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Selective Synthesis Under Microwave Irradiation of Carbohydrate Derivatives Containing Unsaturated Systems

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The selective synthesis of sugars containing vinyl ester- and vinyl ether-type side chains was developed by means of esterification and Wittig olefination procedures. The studies were focused on the anomeric position of D-xylose and on the primary carbon positions of D-glucose and sucrose. Microwave heating was used in both cases, and the results obtained show the usefulness of microwave irradiation for the development of cleaner technologies in carbohydrate chemistry.

Introduction

Carbohydrates are biorenewable resources fundamental to life, which occur in all plants and animals and serve many vital functions, such as energy storage, biological signalling, recognition mechanisms and structural support in the plant kingdom.[1] Common sugars are available in large amounts from natural products, and hence, constitute a suitable renewable source of starting materials in organic synthesis.[2] Among them we can sucrose, glucose and xylose. Sucrose is a major source of cheap chirality and is produced worldwide in large quantities; glucose is the most abundant organic molecule on the planet (predominantly in its polymeric form, cellulose); and xylose is a natural pentose obtained from the xylan-rich portion of hemicelluloses from plant cell walls and fibre. These compounds are highly functionalised molecules with complex stereochemistry due to the presence of several hydroxylated stereogenic centres, which are challenging to chemically differentiate.

Branched-chain sugars are constituents of antibiotics and nucleotides and are of value in the synthesis of optically pure non-carbohydrate natural products.[2–5] Also, the selective derivatisation of sugars with unsaturated moieties is presently one of the easiest methods for the production of potentially biodegradable and biocompatible polymers[6–12] and for the assembly of asymmetric molecules using carbohydrates as chiral auxiliaries.[13–15]

The selective protection of the primary carbon positions of sucrose and D-glucose with TBDPS and TBDMS ethers, followed by the one-step formylation of the silyl ethers with the $POCl_3$·DMF complex (Vilsmeier–Haack complex) has previously been studied.[16] Herein, we present the reaction of such *O*-formyl derivatives with stabilized Wittig reagents to give branched-chain olefinic compounds. Wittig olefination is widely used for the conversion of an aldehyde or ketone into an olefin, but only a few examples can be found in the literature concerning Wittig olefination of less reactive carbonyl groups (esters, amides, anhydrides or lactones).[17–19]

Esters are classically prepared either by the esterification of carboxylic acids with alcohols using acidic catalysis, by transesterification or by alkylation of carboxylate anions.[20–22] This latter method is now applied to sugar bromides by reaction with unsaturated carboxylates prepared in situ from the corresponding carboxylic acid and a suitable base.

Since the 1970s, extensive studies have reported the application of microwave (MW) irradiation in different areas of chemistry, by use of either domestic ovens or monomode reactors.[23–27] Some applications of MW technology in carbohydrate chemistry have also been described.[27–36] Such technology is widely employed in our studies, performed either in the presence or in the absence of solvent, as a means of accelerating the olefination-esterification processes as well as contributing to the overall aim of developing cleaner and more efficient technologies.

Results and Discussion

Wittig Olefination of Sugar Formates

With a view to introducing unsaturated side chains onto carbohydrates, glucose and sucrose derivatives **1**–**4**,[16,37] having an *O*-formyl group at different primary carbon positions, underwent Wittig olefination with stabilized phosphorus ylides **5**–**7** (Scheme 1). The reaction was performed in a multimode microwave oven at 300 W and in the ab-

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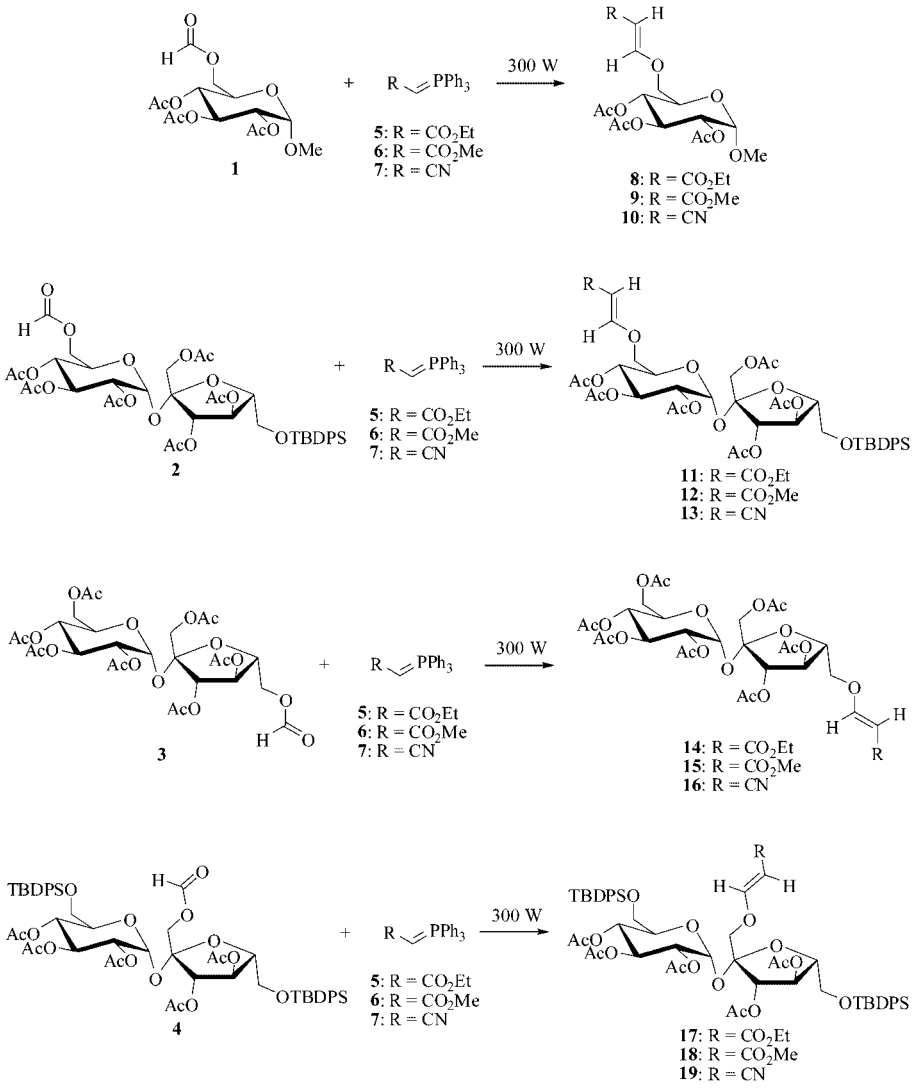


Scheme 1. Wittig olefination of *O*-formylated sugars.

Table 1. Results obtained by the Wittig olefination of sugar derivatives under microwave irradiation.

Entry	Starting sugar	Phosphorane	Reaction time [min]	Product	*E*/*Z*	% Yield[a]
1	**1**	**5**	8	**8**	5.1:1	80
2	**1**	**6**	10	**9**	4.3:1	80
3	**1**	**7**	6	**10**	4.0:1	78
4	**2**	**5**	10	**11**	6.7:1	79
5	**2**	**6**	15	**12**	5.1:1	79
6	**2**	**7**	8	**13**	3.2:1	68
7	**3**	**5**	5	**14**	5.8:1	85
8	**3**	**6**	5	**15**	4.9:1	87
9	**3**	**7**	3	**16**	3.2:1	90
10	**4**	**5**	10	**17**	7.3:1	79
11	**4**	**6**	10	**18**	5.1:1	80
12	**4**	**7**	5	**19**	4.7:1	77

[a] Isolated yield of pure products.

sence of solvent. The results obtained are summarized in Table 1.

Stabilized ylides are known to react readily with aldehydes but slowly or not at all with ketones. In these studies, we have observed that the same chemoselectivity is valid for esters, since only the formyl group underwent Wittig olefination while all the acetyl groups remained unreacted.

The microwave power supplied (300 W) was enough to melt both the sugar and phosphorus ylides **5** and **6**, and hence, the reactions occurred without the need for solvent. Phosphorane **7** is unstable at high temperatures,[27] as it decomposes at 190 °C, but here again, the reaction readily occurred once the sugar melted.

The results obtained are good with slightly higher yields and shorter reaction times for the less-hindered position 6′ of sucrose (Table 1, Entries 7–9).

In all the above reactions both (*E*) and (*Z*) isomers were obtained, with the (*E*) isomer predominating, as expected for stabilized phosphorus ylides.[38–40] The isomers could be easily separated by column chromatography, and their ratio was calculated for the isolated compounds. We also note from our results that the selectivity for the (*E*) isomer is higher for the phosphoranes with an ester group (Table 1, Entries 1, 2, 4, 5, 7, 8, 10 and 11) than it is for the one with a nitrile group (Table 1, Entries 3, 6, 9 and 12).

The Wittig olefination was also tested under conventional heating conditions by refluxing sugar derivatives **1**–**4** with phosphoranes in toluene. The selectivities obtained (Table 2) were similar to those for MW heating. The main advantages of MW irradiation were the large reduction in reaction times, the possibility of decreasing the amount of phosphorane by half and the omission of solvents, thereby representing a greener approach to this olefination.

Table 2. Comparative selectivities for the Wittig olefination under MW and conventional heating.

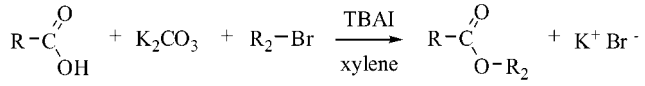
Entry	Starting sugar	Phosphorane	*E*/*Z* (microwave) [a]	*E*/*Z* (conventional) [b]
1	**1**	**5**	5.1:1	6.8:1
2	**1**	**6**	4.3:1	4.8:1
3	**1**	**7**	4.0:1	3.6:1
4	**2**	**5**	6.7:1	6.8:1
5	**2**	**6**	5.1:1	4.1:1
6	**2**	**7**	3.2:1	3.7:1
7	**3**	**5**	5.8:1	6.2:1
8	**4**	**5**	7.3:1	8.0:1

[a] Reaction times were 5–15 min. [b] Reaction conditions: 4 equiv. of phosphorane, toluene, reflux, 24 h.

Esterification of Sugar Bromides

The method described above allows for the introduction of a vinyl ether-type π system at the primary carbon position of sugars. The esterification of sugar bromides represents another possible approach, in which the side chain will be a vinyl ester-type unsaturated system.

The procedure reported in the literature[20,22] involves the reaction of an alkylating agent with a carboxylate prepared in situ from the corresponding carboxylic acid and a base (Scheme 2). As far as we know, such a process is only described for the esterification of alkyl halides with aromatic or saturated carboxylic acids.[20,22] The work presented here extends the methodology to sugar bromides under MW irradiation.



Scheme 2. Esterification of alkyl bromides.

Our studies were directed to the anomeric position of D-xylose and the primary carbon positions of D-glucose and sucrose. These sugars underwent esterification by the reaction of the corresponding bromides with three different unsaturated carboxylic acids: methacrylic acid (**20**), *trans*-crotonic acid (**21**) and *trans*-cinnamic acid (**22**), see Figure 1.

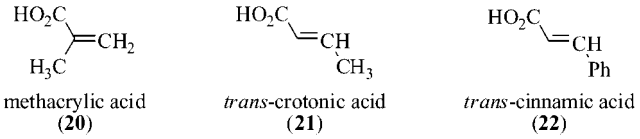


Figure 1. Unsaturated carboxylic acids used for esterification.

The sugar bromides **23**–**28** were prepared by known procedures (Figure 2).[41–43] Sucrose has three different primary OH groups, and its monobromination occurred predominantly at position 6′.

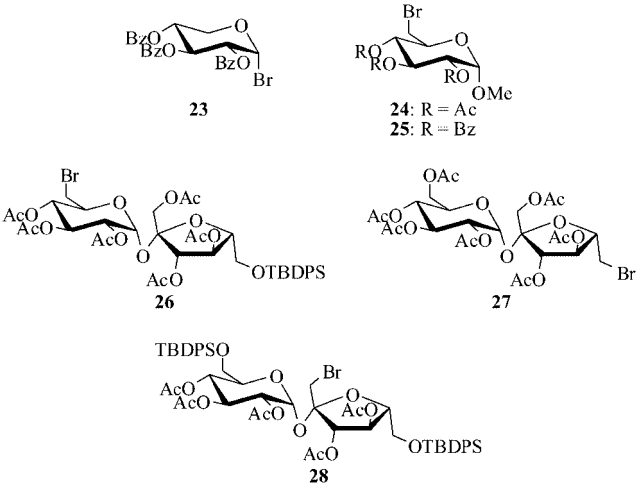
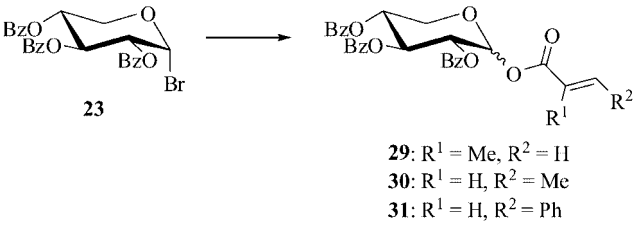


Figure 2. Chemical structure of the sugar bromides used.

In a first approach, we intended to study the anomeric selectivity upon esterification of xylose derivative **23** with different unsaturated esters **20**–**22** under conventional heating. These reactions were carried out in xylene at 90 °C for 30 min. The products obtained (**29**–**31**, Scheme 3) were anomeric mixtures containing an equal proportion of the α and β anomers.



Scheme 3. Esterification of a xylosyl bromide.

In order to find the most efficient method to obtain selectivity in the esterification and greener alternatives for our synthesis, we decided to explore two distinct experimental conditions under MW irradiation; method A: solid-liquid phase-transfer catalysis (PTC) with tetrabutylammonium iodide (TBAI), using K_2CO_3 as the base in the nonpolar solvent xylene or the polar mixture of water/acetone (1:1) or method B: homogeneous mixtures of reagents in pyridine or 1,1,3,3-tetramethylguanidine (TMG), which acts as both the solvent and base catalyst. The results obtained in MW-assisted esterification are summarized in Table 3.

Table 3. Results obtained by MW esterification of xylose derivative **23**.

Entry	Product	Base/solvent	Power [W]	α/β[a]	% Yield[b]
1	**29**	K_2CO_3/xylene	600	1:1.1	65
2	**29**	K_2CO_3/ water/acetone (1:1)	100	1:6.5	70
3	**29**	pyridine	600	–	–
4	**29**	TMG	100	–	–
5	**30**	K_2CO_3/xylene	600	1:1.3	68
6	**30**	K_2CO_3/ water/acetone (1:1)	100	1:6.2	62
7	**30**	pyridine	600	–	–
8	**30**	TMG	100	–	–
9	**31**	K_2CO_3/xylene	600	1:1.3	68
10	**31**	K_2CO_3/ water/acetone (1:1)	100	1:5.2	67
11	**31**	pyridine	600	–	–
12	**31**	TMG	100	–	–

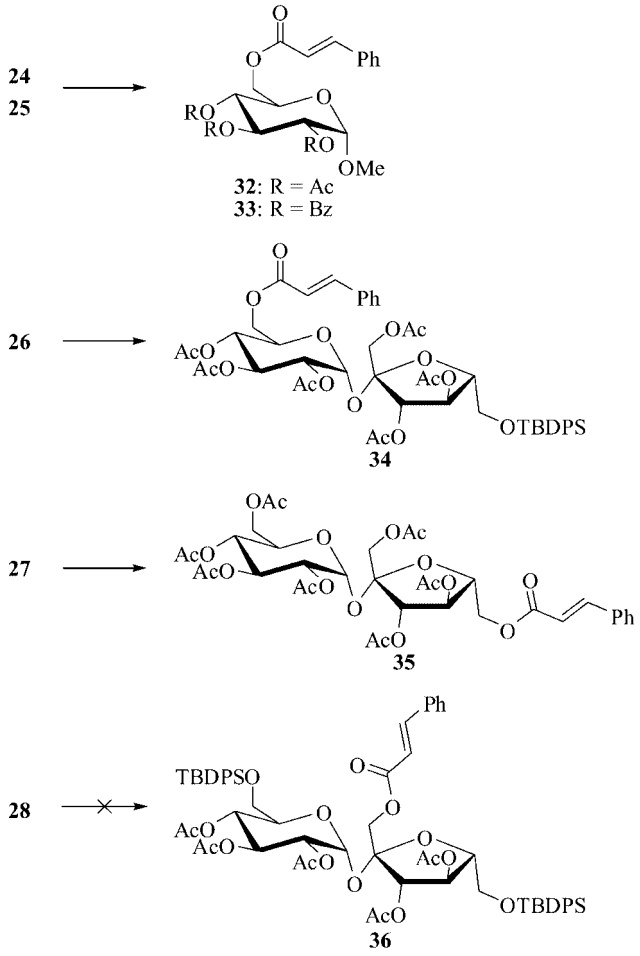
[a] Anomeric ratio was determined by ^{1}H NMR spectroscopy. [b] Isolated yields of pure anomeric mixtures.

By pre-treating the unsaturated acids **20**–**22** with solid K_2CO_3 at room temperature in xylene and then performing the reaction with sugar bromide **23** at 600 W in an open flask (method A), we obtained anomeric mixtures of sugar-derived vinyl esters, with a slight excess of the β anomer (α/β = 1:1.1 for **29**, 1:1.3 for **30** and 1:1.3 for **31**, Table 3, Entries 1, 5 and 9). These results were similar to those obtained under conventional heating, so a better approach could be the use of a different solvent. In this context, when replacing xylene by the polar mixture of water/acetone (1:1) and mixing all the reagents at once in a sealed tube (Table 3, Entries 2, 6 and 10), we observed that irradiation at 100 W for only 5 min led to complete reactions and a pronounced β-selectivity (α/β = 1:6.5 for **29**, 1:6.2 for **30** and 1:5.2 for **31**). These results show an increase in the anomeric selectivity (α/β ≈ 1:6 vs. 1:1) when the esterification was performed in a polar system (water/acetone) compared to a nonpolar one (xylene). As expected, the reaction also occurred under milder conditions with water/acetone since it has better MW absorption than the nonpolar xylene (100 W vs. 600 W).

When we replaced the inorganic base K_2CO_3 with pyridine (Table 3, Entries 3, 7 and 11), after a 5 min reflux at 600 W, we observed that the reaction mixture did not show the presence of the desired products or the starting sugar. For each case, the NMR spectra of the crude products were similar, apart from the presence of different carboxylic acids, and showed traces of the same sugar-derived byproducts.

Additionally, with TMG (Table 3, Entries 4, 8 and 12), after only 5 min at 100 W, all the starting sugar was consumed, but no esterification products were detected by TLC, and only a very complex crude mixture was obtained.

The esterification reaction was also studied at the primary carbon positions of sugar bromides **24**–**28** (Scheme 4), and the results obtained are listed in Table 4.



Scheme 4. Esterification products of glucose and sucrose.

After pre-treating *trans*-cinnamic acid with solid K_2CO_3 at room temperature in xylene and then performing the reaction with glucose bromide **24** in the presence of Ag_2CO_3 at 600 W in an open flask (method A) for 10 min, we obtained a 57% yield of product and recovered 32% of the starting material (Table 4, Entry 1). This method was also tested using lower MW power (100 W and 300 W), but the esterification did not occur, and we only recovered the starting material.

The reaction of glucose derivative **24** according to method A but with the polar solvent water/acetone (with Ag_2CO_3) in a sealed tube at 100 W for 7 min afforded a 17% yield of esterification product **32** and a complex mixture of more polar sugars (showing different degrees of de-

Table 4. Results obtained in the esterification of sugar bromides.

Entry	Starting sugar	Base/solvent	Ag_2CO_3 (equiv.)	**22** (equiv.)	Power [W]	Reaction time [min]	Products	% Yield[a]
1	**24**	K_2CO_3/xylene	2	2	600	10	**32** + **24**	57 + 32
2	**24**	K_2CO_3/ water/acetone (1:1)	2	2	100	7	**32** + **24**	17 + 19
3	**24**	K_2CO_3/ water/acetone (1:1)	2	2	100	30	**32** + **24**	6 + 7
4	**24**	pyridine	2	2	600	10	**32**	67
5	**24**	TMG	–	2	100	5	**32**	74
6	**25**	K_2CO_3/ water/acetone (1:1)	2	2	100	12	**33** + **25**	27 + 7
7	**25**	K_2CO_3/ water/acetone (1:1)	2	2	100	80	**33** + **25**	6 + 3
8	**25**	TMG	–	2	100	30	**33** + **25**	53 + 5
9	**26**	pyridine	4	4	600	60	**34** + **35**	23 + 16
10	**26**	TMG	–	5	100	60	**34**	28
11	**27**	pyridine	3	4	600	30	**35**	58
12	**27**	TMG	–	4	100	30	**35**	32
13	**28**	pyridine	4	5	600	130	–[b]	–[c]
14	**28**	TMG	–	10	100	90	–[b]	–[c]

[a] Isolated yield of pure compounds. [b] No products were obtained. [c] 50% of the starting sugar **28** was recovered.

protection), together with 19% of the starting material (Table 4, Entry 2). When the reaction time was extended to 30 min (15+15) we still recovered 7% of starting material but obtained only a 6% yield of esterification product **32**, and again, a comparable complex mixture of more polar sugars (Table 4, Entry 3). In order to understand which reagent was promoting the acetyl group deprotection, a similar reaction was conducted in the absence of silver salt with an extended reaction time (40 min). This attempt did not yield any esterification product or mixture of more polar sugars like the reactions described above, and only the starting material was recovered. It is reported in the literature[44,45] that acetyl groups can be removed with K_2CO_3/methanol/water at room temperature and our results show that K_2CO_3/acetone/water only removes the protecting group in the presence of the silver salt. Another conclusion we can point out is that, on the contrary to what occurred at the anomeric position of xylose, for the primary carbon position of glucose the presence of a silver salt is essential for the reaction to occur.

When employing method B, the reaction between glucose bromide **24** and 2 equiv. of *trans*-cinnamic acid in the presence of Ag_2CO_3 in refluxing pyridine was complete after 10 min at 600 W, yielding **32** in 67% yield (Table 4, Entry 4). By replacing pyridine with TMG (Table 4, Entry 5), the esterification was faster even under milder conditions (100 W instead of 600 W) and in the absence of silver salt. Purification of the crude mixture afforded the expected product (**32**) in 74% yield.

The same reactions were tested with the benzoyl glucose derivative **25** with analogous results. In aqueous media (method A) after 12 min, we obtained a 27% yield of esterification product **33** and recovered 7% of the starting material (Table 4, Entry 6). When we prolonged the reaction time to 80 min, we still recovered starting material (3%), but the yield of the esterification product diminished (6%, Table 4, Entry 7) due to degradation of the sugar. Performing the reaction with TMG (method B) over 30 min at 100 W yielded 53% of **33** and 5% of the starting material (Table 4, Entry 8).

For the 6-bromosucrose derivative **26**, esterification with 4 equiv. of *trans*-cinnamic acid in refluxing pyridine at 600 W (method B) proceeded in 1 h, showing two major products (Table 4, Entry 9) which were identified as the desired esterification product **34** (23% yield) and a second esterification product (16% yield), in which the TBDPS group and bromide had been removed. This second product was again acetylated, affording **35** in quantitative yield.

Silver salts are reported to remove TBDMS ethers in the presence of TBDPS ethers in 8 h at room temperature.[46] However, by the use of MW irradiation at 600 W, we observed the removal of the more bulky TBDPS group. We can not discard the possibility that the presence of some free bromide in the reaction medium could have contributed to the deprotection as well.[47]

When the reaction of the same sucrose derivative was performed in TMG (Table 4, Entry 10), the starting material was totally consumed after 1 h at 100 W. Purification afforded esterification product **34** in 28% yield and a complex mixture of byproducts resulting from desilylation and random deacetylation.[48]

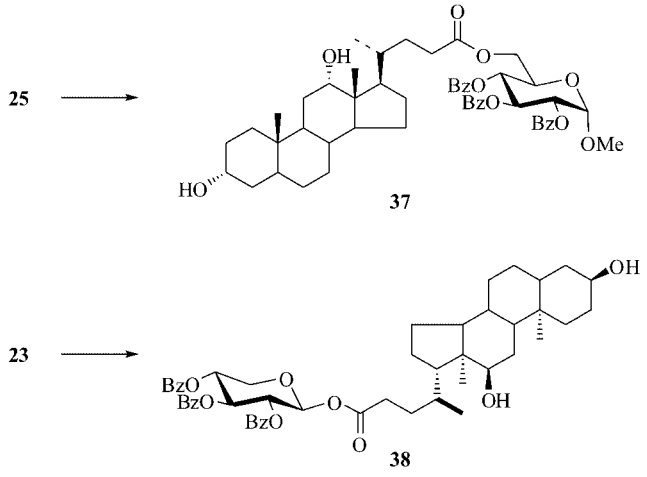
The 6′-bromosucrose derivative **27** reacted completely in refluxing pyridine at 600 W for 30 min (method B), affording product **35** in 58% yield (Table 4, Entry 11), without the detection of any other major secondary product. With TMG (Table 4, Entry 12), the reaction was complete after 30 min at 100 W, but product **35** was isolated in only a 32% yield. This low yield was once more due to the formation of a complex mixture of byproducts.[48] As could be expected by the less-hindered environment at position 6′, the reaction was faster than at position 6; comparison of Entries 9 and 10 with Entries 11 and 12 (Table 4) demonstrates that the time required for completion was two times smaller for **27**.

Applying similar conditions (method B with pyridine or TMG) for the 1′-bromosucrose derivative **28**, no esterification product was detected even after prolonged reaction times, and the starting material was always recovered together with some degradation products (Table 4, Entries 13 and 14). These results reflect the effect of the bulkiness around the bromide group in the esterification reaction, since position 1′ is the most hindered one.

Our studies led us to conclude that the most suitable reaction conditions for each sugar derivative were method A in water/acetone at 100 W for xylose (which showed anomeric selectivity), method B in TMG at 100 W for glucose, and method B in pyridine at 600 W for sucrose.

Synthesis of Steroid Derivatives

The esterification method discussed above can be extended to the synthesis of steroid derivatives, including saponins. Deoxycholic acid is one of the major bile acids produced by the liver. Bile acids have been considered in the preparation of new drugs since bile-acid-conjugated materials can retain the properties of bile acids, such as amphiphilicity, the capacity for self-assembling, high chemical stability and binding ability to bile acids transporters in the intestine[49] (Scheme 5).



Scheme 5. Esterification of deoxycholic acid.

Some preliminary results are shown in Table 5. The esterification reaction between glucose bromide **25** and deoxycholic acid (2 equiv.) with TMG in an open vessel at 100 W (method B) over 20 min gave the desired product **37** in 82% yield (Table 5, Entry 1). When applying method A [water/acetone (1:1)] to xylosyl bromide **23**, all the starting material was consumed in 5 min, and only the β anomer of saponin **38** was formed, in 38% yield, together with some unidentified non-deoxycholate byproducts.

Table 5. Results obtained for the synthesis of deoxycholates.

Entry	Starting sugar	Base/solvent	Reaction time [min]	% Yield[a]
1	**25**	TMG	20	82
2	**23**	K_2CO_3/ water/acetone (1:1)	5	38

[a] Isolated yield of pure product.

Conclusions

We have explored useful MW methodologies for the introduction of unsaturated systems onto carbohydrates. By means of a Wittig olefination, vinyl ether-type chains were selectively appended to the primary carbon positions of sucrose and glucose in short reaction times and without the need for solvents. Similarly, the MW-assisted esterification of sugar bromides allowed for the attachment of vinyl ester-type side chains. In the case of xylose, these studies were directed at the anomeric position, and the anomeric selectivity was analysed for different solvents.

Experimental Section

General Methods: All solvents were purified before use.[50] All reactions were monitored by thin layer chromatography, which was performed with aluminium-backed silica gel Merck 60 F_{254} plates, and compounds were detected by ultraviolet light or by staining with 10% solution of H_2SO_4 in ethanol, followed by heating. Flash chromatography was carried out using silica gel from Macherey–Nagel (Kieselgel 60 M). Preparative layer chromatography was performed with glass plates coated with 1 mm of silica gel (Macherey-Nagel, Kieselgel DGF_{254}). Melting points were determined with a capillary apparatus and are uncorrected. Elemental analyses were performed with Thermo Finnigan-CE Flash EA 1112 CHNS series analyser. NMR spectra were recorded with a Bruker AMX-400 MHz apparatus in $CDCl_3$, using TMS as internal standard, with chemical shift values (δ) in ppm. Structural assignment of all new compounds was made by 2D NMR techniques (COSY 45 and HMQC) using standard pulse sequences and parameters recommended by the manufacturer. The ^{13}C distortionless enhancement by polarization transfer (DEPT 135) spectra were also measured in order to determine the exact ^1H signal multiplicity and to differentiate among CH_3, CH_2, CH and C. Optical rotations were measured at 20 °C with an Optical Activity AA-1000 polarimeter at 589 nm. Microwave experiments were conducted in a Milestone MicroSYNTH apparatus.

General Method for the Wittig Olefination: Wittig reactions were performed at 300 W power, in an open flask and in the absence of solvent, for the times indicated in Table 1. The phosphoranes **5** and **7** were prepared according to known procedures. Phosphorane **6** was purchased from Aldrich.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(1*E*)-3-ethoxy-3-oxo-1-propenyl]-α-D-glucopyranoside (8a) and Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(1*Z*)-3-ethoxy-3-oxo-1-propenyl]-α-D-glucopyranoside (8b): According to the general method, **1** (100 mg, 0.287 mmol) and **5** (200 mg, 2 equiv., 0.574 mmol) were reacted for 8 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **8a** (80.4 mg, 67% yield, colourless oil) and **8b** (15.8 mg, 13% yield, colourless oil). **8a**: $[\alpha]_D^{20}$ = +125.4 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 12.6 Hz, 1 H, 7-H), 5.49 (t, J = 9.7 Hz, 1 H, 3-H), 5.23 (d, J = 12.6 Hz, 1 H, 8-H), 5.03 (t, J = 9.8 Hz, 1 H, 4-H), 4.96 (d, J = 3.4 Hz, 1 H, 1-H), 4.88 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.16 (q, J = 7.1 Hz, 2 H, CH_2-CH_3), 4.04 (td, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 4.0 Hz, 1 H, 5-H), 3.91 (d,

$J_{5,6}$ = 3.9 Hz, 2 H, 6-H), 3.41 (s, 3 H, OCH_3), 2.08, 2.04, 2.01 (3 s, 9 H, 3 CH_3) 1.27 (t, J = 7.1 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 169.9, 169.6 (acetyl *C*=O), 167.3 (EtO-*C*=O), 161.9 (C-7), 97.5 (C-8), 96.6 (C-1), 70.7 (C-2), 69.9 (C-3), 69.5 (C-6), 68.9 (C-4), 67.4 (C-5), 59.9 (*C*H_2-CH_3), 55.5 (O*C*H_3), 20.7 (acetyl *C*H_3), 14.3 (CH_2-*C*H_3) ppm. $C_{18}H_{26}O_{11}$ (418.15): calcd. C 51.67, H 6.26; found C 51.72, H 6.31. **8b**: ^{1}H NMR (100 MHz, $CDCl_3$): δ = 6.53 (d, J = 7.0 Hz, 1 H, 7-H), 5.49 (t, J = 9.7 Hz, 1 H, 3-H), 4.95 (t, J = 9.6 Hz, 1 H, 4-H), 4.94 (d, J = 3.8 Hz, 1 H, 1-H), 4.85 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.84 (d, J = 7.1 Hz, 1 H, 8-H), 4.15 (q, J = 7.1 Hz, 2 H, CH_2-CH_3), 4.09 (m, $J_{4,5}$ = 10.2 Hz, $J_{5,6\alpha}$ = 2.0 Hz, $J_{5,6\beta}$ = 2.6 Hz, 2 H, 5-H, 6α-H), 3.98 (dd, $J_{5,6\beta}$ = 6.7 Hz, $J_{6\alpha,6\beta}$ = 11.4 Hz, 1 H, 6β-H), 3.39 (s, 3 H, OCH_3), 2.08, 2.04, 2.01 (3 s, 9 H, 3 CH_3), 1.27 (t, J = 7.4 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.8 (acetyl *C*=O), 165.1 (EtO-*C*=O), 159.0 (C-7), 96.4 (C-8), 96.3 (C-1), 73.6 (C-6), 70.7 (C-2), 69.8 (C-3), 69.0 (C-4), 68.3 (C-5), 59.5 (*C*H_2-CH_3), 55.3 (O*C*H_3), 20.6, 20.6, 20.5 (acetyl *C*H_3), 14.2 (CH_2-*C*H_3) ppm.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(1*E*)-3-methoxy-3-oxo-1-propenyl]-α-D-glucopyranoside (9a) and Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(1*Z*)-3-methoxy-3-oxo-1-propenyl]-α-D-glucopyranoside (9b): According to the general method, **1** (100 mg, 0.287 mmol) and **6** (192 mg, 2 equiv., 0.574 mmol) were reacted for 10 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **9a** (74.6 mg, 64% yield, colourless needles) and **9b** (17.4 mg, 15% yield, colourless oil). **9a**: m.p. 104–105 °C. $[\alpha]_D^{20}$ = +138.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 12.6 Hz, 1 H, 7-H), 5.49 (t, J = 9.7 Hz, 1 H, 3-H), 5.24 (d, J = 12.6 Hz, 1 H, 8-H), 5.03 (t, J = 9.8 Hz, 1 H, 4-H), 4.95 (d, J = 3.5 Hz, 1 H, 1-H), 4.88 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.04 (td, $J_{4,5}$ = 10.1 Hz, $J_{5,6}$ = 4.0 Hz, 1 H, 5-H), 3.91 (d, $J_{5,6}$ = 3.8 Hz, 2 H, 6-H), 3.70 (s, 3 H, vinyl OCH_3), 3.41 (s, 3 H, Glc OCH_3), 2.08, 2.04, 2.01 (3 s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 169.9, 169.6 (acetyl *C*=O), 167.8 (MeO-*C*=O), 162.1 (C-7), 97.2 (C-8), 96.7 (C-1), 70.7 (C-2), 69.9 (C-3), 69.6 (C-6), 68.9 (C-4), 67.4 (C-5), 55.5 (Glc O*C*H_3), 51.1 (vinyl O*C*H_3), 20.6 (*C*H_3) ppm. $C_{17}H_{24}O_{11}$ (404.13): calcd. C 50.49, H 5.98; found C 50.77, H 6.22. **9b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.54 (d, J = 7.0 Hz, 1 H, 7-H), 5.49 (t, J = 9.7 Hz, 1 H, 3-H), 4.94 (d, J = 3.8 Hz, 1 H, 1-H), 4.94 (t, J = 9.6 Hz, 1 H, 4-H), 4.85 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.0 Hz, 1 H, 2-H), 4.84 (d, J = 7.1 Hz, 1 H, 8-H), 4.10 (m, 2 H, 5-H, 6α-H), 3.99 (dd, $J_{5,6\beta}$ = 6.7 Hz, $J_{6\alpha,6\beta}$ = 11.3 Hz, 1 H, 6β-H), 3.69 (s, 3 H, vinyl OCH_3), 3.39 (s, 3 H, Glc OCH_3), 2.08, 2.04, 2.01 (3 s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.7 (acetyl *C*=O), 165.4 (MeO-*C*=O), 159.1 (C-7), 96.4 (C-8), 96.1 (C-1), 73.7 (C-6), 70.8 (C-2), 69.8 (C-3), 69.0 (C-4), 68.4 (C-5), 55.3 (Glc O*C*H_3), 50.9 (vinyl O*C*H_3), 20.65, 20.61 (*C*H_3) ppm.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(1*E*)-cyanovinyl]-α-D-glucopyranoside (10a) and Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(1*Z*)-cyanovinyl]-α-D-glucopyranoside (10b): According to the general method, **1** (100 mg, 0.287 mmol) and **7** (173 mg, 2 equiv., 0.574 mmol) were reacted for 6 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **10a** (66.7 mg, 63% yield, colourless oil) and **10b** (16.6 mg, 16% yield, colourless oil). **10a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 12.9 Hz, 1 H, 7-H), 5.49 (t, J = 9.8 Hz, 1 H, 3-H), 5.00 (t, J = 9.8 Hz, 1 H, 4-H), 4.95 (d, J = 3.5 Hz, 1 H, 1-H), 4.86 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.72 (d, J = 12.9 Hz, 1 H, 8-H), 4.02 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6\alpha}$ = 3.0 Hz, $J_{5,6\beta}$ = 4.8 Hz, 1 H, 5-H), 3.94 (m, 2 H, 6-H), 3.42 (s, 1 H, OCH_3), 2.08, 2.05, 2.02 (3 s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 169.9, 169.6 (*C*=O), 164.5 (C-7), 116.9 (*C*N), 96.7 (C-1), 76.6 (C-8), 70.5 (C-6), 70.3 (C-2), 69.7 (C-3), 68.6 (C-4), 67.5 (C-5), 55.6 (O*C*H_3), 20.6 (*C*H_3) ppm. **10b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, J = 6.3 Hz, 1 H, 7-H), 5.50 (t, J = 9.6 Hz, 1 H, 3-H), 4.94 (d, J = 3.3 Hz, 1 H, 1-H), 4.90 (t, J = 9.5 Hz, 1 H, 4-H), 4.84 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.40 (d, J = 6.3 Hz, 1 H, 8-H), 4.16 (dd, $J_{5,6\alpha}$ = 1.5 Hz, $J_{6\alpha,6\beta}$ = 10.7 Hz, 1 H, 6α-H), 4.02 (m, 2 H, 5-H, 6β-H), 3.41 (s, 1 H, OCH_3), 2.08, 2.06, 2.02 (3 s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.8, 169.8 (*C*=O), 163.5 (C-7), 114.8 (*C*N), 96.5 (C-1), 74.8 (C-8), 73.3 (C-6), 70.7 (C-2), 69.6 (C-3), 69.0 (C-4), 68.1 (C-5), 55.5 (O*C*H_3), 20.60, 20.58 (*C*H_3) ppm.

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(1*E*)-3-ethoxy-3-oxo-1-propenyl]-6′-*O*-TBDPS-sucrose (11a) and 1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(1*Z*)-3-ethoxy-3-oxo-1-propenyl]-6′-*O*-TBDPS-sucrose (11b): According to the general method, **2** (100 mg, 0.116 mmol) and **5** (80.9 mg, 2 equiv., 0.232 mmol) were reacted for 10 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **11a** (74.3 mg, 69% yield, colourless oil) and **11b** (11.1 mg, 10% yield, colourless oil). **11a**: $[\alpha]_D^{20}$ = +62.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (m, 4 H, Ph-H$_o$), 7.40 (m, 7 H, Ph-H$_{m,p}$, 7-H), 5.60 (d, J = 3.6 Hz, 1 H, 1-H), 5.52 (t, J = 5.8 Hz, 1 H, 4′-H), 5.40 (t, J = 9.8 Hz, 1 H, 3-H), 5.39 (d, J = 5.6 Hz, 1 H, 3′-H), 5.08 (d, J = 12.7 Hz, 1 H, 8-H), 5.03 (t, J = 9.9 Hz, 1 H, 4-H), 4.80 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.24 (m, 1 H, 5-H), 4.14 (m, 5 H, 1′-H, 5′-H, CH_2-CH_3), 3.84 (m, 2 H, 6′-H), 3.71 (dd, $J_{5,6\alpha}$ = 2.3 Hz, $J_{6\alpha,6\beta}$ = 11 Hz, 1 H, 6α-H), 3.63 (dd, $J_{5,6\beta}$ = 4.4 Hz, $J_{6\alpha,6\beta}$ = 11.1 Hz, 1 H, 6β-H), 2.14, 2.10, 2.08, 2.05, 2.01, 1.97 (6 s, 18 H, 6 CH_3), 1.27 (t, J = 7.0 Hz, 3 H, CH_2-CH_3), 1.05 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.7, 169.4 (acetyl *C*=O), 167.3 (EtO-*C*=O), 161.6 (C-7), 135.5 (Ph-*C*$_o$), 132.9 (Ph-*C*$_q$), 129.8 (Ph-*C*$_p$), 127.8 (Ph-*C*$_m$), 103.6 (C-2′), 97.3 (C-8), 89.5 (C-1), 81.5 (C-5′), 76.2 (C-3′), 75.0 (C-4′), 70.1 (C-2), 69.6 (C-3), 68.5 (C-4,6), 68.2 (C-5), 63.7 (C-6′), 62.9 (C-1′), 59.8 (*C*H_2-CH_3), 26.7 (*t*Bu-*C*H_3), 20.8, 20.5 (acetyl *C*H_3), 19.1 (*t*Bu-*C*), 14.3 (CH_2-*C*H_3) ppm. $C_{45}H_{58}O_{19}Si$ (930.33): calcd. C 58.05, H 6.28; found C 58.25, H 6.71. **11b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (m, J = 7.2 Hz, J = 10.4 Hz, 4 H, Ph-H$_o$), 7.41 (m, 6 H, Ph-H$_{m,p}$), 6.20 (d, J = 7.0 Hz, 1 H, 7-H), 5.65 (d, J = 3.6 Hz, 1 H, 1-H), 5.54 (t, J = 5.8 Hz, 1 H, 4′-H), 5.40 (d, J = 6.0 Hz, 1 H, 3′-H), 5.40 (t, J = 9.7 Hz, 1 H, 3-H), 5.08 (t, J = 9.8 Hz, 1 H, 4-H), 4.78 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.66 (d, J = 7.0 Hz, 1 H, 8-H), 4.15 (m, 6 H, 1′-H, 5-H, 5′-H, CH_2-CH_3), 3.90 (dd, $J_{5,6\beta}$ = 3.5 Hz, $J_{6\alpha,6\beta}$ = 12.0 Hz, 1 H, 6β-H), 3.82 (m, $J_{5,6\alpha}$ = 2.4 Hz, 3 H, 6′-H, 6α-H), 2.13, 2.09, 2.08, 2.05, 1.99, 1.96 (6 s, 18 H, 6 CH_3), 1.25 (t, J = 7.0 Hz, 3 H, CH_2-CH_3), 1.04 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 169.8, 169.3 (acetyl *C*=O), 164.9 (EtO-*C*=O), 158.6 (C-7), 135.5 (Ph-*C*$_o$), 132.8 (Ph-*C*$_q$), 129.9 (Ph-*C*$_p$), 127.8 (Ph-*C*$_m$), 103.6 (C-2′), 96.6 (C-8), 89.5 (C-1), 81.3 (C-5′), 76.1 (C-3′), 75.0 (C-4′), 72.7 (C-6), 70.0 (C-2), 69.6 (C-3), 69.0 (C-5), 68.6 (C-4), 63.6 (C-6′), 62.9 (C-1′), 59.5 (*C*H_2-CH_3), 26.6 (*t*Bu-*C*H_3), 20.7, 20.5 (acetyl *C*H_3), 19.1 (*t*Bu-*C*), 14.3 (CH_2-*C*H_3) ppm.

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(1*E*)-3-methoxy-3-oxo-1-propenyl]-6′-*O*-TBDPS-sucrose (12a) and 1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(1*Z*)-3-methoxy-3-oxo-1-propenyl]-6′-*O*-TBDPS-sucrose (12b): According to the general method, **2** (100 mg, 0.116 mmol) and **6** (77.7 mg, 2 equiv., 0.232 mmol) were reacted for 15 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **12a** (70.4 mg, 66% yield, colourless oil) and **12b** (13.8 mg, 13% yield, colourless oil). **12a**: $[\alpha]_D^{20}$ = +61.2 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (m, 4 H, Ph-H$_o$), 7.39 (m, 7 H, Ph-H$_{m,p}$, 7-H), 5.59 (d, J = 3.6 Hz, 1 H, 1-H), 5.51 (t, J = 5.7 Hz, 1 H, 4′-H), 5.39 (m, 2 H, 3′-H, 3-H), 5.08 (d, J =

12.6 Hz, 1 H, 8-H), 5.02 (t, J = 9.9 Hz, 1 H, 4-H), 4.79 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.22 (dt, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 3.7 Hz, 1 H, 5-H), 4.13 (m, 3 H, 1′-H, 5′-H), 3.85 (m, 2 H, 6′-H), 3.68 (m, $J_{5,6\alpha}$ = 2.1 Hz, $J_{5,6\beta}$ = 4.3 Hz, $J_{6\alpha,6\beta}$ = 11.1 Hz, 5 H, 6-H, OCH_3), 2.13, 2.09, 2.07, 2.04, 2.00, 1.96 (6 s, 18 H, 6 CH_3), 1.04 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.7, 169.4 (acetyl *C*=O), 167.7 (MeO-*C*=O), 161.8 (C-7), 135.5 (Ph-C_o), 132.9 (Ph-C_q), 129.8 (Ph-C_p), 127.7 (Ph-C_m), 103.6 (C-2′), 97.0 (C-8), 89.5 (C-1), 81.5 (C-5′), 76.2 (C-3′), 75.0 (C-4′), 70.0 (C-2), 69.6 (C-3), 68.7 (C-6), 68.5 (C-4), 68.2 (C-5), 63.7 (C-6′), 62.9 (C-1′), 51.1 (OCH_3), 26.7 (*t*Bu-CH_3), 20.7, 20.6, 20.5 (CH_3), 19.1 (*t*Bu-*C*) ppm. $C_{44}H_{56}O_{19}Si$ (916.32): calcd. C 57.63, H 6.16; found C 57.55, H 6.41. **12b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (m, 4 H, Ph-H_o), 7.40 (m, 6 H, Ph-$H_{m,p}$), 6.21 (d, J = 7.0 Hz, 1 H, 7-H), 5.64 (d, J = 3.6 Hz, 1 H, 1-H), 5.53 (t, J = 5.8 Hz, 1 H, 4′-H), 5.40 (d, J = 5.9 Hz, 1 H, 3′-H), 5.39 (t, J = 9.9 Hz, 1 H, 3-H), 5.07 (t, J = 9.9 Hz, 1 H, 4-H), 4.77 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.66 (d, J = 7.0 Hz, 1 H, 8-H), 4.50 (dt, $J_{4,5}$ = 10.4 Hz, $J_{5,6}$ = 3.2 Hz, 1 H, 5-H), 4.15 (s, 2 H, 1′-H), 4.10 (dd, J = 5.5 Hz, J = 11.1 Hz, 1 H, 5′-H), 3.91 (dd, $J_{5,6\beta}$ = 3.8 Hz, $J_{6\alpha,6\beta}$ = 12.2 Hz, 1 H, 6β-H), 3.83 (m, $J_{5,6\alpha}$ = 2.7 Hz, 3 H, 6α-H, 6′-H), 3.66 (s, 3 H, OCH_3), 2.14, 2.10, 2.09, 2.06, 2.01, 1.97 (6 s, 18 H, 6 CH_3), 1.05 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 169.8, 169.3 (acetyl *C*=O), 165.4 (MeO-*C*=O), 158.8 (C-7), 135.6 (Ph-C_o), 129.9 (Ph-C_p), 127.8 (Ph-C_m), 103.7 (C-2′), 96.3 (C-8), 89.6 (C-1), 81.3 (C-5′), 76.2 (C-3′), 75.0 (C-4′), 72.9 (C-6), 70.1 (C-2), 69.7 (C-3), 69.1 (C-5), 68.6 (C-4), 63.7 (C-6′), 63.0 (C-1′), 50.9 (OCH_3), 26.7 (*t*Bu-CH_3), 20.8, 20.6 (CH_3), 19.2 (*t*Bu-*C*) ppm.

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(1*E*)-cyanovinyl]-6′-*O*-TBDPS-sucrose (13a) and 1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(1*Z*)-cyanovinyl]-6′-*O*-TBDPS-sucrose (13b): According to the general method, **2** (100 mg, 0.116 mmol) and **7** (70 mg, 2 equiv., 0.232 mmol) were reacted for 8 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **13a** (53.3 mg, 52% yield, colourless oil) and **13b** (16.5 mg, 16% yield, colourless oil). **13a**: $[\alpha]_D^{20}$ = +59.2 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (m, 4 H, Ph-H_o), 7.41 (m, 6 H, Ph-$H_{m,p}$), 6.90 (d, J = 13.0 Hz, 1 H, 7-H), 5.60 (d, J = 3.6 Hz, 1 H, 1-H), 5.51 (t, J = 6.0 Hz, 1 H, 4′-H), 5.40 (d, J = 5.8 Hz, 1 H, 3′-H), 5.37 (t, J = 9.8 Hz, 1 H, 3-H), 4.96 (t, J = 9.9 Hz, 1 H, 4-H), 4.78 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.48 (d, J = 13.0 Hz, 1 H, 8-H), 4.20 (m, 1 H, 5-H), 4.15 (d, J = 12.3 Hz, 1 H, 1′α-H), 4.11 (m, 1 H, 5′-H), 4.09 (d, J = 12.2 Hz, 1 H, 1′β-H), 3.82 (m, 2 H, 6′-H), 3.68 (dd, $J_{5,6\alpha}$ = 2.0 Hz, $J_{6\alpha,6\beta}$ = 11.2 Hz, 1 H, 6α-H), 3.61 (dd, $J_{5,6\beta}$ = 4.5 Hz, $J_{6\alpha,6\beta}$ = 11.2 Hz, 1 H, 6β-H), 2.14, 2.09, 2.07, 2.05, 2.00, 1.97 (6 s, 18 H, 6 CH_3), 1.03 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.6, 169.4 (*C*=O), 164.1 (C-7), 135.5 (Ph-C_o), 132.9 (Ph-C_q), 129.9 (Ph-C_p), 127.8 (Ph-C_m), 117.0 (*C*N), 103.5 (C-2′), 89.4 (C-1), 81.5 (C-5′), 76.3 (C-8), 76.2 (C-3′), 74.8 (C-4′), 69.9 (C-2), 69.5 (C-3), 69.3 (C-6), 68.3 (C-4), 68.1 (C-5), 63.7 (C-6′), 63.1 (C-1′), 26.6 (*t*Bu-CH_3), 20.8, 20.6, 20.5 (CH_3), 19.1 (*t*Bu-*C*) ppm. $C_{43}H_{53}NO_{17}Si$ (883.31): calcd. C 58.43, H 6.04, N 1.58; found C 58.49, H 6.41, N 1.44. **13b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, J = 6.4 Hz, J = 13.2 Hz, 4 H, Ph-H_o), 7.41 (m, 6 H, Ph-$H_{m,p}$), 6.51 (d, J = 6.4 Hz, 1 H, 7-H), 5.68 (d, J = 3.6 Hz, 1 H, 1-H), 5.56 (t, J = 6.1 Hz, 1 H, 4′-H), 5.42 (d, J = 5.8 Hz, 1 H, 3′-H), 5.42 (t, J = 9.8 Hz, 1 H, 3-H), 4.94 (t, J = 9.9 Hz, 1 H, 4-H), 4.76 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.28 (ddd, $J_{4,5}$ = 10.3 Hz, $J_{5,6\beta}$ = 4.7 Hz, $J_{5,6\alpha}$ = 3.4 Hz, 1 H, 5-H), 4.20 (d, J = 6.3 Hz, 1 H, 8-H), 4.19 (d, J = 12.4 Hz, 1 H, 1′α-H), 4.13 (dd, J = 4.8 Hz, J = 10.9 Hz, 1 H, 5′-H), 4.12 (d, J = 12.2 Hz, 1 H, 1′β-H), 3.95 (dd, $J_{5,6\alpha}$ = 3.1 Hz, $J_{6\alpha,6\beta}$ = 11.9 Hz, 1 H, 6α-H), 3.90 (dd, $J_{5',6'\beta}$ = 6.0 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 2 H, 6′α-H, 6β-H), 3.81 (dd, $J_{5',6'\beta}$ = 5.1 Hz, $J_{6'\alpha,6'\beta}$ = 11.1 Hz, 1 H, 6′β-H), 2.16, 2.11, 2.09, 2.06, 2.01, 1.98 (6 s, 18 H, 6 CH_3), 1.06 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 169.9, 169.8, 169.6 (*C*=O), 163.2 (C-7), 135.6 (Ph-C_o), 132.9 (Ph-C_q), 129.9 (Ph-C_p), 127.8, 127.8 (Ph-C_m), 114.8 (*C*N), 103.5 (C-2′), 89.3 (C-1), 81.3 (C-5′), 76.0 (C-3′), 74.7 (C-8), 74.3 (C-4′), 73.0 (C-6), 70.1 (C-2), 69.4 (C-3), 69.0 (C-4), 68.7 (C-5), 63.4 (C-6′), 62.9 (C-1′), 26.7 (*t*Bu-CH_3), 20.8, 20.6, 20.6 (CH_3), 19.2 (*t*Bu-*C*) ppm.

1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(1*E*)-3-ethoxy-3-oxo-1-propenyl]sucrose (14a) and 1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(1*Z*)-3-ethoxy-3-oxo-1-propenyl]sucrose (14b): According to the general method, **3** (100 mg, 0.150 mmol) and **5** (105 mg, 2 equiv., 0.301 mmol) were reacted for 5 min. Flash chromatography with hexane/ethyl acetate (gradient from 2:1 to 1:1) afforded **14a** (79.6 mg, 72% yield, colourless oil) and **14b** (12.5 mg, 13% yield, colourless oil). **14a**: $[\alpha]_D^{20}$ = +59.4 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 12.6 Hz, 1 H, 7-H), 5.62 (d, J = 3.6 Hz, 1 H, 1-H), 5.45 (d, J = 5.9 Hz, 1 H, 3′-H), 5.44 (t, J = 10.0 Hz, 1 H, 3-H), 5.33 (t, J = 5.9 Hz, 1 H, 4′-H), 5.27 (d, J = 12.6 Hz, 1 H, 8-H), 5.05 (t, J = 9.8 Hz, 1 H, 4-H), 4.86 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 4.24 (m, 1 H, 5-H), 4.26 (dd, $J_{5,6}$ = 6.5 Hz, $J_{4,5}$ = 10.2 Hz, 1 H, 5′-H), 4.13 (q, J = 7.1 Hz, 2 H, CH_2-CH_3), 4.13 (m, 5 H, 1′-H, 6-H, 6′β-H), 4.07 (dd, $J_{5',6'\alpha}$ = 4.1 Hz, $J_{6'\alpha,6'\beta}$ = 11.0 Hz, 1 H, 6′α-H), 2.16, 2.11, 2.10, 2.09, 2.08, 2.03, 2.01 (7 s, 21 H, 7 CH_3), 1.25 (t, J = 7.1 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 170.8, 170.3 (acetyl *C*=O), 167.9 (EtO-*C*=O), 162.1 (C-7), 104.8 (C-2′), 98.5 (C-8), 90.9 (C-1), 79.8 (C-5′), 76.3 (C-3′), 75.7 (C-4′), 71.1 (C-6′), 71.0 (C-2), 70.1 (C-3), 69.2 (C-5), 68.9 (C-4), 63.3 (C-1′), 62.5 (C-6), 60.6 (CH_2-CH_3), 21.2 (acetyl CH_3), 15.0 (CH_2-CH_3) ppm. $C_{31}H_{42}O_{20}$ (734.23): calcd. C 50.68, H 5.76; found C 50.48, H 5.83. **14b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (d, J = 7.0 Hz, 1 H, 7-H), 5.59 (d, J = 3.5 Hz, 1 H, 1-H), 5.49 (d, J = 6.7 Hz, 1 H, 3′-H), 5.43 (t, J = 10.0 Hz, 1 H, 3-H), 5.33 (t, J = 6.5 Hz, 1 H, 4′-H), 5.04 (t, J = 9.9 Hz, 1 H, 4-H), 4.88 (m, $J_{7,8}$ = 7.0 Hz, 2 H, 2-H, 8-H), 4.29 (m, 4 H, 5′-H, 6′-H, 5-H), 4.16 (m, 3 H, 1′α-H, 6-H), 4.13 (q, J = 7.3 Hz, 2 H, CH_2-CH_3), 4.06 (d, J = 12.1 Hz, 1 H, 1′β-H), 2.16, 2.10, 2.09, 2.05, 2.01 (5 s, 15 H, 5 CH_3), 1.25 (t, J = 7.1 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.1, 169.7, 169.5 (acetyl *C*=O), 164.8 (EtO-*C*=O), 158.5 (C-7), 103.8 (C-2′), 96.7 (C-8), 90.1 (C-1), 79.5 (C-5′), 75.3 (6′, C-3′), 74.6 (C-4′), 70.1 (C-2), 69.3 (C-3), 68.7 (C-5), 68.2 (C-4), 62.7 (C-1′), 62.0 (C-6), 59 ppm. 5 (CH_2-CH_3), 20.6 (acetyl CH_3), 14.2 (CH_2-CH_3) ppm.

1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(1*E*)-3-methoxy-3-oxo-1-propenyl]sucrose (15a) and 1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(1*Z*)-3-methoxy-3-oxo-1-propenyl]sucrose (15b): According to the general method, **3** (200 mg, 0.301 mmol) and **6** (201 mg, 2 equiv., 0.602 mmol) were reacted for 5 min. Flash chromatography with hexane/ethyl acetate (gradient from 2:1 to 1:1) afforded **15a** (156 mg, 72% yield, colourless oil) and **15b** (31.9 mg, 15% yield, colourless oil). **15a**: $[\alpha]_D^{20}$ = +68.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 12.6 Hz, 1 H, 7-H), 5.64 (d, J = 3.4 Hz, 1 H, 1-H), 5.47 (d, J = 5.8 Hz, 1 H, 3′-H), 5.45 (t, J = 10.1 Hz, 1 H, 3-H), 5.34 (t, J = 5.9 Hz, 1 H, 4′-H), 5.30 (d, J = 12.6 Hz, 1 H, 8-H), 5.06 (t, J = 9.8 Hz, 1 H, 4-H), 4.86 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.26 (m, 2 H, 5′-H, 5-H), 4.17 (m, 5 H, 1′-H, 6-H, 6′β-H), 4.09 (dd, $J_{5',6'\alpha}$ = 3.9 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 1 H, 6′α-H), 3.70 (s, 3 H, OCH_3), 2.17, 2.12, 2.11, 2.10, 2.05, 2.02 (6 s, 18 H, 6 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 169.9, 169.5 (acetyl *C*=O), 167.6 (MeO-*C*=O), 161.6 (C-7), 104.1 (C-2′), 97.4 (C-8), 90.2 (C-1), 79.1 (C-5′), 75.6 (C-3′), 75.0

(C-4′), 70.6 (C-6′), 70.3 (C-2), 69.4 (C-3), 68.5 (C-5), 68.2 (C-4), 62.6 (C-1′), 61.8 (C-6), 51.2 (O*C*H$_3$), 20.6, 20.5 (*C*H$_3$) ppm. $C_{30}H_{40}O_{20}$ (720.21): calcd. C 50.00, H 5.59; found C 50.06, H 5.78. **15b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.59 (d, J = 7.0 Hz, 1 H, 7-H), 5.60 (d, J = 3.3 Hz, 1 H, 1-H), 5.50 (d, J = 6.7 Hz, 1 H, 3′-H), 5.45 (t, J = 10.0 Hz, 1 H, 3-H), 5.35 (t, J = 6.3 Hz, 1 H, 4′-H), 5.05 (t, J = 9.8 Hz, 1 H, 4-H), 4.90 (d, J = 7.0 Hz, 1 H, 8-H), 4.89 (dd, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.32 (m, 1 H, 5′-H), 4.27 (m, 3 H, 5-H, 6′-H), 4.13 (m, 4 H, 6-H, 1′-H), 3.68 (s, 3 H, O*C*H$_3$), 2.17, 2.11, 2.10, 2.06, 2.02 (5 s, 15 H, 5 C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 170.1, 170.0, 169.7, 169.5 (acetyl *C*=O), 165.3 (MeO-*C*=O), 158.6 (C-7), 103.8 (C-2′), 96.6 (C-8), 90.1 (C-1), 79.5 (C-5′), 75.3 (C-3′,6′), 74.7 (C-4′), 70.1 (C-2), 69.3 (C-3), 68.7 (C-5), 68.2 (C-4), 62.7 (C-1′), 62.0 (C-6), 50.8 (O*C*H$_3$), 20.6, 20.5, 20.6 (*C*H$_3$) ppm.

1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(1*E*)-cyanovinyl]sucrose (16a) and 1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(1*Z*)-cyanovinyl]sucrose (16b): According to the general method, **3** (300 mg, 0.451 mmol) and **7** (272 mg, 2 equiv., 0.903 mmol) were reacted for 3 min. Flash chromatography with hexane/ethyl acetate (gradient from 2:1 to 1:1) afforded **16a** (212.6 mg, 69% yield, colourless oil) and **16b** (65.8 mg, 21% yield, colourless oil). **16a**: $[\alpha]_D^{20}$ = +66.4 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, J = 13.0 Hz, 1 H, 7-H), 5.63 (d, J = 3.5 Hz, 1 H, 1-H), 5.51 (d, J = 6.4 Hz, 1 H, 3′-H), 5.46 (t, J = 10.0 Hz, 1 H, 3-H), 5.32 (t, J = 6.2 Hz, 1 H, 4′-H), 5.05 (t, J = 9.8 Hz, 1 H, 4-H), 4.86 (dd, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.1 Hz, 1 H, 2-H), 4.84 (d, J = 13.0 Hz, 1 H, 8-H), 4.26 (m, 3 H, 6′-H, 5′-H), 4.17 (m, 5 H, 5-H, 1′-H, 6-H), 2.15, 2.12, 2.11, 2.10, 2.08, 2.04 (6 s, 18 H, 6 C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.1, 170.0 169.9, 169.8, 169.4 (*C*=O), 163.9 (C-7), 116.9 (*C*N), 104.1 (C-2′), 90.4 (C-1), 78.9 (C-5′), 76.8 (C-2), 75.5 (C-3′), 74.7 (C-4′), 71.3 (C-6′), 70.2 (C-8), 69.1 (C-3), 68.5 (C-5), 68.2 (C-4), 62.3 (C-1′), 61.7 (C-6), 20.5, 20.4 (*C*H$_3$) ppm. $C_{29}H_{37}NO_{18}$ (687.20): calcd. C 50.66, H 5.42, N 2.04; found C 50.69, H 5.63, N 2.04. **16b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (d, J = 6.3 Hz, 1 H, 7-H), 5.59 (d, J = 3.4 Hz, 1 H, 1-H), 5.52 (d, J = 6.8 Hz, 1 H, 3′-H), 5.44 (t, J = 9.9 Hz, 1 H, 3-H), 5.32 (t, J = 6.6 Hz, 1 H, 4′-H), 5.04 (t, J = 9.7 Hz, 1 H, 4-H), 4.88 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 4.45 (d, J = 6.3 Hz, 1 H, 8-H), 4.35 (2 d, $J_{6'\alpha,6'\beta}$ = 11.7 Hz, 2 H, 6′-H), 4.28 (q, J = 5.9 Hz, 1 H, 5′-H), 4.25 (d, J = 11.8 Hz, 1 H, 1′α-H), 4.24 (bt, J = 5.0 Hz, 1 H, 5-H), 4.19 (d, J = 12.1 Hz, 1 H, 6α-H), 4.13 (dd, $J_{5,6\beta}$ = 5.5 Hz, $J_{6\alpha,6\beta}$ = 12.6 Hz, 1 H, 6β-H), 4.05 (d, J = 12.1 Hz, 1 H, 1′β-H), 2.18, 2.14, 2.12, 2.10, 2.06, 2.02 (6 s, 18 H, 6 C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.2, 170.0, 169.7, 169.5 (*C*=O), 163.1 (C-7), 114.9 (*C*N), 103.8 (C-2′), 90.1 (C-1), 79.2 (C-5′), 75.4 (C-8), 75.2 (C-3′), 74.9 (C-6′), 74.7 (C-4′), 70.1 (C-2), 69.2 (C-3), 68.8 (C-5), 68.3 (C-4), 62.7 (C-1′), 62.0 (C-6), 20.6 (*C*H$_3$) ppm.

2,3,3′,4,4′-Penta-*O*-acetyl-1′-*O*-[(1*E*)-3-ethoxy-3-oxo-1-propenyl]-6,6′-di-*O*-TBDPS-sucrose (17a) and 2,3,3′,4,4′-Penta-*O*-acetyl-1′-*O*-[(1*Z*)-3-ethoxy-3-oxo-1-propenyl]-6,6′-di-*O*-TBDPS-sucrose (17b): According to the general method, **4** (100 mg, 0.095 mmol) and **5** (65.9 mg, 2 equiv., 0.189 mmol) were reacted for 10 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **17a** (73.3 mg, 69% yield, colourless oil) and **17b** (10.1 mg, 10% yield, colourless oil). **17a**: $[\alpha]_D^{20}$ = +64.4 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (m, 8 H, Ph-H$_o$), 7.50 (d, J = 12.5 Hz, 1 H, 7-H), 7.36 (m, 12 H, Ph-H$_{m,p}$), 5.58 (d, J = 3.6 Hz, 1 H, 1-H), 5.46 (t, J = 6.0 Hz, 1 H, 4′-H), 5.40 (d, J = 5.9 Hz, 1 H, 3′-H), 5.38 (t, J = 9.6 Hz, 1 H, 3-H), 5.31 (t, J = 9.5 Hz, 1 H, 4-H), 5.24 (d, J = 12.5 Hz, 1 H, 8-H), 4.87 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 4.16 (q, J = 7.1 Hz, 2 H, C*H*$_2$-CH$_3$), 4.05 (d, J = 11.2 Hz, 1 H, 1′α-H), 4.05 (m, 1 H, 5′-H), 3.99 (bd, J = 9.6 Hz, 1 H, 5-H), 3.82 (m, 2 H, 6′α-H, 1′β-H), 3.77 (dd, $J_{5',6'\beta}$ = 6.2 Hz, $J_{6'\alpha,6'\beta}$ = 11.6 Hz, 1 H, 6′β-H), 3.64 (d, $J_{6\alpha,6\beta}$ = 11.0 Hz, 1 H, 6α-H), 3.54 (dd, $J_{5,6\beta}$ = 2.8 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6β-H), 2.10, 2.02, 2.02, 1.99, 1.87 (5 s, 15 H, 5 C*H*$_3$), 1.26 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 1.02 (s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 169.6, 169.2 (acetyl *C*=O), 167.1 (EtO-*C*=O), 161.6 (C-7), 135.7, 135.6 (Ph-C_o), 132.9 (Ph-C_q), 129.8 (Ph-C_p), 127.8 (Ph-C_m), 103.7 (C-2′), 98.2 (C-8), 90.5 (C-1), 81.1 (C-5′), 76.6 (C-3′), 75.3 (C-4′), 70.9 (C-1′), 70.7 (C-5), 70.3 (C-2,3), 68.1 (C-4), 64.1 (C-6′), 61.5 (C-6), 59.9 (*C*H$_2$-CH$_3$), 26.8 (*t*Bu-*C*H$_3$), 20.8, 20.6 (acetyl *C*H$_3$), 19.2 (*t*Bu-*C*), 14.5 (CH$_2$-*C*H$_3$) ppm. $C_{59}H_{74}O_{18}Si_2$ (1126.44): calcd. C 62.86, H 6.62; found C 62.86, H 6.85. **17b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (m, 8 H, Ph-H$_o$), 7.36 (m, 12 H, Ph-H$_{m,p}$), 6.38 (d, J = 6.9 Hz, 1 H, 7-H), 5.66 (d, J = 3.6 Hz, 1 H, 1-H), 5.60 (d, J = 7.5 Hz, 1 H, 3′-H), 5.48 (t, J = 7.4 Hz, 1 H, 4′-H), 5.37 (t, J = 9.8 Hz, 1 H, 3-H), 5.26 (t, J = 9.7 Hz, 1 H, 4-H), 4.92 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.79 (d, J = 6.9 Hz, 1 H, 8-H), 4.24 (d, J = 11.6 Hz, 1 H, 1′α-H), 4.17 (t, J = 7.1 Hz, 2 H, C*H*$_2$-CH$_3$), 4.07 (m, $J_{4',5'}$ = 7.7 Hz, 2 H, 5′-H, 5-H), 3.84 (d, $J_{6'\alpha,6'\beta}$ = 10.8 Hz, 1 H, 6′α-H), 3.83 (d, J = 11.5 Hz, 1 H, 1′β-H), 3.78 (dd, $J_{5',6'\beta}$ = 5.6 Hz, $J_{6'\alpha,6'\beta}$ = 11.4 Hz, 1 H, 6′β-H), 3.69 (dd, $J_{5,6\alpha}$ = 1.4 Hz, $J_{6\alpha,6\beta}$ = 11.1 Hz, 1 H, 6α-H), 3.59 (dd, $J_{5,6\beta}$ = 3.3 Hz, $J_{6\alpha,6\beta}$ = 11.5 Hz, 1 H, 6β-H), 2.11, 2.01, 1.99, 1.95, 1.89 (5 s, 15 H, 5 C*H*$_3$), 1.28 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 1.03, 1.02 (2 s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.0, 169.8, 169.7, 169.2 (acetyl *C*=O), 165.0 (EtO-*C*=O), 158.2 (C-7), 135.6 (Ph-C_o), 132.9, 132.8 (Ph-C_q), 129.8, 129.7 (Ph-C_p), 127.7 (Ph-C_m), 103.4 (C-2′), 97.3 (C-8), 90.2 (C-1), 79.9 (C-5′), 76.2 (C-3′), 74.7 (C-1′), 74.5 (C-4′), 70.6 (C-5), 70.4 (C-3), 70.1 (C-2), 68.3 (C-4), 64.3 (C-6′), 61.7 (C-6), 59.7 (*C*H$_2$-CH$_3$), 27.2, 26.8 (*t*Bu-*C*H$_3$), 20.7, 20.5 (acetyl *C*H$_3$), 19.2 (*t*Bu-*C*), 14.3 (CH$_2$-*C*H$_3$) ppm.

2,3,3′,4,4′-Penta-*O*-acetyl-1′-*O*-[(1*E*)-3-methoxy-3-oxo-1-propenyl]-6,6′-di-*O*-TBDPS-sucrose (18a) and 2,3,3′,4,4′-Penta-*O*-acetyl-1′-*O*-[(1*Z*)-3-methoxy-3-oxo-1-propenyl]-6,6′-di-*O*-TBDPS-sucrose (18b): According to the general method, **4** (100 mg, 0.095 mmol) and **6** (63.2 mg, 2 equiv., 0.189 mmol) were reacted for 10 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **18a** (69.3 mg, 66% yield, colourless oil) and **18b** (13.6 mg, 14% yield, colourless oil). **18a**: $[\alpha]_D^{20}$ = +42.8 (c = 1.0, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (t, J = 7.3 Hz, 8 H, Ph-H$_o$), 7.50 (d, J = 12.5 Hz, 1 H, 7-H), 7.35 (m, 12 H, Ph-H$_{m,p}$), 5.58 (d, J = 3.6 Hz, 1 H, 1-H), 5.46 (t, J = 6.0 Hz, 1 H, 4′-H), 5.40 (d, J = 5.9 Hz, 1 H, 3′-H), 5.37 (t, J = 9.2 Hz, 1 H, 3-H), 5.31 (t, J = 9.5 Hz, 1 H, 4-H), 5.26 (d, J = 12.4 Hz, 1 H, 8-H), 4.87 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 4.06 (m, 2 H, 5′-H, 1′α-H), 3.99 (bd, J = 9.3 Hz, 1 H, 5-H), 3.82 (m, 2 H, 6′α-H, 1′β-H), 3.77 (dd, $J_{5',6'\beta}$ = 6.1 Hz, $J_{6'\alpha,6'\beta}$ = 11.0 Hz, 1 H, 6′β-H), 3.69 (s, 3 H, O*C*H$_3$), 3.64 (bd, $J_{6\alpha,6\beta}$ = 12.1 Hz, 1 H, 6α-H), 3.54 (dd, $J_{5,6\beta}$ = 2.9 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6β-H), 2.11, 2.03, 2.02, 1.99, 1.87 (5 s, 15 H, 5 C*H*$_3$), 1.02 (s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.1, 169.8, 169.6, 169.2 (acetyl *C*=O), 167.6 (MeO-*C*=O), 161.9 (C-7), 135.6, 135.5 (Ph-C_o), 133.1, 133.0, 132.9 (Ph-C_q), 129.7, 129.6 (Ph-C_p), 127.7, 127.7 (Ph-C_m), 103.6 (C-2′), 97.9 (C-8), 90.4 (C-1), 81.1 (C-5′), 76.5 (C-3′), 75.2 (C-4′), 71.1 (C-1′), 70.6 (C-5), 70.3 (C-2,4), 68.1 (C-3), 64.1 (C-6′), 61.4 (C-6), 51.2 (O*C*H$_3$), 26.7 (*t*Bu-*C*H$_3$), 20.8, 20.6, 20.5 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm. $C_{58}H_{72}O_{18}Si_2$ (1112.43): calcd. C 62.57, H 6.52; found C 62.25, H 6.48. **18b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (m, 8 H, Ph-H$_o$), 7.35 (m, 12 H, Ph-H$_{m,p}$), 6.39 (d, J = 6.9 Hz, 1 H, 7-H), 5.66 (d, J = 3.7 Hz, 1 H, 1-H), 5.61 (d, J = 7.3 Hz, 1 H, 3′-H), 5.48 (t, J = 7.3 Hz, 1 H, 4′-H), 5.37 (t, J = 9.8 Hz, 1 H, 3-H), 5.25 (t, J =

9.8 Hz, 1 H, 4-H), 4.91 (dd, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.81 (d, J = 6.9 Hz, 1 H, 8-H), 4.25 (d, J = 11.6 Hz, 1 H, 1′α-H), 4.07 (q, J = 5.6 Hz, 1 H, 5′-H), 4.04 (m, $J_{5,6\alpha}$ = 1.7 Hz, $J_{5,6\beta}$ = 3.5 Hz, 1 H, 5-H), 3.84 (d, J = 11.7 Hz, 1 H, 1′β-H), 3.83 (m, 1 H, 6′α-H), 3.78 (dd, $J_{5',6'\beta}$ = 5.5 Hz, $J_{6'\alpha,6'\beta}$ = 11.3 Hz, 1 H, 6′β-H), 3.70 (s, 3 H, OCH_3), 3.68 (d, $J_{5,6\alpha}$ = 2.0 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6α-H), 3.59 (dd, $J_{5,6\beta}$ = 3.6 Hz, $J_{6\alpha,6\beta}$ = 11.5 Hz, 1 H, 6β-H), 2.11, 2.01, 1.99, 1.95, 1.89 (5 s, 15 H, 5 CH_3), 1.03, 1.02 (2 s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.1, 169.9, 169.8, 169.3 (acetyl *C*=O), 165.5 (MeO-*C*=O), 158.4 (C-7), 135.6 (Ph-C_o), 133.0 (Ph-C_q), 129.8, 129.7, 129.7 (Ph-C_p), 127.7 (Ph-C_m), 103.5 (C-2′), 97.0 (C-8), 90.3 (C-1), 79.9 (C-5′), 76.3 (C-3′), 74.7, 74.6 (C-1′,4′), 70.6 (C-5), 70.4 (C-3), 70.1 (C-2), 68.3 (C-4), 64.3 (C-6′), 61.7 (C-6), 51.0 (O*C*H$_3$), 26.8, 26.7 (*t*Bu-*C*H$_3$), 20.8, 20.7, 20.7, 20.6, 20.5 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm.

2,3,3′,4,4′-Penta-*O*-acetyl-1′-*O*-[(1*E*)-cyanovinyl]-6,6′-di-*O*-TBDPS-sucrose (19a) and 2,3,3′,4,4′-Penta-*O*-acetyl-1′-*O*-[(1*Z*)-cyanovinyl]-6,6′-di-*O*-TBDPS-sucrose (19b): According to the general method, **4** (100 mg, 0.095 mmol) and **7** (57 mg, 2 equiv., 0.189 mmol) were reacted for 5 min. Flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:4) afforded **19a** (64.8 mg, 63% yield, colourless oil) and **19b** (14.2 mg, 14% yield, colourless oil). **19a**: $[\alpha]_D^{20}$ = +48.3 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, J = 7.4 Hz, J = 14.6 Hz, 8 H, Ph-H$_o$), 7.37 (m, 12 H, Ph-H$_{m,p}$), 7.04 (d, J = 12.8 Hz, 1 H, 7-H), 5.56 (d, J = 3.6 Hz, 1 H, 1-H), 5.47 (t, J = 6.4 Hz, 1 H, 4′-H), 5.36 (t, J = 10.0 Hz, 1 H, 3-H), 5.35 (d, J = 6.7 Hz, 1 H, 3′-H), 5.26 (t, J = 9.7 Hz, 1 H, 4-H), 4.86 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.70 (d, J = 12.8 Hz, 1 H, 8-H), 4.05 (d, J = 11.3 Hz, 1 H, 1′α-H), 4.04 (q, J = 6.0 Hz, 1 H, 5′-H), 3.98 (ddd, $J_{5,6\alpha}$ = 2.0 Hz, $J_{5,6\beta}$ = 3.3 Hz, $J_{4,5}$ = 10.1 Hz, 1 H, 5-H), 3.85 (dd, $J_{5',6'\alpha}$ = 5.7 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 1 H, 6′α-H), 3.81 (d, J = 11.3 Hz, 1 H, 1′β-H), 3.78 (dd, $J_{5',6'\beta}$ = 6.1 Hz, $J_{6'\alpha,6'\beta}$ = 11.0 Hz, 1 H, 6′β-H), 3.64 (dd, $J_{5,6\alpha}$ = 2.0 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6α-H), 3.57 (dd, $J_{5,6\beta}$ = 3.5 Hz, $J_{6\alpha,6\beta}$ = 11.7 Hz, 1 H, 6β-H), 2.11, 2.02, 1.99, 1.88 (4 s, 12 H, 4 CH_3), 1.04, 1.02 (2 s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.5, 169.2 (*C*=O), 164.1 (C-7), 135.6, 135.5 (Ph-C_o), 133.0, 132.8, 132.8 (Ph-C_q), 129.9, 129.8 (Ph-C_p), 127.8, 127.7 (Ph-C_m), 116.7 (*C*N), 103.4 (C-2′), 90.5 (C-1), 80.8 (C-5′), 77.3 (C-8), 76.3 (C-3′), 75.0 (C-4′), 71.7 (C-1′), 70.8 (C-5), 70.2, 70.1 (C-2,4), 68.1 (C-3), 64.2 (C-6′), 61.6 (C-6), 26.7 (*t*Bu-*C*H$_3$), 20.7, 20.6, 20.5 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm. $C_{57}H_{69}NO_{16}Si_2$ (1079.42): calcd. C 63.37, H 6.44, N 1.30; found C 63.37, H 6.46, N 1.22. **19b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (m, 8 H, Ph-H$_o$), 7.35 (m, 12 H, Ph-H$_{m,p}$), 6.66 (d, J = 6.4 Hz, 1 H, 7-H), 5.58 (d, J = 3.6 Hz, 1 H, 1-H), 5.45 (t, J = 6.6 Hz, 1 H, 4′-H), 5.36 (d, J = 6.7 Hz, 1 H, 3′-H), 5.35 (t, J = 9.8 Hz, 1 H, 3-H), 5.26 (t, J = 9.7 Hz, 1 H, 4-H), 4.88 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.36 (d, J = 6.3 Hz, 1 H, 8-H), 4.25 (d, J = 11.6 Hz, 1 H, 1′α-H), 4.05 (dd, J = 5.6 Hz, J = 11.9 Hz, 1 H, 5′-H), 4.00 (ddd, $J_{5,6\alpha}$ = 2.0 Hz, $J_{5,6\beta}$ = 3.7 Hz, $J_{4,5}$ = 10.1 Hz, 1 H, 5-H), 3.93 (d, J = 11.6 Hz, 1 H, 1′β-H), 3.83 (dd, $J_{5',6'\alpha}$ = 5.7 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 1 H, 6′α-H), 3.77 (dd, $J_{5',6'\beta}$ = 5.6 Hz, $J_{6'\alpha,6'\beta}$ = 11.2 Hz, 1 H, 6′β-H), 3.67 (dd, $J_{5,6\alpha}$ = 1.6 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6α-H), 3.58 (dd, $J_{5,6\beta}$ = 3.4 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6β-H), 2.10, 2.02, 1.99, 1.88 (4 s, 12 H, 4 CH_3), 1.03, 1.02 (2 s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.1, 169.9, 169.8, 169.7, 169.2 (*C*=O), 163.3 (C-7), 135.7, 135.6 (Ph-C_o), 133.0, 132.9, 132.8 (Ph-C_q), 129.8, 129.8, 129.7 (Ph-C_p), 127.8, 127.7 (Ph-C_m), 114.6 (*C*N), 103.3 (C-2′), 90.4 (C-1), 80.7 (C-5′), 76.8 (C-3′), 75.4 (C-8), 74.7 (C-1′), 74.6 (C-4′), 70.8 (C-5), 70.2, 70.2 (C-2,3), 68.2 (C-4), 64.1 (C-6′), 61.6 (C-6), 26.8, 26.7 (*t*Bu-*C*H$_3$), 20.8, 20.5 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm.

Synthesis of Bromide Derivatives

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-bromo-6-deoxy-6′-*O*-TBDPS-sucrose (26): A solution of 6′-*O*-TBDPS-sucrose[51] (4.56 g, 7.86 mmol) in pyridine (52 mL) was cooled with an ice bath and treated with triphenylphosphane (6.18 g, 3 equiv., 0.024 mol), followed by the dropwise addition (over 30 min) of a solution of carbon tetrabromide (3.91 g, 1.5 equiv., 0.012 mol) in pyridine (12 mL). The reaction mixture was heated to 60 °C and stirred for 1 h. After the addition of methanol (17 mL), the system was allowed to reach room temp. The solvents were removed, and the residue was purified by flash chromatography with ethyl acetate/acetone/water (10:10:0.5) to give 6-bromo-6-desoxy-6′-*O*-TBDPS-sucrose as a colourless oil (3.11 g, 62% yield). A solution of 6-bromo-6-desoxy-6′-*O*-TBDPS-sucrose (3.62 g, 5.62 mmol) in pyridine (100 mL) was cooled with ice and treated with acetic anhydride (3.8 mL, 1.2 equiv./OH, 0.040 mol). The reaction mixture was stirred overnight at room temp. The solvent was removed, and the residue was purified by flash chromatography with hexane/diethyl ether (1:4), yielding a colourless oil, which crystallized from dichloromethane/diethyl ether as colourless needles of **26** (4.8 g, 95% yield). M.p. 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (m, 4 H, Ph-H$_o$), 7.40 (m, 6 H, Ph-H$_{m,p}$), 5.63 (d, J = 3.7 Hz, 1 H, 1-H), 5.54 (t, J = 5.6 Hz, 1 H, 4′-H), 5.40 (t, J = 9.8 Hz, 1 H, 3-H), 5.39 (d, J = 5.6 Hz, 1 H, 3′-H), 5.05 (t, J = 9.7 Hz, 1 H, 4-H), 4.82 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.18 (m and 2 d, $J_{1',1'\beta}$ = 12.3 Hz, 3 H, 1′-H, 5-H), 4.11 (dd, J = 5.9 Hz, J = 11.6 Hz, 1 H, 5′-H), 3.89 (dd, $J_{5',6'\alpha}$ = 5.4 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 1 H, 6′α-H), 3.86 (dd, $J_{5',6'\beta}$ = 6.0 Hz, $J_{6'\alpha,6'\beta}$ = 10.8 Hz, 1 H, 6′β-H), 3.37 (dd, $J_{5,6\alpha}$ = 2.8 Hz, $J_{6\alpha,6\beta}$ = 11.5 Hz, 1 H, 6α-H), 3.23 (dd, $J_{5,6\beta}$ = 4.3 Hz, $J_{6\alpha,6\beta}$ = 11.5 Hz, 1 H, 6β-H), 2.14, 2.10, 2.09, 2.05, 2.01, 1.98 (6 s, 18 H, 6 CH_3), 1.07 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 170.0, 169.9, 169.8, 169.7, 169.3 (*C*=O), 135.6 (Ph-C_o), 133.0, 133.0 (Ph-C_q), 129.9 (Ph-C_p), 127.8, 127.8 (Ph-C_m), 103.8 (C-2′), 89.8 (C-1), 81.5 (C-5′), 76.3 (C-3′), 75.3 (C-4′), 70.6 (C-4), 70.1 (C-2), 69.6 (C-3), 68.6 (C-5), 63.9 (C-6′), 62.9 (C-1′), 31.2 (C-6), 26.8 (*t*Bu-*C*H$_3$), 20.8, 20.7, 20.6, 20.6 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm.

1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-bromo-6′-deoxysucrose (27): A solution of sucrose (2 g, 5.84 mmol) in pyridine (70 mL) was cooled with an ice bath and treated with triphenylphosphane (3.68 g, 2.4 equiv., 0.014 mol), followed by the dropwise addition of a solution of carbon tetrabromide (2.33 g, 1.2 equiv., 7.01 mmol) in pyridine (7 mL). The reaction mixture was heated to 60 °C and stirred for 1.5 h. After re-cooling the mixture with an ice bath, acetic anhydride was added (4.6 mL, 1.2 equiv./OH, 0.049 mol), and the mixture was stirred overnight at room temp. The solvent was removed, and the residue was purified by flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:3 to diethyl ether) to yield **27** as a colourless oil (1.55 g, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75 (d, J = 3.6 Hz, 1 H, 1-H), 5.45 (t, J = 9.9 Hz, 1 H, 3-H), 5.44 (d, J = 5.9 Hz, 1 H, 3′-H), 5.42 (t, J = 5.7 Hz, 1 H, 4′-H), 5.11 (t, J = 9.7 Hz, 1 H, 4-H), 4.87 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 4.36 (dd, $J_{5,6\alpha}$ = 4.4 Hz, $J_{6\alpha,6\beta}$ = 12.1 Hz, 1 H, 6α-H), 4.30 (dd, $J_{5,6\beta}$ = 5.6 Hz, $J_{6\alpha,6\beta}$ = 11.9 Hz, 1 H, 6β-H), 4.30 (m, 1 H, 5-H), 4.21 (dd, J = 5.4 Hz, J = 10.6 Hz, 1 H, 5′-H), 4.19 (m, 2 H, 1′-H), 3.60 (dd, $J_{5',6'\alpha}$ = 2.7 Hz, $J_{6'\alpha,6'\beta}$ = 11.6 Hz, 1 H, 6′α-H), 3.42 (dd, $J_{5',6'\beta}$ = 4.4 Hz, $J_{6'\alpha,6'\beta}$ = 11.5 Hz, 1 H, 6′β-H), 2.17, 2.13, 2.12, 2.11, 2.10, 2.07, 2.02 (7 s, 21 H, 7 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.1, 170.0, 169.9, 169.6, 169.3 (*C*=O), 104.0 (C-2′), 89.8 (C-1), 79.1 (C-5′), 75.7 (C-3′), 74.8 (C-4′), 70.6 (C-4), 70.2 (C-2), 69.5 (C-3), 68.8 (C-5), 63.4 (C-6), 63.0 (C-1′), 31.2 (C-6′), 20.5, 20.7, 20.7, 20.6, 20.6, (*C*H$_3$) ppm.

2,3,3′,4,4′-Penta-*O*-acetyl-1′-bromo-1′-deoxy-6,6′-di-*O*-TBDPS-sucrose (28): A solution of 6,6′-di-*O*-TBDPS-sucrose[51] (2 g, 2.44 mmol) in pyridine (16 mL) was cooled with an ice bath and treated with triphenylphosphane (1.92 g, 3 equiv., 7.33 mmol), followed by the portionwise addition of carbon tetrabromide (1.22 g, 1.5 equiv., 3.66 mmol). The reaction mixture was heated to 60 °C and stirred for 2 d. After re-cooling the mixture with an ice bath, acetic anhydride was added (1.4 mL, 1.2 equiv./OH, 0.015 mol), and the mixture was stirred overnight at room temp. The solvent was removed, and the residue was purified by flash chromatography with hexane/diethyl ether (1:1) to yield **28** as a colourless oil (0.639 g, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (m, 8 H, Ph-H$_o$), 7.36 (m, 12 H, Ph-H$_{m,p}$), 5.65 (d, J = 5.6 Hz, 1 H, 3′-H), 5.63 (d, J = 3.7 Hz, 1 H, 1-H), 5.43 (t, J = 5.8 Hz, 1 H, 4′-H), 5.41 (t, J = 10.1 Hz, 1 H, 3-H), 5.29 (t, J = 9.7 Hz, 1 H, 4-H), 4.89 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.08 (m, 2 H, 5′-H, 5-H), 3.85 (dd, $J_{5',6'\alpha}$ = 5.6 Hz, $J_{6'\alpha,6'\beta}$ = 10.8 Hz, 1 H, 6′α-H), 3.78 (dd, $J_{5',6'\beta}$ = 6.0 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 1 H, 6′β-H), 3.66 (dd, $J_{5,6\alpha}$ = 1.8 Hz, $J_{6\alpha,6\beta}$ = 11.6 Hz, 1 H, 6α-H), 3.60 (d, J = 11.3 Hz, 1 H, 1′α-H), 3.58 (dd, $J_{5,6\beta}$ = 3.5 Hz, $J_{6\alpha,6\beta}$ = 11.2 Hz, 1 H, 6β-H), 3.52 (d, J = 11.6 Hz, 1 H, 1′β-H), 2.11, 2.04, 2.02, 2.00, 1.87 (5 s, 15 H, 5 CH_3), 1.03 (s, 18 H, 2 *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 170.2, 169.7, 169.2 (*C*=O), 135.7, 135.6 (Ph-C_o), 133.0, 132.9 (Ph-C_q), 129.6 (Ph-C_p), 127.7 (Ph-C_m), 104.1 (C-2′), 90.6 (C-1), 81.3 (C-5′), 77.0 (C-3′), 75.6 (C-4′), 70.6 (C-5), 70.3, 70.2 (C-2,3), 68.2 (C-4), 64.2 (C-6′), 61.5 (C-6), 32.6 (C-1′), 26.7 (*t*Bu-*C*H$_3$), 20.8, 20.6 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm.

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-formyl-6′-*O*-TBDPS-sucrose (2): A solution of **26** (3 g, 3.35 mmol) in DMF (67 mL) was treated with sodium formate (1.14 g, 5 equiv., 0.017 mol). The reaction mixture was heated to 110 °C and stirred for 3 h. The solvent was removed, the residue was dissolved in dichloromethane and water, and the product was extracted with dichloromethane. The combined organic layers were dried and concentrated to leave a brown residue, which was subjected to flash chromatography with hexane/diethyl ether (gradient from 1:1 to 1:2 to 1:3 to diethyl ether) to provide a colourless oil. The product (**2**) was crystallized from the oil with dichloromethane/diethyl ether as colourless needles (2.47 g, 86% yield). M.p. 127–128 °C. $[\alpha]_D^{20}$ = +50.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1 H, *H*C=O), 7.65 (m, 4 H, Ph-H$_o$), 7.41 (m, 6 H, Ph-H$_{m,p}$), 5.61 (d, J = 3.7 Hz, 1 H, 1-H), 5.52 (t, J = 6.0 Hz, 1 H, 4′-H), 5.41 (d, J = 5.9 Hz, 1 H, 3′-H), 5.40 (t, J = 10.0 Hz, 1 H, 3-H), 4.99 (t, J = 9.9 Hz, 1 H, 4-H), 4.81 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 4.23 (td, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 3.3 Hz, 1 H, 5-H), 4.11 (m, 5 H, 1′-H, 5′-H, 6-H), 3.87 (dd, $J_{5',6'\alpha}$ = 5.5 Hz, $J_{6'\alpha,6'\beta}$ = 10.9 Hz, 1 H, 6′α-H), 3.84 (dd, $J_{5',6'\beta}$ = 5.8 Hz, $J_{6'\alpha,6'\beta}$ = 11.0 Hz, 1 H, 6′β-H), 2.14, 2.10, 2.09, 2.05, 2.01, 1.98 (6 s, 18 H, 6 CH$_3$), 1.06 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 167.0, 169.8, 169.7, 169.5, 169.3 (acetyl *C*=O), 160.4 (formyl *C*=O), 135.6 (Ph-C_o), 133.0, 132.9 (Ph-C_q), 129.9 (Ph-C_p), 127.8, 127.7 (Ph-C_m), 103.5 (C-2′), 89.5 (C-1), 81.4 (C-5′), 76.1 (C-3′), 75.0 (C-4′), 70.1 (C-2), 69.7 (C-3), 68.4 (C-4), 68.1 (C-5), 63.9 (C-6′), 63.1 (C-6), 61.2 (C-1′), 26.7 (*t*Bu-*C*H$_3$), 20.8, 20.7, 20.6 (*C*H$_3$), 19.2 (*t*Bu-*C*) ppm. $C_{41}H_{52}O_{18}Si$ (860.29): calcd. C 57.20, H 6.09; found C 57.25, H 6.31.

Esterification of Sugar Bromides

Method A (Xylene as Solvent): A mixture of K_2CO_3 (2 equiv.), TBAI (0.2 equiv.), unsaturated carboxylic acid (2 equiv.) and Ag_2CO_3 (2 equiv., added only for D-glucose and sucrose derivatives) in xylene (0.5 mL) was stirred at room temperature in an open vessel. After 5 min, a solution of sugar bromide (1 equiv.) in xylene (0.5 mL) was added and the mixture was placed in a MW reactor at 600 W for 5 min for xylose derivative **23** and for the times indicated in Table 4 for the glucose and sucrose derivatives. After cooling, the reaction mixture was diluted with ethyl acetate, filtered, and the solvent was removed. Preparative chromatography with the eluent system indicated for each case afforded the pure products.

Method A (Water/Acetone as Solvent): A mixture of carboxylic acid (2 equiv.), saturated aqueous K_2CO_3 (0.5 mL), TBAI (0.2 equiv.), Ag_2CO_3 (2 equiv., added only for the D-glucose and sucrose derivatives) and a solution of sugar bromide (1 equiv.) in acetone (0.5 mL) was sealed in a glass tube and placed in a MW reactor at 100 W for 5 min for xylose derivative **23** and for the times indicated in Tables 4 and 5 for the other sugar derivatives. After cooling, the crude mixture was extracted with ethyl acetate, the organic layer was dried with Na_2SO_4 and filtered, and the solvents were evaporated to dryness. The pure products were obtained by preparative layer chromatography with the eluent system indicated for each case.

Method B (Pyridine as Solvent): A mixture of sugar bromide (1 equiv.), unsaturated carboxylic acid (2 equiv.), Ag_2CO_3 (2 equiv., added only for the D-glucose and sucrose derivatives) and pyridine (10 mL) was refluxed in a MW reactor at 600 W for 5 min for xylose derivative **23** and for the times indicated in Table 4 for the glucose and sucrose derivatives. After cooling, the crude mixture was filtered, and the solvents were evaporated to dryness. Preparative chromatography with the eluent system indicated for each case afforded the pure products.

Method B (TMG as Solvent): A mixture of sugar bromide (1 equiv.), carboxylic acid (2 equiv.) and TMG (1 mL) was placed in a MW reactor at 100 W for 5 min for xylose derivative **23** and for the times indicated in Tables 4 and 5 for the other sugar derivatives. After cooling, the crude mixture was purified by preparative chromatography with the eluent system indicated for each case, affording the pure products.

2,3,4-Tri-*O*-benzoyl-1-*O*-methacryloyl-α-D-xylopyranose (29a) and 2,3,4-Tri-*O*-benzoyl-1-*O*-methacryloyl-β-D-xylopyranose (29b): Purification by preparative chromatography (dichloromethane) led to the two anomers **29a** (31% yield after 5 min with method A in xylene and 9% yield after 5 min in water/acetone; colourless oil) and **29b** (34% yield after 5 min with method A in xylene and 61% yield after 5 min in water/acetone; colourless oil). **29a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (m, 6 H, Ph-H$_o$), 7.44 (m, 9 H, Ph-H$_{m,p}$), 6.58 (d, J = 3.6 Hz, 1 H, 1-H), 6.34 (s, 1 H, C=C*H*^{a}H^b), 6.16 (t, J = 9.8 Hz, 1 H, 3-H), 5.76 (s, 1 H, C=CH^a*H*^{b}), 5.55 (dd, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.6 Hz, 1 H, 2-H), 5.49 (ddd, $J_{4,5ax}$ = 10.0 Hz, $J_{4,5eq}$ = 5.6 Hz, $J_{3,4}$ = 10.0 Hz, 1 H, 4-H), 4.27 (dd, $J_{5eq,5ax}$ = 11.2 Hz, $J_{4,5eq}$ = 5.7 Hz, 1 H, 5$_{eq}$-H), 3.96 (t, J = 10.9 Hz, 1 H, 5$_{ax}$-H), 2.01 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 165.5, 165.3, 165.2 (*C*=O), 135.4 (*C* =CH$_2$), 133.5–128.4 (Ph-*C*), 127.4 (C =*C*H$_2$), 89.9 (C-1), 70.2 (C-2), 69.8 (C-3), 69.4 (C-4), 61.2 (C-5), 18.2 (*C*H$_3$) ppm. **29b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (m, 6 H, Ph-H$_o$), 7.45 (m, 9 H, Ph-H$_{m,p}$), 6.19 (s, 1 H, C=C*H*^{a}H^b), 6.16 (d, J = 5.3 Hz, 1 H, 1-H), 5.84 (t, J = 6.8 Hz, 1 H, 3-H), 5.62 (s, 1 H, C=CH^a*H*^{b}), 5.57 (dd, $J_{2,3}$ = 6.8 Hz, $J_{1,2}$ = 5.2 Hz, 1 H, 2-H), 5.40 (ddd, $J_{4,5ax}$ = 6.6 Hz, $J_{4,5eq}$ = 4.0 Hz, $J_{3,4}$ = 6.8 Hz, 1 H, 4-H), 4.50 (dd, $J_{5eq,5ax}$ = 12.4 Hz, $J_{4,5eq}$ = 4.0 Hz, 1 H, 5$_{eq}$-H), 3.93 (dd, $J_{5ax,5eq}$ = 12.4 Hz, $J_{4,5ax}$ = 6.6 Hz, 1 H, 5$_{ax}$-H), 1.91 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 165.2, 165.1, 164.9 (*C*=O), 135.1 (*C* =CH$_2$), 133.4–128.3 (Ph-*C*), 127.6 (C =*C*H$_2$), 92.2 (C-1), 69.6 (C-3), 68.9 (C-2), 68.4 (C-4), 62.12 (C-5), 18.0 (*C*H$_3$) ppm.

2,3,4-Tri-*O*-benzoyl-1-*O*-[(*E*)-3-methyl-2-propenyl]-α-D-xylopyranose (30a) and 2,3,4-Tri-*O*-benzoyl-1-*O*-[(*E*)-3-methyl-2-propenyl]-β-D-xylopyranose (30b): Purification by preparative chromatography (dichloromethane) led to the two anomers **30a** (30% yield after 5 min with method A in xylene and 9% yield after 5 min in water/acetone; colourless oil) and **30b** (38% yield after 5 min with method A in xylene and 53% yield after 5 min in water/acetone; colourless oil). **30a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (m, 6 H, Ph-H$_o$), 7.43 (m, 9 H, Ph-H$_{m,p}$), 7.14 [dq, J = 15.6 Hz, J = 6.9 Hz, 1 H, HC=C(*H*)CH$_3$], 6.59 (d, J = 3.7 Hz, 1 H, 1-H), 6.17 (t, J = 9.8 Hz, 1 H, 3-H), 5.99 [dq, J = 15.5 Hz, J = 1.7 Hz, 1 H, *H*C=C(H)CH$_3$], 5.54 (dd, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.6 Hz, 1 H, 2-H), 5.49 (m, 1 H, 4-H), 4.25 (dd, $J_{5eq,5ax}$ = 11.2 Hz, $J_{4,5eq}$ = 5.8 Hz, 1 H, 5$_{eq}$-H), 3.96 (t, J = 10.9 Hz, 1 H, 5$_{ax}$-H), 1.94 (dd, J = 6.9 Hz, J = 1.7 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 165.5, 165.3, 164.1 (*C*=O), 147.4 [HC =*C*(H)CH$_3$], 133.4–128.4 (Ph-*C*), 121.6 [H*C*=C(H)CH$_3$], 89.4 (C-1), 70.2 (C-2), 69.9 (C-3), 69.5 (C-4), 60.9 (C-5), 18.2 (*C*H$_3$) ppm. **30b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (m, 6 H, Ph-H$_o$), 7.43 (m, 9 H, Ph-H$_{m,p}$), 7.04 [dq, J = 15.5 Hz, J = 6.9 Hz, 1 H, HC=C(*H*)CH$_3$], 6.20 (d, J = 5.1 Hz, 1 H, 1-H), 5.83 [m, 2 H, *H*C=C(H)CH$_3$, 3-H], 5.53 (dd, $J_{2,3}$ = 6.5 Hz, $J_{1,2}$ = 5.2 Hz, 1 H, 2-H), 5.38 (ddd, $J_{4,5ax}$ = 6.4 Hz, $J_{4,5eq}$ = 4.0 Hz, $J_{3,4}$ = 6.4 Hz, 1 H, 4-H), 4.50 (dd, $J_{5eq,5ax}$ = 12.4 Hz, $J_{4,5eq}$ = 4.0 Hz, 1 H, 5$_{eq}$-H), 3.93 (dd, $J_{5ax,5eq}$ = 12.4 Hz, $J_{4,5ax}$ = 6.3 Hz, 1 H, 5$_{ax}$-H), 1.81 (dd, J = 6.9 Hz, J = 1.6 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 165.0, 164.0 (*C*=O), 147.5 [HC=*C*(H)CH$_3$], 133.4–128.4 (Ph-*C*), 121.5 [H*C*=C(H)CH$_3$], 91.7 (C-1), 69.5 (C-2), 68.8 (C-3), 68.4 (C-4), 62.0 (C-5), 18.1 (*C*H$_3$) ppm.

2,3,4-Tri-*O*-benzoyl-1-*O*-[(*E*)-3-phenyl-2-propenyl]-α-D-xylopyranose (31a) and 2,3,4-Tri-*O*-benzoyl-1-*O*-[(*E*)-3-phenyl-2-propenyl]-β-D-xylopyranose (31b): Purification by preparative chromatography (dichloromethane) led to the two anomers **31a** (30% yield after 5 min with method A in xylene and 11% yield after 5 min in water/acetone; colourless oil) and **31b** (38% yield after 5 min with method A in xylene and 56% yield after 5 min in water/acetone; colourless oil). **31a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (m, 6 H, Ph-H$_o$), 7.81 [d, J = 16.0 Hz, 1 H, HC=C(*H*)Ph], 7.47 (m, 14 H, Ph-H$_{m,p}$), 6.67 (d, J = 3.6 Hz, 1 H, 1-H), 6.62 [d, J = 16.0 Hz, 1 H, *H*C=C(H)Ph], 6.24 (t, J = 9.8 Hz, 1 H, 3-H), 5.58 (dd, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.6 Hz, 1 H, 2-H), 5.52 (ddd, $J_{4,5ax}$ = 10.2 Hz, $J_{4,5eq}$ = 5.8 Hz, $J_{3,4}$ = 9.8 Hz, 1 H, 4-H), 4.28 (dd, $J_{5eq,5ax}$ = 11.2 Hz, $J_{4,5eq}$ = 5.8 Hz, 1 H, 5$_{eq}$-H), 4.03 (t, J = 10.9 Hz, 1 H, 5$_{ax}$-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 165.4, 165.3, 164.8 (*C*=O), 147.1 [HC=*C*(H)Ph], 133.9–128.4 (Ph-*C*), 116.5 [H*C*=C(H)Ph], 89.7 (C-1), 70.2 (C-2), 69.9 (C-3), 69.5 (C-4), 61.0 (C-5) ppm. **31b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (m, 5 H, Ph-H$_o$), 7.74 [d, J = 16.0 Hz, 1 H, HC=C(*H*)Ph], 7.44 (m, 15 H, Ph-H$_{m,p}$), 6.41 [d, J = 16.0 Hz, 1 H, *H*C=C(H)Ph], 6.26 (d, J = 5.0 Hz, 1 H, 1-H), 5.83 (t, J = 6.5 Hz, 1 H, 3-H), 5.58 (dd, $J_{2,3}$ = 6.5 Hz, $J_{1,2}$ = 5.1 Hz,1 H, 2-H), 5.40 (ddd, $J_{4,5ax}$ = 6.3 Hz, $J_{4,5eq}$ = 3.9 Hz, $J_{3,4}$ = 6.3 Hz, 1 H, 4-H), 4.54 (dd, $J_{5eq,5ax}$ = 12.4 Hz, $J_{4,5eq}$ = 3.8 Hz, 1 H, 5$_{eq}$-H), 3.96 (dd, $J_{5ax,5eq}$ = 12.4 Hz, $J_{4,5ax}$ = 6.2 Hz, 1 H, 5$_{ax}$-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 165.0, 164.7, 147.0 [HC=*C*(H)Ph], 133.9–128.3 (Ph-*C*), 116.5 [H*C*=C(H)Ph], 91.9 (C-1), 69.5 (C-3), 68.8 (C-2), 68.3 (C-4), 62.0 (C-5) ppm.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[(*E*)-3-phenyl-2-propenyl]-α-D-glucopyranoside (32): Purification by preparative chromatography (hexane/diethyl ether, 1:4) yielded **32** as a colourless oil (57% yield after 10 min with method A in xylene, 17% yield after 7 min in water/acetone, 6% yield after 30 min in water/acetone, 67% yield after 10 min with method B in pyridine and 74% yield after 5 min in TMG). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 [d, J = 16.0 Hz, 1 H, HC=C(*H*)Ph], 7.55 (m, 2 H, Ph-H$_o$), 7.39 (m, 3 H, Ph-H$_{m,p}$), 6.48 [d, J = 16.0 Hz, 1 H, *H*C=C(H)Ph], 5.51 (t, J = 9.7 Hz, 1 H, 3-H), 5.13 (t, J = 9.8 Hz, 1 H, 4-H), 4.98 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.94 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.34 (m, 2 H, 6-H), 4.08 (m, 1 H, 5-H), 3.43 (s, 3 H, OC*H*$_3$), 2.08, 2.05, 2.02 (3 s, 9 H, 3 C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.11, 170.06, 169.6, 166.5 (*C*=O), 145.7 (HC =*C*(H)Ph), 134.2 (Ph-C_q), 130.5 (Ph-C_p), 128.9, 128.2 (Ph-$C_{o,m}$) 117.2 [H*C*=C(H)Ph], 96.8 (C-1), 70.8 (C-2), 70.2 (C-3), 68.8 (C-4), 67.2 (C-5), 62.1 (C-6), 55.5 (O*C*H$_3$), 20.71, 20.68, 20.65 (*C*H$_3$) ppm.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-[(*E*)-3-phenyl-2-propenyl]-α-D-glucopyranoside (33): Purification by preparative chromatography (hexane/diethyl ether, 1:1) yielded **33** as a colourless oil (27% yield after 12 min with method A in water/acetone, 6% yield after 80 min in water/acetone and 53% yield after 30 min with method B in TMG). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (m, 4 H, Ph-H), 7.89 (m, 2 H, Ph-H), 7.71 [d, J = 16.0 Hz, 1 H, HC=C(*H*)Ph], 7.49 (m, 4 H, Ph-H), 7.37 (m, 8 H, Ph-H), 7.27 (m, 2 H, Ph-H), 6.42 [d, J = 16.0 Hz, 1 H, *H*C=C(H)Ph], 6.21 (t, J = 9.9 Hz, 1 H, 3-H), 5.68 (t, J = 9.8 Hz, 1 H, 4-H), 5.34 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 5.28 (d, J = 3.6 Hz, 1 H, 1-H), 4.45 (m, 2 H, 6-H), 4.36 (m, 1 H, 5-H), 3.49 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 165.72, 165.69, 165.2 (*C*=O), 145.5 [HC=*C*(H)Ph], 134.1 (Ph-C_q), 133.3, 133.0, 139.3, 129.8, 129.8 (Ph-*C*H), 129.1, 128.9, 128.8 (Ph-C_q), 128.7, 128.3, 128.2, 128.1 (Ph-*C*H), 117.2 [H*C*=C(H)Ph], 97.0 (C-1), 71.9 (C-2), 70.3 (C-3), 69.6 (C-4), 67.4 (C-5), 62.7 (C-6), 55.6 (O*C*H$_3$) ppm.

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6-*O*-[(*E*)-3-phenyl-2-propenyl]-6′-*O*-TBDPS-sucrose (34): Purification by preparative chromatography (hexane/ethyl acetate, 1:1) yielded **34** as a colourless oil (23% yield after 60 min with method B in pyridine and 28% yield after 60 min in TMG). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 [m, 5 H, HC=C(*H*)Ph, Ph-H$_o$], 7.51 (m, 2 H, Ph-H$_o$), 7.39 (m, 9 H, Ph-H$_{m,p}$), 6.45 [d, J = 16.0 Hz, 1 H, *H*C=C(H)Ph], 5.65 (d, J = 3.5 Hz, 1 H, 1-H), 5.52 (t, J = 5.7 Hz, 1 H, 4′-H), 5.42 (t, J = 9.8 Hz, 1 H, 3-H), 5.41 (d, J = 5.6 Hz, 1 H, 3′-H), 5.08 (t, J = 9.8 Hz, 1 H, 4-H), 4.86 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.18 (m, 6 H, 1′-H, 5-H, 5′-H, 6-H), 3.90 (dd, $J_{5',6'\alpha}$ = 5.6 Hz, $J_{6'\alpha,6'\beta}$ = 11.2 Hz, 1 H, 6′α-H), 3.86 (dd, $J_{5',6'\beta}$ = 5.8 Hz, $J_{6'\alpha,6'\beta}$ = 11.0 Hz, 1 H, 6′β-H), 2.14, 2.10, 2.09, 2.03, 2.01, 1.98 (6 s, 18 H, 6 C*H*$_3$), 1.06 (s, 9 H, *t*Bu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.1, 169.8, 169.5, 166.5 (*C*=O), 145.5 [HC=*C*(H)Ph], 135.6 (Ph-*C*H), 134.4, 133.0 (Ph-C_q), 130.4, 129.9, 128.8, 128.3, 127.8 (Ph-*C*H), 117.4 [H*C*=C(H)Ph], 103.8 (C-2′), 89.8 (C-1), 81.5 (C-5′), 76.2 (C-3′), 75.2 (C-4′), 70.2 (C-2), 69.9 (C-3), 68.4 (5, C-4), 63.9 (C-6′), 62.9 (C-1′), 61.8 (C-6), 26.8 (*t*Bu-*C*H$_3$), 20.8, 20.6 (acetyl *C*H$_3$), 19.2 (*t*Bu-*C*) ppm.

1′,2,3,3′,4,4′,6-Hepta-*O*-acetyl-6′-*O*-[(*E*)-3-phenyl-2-propenyl]-sucrose (35): Purification by preparative chromatography (hexane/ethyl acetate, 1:2) yielded **35** as a colourless oil (58% yield after 30 min with method B in pyridine and 32% yield after 30 min in TMG). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 [d, J = 16.0 Hz, 1 H, HC=C(*H*)Ph], 7.56 (m, 2 H, Ph-H$_o$), 7.39 (m, 3 H, Ph-H$_{m,p}$), 6.53 [d, J = 16.0 Hz, 1 H, *H*C=C(H)Ph], 5.72 (d, J = 3.6 Hz, 1 H, 1-H), 5.48 (m, 2 H, 3-H, 3′-H), 5.38 (t, J = 5.7 Hz, 1 H, 4′-H), 5.14 (t, J = 9.6 Hz, 1 H, 4-H), 4.90 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.34 (m, 5 H, 1′-H, 5-H, 6-H), 4.22 (m, 3 H, 5′-H, 6′-H), 2.19, 2.11, 2.10, 2.09, 2.07, 2.02 (6 s, 18 H, 6 C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.1, 169.9, 169.7, 169.5, 166.5 (*C*=O), 145.7 [HC=*C*(H)Ph], 134.4 (Ph-C_q), 130.4, 128.9, 128.3 (Ph-*C*H), 117.4 [H*C*=C(H)Ph], 104.1 (C-2′), 90.0 (C-1), 79.2 (C-5′), 75.8 (C-3′), 75.1 (C-4′), 70.3 (C-2), 69.7 (C-3), 68.6 (C-5), 68.5 (C-4), 63.6 (C-1′), 62.9 (C-6), 62.0 (C-6′), 20.7, 20.6 (*C*H$_3$) ppm.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-deoxycholyl-α-D-glucopyranoside (37): Purification by preparative chromatography (ethyl acetate) yielded **37** as a colourless oil (82% yield after 20 min with method B in TMG). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 7.3 Hz, 2 H, Ph-H$_o$), 7.94 (d, J = 7.3 Hz, 2 H, Ph-H$_o$), 7.87 (d, J = 7.3 Hz, 2 H, Ph-H$_o$), 7.51 (m, 2 H, Ph-H$_p$), 7.40 (m, 5 H, Ph-H$_{m,p}$), 7.29 (m, 2 H, Ph-H$_m$), 6.15 (t, J = 9.8 Hz, 1 H, 3-H), 5.60 (t, J = 9.7 Hz, 1 H, 4-H), 5.28 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.0 Hz, 1 H, 2-H), 5.24 (d, J = 3.6 Hz, 1 H, 1-H), 4.28 (m, 3 H, 5-H, 6-H), 3.98 (t, J = 2.8 Hz, 1 H, deoxycholyl 12-H), 3.61 (m, 1 H, deoxycholyl 3-H), 3.48 (s, 3 H, OCH_3), 2.34 (m, 2 H, deoxycholyl 23-H), 1.44 (m, 26 H, deoxycholyl-H), 0.94 (m, 6 H, deoxycholyl 19-H, deoxycholyl 21-H), 0.68 (s, 3 H, deoxycholyl 18-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9 (deoxycholyl *C*=O), 165.8, 165.2 (*C*=O), 133.4, 133.1 (Ph-C_p), 129.9, 129.8, 129.7 (Ph-C_o), 129.2, 129.0, 128.9 (Ph-C_q), 128.4, 128.3 (Ph-C_m), 97.1 (C-1), 73.1 (deoxycholyl C-12), 72.0 (C-2), 71.8 (deoxycholyl C-3), 70.4 (C-3), 69.3 (C-4), 67.5 (C-5), 62.4 (C-6), 55.7 (O*C*H$_3$), 48.2 (*C*H), 47.3 (*C*H), 46.5 (*C*), 42.1 (*C*H), 36.4 (*C*H$_2$), 36.0 (*C*H), 35.2 (*C*H$_2$), 35.0 (*C*H), 34.1 (*C*), 33.7 (*C*H), 30.9 (*C*H$_2$), 30.6 (*C*H$_2$), 30.5 (*C*H$_2$), 28.7 (*C*H$_2$), 27.4 (*C*H$_2$), 27.1 (*C*H$_2$), 26.1 (*C*H$_2$), 23.7 (*C*H$_2$), 23.2 (deoxycholyl C-19), 17.3 (deoxycholyl C-21), 12.8 (deoxycholyl C-18) ppm.

2,3,4-Tri-*O*-benzoyl-1-*O*-deoxycholyl-β-D-xylopyranose (38): Purification by preparative chromatography (hexane/ethyl acetate, 1:1) yielded **38** as a colourless oil (38% yield after 5 min with method A in water/acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (m, 6 H, Ph-H$_o$), 7.53 (m, 3 H, Ph-H$_p$), 7.38 (m, 6 H, Ph-H$_m$), 6.12 (d, J = 5.3 Hz, 1 H, 1-H), 5.80 (t, J = 6.8 Hz, 1 H, 3-H), 5.47 (m, 1 H, 2-H), 5.35 (dd, J = 6.5 Hz, J = 10.6 Hz, 1 H, 4-H), 4.47 (dd, J = 4.0 Hz, J = 12.3 Hz, 1 H, 5-H), 3.94 (s, 1 H, deoxycholyl 12-H), 3.89 (dd, J = 6.5 Hz, J = 12.4 Hz, 1 H, 5-H), 3.61 (m, 1 H, deoxycholyl 3-H), 2.34 (m, 2 H, deoxycholyl 23-H), 1.41 (m, 26 H, deoxycholyl-H), 0.91 (m, 6 H, deoxycholyl 19-H, deoxycholyl 21-H), 0.63 (s, 3 H, deoxycholyl 18-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.3 (deoxycholyl *C*=O), 165.5, 165.1, 165.0 (*C*=O), 133.5 (Ph-C_p), 129.9, 129.8 (Ph-C_o), 129.0, 128.97, 128.8 (Ph-C_q), 128.5 (Ph-C_m), 91.6 (C-1), 73.1 (deoxycholyl C-12), 71.7 (deoxycholyl C-3), 69.6 (C-3), 68.9 (C-2), 68.5 (C-4), 62.1 (C-5), 48.1 (*C*H), 47.1 (*C*H), 46.5 (*C*), 42.1 (*C*H), 36.4 (*C*H$_2$), 36.0 (*C*H), 35.2 (*C*H$_2$), 35.0 (*C*H), 34.1 (*C*), 33.6 (*C*H), 31.2 (*C*H$_2$), 30.6 (*C*H$_2$), 30.4 (*C*H$_2$), 28.7 (*C*H$_2$), 27.3 (*C*H$_2$), 27.1 (*C*H$_2$), 26.1 (*C*H$_2$), 23.6 (*C*H$_2$), 23.1 (deoxycholyl C-19), 17.2 (deoxycholyl C-21), 12.7 (deoxycholyl C-18) ppm.

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[1] B. G. Davis, A. J. Fairbanks, *Carbohydrate Chemistry*, vol. 99, 1st ed., Oxford University Press Inc., New York, **2002**.
[2] R. I. Hollingsworth, G. J. Wang, *Chem. Rev.* **2000**, *100*, 4267–4282.
[3] S. A. W. Gruner, E. Locardi, E. Lohof, H. Kessler, *Chem. Rev.* **2002**, *102*, 491–514.
[4] Y. Chapleur, F. Chrétien, in *Preparative Carbohydrate Chemistry* (Ed.: S. Hanessian), Marcel Dekker, New York, **1997**, pp. 207–262.
[5] R. J. Ferrier, S. Middleton, *Chem. Rev.* **1993**, *93*, 2779–2831.
[6] J. R. Dontulwar, D. K. Borikar, B. B. Gogte, *Carbohydr. Polym.* **2006**, *63*, 375–378.
[7] A. Poschalko, T. Rohr, H. Gruber, A. Bianco, G. Guichard, J. P. Briand, V. Weber, D. Falkenhagen, *J. Am. Chem. Soc.* **2003**, *125*, 13415–13426.
[8] M. T. Barros, F. Sineriz, *Synthesis (Stuttgart)* **2002**, 1407–1411.
[9] M. T. Barros, K. T. Petrova, A. M. Ramos, *J. Org. Chem.* **2004**, *69*, 7772–7775.
[10] R. Narain, D. Jhurry, G. Wulff, *Eur. Polym. J.* **2002**, *38*, 273–280.
[11] R. Narain, D. Jhurry, *Polym. Int.* **2002**, *51*, 85–91.
[12] M. J. Carneiro, A. Fernandes, C. M. Figueiredo, A. G. Fortes, A. M. Freitas, *Carbohydr. Polym.* **2001**, *45*, 135–138.
[13] L. L. Huang, M. H. Xu, G. Q. Lin, *J. Org. Chem.* **2005**, *70*, 529–532.
[14] B. H. Wang, H. W. Yu, E. E. Ballard, P. D. Boyle, *Abstr. Pap. Am. Chem. Soc.* **2002**, *223*, B189–B189.
[15] S. C. Pellegrinet, R. A. Spanevello, *Org. Lett.* **2000**, *2*, 1073–1076.
[16] M. M. Andrade, M. T. Barros, *Tetrahedron* **2004**, *60*, 9235–9243.
[17] M. Lakhrissi, Y. Chapleur, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 750–752.
[18] P. J. Murphy, S. E. Lee, *J. Chem. Soc., Perkin Trans. 1* **1999**, 3049–3066.
[19] C. Taillefumier, Y. Chapleur, *Chem. Rev.* **2004**, *104*, 263–292.
[20] A. Loupy, P. Pigeon, M. Ramdani, *Tetrahedron* **1996**, *52*, 6705–6712.
[21] A. Loupy, P. Pigeon, M. Ramdani, P. Jacquault, *Synth. Commun.* **1994**, *24*, 159–165.
[22] C. Villa, E. Mariani, A. Loupy, C. Grippo, G. C. Grossi, A. Bargagna, *Green Chem.* **2003**, *5*, 623–626.
[23] J. Westman, *Org. Lett.* **2001**, *3*, 3745–3747.
[24] C. C. Silveira, M. R. S. Nunes, E. Wendling, A. L. Braga, *J. Organomet. Chem.* **2001**, *623*, 131–136.
[25] S. Frattini, M. Quai, E. Cereda, *Tetrahedron Lett.* **2001**, *42*, 6827–6829.
[26] J. Wu, H. Wu, S. Wei, W.-M. Dai, *Tetrahedron Lett.* **2004**, *45*, 4401–4404.
[27] Y. Lakhrissi, C. Taillefumier, M. Lakhrissi, Y. Chapleur, *Tetrahedron: Asymmetry* **2000**, *11*, 417–421.
[28] C. Limousin, A. Olesker, J. Cleophax, A. Petit, A. Loupy, G. Lukacs, *Carbohydr. Res.* **1998**, *312*, 23–31.
[29] B. C. Bookser, N. B. Raffaele, *J. Org. Chem.* **2007**, *72*, 173–179.
[30] A. Corsaro, U. Chiacchio, V. Pistara, G. Romeo, *Curr. Org. Chem.* **2004**, *8*, 511–538.
[31] M. R. C. Couri, E. A. Evangelista, R. B. Alves, M. A. F. Prado, R. P. F. Gil, M. V. De Almeida, D. S. Raslan, *Synth. Commun.* **2005**, *35*, 2025–2031.
[32] S. K. Das, *Synlett* **2004**, 915–932.
[33] S. K. Das, K. A. Reddy, V. L. N. R. Krovvidi, K. Mukkanti, *Carbohydr. Res.* **2005**, *340*, 1387–1392.
[34] E. Soderberg, J. Westman, S. Oscarson, *J. Carbohydr. Chem.* **2001**, *20*, 397–410.
[35] P. Tiwari, A. K. Misra, *Carbohydr. Res.* **2006**, *341*, 339–350.
[36] A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault, D. Mathe, *Synthesis (Stuttgart)* **1998**, 1213–1234.
[37] For the synthesis of compound **2**, see the Experimental Section.
[38] B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927.
[39] M. Schlosser, B. Schaub, J. de Oliveira-Neto, S. Jeganathan, *Chimia* **1986**, *40*, 244–245.
[40] A. W. Johnson, in *Ylides and imines of Phosphorus*, John Wiley & Sons, New York, **1993**, pp. 294–296.
[41] H. G. Fletcher, C. S. Hudson, *J. Am. Chem. Soc.* **1947**, *69*, 921–924.
[42] N. Belkhouya, C. Fréchou, M. Benazza, D. Beaupère, R. Uzan, G. Demailly, *Tetrahedron Lett.* **1991**, *32*, 3977–3980.
[43] L. Hough, L. Sinchareonkul, A. C. Richardson, F. Akhtar, M. G. B. Drew, *Carbohydr. Res.* **1988**, *174*, 145–160.
[44] J. J. Plattner, R. D. Gless, G. K. Cooper, H. Rapoport, *J. Org. Chem.* **1974**, *39*, 303–311.

[45] J. J. Plattner, R. D. Gless, H. Rapoport, *J. Am. Chem. Soc.* **1972**, *94*, 8613–8615.
[46] A. Orsini, A. Viterisi, A. Bodlenner, J. M. Weibel, P. Pale, *Tetrahedron Lett.* **2005**, *46*, 2259–2262.
[47] M. T. Barros, C. D. Maycock, C. Thomassigny, *Synlett* **2001**, 1146–1148.
[48] K. I. Oyama, T. D. Kondo, *Org. Lett.* **2003**, *5*, 209–212.
[49] S. Lee, K. Kim, T. S. Kumar, J. Lee, S. K. Kim, D. Y. Lee, Y. K. Lee, Y. Byun, *Bioconjugate Chem.* **2005**, *16*, 615–620.
[50] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, New York, **1980**.
[51] H. Karl, C. K. Lee, R. Khan, *Carbohyd. Res.* **1982**, *101*, 31–38.

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