DOI: 10.1002/ejoc.200901286

Horner–Wadsworth–Emmons Reaction of Unprotected Sugars in Water or in the Absence of Any Solvent: One-Step Access to *C*-Glycoside Amphiphiles

Adeline Ranoux,[a,b] Loïc Lemiègre,[a] Maud Benoit,[a] Jean-Paul Guégan,[a] and Thierry Benvegnu*[a]

Keywords: Carbohydrates / *C*-Glycosides / Solvent-free reactions / Surfactants / Green chemistry / Amphiphiles

The synthesis of *C*-glycosides in water or in the absence of any solvent from free sugars and β-keto phosphonates is reported. The methodology permits a one-step access to *C*-glycoside amphiphiles in moderate-to-good yields. The selectivity (α/β and furanoside/pyranoside) is discussed and a process that leads to pure β-*C*-pyranosides is also described.

Introduction

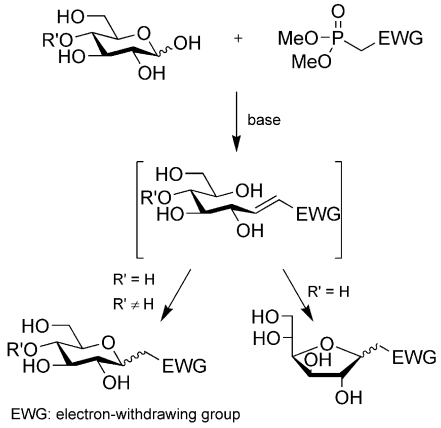
In recent years, *C*-glycosides have gained increasing importance because of their abilities to promote high chemical and enzymatic stabilities and to display interesting biological properties.[1,2] Some of them have been reported to exhibit anti-tumour, anti-bacterial, anti-viral and glycosidase inhibitory activities.[3] The major feature of *C*-glycosides is their unique chemical reactivity. The absence of anomeric effects and principally the resistance of the *C*-anomeric linkage towards acid/enzymatic hydrolysis make them attractive candidates as stable carbohydrate mimetics of *O*-glycosides. However, the synthetic problems posed by the replacement of the *exo*-anomeric oxygen atom by a methylene group still represent a real challenge in carbohydrate chemistry.

Most of the synthetic approaches to *C*-glycosides developed over the past few years are based upon electrophilic or nucleophilic substitutions, transition-metal-mediated *C*-glycosylations, anomeric radical reactions, rearrangements and cycloadditions, and sugar ring formation reactions.[1,2] These methods generally require additional steps before and after the formation of the *C*-glycosidic bond that could involve the activation of the anomeric carbon and/or the protection/deprotection of the hydroxy groups. Recently, a straightforward synthesis of β-δ-*C*-glycosidic β-ketones by condensation of symmetrical or unsymmetrical β-diketones and unprotected sugars in alkaline aqueous solutions has been successfully investigated.[4–7] The synthesis relies on a Knoevenagel condensation between the carbanion of a β-diketone and the formyl group of an unprotected sugar. A *C*-xyloside alcohol resulting from the reduction of a β-keto-*C*-glycoside obtained by this method was found to stimulate sulfated glycosaminoglycan (GAG) synthesis: this has recently been developed in cosmetic skincare products as pro-Xylane™.[8] However, until now, no straightforward approach has been described for the synthesis of amphiphilic *C*-glycosides from unprotected sugars in organic solvent-free media. The development of such an approach could be invaluable for the preparation of green surfactant formulations based on *C*-glycosides.

With the aim of finding an alternative direct synthetic route that does not need organic media either as solvents or as co-solvents even for the introduction of highly hydrophobic chains, we explored the Horner–Wadsworth–Emmons (HWE) reaction of unprotected sugars under unusual conditions. The HWE reaction is a well-known method for the formation of olefins from aldehydes and ketones. In the case of unprotected carbohydrates,[9] the aldehyde is masked in the form of a hemiacetal. Consequently, the HWE reaction has to drive the equilibrium between the cyclic hemiacetalic form and the corresponding ring-opened sugar incorporating the reactive aldehyde functionality to provide an acyclic olefin. Once produced, this hydroxy-olefin can finally cyclize in situ to form the expected four *C*-glycosides (α/β-pyranosides or -furanosides; Scheme 1).

The condensation reactions of phosphonates with unprotected sugars have so far been investigated only in organic solvents and led mainly to *C*-furanoside derivatives.[10,11] Convenient protection of the carbohydrates is necessary to achieve in one step a perfect control of the cyclization to the pyranoside or the furanoside form.[10–12] Therefore the

[a] Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226
Université européenne de Bretagne,
Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France
Fax: +33-2-23238046
E-mail: thierry.benvegnu@ensc-rennes.fr
[b] Armor Protéines,
Le Pont, 35460 Saint Brice en Coglès, France
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901286.



Scheme 1. General route for the formation of both *C*-pyranoside and *C*-furanoside by the HWE reaction.

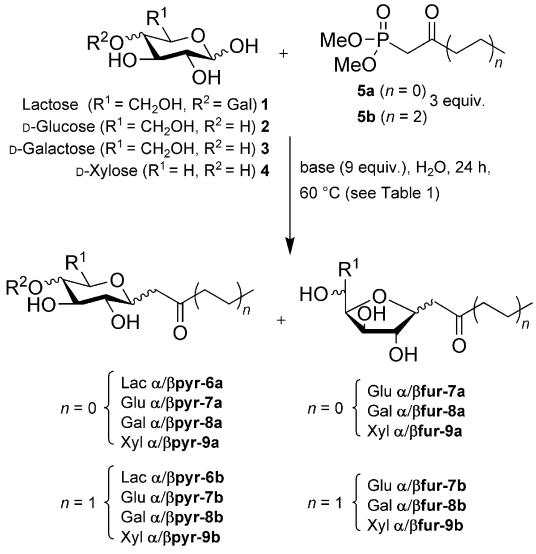
access to six-membered *C*-glycoside amphiphiles in pure form under organic solvent-free conditions and from unprotected sugars remains a challenge.

Results and Discussion

To develop a general and environmentally friendly synthetic route to β-keto-*C*-glycosides we investigated new versions of the HWE reaction in water or in the absence of any solvent from unprotected carbohydrates and commercially or readily available dimethyl 2-oxoalkylphosphonates (see Schemes 2 and 3, Tables 1 and 2). In particular, our major objective was to establish methods that permitted the synthesis of keto-*C*-glycosides with a wide range of alkyl chain lengths in a chemoselective and stereocontrolled manner.[13]

Synthesis Under Aqueous Conditions

Four representative sugars, in terms of disaccharidic and monosaccharidic reactivities [lactose (**1**), D-glucose (**2**), D-galactose (**3**) and D-xylose (**4**)], and two β-keto phosphonates **5a**,**b** with different alkyl chain lengths were selected. The mineral bases K_2CO_3, NaOH and $NaHCO_3$ were considered to furnish the basic conditions required for the HWE reaction (Scheme 2). The results of the HWE reactions performed in water are reported in Table 1.



Scheme 2. Reaction of β-keto phosphonates **5a** and **5b** with lactose (**1**), D-glucose (**2**), D-galactose (**3**), and D-xylose (**4**) in water (Table 1).

Table 1. Reaction of β-keto phosphonates **5a**–**b** with lactose (**1**), D-glucose (**2**), D-galactose (**3**), D-xylose (**4**), in water.

Entry	Phosphonate	Sugar	Base	Product	Yield (%)	Pyr/Fur[a]	α/β (Pyr)[a]
1	**5a**	**1**	K_2CO_3	**6a**	67	100:0	0:100
2	**5a**	**2**	K_2CO_3	**7a**	75	95:5	11:89
3	**5a**	**3**	K_2CO_3	**8a**	85	95:5	15:85
4	**5a**	**4**	K_2CO_3	**9a**	57	100:0	7:93
5	**5a**	**2**	NaOH	**7a**	28	100:0	5:95
6	**5a**	**2**	$NaHCO_3$	**7a**	73	75:25	35:65
7	**5b**	**1**	K_2CO_3	**6b**	35	100:0	13:87
8	**5b**	**2**	K_2CO_3	**7b**	25	95:5	26:74

[a] Determined by ^{1}H NMR spectroscopy.

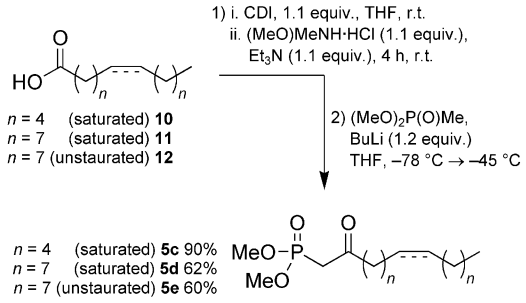
We first studied the reaction of the water-soluble phosphonate **5a** in basic aqueous media (K_2CO_3, 9 equiv.) at 60 °C (Table 1, entries 1–4). The reaction of the disaccharide (lactose **1**) proceeded cleanly to provide the pure β-*C*-pyranoside **βpyr-6a** in 67% yield (Table 1, entry 1). The same conditions applied to monosaccharides **2**–**4** also led to a selective reaction in favour of the β-*C*-pyranosides **βpyr-7a**–**9a**, although careful analysis of the NMR spectra revealed the presence of small amounts of **αpyr-7a**–**9a** and **α/βfur-7a**–**9a** derivatives (Table 1, entries 2–4). Switching the base to sodium hydroxide influenced the pyranoside/furanoside and α/β ratios and led to the *C*-glucoside **pyr-7a** in an α/β ratio of 5:95 (Table 1, entry 5).

The better diastereoselectivity observed with NaOH was reached to the detriment of the yield, which decreased from 75 to 28%. Conversely, the use of a weaker base ($NaHCO_3$) afforded a higher yield, but with a lower β-pyranoside selectivity (Table 1, entry 6). These results can be explained by the existence of a faster equilibration towards the thermodynamic product (β-pyranoside) when a strong base is used. Furthermore, they show that the keto-*C*-glycosides may be sensitive to strong basic media. Therefore the use of K_2CO_3 in HWE reactions of unprotected sugars in water remained a good compromise in terms of yields and selectivities. As expected, the poor solubility of the phosphonate **5b** possessing a C_7 alkyl chain led to lower yields (25–35%) irrespective of the sugar used (Table 1, entries 7–8). Even though these aqueous conditions were found to be efficient for a water-soluble phosphonate, we rapidly sought alternative reaction conditions that would provide a general access to *C*-glycoside surfactants irrespective of the chain length of the phosphonate.

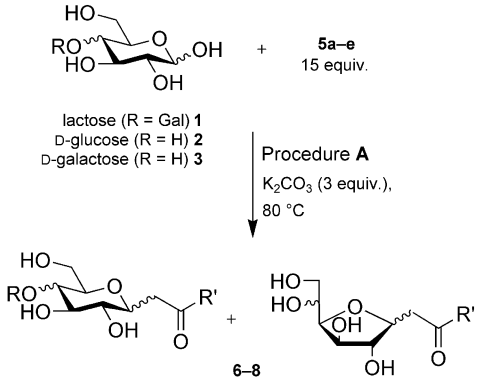
Synthesis Under Solvent-Free Conditions

The development of solvent-free reactions usually requires the use of an excess of reactant. In this case, the consideration of such conditions as a greener process thus implies the recycling of the reactant. With this in mind, we studied the HWE olefination/cyclization process in the phosphonate itself. Our study was based upon the use of phosphonates with carbon chain lengths ranging from C_3 to C_{19} (**5a**–**e**). Non-commercial β-keto phosphonates **5c**–**e** were prepared from the corresponding fatty acids **10**–**12** (Scheme 3). The conversion of **10**–**12** to the Weinreb amides was achieved by reaction with carbonyldiimidazole (CDI) and methoxymethylamine. Then addition of the lithium salt of dimethyl methylphosphonate to the Weinreb amide derivatives led to the desired β-keto phosphonates **5c**–**e** in good yields (60–90% over the two steps).

The β-keto phosphonates **5a**–**e** were then subjected to HWE reactions with various carbohydrates [lactose (**1**), D-glucose (**2**) and D-galactose (**3**)] in the absence of any solvent. As under aqueous conditions, we used potassium carbonate to furnish basic conditions, however, the amount of base was reduced to 3 equiv. for solubility reasons. A minimum of 15 equiv. of phosphonates **5a**–**e** was necessary to afford the corresponding *C*-glycosides in moderate-to-good yields (Scheme 4, Table 2).



Scheme 3. Synthesis of β-keto phosphonates **5a**–**e**.



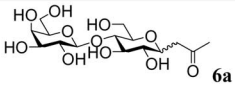
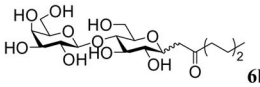
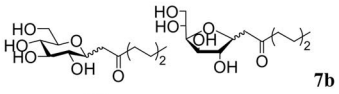
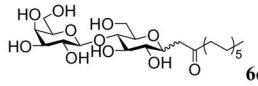
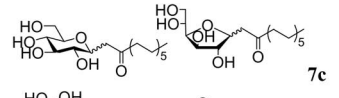
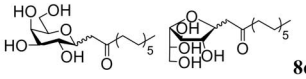
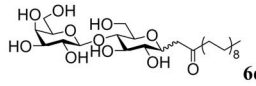
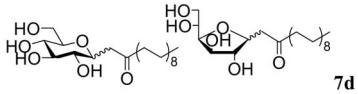
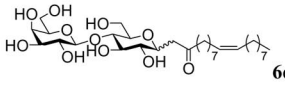
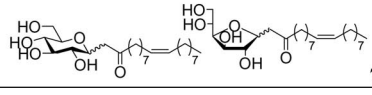
Scheme 4. Reaction of β-keto phosphonates **5a**–**e** with lactose (**1**), D-glucose (**2**) and D-galactose (**3**) following procedure A (see Table 2 for structures).

Under these new conditions, the *C*-lactoside **6a** was obtained in a similar yield (64%) as under aqueous conditions (Table 2, entry 1). However, we observed a dramatic increase in the yield of the *C*-lactoside **6b** possessing a C_7 chain (71 instead of 35%; Table 2, entry 2). This process was then applied to D-glucose leading to the corresponding *C*-glucosides **7b** in 51% yield. Increasing the carbon chain length of the phosphonate (C_{13} **5c** and $C_{19:0}$ **5d**) also led to satisfactory yields for both lactose **1** and the monosaccharides **2** and **3** (48–70%, Table 2, entries 4–8). The reaction proceeded with the same efficiency with the unsaturated phosphonate **5e** ($C_{19:1}$) and sugars **1** and **2** providing *C*-glycosides **6e** and **7e** in 58 and 50% yields, respectively. This methodology therefore affords a simple access to *C*-glycoside amphiphiles that may be incorporated into various surfactant formulations.

As mentioned before, we envisaged a solvent-free HWE reaction, which implies the recycling of the excess phosphonate. We then confirmed the possibility of recovering and reusing the phosphonates **5a**–**e** in other HWE reactions with similar performances. A typical procedure (reduced pressure distillation) afforded 40–78% of recovered phosphonate **5a**–**e**.

In terms of selectivity, note that the reaction of lactose with **5a** or **5b** (15 equiv.) yielded isomers **αpyr-6a** and **αpyr-6b** as the major products (Table 2, entries 1 and 2) instead

Table 2. Reaction of β-keto phosphonates **5a**–**e** with lactose (**1**), D-glucose (**2**) and D-galactose (**3**) in the absence of solvent (procedure A).[a]

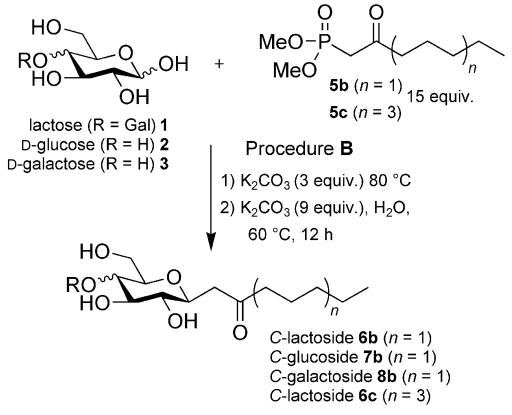
Entry	Phosphonate	Sugar	Product	Yield (%)	Pyr/Fur[b]	α/β (Pyr)[b]
1	**5a**	**1**	 **6a**	64	100:0	63:37
2	**5b**	**1**	 **6b**	71	100:0	68:32
3	**5b**	**2**	 **7b**	51	50:50	65:35[c]
4	**5c**	**1**	 **6c**	50	100:0	80:20
5	**5c**	**2**	 **7c**	48	65:35	80:20
6	**5c**	**3**	 **8c**	64	63:37	95:5
7	**5d**	**1**	 **6d**	70	100:0	61:39
8	**5d**	**2**	 **7d**	63	60:40	81:19
9	**5e**	**1**	 **6e**	58	100:0	50:50
10	**5e**	**2**	 **7e**	50	65:35	89:11

[a] Procedure A: one step, neat, K_2CO_3 (3 equiv.), 80 °C, 24 h. [b] Determined by ^1H NMR spectroscopy. [c] α/β (fur): 67:37.

of the β-pyranoside forms that were obtained quasi-exclusively under aqueous conditions (Table 1, entries 1 and 7). Also, glucose gave a 50:50 pyr/fur ratio and here again the α/β ratio of the *C*-glucoside is in favour of the α isomer both for the pyranoside and furanoside derivatives (Table 2, entry 3). These observations show that equilibration between the four furanoside and pyranoside isomers was reached at a lower rate in the absence of solvent than in aqueous media. The same observations were made in the reactions of dimethyl 2-oxoalkylphosphonates **5c**–**e** with longer alkyl chains, with the α-pyranoside *C*-glycosides predominating (Table 2, entries 4–10).

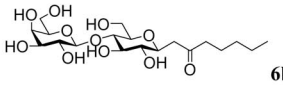
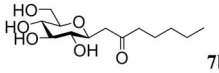
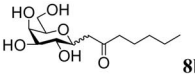
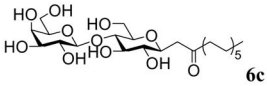
The production of mixtures of isomers or even crude mixtures can be satisfactory enough when these *C*-glycoside amphiphiles are intended to be used in surfactant formulations. However, for a better physicochemical understanding and to widen the range of applications, we elaborated another procedure that permitted selective access to β-pyranosides.

Thus, with the aim of obtaining stereochemically pure compounds we next investigated a stereocontrolled route (procedure B) that involved the same HWE reaction conditions as in procedure A (including the recovery of unreacted phosphonate) followed by treatment with an aqueous base [aq. K_2CO_3 (9 equiv.), 60 °C, 12 h; Scheme 5]. This simple additional basic treatment applied to *C*-lactoside, *C*-glucoside or *C*-galactoside isomer mixtures (**6b**–**8b** and **6c**) yielded pure pyranoside compounds[11] with α/β ratios ranging from 5:95 to 0:100 (Table 3, entries 1–4).



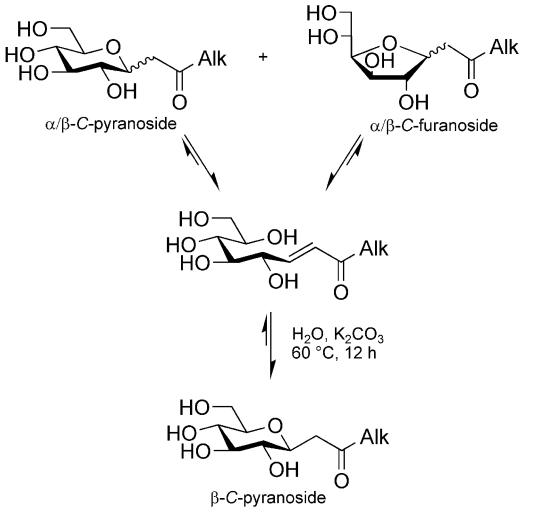
Scheme 5. Reaction of β-keto phosphonates **5b**,**c** with lactose (**1**), D-glucose (**2**) and D-galactose (**3**) following procedure **B**.

Table 3. Selective access to β-pyr-*C*-glycosides **6b**–**8b** and **6c** (procedure B).[a]

Entry	Phosphonate	Sugar	Product	Yield (%)	Pyr/Fur[b]	α/β (Pyr)[b]
1	**5b**	**1**	 **6b**	61	100:0	0:100
2	**5b**	**2**	 **7b**	50	100:0	0:100
3	**5b**	**3**	 **8b**	32	100:0	5:95
4	**5c**	**1**	 **6c**	69	100:0	0:100

[a] Procedure B: i) neat, K_2CO_3 (3 equiv.), 80 °C, 24 h, distillation of the residual phosphonate, ii) H_2O, K_2CO_3 (9 equiv.), 60 °C, 12 h. [b] Determined by ^1H NMR spectroscopy.

These interesting results suggest that the α/β-furanosides and α-pyranosides initially formed in solvent-free reaction media could be isomerized to the thermodynamic β-pyranoside products when heated in basic aqueous solutions. The isomerization pathway would follow a ring-opening/closing equilibrium involving an α,β-unsaturated hydroxy ketone and lead to the thermodynamically favoured β-pyranoside isomer (Scheme 6).



Scheme 6. Isomerization of pyranoside/furanoside mixtures in aqueous basic media (shown for glucoside derivatives).

Conclusions

We have developed a one-step HWE synthesis of amphiphilic *C*-glycosides from unprotected mono- and disaccharides. The general procedure described herein was carried out in the absence of any solvent with recyclable β-keto phosphonates. Moreover, it was applied to the introduction of short (C_3) to long (C_{19}) alkyl chain lengths. Furthermore, the thermodynamic compounds (β-*C*-pyranosides) were obtained by using aqueous basic HWE reaction conditions or by aqueous basic treatment of the solvent-free crude reaction mixture. This methodology represents an environmentally friendly process for the synthesis of *C*-glycoside surfactants covering a wide range of hydrophobic/hydrophilic balances. Physicochemical evaluations of this ecofriendly surfactant family are in progress.

Experimental Section

General: Commercially available chemicals were used without further purification. Analytical TLC was performed on Merck 60 F254 silica gel non-activated plates. A solution of 5% H_2SO_4 in EtOH was used to develop the plates. Merck 60 H (5–40 mm) silica gel was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker Avance III spectrometer. In the NMR data, the numbering and α/β designations are in accordance with carbohydrate nomenclature. "f" and "p" refer to furanoside and pyranoside derivatives respectively. MS spectra were recorded with a Waters Micromass Q-TOF spectrometer equipped with a Z-spray ion source. IR spectra were recorded with a Thermo Nicolet 320 FTIR spectrometer and optical rotations were recorded with a Perkin–Elmer 341 polarimeter.

General Procedure for the Synthesis of Phosphonates 5c–e. Synthesis of the Weinreb Amides: Under nitrogen, carbonyldiimidazole (27.5 mmol, 1.1 equiv.) was added slowly at room temperature to a solution of fatty acid **10**–**12** (25 mmol, 1 equiv.) in anhydrous dichloromethane (250 mL). After 40 min, methoxymethylammonium chloride (27.5 mmol, 1.1 equiv.) and triethylamine (27.5 mmol, 1.1 equiv.) were added. The reaction mixture was stirred at room temperature for 4 h and was quenched by the addition of a saturated solution of ammonium chloride (40 mL). The aqueous phase was extracted by dichloromethane. The combined organic phases were then washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. Flash chromatography on silica gel (dichloromethane) afforded the corresponding amide as a colourless oil.

Synthesis of the Phosphonates 5c–e: Under nitrogen, BuLi (30 mmol, 1.2 equiv., 1.6 M in hexane) was added at –78 °C to a solution of dimethyl methylphosphonate (30 mmol, 1.2 equiv.) in

anhydrous THF (150 mL). The reaction mixture was stirred for 30 min at the same temperature and then a solution of the Weinreb amide (25 mmol, 1 equiv.) in THF (50 mL) was added slowly. The reaction mixture was warmed to –45 °C over 3 h and then a saturated solution of ammonium chloride (40 mL) was added. The aqueous phase was extracted with Et_2O. The combined organic phases were then washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. Flash chromatography on silica gel (DCM/AcOEt, 1:1) afforded the corresponding β-keto phosphonates **5c**–**e**.

Dimethyl 2-Oxotridecylphosphonate (5c). Amide Derivative: Yield 99%. R_f (DCM) = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.67 (s, 3 H, O-CH_3), 3.17 (s, 3 H, N-CH_3), 2.40 [t, J = 7.6 Hz, 2 H, CO(CH_2)], 1.62 (quint., J = 7.6 Hz, 2 H, CH_2), 1.25 [m, 16 H, $(CH_2)_8$], 0.87 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 174.8 (CO), 61.2 (O-CH_3), 32.0 (N-CH_3), 31.9 (CH_2), 29.6, 29.5, 29.41, 29.39, 29.3, 24.7, 22.7 [$(CH_2)_8$], 14.1 (CH_3) ppm. HRMS (ESI$^+$): calcd. for C-1$_4$H$_{29}$NO$_2$ [M + Na]$^+$ 266.2096; found 266.2098; [M + H]$^+$ 244.22765; found 244.2286. $C_{14}H_{29}NO_2$ (243.39): calcd. C 69.09, H 12.01, N 5.75; found C 68.90, H 12.05, N 5.54.

Dimethyl 2-Oxotridecylphosphonate (5c): Yield 91%. White solid. R_f (DCM/AcOEt: 1:1) = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.76 (d, $J_{H,P}$ = 11.2 Hz, 6 H, O-CH_3), 3.07 (d, $J_{H,P}$ = 22.8 Hz, 2 H, P-CH_2), 2.59 [t, J = 7.2 Hz, 2 H, CO(CH_2)], 1.56 (quint., J = 7.2 Hz, 2 H, CH_2), 1.24 [m, 16 H, $(CH_2)_8$], 0.87 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 22.8 ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.1 (d, $J_{C,P}$ = 5.9 Hz, CO), 53.0 (d, $J_{C,P}$ = 6.5 Hz, OCH_3), 44.2 [d, $J_{C,P}$ = 1.4 Hz, CO(CH_2)], 41.2 (d, $J_{C,P}$ = 128 Hz, P-CH_2), 31.9, 29.6, 29.4, 29.30, 28.9 (COCH_2-CH_2), 23.4, 22.6, [$(CH_2)_8$], 14.1 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{15}H_{30}O_4P$ [M + Na]$^+$ 329.18577; found 329.1856; [M + H]$^+$ 307.20382; found 307.2043. $C_{15}H_{31}O_4P$ (306.38): calcd. C 58.80, H 10.20; found C 58.56, H 10.40.

Dimethyl 2-Oxononadecylphosphonate (5d). Amide Derivative: Yield 78%. R_f (DCM) = 0.65. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.67 (s, 3 H, O-CH_3), 3.15 (s, 3 H, N-CH_3), 2.38 [t, J = 7.6 Hz, 2 H, CO(CH_2)], 1.60 (quint., J = 7.6 Hz, 2 H, CH_2), 1.25 [m, 28 H, $(CH_2)_{14}$], 0.85 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 174.9 (CO), 61.2 (O-CH_3), 32.2 (N-CH_3), 31.9 (CH_2), 29.7, 29.52, 29.47, 29.45, 29.44, 29.43, 29.36, 24.7, 22.7 [$(CH_2)_{14}$], 14.1 (CH_3) ppm. HRMS (ESI$^+$): calcd. for C-2$_0$H$_{41}$NO$_2$ [M + Na]$^+$ 350.30350; found 350.3035; [M + H]$^+$ 328.32155; found 328.3214. $C_{20}H_{41}NO_2$ (327.55): calcd. C 73.34, H 12.62, N 4.28; found C 72.94, H 12.31, N 3.88.

Dimethyl 2-Oxononadecylphosphonate (5d): Yield 80%. White solid. R_f (DCM/AcOEt: 1:1) = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.76 (d, $J_{H,P}$ = 11.2 Hz, 6 H, O-CH_3), 3.07 (d, $J_{H,P}$ = 22.8 Hz, 2 H, P-CH_2), 2.59 [t, J = 7.2 Hz, 2 H, CO(CH_2)], 1.55 (quint., J = 6.8 Hz, 2 H, CH_2), 1.24 [m, 28 H, $(CH_2)_{14}$], 0.87 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 22.9 ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.1 (d, $J_{C,P}$ = 5.9 Hz, CO), 53.0 (d, $J_{C\text{-}P}$ = 6.5 Hz, OCH_3), 44.2 [d, $J_{C,P}$ = 1.4 Hz, CO(CH_2)], 41.9 (d, $J_{C,P}$ = 127.7 Hz, P-CH_2), 31.9, 29.6, 29.44, 29.36, 29.32, 28.9, 23.4, 22.7, 14.1 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{21}H_{43}O_4P$ [M + Na]$^+$ 413.27967; found 413.2795; [M + H]$^+$ 391.29772; found 391.2997. $C_{21}H_{43}O_4P$ (390.54): calcd. C 64.58, H 11.10; found C 64.65, H 11.10.

Dimethyl 2-Oxononadec-10-enylphosphonate (5e). Amide Derivative: Yield 77%. R_f (DCM) = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.33 (m, 2 H, CH), 3.66 (s, 3 H, O-CH_3), 3.16 (s, 3 H, N-CH_3), 2.39 [t, J = 7.6 Hz, 2 H, CO(CH_2)], 2.00 (m, 4 H, CH-CH_2), 1.61 (quint., J = 7.6 Hz, 2 H, CH_2), 1.27 (d, J = 19.2 Hz, 20 H, CH_2), 0.87 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.3 (CO), 129.9, 129.7 (2 CH), 61.1 (O-CH_3), 31.90 (N-CH_3), 31.85 (CH_2), 29.72, 29.68, 29.5, 29.4, 29.3, 29.1, 27.2, 24.6, 22.6, 14.1 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{20}H_{39}NO_2$ [M + Na]$^+$ 348.28785; found 348.2880; [M + H]$^+$ 326.30590; found 326.3049.

Dimethyl 2-Oxononadec-10-enylphosphonate (5e): Yield 78%. Colourless oil. R_f (DCM/AcOEt, 1:1) = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.30 (m, 2 H, CH), 3.07 (d, $J_{H,P}$ = 22.8 Hz, 2 H, P-CH_2), 3.76 (d, $J_{H,P}$ = 11.2 Hz, 6 H, O-CH_3), 2.59 [t, J = 7.2 Hz, 2 H, CO(CH_2)], 1.98 [q, J = 6.8 Hz, 4 H, CH(CH_2)], 1.56 (quint., J = 7.2 Hz, 2 H, CH_2), 1.25 [m, 16 H, $(CH_2)_{11}$], 0.85 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 22.9 ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.0 (d, $J_{C,P}$ = 5.9 Hz, CO), 129.9, 129.6 (2 CH), 52.9 (d, $J_{C,P}$ = 6.5 Hz, OCH_3), 44.1 [d, $J_{C,P}$ = 1.4 Hz, CO(CH_2)], 41.8 (d, $J_{C,P}$ = 123 Hz, P-CH_2), 31.8, 29.7, 29.6, 29.4, 29.22, 29.19, 29.0, 28.8, 27.12, 27.07, 23.3, 22.6, 14.0 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{21}H_{41}O_4P$ [M + Na]$^+$ 411.26402; found 411.2641; [M + H]$^+$ 389.28207; found 389.2828.

General Procedure for the HWE Reactions

Syntheses Under Aqueous Conditions: D-Glucose, lactose, D-galactose or D-xylose (1 equiv.) and K_2CO_3 (9 equiv.) were dissolved in water heated at 60 °C. Dimethyl 2-oxoalkylphosphonate (3 equiv.) was added and the reaction mixture was stirred at 60 °C for 24 h. The reaction media was then neutralized with a few drops of a 5% aq. hydrochloric acid solution and freeze-dried. Flash column chromatography on silica gel afforded pure *C*-glycoside.

Syntheses Under Solvent-Free Conditions. Procedure A: D-Glucose, lactose, or D-galactose (1 equiv.) and K_2CO_3 (3 equiv.) were dissolved in dimethyl 2-oxoalkylphosphonate (15 equiv.). The reaction mixture was stirred at 80 °C for 24 h. The excess phosphonate was then removed by distillation under reduced pressure. Flash column chromatography on silica gel afforded the pure *C*-glycoside.

Procedure B: D-Glucose, D-galactose or lactose (1 equiv.) and K_2CO_3 (3 equiv.) were dissolved in dimethyl 2-oxoalkylphosphonate (15 equiv.). The reaction mixture was stirred at 80 °C for 24 h. The excess of phosphonate was then removed by distillation under reduced pressure. Next the residue was dissolved in water (10 mL) in the presence of additional K_2CO_3 (9 equiv.). The reaction mixture was stirred at 60 °C for 12 h. The reaction media was then neutralized with a few drops of a 5% aq. hydrochloric acid solution and freeze-dried. Flash column chromatography on silica gel afforded pure *C*-glycoside.

1-(β-*C*-Lactosyl)-2-propanone (βpyr-6a): Compound **βpyr-6a** was prepared from **1** (100 mg, 0.277 mmol) and **5a** (138 mg, 0.833 mmol) under aqueous conditions (2 mL of water). Flash chromatography on silica gel (EtOAc/MeOH/H_2O, 15:4:1; R_f = 0.30 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **6a** as white crystals in 67% yield (70.9 mg); m.p. 162 °C (decomp.). $[\alpha]_D$ = +4.1 (c = 1, MeOH). IR (KBr): $\tilde{\nu}$ = 1050, 1705, 1945, 3394 cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ = 4.39 (d, J = 7.7 Hz, 1 H, 1′-H), 3.50–3.75 (m, 12 H, 1,3–6,2′–6′-H), 3.24 (t, J = 9.3 Hz, 1 H, 2-H), 2.99 (dd, J = 17.0, 2.9 Hz, 1 H, CH_2), 2.68 (dd, J = 17.0, 9.5 Hz, 1 H, CH_2), 2.23 (s, 3 H, CH_3) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 213.6 (CO), 103.2 (C-1′), 78.72 (C-5), 78.70 (C-5′), 76.1 (C-3), 75.7 (C-3′), 75.4 (C-1), 73.1 (C-2), 72.9 (C-4), 71.3 (C-2′), 68.9 (C-4′), 61.4 (C-6′), 60.4 (C-6), 49.2 (CH_2), 30.2 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{15}H_{26}O_{11}$ [M + Na]$^+$ 405.13728; found 405.1373; [M + K]$^+$ 421.11122; found 421.1127.

1-(*C*-Glucosyl)-2-propanone (7a):[14] A mixture of compounds **α/βpyr-7a** and **α/βfur-7a** was prepared from **2** (100 mg, 0.555 mmol) and **5a** (277 mg, 1.67 mmol) under aqueous conditions (2 mL of water). Flash chromatography on silica gel (EtOAc/MeOH/H_2O, 15:4:1; R_f = 0.51 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **7a** as a colourless oil in 75% yield (91.6 mg). ^{1}H NMR (D_2O, 400 MHz): δ = 5.01 and 4.97 (m, 2 H, 1fα,1fβ-H), 4.55 (d, J = 4.8 Hz, 1 H, 2fα-H), 4.37 (d, J = 4.8 Hz, 1 H, 2fβ-H), 4.17 (m, 1 H, 1pα-H), 3.45–3.90 and 3.40–3.20 (m, 1pβ,2pα,3–6-H), 3.15 (t, J = 9.3 Hz, 1 H, 2pβ-H), 2.95 (dd, J = 16.0, 8.0 Hz, 1 H, pα-CH_2), 2.94 (dd, J = 16.6, 3.2 Hz, 1 H, pβ-CH_2), 2.80 (dd, J = 16.0, 5.2 Hz, 1 H, pα-CH_2), 2.66 (dd, J = 16.6, 9.2 Hz, 1 H, pβ-CH_2), 2.39 (dd, J = 14.0, 8.0 Hz, 1 H, fα-CH_2), 2.34 (dd, J = 14.0, 7.6 Hz, 1 H, fβ-CH_2), 2.20, 2.17, 2.16, 2.14 (s, 3 H, CH_3), 1.94 (dd, J = 14.0, 3.2 Hz, 1 H, fβ-CH_2), 1.88 (dd, J = 14.0, 3.6 Hz, 1 H, fα-CH_2) ppm.

Compound **βpyr-7a** was prepared from **2** (100 mg, 0.555 mmol) and **5a** (277 mg, 1.667 mmol) under aqueous conditions (2 mL of water) and using NaOH instead of K_2CO_3. Flash chromatography on silica gel (EtOAc/MeOH/H_2O, 15:4:1; R_f = 0.51 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **7a** as a colourless oil in 28% yield (34.2 mg). $[\alpha]_D$ = –3.0 (c = 1, MeOH). IR (Nujol): $\tilde{\nu}$ = 1095, 1709, 1940, 3405 cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ = 3.76 (dd, J = 12.2, 2.0 Hz, 1 H, 6-H), 3.72 (td, J = 9.5, 3.2 Hz, 1 H, 1-H), 3.59 (dd, J = 12.4, 5.1 Hz, 1 H, 6-H), 3.40 (t, J = 9.3 Hz, 1 H, 3-H), 3.32 (ddd, J = 8.7, 5.1, 2.0 Hz, 1 H, 5-H), 3.27 (t, J = 8.7 Hz, 1 H, 4-H), 3.15 (t, J = 9.3 Hz, 1 H, 2-H), 2.94 (dd, J = 16.6, 3.2 Hz, 1 H, CH_2), 2.66 (dd, J = 16.6, 9.2 Hz, 1 H, CH_2), 2.20 (s, 3 H,CH_3) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 213.2 (CO), 79.5 (C-5), 77.2 (C-3), 75.3 (C-1), 73.1 (C-2), 69.7 (C-4), 60.7 (C-6), 45.6 (CH_2), 29.8 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_9H_{16}O_6$; [M + Na]$^+$ 243.08446; found 243.0855.

1-(*C*-Galactosyl)-2-propanone (8a):[7] Compounds **α/βpyr-8a** and **α/βfur-8a** were prepared from **3** (100 mg, 0.555 mmol) and **5a** (277 mg, 1.67 mmol) under aqueous conditions (2 mL of water). The crude residue was purified by flash column chromatography (EtOAc/MeOH/H_2O, 15:4:1; R_f = 0.48 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying to afford **8a** as white crystals in 85% yield (103.8 mg). ^{1}H NMR (D_2O, 400 MHz): δ = 4.72 (m, 1 H, 1fα-H), 4.50 (m, 1 H, 1fβ-H, 2fα-H), 4.14 (m, 1 H, 1pα-H), 4.34 (m, 1 H, 2fβ-H), 3.55–3.90 (m, sugars), 3.37 (t, J = 9.6 Hz, 1 H, 2pβ-H), 2.95 [dd, J = 16.8, 2.8 Hz, 1 H, pβ-CH_2(CO)], 2.78 (m, 1 H, pα-CH_2), 2.66 (dd, J = 16.8, 9.2 Hz, 1 H, pβ-CH_2), 2.33 (m, 1 H, fα-CH_2), 2.22 (m, 1 H, fβ-CH_2), 2.19 (s, 3 H, CH_3), 2.18 (m, 1 H, fβ-CH_2), 2.03 (m, 1 H, fα-CH_2) ppm.

Pure **βpyr-8a** was isolated as white crystals. $[\alpha]_D$ = +8.0 (c = 1, MeOH); m.p. 173 °C. IR (KBr): $\tilde{\nu}$ = 1057, 1079, 1145, 1277, 1710, 2865, 2918, 3282, 3384 cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ = 3.88 (d, J = 3.2 Hz, 1 H, 4-H), 3.68 (td, J = 9.2, 2.8 Hz, 1 H, 1-H), 3.66–3.60 (m, 3 H, 5,6-H), 3.55 (dd, J = 9.6, 3.6 Hz, 1 H, 3-H), 3.37 (t, J = 9.6 Hz, 1 H, 2-H), 2.95 (dd, J = 16.8, 2.8 Hz, 1 H, CH_2), 2.66 (dd, J = 16.8, 9.2 Hz, 1 H, CH_2), 2.19 (s, 3 H, CH_3) ppm. ^{13}C NMR (D_2O, 100 MHz): δ = 213.4 (CO), 78.6 (C-5), 75.7 (C-1), 73.8 (C-3), 70.4 (C-2), 69.1 (C-4), 61.2 (C-6), 45.7 (CH_2), 29.8 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_9H_{16}O_6$ [M + Na]$^+$ 243.08446; found 243.0846.

1-(β-*C*-Xylosyl)-2-propanone (βpyr-9a):[7] Compound **βpyr-9a** was prepared from **4** (100 mg, 0.671 mmol) and **5a** (334 mg, 2.01 mmol) under aqueous conditions (2 mL of water). Flash chromatography on silica gel (EtOAc/MeOH, 9:1; R_f = 0.50 with EtOAc/*i*PrOH/H_2O, 6:4:1) followed by freeze-drying afforded **9a** as a yellowish oil in 57% yield (72.3 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.80 (dd, J = 11.2, 5.2 Hz, 1 H, 5-H), 3.56 (td, J = 9.4, 2.8 Hz, 1 H, 1-H), 3.40 (m, 1 H, 4-H), 3.28 (t, J = 9.4 Hz, 1 H, 3-H), 3.14 (t, J = 11.2 Hz, 1 H, 5-H), 3.05 (t, J = 9.4 Hz, 1 H, 2-H), 2.80 (dd, J = 16.0, 2.8 Hz, 1 H, CH_2), 2.54 (dd, J = 16.0, 9.4 Hz, 1 H, CH_2), 2.17 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 210.1 (CO), 79.7 (C-3), 78.2 (C-1), 75.1 (C-2), 71.5 (C-4), 71.0 (C-5), 47.2 (CH_2), 30.7 (CH_3) ppm. HRMS (ESI$^+$): calcd. for C-1$_3H_{24}O_6$ [M + Na]$^+$ 213.07389; found 213.0738.

1-(*C*-Lactosyl)heptan-2-one (6b): A mixture of **α/βpyr-6b** was prepared from **1** (50 mg, 0.139 mmol) and **5b** (462 mg, 2.08 mmol) under solvent-free conditions (Procedure A: yield 71%, 43.2 mg) or from **1** (50 mg, 0.139 mmol) and **5b** (92.5 mg, 0.417 mmol) under aqueous conditions (1 mL of water, 35% yield, 15.2 mg). Flash chromatography on silica gel (CH_2Cl_2/MeOH, 9:1; R_f = 0.55 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **6b** as yellowish crystals. ^{1}H NMR (CD_3OD, 400 MHz): δ = 4.38 (dt, J = 7.6, 5.2 Hz, 1 H, 1α-H), 4.26 (d, J = 7.6 Hz, 1 H, 1′β-H), 4.23 (d, J = 7.6 Hz, 1 H, 1′α-H), 3.95–3.50 (m, 12 H, 1β,2α,3–6,2′–6′-H), 3.05 (t, J = 9.4 Hz, 1 H, 2β-H), 2.85 [dd, J = 16.2, 3.2 Hz, 1 H, β-CH_2(CO)], 2.75 [m, 1 H, α-CH_2(CO)], 2.60 [dd, J = 16.2, 9.2 Hz, 1 H, β-CH_2(CO)], 2.52 [m, 2 H, (CO)CH_2], 1.55 (m, 2 H, CH_2 alkyl), 1.25 (m, 4 H, CH_2 alkyl), 0.85 (t, J = 7.2 Hz, 3 H, CH_3) ppm.

Compound **βpyr-6b** was prepared from **1** (50 mg, 0.139 mmol) and **5b** (462 mg, 2.08 mmol) under solvent-free conditions (Procedure B). Flash chromatography on silica gel (CH_2Cl_2/MeOH, 9:1; R_f = 0.55 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **6b** as a yellowish crystals in 61% yield (37.1 mg). $[\alpha]_D$ = +10.4 (c = 1, MeOH); m.p. 144 °C. IR (neat): $\tilde{\nu}$ = 1055, 1088, 1138, 1374, 1705, 2930, 3381 cm^{-1}. ^{1}H NMR (CD_3OD, 400 MHz): δ = 4.26 (d, J = 7.2 Hz, 1 H, 1′-H), 3.87–3.68 (m, 7 H, 1,5′,6,6′,4-H), 3.60 (ddd, J = 7.2, 4.4, 0.8 Hz, 1 H, 5-H), 3.56–3.47 (m, 3 H, 3′,2′,3-H), 3.36 (t, J = 2.8 Hz, 1 H, 4′-H), 3.05 (t, J = 9.4 Hz, 1 H, 2-H), 2.85 [dd, J = 16.2, 3.2 Hz, 1 H, CH_2(CO)], 2.60 [dd, J = 16.2, 9.2 Hz, 1 H, CH_2(CO)], 1.55 (m, 2 H, CH_2 alkyl), 2.52 [m, 2 H, (CO)CH_2], 1.25 (m, 4 H, CH_2 alkyl), 0.85 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR [$(CD_3)_2CO$, 100 MHz]: δ = 213.5 (CO), 104.7 (C-1′), 80.7 (C-5), 79.9 (C-4′), 77.6 (C-3), 77.0, 74.4 (C-1,5′), 73.4 (C-2), 72.5, 71.7 (C-2′,3′), 70.2 (C-4), 62.6, 61.9 (C-6,6′), 44.3 [CH_2(CO)], 40.4 [(CO)CH_2], 32.3 (CH_2 alkyl), 24.4 (CH_2 alkyl), 23.6 (CH_2 alkyl), 14.8 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{19}H_{34}O_{11}$ [M + Na]$^+$ 461.19988; found 461.1999.

1-(*C*-Glucosyl)heptan-2-one (7b): A mixture of **α/βpyr-7b** and **α/βfur-7b** was prepared from **2** (50 mg, 0.277 mmol) and **5b** (925 mg, 4.17 mmol) under solvent-free conditions (Procedure A: yield 51%, 39.0 mg) or from **2** (50 mg, 0.277 mmol) and **5b** (184.5 mg, 0.831 mmol) under aqueous conditions (1 mL of water, yield 25%, 19.1 mg). Flash chromatography on silica gel (CH_2Cl_2/MeOH, 9:1; R_f = 0.25 with EtOAc/MeOH, 9:1). followed by freeze-drying afforded **7b** as a colourless oil. ^{1}H NMR (CD_3OD, 400 MHz): δ = 4.93 (m, 1 H, 1fα-H), 4.60 (m, 1 H, 1fβ-H), 4.31 (d, J = 3.6 Hz, 1 H, 2fα-H), 4.05 (dt, J = 8.4, 5.2 Hz, 1 H, 1pα-H), 3.85–3.40 (m, sugars), 3.08 (t, J = 8.8 Hz, 1 H, 2pβ-H), 2.84 [dd, J = 16.4, 8.4 Hz, 1 H, pα-CH_2(CO)], 2.80 [dd, J = 15.6, 2.8 Hz, 1 H, pβ-CH_2(CO)], 2.73 [dd, J = 16.4, 5.2 Hz, 1 H, pα-CH_2(CO)], 2.49 [m, 3 H, (CO)-CH_2, pβ-CH_2(CO)], 2.32 [dd, J = 13.6, 7.6 Hz, 1 H, fα-CH_2(CO)], 2.19 [dd, J = 13.6, 7.6 Hz, 1 H, fβ-CH_2(CO)], 1.91 [dd, J = 13.6, 4.8 Hz, 1 H, fβ-CH_2(CO)], 1.78 [m, 1 H, fα-CH_2(CO)], 1.51 (q, J = 7.2 Hz, 2 H, CH_2 alkyl), 1.29 (m, 4 H, CH_2 alkyl), 0.90 (t, J = 7.2 Hz, 3 H, CH_3) ppm.

Compound **βpyr-7b** was prepared from **2** (50 mg, 0.277 mmol) and **5b** (925 mg, 4.17 mmol) under solvent-free conditions (Procedure B). Flash chromatography on silica gel (CH_2Cl_2/MeOH, 9:1; R_f = 0.25 with EtOAc/MeOH, 9:1) followed by freeze-drying afforded **7b** as a colourless oil in 50% yield (34.4 mg). $[\alpha]_D$ = –15.9 (*c* = 1, MeOH). IR (neat): $\tilde{\nu}$ = 1049, 1090, 1382, 1455, 1716, 2884, 2974, 3340 cm^{-1}. ^1H NMR (CD_3OD, 400 MHz): δ = 3.70 (d, *J* = 10.8 Hz, 1 H, 6-H), 3.68 (td, *J* = 9.6, 3.2 Hz, 1 H, 1-H), 3.59 (dd, *J* = 11.0, 5.2 Hz, 1 H, 6-H), 3.36 (t, *J* = 8.6 Hz, 1 H, 3-H), 3.33 (t, *J* = 8.6 Hz, 1 H, 4-H), 3.23 (ddd, *J* = 9.2, 5.2, 2.8 Hz, 1 H, 5-H), 3.08 (t, *J* = 8.8 Hz, 1 H, 2-H), 2.80 [dd, *J* = 15.6, 2.8 Hz, 1 H, CH_2(CO)], 2.49 [m, 3 H, (CO)CH_2, CH_2(CO)], 1.51 (q, *J* = 7.2 Hz, 2 H, CH_2 alkyl), 1.29 (m, 4 H, CH_2 alkyl), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR [$(CD_3)_2CO$, 100 MHz]: δ = 210.0 (CO), 82.1 (C-5), 80.6 (C-3), 78.0 (C-1), 75.9 (C-2), 73.0 (C-4), 64.0 (C-6), 47.3 [CH_2(CO)], 44.6 [(CO)CH_2], 33.1 (CH_2 alkyl), 24.8 (CH_2 alkyl), 24.2 (CH_2 alkyl), 15.2 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{13}H_{24}O_6$ [M + Na]$^+$ 299.14706; found 299.1469.

1-(β-*C*-Galactosyl)heptan-2-one (βpyr-8b): Compound **βpyr-8b** was prepared from **3** (50 mg, 0.277 mmol) and **5b** (925 mg, 4.17 mmol) under solvent-free conditions (Procedure B). Flash chromatography on silica gel (CH_2Cl_2/MeOH, 9:1; R_f = 0.25 with EtOAc/MeOH, 9:1) followed by freeze-drying afforded **8b** as white hygroscopic crystals in 32% yield (24.5 mg). $[\alpha]_D$ = –0.7 (*c* = 1, MeOH). IR (KBr): $\tilde{\nu}$ = 1150, 1333, 1450, 1703, 2855, 2935, 3340 cm^{-1}. ^1H NMR (CD_3OD, 400 MHz): δ = 3.93 (t, *J* = 3.0 Hz, 1 H, 4-H), 3.70–3.60 (m, 3 H, 1,6-H), 3.50–3.45 (m, 3 H, 2,3,5-H), 2.82 [dd, *J* = 15.6, 2.8 Hz, 1 H, CH_2(CO)], 2.53 [dd, *J* = 15.6, 9.2 Hz, 1 H, CH_2(CO)], 2.49 [td, *J* = 7.2, 2.8 Hz, 2 H, (CO)CH_2], 1.53 (q, *J* = 7.6 Hz, 2 H, CH_2 alkyl), 1.28 (m, 4 H, CH_2 alkyl), 0.87 (t, *J* = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR [$(CD_3)_2CO$, 100 MHz]: δ = 210.09 (CO), 80.61 (C-5), 78.46 (C-1), 77.12 (C-3), 73.33 (C-2), 71.45 (C-4), 63.38 (C-6), 47.33 [CH_2(CO)], 44.62 [(CO)CH_2], 33.08, 24.88, 24.16 (CH_2 alkyl), 15.23 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{13}H_{24}O_6$ [M + Na]$^+$ 299.14706; found 299.1474.

1-(*C*-Lactosyl)tridecan-2-one (6c): A mixture of **α/βpyr-6c** was prepared from **1** (25 mg, 0.070 mmol) and **5c** (319 mg, 1.04 mmol) under solvent-free conditions (Procedure A: yield 50%, 18.1 mg). Flash chromatography on silica gel (AcOEt; R_f = 0.56 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **6c** as a yellowish solid. ^1H NMR ($CDCl_3$/CD_3OD, 9:1, 400 MHz): δ = 4.37 (dt, *J* = 8.4, 5.2 Hz, 1 H, 1α-H), 4.25 (d, *J* = 7.2 Hz, 1 H, 1′β-H), 4.22 (d, *J* = 7.2 Hz, 1 H, 1′α-H), 3.80–3.47 (m, 12 H, sugars), 3.06 (t, *J* = 9.6 Hz, 1 H, 2β-H), 2.77 [dd, *J* = 16.0, 2.8 Hz, 1 H, β-CH_2(CO)], 2.68 [m, 2 H, α-CH_2(CO)], 2.51 [dd, *J* = 16.0, 9.2 Hz, 1 H, β-CH_2(CO)], 2.42 [t, *J* = 5.6 Hz, 2 H, (CO)CH_2], 1.45 (m, 2 H, CH_2 alkyl), 1.20 (m, 16 H, CH_2), 0.90 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_3OD, 100 MHz): δ = 212.6, 212.4 (CO), 105.01, 104.97 (C-1′), 80.7, 80.6, 80.1, 77.9, 77.14, 77.07, 74.7, 73.85, 73.62, 73.55, 72.6, 72.0, 70.3, 62.5, 61.94, 61.86, (C-6, C-6′), 46.3 [(CO)CH_2, CH_2(CO)], 44.3, 44.2, 40.4, 33.1, 30.81, 30.75, 30.65, 30.60, 30.5, 30.3, 24.7, 24.6, 23.8 (CH_2 alkyl), 14.5 (CH_3) ppm.

Compound **βpyr-6c** was prepared from **1** (25 mg, 0.070 mmol) and **5c** (319 mg, 1.042 mmol) under solvent-free conditions (Procedure B). Flash chromatography on silica gel (CH_2Cl_2/MeOH, 9:1; R_f = 0.56 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **6c** as a yellowish solid in 69% yield (25.0 mg). $[\alpha]_D$ = –2.4 (*c* = 1, MeOH); m.p. 132 °C. IR (KBr): $\tilde{\nu}$ = 1024, 1076, 1136, 1379, 1464, 1715, 2851, 2920, 3415 cm^{-1}. ^1H NMR ($CDCl_3$/CD_3OD 9:1, 400 MHz): δ = 4.25 (d, *J* = 7.2 Hz, 1 H, 1′-H), 3.80–3.69 (m, 6 H, 5,6,3′,6′-H), 3.65 (td, *J* = 9.2, 2.8 Hz, 1 H, 1-H), 3.57–3.47 (m, 4 H, 3,2′,4′,5′-H), 3.33 (t, *J* = 3.2 Hz, 1 H, 4-H), 3.06 (t, *J* = 9.6 Hz, 1 H, 2-H), 2.77 [dd, *J* = 16.0, 2.8 Hz, 1 H, CH_2(CO)], 2.51 [dd, *J* = 16.0, 9.2 Hz, 1 H, CH_2(CO)], 2.42 [t, *J* = 5.6 Hz, 2 H, CO(CH_2)], 1.45 (m, 2 H, CH_2), 1.20 (m, 16 H, CH_2), 0.90 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_3OD, 100 MHz): δ = 212.29 (CO), 105.12 (C-1′), 80.81, 80.19 (C-4), 77.87, 77.17, 77.09 (C-1), 74.84, 74.76 (C-2), 72.56, 70.40, 62.58, 61.92 (C-6, C-6′), 46.24 [CH_2(CO)], 44.34 [(CO)CH_2], 33.10, 30.78, 30.68, 30.63, 30.50, 24.59, 23.77 (CH_2 alkyl), 14.48 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{25}H_{46}O_{11}$ [M + Na]$^+$ 545.29378; found 545.2941.

1-(*C*-Glucosyl)tridecan-2-one (α/βpyr-7c): A mixture of **α/βpyr-7c** was prepared from **2** (25 mg, 0.139 mmol) and **5c** (637 mg, 2.08 mmol) under solvent-free conditions (Procedure A). Flash chromatography on silica gel (AcOEt; R_f = 0.57 with EtOAc/MeOH, 9:1) followed by freeze-drying afforded **7c** as a yellowish solid in 48% yield (24.0 mg). IR (KBr): $\tilde{\nu}$ = 1081, 1262, 1423, 1713, 2854, 2926, 3396 cm^{-1}. ^1H NMR ($CDCl_3$/CD_3OD: 9:1, 400 MHz): δ = 4.93 (dt, *J* = 8.0, 3.6 Hz, 1 H, 1fα-H), 4.60 (td, *J* = 7.6, 5.2 Hz, 1 H, 1fβ-H), 4.31 (d, *J* = 3.6 Hz, 1 H, 2fα-H), 4.03 (dt, *J* = 7.6, 5.6 Hz, 1 H, 1pα-H), 3.91–3.51 (m, 5 H, sugars), 3.30 (m, 1 H, sugars), 3.07 (t, *J* = 9.2 Hz, 1 H, 2pβ-H), 2.85 [dd, *J* = 16.0, 3.0 Hz, 1 H, pβ-CH_2(CO)], 2.84 [dd, *J* = 16.6, 7.6 Hz, 1 H, pα-CH_2(CO)], 2.73 [dd, *J* = 16.6, 5.6 Hz, 1 H, pα-CH_2(CO)], 2.54 [dd, *J* = 16.0, 9.2 Hz, 1 H, pβ-CH_2(CO)], 2.43 [t, *J* = 5.2 Hz, 2 H, (CO)CH_2], 2.25 [dd, *J* = 14.0, 8.0 Hz, 1 H, fα-CH_2(CO)], 2.15 [dd, *J* = 13.6, 7.6 Hz, 1 H, fβ-CH_2(CO)], 1.91 [dd, *J* = 13.6, 5.2 Hz, 1 H, fβ-CH_2(CO)], 1.77 [dd, *J* = 14.0, 3.6 Hz, 1 H, fα-CH_2(CO)], 1.51 [t, *J* = 6.8 Hz, 2 H, (COCH_2)CH_2], 1.21 (m, 16 H, CH_2), 0.90 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$/CD_3OD: 9:1, 100 MHz): δ = 211.4 (CO), 89.8 (C-2fα), 86.9 (C-1fα), 85.2 (C-1fβ), 82.2, 81.6, 81.1, 80.2, 79.8, 79.2 (C-1pβ), 78.0 (C-2pβ), 77.6 (C-1fβ), 76.6, 75.8, 75.1, 73.9, 73.2, 70.6, 70.4, 69.9, 64.2, 63.8 (C-6), 44.8 [pα-CH_2(CO)], 43.8 [pβ-CH_2(CO)], 42.3 [fα-CH_2(CO)], 42.1 [(CO)CH_2], 39.1 [fβ-CH_2(CO)], 31.8, 29.62, 29.55, 29.47, 29.42, 29.40, 29.3, 29.2, 29.1, 28.9, 24.4, 23.5, 22.6 (CH_2 alkyl), 13.90 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{19}H_{36}O_6$ [M + Na]$^+$ 383.24096; found 383.2407; [M + K]$^+$ 399.21490; found 399.2153.

1-(*C*-Galactosyl)tridecan-2-one (8c): A mixture of compounds **8c** was prepared from **3** (25 mg, 0.139 mmol) and **5c** (637 mg, 2.08 mmol) under solvent-free conditions (Procedure A). Flash chromatography on silica gel (AcOEt; R_f = 0.57 with EtOAc/MeOH, 9:1) followed by freeze-drying afforded **8c** as a yellowish solid in 64% yield (32 mg). IR (KBr): $\tilde{\nu}$ = 1100, 1636, 1910, 3449 cm^{-1}. ^1H NMR ($CDCl_3$/CD_3OD, 9:1, 400 MHz): δ = 4.64 (t, *J* = 5.2 Hz, 1 H, 1fα-H), 4.39 (dd, *J* = 4.8, 0.8 Hz, 1 H, 2fα-H), 4.31 (td, *J* = 6.4, 3.6 Hz, 1 H, 1pα-H), 4.15–3.90 (m, sugars), 3.82 (dd, *J* = 3.6, 0.8 Hz, 1 H, 2pα-H), 3.73–3.52 (m, 5 H, sugars), 2.73 [m, 2 H, pα-CH_2(CO)], 2.40 [t, *J* = 6.5 Hz, 2 H, (CO)CH_2], 2.11 [d, *J* = 14.2 Hz, 1 H, fα-CH_2(CO)], 1.85 [dd, *J* = 14.2, 5.2 Hz, 1 H, fα-CH_2(CO)], 1.47 (t, *J* = 6.8 Hz, 2 H, CH_2 alkyl), 1.17 (m, 16 H, CH_2), 0.80 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$/CD_3OD, 9:1, 100 MHz): determined from HMBC and HSQC experiments: δ = 211.6 (CO), 87.7, 85.8, 83.8, 83.4 (C-1fα), 80.4, 79.1, 78.2, 77.9, 76.9 (C-1pα), 76.7 (C-2pα), 71.9, 63.5, 62.8 (C-6), 43.7 [(CO)CH_2], 42.1 [fα-CH_2(CO)], 41.9 [pα-CH_2(CO)], 31.8, 30.11, 30.05, 29.8, 23.6, 22.60, (CH_2 alkyl), 14.9 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{19}H_{36}O_6$ [M + Na]$^+$ 383.24096; found 383.2409.

1-(*C*-Lactosyl)nonadecan-2-one (6d): A mixture of **α/βpyr-6d** was prepared from **1** (25 mg, 0.070 mmol) and **5d** (406 mg, 1.04 mmol) under solvent-free conditions (Procedure A). Flash chromatography on silica gel (AcOEt/CH_2Cl_2, 1:1, then AcOEt; R_f = 0.69 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded

6d as a white solid in 70% yield (29.0 mg); m.p. 115 °C. IR (KBr): $\tilde{\nu}$ = 1048, 1266, 1422, 1712, 2927, 2975, 3043 cm^{-1}. ^1H NMR ([D_6]DMSO, 400 MHz): δ = 4.35 (dt, J = 8.8, 5.6 Hz, 1 H, 1α-H), 4.23 and 4.21 (d, J = 7.6 Hz, 1 H, 1′α,1′β-H), 3.74–3.33 (m, 11 H, sugars), 3.01 (m, 1 H, 2β-H), 2.75 [dd, J = 16.0, 2.8 Hz, 1 H, β-CH_2(CO)], 2.65 [m, 2 H, α-CH_2(CO)], 2.41 [dd, J = 16.0, 9.6 Hz, 1 H, β-CH_2(CO)], 2.36 [m, 2 H, (CO)CH_2], 1.43 (m, 2 H, CH_2 alkyl), 1.18 (m, 28 H), 0.81 (t, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): determined from HMBC and HSQC experiments: δ = 210.5 (CO), 104.2 (C-1′), 81.5, 75.9, 75.8, 73.7, 72.3, 71.2, 70.6, 68.6, 61.5, 61.4 (C-6, C-6′), 60.9, 45.6 [β-CH_2(CO)], 43.1 [(CO)CH_2], 39.4 [α-CH_2(CO)], 32.6, 31.5, 30.8, 30.1, 29.7, 29.5, 29.4, 29.2, 28.7, 27.6, 26.7, 23.7, 23.4, 22.5, 22.3, 14.2 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{31}H_{58}O_{11}$ [M + Na]$^+$ 629.38768; found 629.3877.

1-(*C*-Glucosyl)nonadecan-2-one (7d): A mixture of compounds **7d** was prepared from **2** (25 mg, 0.139 mmol) and **5d** (812 mg, 2.08 mmol) under solvent-free conditions (Procedure A). Flash chromatography on silica gel (CH_2Cl_2 then CH_2Cl_2/MeOH, 9:1; R_f = 0.43 with CH_2Cl_2/MeOH, 9:1) followed by freeze-drying afforded **7d** as a white solid in 63% yield (38.8 mg). IR (KBr): $\tilde{\nu}$ = 880, 1048, 1268, 1382, 1698, 2539, 2973, 2975, 3331 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.93 (dt, J = 7.6, 3.6 Hz, 1 H, 1fα-H), 4.77 (t, J = 4.8 Hz, 1 H, 1fβ-H), 4.53 (td, J = 7.6, 5.2 Hz, 1 H, 1pα-H), 4.50 (d, J = 4.0 Hz, 1 H, 2fα-H), 4.43 (d, J = 4.4 Hz, 1 H, 2fβ-H), 4.19 (d, J = 3.2 Hz, 1 H, 3pα-H), 4.14 (dd, J = 3.2, 0.8 Hz, 1 H, 3fα-H), 4.10 (m, 1 H, 2pα-H), 3.90–3.35 (m, sugars), 3.03 (t, J = 9.2 Hz, 1 H, 2pβ-H), 2.85 [dd, J = 16.0, 3.6 Hz, 1 H, pβ-CH_2(CO)], 2.84 [dd, J = 16.4, 7.6 Hz, 1 H, pα-CH_2(CO)], 2.70 [dd, J = 16.4, 5.6 Hz, 1 H, pα-CH_2(CO)], 2.52 [dd, J = 16.0, 3.2 Hz, 1 H, pβ-CH_2(CO)], 2.42 [m, 2 H, (CO)CH_2], 2.19 [dd, J = 14.0, 7.6 Hz, 1 H, fα-CH_2(CO)], 2.12 [dd, J = 14.8, 7.6 Hz, 1 H, fβ-CH_2(CO)], 1.96 [dd, J = 14.8, 5.6 Hz, 1 H, fβ-CH_2(CO)], 1.79 [dd, J = 14.0, 3.2 Hz, 1 H, fα-CH_2(CO)], 1.50 (m, 2 H, CH_2 alkyl), 1.21 (m, 28 H, CH_2), 0.81 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 211.1, 210.88, 210.85, 210.7 (CO), 86.5 (C-1pα), 82.2, 81.7 (C-1fα), 81.0, 80.0, 79.8, 79.4, 79.3, 79.0, 76.5, 75.33, 75.25, 74.4, 73.7, 73.2, 73.1, 71.2, 70.4, 69.8, 67.6, 63.8, 63.6, 63.5, 61.1, 61.2, 46.0 [pα-CH_2(CO)], 44.8 [pβ-CH_2(CO)], 43.2 [fα-CH_2(CO)], 42.88 [fβ-CH_2(CO)], 42.87 [(CO)CH_2], 23.1 (CH_2 alkyl), 31.4 (CH_2 alkyl), 29.4–28.6 (CH_2), 22.1, 13.3 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{25}H_{48}O_6$ [M + Na]$^+$ 467.3348; found 467.3346.

1-(*C*-Lactosyl)nonadec-10-en-2-one (6e): A mixture of **α/βpyr-6e** was prepared from **1** (25 mg, 0.070 mmol) and **5e** (404 mg, 1.04 mmol) under solvent-free conditions (Procedure A). Flash chromatography on silica gel (AcOEt/CH_2Cl_2, 1:1, then AcOEt; R_f = 0.67 with EtOAc/*i*PrOH/H_2O, 5:4:1) followed by freeze-drying afforded **6d** as a white solid in 58% yield (24.7 mg); m.p. 98 °C. IR (KBr): $\tilde{\nu}$ = 745, 1078, 1262, 1384, 1708, 2853, 2924, 3364 cm^{-1}. ^1H NMR ($CDCl_3$/CD_3OD, 9:1, 400 MHz): δ = 5.30 (m, 2 H, CH=CH), 4.50 (dt, J = 7.8, 5.5 Hz, 1 H, 1α-H), 4.34 (d, J = 7.6 Hz, 1 H, 1′β-H), 4.31 (d, J = 7.5 Hz, 1 H, 1′α-H), 3.84–3.45 (m, 11 H, sugars), 3.15 (t, J = 8.8 Hz, 1 H, 2β-H), 2.86 [dd, J = 16.0, 2.76 Hz, 1 H, β-CH_2(CO)], 2.79 [m, 2 H, α-CH_2(CO)], 2.57 [dd, J = 16.0, 9.1 Hz, 1 H, β-CH_2(CO)], 2.49 [m, 2 H, (CO)CH_2], 1.99 [m, 4 H, CH_2(CH=CH)], 1.54 (m, 2 H, CH_2 alkyl), 1.27 (m, 11 H, CH_2 alkyl), 0.86 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$/CD_3OD, 1:9, 100 MHz): δ = 211.7, 209.9 (CO), 130.9, 130.6, 130.4, 129.6 (CH=CH), 104.6, 104.5 (C-1′), 80.7, 80.6, 79.6, 78.9, 78.7, 77.5, 76.6, 76.5 (C-1α), 74.3, 74.2, 73.4, 73.1, 72.9, 72.1, 71.5, 69.8, 62.2, 61.7, 45.9 [(CO)CH_2], 43.9 [α-CH_2(CO)], 40.2 [β-CH_2(CO)], 32.6–32.4 (CH_2), 30.5–29.5 (CH_2), 27.9, 23.4, 14.5 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{31}H_{56}O_{11}$ [M + Na]$^+$ 627.37203; found 627.3721.

1-(*C*-Glucosyl)nonadec-10-en-2-one (7e): A mixture of compounds **7e** was prepared from **2** (25 mg, 0.139 mmol) and **5e** (808 mg, 2.08 mmol) under solvent-free conditions (Procedure A). Flash chromatography on silica gel (CH_2Cl_2 then CH_2Cl_2/MeOH, 9:1; R_f = 0.20 with CH_2Cl_2/MeOH, 9:1) followed by freeze-drying afforded **7e** as a colourless oil in 50% yield (30.7 mg). IR (KBr): $\tilde{\nu}$ = 1036, 1264, 1455, 1716, 2854, 2927, 3320 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): assignments were made on the basis of 1D TOCSY experiments: δ = 5.32 (m, 2 H, CH=CH), 4.98 (quint., J = 4.2 Hz, 1 H, 1fα-H), 4.81 (t, J = 4.5 Hz, 1 H, 1fβ-H), 4.50 (d, J = 5.0 Hz, 1 H, 2fα-H), 4.43 (dt, J = 7.0, 3.6 Hz, 1 H, 1pα-H), 4.41 (d, J = 3.9 Hz, 1 H, 2fβ-H), 4.20–4.07 (m, sugars), 4.00–3.75 (m, sugars), 3.72–3.30 (m, sugars), 3.09 (t, J = 8.8 Hz, 1 H, 2pβ-H), 2.89 [dd, J = 17.1, 4.8 Hz, 1 H, pα-CH_2(CO)], 2.83 [dd, J = 15.9, 2.4 Hz, 1 H, pβ-CH_2(CO)], 2.73 [dd, J = 17.1, 6.3 Hz, 1 H, pα-CH_2(CO)], 2.56 [dd, J = 15.9, 9.0 Hz, 1 H, pβ-CH_2(CO)], 2.45 [m, 2 H, (CO)CH_2], 2.26 [dd, J = 14.1, 7.5 Hz, 1 H, fα-CH_2(CO)], 2.11 [dd, J = 15.3, 10.2 Hz, 1 H, fβ-CH_2(CO)], 1.94 [m, 1 H, fβ-CH_2(CO)], 1.93 [m, 4 H, CH_2(CH=CH)], 1.85 [dd, J = 14.1, 3.6 Hz, 1 H, fα-CH_2(CO)], 1.48 (m, 2 H, CH_2 alkyl), 1.21 (m, 20 H, CH_2), 0.89 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): determined from HMBC and HSQC experiments: δ = 210.5 (CO), 129.8 (CH=CH), 86.9 (C-2fα), 89.8 (C-2fβ), 82.6 (C-1fβ), 82.0 (C-1fα), 81.50, 80.2, 81.1, 79.7, 78.2, 77.8, 77.6, 77.0, 76.6 (C-1pα), 75.7, 75.0, 73.5, 71.1, 70.4, 69.6, 64.0, 61.6, 48.9, 48.0, 46.3 [pα-CH_2(CO)], 43.5 [fα-CH_2(CO)], 43.3, 41.8 [pβ-CH_2(CO)], 39.6 [(CO)CH_2], 39.4, 32.6 (CH_2 alkyl), 31.7, 30.7, 29.7, 29.0, 28.8, 28.10, 27.1, 26.5 [CH_2(CH=CH)], 24.4, 23.5, 23.4, 22.6, 22.4, 13.9 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{25}H_{46}O_6$ [M + Na]$^+$ 465.31921; found 465.3193.

Supporting Information (see also the footnote on the first page of this article): ^{13}C NMR spectra of the previously unknown compounds **6a**–**e**, **7b**–**e** and **8a**–**c**.

Acknowledgments

We thank the Association Nationale de la Recherche et de la Technologie (ANRT) and Armor Protéines for a grant to A. R. and for funding.

[1] D. E. Levy, C. Tang, *The Chemistry of C-Glycosides*, Pergamon Press, Tarrytown, NY, **1995**.
[2] M. H. D. Postema, *C-Glycoside Synthesis*, CRC Press, Boca Raton, **1995**.
[3] H. Shao, Z. Wang, E. Lacroix, S.-H. Wu, H. J. Jennings, W. Zou, *J. Am. Chem. Soc.* **2002**, *124*, 2130–2131.
[4] F. Rodrigues, Y. Canac, A. Lubineau, *Chem. Commun.* **2000**, 2049–2050.
[5] Y. Hersant, R. Abou-Jneid, Y. Canac, A. Lubineau, M. Philippe, D. Semeria, X. Radisson, M.-C. Scherrmann, *Carbohydr. Res.* **2004**, *339*, 741–745.
[6] N. Bragnier, M.-C. Scherrmann, *Synthesis* **2005**, 814–818.
[7] I. Riemann, M. A. Papadopoulos, M. Knorst, W. D. Fessner, *Aust. J. Chem.* **2002**, *55*, 147–154.
[8] A. Cavezza, C. Boulle, A. Guéguiniat, P. Pichaud, S. Trouille, L. Ricard, M. Dalko-Csiba, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 845–849.
[9] S. Jarosz, *J. Carbohydr. Chem.* **2001**, *20*, 93–107.
[10] S. Jeanmart, R. J. K. Taylor, *Tetrahedron Lett.* **2005**, *46*, 9043–9048.
[11] A. H. Davidson, L. R. Hughes, S. S. Qureshi, B. Wright, *Tetrahedron Lett.* **1988**, *29*, 693–696.

[12] V. Aucagne, D. Gueyrard, A. Tatibouët, A. Quinsac, P. Rollin, *Tetrahedron* **2000**, *56*, 2647–2654.
[13] The compound numbering used in this article is defined as follows: α and β relate to the configuration at C-1 of the sugar moiety, pyr and fur refer, respectively, to pyranoside and furanoside derivatives and the letter relates to the alkyl chain length.
[14] S. Howard, S. G. Withers, *J. Am. Chem. Soc.* **1998**, *120*, 10326–10331.

Received: November 9, 2009
Published Online: January 18, 2010

