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Convenient Syntheses and Transformations of 2-*C*-Malonyl Carbohydrates

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Abstract: 2-*C*-malonyl carbohydrates were synthesized in only few steps and high yields by radical additions of malonates to glycals. For the first time, the undesired formation of nitrates was completely suppressed with anhydrous cerium ammonium nitrate (CAN) as oxidizing agent. A coherent explanation for the high stereoselectivities of the additions to *gluco*-configured glycals was provided by variation of the substituents in the 3-position. We established steric effects for the face selectivity, and electronic effects strongly influence the reactivity of the double bonds. The scope and limitation of transition-metal-mediated radical reactions in the synthesis of 2-*C*-branched carbohydrates was thoroughly investigated. Thus, unsaturated disaccharides and benzyl-protected glycals were used as substrates for the first time. Finally, the 2-*C*-malonyl carbohydrates were transformed into various products by decarboxylation, saponification and reduction, which afforded interesting precursors for *C*-disaccharides. In this paper we describe the syntheses of more than 40 new 2-*C*-analogues of carbohydrates, which were isolated in high yields in analytically pure form. Therefore, the transition-metal-mediated radical addition of malonates to glycals offers a simple and convenient entry to such important carbohydrate derivatives.

Keywords: carbohydrates · C-glycosides · radicals · synthetic methods · transformations

Introduction

C-Glycosides are of current interest in chemistry, biology, and medicine.[1] They are characterized by the substitution of the interglycosidic oxygen by a carbon atom, resulting in higher stabilities towards enzymatic and chemical hydrolyses. Although many synthetic strategies for simple *C*-glycosides were developed over the years,[2] the preparation of *C*-oligosaccharides is more laborious and depends on a convenient access to the corresponding *C*-branched monosaccharides.[3] For this purpose, carbon substituents can be easily introduced at the anomeric center, whereas *C*-functionalizations at other positions of the carbohydrate require many steps. Especially carboxylic acid side chains are of current interest, since they offer an elegant entry to *C*-oligosaccharides by ring-closing metathesis.[4] Herein, we describe general and convenient syntheses of such *C*-branched carbohydrates in only few steps and high selectivities from easily available precursors.

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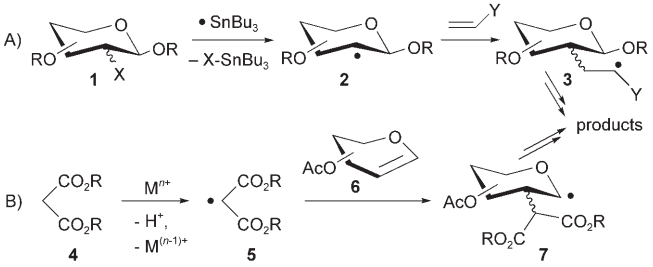
Radical reactions have become an important and versatile tool for the selective formation of carbon–carbon bonds in highly functionalized molecules and have found many applications in natural product chemistry.[5] In context with our studies on transition-metal-mediated radical reactions,[6] we became interested in the synthesis of 2-*C*-branched carbohydrates by this methodology.[7] The introduction of carbon chains at the 2-position of carbohydrates was previously realized by epoxide opening[8] or by rearrangements,[9] however the synthesis of the precursors required many reactions steps. More recently, the cyclopropanation of glycals and subsequent ring opening offered a simpler access,[10] but radical reactions are still a very convenient way for the stereoselective synthesis of 2-*C*-branched carbohydrates. The two different radical strategies are summarized in Scheme 1.

Starting from precursor **1**, the carbohydrate radicals **2** can be generated and added to alkenes to afford the 2-*C*-branched carbohydrates **3** (Scheme 1, pathway A). Although many inter- and intramolecular applications of such reactions have been described,[4d,e,11] the tedious synthesis of the precursors **1**, the high toxicity of the reagents, and the often moderate stereoselectivities are disadvantageous. Therefore, we developed a simple procedure to introduce malonyl substituents at the 2-position of carbohydrates in only one step from commercially available starting materials (Scheme 1, pathway B).[7] The reaction of malonates **4** with $Mn(OAc)_3$



Scheme 1. Radical strategies for the syntheses of 2-*C*-branched carbohydrates. R = protecting group; X = I, HgOAc, PhOC(S)O; Y = acceptor, CH_2SnBu_3; $M^{n+} = Mn^{3+}$, Ce^{4+}.

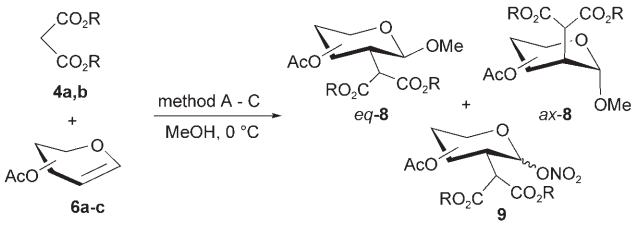
or cerium ammonium nitrate (CAN) generates the electrophilic radicals **5**, which add to glycals **6** to afford 2-*C*-malonyl carbohydrates via the radicals **7** in high yields, regio- and stereoselectivities.

We were able to extend our methodology to 1-substituted glycals,[12] to other CH acidic precursors,[13] and applied transition-metal-mediated radical reactions as the key step in the synthesis of 3-deoxy-D-oct-2-ulosonic acids (KDO).[14] Very recently, we described the decarboxylation of the malonate addition products to carboxylic acids.[15] However, our previous studies were limited to acetylated monosaccharides and no disaccharides were investigated. Furthermore, base stable protecting groups would allow various further transformations of the malonyl sided chain.

Herein we examine the scope and limitations of transition-metal-mediated radical reactions in the synthesis of 2-*C*-branched carbohydrates. The formation of nitrates could be suppressed and a coherent explanation for the high stereoselectivities of the additions by variation of the substituents in the 3-position is provided. Unsaturated disaccharides and benzyl-protected glycals, which are stable under basic reaction conditions, are used as substrates for transition-metal-mediated C–C-bond formations for the first time. Finally, selective transformations of the addition products provide an easy access to a variety of 2-*C*-branched carbohydrates, which can serve as precursors for the synthesis of *C*-glycosides.

Results and Discussion

Optimization and stereoselectivities of the radical additions: The reaction of malonates **4** with glycals **6** and oxidative trapping of the radicals **7** could lead to eight different regio- and stereoisomers (Scheme 1, pathway B). However, our previous studies have shown that the radicals add selectively to the 2-position under orbital control to afford only one regioisomer.[7] Furthermore, the reactions are highly 1,2-*trans* selective, since the methyl glycosides **8** are formed by a neighboring group participation of the malonyl substituents. On the other hand, nitrates **9** were isolated as by-products, which reduced the yields of the desired 2-*C*-analogues **8**. To optimize the reactions and to study the stereoselectivities, we investigated the addition of dimethyl (**4a**) and diisopropyl malonate (**4b**) to the glycals **6a–c** under various conditions (Scheme 2).



6a (*gluco*)	**4a**: R = Me	A	*gluco*-**8a** (62%)	*manno*-**8a** (14%)	*gluco*-**9a** (16%)
6a (*gluco*)	**4a**: R = Me	B	*gluco*-**8a** (41%)	*manno*-**8a** (12%)	*gluco*-**9a** (34%)
6a (*gluco*)	**4a**: R = Me	C	*gluco*-**8a** (80%)	*manno*-**8a** (15%)	-
6a (*gluco*)	**4b**: R = *i*Pr	A	*gluco*-**8b** (68%)	*manno*-**8b** (8%)	*gluco*-**9b** (16%)
6a (*gluco*)	**4b**: R = *i*Pr	B	*gluco*-**8b** (40%)	*manno*-**8b** (8%)	*gluco*-**9b** (38%)
6a (*gluco*)	**4b**: R = *i*Pr	C	*gluco*-**8b** (86%)	*manno*-**8b** (9%)	-
6b (*galacto*)	**4a**: R = Me	A	*galacto*-**8a** (78%)	-	*galacto*-**9a** (8%)
6b (*galacto*)	**4a**: R = Me	B	*galacto*-**8a** (47%)	-	*galacto*-**9a** (35%)
6b (*galacto*)	**4a**: R = Me	C	*galacto*-**8a** (87%)	-	-
6b (*galacto*)	**4b**: R = *i*Pr	A	*galacto*-**8b** (73%)	-	*galacto*-**9b** (17%)
6b (*galacto*)	**4b**: R = *i*Pr	B	*galacto*-**8b** (46%)	-	*galacto*-**9b** (36%)
6b (*galacto*)	**4b**: R = *i*Pr	C	*galacto*-**8b** (88%)	-	-
6c (*arabino*)	**4a**: R = Me	C	-	*arabino*-**8a** (89%)	-
6c (*arabino*)	**4b**: R = *i*Pr	C	-	*arabino*-**8b** (87%)	-

Scheme 2. Addition of malonates **4** to glycals **6**. Method A: 4 equiv CAN; method B: 4 equiv CAN, 0.5 equiv water; method C: 4 equiv anhydrous CAN. Yields of isolated products after column chromatography are indicated in parentheses.

The generation of malonyl radicals from commercially available CAN affords the nitrates **9** as by-products in 8–17% yield (method A). Such nitrates are often observed in transition-metal-mediated radical reactions.[16] In our previous studies we discussed the direct attack of the adduct radicals **7** to the nitrate ligand of CAN as a mechanistic rational.[7] However, an ionic trapping of the anomeric carbenium ion by nitric acid, which is always present in wet CAN, might explain the formation of the nitrates **9** as well. To prove this hypothesis, we added 0.5 equiv of water to the commercially available CAN (method B) and conducted the radical additions under otherwise identical conditions. Indeed, the yields of the nitrates **9** increased to 34–38% (Scheme 2), which is in accordance to an ionic mechanism.

For synthetic applications and further transformations of the 2-*C*-malonyl carbohydrates **8**, it was important to suppress the undesired formation of the nitrates **9**. This was achieved employing anhydrous CAN, derived from drying of the commercially available material in a desiccator under high vacuum. Under such conditions no nitrate **9** was obtained and the methyl glycosides **8** could be isolated in high yields in analytically pure form (method C, Scheme 2). Additionally, separation of the products by column chromatography was much easier. Therefore, the new method C with anhydrous cerium ammonium nitrate represents an improvement for transition-metal-mediated radical reactions in carbohydrate chemistry and was employed for all subsequent malonate additions in this paper.

The attack of the radicals to the double bonds of the glycals **6** proceeds with good to excellent stereoselectivities. Especially tri-*O*-acetyl-D-galactal (**6b**) and di-*O*-acetyl-D-arabinal (**6c**) afford exclusively one diastereomer **8** in high yields (Scheme 2). This can be rationalized by unfavorable interactions of the incoming radicals with a pseudo-axial *O*-acetyl group (Figure 1), which is in accordance to our previous studies.[7]

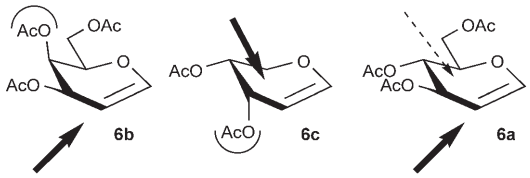
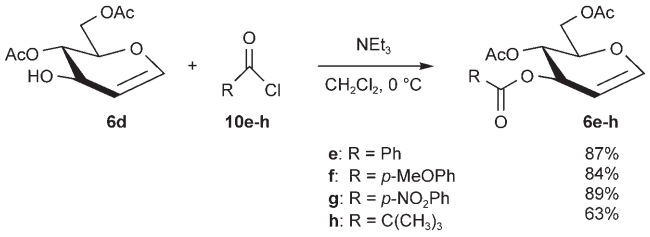


Figure 1. Preferred side of attack for radicals **5** to glycals **6a–c**.

On the other hand, only a moderate influence of the steric demand of dimethyl malonate (**4a**) versus diisopropyl malonate (**4b**) on the stereoselectivities was observed, since the ester groups are too far away from the reaction center. Finally, tri-*O*-acetyl-D-glucal (**6a**) represents an interesting example for the addition of malonates **4**. Although both *O*-acetyl groups are oriented pseudo-equatorial (Figure 1), the *gluco*/*manno* ratio of the methyl glycosides **8** was rather high with values ranging from 84:16 to 91:9.

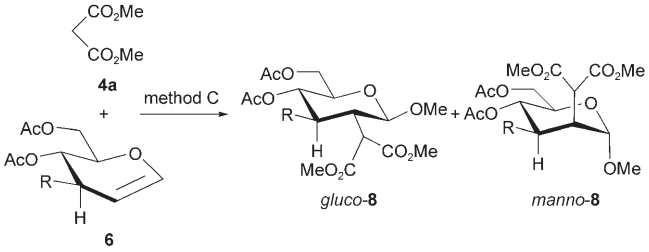
In order to explain the good selectivities in favor of the *gluco* isomers, we synthesized various 3-substituted glycals **6e–h** from 4,6-di-*O*-acetyl-D-glucal (**6d**)[17] by esterification. High yields were obtained with the acid chlorides **10** and triethylamine as base, only the sterically hindered pivaloyl chloride (**10h**) reacted less efficiently (Scheme 3). All glycals were isolated in analytically pure form by column chromatography.



Scheme 3. Synthesis of the glycals **6e–h**.

The radical addition of dimethyl malonate (**4a**) to the *gluco*-configured glycals **6d–h** was performed with anhydrous CAN to suppress the formation of nitrates (method C). Indeed, the methyl glycosides **8** were obtained regioselectively in high yields as sole 1,2-*trans* isomers (Table 1). Only the unprotected glycal **6d** afforded oxidative by-products, due to the labile allylic alcohol. The diastereoselectivities of the additions (*gluco*/*manno* ratios) were compared

Table 1. Addition of dimethyl malonate (**4a**) to various 3-substituted glycals **6**.



Glycal **6**[a]	R	*gluco*/*manno*[b]	*gluco*-**8** [%][c]	*manno*-**8** [%][c]
6a	OAc	84:16	*gluco*-**8a** (80)	*manno*-**8a** (15)
6e	O_2CPh	83:17	*gluco*-**8e** (78)	*manno*-**8e** (16)
6f	$O_2CPhpOMe$	79:21	*gluco*-**8f** (74)	*manno*-**8f** (20)
6g	$O_2CPhpNO_2$	81:19	*gluco*-**8g** (73)	*manno*-**8g** (17)
6h	$O_2C(CH_3)_3$	82:18	*gluco*-**8h** (75)	*manno*-**8h** (16)
6d	OH	94:6	*gluco*-**8d** (45)	*manno*-**8d** (3)
6i	H	54:46	*gluco*-**8i** (47)	*manno*-**8i** (40)

[a] All reactions were performed on a 2 mmol scale with method C (4 equiv anhydr. CAN, MeOH, 0 °C). [b] *gluco*/*manno* ratios determined by ^{1}H NMR analysis of the crude product (600 MHz). [c] Yields of isolated products after column chromatography.

with tri-*O*-acetyl-D-glucal (**6a**) and with the unsubstituted 4,6-di-*O*-acetyl-3-deoxy-D-glucal (**6i**)[18] (Table 1).

Interestingly, the different ester groups in the 3-position have no influence on the facial selectivity of the radical attack. Thus, for all glycals **6a** and **6e–f** the ratio of *gluco*/*manno* is approximately 5:1. Even the sterically most demanding pivaloyl derivative **6h** did not change the diastereoselectivity and the methyl glycoside *gluco*-**8h** was isolated in 75% yield. This can be rationalized by a conformation of the ester groups, where the substituents R are too far away from the reacting double bond (see Scheme 3).

On the other hand, the unprotected 4,6-di-*O*-acetyl-D-glucal (**6d**) exhibits the highest selectivity in favor of the *gluco* isomer (Table 1). An explanation might be the complexation of CAN or the polar solvent to the free OH group, which shields the upper side of the glycal closer to the double bond and hinders the *manno* attack of radicals more efficiently. The fact that the steric influence of the substituents in the 3-position is indeed responsible for the high *gluco* selectivity was finally demonstrated with 4,6-di-*O*-acetyl-3-deoxy-D-glucal (**6i**).[18] Now both faces are not shielded (R = H) and the addition of dimethyl malonate (**4a**) afforded the methyl glycosides **8i** in a *gluco*/*manno* ratio of almost 1:1 (Table 1).

Besides the stereoselectivities, an interesting influence of the benzoate groups on the reactivity of the glycals **6e–g** was established. Thus, the *p*-methoxy substituted derivative **6f** gave complete conversion after 3 h, whereas the reaction of benzoyl glucal **6e** took 6 h and the *p*-nitro substituted

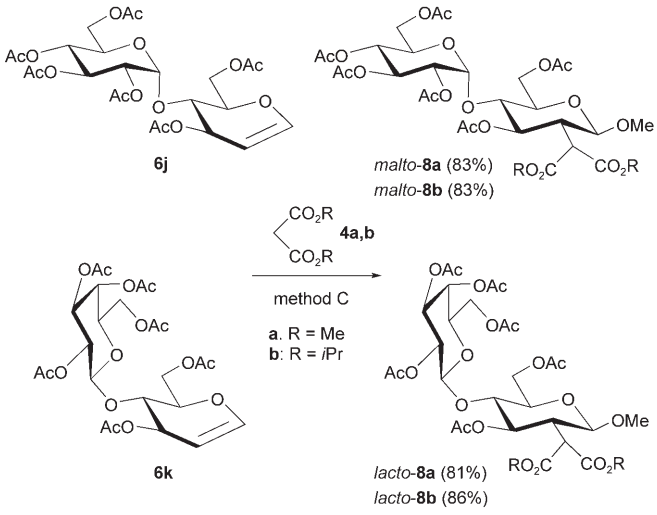
system **6g** even 12 h. These differences in reaction times nicely correlate with the electronic properties of the functional groups. The electrophilic malonyl radicals **5** interact preferentially with the HOMO of the double bond,[5] and therefore electron donors should accelerate the additions. However, the fact that the electronic effects of the *p*-substituents influence the HOMO energies of the glycals **6e–g** through many bonds is a remarkable finding.

In summary, the application of anhydrous CAN (method C) suppressed completely the formation of nitrates **9** and increased the yields of the desired methyl glycosides **8** considerably. A coherent explanation for the high stereoselectivities of the additions to glucals was provided by unfavorable steric interactions of the incoming radicals with the substituents in the 3-position. Although benzoates do not alter the stereochemical course of the reactions, a remarkable influence of the *p*-substituents on the reactivity was established.

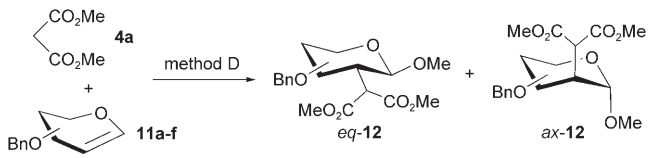
Addition of malonates to unsaturated disaccharides and benzyl-protected glycals: After the successful addition of malonates **4** to the glycals **6a–i** we became interested in the conversion of unsaturated disaccharides **6j–k**, to extend the scope of transition-metal-mediated radical reactions in carbohydrate chemistry. Especially the stability of the glycosidic linkage under the oxidative and acidic conditions in the presence of $Mn(OAc)_3$ or CAN was problematic. We chose hexa-*O*-acetyl-D-maltal (**6j**) and hexa-*O*-acetyl-D-lactal (**6k**) as representative examples, since they are components of many naturally occurring oligosaccharides and can be easily synthesized on a large scale.[19] The addition of dimethyl malonate (**4a**) and diisopropyl malonate (**4b**) was investigated with respect to the stereoeselectivities and yields (Scheme 4).

We conducted the first experiments with $Mn(OAc)_3$ to generate the malonyl radicals **5**, but the acidic reaction conditions led to the partial cleavage of the glycosidic linkages. Commercially available cerium ammonium nitrate afforded the nitrates **9** as by-products and therefore anhydrous CAN (method C) gave again the best results. Thus, the methyl glycosides *malto*-**8** and *lacto*-**8** were obtained as sole products in high yields (Scheme 4). All products were isolated by column chromatography or even simple recrystallization in analytically pure form. The exclusive formation of one stereoisomer can be rationalized by the second sugar ring, which efficiently shields the upper face of the double bond. Therefore, the malonyl radicals **5** can only attack from one side, independent of the steric demand of the ester groups (Me vs *i*Pr). To summarize, we realized the first syntheses of 2-*C*-malonyl disaccharides in only few steps, which clearly extends the scope of transition-metal-mediated C–C-bond formations in carbohydrate chemistry.

For synthetic applications and further transformations of the 2-*C*-malonyl carbohydrates **8** it was necessary to change the *O*-acetyl groups at the sugar ring, since acetates and malonates undergo similar reactions. Especially base stable protective groups, like *O*-benzyl, would allow saponifications and reductions without cleavage. Additionally, the benzyl ethers could be removed selectively by hydrogenolysis.[20] We decided to introduce the protective groups directly into the starting materials, since *O*-benzylated glycals **11** are available from the *O*-acetylated precursors **6** on a large scale by a one-step procedure.[21] However, the stability of benzyl ethers under the oxidative and Lewis-acidic conditions of the radical reactions had to be examined. Indeed, the addition of dimethyl malonate (**4a**) to the glycals **11** in the presence of $Mn(OAc)_3$ or commercially available CAN failed. Even anhydrous CAN (method C) led to partial cleavage of the protective groups and an undesired Ferrier-rearrangement.[22] Therefore, we added four equivalents of $NaHCO_3$ to the reaction mixture (method D) to suppress the formation of such by-products. Under these conditions the addition of dimethyl malonate (**4a**) to the glycals **11** proceeded smoothly and the methyl glycosides **12** were isolated in high yields (Scheme 5). The reactions were applicable for unsaturated hexoses, pentoses, and disaccharides and again the 1,2-*trans* isomers were obtained as the sole products. The stereoselectivities are in accordance to the radical additions to *O*-acetylated glycals **6** and only the *gluco*- and *xylo*-



Scheme 4. Addition of malonates **4** to glycals **6j** and **6k**. Method C: 4 equiv anhydrous CAN, MeOH, 0 °C. Yields of isolated products after column chromatography are indicated in parentheses.

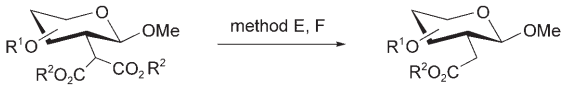


11a (*gluco*)	*gluco*-**12** (78%)	*manno*-**12** (13%)
11b (*galacto*)	*galacto*-**12** (83%)	-
11c (*arabino*)	-	*arabino*-**12** (82%)
11d (*xylo*)	*xylo*-**12** (75%)	*lyxo*-**12** (12%)
11e (*malto*)	*malto*-**12** (81%)	-
11f (*lacto*)	*lacto*-**12** (82%)	-

Scheme 5. Addition of dimethyl malonate (**4a**) to glycals **11**. Method D: 4 equiv anhydrous CAN, 4 equiv $NaHCO_3$, MeOH, 0 °C. Yields of isolated products after column chromatography are indicated in parentheses.

configured glycals **11a** and **11d** afforded diastereomeric mixtures. All products were isolated in analytically pure form after column chromatography and the *O*-benzylated methyl glycosides **12** can be used for further transformations under basic reaction conditions. In summary, in this paper we synthesized more than 20 new 2-*C*-malonyl carbohydrates, which demonstrates the broad applicability of transition-metal-mediated radical reactions in carbohydrate chemistry.

Transformations of the 2-*C*-malonyl carbohydrates: Many transformations of carboxylic acid derivatives are known in literature,[23] and the decarboxylation of malonates is a well established reaction.[24] However, only one example of a 1-*C*-malonyl carbohydrate has been described, which afforded the corresponding methyl acetate in low yield.[25] In a very recent communication, we succeeded in a more efficient demethoxcarbonylation in the presence of lithium iodide for selected methyl glycosides **8a**.[15] Herein we investigate the scope and limitations of this reaction for various 2-*C*-malonyl carbohydrates with methyl **8a** and isopropyl **8b** ester groups as well as *O*-benzyl protected derivatives **12** for the general synthesis of the corresponding acetic esters **13a**, **13b**, and **14** (Scheme 6). First experiments were conducted with the dimethyl malonates **8a** in the presence of lithium iodide at 180 °C (method E). Although carbohydrates are quite labile under thermal conditions, the 2-*C*-branched acetic esters **13a** were isolated in high yields, only the disaccharides *malto*-**8a** and *lacto*-**8a** afforded some decomposition products. We were able to increase the yields slightly by microwave irradiation (method F),[26] but due to the simple



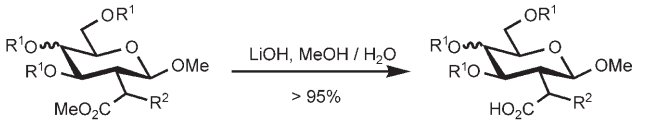
gluco-**8a**	R^1 = Ac	R^2 = Me	E	*gluco*-**13a** (92%)
galacto-**8a**	R^1 = Ac	R^2 = Me	E	*galacto*-**13a** (81%)
xylo-**8a**	R^1 = Ac	R^2 = Me	E	*xylo*-**13a** (81%)
arabino-**8a**	R^1 = Ac	R^2 = Me	E	*arabino*-**13a** (79%)
malto-**8a**	R^1 = Ac	R^2 = Me	E	*malto*-**13a** (73%)
lacto-**8a**	R^1 = Ac	R^2 = Me	E	*lacto*-**13a** (72%)
gluco-**8a**	R^1 = Ac	R^2 = Me	F	*gluco*-**13a** (97%)
gluco-**8b**	R^1 = Ac	R^2 = *i*Pr	E	*gluco*-**13b** (78%)
galacto-**8b**	R^1 = Ac	R^2 = *i*Pr	E	*galacto*-**13b** (80%)
xylo-**8b**	R^1 = Ac	R^2 = *i*Pr	E	*xylo*-**13b** (82%)
arabino-**8b**	R^1 = Ac	R^2 = *i*Pr	E	*arabino*-**13b** (81%)
malto-**8b**	R^1 = Ac	R^2 = *i*Pr	E	*malto*-**13b** (74%)
lacto-**8b**	R^1 = Ac	R^2 = *i*Pr	E	*lacto*-**13b** (71%)
gluco-**12**	R^1 = Bn	R^2 = Me	E	*gluco*-**14** (64%)
gluco-**12**	R^1 = Bn	R^2 = Me	F	*gluco*-**14** (92%)
galacto-**12**	R^1 = Bn	R^2 = Me	F	*galacto*-**14** (85%)
xylo-**12**	R^1 = Bn	R^2 = Me	F	*xylo*-**14** (83%)
arabino-**12**	R^1 = Bn	R^2 = Me	F	*arabino*-**14** (83%)
malto-**12**	R^1 = Bn	R^2 = Me	F	*malto*-**14** (81%)
lacto-**12**	R^1 = Bn	R^2 = Me	F	*lacto*-**14** (79%)

Scheme 6. Syntheses of the acetic esters **13** and **14** by dealkoxcarbonylation of the 2-*C*-malonyl carbohydrates **8** and **12**. Method E: 1.5 equiv LiI, DMSO, 180 °C, 5–7 h; method F: 1.5 equiv LiI, DMSO, microwave, 200 W, 10 bar, 100 °C, 10–20 min. Yields of isolated products after column chromatography are indicated in parentheses.

experimental procedure, the diisopropyl malonates **8b** were treated under thermal conditions as well. Indeed, the 2-*C*-branched carbohydrates **13b** were isolated in analytically pure form in similar yields (Scheme 6). This is a remarkable result, since the iodide has to attack the sterically more hindered isopropyl ester by a S_N2 mechanism. To the best of our knowledge, this is the first example for a cleavage of a diisopropyl malonate under such conditions.

The reaction of the 2-*C*-malonyl carbohydrates **12** at 180 °C (method E) proceeded less efficiently, due to the lability of the benzyl protective groups. Therefore, microwave irradiation (method F) was applied, which afforded the products **14** in high yields under milder conditions (Scheme 6). In summary, 18 different 2-*C*-branched glyco-acetic esters **13** and **14** were synthesized in only two steps from glycals. The products were isolated in high yields as sole diastereomers, which demonstrates the broad applicability of malonate addition and decarboxylation in carbohydrate chemistry.

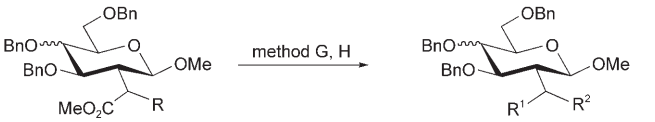
To investigate the potential of further transformations, we selected the *gluco* and *galacto* isomers, which represent common configurations of hexoses in nature. Especially the saponification should provide an easy entry point to malonic and acetic acids. Best conditions were found with 10 equivalents of lithium hydroxide in mixtures of methanol and water, where the products **15**–**18** could be isolated in quantitative yields (Scheme 7). In contrast to the benzylated derivatives, the acetylated starting materials **8a** and **13a** gave access to the completely free methyl glycosides **15** and **17**. Interestingly, the partly protected glyco-acetic acids **18** are suitable precursors for the synthesis of *C*-disaccharides.[4]



gluco-**8a**	(R^1 = Ac, R^2 = CO_2Me)	*gluco*-**15**	(R^1 = H, R^2 = CO_2H)
galacto-**8a**	(R^1 = Ac, R^2 = CO_2Me)	*galacto*-**15**	(R^1 = H, R^2 = CO_2H)
gluco-**12**	(R^1 = Bn, R^2 = CO_2Me)	*gluco*-**16**	(R^1 = Bn, R^2 = CO_2H)
galacto-**12**	(R^1 = Bn, R^2 = CO_2Me)	*galacto*-**16**	(R^1 = Bn, R^2 = CO_2H)
gluco-**13a**	(R^1 = Ac, R^2 = H)	*gluco*-**17**	(R^1 = R^2 = H)
galacto-**13a**	(R^1 = Ac, R^2 = H)	*galacto*-**17**	(R^1 = R^2 = H)
gluco-**14**	(R^1 = Bn, R^2 = H)	*gluco*-**18**	(R^1 = Bn, R^2 = H)
galacto-**14**	(R^1 = Bn, R^2 = H)	*galacto*-**18**	(R^1 = Bn, R^2 = H)

Scheme 7. Syntheses of the malonic acids **15** and **16** and acetic acids **17** and **18**.

Finally, we investigated reductions of the *gluco* and *galacto* isomers **12** and **14**, for the synthesis of further functionalized carbohydrate 2-*C*-analogues. Due to their stability under the basic reaction conditions, the benzyl protective groups were advantageous. Thus, the malonates **12** were reduced with lithium aluminium hydride in good yields to the diols **19** (Scheme 8), which might be used to build up dendritic structures. The same reductions with the acetic esters **14** gave an easy access to the 2-*C*-ethanol carbohydrates **20**. Similar compounds were previously synthesized in literature



gluco-**12**	(R = CO_2Me)	G (85%)	*gluco*-**19** ($R^1 = R^2 = CH_2OH$)
galacto-**12**	(R = CO_2Me)	G (83%)	*galacto*-**19** ($R^1 = R^2 = CH_2OH$)
gluco-**14**	(R = H)	G (83%)	*gluco*-**20** ($R^1 = CH_2OH$, R^2 = H)
galacto-**14**	(R = H)	G (81%)	*galacto*-**20** ($R^1 = CH_2OH$, R^2 = H)
gluco-**14**	(R = H)	H (82%)	*gluco*-**21** (R^1 = CHO, R^2 = H)
galacto-**14**	(R = H)	H (88%)	*galacto*-**21** (R^1 = CHO, R^2 = H)

Scheme 8. Reductions of the methyl esters **12** and **14**. Method G: 3 equiv $LiAlH_4$, 1,4-dioxane, 100 °C, 3 h; method H: 1.2 equiv iBu_2AlH, CH_2Cl_2, −78 °C, 3 h. Yields of isolated products after column chromatography are indicated in parentheses.

by multi-step sequences in only moderate yields,[9a,27] and thus our strategy by radical addition and further transformation is more convenient. Selective syntheses of aldehydes **21**, which again represent suitable precursors for *C*-disaccharides,[28] were finally realized in the presence of diisobutylaluminium hydride (Scheme 8). All reduction products were isolated by column chromatography in high yields in analytically pure form.

Conclusion

We presented a general and convenient entry to carbohydrate 2-*C*-analogues in high yields. The key step is the radical addition of malonates to glycals, which proceeds with high regio- and stereoeselectivity. For the first time, the undesired formation of nitrates was completely suppressed by employing anhydrous CAN. A coherent explanation for the high stereoselectivities of the reactions was provided by variation of the steric demand of substituents in the 3-position of glucals. Additionally, these substituents exhibit a remarkable electronic influence on the reactivity of the double bond.

The applicability of transition-metal-mediated C–C-bond formations was extended to unsaturated disaccharides and benzyl-protected glycals, which allowed further transformations of the 2-*C*-malonyl carbohydrates. For instance the decarboxylation proceeded smoothly under thermal or microwave conditions and afforded acetic esters in high yields. The saponification of the esters opened an easy entry to 2-*C*-branched glyco-malonic and -acetic acids, which represent suitable precursors for the synthesis of *C*-disaccharides. Finally, other functional groups were introduced by reduction to alcohols and aldehydes in high yields.

In summary, the radical addition of malonates to glycals in combination with further transformations offers a general method in carbohydrate chemistry. More than 40 new 2-*C*-analogues were synthesized in only few steps, high yields and with high regio- and stereoselectivities. Due to the importance of the products as precursors for *C*-disaccharides, the herein described syntheses open interesting prospects for future applications in carbohydrate chemistry.

Experimental Section

General methods: All reactions were carried out under argon by using standard Schlenk techniques. Solvents and commercially available chemicals were purified by standard methods or used as purchased. Excess of malonate was removed by a Kugelrohrofen (GKR-50, Büchi). TLC was performed on aluminium sheets silica gel $60F_{254}$ (Merck, Darmstadt). Silica gel (63–200 μm, Woelm, Erlangen (Germany)) was used for column chromatography. Optical rotations were measured on a JASCO P-1020 polarimeter, melting points on a Büchi SMP 20 apparatus (uncorrected). IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. NMR spectra were recorded either on a Bruker AM 250, AC 300, Avance 500 or DMX 600 with $CDCl_3$ as the solvent and internal standard. Elemental analyses were performed on an ELEMENTAR vario EL analysator.

Synthesis of the glycals 6 and 11: The *O*-acetylated glycals **6a–c,j,k** were prepared by the method of Helferich[19a] or Korreda,[19b] 4,6-di-*O*-acetyl-D-glucal (**6d**) by the procedure from Holla[17] and the 3-deoxy-glycal (**6i**) by the method of Fraser-Reid.[18] The benzylated glycals **11a–f** were obtained from the *O*-acetylated precursors **6a–f** by an one-step procedure.[21] The 3-substituted glycals **6e–h** were synthesized by the following procedure: 4,6-di-*O*-acetyl-D-glucal (**6d**) (2.30 g, 10.0 mmol) and triethylamine (1.52 g, 15.0 mmol, 1.5 equiv) were dissolved in dichloromethane (20 mL) at 0 °C. At this temperature the acid chlorides **10e–h** (15 mmol, 1.5 equiv) were added over a period of 1 h and the mixture was stirred at room temperature for 14 h. After dilution with dichloromethane (50 mL), the solution was washed with water (30 mL), diluted aqueous sodium hydrogen carbonate (30 mL) and again water (30 mL), and the organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by column chromatography (pentane/ethyl acetate 7:3) afforded the glycals **6e–h** as colorless oils.

3-*O*-Benzoyl-4,6-di-*O*-acetyl-D-glucal (6e): 2.91 g (87%); R_f = 0.62 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20} = -134.9$ (c = 1.02 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04, 2.07 (2s, 3H each, OAc), 4.23 (dd, J = 11.9, 3.1 Hz, 1H, 6-H), 4.33 (ddd, J = 7.6, 5.5, 3.1 Hz, 1H, 5-H), 4.48 (dd, J = 11.9, 5.5 Hz, 1H, 6′-H), 4.97 (dd, J = 6.1, 3.4 Hz, 1H, 2-H), 5.41 (dd, J = 7.6, 5.9 Hz, 1H, 4-H), 5.53 (ddd, J = 5.9, 3.4, 1.2 Hz, 1H, 3-H), 6.49 (dd, J = 6.1, 1.2 Hz, 1H, 1-H), 7.36–7.58 (m, 3H, arom. H), 7.94–8.02 ppm (m, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.1, 21.2 (2q, OAc), 61.8 (t, C-6), 67.4, 68.5, 74.3 (3d, C-3, C-4, C-5), 99.4 (d, C-1), 128.7, 128.8, 129.3, 129.9, 130.0 (5d, C-arom.), 133.7 (s, C-arom.), 146.2 (d, C-2), 166.3, 169.9, 171.0 ppm (3s, OAc, *C*OOR); IR (KBr): $\tilde{\nu}$ = 2975, 1732, 1651, 1542, 1372, 1231 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{18}O_7$ (334.32): C 61.07, H 5.43; found: C 60.84, H 5.52.

3-*O*-(4-Methoxybenzoyl)-4,6-di-*O*-acetyl-D-glucal (6f): 3.06 g (84%); R_f = 0.79 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20} = -124.2$ (c = 1.35 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.05, 2.10 (2s, 3H each, OAc), 3.85 (s, 3H, OMe), 4.23 (dd, J = 12.0, 3.1 Hz, 1H, 6-H), 4.34 (ddd, J = 7.4, 5.8, 3.1 Hz, 1H, 5-H), 4.51 (dd, J = 12.0, 5.8 Hz, 1H, 6′-H), 5.00 (dd, J = 6.2, 3.2 Hz, 1H, 2-H), 5.42 (dd, J = 7.4, 5.7 Hz, 1H, 4-H), 5.51 (ddd, J = 5.7, 3.2, 1.2 Hz, 1H, 3-H), 6.51 (dd, J = 6.2, 1.2 Hz, 1H, 1-H), 6.91 (dt, J = 11.8, 2.8 Hz, 2H, arom. H), 7.95 ppm (dt, J = 11.8, 2.8 Hz, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.1, 21.2 (2q, OAc), 55.9 (q, OMe), 61.9 (t, C-6), 67.5, 68.0, 74.3 (3d, C-3, C-4, C-5), 99.6 (d, C-1), 114.2, 114.5, 132.2, 133.2 (4d, C-arom.), 122.3 (s, C-arom.), 146.0 (d, C-2), 164.0, 164.9, 169.9, 170.0 ppm (4s, OAc, *C*OOR, C-arom.); IR (film): $\tilde{\nu}$ = 2964, 1782, 1746, 1606, 1512, 1259, 1160 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_8$ (364.35): C 59.34, H 5.53; found: C 59.79, H 5.70.

3-*O*-(4-Nitrobenzoyl)-4,6-di-*O*-acetyl-D-glucal (6g): 3.37 g (89%); R_f = 0.77 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20} = -141.8$ (c = 1.02 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06, 2.10 (2s, 3H each, OAc), 4.25 (dd, J = 12.2, 3.0 Hz, 1H, 6-H), 4.34 (ddd, J = 8.2, 5.5, 3.0 Hz, 1H, 5-H), 4.49 (dd, J = 12.2, 5.5 Hz, 1H, 6′-H), 4.97 (dd, J = 6.2, 3.2 Hz, 1H, 2-H), 5.44 (dd, J = 8.2, 6.0 Hz, 1H, 4-H), 5.60 (ddd, J = 6.0, 3.2, 1.1 Hz, 1H, 3-H), 6.53 (dd, J = 6.2, 1.1 Hz, 1H, 1-H), 8.16 (dt, J = 8.9, 2.1 Hz, 2H, arom. H), 8.28 ppm (dt, J = 8.9, 2.1 Hz, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.1, 21.2 (2q, OAc), 61.7 (t, C-6), 67.2, 70.1, 74.4 (3d, C-3, C-4, C-5), 98.9 (d, C-1), 124.0, 131.3 (4d, C-arom.), 135.4 (s, C-arom.), 146.7 (d, C-

2), 151.1 (s, C-arom.), 164.5 (s, *C*OOR), 169.9, 171.0 ppm (2s, OAc); IR (film): $\tilde{\nu}$ = 3277, 2928, 1655, 1628, 1541, 1266, 1049 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{17}NO_9$ (379.32): C 53.83, H 4.52, N 3.69; found: C 53.68, H 4.67 N 3.61.

3-*O*-Pivaloyl-4,6-di-*O*-acetyl-D-glucal (6h): 1.97 g (63%); R_f = 0.29 (pentane/ethyl acetate 85:15); $[\alpha]_D^{20}$ = −44.6 (*c* = 1.02 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 (s, 9H, $C(CH_3)_3$), 2.03, 2.07 (2s, 3H each, OAc), 4.14 (dd, *J* = 12.0, 2.9 Hz, 1H, 6-H), 4.26 (ddd, *J* = 8.2, 5.9, 2.9 Hz, 1H, 5-H), 4.41 (dd, *J* = 12.0, 5.9 Hz, 1H, 6′-H), 4.82 (dd, *J* = 6.1, 3.0 Hz, 1H, 2-H), 5.24 (dd, *J* = 8.2, 5.9 Hz, 1H, 4-H), 5.27 (ddd, *J* = 5.9, 3.0, 0.9 Hz, 1H, 3-H), 6.43 ppm (dd, *J* = 6.1, 0.9 Hz, 1H, 1-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.7, 20.8 (2q, OAc), 27.0 (3q, $C(CH_3)_3$), 38.7 (s, $C(CH_3)_3$), 61.5 (t, C-6), 67.1, 67.2, 73.9 (3d, C-3, C-4, C-5), 99.1 (d, C-1), 145.5 (d, C-2), 169.5, 170.7 (2s, OAc), 177.8 ppm (s, *C*OOR); IR (film): $\tilde{\nu}$ = 2975, 1746, 1650, 1482, 1369, 1231 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{22}O_7$ (314.33): C 57.32, H 7.05; found: C 57.51, H 7.07.

Addition of dimethyl malonate (4a) or diisopropyl malonate (4b) to acetyl protected glycals 6 with anhydrous CAN (method C): A solution of the acetylated glycal **6** (5.0 mmol) and dimethyl malonate (**4a**) (6.61 g, 50 mmol, 10 equiv) or diisopropyl malonate (**4b**) (9.41 g, 50 mmol, 10 equiv) in dry methanol (20 mL) was cooled to 0°C under an argon atmosphere. At this temperature, a solution of CAN (11.0 g, 20 mmol, 4 equiv), which was dried in a desiccator under high vacuum overnight, in methanol (30 mL) was added dropwise over a period of 6 h until TLC showed complete conversion of the starting material. After stirring for 30 min at 0°C, an ice-cold diluted solution of sodium thiosulfate (200 mL) was added, and the mixture was extracted with dichloromethane (4 × 80 mL). The combined organic phases were dried (Na_2SO_4), concentrated, and the excess of malonate was removed at 0.01 mbar in a Kugelrohrofen. The crude product was purified by column chromatography or medium pressure liquid chromatography (MPLC) and the 2-*C*-malonyl carbohydrates **8** were isolated as colorless oils or solids.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-[(bis-methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-8a): 1.73 g (80%); R_f = 0.45 (pentane/ethyl acetate 1:1); m.p. 100–101°C; $[\alpha]_D^{20}$ = −6.9 (*c* = 1.08 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.98, 1.99, 2.06 (3s, 3H each, OAc), 2.57 (ddd, *J* = 11.6, 8.6, 3.6 Hz, 1H, 2-H), 3.45 (s, 3H, OMe), 3.57 (d, *J* = 3.6 Hz, 1H, 7-H), 3.69 (ddd, *J* = 10.0, 4.6, 2.4 Hz, 1H, 5-H), 3.70, 3.73 (2s, 3H each, COOMe), 4.10 (dd, *J* = 12.2, 2.4 Hz, 1H, 6-H), 4.28 (dd, *J* = 12.2, 4.6 Hz, 1H, 6′-H), 4.95 (d, *J* = 8.6 Hz, 1H, 1-H), 4.98 (dd, *J* = 10.0, 9.0 Hz, 1H, 4-H), 5.27 ppm (dd, *J* = 11.6, 9.0 Hz, 1H, 3-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7 (3q, OAc), 46.3, 48.0 (2d, C-2, C-7), 52.4, 52.5 (2q, COO*Me*), 57.5 (q, OMe), 62.2 (t, C-6), 69.8, 71.3, 71.6 (3d, C-3, C-4, C-5), 101.6 (d, C-1), 168.2, 168.3, 169.7, 170.0, 170.7 ppm (5s, OAc, *C*OOMe); IR (KBr): $\tilde{\nu}$ = 3005, 2951, 1750, 1366, 1227 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{26}O_{12}$ (434.39): C 49.77, H 6.03; found: C 49.51, H 5.92.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)methyl]-α-D-mannopyranoside (*manno*-8a): 325 mg (15%); R_f = 0.43 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}$ = −8.4 (*c* = 1.04 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.02, 2.08, 2.11 (3s, 3H each, OAc), 3.02 (ddd, *J* = 10.1, 4.6, 2.1 Hz, 1H, 2-H), 3.39 (s, 3H, OMe), 3.67 (d, *J* = 10.1 Hz, 1H, 7-H), 3.72, 3.76 (2s, 3H each, COOMe), 3.92 (ddd, *J* = 9.8, 5.6, 2.1 Hz, 1H, 5-H), 4.11 (dd, *J* = 12.1, 2.1 Hz, 1H, 6-H), 4.37 (dd, *J* = 12.1, 5.6 Hz, 1H, 6′-H), 4.68 (d, *J* = 2.1 Hz, 1H, 1-H), 5.26 (dd, *J* = 9.8, 9.2 Hz, 1H, 4-H), 5.46 ppm (dd, *J* = 9.2, 4.6 Hz, 1H, 3-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.3, 20.5, 20.6 (3q, OAc), 40.9, 48.9 (2d, C-2, C-7), 52.3, 52.4 (2q, COO*Me*), 55.3 (q, OMe), 62.4 (t, C-6), 68.7, 69.6, 71.1 (3d, C-3, C-4, C-5), 99.3 (d, C-1), 168.1, 168.3, 169.6, 169.9, 170.3 ppm (5s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$ = 3008, 1748, 1354, 1214 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{26}O_{12}$ (434.39): C 49.77, H 6.03; found: C 49.83, H 5.82.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)methyl]-β-D-galactopyranoside (*galacto*-8a): 1.89 g (87%); R_f = 0.46 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}$ = −4.4 (*c* = 1.17 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.98, 2.02, 2.11 (3s, 3H each, OAc), 2.80 (ddd, *J* = 12.3, 8.8, 3.7 Hz, 1H, 2-H), 3.47 (s, 3H, OMe), 3.66 (d, *J* = 3.7 Hz, 1H, 7-H), 3.71, 3.72 (2s, 3H each, COOMe), 3.87 (ddd, *J* = 7.3, 6.6, 1.0 Hz, 1H, 5-H), 4.12 (dd, *J* = 11.2, 7.3 Hz, 1H, 6-H), 4.17 (dd, *J* = 11.2, 6.6 Hz, 1H, 6′-H), 4.85 (d, *J* = 8.8 Hz, 1H, 1-H), 5.12 (dd, *J* = 12.3, 3.2 Hz, 1H, 3-H), 5.27 ppm (dd, *J* = 3.2, 1.0 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 22.1, 22.3, 22.4 (3q, OAc), 43.5, 49.2 (2d, C-2, C-7), 54.0, 54.1 (2q, COO*Me*), 59.1 (q, OMe), 63.1 (t, C-6), 67.6, 71.2, 72.1 (3d, C-3, C-4, C-5), 103.5 (d, C-1), 170.0, 170.3, 171.3, 171.9, 172.0 ppm (5s, OAc, *C*OOMe); IR (CCl_4): $\tilde{\nu}$ = 3038, 2955, 1748, 1437, 1244 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{26}O_{12}$ (434.39): C 49.77, H 6.03; found: C 49.50, H 6.04.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)methyl]-α-D-arabinopyranoside (*arabino*-8a): 1.61 g (89%); R_f = 0.50 (pentane/ethyl acetate 1:1); m.p. 99–100°C; $[\alpha]_D^{20}$ = −1.5 (*c* = 1.03 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97, 2.12 (2s, 3H each, OAc), 2.84 (ddd, *J* = 11.9, 8.6, 3.9 Hz, 1H, 2-H), 3.45 (s, 3H, OMe), 3.64 (dd, *J* = 13.3, 1.1 Hz, 5-H), 3.68 (d, *J* = 3.9 Hz, 6-H), 3.71, 3.72 (2s, 3H each, COOMe), 4.01 (dd, *J* = 13.2, 2.0 Hz, 1H, 5′-H), 4.73 (d, *J* = 8.6 Hz, 1H, 1-H), 5.13 (dd, *J* = 11.9, 3.3 Hz, 1H, 3-H), 5.17 ppm (ddd, *J* = 13.3, 2.0, 1.1 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.9, 21.4 (2q, OAc), 42.7, 48.2 (2d, C-2, C-6), 52.8, 52.9 (2q, COO*Me*), 57.8 (q, OMe), 64.7 (t, C-5), 67.5, 69.8 (2d, C-3, C-4), 102.5 (d, C-1), 168.9, 169.2, 170.1, 170.8 ppm (4s, OAc, *C*OOMe); IR ($CHCl_3$): $\tilde{\nu}$ = 3012, 2965, 2848, 1750, 1439, 1374, 1298, 1236, 1132, 1093 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{22}O_{10}$ (362.33): C 49.72, H 6.12; found: C 49.48, H 6.02.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)-methyl]-β-D-maltopyranoside (*malto*-8a): 3.0 g (83%); R_f = 0.23 (pentane/ethyl acetate 1:1); m.p. 163–164°C; $[\alpha]_D^{20}$ = +49.1 (*c* = 0.80 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.98, 2.01, 2.03, 2.04, 2.09, 2.13 (6s, 3H each, OAc), 2.41 (ddd, *J* = 11.3, 8.6, 3.7 Hz, 1H, 2-H), 3.35 (d, *J* = 3.7 Hz, 1H, 13-H), 3.43 (s, 3H, OMe), 3.64–3.71 (m, 1H, 5-H), 3.69, 3.74 (2s, 3H each, COOMe), 3.87 (dd, *J* = 9.4, 8.7 Hz, 1H, 4-H), 3.97 (ddd, *J* = 10.2, 4.1, 2.3 Hz, 1H, 11-H), 4.04 (dd, *J* = 12.4, 2.3 Hz, 12-H), 4.23 (dd, *J* = 12.4, 4.1 Hz, 12′-H), 4.26 (dd, *J* = 12.1, 4.3 Hz, 1H, 6-H), 4.46 (dd, *J* = 12.1, 2.8 Hz, 1H, 6′-H), 4.86 (dd, *J* = 10.5, 4.0 Hz, 1H, 8-H), 5.04 (dd, *J* = 10.2, 9.6 Hz, 1H, 10-H), 5.12 (d, *J* = 8.6 Hz, 1H, 1-H), 5.29 (dd, *J* = 11.3, 8.7, 1H, 3-H), 5.32 (d, *J* = 4.0 Hz, 1H, 7-H), 5.33 ppm (dd, *J* = 10.5, 9.6 Hz, 1H, 9-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.4, 20.5, 20.6, 20.7, 20.8, 20.9 (6q, OAc), 47.2, 48.1 (2d, C-2, C-13), 52.4, 52.5 (2q, COO*Me*), 57.5 (q, OMe), 61.5, 63.2 (2t, C-6, C-12), 68.0, 68.4, 69.4, 70.0, 72.0, 73.7, 74.3 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 95.5, 101.3 (2d, C-1, C-7), 168.1, 168.4, 168.7, 169.1, 169.4, 170.1, 170.5, 170.8 ppm (8s, OAc, *C*OOMe); IR (KBr): $\tilde{\nu}$ = 2984, 1744, 1371, 1241, 1042 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{42}O_{20}$ (722.64): C 49.86, H 5.86; found: C 49.65, H 5.87.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)-methyl]-β-D-lactopyranoside (*lacto*-8a): 2.92 g (81%); R_f = 0.28 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$ = −1.4 (*c* = 1.05 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96, 2.04, 2.06, 2.07, 2.12, 2.14 (6s, 3H each, OAc), 2.47 (ddd, *J* = 12.0, 7.8, 3.9 Hz, 1H, 2-H), 3.44 (s, 3H, OMe), 3.51 (d, *J* = 3.9 Hz, 1H, 13-H), 3.61 (ddd, *J* = 9.3, 4.5, 1.8 Hz, 1H, 5-H), 3.70 (dd, *J* = 9.3, 6.3 Hz, 1H, 4-H), 3.71, 3.75 (2s, 3H each, COOMe), 3.87 (t, *J* = 6.8 Hz, 1H, 11-H), 4.04–4.20 (m, 2H, 12-H, 12′-H), 4.17 (dd, *J* = 12.0, 4.5 Hz, 1H, 6-H), 4.46 (d, *J* = 7.8 Hz, 1H, 1-H), 4.48 (dd, *J* = 12.0, 1.8 Hz, 1H, 6′-H), 4.95 (dd, *J* = 10.2, 3.3 Hz, 1H, 8-H), 5.04 (dd, *J* = 9.0, 8.4 Hz, 1H, 10-H), 5.09 (d, *J* = 7.8 Hz, 1H, 7-H), 5.18 (dd, *J* = 11.4, 8.4 Hz, 1H, 9-H), 5.35 ppm (d, *J* = 3.0, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4, 20.5, 20.6, 20.7, 20.8, 20.9 (6q, OAc), 46.7 (d, C-13), 48.3 (d, C-2), 52.3, 52.4 (2q, COO*Me*), 57.4 (q, OMe), 60.8, 62.2 (2t, C-6, C-12), 66.6, 69.1, 69.3, 70.6, 71.0, 71.6, 72.4 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 100.0, 101.4 (2d, C-1, C-7), 168.0, 168.6, 168.8, 169.6, 169.9, 170.0, 170.2, 170.3 ppm (8s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$ = 2957, 1752, 1371, 1228, 1052 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{42}O_{20}$ (722.64): C 49.86, H 5.86; found: C 49.76, H 5.87.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[bis-methylethoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-8b): 2.10 g (86%); R_f = 0.46 (pentane/ethyl acetate 6:4); m.p. 86–87°C; $[\alpha]_D^{20}$ = −7.4 (*c* = 0.99 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.19–1.29 (m, 12H, 2COOCH(CH_3)$_2$), 1.97, 2.00, 2.05 (3s, 3H each, OAc), 2.52 (ddd, *J* = 11.6, 8.6, 3.4 Hz, 1H, 2-H), 3.45 (d, *J* = 3.4 Hz, 1H, 7-H), 3.47 (s, 3H, OMe), 3.64 (ddd, *J* = 10.0, 4.7, 2.4 Hz, 1H, 5-H), 4.05 (dd, *J* = 12.2, 2.4 Hz, 1H, 6-H), 4.25 (dd, *J* =

12.2, 4.7 Hz, 1H, 6′-H), 5.05 (d, J=8.6 Hz, 1H, 1-H), 4.94–5.11 (m, 3H, 4-H, 2 COOC*H*(CH_3)$_2$), 5.18 ppm (dd, J=11.6, 9.0 Hz, 1H, 3-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=22.2, 22.3, 22.4, 22.5, 23.0, 23.2, 23.4 (7q, 3OAc, 4COOCH(CH_3)$_2$), 47.7, 50.4 (2d, C-2, C-7), 63.9 (t, C-6), 69.8, 69.9, 70.7, 71.1, 71.6 (5d, C-3, C-4, C-5, 2COO*C*H(CH_3)$_2$), 103.6 (d, C-1), 168.9, 169.3, 171.4, 171.5, 172.4 ppm (5s, OAc, *C*OOCH(CH_3)$_2$); IR (CCl_4): $\tilde{\nu}$=2982, 2938, 1755, 1374, 1228 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{34}O_{12}$ (490.50): C 53.87, H 6.99; found: C 53.88, H, 6.68.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[bis-methylethoxycarbonyl)methyl]-α-D-mannopyranoside (*manno*-8b): 220 mg (9%); R_f=0.48 (pentane/ethyl acetate 6:4); $[\alpha]_D^{20}$=+21.4 (c=1.02 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.19–1.29 (m, 12H, 2COOCH(C*H*$_3$)$_2$), 1.97, 2.02, 2.03 (3s, 3H each, OAc), 3.08 (ddd, J=10.2, 4.8, 2.3 Hz, 1H, 2-H), 3.36 (s, 3H, OMe), 3.46 (d, J=10.2 Hz, 1H, 7-H), 4.04 (ddd, J=10.4, 5.6, 3.1 Hz, 1H, 5-H), 4.12 (dd, J=12.0, 5.6 Hz, 1H, 6′-H), 4.26 (dd, J=12.0, 3.1 Hz, 1H, 6-H), 4.72 (d, J=2.3 Hz, 1H, 1-H), 4.94–5.11 (m, 3H, 4-H, 2COOC*H*-(CH_3)$_2$), 5.45 ppm (dd, J=8.7, 4.8 Hz, 1H, 3-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=20.7, 20.8, 20.9, 21.0, 21.3, 21.4, 21.5 (7q, 3OAc, 4COOCH-(*C*H$_3$)$_2$), 40.0, 50.0 (2d, C-2, C-7), 61.4 (t, C-6), 67.2, 67.3, 69.7, 69.8, 70.4 (5d, C-3, C-4, C-5, 2 COO*C*H(CH_3)$_2$), 99.5 (d, C-1), 166.3, 166.5, 169.4, 169.6, 170.5 (5s, OAc, *C*OOCH(CH_3)$_2$); IR (CCl_4): $\tilde{\nu}$=2981, 2927, 1752, 1369, 1224 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{34}O_{12}$ (490.50): C 53.87, H 6.99; found: C 53.72, H, 6.78.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(bis-methylethoxycarbonyl)methyl]-β-D-galactopyranoside (*galacto*-8b): 2.16 g (88%); R_f=0.30 (pentane/ethyl acetate 1:1); m.p. 109–110°C; $[\alpha]_D^{20}$=−17.3 (c=1.24 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.20–1.31 (m, 12H, 2COOCH(C*H*$_3$)$_2$), 1.96, 2.04, 2.13 (3s, 3H each, OAc), 2.82 (ddd, J=12.3, 8.8, 3.5 Hz, 1H, 2-H), 3.48 (s, 3H, OMe), 3.60 (d, J=3.5 Hz, 1H, 7-H), 3.87 (ddd, J=7.0, 6.5, 1.0 Hz, 1H, 5-H), 4.13 (dd, J=11.2, 7.0 Hz, 1H, 6-H), 4.18 (dd, J=11.2, 6.5 Hz, 1H, 6′-H), 4.83 (d, J=8.8 Hz, 1H, 1-H), 5.05 (dddd, J=18.9, 12.6, 6.4, 2.2 Hz, 2H, 2COOC*H*(CH_3)$_2$), 5.17 (dd, J=12.3, 3.1 Hz, 1H, 3-H), 5.31 ppm (dd, J=3.1, 1.0 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ=20.8, 21.1, 21.8, 21.9, 22.0, 22.0, 22.1 (7q, OAc, COOCH(*C*H$_3$)$_2$), 42.0, 48.7 (2d, C-2, C-7), 57.8 (q, OMe), 62.0 (t, C-6), 66.6, 69.3, 69.7 (3d, C-3, C-4, C-5), 70.2, 71.0 (2d, COO*C*H(CH_3)$_2$), 102.6 (d, C-1), 168.0, 168.1, 170.0, 170.7, 170.9 ppm (5s, OAc, *C*OOCH(CH_3)$_2$); IR (KBr): $\tilde{\nu}$=2985, 2938, 1732, 1664, 1467, 1376 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{34}O_{12}$ (490.50): C 53.87, H 6.99; found: C 53.88, H, 7.09.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methylethoxycarbonyl)methyl]-α-D-arabinopyranoside (*arabino*-8b): 1.82 g (87%); R_f=0.68 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}$=−11.1 (c=0.98 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.20–1.27 (m, 12H, 2COOCH(C*H*$_3$)$_2$), 1.97, 2.12 (2s, 3H each, OAc), 2.85 (ddd, J=11.9, 8.6, 3.7 Hz, 1H, 2-H), 3.46 (s, 3H, OMe), 3.59 (d, J=3.7 Hz, 1H, 6-H), 3.64 (dd, J=13.4, 1.0 Hz, 1H, 5-H), 4.01 (dd, J=13.4, 1.8 Hz, 1H, 5′-H), 4.71 (d, J=8.6, 1H, 1-H), 5.00–5.08 (m, 2H, 2COOC*H*(CH_3)$_2$), 5.14 (dd, J=11.9, 3.3 Hz, 1H, 3-H), 5.18 ppm (ddd, J=3.3, 1.8, 1.0 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ=20.8, 21.3, 21.6, 21.8, 21.9, 22.0 (6q, OAc, COOCH(*C*H$_3$)$_2$), 42.4, 48.9 (2d, C-2, C-6), 57.4 (q, OMe), 64.7 (t, C-5), 67.6, 69.2, 69.5, 69.9 (4d, C-3, C-4, 2COO*C*H(CH_3)$_2$), 102.7 (d, C-1), 168.0, 168.1, 170.0, 170.8 ppm (4s, OAc, *C*OOCH(CH_3)$_2$); IR ($CHCl_3$): $\tilde{\nu}$=3031, 2984, 2938, 1746, 1459, 1376, 1234, 1181, 1103, 1023 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{30}O_{10}$ (418.44): C 54.54, H 7.23; found: C 54.78, H 7.39.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(bis-methylethoxycarbonyl)methyl]-β-D-maltopyranoside (*malto*-8b): 3.23 g (83%); R_f=0.34 (pentane/ethyl acetate 6:4); m.p. 151–152°C; $[\alpha]_D^{20}$=+49.8 (c=1.02 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.20–1.27 (m, 12H, 2COOCH-(C*H*$_3$)$_2$), 1.96, 1.99, 2.03, 2.04, 2.07, 2.11 (6s, 3H each, OAc), 2.38 (dddd, J=11.4, 8.6, 3.4 Hz, 1H, 2-H), 3.21 (d, J=3.4 Hz, 1H, 13-H), 3.41 (s, 3H, OMe), 3.67 (ddd, J=9.2, 4.4, 2.7 Hz, 1H, 5-H), 3.86 (dd, J=9.2, 8.7 Hz, 1H, 4-H), 3.96 (ddd, J=10.3, 3.9, 2.4 Hz, 1H, 11-H), 4.01 (dd, J=12.5, 2.4 Hz, 12-H), 4.24 (dd, J=12.5, 3.9 Hz, 12′-H), 4.25 (dd, J=12.1, 4.4 Hz, 1H, 6-H), 4.43 (dd, J=12.1, 2.7 Hz, 1H, 6′-H), 4.87 (dd, J=10.3, 3.7 Hz, 1H, 8-H), 4.95–5.09 (m, 2H, COOC*H*(CH_3)$_2$), 5.03 (dd, J=10.3, 9.7 Hz, 1H, 10-H), 5.16 (d, J=8.6 Hz, 1H, 1-H), 5.27 (dd, J=11.4, 8.7 Hz, 1H, 3-H), 5.29 (d, J=3.7, 1H, 7-H), 5.31 ppm (dd, J=10.3, 9.7 Hz, 1H, 9-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=20.9, 21.0, 21.1, 21.2, 21.3, 21.7, 21.8, 21.9, 22.0, 22.1 (10q, OAc, COOCH(*C*H$_3$)$_2$), 47.4, 49.9 (2d, C-2, C-13), 57.5 (q, OMe), 62.0, 63.7 (2t, C-6, C-12), 68.4, 68.8, 69.2, 69.8, 69.9, 70.4, 72.5, 74.0, 75.0 (9d, C-3, C-4, C-5, C-8, C-9, C-10, C-11, COO*C*H(CH_3)$_2$), 95.9, 102.0 (2d, C-1, C-7), 167.6, 168.3, 169.9, 170.1, 170.2, 170.4, 170.6, 171.0 ppm (8s, OAc, *C*OO*i*Pr); IR (KBr): $\tilde{\nu}$=2980, 2958, 1742, 1362, 1212, 1089 cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{50}O_{20}$ (778.75): C 52.44, H 6.47; found: C 52.39, H 6.45.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(bis-methylethoxycarbonyl)methyl]-β-D-lactopyranoside (*lacto*-8b): 3.35 g (86%); R_f=0.30 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$=−1.5 (c=1.09 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.20–1.32 (m, 12H, 2COOCH(C*H*$_3$)$_2$), 1.96, 2.04, 2.06, 2.09, 2.12, 2.14 (6s, 3H each, OAc), 2.46 (dddd, J=11.4, 8.7, 3.6 Hz, 1H, 2-H), 3.38 (d, J=3.6 Hz, 1H, 13-H), 3.43 (s, 3H, OMe), 3.61 (ddd, J=9.3, 5.4, 1.5 Hz, 1H, 5-H), 3.71 (ddd, J=9.6, 6.6, 3.0 Hz, 1H, 11-H), 3.87 (t, J=6.9 Hz, 1H, 4-H), 4.06–4.13 (m, 2H, 12-H 12′-H), 4.17 (dd, J=11.7, 5.4 Hz, 1H, 6-H), 4.45 (d, J=8.7 Hz, 1H, 1-H), 4.47 (dd, J=11.7, 1.5 Hz, 1H, 6′-H), 4.94 (dd, J=10.5, 3.3 Hz, 1H, 8-H), 5.00–5.10 (m, 2H, COOC*H*(CH_3)$_2$), 5.09 (d, J=7.8 Hz, 1H, 7-H), 5.11 (dd, J=10.5, 3.0 Hz, 1H, 10-H), 5.16 (dd, J=11.4, 8.4 Hz, 1H, 9-H), 5.35 ppm (d, J=3.0, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.4, 20.5, 20.7, 20.8, 20.9, 21.0, 21.2, 21.3, 21.5, 21.6 (10q, OAc, COOCH(*C*H$_3$)$_2$), 46.5 (d, C-13), 49.0 (d, C-2), 57.0 (q, OMe), 60.3, 60.8 (2t, C-6, C-12), 62.3, 66.6, 68.8, 69.1, 69.2, 70.6, 70.9, 71.0, 72.5 (9d, C-3, C-4, C-5, C-8, C-9, C-10, C-11, COO*C*H-(CH_3)$_2$), 100.9, 101.7 (2d, C-1, C-7), 167.1, 167.8, 168.8, 169.3, 169.9, 170.0, 170.2, 170.3 ppm (8s, OAc, *C*OO*i*Pr); IR (film): $\tilde{\nu}$=2984, 2939, 1752, 1373, 1227, 1051 cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{50}O_{20}$ (778.75): C 52.44, H 6.47; found: C 52.22, H 6.56.

Addition of dimethyl malonate (4a) to the 3-substituted glycals 6d–i with anhydrous CAN (method C): A solution of the 3-substituted glycal **6** (2.0 mmol) and dimethyl malonate (**4a**) (2.64 g, 20 mmol, 10 equiv) in dry methanol (10 mL) was cooled to 0°C under an argon atmosphere. At this temperature, a solution of CAN (4.4 g, 8.0 mmol, 4 equiv), which was dried in a desiccator under high vacuum overnight, in methanol (12 mL) was added dropwise over a period of 3–12 h until TLC showed complete conversion of the starting material. After stirring for 30 min at 0°C, an ice-cold diluted solution of sodium thiosulfate (100 mL) was added, and the mixture was extracted with dichloromethane (4×30 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated, and the excess of malonate was removed at 0.01 mbar in a Kugelrohrofen. The *gluco*/*manno* ratios were determined by ^{1}H NMR (600 MHz). The crude product was purified by column chromatography or medium pressure liquid chromatography (MPLC) and the 2-*C*-malonyl carbohydrates **8** were isolated as colorless oils or solids.

Methyl 4,6-di-*O*-acetyl-2-deoxy-2-[(bis-methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-8d): 350 mg (45%); m.p. 137–138°C; R_f=0.30 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}$=−34.0 (c=1.21 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=2.05, 2.09 (2s, 3H each, OAc), 2.43 (ddd, J=11.3, 8.5, 3.7 Hz, 1H, 2-H), 2.91 (brs, 1H, OH), 3.44 (s, 3H, OMe), 3.60 (ddd, J=9.2, 4.7, 2.3 Hz, 1H, 5-H), 3.72, 3.74 (2s, 3H each, COOMe), 3.84 (dd, J=11.3, 9.8 Hz, 1H, 3-H), 3.95 (d, J=3.7 Hz, 1H, 7-H), 4.11 (dd, J=12.2, 2.3 Hz, 1H, 6-H), 4.27 (dd, J=12.2, 4.7 Hz, 1H, 6′-H), 4.72 (d, J=8.5 Hz, 1H, 1-H), 4.81 ppm (dd, J=9.8, 9.2 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.2, 21.3 (2q, OAc), 48.7, 49.0 (2d, C-2, C-7), 52.9, 53.0 (2q, COO*Me*), 57.8 (q, OMe), 62.3 (t, C-6), 71.8, 72.1, 73.1 (3d, C-3, C-4, C-5), 102.3 (d, C-1), 169.6, 169.8, 171.3, 171.6 ppm (4s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$=2960, 1744, 1443, 1371, 1040 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_{11}$ (392.35): C 48.98, H 6.17; found: C 48.59, H 6.29.

Methyl 4,6-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)methyl]-α-D-mannopyranoside (*manno*-8d): 25 mg (3%); R_f=0.32 (pentane/ethyl acetate 1:1); NMR signals are overlapped with *gluco* isomer.

Methyl 3-*O*-benzoyl-4,6-di-*O*-acetyl-2-deoxy-2-[(bis-methoxycarbonyl)-methyl]-β-D-glucopyranoside (*gluco*-8e): 775 mg (78%); R_f=0.33 (pentane/ethyl acetate 6:4); $[\alpha]_D^{20}$=−17.8 (c=1.02 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.96, 2.09 (2s, 3H each, OAc), 2.72 (ddd, J=11.7, 8.6, 3.7 Hz, 1H, 2-H), 3.48 (s, 3H, OMe), 3.58 (d, J=3.7 Hz, 1H, 7-H), 3.66, 3.68 (2s, 3H each, COOMe), 3.78 (ddd, J=9.9, 4.6, 2.3 Hz, 1H, 5-H), 4.14 (dd, J=12.3, 2.3 Hz, 1H, 6-H), 4.33 (dd, J=12.3, 4.6 Hz, 1H, 6′-H), 5.09 (d, J=8.6 Hz, 1H, 1-H), 5.21 (dd, J=9.9, 9.2 Hz, 1H, 4-H), 5.53

(dd, $J=11.7$, 9.2 Hz, 1H, 3-H), 7.40–7.60 (m, 3H, arom. H), 7.95–8.00 ppm (m, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=21.0$, 21.3 (2q, OAc), 47.2, 48.7 (2d, C-2, C-7), 53.3, 53.4 (2q, COO*Me*), 58.2 (q, OMe), 62.7 (t, C-6), 70.1, 72.1, 72.5 (3d, C-3, C-4, C-5), 102.3 (d, C-1), 129.0, 129.3, 130.3, 130.4, 134.0 (5d, C-arom.), 130.2 (s, C-arom.), 166.2, 168.6, 168.7, 170.1, 171.3 ppm (5s, OAc, *C*OOMe); IR (film): $\tilde{\nu}=3048$, 2987, 1722, 1602, 1439, 1370, 1094 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{28}O_{12}$ (496.46): C 55.64, H 5.68; found: C 55.97, H 5.84.

Methyl 3-*O*-benzoyl-4,6-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)-methyl]-α-D-mannopyranoside (*manno*-8e): 160 mg (16%); $R_f=0.35$ (pentane/ethyl acetate 6:4); $[\alpha]_D^{20}=+21.4$ ($c=1.02$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=2.01$, 2.11 (2s, 3H each, OAc), 3.33 (ddd, $J=9.5$, 5.0, 2.0 Hz, 1H, 2-H), 3.40, 3.41, 3.73 (3s, 3H each, OMe, COOMe), 3.76 (d, $J=9.5$ Hz, 1H, 7-H), 4.01 (ddd, $J=9.4$, 5.2, 2.3 Hz, 1H, 5-H), 4.17 (dd, $J=12.1$, 2.3 Hz, 1H, 6-H), 4.24 (dd, $J=12.1$, 5.2 Hz, 1H, 6′-H), 4.80 (d, $J=2.0$ Hz, 1H, 1-H), 5.42 (dd, $J=9.4$, 9.1 Hz, 1H, 4-H), 5.66 (dd, $J=9.1$, 5.0 Hz, 1H, 3-H), 7.40–7.60 (m, 3H, arom. H), 7.95–8.00 ppm (m, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=21.3$, 21.4 (2q, OAc), 42.9, 49.9 (2d, C-2, C-7), 53.0, 53.4 (2q, COO*Me*), 56.0 (q, OMe), 62.8 (t, C-6), 68.9, 70.1, 72.1 (3d, C-3, C-4, C-5), 100.0 (d, C-1), 129.0, 129.5, 129.8, 130.4, 134.0 (5d, C-arom.), 130.3 (s, C-arom.), 166.0, 168.6, 168.8, 169.0, 171.4 ppm (5s, OAc, *C*OOMe); IR (film): $\tilde{\nu}=3052$, 2986, 1725, 1602, 1374, 1098 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{28}O_{12}$ (496.46): C 55.64, H 5.68; found: C 55.87, H 5.79.

Methyl 3-*O*-(4-methoxybenzoyl)-4,6-di-*O*-acetyl-2-deoxy-2-[(bis-methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-8f): 780 mg (74%); $R_f=0.55$ (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}=-9.0$ ($c=2.37$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.85$, 2.09 (2s, 3H each, OAc), 2.75 (ddd, $J=11.6$, 8.5, 3.8 Hz, 1H, 2-H), 3.48 (s, 3H, OMe), 3.62 (d, $J=3.8$ Hz, 1H, 7-H), 3.65, 3.68 (2s, 3H each, COOMe), 3.77 (ddd, $J=9.8$, 4.6, 2.4 Hz, 1H, 5-H), 3.84 (s, 3H, arom. OMe), 4.13 (dd, $J=12.3$, 2.4 Hz, 1H, 6-H), 4.13 (dd, $J=12.3$, 4.6 Hz, 1H, 6′-H), 5.09 (d, $J=8.5$ Hz, 1H, 1-H), 5.22 (dd, $J=9.8$, 9.3 Hz, 1H, 4-H), 5.61 (dd, $J=11.6$, 9.3 Hz, 1H, 3-H), 6.91 (dt, $J=8.9$, 1.9, 2H, arom. H), 7.93 ppm (dt, $J=8.9$, 1.9, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=20.6$, 20.9 (2q, OAc), 46.8, 48.4 (2d, C-2, C-7), 52.5, 52.9 (2q, COO*Me*), 55.5, 57.7 (2q, OMe, arom. OMe), 62.3 (t, C-6), 66.1, 69.7, 71.7 (3d, C-3, C-4, C-5), 101.9 (d, C-1), 113.9, 114.0, 131.9, 132.1 (4d, C-arom.), 121.2 (s, C-arom.), 163.9, 165.5, 168.8, 169.7, 169.8, 170.9 ppm (6s, OAc, C-arom., *C*OOMe); IR (film): $\tilde{\nu}=2939$, 1749, 1732, 1598, 1438, 1358, 1081 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{30}O_{13}$ (526.49): C 54.75, H 5.74; found: C 54.58, H 5.72.

Methyl 3-*O*-(4-methoxybenzoyl)-4,6-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)methyl]-α-D-mannopyranoside (*manno*-8f): 210 mg (20%); $R_f=0.58$ (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}=+12.3$ ($c=1.13$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.95$, 2.11 (2s, 3H each, OAc), 3.31 (ddd, $J=9.6$, 5.0, 2.1 Hz, 1H, 2-H), 3.41, 3.43, 3.73 (3s, 3H each, OMe, COOMe), 3.72 (d, $J=9.6$ Hz, 1H, 7-H), 3.85 (s, 3H, arom. OMe), 4.00 (ddd, $J=9.5$, 5.4, 2.4 Hz, 1H, 5-H), 4.16 (dd, $J=12.2$, 2.4 Hz, 1H, 6-H), 4.24 (dd, $J=12.2$, 5.4 Hz, 1H, 6′-H), 4.80 (d, $J=2.1$ Hz, 1H, 1-H), 5.41 (dd, $J=9.5$, 9.3 Hz, 1H, 4-H), 5.62 (dd, $J=9.3$, 5.0 Hz, 1H, 3-H), 6.93 (dt, $J=8.9$, 2.7, 2H, arom. H), 7.89 ppm (dt, $J=8.9$, 2.7, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=20.6$, 20.8 (2q, OAc), 42.5, 49.6 (2d, C-2, C-7), 52.9, 53.0 (2q, COO*Me*), 55.5, 57.7 (2q, OMe, arom. OMe), 62.7 (t, C-6), 66.1, 68.5, 70.3 (3d, C-3, C-4, C-5), 99.6 (d, C-1), 113.9, 114.1, 131.9, 132.2 (4d, C-arom.), 121.6 (s, C-arom.), 163.8, 164.9, 167.9, 168.3, 169.7, 170.8 ppm (6s, OAc, C-arom., *C*OOMe); IR (film): $\tilde{\nu}=2948$, 1764, 1734, 1600, 1442, 1356, 1098 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{30}O_{13}$ (526.49): C 54.75, H 5.74; found: C 54.52, H 5.62.

Methyl 3-*O*-(4-nitrobenzoyl)-4,6-di-*O*-acetyl-2-deoxy-2-[(bis-methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-8g): 790 mg (73%); $R_f=0.62$ (pentane/ethyl acetate 1:1); m.p. 130–131 °C; $[\alpha]_D^{20}=-23.6$ ($c=1.04$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.87$, 2.08 (2s, 3H each, OAc), 2.75 (ddd, $J=11.6$, 8.6, 3.6 Hz, 1H, 2-H), 3.48 (s, 3H, OMe), 3.62 (d, $J=3.6$ Hz, 1H, 7-H), 3.66, 3.68 (2s, 3H each, COOMe), 3.81 (ddd, $J=10.0$, 4.4, 2.3 Hz, 1H, 5-H), 4.14 (dd, $J=12.3$, 2.3 Hz, 1H, 6-H), 4.35 (dd, $J=12.3$, 4.4 Hz, 1H, 6′-H), 5.03 (d, $J=8.6$ Hz, 1H, 1-H), 5.22 (dd, $J=10.0$, 9.0 Hz, 1H, 4-H), 5.61 (dd, $J=11.6$, 9.0 Hz, 1H, 3-H), 8.15 (dt, $J=9.0$, 2.0, 2H, arom. H), 8.29 ppm (dt, $J=9.0$, 2.0, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=20.9$, 21.2 (2q, OAc), 46.8, 48.6 (2d, C-2, C-7), 52.9, 53.0 (2q, COO*Me*), 58.1 (q, OMe), 62.5 (t, C-6), 69.9, 71.9, 73.5 (3d, C-3, C-4, C-5), 102.0 (d, C-1), 124.1, 131.5 (4d, C-arom.), 134.7, 151.3 (2s, C-arom.), 164.4, 168.6, 168.7, 170.1, 171.1 ppm (5s, OAc, C-arom. *C*OOMe); IR (film): $\tilde{\nu}=2957$, 1743, 1726, 1527, 1346, 1276, 1116 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{27}NO_{14}$ (541.46): C 51.02, H 5.03, N 2.59; found: C 50.80, H 5.05, N 2.58.

Methyl 3-*O*-(4-nitrobenzoyl)-4,6-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)methyl]-α-D-mannopyranoside (*manno*-8g): 185 mg (17%); $R_f=0.63$ (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}=+34.5$ ($c=1.03$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.98$, 2.13 (2s, 3H each, OAc), 3.36 (ddd, $J=10.0$, 4.9, 2.2 Hz, 1H, 2-H), 3.43, 3.46, 3.74 (3s, 3H each, OMe, COOMe), 3.73 (d, $J=10.0$ Hz, 1H, 7-H), 4.02 (ddd, $J=9.7$, 5.1, 2.3 Hz, 1H, 5-H), 4.18 (dd, $J=12.2$, 2.3 Hz, 1H, 6-H), 4.26 (dd, $J=12.2$, 5.1 Hz, 1H, 6′-H), 4.80 (d, $J=2.1$ Hz, 1H, 1-H), 5.44 (dd, $J=9.5$, 9.4 Hz, 1H, 4-H), 5.67 (dd, $J=9.0$, 4.9 Hz, 1H, 3-H), 8.12 (dt, $J=9.0$, 2.2, 2H, arom. H), 8.28 ppm (dt, $J=9.0$, 2.2, 2H, arom. H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=21.1$, 21.4 (2q, OAc), 43.2, 50.0 (2d, C-2, C-7), 53.2, 53.4 (2q, COO*Me*), 55.8 (q, OMe), 62.6 (t, C-6), 68.9, 70.4, 71.7 (3d, C-3, C-4, C-5), 100.9 (d, C-1), 124.0, 124.1, 131.1, 131.2 (4d, C-arom.), 133.1, 152.2 (2s, C-arom.), 164.3, 167.5, 167.7, 170.2, 170.4 ppm (5s, OAc, C-arom., *C*OOMe); IR (film): $\tilde{\nu}=2945$, 1746, 1734, 1534, 1343, 1103 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{27}NO_{14}$ (541.46): C 51.02, H 5.03, N 2.59; found: C 51.23, H 5.14, N 2.74.

Methyl 3-*O*-pivaoyl-4,6-di-*O*-acetyl-2-deoxy-2-[(bis-methoxycarbonyl)-methyl]-β-D-glucopyranoside (*gluco*-8h): 715 mg (75%); $R_f=0.35$ (pentane/ethyl acetate 7:3); $[\alpha]_D^{20}=-11.3$ ($c=1.12$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.14$ (s, 9H, C(CH_3)$_3$), 1.97, 2.08 (2s, 3H each, OAc), 2.60 (ddd, $J=11.2$, 8.7, 3.6 Hz, 1H, 2-H), 3.45 (d, $J=3.6$ Hz, 1H, 7-H), 3.47 (s, 3H, OMe), 3.70 (ddd, $J=10.5$, 4.5, 2.2 Hz, 1H, 5-H), 3.71, 3.74 (2s, 3H each, COOMe), 4.10 (dd, $J=12.3$, 2.2 Hz, 1H, 6-H), 4.27 (dd, $J=12.3$, 4.5 Hz, 1H, 6′-H), 5.05 (d, $J=8.7$ Hz, 1H, 1-H), 5.08 (dd, $J=10.5$, 9.2 Hz, 1H, 4-H), 5.15 ppm (dd, $J=11.2$, 9.2 Hz, 1H, 3-H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=21.0$, 21.4 (2q, OAc), 27.3, 27.4, 27.5 (3q, C(CH_3)$_3$), 39.2 (s, *C*(CH$_3$)$_3$), 46.9, 48.5 (2d, C-2, C-7), 52.7, 52.8 (2q, COO*Me*), 58.1 (q, OMe), 62.6 (t, C-6), 69.8, 71.2, 72.1 (3d, C-3, C-4, C-5), 102.2 (d, C-1), 168.4, 169.1, 169.8, 171.1 ppm (4s, OAc, *C*OOMe); IR (film): $\tilde{\nu}=2959$, 1732, 1436, 1366, 1236, 916 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{32}O_{12}$ (476.47): C 52.94, H 6.77; found: C 53.06, H 6.90.

Methyl 3-O-pivaoyl-4,6-di-*O*-acetyl-2-deoxy-2-*C*-[(bis-methoxycarbonyl)-methyl]-α-D-mannopyranoside (*manno*-8h): 150 mg (16%); $R_f=0.33$ (pentane/ethyl acetate 7:3); $[\alpha]_D^{20}=+13.7$ ($c=1.06$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.14$ (s, 9H, C(CH_3)$_3$), 2.02, 2.11 (2s, 3H each, OAc), 3.09 (ddd, $J=7.3$, 4.6, 3.0 Hz, 1H, 2-H), 3.36 (s, 3H, OMe), 3.64 (d, $J=7.3$ Hz, 1H, 7-H), 3.75, 3.76 (3s, 3H each, COOMe), 3.95 (ddd, $J=8.5$, 5.5, 2.4 Hz, 1H, 5-H), 4.11 (dd, $J=12.2$, 2.4 Hz, 1H, 6-H), 4.19 (dd, $J=12.2$, 5.5 Hz, 1H, 6′-H), 4.79 (d, $J=3.0$ Hz, 1H, 1-H), 5.21 (dd, $J=9.0$, 8.5 Hz, 1H, 4-H), 5.40 ppm (dd, $J=9.0$, 4.6 Hz, 1H, 3-H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=21.0$, 21.1 (2q, OAc), 27.3, 27.4, 27.5 (3q, C(CH_3)$_3$), 39.9 (s, *C*(CH$_3$)$_3$), 42.5, 49.2 (2d, C-2, C-7), 52.8, 53.3 (2q, COO*Me*), 55.8 (q, OMe), 63.1 (t, C-6), 67.1, 68.8, 72.0 (3d, C-3, C-4, C-5), 99.5 (d, C-1), 168.6, 169.2, 169.8, 171.0 ppm (4s, OAc, *C*OOMe); IR (film): $\tilde{\nu}=2964$, 1734, 1433, 1362, 1244, 923 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{32}O_{12}$ (476.47): C 52.94, H 6.77; found: C 53.08, H 6.81.

Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-[(bis-methoxycarbonyl)methyl]-β-D-xylohexanoside (*gluco*-8i): 355 mg (47%); $R_f=0.64$ (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}=+16.2$ ($c=1.33$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.59$ (ddd, $J=13.0$, 12.5, 10.8 Hz, 1H, 3-H^{ax}), 2.02, 2.07 (2s, 3H each, OAc), 2.28 (ddd, $J=12.5$, 5.0, 4.0 Hz, 1H, 3-H^{eq}), 2.39 (dddd, $J=13.0$, 8.5, 5.4, 4.0 Hz, 1H, 2-H), 3.45 (s, 3H, OMe), 3.61 (d, $J=5.4$ Hz, 1H, 7-H), 3.65 (ddd, $J=9.8$, 5.2, 2.5 Hz, 1H, 5-H), 3.71, 3.73 (2s, 3H each, COOMe), 4.15 (dd, $J=12.0$, 2.5 Hz, 1H, 6-H), 4.23 (dd, $J=12.0$, 5.2 Hz, 1H, 6′-H), 4.48 (d, $J=8.5$ Hz, 1H, 1-H), 4.78 ppm (ddd, $J=10.8$, 9.8, 5.0 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=20.7$, 20.9 (2q, OAc), 30.4 (t, C-3), 39.9 (d, C-2), 51.4 (d, C-7), 52.4, 52.5 (2q, COO*Me*), 57.0 (q, OMe), 62.8 (t, C-6), 67.0 (d, C-4), 75.0 (d, C-5), 103.6 (d, C-1), 168.2, 168.4, 169.7, 170.8 ppm (4s, OAc, *C*OOMe); IR ($CHCl_3$): $\tilde{\nu}=2956$, 1747,

1436, 1372, 1244, 1039 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_{10}$ (376.36): C 51.06, H 6.43; found: C 50.96, H 6.49.

Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-[(bis-methoxycarbonyl)methyl]-α-D-lyxohexanoside (*manno*-8i): 300 mg (40%); R_f=0.74 (pentane/ethyl acetate 1:1); $[\alpha]_D^{20}$=+93.7 (c=1.11 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.79 (ddd, J=13.5, 4.8, 4.4 Hz, 1H, 3-H^{eq}), 1.99 (ddd, J=13.5, 10.1, 4.2 Hz, 1H, 3-H^{ax}), 2.02, 2.09 (2s, 3H each, OAc), 2.67 (dddd, J=11.1, 4.4, 4.2, 2.0 Hz, 1H, 2-H), 3.38 (s, 3H, OMe), 3.67 (d, J=11.1 Hz, 1H, 7-H), 3.73, 3.80 (2s, 3H each, COOMe), 3.92 (ddd, J=10.0, 5.6, 2.7 Hz, 1H, 5-H), 4.16 (dd, J=12.0, 2.7 Hz, 1H, 6-H), 4.20 (dd, J=12.0, 5.6 Hz, 1H, 6′-H), 4.56 (d, J=2.0 Hz, 1H, 1-H), 4.86 ppm (ddd, J=10.1, 10.0, 4.8 Hz, 1H, 4-H); ^{13}C NMR (63 MHz, $CDCl_3$): δ=20.8, 21.0 (2q, OAc), 26.5 (t, C-3), 38.1 (d, C-2), 51.8 (d, C-7), 52.7, 52.8 (2q, COO*Me*), 55.1 (q, OMe), 63.1 (t, C-6), 64.8 (d, C-4), 68.5 (d, C-5), 99.0 (d, C-1), 168.4, 168.8, 170.5, 170.8 ppm (4s, OAc, *C*OOMe); IR ($CHCl_3$): $\tilde{\nu}$=2956, 1741, 1435, 1372, 1242, 1040 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_{10}$ (376.36): C 51.06, H 6.43; found: C 50.84, H 6.22.

Addition of dimethyl malonate (4a) to the *O*-benzylated glycals 11 (method D): A solution of the benzyl-protected glycal **11** (5.0 mmol), dimethyl malonate (**4a**) (6.61 g, 50 mmol, 10 equiv) and sodium hydrogen carbonate (1.68 g, 20 mmol, 4 equiv) in dry methanol (20 mL) was cooled to 0°C under an argon atmosphere. At this temperature, a solution of CAN (11.0 g, 20 mmol, 4 equiv), which was dried in a desiccator under high vacuum overnight, in methanol (30 mL) was added dropwise over a period of 4–6 h until TLC showed complete conversion of the starting material. After stirring for 30 min at 0°C, an ice-cold diluted solution of sodium thiosulfate (200 mL) was added, and the mixture was extracted with dichloromethane (4×80 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated, and the excess of malonate was removed at 0.01 mbar in a Kugelrohrofen. The crude product was purified by column chromatography (cyclohexane/ethyl acetate) and the 2-*C*-malonyl carbohydrates **12** were isolated in analytically pure form.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-12): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the carbohydrate 2-*C*-analogue *gluco*-**12** as a colorless syrup (2.25 g, 78%); R_f=0.42 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+5.0 (c=1.10 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.43 (ddd, J=12.5, 9.0, 4.0 Hz, 1H, 2-H), 3.38 (s, 3H, OMe), 3.43 (ddd, J=11.5, 4.0, 3.0 Hz, 1H, 5-H), 3.50 (s, 3H, COOMe), 3.58 (dd, J=12.5, 8.5 Hz, 1H, 3-H), 3.62 (s, 3H, COOMe), 3.68 (d, J=3.0 Hz, 2H, 6-H), 3.73 (dd, J=11.5, 8.5 Hz, 1H, 4-H), 3.85 (d, J=4.0 Hz, 1H, 7-H), 4.46 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.49 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.52 (d, J=10.5 Hz, 1H, CH_2-Ph), 4.59 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.66 (d, J=9.0 Hz, 1H, 1-H), 4.69 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.82 (d, J=10.5 Hz, 1H, CH_2-Ph), 7.06–7.30 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=48.0, 48.2 (2d, C-2, C-7), 52.1, 52.2 (2q, COO*Me*), 57.2 (q, OMe), 68.9 (t, C-6), 73.5, 74.6, 74.7 (3t, *C*H$_2$-Ph), 75.0, 80.0, 80.4 (3d, C-3, C-4, C-5), 101.9 (d, C-1), 127.6, 127.7, 127.8, 128.3, 128.4 (15d, arom, C-H), 137.9, 138.1, 138.2 (3s, arom. *C*-CH$_2$O), 169.0, 169.5 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=3025, 2947, 2860, 1729, 1435, 1237 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{38}O_9$ (578.65): C 68.50, H 6.62; found: C 68.75, H 6.58.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)methyl]-α-D-mannopyranoside (*manno*-12): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) afforded the carbohydrate 2-*C*-analogue *manno*-**12** as a colorless syrup (375 mg, 13%); R_f=0.42 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+3.4 (c=0.92 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.14 (ddd, J=10.5, 5.0, 1.5 Hz, 1H, 2-H), 3.27 (s, 3H, OMe), 3.36 (s, 3H, COOMe), 3.58 (ddd, J=9.5, 6.0, 3.5 Hz, 1H, 5-H), 3.64 (s, 3H, COOMe), 3.65–3.70 (m, 2H, 6-H, 6′-H), 3.67 (d, J=5.0 Hz, 1H, 7-H), 3.77 (dd, J=9.5, 4.5 Hz, 1H, 4-H), 4.08 (dd, J=10.5, 4.5 Hz, 1H, 3-H), 4.35 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.38 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.42 (d, J=12.5 Hz, 1H, CH_2-Ph), 4.50 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.54 (d, J=12.5 Hz, 1H, CH_2-Ph), 4.65 (d, J=1.5 Hz, 1H, 1-H), 4.73 (d, J=11.0 Hz, 1H, CH_2-Ph), 7.06–7.31 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=42.2, 49.4 (2d, C-2, C-7), 52.4, 52.7 (2q, COO*Me*), 55.1 (q, OMe), 69.1 (t, C-6), 72.2, 73.3, 74.6 (3t, *C*H$_2$-Ph), 71.4, 73.3, 78.7 (3d, C-3, C-4, C-5), 99.8 (d, C-1), 127.5, 127.6, 127.7, 128.0, 128.2, 128.3 (15d, arom, C-H), 138.0, 138.3 (3s, arom. *C*-CH$_2$O), 168.9, 169.1 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=3060, 3028, 2951, 2864, 1733, 1435, 1267 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{38}O_9$ (578.65): C 68.50, H 6.62; found: C 68.75, H 6.90.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)methyl]-β-D-galactopyranoside (*galacto*-12): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the carbohydrate 2-*C*-analogue *galacto*-**12** as a colorless syrup (2.40 g, 83%); R_f=0.44 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+38.3 (c=1.01 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.91 (ddd, J=12.5, 9.0, 4.0 Hz, 1H, 2-H), 3.34 (s, 3H, OMe), 3.46 (s, 3H, COOMe), 3.53 (ddd, J=11.5, 4.0, 2.5 Hz, 1H, 5-H), 3.57 (dd, J=11.5, 4.0 Hz, 1H, 6-H), 3.60 (s, 3H, COOMe), 3.61 (dd, J=12.5, 6.5 Hz, 1H, 3-H), 3.71 (dd, J=11.5, 2.5 Hz, 1H, 6′-H), 3.88 (dd, J=11.5, 6.5 Hz, 1H, 4-H), 3.88 (d, J=4.0 Hz, 1H, 7-H), 4.28 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.38 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.42 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.50 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.56 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.61 (d, J=9.0 Hz, 1H, 1-H), 4.80 (d, J=12.0 Hz, 1H, CH_2-Ph), 7.15–7.29 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=43.3, 47.8 (2d, C-2, C-7), 51.8, 51.9 (2q, COO*Me*), 56.9 (q, OMe), 68.8 (t, C-6), 70.9, 71.4, 73.3 (3t, *C*H$_2$-Ph), 73.4, 74.2, 78.7 (3d, C-3, C-4, C-5), 102.0 (d, C-1), 127.3, 127.6, 127.7, 127.9, 128.0 128.2, 128.3 (15d, arom, C-H), 137.4, 137.9, 138.6 (3s, arom. *C*-CH$_2$O), 169.2, 169.8 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=3030, 2951, 1956, 1735, 1436, 1286 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{38}O_9$ (578.65): C 68.50, H 6.62; found: C 68.65, H 6.60.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)methyl]-α-D-arabinopyranoside (*arabino*-12): Flash chromatography (cyclohexane/ethyl acetate 8:1→6:1) afforded the carbohydrate 2-*C*-analogue *arabino*-**12** as a colorless syrup (1.88 g, 82%); R_f=0.42 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$=−76.4 (c=0.82 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.97 (ddd, J=13.0, 9.0, 4.5 Hz, 1H, 2-H), 3.32 (d, J=13.0 Hz, 1H, 5-H), 3.42 (s, 3H, OMe), 3.58 (s, 3H, COOMe), 3.67 (s, 3H, COOMe), 3.69 (s, 2H, 4H, 5′-H), 3.98 (d, J=4.5 Hz, 1H, 6-H), 4.13 (dd, J=13.0, 1.5 Hz, 1H, 3-H), 4.26 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.50 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.64 (d, J=12.5 Hz, 1H, CH_2-Ph), 4.66 (d, J=9.0 Hz, 1H, 1-H), 4.75 (d, J=12.5 Hz, 1H, CH_2-Ph), 7.24–7.39 ppm (m, 10H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=43.4, 48.1 (2d, C-2, C-6), 52.0 (2q, COO*Me*), 57.0 (q, OMe), 63.3 (t, C-5), 70.8, 71.0 (2t, *C*H$_2$-Ph), 69.8, 76.7 (2d, C-3, C-4), 102.5 (d, C-1), 127.6, 127.7, 127.9, 128.0, 128.3 (10d, arom, C-H), 137.5, 138.3 (2s, arom. *C*-CH$_2$O), 169.2, 169.9 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=2951, 1731, 1435, 1238 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{30}O_8$ (458.50): C 65.49, H 6.60; found: C 65.67, H 6.70.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)methyl]-β-D-xylopyranoside (*xylo*-12): Flash chromatography (cyclohexane/ethyl acetate 8:1→6:1) gave the carbohydrate 2-*C*-analogue *xylo*-**12** as a colorless syrup (1.72 g, 75%); R_f=0.40 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$=−2.6 (c=0.89 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.33 (ddd, J=12.0, 8.5, 4.0 Hz, 1H, 2-H), 3.20 (dd, J=10.0, 2.0 Hz, 1H, 5-H), 3.34 (s, 3H, OMe), 3.50 (s, 3H, COOMe), 3.57 (ddd, J=5.5, 2.5, 2.0 Hz, 1H, 4-H), 3.61 (s, 3H, COOMe), 3.65 (dd, J=10.0, 2.5 Hz, 1H, 5′-H), 3.85 (d, J=4.0 Hz, 1H, 6-H), 3.93 (dd, J=12.0, 5.5 Hz, 1H, 3-H), 4.46 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.54 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.58 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.60 (d, J=8.5 Hz, 1H, 1-H), 4.85 (d, J=11.0 Hz, 1H, CH_2-Ph), 7.19–7.27 ppm (m, 10H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=47.1, 48.4 (2d, C-2, C-6), 52.2 (2q, COO*Me*), 57.0 (q, OMe), 63.4 (t, C-5), 72.7, 74.6 (2t, *C*H$_2$-Ph), 78.4, 80.2 (2d, C-3, C-4), 102.2 (d, C-1), 127.6, 127.8, 127.9, 128.2, 128.3, 128.5 (10d, arom, C-H), 138.0, 138.2 (2s, arom. *C*-CH$_2$O), 169.0, 169.5 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=3030, 2952, 1735, 1454, 1262 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{30}O_8$ (458.50): C 65.49, H 6.60; found: C 65.51, H 6.57.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)methyl]-α-D-lyxopyranoside (*lyxo*-12): Flash chromatography (cyclohexane/ethyl acetate 8:1→6:1) gave the carbohydrate 2-*C*-analogue *lyxo*-**12** as a colorless syrup (275 mg, 12%); R_f=0.40 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$=+59.7 (c=1.02 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.49 (ddd, J=11.0, 6.0, 3.0 Hz, 1H, 2-H), 3.19 (s, 3H, OMe), 3.44 (s, 3H, COOMe), 3.48 (dd, J=10.5, 3.5 Hz, 1H, 5-H), 3.57 (s, 3H, COOMe), 3.57 (ddd, J=9.0, 5.0, 3.5 Hz, 1H, 4-H), 3.63 (d, J=6.0 Hz, 1H, 6-H), 3.65 (dd, J=10.5, 5.0 Hz, 1H, 5′-H), 3.88 (dd, J=11.0, 9.0 Hz, 1H, 3-H), 4.54 (d, J=

11.5 Hz, 1H, CH_2-Ph), 4.59 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.61 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.84 (d, J=3.0 Hz, 1H, 1-H), 4.95 (d, J=11.0 Hz, 1H, CH_2-Ph), 7.18–7.25 ppm (m, 10H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=45.8, 49.9 (2d, C-2, C-6), 52.2, 52.3 (2q, COO*Me*), 55.2 (q, OMe), 60.2 (t, C-5), 72.8, 74.9 (2t, *C*H_2-Ph), 77.6, 80.2 (2d, C-3, C-4), 99.2 (d, C-1), 127.4, 127.7, 127.8, 128.2, 128.4 (10d, arom, C-H), 138.1, 138.6 (2s, arom. *C*-CH_2O), 168.8, 168.9 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$= 2950, 1732, 1454, 1126 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{30}O_8$ (458.50): C 65.49, H 6.60; found: C 65.55, H 6.56.

Methyl 3,6,8,9,10,12-hexa-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)-methyl]-β-D-maltopyranoside (*malto*-12): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the carbohydrate 2-*C*-analogue *malto*-**12** as a colorless syrup (4.09 g, 81%); R_f=0.38 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+18.7 (c=1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.62 (ddd, J=12.5, 8.5, 4.0 Hz, 1H, 2-H), 3.44 (s, 3H, OMe), 3.46 (ddd, J=6.5, 3.0, 2.5 1H, 5-H), 3.49 (dd, J=7.5, 1.5 Hz, 2H, 12-H, 12′-H), 3.55–3.58 (m, 1H, 11-H), 3.60 (dd, J=11.0, 3.0 Hz, 1H, 6-H), 3.63 (dd, J=11.0, 6.5 Hz, 1H, 4-H), 3.63, 3.65 (2s, 3H each, COOMe), 3.64–3.68 (m, 1H, 8-H), 3.76 (dd, J=11.0, 2.5 Hz, 1H, 6′-H), 3.85 (dd, J=10.5, 8.0 Hz, 1H, 10-H), 3.90 (d, J=4.0 Hz, 1H, 13-H), 3.94 (dd, J=12.5, 6.5 Hz, 1H, 3-H), 4.07 (t, J=8.3 Hz, 1H, 9-H), 4.37 (d, J=12.5 Hz, 1H, CH_2-Ph), 4.45 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.47 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.53 (d, J=6.5 Hz, 2H, CH_2-Ph), 4.55 (s, 4H, CH_2-Ph), 4.74 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.81 (d, J=8.5 Hz, 1H, 1-H), 4.83 (d, J=12.5 Hz, 1H, CH_2-Ph), 5.08 (d, J=11.0 Hz, 1H, CH_2-Ph), 5.30 (d, J=3.5, 1H, 7-H), 7.12–7.32 ppm (m, 30H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=46.8 (d, C-13), 48.5 (d, C-2), 52.2 (2q, COO*Me*), 57.0 (q, OMe), 68.5, 69.5 (2t, C-6, C-12), 73.2, 73.4, 75.0, 75.3, 75.5 (6t, *C*H_2-Ph), 71.1, 72.2, 77.7, 79.6, 80.0, 81.9 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 97.3, 101.6 (2d, C-1, C-7), 127.3, 127.5, 127.6, 127.8, 127.9, 128.2, 128.3 (30d, arom, C-H), 137.9, 138.0, 138.2, 138.3, 138.4, 138.7 (6s, arom. *C*-CH_2O), 168.8, 169.5 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=2863, 1734, 1496, 1142, 1027 cm^{-1}; elemental analysis calcd (%) for $C_{60}H_{66}O_{14}$ (1011.17): C 71.27, H 6.58; found: C 71.37, H 6.49.

Methyl 3,6,8,9,10,12-hexa-*O*-benzyl-2-deoxy-2-*C*-[bis-(methoxycarbonyl)-methyl]-β-D-lactopyranoside (*lacto*-12): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the carbohydrate 2-*C*-analogue *lacto*-**12** as a colorless syrup (4.14 g, 82%); R_f=0.39 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+14.9 (c=0.86 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 2.41 (ddd, J=12.0, 9.0, 4.0 Hz, 1H, 2-H), 3.21 (d, J=2.0 Hz, 1H, 11-H), 3.27 (dd, J=9.0, 3.5 Hz, 1H, 12-H), 3.30 (dd, J=9.0, 4.0 Hz, 1H, 12′-H), 3.36 (s, 3H, OMe), 3.39 (dd, J=11.0, 8.5 Hz, 1H, 4-H), 3.42 (ddd, J=8.5, 2.5, 2.0 1H, 5-H), 3.54 (dd, J=11.0, 2.5 Hz, 1H, 6-H), 3.56, 3.59 (2s, 3H each, COOMe), 3.62 (m, J=11.0, 2.0 Hz, 1H, 6′-H), 3.67 (dd, J=9.5, 8.0 Hz, 1H, 1H, 8-H), 3.79 (dd, J=11.0, 4.0 Hz, 1H, 10-H), 3.82 (d, J=2.5 Hz, 1H, 9-H), 3.93 (dd, J=12.5, 8.5 Hz, 1H, 3-H), 3.95 (d, J=4.0 Hz, 1H, 13-H), 4.16 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.27 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.28 (d, J=10.5 Hz, 1H, CH_2-Ph), 4.31 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.34 (d, J=8.0, 1H, 7-H), 4.45 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.52 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.63 (s, 2H, CH_2-Ph), 4.73 (d, J=4.5 Hz, 2H, CH_2-Ph), 4.75 (d, J=9.0 Hz, 1H, 1-H), 4.88 (d, J=11.5 Hz, 1H, CH_2-Ph), 5.08 (d, J=10.5 Hz, 1H, CH_2-Ph), 7.04–7.28 ppm (m, 30H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=47.7 (d, C-13), 48.4 (d, C-2), 52.1 (2q, COO*Me*), 57.3 (q, OMe), 68.0, 68.1 (2t, C-6, C-12), 72.6, 73.1, 73.4, 74.6, 74.7, 75.3 (6t, *C*H_2-Ph), 73.0, 73.7, 75.2, 77.6, 78.4, 80.1, 82.3 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 101.9, 102.7 (2d, C-1, C-7), 127.2, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4 (30d, arom, C-H), 138.1, 138.4, 138.5, 138.6, 138.7, 139.0 (6s, arom. *C*-CH_2O), 169.2, 169.8 ppm (2s, *C*OOMe); IR (film): $\tilde{\nu}$=3029, 2864, 1734, 1453, 1027 cm^{-1}; elemental analysis calcd (%) for $C_{60}H_{66}O_{14}$ (1011.17): C 71.27, H 6.58; found: C 71.31, H 6.49.

Decarboxylation of the acetyl-protected 2-*C*-malonyl carbohydrates 8 (method E): A solution of the 2-*C*-malonyl carbohydrate **8** (1.0 mmol) and lithium iodide (200 mg, 1.5 mmol) in DMSO (12 mL) was heated to 180°C in a Kugelrohrofen and kept under rotation at this temperature for 5.5–6.5 h. DMSO was removed at 0.01 mbar directly in the Kugelrohrofen. The crude product was purified by column chromatography (cyclohexane/ethyl acetate) and the glyco-acetic esters **13** were isolated in analytically pure form.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-13a): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the methyl ester *gluco*-**13a** as a white solid (345 mg, 92%); R_f=0.43 (cyclohexane/ethyl acetate 1:1); m.p. 75–77°C; $[\alpha]_D^{20}$=+20.3 (c=1.20 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.01, 2.02, 2.08 (3s, 3H each, OAc), 2.27 (dddd, J=11.1, 8.7, 5.7, 2.4 Hz, 1H, 2-H), 2.39–2.43 (m, 2H, 7-H, 7′-H), 3.51 (s, 3H, OMe), 3.67 (s, 3H, COOMe), 3.70 (ddd, J=9.6, 4.5, 2.4 Hz, 1H, 5-H), 4.13 (dd, J=12.3, 2.4 Hz, 1H, 6-H), 4.30 (dd, J=12.3, 4.5 Hz, 1H, 6′-H), 4.47 (d, J=8.7 Hz, 1H, 1-H), 4.99 (dd, J=9.6, 9.3 Hz, 1H, 4-H), 5.12 ppm (dd, J=11.1, 9.3 Hz, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5, 20.6 (3q, OAc), 31.5 (t, C-7), 43.2 (d, C-2), 51.6 (q, COO*Me*), 57.1 (q, OMe), 62.2 (t, C-6), 69.6, 71.6, 72.9 (3d, C-3, C-4, C-5), 103.0 (d, C-1), 169.7, 170.3, 170.6, 171.6 ppm (4s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$=3002, 2972, 1751, 1372, 1237 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_{10}$ (376.36): C 51.06, H 6.43; found: C 51.03, H 6.57.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-galactopyranoside (*galacto*-13a): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the methyl ester *galacto*-**13a** as a colorless syrup (305 mg, 81%); R_f=0.45 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$= −0.84 (c=1.02 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.99, 2.05, 2.14 (3s, 3H each, OAc), 2.42 (dddd, J=11.1, 8.4, 4.8, 3.0 Hz, 1H, 2-H), 2.36–2.49 (m, 2H, 7-H, 7′-H), 3.52 (s, 3H, OMe), 3.67 (s, 3H, COOMe), 3.87 (ddd, J=6.9, 6.6, 0.9 Hz, 1H, 5-H), 4.12 (dd, J=11.1, 6.9 Hz, 1H, 6-H), 4.20 (dd, J=11.1, 6.6 Hz, 1H, 6′-H), 4.40 (d, J=8.4 Hz, 1H, 1-H), 4.92 (dd, J=11.4, 3.3 Hz, 1H, 3-H), 5.29 ppm (dd, J=3.3, 0.9 Hz, 1H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5, 20.6 (3q, OAc), 31.4 (t, C-7), 38.6 (d, C-2), 51.6 (q, COO*Me*), 57.2 (q, OMe), 61.6 (t, C-6), 65.8, 70.6, 71.3 (3d, C-3, C-4, C-5), 103.6 (d, C-1), 170.0, 170.3, 170.4, 171.9 ppm (4s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$=2956, 2849, 1747, 1372, 1244 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_{10}$ (376.36): C 51.06, H 6.43; found: C 51.54, H 6.53.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-xylopyranoside (*xylo*-13a): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the methyl ester *xylo*-**13a** as a colorless syrup (245 mg, 81%); R_f=0.47 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$=+26.82 (c=1.08 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.03, 2.05 (2s, 3H each, OAc), 2.25 (dddd, J=10.2, 7.8, 4.2, 1.2 Hz, 1H, 2-H), 2.43 (d, J=6.0, 2H, 6-H), 3.36 (dd, J=11.7, 8.7 Hz, 1H, 5-H), 3.46 (s, 3H, OMe), 3.67 (s, 3H, COOMe), 4.11 (dd, J=11.7, 5.4 Hz, 1H, 5′-H), 4.39 (d, J=7.8 Hz, 1H, 1-H), 4.89 (ddd, J=8.7, 8.4, 5.4 Hz, 1H, 4-H), 5.05 ppm (dd, J=10.2, 8.4 Hz, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.7, 20.8 (2q, OAc), 32.2 (t, C-6), 42.2 (d, C-2), 51.7 (q, COO*Me*), 56.8 (q, OMe), 62.3 (t, C-5), 70.2, 72.1 (2d, C-3, C-4), 103.2 (d, C-1), 170.0, 170.2, 171.8 ppm (3s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$=2955, 2849, 1747, 1372, 1244 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{20}O_8$ (304.29): C 51.31, H 6.62; found: C 51.72, H 6.73.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-arabinopyranoside (*arabino*-13a): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the methyl ester *arabino*-**13a** as a colorless syrup (240 mg, 79%); R_f=0.48 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$=−26.85 (c=1.22 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02, 2.14 (2s, 3H each, OAc), 2.42 (t, J=5.7, 2H, 6-H), 2.52 (dddd, J=11.4, 8.4, 3.6, 1.5 Hz, 1H, 2-H), 3.50 (s, 3H, OMe), 3.65 (dd, J=13.2, 1.2 Hz, 1H, 5-H), 3.67 (s, 3H, COOMe), 4.05 (dd, J=13.2, 2.4 Hz, 1H, 5′-H), 4.30 (d, J=8.4 Hz, 1H, 1-H), 4.91 (dd, J=11.4, 3.3 Hz, 1H, 3-H), 5.17 ppm (ddd, J=3.3, 2.4, 1.2 Hz, 1H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.6, 20.9 (2q, OAc), 31.7 (t, C-6), 39.0 (d, C-2), 51.6 (q, COO*Me*), 57.0 (q, OMe), 64.2 (t, C-5), 66.8, 71.0 (2d, C-3, C-4), 103.8 (d, C-1), 170.1, 170.4, 172.0 ppm (3s, OAc, *C*OOMe); IR (film): $\tilde{\nu}$=2955, 2847, 1742, 1373, 1249 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{20}O_8$ (304.29): C 51.31, H 6.62; found: C 51.40, H 6.60.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(methoxycarbonyl)-methyl]-β-D-maltopyranoside (*malto*-13a): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the methyl ester *malto*-**13a** as a white solid (485 mg, 73%). R_f=0.26 (cyclohexane/ethyl acetate 1:1); m.p.

144–146 °C; $[\alpha]_D^{20} = +72.8$ ($c = 1.07$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.00$, 2.03, 2.06, 2.10, 2.14 (6 s, 3 H each, OAc), 2.07 (dddd, $J = 11.1$, 8.7, 5.7, 5.4 Hz, 1 H, 2-H), 2.31 (dd, $J = 16.4$, 5.7 Hz, 1 H, 13-H), 2.41 (dd, $J = 16.4$, 5.4 Hz, 1 H, 13′-H), 3.48 (s, 3 H, OMe), 3.66 (s, 3 H, COOMe), 3.68 (ddd, $J = 9.3$, 4.5, 2.7 Hz, 1 H, 5-H), 3.90 (dd, $J = 9.3$, 8.7 Hz, 1 H, 4-H), 3.98 (ddd, $J = 10.2$, 3.6, 2.4 Hz, 1 H, 11-H), 4.05 (dd, $J = 12.3$, 2.1 Hz, 1 H, 12-H), 4.26 (dd, $J = 12.3$, 4.5 Hz, 1 H, 12′-H), 4.26 (dd, $J = 12.0$, 4.5 Hz, 1 H, 6-H), 4.47 (dd, $J = 12.0$, 2.7 Hz, 1 H, 6′-H), 4.49 (d, $J = 8.7$ Hz, 1 H, 1-H), 4.89 (dd, $J = 10.5$, 3.9 Hz, 1 H, 8-H), 5.05 (dd, $J = 10.5$, 9.3 Hz, 1 H, 10-H), 5.20 (dd, $J = 11.1$, 8.7 Hz, 1 H, 3-H), 5.35 (d, $J = 3.9$ Hz, 1 H, 7-H), 5.35 ppm (dd, $J = 10.5$, 9.3 Hz, 1 H, 9-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$, 20.8, 20.9 (6 q, OAc), 31.4 (t, C-13), 43.9 (d, C-2), 51.6 (q, COO*Me*), 57.1 (q, OMe), 61.6, 63.2 (2 t, C-6, C-12), 68.1, 68.4, 69.4, 70.0, 72.2, 74.0, 75.3 (7 d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 95.5, 102.7 (2 d, C-1, C-7), 169.4, 169.8, 169.9, 170.4, 170.5, 171.0, 171.7 ppm (7 s, OAc, *C*OOMe); IR (film): $\tilde{\nu} = 2960$, 1746, 1371, 1230, 1042 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{40}O_{18}$ (664.61): C 50.60, H 6.07; found: C 50.34, H 6.08.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(methoxycarbonyl)-methyl]-β-D-lactopyranoside (*lacto*-13a): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the methyl ester *lacto*-**13a** as a colorless syrup (480 mg, 72 %); $R_f = 0.29$ (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20} = +13.7$ ($c = 1.03$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.96$, 2.05, 2.06, 2.07, 2.12, 2.15 (6 s, 3 H each, OAc), 2.22 (dddd, $J = 10.8$, 8.7, 5.7, 2.4 Hz, 1 H, 2-H), 2.38 (dd, $J = 5.7$, 3.0 Hz, 2 H, 13-H), 3.34 (dd, $J = 10.8$, 0.9 Hz, 1 H, 4-H), 3.47 (s, 3 H, OMe), 3.57 (ddd, $J = 9.9$, 5.1, 2.1 Hz, 1 H, 5-H), 3.66 (s, 3 H, COOMe), 3.67–3.73 (m, 1 H, 11-H), 3.84–3.91 (m, 1 H, 12-H), 4.04–4.20 (m, 2 H, 6-H, 12′-H), 4.38 (d, $J = 8.7$ Hz, 1 H, 1-H), 4.44–4.52 (m, 1 H, 6′-H), 4.45 (dd, $J = 7.8$, 2.4 Hz, 1 H, 8-H), 4.95 (dd, $J = 10.5$, 3.3 Hz, 1 H, 10-H), 5.07 (d, $J = 7.8$ Hz, 1 H, 7-H), 5.07 (dd, $J = 2.4$, 1.2 Hz, 1 H, 9-H), 5.35 ppm (dd, $J = 3.3$, 0.9 Hz, 1 H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$, 20.8, 21.0 (6 q, OAc), 31.9 (t, C-13), 43.6 (d, C-2), 51.6 (q, COO*Me*), 57.1 (q, OMe), 60.3, 60.8 (2 t, C-6, C-12), 62.3, 66.7, 69.2, 70.6, 71.0, 72.7, 76.9 (7 d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 101.0, 103.1 (2 d, C-1, C-7), 169.0, 170.0, 170.1, 170.3, 170.4, 171.8 ppm (7 s, OAc, *C*OOMe); IR (film): $\tilde{\nu} = 2957$, 1751, 1372, 1229, 1050 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{40}O_{18}$ (664.61): C 50.60, H 6.07; found: C 50.67, H 6.20.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(methylethoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-13b): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the isopropyl ester *gluco*-**13b** as a white solid (315 mg, 78 %); $R_f = 0.45$ (cyclohexane/ethyl acetate 1:1); m.p. 66–69 °C; $[\alpha]_D^{20} = +12.2$ ($c = 1.01$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$–1.26 (m, 6 H, COOCH(CH_3)$_2$), 2.01, 2.03, 2.08 (3 s, 3 H each, OAc), 2.27 (dddd, $J = 10.8$, 8.1, 5.7, 4.8 Hz, 1 H, 2-H), 2.34 (dd, $J = 15.6$, 5.7 Hz, 1 H, 7-H), 2.41 (dd, $J = 15.6$, 4.8 Hz, 1 H, 7′-H), 3.50 (s, 3 H, OMe), 3.68 (ddd, $J = 9.9$, 4.8, 2.4 Hz, 1 H, 5-H), 4.12 (dd, $J = 12.0$, 2.4 Hz, 1 H, 6-H), 4.31 (dd, $J = 12.0$, 4.8 Hz, 1 H, 6′-H), 4.47 (d, $J = 8.1$ Hz, 1 H, 1-H), 4.95–5.03 (m, 1 H, COOC*H*(CH$_3$)$_2$), 4.99 (dd, $J = 9.9$, 9.3 Hz, 1 H, 4-H), 5.12 ppm (dd, $J = 10.8$, 9.3 Hz, 1 H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$, 20.7 (3 q, OAc), 21.7 (2 q, COOCH(*C*H$_3$)$_2$), 32.1 (t, C-7), 43.2 (d, C-2), 57.1 (q, OMe), 62.3 (t, C-6), 68.0 (d, COO*C*H(CH$_3$)$_2$), 69.8, 71.7, 72.9 (3 d, C-3, C-4, C-5), 103.3 (d, C-1), 169.7, 170.2, 170.7 ppm (4 s, OAc, *C*OOCH(CH$_3$)$_2$); IR (film): $\tilde{\nu} = 2980$, 1748, 1720, 1371, 1250 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{28}O_{10}$ (404.41): C 53.46, H 6.98; found: C 53.63, H 7.08.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(methylethoxycarbonyl)methyl]-β-D-galactopyranoside (*galacto*-13b): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the isopropyl ester *galacto*-**13b** as a colorless syrup (325 mg, 80 %); $R_f = 0.47$ (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20} = -3.4$ ($c = 1.04$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$–1.26 (m, 6 H, COOCH(CH_3)$_2$), 2.00, 2.05, 2.13 (3 s, 3 H each, OAc), 2.32 (dd, $J = 15.3$, 6.3 Hz, 1 H, 7-H), 2.39 (dd, $J = 15.3$, 4.8 Hz, 1 H, 7′-H), 2.48 (dddd, $J = 11.7$, 8.4, 6.3, 4.8 Hz, 1 H, 2-H), 3.52 (s, 3 H, OMe), 3.87 (ddd, $J = 6.9$, 6.6, 0.9 Hz, 1 H, 5-H), 4.14 (dd, $J = 11.1$, 6.9 Hz, 1 H, 6-H), 4.20 (dd, $J = 11.1$, 6.6 Hz, 1 H, 6′-H), 4.40 (d, $J = 8.4$ Hz, 1 H, 1-H), 4.91 (dd, $J = 11.7$, 3.0 Hz, 1 H, 3-H), 4.95–5.04 (m, 1 H, COOC*H*(CH$_3$)$_2$), 5.30 ppm (dd, $J = 3.0$, 0.9 Hz, 1 H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.5$, 20.6 (3 q, OAc), 21.7 (2 q, COOCH(*C*H$_3$)$_2$), 31.9 (t, C-7), 38.5 (d, C-2), 57.1 (q, OMe), 61.6 (t, C-6), 65.8 (d, COO*C*H(CH$_3$)$_2$), 67.9, 70.6, 71.3 (3 d, C-3, C-4, C-5), 103.7 (d, C-1), 170.0, 170.3, 170.4, 170.9 ppm (4 s, OAc, *C*OOCH(CH$_3$)$_2$); IR (film): $\tilde{\nu} = 2982$, 2939, 1749, 1374, 1245 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{28}O_{10}$ (404.41): C 53.46, H 6.98; found: C 53.29, H 7.11.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(methylethoxycarbonyl)methyl]-β-D-xylopyranoside (*xylo*-13b): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the isopropyl ester *xylo*-**13b** as a colorless syrup (273 mg, 82 %); $R_f = 0.51$ (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20} = -19.4$ ($c = 1.05$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$–1.26 (m, 6 H, COOCH(CH_3)$_2$), 2.03, 2.05 (2 s, 3 H each, OAc), 2.24 (dddd, $J = 10.2$, 7.5, 5.9, 3.8 Hz, 1 H, 2-H), 2.38 (dd, $J = 5.9$, 3.8 Hz, 2 H, 6-H), 3.36 (dd, $J = 12.0$, 8.7 Hz, 1 H, 5-H), 3.46 (s, 3 H, OMe), 4.10 (dd, $J = 12.0$, 5.1 Hz, 1 H, 5′-H), 4.40 (d, $J = 7.5$ Hz, 1 H, 1-H), 4.89 (ddd, $J = 8.7$, 8.3, 5.1 Hz, 1 H, 4-H), 4.95–5.03 (m, 1 H, COOC*H*(CH$_3$)$_2$), 5.06 ppm (dd, $J = 10.2$, 8.3 Hz, 1 H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$ (2 q, OAc), 21.7 (2 q, COOCH(*C*H$_3$)$_2$), 32.7 (t, C-6), 42.1 (d, C-2), 56.8 (q, OMe), 62.2 (t, C-5), 68.0 (d, COO*C*H(CH$_3$)$_2$), 70.2, 71.9 (2 d, C-3, C-4), 103.3 (d, C-1), 170.0, 170.1, 170.8 ppm (3 s, OAc, *C*OOCH(CH$_3$)$_2$); IR (film): $\tilde{\nu} = 2982$, 2937, 1749, 1373, 1242 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_8$ (332.35): C 54.21, H 7.28; found: C 54.43, H 7.30.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(methylethoxycarbonyl)methyl]-β-D-arabinopyranoside (*arabino*-13b): Flash chromatography (cyclohexane/ethyl acetate 4:1→3:1) gave the isopropyl ester *arabino*-**13b** as a colorless syrup (270 mg, 81 %); $R_f = 0.50$ (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20} = -25.7$ ($c = 1.08$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.22$–1.26 (m, 6 H, COOCH(CH_3)$_2$), 2.02, 2.13 (2 s, 3 H each, OAc), 2.34 (dd, $J = 15.3$, 6.3 Hz, 1 H, 6-H), 2.42 (dd, $J = 15.3$, 4.8 Hz, 1 H, 6′-H), 2.52 (dddd, $J = 11.4$, 8.4, 6.3, 4.8 Hz, 1 H, 2-H), 3.50 (s, 3 H, OMe), 3.64 (dd, $J = 13.2$, 1.2 Hz, 1 H, 5-H), 4.05 (dd, $J = 13.2$, 2.4 Hz, 1 H, 5′-H), 4.31 (d, $J = 8.4$ Hz, 1 H, 1-H), 4.91 (dd, $J = 11.4$, 3.3 Hz, 1 H, 3-H), 4.96–5.04 (m, 1 H, COOC*H*(CH$_3$)$_2$), 5.17 ppm (ddd, $J = 3.3$, 2.4, 1.2 Hz, 1 H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$, 20.9 (2 q, OAc), 21.7 (2 q, COOCH(*C*H$_3$)$_2$), 32.2 (t, C-6), 39.0 (d, C-2), 57.0 (q, OMe), 64.2 (t, C-5), 66.9 (d, COO*C*H(CH$_3$)$_2$), 67.9, 71.1 (2 d, C-3, C-4), 103.9 (d, C-1), 170.1, 170.41, 171.1 ppm (3 s, OAc, *C*OOCH(CH$_3$)$_2$); IR (film): $\tilde{\nu} = 2981$, 2937, 1747, 1374, 1246 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_8$ (332.35): C 54.21, H 7.28; found: C 54.38, H 7.36.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(methylethoxycarbonyl)methyl]-β-D-maltopyranoside (*malto*-13b): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the isopropyl ester *malto*-**13b** as a white solid (512 mg, 74 %); $R_f = 0.28$ (cyclohexane/ethyl acetate 1:1); m.p. 146–149 °C; $[\alpha]_D^{20} = +65.6$ ($c = 1.00$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.21$–1.25 (m, 6 H, COOCH(CH_3)$_2$), 2.00, 2.02, 2.04, 2.06, 2.10, 2.14 (6 s, 3 H each, OAc), 2.25 (dd, $J = 16.5$, 5.7 Hz, 1 H, 13-H), 2.30 (dddd, $J = 10.8$, 8.7, 5.7, 5.1 Hz, 1 H, 2-H), 2.36 (dd, $J = 16.5$, 5.1 Hz, 1 H, 13′-H), 3.47 (s, 3 H, OMe), 3.66 (ddd, $J = 9.3$, 4.5, 2.7 Hz, 1 H, 5-H), 3.94 (dd, $J = 9.3$, 8.7 Hz, 1 H, 4-H), 3.99 (ddd, $J = 10.2$, 3.8, 2.4 Hz, 1 H, 11-H), 4.05 (dd, $J = 12.3$, 2.4 Hz, 1 H, 12-H), 4.24 (dd, $J = 12.3$, 3.8 Hz, 1 H, 12′-H), 4.28 (dd, $J = 12.0$, 4.5 Hz, 1 H, 6-H), 4.48 (dd, $J = 12.0$, 2.7 Hz, 1 H, 6′-H), 4.48 (d, $J = 8.7$ Hz, 1 H, 1-H), 4.90 (dd, $J = 10.7$, 3.9 Hz, 1 H, 8-H), 4.96–5.08 (m, 1 H, COOC*H*(CH$_3$)$_2$), 5.02 (dd, $J = 10.7$, 9.3 Hz, 1 H, 10-H), 5.20 (dd, $J = 10.8$, 8.7 Hz, 1 H, 3-H), 5.35 ppm (dd, $J = 10.7$, 9.3 Hz, 1 H, 9-H), 5.36 (d, $J = 3.6$ Hz, 1 H, 7-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$, 20.8, 20.9 (6 q, OAc), 21.7 (2 q, COOCH(*C*H$_3$)$_2$), 32.0 (t, C-13), 43.8 (d, C-2), 57.0 (q, OMe), 61.6, 63.3 (2 t, C-6, C-12), 68.0 (d, COO*C*H(CH$_3$)$_2$), 68.1, 68.4, 69.5, 70.0, 72.2, 74.1, 75.3 (7 d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 95.5, 102.9 (2 d, C-1, C-7), 169.4, 169.8, 170.3, 170.5, 170.8 ppm (7 s, OAc, *C*OOCH(CH$_3$)$_2$); IR (film): $\tilde{\nu} = 2980$, 1747, 1373, 1231, 1045 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{44}O_{18}$ (692.66): C 52.02, H 6.40; found: C 52.20, H 6.39.

Methyl 3,6,8,9,10,12-hexa-*O*-acetyl-2-deoxy-2-*C*-[(methylethoxycarbonyl)methyl]-β-D-lactopyranoside (*lacto*-13b): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the isopropyl ester *lacto*-**13b** as a white solid (492 mg, 71 %); $R_f = 0.30$ (cyclohexane/ethyl acetate 1:1); m.p. 48–51 °C; $[\alpha]_D^{20} = +17.0$ ($c = 1.05$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.21$–1.28 (m, 6 H, COOCH(CH_3)$_2$), 1.96, 2.04, 2.05, 2.06, 2.12, 2.15

(6 s, 3H each, OAc), 2.23 (dddd, J=10.8, 8.7, 6.0, 4.8 Hz, 1H, 2-H), 2.32 (dd, J=16.5, 6.0 Hz, 1H, 13-H), 2.37 (dd, J=16.5, 4.8 Hz, 1H, 13′-H), 3.36 (ddd, J=11.4, 6.6, 2.1 Hz, 1H, 5-H), 3.46 (s, 3H, OMe), 3.57 (ddd, J=9.6, 4.8, 1.8 Hz, 1H, 11-H), 3.69 (dd, J=9.6, 9.0 Hz, 1H, 4-H), 3.84–3.90 (m, 1H, 12-H), 4.08–4.18 (m, 3H, 6-H, 12′-H), 4.38 (d, J=8.7 Hz, 1H, 1-H), 4.95 (dd, J=7.8, 3.5 Hz, 1H, 8-H), 5.00–5.10 (m, 1H, COOC*H*-(CH_3)$_2$), 5.17 (dd, J=10.8, 3.5 Hz, 1H, 10-H), 5.35 (d, J=7.8 Hz, 1H, 7-H), 5.42 (dd, J=10.8, 3.5 Hz, 1H, 3-H), 5.48 ppm (dd, J=3.0, 0.9 Hz, 1H, 9-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5, 20.6, 20.8, 20.9 (6q, OAc), 21.7 (2q, COOCH(*C*H$_3$)$_2$), 32.4 (t, C-13), 43.5 (d, C-2), 57.0 (q, OMe), 60.4, 60.8 (2t, C-6, C-12), 62.3 (d, COO*C*H(CH$_3$)$_2$), 66.7, 68.0, 69.2, 70.7, 71.1, 72.7 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 101.0, 103.4 (2d, C-1, C-7), 169.0, 170.0, 170.1, 170.3, 170.4, 170.9 ppm (7s, OAc, *C*OOCH-(CH$_3$)$_2$); IR (film): $\tilde{\nu}$=2983, 2940, 1744, 1372, 1232, 1048 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{44}O_{18}$ (692.66): C 52.02, H 6.40; found: C 52.02, H 6.46.

Decarboxylation of the benzyl-protected 2-*C*-malonyl carbohydrates 12 under microwave irradiation (method F): A solution of the 2-*C*-malonyl carbohydrate **12** (1.0 mmol) and lithium iodide (200 mg, 1.5 mmol) in DMSO (6 mL) was heated to 100 °C with a microwave oven (power: 200 W; pressure: 10 bar) and kept stirred for 10–18 minutes. DMSO was removed at 0.01 mbar and the crude product was purified by flash chromatography (cyclohexane/ethyl acetate) to afford the glyco-acetic esters **14** in analytically pure form.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-glucopyranoside (*gluco*-14): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the methyl ester *gluco*-**14** as a colorless syrup (480 mg, 92%); R_f=0.42 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+14.2 (c=0.97 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.09 (dddd, J=10.8, 8.7, 5.7, 5.4 Hz, 1H, 2-H), 2.39 (dd, J=15.3, 5.7 Hz, 1H, 7-H), 2.47 (dd, J=15.3, 5.4 Hz, 1H, 7′-H), 3.41 (s, 3H, OMe), 3.43 (ddd, J=9.3, 5.4, 3.9 Hz, 1H, 5-H), 3.45 (dd, J=10.8, 2.1 Hz, 1H, 3-H), 3.49 (s, 3H, COOMe), 3.56 (dd, J=9.3, 2.1 Hz, 1H, 4-H), 3.67–3.70 (m, 2H, 6-H, 6′-H), 4.22 (d, J=8.7 Hz, 1H, 1-H), 4.50 (d, J=12.3 Hz, 1H, C*H*$_2$-Ph), 4.51 (d, J=11.1 Hz, 1H, C*H*$_2$-Ph), 4.54 (d, J=11.7 Hz, 1H, C*H*$_2$-Ph), 4.59 (d, J=12.0 Hz, 1H, C*H*$_2$-Ph), 4.71 (d, J=10.8 Hz, 1H, C*H*$_2$-Ph), 4.84 (d, J=11.1 Hz, 1H, C*H*$_2$-Ph), 7.09–7.30 ppm (m, 15H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.9 (t, C-7), 44.8 (d, C-2), 51.4 (q, COO*Me*), 56.9 (q, OMe), 69.0 (t, C-6), 73.5, 74.7, 74.8 (3t, *C*H$_2$-Ph), 75.2, 79.9, 82.1 (3d, C-3, C-4, C-5), 103.4 (d, C-1), 127.6, 127.7, 127.8, 128.3, 128.4 (15d, arom, C-H), 138.0, 138.2, 138.3 (3s, arom. *C*-CH$_2$O), 172.6 ppm (s, *C*OOMe); IR (film): $\tilde{\nu}$=3030, 2949, 1736, 1452, 1260 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{36}O_7$ (520.62): C 71.52, H 6.97; found: C 71.45, H 7.06.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-galactopyranoside (*galacto*-14): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the methyl ester *galacto*-**14** as a colorless syrup (440 mg, 85%); R_f=0.44 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+47.5 (c=0.95 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.55 (dddd, J=11.1, 8.4, 6.3, 4.8 Hz, 1H, 2-H), 2.44–2.66 (m, 2H, 7-H, 7′-H), 3.44 (s, 3H, OMe), 3.47 (dd, J=11.1, 6.9 Hz, 1H, 6-H), 3.55 (s, 3H, COOMe), 3.56 (dd, J=11.1, 5.4 Hz, 1H, 6′-H), 3.63 (dd, J=11.1, 3.3 Hz, 1H, 3-H), 3.66 (ddd, J=6.9, 5.4, 0.6 Hz, 1H, 5-H), 3.93 (d, J=2.4 Hz, 1H, 4-H), 4.27 (d, J=8.4 Hz, 1H, 1-H), 4.39 (d, J=11.4 Hz, 1H, C*H*$_2$-Ph), 4.47 (d, J=3.9 Hz, 2H, C*H*$_2$-Ph), 4.58 (d, J=11.7 Hz, 1H, C*H*$_2$-Ph), 4.68 (d, J=11.4 Hz, 1H, C*H*$_2$-Ph), 4.88 (d, J=11.7 Hz, 1H, C*H*$_2$-Ph), 7.23–7.37 ppm (m, 15H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.5 (t, C-7), 39.9 (d, C-2), 51.2 (q, COO*Me*), 56.8 (q, OMe), 69.1 (t, C-6), 70.6, 73.5, 73.6 (3t, *C*H$_2$-Ph), 71.5, 74.2, 80.3 (3d, C-3, C-4, C-5), 103.8 (d, C-1), 127.4, 127.8, 127.9, 128.0, 128.1, 128.4 (15d, arom, C-H), 137.7, 138.0, 138.7 (3s, arom. *C*-CH$_2$O), 173.0 ppm (s, *C*OOMe); IR (film): $\tilde{\nu}$=3030, 2919, 1735, 1453, 1259 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{36}O_7$ (520.62): C 71.52, H 6.97; found: C 71.58, H 7.01.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-β-D-xylopyranoside (*xylo*-14): Flash chromatography (cyclohexane/ethyl acetate 8:1→6:1) gave the methyl ester *xylo*-**14** as a colorless syrup (330 mg, 83%); R_f=0.40 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$=−7.7 (c=0.98 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.01 (dddd, J=11.5, 8.5, 6.0, 5.0 Hz, 1H, 2-H), 2.40 (dd, J=15.5, 6.0 Hz, 1H, 6-H), 2.46 (dd, J=15.5, 5.0 Hz, 1H, 6′-H), 3.18 (dd, J=10.0, 5.0 Hz, 1H, 5-H), 3.36 (s, 3H, OMe), 3.39 (dd, J=10.5, 8.0 Hz, 1H, 5′-H), 3.49 (s, 3H, COOMe), 3.56 (ddd, J=13.0, 8.0, 5.0 Hz, 1H, 4-H), 3.95 (dd, J=11.5, 5.0 Hz, 1H, 3-H), 4.18 (d, J=8.5 Hz, 1H, 1-H), 4.54 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 4.55 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 4.60 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 4.86 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 7.20–7.28 ppm (m, 10H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=32.3 (t, C-6), 43.8 (d, C-2), 51.4 (q, COO*Me*), 56.7 (q, OMe), 63.4 (t, C-5), 72.7, 74.5 (2t, *C*H$_2$-Ph), 79.5, 80.3 (2d, C-3, C-4), 103.9 (d, C-1), 127.6, 127.8, 128.0, 128.3, 128.5 (10d, arom, C-H), 138.1, 138.4 (2s, arom. *C*-CH$_2$O), 172.7 ppm (s, *C*OOMe); IR (film): $\tilde{\nu}$=3030, 2951, 1733, 1454, 1202 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{28}O_6$ (400.47): C 68.98, H 7.05; found: C 68.80, H 6.97.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)methyl]-?-D-arabinopyranoside (*arabino*-14): Flash chromatography (cyclohexane/ethyl acetate 8:1→6:1) gave the methyl ester *arabino*-**14** as a colorless syrup (332 mg, 83%); R_f=0.42 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$=−2.0 (c=1.04 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.49 (dddd, J=13.0, 8.0, 6.5, 4.0 Hz, 1H, 2-H), 2.42–2.55 (m, 2H, 6-H, 6′-H), 3.18 (dd, J=12.5, 3.0 Hz, 1H, 5-H), 3.39 (s, 3H, OMe), 3.45 (ddd, J=4.0, 3.0, 2.5 Hz, 1H, 4-H), 3.51 (s, 3H, COOMe), 3.60 (dd, J=12.5, 4.0 Hz, 1H, 5′-H), 4.09 (dd, J=13.0, 2.5 Hz, 1H, 3-H), 4.18 (d, J=8.0 Hz, 1H, 1-H), 4.24 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 4.47 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 4.56 (d, J=12.5 Hz, 1H, C*H*$_2$-Ph), 4.69 (d, J=12.5 Hz, 1H, C*H*$_2$-Ph), 7.18–7.33 ppm (m, 10H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.5 (t, C-6), 40.0 (d, C-2), 51.3 (q, COO*Me*), 56.7 (q, OMe), 63.2 (t, C-5), 70.8, 70.9 (2t, *C*H$_2$-Ph), 69.7, 78.0 (2d, C-3, C-4), 104.0 (d, C-1), 127.6, 127.7, 127.9, 128.3 (10d, arom, C-H), 137.8, 138.3 (2s, arom. *C*-CH$_2$O), 173.0 ppm (s, *C*OOMe); IR (film): $\tilde{\nu}$=2950, 1735, 1497, 1203 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{28}O_6$ (400.47): C 68.98, H 7.05; found: C 68.91, H 7.07.

Methyl 3,6,8,9,10,12-hexa-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)-methyl]-β-D-maltopyranoside (*malto*-14): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the methyl ester *malto*-**14** as a colorless syrup (770 mg, 81%); R_f=0.38 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+4.0 (c=0.96 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.26 (dddd, J=12.5, 8.5, 6.5, 4.5 Hz, 1H, 2-H), 2.32 (d, J=15.5, 6.5 Hz, 1H, 13-H), 2.52 (d, J=15.5, 4.5 Hz, 1H, 13′-H), 3.38 (dd, J=6.5, 3.0 Hz, 2H, 12-H, 12′-H), 3.39 (s, 3H, OMe), 3.42 (ddd, J=6.5, 3.0, 2.5 Hz, 1H, 5-H), 3.52 (dd, J=10.0, 3.0 Hz, 1H, 11-H), 3.49 (1s, 3H, COOMe), 3.56 (dd, J=11.0, 2.5 Hz, 1H, 6-H), 3.63 (dd, J=10.5, 6.5 Hz, 1H, 4-H), 3.61–3.66 (m, 1H, 8-H), 3.70 (dd, J=11.0, 3.0 Hz, 1H, 6′-H), 3.76 (dd, J=10.5, 8.0 Hz, 1H, 10-H), 3.83 (dd, J=12.5, 6.5 Hz, 1H, 3-H), 4.01 (t, J=8.5 Hz, 1H, 9-H), 4.22 (d, J=8.5 Hz, 1H, 1-H), 4.29 (d, J=12.0 Hz, 1H, C*H*$_2$-Ph), 4.39 (d, J=11.0 Hz, 1H, C*H*$_2$-Ph), 4.46 (d, J=12.0 Hz, 1H, C*H*$_2$-Ph), 4.48 (d, J=4.5 Hz, 5H, C*H*$_2$-Ph), 4.69 (d, J=10.5 Hz, 1H, C*H*$_2$-Ph), 4.73 (d, J=11.0 Hz, 1H, C*H*$_2$-Ph), 4.80 (d, J=10.5 Hz, 1H, C*H*$_2$-Ph), 4.88 (d, J=11.0 Hz, 1H, C*H*$_2$-Ph), 5.33 (d, J=3.5, 1H, 7-H), 7.05–7.26 ppm (m, 30H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=32.0 (t, C-13), 43.2 (d, C-2), 51.4 (q, COO*Me*), 56.7 (q, OMe), 68.5, 69.5 (2t, C-6, C-12), 71.1, 73.1, 73.3, 73.4, 75.0, 75.5 (6t, *C*H$_2$-Ph), 71.1, 74.4, 75.2, 77.7, 79.6, 81.7, 81.9 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 96.9, 103.4 (2d, C-1, C-7), 127.3, 127.4, 127.5, 127.6, 127.8, 128.0, 128.2, 128.3 (30d, arom, C-H), 138.0, 138.3, 138.4, 138.5, 138.7 (6s, arom. *C*-CH$_2$O), 172.6 ppm (s, *C*OOMe); IR (film): $\tilde{\nu}$=3029, 2863, 1734, 1496, 1053 cm^{-1}; elemental analysis calcd (%) for $C_{58}H_{64}O_{12}$ (953.13): C 73.09, H 6.77; found: C 73.37, H 6.79.

Methyl 3,6,8,9,10,12-hexa-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)-methyl]-β-D-lactopyranoside (*lacto*-14): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) gave the methyl ester *lacto*-**14** as a colorless syrup (750 mg, 79%); R_f=0.39 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$=+32.6 (c=1.01 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.04 (dddd, J=12.5, 8.5, 6.0, 4.5 Hz, 1H, 2-H), 2.45 (d, J=15.5, 6.0 Hz, 1H, 13-H), 2.54 (d, J=15.5, 4.5 Hz, 1H, 13′-H), 3.25–3.29 (m, 1H, 11-H), 3.27 (ddd, J=8.5, 4.5, 1.5 1H, 5-H), 3.32 (dd, J=9.5, 2.5 Hz, 2H, 12-H, 12′-H), 3.39 (s, 3H, OMe), 3.40 (dd, J=11.0, 8.5 Hz, 1H, 6-H), 3.49 (s, 3H, COOMe), 3.64 (dd, J=8.5, 6.5 Hz, 1H, 4-H), 3.69 (dd, J=9.5, 8.0 Hz, 1H, 8-H), 3.79 (dd, J=10.5, 4.0 Hz, 1H, 10-H), 3.83 (d, J=2.5 Hz, 1H, 6′-H), 3.94 (dd, J=12.5, 6.5 Hz, 1H, 3-H), 3.91 (t, J=9.0 Hz, 1H, 7-H), 4.15 (d, J=11.5 Hz, 1H, C*H*$_2$-Ph), 4.25 (d, J=12.0 Hz, 1H, C*H*$_2$-Ph), 4.26 (d, J=

8.5 Hz, 1H, 1-H), 4.32 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.35 (d, J=3.5, 1H, 9-H), 4.39 (d, J=10.5 Hz, 1H, CH_2-Ph), 4.45 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.51 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.63 (d, J=1.5 Hz, 2H, CH_2-Ph), 4.74 (d, J=4.5 Hz, 2H, CH_2-Ph), 4.88 (d, J=11.5 Hz, 1H, CH_2-Ph), 5.07 (d, J=10.5 Hz, 1H, CH_2-Ph), 7.05–7.28 ppm (m, 30H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.8 (t, C-13), 44.5 (d, C-2), 51.3 (q, COO*Me*), 56.8 (q, OMe), 68.1, 68.3 (2t, C-6, C-12), 72.7, 73.1, 73.4, 74.4, 74.6, 75.3 (6t, CH_2-Ph), 73.0, 73.8, 75.5, 77.5, 80.0, 80.1, 82.4 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 102.8, 103.4 (2d, C-1, C-7), 127.1, 127.2, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3 (30d, arom, C-H), 138.1, 138.5, 138.6, 138.8, 138.9, 139.1 (6s, arom. C-CH$_2$O), 172.8 ppm (s, COOMe); IR (film): $\tilde{\nu}$=3029, 2863, 1734, 1496, 1054 cm^{-1}; elemental analysis calcd (%) for $C_{58}H_{64}O_{12}$ (953.13): C 73.09, H 6.77; found: C 73.32, H 6.70.

Saponification of the acetyl-protected methyl esters 8a and 13a: A solution of the acetyl-protected methyl ester **8a** or **13a** (1.0 mmol) and LiOH·H_2O (420 mg, 10.0 mmol) in MeOH/H_2O (1:4, 10 mL) was stirred overnight at room temperature. Then the pH value was adjusted to 3–4 with amberlite IR-120. Finally the polar product was isolated after freeze drying.

Methyl 2-deoxy-2-*C*-[malonic acid]-β-D-glucopyranoside (*gluco*-15): Freeze drying afforded the malonic acid *gluco*-**15** quantitatively as a light yellow syrup; $[\alpha]_D^{20}$=−22.6 (c=1.03 in D_2O); ^{1}H NMR (300 MHz, D_2O): δ=2.22 (ddd, J=11.1, 9.0, 4.2 Hz, 1H, 2-H), 3.23 (dd, J=9.6, 9.0 Hz, 1H, 4-H), 3.29 (ddd, J=9.6, 5.4, 2.1 Hz, 1H, 5-H), 3.32 (dd, J=11.1, 9.0 Hz, 1H, 3-H), 3.38 (s, 3H, OMe), 3.60 (dd, J=12.3, 5.4 Hz, 1H, 6-H), 3.65 (d, J=4.2 Hz, 1H, 7-H), 3.84 (dd, J=12.3, 2.1 Hz, 1H, 6′-H), 4.57 ppm (d, J=9.0 Hz, 1H, 1-H); ^{13}C NMR (75 MHz, D_2O): δ=49.2 (2d, C-2, C-7), 57.7 (q, OMe), 61.4 (t, C-6), 71.6, 73.1, 76.2 (3d, C-3, C-4, C-5), 102.9 (d, C-1), 174.8, 175.6 ppm (2s, COOH); IR (film): $\tilde{\nu}$=3358, 2935, 1705, 1389, 1218 cm^{-1}; HR-MS(ES): m/z: calcd for $C_{10}H_{16}O_9Li$: 287.0954; found 287.0974 [M+Li]$^+$.

Methyl 2-deoxy-2-*C*-[malonic acid]-β-D-galactopyranoside (*galacto*-15): Freeze drying afforded the malonic acid *galacto*-**15** quantitatively as a light yellow syrup; $[\alpha]_D^{20}$=−10.3 (c=0.82 in D_2O); ^{1}H NMR (500 MHz, D_2O): δ=2.35 (ddd, J=11.5, 9.0, 3.5 Hz, 1H, 2-H), 3.34 (s, 3H, OMe), 3.46 (ddd, J=7.5, 4.5, 2.0 Hz, 1H, 5-H), 3.59 (dd, J=11.5, 7.5 Hz, 1H, 6-H), 3.62 (dd, J=3.0, 2.0 Hz, 1H, 4-H), 3.65 (dd, J=11.5, 4.5 Hz, 1H, 6′-H), 3.69 (d, J=3.5 Hz, 1H, 7-H), 3.80 (dd, J=11.5, 3.0 Hz, 1H, 3-H), 4.37 ppm (d, J=9.0 Hz, 1H, 1-H); ^{13}C NMR (125 MHz, D_2O): δ=45.4, 45.5 (2d, C-2, C-7), 57.7 (q, OMe), 61.7 (t, C-6), 68.3, 70.2, 75.4 (3d, C-3, C-4, C-5), 103.5 (d, C-1), 176.7, 177.5 ppm (2s, COOH); IR (film): $\tilde{\nu}$= 3370, 2941, 1699, 1386, 1237 cm^{-1}; HR-MS(ES): m/z: calcd for $C_{10}H_{16}O_9Na$: 303.0692; found 303.0721 [M+Na]$^+$.

Methyl 2-deoxy-2-*C*-[acetic acid]-β-D-glucopyranoside (*gluco*-17): Freeze drying afforded the acetic acid *gluco*-**17** quantitatively as a light yellow syrup; $[\alpha]_D^{20}$=−23.1 (c=0.88 in D_2O); ^{1}H NMR (300 MHz, D_2O): δ=2.09 (dd, J=14.7, 7.2 Hz, 1H, 7-H), 2.37 (dd, J=14.7, 4.8 Hz, 1H, 7′-H), 3.22 (dddd, J=11.1, 8.7, 7.2, 4.8 Hz, 1H, 2-H), 3.24 (dd, J=9.6, 9.0 Hz, 1H, 4-H), 3.25 (dd, J=11.1, 9.0 Hz, 1H, 3-H), 3.27 (ddd, J=9.6, 5.7, 1.8 Hz, 1H, 5-H), 3.35 (s, 3H, OMe), 3.59 (dd, J=12.3, 5.7 Hz, 1H, 6-H), 3.79 (dd, J=12.3, 1.8 Hz, 1H, 6′-H), 4.24 ppm (d, J=8.7 Hz, 1H, 1-H); ^{13}C NMR (75 MHz, D_2O): δ=36.2 (t, C-7), 46.0 (d, C-2), 57.6 (q, OMe), 61.5 (t, C-6), 71.3, 75.1, 76.1 (3d, C-3, C-4, C-5), 105.0 (d, C-1), 181.6 ppm (s, COOH); IR (film): $\tilde{\nu}$=3226, 1561, 1409, 1074 cm^{-1}; HR-MS(ES): m/z: calcd for $C_9H_{16}O_7Na$: 259.0794; found 2596.0807 [M+Na]$^+$.

Methyl 2-deoxy-2-*C*-[acetic acid]-β-D-galactopyranoside (*galacto*-17): Freeze drying afforded the acetic acid *galacto*-**17** quantitatively as a light yellow syrup; $[\alpha]_D^{20}$=−9.0 (c=0.98 in D_2O); ^{1}H NMR (300 MHz, D_2O): δ=2.08 (dddd, J=11.2, 8.7, 7.8, 4.5 Hz, 1H, 2-H), 2.27 (dd, J=15.3, 7.8 Hz, 1H, 7-H), 2.56 (dd, J=15.3, 4.5 Hz, 1H, 7′-H), 3.41 (s, 3H, OMe), 3.50 (dd, J=11.2, 3.3 Hz, 1H, 3-H), 3.55 (ddd, J=6.9, 5.4, 1.5 Hz, 1H, 5-H), 3.66 (dd, J=11.7, 5.4 Hz, 1H, 6-H), 3.73 (dd, J=11.7, 6.9 Hz, 1H, 6′-H), 3.69 (dd, J=3.3, 1.5 Hz, 1H, 4-H), 4.24 ppm (d, J=8.7 Hz, 1H, 1-H); ^{13}C NMR (75 MHz, D_2O): δ=33.2 (t, C-7), 41.2 (d, C-2), 57.6 (q, OMe), 61.7 (t, C-6), 68.0, 71.9, 75.5 (3d, C-3, C-4, C-5), 105.0 (d, C-1), 178.2 ppm (s, COOH); IR (film): $\tilde{\nu}$=3367, 2939, 1704, 1387, 1228 cm^{-1}; HR-MS(ES): m/z: calcd for $C_9H_{16}O_7Na$: 259.0794; found 259.0793 [M+Na]$^+$.

Saponification of the benzyl-protected methyl esters 12 and 14: A solution of the benzyl-protected methyl ester **12** or **14** (1.0 mmol) and LiOH·H_2O (420 mg, 10.0 mmol) in MeOH/H_2O 4:1 (10 mL) was heated under reflux until TLC showed complete conversion of the starting material. After cooling to room temperature, the pH value was adjusted to 3–4 with Amberlite IR-120, and the solvent was removed under high vacuum.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[malonic acid]-β-D-glucopyranoside (*gluco*-16): The malonic acid *gluco*-**16** was isolated quantitatively without chromatography as a light yellow syrup; $[\alpha]_D^{20}$=−7.0 (c=0.92 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.43 (ddd, J=11.5, 9.0, 3.5 Hz, 1H, 2-H), 3.36 (s, 3H, OMe), 3.41 (ddd, J=11.5, 4.0, 3.0 Hz, 1H, 5-H), 3.59 (t, J=9.5 Hz, 1H, 3-H), 3.65 (d, J=3.5 Hz, 1H, 7-H), 3.68 (d, J= 2.5 Hz, 2H, 6-H, 6′-H), 3.87 (dd, J=11.5, 9.0 Hz, 1H, 4-H), 4.44 (d, J= 11.0 Hz, 1H, CH_2-Ph), 4.45 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.46 (d, J= 9.0 Hz, 1H, 1-H), 4.54 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.62 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.69 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.86 (d, J=11.0 Hz, 1H, CH_2-Ph), 7.04–7.27 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=45.2, 48.5 (2d, C-2, C-7), 57.2 (q, OMe), 68.4 (t, C-6), 73.4, 74.7, 75.0 (3t, CH_2-Ph), 74.5, 79.9, 80.0 (3d, C-3, C-4, C-5), 101.9 (d, C-1), 127.6, 127.7, 127.8, 128.1, 128.4 (15d, arom, C-H), 137.3, 137.7, 137.9 (3s, arom. C-CH$_2$O), 171.7, 174.0 ppm (2s, COOH); IR (film): $\tilde{\nu}$=3416, 2930, 1713, 1453, 1209 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{34}O_9$ (550.60): C 67.62, H 6.22; found: C 67.35, H 6.26.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[malonic acid]-β-D-galactopyranoside (*galacto*-16): The malonic acid *galacto*-**16** was isolated quantitatively without chromatography as a light yellow syrup; $[\alpha]_D^{20}$=+6.7 (c=1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.00 (ddd, J=12.5, 9.0, 4.5 Hz, 1H, 2-H), 3.19 (ddd, J=11.5, 4.0, 2.5 Hz, 1H, 5-H), 3.35 (s, 3H, OMe), 3.52 (dd, J=12.5, 6.5 Hz, 1H, 3-H), 3.56 (dd, J=11.5, 6.5 Hz, 1H, 4-H), 3.77–3.87 (m, 2H, 6-H, 6′-H), 4.30 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.40 (d, J=9.0 Hz, 1H, 1-H), 4.42 (d, J=4.5 Hz, 1H, 7-H), 4.46 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.53 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.59 (d, J=11.0 Hz, 1H, CH_2-Ph), 4.62 (d, J=11.5 Hz, 1H, CH_2-Ph), 4.75 (d, J=11.0 Hz, 1H, CH_2-Ph), 7.12–7.32 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=43.9, 45.8 (2d, C-2, C-7), 57.0 (q, OMe), 68.7 (t, C-6), 72.0, 73.3, 74.3 (3t, CH_2-Ph), 71.4, 73.2, 78.9 (3d, C-3, C-4, C-5), 102.5 (d, C-1), 127.6, 127.7, 127.8, 127.9, 128.0 128.1, 128.3, 128.6 (15d, arom, C-H), 137.3, 137.6, 138.1 (3s, arom. C-CH$_2$O), 173.7, 175.1 ppm (2s, COOH); IR (film): $\tilde{\nu}$=2870, 1713, 1454, 1207 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{34}O_9$ (550.60): C 67.62, H 6.22; found: C 67.35, H 6.30.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[acetic acid]-β-D-glucopyranoside (*gluco*-18): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the acetic acid *gluco*-**18** quantitatively as a colorless syrup; R_f=0.40 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$=+1.4 (c=1.07 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.16 (ddt, J=10.8, 8.7, 5.4 Hz, 1H, 2-H), 2.48 (dd, J=15.6, 5.4 Hz, 1H, 7-H), 2.55 (dd, J=15.6, 5.4 Hz, 1H, 7′-H), 3.48 (s, 3H, OMe), 3.50 (ddd, J=9.3, 5.4, 3.9 Hz, 1H, 5-H), 3.56 (dd, J= 10.8, 9.0 Hz, 1H, 3-H), 3.64 (dd, J=9.3, 9.0 Hz, 1H, 4-H), 3.76 (d, J= 2.4 Hz, 2H, 6-H), 4.30 (d, J=8.7 Hz, 1H, 1-H), 4.56 (d, J=12.3 Hz, 1H, CH_2-Ph), 4.58 (d, J=10.8 Hz, 1H, CH_2-Ph), 4.64 (d, J=11.1 Hz, 1H, CH_2-Ph), 4.65 (d, J=12.3 Hz, 1H, CH_2-Ph), 4.77 (d, J=10.5 Hz, 1H, CH_2-Ph), 4.91 (d, J=11.1 Hz, 1H, CH_2-Ph), 7.16–7.37 ppm (m, 15H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.6 (t, C-7), 44.5 (d, C-2), 56.9 (q, OMe), 68.8 (t, C-6), 73.4, 74.7, 75.0 (3t, CH_2-Ph), 74.6, 79.7, 81.6 (3d, C-3, C-4, C-5), 103.2 (d, C-1), 127.5, 127.7, 127.8, 128.3, 128.4 (15d, arom, C-H), 137.9, 138.0 (3s, arom. C-CH$_2$O), 178.3 ppm (s, COOH); IR (film): $\tilde{\nu}$=3027, 2947, 1735, 1462, 1263 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{34}O_7$ (506.59): C 71.13, H 6.76; found: C 71.32, H 6.89.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[acetic acid]-β-D-galactopyranoside (*galacto*-18): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the acetic acid *galacto*-**18** quantitatively as a colorless syrup; R_f=0.42 (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}$=+48.3 (c=1.02 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.30 (dd, J=16.0, 5.0 Hz, 1H, 7-H), 2.59 (dd, J=16.0, 3.0 Hz, 1H, 7′-H), 2.78 (dddd, J=12.0, 8.5, 5.0, 3.0 Hz, 1H, 2-H), 3.22 (s, 3H, OMe), 3.54–3.57 (m, 1H, 5-H), 3.56 (dd, J=9.0, 5.5 Hz, 2H, 6-H, 6′-H), 3.81 (t, J=6.5 Hz, 1H, 3-H), 3.88 (s, 1H, 4-H), 4.36 (d, J=12.0 Hz, 1H, CH_2-Ph), 4.45 (d, J=8.5 Hz, 1H, 1-H),

4.47 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.61 (d, $J=12.0$ Hz, 1H, CH_2-Ph), 4.75 (d, $J=3.5$ Hz, 2H, CH_2-Ph), 4.79 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 7.14–7.28 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=32.3$ (t, C-7), 37.3 (d, C-2), 55.2 (q, OMe), 69.4 (t, C-6), 71.4, 73.5, 74.4 (3t, *C*H_2-Ph), 69.5, 71.8, 78.1 (3d, C-3, C-4, C-5), 100.1 (d, C-1), 127.5, 127.7, 127.8, 128.0, 128.2, 128.4 (15d, arom, C-H), 137.7, 138.0, 138.7 (3s, arom. *C*-CH_2O), 178.4 ppm (s, *C*OOH); IR (film): $\tilde{\nu}=3030$, 2913, 1706, 1454, 1077 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{34}O_7$ (506.59): C 71.13, H 6.76; found: C 71.27, H 6.86.

Reduction of the *C*-analogues 12 and 14 with lithium aluminum hydride (method G): A suspension of the 2-*C*-analogue **12** or **14** (1.0 mmol) and lithium aluminium hydride (115 mg, 3 mmol) in 1,4-dioxane (10 mL) was stirred at reflux for 3–4 h until TLC showed complete conversion of the starting material. Ethyl acetate (2 mL) and water (12 mL) were added sequentially. The mixture was filtered over Celite and was extracted with dichloromethane (4×10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated, and the alcohols **19** and **20** were isolated in analytically pure form by column chromatography.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[bis-(methanol)methyl]-β-D-glucopyranoside (*gluco*-19): Flash chromatography (cyclohexane/ethyl acetate 3:3→2:3) gave the diol *gluco*-**19** as a white solid (445 mg, 85%); $R_f=0.40$ (cyclohexane/ethyl acetate 1:3); m.p. 68–70°C; $[\alpha]_D^{20}=+0.3$ ($c=0.94$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.88$ (ddd, $J=12.0$, 9.0, 5.0 Hz, 1H, 2-H), 2.23 (t, $J=5.5$ Hz, 1H, 8-H), 2.94 (dd, $J=7.0$, 4.0 Hz, 1H, 8′-H), 3.47 (ddd, $J=10.0$, 6.5, 3.0 Hz, 1H, 5-H), 3.53 (s, 3H, OMe), 3.65 (dd, $J=9.0$, 8.5 Hz, 2H, 9-H, 9′-H), 3.72 (t, $J=5.5$ Hz, 1H, 3-H), 3.76 (d, $J=3.5$ Hz, 2H, 6-H, 6′-H), 3.79–3.84 (m, 1H, 4-H), 3.81 (d, $J=5.0$ Hz, 1H, 7-H), 4.38 (d, $J=9.0$ Hz, 1H, 1-H), 4.59 (d, $J=12.5$ Hz, 1H, CH_2-Ph), 4.61 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.67 (d, $J=12.5$ Hz, 1H, CH_2-Ph), 4.70 (d, $J=11.0$ Hz, 1H, CH_2-Ph), 4.79 (d, $J=11.0$ Hz, 1H, CH_2-Ph), 4.98 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 7.16–7.39 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=39.8$ (d, C-7), 49.1 (d, C-2), 56.4 (q, OMe), 62.6, 66.0, 68.9 (3t, C-6, C-8, C-9), 73.5, 74.6 (3t, *C*H_2-Ph), 75.1, 80.2, 80.3 (3d, C-3, C-4, C-5), 102.3 (d, C-1), 127.5, 127.6, 127.7, 127.8, 128.0, 128.3, 128.4, 128.5 (15d, arom, C-H), 138.0, 138.1 ppm (3s, arom. *C*-CH_2O); IR (film): $\tilde{\nu}=3089$, 2864, 1495, 1450, 1070 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{38}O_7$ (522.63): C 71.24, H 7.33; found: C 71.44, H 7.43.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[bis-(methanol)methyl]-β-D-galactopyranoside (*galacto*-19): Flash chromatography (cyclohexane/ethyl acetate 3:3→2:3) gave the diol *galacto*-**19** as a white solid (435 mg, 83%); $R_f=0.42$ (cyclohexane/ethyl acetate 1:3); m.p. 92–95°C; $[\alpha]_D^{20}=-18.9$ ($c=0.96$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.23$ (ddd, $J=11.7$, 9.0, 5.4 Hz, 1H, 2-H), 2.15–2.30 (m, 2H, 8-H, 8′-H), 3.39 (s, 3H, OMe), 3.45 (ddd, $J=11.7$, 4.5, 2.4 Hz, 1H, 5-H), 3.65 (d, $J=5.4$ Hz, 1H, 7-H), 3.72 (dd, $J=4.8$, 0.9 Hz, 2H, 9-H, 9′-H), 3.56 (d, $J=5.4$ Hz, 2H, 6-H, 6′-H), 3.72 (dd, $J=9.0$, 5.0 Hz, 1H, 4-H), 3.81 (d, $J=1.8$ Hz, 1H, 3-H), 4.28 (d, $J=9.0$ Hz, 1H, 1-H), 4.33 (d, $J=11.4$ Hz, 1H, CH_2-Ph), 4.40 (d, $J=2.7$ Hz, 2H, CH_2-Ph), 4.52 (d, $J=11.7$ Hz, 1H, CH_2-Ph), 4.66 (d, $J=11.4$ Hz, 1H, CH_2-Ph), 4.78 (d, $J=11.7$ Hz, 1H, CH_2-Ph), 7.14–7.30 ppm (m, 15H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=39.3$ (d, C-7), 44.4 (d, C-2), 56.4 (q, OMe), 63.6, 65.5, 69.0 (3t, C-6, C-8, C-9), 71.2, 73.5, 74.4 (3t, *C*H_2-Ph), 70.4, 73.5, 78.8 (3d, C-3, C-4, C-5), 102.8 (d, C-1), 127.5, 127.8, 128.0, 128.1, 128.4, 128.6 (15d, arom, C-H), 137.1, 137.9, 138.6 ppm (3s, arom. *C*-CH_2O); IR (film): $\tilde{\nu}=3085$, 2851, 1453, 1277, 1067 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{38}O_7$ (522.63): C 71.24, H 7.33; found: C 71.46, H 7.40.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[ethanol]-β-D-glucopyranoside (*gluco*-20): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the alcohol *gluco*-**20** as a colorless syrup (410 mg, 83%); $R_f=0.38$ (cyclohexane/ethyl acetate 1:1); $[\alpha]_D^{20}=+0.3$ ($c=0.87$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.63$ (dddd, $J=10.0$, 8.5, 6.0, 2.0 Hz, 1H, 2-H), 1.76–1.88 (m, 2H, 7-H), 3.32–3.38 (m, 2H, 8-H), 3.46 (ddd, $J=10.0$, 4.5, 3.0 Hz, 1H, 5-H), 3.52 (s, 3H, OMe), 3.62–3.68 (m, 2H, 3-H, 4-H), 3.75 (t, $J=2.8$ Hz, 2H, 6-H), 4.14 (d, $J=8.5$ Hz, 1H, 1-H), 4.57 (d, $J=12.5$ Hz, 1H, CH_2-Ph), 4.59 (d, $J=10.5$ Hz, 1H, CH_2-Ph), 4.64 (d, $J=12.5$ Hz, 1H, CH_2-Ph), 4.65 (d, $J=11.0$ Hz, 1H, CH_2-Ph), 4.77 (d, $J=11.0$ Hz, 1H, CH_2-Ph), 4.95 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 7.17–7.36 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=30.7$ (t, C-7), 45.9 (d, C-2), 56.7 (q, OMe), 61.8 (t, C-8), 69.0 (t, C-6), 73.5, 74.6, 75.0 (3t, *C*H_2-Ph), 75.2, 79.7, 83.2 (3d, C-3, C-4, C-5), 104.7 (d, C-1), 127.6, 127.8, 127.9, 128.3, 128.4 (15d, arom, C-H), 138.0, 138.2 ppm (3s, arom. *C*-CH_2O); IR (film): $\tilde{\nu}=3088$, 2893, 2360, 1496, 1361, 1054 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{36}O_6$ (492.61): C 73.15, H 7.37; found: C 73.15, H 7.33.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[ethanol]-β-D-galactopyranoside (*galacto*-20): Flash chromatography (cyclohexane/ethyl acetate 3:1→2:1) gave the alcohol *galacto*-**20** as a white solid (400 mg, 81%); $R_f=0.40$ (cyclohexane/ethyl acetate 1:1); m.p. 67–69°C; $[\alpha]_D^{20}=-20.9$ ($c=0.68$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.61$ (dddd, $J=11.5$, 9.0, 6.0, 3.0 Hz, 1H, 2-H), 1.80–1.87 (m, 1H, 7-H), 2.14–2.22 (m, 1H, 7′-H), 2.71 (t, $J=5.5$ Hz, 1H, 8-H), 3.22 (dd, $J=11.5$, 2.5 Hz, 1H, 8′-H), 3.49 (s, 3H, OMe), 3.53 (dt, $J=5.5$, 0.5 Hz, 1H, 5-H), 3.63 (dd, $J=9.0$, 5.5 Hz, 1H, 4-H), 3.67 (dd, $J=9.5$, 7.5 Hz, 2H, 6-H, 6′-H), 3.93 (d, $J=2.0$ Hz, 1H, 3-H), 4.09 (d, $J=9.0$ Hz, 1H, 1-H), 4.42 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.45 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.49 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.60 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.73 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 4.86 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 7.22–7.37 ppm (m, 15H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=30.7$ (t, C-7), 41.2 (d, C-2), 56.7 (q, OMe), 62.2 (t, C-8), 69.1 (t, C-6), 70.2, 73.6, 74.3 (3t, *C*H_2-Ph), 71.5, 77.2, 81.7 (3d, C-3, C-4, C-5), 105.1 (d, C-1), 127.5, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4, 128.5 (15d, arom, C-H), 137.3, 137.9, 138.6 ppm (3s, arom. *C*-CH_2O); IR (film): $\tilde{\nu}=3088$, 2894, 1496, 1361, 1053 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{36}O_6$ (492.61): C 73.15, H 7.37; found: C 73.25, H 7.46.

Reduction of the *C*-analogues 14 with diisobutyl aluminum hydride (method H): A solution of the 2-*C*-analogue **14** (1.0 mmol) in dry dichloromethane (10 mL) was cooled to −78°C under an argon atmosphere. At this temperature DIBAL (1.2 mL, 1.2 mmol) was added to the solution, which was stirred at low temperature until TLC showed complete conversion of the starting material. 2-Propanol (2 mL) was added to quench the reaction and water (10 mL) was added sequentially. The mixture was extracted with dichloromethane (4×10 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography to afford the aldehydes **21** in analytically pure form.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-(formylmethyl)-β-D-glucopyranoside (*gluco*-21): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) afforded the aldehyde *gluco*-**21** as a colorless syrup (403 mg, 82%); $R_f=0.40$ (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}=+8.6$ ($c=1.05$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.21$ (dddd, $J=10.5$, 8.5, 6.0, 2.5 Hz, 1H, 2-H), 2.31 (ddd, $J=16.0$, 6.0, 2.5 Hz, 1H, 7-H), 2.39 (ddd, $J=16.0$, 6.0, 2.5 Hz, 1H, 7′-H), 3.31 (dd, $J=10.5$, 9.0 Hz, 1H, 3-H), 3.38 (s, 3H, OMe), 3.38–3.41 (m, 1H, 6′-H), 3.40 (dt, $J=9.5$, 3.5 Hz, 1H, 5-H), 3.61 (dd, $J=9.5$, 9.0 Hz, 1H, 4-H), 3.69 (d, $J=3.5$ Hz, 2H, 6-H, 6′-H), 4.08 (d, $J=8.5$ Hz, 1H, 1-H), 4.47 (d, $J=11.0$ Hz, 1H, CH_2-Ph), 4.49 (d, $J=12.5$ Hz, 1H, CH_2-Ph), 4.50 (d, $J=11.0$ Hz, 1H, CH_2-Ph), 4.58 (d, $J=12.5$ Hz, 1H, CH_2-Ph), 4.72 (d, $J=10.5$ Hz, 1H, CH_2-Ph), 4.80 (d, $J=11.5$ Hz, 1H, CH_2-Ph), 7.09–7.30 (m, 15H, arom. H), 9.47 ppm (t, $J=2.5$ Hz, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=42.2$ (t, C-7), 43.8 (d, C-2), 56.8 (q, OMe), 68.8 (t, C-6), 73.5, 74.7, 74.9 (3t, *C*H_2-Ph), 75.2, 79.8, 82.3 (3d, C-3, C-4, C-5), 103.7 (d, C-1), 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5 (15d, arom, C-H), 137.7, 137.9, 138.1 (3s, arom. *C*-CH_2O), 201.0 ppm (s, *C*HO); IR (film): $\tilde{\nu}=3029$, 2863, 1721, 1496, 1050 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{34}O_6$ (490.59): C 73.45, H 6.99; found: C 72.98, H 7.04.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-(formylmethyl)-β-D-galactopyranoside (*galacto*-21): Flash chromatography (cyclohexane/ethyl acetate 10:1→8:1) afforded the aldehyde *galacto*-**21** as a colorless syrup (430 mg, 88%); $R_f=0.44$ (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}=+13.9$ ($c=0.96$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.31$ (ddd, $J=16.8$, 6.6, 3.0 Hz, 1H, 7-H), 2.53 (ddd, $J=16.8$, 6.6, 3.0 Hz, 1H, 7′-H), 2.86 (dddd, $J=10.2$, 7.8, 6.6, 3.0 Hz, 1H, 2-H), 3.21 (s, 3H, OMe), 3.47–3.54 (m, 1H, 3-H), 3.54 (d, $J=4.5$ Hz, 1H, 6-H), 3.57 (ddd, $J=9.3$, 6.9, 2.7 Hz, 1H, 5-H), 3.81 (t, $J=6.9$ Hz, 1H, 6′-H), 3.89 (d, $J=1.2$ Hz, 1H, 4-H), 4.34 (d, $J=11.7$ Hz, 1H, CH_2-Ph), 4.36 (d, $J=11.7$ Hz, 1H, CH_2-Ph), 4.44 (d, $J=11.7$ Hz, 1H, CH_2-Ph), 4.46 (d, $J=11.4$ Hz, 1H, CH_2-Ph), 4.57 (d, $J=$

11.4 Hz, 1H, CH_2-Ph), 4.68 (d, J=7.8 Hz, 1H, 1-H), 4.78 (d, J=11.7 Hz, 1H, CH_2-Ph), 7.15–7.30 (m, 15H, arom. H), 9.59 ppm (dd, J=5.0, 1.5 Hz, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.2 (t, C-2), 42.3 (t, C-7), 55.1 (q, OMe), 69.3 (t, C-6), 71.3, 73.5, 74.4 (3t, CH_2-Ph), 69.6, 71.9, 78.0 (3d, C-3, C-4, C-5), 100.4 (d, C-1), 127.5, 127.7, 127.8, 127.9, 128.2, 128.4, 128.5 (15d, arom, C-H), 137.6, 138.0, 138.6 (3s, arom. C-CH_2O), 201.5 ppm (s, CHO); IR (film): $\tilde{\nu}$=3030, 2870, 1721, 1496, 1050 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{34}O_6$ (490.59): C 73.45, H 6.99; found: C 73.25, H 7.15.

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[1] a) M. H. D. Postema, *C-Glycoside Synthesis*, CRC Press, Boca Raton, **1995**; b) D. E. Levy, C. Tang, *The Chemistry of C-Glycosides*, Elsevier, Oxford, **1995**.

[2] Reviews: a) S. Hanessian, A. G. Pernet, *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111–188; b) M. H. D. Postema, *Tetrahedron* **1992**, *48*, 8545–8599; c) J.-M. Beau, T. Gallagher, *Top. Curr. Chem.* **1997**, *187*, 1–54; d) F. Nicotra, *Top. Curr. Chem.* **1997**, *187*, 55–83; e) Y. Du, R. J. Linhardt, I. R. Vlahov, *Tetrahedron* **1998**, *54*, 9913–9959.

[3] Reviews of *C*-saccharide synthesis: a) M. McKee, L. Liu, M. H. D. Postema, *Curr. Org. Chem.* **2001**, *5*, 1133–1167; b) X. Yuan, R. J. Linhardt, *Curr. Top. Med. Chem.* **2005**, *5*, 1393–1430.

[4] a) M. H. D. Postema, D. Calimente, *Tetrahedron Lett.* **1999**, *40*, 4755–4759; b) M. H. D. Postema, D. Calimente, L. Liu, T. L. Behrmann, *J. Org. Chem.* **2000**, *65*, 6061–6068; c) L. Liu, M. H. D. Postema, *J. Am. Chem. Soc.* **2001**, *123*, 8602–8603; d) M. H. D. Postema, J. L. Piper, L. Liu, J. Shen, M. Faust, P. Andreana, *J. Org. Chem.* **2003**, *68*, 4748–4754; e) M. H. D. Postema, J. L. Piper, V. Komanduri, L. Liu, *Angew. Chem.* **2004**, *116*, 2975–2978; *Angew. Chem. Int. Ed.* **2004**, *43*, 2915–2918.

[5] Books: a) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon Press, Oxford, **1986**; b) J. Fossey, D. Lefort, J. Sorba, *Free Radicals in Organic Chemistry*, Wiley, Chichester, **1995**; c) D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, **1996**; d) T. Linker, M. Schmittel, *Radikale und Radikalionen in der Organischen Synthese*, Wiley-VCH, Weinheim, **1998**; e) *Radicals in Organic Synthesis* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**; f) S. Z. Zard, Radical Reactions in Organic Synthesis, Oxford University Press, New York, **2003**; g) A. Gansäuer, *Radicals in Synthesis, Top. Curr. Chem.* **2006**, *263*, whole volume.

[6] a) U. Linker, B. Kersten, T. Linker, *Tetrahedron* **1995**, *51*, 9917–9926; b) T. Linker, B. Kersten, U. Linker, K. Peters, E.-M. Peters, H.-G. von Schnering, *Synlett* **1996**, 468–470; c) T. Linker, U. Linker, *Angew. Chem.* **2000**, *112*, 934–936; *Angew. Chem. Int. Ed.* **2000**, *39*, 902–904; d) T. Linker, *J. Organomet. Chem.* **2002**, *661*, 159–167; recent review of CAN in radical reactions: V. Nair, A. Deepthi, *Chem. Rev.* **2007**, *107*, 1862–1891.

[7] a) T. Linker, K. Hartmann, T. Sommermann, D. Scheutzow, E. Ruckdeschel, *Angew. Chem.* **1996**, *108*, 1819–1821; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1730–1732; b) T. Linker, T. Sommermann, F. Kahlenberg, *J. Am. Chem. Soc.* **1997**, *119*, 9377–9384.

[8] a) S. Hanessian, P. Dextraze, *Can. J. Chem.* **1972**, *50*, 226–232; b) B. Fraser-Reid, L. Magdzinski, B. F. Molino, D. R. Mootoo, *J. Org. Chem.* **1987**, *52*, 4495–4504; c) D. Kubota, O. Mitsunobu, *Chem. Lett.* **1997**, 517–518; d) X. Li, T. Uchiyama, C. R. H. Raetz, O. Hindsgaul, *Org. Lett.* **2003**, *5*, 539–541.

[9] a) K. Krohn, U. Flörke, D. Gehle, *J. Carbohydr. Chem.* **2002**, *21*, 431–443; b) H. Shao, S. Ekthawatchai, S.-H. Wu, W. Zou, *Org. Lett.* **2004**, *6*, 3497–3499.

[10] Review: G. S. Cousins, J. O. Hoberg, *Chem. Soc. Rev.* **2000**, *29*, 165–174; a) C. V. Ramana, M. Nagarajan, *Synlett* **1997**, 763–764; b) J. Beyer, R. Madsen, *J. Am. Chem. Soc.* **1998**, *120*, 12137–12138; c) J. Beyer, P. R. Skaanderup, *J. Am. Chem. Soc.* **2000**, *122*, 9575–9583; d) P. R. Sridhar, K. C. Ashalu, S. Chandrasekaran, *Org. Lett.* **2004**, *6*, 1777–1779; e) S. D. Haveli, P. R. Sridhar, P. Suguna, S. Chandrasekaran, *Org. Lett.* **2007**, *9*, 1331–1334.

[11] a) B. Giese, K. Gröninger, *Tetrahedron Lett.* **1984**, *25*, 2743–2746; b) B. Giese, *Pure Appl. Chem.* **1988**, *60*, 1655–1658; c) B. Giese, *Angew. Chem.* **1989**, *101*, 993–1172; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 969–980; d) J. Cossy, S. Ibji, *Carbohydr. Res.* **1996**, *291*, 189–196.

[12] V. Gyóllai, D. Schanzenbach, L. Somsák, T. Linker, *Chem. Commun.* **2002**, 1294–1295.

[13] T. Sommermann, B. G. Kim, K. Peters, E.-M. Peters, T. Linker, *Chem. Commun.* **2004**, 2624–2625.

[14] a) K. Hartmann, B. G. Kim, T. Linker, *Synlett* **2004**, 2728–2731; b) B. G. Kim, U. Schilde, T. Linker, *Synthesis* **2005**, 1507–1513.

[15] J. Yin, J. Spindler, T. Linker, *Chem. Commun.* **2007**, 2712–2713.

[16] a) R. U. Lemieux, R. M. Ratcliffe, *Can. J. Chem.* **1979**, *57*, 1244–1251; b) V. Nair, J. Mathew, *J. Chem. Soc. Perkin Trans. 1* **1995**, 1881–1882; c) V. Nair, J. Mathew, J. Prabhakaran, *Chem. Soc. Rev.* **1997**, *26*, 127–132; d) V. Nair, L. Balagopal, R. Rajan, J. Mathew, *Acc. Chem. Res.* **2004**, *37*, 21–30.

[17] W. E. Holla, *J. Carbohydr. Chem.* **1990**, *9*, 113–119. We thank Dr. Holla (Novartis) for a generous gift of crude glycal **6d**.

[18] B. Fraser-Reid, S. Y.-K. Tam, B. Radatus, *Can. J. Chem.* **1975**, *53*, 2005–2016.

[19] a) B. Helferich, E. N. Mulcahy, H. Ziegler, *Chem. Ber.* **1954**, *87*, 233–237; b) B. K. Shull, Z. Wu, M. Koreeda, *J. Carbohydr. Chem.* **1996**, *15*, 955–964; c) S. A. Mitchell, M. R. Pratt, V. J. Hruby, R. Polt. *J. Org. Chem.* **2001**, *66*, 2327–2342.

[20] P. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis*, 4th ed., Wiley, Hoboken, **2007**.

[21] a) A. G. Tolstikov, N. V. Khakhalina, L. V. Spirikhin, *Synthesis* **1988**, 221–222; b) M. Chmielewski, I. Fokt, J. Grodner, G. Grynkiewicz, W. Szeja, *J. Carbohydr. Chem.* **1989**, *8*, 735–744; c) S. Messaoudi, F. Anizon, B. Pfeiffer, R. Golsteyn, M. Prudhomme, *Tetrahedron Lett.* **2004**, *45*, 4643–4647; d) S. K. Madhusudan, G. Agnihotri, D. S. Negi, A. K. Misra, *Carbohydr. Res.* **2005**, *340*, 1373–1377.

[22] a) R. J. Ferrier, N. Prasad, *J. Chem. Soc. C* **1969**, 581–586; b) R. D. Dawe, B. Fraser-Reid, *J. Chem. Soc. Chem. Commun.* **1981**, 1180–1181; c) K. Inaba, S. Matsumura, S. Yoshikawa, *Chem. Lett.* **1991**, 485–488.

[23] R. Sustmann, H.-G. Korth in *Houben-Weyl, Methoden der Organischen Chemie, Vol. E5* (Ed.: J. Falbe), Thieme, Stuttgart, **1985**, pp. 193–470.

[24] Reviews: a) A. P. Krapcho, *Synthesis* **1982**, 805–822; b) A. P. Krapcho, *Synthesis* **1982**, 893–914.

[25] K.-I. Kim, R. I. Hollingsworth, *Tetrahedron Lett.* **1994**, *35*, 1031–1032.

[26] *Microwaves in Organic Synthesis* (Ed.: A. Loupy), Wiley-VCH, Weinheim, 2nd ed., **2006**.

[27] a) L. I. Kudryashov, M. A. Cclenov, N. K. Kochetkov, *Izvestiya Akademii Nauk SSSR, Seria Khimicheskaya* **1965**, *1*, 75–79; b) J. K. Dickson, B. Fraser-Reid, *J. Chem. Soc. Chem. Commun.* **1990**, 1440–1443; c) O. Jarreton, T. Skrydstrup, J.-F. Espinosa, J. Jiménez-Barbero, J.-M. Beau, *Chem. Eur. J.* **1999**, *5*, 430–441; d) C. Clarke, R. J. Woods, J. Gluska, A. Cooper, M. A. Nutley, G.-J. Boons, *J. Am. Chem. Soc.* **2001**, *123*, 12238–12247.

[28] S. L. Krintel, J. Jiménez-Barbero, T. Skrydstrup, *Tetrahedron Lett.* **1999**, *40*, 7565–7568.

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