The Addition of Malonates to Glycals: A General and Convenient Method for the Synthesis of 2-*C*-Branched Carbohydrates

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Abstract: A general and convenient synthesis of carbohydrate 2-*C*-analogs by addition of malonates to glycals is described. The method is applicable to glycals derived from hexoses and pentoses and is characterized by easily available precursors. The reactions are mediated by manganese(III) or cerium(IV) and proceed *via* intermediarily generated malonyl radicals. All additions exhibit a very high degree of regioselectivity, since only 2-*C*-branched sugars were obtained. This result can be best rationalized by favorable orbital interactions between the SOMO of the malonyl radical and the HOMO of the double bond. Variation of the steric demand of the malonate or the glycal allows the stereoselectivities to be increased up to >98%. Highest selectivities were obtained with tri-*O*-acetyl-D-galactal and di-*O*-acetyl-D-arabinal, where the attack occurs exclusively from one face of the carbohydrate. For all cerium(IV)-mediated reactions, methyl glycosides are formed as main products in 73−89% yield, which can be isolated in analytically pure form on a gram scale. Strong evidence was found for a ligand transfer rather than electron transfer during the formation of carbohydrate 1-nitrates, which sheds light on the mechanism of transition-metal-mediated radical reactions. In terms of starting materials, stereoselectivities, and yields, the herein described method for the synthesis of carbohydrate 2-*C*-analogs is superior to literature known procedures.

Introduction

C-Branched sugars are of current interest in carbohydrate chemistry. During the last 20 years, many methods have been developed for the synthesis of *C*-glycosides in which a carbon atom substitutes the glycosidic oxygen.[2] However, *C*-functionalizations at other positions of the sugar ring require many steps[3] or the use of toxic tin and mercury compounds.[4] Herein we present a practical and general protocol for the synthesis of 2-*C*-analogs of carbohydrates, which is notable for easily available starting materials, high yields, and good stereoselectivities.

We chose glycals as ideal substrates for this purpose, since these chiral building blocks can be prepared on a multigram scale and are known to serve as precursors for a broad variety of optically active products.[5] Among the various transforma-

tions, cycloadditions,[6] epoxidations,[7] the addition of heteroatoms,[8] and acid-induced rearrangements[9] are the most important reactions. Furthermore, *C*-glycosides can be conveniently synthesized from glycals.[10] However, the direct *C*-functionalization of the 2-position of glycals was unexplored until very recently.

During the course of our investigations on manganese(III)-mediated radical reactions,[11] we revealed the first application of this methodology in carbohydrate chemistry.[12] Thus, addition of dimethyl malonate (**2a**) to tri-*O*-acetyl-D-glucal (**1a**) proceeds

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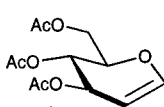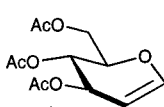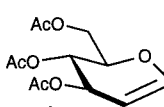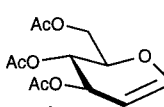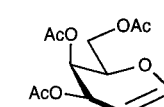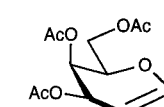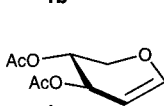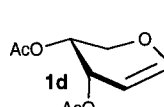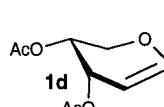
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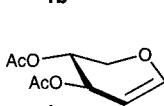
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Table 1. Addition of Malonates **2** to Glycals **1**

1	2	R	method[a]	dr α : β[b]	R'	3 (%)[c]	3 (%)[c]	4 (%)[c]	5 (%)[c]
1a	2a	Me	A	79 : 21	Ac	gluco-**3a** (52)[d]	manno-**3a** (14)[e]	(10)[f]	-
	2b	i-Pr	A	84 : 16	Ac	gluco-**3b** (57)[g]	manno-**3b** (11)[h]	(11)[i]	-
1a	2a	Me	B	85 : 15	Me	gluco-**3a** (62)	manno-**3a** (14)	-	gluco-**5a** (16)
	2b	i-Pr	B	91 : 9	Me	gluco-**3b** (68)	manno-**3b** (8)	-	gluco-**5b** (16)
1b	2a	Me	B	>98 : 2	Me	galacto-**3a** (78)	-	-	galacto-**5a** (8)
	2b	i-Pr	B	>98 : 2	Me	galacto-**3b** (73)	-	-	galacto-**5b** (17)
1c	2a	Me	B	93 : 7	Me	xylo-**3a** (81)[j]	lyxo-**3a** (6)	-	-
	2b	i-Pr	B	87 : 13	Me	xylo-**3b** (75)[k]	lyxo-**3b** (11)	-	-
1d	2a	Me	B	<2 : 98	Me	arabino-**3a** (89)[l]	-	-	-
	2b	i-Pr	B	<2 : 98	Me	arabino-**3b** (87)[l]	-	-	-

[a] Method A; 2−4 equiv of Mn(OAc)$_3$·2H$_2$O, HOAc, 95 °C; method B; 3−6 equiv of CAN, MeOH, 0 °C. [b] Diastereomeric ratios (dr related to attack of malonyl radicals) determined by ^{1}H NMR analysis of the crude product (600 MHz). [c] Yield of isolated product after column chromatography. [d] α:β = 16:84. [e] α:β = 71:29. [f] α:β = 10:90. [g] α:β = 8:92. [h] α:β >97:3. [i] α:β = 7:93. [j] α:β = 5:95. [k] α:β = 3:97. [l] α:β = 92:8.
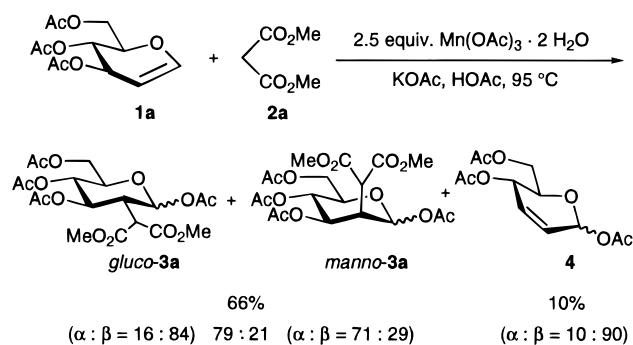
Scheme 1

with very high regioselectivity to afford the *C*-analogs **3a** in 66% yield (Scheme 1). However, four diastereomers are formed with only moderate selectivity. Furthermore, the unsaturated carbohydrates **4** result from an acid-catalyzed Ferrier rearrangement[9] under the drastic reaction conditions.

Herein we describe a new methodology to remarkably increase the stereoselectivities of the additions and to suppress the undesired Ferrier rearrangement. Furthermore, for the first time the transition-metal-mediated addition of malonates **2** was extended to tri-*O*-acetyl-D-galactal (**1b**) and glycals **1c** and **1d** derived from pentoses. Finally, mechanistic details will be presented to rationalize the regio- and stereoselectivities of the reactions.

Results

Glycals **1a**−**d** were synthesized from D-glucose, D-galactose, D-xylose, and D-arabinose, respectively, according to the method described by Helferich.[13] First attempts to obtain higher stereoselectivities were performed by addition of the sterically more demanding diisopropyl malonate (**2b**) to tri-*O*-acetyl-D-glucal (**1a**) in the presence of manganese(III) acetate dihydrate (method A, Table 1). Indeed, the *gluco:manno* ratio was slightly increased from 79:21 to 84:16, but again the unsaturated carbohydrate **4** was formed in 11% yield. The product ratios were determined by 600 MHz ^{1}H NMR spectroscopy directly on the crude reaction mixture after evaporation of the solvent. The rearranged products **4** could be easily removed by column chromatography, but a complete separation of the diastereomeric *C*-analogs **3b** was not possible. However, the configuration of the addition products was unequivocally established by the assignment of all coupling constants of the ring protons by means of 1D TOCSY NMR spectroscopy.[14] Furthermore, the main products *β-gluco*-**3a** and *β-gluco*-**3b**, derived from addition of malonates **2** to tri-*O*-acetyl-D-glucal (**1a**) in the presence of manganese(III) acetate dihydrate (method A), could be finally isolated in analytically pure form by crystallization.

β-*gluco*-**3a**   β-*gluco*-**3b**
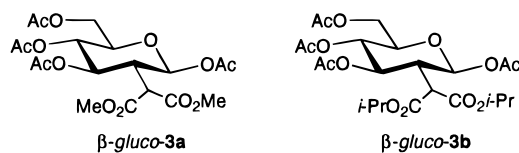
To overcome the problem of acid-catalyzed Ferrier rearrangements, milder reaction conditions were next employed.
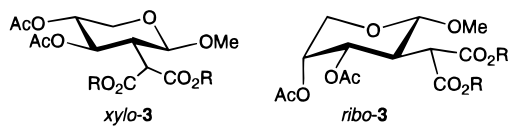
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Scheme 2
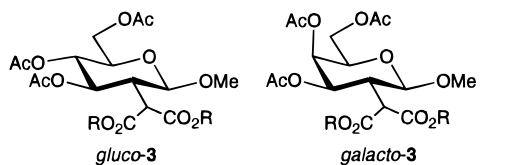
	gluco-3	*galacto-3*
a: R = Me	$J_{1,2}$ = 8.6 Hz; $J_{2,3}$ = 11.6 Hz	$J_{1,2}$ = 8.8 Hz; $J_{2,3}$ = 12.3 Hz
b: R = *i*-Pr	$J_{1,2}$ = 8.6 Hz; $J_{2,3}$ = 11.6 Hz	$J_{1,2}$ = 8.8 Hz; $J_{2,3}$ = 12.3 Hz

	xylo-3	*ribo-3*
a: R = Me	$J_{1,2}$ = 7.8 Hz; $J_{2,3}$ = 10.8 Hz	$J_{1,2}$ = 8.6 Hz; $J_{2,3}$ = 11.9 Hz
b: R = *i*-Pr	$J_{1,2}$ = 7.6 Hz; $J_{2,3}$ = 10.4 Hz	$J_{1,2}$ = 8.6 Hz; $J_{2,3}$ = 11.9 Hz

Ceric(IV) ammonium nitrate (CAN) turned out to be the reagent of choice (method B), since radical generation from CH-acidic substrates takes place even in methanol at low temperatures.[15] Thus, the addition of malonates **2** to tri-*O*-acetyl-D-glucal (**1a**) afforded the C−C bond-formation products **3** and **5** highly regioselectively in 92% yield without competing Ferrier rearrangement (Table 1). Furthermore, due to the lower reaction temperature higher stereoselectivities were obtained with cerium(IV) than with manganese(III). Again, the sterically more hindered diisopropyl malonate (**2b**) favors the formation of the *gluco*-configured products **3b** and **5b** compared to dimethyl malonate (**2a**). Finally, another advantage of the cerium(IV)-mediated reactions is reflected in the easy separation of the nitrates **5** from the *gluco*-configured main products by column chromatography.

Although the reactions with diisopropyl malonate (**2b**) provide higher stereoselectivities than the analogous additions of dimethyl malonate (**2a**), *manno* isomers **3b** are still formed as side products by β-attack to the glucal **1a**. To further increase the selectivities and to elucidate the scope and limitations of our method, other glycals were next tested. Thus, tri-*O*-acetyl-D-galactal (**1b**) was found to be an especially attractive substrate for the cerium(IV)-mediated radical reactions, since no *talo* isomers could be detected with both malonates (Table 1). Finally, we investigated for the first time additions of malonates **2** to glycals **1c** and **1d** derived from pentoses. Indeed, a smooth reaction takes place at 0 °C in the presence of ceric(IV) ammonium nitrate (CAN), and the formation of rearrangement products **4** was suppressed completely (Table 1). The 2-*C*-analogs **3** were isolated in even higher yields compared to the additions to glycals **1a** and **1b**, since no nitrates **5** are formed.

The configuration of all products was established by complete assignment of the coupling constants of the ring protons by 600 MHz ^{1}H NMR spectroscopy. Furthermore, for some methyl glycosides X-ray structures were obtained.[16] As expected, *gluco*, *galacto*, and *xylo* isomers **3** prefer the $^4C_1$ conformation, which is revealed by the large $J_{1,2}$ and $J_{2,3}$ H−H coupling constants (Scheme 2). On the other hand, the $^1C_4$ conformation is favored for the α-*arabino* configured products, which can be rationalized by the preferred equatorial orientation

Scheme 3
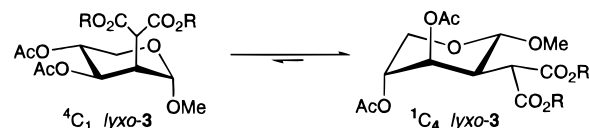
a: R = Me	$J_{1,2}$ = 7.2 Hz;	$J_{2,3}$ = 3.7 Hz
b: R = *i*-Pr	$J_{1,2}$ = 7.0 Hz;	$J_{2,3}$ = 3.4 Hz

Scheme 4
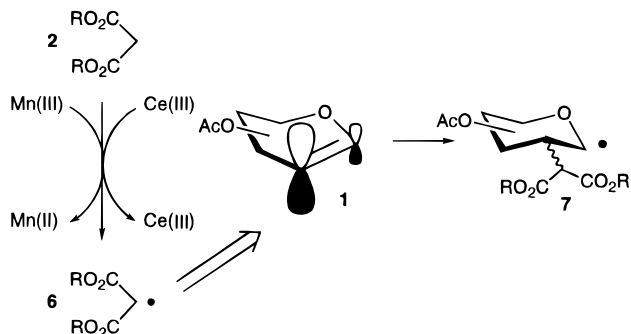
of substituents.[17] An interesting example is provided by the *lyxo*-configurated methyl glycosides **3**, since both conformers have two equatorial substituents (Scheme 3). Due to the anomeric effect,[18] the $^4C_1$ conformation should be slightly favored. However, the $J_{1,2}$ H−H coupling constants of 7.0−7.2 Hz indicate that the equilibrium is shifted toward the $^1C_4$ conformation, which documents the importance of the equatorial orientation of the sterically demanding malonyl substituents.

For synthetic applications it is important that the major products **3** and **5** can be isolated by column chromatography or simply by crystallization in analytically pure form on a gram scale. Therefore, the herein presented methodology provides a convenient and general route to 2-*C*-analogs of carbohydrates, which in terms of steps and yield is superior to literature known procedures.[3,4]

Discussion

As shown in Table 1, all reactions of glycals **1** with malonates **2** afford exclusively 2-*C*-branched carbohydrates, and no addition to the 1-position is observed. These high regioselectivities are interesting from the mechanistic point of view (Scheme 4). In the first step, malonyl radicals **6** are generated from malonates **2** and manganese(III) (method A) or cerium(IV) (method B) by an inner-sphere electron transfer.[11] Such acceptor-substituted radicals are characterized by the low energy of the SOMO and exhibit electrophilic character.[15a,19] Thus, the interaction with the HOMO of the double bond becomes predominant, which has the largest coefficient at the 2-position of glycals. This explains the highly regioselective addition of malonates **2** to afford the adduct radicals **7** and reveals the importance of orbital interactions in radical reactions, since for steric reasons, attack at the 1-position should be favored. Furthermore, the transition-metal-mediated radical reactions described herein represent typical examples of an *Umpolung*, since the palladium-catalyzed addition of β-diketones and

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Scheme 5
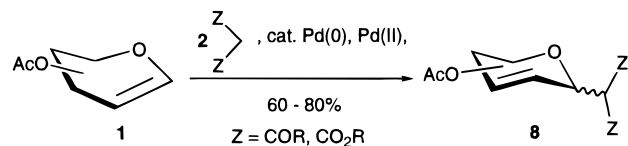
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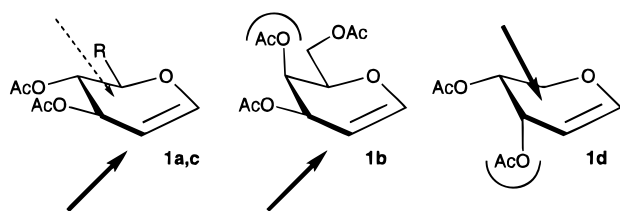
Scheme 7
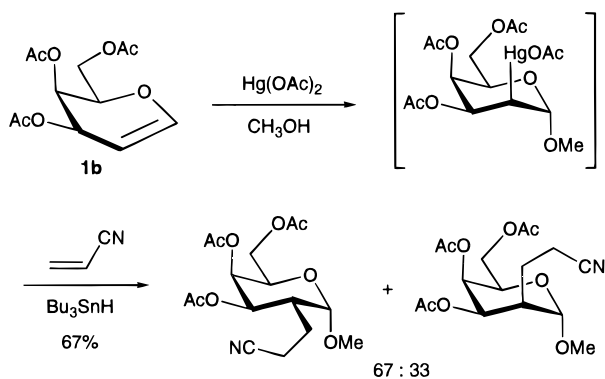
malonates **2** to glycals **1** affords exclusively *C*-glycosides **8** (Scheme 5).[2c,20]

Apart from the excellent regioselectivities, the addition of malonates to the 2-position exhibits a good to high degree of stereoselectivity (Table 1). Due to the lower reaction temperatures, cerium(IV)-mediated reactions (method B) are more selective than the corresponding additions in the presence of manganese(III) acetate dihydrate (method A). The observed preferred attack of malonyl radicals **6** to the double bond of the glycals can be best rationalized by steric interactions. Although the change from dimethyl malonate (**1a**) to diisopropyl malonate (**1b**) only slightly alters the $\alpha{:}\beta$ ratio, the substitution pattern of the glycals **1** has a strong influence on the stereoselectivity. Thus, in all examined reactions the radicals add preferentially *trans* to the acetate group in the 3-position (Scheme 6). Due to the similar substitution pattern of tri-*O*-acetyl-D-glucal (**1a**) and di-*O*-acetyl-D-xylal (**1c**), *gluco/manno* and *xylo/lyxo* mixtures were obtained in approximately the same ratios (Table 1). On the other hand, highest stereoselectivities were observed 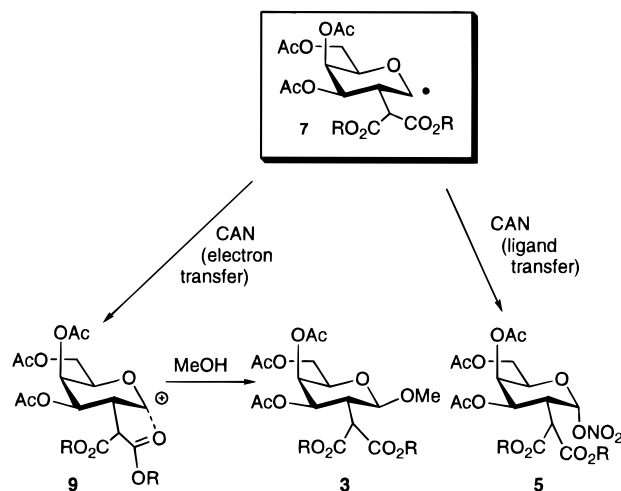with tri-*O*-acetyl-D-galactal (**1b**) and di-*O*-acetyl-D-arabinal (**1d**), since two ester groups shield the same face of the carbohydrate. Furthermore, in both cases one substituent is orientated *pseudo* axial, which results in severe steric interactions with the malonyl radicals **6** and, thus, *galacto-* and *arabino*-configured products are formed exclusively. The herein described high selectivities are in accordance with cycloadditions[6] and epoxidations[7] of galactal and arabinal derivatives. However, the similar cerium(IV)-mediated azidonitration of tri-*O*-acetyl-D-galactal (**1b**) affords only a product mixture.[8b] Furthermore, compared to the tin-mediated synthesis of carbohydrate 2-*C*-analogs (Scheme 7),[4b] which also proceeds *via* radical intermediates, our method is superior in terms of yield and stereoselectivity.

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Scheme 8

Finally, the formation of methyl glycosides **3** and nitrates **5** is interesting from the mechanistic point of view. The adduct radical **7** is readily oxidized by CAN to the cation **9**, which is trapped by the solvent to afford the methyl glycoside **3**. The exclusive formation of β-galactosides, β-glucosides, and α-mannosides **3** can be rationalized by a neighboring group participation of the malonyl substituent (Scheme 8). Such effects are not present in heteroatom additions to glycals, and, therefore, product mixtures result.[8]

On the other hand, the nitrates **5** are exclusively obtained as α-anomers and cannot be formed *via* the intermediate **9**. A direct ligand transfer from CAN without participation of cations is more likely (Scheme 8), which would explain the high stereoselectivity, since carbohydrate radicals like **7** are preferentially trapped from the α-face.[21] To further prove this hypothesis, we conducted the additions in the presence of 10 equiv of sodium nitrate. Indeed, no influence on the product distribution was observed. Thus, the previously postulated ionic mechanism for the formation of nitrates[15] can be ruled out, which is important for the mechanistic understanding of transition-metal-mediated radical reactions. For the addition of malonates in the presence of manganese(III) acetate dihydrate, a differentiation between electron and ligand transfer is not possible, since trapping of the intermediary cations **9** by the solvent acetic acid affords the same product.

Interestingly, with the pentose derived glycals **1c** and **1d** no nitrates **5** were obtained (Table 1). One explanation could be the slower oxidation of the adduct radicals *gluco-* and *galacto-***7** to the cations **9** compared to the corresponding *xylo* and *arabino* isomers and, thus, a ligand transfer cannot compete. However, no mechanistic rational for such a difference in the oxidation potentials exists in the literature. It is more likely that *xylo-*, *lyxo-*, and *arabino*-configured nitrates **5** are formed as intermediates and are subsequently trapped by the solvent methanol *via* a S_N2 reaction (Scheme 9). Indeed, small amounts of the methyl glycosides α-*lyxo*-**3** and β-*arabino*-**3** were isolated, whereas the addition to tri-*O*-acetyl-D-glucal (**1a**) and tri-*O*-acetyl-D-galactal (**1b**) proceeds exclusively 1,2-*trans* selective (Table 1). Further evidence for this mechanistic hypothesis is provided by the literature known reaction of carbohydrate 1-nitrates with nucleophiles like halides.[8b] This reaction opens up interesting prospects for the synthesis of useful glycosyl donors.

Conclusion

The addition of malonates to glycals provides a general and convenient entry to carbohydrate 2-*C*-analogs. Our methodol-

Scheme 9
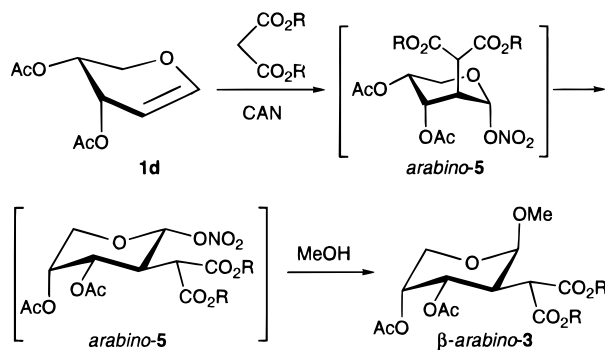
ogy is applicable to glycals derived from hexoses and pentoses and is characterized by easily available precursors. The generation of malonyl radicals by ceric(IV) ammonium nitrate (CAN) is superior to manganese(III)-mediated additions in terms of milder reaction conditions and yields. All reactions exhibit a very high degree of regioselectivity, since only 2-*C*-branched sugars were obtained. This result can be best rationalized by favorable orbital interactions between the SOMO of the malonyl radical and the HOMO of the double bond.

A moderate influence of the malonic ester groups on the stereoselectivities was observed. On the other hand, the substitution pattern of the glycals strongly alters the diastereomeric ratios. High stereoselectivities were obtained with tri-*O*-acetyl-D-glucal and di-*O*-acetyl-D-xylal. Furthermore, the addition of malonates to the corresponding unsaturated *galacto* and *arabino* derivatives occurs exlusively from one face of the carbohydrate. For all cerium(IV)-mediated reactions, methyl glycosides are formed as main products in 73−89% yield, which can be isolated in analytically pure form on a gram scale. The addition of malonates to tri-*O*-acetyl-D-glucal and tri-*O*-acetyl-D-galactal affords nitrates as side products. Strong evidence was found for a ligand transfer rather than electron transfer during the formation of these compounds, which sheds light on the mechanism of transition-metal-mediated radical reactions.

Experiments are currently in progress, to extend our methodology to other CH-acidic radical precursors and to trap intermediary cations by various nucleophiles. Furthermore, the addition of malonates to glycals should open up interesting prospects for the synthesis of *C*-disaccharides, since malonates and related CH-acidic substrates can be conveniently linked to the 1-position of various carbohydrates.[20,22]

Experimental Section

Solvents and commercially available chemicals were purified by standard methods or used as purchased. TLC was performed on aluminum sheets silica gel 60F$_{254}$ (Merck, Darmstadt). Silica gel (63−200 μm, Woelm, Erlangen) was used for column chromatography. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter; melting points were measured on a Büchi SMP 20 apparatus (uncorrected). IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. NMR spectra were recorded on either a Bruker AM 250 or DMX 600 with CDCl$_3$ as the solvent and internal standard. Combustion analyses were carried out at the Microanalytical Division of the Institute of Organic Chemistry, University of Giessen, Germany.

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3,4,6-Tri-*O*-acetyl-D-glucal (1a), 3,4,6-Tri-*O*-acetyl-D-galactal (1b), 3,4-Di-*O*-acetyl-D-xylal (1c), and 3,4-Di-*O*-acetyl-D-arabinal (1d). Compounds **1a−d** were prepared by the method described by Helferich.[13] D-galactal **1b** could not be crystallized from the crude product mixture and was therefore purified by column chromatography (petroleum ether/ethyl acetate 7:3 → 6:4) as well as D-xylal **1c** and D-arabinal **1d** (petroleum ether/ethyl acetate 6:4), which in the original procedure were purified by distillation.

General Procedure for Manganese(III)-Mediated Additions. A solution of glycal **1a** (1.36 g, 5.0 mmol), malonate **2** (50 mmol), and potassium acetate (1.75 g, 18 mmol) in acetic acid (20 mL) was heated to 90 °C under an argon atmosphere. At this temperature solid manganese(III) acetate dihydrate (2.68 g, 10 mmol, 2.0 equiv) was added, and stirring was continued until the dark brown color of the mixture changed to pale yellow. An additional amount of manganese(III) acetate dihydrate (2.68 g, 10 mmol, 2.0 equiv) was added until TLC showed complete conversion of the starting material. After cooling to room temperature, a diluted solution of sodium thiosulfate (300 mL) was added, and the mixture was extracted with dichloromethane (4 × 80 mL). The combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate (2 × 50 mL) and dried (Na$_2$SO$_4$), and the solvent was evaporated. The excess of malonate was removed at 0.01 mbar. The crude product was purified by column chromatography (petroleum ether/ethyl acetate).

General Procedure for Cerium(IV)-Mediated Additions. A solution of glycal **1a,b** (1.36 g, 5.0 mmol) or **1c,d** (1.00 g, 5.0 mmol) and malonate **2** (50 mmol) in methanol (10 mL) was cooled to 0 °C under an argon atmosphere. At this temperature a solution of ceric(IV) ammonium nitrate (3−6 equiv) in methanol (20−40 mL) was added dropwise over a period of 4−8 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$_2$SO$_4$) and concentrated, and the excess of malonate was removed at 0.01 mbar. The crude product was purified by column chromatography (petroleum ether/ethyl acetate).

Addition of Dimethyl Malonate (2a) to 3,4,6-Tri-*O*-acetyl-D-glucal (1a) in the Presence of Manganese(III) Acetate Dihydrate. Column chromatography (PE/EA 7:3 → 5:5) afforded 350 mg (15%) of *β-gluco*-**3a**, 1.18 g (51%) of a diastereomeric mixture of *gluco*-**3a** (α:β = 16: 84) and *manno*-**3a** (α:β = 71:29), and 140 mg (10%) of rearranged product **4** (α:β = 10:90). Crystallization of the diastereomeric mixture from ethanol gave the β-glucoside *β-gluco*-**3a** as colorless needles, mp 139−141 °C.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-α-D-glucopyranose (α-*gluco*-3a). TLC (petroleum ether/ethyl acetate 6:4) R_f 0.17. ^{1}H NMR δ 1.99, 2.02, 2.05, 2.07 (4s, 3 H each, OAc), 3.03 (ddd, J = 11.6, 7.0, 3.2 Hz, 1 H, 2-H), 3.43 (d, J = 7.0 Hz, 1 H, 7-H), 3.74, 3.75 (2s, 3 H each, OMe), 3.96−4.15 (m, 1 H, 5-H), 4.23−4.31 (m, 2 H, 6-H, 6′-H), 5.04 (t, J = 9.3 Hz, 1 H, 4-H), 5.51 (dd, J = 11.6, 9.3 Hz, 1 H, 3-H), 6.37 (d, J = 3.2 Hz, 1 H, 1-H). ^{13}C NMR δ 20.6, 20.7, 20.8, 21.0 (4q, OAc), 42.8 (d, C-2), 50.4 (d, C-7), 52.9, 53.1 (2q, OMe), 62.1 (t, C-6), 69.0, 69.8, 70.5 (3d, C-3, C-4, C-5), 91.5 (d, C-1), 167.4, 168.2, 168.3, 168.4, 169.7, 170.6 (6s, OAc, CO$_2$Me).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-β-D-glucopyranose (β-*gluco*-3a). [α]$^{20}_D$ = +9.5 (*c* 1.53, CHCl$_3$). TLC (petroleum ether/ethyl acetate 6:4) R_f 0.12. ^{1}H NMR δ 1.99, 2.02, 2.05, 2.07 (4s, 3 H each, OAc), 2.77 (ddd, J = 11.5, 9.2, 3.3 Hz, 1 H, 2-H), 3.52 (d, J = 3.3 Hz, 1 H, 7-H), 3.74, 3.75 (2s, 3 H each, OMe), 3.84 (ddd, J = 10.1, 4.3, 2.1 Hz, 1 H, 5-H), 4.05 (dd, J = 12.5, 2.1 Hz, 1 H, 6-H), 4.31 (dd, J = 12.5, 4.3 Hz, 1 H, 6′-H), 5.02 (dd, J = 10.0, 9.0 Hz, 1 H, 4-H), 5.33 (dd, J = 11.5, 9.0 Hz, 1 H, 3-H), 6.18 (d, J = 9.2 Hz, 1 H, 1-H). ^{13}C NMR δ 20.4, 20.5, 20.6, 20.7 (4q, OAc), 44.6 (d, C-2), 47.5 (d, C-7), 52.6, 52.7 (2q, OMe), 61.7 (t, C-6), 69.1, 70.9, 72.4 (3d, C-3, C-4, C-5), 91.9 (d, C-1), 167.4, 168.1, 168.2, 169.8, 169.9, 170.6 (6s, OAc, CO$_2$Me). IR (KBr) ν 3005, 2951, 1750, 1366, 1227. Anal. Calcd for C$_{19}$H$_{26}$O$_{13}$: C, 49.35; H, 5.67. Found: C, 49.39; H, 5.35.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-α-D-mannopyranose (α-*manno*-3a). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.14. ^{1}H NMR δ 2.02, 2.04, 2.05, 2.06 (4s, 3 H each,

OAc), 3.15 (ddd, $J = 10.0, 4.9, 2.3$ Hz, 1 H, 2-H), 3.72 (d, $J = 10.0$ Hz, 1 H, 7-H), 3.74, 3.75 (2s, 3 H each, OMe), 3.90 (ddd, $J = 9.8, 4.7, 2.5$ Hz, 1 H, 5-H), 4.08 (dd, $J = 12.4, 2.5$ Hz, 1 H, 6-H), 4.21 (dd, $J = 12.4, 4.7$ Hz, 1 H, 6′-H), 5.35 (t, $J = 9.5$ Hz, 1 H, 4-H), 5.49 (dd, $J = 9.5, 4.9$ Hz, 1 H, 3-H), 6.11 (d, $J = 2.3$ Hz, 1 H, 1-H). ^{13}C NMR δ 20.6, 20.7, 20.9, 21.0 (4q, OAc), 41.5 (d, C-2), 48.9 (d, C-7), 52.8, 52.9 (2q, OMe), 61.6 (t, C-6), 65.4, 69.3, 70.3 (3d, C-3, C-4, C-5), 90.9 (d, C-1), 167.7, 168.0, 168.1, 168.4, 169.7, 170.5 (6s, OAc, CO_2Me).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-*β*-D-mannopyranose (*β-manno*-3a). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.13. ^{1}H NMR δ 1.99, 2.02, 2.05, 2.07 (4s, 3 H each, OAc), 3.33 (ddd, $J = 11.0, 4.4, 3.0$ Hz, 1 H, 2-H), 3.68 (d, $J = 11.0$ Hz, 1 H, 7-H), 3.73, 3.75 (2s, 3 H each, OMe), 4.25−4.41 (m, 3 H, 5-H, 6-H, 6′-H), 5.18 (dd, $J = 6.6, 4.4$ Hz, 1 H, 3-H), 5.22 (dd, $J = 6.6, 6.1$ Hz, 1 H, 4-H), 6.04 (d, $J = 3.0$ Hz, 1 H, 1-H). ^{13}C NMR δ 20.6, 20.7, 20.8, 20.9 (4q, OAc), 41.8 (d, C-2), 48.0 (d, C-7), 52.8, 52.9 (2q, OMe), 62.5 (t, C-6), 65.3, 69.3, 69.6 (3d, C-3, C-4, C-5), 90.2 (d, C-1), 167.6, 168.0, 168.3, 168.4, 169.7, 170.5 (6s, OAc, CO_2Me).

1,4,6-Tri-*O*-acetyl-1,5-anhydro-2,3-dideoxy-*α*-D-*erythro*-hex-2-enitol (*α*-4). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.17. ^{1}H NMR δ 2.06, 2.07, 2.08 (3s, 3 H each, OAc), 4.00−4.40 (m, 3 H, 5-H, 6-H, 6′-H), 5.09−5.18 (m, 1 H, 4-H), 5.91 (ddd, $J = 10.6, 2.7, 0.9$ Hz, 1 H, 3-H), 6.12 (ddd, $J = 10.5, 4.3, 1.2$ Hz, 1 H, 2-H), 6.37 (dd, $J = 1.2, 0.8$ Hz, 1 H, 1-H). ^{13}C NMR δ 20.7, 20.9, 21.1(3q, OAc), 63.0 (d, C-5), 63.1 (t, C-6), 73.0 (d, C-4), 87.3 (d, C-1), 126.2, 128.2 (2d, C-2, C-3), 169.6, 170.1, 170.2 (3s, OAc).

1,4,6-Tri-*O*-acetyl-1,5-anhydro-2,3-dideoxy-*β*-D-*erythro*-hex-2-enitol (*β*-4). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.17. ^{1}H NMR δ 2.06, 2.07, 2.08 (3s, 3 H each, OAc), 4.08 (ddd, $J = 9.5, 4.6, 2.8$ Hz, 1 H, 5-H), 4.23 (ddd, $J = 12.3, 4.6, 1.7$ Hz , 2 H, 6′-H, 6-H), 5.35 (ddd, $J = 9.6, 3.3, 1.7$ Hz, 1 H, 4-H), 5.84 (ddd, $J = 10.2, 2.8, 2.0$ Hz, 1 H, 3-H), 6.02 (d, $J = 10.1$, 1 H, 2-H), 6.28 (dd, $J = 1.4, 1.2$ Hz, 1 H, 1-H). ^{13}C NMR δ 20.7, 21.0 (2q, OAc), 62.5 (t, C-6), 64.5 (d, C-5), 68.8 (d, C-4), 88.0 (d, C-1), 125.8, 130.5 (2d, C-2, C-3), 170.1, 170.7 (2s, OAc).

Addition of Diisopropyl Malonate (2b) to 3,4,6-Tri-*O*-acetyl-D-glucal (1a) in the presence of Manganese(III) Acetate Dihydrate. Column chromatography (PE/EA 7:3 → 5:5) afforded 82 mg (6%) of unreacted glucal **1a**, 302 mg (13%) of *β-gluco*-**3b**, 1.35 g (55%) of a diastereomeric mixture of *gluco*-**3b** (α:β = 18:82) and α-*manno*-**3b** in a 80:20 ratio, and 141 mg (11%) of rearranged product **4** (α:β = 7:93). Crystallization of the diastereomeric mixture from ethanol gave the *β*-glucoside *β-gluco*-**3b** as colorless needles, mp 161−162 °C.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-*α*-D-glucopyranose (*α-gluco*-3b). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.62. ^{1}H NMR δ 1.22−1.29 (m, 12 H, CO₂CH(CH_3)₂), 1.98, 2.02, 2.04, 2.05 (4s, 3 H each, OAc), 3.01 (ddd, $J = 11.3, 7.7, 3.3$ Hz, 1 H, 2-H), 3.33 (d, $J = 7.7$ Hz, 1 H, 7-H), 3.97−4.18 (m, 1 H, 5-H), 4.25−4.33 (m, 2 H, 6-H, 6′-H), 5.04 (t, $J = 9.3$ Hz, 1 H, 4-H), 4.96−5.12 (m, 2 H, CO₂CH(CH₃)₂), 5.50 (dd, $J = 11.6, 9.3$ Hz, 1 H, 3-H), 6.40 (d, $J = 3.3$ Hz, 1 H, 1-H). ^{13}C NMR δ 22.1, 22.2, 22.3, 22.4, 23.2, 23.3, 23.4, 23.5 (8q, OAc, CO₂CH(CH_3)₂), 42.8 (d, C-2), 50.4 (d, C-7), 62.1 (t, C-6), 70.9, 71.0 (2d, CO₂CH(CH₃)₂), 69.0, 69.8, 70.5 (3d, C-3, C-4, C-5), 91.5 (d, C-1), 167.6, 168.1, 168.2, 168.4, 169.7, 170.6 (6s, OAc, CO_2iPr).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-*β*-D-glucopyranose (*β-gluco*-3b). [α]$^{20}_D$ = + 22.6 (c 0.98, CHCl₃). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.61. ^{1}H NMR δ 1.23−1.27 (m, 12 H, CO₂CH(CH_3)₂), 1.99, 2.03, 2.05, 2.06 (4s, 3 H each, OAc), 2.76 (ddd, $J = 11.5, 9.2, 3.1$ Hz, 1 H, 2-H), 3.42 (d, $J = 3.1$ Hz, 1 H, 7-H), 3.83 (ddd, $J = 10.1, 4.5, 2.2$ Hz, 1 H, 5-H), 4.06 (dd, $J = 12.5, 2.2$ Hz, 1 H, 6-H), 4.32 (dd, $J = 12.5, 4.5$ Hz, 1 H, 6′-H), 5.02 (dd, $J = 10.1, 8.9$ Hz, 1 H, 4-H), 5.03−5.12 (m, 2 H, CO₂CH(CH₃)₂), 5.30 (dd, $J = 11.5, 8.9$ Hz, 1 H, 3-H), 6.19 (d, $J = 9.2$ Hz, 1 H, 1-H). ^{13}C NMR δ 22.1, 22.2, 22.3, 22.4, 23.2, 23.3, 23.4, 23.5 (8q, OAc, CO₂CH(CH_3)₂), 46.1, 50.1 (2d, C-2, C-7), 63.4 (t, C-6), 70.8, 70.9 (2d, CO₂CH(CH₃)₂), 71.2, 72.8, 74.2 (3d, C-3, C-4, C-5), 93.7 (d, C-1), 168.1, 168.9, 169.8, 171.3, 171.5, 172.3 (6s, OAc, CO_2iPr). IR (KBr) ν 3032, 2984, 1747, 1370, 1242. Anal. Calcd for C₂₃H₃₄O₁₃: C, 53.28; H, 6.60. Found: C, 53.24; H, 6.29.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-*α*-D-mannopyranose (*α-manno*-3b). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.59. ^{1}H NMR δ 1.19−1.28 (m, 12 H, CO₂CH(CH_3)₂), 2.01, 2.04, 2.05, 2.07 (4s, 3 H each, OAc), 3.13 (ddd, $J = 9.9, 5.0, 2.3$ Hz, 1 H, 2-H), 3.60 (d, $J = 9.7$ Hz, 1 H, 7-H), 3.97−4.18 (m, 1 H, 5-H), 4.25−4.33 (m, 2 H, 6-H, 6′-H), 4.96−5.12 (m, 2 H, CO₂CH(CH₃)₂), 5.35 (t, $J = 9.5$ Hz, 1 H, 4-H), 5.49 (dd, $J = 9.5, 5.0$ Hz, 1 H, 3-H), 6.11 (d, $J = 2.3$ Hz, 1 H, 1-H). ^{13}C NMR δ 20.6, 20.7, 20.8, 20.9 (4q, OAc), 23.2, 23.3, 23.4, 23.5 (4q, CO₂CH(CH_3)₂), 41.5, 48.9 (2d, C-2, C-7), 61.6 (t, C-6), 69.9, 70.0 (2d, CO₂CH(CH₃)₂), 65.4, 69.3, 70.3 (3d, C-3, C-4, C-5), 90.9 (d, C-1), 167.7, 168.0, 168.1, 168.4, 169.7, 170.5 (6s, OAc, CO_2iPr).

Addition of Dimethyl Malonate (2a) to 3,4,6-Tri-*O*-acetyl-D-glucal (1a) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 7:3 → 5:5) afforded 370 mg (16%) of *gluco*-**5a**, 1.35 g (62%) of *gluco*-**3a**, and 350 mg (16%) of *manno*-**3a** containing a small amount of *gluco*-**3a** as colorless oils. *Gluco*-**3a** could be crystallized from ethanol as colorless crystals, mp 100−101 °C.

Methyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-[(bis(methoxycarbonyl))methyl]-*β*-D-glucopyranoside (*gluco*-3a). [α]$^{20}_D$ = −6.9 (c 1.08, CHCl₃). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.45. ^{1}H NMR δ 1.98, 1.99, 2.06 (3s, 3 H each, OAc), 2.57 (ddd, $J = 11.6, 8.6, 3.6$ Hz, 1 H, 2-H), 3.45 (s, 3 H, OMe), 3.57 (d, $J = 3.6$ Hz, 1 H, 7-H), 3.69 (ddd, $J = 10.0, 4.6, 2.4$ Hz, 1 H, 5-H), 3.70, 3.73 (2s, 3 H each, CO₂Me), 4.10 (dd, $J = 12.2, 2.4$ Hz, 1 H, 6-H), 4.28 (dd, $J = 12.2, 4.6$ Hz, 1 H, 6′-H), 4.95 (d, $J = 8.6$ Hz, 1 H, 1-H), 4.98 (dd, $J = 10.0, 9.0$ Hz, 1 H, 4-H), 5.27 (dd, $J = 11.6, 9.0$ Hz, 1 H, 3-H). ^{13}C NMR δ 20.5, 20.6, 20.7 (3q, OAc), 46.3, 48.0 (2d, C-2, C-7), 52.4, 52.5 (2q, CO₂Me), 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 (5s, OAc, CO_2Me). IR (KBr) ν 3005, 2951, 1750, 1366, 1227. Anal. Calcd for C₁₈H₂₆O₁₂: 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*-3b). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.44. ^{1}H NMR δ 2.02, 2.08, 2.11 (3s, 3 H each, OAc), 3.02 (ddd, $J = 10.1, 4.6, 2.1$ Hz, 1 H, 2-H), 3.39 (s, 3 H, OMe), 3.67 (d, $J = 10.1$ Hz, 1 H, 7-H), 3.72, 3.76 (2s, 3 H each, CO₂Me), 3.92 (ddd, $J = 9.8, 5.6, 2.1$ Hz, 1 H, 5-H), 4.11 (dd, $J = 12.1, 2.1$ Hz, 1 H, 6′-H), 4.37 (dd, $J = 12.1, 5.6$ Hz, 1 H, 6-H), 4.68 (d, $J = 2.1$ Hz, 1 H, 1-H), 5.26 (dd, $J = 9.8, 9.2$ Hz, 1 H, 4-H), 5.46 (dd, $J = 9.2, 4.6$ Hz, 1 H, 3-H). ^{13}C NMR δ 20.3, 20.5, 20.6 (3q, OAc), 40.9, 48.9 (2d, C-2, C-7), 52.3, 52.4 (2q, CO₂Me), 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 (5s, OAc, CO_2Me).

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-1-*O*-nitro-*α*-D-glucose (*gluco*-5a). [α]$^{20}_D$ = +138.7 (c 0.86, CHCl₃). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.47. ^{1}H NMR δ 2.01, 2.03, 2.10 (3s, 3 H each, OAc), 3.09 (ddd, $J = 12.0, 6.1, 3.7$ Hz, 1 H, 2-H), 3.58 (d, $J = 6.1$ Hz, 1 H, 7-H), 3.76, 3.78 (2s, 3 H each, CO₂Me), 4.08 (dd, $J = 12.6, 2.2$ Hz, 1 H, 6-H), 4.17 (ddd, $J = 10.3, 4.0, 2.2$ Hz, 1 H, 5-H), 4.33 (dd, $J = 12.6, 4.0$ Hz, 1 H, 6′-H), 5.07 (dd, $J = 10.3, 9.3$ Hz, 1 H, 4-H), 5.45 (dd, $J = 12.0, 9.3$ Hz, 1 H, 3-H), 6.70 (d, $J = 3.7$ Hz, 1 H, 1-H). ^{13}C NMR δ 20.4, 20.5, 20.6 (3q, OAc), 42.1, 49.1 (2d, C-2, C-7), 53.0, 53.2 (2q, CO₂Me), 61.3 (t, C-6), 68.9, 69.4, 70.3 (3d, C-3, C-4, C-5), 97.3 (d, C-1), 167.2, 167.4, 169.5, 169.7, 170.5 (5s, OAc, CO_2Me). IR (CHCl₃) ν 3005, 2951, 1750, 1366, 1227. Anal. Calcd for C₁₇H₂₃NO₁₄: C, 43.88; H, 4.98; N, 3.01. Found: C, 44.12; H, 5.14; N, 2.79.

Addition of Diisopropyl Malonate (2b) to 3,4,6-Tri-*O*-acetyl-D-glucal (1a) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 7:3 → 5:5) afforded 331 mg (16%) of *gluco*-**5b** and 1.97 g (76%) of a diastereomeric mixture of compounds *gluco*-**3b** and *manno*-**3b** in a 89:11 ratio as colorless oils. Crystallization of the diastereomeric mixture from ethanol gave *gluco*-**3b** as colorless needles, mp 86−87 °C.

Methyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[bis(methylethoxycarbonyl))methyl]-*β*-D-glucopyranoside (*gluco*-3b). [α]$^{20}_D$ = −7.4 (c 0.99, CHCl₃). TLC (petroleum ether/ethyl acetate 6:4) R_f 0.46. ^{1}H NMR δ 1.19−1.29 (m, 12 H, 2 CO₂CH(CH_3)₂), 1.97, 2.00, 2.05 (3s, 3 H each, OAc), 2.52 (ddd, $J = 11.6, 8.6, 3.4$ Hz, 1 H, 2-H), 3.45 (d, $J = 3.4$ Hz, 1 H, 7-H), 3.47 (s, 3 H, OMe), 3.64 (ddd, $J = 10.0, 4.7, 2.4$ Hz,

1 H, 5-H), 4.05 (dd, *J* = 12.2, 2.4 Hz, 1 H, 6-H), 4.25 (dd, *J* = 12.2, 4.7 Hz, 1 H, 6′-H), 5.05 (d, *J* = 8.6 Hz, 1 H, 1-H), 4.94−5.11 (m, 3 H, 4-H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.18 (dd, *J* = 11.6, 9.0 Hz, 1 H, 3-H). ^{13}C NMR δ 22.2, 22.3, 22.4, 22.5, 23.0, 23.2, 23.4 (7q, OAc, CO$_2$CH-(*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, 2 CO$_2$*C*H(CH$_3$)$_2$), 103.6 (d, C-1), 168.9, 169.3, 171.4, 171.5, 172.4 (5s, OAc, *C*O$_2$iPr). IR (KBr) ν 2982, 2938, 1755, 1374, 1228. Anal. Calcd for C$_{22}$H$_{34}$O$_{12}$: C, 53.89; H, 6.98. 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*-3b). TLC (petroleum ether/ethyl acetate 6:4) *R$_f$* 0.48. ^{1}H NMR δ 1.19−1.29 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 1.97, 2.02, 2.03 (3s, 3 H each, OAc), 3.08 (ddd, *J* = 10.2, 4.8, 2.3 Hz, 1 H, 2-H), 3.36 (s, 3 H, OMe), 3.46 (d, *J* = 10.2 Hz, 1 H, 7-H), 4.04 (ddd, *J* = 10.4, 5.6, 3.1 Hz, 1 H, 5-H), 4.12 (dd, *J* = 12.0, 5.6 Hz, 1 H, 6′-H), 4.26 (dd, *J* = 12.0, 3.1 Hz, 1 H, 6-H), 4.72 (d, *J* = 2.3 Hz, 1 H, 1-H), 4.94−5.11 (m, 3 H, 4-H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.45 (dd, *J* = 8.7, 4.8 Hz, 1 H, 3-H). ^{13}C NMR δ 20.7, 20.8, 20.9, 21.0, 21.3, 21.4, 21.5 (7q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 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 CO$_2$*C*H(CH$_3$)$_2$), 99.5 (d, C-1), 166.3, 166.5, 169.4, 169.6, 170.5 (5s, OAc, *C*O$_2$iPr).

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*C*-[bis(methylethoxycarbonyl))methyl]-1-*O*-nitro-α-D-glucose (*gluco*-5b). [α]$^{20}_D$ = +110.4 (*c* 1.00, CHCl$_3$). TLC (petroleum ether/ethyl acetate 6:4) *R$_f$* 0.54. ^{1}H NMR δ 1.18−1.27 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 1.98, 2.01, 2.09 (3s, 3 H each, OAc), 3.06 (ddd, *J* = 11.9, 6.7, 3.7 Hz, 1 H, 2-H), 3.47 (d, *J* = 6.7 Hz, 1 H, 7-H), 4.06 (dd, *J* = 12.5, 2.2 Hz, 1 H, 6-H), 4.14 (ddd, *J* = 10.0, 4.0, 2.2 Hz, 1 H, 5-H), 4.31 (dd, *J* = 12.5, 4.0 Hz, 1 H, 6′-H), 4.94−5.10 (m, 3 H, 4-H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.40 (dd, *J* = 11.9, 9.5 Hz, 1 H, 3-H), 6.75 (d, *J* = 3.7 Hz, 1 H, 1-H). ^{13}C NMR δ 20.7, 20.8, 20.9, 21.0, 21.1, 21.3, 21.8 (7q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 42.1, 50.6 (2d, C-2, C-7), 61.8 (t, C-6), 65.3, 65.4 (2d, CO$_2$*C*H(CH$_3$)$_2$), 69.4, 70.3, 70.7 (3d, C-3, C-4, C-5), 98.0 (d, C-1), 166.7, 167.2, 169.4, 169.8, 170.8 (5s, OAc, *C*O$_2$iPr). IR (Film) ν 2985, 2934, 1748, 1670, 1374, 1233. Anal. Calcd for C$_{21}$H$_{31}$NO$_{14}$: C, 48.36; H, 5.99; N, 2.68. Found: C, 48.27; H, 5.86; N, 2.59.

Addition of Dimethyl Malonate (2a) to 3,4,6-Tri-*O*-acetyl-D-galactal (1b) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 7:3 → 5:5) afforded 1.73 g (79%) of *galacto*-3a and 312 mg (16%) of *galacto*-5a as colorless oils.

Methyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-β-D-galactopyranoside (*galacto*-3a). [α]$^{20}_D$ = −4.4 (*c* 1.17, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.46. ^{1}H NMR δ 1.98, 2.02, 2.11 (3s, 3 H each, OAc), 2.80 (ddd, *J* = 12.3, 8.8, 3.7 Hz, 1 H, 2-H), 3.47 (s, 3 H, OMe), 3.66 (d, *J* = 3.7 Hz, 1 H, 7-H), 3.71, 3.72 (2s, 3 H each, CO$_2$Me), 3.87 (ddd, *J* = 7.3, 6.6, 1.0 Hz, 1 H, 5-H), 4.12 (dd, *J* = 11.2, 7.3 Hz, 1 H, 6-H), 4.17 (dd, *J* = 11.2, 6.6 Hz, 1 H, 6′-H), 4.85 (d, *J* = 8.8 Hz, 1 H, 1-H), 5.12 (dd, *J* = 12.3, 3.2 Hz, 1 H, 3-H), 5.27 (dd, *J* = 3.2, 1.0 Hz, 1 H, 4-H). ^{13}C NMR δ 22.1, 22.3, 22.4 (3q, OAc), 43.5, 49.2 (2d, C-2, C-7), 54.0, 54.1 (2q, CO$_2$*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 (5s, OAc, *C*O$_2$Me). IR (CCl4) ν 3038, 2955, 1748, 1437, 1244. Anal. Calcd for C$_{18}$H$_{26}$O$_{12}$: C, 49.77; H, 6.03. Found: C, 49.50; H, 6.04.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-1-*O*-nitro-α-D-galactose (*galacto*-5a). [α]$^{20}_D$ = +58.7 (*c* 1.00, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.51. ^{1}H NMR δ 1.98, 2.02, 2.12 (3s, 3 H each, OAc), 3.27 (ddd, *J* = 12.5, 6.5, 3.8 Hz, 1 H, 2-H), 3.55 (d, *J* = 6.5 Hz, 1 H, 7-H), 3.72, 3.74 (2s, 3 H each, CO$_2$Me), 3.80 (ddd, *J* = 7.5, 6.4, 1.1 Hz, 1 H, 5-H), 4.08 (dd, *J* = 11.2, 6.4 Hz, 1 H, 6-H), 4.17 (dd, *J* = 11.2, 7.5 Hz, 1 H, 6′-H), 5.28 (dd, *J* = 12.5, 3.2 Hz, 1 H, 3-H), 5.42 (dd, *J* = 3.2, 1.1 Hz, 1 H, 4-H), 6.70 (d, *J* = 3.8 Hz, 1 H, 1-H). ^{13}C NMR δ 22.1, 22.2, 22.4 (3q, OAc), 39.0, 50.2 (2d, C-2, C-7), 54.5, 54.8 (2q, CO$_2$*Me*), 62.9 (t, C-6), 67.6, 69.0, 70.6 (3d, C-3, C-4, C-5), 99.8 (d, C-1), 169.1, 169.4, 170.9, 171.6, 172.1 (5s, OAc, *C*O$_2$Me). IR (CCl4) ν 2958, 1748, 1659, 1437, 1229.

Addition of Diisopropyl Malonate (2b) to 3,4,6-Tri-*O*-acetyl-D-galactal (1b) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 7:3 → 6:4) afforded 2.22 g of a 79:21 mixture of *galacto*-3b (73%) and *galacto*-5b (17%) as a

colorless oil. Crystallization from petroleum ether/ethyl acetate gave *galacto*-3b as colorless needles, mp 109−110 °C.

Methyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-[bis(methylethoxycarbonyl))methyl]-β-D-galactopyranoside (*galacto*-3b). [α]$^{20}_D$ = −17.3 (*c* 1.24, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.30. ^{1}H NMR δ 1.20−1.31 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 1.96, 2.04, 2.13 (3s, 3 H each, OAc), 2.82 (ddd, *J* = 12.3, 8.8, 3.5 Hz, 1 H, 2-H), 3.48 (s, 3 H, OMe), 3.60 (d, *J* = 3.5 Hz, 1 H, 7-H), 3.87 (ddd, *J* = 7.0, 6.5, 1.0 Hz, 1 H, 5-H), 4.13 (dd, *J* = 11.2, 7.0 Hz, 1 H, 6-H), 4.18 (dd, *J* = 11.2, 6.5 Hz, 1 H, 6′-H), 4.83 (d, *J* = 8.8 Hz, 1 H, 1-H), 5.05 (dddd, *J* = 18.9, 12.6, 6.4, 2.2 Hz, 2 H, CO$_2$C*H*(CH$_3$)$_2$), 5.17 (dd, *J* = 12.3, 3.1 Hz, 1 H, 3-H), 5.31 (dd, *J* = 3.1, 1.0 Hz, 1 H, 4-H). ^{13}C NMR δ 20.8, 21.1, 21.8, 21.9, 22.0, 22.0, 22.1 (7q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 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, CO$_2$*C*H(CH$_3$)$_2$), 102.6 (d, C-1), 168.0, 168.1, 170.0, 170.7, 170.9 (5s, OAc, *C*O$_2$iPr). IR (KBr) ν 2985, 2938, 1732, 1664, 1467, 1376. Anal. Calcd for C$_{22}$H$_{34}$O$_{12}$: C, 53.89; H, 6.98. Found: C, 53.88; H, 7.09.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-1-*O*-nitro-α-D-galactose (*galacto*-5b). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.31. ^{1}H NMR δ 1.20−1.31 (m, 12 H, 2CO$_2$CH-(C*H$_3$*)$_2$), 1.96, 2.03, 2.14 (3s, 3 H each, OAc), 3.30 (ddd, *J* = 12.0, 6.1, 3.7 Hz, 1 H, 2-H), 3.44 (d, *J* = 6.1 Hz, 1 H, 7-H), 4.07−4.14 (m, 3 H, 5-H; 6-H; 6′-H), 5.05 (dddd, *J* = 18.9, 12.5, 6.4, 2.5 Hz, 2 H, 2CO$_2$C*H*(CH$_3$)$_2$), 5.32 (dd, *J* = 12.5, 2.9 Hz, 1 H, 3-H), 5.44 (dd, *J* = 2.9, 1.0 Hz, 1 H, 4-H), 6.74 (d, *J* = 3.7 Hz, 1 H, 1-H). ^{13}C NMR δ 20.8, 20.9, 21.0, 21.8, 21.9, 22.0, 22.1 (7q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 37.3, 50.1 (2d, C-2, C-7), 61.7 (t, C-6), 66.4, 68.1, 69.7, 70.0, 70.6 (5d, C-3, C-4, C-5, 2 CO$_2$*C*H(CH$_3$)$_2$), 98.9 (d, C-1), 166.9, 167.1, 169.7, 170.4, 170.7 (5s, OAc, *C*O$_2$iPr). IR (CCl4) ν 2991, 2933, 1750, 1662, 1452, 1233.

Addition of Dimethyl Malonate (2a) to 3,4-Di-*O*-acetyl-D-xylal (1c) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 7:3 → 6:4) afforded 1.12 g of pure β-*xylo*-3a (61%), 75 mg of α-*lyxo*-3a with traces of β-*xylo*-3a (4%), and 443 mg of a mixture of β-*xylo*-3a, α-*lyxo*-3a, and α-*xylo*-3a in a 65:17:18 (16%, 4%, 4%) ratio as colorless oils.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-β-xylopyranoside (β-*xylo*-3a). [α]$^{20}_D$ = −24.4 (*c* 0.90, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.55. ^{1}H NMR δ 2.02, 2.03 (2s, 3 H each, OAc), 2.52 (ddd, *J* = 10.8, 7.8, 4.5 Hz, 1 H, 2-H), 3.38 (dd, *J* = 11.8, 9.0 Hz, 1H, 5-H), 3.42 (s, 3 H, OMe), 3.59 (d, *J* = 4.5 Hz, 1 H, 6-H), 3.72, 3.74 (2s, 3 H each, CO$_2$Me), 4.08 (dd, *J* = 11.8, 5.3 Hz, 1 H, 5′-H), 4.86 (d, *J* = 7.8 Hz, 1 H, 1-H), 4.89 (ddd, *J* = 9.0, 8.3, 5.3 Hz, 1 H, 4-H), 5.22 (dd, *J* = 10.8, 8.3 Hz, 1 H, 3-H). ^{13}C NMR δ 21.0, 21.2 (2q, OAc), 45.8, 48.8 (2d, C-2, C-6), 52.8, 52.9 (2q, CO$_2$Me), 57.5 (q, OMe), 62.7 (t, C-5), 70.8, 70.9 (2d, C-3, C-4), 102.0 (d, C-1), 168.7, 168.9, 170.3, 170.5 (4s, OAc, *C*O$_2$Me). IR (CHCl$_3$) ν 3038, 3015, 2955, 1754, 1437, 1371, 1160, 1048. Anal. Calcd for C$_{15}$H$_{22}$O$_{10}$: C, 49.72; H, 6.12. Found: C, 49.44; H, 6.22.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-D-lyxopyranoside (α-*lyxo*-3a). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.39. ^{1}H NMR δ 2.05, 2.11 (2s, 3 H each, OAc), 2.96 (ddd, *J* = 9.3, 7.1, 3.5 Hz, 1 H, 2-H), 3.42 (s, 3 H, OMe), 3.50 (d, *J* = 9.3 Hz, 1 H, 6-H), 3.72, 3.74 (2s, 3 H each, CO$_2$Me), 3.84 (dd, *J* = 12.6, 2.2 Hz, 1 H, 5-H), 3.90 (dd, *J* = 12.6, 3.3 Hz, 1 H, 5′-H), 4.59 (d, *J* = 7.1 Hz, 1 H, 1-H), 4.79 (ddd, *J* = 5.0, 3.3, 2.2 Hz, 1 H, 4-H), 5.31 (dd, *J* = 5.0, 3.5 Hz, 1 H, 3-H). ^{13}C NMR δ 20.7, 21.0 (2q, OAc), 41.4, 50.0 (2d, C-2, C-6), 52.6, 52.8 (2q, CO$_2$Me), 56.7 (q, OMe), 62.6 (t, C-5), 66.8, 69.2 (2d, C-3, C-4), 100.7 (d, C-1), 166.2, 167.1, 167.9, 168.2 (4s, OAc, *C*O$_2$Me).

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-α-D-xylopyranoside (α-*xylo*-3a). TLC (petroleum ether/ethyl acetate 5:5) *R$_f$* 0.56. ^{1}H NMR δ 1.96, 1.99 (2s, 3 H each, OAc), 2.74 (ddd, *J* = 10.9, 6.4, 3.0 Hz, 1 H, 2-H), 3.27 (s, 3 H, OMe), 3.51 (d, *J* = 6.4 Hz, 1 H, 6-H), 3.60−3.63 (m, 1 H, 5-H), 3.72, 3.74 (2s, 3 H each, CO$_2$Me), 4.20−4.22 (m, 1 H, 5′-H), 4.96 (d, *J* = 3.0 Hz, 1 H, 1-H), 5.39−5.41 (m, 1 H, 4-H), 5.46 (dd, *J* = 10.9, 9.3 Hz, 1 H, 3-H). ^{13}C NMR δ 20.9, 21.0 (2q, OAc), 43.9, 50.0 (2d, C-2, C-6), 52.7, 52.8 (2q, CO$_2$Me), 55.3 (q, OMe), 58.9 (t, C-5), 66.9, 69.5 (2d, C-3, C-4), 98.8 (d, C-1), 167.9, 168.2, 169.8, 170.1 (4s, OAc, *C*O$_2$Me).

Addition of Diisopropyl Malonate (2b) to 3,4-Di-*O*-acetyl-D-xylal (1c) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 8.5:1.5 → 7:3) afforded 1.19 g of pure β-*xylo*-**3b** (57%), 142 mg of α-*lyxo*-**3b** with traces of α-*xylo*-**3b** (7%), and 469 mg of a mixture of β-*xylo*-**3b**, α-*lyxo*-**3b**, and α-*xylo*-**3b** in a 65:17:18 (16%, 4%, 2%) ratio as colorless oils.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-β-D-xylopyranoside (β-*xylo*-3b). [α]$^{20}_D$ = −23.3 (*c* 0.98, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.72. ^{1}H NMR δ 1.20−1.27 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 2.01, 2.03 (2s, 3 H each, OAc), 2.51 (ddd, *J* = 10.4, 7.6, 4.7 Hz, 1 H, 2-H), 3.40 (s, 3 H, OMe), 3.48 (d, *J* = 4.7 Hz, 1 H, 6-H), 4.07 (dd, *J* = 11.6, 5.2 Hz, 1 H, 5-H), 4.88 (ddd, *J* = 9.0, 8.3, 5.2 Hz, 1 H, 4-H), 4.92 (d, *J* = 7.6, 1 H, 1-H), 4.99−5.08 (m, 2 H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.02 (dd, *J* = 11.6, 9.0 Hz, 1 H, 5′-H), 5.16 (dd, *J* = 10.4, 8.3 Hz, 1 H, 3-H). ^{13}C NMR δ 21.1, 21.2, 21.3, 21.8, 22.0, 22.1 (6q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 45.3, 49.7 (2d, C-2, C-6), 57.2 (q, OMe), 62.4 (t, C-5), 69.5, 69.8, 70.6, 70.9 (4d, C-3, C-4, 2 CO$_2$*C*H(CH$_3$)$_2$), 102.1 (d, C-1), 167.7, 168.0, 170.1, 170.5 (4s, OAc, *CO$_2$iPr). IR (CHCl$_3$) ν 3023, 2985, 2938, 1744, 1457, 1375, 1232, 1209, 1102, 1051. Anal. Calcd for C$_{19}$H$_{30}$O$_{10}$: C, 54.54; H, 7.23. Found: C, 54.61; H, 7.24.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[bis(methylethoxycarbonyl))methyl-α-D-lyxopyranoside (α-*lyxo*-3b). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.69. ^{1}H NMR δ 1.20−1.26 (m, 12 H, 2CO$_2$CH(C*H$_3$*)$_2$), 2.04, 2.10 (2s, 3 H each, OAc), 2.94 (ddd, *J* = 7.0, 5.8, 3.4 Hz, 1 H, 2-H), 3.39 (d, *J* = 5.8 Hz, 1 H, 6-H), 3.40 (s, 3 H, OMe), 3.82 (dd, *J* = 12.6, 3.0 Hz, 1 H, 5-H), 3.88 (ddd, *J* = 12.6, 3.8 Hz, 1 H, 5′-H), 4.61 (d, *J* = 7.0, 1 H, 1-H), 4.80 (ddd, J = 9.0, 3.8, 3.0 Hz, 1 H, 4-H), 4.99−5.09 (m, 2 H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.34 (dd, *J* = 9.0, 3.4 Hz, 1 H, 3-H). ^{13}C NMR δ 20.6, 20.9, 21.1, 21.3, 21.4, 21.5 (6q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 40.9, 50.7 (2d, C-2, C-6), 56.3 (q, OMe), 62.4 (t, C-5), 66.0, 69.0, 69.2, 69.3 (4d, C-3, C-4, 2CO$_2$*C*H(CH$_3$)$_2$), 100.7 (d, C-1), 167.0, 167.2, 169.0, 169.7 (4s, OAc, *CO$_2$iPr).

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[bis(methylethoxycarbonyl))methyl]-α-D-xylopyranoside (α-*xylo*-3b). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.72. ^{1}H NMR δ 1.20−1.27 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 1.95, 1.98 (2s, 3 H each, OAc), 2.72 (ddd, *J* = 11.1, 6.9, 3.2 Hz, 1 H, 2-H), 3.26 (s, 3 H, OMe), 3.51 (d, *J* = 6.9 Hz, 1 H, 6-H), 3.60 (dd, *J* = 12.2, 9.1 Hz, 1 H, 5-H), 4.86 (d, *J* = 3.2 Hz, 1 H, 1-H), 4.99−5.08 (m, 3 H, 4-H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.12 (dd, *J* = 12.2, 6.0 Hz, 1 H, 5′-H), 5.46 (dd, *J* = 11.1, 9.5 Hz, 1 H, 3-H). ^{13}C NMR δ 20.7, 20.8, 21.5, 21.6, 21.8, 22.0 (6q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 43.5, 51.2 (2d, C-2, C-6), 55.0 (q, OMe), 58.9 (t, C-5), 69.2, 69.6, 70.3, 70.6 (4d, C-3, C-4, 2 CO$_2$*C*H(CH$_3$)$_2$), 100.0 (d, C-1), 167.0, 167.4, 169.5, 170.1 (4s, OAc, *CO$_2$iPr).

Addition of Dimethyl Malonate (2a) to 3,4-Di-*O*-acetyl-D-arabinal (1d) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 7:3 → 6:4) afforded 1.13 g of pure α-*arabino*-**3a** (61%) and 503 mg of a mixture of α-*arabino*-**3a** and β-ara*bino*-**3a** in a 75:25 (21%, 7%) ratio as colorless oils. Crystallization from ethanol gave α-*arabino*-**3a** as colorless needles, mp 99−100 °C.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-α-D-arabinopyranoside (α-*arabino*-3a). [α]$^{20}_D$ = −1.5 (*c* 1.03, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.50. ^{1}H NMR δ 1.97, 2.12 (2s, 3 H each, OAc), 2.84 (ddd, *J* = 11.9, 8.6, 3.9 Hz, 1 H, 2-H), 3.45 (s, 3 H, 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, 3 H each, CO$_2$Me), 4.01 (dd, *J* = 13.2, 2.0 Hz, 1 H, 5′-H), 4.73 (d, *J* = 8.6 Hz, 1 H, 1-H), 5.13 (dd,

J = 11.9, 3.3 Hz, 1 H, 3-H), 5.17 (ddd, *J* = 13.3, 2.0, 1.1 Hz, 1 H, 4-H). ^{13}C NMR δ 20.9, 21.4 (2q, OAc), 42.7, 48.2 (2d, C-2, C-6), 52.8, 52.9 (2q, CO$_2$*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 (4s, OAc, *CO$_2$Me). IR (CHCl$_3$) ν 3012, 2965, 2848, 1750, 1439, 1374, 1298, 1236, 1132, 1093. Anal. Calcd for C$_{15}$H$_{22}$O$_{10}$: C, 49.72; H, 6.12. Found: C, 49.48; H, 6.02.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methoxycarbonyl))methyl]-β-D-arabinopyranoside (β-*arabino*-3a). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.52. ^{1}H NMR δ 1.95, 2.13 (2s, 3 H each, OAc), 3.08 (ddd, *J* = 11.9, 6.0, 3.2 Hz, 1 H, 2-H), 3.41 (s, 3 H, OMe), 3.68−3.70 (m, 1 H, 5-H), 3.72, 3.77 (2s, 3 H each, CO$_2$Me), 3.84 (d, *J* = 6.0 Hz, 1 H, 6-H), 4.01−4.04 (m, 1 H, 5′-H), 4.90 (ddd, *J* = 10.8, 5.3, 3.0 Hz, 1 H, 4-H), 5.04 (d, *J* = 3.2 Hz, 1 H, 1-H), 5.35 (dd, *J* = 11.9, 3.0 Hz, 1 H, 3-H). ^{13}C NMR δ 20.6, 20.8 (2q, OAc), 39.5, 49.7 (2d, C-2, C-6), 52.6, 52.7 (2q, CO$_2$*Me*), 56.4 (q, OMe), 60.6 (t, C-5), 65.3, 67.9 (2d, C-3, C-4), 99.4 (d, C-1), 168.2, 168.8, 169.8, 170.0 (4s, OAc, *CO$_2$Me).

Addition of Diisopropyl Malonate (2b) to 3,4-Di-*O*-acetyl-D-arabinal (1d) in the Presence of Ceric(IV) Ammonium Nitrate. Column chromatography (hexane/ethyl acetate 6:4) afforded 1.18 g of pure α-*arabino*-**3b** (56%) and 644 mg of a mixture of α-*arabino*-**3b** and β-*arabino*-**3b** in a 77:23 (24%, 7%) ratio as colorless oils.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-α-D-arabinopyranoside (α-*arabino*-3b). [α]$^{20}_D$ = −11.1 (*c* 0.98, CHCl$_3$). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.68. ^{1}H NMR δ 1.20−1.27 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 1.97, 2.12 (2s, 3 H each, OAc), 2.85 (ddd, *J* = 11.9, 8.6, 3.7 Hz, 1 H, 2-H), 3.46 (s, 3 H, OMe), 3.59 (d, *J* = 3.7 Hz, 1 H, 6-H), 3.64 (dd, *J* = 13.4, 1.0 Hz, 1 H, 5-H), 4.01 (dd, *J* = 13.4, 1.8 Hz, 1 H, 5′-H), 4.71 (d, *J* = 8.6, 1 H, 1-H), 5.00−5.08 (m, 2 H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.14 (dd, *J* = 11.9, 3.3 Hz, 1 H, 3-H), 5.18 (ddd, *J* = 3.3, 1.8, 1.0 Hz, 1 H, 4-H). ^{13}C NMR δ 20.8, 21.3, 21.6, 21.8, 21.9, 22.0 (6q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 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, 2 CO$_2$*C*H(CH$_3$)$_2$), 102.7 (d, C-1), 168.0, 168.1, 170.0, 170.8 (4s, OAc, *CO$_2$CH(CH$_3$)$_2$). IR (CHCl$_3$) ν 3031, 2984, 2938, 1746, 1459, 1376, 1234, 1181, 1103, 1023. Anal. Calcd for C$_{19}$H$_{30}$O$_{10}$: C, 54.54; H, 7.23. Found: C, 54.78; H, 7.39.

Methyl-3,4-di-*O*-acetyl-2-deoxy-2-*C*-[(bis(methylethoxycarbonyl))methyl]-β-D-arabinopyranoside (β-*arabino*-3b). TLC (petroleum ether/ethyl acetate 5:5) R_f 0.70. ^{1}H NMR δ 1.22−1.30 (m, 12 H, 2 CO$_2$CH(C*H$_3$*)$_2$), 1.94, 2.12 (2s, 3 H each, OAc), 3.09 (ddd, *J* = 12.0, 6.1, 3.0 Hz, 1 H, 2-H), 3.30 (s, 3 H, OMe), 3.38 (d, *J* = 6.1 Hz, 1 H, 6-H), 3.93 (dd, *J* = 12.8, 2.0 Hz, 1 H, 5-H), 5.02−5.09 (m, 3 H, 5′-H, 2 CO$_2$C*H*(CH$_3$)$_2$), 5.26−5.28 (m, 1 H, 4-H), 5.29 (d, *J* = 3.0 Hz, 1 H, 1-H), 5.40 (dd, *J* = 12.0, 3.2 Hz, 1 H, 3-H). ^{13}C NMR δ 20.3, 20.4, 21.2, 21.3, 21.4, 21.5 (6q, OAc, CO$_2$CH(*CH$_3$*)$_2$), 39.0, 50.1 (2d, C-2, C-6), 55.0 (q, OMe), 60.5 (t, C-5), 67.6, 68.0, 68.9, 69.0 (4d, C-3, C-4, 2CO$_2$*C*H(CH$_3$)$_2$), 99.7 (d, C-1), 167.1, 167.3, 169.4, 169.6 (4s, OAc, *CO$_2$CH(CH$_3$)$_2$).