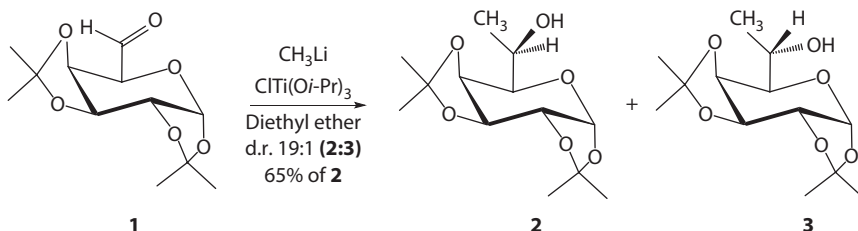


# 31 Stereoselective Synthesis of 7-Deoxy-1,2;3,4-di-O-isopropylidene-D-glycero- $\alpha$ -D-galactohexopyranose

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The addition of organometallic reagents to 1,2,3,4-di-*O*-isopropylidene- $\alpha$ -D-*galacto*-1,6-dialdo-hexopyranose **1** provides higher-carbon heptopyranoses that have been used in the synthesis of sialoside probes for neuraminidase inhibition,<sup>1,2</sup> immunologically relevant disaccharides,<sup>3</sup> substrates for glycosidases used in kinetic resolution,<sup>4</sup> trisaccharides used to assess monoclonal antibody binding,<sup>5</sup> and other targets containing chain-extended sugars.<sup>6</sup> The addition of methylmagnesium halides to **1**, as well as the addition of methyllithium and methylmanganese halides,<sup>7</sup> gives mixtures of the  $\alpha$ -D-*glycero* **2** and  $\beta$ -L-*glycero* **3** diastereomers. An extensive study by Tolsitkov and coworkers revealed very high diastereoselectivity for the addition of methylmanganese iodide to **1** to give a 97:3 ratio in favor of the  $\beta$ -L-*glycero* isomer **3**.<sup>7</sup> In spite of the variety of conditions that have been examined, a highly stereoselective route to **2** based on the addition of an organometallic reagent to **1** has not been achieved. Methylation conditions typically favor the formation of **3**, which is predicted on the basis of chelation control involving metal binding with the aldehyde and ring oxygens and alkylation from the less hindered side of the carbonyl group.<sup>7</sup> The highest ratios of **2**:**3** are only on the order of 2.5:1 to 3:1 and have been achieved using methylmagnesium chloride or methyllithium in diethyl ether. Herein, we wish to report a highly stereoselective synthesis of **2** using methyl(triisopropoxy)titanium<sup>8</sup> CH<sub>3</sub>Ti(Oi-Pr)<sub>3</sub> as the methylating agent.

Our choice of methyl(triisopropoxy)titanium<sup>9</sup> was based on our previous work<sup>10</sup> on the addition of organometallic reagents to pentodialdo-1,4-furanoses, in which we observed high Felkin–Anh stereoselectivity when methyl(triisopropoxy)titanium<sup>9</sup>

**TABLE 31.1**  
**Comparison of <sup>1</sup>H NMR Data of **2** with Data Reported for **2** and **3****

Compound <b>3</b> <sup>5</sup>	Compound <b>2</b> <sup>5</sup>	Compound <b>2</b> (This Work, Method b)
$\delta$ 5.58 (d, 1H, $J=4.6$ Hz, H-1)	$\delta$ 5.55 (d, 1H, $J=5$ Hz, H-1)	5.56 (d, 1H, $J=5.1$ Hz, H-1)
$\delta$ 4.59 (dd, 1H, $J=8.0, 2.1$ Hz, H-3)	$\delta$ 4.62 (dd, 1H, $J=8.0, 2.2$ Hz, H-3)	4.62 (dd, 1H, $J=7.8, 2.4$ Hz, H-3)
$\delta$ 4.32 (dd, 1H, H-2)	$\delta$ 4.30 (dd, 1H, H-2)	4.32 (dd, 1H, $J=4.8, 2.4$ Hz, H-2)
$\delta$ 4.26 (dd, 1H, $J=2.0$ Hz, H-4)	$\delta$ 4.46 (dd, 1H, $J=2.0$ Hz, H-4)	4.47 (dd, 1H, $J=7.5, 2.4$ Hz, H-4)
$\delta$ 3.99 (m, 1H, H-6)	$\delta$ 3.96 (m, 1H, H-6)	3.97 (m, 1H, H-6)
$\delta$ 3.48 (dd, 1H, $J=6.8$ Hz, H-5)	$\delta$ 3.50 (dd, 1H, $J=7.2$ Hz, H-5)	3.51 (dd, 1H, $J=7.5, 1.8$ Hz, H-5)
$\delta$ 1.50 (CH <sub>3</sub> , singlet)	$\delta$ 1.51 (CH <sub>3</sub> , singlet)	$\delta$ 1.52 (CH <sub>3</sub> , singlet)
$\delta$ 1.44 (CH <sub>3</sub> , singlet)	$\delta$ 1.45 (CH <sub>3</sub> , singlet)	$\delta$ 1.47 (CH <sub>3</sub> , singlet)
$\delta$ 1.32 (CH <sub>3</sub> , singlet)	$\delta$ 1.36 (CH <sub>3</sub> , singlet)	$\delta$ 1.36 (CH <sub>3</sub> , singlet)
	$\delta$ 1.32 (overlap with $\delta$ 1.29)	$\delta$ 1.33 (CH <sub>3</sub> , singlet)
$\delta$ 1.26 (d, 3H, $J=6$ Hz, C-7)	$\delta$ 1.29 (overlap with $\delta$ 1.32)	1.31 (d, 3H, $J=6.3$ Hz, C-7) 2.29 (d, 1H, $J=6.0$ Hz, OH)

Source: Lemieux, R.U. et al., *Can. J. Chem.*, 60, 81–86, 1982.

was used. The conversion, as described in the section “Experimental Methods,” gave **2** in a ratio of approximately 19:1, as determined by integration of the C-6 hydroxyl group proton at 2.34 and 2.73 ppm, respectively, in the  $^1\text{H}$  Nuclear Magnetic Resonance (NMR) spectrum of the crude product. Unchanged aldehyde **1** (~5%) was also present.

Pure, title compound **2** was isolated by flash chromatography and its isomeric identity and purity were proven by x-ray analysis of the crystalline *p*-bromobenzoate **4**. As noted by Lemieux,<sup>5</sup> many of the proton chemical shifts for **2** and **3** are nearly identical; however, the H-4 resonances are sufficiently resolved in spectra of the two diastereomers<sup>5</sup> ( $\delta$  4.47 in **2** and  $\delta$  4.26 in **3**, Table 31.1). A comparison of  $^1\text{H}$  NMR data of **2** with those reported previously<sup>5</sup> for **2** and **3** is given in Table 31.1, which proves that the identity of the material described here is consistent with that reported by Lemieux and coworkers.<sup>5</sup> Nevertheless, we cannot explain the difference in the  $[\alpha]_{\text{D}}$  values found for the two materials synthesized independently. Herein, we describe a gram-scale, stereoselective synthesis of the title compound **2** and further illustrate the Felkin–Anh (nonchelation) selectivity in reactions of dialdopyranose sugars with methyl(triisopropoxy)titanium.

## EXPERIMENTAL METHODS

### GENERAL METHODS

Chlorotitanium triisopropoxide, 97% (CAS number 20717-86-6), was purchased from Strem Chemicals and stored in a nitrogen glove box at room temperature. All other reagents were purchased from Sigma-Aldrich, including anhydrous diethyl ether and anhydrous dichloromethane (Sure/Seal™). Thin-layer chromatography (TLC) was performed on aluminum-backed silica gel 60 F<sub>254</sub> plates (Merck KGaA 64271 Darmstadt). Visualization of spots was facilitated by dipping the TLC plates in Hanessian’s stain [3 g Ce(SO<sub>4</sub>)<sub>2</sub>, 10 g (NH<sub>4</sub>)Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O, H<sub>2</sub>O, 450 mL, conc. H<sub>2</sub>SO<sub>4</sub>, 50 mL] followed by heating with a heat gun. Column chromatography was performed on silica gel 60 Å (Fluka, 40–63  $\mu\text{m}$  particle size). NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer in CDCl<sub>3</sub>.  $^1\text{H}$  and  $^{13}\text{C}$  spectra (300 and 75 MHz, respectively) were referenced to Tetra Methyl Silane (TMS) ( $\delta$ =0.0 ppm) and CDCl<sub>3</sub> ( $\delta$ =76.9 ppm). Signal-nuclei assignments were confirmed using Distortion less Enhancement by polarization Transfer (DEPT) and 2D experiments. Optical rotations were measured at 23°C using Perkin–Elmer 241 and Jasco p-2000 polarimeters.

### 7-Deoxy-1,2;3,4-di-*O*-isopropylidene-*D*-glycero- $\alpha$ -*D*-galacto-heptopyranose (**2**)

#### Method A

In a nitrogen glove box, chlorotitanium triisopropoxide (23.3 g, 89.4 mmol, ~6 equiv.)\* was added to a Schlenk flask equipped with a Teflon plug and a magnetic stir bar. The Schlenk flask was fitted with a rubber septum and removed from the

\* An excess of chlorotitanium triisopropoxide and methylolithium over the 6 equivalents of each may be needed for the methylation of **1** to go to completion.

glove box. The Schlenk flask was then connected to a Schlenk line, and argon was introduced into the flask. Anhydrous diethyl ether (55 mL) was dispensed into the flask using a syringe. The mixture was stirred at room temperature until the solids dissolved, then chilled to  $-50^{\circ}\text{C}$  (dry ice/acetone bath). Under an argon counterflow, the septum was replaced with a dropping funnel (itself capped with a septum). Methylolithium (57 mL of 1.6 M methylolithium in diethyl ether, 91 mmol,  $\sim 6$  equiv.) was added to the dropping funnel via cannula transfer. Methylolithium was added dropwise at a rate that the temperature of the cooling bath did not rise above  $-50^{\circ}\text{C}$ . When the addition was complete, the light yellow reaction mixture was stirred for 1 h (the reaction warmed to  $-25^{\circ}\text{C}$  during this time) and a white precipitate formed. Under an argon counterflow, the dropping funnel was removed and replaced with a stopper. While maintaining the cooling bath at  $-25^{\circ}\text{C}$ , diethyl ether was removed *in vacuo* (using the Schlenk line, with a liquid nitrogen-cooled trap to collect the solvent). When the solvent was removed, methyl(triisopropoxy)titanium thus formed was kept under argon, and the flask's stopper was replaced with a septum.

Methyl(triisopropoxy)titanium was suspended in anhydrous dichloromethane (35 mL), and the Schlenk flask was placed in a dry ice/acetone bath ( $-78^{\circ}\text{C}$ ). A solution of 1,2;3,4-di-*O*-isopropylidene- $\alpha$ -D-galacto-1,6-dialdo-hexopyranose **1** (3.8 g, 14.7 mmol),\* prepared by TEMPO/BAIB oxidation,<sup>11</sup> in anhydrous dichloromethane (15 mL) was added dropwise via a syringe while maintaining the cooling bath at  $-78^{\circ}\text{C}$ . The cooling bath was left in place to allow the temperature to rise slowly over a period of 22 h under argon (a needle was affixed to an argon balloon and was inserted through the septum of the Schlenk flask in order to avoid pressure buildup). The temperature of the bath at this point had reached  $-5^{\circ}\text{C}$ . In order to quench the reaction, a few drops of water were added slowly with stirring to the reaction mixture. Once vigorous effervescence subsided, additional water (95 mL) was added, followed by diethyl ether (200 mL). The entire mixture (including the solids formed) was transferred into an Erlenmeyer flask (500 mL) equipped with a large stirring bar and the mixture was stirred vigorously for 10 min. After filtration, the solids were washed with diethyl ether (125 mL), the filtrate was transferred into a separatory funnel, the layers were separated, and the aqueous phase was washed with diethyl ether ( $2 \times 25$  mL). Combined organic extracts were washed successively with  $\text{H}_2\text{O}$  (50 mL) and saturated NaCl solution (20 mL), dried ( $\text{MgSO}_4$ ), and filtered through a pad of silica gel. The silica gel was rinsed with additional diethyl ether (100 mL) and the filtrate was concentrated to yield crude **2** as a light yellow oil. Chromatography (1:1 ethyl acetate/hexanes) yielded 2.63 g of **2** as a colorless oil (65.1%). Small amounts of impurities were evident in the NMR spectrum, but the material produced correct analytical figures.

$[\alpha]_{\text{D}} = -37.8$  ( $c$  0.4,  $\text{CHCl}_3$ ), lit.  $[\alpha]_{\text{D}}^{\dagger} = -34.8$  ( $c$  0.3,  $\text{CHCl}_3$ ), for nearly pure substance.

\* Aldehyde **1** is unstable and it should be prepared freshly before use. See also reference 12.

<sup>†</sup> The optical rotation for **2** reported by Lemieux and coworkers<sup>5</sup> is for a white solid, mp  $57$ – $58^{\circ}\text{C}$ , that was obtained by a sequence consisting of benzylation of **2** and debenzoylation of the benzoate **4**. Gateau-Olesker and coworkers<sup>13</sup> independently synthesized **2** and obtained it in a non crystalline form.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.31 (d, 3H,  $J_{7,6}=6.3$  Hz, (C-7)  $\text{H}_3$ ), 1.33, 1.36, 1.47, 1.52 (4s, 12H, 4  $\times$  isopropylidene  $\text{CH}_3$ ), 2.29 (d, 1H,  $J_{\text{OH},6}=6.0$  Hz, OH), 3.51 (dd, 1H,  $J_{5,6}=7.5$  Hz,  $J_{5,4}=1.8$  Hz, H-5), 3.96 (m, 1H, H-6), 4.32 (dd, 1H,  $J_{2,1}=5.4$  Hz,  $J_{2,3}=2.4$  Hz, H-2), 4.47 (dd, 1H,  $J_{4,3}=8.1$  Hz,  $J_{4,5}=2.4$  Hz, H-4), 4.62 (dd, 1H,  $J_{3,4}=7.8$  Hz,  $J_{3,2}=2.4$  Hz, H-3), 5.56 (d, 1H,  $J_{1,2}=5.1$  Hz, H-1).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  109.2, 108.5 (quaternary C of isopropylidene), 96.4 (C-1), 71.2 (C-5), 70.7 (C-4), 70.6 (C-3), 70.4 (C-2), 66.4 (C-6), 25.9, 25.9, 24.9, 24.4 (4  $\times$  isopropylidene  $\text{CH}_3$ ), 20.3 (C-7)

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_6$ : C, 56.92; H, 8.08. Found: C, 57.19; H, 8.29.

### Method B

The 4-bromobenzoate **4** (0.98 g, 2.1 mmol) was dissolved in anhydrous methanol (10 mL). Sodium methoxide solution (0.26 g, 25 wt% in methanol) was added, and the solution was stirred at room temperature. TLC analysis (1:1 ethyl acetate: hexanes) indicated the presence of some starting material; therefore, additional 0.23 g of sodium methoxide solution (overall 0.49 g, 25 wt% in methanol, 2.3 mmol, 1.1 equiv.) was added and the reaction was stirred overnight. After 12 h, all starting material was consumed and the reaction mixture had turned yellow. The mixture was neutralized by adding, in small portions, Dowex 50WX8-200 ( $\text{H}^+$ ), until neutral pH was achieved. The mixture was filtered and the filtrate was concentrated to yield a solid residue containing 4-bromomethyl benzoate as the major impurity. Chromatography (2:3 ethyl acetate/hexanes) yielded 0.54 g (91.5%) of **2** as colorless oil, which was dried overnight in a vacuum oven at  $50^\circ\text{C}$ .

$[\alpha]_{\text{D}} = -66.9$  ( $c$ , 0.3,  $\text{CHCl}_3$ ), lit.  $[\eta]^*$   $[\alpha]_{\text{D}} = -34.8$  ( $c$  0.3,  $\text{CHCl}_3$ ), for nearly pure substance.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.31 (d, 3H,  $J_{7,6}=6.3$  Hz, (C-7)  $\text{H}_3$ ), 1.33, 1.36, 1.47, 1.52 (4s, 12H, 4  $\times$  isopropylidene  $\text{CH}_3$ ), 2.29 (d, 1H,  $J_{\text{OH},6}=6.0$  Hz, OH), 3.51 (dd, 1H,  $J_{5,6}=7.5$  Hz,  $J_{5,4}=1.8$  Hz, H-5), 3.97 (m, 1H, H-6), 4.32 (dd, 1H,  $J_{2,1}=4.8$  Hz,  $J_{2,3}=2.4$  Hz, H-2), 4.47 (dd, 1H,  $J_{4,3}=7.5$  Hz,  $J_{4,5}=2.4$  Hz, H-4), 4.62 (dd, 1H,  $J_{3,4}=7.8$  Hz,  $J_{3,2}=2.4$  Hz, H-3), 5.56 (d, 1H,  $J_{1,2}=5.1$  Hz, H-1).

$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  109.3, 108.5 (quaternary C of isopropylidene), 96.4 (C-1), 71.0 (C-5), 70.8 (C-4), 70.6 (C-3), 70.4 (C-2), 66.9 (C-6), 25.9, 25.9, 24.9, 24.4 (4  $\times$  isopropylidene  $\text{CH}_3$ ), 20.3 (C-7).

$^1\text{H NMR}$  spectra of compound **2** prepared by method A (top spectrum) and method B (bottom spectrum) as well as the  $^{13}\text{C NMR}$  spectrum for **2** prepared by method B are provided.

### 6-O-(4-Bromobenzoyl)-7-deoxy-1,2;3,4-di-O-isopropylidene-D-glycero- $\alpha$ -D-galacto-heptopyranose (**4**)

To a solution of **2** (2.63 g, 9.58 mmol) in anhydrous pyridine (80 mL) was added 4-bromobenzoyl chloride (3.16 g, 14.4 mmol, 1.5 equiv.). The reaction was stirred at room temperature overnight. TLC analysis indicated majority of the starting

\* The optical rotation for **2** reported by Lemieux and coworkers<sup>5</sup> is for a white solid, mp  $57\text{--}58^\circ\text{C}$ , that was obtained by a sequence consisting of benzylation of **2** and debenzoylation of the benzoate **4**. Gateau-Olesker and coworkers<sup>12</sup> independently synthesized **2** and obtained it in a noncrystalline form.

material was consumed (1:1 Ethyl acetate/hexanes). Excess pyridine was removed under reduced pressure to yield white solids. Hexanes (10 mL) were added to the solids and, after brief manual swirling, the mixture was filtered through a medium-porosity sintered glass funnel. Solids remaining in the flask were combined with the bulk in the funnel using nine additional portions of hexanes (10 mL, 100 mL of hexane overall), rubbing the combined solids with hexanes after addition of each portion, and the combined filtrates were concentrated. If more solids appeared in the filtrate, the filtration was repeated (to remove any solid). Concentration of the clear solution yielded 2.6 g of a yellow oil. Crystallization from methanol (15 mL) gave 1.27 g of a white solid,  $[\alpha]_D = -68.7$  ( $c$  0.3,  $\text{CHCl}_3$ ); mp 93.5°C–95.5°C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.26 (s, 3H, isopropylidene  $\text{CH}_3$ ), 1.34 (s, 3H, isopropylidene  $\text{CH}_3$ ), 1.43 (s, 3H, isopropylidene  $\text{CH}_3$ ), 1.44 (d, 3H,  $J=6.3$  Hz, (C-7) $\text{H}_3$ ), 1.53 (s, 3H, isopropylidene  $\text{CH}_3$ ), 3.86 (dd, 1H,  $J=7.5$  Hz, 1.8 Hz, H-5), 4.33 (m, 2H, H-2, H-4), 4.61 (dd, 1H,  $J=8.1$  Hz, 2.4 Hz, H-3), 5.24 (dq, 1H,  $J=7.5$  Hz, 6.3 Hz, H-6), 5.56 (d, 1H,  $J=5.1$  Hz, H-1), 7.57 (d, 1H,  $J=8.1$  Hz, aromatic), 7.89 (d, 1H,  $J=8.1$  Hz, aromatic).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  164.7 (ester carbonyl), 131.7, 131.1, 129.4, 128.0 (aromatic), 109.5, 108.7 (quaternary C of isopropylidene), 96.4 (C-1), 70.7 (C-2), 70.7 (C-3), 70.6 (C-4), 70.1 (C-6), 69.8 (C-5), 26.1, 26.0, 24.9, 24.4 (4 $\times$  isopropylidene  $\text{CH}_3$ ), 17.0 (C-7).

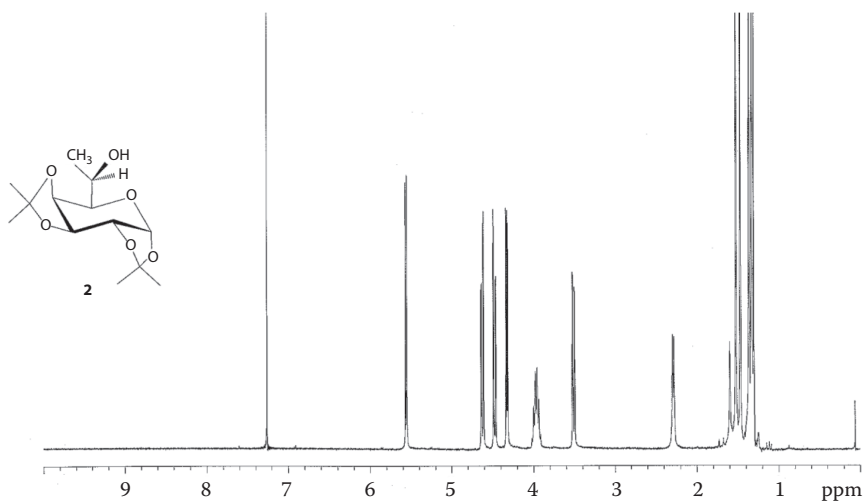
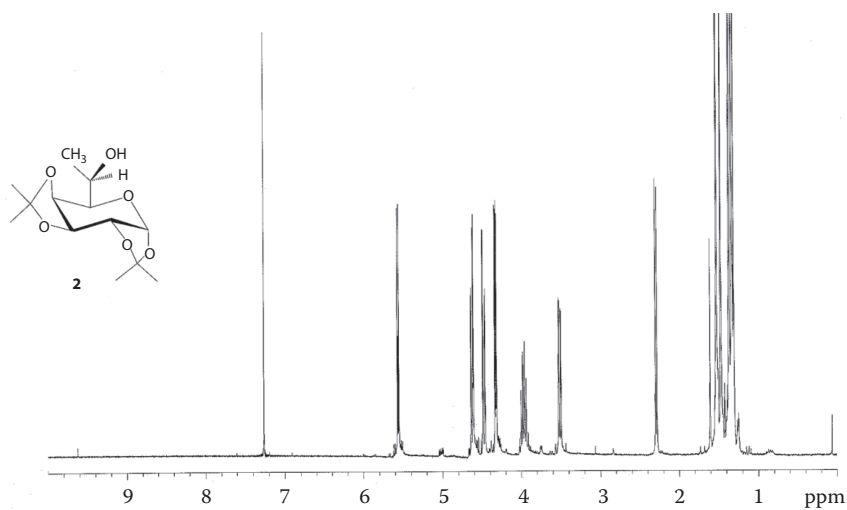
*Anal.* Calcd for  $\text{C}_{20}\text{H}_{25}\text{BrO}_7$ : C, 52.53; H, 5.51; Br, 17.47. Found: C, 52.43; H, 5.36; Br, 17.39.

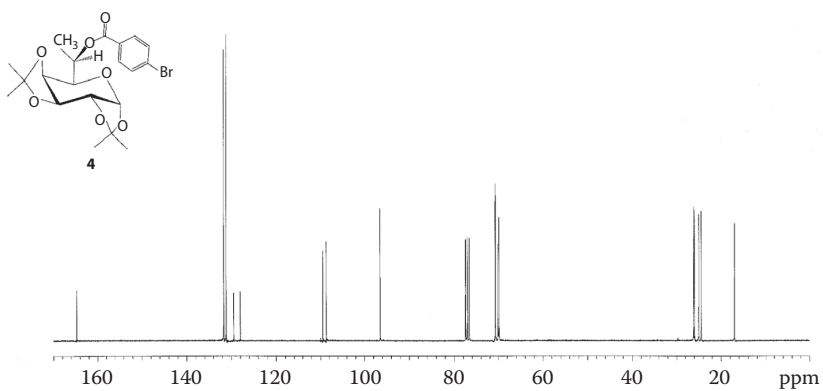
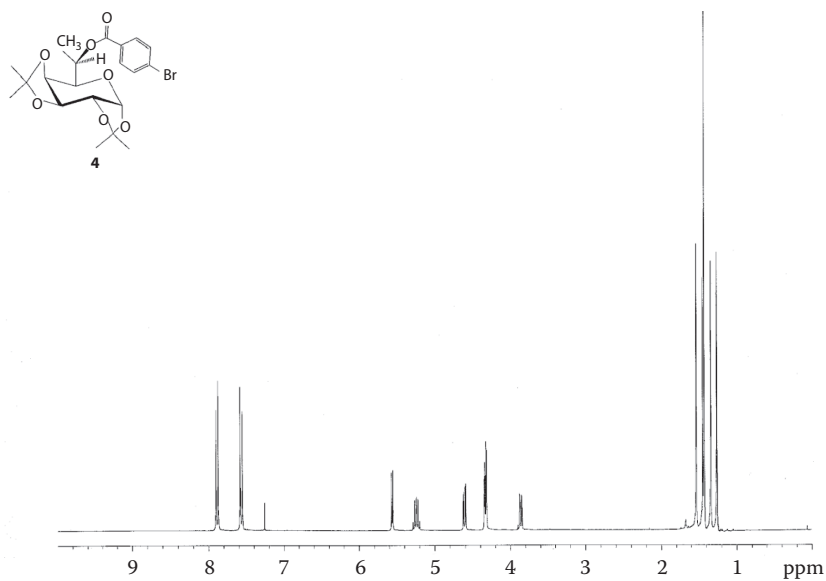
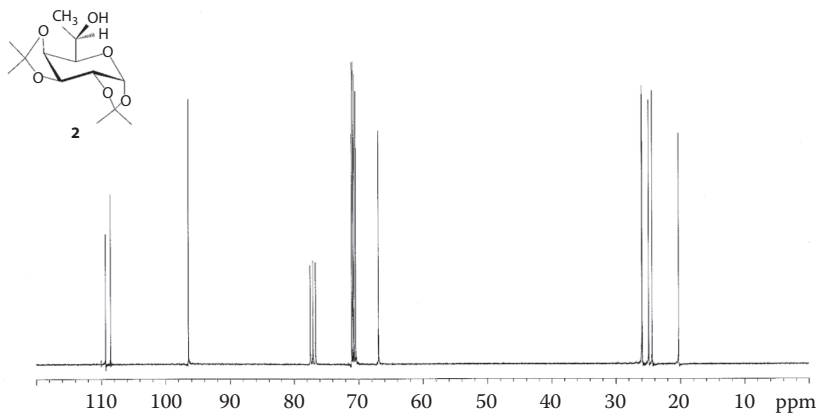
### X-Ray Structural Analysis

A single colorless shard ( $0.15 \times 0.17 \times 0.24$  mm<sup>3</sup>) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Bruker-AXS Kappa APEX II CCD diffractometer with  $0.71073$  Å Mo-K $\alpha$  radiation. Unit cell parameters were obtained from 60 data frames,  $0.5^\circ$   $\phi$ , from three different sections of the Ewald sphere yielding  $a=13.3815(10)$ ,  $b=19.0003(14)$ ,  $c=25.1987(19)$  Å,  $V=6406.8(8)$  Å<sup>3</sup>. 141,249 reflections ( $R_{int}=0.0838$ ) were collected (14,146 unique) over  $\theta=1.342^\circ$ – $27.122^\circ$ . The systematic absences in the data were consistent with the noncentrosymmetric, orthorhombic space group  $P2_12_12_1$ . The data set was treated with SADABS absorption corrections based on redundant multiscan data (Sheldrick, G. Bruker-AXS, 2012);  $T_{max}/T_{min}=1.12$ . The asymmetric unit contains three independent molecules yielding  $Z'=3$  and  $Z=12$ . All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions with methyl groups allowed to rotate freely. To confirm the absolute structure, the data were passed through one round of refinement as a racemic twin with the twin ratio parameter allowed to refine freely; this parameter corresponds to the Flack  $x$  parameter and refined to 0.004(5), which confirms that the correct absolute configuration was identified and that the crystal is enantiomerically pure. The goodness of fit on  $F^2$  was 1.021 with  $R_1=0.0326$  (for  $I > 2\sigma(I)$ ) and  $wR_2=0.0618$  (all data). The largest difference peak and hole are 0.0287 and  $-0.372$  e/Å<sup>3</sup>.

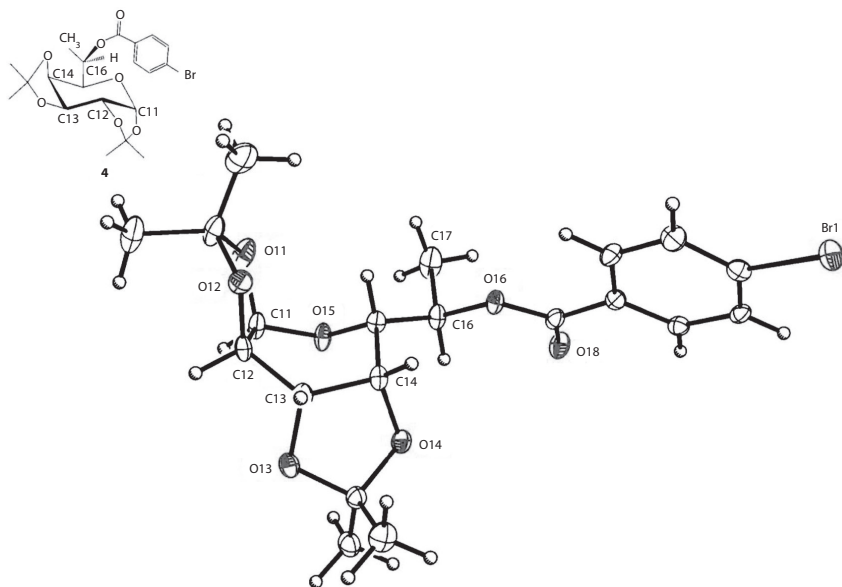
**ACKNOWLEDGMENTS**

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