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Syntheses of β-D-Gal*f*-(1→6)-β-D-Gal*f*-(1→5)-D-Gal*f* and β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-D-Gal*f*, Trisaccharide Units in the Galactan of *Mycobacterium tuberculosis*

Lucía Gandolfi-Donadío, Carola Gallo-Rodriguez, and Rosa M. de Lederkremer*

CIHIDECAR, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina

lederk@qo.fcen.uba.ar

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The galactofuran is a crucial constituent of the cell wall of mycobacteria. An efficient synthesis of the two trisaccharide units of the galactan is described. The strategy relies on the use of substituted D-galactono-1,4-lactones as precursors for the internal and the reducing galactofuranoses. Dec-9-enyl β-D-Gal*f*-(1→6)-β-D-Gal*f*-(1→5)-β-D-Gal*f* (**2**) and dec-9-enyl β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-β-D-Gal*f* (**9**) so far reported as convenient substrates for the galactofuranosyl transferase, and possibly useful for immunological studies, were obtained by the trichloroacetimidate method of glycosylation.

Introduction

Mycobacterial diseases such as tuberculosis and leprosy have reemerged in the last years because of the appearance of multi-drug-resistant strains of *Mycobacterium* and the relation of tuberculosis with AIDS.[1] New approaches for the treatment of tuberculosis are needed. Integrity of the mycobacterial cell wall is essential for viability of mycobacteria,[2] and thus, it is a good target for the development of antimycobacterial drugs.

The cell wall of *Mycobacterium tuberculosis* is composed of an outer lipidic layer of mycolic acid linked via an arabinogalactan (AG) to the inner layer of peptidoglycan.[3] Particularly interesting is the AG with both component sugars, arabinose (Ara) and galactose (Gal), present in the furanose configuration. This structural feature offers an ideal approach for developing an anti-TB drug. Galactose, although abundant in nature, is only present in the pyranose configuration in mammals, and thus, the oligosaccharide biosynthesis would not be affected by a drug interfering with biosynthesis of the galactan in mycobacteria. At least two enzymes are necessary for the construction of a galactofuranosyl linkage in microorganisms. The *E. coli* enzyme UDP-galactopyranose mutase,[4] which converts UDP-Gal*p* into UDP-Gal*f*, was recently crystallized, and its structure has been determined.[5] This activity was also demonstrated in *Klebsiella* sp.[6] and mycobacteria.[7] A bifunctional UDP-galactofuranose transferase responsible for the construction of β-D-Gal*f*-(1→5)-D-Gal*f* and β-D-Gal*f*-(1→6)-D-Gal*f* linkages in *M. tuberculosis* was recently identified.[8] The synthetic dec-9-enyl glycosides of the disaccharides, β-D-Gal*f*-(1→5)-β-D-Gal*f*-*O*-$C_{10:1}$ and β-D-Gal*f*-(1→6)-β-D-Gal*f*-*O*-$C_{10:1}$, were used as acceptors. The trisaccharides resulting from the enzymatic reaction were characterized after permethylation and fast atom bombardment mass spectrometry.

Several methods have been described for the synthesis of glycosides of galactofuranose disaccharides.[9−15]

The synthesis of oligosaccharide units of the *M. tuberculosis* AG is a topic of increasing interest.[16−18]

In the present paper, we describe the first chemical

* To whom correspondence should be addressed. Fax: 5411-4576-3352.

(1) (a) World Health Organization. In *Anti-tuberculosis Drug Resistance in the World;* The WHO/IUATLD Global Project on Anti-tuberculosis Resistance Surveillance. WHO (Publication WHO/TB/97.229): Geneva, Switzerland, 1997. (b) Butler, D. *Nature* **2000**, *406*, 670.

(2) Pan, F.; Jackson, M.; Ma, Y., McNeil, M. *J. Bacteriol.* **2001**, *183*, 3991.

(3) Crick, D. C.; Mahaprata, S.; Brennan, P. J. *Glycobiology* **2001**, *11*, 107.

(4) Nassau, P. M.; Martín, S. L.; Brown, R. E.; Weston, A.; Monsey, D.; MacNeil, M.; Duncan, K. *J. Bacteriol.* **1996**, *178*, 1047.

(5) Sanders, D. A. R.; Staines, A. G.; MacMahon, S. A.; MacNeil, M. R.; Whitfield, C.; Naismith, J. H. *Nature Struct. Biol.* **2001**, *8*, 858.

(6) Koplin, R.; Brisson, J. R.; Whitfield, C. *J. Biol. Chem.* **1997**, *272*, 4121.

(7) Weston, A.; Stern, R. J.; Lee, R. E.; Nassau, P. M.; Monsey, D.; Martin, S. L.; Scherman, M. S.; Besra, G. S.; Duncan, K.; McNeil, M. R. *Tuber. Lung. Dis.* **1997**, *78*, 123.

(8) Kremer, L.; Dover: L. G.; Morehouse, C.; Hitchin, P.; Everett, M.; Morris, H. R.; Dell, A.; Brennan, J.; MacNeil, M. R.; Flaherty, C.; Duncan, K.; Besra, G. S. *J. Biol. Chem.* **2001,** *276*, 26430.

(9) Veeneman, G. H.; Notermans, S.; Hoogerhout, P.; van Boom, J. H. *Trav. Chim. Pays-Bas* **1989**, *108*, 344.

(10) Marino, C.; Varela, O.; de Lederkremer, R. M. *Carbohydr. Res.* **1989**, *190*, 65.

(11) de Lederkremer, R. M.; Marino, C.; Varela, O. *Carbohydr. Res.* **1990**, *200*, 227.

(12) Velty, R.; Benvegnu, T.; Gelin, M.; Privat, E.; Plusquellec, D. *Carbohydr. Res.* **1997**, *299*, 7.

(13) Choudhury, A. K.; Roy, N. *Carbohydr. Res.* **1998**, *308*, 207.

(14) McAuliffe, J. C.; Hindsgaul, O. *J. Org. Chem.* **1997**, *62*, 1234.

(15) Gallo-Rodriguez, C.; Gandolfi, L.; de Lederkremer, R. M. *Org. Lett.* **1999**, *1*, 245.

(16) Gurjar, M. K.; Reddy, L. K.; Hotha, S. *J. Org. Chem.* **2001**, *66*, 4657.

(17) Yin, H.; D'Souza, F. W.; Lowary, T. L. *J. Org. Chem.* **2002**, *67*, 892.

(18) Pathak, A. K.; Pathak, V.; Seitz, L.; Maddry, J. A.; Gurcha, S. S.; Besra, G. S.; Suling, W. J.; Reynolds, R. C. *Bioorg. Med. Chem.* **2001**, *9*, 3129.

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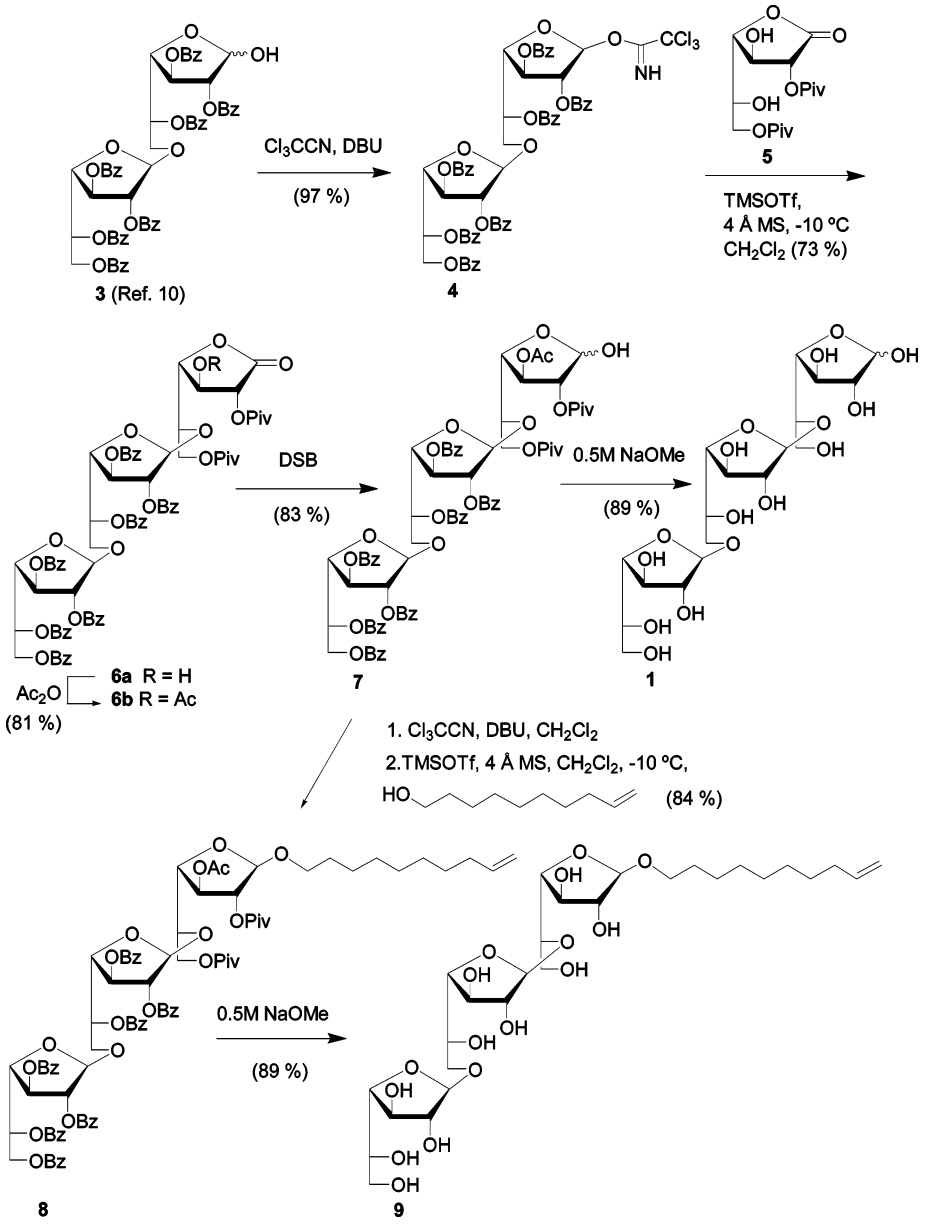
SCHEME 1



synthesis of β-D-Gal*f*-(1→6)-β-D-Gal*f*-(1→5)-D-Gal*f* (**1**) and the decenyl glycosides of **1** and of β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-β-D-Gal*f* (**2**). The oligosaccharides will be useful for studies on the biosynthesis of the galactan and of the Ara*f* attachment to the galactan in *M. tuberculosis* and its inhibition. In addition, the dec-9-enyl spacer provides a good intermediate for coupling to other molecules or solid matrixes in order to investigate the immunological properties of the trisaccharides.

Results and Discussion

The synthetic strategy utilized commercially available D-galactono-1,4-lactone as a template for the internal galactofuranose ring. This approach was recently used for the synthesis of a trisaccharide containing an internal Gal*f*, present in glycoinositolphospholipids of *Leishmania*.[19] The lactone, besides being a stable precursor for the reducing sugar, is selectively substituted by acylation reactions.[20] The disaccharide moieties Gal*f*-(β1→5)-Gal*f*[11] and Gal*f*-(β1→6)-Gal*f*[10] have been previously synthesized in our laboratory. Synthesis of trisaccharide **1** was performed according to Scheme 1 from disaccharide derivative **3**.[10] Tin(IV) chloride-promoted glycosylation of 2,3,5-tri-*O*-benzoyl-6-*O*-trityl-D-galactono-1,4-lactone with penta-*O*-benzoyl-α,β-D-galactofuranose, followed by diisoamylborane (DSB) reduction of the glycosyl lactone derivative, afforded **3** in 75% yield. It is worth noting that the two condensing residues were obtained crystalline in one step from inexpensive commercially available materials.[10]

The advantage of this strategy relies on the straightforward synthesis of the disaccharide precursor, with the free anomeric OH, suited for activation as the trichloro-

(19) Gandolfi-Donadio, L.; Gallo-Rodriguez, C.; de Lederkremer, R. M. *J. Org. Chem.* **2002**, *67*, 4430.
(20) Gallo, C.; Jeroncic, L.; Varela, O.; de Lederkremer, R. M. *J. Carbohydr. Chem.* **1993**, *12*, 841.

TABLE 1. ^{1}H NMR (500 MHz, $CDCl_3$) Chemical Shifts for Compounds 6a,b, 8, 10, 11, 15, and 17

		δ (ppm), J (Hz)						
compd		H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{5,6b}$)	H-6b ($J_{6a,6b}$)
6a	Gal-one		5.38	4.75	4.31	4.61	4.39	4.38
			(8.6)	(8.0)	(3.4)	(3.7)	(8.4)	nd
	Gal*f*′	5.60	5.52	5.69	4.75	5.87	4.19	4.09
			(1.3)	(4.5)	nd	(5.9)	(6.1)	(11.2)
	Gal*f*″	5.42	5.39	5.58	5.80	6.08	4.75	4.75
			(1.4)	(5.1)	(3.2)	nd	nd	nd
6b	Gal-one		5.57	5.69	4.48	4.14	4.37	4.35
			(8.0)	(7.8)	(3.1)	(6.1)	(5.9)	(11.8)
	Gal*f*′	5.54	5.48	5.75	4.76	5.91	4.25	3.97
			(1.1)	(3.5)	(5.2)	(4.7)	(6.8)	(11.2)
	Gal*f*″	5.37	5.35	5.53	4.83	6.10	4.74−4.75	4.74−4.75
			(1.5)	(5.0)	(3.4)	(5.7)	(5.7)	nd
8	Gal*f*	4.93	5.06	5.24	4.22−4.26	4.22−4.26	4.38	4.29
		(0.9)	(2.5)	(6.2)	nd	(4.2)	(6.5)	(11.7)
	Gal*f*′	5.59	5.54	5.66	4.81	5.98	4.21	4.08
			(1.4)	(4.6)	(4.2)	(3.7)	(7.5)	(11.4)
	Gal*f*″	5.38	5.37	5.57	4.79	6.06	4.74−4.75	4.74−4.75
			(1.4)	(5.0)	(3.4)	(5.7)	(5.7)	nd
10	Gal-one		5.44	4.55	4.34	4.17	4.39	4.36
			(8.5)	(7.9)	(3.3)	(6.1)	(6.1)	(11.6)
	Gal*f*′	5.59	5.49	5.64	4.74	5.99	4.82−4.83	4.82−4.83
		-	(1.0)	(4.7)	(3.1)	(4.9)	(4.9)	nd
11	Gal-one		5.60	5.72	4.52	4.18	4.40	4.37
			(8.0)	(7.8)	(3.1)	(6.1)	(5.8)	(12.0)
	Gal*f*′	5.60	5.53	5.72	4.85	6.09	4.76	4.69
		-	(1.3)	(4.0)	(3.8)	(3.5)	(7.6)	(12.2)
15	Gal-one		6.10	5.80	5.04	5.76	4.01	3.90
			(5.8)	(4.9)	(2.2)	(7.8)	(6.0)	(10.3)
	Gal*f*′	5.06	5.04	5.28	4.37	4.25−4.30	4.40	4.25−4.30
		-	(1.9)	(5.8)	(4.5)	nd	nd	nd
	Gal*f*″	5.59	5.55	5.70	4.86	6.09	4.79	4.73
		-	(1.5)	(5.3)	(3.3)	(3.7)	(7.6)	(12.0)
17	Gal*f*	5.26	5.43	5.54	4.57	5.84	4.06	3.93
			(1.3)	(5.1)	(3.4)	(5.5)	(7.2)	(10.7)
	Gal*f*′	5.05	5.02	5.26	4.33	4.27	4.39	4.27
			(2.4)	(6.1)	(3.9)	nd	nd	nd
	Gal*f*″	5.62	5.57	5.66	4.88	6.08	4.76	4.71
			(1.7)	(5.2)	(3.3)	(3.9)	(7.6)	(12.0)

acetimidate. The trichloroacetimidate method[21] has been successfully used for β-galactofuranosyl glycosylation.[13,15,19,22,23] Treatment of **3** with Cl_3CCN and DBU afforded the imidate **4** as a 9:1 β/α mixture (Scheme 1).

As the precursor of the 5-linked galactofuranose, the reducing end of the target trisaccharide **1**, a selectively protected derivative of D-galactono-1,4-lactone, was used. Crystalline 2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone[20] (**5**) was obtained by pivaloylation of D-galactono-1,4-lactone at −23 °C in 71% yield. Selective glycosylation of the exocyclic OH-5 of **5** with trichloroacetimidate **4** gave **6a**, purified by column chromatography in 70% yield. No product of condensation at OH-3 of **5** was detected. The ^{13}C NMR spectrum of **6a** showed the C-1″ and C-1′ β-furanosic centers at 106.4 and 105.7 ppm. In the ^{1}H NMR spectrum, H-1″ and H-1′ appeared as singlets at 5.60 and 5.42 ppm and H-2′ and H-2″ as doublets with $J_{2,3}<1.5$ Hz at 5.52 and 5.39 ppm, characteristic of β-Gal*f* linkages. Acetylation of OH-3 of compound **6a** and comparison of ^{1}H NMR spectra confirmed the structure, and the signal of H-3 was shifted 1 ppm downfield in **6b** (Table 1). Reduction of the trisaccharide lactone derivative **6b** with DSB yielded the furanoic derivative **7** conveniently protected for further coupling in 83% yield. The free trisaccharide **1** was obtained by deprotection of **7** with sodium methoxide. The ^{13}C NMR spectrum showed both anomers of **1**. The two signals for C-1 appeared at 96.6 (C-1α) and 102.5 ppm (C-1β). The other two anomeric carbons gave signals at 107.3 and 109.4 ppm.

To synthesize the decenyl glycoside of **1**, the trichloroacetimidate method was used. Glycosylation of **7** with 9-decen-1-ol in the presence of TMSOTf afforded **8** in 87% yield. The structure was confirmed by the NMR spectra (Tables 1 and 2). Deprotection of **8** with NaOMe in MeOH gave dec-9-enyl β-D-Gal*f*(1→6)-β-D-Gal*f*(1→5)-β-D-Gal*f* (**9**) as a highly hygroscopic syrup in 89% yield. The NMR spectra showed the characteristic resonances for the anomeric configurations of the three furanose rings. In the ^{1}H NMR spectrum, the three anomeric protons gave signals at 5.28 (H-1′), 5.08 (H-1″) and 4.97 (H-1) ppm. The ^{13}C NMR spectrum showed the anomeric carbons at 108.5, 107.9, and 107.8 ppm, characteristic of β-D-galactofuranosides.

For the synthesis of the decenyl glycoside of β-D-Gal*f*(1→5)-β-D-Gal*f*(1→6)-β-D-Gal*f* **2**, a similar strategy

(21) Schmidt, R. R.; Jung, K.-H. In *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: New York, 1997; pp 283−312.

(22) Gelin, M.; Ferrieres, V.; Plusquellec, D. *Carbohydr. Lett.* **1997**, *2*, 381.

(23) Gallo-Rodriguez, C.; Gil-Libarona, M. A.; Mendoza, V. M.; de Lederkremer, R. M. *Tetrahedron* **2002**, *58*, 9373.

SCHEME 2

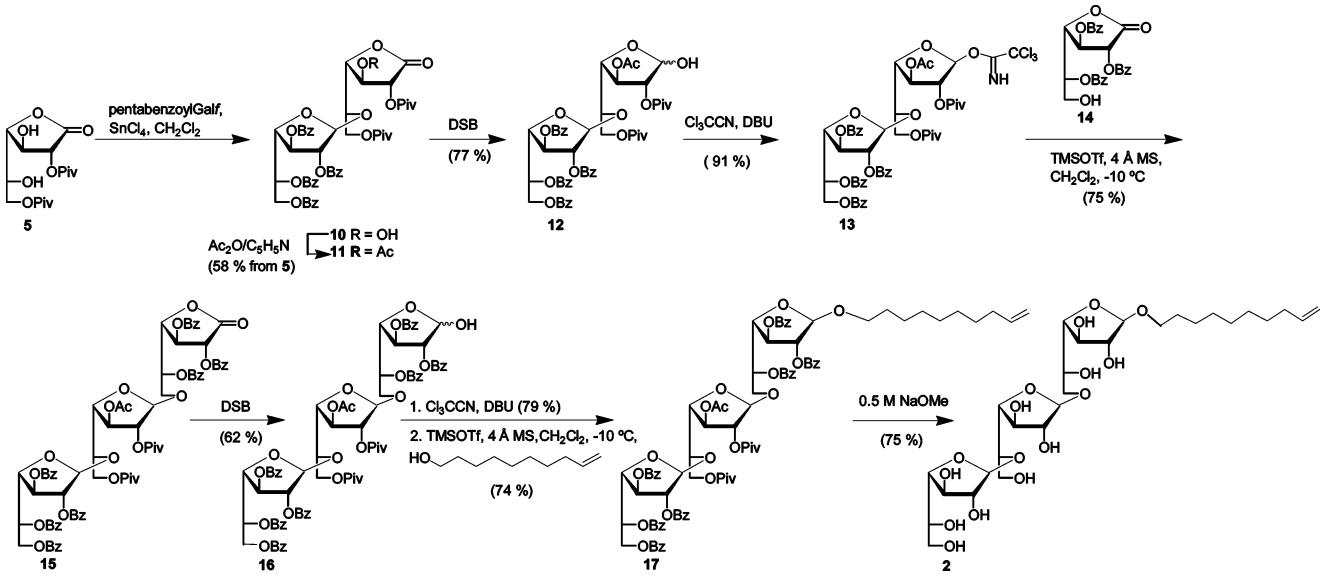


TABLE 2. ^{13}C NMR (125.8 MHz, $CDCl_3$) Chemical Shifts for Compounds 6a,b, 8, 10, 11, 15, and 17

compd		C-1	C-2	C-3	C-4	C-5	C-6
6a	Gal-one	168.3	75.4	72.0	79.4	72.2	62.7
	Gal*f*′	105.8	81.8	76.9	82.9	71.1	66.2
	Gal*f*″	106.4	81.9	77.5	82.0	70.3	63.8
6b	Gal-one	169.2	72.2	72.0	77.1	72.5	62.5
	Gal*f*′	106.4	81.5	76.9	84.5	72.1	67.3
	Gal*f*″	106.6	81.9	77.7	82.1	70.5	63.8
8	Gal*f*	105.4	81.6	76.3	80.3	73.2	63.9
	Gal*f*′	105.7	81.8	77.7	82.7	71.8	67.5
	Gal*f*″	106.7	81.9*	77.5	82.0*	70.5	63.7
10	Gal-one	168.5	75.3	72.1	79.4	72.0	62.3
	Gal*f*′	105.5	81.9	77.7	83.7	70.7	63.6
11	Gal-one	169.5	72.3	72.0	77.2	72.2	62.3
	Gal*f*′	106.1	81.8	77.4	83.8	70.6	63.9
15	Gal-one	169.7	74.4	74.2	81.2§	70.2	63.6
	Gal*f*′	105.4	79.0§	76.0	81.4	73.6	63.8
	Gal*f*″	105.9	82.0	77.6	81.9	70.3	63.8
17	Gal*f*	105.9	82.1	77.6	81.3	71.2	66.0
	Gal*f*′	105.6	81.2	76.0	81.2	73.0	64.3
	Gal*f*″	105.7	82.0	77.8	82.1	70.4	63.8

*,§ Signals may be interchanged.

was used (Scheme 2). Thus, the 2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (**5**) was used for the first glycosylation step with penta-*O*-benzoyl-D-galactofuranose[24] and $SnCl_4$ as promoter. We have previously used the di-*O*-benzoyl lactone derivative as acceptor. In the present case, the pivaloyl groups favored the selective glycosylation of the exocyclic HO-5, affording **10** in 73% yield. The NMR spectra for **10** were in agreement with those reported for the analogous disaccharide derivative.[11] Compound **10** was acetylated and reduced with DSB to afford the acetylated *β*-D-Gal*f* (1→5)-D-Gal*f* **12,** having OH-1 free, in 74% yield. Analogous to the preparation of **6a**, the trichloroacetimidate method was chosen for glycosylation with the convenient derivative **14**, easily prepared from D-galactono-1,4-lactone.[25]

The lactonic trisaccharide **15** was obtained in 74% yield after purification by column chromatography. Reduction with DSB produced the trisaccharide **16** conveniently protected for further coupling.

The furanoic structure of the reducing end was conserved by conversion to the decenyl glycoside, a convenient derivative for the synthesis of neoglycoconjugates. The trichloroacetimidate method was used for glycosylation of 9-decen-1-ol in the presence of TMSOTf to afford **17** in 74% yield. The structure of **17** was confirmed by the NMR spectra (Tables 1 and 2). The one-step deprotection procedure gave dec-9-enyl *β*-D-Gal*f*-(1→5)-*β*-D-Gal*f*-(1→6)-*β*-D-Gal*f* (**2**) as a syrup of $[\alpha]_D$ −80.9. All *β*-anomeric configurations in **2** were evident in the NMR spectra. The three anomeric carbons appeared at 107.8 (C-1′) and 107.1 (C-1, C-1″). The trisaccharide glycosides **2** and **9** could be distinguished by TLC with 1-propanol−EtOH−H_2O 7:1:1 as solvent (R_f 0.77 and R_f 0.74 respectively). Compounds **2** and **9** have been previously obtained in biosynthetic studies and characterized as the fully methylated derivatives.[8] The possibility to count with the synthetic products will facilitate studies on the properties of the galactofuranosyl transferases involved in mycobacterial galactan polymerization. The protected trisaccharides **7** and **16** could be used for the construction of higher oligosaccharides.

Conclusion

We have synthesized for the first time the two isomeric galactofuranose trisaccharides that are the products of the galactofuranosyl transferases forming Gal*f*(*β*1→5)-Gal*f* and Gal*f*(*β*1→6)Gal*f* units in *M. tuberculosis*. The trisaccharides are potentially useful for testing the action of inhibitors on the enzymatic reactions. The syntheses are simple and give good yields. They are based on the glycosylaldonolactone approach for the construction of the internal galactofuranose and the trichloroacetimidate method for its glycosylation. In addition, the dec-9-enyl aglycon can be converted to an aldehyde by ozonolysis, thus providing a good spacer for reductive coupling to protein or an aminofunctionalized affinity material.[26,27] The synthetic neoglycoproteins would be used for studies on the immunoreactivities of the galactofuranose trisaccharides.

(24) Gallo-Rodriguez, C.; Varela, O.; Lederkremer, R. M. *Carbohydr. Res.* **1998**, *305*, 163.
(25) Du Mortier, C.; Varela, O.; de Lederkremer, R. M. *Carbohydr. Res.* **1989**, *189*, 79.

Experimental Section

General Methods. TLC was performed on 0.2 mm silica gel 60 F254 aluminum-supported plates. Detection was effected by exposure to UV light or by spraying with 5% (v/v) sulfuric acid in EtOH and charring. Column chromatography was performed on silica gel 60 (230−400 mesh). Melting points are uncorrected. Optical rotations were measured at 25 °C. Mass spectra were recorded on a 70-SE-4F mass spectrometer. NMR spectra were recorded at 200 MHz (^{1}H) and 50.3 MHz (^{13}C) or at 500 MHz (^{1}H) and 125.8 MHz (^{13}C). Assigments were supported by ^{1}H−^{1}H NMR and/or ^{1}H−^{13}C NMR correlational spectra.

2,6-Di-*O*-pivaloyl-D-galactono-1,4-lactone (5). To a stirred solution of D-galactono-1,4-lactone (534 mg, 3.0 mmol) in dry pyridine (10 mL), cooled to −23 °C, was added pivaloyl chloride (0.89 mL, 7.5 mmol) during 2 h. After 3 h of stirring at −23 °C, the mixture was poured into ice−water (100 g), and the stirring was continued for 1 h. The mixture was extracted with CH_2Cl_2 (2 × 70 mL), and the organic layer was sequentially washed with 5% HCl (70 mL), water (70 mL), saturated aq $NaHCO_3$ (70 mL), and water, dried ($MgSO_4$), and concentrated. The residue partially crystallized upon addition of hexane, affording **5** (820 mg, 79%), which after recrystallization from MeOH−water gave the following data: mp 133−134 °C; $[\alpha]_D$ −63.7 (*c* 1, $CHCl_3$) (lit.[13] mp 133−134 °C, $[\alpha]_D$ −63.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (d, 1 H, J = 7.9 Hz, H-2), 4.55 (t, 1 H, J = 7.7 Hz, H-3), 4.37 (dd, 1 H, J = 6.4, 11.9 Hz, H-6a), 4.27 (dd, 1 H, J = 7.7, 2.9 Hz, H-4), 4.24 (dd, 1H, J = 4.4, 11.9 Hz, H-6b), 4.07 (ddd, J = 2.9, 6.4, 4.4 Hz, H-5); ^{13}C NMR ($CDCl_3$, 25.3 MHz) δ 168.8, 80.7, 76.3, 72.4, 68.2, 64.9.

2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (6a). To a stirred solution of 2,3,5,6-tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranose[10] (**3**) (2.32 g, 2.17 mmol) and trichloroacetonitrile (1.07 mL, 10.7 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C was slowly added DBU (154 μL, 1.08 mmol). After 1.5 h, the solution was concentrated at room temperature under reduced pressure, and the residue was purified by column chromatography (40:1:0.4 toluene−EtOAc−TEA) to give 2.56 g (97%) of *O*-(2,3,5,6-tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl)-D-galactofuranosyl) trichloroacetimidate (**4**) as an amorphous solid. Compound **4** was stable for 1 week at −20 °C: R_f 0.60 (9:1:0.09 toluene−EtOAc−TEA); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.76 (s, N*H*, 0.9 H), 8.68 (s, N*H*, 0.1 H), 8.06−7.16 (m, 35 H, aromatic), 6.79 (d, 0.1 H, J = 4.8 Hz, H-1 α anomer), 6.68 (bs, 0.9 H, H-1 β anomer), 6.05 (m, 0.9 H, H-5′), 5.98 (ddd, 0.9 H, J = 3.7, 6.0, 6.4 Hz, H-5), 5.73 (dd, 0.9 H, J = 1.8, 4.0 Hz, H-3), 5.72 (d, 0.9 H, J = 1.8 Hz, H-2), 5.57 (dd, 0.9 H, J = 2.0, 5.2 Hz, H-3′), 5.36 (bs, 0.9 H, H-1′), 5.35 (d, 0.9 H, J = 2.0 Hz, H-2′), 4.88 (dd, 0.9 H, J = 4.0, 3.7 Hz, H-4), 4.77−4.70 (m, 0.9 × 3 H, H-4′, H-6a′, H-6b′), 4.22 (dd, 0.9 H, J = 6.0, 10.6 Hz, H-6a), 4.03 (dd, 0.9 H, J = 6.4, 10.6 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 166.1−165.1 (*C*OPh), 160.4 (*C*=NH), 133.6−130.2 (aromatic), 106.0 (C-1′), 103.1 (C-1), 84.9 (C-4), 82.0, 81.9, 80.9, 77.5, 76.9, 70.9, 70.2, 65.8 (C-6), 63.9 (C-6′).

A vigorously stirred suspension of dried **4** (1.09 g, 0.90 mmol), 2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (**5**, 0.45 g, 1.30 mmol), and 4 Å powdered molecular sieves (0.7 g) in anhyd CH_2Cl_2 (35 mL) was cooled to −10 °C, and TMSOTf (64 μL, 0.35 mmol) was slowly added. After 1 h, the mixture was quenched by addition of saturated aq $NaHCO_3$ (15 mL). After dilution with CH_2Cl_2 (150 mL) and additional saturated aq $NaHCO_3$, the organic phase was separated and washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (15:1 toluene−EtOAc) to give 0.906 g of 2,3,5,6-tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (**6a**) (73% yield) as an amorphous solid that precipitated from EtOH upon cooling: R_f 0.40 (5:1 toluene−EtOAc); $[\alpha]_D$ −35.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for the protecting groups are listed δ 7.52−7.16 (35 H, aromatic), 1.18, 1.01 (2s, 18 H, $(CH_3)_3CCO$)); ^{13}C NMR ($CDCl_3$, 125.8 MHz, Table 2) only the values for the protecting groups are listed δ 178.0 ($(CH_3)_3CCO$), 166.2−165.1 (*C*OPh), 133.5−128.2 (aromatic), 38.7, 38.6-($(CH_3)_3CCO$), 27.0, 26.7 ($(CH_3)_3CCO$).

Anal. Calcd for $C_{77}H_{74}O_{25}$: C, 66.09; H, 5.33. Found: C, 65.91; H, 5.30.

2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (6b). To a solution of **6a** (0.6 g, 0.43 mmol) in dry pyridine (4.9 mL) cooled at 0 °C was added dropwise acetic anhydride (4.9 mL). The mixture was kept at room temperature for 30 min and cooled at 0 °C, and then MeOH (2 mL) was slowly added. After 0.5 h of stirring at room temperature, the solution was coevaporated with toluene to dryness. The residue crystallized upon addition of EtOH−H_2O to give **6b** (0.5 g, 81%): mp 81−83 °C (EtOH−H_2O); R_f 0.48 (5:1 toluene−EtOAc); $[\alpha]_D$ −52.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for the protecting groups are listed: δ 7.54−7.21 (35 H, aromatic), 1.94 (CH_3CO), 1.18, 0.98 (2s, 18 H, $(CH_3)_3CCO$)); ^{13}C NMR ($CDCl_3$, 125.8 MHz, Table 2) only the values for the protecting groups are listed δ 177.9, 177.1 ($(CH_3)_3CCO$), 167.9 (CH_3CO), 166.0−165.1 (*C*OPh), 133.1−127.7 (aromatic), 38.8, 38.4 ($(CH_3)_3CCO$), 27.0, 26.9 ($(CH_3)_3CCO$), 20.3 (CH_3).

Anal. Calcd for $C_{79}H_{76}O_{26}$: C, 65.83; H, 5.31. Found: C, 65.84; H, 5.34.

2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-D-galactofuranose (7). A solution of bis(2-butyl-3-methyl)borane (3.55 mmol) in anhyd THF (1.1 mL) cooled to 0 °C and under an argon atmosphere was added to a flask containing compound **6b** (873 mg, 0.60 mmol) previously dried. The resulting solution was stirred for 20 h at room temperature and then processed as previously described.[28] The organic layer was washed with water, dried (Mg_2SO_4), and concentrated. Boric acid was eliminated by coevaporation with MeOH (5 × 5 mL) at room temperature to give **7** (720 mg; 83%) as a syrup: R_f 0.41 (4:1 toluene−EtOAc); $[\alpha]_D$ −23.7 (*c* 1, $CHCl_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 178.0, 177.9 ($(CH_3)_3CCO$), 169.8, 169.9 (CH_3CO), 166.1−165.2 (*C*OPh), 134.0−128.2 (aromatic), 106.5, 106.0 (C-1′), 105.5 (C-1″), 100.6 (C-1, β anomer), 95.2 (C-1, α anomer), 82.2, 82.0, 81.9, 81.8, 81.7, 81.5, 80.1, 77.4, 75.5, 75.4, 74.4, 71.5, 71.1, 70.3, 70.2, 66.8, 66.1, 64.0, 63.7, 63.1, 38.7, 38.5 ($(CH_3)_3CCO$), 27.2, 27.1, 26.9 ($(CH_3)_3CCO$), 20.6 (CH_3CO).

Anal. Calcd for $C_{79}H_{78}O_{26}$: C, 65.73; H, 5.45. Found: C, 65.53; H, 5.35.

***β*-D-Galactofuranosyl-(1→6)-*β*-D-galactofuranosyl-(1→5)-*β*-D-galactofuranose (1).** Compound **7** (103 mg, 0.071 mmol) was suspended in 0.5 M NaOMe in MeOH solution (0.86 mL) cooled at 0 °C. After being for 3 h at 0 °C and 2 h at room temperature, the solution was cooled at −15 °C and water (0.18 mL) was added. The solution was passed through a column containing BIO-RAD AG 50W-X12, 100−200 mesh, H^+ form (3 mL), and washed with MeOH/H_2O 9:1. The solvent was evaporated and the methyl benzoate eliminated by five successive coevaporations with water and further purified by through a C8-Maxi-Clean cartridge and lyophilized. The trisaccharide **1** (32 mg, 89%) was obtained as a hygroscopic syrup: R_f 0.34 (3:2 EtOH−NH_3), $[\alpha]_D$ −85.7 (*c* 1, H_2O); ^{13} C NMR (125.8 MHz) δ 109.4 (C-1″), 107.3 (C-1′), 102.5 (C-1, β

(26) Routier, F. H.; Nikolaev, A. V.; Ferguson, M. A. J. *Glycoconjugate J.* **1999**, *16*, 773.

(27) Ragupathi, G.; Coltart, D. M.; Williams, L. J.; Koide, F.; Kagan, E.; Allen, J.; Harris, C.; Glunz, P. W.; Livingston, P. O.; Danishefsky, S. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 13699.

(28) Lerner, L. M. *Methods Carbohydr. Chem.* **1972**, *6*, 131−134.

anomer), 96.6 (C-1, α anomer); HRMS calcd for $C_{18}H_{32}O_{16}$ [M + Na]$^+$ 527.1588, found [M + Na]$^+$ 527.1589.

1-Decenyl 2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-*β*-D-galactofuranoside (8). To a stirred solution of **7** (400 mg, 0.28 mmol) and trichloroacetonitrile (0.14 mL, 1.4 mmol) in CH_2Cl_2 (8 mL) cooled to 0 °C was slowly added DBU (19.9 μL, 0.13 mmol). After 45 min, the solution was carefully concentrated under reduced pressure at room temperature, and the residue was purified by column chromatography (30:1:0.3 toluene−EtOAc−TEA) to give 372 mg (84%) of the trichloroacetimidate of **7** as a syrup: R_f 0.75 (4:1:0.04 toluene−EtOAc−TEA); ^{1}H NMR ($CDCl_3$, 200 MHz) anomeric region δ 8.74 (N*H*, 0.15 H), 8.64 (N*H*, 0.85 H), 8.06−7.19 (m, 35 H), 6.50 (d, 0.15 H, J = 4.8 Hz, H-1 α anomer), 6.26 (bs, 0.85 H, H-1 β anomer), 6.07 (m, 2 H, H-5′, H-5″), 5.56 (m, 2 H), 5.54 (bs, 1 H), 5.49 (d, 1 H, J = 1.1 Hz), 5.40−5.26 (m, 4 H), 4.86−4.69 (m, 4 H), 4.47−4.03 (m, 6 H).

A vigorously stirred suspension of the trichloroacetimidate of **7** (367 mg, 0.23 mmol), 9-decen-1-ol (55.4 μL, 0.31 mmol), and 4 Å powdered molecular sieves (0.5 g) in anhyd CH_2Cl_2 (8 mL) was cooled to −10 °C, and TMSOTf (12 μL, 0.066 mmol) was slowly added. After 30 min, the mixture was quenched by addition of saturated aq $NaHCO_3$ (10 mL) and processed as above. The product was washed with cold hexane to eliminate the alcohol affording **8** as a chromatographically homogeneous syrup (315 mg, 87%). An amorphous solid was obtained by cooling a hot solution of the syrup in EtOH: R_f 0.47 (9:1, toluene/EtOAc); $[\alpha]_D$ −35.6 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) (only the values for the protecting groups are listed) δ 8.01−7.24 (m, 35 H, aromatic), 5.81 (ddt, 1 H, J = 6.8, 10.3, 17.0 Hz, C*H*-ethylenic), 4.97 (ddt, 1 H, J = 1.6, 2.2, 17.0 Hz, CH_2-ethylenic), 4.93 (ddt, 1 H, J = 1.4, 2.2, 10.3 Hz, CH_2-ethylenic), 3.61 (dt, 1 H, J = 6.8, 9.6 Hz, CH_2O), 3.37 (m, 1 H, J = 6.6, 9.6 Hz, CH_2O), 2.02 (m, 2H, CH_2), 1.94 (s, 3 H, CH_3), 1.51 (m, 2 H, CH_2), 1.35 (2 H, CH_2), 1.25 (m, 10 H, CH_2), 1.19, 1.09 (2s, 18 H, ((C*H*$_3$)$_3$CCO)). ^{13} C NMR ($CDCl_3$, 125.8 MHz, Table 2) (only the values for protecting groups are listed) δ 178.0, 177.3 ((CH_3)$_3$C*C*O), 169.8 (CH_3*C*O), 165.8−165.1 (*C*OPh), 139.1 (*C*H-ethylenic), 133.3−128.3 (aromatic), 114.1 (*C*H$_2$-ethylenic), 67.8 (CH_2O), 38.7, 38.5, ((CH_3)$_3$*C*CO), 33.7, 29.4, 29.3, 29.1, 28.9, 26.0 (7 × CH_2), 27.1, 26.9 ((CH_3)$_3$-CCO), 20.6 (CH_3).

Anal. Calcd for $C_{89}H_{96}O_{26}$: C, 67.58; H, 6.12. Found: C, 67.62; H, 6.00.

1-Decenyl *β*-D-Galactofuranosyl-(1→6)-*β*-D-galactofuranosyl-(1→5)-*β*-D-galactofuranoside (9). Compound **8** (234 mg, 0.15 mmol) was suspended in 0.55 M NaOMe in MeOH solution (3.0 mL) cooled at 0 °C. After the mixture was stirred 1 h at 0 °C and 1 h at room temperature, water (0.5 mL) was added and the solution processed as for **1**. Glycoside **9** (86 mg, 89%) was obtained as a hygroscopic syrup: R_f 0.74 (7:1:1 *n*-propanol−EtOH−H_2O); $[\alpha]_D$ −85.7 (*c* 1, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ 5.88 (ddt, 1 H, J = 6.8, 10.0, 16.9 Hz, C*H*-ethylenic), 5.28 (bs, 1 H, H-1′), 5.08 (bs, 1 H, H-1″), 5.02 (m, 2 H, CH_2- ethylenic), 4.97(bs, 1 H, H-1), 4.19−3.68 (20 H), 2.07 (m, 2 H, CH_2), 1.62 (m, 2 H, CH_2), 1.41−1.34 (m, 10 H, CH_2 × 5); ^{13} C NMR (125.8 MHz) δ 140.1 (*C*H-ethylenic), 114.6 (CH_2-ethylenic), 108.5 (C-1″), 107.9 (C-1′), 107.8 (C-1), 83.6, 83.5, 82.1, 81.9, 81.8, 81.5, 77.3, 77.2, 76.4, 71.4, 70.2, 69.8 (C-6′), 68.9 (O*C*H$_2$), 63.3 (C-6), 62.3 (C-6″), 34.0, 29.6, 29.4, 29.3, 29.1, 26.1 (*C*H$_2$ × 7); HRMS calcd for $C_{28}H_{50}O_{16}Na$ [M + Na]$^+$ 665.2997, found [M + Na]$^+$ 665.2992.

2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (11). To a solution of penta-*O*-benzoyl-D-galactofuranose[24] (5.48 g, 7.8 mmol) in dry CH_2Cl_2 (80 mL) was added $SnCl_4$ (1.4 mL, 7.8 mmol), and the solution was stirred for 10 min at 0 °C. A solution of compound **5** (3.77 g, 10.89 mmol) in CH_2Cl_2 (20 mL) was then slowly added, and the mixture was stirred for 3 h at room temperature until examination by TLC showed a main spot (R_f 0.46; 5:1, toluene−EtOAc). The solution was poured into aq $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 200 mL). The organic extract was washed with water (3 × 100 mL), dried ($MgSO_4$), filtered, and evaporated affording 2,3,5,6-tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (**10**): ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) (only the values for the protecting groups are listed) δ 8.08−7.22 (m, 20 H), 1.17, 1.03 (2s, 18H, (CH_3)$_3$CCO); ^{13}C NMR ($CDCl_3$, 125.8 MHz, Table 2) only the values for the protecting groups are listed δ 178.2, 177.9 ((CH_3)$_3$C*C*O), 168.4 (C-1), 167.2−165.3 (*C*OPh), 133.7−128.2 (aromatic), 38.7, 38.6 ((CH_3)$_3$*C*CO), 27.0, 26.7 ((CH_3)$_3$CCO). The product was dissolved in dry pyridine (56.5 mL) and cooled to 0 °C. Acetic anhydride (56.5 mL) was added dropwise to this solution. The mixture was kept at room temperature for 1 h and cooled to 0 °C, and then MeOH (20 mL) was slowly added. After 0.5 h of stirring at room temperature, the solution was coevaporated with toluene to eliminate pyridine and the residue was purified by column chromatography (20:1 toluene−EtOAc) to give 4.34 g (58% from **5**) of **11** as a syrup: R_f 0.27 (5:1 toluene−EtOAc); $[\alpha]_D$ −52.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) (only the protecting groups are listed) δ 8.05−7.16 (m, 20 H, aromatic), 2.05 (s, 3H, CH_3), 1.19, 1.01 (2s, 18 H, (CH_3)$_3$CCO); ^{13}C NMR ($CDCl_3$, 125.8 MHz, Table 2) (only the values for the protecting groups are listed) δ 177.9, 177.1 ((CH_3)$_3$C*C*O), 169.5 (C-1), 167.9 (CH_3*C*O), 166.1−165.2 (*C*OPh), 133.6−128.2 (aromatic), 38.5 ((CH_3)$_3$C*C*O), 27.1, 26.6 ((CH_3)$_3$C*C*O), 20.4 (*C*H$_3$-CO). Anal. Calcd for $C_{52}H_{54}O_{18}$: C, 64.59; H, 5.63. Found: C, 64.59; H, 5.60.

2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-D-galactofuranose (12). The lactone **11** (1.95 g, 2.01 mmol) with a solution of bis(2-butyl-3-methyl)borane (13.9 mmol) in anhyd THF (4.1 mL) was reduced as described for **7**. Purification of the crude by column chromatography gave **12** (1.5 g, 77%) as a syrup: R_f 0.23 (5:1 toluene−EtOAc); $[\alpha]_D$ −19.9 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20−7.15 (m, 20 H, aromatic), 6.06 (m, 1 H, H-5′), 5.71 (dd, 0.5 H, J = 1.7, 5.5 Hz), 5.67 (bs, 0.5 H), 5.67 (dd, 0.5 H, J = 1.6, 5.5 Hz), 5.61 (dd, 0.5 H, J = 5.2, 6.5 Hz), 5.57 (bs, 0.5 H), 5.56 (d, 0.5 H, J = 1.7 Hz), 5.55 (d, 0.5 H, J = 1.6 Hz), 5.47 (d, 0.5 H, J = 4.7 Hz, H-1 α anomer), 5.34 (bs, 0.5 H, H-1 β anomer), 5.26 (dd, 0.5 H, J = 2.7, 6.0 Hz), 5.11−5.07 (m,1 H), 4.96 (dd, 0.5 H, J = 3.4, 5.6 Hz), 4.88 (dd, 0.5 H, J = 5.5, 3.3 Hz), 4.86−4.79 (m, 1 H), 4.77−4.69 (m, 1 H), 4.46−4.20 (m, 3.5 H), 4.11 (dd, 0.5 H, J = 4.5, 5.2 Hz), 2.03, 1.98 (2s, 6 H), 1.17, 1.16, 1.11 (3s, 18 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 178.0, 177.4 ((CH_3)$_2$C*C*O), 170.2, 169.9 (CH_3*C*O), 166.3−165.2 (*C*OPh), 133.5−128.2 (aromatic), 105.5, 105.6 (C-1′of α and β anomers), 100.6 (C-1β), 95.9 (C-1α), 82.2, 82.0, 81.9, 81.5, 81.1, 80.0, 77.5, 77.4, 76.2, 75.2, 74.1, 70.2, 63.7, 63.8, 63.6, 63.2, 38.7, 38.5 ((CH_3)$_2$*C*CO), 27.0, 26.9 ((CH_3)$_2$CCO), 20.6 (*C*H$_3$CO).

Anal. Calcd for $C_{52}H_{56}O_{18}$: C, 64.45; H, 5.83. Found: C, 64.55; H, 5.86.

2,3,5,6-Tetra-*O*-benzoyl-*β*-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-*β*-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-D-galactono-1,4-lactone (15). To a stirred solution of **12** (1.17 g, 1.21 mmol) and trichloroacetonitrile (0.6 mL, 6.0 mmol) in CH_2Cl_2 (50 mL), cooled to 0 °C, was slowly added DBU (86 μL, 0.6 mmol). After 30 min, the solution was concentrated under reduced pressure at room temperature, and the residue was purified by column chromatography (10:1:0.1 toluene−EtOAc−TEA) to give 1.22 g of trichloroacetimidate **13** (91%) as a syrup: R_f 0.50 (2:1 hexanes−EtOAc);^{1}H NMR ($CDCl_3$, 200 MHz) anomeric region δ 8.87 (s, 0.2 H, N*H*), 8.59 (s, 0.8 H, N*H*), 6.56 (d, 0.2 H, J = 4.5 Hz, H-1α anomer), 6.27 (bs, 0.8H, H-1β anomer); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 169.7 (*C*OCH$_3$), 165.7−165.3 (*C*OPh), 160.2 (C═NH), 133.5−128.3 (aromatic), 105.5 (C-1′), 102.6 (C-1), 83.3, 82.2, 81.8, 80.3, 77.7, 75.8, 73.6, 70.4, 64.1, 63.6 (C-6, C-6′), 38.7 (*C*(CH$_3$)$_3$), 20.5 (*C*H$_3$), 27.1, 26.7 (C(*C*H$_3$)$_3$). A vigorously stirred suspension of **13** (1.18 g, 1.06 mmol), 2,3,5-tri-*O*-benzoyl-D-galactono-1,4-lactone[25] (**14**, 0.64 g, 1.31 mmol), 4 Å powdered molecular sieves (1.2 g) in anhyd CH_2Cl_2 (70 mL) was cooled to −10 °C,

and TMSOTf (62 μL, 0.34 mmol) was slowly added. After 1 h, the reaction was quenched by addition of $NaHCO_3$, and the mixture was processed as usual. The product was purified by column chromatography (15:1 toluene−EtOAc) to give 1.14 g of **15** (75% yield) that crystallized from EtOH: mp 82−83 °C (EtOH); R_f 0.56 (5:1 toluene−EtOAc); $[\alpha]_D$ −24.3 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) (only the values for the protecting groups are listed) δ 8.08−7.15 (m, 35 H), 1.86 (s, 3 H, CH_3CO), 1.16, 1.07 (2s, 18 H, $(CH_3)_3CCO$); ^{13}C NMR ($CDCl_3$, 125.8 MHz, Table 2) (only the values for the protecting groups are listed) δ 178.0 ($(CH_3)_3CCO$), 169.0 (CH_3CO), 166.1−164.9 (*C*OPh), 133.9−128.0 (aromatic), 38.7, 38.5 ($(CH_3)_3CCO$), 27.1, 26.8 ($(CH_3)_3CCO$), 20.4 (CH_3CO).

Anal. Calcd for $C_{79}H_{76}O_{26}$: C, 65.83; H, 5.31. Found: C, 65.90; H, 5.32.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-D-galactofuranose (16). Compound **15** (0.81 g, 0.56 mmol) was reduced as described for **7** to give **16** (0.50 g, 62%) as an amorphous solid: R_f 0.34 (5:1 toluene−EtOAc); $[\alpha]_D$ −19.7 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.06−7.24 (m, 35 H, aromatic), 6.07 (m, 1 H, H-5″), 5.76 (m, 1 H, H-5), 5.73 (bs, 1 H, H-1), 5.67 (dd, 1 H, *J* = 1.6, 5.5 Hz, H-3″), 5.66 (bs, 1 H, H-1″), 5.59 (d, 1 H, *J* = 1.6 Hz, H-2″), 5.53 (m, 2 H, H-3, H-2), 5.23 (dd, 1 H, *J* = 1.7, 5.9 Hz, H-3′), 5.08 (d, 1 H, *J* = 1.7 Hz, H-2′), 5.01 (s, 1 H, H-1′), 4.94 (dd, 1 H, *J* = 3.9, 5.5 Hz, H-4″), 4.80 (dd, 1 H, *J* = 3.6, 12.2 Hz, H-6a″), 4.74 (dd, 1 H, *J* = 2.2, 5.3 Hz, H-4), 4.69 (dd, 1 H, *J* = 7.6, 12.2 Hz, H-6b″), 4.66 (dd, 1 H, *J* = 2.2, 12.2 Hz, H-6a′), 4.45 (dd, 1 H, *J* = 3.9, 5.9 Hz, H-4′), 4.34 (m, 1 H, H-5′), 4.24 (dd, 1 H, *J* = 7.3, 12.2 Hz, H-6b′), 4.06 (t, 1 H, *J* = 8.8 Hz, H-6a), 3.83 (dd, 1 H, *J* = 8.8, 5.7 Hz, H-6b), 1.86 (s, 3 H, CH_3), 1.16, 1.05 (2s, 18 H, $(CH_3)_3CCO$); ^{13}C NMR (50.3 MHz) δ 179.3, 177.2 ($(CH_3)_3CCO$), 170.1 (CH_3CO), 166.2−165.2 (Ph*C*O), 135.5−128.2 (aromatic), 105.1 (C-1″), 104.3 (C-1′), 100.6 (C-1, β anomer), 95.5 (C-1, α anomer), 82.1, 82.0, 81.6, 80.9, 80.6, 77.9, 76.0, 72.9, 70.5, 70.4, 66.2, 63.8, 62.9, 38.8, 38.5 ($(CH_3)_3CCO$), 27.0, 26.8 ($(CH_3)_3CCO$), 20.3 (CH_3CO).

Anal. Calcd for $C_{79}H_{78}O_{26}$: C, 65.73; H, 5.45. Found: C, 65.68; H, 5.44.

1-Decenyl 2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (17). To a stirred solution of **16** (365 mg, 0.25 mmol) and trichloroacetonitrile (0.13 mL, 1.3 mmol) in CH_2Cl_2 (8 mL), cooled to 0 °C, was slowly added DBU (18.5 μL, 0.12 mmol). After 1 h, the solution was concentrated under reduced pressure, and the residue was purified by column chromatography (30:1:0.3 toluene−EtOAc−TEA) to give 309 mg of the trichloroacetimidate of **16** (79%) as a syrup: R_f 0.50 (5:1:0.05 toluene−EtOAc−TEA); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.82 (s, 1H, N*H*), 8.10−7.16 (m, 35 H), 6.66 (s, 1 H, H-1), 6.08 (m, 1 H, H-5″), 5.89 (m, 1 H, H-5), 5.72 (d, 1 H, *J* = 0.8 Hz, H-2), 5.67−5.65 (m, 2 H, H-3, H-3″), 5.62 (s, 1 H, H-1″), 5.59 (d, 1 H, *J* = 1.3 Hz, H-2″), 5.24 (dd, 1 H, *J* = 2.4, 6.4 Hz, H-3′), 5.01 (s, 1 H, H-1′), 4.99 (d, 1 H, *J* = 2.4 Hz, H-2′), 4.86 (dd, 1 H, *J* = 3.6, 4.9 Hz), 4.80 (dd, 1 H, *J* = 3.3, 4.0 Hz), 4.75 (dd, 1 H, *J* = 3.7, 12.0 Hz, H-6a″), 4.69 (dd, 1 H, *J* = 7.7, 12.0 Hz, H-6b″), 4.42 (dd, 1 H, *J* = 3.3, 11.8 Hz, H-6a′), 4.31−4.26 (m, 2 H, H-6b′, H-4′), 4.22 (m, 1 H, H-5′), 4.06 (dd, 1 H, *J* = 6.5, 10.2 Hz, H-6a), 3.88 (dd, 1 H, *J* = 6.8, 10.2 Hz, H-6b), 1.84 (s, 3 H, CH_3), 1.14, 1.00 (2s, 18 H, $(CH_3)_3CCO$).

Glycosylation of 9-decen-1-ol (45.8 μL, 0.25 mmol) with the trichloroacetimidate of **16** (299 mg, 0.19 mmol) using TMSOTf as catalyst, 4 Å powedered molecular sieves, and CH_2Cl_2 (8 mL) cooled at −10 °C afforded **17** (222 mg, 74%) as an amorphous solid: R_f 0.45 (9:1, toluene/EtOAc); $[\alpha]_D$ −36.0 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) (only the values for protecting groups are listed) δ 8.15−7.24 (m, 35 H, aromatic), 5.79 (ddt, 1 H, *J* = 17.1, 10.2, 6.7 Hz, C*H*-ethylenic), 4.97 (ddt, 1 H, *J* = 17.1, 2.2, 1.5 Hz, CH_2-ethylenic), 4.91 (ddt, 1 H, *J* = 10.2, 2.2, 1.1 Hz, CH_2-ethylenic), 3.76 (dt, 1 H, *J* = 6.7, 9.6 Hz, CH_2O), 3.53 (dt, 1 H, *J* = 6.5, 9.6 Hz, CH_2O), 2.01 (m, 2H, CH_2), 1.86 (s, 3 H, CH_3), 1.67 (m, 4 H, CH_2), 1.35 (m, 10 H, CH_2), 1.14, 1.02 (2s, 18 H, $(CH_3)_3CCO$); ^{13}C NMR ($CDCl_3$, 125.8 MHz, Table 2) (only the values for protecting groups are listed) δ 177.9, 177.0 ($(CH_3)_3CCO$), 169.9 (CH_3CO), 166.1−165.1 (*C*OPh), 139.1 (CH-ethylenic), 133.4−128.3 (aromatic), 114.1 (CH_2-ethylenic), 67.7 (CH_2O), 38.7, 38.4, ($(CH_3)_3CCO$), 33.7, 29.5, 29.4, 29.1, 28.9, 27.0, 26.1 (CH_2 × 7), 26.8, 26.1 ($(CH_3)_3CCO$), 20.4 (CH_3). Anal. Calcd for $C_{89}H_{96}O_{26}$: C, 67.58; H, 6.12. Found: C, 67.84; H, 6.09.

1-Decenyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranoside (2). Compound **17** (177 mg, 0.112 mmol) was deacylated with NaOMe in MeOH to afford glycoside **2** (54 mg, 75%) as a hygroscopic syrup: R_f 0.77 (7:1:1 *n*-propanol−EtOH−H_2O); $[\alpha]_D$ −80.9 (*c* 1, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ 5.79 (ddt, 1H, *J* = 16.9, 10.4, 6.5 Hz, CH-ethylenic), 5.16 (d, *J* = 1.8 Hz, 1 H, H-1″), 4.95 (bs, 1 H), 4.91 (bs, 1 H), 4.93 (m, 1 H, CH_2-ethylenic), 4.06−3.46 (21 H), 1.99 (m, 2 H, CH_2), 1.54 (m, 2 H, CH_2), 1.33−1.26 (m, CH_2 × 5). ^{13}C NMR (125.8 MHz) δ 139.6 (*C*H-ethylenic), 114.1 (CH_2-ethylenic), 107.8 (C-1′), 107.1 (C-1, C-1″), 82.7, 82.6, 81.9, 81.2, 81.1, 76.7, 76.6, 76.5, 75.8, 70.5, 69.5, 69.3, 68.3 (C-6, OCH_2), 62.8, 61.1 (C-6′, C-6″), 33.3, 28.9, 28.8, 28.6, 28.4, 25.4 (CH_2 × 7); HRMS calcd for $C_{28}H_{50}O_{16}Na$ $[M + Na]^+$ 665.2997, found $[M + Na]^+$ 665.2998.

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Supporting Information Available: ^{1}H-^{1}H and ^{1}H-^{13}C 2D correlation spectra for **6a**, **6b**, **8**, **10**, **11**, **15** and **17.** This material is available free of charge via the Internet at http://pubs.acs.org.

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