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Phthalic Anhydride-Mediated Direct Glycosylation of Anomeric Hydroxy Arabinofuranose: Synthesis of Repeating Oligoarabinofuranoside and Tetradecasaccharide Arabinan Motif of Mycobacterial Cell Wall

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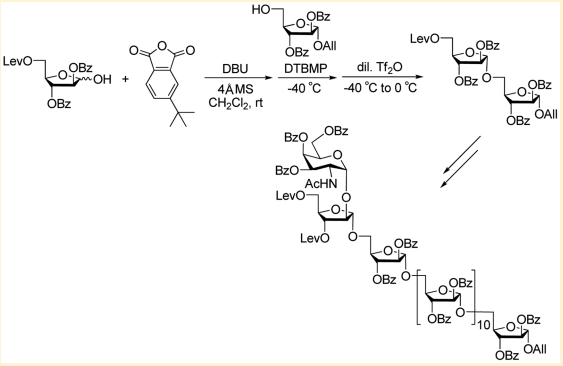
Supporting Information

ABSTRACT: An efficient direct phthalic anhydride-mediated one-pot glycosylation method employing anomeric hydroxy arabinofuranose as glycosyl donor and triflic anhydride as activating agent has been developed. This method afforded the desired di- and oligoarabinofuranosides in good yields even in gram scale glycosylation when *t*-butylphthalic anhydride was used. Moreover, our new method can be further extended to the syntheses of repeating oligoarabinofuranoside and tetradecasaccharide arabinan motif found in mycobacterial cell wall.



Mycobacterial infections have received significant attention due to their increasing incidence over the world. In particular, *Mycobacterium tuberculosis*, the causative agent of tuberculosis, is the most well-known pathogenic strain of mycobacteria.[1] Recently, tuberculosis (TB) has "reappeared" as a major threat to human health. Successful treatment of TB requires a regimen of multiple antibiotics that must be administered over a number of months,[2] and failure to complete this process is a major cause of drug resistance.[3] Inhibition of the biosynthesis of the mycobacterial cell wall represents an exciting therapeutic opportunity for the development of new drugs to combat TB.[4] In particular, assembly of the carbohydrate sections of the cell wall, many of which are unique to mycobacteria, has been a field of intense interest over recent years. Several research groups have been attempting to inhibit mycobacterial cell wall biosynthesis by inhibition of particular enzymes involved in the proposed biosynthetic pathways.[5]

Two major components of the mycobacterial cell wall are arabinogalactan and lipoarabinomannam, both of which have mycobacterial arabinan moiety as a common constituent containing large domains of D-arabinofuranose (Ara*f*) units that are predominantly linked $\alpha(1 \rightarrow 5)$ as shown in Figure 1.[6] In addition, the further complexity have been found at the 2-*O*-position of inner 3,5-branched-Ara*f* connected by 2-amino-2-deoxy-galactose ($GalNH_2$) or succinate ester in arabinan domain.[6b,7] Recently, Lowary group reported the synthesis of the tetrasaccharide containing both $GalNH_2$ anomers attached to the triarabinofuranoside (3,5-branched-Ara*f*) and the elucidation of $GalNH_2$ connected by α-linkage to core Ara*f* by the comparison with natural arabinan by NMR spectra.[8] Although many groups have achieved the synthesis of

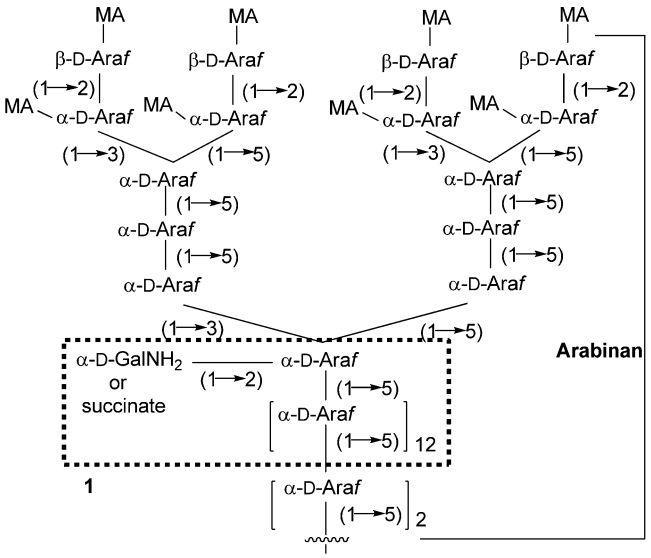


Figure 1. Structure of a mycobacterial arabinan terminus and tetradecasaccharide **1**.

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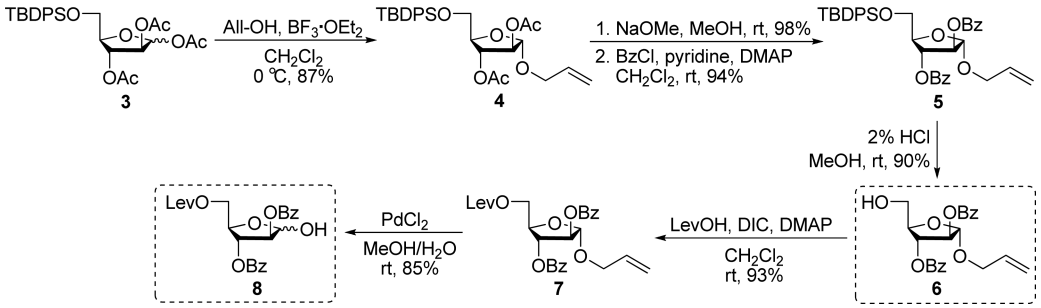
Scheme 1. Synthesis of C-1 Hydroxy Sugar 8 and Glycosyl Acceptor 6



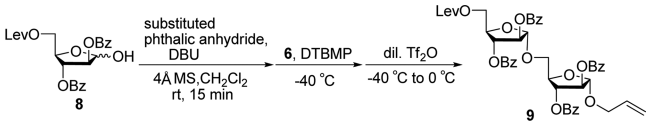
oligosaccharide arabinan motifs of mycobacterial cell wall,[9−28] there is no previous study for the synthesis of oligofuranoside containing $GalNH_2$ except this report as far as we know. In addition, because the formation of furanosyl linkage is generally more difficult than that of pyranosyl linkage, the leaving groups at furanosyl donors have been essential for the successful furanosylation and most of them have employed only a few representative leaving groups, such as thioaryl or alkylate,[9−23,29] pentenyl,[23−26] and trichloroacetimidate.[9,17,30] Accordingly, there still remains a need for new and efficient furanosylation methodologies. In our efforts to develop the furanosylation method, we achieved recently an efficient direct furanosylation protocol. We herein describe the direct phthalic anhydride-mediated one-pot furanosylation method employing anomeric hydroxy arabinofuranose as glycosyl donor and the efficient synthesis of repeating oligoarabinofuranoside using our new method. We also report the synthesis of suitably protected compound **2** of tetradecasaccharide **1**, which is composed of α-$GalNH_2$ and $\alpha(1 \rightarrow 5)$-$(Araf)_{13}$, for selective deprotection at 3,5-O positions to be connected with $\alpha(1 \rightarrow 3)$-$(Araf)_n$ and $\alpha(1 \rightarrow 5)$-$(Araf)_n$ in arabinan domain (Figure 1).

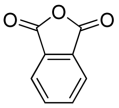
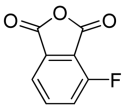
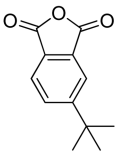
For the preparation of arabinofuranosyl acceptor **6** and donor **8**, compound **3**[31] was transformed in 87% yield to the corresponding allyl glycoside **4** on treatment of allyl alcohol and $BF_3{\cdot}OEt_2$ (Scheme 1). Removal of the acetyl groups in **4** was achieved by stirring with NaOMe in MeOH, affording diol in 98% yield. The resulting diol was then converted to compound **5** upon reaction with BzCl and pyridine in CH_2Cl_2. The fully protected glycoside **5** was transformed upon treatment with 2% HCl to give the glycosyl acceptor **6** in 90% yield. For the selective deprotection with Bz group at later stage, the levulinylation of compound **6** was conducted to give **7** in 93% yield prior to the Pd-catalyzed cleavage of the allyl ether group providing **8** with free anomeric hydroxyl group in 85% yield.

The one-pot direct mannosylation protocol,[32] which was developed by our group, was applied to the arabinosylation of C-1 hydroxy arabinofuranose employing various phthalic anhydrides (Table 1). In those experiments, the arabinosylation with compound **8** was carried out by a sequence of three steps in one-pot in CH_2Cl_2: (1) stirring the solution of **8**, substituted phthalic anhydride, and DBU in the presence of 4 Å molecular sieves for 15 min at room temperature in CH_2Cl_2, (2) addition of DTBMP and **6** to the above solution at −40 °C and stirring the resulting solution, and (3) slow addition of Tf_2O at −40 °C and stirring the reaction mixture at −40 to 0 °C. The reaction of **8** with **6** under the modified condition afforded α-diarabinofuranoside **9**.

At first, when phthalic anhydride was used, the reaction afforded desired disaccharide **9** along with self-condensed ester

Table 1. Synthesis of α-Diarabinofuranoside 9 Employing Various Substituted Phthalic Anhydrides



8 (Scale)	substituted phthalic anhydride	**9** (Yield)[a]
60 mg		83%
110 mg		83%
279 mg		62%
603 mg		57%
70 mg		86%
150 mg		80%
245 mg		70%
578 mg		36%
65 mg		75%
528 mg		68%
845 mg		70%
1.35 g		73%

[a]Isolated yield.

and decomposed donor. In the reactions up to 110 mg scale, disaccharide **9** was obtained in high yield. However, gradual decrease of product yield was observed as the reaction scale increased. When we changed phthalic anhydride to 3-fluorophthalic anhydride,[33] we obtained slightly better results up to 245 mg scale, but not at larger scale. On the other hand, coupling reaction with *t*-butylphthalic anhydride produced the desired disaccharide **9** in 68−75% yield independent to the scale of anomeric hydroxy sugar **8**. Although the reason that *t*-butylphthalic anhydride is better activator than others is not clear, these surprising results encouraged us to prepare the repeating oligoarabinofuranoside by one-pot direct glycosylation.

Toward the synthesis of triarabinofuranoside, compound **9** was converted into disaccharide anomeric hydroxy sugar **10** as

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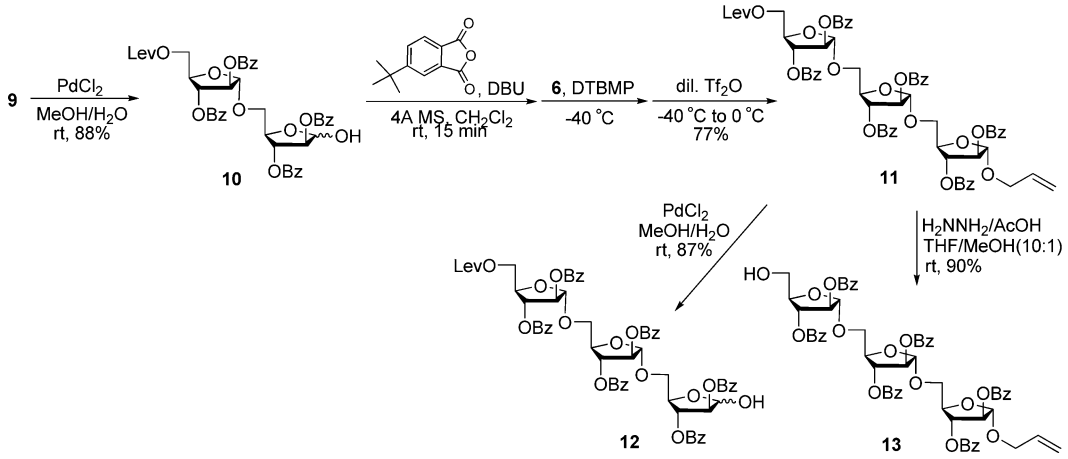
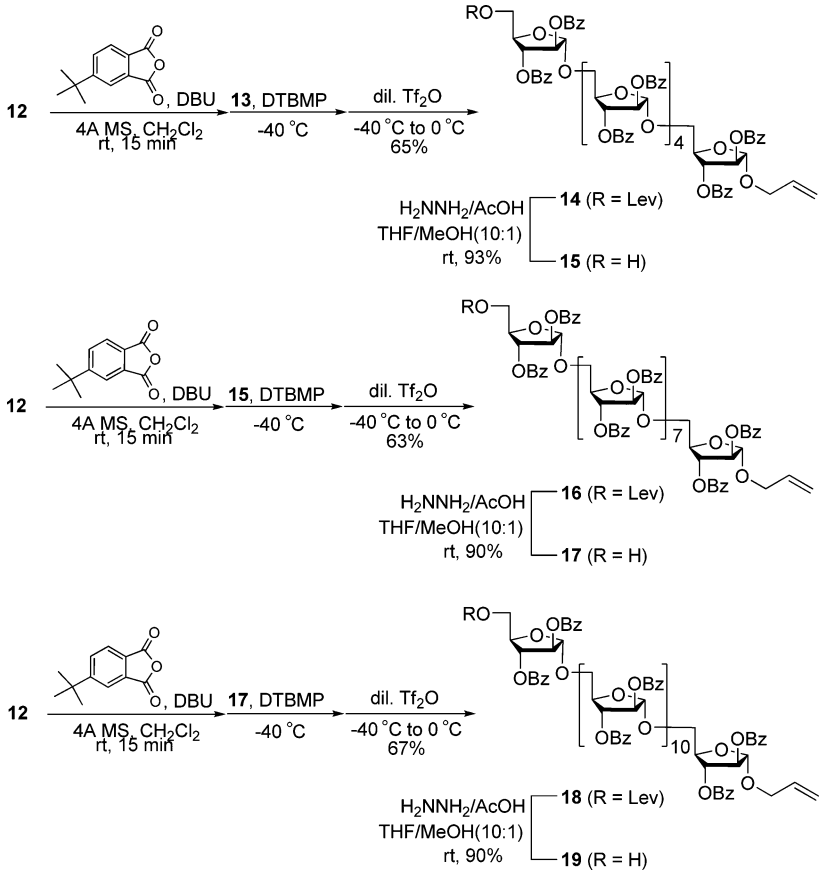
Scheme 2. Synthesis of Trisaccharide C-1 Hydoxy Sugar 12 and Trisaccharide Acceptor 13



Scheme 3. Synthesis of Dodecasaccharide Acceptor 19



the next glycosyl donor upon deallylation over $PdCl_2$ in MeOH (Scheme 2). Reaction of anomeric hydroxy sugar **10** and acceptor **6** under the standard glycosylation conditions afforded α-trisaccharide **11** in 77% yield. The NMR spectrum of **11** in $CDCl_3$ showed three anomeric carbon peaks at δ 104.9, 105.9, and 106.1. For the preparation of trisaccharide donor and acceptor suited for the synthesis of the repeating oligosaccharide, compound **11** was transformed to anomeric hydroxy sugar **12** and **13** by deallylation and delevulinylation, respectively.

Repetitive glycosylation of the trisaccharide anomeric hydroxy sugar **12** with the trisaccharide **13** as an acceptor resulted α-hexasaccharide **14** in 65% yield, which then was converted into the hexasaccharide acceptor **15** by removal of its levulinyl group with hydrazine (Scheme 3). Glycosylation of the trisaccharide donor **12** with the glycosyl acceptor **15** afforded α-nonasaccharide **16** in 63% yield. Deprotection of the levulinyl group in **16** with hydrazine gave the nonasaccharide acceptor **17** in 90% yield. The arabinosylation of the trisaccharide donor **12** with the nonasaccharide acceptor **17** proceeded smoothly under the standard conditions to afford dodecasaccharide **18** in 67% yield. Deprotection of the levulinyl group proceeded uneventfully to give dodecasaccharide acceptor **19** in 90% yield. This new protocol would be considered as

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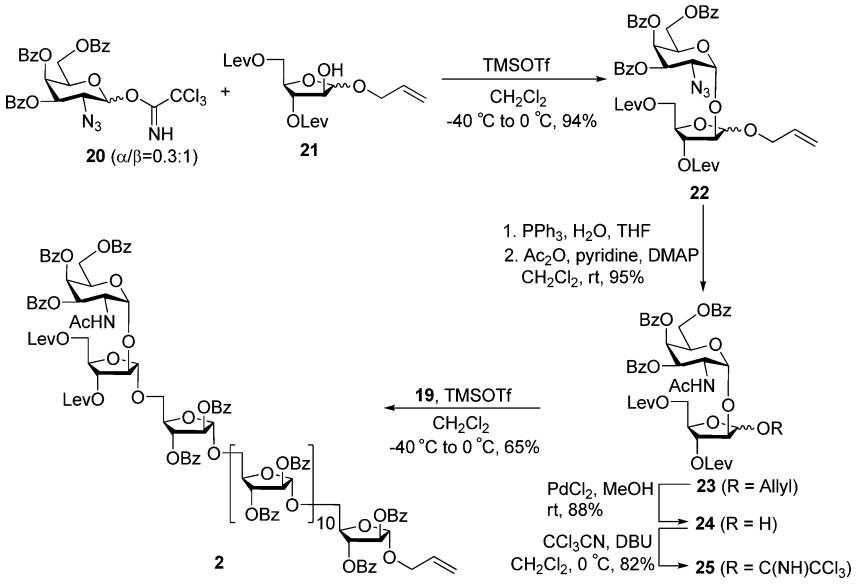
Scheme 4. Synthesis of Tetradecasaccharide 2 in Arabinan



one of the most convenient and efficient methods to prepare oligoarabinofuranoside.

For the synthesis of the tetradecasaccharide **2** in arabinan, the suitably protected α-GalNH$_2$-(1 → 2)-arabinofuranosyl trichloroacetimidate **25** was prepared from 2-azido-galactosyl trichloroacetimidate **20**[34] and arabinofuranosyl acceptor **21**[34] (Scheme 4). The crucial stereoselective α-galactosylation was readily achieved by activation of the glycosyl donor **20** with TMSOTf, followed by the addition of the acceptor **21**. The desired α-disaccharide **22** was obtained in 94% yield. Reduction of the azide group by treatment of **22** with Ph_3P and acetylation of the resulting amine afforded the *N*-acetyl protected disaccharide **23**. Compound **23** was converted into disaccharide anomeric hydroxy sugar **24** by deallylation over $PdCl_2$ in MeOH. Subsequent treatment with trichloroacetonitrile and DBU provided the expected trichloroacetimidate donor **25**. Finally, the coupling of the disaccharide donor **25** and the dodecasaccharide acceptor **19** in the presence of TMSOTf afforded the desired suitably protected tetradecasaccharide **2** in 65% yield.

In conclusion, we have established a reliable direct one-pot gycosylation of C-1 hydroxy arabinofuranose without a leaving group at furanosyl donor by employing *t*-butylphthalic anhydride as activator in good yield even in gram scale reaction. The power of the present arabinofuranosylation method was demonstrated by the efficient synthesis of repeating oligoarabinofuranoside and tetradecasaccharide arabinan motif found in mycobacterial cell wall.

■ EXPERIMENTAL SECTION

General Information. All reactions were conducted under a positive pressure of dry argon with dry, freshly distilled solvents unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Dichloromethane and acetonitrile were distilled from calcium hydride. Ethyl acetate and hexane were distilled. Flash column chromatography was performed employing 230−400 mesh silica gel. Thin-layer chromatography was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm) and a typical TLC indication solution (cerium sulfate/molybdic acid solution). NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS).

Allyl 2,3-Di-O-acetyl-5-O-t-butyldiphenylsilyl-α-D-arabinofuranoside (4). To a solution of compound **3**[31] (7.65 g, 14.9 mmol) in CH_2Cl_2 (50 mL) were added allyl alcohol (2.02 mL, 29.7 mmol) and $BF_3{\cdot}Et_2O$ (2.83 mL, 22.3 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic layer was washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **4** (6.63 g, 87%) as a colorless oil. R_f = 0.73 (hexane/EtOAc, 3:1, v/v); $[\alpha]_D^{20}$ = +34.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 9H), 2.03 (s, 3H), 2.06 (s, 3H), 3.87 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.91 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.04 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.15 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.21 (dd, *J* = 13.2, 4.8 Hz, 1H), 5.07 (s, 1H), 5.11 (d, *J* = 1.2 Hz, 1H), 5.20 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.26 (dd, *J* = 5.2, 0.8 Hz 1H), 5.32 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.85−5.97 (m, 1H), 7.34−7.45 (m, 6H), 7.68−7.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 20.85, 20.90, 26.8, 63.3, 67.9, 77.2, 82.2, 82.8, 104.8, 117.4, 127.7, 127.8, 129.78, 129.81, 133.35, 133.39, 134.0, 135.75, 135.78, 169.9, 170.2. Anal. Calcd for $C_{28}H_{36}O_7Si$: C, 65.60; H, 7.08. Found: C, 65.55; H, 7.21.

Allyl 2,3-Di-O-benzoyl-5-O-t-butyldiphenylsilyl-α-D-arabinofuranoside (5). A mixture of compound **4** (8.29 g, 16.2 mmol) and NaOMe (175 mg, 3.23 mmol) in MeOH (50 mL) was stirred at room temperature for 1 h. The reaction mixture was neutralized with DOWEX CCR-3 (H^+ mode) resin, filtered through Celite, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford allyl 5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranoside (6.79 g, 98%) as a colorless oil. R_f = 0.30 (hexane/EtOAc, 3:1, v/v); $[\alpha]_D^{20}$ = +184.3 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 9H), 3.00 (d, *J* = 11.2 Hz, 1H), 3.75 (dd, *J* = 11.6, 1.2 Hz, 1H), 3.83 (dd, *J* = 11.6, 2.4 Hz, 1H), 4.01−4.09 (m, 2H), 4.11−4.19 (m, 3H), 4.24 (dd, *J* = 12.8 5.2 Hz, 1H), 5.14 (s, 1H), 5.20 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.84−5.96 (m, 1H), 7.37−7.48 (m, 6H), 7.65−7.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 26.8, 64.2, 68.2, 78.1, 78.6, 87.6, 107.6, 117.8, 128.0, 128.1, 130.2, 130.3, 131.9, 132.0, 133.8, 135.7, 135.8. Anal. Calcd for $C_{24}H_{32}O_5Si$: C, 67.26; H, 7.53. Found: C, 67.25; H, 7.45.

To a solution of allyl 5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranoside (6.79 g, 15.8 mmol) in CH_2Cl_2 (50 mL) were added benzoyl chloride (5.52 mL, 47.5 mmol), pyridine (7.69 mL, 95.1 mmol), and 4-dimethylaminopyridine (387 mg, 3.17 mmol). After stirring at room

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temperature for 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layer was washed with 1N HCl (2 × 30 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL); dried over $MgSO_4$; and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 8:1) to afford compound **5** (9.49 g, 94%) as a white solid. R_f = 0.45 (hexane/EtOAc, 8:1, v/v); mp 113−114 °C; $[\alpha]_D^{20}$ = −92.7(c 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 9H), 4.01−4.09 (m, 2H), 4.12 (dd, J = 8.8, 6.0 Hz, 1H), 4.26−4.34 (m, 1H), 4.43 (dd, J = 9.6, 4.4 Hz, 1H), 5.22 (dd, J = 10.8, 1.6 Hz, 1H), 5.29 (s, 1H), 5.37 (dd, J = 17.2, 1.6 Hz, 1H), 5.53 (d, J = 1.2 Hz, 1H), 5.67 (dd, J = 5.2, 1.2 Hz, 1H), 5.90−6.03 (m, 1H), 7.29−7.58 (m, 12H), 7.71−7.77 (m, 4H), 7.96−8.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 26.9, 63.7, 67.9, 77.5, 82.6, 83.1, 105.0, 117.4, 127.8, 128.4, 128.9, 129.3, 129.6, 129.8, 130.0, 130.6, 133.2, 133.3, 133.4, 134.0, 134.6, 135.7, 165.5, 165.7. Anal. Calcd for $C_{38}H_{40}O_7Si$: C, 71.67; H, 6.33. Found: C, 71.63; H, 6.15.

*Allyl 2,3-Di-O-benzoyl-α-D-arabinofuranoside (**6**).* To a solution of compound **5** (7.26 g, 11.4 mmol) in CH_2Cl_2 (10 mL) was added 2% HCl (40 mL) in MeOH (40 mL). The resulting solution was stirred at room temperature for 10 h, and then the reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (3 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **6** (4.09 g, 90%) as a colorless oil. R_f = 0.30 (hexane/EtOAc, 3:1, v/v); $[\alpha]_D^{20}$ = −34.7 (c 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (dd, J = 7.6, 5.2 Hz, 1H), 3.94−4.06 (m, 2H), 4.12 (dd, J = 13.2, 6.0 Hz, 1H), 4.30 (dd, J = 13.2, 4.8 Hz, 1H), 4.35 (dd, J = 8.8, 4.4 Hz, 1H), 5.22 (dd, J = 10.4, 1.6 Hz, 1H), 5.30 (s, 1H), 5.37 (dd, J = 17.2, 1.6 Hz, 1H), 5.46 (d, J = 4.8 Hz, 1H), 5.57 (d, J = 1.2 Hz, 1H), 5.89−6.01 (m, 1H), 7.42−7.49 (m, 4H), 7.55−7.62 (m, 2H), 8.02−8.11 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.5, 68.0, 78.0, 82.1, 83.8, 104.9, 117.6, 128.6, 128.7, 129.2, 129.3, 130.0, 130.1, 133.7, 133.8, 165.5, 166.4. Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.26; H, 5.54.

*Allyl 2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranoside (**7**).* To a solution of compound **6** (7.80 g, 19.6 mmol) in CH_2Cl_2 (50 mL) were added levulinic acid (3.41 g, 29.4 mmol), *N*,*N*-diisopropylcarbodimide (4.55 mL, 29.4 mmol), and 4-dimethylaminopyridine (239 mg, 1.96 mmol). After stirring at room temperature for 4 h, the reaction mixture was quenched with H_2O (30 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **7** (9.04 g, 93%) as a colorless oil. R_f = 0.25 (hexane/EtOAc, 3:1, v/v); $[\alpha]_D^{20}$ = −6.6 (c 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.59−2.65 (m, 2H), 2.71−2.77 (m, 2H), 4.12 (dd, J = 13.2, 6.0 Hz, 1H), 4.31 (dd, J = 12.8, 4.8 Hz, 1H), 4.41 (dd, J = 11.6, 5.6 Hz, 1H), 4.48 (dd, J = 8.4, 5.2 Hz, 1H), 4.57 (dd, J = 11.6, 3.6 Hz, 1H), 5.23 (dd, J = 10.4, 1.6 Hz, 1H), 5.31 (s, 1H), 5.38 (dd, J = 17.2, 1.6 Hz, 1H), 5.42 (d, J = 4.8 Hz, 1H), 5.53 (d, J = 0.8 Hz, 1H), 5.89−6.02 (m, 1H), 7.43−7.50 (m, 4H), 7.56−7.63 (m, 2H), 8.04−8.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 29.9, 38.0, 63.9, 68.1, 77.9, 81.1, 81.9, 105.1, 117.5, 128.6, 128.7, 129.2, 129.3, 130.0, 130.1, 133.65, 133.74, 133.8, 165.5, 165.9, 172.6, 206.5. Anal. Calcd for $C_{27}H_{28}O_9$: C, 65.31; H, 5.68. Found: C, 65.23; H, 5.66.

*2,3-Di-O-benzoyl-5-O-levulinyl-α/β-D-arabinofuranose (**8**).* A mixture of compound **7** (7.04 g, 14.2 mmol) and $PdCl_2$ (503 mg, 2.84 mmol) in MeOH/H_2O (100 mL, 10:1, v/v) was stirred at room temperature for 8 h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:2) to afford compound **8** (5.51 g, 85%, α/β = 2:1) as a colorless amorphous form. R_f = 0.20 (hexane/EtOAc, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.18 (s, 1.5H), 2.58−2.88 (m, 6H), 3.85 (d, J = 3.6 Hz, 1H), 4.26−4.31 (m, 0.5H), 4.35−4.45 (m, 2H), 4.58 (dd, J = 11.6, 3.6 Hz, 1H), 4.61−4.66 (m, 1H), 4.72 (dd, J = 12.0, 4.0 Hz, 0.5H), 5.41 (d, J = 4.0 Hz, 1H), 5.50 (dd, J = 6.8, 4.4 Hz, 0.5H), 5.52 (s, 1H), 5.66 (d, J = 4.0 Hz, 1H), 5.80 (t, J = 4.8 Hz, 0.5H), 5.86 (t, J = 6.0 Hz, 0.5H), 7.40−7.49 (m, 6H), 7.53−7.62 (m, 3H), 8.03−8.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 28.0, 29.89, 29.93, 37.96, 38.02, 64.0, 64.6, 75.9, 77.5, 77.9, 78.8, 81.2, 82.3, 95.2, 101.0, 128.57, 128.61, 128.63, 128.7, 129.0, 129.1, 129.96, 130.04, 130.1, 133.6, 133.70, 133.72, 133.8, 165.6, 165.9, 165.95, 166.02, 172.6, 172.8, 206.8, 207.8. HRMS (ESI) calcd for $C_{24}H_{24}O_9Na$ $[M + Na]^+$: 479.1318. Found: 479.1317.

*Allyl (2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**9**).* A solution of **8** (1.35 g, 2.96 mmol, 1.0 equiv), *t*-butylphthalic anhydride (906 mg, 4.44 mmol, 1.5 equiv), and DBU (0.538 mL, 3.55 mmol, 1.2 equiv) in CH_2Cl_2 (15 mL) in the presence of 4 Å molecular sieves was stirred for 15 min at room temperature and cooled down to −40 °C. Then a solution of a glycosyl acceptor **6** (1.53 g, 3.84 mmol, 1.3 equiv) and DTBMP (1.52 g, 7.39 mmol, 2.5 equiv) in CH_2Cl_2 (15 mL) were added sequentially at −40 °C and the resulting solution was stirred for further 15 min at −40 °C. After dropwise addition of a solution of Tf_2O (0.647 mL, 3.84 mmol, 1.3 equiv) in CH_2Cl_2 (6.5 mL) to the above solution via cannula, the reaction mixture was stirred at −40 °C for 15 min, allowed to warm up over 1 h to 0 °C, quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to afford compound **9** (1.81 g, 73%) as a colorless oil. R_f = 0.45 (hexane/EtOAc, 3:2, v/v); $[\alpha]_D^{20}$ = −2.8 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.56−2.63 (m, 2H), 2.68−2.75 (m, 2H), 3.96 (dd, J = 11.2, 2.8 Hz, 1H), 4.09 (dd, J = 12.8, 6.0 Hz, 1H), 4.22 (dd, J = 11.2, 4.4 Hz, 1H), 4.28 (dd, J = 13.2, 4.8 Hz, 1H), 4.40 (dd, J = 12.0, 5.2 Hz, 1H), 4.48 (dd, J = 7.2, 4.4 Hz, 1H), 4.53−4.65 (m, 2H), 5.21 (dd, J = 10.4, 0.8 Hz, 1H), 5.28 (s, 1H), 5.35 (dd, J = 17.2, 1.2 Hz, 1H), 5.40 (d, J = 4.4 Hz, 1H), 5.43 (s, 1H), 5.55 (s, 1H), 5.61 (s, 1H), 5.63 (d, J = 5.2 Hz, 1H), 5.88−6.01 (m, 1H), 7.24−7.64 (m, 12H), 7.90−8.11 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.9, 38.0, 63.8, 66.3, 67.9, 77.5, 77.8, 81.3, 81.5, 82.0, 82.1, 104.9, 106.0, 117.5, 128.5, 128.58, 128.63, 128.7, 129.1, 129.15, 129.23, 129.4, 129.92, 129.94, 130.00, 130.03, 133.5, 133.55, 133.59, 133.7, 133.9, 165.2, 165.5, 165.80, 165.83, 172.6, 206.5. Anal. Calcd for $C_{46}H_{44}O_{15}$: C, 66.02; H, 5.30. Found: C, 66.00; H, 5.28.

*(2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-2,3-di-O-benzoyl-α/β-D-arabinofuranose (**10**).* A mixture of compound **9** (8.55 g, 10.2 mmol) and $PdCl_2$ (362 mg, 2.04 mmol) in MeOH/H_2O (100 mL, 10:1, v/v) was stirred at room temperature for 8 h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to afford compound **10** (7.16 g, 88%, α/β = 2:1) as a colorless amorphous form. R_f = 0.30 (hexane/EtOAc, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.127 (s, 3H), 2.133 (s, 1.5H), 2.55−2.65 (m, 3H), 2.68−2.76 (m, 3H), 3.73 (d, J = 3.6 Hz, 1H), 3.96 (dd, J = 11.2, 2.8 Hz, 1H), 4.00 (dd, J = 11.6, 2.4 Hz, 0.5H), 4.19 (dd, J = 11.2, 4.8 Hz, 1H), 4.23 (dd, J = 9.6, 4.4 Hz, 0.5H), 4.29−4.33 (m, 0.5H), 4.35 (d, J = 7.6 Hz, 0.5H), 4.37−4.44 (m, 1.5H), 4.55−4.69 (m, 4H), 5.38−5.44 (m, 2.5H), 5.47 (d, J = 4.4 Hz, 0.5H), 5.52−5.57 (m, 2H), 5.58−5.65 (m, 3H), 5.77 (dd, J = 7.2, 4.8 Hz, 0.5H), 5.98 (t, J = 6.0 Hz, 0.5H), 7.28−7.61 (m, 18H), 7.93−8.08 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.9, 38.0, 63.77, 63.82, 66.7, 67.8, 75.8, 77.45, 77.50, 77.7, 78.0, 79.9, 81.0, 81.2, 81.5, 82.0, 82.1, 82.5, 95.3, 100.9, 106.1, 106.4, 128.4, 128.48, 128.52, 128.54, 128.60, 128.63, 128.7, 128.88, 128.94, 128.99, 129.03, 129.11, 129.14, 129.2, 129.88, 129.93, 129.98, 130.01, 130.1, 133.5, 133.56, 133.59, 133.64, 133.7, 133.9, 165.2, 165.6, 165.7, 165.76, 165.79, 165.87, 165.94, 166.0, 172.58, 172.60, 206.7, 206.8. HRMS (ESI) calcd for $C_{43}H_{40}O_{15}Na$ $[M + Na]^+$: 819.2265. Found: 819.2265.

*Allyl [(2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**11**).* A solution of **10** (966 mg, 1.21 mmol, 1.0 equiv), *t*-butylphthalic anhydride (371 mg, 1.82 mmol, 1.5 equiv), and DBU (0.220 mL, 1.45 mmol, 1.2 equiv) in CH_2Cl_2 (15 mL) in the presence of 4 Å molecular sieves was stirred for 15 min at

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room temperature and cooled down to −40 °C. Then a solution of a glycosyl acceptor **6** (628 mg, 1.58 mmol, 1.3 equiv) and DTBMP (622 mg, 3.03 mmol, 2.5 equiv) in CH_2Cl_2 (10 mL) were added sequentially at −40 °C and the resulting solution was stirred for further 15 min at −40 °C. After dropwise addition of a solution of Tf_2O (0.265 mL, 1.58 mmol, 1.3 equiv) in CH_2Cl_2 (3 mL) to the above solution via cannula, the reaction mixture was stirred at −40 °C for 15 min, allowed to warm up over 1 h to 0 °C, quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:2) to afford compound **11** (1.10 g, 77%) as a colorless amorphous form. R_f = 0.40 (hexane/EtOAc, 1:1, v/v); $[\alpha]_D^{20}$ = +4.0 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.55−2.61 (m, 2H), 2.67−2.73 (m, 2H), 3.93 (dd, J = 10.8, 2.4 Hz, 1H), 3.96 (dd, J = 10.8, 2.8 Hz, 1H), 4.09 (dd, J = 13.2, 6.0 Hz, 1H), 4.16−4.24 (m, 2H), 4.24−4.31 (m, 1H), 4.39 (dd, J = 11.2, 4.8 Hz, 1H), 4.43−4.49 (m, 1H), 4.52−4.65(m, 3H), 5.20 (dd, J = 10.4, 1.2 Hz, 1H), 5.27 (s, 1H), 5.35 (dd, J = 17.2, 1.6 Hz, 1H), 5.38−5.42 (m, 2H), 5.44 (s, 1H), 5.55 (d, J = 1.2 Hz, 1H), 5.60 (s, 1H), 5.61−5.67 (m, 3H), 5.87−6.00 (m, 1H), 7.24−7.30 (m, 4H), 7.37−7.61 (m, 14H), 7.88−7.94 (m, 4H), 7.99−8.08 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.9, 38.0, 63.7, 66.0, 66.2, 67.9, 77.4, 77.8, 81.2, 81.6, 81.7, 82.0, 82.1, 104.9, 105.9, 106.1, 117.4, 128.39, 128.41, 128.5, 128.6, 128.7, 129.0, 129.2, 129.3, 129.4, 129.88, 129.92, 129.97, 130.01, 133.3, 133.4, 133.5, 133.7, 133.9, 165.2, 165.3, 165.5, 165.75, 165.80, 172.6, 206.4. Anal. Calcd for $C_{65}H_{60}O_{21}$: C, 66.32; H, 5.14. Found: C, 66.40; H, 5.25.

*[(2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α/β-D-arabinofuranose (**12**).* A mixture of compound **11** (3.98 g, 3.38 mmol) and $PdCl_2$ (120 mg, 0.677 mmol) in MeOH/H_2O (40 mL, 10:1, v/v) was stirred at room temperature for 8 h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to afford compound **12** (3.35 g, 87%, α/β= 2:1) as a colorless oil. R_f = 0.28 (hexane/EtOAc, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 9H), 2.55−2.62 (m, 6H), 2.68−2.72 (m, 6H), 3.28 (d, J = 3.6 Hz, 1H), 3.90−3.99 (m, 5H), 4.01 (dd, J = 11.6, 2.8 Hz, 1H), 4.14−4.24 (m, 6H), 4.26−4.31 (m, 1H), 4.37−4.43 (m, 3H), 4.53−4.64 (m, 10H), 4.67−4.72 (m, 1H), 5.38−5.45 (m, 9H), 5.52−5.63 (m, 16H), 5.68 (d, J = 5.2 Hz, 1H), 5.76 (dd, J = 7.6, 4.8 Hz, 1H), 5.97 (t, J = 6.0 Hz, 1H), 7.27−7.60 (m, 54H), 7.90−8.07 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 29.9, 38.0, 63.8, 66.4, 66.5, 67.5, 75.8, 77.1, 77.4, 77.5, 77.8, 78.2, 80.1, 81.2, 81.3, 81.6, 81.8, 81.9, 82.1, 82.3, 82.5, 95.4, 101.0, 105.97, 106.04, 106.1, 106.3, 128.45, 128.51, 128.54, 128.61, 128.63, 128.65, 128.68, 128.9, 129.05, 129.07, 129.11, 129.16, 129.18, 129.22, 129.24, 129.3, 129.96, 130.00, 130.02, 130.1, 133.39, 133.43, 133.5, 133.58, 133.61, 133.7, 133.8, 165.3, 165.4, 165.7, 165.79, 165.82, 165.9, 166.0, 166.1, 172.6, 206.5. Anal. Calcd for $C_{62}H_{56}O_{21}$: C, 65.49; H, 4.96. Found: C, 65.50; H, 4.75.

*Allyl [(2,3-Di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**13**).* A solution of compound **11** (4.21 g, 3.58 mmol) and 66% hydrazine-acetic acid (1:2, v/v, 15 mL) in THF-MeOH (10:1, v/v, 44 mL) was stirred at room temperature for 1h. The solvent was removed and the resulting oil was dissolved in EtOAc (70 mL). The EtOAc solution was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc, 2:1) to afford compound **13** (3.48 g, 90%) as a colorless amorphous form. R_f = 0.63 (hexane/EtOAc, 1:1, v/v); $[\alpha]_D^{20}$ = −5.3 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (brs, 1H), 3.89−4.04 (m, 4H), 4.09 (dd, J = 13.2, 6.0 Hz, 1H), 4.16−4.24 (m, 2H), 4.25−4.32 (m, 1H), 4.43−4.51 (m, 2H), 4.63(dd, J = 7.2, 4.4 Hz, 1H), 5.20 (dd, J = 10.8, 1.2 Hz, 1H), 5.27 (s, 1H), 5.35 (dd, J = 17.2, 1.6 Hz, 1H), 5.40−5.45 (m, 3H), 5.56 (s, 1H), 5.61−5.68 (m, 4H), 5.87−6.00 (m, 1H), 7.23−7.31 (m, 4H), 7.37−7.61 (m, 14H), 7.87−7.94 (m, 4H), 8.00−8.08 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.4, 66.0, 66.2, 67.9, 77.4, 77.5, 77.8, 81.7, 81.8, 82.00, 82.02, 82.1, 83.8, 104.9, 105.86, 105.91, 117.5, 128.39, 128.42, 128.56, 128.63, 129.07, 129.14, 129.16, 129.19, 129.3, 129.4, 129.88, 129.93, 129.97, 130.01, 133.35, 133.41, 133.5, 133.57, 133.64, 133.9, 165.2, 165.3, 165.5, 165.80, 165.84, 166.2. Anal. Calcd for $C_{60}H_{54}O_{19}$: C, 66.78; H, 5.04. Found: C, 66.81; H, 4.87.

*Allyl [(2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**14**).* A solution of **12** (942 mg, 0.828 mmol, 1.0 equiv), *t*-butylphthalic anhydride (254 mg, 1.24 mmol, 1.5 equiv), and DBU (0.151 mL, 0.994 mmol, 1.2 equiv) in CH_2Cl_2 (15 mL) in the presence of 4 Å molecular sieves was stirred for 15 min at room temperature and cooled down to −40 °C. Then a solution of a glycosyl acceptor **13** (1.16 g, 1.08 mmol, 1.3 equiv) and DTBMP (425 mg, 2.07 mmol, 2.5 equiv) in CH_2Cl_2 (15 mL) were added sequentially at −40 °C and the resulting solution was stirred for further 15 min at −40 °C. After dropwise addition of a solution of Tf_2O (0.181 mL, 1.08 mmol, 1.3 equiv) in CH_2Cl_2 (2 mL) to the above solution via cannula, the reaction mixture was stirred at −40 °C for 15 min, allowed to warm up over 1 h to 0 °C, quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:2) to afford compound **14** (1.19 g, 65%) as a colorless amorphous form. R_f = 0.35 (hexane/EtOAc, 1:1, v/v); $[\alpha]_D^{20}$ = +3.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.53−2.61 (m, 2H), 2.66−2.73 (m, 2H), 3.85−3.96 (m, 5H), 4.08 (dd, J = 12.8, 5.6 Hz, 1H), 4.12−4.22 (m, 5H), 4.27 (dd, J = 13.2, 4.8 Hz, 1H), 4.37 (dd, J = 11.2, 4.8 Hz, 1H), 4.43−4.49 (m, 1H), 4.51−4.63 (m, 6H), 5.20 (d, J = 10.4 Hz, 1H), 5.26 (s, 1H), 5.31−5.42 (m, 7H), 5.53−5.66 (m, 11H), 5.87−5.99 (m, 1H), 7.20−7.61 (m, 36H), 7.83−8.08 (m. 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 29.9, 38.0, 63.8, 65.9, 66.0, 66.2, 67.9, 77.3, 77.36, 77.41, 77.7, 81.2, 81.5, 81.7, 82.0, 82.1, 82.2, 104.9, 105.9, 106.0, 106.1, 117.5, 128.4, 128.6, 128.7, 129.0, 129.15, 129.21, 129.3, 129.4, 129.99, 130.03, 133.25, 133.31, 133.4, 133.48, 133.52, 133.7, 133.9, 165.19, 165.24, 165.3, 165.5, 165.7, 165.75, 165.77, 165.82, 172.6, 206.5. Anal. Calcd for $C_{122}H_{108}O_{39}$: C, 66.66; H, 4.95. Found: C, 66.53; H, 5.14.

*Allyl [(2,3-Di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**15**).* A solution of compound **14** (2.24 g, 1.02 mmol) and 66% hydrazine-acetic acid (1:2, v/v, 9 mL) in THF-MeOH (10:1, v/v, 22 mL) was stirred at room temperature for 1 h. The solvent was removed and the resulting oil was dissolved in EtOAc (30 mL). The EtOAc solution was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (30 mL), dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc/CH_2Cl_2, 5:2:2) to afford compound **15** (1.99 g, 93%) as a colorless amorphous form. R_f = 0.23 (hexane/EtOAc/CH_2Cl_2, 5:2:2, v/v/v); $[\alpha]_D^{20}$ = +7.4 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (brs, 1H), 3.87−4.01 (m, 7H), 4.08 (dd, J = 13.2, 6.0 Hz, 1H), 4.13−4.22 (m, 5H), 4.27 (dd, J = 13.2, 4.8 Hz, 1H), 4.43−4.49 (m, 2H), 4.55−4.63 (m, 4H), 5.20 (d, J = 10.4 Hz, 1H), 5.27 (s, 1H), 5.31−5.44 (m, 7H), 5.56 (s, 1H), 5.60−5.67 (m, 10H), 5.87−6.00 (m, 1H), 7.20−7.59 (m, 36H), 7.83−8.08 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.4, 65.9, 66.0, 66.2, 67.9, 77.3, 77.35, 77.39, 77.8, 81.7, 81.8, 82.0, 82.1, 82.2, 83.7, 104.9, 105.7, 105.89, 105.94, 106.0, 117.4, 128.0, 128.3, 128.4, 128.5, 128.6, 128.9, 129.06, 129.09, 129.14, 129.17, 129.21, 129.3, 129.4, 129.6, 129.85, 129.92, 129.95, 130.00, 133.2, 133.25, 133.27, 133.4, 133.45, 133.50, 133.6, 133.9, 165.19, 165.22, 165.3, 165.5, 165.69, 165.72, 165.8, 166.1. Anal. Calcd for $C_{117}H_{102}O_{37}$: C, 66.92; H, 4.90. Found: C, 66.97; H, 5.10.

Allyl [(2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-

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*benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**16**).* A solution of **12** (859 mg, 0.755 mmol, 1.0 equiv), *t*-butylphthalic anhydride (231 mg, 1.13 mmol, 1.5 equiv), and DBU (0.137 mL, 0.907 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) in the presence of 4 Å molecular sieves was stirred for 15 min at room temperature and cooled down to −40 °C. Then a solution of a glycosyl acceptor **15** (2.06 g, 0.982 mmol, 1.3 equiv) and DTBMP (388 mg, 1.89 mmol, 2.5 equiv) in CH_2Cl_2 (15 mL) were added sequentially at −40 °C and the resulting solution was stirred for further 15 min at −40 °C. After dropwise addition of a solution of Tf_2O (0.165 mL, 0.982 mmol, 1.3 equiv) in CH_2Cl_2 (2 mL) to the above solution via cannula, the reaction mixture was stirred at −40 °C for 15 min, allowed to warm up over 1 h to 0 °C, quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH_2Cl_2, 5:2:2) to afford compound **16** (1.53 g, 63%) as a colorless amorphous form. R_f = 0.38 (hexane/EtOAc/CH_2Cl_2, 2:1:1, v/v/v); $[\alpha]_D^{20}$ = +0.25 (c 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.53−2.60 (m, 2H), 2.65−2.72 (m, 2H), 3.84−3.95 (m, 8H), 4.07 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.11−4.21 (m, 8H), 4.27 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.37 (dd, *J* = 10.8, 4.4 Hz, 1H), 4.43−4.48 (m, 1H), 4.50−4.63 (m, 9H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.26 (s, 1H), 5.31−5.42 (m, 10H), 5.54 (s, 1H), 5.57 (s, 1H), 5.59−5.66 (m, 15H), 5.86−5.99 (m, 1H), 7.18−7.60 (m, 54H), 7.81−8.08 (m. 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.9, 38.0, 63.7, 65.9, 66.0, 66.1, 67.9, 77.2, 77.3, 77.4, 77.7, 81.2, 81.5, 81.6, 81.7, 82.0, 82.1, 82.2, 104.9, 105.9, 106.0, 106.1, 117.5, 128.36, 128.41, 128.6, 128.7, 129.0, 129.1, 129.21, 129.24, 129.4, 129.9, 129.98, 130.02, 133.2, 133.3, 133.4, 133.46, 133.52, 133.7, 133.9, 165.17, 165.20, 165.3, 165.5, 165.69, 165.71, 165.73, 165.75, 165.80, 172.6, 206.4. Anal. Calcd for $C_{179}H_{156}O_{57}$: C, 66.79; H, 4.88. Found: C, 66.72; H, 4.92.

*Allyl [(2,3-Di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**17**).* A solution of compound **16** (2.50 g, 0.777 mmol) and 66% hydrazine-acetic acid (1:2, v/v, 9 mL) in THF-MeOH (10:1, v/v, 22 mL) was stirred at room temperature for 1 h. The solvent was removed and the resulting oil was dissolved in EtOAc (30 mL). The EtOAc solution was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (30 mL), dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc/CH_2Cl_2, 5:2:2) to afford compound **17** (2.19 g, 90%) as a colorless amorphous form. R_f = 0.18 (hexane/EtOAc/CH_2Cl_2, 5:2:2, v/v/v); $[\alpha]_D^{20}$ = +0.29 (c 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (brs, 1H), 3.85−4.00 (m, 10H), 4.08 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.12−4.21 (m, 8H), 4.27 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.42−4.48 (m, 2H), 4.53−4.62 (m, 7H), 5.19 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.26 (s, 1H), 5.31−5.42 (m, 10H), 5.55 (s, 1H), 5.59−5.65 (m, 16H), 5.87−5.99 (m, 1H), 7.18−7.59 (m, 54H), 7.83−8.05 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.4, 65.9, 66.0, 66.2, 67.9, 77.3, 77.35, 77.40, 77.8, 81.6, 81.7, 81.8, 81.9, 82.0, 82.1, 82.2, 83.7, 104.9, 105.7, 105.9, 106.0, 117.5, 128.36, 128.42, 128.56, 128.60, 129.06, 129.09, 129.14, 129.18, 129.22, 129.3, 129.4, 129.87, 129.94, 129.98, 130.03, 133.2, 133.3, 133.4, 133.47, 133.54, 133.6, 133.9, 165.21, 165.23, 165.3, 165.5, 165.70, 165.74, 165.76, 165.81, 166.2. Anal. Calcd for $C_{174}H_{150}O_{55}$: C, 66.96; H, 4.84. Found: C, 66.93; H, 4.82.

*Allyl [(2,3-Di-O-benzoyl-5-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**18**).* A solution of **12** (490 mg, 0.431 mmol, 1.0 equiv), *t*-butylphthalic anhydride (132 mg, 0.646 mmol, 1.5 equiv), and DBU (78.3 μL, 0.517 mmol, 1.2 equiv) in CH_2Cl_2 (7 mL) in the presence of 4 Å molecular sieves was stirred for 15 min at room temperature and cooled down to −40 °C. Then a solution of a glycosyl acceptor **17** (1.75 g, 0.560 mmol, 1.3 equiv) and DTBMP (221 mg, 1.08 mmol, 2.5 equiv) in CH_2Cl_2 (15 mL) were added sequentially at −40 °C and the resulting solution was stirred for further 15 min at −40 °C. After dropwise addition of a solution of Tf_2O (94.2 μL, 0.560 mmol, 1.3 equiv) in CH_2Cl_2 (1 mL) to the above solution via cannula, the reaction mixture was stirred at −40 °C for 15 min, allowed to warm up over 1 h to 0 °C, quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH_2Cl_2, 2:1:1) to afford compound **18** (1.23 g, 67%) as a colorless amorphous form. R_f = 0.23 (hexane/EtOAc/CH_2Cl_2, 2:1:1, v/v/v); $[\alpha]_D^{20}$ = +0.33 (c 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.53−2.60 (m, 2H), 2.65−2.72 (m, 2H), 3.84−3.95 (m, 10H), 4.08 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.12−4.21 (m, 10H), 4.27 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.38 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.43−4.48 (m, 1H), 4.52−4.62 (m, 11H), 5.19 (d, *J* = 11.2 Hz, 1H), 5.26 (s, 1H), 5.31−5.42 (m, 12H), 5.54−5.68 (m, 22H), 5.87−5.99 (m, 1H), 7.18−7.59 (m, 72H), 7.82−8.08 (m, 48H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.9, 38.0, 63.7, 65.9, 66.0, 66.2, 67.9, 77.26, 77.32, 77.36, 77.42, 77.7, 81.2, 81.5, 81.6, 81.7, 82.0, 82.1, 82.18, 82.19, 104.9, 105.9, 106.0, 106.1, 117.5, 128.35, 128.42, 128.55, 128.59, 128.7, 129.0, 129.16, 129.23, 129.4, 129.86, 129.93, 129.98, 130.02, 133.2, 133.4, 133.45, 133.50, 133.7, 133.9, 165.2, 165.3, 165.5, 165.7, 165.75, 165.79, 172.6, 206.4. Anal. Calcd for $C_{236}H_{204}O_{75}$: C, 66.85; H, 4.85. Found: C, 66.81; H, 4.92. MALDI-TOF: Calcd for $C_{236}H_{204}O_{75}Na$ $[M+Na]^+$: 4263.09, Found: 4263.13.

*Allyl [(2,3-Di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**19**).* A solution of compound **18** (1.88 g, 0.443 mmol) and 66% hydrazine-acetic acid (1:2, v/v, 6 mL) in THF-MeOH (10:1, v/v, 11 mL) was stirred at room temperature for 1 h. The solvent was removed and the resulting oil was dissolved in EtOAc (30 mL). The EtOAc solution was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (30 mL), dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc/CH_2Cl_2, 2:1:1) to afford compound **19** (1.66 g, 90%) as a colorless amorphous form. R_f = 0.23 (hexane/EtOAc/CH_2Cl_2, 2:1:1, v/v/v); $[\alpha]_D^{20}$ = +0.21 (c 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.82−4.02 (m, 13H), 4.08 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.11−4.22 (m, 11H), 4.27 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.42−4.48 (m, 2H), 4.51−4.63 (m, 10H), 5.20 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.26 (s, 1H), 5.30−5.43 (m, 13H), 5.55 (s, 1H), 5.56−5.68 (m, 22H), 5.87−5.99 (m, 1H), 7.16−7.60 (m, 72H), 7.81−8.07 (m, 48H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.4, 65.86, 65.91, 66.0, 66.2, 67.9, 77.2, 77.3, 77.4, 77.8, 81.6, 81.7, 81.8, 81.9, 82.0, 82.1, 82.2, 83.7, 104.9, 105.7, 105.88, 105.92, 106.0, 117.5, 128.35, 128.38, 128.42, 128.56, 128.59, 128.62, 128.63, 129.05, 129.08, 129.12, 129.2, 129.3, 129.4, 129.86, 129.93, 129.97, 130.02, 133.2, 133.27, 133.29, 133.4, 133.45, 133.51, 133.53, 133.6, 133.9, 165.18, 165.21, 165.3, 165.5, 165.68, 165.72, 165.74, 165.8, 166.2. Anal. Calcd for $C_{231}H_{198}O_{73}$: C, 66.98; H, 4.82. Found: C, 66.96; H, 4.77. MALDI-TOF: Calcd for $C_{231}H_{198}O_{73}Na$ $[M+Na]^+$: 4164.99, Found: 4164.74.

*p-Methoxyphenyl 3,4,6-tri-O-acetyl-2-deoxy-2-azido-α/β-D-glucopyranoside (**S2**).* To a stirred mixture of acetyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-azido-α/β-D-glucopyranoside (**S1**)[35] (4.09 g, 11.0 mmol) and *p*-methoxyphenol (2.04 g, 16.4 mmol) in CH_2Cl_2 (50 mL) was added dropwise TfOH (0.97 mL, 11.0 mmol) at 0 °C for 30 min. The reaction mixture was stirred at room temperature for 5 h, quenched

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with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to afford compound **S2** (4.13 g, 86%, α/β = 10:1): α form, colorless amorphous form. R_f = 0.28 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 2111, 1747, 1507, 1367, 1212, 1034, 829 cm^{-1}; $[\alpha]_D^{20}$ = +1.78 (c 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.06 (s, 3H), 2.12 (s, 3H), 3.45 (dd, J = 10.8, 3.2 Hz, 1H), 3.78 (s, 3H), 4.08 (d, J = 12.0 Hz, 1H), 4.17−4.23 (m, 1H), 4.29 (dd, J = 12.4, 4.8 Hz, 1H), 5.13 (t, J = 9.6 Hz, 1H), 5.51 (d, J = 3.2 Hz, 1H), 5.69 (t, J = 10.0 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 20.7, 20.8, 55.7, 60.8, 61.8, 68.3, 68.5, 70.4, 97.5 (J_{C-H} = 174.1 Hz), 114.8, 118.0, 150.1, 155.8, 169.7, 170.1, 170.5. Anal. Calcd for $C_{19}H_{23}N_3O_9$: C, 52.17; H, 5.30; N, 9.61. Found: C, 52.17; H, 5.33; N, 9.48.β form, colorless amorphous form, R_f = 0.20 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 2113, 1748, 1507, 1367, 1212, 1037, 829 cm^{-1}; $[\alpha]_D^{20}$ = +0.13 (c 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 3.72−3.82 (m, 2H), 3.77 (s, 3H), 4.14 (dd, J = 12.0, 2.0 Hz, 1H), 4.30 (dd, J = 12.0, 5.2 Hz, 1H), 4.82 (d, J = 8.0 Hz, 1H), 5.01−5.10 (m, 2H), 6.81−6.87 (m, 2H), 7.00−7.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 20.69, 20.70, 55.6, 62.0, 63.6, 68.4, 71.9, 72.4, 101.6 (J_{C-H} = 165.9 Hz), 114.7, 118.8, 150.8, 156.0, 169.6, 169.9, 170.5. Anal. Calcd for $C_{19}H_{23}N_3O_9$: C, 52.17; H, 5.30; N, 9.61. Found: C, 52.14; H, 5.25; N, 9.49.

*p-Methoxyphenyl 4,6-O-benzylidene-2-deoxy-2-azido-α-D-glucopyranoside (**S3**).* A mixture of compound **S2** (5.75 g, 13.1 mmol) and NaOMe (142 mg, 2.63 mmol) in MeOH−CH_2Cl_2 (10:1, v/v, 55 mL) was stirred at room temperature for 1 h. The reaction mixture was neutralized with DOWEX CCR-3 (H^+ mode) resin, filtered through Celite, and concentrated in vacuo. R_f = 0.08 (hexane/EtOAc, 1:2, v/v); ^1H NMR (400 MHz, CD_3OD) δ 3.24 (dd, J = 10.4, 3.2 Hz, 1H), 3.47 (t, J = 8.8 Hz, 1H), 3.69−3.81 (m, 3H), 3.75 (s, 3H), 4.03 (dd, J = 10.4, 8.8 Hz, 1H), 5.41 (d, J = 3.2 Hz, 1H), 6.81−6.88 (m, 2H), 7.04−7.10 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 54.0, 60.1, 62.3, 69.7, 70.5, 72.4, 97.7, 113.5, 117.4, 150.2, 154.8.

The residue was dissolved in DMF (30 mL) containing benzaldehyde dimethyl acetal (2.90 mL, 19.3 mmol) and CSA (599 mg, 2.58 mmol), and the solution was stirred for 10 h at 60−65 °C. The reaction mixture was quenched with water (5 mL) and diluted with EtOAc (50 mL). The combined organic layer was washed with saturated aqueous NH_4Cl and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **S3** (4.78 g, 91%) as a white solid. R_f = 0.30 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 3371, 3014, 2108, 1508, 1377, 1209, 1108, 1094, 1034, 1019, 982, 831 cm^{-1}; $[\alpha]_D^{20}$ = +1.10 (c 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.96 (d, J = 2.0 Hz, 1H), 3.38 (dd, J = 10.0, 3.6 Hz, 1H), 3.58 (t, J = 9.2 Hz, 1H), 3.73 (t, J = 10.0 Hz, 1H), 3.88 (s, 3H), 4.00−4.09 (m, 1H), 4.25 (dd, J = 10.4, 4.8 Hz, 1H), 4.39 (dt, J = 9.6, 2.0 Hz, 1H), 5.43 (d, J = 3.6 Hz, 1H), 5.55 (s, 1H), 6.82−6.88 (m, 2H), 7.00−7.05 (m, 2H), 7.35−7.41 (m, 3H), 7.46−7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 63.0, 63.1, 68.78, 68.84, 81.8, 98.4 (J_{C-H} = 173.8 Hz), 102.3, 114.9, 118.3, 126.4, 128.5, 129.6, 136.9, 150.4, 155.7. Anal. Calcd for $C_{20}H_{21}N_3O_6$: C, 60.14; H, 5.30; N, 10.52. Found: C, 60.15; H, 5.32; N, 10.47.

*p-Methoxyphenyl 3-O-benzoyl-4,6-O-benzylidene-2-deoxy-2-azido-α-D-glucopyranoside (**S4**).* To a solution of compound **S3** (5.46 g, 13.7 mmol) in CH_2Cl_2 (50 mL) were added benzoyl chloride (3.17 mL, 27.3 mmol), pyridine (4.42 mL, 54.7 mmol), and 4-dimethylaminopyridine (334 mg, 2.73 mmol). After stirring at room temperature for 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layer was washed with 1N HCl (2 × 30 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL); dried over $MgSO_4$; and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **S4** (6.51 g, 95%) as a white solid. R_f = 0.35 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 3011, 2109, 1728, 1507, 1367, 1214, 1179, 1094, 1035, 828 cm^{-1}; $[\alpha]_D^{20}$ = +1.80 (c 0.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.50 (dd, J = 10.4, 3.2 Hz, 1H), 3.76 (s, 3H), 3.80 (t, J = 10.0 Hz, 1H), 3.89 (t, J = 9.6 Hz, 1H), 4.19−4.33 (m, 2H), 5.53 (s, 1H), 5.58 (d, J = 3.6 Hz, 1H), 6.07 (t, J = 10.0 Hz, 1H), 6.82−6.89 (m, 2H), 7.05−7.12 (m, 2H), 7.25−7.32 (m, 3H), 7.37−7.47 (m, 4H), 7.52−7.59 (m, 1H), 8.08−8.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 61.8, 63.5, 68.7, 69.5, 79.5, 98.6 (J_{C-H} = 174.1 Hz), 101.8, 114.8, 118.1, 126.2, 128.3, 128.5, 129.2, 129.5, 130.0, 133.4, 136.8, 150.1, 155.7, 165.6. Anal. Calcd for $C_{27}H_{25}N_3O_7$: C, 64.41; H, 5.00; N, 8.35. Found: C, 64.47; H, 5.02; N, 8.34.

*p-Methoxyphenyl 3-O-benzoyl-2-deoxy-2-azido-α-D-glucopyranoside (**S5**).* To a solution of compound **S4** (6.17 g, 12.3 mmol) in MeOH-1,4-dioxane (2:1, v/v, 90 mL) was added p-TsOH·H_2O (233 mg, 1.23 mmol). The mixture was stirred for 1 h at 65−70 °C, neutralized with Et_3N, and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 1:6) to afford compound **S5** (4.71 g, 93%) as a white solid. R_f = 0.55 (hexane/EtOAc, 1:6, v/v); IR ($CHCl_3$ film) 3337, 2974, 2110, 1508, 1380, 1216, 1088, 1046, 880 cm^{-1}; $[\alpha]_D^{20}$ = +1.88 (c 0.4, CH_3OH); ^1H NMR (400 MHz, CD_3CD) δ 3.51 (dd, J = 10.4, 3.6 Hz, 1H), 3.77 (s, 3H), 3.81−3.96 (m, 4H), 5.57 (d, J = 3.6 Hz, 1H), 5.80 (dd, J = 10.6, 8.4 Hz, 1H), 6.84−6.91 (m, 2H), 7.11−7.17 (m, 2H), 7.47−7.53 (m, 2H), 7.59−7.66 (m, 1H), 8.10−8.15 (m, 2H); ^{13}C NMR (100 MHz, CD_3CD) δ 54.4, 60.0, 60.7, 67.6, 72.5, 72.7, 97.7 (J_{C-H} = 174.1 Hz), 113.9, 117.6, 127.7, 129.0, 129.1, 132.6, 150.0, 155.0, 165.8. Anal. Calcd for $C_{20}H_{21}N_3O_7$: C, 57.83; H, 5.10; N, 10.12. Found: C, 57.86; H, 5.14; N, 10.08.

*p-Methoxyphenyl 3,6-di-O-benzoyl-2-deoxy-2-azido-α/β-D-glucopyranoside (**S6**).* To a solution of compound **S5** (3.44 g, 8.28 mmol) in CH_2Cl_2-pyridine (5:3, v/v, 24 mL) was added benzoyl chloride (0.962 mL, 8.28 mmol) at 0 °C. After stirring at 0 °C for 3 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layer was washed with 1N HCl (2 × 20 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL); dried over $MgSO_4$; and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 1:1) to afford compound **S6** (3.69 g, 86%) as a white solid. R_f = 0.70 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 3415, 2106, 1702, 1508, 1451, 1269, 1221, 1117, 1083, 1070, 1038, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.50 (d, J = 5.2 Hz, 1H, OHα), 3.54 (dd, J = 10.4, 3.2 Hz, 1H, Hα-2), 3.61 (d, J = 4.8 Hz, 0.25H, OHβ), 3.74 (s, 3.75H, OMeα,β), 3.80−3.93 (m, 1.75H, Hα-4, Hβ-2, 4, 5), 4.25−4.32 (m, 1H, Hα-5), 4.56−4.76 (m, 2.5H, Hα-6a,6b, Hβ-6a, 6b), 4.95 (d, J = 8.0 Hz, 0.25H, Hβ-1), 5.21 (dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.2 Hz, 0.25H, Hβ-3), 5.55 (d, J = 3.6 Hz, 1H, Hα-1), 5.82 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 9.6 Hz, 1H, Hα-3), 6.70−6.80 (m, 2.5H), 7.02−7.13 (m, 2.5H), 7.39−7.48 (m, 5H), 7.54−7.62 (m, 2.5H), 7.95−8.14 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 62.1, 63.6, 63.75, 63.81, 69.8, 70.0, 71.1, 73.9, 74.5, 76.2, 97.8 (J_{C-H} = 174.4 Hz), 101.7 (J_{C-H} = 165.6 Hz), 114.7, 114.8, 118.3, 118.8, 128.49, 128.53, 128.6, 129.0, 129.1, 129.7, 129.9, 130.2, 133.39, 133.43, 133.8, 133.9, 150.2, 151.0, 155.7, 155.9, 166.8, 166.9, 167.1, 167.2. Anal. Calcd for $C_{27}H_{25}N_3O_8$: C, 62.42; H, 4.85; N, 8.09. Found: C, 62.39; H, 4.78; N, 8.07.

*p-Methoxyphenyl 3,6-di-O-benzoyl-2-deoxy-2-azido-α/β-D-galactopyranoside (**S7**).* To a solution of compound **S6** (5.04 g, 9.71 mmol) in CH_2Cl_2-pyridine (10:3, v/v, 39 mL) was added dropwise Tf_2O (4.09 mL, 24.3 mmol) at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with 1N HCl (2 × 20 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL); dried over $MgSO_4$; and concentrated in vacuo. To the brown foam were added dry DMF (40 mL) and $NaNO_2$ (6.69 g, 97.1 mmol), and the mixture was stirred for 2 h at room temperature. The mixture was diluted with EtOAc (100 mL), washed with 1N HCl (2 × 50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL); dried over $MgSO_4$; filtered; and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **S7** (4.41 g, 88%) as a white solid. R_f = 0.25 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 3465, 2112, 1717, 1507, 1451, 1316, 1270, 1213, 1117, 1095, 1039, 829 cm^{-1}; ^1H NMR (400 MHz,

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$CDCl_3$) δ 3.74 (s, 3.6H, OMeα,β), 4.03 (t, J = 6.0 Hz, 0.2H, Hβ), 4.10 (dd, J = 10.8, 3.2 Hz, 1H, Hα-2), 4.25 (dd, J = 10.8, 8.4 Hz, 0.2H, Hβ), 4.28 (d, J = 2.8 Hz, 0.2H, Hβ), 4.42−4.69 (m, 4.4H, Hα-4, 5, 6a, 6b, Hβ-6a, 6b), 4.87 (d, J = 8.0 Hz, 0.2H, Hβ-1), 5.03 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 2.8 Hz, 0.2H, Hβ-3), 5.60 (d, J = 3.2 Hz, 1H, Hα-1), 5.75 (dd, $J_{2,3}$ = 11.2 Hz, $J_{3,4}$ = 2.8 Hz, 1H, Hα-3), 6.70−6.79 (m, 2.4H), 7.04−7.12 (m, 2.4H), 7.34−7.62 (m, 7.2H), 7.83−8.14 (m, 4.8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 57.6, 60.9, 63.1, 63.7, 66.4, 67.5, 69.0, 71.3, 72.7, 74.1, 98.1 (J_{C-H} = 175.2 Hz), 102.1 (J_{C-H} = 165.3 Hz), 114.6, 114.8, 118.5, 118.9, 128.5, 128.57, 128.59, 128.7, 129.15, 129.24, 129.5, 129.6, 129.9, 130.1, 130.3, 133.4, 133.5, 133.75, 133.80, 150.4, 151.1, 155.6, 155.9, 165.8, 166.6, 166.7. Anal. Calcd for $C_{27}H_{25}N_3O_8$: C, 62.42; H, 4.85; N, 8.09. Found: C, 62.43; H, 4.82; N, 8.01.

*p-Methoxyphenyl 3,4,6-tri-O-benzoyl-2-deoxy-2-azido-α/β-D-galactopyranoside (**S8**).* To a solution of compound **S7** (2.96 g, 5.70 mmol) in pyridine (20 mL) were added benzoyl chloride (1.98 mL, 17.1 mmol) and 4-dimethylaminopyridine (139 mg, 1.14 mmol). After stirring at 40 °C for 14 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and diluted with CH_2Cl_2 (50 mL). The combined organic layer was washed with 1N HCl (2 × 20 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL); dried over $MgSO_4$; filtered; and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 5:1) to afford compound **S8** (3.30 g, 93%) as a colorless amorphous form. R_f = 0.20 (hexane/EtOAc, 5:1, v/v); IR ($CHCl_3$ film) 2112, 1723, 1602, 1506, 1451, 1315, 1264, 1212, 1178, 1107, 1068, 1039, 1026, 828 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.74 (s, 2.1H), 4.09 (dd, J = 11.2, 3.2 Hz, 1H), 4.27 (dd, J = 10.8, 8.0 Hz, 0.7H), 4.34 (dd, J = 6.8, 6.0 Hz, 0.7H), 4.39 (dd, J = 11.6, 4.8 Hz, 1H), 4.48 (dd, J = 11.6, 5.2 Hz, 0.7H), 4.59 (dd, J = 11.2, 8.0 Hz, 1H), 4.65 (dd, J = 11.6, 8.0 Hz, 0.7H), 4.78 (dd, J = 7.6, 4.8 Hz, 1H), 5.02 (d, J = 8.0 Hz, 0.7H), 5.34 (dd, J = 10.8, 3.2 Hz, 0.7H), 5.73 (d, J = 3.2 Hz, 1H), 5.93 (d, J = 3.2 Hz, 0.7H), 6.00−6.09 (m, 2H), 6.72−6.79 (m, 3.4H), 7.09−7.15 (m, 3.4H), 7.29−7.63 (m, 15.3H), 7.87−8.11 (m, 10.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.60, 55.63, 58.2, 61.3, 62.4, 62.8, 67.3, 68.1, 68.6, 68.9, 71.67, 71.69, 98.1 (J_{C-H} = 175.9 Hz), 102.0 (J_{C-H} = 168.3 Hz), 114.7, 114.8, 118.4, 118.8, 128.4, 128.5, 128.9, 128.99, 129.03, 129.1, 129.46, 129.49, 129.8, 129.9, 130.0, 130.2, 133.3, 133.4, 133.50, 133.52, 133.76, 133.79, 150.2, 150.9, 155.7, 155.9, 165.36, 165.43, 166.0. Anal. Calcd for $C_{34}H_{29}N_3O_9$: C, 65.48; H, 4.69; N, 6.74. Found: C, 65.45; H, 4.67; N, 6.66.

*3,4,6-Tri-O-benzoyl-2-deoxy-2-azido-α/β-D-galactopyranose (**S9**).* To a solution of compound **S8** (4.56 g, 7.31 mmol) and ceric ammonium nitrate (20.0 g, 36.6 mmol) in toluene-MeCN-H_2O (1:1.6:1, v/v/v, 180 mL) was stirred at room temperature for 1 h. The mixture was diluted with water (100 mL) and washed with CH_2Cl_2 (2 × 150 mL). The combined organic layer was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **S9** (3.02 g, 80%, α/β = 1.5:1) as a white solid. R_f = 0.25 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 3446, 3014, 2115, 1727, 1452, 1316, 1270, 1215, 1093, 1069, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99−4.05 (m, 2.5H), 4.24 (t, J = 6.4 Hz, 1H), 4.30−4.46 (m, 4H), 4.59 (dd, J = 11.2, 6.4 Hz, 1.5H), 4.64 (dd, J = 11.2, 6.4 Hz, 1H), 4.80 (t, J = 6.8 Hz, 1.5H), 4.92 (d, J = 7.6 Hz, 1H), 5.13 (brs, 1H), 5.28 (dd, J = 10.8, 3.2 Hz, 1H), 5.62 (d, J = 2.4 Hz, 1.5H), 5.86 (dd, J = 11.2, 3.2 Hz, 1.5H), 5.91 (d, J = 3.2 Hz, 1H), 6.03 (d, J = 2.8 Hz, 1.5H), 7.30−7.62 (m, 22.5H), 7.87−8.08 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.9, 62.2, 62.5, 62.7, 66.9, 67.5, 68.7, 69.1, 71.3, 71.9, 92.7 (J_{C-H} = 174.4 Hz), 96.7 (J_{C-H} = 163.6 Hz), 128.45, 128.47, 128.50, 128.54, 128.7, 128.9, 128.97, 129.00, 129.2, 129.3, 129.8, 129.86, 129.88, 130.0, 133.4, 133.5, 133.6, 133.7, 133.8, 165.61, 165.64, 166.4. Anal. Calcd for $C_{27}H_{23}N_3O_8$: C, 62.67; H, 4.48; N, 8.12. Found: C, 62.64; H, 4.58; N, 8.04.

*3,4,6-Tri-O-benzoyl-2-deoxy-2-azido-α/β-D-galactopyranosyl trichloroacetimidate (**20**).* To a solution of compound **S9** (735 mg, 1.42 mmol) and CCl_3CN (1.42 mL, 14.2 mmol) in CH_2Cl_2 (5 mL) was added K_2CO_3 (336 mg, 2.41 mmol). After stirred at room temperature for 30 min, the reaction mixture was heated at 30 °C for 5 h, filtered through Celite, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to afford compound **20** (784 mg, 83%, α/β= 0.3:1) as a colorless amorphous form. R_f = 0.43 (hexane/EtOAc, 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (dd, J = 10.4, 8.4 Hz, 1H), 4.33 (dd, J = 10.8, 3.6 Hz, 0.3H), 4.36−4.42 (m, 2.3H), 4.56 (dd, J = 11.6, 7.2 Hz, 0.3H), 4.65 (dd, J = 13.6, 9.2 Hz, 1H), 4.79 (t, J = 6.4 Hz, 0.3H), 5.37 (dd, J = 10.4, 3.6 Hz, 1H), 5.82 (dd, J = 10.8, 3.2 Hz, 0.3H), 5.91 (d, J = 8.4 Hz, 1H, Hβ-1), 5.95 (d, J = 3.2 Hz, 1H), 6.10 (d, J = 2.8 Hz, 0.3H), 6.71 (d, J = 3.6 Hz, 0.3H, Hα-1), 7.32−7.67 (m, 11.7H), 7.86−8.09 (m, 7.8H), 8.84 (s, 0.3H, NH-α), 8.85 (s, 1H, NH-β); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.9, 61.2, 61.7, 62.3, 67.1, 68.0, 69.5, 69.9, 72.0, 72.3, 94.9 (Cα-1), 97.1 (Cβ-1), 128.5, 128.6, 128.8, 128.86, 128.93, 129.0, 129.1, 129.5, 129.7, 129.87, 129.94, 130.0, 130.1, 133.4, 133.7, 133.86, 133.92, 160.85, 160.89, 165.3, 165.4, 166.0. Anal. Calcd for $C_{29}H_{23}Cl_3N_4O_8$: C, 52.62; H, 3.50; N, 8.46. Found: C, 52.64; H, 3.51; N, 8.37.

*1,2-O-isopropylidene-3,5-di-O-levulinyl-β-D-arabinofuranose (**S11**).* To a solution of 1,2-*O*-isopropylidene-α/β-D-arabinofuranose (**S10**)[23] (4.71 g, 24.8 mmol) in CH_2Cl_2 (70 mL) were added levulinic acid (8.63 g, 74.3 mmol), *N,N*-diisopropylcarbodimide (11.5 mL, 74.3 mmol) and 4-dimethylaminopyridine (605 mg, 4.95 mmol). After stirred at room temperature for 4 h, the reaction mixture was quenched with H_2O (30 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 70 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc/CH_2Cl_2, 1:2:3) to afford compound **S11** (8.80 g, 92%) as a colorless oil. R_f = 0.43 (hexane/EtOAc/CH_2Cl_2, 1:2:3, v/v/v); $[\alpha]_D^{20}$ = +0.087 (c 2.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.56 (s, 3H), 2.19 (s, 3H), 2.20 (s, 3H), 2.55−2.66 (m, 4H), 2.73−2.83 (m, 4H), 4.23−4.33 (m, 3H), 4.61 (d, J = 3.6 Hz, 1H), 5.08 (s, 1H), 5.93 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.8, 27.8, 27.9, 29.89, 29.93, 37.8, 38.0, 63.9, 77.6, 82.8, 84.4, 106.0, 113.2, 171.8, 172.4, 206.5, 206.6. Anal. Calcd for $C_{18}H_{26}O_9$: C, 55.95; H, 6.78. Found: C, 55.97; H, 6.79.

*Allyl 3,5-di-O-levulinyl-α/β-D-arabinofuranoside (**21**).* To a solution of compound **S11** (6.36 g, 16.5 mmol) in CH_2Cl_2 (100 mL) were added allyl alcohol (2.24 mL, 32.9 mmol) and *p*-TsOH·H_2O (4.70 g, 24.7 mmol) at room temperature. The resulting solution was stirred at room temperature for 5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The combined organic layer was washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH_2Cl_2, 1:2:3) to afford compound **21** (5.09 g, 80%, α/β= 1:0.2) as a colorless oil. R_f = 0.18 (hexane/EtOAc/CH_2Cl_2, 1:2:3, v/v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16−2.23 (m, 7.2H), 2.58−2.65 (m, 4.8H), 2.75−2.81 (m, 4.8H), 3.02 (d, J = 8.8 Hz, 0.2H), 3.49 (d, J = 5.2 Hz, 1H), 4.01 (dd, J = 13.2, 6.0 Hz, 1H), 4.05−4.13 (m, 0.4H), 4.17−4.30 (m, 4.6H), 4.31 (dd, J = 7.6, 4.0 Hz, 0.2H), 4.40−4.47 (m, 1H), 4.75 (dd, J = 4.8, 1.6 Hz, 1H), 5.03−5.08 (m, 1.4H), 5.20 (dd, J = 10.4, 1.2 Hz, 1H), 5.22 (dd, J = 10.0, 0.8 Hz, 0.2H), 5.31 (dd, J = 17.2, 1.2 Hz, 1.2H), 5.85−5.97 (m, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.77, 27.83, 29.78, 29.81, 29.9, 37.75, 37.82, 37.9, 63.3, 65.5, 68.0, 68.7, 76.3, 79.1, 79.4, 79.8, 80.5, 80.8, 100.3, 107.0, 117.2, 118.0, 133.4, 134.0, 172.4, 172.8, 173.1, 206.5, 206.7, 207.1. Anal. Calcd for $C_{18}H_{26}O_9$: C, 55.95; H, 6.78. Found: C, 55.83; H, 6.89.

*Allyl (3,4,6-Tri-O-benzoyl-2-deoxy-2-azido-α-D-galactopyranosyl)-(1 → 2)-3,5-di-O-levulinyl-α/β-D-arabinofuranoside (**22**).* A mixture of a galactosyl trichloroacetimidate donor **20** (2.33 g, 3.52 mmol) and an arabinosyl acceptor **21** (1.05 g, 2.71 mmol) in CH_2Cl_2 (10 mL) was stirred for 5 min at room temperature and cooled down to −40 °C. After the addition of TMSOTf (0.192 mL, 1.06 mmol), the reaction mixture was stirred at −40 °C for 1 h, allowed to warm up over 30 min to 0 °C, quenched with triethylamine and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to afford compound **22** (2.26 g, 94%): α-α form: colorless amorphous form, R_f = 0.35 (hexane/EtOAc, 1:1, v/v); IR

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($CHCl_3$ film) 3022, 2113, 1720, 1602, 1452, 1360, 1315, 1268, 1155, 1094, 1068, 1026 cm^{-1}; $[\alpha]_D^{20}$ = +1.40 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 6H), 2.53−2.80 (m, 8H), 3.96 (dd, J = 13.2, 6.0 Hz, 1H), 4.06 (dd, J = 11.2, 3.2 Hz, 1H), 4.19 (dd, J = 12.8, 4.8 Hz, 1H), 4.25−4.37 (m, 4H), 4.43 (dd, J = 10.4, 2.4 Hz, 1H), 4.55−4.63 (m, 2H), 5.07 (d, J = 3.6 Hz, 1H), 5.18 (d, J = 10.4 Hz, 1H), 5.26 (s, 1H), 5.28 (d, J = 16.0 Hz, 1H), 5.53 (d, J = 3.2 Hz, 1H), 5.71 (dd, J = 11.2, 2.8 Hz, 1H), 5.80−5.92 (m, 1H), 5.99 (d, J = 2.8 Hz, 1H), 7.30−7.65 (m, 9H), 7.84−8.05 (m. 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.8, 29.9, 37.9, 38.0, 58.1, 62.6, 63.5, 67.9, 68.0, 68.4, 69.1, 77.9, 79.9, 85.5, 97.5 (J_{C-H} = 178.6 Hz), 105.2, 117.5, 128.4, 128.5, 128.7, 129.0, 129.1, 129.5, 129.86, 129.91, 133.3, 133.5, 133.7, 133.9, 165.4, 166.0, 172.4, 172.6, 206.2, 206.6. Anal. Calcd for $C_{45}H_{47}N_3O_{16}$: C, 61.01; H, 5.35; N, 4.74. Found: C, 61.02; H, 5.41; N, 4.62. α-β form: colorless oil, R_f = 0.23 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 3021, 2113, 1720, 1452, 1360, 1316, 1268, 1215, 1156, 1094, 1068, 1026 cm^{-1}; $[\alpha]_D^{20}$ = +0.77 (c 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.175 (s, 3H), 2.184 (s, 3H), 2.58−2.66 (m, 4H), 2.72−2.82 (m, 4H), 3.87 (dd, J = 11.2, 3.2 Hz, 1H), 3.95 (dd, J = 12.8, 6.0 Hz, 1H), 4.06−4.13 (m, 1H), 4.22 (dd, J = 11.6, 7.6 Hz, 1H), 4.27−4.35 (m, 3H), 4.41−4.50 (m, 2H), 4.84 (t, J = 6.4 Hz, 1H), 5.07−5.14 (m, 2H), 5.28 (d, J = 17.2 Hz, 1H), 5.35 (d, J = 3.2 Hz, 1H), 5.38 (dd, J = 7.2, 6.0 Hz, 1H), 5.85 (dd, J = 11.2, 3.2 Hz, 1H), 5.84−5.95 (m, 1H), 6.02 (d, J = 1.6 Hz, 1H), 7.29−7.65 (m, 9H), 7.84−8.04 (m. 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8, 28.0, 29.9, 30.0, 37.99, 38.01, 57.9, 61.8, 65.9, 67.8, 68.3, 68.4, 68.5, 76.5, 78.4, 83.6, 99.8 (J_{C-H} = 179.5 Hz), 100.7, 117.8, 128.4, 128.6, 128.7, 129.1, 129.2, 129.3, 129.8, 129.9, 133.39, 133.43, 133.5, 133.7, 165.3, 165.4, 166.0, 172.4, 172.5, 206.5, 206.7. Anal. Calcd for $C_{45}H_{47}N_3O_{16}$: C, 61.01; H, 5.35; N, 4.74. Found: C, 61.07; H, 5.20; N, 4.67.

*Allyl (3,4,6-Tri-O-benzoyl-2-deoxy-2-acetamido-α-D-galactopyranosyl)-(1 → 2)-3,5-di-O-levulinyl-α/β-D-arabinofuranoside (**23**).* To a solution of compound **22** (1.47 g, 1.66 mmol) in dry THF (10 mL) was added PPh_3 (653 mg, 2.49 mmol) at 0 °C. After added H_2O (59.7 μL, 3.32 mmol), the reaction mixture was stirred at room temperature for 1 h, quenched with water, and then extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Colorless oil, R_f = 0.45 (hexane/EtOAc, 1:2, v/v). To a solution of amine compound (1.72 g, 2.00 mmol) in CH_2Cl_2 (20 mL) were added Ac_2O (0.377 mL, 4.00 mmol), pyridine (0.647 mL, 8.00 mmol), and 4-dimethylaminopyridine (48.8 mg, 0.400 mmol). After stirring at room temperature for 5 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was washed with 1N HCl (20 mL), saturated aqueous $NaHCO_3$ (20 mL), and brine (20 mL); dried over $MgSO_4$; and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 1:4) to afford compound **23** (1.71 g, 95%): α-α form: colorless amorphous form, R_f = 0.18 (hexane/EtOAc, 1:4, v/v); IR ($CHCl_3$ film) 3378, 3019, 1721, 1677, 1602, 1521, 1452, 1364, 1316, 1269, 1215, 1157, 1112, 1068, 1026 cm^{-1}; $[\alpha]_D^{20}$ = +1.28(c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.11 (s, 3H), 2.15 (s, 3H), 2.55−2.84 (m, 8H), 3.84 (dd, J = 12.4, 5.2 Hz, 1H), 4.09 (dd, J = 12.4, 3.6 Hz, 1H), 4.18 (s, 1H), 4.26−4.40 (m, 3H), 4.43 (dd, J = 11.6, 3.6 Hz, 1H), 4.53−4.66 (m, 2H), 4.95−5.05 (m, 2H), 5.15 (d, J = 10.4 Hz, 1H), 5.18−5.28 (m, 3H), 5.52 (dd, J = 10.8 2.0 Hz, 1H), 5.75−5.87 (m, 1H), 5.94 (s, 1H), 6.60 (d, J = 9.2 Hz, 1H), 7.28−7.70 (m, 9H), 7.82−8.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 27.8, 28.0, 29.7, 37.8, 37.9, 47.8, 62.5, 62.8, 67.9, 68.1, 68.4, 69.3, 78.3, 78.6, 88.8, 100.0 (J_{C-H} = 174.1 Hz), 104.9, 117.3, 128.36, 128.40, 128.44, 128.56, 128.60, 129.1, 129.2, 129.5, 129.8, 130.0, 131.9, 131.96, 132.01, 132.1, 133.0, 133.2, 133.3, 133.5, 133.7, 165.7, 166.0, 166.1, 170.7, 172.4, 172.6, 206.1, 206.9. Anal. Calcd for $C_{47}H_{51}NO_{17}$: C, 62.59; H, 5.70; N, 1.55. Found: C, 62.62; H, 5.78; N, 1.40. α-β form: colorless oil, IR ($CHCl_3$ film) 3378, 3019, 1720, 1677, 1602, 1522, 1452, 1366, 1316, 1268, 1216, 1158, 1112, 1068, 1026 cm^{-1}; $[\alpha]_D^{20}$ = +0.56 (c 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 2.53−2.65 (m, 4H), 2.74−2.82 (m, 4H), 3.95 (dd, J = 12.8, 6.0 Hz, 1H), 4.13−4.24 (m, 3H), 4.25−4.36 (m, 3H), 4.48 (dd, J = 11.2, 6.0 Hz, 1H), 4.73 (t, J = 6.4 Hz, 1H), 4.95−5.03 (m, 1H), 5.08−5.14 (m, 2H), 5.18 (d, J = 3.6 Hz, 1H), 5.29 (dd, J = 17.2, 1.2 Hz, 1H), 5.47 (dd, J = 7.2, 5.6 Hz, 1H), 5.59 (dd, J = 11.2, 3.2 Hz, 1H), 5.82−5.94 (m, 1H), 5.95 (d, J = 2.4 Hz, 1H), 6.35 (d, J = 9.6 Hz, 1H), 7.28−7.61 (m, 9H), 7.84−8.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 27.9, 28.2, 29.7, 29.9, 38.0, 38.2, 47.8, 62.2, 65.4, 67.9, 68.37, 68.44, 69.5, 77.0, 77.4, 84.2, 100.4 (J_{C-H} = 178.7 Hz), 100.5, 117.7, 128.4, 128.6, 128.7, 129.3, 129.40, 129.44, 129.7, 129.9, 130.0, 133.25, 133.34, 133.4, 133.5, 165.8, 166.0, 166.2, 170.5, 172.51, 172.53, 206.4, 206.6. Anal. Calcd for $C_{47}H_{51}NO_{17}$: C, 62.59; H, 5.70; N, 1.55. Found: C, 62.55; H, 5.73; N, 1.43.

*(3,4,6-Tri-O-benzoyl-2-deoxy-2-acetamido-α-D-galactopyranosyl)-(1 → 2)-3,5-di-O-levulinyl-α/β-D-arabinofuranose (**24**).* A mixture of compound **23** (1.30 g, 1.20 mmol) and $PdCl_2$ (42.5 mg, 0.24 mmol) in MeOH (10 mL) was stirred at room temperature for 8 h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:4) to afford compound **24** (1.09 g, 88%, α/β = 1:1) as a colorless amorphous form. R_f = 0.10 (hexane/EtOAc, 1:4, v/v); IR ($CHCl_3$ film) 3378, 3019, 1720, 1678, 1524, 1452, 1362, 1316, 1270, 1215, 1158, 1112, 1069, 1026 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (s, 3H), 1.91 (s, 3H), 2.11 (s, 3H), 2.16 (s, 6H), 2.18 (s, 3H), 2.54−2.85 (m, 16H), 3.43 (s, 1H), 4.10 (dd, J = 9.2, 5.2 Hz, 1H), 4.15 (dd, J = 6.4, 4.4 Hz, 1H), 4.18 (s, 1H), 4.25 (dd, J = 12.0, 5.2 Hz, 1H), 4.29 (dd, J = 11.2, 6.4 Hz, 1H), 4.32−4.40 (m, 3H), 4.43 (dd, J = 9.2, 4.4 Hz, 1H), 4.49 (dd, J = 12.0, 4.0 Hz, 1H), 4.56−4.66 (m, 4H), 4.91 (t, J = 6.4 Hz, 1H), 4.95−5.04 (m, 3H), 5.21 (s, 1H), 5.25 (d, J = 2.0 Hz, 1H), 5.42−5.48 (m, 2H), 5.51 (dd, J = 11.2, 3.2 Hz, 1H), 5.56−5.62 (m, 2H), 5.89−5.94 (m, 2H), 6.53 (d, J = 8.8 Hz, 1H), 6.58 (d, J = 8.8 Hz, 1H), 7.28−7.64 (m, 18H), 7.81−8.11 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 28.0, 28.05, 28.12, 28.2, 29.7, 29.8, 29.9, 38.06, 38.10, 38.2, 47.9, 48.0, 62.6, 62.9, 63.0, 64.4, 67.9, 68.1, 68.4, 68.5, 69.3, 69.6, 76.5, 77.6, 78.4, 78.9, 83.6, 88.7, 96.1, 99.88, 99.93, 101.0, 128.46, 128.49, 128.6, 128.7, 129.2, 129.3, 129.4, 129.5, 129.6, 129.86, 129.89, 129.92, 130.0, 130.1, 133.3, 133.41, 133.44, 133.57, 133.64, 165.88, 165.90, 166.22, 166.24, 166.3, 166.5, 172.5, 172.6, 172.7, 172.8, 206.5, 206.6, 207.3, 207.9. Anal. Calcd for $C_{44}H_{47}NO_{17}$: C, 61.32; H, 5.50; N, 1.63. Found: C, 61.30; H, 5.57; N, 1.50.

*(3,4,6-Tri-O-benzoyl-2-deoxy-2-acetamido-α-D-galactopyranosyl)-(1 → 2)-3,5-di-O-levulinyl-α/β-D-arabinofuranosyl trichloroacetimidate (**25**).* To a solution of compound **24** (498 mg, 0.578 mmol) in CH_2Cl_2 (5 mL) were added Cl_3CCN (0.579 mL, 5.78 mmol) and DBU (8.75 μL, 0.0578 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:4) to afford compound **25** (474 mg, 82%) as a colorless amorphous form. R_f = 0.30 (hexane/EtOAc, 1:4, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 2.53−2.78 (m, 6H), 2.80−2.85 (m, 2H), 4.31−4.41 (m, 2H), 4.48 (s, 1H), 4.52 (dd, J = 12.0, 4.8 Hz, 1H), 4.57 (dd, J = 8.4, 4.0 Hz, 1H), 4.63 (dd, J = 11.6, 6.8 Hz, 1H), 4.72 (t, J = 6.4 Hz, 1H), 4.97−5.04 (m, 1H), 5.06 (d, J = 4.4 Hz, 1H), 5.44 (d, J = 3.6 Hz, 1H), 5.55 (dd, J = 11.2, 3.2 Hz, 1H), 5.97 (d, J = 2.4 Hz, 1H), 6.49 (s, 1H), 6.57 (d, J = 9.2 Hz, 1H), 7.28−7.70 (m, 9H), 7.80−8.09 (m, 6H), 8.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 27.8, 28.1, 29.76, 29.81, 37.8, 38.1, 48.1, 62.4, 62.6, 68.25, 68.30, 69.1, 77.3, 82.6, 85.9, 99.2 (J_{C-H} = 175.1 Hz), 104.5, 128.49, 128.53, 128.65, 128.70, 129.1, 129.2, 129.6, 129.86, 129.89, 130.1, 132.0, 132.05, 132.12, 132.2, 133.2, 133.4, 133.6, 160.3, 165.8, 166.1, 166.3, 170.8, 172.4, 172.8, 206.1, 207.3. Anal. Calcd for $C_{46}H_{47}Cl_3N_2O_{17}$: C, 54.91; H, 4.71; N, 2.78. Found: C, 54.89; H, 4.77; N, 2.59.

Allyl [(3,4,6-Tri-O-benzoyl-2-deoxy-2-acetamido-α-D-galactopyranosyl)-(1 → 2)-(3,5-di-O-levulinyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofuranosyl)-(1 → 5)-(2,3-di-O-benzoyl-α-D-arabinofura-

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nosyl)]-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (2). A mixture of donor **25** (73.9 mg, 0.0734 mmol) and acceptor **19** (234 mg, 0.0565 mmol) in CH_2Cl_2 (3 mL) was stirred for 5 min at room temperature and cooled down to −40 °C. After the addition of TMSOTf (4.0 μL, 0.0220 mmol), the reaction mixture was stirred at −40 °C for 1 h, allowed to warm up over 30 min to 0 °C, quenched with triethylamine, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:4) to afford compound **2** (182 mg, 65%) as a colorless amorphous form. R_f = 0.60 (hexane/EtOAc, 1:4, v/v); IR ($CHCl_3$ film) 3022, 2925, 1718, 1601, 1452, 1366, 1315, 1261, 1177, 1108, 1070, 1026, 962, 857 cm^{-1}; $[\alpha]_D^{20}$ = +0.44 (c 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.26−2.45 (m, 2H), 2.48−2.82 (m, 6H), 3.59 (d, *J* = 8.8 Hz, 1H), 3.83−3.97 (m, 12H), 4.05−4.23 (m, 13H), 4.25−4.33 (m, 3H), 4.35 (dd, *J* = 11.2, 5.2 Hz, 1H), 4.43 (dd, *J* = 13.2, 4.4 Hz, 1H), 4.45−4.50 (m, 2H), 4.53−4.68 (m, 13H), 4.92 (d, *J* = 4.8 Hz, 1H), 4.94−5.02 (m, 1H), 5.16 (d, *J* = 2.8 Hz, 1H), 5.20 (dd, *J* = 15.2, 4.0 Hz, 1H), 5.26−5.43 (m, 13H), 5.46−5.53 (m, 3H), 5.55−5.59 (m, 2H), 5.61−5.69 (m, 20H), 5.88−6.01 (m, 1H), 5.93 (d, *J* = 1.6 Hz, 1H), 6.59 (d, *J* = 9.2 Hz, 1H), 7.18−7.71 (m, 81H), 7.81−8.10 (m. 54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 27.7, 28.1, 29.6, 29.7, 37.7, 38.0, 47.9, 62.4, 62.9, 65.3, 65.8, 66.0, 66.1, 67.8, 68.2, 68.4, 69.1, 69.3, 77.0, 77.2, 77.3, 77.4, 78.6, 78.8, 81.6, 81.8, 81.9, 82.0, 82.1, 89.0, 100.4 (J_{C-H} = 175.5 Hz), 104.9, 105.5, 105.6, 105.8, 105.85, 105.94, 117.4, 128.3, 128.42, 128.44, 128.5, 128.7, 129.1, 129.2, 129.28, 129.32, 129.4, 129.5, 129.6, 129.8, 129.9, 129.95, 130.04, 132.0, 132.1, 132.2, 133.18, 133.24, 133.3, 133.4, 133.5, 133.7, 133.8, 165.1, 165.15, 165.21, 165.46, 165.49, 165.55, 165.63, 165.7, 165.75, 165.79, 166.0, 166.1, 170.7, 172.6, 172.7, 206.1, 207.1. MALDI-TOF: Calcd for $C_{275}H_{243}NO_{89}Na$ $[M+Na]^+$: 5008.81, Found: 5008.34.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01723.

Scheme S1 for the synthesis of compound **20**, Scheme S2 for the synthesis of compound **21**, and ^1H and ^{13}C NMR spectra for all reported compounds (PDF)

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Notes

The authors declare no competing financial interest.

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