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Concise Synthesis of a Pentasaccharide Related to the Anti-Leishmanial Triterpenoid Saponin Isolated from *Maesa balansae*†

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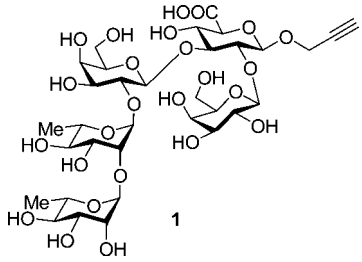

Concise synthesis of the glycone part (a pentasaccharide) of the anti-leishmanial triterpenoid saponin isolated from *Maesa balansae* is reported. A late-stage TEMPO-mediated oxidation of a primary hydroxyl group to carboxylic acid has been achieved under phase-transfer conditions. Glycosylations were performed either by thioglycoside or glycosyl trichloroacetimidate activation using sulfuric acid immobilized on silica (H_2SO_4−silica) in conjunction with *N*-iodosuccinimide and alone, respectively. H_2SO_4−silica was proved to be a better choice as promoter than conventional Lewis acid promoters such as TfOH or TMSOTf.

Saponins, glycosylated secondary metabolites in plants,[1] are synthesized routinely during their normal program of growth and development. Because of their intense antifungal properties, it is believed that these molecules act as natural chemical barriers in plants against fungal attack.[2] In addition to their natural protective activity, many of them are exploited as sources for drugs, e.g., ginseng and liquorice, or food crops such as legumes and oats.[3] Therefore, this class of compounds is commercially attractive for diverse reasons. However, the detailed genetic machinery responsible for the elaboration of this important family is largely uncharacterized till date. Although a broad range of architectural diversity is observed in the saponin family, one common feature shared by all saponins is the presence of a sugar chain attached to the 3-position of the aglycon moiety. Sugar chains differ substantially from saponin to saponin; they are often branched and consist of up to five sugar units (usually selected from glucose, rhamnose, arabinose, xylose, or glucuronic acid).[4] The glycosylation step is believed to happen at the final stage of the saponin biosynthesis, and the saponin bioactivity largely depends on the glycosylation pattern.[5] Therefore, a clear elucidation of the biosynthetic formation of the glycone chain as well as the enzymes involved in the whole process is of absolute necessity. Moreover, to explore the medicinal activities associated with many of the saponins, chemical synthesis of the saccharide fragments will be useful.

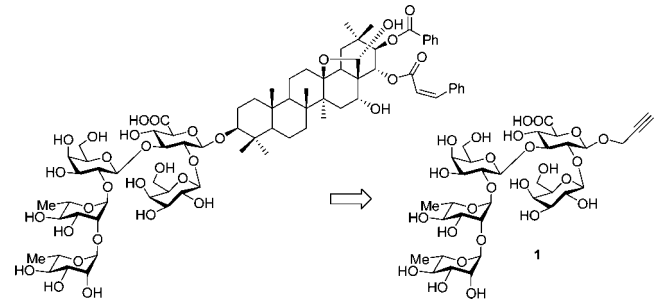

FIGURE 1. Structure of maesabalide I and synthetic target.

Recently, De Kimpe et al.[6] reported the isolation and characterization of six triterpenoid saponins (maesabalides I−IV)[7] isolated from the Vietnamese medicinal plant *Maesa balansae* that showed intense in vitro and in vivo anti-leishmanial activity against intracellular *Leishmania infantum* amastigotes.[8] To determine the structure−activity relationship for the saponins, they have evaluated some semisynthetic analogs of the same. However, they focused on the modification of the aglycon part only. As Leishmaniasis is a growing threat to the public health with about 350 million people living in endemic areas and an annual incidence of about 2 million cases.[9] Inadequate resources are available to tackle this disease, with treatment options limited to pentavalent antimonials as first-line chemotherapeutics and to amphotericin and pentamidine as second-line chemotherapeutics, and novel drug leads are highly needed[10] to combat this deadly disease. In order to exploit the scopes arisen from the identification of anti-leishmanial saponins from *Maesa balansae*, here we report the concise chemical synthesis of the pentasaccharide side chain (Figure 1), aiming for the elucidation of the biosynthetic pathway of

† Dedicated to Prof. Sushanta Dattagupta, Director, IISER-K on the occasion of his 60th birthday.

(1) Price, K. R.; Johnson, I. T.; Fenwick, G. R. *CRC Crit. Rev. Food Sci. Nutr.* **1987**, *26*, 27–133.
(2) Papadopoulou, K.; Melton, R. E.; Legget, M.; Daniels, M. J.; Osbourn, A. E *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12923–12928.
(3) Haralampidis, K.; Trojanowska, M.; Osbourn, A. E. *Adv. Biochem. Eng. Biotechnol.* **2002**, *75*, 31–49.
(4) Hostettmann, K. A.; Marston, A. Saponins. *Chemistry and Pharmacology of Natural Products*; Cambridge University Press: Cambridge, UK, 1995.
(5) (a) Paczkowski, C.; Wojciechowski, Z. A. *Phytochemistry* **1994**, *35*, 1429–1434. (b) Wojciechowski, Z. A. *Phytochemistry* **1975**, *14*, 1749–1753.
(6) Germonprez, N.; Maes, L.; Van Puyvelde, L.; Van Tri, M.; Tuan, D. A.; De Kimpe, N. *J. Med. Chem.* **2005**, *48*, 32–37.
(7) Germonprez, N.; Van Puyvelde, L.; Maes, L.; De Kimpe, N. *Tetrahedron* **2004**, *60*, 219–228.
(8) Maes, L.; Vanden Berghe, D.; Germonprez, N.; Quirijnen, L.; Cos, P.; De Kimpe, N.; Van Puyvelde, L. *Antimicrob. Agents Chemother.* **2004**, *48*, 130–136.
(9) Desjeux, P *Trans. R. Soc. Trop. Med. Hyg.* **2001**, *95*, 239–243.
(10) Guerin, P.; Olliaro, J. P.; Sundar, S.; Boelaert, M.; Croft, S. L.; Desjeux, P.; Wasunna, M. K.; Bryceson, A. D. *Lancet Infect. Dis.* **2002**, *2*, 494–501.

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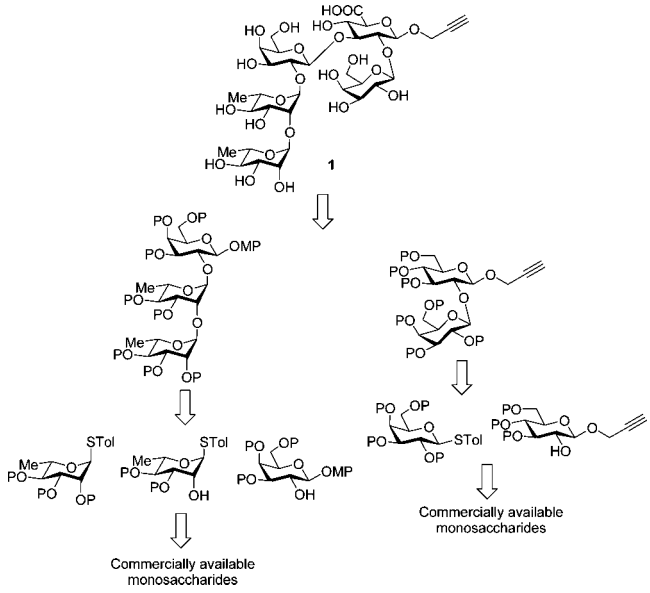


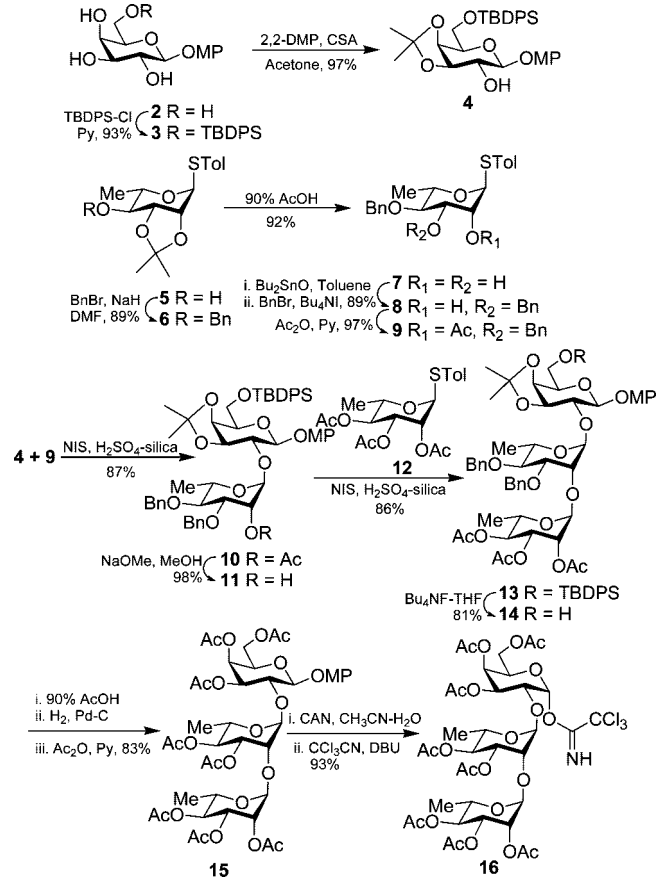
FIGURE 2. Retrosynthetic analysis for the target oligosaccharides.

the saponin concerned as well as further medicinal use if found suitable. It is worth noting that all of the six saponins (maesabalides I−IV) have the same side chain oligosaccharides.

For the synthesis of the target pentasaccharide (**1**), a 3 + 2 disconnection was planned where the protected trisaccharide can be coupled to the disaccharide acceptor. The reducing end glycoside is always an important factor for oligosaccharide synthesis since this will ultimately determine the possibility of further conjugate formation. Here we opted for propargyl glycosides as they can be converted to suitable glycoconjugates as required through simple multicomponent reactions or cycloaddition reactions.[11] Many of these reactions can be done in aqueous media, and therefore, modifications are possible even after global deprotection of the oligosaccharide target.[12] Moreover, propargyl glycoside can be effectively cleaved to obtain the corresponding hemiacetal.[13,29] The glycosylation strategies are so chosen that the trisaccharide can be converted to its corresponding glycosyl trichloroacetimidate for the final glycosylation. For other glycosylations, activation of thioglycosides were preferred as thioglycosides are stable enough for required protecting group manipulations and can be activated efficiently to provide required glycosidic bond. A TEMPO-mediated late-stage oxidation of the required primary hydroxyl group to carboxylic acid was planned to afford the target uronic acid moiety. This 3 + 2 route would provide the tri- and disaccharide fragments also, which are useful for biological evaluation. The planned retrosynthetic analysis for the total synthesis of the pentasaccharide **1** is furnished below (Figure 2).

Synthesis of the trisaccharide fragment was commenced with known *p*-methoxyphenyl β-D-glactopyranoside (**2**).[14] Protection of the primary OH with a TBDPS group using TBDPS-Cl in

SCHEME 1. Synthesis of Trisaccharide Donor



pyridine[15] (isolated yield, 93%) followed by 3,4-isopropylidene formation using 2,2-dimethoxypropane and 10-camphorsulfonic acid in acetone[16] furnished the acceptor, *p*-methoxyphenyl 6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-β-D-glactopyranoside (**4**), in 97% yield. For the synthesis of the rhamnose donor, known *p*-tolyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (**5**)[17] was benzylated using BnBr and NaH in dry DMF[18] to afford *p*-tolyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (**6**) in 89% yield. Removal of isopropylidene acetal by 80% AcOH at 80 °C[19] (isolated yield, 92%) followed by selective benzylation through stannylene acetal using Bu_2SnO in toluene and then BnBr in the presence of tetrabutylammonium iodide[20] furnished *p*-tolyl 3,4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**8**) in 89% yield. Acetylation of compound **8** using Ac_2O in pyridine[21] afforded the target donor, *p*-tolyl 2-*O*-acetyl-3,4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**9**), in 97% yield (Scheme 1).

Glycosylation between acceptor **4** and donor **9** was achieved through thioglycoside activation by *N*-iodosuccinimide in the presence of H_2SO_4−silica[22] to afford the disaccharide **10** in 87% yield. Use of H_2SO_4−silica in conjunction with *N*-iodosuccinimide was found to be advantageous as it replaces the use of Lewis acids such as TfOH[23] or TMSOTf.[24] The same glyco-

(11) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew.Chem., Int. Ed.* **2002**, *41*, 2596–2599. (b) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064. (c) Saxon, E.; Bertozzi, C. R. *Science* **2000**, *287*, 2007–2010.

(12) Mandal, S.; Gauniyal, H. M.; Pramanik, K.; Mukhopadhyay, B. *J. Org. Chem.* **2007**, *72*, 9753–9756.

(13) Hotha, S.; Kashyap, S. *J. Am. Chem. Soc.* **2006**, *128*, 9620–9621.

(29) For corresponding á-isomer Izumi, M.; Fukase, K.; Kusumoto, S *Synlett* **2002**, *9*, 1409–1416.

(14) Ohlsson, J.; Magnusson, G. *Carbohydr. Res.* **2000**, *329*, 49–55.

(15) Limberg, G.; Thiem, J. *Carbohydr. Res.* **1995**, *275*, 107–115.

(16) Lipták, A.; Imre, J.; Nánási, P. *Carbohydr. Res.* **1981**, *92*, 154–156.

(17) Mukhopadhyay, B.; Field, R. A. *Carbohydr. Res.* **2006**, *341*, 1697–1701.

(18) Thollas, B.; Biosset, C. *Synlett* **2007**, *11*, 1736–1738.

(19) Gent, P. A.; Gigg, R. *J. Chem. Soc., Perkin Trans. I* **1974**, 1446–1455.

(20) Faure, R.; Shiao, T. C.; Damerval, S.; Roy, R. *Tettrahedron Lett.* **2007**, *48*, 2385–2388.

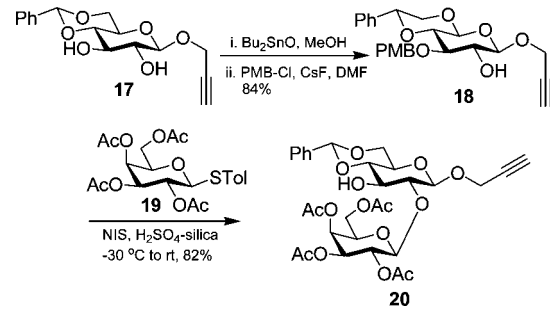
(21) Hudson, C. S.; Dale, J. K. *J. Am. Chem. Soc.* **1915**, *37*, 1264–1270.

sylation reaction in the presence of TfOH and TMSOTf produced 78% and 81% yields, respectively. Moreover, both TfOH and TMSOTf needed to be diluted with CH_2Cl_2 to obtain the required amount, whereas for H_2SO_4−silica simple weighing was enough. Zemplén de-O-acetylation of the disaccharide **10** using NaOMe in methanol afforded the required disaccharide acceptor **11** in 98% yield. Compound **11** was then coupled with known *p*-tolyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (**12**)[25] using the same thioglycoside activation protocol as above to get the protected trisaccharide **13** in 86% yield. Our experience with CAN-mediated oxidative cleavage of *p*-methoxyphenyl group suggests that isopropylidene acetals or silyl protections are not well tolerated. Therefore, the TBDPS group was removed using Bu_4NF in THF[26] to afford the trisaccharide **14** in 81% isolated yield. Further, the isopropylidene acetal was hydrolyzed using 80% AcOH at 80 °C[17] followed by Pd−C promoted hydrogenolysis of the benzyl protections. The resulting compound was acetylated using Ac_2O in pyridine to afford trisaccharide **15** in 83% yield. Now the CAN-mediated[27] oxidative cleavage of the *p*-methoxyphenyl group followed by reaction with trichloroacetonitrile in the presence of DBU[28] afforded the glycosyl trichloroacetimidate donor **16** in 79% yield (Scheme 1).

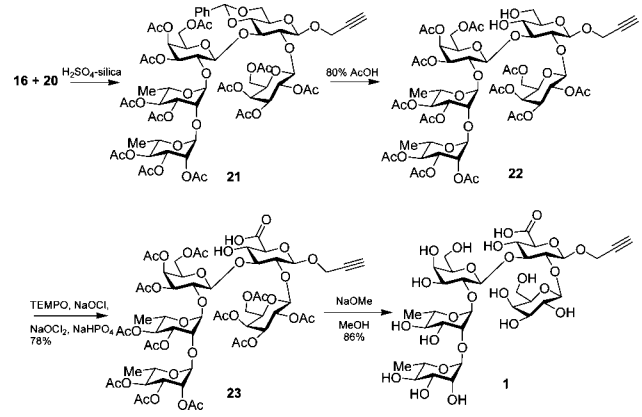
For the synthesis of the disaccharide acceptor, propargyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**17**)[29] was selectively protected at the 3-O-position with *p*-methoxybenzyl group via its 2,3-stannylene acetal to afford the required 2-ol acceptor **18** in 84% yield. The regioselectivity of the *p*-methoxybenzyl group at the 3-position was further confirmed by acetylation of the free OH group and careful adjudication of ^1H and $^1H-^1H$ COSY spectra. Disaccharide acceptor **18** was coupled with known galactosyl donor **19** using *N*-iodosuccinimide in the presence of H_2SO_4−silica.[20] After complete conversion of the acceptor at −30 °C in 45 min, the temperature of the solution was raised to room temperature and stirred for an additional hour when the *p*-methoxybenzyl group was cleaved completely to furnish the target disaccharide acceptor **20** in 82% yield (Scheme 2).

Glycosylation of trisaccharide donor **16** and acceptor **20** was achieved through trichloroacetimidate activation using H_2SO_4−silica at −40 °C for 6 h. The reaction proceeded smoothly to furnish the protected pentasaccharide **21**. However, a trehalose type of compound resulted from the coupling between donor hemiacetal, and unreacted donor was formed (<5%) as confirmed by mass spectroscopy that could not be separated by chromatography. Therefore, the scheme was continued to the next step without having clean NMR spectra

SCHEME 2. Synthesis of Disaccharide Acceptor



SCHEME 3. Synthesis of Pentasaccharide, Oxidation, and Deprotection



at this stage. Opening of the benzylidene acetal using 80% AcOH at 80 °C[30] afforded the diol **22**, and the trehalose impurity generated in the previous step was successfully removed. Required oxidation of the primary-OH group was achieved by a TEMPO-mediated oxidation under phase transfer conditions by following a recent protocol developed by Huang et al.[31] It is worth noting that the oxidation was absolutely selective to the primary-OH without affecting the secondary-OH present adjacent to it. Use of 2-methyl-2-butene as used in Huang's protocol is also found to be optional as 78% yield of the target uronic acid derivative **23** was achieved without it. Finally, global deprotection through Zemplén de-O-acetylation afforded target pentasaccharide **1** in 86% yield (Scheme 3).

In conclusion, we have accomplished the total synthesis of the pentasaccharide glycone part of the anti-leishmanial triterpenoid saponin isolated from *Maesa balasae* as its propargyl glycoside. H_2SO_4−silica has been utilized as the acid source in conjunction with *N*-iodosuccinimide for activation of thioglycoside and alone for trichloroacetimidate donors and found to be a better user-friendly alternative of the conventional Lewis acids. The propargyl glycoside at the reducing end will provide the scope of making various types of glycoconjugates in future to asses the biological activity of the oligosaccharide in question.

Experimental Section

***p*-Methoxyphenyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranoside (15).** A solution of compound **14** (1.2 g, 1.3 mmol) in AcOH−H_2O (9:1, 20 mL) was stirred at

(22) **Preparation of H_2SO_4−Silica.** To a slurry of silica gel (10 g, 200−400 mesh) in dry diethyl ether (50 mL) was added commercially available concentrated H_2SO_4 (1 mL), and the slurry was shaken for 5 min. The solvent was evaporated under reduced pressure, resulting in free flowing H_2SO_4−silica, which was dried at 110 °C for 3 h and used for the reactions. For the use of H_2SO_4−silica in various carbohydrate reactions, see: (a) Rajput, V. K.; Roy, B.; Mukhopadhyay, B. *Tetrahedron Lett.* **2006**, *47*, 6987–6991. (b) Rajput, V. K.; Mukhopadhyay, B. *Tetrahedron Lett.* **2006**, *47*, 5939–5941. (c) Mukhopadhyay, B. *Tetrahedron Lett.* **2006**, *47*, 4337–4341. (d) Roy, B.; Mukhopadhyay, B. *Tetrahedron Lett.* **2007**, *48*, 3783–3787.

(23) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331–1334.

(24) Terada, T.; Ishida, H.; Kiso, M.; Hasegawa, A. *J. Carbohydr. Chem.* **1995**, *14*, 751–768.

(25) Cumpstey, I.; Fairbanks, A. J.; Redgrave, A. J. *Tetrahedron* **2004**, *60*, 9061–9074.

(26) Neumann, K. W.; Tamura, J.-I.; Ogaya, T. *Glycoconjugate J.* **1996**, *13*, 933–936.

(27) Classon, B.; Garegg, P. J.; Samuelson, B *Acta Chem. Scand. Ser. B.* **1984**, *38*, 419–422.

(28) Kerékgyártó, J.; Szurmai, Z.; Lipták, A. *Carbohydr. Res.* **1993**, *245*, 65–80.

(30) Medgyes, G.; Jerkovich, G.; Kuszmann, J. *Carbohydr. Res.* **1989**, *186*, 225–239.

(31) Huang, L.; Teumelsan, N.; Huang, X. *Chem. Eur. J.* **2006**, *12*, 5246–5252.

85 °C for 3 h. After the removal of solvents in vacuo, the residue was dissolved MeOH (1:2, 15 mL), $Pd(OH)_2$ (50 mg) was added, and the mixture was stirred under H_2 atmosphere for 6 h. The mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo. The residue was dissolved in dry pyridine (15 mL), Ac_2O (10 mL) was added, and the solution was stirred at room temperature for 3 h. The solvents were evaporated and coevaporated with toluene to remove traces of pyridine. The residue was purified by flash chromatography using *n*-hexane−EtOAc (3:1) to afford pure compound **15** (1.1 g, 83%) as white foam. $[\alpha]^{25}_D$ +67 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.95, 6.76 (2d, 4H, J = 9.0 Hz, $C_6H_4OCH_3$), 5.32 (bs, 1H, H-4), 5.24 (dd, 1H, J = 2.1 Hz, 8.7 Hz, H-3″), 5.22 (bs, 1H, H-2″), 5.20−4.94 (m, 5H, H-1″, H-3, H-3′, H-4′, H-4″), 4.87 (d, 1H, J = 7.8 Hz, H-1), 4.75 (bs, 1H, H-1′), 4.17−4.02 (m, 4H, H-2′, H-5′, H-5″, H-6a), 3.95 (m, 3H, H-2, H-5, H-6b), 3.74 (s, 3H, $C_6H_4OCH_3$), 2.12, 2.10, 2.01(3), 1.99, 1.96(2) (8s, 24H, 8 × $COCH_3$), 1.21 (d, 3H, J = 6.0 Hz, C−CH_3), 1.18 (d, 3H, J = 6.3 Hz, C−CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 169.7, 169.4(2), 169.2(3), 169.1(2) (8 × $COCH_3$), 155.7, 150.7, 118.5 (2), 114.5(2) (ArC), 100.8 (C-1), 99.4 (C-1″), 99.1 (C-1′), 77.4, 73.4, 73.1, 71.1, 70.8, 70.6, 70.2, 69.8, 68.5, 67.1, 67.0, 66.8, 61.1 (C-6), 55.3 ($C_6H_4OCH_3$), 20.7(3), 20.6(3), 20.5(2) (8 × $COCH_3$), 17.4, 17.3 (2 × C-CH_3). HRMS calcd for $C_{41}H_{54}O_{23}Na$ $(M + Na)^+$ 937.2954; found 937.2952.

Propargyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→2)-4,6-*O*-benzylidene-β-D-glucopyranoside (20). A mixture of compound **18** (2 g, 4.7 mmol), compound **19** (2.6 g, 5.6 mmol), and MS 4Å (2 g) in dry CH_2Cl_2 (25 mL) was stirred under nitrogen for 1 h. NIS (1.5 g, 6.7 mmol) was added, and the mixture was cooled to −40 °C followed by addition of H_2SO_4−silica (40 mg). The mixture was allowed to stir at −40 °C for 6 h when TLC showed complete consumption of the acceptor **18**. At this point H_2SO_4−silica (30 mg) was added, the reaction temperature was raised to room temperature, and the mixture was stirred for an additional 2 h. The mixture was filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (20 mL) and washed successively with $Na_2S_2O_3$ (2 × 50 mL), $NaHCO_3$ (2 × 50 mL), and brine (50 mL). The organic layer was collected, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by flash chromatography using *n*-hexane−EtOAc (3:1) to afford pure compound **20** (2.4 g, 82%). $[\alpha]^{25}_D$ +47 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.49−7.34 (m, 5H, ArH), 5.53 (s, 1H, C*H*Ph), 5.39 (bd, 1H, J = 2.7 Hz, H-4′), 5.23 (dd, 1H, J = 8.1 Hz, 10.5 Hz, H-2′), 5.06 (dd, 1H, J = 2.7 Hz, 10.5 Hz, H-3′), 4.81 (d, 1H, J = 8.1 Hz, H-1′), 4.67 (d, 1H, J = 7.8 Hz, H-1), 4.47 (dd, 1H, J = 2.4 Hz, 12.6 Hz, H-6a′), 4.45−4.30 (m, 3H, H-2, H-5′, H-6b′), 4.21 (m, 2H, OCH_2-C≡CH), 4.10 (m, 2H, H-6a, H-6b), 3.86 (t, 1H, J = 10.2 Hz, H-3), 3.79 (t, 1H, J = 10.2 Hz, H-4), 3.48 (m, 1H, H-5), 2.95 (bs, 1H, O*H*), 2.53 (t, 1H, J = 2.4 Hz, OCH_2−C≡C*H*), 2.15, 2.06, 2.04, 1.98 (4s, 12H, 4 × $COCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 170.7, 170.2, 170.1, 170.0 (4 × $COCH_3$), 136.8, 129.2, 128.2(2), 126.2(2) (ArC), 101.9 (*C*HPh), 101.7 (C-1′), 100.9 (C-1), 83.5, 79.7, 78.2 (OCH_2-*C*≡CH), 75.6, 72.1, 70.9, 70.7, 69.7, 68.4, 66.9, 66.1, 61.2, 56.9, 20.9, 20.6(2), 20.5 (4 × $COCH_3$). HRMS calcd for $C_{30}H_{36}O_{15}Na$ $(M + Na)^+$ 659.1952; found 659.1954.

Propargyl α-L-Rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-2-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosiduronic Acid (1). To a solution of the protected pentasaccharide **23** (450 mg, 0.33 mmol) in dry MeOH (5 mL) was added NaOMe (50 mg, 0.7 mmol), and the solution was stirred at room temperature for 4 h. The solution was neutralized with DOWEX 50W H+ resin and filtered through a cotton plug. The filtrate was evaporated and washed with CH_2Cl_2 (5 mL), removing the TEMPO salt to afford compound **1** (240 mg, 86%) in 99% yield. ^{1}H NMR (D_2O, 400 MHz) δ: 5.80 (d, 1H, J = 7.2 Hz, H-1^c), 5.18 (bs, 1H, H-1^d), 4.98 (d, 1H, J = 1.6 Hz, H-1^e), 4.38 (d, 1H, J = 7.2 Hz, H-1^b), 4.34 (d, 1H, J = 7.6 Hz, H-1^a), 4.06−3.96 (m, 8H, H-2^d, H-2^e, H-3^a, H-4^b, H-5^e, H-6^c, CH_2-C≡CH), 3.94-.55 (m, 16H, H-2^a, H-2^b, H-2^c, H-3^b, H-3^c, H-3^d, H-3^e, H-4^a, H-4^c, H-5^a, H-5^b, H-5^c, H-5^d, H-6^b, H-6′^{b}, H-6′^{c}), 3.48 (t, 2H, J = 9.6 Hz, H-4^d, H-4^e), 1.94 (bs, 1H, CH_2−C≡C*H*), 1.37 (d, 3H, J = 6.0 Hz, C−CH_3), 1.32 (d, 3H, J = 6.0 Hz, C−CH_3). ^{13}C NMR (D_2O, 100 MHz) δ: 175.4 (*C*OOH), 102.8 (C-1^a), 101.9 (C-1^b), 100.8 (C-1^c), 99.4 (C-1^d), 96.0 (C-1^e), 79.6, 78.2, 77.5, 76.3, 75.7, 75.0, 74.6(2), 74.5, 73.2, 73.0, 72.3, 72.1, 71.4, 70.8, 70.2(2), 69.8, 69.3, 68.6(2), 61.3, 60.4, 56.3, 17.1, 16.7 (2 × $COCH_3$). HRMS calcd for $C_{33}H_{52}O_{25}Na$ $(M + Na)^+$ 871.2695; found 871.2698.

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Supporting Information Available: Experimental details and copies of ^{1}H and ^{13}C spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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