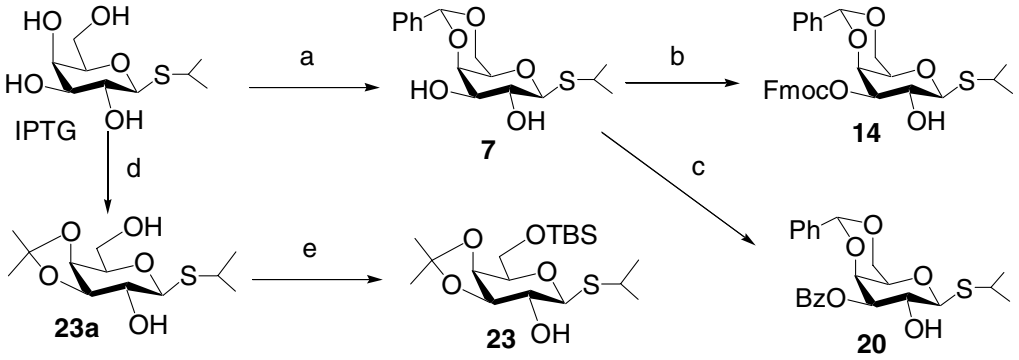
Supplementary materials

Experimental Details and Compound Characterization

1. Preparation of donors

Donors **1** and **18** were synthesized according to literature methods (Ekelöf, K.; Oscarson, S. *J. Org. Chem.* **1996**, *61*, 7711); Donors **4**, **12** and **16** were synthesized according to literature methods (Jiang, L.; Chan, T.-H. *J. Org. Chem.* **1998**, *63*, 6035 and Du, Y.; Zhang, M.; Kong, F. *Org. Lett.* **2000**, *2*, 3797); Donor **25** was prepared according to literature methods (Zegelaar-Jaarsveld, K.; van der Plas, S. C.; van der Marel, G. A.; van Boom, J. H. *J. Carbohydr. Chem.* **1996**, *15*, 591); Donors **7**, **14**, **20** and **23** were prepared according to the following Scheme:



Reagents and conditions: a) 1.2 equiv of $PhCH(OMe)_2$, 0.2 equiv of CSA, DMF, 0 °C — rt, 82%; b) 1.2 equiv of FmocCl, catalytic amount of DMAP, Pyr, 0 °C — rt, 87%; c) 1.1 equiv of BzCl, Pyr, 0 °C, 90%; d) 1.5 equiv of $CH_3C(OMe)_2CH_3$, 0.2 equiv of CSA, acetone, rt, 40%; e) 1.05 equiv of TBSCl, Pyr, 0 °C, 85%.

2. General procedure for the preparation of alkyl or steroidal glycosides using partially protected thioglycosides

To the solution of thioglycosyl donor (1 mmol) and ROH (1 mmol) in anhydrous dichloromethane (2 mL) at - 42 °C, 1.1 mmol of NIS and a catalytic amount of TMSOTf

(0.1 equiv.) were added under a N_2 protection. The reaction mixture was stirred under these conditions for 45 min at which time TLC indicated the reaction was complete. The mixture was then neutralized with Et_3N and concentrated to dryness. The residue was subject to column chromatography on silica gel with petroleum ether/EtOAc (6/1 - 3/1) as the eluent to get desired product.

6'-*C*-azido-hexyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside 3

a white solid; $[\alpha]_D^{25}$ + 7° (*c* 1, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C): δ 1.39-1.43 (m, 4 H, C*H*$_2$C*H*$_2$), 1.60-1.69 (m, 4 H, C*H*$_2$C*H*$_2$), 3.27 (t, 2 H, *J* 6.9 Hz, C*H*$_2$N$_3$), 3.51-3.56 (m, 1 H, OC*H*$_2$CH$_2$), 3.77-3.82 (m, 1 H, OC*H*$_2$CH$_2$), 4.31 (dd, 1 H, *J* 3.0, 1.7 Hz, H-2), 4.34 (m, 1 H, H-5), 4.48 (dd, 1 H, *J* 12.0, 5.6 Hz, H-6a), 4.60 (dd, 1 H, *J* 12.0, 3.0 Hz, H-6b), 4.97 (s, 1 H, *J* 1.6 Hz, H-1), 5.68 (dd, 1 H, *J* 10.0, 3.1 Hz, H-3), 5.92 (t, 1 H, *J* 10.0 Hz, H-4), 7.34-8.04 (15 H, *Ph*).

Octyl 3,6-di-*O*-benzoyl-β-D-galactopyranoside 6

a white solid; $[\alpha]_D^{25}$ + 3° (*c* 2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 3 H, C*H*$_3$), 1.21-1.36 (m, 10 H, C*H*$_2$C*H*$_2$), 1.60-1.67 (m, 2 H, OCH$_2$C*H*$_2$), 3.53-3.60 (m, 1 H, OC*H*$_2$CH$_2$), 3.89-3.98 (m, 2 H, H-5 and OC*H*$_2$CH$_2$), 4.04 (dd, 1 H, *J* 10.2, 7.7 Hz, H-2), 4.22 (d, 1 H, *J* 3.1 Hz, H-4), 4.42 (d, 1 H, *J* 7.7 Hz, H-1), 4.55 (dd, 1 H, *J* 11.4, 6.4 Hz, H-6a), 4.63 (dd, 1 H, *J* 11.4, 6.6 Hz, H-6b), 5.14 (dd, 1 H, *J* 10.2, 3.1 Hz, H-3), 7.40-8.10 (10 H, *Ph*).

6'-*O*-*Tert*-butyldimethylsilyl-hexyl 4,6-di-*O*-benzylidene-β-D-galactopyranoside 9

a colorless oil; $[\alpha]_D^{25}$ - 8° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.05, 0.07 (2 s, 6 H, (C*H*$_3$)$_2$Si), 0.89 (s, 9 H, (C*H*$_3$)$_3$C), 1.34-1.39 (m, 4 H, C*H*$_2$C*H*$_2$), 1.48-1.56 (m, 2 H, C*H*$_2$C*H*$_2$), 1.62-1.68 (m, 2 H, C*H*$_2$C*H*$_2$), 3.48-3.55 (m, 2 H, H-2, H-3), 3.60 (t, 2 H, *J* 6.5

Hz, -C*H*$_2$N$_3$), 3.68-3.77 (m, 2 H, H-5, OC*H*$_2$CH$_2$), 3.94-3.40 (m, 1 H, OC*H*$_2$CH$_2$), 4.09 (br d, 1 H, *J* 12.4 Hz, H-6a), 4.22 (br d, 1 H, H-4), 4.28 (d, 1 H, *J* 7.2 Hz, H-1), 4.34 (br d, 1 H, *J* 12.4 Hz, H-6b), 5.56 (s, 1 H, PhC*H*), 7.35-7.52 (5 H, *Ph*).

Diosgenyl 3,6-di-*O*-benzoyl-β-D-galactopyranoside 11

a white solid; $[\alpha]_D^{25}$ - 30° (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ0.789 (s, 3 H, C*H*$_3$), 0.792 (d, 3 H, J 6.0 Hz, C*H*$_3$), 0.87-0.95 (m, 2 H), 0.98 (d, 3 H, *J* 6.9 Hz, C*H*$_3$), 1.00 (s, 3 H, C*H*$_3$), 1.04-2.38 (m, 22 H), 3.38 (t, 1 H, *J* 10.9 Hz, H-26a), 3.48 (dd, 1 H, *J* 9.4, 3.3 Hz, H-26b), 3.56-3.63 (m, 1 H, H-3α), 3.95-4.05 (m, 2 H, H-2, H-5), 4.22 (d, 1 H, *J* 3.2 Hz, H-4), 4.42 (q, 1 H, *J* 7.3 Hz, H-16), 4.53 (d, 1 H, *J* 7.7 Hz, H-1), 4.54-4.64 (m, 2 H, H-6a, H-6b), 5.15 (dd, 1 H, *J* 10.1, 3.2 Hz, H-3), 5.34 (m, H-6 of diosgenyl), 7.40-8.11 (10 H, *Ph*).

Diosgenyl 3,6-di-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside 13

a colorless oil; $[\alpha]_D^{25}$ - 52° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ0.71, 0.76, 0.13, 0.14 (4 s, 12 H, -(C*H*$_3$)$_2$Si), 0.784 (s, 3 H, C*H*$_3$), 0.788 (d, 3 H, *J* 4.9 Hz, C*H*$_3$), 0.87-0.94 (m, 22 H, two protons of diosgenyl and (C*H*$_3$)$_3$C), 0.97 (d, 3 H, *J* 6.9 Hz, C*H*$_3$), 1.01 (s, 3 H, C*H*$_3$), 1.04-2.40 (m, 22 H), 3.37 (t, 1 H, *J* 10.9 Hz, H-26a), 3.45-3.58 (m, 4 H, H-26b and H-3α of diosgenyl, H-2, H-5), 3.62 (dd, 1 H, *J* 9.0, 3.2 Hz, H-3), 3.78 (d, 1 H, *J* 3.2 Hz, H-4), 3.81 (dd, 1 H, *J* 10.2, 6.2 Hz, H-6a), 3.89 (dd, 1 H, *J* 10.2, 6.3 Hz, Hz, H-6b), 4.30 (d, 1 H, *J* 7.6 Hz, H-1), 4.41 (q, 1 H, *J* 7.3 Hz, H-16), 5.34 (m, 1 H, H-6 of diosgenyl).

Diosgenyl 3-*O*-fluorenylmethoxycarbonyl-4,6-*O*-bezylidiene-β-D-galactopyranoside 15

a white solid; $[\alpha]_D^{25}$ - 34° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ0.788 (s, 3 H, C*H*$_3$), 0.789 (d, 3 H, *J* 6.2 Hz, C*H*$_3$), 0.89-0.96 (m, 2 H), 0.97 (d, 3 H, *J* 6.9 Hz, C*H*$_3$), 1.03 (s, 3 H,

CH_3), 1.04-2.38 (m, 22 H), 3.37 (t, 1 H, *J* 10.9 Hz, H-26a), 3.46-3.50 (m, H-26b, H-5), 3.55-3.66 (m, 1 H, H-3α), 4.04-4.09 (m, 2 H, H-2, H-6a), 4.27-4.34 (m, 2 H, H-6b, C*H* of Fmoc), 4.35-4.50 (m, 5 H, H-16 of diosgenyl, H-1, H-4, CH_2 of Fmoc), 4.75 (dd, 1 H, *J* 10.2, 3.7 Hz, H-3), 5.34 (m, H-6 of diosgenyl), 5.51 (s, 1 H, PhCH_2), 7.42-8.11 (10 H, *Ph*).

Diosgenyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside 17

a white solid; $[\alpha]_D^{25}$ - 38° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ0.79 (s, 3 H, CH_3), 0.80 (d, 3 H, *J* 5.4 Hz, CH_3), 0.89-0.96 (m, 2 H), 0.98 (d, 3 H, *J* 7.0 Hz, CH_3), 0.99 (s, 3 H, CH_3), 1.04-2.38 (m, 22 H), 3.38 (t, 1 H, *J* 10.9 Hz, H-26a), 3.48 (dd, 1 H, *J* 11.3, 5.1 Hz, H-26b), 3.53-3.59 (m, 1 H, H-3α), 3.68 (dd, 1 H, *J* 9.2, 7.8 Hz, H-2), 3.73-3.79 (m, 2 H, H-4, H-5), 4.42 (q, 1 H, *J* 7.4 Hz, H-16), 4.55 (d, 1 H, *J* 7.8 Hz, H-1), 4.61-4.71 (m, 2 H, H-6a, H-6b), 5.21 (t, 1 H, *J* 9.2 Hz, H-3), 5.34 (m, H-6 of diosgenyl), 7.42-8.11 (10 H, *Ph*).

Diosgenyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside 19

a colorless oil; $[\alpha]_D^{25}$ - 64° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ0.78 (d, 3 H, *J* 6.2 Hz, CH_3), 0.79 (s, 3 H, CH_3), 0.90-0.97 (m, 2 H), 0.97 (d, 3 H, *J* 6.9 Hz, CH_3), 1.03 (s, 3 H, CH_3), 1.04-2.38 (m, 22 H), 3.38 (t, 1 H, *J* 10.9 Hz, H-26a), 3.47 (dd, 1 H, *J* 11.0, 5.4 Hz, H-26b), 3.50-3.62 (m, 5 H, H-3α of diosgenyl, H-2, H-3, H-4, H-5), 3.66 (dd, 1 H, *J* 10.8, 5.0 Hz, H-6a), 3.73 (dd, 1 H, *J* 10.8, 1.9 Hz, H-6b), 4.35 (d, 1 H, *J* 7.5 Hz, H-1), 4.42 (q, 1 H, *J* 7.4 Hz, H-16), 4.50-4.95 (m, 6 H, PhCH_2), 5.34 (m, 1 H, H-6 of diosgenyl), 7.16-7.38 (15 H, *Ph*).

Cholest-5-en-yl 3-*O*-benzoyl-4,6-di-*O*-benzylidiene-β-D-galactopyranoside 22

a white solid; $[\alpha]_D^{25}$ + 20° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ0.68 (s, 3 H, CH_3), 0.86 (d,

3 H, *J* 1.8 Hz, CH_3), 0.87 (d, 3 H, *J* 1.7 Hz, CH_3), 0.92 (d, 3 H, *J* 6.5 Hz, CH_3), 1.01 (s, 3 H, CH_3), 3.57 (br s, 1 H, H-5), 3.60-3.70 (m, 1 H, H-3α), 4.10 (dd, 1 H, *J* 12.4, 1.6 Hz, H-6a), 4.14 (dd, 1 H, *J* 10.1, 7.8 Hz, H-2), 4.34 (dd, 1 H, *J* 12.4, 1.3 Hz, H-6b), 4.48 (d, 1 H, *J* 3.8 Hz, H-4), 4.55 (d, 1 H, *J* 7.8 Hz, H-1), 5.16 (dd, 1 H, *J* 10.1, 3.8 Hz, H-3), 5.38 (dd, 1 H, H-6 of cholesterol), 5.51 (s, 1 H, PhCH_2), 7.30-8.11 (m, 10 H, *Ph*).

Cholest-5-en-yl 3,4-di-*O*-isopropylidene-β-D-fucopyranoside 26

a colorless oil; $[\alpha]_D^{25}$ - 5° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 3 H, CH_3), 0.85 (d, 3 H, *J* 1.7 Hz, CH_3), 0.87 (d, 3 H, *J* 1.7 Hz, CH_3), 0.91 (d, 3 H, *J* 6.5 Hz, CH_3), 1.00 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3 of isopropylidene), 1.40 (d, 3 H, *J* 6.6 Hz, H-6 of fucose), 1.53 (s, 3 H, CH_3 of isopropylidene), 3.51 (dd, 1 H, *J* 8.2, 7.4 Hz, H-2), 3.53-3.59 (m, 1 H, H-3α), 3.82-3.88 (m, 1 H, H-5), 3.99 (dd, 1 H, *J* 5.4, 2.1 Hz, H-4), 4.04 (dd, 1 H, *J* 7.4, 5.4 Hz, H-3), 4.25 (d, 1 H, *J* 8.2Hz, H-4), 4.55 (d, 1 H, *J* 8.2 Hz, H-1), 5.38 (dd, 1 H, H-6 of cholesterol).

3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose 28

a colorless oil; $[\alpha]_D^{25}$ - 41° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.29, 1.33, 1.45, 1.54 (4 s, 12 H, CH_3), 3.46-3.501 (m, 1 H, H-5'), 3.56-3.62 (m, 3 H, H-2', H-6a, H-6a'), 3.66-3.78 (m, 3 H, H-3', H-4', H-6b'), 4.00-4.06 (m, 1 H, H-5), 4.10 (dd, 1 H, *J* 11.1, 3.4 Hz, H-6b), 4.22 (dd, 1 H, *J* 8.0, 1.9 Hz, H-4), 4.32 (dd, 1 H, *J* 5.0, 2.4 Hz, H-2), 4.34 (d, 1 H, *J* 8.6 Hz, H-1), 4.50, 5.02 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.52 (d, 1 H, *J* 12.2 Hz, one proton of PhCH_2), 4.58-4.63 (m, 2 H, H-3 and one proton of PhCH_2), 4.80, 5.02 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 5.55 (d, 1 H, *J* 5.0 Hz, H-1), 7.13-7.40 (m, 15 H, *Ph*).

3,6-Di-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose 29

a colorless oil; ^{1}H NMR ($CDCl_3$): (α:β = 1:2) δ1.25, 1.33, 1.41, 1.55 (4 s, 4 × 0.99 H, CH_3 of isopropylidene), 1.31, 1.44, 1.54 (3 s, 4 δ2.01 H, CH_3 of isopropylidene), 3.75-4.37 (m, 8 H), 4.49-4.67 (m, 3.67 H, H-1' of β isomer, H-3, H-6a', H-6b'), 5.07 (d, 0.33 H, *J* 5.0 Hz, H-1' of α isomer), 5.15 (dd, 0.67 H, *J* 10.0, 2.8 Hz, H-3' of β isomer), 5.36 (dd, 0.33 H, *J* 10.0, 2.8 Hz, H-3' of α isomer), 5.52 (d, 0.33 H, *J* 5.0 Hz, H-1 of α isomer), 5.54 (d, 0.67 H, *J* 5.0 Hz, H-1 of β isomer), 7.41-8.12 (m, 10 H, *Ph*).

Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside 33

a colorless oil; $[\alpha]_D^{25}$ + 11° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ3.18-3.22 (m, 1 H, H-5), 3.35 (s, 3 H, OCH_3), 3.38-3.51 (m, 5 H), 3.54-3.68 (m, 2 H), 3.75-3.79 (m, 1 H, H-5), 3.93-3.99 (m, 3 H), 4.54 (d, 1 H, *J* 7.2 Hz, H-1'), 4.57 (d, 1 H, *J* 4.0 Hz, H-1), 4.38, 4.42, 4.49, 4.53, 4.58, 4.65, 4.72, 4.77, 4.78, 4.87, 4.88, 5.00 (12 d, 6 × 2 H, *J* 11.0, 11.4, 11.5, 11.8, 12.1, 12.2 Hz, 6 × PhCH_2), 7.15-7.34 (m, 30 H, *Ph*).

3. Preparation of diosgenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-[2,3,4-tri-*O*-acetyl-α-L-rhamanopyranosyl-(1→2)]-3,6-di-*O*-benzoyl-β-D-galactopyranoside 38

To a solution of **11** (185 mg, 0.235 mmol) and **36** (107 mg, 0.247 mmol) in anhydrous CH_2Cl_2 (3 mL) at - 42 °C, TMSOTf (3 μL, 0.017 mmol) was added under nitrogen protection. The mixture was stirred under these conditions for 45 min, at the end of which

time TLC indicated the donor was completely consumed. The temperature was raised to 0 °C, and a solution of **37** (262 mg, 0.354 mmol) in CH_2Cl_2 (2 mL) was cannulated into the reaction mixture. An additional amount of TMSOTf (4 μL, 0.022 mmol) was slowly dropped into the mixture, stirred for another 3 h, neutralized with triethylamine, and concentrated. Column chromatography (petroleum ether/EtOAc, 3:1) of the residue gave **38** (265 mg, 68.7%) as an amorphous solid: $[\alpha]_D^{25}$ - 6 ° (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C): δ 0.78 (s, 3 H, C*H*$_3$), 0.79 (d, 3 H, *J* 6.1 Hz, C*H*$_3$), 0.97 (s, 3 H, C*H*$_3$), 0.98 (d, 3 H, *J* 6.7 Hz, C*H*$_3$), 1.13 (d, 1 H, *J* 6.2 Hz, H-6^{II}), 1.77, 1.85, 2.00 (3 s, 3 × 3 H, C*H*$_3$CO), 2.24 (dt, 1 H), 2.36 (dd, 1 H), 3.38 (t, 1 H, *J* 10.9 Hz, H-26a), 3.48 (dd, 1 H, *J* 10.9, 5.1 Hz, H-26b), 3.52-3.61 (m, 1 H, H-3α), 3.92-4.02 (m, 3 H, H-2, H-5^{I}, H-5^{II}), 4.30-4.47 (m, 6 H, H-1^{II}, H-4^{I}, H-5^{III}, H-6a$^{I/III}$, H-6b$^{I/III}$, H-16), 4.4.51-4.58 (m, 2 H, H-1^{I}, H-6a$^{III/I}$), 4.67 (dd, 1 H, *J* 11.8, 4.9 Hz, H-6b$^{III/I}$), 4.80 (dd, 1 H, *J* 3.5, 1.6 Hz, H-2^{II}), 4.87 (d, 1 H, *J* 7.7 Hz, H-1^{III}), 4.89 (t, 1 H, *J* 10.0 Hz, H-4^{II}), 5.08 (dd, 1 H, *J* 10.0, 3.5 Hz, H-3^{II}), 5.20 (dd, 1 H, *J* 10.1, 2.8 Hz, H-3^{I}), 5.29 (m, 1 H, H-6), 5.57 (dd, 1 H, *J* 9.9, 7.7 Hz, H-2^{III}), 5.62 (t, 1 H, *J* 10.1 Hz, H-4^{III}), 5.79 (t, 1 H, *J* 9.7 Hz, H-3^{III}), 7.27-8.01 (30 H, *Ph*). ^{13}C NMR (100 Hz, CCl_3D, 25 °C): δ 14.09, 14.50, 16.26, 17.10, 17.16 (*C*-6^{II}), 19.21, 20.37, 20.56, 20.79, 28.79, 29.58, 29.66, 30.29, 31.39, 31.82, 32.06, 36.80, 36.98, 37.42, 38.36, 39.76, 40.24, 41.60, 49.97, 56.46, 62.26 (*C*-6$^{I/II}$), 63.65 (*C*-6$^{II/I}$), 66.10, 66.83, 68.93 (*C*-3^{II}), 69.13 (*C*-3^{III}), 69.19 (*C*-4^{II}), 71.16 (*C*-2^{II}), 71.68 , 72.10, 72.38, 72.64, 72.70, 74.30, 76.52, 79.22, 80.78, 97.48 (*C*-1^{II}), 99.82 (*C*-1^{I}), 101.34 (*C*-1^{III}), 109.26, 121.71 (*C*-6), 140.30 (*C*-5), 164.96, 165.12, 165.67, 165.82, 165.89 (6 C, Ph*C*O, some overlapped), 169.40, 169.69, 170.02 (3 C, CH_3*C*O). Anal. Calcd for $C_{93}H_{102}O_{26}$: C, 68.28; H, 6.29%. Found: C, 68.63; H, 6.21%.

4. Preparation of diosgenyl β-D-glucopyranosyl-(1→4)-[α-L-rhamanopyranosyl-

(1→2)]-β-D-galactopyranoside 39

To a solution of compound **38** (225 mg, 0.138 mmol) in MeOH (6 mL) aqueous 1 N NaOH was added until the pH was 10. The mixture was stirred at rt for 6 h, then neutralized with Amberlite IR-120 (H^+). The solvents were filtered, and the filtrate was concentrated to dryness under diminished pressure. The residue was subjected to column chromatography on silica gel with CH_2Cl_2/MeOH (5:2) as the eluent to give **39** as a white solid (112 mg, 92.3%): $[\alpha]_D^{25}$ – 78° (*c* 0.25, CH_3OH); ^{1}H NMR (400 Hz, d_6-DMSO): δ 0.73 (s, 3 H, CH_3), 0.74 (d, 3 H, *J* 6.1 Hz, CH_3), 0.91 (d, 3 H, *J* 6.9 Hz, CH_3), 0.96 (s, 3 H, CH_3), 1.09 (d, 1 H, *J* 6.2 Hz, H-6^{II}), 2.95-3.25 (m, 6 H), 3.26-3.50 (m, 8 H), 3.55-3.74 (m, 4 H), 3.79 (d, 1 H, *J* 3.2 Hz, H-4^{I}), 3.98 (q, 1 H, *J* 6.2 Hz, H-5^{II}), 4. 26 (d, 1 H, *J* 7.7 Hz, H-1^{III}), 4.29 (s, 1 H, *J* 4.6 Hz, O*H*), 4.36 (d, 1 H, *J* 7.8 Hz, H-1^{I}), 4.39 (m, 1 H, H-16), 4.49, 4.60, 4.62, 4.68, 4.79 (5 s, 5 H, *J* 5.8, 4.2, 4.8, 4.4, 9.0 Hz, O*H*), 4.96 (br s, 1 H, H-1^{II}), 4.97, 5.01 (2 s, 2 H, *J* 5.3, 5.0 Hz, O*H*), 5.31 (m, H-6); 5.53 (s, 1 H, *J* 3.7 Hz, O*H*); ^{13}C NMR (100 Hz, d_6-DMSO): δ14.61, 15.98, 17.05, 17.72, 18.91, 20.37, 28.46, 29.10, 29.78, 30.96 (2 C), 31.45, 31.49, 36.38, 36.79, 37.59, 38.36, 39.76, 40.24, 41.08, 48.58, 49.57, 55.76, 59.49, 61.49, 61.80, 65.91, 67.96, 70.50, 70.63, 71.93, 73.50, 74.21, 75.43, 76.09, 76.73, 76.77, 78.91, 80.16, 98.36 (*C*-1^{I}), 100.34 (*C*-1^{III}), 105.09 (*C*-1^{II}), 108.38, 121.16 (*C*-6), 140.31 (*C*-5). MALDITOF-MS found for $C_{45}H_{72}O_{17}$: 907.3 $(M + Na)^+$.