Direct Synthesis of the β -L-Rhamnopyranosides

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General Procedures. All solvents were dried and distilled by standard procedures. ^1H and ^{13}C

NMR spectra were recorded at 500 and 125 MHz, respectively, with CDCl_3 as solvent unless

otherwise stated. All the reactions were run under argon atmosphere unless otherwise stated.

The donors were dried overnight in a vacuum oven at approx. 45 $^\circ\text{C}$, as were acceptors for

examples **23-29**. BSP was placed on a vacuum pump for 3 h at room temperature prior to use, as

was TTBP and cholestanol. Triflic anhydride was distilled over P_2O_5 . Optical rotations were

recorded on an Autopol polarimeter in CH₂Cl₂ unless otherwise stated. Microanalyses were carried out by Midwest Microlabs, Indianapolis, IN. All the mass spectra were recorded by the Regional Resource Center at the University of Illinois at Chicago.

Phenyl 2,3,4-tri-*O*-acetyl-1-thio- β -L-rhamnopyranoside (2). To a solution of thiophenol (16.5 mL, 160.3 mmol) in HMPA (54 mL), NaH (9.6g, 240.4 mmol) was added slowly at 0 °C. After stirring for 5 min, **1**^{1,2} (28.3 g, 80.1 mmol) in HMPA (50 mL) was added through a pressure addition funnel over a period of 15 min. After 40 min TLC indicated the disappearance of starting material and the reaction was quenched slowly by adding water followed by ethyl acetate. The aqueous layer was then extracted twice with ethyl acetate, and the combined organic extracts were washed with brine, and dried (Na₂SO₄). Column chromatography (hexanes/ethyl acetate, 3:1) afforded **3** (23.9 g, 78%) as an oil. $[\alpha]_D^{25} +65.4$ (*c*, 0.72, CHCl₃); ¹H NMR δ : 7.48-7.45 (m, 2H) 7.31-7.24 (m, 3H), 5.63-5.62 (dd, *J* = 1.5 Hz, 1H), 5.11-5.07 (t, *J* = 10.5, 9.5 Hz, 1H), 4.99-4.97 (dd, *J* = 3.5, 4.0 Hz, 1H), 4.88-4.87 (d, *J* = 1.0 Hz), 3.55-3.50 (m, 1H), 2.17 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.29-1.28 (d, *J* = 6 Hz, 3H); ¹³C NMR δ : 170.7, 170.5, 170.2, 133.7, 132.4, 129.5, 128.4, 85.7 (*J*_{CH} = 153.4 Hz), 75.3, 72.2, 71.4, 70.6, 21.2, 21.0, 18.2; ESIHRMS Calcd. for C₁₈H₂₂O₇NaS [M+Na]⁺: 405.0984. Found: 405.0996.

Phenyl 1-thio- β -L-rhamnopyranoside (3). To a solution of **2** (23.2 g, 60.6 mmol) in methanol (202 mL), was added a solution of sodium methoxide (0.28 g, 12.1 mmol in 50 mL of methanol, or 0.2 eq of commercial sodium methoxide in 50 mL of methanol) at room temperature.² After stirring for 3 h the reaction mixture was neutralized with Amberlyst 15 ion exchange resin, filtered, and concentrated under reduced pressure. Recrystallization from hexanes yielded **3** (14.8 g, 95%) as a white solid. $[\alpha]_D^{25} +98.6$ (*c*, 0.94, MeOH); Mp 149 °C; ¹H NMR (DMSO-d₆) δ : 7.36-7.16 (m, 5H), 5.01 (s, 1H), 5.00-4.99 (d, *J* = 6.0 Hz, 1H), 4.84-4.83 (d, *J* = 5.0 Hz, 1H),

4.80-4.79 (d, $J = 5.5$ Hz, 1H), 3.83-3.81 (m, 1H), 3.26-3.20 (m, 1H), 1.17-1.16 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (DMSO- d_6) δ : 137.4, 129.8, 129.1, 126.8, 86.9, 76.8, 74.8, 73.3, 72.4, 19.0; ESIHRMS Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_4\text{NaS}$ $[\text{M}+\text{Na}]^+$: 279.0667. Found: 279.0677.

Phenyl 2,3-*O*-isopropylidene-1-thio- β -L-rhamnopyranoside (4). To a solution of **3** (7.7 g, 30.0 mmol) in acetone³ (150 mL) was added 2,2-dimethoxypropane (4.0 mL, 32.5 mmol) and CSA (1.4 g, 6.0 mmol). The reaction mixture was stirred for 12 h at room temperature after which Et_3N was added (3 mL), and the reaction contents concentrated under reduced pressure. Dichloromethane was added to the reaction mixture, along with saturated aqueous NaHCO_3 . After stirring for 10 min the reaction mixture was extracted with CH_2Cl_2 . The organic washed with brine, and dried (NaSO_4). Concentration under reduced pressure afforded a yellowish-white solid which was recrystallized from hexanes to yield **4** as a white solid (7.0 g, 79%). $[\alpha]_D^{25} +116.2$ (c, 0.52); Mp 141 °C; ^1H NMR δ : 7.55-7.54 (d, $J = 8.5$ Hz, 2H), 7.33-7.26 (m, 3H), 5.05-5.04 (d, $J = 2.5$ Hz, 1H), 4.44-4.43 (dd, $J = 2.5$ Hz, 2 Hz), 4.02-4.00 (dd, $J = 5.5$ Hz, 6 Hz, 1H), 3.54-3.51 (dd, $J = 7.5$ Hz, 1H), 3.32-3.27 (m, 1H), 1.60 (s, 3H), 1.42 (s, 3H), 1.38-1.37 (d, $J = 6$ Hz, 3H); ^{13}C NMR δ : 135.5, 131.4, 129.4, 127.6, 111.2, 84.3, 75.2, 69.3, 28.61, 26.8, 18.2. Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80. Found: C, 60.92; H, 6.78.

Phenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio- β -L-rhamnopyranoside (5). To a solution of **4** (5.0 g, 16.9 mmol) in THF (169 mL) was added a 60% dispersion of NaH (1.35g, 33.8 mmol) slowly at 0 °C. After stirring for 5 min, the reaction mixture was taken off the ice bath, benzyl bromide was added (3.13 mL, 27.0 mmol) and the reaction refluxed overnight. The reaction mixture was quenched slowly by adding drops of ammonium chloride, and extracted with ethyl acetate. The combined organic layers were washed with brine and dried (NaSO_4), and the solvent removed under reduced pressure. Column chromatography over silica gel (hexanes/ethyl

acetate, 10:1) afforded **5** (5.7g, 87%) as a white solid. $[\alpha]_D^{25} +90.1$ (*c*, 0.44); Mp 125 °C; ^1H NMR δ : 7.54-7.52 (d, *J* = 8.0 Hz, 2H), 7.36-7.25 (m, 8H), 5.02-5.01 (d, *J* = 1.5 Hz, 1H), 4.88-4.86 (d, *J* = 11.5 Hz, 1H), 4.65-4.63 (d, *J* = 11.5 Hz, 1H), 4.45-4.43 (dd, *J* = 2.5 Hz, 2 Hz, 1H), 4.25-4.22 (t, *J* = 6.0 Hz, 5.5 Hz, 1H), 3.38-3.34 (m, 1H), 1.37-1.36 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR δ : 138.5, 135.6, 131.3, 129.3, 128.8, 128.5, 128.2, 127.8, 84.5, 80.9, 80.4, 77.1, 76.8, 75.0, 73.4, 28.4, 26.8, 18.9. Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_4\text{S}$: C, 68.37; H, 6.78. Found: C, 68.31; H, 6.74.

Phenyl 4-*O*-benzyl-1-thio- β -L-rhamnopyranoside (6). To a solution of **5** (4.9 g, 12.7 mmol) in methanol (64 mL) was added trifluoroacetic acid⁴ (0.39 mL, 5.1 mmol), and the contents refluxed for 8 h after which time the reaction showed the complete consumption of the starting material. The mixture was then cooled to room temperature and diluted with ethyl acetate. A saturated solution of NaHCO_3 was added until effervescence ceased after which the organic layers were washed with brine and dried (NaSO_4). Concentration under reduced pressure afforded a white solid which was recrystallized from hexanes to yield **6** (3.9 g, 90%) as white solid. $[\alpha]_D^{25} +86.3$ (*c*, 0.80); Mp 157 °C; ^1H NMR δ : 7.51-7.26 (m, 10H), 4.82 (s, 1H), 4.81-4.79 (d, *J* = 11.5 Hz, 1H), 4.76-4.74 (d, *J* = 11.0 Hz, 1H), 4.16-4.15 (d, *J* = 2.5 Hz, 1H), 3.67-3.66 (m, 1H), 3.40-3.38 (m, 1H), 2.53-2.46 (br. s., 2H), 1.42-1.41 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR δ : 138.5, 134.6, 131.8, 129.5, 129.1, 128.5, 128.4, 128.0, 87.1, 81.6, 76.3, 75.6, 75.3, 73.1, 18.7. Anal. Calcd. for: $\text{C}_{19}\text{H}_{22}\text{O}_4\text{S}$: C, 65.87; H, 6.40. Found: C, 66.07; H, 6.47.

Phenyl 3,4-di-*O*-benzyl-1-thio- β -L-rhamnopyranoside (7). To a solution of **6** (3.5 g, 10.1 mmol) in benzene (101 mL) was added dibutyltin oxide (3.0 g, 12.1 mmol) followed by heating to reflux using a Dean-Stark apparatus for 3 h, until all the water has been removed from the mixture.⁵ The contents were then cooled to room temperature and the solvent removed under reduced pressure. DMF was then added (101 mL) along with CsF (3.1 g, 20.2 mmol) followed

by benzyl bromide (1.52 mL, 13.1 mmol). The reaction mixture was stirred for 18 h and then diluted with ethyl acetate. The organic layer was washed with water, brine, dried (NaSO₄), and concentrated under reduced pressure. Column chromatography (hexanes/ethyl acetate, 9:1) afforded **7** (3.1 g, 71%) as a white solid. $[\alpha]_D^{25} +46.8$ (c, 1.09); Mp 103 °C; ¹H NMR δ: 7.51-7.24 (m, 15H), 4.92-4.89 (d, *J* = 11.0 Hz, 1H), 4.76-4.65 (m, 4H), 4.28-4.28 (d, *J* = 2.5 Hz, 1H), 3.60-3.57 (dd, *J* = 3.5 Hz, 3.0 Hz, 1H), 3.55-3.52 (t, *J* = 8.5 Hz, 9 Hz, 1H), 3.40-3.35 (m, 1H), 2.66 (br. s., 1H), 1.39-1.37 (d, *J* = 6.5 Hz, 3H); ¹³C NMR δ: 138.6, 137.9, 135.3, 131.5, 129.4, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 127.7, 86.8, 82.8, 79.8 76.3, 76.0, 72.3, 70.6, 18.6. Anal. Calcd. for C₂₆H₂₈O₄S: C, 71.53; H, 6.46. Found: C, 71.37; H, 6.47.

Typical sulfonylation procedure for compounds 8-12: To a solution of **8** in CH₂Cl₂ (0.1 M in substrate) was added Et₃N (3 eq) followed by the sulfonyl chloride (1.5 eq) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred until the starting material was consumed. The reaction mixture was then quenched with a saturated aqueous solution of NaHCO₃ and extracted with CH₂Cl₂. The combined organic layer was then dried (Na₂SO₄). Concentration under reduced pressure and column chromatography over silica gel (hexanes/ethyl acetate) afforded the respective sulfonylated products. For compounds **13** and **15** collidine was used as a base and the crude reaction mixture was washed twice with a saturated aqueous CuSO₄ solution before concentration.

Phenyl 3,4-di-*O*-benzyl-2-*O*-(4-bromobenzenesulfonyl)-1-thio-β-L-rhamnopyranoside (8**).**

The reaction of **7** (0.211 g, 0.484 mmol) with 4-bromobenzenesulfonyl chloride for 24 h gave **8** (0.270 g, 85%) as a white solid. $[\alpha]_D^{25} +59.5$ (c, 0.81); Mp 137 °C; ¹H NMR δ: 7.87-7.86 (d, *J* = 8.5 Hz, 2H), 7.59-7.57 (d, *J* = 9.0 Hz, 2H), 7.46-7.22 (m, 15H), 5.48-5.47 (d, *J* = 3.0 Hz, 1H), 4.94-4.91 (d, *J* = 11.0 Hz, 1H), 4.85-4.83 (d, *J* = 11.0 Hz, 1H), 4.78 (s, 1H), 4.59-4.56 (m, 2H),

3.63-3.60 (dd, $J = 2.5$ Hz, 1H), 3.40-3.35 (m, 2H), 1.33-1.32 (d, $J = 5.5$ Hz, 3H); ^{13}C NMR δ : 138.3, 137.6, 137.0, 134.2, 132.4, 131.9, 130.1, 129.5, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 85.5, 81.3, 80.4, 79.0, 76.9, 75.9, 72.9, 18.5; ESIHRMS Calcd. for $\text{C}_{32}\text{H}_{31}\text{BrO}_6\text{NaS}_2$ $[\text{M}+\text{Na}]^+$: 677.0643. Found: 677.0659.

Phenyl 3,4-di-*O*-benzyl-2-*O*-(4-fluorobenzenesulfonyl)-1-thio- β -L-rhamnopyranoside (9).

The reaction of **7** (0.185 g, 0.424 mmol) with 4-fluorobenzenesulfonyl chloride for 24 h gave **9** (0.209 g, 83%) as a white solid. $[\alpha]_{\text{D}}^{25} +64.8$ (c , 0.29); Mp 129 °C; ^1H NMR δ : 8.08-8.05 (m, 2H), 7.49-7.11 (m, 17H), 5.53-5.52 (d, $J = 2.5$ Hz, 1H), 4.99-4.97 (d, $J = 11.5$ Hz, 1H), 4.90-4.88 (d, $J = 10.5$ Hz, 1H), 4.83-4.82 (d, $J = 0.5$ Hz, 1H), 4.62-4.60 (d, $J = 10.5$ Hz, 1H), 3.68-3.66 (dd, $J = 3.0$ Hz, 1H), 3.48-3.39 (m, 2H), 1.37-1.36 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR δ : 138.4, 137.8, 134.3, 134.1, 131.8, 131.5, 131.4, 129.6, 128.89, 128.86, 128.7, 128.6, 128.4, 128.3, 128.2, 116.5, 116.4, 85.5, 81.4, 80.3, 79.1, 76.9, 76.0, 72.9, 18.6. Anal. Calcd. for $\text{C}_{32}\text{H}_{31}\text{FO}_6\text{S}_2$: C, 64.63; H, 5.25. Found: C, 64.84; H, 5.32.

Phenyl 3,4-di-*O*-benzyl-2-*O*-tresyl-1-thio- β -L-rhamnopyranoside (10). The reaction of **7** (0.410 g, 0.939 mmol) with tresyl chloride for 4 h at 0 °C and 3 hrs at rt. gave **9** (0.328 g, 60%) as an oil. $[\alpha]_{\text{D}}^{25} +39.3$ (c , 1.08); ^1H NMR δ : 7.54-7.52 (m, 2H), 7.34-7.31 (m, 13H), 5.44-5.43 (d, $J = 3.0$ Hz, 1H), 4.91-4.89 (d, $J = 11.0$ Hz, 1H), 4.82 (s, 1H), 4.81-4.79 (d, $J = 10.5$ Hz, 1H), 4.72-4.69 (m, 2H), 4.19-4.11 (m, 1H), 4.02-3.94 (m, 1H), 3.67-3.65 (dd, $J = 3.0$ Hz, 1H), 3.50-3.40 (m, 2H), 1.40-1.39 (d, $J = 5.5$ Hz, 3H); ^{13}C NMR δ : 138.1, 136.9, 133.6, 132.3, 129.6, 129.2, 128.9, 128.9, 128.6, 128.5, 85.3, 83.1, 81.4, 79.4, 77.0, 76.0, 74.1, 18.5; ESIHRMS Calcd. for $\text{C}_{28}\text{H}_{29}\text{F}_3\text{O}_6\text{NaS}$ $[\text{M}+\text{Na}]^+$: 605.1255. Found: 605.1261.

Phenyl 3,4-di-*O*-benzyl-2-*O*-(4-cyanobenzenesulfonyl)-1-thio- β -L-rhamnopyranoside (11).

The reaction of **7** (0.289 g, 0.662 mmol) with 4-cyanobenzenesulfonyl chloride for 36 h gave **11**

(0.33g, 82%) as a white solid. $[\alpha]_D^{25} +55.5$ (*c*, 0.71); Mp 137 °C; ^1H NMR δ : 8.09-8.07 (m, 2H), 7.69-7.67 (m, 2H), 7.45-7.22 (m, 15H), 5.49-5.48 (d, *J* = 2.5 Hz, 1H), 4.89-4.86 (d, *J* = 11.5 Hz, 1H), 4.83-4.81 (d, *J* = 10.5 Hz, 1H), 4.79-4.78 (d, *J* = 1.0 Hz, 1H), 4.59-4.57 (d, *J* = 11.0 Hz, 2H), 3.64-3.61 (m, 1H), 3.40-3.37 (m, 2H), 1.34-1.33 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR δ : 142.0, 138.2, 137.5, 133.8, 132.9, 132.1, 129.6, 129.1, 128.91, 128.86, 128.6, 128.54, 128.48, 128.37, 117.7, 117.4, 85.4, 81.4, 81.2, 79.2, 76.9, 76.0, 73.2, 18.5; ESIHRMS Calcd. for $\text{C}_{33}\text{H}_{31}\text{NO}_6\text{NaS}_2$ $[\text{M}+\text{Na}]^+$: 624.1491. Found: 624.1475.

Phenyl 3,4-di-*O*-benzyl-2-*O*-(4-trifluoromethylbenzenesulfonyl)-1-thio- β -L-

rhamnopyranoside (12). The reaction of **7** (0.32 g, 0.733 mmol) with 4-trifluoromethylbenzenesulfonyl chloride for 36 h gave **12** (0.364 g, 77%) as a white solid. $[\alpha]_D^{25} +52.9$ (*c*, 0.79); Mp 143 °C; ^1H NMR δ : 8.13-8.12 (m, 2H), 7.70-7.69 (d, *J* = 8.5 Hz, 1H), 7.45-7.21 (m, 15H), 5.52-5.51 (m, 1H), 4.93-4.91 (d, *J* = 11.5 Hz, 1H), 4.83-4.81 (d, *J* = 10.5 Hz, 1H), 4.797-4.796 (d, *J* = 0.5 Hz, 1H), 4.59-4.58 (d, *J* = 2.5 Hz, 1H), 4.57-4.56 (d, *J* = 2.5 Hz, 1H), 3.64-3.62 (m, 1H), 3.42-3.37 (m, 2H), 1.34-1.33 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR δ : 141.4, 138.2, 137.6, 134.0, 131.9, 129.6, 129.1, 128.88, 128.81, 128.7, 128.5, 128.43, 128.36, 128.33, 126.30, 126.28, 85.4, 81.3, 80.9, 79.1, 76.9, 75.9, 73.0, 18.5; ESIHRMS Calcd. for $\text{C}_{33}\text{H}_{31}\text{F}_3\text{O}_6\text{NaS}$ $[\text{M}+\text{Na}]^+$: 667.1412. Found: 667.1443.

General Procedure For Coupling Phenyl 3,4-di-*O*-benzyl-2-*O*-(sulfonyl)-1-thio- β -L-rhamnopyranoside with Cholesterol:

To a solution of substrate in CH_2Cl_2 (.03 M in substrate), BSP, and TTBP was added and the reaction cooled to -60 °C, after which Tf_2O (1.1equiv) was added slowly. After 30 min of stirring at -60 °C, cholesterol (2 eq) in CH_2Cl_2 (2 M in substrate) was added slowly over a period of 1 min. The cloudy reaction mixture was stirred for further 30 min at -60 °C, then the reaction

mixture was removed from the dry ice/acetone bath and left to stir for another 15 min. The clear orange solution was then quenched by adding a saturated aqueous solution of NaHCO₃. Brine was then added and the contents were extracted with CH₂Cl₂. The combined organic layer was dried (Na₂SO₄) and the solvent removed under reduced pressure. Purification by silica gel column chromatography (hexanes/ethyl acetate) afforded the corresponding alpha/beta rhamnosides.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-bromobenzenesulfonyl)- α -L-rhamnopyranoside

(13 α). White solid. $[\alpha]_D^{25}$ -32.7 (*c*, 0.77); Mp 127 °C; ¹H NMR δ : 7.90-7.89 (m, 2H), 7.32-7.21 (m, 10H), 7.00-6.97 (m, 2H), 4.98-4.97 (d, *J* = 1.4 Hz, 1H), 4.85-4.83 (d, *J* = 10.0 Hz, 1H), 4.78-4.77 (t, *J* = 3.0 Hz, 1H), 4.58-4.56 (d, *J* = 10.5 Hz, 1H), 4.50-4.45 (q, *J* = 11.5 Hz, 2H), 3.91-3.89 (dd, *J* = 3.4 Hz, 1H), 3.79-3.74 (m, 1H), 3.52-3.46 (m, 1H), 3.41-3.37 (t, *J* = 9.0 Hz, 1H), 1.97-0.56 (m, 50H); ¹³C NMR δ : 138.5, 138.2, 133.1, 131.3, 131.2, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 116.8, 116.6, 95.5 (*J*_{CH} = 169.3Hz), 80.3, 76.9, 76.0, 72.5, 68.2, 56.9, 56.8, 54.7, 45.0, 39.9, 37.4, 36.6, 36.0, 35.9, 29.4, 29.2, 28.7, 28.4, 24.6, 24.2, 23.2, 23.0, 21.6, 19.1, 18.2, 12.7, 12.5; ESIHRMS Calcd. for C₅₃H₇₃BrO₇NaS [M+Na]⁺: 950.4604. Found: 950.4595.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-bromobenzenesulfonyl)- β -L-rhamnopyranoside

(13 β). White solid. $[\alpha]_D^{25}$ +74.7 (*c*, 0.59); Mp 152 °C; ¹H NMR δ : 7.84-7.82 (d, *J* = 9.0 Hz, 2H), 7.59-7.26 (m, 12H), 5.12-5.11 (d, *J* = 3.5 Hz, 1H), 4.98-4.96 (d, *J* = 11.5 Hz, 1H), 4.92-4.90 (d, *J* = 10.5 Hz, 1H), 4.60-4.56 (m, 2H), 4.51 (s, 1H), 3.61-3.59 (dd, *J* = 3.0 Hz, 1H), 3.48-3.40 (m, 2H), 3.32-3.27 (m, 1H), 1.97-0.53 (m, 50H); ¹³C NMR δ : 143.4, 138.6, 138.0, 137.8, 137.0, 134.1, 132.3, 131.8, 130.2, 129.9, 129.2, 128.83, 128.80, 128.60, 128.57, 128.49, 128.2, 128.0, 96.2 (*J*_{CH} = 156.2Hz), 80.1, 79.7, 79.2, 78.1, 76.0, 72.24, 72.20, 56.9, 56.7, 54.7, 45.1, 43.0, 40.4, 39.9, 37.2, 36.6, 36.2, 35.93, 35.88, 32.4, 29.1, 28.7, 28.4, 28.0, 24.6, 24.3, 23.3, 23.0, 21.6,

19.1, 18.4, 12.8, 12.5; ESIHRMS Calcd. for $C_{53}H_{73}BrO_7NaS$ $[M+Na]^+$: 950.4604. Found: 950.4591.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-fluorobenzenesulfonyl)- α -L-rhamnopyranoside

(14 α). White solid. $[\alpha]_D^{25}$ -66.3 (*c*, 0.97); Mp 178 °C; 1H NMR δ : 7.93-7.90 (m, 2H), 7.32-7.21 (m, 10H), 7.02-6.99 (m, 2H), 4.99-4.98 (d, *J* = 1.5 Hz, 1H), 4.85-4.83 (d, *J* = 10.5 Hz, 1H), 4.79-4.78 (t, *J* = 3.0 Hz, 1H), 4.58-4.56 (d, *J* = 10.5 Hz, 1H), 4.50-4.45 (q, *J* = 11.5 Hz, 2H), 3.91-3.89 (dd, *J* = 3.5 Hz, 1H), 3.79-3.74 (m, 1H), 3.52-3.46 (m, 1H), 3.41-3.37 (t, *J* = 9.0 Hz, 1H), 1.97-0.56 (m, 50H); ^{13}C NMR ($CDCl_3$) δ : 138.51, 138.2, 133.1, 131.3, 131.2, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 116.8, 116.6, 95.5 (J_{CH} = 170.9Hz), 80.3, 76.9, 76.0, 72.5, 68.2, 56.9, 56.7, 54.7, 45.0, 39.9, 37.4, 36.6, 36.0, 35.9, 29.4, 29.2, 28.7, 28.4, 24.6, 24.2, 23.2, 23.0, 21.6, 19.1, 18.2, 12.7, 12.5; ESIHRMS Calcd. for $C_{53}H_{73}FO_7NaS$ $[M+Na]^+$: 895.4959. Found: 895.4950.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-fluorobenzenesulfonyl)- β -L-rhamnopyranoside

(14 β). White solid. $[\alpha]_D^{25}$ +38.5 (*c*, 1.04); Mp 164 °C; 1H NMR δ : 8.02-7.99 (m, 2H), 7.58-7.26 (m, 10H), 7.12-7.09 (m, 2H), 5.17-5.16 (d, *J* = 2.5 Hz, 1H), 4.99-4.97 (d, *J* = 11.5 Hz, 1H), 4.93-4.91 (d, *J* = 10.5 Hz, 1H), 4.61-4.60 (d, *J* = 5.0 Hz, 1H), 4.58-4.57 (d, *J* = 5.0 Hz, 1H), 4.54 (s, 1H), 3.63-3.60 (dd, *J* = 2.5 Hz, 1H), 3.51-3.47 (m, 1H), 3.45-3.41 (t, *J* = 9.5 Hz, 1H), 3.34-3.28 (m, 1H), 1.97-0.55 (m, 50H); ^{13}C NMR δ : 138.6, 138.0, 137.0, 134.8, 134.1, 131.9, 131.5, 131.4, 129.9, 129.2, 128.83, 128.80, 128.61, 128.57, 128.2, 128.0, 116.3, 116.1, 96.3 (J_{CH} = 153.3Hz), 80.2, 79.7, 78.9, 78.2, 76.0, 72.3, 72.2, 54.7, 45.1, 43.0, 40.4, 40.0, 37.1, 36.6, 36.2, 36.0, 35.91, 35.88, 32.5, 29.0, 28.7, 28.5, 28.0, 24.6, 24.3, 23.3, 23.1, 23.0, 21.7, 19.1, 18.4, 12.6, 12.5; ESIHRMS Calcd. for $C_{53}H_{73}FO_7NaS$ $[M+Na]^+$: 895.4979. Found: 895.4959.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-cyanobenzenesulfonyl)- α -L-rhamnopyranoside

(15 α). White solid. $[\alpha]_D^{25}$ 68.5 (*c*, 0.61); Mp 160 °C; ^1H NMR δ : 7.96-7.93 (m, 2H), 7.66-7.15 (m, 12H), 5.06 (s, 1H), 4.84-4.77 (m, 2H), 4.60-4.51 (t, J = 10.8 Hz, 2H), 4.43-4.38 (d, J = 16.2 Hz, 1H), 3.93-3.89 (dd, J = 6.0 Hz, 1H), 3.83-3.74 (m, 1H), 3.57-3.48 (m, 1H), 3.41-3.34 (t, J = 9.3 Hz, 1H), 1.98-0.57 (m, 50H); ^{13}C NMR δ : 144.4, 141.2, 138.3, 137.9, 135.8, 132.9, 132.0, 130.7, 129.7, 129.4, 128.9, 128.4, 128.3, 127.9, 124.7, 117.53, 117.45, 95.7 (J_{CH} = 168.5Hz), 80.5, 79.0, 77.9, 76.0, 73.0, 68.3, 56.9, 56.7, 54.7, 45.0, 43.0, 40.4, 39.9, 37.4, 36.6, 36.2, 36.0, 35.9, 34.3, 32.5, 29.5, 29.2, 28.7, 28.4, 24.6, 24.3, 23.2, 23.0, 21.6, 19.1, 18.2, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{54}\text{H}_{73}\text{NO}_7\text{NaS}$ $[\text{M}+\text{Na}]^+$: 902.5005. Found: 902.4984.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-cyanobenzenesulfonyl)- β -L-rhamnopyranoside

(15 β). White solid. $[\alpha]_D^{25}$ +32.5 (*c*, 0.91); Mp 142 °C; ^1H NMR (300MHz) δ : 8.10-8.07 (m, 2H), 7.73-7.69 (m, 2H), 7.40-7.26 (m, 10H), 5.16-5.15 (d, J = 2.1 Hz, 1H), 4.95-4.88 (t, J = 10.5 Hz, 2H), 4.62-4.57 (dd, J = 2.1 Hz, 2H), 4.54 (s, 1H), 3.64-3.60 (dd, J = 11.1 Hz, 1H), 3.51-3.26 (m, 3H), 1.96-0.52 (m, 50H); ^{13}C NMR δ : 142.9, 138.5, 137.8, 132.8, 129.2, 128.9, 128.8, 128.7, 128.5, 128.34, 128.25, 117.7, 117.0, 96.1 (J_{CH} = 153.7Hz), 80.0, 79.8, 78.3, 76.0, 72.4, 72.3, 56.9, 56.7, 54.7, 45.1, 43.0, 40.4, 39.9, 37.1, 36.6, 36.2, 36.0, 35.91, 35.86, 32.4, 29.1, 28.7, 28.4, 28.1, 24.6, 24.3, 23.3, 23.0, 21.6, 19.1, 18.4, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{54}\text{H}_{73}\text{NO}_7\text{SNa}$ $[\text{M}+\text{Na}]^+$: 902.5005. Found: 902.5042.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-trifluoromethylbenzenesulfonyl)- α -L-

rhamnopyranoside (16 α). White solid. $[\alpha]_D^{25}$ -35.4 (*c*, 0.57); Mp 149 °C; ^1H NMR δ : 7.96-7.93 (m, 1H), 7.68-7.64 (m, 1H), 7.54-7.15 (m, 12H), 5.06 (s, 1H), 4.84-4.81 (m, 2H), 4.60-4.51 (m, 2H), 4.39-4.37 (d, J = 7.5 Hz, 1H), 3.93-3.89 (dd, J = 3.6 Hz, 1H), 3.83-3.74 (m, 1H), 3.57-3.48 (m, 1H), 3.41-3.34 (t, J = 9.3 Hz, 1H), 1.98-0.57 (m, 50H); ^{13}C NMR δ : 144.45, 141.08,

138.34, 137.94, 135.8, 132.93, 131.9, 130.7, 129.7, 129.5, 128.8, 128.5, 128.3, 127.8, 124.6, 117.53, 117.45, 95.9 ($J_{\text{CH}} = 169.1\text{Hz}$), 80.5, 79.2, 77.8, 75.9, 73.0, 68.3, 56.8, 56.7, 54.7, 45.0, 43.0, 40.4, 39.9, 37.4, 36.6, 36.2, 36.0, 35.9, 34.3, 32.5, 29.5, 29.2, 28.7, 28.4, 24.6, 24.3, 23.2, 22.9, 21.6, 19.0, 18.2, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{54}\text{H}_{73}\text{O}_7\text{NaS}$ $[\text{M}+\text{Na}]^+$: 945.4927. Found: 945.4940.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-(4-trifluoromethylbenzenesulfonyl)- β -L-

rhamnopyranoside (16 β). White solid. $[\alpha]_{\text{D}}^{25} +40.1$ (c , 1.01); Mp 152 °C; ^1H NMR δ : 8.14-8.12 (d, $J = 8.5$ Hz, 2H), 7.74-7.73 (d, $J = 8.5$ Hz, 2H), 7.48-7.29 (m, 10H), 5.20-5.19 (d, $J = 3.0$ Hz, 1H), 5.01-4.93 (dd, $J = 11.5$ Hz, 2H), 4.64-4.61 (dd, $J = 5.5$ Hz, 2H), 4.56 (s, 1H), 3.66-3.64 (dd, $J = 2.5$ Hz, 1H), 3.48-3.44 (m, 2H), 3.35-3.32 (m, 1H), 1.99-0.56 (m, 50H); ^{13}C NMR δ : 143.0, 138.7, 137.9, 132.7, 129.1, 128.8, 128.8, 128.6, 128.5, 128.3, 128.3, 117.7, 117.0, 96.4 ($J_{\text{CH}} = 153.5\text{Hz}$), 80.0, 79.8, 78.3, 76.0, 72.4, 72.3, 56.9, 56.7, 54.7, 45.1, 43.0, 40.4, 39.9, 37.1, 36.6, 36.1, 36.0, 35.9, 35.8, 32.4, 29.1, 28.7, 28.4, 28.1, 24.6, 24.3, 23.3, 22.9, 21.6, 19.1, 18.4, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{54}\text{H}_{73}\text{O}_7\text{NaS}$ $[\text{M}+\text{Na}]^+$: 945.4927. Found: 945.4938.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-tresyl- α -L-rhamnopyranoside (17 α). White solid.

$[\alpha]_{\text{D}}^{25} -30.2$ (c , 0.64); Mp 122 °C; ^1H NMR δ : 7.34-7.25 (m, 10H), 5.04-5.02 (m, 2H), 4.89-4.86 (d, $J = 10.2$ Hz, 1H), 4.73 (s, 2H), 4.66-4.63 (d, $J = 10.5$ Hz, 1H), 4.10-3.96 (m, 2H), 3.89-3.75 (m, 2H), 3.58-3.49 (m, 1H), 3.41-3.35 (t, $J = 9.6$ Hz, 1H), 1.97-0.56 (m, 50H); ^{13}C NMR δ : 138.3, 137.4, 129.1, 128.9, 128.7, 128.5, 128.4, 95.8 ($J_{\text{CH}} = 168.7\text{Hz}$), 81.1, 80.5, 78.4, 77.3, 76.0, 74.2, 68.5, 56.9, 56.7, 54.7, 45.0, 43.0, 40.4, 39.9, 37.4, 36.6, 36.2, 36.0, 35.9, 34.4, 32.5, 32.0, 30.0, 29.5, 29.2, 28.7, 28.4, 24.6, 24.3, 23.2, 23.1, 23.0, 21.7, 19.1, 18.1, 14.5, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{49}\text{H}_{71}\text{F}_3\text{O}_7\text{NaS}$ $[\text{M}+\text{Na}]^+$: 883.4783. Found: 883.4773.

3 β -Cholestanyl 3,4-di-*O*-benzyl-2-*O*-tresyl- β -L-rhamnopyranoside (17 β). White solid.

$[\alpha]_D^{25} +60.4$ (*c*, 0.81); Mp 141 °C; ^1H NMR δ : 7.40-7.25 (m, 10H), 5.11-5.10 (d, $J = 3.0$ Hz, 1H), 4.92-4.89 (d, $J = 10.8$ Hz, 1H), 4.86-4.83 (d, $J = 10.8$ Hz, 1H), 4.62-4.54 (m, 3H), 4.34-4.10 (m, 2H), 3.75-3.64 (m, 1H), 3.63-3.59 (dd, $J = 3.0$ Hz), 3.48-3.28 (m, 2H), 1.93-0.57 (m, 50H); ^{13}C NMR δ : 138.5, 137.5, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 95.9 ($J_{\text{CH}} = 154.1\text{Hz}$), 80.9, 79.7, 79.6, 78.7, 76.0, 72.3, 72.3, 56.9, 56.7, 54.8, 54.4, 45.3, 43.0, 40.4, 39.9, 37.1, 36.6, 36.2, 36.1, 36.0, 35.9, 32.4, 29.1, 28.7, 28.4, 28.1, 24.6, 24.3, 23.2, 23.0, 21.7, 19.1, 18.3, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{49}\text{H}_{71}\text{F}_3\text{O}_7\text{NaS}$ $[\text{M}+\text{Na}]^+$: 883.4783. Found: 883.4770.

Phenyl 3-*O*-benzyl-1-thio- β -L-rhamnopyranoside (18). To a solution of **3** (2.3 g, 9.0 mmol) in benzene (45 mL) was added dibutyltin oxide (2.5 g, 9.9 mmol) followed by heating to reflux in a Dean-Stark apparatus for 3 h, until all the water had been removed from the mixture. The contents were then cooled to room temperature and the solvent removed under reduced pressure, DMF was then added (45 mL) along with CsF (2.7 g, 18.0 mmol) followed by benzyl bromide (1.1 mL, 9.9 mmol). The reaction was stirred for 18 h and then diluted with ethyl acetate. The organic layer washed with water, brine, dried (NaSO_4), and concentrated under reduced pressure. Column chromatography on silica gel (hexanes/ethyl acetate, 3:1) yielded **7** (2.2 g, 71%) as an oil. $[\alpha]_D^{25} +34.2$ (*c*, 1.21, CHCl_3); ^1H NMR δ : 7.51-7.26 (m, 10H), 4.80-4.79 (d, $J = 1.0$ Hz, 1H), 4.78-4.75 (d, $J = 12.0$ Hz, 1H), 4.59-4.56 (d, $J = 11.5$ Hz, 1H), 4.30-4.29 (d, $J = 2.5$ Hz, 1H), 3.65-3.61 (t, $J = 9.5$ Hz, 9.0 Hz, 1H), 3.39-3.33 (m, 2H), 1.39-1.38 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR δ : 137.7, 135.2, 131.5, 129.4, 129.2, 128.8, 128.5, 127.8, 87.1, 82.6, 76.6, 71.9, 71.7, 69.8, 18.4; ESIHRMS Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{NaS}$ $[\text{M}+\text{Na}]^+$: 369.1137. Found: 369.1150.

Phenyl 3-*O*-benzyl-2-*O*-(4-trifluoromethylbenzenesulfonyl)-1-thio- β -L-rhamnopyranoside (19). To a solution of **18** (2.0 g, 5.8 mmol) in CH_2Cl_2 (23 mL) was added collidine (1.9 mL,

14.5 mmol), KI (1.9 g, 11.6 mmol), Ag₂O⁶ (2.7 g, 11.6 mmol), and 4-trifluoromethylbenzenesulfonyl chloride (1.8 g, 7.5 mmol) sequentially at 0 °C. The reaction mixture was then stirred for 1 h at 0 °C, then allowed to warm to room temperature and stirred for an additional 36 h after which time the contents were filtered and the filtrate washed with a saturated solution of NaHCO₃, brine, dried (Na₂SO₄), and preloaded onto silica gel. Loading on a silica gel column and eluting with toluene/ethyl acetate (10/1) gave **18** (1.8 g, 55%) as a white solid. $[\alpha]_D^{25} +63.8^\circ$ (*c*, 0.57); Mp 145 °C; ¹H NMR δ: 8.31-8.29 (d, *J* = 8.0 Hz, 1H), 7.89-7.88 (d, *J* = 8.0 Hz, 1H), 7.69-7.64 (m, 2H), 7.40-7.26 (m, 10H), 5.49-5.48 (d, *J* = 3.0 Hz, 1H), 4.89-4.86 (d, *J* = 11.5 Hz, 1H), 4.80 (s, 1H), 4.43-4.40 (d, *J* = 11.0 Hz, 1H), 3.63-3.59 (t, *J* = 9.0 Hz, 9.5 Hz, 1H), 3.41-3.36 (m, 2H), 1.38-1.37 (d, *J* = 7.0 Hz, 3H); ¹³C NMR δ: 137.6, 136.3, 134.4, 133.9, 132.3, 132.0, 131.6, 129.6, 129.4, 129.0, 128.7, 128.8, 128.6, 128.6, 128.2, 123.9, 121.7, 85.4, 80.4, 72.3, 71.3, 18.5. Anal. Calcd. for C₂₆H₂₅O₆S₂: C, 56.31; H, 4.54. Found: C, 56.50; H, 4.58.

Phenyl 3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)-1-thio-β-L-rhamnopyranoside

(20). Following the above procedure, **20** was obtained as a white solid (52%). $[\alpha]_D^{25} +80.9^\circ$ (*c*, 0.34); Mp 139 °C; ¹H NMR δ: 8.29-8.28 (d, *J* = 7.5 Hz, 1H), 7.89-7.88 (d, *J* = 8.0 Hz, 1H), 7.69-7.64 (m, 2H), 7.40-7.26 (m, 10H), 5.49-5.48 (d, *J* = 3.0 Hz, 1H), 4.89-4.86 (d, *J* = 11.5 Hz, 1H), 4.80 (s, 1H), 4.43-4.40 (d, *J* = 11.0 Hz, 1H), 3.63-3.59 (t, *J* = 9.0 Hz, 9.5 Hz, 1H), 3.41-3.36 (m, 2H), 1.38-1.37 (d, *J* = 7.0 Hz, 3H); ¹³C NMR δ: 137.3, 136.4, 134.3, 133.8, 132.3, 132.0, 131.6, 129.5, 129.3, 129.0, 128.8, 128.71, 128.68, 128.6, 128.2, 123.9, 121.7, 85.4, 80.5, 72.3, 71.3, 18.5. Anal. Calcd. for C₂₆H₂₅O₆S₂: C, 56.31; H, 4.54. Found: C, 55.87; H, 4.52.

Phenyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(4-trifluoromethylbenzenesulfonyl)-1-thio-β-L-

rhamnopyranoside (21). To a solution of **19** (1.5 g, 2.7 mmol) in CH₂Cl₂ (27 mL) was added DMAP (1 g, 8.1 mmol) followed by benzoyl chloride (0.44 mL, 3.8 mmol) at 0 °C. After

stirring for 5 min at 0 °C the reaction was allowed to reach room temperature and after 3 h TLC showed complete consumption of starting material. The reaction mixture was then quenched with a saturated aqueous solution of NaHCO₃, and the organic layers washed with brine, dried (Na₂SO₄) and chromatographed (hexanes/ethyl acetate/dichloromethane 8/2/1) to afford **21** (1.6 g, 90%) as a white solid. $[\alpha]_D^{25} +47.3$ (c, 0.42); Mp 177 °C; ¹H NMR (400 MHz) δ : 8.14-8.12 (d, J = 8.4 Hz, 2H), 7.94-7.91 (d, J = 9.6 Hz, 2H), 7.68-7.04 (m, 15H), 5.58-5.57 (d, J = 2.0 Hz, 1H), 5.28-5.23 (t, J = 9.2 Hz, 1H), 4.90, (s, 1H), 4.69-4.66 (d, J = 12.8 Hz, 1H), 4.43-4.40 (d, J = 12.0 Hz, 1H), 3.72-3.69 (dd, J = 2.8 Hz, 1H), 3.62-3.58 (m, 1H), 1.30-1.28 (d, J = 7.2 Hz, 3H); ¹³C NMR δ : 142.5, 137.6, 133.8, 133.7, 132.0, 130.1, 129.9, 129.7, 128.8, 128.7, 128.5, 128.3, 126.36, 126.33, 122.5, 85.7, 80.1, 75.7, 72.3, 18.2. Anal. Calcd. for C₃₃H₂₉F₃O₇S₂: C, 60.17; H, 4.44. Found: C, 60.22; H, 4.46.

Phenyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)-1-thio- β -L-rhamnopyranoside (22**).** Following the above procedure, **22** was obtained as a foam (88%). $[\alpha]_D^{25} +65.5$ (c, 0.42); ¹H NMR δ : 8.28-8.26 (m, 1H), 7.92-7.91 (m, 2H), 7.81-7.79 (m, 1H), 7.59-6.97 (m, 15H), 5.56-5.55 (d, J = 4.0 Hz, 1H), 5.35-5.31 (t, J = 9.5 Hz, 1H), 4.88 (s, 1H), 4.50-4.48 (d, J = 12.5 Hz, 1H), 4.33-4.31 (d, J = 12.5 Hz, 1H), 3.68-3.66 (dd, J = 3.5 Hz, 1H), 3.63-3.57 (m, 1H), 1.32-1.31 (d, J = 6.0 Hz, 3H); ¹³C NMR δ : 141.3, 137.0, 134.0, 133.8, 132.1, 130.2, 129.9, 129.6, 128.9, 128.8, 128.5, 128.4, 126.36, 126.33, 122.5, 85.7, 80.1, 75.8, 72.3, 18.2. Anal. Calcd. for C₃₃H₂₉F₃O₇S₂: C, 60.17; H, 4.44. Found: C, 60.11; H, 4.39.

Procedure for Coupling Phenyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)-1-thio- β -L-rhamnopyranoside with Cholesterol: To a solution of substrate in CH₂Cl₂ (0.03M in substrate) under argon atmosphere, BSP (1.1 eq) and TTBP (3 eq) were added and the reaction mixture cooled to -60 °C, after which Tf₂O (1.1 eq) was added slowly.

After 1 h of stirring at -60 °C, cholestanol (3 eq) in CH₂Cl₂ (2 M in substrate) was added slowly over a period of 1 min. The viscous reaction mixture was stirred for further 2.5 h at -60°C, after which the reaction mixture was allowed to warm with stirring to room temperature over 1 h. The clear orange solution was then quenched by adding a saturated aqueous solution of NaHCO₃. Brine was then added and the contents were extracted with CH₂Cl₂. The combined organic layer was dried (Na₂SO₄) and the solvent removed under reduced pressure. Purification by silica gel column chromatography (hexanes/ethyl acetate) afforded the corresponding alpha/beta rhamnosides.

3 β -Cholestanyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- α -L-rhamnopyranoside (23 α). Oil. $[\alpha]_D^{25}$ -18.2 (*c*, 0.50); ¹H NMR δ : 8.24-8.22 (d, *J* = 8.0 Hz, 1H), 7.98-7.96 (m, 2H), 7.71-7.69 (d, *J* = 7.5 Hz, 1H), 7.57-7.40 (m, 5H), 7.17-7.07 (m, 3H), 6.95-6.94 (m, 2H), 5.30-5.26 (t, *J* = 10.0 Hz, 1H), 5.204-5.200 (d, *J* = 2.0 Hz, 1H), 5.01-5.00 (m, 1H), 4.33-4.27 (q, *J* = 11.5 Hz, *J* = 8.5 Hz, 2H), 3.97-3.91 (m, 2H), 3.62-3.55 (m, 1H), 1.98-0.60 (m, 50H); ¹³C NMR δ : 165.8, 137.7, 135.6, 133.8, 133.5, 132.3, 132.1, 130.2, 128.9, 128.6, 127.9, 123.8, 121.6, 96.3, 78.2, 77.9, 74.8, 73.2, 72.1, 67.3, 56.9, 56.7, 54.7, 45.0, 43.0, 40.4, 39.9, 37.4, 36.6, 36.2, 36.0, 35.9, 34.5, 32.5, 29.6, 29.2, 28.7, 28.4, 24.7, 24.2, 23.3, 23.0, 21.7, 19.1, 17.8, 12.8, 12.5; ESIHRMS Calcd. for C₅₄H₇₁O₈NaS [M+Na]⁺: 959.4719. Found: 959.4742.

3 β -Cholestanyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- β -L-rhamnopyranoside (23 β). White solid. $[\alpha]_D^{25}$ +43.2 (*c*, 0.89); Mp 139 °C; ¹H NMR δ : 8.08-8.06 (d, *J* = 10.0 Hz, 2H), 7.67-7.66 (d, *J* = 9.5 Hz, 2H), 7.35-7.26 (m, 10H), 5.17-5.16 (d, *J* = 3.5 Hz, 1H), 4.98-4.93 (t, *J* = 12.0 Hz, 1H), 4.83-4.80 (d, *J* = 15.5 Hz, 1H), 4.56 (s, 1H), 4.48-4.45 (d, *J* = 15.5 Hz, 1H), 3.56-3.48 (m, 2H), 3.38-3.30 (m, 1H), 2.00-0.53 (m, 50H); ¹³C NMR

δ : 169.5, 141.6, 137.3, 128.5, 128.4, 127.9, 127.8, 125.7, 95.6, 78.3, 77.9, 76.3, 72.0, 71.4, 70.7, 56.5, 56.3, 54.3, 44.8, 42.6, 40.0, 39.5, 36.7, 36.2, 35.8, 35.5, 35.4, 35.4, 32.0, 28.5, 28.2, 28.0, 27.5, 24.2, 23.8, 22.8, 22.6, 21.2, 20.9, 18.7, 17.5, 12.2, 12.1; ESIHRMS Calcd. for $C_{54}H_{71}O_8NaS$ $[M+Na]^+$: 959.4719. Found: 959.4725.

General Procedure for Coupling Phenyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)-1-thio- β -L-rhamnopyranoside with Acceptors: To a solution of substrate in CH_2Cl_2 (0.03M in substrate) BSP (1.1 eq) and TTBP (3 eq) were added and the reaction mixture cooled to $-60^\circ C$, after which Tf_2O (1.1 eq) was added slowly. After 1 h of stirring at $-60^\circ C$, the acceptor (3 eq) in CH_2Cl_2 (2 M in substrate) was added slowly over a period of 1 min. The reaction mixture was stirred for further 2.5 h at $-60^\circ C$, after which the reaction mixture was allowed to warm with stirring to room temperature over 1 h. The clear orange solution was then quenched by adding a saturated aqueous solution of $NaHCO_3$. Brine was then added and the contents were extracted with CH_2Cl_2 . The combined organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by silica gel column chromatography (hexanes/ethyl acetate, unless otherwise noted) afforded the corresponding alpha/beta rhamnosides.

1-Adamantyl 4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- β -L-rhamnopyranoside (24). White solid. $[\alpha]_D^{25} +50.3$ (c , 0.90); Mp $140^\circ C$; 1H NMR δ : 8.35-8.34 (m, 1H), 7.96-7.94 (m, 2H), 7.78-7.76 (m, 2H), 7.60-7.42 (m, 5H), 7.16-7.06 (m, 4H), 5.32-5.28 (t, $J = 9.5$ Hz, 1H), 5.18-5.17 (d, $J = 3.0$ Hz, 1H), 4.83 (s, 1H), 4.63-4.61 (d, $J = 12.5$ Hz, 1H), 4.42-4.40 (d, $J = 12.5$ Hz, 1H), 3.74-3.71 (dd, $J = 2.5$ Hz, 1H), 3.58-3.52 (m, 1H), 2.08-2.04 (m, 3H), 1.71-1.50 (m, 11H), 1.27-1.24 (m, 4H); ^{13}C NMR δ : 165.7, 137.7, 137.5, 133.6, 133.0, 132.4, 131.8, 130.2, 128.8, 128.7, 128.6, 128.2, 128.11, 128.08, 128.0, 126.2, 124.1, 121.9, 91.6

($J_{\text{CH}} = 152.5\text{Hz}$), 80.5, 76.4, 75.9, 73.1, 71.2, 70.9, 60.8, 45.8, 42.4, 36.5, 32.2, 31.2, 31.1, 25.7, 23.1, 18.3, 14.6, 14.6; ESIHRMS Calcd. for $\text{C}_{37}\text{H}_{39}\text{F}_3\text{O}_8\text{NaS}$ $[\text{M}+\text{Na}]^+$: 723.2215. Found: 723.2224.

Methyl 6-*O*-[4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- α -L-rhamnopyranosyl]-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (25 α). Oil. $[\alpha]_{\text{D}}^{25} -30.2$ (c , 0.41); ^1H NMR δ : 8.22-8.20 (m, 1H), 7.97-7.95 (m, 2H), 7.73-7.71 (m, 1H), 7.59-7.26 (m, 20H), 7.14-7.06 (m, 3H), 6.94-6.92 (m, 2H), 5.30-5.26 (t, $J = 10.0$ Hz, 1H), 5.12-5.11 (d, $J = 2.0$ Hz, 1H), 5.04-5.02 (m, 2H), 4.94-4.92 (d, $J = 11.0$ Hz, 1H), 4.86-4.81 (m, 2H), 4.72-4.69 (d, $J = 12.0$ Hz, 1H), 4.62-4.61 (d, $J = 3.5$ Hz, 1H), 4.55-4.53 (d, $J = 11.0$ Hz, 1H), 4.30-4.23 (q, $J = 12.5$ Hz, 2H), 4.04-4.01 (t, $J = 9.0$ Hz, 1H), 3.90-3.76 (m, 4H), 3.60-3.51 (m, 2H), 3.40-3.36 (m, 4H), 1.19-1.18 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR δ : 165.7, 139.0, 138.5, 138.3, 137.4, 135.5, 133.9, 133.6, 132.4, 132.1, 130.2, 130.1, 129.2, 129.0, 128.9, 128.8, 128.73, 128.67, 128.64, 128.59, 128.52, 128.45, 128.4, 128.3, 128.2, 128.0, 123.8, 121.6, 98.3, 98.2 ($J_{\text{CH}} = 169.3\text{Hz}$), 82.4, 80.3, 78.2, 76.3, 75.6, 74.0, 73.8, 72.9, 71.9, 70.6, 67.4, 67.2, 55.6, 53.9, 30.1, 17.8; ESIHRMS Calcd. for $\text{C}_{55}\text{H}_{55}\text{O}_{13}\text{F}_3\text{NaS}$ $[\text{M}+\text{Na}]^+$: 1035.3213. Found: 1035.3218.

Methyl 6-*O*-[4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- β -L-rhamnopyranosyl]-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (25 β). Oil. $[\alpha]_{\text{D}}^{25} +22.9$ (c , 0.86); ^1H NMR (400MHz) δ : 8.21-8.19 (d, $J = 7.6$ Hz, 1H), 7.95-7.93 (m, 2H), 7.65-7.57 (m, 2H), 7.46-7.01 (m, 29H), 5.40-5.39 (d, $J = 2.0$ Hz, 1H), 5.30-5.25 (t, $J = 9.2$ Hz, 1H), 5.00-4.79 (m, 4H), 4.74-4.62 (m, 3H), 4.57-4.46 (m, 3H), 4.36-4.33 (d, $J = 13.2$ Hz, 1H), 4.26-4.23 (dd, $J = 2.0$ Hz, 1H), 3.92-3.87 (t, $J = 9.2$ Hz, 1H), 3.68-3.61 (m, 3H), 3.55-3.48 (m, 2H), 3.44-3.39 (t, $J = 10.0$ Hz, 1H), 3.35 (s, 3H), 1.25-.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR δ : 165.1, 139.1, 138.6, 136.8, 133.2, 131.9, 130.9, 129.8, 128.5, 128.42, 128.36, 128.34, 128.22, 128.16, 128.0, 127.99,

127.95, 127.89, 125.9, 127.7, 127.5, 127.5, 98.3, 97.8, 82.0, 81.7, 79.9, 79.6, 75.6, 75.5, 75.0, 74.9, 73.4, 72.4, 71.0, 70.8, 70.6, 69.8, 67.1, 61.9, 55.2, 17.5; ESIHRMS Calcd. for $C_{55}H_{55}O_{13}F_3NaS$ $[M+Na]^+$: 1035.3213. Found: 1035.3209

Methyl 3-*O*-[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- α -L-rhamnopyranosyl)]- 2,4,6-tri-*O*-benzyl- α -D-mannopyranoside (26 α). Oil. $[\alpha]_D^{25}$ -23.1 (*c*, 0.67); 1H NMR δ : 8.16-8.14 (d, J = 8.5 Hz, 1H), 7.74-7.70 (m, 3H), 7.56-7.17 (m, 20H), 7.10-6.99 (m, 5H), 6.88-6.87 (d, J = 7.0 Hz, 2H), 5.37-5.36 (d, J = 1.0 Hz, 1H), 5.32-5.28 (t, J = 10.0 Hz, 1H), 5.03-5.02 (m, 1H), 4.85-4.84 (d, J = 1.5 Hz, 1H), 4.82-4.75 (q, J = 12.5 Hz, 2H), 4.74-4.71 (d, J = 12.0 Hz, 1H), 4.62-4.55 (m, 2H), 4.45-4.43 (d, J = 11.0 Hz, 1H), 4.21-3.92 (m, 7H), 3.85-3.72 (m, 3H), 3.35 (s, 3H), 1.13-1.12 (d, J = 6.0 Hz, 3H); ^{13}C NMR δ : 165.7, 138.8, 138.7, 138.4, 137.2, 135.3, 134.0, 133.5, 132.4, 132.1, 130.2, 130.0, 128.9, 128.0, 127.98, 127.93, 127.7, 123.8, 121.6, 99.1 (J_{CH} = 170.2 Hz), 93.9 (J_{CH} = 170.9 Hz), 77.3, 75.5, 75.2, 74.3, 74.2, 74.0, 73.9, 73.6, 72.6, 71.9, 71.7, 69.4, 67.5, 55.4, 17.7; ESIHRMS Calcd. for $C_{55}H_{55}O_{13}F_3KS$ $[M+K]^+$: 1051.2953. Found: 1051.2914.

Methyl 3-*O*-[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- β -L-rhamnopyranosyl)]- 2,4,6-tri-*O*-benzyl- α -D-mannopyranoside (26 β). Oil. $[\alpha]_D^{25}$ +35.2 (*c*, 0.72); 1H NMR δ : 8.24-8.23 (m, 1H), 7.92-7.90 (m, 2H), 7.67-7.56 (m, 2H), 7.45-7.05 (m, 24H), 6.90-6.88 (m, 2H), 5.28-5.25 (t, J = 10.0 Hz, 1H), 5.13-5.12 (d, J = 3.0 Hz, 1H), 4.87-4.84 (d, J = 12.5 Hz, 1H), 4.79-4.74 (m, 2H), 4.72-4.68 (m, 2H), 4.65-4.64 (d, J = 2.0 Hz, 1H), 4.60-4.56 (m, 2H), 4.30-4.27 (d, J = 12.5 Hz, 1H), 4.14-4.11 (m, 2H), 4.02-3.99 (dd, J = 3.0 Hz, 1H), 3.95-3.91 (t, J = 9.5 Hz, 1H), 3.89-3.88 (m, 1H), 3.78-3.76 (m, 3H), 3.50-3.47 (m, 1H), 3.41-3.39 (dd, J = 3.0 Hz, 1H), 3.36-3.31 (m, 4H), 1.26-1.24 (d, J = 8.0 Hz, 3H); ^{13}C NMR δ : 165.6, 139.5, 139.4, 138.8, 137.1, 136.9, 134.0, 133.9, 133.6, 133.5, 133.1, 132.38, 132.36, 132.2, 132.1, 132.1,

131.4, 130.2, 130.1, 130.0, 129.4, 129.0, 128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.32, 128.25, 128.2, 128.1, 128.04, 128.02, 127.98, 127.9, 127.73, 127.65, 124.0, 121.8, 100.7 ($J_{\text{CH}} = 159.8$ Hz), 99.1 ($J_{\text{CH}} = 171.0$ Hz), 85.8, 78.6, 77.3, 76.6, 75.3, 75.2, 73.9, 73.5, 72.7, 72.3, 71.6, 71.2, 69.8, 55.1, 18.1; ESIHRMS Calcd. for $\text{C}_{55}\text{H}_{55}\text{O}_{13}\text{F}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 1035.3213, Found: 1035.3236.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O* –[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- α -L-rhamnopyranosyl)]- α -D-mannopyranoside (27 α).

Was chromatographed with toluene/ethyl acetate and obtained as an oil. $[\alpha]_{\text{D}}^{25} -35.6$ (c , 0.45); ^1H NMR δ : 8.27-8.25 (d, $J = 8.0$ Hz, 1H), 7.93-7.92 (m, 2H), 7.75-7.73 (d, $J = 7.5$ Hz, 1H), 7.58-7.12 (m, 20H), 6.99-6.97 (m, 2H), 5.65 (s, 1H), 5.31-5.27 (t, $J = 9.5$ Hz, 1H), 5.17-5.16 (d, $J = 2.0$ Hz, 1H), 5.11-5.10 (m, 1H), 4.82-4.80 (d, $J = 12.0$ Hz, 1H), 4.72-4.68 (m, 2H), 4.39-4.29 (m, 4H), 4.19-4.18 (m, 1H), 4.01-3.98 (m, 3H), 3.90-3.86 (t, $J = 10.0$ Hz, 1H), 3.82-3.79 (m, 1H), 3.41 (s, 3H), 1.07-1.05 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR δ : 165.8, 138.5, 137.9, 137.6, 135.4, 133.9, 133.5, 132.4, 132.1, 130.2, 130.1, 129.4, 128.7, 128.7, 128.6, 128.6, 128.1, 128.0, 126.5, 123.8, 121.6, 102.0 ($J_{\text{CH}} = 161.0$ Hz), 99.4 ($J_{\text{CH}} = 167.2$ Hz), 96.9 ($J_{\text{CH}} = 170.5$ Hz), 79.1, 74.9, 74.6, 74.2, 73.5, 72.8, 72.2, 69.3, 67.6, 64.4, 55.6, 17.7; ESIHRMS Calcd. for $\text{C}_{48}\text{H}_{47}\text{F}_3\text{O}_{13}\text{NaS}$ $[\text{M}+\text{Na}]^+$: 943.2587. Found: 943.2598.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O* –[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- β -L-rhamnopyranosyl)]- α -D-mannopyranoside (27 β).

Oil. $[\alpha]_{\text{D}}^{25} +25.9$ (c , 0.60); ^1H NMR δ : 8.36-8.34 (m, 1H), 7.94-7.92 (m, 2H), 7.79-7.77 (m, 1H), 7.59-7.26 (m, 15H), 7.16-7.05 (m, 3H), 6.96-6.94 (d, $J = 7.5$ Hz, 2H), 5.68 (s, 1H), 5.47-5.46 (d, $J = 3.0$ Hz, 1H), 5.28-5.24 (t, $J = 9.5$ Hz, 1H), 4.98-4.95 (d, $J = 12.0$ Hz, 1H), 4.89 (s, 1H), 4.67-4.63 (m, 2H), 4.44-4.41 (d, $J = 12.5$ Hz, 1H), 4.32-4.29 (t, $J = 9.5$ Hz, 1H), 4.25-4.12

(m, 3H), 4.01-3.98 (dd, $J = 3.0$ Hz, 1H), 3.83-3.72 (m, 2H), 3.49-3.47 (dd, $J = 3.0$ Hz, 1H), 3.46-3.39 (m, 1H), 3.33 (s, 3H), 1.28-1.27 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR δ : 165.6, 139.3, 138.2, 137.4, 137.3, 133.6, 133.0, 132.4, 131.5, 130.2, 130.1, 129.4, 129.2, 129.1, 128.9, 128.84, 128.80, 128.67, 128.62, 128.4, 128.31, 128.27, 128.2, 128.1, 128.06, 128.0, 127.97, 127.89, 126.6, 124.1, 121.9, 101.9 ($J_{\text{CH}} = 163.8\text{Hz}$), 101.3 ($J_{\text{CH}} = 172.3\text{Hz}$), 99.0 ($J_{\text{CH}} = 157.3\text{Hz}$), 79.4, 78.0, 77.0, 76.9, 76.4, 74.0, 72.8, 71.4, 71.2, 69.3, 64.4, 55.1, 18.0; ESIHRMS Calcd. for $\text{C}_{48}\text{H}_{47}\text{F}_3\text{O}_{13}\text{SNa}$ $[\text{M}+\text{Na}]^+$: 943.2587. Found: 943.2542.

Methyl 4-*O*-[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- α -L-rhamnopyranosyl)]-2,3-*O*-isopropylidene- α -L-rhamnopyranoside (28 α). Foam. $[\alpha]_D^{25} -55.2$ (c , 0.58); ^1H NMR δ : 8.27-8.25 (d, $J = 8.0$ Hz, 1H), 7.94-7.92 (m, 2H), 7.76-7.74 (d, $J = 7.5$ Hz, 1H), 7.58-7.40 (m, 5H), 7.17-6.98 (m, 5H), 5.48-5.47 (d, $J = 2.0$ Hz, 1H), 5.30-5.26 (t, $J = 10.0$ Hz, 1H), 5.20-5.19 (t, $J = 2.5$ Hz, 1H), 4.87 (s, 1H), 4.39-4.37 (d, $J = 12.0$ Hz, 1H), 4.30-4.27 (d, $J = 12.5$ Hz, 1H), 4.12-4.11 (d, $J = 2.5$ Hz, 1H), 3.91-3.87 (m, 2H), 3.66-3.63 (m, 1H), 3.48-3.44 (m, 1H), 3.39 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.27-1.26 (d, $J = 6.0$ Hz, 3H), 1.22-1.21 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR δ : 165.7, 137.5, 135.9, 133.8, 133.5, 132.4, 132.3, 130.2, 128.8, 128.7, 128.6, 128.5, 128.1, 128.0, 110.2, 98.4, 97.6, 79.7, 78.2, 76.5, 74.1, 72.8, 71.8, 68.1, 64.3, 55.4, 28.3, 26.8, 18.2, 17.9. Anal. Calcd. for $\text{C}_{37}\text{H}_{41}\text{F}_3\text{O}_{12}\text{S}$: C, 57.96; H, 5.39. Found: C, 57.66; H, 5.23.

Methyl 4-*O*-[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)- β -L-rhamnopyranosyl)]-2,3-*O*-isopropylidene- α -L-rhamnopyranoside (28 β). Oil. $[\alpha]_D^{25} +30.7$ (c , 0.64); ^1H NMR δ : 8.29-8.27 (m, 1H), 7.96-7.94 (m, 2H), 7.76-7.74 (m, 1H), 7.60-7.52 (m, 3H), 7.46-7.42 (m, 2H), 7.18-6.98 (m, 5H), 5.34-5.33 (d, $J = 4.0$ Hz, 1H), 5.32-5.27 (t, $J = 11.5$ Hz, 1H), 4.81-4.80 (d, $J = 2.5$ Hz, 1H), 4.48-4.45 (d, $J = 15.5$ Hz, 1H), 4.34-4.31 (d, $J = 15.0$ Hz,

1H), 4.18-4.15 (t, $J = 8.0$ Hz, 1H), 4.06-4.04 (d, $J = 7.5$ Hz, 1H), 3.71-3.67 (dd, $J = 4.0$ Hz, 1H), 3.57-3.47 (m, 2H), 3.42-3.38 (m, 1H), 3.34 (s, 3H), 1.50 (s, 3H), 1.31 (s, 3H), 1.30-1.28 (d, $J = 7.5$ Hz, 3H), 1.27-1.25 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR δ : 165.7, 137.3, 137.2, 133.7, 133.1, 132.2, 131.6, 130.2, 130.1, 128.8, 128.6, 128.4, 128.3, 128.21, 128.18, 128.12, 128.06, 124.0, 121.8, 109.3, 98.5 ($J_{\text{CH}} = 154.7\text{Hz}$), 98.0 ($J_{\text{CH}} = 167.0\text{Hz}$), 83.2, 78.4, 76.7, 76.5, 76.1, 73.0, 71.5, 64.2, 55.1, 28.5, 26.6, 18.1, 18.0. Anal. Calcd. for $\text{C}_{37}\text{H}_{41}\text{F}_3\text{O}_{12}\text{S}$: C, 57.96; H, 5.39. Found: C, 58.03; H, 5.39.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)]- α -L-rhamnopyranosyl)- α -D-glucopyranoside (29 α). Oil. $[\alpha]_{\text{D}}^{25} -41.0$ (c, 0.96); ^1H NMR δ : 8.20-8.17 (d, $J = 10.5$ Hz, 1H), 7.83-7.80 (m, 2H), 7.69-7.68 (d, $J = 8.5$ Hz, 1H), 7.57-7.10 (m, 20H), 6.97-6.94 (m, 2H), 5.36-5.35 (d, $J = 3.0$ Hz, 1H), 5.26-5.22 (t, $J = 11.5$ Hz, 1H), 5.09-5.06 (d, $J = 14.0$ Hz, 1H), 5.04-5.03 (m, 1H), 4.75-4.56 (m, 6H), 4.30-4.23 (q, $J = 14.0$ Hz, 5.5 Hz, 2H), 4.16-4.00 (m, 2H), 3.93-3.90 (dd, $J = 3.5$ Hz, 1H), 3.85-3.80 (t, $J = 11.5$ Hz, 1H), 3.75-3.72 (m, 2H), 3.64-3.60 (dd, $J = 5.0$ Hz, 1H), 3.41 (s, 3H), 0.88-0.87 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR δ : 165.3, 138.5, 137.9, 137.0, 135.0, 133.5, 133.1, 132.0, 131.6, 129.7, 128.8, 128.5, 128.14, 128.07, 128.03, 127.96, 127.7, 127.62, 127.57, 127.3, 123.7, 120.9, 97.9 ($J_{\text{CH}} = 172.3\text{Hz}$), 97.0 ($J_{\text{CH}} = 170.3\text{Hz}$), 80.2, 79.7, 77.0, 75.3, 73.8, 73.7, 73.4, 73.3, 72.4, 71.5, 69.9, 68.3, 67.4, 55.4, 17.0; ESIHRMS Calcd. for $\text{C}_{55}\text{H}_{55}\text{F}_3\text{O}_{13}\text{NaS}$ $[\text{M}+\text{Na}]^+$: 1035.3213. Found: 1035.3208.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[(4-*O*-benzoyl-3-*O*-benzyl-2-*O*-(2-trifluoromethylbenzenesulfonyl)]- β -L-rhamnopyranosyl)- α -D-glucopyranoside (29 β). Oil. $[\alpha]_{\text{D}}^{25} +19.4$ (c, 0.60); ^1H NMR (400MHz) δ : 8.14-8.12 (m, 1H), 7.91-7.89 (m, 2H), 7.78-7.76 (m, 1H), 7.59-7.00 (m, 24H), 5.18-5.13 (t, $J = 10.4$ Hz, 1H), 5.09-5.06 (d, $J = 11.6$ Hz, 1H), 4.96-4.95 (d, $J =$

2.8 Hz, 1H), 4.76-4.63 (m, 4H), 4.57-4.43 (m, 4H), 4.18-4.15 (d, $J = 12.0$ Hz, 1H), 3.70-3.57 (m, 2H), 3.48-3.44 (m, 2H), 3.39-3.28 (m, 5H), 1.11-1.09 (d, $J = 6.4$ Hz, 3H); 400MHz ^{13}C NMR δ : 165.2, 138.9, 138.4, 137.8, 137.0, 136.9, 133.2, 132.7, 131.8, 129.72, 129.68, 128.7, 128.5, 128.3, 128.18, 128.15, 128.1, 127.9, 127.7, 127.5, 127.5, 127.3, 98.2 ($J_{\text{CH}} = 154.7\text{Hz}$), 97.7 ($J_{\text{CH}} = 167.0\text{Hz}$), 81.5, 79.7, 78.2, 77.2, 76.2, 75.5, 75.2, 73.3, 73.1, 72.3, 71.1, 70.6, 68.9, 68.0, 55.2, 17.4; ESIHRMS Calcd. for $\text{C}_{55}\text{H}_{55}\text{F}_3\text{O}_{13}\text{NaS}$ $[\text{M}+\text{Na}]^+$: 1035.3213 Found: 1035.3217.

General Procedure for Desulfonylation of Selected β -L-rhamnopyranosides. To a solution of substrate in THF (0.1 M in substrate) was added anhydrous 2-propanol (7 eq), and 7% sodium amalgam⁷ (5 times wt. of substrate). After 72 h the reaction was complete and the reaction mixture filtered, extracted with ethyl acetate, and washed with brine. The combined organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by silica gel column chromatography (hexanes/ethyl acetate) afforded the corresponding diols.

3 β -Cholestanyl 3-*O*-benzyl- β -L-rhamnopyranoside (30). White solid. $[\alpha]_{\text{D}}^{25} +35.6$ (c , 0.98); Mp 118 °C; ^1H NMR δ : 7.38-7.36 (m, 5H), 4.82-4.79 (d, $J = 11.5$ Hz, 1H), 4.55-4.53 (m, 2H), 4.08-4.07 (d, $J = 2.5$ Hz, 1H), 3.70-3.61 (m, 2H), 3.31-3.24 (m, 2H), 2.32-2.23 (bd, 2H), 1.97-0.56 (m, 50H); ^{13}C NMR δ : 138.0, 129.1, 128.5, 128.4, 97.7, 81.6, 78.1, 72.0, 71.7, 71.2, 68.6, 56.9, 56.7, 54.8, 45.3, 43.0, 40.5, 39.9, 37.3, 36.6, 36.2, 36.0, 35.9, 32.5, 29.1, 28.7, 28.4, 28.2, 24.6, 24.2, 23.3, 23.0, 21.7, 19.1, 18.2, 12.7, 12.5; ESIHRMS Calcd. for $\text{C}_{40}\text{H}_{64}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 647.4651. Found: 647.4677.

1-Adamantyl 3-*O*-benzyl- β -L-rhamnopyranoside (31). White solid. $[\alpha]_{\text{D}}^{25} +20.3$ (c , 1.21); Mp 129 °C; ^1H NMR δ : 7.36-7.26 (m, 5H), 4.81-4.78 (d, $J = 15.0$ Hz, 1H), 4.71-4.70 (d, $J = 1.5$ Hz, 1H), 4.54-4.51 (d, $J = 15.5$ Hz, 1H), 3.98-3.97 (d, $J = 5.0$ Hz, 1H), 3.63-3.59 (t, $J = 12.0$ Hz, 1H), 3.32-3.22 (m, 2H), 2.50 (bs, 2H), 2.14 (bs, 3H), 1.86-1.76 (q, $J = 14.0$ Hz, 6H), 1.65-1.57

(m, 6H), 1.33-1.32 (d, $J = 8.5$ Hz, 3H); ^{13}C NMR δ : 137.7, 128.6, 128.0, 92.5, 81.3, 75.4, 71.3, 71.2, 70.6, 69.2, 42.4, 36.2, 30.6, 18.0; ESIHRMS Calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 411.2147. Found: 411.2157.

Methyl 6-*O*-(3-*O*-benzyl- β -L-rhamnopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside

(32). White solid. $[\alpha]_D^{25} +43.2$ (c , 0.43); Mp 153 °C; ^1H NMR (300MHz) δ : 7.35-7.26 (m, 20H), 5.04-5.39 5.07 (d, $J = 11.5$ Hz, 1H), 4.76-4.74 (d, $J = 12.0$ Hz, 1H), 4.68-4.51 (m, 7H), 4.28-4.26 (d, $J = 11.5$ Hz, 1H), 4.00-3.98 (q, $J = 8.4$ Hz), 3.92-3.87 (t, $J = 9.2$ Hz, 1H), 3.68-3.61 (m, 3H), 3.55-3.48 (m, 2H), 3.44-3.39 (t, $J = 10.0$ Hz, 1H), 3.35 (s, 3H), 1.25-.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (300MHz) δ : 138.9, 138.3, 137.7, 128.6, 128.57, 128.50, 128.3, 128.1, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 100.6, 97.8, 81.7, 81.4, 79.8, 76.5, 75.7, 73.3, 73.2, 71.7, 71.1, 70.8, 69.5, 68.8, 67.6, 55.2, 17.6; ESIHRMS Calcd. for $\text{C}_{41}\text{H}_{48}\text{O}_{10}\text{Na}$ $[\text{M}+\text{Na}]^+$: 723.3145. Found: 723.3132.

Methyl 3-*O*-(3-*O*-benzyl- β -L-rhamnopyranosyl)- 2,4,6-tri-*O*-benzyl- α -D-mannopyranoside

(33). Oil. $[\alpha]_D^{25} +23.7$ (c , 0.43); ^1H NMR (300MHz) δ : 7.31-7.22 (m, 20H), 5.09-5.07 (d, $J = 11.5$ Hz, 1H), 4.77-4.75 (d, $J = 12.0$ Hz, 1H), 4.68-4.51 (m, 7H), 4.28-4.26 (d, $J = 11.5$ Hz, 1H), 4.00-3.97 (q, $J = 8.0$) 3.87-3.86 (d, $J = 2.5$ Hz, 1H), 3.81-3.75 (m, 2H), 3.67-3.66 (m, 1H), 3.58-3.54 (d, $J = 3.0$ Hz, 1H), 3.49-3.46 (t, $J = 9.5$ Hz, 1H), 3.39 (s, 3H), 3.14-3.08 (m, 1H), 3.00-2.98 (dd, $J = 3.0$ Hz, 1H), 2.05 (bs, 2H), 1.23-1.22 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (300MHz) δ : 138.9, 138.5, 137.61, 137.60, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 100.7, 97.8, 81.9, 81.5, 79.8, 76.5, 75.6, 73.2, 73.1, 71.7, 71.0, 70.8, 69.5, 68.8, 67.6, 55.2, 17.6; ESIHRMS Calcd. for $\text{C}_{41}\text{H}_{48}\text{O}_{10}\text{Na}$ $[\text{M}+\text{Na}]^+$: 723.3145. Found: 723.3139.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(3-*O*-benzyl- β -L-rhamnopyranosyl)- α -D-

mannopyranoside (34). Oil. $[\alpha]_D^{25} +48.9$ (c , 0.79); ^1H NMR (300MHz) δ : 7.57-7.25 (m, 15H),

5.66 (s, 1H), 4.98-4.95 (d, $J = 12.0$ Hz, 1H), 4.87 (s, 1H), 4.67-4.63 (m, 3H), 4.44-4.41 (d, $J = 12.5$ Hz, 1H), 4.32-4.29 (t, $J = 9.5$ Hz, 1H), 4.25-4.12 (m, 7H), 4.01-3.98 (dd, $J = 3.0$ Hz, 1H), 3.83-3.72 (m, 2H), 3.49-3.47 (dd, $J = 3.0$ Hz, 1H), 3.46-3.39 (m, 1H), 3.33 (s, 3H), 1.28-1.27 (d, $J = 6.5$ Hz, 3H); 300MHz ^{13}C NMR δ : 138.9, 138.5, 137.61, 137.60, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 101.7, 101.0, 99.0, 79.43, 77.96, 76.5, 75.6, 73.2, 73.1, 71.7, 71.0, 70.8, 69.5, 68.8, 67.6, 55.2, 17.6; ESIHRMS Calcd. for $\text{C}_{34}\text{H}_{40}\text{O}_{10}\text{Na}$ $[\text{M}+\text{Na}]^+$: 631.2519. Found: 631.2527.

Methyl 4-*O*-(3-*O*-benzyl- β -L-rhamnopyranosyl)-2,3-*O*-isopropylidene- α -L-

rhamnopyranoside (35). Oil. $[\alpha]_{\text{D}}^{25} +50.2$ (c, 0.49); ^1H NMR δ : 7.39-7.30 (m, 5H), 4.86-4.80 (m, 2H), 4.60-4.59 (d, $J = 1.5$ Hz, 1H), 4.56-4.53 (d, $J = 14.5$ Hz, 1H), 4.29-4.26 (q, $J = 7.0$ Hz, $J = 1.5$ Hz, 1H), 4.14-4.11 (m, 2H), 3.72-3.61 (m, 2H), 3.51-3.47 (dd, $J = 9.5$ Hz, 1H), 3.36 (s, 3H), 3.33-3.26 (m, 2H), 2.23 (s, 2H), 1.52 (s, 3H), 1.36-1.35 (dd, $J = 7.5$ Hz, 3H), 1.33 (s, 3H), 1.28-1.27 (d, $J = 8.0$ Hz, 3H); ^{13}C NMR δ : 137.6, 128.7, 128.2, 128.0, 109.1, 99.6, 98.1, 81.3, 81.2, 76.5, 76.0, 72.1, 71.2, 70.9, 67.6, 64.4, 54.9, 28.0, 26.2, 17.7, 17.6; ESIHRMS Calcd. for $\text{C}_{23}\text{H}_{34}\text{O}_9\text{Na}$ $[\text{M}+\text{Na}]^+$: 477.2101. Found: 477.2113.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3-*O*-benzyl- β -L-rhamnopyranosyl)- α -D-glucopyranoside

(36). White solid. $[\alpha]_{\text{D}}^{25} +47.8$ (c, 0.84); Mp 163 °C; ^1H NMR δ : 7.36-7.26 (m, 20H), 5.09-5.07 (d, $J = 11.5$ Hz, 1H), 4.77-4.75 (d, $J = 12.0$ Hz, 1H), 4.68-4.51 (m, 7H), 4.28-4.26 (d, $J = 11.5$ Hz, 1H), 4.00-3.97 (q, $J = 8.5$ Hz, $J = 1.0$ Hz, 1H) 3.87-3.86 (d, $J = 2.5$ Hz, 1H), 3.81-3.75 (m, 2H), 3.67-3.66 (m, 1H), 3.56-3.53 (dd, $J = 3.0$ Hz, 1H), 3.49-3.46 (t, $J = 9.5$ Hz, 1H), 3.39 (s, 3H), 3.14-3.08 (m, 1H), 3.00-2.98 (dd, $J = 3.0$ Hz, 1H), 2.09 (bs, 2H), 1.23-1.22 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR δ : 138.8, 138.3, 137.9, 137.6, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.76, 127.6, 127.5, 100.7, 97.8, 81.7, 81.4, 79.9, 76.5, 75.7, 73.4, 73.2, 71.7, 71.1, 70.8,

69.5, 68.8, 67.6, 55.2, 17.6. Anal. Calcd. for $C_{41}H_{48}O_{10}$: C, 70.27; H, 6.90. Found: C, 69.98; H, 6.86.

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