Supplementary information

Experimental

General experimental methods have been previously described.[1] Anhydrous pyridine and DMF were purchased from Sigma Aldrich and used without further purification. All non-aqueous reactions were performed under an atmosphere of nitrogen. The numbering system used to name each compounds has been used to assign the NMR spectra; the numbering of the core ring is not marked with a dash in each case. Analytical HPLC was conducted on a Dionex HPLC system with diode array detection; unless otherwise stated, the column oven was set at 24 °C. An Econosil columns (silica particle size: 10 μm) was used for analytical (4.6 × 250 mm) work, and a Chiracel OD column (4.6 × 250 mm) was used for chiral analytical HPLC; samples were calibrated against external standard samples dissolved in isopropanol. Semi-preparative HPLC was conducted with a Waters 2525 binary gradient pump with detection by a Micromass ZQ mass spectrometer; an XTerra® preparative HPLC column (19 × 50 mm) was used. Preparative HPLC was generally conducted on a Gilson HPLC machine using a gradient of 90 → 95% MeCN in H_2O over 30 min detecting at 200 nm on a Thermohypersil 250 × 21.2 mm, 8 μ, Hyperprep® HS C18 column. Microanalyses were carried out by staff of the Department of Chemistry using a Carlo Erba 1106 automatic analyser.

4,8-Dioxa-tricyclo[5.1.0.0^{3,5}]octane *or cis*-1,4-Cyclohexadiene dioxide[2a] 12

A solution of 1,4-cyclohexadiene (5.0 g, 62 mmol) in dichloromethane (13 mL) was added dropwise to a solution of *m*-chloroperbenzoic acid (31.0 g, 125 mmol, 2 eq., 70 % in weight) in dichloromethane (120 mL) cooled at 0 ˚C. The rate of the addition was such that the temperature of the reaction mixture did not exceed 4 ˚C. The reaction was stirred for 8 h at 0 ˚C and allowed to warm to room temperature over 14 h. The reaction mixture was filtered, and the cake washed with dichloromethane (100 mL). The filtrate was stirred with a saturated aqueous solution of sodium sulfite (100 mL) over 30 min and then extracted with dichloromethane. The organic layer was stirred with calcium hydroxide (8.0 g) for 30 min, filtered, the cake washed with dichloromethane (100 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (gradient elution: 1:0.8:0.2 → 6:3.8:0.2 → 7:2.8:0.2 dichloromethane−petrol−Et_3N) to give the diepoxide **12** (4.1 g, 59%) as colourless prisms, m.p. 54-56 °C (from dichloromethane) (lit.[3] 59-60 °C); R_f 0.25 (7:3 dichloromethane−petrol); ν_{max}/cm^{-1} (film) 2960, 1278 and 1023; δ_H (300 MHz, $CDCl_3$) 3.09 (4H, d, *J* 1.0, 1-H, 2-H, 4-H and 5-H), 2.74 (2H, d, *J* 17.1, 3-H_{cis} and 6-H_{cis}), 2.28 (2H, dd, *J* 17.1 and 1.0, 3-H_{trans} and 6-H_{trans}); δ_C (75 MHz, $CDCl_3$) 49.6 (*C*HO), 23.9 (*C*H_2); *m/z* (EI) 112.1 (20%, M^+), 55.1 (100) and 39.1 (50); (Found: M^+, 112.0520. $C_6H_8O_2$ requires *M*, 112.0519).

(1*R*,2*R*,4*R*,5*R*)-2,5-Diazido-cyclohexane-1,4-diol 13

The diepoxide **12** (4.7 g, 41.5 mmol) was dissolved in dry ether (24 mL) in a flame dried round bottom flask. The (salen)Cr(III)Cl complex (*S*,*S*)-**16** (0.53 g, 0.8 mmol, 0.02 eq.) and trimethylsilylazide (11.5 mL, 87.1 mmol, 2.1 eq.) were added to the reaction mixture, which was stirred for 24 hr, (*S*,*S*)-**16** (0.53 mg, 0.8 mmol, 0.02 eq.) and trimethylsilylazide (11.5 mL, 87.1 mmol, 2.1 eq.) added and the reaction stirred for two days at room temperature. The crude reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (gradient elution: 0.98:0:0.2 → 1:0.98:0.2 petrol−EtOAc−Et_3N) to give the corresponding bis silyl ether (9.7 g, 68%), which was dissolved in dry methanol (94 mL), trifluoroacetic acid (1.8 mL, 24 μmol) added dropwise and stirred for 18 h. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and recrystallisation from dichloromethane to give the *diol* **13** (4.6 g, 57%) as colourless prisms, m.p. 139-141 °C (from dichloromethane); R_f 0.56 (6:4 petrol−EtOAc); $[\alpha]_D$ −21.4 (c. 1.05 in MeOH); (Found C, 36.45; H, 5.15; N, 42.55; $C_6H_{10}N_6O_2$ requires C, 36.36; H, 5.09; N, 42.41%); ν_{max}/cm^{-1} (film) 3339, 2933, 2104, 1256, 1010; δ_H (300 MHz, MeOD) 3.66-3.50 (4H, m, 1-H ,2-H ,4-H and 5-H), 1.89-1.77 (2H, m, 3-H or 6-H) and 1.75-1.62 (2H, m, 3-H or 6-H); δ_C (75 MHz, MeOD) 69.6-63.5 (1/4-*C*HO and 2/5-*C*N_3) and 33.6 (3/6-*C*H_2); *m/z* (ES) 221.0 (100%, MNa^+). The sample was shown to have 70 ± 10% ee by chiral HPLC (Chiralcel OD column; elution with 3:97 isopropanol−hexane).

(1*S*,2*S*,4*S*,5*S*)-2,5-Diazido-cyclohexane-1,4-diol 13'

By the same general method, the diepoxide **12** (2.1 g, 18.5 mmol), (*R*,*R*)-**16** (0.23 g, 0.4 mmol, 0.02 eq.), trimethylsilylazide (5.1 mL, 38.9 mmol, 2.1 eq.), and trifluoroacetic acid (345 μL, 4.2 μmol) gave the *diol* **13'** (0.90 g, 25%) as colourless prisms, $[\alpha]_D$ +21.7 (c. 1.40 in MeOH), spectroscopically identical to **13** obtained previously. The sample was shown to have 70 ± 10% ee by chiral HPLC (Chiralcel OD column; elution with 3:97 isopropanol−hexane).

(1*R*,2*R*,4*R*,5*R*)-1,5-Diazido-2,4-bis-trimethylsilanyloxy-cyclohexane

The diepoxide[2b] **14** (168 mg, 3.0 mmol), (*S,S*)-*N-N'*-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexane-diaminochromium(III) chloride (84 mg, 0.12 mmol) and azidotrimethylsilane (1.2 mL, 9 mmol) were dissolved in ether (1 mL) and stirred for 48 h. Azidotrimethylsilane (600 μL, 4.5 mmol) was added, the reaction mixture stirred for a further 16 h and then evaporated under reduced pressure to give a crude product, which was purified by flash chromatography, eluting with 79:20:1 petrol−EtOAc−Et_3N to give the *diazide* (662 mg, 70%) as a yellow oil, R_f 0.8 (8:2, petrol–EtOAc); $[\alpha]_D^{20} -4.7$ (*c* 1.2 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 2958, 2903, 2496, 2102 and 1703; δ_H (500 MHz; $CDCl_3$) 3.70 (2H, q, *J* 5.7, 2-CH and 4-CH), 3.37 (2H, q, *J* 5.7, 1-CH and 5-CH), 1.72 (2H, t, *J* 5.7, 3-CH_2), 1.61 (2H, t, *J* 5.7, 5-CH_2) and 0.00 (18H, s, TMS); δ_C (75 MHz; $CDCl_3$) 69.7, 61.7, 36.9, 29.2 and 0.00; *m/z* (ES) 315 (100%, M-N_2^+); (Found: M-N_2^+ 315.1670; $C_{12}H_{27}N_6O_2Si_2$ requires *M-N*$_2$, 315.1673).

(1*R*,3*R*,4*R*,6*R*)-4,6-Diazidocyclohexane-1,3-diol[3] 15

Trifluoroacetic acid (2 μL) was added to a solution of (1*R*,2*R*,4*R*,5*R*)-1,5-Diazido-2,4-bis-trimethylsilanyloxy-cyclohexane (534 mg, 1.7 mmol) dissolved in MeOH (2 mL), and the reaction mixture was stirred for 35 min. The reaction mixture was evaporated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 7:3 petrol−EtOAc to give the diazide[3] **15** (327 mg, 97%) as colourless prisms, mp 97-98 °C (from MeOH–CH_2Cl_2, lit.[3] 96 ºC); R_f 0.25 (7:3, petrol–EtOAc); $[\alpha]_D^{20} -5.7$ (*c* 1.2 in CH_2Cl_2);

(Found: C, 36.6; H, 5.20; N, 42.3%; $C_{14}H_{14}N_2O$ requires C, 36.4; H, 5.10; N, 42.4%), spectroscopically identical to the racemate obtained previously. Analysis by chiral HPLC showed that the sample had >98%ee.

(1*S*,3*S*,4*S*,6*S*)-4,6-Diazidocyclohexane-1,3-diol[3] 15'

Azidotrimethylsilane (15.5 mL, 117 mmol) was added dropwise to a stirred solution of the diepoxide **14** (6.25 g, 55.8 mmol) and (*R,R*)-*N-N'*-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexane-diaminochromium(III) chloride (4 mol%, 705 mg, 1.12 mmol) in ether (19 mL) and stirred for 96 h and concentrated under reduced pressure to give a crude product, which was purified by flash chromatography, eluting with 99:10:1 petrol–EtOAc–Et_3N to give the TMS protected diol as a yellow oil. The TMS-protected diol was dissolved in 0.05% TFA in MeOH (80 mL), stirred for 16 h and evaporated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 8:2 petrol–EtOAc and recrystallised from CH_2Cl_2–MeOH to give the *diol*[3] **15'** (4.44 g, 49%) as colourless prisms; mp 98-99 °C (from MeOH–CH_2Cl_2, lit.[3] 96 ºC); R_f 0.25 (7:3, petrol–EtOAc); $[\alpha]_D^{20}$ $+5.6$ (*c* 1.0 in CH_2Cl_2), spectroscopically identical to the racemate obtained previously. Analysis by chiral HPLC showed that the sample had >98%ee.

(1*R*,3*S*,4*S*,6*R*)-Diazidocyclohexane-3,6-diol

Azidotrimethylsilane (9.42 mL, 71.4 mmol) was added dropwise to stirred solution of the diepoxide **14** (2.0 g, 17.9 mmol) and (*R,R*)-*N-N'*-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexane-diaminochromium(III) chloride (4 mol%, 451 mg, 0.714 mmol) in ether (36 mL). After 96 h, the reaction mixture was filtered through a short pad of silica, and the crude residue treated with 0.05% TFA in MeOH (50 mL) for 30 min. The reaction mixture was concentrated under reduced pressure to give a crude product, which was recrystallised (twice) from crude (CH_2Cl_2–MeOH) and the mother liquor purified by flash chromatography eluting with 7:3 petrol–EtOAc to give the *centrosymmetric diol* **17** (183 mg, 5%) as colourless plates, m.p. 158-160 °C (from CH_2Cl_2–MeOH); R_f 0.2 (7:3 petrol–EtOAc); (Found : C, 36.8; H, 5.05; N, 42.3; $C_6H_{10}N_6O_2$ requires C, 36.4; H, 5.10; N, 42.4%); ν_{max}/cm^{-1} (thin film) 3376, 2939, 2906 and 2105; δ_H (300 MHz; d_4-MeOD) 3.51 (2H, ddd, *J* 12.5, 9.5 and 4.5, 3-H and 6-H), 3.27 (2H, ddd, *J* 12.5, 9.5 and 4.5, 1-H and 4-H), 2.03 (2H, app dt, ^2J 12.5 and *J* 4.5, 2-H and 5-H) and 1.22 (2H, app q, ^2J and *J* 12.5, 2-H and 5-H); δ_C (75 MHz; d_4-MeOD) 73.0, 65.3 and 37.7; *m/z* (ES^-) 197 [100%, $(M-H)^-$]; (Found: [M–H] 197.0789; $C_6H_{10}N_6O_2$ requires *M–H*, 197.0792).

(1*R*, 3*S*,4*S*,6*R*)-Diazidocyclohexane-3,6-diacetate 18

Triethylamine (1 mL) and acetic anhydride (1 mL) were added to the centrosymmetric diol **17** (50.0 mg, 0.25 mmol) and the reaction stirred for 1.5 h. The reaction mixture was evaporated under reduced pressure to give a crude product which was purified by flash chromatography eluting with 9:1 petrol–EtOAc to give the *diacetate* **18** (57.9 mg, 82%) as colourless plates, m.p. 151-152 °C (from petrol–Et_2O); R_f 0.20 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} (solid phase) 2967, 2102, 1735 and 1455; δ_H (300 MHz; $CDCl_3$) 4.74 (2H, ddd, *J* 12.4, 9.9 and 4.6, 3-H and 6-H), 3.55 (2H, ddd, *J* 12.4, 9.9 and 4.6, 1-H and 4-H), 2.39 (2H, app dt, *J* 12.4 and 4.6, 2-H and 5-H), 2.12 (6H, s, OAc) and 1.46 (2H, app q, *J* 12.6, 2-H and 5-H); δ_C (75 MHz; $CDCl_3$) 170.4, 72.8, 60.2, 33.3 and 21.4; *m/z* (ES) 300 (100%, MNH_4^+); (Found: MNH_4^+, 300.1415; $C_{10}H_{14}N_6O_2$ requires *MNH_4*, 300.1415).

(1*S*,3*R*,4*R*,6*S*)-Diazidocyclohexane-3-ol-6-acetate 19

Porcine liver esterase (54 µl, 10 $mgml^{-1}$, 184 Umg^{-1}, 100 U) was added to a stirred solution of the diacetate (65 mg, 0.23 mmol) suspended in aqueous Tris.HCl buffer (9 mL, 250 mM, pH 7.5) and DMSO (1 mL). After 16 h, water (10 mL) was added and the reaction mixture extracted with ether (3 × 30 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 8:2 petrol–EtOAc to the *hydroxy acetate* **19** (25 mg, 46%) as a colourless oil, R_f 0.20 (8:2 petrol–EtOAc); $[\alpha]_D^{20} + 0.60$ (*c* 0.66 in MeOH); ν_{max}/cm^{-1} (thin film) 3357, 2928, 2098 and 1740; δ_H (500 MHz; $CDCl_3$) 4.75 (1H, ddd, *J* 11.7, 9.9 and 4.7, 6-H), 3.53-3.48 (2H, m, 3-H and 1-H), 3.35 (1H, ddd, *J* 11.7, 9.9 and 4.7, 4-H), 2.45 (1H, s, OH), 2.40 (1H, dt, *J* 11.7 and 4.7, 5-H), 2.30 (1H, dt, 11.7 and 4.7, 2-H) and 1.45 (2H, 2 × app q, *J* 11.7, 5-H and 2-H); δ_C

(75 MHz; $CDCl_3$) 170.6, 73.3, 71.4, 63.6, 60.5, 35.6, 32.8 and 21.4; *m/z* (ES) 258 (100%, MNH_4^+); (Found: MNH_4^+ 258.1309; $C_8H_{12}N_6O_3$ requires *MNH_4*, 258.1309).

(1*R*,2*R*,4*S*,5*S*)-4-(acetyloxy)-2,5-diazidocyclohexyl-1-(1'*S*)-camphanic acid ester 20a

(1*S*)-(−)-Camphanic chloride (8.3 mg, 38.5 μmol) was added in one portion to a stirred solution of the alcohol **19** (6.6 mg, 27.5 μmol) and dimethylaminopyridine (0.7 mg, 5.5 μmol) in pyridine (1 mL) at 0 °C. After 4 h, the reaction mixture was concentrated under reduced pressure and the crude residue redissolved in CH_2Cl_2 (25 mL), washed with aqueous hydrochloric acid (25 mL of a 1 M solution), saturated aqueous sodium bicarbonate (25 mL), brine (25 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude product, which was purified by flash chromatography (gradient elution 8:2→7:3 petrol−Et_2O) to give the *(1'S)-camphanic ester* **20a** (6.5 mg, 56%) as colourless needles, m.p. 186-187 °C (from petrol−Et_2O); R_f 0.15 (7:3 petrol−Et_2O); $[\alpha]_D^{20}$ −10.0 (*c* 0.16 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 2928, 2106, 1785 and 1751; δ_H (500 MHz; $CDCl_3$) 4.88-4.71 (2H, m, 4-H and 1-H), 3.65-3.55 (2H, m, 5-H and 2-H), 2.52-2.38 (3H, m, 6-H, 3-H and 4'-H or 3'-H), 2.13 (3H, s, OAc), 2.10-1.91 (2H, m, 4'-H and 3'-H), 1.71 (1H, ddd, ^2J 13.2, *J* 12.9 and 4.2, 4'-H or 3'-H), 1.50 (2H, m, 6-H and 3-H), 1.13 (3H, s, 6'-Me), 1.07 (3H, s, 9'-H or 8'-H) and 1.00 (3H, s, 9'-H or 8'-H); δ_C (75 MHz, $CDCl_3$) 178.2, 170.4, 167.2, 91.2, 73.5, 72.7, 60.2, 60.1, 55.3, 55.0, 33.3, 31.1, 29.3, 21.3, 17.3, 17.0 and 10.1 (1 carbon signal missing or overlapped); *m/z* (ES) 438 (100%, MNH_4^+), 421 (40, MH^+) and 443 (40, MNa^+); (Found: MNa^+ 443.1670; $C_{18}H_{24}N_6O_6$ requires *MNa*, 443.1655).

(1*R*,2*R*,4*S*,5*S*) 4-(Acetyloxy)-2,5-diazidocyclohexyl-1-(1'*R*)-camphanic acid ester 20b

By the same general method, the alcohol **19** (19 mg, 0.079 mmol) was converted into the *(1'R)-camphanic ester* **20b** (25.2 mg, 76%) as colourless plates, m.p. 185-186 °C (from petrol−EtOAc); R_f 0.50 (8:2 petrol−EtOAc); $[\alpha]_D^{20}$ +24.5 (*c* 0.62 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 2961, 2928, 2104, 1783 and 1737; δ_H (300 MHz; $CDCl_3$) 4.89 (1H, ddd, *J* 14.6, 12.1 and 4.7, 1-H), 4.76 (1H, ddd, *J* 14.4, 12.1, 4.5, 4-H), 3.67-3.56 (2H, m, 5-H and 2-H), 2.51-2.33 (3H, m, 3'-H or 4'-H and, 3-H and 6-H), 2.14 (3H, s, OAc), 2.14-2.03 (1H, m, 3'-H or 4'-H), 1.95 (1H, ddd, ^{2}J 13.2, J 10.7 and 4.5, 3'-H or 4'-H), 1.71 (1H, ddd, ^{2}J 13.2, J 10.7 and 4.5, 3'-H or 4'-H), 1.51 (2H, m, 6-H and 3-H), 1.11 (3H, s, 6'-Me), 1.07 (3H, s, 8'-Me or 9'-Me) and 0.97 (3H, s 8'-H or 9'-H); δ_C (75 MHz, $CDCl_3$) 177.9, 170.0, 166.8, 90.7, 72.8, 72.3, 60.1, 59.5, 54.8, 54.5, 32.8, 32.5, 30.6, 28.9, 20.9, 16.7, 16.6 and 9.7; *m/z* (ES) 438 (100%, MNH_4^+); (Found: MNa^+ 443.1669; $C_{18}H_{24}N_6O_6$ requires *MNa*, 443.1655).

Phenyl-2,3,4,6-tetraol-1-thio-β-L-glycopyranoside

A catalytic amount of sodium methoxide (0.90 g, 0.2 eq., 17.0 mmol) was added to a solution of phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-L-glycopyranoside (37.0 g, 84.0 mmol) dissolved in dry MeOH (158 mL). The reaction mixture was stirred at room temperature 18 h and concentrated under reduced pressure. The residue was pre-absorbed on silica and filtered through a short pad of silica (gradient elution 9:1 → 8:2 EtOAc−MeOH). The filtrate was then concentrated under reduced pressure and phenyl-2,3,4,6-tetraol-1-thio-β-D-glycopyranoside (21.3 g, 93%) was obtained as a colourless foam, which has been used without any further purification.

Phenyl-6-*O*-toluenesulfonyl-2,3,4-triol-1-thio-β-L-glycopyranoside

A solution of *p*-toluenesulfonyl chloride (20.0 g, 1.3 eq., 112 mmol) in dry pyridine (150 mL) was added dropwise to a solution of phenyl-2,3,4,6-tetraol-1-thio-β-D-glycopyranoside (23.4 g, 86.0 mmol) in dry pyridine (357 mL) at 0 ºC. After 5 h stirred at 0 ºC, the reaction was warmed to ambient temperature and stirred for an additional 18 h. The reaction was then quenched with methanol (50 mL) and concentrated under reduced pressure. The residue was dissolved in dichloromethane (150 mL) and washed sequentially with a saturated aqueous sodium hydrogen carbonate solution (100 mL), 1 M hydrochloric acid solution (100 mL) and saturated aqueous sodium hydrogen carbonate solution (2×100 mL). The aqueous layers were extracted with dichloromethane (2×100 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient elution 6:4 → 0:1 petrol−EtOAc) to provide phenyl-6-*O*-toluenesulfonyl-2,3,4-triol-1-thio-β-L-glycopyranoside (21.8 g, 60%) as colourless foam; $[\alpha]_D$ +40.0 (c. 0.22 in $CHCl_3$).

Phenyl-6-azido-6-deoxy-2,3,4-triol-1-thio-β-L-glycopyranoside

Sodium azide (4.84 g, 1.2 eq., 74.0 mmol) was added to a solution of phenyl-6-*O*-toluenesulfonyl-2,3,4-triol-1-thio-β-L-glycopyranoside (26.4 g, 62.0 mmol) in dry DMF (250 mL). The reaction was heated at 80 ºC during 8 h. After cooling at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (100 mL) and washed with a saturated aqueous sodium hydrogen carbonate solution (100 mL) and brine (100 mL), the aqueous layers were backwashed with ethyl acetate (2×100 mL) and the combined organic layers were dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with pure ethyl acetate to provide phenyl-6-azido-6-deoxy-2,3,4-triol-1-thio-β-D-glycopyranoside (14.1 g, 48%) as a colourless foam, $[\alpha]_D$ +15.6 (c. 1.00 in $CHCl_3$).

Phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glycopyranoside 21B

Benzoyl chloride (4.1 mL, 3.0 eq., 35.4 mmol) was added dropwise at 0 ºC to a stirred solution of phenyl-6-azido-6-deoxy-2,3,4-triol-1-thio-β-D-glycopyranoside (3.50 g, 11.8 mmol), triethylamine (6.6 mL, 4 eq., 47.2 mmol) and dimethylaminopyridine (0.14 g, 0.1 eq., 1.18 mmol) in dichloromethane (30 mL). The reaction mixture was warmed to room temperature over 18 h before being concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient elution 9:1 → 8:2 petrol−EtOAc) to provide 2-azidomethyl-3,4,5-tris-benzoyloxy-6-phenylsulfanyl-tetrahydro-pyran (4.37 g, 61%), as colourless prisms, mp 43-44 °C; R_f 0.41 (8:2 petrol−EtOAc); $[\alpha]_D$ +30.8 (c. 1.18 in $CHCl_3$); (Found C, 65.25; H, 4.5; N, 6.7; S, 5.2; $C_{33}H_{27}N_3O_7S$ requires C, 65.01; H, 4.46; N, 6.89; S, 5.26%); ν_{max}/cm^{-1} (film) 3155, 2959, 2107, 1734, 1278, 1091, 908, 733, 650; δ_H (300 MHz, $CDCl_3$) 7.90 (2H, d, *J* 8.7, Bz 3-H and 5-H), 7.83 (2H, d, *J* 8.7, Bz 3-H and 5-H), 7.71 (2H, d, *J* 8.7, Bz 3-H and 5-H), 7.50-7.41 (3H, m, Bz 4-H), 7.37-7.16 (11H, m, Ph), 5.81 (1H, t, *J* 9.7, 3-H), 5.39 (1H, t, *J* 9.7, 2-H or 4-H), 5.38 (1H, t, *J* 9.7, 2-H or 4-H), 4.97 (1H, d, *J*

10.2, 1-H), 3.89 (1H, ddd, *J* 9.7, 6.7 and 3.1, 5-H), 3.45 (1H, dd, *J* 13.3 and 6.7, 6-H_A) and 3.36 (1H, dd, *J* 13.3 and 3.1, 6-H_B); δ_C (75 MHz, $CDCl_3$) 164.7, 164.2, 163.9, 132.8, 132.6, 132.4, 129.9, 128.8, 128.7, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.2, 85.2, 76.6, 72.9, 69.3, 68.8 and 50.4(3 aromatic peaks overlapped or missing); *m/z* (ES) 632.6 (20%, MNa^+) and 105.9 (100%, $PhCO^+$).

Phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzyl-1-thio-β-D-glycopyranoside 21A'

Benzyl bromide (7.2 mL, 2.6 eq., 60.5 mmol) was added at 0 ºC to a stirred solution of phenyl-6-azido-6-deoxy-2,3,4-triol-1-thio-α-D-glycopyranoside (7.07 g, 23.8 mmol) in dimethylformamide (104 mL), and followed by an portionwise addition of sodium hydride (2.36 g, 2.5 eq., 59.0 mmol). After 1 h, the reaction mixture was allowed to slowly warm to room temperature. After 3 h, additional portions of benzyl bromide (2.8 mL, 1.0 eq., 23.5 mmol) and sodium hydride (0.76 g, 0.8 eq., 19.0 mmol) were added. After 1 h, TLC showed no more starting material, the reaction mixture was quenched with methanol (50 mL) and the reaction was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (100 mL), washed with a saturated aqueous ammonium chloride solution (50 mL) and brine (2 ×50 mL). The organic layer was dried (Na_2SO_4), concentrated under reduced pressure, the crude mixture was purified by flash chromatography on silica gel (9:1 petrol−EtOAc) and recrystallised from EtOH to provide phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzyl-1-thio-β-D-glycopyranoside, as colourless needles (3.63 g, 27%), $[\alpha]_D$ −16.0 (c. 0.60 in $CHCl_3$).

Phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzoyl-1-thio-β-L-glycopyranoside 21B'

Benzoyl chloride (8.2 mL, 3.0 eq., 70.8 mmol) was added dropwise at 0 ºC to a solution of phenyl-6-azido-6-deoxy-2,3,4-triol-1-thio-β-D-glycopyranoside (7.06 g, 23.6 mmol), triethylamine (13.2 mL, 4 eq., 94.4 mmol) and dimethylaminopyridine (0.28 g, 0.1 eq., 2.36 mmol) in dichloromethane (60 mL). The reaction mixture was warmed to room temperature over 18 h then concentrated under reduced pressure, and residue was purified by flash chromatography on silica gel (gradient elution 9:1 to 8:2 petrol−EtOAc) to provide phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glycopyranoside, as colourless prisms (9.50 g, 66%), $[\alpha]_D$ −14.4 (c. 1.08 in $CHCl_3$).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-phenylthio-β-D-glucopyranoside[4] 24

Zinc (II) iodide (76.92 g, 240.4 mmol) and phenylthiotrimethylsilane (25.0 g, 137 mmol) were added to a stirred suspension of D-glucosamine pentaacetate (13.36 g, 34.34 mmol) in dichloroethane (250 mL) and the reaction mixture heated to 50 °C for 8 h. The reaction mixture was allowed to cool, diluted with CH_2Cl_2 (100 mL), filtered through celite and the filtrate was washed with saturated aqueous sodium hydrogen carbonate solution (250 mL), water (250 mL), dried (Na_2SO_4), filtered and evaporated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 4:6 petrol−EtOAc to give the 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-phenylthio-β-D-glucopyranoside[4] **24** (7.01 g, 47%) as colourless prisms, m.p. 207-209 °C [from EtOAc−petrol, lit.[4] 210-212 °C (from EtOAc−petrol)]; R_f 0.30 (75:25 petrol−EtOAc); $[\alpha]_D^{20}$ − 22.4 [*c* 1.6 in $CHCl_3$, lit.[4] −24.0 (*c* 1.0, $CHCl_3$)]; ν_{max}/cm^{-1} (thin film) 3305, 3078, 2951, 1747 and 1661; δ_H (300 MHz; $CDCl_3$); 7.50-7.48 (2H, m, SPh), 7.31-7.28 (3H, m, SPh), 5.60 (1H, d, *J* 9.2, N*H*Ac), 5.22 (1H, t, *J* 9.2, 3-H), 5.06 (1H, t, *J* 9.2, 4-H), 4.85 (1H, d, *J* 10.2, 1-H), 4.23 (1H, dd, ^2J 12.2 and *J* 5.6, 6-H), 4.16 (1H, dd, ^2J 12.2 and *J* 5.6, 6-H), 4.03 (1H, app. dd, *J* 10.2 and 9.2, 2-H), 3.72 (1H, dt, *J* 9.2 and 5.6, 5-H), 2.08 (3H, s, OAc), 2.02 (3H, s, OAc), 2.01 (3H, s, OAc) and 1.99 (3H, s, NAc); *m/z* (ES) 439 (100%, MH^+).

Phenyl-6-*O*-toluenesulfonyl-2-azido-2-deoxy-3,4-diol-β-D-glycopyranoside[5] 25

The glucosamine **24** (6.98 g, 15.9 mmol) was heated under reflux conditions in aqueous sodium hydroxide (150 mL of a 2 M solution) for 24 h. The resulting solution was cooled on ice, neutralised to pH 7 with aqueous hydrochloric acid (2 M), filtered through a short pad of silica eluting with EtOAc−MeOH−H_2O 7:2:1 (200 mL), and evaporated under reduced pressure to give the free amine. Dimethylaminopyridine (3.88 g, 31.8 mmol) was added and the reaction mixture was redissolved in methanol (200 mL), and a solution of trifluoromethanesulfonic azide (35.46 mmol) in CH_2Cl_2 (76 mL) was added dropwise. The reaction mixture was stirred for 16 h, evaporated under reduced pressure and the resulting residue was redissolved in EtOAc (100 mL), washed with water (2 × 75 mL), and the combined aqueous washings extracted with EtOAc (2 × 75 mL). The combined organic extracts were dried ($NaSO_4$), filtered and evaporated under reduced pressure. The residue was dissolved in pyridine (100 mL), cooled to 0 °C and *p*-toluene sulfonyl chloride (4.18 g, 21.9 mmol) dissolved in pyridine (100 mL) was added dropwise *via* cannula. After stirring for 8 h, MeOH (20 mL) was added and the reaction mixture evaporated under reduced pressure to give a crude product, which was pre-absorbed onto silica and purified by flash chromatography eluting with 6:4 petrol–EtOAc to give the azide[5] **25** (3.58 g, 69%) as a colourless oil, R_f 0.20 (6:4 petrol–EtOAc); $[\alpha]_D^{20}$ $+40.8$ (*c* 1.51 in MeOH); ν_{max}/cm^{-1} (thin film) 3401, 3060, 2917, 2113 and 1597; δ_H (300 MHz; $CDCl_3$) 7.81 (2H, d, *J* 8.2, OTs), 7.48 (2H, dd, *J* 7.8 and 1.8, Ph), 7.35-7.25 (5H, m, Ph and OTs), 4.41 (1H, d, *J* 10.1, 1-H), 4.30 (1H, br s, 5-H), 3.49-3.37 (6H, m, 6-H, 4-H, 3-H and OH), 3.21 (1H, t, *J* 10.1, 2-H) and 2.42 (3H, s, Me); δ_C (75 MHz, $CDCl_3$) 133.3, 132.1, 130.0, 129.4, 129.0, 128.5, 128.0, 126.0, 86.2, 77.0, 76.6, 69.1, 68.4, 64.5 and 21.7; *m/z* (ES) 469 (100%, MNH_4^+); (Found: MNH_4^+ 469.1198; $C_{19}H_{25}N_4O_6S_2$ requires *MNH_4*, 469.1216).

***S*-Phenyl-6-*O*-toluenesulfonyl-2-azido-2-deoxy-3,4-di-*O*-benzyl-β-D-glycopyranoside[5] 26**

Sodium azide (598 mg, 9.2 mmol) was added to a stirred solution of the tosylate **25** (3.193 g, 7.1 mmol) in DMF (100 mL) and the reaction mixture heated to 80 °C for 18 h. The reaction mixture was concentrated under reduced pressure and the residue redissolved in EtOAc (100 mL), washed with saturated aqueous sodium bicarbonate solution (100 mL), then the aqueous layer extracted with EtOAc (2 × 100 mL) and the combined organic extracts dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the product[5] (2.03 g, 89%), which was used without further purification.

***S*-Phenyl-6,2-azido-6,2-deoxy-3,4-di-*O*-benzyl-β-D-glycopyranoside[5] 21G**

Sodium hydride (60% dispersion in mineral oil, 2.54 g, 63.4 mmol) was added portionwise to a stirred solution of the sugar **26** (2.04 g, 6.34 mmol) and *tert*-butyl ammonium iodide (468 mg, 1.27 mmol) in DMF (100 mL) at 0 °C. After 1h, benzyl bromide (3.77 mL, 31.7 mmol) was added dropwise and the reaction stirred at room temperature for 1 h. The reaction was quenched with saturated ammonium chloride (100 mL), extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic extracts washed with water (200 mL), brine (200 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude product, which was purified by flash chromatography (gradient elution 9:1 → 7:3 petrol−EtOAc) to give the benzylated sugar[5] **21G** (484 mg, 31%) as a colourless oil, R_f 0.20 (9:1 petrol−EtOAc); $[\alpha]_D^{20} +6.46$ (*c* 0.99 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3063, 3031, 2916, 2868 and 2109; δ_H (300 MHz; $CDCl_3$) 7.72-7.69 (2H, m, Ph), 7.46-7.31 (13H, m, Ph), 4.97 (1H, d, ^2J 10.5, CH_2Ph), 4.93 (1H, d, ^2J 11.0, CH_2Ph), 4.90 (1H, d, ^2J 11.0, CH_2Ph), 4.67 (1H, d, ^2J 10.5, CH_2Ph), 4.48 (1H, d, *J* 10.0, 1-H), 3.66-3.53 (4H, m, 6-H, 5-H, 4-H and 3-H) and 3.43-3.36 (2H, m, 6-H and 2-H); δ_C (75 MHz; $CDCl_3$) 137.9, 137.8, 135.0, 130.6, 129.6, 129.3, 129.1, 128.7, 128.6, 128.4, 86.4, 85.4, 78.8, 78.3, 76.4, 75.7, 65.4 and 51.6 (two carbon signals missing or overlapped); *m/z* (ES) 525 (100%, MNa^+); (Found: MNa^+ 525.1706; $C_{26}H_{26}N_6O_3S$ requires MNa^+, 525.1685).

General procedure for glycosylation (Method A)

The glycosyl donor (0.43 mmol) and the acceptor (0.34 mmol), both freshly dried azeotropically by removal of toluene, were dissolved in dry dichloromethane (2.6 mL) and transferred with a syringe into a flame dried round bottom flask containing activated 4 Å molecular sieves. The reaction mixture was cooled to 0 °C, *N*-iodosuccinimide (104 mg, 0.46 mmol) and silver(I) trifluoromethanesulfonate (9 mg, 0.03 mmol) added simultaneously, stirred for 2 h and quenched with Et_3N (1 mL). The reaction mixture was filtered through celite, eluting with dichloromethane (15 mL), washed with a solution of 10% aqueous $Na_2S_2O_3$ solution (2×10 mL) and brine (2×10 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure to give a crude product.

General procedure for glycosylation (Method B)

The glycosyl donor (5.57 mmol) and the acceptor (7.06 mmol), both freshly dried azeotropically by removal of toluene, were dissolved in dry dichloromethane (13 mL) and diethyl ether (40 mL) respectively, and transferred with a syringe into a flame dried round bottom flask containing activated 4 Å molecular sieves. The reaction mixture was cooled to 0 °C, *N*-iodosuccinimide (1.63 g, 7.23 mmol) and silver(I) trifluoromethanesulfonate (286 mg, 1.11 mmol) added simultaneously, stirred for 3 h and quenched with Et_3N (5 mL). The reaction mixture was filtered through celite, eluting with dichloromethane (50 mL), washed with a solution of 10% aqueous $Na_2S_2O_3$ solution (2×50 mL) and brine (2×50 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure to give a crude product.

General procedure for glycosylation with a trichloroacetimidate donor (Method C)
A solution of the trichloroacetimidate donor (1 equivalent), the acceptor (1.2 equivalents) and powdered 4 Å molecular sieves (80 mg) in dichloromethane (5 ml) were stirred at room temperature for 1 h. The reaction mixture was cooled to −60 °C and boron trifluoride diethyl etherate (0.1 equivalents) was added dropwise. The reaction was stirred at −60 °C for 2 h and then quenched with solid $NaHCO_3$ and stirred for 15 min. The mixture was filtered through celite, washing with dichloromethane and EtOAc, and the solvent was removed under reduced pressure to yield a crude product.

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-2,3-diacetoxy-4,6-diazido-cyclohexanol 27A
By method A, the glycosyl donor **21A** (242 mg, 1.2 eq., 0.43 mmol) and the acceptor **11** (100 mg, 1.0 eq., 0.34 mmol), gave a crude product which was purified by flash chromatography on silica gel (gradient elution 9:1 → 8:2 petrol−EtOAc) to give **27A** (0.16 g, 65%) as a yellow oil, R_f 0.51 (7:3 petrol−EtOAc); $[\alpha]_D$ +34.2 (c. 1.10 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2931, 2103, 1756, 1234 and 1071; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (15H, m, Ph), 5.18 (1H, dd, *J* 9.8 and 9.4, 1-H), 5.13 (1H, d, *J* 3.4, 1'-H), 4.96 (1H, dd, *J* 10.2 and 9.8, 2-H), 4.89 (1H, d, *J* 11.1, CH_AHPh), 4.86 (1H, d, *J* 11.1, CH_BHPh), 4.78 (1H, d, *J* 11.1, $CHH_{B'}Ph$), 4.71 (1H, d, *J*

12.0, C*H_C*HPh), 4.64 (1H, d, *J* 12.0, CH*H_{C'}*Ph), 4.59 (1H, d, *J* 11.1, CH*H_{A'}*Ph), 4.12 (1H, d, *J* 9.4, 5'-H), 3.96 (1H, t, *J* 9.4, 3'-H), 3.64-3.47 (6H, m, 2'-H, 4'-H, 6'-H_A, 3-H, 4-H and 6-H), 3.37 (1H, dd, *J* 13.3 and 4.7, 6'-H_B), 2.37 (1H, ddd, *J* 12.8, 4.7 and 4.3, 5-H_A), 2.08 (3H, s, CH_3), 1.86 (3H, s, CH_3) and 1.56 (1H, q, *J* 12.8, 5-H_B); δ_C (125 MHz, $CDCl_3$) 169.8 (C=O), 169.6 (C=O), 138.4, 138.0, 137.7 (*o*-Ph), 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 97.9 (1'-C), 81.3 (3'-C), 79.8 (4'-C), 78.2, 78.1 (2'-C and 3-C), 76.0 (CH$_2$Ph), 75.5 (CH$_2$Ph), 74.1 (2-C), 73.8 (CH$_2$Ph), 73.2 (1-C), 71.1 (5'-C), 60.0, 57.8 (4-C and 6-C), 51.2 (6'-C), 32.3 (5-C), 20.7 (CH_3) and 20.6 (CH_3); *m/z* (ES) 778.3 (76%, MNa^+) and 430.2 (100); (Found: MNa^+, 778.2921. $C_{37}H_{41}O_9N_9$ requires *MNa*, 778.2925).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-2,3-diacetoxy-4,6-diazido-cyclohexanol 27A'

By method A, the glycosyl donor **21A'** (0.46 g, 1.2 eq., 0.81 mmol) and the acceptor **11** (0.20 g, 1.0 eq., 0.67 mmol) gave a crude product which was purified by flash chromatography on silica gel (gradient elution 9:1 to 8:2 petrol−EtOAc) to give **27A'** (0.28 g, 55%) as a yellow oil; R_f 0.51 (7:3 petrol−EtOAc); $[\alpha]_D$ −25.0 (c. 0.16 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2925, 2103, 1754, 1234 and 1072; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (15H, m, Ph), 5.09 (1H, d, *J* 3.4, 1'-H), 5.04 (1H, t, *J* 9.4, 2-H), 4.95 (1H, d, *J* 10.7, CH_AHPh), 4.88 (1H, d, *J* 11.1, CH_BHPh), 4.87 (1H, dd, *J* 9.8 and 8.6, 3-H), 4.78 (1H, d, *J* 11.9, CH_CHPh), 4.76 (1H, d, *J* 11.1, CH$H_{B'}$Ph), 4.71 (1H, d, *J* 11.9, CH$H_{C'}$Ph), 4.57 (1H, d, *J* 10.7, CH$H_{A'}$Ph), 3.97 (1H, t, *J* 9.4, 3'-H), 3.82 (1H, dt, *J* 9.8 and 2.5, 5'-H), 3.60-3.47 (6H, m, 2'-H, 4'-H, 6'-H, 1-H, 4-H and 6-H), 3.35 (1H, dd, *J* 13.7 and 2.7, 6'-H), 2.28 (1H, ddd, *J* 12.8, 4.7 and 4.3, 5-H_A), 2.07 (3H, s, CH_3), 2.02 (3H, s, CH_3) and 1.44 (1H, q, *J* 12.8, 5-H_B); δ_C (125 MHz, $CDCl_3$) 170.0 (C=O), 169.8 (C=O), 138.6, 138.4, 138.1 (*o*-Ph), 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6 (Ph), 98.9 (1'-C), 81.9 (2'-C), 80.8 (3'-C), 77.2 (4'-C and 1-C), 75.5 (CH$_2$Ph), 75.2 (CH$_2$Ph), 74.6 (3-C), 73.5 (CH$_2$Ph), 73.2 (2-C), 70.9 (5'-C) ,60.2, 58.1 (4-C and 6-C), 50.8 (6'-C), 31.9 (5-C), 20.7 (CH_3) and 20.6 (CH_3); *m/z* (ES) 778.3 (97%, MNa^+) and 430.2 (100); (Found: MNa^+, 778.2891. $C_{37}H_{41}O_9N_9Na$ requires *MNa*, 778.2925).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzoyl-α-D-glucopyranosyl)-2,3-diacetoxy-4,6-diazido-cyclohexanol 27B

By method A, the glycosyl donor **21B** (102 mg, 1.2 eq., 0.16 mmol) and the acceptor **11** (42 mg, 1.0 eq., 0.14 mmol) gave a crude product was purified by flash chromatography on silica gel, eluting with 8:2 petrol−EtOAc, to give **27B** (83.5 mg, 75%) as a yellow oil; R_f 0.53 (6:4 petrol−EtOAc); $[\alpha]_D$ −16.5 (c. 1.04 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2931, 2103, 1735, 1642, 1260 and 1069; δ_H (500 MHz, $CDCl_3$) 7.96 (2H, d, *J* 7.6, Ph 2-H and 6-H), 7.91 (2H, d, *J* 7.6, Ph 2-H and 6-H), 7.80 (2H, d, *J* 7.6, Ph 2-H and 6-H), 7.56-7.46 (2H, m, Ph 4-H), 7.41-7.33 (5H, m, Ph), 7.31-7.26 (2H, m, Ph 3-H and 5-H), 5.88 (1H, t, *J* 9.6, 3'-H), 5.45-5.38 (2H, m, 2'-H and 4'-H), 5.17 (1H, d, *J* 7.9, 1'-H), 5.04-4.94 (2H, m, 1-H and 3-H), 3.94 (1H, dd, *J* 7.6 and 7.4, 5'-H), 3.65 (1H, dd, *J* 9.4 and 9.2, 2-H), 3.54 (1H, dd, *J* 13.5 and 7.4, 6'-H_A), 3.51-3.39 (3H, m, 6'-H_B, 4-H and 6-H), 2.31-2.23 (1H, m, 5-H_A), 2.13 (3H, s, CH_3), 2.07 (3H, s, CH_3) and 1.54 (1H, q, *J* 12.6, 5-H_B); δ_C (125 MHz, $CDCl_3$) 169.7 (C=O Ac), 169.6 (C=O Ac), 165.7 (C=O Bz), 165.3 (C=O Bz), 164.9 (C=O Bz), 133.7, 133.3 (4-*C* Ph), 129.9, 129.8, 129.7 (2*C* and 6*C* Ph), 129.1, 128.7, 128.5 (1-*C* Ph), 128.5, 128.4, 128.3 (3*C* and 5*C* Ph), 100.6 (1'-C), 79.1 (2-C), 73.6 (5'-C and 3-C), 72.7 (3'-C), 72.0 (4'-C), 71.1 (1-C), 70.2 (2'-C), 60.1, 57.8 (4-C and 6-C), 51.3 (6'-C), 32.3 (5-C), 20.8 (CH_3), 20.7 (CH_3) (1 aromatic peak overlapped or missing); *m/z* (ES) 820.2 (100%, MNa^+) and 500.2 (79); (Found: MNa^+, 820.2270. $C_{37}H_{35}O_{12}N_9$ requires *MNa*, 820.2303).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-2,3-ol 31A

A catalytic amount of sodium methoxide (3 mg, 0.2 eq., 0.06 mmol) was added to a solution of the diacetylated glycoside **4A** (165 mg, 0.22 mmol) in dry MeOH (1.4 mL). The reaction mixture was stirred at room temperature for 18h and concentrated under reduced pressure. The crude product was pre-absorbed on silica and filtered through a short pad of silica (gradient elution 9:1 to 8:2 EtOAc−MeOH) to give **31A** (67 mg, 65%) as a yellow oil; R_f 0.26 (7:3 petrol−EtOAc); $[\alpha]_D$ +60.9 (c. 1.05 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3429, 2919, 2102, 1262 and 1069; δ_H (300 MHz, $CDCl_3$) 7.40-7.20 (15H, m, Ph), 4.96 (1H, d, *J* 3.6, 1'-H), 4.93-4.85 (3H, m, C*H*$_2$Ph), 4.74 (1H, d, *J* 11.8, C*H*$_A$HPh), 4.62 (2H, d, *J* 10.8, C*H*$_2$Ph), 4.11-3.98 (2H, m, 3'-H and 4'-H), 3.63-3.50 (3H, m, 2'-H, 5'-H and 6'-H), 3.47-3.15 (6H, m, 6'-H, 1-H, 2-H, 3-H, 4-H and 6-H), 2.29 (1H, ddd, *J* 12.8, 4.6 and 4.1, 5-H_A) and 1.46 (1H, q, *J* 12.8, 5-H_B); δ_C (75 MHz, $CDCl_3$), 138.1 (*o*-Ph×3), 129.2, 128.9, 128.5, 128.3, 128.1 (Ph), 101.4 (1'-C), 85.7 (1-C), 82.5 (3'-C), 79.8 (2'-C), 78.7 (5'-C), 76.0, 75.8 (2-C and 3-C), 75.1 (*C*H$_2$Ph), 71.5 (4'-C), 60.1, 59.8 (4-C and 6-C), 51.5 (6'-C) and 32.7 (5-C) (4 aromatic peaks overlapped or missing); *m/z* (ES) 694.3 (81%, MNa^+) and 430.2 (100); (Found: MNa^+, 694.2736. $C_{33}H_{37}O_7N_9$ requires *MNa*, 694.2714).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-4,6-diazido-cyclohexan-2,3-ol 31A'

By the same method, **27A'** (50.9 mg, 0.07 mmol) gave **31A'** (39.9 mg, 89%) as a yellow oil; R_f 0.26 (7:3 petrol−EtOAc); $[\alpha]_D$ −27.4 (c. 0.57 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3437, 2923, 2104, 1260 and 1070; δ_H (500 MHz, $CDCl_3$) 7.45-7.20 (15H, m, Ph), 5.04 (1H, d, *J* 3.8, 1'-H), 4.98 (1H, d, *J* 11.1, C*H*$_A$HPh), 4.90 (1H, d, *J* 11.1, C*H*$_B$HPh), 4.79 (1H, d, *J* 11.1, CH*H*$_{A'}$Ph), 4.77 (1H, d, *J* 12.0, C*H*$_C$HPh), 4.71 (1H, d, *J* 12.0, CH*H*$_{C'}$Ph), 4.57 (1H, d, *J* 11.1, CH*H*$_{B'}$Ph), 4.06-3.98 (2H, m, 3'-H and 5'-H), 3.61-3.55 (2H, m, 2'-H and 6'-H_A), 3.50-3.36 (5H, m, 4'-H, 2-H, 3-H, 4-H and 6-H), 3.33 (1H, dd, *J* 12.8 and 6.4, 6'-H_B), 3.28-3.23 (1H, m, 1-H), 2.28 (1H, dt, *J* 12.3 and 4.3, 5-H_A) and 1.44 (1H, q, *J* 12.3, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.5, 137.8, 137.7 (*o*-Ph), 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7 (Ph), 98.0 (1'-C), 85.5 (1-C), 81.1 (3'-C), 79.8 (2'-C), 78.1 (4'-C), 75.8 (3-C), 75.7 (*C*H$_2$Ph), 75.3 (*C*H$_2$Ph), 74.7 (*C*H$_2$Ph), 73.6 (2-C), 71.1 (5'-C), 59.7, 59.5 (4-C and 6-C), 51.7 (6'-C) and 32.4 (5-C) (2 aromatic peaks overlapped or missing); *m/z* (ES) 694.2 (100%, MNa^+) and 430.2 (78); (Found: MNa^+, 694.2681. $C_{33}H_{37}O_7N_9$ requires *MNa*, 694.2714).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AA

By method A, the glycosyl donor **21A** (51 mg, 1.2 eq., 0.09 mmol) and the acceptor **31A** (50 mg, 1.0 eq., 0.08 mmol), gave a crude mixture which was purified by flash chromatography on silica gel (9:1 petrol−EtOAc) to give **27AA** (54 mg, 62%) as a yellow foam, R_f 0.46 (7:3 petrol−EtOAc); $[\alpha]_D$ +88.0 (c. 1.10 in $CHCl_3$), ν_{max}/cm^{-1} (film) 3446, 2925, 2103, 1154 and 1070; δ_H (500 MHz, $CDCl_3$) 7.40-7.10 (30H, m, Ph), 5.29 (1H, d, *J* 3.4, 1''-H), 5.12 (1H, d, *J* 3.4, 1'-H), 5.01 (1H, d, *J* 10.7, CH_AHPh), 4.94 (1H, d, *J* 11.1, CH_BHPh), 4.91-4.76 (8H, m, CH_2Ph), 4.61 (1H, d, *J* 11.1, CH_CHPh), 4.57 (1H, d, *J* 11.1, CHH_DPh), 4.34 (1H, ddd, *J* 9.8, 4.3 and 2.6, 5'-H), 4.09 (1H, ddd, *J* 9.9, 3.4 and 2.6, 5''-H), 4.01 (1H, dd, *J* 9.8 and 9.4, 3'-H), 3.97 (1H, dd, *J* 9.8 and 9.4, 3''-H), 3.61-3.52 (6H, m, 2'-H, 2''-H, 4''-H, 6''-H, 2-H and 4-H), 3.49-3.39 (3H, m, 4'-H, 3-H, and 6''-H), 3.31-3.23 (3H, m, 6'-H, 1-H and 6-H), 3.19 (1H, dd, *J* 13.2 and 4.3, 6'-H), 2.41 (1H, dt, *J* 12.4, and 4.3, 5-H_A) and 1.61 (1H, q, *J* 12.4, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.7, 138.4, 138.0, 137.9, 137.1, 137.2 (*o*-Ph), 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (Ph), 100.4 (1'-C), 97.5 (1''-C), 84.9 (1-C), 81.8 (3''-C), 81.6 (3'-C), 80.3 (3-C), 79.8 (2'-C and 2''-C), 78.3 (4'-C and 4''-C), 75.6 (*C*H_2Ph), 75.4 (*C*H_2Ph), 75.3 (*C*H_2Ph), 74.4 (2-C), 74.2 (*C*H_2Ph), 73.3 (*C*H_2Ph), 71.0 (5''-C), 70.2 (5'-C), 60.2 (4-C), 58.9 (6-C), 51.2 (6''-C), 51.1 (6'-C) and 32.2 (5-C) (nine peaks overlapped or missing); *m/z* (ES) 1151.9 (100%, MNa^+) and 430.4 (100); (Found: MNa^+, 1151.4712. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzyl-α-L-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AA'

By method A, the glycosyl donor **21A'** (67 mg, 1.2 eq., 0.12 mmol) and the acceptor **31A** gave a crude mixture was purified by flash chromatography on silica gel (9:1 petrol−EtOAc) to give **27AA'** (56 mg, 50%) as a yellow foam, R_f 0.55 (7:3 petrol−EtOAc); ν_{max}/cm^{-1} (film) 3421, 2923, 2102, 1152 and 1069; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (30H, m, Ph), 5.35 (2H, d, *J* 3.7, 1'-H and 1''-H), 4.94 (2H, d, *J* 10.9, CH_AHPh), 4.90 (2H, d, *J* 11.4, CH_BHPh), 4.84 (2H, d, *J* 10.9, CH$H_{A'}$Ph), 4.65 (2H, d, *J* 11.3, CH_CHPh), 4.62 (2H, d, *J* 11.4, CH$H_{B'}$Ph), 4.59 (2H, d, *J* 11.3, CH$H_{C'}$Ph), 4.14 (2H, ddd, *J* 9.9, 3.9 and 2.5, 5'-H and 5''-H), 4.06 (2H, t, *J* 9.3, 4'-H and 4"-H), 3.74 (1H, t, *J* 8.6, 2-H), 3.60-3.50 (6H, m, 2'-H, 2"-H, 4'-H, 4"-H, 6'-H_A and 6"-H_A), 3.45-3.37 (4H, m, 1-H, 3-H, 4-H and 6-H), 3.35 (2H, dd, *J* 10.0 and 4.2, 6'-H_B and 6"-H_B), 2.41 (1H, dt, *J* 12.6, and 4.1, 5-H_A) and 1.60 (1H, q, *J* 12.6, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.5, 137.9, 137.2 (*o*-Ph), 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7 (Ph), 98.8 (1'-C and 1"-C), 82.0-81.8 (1-C, 3-C, 3'-C and 3"-C), 79.8 (2'-C and 2"-C), 78.1 (4'-C and 4"-C), 76.7 (2-C), 75.7 (CH$_2$Ph), 75.2 (CH$_2$Ph), 73.7 (CH$_2$Ph), 70.8 (5'-C and 5"-C), 58.9 (4-C and 6-C), 51.3 (6'-C and 6"-C) and 32.4 (5-C) (2 aromatic peaks overlapped or missing); *m/z* (ES) 1151.6 (20%, MNa^+), and 947.4 (100, M-2Bn); (Found: MNa^+, 1151.4724. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'A

By method A, the glycosyl donor **21A** (91 mg, 1.2 eq., 0.16 mmol) and the acceptor **31A'** (89 mg, 1.0 eq., 0.13 mmol) gave a crude product which was purified by flash chromatography on silica gel (9:1 petrol−EtOAc) to give **27A'A** (31 mg, 21%) as a yellow foam, R_f 0.44 (7:3 petrol−EtOAc); ν_{max}/cm^{-1} (film) 3469, 2923, 2104 and 1070; δ_H (500 MHz, $CDCl_3$) δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (30H, m, Ph), 5.21 (2H, d, *J* 3.9, 1'-H and 1"-H), 4.98 (2H, d, *J* 11.1, CH_AHPh), 4.89 (2H, d, *J* 11.1, CH_BHPh), 4.79 (2H, d, *J* 11.1, CH$H_{B'}$Ph), 4.78 (2H, d, *J* 11.5, CH_CHPh), 4.74 (2H, d, *J* 11.5, CH$H_{C'}$Ph), 4.58 (2H, d, *J* 11.1, CH$H_{A'}$Ph), 4.25-4.19 (2H, m, 5'-H and 5"-H), 3.99 (2H, dd, *J* 9.4 and 8.9, 3'-H and 3"-H), 3.60-3.48 (8H, m, 2'-H, 2"-H, 4'-H, 4"-H, 6'-H_A, 6"-H_A, 4-H and 6-H), 3.46 (1H, t, *J* 9.4, 2-H), 3.36 (2H, t, *J* 9.4, 1-H and 3-H), 3.33 (2H, dd, *J* 13.2 and 5.1, 6'-H_B and 6"-H_B), 2.34 (1H, ddd, *J* 12.8, 4.7 and 4.1, 5-H_A) and 1.53 (1H, q, *J* 12.8, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.6, 137.9, 137.8 (*o*-Ph), 128.5, 128.4, 128.0, 127.9 (Ph), 97.6 (1'-C and 1"-C), 82.9 (1-C and 3-C), 81.4 (3'-C and 3"-C), 79.8 (2'-C and 2"-C), 78.2 (4'-C and 4"-C), 75.6 (CH$_2$Ph), 75.2 (CH$_2$Ph), 73.5, 73.2 (CH$_2$Ph and 2-C), 70.7 (5'-C and 5"-C), 59.7 (4-C and 6-C), 51.4 (6'-C and 6"-C) and 29.7 (5-C) (five aromatic peaks overlapped or missing); *m/z* (ES) 1151.6 (65%, MNa^+) and 430.3 (100); (Found: MNa^+, 1151.4711. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzyl-α-L-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'A'

By method A, the glycosyl donor **21A'** (119 mg, 1.2 eq., 0.21 mmol) and the acceptor **31A'** (117 mg, 1.0 eq., 0.17 mmol) gave a crude product which was purified by flash chromatography on silica gel (9:1 petrol−EtOAc) to give **27A'A'** (49 mg, 26%) as a yellow oil, $[\alpha]_D$ −71.6 (c. 0.91 in $CHCl_3$), spectroscopically identical to **27AA** reported previously.

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzoyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AB

By method A, the glycosyl donor **21B** (85 mg, 1.2 eq., 0.14 mmol) and the acceptor **31A** (78 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and preparative HPLC to give **27AB** (69 mg, 51%) as a colourless foam, R_f 0.45 (7:3 petrol−EtOAc); $[\alpha]_D$ +32.1 (c. 0.09 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3460, 2920, 2104, 1736, 1261 and 1068; δ_H (500 MHz, $CDCl_3$) 7.94 (2H, dd, *J* 7.2 and 1.1, Bz), 7.88 (2H, dd, *J* 7.2 and 1.1, Bz), 7.84 (2H, dd, *J* 7.2 and 1.1, Bz), 7.55-7.20 (24H, m, Ph), 5.89 (1H, t, *J* 9.5, 3''-H), 5.51-5.46 (2H, m, 2''-H and 4''-H), 5.45 (1H, d, *J* 8.0, 1''-H), 4.94 (1H, d, *J* 3.5, 1'-H), 4.91 (1H, d, *J* 10.9, CH_AHPh), 4.90-4.81 (3H, m, CH_BHPh, CH_CHPh and $CHH_{C'}$Ph), 4.73 (1H, d, *J* 11.1, $CHH_{B'}$Ph), 4.60 (1H, d, *J* 10.9, $CHH_{A'}$Ph), 4.54 (1H, d, *J* 1.2, OH), 4.03-3.97 (2H, m, 5'-H and 5''-H), 3.92 (1H, t, *J* 9.3, 3'-H), 3.81 (1H, t, *J* 9.4, 3-H), 3.64-3.58 (2H, m, 2'-H and 6''-H), 3.58-3.52 (2H, m, 4'-H and 6'-H), 3.43-3.37 (3H, m, 6'-H, 2-H and 4-H), 3.35 (1H, dd, *J* 13.7 and 2.1, 6''-H), 3.16-3.02 (2H, m, 1-H and 6-H), 2.24-2.15 (1H, m, 5-H_A) and 1.45-1.33 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 165.8, 165.4 (3×C=O Bz), 138.3, 137.8, 136.6 (*o*-Ph), 133.7, 133.3, 133.0 (*o*-Bz), 129.9, 129.8, 129.5, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6 (Ph), 101.2 (1'-C), 100.3 (1''-C), 86.2 (1-C), 82.1 (3'-C), 80.3 (3-C), 79.7 (2'-C), 78.2 (4'-C), 76.2 (2-C), 75.6 (CH_2Ph), 75.3 (CH_2Ph), 75.0 (CH_2Ph), 74.2 (5'-C), 72.7 (3''-C), 72.1 (4''-C), 71.0 (5''-C), 70.5 (2''-C), 58.9 (6-C), 57.9 (4-C), 51.5, 51.1 (6'-C and 6''-C) and 32.3 (5-C) (three aromatic peaks overlapped or missing); *m/z* (ES) 1194.2 (24%, MNa^+) and 429.8 (98); (Found: MNa^+, 1193.4080. $C_{60}H_{58}O_{14}N_{12}$ requires *MNa*, 1193.4093).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzoyl-β-L-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AB'

By method A, the glycosyl donor **21B'** (85 mg, 1.2 eq., 0.14 mmol) and the acceptor **31A** (78 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and preparative HPLC to give **27AB'** (38 mg, 28%) as a colourless foam, R_f 0.48 (7:3 petrol−EtOAc); $[\alpha]_D$ +45.3 (c. 0.98 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3475, 2926, 2104, 1733, 1261 and 1069; δ_H (500 MHz, $CDCl_3$) 7.99 (2H, dd, *J* 7.3 and 1.0, Bz), 7.92 (2H, dd, *J* 7.3 and 1.0, Bz), 7.81 (2H, br d, *J* 7.3, Bz), 7.56-7.23 (24H, m, Ph), 5.91 (1H, t, *J* 9.7, 3''-H), 5.57 (1H, dd, *J* 9.7 and 8.0, 2''-H), 5.55 (1H, d, *J* 3.8, 1'-H), 5.50 (1H, t, *J* 9.7, 4''-H), 5.14 (1H, d, *J* 8.0, 1''-H), 4.98 (1H, d, *J* 10.9, CH_AHPh), 4.90 (1H, d, *J* 11.2, CH_BHPh), 4.86 (1H, d, *J* 11.7, CH_CHPh), 4.80 (1H, d, *J* 10.9, $CHH_{A'}Ph$), 4.73 (1H, d, *J* 11.7, $CHH_{C'}Ph$), 4.59 (1H, d, *J* 11.2, $CHH_{B'}Ph$), 4.15 (1H, ddd, *J* 9.9, 4.4 and 2.3, 5'-H), 4.00 (1H, t, *J* 9.3, 3'-H), 3.94 (1H, ddd, *J* 9.7, 6.9 and 2.7, 5''-H), 3.75 (1H, dd, *J* 8.6 and 8.3, 2-H), 3.57 (1H, dd, *J* 9.3 and 3.8, 1'-H), 3.53-3.47 (5H, m, 4'-H, 6'-H, 6''-H and 1-H), 3.47-3.34 (4H, m, 6'-H, 3-H, 4-H and 6-H), 2.32-2.25 (1H, m, 5-H_A) and 1.52 (1H, q, *J* 12.4, 5-H_B); δ_C (125 MHz, $CDCl_3$) 165.7, 165.3, 165.1 (C=O Bz), 138.7, 138.1, 137.7 (*o*-Ph), 133.8, 133.4 (*o*-Bz), 129.9, 129.8, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8 (Ph), 101.5 (1''-C), 97.9 (1'-C), 84.5 (3-C), 81.5 (3'-C), 80.5 (1-C), 79.4 (2'-C), 78.1 (4'-C), 75.7 (C_AH_2Ph), 75.1 (C_BH_2Ph), 74.8 (2-C), 73.8 (5''-C), 72.9 (C_CH_2Ph), 72.6 (3''-C), 71.7 (2''-C), 70.7 (5'-C), 69.9 (4''-C), 59.2, 58.7 (4-C and 6-C), 51.4, 51.3 (6'-C and 6''-C) and 32.1 (5-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1193.7 (52%, MNa^+) and 430.3 (100); (Found: MNa^+, 1193.4125. $C_{60}H_{58}O_{14}N_{12}$ requires *MNa*, 1193.4093).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzoyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'B

By method A, the donor **21B** (88 mg, 1.2 eq., 0.15 mmol) and the acceptor **31A'** (81 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and preparative HPLC to give **27A'B** (45 mg, 32%) as a colourless foam; R_f 0.38 (7:3 petrol/EtOAc); $[\alpha]_D$ −32.4 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3461, 2924, 2106, 1733, 1261 and 1069; δ_H (500 MHz, $CDCl_3$) 7.95 (2H, d, *J* 7.3, Bz), 7.91 (2H, d, *J* 7.4, Bz), 7.80 (2H, d, *J* 7.4, 3''C-Bz), 7.52 (1H, dd, *J* 7.5 and 7.4, Ph), 7.44-7.21 (23H, m, Ph), 5.90 (1H, t, *J* 9.6, 3''-H), 5.51 (1H, dd, *J* 9.6 and 8.0, 2''-H), 5.49 (1H, t, *J* 9.6, 4''-H), 5.43 (1H, d, *J* 8.0, 1''-H), 5.01 (1H, d, *J* 3.5, 1'-H), 4.93 (1H, d, *J* 10.9, 3'C-CH_AHPh), 4.89 (1H, d, *J* 10.9, 4'C-CH_BHPh), 4.75 (1H, d, *J* 10.9, 3'C-CH$H_{A'}$Ph), 4.70 (2H, s, 2'C-CH_2Ph), 4.54 (1H, d, *J* 10.9, 4'C-CH$H_{B'}$Ph), 4.00 (1H, ddd, *J* 9.7, 7.5 and 2.2, 5''-H), 3.90 (1H, t, *J* 9.4, 3'-H), 3.89-3.84 (1H, m, 5'-H), 3.76-3.70 (2H, m, OH and 3-H), 3.60 (1H, dd, *J* 13.4 and 7.5, 6''-H_A), 3.54 (1H, dd, *J* 9.4 and 3.5, 2'-H), 3.46 (1H, dd, *J* 9.6 and 9.3, 4'-H), 3.45-3.33 (4H, m, 2-H, 4-H, 6-H and 6''-H_B), 3.23 (1H, t, *J* 9.4, 1-H), 3.14 (2H, d, J 3.5, 6'-H), 2.17 (1H, dt, *J* 13.5 and 4.5, 5-H_A) and 1.57 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 165.8, 165.3, 165.0 (C=O Bz), 138.5, 137.7 (*o*-Ph), 133.6, 133.3, 133.2 (*o*-Bz), 129.9, 129.8, 129.7, 129.3, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7 (Ph), 100.8 (1''-C), 98.3 (1'-C), 85.4 (1-C), 81.3 (3-C), 80.9 (3'-C), 79.6 (2'-C_2), 77.7 (4'-C), 75.6 (3''-C*C*H_2Ph), 75.3 (4''-C*C*H_2Ph), 75.2 (2-C), 74.1 (5''-C), 73.5 (2''-C*C*H_2Ph), 72.7 (3''-C), 72.3 (2''-C), 71.0 (5'-C), 70.3 (4''-C), 59.5 (6-C), 58.0 (4-C), 51.5 (6''-C), 51.0 (6'-C) and 32.4 (5-C) (seven aromatic peaks overlapped or missing); *m/z* (ES) 1193.6 (55%, MNa^+), 1151.7 (57) and 430.3 (100); (Found: MNa^+, 1193.4102. $C_{60}H_{58}O_{14}N_{12}$ requires *MNa*, 1193.4093).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzoyl-β-L-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'B'

By method A, the glycosyl donor **21B'** (88 mg, 1.2 eq., 0.15 mmol) and the acceptor **31A'** (81 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and preparative HPLC to give **27A'B'** (36 mg, 26%) as a colourless foam; R_f 0.32 (7:3 petrol−EtOAc); $[\alpha]_D$ −29.6 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3490, 2924, 2104, 1735, 1261 and 1092; δ_H (500 MHz, $CDCl_3$) 8.00 (2H, d, *J* 7.5, Bz), 7.92 (2H, d, *J* 7.5, Bz), 7.81 (2H, d, *J* 7.5, 3"C-Bz), 7.56-7.49 (2H, m, Ph), 7.45-7.23 (22H, m, Ph), 5.90 (1H, t, *J* 9.7, 3"-H), 5.54 (1H, dd, *J* 9.7 and 8.0, 2"-H), 5.48 (1H, t, *J* 9.7, 4"-H), 5.32 (1H, d, *J* 3.6, 1'-H), 5.07 (1H, d, *J* 8.0, 1"-H), 4.98 (1H, d, *J* 10.9, 3'-CCH_AHPh), 4.89 (1H, d, *J* 11.1, 4'-CCH_BHPh), 4.84 (1H, d, *J* 11.8, 2'-CCH_CHPh), 4.82 (1H, d, *J* 10.9, 3'-CCH$H_{A'}$Ph), 4.74 (1H, d, *J* 11.8, 2'-CCH$H_{C'}$Ph), 4.60 (1H, d, *J* 11.1, 4'-CCH$H_{B'}$Ph), 4.51-4.44 (1H, m, 5'-H), 4.00 (1H, t, *J* 9.4, 3'-H), 3.99-3.94 (1H, m, 5"-H), 3.68 (1H, d, *J* 1.2, OH), 3.61-3.49 (6H, m, 2-H, 6-H, 2'-H, 6'-H_A and 6"-H), 3.49 (1H, t, *J* 9.5, 4'-H), 3.44 (1H, t, *J* 9.4, 1-H), 3.40-3.32 (3H, m, 3-H, 4-H and 6'-H_B), 2.31-2.23 (1H, m, 5-H_A) and 1.58-1.49 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 165.7, 165.3, 165.1 (C=O Bz), 138.7, 138.1, 137.9 (*o*-Ph), 133.8, 133.4 (*o*-Bz), 129.9, 129.8, 129.0, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6 (Ph), 101.9 (1"-C), 97.5 (1'-C), 85.7 (3-C), 81.6 (3'-C), 80.1 (1-C), 79.7 (2'-C), 78.2 (4'-C), 75.6 (3'-C*C*H_2Ph), 75.1 (4'-C*C*H_2Ph), 73.6 (5"-C), 73.2 (2'-C*C*H_2Ph), 72.6 (3"-C), 72.5 (2-C), 71.7 (2"-C), 70.2 (5'-C), 69.9 (4"-C), 59.9 (6-C), 59.0 (4-C), 51.4 (6"-C), 51.1 (6'-C) and 31.8 (5-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1193.6 (75%, MNa^+), 1188.7 (55) and 430.3 (100); (Found: MNa^+, 1193.4081. $C_{60}H_{58}O_{14}N_{12}$ requires *MNa*, 1193.4093).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AC

By method A, the glycosyl donor **21C** (79 mg, 1.2 eq., 0.14 mmol) and the acceptor **31A** (78 mg, 1.0 eq., 0.12 mmol), gave a crude product which was purified by flash chromatography on silica gel (8:2 petrol−EtOAc) and preparative HPLC to give **27AC** (40 mg, 30%) as a colourless foam, R_f 0.58 (7:3 petrol−EtOAc); $[\alpha]_D$ +76.7 (c. 0.97 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3453, 2924, 2106, 1154 and 1071; δ_H (500 MHz, $CDCl_3$) 7.48-7.10 (30H, m, Ph), 5.27 (1H, d, *J* 3.5, 1''-H), 5.11 (1H, d, *J* 3.5, 1'-H), 4.90 (1H, d, *J* 10.9, 3'-CCH_AHPh), 4.89 (1H, d, *J* 11.0, 2''-CCH_BHPh), 4.84 (1H, d, *J* 10.9, 3'-CCH$H_{A'}$Ph), 4.82 (1H, d, *J* 11.9, CH_CHPh), 4.79 (1H, d, *J* 10.5, 4''-CCH_DHPh), 4.73 (1H, d, *J* 11.9, CH$H_{C'}$Ph), 4.69 (1H, d, *J* 11.7, CH_EHPh), 4.65 (1H, d, *J* 11.7, CH$H_{E'}$Ph), 4.60 (1H, d, *J* 11.0, 2''-CCH$H_{B'}$Ph), 4.55 (1H, d, *J* 12.1, 6''-CCH_FHPh), 4.42 (1H, d, *J* 10.5, 4''-CCH$H_{D'}$Ph), 4.36 (1H, d, *J* 12.1, 6''-CCH$H_{F'}$Ph), 4.26 (1H, m, 5''-H), 4.09 (1H, ddd, *J* 9.8, 3.3 and 2.7, 5'-H), 3.98 (1H, t, *J* 9.4, 3'-H), 3.89 (1H, t, *J* 9.9, 3''-H), 3.59 (1H, dd, *J* 10.9 and 2.8, 6''-H), 3.56-3.49 (5H, m, 2'-H, 4'-H, 6'-H, 2-H and 6-H), 3.49-3.43 (2H, m, 4''-H and 6''-H), 3.43-3.36 (3H, m, 2''-H, 6'-H and 1-H), 3.31-3.22 (2H, m, 3-H and 4-H), 2.40-2.34 (1H, m, 5-H_A) and 1.57 (1H, q, *J* 12.5, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.4, 137.9, 137.7, 137.4, 137.1 (*o*-Ph), 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (Ph), 100.0 (1''-C), 96.9 (1'-C), 84.3 (3-C), 81.8 (3'-C), 80.7 (1-C), 79.6, 78.2 (2'-C and 4'-C), 77.3 (2''-C), 76.3 (4''-C), 75.6 (C_AH_2Ph), 75.3 (C_DH_2Ph), 75.1 (C_BH_2Ph), 74.6 (2-C), 74.0 (C_EH_2Ph), 73.6 (C_FH_2Ph), 72.9 (C_CH_2Ph), 70.9 (5'-C), 70.4 (5''-C), 68.0 (6''-C), 65.4 (3''-C), 60.2 (6-C), 58.8 (4-C), 51.2 (6'-C) and 32.2 (5-C) (nine aromatic peaks overlapped or missing); *m/z* (ES) 1151.4 (71%, MNa^+), 586.8 (41) and 429.8 (100); (Found: MNa^+, 1151.4667. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

Also obtained was (1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol **27Ad** (15 mg, 11%) as a colourless foam, R_f 0.58 (7:3 petrol−EtOAc); $[\alpha]_D$ +52.4 (c. 1.16 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3429, 2922, 2104, 1151 and 1070; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (30H, m, Ph), 5.04 (1H, d, *J* 3.5, 1'-H), 4.96 (1H, d, *J* 10.9, CH_AHPh), 4.91 (1H, d, *J* 8.0, 1''-H), 4.90 (1H, d, *J* 11.2, CH_BHPh), 4.89 (1H, d, *J* 10.9, CH$H_{A'}$Ph), 4.85 (1H, d, *J* 11.5, CH_CHPh), 4.81 (1H, d, *J* 10.7, CH_DHPh), 4.77 (1H, d, *J* 11.5, CH$H_{C'}$Ph), 4.76 (1H, d, *J* 11.6, CH_EHPh), 4.68 (1H, d, *J* 12.1, 6''-CCH_FHPh), 4.66 (1H, d, *J* 11.6, CH$H_{E'}$Ph), 4.64-4.57 (3H, m, 6''-CCH$H_{F'}$Ph, CH$H_{D'}$Ph and CH$H_{B'}$Ph), 4.10-4.08 (1H, m, 5'-H), 4.01 (1H, t, *J* 9.4, 3'-H), 3.81-3.73 (2H, m, 5''-H and 6''-H), 3.70 (1H, t, *J* 9.5, 3-H), 3.60-3.54 (3H, m, 2'-H, 3''-H and 6'-H), 3.54-3.46 (4H, m, 4'-H, 4''-H, 6''-H, and 2-H), 3.41 (1H, dd, *J* 13.2 and 4.2, 6'-H), 3.34-3.20 (3H, m, 2''-H, 4-H and 6-H), 3.17 (1H, dd, *J* 9.7 and 9.2, 1-H), 2.25 (1H, dt, *J* 13.4 and 4.4, 5-H_A) and 1.43-1.34 (1H, m, 5-H_B); δ_C (125 MHz,

$CDCl_3$) 138.3, 137.9, 137.7, 137.4, 136.7 (*o*-Ph), 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6 (Ph), 102.6 (1''-C), 100.2 (1'-C), 84.2 (1-C), 82.0 (3'-C), 80.3, 80.2 (3-C and 2''-C), 79.2 (2'-C), 78.2 (4'-C), 76.5 (2-C), 76.4 (4''-C), 75.6 (CH$_2$Ph), 74.9 (CH$_2$Ph), 74.5 (CH$_2$Ph), 74.2 (CH$_2$Ph), 73.5 (CH$_2$Ph), 70.9 (6''-CCH$_2$Ph), 70.9 (5'-C), 68.6 (3''-C, 5''-C and 6''-C), 59.1 (6-C), 58.4 (4-C), 50.8 (6'-C) and 32.3 (5-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1151.2 (12%, MNa^+) and 430.1 (100); (Found: MNa^+, 1151.4734. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-acetoxy-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AD

By method A, the glycosyl donor **21D** (59 mg, 1.2 eq., 0.14 mmol) and the acceptor **31A** (78 mg, 1.0 eq., 0.12 mmol), gave a crude product which was purified by flash chromatography on silica gel (gradient elution 8:2 to 7:3 to 6:4 petrol−EtOAc) to give **27AD** (61 mg, 54%) as a colourless foam, R_f 0.40 (6:4 petrol−EtOAc); $[\alpha]_D$ +27.3 (c. 0.06 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3412, 2920, 2106, 1749, 1223 and 1068; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (15H, m, Ph), 5.03 (1H, t, *J* 10.1, 4''-H), 5.00 (1H, d, *J* 3.5, 1'-H), 4.92-4.88 (4H, m, 1''-H, 2''-H, CH_AHPh and CH_BHPh), 4.87 (2H, d, *J* 10.8, CH$H_{A'}$Ph and CH_CHPh), 4.75 (1H, d, *J* 11.5, CH$H_{B'}$Ph), 4.62 (1H, d, *J* 10.8, CH$H_{C'}$Ph), 4.36 (1H, br s, OH), 4.22 (2H, d, *J* 3.4, 6''-H), 4.09-4.04 (1H, m, 5'-H), 4.01 (1H, dd, *J* 9.8 and 9.3, 3'-H), 3.69-3.64 (1H, m, 5''-H), 3.64-3.58 (3H, m, 2'-H, 3''-H and 4'-H), 3.58-3.52 (2H, m, 6'-H and 3-H), 3.48 (1H, dd, *J* 9.1 and 8.4, 2-H), 3.42 (1H, dd, *J* 13.3 and 3.9, 6'-H), 3.38-3.31 (1H, m, 4-H), 3.24-3.18 (1H, m, 6-H), 3.14 (1H, dd, J 9.6 and 9.1, 1-H), 2.28-2.22 (1H, m, 5-H_A), 2.14 (3H, s, 4''-COCOCH_3), 2.08 (3H, s, 6''-COCOCH_3), 1.95 (3H, s, 2''-COCOCH_3) and 1.43-1.33 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 170.8, 169.2, 169.1 (C=O), 138.2, 137.7, 136.9 (*o*-Ph), 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.6 (Ph), 100.9 (1''-C and 1'-C), 85.6 (1-C), 82.0 (3'-C), 81.6 (3-C), 79.7, 78.4 (2'-C and 4'-C), 75.9 (2-C), 75.6 (CH$_2$Ph), 75.3 (CH$_2$Ph), 74.9 (CH$_2$Ph), 72.4 (5''-C), 71.6 (2''-C), 71.1 (5'-C), 68.5 (4''-C), 64.4 (3''-C), 61.9 (6''-C), 58.9 (6-C), 58.3 (4-C), 51.1 (6'-C), 32.4 (5-C), 20.8, 20.7, 20.6 (CH$_3$) (one aromatic peak overlapped or missing); *m/z*

(ES) 1007.3 (54%, MNa^+), 1006.3 (100) and 429.7 (87); (Found: MNa^+, 1007.3596. $C_{45}H_{52}O_{14}N_{12}$ requires *MNa*, 1007.3624).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'C

By method A, the glycosyl donor **21C** (82 mg, 1.2 eq., 0.15 mmol) and the acceptor **31A'** (81 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (gradient elution 9:1 to 8:2 petrol−EtOAc) and preparative HPLC to give **27A'C** (55 mg, 40%) as a colourless foam, R_f 0.60 (7:3 petrol−EtOAc); $[\alpha]_D$ +12.2 (c. 0.92 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3475, 2920, 2107 and 1071; δ_H (500 MHz, $CDCl_3$) 7.45-7.11 (30H, m, Ph), 5.27 (1H, d, *J* 3.6, 1'-H), 5.10 (1H, d, *J* 3.5, 1''-H), 4.94 (1H, d, *J* 10.9, CH_AHPh), 4.83 (1H, d, *J* 11.2, CH_BHPh), 4.81-4.70 (6H, m, CH_2Ph), 4.53 (1H, d, *J* 10.9, CH_CHPh), 4.51 (1H, d, *J* 12.5, CH_DHPh), 4.43 (1H, d, *J* 12.5, $CHH_{D'}Ph$), 4.39 (1H, d, *J* 10.7, CH_EHPh), 4.34-4.29 (1H, m, 5'-H), 4.16 (1H, d, *J* 3.1, OH), 4.14-4.09 (1H, m, 5''-H), 3.96 (1H, t, *J* 9.3, 3'-H), 3.90 (1H, dd, *J* 10.0 and 9.9, 3''-H), 3.56 (1H, dd, *J* 9.8 and 3.7, 2'-H), 3.54-3.49 (4H, m, 2-H, 6-H, and 6''-H), 3.49-3.41 (3H, m, 4-H, 4'-H and 6'-H), 3.41-3.35 (2H, m, 1-H and 2''-H), 3.31 (1H, dd, *J* 9.9 and 9.8, 4''-H), 3.30 (1H, dd, *J* 9.8 and 9.3, 3-H), 3.27 (1H, dd, *J* 13.7 and 4.8, 6'-H), 2.34-2.28 (1H, m, $5\text{-}H_A$) and 1.51 (1H, q, *J* 12.8, $5\text{-}H_B$); δ_C (125 MHz, $CDCl_3$) 138.6, 137.9, 137.8, 137.6, 137.5, 137.4 (*o*-Ph), 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6 (Ph), 97.4, 97.3 (1''-C and 1'-C), 84.8 (3-C), 81.6, 81.5 (3'-C and 1-C), 79.7 (2'-C), 78.2 (4'-C), 77.6 (2''-C), 76.3 (4''-C), 75.6 (CH_2Ph), 75.2 (CH_2Ph), 74.9 (CH_2Ph), 73.4 (2-C), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 73.1 (CH_2Ph), 70.8 (5''-C), 70.4 (5'-C), 67.9 (6''-C), 65.2 (3''-C), 59.9 (6-C), 59.7 (4-C), 51.4 (6'-C), 32.2 (5-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1151.8 (55%, MNa^+), 496.3 (65), 430.3 (100) and 401.0 (70); (Found: MNa^+, 1151.4756. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

Also obtained was (1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-

4,6-diazido-cyclohexan-1,2,3-ol **27A'd** (17 mg, 12%) as a colourless foam, R_f 0.60 (7:3 petrol−EtOAc); $[\alpha]_D$ −16.7 (c. 1.03 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3468, 2919, 2105, 1261 and 1070; δ_H (500 MHz, $CDCl_3$) 7.39-7.18 (30H, m, Ph), 5.18 (1H, d, *J* 3.6, 1'-H), 4.99 (1H, d, *J* 10.9, CH_AHPh), 4.92 (1H, d, *J* 10.8, CH_BHPh), 4.85 (1H, d, *J* 10.9, CH_CHPh), 4.84 (1H, d, *J* 10.9, $CHH_{A'}$Ph), 4.82-4.76 (4H, m, CH_2Ph), 4.77 (1H, d, *J* 5.3, 1"-H), 4.72 (1H, d, *J* 11.6, CH_DHPh), 4.67 (1H, d, *J* 12.2, CH_EHPh), 4.58 (1H, d, *J* 12.2, $CHH_{E'}$Ph), 4.57 (1H, d, *J* 10.8, $CHH_{B'}$Ph), 4.10-4.05 (1H, m, 5'-H), 3.93 (1H, t, *J* 9.4, 3'-H), 3.77-3.72 (2H, m, 6"-H), 3.69 (1H, d, *J* 2.5, OH), 3.60-3.42 (8H, m, 2-H, 3-H, 6-H, 2'-H, 4'-H, 3"-H, 4"-H and 5"-H), 3.36 (1H, dd, *J* 13.1 and 2.4, 6'-H), 3.34-3.28 (3H, m, 1-H, 4-H and 2"-H), 3. 22 (1H, dd, *J* 13.1 and 4.4, 6'-H), 2.28-2.22 (1H, m, 5-H_A) and 1.45-1.35 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.3, 137.8 (*o*-Ph), 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7 (Ph), 103.5 (1"-C), 97.7 (1'-C), 83.7 (3-C), 81.9 (2"-C), 81.5 (3'-C), 80.3 (1-C), 79.7 (2'-C), 78.1 (4'-C), 75.9 (2-C), 75.7 (*C*H_2Ph), 75.3 (4"-C), 74.9 (*C*H_2Ph), 73.6 (*C*H_2Ph), 73.4 (*C*H_2Ph), 70.4 (5'-C), 68.8 (3"-C), 68.6 (6"-C), 60.1 (6-C), 58.2 (4-C), 51.1 (6'-C) and 32.3 (5-C) (sixteen peaks overlapped or missing); *m/z* (ES) 1151.7 (30%, MNa^+), 1101.7 (32) and 430.3 (100); (Found: MNa^+, 1151.4681. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-acetoxy-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'D

By method A, the glycosyl donor **21D** (61 mg, 1.2 eq., 0.15 mmol) and the acceptor **31A'** (81 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (gradient elution 7:3 to 6:4 petrol−EtOAc) and preparative HPLC to give **27A'D** (44 mg, 37%) as a colourless foam, R_f 0.25 (7:3 petrol−EtOAc); $[\alpha]_D$ −23.6 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3486, 2916, 2106, 1751, 1222 and 1069; δ_H (500 MHz, $CDCl_3$) 7.41-7.24 (15H, m, Ph), 5.05 (1H, d, *J* 3.8, 1'-H), 5.04 (1H, dd, *J* 9.9 and 9.6, 4"-H), 4.98 (1H, d, *J* 7.9, 1"-H), 4.97 (1H, d, *J* 10.9, CH_AHPh), 4.91 (1H, dd, *J* 10.1 and 7.9, 2"-H), 4.90 (1H, d, *J* 11.0, CH_BHPh), 4.79 (1H, d, *J* 10.9, $CHH_{A'}$Ph), 4.76 (1H, d, *J* 11.8, CH_CHPh), 4.73 (1H, d, *J* 11.8, $CHH_{C'}$Ph), 4.56 (1H, d, *J* 11.0, $CHH_{B'}$Ph), 4.23-4.20 (2H, m, 6''-H), 4.05-4.01 (1H, m, 5'-H), 4.00 (1H, t, *J* 9.3, 3'-H), 3.83 (1H, d, *J* 2.5, OH), 3.68-3.64 (1H, m, 5''-H), 3.63 (1H, t, *J* 10.1, 3''-H), 3.57 (1H, dd, *J* 9.3 and 3.8, 2'-H), 3.55 (1H, dd, *J* 9.3 and 9.1, 3-H), 3.53-3.38 (3H, m, 2-H, 6-H and 6'-H), 3.41 (1H, dd, *J* 9.7 and 9.3, 4'-H), 3.38-3.34 (1H, m, 4-H), 3.31 (1H, dd, *J* 13.0 and 6.7, 6'-H), 3.24 (1H, t, *J* 9.2, 1-H), 2.20 (1H, dt, *J* 13.5 and 4.5, 5-H_A), 2.12 (6H, s, CH_3), 2.08 (3H, s, CH_3) and 1.37-1.27 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 170.8, 169.2, 169.2 (C=O), 138.4, 137.8, 137.6 (*o*-Ph), 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8 (Ph), 100.8 (1''-C), 98.4 (1'-C), 85.6 (1-C), 81.6 (3-C), 81.0 (3'-C), 79.7 (2'-C), 78.1 (4'-C), 75.7 ($C_A H_2$Ph), 75.3 ($C_B H_2$Ph), 75.0 (2-C), 73.6 ($C_C H_2$Ph), 72.5 (5''-C), 71.6 (2''-C), 71.2 (5'-C), 68.4 (4''-C), 64.3 (3''-C), 61.8 (6''-C), 59.4 (6-C), 58.3 (4-C), 51.8 (6'-C), 32.5 (5-C), 20.7, 20.7 and 20.6 (CH_3) (two aromatic peaks overlapped or missing); *m/z* (ES) 1007.5 (60%, MNa^+), and 430.3 (100); (Found: MNa^+, 1007.3625. $C_{45}H_{52}O_{14}N_{12}$ requires *MNa*, 1007.3624).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(2''-Azido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AE

By method A, the glycosyl donor **21E** (79 mg, 1.2 eq., 0.14 mmol) and the acceptor **31A** (78 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (gradient elution: 8:2 → 7:3 petrol−EtOAc) and preparative HPLC to give **27AE** (31 mg, 24%) as a colourless foam, R_f 0.50 (7:3 petrol−EtOAc); $[\alpha]_D$ +64.2 (c. 0.99 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3459, 2923, 2106, 1154 and 1069; δ_H (500 MHz, $CDCl_3$) 7.40-7.00 (30H, m, Ph), 5.33 (1H, d, *J* 3.7, 1''-H), 5.07 (1H, d, *J* 3.5, 1'-H), 4.92-4.87 (4H, m, CH_2Ph), 4.86 (1H, d, *J* 11.0, CH_AHPh), 4.83 (1H, d, *J* 10.8, CH_BHPh), 4.73 (1H, d, *J* 11.6, CH_CHPh), 4.68 (1H, d, *J* 11.6, $CHH_{C'}$Ph), 4.61 (1H, d, *J* 11.0, $CHH_{A'}$Ph), 4.57 (1H, d, *J* 12.1, CH_DHPh), 4.52 (1H, d, *J* 10.8, $CHH_{B'}$Ph), 4.40 (1H, d, *J* 12.1, $CHH_{D'}$Ph), 4.35 (1H, d, *J* 1.6, OH), 4.33-4.28 (1H, m, 5''-H), 4.11-4.05 (1H, m, 5'-H), 3.99 (1H, t, *J* 9.4, 3'-H), 3.96 (1H, dd, *J* 10.0 and 9.3, 3''-H), 3.75 (1H, dd, *J* 9.7 and 9.3, 4''-H), 3.65 (1H, dd, *J* 10.7 and 3.0, 6''-H), 3.59-3.50 (6H, m, 2'-H, 4'-H, 6'-H, 6''-H, 2-H and 4-H), 3.46-3.36 (3H, m, 2''-H, 6'-H and 1-H), 3.30-3.25 (1H, m, 6-H), 3.22 (1H, m, 3-H), 2.38 (1H, dt, *J* 13.1 and 4.3, 5-H_A)

and 1.67-1.50 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.4, 138.1, 138.0, 137.9, 137.8, 137.0 (*o*-Ph), 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7 (Ph), 100.4 (1''-C), 98.7 (1'-C), 84.9 (3-C), 81.9 (3'-C), 80.8 (1-C), 80.3 (3''-C), 79.7 (2'-C), 78.2, 78.1 (4'-C and 4''-C), 75.6 (*C*H_2Ph), 75.5 (*C*H_2Ph), 75.3 (*C*H_2Ph), 75.2 (*C*H_2Ph), 74.4, 74.3 (*C*H_2Ph and 2-C), 73.5 (*C*H_2Ph), 71.0, 70.9 (5'-C and 5''-C), 68.1 (6''-C), 63.6 (2''-C), 60.9 (4-C), 58.8 (6-C), 51.2 (6'-C) and 32.5 (5-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1151.8 (100%, MNa^+), and 430.3 (89); (Found: MNa^+, 1151.4741. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

Also obtained was (1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(2''-Azido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol **27Af** (32 mg, 24%) as a colourless foam, R_f 0.50 (7:3 petrol−EtOAc); $[\alpha]_D$ +57.6 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3435, 2919, 2107 and 1069; δ_H (500 MHz, $CDCl_3$) 7.42-7.14 (30H, m, Ph), 5.07 (1H, d, *J* 3.5, 1'-H), 4.96 (1H, d, *J* 11.0, CH_AHPh), 4.93-4.89 (3H, m, CH$H_{A'}$Ph, CH_BHPh and CH_CHPh), 4.88 (1H, d, *J* 11.4, CH_DHPh), 4.86 (1H, d, *J* 11.2, CH$H_{B'}$Ph), 4.81 (1H, d, *J* 11.8, CH_EHPh), 5.11 (1H, d, *J* 4.0, 1''-H), 4.72 (1H, d, *J* 11.4, CH$H_{D'}$Ph), 4.68 (1H, d, *J* 12.2, CH_FHPh), 4.64-4.59 (2H, m, CH$H_{C'}$Ph and CH$H_{E'}$Ph), 4.60 (1H, d, *J* 12.2, CH$H_{F'}$Ph), 4.10 (1H, br d, *J* 9.6, 5'-H), 4.03 (1H, t, *J* 9.3, 3'-H), 3.81-3.78 (1H, m, 6''-H_A), 3.75 (1H, dd, *J* 11.3 and 4.5, 6''-H_B), 3.71-3.63 (3H, m, 3''-H, 2-H and 3-H), 3.60 (1H, dd, J 9.3 and 3.5, 2'-H), 3.58-3.52 (2H, m, 4'-H and 6'-H), 3.50-3.36 (5H, m, 2''-H, 4''-H, 5''-H, 6'-H and 4-H), 3.30-3.22 (1H, m, 6-H), 3.20-3.14 (1H, m, 1-H), 2.29-2.22 (1H, m, 5-H_A) and 1.38 (1H, q, *J* 12.8, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.5, 138.3, 138.0, 137.9, 137.8, 136.9 (*o*-Ph), 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 (Ph), 101.5 (1''-C), 100.5 (1'-C), 84.6 (1-C), 83.1 (4''-C), 82.0 (3'-C), 80.7 (3-C), 79.8 (2'-C), 78.3 (4'-C), 77.9 (3''-C), 76.3 (2-C), 75.6 (5''-C), 75.5 (*C*H_2Ph), 75.4 (*C*H_2Ph), 75.3 (*C*H_2Ph), 75.1 (*C*H_2Ph), 74.7 (*C*H_2Ph), 73.5 (*C*H_2Ph), 70.9 (5'-C), 68.8 (6''-C), 66.0 (2''-C), 58.9 (6-C), 58.3 (4-C), 51.2 (6'-C) and 32.3 (5-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1151.9 (100%, MNa^+) and 430.4 (89); (Found: MNa^+, 1151.4698. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(2''-Phthalimido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27AF

By method A, the glycosyl donor **21F** (72 mg, 1.2 eq., 0.11 mmol) and the acceptor **31A** (60 mg, 1.0 eq., 0.09 mmol) gave a crude product which was purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and preparative HPLC to give **27AF** (56 mg, 51%) as a colourless foam, R_f 0.50 (7:3 petrol−EtOAc); $[\alpha]_D$ +63.8 (c. 1.01 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3432, 2926, 2105, 1715, 1388 and 1070; δ_H (500 MHz, $CDCl_3$) 7.42-7.17 (30H, m, Ph), 6.98 (2H, d, *J* 7.1, 2-H_{Phth}), 6.98 (2H, t, *J* 7.1, 3-H_{Phth}), 5.51 (1H, d, *J* 8.5, 1''-H), 4.84 (1H, d, *J* 3.8, 1'-H), 4.79 (1H, d, *J* 11.7, CH_BHPh), 4.72 (1H, d, *J* 10.9, CH_CHPh), 4.69 (1H, d, *J* 12.2, CH_DHPh), 4.68 (1H, d, *J* 11.8, CH$H_{A'}$Ph), 4.65-4.63 (3H, m), 4.59 (1H, d, *J* 12.2, CH$H_{D'}$Ph), 4.56 (1H, d, *J* 12.1, CH_EHPh), 4.54 (1H, d, *J* 10.9, CH$H_{C'}$Ph), 4.47 (1H, t, *J* 10.5, 3''-H), 4.45 (1H, d, *J* 11.7, CH$H_{B'}$Ph), 4.40 (1H, d, *J* 12.1, CH$H_{E'}$Ph), 4.27 (1H, dd, J 10.5 and 8.5, 2''-H), 4.05 (1H, d, *J* 1.1, OH), 3.95 (1H, ddd, *J* 9.6, 4.0 and 2.8, 5'-H), 3.88-3.80 (3H, m, 4''-H and 6''-H), 3.77 (1H, t, *J* 9.4, 3'-H), 3.75-3.70 (1H, m, 5''-H), 3.53 (1H, t, *J* 9.5, 3-H), 3.49 (1H, dd, *J* 13.4 and 2.8, 6'-H), 3.43 (1H, dd, *J* 9.6 and 9.4, 4'-H), 3.39 (1H, dd, *J* 9.4 and 3.8, 2'-H), 3.35 (1H, dd, *J* 13.4 and 4.0, 6'-H), 3.33-3.23 (2H, m, 2-H and 4-H), 3.15 (1H, m, 6-H), 3.04 (1H, dd, *J* 9.6 and 9.4, 1-H), 2.24-2.16 (1H, m, 5-H_A) and 1.38-1.28 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 166.6 (C=O), 138.5, 138.4, 138.1, 138.0, 137.9 (*o*-Ph), 133.4, 131.9 (*o*-Phth), 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3 (Ph), 100.1 (1'-C), 98.6 (1''-C), 84.1 (1-C), 81.7 (3'-C and 3-C), 79.6 (4''-C), 79.2 (3''-C), 78.6 (2'-C), 78.0 (4'-C), 75.5 (2-C), 75.4 (5''-C), 75.2 (CH$_2$Ph), 75.1 (CH$_2$Ph), 75.0 (CH$_2$Ph), 74.8 (CH$_2$Ph), 73.5 (CH$_2$Ph), 70.8 (5'-C), 68.9 (6''-C), 59.2 (6-C), 58.4 (4-C), 55.9 (2''-C), 51.1 (6'-C) and 32.4 (5-C) (ten peaks overlapped or missing); *m/z* (ES) 1256.0 (40%, MNa^+), 454.4 (25) and 348.3 (100); (Found: MNa^+, 1255.4885. $C_{64}H_{68}O_{13}N_{10}$ requires *MNa*, 1255.4865).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(2''-Azido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'E

By method A, the glycosyl donor **21E** (82 mg, 1.2 eq., 0.14 mmol) and the acceptor **31A'** (81 mg, 1.0 eq., 0.12 mmol) gave a crude product which was purified by flash chromatography on silica gel (8:2 petrol−EtOAc) and preparative HPLC to give **27A'E** (25 mg, 19%; >90:10 mixture of diastereomers) as a colourless foam, R_f 0.57 (7:3 petrol−EtOAc); ν_{max}/cm^{-1} (film) 3473, 2920, 2106 and 1070; δ_H (500 MHz, $CDCl_3$) 7.48-7.07 (30H, m, Ph), 5.24 (1H, d, *J* 4.3, 1'-H), 5.22 (1H, d, *J* 4.6, 1''-H), 4.96 (1H, d, *J* 11.0, CH_AHPh), 4.88 (1H, d, *J* 10.6, CH_BHPh), 4.85 (1H, d, *J* 10.9, CH_CHPh), 4.84 (1H, d, *J* 10.6, CH$H_{B'}$Ph), 4.79 (1H, d, *J* 11.6, CH_DHPh), 4.77 (1H, d, *J* 10.9, CH_EHPh), 4.75-4.71 (2H, m, CH$H_{A'}$Ph and CH$H_{D'}$Ph), 4.54 (1H, d, *J* 10.9, CH$H_{C'}$Ph), 4.52 (1H, d, *J* 12.5, 6''-CCH_FHPh), 4.46 (1H, d, *J* 10.8, CH$H_{E'}$Ph), 4.44 (1H, d, *J* 12.5, 6''-CCH$H_{F'}$Ph), 4.28 (1H, ddd, *J* 9.9, 4.9 and 2.3, 5'-H), 4.19 (1H, ddd, *J* 9.9, 3.4 and 3.0, 5''-H), 4.10 (1H, d, *J* 3.3, OH), 3.98 (1H, t, *J* 9.4, 3'-H), 3.96 (1H, dd, *J* 9.9 and 9.4, 3''-H), 3.63-3.53 (5H, m, 6-H, 2'-H, 4''-H and 6''-H), 3.53-3.49 (3H, m, 2-H, 6'-H_A and 2''-H), 3.49-3.40 (2H, m, 4-H and 4'-H), 3.35 (1H, t, *J* 9.4, 1-H), 3.34 (1H, dd, *J* 9.5 and 9.1, 3-H), 3.29 (1H, dd, *J* 13.0 and 5.0, 6'-H_B), 2.36-2.30 (1H, m, 5-H_A) and 1.52 (1H, q, *J* 12.8, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.6, 137.9, 137.8, 137.7 (*o*-Ph), 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8 (Ph), 98.8 (1''-C), 97.5 (1'-C), 84.2 (3-C), 82.5 (1-C), 81.5 (3'-C), 80.4 (3''-C), 79.7 (2'-C), 78.3 (4''-C), 78.2 (4'-C), 75.7 (CH$_2$Ph), 75.6 (CH$_2$Ph), 75.2 (CH$_2$Ph), 75.1 (CH$_2$Ph), 73.5, 73.4, 73.3 (CH$_2$Ph and 2-C), 71.4 (5''-C), 70.6 (5'-C), 67.9 (6''-C), 63.9 (2''-C), 60.3-59.8 (4-C and 6-C), 51.4 (6'-C) and 32.4 (5-C) (13 aromatic peaks overlapped or missing); *m/z* (ES) 1151.7 (80%, MNa^+), 609.4 (54) and 430.3 (100); (Found: MNa^+, 1151.4666. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

Also obtained was (1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(2''-Azido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol **27A'f** (36 mg, 26%; >85:15 mixture of diastereomers) as a colourless foam, R_f 0.57 (7:3 petrol−EtOAc); ν_{max}/cm^{-1} (film) 3480, 2918, 2108 and 1070; δ_H (500 MHz, $CDCl_3$) 7.41-7.15 (30H, m, Ph), 5.12 (1H, d, *J* 3.5, 1'-H), 4.98 (1H, d, *J* 10.9, C*H_A*HPh), 4.90 (1H, d, *J* 10.9, C*H_B*HPh), 4.87 (1H, d, *J* 10.7, C*H_C*HPh), 4.83-4.74 (5H, m, CH_2Ph), 4.78 (1H, d, *J* 5.1, 1"-H), 4.66 (1H, d, *J* 12.2, C*H_D*HPh), 4.63-4.54 (3H, m, CH_2Ph), 4.18-4.12 (1H, m, 5'-H), 4.05-3.98 (1H, m, 3'-H), 4.04 (1H, d, *J* 2.7, OH), 3.80-3.75 (1H, m, 6"-H_A), 3.73 (1H, dd, *J* 11.2 and 4.5, 6"-H_B), 3.68-3.55 (5H, m, 2-H, 3-H, 2'-H, 6'-H_A and 4"-H), 3.50-3.43 (5H, m, 6-H, 4'-H, 2"-H, 3"-H and 5"-H), 3.43-3.33 (2H, m, 4-H and 6'-H_B), 3.30 (1H, dd, *J* 9.2 and 9.0, 1-H), 2.26-2.18 (1H, m, 5-H_A) and 1.34 (1H, q, *J* 12.9, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.6, 138.5, 137.9, 137.8, 137.7 (*o*-Ph), 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5 (Ph), 101.9 (1"-C), 97.8 (1'-C), 84.3 (1-C), 83.2 (3"-C), 82.2 (3-C), 81.3 (3'-C), 79.7 (2'-C), 78.1 (4'-C), 77.9 (4"-C), 75.7 (*C*H_2Ph), 75.6 (*C*H_2Ph), 75.4 (5"-C), 75.2 (2-C), 75.0 (*C*H_2Ph), 73.5 (*C*H_2Ph), 70.9 (5'-C), 68.8 (6"-C), 66.1 (2"-C), 59.7 (6-C), 58.3 (4-C), 51.5 (6'-C) and 32.4 (5-C) (twelve peaks overlapped or missing); *m/z* (ES) 1151.7 (88%, MNa^+) and 430.3 (100); (Found: MNa^+, 1151.4746. $C_{60}H_{64}O_{11}N_{12}$ requires *MNa*, 1151.4715).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-L-glucopyranosyl)-3-*O*-(2''-Phthalimido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexan-1,2,3-ol 27A'F

By method A, the glycosyl donor **21F** (97 mg, 1.2 eq., 0.15 mmol) and the acceptor **31A'** (81 mg, 1.0 eq., 0.14 mmol) gave a crude product which was purified by flash chromatography on silica gel (7:3 petrol−EtOAc) and preparative HPLC to give **27A'F** (62 mg, 42%) as a colourless foam, R_f 0.41 (7:3 petrol/EtOAc); $[\alpha]_D$ −2.0 (c. 0.92 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3477, 2923, 2106, 1715 and 1071; δ_H (500 MHz, $CDCl_3$) 7.38-7.14 (30H, m, Ph), 6.99-6.80 (4H, m, H_{Phth}), 5.49 (1H, d, *J* 8.5, 1"-H), 5.00 (1H, d, *J* 3.5, 1'-H), 4.90 (1H, d, *J* 11.0, CH_AHPh), 4.84 (1H, d, *J* 10.9, CH_BHPh), 4.82 (1H, d, *J* 11.8, CH_CHPh), 4.78 (1H, d, *J* 12.1, CH_DHPh), 4.71 (1H, d, *J* 11.0, CH$H_{A'}$Ph), 4.67 (1H, d, *J* 12.1, 6"-CCH_EHPh), 4.66 (1H, d, *J* 11.8, CH_FHPh), 4.64 (1H, d, *J* 11.8, CH$H_{C'}$Ph), 4.62 (1H, d, *J* 11.8, CH$H_{F'}$Ph), 4.60 (1H, d, *J* 12.1, 6"-CCH$H_{E'}$Ph), 4.51 (1H, d, *J* 10.9, CH$H_{B'}$Ph), 4.42 (1H, d, *J* 12.1, CH$H_{D'}$Ph), 4.37 (1H, dd, *J* 10.6 and 8.7, 3"-H), 4.24 (1H, dd, *J* 10.6 and 8.5, 2"-H), 3.93-3.88 (1H, m, 5'-H), 3.87 (1H, dd, *J* 9.5 and 9.3, 3'-H), 3.83-3.73 (3H, m, 4"-H and 6"-H), 3.71-3.66 (1H, m, 5"-H), 3.52-3.45 (3H, m, 3-H, 2'-H and OH), 3.42 (1H, dd, *J* 9.5 and 9.4, 4'-H), 3.37-3.30 (1H, m, 6-H), 3.30-3.21 (2H, m, 2-H and 4-H), 3.19 (1H, t, *J* 9.4, 1-H), 3.09 (1H, dd, *J* 13.3 and 4.1, 6'-H_A), 2.99 (1H, dd, *J* 13.3 and 2.2, 6'-H_B), 2.18-2.11 (1H, m, 5-H_A) and 1.34-1.25 (1H, m, 5-H_B); δ_C (125 MHz, $CDCl_3$) 138.1, 137.9, 137.5, 137.4, 137.2 (*o*-Ph), 128.6, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 127.0, 129.8 (Ph), 97.6 (1"-C), 97.1 (1'-C), 83.1 (1-C), 81.3 (3-C), 80.7 (3'-C), 79.2 (4"-C), 78.9 (2'-C), 78.2 (3"-C), 77.2 (4'-C), 75.1 (CH$_2$Ph), 74.7 (5"-C), 74.6 (CH$_2$Ph), 74.5 (CH$_2$Ph), 74.3 (CH$_2$Ph), 73.4 (2-C), 72.9, 72.8 (CH$_2$Ph), 70.1 (5'-C), 68.2 (6"-C), 59.1 (6-C), 57.5 (4-C), 55.4 (2"-C), 50.3 (6'-C) and 31.8 (5-C) (thirteen peaks overlapped or missing); *m/z* (ES) 1255.8 (50%, MNa^+) and 348.2 (100); (Found: MNa^+, 1255.4866. $C_{68}H_{68}O_{13}N_{10}$ requires *MNa*, 1255.4865).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol 28A

By method B, the glycosyl donor **21A** (3.16 g, 1.0 eq., 5.57 mmol) and the acceptor **13** (1.40 g, 1.2 eq., 7.06 mmol) gave a crude product which was purified by flash chromatography on silica gel (gradient elution: 9:1, 8:2 → 7:3 petrol−EtOAc) to give a mixture of diastereomeric monoglycosylated products (1.17 g, 32%; *ca.* 70:15:15 **28A** : **28b** : **28'A**) and a mixture of diastereomeric diglycosylated products (1.98 g, 32%; *ca.* 70:20:10 **28AA** : **28Ab** : **28'AA**).

For analytical purposes, a sample (201 mg) of the mixture of diastereomeric monoglycosylated products was purified by preparative HPLC to give **28A** (82.5 mg, 13%) as a yellow oil, R_f 0.34 (8:2 petrol−EtOAc); $[\alpha]_D$ +41.8 (c. 0.90 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3450, 2927, 2102, 1756, 1255 and 1071; δ_H (500 MHz, $CDCl_3$) 7.40-7.25 (15H, m, Ph), 4.98 (1H, d, *J* 10.9, CH_AHPh), 4.91 (1H, d, *J* 10.9, CH_BHPh), 4.84 (1H, d, *J* 3.3, 1'-H), 4.83 (1H, d, *J* 10.9, CH$H_{A'}$Ph), 4.78 (1H, d, *J* 11.8, CH_CHPh), 4.62 (1H, d, *J* 11.8, CH$H_{C'}$Ph), 4.58 (1H, d, *J* 10.9, CH$H_{B'}$Ph), 3.92 (1H, t, *J* 9.3, 3'-H), 3.87-3.81 (1H, m, 5'-H), 3.75-3.64 (3H, m, 1-H, 4-H, 2-H or 5-H), 3.59-3.54 (1H, m, 2-H or 5-H), 3.33 (1H, dd, *J* 9.3 and 3.3, 2'-H), 3.47 (1H, dd, *J* 13.1 and 2.4, 6'-H_A), 3.50-3.42 (1H, m, 4'-H), 3.34 (1H, dd, *J* 13.1 and 5.7, 6'-H_B), 2.07-2.00 (1H, m, 3-H or 6-H), 2.00-1.95 (1H, m, 3-H or 6-H), 1.94-1.88 (1H, m, 3-H or 6-H) and

1.88-1.80 (1H, m, 3-H or 6-H); δ_C (125 MHz, $CDCl_3$) 138.5, 138.1, 137.7 (*o*-Ph), 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8 (Ph), 97.4 (1'-C), 81.4 (3'-C), 80.2 (2'-C), 77.3 (4'-C), 75.7 (C_AH_2Ph), 75.4 (C_BH_2Ph), 74.7 (1-C or 4-C), 73.9 (C_CH_2Ph), 71.0 (5'-C), 68.6 (1-C or 4-C), 61.9, 59.0 (2-C and 5-C), 51.4 (6'-C), 32.1, 30.8 (3-C and 6-H) (one aromatic peak overlapped or missing); *m/z* (ES) 677.9 (50, MNa^+), 672.9 (100, MNH_4^+) and 429.9 (58); (Found: MNa^+, 678.2781 $C_{33}H_{37}O_6N_9$ requires *MNa*, 678.2765).

Also obtained was *(1S,2S,4S,5S)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28'A** (20.3 mg, 3%) as a yellow oil, R_f 0.34 (8:2 petrol−EtOAc); $[\alpha]_D$ +54.0 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3453, 2926, 2102, 1255 and 1071; δ_H (500 MHz, $CDCl_3$) 7.40-7.25 (15H, m, Ph), 4.98 (1H, d, *J* 10.9, CH_AHPh), 4.91 (1H, d, *J* 11.0, CH_BHPh), 4.83 (1H, d, *J* 10.9, $CHH_{A'}Ph$), 4.81 (1H, d, *J* 3.9, 1'-H), 4.79 (1H, d, *J* 11.9, CH_CHPh), 4.63 (1H, d, *J* 11.9, $CHH_{C'}Ph$), 4.58 (1H, d, *J* 11.0, $CHH_{B'}Ph$), 3.92 (1H, t, *J* 9.3, 3'-H), 3.88-3.86 (2H, m, 2-H and 5-H), 3.85-3.81 (1H, m, 5'-H), 3.80-3.73 (2H, m, 1-H and 4-H), 3.54 (1H, dd, *J* 9.3 and 3.6, 2'-H), 3.47 (1H, dd, *J* 13.1 and 2.3, 6'-H_A), 3.46-3.42 (1H, m, 4'-H), 3.32 (1H, dd, *J* 13.1 and 5.8, 6'-H_B), 2.14-2.08 (1H, br. s, O*H*), 2.08-1.99 (2H, m, 3-H_A and 6-H_A), 1.99-1.91 (1H, m, 3-H_B or 6-H_B) and 1.77-1.69 (1H, m, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.5, 138.1, 137.7 (*o*-Ph), 128.9, 128.8, 128.4, 128.1, 127.9, 127.8 (Ph), 95.9 (1'-C), 81.4 (3'-C), 79.7 (2'-C), 78.2 (4'-C), 75.6 (C_AH_2Ph), 75.4 (C_BH_2Ph), 73.8 (C_CH_2Ph), 73.4 (1-C or 4-C), 70.9 (5'-C), 68.9 (1-C or 4-C), 61.7, 59.8 (2-C and 5-C), 51.3 (6'-C), 32.4 and 28.8 (3-C and 6-H) (two aromatic peaks overlapped or missing); *m/z* (ES) 678.3 (35%, MNa^+), 673.3 (67, MNH_4^+) and 430.2 (100); (Found: MNa^+, 678.2780. $C_{33}H_{37}O_6N_9$ requires *MNa*, 678.2765).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-β-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28b** (22.3 mg, 4%; 90:10 mixture of diastereoisomers) as a yellow oil, R_f 0.34 (8:2 petrol−EtOAc); $[\alpha]_D$ +1.4 (c. 1.10 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3435,2917, 2101, 1756, 1254, 1070, 736 and 698; δ_H (500 MHz, $CDCl_3$) 7.40-7.25 (15H, m, Ph), 4.94 (1H, d, *J* 10.9, CH_AHPh), 4.87 (1H, d, *J* 11.0, CH_BHPh), 4.85 (1H, d, *J* 11.0, CH_CHPh), 4.82 (1H, d, *J* 10.9, $CHH_{A'}Ph$), 4.78 (1H, d, *J* 11.0, $CHH_{C'}Ph$), 4.58 (1H, d, *J* 11.0, $CHH_{B'}Ph$), 4.51 (1H, d, *J* 7.8, 1'-H), 4.03-3.98 (1H, m, 2-H or 5-H), 3.95-3.91

(1H, m, 1-H or 4-H), 3.75-3.63 (3H, m, 1-H or 4-H, 3'-H and 2-H or 5-H), 3.51-3.41 (5H, m, 2-H or 5-H, 2'-H, 4'-H, 5'-H, 6'-H_A), 3.28 (1H, dd, *J* 13.1 and 5.7, 6'-H_B), 2.10-2.01 (2H, m, 3-H_A and 6-H_A), 1.93 (1H, ddd, *J* 13.9, 10.5 and 3.3, 3-H_B or 6-H_B) and 1.75 (1H, ddd, *J* 14.0, 11.3 and 2.6, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.5, 138.1, 137.7 (*o*-Ph), 128.9, 128.8, 128.5, 128.2, 128.1, 128.0 (Ph), 102.3 (1'-C), 84.4 (3'-C), 82.1 (2'-C), 78.2 (4'-C), 75.8 (C_AH_2Ph), 75.3 (C_CH_2Ph), 75.2 (C_BH_2Ph), 75.1 (1-C or 4-C), 74.8 (5'-C), 68.6 (1-C or 4-C), 61.9, 59.9 (2-C and 5-C), 51.2 (6'-C) and 32.1, 29.5 (3-C and 6-H) (two aromatic peaks overlapped or missing); *m/z* (ES) 678.3 (35%, MNa^+), 673.3 (67, MNH_4^+) and 430.2 (100); (Found: MNa^+, 678.2781. $C_{33}H_{37}O_6N_9$ requires *MNa*, 678.2765).

For analytical purposes, a sample (424 mg) of the mixture of diastereomeric diglycosylated products was purified by preparative HPLC to give *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28AA** (200.2 mg, 15%) as a yellow oil, R_f 0.53 (8:2 petrol−EtOAc); $[\alpha]_D$ +46.4 (c. 1.12 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2922, 2102, 1285 and 1072; δ_H (500 MHz, $CDCl_3$) 7.40-7.10 (30H, m, Ph), 5.02 (2H, d, *J* 10.9, CH_AHPh), 4.95-4.90 (4H, m, 1'-H, 1''-H and CH_BHPh), 4.85 (2H, d, *J* 10.9, $CHH_{A'}$Ph), 4.77 (2H, d, *J* 11.8, CH_CHPh), 4.68 (2H, d, *J* 11.8, $CHH_{C'}$Ph), 4.58 (2H, d, *J* 10.9, $CHH_{B'}$Ph), 3.97 (2H, t, *J* 9.3, 3'-H and 3''-H), 3.88-3.83 (2H, m, 5'-H and 5''-H), 3.70-3.63 (4H, m, 1-H, 2-H, 4-H and 5-H), 3.54 (2H, dd, *J* 9.3 and 3.6, 2'-H and 2''-H), 3.48-3.41 (4H, m, 4'-H, 4''-H, 6'-H_A and 6''-H_A), 3.34 (2H, dd, *J* 13.1 and 5.8, 6'-H_B and 6''-H_B), 2.12-2.02 (2H, m, 3-H_A and 6-H_A) and 1.98-1.89 (2H, m, 3-H_B and 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.6, 138.1, 137.8 (*o*-Ph), 129.1, 128.6, 128.4, 128.5, 128.3, 128.1, 127.9, 127.7 (Ph), 97.8 (1'-C and 1''-C), 81.4 (3'-C and 3''-C), 80.0 (2'-C and 2''-C), 78.4 (4'-C and 4''-C), 75.7 (C_AH_2Ph), 75.4 (C_BH_2Ph), 74.9 (1-C and 4-C), 73.6 (C_CH_2Ph), 70.9 (5'-C and 5''-C), 59.5 (2-C and 5-C), 51.5 (6'-H and 6''-C) and 31.4 (3-C and 6-C) (one aromatic peak overlapped or missing); *m/z* (ES) 1135.4 (80, MNa^+) and 430.2 (100); (Found: MNa^+, 1135.4800. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1S,2S,4S,5S)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzyl-α-D-glucopyranosyl)-2,5-*

diazido-cyclohexane-1,4-diol **28'AA** (31.7 mg, 2%) as a yellow oil, R_f 0.53 (8:2 petrol−EtOAc); $[\alpha]_D$ +61.6 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2925, 2102, 1086 and 1072; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (30H, m, Ph), 5.02 (2H, d, *J* 10.8, CH_AHPh), 4.92 (2H, d, *J* 11.1, CH_BHPh), 4.84 (2H, d, *J* 10.8, $CHH_{A'}Ph$), 4.81 (2H, d, *J* 12.0, CH_CHPh), 4.79 (2H, d, *J* 4.9, 1'-H and 1''-H), 4.63 (2H, d, *J* 12.0, $CHH_{C'}Ph$), 4.60 (2H, d, *J* 11.1, $CHH_{B'}Ph$), 4.00 (2H, t, *J* 9.3, 3'-H and 3''-H), 3.97-3.90 (2H, m, 5'-H and 5''-H), 3.87-3.81 (2H, m, 2-H and 5-H), 3.75-3.68 (2H, m, 1-H and 4-H), 3.58-3.53 (2H, m, 2'-H and 2''-H), 3.51-3.43 (4H, m, 4'-H, 4''-H, 6'-H_A and 6''-H_A), 3.43 (2H, dd, *J* 13.1 and 5.5, 6'-H_B and 6''-H_B), 2.00-1.92 (2H, m, 3-H_A and 6-H_A) and 1.89-1.81 (2H, m, 3-H_B and 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.4, 137.9 (*o*-Ph), 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7 (Ph), 95.5 (1'-C and 1''-C), 81.6 (3'-C and 3''-C), 79.7 (2'-C and 2''-C), 78.3 (4'-C and 4''-C), 75.8 (C_AH_2Ph), 75.2 (C_BH_2Ph), 73.9 (C_CH_2Ph), 73.4 (1-C and 4-C), 70.8 (5'-C and 5''-C), 59.7 (2-C and 5-C), 51.3 (6'-H and 6''-C) and 29.6 (3-C and 6-C) (two aromatic peaks overlapped or missing); *m/z* (ES) 1135.4 (69, M^++Na), 1085.5 (60) and 430.2 (100); (Found: MNa^+, 1135.4792. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-β-D-glucopyranosyl) -4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28Ab** (69.6 mg, 16%; 80:20 mixture of diastereoisomers) as a yellow oil, R_f 0.53 (8:2 petrol−EtOAc); $[\alpha]_D$ +18.0 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2917, 2102, 1285 and 1072; δ_H (500 MHz, $CDCl_3$) 7.45-7.20 (30H, m, Ph), 5.03 (1H, d, *J* 3.4, 1''-H), 4.99 (1H, d, *J* 10.9, CH_AHPh), 4.94 (1H, d, *J* 11.0, CH_BHPh), 4.90 (1H, d, *J* 10.9, CH_CHPh), 4.88 (1H, d, *J* 10.8, CH_EHPh), 4.87 (1H, d, *J* 11.0, CH_DHPh), 4.82 (1H, d, *J* 11.0, $CHH_{B'}Ph$), 4.81 (1H, d, *J* 10.8, $CHH_{E'}Ph$), 4.79 (1H, d, *J* 10.9, $CHH_{A'}Ph$), 4.75 (2H, d, *J* 11.6, CH_FHPh and $CHH_{F'}Ph$), 4.58 (1H, d, *J* 11.0, $CHH_{D'}Ph$), 4.57 (1H, d, *J* 10.9, $CHH_{C'}Ph$), 4.51 (1H, d, *J* 7.7, 1'-H), 4.00-3.94 (2H, m, 3''-H and 2-H or 5-H), 3.91-3.84 (2H, m, 4''-H and 1-H or 4-H), 3.69-3.62 (3H, m, 1-H or 4-H, 3'-H and 2-H or 5-H), 3.54 (1H, dd, *J* 9.7 and 3.4, 2''-H), 3.51-3.40 (6H, m, 2'-H, 4'-H, 5'-H, 6'-H_A, 5''-H and 6''-H_A), 3.34 (1H, dd, *J* 13.1 and 5.6, 6''-H_B), 3.31-3.26 (1H, m, 6'-H_B), 2.13-1.93 (3H, m, 3-H and 6-H) and 1.87-1.78 (1H, m, 3-H or 6-H); δ_C (125 MHz, $CDCl_3$) 138.4, 137.9, 137.7, 137.4, 137.1 (*o*-Ph), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (Ph), 102.6 (1'-C), 98.2 (1"-C), 84.4 (3'-C), 82.1 (2'-C), 81.4 (3"-C), 80.1 (2"-C), 78.3 (4'-C), 76.5 (1-C or 4-C), 75.6 (C_BH$_2$Ph and C_EH$_2$Ph), 75.5 (4"-C and C_AH$_2$Ph), 75.1 (C_CH$_2$Ph and C_DH$_2$Ph), 74.6 (5'-C and 5"-C), 73.2 (C_FH$_2$Ph), 70.8 (1-C or 4-C), 60.2, 60.1 (2-C and 5-C), 51.4 (6'-C and 6"-C), 31.4 and 30.2 (3-C and 6-C) (12 aromatic peaks overlapped or missing); *m/z* (ES) 1135.6 (100, M^++Na), 575.2 (67) and 430.3 (100); (Found: MNa^+, 1135.4806. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)- 4-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzyl-α-L-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol 28AA'

By method A, the glycosyl donor **21A'** (242 mg, 1.2 eq., 0.43 mmol) and the acceptor **28A** (233 mg, 1.0 eq., 0.36 mmol; *ca.* 70:15:15 **28A** : **28b** : **28'A**) gave a crude mixture which was purified by flash chromatography on silica gel (8:2 petrol−EtOAc) and preparative HPLC to give **28AA'** (83.4 mg, 21%) as a yellow oil, R_f 0.33 (8:2 petrol−EtOAc); $[\alpha]_D$ –11.2 (c. 1.00 in CHCl$_3$); ν_{max}/cm^{-1} (film) 3031, 2922, 2102, 1285 and 1072; δ_H (500 MHz, CDCl$_3$) 7.45-7.20 (30H, m, Ph), 5.02 (1H, d, *J* 10.9, CH_AHPh), 5.01 (1H, d, *J* 10.9, CH_BHPh), 4.95 (1H, d, *J* 3.6, 1'-H or 1"-H), 4.92 (1H, d, *J* 11.8, CH_CHPh), 4.91 (1H, d, *J* 10.7, CH_DHPh), 4.85 (1H, d, *J* 10.9, CH$H_{A'}$Ph), 4.84 (1H, d, *J* 10.9, CH$H_{B'}$Ph), 4.81 (1H, d, *J* 3.7, 1'-H or 1"-H), 4.79 (1H, d, *J* 11.9, CH_EHPh), 4.77 (1H, d, *J* 11.9, CH_FHPh), 4.72 (1H, d, *J* 11.9, CH$H_{F'}$Ph), 4.63 (1H, d, *J* 11.9, CH$H_{E'}$Ph), 4.59 (1H d, *J* 11.8, CH$H_{C'}$Ph), 4.58 (1H d, *J* 10.7, CH$H_{D'}$Ph), 3.98 (1H, t, *J* 9.3, 3'-H or 3"-H), 3.97 (1H, t, *J* 9.3, 3'-H or 3"-H), 3.92-3.85 (2H, m, 5'-H and 5"-H), 3.84-3.78 (1H, m, 2-H or 5-H), 3.77-3.65 (3H, m, 1-H, 4-H and 2-H or 5-H), 3.55 (2H, dd, *J* 9.3 and 3.6, 2'-H and 2"-H), 3.51-3.42 (4H, m, 4'-H, 4"-H, 6'-H_A and 6"-H_A), 3.38-3.30 (2H, m, 6'-H_B and 6"-H_B), 2.07-1.99 (3H, m, 3-H and 6-H) and 1.84-1.77 (1H, m, 3-H or 6-H); δ_C (125 MHz, CDCl$_3$) 138.6, 138.5, 138.1, 138.0, 137.9, 137.8 (*o*-Ph), 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7 (Ph), 98.1, 95.8 (1'-C and 1"-C), 81.6, 81.4 (3'-C and 3"-C), 80.1, 79.7 (2'-C and 2"-C), 78.3, 78.2 (4'-C and 4"-C), 75.8 (1-C and 4-C), 75.7, 75.6 (C_CH$_2$Ph and C_DH$_2$Ph), 75.4, 75.2 (C_AH$_2$Ph and C_BH$_2$Ph), 73.8, 73.5 (C_EH$_2$Ph and C_FH$_2$Ph), 73.4 (1-C and 4-C), 70.9 (5'-C and 5"-C), 59.9, 59.7 (2-C and 5-C), 51.5, 51.3

(6'-H and 6"-C), 31.7 and 29.5 (3-C and 6-C) (nine aromatic peaks overlapped or missing); *m/z* (ES) 1135.5 (45, MNa^+) and 430.2 (100); (Found: MNa^+, 1135.4784. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1S,2S,4S,5S)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzyl-α-L-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28'AA'** (22.0 mg, 5%) as a yellow oil, R_f 0.33 (8:2 petrol−EtOAc); $[\alpha]_D$ +4.4 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3031, 2917, 2102, 1285 and 1071; δ_H (500 MHz, $CDCl_3$) 7.45-7.20 (30H, m, Ph), 5.00 (1H, d, *J* 10.9, CH_AHPh), 4.99 (1H, d, *J* 4.6, 1"-H), 4.93 (1H, d, *J* 10.9, CH_BHPh), 4.91 (1H, d, *J* 11.0, CH_CHPh), 4.89 (1H, d, *J* 11.1, CH_DHPh), 4.87 (1H, d, *J* 11.0, CH_FHPh), 4.80 (2H, d, *J* 10.9, CH$H_{A'}$Ph and CH$H_{B'}$Ph), 4.77 (1H, d, *J* 11.1, CH$H_{D'}$Ph), 4.75 (1H, d, *J* 11.8, CH_FHPh), 4.72 (1H, d, *J* 11.8, CH$H_{F'}$Ph), 4.59 (1H, d, *J* 11.0, CH$H_{E'}$Ph), 4.56 (1H, d, *J* 11.0, CH$H_{C'}$Ph), 4.55 (1H, d, *J* 5.2, 1'-H), 3.95 (1H, t, *J* 9.3, 3"-H), 3.84-3.78 (2H, m, 5"-H and 1-H or 4-H), 3.78-3.73 (1H, m, 2-H or 5-H), 3.73-3.62 (4H, m, 1-H or 4-H, 3'-H, and 2-H or 5-H), 3.56-3.39 (7H, m, 2"-H, 2'-H, 4'-H, 5'-H, 6'-H_A, 4"-H and 6"-H_A), 3.34-3.27 (2H, m, 6"-H_B and 6'-H_B), 2.26-2.19 (1H, m, 3-H or 6-H) and 2.04-1.92 (3H, m, 3-H and 6-H); δ_C (125 MHz, $CDCl_3$) 138.5, 138.2, 138.1, 137.9, 137.7, 137.6 (*o*-Ph), 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7 (Ph), 103.6 (1'-C), 97.8 (1"-C), 84.4 (3'-C), 82.2 (2'-C), 81.4 (3"-C), 79.9 (2"-C), 78.2, 77.9 (4'-C and 4"-C), 75.9, 75.6, 75.4, 75.3, 75.2, 74.4 (5'-C), 73.4, 70.8 (5"-C), 59.8, 59.6 (2-C and 5-C), 51.4, 51.1 (6'-C and 6"-C), 31.6 and 31.4 (3-C and 6-C) (11 aromatic peaks overlapped or missing); *m/z* (ES) 1135.9 (55, MNa^+) and 430.3 (100); (Found: MNa^+, 1135.4769. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-β-D-glucopyranosyl) -4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzyl-α-L-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28A'b** (40.3 mg, 10%) as a yellow oil, R_f 0.33 (8:2 petrol−EtOAc); $[\alpha]_D$ –24.0 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3031, 2920, 2102, 1285 and 1071; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (30H, m, Ph), 4.96 (1H, d, *J* 10.8, CH_AHPh), 4.95 (1H, d, *J* 10.6, CH_BHPh), 4.92 (1H, d, *J* 10.6, CH_CHPh), 4.88 (2H, d, *J* 10.8, CH_DHPh and CH$H_{A'}$Ph), 4.84 (1H, d, *J* 11.7, CH_EHPh), 4.83 (1H, d, *J* 4.1, 1"-H), 4.82 (1H, d, *J* 10.6, CH$H_{C'}$Ph), 4.79 (1H, d, *J* 11.7, CH$H_{E'}$Ph), 4.78 (1H, d, *J* 10.2, CH_FHPh), 4.68 (1H, d, *J* 10.2, CH$H_{F'}$Ph), 4.61 (1H, d, J 10.6, CH$H_{B'}$Ph), 4.69 (1H, d, J 10.8, CH$H_{D'}$Ph), 4.52 (1H, d, J 7.7, 1'-H), 4.03-3.94 (2H, m, 3"-H and 2-H or 5-H), 3.94-3.86 (1H, m, 1-H or 4-H), 3.75-3.62 (3H, m, 1-H or 4-H, 3'-H and 2-H or 5-H), 3.56 (1H, dd, *J* 9.7 and 3.6, 2"-H), 3.53-3.42 (7H, m, 2'-H, 4'-H, 4"-H, 5'-H, 5"-H, 6'-H_A and 6"-H_A), 3.42-3.25 (2H, m, 6'-H_B and 6"-H_B), 2.09-1.93 (3H, m, 3-H and 6-H) and 1.93-1.81 (1H, m, 3-H or 6-H); δ_C (125 MHz, $CDCl_3$) 138.9, 138.6, 138.4, 138.3, 138.0 (*o*-Ph), 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (Ph), 103.0 (1'-C), 94.9 (1"-C), 84.8 (3'-C), 82.6 (2'-C), 82.1 (3"-C), 80.1 (2"-C), 78.5, 78.4 (4'-C and 4"-C), 76.2, 76.1, 75.9, 75.6, 75.5, 74.9, 73.4 (C_AH$_2$Ph, C_BH$_2$Ph, C_DH$_2$Ph, C_EH$_2$Ph, C_FH$_2$Ph, 1-C and 4-C), 74.2 (5'-C and 5"-C), 71.0 (C_CH$_2$Ph), 60.1 (2-C and 5-C), 51.7, 51.6 (6'-H and 6"-C), 30.9, 29.4 (3-C and 6-C) (10 aromatic peaks overlapped or missing); *m/z* (ES) 1135.5 (40, MNa^+), 1085.5 (35) and 430.2 (100); (Found: MNa^+, 1135.4758. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzoyl-β-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol 28AB

By method A, glycosyl donor **21B** (260 mg, 1.2 eq., 0.43 mmol) and the acceptor **28A** (233 mg, 0.36 mmol; *ca.* 70:15:15 **28A** : **28b** : **28'A**) gave a crude mixture which was purified by flash chromatography on silica gel (gradient elution: 7:3 → 6:4 petrol−EtOAc) and preparative HPLC to give **28AB** (185 mg, 45%) as a yellow oil, R_f 0.35 (7:3 petrol−EtOAc); $[\alpha]_D$ –6.67 (c. 1.14 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2929, 2101, 1732, 1259 and 1070; δ_H (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 7.3, Bz), 7.92 (2H, d, *J* 7.5, OBz), 7.84 (2H, d, *J* 7.4, Bz), 7.56-7.47 (1H, m, Bz), 7.47-7.14 (23H, m, Ar), 5.92 (1H, t, *J* 9.7, 3"-H), 5.60-5.43 (2H, m, 2"-H and 4"-H), 4.96 (1H, d, *J* 10.8, CH_AHPh), 4.95 (1H, d, *J* 6.8, 1"-H), 4.92 (1H, d, *J* 11.0, CH_BHPh), 4.89 (1H, d, *J* 4.6, 1'-H), 4.78 (1H, d, *J* 10.8, CH$H_{A'}$Ph), 4.67-4.55 (3H, m, CH$H_{B'}$Ph, CH_CHPh and CH$H_{C'}$Ph), 4.06-3.96 (1H, m, 5"-H), 3.96-3.90 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.88 (1H, t, *J* 9.5, 3'-H), 3.84-3.77 (1H, m, 5'-H), 3.62-3.51 (2H, m, 6"-H_A and 1-H or 4-H), 3.51-3.42 (2H, m, 2'-H and 6'-H_A), 3.44-3.30 (4H, m, 4'-H, 2-H or 5-H, 6'-

H_B and 6"-H_B), 2.14-1.84 (3H, m, 3-H and 6-H) and 1.76-1.62 (1H, m, 3-H or 6-H); δ_C (125 MHz, $CDCl_3$) 166.2, 165.7, 165.4 (*C*=O), 139.1, 138.6, 138.4 (*o*-Ph), 134.2, 134.1, 133.8(*o*-Bz), 130.3, 130.2, 130.1, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 100.7 (1"-C), 98.3 (1'-C), 81.7 (3'-C), 80.5 (2'-C), 78.5 (4'-C), 76.9 (1-C or 4-C), 76.2, 76.1 (C_AH_2Ph and C_BH_2Ph), 75.8 (1-C or 4-C), 74.8 (5"-C), 73.5 (C_CH_2Ph), 72.7 (3"-C), 72.2 (2"-C), 71.2 (5'-C), 70.5 (4"-C), 60.1, 60.0 (2-C and 5-C), 51.8, 51.7 (6'-H and 6"-C), 31.6 and 30.7 (3-C and 6-C) (three aromatic peaks overlapped or missing); *m/z* (ES) 1177.4 (60, MNa^+), 760.3 (27) and 430.2 (100); (Found: MNa^+, 1177.4193. $C_{60}H_{58}O_{13}N_{12}$ requires *MNa*, 1177.4144).

Also obtained was *(1S,2S,4S,5S)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzoyl-β-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28'AB** (11.3 mg, 3%) as a yellow oil, R_f 0.35 (7:3 petrol−EtOAc); $[\alpha]_D$ +24.8 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2926, 2103, 1734, 1260 and 1070; δ_H (500 MHz, $CDCl_3$) 7.98 (2H, dd, *J* 7.2 and 1.4, Bz), 7.91 (2H, dd, *J* 7.2 and 1.0, Bz), 7.81 (2H, dd, *J* 7.3 and 1.3, Bz), 7.57-7.17 (24H, m, Ph), 5.88 (1H, t, *J* 9.7, 3"-H), 5.58-5.44 (2H, m, 2"-H and 4"-H), 5.05 (1H, d, *J* 8.0, 1"-H), 4.97 (1H, d, *J* 10.9, CH_AHPh), 4.91 (1H, d, *J* 11.1, CH_BHPh), 4.83 (1H, d, *J* 10.9, $CHH_{A'}$Ph), 4.71 (1H, d, *J* 11.8, CH_CHPh), 4.69 (1H, d, *J* 4.5, 1'-H), 4.58 (1H, d, *J* 11.1, $CHH_{B'}$Ph), 4.52 (1H, d, *J* 11.8, $CHH_{C'}$Ph), 4.04-3.93 (1H, m, 5"-H), 3.92 (1H, t, *J* 9.4, 3'-H), 3.89-3.69 (3H, m, 1-H or 4-H, 5'-H and 2-H or 5-H), 3.69-3.57 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.52-3.37 (5H, m, 2'-H, 4'-H, 6'-H_A, 6"-H_A and 6"-H_B), 3.31 (1H, dd, *J* 13.1 and 5.4, 6'-H_B), 2.25-2.08 (2H, m, 3-H or 6-H), 1.94-1.82 (1H, m, 3-H_A or 6-H_A) and 1.75-1.53 (1H, m, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 165.7, 165.3, 165.1 (*C*=O), 138.5, 137.9, 137.8 (*o*-Ph), 133.7, 133.3 (*o*-Bz), 129.9, 129.8, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7 (Ph), 102.1 (1"-C), 95.8 (1'-C), 81.4 (3'-C), 79.4 (2'-C), 78.1 (4'-C), 77.0 (1-C or 4-C), 75.7 (C_AH_2Ph), 75.2 (C_BH_2Ph), 73.7, 73.6 (C_CH_2Ph and 1-C or 4-C), 73.1 (3"-C), 72.6 (5"-C), 71.8 (2"-C or 4"-C), 70.8 (5'-C), 69.9 (2"-C or 4"-C), 59.9 (2-C and 5-C), 51.2 (6'-C and 6"-C), 31.8 and 29.4 (3-C and 6-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1177.5 (95, MNa^+), 760.5 (20) and 430.2 (100); (Found: MNa^+, 1177.4186. $C_{60}H_{58}O_{13}N_{12}$ requires *MNa*, 1177.4144).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-β-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzoyl-β-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28Bb** (20.8 mg, 5%; 90:10 mixture of diastereomers) as a yellow oil, R_f 0.35 (7:3 petrol−EtOAc); $[\alpha]_D$ +9.1 (c. 1.10 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2924, 2103, 1735, 1260 and 1069; δ_H (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 7.1, Bz), 7.91 (2H, d, *J* 8.2, Bz), 7.81 (2H, d, *J* 7.4, Bz), 7.58-7.22 (24H, m, Ph), 5.87 (1H, t, *J* 9.7, 3"-H), 5.59-5.41 (2H, m, 2"-H and 4"-H), 4.98 (1H, d, *J* 7.9, 1"-H), 4.98-4.85 (3H, m, CH_AHPh, CH_BHPh and CH_CHPh), 4.73 (1H, d, *J* 10.8, $CHH_{A'}$Ph), 4.55 (2H, d, *J* 10.9, $CHH_{B'}$Ph, and $CHH_{C'}$Ph), 4.43 (1H, d, *J* 7.4, 1'-H), 4.07-3.94 (1H, m, 5"-H), 3.94-3.85 (2H, m, 3'-H and 2-H or 5-H), 3.85-3.69 (2H, m, 5'-H and 1-H or 4-H), 3.64-3.52 (2H, m, 6"-H_A and 1-H or 4-H), 3.52-3.19 (6H, m, 2'-H, 4'-H, 2-H or 5-H, 6'-H and 6"-H_B), 2.17-2.07 (1H, m, 3-H_A or 6-H_A), 2.07-1.96 (1H, m, 3-H_A or 6-H_A) and 1.94-1.78 (2H, m, 3-H_B and 6-H_B); *m/z* (ES) 1177.4 (100, MNa^+), 760.3 (20), 487.2 (48) and 430.2 (98); (Found: MNa^+, 1177.4180. $C_{60}H_{58}O_{13}N_{12}$ requires *MNa*, 1177.4144).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzoyl-β-L-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol 28AB'

By method A, the glycosyl donor **21B'** (260 mg, 1.2 eq., 0.43 mmol) and the acceptor **28A** (233 mg, 1.0 eq., 0.36 mmol; *ca.* 70:15:15 **28A** : **28b** : **28'A**) gave a crude product which was purified by flash chromatography on silica gel (8:2 petrol−EtOAc) and preparative HPLC to give **28AB'** (171.5 mg, 42%) as a yellow oil, R_f 0.52 (7:3 petrol−EtOAc); $[\alpha]_D$ +28.6 (c. 1.09 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2927, 2102, 1732, 1259 and 1070; δ_H (500 MHz, $CDCl_3$) 7.97 (2H, dd, *J* 7.3 and 1.0, Bz), 7.92 (2H, dd, *J* 7.3 and 1.0, Bz), 7.82 (2H, d, *J* 7.3, Bz), 7.51 (1H, t, *J* 7.3, Bz), 7.45 (1H, d, *J* 7.3, Bz), 7.42-7.13 (22H, m, Ph), 5.89 (1H, t, *J* 9.7, 3"-H), 5.56-5.48 (2H, m, 2"-H and 4"-H), 5.01 (1H, d, *J* 7.9, 1"-H), 5.00 (1H, d, *J* 11.0, CH_AHPh), 4.90 (1H, d, *J* 10.9, CH_BHPh), 4.83 (1H, d, *J* 11.0, $CHH_{A'}$Ph), 4.80 (1H, d, *J* 2.9, 1'-H), 4.76 (1H, d, *J* 11.9, CH_CHPh), 4.63 (1H, d, *J* 11.9, $CHH_{C'}$Ph), 4.55 (1H, d, *J* 10.9, $CHH_{B'}$Ph), 4.01-3.95 (1H, m, 5"-H), 3.89 (1H, t, *J* 9.3, 3'-H), 3.80-3.74 (1H, m, 5'-H), 3.71-3.66 (1H, m, 1-H or 4-H), 3.66-3.62 (1H, m, 2-H or 5-H), 3.62-3.55 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.55-3.47 (2H, m, 2'-H and 6''-H_A), 3.45 (1H, dd, *J* 13.4 and 2.6, 6''-H_B), 3.40 (1H, t, *J* 9.4, 4'-H), 3.33 (1H, dd, *J* 13.1 and 2.2, 6'-H_A), 3.24 (1H, dd, *J* 13.1 and 5.6, 6'-H_B), 2.25-2.17 (1H, m, 3-H_A or 6-H_A), 2.13-2.05 (1H, m, 3-H_B or 6-H_B) and 1.91-1.77 (2H, m, 3-H or 6-H); δ_C (125 MHz, $CDCl_3$) 165.8, 165.3, 165.2 (*C*=O), 138.6, 138.2, 137.8 (*o*-Ph), 133.7, 133.4, 133.3 (*o*-Bz), 129.9, 129.8, 129.7, 129.2, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7 (Ph), 101.9 (1''-C), 97.6 (1'-C), 81.3 (3'-C), 80.1 (2'-C), 78.2 (4'-C), 77.2 (1-C or 4-C), 75.7 (C_AH_2Ph), 75.3 (C_BH_2Ph), 74.6 (1-C or 4-C), 73.9, 73.7 (5''-C and C_CH_2Ph), 72.6 (3''-C), 71.9 (2''-C), 70.8 (5'-C), 70.1 (4''-C), 59.8, 59.3 (2-C and 5-C), 51.3, 51.2 (6'-H and 6''-C), 31.6 and 31.3 (3-C and 6-C) (four aromatic peaks overlapped or missing); *m/z* (ES) 1177.5 (55, MNa^+) and 430.3 (100); (Found: MNa^+, 1177.4180. $C_{60}H_{58}O_{13}N_{12}$ requires *MNa*, 1177.4144).

Also obtained was *(1S,2S,4S,5S)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzoyl-β-L-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28'AB'** (12.2 mg, 3%) as a yellow oil, R_f 0.52 (7:3 petrol−EtOAc); $[\alpha]_D$ +70.4 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2917, 2103, 1734, 1259 and 1069; δ_H (500 MHz, $CDCl_3$) 7.96 (2H, dd, *J* 7.3 and 1.2, Bz), 7.92 (2H, dd, *J* 7.3 and 1.1, Bz), 7.83 (2H, dd, *J* 7.2 and 1.1, Bz), 7.53 (1H, dd, *J* 7.4 and 7.3, Bz), 7.49 (1H, dd, *J* 7.4 and 7.3, Bz), 7.44 (1H, dd, *J* 7.5 and 7.4, Bz), 7.41-7.23 (21H, m, Ph), 5.89 (1H, t, *J* 9.7, 3''-H), 5.50 (1H, dd, *J* 9.7 and 7.9, 2''-H), 5.49 (1H, t, *J* 9.7, 4''-H), 4.95 (1H, d, *J* 7.9, 1''-H), 4.94 (1H, d, *J* 11.4, CH_AHPh), 4.89 (1H, d, *J* 11.1, CH_BHPh), 4.79-4.74 (3H, m, CH$H_{A'}$Ph, CH_CHPh and 1'-H), 4.61 (1H, d, *J* 11.9, CH$H_{C'}$Ph), 4.57 (1H, d, *J* 11.1, CH$H_{B'}$Ph), 4.00 (1H, ddd, *J* 9.7, 7.3 and 2.3, 5''-H), 3.97-3.92 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.89 (1H, t, *J* 9.3, 3'-H), 3.86-3.80 (1H, m, 5'-H), 3.63-3.58 (1H, m, 1-H or 4-H), 3.56 (1H, dd, *J* 13.6 and 7.3, 6''-H_A), 3.53-3.47 (2H, m, 2'-H and 2-H or 5-H), 3.42 (1H, t, *J* 9.3, 4'-H), 3.40-3.35 (2H, m, 6'-H_A and 6''-H_B), 3.28 (1H, dd, *J* 13.1 and 5.1, 6'-H_B), 1.95-1.82 (3H, m, 3-H and 6-H) and 1.80-1.73 (1H, m, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 165.7, 165.3, 164.9 (*C*=O), 138.6, 137.9 (*o*-Ph), 133.7, 133.6, 133.4 (*o*-Bz), 129.9, 129.8, 129.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6 (Ph), 100.6 (1''-C), 95.0 (1'-C), 81.5 (3'-C), 79.7 (2'-C), 78.1 (4'-C), 76.3 (1-C or

4-C), 75.7 (C_AH$_2$Ph), 75.0 (C_BH$_2$Ph), 74.3 (5''-C), 73.7 (C_CH$_2$Ph), 73.2 (1-C or 4-C), 72.4 (3''-C), 71.8 (2''-C), 70.6 (5'-C), 70.1 (4''-C), 59.6, 59.4 (2-C and 5-C), 51.3, 51.2 (6'-H and 6''-C), 30.5 and 29.1 (3-C and 6-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1177.8 (69, MNa^+) and 430.2 (100); (Found: MNa^+, 1177.4167. $C_{60}H_{58}O_{13}N_{12}$ requires *MNa*, 1177.4144).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-β-D-glucopyranosyl)-4-O-(6''-Azido-6''-deoxy-2'',3'',4''-tri-O-benzoyl-β-L-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28bB'** (36.3 mg, 9%; 90:10 mixture of diastereomers) as a yellow oil, R_f 0.52 (7:3 petrol−EtOAc); $[\alpha]_D$ +5.8 (c. 1.04 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2923, 2103, 1733, 1260 and 1070; δ_H (500 MHz, $CDCl_3$) 7.98-7.89 (4H, m, Bz), 7.83-7.78 (2H, m, Bz), 7.56-7.20 (24H, m, Ph), 5.88 (1H, t, *J* 9.7, 3''-H), 5.56-5.47 (2H, m, 2''-H and 4''-H), 5.04 (1H, d, *J* 7.9, 1''-H), 4.93 (1H, d, *J* 10.9, CH_AHPh), 4.85 (1H, d, *J* 11.1, CH_BHPh), 4.80 (1H, d, *J* 10.9, CH$H_{A'}$Ph), 4.76 (1H d, *J* 10.9, CH_CHPh), 4.70 (1H, d, *J* 10.9, CH$H_{C'}$Ph), 4.56 (1H, d, *J* 11.1, CH$H_{B'}$Ph), 4.44 (1H, d, *J* 7.7, 1'-H), 4.01-3.95 (2H, m, 5''-H and 2-H or 5-H), 3.87-3.82 (1H, m, 1-H or 4-H), 3.78-3.70 (1H, m, 1-H or 4-H), 3.64-3.58 (1H, m, 3'-H), 3.52-3.46 (3H, m, 2-H or 5-H, 6''-H), 3.46-3.38 (4H, m, 2'-H, 4'-H, 5'-H and 6'-H_A), 3.27 (1H, dd, *J* 12.7 and 4.3, 6'-H_B), 2.28-2.18 (1H, m, 3-H_A or 6-H_A), 2.15-2.06 (1H, m, 3-H_B or 6-H_B), 1.97-1.90 (1H, m, 3-H_A or 6-H_A) and 1.80-1.71 (1H, m, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 165.7, 165.3, 165.1 (*C*=O), 138.2, 137.7, 137.6 (*o*-Ph), 133.7, 133.3, 133.2 (OBz), 129.9, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8 (Ph), 102.4, 102.1 (1''-C and 1'-C), 84.5 (3'-C), 81.9 (2'-C), 78.1, 77.9 (4'-C and 1-C or 4-C), 75.7 (C_AH$_2$Ph), 75.3, 75.2, 75.0 (C_BH$_2$Ph, C_CH$_2$Ph and 1-C or 4-C), 74.6 (5'-C), 73.7 (5''-C), 72.7 (3''-C), 71.8 (2''-C), 70.0 (4''-C), 60.2, 60.0 (2-C and 5-C), 51.3 (6'-H and 6''-C), 31.8 and 30.2 (3-C and 6-C) (eight aromatic peaks overlapped or missing); *m/z* (ES) 1177.5 (57, MNa^+), 760.3 (22) and 430.2 (100); (Found: MNa^+, 1177.4175. $C_{60}H_{58}O_{13}N_{12}$ requires *MNa*, 1177.4144).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol 28AC

By method A, the glycosyl donor **21C** (242 mg, 1.2 eq., 0.43 mmol) and the acceptor **28A** (233 mg, 1.0 eq., 0.36 mmol; *ca.* 70:15:15 **28A** : **28b** : **28'A**) gave a crude mixture which was purified by flash chromatography on silica gel (8:2 petrol−EtOAc) and preparative HPLC to give **28AC** (117.2 mg, 30%) as a yellow oil, R_f 0.43 (8:2 petrol−EtOAc); $[\alpha]_D$ +58.0 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3031, 2924, 2106, 1254 and 1073; δ_H (500 MHz, $CDCl_3$) 7.40-7.25 (30H, m, Ph), 5.00 (1H, d, *J* 10.9, 3'C-CH_AHPh), 4.91 (1H, d, *J* 10.9, 2"C-CH_BHPh), 4.89 (2H, br s, 1'-H and 1"-H), 4.82 (1H, d, *J* 10.9, 3'C-CH$H_{A'}$Ph), 4.81 (1H, d, *J* 10.5, 4"C-CH_CHPh), 4.77 (1H, d, *J* 11.9, CH_DHPh), 4.74 (1H, d, *J* 11.8, CH_EHPh), 4.66 (1H, d, *J* 11.9, CH$H_{D'}$Ph), 4.65 (1H, d, *J* 11.8, CH$H_{E'}$Ph), 4.61 (1H, d, *J* 12.1, 6"C-CH_FHPh), 4.57 (1H, d, *J* 10.9, 2"C-CH$H_{B'}$Ph), 4.47 (1H, d, *J* 12.1, 6"C-CH$H_{F'}$Ph), 4.44 (1H, d, *J* 10.5, 4"C-CH$H_{C'}$Ph), 3.95 (1H, t, *J* 9.3, 3'-H), 3.89 (1H, t, *J* 9.9, 3"-H), 3.85-3.81 (1H, m, 5'-H), 3.81-3.77 (1H, m, 5"-H), 3.72 (1H, dd, *J* 10.6 and 3.5, 6"-H_A), 3.66-3.59 (4H, m, 1-H, 2-H, 4-H and 5-H), 3.60 (1H, dd, *J* 10.6 and 2.0, 6"-H_B), 3.51 (1H, dd, *J* 9.3 and 3.6, 2'-H), 3.47-3.40 (3H, m, 4'-H, 4"-H and 6'-H_A), 3.37 (1H, dd, *J* 10.0 and 3.6, 2"-H), 3.32 (1H, dd, *J* 13.1 and 5.7, 6'-H_B), 2.07-1.98 (2H, m, 3-H_A and 6-H_A) and 1.95-1.84 (2H, m, 3-H_B and 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.6, 138.1, 137.8, 137.7, 136.6, 137.5 (*o*-Ph), 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7 (Ph), 97.7, 97.2 (1'-C and 1"-C), 81.4 (3'-C), 79.9 (2'-C), 78.3 (4'-C), 77.8 (2"-C), 76.3 (4"-C), 75.7 (C_AH$_2$Ph), 75.3, 75.1, 74.8 (C_BH$_2$Ph, 1-C, 4-C and C_CH$_2$Ph), 73.7, 73.5, 73.4 (C_DH$_2$Ph, C_EH$_2$Ph and C_FH$_2$Ph), 70.9, 70.8 (5'-C and 5"-C), 68.1 (6"-C), 65.2 (3"-C), 59.5 (2-C and 5-C), 51.4 (6'-H), 31.3 and 31.3 (3-C and 6-C) (nine aromatic peaks overlapped or missing); *m/z* (ES) 1135.5 (38, MNa^+) and 430.2 (100); (Found: MNa^+, 1135.4814. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1S,2S,4S,5S)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(3''-Azido-3''-deoxy-2'',4'',6''-tri-O-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28'AC** (15.3 mg, 4%; 90:10 mixture of diastereomers) as a yellow oil, R_f 0.43 (8:2 petrol−EtOAc); $[\alpha]_D$ +60.8 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2924, 2105, 1255 and 1073; δ_H (500 MHz, $CDCl_3$) 7.40-7.20 (30H, m, Ph), 5.00 (1H, d, *J* 10.9, CH_AHPh), 4.92 (1H, d, *J* 11.1, CH_BHPh), 4.84 (1H, d, *J* 9.9, CH_CHPh), 4.82 (1H, d, *J* 10.9, CH$H_{A'}$Ph), 4.81 (1H, d, *J* 12.0, CH_DHPh), 4.78 (1H, d, *J* 12.0, CH_EHPh), 4.77 (2H, d, *J* 2.7, 1'-H and 1"-H), 4.65-4.57 (4H, m, CH$H_{B'}$Ph, CH$H_{C'}$Ph, CH$H_{E'}$Ph and CH_FHPh), 4.48-4.43 (2H, m, CH$H_{C'}$Ph and CH$H_{F'}$Ph), 3.97 (1H, t, *J* 9.3, 3'-H), 3.90 (1H, t, *J* 10.0, 3"-H), 3.89-3.84 (1H, m, 5'-H), 3.83-3.76 (2H, m, 1-H or 4-H and 2-H and 5-H), 3.73 (1H, dd, *J* 10.7 and 3.5, 6"-H_A), 3.71-3.65 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.63 (1H, dd, *J* 10.7 and 1.9, 6"-H_B), 3.61-3.55 (1H, m, 5"-H), 3.53 (1H, m, 2'-H), 3.50-3.42 (3H, m, 4'-H, 4"-H, 6'-H_A), 3.39 (1H, m, 2"-H), 3.33 (1H, dd, *J* 13.2 and 5.5, 6'-H_B), 1.95-1.88 (2H, m, 3-H_A and 6-H_A) and 1.84-1.76 (2H, m, 3-H_B and 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.4, 137.9 (*o*-Ph), 128.9, 128.4, 128.3, 128.1, 127.9, 127.8 (Ph), 96.1, 94.1 (1'-C and 1"-C), 81.5 (3'-C), 79.6 (2'-C), 78.2 (4'-C), 77.9 (2"-C), 76.2 (4"-C), 75.7 (C_AH$_2$Ph), 75.3 (C_CH$_2$Ph), 75.1 (C_BH$_2$Ph), 74.8, 74.1, 73.8 (C_DH$_2$Ph, C_EH$_2$Ph and C_FH$_2$Ph), 73.4 (1-C and 4-C), 70.7 (5'-C), 68.5 (5"-C), 68.3 (6"-C), 65.2 (3"-C), 59.7 (2-C and 5-C), 51.4 (6'-H), 29.7 and 29.4 (3-C and 6-C) (sixteen aromatic peaks overlapped or missing); *m/z* (ES) 1135.5 (30, MNa^+), 955.4 (25) and 430.2 (100); (Found: MNa^+, 1135.4783. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-β-D-glucopyranosyl)-4-O-(3''-Azido-3''-deoxy-2'',4'',6''-tri-O-benzyl-α-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28bC** (29.7 mg, 8%; *ca.* 90:10 mixture of diastereomers) as a yellow oil, R_f 0.43 (8:2 petrol−EtOAc); $[\alpha]_D$ +24.0 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3031, 2920, 2105, 1255 and 1072; δ_H (500 MHz, $CDCl_3$) 7.45-7.25 (30H, m, Ph), 4.99 (1H, d, *J* 3.4, 1"-H), 4.94 (1H, d, *J* 10.9), 4.86 (1H, d, *J* 11.8), 4.85 (1H, d, *J* 10.9), 4.81 (1H, d, *J* 10.9), 4.79 (1H, d, *J* 10.5), 4.75 (1H, d, *J* 10.9), 4.73-4.72 (2H, m), 4.62 (1H, d, *J* 12.1), 4.57 (1H, d, *J* 11.8), 4.49 (1H, d, *J* 7.7, 1'-H), 4.46 (1H, d, *J* 12.1), 4.41 (1H, d, *J* 10.5), 3.92-3.82 (3H, m, 3'-H, 1-H or 4-H and 2-H or 5-H), 3.82-3.76 (1H, m, 5'-H), 3.70 (1H, dd, *J* 10.6 and 3.5, 6"-H_A), 3.66-3.62 (1H, m, 3"-H), 3.62-3.56 (3H, m, 6"-H_B, 1-H or 4-H and 2-H or 5-H), 3.50-3.40 (5H, m, 2'-H, 5"-H, 4'-H, 4"-H and 6'-H_A), 3.37 (1H, dd, *J* 10.0 and 3.4, 2"-H), 3.27 (1H, dd, *J* 12.3 and 5.0, 6'-H_B), 2.06-1.90 (3H, m, 3-H and 6-H) and 1.86-1.78 (1H, m, 3-H or 6-H); δ_C (125 MHz, $CDCl_3$) 137.8, 137.7, 137.5 (*o*-Ph), 128.2, 128.1, 128.0, 127.9, 127.6, 127.5 (Ph), 102.5 (1'-C), 97.5 (1"-C), 84.4 (3'-C), 82.1 (2'-C), 78.1 (4'-C), 77.7 (2"-C), 76.3 (4"-C and 1-C or 4-C), 75.3 (C_AH$_2$Ph, C_BH$_2$Ph, C_CH$_2$Ph, C_DH$_2$Ph and 1-C or 4-C), 74.7 (5"-C), 73.6 (C_FH$_2$Ph), 72.9 (C_EH$_2$Ph), 70.6 (5'-C), 68.2 (6"-C), 65.3 (3"-C), 59.8 (2-C and 5-C), 51.3 (6'-

H), 31.5 and 30.6 (3-C and 6-C) (15 aromatic peaks overlapped or missing); *m/z* (ES) 1135.6 (100, MNa^+), 575.1 (27) and 430.2 (98); (Found: MNa^+, 1135.4783. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

Also obtained was *(1R,2R,4R,5R)-1-O-(6'-Azido-6'-deoxy-2',3',4'-tri-O-benzyl-α-D-glucopyranosyl)-4-O-(3''-Azido-3''-deoxy-2'',4'',6''-tri-O-benzyl-β-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol* **28Ad** (42.4 mg, 11%) as a yellow oil, R_f 0.43 (8:2 petrol−EtOAc); $[\alpha]_D$ +4.00 (c. 1.00 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2918, 2104, 1256 and 1072; δ_H (500 MHz, $CDCl_3$) 7.45-7.25 (30H, m, Ph), 5.03 (1H, d, *J* 3.5, 1'-H), 5.00 (1H, d, *J* 10.9, 3'C-CH_AHPh), 4.91 (1H, d, *J* 10.9, 4'C-CH_BHPh), 4.85 (1H, d, *J* 10.8, CH_CHPh), 4.81 (1H, d, *J* 10.6, 4"C-CH_DHPh), 4.80 (1H, d, *J* 10.9, 3'C-CH$H_{A'}$Ph), 4.77 (1H, d, *J* 10.8, CH$H_{C'}$Ph), 4.75 (2H, d, *J* 11.8, CH_EHPh), 4.59 (1H, d, *J* 12.0, 6"C-CH_FHPh), 4.57 (1H, d, *J* 10.9, 4'C-CH$H_{B'}$Ph), 4.55 (1H, d, *J* 10.6, 4"C-CH$H_{D'}$Ph), 4.54 (1H, d, *J* 12.0, 6"C-CH$H_{F'}$Ph), 4.60 (1H, d, *J* 7.7, 1"-H), 4.00-3.94 (2H, m, 3'-H and 2-H or 5-H), 3.91-3.84 (2H, m, 5'-H and 1-H or 4-H), 3.69-3.63 (4H,m, 2-H or 5-H, 1-H or 4-H and 6"-H), 3.56 (1H, dd, *J* 9.7 and 3.6, 2'-H), 3.55 (1H, t, *J* 9.5, 3"-H), 3.48-3.41 (4H, m, 4'-H, 4"-H, 6'-H_A and 5"-H), 3.33 (1H, dd, *J* 10.6 and 5.8, 6'-H_B), 3.28 (1H, dd, *J* 9.7 and 7.7, 2"-H), 2.12-2.00 (3H, m, 3-H and 6-H) and 1.87-1.79 (1H, m, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.4, 137.4 (*o*-Ph), 128.4, 128.3, 128.2, 128.1, 128.0, 127.9 (Ph), 102.5 (1"-C), 98.0 (1'-C), 81.5 (3'-C), 80.1 (2'-C and 2"-C), 78.3 (4'-C), 76.1 (1-C or 4-C), 76.1 (4"-C, C_AH_2Ph and, C_DH_2Ph), 75.3 (1-C or 4-C, C_BH_2Ph, and C_CH_2Ph), 73.4 (C_FH_2Ph), 73.1 (C_EH_2Ph), 70.9 (5'-C), 68.7 (5"-C), 68.6 (6"-C), 68.5 (3"-C), 60.0 (2-C and 5-C), 51.6 (6'-H), 30.8 and 30.2 (3-C and 6-C) (16 aromatic peaks overlapped or missing); *m/z* (ES) 1135.6 (100, MNa^+), 575.1 (27) and 430.2 (98); (Found: MNa^+, 1135.4782. $C_{60}H_{64}O_{10}N_{12}$ requires *MNa*, 1135.4766).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-(3''-Azido-3''-deoxy-2'',4'',6''-tri-*O*-acetoxy-β-D-glucopyranosyl)-2,5-diazido-cyclohexane-1,4-diol 28AD

By method A, the glycosyl donor **21D** (181 mg, 1.2 eq., 0.43 mmol) and the acceptor **28A** (233 mg, 1.0 eq., 0.36 mmol; *ca.* 70:15:15 **28A** : **28b** : **28'A**) gave a crude product which was purified by flash chromatography on silica gel (gradient elution: 9:1 → 7:3 petrol−EtOAc) and preparative HPLC to give **28AD** (29.0 mg, 8%) as a yellow oil, R_f 0.10 (8:2 petrol−EtOAc); $[\alpha]_D$ +13.7 (c. 0.99 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2929, 2106, 1752, 1218 and 1040; δ_H (500 MHz, $CDCl_3$) 7.40-7.25 (15H, m, Ph), 5.01-4.99 (1H, m, 1'-H), 4.98 (1H, dd, *J* 10.2 and 9.5, 4"-H), 4.97 (1H, d, *J* 10.9, CH_AHPh), 4.91 (1H, dd, *J* 11.1, CH_BHPh), 4.90 (1H, dd, *J* 10.2 and 7.9, 2"-H), 4.82 (1H, d, *J* 10.9, $CHH_{A'}Ph$), 4.75 (1H, d, *J* 11.8, CH_CHPh), 4.71 (1H, d, *J* 11.8, $CHH_{C'}Ph$), 4.57 (1H, dd, *J* 11.1, $CHH_{B'}Ph$), 4.56 (1H, dd, *J* 7.9, 1"-H), 4.20 (1H, dd, *J* 12.6 and 5.1, 6"-H_A), 4.15 (1H, dd, *J* 12.6 and 2.6, 6"-H_B), 3.96 (1H, t, *J* 9.3, 3'-H), 3.89-3.82 (2H, m, 5'-H and 2-H or 5-H), 3.80-3.75 (1H, m, 1-H or 4-H), 3.70-3.63 (1H, m, 5"-H), 3.63 (1H, t, *J* 10.2, 3"-H), 3.63-3.60 (1H, m, 1-H or 4-H), 3.60-3.55 (1H, m, 2-H or 5-H), 3.53 (1H, dd, J 9.3 and 3.6, 2'-H), 3.50-3.40 (2H, m, 4'-H and 6'-H_A), 3.34 (1H, dd, *J* 13.1 and 5.7, 6'-H_B), 2.17 (3H, s, Me), 2.12 (6H, s, Me), 2.06-1.94 (3H, m, 3-H and 6-H) and 1.83-1.76 (1H, m, 3-H_B or 6-H_B); δ_C (125 MHz, $CDCl_3$) 138.6, 138.1, 137.8 (*o*-Ph), 128.5, 128.3, 128.0, 127.9, 127.5 (Ph), 100.3 (1"-C), 97.8 (1'-C), 81.3 (3'-C), 80.1 (2'-C), 78.1 (4'-C), 75.8, 75.6 (1-C and 4-C), 75.5 (C_AH_2Ph), 75.1 (C_BH_2Ph), 73.1 (C_CH_2Ph), 72.8 (5"-C), 71.1 (2"-C), 70.9 (5'-C), 68.5 (4"-C), 64.2 (3"-C), 61.9 (6"-C), 59.8 (2-C and 5-C), 51.3 (6'-H), 30.7, 30.4 (3-C and 6-C), 20.6 and 20.5 (Me) (7 peaks overlapped or missing); *m/z* (ES) 991.7 (100, MNa^+) and 430.3 (82); (Found: MNa^+, 991.3668. $C_{45}H_{52}O_{13}N_{12}$ requires *MNa*, 991.3675).

(1*S*,3*S*,4*S*,6*S*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol 29A

By method B, the glycosyl donor **21A** (551 mg, 1.0 eq., 0.97 mmol) and the acceptor **15** (192 mg, 1.0 eq., 0.97 mmol) gave a crude product, which was purified by flash chromatography (gradient elution 9:1 → 7:3 petrol–EtOAc) to give the *glycosidated product* **29A** (179.6 mg, 29%) as a colourless oil, R_f 0.15 (7:3 petrol–EtOAc); $[\alpha]_D^{20}$ + 54.3 (*c* 2.07 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3445, 3031, 2928 and 2105; δ_H (500 MHz; $CDCl_3$) 7.49-7.23 (15H, m, PhH), 4.97 (1H, d, ^2J 10.8, CH_2Ph), 4.90 (1H, d, ^2J 10.9, CH_2Ph), 4.85 (1H, d, *J* 3.6, 1'-H), 4.82 (1H, d, ^2J 10.8, CH_2Ph), 4.77 (1H, d, ^2J 11.6, CH_2Ph), 4.59 (1H, d, ^2J 10.9, CH_2Ph), 4.57

(1H, d, ^2J 11.6, *CH₂*Ph), 3.91 (1H, t, *J* 9.3, 3'-H), 3.84-3.42 (9H, m, 1-H, 3-H, 4-H, 6-H, 6'-H, 5'-H, 4'-H and 2'-H) and 2.13-1.70 (4H, m, 5-H_2 and 2-H_2); δ_C (75 MHz, $CDCl_3$) 138.9, 138.4, 138.2, 130.4, 129.4, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 95.7, 81.9, 80.3, 78.7, 78.6, 76.2, 75.7, 74.1, 71.4, 69.1, 62.1, 51.7, 32.2 and 30.0 (1 carbon signal missing or overlapped); *m/z* (ES) 674 (100%, MNH_4^+) and 679 (40, MNa^+); (Found: MNa^+ 678.2741; $C_{33}H_{37}N_9O_6$ requires *MNa* 678.2765).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol 29'A

By method B, the diol **15'** (1.07 g, 5.39 mmol) and the donor **21A** (2.55 g, 4.49 mmol) gave a crude product, which was pre-absorbed onto silica and purified by flash chromatography (gradient elution 9:1 → 6:4 petrol–EtOAc) to give the *glycosidated product* **29'A** (429.4 mg, 15%) as a colourless oil, R_f 0.15 (8:2 petrol–EtOAc); $[\alpha]_D^{20}$ + 28.1 (*c* 2.05 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3448, 3031, 2927 and 2103; δ_H (500 MHz; $CDCl_3$) 7.37-7.24 (15H, m, PhH), 4.97 (1H, d, ^2J 10.9, CH_2Ph), 4.90 (1H, d, ^2J 11.0, CH_2Ph), 4.83 (1H, d, *J* 3.6, 1'-H), 4.81 (1H, d, ^2J 10.9, CH_2Ph), 4.78 (1H, d, ^2J 11.7, CH_2Ph), 4.61 (1H, ^2J 11.7, CH_2Ph), 4.57 (1H, ^2J 11.0, *CH₂*Ph), 3.90 (1H, t, *J* 9.2, 3'-H), 3.86-3.82 (2H, m, 4'-H and 1-H), 3.81-3.74 (2H, m, 5'-H and 3-H), 3.59 (1H, dd, *J* 9.2 and 4.7, 6-H), 3.54-3.50 (2H, m, 2'-H and 4-H), 3.44 (1H, dd, ^2J 13.1 and *J* 5.5, 6'$_a$-H), 3.31 (1H, dd, ^2J 13.1 and *J* 5.9, 6'$_b$-H), 2.13 (1H, br s, OH), 2.01-1.95 (3H, m, 2-H_a and 5-H_2) and 1.87 (1H, m, 2-H_b); δ_C (75 MHz, $CDCl_3$) 138.4, 138.1, 137.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 97.4, 81.4, 80.2, 78.2, 75.7, 75.3, 75.1, 73.8, 70.9, 69.0, 61.5, 58.8, 51.3, 34.0 and 29.2; *m/z* (ES) 679 (100%, MNa^+); (Found: MNa^+ 678.2739; $C_{33}H_{37}N_9O_6$ requires *MNa*, 678.2765).

Also obtained (1*R*,3*R*,4*R*,6*R*)-1,3-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol **29'AA** (73.7 mg, 2%) as a colourless amorphous solid, R_f 0.20 (8:2 petrol–Et_2O); $[\alpha]_D^{20}$ + 49.3 (*c* 2.02 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3064, 3031, 2917 and 2102; δ_H (500 MHz; $CDCl_3$) 7.34-7.24 (30H, m, PhH), 4.98 (2H, d, ^2J 10.9, CH_2Ph), 4.93 (2H, d, ^2J 3.6, 1'-H), 4.89 (2H, d, ^2J 11.0, CH_2Ph), 4.81 (2H, d, ^2J 10.9, CH_2Ph), 4.77 (2H, d, ^2J 11.7, CH_2Ph), 4.67 (2H, d, ^2J 11.7, CH_2Ph), 4.57 (2H, ^2J 11.0, C*H*$_2$Ph), 3.94 (2H, t, *J* 9.1, 3'-H), 3.85-3.82 (2H, m, 5'-H), 3.72 (2H, app. q, *J* 5.9, 1-H and 3-H), 3.58 (2H, app. q, *J* 5.9, 6-H and 4-H), 3.52 (2H, dd, *J* 9.1 and 3.6, 2'-H), 3.44 (2H, t, *J* 9.1, 4-H), 3.42 (2H, dd, ^2J 13.1 and *J* 4.9, 6'$_a$-H), 3.29 (2H, dd, ^2J 13.1 and *J* 5.5, 6'$_b$-H), 2.01 (2H, app. t, *J* 5.9, 2-H) and 1.96 (2H, app. t, *J* 5.9, 5-H); δ_C (75 MHz, $CDCl_3$) 139.0, 138.5, 138.3, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 98.0, 81.9, 80.5, 78.6, 76.1, 75.7, 74.0, 71.5, 59.5, 51.8, 33.5 and 29.9 (2 carbon missing or overlapped); *m/z* (ES) 1135 (100%, MNH_4^+); (Found: MNa^+ 1135.4719; $C_{60}H_{64}N_{12}O_{10}$ requires *MNa*, 1135.4766).

Also obtained (1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzyl-α-D-glucopyranosyl)-3-*O*-(6''-Azido-6''-deoxy-2'',3'',4''-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol **29'Ab** (42.5 mg, 1%) as a colourless amorphous solid, R_f 0.20 (8:2 petrol–Et_2O); $[\alpha]_D^{20} + 28.2$ (*c* 2.13 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3064, 3031, 2917 and 2102; δ_H (500 MHz; $CDCl_3$) 7.33-7.25 (30H, m, Ph), 4.96 (1H, d, ^2J 10.7, C*H*$_2$Ph), 4.90 (1H, d, ^2J 11.1, C*H*$_2$Ph), 4.88 (1H, d, ^2J 10.7, C*H*$_2$Ph), 4.87 (1H, d, ^2J 10.7, C*H*$_2$Ph), 4.85 (1H, d, ^2J 11.1, C*H*$_2$Ph), 4.83 (1H, d, *J* 3.6, 1'-H), 4.78 (1H, ^2J 10.7, C*H*$_2$Ph), 4.77 (1H, d, ^2J 10.7, C*H*$_2$Ph), 4.73 (1H, d, ^2J 11.4, C*H*$_2$Ph), 4.62 (1H, d, ^2J 11.4, C*H*$_2$Ph), 4.59 (1H, d, ^2J 11.4, C*H*$_2$Ph), 4.56 (1H, d, ^2J 11.4, C*H*$_2$Ph), 4.55 (1H, d, ^2J 10.7, C*H*$_2$Ph), 4.54 (1H, d, *J* 7.7, 1''-H), 4.02-3.99 (1H, m, 1-H or 3-H), 3.94 (2H, t, *J* 9.3, 3''-H and 3'-H), 3.87-3.81 (3H, m, 3-H or 1-H, 5''-H and 5'-H), 3.67-3.62 (4H, m, 6-H, 4-H, 4''-H and 4'-H), 3.47-3.38 (4H, m, 2'-H, 2''-H, 6$_a$''-H and 6$_b$''-H, or 6$_a$'-H and 6$_b$'-H), 3.36 (1H, dd, ^2J 13.1 and *J* 2.2, 6$_a$''-H or 6'$_a$-H), 3.26 (1H, dd, ^2J 13.1 and *J* 5.6, 6''$_b$-H or 6'$_b$-H), 2.16-2.12 (1H, m, 2-H$_a$), 2.06-2.02 (1H, m, 2-H$_b$) and 1.98-1.90 (2H, m, 5-H$_2$); δ_C (75 MHz, $CDCl_3$) 139.0, 138.7, 138.6, 138.5, 138.3, 138.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 101.8, 98.6, 84.8, 82.4, 81.7, 80.5, 78.6, 78.4, 76.2, 76.0, 75.7, 75.6, 75.4, 75.0, 73.5, 71.3, 60.2, 59.7, 52.0, 51.6, 31.7 and 30.2 (11 signals missing or overlapped); *m/z* (ES) 1131 (100%, MNH_4^+); (Found: MNH_4^+ 1130.5013; $C_{60}H_{64}N_{12}O_{10}$ requires MNH_4^+, 1130.5212).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Azido-6'-deoxy-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl)-2,4-diazido-cyclohexane-1,5-diol 29'B

By method A, the diol **15'** (313 mg, 1.58 mmol) and the donor **21B** (481.8 mg, 0.79 mmol) gave a crude product, which was pre-absorbed onto silica and purified by flash chromatography (gradient elution 9:1 → 7:3 petrol–EtOAc) and then by LC-MS to give the *glycosidated product* **29'B** (46.8 mg, 8%) as a yellow oil, R_f 0.10 (7:3 petrol–EtOAc); $[\alpha]_D^{20}$ -41.7 (*c* 1.17 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3496, 2925, 2103, 1733 and 1601; δ_H (500 MHz; $CDCl_3$) 7.95 (2H, d, *J* 7.2, Ph), 7.91 (2H, d, *J* 7.4, Ph), 7.82 (2H, d, *J* 7.3, Ph), 7.53 (2H, dd, *J* 7.4 and 6.6, Ph), 7.45-7.35 (4H, m, Ph), 7.30-7.24 (2H, m, Ph), 7.18-7.14 (1H, m, Ph), 5.89 (1H, t, *J* 8.1, 3'-H), 5.49 (1H, t, *J* 8.1, 4'-H or 2'-H), 5.47 (1H, t, *J* 8.1, 4'-H or 2'-H), 4.93 (1H, d, *J* 8.1, 1'-H), 4.03-3.98 (4H, m, 5'-H, 5-H, 1-H and OH), 3.56 (1H, dd, ^2J 13.7 and *J* 7.7, 6'$_a$-H), 3.42-3.38 (2H, m, 4-H and 2-H), 3.34 (1H, dd, ^2J 13.7 and *J* 2.3, 6'$_a$-H), 2.01 (1H, dt, *J* 13.9 and 3.7, 6_a-H), 1.90-1.84 (2H, m, 6_b-H and 3_a-H) and 1.72-1.64 (1H, m, 3_b-H); δ_C (75 MHz, $CDCl_3$) 165.7, 165.3, 165.0, 133.8, 133.6, 133.4, 129.9, 129.8, 129.7, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 100.1, 75.6, 74.3, 72.2, 71.7, 70.3, 68.8, 61.7, 59.4, 51.2, 32.3 and 29.2; *m/z* (ES) 715 (100%, MNH_4^+); (Found: MNH_4^+ 715.2588; $C_{33}H_{31}N_9O_9$ requires *MNH_4*, 715.2556).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(2'-Phthalimido-2'-deoxy-3',4',6'-tri-*O*-benzyl-β-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol 29'F

By method A, the diol **15'** (33 mg, 0.17 mmol), the donor **21F** (128 mg, 0.19 mmol) gave a crude product, which was pre-absorbed onto silica and purified by flash chromatography eluting with 7:3 petrol–EtOAc to give the *glycosidated product* **29'F** (65 mg, 45%) at a yellow oil, R_f 0.15 (7:3 petrol–EtOAc); $[\alpha]_D^{20}$ -9.6 (*c* 1.8 in CH_2Cl_2); ν_{max}/cm^{-1} (thin film) 3468, 2930, 2102, 1775 and 1712; δ_H (500 MHz; $CDCl_3$) 7.77-7.59 (2H, m, phthal-H), 7.39-7.22 (12H, m, phthal-H and Ph), 7.01-6.95 (2H, m, Ph), 6.91-6.81 (3H, m, Ph), 5.23 (1H, d, *J* 8.4, 1'-H), 4.84 (1H, d, ^2J 10.8, C*H*Ph), 4.79 (1H, d, ^2J 12.1, C*H*Ph), 4.64 (1H, d, ^2J 10.8, C*H*Ph), 4.62 (1H, d, ^2J 12.1, C*H*Ph), 4.60 (1H, d, ^2J 12.1, C*H*Ph), 4.44 (1H, d, ^2J 12.1, C*H*Ph), 4.32 (1H, dd, *J* 10.7 and 8.7, 3'-H), 4.14 (1H, dd, *J* 10.7 and 8.4, 2'-H), 3.92-3.83 (2H, m, 6'-H_a and 1-H), 3.78-3.71 (3H, m, 4'-H, 5'-H and 3-H), 3.64 (1H, dd, ^2J 9.9 and *J* 3.7, 6'-H_b), 3.31 (1H, app td, *J* 10.9 and 4.1, 4-H), 3.21 (1H, app td, *J* 9.9 and 4.1, 6-H), 2.10

(1H, br s, OH), 1.93-1.86 (1H, m, 5-H_a), 1.74 (1H, app dd, *J* 10.5 and 4.1, 5-H_b), 1.71-1.62 (1H, m, 2-H_a) and 1.61-1.49 (1H, m, 2-H_b); δ_C (75 MHz, $CDCl_3$) 138.3, 134.4, 131.7, 128.9, 128.5, 128.4, 128.2, 127.8, 123.8, 97.6, 79.9, 75.5, 75.4, 73.9, 69.1, 68.9, 62.0, 59.8, 56.3, 35.6, 32.7, 29.4 and 29.3 (seven carbon signals missing or overlapped); *m/z* (ES) 778 (100%, MNH_4^+); (Found: MNH_4^+ 777.3376; $C_{41}H_{41}N_7O_8$ requires *MNH_4*, 777.3360).

(1*S*,3*S*,4*S*,6*S*)-1-*O*-(2',6'-Azido-2',6'-deoxy-3',4'-di-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol 29G

By Method B, the acceptor **15** (113 mg, 0.57 mmol) and the donor **21G** (191.2 mg, 0.381 mmol) gave a crude product, which was purified by flash chromatography (gradient elution 9:1→8:2 petrol–EtOAc) to give the *glycosidated product* **29G** (31.8 mg, 14%) as a colourless oil, R_f 0.15 (8:2 petrol–Et_2O); $[\alpha]_D^{20}$ +18.9 (*c* 1.4 in MeOH); ν_{max}/cm^{-1} (thin film) 3379, 2923, 2104 and 1448; δ_H (500 MHz; $CDCl_3$) 7.39-7.25 (10H, m, Ph), 5.00 (1H, d, *J* 3.6, 1'-H), 4.91-4.85 (3H, m, CH_2Ph), 4.59 (1H, d, ^2J 11.0, CH_2Ph), 3.92 (1H, dd, *J* 10.2 and 9.1, 3'-H), 3.89-3.86 (2H, m, 5'-H and 1-H), 3.83-3.73 (2H, m, 3-H and 4-H or 6-H), 3.57 (1H, dt, *J* 13.0 and 4.1, 4-H or 6-H), 3.51 (1H, app t, *J* 9.1, 4'-H), 3.47 (1H, dd, ^2J 13.1 and *J* 2.4, 6'$_a$-H), 3.40 (1H, dd, *J* 10.2 and 3.6, 2'-H), 3.33 (1H, dd, ^2J 13.1 and *J* 5.7, 6'$_b$-H), 2.19 (1H, br s, OH), 2.09 (1H, dt, ^2J 13.9 and *J* 4.9, 2-H_a), 2.04-1.97 (2H, m, 2-H_b and 5-H_a) and 1.89 (1H, ddd, ^2J 12.8, and *J* 9.3 and 3.3, 5-H_b); δ_C (75 MHz, $CDCl_3$) 137.6, 137.3, 129.3, 128.6, 128.5, 128.2, 128.1, 124.9, 102.1, 82.6, 77.9, 76.7, 75.7, 75.2, 74.8, 69.0, 66.4, 61.4, 59.7, 51.1, 34.5 and 29.5; *m/z* (ES) 563 (100%, $M^+ - N_2$) and 613 (60, MNa^+); (Found: MNa^+ 613.2361; $C_{26}H_{30}N_{12}O_5$ requires *MNa*, 613.2360).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(2',6'-Azido-2',6'-deoxy-3',4'-di-*O*-benzyl-α-D-glucopyranosyl)-4,6-diazido-cyclohexane-1,3-diol 29'G

By Method B, the acceptor **15'** (113 mg, 0.57 mmol) and the donor **21G** (191.2 mg, 0.381 mmol) gave a crude product, which was purified by flash chromatography (gradient elution 9:1→8:2 petrol–EtOAc) to give the *glycosidated product* **29'G** (58.7 mg, 26%) as a colourless oil, R_f 0.15 (8:2 petrol–Et_2O); $[\alpha]_D^{20}$ +57.4 (*c* 2.3 in MeOH); ν_{max}/cm^{-1} (thin film)

3379, 2923, 2104 and 1448; δ_H (500 MHz; $CDCl_3$) 7.39-7.25 (10H, m, Ph), 5.00 (1H, d, 3.6, 1'-H), 4.91-4.85 (3H, m, C*H*$_2$Ph), 4.59 (1H, d, ^2J 11.0, C*H*$_2$Ph), 3.92 (1H, dd, *J* 10.2 and 9.1, 3'-H), 3.89-3.86 (2H, m, 5'-H and 1-H), 3.83-3.73 (2H, m, 6-H or 4-H and 3-H), 3.57 (1H, dt, ^2J 13.0 and *J* 4.1, 6-H or 4-H), 3.51 (1H, d, *J* 9.1, 4'-H), 3.47 (1H, dd, ^2J 13.1 and *J* 2.4, 6'$_a$-H), 3.40 (1H, dd, *J* 10.2 and 3.6, 2'-H), 3.33 (1H, dd, ^2J 13.1 and *J* 5.7, 6'$_b$-H), 2.19 (1H, br s, OH), 2.09 (1H, dt, ^2J 13.9 and *J* 4.9, 2-H$_a$), 2.04-1.97 (2H, m, 5-H$_a$ and 2-H$_b$) and 1.89 (1H, ddd, ^2J 12.8, and *J* 9.3 and 3.3, 5-H$_b$); δ_C (75 MHz, $CDCl_3$) 137.9, 137.7, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 98.3, 80.3, 79.2, 75.9, 71.9, 69.4, 63.8, 61.9, 59.3, 51.5, 34.3 and 29.8 (5 missing or overlapped); *m/z* (ES) 613 (100%, MNa^+) and 563 (80, (M^+–N_2); (Found: MNa^+ 613.2369; $C_{26}H_{30}N_{12}O_5$ requires *MNa*, 613.2360).

5'-(2''-Phthalimido-2''-deoxy-3'',4'',6''-tri-*O*-benzyl-β-D-glucopyranosyl)-1',3',2,6-tetraazido-6',3,4-tri-*O*-benzyl Neamine 30GF

By Method A, the donor **21F** (103 mg, 0.15 mmol) and the acceptor **30G** (106 mg, 0.15 mmol) gave a crude product which was purified by column chromatography (gradient elution: 0 : 10 → 2 : 8 EtOAc–petrol) to yield **30GF** (31 mg, 16%) as a yellow oil, R_f 0.4 (2 : 8 EtOAc–petrol); $[\alpha]_D$ +83.1 (c. 0.52, $CHCl_3$); ν_{max}/cm^{-1} (thin film) 3031, 2924, 2103 (azide), 1775 (C=O) and 1713 (C=O); δ_H (500 MHz; $CDCl_3$) 7.79-7.77 (1H, m, Phth), 7.68-7.63 (3H, m, Phth), 7.50-7.48 (2H, m, Ph), 7.39-7.16 (23H, m, Ph), 6.99-6.97 (2H, m, Ph), 6.92-6.86 (3H, m, Ph), 5.66 (1H, d, *J* 7.4, 1''-H), 5.45 (1H, d, *J* 3.8, 1-H), 4.86-4.76 (5H, m, PhC*H* × 5), 4.68-4.47 (6H, m, PhC*H* × 6), 4.43-4.38 (3H, m, PhC*H*, 3''- and 2''-H), 4.27 (1H, t, *J* 8.8, 5'-H), 4.21-4.20 (1H, m, 5-H), 3.98 (1H, t, *J* 9.2, 3-H), 3.83-3.70 (2H, m, 4''- and 6''$_A$-H), 3.72 (1H, dd, J, 6''$_B$-H), 3.55 (1H, t, *J* 9.2, 4-H), 3.45-3.31 (7H, m, 5''-, 2-, 4'-, 1'-, 3'-, 6$_A$- and 6$_B$-H), 3.14 (1H, t, *J* 9.1, 6'-H), 2.22 (1H, app dt, *J* 13.0 and 4.3, 2'$_A$-H) and 1.41 (1H, app q, *J* 13.0, 2'$_B$-H); δ_C (125 MHz; $CDCl_3$) 168.2 (*C*=O), 167.7, 138.4, 138.1, 138.1, 138.0, 137.8, 137.4, 133.8, 133.7, 131.9, 131.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.6, 127.5, 127.5, 123.6, 123.1, 98.8 (1-C), 95.6 (1'-C), 83.8 (6'-C), 79.9 (4''-C), 79.1, 78.5 (4-C), 76.7 (4'-C), 75.6 (5'-C), 75.1 (5''-C), 74.9 (*C*H$_2$), 74.9 (*C*H$_2$), 74.7 (*C*H$_2$), 74.7 (*C*H$_2$), 74.4 (*C*H$_2$), 72.8 (*C*H$_2$), 70.9 (5-C), 68.9 (6''-C), 62.5 (2-C), 60.7 (1'-

C), 58.8 (6'-C), 56.3 (2'-C), 51.1 (6-C) and 31.8 (2'-C); *m/z* (ES) 1280.3 (100%, MNa^+); Found MNa^+ 1280.4944; $C_{68}H_{67}N_{13}O_{12}$ requires MNa^+ 1280.4930.

4'-(2",3",4",6"-tetra-*O*-acetyl-β-D-glucopyranosyl)-1',3',2,6,-tetraazido-6',3,4-tri-*O*-benzyl Neamine 30GH

By Method C, the trichloroacetimidate **21H** (90 mg, 0.18 mmol) and the acceptor **30G** (152 mg, 0.21 mmol) gave a crude product which was purified by column chromatography (gradient elution: 1 : 9 → 3 : 7 EtOAc–petrol) to yield **30GH** (40 mg, 22%) as a colourless oil, R_f 0.15 (2 : 8 EtOAc–petrol); $[\alpha]_D$ +98.5 (*c* 0.28, $CHCl_3$); ν_{max}/cm^{-1} (Thin film) 3031, 2936, 2105 (azide), 1758 (C=O) and 1366; δ_H (500 MHz; $CDCl_3$) 7.53-7.25 (15H, m, Ph × 3), 5.68 (1H, d, *J* 3.8, 1-H), 5.22 (1H, d, *J* 7.6, 1"-H), 5.14 (1H, dd, *J* 9.5 and 8.9, 4"-H), 5.08 (1H, dd, *J* 9.5 and 9.3, 3"-H), 5.04 (1H, dd, *J* 9.3 and 7.6, 2"-H), 4.95 (1H, d, *J* 9.6, $PhCH_A$), 4.89 (1H, d, *J* 11.4, $PhCH_B$), 4.88-4.83 (2H, m, Ph*CH* ×2), 4.68 (1H, d, *J* 9.6, $PhCH_A$), 4.61 (1H, d, *J* 11.4, $PhCH_B$), 4.28 (1H, dd, *J* 12.5 and 4.2, $6"_A$-H), 4.24-4.21 (1H, m, 5-H), 4.12 (1H, app t, *J* 9.4, 5'-H), 4.10-4.01 (2H, m, $6"_B$- and 3-H), 3.57 (1H, dd, *J* 9.8 and 9.4, 4'-H), 3.51-3.41 (4H, m, 1'-, 3'-, 6_A- and 4-H), 3.38-3.34 (3H, m, 6'-, 6_B and 5"-H), 3.22 (1H, dd, *J* 10.3 and 3.8, 2-H), 2.73 (1H, app dt, *J* 12.7 and 4.5, $2'_B$-H), 2.11 (3H, s, O*Ac*), 2.02 (3H, s, O*Ac*), 2.01 (3H, s, O*Ac*), 2.00 (3H, s, O*Ac*) and 1.50 (1H, app q, *J* 12.7, $2'_A$-H); δ_C (125 MHz; $CDCl_3$) 170.7 (*C*=O), 170.2 (*C*=O), 169.3 (*C*=O), 168.9 (*C*=O), 137.7, 137.7, 136.7, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 98.9 (1"-C), 97.8 (1-C), 85.0, 79.2, 78.6, 77.8, 75.8 ($PhCH_2$), 75.7, 75.2 ($PhCH_2$), 75.0 ($PhCH_2$), 72.8, 72.2, 71.6, 71.0, 68.0, 62.7 (2-C), 61.7 (6"-C), 60.7, 59.4, 51.1 (6-C), 32.4 (2'-C), 21.0 (CH_3), 20.9 (CH_3), 20.6 (CH_3) and 20.5 (CH_3); *m/z* (ES) 1049.3 (100%, MNa^+); Found MNa^+ 1049.3770; $C_{47}H_{54}N_{12}O_{15}$ requires MNa^+ 1049.3729.

5'-(2",3",4",6"-tetra-*O*-acetyl-β-L-glucopyranosyl)-1',3',2,6,-tetraazido-6',3,4-tri-*O*-benzyl Neamine 30GH'

By Method C, the trichloroacetimidate donor **21H'** (176 mg, 0.36 mmol) and the acceptor **30G** (300 mg, 0.43 mmol) gave a crude product which was purified by column chromatography (gradient elution: 1 : 9 → 3 : 7 EtOAc−petrol) to yield **30GH'** (0.141 g, 38%) as a colourless oil, R_f 0.15 (2 : 8 EtOAc−petrol); $[\alpha]_D$ +84.7 (*c* 0.67, $CHCl_3$); ν_{max}/cm^{-1} (Thin film) 3032, 2939, 2105 (azide), 1758 (C=O) and 1367; δ_H (500 MHz; $CDCl_3$) 7.41-7.25 (15H, m, Ph × 3), 5.53 (1H, d, *J* 3.9, 1-H), 5.34 (1H, d, *J* 8.0, 1''-H), 5.19 (1H, t, *J* 9.5, 3''-H), 5.05 (1H, dd, *J* 9.5 and 8.0, 2''-H), 5.03 (1H, dd, *J* 9.5 and 9.2, 4''-H), 4.95 (1H, d, *J* 11.1, $PhCH_A$), 4.93 (1H, d, *J* 12.2, $PhCH_B$), 4.90 (1H, d, *J* 12.2, $PhCH_B$), 4.88 (1 H, d, *J* 11.2, $PhCH_C$), 4.68 (1H, d, *J* 11.1, $PhCH_A$), 4.64 (1H, d, *J* 11.2, $PhCH_C$), 4.37-4.34 (1H, m, 5-H), 4.06 (1H, dd, *J* 12.2 and 4.7, $6''_A$-H), 4.00-3.94 (3H, m, 5'-, 3- and $6''_B$-H), 3.70-3.66 (1H, m, 5''-H), 3.64 (1H, t, *J* 9.5, 4-H), 3.61 (1H, t, *J* 9.7, 4'-H), 3.54 (1H, dd, *J* 10.0 and 3.9, 2-H), 3.55-3.52 (1H, m, 6_A-H), 3.44-3.40 (1H, m, 1'-H), 3.39-3.36 (1H, m, 3-H '), 3.33-3.32 (1H, m, 6_B-H), 3.30 (1H, t, *J* 9.5, 6'-H), 2.26 (1H, app dt, *J* 13.0, 4.5, $2'_A$-H), 2.06 (3H, s, OAc), 2.01 (3H, s, OAc), 2.00 (3H, s, OAc), 1.96 (3H, s, OAc) and 1.42 (1H, app q, *J* 13.0, $2'_B$-H); δ_C (75 MHz; $CDCl_3$) 170.5 (CH_3CO), 169.9 (CH_3CO), 169.4 (CH_3CO), 169.0 (CH_3CO), 137.9, 137.5, 137.4, 128.5, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 99.3 (1''-C), 96.8 (1-C), 81.7, 81.5, 80.2, 78.5, 78.2, 75.7, 75.5, 75.2, 72.9, 72.1, 71.9, 71.6, 68.7, 63.7 (2-C), 62.0 (6''-C), 59.5, 59.0, 50.7 (6-C), 32.2 (2'-C), 20.6 (CH_3CO), 20.6 (CH_3CO), 20.6 (CH_3CO) and 20.5 (CH_3CO) (two aromatic peaks overlapped or missing); *m/z* (ES) 1049.2 (100%, MNa^+); Found MNa^+ 1049.3710; $C_{47}H_{54}N_{12}O_{15}$ requires MNa^+ 1049.3729.

General procedure for the deprotection of benzylated aminoglycoside derivatives (Method D)

The perbenzylated azidoaminoglycoside (0.12 mmol) was dissolved in a solution of THF (3.6 mL), and 0.1 M aqueous sodium hydroxide solution (0.3 mL) and trimethylphosphine (0.82 mL, 1 M in THF, 6 eq., 0.82 mmol) were added. The reaction was stirred at 50 °C for 2 h and followed by TLC (elution: 2:1 *i*PrOH−NH_4OH). The reaction mixture was cooled to room temperature and loaded onto a short column (4 cm silica and 1 cm of celite) and eluted (gradient elution 1:0:0 → 1:1:0 → 0:1:0 → 0:2:1 THF−MeOH−NH_4OH). The fractions containing required product were collected, concentrated under reduced pressure, dissolved in a degassed solution of 1:1 AcOH−H_2O (4 mL) and $Pd(OH)_2/C$ (20% Degussa type) was added. The reaction was stirred at room temperature under atmospheric pressure of hydrogen. After 2 days, the reaction mixture was filtered through a short pad of celite, eluted with water, and the filtrate was concentrated under reduced pressure.

General procedure for the debenzoylation (Method E)

Sodium methoxide (0.5 eq.) was added to a solution of benzylated aminoglycoside (0.22 mmol) in dry MeOH (1.4 mL). The reaction mixture was stirred at room temperature for 18h and concentrated under reduced pressure.

General procedure for the removal of a phthalimide group (Methods F)

Hydrazine acetate (83.0 mg, 0.90 mmol) was added in one portion to a stirred solution of the protected aminoglycoside (55.6 mg, 0.45 mmol) in toluene (0.8 ml) and ethanol (1.2 ml). The reaction mixture was heated at reflux at 110 °C for 5 days. The reaction was allowed to cool to room temperature and the solvent was removed under reduced pressure. The resulting residue was redissolved in 1:1 dichloromethane−ethanol (1:1) and washed with water (20 ml), and the aqueous layer was back-washed with dichloromethane−ethanol (10 ml, 1:1). The combined organic fractions were dried (Na_2SO_4) and the solvent removed under reduced pressure to give the crude product which was purified by column chromatography (elution: 7:3 petrol−EtOAc) to yield a solution of the crude product which was evaporated under reduced pressure.

Alternative procedure for the deprotection of benzylated aminoglycosides (Method G)

The perbenzylated azidoaminoglycoside (142.4 mg, 0.12 mmol) was dissolved in 1:1:1 EtOAc−MeOH−H_2O (6 mL), $Pd(OH)_2/C$ (150 mg) was added and the reaction was stirred under an atmospheric pressure of hydrogen. After two days, the reaction mixture was filtered through a short pad of celite, eluting sequentially with ethyl acetate, methanol and water. The filtrate was concentrated under reduced pressure, redissolved in a degassed solution of 1:1 AcOH−H_2O (4 mL), $Pd(OH)_2/C$ (20% Degussa type) added and the reaction mixture stirred under an atmospheric of hydrogen. After 2 days, the reaction mixture was filtered under a short pad of celite, eluting with water. The filtrate was concentrated under reduced pressure to give a crude product.

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4,6-diamino-cyclohexan-2,3-ol, tri-acetate salt 6A

By method D, **31A** (78.7 mg, 0.12 mmol) gave the aminoglycoside **6A** (51.9 mg, 86%) as an orange oil, $[\alpha]_D$ +13.3 (c. 0.15 in H_2O); δ_H (500 MHz, D_2O) 5.46 (1H, d, *J* 3.1, 1'-H), 3.96 (1H, t, *J* 8.2, 1-H), 3.69 (1H, dd, *J* 9.7 and 9.2, 4'-H), 3.64-3.24 (6H, m, 2'-H, 3'-H, 5'-H, 6'-H, 4-H and 6-H), 3.18-3.00 (3H, m, 6'-H, 2-H and 3-H), 2.21 (1H, broad d, *J* 12.3, 5-H_A), 1.85 (9H, s, 3 $OCOCH_3$) and 1.51-1.40 (1H, m, 5-H_B); δ_C (75 MHz, D_2O) 182 (C=O), 97.9 (1'-C), 82.6 (1-C), 75.2 (2'-C), 74.3 (3'-C), 72.6 (4'-C), 71.5-71.4 (2-C and 3-C), 61.3 (5'-C), 50.7, 48.7 (4-C and 6-C), 40.8 (6'-C), 31.8 (5-C), 23.7, 23.2 (CH_3); *m/z* (ES) 324.3 (40%, MH^+), 203.7 (100); (Found: MNa^+, 346.1588. $C_{12}H_{25}O_7N_3$ requires *MNa*, 346.1590).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-4,6-diamino-cyclohexan-2,3-ol, tri-acetate salts 6A'

By method D, **31A'** (57.9 mg, 0.09 mmol) gave the aminoglycoside **6A'** (23.3 mg, 51%) as an orange oil, $[\alpha]_D$ −26.7 (c. 0.15 in H_2O); δ_H (500 MHz, D_2O) 5.03 (1H, s, 1'-H), 4.07 (1H, m, 1-H), 3.68-3.55 (3H, m, 4'-H, 2'-H and 3'-H), 3.47-3.35 (5H, m, 5'-H, 6'-H, 2-H, 4-H and 6-H), 3.18-3.00 (2H, m, 6'-H and 3-H), 2.18 (1H, broad d, *J* 13.0, 5-H_A), 1.88 (9H, s, $OCOCH_3$) and 1.54-1.45 (1H, m, 5-H_B); δ_C (75 MHz, D_2O) 181.0 (C=O), 101.4 (1'-C), 85.6 (1-C), 74.7 (2'-C), 74.3 (3'-C), 73.1 (4'-C), 71.9, 71.2 (3-C and 2-C), 68.4 (5'-C), 51.1, 50.7 (4-C and 6-C), 40.6 (6'-C), 31.8 (5-C), 23.6, 23.1 (CH_3); *m/z* (ES) 324.3 (40%, MH^+) and 203.7 (100); (Found: MNa^+, 346.1584. $C_{12}H_{25}O_7N_3$ requires *MNa*, 346.1590).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-α-L-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol, tetra-acetate salt 6A'A'

By method D, **27 A'A'** (142 mg, 0.13 mmol) gave the aminoglycoside **6A'A'** (37.3 mg, 41%) as an orange oil; $[\alpha]_D$ –26.7 (c. 0.18 in H_2O); δ_H (500 MHz, D_2O) 5.51 (1H, br s, 1"-H), 5.06 (1H, br s, 1'-H), 4.11 (1H, m, 1-H), 3.92 (1H, m, 2'-H), 3.75-3.50 (10H, m, 2"-H, 3'-H, 3"-H, 4'-H, 4"-H, 5'-H, 5"-H, 3-H, 4-H and 6-H), 3.40-3.25 (4H, m, 6'-H, 6"-H and 2-H), 3.20-3.15 (1H, br m, 6'-H), 2.20-2.35 (1H, br m, 5-H_A), 1.88 (12H, s, OCOCH_3) and 1.60-1.50 (1H, m, 5-H_B); *m/z* (ES) 506.9 (100%, MNa^+), 484.9 (70, MH^+); (Found: MNa^+, 507.2272. $C_{18}H_{36}O_{11}N_4$ requires *MNa*, 507.2278).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6’-Amino-6’-deoxy-2’,3’,4’-triol-α-D-glucopyranosyl)-3-*O*-(6’’-Amino-6’’-deoxy-2’’,3’’,4’’-triol-α-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol, tetra-acetate salt 6AA

By method D, **27AA** (135 mg, 0.12 mmol gave the aminoglycoside **6AA** (21.7 mg, 25%) as a brown oil, $[\alpha]_D$ +20.2 (c. 0.21 in H_2O), spectroscopically identical to the enantiomer (**27A’A’**) prepared previously.

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6’-Amino-6’-deoxy-2’,3’,4’-triol-α-D-glucopyranosyl)-3-*O*-(6’’-Amino-6’’-deoxy-2’’,3’’,4’’-triol-α-L-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol, tetra-acetate salt 6AA’

By method D, **27AA’** (130 mg, 0.12 mmol) gave the aminoglycoside **6AA’** (66.8 mg, 77%) as a brown oil, δ_H (500 MHz, D_2O) 5.50 (2H, broad s, 1'-H and 1"-H), 3.91 (1H, broad s, 1-H), 3.71-3.51 (7H, m, 2'-H, 2"-H, 3'-H, 3"-H, 4'-H, 4"-H, and 2-H), 3.45-3.20 (8H, m, 5'-H, 5"-H, 6'-H, 6"-H, 4-H and 6-H), 3.18-3.00 (1H, m, 3-H), 2.40-2.30 (1H, m, 5-H_A), 1.82 (12H, s, OCOCH_3) and 1.70-1.60 (1H, m, 5-H_B); δ_C (75 MHz, D_2O) 181.9 (C=O), 103.9 (1'-C), 80.6 (1-C), 75.6, 73.7, 72.7 (2'-C, 3'-C and 4'-C), 71.2, 71.1 (3-C and 2-C), 69.1 (5'-C), 48.2 (4-C and 6-C), 40.6 (6'-C), 29.4 (5-C) and 23.5 (CH_3); *m/z* (ES) 485.5 (60%, MH^+), 324.3 (53), 203.7 (100) and 143.1 (84); (Found: MNa^+, 507.2153. $C_{18}H_{36}O_{11}N_4$ requires *MNa*, 507.2150).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-α-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol, tetra-acetate salt 6A'A

By method D, **27A'A** (101 mg, 0.09 mmol) gave the aminoglycoside **6A'A** (29.6 mg, 46%) as an orange oil, δ_H (500 MHz, D_2O) 5.07 (2H, br s, 1'-H and 1''-H), 4.06 (1H, m, 1-H), 3.88-3.60 (8H, m, 3'-H, 3''-H, 4'-H, 4''-H, 5'-H, 5''-H, 4-H and 6-H), 3.50-3.10 (7H, m, 2'-H, 2''-H, 6'-H, 6''-H and 2-H), 2.20-2.30 (1H, br m, 5-H_A), 1.90 (12H, s, OCOCH_3) and 1.60-1.50 (1H, m, 5-H_B); *m/z* (ES) 506.9 (100%, MNa^+), 484.9 (85, MH^+) and 298.9 (68); (Found: MH^+, 485.2473. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-3-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol, tetra-acetate salt 6AB

By methods E and D, **27AB** (69 mg, 0.06 mmol) gave the aminoglycoside **6AB** (16 mg, 37%) as a brown oil, $[\alpha]_D$ –126 (c. 1.00 in H_2O); δ_H (500 MHz, D_2O) 5.40 (1H, broad s, 1'-H or 1''-H), 4.75 (1H, broad s, 1'-H or 1''-H), 3.95-3.20 (10H, m), 3.20-3.05 (1H, m), 2.40-2.30 (1H, m, 5-H_A), 2.20 (12H, s, CH_3) and 1.80-1.70 (1H, m, 5-H_B); *m/z* (ES) 485.1 (10%, MH^+), 177.7 (60) and 141.7 (100); (Found: MH^+, 485.2452. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-3-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-L-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6AB'

By methods E and D, 27**AB'** (51 mg, 0.04 mmol) gave the aminoglycoside **6AB'** (16.9 mg, 58%) as a brown oil, $[\alpha]_D$ 20.0 (c. 0.58 in H_2O); δ_H (500 MHz, D_2O) 4.80-4.65 (2H, broad m, 1'-H and 1''-H), 3.90-3.10 (11H, m), 2.50-2.40 (1H, m, 5-H_A), 2.01 (12H, s, CH_3) and 1.60-1.50 (1H, m, 5-H_B); *m/z* (ES) 485.1 (8%, MH^+), 346.7 (25) and 231.7 (50); (Found: MH^+, 485.2456. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6A'B

By methods E and D, **27A'B** (45 mg, 0.04 mmol) gave the aminoglycoside **6A'B** (14 mg, 48%) as a brown oil; $[\alpha]_D$ –40.0 (c. 1.3 in H_2O); δ_H (500 MHz, D_2O) 4.75 (1H, broad s, 1'-H), 4.52 (1H, d, *J* 7.2, 1"-H), 3.79-3.50 (2H, m), 3.50-3.28 (5H, m), 3.28-2.78 (10H, m), 2.23-2.09 (1H, m, 5-H_A), 1.63 (12H, s, CH_3) and 1.53-1.38 (1H, m, 5-H_B); δ_C (75 MHz, D_2O) 183.0 (C=O), 102.8, 101.3 (1'-C and 1"-C), 83.8, 75.3, 74.0, 73.3, 73.0, 71.9, 71.0, 68.8, 50.8, 49.2, 40.6 (CH_2), 30.6 and 23.6 (CH_3); *m/z* (ES) 485.1 (32%, MH^+); (Found: MH^+, 485.2455. $C_{18}H_{37}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-L-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6A'B'

By methods E and D, 27**A'B'** (36 mg, 0.03 mmol) gave the aminoglycoside **6A'B'** (7.2 mg, 33%) as a brown oil, $[\alpha]_D$ –57.2 (c. 0.72 in H_2O); δ_H (500 MHz, D_2O) 5.25-5.11 (1H, m, 1'-H or 1"-H), 4.86-4.75 (1H, m, 1'-H or 1"-H), 4.19-3.69 (4H, m), 3.69-3.25 (13H, m), 2.59-2.50 (1H, m, 5-H), 2.13 (12H, s, CH_3) and 2.13-1.90 (1H, m, 5-H); *m/z* (ES) 485.1 (10%, MH^+) and 143.0 (100); (Found: MH^+, 485.2463. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-3-*O*-(3''-Amino-3''-deoxy-2'',4'',6''-triol-β-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6AD

By methods E and D, 27**AD** (61.2 mg, 0.06 mmol) gave the aminoglycoside **6AD** (22 mg, 51%) as a brown oil, $[\alpha]_D$ –43.3 (c. 0.12 in H_2O); δ_H (500 MHz, D_2O) 5.58-5.48 (1H, m, 1"-H), 5.00-4.88 (1H, m, 1'-H), 4.00-3.48 (12H, m), 3.48-3.29 (3H, m), 3.29-3.08 (2H, m, 3"-H and 6"-H_A), 2.55-2.39 (1H, m, 5-H_A), 2.05-1.81 (1H, m, 5-H_B) and 1.93 (12H, s, CH_3); δ_C (75 MHz, D_2O) 180.0 (C=O), 106.1-103.9 (1"-C and 1'-C), 77.2, 71.1, 69.9, 66.1, 60.4, 57.9

(CH_2), 49.2, 40.7 (CH_2), 27.5 (CH_2) and 22.8 (CH_3); *m/z* (ES) 507.2 (50%, MNa^+) and 485.1 (100%, M^++H); (Found: MNa^+, 507.2300. $C_{18}H_{36}O_{11}N_4$ requires *MNa*, 507.2278).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(3''-Amino-3''-deoxy-2'',4'',6''-triol-β-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6A'D

By methods E and D, **27A'D** (43.6 mg, 0.04 mmol) gave the aminoglycoside **6A'D** (19.4 mg, 67%) as a brown oil, $[\alpha]_D$ –32.8 (c. 1.28 in H_2O); δ_H (500 MHz, D_2O) 5.07-5.00 (1H, m, 1''-H), 4.85-4.75 (1H, m, 1'-H), 4.07-3.96 (1H, m), 3.96-3.42 (12H, m), 3.42-3.25 (2H, m), 3.25-3.10 (2H, m), 2.50-2.38 (1H, m, 5-H_A), 2.00 (12H, s, CH_3) and 2.00-1.83 (1H, m, 5-H_B); *m/z* (ES) 507.1 (23%, MNa^+) and 485.1 (65%, MH^+); (Found: MH^+, 485.2467. $C_{18}H_{37}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(3''-Amino-3''-deoxy-2'',4'',6''-triol-α-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6A'C

By method D, **27A'C** (54.9 mg, 0.05 mmol) gave the aminoglycoside **6A'C** (31.9 mg, 88%) as a brown oil; $[\alpha]_D$ +10.0 (c. 0.84 in H_2O); δ_H (500 MHz, D_2O) 5.01 (1H, d, *J* 3.2, 1''-H), 5.00 (1H, broad s, 1'-H), 4.05-3.95 (1H, m), 3.90-3.80 (1H, m, 2''-H), 3.80-3.50 (7H, m), 3.50-3.05 (8H, m), 2.45-2.38 (1H, m, 5-H_A), 1.99 (12H, s, CH_3) and 1.99-1.80 (1H, m, 5-H_B); δ_C (75 MHz, D_2O) 180.7 (C=O), 102.1, 99.2 (1'-C and 1''-C), 83.8, 73.2, 72.0, 70.9, 68.5, 65.9, 60.4 (CH_2), 50.3, 40.5 (CH_2), 27.9 (CH_2) and 22.9 (CH_3); *m/z* (ES) 485.3 (100%, MH^+), 396.3 (50) and 324.2 (40); (Found: MH^+, 485.2482. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-3-*O*-(2''-Amino-2''-deoxy-3'',4'',6''-triol-α-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6AE

By method D, 27**AE** (29 mg, 0.03 mmol) gave the aminoglycoside **6AE** (13.8 mg, 63%) as a brown oil; $[\alpha]_D$ +34.8 (c. 1.38 in H_2O); δ_H (500 MHz, D_2O) 5.51-5.50 (1H, m, 1'-H), 4.80-

4.72 (1H, m, 1''-H), 4.12-3.37 (14H, m), 3.36-3.10 (3H, m), 2.61-2.50 (1H, m, 5-H_A), 1.98 (12H, s, CH_3) and 1.77-1.65 (1H, m, 5-H_B); δ_C (75 MHz, D_2O) 181.7, 180.5 (C=O), 104.2 (1''-C), 95.9 (1'-C), 79.4, 73.6, 72.7, 72.1, 69.1, 60.8 (CH_2), 54.4, 50.0, 40.7 (CH_2), 22.6 (CH_2) and 20.7 (CH_3); *m/z* (ES) 507.1 (20%, MNa^+), 485.1 (100%, MH^+) and 324.1 (60); (Found: MH^+, 485.2451. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(2''-Amino-2''-deoxy-3'',4'',6''-triol-α-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6A'E

By method D, 27**A'E** (36.2 mg, 0.32 mmol) gave the aminoglycoside **6A'E** (12.9 mg, 6%) as a brown oil; $[\alpha]_D$, 204.4 (c. 0.64 in H_2O); δ_H (500 MHz, D_2O) 5.42-5.37 (1H, m, 1'-H), 5.04-5.00 (1H, m, 1''-H), 4.00-3.53 (7H, m), 3.53-3.25 (5H, m), 3.17-3.05 (1H, m, 2''-H), 2.43-2.30 (1H, m, 5-H_A), 1.93 (12H, s, CH_3) and 1.80-1.68 (1H, m, 5-H_B); *m/z* (ES) 485.2 (100, MH^+) and 324.2 (40); (Found: MH^+, 485.2459. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2457).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-3-*O*-(2''-Amino-2''-deoxy-3'',4'',6''-triol-β-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6AF

By methods F and D, **27AF** (55.6 mg, 0.45 mmol) gave the aminoglycoside **6AF** (13.2 mg, 4%) as a brown oil; $[\alpha]_D$ +15.7 (c. 1.32 in H_2O); δ_H (500 MHz, D_2O) 5.45 (1H, d, *J* 3.3, 1'-H), 4.91 (1H, d, *J* 8.3, 1''-H), 3.96-3.79 (4H, m), 3.71-3.25 (11H, m), 3.14-3.03 (2H, m, 6'-H and 2''-H), 2.50-2.40 (1H, m, 5-H_A), 1.96 (12H, s, CH_3) and 1.89-1.79 (1H, m, 5-H_B); *m/z* (ES) 485.1 (18%, MH^+) and 101.0 (100); (Found: MH^+, 485.2446. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*S*,3*S*,4*R*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-L-glucopyranosyl)-3-*O*-(2''-Amino-2''-deoxy-3'',4'',6''-triol-β-D-glucopyranosyl)-4,6-diamino-cyclohexan-1,2,3-ol tetra-acetate salt 6A'F

By methods F and D, 27**A'F** (62.4 mg, 0.51 mmol) gave the aminoglycoside **6A'F** (13.2 mg, 4%) as a brown oil, $[\alpha]_D$ –53.9 (c. 0.75 in H_2O); δ_H (500 MHz, D_2O) 5.00 (1H, d, *J* 2.5, 1'-H), 4.93 (1H, d, *J* 8.4, 1"-H), 4.08-3.96 (1H, m, 6"-H_A), 3.96-3.55 (7H, m, 2-H, 2'-H, 6'-H, 4"-H, 5"-H and 6"-H), 3.55-3.04 (6H, m, 1-H, 3-H, 4-H, 6-H, 3'-H and 4'-H), 2.53-2.39 (1H, m, 5-H_A), 1.98-1.75 (1H, m, 5-H_B) and 1.90 (12H, s, CH_3); δ_C (75 MHz, D_2O) 180.9 (C=O), 102.2, 99.8 (1'-C and 1"-C), 83.8, 79.8, 76.9, 73.5, 73.0, 72.1, 71.9, 70.8, 69.8, 68.9, 60.7 (CH_2), 56.0, 50.6, 48.7, 40.5 (CH_2), 30.6, 27.9 (CH_2) and 23.1 (CH_3); *m/z* (ES) 507.2 (16%, MNa^+), 485.1 (88%, MH^+), 284.2 (78) and 263.7 (100); (Found: MH^+, 485.2448. $C_{18}H_{36}O_{11}N_4$ requires *MH*, 485.2459).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-α-D-glucopyranosyl)-2,5-diamino-cyclohexanol, tetra-acetate salt 7AA

By method G, **28AA** (142.4 mg, 0.12 mmol) gave the aminoglycoside **7AA** (77.0 mg, 85% after two steps) as an orange oil, $[\alpha]_D$ +47.6 (c. 1.10 in H_2O); δ_H (300 MHz, D_2O) 5.00 (2H, d, *J* 2.9, 1'-H and 1"-H), 4.08-3.96 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.88-3.76 (2H, m, 5'-H and 5"-H), 3.69-3.56 (4H, m, 3'-H, 3"-H, 1-H or 4-H and 2-H or 5-H), 3.56-3.46 (2H, m, 2'-H and 2"-H), 3.35-3.21 (4H, m, 4'-H, 4"-H, 6'-H_A and 6"-H_A), 3.14-3.02 (2H, m, 6'-H_B and 6"-H_B), 2.34-2.10 (4H, m, 3-H and 6-H) and 1.88 (12H, s, 4 $OCOCH_3$); δ_C (75 MHz, D_2O) 180.0 (C=O), 99.5 (1'-C and 1"-C), 73.4, 72.4, 71.3, 71.2, 68.9 (5'-C and 5"-C), 49.1 (2-C and 5-C), 40.6 (6'-C and 6"-C), 29.9 (3-C and 6-C) and 22.7 (CH_3); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2535; $C_{18}H_{37}N_4O_{10}$ requires *MH*, 469.2510).

(1*S*,2*S*,4*S*,5*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-α-D-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetra-acetate salt 7'AA

By method G, **28'AA** (93.0 mg, 0.08 mmol) gave the aminoglycoside **7'AA** (50.0 mg, 84% after two steps) as an orange oil; $[\alpha]_D$ +91.2 (c. 1.00 in H_2O); δ_H (300 MHz, D_2O) 5.03 (2H, d, *J* 2.9, 1'-H and 1"-H), 4.09-3.94 (2H, m, 1-H or 4-H and 2-H or 5-H), 3.75-3.66 (2H, m, 5'-

H and 5''-H), 3.66-3.54 (4H, m, 3'-H, 3''-H, 1-H or 3-H and 2-H or 5-H), 3.54-3.40 (2H, m, 2'-H and 2''-H), 3.31-3.16 (4H, m, 4'-H, 4''-H, 6'-H_A and 6''-H_A), 3.11-3.00 (2H, m, 6'-H_B and 6''-H_B), 2.25-2.00 (4H, m, 3-H and 6-H) and 1.92 (12H, s, 4 $OCOCH_3$); δ_C (75 MHz, D_2O) 180.0 (C=O), 95.9 (1'-C and 1''-C), 72.2, 71.3, 70.9, 70.3, 68.8, 49.5 (2-C and 5-C),40.6 (6'-C and 6''-C), 27.5 (3-C and 6-C) and 24.4 (CH_3); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2534; $C_{18}H_{37}N_4O_{10}$ requires *MH*, 469.2510).

(1*S*,2*S*,4*S*,5*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-α-L-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetra-acetate salt 7'AA'

By method G, **28'AA'**(40.3 mg, 36.14 μmol) was converted into the *acetate salt of aminoglycoside* **7'AA'** (17.3 mg, 68%) as a colourless amorphous solid; $[\alpha]_D^{20}$ $+12.7$ (*c* 1.23 in H_2O); δ_H (500 MHz; D_2O) 5.05-2.12 (20H, m) and 1.95 (12H, s, OAc); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2534; $C_{18}H_{37}N_4O_{10}$ requires *MH*, 469.2510).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-D-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetraacetate salt 7AB

By methods E and G, **28AB** (185.0 mg, 0.16 mmol) gave the aminoglycoside **7AB** (87.6 mg, 77% after two steps) as an orange oil, $[\alpha]_D$ +11.9 (c. 0.97 in H_2O); δ_H (300 MHz, D_2O) 5.08-5.00 (2H, m, 1'-H or 1''-H and H), 4.64-4.35 (2H, m, 1'-H or 1''-H and H), 4.35-4.00 (2H, m), 4.00-3.00 (12H, m), 3.00-2.50 (4H, m), 2.34-2.03 (2H, m), 1.91 (12H, s, 4 $OCOCH_3$), 1.91-1.75 (2H, m, 3-H and 6-H) and 1.36-1.09 (2H, m, 3-H and 6-H); δ_C (75 MHz, D_2O) 180.6-180.3-179.8 (C=O), 100.2-98.0 (1'-C and 1''-C), 75.2, 72.7, 72.4, 71.4, 70.9, 50.1, 49.6, 33.7 (3-C and 6-C) and 22.6 (CH_3); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2503; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2504).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-L-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetraacetate salt 7AB'

By methods E and G, **28AB'** (171.0 mg, 0.15 mmol) gave the aminoglycoside **7AB'** (87.8 mg, 83% over two steps) as an orange oil, $[\alpha]_D$ +38.4 (c. 0.97 in H_2O); δ_H (300 MHz, D_2O) 5.04 (1H, br s, 1'-H), 4.56 (1H, d, *J* 7.7, 1''-H), 4.21-4.08 (1H, m, 1-H or 2-H or 4-H or 5-H), 4.08-3.97 (1H, m, 1-H or 2-H or 4-H or 5-H), 3.89-3.78 (2H, m, 5'-H and 5''-H), 3.71-3.43 (5H, m, 1-H or 2-H or 4-H or 5-H, 2'-H, 3'-H and 3''-H), 3.43-3.19 (5H, m, 2''-H, 4'-H, 4''-H, 6'-H_A and 6''-H_A), 3.19-3.00 (2H, m, 6'-H_B and 6''-H_B), 2.37-2.07 (4H, m, 3-H and 6-H) and 1.89 (12H, s, 4 $OCOCH_3$); δ_C (75 MHz, D_2O) 180.1 (C=O), 102.6, 99.7 (1'-C and 1-C), 75.3, 73.8, 73.0, 72.4, 72.3, 71.3, 69.9, 49.2, 40.6, 29.9 and 22.6 (CH_3); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2503; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2504).

(1*S*,2*S*,4*S*,5*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(6''-Amino-6''-deoxy-2'',3'',4''-triol-β-L-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetraacetate salt 7'AB'

By method E and G, **28'AB'** (12.2 mg, 10.56 μmol) was converted into the *acetate salt of aminoglycoside* **7'AB'** (7.3 mg, 98%) as a colourless amorphous solid; $[\alpha]_D^{20} +36.3$ (*c* 0.39 in H_2O); δ_H (500 MHz; $CDCl_3$) 5.18-1.14 (34H, m); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2503; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2504).

(1*R*,2*R*,4*R*,5*R*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(3''-Amino-3''-deoxy-2'',4'',6''-triol-α-D-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetraacetate salt 7AC

By method G, **28AC** (117.2 mg, 0.11 mmol) gave **7AC** (59.0 mg, 79% over two steps) as an orange oil, $[\alpha]_D$ +65.0 (c. 0.84 in H_2O); δ_H (300 MHz, D_2O) 5.16-5.00 (2H, m, 1'-H and 1''-H), 4.25-4.00 (2H, m), 3.94-3.44 (8H, m, 2'-H, 3'-H, 4'-H, 5'-H, 2''-H, 3''-H, 4''-H and 5''-H), 3.44-3.00 (4H, m, 6'-H, and 6''-H), 3.00-2.59 (2H, m), 2.41-2.15 (3H, m, 3-H and 6-H), 1.96 (12H, s, 4 $OCOCH_3$) and 1.30-1.34 (1H, m, 3-H_B or 6-H_B); δ_C (75 MHz, D_2O) 179.4 (C=O), 99.3, 98.8 (1'-C and 1"-C), 74.0, 72.9, 72.4, 71.2, 68.8, 68.1, 66.0, 60.2, 55.2, 49.3, 49.1, 40.6, 30.0, 29.8, 27.2 and 22.4 (CH_3); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+, 469.2499; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

(1*S*,2*S*,4*S*,5*S*)-1-*O*-(6'-Amino-6'-deoxy-2',3',4'-triol-α-D-glucopyranosyl)-4-*O*-(3''-Amino-3''-deoxy-2'',4'',6''-triol-α-D-glucopyranosyl)-2,5-diamino-cyclohexane-1,4-diol, tetraacetate salt 7'AC

By method G, **28'AC** (15.3 mg, 13.75 µmol) was converted into the *acetate salt of aminoglycoside* **7'AC** (7.1 mg, 73%) as a colourless amorphous solid; $[\alpha]_D^{20} + 3.4$ (*c* 0.37 in H_2O); δ_H (500 MHz; $CDCl_3$) 5.15-1.11 (32H, m); *m/z* (ES) 469 (100%, MH^+); (Found: MH^+ 469.2505; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2504).

(1*S*,3*S*,4*S*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8A

By method G, **29A** (124.1 mg, 0.189 mmol) was converted into the *acetate salt of aminoglycoside* **8A** (38.2 mg, 42%) as a colourless amorphous solid; $[\alpha]_D^{20} + 20.0$ (*c* 0.96 in H_2O); δ_H (500 MHz; D_2O) 5.11 (1H, d, *J* 3.1, 1'-H), 4.12-3.05 (10H, m, 6'-H, 5'-H, 4'-H, 3'-H, 2'-H, 1-H, 3-H, 4-H and 6-H), 2.72-2.67 (1H, m, 5-H or 2-H), 2.22-2.15 (3H, m, 5-H and 2-H) and 1.84 (9H, s, OAc); *m/z* (ES) 307 (100%, MH^+); (Found: MH^+ 307.1817; $C_{12}H_{26}N_4O_5$ requires *MH*, 307.1981).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'A

By method G, **29'A** (22.1 mg, 33.7 µmol) was converted into the *acetate salt of aminoglycoside* **8'A** (16.8 mg, 100%) as a colourless amorphous solid; $[\alpha]_D^{20} + 50.5$ (*c* 1.68 in H_2O); δ_H (500 MHz; D_2O) 5.31 (1H, br s, 1'-H), 4.24 (1H, br s, 3'-H) 4.00-3.96 (1H, m, 5'-H), 3.87-3.80 (3H, m, 3-H, 1-H and 4-H or 6-H), 3.73-3.71 (1H, m, 4-H or 6-H), 3.45-3.32 (3H, m, 6_a'-H, 4'-H and 2'-H), 3.21 (1H, dd, ^2J 13.5 and *J* 6.9, 6_b'-H), 2.27-2.15 (4H, m, 5-H and 2-H) and 1.96 (9H, s, OAc); *m/z* (ES) 307 (100%, MH^+); (Found: MH^+ 307.1813; $C_{12}H_{26}N_4O_5$ requires *MH*, 307.1981).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(2',6'-Amino-2',6'-deoxy-α-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8G

By method G, **29G** (31.8 mg, 53.84 μmol) was converted into the *acetate salt of aminoglycoside* **8G** (29 mg, 100%) as a colourless amorphous solid; $[\alpha]_D^{20}$ +10.4 (*c* 1.31 in H_2O); δ_H (500 MHz; D_2O) 4.70-1.25 (15H, m) and 1.77 (12H, s, OAc); *m/z* (ES) 307 (100%, MH^+); (Found: MH^+ 307.1823; $C_{12}H_{26}N_4O_5$ requires *MH*, 307.1981).

(1*S*,3*S*,4*S*,6*S*)-1-*O*-(2',6'-Amino-2',6'-deoxy-α-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'G

By method G, **29'G** (57.8 mg, 97.9 μmol) was converted into the *acetate salt of aminoglycoside* **8'G** (35.9 mg, 67%) as a colourless amorphous solid; $[\alpha]_D^{20}$ +18.5 (*c* 1.64 in H_2O); δ_H (500 MHz; D_2O) 5.03 (1H, d, *J* 3.1, 1'-H), 4.14-4.12 (1H, m, 3'-H), 4.07-4.01 (1H, m, 5'-H), 3.88-3.83 (1H, m, 1-H), 3.69-3.63 (2H, m, 3-H and 4-H or 6-H), 3.56 (1H, dd, ^2J 11.1 and *J* 3.6, 6_a'-H), 3.42-3.30 (3H, m, 4'H, 2'-H and 4-H or 6-H), 3.15 (1H, dd, ^2J 11.1 and *J* 7.6 , 6_b'-H), 2.26-2.24 (2H, m, 5-H or 2-H), 2.16-2.12 (1H, m, 5-H or 2-H), 2.06-2.03 (1H, m, 5-H or 2-H) and 1.99 (12H, s, OAc); δ_C (75 MHz, D_2O) 178.0, 95.6, 73.6, 71.0, 69.4, 65.9, 53.6, 50.5, 47.9, 40.3, 33.7, 26.9 and 21.4 (one carbon signal missing or overlapped); *m/z* (ES) 307.4 (100%, MH^+); (Found: MH^+ 307.1969; $C_{12}H_{26}N_4O_5$ requires *MH*, 307.1981).

(1*S*,3*S*,4*S*,6*S*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-3-*O*-(6''-amino-6''-deoxy-α-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8AA

By method G, **29AA** (26 mg, 22.5 μmol) was converted into the *acetate salt of aminoglycoside* **8AA** (15.7 mg, 98%) as a colourless amorphous solid; $[\alpha]_D^{20}$ + 2.3 (*c* 1.57 in H_2O); δ_H (500 MHz; D_2O) 5.09-1.14 (34H, m); *m/z* (ES) 469 (100%, M^+); (Found: MH^+ 469.2512; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

(1*R*,3*R*,4*R*,6*R*)-1,3-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'AA

By method G, **29'AA** (70.8 mg, 63.61 μmol) was converted into the *acetate salt of aminoglycoside* **8'AA** (26 mg, 58%) as a colourless amorphous solid; $[\alpha]_D^{20} + 77.5$ (*c* 0.96 in H_2O); δ_H (500 MHz; D_2O) 5.05 (2H, br s, 1'-H), 4.22-2.23 (20H, m) and 1.87 (12H, s, OAc); *m/z* (ES) 469 (100%, M^+); (Found: MH^+ 469.2513; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-3-*O*-(6''-amino-6''-deoxy-α-L-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'AA'

By method G, **29'AA'** (45.8 mg, 0.041 mmol) was converted into the *acetate salt of aminoglycoside* **8'AA'** (22.4 mg, 77%) as a colourless amorphous solid; $[\alpha]_D^{20} - 3.8$ (*c* 0.85 in H_2O); δ_H (500 MHz; D_2O) 5.24 (1H, d, *J* 3.9, 1'-H or 1''-H), 5.16 (1H, *J* d, 3.9, 1'-H or 1''-H), 4.42-1.31 (32H, m, 6''-H, 6'-H, 6-H, 5''-H, 5'-H, 5-H, 4''-H, 4'-H, 4-H, 3''-H, 3'-H, 3-H, 2''-H, 2'-H, 2-H, 1-H and OAc); *m/z* (ES) 469.5 (100%, MH^+); *m/z* (ES) 469 (100%, M^+); (Found: MH^+ 469.2513; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-3-*O*-(6''-amino-6''-deoxy-β-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'AB

By method E and G, **29'AB** (22.9 mg, 19.8 μmol) was converted into the *acetate salt of aminoglycoside* **8'AB** (8.3 mg, 59%) as a colourless amorphous solid; $[\alpha]_D^{20} + 10.6$ (*c* 0.83 in H_2O); δ_H (500 MHz; D_2O) 5.09 (2H, br s, 1'-H and 1''-H), 4.46-2.03 (20H, m) and 1.93 (12H, s, OAc); *m/z* (ES) 469 (100%, M^+); (Found: MH^+ 469.2513; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-3-*O*-(6''-amino-6''-deoxy-β-L-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'AB'

By method E and G, **29'AB'** (67.3 mg, 58.3 μmol) was converted into the *acetate salt of aminoglycoside* 8**'AB'** (40.3 mg, 97%) as a colourless amorphous solid; $[\alpha]_D^{20} + 8.09$ (*c* 0.89

in H_2O); δ_H (500 MHz; D_2O) 5.18-1.75 (34H, m); *m/z* (ES) 469 (100%, M^+); (Found: MH^+ 469.2510; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

(1*R*,3*R*,4*R*,6*R*)-1-*O*-(6'-Amino-6'-deoxy-α-D-glucopyranosyl)-3-*O*-(3''-amino-3''-deoxy-β-D-glucopyranosyl)-4,6-diamino-cyclohexane-1,3-diol 8'AC

By method G, **29'AC** (79.9 mg, 0.072 mmol) was converted into the *acetate salt of aminoglycoside* 8**'AC** (30.3 mg, 59%) as a colourless amorphous solid; $[\alpha]_D^{20} + 63.9$ (*c* 1.1 in H_2O); δ_H (500 MHz; D_2O) 5.20-5.11 (2H, m, 1'-H and 1''-H), 4.42-2.79 (14H, m, 6''-H, 6'-H, 6-H, 5''-H, 5'-H, 4''-H, 4'-H, 4-H, 3''-H, 3'-H, 3-H, 2''-H, 2'-H and 1-H), 2.45-2.31 (4H, m, 5-H and 2-H) and 2.01 (12H, s, OAc); *m/z* (ES) 469 (100%, M^+); (Found: MH^+ 469.2515; $C_{18}H_{36}N_4O_{10}$ requires *MH*, 469.2510).

5'-(β-D-Glucopyranosyl)-Neamine, tetraacetate salt 9GH

By Methods E and D, **30GH** (57 mg, 0.056 mmol) gave the aminoglycoside **9GH** (19 mg, 48%) as a yellow-brown oil, R_f 0.05 (2:1 ^{i}PrOH–NH_4OH); $[\alpha]_D$ +37.7 (*c* 0.35, H_2O); δ_H (500 MHz; D_2O) 5.92 (1H, br s, 1-H), 5.01 (1H, d, *J* 8.9, 1"-H), 4.04 (1H, t, *J* 8.9, 5'-H), 3.94 (1H, t, *J* 8.9, 3-H), 3.92 (1H, t, *J* 8.9, 4'-H), 3.89-3.84 (1H, m, 5-H), 3.83 (1H, br d, *J* 12.3, $6''_B$-H), 3.76 (1H, dd, *J* 9.4 and 8.9, 6'-H), 3.72 (1H, br d, *J* 12.3, $6''_A$-H), 3.46 (1H, br dd, *J* 9.4, 3"-H), 3.43 (1H, m, 3'-H), 3.42-3.40 (4H, m, 4-, 2-, 4"- and 5"-H), 3.39-3.35 (1H, m, 6_B-H), 3.31 (1H, br dd, *J* 9.4 and 8.9, 2"-H), 3.27-3.24 (1H, m, 1'-H), 3.22 (1H, br dd, *J* 13.7 and 4.7, 6_A-H), 2.41-2.36 (1H, m, $2'_A$-H), 1.89 (12H, br s, OAc × 4) and 1.77 (1H, app q, *J* 12.4, $2'_B$-H); δ_C (75 MHz; D_2O) 180.7 (*C*=O), 103.0 (1"-C), 95.8 (1-C), 81.0 (5'-C), 76.7, 75.9, 73.7, 73.4, 70.8, 69.6, 69.4, 68.5, 60.0 (6"-C), 53.7, 49.9, 49.0, 40.3 (6-C), 28.8 (2'-C) and 23.0 (CH_3); *m/z* (ES) 485.2 (100%, MH^+); Found MH^+ 485.2454; $C_{18}H_{36}N_4O_{11}$ requires MH^+ 485.2459.

5'-(2"-amino-2"-deoxy-*β*-D-glucopyranosyl)-Neamine, tetraacetate salt 9GF

By Method F and D, **30GF** (0.128 g, 0.1 mmol) gave the aminoglycoside **9GF** (42 mg, 42%) as a yellow-brown oil; R_f 0.05 (2 : 1 ^{i}PrOH–NH_4OH); $[\alpha]_D$ +20.0 (*c* 0.46, H_2O); δ_H (500 MHz; D_2O) 5.84 (1H, d, *J* 3.4, 1-H), 5.16 (1H, d, *J* 8.1, 1"-H), 4.05 (1H, t, *J* 9.1, 5'-H), 3.97

(1H, t, *J* 9.1, 4'-H), 3.90 (1H, t, *J* 9.1, 3-H), 3.79-3.68 (4H, m, 5-, 6'-, 6"$_A$- and 6"$_B$-H), 3.60 (1H, t, *J* 8.7, 3"-H), 3.46-3.41 (2H, m, 4"- and 3'-H), 3.40-3.34 (3H, m, 2-, 4- and 5"-H), 3.31 (1H, dd, *J* 13.6 and 3.1, 6$_A$-H), 3.24 (1H, m, 1'-H), 3.19 (1H, dd, *J* 13.6 and 5.8, 6$_B$-H), 3.11 (1H, dd, *J* 8.7 and 8.1, 2"-H), 2.36-2.33 (1H, m, 2'$_A$-H), 1.92 (15H, s, AcO × 5) and 1.76 (1H, app q, *J* 12.2, 2'$_B$-H); δ_C (125 MHz; D_2O) 179.7 (CH_3*C*O), 102.3 (1"-C), 97.8 (1-C), 82.9 (5'-C), 79.2 (5"-C), 77.1 (4'-C), 75.3 (6'-C), 74.4 (3"-C), 72.0 (5-C), 71.7 (4"-C), 70.6 (3-C), 61.8 (6"-C), 58.3 (2"-C), 55.8 (2-C), 52.5 (1'-C), 51.2 (3'-C), 42.5 (6-C), 30.7 (2'-C) and 23.2 (*C*H_3CO); *m/z* (ES) 485.2 (100%, MH^+); Found MH^+ 485.2474; $C_{18}H_{36}N_4O_{11}$ requires MH^+ 485.2459.

5'-(*β*-L-glucopyranosyl)-Neamine, tetraacetate salt 9GH'

By Methods E and D, **30GH'** (129 mg, 0.13 mmol) gave the aminoglycoside **9GH'** (44 mg, 61%) as a yellow-brown oil, R_f 0.05 (2:1 ^{i}PrOH–NH_4OH); $[\alpha]_D$ +45.0 (*c* 0.4 in H_2O);); δ_H (500 MHz; D_2O) 5.92 (1H, d, *J* 3.6, 1-H), 4.71 (1H, d, *J* 7.9, 1"-H), 3.98 (1H, t, *J* 9.5, 4'-H), 3.94-3.91 (1H, m, 5-H), 3.92-3.89 (1H, m 5'-H), 3.89-3.86 (1H, m, 6"$_A$-H), 3.71 (1H, t, *J* 9.7, 6'-H), 3.58 (1H, dd, *J* 8.4 and 4.9, 6"$_B$-H), 3.47 (1H, t, *J* 9.2, 3"-H), 3.48-3.45 (1H, m, 5"-H), 3.42 (1H, t, *J* 9.1, 4-H), 3.39-3.34 (5H, m, 2-, 2"-, 3'-, 6$_A$- and 3-H), 3.31 (1H, t, *J* 9.2, 4"-H), 3.29-3.26 (1H, m, 1'-H), 3.22 (1H, dd, *J* 13.7 and 6.8, 6$_B$-H), 2.35-2.32 (1H, m, 2'$_A$-H), 1.89 (12H, s, AcO × 4) and 1.77 (1H, app q, *J* 12.5, 2'$_B$-H); δ_C (125 MHz; D_2O) 181.2 (CH_3*C*O), 102.3 (1"-C), 95.7 (1-C), 86.2 (5'-C), 77.4 (4'-C), 76.7 (5"-C), 76.2 (3"-C), 73.8 (2"-C), 72.0 (6'-C), 70.7 (4-C), 69.9 (2-C), 69.8 (4"-C), 68.6 (5-C), 61.0 (6"-C), 53.6 (3-C), 50.1 (1'-C), 48.9 (3'-C), 40.3 (6-C), 29.1 (2'-C) and 23.9 (*C*H_3CO); *m/z* (ES) 484.2 (100%, MH^+); Found MH^+ 484.2639; $C_{18}H_{37}N_5O_{10}$ requires MH^+ 484.2619.

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