Supplementary Material (ESI) for Organic & Biomolecular Chemistry


**Supporting Information**

# Nucloside triphosphate mimicry:- A sugar triazolyl nucleoside as an ATP-competitive inhibitor of *B. anthracis* pantothenate kinase

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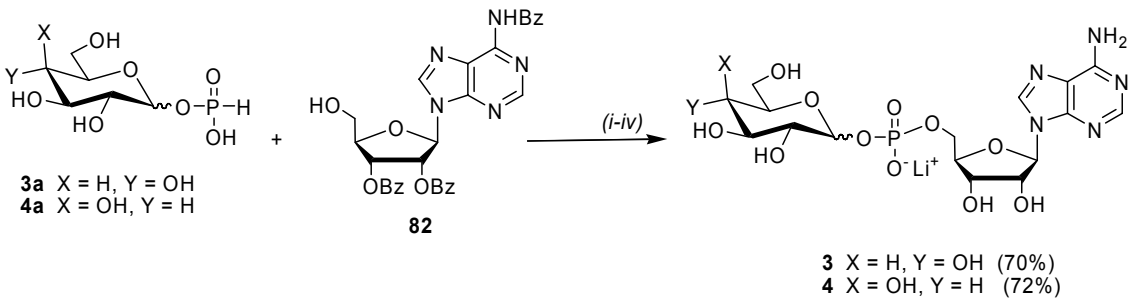
**Contents**

Experimental procedures




*Reagents and conditions: (i) Pivaloyl chloride, pyridine; (ii) $I_2$, pyridine, $H_2O$; (iii) $NH_{3(aq)}$; (iv) 2% $LiClO_4$, acetone*.

**Adenosine 5'-(α/β-D-glucopyranosyl phosphate) (3)**
Benzoylated glucosyl 1-H-phosphonate **3a** [1] (244 mg, 1.0 mmol) and protected adenosine **82** (382 mg, 0.66 mmol) were co-evaporated with anhydrous pyridine (3×10 mL) and dissolved in pyridine (8 mL). Pivaloyl chloride (0.216 mL, 1.65 mmol) was added and stirred for 10 min before adding a solution of iodine (0.5 g, 2 mmol) pyridine/water (95:5, 5.84 mL). After 15 min the solution was diluted with chloroform (200 mL), washed with 0.5 M $Na_2S_2O_3$ (2×100 mL), 0.5 M $Et_4NHCO_3$ (2×100 mL), dried ($Na_2SO_4$) and evaporated. The residue was purified by silica chromatography (0-15% MeOH in $CH_2Cl_2$) and then dissolved in methanol (4 mL) and added to an excess of concentrated aqueous ammonia (50 mL). The mixture was left at room temperature overnight and then evaporated. The residue was suspended in water (2 mL), centrifuged to remove the non-soluble components, and the product was precipitated as a lithium salt by addition of $LiClO_4$ (2% w/v) in acetone (20 mL). The resulting precipitate was washed with acetone and dried *in vacuo* to give **3** as a white solid (236 mg, 70%).The preparation contained 23% of β-anomer. $^1$H NMR ($D_2O$): 3.26 (t, 1H, *J* 9.3, H-4"), 3.38 (dt, 1H, *J* 10.3, 3.3, H-2"), 3.51 (t, 1H, *J* 4.6, H-3"), 3.53 (d, 1H, *J* 1.6, H-6a"), 3.57 (s, 1H, H-6b"), 3.61 (dt, 1H, *J* 7.6, 2.3, H-5"), 4.04 (dd, 2H, *J* 4.2, 3.1, H-5'), 4.23 (t, 1H, *J* 3.4, H-4'), 4.36 (dd, 1H, *J* 4.9, 4.0, H-3'), 4.59 (t, 1H, *J* 5.3, H-2'), 5.30 (dd, 1H, *J* 3.8, 3.5, H-1"), 5.92 (d, 1H, *J* 5.5, H-1'), 7.98 (s, 1H, H-8), 8.26 (s, 1H, H-2). $^{13}$C NMR ($D_2O$): 60.81 (C-6"), 65.37 (d, *J* 5.2, C-5'), 69.68 (C-4"), 70.82 (C-3'), 71.80 (d, *J* 7.9, C-2"), 73.00, 73.35 (C-2' and C-3"), 74.69 (C-5"), 84.23 (d, *J* 9.1, C-4'), 87.59 (C-1'), 95.82 (d, *J* 6.3, C-1"), 119.02 (C-5), 140.12 (C-8), 149.41 (C-6), 153.29 (C-2), 155.93 (C-4). $^{31}$P NMR ($D_2O$): -0.49 (β-anomer) and -0.30 (α-anomer). HRMS ($ES^-$) *m/z* calc. for $C_{16}H_{23}N_5O_{12}P$ ($M\text{-}Li^+$): 508.1086; found 508.1095.

**Adenosine 5'-(α/β-D-galactopyranosyl phosphate) (4)**
Was prepared from galactosyl 1-H-phosphonate **4a** using the same procedure described for **3** and was isolated as a white solid (243 mg, 72%). The preparation contained 31% of β-anomer. $^1$H NMR ($D_2O$): 3.46 (d, 2H, *J* 6.5, H-6"), 3.62 (m, 1H, H-2"), 3.79 (d, 1H. *J* 2.9, H-3"), 3.85 (t, 1H, *J* 6.2, H-5"), 4.03 (m, 3H, H-4", H-5'), 4.22 (m, 1H, H-4'), 4.36 (t, 1H, *J* 4.5, H-3'), 4.62 (t, 1H, *J* 5.3, H-2'), 5.36 (dd, 1H, *J* 7.2, 3.5, H-1"), 5.95 (d, 1H, *J* 5.6, H-1'), 8.04 (s, 1H, H-8), 8.28 (s, 1H, H-2). $^{13}$C NMR ($D_2O$): 61.38 (C-6"), 65.37 (d, *J* 5.2, C-5'), 68.64 (d, *J* 7.8, C-2"), 69.51 (C-3', C-4"), 70.85, 72.47 (C-2', C-3"), 74.67 (C-5"), 84.33 (d, *J* 8.9, C-4'), 87.56 (C-1'), 96.09 (d, *J* 6.4, C-1"), 119.10 (C-5), 140.25 (C-8), 149.54 (C-6), 153.38 (C2-), 156.05 (C-4). $^{31}$P NMR ($D_2O$): -0.46 (β-anomer) and -0.14 (α-anomer). HRMS ($ES^-$) *m/z* calc. for $C_{16}H_{23}N_5O_{12}P$ ($M\text{-}Li^+$): 508.1086; found 508.1086.

**5'-Azido-5'-deoxyadenosine (14)**
A 9:1 mixture of TFA/$H_2O$ (10 ml) was added to compound **13**[2] (1.25 g, 3.76 mmol) at 0 ºC and stirred for 5 minutes. This was then lifted out of the ice bath and stirred for a further 20 minutes, then concentrated *in vacuo* and coevaporated

with ethanol (2 x 20 ml) and $Et_2O$ (20 ml). This was then dissolved in methanol and passed through a column containing Dowex 550A OH anion exchange resin. Ten column volumes of methanol were then washed through, and the combined washings concentrated *in vacuo* and purified by chromatography (EtOAc/$CH_2Cl_2$/MeOH 9:3:2 as eluent) to yield **14** (690 mg, 2.36 mmol, 63%) as a white solid: IR (KBr) $cm^{-1}$ 2104 ($N_3$); $[\alpha]_D^{20}$ = +54.7 (c = 1.0, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 8.29 (s, 1H, H-8), 8.22 (s, 1H, H-2), 6.02 (d, 1H, *J* 4.5, H-1'), 4.79 (t, 1H, *J* 5.0, H-2'), 4.37 (t, 1H, *J* 5.0, H-3'), 4.18 (dt, 1H, *J* 4.5, 4.5, H-4'), 3.67 (dd, 1H, *J* 13.0, 5.0, H-5'a), 3.63 (dd, 1H, *J* 13.0, 4.0, H-5'b); $\delta_C$ (125 MHz, $CD_3OD$) 157.42 (C-6), 153.99 (C-2), 150.73 (C-4), 141.39 (C-8), 120.64 (C-5), 90.42 (C-1'), 84.69 (C-4'), 75.04 (C-2'), 72.39 (C-3'), 53.21 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{10}H_{13}N_8O_3$ ($M+H^+$): 293.1111; found 293.1126; *m/z* 209 (100%), 293 (13%, $M+H^+$).

**Prop-2-ynyl-α-D-glucopyranoside (15)**
Propargyl alcohol (20.84 mL, 358 mmol) and acetyl chloride (257 μL, 3.61 mmol) were stirred together for 30 minutes followed by addition of D-glucose (5 g, 27.75 mmol). This was heated to 120 °C and stirred for 2 days. The reaction mixture was then concentrated *in vacuo* and purified by chromatography (EtOAc/MeOH 19:1 as eluent) to yield **15** (1.45 g, 24%) as a yellow solid. mp 79-81 °C (EtOAc/MeOH) (Lit.[3] 77-79 °C); $[\alpha]_D^{20}$ = +146.4 (c = 1.115, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 5.00 (d, 1H, *J* 3.5, H-1), 4.32 (dd, 1H, *J* 15.5, 2.0, H-1'a), 4.29 (dd, 1H, *J* 15.5, 2.0, H-1'b), 3.81 (dd, 1H, *J* 12.0, 2.5, H-6a), 3.68 (dd, 1H, *J* 12.0, 5.5, H-6b), 3.63 (t, 1H, *J* 9.0, H-3), 3.57 (ddd, 1H, *J* 10.0, 5.5, 2.5, H-5), 3.42 (dd, 1H, *J* 9.5, 3.5, H-2), 3.31 (dd, 1H, *J* 10.0, 9.0, H-4, overlapping $CHD_2OD$), 2.86 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (125 MHz, $CD_3OD$) 98.62 (C-1), 80.13 (C-2'), 76.11 (C-3'), 75.01 (C-3), 74.13 (C-5), 73.33 (C-2), 71.67 (C-4), 62.54 (C-6), 55.26 (C-1'); HRMS (CI) *m/z* calc. for $C_9H_{18}NO_6$ ($M+NH_4^+$): 236.11341; found 236.11357; *m/z* 236 (100%, $M+NH_4^+$).

**Prop-2-ynyl-2-acetamido-2-deoxy-α-D-glucoside (16)**
*N*-Acetyl-D-glucosamine (2 g, 9.04 mmol) was dissolved in propargyl alcohol (10 mL) followed by the addition of acetyl chloride (0.5 mL, 7.01 mmol). This was heated to 100 °C and stirred for 3 days. The reaction mixture was then concentrated *in vacuo* and purified by chromatography (EtOAc/MeOH 9:1 as eluent) to yield **16** (690 mg, 29%) as a pale yellow solid: mp 170-172 °C (EtOAc/MeOH); $R_f$ = 0.22 (EtOAc/MeOH 4:1); $[\alpha]_D^{20}$ = +145.6 (c = 1.04, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 4.99 (d, 1H, *J* 3.5, H-1), 4.30 (dd, 1H, *J* 16.0, 2.5, H-1'a), 4.25 (dd, 1H, *J* 16.0, 2.5, H-1'b), 3.94 (dd, 1H, *J* 10.5, 3.5, H-2), 3.82 (dd, 1H, *J* 11.5, 2.0, H-6a), 3.69 (dd, 1H, *J* 12.0, 5.5, H-6b), 3.65 (dd, 1H, *J* 11.0, 9.0, H-3), 3.58 (ddd, 1H, *J* 10.0, 5.5, 2.0, H-5), 3.37 (dd, 1H, *J* 10.0, 9.0, H-4), 2.86 (t, 1H, *J* 2.0, H-3'), 1.99 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 173.77 (C=O), 97.16 (C-1), 80.08 (C-2'), 76.09 (C-3'), 74.35 (C-5), 72.68 (C-3), 72.27 (C-4), 62.64 (C-6), 55.39 (C-1'), 55.15 (C-2), 22.59 ($CH_3$); HRMS (CI) *m/z* calc. for $C_{11}H_{18}NO_6$ ($M+H^+$): 260.11341; found 260.11241; *m/z* 260 (74%, $M+H^+$).

**Prop-2-ynyl-α-D-mannopyranoside (17)**
Propargyl alcohol (8.34 mL, 143 mmol) and acetyl chloride (103 μL, 1.44 mmol) were stirred together for 30 minutes followed by addition of D-mannose (2 g, 11.10 mmol). This was stirred at 110 °C for 24 hours. The reaction mixture was then concentrated *in vacuo* and purified by chromatography (EtOAc/MeOH 19:1 as eluent) to yield **17** (760 mg, 31%) as a yellow solid: mp 110-113 ºC (EtOAc/MeOH); $R_f$ = 0.31 (EtOAc/MeOH 9:1); $[\alpha]_D^{20}$ = +115.6 (c = 0.895, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 4.96 (d, 1H, *J* 1.5, H-1), 4.27 (d, 2H, *J* 2.0, H-1'), 3.84 (dd, 1H, *J* 12.0, 2.5, H-6a), 3.79 (dd, 1H, *J* 3.0, 1.5, H-2), 3.71 (dd, 1H, *J* 11.5, 6.0, H-6b), 3.66 (dd, 1H, *J* 10.0, 3.0, H-3), 3.62 (t, 1H, *J* 9.5, H-4), 3.51 (ddd, 1H, *J* 9.5, 6.0, 2.0, H-5), 2.86 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (125 MHz, $CD_3OD$) 99.83 (C-1), 80.06 (C-2'), 76.02 (C-3'), 75.13 (C-5), 72.51 (C-3), 72.05 (C-2), 68.49 (C-4), 62.86 (C-6), 54.84 (C-1'); HRMS (CI) *m/z* calc. for $C_9H_{18}NO_6$

($M+NH_4^+$): 236.11341; found 236.11388; *m/z* 236 (100%, $M+NH_4^+$).

**Prop-2-ynyl-L-arabinopyranoside (18)**
Propargyl alcohol (10 mL) and acetyl chloride (123 μL, 1.73 mmol) were stirred together for 30 minutes followed by addition of L-arabinose (2 g, 13.32 mmol). This was heated to 110 °C and stirred for 24 hours. The reaction mixture was then concentrated *in vacuo* and purified by chromatography (EtOAc/MeOH 19:1 as eluent) to yield **18** (1.10 g, 44%) as a yellow solid with an α/β ratio of 1:2.9: $\delta_H$ (500 MHz, $CD_3OD$) 4.99 (d, 1H, *J* 3.5, H-1β), 4.42 (d, 1H, *J* 6.5, H-1α), 4.38 (dd, 1H, *J* 16.0, 2.5, H-1'aα), 4.33 (dd, 1H, *J* 16.0, 2.5, H-1'bα), 4.29 (dd, 1H, *J* 16.0, 2.5, H-1'aβ), 4.25 (dd, 1H, *J* 16.0, 2.5, H-1'bβ), 3.88-3.86 (m, 1H, H-4β), 3.87 (dd, 1H, *J* 12.0, 3.5, H-5aα), 3.83 (dd, 1H, *J* 12.5, 1.5, H-5aβ), 3.83-3.82 (m, 1H, H-4α), 3.80 (dd, 1H, *J* 9.5, 3.5, H-2β), 3.76 (dd, 1H, *J* 10.0, 3.5, H-3β), 3.60 (dd, 1H, *J* 12.0, 2. 5, H-5bβ), 3.57 (dd, 1H, *J* 9.0, 6.0, H-2α), 3.56-3.53 (m, 1H, H-3α), 3.54 (dd, 1H, *J* 12.0, 1.5, H-5bα), 2.864 (t, 1H, *J* 2.5, H-3'α), 2.863 (t, 1H, *J* 2.5, H-3'β); $\delta_C$ (125 MHz, $CD_3OD$) 102.45 (C-1α), 99.33 (C-1β), 80.11 (C-2'β), 80.00 (C-2'α), 76.23 (C-3'α), 76.10 (C-3'β), 74.09 (C-2α), 72.21 (C-3α), 70.72 (C-2β), 70.64 (C-4β), 70.06 (C-3β), 69.43 (C-4α), 66.74 (C-5α), 64.55 (C-5β), 56.21 (C-1'α), 55.50 (C-1'β); HRMS (CI) *m/z* calc. for $C_8H_{16}NO_5$ ($M+NH_4^+$): 206.10285; found 206.10242; *m/z* 206 (100%, $M+NH_4^+$).

**Prop-2-ynyl-α-D-xylopyranoside (19)**
Propargyl alcohol (25 mL) and acetyl chloride (310 μL, 4.3 mmol) were stirred together for 30 minutes followed by addition of D-xylose (5 g, 33.3 mmol). This was stirred at 110 °C for 26 hours. The reaction mixture was then concentrated *in vacuo* and the resulting dark brown oil purified by chromatography (EtOAc/hexane 19:1 to 24:1 as eluent) to yield **19** (513 mg, 2.73 mmol, 8%) as a white fluffy solid. (An anomeric mixture of **19** (1.5 g, 24%) α/β = 3:2) was also obtained: mp 134-135 °C (MeOH); $R_f$ = 0.33 (EtOAc/MeOH 19:1); $[\alpha]_D^{20}$ = +173.9 (c = 0.848, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 4.92 (d, 1H, *J* 4.0, H-1), 4.29 (dd, 1H, *J* 15.5, 2.0, H-1'a), 4.25 (dd, 1H, *J* 15.5, 2.0, H-1'b), 3.59-3.53 (m, 2H, H-3, H-5a), 3.51-3.44 (m, 2H, H-4, H-5b ), 3.39 (dd, 1H, *J* 9.5, 3.5, H-2), 2.85 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (125 MHz, $CD_3OD$) 99.0 (C-1), 80.0 (C-2'), 76.1 (C-3'), 75.1 (C-3), 73.4 (C-2), 71.5 (C-4), 63.4 (C-5), 55.4 (C-1'); HRMS (CI) *m/z* calc. for $C_8H_{16}NO_5$ ($M+NH_4^+$): 206.10285; found 206.10230; *m/z* 206 (100%, $M+NH_4^+$).

**Prop-2-ynyl-4,6-*O*-benzylidene-α-D-galactopyranoside (21) & Prop-2-ynyl-4,6-*O*-benzylidene-β-D-galactopyranoside (22)**
Propargyl alcohol (20.8 mL, 358 mmol) and acetyl chloride (257 μL, 3.61 mmol) were stirred together for 30 minutes followed by addition of D-galactose (5 g, 27.75 mmol). This was heated to 110 °C and stirred for 2 days. The reaction mixture was then concentrated *in vacuo* and purified by chromatography (EtOAc/MeOH 9:1 as eluent) to yield α/β-propargyl galactoside **20** (1.92 g, 8.80 mmol, 32%) as a yellow oil with an α/β ratio of 3:1. To a heterogeneous mixture of this, in dry acetonitrile (50 mL), was added *p*-toluenesulfonic acid (60.6 mg, 0.352 mmol) followed by *α,α*-dimethoxytoluene (1.58 mL, 10.56 mmol). The mixture gradually became homogeneous as the reaction progressed. After stirring for 19 hours, triethylamine (49.1 μL, 0.352 mmol) was added and stirring was continued for 10 minutes. The reaction mixture was then concentrated *in vacuo* to yield a dark orange oil which was purified by chromatography (EtOAc/hexane 3:1 to 9:1 as eluent). This yielded both **21** (1.56 g, 58%) and **22** (300 mg, 11%) as white solids:
**21:** mp 128-129 °C (EtOAc/hexane); $[\alpha]_D^{20}$ = +149.6 (c = 1.02, EtOAc); $\delta_H$ (500 MHz, $CDCl_3$) 7.50-7.48 (m, 2H, Ar H-2, Ar H-6), 7.39-7.35 (m, 3H, Ar H-3, Ar H-4, Ar H-5), 5.55 (s, 1H, PhC-H), 5.20 (d, 1H, *J* 3.5, H-1), 4.31 (d, 2H, *J* 2.5, H-1'), 4.27 (dd, 1H, *J* 12.5, 1.5, H-6a), 4.26 (dd, 1H, *J* 3.5, 1.0, H-4), 4.06 (dd, 1H, *J* 12.5, 1.5, H-6b), 3.96 (dd, 1H, *J* 10.0, 3.5, H-2), 3.91 (dd, 1H, *J* 10.0, 3.5, H-3), 3.77 (d, 1H, *J* 1.0, H-5), 2.46 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (125 MHz, $CDCl_3$) 137.46 (Ar C-1), 129.20 (Ar C-4), 128.24 (Ar C-3, Ar C-5), 126.25 (Ar C-2, Ar C-6), 101.26 ($ArC(OR)_2$), 98.29 (C-1), 78.70 (C-2'), 75.81 (C-4), 75.05 (C-3'), 69.72

(C-2), 69.46 (C-3), 69.15 (C-6), 63.35 (C-5), 55.44 (C-1'); HRMS (CI) *m/z* calc. for $C_{16}H_{19}O_6$ ($M+H^+$): 307.1176; found 307.1177; *m/z* 324 (100%, $M+NH_4^+$), 307 (76%, $M+H^+$).
**22:** mp 177-178 °C (EtOAc/hexane); $[\alpha]_D^{20}$ = -68.1 (c = 1.00, EtOAc); $\delta_H$ (500 MHz, $CDCl_3$) 7.51-7.49 (m, 2H, Ar H-2, Ar H-6), 7.38-7.36 (m 3H, Ar H-3, Ar H-4, Ar H-5), 5.56 (s, 1H, PhC-H), 4.56 (d, 1H, *J* 7.5, H-1), 4.48 (dd, 1H, *J* 16.0, 2.5, H-1'a), 4.44 (dd, 1H, *J* 16.0, 2.5, H-1'b), 4.35 (dd, 1H, *J* 12.5, 1.0, H-6a), 4.23 (d, 1H, *J* 3.0, H-4), 4.10 (dd, 1H, *J* 12.5, 1.5, H-6b), 3.80 (dd, 1H, *J* 9.5, 7.5, H-2), 3.77-3.72 (m, 1H, H-3), 3.53 (s, 1H, H-5), 2.48 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (125 MHz, $CDCl_3$) 137.36 (Ar C-1), 129.26 (Ar C-4), 126.24 (Ar C-3, Ar C-5), 126.35 (Ar C-2, Ar C-6), 101.45 ($ArC(OR)_2$), 100.10 (C-1), 78.67 (C-2'), 75.34 (C-3'), 75.20 (C-4), 72.69 (C-3), 71.50 (C-2), 69.06 (C-6), 66.83 (C-5), 55.67 (C-1'); HRMS (CI) *m/z* calc. for $C_{16}H_{19}O_6$ ($M+H^+$): 307.1176; found 307.1176; *m/z* 324 (100%, $M+NH_4^+$), 307 (21%, $M+H^+$).

**Prop-2-ynyl-α-D-galactopyranoside (23)**
Compound **21** (800 mg, 2.61 mmol) was dissolved in 80% aqueous acetic acid (60 mL) and stirred at 80 °C for 4 hours. The reaction mixture was then concentrated *in vacuo* to yield a clear oil that was purified by chromatography (EtOAc/MeOH 9:1 as eluent) to yield **23** (420 mg, 74%) as a white solid: mp 102-104 °C (EtOAc/MeOH); $[\alpha]_D^{20}$ = +166.1 (c = 1.045, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 5.02 (dd, 1H, *J* 3.5, H-1), 4.32 (dd, 1H, *J* 16.0, 2.5, H-1'a), 4.29 (dd, 1H, *J* 15.5, 2.5, H-1'b), 3.90 (dd, 1H, *J* 3.0, 0.5, H-4), 3.82-3.78 (m, 2H, H-2, H-5), 3.726 (dd, 1H, *J* 11.5, 6.5, H-6a), 3.728 (dd, 1H, *J* 10.0, 3.5, H-3), 3.68 (dd, 1H, *J* 11.0, 5.5, H-6b), 2.86 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (125 MHz, $CD_3OD$) 98.81 (C-1), 80.16 (C-2'), 76.06 (C-3'), 72.84 (C-5), 71.43 (C-3), 71.06 (C-4), 69.99 (C-2), 62.69 (C-6), 55.28 (C-1'); HRMS (CI) *m/z* calc. for $C_9H_{18}NO_6$ ($M+NH_4^+$): 236.1129; found 236.1132; *m/z* 236 (83%, $M+NH_4^+$)

**Prop-2-ynyl-2,3,5-tri-*O*-acetyl-β-D-ribofuranoside (25)**
β-D-ribofuranose tetra-acetate **24** (2 g, 6.28 mmol) was dissolved in dry dichloromethane (40 mL) and stirred at 0 °C followed by addition of propargyl alcohol (439 μL, 7.54 mmol) and boron trifluoride diethyl etherate (1.19 mL, 9.42 mmol). This was stirred at room temperature for 24 hours. Anhydrous potassium carbonate (1.4 g) was then added and stirring continued for 30 minutes, followed by filtration. The filtrate was washed with water (2 x 100 mL), and the combined aqueous layers back-extracted with dichloromethane (50 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield a pale brown oil which was purified by chromatography (hexane/EtOAc 7:3 as eluent) to give **25** (950 mg, 48%) as a colourless oil: $[\alpha]_D^{20}$ = -31.9 (c = 1.067, dichloromethane); $\delta_H$ (500 MHz, $CD_3OD$) 5.35 (dd, 1H, *J* 7.0, 5.0, H-3), 5.28 (broad dd, 1H, *J* 4.5, 1.0, H-2), 5.20 (s, 1H, H-1), 4.35-4.28 (m, 2H, H-5a, H-4), 4.28 (dd, 1H, *J* 16.0, 2.5, H-1'a), 4.22 (dd, 1H, *J* 16.0, 2.5, H-1'b), 4.12 (dd, 1H, *J* 12.0, 5.5, H-5b), 2.44 (t, 1H, *J* 2.5, H-3'), 2.11 (s, 3H, $CH_3$), 2.09 (s, 3H, $CH_3$), 2.04 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 170.57 (C=O), 169.55 (C=O), 169.45 (C=O), 103.18 (C-1), 78.87 (C-4), 78.31 (C-2'), 75.11 (C-3'), 74.73 (C-2), 71.22 (C-3), 64.01 (C-5), 54.42 (C-1'), 20.74 ($CH_3$), 20.52 ($CH_3$), 20.45 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{14}H_{22}NO_8$ ($M+NH_4^+$): 332.1340; found 332.1339; *m/z* 667 (23%, $2M+K^+$), 651 (100%, $2M+Na^+$), 353 (13%, $M+K^+$), 337 (56%, $M+Na^+$).

**Prop-2-ynyl-β-D-ribofuranoside (26)**
To a solution of **25** (700 mg, 2.23 mmol) in dry methanol (10 mL), a solution of sodium methoxide (120 mg, 2.23 mmol) in dry methanol (5 mL) was added. This was stirred at room temperature for 18 hours followed by addition of DOWEX HCR-W2 $H^+$ resin (1.7 g). Stirring was continued for 10 minutes, then this was filtered and concentrated *in vacuo* to yield **26** (384 mg, 91%) as a white solid: mp 101 °C (MeOH) (Lit. 102-103 °C); $R_f$ = 0.41 (EtOAc/MeOH 8:2); $[\alpha]_D^{20}$ = -91.4 (c = 1.095, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 5.06 (s, 1H, H-1), 4.27 (dd, 1H, *J* 16.0, 2.5, H-1'a), 4.24 (dd, 1H, *J* 16.0, 2.5, H-1'b), 4.07 (dd, 1H, *J* 7.5, 5.0, H-3), 3.96 (m, 1H, *J* 7.0, 6.5, 3.5, H-4), 3.92 (d, 1H, *J* 5.0, H-2), 3.73 (dd, 1H, *J* 12.0,

3.5, H-5a), 3.55 (dd, 1H, *J* 12.0, 6.5, H-5b), 2.82 (t, 1H, *J* 2.0, H-3'); $\delta_C$ (125 MHz, $CD_3OD$) 106.53 (C-1), 84.99 (C-4), 80.22 (C-2'), 76.27 (C-2), 75.82 (C-3'), 72.51 (C-3), 64.77 (C-5), 54.80 (C-1'); HRMS (CI) *m/z* calc. for $C_8H_{16}NO_5$ ($M+NH_4^+$): 206.1023; found 206.1025; *m/z* 206 (100%, $M+NH_4^+$).

**Prop-2-ynyl-β-D-galactopyranoside (27c)**
To a solution of **27b**[4] (590 mg, 1.53 mmol) in dry methanol (6 mL), a solution of sodium methoxide (83 mg, 1.53 mmol) in dry methanol (4 mL) was added. This was stirred at room temperature for 3 hours followed by addition of DOWEX HCR-W2 $H^+$ resin (1.4 g). Stirring was continued for 10 minutes, then this was filtered and concentrated *in vacuo* to yield **27c** (323 mg, 97%) as a white solid: $R_f$ = 0.32 (EtOAc/MeOH 4:1); $\delta_H$ (500 MHz, $CD_3OD$) 4.44 (dd, 1H, *J* 15.5, 2.5, H-1a), 4.41 (d, 1H, *J* 8.0, H-1), 4.40 (dd, 1H, *J* 15.5, 2.0, H-1'b), 3.83 (dd, 1H, *J* 3.0, 1.0, H-4), 3.76 (dd, 1H, *J* 11.0, 6.5, H-6a), 3.71 (dd, 1H, *J* 11.0, 5.0, H-6b), 3.53 (dd, 1H, *J* 9.5, 7.5, H-2), 3.51 (ddd, 1H, *J* 6.5, 5.5, 1.0, H-5), 3.48 (dd, 1H, *J* 10.0, 3.5, H-3), 2.84 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (75 MHz, $CD_3OD$) 102.76 (C-1), 80.20 (C-2'), 76.87 (C-5), 76.12 (C-3'), 74.96 (C-3), 72.30 (C-2), 70.32 (C-4), 62.55 (C-6), 56.51 (C-1'); MS ($ES^-$) *m/z* 217 (60%, $M-H^+$).

**Prop-2-ynyl-2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (28b)**
β-D-xylose tetra-acetate **28a** (3 g, 9.43 mmol) was dissolved in dry dichloromethane (60 mL) and stirred at 0 °C followed by addition of propargyl alcohol (660 μL, 11.31 mmol) and boron trifluoride diethyl etherate (1.78 mL, 14.14 mmol). This was stirred at room temperature for 18 hours. Anhydrous potassium carbonate (2.5 g) was then added and stirring continued for 30 minutes, followed by filtration. The filtrate was washed with water (2 x 75 mL), and the combined aqueous layers back-extracted with dichloromethane (2 x 40 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield a pale yellow solid which was purified by chromatography (hexane/EtOAc 7:3 to 3:2 as eluent). This afforded **28b** (2.05 g, 69%) as a white solid: mp 114-116 °C (EtOAc/hexane); $[\alpha]_D^{20}$ = -75.4 (c = 1.01, $CHCl_3$); $\delta_H$ (500 MHz, $CDCl_3$) 5.18 (t, 1H, *J* 8.5, H-3), 4.94 (dt, 1H, *J* 8.5, 5.0, H-4), 4.93 (dd, 1H, *J* 8.5, 7.0, H-2), 4.75 (d, 1H, *J* 7.0, H-1), 4.33 (d, 2H, *J* 2.5, H-1'), 4.13 (dd, 1H, *J* 11.5, 5.0, H-5a), 3.40 (dd, 1H, *J* 11.5, 8.5, H-5b), 2.45 (t, 1H, *J* 2.5, H-3'), 2.07 (s, 3H, $CH_3$), 2.05 (s, 3H, $CH_3$), 2.04 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CDCl_3$) 169.99, 169.81, 169.44 (C=O), 98.26 (C-1), 78.27 (C-2'), 75.23 (C-3'), 71.21 (C-3), 70.41 (C-2), 68.85 (C-4), 62.06 (C-5), 55.59 (C-1'), 20.70 (3 x $CH_3$); HRMS (CI) *m/z* calc. for $C_{14}H_{22}NO_8$ ($M+NH_4^+$): 332.13454; found 332.13467; *m/z* 332 (100%, $M+NH_4^+$)

**Prop-2-ynyl-β-D-xylopyranoside (28c)**
To a solution of **28b** (222 mg, 0.697 mmol) in dry methanol (4 mL), a solution of sodium methoxide (38 mg, 0.697 mmol) in dry methanol (2 mL) was added. This was stirred at room temperature for 4 hours followed by addition of DOWEX HCR-W2 $H^+$ resin (600 mg). Stirring was continued for 10 minutes, then this was filtered and concentrated *in vacuo* to yield **28c** (128 mg, 98%) as a white solid: mp 122-123 °C (MeOH); $[\alpha]_D^{20}$ = -92.0 (c = 1.015, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 4.41 (d, 1H, *J* 7.5, H-1), 4.38 (dd, 1H, *J* 15.5, 2.5, H-1'a), 4.33 (dd, 1H, *J* 16.0, 2.5, H-1'b), 3.87 (dd, 1H, *J* 11.5, 5.0, H-5a), 3.49 (ddd, 1H, *J* 10.0, 9.0, 5.5, H-4), 3.32 (t, 1H, *J* 9.0, H-3), 3.19 (dd, 1H, *J* 11.5, 10.0, H-5b), 3.18 (dd, 1H, *J* 9.0, 7.5, H-2), 2.87 (t, 1H, *J* 2.5, H-3'); $\delta_C$ (75 MHz, $CD_3OD$) 102.86 (C-1), 79.91 (C-2'), 77.73 (C-3), 76.31 (C-3'), 74.70 (C-2), 71.20 (C-4), 67.00 (C-5), 56.55 (C-1'); HRMS (CI) *m/z* calc. for $C_8H_{16}NO_5$ ($M+NH_4^+$): 206.10285; found 206.10347; *m/z* 206 (100%, $M+NH_4^+$).

**Prop-2-ynyl-3,4,6-tri-*O*-acetyl-2-acetylamino-2-deoxy-β-D-glucoside (30)**
To a solution of 3,4,6-Tri-*O*-acetyl-2-acetamido-2-deoxy-α-D-glucopyranosyl bromide **29** [5] (200 mg, 0.488 mmol) in dry dichloromethane (6 mL) containing 4Å molecular sieves was added propargyl alcohol (43 μL, 0.739 mmol) *via* syringe. This was cooled to 0 ºC, followed by the addition of silver triflate (188 mg, 0.731 mmol), and stirred vigorously at 0 ºC for 2 hours. The reaction mixture was then

passed through celite to remove solids, and the celite washed through with dichloromethane (50 mL). The organic solvent was then washed with saturated aqueous sodium bicarbonate solution (50 mL) and brine (50 mL), then dried ($MgSO_4$), filtered and concentrated and purified by chromatography (EtOAc/hexane 8:2 as eluent) to yield **30** (56 mg, 30%) as a white solid: mp 189-190 °C (EtOAc/hexane); $R_f$ = 0.21 (EtOAc/hexane 4:1); $[\alpha]_D^{20}$ = -8.3 (c = 1.4, $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$) 5.65 (d, 1H, *J* 9.0, NH), 5.27 (dd, 1H, *J* 10.5, 9.3, H-3), 5.08 (t, 1H, *J* 9.6, H-4), 4.84 (d, 1H, *J* 8.4, H-1), 4.37 (d, 2H, *J* 2.4, H-1'), 4.27 (dd, 1H, *J* 12.3, 4.8, H-6a), 4.13 (dd, 1H, *J* 12.0, 2.1, H-6b), 3.95 (dt, 1H, *J* 10.2, 8.7, H-2), 3.72 (ddd, 1H, *J* 9.9, 4.5, 2.4, H-5), 2.47 (t, 1H, *J* 2.1, H-3'), 2.08 (s, 3H, $CH_3$), 2.03 (s, 3H, $CH_3$), 2.02 (s, 3H, $CH_3$), 1.96 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CDCl_3$) 170.89**,** 170.64, 170.25, 169.31 (C=O), 98.30 (C-1), 78.47 (C-2'), 75.33 (C-3'), 72.39 (C-3), 71.95 (C-5), 68.46 (C-4), 61.92 (C-6), 55.86 (C-1'), 54.25 (C-2), 23.31 ($CH_3$), 20.70 ($CH_3$), 20.64 ($CH_3$), 20.59 ($CH_3$); HRMS (CI) *m/z* calc. for $C_{17}H_{24}NO_9$ ($M+H^+$): 386.14511; found 386.14532; *m/z* 386 (100%, $M+H^+$), 403 (40, $M+NH_4^+$).

**Prop-2-ynyl-2-acetamido-2-deoxy-β-D-glucoside (31)**
To a solution of **30**[6] (78 mg, 0.202 mmol) in dry methanol (0.5 mL), a solution of sodium methoxide (11 mg, 0.202 mmol) in dry methanol (0.5 mL) was added. This was stirred at room temperature for 20 hours followed by addition of DOWEX-$H^+$ resin (0.5 g). Stirring was continued for 10 minutes, then this was filtered and concentrated *in vacuo* to yield **31** (52 mg, 100%) as an off-white solid: mp 144-145 °C (MeOH); $[\alpha]_D^{20}$ = -48.0 (c = 1.03, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 4.60 (d, 1H, *J* 8.5, H-1), 4.38 (dd, 1H, *J* 16.0, 2.5, H-1'a), 4.35 (dd, 1H, *J* 16.0, 2.5, H-1'b), 3.88 (dd, 1H, *J* 12.0, 2.0, H-6a), 3.68 (dd, 1H, *J* 12.0, 5.5, H-6b), 3.66 (dd, 1H, *J* 10.5, 8.5, H-2), 3.49 (dd, 1H, *J* 10.0, 8.0, H-3), 3.34-3.30 (m, 1H, H-4), 3.28 (ddd, 1H, *J* 10.0, 6.0, 2.0, H-5), 2.84 (t, 1H, *J* 2.5, H-3'), 1.99 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 173.89 (C=O), 100.52 (C-1), 80.09 (C-2'), 78.08 (C-5), 76.19 (C-3'), 75.96 (C-3), 72.13 (C-4), 62.79 (C-6), 57.15 (C-2), 56.52 (C-1'), 23.03 ($CH_3$); HRMS (CI) *m/z* calc. for $C_{11}H_{18}NO_6$ ($M+H^+$): 260.11341; found 260.11419; *m/z* 260 (100%, $M+H^+$).

**3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide (33)**
Compound **32**[7] (1 g, 2.68 mmol) and titanium(IV) bromide (1.18 g, 3.21 mmol) were dissolved in a mixture of dichloromethane (40 mL) and ethyl acetate (8 mL). This was stirred for 3 days, then acetonitrile (20 mL) was added, followed by sodium methoxide (840 mg, 15.54 mmol). Stirring was continued until the red colour disappeared, then the reaction mixture was filtered and concentrated to yield a dark orange oil which was purified by automated chromatography (hexane/EtOAc 3:1 to 18:7 as eluent) to recover unreacted starting material **32** (395 mg, 40%) and the desired product **33** (326 mg, 31%) as pale yellow oil: $[\alpha]_D^{20}$ = +198.0 (c = 1.2, $CHCl_3$) (Lit. [8] $[\alpha]_D^{20}$ = +184.0 (c = 1.2, $CHCl_3$)); $\delta_H$ (500 MHz, $C_6D_6$) 5.69 (d, 1H, *J* 4.0, H-1), 5.62 (t, 1H, *J* 10.5, H-3), 5.08 (t, 1H, *J* 10.5, H-4), 4.21 (dd, 1H, *J* 13.0, 4.5, H-6a), 4.08 (ddd, 1H, *J* 10.5, 4.0, 2.0, H-5), 3.82 (dd, 1H, *J* 12.5, 2.0, H-6b), 2.73 (dd, 1H, *J* 10.5, 4.0, H-2), 1.70 (s, 3H, $CH_3$), 1.69 (s, 3H, $CH_3$), 1.64 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $C_6D_6$) 169.66, 169.35, 169.18 (C=O), 87.97 (C-1), 72.98 (C-5), 71.86 (C-3), 67.48 (C-4), 62.30 (C-2), 60.84 (C-6), 20.13, 20.07, 20.02 ($CH_3$).

**Prop-2-ynyl-3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranoside (34)**
To a solution of compound **33** (655 mg, 1.66 mmol) in dry dichloromethane (18 mL) containing 4Å molecular sieves (500 mg) was added propargyl alcohol (145 µL, 2.49 mmol) *via* syringe. This was cooled to 0 ºC, followed by the addition of silver triflate (640 mg, 2.49 mmol), and stirred vigorously at 0 ºC for 80 minutes. The reaction mixture was then passed through celite to remove solids, and the celite washed through with dichloromethane (50 mL). The organic solvent was then washed with saturated sodium bicarbonate solution (200 mL) and brine (200 mL), then dried ($MgSO_4$), filtered and concentrated to yield a colourless oil that was purified by chromatography (hexane/EtOAc 7:3 as eluent) to yield **34** (539

mg, 88%) as a colourless oil with an α/β ratio of 1.1:1: $R_f$ = 0.32 (hexane/EtOAc 7:3); IR (KBr) $cm^{-1}$ 2113 ($N_3$); $\delta_H$ (500 MHz, $CDCl_3$) 5.48 (dd, 1H, *J* 10.5, 9.5, H-3α), 5.21 (d, 1H, *J* 3.5, H-1α), 5.06 (t, 1H, *J* 9.5, H-4α), 5.05-4.98 (m, 2H, H-3β, H-4β), 4.66 (d, 1H, *J* 8.0, H-1β), 4.46 (dd, 1H, *J* 16.0, 2.5, H-1'aβ), 4.42 (dd, 1H, *J* 16.0, 2.5, H-1'bβ), 4.33 (d, 2H, *J* 2.5, H-1'α), 4.28 (dd, 2H, *J* 12.5, 4.5, H-6aα, H-6aβ), 4.14 (m, 3H, H-5β, H-6bα, H-6bβ), 3.69 (ddd, 1H, *J* 9.5, 5.0, 2.0, H-5α), 3.55-3.48 (m, 1H, H-2β), 3.42 (dd, 1H, *J* 10.5, 3.5, H-2α), 2.52 (t, 1H, *J* 2.5, H-3'β), 2.50 (t, 1H, *J* 2.5, H-3'α), 2.09-2.07 (m, 12H, $CH_3$α x 2, $CH_3$β x 2), 2.03 (s, 3H, $CH_3$α), 2.01 (s, 3H, $CH_3$β); $\delta_C$ (125 MHz, $CDCl_3$) 170.59, 169.95, 169.66, 169.60 (C=O x 6), 99.29 (C-1β), 96.49 (C-1α), 77.77, 77.69 (C-2'α, C-2'β), 75.96, 75.75 (C-3'α, C-3'β), 72.57 (C-3β), 71.97 (C-5α), 70.42 (C-3α), 68.45, 68.32, 68.17 (C-4α, C-4β, C-5β), 63.37 (C-2β), 61.74 (C-6β), 61.69 (C-6α), 60.71 (C-2α), 56.21 (C-1'β), 55.45 (C-1'α), 20.71, 20.68, 20.59, 20.57 ($CH_3$ x 6); HRMS ($ES^+$) *m/z* calc. for $C_{15}H_{20}N_3O_8$ ($M+H^+$): 370.1250; found 370.1260; *m/z* 370 (70%, $M+H^+$).

**Prop-2-ynyl-2-azido-2-deoxy-D-glucopyranoside (35)**
Methanol (8 mL) was added to a mixture of compound **34** (460 mg, 1.25 mmol) and sodium methoxide (68 mg, 1.26 mmol) in a 25 mL round bottomed flask, and this was sonicated for 3 minutes, followed by addition of DOWEX HCR-W2 $H^+$ resin (1.2 g). This was stirred for 15 minutes, then filtered and concentrated *in vacuo* to yield **35** (284 mg, 94%) as a colourless oil: $R_f$ = 0.63 (EtOAc/MeOH 19:1); IR (KBr) $cm^{-1}$ 2118 ($N_3$); $\delta_H$ (500 MHz, $CD_3OD$) 5.10 (d, 1H, *J* 3.5, H-1α), 4.54 (d, 1H, *J* 8.5, H-1β), 4.44 (d, 2H, *J* 2.5, H-1'β), 4.33 (dd, 1H, *J* 15.5, 2.0, H-1'aα), 4.29 (dd, 1H, *J* 16.0, 2.5, H-1'bα), 3.86 (dd, 1H, *J* 12.0, 2.5, H-6aβ), 3.81 (dd, 1H, *J* 10.5, 9.0, H-3α), 3.81 (dd, 1H, *J* 12.0, 2.5, H-6aα), 3.69 (dd, 1H, *J* 12.0, 5.5, H-6bα), 3.67 (dd, 1H, *J* 12.0, 5.5, H-6bβ), 3.58 (ddd, 1H, *J* 10.0, 5.0, 2.0, H-5α), 3.37 (dd, 1H, *J* 10.5, 9.0, H-4α), 3.32-3.26 (m, 2H, H-3β, H-4β), 3.25 (ddd, 1H, *J* 9.5, 5.5, 2.0, H-5β), 3.17 (dd, 1H, *J* 10.5, 3.0, H-2α), 3.16 (dd, 1H, *J* 9.5, 8.5, H-2β), 2.91 (t, 1H, *J* 2.5, H-3'β), 2.89 (t, 1H, *J* 2.5, H-3'α); $\delta_C$ (125 MHz, $CD_3OD$) 100.83 (C-1β), 97.78 (C-1α), 79.72, 79.68 (C-2'α, C-2'β), 78.14 (C-5β), 76.47, 76.44, 76.32 (C-3β, C-3'α, C-3'β), 74.39 (C-5α), 72.66 (C-3α), 71.99 (C-4α), 71.52 (C-4β), 67.92 (C-2β), 64.39 (C-2α), 62.56, 62.35 (C-6α, C-6β), 56.66 (C-1'β), 55.36 (C-1'α).

**Prop-2-ynyl-2-amino-2-deoxy-D-glucopyranoside (36)**
Compound **35** (210 mg, 0.863 mmol) was dissolved in ethanol (6 mL) and water (3 mL), followed by the addition of zinc dust (73 mg, 1.12 mmol) and ammonium chloride (106 mg, 1.98 mmol). This was refluxed at 90 ºC for 15 minutes, then allowed to cool to room temperature. The reaction mixture was filtered to remove zinc, then passed through a column containing Dowex 550A OH anion exchange resin to remove ammonium chloride. Methanol was washed through the column until the product stopped eluting. The combined washings were concentrated *in vacuo*, and the residue dissolved in a small volume of water and freeze-dried to obtain **36** (127 mg, 68%) as a white solid: $\delta_H$ (500 MHz, $CD_3OD$) 4.99 (d, 1H, *J* 3.5, H-1α), 4.42 (d, 1H, *J* 8.0, H-1β), 4.47-4.37 (m, 2H, H-1'β), 4.34-4.24 (m, 2H, H-1'α), 3.87 (dd, 1H, *J* 12.0, 2.0, H-6aβ), 3.81 (dd, 1H, *J* 12.0, 2.5, H-6aα), 3.70-3.65 (m, 2H, H-6bα, H-6bβ), 3.57 (ddd, 1H, *J* 9.5, 5.5, 2.5, H-5α), 3.44 (dd, 1H, *J* 10.0, 9.5, H-3α), 3.29-3.24 (m, 4H, H-3β, H-4α, H-4β, H-5β), 2.89 (t, 1H, *J* 2.5, H-3'β), 2.87 (t, 1H, *J* 2.0, H-3'α), 2.62 (dd, 1H, *J* 10.0, 3.5, H-2α), 2.61-2.57 (m, 1H, H-2β); $\delta_C$ (125 MHz, DMSO-$d_6$) 101.62 (C-1β), 97.41 (C-1α), 79.86, 79.76 (C-2'α, C-2'β), 77.16, 77.09, 77.03 (C-3'α, C-3'β, C-5β), 76.35 (C-3β), 74.93 (C-3α), 73.44 (C-5α), 70.15, 69.98 (C-4α, C-4β), 61.06, 60.72 (C-6α, C-6β), 57.01 (C-2β), 55.94 (C-2α), 54.79 (C-1'β), 53.33 (C-1'α); HRMS ($ES^+$) *m/z* calc. for $C_9H_{16}NO_5$ ($M+H^+$): 218.1028; found 218.1055; *m/z* 218 (23%, $M+H^+$).

**Propargyl glycoside couplings with 5'-azido-5'-deoxyadenosine 14**
Adenosine-based sugar-triazole-nucleosides were prepared using the general procedure below (using compound **37** as an example).

**5'-Deoxy-5'-[4-(α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (37)**

Prop-2-ynyl-α-D-glucopyranoside **15** (29.0 mg, 0.133 mmol) and 5'-azido-5'-deoxyadenosine **14** (42.7 mg, 0.146 mmol) were measured into a sample vial, followed by copper(I) bromide (1 mg, 6.6 μmol). Aqueous sodium ascorbate solution (40 mM, 332 μL, 13.3 μmol) and a solution of TBTA in acetonitrile (20 mM, 333 μL, 6.6 μmol) was added, followed by methanol (700 μL), acetonitrile (367 μL) and water (368 μL). The sample vial was sealed, the lid pierced with a syringe needle, and the reaction mixture was sonicated for 30 minutes until reaction completion. This was concentrated *in vacuo* and purified by automated chromatography (EtOAc/MeOH 7:3 as eluent) to yield **37** (49 mg, 72%) as a white solid: $[\alpha]_D^{20}$ = +75.4 (c = 1.085, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.15, 8.07, 7.98 (3 x s, 3H, H-2, H-8, H-5'''), 5.89 (d, 1H, *J* 5.0, H-1'), 4.78-4.70 (m, 2H, H-5'), 4.75 (d, 1H, *J* 3.5, H-1''), 4.62 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.51 (t, 1H, *J* 5.0, H-2'), 4.43 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.28 (dt, 1H, *J* 6.0, 4.5, H-4'), 4.23 (t, 1H, *J* 4.5, H-3'), 3.60 (dd, 1H, *J* 11.5, 1.5, H-6''a), 3.44 (dd, 1H, *J* 11.5, 5.5, H-6''b), 3.40 (ddd, 1H, *J* 9.5, 5.5, 2.0, H-5''), 3.39 (t, 1H, *J* 9.5, H-3''), 3.19 (dd, 1H, *J* 9.5, 4.0, H-2''), 3.06 (t, 1H, *J* 9.0, H-4''); $\delta_C$ (125 MHz, $CD_3OD$) 157.42 (C-6), 154.16 (C-2), 150.55 (C-4), 145.40 (C-4'''), 141.07 (C-8), 127.14 (C-5'''), 120.44 (C-5), 99.92 (C-1''), 90.51 (C-1'), 83.47 (C-4'), 75.02, 74.90 (C-2', C-3''), 74.06, 73.77 (C-2'', C-5''), 72.07, 72.03 (C-3', C-4''), 62.77 (C-6''), 61.34 ($CH_2$), 52.06 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{19}H_{25}N_8O_9$ ($M-H^+$): 509.1744; found 509.1735; *m/z* 509 (23%, $M-H^+$).

**5'-Deoxy-5'-[4-(β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (38)**

Was prepared from prop-2-ynyl-β-D-glucopyranoside (30.5 mg, 0.140 mmol) and 5'-azido-5'-deoxyadenosine **14** (44.9 mg, 0.154 mmol) as described for **37** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **38** (61 mg, 85%) was obtained as a white solid: $[\alpha]_D^{20}$ = -2.7 (c = 0.919, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.17 (s, 1H, H-2), 7.87, 7.82 (2 x s, 2H, H-8, H-5'''), 5.98 (d, 1H, *J* 4.0, H-1'), 4.93 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.87 (dd, 1H, *J* 15.0, 5.0, H-5'a), 4.80 (dd, 1H, *J* 15.0, 3.5, H-5'b), 4.65 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.45 (t, 1H, *J* 5.5, H-3'), 4.41 (dd, 1H, *J* 5.0, 4.0, H-4'), 4.39-4.36 (m, 1H, H-2'), 4.38 (d, 1H, *J* 8.0, H-1''), 3.88 (dd, 1H, *J* 12.0, 1.5, H-6''a), 3.67 (dd, 1H, *J* 12.0, 5.5, H-6''b), 3.38 (t, 1H, *J* 9.0, H-3''), 3.33-3.26 (m, 2H, H-4'', H-5'', overlapping $CD_3OD$ peak), 3.22 (dd, 1H, *J* 9.0, 8.0, H-2''); $\delta_C$ (125 MHz, $CD_3OD$) 157.34 (C-6), 154.19 (C-2), 150.58 (C-4), 145.65 (C-4'''), 141.38 (C-8), 126.95 (C-5'''), 119.94 (C-5), 103.88 (C-1''), 90.53 (C-1'), 83.47 (C-4'), 78.08, 77.87 (C-3'', C-5''), 74.93, 74.70 (C-2', C-2''), 71.91 (C-3'), 71.64 (C-4''), 63.10 ($CH_2$), 62.75 (C-6''), 51.98 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{27}N_8O_9$ ($M+H^+$): 511.1901; found 511.1901; *m/z* 533 (50%, $M+Na^+$), 511 (90%, $M+H^+$).

**5'-Deoxy-5'-[4-(α-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (39)**

Was prepared from prop-2-ynyl-α-D-galactopyranoside **23** (20.3 mg, 0.093 mmol) and 5'-azido-5'-deoxyadenosine **14** (29.9 mg, 0.102 mmol) as described for **37** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **39** (40 mg, 84%) was obtained as a white solid: $[\alpha]_D^{20}$ = +95.0 (c = 0.943, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.15, 8.05, 8.00 (3 x s, 3H, H-2, H-8, H-5'''), 5.90 (d, 1H, *J* 5.0, H-1'), 4.77 (d, 1H, *J* 3.5, H-1''), 4.76-4.70 (m, 2H, H-5'), 4.63 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.52 (t, 1H, *J* 5.0, H-2'), 4.43 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.28 (dt, 1H, *J* 6.5, 4.5, H-4'), 4.24 (t, 1H, *J* 5.0, H-3'), 3.69 (dd, 1H, *J* 3.0, 1.0, H-4''), 3.63 (m, 1H, H-5''), 3.59 (dd, 1H, *J* 10.5, 4.0, H-2''), 3.54-3.48 (m, 2H, H-3'', H-6''a, overlapping HOD peak), 3.45 (dd, 1H, *J* 10.5, 7.0, H-6''b); $\delta_C$ (125 MHz, DMSO-$d_6$) 155.93 (C-6), 152.89 (C-2), 149.29 (C-4), 143.92 (C-4'''), 139.72 (C-8), 125.04 (C-5'''), 119.96 (C-5), 98.50 (C-1''), 87.83 (C-1'), 82.22 (C-4'), 72.77 (C-2'), 71.39 (C-5''), 70.80 (C-3'), 69.44 (C-3''), 68.83 (C-4''), 68.33 (C-2''), 60.63 (C-6''), 59.94 ($CH_2$), 51.24 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{19}H_{25}N_8O_9$ ($M-H^+$): 509.1744; found 509.1756; *m/z* 509 (100%, $M-H^+$).

**5'-Deoxy-5'-[4-(α-D-mannopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (41)**
Was prepared from prop-2-ynyl-α-D-mannopyranoside **17** (27.4 mg, 0.126 mmol) and 5'-azido-5'-deoxyadenosine **14** (40.4 mg, 0.138 mmol) as described for **37** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **41** (55 mg, 86%) was obtained as a white solid: $[\alpha]_D^{20}$ = +67.1 (c = 1.436, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.18, 8.14 (2 x s, 2H, H-2, H-8), 7.94 (s, 1H, H-5'''), 5.89 (d, 1H, *J* 5.5, H-1'), 4.75-4.68 (m, 2H, H-5'), 4.72 (d, 1H, *J* 1.5, H-1''), 4.582 (t, 1H, *J* 5.5, H-2'), 4.579 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.44 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.30-4.23 (m, 2H, H-3', H-4'), 3.68-3.60 (m, 1H, H-6''a, overlapping HOD peak), 3.55 (dd, 1H, *J* 3.0, 1.5, H-2''), 3.48-3.40 (m, 2H, H-3'', H-6''b), 3.39-3.32 (m, 2H, H-4'', H-5''); $\delta_C$ (125 MHz, DMSO-$d_6$) 156.06 (C-6), 153.00 (C-2), 149.45 (C-4), 143.72 (C-4'''), 140.13 (C-8), 125.10 (C-5'''), 119.20 (C-5), 99.22 (C-1''), 87.98 (C-1'), 82.46 (C-4'), 74.13 (C-5''), 72.75 (C-2'), 70.98 (C-3''), 70.86 (C-3'), 70.22 (C-2''), 67.02 (C-4''), 61.31 (C-6''), 59.19 ($CH_2$), 51.56 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{27}N_8O_9$ ($M+H^+$): 511.1901; found 511.1890; *m/z* 533 (18%, $M+Na^+$), 511 (100%, $M+H^+$).

**5'-Deoxy-5'-[4-(α-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (42)**
Was prepared from prop-2-ynyl-α-D-xylopyranoside **19** (25.8 mg, 0.137 mmol) and 5'-azido-5'-deoxyadenosine **14** (44.1 mg, 0.151 mmol) as described for **37**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **42** (58 mg, 88%) was obtained as a white solid: $[\alpha]_D^{20}$ = +82.1 (c = 1.199, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.14, 8.06, 7.96 (3 x s, 3H, H-2, H-8, H-5'''), 5.89 (d, 1H, *J* 5.0, H-1'), 4.77-4.72 (m, 2H, H-5'), 4.72 (d, 1H, *J* 3.5, H-1''), 4.58 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.52 (t, 1H, *J* 5.0, H-2'), 4.43 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.28 (m, 1H, H-4'), 4.23 (t, 1H, *J* 5.0, H-3'), 3.41 (dd, 1H, *J* 9.5, 4.5, H-5''a), 3.34 (t, 1H, *J* 9.0, H-3''), 3.33-3.24 (m, 2H, H-4'', H-5''b), 3.19 (dd, 1H, *J* 9.0, 3.5, H-2''); $\delta_C$ (125 MHz, DMSO-$d_6$) 156.02 (C-6), 153.04 (C-2), 149.40 (C-4), 143.85 (C-4'''), 139.95 (C-8), 125.29 (C-5'''), 119.07 (C-5), 98.65 (C-1''), 88.00 (C-1'), 82.37 (C-4'), 73.27 (C-3''), 72.86 (C-2'), 71.92 (C-2''), 70.87 (C-3'), 70.00 (C-4''), 62.09 (C-5''), 60.18 ($CH_2$), 51.36 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_8O_8$ ($M+H^+$): 481.1795; found 481.1794; *m/z* 983 (38%, $2M+Na^+$), 503 (96%, $M+Na^+$), 481 (68%, $M+H^+$).

**5'-Deoxy-5'-[4-(β-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (43)**
Was prepared from prop-2-ynyl-β-D-xylopyranoside **28c** (23.4 mg, 0.124 mmol) and 5'-azido-5'-deoxyadenosine **14** (39.9 mg, 0.137 mmol) as described for **37** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **43** (51 mg, 85%) was obtained as a white solid: $[\alpha]_D^{20}$ = -10.9 (c = 1.312, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.18, 8.15 (2 x s, 2H, H-2, H-8), 7.94 (s, 1H, H-5'''), 5.89 (d, 1H, *J* 5.5, H-1'), 4.76-4.72 (m, 2H, H-5'), 4.72 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.60 (t, 1H, *J* 5.5, H-2'), 4.51 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.28-4.22 (m, 2H, H-3', H-4'), 4.19 (d, 1H, *J* 8.0, H-1''), 3.69 (dd, 1H, *J* 11.5, 5.5, H-5''a), 3.30-3.26 (m, 1H, H-4''), 3.11-3.01 (m, 2H, H-3'', H-5''b), 2.94 (t, 1H, *J* 8.5, H-2''); $\delta_C$ (125 MHz, DMSO-$d_6$) 155.98 (C-6), 152.63 (C-2), 149.18 (C-4), 143.53 (C-4'''), 139.74 (C-8), 124.80 (C-5'''), 119.05 (C-5), 102.80 (C-1''), 87.68 (C-1'), 82.26 (C-4'), 76.38 (C-3''), 73.08 (C-2''), 72.53 (C-2'), 70.84 (C-3'), 69.46 (C-4''), 65.63 (C-5''), 61.27 ($CH_2$), 51.22 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_8O_8$ ($M+H^+$): 481.1795; found 481.1799; *m/z* 983 (12%, $2M+Na^+$), 961 (7%, $2M+H^+$), 503 (32%, $M+Na^+$), 481 (100%, $M+H^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (44)**
Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-α-D-glucoside **16** (28.3 mg, 0.109 mmol) and 5'-azido-5'-deoxyadenosine **14** (35.1 mg, 0.120 mmol) as described for **37** Following automated chromatography (EtOAc/MeOH 7:3 as

eluent), **44** (48 mg, 80%) was obtained as a white solid: $[\alpha]_D^{20}$ = +86.0 (c = 1.392, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.15, 8.11 (2 x s, 2H, H-2, H-8), 7.96 (s, 1H, H-5'''), 5.89 (d, 1H, *J* 5.5, H-1'), 4.75-4.71 (m, 3H, H-5', H-1''), 4.60 (d, 1H, *J* 12.5, OC$\underline{H}_A H_B$), 4.49 (t, 1H, *J* 5.0, H-2'), 4.42 (d, 1H, *J* 12.5, OC$H_A\underline{H}_B$), 4.30-4.23 (m, 2H, H-3', H-4'), 3.69-3.60 (m, 2H, H-2'', H-6''a), 3.52-3.40 (m, 3H, H-6''b, H-3'', H-5''), 3.14 (dd, 1H, *J* 9.5, 9.0, H-4''), 1.73 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, DMSO-$d_6$) 170.33 (C=O), 156.06 (C-6), 153.09 (C-2), 149.49 (C-4), 143.83 (C-4'''), 140.00 (C-8), 125.22 (C-5'''), 119.11 (C-5), 96.49 (C-1''), 87.90 (C-1'), 82.47 (C-4'), 73.08, 72.84 (C-2', C-5''), 70.92, 70.78, 70.56 (C-3', C-3'', C-4''), 60.94 (C-6''), 60.09 ($CH_2$), 53.81 (C-2''), 51.53 (C-5'), 22.62 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{21}H_{30}N_9O_9$ ($M+H^+$): 552.2166; found 552.2150; *m/z* 574 (35%, $M+Na^+$), 552 (100%, $M+H^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (45)**
Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-β-D-glucoside **31** (18.8 mg, 0.073 mmol) and 5'-azido-5'-deoxyadenosine **14** (23.3 mg, 0.08 mmol) as described for **37**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **45** (21 mg, 53%) was obtained as a white solid: $[\alpha]_D^{20}$ = +5.5 (c = 1.08, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.21, 8.15 (2 x s, 2H, H-2, H-8), 7.83 (s, 1H, H-5'''), 5.89 (d, 1H, *J* 5.5, H-1'), 4.77-4.68 (m, 2H, H-5'), 4.73 (d, 1H, *J* 12.0, OC$\underline{H}_A H_B$), 4.57 (t, 1H, *J* 5.0, H-2'), 4.51 (d, 1H, *J* 11.5, OC$H_A\underline{H}_B$), 4.36 (d, 1H, *J* 8.0, H-1''), 4.29-4.23 (m, 2H, H-3', H-4'), 3.65-3.62 (m, 1H, H-6''a), 3.45 (dd, 1H, *J* 12.0, 6.5, H-6''b), 3.39 (dd, 1H, *J* 10.5, 8.5, H-2''), 3.26 (dd, 1H, *J* 10.0, 8.5, H-3''), 3.15-3.03 (m, 2H, H-4'', H-5''), 1.66 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, DMSO-$d_6$) 169.87 (C=O), 156.04 (C-6), 152.96 (C-2), 149.43 (C-4), 144.00 (C-4'''), 140.17 (C-8), 124.91 (C-5'''), 119.21 (C-5), 100.38 (C-1''), 87.95 (C-1'), 82.54 (C-4'), 77.04 (C-5''), 74.15 (C-3''), 72.67 (C-2'), 70.99, 70.64 (C-3', C-4''), 61.43, 61.16 (C-6'', $CH_2$), 55.39 (C-2''), 51.64 (C-5'), 22.95 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{21}H_{30}N_9O_9$ ($M+H^+$): 552.2166; found 552.2165; *m/z* 574 (70%, $M+Na^+$), 552 (100%, $M+H^+$).

**5'-Deoxy-5'-[4-(L-arabinopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (46)**
Was prepared from prop-2-ynyl-L-arabinopyranoside **18** (27.4 mg, 0.146 mmol) and 5'-azido-5'-deoxyadenosine **14** (46.8 mg, 0.160 mmol) as described for **31** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **46** (59 mg, 84%) was obtained as a white solid with an α/β ratio of 1:3: $[\alpha]_D^{20}$ = +92.2 (c = 1.194, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.15, 8.14, 8.06, 7.95, 7.92 (5 x s, 6H, H-2α, H-2β, H-8α, H-8β, H-5'''α, H-5'''β), 5.89 (d, 2H, H-1'α, H-1'β), 4.80-4.67 (m, 6H, H-1''β, H-5'aα, H-5'aβ, H-5'aα, H-5'bα, OC$\underline{H}_A H_B$α), 4.57 (d, 1H, *J* 12.5, OC$\underline{H}_A H_B$β), 4.53 (t, 2H, *J* 5.0, H-2'α, H-2'β), 4.48 (d, 1H, *J* 12.5, OC$H_A\underline{H}_B$α), 4.42 (d, 1H, *J* 12.0, OC$H_A\underline{H}_B$β), 4.30-4.20 (m, 4H, H-3'α, H-3'β, H-4'α, H-4'β), 4.17-4.13 (m, 1H, H-1''α), 3.72-3.50 (m, 6H, H-2''β, H-3''β, H-4''α, H-4''β, H-5''aα, H-5''β), 3.44-3.38 (m, 1H, H-5''bβ), 3.38-3.32 (m, 1H, H-5''bα), 3.32-3.28 (m, 2H, H-2''α, H-3''α); $\delta_C$ (125 MHz, DMSO-$d_6$) 156.06 (C-6), 153.10 (C-2), 149.47 (C-4α), 149.42 (C-4β), 143.99 (C-4'''β), 143.89 (C-4'''α), 140.16 (C-8α), 140.02 (C-8β), 125.34 (C-5'''), 119.09 (C-5), 102.56 (C-1''α), 99.17 (C-1''β), 87.97 (C-1'β), 87.85 (C-1'α), 82.56 (C-4'α), 82.41 (C-4'β), 72.85 (C-2'β), 72.76 (C-2'α), 72.53 (C-2''α), 70.94 (C-3'α), 70.90 (C-3'β), 70.56 (C-3''α), 69.02 (C-2''β), 68.64 (C-4''β), 68.44 (C-3''β), 67.71 (C-4''α), 65.55 (C-5''α), 63.37 (C-5''β), 61.14 ($CH_2$α), 60.37 ($CH_2$β), 51.49 (C-5'α), 51.36 (C-5'β); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_8O_8$ ($M+H^+$): 481.1795; found 481.1787; *m/z* 983 (44%, $2M+Na^+$), 961 (8%, $2M+H^+$), 503 (32%, $M+Na^+$), 481 (100%, $M+H^+$).

**5'-Deoxy-5'-[4-(β-D-ribofuranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (47)**

Was prepared from prop-2-ynyl-β-D-ribofuranoside **26** (28.6 mg, 0.152 mmol) and 5'-azido-5'-deoxyadenosine **14** (48.9 mg, 0.167 mmol) as described for **37**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **47** (52 mg, 71%) was obtained as a white solid: $[\alpha]_D^{20}$ = -9.9 (c = 1.184, DMSO); $\delta_H$ (500 MHz, DMSO-$d_6$) 8.22 (s, 1H, H-8), 8.14 (s, 1H, H-2), 7.89 (s, 1H, H-5'''), 5.88 (d, 1H, *J* 5.5, H-1'), 4.80 (s, 1H, H-1''), 4.76-4.69 (m, 2H, H-5'), 4.61 (d, 1H, *J* 12.5, OC$\underline{H}_A$H$_B$), 4.59 (t, 1H, *J* 5.0, H-2'), 4.38 (d, 1H, *J* 12.5, OCH$_A\underline{H}_B$), 4.27 (dd, 1H, *J* 6.0, 4.5, H-4'), 4.24 (t, 1H, *J* 4.5, H-3'), 3.84 (dd, 1H, *J* 6.5, 4.5, H-3''), 3.76 (dt, 1H, *J* 6.5, 4.0, H-4''), 3.68 (d, 1H, *J* 5.0, H-2''), 3.52 (dd, 1H, *J* 12.0, 4.0, H-5''a), 3.34 (dd, 1H, *J* 12.0, 6.5, H-5''b); $\delta_C$ (125 MHz, DMSO-$d_6$) 156.10 (C-6), 153.03 (C-2), 149.47 (C-4), 143.88 (C-4''), 140.22 (C-8), 125.06 (C-5'''), 119.25 (C-5), 106.25 (C-1''), 87.93 (C-1'), 83.81 (C-4''), 82.58 (C-4'), 74.38 (C-2''), 72.69 (C-2'), 70.99, 70.97 (C-3', C-3''), 63.23 (C-5''), 59.62 ($CH_2$), 51.59 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_8O_8$ ($M+H^+$): 481.1795; found 481.1794; *m/z* 983 (15%, $2M+Na^+$), 961 (3%, $2M+H^+$), 503 (48%, $M+Na^+$), 481 (100%, $M+H^+$).

**5'-Deoxy-5'-[4-(2-amino-2-deoxy-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]adenosine (48)**
Was prepared from prop-2-ynyl-2-amino-2-deoxy-D-glucopyranoside **36** (37.2 mg, 0.171 mmol) and 5'-azido-5'-deoxyadenosine **14** (55.1 mg, 0.188 mmol) as described for **37**. Following automated chromatography (EtOAc/MeOH 7:3 to 100% MeOH as eluent), **48** (42 mg, 48%) was obtained as a white solid with an α/β ratio of (1.1:1): $\delta_H$ (500 MHz, DMSO-$d_6$) 8.23-8.00 (m, 6H, H-2α, H-2β, H-8α, H-8β, H-5'''α, H-5'''β), 5.900, 5.897 (2 x d, 2H, *J* 5.5, H-1'α, H-1'β), 4.81 (d, 1H, *J* 12.5, OC$\underline{H}_A$H$_B$β), 4.78-4.69 (m, 5H, H-5'aα, H-5'aβ, H-5'bα, H-5'bβ, H-1''α), 4.64 (d, 1H, *J* 12.0, OC$\underline{H}_A$H$_B$α), 4.59, 4.58 (2 x t, 2H, *J* 5.0, H-2'α, H-2'β), 4.55 (d, 1H, *J* 12.0, OCH$_A\underline{H}_B$β), 4.45 (d, 1H, *J* 12.5, OCH$_A\underline{H}_B$α), 4.30-4.12 (m, 5H, H-1''β, H-3'α, H-3'β, H-4'α, H-4'β), 3.70-3.60 (m, 2H, H-6''aα, H-6''aβ), 3.50-3.20 (m, 3H, H-5''α, H-6''bα, H-6''bβ, overlapping HOD peak), 3.20-3.00 (m, 5H, H-3''α, H-3''β, H-4''α, H-4''β, H-5''β), 2.63-2.30 (m, 2H, H-2''α, H-2''β); $\delta_C$ (125 MHz, DMSO-$d_6$) 155.97 (C-6), 152.59 (C-2), 149.21 (C-4), 145.46, 143.64 (C-4'''α, C-4'''β), 139.71, 139.61 (C-8α, C-8β), 124.69, 124.54 (C-5'''α, C-5'''β), 119.09, 118.96 (C-5α, C-5β), (anomeric carbons hidden in baseline noise), 87.68, 87.61 (C-1'α, C-1'β), 82.22, 82.16 (C-4'α, C-4'β), 77.05 (C-5''β), 73.23-70.02 (C-2'α, C-2'β, C-3'α, C-3'β, C-3''α, C-3''β, C-4''α, C-4''β, C-5''α), 61.34, 61.06, 60.88, 59.66, 59.64 ($CH_2$α, $CH_2$β, C-2''α, C-2''β, C-6''α, C-6''β), 51.24 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{28}N_9O_8$ ($M+H^+$): 510.2061; found 510.2070; *m/z* 510 (100%, $M+H^+$).

**Propargyl glycoside couplings with 5'-azido-5'-deoxythymidine (18)**
Thymidine-based sugar-triazole-nucleosides were prepared using the general procedure below (using compound **33** as an example).

**5'-Deoxy-5'-[4-(α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (49)**
Prop-2-ynyl-α-D-glucopyranoside **15** (80.8 mg, 0.370 mmol) and 5'-azido-5'-deoxythymidine **8** (108.8 mg, 0.407 mmol) were dissolved in MeOH (2 mL). Aqueous $CuSO_4$ solution (0.05 M, 370 μL, 18.5 μmol) was added followed by aqueous sodium ascorbate solution (0.1 M, 370 μL, 37.0 μmol). This was stirred for 3 days then concentrated *in vacuo* and purified by automated chromatography (EtOAc/MeOH 3:1 as eluent) to yield **49** (109 mg, 61%) as a white solid: $[\alpha]_D^{20}$ = +104.2 (c = 0.95, MeOH) (Lit.[9] +108);; $\delta_H$ (500 MHz, $CD_3OD$) 8.04 (s, 1H, H-5'''), 7.28 (d, 1H, *J* 1.0, H-6), 6.18 (t, 1H, *J* 7.0, H-1'), 4.90 (d, 1H, *J* 4.0, H-1''), 4.82 (d, 1H, *J* 12.0, OC$\underline{H}_A$H$_B$), 4.78 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.70 (dd, 1H, *J* 14.5, 7.0, H-5'b), 4.67 (d, 1H, *J* 12.5, OCH$_A\underline{H}_B$), 4.41 (dt, 1H, *J* 6.5, 4.5, H-3'), 4.17 (dt, 1H, *J* 7.0, 4.0, H-4'), 3.80 (dd, 1H, *J* 11.5, 2.5, H-6''a), 3.66 (dd, 1H, *J* 12.0, 5.5, H-6''b), 3.62 (t, 1H, *J* 9.0, H-3''), 3.58 (ddd, 1H, *J* 9.5, 5.5, 2.0, H-5''), 3.39 (dd, 1H, *J* 9.5, 3.5, H-2''), 3.28 (dd, 1H, *J* 10.0, 9.0, H-4''), 2.30 (ddd, 1H, *J* 14.0, 6.5, 6.5, H-2'a), 2.27 (ddd, 1H, *J* 13.5, 6.5, 5.0, H-2'b), 1.89 (d, 3H, *J* 1.0,

$CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.35 (C-4), 152.18 (C-2), 145.73 (C-4'''), 138.35 (C-6), 126.37 (C-5'''), 111.94 (C-5), 99.78 (C-1''), 87.19 (C-1'), 85.59 (C-4'), 75.09 (C-3''), 74.07 (C-5''), 73.56 (C-2''), 72.50 (C-3'), 71.87 (C-4''), 62.77 (C-6''), 61.55 ($CH_2$), 52.72 (C-5'), 39.60 (C-2'), 12.46 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{28}N_5O_{10}$ ($M+H^+$): 486.1831; found 486.1825; *m/z* 524 (17%, $M+K^+$), 508 (35%, $M+Na^+$).

**5'-Deoxy-5'-[4-(β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (50)**
Was prepared from prop-2-ynyl-β-D-glucopyranoside (23.5 mg, 0.108 mmol) and 5'-azido-5'-deoxythymidine **8** (31.7 mg, 0.119 mmol) as described for **49**. Reaction time 44 hours. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **50** (46 mg, 88%) was obtained as a white solid: $R_f$ = 0.23 (EtOAc/MeOH 7:3); $[\alpha]_D^{20}$ = +23.7 (c = 0.985, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 8.03 (s, 1H, H-5'''), 7.24 (d, 1H, *J* 1.0, H-6), 6.19 (t, 1H, *J* 7.0, H-1'), 4.97 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.77 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.78 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.70 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.41 (dt, 1H, *J* 6.0, 5.0, H-3'), 4.37 (d, 1H, *J* 7.5, H-1''), 4.15 (dt, 1H, *J* 7.0, 4.5, H-4'), 3.88 (dd, 1H, *J* 12.5, 2.0, H-6''a), 3.66 (dd, 1H, *J* 12.0, 6.0, H-6''b), 3.34 (t, 1H, *J* 9.0, H-3''), 3.29-3.26 (m, 2H, H-4'', H-5''), 3.20 (dd, 1H, *J* 9.0, 7.5, H-2''), 2.27 (dd, 2H, *J* 6.5, 6.0, H-2'), 1.89 (d, 3H, *J* 1.0, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.38 (C-4), 152.22 (C-2), 145.83 (C-4'''), 138.28 (C-6), 126.56 (C-5'''), 112.02 (C-5), 103.66 (C-1''), 87.00 (C-1'), 85.47 (C-4'), 78.11, 78.03 (C-3'', C-5''), 75.06 (C-2''), 72.40 (C-3'), 71.67 (C-4''), 63.03 ($CH_2$), 62.92 (C-6''), 52.59 (C-5'), 39.56 (C-2'), 12.56 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{28}N_5O_{10}$ ($M+H^+$): 486.1831; found 486.1833; *m/z* 524 (19%, $M+K^+$), 508 (32%, $M+Na^+$).

**5'-Deoxy-5'-[4-(α-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (51)**
Was prepared from prop-2-ynyl-α-D-galactopyranoside **23** (60 mg, 0.275 mmol) and 5'-azido-5'-deoxythymidine **8** (80.8 mg, 0.302 mmol) as described for **49**. Reaction time 18 hours. Following automated chromatography (EtOAc/MeOH 9:1 as eluent), **51** (90 mg, 68%) was obtained as a white solid: $[\alpha]_D^{20}$ = +110.2 (c = 1.05, MeOH) (Lit.[9] +110); $\delta_H$ (500 MHz, $CD_3OD$) 8.05 (s, 1H, H-5'''), 7.28 (d, 1H, *J* 1.0, H-6), 6.19 (t, 1H, *J* 6.5, H-1'), 4.94 (d, 1H, *J* 4.0, H-1''), 4.82 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.78 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.70 (dd, 1H, *J* 14.0, 7.0, H-5'b), 4.66 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.42 (dt, 1H, *J* 6.5, 5.0, H-3'), 4.17 (dt, 1H, *J* 7.0, 4.0, H-4'), 3.87 (dd, 1H, *J* 3.0, 1.0, H-4''), 3.82 (ddd, 1H, *J* 6.5, 5.0, 1.0, H-5''), 3.78 (dd, 1H, *J* 10.5, 4.0, H-2''), 3.73 (dd, 1H, *J* 11.0, 7.0, H-6''a), 3.72 (dd, 1H, *J* 10.5, 3.5, H-3''), 3.68 (dd, 1H, *J* 11.5, 5.5, H-6''b), 2.30 (ddd, 1H, *J* 13.5, 6.5, 6.5, H-2'a), 2.27 (ddd, 1H, *J* 14.0, 7.0, 5.0, H-2'b), 1.89 (d, 3H, *J* 1.5, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.35 (C-4), 152.19 (C-2), 145.74 (C-4'''), 138.36 (C-6), 126.39 (C-5'''), 111.92 (C-5), 100.02 (C-1''), 87.11 (C-1'), 85.56 (C-4'), 72.81 (C-5''), 72.47 (C-3'), 71.47 (C-3''), 71.14 (C-4''), 70.21 (C-2''), 62.88 (C-6''), 61.55 ($CH_2$), 52.69 (C-5'), 39.56 (C-2'), 12.48 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{28}N_5O_{10}$ ($M+H^+$): 486.1831; found 486.1828; *m/z* 486 (47%, $M+H^+$).

**5'-Deoxy-5'-[4-(β-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (52)**
Was prepared from prop-2-ynyl-β-D-galactopyranoside **27c** (80 mg, 0.37 mmol) and 5'-azido-5'-deoxythymidine **8** (98 mg, 0.37 mmol) as described for **49**. Reaction time 19 hours. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **52** (97 mg, 54%) was obtained as an off-white solid: mp 175-178 °C (EtOAc/MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 8.03 (s, 1H, H-5'''), 7.25 (s, 1H, H-6), 6.19 (t, 1H, *J* 7.0, H-1'), 4.97 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.77 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.78 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.69 (dd, 1H, *J* 14.5, 7.0, H-5'b), 4.41 (dt, 1H, *J* 5.5, 5.0, H-3'), 4.33 (d, 1H, *J* 8.0, H-1''), 4.15 (dt, 1H, *J* 7.0, 4.5, H-4'),

3.82 (d, 1H, *J* 3.5, H-4''), 3.79 (dd, 1H, *J* 11.5, 7.5, H-6''a), 3.72 (dd, 1H, *J* 11.5, 5.0, H-6''b), 3.54 (m, 2H, H-2'', H-5''), 3.46 (dd, 1H, *J* 10.0, 3.5, H-3''), 2.27 (dd, 2H, *J* 6.5, 6.0, H-2'), 1.89 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.36 (C-4), 152.20 (C-2), 145.94 (C-4'''), 138.27 (C-6), 126.54 (C-5'''), 112.01 (C-5), 104.23 (C-1''), 86.97 (C-1'), 85.54 (C-4'), 76.89 (C-5''), 74.96 (C-3''), 72.46 (C-2''), 72.41 (C-3'), 70.38 (C-4''), 63.00 ($CH_2$), 62.67 (C-6''), 52.63 (C-5'), 39.56 (C-2'), 12.51 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{27}N_5O_{10}Na$ ($M+Na^+$): 508.1650; found 508.1655; *m/z* 508 (100%, $M+Na^+$).

**5'-Deoxy-5'-[4-(α-D-mannopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (53)**

Was prepared from prop-2-ynyl-α-D-mannopyranoside **17** (40.7 mg, 0.187 mmol) and 5'-azido-5'-deoxythymidine **8** (54.8 mg, 0.205 mmol) as described for **49**. Reaction time 24 hours. Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **53** (56 mg, 62%) was obtained as a white solid: Mpt 131-133 ºC (EtOAc/MeOH); $[\alpha]_D^{20}$ = +79.8 (c = 1.13, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 8.02 (s, 1H, H-5'''), 7.25 (d, 1H, *J* 1.0, H-6), 6.17 (t, 1H, *J* 6.5, H-1'), 4.86 (d, 1H, *J* 1.5, H-1''), 4.79 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.78 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.70 (dd, 1H, *J* 14.0, 6.5, H-5'b), 4.65 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.42 (dt, 1H, *J* 6.0, 5.0, H-3'), 4.16 (dt, 1H, *J* 6.5, 4.5, H-4'), 3.84 (dd, 1H, *J* 12.0, 2.5, H-6''a), 3.78 (dd, 1H, *J* 3.0, 1.5, H-2''), 3.71 (dd, 1H, *J* 12.0, 6.0, H-6''b), 3.66 (dd, 1H, *J* 9.0, 3.5, H-3''), 3.60 (t, 1H, *J* 9.5, H-4''), 3.55 (ddd, 1H, *J* 9.5, 5.5, 2.0, H-5''), 2.32-2.27 (m, 2H, H-2'), 1.89 (d, 3H, *J* 1.0, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.34 (C-4), 152.16 (C-2), 145.47 (C-4'''), 138.37 (C-6), 126.49 (C-5'''), 111.92 (C-5), 100.88 (C-1''), 87.24 (C-1'), 85.52 (C-4'), 75.05 (C-5''), 72.56 (C-3''), 72.41 (C-3'), 72.08 (C-2''), 68.69 (C-4''), 63.06 (C-6''), 60.76 ($CH_2$), 52.60 (C-5'), 39.60 (C-2'), 12.45 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{19}H_{27}N_5O_{10}$ ($M+H^+$): 486.1831; found 486.1832; *m/z* 508 (16%, $M+Na^+$).

**5'-Deoxy-5'-[4-(α-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (54)**

Was prepared from prop-2-ynyl-α-D-xylopyranoside **19** (59.7 mg, 0.317 mmol) and 5'-azido-5'-deoxythymidine **8** (84.8 mg, 0.317 mmol) as described for **49**. Reaction time 24 hours. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **54** (87 mg, 60%) was obtained as a white solid: $[\alpha]_D^{20}$ = +121.7 (c = 1.00, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 8.04 (s, 1H, H-5'''), 7.29 (d, 1H, *J* 1.5, H-6), 6.18 (t, 1H, *J* 6.5, H-1'), 4.85 (d, 1H, *J* 3.5, H-1''), 4.79 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.78 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.70 (dd, 1H, *J* 14.5, 7.0, H-5'b), 4.65 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.41 (dt, 1H, *J* 6.0, 4.5, H-3'), 4.17 (dt, 1H, *J* 7.0, 4.5, H-4'), 3.57-3.52 (m, 2H, H-3'', H-5''a), 3.50-3.45 (m, 2H, H-4'', H-5''b), 3.37 (dd, 1H, *J* 9.5, 4.0, H-2''), 2.32-2.27 (m, 2H, H-2'), 1.89 (d, 3H, *J* 1.0, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.36 (C-4), 152.19 (C-2), 145.74 (C-4'''), 138.36 (C-6), 126.34 (C-5'''), 111.93 (C-5), 100.10 (C-1''), 87.20, 87.12 (C-1'), 85.58 (C-4'), 75.16 (C-3''), 73.58 (C-2''), 72.49 (C-3'), 71.55 (C-4''), 63.33 (C-5''), 61.66 ($CH_2$), 52.71 (C-5'), 39.57 (C-2'), 12.51, 12.45 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_5O_9Na$ ($M+Na^+$): 478.1544; found 478.1547; *m/z* 494 (28%, $M+K^+$), 478 (100%, $M+Na^+$).

**5'-Deoxy-5'-[4-(β-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (55)**

Was prepared from prop-2-ynyl-β-D-xylopyranoside **28c** (50 mg, 0.266 mmol) and 5'-azido-5'-deoxythymidine **8** (71 mg, 0.266 mmol) as described for **49**. Reaction time 19 hours. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **55** (69 mg, 57%) was obtained as a white solid: $[\alpha]_D^{20}$ = -7.3 (c = 0.99, $H_2O$); $\delta_H$ (500 MHz, $CD_3OD$) 8.00 (s, 1H, H-5'''), 7.24 (s, 1H, H-6), 6.18 (t, 1H, *J* 7.0, H-1'), 4.91 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.77 (dd, 1H, *J* 14.5, 4.5, H-5'a), 4.73 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.70 (dd, 1H, *J* 14.0, 6.5, H-5'b), 4.41 (dt, 1H, *J* 5.5, 5.0, H-3'), 4.32 (d, 1H, *J* 7.5, H-1''), 4.16 (dt, 1H, *J* 6.5, 4.5, H-4'), 3.87 (dd, 1H, *J* 11.5, 5.5, H-5''a), 3.48 (ddd, 1H, *J* 10.0, 9.0, 5.5, H-4''), 3.23-3.18 (m, 2H, H-2'', H-5''b), 2.27 (dd, 2H, *J* 6.5, 6.0, H-2'), 1.89 (s, 3H, $CH_3$); $\delta_C$ (125 MHz,

$CD_3OD$) 166.36 (C-4), 152.22 (C-2), 145.82 (C-4'''), 138.23 (C-6), 126.39 (C-5'''), 112.02 (C-5), 104.41 (C-1''), 87.01 (C-1'), 85.54 (C-4'), 77.83 (C-3''), 74.89 (C-2''), 72.41 (C-3'), 71.22 (C-4''), 67.07 (C-5''), 63.08 ($CH_2$), 52.60 (C-5'), 39.58 (C-2'), 12.47 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_5O_9Na$ ($M+Na^+$): 478.1544; found 478.1541; *m/z* 494 (10%, $M+K^+$), 478 (44%, $M+Na^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (56)**

Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-α-D-glucoside **16** (70 mg, 0.27 mmol) and 5'-azido-5'-deoxythymidine **8** (72.2 mg, 0.27 mmol) as described for **49**. Reaction time 21 hours. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **56** (116 mg, 82%) was obtained as a white solid: $[\alpha]_D^{20}$ = +127.8 (c = 0.95, MeOH) (Lit.[9] +127.8); $\delta_H$ (500 MHz, $CD_3OD$) 8.00 (s, 1H, H-5'''), 7.30 (s, 1H, H-6), 6.18 (t, 1H, *J* 6.5, H-1'), 4.88 (d, 1H, *J* 3.5, H-1''), 4.79 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.78 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.70 (dd, 1H, *J* 14.5, 7.0, H-5'b), 4.62 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.41 (dt, 1H, *J* 6.5, 4.5, H-3'), 4.16 (dt, 1H, *J* 7.5, 4.0, H-4'), 3.90 (dd, 1H, *J* 11.0, 3.5, H-2''), 3.82 (dd, 1H, J 12.0, 2.0, H-6''a), 3.68 (dd, 1H, *J* 11.5, 6.0, H-6''b), 3.65-3.59 (m, 2H, H-3'', H-5''), 3.35 (dd, 1H, *J* 9.5, 8.0, H-4''), 2.33 (ddd, 1H, *J* 14.0, 6.5, 6.5, H-2'a), 2.28 (ddd, 1H, *J* 14.0, 6.5, 5.0, H-2'b), 1.94 (s, 3H, $OCH_3$), 1.89 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 173.73 (C=O), 166.34 (C-4), 152.18 (C-2), 145.37 (C-4'''), 138.41 (C-6), 126.24 (C-5'''), 111.94 (C-5), 98.06 (C-1''), 87.27 (C-1'), 85.62 (C-4'), 74.27 (C-5''), 72.84 (C-3''), 72.52 (C-4''), 72.40 (C-3'), 62.83 (C-6''), 61.18 ($CH_2$), 55.28 (C-2''), 52.79 (C-5'), 39.54 (C-2'), 22.62 ($OCH_3$), 12.45 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{21}H_{30}N_6O_{10}$ ($M+H^+$): 527.2096; found 527.2089; *m/z* 565 (29%, $M+K^+$), 549 (59%, $M+Na^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (57)**

Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-β-D-glucopyranoside **31** (42 mg, 0.162 mmol) and 5'-azido-5'-deoxythymidine **8** (43.3 mg, 0.162 mmol) as described for **49**. Reaction time 24 hours. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **57** (42 mg, 49%) was obtained as a white solid: $R_f$ = 0.13 (EtOAc/MeOH 7:3); mp 175-177 ºC (EtOAc/MeOH); $[\alpha]_D^{20}$ = +34.1 (c = 0.967, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 7.96 (s, 1H, H-5'''), 7.26 (d, 1H, *J* 1.0, H-6), 6.19 (t, 1H, *J* 7.0, H-1'), 4.91 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.77 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.72 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$),, 4.69 (dd, 1H, *J* 14.5, 7.0, H-5'b), 4.50 (d, 1H, *J* 8.5, H-1''), 4.41 (dt, 1H, *J* 6.5, 4.5, H-3'), 4.15 (dt, 1H, *J* 7.0, 4.5, H-4'), 3.89 (dd, 1H, *J* 11.5, 2.0, H-6''a), 3.68 (dd, 1H, *J* 11.5, 5.5, H-6''b), 3.65 (dd, 1H, *J* 10.5, 8.5, H-2''), 3.44 (dd, 1H, *J* 10.5, 8.5, H-3''), 3.34-3.28 (m, 2H, H-4'', H-5''), 2.29-2.26 (m, 2H, H-2'), 1.92 (s, 3H, $OCH_3$), 1.89 (d, 3H, *J* 1.0, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 173.83 (C=O), 166.34 (C-4), 152.21 (C-2), 145.84 (C-4'''), 138.29 (C-6), 126.45 (C-5'''), 112.00 (C-5), 101.81 (C-1''), 87.10 (C-1'), 85.61 (C-4'), 78.16 (C-5''), 76.04 (C-3''), 72.50 (C-3'), 72.23 (C-4''), 62.92 ($CH_2$), 62.79 (C-6''), 57.39 (C-2''), 52.68 (C-5'), 39.55 ($OCH_3$), 12.48 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{21}H_{30}N_6O_{10}Na$ ($M+Na^+$): 549.1916; found 549.1915; *m/z* 565 (32%, $M+K^+$), 549 (75%, $M+Na^+$), 527 (5%, $M+H^+$).

**5'-Deoxy-5'-[4-(L-arabinopyranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (58)**

Was prepared from prop-2-ynyl-L-arabinopyranoside **18** (90 mg, 0.478 mmol) and 5'-azido-5'-deoxythymidine **8** (140.6 mg, 0.526 mmol) as described for **49**. Reaction time 2 days. Following automated chromatography (EtOAc/MeOH 3:1 as eluent), **58** (127 mg, 58%) was obtained as a white solid with an α/β ratio of approximately 1:3: $\delta_H$ (500 MHz, $CD_3OD$) 8.02 (s, 1H, H-5'''β), 8.00 (s, 1H, H-5'''α), 7.27 (d, 1H, *J* 1.0, H-6β), 7.25 (d, 1H, *J* 1.0, H-6α), 6.18 (t, 1H, *J* 6.5, H-1'), 4.913 (d, 1H, *J* 3.0, H-1''β), 4.911 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B\alpha$), 4.79 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B\beta$), 4.80-4.74 (m, 3H, $OCH_A\underline{H}_B\alpha$, H-5'aα, H-5'aβ), 4.72-4.68 (m, 2H, H-5'bα, H-5'bβ), 4.64 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B\beta$), 4.41 (m, 1H, H-3'), 4.30 (d, 1H, *J* 6.5, H-1''α), 4.16 (m, 1H, H-4'), 3.89 (dd, 1H, *J* 12.5, 3.0, H-5''aα), 3.85-

3.80 (m, 3H, H-4''α, H-4''β, H-5''aβ), 3.78 (dd, 1H, *J* 10.0, 3.5, H-2''β), 3.74 (dd, 1H, *J* 10.0, 3.5, H-3''β), 3.60-3.54 (m, 3H, H-2''α, H-5''bα, H-5''bβ), 3.51 (dd, 1H, *J* 9.0, 3.5, H-3''α), 2.29-2.26 (m, 2H, H-2'), 1.89 (d, 3H, *J* 1.0, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.35 (C-4α), 166.31 (C-4β), 152.20 (C-2), 145.93 (C-4'''α), 145.81 (C-4'''β), 138.31 (C-6β), 138.27 (C-6α), 126.38 (C-5'''α), 126.31 (C-5'''β), 111.99 (C-5α), 111.94 (C-5β), 104.16 (C-1''α), 100.56 (C-1''β), 87.11 (C-1'β), 87.04 (C-1'α), 85.58 (C-4'), 74.28 (C-2''α), 72.48 (C-3'β), 72.43, 72.40 (C-3'α, C-3''α), 70.82 (C-2''β), 70.69 (C-4''β), 70.32 (C-3''β), 69.70 (C-4''α), 67.10 (C-5''α), 64.48 (C-5''β), 62.82 ($CH_2$α), 61.82 ($CH_2$β), 52.69 (C-5'β), 52.63 (C-5'α), 39.60 (C-2'), 12.45 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{25}N_5O_9Na$ ($M+Na^+$): 478.1544; found 478.1550; *m/z* 949 (5%, $2M+K^+$), 933 (31%, $2M+Na^+$), 494 (16%, $M+K^+$), 478 (100%, $M+Na^+$).

**5'-Deoxy-5'-[4-(β-D-ribofuranosyloxymethyl)-1,2,3-triazol-1-yl]thymidine (59)**
Was prepared from prop-2-ynyl-β-D-ribofuranoside **26** (64.6 mg, 0.343 mmol) and 5'-azido-5'-deoxythymidine **8** (100.9 mg, 0.378 mmol) as described for **49**. Reaction time 24 hours. Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **59** (126 mg, 81%) was obtained as a white solid: $[\alpha]_D^{20}$ = +23.5 (c = 0.953, MeOH); $\delta_H$ (500 MHz, $CD_3OD$) 7.97 (s, 1H, H-5'''), 7.21 (d, 1H, *J* 1.5, H-6), 6.19 (t, 1H, *J* 7.0, H-1'), 4.95 (s, 1H, H-1''), 4.81 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.77 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.69 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.61 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.41 (m, 1H, H-3'), 4.16 (dt, 1H, *J* 7.0, 4.0, H-4'), 4.08 (dd, 1H, *J* 7.0, 4.5, H-3''), 3.97 (ddd, 1H, *J* 7.0, 6.0, 3.0, H-4''), 3.90 (d, 1H, *J* 4.5, H-2''), 3.74 (dd, 1H, *J* 12.0, 3.5, H-5''a), 3.56 (dd, 1H, *J* 12.0, 6.0, H-5''b), 2.27 (m, 2H, H-2'), 1.88 (d, 3H, *J* 1.0, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 166.32 (C-4), 152.21 (C-2), 145.82 (C-4'''), 138.15 (C-6), 126.32 (C-5'''), 111.99 (C-5), 108.09 (C-1''), 86.98 (C-1'), 85.52 (C-4'), 85.20 (C-4''), 76.38 (C-2''), 72.48, 72.43 (C-3'', C-3'), 64.72 (C-5''), 61.23 ($CH_2$), 52.57 (C-5'), 39.61 (C-2'), 12.47 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{26}N_5O_9$ ($M+H^+$): 456.1726; found 456.1725; *m/z* 478 (11%, $M+Na^+$), 456 (3%, $M+H^+$).

**Propargyl glycoside couplings with 5'-azido-5'-deoxyuridine (7)**
Uridine-based sugar-triazole-nucleosides were prepared using the general procedure below (using compound **60** as an example).

**5'-Deoxy-5'-[4-(α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (60)**
Prop-2-ynyl-α-D-glucopyranoside **15** (35.2 mg, 0.161 mmol) and 5'-azido-5'-deoxyuridine **7** (47.8 mg, 0.177 mmol) were measured into a sample vial, followed by copper(I) bromide (1.2 mg, 8.1 μmol). Aqueous sodium ascorbate solution (40 mM, 403 μL, 16.1 μmol) and a solution of TBTA in acetonitrile (20 mM, 403 μL, 8.1 μmol) was added, followed by methanol (700 μL), acetonitrile (297 μL) and water (297 μL). The sample vial was sealed, the lid pierced with a syringe needle, and the reaction mixture was sonicated for 30 minutes. This was concentrated *in vacuo* and purified by automated chromatography (EtOAc/MeOH 4:1 as eluent) to yield **60** (58 mg, 74%) as a white solid: $[\alpha]_D^{20}$ = +109.1 (c = 0.748, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.05 (s, 1H, H-5'''), 7.39 (d, 1H, *J* 8.0, H-6), 5.719 (d, 1H, *J* 4.0, H-1'), 5.715 (d, 1H, *J* 8.0, H-5), 4.91 (d, 1H, *J* 3.5, H-1''), 4.83 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.82 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.72 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.66 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.25 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.18 (dd, 1H, *J* 5.5, 4.0, H-2'), 4.11 (t, 1H, *J* 6.0, H-3'), 3.81 (dd, 1H, *J* 12.0, 2.5, H-6''a), 3.67 (dd, 1H, *J* 12.0, 6.0, H-6''b), 3.63 (t, 1H, *J* 9.5, H-3''), 3.59 (ddd, 1H, *J* 10.0, 5.5, 2.0, H-5''), 3.40 (dd, 1H, *J* 10.0, 4.0, H-2''), 3.29 (m, 1H, H-4'' overlapping MeOD peak); $\delta_C$ (125 MHz, $CD_3OD$) 166.20 (C-4), 152.09 (C-2), 145.70 (C-4'''), 143.44 (C-6), 126.64 (C-5'''), 103.11 (C-5), 99.71 (C-1''), 93.49 (C-1'), 82.96 (C-4'), 75.06 (C-3''), 74.21 (C-2'), 74.07 (C-5''), 73.54 (C-2''), 71.93 (C-3'), 71.85 (C-4''), 62.74 (C-6''), 61.43 ($CH_2$), 52.51 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{24}N_5O_{11}$ ($M-H^+$): 486.1472; found 486.1465; *m/z* 486 (100%, $M-H^+$).

**5'-Deoxy-5'-[4-(β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (61)**
Was prepared from prop-2-ynyl-β-D-glucopyranoside (29.0 mg, 0.133 mmol) and

5'-azido-5'-deoxyuridine **7** (39.4 mg, 0.146 mmol) as described for **60**. Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **61** (59 mg, 91%) was obtained as a white solid: $[\alpha]_D^{20}$ = +9.3 (c = 0.795, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.03 (s, 1H, H-5'''), 7.30 (d, 1H, *J* 8.0, H-6), 5.75-5.72 (m, 2H, H-1', H-5), 4.97 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.81 (dd, 1H, *J* 15.0, 4.0, H-5'a), 4.78 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.73 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.39 (d, 1H, *J* 7.5, H-1''), 4.24 (dt, 1H, *J* 6.0, 3.0, H-4'), 4.13-4.07 (m, 2H, H-2', H-3'), 3.89 (dd, 1H, *J* 12.0, 2.0, H-6''a), 3.68 (m, 1H, H-6''b), 3.35 (t, 1H, *J* 9.0, H-3''), 3.34-3.26 (m, 2H, H-4'', H-5'', overlapping solvent peak), 3.21 (dd, 1H, *J* 9.0, 8.0, H-2''); $\delta_C$ (125 MHz, $CD_3OD$) 166.21 (C-4), 152.17 (C-2), 145.80 (C-4'''), 143.26 (C-6), 126.88 (C-5'''), 103.64 (C-1''), 103.22 (C-5), 93.09 (C-1'), 82.97 (C-4'), 78.14, 78.05 (C-3'', C-5''), 75.09 (C-2''), 74.22 (C-2'), 71.91 (C-3'), 71.67 (C-4''), 62.98, 62.85 (C-6'', $CH_2$), 52.41 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{24}N_5O_{11}$ ($M\text{-}H^+$): 486.1472; found 486.1459; *m/z* 486 (65%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(α-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (62)**

Was prepared from prop-2-ynyl-α-D-galactopyranoside **23** (28.2 mg, 0.129 mmol) and 5'-azido-5'-deoxyuridine **7** (38.3 mg, 0.142 mmol) as described for **60**. Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **62** (51 mg, 81%) was obtained as a white solid: $[\alpha]_D^{20}$ = +127.7 (c = 0.830, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.04 (s, 1H, H-5'''), 7.39 (d, 1H, *J* 8.0, H-6), 5.72 (d, 1H, *J* 4.5, H-1'), 5.71 (d, 1H, *J* 8.0, H-5), 4.94 (d, 1H, *J* 3.5, H-1''), 4.83 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.82 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.72 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.65 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.25 (dt, 1H, *J* 6.0, 3.5, H-4'), 4.19 (dd, 1H, *J* 6.0, 4.0, H-2'), 4.11 (t, 1H, *J* 6.0, H-3'), 3.88 (dd, 1H, *J* 3.5, 1.0, H-4''), 3.84 (m, 1H, H-5''), 3.78 (dd, 1H, *J* 10.0, 4.0, H-2''), 3.73 (dd, 1H, *J* 11.0, 7.0, H-6''a), 3.72 (dd, 1H, *J* 10.0, 3.5, H-3''), 3.69 (dd, 1H, *J* 11.5, 5.5, H-6''b); $\delta_C$ (125 MHz, $CD_3OD$) 166.30 (C-4), 152.19 (C-2), 145.73 (C-4'''), 143.44 (C-6), 126.65 (C-5'''), 103.11 (C-5), 99.96 (C-1''), 93.50 (C-1'), 82.93 (C-4'), 74.22 (C-2'), 72.82 (C-5''), 71.93 (C-3'), 71.48 (C-3''), 71.15 (C-4''), 70.23 (C-2''), 62.90 (C-6''), 61.47 ($CH_2$), 52.49 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{24}N_5O_{11}$ ($M\text{-}H^+$): 486.1472; found 486.1469; *m/z* 486 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(β-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (63)**

Was prepared from prop-2-ynyl-β-D-galactopyranoside **27c** (27.9 mg, 0.128 mmol) and 5'-azido-5'-deoxyuridine **7** (37.9 mg, 0.141 mmol) as described for **60**. Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **63** (54 mg, 87%) was obtained as a white solid: $[\alpha]_D^{20}$ = +18.2 (c = 0.845, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.03 (s, 1H, H-5'''), 7.34 (d, 1H, *J* 8.0, H-6), 5.75-5.72 (m, 2H, H-1', H-5), 4.97 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.81 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.80 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.72 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.34 (d, 1H, *J* 7.5, H-1''), 4.24 (dt, 1H, *J* 6.5, 3.0, H-4'), 4.14-4.09 (m, 2H, H-2', H-3'), 3.82 (m, 1H, H-4''), 3.79 (dd, 1H, *J* 11.5, 7.0, H-6''a), 3.72 (dd, 1H, *J* 11.5, 5.0, H-6''b), 3.57-3.51 (m, 2H, H-2'', H-5''), 3.46 (dd, 1H, *J* 10.0, 3.5, H-3''); $\delta_C$ (125 MHz, $CD_3OD$) 166.17 (C-4), 152.15 (C-2), 145.94 (C-4'''), 143.28 (C-6), 126.83 (C-5'''), 104.21 (C-1''), 103.22 (C-5), 93.12 (C-1'), 83.01 (C-4'), 76.93 (C-5''), 74.99 (C-3''), 74.21 (C-2'), 72.50 (C-2''), 71.92 (C-3'), 70.43 (C-4''), 62.94 ($CH_2$), 62.71 (C-6''), 52.46 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{24}N_5O_{11}$ ($M\text{-}H^+$): 486.1472; found 486.1471; *m/z* 486 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(α-D-mannopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (64)**

Was prepared from prop-2-ynyl-α-D-mannopyranoside **17** (29.6 mg, 0.136 mmol) and 5'-azido-5'-deoxyuridine **7** (40.2 mg, 0.149 mmol) as described for **60** Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **64** (53 mg, 80%) was obtained as a white solid: $[\alpha]_D^{20}$ = +80.5 (c = 0.819, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.02 (s, 1H, H-5'''), 7.39 (d, 1H, *J* 8.0, H-6), 5.69 (d, 1H, *J* 4.0, H-1'), 5.68 (d, 1H, *J* 8.0, H-5), 4.87 (d, 1H, *J* 1.5, H-1''), 4.81 (dd, 1H, *J* 15.0, 3.5,

H-5'a), 4.79 (d, 1H, *J* 13.0, OC$\underline{H}_A H_B$), 4.73 (dd, 1H, *J* 14.5, 6.0, H-5'b), 4.65 (d, 1H, *J* 12.5, OC$H_A\underline{H}_B$), 4.23 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.20 (dd, 1H, *J* 6.0, 4.0, H-2'), 4.12 (dd, 1H, *J* 6.5, 5.5, H-3'), 3.86 (dd, 1H, *J* 11.5, 2.0, H-6''a), 3.79 (dd, 1H, *J* 3.5, 2.0, H-2''), 3.70 (dd, 1H, *J* 11.5, 6.0, H-6''b), 3.67 (dd, 1H, *J* 9.0, 3.5, H-3''), 3.61 (t, 1H, *J* 9.0, H-4''), 3.56 (ddd, 1H, *J* 9.5, 6.0, 2.0, H-5''); $\delta_C$ (125 MHz, $CD_3OD$) 166.17 (C-4), 152.04 (C-2), 145.40 (C-4'''), 143.61 (C-6), 126.82 (C-5'''), 103.04 (C-5), 100.63 (C-1''), 93.91 (C-1'), 82.86 (C-4'), 75.07 (C-5''), 74.19 (C-2'), 72.56 (C-3''), 72.11 (C-2''), 71.82 (C-3'), 68.70 (C-4''), 63.07 (C-6''), 60.58 ($CH_2$), 52.34 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{24}N_5O_{11}$ ($M\text{-}H^+$): 486.1472; found 486.1458; *m/z* 486 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(β-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (66)**
Was prepared from prop-2-ynyl-β-D-xylopyranoside **28c** (35.1 mg, 0.187 mmol) and 5'-azido-5'-deoxyuridine **7** (55.2 mg, 0.205 mmol) as described for **60**. Following automated chromatography (EtOAc/MeOH 17:3 to 4:1 as eluent), **66** (80 mg, 94%) was obtained as a white solid: $[\alpha]_D^{20}$ = -1.7 (c = 0.784, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.00 (s, 1H, H-5'''), 7.33 (d, 1H, *J* 8.0, H-6), 5.75-5.69 (m, 2H, H-1', H-5), 4.93-4.89 (m, 1H, OC$\underline{H}_A H_B$ overlapping HOD peak), 4.81 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.74 (d, 1H, *J* 12.5, OC$H_A\underline{H}_B$), 4.72 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.34 (d, 1H, *J* 7.5, H-1''), 4.24 (dt, 1H, *J* 6.0, 3.0, H-4'), 4.13-4.09 (m, 2H, H-2', H-3'), 3.88 (dd, 1H, *J* 11.5, 5.5, H-5''a), 3.49 (ddd, 1H, *J* 10.0, 8.5, 5.0, H-4''), 3.33-3.28 (m, 1H, H-3'' overlapping MeOD peak), 3.22 (dd, 1H, *J* 11.5, 10.5, H-5''b), 3.19 (dd, 1H, *J* 9.0, 7.5, H-2''); $\delta_C$ (125 MHz, $CD_3OD$) 166.11 (C-4), 152.12 (C-2), 145.76 (C-4'''), 143.29 (C-6), 126.70 (C-5'''), 104.35 (C-1''), 103.17 (C-5), 93.11 (C-1'), 83.02 (C-4'), 77.85 (C-3''), 74.92 (C-2''), 74.17 (C-2'), 71.92 (C-3'), 71.22 (C-4''), 67.10 (C-5''), 62.97 ($CH_2$), 52.46 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{17}H_{22}N_5O_{10}$ ($M\text{-}H^+$): 456.1367; found 456.1361; *m/z* 456 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (67)**
Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-α-D-glucoside **16** (31.5 mg, 0.122 mmol) and 5'-azido-5'-deoxyuridine **7** (36.0 mg, 0.134 mmol) as described for **60** Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **67** (58 mg, 90%) was obtained as a white solid: $[\alpha]_D^{20}$ = +130.1 (c = 0.864, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.00 (s, 1H, H-5'''), 7.43 (d, 1H, *J* 8.0, H-6), 5.71 (d, 1H, *J* 4.0, H-1'), 5.70 (d, 1H, *J* 8.0, H-5), 4.87 (d, 1H, *J* 3.5, H-1''), 4.82 (dd, 1H, *J* 14.0, 3.5, H-5'a), 4.79 (d, 1H, *J* 12.5, OC$\underline{H}_A H_B$), 4.72 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.63 (d, 1H, *J* 12.5, OC$H_A\underline{H}_B$), 4.24 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.22 (dd, 1H, *J* 6.0, 4.0, H-2'), 4.10 (t, 1H, *J* 6.0, H-3'), 3.90 (dd, 1H, *J* 11.0, 4.0, H-2''), 3.83 (dd, 1H, *J* 12.0, 2.0, H-6''a), 3.69 (dd, 1H, *J* 12.0, 6.0, H-6''b), 3.64 (dd, 1H, *J* 10.5, 9.0, H-3''), 3.61 (ddd, 1H, *J* 9.5, 6.0, 2.5, H-5''), 3.35 (m, 1H, H-4'', overlapping MeOH peak), 1.94 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 173.79 (C=O), 166.15 (C-4), 152.05 (C-2), 145.34 (C-4'''), 143.54 (C-6), 126.52 (C-5'''), 103.08 (C-5), 97.85 (C-1''), 93.69 (C-1'), 82.98 (C-4'), 74.29 (C-5''), 74.17 (C-2'), 72.79 (C-3''), 72.38 (C-4''), 71.97 (C-3'), 62.81 (C-6''), 61.03 ($CH_2$), 55.27 (C-2''), 52.57 (C-5'), 22.63 ($CH_3$); HRMS ($ES^-$) *m/z* calc. for $C_{20}H_{27}N_6O_{11}$ ($M\text{-}H^+$): 527.1738; found 527.1738; *m/z* 527 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (68)**
Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-β-D-glucoside **31** (24.0 mg, 0.093 mmol) and 5'-azido-5'-deoxyuridine **7** (27.4 mg, 0.102 mmol) as described for **60** Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **68** (37 mg, 76%) was obtained as a white solid: $[\alpha]_D^{20}$ = +10.3 (c = 0.602, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 7.95 (s, 1H, H-5'''), 7.34 (d, 1H, *J* 8.0, H-6), 5.75 (d, 1H, *J* 3.0, H-1'), 5.74 (d, 1H, *J* 7.5, H-5), 4.93 (d, 1H, *J* 12.0, OC$\underline{H}_A H_B$), 4.79 (dd, 1H, *J* 15.0, 3.5, H-5'a), 4.72 (dd, 1H, *J* 15.0, 6.0, H-5'b), 4.71 (d, 1H, *J* 12.0, OC$H_A\underline{H}_B$), 4.51 (d, 1H, *J* 8.5, H-1''), 4.27-4.21 (m, 1H, H-4'), 4.10 (m, 1H, H-3'), 4.03 (m, 1H, H-2'), 3.91 (m, 1H, H-6''a), 3.73-3.64 (m, 2H, H-2'', H-6''b),

3.44 (m, 1H, H-3''), 3.37-3.26 (m, 2H, H-4'', H-5'', overlapping MeOD peak); $\delta_C$ (125 MHz, $CD_3OD$) 173.93 (C=O), 166.16 (C-4), 152.24 (C-2), 145.75 (C-4'''), 143.35 (C-6), 126.83 (C-5'''), 103.24 (C-5), 102.02 (C-1''), 92.82 (C-1'), 83.08 (C-4'), 78.19 (C-5''), 76.03 (C-3''), 73.95 (C-3'), 72.25 (C-4''), 72.01 (C-3'), 62.93, 62.83 (C-6'', $CH_2$), 57.33 (C-2''), 52.53 (C-5'), 23.03 ($CH_3$); HRMS ($ES^-$) *m/z* calc. for $C_{20}H_{27}N_6O_{11}$ ($M\text{-}H^+$): 527.1738; found 527.1741; *m/z* 527 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(L-arabinopyranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (69)**
Was prepared from prop-2-ynyl-L-arabinopyranoside **18** (29.1 mg, 0.155 mmol) and 5'-azido-5'-deoxyuridine **7** (45.8 mg, 0.170 mmol) as described for **60**. Following automated chromatography (EtOAc/MeOH 83:17 as eluent), **69** (57 mg, 81%) was obtained as a white solid with an α/β ratio of approximately 1:3: $[\alpha]_D^{20}$ = +106.4 (c = 0.845, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.02 (s, 1H, H-5'''β), 8.01 (s, 1H, H-5'''α), 7.39 (d, 1H, *J* 8.5, H-6β), 7.35 (d, 1H, *J* 8.0, H-6α), 5.76-5.68 (m, 4H, H-1'α, H-1'β, H-5α, H-5β), 4.92 (d, 1H, *J* 3.0, H-1''β), 4.91-4.69 (m, 7H, H-5'aα, H-5'aβ, H-5'bα, H-5'bβ, $OCH_AH_B$α, $OCH_AH_B$α, $OCH_AH_B$β), 4.64 (d, 1H, *J* 12.5, $OCH_AH_B$β), 4.32 (d, 1H, *J* 7.0, H-1''α), 4.25 (dt, 2H, *J* 6.5, 3.5, H-4'α, H-4'β), 4.18 (dd, 1H, *J* 5.5, 4.0, H-2'β), 4.15-4.09 (m, 3H, H-2'α, H-3'α, H-3'β), 3.89 (dd, 1H, *J* 12.5, 3.0, H-5''aα), 3.86-3.79 (m, 3H, H-4''α, H-4''β, H-5''aβ), 3.78 (dd, 1H, *J* 9.5, 3.0, H-2''β), 3.75 (dd, 1H, *J* 9.5, 3.0, H-3''β), 3.59 (dd, 1H, *J* 12.5, 2.5, H-5''bβ), 3.60-3.55 (m, 2H, H-2''α, H-5''bα), 3.52 (dd, 1H, *J* 8.5, 3.0, H-3''α); $\delta_C$ (125 MHz, $CD_3OD$) 166.08 (C-4), 152.09 (C-2), 145.86 (C-4'''), 143.39 (C-6β), 143.32 (C-6α), 126.64 (C-5'''), 104.14 (C-1''α), 103.13 (C-5), 100.51 (C-1''β), 93.41 (C-1'β), 93.18 (C-1'α), 82.99 (C-4'), 74.29 (C-2''α), 74.22 (C-2'β), 74.18 (C-2'α), 72.43 (C-3''α), 71.95 (C-3'β), 71.92 (C-3'α), 70.82 (C-2''β), 70.69 (C-4''β), 70.32 (C-3''β), 69.71 (C-4''α), 67.10 (C-5''α), 64.49 (C-5''β), 62.77 ($CH_2$α), 61.74 ($CH_2$β), 52.50 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{17}H_{22}N_5O_{10}$ ($M\text{-}H^+$): 456.1367; found 456.1370; *m/z* 456 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(β-D-ribofuranosyloxymethyl)-1,2,3-triazol-1-yl]uridine (70)**
Was prepared from prop-2-ynyl-β-D-ribofuranoside **26** (31.5 mg, 0.167 mmol) and 5'-azido-5'-deoxyuridine **7** (49.6 mg, 0.184 mmol) as described for **60**. Following automated chromatography (EtOAc/MeOH 4:1 as eluent), **70** (62 mg, 80%) was obtained as a white solid: $[\alpha]_D^{20}$ = +3.1 (c = 0.794, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 7.97 (s, 1H, H-5'''), 7.32 (d, 1H, *J* 8.0, H-6), 5.74 (d, 1H, *J* 3.5, H-1'), 5.69 (d, 1H, *J* 7.5, H-5), 4.96 (s, 1H, H-1''), 4.81 (dd, 1H, *J* 15.0, 3.0, H-5'a), 4.81 (d, 1H, *J* 12.0, $OCH_AH_B$), 4.72 (dd, 1H, *J* 14.5, 6.0, H-5'b), 4.62 (d, 1H, *J* 12.5, $OCH_AH_B$), 4.24 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.14 (dd, 1H, *J* 5.5, 4.0, H-2'), 4.11 (t, 1H, *J* 6.0, H-3'), 4.09 (dd, 1H, *J* 7.0, 5.0, H-3''), 3.96 (dt, 1H, *J* 6.5, 3.0, H-4''), 3.91 (d, 1H, *J* 5.0, H-2''), 3.74 (dd, 1H, *J* 12.0, 3.0, H-5''a), 3.56 (dd, 1H, *J* 12.0, 6.5, H-5''b); $\delta_C$ (125 MHz, $CD_3OD$) 166.08 (C-4), 152.15 (C-2), 145.87 (C-4'''), 143.18 (C-6), 126.56 (C-5'''), 108.16 (C-1''), 103.15 (C-5), 93.12 (C-1'), 85.22 (C-4''), 82.98 (C-4'), 76.41 (C-2''), 74.24 (C-2'), 72.44 (C-3''), 71.93 (C-3'), 64.67 (C-5''), 61.26 ($CH_2$), 52.40 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{17}H_{22}N_5O_{10}$ ($M\text{-}H^+$): 456.1367; found 456.1377; *m/z* 456 (100%, $M\text{-}H^+$).

**Propargyl glycoside couplings with 5'-azido-5'-deoxycytidine (11)**
Cytidine-based sugar-triazole-nucleosides were prepared using the general procedure below (using compound **71** as an example).

**5'-Deoxy-5'-[4-(α-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (71)**
Prop-2-ynyl-α-D-glucopyranoside **15** (32.0 mg, 0.147 mmol) and 5'-azido-5'-deoxycytidine **11** (43.3 mg, 0.161 mmol) were measured into a sample vial, followed by copper(I) bromide (1.1 mg, 7.3 μmol). Aqueous sodium ascorbate solution (40 mM, 367 μL, 14.7 μmol) and a solution of TBTA in acetonitrile (20 mM, 367 μL, 7.3 μmol) was added, followed by methanol (700 μL), acetonitrile (333 μL) and water (333 μL). The sample vial was sealed, the lid pierced with a syringe needle, and the reaction mixture was sonicated for 40 minutes until

reaction completion. This was concentrated *in vacuo* and purified by automated chromatography (EtOAc/MeOH 7:3 as eluent) to yield **71** (43 mg, 60%) as a white solid: $[\alpha]_D^{20}$ = +117.7 (c = 1.496, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.07 (s, 1H, H-5'''), 7.22 (d, 1H, *J* 7.5, H-6), 5.90 (d, 1H, *J* 7.5, H-5), 5.71 (d, 1H, *J* 3.0, H-1'), 4.91 (d, 1H, *J* 3.5, H-1''), 4.89-4.81 (m, 2H, H-5'a, $OC\underline{H}_AH_B$), 4.75 (dd, 1H, *J* 14.5, 6.0, H-5'b), 4.66 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.27 (dt, 1H, *J* 7.0, 3.0, H-4'), 4.14 (dd, 1H, *J* 5.5, 3.0, H-2'), 4.08 (dd, 1H, *J* 6.5, 5.5, H-3'), 3.81 (dd, 1H, *J* 12.0, 2.5, H-6''a), 3.67 (dd, 1H, *J* 12.0, H-6''b), 3.64 (t, 1H, *J* 9.5, H-3''), 3.61 (ddd, 1H, *J* 9.5, 6.0, 2.5, H-5''), 3.41 (dd, 1H, *J* 9.5, 3.5, H-2''), 3.32-3.27 (m, 1H, H-4'', overlapping MeOD peak); $\delta_C$ (125 MHz, $CD_3OD$) 167.75 (C-4), 158.16 (C-2), 145.67 (C-4'''), 143.31 (C-6), 126.80 (C-5'''), 99.72 (C-1''), 96.42 (C-5), 94.49 (C-1'), 82.57 (C-4'), 74.99 (C-3''), 74.85 (C-2'), 74.08 (C-5''), 73.54 (C-2''), 71.94 (C-3'), 71.88 (C-4''), 62.74 (C-6''), 61.41 ($CH_2$), 52.32 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{25}N_6O_{10}$ ($M\text{-}H^+$): 485.1632; found 485.1629; *m/z* 485 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (72)**
Was prepared from prop-2-ynyl-β-D-glucopyranoside (30.4 mg, 0.139 mmol) and 5'-azido-5'-deoxycytidine **11** (41.4 mg, 0.153 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **72** (54 mg, 80%) was obtained as a white solid: $\delta_H$ (500 MHz, $CD_3OD$) 8.04 (s, 1H, H-5'''), 7.24 (d, 1H, *J* 7.5, H-6), 5.91 (d, 1H, *J* 7.5, H-5), 5.73 (d, 1H, *J* 3.5, H-1'), 4.98 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.83 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.78 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.75 (dd, 1H, *J* 15.0, 6.5, H-5'b), 4.40 (d, 1H, *J* 7.5, H-1''), 4.26 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.10 (dd, 1H, *J* 6.0, 3.5, H-2'), 4.06 (dd, 1H, *J* 6.0, 5.5, H-3'), 3.89 (dd, 1H, *J* 12.0, 2.0, H-6''a), 3.69 (m, 1H, H-6''b), 3.36 (t, 1H, *J* 8.5, H-3''), 3.30-3.26 (m, 2H, H-4'', H-5'', partially overlapping MeOD peak), 3.21 (dd, 1H, *J* 9.5, 8.0, H-2''); 167.76 (C-4), 158.21 (C-2), 145.82 (C-4'''), 143.41 (C-6), 126.93 (C-5'''), 103.71 (C-1''), 96.50 (C-5), 94.29 (C-1'), 82.68 (C-4'), 78.09, 78.02 (C-3'', C-5''), 75.09 (C-2''), 74.72 (C-2'), 71.98 (C-3'), 71.62 (C-4''), 63.04 ($CH_2$), 62.76 (C-6''), 52.37 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{25}N_6O_{10}$ ($M\text{-}H^+$): 485.1632; found 485.1620; *m/z* 485 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(α-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (73)**
Was prepared from prop-2-ynyl-α-D-galactopyranoside **23** (27.4 mg, 0.126 mmol) and 5'-azido-5'-deoxycytidine **11** (37.0 mg, 0.138 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **73** (41 mg, 67%) was obtained as a white solid: $[\alpha]_D^{20}$ = +126.3 (c = 1.203, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.06 (s, 1H, H-5'''), 7.26 (d, 1H, *J* 7.5, H-6), 5.90 (d, 1H, *J* 7.5, H-5), 5.71 (d, 1H, *J* 3.5, H-1'), 4.94 (d, 1H, *J* 3.5, H-1''), 4.89-4.77 (m, 2H, H-5'a, $OC\underline{H}_AH_B$, buried under HOD peak), 4.74 (dd, 1H, *J* 14.5, 6.5, H-5'a), 4.65 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.27 (dt, 1H, *J* 7.0, 3.5, H-4'), 4.15 (dd, 1H, *J* 5.5, 3.0, H-2'), 4.08 (dd, 1H, *J* 7.0, 5.5, H-3'), 3.88 (dd, 1H, *J* 3.0, 0.5, H-4''), 3.87-3.83 (m, 1H, H-5''), 3.79 (dd, 1H, *J* 10.5, 4.0, H-2''), 3.735 (dd, 1H, *J* 11.5, 6.5, H-6''a), 3.733 (dd, 1H, *J* 10.5, 3.5, H-3''), 3.69 (dd, 1H, *J* 11.5, 5.5, H-6''b); $\delta_C$ (125 MHz, $CD_3OD$) 167.79 (C-4), 158.18 (C-2), 145.71 (C-4'''), 143.38 (C-6), 126.75 (C-5'''), 99.98 (C-1''), 96.41 (C-5), 94.55 (C-1'), 82.64 (C-4'), 74.84 (C-2'), 72.80 (C-5''), 72.01 (C-3'), 71.46 (C-3''), 71.16 (C-4''), 70.23 (C-2''), 62.90 (C-6''), 61.42 ($CH_2$), 52.40 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{25}N_6O_{10}$ ($M\text{-}H^+$): 485.1632; found 485.1639; *m/z* 485 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(β-D-galactopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (74)**
Was prepared from prop-2-ynyl-β-D-galactopyranoside **27c** (29.5 mg, 0.135 mmol) and 5'-azido-5'-deoxycytidine **11** (39.9 mg, 0.149 mmol) as described for **71** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **74** (46 mg, 70%) was obtained as a white solid: $[\alpha]_D^{20}$ = +30.2 (c = 2.408, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.04 (s, 1H, H-5'''), 7.09 (d, 1H, *J* 7.5, H-6), 5.97 (d, 1H, *J* 7.5, H-5), 5.76 (d, 1H, *J* 2.5, H-1'), 5.00 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.84 (dd, 1H, *J*

14.5, 3.0, H-5'a), 4.78 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.77 (dd, 1H, *J* 14.5, 5.5, H-5'b), 4.37 (d, 1H, *J* 7.5, H-1''), 4.26 (dt, 1H, *J* 5.5, 3.5, H-4'), 4.05-4.00 (m, 2H, H-2', H-3'), 3.84 (dd, 1H, *J* 3.5, 1.0, H-4''), 3.80 (dd, 1H, *J* 11.5, 7.0, H-6''a), 3.73 (dd, 1H, *J* 11.0, 5.0, H-6''b), 3.57-3.52 (m, 2H, H-2'', H-5''), 3.48 (dd, 1H, *J* 10.0, 3.5, H-3''); $\delta_C$ (125 MHz, $CD_3OD$) 167.74 (C-4), 158.22 (C-2), 145.85 (C-4'''), 143.09 (C-6), 127.08 (C-5'''), 104.30 (C-1''), 96.73 (C-5), 93.87 (C-1'), 82.54 (C-4'), 76.90 (C-5''), 74.95 (C-3''), 74.84 (C-2'), 72.56 (C-2''), 71.80 (C-3'), 70.46 (C-4''), 62.90 ($CH_2$), 62.73 (C-6''), 52.10 (C-5'); HRMS ($ES^-$) *m/z* calc. for $C_{18}H_{25}N_6O_{10}$ ($M\text{-}H^+$): 485.1632; found 485.1607; *m/z* 485 (100%, $M\text{-}H^+$).

**5'-Deoxy-5'-[4-(α-D-mannopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (75)**
Was prepared from prop-2-ynyl-α-D-mannopyranoside **17** (30.2 mg, 0.138 mmol) and 5'-azido-5'-deoxycytidine **11** (40.8 mg, 0.152 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **75** (51 mg, 76%) was obtained as a white solid: $[\alpha]_D^{20}$ = +87.5 (c = 1.155, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.03 (s, 1H, H-5'''), 7.30 (d, 1H, *J* 7.5, H-6), 5.86 (d, 1H, *J* 7.5, H-5), 5.69 (d, 1H, *J* 3.0, H-1'), 4.86 (d, 1H, *J* 2.0, H-1''), 4.84 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.80 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.75 (dd, 1H, *J* 15.0, 6.5, H-5'b), 4.65 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.26 (dt, 1H, *J* 7.0, 3.5, H-4'), 4.17 (dd, 1H, *J* 6.0, 3.5, H-2'), 4.09 (dd, 1H, *J* 7.0, 6.0, H-3'), 3.86 (dd, 1H, *J* 12.0, 2.0, H-6''a), 3.80 (dd, 1H, *J* 3.5, 2.0, H-2''), 3.71 (dd, 1H, *J* 11.5, 5.5, H-6''b), 3.69 (dd, 1H, *J* 9.0, 3.5, H-3''), 3.61 (t, 1H, *J* 9.5, H-4''), 3.57 (ddd, 1H, *J* 9.5, 6.0, 2.5, H-5''); $\delta_C$ (125 MHz, $CD_3OD$) 167.76 (C-4), 158.11 (C-2), 145.46 (C-4'''), 143.61 (C-6), 126.77 (C-5'''), 100.84 (C-1''), 96.32 (C-5), 94.82 (C-1'), 82.62 (C-4'), 75.08 (C-5''), 74.74 (C-2'), 72.52 (C-3''), 72.05, 72.02 (C-3', C-2''), 68.72 (C-4''), 63.06 (C-6''), 60.72 ($CH_2$), 52.39 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{18}H_{27}N_6O_{10}$ ($M+H^+$) 487.1789; found 487.1801; *m/z* 509 (100%, $M+Na^+$), 487 (59%, $M+H^+$).

**5'-Deoxy-5'-[4-(α-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (76)**
Was prepared from prop-2-ynyl-α-D-xylopyranoside **19** (23.1 mg, 0.123 mmol) and 5'-azido-5'-deoxycytidine **11** (36.2 mg, 0.135 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **76** (46 mg, 82%) was obtained as a white solid: $[\alpha]_D^{20}$ = + 113.0 (c = 1.495, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.05 (s, 1H, H-5'''), 7.23 (d, 1H, *J* 7.5, H-6), 5.89 (d, 1H, *J* 7.5, H-5), 5.72 (d, 1H, *J* 3.5, H-1'), 4.88-4.80 (m, 1H, H-5'a, overlapping HOD peak), 4.86 (d, 1H, *J* 3.5, H-1''), 4.81 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.75 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.63 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.27 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.14 (dd, 1H, *J* 5.5, 3.0, H-2'), 4.08 (dd, 1H, *J* 6.5, 6.0, H-3'), 3.60-3.44 (m, 4H, H-3'', H-4'', H-5''a, H-5''b), 3.39 (dd, 1H, *J* 9.5, 4.0, H-2''); $\delta_C$ (125 MHz, $CD_3OD$) 167.77 (C-4), 158.17 (C-2), 145.70 (C-4'''), 143.33 (C-6), 126.77 (C-5'''), 100.10 (C-1''), 96.41 (C-5), 94.46 (C-1'), 82.62 (C-4'), 75.11 (C-3''), 74.84 (C-2'), 73.61 (C-2''), 71.97 (C-3'), 71.61 (C-4''), 63.36 (C-5''), 61.60 ($CH_2$), 52.33 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{17}H_{24}N_6O_9Na$ ($M+Na^+$): 479.1502; found 479.1553; *m/z* 479 (30%, $M+Na^+$).

**5'-Deoxy-5'-[4-(β-D-xylopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (77)**
Was prepared from prop-2-ynyl-β-D-xylopyranoside **28c** (27.1 mg, 0.144 mmol) and 5'-azido-5'-deoxycytidine **11** (42.5 mg, 0.158 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **77** (53 mg, 81%) was obtained as a white solid: $[\alpha]_D^{20}$ = +16.3 (c = 2.074, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.01 (s, 1H, H-5'''), 7.29 (d, 1H, *J* 8.0, H-6), 5.88 (d, 1H, *J* 7.5, H-5), 5.71 (d, 1H, *J* 3.0, H-1'), 4.91 (d, 1H, *J* 12.0, $OC\underline{H}_AH_B$), 4.87-4.80 (m, 1H, H-5'a, overlapping HOD peak), 4.77-4.70 (m, 1H, H-5'b), 4.73 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.33 (d, 1H, *J* 7.5, H-1''), 4.26 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.14 (dd, 1H, *J* 5.5, 3.5, H-2'), 4.07 (dd, 1H, *J* 6.5, 6.0, H-3'), 3.88 (dd, 1H, *J* 11.5, 5.0, H-5''a), 3.49 (ddd, 1H, *J* 10.0, 8.5, 5.5, H-4''), 3.34-3.28 (m, 1H, H-3'', overlapping $CD_3OD$ peak), 3.22 (dd, 1H, *J* 11.5, 10.0, H-5''b), 3.20 (dd, 1H, *J* 9.0, 8.0, H-2''); $\delta_C$ (125 MHz, $CD_3OD$) 167.77 (C-4), 158.17 (C-2), 145.80 (C-4'''), 143.53 (C-6), 126.72 (C-5'''), 104.39 (C-1''), 96.39 (C-5), 94.53 (C-1'), 82.72 (C-4'),

77.83 (C-3''), 74.90 (C-2''), 74.74 (C-2'), 72.02 (C-3'), 71.24 (C-4''), 67.08 (C-5''), 63.04 ($CH_2$), 52.44 (C-5'); HRMS ($ES^+$) *m/z* calc. for $C_{17}H_{24}N_6O_9Na$ ($M+Na^+$): 479.1502; found 479.1503; *m/z* 935 (30%, $2M+Na^+$), 913 (22%, $2M+H^+$), 479 (100%, $M+Na^+$), 457 (14%, $M+H^+$).

**5'-Deoxy-5'-[4-(2-acetylamino-2-deoxy-β-D-glucopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (79)**
Was prepared from prop-2-ynyl-2-acetylamino-2-deoxy-β-D-glucoside **31** (18.9 mg, 0.073 mmol) and 5'-azido-5'-deoxycytidine **11** (21.5 mg, 0.080 mmol) as described for **71** Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **79** (26 mg, 68%) was obtained as a white solid: $[\alpha]_D^{20}$ = +23.5 (c = 0.732, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.00 (s, 1H, H-5'''), 7.06 (d, 1H, *J* 7.5, H-6), 5.89 (d, 1H, *J* 7.5, H-5), 5.75 (d, 1H, *J* 3.5, H-1'), 4.92 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.83 (dd, 1H, *J* 14.5, 4.0, H-5'a), 4.75 (dd, 1H, *J* 14.5, 5.5, H-5'b), 4.73 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B$), 4.52 (d, 1H, *J* 8.0, H-1''), 4.26 (dt, 1H, *J* 6.0, 3.5, H-4'), 4.09 (t, 1H, *J* 6.0, H-3'), 4.01 (dd, 1H, *J* 5.5, 3.0, H-2'), 3.91 (dd, 1H, *J* 12.5, 2.0, H-6''a), 3.73-3.66 (m, 2H, H-6''b, H-2''), 3.44 (dd, 1H, *J* 10.0, 8.5, H-3''), 3.38-3.30 (m, 2H, H-4'', H-5'', partially buried under MeOD peak), 1.94 (s, 3H, $CH_3$); $\delta_C$ (125 MHz, $CD_3OD$) 173.89 (C=O), 167.76 (C-4), 158.23 (C-2), 145.69 (C-4'''), 143.07 (C-6), 127.28 (C-5'''), 102.08 (C-1''), 96.59 (C-5), 93.86 (C-1'), 82.51 (C-4'), 78.15 (C-5''), 76.17 (C-3''), 74.73 (C-2'), 72.11 (C-4''), 71.89 (C-3'), 62.88, 62.83 (C-6'', $CH_2$), 57.24 (C-2''), 52.11 (C-5'), 23.05 ($CH_3$); HRMS ($ES^+$) *m/z* calc. for $C_{20}H_{30}N_7O_{10}$ ($M+H^+$): 528.2054; found 528.2067; *m/z* 550 (100%, $M+Na^+$), 528 (53%, $M+H^+$).

**5'-Deoxy-5'-[4-(L-arabinopyranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (80)**
Was prepared from prop-2-ynyl-L-arabinopyranoside **18** (28.9 mg, 0.154 mmol) and 5'-azido-5'-deoxycytidine **11** (45.3 mg, 0.169 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **80** (56 mg, 80%) was obtained as a white solid with an α/β ratio of approximately 1:3: $[\alpha]_D^{20}$ = +113.7 (c = 1.380, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 8.04 (s, 1H, H-5'''β), 8.02 (s, 1H, H-5'''α), 7.27 (d, 1H, *J* 7.5, H-6β), 7.14 (d, 1H, *J* 7.5, H-6α), 6.0-5.87 (m, 2H, H-5α, H-5β), 5.75 (d, 1H, *J* 3.0, H-1'α), 5.72 (d, 1H, *J* 3.5, H-1'β), 4.94-4.90 (m, 2H, $OC\underline{H}_AH_B\alpha$, H-1''β), 4.89-4.71 (m, 6H, H-5'aα, H-5'aβ, H-5'bα, H-5'bβ, $OCH_A\underline{H}_B\alpha$, $OC\underline{H}_AH_B\beta$), 4.63 (d, 1H, *J* 12.0, $OCH_A\underline{H}_B\beta$), 4.33 (d, 1H, *J* 7.0, H-1''α), 4.20-4.24 (m, 2H, H-4'α, H-4'β), 4.15 (dd, 1H, *J* 5.5, 3.5, H-2'β), 4.09-4.02 (m, 3H, H-2'α, H-3'α, H-3'β), 3.90 (dd, 1H, *J* 12.5, 2.5, H-5''aα), 3.87-3.81 (m, 3H, H-4''β, H-5''aβ, H-4''α), 3.79 (dd, 1H, *J* 10.0, 3.5, H-2''β), 3.76 (dd, 1H, *J* 10.0, 3.0, H-3''β), 3.61-3.55 (m, 3H, H-5''bβ, H-2''α, H-5''bα), 3.53 (dd, 1H, *J* 9.0, 3.5, H-3''α); $\delta_C$ (125 MHz, $CD_3OD$) 167.77 (C-4), 158.17 (C-2), 145.73 (C-4'''), 143.34 (C-6β), 143.17 (C-6α), 126.93 (C-5'''α), 126.73 (C-5'''β), 104.24 (C-1''α), 100.52 (C-1''β), 96.43 (C-5), 94.47 (C-1'β), 93.98 (C-1'α), 82.67 (C-4'β), 82.56 (C-4'α), 74.84 (C-2'β), 74.81 (C-2'α), 74.26 (C-2''α), 72.48 (C-3''α), 72.01 (C-3'β), 71.82 (C-3'α), 70.77, 70.73 (C-2''β, C-4''β), 70.29 (C-3''β), 69.83 (C-4''α), 67.19 (C-5''α), 64.48 (C-5''β), 62.73 ($CH_2\alpha$), 61.64 ($CH_2\beta$), 52.40 (C-5'β), 52.15 (C-5'α); HRMS ($ES^+$) *m/z* calc. for $C_{17}H_{25}N_6O_9$ ($M+H^+$): 457.1683; found 457.1688; *m/z* 935 (25%, $2M+Na^+$), 913 (55%, $2M+H^+$), 457 (56%, $M+H^+$).

**5'-Deoxy-5'-[4-(β-D-ribofuranosyloxymethyl)-1,2,3-triazol-1-yl]cytidine (81)**
Was prepared from prop-2-ynyl-β-D-ribofuranoside **26** (28.2 mg, 0.150 mmol) and 5'-azido-5'-deoxycytidine **11** (44.2 mg, 0.165 mmol) as described for **71**. Following automated chromatography (EtOAc/MeOH 7:3 as eluent), **81** (48 mg, 70%) was obtained as a white solid: $[\alpha]_D^{20}$ = +20.7 (c = 1.065, DMSO); $\delta_H$ (500 MHz, $CD_3OD$) 7.98 (s, 1H, H-5'''), 7.29 (d, 1H, *J* 7.5, H-6), 5.86 (d, 1H, *J* 7.5, H-5), 5.71 (d, 1H, *J* 3.5, H-1'), 4.97 (s, 1H, H-1''), 4.83 (dd, 1H, *J* 14.5, 3.5, H-5'a), 4.81 (d, 1H, *J* 12.5, $OC\underline{H}_AH_B$), 4.74 (dd, 1H, *J* 14.5, 6.5, H-5'b), 4.63 (d, 1H, *J* 12.5, $OCH_A\underline{H}_B$), 4.26 (dt, 1H, *J* 6.5, 3.5, H-4'), 4.15 (dd, 1H, *J* 5.5, 3.5, H-2'), 4.09 (dd, 1H, *J* 7.0, 4.5, H-3''), 4.07 (dd, 1H, *J* 6.5, 6.0, H-3'), 3.97 (ddd, 1H, *J* 7.0, 6.0, 3.0, H-4''), 3.91 (d, 1H, *J* 5.0, H-2''), 3.74 (dd, 1H, *J* 12.0, 3.5, H-5''a), 3.57 (dd, 1H, *J* 12.0, 6.5, H-5''b); $\delta_C$ (125 MHz, $CD_3OD$) 167.78 (C-4), 158.18

(C-2), 145.85 (C-4’’’), 143.53 (C-6), 126.58 (C-5’’’), 108.09 (C-1’’), 96.35 (C-5), 94.54 (C-1’), 85.19 (C-4’’), 82.69 (C-4’), 76.37 (C-2’’), 74.74 (C-2’), 72.44 (C-3’’), 72.04 (C-3’), 64.68 (C-5’’), 61.23 ($CH_2$), 52.40 (C-5’); HRMS ($ES^-$) *m/z* calc. for $C_{17}H_{23}N_6O_9$ ($M\text{-}H^+$): 455.1527; found 455.1559; *m/z* 455 (25%, $M\text{-}H^+$).

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