1. Numbering system

2. Comprehensive experimental section

When a compound is obtained as a mixture of epimers, two situations may happen:
1) One of both epimers is largely predominant: in this case, only one is described.
2) The epimers are both present in substantial quantities: if the distinction between a major epimer and a minor one is possible, they are marked by symbols : * (major) and ° (minor).

“eq” and “ax” are used for description of respectively equatorial and axial protons.

3-(2-Acetamido-4,6-\(\text{O}-(R)\)-benzylidene-3-\(\text{O}\)-tert-butyldimethylsilyl-2-deoxy-\(\alpha\)-D-glucopyranosyl)-prop-1-ene 2\(\alpha\) and 3-(2-acetamido-4,6-\(\text{O}-(R)\)-benzylidene-3-\(\text{O}\)-tert-butyldimethylsilyl-2-deoxy-\(\beta\)-D-glucopyranosyl)-prop-1-ene 2\(\beta\)

To a solution of 1 (6.00 g, 18 mmol) in DMF (180 mL) were added tert-butyldimethylsilyl chloride (6.78 g, 45 mmol, 2.5 eq.) and imidazole (4.90 g, 72 mmol, 4 eq.). The reaction mixture was stirred at r.t. for 16 h and concentrated to dryness. The residue was then dissolved in CH\(_2\)Cl\(_2\) and washed with saturated aqueous NH\(_4\)Cl solution, dried (MgSO\(_4\)) and concentrated. Purification by flash chromatography (CH\(_2\)Cl\(_2\)/acetone, 9:1) afforded 2\(\beta\) (480 mg, 6%, white solid): \(R_f\) 0.72 (CH\(_2\)Cl\(_2\)/acetone = 9:1); mp 159 °C; [\(\alpha\)]\(_D\)\(^{20}\) - 58 (c 1.0, CH\(_2\)Cl\(_2\))
Further elution afforded 2α (7.19 g, 89%, white solid): Rf 0.62 (CH₂Cl₂/acetone = 9:1); mp 210 °C; [α]D²⁰ = 21° (c 1.0, CH₂Cl₂). ¹H NMR δ 7.50-7.45 (m, 2H, H₆'), 7.38-7.33 (m, 3H, H₅'), 7.18 (s, 3H, H₃'), 5.77 (dd, 1H, JH₁H₂ = 17.1 Hz, H₂', JH₁H₃₃ = 10.3 Hz, H₃'), 5.50 (s, 1H, H₇), 5.49 (d, 1H, JH₇H₆₂ = 7.1 Hz, H₂), 5.14 (dm, 1H, JH₁H₂ = 17.1 Hz, H₁), 5.11 (dm, 1H, JH₁H₂ = 10.3 Hz, H₁cis), 4.35 (dd, 1H, JH₁H₃₃ = 10.7 Hz, H₁cis), 5.6 Hz, JH₁H₃₃ = 5.6 Hz, JH₁H₃₃ = 4.8 Hz, JH₁H₃₃ = 4.24-4.18 (m, 2H, H₂', H₆'eq), 3.84 (dd, 1H, JH₂₃'H₄ = 10.0 Hz, JH₂₃'H₄ = 8.3 Hz, H₃'), 3.69 (dd, 1H, JH₂₃'H₄ = 8.3 Hz, H₃'), 3.69 (dd, 1H, JH₂₃'H₄ = 9.7 Hz, H₁'), 4.22 (dd, 1H, JH₂₃'H₄ = 9.7 Hz, H₁'), 4.18 (dd, 1H, JH₂₃'H₄ = 14.8 Hz, H₂'), 3.77 (s, 9H, SiBu), 2.62 (dd, 1H, JH₂₃'H₂₆ = 14.3 Hz, JH₂₃'H₁ = 14.3 Hz, H₂'), 2.30 (s, 3H, CH₃CO), 2.19 (s, 3H, CH₃CO), 1.99 (s, 3H, CH₃CO), 0.84 (s, 9H, SiBu), 0.07, 0.00 (2s, 6H, SiMe). ¹³C NMR δ 170.2 (CH₂CO), 137.3, 129.2, 128.3, 126.4 (C₆'), 123.3 (C₅'), 122.3 (C₄'), 119.4 (C₃), 118.4 (C₂), 105.2 (C₁), 60.2 (C₀), 55.3 (C₂'), 31.3 (C₃), 25.8 (CH₂CO), 18.3 (SiBu), -3.7, -4.7 (SiMe). MS (ESI): m/z = 917 [2M+Na⁺] 100%; HRMS calcd for C₂₄H₂₇Na₂O₄Si₂ 470.2339, found 470.2336.

**Methyl 2-(2-acetamido-4,6-O-(R)-benzylidene-3-O-tert-butyl dimethylsilyl-2-deoxy-α-D-glucopyranosyl)acetate 3**

To a solution of 2α (2.00 g, 4.47 mmol) in CH₂Cl₂ (55 mL) was added a solution of sodium hydroxide (1.79 g, 44.7 mmol, 10 eq.) in methanol (25 mL). Ozone was bubbled through the solution at 78 °C for 3 h until it became blue. The solution was then purged with argon, warmed to r.t., diluted with CH₂Cl₂ and washed with saturated aqueous NaHCl solution. Aqueous phase was back-extracted with CH₂Cl₂. Combined organic extracts were dried (MgSO₄) and concentrated. Purification by flash chromatography (CH₂Cl₂/acetone, 9:1) afforded ester 3 (1.44 g, 67%, white solid): Rf 0.37 (CH₂Cl₂/acetone = 9:1); mp 198 °C; [α]D²⁰ = 21° (c 1.0, CH₂Cl₂); IR 1743 cm⁻¹; ¹H NMR δ 7.49-7.45 (m, 2H, H₆'), 7.37-7.33 (m, 3H, H₅'), 5.52 (d, 1H, JH₇H₆₂ = 7.0 Hz, H₃'), 5.50 (s, 1H, H₇), 4.78 (dd, 1H, JH₁H₂ = 9.4 Hz, JH₁H₃₃ = 5.5 Hz, H₁'), 4.22 (dd, 1H, JH₂₃'H₄ = 9.7 Hz, H₂', JH₂₃'H₄ = 7.0 Hz, JH₂₃'H₄ = 5.7 Hz, H₃'), 4.20 (dd, 1H, JH₁H₂ = 9.4 Hz, JH₆'eqH₆'ax = 3.5 Hz, H₆'eq), 3.81 (dd, 1H, JH₁H₂ = 9.7 Hz, JH₆'eqH₆'ax = 8.8 Hz, H₃'), 3.70 (s, 3H, OMMe), 3.69-3.62 (m, 2H, H₅', H₆'ax), 2.53 (dd, 1H, JH₁H₂ = 9.2 Hz, JH₆'eqH₆'ax = 8.8 Hz, H₃'), 2.73 (dd, 1H, JH₂₃'H₂₆ = 14.3 Hz, JH₂₃'H₁ = 9.4 Hz, H₂a), 2.62 (dd, 1H, JH₂₃'H₂₆ = 14.3 Hz, JH₂₃'H₁ = 14.3 Hz, H₂a), 1.97 (s, 3H, CH₃CO), 0.83 (s, 9H, SiBu), 0.05, -0.02 (2s, 6H, SiMe); ¹³C NMR δ 171.2 (C₁), 170.3 (CH₂CO), 137.3, 129.2, 128.3, 126.4 (C₆'), 102.1 (C₇'), 83.1 (C₆'), 72.3 (C₅'), 70.4 (C₄'), 69.3 (C₀), 64.9
(3-N-tert-Butyloxycarbonyl-2',3'-O-isopropylidene)-uridine 6
To a solution of 2',3'-O-isopropylidene-uridine (1.50 g, 5.3 mmol) in THF (30 mL) were added at 0 °C trimethylsilyl chloride (1.35 mL, 10.6 mmol, 2 eq.) and DIEA (1.85 mL, 10.6 mmol, 2 eq.). The reaction mixture was stirred at r.t. for 1 h and hydrolyzed with saturated aqueous NH4Cl solution. Aqueous phase was extracted with EtOAc and organic phase was dried (MgSO4) and concentrated in vacuo. The residue was taken up in THF (30 mL). Di-tert-butyl dicarbonate (1.27 g, 5.8 mmol, 1.1 eq.), Et3N (820 μL, 5.8 mmol, 1.1 eq.) and DMAP cat. were successively added. The mixture was stirred at r.t. for 3 h, then cooled to 0 °C and stirred with 1 M aqueous HCl solution for 5 min. After dilution with EtOAc and decantation, organic phase was washed with saturated aqueous NaCl solution, dried (MgSO4) and concentrated. Purification by flash chromatography (cyclohexane/acetone, 2:1) afforded 6 (1.67 g, 82%, white solid): Rf 0.26 (cyclohexane/acetone = 2:1); [α]D20 -23 (c 1.0, CH2Cl2);

1H NMR δ 7.48 (d, 1H, JH6-H5 = 8.2 Hz, H6), 5.71 (d, 1H, JH5-H6 = 8.2 Hz, H5), 5.66 (d, 1H, JH1'-H2' = 2.9 Hz, H1'), 4.94 (dd, 1H, JH2'-H3' = 6.4 Hz, JH2'-H1' = 2.9 Hz, H2'), 4.89 (dd, 1H, JH3'-H2' = 6.4 Hz, JH3'-H4' = 3.2 Hz, H3'), 4.29 (dd, 1H, JH4'-H5'b = 3.5 Hz, JH4'-H3' = 3.2 Hz, H4'), 3.90 (dd, 1H, JH5'a-H5'b = 12.0 Hz, JH5'a-OH = 3.8 Hz, JH5'a-H4' = 2.4 Hz, H5'a), 3.78 (ddd, 1H, JH5'b-H5'a = 12.0 Hz, JH5'b-OH = 6.4 Hz, JH5'b-H4' = 3.5 Hz, H5'b), 2.81 (dd, 1H, JOH-H5'b = 6.4 Hz, JOH-H5'a = 3.8 Hz, OH), 1.58 (s, 9H, CMe3), 1.55, 1.34 (2s, 6H, CMe2);

13C NMR δ 160.5 (C4), 148.7 (C2), 147.5 (COBoc), 141.7 (C6), 114.5 (CMe2), 102.5 (C5), 95.7 (C1'), 87.4 (CMe3), 87.1 (C4'), 84.1 (C2'), 80.4 (C3'), 62.7 (C5'), 27.6 (CMe2); MS (ESI): m/z = 791 [2M+Na] + 100%; HRMS calcd for C17H24N2NaO8+ 407.1430, found 407.1431.

Benzyl (3-N-tert-butyloxycarbonyl-2',3'-O-isopropylidene)-uridin-5'-yl methylphosphonate 7
At 0 °C, diisopropyl azodicarboxylate (DIAD) (320 μL, 1.6 mmol, 1.5 eq.) was added dropwise to a solution of 5 (200 mg, 1.1 mmol, 1 eq.), 6 (413 mg, 1.1 mmol, 1 eq.) and PPh3 (423 mg, 1.6 mmol, 1.5 eq.) in THF (10 mL). The reaction mixture was stirred at r.t. for 3 h then concentrated. Purification by flash chromatography (EtOAc/cyclohexane, 2:1) afforded 7 (400 mg, 67%, white solid) as a mixture of epimers (d.r. = 54/46): Rf 0.13 (EtOAc/cyclohexane = 2:1);

1H NMR δ 7.39-7.33 (m, 5H, Har), 7.32, 7.30 (2d, 1H, JH6-H5 = 8.1 Hz, H6*), 5.70, 5.66 (2d, 1H, JH5-H6 = 8.1 Hz, H5*), 5.70-5.68 (m, 1H, H1'), 5.12-5.04 (m, 2H, CH2Ph), 4.87, 4.80 (2dd, 1H, JH2'-H3' = 6.4 Hz, JH2'-H1' = 2.2 Hz, H2'*, H2*'), 4.77, 4.71 (2dd, 1H, JH3'-H2' = 6.4 Hz, JH3'-H4' = 3.7 Hz, H3', H3*), 4.32-4.28 (m, 1H, H4'), 4.25-4.15, 4.15-4.07 (2m, 2H, H5'), 1.59 (2s, 9H, tBu*), 1.54 (bs, 3H, CH3), 1.48 (2d, 3H, JCH3-P = 17.6 Hz, CH3*), 1.33 (2s, 3H, CMeth*, CMeth*); 13C NMR δ 160.3 (C4), 148.3 (C2), 147.5 (COBoc), 140.8, 140.7 (C6*, C6°), 136.2, 136.2 (2d, JCarb-P = 5.0 Hz, CCarb*, CCarb°), 128.9, 128.8, 128.1 (CHar), 114.8 (CMeth), 102.3 (C3), 94.5, 94.4 (C1°, C1*), 87.2 (CMeth), 85.8, 85.7 (2d, JC4'-P = 7.0 Hz, C4°, C4*), 84.7, 84.6 (C2°, C2*), 80.6, 80.5 (C3°, C3*), 67.8, 67.7 (2d, JC2HPh-P = 6.0 Hz, CH2Ph, CH2Ph°), 64.8, 64.7 (2d, JC5'-P = 6.0 Hz, C5°, C5*), 27.6 (CMeth), 27.3, 25.5, 25.4 (CMeth), 11.5, 11.5 (2d, JCH3-P = 144.0 Hz, CH3*, CH3°); 31P NMR (202 MHz, CDCl3) δ 32.6 (s, 0.46P, P°), 32.4 (s, 0.54P, P°); MS
**Benzyl (R)-citronellyl methylphosphonate 8**

At 0 °C, DIAD (880 μL, 4.4 mmol, 1.5 eq.) was added dropwise to a solution of 5 (550 mg, 3 mmol, 1 eq.), (R)-citronellol (540 μL, 3 mmol, 1 eq.) and PPh 3 (1.16 g, 4.4 mmol, 1.5 eq.) in THF (25 mL). The reaction mixture was stirred at r.t. for 1 h 30 then concentrated. Purification by flash chromatography (EtOAc/cyclohexane, 2:1) afforded 8 (920 mg, 95%, colorless oil) as a mixture of epimers (d.r. = 1/1): Rf 0.44, 0.31 (EtOAc/cyclohexane, 2:1); 1H NMR δ 7.41-7.28 (m, 5H, H ar), 5.12-5.02 (m, 3H, CH 2Ph, H6), 4.10-3.90 (m, 2H, H 1), 2.04-1.87 (m, 2H, H5), 1.72-1.64 (m, 1H, H2a), 1.67 (s, 3H, H8), 1.59 (s, 3H, H9), 1.58-1.51 (m, 1H, H3), 1.48 (d, 3H, JCH3-P = 17.5 Hz, CH 3P), 1.36-1.26, 1.20-1.11 (2m, 2H, H4), 0.88 (2d, 3H, JH10-H3 = 6.6 Hz, H10); 13C NMR δ 136.7 (d, JCq-P = 5.7 Hz, Cq), 131.5 (C7), 128.7, 128.5, 128.0 (CH ar), 124.7 (C6), 67.2 (d, JCH2Ph-P = 5.7 Hz, CH2Ph), 64.2 (d, JC1-P = 6.2 Hz, C1), 37.5 (d, JC2-P = 6.3 Hz, C2), 37.1 (C4), 29.2 (C 3), 25.8 (C 8), 25.5 (C 5), 19.4 (C10), 17.8 (C9), 11.5, 11.5 (2d, JCH3-P = 144.5 Hz, CH3P); 31 P NMR δ 31.5, 31.5 (2s); MS (ESI): m/z = 671 [2M+Na] + 100%; HRMS calcd for C 18H29NaO3P+ 347.1752, found 347.1746.

**Dibenzyl 3-(2-acetamido-4,6-O-(R)-benzylidene-3-O-tert-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-2-oxopropylphosphonate 11**

To a solution of 17 (890 mg, 3.2 mmol, 3.25 eq.) in THF (15 mL) was added dropwise nBuLi (1.5 mL, 3.43 mmol, 3.5 eq.) at - 78 °C. After 1 h stirring at - 78 °C, the mixture was added to a cold solution of 3 (475 mg, 0.99 mmol, 1 eq.) in THF (3 mL). The reaction mixture was slowly warmed to r.t. overnight and quenched with saturated aqueous NH 4Cl solution. Aqueous phase was extracted with EtOAc and combined organic layers were dried (MgSO 4) and concentrated. Purification by flash chromatography (CH 2Cl2/acetone, 8:2) afforded 11 (600 mg, 83%, white solid): Rf 0.47 (CH2Cl2/acetone = 8:2); [α]D 20 + 26 (c 1.0, CH2Cl2); IR (cm⁻¹) 1718 (CO), 1250 (PO); 1H NMR δ 7.51-7.47 (m, 2H, H ar), 7.42-7.30 (m, 13H, H ar), 6.62 (d, JNH-H2' = 8.7 Hz, NH), 5.50 (s, 1H, H 7'), 5.12, 5.02 (AB from ABX, 2H, JAB = 11.6 Hz, J A-P = 9.5 Hz, CH2Ph), 5.01 (d, 2H, JH-P = 8.4 Hz, CH2Ph), 4.78 (ddd, 1H, JH2'-H3' = 9.8 Hz, JH2'-NH = 8.7 Hz, H2'), 4.15 (dd, 1H, JH6'eq-H6'ax = 10.3 Hz, JH6'eq-H5' = 4.3 Hz, H6'eq), 3.83 (dd, 1H, JH3'-H2' = 9.8 Hz, JH3'-H4' = 8.3 Hz, H3'), 3.65 (dd, 1H, JH6'ax-H6'eq = 10.3 Hz, JH6'ax-H1' = 9.6 Hz, H6'ax), 3.51 (dd, 1H, JH4'-H5' = 9.6 Hz, JH4'-H3' = 8.3 Hz, H4'), 3.47 (ddd, 1H, JH5'-'H4' = 9.6 Hz, JH5'-H6'eq = 9.2 Hz, JH5'-H3' = 4.3 Hz, H3'), 3.19 (dd, 1H, JH3a-H3b = 17.1 Hz, JH3a-H1' = 8.0 Hz, H3a), 3.10, 3.05 (AB from ABX, 2H, JAB = 13.5 Hz, J A-P = 23.2 Hz, J B-P = 21.9 Hz, H1a, H1b), 2.63 (dd, 1H, JH3b-H3a = 17.1 Hz, JH3b-H1' = 5.1 Hz, H3b), 1.85 (s, 3H, CH3CO), 0.83 (s, 9H, SiBu), 0.10, 0.01 (2s, 6H, SiMe); 13C NMR δ 197.4 (d, JC2-P = 4.7 Hz, C2), 170.7 (CH3CO), 137.4 (Cqar), 135.4, 135.3 (2d, JCq-P = 6.0 Hz, Cqar), 129.2, 129.1, 129.0, 128.9, 128.5, 128.2, 128.4 (CHqar), 102.0 (C7'), 83.4 (C4'), 70.5 (C7'), 70.1 (C3'), 69.3 (C6'), 68.6, 68.5 (2d, JCH2Ph-P = 6.5 Hz, CH2Ph), 65.7 (C5'), 54.0 (C2'), 43.9 (C3'), 42.9 (d, JCH3-P = 124.8 Hz, C1'), 25.8 (SiBu), 23.0 (CH3CO), 18.2 (SiBu), -3.9, -4.7 (SiMe); 31P NMR δ 21.4 (s); MS (ESI): m/z = 1469 [2M+Na] + 100%; HRMS calcd for C38H50NNaO9PSi+ 746.2890, found 746.2898.
Benzyl 3-(2-acetamido-4,6-O-(R)-benzylidene-3-O-tert-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-2-oxopropylphosphonate 12

To a solution of 11 (600 mg, 0.83 mmol) in toluene (8 mL) was added DABCO (110 mg, 0.99 mmol, 1.2 eq.). The reaction mixture was then refluxed for 7 h and concentrated. The residue was taken up in methanol, acidified with DOWEX H⁺ (50WX8-100) ion exchange resin. Methanol was removed in vacuo to afford 12 (475 mg, 90%, white solid): [α]D 20 + 18 (c 1.0, CH2Cl2); 1H NMR (acetone-d6) δ 7.54-7.32 (m, 11H, NH, Har), 5.62 (s, 1H, Hγ), 5.18-5.08 (m, 2H, CH2Ph), 4.66 (ddd, 1H, JH1′-H3a = 6.8 Hz, JH1′-H3b = 6.3 Hz, JH1′-H2′ = 5.9 Hz, H1′), 4.28 (ddd, 1H, JH2′-H3′ = 10.0 Hz, JH2′-NH = 9.4 Hz, JH2′-H1′ = 5.9 Hz, H2′), 4.09 (dd, 1H, JH6′-eq-H6′ax = 9.7 Hz, JH6′-eq-H5′ = 4.5 Hz, H6′eq), 3.99 (dd, 1H, JH3′-H4′ = 10.0 Hz, JH3′-H4′ = 8.9 Hz, H3′), 3.68 (dd, 1H, JH6′ax-H5′ = 5.8 Hz, H6′ax), 3.62 (ddd, 1H, JH5′-H6′ax = 9.7 Hz, H5′-H6′ax = 4.5 Hz, H5′), 3.52 (dd, 1H, JH4′-H5′ = 9.2 Hz, JH4′-H5′ = 8.9 Hz, H4′), 3.37 (dd, 1H, JH1α-H1β = 22.8 Hz, JH1α-H1β = 13.4 Hz, H1α), 3.35 (dd, 1H, JH3α-H3β = 17.1 Hz, JH3α-H1′ = 6.8 Hz, H3α), 3.24 (dd, 1H, JH1β-H1α = 21.9 Hz, JH1β-H1α = 13.4 Hz, H1β), 3.00 (dd, 1H, JH3β-H3α = 17.1 Hz, JH3β-H1′ = 6.3 Hz, H3β), 1.84 (s, 3H, CH3CO), 0.82 (s, 9H, SiMe3), 0.08 (0.02, 6H, SiMe); 13C NMR (acetone-d6) δ 199.9 (d, JC2-P = 5.0 Hz, C2), 170.5 (CH2CO), 139.0 (Cqa), 137.6 (Cqα), 129.7, 129.2, 129.0, 128.7, 127.3 (CHar), 102.5 (C7′), 84.4 (C4′), 72.0 (C1′), 69.7 (C6′), 68.0 (d, JC2Hβ-P = 5.0 Hz, CH2Ph), 65.9 (C5′), 54.6 (C2′), 43.8 (d, JC1-P = 124.0 Hz, C1), 34.5 (C5), 26.3 (SiBu3), 23.1 (CH2CO), 18.8 (SiBu3), -3.8, -4.5 (SiMe3); 31P NMR (acetone-d6) δ 18.8 (s); MS (ESI): m/z = 632 [M-H] - 100%; HRMS calcd for C31H43NO9PSi- 632.2445, found 632.2460.

Dibenzy 3-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-2-oxopropylphosphonate 13

To a suspension of 11 (100 mg, 0.14 mmol) in water (5 mL) was added trifluoroacetic acid (5 mL) at 0 °C. The reaction mixture was stirred at r.t. for 1 h and concentrated. Purification by flash chromatography (CH2Cl2/MeOH, 85:15) and lyophilization afforded 13 (70 mg, 97%, white solid): Rf 0.48 (CH2Cl2/MeOH = 85:15); [α]D 20 + 38 (c 1.0, CH2Cl2); 1H NMR (DMSC-d6) δ 7.67 (d, 1H, JH3N-H2′ = 7.8 Hz, NH), 7.41-7.31 (m, 10H, Har), 5.07-4.98 (m, 5H, H4′-OH4′ = 5.3 Hz, H4′), 4.44 (dd, 1H, JH3O-H6′b = 6.0 Hz, JH3O-H6′a = 5.8 Hz, OH4′), 4.40 (ddd, 1H, JH1′-H3a = 9.1 Hz, JH1′-H2′ = 5.6 Hz, JH1′-H3b = 4.6 Hz, H1′), 3.71 (ddd, 1H, JH2′-H3′ = 10.0 Hz, JH2′-NH = 7.8 Hz, JH2′-H1′ = 5.6 Hz, H2′), 3.56 (ddd, 1H, JH6′a-OH6′ = 5.8 Hz, JH6′a-H5′ = 2.5 Hz, H6′a), 3.50 (dd, 1H, JH1α-H1β = 21.8 Hz, H1α), 14.4 Hz, H1α), 3.47 (dd, 1H, JH6′b-H6′a = 11.6 Hz, JH6′b-OH6′ = 6.0 Hz, JH6′b-H5′ = 5.7 Hz, H6′b), 3.41 (dd, 1H, JH1β-H1α = 21.5 Hz, H1α), 14.4 Hz, H1β), 3.40 (ddd, 1H, JH3′-H2′ = 10.0 Hz, JH3′-H4′ = 8.0 Hz, JH3′-OH3′ = 5.3 Hz, H3′), 3.35 (dd, 1H, JH5′-H4′ = 8.8 Hz, JH5′-H6′b = 5.7 Hz, JH5′-H6′a = 2.5 Hz, H5′), 3.15 (ddd, 1H, JH1′-H4′ = 8.8 Hz, JH4′-H3′ = 8.0 Hz, JH4′-OH4′ = 5.3 Hz, H4′), 2.90 (dd, 1H, JH3α-H3β = 16.1 Hz, JH3α-H1′ = 9.1 Hz, H3α), 2.66 (dd, 1H, JH3β-H3α = 16.1 Hz, JH3β-H1′ = 4.6 Hz, H3β), 1.77 (s, 3H, CH2CO); 13C NMR (DMSC-d6) δ 200.5 (d, JC2-P = 6.0 Hz, C2), 169.3 (CH2CO), 136.2 (d, JCC=P = 6.0 Hz, Ccar), 128.4, 128.2, 127.7 (CHar), 74.9 (C5′), 70.6 (C4′), 70.3 (C3′), 69.3 (C1′), 67.0, 66.9 (2d, JCH2Ph-P = 6.0 Hz, CH2Ph), 60.9 (C6′), 52.6 (C2′), 41.8 (d, JC1-P = 126.0 Hz, C1), 41.4 (C3), 22.6 (CH2CO); 31P NMR (DMSC-d6) δ 21.8 (s); MS (ESI): m/z = 544 [M+Na]+ 100%; HRMS calcd for C25H32NNaO9P+ 544.1712, found 544.1707.

Benzyl 3-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-2-oxopropylphosphonate 14
To a solution of 13 (34 mg, 65 μmol) in toluene (1 mL) was added DABCO (9 mg, 78 μmol, 1.2 eq.). The reaction mixture was then refluxed for 4 h and concentrated. The residue was taken up in water, acidified with DOWEX H⁺ (50WX8-100) ion exchange resin. Water was removed in vacuo to afford 14 (25 mg, 88%, white solid): 1H NMR (DMSO-d6) δ 7.73 (d, 1H, J_B'-H2' = 8.0 Hz, H_B'), 7.42-7.28 (m, 5H, H_ar), 4.94 (d, 2H, J_CH2Ph-P = 7.5 Hz, CH2Ph), 4.66 (ddd, 1H, J_H1'-H3a = 8.3 Hz, J_H1'-H3b = J_H1'-H2' = 5.2 Hz, H_1'), 3.72 (ddd, 1H, 1H, J_H2'-H3' = 5.2 Hz, H_2'), 3.56 (dd, 1H, J_H6'b-H6'a = 11.5 Hz, J_H6'b-H5' = 5.7 Hz, H_6'b), 3.41 (dd, 1H, J_H3'-H2' = 10.3 Hz, J_H3'-H4' = 8.1 Hz, H_3'), 3.38 (ddd, 1H, J_H2'-H3' = 10.3 Hz, J_H2'-NH = 8.0 Hz, J_H2'-H2' = 5.2 Hz, H_2'), 3.28 (dd, 1H, J_H6'b-H6'a = 11.5 Hz, J_H6'b-H5' = 5.7 Hz, H_6'b), 2.88 (dd, 1H, J_H3a-H3b = 16.2 Hz, J_H3a-H1' = 8.3 Hz, H_3a), 2.75 (dd, 1H, J_H3b-H3a = 16.2 Hz, J_H3b-H1' = 5.2 Hz, H_3b), 1.76 (s, 3H, CH3CO); 13C NMR (DMSO-d6) δ 201.5 (d, J_C2-P = 5.5 Hz, C_2), 169.3 (CH3CO), 137.2 (d, J_Cq-P = 7.0 Hz, Cqar), 128.3, 127.8, 127.4 (CH ar), 74.8 (C_5'), 70.8 (C_4'), 70.4 (C_3'), 69.5 (C_1'), 66.1 (d, J_CH2Ph-P = 5.0 Hz, CH2Ph), 61.0 (C_6), 52.7 (C_2'), 43.9 (d, J_Cp-P = 120.0 Hz, C_1), 41.1 (C_3), 22.6 (CH3CO), 31P NMR (DMSO-d6) δ 16.2 (s); MS (ESI): m/z = 430 [M-H⁺] 100%;.

3-N-tert-Butyloxycarbonyl-1-(5'-hydroxypentyl)-uracil 17

To a solution of 1-(5'-hydroxypentyl)uracil (500 mg, 2.5 mmol) in THF (10 mL) were added at 0 °C trimethylsilyl chloride (650 μL, 5.0 mmol, 2 eq.) and DIEA (880 μL, 5.0 mmol, 2 eq.). The reaction mixture was stirred at r.t. for 1 h 30 and hydrolyzed with saturated aqueous NH4Cl solution. Aqueous phase was extracted with EtOAc and the organic layer was dried (MgSO4) and concentrated in vacuo. The residue was taken up in THF (10 mL). Boc2O (606 mg, 2.8 mmol, 1.1 eq.), Et3N (390 μL, 2.8 mmol, 1.1 eq.) and DMAP cat. were successively added. The mixture was stirred at r.t. for 16 h, then cooled to 0 °C and stirred with 1 M aqueous HCl solution for 2 min. After dilution with EtOAc and decantation, organic phase was washed with saturated aqueous NaCl solution, dried (MgSO4) and concentrated. Purification by flash chromatography (CH2Cl2/MeOH, 9:1) afforded 17 (498 mg, 66%, yellow oil): Rf 0.54 (CH2Cl2/MeOH, 9:1); 1H NMR δ 7.12 (d, 1H, J_H6-H5 = 8.0 Hz, H_6), 5.70 (d, 1H, J_H5-H6 = 8.0 Hz, H_5), 3.73 (t, 2H, J_H1'-H2' = 7.4 Hz, H_1'), 3.68-3.61 (m, 2H, H_2'), 1.74 (tt, 2H, J_H2'-H3' = 7.7 Hz, J_H2'-H1' = 7.4 Hz, H_2'), 1.65-1.56 (m, 2H, H_3'), 1.60 (s, 9H, CMe3), 1.47-1.39 (m, 2H, H_3'); 13C NMR δ 160.9 (C_4'), 149.2 (C_2), 148.0 (COBoc), 143.7 (C_6), 102.0 (C_5), 86.9 (CMe3), 62.5 (C_3'), 49.4 (C_1'), 32.1 (C_4'), 28.8 (C_2'), 27.6 (CMe3'), 22.9 (C_3'); MS (ESI): m/z = 321 [M+Na⁺] 100%; HRMS calcd for C14H22N2NaO5⁺ 321.1426, found 321.1425.
3. $^1H$, $^{13}C$ and $^{31}P$ NMR Spectra

Compound 2α ($^1H$, $^{13}C$)
Compound 3 ($^1$H, $^{13}$C)
Compound 6 (\(^1\text{H}, \, ^{13}\text{C}\))
Compound 7 ($^1$H, $^{13}$C, $^{31}$P)
Compound 8 (\(^1\text{H}, \, ^{13}\text{C}, \, ^{31}\text{P}\))
Compound 9 (\(^1\text{H}, \quad \text{\textsuperscript{13}C}, \quad \text{\textsuperscript{31}P}\)
Compound 10 ($^1$H, $^{13}$C, $^{31}$P)
Compound 11 ($^1$H, $^{13}$C, $^{31}$P)
Compound 12 ($^1$H, $^{13}$C, $^{31}$P)
Compound 13 ($^1$H, $^{13}$C, $^{31}$P)
Compound 15 (\(^{1}H, ^{13}C, ^{31}P\))
Compound 16 ($^1$H, $^{13}$C, $^{31}$P)
Compound 17 \((^1H, ^{13}C)\)
Compound 18 \((^1H, ^{13}C, ^{31}P)\)
Compound 19 ($^1$H, $^{13}$C, $^{31}$P)
Compound 20 ($^1$H, $^{13}$C, $^{31}$P)
Compound 21 ($^1$H, $^{13}$C, $^{31}$P)
Compound 22 ($^1$H, $^{13}$C, $^{31}$P)
Compound 23 (\(^1\text{H}, \^{13}\text{C}, \^{31}\text{P}\))
Compound 24 (\( ^1\text{H}, ^{13}\text{C}, ^{31}\text{P} \))
Compound 25 ($^1$H, $^{13}$C, $^{31}$P)
Compound 26 ($^1$H, $^{13}$C, $^{31}$P)