SUPPORTING INFORMATION

Deoxyuridine Triphosphate Nucleotidohydrolase as a Potential Antiparasitic Drug Target

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General Experimental is as described in the main article.

Some of the compounds have been previously reported in the literature and are listed with their corresponding CAS numbers in section 3 of this document. However, for the purpose of this work all compounds were thoroughly characterised.

2'-Deoxyuridine 5'-diphenylphosphate (1a)

Dowex® WX-2-200 resin was added to a solution of the 3'-silylated precursor 3a (0.88 g, 1.53 mmol) in CH₃OH (15 mL) and the suspension was stirred overnight at room temperature. The crude mixture was filtered, reduced in vacuo and purified by flash column chromatography eluting with 10% CH₃OH in CHCl₃. Compound 1a was obtained as a white solid (0.62 g, 88%) from the fractions with R<sub>f</sub> = 0.28 (10% CH₃OH/CHCl₃). Mp 53-60°C; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 1.93-2.10 (1H, m, 2'<sup>CH</sup>H), 2.18-2.26 (1H, m, 2''<sup>CH</sup>H), 4.05 (1H, d, J = 6.7 Hz, 5'<sup>CH</sup>H), 4.30-4.40 (1H, m, 4'-H), 4.41-4.52 (2H, m, 5'<sup>CH</sup>H and 3'<sup>CH</sup>H), 5.45 (1H, d, J = 8.1 Hz, 5-H), 6.17 (1H, t, J = 6.8 Hz, 1'-H), 7.17-7.38 (10H, m, Ph-H), 7.49 (1H, d, J = 8.1 Hz, 6-H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 41.1 (2'<sup>CH</sup>₂), 70.3 (d, J = 6.0 Hz, 5'<sup>CH</sup>₂), 72.1 (3'<sup>CH</sup>), 86.5 (d, J = 7.5 Hz, 4'-CH), 87.2 (1'-CH), 103.3 (5-C), 121.52, 121.54, 121.58 and 121.61 (Ph-CH), 127.5 (Ph-CH), 131.54 and 131.59 (Ph-CH), 142.3 (6-CH), 152.1 (d, J = 6.8 Hz, Ph-C), 152.4 (2-C), 166.4 (4-C); <sup>31</sup>P NMR(121 MHz, CD<sub>3</sub>OD) δ -10.8; IR (KBr) 3059, 1693, 1284, 1188, 690, 762 cm<sup>-1</sup>; Anal. (C<sub>21</sub>H<sub>21</sub>O₈N₂P) H, N; Calcd C, 54.79; Found 54.18%.

2'-Deoxyuridine 5'-diethylphosphate (1b)

A procedure identical to the one used for 1a was employed. Compound 1b was obtained as a clear viscous liquid (0.44 g, 90%) from the 3'-silylated precursor 3b (0.65 g, 1.36 mmol). Flash column chromatography was carried out using 0→5% CH₃OH in CHCl₃. R<sub>f</sub>(5% CH₃OH/CHCl₃) 0.29; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 1.35 (6H, t, J = 7.0 Hz, 2 x OCH₂CH₃H₂), 2.20-2.40 (2H, m, 2''-H), 4.08-4.28 (7H, m, 2 x OCH₂CH₃, 5'-H and 4'-H), 4.42 (1H, m, 3'-H), 5.74 (1H, d, J = 8.1 Hz, 5-H), 6.28 (1H, t, J = 6.7 Hz, 1'-H), 7.66 (1H, d, J = 8.1 Hz, 6-H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)
δ 17.0 (d, J = 6.8 Hz, OCH$_2$CH$_3$), 41.3 (d, J = 17.3 Hz, OCH$_2$CH$_3$), 66.2 (2'-CH$_2$), 68.7 (5'-CH$_2$), 72.2 (3'-CH), 86.7 (1'-CH), 87.2 (4'-CH), 103.4 (5'-CH), 142.6 (6'-CH), 152.5 (2-C), 166.4 (4-C); $^{31}$P NMR (121 MHz, CD$_3$OD) δ -0.1; IR (film) 3434, 1686, 1648, 1275, 1032 cm$^{-1}$; MS (CI) m/z 382 ([M+NH$_4^+$], 80%); (ES$^+$) calcd for C$_{13}$H$_{22}$N$_2$O$_8$P$^+$ (M+H)$^+$ 365.1114, found 365.1118.

5'-O-Diethylphosphonoacetyl-2'-deoxyuridine (1c)

A mixture of 2'-deoxyuridine (2.00 g, 8.77 mmol) and diethylphosphonoacetic acid (2.58 g, 13.16 mmol) in dry DMF (40 mL) was treated dropwise with a solution of EDCI (2.86 g, 14.91 mmol) in dry DMF (40 mL). The resulting mixture was stirred at room temperature for 6 h. The solvent was reduced in vacuo and the crude product purified by flash column chromatography eluting with 5% CH$_3$OH in CHCl$_3$. The fractions with R$_f$ = 0.40 (15% CH$_3$OH/CHCl$_3$) yielded compound 1c as a white hygroscopic solid (2.58 g, 73%).

$^1$H NMR (300 MHz, CD$_3$OD) δ 1.41 (6H, t, J = 7.1 Hz, 2 x OCH$_2$CH$_3$), 2.36 (2H, m, 2'-H), 3.21-3.28 (2H, d, J = 21.6 Hz, PCH$_2$), 4.12-4.28 (5H, m, 2 x OCH$_2$CH$_3$ and 5'-CH$_2$), 4.35-4.50 (3H, m, 5'-CH$_2$ and 3'-H and 4'-H), 5.81 (1H, d, J = 8.1 Hz, 5'-H), 6.32 (1H, t, J = 6.7 Hz, 1'-H), 7.82 (1H, d, J = 8.1 Hz, 6'-H); $^{13}$C NMR (75 MHz, CD$_3$OD) δ 17.0 (d, J = 6.0 Hz, OCH$_2$CH$_3$), 33.8 (d, J = 15.8 Hz, PCH$_2$), 41.1 (2'-CH$_2$), 64.8 (d, J = 6.8 Hz, OCH$_2$CH$_3$), 66.5 (5'-CH$_2$), 72.5 (3'-CH), 86.0 (1'-CH), 87.1 (4'-CH), 103.4 (5'-CH), 142.8 (6'-CH), 152.5 (2-C), 166.5 (4-C), 167.3 (d, J = 6.0 Hz, COO); $^{31}$P NMR (121 MHz, CD$_3$OD) δ 22.2; IR (film) 3428, 1709, 1691, 1678, 1279, 1024 cm$^{-1}$; MS (CI) m/z 424 ([M+NH$_4^+$], 60%), 407 ([M+H]$^+$, 100%); HRMS (ES$^+$) calcd for C$_{15}$H$_{24}$N$_2$O$_9$P$^+$ (M+H)$^+$ 407.1214, found 407.1222.

5'-Acetyl-2'-deoxyuridine (1d)

Tetra-n-butyrammonium fluoride (1.35 g, 5.17 mmol) was added to a solution of 6 (0.99 g, 2.59 mmol) in THF (10 mL) and the mixture was stirred at room temperature overnight. The reaction mixture was reduced in vacuo and purified by flash column chromatography eluting with 0-10% CH$_3$OH in CHCl$_3$. Compound 1d was obtained as a yellow viscous liquid (0.50 g, 72%) from the fractions with R$_f$ = 0.30 (10% CH$_3$OH/CHCl$_3$). $^1$H NMR (300 MHz, CD$_3$OD) δ 2.10 (3H, s, CH$_3$), 2.22-2.40 (2H, m, 2'-H), 4.12 (1H, m, 5'-CH$^2$H), 4.32 (2H, m, 4'-H and 5'-CH$^2$H), 4.41 (1H, m, 3'-H), 7.10 (1H, d, J = 8.1 Hz, 6'-H), 7.80 (1H, d, J = 8.1 Hz, 5'-H); $^{13}$C NMR (75 MHz, CD$_3$OD) δ 17.0 (d, J = 6.0 Hz, OCH$_2$CH$_3$), 33.8 (d, J = 15.8 Hz, PCH$_2$), 41.1 (2'-CH$_2$), 64.8 (d, J = 6.8 Hz, OCH$_2$CH$_3$), 66.5 (5'-CH$_2$), 72.5 (3'-CH), 86.0 (1'-CH), 87.1 (4'-CH), 103.4 (5'-CH), 142.8 (6'-CH), 152.5 (2-C), 166.5 (4-C), 167.3 (d, J = 6.0 Hz, COO); $^{31}$P NMR (121 MHz, CD$_3$OD) δ 22.2; IR (film) 3428, 1709, 1691, 1678, 1279, 1024 cm$^{-1}$; MS (CI) m/z 424 ([M+NH$_4^+$], 60%), 407 ([M+H]$^+$, 100%); HRMS (ES$^+$) calcd for C$_{15}$H$_{24}$N$_2$O$_9$P$^+$ (M+H)$^+$ 407.1214, found 407.1222.
5.75 (1H, d, \(J = 8.1\) Hz, 5-H), 6.28 (1H, t, \(J = 6.6\) Hz, 1’-H), 7.75 (1H, d, \(J = 8.1\) Hz, 6-H); \(^{13}\)C NMR (75 MHz, CD\(_3\)OD) \(\delta\) 21.2 (CH\(_3\)), 41.2 (2’-CH\(_2\)), 65.5 (5’-CH\(_2\)), 72.6 (3’-CH), 86.2 (1’-CH), 87.3 (4’-CH), 103.3 (5-CH), 142.4 (6-CH), 152.5 (2-C), 166.5 (4-C), 172.8 (COO); IR (film) 3449, 1720, 1700, 1669 cm\(^{-1}\); MS (Cl) m/z 271 ([M+H]\(^{+}\), 50%), 288 ([M+NH\(_4\)]\(^{+}\), 100%); HRMS (ES\(^{+}\)) cale for \(\text{C}_{11}\text{H}_{13}\text{N}_{2}\text{O}_{5}\)\(^{+}\) (M+H)\(^{+}\) 271.0925, found 271.0927.

5’-O-Pentanoyl-2’-deoxyuridine (1e)
A procedure identical to the one used for 1d was employed. Compound 1e was obtained as pale orange/brown crystals (0.45 g, 68%) from 7 (0.90 g, 2.12 mmol). Flash column chromatography was carried out using 0→5% CH\(_3\)OH in CHCl\(_3\). \(R_f\) (10% CH\(_3\)OH/CHCl\(_3\)) 0.21; Mp 75-77ºC; \(^1\)H NMR (300 MHz, CD\(_3\)OD) \(\delta\) 0.90 (3H, t, \(J = 7.3\) Hz, CH\(_3\)), 1.25-1.37 (2H, m, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.50-1.60 (2H, m, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.13-2.35 (4H, m, 2’-H and CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 4.03 (1H, m, 5’-CH\(_2\)), 4.18-4.31 (3H, m, 5’-CH\(_2\)), 4.18-4.31 (3H, m, 5’-CH\(_2\)H, 4’-H and 3’-H), 5.66 (1H, d, \(J = 8.1\) Hz, 5-H), 6.18 (1H, t, \(J = 6.6\) Hz, 1’-H), 7.65 (1H, d, \(J = 8.1\) Hz, 6-H); \(^{13}\)C NMR (75 MHz, CD\(_3\)OD) \(\delta\) 14.5 (CH\(_3\)), 23.7 (CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 28.5 (CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 35.0 (CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 41.3 (2’-CH\(_2\)), 65.3 (5’-CH\(_2\)), 72.6 (3’-CH), 86.3 (1’-CH), 87.3 (4’-CH), 103.2 (5-CH), 142.4 (6-CH), 152.4 (2-C), 166.5 (4-C), 175.4 (COO); IR (KBr) 3386, 1736, 1707, 1667 cm\(^{-1}\); MS (El) m/z 312 (M\(^+\), 100%); MS (Cl) m/z 330 ([M+NH\(_4\)]\(^+\), 60%), 313 ([M+H]\(^{+}\), 40%). HRMS (ES\(^{+}\)) cale for \(\text{C}_{14}\text{H}_{21}\text{N}_{2}\text{O}_{6}\)\(^{+}\) (M+H)\(^{+}\) 313.1394, found 313.1394.

5’-O-Benzoyl-2’-deoxyuridine (1f)
Dowex\(^{®}\) WX-2-200 resin was added to a solution of the 3’-silylated precursor 3a (0.78g, 1.75 mmol) in CH\(_3\)OH (15 mL) and the suspension was stirred overnight at room temperature. The crude mixture was filtered, reduced \textit{in vacuo} and purified by flash column chromatography eluting with 10% CH\(_3\)OH in CHCl\(_3\). Compound 1f was obtained as a white solid (0.49 g, 80%) from the fractions with \(R_f = 0.20\) (10% CH\(_3\)OH/CHCl\(_3\)). Mp 158-160ºC; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 2.24 (2H, m, 2’-H), 4.08 (1H, dd, \(J = 4.1, 9.3\) Hz, 5’-CH\(_2\)), 4.38-4.56 (3H, m, 3’-H, 4’-H and 5’-CH\(_2\)), 5.55 (1H, d, \(J = 8.0\) Hz, 5-H), 6.20 (1H, t, \(J = 6.6\) Hz, 1’-H), 7.54 (2H, m, Ph-H), 7.68 (2H, m, 6-H and Ph-H), 7.99 (2H, d, \(J = 7.3\) Hz, Ph-H); \(^{13}\)C NMR (75 MHz,
DMSO-\textit{d}_6 \delta 39.1 (2'-CH\textsubscript{2}), 64.8 (5'-CH\textsubscript{2}), 70.4 (3’-CH), 84.1 (1’-CH), 84.7 (4’-CH), 102.3 (5-CH), 129.2 (Ph-CH), 129.6 (Ph-CH), 129.7 (Ph-C), 133.9 (Ph-CH), 140.9 (6-CH), 150.7 (2-C), 163.4 (4-C), 165.9 (COO); IR (KBr) 3377, 1722, 1667, 1632 cm\textsuperscript{-1}; MS (Cl) m/z 350 ([M+NH\textsubscript{4}]\textsuperscript{+}, 100%), 333 ([M+H]\textsuperscript{+}, 60%); HRMS (ES\textsuperscript{+}) calcd for C\textsubscript{16}H\textsubscript{20}N\textsubscript{3}O\textsubscript{6} (M+NH\textsubscript{4})\textsuperscript{+} 350.1347, found 350.1352.

\textbf{5’-O-Tosyl-2’-deoxyuridine (1g)}

Tosyl chloride (4.60 g, 24.12 mmol) was added portion-wise to an ice-cold solution of 2’-deoxyuridine (5.00 g, 21.93 mmol) in dry pyridine/DCM (1:1) (50 mL). The reaction mixture was stirred at 0\degree C for 1h and then kept at 4\degree C for another 23h. The solvent was removed \textit{in vacuo} and the crude syrup was repetitively washed with Et\textsubscript{2}O (5 x 50 mL) and H\textsubscript{2}O (5 x 100 mL). The residue was dissolved in CHCl\textsubscript{3} (100 mL) and petroleum ether (35-60\degree C) was slowly added under stirring. The product precipitated out as a white solid which was collected by filtration and chromatographed on a silica gel column eluting with 0\rightarrow 10% CH\textsubscript{3}OH in CHCl\textsubscript{3}. Compound 1g was obtained as a white solid (5.32 g, 64%) from the fractions with \textit{Rf} = 0.24 (10% CH\textsubscript{3}OH/CHCl\textsubscript{3}). Mp 155-156\degree C (lit\textsuperscript{1} 163-164\degree C); \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6) \delta 2.03-2.16 (2H, m, 2’-H), 2.40 (3H, s, CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{4}), 3.85 (1H, m, 4’-H), 4.12-4.26 (3H, m, 5’-H and 3’-H), 5.58 (1H, d, \textit{J} = 8.1 Hz, 5-H), 6.10 (1H, t, \textit{J} = 6.8 Hz, 1’-H), 7.46 (3H, m, 6-H and Ph-H), 7.80 (2H, m, Ph-H); \textsuperscript{13}C NMR (75 MHz, DMSO-\textit{d}_6) \delta 21.5 (CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{4}), 38.7 (2’-CH\textsubscript{2}), 70.2 (5’-CH\textsubscript{2}), 70.4 (3’-CH), 83.6 (1’-CH), 84.7 (4’-CH), 102.4 (5-CH), 128.0 (Ar-CH), 130.6 (Ar-CH), 132.4 (Ar-C), 140.9 (6-CH), 145.9 (Ar-C), 150.7 (2-C), 163.35 (4-C); IR (KBr) 3376, 3063, 1726, 1694, 1381, 1181 cm\textsuperscript{-1}; Anal. (C\textsubscript{16}H\textsubscript{19}O\textsubscript{7}N\textsubscript{2}S) C, H, N, S.

\textbf{5’-O-Sulfamoyl-2’-deoxyuridine (1h)}

A catalytic amount of bis(acetonitrile)dichloropalladium (II) and 1M HCl (2 mL) were added to a solution of 3e (0.49 g, 1.16 mmol) in acetone (10 mL). After stirring the mixture overnight at room temperature the solvent was reduced \textit{in vacuo} and the crude was purified by flash column chromatography eluting with 5\rightarrow 10% CH\textsubscript{3}OH/CHCl\textsubscript{3}. Compound 1h was obtained as a white solid (0.32 g, 90%) from the fractions with \textit{Rf} = 0.34 (20% CH\textsubscript{3}OH/CHCl\textsubscript{3}). Mp 68-70\degree C; \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}OD) \delta 2.15-2.37 (2H, m, 2’-H), 4.14-4.18 (1H, m, 3’-H), 4.26-4.37 (2H, m, 4’-H and 5’-CH\textsubscript{2}H), 4.43-4.47 (1H, m, 5’-CH\textsubscript{2}H), 5.74 (1H, d, \textit{J} = 8.1 Hz, 5-H), 6.28-6.35
(1H, t, J = 6.8 Hz, 1'-CH), 7.77 (1H, d, J = 8.1 Hz, 6-H); 13C NMR (75 MHz, CD3OD) δ 41.3 (2'-CH2), 70.2 (5'-CH2), 72.7 (3'-CH), 86.3 (1'-CH), 87.2 (4'-CH), 103.4 (5'-CH), 142.4 (6'-CH), 152.5 (2'-C), 166.6 (4'-C); IR (KBr) 3207, 1692, 1687, 1370, 1182 cm⁻¹; MS (CI) m/z 325 ([M+NH4]⁺, 100%), 308 ([M+H]⁺, 100%); HRMS (ES⁺) calc for C9H14N3O2S⁺ (M+H)⁺ 308.0547, found, 308.0554.

5'-O-Sulfamoylcarbamoyl-2'-deoxyuridine tetrabutylammonium salt (1i)

A procedure identical to the one used for 1d was employed. Compound 1i was obtained as white crystals (0.50 g, 66%) from the 3'-silylated precursor 3d (0.60 g, 1.29 mmol). Flash column chromatography was carried out using 5→15% CH3OH in CHCl3. Mp 58-60°C; 1H NMR (300 MHz, DMSO-d6) δ 0.94 (12H, t, J = 7.3 Hz, N⁺[(CH2)3]H4), 1.25-1.37 (8H, m, N⁺[(CH2)3]H4), 1.55 (8H, s, N⁺[(CH2)3]H4), 3.91-4.03 (2H, m, 2'-H), 3.14-3.37 (8H, m, N⁺[(CH2)3]H4), 3.91-4.03 (3H, m, 4'-H and 5'H), 4.22 (1H, m, 3'-H), 5.35 (1H, bs, 3'-OH), 5.63 (2H, d, J = 8.1 Hz, 5-H), 5.75 (2H, bs, NH2), 6.19 (1H, t, J = 7.0 Hz, 1'-H), 7.81 (1H, d, J = 8.1 Hz, 6-H); 13C NMR (75 MHz, DMSO-d6) δ 13.9 (N⁺[(CH2)3]H4), 19.6 (N⁺[(CH2)3]H4), 23.4 (N⁺[(CH2)3]H4), 39.4 (N⁺[(CH2)3]H4), 57.9 (2'-CH2), 64.2 (5'-CH2), 71.3 (3'-CH), 84.4 (1'-CH), 85.3 (4'-CH), 102.5 (5'-CH), 141.1 (6'-CH), 150.9 (2'-C), 163.5 (4'-C); IR (KBr) 1738, 1714, 1696, 1651, 1628, 1378, 1163 cm⁻¹; MS (ES⁺) m/z 349 ([M-H]⁻, 100%); MS (ES⁺) m/z 242 (N⁺[(CH2)3]H4, 100%); HRMS (ES⁺) calc for C16H13N4O8S⁺ (M+H)⁺ 349.0449, found 349.0459.

5'-O-Trityl-2'-deoxyuridine (1j)

2'-Deoxyuridine (1.00 g, 4.39 mmol) and trityl chloride (1.34 g, 4.83 mmol) were stirred in dry pyridine (20 mL) at 50°C overnight. The reaction mixture was poured into ice-H2O (100 mL) under vigorous stirring and then filtered. The precipitate was dissolved in EtOAc (100 mL) then the solution was washed with 0.5M HCl (100 mL) and H2O (100 mL), dried (Na2SO4) and reduced in vacuo. The residue was washed with toluene to leave the title compound 1j as a pale yellow solid (1.99 g, 97%). For analytical purposes, the compound was further purified by flash column chromatography eluting with 5→10% CH3OH in CHCl3. Rf (10% CH3OH/CHCl3) 0.49; 1H NMR (300 MHz, CDCl3) δ 2.34 (1H, m, 2'-CH2H), 2.45 (1H, m, 2'-CH2H), 3.51 (2H, m, 5'-H), 4.12 (1H, m, 4'-H), 4.64 (1H, m, 3'-H), 5.47 (1H, d, J = 8.1 Hz, 3'-H).
5'-H), 6.40 (1H, t, J = 6.3 Hz, 1'-H), 7.22-7.49 (15H, m, Ph-H), 7.86 (1H, d, J = 8.1 Hz, 6-H), 9.37 (1H, s, 3-NH); 13C NMR (75 MHz, CDCl3) δ 41.6 (2'-CH2), 63.5 (5'-CH2), 71.8 (3'-CH), 85.5 (4'-CH), 86.4 (1'-CH), 88.0 (Ph), 127.9 (Ph-CH), 128.7 (Ph-CH), 129.5 (Ph-CH), 140.7 (6-CH), 143.7 (Ph-C), 153.2 (2-C), 163.9 (4-C).

5'-O-Triisopropylsilyl-2'-deoxyuridine (1k)

Imidazole (0.183 g, 2.69 mmol) was added to a solution of 2'-deoxyuridine (0.272 g, 1.19 mmol) in dry DMF (5 mL). The mixture was cooled in an ice-salt bath before triisopropylsilyle chloride (0.28 mL, 1.31 mmol) was added dropwise via a syringe. The reaction mixture was kept at 0ºC for 3h and then stirred at room temperature for 22h. After addition of H2O (5 mL), the crude mixture was extracted with CHCl3 (2 x 10 mL). The combined organic layers were dried over MgSO4 and concentrated in vacuo. The crude oil was further purified by silica gel chromatography (ISOLUTE SI column) eluting with 0→10% CH3OH in CHCl3. The title compound 1k was obtained as a crystalline white solid (0.366 g, 74%) from the fractions with Rf = 0.25 (10% CH3OH in CHCl3). 1H NMR (300 MHz, CDCl3) δ 1.08 (21H, m, iPr-H), 2.18 (1H, m, 2'-CHH), 2.49 (1H, m, 2'-CHH), 3.97 (2H, m, 5'-H), 4.08 (1H, m, 4'-H), 4.56 (1H, m, 3'-H), 5.70 (1H, d, J = 8.1 Hz, 5-H), 6.38 (1H, t, J = 6.2 Hz, 1'-H), 7.96 (1H, d, J = 8.1 Hz, 6-H), 10.16 (1H, bs, 3-NH); 13C NMR (75 MHz, CDCl3) δ 12.7 (iPr-CH), 18.4 (iPr-CH3), 41.9 (2'-CH2), 63.8 (5'-CH2), 71.7 (3'-CH), 85.7 (1'-CH), 88.0 (4'-CH), 102.5 (5-CH), 140.9 (6-CH), 151.1 (2-C), 164.5 (4-C). MS (ES+) m/z 790 ([2M+Na]+, 10%), 407 ([M+Na]+, 100%); HRMS (ES+) calcd for C18H32N2O5SiNa+ (M+Na)+ 407.1973, found 407.1988; Mp 152-153ºC; Anal. (C18H32N2O5Si) C, H, N.

5'-O-tert-Butyldiphenylsilyl-2'-deoxyuridine (1l)

A solution of tert-butyldiphenylsilyl chloride (0.710 g, 2.58 mmol) and imidazole (0.342 g, 5.69 mmol) in dry DMF (4 mL) was added dropwise at 0ºC to a cooled solution of 2'-deoxyuridine (0.530 g, 2.32 mmol) in dry DMF (5 mL). The reaction mixture was stirred at 0ºC for 2h and then at room temperature for 15h. The reaction was quenched by addition of H2O (15 mL). The crude mixture was extracted with CHCl3 (2 x 15 mL). The combined organic layers were dried over MgSO4 and concentrated in vacuo. The crude oil was chromatographed on a silica gel column (ISOLUTE SI) eluted with a gradient of 0→10% CH3OH in CHCl3. Compound 1l
was obtained as a white crystalline solid (0.823 g, 76%) from the fractions with \( R_f = 0.26 \) (10% \( \text{CH}_3\text{OH/CHCl}_3 \)). Mp 75-78°C; \(^1\text{H} \) NMR (300 MHz, CDCl\(_3\)) \( \delta 1.14 \) [9H, m, C(CH\(_3\))\(_3\)], 2.27 (1H, m, 2'-CH\(_2\H_2\)), 2.50 (1H, m, 2'-CH\(_2\H_2\)), 2.69 (1H, bs, 3'-OH), 2.90 (1H, m, 4'-H), 4.05 (2H, m, 5'-H), 4.60 (1H, m, 3'-H), 5.52 (1H, d, \( J = 8.1 \) Hz, 5'-H), 6.41 (1H, t, \( J = 6.4 \) Hz, 1'-H), 7.48 (6H, m, Ph-H), 7.70 (4H, m, Ph-H), 7.87 (1H, d, \( J = 8.1 \) Hz, 6-H), 9.34 (1H, bs, 3'-NH); \(^13\text{C} \) NMR (75 MHz, CDCl\(_3\)) \( \delta 19.7 \) [C(CH\(_3\))\(_3\)], 27.4 [C(CH\(_3\))\(_3\)], 41.7 (2'-CH\(_2\)), 64.1 (5'-CH\(_2\)), 71.9 (3'-CH), 85.4 (1'-CH), 87.5 (4'-CH), 102.6 (5'-CH), 128.4 (Ph-CH), 128.5 (Ph-CH), 130.6 (Ph-CH), 132.7 (Ph-C), 133.1 (Ph-C), 135.8 (Ph-C), 136.0 (Ph-CH), 140.5 (6-CH), 150.9 (2-C), 163.9 (4-C); MS (ES\(^+\)) m/z 489 ([M+Na\(^+\)], 100%); HRMS (ES\(^+\)) calcd for C\(_{25}\)H\(_{34}\)N\(_3\)O\(_5\)Si (M+Na\(^+\)) 484.2259, found 484.2262; Anal. (C\(_{25}\)H\(_{30}\)N\(_2\)O\(_5\)Si, 0.30 HCl, 0.20 H\(_2\)O) C, H, N, Cl.

**5'-Diethylphosphonoacetylamino-2',5'-dideoxyuridine (2b)**

A solution of EDCI (2.15 g, 11.23 mmol) in dry DMF (40 mL) was added dropwise to a solution of 5'-amino-2',5'-dideoxyuridine \( 2k \) (1.50 g, 6.61 mmol) and diethylphosphonoacetic acid (1.94 g, 9.91 mmol) in dry DMF (40 mL). The mixture was stirred at room temperature overnight. The solvent was removed \( \text{in vacuo} \) and the crude product purified by flash column chromatography eluting with 5% \( \text{CH}_3\text{OH} \) in CHCl\(_3\). Compound \( 2b \) was obtained as a white hygroscopic solid (1.50 g, 56%) from the fractions with \( R_f = 0.27 \) (15% \( \text{CH}_3\text{OH/CHCl}_3 \)). \(^1\text{H} \) NMR (300 MHz, CD\(_2\)OD) \( \delta 1.38 \) (6H, t, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 2.27 (2H, m, 2'-H), 2.95-3.03 (2H, d, \( J = 21.7 \) Hz, PC\(_{\text{H}_2}\)), 3.51 (2H, m, 5'-H), 3.94 (1H, m, 3'-H), 4.12-4.23 (4H, m, OCH\(_2\)CH\(_3\)), 4.30 (1H, m, 4'-H), 5.73 (1H, d, \( J = 8.1 \) Hz, 5'-H), 6.20 (1H, t, \( J = 6.9 \) Hz, 1'-H), 7.75 (1H, d, \( J = 8.1 \) Hz, 6-H); \(^13\text{C} \) NMR (75 MHz, CD\(_2\)OD) \( \delta 17.1 \) (d, \( J = 6.8 \) Hz, OCH\(_2\)CH\(_3\)), 36.0 (d, \( J = 134.3 \) Hz, PC\(_{\text{H}_2}\)), 40.6 (2'-CH\(_2\)), 43.0 (5'-CH\(_2\)), 64.5 (d, \( J = 6.8 \) Hz, OCH\(_2\)CH\(_3\)), 73.2 (3'-CH), 86.9 (1'-CH), 87.3 (4'-CH), 103.3 (5'-CH), 143.3 (6-CH), 152.5 (2-C), 161.8 (4-C), 167.6 (d, \( J = 6.0 \) Hz, CONH); \(^31\text{P} \) NMR (121 MHz, CD\(_2\)OD) \( \delta 24.2 \); IR (KBr) 3336, 1717, 1698, 1670, 1272, 1027 cm\(^{-1}\); MS (ES\(^+\)) m/z 428([M+Na\(^+\)], 10%); HRMS (ES\(^+\)) calcd for C\(_{18}\)H\(_{24}\)N\(_3\)O\(_8\)NaP\(^+\) (M+Na\(^+\)) 428.1193, found 428.1206.
5'-{(1-Adamantoyl)amino-2',5'-dideoxyuridine (2c)}
The amine 2k (0.232 g, 1.02 mmol) was taken in a mixture of dry pyridine (3 mL) and dry DMF (3 mL). 1-Adamantanecarbonyl chloride (0.230 g, 1.16 mmol) was added in one portion and the reaction mixture was stirred at room temperature for 26 h. After removal of the solvent in vacuo, the crude product was purified by flash column chromatography (ISOLUTE SI column) eluting with 0→20% CH$_3$OH in CHCl$_3$. The fractions with $R_f = 0.28$ (10% CH$_3$OH/CHCl$_3$) yielded compound 2c as a white crystalline solid (0.212 g, 53%). Mp 126-129ºC; $^1$H NMR (300 MHz, CD$_3$OD) $\delta$ 1.73-1.93 (12H, m, adamantyl-H), 2.08 (3H, s, adamantyl-H), 2.17-2.43 (2H, m, 2'-H), 3.51 (2H, t, $J = 5.7$ Hz, 5'-H), 4.01 (1H, m, 4'-H), 4.30 (1H, m, 3'-H), 5.77 (1H, d, $J = 8.1$ Hz, 5-H), 6.22 (1H, t, $J = 6.5$ Hz, 1'-H), 7.78 (1H, d, $J = 8.1$ Hz, 6-H); $^{13}$C NMR (75 MHz, CD$_3$OD) $\delta$ 30.0 (adamantyl-CH), 38.0 (adamantyl-CH$_2$), 40.6 (adamantyl-CH$_2$), 40.7 (2'-CH$_2$), 42.3 (adamantyl-C), 427 (5'-CH$_2$), 73.4 (3'-CH), 87.0 (1'-CH), 87.6 (4'-CH), 103.2 (5-CH), 143.0 (6-CH), 152.4 (2-C), 166.6 (4-C), 181.6 (CONH); MS (ES$^+\vert$) m/z 412 ([M+Na]$^+$, 62%); HRMS (ES$^+$) calcd for C$_{20}$H$_{27}$N$_3$O$_5$Na$^+$ (M+Na)$^+$ 412.1843, found 412.1856; Anal. (C$_{20}$H$_{27}$N$_3$O$_5$, 1.7 HCl) C, H, N, Cl.

5'-Acetylamino-2',5'-dideoxyuridine (2d)
A procedure identical to the one used for 2a was employed. Compound 2d was obtained as hygroscopic crystals (0.25 g, 52%) from the amine 2k (0.40 g, 1.76 mmol) and acetyl chloride (0.13 mL, 1.76 mmol). Flash column chromatography was carried out using 0→15% CH$_3$OH in CHCl$_3$. $R_f$ (15% CH$_3$OH/CHCl$_3$) 0.20; Mp 163-165ºC; $^1$H NMR (300 MHz, CD$_3$OD) $\delta$ 2.00 (3H, s, CH$_3$), 2.22-2.35 (2H, m, 2'-H), 3.48 (2H, m, 5'-H), 3.62-3.90 (1H, m, 4'-H), 4.27 (1H, m, 3'-H), 5.74 (1H, d, $J = 8.1$ Hz, 5-H), 6.20 (1H, t, $J = 6.8$ Hz, 1'-H), 7.72 (1H, d, $J = 8.1$ Hz, 6-H); $^{13}$C NMR (75 MHz, CD$_3$OD) $\delta$ 23.0 (CH$_3$), 40.6 (2'-CH$_2$), 42.9 (5'-CH$_2$), 73.4 (3'-CH), 87.0 (1'-CH), 87.6 (4'-CH), 103.3 (5-CH), 143.1 (6-CH), 152.5 (2-C), 166.6 (4-C), 174.1 (CONH); IR (KBr) 3297, 1726, 1664, 1644 cm$^{-1}$; MS (CI) m/z 287 ([M+NH$_4^+$]$^+$, 5%), 270 ([M+H]$^+$, 45%); HRMS (ES$^+$) calcd for C$_{11}$H$_{16}$N$_3$O$_5^+$ (M+H)$^+$ 270.1084, found 270.1088.

5'-Benzoylamino-2',5'-dideoxyuridine (2f)
A procedure identical to the one used for 2a (except for the solvent mixture) was employed. Compound 2f was obtained as a white solid (0.25 g, 34.2%) from the
amine 2k (0.50 g, 4.41 mmol) and benzoyl chloride (0.51 mL, 4.41 mmol) in dry DMF/pyridine (1:1) (20 mL). Flash column chromatography was carried out using 0→10% CH$_3$OH in CHCl$_3$. R$_f$ (8% CH$_3$OH/CHCl$_3$) 0.38; Mp 193-195ºC; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 2.14 (2H, m, 2'-H), 3.41-3.55 (2H, m, 5'-H), 3.92 (1H, m, 4'-H), 4.24 (1H, m, 5'-H), 5.36 (1H, d, $J$ = 4 Hz, CO$_2$NH), 5.61 (1H, d, $J$ = 8.1 Hz, 5-H), 6.13 (1H, t, $J$ = 6.9 Hz, 1'-H), 7.45-7.57 (3H, m, Ph-H), 7.74 (1H, d, $J$ = 8.1 Hz, 6-H), 7.86 (2H, m, Ph-H); $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 38.9 (2'-CH$_2$), 42.1 (5'-CH$_2$), 71.7 (3'-CH), 84.8 (1'-CH), 85.4 (4'-CH), 102.2 (5-CH), 127.6 (Ph-CH), 128.7 (Ph-CH), 131.6 (Ph-CH), 134.6 (Ph-C), 141.2 (6-CH), 150.8 (2-C), 163.4 (4-C), 166.9 (CONH); IR (KBr) 3408, 3336, 1726, 1666, 1632 cm$^{-1}$; MS (CI) m/z 349 ([M+NH$_4$]$^+$, 5%), 332 ([M+H]$^+$, 100%); HRMS (ES$^+$) calcd for C$_{16}$H$_{18}$O$_5$N$_3$+ (M+H)$^+$ 332.1241, found 332.1248.

5'-Tosylamino-2',5'-dideoxyuridine (2g)

A procedure identical to the one used for 2a (except for the reaction temperature) was employed. Compound 2g was obtained as a white solid (0.25 g, 37%) from the reaction of the amine 2k (0.40 g, 1.76 mmol) and tosyl chloride (0.34 g, 1.78 mmol) in DMF/pyridine (4:1) (20 mL) at 0-4ºC. Flash column chromatography was carried out using 0→10% CH$_3$OH in CHCl$_3$. R$_f$ (15% CH$_3$OH/CHCl$_3$) 0.52. Mp 166-168ºC; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 2.06-2.14 (2H, m, 2'-H), 2.35 (3H, s, CH$_3$C$_6$H$_4$), 2.85-2.97 (1H, m, 5'-CH$_2$H), 3.06-3.15 (1H, m, 5'-CH$_2$H), 3.65 (1H, m, 3'-H), 4.15 (1H, m, 4'-H), 5.44 (1H, d, $J$ = 4.2 Hz, SO$_2$NH), 5.57 (1H, d, $J$ = 8.1 Hz, 5-H), 6.05 (1H, t, $J$ = 6.9 Hz, 1'-H), 7.37 (2H, d, $J$ = 8.1 Hz, Ar-H), 7.59 (1H, d, $J$ = 8.1 Hz, 6-H), 7.66 (2H, d, $J$ = 8.1 Hz, Ar-H); $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 21.8 (CH$_3$C$_6$H$_4$), 38.7 (2'-CH$_2$), 45.0 (5'-CH$_2$), 71.2 (3'-CH), 84.7 (1'-CH), 85.2 (4'-CH), 102.2 (5-CH), 126.8 (Ar-CH), 130.0 (Ar-CH), 137.8 (Ar-C), 141.4 (6-CH), 143.2 (Ar-C), 150.7 (2-C), 163.6 (4-C); IR (KBr) 3354, 1727, 1676, 1328, 1158 cm$^{-1}$; MS (CI) m/z 399 ([M+NH$_4$]$^+$, 100%), 382 ([M+H]$^+$, 30%); HRMS (ES$^+$) calcd for C$_{16}$H$_{20}$O$_6$N$_3$S$^+$ (M+H)$^+$ 382.1067, found 382.1073.

5'-Methanesulfonylamino-2',5'-dideoxyuridine (2h)

A procedure identical to the one used for 2a (except for the reaction temperature) was employed. Compound 2h was obtained as a pale yellow solid (0.26 g, 51%) from the
reaction of the amine 2k (0.40 g, 1.76 mmol) and methanesulfonyl chloride (0.14 mL, 1.76 mmol) in DMF/pyridine (4:1) (20 mL) at 0-4°C. Flash column chromatography was carried out using 0→5% CH₃OH in CHCl₃. Rⱽ (8% CH₃OH/CHCl₃) 0.26; Mp 250°C (dec); ¹H NMR (300 MHz, DMSO-d₆) δ 2.09-2.14 (2H, m, 2'-H), 2.30 (1H, s, 3'-OH), 2.92 (3H, s, CH₃), 3.07-3.25 (2H, m, 5'-H), 3.77-3.81 (1H, m, 4'-H), 4.14-4.22 (1H, t, J = 6.9 Hz, 1'-H), 7.86 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, DMSO-d₆) δ 38.7 (2'-CH₂), 39.9 (CH₃), 44.9 (5'-CH₂), 71.2 (3'-CH), 84.6 (1'-CH), 85.2 (4'-CH), 141.3 (6-CH), 150.8 (2-C), 163.4 (4-C); IR (KBr) 3317, 1718, 1656, 1310, 1143 cm⁻¹; MS (CI) m/z 323 ([M+NH₄]⁺, 100%), 306 ([M+H]⁺, 60%); HRMS (ES⁺) calcd for C₁₀H₁₆O₅N₃S⁺ (M+H)⁺ 306.0754, found 306.0749.

5'-Benzylamino-2',5'-dideoxyuridine (2i)
The tosylate 1g (0.302 g, 0.79 mmol) and benzylamine (6 mL, 54.9 mmol) were heated at 40°C for 24h. Then the reaction mixture was co-evaporated with DMF (4 x 20 mL) and the crude product purified by ion exchange chromatography using a column of H⁺ resin Dowex 50WX8-200 eluted with 50% CH₃OH in H₂O and then with 2% NH₃ in H₂O. The fractions with Rⱽ = 0.37 (20% CH₃OH/CHCl₃) yielded compound 2i as a white crystalline solid (0.112 g, 45%). Mp 70-72°C; ¹H NMR (300 MHz, CD₃OD) δ 2.17-2.33 (2H, m, 2'-H), 4.00 (1H, m, 4'-H), 4.23 (1H, m, 3'-H), 5.66 (1H, d, J = 8.1 Hz, 5-H), 6.21 (1H, t, J = 6.6 Hz, 1'-H), 7.20-7.41 (5H, m, Ph-H), 7.63 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, CD₂OD) δ 40.4 (2'-CH₂), 52.1 (5'-CH₂ or CH₂Ph), 54.8 (5'-CH₂ or CH₂Ph), 73.8 (3'-CH), 87.1 (1' or 4'-CH), 87.3 (4' or 1'-CH), 103.3 (5-CH), 128.8 (Ph-CH), 129.99 (Ph-CH), 130.04 (Ph-CH), 143.0 (6-CH), 152.5 (2-C), 166.6 (4-C); MS (ES⁺) m/z 340 ([M+Na]⁺, 5%), 318 ([M+H]⁺, 100%); HRMS (ES⁺) calcd for C₁₆H₂₀N₅O₄⁺ (M+H)⁺ 318.1448, found 318.1465.

5'-Amino-2',5'-dideoxyuridine (2k)
The azide 9 (6.00 g, 23.72 mmol) was taken in EtOH/H₂O (1:1) (150 mL) and hydrogenated in the presence of 5% Pd/C at room temperature for 6h. The reaction mixture was filtered through a Celite pad and reduced in vacuo. The crude product was washed with CHCl₃ and Et₂O to yield compound 2k as a pale yellow solid (4.98

S11
g, 53%). R<sub>f</sub> (30% CH<sub>3</sub>OH, 10% Et<sub>3</sub>N in CHCl<sub>3</sub>) 0.17; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O) δ 2.17 (2H, t, J = 6.8 Hz, 2'-H), 2.67 (2H, m, 5'-H), 3.78 (1H, m, 4'-H), 4.17 (1H, m, 3'-H), 5.62 (1H, d, J = 7.9 Hz, 5-H), 6.02 (1H, t, J = 6.8 Hz, 1'-H), 7.40 (1H, d, J = 7.9 Hz, 6-H); <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O) δ 38.4 (2'-CH<sub>2</sub>), 42.7 (5'-CH<sub>2</sub>), 71.8 (3'-CH), 85.9 (4'-CH or 1'-CH), 86.3 (1'-CH or 4'-CH), 102.8 (5-CH), 141.8 (6-CH), 155.3 (2-C), 171.4 (4-C); MS (Cl) m/z 228 ([M+H]<sup>+</sup>, 80%); HRMS (ES<sup>+</sup>) calcld for C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>N<sub>3</sub> <sup>+</sup>(M+H)<sup>+</sup> 228.0979, found 228.0987.

3'-O-tert-Butyldimethylsilyl-2' deoxyuridine 5'-diphenylphosphate (3a)

Chlorodiphenylphosphate (1.23 g, 4.60 mmol) was added dropwise to a solution of compound 3f (1.43 g, 4.18 mmol) in dry pyridine (50 mL) and the reaction was stirred overnight at room temperature. The reaction mixture was diluted with CHCl<sub>3</sub> (200 mL) and washed with H<sub>2</sub>O (2 x 100 mL), saturated aqueous NaHCO<sub>3</sub> (2 x 100 mL) and again with H<sub>2</sub>O (2 x 100 mL). The CHCl<sub>3</sub> layer was dried over Na<sub>2</sub>SO<sub>4</sub> and reduced in vacuo. Further purification was carried out by flash column chromatography, eluting with 5% CH<sub>3</sub>OH in CHCl<sub>3</sub>. Compound 3a was obtained as a brown gum (2.25 g, 94%) from the fractions with R<sub>f</sub> = 0.39 (10% CH<sub>3</sub>OH/CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.11 [6H, s, Si(CH<sub>3</sub>)<sub>2</sub>], 0.93 [9H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.96 (1H, m, 2'-CHH), 2.30 (1H, m, 2'-CHH), 4.11 (1H, m, 5'-CHH), 4.40 (2H, m, 4'-H, 5'-CHH), 4.54 (1H, m, 3'-H), 5.58 (1H, d, J = 8.2 Hz, 5-H), 6.32 (1H, t, J = 6.7 Hz, 1-H), 7.24-7.40 (11H, m, 6-H and Ph-H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ -4.5 (SiCH<sub>3</sub>), -4.3 (SiCH<sub>3</sub>), 18.3 (C(CH<sub>3</sub>)<sub>3</sub>), 26.1 (C(CH<sub>3</sub>)<sub>3</sub>), 41.3 (2'-CH<sub>2</sub>), 67.9 (d, J = 6.5 Hz, 5'-CH<sub>2</sub>), 71.8 (3'-CH), 85.5 (1'-CH), 85.6 (d, J = 8.0 Hz, 4'-CH), 103.1 (5-CH), 120.27, 120.31, 120.34, 120.38 and 120.45 (Ph-CH), 126.2 (Ph-CH), 130.38 and 130.44 (Ph-CH), 139.9 (6-CH), 150.7 (d, J = 7.5 Hz, Ph-C), 150.9 (2-C), 160.3, 164.1 (4-C); <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ -10.6; Anal. (C<sub>27</sub>H<sub>35</sub>O<sub>6</sub>N<sub>3</sub>SiP) C, H, N.

3'-O-tert-Butyldimethylsilyl-2' deoxyuridine 5'-diethylphosphate (3b)

A procedure identical to the one used for 3a was employed. Compound 3b was obtained as a brownish viscous oil (0.77 g, 69%) from the reaction of 3f (0.80 g, 2.33 mmol) with diethylchlorophosphate (0.37 mL, 2.57 mmol). Flash column chromatography was carried out using 0→5% CH<sub>3</sub>OH in CHCl<sub>3</sub>. R<sub>f</sub> (5% CH<sub>3</sub>OH/CHCl<sub>3</sub>) 0.42; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.15 [6H, s, Si(CH<sub>3</sub>)<sub>2</sub>], 0.98 [9H,
A solution of EDCI (0.95 g, 4.97 mmol) in dry DMF (20 mL) was added dropwise to a solution of 3f (1.00 g, 2.92 mmol) and diethylphosphonoacetic acid (0.86 g, 4.39 mmol) in DMF (20 mL). The reaction mixture was stirred at room temperature overnight. H₂O (20 mL) was added and the resulting mixture was extracted with CHCl₃ (2 x 60 mL). The organic layers were washed with H₂O, dried over Na₂SO₄ and reduced in vacuo. Further purification was carried out by flash column chromatography eluting with 0→5% CH₃OH in CHCl₃. The fractions with Rf = 0.42 (10% CH₃OH/CHCl₃) yielded compound 3c as pale yellow viscous liquid (1.17 g, 77%). ¹H NMR (300 MHz, CDCl₃) δ 0.13 [6H, s, Si(CH₃)₂], 0.94 [9H, s, C(CH₂)₃], 1.39 (6H, m, OCH₂CH₂), 2.20-2.37 (2H, m, 2'-H), 2.94-3.01 (2H, d, J = 22.1 Hz, PCH₃), 4.10 (1H, m, 4'-H), 4.16-4.26 (4H, m, OCH₂CH₂), 4.32 (1H, m, 5'-CHH), 4.44 (2H, m, 5'-CHH and 3'-CH), 5.84 (1H, d, J = 8.1 Hz, 5-H), 6.33 (1H, t, J = 6.6 Hz, 1'-H), 7.73 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, CDCl₃) δ −4.5 (Si(CH₃)₂), −4.3 (Si(CH₃)₂), 16.8 (d, J = 60.0 Hz, OCH₂CH₂), 18.3 [C(CH₃)₃], 26.1 [C(CH₂)₃], 34.8 (d, J = 133.5 Hz, PCH₃), 41.2 (2'-CH₂), 63.4 (d, J = 67.5 Hz, OCH₂CH₂), 64.6 (5'-CH₂), 71.8 (3'-CH), 84.9 (1'-CH), 85.3 (4'-CH), 103.2 (5-CH), 140.8 (6-CH), 150.6 (2-C), 163.5 (COO), 165.9 (4-C); ³¹P NMR (121 MHz, CDCl₃) δ 20.2; IR (film) 1676, 1253, 1020 cm⁻¹; MS (ES⁺) m/z 543 ([M+Na]⁺, 100%); HRMS (ES⁺) calcd for C₁₉H₁₈N₂O₃PSi⁺ (M+H)⁺ 543.1897, found 543.1897.

3'-O-tert-Butyldimethylsilyl-5'-O-sulfamoylcarbamoyl-2'-deoxyuridine (3d)
A solution of 3f (5.00 g, 14.62 mmol) in CH₃CN (100 mL) was reacted with chlorosulfonylisocyanate (1.40 mL, 16.08 mmol) at -20°C for 2h. The mixture was
then treated at -20°C with a saturated solution of NH₃ in CH₂CN added dropwise until the solution had reached pH 11. The reaction mixture was allowed to warm up and was to and was stirred at room temperature for 2h. Compound 3d precipitated out, and after filtration and drying was obtained as a white solid (4.80 g, 74%). Rᵣ (20% CH₃OH/CHCl₃) 0.42; Mp: 130-132°C; ¹H NMR (300 MHz, CD₂OD) 0.13 [6H, s, Si(CH₃)₂], 0.92 [9H, s, C(CH₃)₃], 2.08-2.15 (1H, m, 2’-CHH), 2.24-2.33 (1H, m, 2’-CHH), 3.96 (1H, m, 4’-H), 4.03-4.12 (2H, m, 5’-H), 4.43 (1H, m, 3’-H), 5.68 (1H, d, J = 8.1 Hz, 5-H), 6.21 (1H, t, J = 6.9 Hz, 1’-H), 7.79 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, CD₂OD) –4.6 (SiCH₃), –4.5 (SiCH₃), 18.0 [C(CH₃)₃], 26.0 [C(CH₃)₃], 39.6 (2’-CH₂), 64.1 (5’-CH₂), 72.7 (3’-CH), 84.3 (1’-CH), 85.1 (4’-CH), 102.5 (5-CH), 141.1 (6-CH), 150.4 (2-C), 163.4 (4-C); IR (KBr) 1736, 1717, 1696, 1673 1620, 1163, 1556, 1388 cm⁻¹; MS (Cl) m/z 482 ([M+NH₄]⁺, 80%), 465 ([M+H]⁺, 40%); HRMS (ES⁺) calcd for C₁₆H₂₉N₄O₈SSi⁺ (M+H)⁺ 465.1470, found 465.1479.

3’-O-tert-Butyldimethylsilyl-2’-deoxyuridine (3f)

Diethylaluminium chloride (Et₂AlCl 1.8 M in hexanes) (10.60 mL, 18.12 mmol) was added dropwise to a stirred solution of 3g (3.72 g, 6.36 mmol) in CHCl₃ (100 mL). After 45 min further Et₂AlCl (3.72 mL, 6.36 mmol) was added dropwise. After 10 min, saturated aqueous NaHCO₃ (30 mL) was slowly added and the mixture was left to stand for 1h. The layers were separated and the aqueous phase was extracted with CHCl₃ (100 mL). The combined organic phases were dried over Na₂SO₄ and reduced in vacuo. A short silica column eluting with 0 5% CH₃OH in CHCl₃ afforded 3e as a white solid (1.59g, 73%). Rᵣ (5% CH₃OH/CHCl₃) 0.13; ¹H NMR (300 MHz, CDCl₃) δ 0.20 [6H, s, Si(CH₃)₂], 1.02 [9H, s, C(CH₃)₃], 2.40 (2H, m, 2’-H), 3.87 (1H, dd, J = 3.3, 12.5 Hz, 5’CHH), 4.04 (2H, m, 4’-H and 5’-CHH), 4.60 (1H, dd, J = 5.1, 8.8 Hz, 3’-H), 5.85 (1H, d, J = 8.1 Hz, 5-H), 6.30 (1H, t, J = 6.6 Hz, 1’-H), 7.79 (1H, d, J = 8.1 Hz, 6-H), 9.37 (1H, s, 3-NH) ; ¹³C NMR (75MHz, CDCl₃) δ -4.5 (SiCH₃), -4.3 (SiCH₃), 18.4 [C(CH₃)₃], 26.1 [C(CH₃)₃], 41.3 (2’-CH₂), 62.2 (5’-CH₂), 71.8 (3’-CH), 87.1 (4’-CH), 88.1 (1’-CH), 102.8 (5-CH), 141.6 (6-CH), 150.7 (2-C), 164.0 (4-C); MS (APCI) m/z 342 (M⁺, 50%).
3’-O-tert-Butyldimethylsilyl-5’-O-trityl-2’-deoxyuridine (3g)

Compound 1j (0.70 g, 1.49 mmol) in dry DMF (3 mL) was added dropwise to a stirred solution of tert-butyldimethylsilyl chloride (0.25 g, 1.65 mmol) and imidazole (0.22 g, 3.28 mmol) in dry DMF (3 mL), cooled at 0°C. The reaction mixture was allowed to warm up and stirred overnight at room temperature. H2O (10 mL) was added and the mixture was extracted with Et2O (2 x 50 mL). The combined organic extracts were washed with saturated NaHCO3 (50 mL) and H2O (50 mL), dried over Na2SO4 and reduced in vacuo. A flash silica column eluting with 3% CH3OH in CHCl3 afforded compound 3f as white foam (0.65 g, 74%). Rf (3% CH3OH/CHCl3) 0.33; 1H NMR (300 MHz, CDCl3) δ -0.05 (3H, s, SiCH3), 0.00 (3H, s, SiCH3), 0.85 [9H, s, C(CH3)3], 2.12-2.20 (1H, m, 2’-CH), 2.31-2.39 (1H, m, 2’-CH), 3.33 (1H, dd, J = 2.8, 10.7 Hz, 5’-CH), 3.46 (1H, dd, J = 2.8, 10.7 Hz, 5’-CH), 3.92 (1H, dt, J = 2.8, 4.4 Hz, 4’-H), 4.51 (1H, dd, J = 2.8, 10.7 Hz, 3’-H), 5.34 (1H, d, J = 8.1 Hz, 5-H), 6.26 (1H, t, J = 6.0 Hz, 1’-H), 7.23-7.39 (15H, m, Ph-H), 7.85 (1H, d, J = 8.1 Hz, 6-H), 9.11 (1H, s, 3-NH) ; 13C NMR (75MHz, CDCl3) 4.5 (SiCH3), 4.2 (SiCH3), 18.4 [C(CH3)3], 6.17 [C(CH3)3], 42.2 (2’-CH2), 62.3 (5’-CH2), 71.4 (3’-CH), 85.6 (4’-CH) 86.8 (1’-CH), 87.9 (Ph3C), 102.7 (5-CH), 127.9 (Ph-CH), 128.5 (Ph-CH), 129.2 (Ph-CH), 140.6 (6-CH), 143.6 (Ph-C), 150.7 (2-C), 163.8 (4-C); MS (APCI) m/z 607 ([M+Na]+, 100%),341 (M-PhC+, 75%), 243 (PhC+, 50%).

3’-O-tert-Butyldimethylsilyl-5’-tritylamino-2’,5’-dideoxyuridine (3h)

A solution of compound 2j (0.172 g, 0.37 mmol) in dry DMF (2 mL) was added dropwise to an ice cold solution of tert-butyldimethylsilyl chloride (68 mg, 0.45 mmol) and imidazole (60 mg, 0.88 mmol) in dry DMF (2 mL). The reaction mixture was stirred at 0°C for 2h and at room temperature for a further 20h. It was then partitioned between H2O (10 mL) and Et2O (2 x 20 mL). The combined organic layers were washed with a saturated aqueous solution of NaHCO3 (15 mL), dried over MgSO4 and concentrated in vacuo. The white solid obtained was further purified by flash column chromatography (ISOLUTE SI column) eluting with 0→10% CH3OH in CHCl3. The fractions with Rf = 0.69 (10% CH3OH/CHCl3) yielded compound 3h as a white solid (0.154 g, 72%). Mp 98-101°C; 1H NMR (300 MHz, CDCl3) δ 0.00-0.02 [6H, 2 x s, Si(CH3)2], 0.86 [9H, s, C(CH3)3], 1.90 (2H, m, 2’-H), 2.11-2.35 (2H, m, 5’-H), 2.59 (1H, bd, J = 13 Hz, Ph3CNH), 4.06 (2H, m, 3’-H and 4’-H), 5.65 (1H, d, J
from the reaction of 3' after flash chromatography (0 → 2% CH₃OH in CHCl₃) as a white solid (0.30 g, 77%) from the reaction of 3'-fluoro-2',3'-dideoxyuridine (0.30 g, 1.43 mmol) in dry DMF (5 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of H₂O (10 mL). The crude mixture was extracted with CHCl₃ (2 x 30 mL). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude oil was chromatographed on a silica gel column eluted with a gradient of 0 → 6% CH₃OH in CHCl₃. Compound 4a was obtained as white crystals (0.25 g, 82%) from the fractions with R f = 0.65 (10% CH₃OH/CHCl₃). Mp 112-115°C; ³¹P NMR (300 MHz, CDCl₃) δ 0.20 [6H, s, Si(CH₃)₂], 0.10 [9H, s, C(CH₃)₃], 2.04-2.14 (1H, m, 2'-CHH), 2.70-2.83 (1H, m, 2'-CHH), 3.92-4.03 (2H, m, 5'-H), 4.40-4.49 (1H, d, J = 27.0 Hz, 4'-H), 5.18-5.38 (1H, dd, J = 4.7, 53.7 Hz, 3'-H), 5.81 (1H, d, J = 8.1 Hz, 5'-CH), 6.50-6.55 (1H, m, 1'-H), 7.94 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, CDCl₃) δ -5.2 (SiCH₃), -5.1 (SiCH₃), 18.7 [C(CH₃)₃], 26.2 [C(CH₂)₃], 39.9 (d, J = 21.0 Hz, 2'-CH₂), 63.9 (d, J = 11.3 Hz, 5'-CH₂), 85.7 (d, J = 2.8 Hz, 4'-CH), 88.1 (1'-CH), 95.0 (o, J = 176.3 Hz, 5'-CH), 103.1 (5'-CH), 140.2 (6'-CH), 146.6 (2'-CH), 163.8 (4'-C); ¹⁹F NMR (282 MHz, CDCl₃) δ -175.6 (m, 3'-F); IR (KBr) 1705, 1689, 1126 cm⁻¹; MS (Cl) m/z 362 ([M+NH₄]^⁺, 30%), 345 ([M+H]^⁺, 100%); HRMS (ES⁺) calcd for C₁₃H₂₆N₂O₄SiF⁺ (M+H)^⁺ 345.1640, found 345.1648.

5'-O-Trityl-2',3'-dideoxy-3'-fluorouridine (4e)

A procedure similar to the one used for 1j was employed. Compound 4e was obtained after flash chromatography (0 → 2% CH₃OH in CHCl₃) as a white solid (0.48 g, 77%) from the reaction of 3'-fluoro-2',3'-dideoxyuridine (0.30 g, 1.30 mmol) with trityl...
chloride (0.44 g, 1.57 mmol) in dry pyridine (20 mL). R<sub>f</sub> (10% CH<sub>3</sub>OH/CHCl<sub>3</sub>) 0.52; Mp 128-130°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.27-2.50 (1H, m, 2'-CH<sub>f</sub>H), 2.78-2.92 (1H, m, 2'-CH<sub>f</sub>H), 3.53-3.63 (2H, m, 5'-H), 4.41-4.51 (1H, d, J = 27.3 Hz, 4'-H), 5.33-5.53 (2H, m, 3'-H and 5'-H), 6.50-6.55 (1H, m, 1'-H), 7.46 (15H, m, Ph-H), 7.80 (1H, d, J = 8.1 Hz, 6-H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 39.6 (d, J = 21.0 Hz, 2'-CH<sub>f</sub>), 63.8 (d, J = 10.5 Hz, 5'-CH<sub>f</sub>), 84.7 (d, J = 25.5 Hz, 4'-CH), 85.4 (1'-CH), 88.3 (Ph<sub>3</sub>C), 94.6 (d, J = 177.0 Hz, 3'-CH), 103.1 (5-CH), 128.1 (Ph-CH), 128.6 (Ph-CH), 129.0 (Ph-CH), 140.2 (6-CH), 143.3 (Ph-C), 150.7 (2-C), 163.5 (4-C); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -174.3 (m, 3'-F); IR (KBr) 1732, 1702, 1689, 1108 cm<sup>-1</sup>; MS (Cl) m/z 490 ([M+NH<sub>4</sub>]<sup>+</sup>, 80%), 473 ([M+H]<sup>+</sup>, 50%); HRMS (EI<sup>+</sup>) calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>F<sup>+</sup> (M<sup>+</sup>) 472.1738, found 472.1797.

5'-O-Palmitoyl-2',3'-dideoxy-2',3'-dideoxyuridine (5c)
A procedure identical to the one used for 3a was employed. Compound 5c was obtained as a white solid (0.59 g, 44%) from the reaction of 5i (0.30 g, 1.43 mmol) with palmitoyl chloride (0.48 mL, 1.57 mmol). Flash column chromatography was carried out using 0→3% CH<sub>3</sub>OH in CHCl<sub>3</sub>. R<sub>f</sub> (7% CH<sub>3</sub>OH/CHCl<sub>3</sub>) 0.48; Mp 121-123°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.93 (3H, t, J = 0.9 Hz, palmitoyl-H), 1.30 (24H, s, palmitoyl-H), 1.65 (2H, m, palmitoyl-H), 2.35 (2H, t, J = 7.5 Hz, palmitoyl-H), 4.28 (1H, dd, J = 3.7, 12.4 Hz, 5'-CH<sub>f</sub>H), 4.43 (1H, J = 3.7, 12.4 Hz, 5'-CH<sub>f</sub>H), 5.12 (1H, m, 4'-H), 5.78 (1H, d, J = 8.1 Hz, 5-H), 5.97 (1H, m, 1'-H), 6.34 (1H, m, 2'-H), 7.06 (1H, m, 3'-H), 7.55 (1H, d, J = 8.1 Hz, 6-H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ 14.6 (palmitoyl-CH<sub>3</sub>), 23.1 (palmitoyl-CH<sub>2</sub>), 25.3 (palmitoyl-CH<sub>2</sub>), 29.6 (palmitoyl-CH<sub>2</sub>), 29.7 (palmitoyl-CH<sub>2</sub>), 29.8 (palmitoyl-CH<sub>2</sub>), 29.9 (palmitoyl-CH<sub>2</sub>), 30.0 (palmitoyl-CH<sub>2</sub>), 30.1 (palmitoyl-CH<sub>2</sub>), 30.1 (palmitoyl-CH<sub>2</sub>), 32.4 (palmitoyl-CH<sub>2</sub>), 34.5 (palmitoyl-CH<sub>2</sub>), 64.8 (5'-CH<sub>f</sub>), 85.0 (1'-CH), 90.4 (4'-CH), 103.0 (5-CH), 127.5 (2'-CH), 133.9 (3'-CH), 140.4 (6-CH), 151.1 (2-C), 163.6 (4-C), 173.7 (COO); IR (KBr) 1732, 1702, 1698 cm<sup>-1</sup>; MS (ES<sup>+</sup>) m/z 471 ([M+Na]<sup>+</sup>, 100%); HRMS (ES<sup>+</sup>) calcd for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>O<sub>5</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 471.2829, found 471.2838.

5'-O-Sulfamoyl-2',3'-dideoxy-2',3'-dideoxyuridine (5e)
A procedure identical to the one used for 3e was employed. Compound 5e was obtained as a pale yellow hygroscopic solid (0.52 g, 76%) from the reaction of 5i (0.50 g, 2.38 mmol) with sulfamoyl chloride (0.55 g, 4.76 mmol). Flash column
chromatography was carried out using 5→12% CH₃OH in CHCl₃. R_f (15% CH₃OH/CHCl₃) 0.42; ¹H NMR (300 MHz, CD₃OD) δ 4.32 (2H, m, 5'-H), 5.03 (1H, m, 4'-H), 5.85 (1H, d, J = 8.1 Hz, 5-H), 6.05 (1H, m, 1'-H), 6.15 (1H, m, 2'-H), 7.02 (1H, m, 3'-H), 7.76 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, CD₃OD) δ 70.6 (5'-CH₃), 86.0 (4'-CH), 91.6 (1'-CH), 103.4 (5-CH), 128.2 (2'-CH), 135.3 (3'-CH), 143.3 (6-CH), 153.1 (2-C), 161.4 (4-C); IR (film) 1702, 1692, 1621, 1373, 1150 cm⁻¹; MS (ES⁺) m/z 326 ([M+37Cl⁺, 20%), 324 ([M+35Cl⁺, 60%), 288 ([M-H⁻, 100%); HRMS (ES⁺) calcd for C₁₉H₁₅N₄O₆S⁺ (M+NH₄)⁺ 307.0707, found 307.0714.

5'-O-tert-Butyldimethylsilanyl-2',3'-didehydro-2',3'-dideoxyuridine (5f)

Compound 14 (6.19 g, 15.48 mmol) was suspended in trimethyl phosphite (50 mL) under nitrogen. The reaction mixture was heated at 118ºC for 5h after which it was reduced in vacuo. The crude product was then suspended in n-hexane, filtered and washed with n-hexane. Further purification by flash column chromatography eluting with 0→5% CH₃OH in CHCl₃ afforded compound 5f as a white solid (4.16 g, 84%). R_f (5% CH₃OH/CHCl₃) 0.26; Mp 156-159ºC (lit.² 158-159ºC); ¹H NMR (300 MHz, DMSO-d₆) δ 0.12 [6H, s, Si(CH₃)₂], 0.94 [9H, s, C(CH₃)₃], 3.85-4.01 (2H, m, 5'-H), 4.95 (1H, m, 4'-H), 5.73 (1H, dd, J = 2.5, 8.1 Hz, 5-H), 5.89 (1H, m, 2'-H), 6.34 (1H, m, 3'-H), 7.07 (1H, m, 1'-H), 7.92 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, DMSO-d₆) δ −5.1 (Si(CH₃)₂), −4.9 (Si(CH₃)₂), 19.0 [C(CH₃)₃], 26.3 [C(CH₃)₃], 64.6 (5'-CH₂), 87.7 (1'-CH), 90.1 (4'-CH), 102.8 (5-CH), 127.0 (2'-CH), 134.7 (3'-CH), 141.6 (6-CH), 151.1 (2-C), 163.8 (4-C); IR (film) 1679, 1681, 1629 cm⁻¹; MS (Cl) m/z 342 ([M+NH₄⁺, 50%), 325 ([M+H⁺, 100%); HRMS (ES⁺) calcd for C₁₅H₂₅N₂O₄Si⁺ (M+H)⁺ 325.1578, found 325.1574.

5'-O-tert-Butyldiphenylsilyl-2',3'-didehydro-2',3'-dideoxyuridine (5g)

A procedure identical to the one used for 11 was employed. Compound 5g was obtained as a colourless viscous oil (0.46 g, 73%) from the reaction of 5i (0.30 g, 1.43 mmol) with tert-butyldiphenylsilyl chloride (0.41 mL, 1.57 mmol) and imidazole (0.21 g, 3.14 mmol). Flash column chromatography was carried out using 0→3% CH₃OH in CHCl₃. R_f (10% CH₃OH/CHCl₃) 0.73; ¹H NMR (300 MHz, CD₃OD) δ 1.15 [9H, s, C(CH₃)₃], 3.95 (1H, dd, J = 2.9, 11.7 Hz, 5'-CH(HP)), 4.06 (1H, dd, J = 2.9, 11.7 Hz, 5'-CH(HP)), 4.97 (1H, m, 4'-H), 5.26 (1H, d, J = 8.1 Hz, 5-H), 5.58 (1H, m, 1'-
H), 6.38 (1H, m, 2'-H), 7.10 (1H, m, 3'-H), 7.34-7.55 (6H, m, Ph-H), 7.66-7.81 (5H, m, Ph-H and 6-H); $^{13}$C NMR (300 MHz, CD$_2$OD) $\delta$ 19.8 [C(CH$_3$)$_3$], 27.4 [C(CH$_3$)$_2$H], 65.4 (5'-CH$_2$), 87.6 (1'-CH), 90.1 (4'-CH), 103. (5'-CH), 127.0 (2'-CH), 128.3 (Ph-CH), 128.4 (Ph-CH), 130.5 (Ph-CH), 130.6 (Ph-CH), 132.8 (Ph-C), 133.5 (Ph-C), 135.8 (Ph-CH), 136.0 (6-CH), 151.0 (2-C), 163.4 (4-C); IR (film) 1697 cm$^{-1}$; MS (Cl) m/z 466 ([M+NH$_4$]$^+$, 100%), 449 ([M+H]$^+$, 50%); HRMS (ES$^+$) calcd for C$_{25}$H$_{32}$O$_4$Si$^+$ (M+H)$^+$ 449.1891, found 449.1894.

2',3'-Didehydro-2',3'-dideoxyuridine (5i)

Tetra-$n$-butylammonium fluoride (7.99 g, 30.56 mmol) was added to a solution of 5f (9.00 g, 27.28 mmol) in THF (50 mL) and the mixture was stirred at room temperature overnight. The reaction mixture was reduced in vacuo and purified by flash column chromatography eluting with 5$\rightarrow$10% CH$_3$OH in CHCl$_3$. Compound 5i was obtained as a white solid (3.99 g, 78%) from the fractions with $R_f = 0.23$ (10% CH$_3$OH/CHCl$_3$). Mp: 148-150°C (lit$^2$ 151°C); $^1$H NMR (300 MHz, CD$_2$OD) $\delta$ 3.32 (1H, m, 5'-CH/H), 3.70-3.82 (2H, m, 5'-CH/H and 4'-H), 5.66 (1H, d, $J = 8.1$ Hz, 5'-CH), 5.95 (1H, m, 1'-H), 6.42 (1H, m, 2'-H), 6.96 (1H, m, 3'-H), 7.91 (1H, d, $J = 8.1$ Hz, 6'-CH); $^{13}$C NMR (300 MHz, CD$_2$OD) $\delta$ 64.2 (5'-CH$_2$), 89.5 (4'-CH), 91.7 (1'-CH), 102.9 (5'-CH), 127.5 (2'-CH), 136.5 (3'-CH), 143.6 (6-CH), 153.1 (2-C), 166.8 (4-C); IR (KBr) 1701, 1674, 1614 cm$^{-1}$; MS (Cl) m/z 228 ([M+NH$_4$]$^+$, 50%), 211 ([M+H]$^+$, 40%); HRMS (ES$^+$) calcd for C$_9$H$_{17}$N$_2$O$_4$Si$^+$ (M+H)$^+$ 211.0713, found 211.0718.

5'-O-Trityl-2',3'-didehydro-2',3'-dideoxyuridine (5j)

A procedure similar to the one used for 1j was employed. Compound 5j was obtained as white crystals (0.37 g, 58%) from the reaction of 5i (0.30 g, 1.43 mmol) with trityl chloride (0.44 g, 1.57 mmol) in dry pyridine (10 mL). Flash column chromatography was carried out using 0$\rightarrow$3% CH$_3$OH in CHCl$_3$. $R_f$ (10% CH$_3$OH/CHCl$_3$) 0.30; Mp 68°C; $^1$H NMR (300 MHz, CD$_2$OD) $\delta$ 3.56 (2H, m, 5'-H), 5.02 (1H, m, 4'-H), 5.08 (1H, m, 5-H), 5.93 (1H, m, 1'-H), 6.40 (1H, m, 2'-H), 7.09 (1H, m, 3'-H), 7.30-7.44 (15H, m, Ph-H), 7.87 (1H, d, $J = 8.1$ Hz, 6'-H); $^{13}$C NMR (300 MHz, CD$_2$OD) $\delta$ 64.8 (5'-CH$_2$), 86.4 (1'-CH), 87.8 (Ph$_3$C), 90.0 (4'-CH), 102.7 (5'-CH), 126.8 (Ph-CH), 127.8 (2'-CH), 128.4 (Ph-CH), 129.2 (Ph-CH), 134.9 (3'-CH), 141.8 (6-CH), 143.5 (Ph-C), 151.0 (2-C), 160.0 (4-C); IR (KBr) 1692, 1681 cm$^{-1}$; MS (Cl) m/z 470.
([M+NH₄]⁺, 100%), 453 ([M+H]⁺, 20%); HRMS (ES⁺) calcd for C₂₈H₂₅N₂O₄⁺ (M+H)⁺ 453.1809, found 453.1807.

3'-O-tert-Butyldimethylsilyl-5'-O-acetyl-2'-deoxyuridine (6)

Acetyl chloride (0.15 mL, 2.11 mmol) was added dropwise at room temperature to a stirred solution of 3f (0.60 g, 1.75 mmol) in dry DCM/pyridine (1:1) (20 mL). After 5h, the reaction was quenched by addition of saturated aqueous NaHCO₃ (10 mL). The reaction mixture was diluted with CH₂Cl₂ (100 mL) and the organic phase was washed with saturated NaHCO₃ (2 x 50 mL), dried over Na₂SO₄ and concentrated in vacuo. After co-evaporation with toluene the resulting crude oil was purified by flash column chromatography eluting with 0→8% CH₃OH in CHCl₃. The fractions with Rf = 0.63 (8% CH₃OH/CHCl₃) yielded compound 6 as a viscous colourless liquid (0.50 g, 74%). ¹H NMR (300 MHz, CD₃OD) δ 0.04 [6H, s, Si(CH₃)₂], 0.84 [9H, s, C(CH₃)₃], 2.01 (3H, s, CH₃), 2.14 (1H, m, 2'-H), 4.12-4.24 (2H, m, 4'-H and 5'-CH₂H), 4.36-4.40 (1H, m, 3'-H), 5.66 (1H, d, J = 8.1 Hz, 5'-H), 6.14 (1H, t, J = 6.6 Hz, 1'-H), 7.61 (1H, d, J = 8.1 Hz, 6-H); ¹³C NMR (75 MHz, CD₃OD) δ -4.3 (SiCH₃), -4.1 (SiCH₂), 19.2 [C(CH₃)₃], 20.1 (CH₂CO), 26.7 [C(CH₃)₃], 41.6 (2'-CH₂), 65.5 (5'-CH₂), 74.0 (3'-CH), 86.7 (1'-CH), 87.3 (4'-CH), 103.4 (5'-CH), 142.5 (6'-CH), 152.5 (2'-C), 166.4 (4'-C), 172.6 (COO); IR (neat) 1660 cm⁻¹; MS (Cl) m/z 402 ([M+NH₄]⁺, 70%), 385 ([M+H]⁺, 50%); HRMS (ES⁺) calcd for C₁₇H₂₉N₂O₅Si⁺ (M+H)⁺ 385.1789, found 385.1792.

3'-O-tert-Butyldimethylsilyloxy-5'-O-pentoyl-2'-deoxyuridine (7)

A procedure identical to the one used for 6 was employed. Compound 7 (contaminated by small amounts of 3'-O-tert-butyldimethylsilyl-3-N-pentoyl-5'-pentoyloxy-2'-deoxyuridine) was obtained as a yellowish viscous liquid (0.90 g, 96%) from the reaction of 3f (0.76 g, 2.21 mmol) with valeryl chloride (0.32 mL, 2.65 mmol). Flash column chromatography was carried out using 2→5% CH₃OH in CHCl₃, Rf (10% CH₃OH/CHCl₃) 0.40; ¹H NMR (300 MHz, CDCl₃) δ 0.13 [6H,s, Si(CH₃)₂], 0.94-1.01 [12H, m, C(CH₃)₃ and CH₂CH₂CH₂CH₂H₂], 1.35-1.47 (2H, m, CH₂CH₂CH₂CH₂CH₂), 1.65-1.70 (2H, m, CH₂CH₂CH₂CH₂CH₂), 1.73-1.81 (1H, m, 2'-CH₂H), 2.07-2.14 (1H, m, 2'-CH₂H), 2.27-2.40 (2H, m, CH₂CH₂CH₂CH₂), 4.11-4.17 (1H, m, 5'-CH₂H), 4.25-4.38 (3H, m, 5'-CH₂H, 4'-H and 3'-H), 5.80 (1H, m, 5'-H), 6.27 (1H,
m, 1'-H), 7.58 (1H, d, J = 8.2 Hz, 6-H); 13C NMR (75 MHz, CDCl3) δ -4.5 (SiCH3), 4.3 (SiCH3), 14.2 (CH2CH2CH2CH3), 18.4 [C(CH3)3], 22.7 (CH2CH2CH2CH3), 26.1 [C(CH3)3], 27.4 (CH2CH2CH2CH3), 34.3 (CH2CH2CH2CH3), 41.6 (2'-CH2), 63.5 (5'-CH2), 72.0 (3'-CH), 85.4 (1'-CH), 86.0 (4'-CH), 102.8 (5'-CH), 139.8 (6'-CH), 150.4 (2-C), 163.6 (4-C), 173.6 (COO); MS (Cl) m/z 444 ([M+NH4]+, 70%), 427 ([M+H]+, 30%); HRMS (ESI) calced for C20H38N2O6Si+ (M+H)+ 427.2260, found 427.2260.

5'-O-Benzoyl-3’-O-tert-Butyldimethylsilyloxy-2’-deoxyuridine (8)
A procedure identical to the one used for 6 was employed. Compound 8 was obtained as a pale yellow hygroscopic solid (0.77 g, 99%) from the reaction of 3f (0.60 g, 1.75 mmol) with benzoyl chloride (0.29 mL, 2.11 mmol). Flash column chromatography was carried out using 0→5% CH3OH in CHCl3. Rf (5% CH3OH/CHCl3) 0.41; 1H NMR (300 MHz, CD3OD) δ 0.13 [6H, s, Si(CH3)2], 0.93 [9H, s, C(CH3)3], 2.31-2.36 (2H, m, 2’-H), 4.19 (1H, dd, J = 4.4, 8.4 Hz, 5’-CH(H)), 4.49-4.62 (3H, m, 3’-CH, 4’-H and 5’-CH(H)), 5.59 (1H, d, J = 8.1 Hz, 5-H), 6.23 (1H, t, J = 5.6 Hz, 1’-H), 7.41-7.72 (6H, m, 6-H and Ph-H); 13C NMR (75 MHz, CD3OD) δ -4.4 (SiCH3), 19.2 [C(CH3)3], 26.6 [C(CH3)3], 41.7 (2’-CH2), 65.3 (5’-CH2), 73.8 (3’-CH), 86.6 (4’-CH) 87.5 (1’-CH), 103.3 (5-CH), 129.9 (Ph-CH), 130.2 (Ph-CH), 131.0 (Ph-CH), 131.1 (Ph-CH), 135.1 (Ph-CH), 142.5 (6-CH), 150.4 (2-C), 152.4 (Ph-C), 166.5 (4-C), 168.0 (COO); IR (KBr) 1725, 1704, 1692 cm⁻¹; MS (Cl) m/z 464 ([M+NH4]+, 70%), 447 ([M+H]+, 50%); HRMS (ESI) calced for C22H31N2O6Si+ (M+H)+ 447.1946, found 447.1947.

5’-Azido-2’,5’-dideoxyuridine (9)
The tosylate 1g (6.85 g, 44.03 mmol) was reacted with sodium azide (11.45 g, 176.18 mmol) in dry DMF (100 mL) at 90°C overnight. The reaction mixture was cooled in an ice bath and then filtered. The filtrate was reduced in vacuo and the residue was co-evaporated several times with EtOH and washed with iPrOH/EtOH (1:1) (3 x 100 mL). The filtrates were reduced in vacuo to yield compound 9. An analytical sample was obtained by flash column chromatography eluting with 5%→15% CH3OH in CHCl3. Compound 9 was obtained as a white solid (0.47 g, 59%) from the fractions with Rf = 0.50 (20% CH3OH/CHCl3). Mp 136-138°C (lit1 140-141°C); 1H NMR (300 MHz, CD3OD) δ 2.28-2.34 (2H, m, 2’-H), 3.55-3.69 (2H, m, 5’-H), 3.96-4.02 (1H, m,
3'-H), 4.34-4.39 (1H, m, 4'-H), 5.74-5.78 (1H, m, 5-H), 6.23-6.30 (1H, m, 1'-H), 7.73-7.78 (1H, m, 6-H); 13C NMR (75 MHz, CD3OD) δ 40.8 (2'-CH2), 53.7 (5'-CH2), 72.8 (3'-CH), 86.8 (1'-CH), 87.0 (4'-CH), 103.4 (5-CH), 142.6 (6-CH), 152.5 (2-C), 166.5 (4-C); IR (KBr) 3373, 2097, 1722, 1668 cm⁻¹.

5'-O-Tosyl-2',3'-dideoxy-3'-fluorouridine (10)
Tosyl chloride (0.194 g, 1.02 mmol) was added to an ice-cold solution of 3'-fluoro-2',3'-dideoxyuridine (0.205 g, 0.89 mmol) in dry pyridine (1 mL). The reaction mixture was stirred at 0ºC for 7h and then kept at 4ºC for 40h. The solvent was removed in vacuo and the crude syrup chromatographed (ISOLUTE SI column) using 0→5% CH3OH in CHCl3. Compound 10 (contaminated with traces of an impurity likely to be 5'-chloro-3'-fluoro-2',3',5'-trideoxyuridine) was obtained as a white solid (0.269 g, 79%). Rf (10% CH3OH/CHCl3) 0.63; 1H NMR (300 MHz, CDCl3) δ 2.26 (1H, m, 2'-CHH), 2.61 (3H, s, CH3C6H4), 2.77 (1H, m, 2'-CHH), 4.40 (2H, m, 5'-H), 4.55 (2H, d, J = 26.2 Hz, 4'-H), 5.37 (1H, dd, J = 5.2, 53.1 Hz, 3'-OH), 5.88 (1H, d, J = 8.1 Hz, 5-H), 6.50 (1H, m, 1'-H), 7.50-7.60 (3H, m, 6-H and Ar-H), 7.92 (2H, d, J = 8.4 Hz, Ar-H), 9.50 (1H, bs, 3'-NH); 13C NMR (75 MHz, CDCl3) δ 22.2 (CH3C6H4), 38.6 (d, J = 10.9 Hz, 3'-CH), 85.5 (d, J = 27.6 Hz, 4'-CH2), 85.7 (1'-CH), 93.8 (d, J = 180.5 Hz, 3'-CH), 103.7 (5-CH), 128.3 (Ar-CH), 130.7 (Ar-CH), 132.4 (Ar-C), 139.6 (6-CH), 146.4 (Ar-C), 150.6 (2-C), 163.4 (4-C); 19F NMR (282 MHz, CDCl3) δ -174.7 (m, 3'-F); MS (ES⁺) m/z 791 ([2M+Na]⁺, 6%), 407 ([M+Na]⁺; 24%), 87 (100%);

5'-Azido-3'-fluoro-2',3',5'-trideoxyuridine (11)
A procedure similar to the one used for 9 was employed. Compound 11 was obtained as a crude yellow gum (0.166 g) from the reaction of the tosylate 10 (0.137 g, 0.36 mmol) and sodium azide (0.098 g, 1.51 mmol) in dry DMF (3 mL). This crude product (contaminated by iPrOH, DMF and tosic acid) was used in the next step without further purification. 1H NMR (300 MHz, CD3OD) δ 2.41-2.68 (2H, m, 2'-H), 3.68 (2H, m, 5'-H), 4.32 (1H, dtd, J = 1.3, 4.8, 26.5 Hz, 4'-H), 5.25 (1H, dm, J = 53.8 Hz, 3'-H), 5.78 (1H, d, J = 8.2 Hz, 5-H), 6.30 (1H, m, 1'-H), 7.73 (1H, d, J = 8.2 Hz, 6-H); 13C NMR (75 MHz, CD3OD) δ 38.6 (d, J = 22.8 Hz, 2'-CH2), 53.5 (d, J = 10.1 Hz, 5'-CH2), 84.9 (d, J = 26.3 Hz, 4'-CH), 87.3 (1'-CH), 95.8 (d, J = 177.6 Hz, 3'-H).
CH), 103.8 (5'-CH), 143.8 (6-CH), 153.4 (2-C), 167.6 (4-C); $^{19}$F NMR (282 MHz, CD$_3$OD) δ -176.9 (m, 3'-F); IR (KBr) 3388, 3009, 2112, 1691 cm$^{-1}$; MS (ES$^+$) m/z 533 ([2M+Na]$^+$; 16%), 278 ([M+Na]$^+$; 7%);

5'-Amino-3'-fluoro-2',3',5'-trideoxyuridine (12)

A procedure identical to the one used for 2k was employed. Compound 12 was obtained as a crude pale yellow solid (0.130 g, 96%) from the hydrogenolysis of the azide 11 (0.150 g, 0.59 mmol) in EtOH/H$_2$O (1:1, 4mL) using 5%Pd/C as catalyst. The crude product was used in the next step without further purification. $^1$H NMR (300 MHz, D$_2$O) δ 2.25 (1H, m, 2'-H), 2.51 (1H, m, 2'-H), 2.72 - 2.87 (2H, m, 5'-H), 4.18 (1H, dt, $J$ = 6.6, 26.5 Hz, 4'-H), 5.14 (1H, dd, $J$ = 5.2, 53.4 Hz, 3'-H), 5.71 (1H, d, $J$ = 7.9 Hz, 5'-H), 6.14 (1H, dd, $J$ = 5.7, 9.0 Hz, 1'-H), 7.49 (1H, d, $J$ = 7.9 Hz, 6'-H); $^{13}$C NMR (75 MHz, D$_2$O) δ 36.5 (d, $J$ = 20.7 Hz, 2'-CH$_2$), 42.4 (d, $J$ = 9.8 Hz, 5'-CH$_2$), 84.9 (d, $J$ = 24.1 Hz, 4'-CH), 86.6 (1'-CH), 94.7 (d, $J$ = 175.9 Hz, 3'-CH), 103.0 (5-CH), 141.6 (6-CH), 155.4 (2-C), 171.4 (4-C).

5'-O-(tert-Butyldimethylsilyl)uridine (13)

$^{t}$er$t$-Butyldimethylsilylchloride (7.68 g, 51.23 mmol) and imidazole (6.97 g, 102.46 mmol) in dry DMF was added dropwise to a stirred solution of uridine (10.00 g, 40.98 mmol) in dry DMF under ice-bath cooling. After 1.5h, H$_2$O (100 mL) was added and the mixture was extracted with EtOAc (2 x 300 mL). The combined organic extracts were washed with saturated aqueous NaHCO$_3$ (300 mL), H$_2$O (300 mL), dried over Na$_2$SO$_4$ and reduced in vacuo. Purification by flash column chromatography eluting with 5% CH$_3$OH in CHCl$_3$ gave the compound 13 as a white solid (10.50 g, 75%). $R_f$ (10% CH$_3$OH/CHCl$_3$) 0.36; Mp 105-108°C (lit.$^2$ 106-107°C) $^1$H NMR (300 MHz, CDCl$_3$) δ 0.20 [6H, s, Si(CH$_3$)$_2$], 1.00 [9H, s, C(CH$_3$)$_3$], 3.94 (1H, m, 5'-CH$_2$), 4.13 (1H, m, 5'-CH$_2$), 4.22 (1H, m, 4'-H), 4.30-4.36 (2H, m, 2'-H and 3'-H), 5.74 (1H, d, $J$ = 8.1 Hz, 5-CH), 6.00 (1H, d, $J$ = 2.2 Hz, 1'-H), 8.19 (1H, d, $J$ = 8.1 Hz, 6-H); $^{1}$C NMR (75 MHz, CDCl$_3$) δ -5.1 [Si(CH$_3$)$_2$], 18.9 [C(CH$_3$)$_3$], 26.35 [C(CH$_3$)$_3$], 62.1 (5'-CH$_2$), 69.1 (2'-CH), 76.0 (3'-CH), 85.2 (1'-CH), 90.8 (4'-CH), 102.5 (5-CH), 141.0 (6-CH), 151.7 (2-C), 164.5 (4-C); IR (KBr) 3361, 1704, 1693 cm$^{-1}$; MS (Cl) m/z 376 ([M+NH$_4$]$^+$, 30%), 359 ([M+H]$^+$, 100%); HRMS (ES$^+$) calcd for C$_{15}$H$_{27}$N$_2$O$_6$Si$^+$ (M+H)$^+$ 359.1633, found 359.1634.
5'-O-(\textit{tert}-Butyldimethylsilyl)uridine \(2',3'\)-O-thiocarbonate (14)

A solution of 1,1'-thiocarbonylimidazole (9.31g, 52.21 mmol) in dry CHCl\(_3\) (60 mL) was added dropwise to a solution of 13 (17.80 g, 49.73 mmol) in dry CHCl\(_3\) (60 mL). The reaction mixture was stirred overnight at room temperature, then diluted with CHCl\(_3\) (200 mL) and extracted with H\(_2\)O (200 mL). The organic layer was washed with H\(_2\)O (200 mL), dried over Na\(_2\)SO\(_4\) and reduced \textit{in vacuo}. The crude product was purified by flash column chromatography eluting with 0→2% CH\(_3\)OH/CHCl\(_3\). The fractions with \(R_f = 0.59\) (10% CH\(_3\)OH/CHCl\(_3\)) afforded a crystalline residue, which was suspended in toluene and filtered to give compound 15 as a white solid (11.83 g, 60%). Mp 143-146\(^\circ\)C (lit\(^2\) 144-147\(^\circ\)C); \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 0.00 [6H, s, Si(CH\(_3\))\(_2\)], 0.82 [9H, s, C(CH\(_3\))\(_3\)] 3.78 (2H, m, 5'-H), 4.36 (1H, m, 4'-H), 5.51 (1H, dd, \(J = 3.1, 7.4\) Hz, 3'-H), 5.62 (1H, m, 2'-H), 5.90 (1H, d, \(J = 8.1\) Hz, 5-H), 5.97 (1H, m, 1'-H), 8.19 (1H, d, \(J = 8.1\) Hz, 6-H); \(^1\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 5.2 (SiCH\(_3\)), -5.1 (SiCH\(_3\)), 18.3 [C(CH\(_3\))\(_3\)], 26.1 [C(CH\(_3\))\(_3\)], 62.9 (5'-CH\(_2\)), 86.9 (3'-CH), 87.2 (4'-CH), 89.3 (2'-CH), 93.4 (1'-CH), 102.0 (5-CH), 143.5 (6-CH), 150.8 (2-C), 163.7 (4-C); IR (KBr) 1698, 1694, 1145 cm\(^{-1}\); MS (ES\(^\text{+}\)) m/z 399 ([M-H]\(^+\), 100%); MS (ES\(^\text{+}\)) m/z 423 ([M+Na]\(^+\), 60%); HRMS (ES\(^\text{+}\)) calcd for C\(_{16}\)H\(_{25}\)N\(_2\)O\(_6\)SSi\(^+\) (M+H\(^+\)) 401.1197, found 401.1199.
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S25
3. List of known compounds and their CAS number.

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