

Synthesis of spiroacetal-nucleosides as privileged natural product-like scaffolds

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Supplementary Information

General

Experiments requiring anhydrous conditions were performed under a dry nitrogen atmosphere using flame-dried apparatus and standard techniques in handling air- and moisture-sensitive materials unless otherwise stated. Solvents used for reactions, extractions and chromatographic purifications were distilled (except for diethyl ether), unless otherwise stated. Commercial reagents were analytical grade or were purified by standard procedures prior to use.³⁸ Microwave reactions were conducted in sealed reaction vessels using a Discover[®] LabMate microwave synthesiser (CEM Corporation) at the temperature stated. The progress of reactions was monitored by analytical thin layer chromatography (TLC) using Kieselgel 60 F₂₅₄ (Merck) silica plates with visualisation by ultraviolet irradiation (365 nm) followed by staining with ethanolic vanillin. Separation of mixtures was performed by flash chromatography using Kieselgel S 63–100 μm (Riedel-de-Hahn) silica gel with the indicated eluent or by PLC using Kieselgel 60 F₂₅₄ (Merck) silica plates with the indicated eluent. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected. Mass spectra were recorded on a VG-70SE mass spectrometer at a nominal accelerating voltage of 70 eV for low resolution and at a nominal resolution of 5000 to 10000 as appropriate for high resolution. Ionisation was effected using electron impact (EI⁺), fast atom bombardment (FAB⁺) using 3-nitrobenzyl alcohol as the matrix or chemical ionisation (CI⁺) using ammonia as a carrier gas. Major and significant fragments are quoted in the form $x(y)$, where x is the mass to charge ratio (m/z) and y is the percentage abundance relative to the base peak (100%). Infrared spectra were obtained using a Perkin Elmer Spectrum 1000 Fourier Transform Infrared spectrometer as a thin film between sodium chloride plates. Absorption peaks are reported as wavenumbers (ν , cm^{-1}). NMR spectra were recorded on either a Bruker DRX300 spectrophotometer operating at 300 MHz for ^1H nuclei and 75 MHz for ^{13}C nuclei, or on a Bruker DRX400 spectrophotometer operating at 400 MHz for ^1H nuclei and 100 MHz for ^{13}C nuclei, at ambient temperature. ^1H NMR chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane peak (δ 0.00 ppm). ^{13}C NMR chemical shifts are reported in ppm relative to the chloroform peak (δ 77.0 ppm). Decoupled ^{19}F NMR spectra were recorded on a Bruker DRX300 spectrophotometer operating at 282 MHz and data are expressed in ppm relative to CFCl_3 peak (δ 0.00 ppm).

Spectroscopic characterisation data of acetoxy-spiroacetal 10

(2*R**,6*S**,8*S**)-8-(*tert*-Butyldiphenylsilyloxymethyl)-2-acetoxy-1,7-dioxaspiro[5.5]undecane (10)

M.p.: 106.9–108.5 °C. HRMS (FAB): $[M - H]^+$, 481.2407, $C_{28}H_{37}O_5Si$ requires 481.2410. $\nu_{\max}$ (film)/ cm^{-1} : 2932 (C–H), 1754(C=O), 1428, 1367, 1226, 1199, 1113 (C–O), 1078 (C–O), 973, 702. δ_H (400 MHz; $CDCl_3$): 1.05 (9 H, s, $OSiPh_2^tBu$), 1.31–1.40 (1 H, m, 9- H_A), 1.40–1.54 (3 H, m, 3- H_A , 5- H_A and 11- H_A), 1.59–1.72 (4 H, m, 4- H_A , 5- H_B , 9- H_B and 10- H_A), 1.72–1.82 (2 H, m, 3- H_B and 11- H_B), 1.87–1.96 (1 H, m, 10- H_B), 1.96–2.07 (1 H, m, 4- H_B), 2.11 (3 H, s, $COCH_3$), 3.64 (1 H, dd, J_{AB} 10.4 and $J_{2-CH_{2,2}}$ 4.2, 8- CH_AH_BO), 3.69 (1 H, dd, J_{AB} 10.4 and $J_{2-CH_{2,2}}$ 5.8, 8- CH_AH_BO), 4.16–4.23 (1 H, m, 8-H), 6.00 (1 H, dd, $J_{2ax,3ax}$ 10.1 and $J_{2ax,3eq}$ 2.6, 2- H_{ax}), 7.36–7.44 (6 H, m, Ph), 7.72–7.77 (4 H, m, Ph). δ_C (100 MHz; $CDCl_3$): 17.4 (CH_2 , C-4), 18.2 (CH_2 , C-10), 19.2 (C, $OSiPh_2^tBu$), 21.3 (CH_3 , $COCH_3$), 26.6 (CH_2 , C-9), 26.7 (CH_3 , $OSiPh_2^tBu$), 29.5 (CH_2 , C-3), 34.6 (CH_2 , C-5), 34.9 (CH_2 , C-11), 67.2 (CH_2 , 8- CH_2O), 70.7 (CH, C-8), 90.2 (CH, C-2), 99.1 (C, C-6), 127.5 (CH, Ph), 129.4 (CH, Ph), 129.4 (CH, Ph), 133.9 (C, Ph), 135.7 (CH, Ph), 135.7 (CH, Ph), 169.3 (C=O, $COCH_3$). m/z (FAB): 481 ($[M - H]^+$, 1%), 423 ($M - OAc$, 66), 405 ($M - Ph$, 4), 365 (59), 241 (33), 207 (55), 199 (55), 197 (36), 167 (32), 149 (29), 137 (76), 135 (100), 121 (41).

Spectroscopic characterisation data of spiroacetal nucleosides 15

1-((2'*S**,6'*S**,8'*S**)-8'-(*tert*-Butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)-5-fluorocytidine (15a)

HRMS (FAB): found MH^+ , 552.2688, $C_{30}H_{39}FN_3O_4Si$ requires 552.2694. $\nu_{\max}$ (film)/ cm^{-1} : 3297 (N–H), 3072 (N–H), 2931 (C–H), 1688 (C=O), 1626, 1514, 1112 (C–O), 982, 703. δ_H (300 MHz; $CDCl_3$): 1.06 (9 H, s, $OSiPh_2^tBu$), 1.21–1.25 (1 H, m, 3'- H_A), 1.41–1.52 (3 H, m, 5'- H_A , 9'- H_A and 11'- H_A), 1.56–1.74 (5 H, m, 4'- H_A , 5'- H_B , 9'- H_B , 10'- H_A and 11'- H_B), 1.80–1.88 (1 H, m, 10'- H_B), 2.05–2.12 (2 H, m, 3'- H_B and 4'- H_B), 3.65 (1 H, dd, J_{AB} 10.2 and $J_{8'CH_2,8'}$ 4.8, 8'- CH_AH_BO), 3.72 (1 H, dd, J_{AB} 10.2 and $J_{8'CH_2,8'}$ 4.2, 8'- CH_AH_BO), 3.74–3.85 (1 H, m, 8'-H), 5.87 (1 H, ddd, $J_{2'ax,3'ax}$ 10.8, $J_{2'ax,3'eq}$ 2.3 and $J_{2'ax,5F}$ 2.0, 2'- H_{ax}), 7.33–7.42 (6 H, m, Ph), 7.54 (1 H, d, $J_{6,5F}$ 6.4, 6-H), 7.68–7.74 (4 H, m, Ph). δ_C (75 MHz; $CDCl_3$): 17.9 (CH_2 , C-4'), 18.1 (CH_2 , C-10'), 19.3 (C, $OSiPh_2^tBu$), 26.6 (CH_2 , C-

9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 30.9 (CH₂, C-3'), 34.9 (CH₂, C-5' or C-11'), 35.0 (CH₂, C-5' or C-11'), 66.9 (CH₂, 8'-CH₂O), 70.4 (CH, C-8'), 77.8 (CH, C-2'), 99.1 (C, C-6'), 125.6 (CH, d, *J*_{6,5F} 31.3, C-6), 127.5 (CH, Ph), 127.6 (CH, Ph), 129.5 (CH, Ph), 133.9 (C, Ph), 133.9 (C, Ph), 135.6 (CH, Ph), 135.7 (CH, Ph), 136.3 (C, d, *J*_{5,5F} 241.3, C-5), 153.4 (C, C-2), 157.5 (C, *J*_{4,5F} 13.6, C-4). δ_F (282 MHz; CFCl₃): -170.2 (CF, 5-F). *m/z* (FAB): 552 (MH⁺, 1%), 494 (M - ^{*t*}Bu, 7), 474 (M - Ph, 1), 423 (C₂₆H₃₅O₃Si, 27), 239 (SiPh₂^{*t*}Bu, 7), 207 (29), 197 (35), 135 (100), 130 (31).

4-*N*-Acetyl-1-[(2'S*,6'S*,8'S*)-8'-(*tert*-butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]cytidine (15b)

HRMS (FAB): found MH⁺, 576.2895, C₃₂H₄₂N₃O₅Si requires 576.2894. $\nu_{\max}$ (film)/cm⁻¹: 3232 (N-H), 2932 (C-H), 1716 (C=O), 1668 (C=O), 1626, 1563, 1495, 1113 (C-O), 984, 703. δ_H (400 MHz; CDCl₃): 1.06 (9 H, s, OSiPh₂^{*t*}Bu), 1.18–1.24 (1 H, m, 3'-H_A), 1.24–1.44 (3 H, m, 5'-H_A, 9'-H_A and 11'-H_A), 1.47–1.75 (6 H, m, 4'-H_A, 5'-H_B, 9'-H_B, 10'-H_A, 10'-H_B and 11'-H_B), 1.96–2.07 (2 H, m, 3'-H_B and 4'-H_B), 2.17 (3 H, s, COCH₃), 3.52 (1 H, dd, *J*_{AB} 10.2 and *J*_{8'-CH₂,8'} 4.8, 8'-CH_AH_BO), 3.61 (1 H, dd, *J*_{AB} 10.2 and *J*_{8'-CH₂,8'} 4.8, 8'-CH_AH_BO), 3.63–3.69 (1 H, m, 8'-H), 5.85 (1 H, dd, *J*_{2'ax,3'ax} 10.7 and *J*_{2'ax,3'eq} 2.0, 2'-H_{ax}), 7.24–7.34 (7 H, m, Ph and 5-H), 7.58–7.62 (4 H, m, Ph), 7.81 (1 H, d, *J*_{6,5} 7.5, 6-H), 9.76 (1 H, br s, NH). δ_C (100 MHz; CDCl₃): 17.8 (CH₂, C-4'), 18.0 (CH₂, C-10'), 19.2 (C, OSiPh₂^{*t*}Bu), 24.9 (CH₃, COCH₃), 26.6 (CH₂, C-9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 31.1 (CH₂, C-3'), 34.8 (CH₂, C-5' or C-11'), 35.0 (CH₂, C-5' or C-11'), 66.9 (CH₂, 8'-CH₂O), 70.6 (CH, C-8'), 78.4 (CH, C-2'), 96.6 (CH, C-5), 99.2 (C, C-6'), 127.5 (CH, Ph), 127.6 (CH, Ph), 129.5 (CH, Ph), 133.8 (C, Ph), 135.6 (CH, Ph), 135.7 (CH, Ph), 144.7 (CH, C-6), 154.6 (C, C-2), 162.4 (C, C-4), 170.9 (C, NCOCH₃). *m/z* (FAB): 576 (MH⁺, 6%), 423 (C₂₆H₃₅O₃Si, 42), 405 (21), 207 (40), 199 (29), 197 (33), 154 (80), 135 (100).

1-[(2'S*,6'S*,8'S*)-8'-(*tert*-Butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]thymidine (15c)

HRMS (FAB): found MH⁺, 549.2784, C₃₁H₄₁N₂O₅Si requires 549.2785. $\nu_{\max}$ (film)/cm⁻¹: 3180 (N-H), 2930 (C-H), 1713 (C=O), 1694 (C=O), 1428, 1270 (C-O), 1112 (C-O), 981, 702. δ_H (300 MHz; CDCl₃): 1.06 (9 H, s, OSiPh₂^{*t*}Bu), 1.35–1.43 (1 H, m, 9'-H_A), 1.43–1.53 (3 H, m, 3'-H_A, 5'-H_A and 11'-H_A), 1.54–1.76 (5 H, m, 4'-H_A, 5'-H_B, 9'-H_B, 10'-H_A and 11'-H_B), 1.79–1.90 (2 H, m, 3'-H_B and 10'-H_B), 1.95 (3 H, d, *J*_{5-CH₃,6} 1.2, 5-CH₃), 2.06–2.16 (1 H, m, 4'-H_B), 3.65 (1 H, dd, *J*_{AB} 10.5 and *J*_{8'-CH₂,8'} 4.5, 8'-CH_AH_BO), 3.71 (1 H, dd, *J*_{AB} 10.5 and *J*_{8'-CH₂,8'} 5.2, 8'-CH_AH_BO), 3.85–3.93 (1 H, m, 8'-H), 5.95 (1 H, dd, *J*_{2'ax,3'ax} 11.1 and *J*_{2'ax,3'eq} 2.5, 2'-H_{ax}), 7.25 (1 H, d, *J*_{6,5-CH₃} 1.2, 6-H), 7.33–7.46

(6 H, m, Ph), 7.71–7.76 (4 H, m, Ph), 8.29 (1 H, br s, NH). δ_c (75 MHz; CDCl₃): 12.6 (CH₃, 5-CH₃), 18.0 (CH₂, C-4'), 18.1 (CH₂, C-10'), 19.3 (C, OSiPh₂^{*t*}Bu), 26.5 (CH₂, C-9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 30.1 (CH₂, C-3'), 34.7 (CH₂, C-5' or C-11'), 34.8 (CH₂, C-5' or C-11'), 67.0 (CH₂, 8'-CH₂O), 70.6 (CH, C-8'), 76.5 (CH, C-2'), 99.0 (C, C-6'), 110.4 (C, C-5), 127.5 (CH, Ph), 127.6 (CH, Ph), 129.5 (CH, Ph), 133.8 (C, Ph), 135.7 (CH, Ph), 135.7 (CH, Ph), 136.1 (CH, C-6), 146.9 (C, C-2), 163.6 (C, C-4). m/z (FAB): 549 (MH⁺, 1%), 491 (M – ^{*t*}Bu, 14), 471 (M – Ph, 3), 423 (C₂₆H₃₅O₃Si, 17), 199 (38), 197 (38), 165 (22), 135 (100), 122 (21).

1-((2'S*,6'S*,8'S*)-8'-(*tert*-Butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)uridine (15d)

M.p.: 208.3–210.1 °C. HRMS (FAB): found MH⁺, 535.2633, C₃₀H₃₉N₂O₅Si requires 535.2628. $\nu_{\max}$ (film)/cm⁻¹: 3376 (N–H), 2919 (C–H), 1689 (C=O), 1668 (C=O), 1456, 1377, 1267 (C–O), 1103 (C–O), 982, 699. δ_H (300 MHz; CDCl₃): 1.07 (9 H, s, OSiPh₂^{*t*}Bu), 1.31–1.38 (1 H, m, 9'-H_A), 1.41–1.51 (3 H, m, 3'-H_A, 5'-H_A and 11'-H_A), 1.56–1.76 (5 H, m, 4'-H_A, 5'-H_B, 9'-H_B, 10'-H_A and 11'-H_B), 1.80–1.94 (2 H, m, 3'-H_B and 10'-H_B), 2.07–2.16 (1 H, m, 4'-H_B), 3.63 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 4.5, 8'-CH_AH_BO), 3.72 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 5.3, 8'-CH_AH_BO), 3.82–3.89 (1 H, m, 8'-H), 5.73 (1 H, d, $J_{5,6}$ 8.2, 5-H), 5.94 (1 H, dd, $J_{2'_{ax},3'_{ax}}$ 11.1 and $J_{2'_{ax},3'_{eq}}$ 2.5, 2'-H_{ax}), 7.33–7.42 (6 H, m, Ph), 7.46 (1 H, d, $J_{6,5}$ 8.2, 6-H), 7.70–7.76 (4 H, m, Ph), 8.17 (1 H, br s, NH). δ_c (75 MHz; CDCl₃): 17.9 (CH₂, C-4'), 18.0 (CH₂, C-10'), 19.3 (C, OSiPh₂^{*t*}Bu), 26.5 (CH₂, C-9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 30.3 (CH₂, C-3'), 34.7 (CH₂, C-5'), 34.8 (CH₂, C-11'), 67.0 (CH₂, 8'-CH₂O), 70.7 (CH, C-8'), 76.8 (CH, C-2'), 99.1 (C, C-6'), 102.1 (CH, C-5), 127.6 (CH, Ph), 129.5 (CH, Ph), 129.5 (CH, Ph), 133.8 (C, Ph), 135.7 (CH, Ph), 135.7 (CH, Ph), 140.3 (CH, C-6), 149.7 (C, C-2), 162.8 (C, C-4). m/z (FAB): 535 (MH⁺, 3%), 477 (M – ^{*t*}Bu, 11), 457 (M – Ph, 3), 423 (C₂₆H₃₅O₃Si, 19), 239 (SiPh₂^{*t*}Bu, 8), 199 (35), 197 (35), 135 (100), 105 (32), 91 (73).

1-((2'S*,6'S*,8'S*)-8'-(*tert*-Butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)-5-fluorouridine (15e)

HRMS (FAB): found MH⁺, 553.2540, C₃₀H₃₈FN₂O₅Si requires 553.2534. $\nu_{\max}$ (film)/cm⁻¹: 3187 (N–H), 3063 (N–H), 2918 (C–H), 1712 (C=O), 1694 (C=O), 1673 (C=O), 1260 (C–O), 1112 (C–O), 987, 700. δ_H (300 MHz; CDCl₃): 1.06 (9 H, s, OSiPh₂^{*t*}Bu), 1.28–1.37 (1 H, m, 9'-H_A), 1.37–1.52 (3 H, m, 3'-H_A, 5'-H_A and 11'-H_A), 1.57–1.75 (5 H, m, 4'-H_A, 5'-H_B, 9'-H_B, 10'-H_A and 11'-H_B), 1.75–1.96 (2 H, m, 3'-H_B and 10'-H_B), 2.03–2.17 (1 H, m, 4'-H_B), 3.62 (1 H, dd, J_{AB} 10.5 and $J_{8'-CH_2,8'}$ 4.5, 8'-CH_AH_BO), 3.70 (1 H, dd, J_{AB} 10.5 and $J_{8'-CH_2,8'}$ 5.5, 8'-CH_AH_BO), 3.79–3.88 (1 H, m, 8'-H), 5.92 (1 H,

ddd, $J_{2'ax,3'ax}$ 11.0, $J_{2'ax,3'eq}$ 2.4 and $J_{2',5F}$ 2.3, 2'-H_{ax}), 7.34–7.44 (6 H, m, Ph), 7.52 (1 H, d, $J_{6,5F}$ 6.3, 6-H), 7.70–7.75 (4 H, m, Ph), 8.45 (1 H, br s, NH). δ_c (100 MHz; CDCl₃): 17.8 (CH₂, C-4'), 18.0 (CH₂, C-10'), 19.2 (C, OSiPh₂^{*t*}Bu), 26.4 (CH₂, C-9'), 26.7 (CH₃, OSiPh₂^{*t*}Bu), 30.2 (CH₂, C-3'), 34.6 (CH₂, C-5' or C-11'), 34.8 (CH₂, C-5' or C-11'), 67.0 (CH₂, 8'-CH₂O), 70.8 (CH, C-8'), 77.2 (CH, C-2'), 99.3 (C, C-6'), 124.6 (CH, d, $J_{6,5F}$ 33.6, C-6), 127.6 (CH, Ph), 129.5 (CH, Ph), 129.5 (CH, Ph), 133.7 (C, Ph), 135.7 (CH, Ph), 140.3 (C, d, $J_{5,5F}$ 236.5, C-5), 148.2 (C, C-2), 156.6 (C, $J_{4,5F}$ 26.7, C-4). δ_f (282 MHz; CFCl₃): -165.8 (CF, F-5). m/z (FAB): 553 (MH⁺, 4%), 495 (M – ^{*t*}Bu, 23), 475 (M – Ph, 7), 423 (C₂₆H₃₅O₃Si, 48), 199 (45), 197 (42), 169 (22), 135 (100), 121 (33), 105 (26), 89 (41).

6-*N*-Benzoyl-9-((2'*S,6'*S**,8'*S**)-8'-(*tert*-butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)adenosine (15f)**

HRMS (FAB): found MH⁺, 662.3162, C₃₈H₄₄N₅O₄Si requires 662.3163. ν_{max} (film)/cm⁻¹: 3070 (N–H), 2929 (C–H), 1696 (C=O), 1610, 1582, 1256, 1112 (C–O), 980, 704. δ_H (400 MHz; CDCl₃): 1.09 (9 H, s, OSiPh₂^{*t*}Bu), 1.28–1.34 (1 H, m, 9'-H_A), 1.46–1.54 (1 H, m, 11'-H_A), 1.55–1.66 (3 H, m, 5'-H_A, 9'-H_B and 10'-H_A), 1.73–1.85 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 2.02–2.11 (1 H, m, 3'-H_A), 2.12–2.18 (1 H, m, 3'-H_B), 2.19–2.28 (1 H, m, 4'-H_B), 3.68 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 4.3, 8'-CH_AH_BO), 3.77 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 6.2, 8'-CH_AH_BO), 4.05–4.11 (1 H, m, 8'-H), 6.22 (1 H, dd, $J_{2'ax,3'ax}$ 11.1 and $J_{2'ax,3'eq}$ 2.6, 2'-H_{ax}), 7.36–7.44 (6 H, m, OSiPh₂^{*t*}Bu), 7.53 (2 H, t, J 7.4, C_{OPh}), 7.62 (1 H, t, J 7.4 C_{OPh}), 7.74–7.80 (4 H, m, OSiPh₂^{*t*}Bu), 8.05 (2 H, d, J 7.4, C_{OPh}), 8.22 (1 H, s, 8-H), 8.78 (1 H, s, 2-H), 9.05 (1 H, s, NH). δ_c (100 MHz; CDCl₃): 18.1 (CH₂, C-10'), 18.2 (CH₂, C-4'), 19.3 (C, OSiPh₂^{*t*}Bu), 26.6 (CH₂, C-9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 30.8 (CH₂, C-3'), 34.6 (CH₂, C-5'), 34.7 (CH₂, C-11'), 67.2 (CH₂, 8'-CH₂O), 71.0 (CH, C-8'), 76.4 (CH, C-2'), 98.9 (C, C-6'), 123.0 (CH, C-5), 127.6 (CH, OSiPh₂^{*t*}Bu), 127.9 (CH, C_{OPh}), 128.8 (CH, C_{OPh}), 129.5 (CH, OSiPh₂^{*t*}Bu), 129.6 (CH, OSiPh₂^{*t*}Bu), 132.7 (CH, C_{OPh}), 133.8 (2 x C, OSiPh₂^{*t*}Bu and C_{OPh}), 135.7 (CH, OSiPh₂^{*t*}Bu), 141.1 (CH, C-8), 149.3 (C, C-6), 151.7 (C, C-4), 152.6 (CH, C-2), 164.7 (C, C_{OPh}). m/z (FAB): 662 (MH⁺, 6%), 604 (M – ^{*t*}Bu, 5), 584 (M – Ph, 1), 423 (C₂₆H₃₅O₃Si, 3), 240 (100), 197 (15), 135 (41), 105 (29).

2-*N*-Acetyl-9-((2'*S,6'*S**,8'*S**)-8'-(*tert*-butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)guanosine (15g)**

HRMS (FAB): found MH⁺, 616.2958, C₃₃H₄₂N₅O₅Si requires 616.2955. ν_{max} (film)/cm⁻¹: 3148 (N–H), 3049 (N–H), 2932 (C–H), 1682 (C=O), 1613, 1556, 1257, 1233, 1112 (C–O), 979, 703. δ_H (300 MHz; CDCl₃): 1.13 (9 H, s, OSiPh₂^{*t*}Bu), 1.29–1.34 (1 H, m, 9'-H_A), 1.46–1.66 (4 H, m, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.73–1.89 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.80 (3 H, s, COCH₃),

1.90–2.02 (2 H, m, 3'-H), 2.16–2.30 (1 H, m, 4'-H_B), 3.69 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 3.7, 8'-CH_AH_BO), 3.80 (1 H, dd, J_{AB} 10.4 and $J_{8'CH_2-8'}$ 7.2, 8'-CH_AH_BO), 3.94–4.03 (1 H, m, 8'-H), 6.00 (1 H, dd, $J_{2'ax,3'ax}$ 10.6 and $J_{2'ax,3'eq}$ 2.6, 2'-H_{ax}), 7.34–7.44 (6 H, m, Ph), 7.50 (1 H, br s, NH), 7.74–7.80 (4 H, m, Ph), 7.90 (1 H, br s, 8-H), 11.76 (1 H, br s, NH). δ_C (75 MHz; CDCl₃): 18.0 (CH₂, C-10'), 18.3 (CH₂, C-4'), 19.5 (C, OSiPh₂^{*t*}Bu), 24.0 (CH₃, COCH₃), 26.6 (CH₂, C-9'), 27.0 (CH₃, OSiPh₂^{*t*}Bu), 31.5 (CH₂, C-3'), 34.5 (CH₂, C-5'), 34.6 (CH₂, C-11'), 67.7 (CH₂, 8'-CH₂O), 71.1 (CH, C-8'), 76.0 (CH, C-2'), 98.8 (C, C-6'), 121.1 (C, C-5), 127.9 (CH, Ph), 129.9 (CH, Ph), 133.9 (C, Ph), 134.3 (C, Ph), 135.4 (CH, Ph), 137.1 (CH, C-8), 146.6 (C, C-2), 147.5 (C, C-4), 155.5 (C, C-6), 170.8 (C, NCOMe). m/z (FAB): 616 (MH⁺, 15%), 538 (M – Ph, 1), 423 (C₂₆H₃₅O₃Si, 51), 207 (32), 198 (28), 194 (100), 136 (43), 135 (87).

2-*N*-Acetyl-7-[(2*S,6*S**,8*S**)-8'-(*tert*-butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]guanosine (15h)**

HRMS (FAB): found MH⁺, 616.2949, C₃₃H₄₂N₅O₅Si requires 616.2955. ν_{max} (film)/cm⁻¹: 3134 (N–H), 3070 (N–H), 2931 (C–H), 1694 (C=O), 1621, 1547, 1257, 1212, 1112 (C–O), 981, 703. δ_H (300 MHz; CDCl₃): 1.07 (9 H, s, OSiPh₂^{*t*}Bu), 1.42–1.50 (1 H, m, 9'-H_A), 1.52–1.70 (4 H, m, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.70–1.89 (5 H, m, 3'-H_A, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 2.14–2.35 (2 H, m, 3'-H_B and 4'-H_B), 2.38 (3 H, s, COCH₃), 3.70 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 4.7, 8'-CH_AH_BO), 3.78 (1 H, dd, J_{AB} 10.4 and $J_{8'CH_2-8'}$ 4.8, 8'-CH_AH_BO), 3.85–4.92 (1 H, m, 8'-H), 6.11 (1 H, dd, $J_{2'ax,3'ax}$ 10.8 and $J_{2'ax,3'eq}$ 2.1, 2'-H_{ax}), 7.34–7.43 (6 H, m, Ph), 7.70–7.78 (4 H, m, Ph), 8.05 (1 H, s, 8-H), 10.87 (1 H, br s, NH), 12.23 (1 H, br s, NH). δ_C (75 MHz; CDCl₃): 17.9 (CH₂, C-4'), 18.1 (CH₂, C-10'), 19.3 (C, OSiPh₂^{*t*}Bu), 24.6 (CH₃, COCH₃), 26.6 (CH₂, C-9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 32.4 (CH₂, C-3'), 34.7 (CH₂, C-5'), 34.9 (CH₂, C-11'), 67.0 (CH₂, 8'-CH₂O), 70.8 (CH, C-8'), 79.5 (CH, C-2'), 99.1 (C, C-6'), 111.3 (C, C-5), 127.6 (CH, Ph), 129.5 (CH, Ph), 133.8 (C, Ph), 135.7 (CH, Ph), 135.7 (CH, Ph), 141.0 (CH, C-8), 147.8 (C, C-2), 152.6 (C, C-6), 156.8 (C, C-4), 173.0 (C, NCOMe). m/z (FAB): 616 (MH⁺, 9%), 558 (12), 538 (M – Ph, 3), 423 (C₂₆H₃₅O₃Si, 17), 405 (19), 207 (17), 197 (21), 194 (100), 136 (33), 135 (65).

Spectroscopic characterisation data of spiroacetal nucleosides

11

1- $\{(2'S^*,6'S^*,8'S^*)\text{-}8'\text{-(Hydroxymethyl)}\text{-}1',7'\text{-dioxaspiro[5.5]undecan-2'-yl}\}$ -5-fluorocytidine (11a)

HRMS (FAB): found MH^+ , 314.1506, $C_{14}H_{21}FN_3O_4$ requires 314.1516. $\nu_{\max}$ (film)/ cm^{-1} : 3354br (O–H), 3195 (N–H), 3101 (N–H), 2927 (C–H), 1678 (C=O), 1602 (C=N), 1511, 1201 (C–O), 1133 (C–O), 979. δ_H (300 MHz; $CDCl_3$): 1.27–1.35 (1 H, m, 9'-H_A), 1.37–1.52 (3 H, m, 3'-H_A, 5'-H_A and 11'-H_A), 1.52–1.65 (2 H, m, 9'-H_B and 10'-H_A), 1.65–1.86 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.90–1.99 (1 H, m, 3'-H_B), 2.00–2.61 (4 H, m, 4'-H_B, NH₂ and OH), 3.55 (1 H, dd, J_{AB} 11.6 and $J_{8'CH_2,8'}$ 6.3, 8'-CH_AH_BO), 3.66 (1 H, dd, J_{AB} 11.6 and $J_{8'CH_2,8'}$ 3.4, 8'-CH_AH_BO), 3.84–3.90 (1 H, m, 8'-H), 6.03 (1 H, d, $J_{2'ax,3'ax}$ 10.8, 2'-H_{ax}), 7.51 (1 H, d, $J_{6,5F}$ 5.8, 6-H). δ_C (100 MHz; $CDCl_3$ with a drop of CD_3OD): 18.1 (2 x CH₂, C-4' and C-10'), 26.4 (CH₂, C-9'), 30.2 (CH₂, C-3'), 34.4 (CH₂, C-5' or C-11'), 34.6 (CH₂, C-5' or C-11'), 65.8 (CH₂, 8'-CH₂O), 70.9 (CH, C-8'), 77.2 (CH, C-2'), 99.2 (C, C-6'), 125.6 (CH, d, $J_{6,5F}$ 31.2, C-6), 136.6 (C, d, $J_{5,5F}$ 242.3, C-5), 153.8 (C, C-2), 157.4 (C, $J_{4,5F}$ 14.5, C-4). δ_F (282 MHz; $CFCl_3$): -168.52 (CF, 5-F). m/z (FAB): 314 (MH^+ , 21%), 185 ($C_{10}H_{17}O_3$, 64), 156 (37), 149 (28), 138 (49), 137 (90), 130 (100).

1- $\{(2'S^*,6'S^*,8'S^*)\text{-}8'\text{-(Hydroxymethyl)}\text{-}1',7'\text{-dioxaspiro[5.5]undecan-2'-yl}\}$ cytidine (11b)

HRMS (FAB): found MH^+ , 296.1605, $C_{14}H_{22}FN_3O_4$ requires 296.1610. $\nu_{\max}$ (film)/ cm^{-1} : 3354br (O–H), 3205 (N–H), 2929 (C–H), 1646 (C=O), 1493, 1203 (C–O), 979. δ_H (300 MHz; $CDCl_3$): 1.32–1.37 (1 H, m, 9'-H_A), 1.40–1.62 (5 H, m, 3'-H_A, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.64–1.76 (3 H, m, 4'-H_A, 5'-H_B and 11'-H_B), 1.77–1.85 (1 H, m, 10'-H_B), 1.87–1.95 (1 H, m, 3'-H_B), 2.04–2.39 (4 H, m, 4'-H_B, NH₂ and OH), 3.55 (1 H, dd, J_{AB} 11.5 and $J_{8'CH_2,8'}$ 6.6, 8'-CH_AH_BO), 3.67 (1 H, dd, J_{AB} 11.5 and $J_{8'CH_2,8'}$ 3.5, 8'-CH_AH_BO), 3.86–3.94 (1 H, m, 8'-H), 5.86 (1 H, d, $J_{5,6}$ 7.5, 5-H), 6.10 (1 H, dd, $J_{2'ax,3'ax}$ 11.2 and $J_{2'ax,3'eq}$ 2.0, 2'-H_{ax}), 7.50 (1 H, d, $J_{6,5}$ 7.5, 6-H). δ_C (75 MHz; $CDCl_3$): 18.2 (CH₂, C-10'), 18.5 (CH₂, C-4'), 26.2 (CH₂, C-9'), 30.1 (CH₂, C-3'), 34.6 (CH₂, C-5' or C-11'), 34.8 (CH₂, C-5' or C-11'), 66.1 (CH₂, 8'-CH₂O), 70.7 (CH, C-8'), 76.7 (CH, C-2'), 94.8 (CH, C-5), 99.1 (C, C-6'), 141.5 (CH, C-6), 165.6 (C, C-2), 165.3 (C, C-4). m/z (FAB): 296 (MH^+ , 10%), 185 ($C_{10}H_{17}O_3$, 12), 155 (45), 149 (32), 138 (56), 137 (100), 120 (20), 112 (68), 91 (37).

1-((2'S*,6'S*,8'S*)-8'-(Hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)thymidine (11c)

HRMS (FAB): found MH^+ , 310.1525, $C_{15}H_{22}N_2O_5$ requires 310.1529. $\nu_{\max}$ (film)/ cm^{-1} : 3444br (O–H), 3184 (N–H), 3044, 2945 (C–H), 1694 (C=O), 1682 (C=O), 1272 (C–O), 1092, 980. δ_H (400 MHz; $CDCl_3$): 1.23–1.34 (1 H, m, 9'-H_A), 1.44–1.52 (2 H, m, 5'-H_A and 11'-H_A), 1.56–1.65 (3 H, m, 3'-H_A, 9'-H_B and 10'-H_A), 1.65–1.87 (5 H, m, 3'-H_B, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.96 (3 H, d, $J_{5-CH_3,6}$ 1.1, 5-CH₃), 2.04–2.18 (1 H, m, 4'-H_B), 2.63 (1 H, t, $J_{OH,8'-CH_2}$ 5.5, OH), 3.59–3.64 (2 H, m, 8'-CH₂O), 3.82–3.89 (1 H, m, 8'-H), 6.03 (1 H, dd, $J_{2'ax,3'ax}$ 11.3, $J_{2'ax,3'eq}$ 2.2, 2'-H_{ax}), 7.22 (1 H, d, $J_{6,5-CH_3}$ 1.1, 6-H), 9.21 (1 H, br s, NH). δ_C (100 MHz; $CDCl_3$): 12.6 (CH₃, 5-CH₃), 18.1 (CH₂, C-4'), 18.4 (CH₂, C-10'), 26.5 (CH₂, C-9'), 29.3 (CH₂, C-3'), 34.4 (CH₂, C-5' or C-11'), 34.7 (CH₂, C-5' or C-11'), 66.0 (CH₂, 8'-CH₂O), 70.9 (CH, C-8'), 75.8 (CH, C-2'), 99.2 (C, C-6'), 111.2 (C, C-5), 135.8 (CH, C-6), 150.9 (C, C-2), 163.6 (C, C-4). m/z (FAB): 311 (MH^+ , 1%), 293 (M – OH, 7), 185 ($C_{10}H_{17}O_3$, 100), 127 (24), 99 (12).

1-((2'S*,6'S*,8'S*)-8'-(Hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)uridine (11d)

HRMS (FAB): found MH^+ , 297.1441, $C_{14}H_{21}N_2O_5$ requires 297.1451. $\nu_{\max}$ (film)/ cm^{-1} : 3439br (O–H), 3055 (N–H), 2926 (C–H), 1694 (C=O), 1682 (C=O), 1463, 1385, 1271 (C–O), 1204 (C–O), 1048, 982. δ_H (400 MHz; $CDCl_3$): 1.29–1.37 (1 H, m, 9'-H_A), 1.45–1.52 (2 H, m, 5'-H_A and 11'-H_A), 1.53–1.64 (3 H, m, 3'-H_A, 9'-H_B and 10'-H_A), 1.66–1.82 (5 H, m, 4'-H_A, 5'-H_B, 10'-H_B, 11'-H_B and OH), 1.82–1.88 (1 H, m, 3'-H_B), 2.08–2.17 (1 H, m, 4'-H_B), 3.59 (1 H, dd, J_{AB} 11.5 and $J_{8'-CH_2,8'}$ 6.0, 8'-CH_AH_BO), 3.72 (1 H, dd, J_{AB} 11.5 and $J_{8'-CH_2,8'}$ 4.0, 8'-CH_AH_BO), 3.81–3.87 (1 H, m, 8'-H), 5.76 (1 H, d, $J_{5,6}$ 8.2, 5-H), 5.99 (1 H, dd, $J_{2'ax,3'ax}$ 11.3 and $J_{2'ax,3'eq}$ 2.3, 2'-H_{ax}), 7.43 (1 H, d, $J_{6,5}$ 8.2, 6-H), 8.86 (1 H, br s, NH). δ_C (75 MHz; $CDCl_3$): 18.1 (CH₂, C-10'), 18.3 (CH₂, C-4'), 26.2 (CH₂, C-9'), 29.6 (CH₂, C-3'), 34.4 (CH₂, C-5' or C-11'), 34.7 (CH₂, C-5' or C-11'), 66.0 (CH₂, 8'-CH₂O), 70.9 (CH, C-8'), 76.2 (CH, C-2'), 99.3 (C, C-6'), 102.7 (CH, C-5), 140.1 (CH, C-6), 150.4 (C, C-2), 162.7 (C, C-4). m/z (FAB): 297 (MH^+ , 6%), 185 ($C_{10}H_{17}O_3$, 34), 155 (31), 138 (41), 137 (78), 120 (17), 102 (100), 91 (19).

1-((2'S*,6'S*,8'S*)-8'-(Hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)-5-fluorouridine (11e)

HRMS (FAB): found MH^+ , 315.1356, $C_{14}H_{20}FN_2O_5$ requires 315.1356. $\nu_{\max}$ (film)/ cm^{-1} : 3444br (O–H), 3198 (N–H), 3064 (N–H), 2929 (C–H), 1714 (C=O), 1666 (C=O), 1373, 1265 (C–O), 1203, 1093 (C–O), 982. δ_H (400 MHz; $CDCl_3$): 1.29–1.39 (1 H, m, 9'-H_A), 1.43–1.60 (5 H, m, 3'-H_A,

5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.68–1.91 (5 H, m, 3'-H_A, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.98–2.18 (2 H, m, 4'-H_B and OH), 3.58 (1 H, dd, J_{AB} 11.6 and $J_{8'-CH_2,8'}$ 6.1, 8'-CH_AH_BO), 3.66 (1 H, dd, J_{AB} 11.6 and $J_{8'-CH_2,8'}$ 3.7, 8'-CH_AH_BO), 3.78–3.85 (1 H, m, 8'-H), 5.96 (1 H, ddd, $J_{2'ax,3'ax}$ 11.2, $J_{2'ax,3'eq}$ 2.1, $J_{2',5F}$ 2.1, 2'-H_{ax}), 7.48 (1 H, d, $J_{6,5F}$ 6.1, 6-H), 8.88 (1 H, br s, NH). δ_C (100 MHz; CDCl₃): 18.0 (CH₂, C-10'), 18.1 (CH₂, C-4'), 26.1 (CH₂, C-9'), 29.6 (CH₂, C-3'), 34.4 (CH₂, C-5' or C-11'), 34.6 (CH₂, C-5' or C-11'), 66.0 (CH₂, 8'-CH₂O), 71.0 (CH, C-8'), 76.7 (CH, C-2'), 99.5 (C, C-6'), 124.8 (CH, d, $J_{6,5F}$ 33.5, C-6), 141.0 (C, d, $J_{5,5F}$ 238.5, C-5), 148.8 (C, C-2), 156.3 (C, C-4). δ_F (282 MHz; CFCl₃): -165.6 (CF, 5-F). m/z (FAB): 315 (MH⁺, 3%), 185 (C₁₀H₁₇O₃, 24), 155 (40), 138 (50), 137 (100), 136(21), 91(24), 90 (24).

6-*N*-Benzoyl-9-[(2'*S,6'*S**,8'*S**)-8'-(hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]adenosine (11f)**

HRMS (FAB): found MH⁺, 424.1974, C₂₂H₂₆N₅O₄ requires 424.1985. ν_{max} (film)/cm⁻¹: 3395 (O–H), 3057 (N–H), 2932 (C–H), 1698 (C=O), 1614, 1582, 1455, 1258 (C–O), 1227 (C–O), 1097, 980. δ_H (300 MHz; CDCl₃): 1.32–1.40 (1 H, m, 9'-H_A), 1.45–1.66 (4 H, m, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.70–1.91 (5 H, m, 4'-H_A, 5'-H_B, 10'-H_B, 11'-H_B and OH), 2.10–2.27 (3 H, m, 3'-H_A, 3'-H_B and 4'-H_B), 3.63 (1 H, dd, J_{AB} 11.6 and $J_{8'-CH_2,8'}$ 7.0, 8'-CH_AH_BO), 3.78 (1 H, dd, J_{AB} 11.6 and $J_{8'-CH_2,8'}$ 2.9, 8'-CH_AH_BO), 3.99–4.07 (1 H, m, 8'-H), 6.23 (1 H, d, $J_{2'ax,3'ax}$ 9.5, 2'-H_{ax}), 7.53 (2 H, t, J 7.2, Ph), 7.61 (1 H, t, J 7.2, Ph), 8.04 (2 H, d, J 7.2, Ph), 8.25 (1 H, s, 8-H), 8.80 (1 H, s, 2-H), 9.11 (1 H, br s, NH). δ_C (100 MHz; CDCl₃): 18.2 (CH₂, C-10'), 18.6 (CH₂, C-4'), 26.0 (CH₂, C-9'), 30.4 (CH₂, C-3'), 34.3 (CH₂, C-5'), 34.5 (CH₂, C-11'), 66.2 (CH₂, 8'-CH₂O), 71.3 (CH, C-8'), 75.6 (CH, C-2'), 99.3 (C, C-6'), 123.0 (C, C-5), 127.9 (CH, Ph), 128.8 (CH, Ph), 132.8 (CH, Ph), 133.6 (C, Ph), 141.0 (CH, C-8), 149.6 (C, C-6), 151.6 (C, C-4), 152.7 (CH, C-2), 164.6 (C, C=O). m/z (FAB): 424 (MH⁺, 8%), 185 (C₁₀H₁₇O₃, 3), 155 (40), 135 (51), 137 (100), 120 (20).

2-*N*-Acetyl-9-[(2'*S,6'*S**,8'*S**)-8'-(hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]guanosine (11g)**

HRMS (FAB): found MH⁺, 378.1780, C₁₇H₂₄N₅O₅ requires 378.1777. ν_{max} (film)/cm⁻¹: 3390br (O–H), 3210 (N–H), 3050 (N–H), 2941 (C–H), 1681 (C=O), 1613, 1557, 1411, 1260 (C–O), 1235 (C–O), 978. δ_H (300 MHz; CDCl₃): 1.15–1.23 (1 H, m, 9'-H_A), 1.46–1.66 (4 H, m, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.66–1.89 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.97–2.04 (2 H, m, 3'-H), 2.06–2.16 (1 H, m, 4'-H_B), 2.24 (3 H, s, COCH₃), 2.47 (1 H, br s, OH), 3.66 (1 H, dd, J_{AB} 11.1 and $J_{8'-CH_2,8'}$ 4.9, 8'-CH_AH_BO), 3.75 (1 H, dd, J_{AB} 11.1 and $J_{8'-CH_2,8'}$ 6.8, 8'-CH_AH_BO), 4.16–4.26 (1 H, m, 8'-H), 5.90

(1 H, dd, $J_{2'ax,3'ax}$ 9.7 and $J_{2'ax,3'eq}$ 3.5, 2'-H_{ax}), 7.87 (1 H, s, 8-H), 10.14 (1 H, br s, NH), 11.97 (1 H, br s, NH). δ_c (75 MHz; CDCl₃): 18.2 (CH₂, C-10'), 18.8 (CH₂, C-4'), 24.2 (CH₃, COCH₃), 26.9 (CH₂, C-9'), 29.6 (CH₂, C-3'), 34.3 (CH₂, C-5'), 34.8 (CH₂, C-11'), 66.6 (CH₂, 8'-CH₂O), 70.8 (CH, C-8'), 75.0 (CH, C-2'), 99.3 (C, C-6'), 120.5 (C, C-5), 136.6 (CH, C-8), 147.8 (C, C-2), 148.2 (C, C-4), 155.5 (C, C-6), 170.9 (C, NCOMe). m/z (FAB): 378 (MH⁺, 6%), 194 (38), 185 (C₁₀H₁₇O₃, 11), 155 (46), 139 (24), 138 (53), 137 (100), 90 (24).

2-*N*-Acetyl-7-[(2'*S,6'*S**,8'*S**)-8'-(hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]guanosine (11h)**

HRMS (FAB): found MH⁺, 378.1784, C₁₇H₂₄N₅O₅ requires 378.1777. ν_{max} (film)/cm⁻¹: 3429br (N-H and O-H), 2946 (C-H), 1673 (C=O), 1625, 1548, 1259, 1217 (C-O), 981, 732. δ_H (300 MHz; CDCl₃): 1.27–1.34 (1 H, m, 9'-H_A), 1.46–1.70 (4 H, m, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.70–1.85 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.89–2.00 (1 H, m, 3'-H_A), 2.10–2.18 (1 H, m, 3'-H_B), 2.18–2.25 (1 H, m, 4'-H_B), 2.40 (3 H, s, COCH₃), 2.79 (1 H, br s, OH), 3.54–3.64 (1 H, m, 8'-CH_AH_BO), 3.73 (1 H, dd, J_{AB} 11.5 and $J_{8'-CH_2,8'}$ 3.1, 8'-CH_AH_BO), 3.84–4.04 (1 H, m, 8'-H), 6.38 (1 H, dd, $J_{2'ax,3'ax}$ 11.1 and $J_{2'ax,3'eq}$ 2.1, 2'-H_{ax}), 8.12 (1 H, s, 8-H), 10.62 (1 H, br s, NH), 12.30 (1 H, br s, NH). δ_c (100 MHz; CDCl₃): 18.3 (CH₂, C-10'), 18.5 (CH₂, C-4'), 24.6 (CH₃, COCH₃), 26.4 (CH₂, C-9'), 31.3 (CH₂, C-3'), 34.5 (CH₂, C-5'), 34.6 (CH₂, C-11'), 66.4 (CH₂, 8'-CH₂O), 71.1 (CH, C-8'), 77.9 (CH, C-2'), 99.2 (C, C-6'), 111.4 (C, C-5), 141.5 (CH, C-8), 147.6 (C, C-2), 152.9 (C, C-6), 156.7 (C, C-4), 173.0 (C, NCOMe). m/z (FAB): 378 (MH⁺, 25%), 194 (100), 165 (28), 124 (53), 120 (75).

9-[(2'*S,6'*S**,8'*S**)-8'-(*tert*-Butyldiphenylsilyloxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl]adenosine (15i)**

M.p.: 65.5–66.9 °C. HRMS (FAB): found MH⁺, 558.2908, C₃₁H₄₀N₅O₃Si requires 558.2900. ν_{max} (film)/cm⁻¹: 3323 (N-H), 3164 (N-H), 2931 (C-H), 2856 (C-H), 1645 (C=O), 1698, 1427, 1228, 1112 (C-O), 980, 702. δ_H (300 MHz; CDCl₃): 1.08 (9 H, s, OSiPh₂^{*t*}Bu), 1.31–1.39 (1 H, m, 9'-H_A), 1.42–1.53 (1 H, m, 11'-H_A), 1.53–1.67 (3 H, m, 5'-H_A, 9'-H_B and 10'-H_A), 1.71–1.86 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.95–2.06 (1 H, m, 3'-H_A), 2.06–2.16 (1 H, m, 3'-H_B), 2.16–2.26 (1 H, m, 4'-H_B), 3.67 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 4.5, 8'-CH_AH_BO), 3.77 (1 H, dd, J_{AB} 10.4 and $J_{8'-CH_2,8'}$ 5.8, 8'-CH_AH_BO), 4.01–4.10 (1 H, m, 8'-H), 5.74 (2 H, br s, NH₂), 6.09 (1 H, dd, $J_{2'ax,3'ax}$ 10.8 and $J_{2'ax,3'eq}$ 2.8, 2'-H_{ax}), 7.34–7.42 (6 H, m, Ph), 7.73–7.79 (4 H, m, Ph), 8.01 (1 H, s, 8-H), 8.33 (1 H, s, 2-H). δ_c (75 MHz; CDCl₃): 18.1 (CH₂, C-10'), 18.3 (CH₂, C-4'), 19.3 (C, OSiPh₂^{*t*}Bu), 26.7 (CH₂, C-9'), 26.8 (CH₃, OSiPh₂^{*t*}Bu), 30.9 (CH₂, C-3'), 34.6 (CH₂, C-5'), 34.8 (CH₂, C-11'), 67.2 (CH₂, 8'-CH₂O),

70.9 (CH, C-8'), 76.4 (CH, C-2'), 98.8 (C, C-6'), 119.6 (CH, C-5), 127.6 (CH, Ph), 129.5 (CH, Ph), 129.5 (CH, Ph), 133.8 (C, Ph), 135.7 (CH, Ph), 138.8 (CH, C-8), 149.8 (C, C-4), 153.0 (CH, C-2), 155.3 (C, C-6). m/z (FAB): 558 (MH^+ , 20%), 500 ($M - ^iBu$, 15), 423 ($C_{26}H_{35}O_3Si$, 4), 137 (47), 136 (100), 135 (40).

9-((2'S*,6'S*,8'S*)-8'-(Hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)adenosine (11i)

M.p.: 81.2–82.7 °C. HRMS (FAB): found MH^+ , 320.1727, $C_{15}H_{22}N_5O_3$ requires 320.1723. ν_{max} (film)/ cm^{-1} : 3335br and 3194br (N–H and O–H), 2943 (C–H), 1651, 1600, 1227 (C–O), 1048, 980. δ_H (400 MHz; CD_3OD): 1.23–1.31 (1 H, m, 9'- H_A), 1.43–1.51 (1 H, m, 11'- H_A), 1.51–1.60 (2 H, m, 9'- H_B and 10'- H_A), 1.60–1.69 (1 H, m, 5'- H_A), 1.69–1.82 (4 H, m, 4'- H_A , 5'- H_B , 10'- H_B and 11'- H_B), 2.00–2.06 (1 H, m, 3'- H_A), 2.11–2.29 (2 H, m, 3'- H_B and 4'- H_B), 3.58 (1 H, dd, J_{AB} 11.6 and $J_{8'-CH_2,8'}$ 5.9, 8'- CH_AH_BO), 3.62 (1 H, dd, J_{AB} 11.6 and $J_{8'-CH_2,8'}$ 4.3, 8'- CH_AH_BO), 3.91–3.98 (1 H, m, 8'-H), 6.06 (1 H, dd, $J_{2'ax,3'ax}$ 10.8 and $J_{2'ax,3'eq}$ 2.5, 2'- H_{ax}), 8.20 (1 H, s, 2-H), 8.31 (1 H, s, 8-H). δ_C (100 MHz; CD_3OD): 19.3 (CH_2 , C-10'), 19.4 (CH_2 , C-4'), 27.7 (CH_2 , C-9'), 31.5 (CH_2 , C-3'), 35.6 (CH_2 , C-5'), 35.8 (CH_2 , C-11'), 66.7 (CH_2 , 8'- CH_2O), 72.3 (CH, C-8'), 77.6 (CH, C-2'), 100.4 (C, C-6'), 120.1 (CH, C-5), 140.8 (CH, C-8), 150.3 (C, C-4), 154.0 (CH, C-2), 157.4 (C, C-6). m/z (FAB): 320 (MH^+ , 100%), 275 (12), 185 (31), 169 (41), 120 (35).

9-((2'S*,6'S*,8'S*)-8'-(Hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)guanosine (11j)

HRMS (FAB): found MH^+ , 336.1664, $C_{15}H_{22}N_5O_4$ requires 336.1672. ν_{max} (film)/ cm^{-1} : 3412br (O–H and N–H), 2936 (C–H), 1693 (C=O), 1652, 1532, 1214 (C–O), 1182 (C–O), 978. δ_H (300 MHz; CD_3OD): 1.19–1.30 (1 H, m, 9'- H_A), 1.42–1.53 (1 H, m, 11'- H_A), 1.54–1.68 (3 H, m, 5'- H_A , 9'- H_B and 10'- H_A), 1.68–1.89 (4 H, m, 4'- H_A , 5'- H_B , 10'- H_B and 11'- H_B), 1.96–2.05 (1 H, m, 3'- H_A), 2.05–2.16 (1 H, m, 3'- H_B), 2.16–2.30 (1 H, m, 4'- H_B), 3.58 (1 H, dd, J_{AB} 11.3 and $J_{8'-CH_2,8'}$ 4.7, 8'- CH_AH_BO), 3.64 (1 H, dd, J_{AB} 11.3 and $J_{8'-CH_2,8'}$ 5.6, 8'- CH_AH_BO), 3.99–4.07 (1 H, m, 8'-H), 5.91 (1 H, dd, $J_{2'ax,3'ax}$ 10.8 and $J_{2'ax,3'eq}$ 2.7, 2'- H_{ax}), 7.92 (1 H, s, 8-H). δ_C (75 MHz; CD_3OD): 19.3 (CH_2 , C-10'), 19.4 (CH_2 , C-4'), 27.9 (CH_2 , C-9'), 31.1 (CH_2 , C-3'), 35.6 (CH_2 , C-5'), 35.9 (CH_2 , C-11'), 66.8 (CH_2 , 8'- CH_2O), 72.1 (CH, C-8'), 76.8 (CH, C-2'), 100.1 (C, C-6'), 117.5 (C, C-5), 137.4 (CH, C-8), 152.9 (C, C-4), 155.5 (C, C-2), 159.5 (C, C-6). m/z (FAB): 358 ($MH + Na$, 24%), 336 (MH^+ , 15), 185 ($C_{10}H_{17}O_3$, 14), 176 (21), 174 (46), 152 (100), 120 (29).

7-((2'S*,6'S*,8'S*)-8'-(Hydroxymethyl)-1',7'-dioxaspiro[5.5]undecan-2'-yl)guanosine (11k)

HRMS (FAB): found MH^+ , 336.1673, $C_{15}H_{22}N_5O_4$ requires 336.1672. ν_{max} (film)/ cm^{-1} : 3308br (N–H and O–H), 2923 (C–H), 1673 (C=O), 1459, 1392, 1220 (C–O), 1090, 977. δ_H (400 MHz; $CDCl_3$ with drops of CD_3OD): 1.12–1.19 (1 H, m, 9'-H_A), 1.38–1.57 (4 H, m, 5'-H_A, 9'-H_B, 10'-H_A and 11'-H_A), 1.64–1.79 (4 H, m, 4'-H_A, 5'-H_B, 10'-H_B and 11'-H_B), 1.79–1.88 (1 H, m, 3'-H_A), 2.01–2.09 (1 H, m, 3'-H_B), 2.09–2.20 (1 H, m, 4'-H_B), 3.49–3.58 (2 H, m, 8'-CH₂O), 3.83–3.89 (1 H, m, 8'-H), 6.18 (1 H, dd, $J_{2'ax,3'ax}$ 11.2 and $J_{2'ax,3'eq}$ 2.1, 2'-H_{ax}), 7.99 (1 H, br s, 8-H). δ_C (100 MHz; $CDCl_3$ with drops of CD_3OD): 18.4 (CH₂, C-10'), 18.5 (CH₂, C-4'), 26.7 (CH₂, C-9'), 31.7 (CH₂, C-3'), 34.6 (CH₂, C-5'), 34.8 (CH₂, C-11'), 66.2 (CH₂, 8'-CH₂O), 71.1 (CH, C-8'), 78.2 (CH, C-2'), 99.4 (C, C-6'), 125.9 (C, C-5), 141.2 (CH, C-8), 153.4 (C, C-4), 155.4 (C, C-2), 159.5 (C, C-6). m/z (FAB): 336 (MH^+ , 13%), 152 (100), 124 (63), 120 (81).

References

1. W. L. F. Armarego and D. D. Perrin, Purification of Laboratory Chemicals, 4th edn., Pergamon, Oxford, UK, 1997.