A Novel Method for the Synthesis of Dinucleoside Boranophosphates by a Boranophosphotriester Method

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General Information.

^1H NMR spectra were obtained at 300 MHz with tetramethylsilane (TMS) as an internal standard in CDCl_3 , with TMS as an internal standard in CD_3CN , and with 2,2,3,3- d_4 -3-(trimethylsilyl)propionic acid sodium salt (TSP- d_4) as an external standard in D_2O . ^{13}C NMR spectra were obtained at 75.45 MHz with CDCl_3 as an internal standard (δ 77.0) in CDCl_3 , with TMS as an external standard in CD_3CN , and with DSS as an external standard in D_2O . ^{31}P NMR spectra were obtained at 121.5 MHz using 85% H_3PO_4 as an external standard. Organic solvents were purified and dried by appropriate procedures.

***O*⁶-Diphenylcarbamoyl-*N*²-phenylacetyl-2'-deoxyguanosine.**

*N*²-Phenylacetyl-2'-deoxyguanosine (7.71 g, 20 mmol) was dried by repeated coevaporation with dry toluene followed by dry pyridine, and finally dissolved in dry CH₃CN (200 mL). To the solution was added hexamethyl disilazane (16.8 mL, 80 mmol). After being refluxed for 3 h, the reaction mixture was concentrated to dryness under reduced pressure, coevaporated with dry EtOH for two times, and then dissolved in dry pyridine (200 mL). To the solution were successively added 4-dimethylaminopyridine (244 mg, 2 mmol), *i*-Pr₂NEt (5.1 mL, 30 mmol), diphenylcarbamoyl chloride (5.56 g, 24 mmol). After being stirred at rt for 17 h, the mixture was diluted with MeOH (20 mL) and concentrated to dryness under reduced pressure. The mixture was dissolved in CHCl₃ (200 mL) and washed with phosphate buffer (pH 7.0, 3 x 200 mL), and the aqueous layer was back-extracted with CHCl₃ (3 x 100 mL). The organic layer and washings were combined, dried over Na₂SO₄, filtered, and concentrated to dryness under reduced pressure. To the solution of the residue was dissolved in MeOH-CHCl₃ (1:1, v/v, 200 mL) was added TFA (2 mL), and the solution was stirred at rt for 10 min. The mixture was diluted with CHCl₃ (100 mL) and washed with sat NaHCO₃ aq (3 x 200 mL), and the aqueous layer was back-extracted with CHCl₃ (5 x 100 mL). The organic layer and washings were combined, dried over Na₂SO₄, filtered, and concentrated until crystallization began. After the solution was cooled at 0 °C, filtration obtained *O*⁶-diphenylcarbamoyl-*N*²-phenylacetyl-2'-deoxyguanosine (10.12 g, 87 %) as a white powder: ¹H NMR (DMSO) δ 10.96 (1H, s), 8.65 (1H, s), 7.60-7.17 (15H, m), 6.35 (1H, t, *J* = 6.0Hz), 5.32 (1H, d, *J* = 3.0Hz), 4.89 (1H, t, *J* = 4.5Hz), 4.43 (1H, bs), 3.89-3.81 (1H, bs), 3.79 (2H, s), 3.65-3.45 (2H, m), 2.81-2.68 (1H, m), 2.36-2.25 (1H, m); ¹³C NMR (DMSO) δ 151.5, 137.5, 136.9, 134.5, 132.6, 126.8, 126.3, 124.1, 118.0, 112.9, 111.9, 111.8, 110.8, 109.8, 103.0, 70.7, 70.4, 66.2, 65.9, 53.1, 53.0, 44.0, 25.6, 22.8, 22.6, 22.3, 22.0, 21.7, 21.4, 21.2; IR (KBr) 3452, 2957, 1678, 1609, 1563, 1484, 1454, 1421, 1399, 1362, 1302, 1253, 1220, 1159, 1127, 1115, 1086, 1058,

1012, 951, 902, 848, 786, 731, 705, 644 cm^{-1} . Anal. Calcd. for $\text{C}_{31}\text{H}_{28}\text{N}_6\text{O}_6 \cdot 1/3\text{H}_2\text{O} \cdot 1/3\text{CHCl}_3$: C, 60.08; H, 4.67; N, 13.42. Found: C, 59.85; H, 4.55; N, 13.18.

5'-Dimethoxytrityl- O^6 -diphenylcarbamoyl- N^2 -phenylacetyl-2'-deoxyguanosine (1, $B^1 = O^6$ -diphenylcarbamoyl- N^2 -phenylacetylguanin-9-yl).

O^6 -Diphenylcarbamoyl- N^2 -phenylacetyl-2'-deoxyguanosine (8.71 g, 15 mmol) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (157.5 mL). To the solution was added DMTr-Cl (5.33 g, 15.75 mmol), and the solution was stirred at rt for 2 h. After concentrated to dryness under reduced pressure, the residue was dissolved in CHCl_3 (200 mL). The reaction mixture was washed with sat NaHCO_3 aq (3 x 200 mL), and the aqueous layer was back-extracted with CHCl_3 (3 x 200 mL). The organic layer and washings were combined, dried over Na_2SO_4 , filtered, and concentrated to dryness under reduced pressure. The residue was chromatographed on silica gel (150 g) using a gradient of MeOH (0-3%) in CH_2Cl_2 as an eluent. The fractions containing 5'-Dimethoxytrityl- O^6 -diphenylcarbamoyl- N^2 -phenylacetyl-2'-deoxyguanosine (1, $B^1 = O^6$ -diphenylcarbamoyl- N^2 -phenylacetylguanin-9-yl) were combined and concentrated to dryness under reduced pressure to obtain **1** ($B^1 = O^6$ -diphenylcarbamoyl- N^2 -phenylacetylguanin-9-yl) (11.76 g, 89%) as a colorless foam: ^1H NMR (CDCl_3) δ 8.10 (1H, s), 8.04 (1H, bs), 7.44-7.16 (24H, m), 6.76 (4H, d, $J = 9.0\text{Hz}$), 6.51 (1H, t, $J = 6.5\text{Hz}$), 4.72-4.65 (1H, m), 4.18-4.12 (1H, m), 3.88 (2H, s), 3.71 (6H, s), 3.42-3.30 (2H, m), 3.07 (1H, bs), 2.73-2.62 (1H, m), 2.58-2.48 (1H, m); ^{13}C NMR (CDCl_3) δ 169.6, 158.5, 155.9, 154.4, 151.5, 150.4, 144.5, 142.7, 141.7, 135.7, 135.6, 133.8, 130.0, 130.0, 129.5, 129.1, 128.9, 128.1, 127.8, 127.4, 126.9, 125.7, 121.7, 113.1, 86.5, 84.4, 72.3, 63.9, 55.2, 44.4, 40.6; IR (KBr) 3407, 3062, 2933, 2837, 1742, 1620, 1509, 1493, 1446, 1410, 1335, 1303, 1251, 1185, 1062, 1033, 1004, 985, 939, 830, 790, 757, 700, 645 cm^{-1} . Anal. Calcd. for $\text{C}_{52}\text{H}_{46}\text{N}_6\text{O}_8 \cdot \text{H}_2\text{O} \cdot 0.5\text{CHCl}_3$: C, 65.31; H, 4.93; N, 8.68. Found: C, 65.33; H, 4.83; N, 8.68.

5'-*O*-Dimethoxytrityl-*N*⁴-benzoyl-2'-deoxycytidin-3'-yl dimethyl boranophosphate (3, B¹ = *N*⁴-benzoylcytosin-1-yl).

¹H NMR (CDCl₃) δ 8.66 (1H, bs), 8.19 (1H, d, *J* = 7.5 Hz), 7.94-7.18 (15H, m), 6.86 (4H, d, *J* = 4.2 Hz), 6.34 (1H, t, *J* = 6.5 Hz), 5.16-5.06 (1H, m), 4.39-4.32 (1H, m), 3.80 (6H, s), 3.72, 3.68 (3H, 2d, *J*_{POCH} = 9.0 Hz and 9.0 Hz), 3.51-3.47 (2H, m), 2.96-2.85 (1H, m), 2.42-2.30 (1H, m), 1-0 (3H, bq); ¹³C NMR (CDCl₃) δ 162.1, 158.7, 144.3, 143.8, 135.1, 134.9, 133.2, 130.1, 130.0, 129.9, 129.1, 128.1, 127.5, 127.3, 113.4, 113.3, 96.4, 87.2, 87.1, 87.0, 85.5, 62.5, 62.4, 55.3, 55.2, 53.4, 53.3, 53.2, 40.8; ³¹P NMR (CDCl₃) δ 119.8-116.4 (m). IR (KBr) 3434, 2954, 2838, 2400, 1698, 1663, 1609, 1561, 1509, 1486, 1446, 1396, 1303, 1253, 1178, 1116, 1033, 830, 756, 705 cm⁻¹. Anal. Calcd. for C₃₉H₄₃BN₃O₉P·H₂O: C, 61.83; H, 5.99; N, 5.55. Found: C, 61.61; H, 5.84; N, 5.79.

5'-*O*-Dimethoxytrityl-*O*⁶-diphenylcarbamoyl-*N*²-phenylacetyl-2'-deoxyguanosin-3'-yl methyl 2-(trimethylsilyl)ethyl boranophosphate (19, B¹ = *O*⁶-diphenylcarbamoyl-*N*²-phenylacetylguanin-9-yl).

¹H NMR (CDCl₃) δ 8.10 (1H, s), 7.91 (1H, bs), 7.46-7.14 (24H, m), 6.78 (4H, d, *J* = 9.0 Hz), 6.41 (1H, t, *J* = 7.5 Hz), 5.21 (1H, m), 4.32 (1H, m), 4.18-4.06 (2H, m), 3.98 (2H, s), 3.74 (6H, s), 3.69, 3.65 (3H, 2d, *J*_{POCH} = 9.0 Hz and 9.0 Hz), 3.46-3.31 (2H, m), 2.97-2.82 (1H, m), 2.74-2.60 (1H, m), 1.11-1.01 (2H, m), 1-0 (3H, bq), 0.04, 0.03 (9H, 2s); ³¹P NMR (CDCl₃) δ 119.02-115.61 (m). Anal. Calcd. for C₅₈H₆₄BN₆O₁₀PSi: C, 64.80; H, 6.00; N, 7.82. Found: C, 64.85; H, 5.91; N, 7.90.

Triethylammonium 5'-*O*-dimethoxytrityl-*N*⁴-benzoyl-2'-deoxycytidin-3'-yl methyl boranophosphate (4, B¹ = *N*⁴-benzoylcytosin-1-yl).

¹H NMR (CDCl₃) δ 12.50 (1H, bs), 8.70 (1H, bs), 8.24 (1H, q, *J* = 7.0 Hz), 7.90, 7.87 (2H, 2m), 7.65-7.11 (13H, m), 6.94-6.79 (4H, m), 6.36-6.26 (1H, m), 5.04 (1H, m), 4.41-4.31 (1H, m), 3.79, 3.78 (6H,

2s), 3.48, 3.44 (3H, 2d, $J_{\text{POCH}} = 12.0$ Hz and 12.0 Hz), 3.52-3.44 (2H, m), 3.04 (6H, q, $J = 7.0$ Hz), 2.90-2.78 (1H, m), 2.41-2.28 (1H, m), 1.31 (9H, t, $J = 7.5$ Hz), 1-0 (3H, bq); ^{13}C NMR (CDCl_3) δ 161.9, 158.6, 144.9, 144.1, 144.0, 135.5, 135.4, 135.3, 135.2, 133.0, 130.1, 129.0, 128.2, 128.0, 127.5, 127.1, 126.6, 113.3, 113.2, 109.7, 109.5, 96.2, 87.4, 87.2, 86.9, 86.8, 86.1, 85.7, 72.9, 72.7, 72.1, 71.9, 62.8, 55.2, 55.1, 50.3, 50.1, 45.4, 45.3, 41.4, 8.6, 8.5, 8.4; ^{31}P NMR (CDCl_3) δ 98.93-93.67 (m). IR (KBr) 3424, 2942, 2838, 2679, 2363, 1698, 1655, 1608, 1562, 1486, 1395, 1303, 1253, 1177, 1116, 1071, 1033, 915, 831, 790, 757, 706, 660 cm^{-1} . Anal. Calcd. for $\text{C}_{44}\text{H}_{56}\text{BN}_4\text{O}_9\text{P} \cdot 2.5\text{H}_2\text{O}$: C, 60.62; H, 7.05; N, 6.43. Found: C, 60.85; H, 6.79; N, 6.47.

Tributylammonium 5'-*O*-dimethoxytrityl-*O*⁶-diphenylcarbamoyl-*N*²-phenylacetyl-2'-deoxyguanosin-3'-yl methyl boranophosphate (20, $\text{B}^1 = \text{O}^6$ -diphenylcarbamoyl-*N*²-phenylacetylguanine-9-yl).

^1H NMR (CDCl_3) δ 12.52 (1H, bs), 8.08 (1H, bs), 8.02 (1H, d, $J = 9.0$ Hz), 7.51-7.09 (24H, m), 6.75 (4H, d, $J = 9.0$ Hz), 6.45, 6.41 (1H, dd, $J_{1',2'}/J_{1',2''} = 6.3$ Hz and 12.9 Hz), 5.10 (1H, m), 4.37 (1H, d, $J = 15.0$ Hz), 4.02 (2H, s), 3.69 (6H, s), 3.49, 3.42 (3H, 2d, $J_{\text{POCH}} = 12.0$ Hz and 9.0 Hz), 3.38-3.28 (2H, m), 2.93-2.80 (6H, m), 2.82-2.63 (2H, m), 1.71-1.52 (6H, m), 1.33 (6H, q, $J = 8.0$ Hz), 0.92 (9H, t, $J = 7.5$ Hz), 1-0 (3H, bq); ^{13}C NMR (CDCl_3) δ 170.0, 158.3, 155.8, 154.5, 151.6, 150.3, 144.4, 142.4, 142.3, 141.6, 135.6, 135.5, 134.2, 130.1, 129.9, 129.4, 129.3, 129.1, 129.0, 128.7, 128.6, 128.0, 127.7, 127.0, 126.7, 126.0, 125.5, 121.2, 121.1, 113.5, 113.0, 86.4, 86.3, 86.2, 86.1, 85.7, 85.6, 84.4, 84.2, 73.9, 73.6, 63.8, 63.7, 55.0, 51.5, 50.0, 49.9, 49.8, 49.7, 43.7, 40.0, 39.8, 24.9, 20.0, 13.5; ^{31}P NMR (CDCl_3) δ 99.09-93.23 (m). IR (KBr) 3442, 2961, 2874, 2838, 2363, 1743, 1619, 1509, 1494, 1455, 1384, 1335, 1303, 1251, 1223, 1185, 1065, 1033, 987, 943, 831, 789, 758, 701, 645 cm^{-1} . Anal. Calcd. for $\text{C}_{65}\text{H}_{79}\text{BN}_7\text{O}_{10}\text{P}$: C, 67.29; H, 6.86; N, 8.45. Found: C, 67.00; H, 6.98; N, 8.22.

5'-O-Dimethoxytrityl-*N*⁴-benzoyl-2'-deoxycytidin-3'-yl 3'-O,*N*³-dibenzoylthymidin-5'-yl methyl boranophosphate (6, B¹ = *N*⁴-benzoylcytosin-1-yl, B² = *N*³-benzoylthymin-1-yl).

¹H NMR (CDCl₃) δ 8.69 (1H, bs), 8.20-8.13 (1H, m), 8.06-7.16 (26H, m), 6.91-6.82 (4H, m), 6.54-6.46 (1H, m), 6.34 (1H, t, *J* = 6.0 Hz), 5.55-5.40 (1H, m), 5.23-5.14 (1H, m), 4.52-4.24 (4H, m), 3.93-3.64 (9H, m), 3.56-3.46 (2H, m), 3.06-2.89 (1H, m), 2.69-2.52 (1H, m), 2.47-2.25 (1H, m), 2.03, 2.00 (3H, 2s), 1-0 (3H, bq); ¹³C NMR (CDCl₃) δ 168.7, 166.0, 162.6, 162.2, 158.7, 149.4, 144.3, 143.8, 130.5, 130.0, 129.7, 129.1, 128.9, 128.8, 128.6, 128.4, 128.0, 127.5, 127.2, 113.4, 112.1, 96.4, 87.3, 87.0, 85.7, 85.4, 84.7, 84.6, 82.8, 78.1, 77.8, 74.7, 65.9, 65.4, 64.8, 62.7, 62.5, 55.2, 54.2, 54.0, 40.9, 40.7, 37.3, 37.2, 29.7, 14.0, 12.6; ³¹P NMR (CDCl₃) δ 121.21-117.55 (m). IR (KBr) 3441, 2953, 2837, 2401, 1751, 1703, 1663, 1561, 1509, 1485, 1448, 1397, 1300, 1254, 1178, 1110, 1071, 1031, 828, 763, 714 cm⁻¹. Anal. Calcd. for C₆₂H₆₁BN₅O₁₅P·2/3CHCl₃: C, 60.82; H, 5.02; N, 5.66. Found: C, 60.42; H, 5.15; N, 5.59.

5'-O-Dimethoxytrityl-*O*⁶-diphenylcarbamoyl-*N*²-phenylacetyl-2'-deoxyguanosin-3'-yl 3'-O,*N*³-dibenzoylthymidin-5'-yl methyl boranophosphate (6, B¹ = *O*⁶-diphenylcarbamoyl-*N*²-phenylacetylguanin-9-yl, B² = *N*³-benzoylthymin-1-yl).

¹H NMR (CDCl₃) δ 8.13-7.11 (36H, m), 6.82-6.71 (4H, m), 6.55-6.36 (2H, m), 5.54-5.42 (1H, m), 5.38-5.28 (1H, m), 4.50-4.20 (4H, m), 3.89-3.64 (11H, m), 3.52-3.34 (2H, m), 3.08-2.88 (1H, m), 2.79-2.67 (1H, m), 2.67-2.50 (1H, m), 2.43-2.21 (1H, m), 2.03, 2.01 (3H, 2s), 1-0 (3H, bq); ¹³C NMR (CDCl₃) δ 168.7, 166.0, 162.6, 158.6, 156.0, 154.3, 151.8, 150.3, 149.4, 144.2, 143.9, 142.4, 142.2, 141.7, 135.3, 135.1, 134.7, 134.6, 134.0, 133.8, 132.1, 131.4, 130.4, 130.0, 129.6, 129.5, 129.4, 129.1, 128.8, 128.6, 128.0, 127.9, 127.3, 127.0, 125.6, 121.6, 113.2, 112.1, 112.0, 86.8, 85.2, 84.9, 84.7, 84.5, 84.3, 83.0, 78.5, 78.3, 74.8, 66.0, 65.6, 63.2, 55.1, 54.3, 54.2, 44.2, 39.0, 37.3, 37.1, 12.6; ³¹P NMR (CDCl₃) δ 120.94-117.46 (m). IR (KBr) 3440, 2952, 2837, 2401, 1750, 1705, 1664, 1622, 1509, 1493,

1450, 1396, 1272, 1179, 1109, 1032, 831, 790, 761, 700 cm^{-1} . Anal. Calcd. for $\text{C}_{77}\text{H}_{72}\text{BN}_8\text{O}_{16}\text{P}\cdot 1/3\text{CHCl}_3$: C, 64.19; H, 5.04; N, 7.74. Found: C, 64.26; H, 5.23; N, 7.64.

5'-O-Dimethoxytrityl- N^3 -benzoylthymidin-3'-yl 3'-O, N^3 -dibenzoylthymidin-5'-yl methyl boranophosphate (6, $\text{B}^1 = \text{B}^2 = N^3$ -benzoylthymidin-1-yl).

^1H NMR (CDCl_3) δ 8.00-7.26 (26H, m), 6.90-6.83 (4H, m), 6.49-6.41 (2H, m), 5.51-5.35 (1H, m), 5.30-5.23 (1H, m), 4.47-4.19 (4H, m), 3.49, 3.72 (3H, 2d, $J_{\text{POCH}} = 12.0$ Hz and 12.0 Hz), 3.80-3.77 (6H, m), 3.55-3.46 (2H, m), 2.73-2.21 (4H, m), 2.00, 1.99 (3H, 2s), 1.51, 1.50 (3H, 2s), 1-0 (3H, bq); ^{13}C NMR (CDCl_3) δ 168.8, 168.7, 166.0, 162.6, 162.5, 158.8, 149.3, 149.2, 143.9, 135.0, 134.9, 134.6, 134.5, 133.7, 131.4, 130.8, 130.4, 130.0, 129.7, 129.1, 128.7, 128.5, 128.1, 128.0, 127.3, 113.4, 112.1, 112.0, 111.7, 111.6, 87.4, 84.9, 84.8, 84.7, 84.6, 84.5, 82.9, 82.8, 82.7, 78.8, 78.7, 78.6, 78.5, 74.5, 65.8, 65.5, 63.3, 63.2, 55.2, 54.1, 39.7, 39.5, 37.2, 37.0, 12.5, 11.8; ^{31}P NMR (CDCl_3) δ 121.18-117.40 (m). IR (KBr) 3448, 2954, 2837, 2401, 1751, 1705, 1664, 1601, 1509, 1447, 1396, 1366, 1254, 1178, 1108, 1071, 1032, 914, 829, 791, 763, 715, 687 cm^{-1} . Anal. Calcd. for $\text{C}_{63}\text{H}_{62}\text{BN}_4\text{O}_{16}\text{P}\cdot 2\text{CHCl}_3$: C, 61.28; H, 5.38; N, 4.40. Found: C, 61.02; H, 5.10; N, 4.45.

5'-O-Dimethoxytrityl- N^3 -benzoylthymidin-3'-yl 3'-O-*t*-butyldimethylsilyl- N^4 -benzoylcytidin-5'-yl methyl boranophosphate (6, $\text{B}^1 = N^3$ -benzoylthymidin-1-yl, $\text{B}^2 = N^4$ -benzoylcytosin-1-yl).

^1H NMR (CDCl_3) δ 9.00-8.65 (1H, bs), 8.09-7.22 (23H, m), 6.91-6.82 (4H, m), 6.49-6.41 (1H, m), 6.26-6.19 (1H, m), 5.31-5.20 (1H, m), 4.39-4.00 (5H, m), 3.79 (6H, s), 3.75, 3.67 (3H, 2d, $J_{\text{POCH}} = 11.1$ Hz and 11.4 Hz), 3.62-3.46 (2H, m), 2.71-2.45 (3H, m), 2.25-2.21 (1H, m), 1.50, 1.47 (3H, 2s), 0.88, 0.86 (9H, 2s), 0.10-0.04 (6H, m), 1-0 (3H, bq); ^{13}C NMR (CDCl_3) δ 168.8, 162.6, 162.2, 158.7, 154.5, 149.2, 143.9, 134.9, 133.0, 131.4, 130.8, 130.3, 129.9, 129.4, 129.0, 128.8, 128.7, 128.2, 128.0, 127.9, 127.5, 127.2, 113.3, 111.6, 111.5, 96.6, 87.3, 86.9, 85.1, 84.9, 84.8, 84.4, 78.5, 78.3, 70.2, 68.0, 64.7, 63.1, 55.2, 53.7, 41.4, 39.5, 39.4, 38.6, 30.2, 29.5, 28.8, 25.5, 23.6, 22.8, 17.8, 13.9, 11.7, 10.8, -4.8, -

5.1; ^{31}P NMR (CDCl_3) δ 121.86-117.78 (m). Anal. Calcd. for $\text{C}_{61}\text{H}_{71}\text{BN}_5\text{O}_{14}\text{PSi}\cdot 2/3\text{CHCl}_3$: C, 59.36; H, 5.79; N, 5.61. Found: C, 59.53; H, 5.89; N, 5.55.

5'-*O*-Dimethoxytrityl- N^3 -benzoylthymidin-3'-yl 3'-*O*-benzoyl- N^6 -diphenylcarbamoyl- N^2 -phenylacetyl-2'-deoxyguanosin-5'-yl methyl boranophosphate (6, $\text{B}^1 = N^3$ -benzoylthymidin-1-yl, $\text{B}^2 = N^6$ -diphenylcarbamoyl- N^2 -phenylacetylguanin-9-yl).

^1H NMR (CDCl_3) δ 8.20-7.18 (37H, m), 6.89-6.80 (4H, m), 6.48-6.35 (2H, m), 5.82-5.69 (1H, m), 5.26-5.16 (1H, m), 4.45-4.37 (2H, m), 4.28, 4.20 (2H, 2s), 3.92 (2H, s), 3.79-3.74 (6H, m), 3.48-3.38 (2H, m), 3.30-3.13 (1H, m), 2.76-2.35 (3H, m), 1.48-1.43 (3H, m), 1-0 (3H, bq); ^{13}C NMR (CDCl_3) δ 169.0, 165.9, 165.8, 162.8, 158.8, 156.1, 154.3, 151.7, 150.3, 149.3, 144.8, 144.0, 142.9, 142.8, 141.6, 135.2, 135.0, 133.8, 133.6, 131.5, 130.5, 130.0, 129.7, 129.5, 129.1, 129.0, 128.5, 128.1, 128.0, 127.4, 127.2, 127.0, 121.8, 113.4, 111.6, 87.3, 85.0, 84.9, 84.7, 84.6, 83.7, 83.6, 78.2, 74.9, 66.1, 63.3, 63.2, 55.3, 53.7, 44.5, 44.5, 39.6, 39.4, 36.7, 11.8, 0.0; ^{31}P NMR (CDCl_3) δ 120.50-117.06 (m). Anal. Calcd. for $\text{C}_{77}\text{H}_{72}\text{BN}_8\text{O}_{16}\text{P}\cdot 1/2\text{CHCl}_3$: C, 63.45; H, 4.98; N, 7.64. Found: C, 63.71; H, 5.25; N, 7.62.

Triethylammonium 2'-deoxyadenosin-3'-yl thymidin-5'-yl boranophosphate (27, $\text{B}^1 = \text{adenin-9-yl}$, $\text{B}^2 = \text{thymidin-1-yl}$).

^1H NMR (D_2O) δ 8.22 (1H, s), 8.08 (1H, s), 7.55, 7.45 (1H, 2s), 6.33 (1H, t, $J = 6.0$ Hz), 6.20, 6.15 (1H, dd, $J_{1',2'}/J_{1',2''} = 6.8$ Hz and 13.4 Hz), 5.03-4.93 (1H, m), 4.56-4.48 (1H, m), 4.33-4.24 (1H, m), 4.15-4.04 (2H, m), 3.90-3.75 (2H, m), 3.58, 3.55 (1H, 2s), 3.18 (6H, q, $J = 7.0$ Hz), 2.88-2.60 (2H, m), 2.32-2.23 (2H, m), 1.71 (3H, s), 1.26 (9H, t, $J = 7.5$ Hz), 1-0 (3H, bq); ^{13}C NMR (D_2O) δ 168.6, 168.5, 157.8, 154.5, 154.0, 150.9, 150.6, 143.3, 142.9, 139.6, 139.4, 121.6, 113.9, 113.8, 89.8, 89.7, 89.6, 89.4, 89.3, 89.2, 89.1, 87.9, 87.8, 87.7, 87.6, 87.5, 87.1, 76.4, 76.1, 75.0, 72.9, 65.5, 64.3, 63.9, 63.8, 57.8, 52.8, 52.8, 49.4, 42.6, 41.6, 41.5, 41.3, 33.0, 28.3, 17.5, 14.4, 14.2, 13.4, 11.4, 10.9; ^{31}P NMR (D_2O)

δ 95.88-90.73 (m). FAB⁺ m/z calcd for C₂₀H₃₀BN₇O₉P [M+H]⁺ 554.1936, found 554.1923. UV (H₂O)

$\lambda_{\max}$: 261.2 nm; $\epsilon_{261.2}$: 21800.

Triethylammonium 2'-deoxycytidin-3'-yl thymidin-5'-yl boranophosphate (27, B¹ = cytosine-1-yl, B² = thymine-1-yl).

¹H NMR (D₂O) δ 7.92-7.90 (1H, m), 7.72, 7.66 (1H, 2s), 6.31, 6.26 (1H, dd, $J_{1',2'}/J_{1',2''}$ = 7.1 Hz and 14.3 Hz), 6.18 (1H, t, J = 7.5 Hz), 6.07, 6.04 (1H, 2m), 4.90-4.82 (1H, m), 4.58-4.51 (1H, m), 4.22-4.00 (4H, m), 3.88-3.71 (2H, m), 3.19 (6H, q, J = 7.0 Hz), 2.61-2.28 (4H, m), 1.90 (3H, s), 1.27 (9H, t, J = 7.5 Hz), 1-0 (3H, bq); ¹³C NMR (D₂O) δ 169.1, 169.0, 166.4, 156.9, 154.3, 145.1, 140.0, 139.9, 114.2, 114.1, 98.4, 89.1, 88.8, 88.2, 88.1, 87.8, 87.6, 75.3, 74.6, 73.5, 73.4, 65.5, 64.4, 64.3, 63.5, 49.4, 41.7, 41.5, 41.4, 14.6, 14.5, 11.0; ³¹P NMR (D₂O) δ 95.56-90.36 (m). FAB⁺ m/z calcd for C₁₉H₃₀BN₅O₁₀P [M+H]⁺ 530.1823, found 530.1837. UV (H₂O) $\lambda_{\max}$: 269.6 nm; $\epsilon_{269.6}$: 15700.

O6-diphenylcarbamoyl-N2-phenylacetyl-2'-deoxyguanosine

1H NMR spectrum (DMSO-d4)

¹³C NMR spectrum (DMSO-d₄)

1 (B¹ = O6-diphenylcarbamoyl-N²-phenylacetylguanine-9-yl)

¹H NMR spectrum (CDCl₃)

¹³C NMR spectrum (CDCl₃)

^1H NMR spectrum (CDCl_3) ^{13}C NMR spectrum (CDCl_3) ^{31}P NMR spectrum (CDCl_3)

17

¹H NMR spectrum (CDCl₃) ¹³C NMR spectrum (CDCl₃) ³¹P NMR spectrum (CDCl₃)

1 (B¹ = N6-benzoyladenine-9-yl)

¹³C NMR spectrum (CDCl₃)

¹H NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

1 (B' = N4-benzoylcytosin-1-yl)

¹H NMR spectrum (CDCl₃) ¹³C NMR spectrum (CDCl₃) ³¹P NMR spectrum (CDCl₃)

19 (B¹ = N³-benzoylthymine-1-yl)

¹H NMR spectrum (CDCl₃)

¹³C NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

19 (B¹ = O6-diphenylcarbamoyl-N²-phenylacetylguanine-9-yl)

¹H NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

4 (B¹ = N6-benzoyladenine-9-yl)¹H NMR spectrum (CDCl₃) ¹³C NMR spectrum (CDCl₃) ³¹P NMR spectrum (CDCl₃)

4 (B¹ = N4-benzoylcytosin-1-yl)¹H NMR spectrum (CDCl₃) ¹³C NMR spectrum (CDCl₃) ³¹P NMR spectrum (CDCl₃)

20 (B¹ = O⁶-diphenylcarbamoyl-N²-phenylacetylguanine-9-yl) ¹³C NMR spectrum (CDCl₃)¹H NMR spectrum (CDCl₃) ³¹P NMR spectrum (CDCl₃)

20 (B¹ = N³-benzoylthymine-1-yl)¹H NMR spectrum (CDCl₃) ¹³C NMR spectrum (CDCl₃) ³¹P NMR spectrum (CDCl₃)

6 (B¹ = N6-benzoyladenine-9-yl, B² = N3-benzoylthymine-1-yl)

¹H NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

6 (B¹ = N4-benzoylcytosin-1-yl, B² = N3-benzoylthymine-1-yl

6 (B¹ = O6-diphenylcarbamoyl-N2-phenylacetylguanin-9-yl, $\square$
 B² = N3-benzoylthymine-1-yl)

¹³C NMR spectrum (CDCl₃)

¹H NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

6 (B¹ = B² = N³-benzoylthymine-1-yl)

¹H NMR spectrum (CDCl₃)

¹³C NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

6 (B¹ = N3-benzoylthymine-1-yl, B² = N6-benzoyladenine-9-yl)

¹H NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

6 (B¹ = N3-benzoylthymine-1-yl, B² = N4-benzoylcytosine-1-yl)

¹³C NMR spectrum (CDCl₃)

¹H NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

6 (B^1 = N³-benzoylthymine-1-yl, B^2 = O⁶-diphenylcarbamoyl-N²-phenylacetylguanine-9-yl)

¹H NMR spectrum (CDCl₃)

¹³C NMR spectrum (CDCl₃)

³¹P NMR spectrum (CDCl₃)

27 (B¹ = B² = thimin-1-yl)¹H NMR spectrum (D₂O) ¹³C NMR spectrum (D₂O) ³¹P NMR spectrum (D₂O)

6 (B¹ = adenin-9-yl, B² = thymine-1-yl)

¹H NMR spectrum (D₂O)

¹³C NMR spectrum (D₂O)

³¹P NMR spectrum (D₂O)

6 (B¹ = cytosin-1-yl, B² = thymine-1-yl)¹H NMR spectrum (D₂O) ¹³C NMR spectrum (D₂O) ³¹P NMR spectrum (D₂O)

6 (B¹ = guanine-9-yl, B² = thymine-1-yl)

¹H NMR spectrum (D₂O)

¹³C NMR spectrum (D₂O)

³¹P NMR spectrum (D₂O)