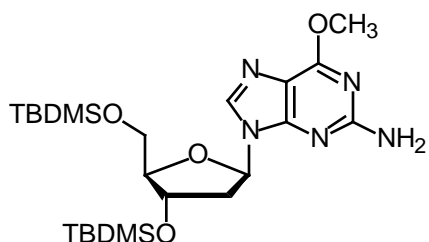


Thin-layer chromatography was performed on 250 μ silica plates, while column chromatographic purifications were performed on 200-300 mesh silica gel. All reagents were obtained from commercial sources and used without further purification. Compound **2** was prepared as described in the literature.⁷ NMR spectra were recorded at 500 MHz in deacidified CDCl₃. Deacidification was performed by percolating the solvent through a bed of solid NaHCO₃ and basic alumina. Chemical shifts (δ) are in ppm and coupling constants (J) are in Hz.

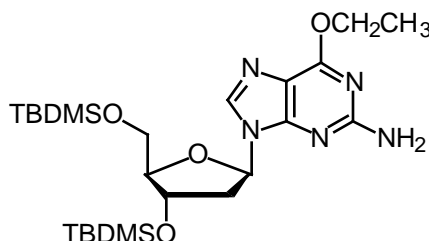
***O*⁶-Methyl-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4a**



Colorless solid, R_f (silica/CH₂Cl₂) = 0.38. ¹H NMR: 7.92 (s, 1H₈), 6.33 (t, 1H_{1'}, J = 6.5), 4.84 (s, 2H, NH₂), 4.60 (m, 1H_{3'}), 4.07 (s, 3H, OCH₃), 3.98 (app q, 1H_{4'}, J_{app} = 3.9), 3.82 (dd, 1H_{5'}, J = 4.3, 11.1), 3.76 (dd, 1H_{5'}, J = 3.2, 11.1), 2.58 (app quint, 1H_{2'}, J_{app} = 6.8), 2.36 (ddd, 1H_{2'}, J = 3.8, 6.1, 13.0), 0.92 (s, 18H, *tert*-Bu), 0.11, 0.09, 0.08 (3s, 12H,

SiCH₃). HRMS Calcd for C₂₃H₄₄N₅O₄Si₂ (M⁺ + 1): 510.2932, found: 510.2946.

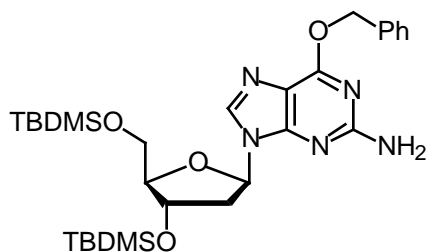
***O*⁶-Ethyl-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4b**



Colorless solid, R_f (silica/1% MeOH in CH₂Cl₂) = 0.23. ¹H NMR: 7.91 (s, 1H₈), 6.33 (t, 1H_{1'}, J = 6.6), 4.80 (s, 2H, NH₂), 4.59 (m, 1H_{3'}), 4.55 (q, 2H, OCH₂, J = 7.1), 3.98 (app q, 1H_{4'}, J_{app} = 3.5), 3.82 (dd, 1H_{5'}, J = 4.3, 11.1), 3.76 (dd, 1H_{5'}, J = 3.2, 11.1), 2.58 (app quint, 1H_{2'}, J_{app} = 6.5), 2.36 (ddd, 1H_{2'}, J = 3.7, 6.1, 13.0), 0.92 (s, 18H, *tert*-Bu), 0.11-

0.09(3s, 12H, SiCH₃). HRMS Calcd for C₂₄H₄₆N₅O₄Si₂ (M⁺ + 1): 524.3088, found: 524.3076.

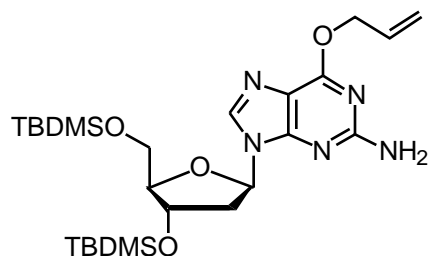
***O*⁶-Benzyl-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4c**



Clear crystalline solid, R_f (silica/2.5% MeOH in CH₂Cl₂) = 0.66. ¹H NMR: 7.95 (s, 1H₈), 7.50 (d, 2H, ArH, J = 8.3), 7.33 (m, 3H, ArH), 6.34 (t, 1H_{1'}, J = 6.4), 5.59 (d, 1H, OCH₂, J = 12.3), 5.56 (d, 1H, OCH₂, J = 12.3), 5.06 (s, 2H, NH₂), 4.59 (m, 1H_{3'}), 3.98 (app q, 1H_{4'}, J_{app} = 3.2), 3.83 (dd, 1H_{5'}, J = 4.2, 11.2), 3.75 (dd, 1H_{5'}, J = 3.1, 11.2), 2.55 (app

quint, 1H₂, $J_{\text{app}} = 6.0$), 2.38 (ddd, 1H₂, $J = 4.0, 6.1, 13.1$), 0.913, 0.908 (2s, 18H, *tert*-Bu), 0.10-0.08 (3s, 12H, SiCH₃). HRMS Calcd for C₂₉H₄₈N₅O₄Si₂ (M⁺ + 1): 586.3245, found: 586.3224.

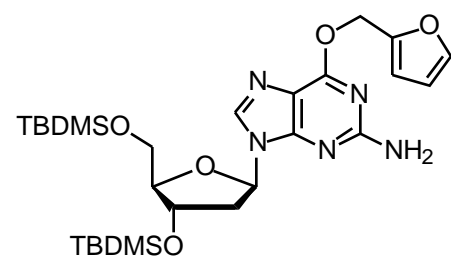
*O*⁶-Allyl-3',5'-bis-*O*-*tert*-butyldimethylsilyl-2'-deoxyguanosine 4d



White solid, R_f (silica/CH₂Cl₂) = 0.10. ¹H NMR: 7.91 (s, 1H₈), 6.32 (d, 1H₁, $J = 6.5$), 6.13 (tdd, 1H, =CH, $J = 5.7, 10.4, 17.2$), 5.33 (dd, 1H, =CH_{trans}, $J = 1.5, 17.2$), 5.26 (dd, 1H, =CH_{cis}, $J = 1.5, 10.4$), 5.01 (d, 2H, OCH₂, $J = 5.7$), 4.82 (s, 2H, NH₂), 4.59 (m, 1H_{3'}), 3.98 (app q, 1H_{4'}, $J_{\text{app}} = 3.3$), 3.81 (dd, 1H_{5'}, $J = 4.3, 11.1$), 3.75 (dd, 1H_{5'}, $J = 3.2, 11.1$), 2.56

(app quint, 1H₂, $J_{\text{app}} = 6.0$), 2.35 (ddd, 1H₂, $J = 3.7, 6.1, 13.1$), 0.913, 0.910 (2s, 18H, *tert*-Bu), 0.11, 0.080, 0.075 (3s, 12H, SiCH₃). HRMS Calcd for C₂₅H₄₆N₅O₄Si₂ (M⁺ + 1): 536.3088, found: 536.3074.

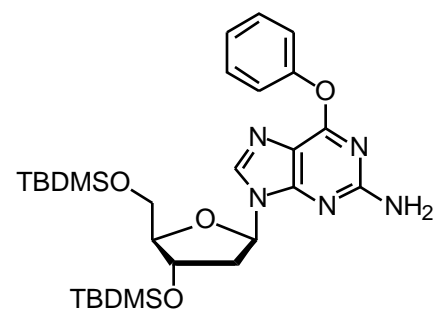
*O*⁶-(2-Furylmethyl)-3',5'-bis-*O*-*tert*-butyldimethylsilyl-2'-deoxyguanosine 4e



Yellow waxy solid, R_f (silica/2% MeOH in CH₂Cl₂) = 0.65. ¹H NMR: 7.91 (s, 1H₈), 7.41 (dd, 1H_{furan}, $J = 0.7, 1.8$), 6.48 (d, 1H_{furan}, $J = 3.2$), 6.35 (m, 1H_{furan}), 6.31 (t, 1H₁, $J = 6.6$), 5.51 (d, 1H, OCH₂, $J = 13.0$), 5.48 (d, 1H, OCH₂, $J = 13.0$), 4.86 (s, 2H, NH₂), 4.59 (m, 1H_{3'}), 3.97 (app q, 1H_{4'}, $J_{\text{app}} = 3.2$), 3.81 (dd, 1H_{5'}, $J = 4.3, 11.2$), 3.75 (dd, 1H_{5'},

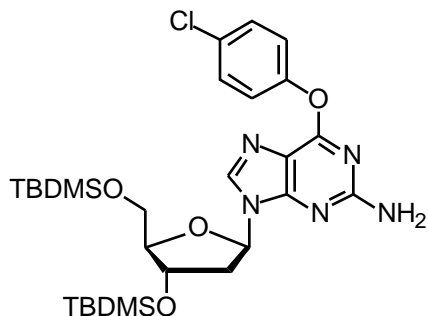
$J = 3.2, 11.2$), 2.55 (app quint, 1H₂, $J_{\text{app}} = 6.0$), 2.34 (ddd, 1H₂, $J = 3.8, 6.0, 13.1$), 0.914, 0.908 (2s, 18H, *tert*-Bu), 0.10, 0.08, 0.07 (3s, 12H, SiCH₃). HRMS Calcd for C₂₇H₄₆N₅O₅Si₂ (M⁺ + 1): 576.3037, found: 576.3030.

*O*⁶-Phenyl-3',5'-bis-*O*-*tert*-butyldimethylsilyl-2'-deoxyguanosine 4f



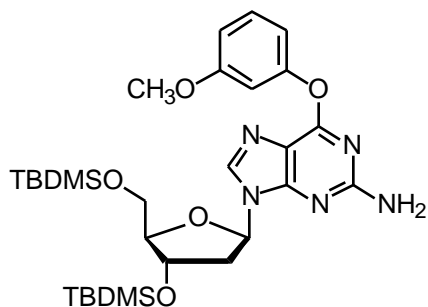
Colorless solid, R_f (silica/CH₂Cl₂) = 0.42. ¹H NMR: 8.02 (s, 1H₈), 7.41 (t, 1H, ArH, $J = 3.0$), 7.26 (t, 1H, ArH, $J = 3.0$), 7.25 (d, 1H, ArH, $J = 1.8$), 6.36 (t, 1H₁, $J = 6.0$), 4.80 (s, 2H, NH₂), 4.62 (m, 1H_{3'}), 4.00 (app q, 1H_{4'}, $J_{\text{app}} = 3.3$), 3.85 (dd, 1H_{5'}, $J = 4.3, 11.2$), 3.78 (dd, 1H_{5'}, $J = 3.2, 11.2$), 2.60 (app quint, 1H₂, $J_{\text{app}} = 6.6$), 2.39 (ddd, 1H₂, $J = 3.9, 6.1, 13.0$), 0.933, 0.928 (2s, 18H, *tert*-Bu), 0.12, 0.11 (2s, 12H, SiCH₃).

HRMS Calcd for C₂₈H₄₆N₅O₄Si₂ (M⁺ + 1): 572.3088, found: 572.3104.

***O*⁶-(4-Chlorophenyl)-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4g**

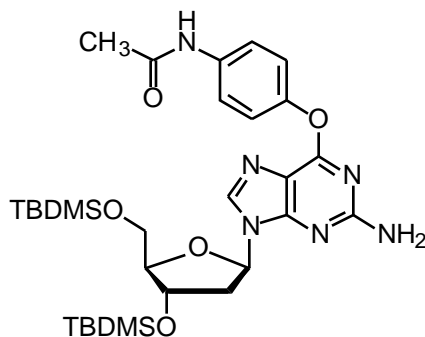
Clear solid, R_f (silica/2% EtOAc in CH_2Cl_2) = 0.47. ^1H NMR: 8.03 (s, 1H₈), 7.37 (d, 2H, ArH, J = 8.8), 7.20 (d, 2H, ArH, J = 8.8), 6.36 (t, 1H_{1'}, J = 6.5), 4.80 (s, 2H, NH₂), 4.62 (m, 1H_{3'}), 4.00 (app q, 1H_{4'}, J_{app} = 3.4), 3.85 (dd, 1H_{5'}, J = 4.2, 11.2), 3.78 (dd, 1H_{5'}, J = 3.1, 11.2), 2.59 (app quint, 1H_{2'}, J_{app} = 5.9), 2.39 (ddd, 1H_{2'}, J = 3.9, 6.1, 13.0), 0.932, 0.928 (2s, 18H, *tert*-Bu), 0.12, 0.11 (2s, 12H, SiCH₃). HRMS Calcd for

$\text{C}_{28}\text{H}_{45}\text{ClN}_5\text{O}_4\text{Si}_2$ ($M^+ + 1$): 606.2699, found: 606.2704.

***O*⁶-(3-Methoxyphenyl)-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4h**

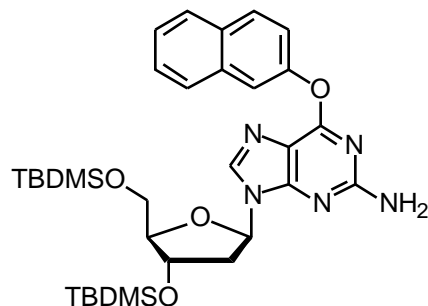
White foam, R_f (silica/ CH_2Cl_2) = 0.37. ^1H NMR: 8.00 (s, 1H₈), 7.29 (t, 1H, ArH, J = 8.1), 6.85 (ddd, 1H, ArH, J = 0.9, 2.1, 8.1), 6.79 (m, 2H, ArH), 6.34 (t, 1H_{1'}, J = 6.5), 4.79 (s, 2H, NH₂), 4.60 (m, 1H_{3'}), 3.98 (app q, 1H_{4'}, J_{app} = 4.0), 3.82 (dd, 1H_{5'}, J = 4.3, 11.2), 3.80 (s, 3H, OCH₃), 3.76 (dd, 1H_{5'}, J = 3.2, 11.2), 2.58 (app quint, 1H_{2'}, J_{app} = 5.9), 2.37 (ddd, 1H_{2'}, J = 3.8, 6.1, 13.0), 0.302, 0.298 (2s, 18H, *tert*-Bu), -0.291, -

0.300, -0.301 (3s, 12H, SiCH₃). HRMS Calcd for $\text{C}_{29}\text{H}_{48}\text{N}_5\text{O}_5\text{Si}_2$ ($M^+ + 1$): 602.3194, found: 602.3181.

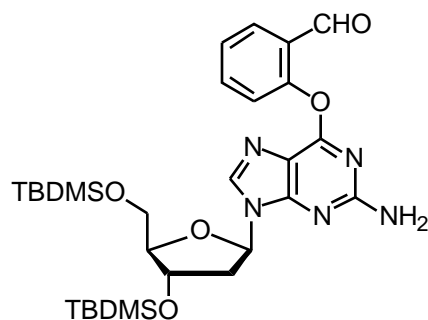
***O*⁶-(4-Acetylaminophenyl)-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4i**

Light cream foam, R_f (silica/5% MeOH in CH_2Cl_2) = 0.15. ^1H NMR: 8.02 (s, 1H₈), 7.53 (d, 2H, ArH, J = 8.8), 7.31 (s, 1H, NH), 7.20 (d, 2H, ArH, J = 8.8), 6.35 (t, 1H_{1'}, J = 6.5), 4.83 (s, 2H, NH₂), 4.61 (m, H_{3'}), 4.00 (app q, 1H_{4'}, J_{app} = 3.6), 3.84 (dd, 1H_{5'}, J = 4.2, 11.2), 3.78 (dd, 1H_{5'}, J = 3.1, 11.2), 2.59 (app quint, 1H_{2'}, J_{app} = 6.3), 2.39 (ddd, 1H_{2'}, J = 3.9, 6.0, 13.0), 2.20 (s, 3H, COCH₃), 0.93, 0.92 (2s, 18H,

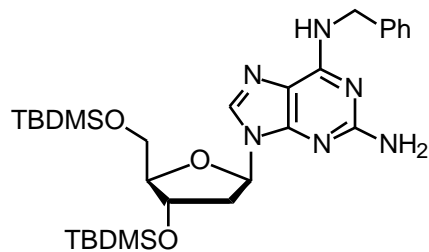
tert-Bu), 0.11, 0.10 (2s, 12H, SiCH₃). HRMS Calcd for $\text{C}_{30}\text{H}_{49}\text{N}_6\text{O}_5\text{Si}_2$ ($M^+ + 1$): 629.3303, found: 629.3275.

***O*⁶-(2-Naphthyl)-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4j**

Pale yellow thick oil, R_f (silica/2% EtOAc in CH_2Cl_2) = 0.37. ^1H NMR: 8.05 (s, 1H₈), 7.88 (d, 2H, ArH, J = 8.9), 7.83 (d, 1H, ArH, J = 7.7), 7.70 (d, 1H, ArH, J = 2.2), 7.52-7.46 (m, 2H, ArH), 7.40 (dd, 1H, ArH, J = 2.2, 8.9), 6.37 (t, 1H_{1'}, J = 6.5), 4.77 (s, 2H, NH₂), 4.63 (m, 1H_{3'}), 4.01 (app q, 1H_{4'}, J_{app} = 3.3), 3.86 (dd, 1H_{5'}, J = 4.3, 11.2), 3.79 (dd, 1H_{5'}, J = 3.2, 11.2), 2.61 (app quint, 1H_{2'}, J = 6.4), 2.40 (ddd, 1H_{2'}, J = 3.9, 6.1, 13.1), 0.94, 0.93 (2s, 18H, *tert*-Bu), 0.12, 0.11 (2s, 12H, SiCH₃). HRMS Calcd for C₃₂H₄₈N₅O₄Si₂ (M^+ + 1): 622.3245, found: 622.3271.

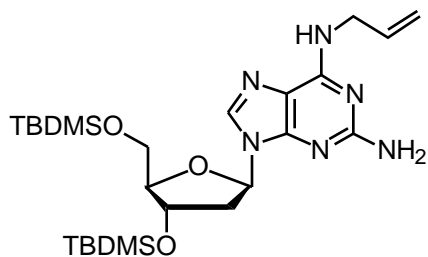
***O*⁶-(2-Formylphenyl)-3',5'-bis-*O*-tert-butyldimethylsilyl-2'-deoxyguanosine 4k**

Pale yellow solid, R_f (silica/2% MeOH in CH_2Cl_2) = 0.40. ^1H NMR: 10.25 (s, 1H, CHO), 8.06 (s, 1H₈), 7.98 (dd, 1H, ArH, J = 2.0, 7.7), 7.66 (dt, 1H, ArH, J = 2.0, 7.5), 7.40 (t, 1H, ArH, J = 7.5), 7.30 (d, 1H, ArH, J = 8.2), 6.35 (t, 1H_{1'}, J = 6.4), 4.79 (s, 2H, NH₂), 4.62 (m, 1H_{3'}), 4.01 (app q, 1H_{4'}, J_{app} = 3.6), 3.86 (dd, 1H_{4'}, J_{app} = 3.6), 3.86 (dd, 1H_{5'}, J = 4.2, 11.2), 3.78 (dd, 1H_{5'}, J = 3.2, 11.2), 2.61 (app quint, 1H_{2'}, J = 6.8), 2.40 (ddd, 1H_{2'}, J = 3.9, 6.1, 13.1), 0.93, 0.92 (2s, 18H, *tert*-Bu), 0.12-0.11 (3s, 12H, SiCH₃). HRMS Calcd for C₂₉H₄₆N₅O₅Si₂ (M^+ + 1): 600.3037, found: 600.3038.

2-Amino-6-(benzylamino)-9-[2-deoxy-3,5-bis-*O*-(*tert*-butyldimethylsilyl)-*D*-erythro-pentofuranosyl]purine 5a

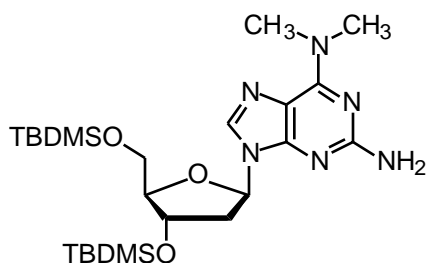
Colorless powder, R_f (silica/3% MeOH in CH_2Cl_2) = 0.49. ^1H NMR: 7.76 (s, 1H₈), 7.33 (5H, m, ArH), 6.31 (t, 1H_{1'}, J = 6.6), 5.83 (1H, s, NH), 4.79 (2H, s, NH₂), 4.70 (2H, s, NCH₂), 4.59 (m, 1H_{3'}), 3.98 (app q, 1H_{4'}, J_{app} = 4.1), 3.82 (dd, 1H_{5'}, J = 4.5, 11.1), 3.76 (dd, 1H_{5'}, J = 3.4, 11.1), 2.59 (app quint, 1H_{2'}, J_{app} = 6.1), 2.35 (ddd, 1H_{2'}, J = 3.7, 6.0, 13.0), 0.92 (2s, 18H, *tert*-Bu), 0.11, 0.08, 0.08 (3s, 12H, SiCH₃). HRMS Calcd for C₂₉H₄₈N₆NaO₃Si₂ (M^+ + Na): 607.3224, found: 607.3233.

2-Amino-6-(allylamino)-9-[2-deoxy-3,5-bis-*O*-(*tert*-butyldimethylsilyl)- *D*-erythro-pento-furanosyl]purine 5b



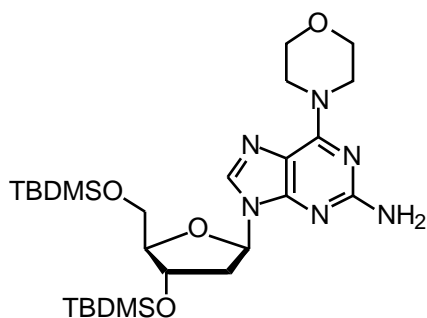
Light yellowish powder, R_f (silica/3%MeOH in CH_2Cl_2) = 0.24. ^1H NMR: 7.77 (s, 1H₈), 6.30 (t, 1H_{1'}, J = 6.8), 5.87 (tdd, 1H, =CH, J = 6.0, 10.3, 17.0), 5.58 (br s, NH), 5.28 (dd, 1H, =CH_{trans}, J = 1.2, 17.0), 5.16 (d, 1H, =CH_{cis}, J = 1.2, 10.3), 4.67 (br s, 2H, NCH₂), 4.59 (m, 1H_{3'}), 4.23 (br s, NH₂), 3.97 (app q, 1H_{4'}, J_{app} = 3.5), 3.82 (dd, 1H_{5'}, J = 4.5, 11.0), 3.76 (dd, 1H_{5'}, J = 3.3, 11.0), 2.60 (app quint, 1H_{2'}, J_{app} = 7.0), 2.34 (ddd, 1H_{2'}, J = 3.5, 5.9, 12.9), 0.92 (2s, 18H, *tert*-Bu), 0.11, 0.09, 0.08 (3s, 12H, SiCH₃). HRMS Calcd for $\text{C}_{25}\text{H}_{47}\text{N}_6\text{O}_3\text{Si}_2$ ($M^+ + 1$): 535.3248, found: 535.3262.

2-Amino-6-(dimethylamino)-9-[2-deoxy-3,5-bis-*O*-(*tert*-butyldimethylsilyl)- *D*-erythro-pento-furanosyl]purine 5c



Colorless powder, R_f (silica/3%MeOH in CH_2Cl_2) = 0.47. ^1H NMR: 7.71 (s, 1H₈); 6.33 (t, 1H_{1'}, J = 6.1); 4.58 (s, NH₂); 4.58 (m, 1H_{3'}); 3.98 (app q, 1H_{4'}, J_{app} = 4.0); 3.78 (dd, 1H_{5'}, J = 4.6, 11.1); 3.75 (dd, 1H_{5'}, J = 3.8, 11.1); 3.45 (s, 6H, NCH₃); 2.57 (app quint, 1H_{2'}, J_{app} = 6.6); 2.34 (ddd, 1H_{2'}, J = 3.4, 6.0, 13.1); 0.92, 0.91 (2s, 18H, *tert*-Bu); 0.11, 0.08, 0.07 (3s, 12H, SiCH₃). HRMS Calcd for $\text{C}_{24}\text{H}_{47}\text{N}_6\text{O}_3\text{Si}_2$ ($M^+ + 1$): 523.3248, found: 523.3224.

2-Amino-6-morpholino-9-[2-deoxy-3,5-bis-*O*-(*tert*-butyldimethylsilyl)- *D*-erythro-pento-furanosyl]purine 5d



Colorless powder, R_f (silica/3%MeOH in CH_2Cl_2) = 0.27. ^1H NMR: 7.73 (s, 1H₈), 6.33 (t, 1H_{1'}, J = 6.7), 4.61 (s, NH₂), 4.58 (m, 1H_{3'}), 4.23 (br s, 4H, NCH₂), 3.97 (app q, 1H_{4'}, J_{app} = 4.1), 3.80 (t, 4H, OCH₂, J = 4.9), 3.78 (dd, 1H_{5'}, J = 4.6, 11.1), 3.75 (dd, 1H_{5'}, J = 3.6, 11.1), 2.56 (app quint, 1H_{2'}, J_{app} = 6.5), 2.34 (ddd, 1H_{2'}, J = 3.4, 6.0, 13.0), 0.92, 0.91 (2s, 18H, *tert*-Bu), 0.10, 0.08, 0.07 (3s, 12H, SiCH₃). HRMS Calcd for $\text{C}_{26}\text{H}_{49}\text{N}_6\text{O}_4\text{Si}_2$ ($M^+ + 1$): 565.3354, found: 565.3377.