

Supporting Information.

Mass spectra and NMR data for selected compounds.

[1- β -d-(1-Deazapurin-9-yl)-5'-(dimethoxytrityl)-2'-deoxyribofuranos-3'-yl]-2-cyanoethyl-N,N-bis(isopropylamino)phosphoramidite. This compound was obtained as a colorless oil, yield 57 %. MS (ESI-, MeCN, LiCl added): 772 (M +35 [Cl]). MS (ESI, MeCN, LiCl added, pos.): 744 (M+7 [Li]) calcd 744. ³¹P NMR (400 MHz, MeCN-d₃): 148.97 (s, 1st diastereoisomer), 148.87 (s, 2nd diastereoisomer).

[1- β -d-(2-Oxopyridin-1-yl)-5'-(dimethoxytrityl)-2'-deoxyribofuranos-3'-yl]-2-cyanoethyl-N,N-bis(isopropylamino)phosphoramidite. This compound was obtained as a colorless oil, yield 89 %. MS (ESI-, MeCN, LiCl added): 748 (M+35 [Cl]). MS (ESI+, MeCN, LiCl added): 720 (M +7 [Li]) calcd 720. ³¹P NMR (400 MHz, MeCN-d₃): 149.07 (s, 1st diastereoisomer), 149.01 (s, 2nd diastereoisomer).

2'-deoxynebularine-5'-triphosphate. MS (MALDI-): 475 (M-1) calcd 475. ³¹P NMR (400 MHz, D₂O): - 10.34 (bs, 2P, α -P and γ -P), -22.3 (bs, 1P, β -P).

1- β -d-(1-deazapurin-9-yl)-2'-deoxyribofuranose-5'-triphosphate. MS (MALDI-): 474 (M-1) calcd 474. ³¹P NMR (400 MHz, D₂O): - 9.92 (bs, 1P, γ -P), - 10.40 (bs, 1P, α -P), - 22.43 (bs, 1P, β -P).

1- β -d-(2-amino-1-deazapurin-9-yl)-2'-deoxyribofuranose -5'-triphosphate. MS (MALDI-): 489 (M - 1) calcd 489. ³¹P NMR (400 MHz, D₂O): - 9.81 (bs, 1P, γ -P), - 10.41 (bd, 1P, J = 46.4 Hz, α -P), - 22.32 (bs, 1P, β -P).

1- β -(2-oxopyridin-1-yl)-2'-deoxyribofuranose-5'-triphosphate. MS (MALDI-): 450 (M-1) calcd 450. ³¹P NMR (400 MHz, D₂O): - 9.94 (bs, 1P, γ -P), - 10.49 (bd, 1P, J = 50.0 Hz, α -P), - 22.36 (bs, 1P, β -P).