Supporting Information for

Preparation of highly substituted 6-arylpurine ribonucleosides by Ni-catalyzed cyclotrimerization. The scope of the reaction.

Pavel Turek, Petr Novák, Radek Pohl, Michal Hocek, and Martin Kotora

Contents

I.	General Methods.	S - 1
II.	Synthesis of Protected 9-(β-D-Ribofuranosyl)-6-alkynylpurines 1.	S - 2
III.	Synthesis of Protected 9-(β-D-Ribofuranosyl)-6-arylpurines 3.	S - 4
IV.	Deprotection of the Acetylated 9-(β-D-Ribofuranosyl)-6-arylpurines.	S - 15
V.	Cyclotrimerization of Unprotected 9-(β-D-Ribofuranosyl)-6-alkynylpurines.	S - 20
VI.	References.	S - 21
VII.	Spectra of the Prepared Compounds.	S - 22

I. General Methods.

All solvents were used as obtained unless otherwise noted. THF and toluene were distilled from sodium and benzophenone, and acetonitrile from CaH_2 under Ar. Starting diynes **2** that were not commercially available were prepared by standard procedures by the reaction of propargyl bromide with the corresponding C-acids under basic conditions.¹ $\text{CoBr}(\text{PPh}_3)_3$ ² and $\text{NiBr}_2(\text{PPh}_3)_2$ ³ were prepared according to the previously reported procedures. All other reagents were obtained from commercial sources. ^1H (400 or 500 MHz) and ^{13}C NMR (100.6 or 125.8 MHz) spectra were recorded as solutions in CDCl_3 with Me_4Si as an internal standard or as solutions in $\text{DMSO}-d_6$ referenced to the residual solvent signal. Chemical shifts are given in δ -scale, coupling constants J are given in Hz. Melting points (uncorrected) were determined using a Kofler apparatus. Infrared spectra were recorded as CHCl_3 solutions or as KBr tablets and are reported in wave numbers (cm^{-1}). Fluka 60 silica gel was used for flash chromatography. TLC was performed on silica gel 60 F_{254} -coated aluminum sheets. All cyclotrimerization reactions were carried out under an argon atmosphere using Schlenk-tube technique.

II. Synthesis of Protected 9-(β -D-Ribofuranosyl)-6-alkynylpurines 1.

General procedure for cross-coupling reactions of 6-chloropurine with acetylenes.

Triethylamine (4 ml) and DMF (20 ml) were added to an argon purged mixture of 6-chloro-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)purine (3.7 g, 9 mmol), CuI (104 mg, 0.54 mmol), [PdCl₂(PPh₂)₂] (128 mg, 0.18 mmol), acetylene (10.8 mmol) and the mixture was stirred at 60 °C for 6 h. Solvents were evaporated under reduced pressure and the residue was chromatographed on silica gel column.

6-(Phenylethynyl)-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (1a).

Column chromatography on silica gel (hexane/EtOAc 1/2) afforded 3.5 g (80%) of a yellowish oil, which after co-evaporation with diethyl ether formed a white foam. Experimental data were in accordance with the published data.⁴

6-(Hex-1-yn-1-yl)-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (1b).

Column chromatography on silica gel (hexane/EtOAc 2/3) afforded 3.3 g (80%) of a yellowish oil: $[\alpha]_D$ -19.4 (*c* 0.24, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 0.96 (t, 3H, J_{vic} = 7.3, CH₃CH₂CH₂CH₂-), 1.53 and 1.71 (2 $\times$ m, 2 $\times$ 2H, CH₃CH₂CH₂CH₂-), 2.08, 2.12 and 2.16 (3 $\times$ s, 3 $\times$ 3H, CH₃CO), 2.61 (t, 2H, J_{vic} = 7.2, CH₃CH₂CH₂CH₂-), 4.35-4.50 (m, 3H, H-4' and H-5'), 5.67 (dd, 1H, $J_{3',2'}$ = 5.5, $J_{3',4'}$ = 4.4, H-3'), 5.96 (t, 1H, $J_{2',3'}$ = 5.5, $J_{2',1'}$ = 5.3, H-2'), 6.24 (d, 1H, $J_{1',2'}$ = 5.3, H-1'), 8.25 (s, 1H, H-8), 8.91 (s, 1H, H-2); ¹³C NMR (100.6 MHz, CDCl₃) δ 13.56 (CH₃CH₂CH₂CH₂-), 19.63 (CH₃CH₂CH₂CH₂-), 20.34, 20.50 and 20.72 (CH₃CO), 22.10 and 30.09 (CH₃CH₂CH₂CH₂-), 62.95 (CH₂-5'), 70.55 (CH-3'), 73.04 (CH-2'), 75.89 (Pur-C $\equiv$ C-Bu), 80.44 (CH-4'), 86.42 (CH-1'), 102.32 (Bu-C $\equiv$ C-Pur), 134.89 (C-5), 143.03 (C-6), 143.18 (CH-8), 150.91 (C-4) 152.82 (CH-2), 169.29, 169.52 and 170.24 (CO); IR (CHCl₃) ν 2999, 2962, 2232, 1751, 1585, 1374, 1245, 1235, 1048 cm⁻¹; MS (FAB,

m/z (rel.%) 459 ($M^+ + H$, 22), 259 (21), 201 (100), 139 (85), 97 (76); HR-MS (FAB) calcd for $C_{22}H_{27}N_4O_7$ [$M^+ + H$] 459.1880, found 459.1899. R_f (hexane/EtOAc 1/3) = 0.44.

6-[(Trimethylsilyl)ethynyl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (1c).

Column chromatography on silica gel (hexane/EtOAc 1/1) afforded 3.16 g (74%) of a yellowish oil, which after co-evaporation with diethyl ether formed a white foam. Experimental data were in accordance with the published data.⁵

III. Synthesis of Protected 9-(β -D-Ribofuranosyl)-6-arylpurines.

General procedure for Ni(cod)₂/2PPh₃ catalyzed cyclotrimerization of 6-alkynylpurines **1** with diynes **2**. Method A.

Into a mixture of Ni(cod)₂ (0.04 mmol, 11 mg) and PPh₃ (0.10 mmol, 26 mg) was added a solution of 6-alkynylpurine **1** (0.20 mmol) and diyne **2** (0.22 mmol) in dry MeCN (4 mL). The reaction mixture was initially stirred at 20°C for 24 h or until the consumption of the starting material (TLC). Then the solvent was evaporated under the reduced pressure and residue was subjected to column chromatography.

General procedure for NiBr₂(dppe)/Zn catalyzed cyclotrimerization of 6-alkynylpurines **1** with diynes **2**. Method B.

Into a solution of 6-alkynylpurine **1** (0.20 mmol), diyne **2** (0.22 mmol) and NiBr₂(dppe) (0.04 mmol, 25 mg) in dry MeCN (4 mL) under Ar was added Zn powder (10 mg, 0.16 mmol). The reaction mixture was initially stirred at 20°C for 24 h or until the consumption of the starting material (TLC). Then the solvent was evaporated under the reduced pressure and residue was subjected to column chromatography.

General procedure for CoBr(PPh₃)₃ catalyzed cyclotrimerization of 6-alkynylpurines **1** with diynes **2**. Method C.

Into a solution of 6-alkynylpurine **1** (0.20 mmol), diyne **2** (0.22 mmol) in dry toluene (4 mL) under Ar was added CoBr(PPh₃)₃ (0.04 mmol, 37 mg). The reaction mixture was initially stirred at 20°C for 24 h or until the consumption of the starting material (TLC). Then the solvent was evaporated under the reduced pressure and residue was subjected to column chromatography.

6-[6-Phenyl-2,2-di(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (**3aa**). (Method A)

Column chromatography on silica gel (diethyl ether) afforded 116 mg (81%) of a white foam: $[\alpha]_D$ -22.8 (*c* 0.23, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.28 (t, 6H, *J*_{vic} = 7.1, CH₃CH₂), 2.09, 2.10 and 2.15 (3×s, 3×3H, CH₃CO), 3.70 and 3.72 (2×s, 2×2H, H-7'' and H-9''), 4.23 (q, 4H, *J*_{vic} = 7.1, CH₂CH₃), 4.36 (dd, 1H, *J*_{gem} = 13.1, *J*_{5'b,4'} = 5.3, H-5'b), 4.43-4.49 (m, 2H, H-5'a and H-4'), 5.67 (t, 1H, *J*_{3',2'} = 5.3, *J*_{3',4'} = 4.9, H-3'), 5.90 (t, 1H, *J*_{2',3'} = 5.3, *J*_{2',1'} = 5.0, H-2'), 6.19 (d, 1H, *J*_{1',2'} = 5.0, H-1'), 7.12 (m, 5H, Ph), 7.38 (s, 1H, H-3''), 7.60 (s, 1H, H-6''),

8.03 (s, 1H, H-8), 8.83 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, CDCl_3) δ 14.02 (CH_3CH_2), 20.38, 20.51 and 20.74 (CH_3CO); 40.19 and 40.43 ($\text{CH}_2\text{-7''}$ and $\text{CH}_2\text{-9''}$); 60.60 (C-8''); 61.82 (CH_2CH_3), 62.93 ($\text{CH}_2\text{-5'}$), 70.46 (CH-3'), 73.11 (CH-2'), 80.23 (CH-4'), 86.44 (CH-1'), 126.45 ($\text{CH-}p\text{-Ph}$), 126.66 and 126.72 (CH-3'' and CH-6''), 127.82 ($\text{CH-}o\text{-Ph}$), 129.21 ($\text{CH-}m\text{-Ph}$), 132.81 (C-5), 133.05 (C-1''), 139.35 (C-5''), 141.19 and 141.21 (C-*i*-Ph and C-2''), 142.37 (CH-8), 142.45 (C-4''), 150.92 (C-4), 152.44 (CH-2), 159.77 (C-6), 169.27, 169.53 and 170.28 (COCH_3), 172.42 (COOEt); IR (CHCl_3) ν 3031, 2986, 1750, 1732, 1588, 1369, 1248, 1097, 1069, 1052 cm^{-1} ; MS (FAB, m/z (rel.%)) 715 ($\text{M}^+\text{+H}$, 5), 457 (15), 139 (76), 97 (100); HR-MS (FAB) calcd for $\text{C}_{37}\text{H}_{38}\text{N}_4\text{O}_{11}$ [$\text{M}^+\text{+H}$] 715.2615, found 715.2632. EA calcd for $\text{C}_{37}\text{H}_{38}\text{N}_4\text{O}_{11}$: C 62.18, H 5.36, N 7.84; found: C 61.88, H 5.34, N 7.58. $R_f(1/4 \text{ hexane/EtOAc}) = 0.45$. (**Method B**, yield 37%.)

6-[6-Phenyl-(2,2-diacetylindan-5-yl)]-9-(2,3,5-tri-O-acetyl- β -D-ribofuranosyl)-9H-purine (3ab). (Method A)

Column chromatography on silica gel (15/1 diethyl ether/acetone) afforded 113 mg (86%) of a white foam: $[\alpha]_D -23.3$ (c 0.24, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 2.09, 2.10 and 2.15 (3s, 3 $\times$ 3H, CH_3COO), 2.22 (s, 3H, CH_3CO), 3.63 and 3.64 (2s, 2 $\times$ 2H, H-7'' and H-9''), 4.35 (dd, 1H, $J_{\text{gem}} = 13.0$, $J_{5'b,4'} = 5.3$, H-5'b), 4.42-4.49 (m, 2H, H-5'a and H-4'), 5.67 (t, 1H, $J_{3',2'} = 5.5$, $J_{3',4'} = 5.1$, H-3'), 5.90 (t, 1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 5.0$, H-2'), 6.18 (d, 1H, $J_{1',2'} = 5.0$, H-1'), 7.08-7.16 (m, 5H, Ph), 7.39 (s, 1H, H-3''), 7.61 (s, 1H, H-6''), 8.03 (s, 1H, H-8), 8.83 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, CDCl_3) δ 20.39, 20.51 and 20.74 (CH_3COO), 26.59 (CH_3CO), 37.37 and 37.58 ($\text{CH}_2\text{-7''}$ and $\text{CH}_2\text{-9''}$), 62.92 ($\text{CH}_2\text{-5'}$), 70.45 (CH-3'), 73.13 (CH-2'), 74.99 (C-8''), 80.23 (CH-4'), 86.52 (CH-1'), 126.56 ($\text{CH-}p\text{-Ph}$), 126.88 and 126.97 (CH-3'' and CH-6''), 127.88 ($\text{CH-}o\text{-Ph}$), 129.18 ($\text{CH-}m\text{-Ph}$), 132.82 (C-5), 133.30 (C-1''), 138.99 (C-5''), 141.03 (C-*i*-Ph), 141.45 (C-2''), 142.12 (C-4''), 142.46 (CH-8), 150.94 (C-4), 152.46 (CH-2), 159.57 (C-6), 169.28, 169.53 and 170.27 (CH_3COO), 204.53 (COCH_3); IR (CHCl_3) ν 3028, 2993, 1751, 1701, 1588, 1373, 1243, 1232, 1099, 1072, 1048 cm^{-1} ; MS (EI, m/z (rel.%)) 654 (M^+ , 3), 611 (12), 395 (10), 353 (32),

311 (10), 139 (15), 97 (35), 43 (100); HR-MS (EI) calcd for $C_{35}H_{34}N_4O_9$ [M^+] 654.2326, found 654.2354. R_f (EtOAc) = 0.38. (**Method B**, yield 62%.)

6-[6-Phenyl-2-acetyl-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ac). (Method A)

Column chromatography on silica gel (diethyl ether) afforded 115 mg (84%) of a white foam: $[\alpha]_D -29.0$ (c 0.24, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ 1.29 (t, 3H, $J_{vic} = 7.1$, CH_3 -Et), 2.09, 2.10 and 2.15 (3 $\times$ s, 3 $\times$ 3H, CH_3 -OAc), 2.27 (s, 3H, CH_3 -Ac), 3.61, 3.62, 3.66 and 3.69 (4 $\times$ d, 4 $\times$ 1H, $J_{gem} = 16.7$, H-7'' and H-9''), 4.25 (q, 2H, $J_{vic} = 7.1$, CH_2 -Et), 4.35 (dd, 1H, $J_{gem} = 13.1$, $J_{5'b4'} = 5.3$, H-5'b), 4.43-4.48 (m, 2H, H-5'a and H-4'), 5.67 (t, 1H, $J_{3'2'} = 5.3$, $J_{3'4'} = 5.1$, H-3'), 5.91 (t, 1H, $J_{2'3'} = 5.3$, $J_{2'1'} = 5.0$, H-2'), 6.19 (d, 1H, $J_{1'2'} = 5.0$, H-1'), 7.12 (m, 5H, Ph), 7.38 (s, 1H, H-3''), 7.60 (s, 1H, H-6''), 8.03 (s, 1H, H-8), 8.82 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 14.02 (CH_3 -Et), 20.38, 20.51 and 20.74 (CH_3 -OAc), 26.15 (CH_3 -Ac), 38.71 and 38.92 (CH_2 -7'' and CH_2 -9''), 61.96 (CH_2 -Et), 62.92 (CH_2 -5'), 67.12 (C-8''), 70.44 (CH -3'), 73.11 (CH -2'), 80.21 (CH -4'), 86.46 (CH -1'), 126.48 (CH -*p*-Ph), 126.78 and 126.82 (CH -3'' and CH -6''), 127.83 (CH -*o*-Ph), 129.19 (CH -*m*-Ph), 132.81 (C-5), 133.12 (C-1''), 139.14 (C-5''), 141.13 (C-*i*-Ph), 141.29 (C-2''), 142.29 (C-4''), 142.40 (CH -8), 150.91 (C-4), 152.43 (CH -2), 159.68 (C-6), 169.28, 169.53 and 170.27 (C=O from OAc), 172.12 (C=O from COOEt), 202.46 (C=O from Ac); IR ($CHCl_3$) ν 3030, 2988, 1750, 1714, 1588, 1370, 1235, 1207, 1097, 1073, 1048 cm^{-1} ; MS (EI, m/z (rel.%)) 684 (M^+ , 6), 425 (17), 139 (20), 97 (35), 57 (30), 43 (100); HR-MS (EI) calcd for $C_{36}H_{36}N_4O_{10}$ [M^+] 684.2431, found 684.2407. EA calcd for $C_{36}H_{36}N_4O_{10}$: C 63.15, H 5.30, N 8.18; found: C 63.03, H 5.23, N 7.92. R_f (EtOAc) = 0.49. (**Method B**, yield 48%.)

6-[6-Phenyl-2-cyano-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ad). (Method A)

Column chromatography on silica gel (diethyl ether) afforded 114 mg (85%) of a white foam: $[\alpha]_D -29.2$ (c 0.25, $CHCl_3$), 1H NMR (500 MHz, $CDCl_3$) δ 1.37 (t, 3H, $J_{vic} = 7.1$, CH_3CH_2), 2.09, 2.10 and 2.15 (3 $\times$ s, 3 $\times$ 3H, CH_3CO), 3.69, 3.71, 3.82 and 3.84 (4 $\times$ d, 4 $\times$ 1H, $J_{gem} = 16.6$, H-7'' and H-9''), 4.33 (q, 2H, $J_{vic} = 7.1$, CH_2CH_3), 4.36 (dd, 1H, $J_{gem} = 13.1$, $J_{5'b4'} = 5.3$, H-5'b), 4.44-4.49 (m, 2H, H-5'a and H-4'), 5.68 (t, 1H, $J_{3'2'} = 5.5$, $J_{3'4'} = 5.0$, H-3'), 5.91 (t,

1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 4.9$, H-2'), 6.19 (d, 1H, $J_{1',2'} = 4.9$, H-1'), 7.14 (m, 5H, Ph), 7.43 (s, 1H, H-3''), 7.66 (s, 1H, H-6''), 8.05 (s, 1H, H-8), 8.83 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, CDCl_3) δ 13.97 (CH_3CH_2), 20.39, 20.51 and 20.75 (CH_3CO), 42.90 and 42.97 (CH_2 -7'' and CH_2 -9''), 47.52 (C-8''), 62.92 (CH_2 -5'), 63.36 (CH_2CH_3), 70.42 (CH -3'), 73.13 (CH -2'), 80.23 (CH -4'), 86.55 (CH -1'), 120.34 (CN), 126.75 (CH -*p*-Ph), 126.89 and 126.99 (CH -3'' and CH -6''), 127.94 (CH -*o*-Ph), 129.16 (CH -*m*-Ph), 132.81 (C-5), 133.92 (C-1''), 137.39 (C-5''), 140.45 (C-*i*-Ph), 140.70 (C-2''), 142.14 (C-4''), 142.60 (CH-8), 151.00 (C-4), 152.45 (CH-2), 159.15 (C-6), 168.21 (COOEt), 169.30, 169.54 and 170.27 (COCH_3); IR (CHCl_3) ν 3029, 2989, 2247, 1749, 1588, 1371, 1232, 1098, 1062, 1050 cm^{-1} ; MS (FAB, m/z (rel.%)) 668 ($\text{M}^+ + \text{H}$, 17), 410 (78), 139 (85), 97 (100); HR-MS (FAB) calcd for $\text{C}_{35}\text{H}_{34}\text{N}_5\text{O}_9$ [$\text{M}^+ + \text{H}$] 668.2357, found 668.2346. EA calcd for $\text{C}_{35}\text{H}_{33}\text{N}_5\text{O}_9$: C 62.96, H 4.98, N 10.49; found: C 62.57, H 4.96, N 10.11. R_f (hexane/EtOAc 1/3) = 0.47. (**Method B**, yield 35%.)

6-[6-Phenyl-1,3-dihydro-2-tosyl-2H-indol-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9H-purine (3ae). (Method A)

Column chromatography on silica gel (diethyl ether) afforded 70 mg (48%) of a white foam: $[\alpha]_D -30.7$ (c 0.15, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 2.085, 2.089 and 2.147 (3 $\times$ s, 3 $\times$ 3H, CH_3CO), 2.43 (s, 3H, CH_3), 4.35 (dd, 1H, $J_{\text{gem}} = 13.1$, $J_{5'b,4'} = 5.3$, H-5'b), 4.43-4.48 (m, 2H, H-5'a and H-4'), 4.74 (s, 4H, H-7'' and H-9''), 5.67 (t, 1H, $J_{3',2'} = 5.6$, $J_{3',4'} = 4.8$, H-3'), 5.89 (t, 1H, $J_{2',3'} = 5.6$, $J_{2',1'} = 4.8$, H-2'), 6.17 (d, 1H, $J_{1',2'} = 4.8$, H-1'), 7.05-7.15 (m, 5H, Ph), 7.33 (m, 2H, H-*m*-Tos), 7.34 (s, 1H, H-3''), 7.57 (s, 1H, H-6''), 7.79 (m, 2H, H-*o*-Tos), 8.03 (s, 1H, H-8), 8.80 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.38, 20.49 and 20.72 (CH_3CO), 21.50 (CH_3), 53.62 and 53.79 (CH_2 -7'' and CH_2 -9''), 62.89 (CH_2 -5'), 70.40 (CH -3'), 73.15 (CH -2'), 80.22 (CH -4'), 86.63 (CH -1'), 125.01 and 125.17 (CH -3'' and CH -6''), 126.87 (CH -*p*-Ph), 127.55 (CH -*o*-Tos), 127.96 (CH -*o*-Ph), 129.09 (CH -*m*-Ph), 129.91 (CH -*m*-Tos), 132.83 (C-5), 133.50 (C-*i*-Tos), 133.95 (C-1''), 135.32 (C-5''), 138.16 (C-4''), 140.43 (C-*i*-Ph), 142.13 (C-2''), 142.72 (CH-8), 143.85 (C-*p*-Tos), 150.99 (C-4), 152.42 (CH-2), 158.88 (C-6), 169.29, 169.52 and 170.23 (CO); IR (CHCl_3) ν 3031,

2994, 1751, 1588, 1374, 1348, 1333, 1247, 1164, 1098, 1066, 1049 cm^{-1} ; MS (FAB, m/z (rel.%)) 726 ($M^+ + H$, 60), 468 (88), 139 (100), 97 (92); HR-MS (FAB) calcd for $C_{37}H_{38}N_4O_{11}$ [$M^+ + H$] 726.2234, found 726.2200. R_f (1/3 hexane/EtOAc) = 0.45. (**Method B**, yield 70%.)

6-[6-Phenyl-1,3-dihydro-2-phenyl-2*H*-indol-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3af). (Method A)

Column chromatography on silica gel (diethyl ether) afforded 47 mg (36%) of a white foam: $[\alpha]_D -33.4$ (c 0.16, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 2.10 (s, 6H, CH_3CO), 2.16 (s, 3H, CH_3CO), 4.36 (dd, 1H, $J_{\text{gem}} = 13.0$, $J_{5'b,4'} = 5.3$, H-5'b), 4.44-4.50 (m, 2H, H-5'a and H-4'), 4.77 (s, 4H, H-7'' and H-9''), 5.69 (t, 1H, $J_{3',2'} = 5.5$, $J_{3',4'} = 4.9$, H-3'), 5.92 (t, 1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 4.9$, H-2'), 6.20 (d, 1H, $J_{1',2'} = 4.9$, H-1'), 6.72 (m, 2H, H-*o*-Ph-8''), 6.78 (m, 1H, H-*p*-Ph-8''), 7.13-7.20 (m, 5H, Ph-2''), 7.33 (m, 2H, H-*m*-Ph-8''), 7.53 (s, 1H, H-3''), 7.76 (s, 1H, H-6''), 8.06 (s, 1H, H-8), 8.86 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.40, 20.51 and 20.75 (CH_3CO), 53.52 and 53.71 (CH_2 -7'' and CH_2 -9''), 62.92 (CH_2 -5'), 70.43 (CH -3'), 73.15 (CH -2'), 80.23 (CH -4'), 86.57 (CH -1'), 111.62 (CH -*o*-Ph-8''), 116.33 (CH -*p*-Ph-8''), 125.06 (CH -3''), 125.21 (CH -6''), 126.68 (CH -*p*-Ph-2''), 127.95 (CH -*m*-Ph-2''), 129.25 (CH -*o*-Ph-2''), 129.42 (CH -*m*-Ph-8''), 132.91 (C-5), 133.36 (C-1''), 137.27 (C-5'), 140.19 (C-4'), 140.99 (C-*i*-Ph-2''), 141.53 (C-2''), 142.59 (CH -8), 147.01 (C-*i*-Ph-8''), 150.99 (C-4), 152.48 (CH -2), 159.50 (C-6), 169.31, 169.55 and 170.28 (CO); IR (CHCl_3) ν 3030, 1752, 1589, 1501, 1377, 1240, 1098, 1060, 1049 cm^{-1} ; MS (EI, m/z (rel.%)) 647 (M^+ , 16), 388 (14), 43 (100); HR-MS (EI) calcd for $C_{36}H_{33}N_5O_7$ [M^+] 647.2380, found 647.2361. R_f (hexane/EtOAc 1/1) = 0.35. (**Method B**, yield 69%. **Method C**, yield 30%.)

6-[6-Phenyl-1,3-dihydroisobenzofuran-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ag). (Method A)

Column chromatography on silica gel (diethyl ether/acetone 20/1) afforded 81 mg (71%) of a white foam: $[\alpha]_D -26.3$ (c 0.19, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 2.10 (s, 6H, CH_3CO), 2.15 (s, 3H, CH_3CO), 4.36 (dd, 1H, $J_{\text{gem}} = 13.0$, $J_{5'b,4'} = 5.3$, H-5'b), 4.44-4.50 (m, 2H, H-5'a and H-4'), 5.23 (s, 4H, H-7'' and H-9''), 5.68 (t, 1H, $J_{3',2'} = 5.5$, $J_{3',4'} = 4.9$, H-3'), 5.92 (t, 1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 4.9$, H-2'), 6.20 (d, 1H, $J_{1',2'} = 4.9$, H-1'), 7.14 (m, 5H, Ph), 7.42 (s, 1H, H-

3''), 7.66 (s, 1H, H-6''), 8.06 (s, 1H, H-8), 8.84 (s, 1H, H-2; ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.38, 20.49 and 20.72 (CH_3CO), 62.90 (CH_2 -5'), 70.43 (CH -3'), 73.14 (CH -2'), 73.39 and 73.48 (CH_2 -7' and CH_2 -9''), 80.22 (CH -4'), 86.57 (CH -1'), 123.41 (CH -3''), 123.59 (CH -6''), 126.68 (CH -*p*-Ph), 127.92 (CH -*m*-Ph), 129.22 (CH -*o*-Ph), 132.90 (C-5), 133.50 (C-1''), 138.40 (C-5''), 140.95 (C-*i*-Ph), 141.38 (C-2''), 141.73 (C-4''), 142.59 (CH -8), 150.99 (C-4), 152.44 (CH -2); 159.47 (C-6); 169.28, 169.52 and 170.25 (CO). IR (CHCl_3) ν 3030, 3010, 2995, 1751, 1589, 1371, 1247, 1098, 1048 cm^{-1} ; MS (FAB, m/z (rel.%)) 573 ($\text{M}^+ + \text{H}$, 5), 315 (16), 279 (14), 55 (100); HR-MS (FAB) calcd for $\text{C}_{30}\text{H}_{29}\text{N}_4\text{O}_8$ [$\text{M}^+ + \text{H}$] 573.1985, found 573.1971. EA calcd for $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_8$: C 62.93, H 4.93, N 9.79; found: C 62.55, H 5.00, N 9.10. R_f (EtOAc) = 0.35. (**Method B**, yield 45%. **Method C**, yield 80%.)

6-[6-Phenyl-2-[(1,1-dimethylethoxy)carbonyl]amino]-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ah). (Method A**)**

Column chromatography on silica gel (diethyl ether) afforded 133 mg (88%) of a white foam: $[\alpha]_{\text{D}} -29.9$ (c 0.30, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 1.29 (t, 3H, $J_{\text{vic}} = 7.1$, CH_3CH_2), 1.44 (s, 9H, $(\text{CH}_3)_3\text{C}$), 2.09, 2.10 and 2.15 (3 $\times$ s, 3 $\times$ 3H, CH_3CO), 3.31, 3.33, 3.71 and 3.76 (4 $\times$ d, 4H, $J_{\text{gem}} = 16.6$, H-7' and H-9''), 4.26 (q, 2H, $J_{\text{vic}} = 7.1$, CH_2 -Et), 4.36 (dd, 1H, $J_{\text{gem}} = 13.1$, $J_{5'b,4'} = 5.3$, H-5'b), 4.43-4.49 (m, 2H, H-5'a and H-4'), 5.15 (bs, 1H, NH), 5.68 (t, 1H, $J_{3',2'} = 5.4$, $J_{3',4'} = 5.0$, H-3'), 5.90 and 5.91 (2 $\times$ t, 1H, $J_{2',3'} = 5.4$, $J_{2',1'} = 5.0$, H-2' diastereomeric), 6.19, 6.20 (2 $\times$ d, 1H, $J_{1',2'} = 5.0$, H-1' diastereomeric), 7.08-7.16 (m, 5H, Ph), 7.39 (s, 1H, H-3''), 7.61 (s, 1H, H-6''), 8.04, 8.05 (2 $\times$ s, 1H, H-8 diastereomeric), 8.83 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, CDCl_3) δ 14.15 (CH_3CH_2), 20.38, 20.51 and 20.74 (CH_3CO), 28.26 ($(\text{CH}_3)_3\text{C}$), 43.50 (br, CH_2 -7' and CH_2 -9''), 61.65 (CH_2CH_3), 62.92 (CH_2 -5'), 66.25 (C-8''), 70.45 (CH -3'), 73.12 (CH -2'), 80.23 (CH -4' and $\text{C}(\text{CH}_3)_3$), 86.47 and 86.50 (CH -1' diastereomeric), 126.50 (CH -*p*-Ph), 127.05 (CH -3'' and CH -6''), 127.86 (CH -*o*-Ph), 129.21 (CH -*m*-Ph), 132.83 (C-5), 133.10 (C-1''), 139.14 (C-5''), 141.14 (C-*i*-Ph), 141.31 (C-2''), 142.41 (C-4''), 142.46 (CH -8), 150.93 (C-4), 152.45 (CH -2), 154.90 (HNCOO), 159.72 (C-6), 169.29, 169.54 and 170.29 (COCH_3), 173.17 (COOEt); IR (CHCl_3) ν 3448, 3029, 2983, 1749, 1714, 1588, 1494, 1369,

1247, 1161, 1063, 1050 cm^{-1} ; MS (FAB, m/z (rel.%)) 758 ($M^+ + H$, 10), 444 (110), 139 (43), 97 (42), 57 (100); HR-MS (FAB) calcd for $C_{39}H_{44}N_5O_{11}$ [$M^+ + H$] 758.3037, found 758.3046. R_f (hexane/EtOAc 1/3) = 0.59.

6-[3-Phenyl-5,6,7,8-tetrahydronaphthalen-2-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ai). (Method A)

Column chromatography on silica gel (toluene/diethyl ether 1/1) afforded 15 mg (13%) of a colourless oil: $[\alpha]_D -73.7$ (c 0.07, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 1.86 (m, 4H, H-8'', 9''), 2.09, 2.10 and 2.15 (3s, 3x3H, CH_3CO), 2.88 (m, 4H, H-7'', 10''), 4.36 (m, 1H, H-5'b), 4.43-4.49 (m, 2H, H-5'a and H-4'), 5.68 (dd, 1H, $J_{3',2'} = 5.5$, $J_{3',4'} = 4.8$, H-3'), 5.91 (t, 1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 5.1$, H-2'), 6.20 (d, 1H, $J_{1',2'} = 5.1$, H-1'), 7.09-7.15 (m, 5H, Ph), 7.25 (s, 1H, H-3''), 7.48 (s, 1H, H-6''), 8.03 (s, 1H, H-8), 8.83 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.39, 20.51 and 20.73 (CH_3CO), 23.10 and 23.15 (CH_2 -8'', 9''), 29.05 and 29.41 (CH_2 -7'', 10''), 62.95 (CH_2 -5'), 70.49 (CH -3'), 73.13 (CH -2'), 80.23 (CH -4'), 86.41 (CH -1'), 126.24 (CH -*p*-Ph), 127.79 and 129.16 (CH -*o,m*-Ph); 131.19 (C-1''), 131.53 and 131.70 (CH -3'' and CH -6''), 132.87 (C-5), 136.39 (C-5''), 139.00 (C-2''), 139.35 (C-4''), 141.27 (C-*i*-Ph), 142.25 (CH -8), 150.90 (C-4), 152.45 (CH -2), 159.92 (C-6), 169.29, 169.54 and 170.29 (CO); IR (CHCl_3) ν 2929, 1751, 1588, 1373, 1237, 1110, 1075, 1047 cm^{-1} ; MS (FAB, m/z (rel.%)) 585 ($M^+ + H$, 33), 327 (100), 139 (43), 97 (43); HR-MS (FAB) calcd for $C_{32}H_{33}N_4O_7$ [$M^+ + H$] 585.2349, found 585.2366. R_f (hexane/EtOAc 1/2) = 0.61.

6-[6-Butyl-2,2-di(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ba). (Method A)

Column chromatography on silica gel (toluene/diethyl ether 1/1) afforded 118 mg (85%) of a colourless oil: $[\alpha]_D -26.8$ (c 0.16, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 0.73 (t, 3H, $J_{\text{vic}} = 7.3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.17 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.26 (t, 6H, $J_{\text{vic}} = 7.1$, CH_3CH_2), 1.42 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 2.11, 2.13 and 2.17 (3s, 3x3H, CH_3CO), 2.74 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 3.635 and 3.644 (2s, 2x2H, H-7'' and H-9''), 4.21 (q, 4H, $J_{\text{vic}} =$

7.1, CH_2CH_3), 4.41 (dd, 1H, $J_{\text{gem}} = 12.9$, $J_{5'b,4'} = 5.2$, H-5'b), 4.47-4.52 (m, 2H, H-5'a and H-4'), 5.73 (t, 1H, $J_{3',2'} = 5.5$, $J_{3',4'} = 4.8$, H-3'), 6.01 (t, 1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 5.1$, H-2'), 6.29 (d, 1H, $J_{1',2'} = 5.1$, H-1'), 7.22 (s, 1H, H-3''), 7.41 (s, 1H, H-6''), 8.21 (s, 1H, H-8), 9.03 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, CDCl_3) δ 13.74 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 14.01 (CH_3CH_2), 20.41, 20.53 and 20.75 (CH_3CO), 22.42 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 32.89 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 33.59 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 40.13 and 40.46 (CH_2 -7'' and CH_2 -9''), 60.53 (C-8''), 61.72 (CH_2CH_3), 63.01 (CH_2 -5'), 70.54 (CH-3'), 73.14 (CH-2'), 80.33 (CH-4'), 86.55 (CH-1'), 125.83 and 126.31 (CH-3'' and CH-6''), 132.85 (C-5), 133.19 (C-1''), 137.57 (C-5''), 141.00 (C-2''), 142.17 (C-4''), 142.63 (CH-8), 151.17 (C-4), 152.50 (CH-2), 160.11 (C-6), 169.36, 169.57 and 170.30 (COCH_3), 171.57 (COOEt); IR (CHCl_3) ν 3030, 2985, 1750, 1731, 1588, 1369, 1276, 1245, 1097, 1068, 1052 cm^{-1} ; MS (FAB, m/z (rel. %)) 695 ($\text{M}^+ + \text{H}$, 18), 437 (55), 139 (100), 97 (100); HR-MS (FAB) calcd for $\text{C}_{35}\text{H}_{43}\text{N}_4\text{O}_{11}$ [$\text{M}^+ + \text{H}$] 695.2928, found 695.2935. R_f (hexane/EtOAc 1/2) = 0.66. (**Method B**, yield 23%.)

6-[6-Butyl-2-cyano-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9H-purine (3bd). (Method A**)**

Column chromatography on silica gel (toluene/diethyl ether 1/1) afforded 50 mg (39%) of a colourless oil: $[\alpha]_D -17.5$ (c 0.17, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.75 (t, 3H, $J_{\text{vic}} = 7.3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.18 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.35 (t, 3H, $J_{\text{vic}} = 7.1$, CH_3CH_2), 1.44 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 2.12, 2.13 and 2.17 (3 $\times$ s, 3 $\times$ 3H, CH_3CO), 2.76 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 3.61, 3.63, 3.74 and 3.77 (4 $\times$ d, 4 $\times$ 1H, $J_{\text{gem}} = 16.6$, H-7'' and H-9''), 4.31 (q, 2H, $J_{\text{vic}} = 7.1$, CH_2CH_3), 4.41 (dd, 1H, $J_{\text{gem}} = 13.0$, $J_{5'b,4'} = 5.2$, H-5'b), 4.48-4.52 (m, 2H, H-5'a and H-4'), 5.73 (t, 1H, $J_{3',2'} = 5.5$, $J_{3',4'} = 4.9$, H-3'), 6.01 (t, 1H, $J_{2',3'} = 5.5$, $J_{2',1'} = 5.0$, H-2'), 6.29 (d, 1H, $J_{1',2'} = 5.0$, H-1'), 7.27 (s, 1H, H-3''), 7.47 (s, 1H, H-6''), 8.23 (s, 1H, H-8), 9.04 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, CDCl_3) δ 13.72 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 13.95 (CH_3CH_2), 20.41, 20.53 and 20.75 (CH_3CO), 22.39 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 32.89 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 33.50 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 42.89 and 42.99 (CH_2 -7'' and CH_2 -9''), 47.45 (C-8''), 62.98 (CH_2 -5'), 63.24 (CH_2CH_3), 70.49 (CH-3'), 73.16 (CH-2'), 80.31 (CH-4'), 86.65 (CH-1'), 120.52 (CN), 126.07 (CH-3''), 126.59 (CH-6''), 132.83 (C-5), 134.06 (C-1''), 135.66 (C-5''), 140.19 (C-4''), 142.09 (C-2''), 142.87 (CH-8), 151.24 (C-4), 152.52 (CH-2), 159.46 (C-6), 168.36 (COOEt), 169.38, 169.58 and

170.29 (COCH₃); IR (CHCl₃) ν 3029, 2989, 2246, 1749, 1588, 1371, 1232, 1097, 1064 cm⁻¹; MS (FAB, m/z (rel.%)) 648 (M⁺+H, 19), 390 (74), 259 (24), 139 (100), 97 (76); HR-MS (FAB) calcd for C₃₃H₃₈N₅O₉ [M⁺+H] 648.2670, found 648.2648. R_f(hexane/EtOAc 1/2) = 0.61.

6-[6-Butyl-1,3-dihydroisobenzofuran-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3bg). (Method A)

Column chromatography on silica gel (diethyl ether/acetone 12/1) afforded 24 mg (22%) of a yellowish oil: $[\alpha]_D$ -25.5 (*c* 0.22, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 0.75 (t, 3H, *J*_{vic} = 7.4, CH₃CH₂CH₂CH₂), 1.20 and 1.45 (2×m, 2×2H, CH₃CH₂CH₂CH₂), 2.12, 2.13 and 2.17 (3×s, 3×3H, CH₃CO), 2.79 (m, 2H, CH₃CH₂CH₂CH₂), 4.41 (dd, 1H, *J*_{gem} = 13.0, *J*_{5'b,4'} = 5.3, H-5'b), 4.43-4.53 (m, 2H, H-5'a and H-4'), 5.16 (s, 4H, H-7'' and H-9''), 5.74 (t, 1H, *J*_{3',2'} = 5.5, *J*_{3',4'} = 4.9, H-3'), 6.02 (t, 1H, *J*_{2',3'} = 5.5, *J*_{2',1'} = 5.0, H-2'), 6.30 (d, 1H, *J*_{1',2'} = 5.0, H-1'), 7.27 (s, 1H, H-3''), 7.47 (s, 1H, H-6''); 8.23 (s, 1H, H-8), 9.06 (s, 1H, H-2); ¹³C NMR (100.6 MHz, CDCl₃) δ 13.73 (CH₃CH₂CH₂CH₂), 20.41, 20.53 and 20.75 (CH₃CO), 22.38 (CH₃CH₂CH₂CH₂), 32.92 (CH₃CH₂CH₂CH₂), 33.61 (CH₃CH₂CH₂CH₂), 62.99 (CH₂-5'), 70.51 (CH-3'), 73.17 (CH-2'), 73.40 and 73.48 (CH₂-7'' and CH₂-9''), 80.32 (CH-4'), 86.68 (CH-1'), 122.56 (CH-3''), 123.22 (CH-6''), 132.92 (C-5), 133.54 (C-1''), 136.75 (C-5''), 141.13 (C-4''), 141.59 (C-2''), 142.87 (CH-8), 151.24 (C-4), 152.52 (CH-2), 159.81 (C-6), 169.39, 169.57 and 170.29 (CO); IR (CHCl₃) ν 3030, 2960, 1751, 1588, 1372, 1232, 1098, 1049 cm⁻¹; MS (FAB, m/z (rel.%)) 553 (M⁺+H, 30), 295 (68), 259 (27), 139 (100), 97 (79); HR-MS (FAB) calcd for C₂₈H₃₃N₄O₈ [M⁺+H] 553.2298, found 553.2279. R_f(EtOAc) = 0.60. (**Method C**, yield 28%.)

6-[6-Trimethylsilyl-2,2-di(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ca). (Method A)

Column chromatography on silica gel (toluene/diethyl ether 1/1) afforded 94 mg (66%) of a white foam: $[\alpha]_D$ -21.7 (*c* 0.28, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 0.15 (s, 9H, (CH₃)₃Si), 1.27 (t, 6H, *J*_{vic} = 7.1, CH₃CH₂), 2.11, 2.13 and 2.17 (3×s, 3×3H, CH₃CO), 3.67 and 3.72 (2×s, 2×2H, H-7'' and H-9''), 4.22 (q, 4H, *J*_{vic} = 7.1, CH₂CH₃), 4.41 (dd, 1H, *J*_{gem} = 12.9, *J*_{5'b,4'} = 5.1, H-5'b), 4.46-4.52 (m, 2H, H-5'a and H-4'), 5.73 (dd, 1H, *J*_{3',2'} = 5.6, *J*_{3',4'} =

4.6, H-3'), 6.00 (t, 1H, $J_{2',3'} = 5.6$, $J_{2',1'} = 5.2$, H-2'), 6.31 (d, 1H, $J_{1',2'} = 5.2$, H-1'), 7.65 (s, 1H, H-3''), 8.22 (s, 1H, H-6''), 8.26 (s, 1H, H-8); 8.95 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, CDCl_3) δ 1.62 ((CH_3) $_3$ Si), 14.01 (CH_3CH_2), 20.39, 20.53 and 20.76 (CH_3CO), 40.49 and 40.55 (CH_2 -7'' and CH_2 -9''), 60.28 (C-8''), 61.75 (CH_2CH_3), 63.01 (CH_2 -5'), 70.57 (CH-3'), 73.18 (CH-2'), 80.34 (CH-4'), 86.41 (CH-1'), 127.35 (CH-6''), 131.79 (C-5), 132.00 (CH-3''), 139.96 and 140.09 (C-1'' and C-2''), 140.89 (C-5''), 141.80 (C-4''), 142.39 (CH-8), 151.54 (CH-2), 151.58 (C-4), 158.88 (C-6), 169.33, 169.55 and 170.29 (COCH_3), 172.42 (COOEt); IR (CHCl_3) ν 3030, 2986, 1750, 1732, 1585, 1577, 1369, 1247, 1193, 1069, 1052 cm^{-1} ; MS (FAB, m/z (rel.%)) 711 ($\text{M}^+\text{+H}$, 17), 437 (13), 139 (7), 97 (12), 73 (100); HR-MS (FAB) calcd for $\text{C}_{34}\text{H}_{43}\text{N}_4\text{O}_{11}\text{Si}$ [$\text{M}^+\text{+H}$] 711.2698, found 711.2709. EA calcd for $\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_{11}\text{Si}$: C 57.45, H 5.96, N 7.88; found: C 57.30, H 5.90, N 7.81. R_f (hexane/EtOAc 1/2) = 0.60. (**Method B**, yield 18%.)

6-[6-Trimethylsilyl-1,3-dihydro-2-tosyl-2H-indol-5-yl]-9-(2,3,5-tri-O-acetyl-β-D-ribofuranosyl)-9H-purine (3ce). (Method A)

Column chromatography on silica gel (toluene/diethyl ether 1/1) afforded 33 mg (23%) of a yellowish oil: $[\alpha]_D -21.8$ (c 0.17, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 0.12 (s, 9H, (CH_3) $_3$ Si), 2.10, 2.12 and 2.17 (3×s, 3×3H, CH_3CO), 2.41 (s, 3H, CH_3 -Tos), 4.40 (dd, 1H, $J_{\text{gem}} = 12.9$, $J_{5'b,4'} = 5.2$, H-5'b), 4.46-4.52 (m, 2H, H-5'a and H-4'), 4.69-4.73 (m, 4H, H-7'' and H-9''), 5.72 (dd, 1H, $J_{3',2'} = 5.6$, $J_{3',4'} = 4.7$, H-3'), 5.98 (t, 1H, $J_{2',3'} = 5.6$, $J_{2',1'} = 5.0$, H-2'), 6.29 (d, 1H, $J_{1',2'} = 5.0$, H-1'), 7.32 (m, 2H, H-*m*-Tos), 7.61 (s, 1H, H-3''), 7.78 (m, 2H, H-*o*-Tos), 8.17 (s, 1H, H-6''), 8.24 (s, 1H, H-8), 8.95 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.46 ((CH_3) $_3$ Si), 20.40, 20.53 and 20.76 (CH_3CO), 21.48 (CH_3 -Tos), 53.82 (CH_2 -7'' and CH_2 -9''), 62.97 (CH_2 -5'), 70.50 (CH-3'), 73.21 (CH-2'), 80.33 (CH-4'), 86.62 (CH-1'), 125.57 (CH-6''), 127.60 (CH-*o*-Tos), 129.85 (CH-*m*-Tos), 130.25 (CH-3''), 131.86 (C-5), 133.50 (C-*i*-Tos), 136.92 (C-5''), 137.50 (C-4''), 140.71 (C-1''), 141.38 (C-2''), 142.77 (CH-8), 143.75 (C-*p*-Tos), 151.60 (CH-2 and C-4), 158.16 (C-6), 169.37, 169.57 and 170.27 (CO); IR (CHCl_3) ν 3031, 3001, 1751, 1586, 1374, 1348, 1331, 1230, 1164, 1099, 1066, 1049 cm^{-1} ; MS (FAB, m/z (rel.%))

722 ($M^+ + H$, 30), 448 (17), 139 (70), 97 (71), 73 (100); HR-MS (FAB) calcd for $C_{34}H_{40}N_5O_9Si$ [$M^+ + H$] 722.2316, found 722.2329. R_f (hexane/EtOAc 1/2) = 0.56. (**Method B**, yield 41%.)

6-[6-Trimethylsilyl-1,3-dihydroisobenzofuran-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3cg). (Method A)

Column chromatography on silica gel (diethyl ether) afforded 17 mg (15%) of a white foam: $[\alpha]_D +25.8$ (c 0.21, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H, $(CH_3)_3Si$), 2.11, 2.13 and 2.17 (3 $\times$ s, 3 $\times$ 3H, CH_3CO), 4.41 (dd, 1H, $J_{gem} = 12.9$, $J_{5'b,4'} = 5.2$, H-5'b), 4.47-4.52 (m, 2H, H-5'a and H-4'), 5.21 (m, 4H, H-7'' and H-9''), 5.73 (dd, 1H, $J_{3',2'} = 5.6$, $J_{3',4'} = 4.7$, H-3'), 6.01 (t, 1H, $J_{2',3'} = 5.6$, $J_{2',1'} = 5.1$, H-2'), 6.31 (d, 1H, $J_{1',2'} = 5.1$, H-1'), 7.70 (s, 1H, H-3''), 8.27 (s, 2H, H-8 and H-6''), 8.98 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 1.59 ($(CH_3)_3Si$), 20.40, 20.53 and 20.76 (CH_3CO), 63.00 (CH_2-5'), 70.54 ($CH-3'$), 73.21 ($CH-2'$), 73.57 (CH_2-7'' and CH_2-9''), 80.35 ($CH-4'$), 86.55 ($CH-1'$), 124.11 ($CH-6''$), 128.60 ($CH-3''$), 131.89 (C-5), 140.09, 140.35, 140.67 and 140.78 (C-1'', C-2'', C-4'' and C-5''), 142.62 ($CH-8$), 151.60 ($CH-2$), 151.62 (C-4), 158.65 (C-6), 169.36, 169.56 and 170.28 (CO); IR ($CHCl_3$) ν 3008, 1751, 1586, 1374, 1247, 1048 cm^{-1} . MS (FAB, m/z (rel.%)): 569 ($M^+ + H$, 15), 285 (8), 266 (7), 73 (100). HR-MS (FAB) calcd for $C_{27}H_{33}N_4O_8Si$ [$M^+ + H$] 569.2068, found 569.2087. R_f (hexane/EtOAc 1/2) = 0.37. (**Method C**, yield 55%.)

IV. Deprotection of the Acetylated 9-(β -D-Ribofuranosyl)-6-arylpurines.

General Procedure for Deprotection of (2,3,5-Tri-*O*-acetyl- β -D-ribofuranosyl)-6-arylpurines.

The prepared 6-aryl-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine **3xy** (0.2 mmol) in methanol (8 ml) was treated with 1 M methanolic sodium methoxide (40 μ l, 0.040 mmol) at room temperature for 1 h. The mixture was evaporated with silica gel and chromatographed on a silica column affording the corresponding 6-aryl-9-(β -D-ribofuranosyl)-9*H*-purine **4xy**.

6-[6-Phenyl-2,2-di(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9*H*-purine (**4aa**).

Column chromatography on silica gel (EtOAc) afforded 90 mg (76%) of a white foam: $[\alpha]_D -30.4$ (*c* 0.13, MeOH); ^1H NMR (500 MHz, DMSO-*d*₆) δ 1.21 (t, 6H, $J_{\text{vic}} = 7.1$, CH₃CH₂), 3.56 (ddd, 1H, $J_{\text{gem}} = 12.0$, $J_{5'b,\text{OH}} = 6.0$, $J_{5'b,4'} = 4.1$, H-5'b), 3.61 (s, 2H, H-7''), 3.64 (s, 2H, H-9''), 3.67 (ddd, 1H, $J_{\text{gem}} = 12.0$, $J_{5'a,\text{OH}} = 5.1$, $J_{5'a,4'} = 4.1$, H-5'a), 3.96 (q, 1H, $J_{4',5'} = 4.1$, $J_{4',3'} = 3.5$, H-4'), 4.15 (td, 1H, $J_{3',2'} = 5.8$, $J_{3',\text{OH}} = 5.0$, $J_{3',4'} = 3.5$, H-3'), 4.20 (q, 4H, $J_{\text{vic}} = 7.1$, CH₂CH₃), 4.58 (q, 1H, $J_{2',\text{OH}} = 6.1$, $J_{2',1'} = 5.8$, $J_{2',3'} = 5.8$, H-2'), 5.07 (t, 1H, $J_{\text{OH},5'} = 6.0$, 5.1, OH-5'), 5.22 (d, 1H, $J_{\text{OH},3'} = 5.0$, OH-

3'), 5.49 (d, 1H, $J_{\text{OH},2'} = 6.1$, OH-2'), 6.00 (d, 1H, $J_{1',2'} = 5.8$, H-1'), 7.03 (m, 2H, H-*o*-Ph), 7.09-7.17 (m, 3H, H-*m,p*-Ph), 7.40 (s, 1H, H-3''), 7.54 (s, 1H, H-6''), 8.68 (s, 1H, H-8), 8.75 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, DMSO-*d*₆) δ 14.02 (CH₃CH₂), 39.51 (CH₂-7'' overlapped by DMSO-*d*₆), 39.94 (CH₂-7'' overlapped by DMSO-*d*₆), 59.94 (C-8''), 61.44 (CH₂-5'), 61.71 (CH₂CH₃), 70.44 (CH-3'), 73.75 (CH-2'), 85.86 (CH-4'), 87.61 (CH-1'), 126.38 (CH-3''), 126.67 (CH-*p*-Ph), 127.03 (CH-6''), 128.00 (CH-*m*-Ph), 128.93 (CH-*o*-Ph), 132.46 (C-5), 133.42 (C-1''), 138.91 (C-5''), 140.57 (C-2''), 141.01 (C-*i*-Ph), 141.94 (C-4''), 144.79 (CH-8), 151.32 (C-4), 151.65 (CH-2), 158.33 (C-6), 171.02 (CO); KBr ν 3296, 3235, 1731, 1589, 1248, 1072 cm⁻¹; MS (FAB, *m/z* (rel.%)) 589 ($\text{M}^+ + \text{H}$, 26), 457 (100); HR-MS (FAB) calcd for C₃₁H₃₃N₄O₈ [$\text{M}^+ + \text{H}$] 589.2298, found 589.2296. R_f (EtOAc/MeOH 10/1) = 0.47.

6-[6-Phenyl-2-acetyl-2-(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9*H*-purine (**4ac**).

Column chromatography on silica gel (EtOAc/MeOH 10/1) afforded 92 mg (82%) of a white foam: $[\alpha]_D -40.1$ (*c* 0.19, MeOH); ^1H NMR (500 MHz, DMSO-*d*₆) δ 1.22 (t, 3H, $J_{\text{vic}} = 7.1$,

CH_3CH_2), 2.26 (s, 3H, CH_3CO), 3.51-3.70 (m, 6H, H-5', H-7'' and H-9''), 3.96 (q, 1H, $J_{4',5'} = 4.0$, $J_{4',3'} = 3.6$, H-4'), 4.15 (td, 1H, $J_{3',\text{OH}} = 5.0$, $J_{3',2'} = 4.9$, $J_{3',4'} = 3.6$, H-3'), 4.21 (q, 2H, $J_{\text{vic}} = 7.1$, CH_2CH_3), 4.59 (q, 1H, $J_{2',\text{OH}} = 6.2$, $J_{2',1'} = 5.8$, $J_{2',3'} = 4.9$, H-2'), 5.09 (t, 1H, $J_{\text{OH},5'} = 5.5$, OH-5'), 5.25 (d, 1H, $J_{\text{OH},3'} = 5.0$, OH-3'), 5.51 (d, 1H, $J_{\text{OH},2'} = 6.2$, OH-2'), 6.00 (d, 1H, $J_{1',2'} = 5.8$, H-1'), 7.02 (m, 2H, H-*o*-Ph), 7.09-7.17 (m, 3H, H-*m,p*-Ph), 7.38 (s, 1H, H-3''), 7.53 (s, 1H, H-6''), 8.68 (s, 1H, H-8), 8.75 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, $\text{DMSO}-d_6$) δ 14.04 (CH_3CH_2), 26.33 (CH_3CO), 38.20 and 38.49 (CH_2 -7'' and CH_2 -9''), 61.46 (CH_2 -5'), 61.84 (CH_2CH_3), 66.54 (C-8''), 70.47 (CH-3'), 73.77 (CH-2'), 85.89 (CH-4'), 87.61 (CH-1'), 126.46 (CH-3''), 126.69 (CH-*p*-Ph), 127.12 (CH-6''), 128.04 (CH-*m*-Ph), 128.96 (CH-*o*-Ph), 132.48 (C-5), 133.36 (C-1'), 139.11 (C-5''), 140.52 (C-2''), 141.08 (C-*i*-Ph), 142.15 (C-4''), 144.85 (CH-8), 151.35 (C-4), 151.69 (CH-2), 158.38 (C-6), 171.90 (COOEt), 202.77 (COMe); IR (KBr) ν 3418, 1734, 1713, 1587, 1329, 1237, 1216, 1088, 1074 cm^{-1} ; MS (FAB, m/z (rel.%)) 559 ($\text{M}^+ + \text{H}$, 55), 427 (100); HR-MS (FAB) calcd for $\text{C}_{31}\text{H}_{33}\text{N}_4\text{O}_8$ [$\text{M}^+ + \text{H}$] 559.2193, found 559.2214. $R_f(\text{EtOAc}/\text{MeOH } 10/1) = 0.47$.

6-[6-Phenyl-2-cyano-2-(carboxymethyl)indan-5-yl]-9-(β-D-ribofuranosyl)-9H-purine (4ad).

Column chromatography on silica gel (EtOAc) afforded 65 mg (60%) of a white amorphous solid: mp 121-126°C; $[\alpha]_D -42.3$ (c 0.15, MeOH); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 3.56 (ddd, 1H, $J_{\text{gem}} = 12.0$, $J_{5'b,\text{OH}} = 6.0$, $J_{5'b,4'} = 4.1$, H-5'b), 3.67 (ddd, 1H, $J_{\text{gem}} = 12.0$, $J_{5'a,\text{OH}} = 5.0$, $J_{5'a,4'} = 4.1$, H-5'a), 3.71, 3.74, 3.76 and 3.79 (4×d, 4H, $J_{\text{gem}} = 16.5$, H-7'' and H-9''), 3.84 (s, 3H, CH_3O), 3.96 (q, 1H, $J_{4',5'} = 4.1$, $J_{4',3'} = 3.7$, H-4'), 4.15 (td, 1H, $J_{3',2'} = 4.9$, $J_{3',\text{OH}} = 4.9$, $J_{3',4'} = 3.7$, H-3'), 4.59 (q, 1H, $J_{2',\text{OH}} = 6.1$, $J_{2',1'} = 5.8$, $J_{2',3'} = 4.9$, H-2'), 5.07 (t, 1H, $J_{\text{OH},5'} = 6.0$, 5.0, OH-5'), 5.22 (d, 1H, $J_{\text{OH},3'} = 4.9$, OH-3'), 5.49 (d, 1H, $J_{\text{OH},2'} = 6.1$, OH-2'), 6.00 (d, 1H, $J_{1',2'} = 5.8$, H-1'), 7.05 (m, 2H, H-*o*-Ph), 7.11-7.18 (m, 3H, H-*m,p*-Ph), 7.47 (s, 1H, H-3''), 7.62 (s, 1H, H-6''), 8.69 (s, 1H, H-8), 8.77 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, $\text{DMSO}-d_6$) δ 42.41 and 42.62 (CH_2 -7'' and CH_2 -9''), 47.62 (C-8''), 54.11 (CH_3O), 61.46 (CH_2 -5'), 70.44 (CH-3'), 73.77 (CH-2'), 85.86 (CH-4'), 87.63 (CH-1'), 120.95 (CN), 126.65 (CH-3''), 126.82 (CH-*p*-Ph), 127.28 (CH-6''), 128.05 (CH-*m*-Ph), 128.93 (CH-*o*-Ph), 132.45 (C-5), 133.90 (C-

1"), 137.67 (C-5"), 140.67 and 140.78 (C-2" and C-4"), 141.09 (C-*i*-Ph), 144.90 (CH-8), 151.38 (C-4), 151.68 (CH-2), 158.02 (C-6), 168.68 (CO); IR (KBr) ν 3295, 2246, 1747, 1588, 1435, 1330, 1240, 1215, 1088, 1074, 1057 cm^{-1} ; MS (FAB, m/z (rel.%)) 528 ($M^+ + H$, 18), 396 (100); HR-MS (FAB) calcd for $C_{28}H_{26}N_5O_6$ [$M^+ + H$] 528.1883, found 528.1897. $R_f(\text{EtOAc/MeOH } 10/1) = 0.40$.

6-[6-Phenyl-1,3-dihydro-2-tosyl-2*H*-indol-5-yl]-9-(β -D-ribofuranosyl)-9*H*-purine (4ae).

Column chromatography on silica gel (EtOAc) afforded 78 mg (65%) of a white amorphous solid: mp 147-152°C; $[\alpha]_D -33.5$ (c 0.18, MeOH); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 2.38 (s, 3H, CH_3), 3.54 (ddd, 1H, $J_{\text{gem}} = 12.2$, $J_{5'b,\text{OH}} = 6.1$, $J_{5'b,4'} = 4.3$, H-5'b), 3.66 (ddd, 1H, $J_{\text{gem}} = 12.2$, $J_{5'a,\text{OH}} = 5.2$, $J_{5'a,4'} = 4.2$, H-5'a), 3.95 (q, 1H, $J_{4',5'b} = 4.3$, $J_{4',5'a} = 4.2$, $J_{4',3'} = 3.8$, H-4'), 4.14 (q, 1H, $J_{3',2'} = 5.4$, $J_{3',\text{OH}} = 4.7$, $J_{3',4'} = 3.8$, H-3'), 4.57 (q, 1H, $J_{2',\text{OH}} = 6.1$, $J_{2',1'} = 5.8$, $J_{2',3'} = 5.4$, H-2'), 4.68 and 4.70 (2 $\times$ bs, 2 $\times$ 2H, H-7" and H-9"), 5.08 (t, 1H, $J_{\text{OH},5'b} = 6.1$, $J_{\text{OH},5'a} = 5.2$, OH-5'), 5.25 (d, 1H, $J_{\text{OH},3'} = 4.7$, OH-3'), 5.51 (d, 1H, $J_{\text{OH},2'} = 6.1$, OH-2'), 5.98 (d, 1H, $J_{1',2'} = 5.8$, H-1'), 6.99 (m, 2H, *m*-H-Ph), 7.10-7.15 (m, 3H, *o*-+ *p*-H-Ph), 7.41 (s, 1H, H-6"), 7.45 (m, 2H, *m*-H-Tos), 7.55 (s, 1H, H-3"), 7.80 (m, 2H, *o*-H-Tos), 8.67 (s, 1H, H-8), 8.75 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$) δ 21.20 (CH_3), 53.50 and 53.67 (CH_2 -7" and CH_2 -9"), 61.42 (CH_2 -5'), 70.43 (CH -3'), 73.76 (CH -2'), 85.87 (CH -4'), 87.61 (CH -1'), 125.08 (CH -6"), 125.65 (CH -3"), 126.94 (CH -*p*-Ph), 127.68 (CH -*o*-Tos), 128.08 (CH -*o*-Ph), 128.90 (CH -*m*-Ph), 130.27 (CH -*m*-Tos), 132.43 (C-5), 133.06 (C-*i*-Tos), 134.12 and 135.06 (C-2" and C-4"), 137.90 (C-5"), 140.57 (C-*i*-Ph), 141.23 (C-1"), 144.04 (C-*p*-Tos), 144.99 (CH-8), 151.36 (C-4), 151.70 (CH-2), 157.77 (C-6); IR (KBr) ν 3429, 3260, 1587, 1332, 1162, 1096, 1074, 1056 cm^{-1} ; MS (FAB, m/z (rel.%)) 600 ($M^+ + H$, 13), 468 (100); HR-MS (FAB) calcd for $C_{31}H_{30}N_5O_6S$ [$M^+ + H$] 600.1917, found 600.1938. $R_f(\text{EtOAc/MeOH } 10/1) = 0.36$.

6-[6-Phenyl-1,3-dihydroisobenzofuran-5-yl]-9-(β -D-ribofuranosyl)-9*H*-purine (4ag).

Column chromatography on silica gel (EtOAc/MeOH 10/1) afforded 76 mg (85%) of a white amorphous solid: mp 138-141°C; $[\alpha]_D -36.6$ (c 0.14, MeOH); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 3.56 (ddd, 1H, $J_{\text{gem}} = 12.0$, $J_{5'b,\text{OH}} = 6.0$, $J_{5'b,4'} = 4.1$, H-5'b), 3.67 (ddd, 1H, $J_{\text{gem}} = 12.0$,

$J_{5'a,OH} = 5.2$, $J_{5'a,4'} = 4.1$, H-5'a), 3.96 (q, 1H, $J_{4',5'} = 4.1$, $J_{4',3'} = 3.4$, H-4'), 4.15 (td, 1H, $J_{3',2'} = 5.1$, $J_{3',OH} = 5.0$, $J_{3',4'} = 3.4$, H-3'), 4.59 (q, 1H, $J_{2',OH} = 6.2$, $J_{2',1'} = 5.8$, $J_{2',3'} = 5.1$, H-2'), 5.09 (t, 1H, $J_{OH,5'} = 6.0$, 5.2, OH-5'), 5.13 (m, 4H, H-7'' and H-9''), 5.25 (d, 1H, $J_{OH,3'} = 5.0$, OH-3'), 5.51 (d, 1H, $J_{OH,2'} = 6.2$, OH-2'), 6.00 (d, 1H, $J_{1',2'} = 5.8$, H-1'), 7.06 (m, 2H, H-*o*-Ph), 7.10-7.19 (m, 3H, H-*m,p*-Ph), 7.48 (s, 1H, H-3''), 7.63 (s, 1H, H-6''), 8.70 (s, 1H, H-8), 8.77 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, DMSO- d_6) δ 61.45 (CH₂-5'), 70.46 (CH-3'), 72.57 and 72.72 (H-7'' and H-9''), 73.76 (CH-2'), 85.88 (CH-4'), 87.62 (CH-1'), 123.39 (CH-3''), 124.06 (CH-6''), 126.81 (CH-*p*-Ph), 128.06 (CH-*m*-Ph), 129.01 (CH-*o*-Ph), 132.54 (C-5), 133.77 (C-1''), 138.24 (C-5''), 140.97 and 140.98 (C-2'' and C-*i*-Ph), 141.18 (C-4''), 144.93 (CH-8), 151.37 (C-4), 151.69 (CH-2), 158.24 (C-6); IR (KBr) ν 3435, 1589, 1331, 1208, 1088, 1076, 1048 cm^{-1} ; MS (FAB, m/z (rel.%)) 447 ($M^+ + H$, 69), 315 (100); HR-MS (FAB) calcd for $\text{C}_{24}\text{H}_{23}\text{N}_4\text{O}_5$ [$M^+ + H$] 447.1668, found 447.1658. R_f (EtOAc/MeOH 5/1) = 0.59.

6-[6-Butyl-2,2-di(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9H-purine (4ba).

Column chromatography on silica gel (EtOAc) afforded 100 mg (88%) of a white amorphous solid: mp 65-68°C; $[\alpha]_D -24.2$ (c 0.14, MeOH); ^1H NMR (500 MHz, DMSO- d_6) δ 0.65 (t, 3H, $J_{\text{vic}} = 7.3$, CH₃CH₂CH₂CH₂), 1.09 (m, 2H, CH₃CH₂CH₂CH₂), 1.19 (t, 6H, $J_{\text{vic}} = 7.1$, CH₃CH₂), 1.32 (m, 2H, CH₃CH₂CH₂CH₂), 2.68 (m, 2H, CH₃CH₂CH₂CH₂), 3.52 (bs, 2H, H-7''), 3.56 (bs, 2H, H-9''), 3.59 (ddd, 1H, $J_{\text{gem}} = 12.1$, $J_{5'b,OH} = 6.0$, $J_{5'b,4'} = 4.1$, H-5'b), 3.70 (ddd, 1H, $J_{\text{gem}} = 12.1$, $J_{5'a,OH} = 5.2$, $J_{5'a,4'} = 4.2$, H-5'a), 4.00 (q, 1H, $J_{4',5'} = 4.2$, 4.1, $J_{4',3'} = 3.4$, H-4'), 4.17 (q, 4H, $J_{\text{vic}} = 7.1$, CH₂CH₃), 4.20 (td, 1H, $J_{3',OH} = 5.0$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.4$, H-3'), 4.67 (q, 1H, $J_{2',OH} = 6.0$, $J_{2',1'} = 5.8$, $J_{2',3'} = 4.8$, H-2'), 5.12 (t, 1H, $J_{OH,5'} = 6.0$, 5.2, OH-5'), 5.27 (d, 1H, $J_{OH,3'} = 5.0$, OH-3'), 5.57 (d, 1H, $J_{OH,2'} = 6.0$, OH-2'), 6.08 (d, 1H, $J_{1',2'} = 5.8$, H-1'), 7.27 (s, 1H, H-3''), 7.40 (s, 1H, H-6''), 8.82 (s, 1H, H-8), 8.98 (s, 1H, H-2); ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 13.69 (CH₃CH₂CH₂CH₂), 14.05 (CH₃CH₂), 21.97 (CH₃CH₂CH₂CH₂), 32.37 (CH₃CH₂CH₂CH₂), 33.24 (CH₃CH₂CH₂CH₂), 39.70 (CH₂-7''), 39.99 (CH₂-9''), 59.90 (C-8''), 61.46 (CH₂-5'), 61.68 (CH₂CH₃), 70.51 (CH-3'), 73.85 (CH-2'), 85.92 (CH-4'), 87.74 (CH-1'), 125.70 (CH-3''), 126.74 (CH-6''), 132.32 (C-5), 133.70 (C-1''); 137.16 (C-5''), 140.58 (C-2''), 141.59 (C-4''), 145.02 (CH-8), 151.59 (C-

4), 151.80 (CH-2), 158.34 (C-6), 171.12 (COOEt); IR (KBr) ν 3398, 1733, 1586, 1249, 1190, 1072, 1053 cm^{-1} ; MS (FAB, m/z (rel.%)) 569 ($M^+ + H$, 50), 437 (100); HR-MS (FAB) calcd for $C_{29}H_{37}N_4O_8$ [$M^+ + H$] 569.2611, found 569.2600. R_f (EtOAc/MeOH 10/1) = 0.50.

6-[6-Trimethylsilyl-2,2-di(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9H-purine (4ca).

Column chromatography on silica gel (EtOAc) afforded 95 mg (81%) of a white amorphous solid: mp 81-84°C; $[\alpha]_D -9.5$ (c 0.19, MeOH); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 0.11 (s, 9H, $(\text{CH}_3)_3\text{Si}$), 1.19 (t, 6H, $J_{\text{vic}} = 7.1$, CH_3CH_2), 3.58 and 3.59 (2×s, 2×2H, H-7'' and H-9''), 3.60 (ddd, 1H, $J_{\text{gem}} = 11.4$, $J_{5'b,\text{OH}} = 5.8$, $J_{5'b,4'} = 4.1$, H-5'b), 3.71 (ddd, 1H, $J_{\text{gem}} = 11.4$, $J_{5'a,\text{OH}} = 4.9$, $J_{5'a,4'} = 4.1$, H-5'a), 4.00 (q, 1H, $J_{4',5'} = 4.1$, $J_{4',3'} = 3.5$, H-4'), 4.17 (q, 4H, $J_{\text{vic}} = 7.1$, CH_2CH_3), 4.21 (q, 1H, $J_{3',\text{OH}} = 5.1$, $J_{3',2'} = 4.7$, $J_{3',4'} = 3.5$, H-3'), 4.66 (q, 1H, $J_{2',\text{OH}} = 6.0$, $J_{2',1'} = 5.7$, $J_{2',3'} = 4.7$, H-2'), 5.13 (t, 1H, $J_{\text{OH},5'} = 5.8$, 4.9, OH-5'), 5.27 (d, 1H, $J_{\text{OH},3'} = 5.1$, OH-3'), 5.58 (d, 1H, $J_{\text{OH},2'} = 6.0$, OH-2'), 6.10 (d, 1H, $J_{1',2'} = 5.7$, H-1'), 7.65 (s, 1H, H-3''), 8.25 (s, 1H, H-6''), 8.89 (s, 1H, H-8), 8.97 (s, 1H, H-2); ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$) δ 1.98 ($(\text{CH}_3)_3\text{Si}$), 14.04 (CH_3CH_2), 40.12 (CH_2 -7'' and CH_2 -9''), 59.75 (C-8''), 61.41 (CH_2 -5'), 61.71 (CH_2CH_3), 70.47 (CH-3'), 73.92 (CH-2'), 85.90 (CH-4'), 87.75 (CH-1'), 127.36 (CH-6''), 131.28 (C-5), 131.73 (CH-3''), 139.27 (C-2''), 140.28 (C-1''), 140.80 (C-5''), 141.52 (C-4''), 145.02 (CH-8), 151.02 (CH-2), 152.02 (C-4), 156.98 (C-6), 171.08 (COOEt); IR (KBr) ν 3425, 3270, 1733, 1582, 1247, 1210, 1190, 1071, 1053 cm^{-1} ; MS (FAB, m/z (rel.%)) 585 ($M^+ + H$, 15), 453 (32), 73 (100); HR-MS (FAB) calcd for $C_{28}H_{37}N_4O_8\text{Si}$ [$M^+ + H$] 585.2381, found 585.2366. R_f (EtOAc) = 0.42.

V. Cyclotrimerization of Unprotected 9-(β -D-Ribofuranosyl)-6-alkynylpurines.

General procedure for $\text{Ni}(\text{cod})_2/2\text{PPh}_3$ catalyzed cyclotrimerization of 6-alkynylpurine **5** with diynes **2**.

Into a mixture of $\text{Ni}(\text{cod})_2$ (0.04 mmol, 11 mg) and PPh_3 (0.10 mmol, 26 mg) was added a solution of 6-alkynyl-9-(β -D-ribofuranosyl)-9*H*-purine **5**⁶ (0.20 mmol) and diyne **2** (0.22 mmol) in dry MeCN (4 mL). The reaction mixture was initially stirred at 20°C for 24 h or until the consumption of the starting material (TLC). The mixture was evaporated with silica gel and chromatographed on a silica column affording the corresponding 6-aryl-9-(β -D-ribofuranosyl)-9*H*-purine **4xy**.

6-[6-Phenyl-2,2-di(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9*H*-purine (**4aa**).

Column chromatography on silica gel (EtOAc) afforded 36 mg (31%) of a white foam.

6-[6-Phenyl-2-acetyl-2-(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9*H*-purine (**4ac**).

Column chromatography on silica gel (EtOAc/MeOH 10/1) afforded 50 mg (45%) of a white foam.

VI. References.

1. (a) Kotha, S.; Brahmachary, E. *J. Org. Chem.* **2000**, *65*, 1359–1365. (b) Kotha, S.; Mohanraja, K.; Durani, S. *Chem. Commun.* **2000**, 1910–1911. (c) Oediger, H.; Miller, F. *Liebigs Ann. Chem.* **1976**, 348–351.
2. Aresta, M.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1969**, *3*, 227–231.
3. Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of Transition Metal in Organic Synthesis*; Springer: Berlin, 1998.
4. Turek, P.; Katora, M.; Hocek, M.; Votruba, I. *Collect. Czech. Chem. Commun.* **2005**, *70*, 339–349.
5. Nauš, P.; Votruba, I.; Hocek, M. *Collect. Czech. Chem. Commun.* **2004**, *69*, 1955–1970.
6. Compound **5** was prepared essentially as described before: Koyama, S.; Kumazawa, Z.; Kashimura, N. *Nucl. Acid Res., Symp. Ser.* **1982**, *11*, 41–44.

VII. Spectra of the Prepared Compounds.

6-(Hex-1-yn-1-yl)-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (1b).

6-[6-Phenyl-2,2-di(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9H-purine (3aa).

6-[6-Phenyl-(2,2-diacetylyndan-5-yl)]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ab).

6-[6-Phenyl-2-acetyl-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ac).

6-[6-Phenyl-2-cyano-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ad).

6-[6-Phenyl-1,3-dihydro-2-tosyl-2*H*-indol-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ae).

6-[6-Phenyl-1,3-dihydro-2-phenyl-2*H*-indol-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3af).

6-[6-Phenyl-1,3-dihydroisobenzofuran-5-yl)]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ag).

6-[6-Phenyl-2-[[[(1,1-dimethylethoxy)carbonyl]amino]-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ah).

6-[3-Phenyl-5,6,7,8-tetrahydronaphthalen-2-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ai).

6-[6-Butyl-2,2-di(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ba).

6-[6-Butyl-2-cyano-2-(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3bd).

6-[6-Butyl-1,3-dihydroisobenzofuran-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3bg).

6-[6-Trimethylsilyl-2,2-di(carboxyethyl)indan-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ca).

6-[6-Trimethylsilyl-1,3-dihydro-2-tosyl-2*H*-indol-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3ce).

6-[6-Trimethylsilyl-1,3-dihydroisobenzofuran-5-yl]-9-(2,3,5-tri-*O*-acetyl- β -D-ribofuranosyl)-9*H*-purine (3cg).

6-[6-Phenyl-2-acetyl-2-(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9H-purine (4ac).

6-[6-Phenyl-2-cyano-2-(carboxymethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9H-purine (4ad).

6-[6-Phenyl-1,3-dihydro-2-tosyl-2H-indol-5-yl]-9-(β-D-ribofuranosyl)-9H-purine (4ae).

6-[6-Phenyl-1,3-dihydroisobenzofuran-5-yl]-9-(β-D-ribofuranosyl)-9H-purine (4a).

6-[6-Butyl-2,2-di(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9H-purine (4ba).

6-[6-Trimethylsilyl-2,2-di(carboxyethyl)indan-5-yl]-9-(β -D-ribofuranosyl)-9H-purine (4ca).