Supporting Information

Selective Magnesiation of Chloro-Iodopurines: An Efficient Approach to New Purine Derivatives.

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General. All reactions were performed under a nitrogen atmosphere. NMR spectra were measured on a Varian Gemini 300 (^1H , 300.07 MHz; ^{13}C , 75.46 MHz), a Bruker AMX3 400 (^1H , 400.13 MHz and ^{13}C , 100.62 MHz) or a Bruker DRX 500 Avance (^1H , 500.13 MHz and ^{13}C , 125.77 MHz) spectrometer at 298 K. Unambiguous assignment of the NMR signals is based on $^{13}\text{C}\{^1\text{H}\}$, ^{13}C APT, COSY, HMQC and ^{13}C HMBC spectra. IR spectra were recorded on Nicolet 750 FT-IR. Mass spectra were measured on ZAB-SEQ (VG Analytical). The solvents were dried and degassed by standard procedures, silica gel (ICN SiliTech, 32-63) was used for column chromatography. 6-Chloro-2-iodo-9-isopropylpurine (**1**)¹ and 9-benzyl-2,6-dichloropurine² were prepared by the reported procedures, other compounds were purchased.

9-Benzyl-2-chloro-6-iodopurine (4**)**³ 9-Benzyl-2,6-dichloropurine (1.48 g, 5.3 mmol) was added under stirring to the ice cooled 57% hydroiodic acid (10 ml) and the suspension was stirred 90 min at 0°C. The reaction mixture was then diluted with water; the product was filtered off, washed with cool water a small amount of acetone. Such obtained solid was then suspended in 50 ml of water and pH was adjusted to 9 by addition of aq. ammonia. The product was filtered off, washed with small amount of water and dried on air yielding 1.698 g (86%) of the product as a white crystals. M.p.: 152-155°C (toluene). ^1H NMR (300 MHz, CDCl_3) δ = 5.38 (s, 2H, CH_2Ph), 7.26-7.40 (m, 5H, ArH), 8.05 (s, 1H, H-8 Pu).

Typical procedure: Preparation of 6-chloro-9-isopropyl-2-(3-nitrophenylhydroxymethyl)purine (2c**).** To the solution of **1** (0.286 g, 0.887 mmol) in THF (10 ml) was at -78°C added *i*PrMgCl (0.49 ml, 0.98 mmol of 2M solution in diethylether) and the mixture was stirred at this temperature. After 30 min all **1** was consumed (TLC) and 3-nitrobenzaldehyde (0.204g, 1.35 mmol) was added. The reaction mixture was stirred 10 h at -80°C, and then allowed to warm to a room temperature and quenched with saturated solution of NH_4Cl (10 ml). Organic phase was separated and water was extracted with dichloromethane (2x10 ml). Combined organic extracts were dried over MgSO_4 , the solvent was then evaporated and pure **2c** was obtained by chromatography on silica (15 g, hexane - ethylacetate 1:2) as white foam 0.213 g (69%). ^1H NMR (500 MHz, CDCl_3) δ = 1.65 (m, 6H, 2CH_3), 4.83 (d, J = 5.9 Hz, 1H, OH), 4.92 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 6.04 (d, J = 5.6 Hz, 1H, CH-O), 7.51 (m, 1H, ArH), 7.97 (d, J = 7.6 Hz, 1H, ArH), 8.11 (d, J = 7.0 Hz, 1H, ArH), 8.18 (s, 1H, H-8 Pu), 8.49 (s, 1H, ArH). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 22.4 (CH_3), 48.4 ($\text{CH}(\text{CH}_3)_2$), 74.2 (CH-O), 121.7 (CH Ar), 122.7 (CH Ar), 129.2 (CH Ar), 131.1 (C-5 Pu), 132.8 (CH Ar), 143.6 (C-8 Pu), 144.0 (C_q Ar), 148.2 (C_q Ar), 151.2 and 151.7 (C-6 Pu and C-4 Pu), 162.6 (C-2 Pu). IR (CHCl_3): 3476, 3016, 1593, 1562, 1532, 1374, 1352 cm^{-1} . HR-MS (EI): Calculated for $\text{C}_{12}\text{H}_{14}\text{N}_5\text{O}_3\text{Cl}$ 347.0785; Found 347.0771.

2a: ^1H NMR (300 MHz, CDCl_3) δ = 1.65 (d, J = 6.9 Hz, 6H, 2CH_3), 4.54 (d, J = 6.9 Hz, 1H, OH), 4.91 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 5.96 (d, J = 6.6 Hz, 1H, CH-O), 7.23-7.35 (m, 3H, PhH), 7.54 (d, J = 7.4 Hz, 2H, PhH), 8.14 (s, 1H, H-8 Pu).

Compound was characterized as 4-nitrobenzoate: White foam, ^1H NMR (500 MHz, CDCl_3) δ = 1.60 (m, 6H, 2CH_3), 4.83 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 7.06 (s, 1H, CH-O), 7.40 (m, 3H, PhH), 7.60 (d, J = 7.3 Hz, 2H, PhH), 8.12 (s, 1H, H-8 Pu), 8.32 (d, J = 8.9 Hz, 2H, ArH), 8.35 (d, J = 8.9 Hz, 2H, ArH). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 22.2 (CH_3), 22.3 (CH_3), 48.3

¹ Legraverend, M.; Ludwig, O.; Bisagni, E.; Leclerc, S.; Meijer, L.; Giocanti, N.; Sadri, R.; Favaudon, V. *Bioorg. Med. Chem.* **1999**, 7, 1281.

² Gundersen, L.-L.; Langli, G.; Rise, F. *Tetrahedron Lett.* **1995**, 36, 1945.

³ Toyota, A.; Katagiri, N.; Kaneko, Ch. *Synth. Commun.* **1993**, 23, 1295.

(CH(CH₃)₂), 79.2 (CH-O), 123.6 (CH Ar), 127.8 (CH Ar), 128.7 (CH Ar), 128.9 (CH Ar), 130.9 (C-5 Pu), 131.0 (CH Ar), 135.4 (C_q Ar), 136.9 (C_q Ar), 143.2 (C-8 Pu), 150.7 and 151.2 and 151.7 (C-4 Pu and C-2 Pu and C_q Ar), 160.5 (C-6 Pu), 164.1 (C=O). IR (CHCl₃): 2990, 2940, 1730, 1609, 1594, 1562, 1531, 1496, 1458, 1393, 1349, 1321, 1305, 1268, 1173, 1149, 1117, 1103 cm⁻¹. HR-MS (EI): Calculated for C₂₂H₁₈N₅O₄Cl: 451.1047; Found 451.1044.

2b: ¹H NMR (300 MHz, CDCl₃) δ = 0.77 (d, J = 6.9 Hz, 3H, CH₃), 1.08 (d, J = 6.9 Hz, 3H, CH₃), 1.66 (m, 6H, 2CH₃), 2.32 (m, 1H, CH(CH₃)₂), 3.71 (d, J = 7.6 Hz, 1H, OH), 4.73 (m, 1H, CH-O), 4.92 (m, 1H, CH(CH₃)₂), 8.15 (s, 1H, H-8 Pu).

Compound was characterized as 4-nitrobenzoate: White foam, ¹H NMR (500 MHz, CDCl₃) δ = 1.06 (d, J = 6.8 Hz, 3H, CH₃), 1.09 (d, J = 6.9 Hz, 3H, CH₃), 1.56 (m, 6H, 2CH₃), 2.66 (m, 1H, CH(CH₃)₂), 4.77 (m, 1H, CH(CH₃)₂), 5.88 (d, J = 5.4 Hz, 1H, CH-O), 8.15 (s, 1H, H-8 Pu), 8.31 (s, 4H, ArH). ¹³C NMR (125.76 MHz, CDCl₃) δ = 17.3 (CH₃), 19.3 (CH₃), 22.1 (CH₃), 22.2 (CH₃), 32.4 (CH(CH₃)₂), 48.4 (CH(CH₃)₂), 81.8 (CH-O), 123.5 (CH Ar), 130.8 (C-5 Pu), 131.0 (CH Ar), 135.8 (C_q Ar), 143.2 (C-8 Pu), 150.6 and 150.9 and 151.5 (C_q Ar and C-2 Pu and C-4 Pu), 160.8 (C-6 Pu), 164.6 (C=O). IR (CHCl₃): 2983, 2936, 1728, 1597, 1561, 1531, 1493, 1394, 1348, 1302, 1284, 1268, 1121, 1104, 1016 cm⁻¹. HR-MS (EI): Calculated for C₁₉H₂₀N₅O₄Cl: 417.1204; Found 417.1191.

2d: ¹H NMR (500 MHz, CDCl₃) δ = 1.63 (m, 6H, 2CH₃), 3.76 (s, 3H, O-CH₃), 4.49 (d, J = 8.8 Hz, 1H, OH), 4.91 (m, 1H, CH(CH₃)₂), 5.91 (d, J = 6.7 Hz, 1H, CH-O), 6.85 (d, J = 8.7 Hz, 2H, ArH), 7.43 (d, J = 8.7 Hz, 2H, ArH), 8.13 (s, 1H, H-8 Pu). ¹³C NMR (125.76 MHz, CDCl₃) δ = 22.4 (CH₃), 22.5 (CH₃), 48.1 (CH(CH₃)₂), 55.2 (O-CH₃), 75.1 (CH-O), 113.8 (CH Ar), 127.8 (CH Ar), 130.7 (C-5 Pu), 134.2 (C_q Ar), 143.1 (C-8 Pu), 151.0 and 151.6 and 159.2 and 164.4 (C-2 Pu and C-4 Pu and C_q Ar and C-6 Pu). IR (CHCl₃): 3488, 2937, 2839, 1612, 1595, 1560, 1512, 1495, 1460, 1393, 1375, 1331, 1304, 1248, 1173, 1148, 1035 cm⁻¹. HR-MS (EI): Calculated for C₁₆H₁₇N₄O₂Cl: 332.1040; Found 332.1037.

2e: ¹H NMR (300 MHz, CDCl₃) δ = 1.67 (d, J = 6.6 Hz, 6H, 2CH₃), 4.11 (d, J = 6.6 Hz, 1H, OH), 4.95 (m, 1H, CH(CH₃)₂), 5.56 (m, 1H, CH-O), 6.50 (dd, J₁ = 5.5 Hz, J₂ = 15.7 Hz, 1H, -CH=), 6.9 (d, J = 15.7 Hz, 1H, -CH=), 7.19-7.32 (m, 3H, ArH), 7.40 (m, 2H, ArH), 8.17 (s, 1H, H-8 Pu).

Compound was characterized as 4-nitrobenzoate: White foam, ¹H NMR (500 MHz, CDCl₃) δ = 1.62 (m, 6H, 2CH₃), 4.89 (m, 1H, CH(CH₃)₂), 6.67 (dd, J₁ = 7.7 Hz, J₂ = 15.6 Hz, 1H, CH=), 6.75 (d, J = 7.7 Hz, 1H, CH-O), 6.98 (d, J = 15.7 Hz, 1H, CH=), 7.26-7.35 (m, 3H, ArH), 7.45 (m, 2H, ArH), 8.22 (s, 1H, H-8 Pu), 8.28-8.35 (m, 5H, ArH). ¹³C NMR (100.6 MHz, CDCl₃) δ = 22.3 (CH₃), 22.4 (CH₃), 48.3 (CH(CH₃)₂), 78.6 (CH-O), 123.6 (CH), 124.1 (CH), 126.9 (CH), 128.5 (CH), 128.6 (CH), 131.0 (C-5 Pu), 131.1 (CH), 135.4 (CH), 135.5 (C_q Ar), 135.8 (C_q Ar), 143.4 (C-8 Pu), 150.7, 151.4 and 151.8 (C-4 Pu, C-2 Pu and C_q Ar), 160.2 (C-6 Pu), 164.0 (C=O). IR (CHCl₃): 2989, 1728, 1594, 1561, 1530, 1496, 1393, 1349, 1274, 1117, 1103 cm⁻¹. HR-MS (EI): Calculated for C₂₄H₂₀N₅O₄Cl: 477.1204; Found 477.1201.

2f: ¹H NMR (400 MHz, CDCl₃) δ = 1.64 (d, J = 6.8 Hz, 6H, 2CH₃), 3.94 (dd, J₁ = 4.0 Hz, J₂ = 10.0 Hz, 1H, CH₂), 4.01 (dd, J₁ = 3.3 Hz, J₂ = 10.0 Hz, 1H, CH₂), 4.53 (d, J = 12.3 Hz, 1H, CH₂), 4.64 (d, J = 12.3 Hz, 1H, CH₂), 4.92 (m, 1H, CH(CH₃)₂), 5.08 (m, 1H, CH-O), 7.24 (m, 5H, ArH), 8.16 (s, 1H, H-8 Pu). ¹³C NMR (100.6 MHz, CDCl₃) δ = 22.5 (CH₃), 48.0 (CH(CH₃)₂), 73.3 (CH-O), 73.4 (CH₂), 73.7 (CH₂), 127.5 (CH Ar), 128.2 (CH Ar), 130.7 (C-5), 138.0 (C_q Ar), 143.0 (C-8 Pu), 151.0, 151.5 and 162.7 (C-4 Pu, C-6 Pu and C-2 Pu). IR (CHCl₃): 3500, 3013, 2936, 2866, 1595, 1562, 1496, 1454, 1393, 1375, 1330, 1173, 1115 cm⁻¹. HR-MS (EI): Calculated for C₁₇H₁₉N₄O₂Cl: 346.1197; Found 346.1222.

2g: ¹H NMR (300 MHz, CDCl₃) δ = 1.63 (d, J = 6.9 Hz, 6H, 2CH₃), 1.99 (s, 3H, CH₃), 4.15 (d, J = 5.5 Hz, 1H, OH), 4.42 (dd, J₁ = 6.1 Hz, J₂ = 11.6 Hz, 1H, CH₂), 4.60 (dd, J₁ = 3.3 Hz, J₂ = 11.3 Hz, 1H, CH₂), 4.90 (m, 1H, CH(CH₃)₂), 5.09 (m, 1H, CH-O), 8.19 (s, 1H, H-8 Pu). ¹³C NMR (75.46 MHz, CDCl₃) δ = 20.7 (CH₃), 22.4 (CH₃), 48.1 (CH(CH₃)₂), 67.6 (CH₂), 71.6 (CH-O), 130.9 (C-5 Pu), 143.4 (C-8 Pu), 150.9, 151.5 and 161.4 (C-2 Pu, C-4 Pu and C-6 Pu), 170.8 (C=O). IR (CHCl₃): 3486, 3018, 2987, 1740, 1595, 1562, 1495, 1460, 1393, 1376, 1331, 1174, 1148, 1110, 1045 cm⁻¹. HR-MS (EI): Calculated for C₁₂H₁₅N₄O₃Cl: 299.0911; Found 299.0916.

3: To the solution of **1** (0.18 g, 0.56 mmol) in THF (8 ml) was at 0°C added *i*PrMgCl (0.31 ml, 0.62 mmol of 2M solution in diethylether) and the mixture was stirred at this temperature. After 20 min benzaldehyde (0.11 ml, 1.0 mmol) was added and the reaction mixture was stirred 12 h at room temperature. Then saturated solution of NH₄Cl (10 ml) was added, organic phase was separated and water was extracted with dichloromethane (3x10 ml). Combined organic extracts were dried over MgSO₄, the solvent was then evaporated and pure **3** was obtained by chromatography on silica (hexane - ethylacetate 1:2) as white crystals (0.146 g, 86%). M.p.: 162-165°C (dichloromethane/heptane). ¹H NMR (300 MHz, CDCl₃) δ = 1.32 (d, J = 6.9 Hz, 3H, CH₃), 1.42 (d, J = 6.8 Hz, 3H, CH₃), 4.68 (m, 1H, CH(CH₃)₂), 5.37 (br s, 1H, OH), 6.25 (s, 1H, CH-O), 7.32 (m, 5H, ArH), 8.66 (s, 1H, H-2 Pu). ¹³C NMR (75.46 MHz, CDCl₃) δ = 20.1 (CH₃), 20.3 (CH₃), 50.1 (CH(CH₃)₂), 70.4 (CH-O), 126.3 (CH Ar), 128.6 (CH Ar), 128.9 (CH Ar), 130.7 (C-5 Pu), 138.9 (C_q Ar), 151.1 (C-2 Pu), 150.1, 153.5, 157.7 (C-4 Pu, C-8 Pu, C-6 Pu). IR (CHCl₃): 3279, 3008, 1597, 1561, 1495, 1452, 1432, 1402, 1372, 1352, 1254, 1154, 1095, 1051, 984, 706 cm⁻¹. Anal. Calcd for C₁₅H₁₅ClN₄O: C, 59.51; H, 4.99; N, 18.51. Found: C, 59.45; H, 4.99; N, 18.51.

5: To the solution of **4** (0.221 g, 0.60 mmol) in THF (10 ml) cooled to -80°C the *i*PrMgCl (0.33 ml, 0.66 mmol of 2M solution in diethylether) was added via syringe and the resulted mixture was stirred at this temperature for 30 min at -80°C . Then saturated solution of NH_4Cl (10 ml) was added and the mixture was allowed to warm to a room temperature. The organic phase was then separated and water was extracted with dichloromethane (2x10 ml). Combined organic extracts were dried over MgSO_4 , the solvent was then evaporated and pure **5** was obtained by chromatography on silica (hexane - ethylacetate 1:2) as white crystals 0.121g (83%). M.p.: $148\text{--}150^{\circ}\text{C}$ (dichloromethane/heptane). ^1H NMR (300 MHz, CDCl_3) δ = 5.42 (s, 2H, CH_2Ph), 7.31–7.39 (m, 5H, ArH), 8.04 (s, 1H, *H*-8 Pu), 8.99 (s, 1H, *H*-6 Pu). ^{13}C NMR (75.46 MHz, CDCl_3) δ = 47.4 (CH_2Ph), 128.1 (CH Ar), 128.9 (CH Ar), 129.3 (CH Ar), 133.0 (C-5 Pu), 134.3 (C_q Ar), 145.7 (C-8 Pu), 150.2 (C-6 Pu), 153.2 (C-4 Pu), 154.6 (C-2 Pu). IR (CHCl_3): 3006, 1601, 1573, 1505, 1350, 1246, 1137 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_9\text{ClN}_4$: C, 58.91; H, 3.71; N, 22.90. Found: C, 58.90; H, 3.78; N, 22.92.

6: To the solution of **4** (0.174 g, 0.47 mmol) in THF (8 ml) was at -78°C added *i*PrMgCl (0.26 ml, 0.52 mmol of 2M solution in diethylether) and the mixture was stirred at this temperature. After 30 min benzaldehyde (0.08 ml, 0.71 mmol) was added. The reaction mixture was stirred 12 h at -80°C , and then quenched with saturated solution of NH_4Cl (10 ml). Organic phase was separated and water was extracted with dichloromethane (3x10 ml). Combined organic extracts were dried over MgSO_4 , the solvent was then evaporated and pure **6** was obtained by chromatography on silica (hexane - ethylacetate 1:2) as yellow foam 0.086 g (52%). ^1H NMR (300 MHz, CDCl_3) δ = 4.83 (d, *J* = 8.0 Hz, 1H, OH), 5.37 (s, 2H, CH_2Ph), 6.30 (d, *J* = 8.0 Hz, 1H, CH-O), 7.23–7.39 (m, 8H, ArH), 7.61 (m, 2H, ArH), 7.93 (s, 1H, *H*-8 Pu).

Compound was characterized as 4-nitrobenzoate: ^1H NMR (500 MHz, CDCl_3) δ = 5.36 (s, 2H, CH_2Ph), 7.31–7.41 (m, 9H, 8H ArH + 1H CH-O), 7.79 (d, *J* = 7.2 Hz, 2H, ArH), 7.99 (s, 1H, *H*-8 Pu), 8.30 (d, *J* = 8.8 Hz, 2H, ArH), 8.39 (d, *J* = 8.8 Hz, 2H, ArH). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 47.6 (CH_2Ph), 76.6 (CH-O), 123.5 (CH Ar), 127.9 (CH Ar), 128.3 (CH Ar), 128.9 (CH Ar), 128.9 (CH Ar), 129.1 (CH Ar), 129.3 (CH Ar), 129.7 (C-5 Pu), 131.3 (CH Ar), 134.2 (C_q Ar), 135.2 (C_q Ar), 136.1 (C_q Ar), 145.3 (C-8 Pu), 150.7 (C_q Ar), 153.9, 154.3, 159.4 (C-4 Pu, C-2 Pu, C-6 Pu), 164.1 (C=O). IR (CHCl_3): 3032, 2930, 1731, 1591, 1531, 1498, 1457, 1348, 1320, 1267, 1240, 1103 cm^{-1} . M^+ (EI): 499.

Typical procedure: Preparation of 9-benzyl-6-cyclopentylpurine (7c). To the solution of **4** (0.093 g, 0.25 mmol) in THF (5 ml) cooled to -80°C the cyclopropylmagnesium chloride (0.26 ml, 0.52 mmol of 2M solution in diethylether) was added via syringe and the resulted mixture was stirred at this temperature for 30 min. The acetone/dry ice bath was then replaced with ice bath and the stirring was continued for another 15 min. Then saturated solution of NH_4Cl (10 ml) was added, organic phase was separated and water was extracted with dichloromethane (2x10 ml). Combined organic extracts were dried over MgSO_4 , the solvent was then evaporated and pure **7c** was obtained by chromatography on silica (9 g, hexane - ethylacetate 1:2) as white crystals 0.055g (79%). M.p.: $44\text{--}47^{\circ}\text{C}$ (diethylether/heptane). ^1H NMR (400 MHz, CDCl_3) δ = 1.77 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 2.07–2.15 (m, 4H, 2 CH_2), 3.89 (m, 1H, CH), 5.42 (s, 2H, CH_2Ph), 7.32 (m, 5H, PhH), 7.98 (s, 1H, *H*-8 Pu), 8.92 (s, 1H, *H*-2 Pu). ^{13}C NMR (100.6 MHz, CDCl_3) δ = 26.3 (CH_2), 32.7 (CH_2), 42.6 (CH), 47.2 (CH_2Ph), 127.9 (CH Ph), 128.5 (CH Ph), 129.1 (CH Ph), 132.2 (C-5 Pu), 135.3 (C_q Ph), 143.2 (C-8 Pu), 150.7 (C-4 Pu), 152.8 (C-2 Pu), 166.4 (C-6 Pu). IR (CHCl_3): 2967, 2872, 1593, 1499, 1456, 1407, 1332 cm^{-1} . HR-MS (EI): Calculated for $\text{C}_{17}\text{H}_{18}\text{N}_4$ 278.1531; Found 278.1546.

Compounds **7a**,⁴ **7d**,⁴ and **7e**⁵ are known compounds.

7b: White crystals, m.p.: $65\text{--}68^{\circ}\text{C}$ (diethylether/heptane). ^1H NMR (500 MHz, CDCl_3) δ = 0.89 (t, *J* = 7.5 Hz, 3H, CH_3), 1.43 (d, *J* = 6.9 Hz, 3H, CH_3), 1.81 (m, 1H, CH_2), 2.00 (m, 1H, CH_2), 3.67 (m, 1H, CH), 5.44 (s, 2H, CH_2Ph), 7.35 (m, 5H, ArH), 8.00 (s, 1H, *H*-8 Pu), 8.96 (s, 1H, *H*-2 Pu). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 12.2 (CH_3), 19.1 (CH_3), 28.8 (CH_2), 38.7 (CH), 47.2 (CH_2Ph), 127.9 (CH Ar), 128.6 (CH Ar), 129.1 (CH Ar), 132.1 (C-5 Pu), 135.2 (C_q Ar), 143.3, 152.7 (C-2 Pu, C-8 Pu), 150.8, 167.0 (C-4 Pu, C-6 Pu). IR (CHCl_3): 2971, 2935, 2877, 1592, 1499, 1464, 1456, 1407, 1331, 1197 cm^{-1} . HR-MS (EI): Calculated for $\text{C}_{16}\text{H}_{18}\text{N}_4$: 266.1531; Found 266.1545.

8 and 9: To the solution of **4** (0.168 g, 0.45 mmol) in THF (5 ml) cooled to 0°C the allylmagnesium bromide (0.95 ml, 0.95 mmol of 1M solution in diethylether) was added via syringe and the resulted mixture was stirred at this temperature for 20 min. Then saturated solution of NH_4Cl (10 ml) was added, organic phase was separated and water was extracted with dichloromethane (2x10 ml). Combined organic extracts were dried over MgSO_4 , the solvent was then evaporated and chromatography on silica (hexane - ethylacetate 1:2) afforded 8-allyl-9-benzyl-7,8-dihydro-2-chloro-6-jodopurine **9** (0.069 g, 37%) as an yellow oil and 8-allyl-9-benzyl-7,8-dihydro-2-chloropurine **8** (0.048 g, 37%) as a yellowish crystals.

⁴ D'esaubry, L.; Bourguignon, J.-J. *Tetrahedron Lett.* **1995**, 36, 7875.

⁵ Gundersen, L.-L.; Bakkestuen, A. K.; Aasen, A. J.; Øverås, H., Rise, F. *Tetrahedron* **1994**, 50, 9743.

8: M.p. 135-138°C (dichloromethane - heptane). ^1H NMR (300 MHz, CDCl_3) δ = 2.39 (m, 1H, CH_2), 2.51 (m, 1H, CH_2), 4.09 (br s, 1H, NH), 4.26 (d, J = 15.5 Hz, 1H, CH_2Ph), 5.03 (d, J = 15.5 Hz, 1H, CH_2Ph), 5.16-5.24 (m, 3H, $=\text{CH}_2$ + NH-CH-N), 5.67 (m, 1H, $=\text{CH-}$), 7.11 (s, 1H, H -6 Pu), 7.27-7.36 (m, 5H, ArH). ^{13}C NMR (75.46 MHz, CDCl_3) δ = 39.3 (CH_2), 45.2 (CH_2Ph), 76.1 (NH-CH-N), 120.5 ($=\text{CH}_2$), 126.8 (CH Ar), 128.0 (CH Ar), 128.1 (CH Ar), 128.9 (C -6 Pu), 130.2 (C -5 Pu), 130.4 ($=\text{CH-}$), 135.2 ($C_q \text{ Ar}$), 150.3 (C -2 Pu), 160.9 (C -4 Pu). IR (CHCl_3): 3428, 3009, 1613, 1581, 1528, 1455, 1368, 1296, 1273 cm^{-1} . HR-MS (EI): Calculated for $\text{C}_{15}\text{H}_{13}\text{ClN}_4$: 284.0829; Found 284.0823.

9: ^1H NMR (300 MHz, CDCl_3) δ = 2.43 (m, 1H, CH_2), 2.54 (m, 1H, CH_2), 3.95 (br s, 1H, NH), 4.22 (d, J = 15.7 Hz, 1H, CH_2Ph), 4.99 (d, J = 15.4 Hz, 1H, CH_2Ph), 5.24 (m, 3H, $=\text{CH}_2$ + NH-CH-N), 5.70 (m, 1H, $=\text{CH-}$), 7.25-7.39 (m, 5H, ArH). ^{13}C NMR (75.46 MHz, CDCl_3) δ = 39.2 (CH_2), 45.6 (CH_2Ph), 76.3 (NH-CH-N), 120.8 ($=\text{CH}_2$), 128.1 (CH Ar), 128.2 (CH Ar), 128.9 (CH Ar), 129.9 (C -5 Pu and $=\text{CH-}$), 134.6 ($C_q \text{ Ar}$), 148.5, 157.6, 160.7 (C -2 Pu, C -4 Pu, C -6 Pu).

Typical procedure: Preparation of 9-benzyl-2-(phenylhydroxymethyl)-6-isopropylpurine (10a). To the solution of 0.129g (0.35 mmol) of **4** in THF (3.5 ml) cooled to -80°C the isopropylmagnesium chloride (0.19 ml, 0.38 mmol of 2M solution in diethylether) was added via syringe and the resulted mixture was stirred at this temperature for 30 min. The acetone/dry ice bath was then replaced with ice bath, the stirring was continued for 15 min and the benzaldehyde (0.09 ml, 0.89 mmol) was added. The resulted mixture was stirred at 0°C for 12 h, then quenched with saturated solution of NH_4Cl (10ml), organic phase was separated and water was extracted with dichloromethane (3x10 ml). Combined organic extracts were dried over MgSO_4 , the solvent was then evaporated and pure **10** was obtained by chromatography on silica (10g, hexane - ethylacetate 1:2) as a yellow oil. ^1H NMR (300 MHz, CDCl_3) δ = 1.44 (d, J = 6.9 Hz, 6H, 2CH_3), 3.77 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 5.36 (s, 2H, CH_2Ph), 5.94 (d, J = 6.1 Hz, 1H, CH-O), 7.25-7.35 (m, 8H, PhH), 7.59 (m, 2H, PhH), 7.94 (s, 1H, H -8 Pu).

The compound was characterized as 4-nitrobenzoate: ^1H NMR (500 MHz, CDCl_3) δ = 1.31 (d, J = 6.9 Hz, 3H, CH_3), 1.39 (d, J = 6.9 Hz, 3H, CH_3), 3.70 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 5.30 (d, J = 15.0 Hz, 1H, CH_2Ph), 5.35 (d, J = 15.0 Hz, 1H, CH_2Ph), 7.12 (s, 1H, CH-O), 7.26-7.41 (m, 8H, ArH), 7.71 (d, J = 7.2 Hz, 2H, ArH), 7.94 (s, 1H, H -8 Pu), 8.31 (d, J = 8.8 Hz, 2H, ArH), 8.36 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 21.0 (CH_3), 21.3 (CH_3), 31.7 ($\text{CH}(\text{CH}_3)_2$), 47.3 (CH_2Ph), 79.8 (CH-O), 123.6 (CH Ar), 127.8 (CH Ar), 128.1 (CH Ar), 128.5 (CH Ar), 129.0 (CH Ar), 130.4 (C -5 Pu), 130.9 (CH Ar), 135.2 ($C_q \text{ Ar}$), 136.0 ($C_q \text{ Ar}$), 137.9 ($C_q \text{ Ar}$), 143.4 (C -8 Pu), 150.6 ($C_q \text{ Ar}$), 151.4 (C -4 Pu), 160.7 and 164.3 (C=O and C -2 Pu), 167.4 (C -6 Pu). IR (CHCl_3): 3030, 2975, 1729, 1591, 1531, 14987, 1457, 1402, 1350, 1269, 1119, 1103 cm^{-1} . HR-MS (EI): Calculated for $\text{C}_{29}\text{H}_{25}\text{N}_5\text{O}_5$: 507.1907; Found 507.1901.

10b: ^1H NMR (300 MHz, CDCl_3) δ = 1.77 (m, 2H, CH_2), 1.90-2.17 (m, 6H, CH_2), 3.88 (m, 1H, CH), 5.28 (d, J = 6.1 Hz, 1H, OH), 5.36 (s, 2H, CH_2Ph), 5.83 (d, J = 6.3 Hz, 1H, CH-O), 5.91 (m, 2H, $\text{O-CH}_2\text{-O}$), 6.76 (d, J = 8.0 Hz, 1H, ArH), 7.05 (m, 2H, ArH), 7.32 (m, 5H, ArH), 7.94 (s, 1H, H -8 Pu).

The compound was characterized as 4-nitrobenzoate: ^1H NMR (500 MHz, CDCl_3) δ = 1.66-2.08 (m, 8H, 4CH_2), 3.84 (m, 1H, CH), 5.31 (d, J = 15.0 Hz, 1H, CH_2Ph), 5.36 (d, J = 15.0 Hz, 1H, CH_2Ph), 5.96 (m, 2H, $\text{O-CH}_2\text{-O}$), 6.81 (d, J = 8.0 Hz, 1H, ArH), 7.00 (s, 1H, ArH), 7.16 (m, 1H, ArH), 7.20 (d, J = 1.4 Hz, 2H, ArH), 7.28 (m, 5H, ArH), 7.92 (s, 1H, H -8 Pu), 8.30 (d, J = 8.9 Hz, 2H, ArH), 8.33 (d, J = 9.0 Hz, 2H, ArH). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 26.1 (CH_2), 26.2 (CH_2), 32.6 (CH_2), 32.7 (CH_2), 42.3 (CH), 47.3 (CH_2Ph), 79.6 (CH-O), 101.2 ($\text{O-CH}_2\text{-O}$), 108.1 (CH Ar), 108.2 (CH Ar), 121.9 (CH Ar), 123.5 (CH Ar), 128.1 (CH Ar), 128.5 (CH Ar), 129.0 (CH Ar), 130.9 (CH Ar), 131.7 (C -5 Pu), 135.2 ($C_q \text{ Ar}$), 135.9 ($C_q \text{ Ar}$), 143.4 (C -8 Pu), 147.7 ($C_q \text{ Ar}$), 147.8 ($C_q \text{ Ar}$), 150.6 ($C_q \text{ Ar}$), 151.1 (C -4 Pu), 160.6, 164.2 (C=O , C -2 Pu), 166.7 (C -6 Pu). IR (CHCl_3): 3021, 2964, 2871, 1727, 1591, 1531, 1504, 1491, 1446, 1404, 1349, 1320, 1278, 1268, 1249, 1118, 1103 cm^{-1} . M^+ (EI): 577.

10c: (mixture of two diastereoisomers): ^1H NMR (300 MHz, CDCl_3) δ = 0.86 (m, 3H, CH_3), 1.41 (d, J = 6.1 Hz, 3H, CH_3), 1.99 (m, 2H, CH_2), 3.57 (m, 1H, CH), 5.37 (s, 2H, CH_2Ph), 5.47 (br s, 1H, OH), 6.02 (br s, 1H, CH-O), 7.35 (m, 5H, ArH), 7.53 (m, 1H, ArH), 7.69 (d, J = 7.7 Hz, 1H, ArH), 7.98 (s, 1H, H -8 Pu), 8.13 (m, 1H, ArH), 8.55 (s, 1H, ArH).

The compound was characterized as 4-nitrobenzoate: ^1H NMR (500 MHz, CDCl_3) δ = 0.76 and 0.83 (t, J = 7.5 Hz, 3H, CH_3), 1.31 and 1.36 (d, J = 6.9 and 7.89 Hz, 3H, CH_3), 1.65-1.78 and 1.84-2.00 (m, 2H, CH_2), 3.52 (m, 1H, CH), 5.35 (m, 2H, CH_2Ph), 7.29 (m, 5H, ArH), 7.58 (t, J = 8.0 Hz, 1H, ArH), 7.99 (s, 1H, H -8 Pu), 8.08 (d, J = 7.2 Hz, 1H, ArH), 8.21 (d, J = 8.2 Hz, 1H, ArH), 8.35 (m, 4H, ArH), 8.64 (s, 1H, ArH). ^{13}C NMR (125.76 MHz, CDCl_3) δ = 11.9 (CH_3), 12.0 (CH_3), 28.4 (CH_3), 28.7 (CH_3), 38.4 (CH), 38.5 (CH), 47.5 (CH_2Ph), 78.4 (CH-O), 122.8 (CH Ar), 123.4 (CH Ar), 123.7 (CH Ar), 128.1 (CH Ar), 128.6 (CH Ar), 129.0 (CH Ar), 129.4 (CH Ar), 131.0 (CH Ar), 131.2 (C -5 Pu), 133.8 (CH Ar), 135.0 ($C_q \text{ Ar}$), 135.3 ($C_q \text{ Ar}$), 143.8 (C -8 Pu), 140.0, 148.3, 150.7, 151.3, 159.4 (C -4 Pu, $C_q \text{ Ar}$), 164.0 (C=O), 167.3 (C -6 Pu). IR (CHCl_3): 2971, 1733, 1592, 1533, 1352, 1266, 1102 cm^{-1} .