Supporting Information

Direct C-H Borylation and C-H Arylation of Pyrrolo[2,3-d]pyrimidines: Synthesis of 6,8-Disubstituted 7-deazapurines.

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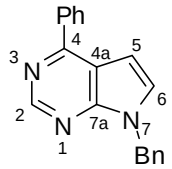
Preparation of starting compounds

7-benzyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine

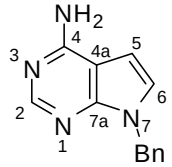
(9-benzyl-6-phenyl-7-deazapurine) (2)



Dry toluene (26 ml) was added to a stirred solution of potassium carbonate (1.109 g, 8.02 mmol), 9-benzyl-6-chloro-7-deazapurine **5** (1.5 g, 6.17 mmol) and phenylboronic acid (1.129 g, 9.26 mmol) under Ar. The mixture was stirred for 3 h at temperature 110°C and then filtered and evaporated. The crude mixture was separated by flash chromatography on silica gel using hexanes/EtOAc 3:1 for elution to give product **2** (1.67 g, 95 %) as yellowish solid. Crystalization in hexan/EtOAc gave yellowish crystals. M.p. 75-78 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 5.51 (s, 2H, CH_2); 6.83 (d, 1H, $J_{5,6}$ = 3.7, H-5); 7.23 (d, 1H, $J_{6,5}$ = 3.7, H-6); 7.25 (m, 2H, H-*o*-Bn); 7.29 (m, 1H, H-*p*-Bn); 7.33 (m, 2H, H-*m*-Bn); 7.51 (m, 1H, H-*p*-Ph); 7.55 (m, 2H, H-*m*-Ph); 8.13 (m, 2H, H-*o*-Ph); 9.01 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 47.98 (CH_2Ph); 100.83 (CH-5); 115.64 (C-4a); 127.60 (CH-*o*-Bn); 127.96 (CH-*p*-Bn); 128.72 and 128.74 (CH-6 and CH-*m*-Ph); 128.84 and 128.85 (CH-*m*-Bn and CH-*o*-Ph); 129.96 (CH-*p*-Ph); 136.81 (C-*i*-Bn); 138.23 (C-*i*-Ph); 151.72 (CH-2); 151.83 (C-7a); 157.57 (C-4). IR ($CHCl_3$): 3067, 2983, 1585, 1564, 1515, 1497, 1466, 1455, 1442, 1423, 1390, 1345, 1302, 1250, 1157. HRMS (ESI) calculated for $C_{19}H_{15}N_3$: 286.1339; found: 286.1339.

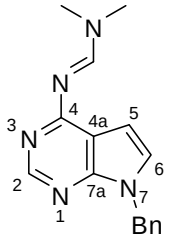
7-benzyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-amine

(6-amino-9-benzyl-7-deazapurine) (3)



Dry DMF (6 ml) was added to a stirred solution of potassium carbonate (0.974 g. 7.05 mmol) and 6-amino-7-deazapurine (0.315 g, 2.35 mmol) under Ar. After 20 min, benzyl chloride (0.41 ml, 3.53 mmol) was added and the resulting mixture was stirred for 2 h at temperature110°C, filtered and evaporated. The crude mixture was separated by flash chromatography on silica gel using $CHCl_3$/CH_3OH 10:1 for elution to give product **3** (275 mg, 53%) as brown solid. Crystalization in hexan/EtOAc gave brownish crystals. M.p. 174-178 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 5.39 (s, 2H, CH_2); 5.41 (bs, 2H, NH_2); 6.38 (d, 1H, $J_{5,6}$ = 3.6, H-5); 6.93 (d, 1H, $J_{6,5}$ = 3.6, H-6); 7.19 (m, 2H, H-*o*-Bn); 7.28 (m, 1H, H-*p*-Bn); 7.31 (m, 2H, H-*m*-Bn); 8.36 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 47.92 (CH_2Ph); 97.98 (CH-5); 102.97 (C-4a); 124.67 (CH-6); 127.40 (CH-*o*-Bn); 127.73 (CH-*p*-Bn); 128.72 (CH-*m*-Bn); 137.15 (C-*i*-Bn); 150.49 (C-7a); 151.92 (CH-2); 156.75 (C-4). IR($CHCl_3$): 3416, 2977, 1619, 1588, 1564, 1511, 1471, 1455, 1398, 1356, 1337, 1265, 991, 897, 705, 665. HRMS (ESI) calculated for $C_{13}H_{12}N_4$: 225.1135; found: 225.1135

7-benzyl-4-[(*N,N*-dimethylaminomethylidene)amino]-7*H*-pyrrolo[2,3-*d*]pyrimidine (4)

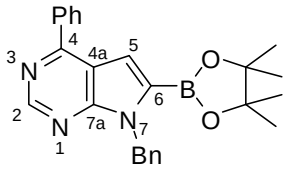


1,1-dimethoxy-*N,N*-dimethylmethanamine (1.7 ml, 12.7 mmol) was added to a flask containing 6-amino-9-benzyl-7-deazapurine **3** (275 mg, 1.27 mmol). The reaction mixture was stirred for 2 h (complete consumption of starting material according to TLC), evaporated and purified by silica gel flash chromatography ($CHCl_3/CH_3OH$ 10:1) to give **4** (315 mg, 89%) as white solid. Crystalization in hexan/EtOAc gave white crystals. M.p. 184-187 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.17 (s, 3H, CH_3N); 3.21 (d, 3H, ^4J = 0.7, CH_3N); 5.43 (s, 2H, CH_2); 6.67 (d, 1H, $J_{5,6}$ = 3.5, H-5); 6.99 (d, 1H, $J_{6,5}$ = 3.5, H-6); 7.17 (m, 2H, H-*o*-Bn); 7.26 (m, 1H, H-*p*-Bn); 7.30 (m, 2H, H-*m*-Bn); 8.53 (s, 1H, H-2); 8.79 (bs, 1H, HC=N). ^{13}C NMR (151 MHz, $CDCl_3$): 34.82, 41.00 (CH_3N); 47.82 (CH_2Ph); 100.07 (CH-5); 111.43 (C-4a); 125.57 (CH-6); 127.29 (CH-*o*-Bn); 127.61 (CH-*p*-Bn); 128.68 (CH-*m*-Bn); 137.40 (C-*i*-Bn); 151.58 (CH-2); 151.88 (C-7a); 156.55 (HC=N); 160.72 (C-4). IR($CHCl_3$): 2971, 1672, 1629, 1576, 1447, 1425, 1382, 1344, 1254, 1112. HRMS (ESI) calculated for $C_{16}H_{17}N_5$: 280.1557; found: 280.1558

Borylation of deazapurines. General Procedure:

7-Deazapurines **2-5** (2 mmol, 1 equiv.), bispinacolatodiboron (0.609 g, 2.4 mmol, 1.2 equiv.), $[Ir(COD)OMe]_2$ (66 mg, 0.1 mmol, 5 mol %) and 4,4'-di-tert-butyl-2,2'-bipyridine (54 mg, 0.2 mmol, 10 mol %) were dissolved in dry THF (15 ml) under Ar. The solution was heated at 80 °C in a septum-sealed flask for 20 hours. The solvent was evaporated and the residue was purified by silica gel flash chromatography.

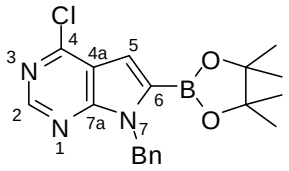
7-benzyl-4-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (9-benzyl-6-phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-deazapurine) (6)



9-Benzyl-6-phenyl-7-deazapurine **2** (570 mg, 2 mmol) was used as starting compound to give product **6** (698 mg, 85%) as white foam after chromatography hexane/EtOAc 5:1. Crystalization in hexan/EtOAc gave white crystals.

M.p. 128-134 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 1.28 (s, 12H, CH_3); 5.81(s, 2H, CH_2); 7.17-7.26 (m, 5H, H-*o,m,p*-Bn); 7.46 (s, 1H, H-5); 7.50 (m, 1H, H-*p*-Ph); 7.54 (m, 2H, H-*m*-Ph); 8.16 (m, 2H, H-*o*-Ph); 9.02 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 24.65 ($(CH_3)_2C$); 47.17 (CH_2Ph); 84.39 ($C(CH_3)_2$); 113.54 (CH-5); 115.44 (C-4a); 127.14 (CH-*p*-Bn); 127.28 (CH-*o*-Bn); 128.25 (CH-*m*-Bn); 128.71 (CH-*m*-Ph); 129.06 (CH-*o*-Ph); 130.10 (CH-*p*-Ph); 132.15 (C-6); 138.16 (C-*i*-Ph); 138.79 (C-*i*-Bn); 152.94 (CH-2); 154.25 (C-7a); 158.73 (C-4). IR($CHCl_3$):2983, 1562, 1525, 1468, 1449, 1428, 1382, 1374, 1335, 1139. HRMS (ESI) calculated for $C_{25}H_{26}BN_3O_2$: 412.2191; found: 412.2192.

7-benzyl-4-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (9-benzyl-6-chloro-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-deazapurine) (7)



9-Benzyl-6-chloro-7-deazapurine **5** (486 mg, 2 mmol) and bispinacolatodiboron (0.762 g, 3.0 mmol, 1.5 equiv.), $[Ir(COD)OMe]_2$ (106 mg, 0.1 mmol, 8 mol %) and 4,4'-di-tert-butyl-2,2'-bipyridine (86 mg, 0.2 mmol, 16 mol %) were used. The residue after C-H activation was purified by silica gel flash chromatography (hexane/EtOAc 5:1→ ethyl acetate/hexanes 1:1) to give product **7** (390 mg, 53%) as white solid. Crystalization in hexan/EtOAc gave white crystals.

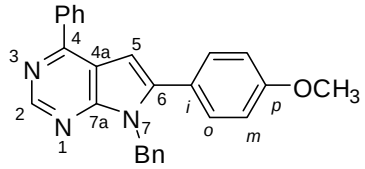
M.p. 172-175 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 1.28 (s, 12H, CH_3); 5.75 (s, 2H, CH_2); 7.16-7.25 (m, 6H, H-5 and H-*o,m,p*-Bn); 8.68 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 24.62 ($(\mathbf{C}H_3)_2C$); 47.60 (CH_2Ph); 84.56 ($\mathbf{C}(CH_3)_2$); 112.23 (CH-5); 117.21 (C-4a); 127.22 (CH-*o*-Bn); 127.34 (CH-*p*-Bn); 128.30 (CH-*m*-Bn); 132.79 (C-6); 138.12 (C-*i*-Bn); 151.91 (CH-2); 153.28 and 153.42 (C-4 and C-7a). IR($CHCl_3$): 2984, 1579, 1541, 1525, 1469, 1430, 1374, 1355, 1330, 1259, 1177, 1137. HRMS (ESI) calculated for $C_{19}H_{21}BClN_3O_2$: 370.1499; found: 370.1488.

Suzuki coupling arylboronic ester with aryl halogens. General procedure:

Aryl halide (0.269 mmol, 1.1 equiv.), **6** (100 mg, 0.244 mmol, 1 equiv.), $Pd(dppf)Cl_2$ (9 mg, 0.0112 mmol, 5 mol %), K_2CO_3 (135 mg, 0.976 mmol, 4 equiv.) were combined in DMF (4 mL) and stirred under argon at 90 °C for 1 h. The solvent was removed under reduced pressure, the residue was purified by silica gel flash chromatography (hexane/EtOAc 5/1) to give products **8a-8g.**

7-benzyl-6-(4-methoxyphenyl)-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-6-phenyl-8-(4-methoxyphenyl)-7-deazapurine) (8a)

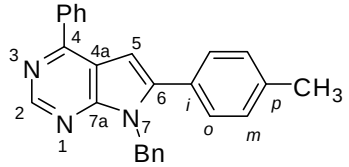


Product **8a** (83 mg, 87%) was obtained as yellow solid. Crystalization in hexan/EtOAc gave yellowish crystals.

M.p. 116-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 3.85 (s, 3H, CH_3O); 5.56 (s, 2H, CH_2); 6.85 (s, 1H, H-5); 6.93 (m, 2H, H-*m*-C_6H_4OMe); 7.00 (m, 2H, H-*o*-Bn); 7.19-7.26 (m, 3H, H-*m,p*-Bn); 7.32 (m, 2H, H-*o*-C_6H_4OMe); 7.51 (m, 1H, H-*p*-Ph); 7.55 (m, 2H, H-*m*-Ph); 8.17 (m, 2H, H-*o*-Ph); 8.98 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.10 (CH_2Ph); 55.35 (CH_3O); 99.96 (CH-5); 114.12 (CH-*m*-C_6H_4OMe); 115.90 (C-4a); 123.65 (C-*i*-C_6H_4OMe); 126.58 (CH-*o*-Bn); 127.35 (CH-*p*-Bn); 128.61 (CH-*m*-Bn); 128.74 (CH-*m*-Ph); 128.80 (CH-*o*-Ph); 129.89 (CH-*p*-Ph); 130.63 (CH-*o*-C_6H_4OMe); 137.60 (C-*i*-Bn); 138.30 (C-*i*-Ph); 142.92 (C-6); 151.49 (CH-2); 153.38 (C-7a); 156.51 (C-4); 160.18 (C-*p*-C_6H_4OMe). IR($CHCl_3$): 3010, 1612, 1567, 1498, 1464, 1455, 1441, 1419, 1344, 1293, 1251, 1177, 1032, 838. HRMS (ESI) calculated for $C_{26}H_{21}N_3O$: 392.1757; found: 392.1764.

7-benzyl-4-phenyl-6-p-tolyl-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-6-phenyl-8-p-tolyl-7-deazapurine) (8b)

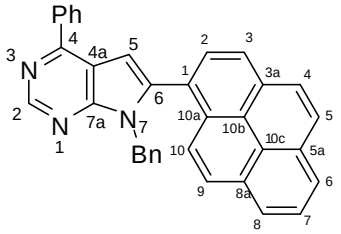


Product **8b** (83 mg, 90%) was obtained as yellow solid. Crystalization in hexan/EtOAc gave yellowish crystals.

M.p. 125-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 2.40 (s, 3H, CH_3); 5.56 (s, 2H, CH_2); 6.87 (s, 1H, H-5); 7.00 (m, 2H, H-*o*-Bn); 7.19-7.26 (m, 5H, H-*m,p*-Bn and H-*m*-C_6H_4Me); 7.30 (m, 2H, H-*o*-C_6H_4Me); 7.50 (m, 1H, H-*p*-Ph); 7.55 (m, 2H, H-*m*-Ph); 8.17 (m, 2H, H-*o*-Ph); 8.99 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.29 (CH_3); 46.13 (CH_2Ph); 100.21 (CH-5); 115.87 (C-4a); 126.60 (CH-*o*-Bn); 127.32 (CH-*p*-Bn); 128.43 (C-*i*-C_6H_4Me); 128.57 (CH-*m*-Bn); 128.73 (CH-*m*-Ph); 128.80 (CH-*o*-Ph); 129.18 (CH-*o*-C_6H_4Me); 129.37 (CH-*m*-C_6H_4Me); 129.89 (CH-*p*-Ph); 137.59 (C-*i*-Bn); 138.32 (C-*i*-Ph); 139.02 (C-*p*-C_6H_4Me); 143.11 (C-6); 151.58 (CH-2); 153.45 (C-7a); 156.65 (C-4). IR($CHCl_3$): 3066, 2983, 1567, 1497, 1463, 1454, 1441, 1420, 1344, 1267, 699. HRMS (ESI) calculated for $C_{26}H_{21}N_3$: 376.1819; found: 376.1808.

7-benzyl-4-phenyl-6-(pyren-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-6-phenyl-8-(pyren-1-yl)-7-deazapurine) (8c)

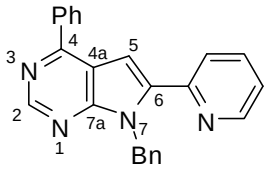


Product **8c** (93 mg, 79%) was obtained as yellow oil which solidified on standing.

M.p. 57-76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 5.13 and 5.67 (2 × bd, 2H, J_{gem} = 15.6, CH_2); 6.65 (m, 2H, H-*o*-Bn); 6.95 (m, 2H, H-*m*-Bn); 7.01 (m, 1H, H-*p*-Bn); 7.08 (s, 1H, H-5); 7.48 (m, 1H, H-*p*-Ph); 7.53 (m, 2H, H-*m*-Ph); 7.81 (d, 1H, $J_{2,3}$ = 7.8, H-2-pyr); 7.84 (d, 1H, $J_{10,9}$ = 9.2, H-10-pyr); 7.98 (d, 1H, $J_{9,10}$ = 9.2, H-9-pyr); 8.03 (t, 1H, $J_{7,6}$ = $J_{7,8}$ = 7.6, H-7-pyr); 8.09 (d, 1H, $J_{4,5}$ = 9.0, H-4-pyr); 8.12 (d, 1H, $J_{3,2}$ = 7.8, H-3-pyr); 8.14 (d, 1H, $J_{5,4}$ = 9.0, H-5-pyr); 8.18 (dd, 1H, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.1, H-6-pyr); 8.18 (m, 3H, H-8-pyr and H-*o*-Ph); 9.12 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.31 (CH_2Ph); 102.70 (CH-5); 115.93 (C-4a); 124.23 (CH-3-pyr); 124.35 (CH-10-pyr); 124.39 (C-10c-pyr); 124.52 (C-10b-pyr); 125.61 (CH-6-pyr); 125.76 (C-1-pyr); 125.80 (CH-8-pyr); 126.34 (CH-7-pyr); 127.19 (CH-*o*-Bn); 127.22, 127.23 (CH-*p*-Bn and CH-4-pyr); 128.17 (CH-*m*-Bn); 128.43 (CH-5-pyr); 128.57 (CH-2,9-pyr); 128.77 (CH-*m*-Ph); 128.88 (CH-*o*-Ph); 129.97 (CH-*p*-Ph); 130.31 (C-10a-pyr); 130.71 (C-8a-pyr); 131.20 (C-5a-pyr); 131.93 (C-3a-pyr); 137.06 (C-*i*-Bn); 138.28 (C-*i*-Ph); 141.02 (C-6); 151.80 (CH-2); 153.07 (C-7a); 156.94 (C-4). IR($CHCl_3$): 3407, 3047, 3000, 1604, 1585, 1559, 1497, 1463, 1455, 1435, 1421, 1342, 1263, 1244, 1054, 851. HRMS (ESI) calculated for $C_{35}H_{23}N_3$: 486.1965; found: 486.1958.

7-benzyl-4-phenyl-6-(pyridin-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-6-phenyl-8-(pyridin-2-yl)-7-deazapurine) (8d)

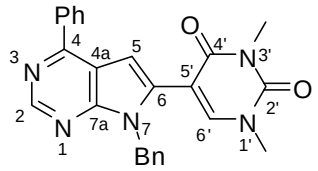


Product **8d** (84 mg, 95%) was obtained as yellowish solid. Crystalization in hexan/EtOAc gave white crystals.

M.p. 105-110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 6.17 (s, 2H, CH_2); 7.02 (m, 2H, H-*o*-Bn); 7.10-7.16 (m, 3H, H-*m,p*-Bn); 7.17 (s, 1H, H-5); 7.25 (ddd, 1H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 4.8, $J_{5,3}$ = 1.3, H-5-py); 7.52 (m, 1H, H-*p*-Ph); 7.56 (m, 2H, H-*m*-Ph); 7.63 (ddd, 1H, $J_{3,4}$ = 7.9, $J_{3,5}$ = 1.3, $J_{3,6}$ = 1.0, H-3-py); 7.70 (ddd, 1H, $J_{4,3}$ = 7.9, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.9, H-4-py); 8.16 (m, 2H, H-*o*-Ph); 8.70 (ddd, 1H, $J_{6,5}$ = 4.8, $J_{6,4}$ = 1.9, $J_{6,3}$ = 1.0, H-6-py); 9.03 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.28 (CH_2Ph); 102.08 (CH-5); 115.50 (C-4a); 122.86 (CH-5-py); 123.39 (CH-3-py); 127.04 (CH-*p*-Bn); 127.07 (CH-*o*-Bn); 128.26 (CH-*m*-Bn); 128.79 (CH-*m*-

Ph); 128.83 (CH-*o*-Ph); 130.05 (CH-*p*-Ph); 136.76 (CH-4-py); 138.14 (C-*i*-Ph); 138.17 (C-*i*-Bn); 139.79 (C-6); 149.22 (CH-6-py); 151.12 (C-2-py); 152.31 (CH-2); 153.89 (C-7a); 157.68 (C-4). IR($CHCl_3$): 3066, 2985, 1587, 1566, 1497, 1462, 1442, 1348, 1323, 1272, 1248. HRMS (ESI) calculated for $C_{24}H_{18}N_4$: 363.1604; found: 363.1603. Anal. calculated for $C_{24}H_{18}N_4$ (362.43): C 79.54%, H 5.01%, N 15.46%, found: C 79.02%, H 4.92%, N 15.05%.

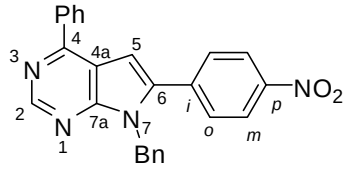
5-(7-benzyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-6-yl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (9-benzyl-6-phenyl-8-(1,3-dimethyluracil-5-yl)-7-deazapurine) (8e)



Product **8e** (95 mg, 92%) was obtained as white solid. Crystalization in hexan/EtOAc gave white crystals.

M.p. 169-176 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.24 (s, 3H, CH_3-1´); 3.44 (s, 3H, CH_3-3´); 5.60 (s, 2H, CH_2); 6.83 (s, 1H, H-5); 6.92 (s, 1H, H-6´); 6.96 (m, 2H, H-*o*-Bn); 7.19-7.25 (m, 3H, H-*m,p*-Bn); 7.51 (m, 1H, H-*p*-Ph); 7.54 (m, 2H, H-*m*-Ph); 8.13 (m, 2H, H-*o*-Ph); 9.02 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 28.36 (CH_3-3´); 37.10 (CH_3-1´); 46.42 (CH_2Ph); 102.69 (CH-5); 105.86 (C-5´); 115.22 (C-4a); 126.92 (CH-*o*-Bn); 127.44 (CH-*p*-Bn); 128.59 (CH-*m*-Bn); 128.76 and 128.80 (CH-*o,m*-Ph); 130.04 (CH-*p*-Ph); 134.11 (C-6); 137.91 (C-*i*-Bn); 138.06 (C-*i*-Ph); 143.58 (CH-6´); 151.09 (C-2´); 152.10 (CH-2); 153.22 (C-7a); 157.31 (C-4); 161.71 (C-4´). IR($CHCl_3$): 3029, 3013, 1710, 1661, 1585, 1565, 1497, 1464, 1456, 1442, 1433, 1342, 1249, 1232. HRMS (ESI) calculated for $C_{25}H_{21}N_5O_2$: 424.1768; found: 424.1764. Anal. calculated for $C_{25}H_{21}N_5O_2$ (423.47): C 70.91%, H 5.00%, N 16.54%, found: C 70.51%, H 4.87%, N 16.31%.

7-benzyl-6-(4-nitrophenyl)-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (9-benzyl-6-phenyl-8-(4-nitrophenyl)-7-deazapurine) (8f)

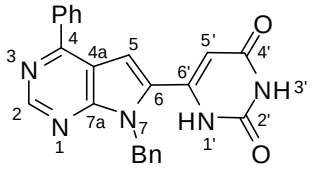


Product **8f** (90 mg, 91%) was obtained as yellow solid. Crystalization in hexan/EtOAc gave yellow crystals.

M.p. 212-219 °C ^{1}H NMR (500 MHz, $CDCl_3$): 5.62 (s, 2H, CH_2); 6.96 (m, 2H, H-*o*-Bn); 7.03 (s, 1H, H-5); 7.22-7.26 (m, 3H, H-*m,p*-Bn); 7.53-7.60 (m, 5H, H-*m,p*-Ph, H-*o*-$C_6H_4NO_2$); 8.17 (m, 2H, H-*o*-Ph); 8.26 (m, 2H, H-*m*-$C_6H_4NO_2$); 9.06 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.45 (CH_2Ph); 102.67 (CH-5); 115.56 (C-4a); 123.93 (CH-*m*-$C_6H_4NO_2$); 126.43 (CH-*o*-Bn); 127.79 (CH-*p*-Bn); 128.86, 128.88 and 128.92 (CH-*m*-Bn and CH-*o,m*-Ph); 129.88 (CH-*o*-$C_6H_4NO_2$); 130.35 (CH-*p*-Ph); 136.93 (C-*i*-Bn); 137.87

(C-*i*-Ph and C-*i*-$C_6H_4NO_2$); 140.11 (C-6); 147.82 (C-*p*-$C_6H_4NO_2$); 152.58 (CH-2); 154.00 (C-7a); 158.01 (C-4). IR($CHCl_3$): 3032, 2987, 1602, 1585, 1566, 1522, 1497, 1485, 1463, 1454, 1442, 1421, 1348. HRMS (ESI) calculated for $C_{25}H_{18}N_4O_2$: 407.1503; found: 407.1499.

6-(7-benzyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-6-yl)pyrimidine-2,4(1*H*,3*H*)-dione (8g)
(9-benzyl-6-phenyl-8-(uracil-6-yl)-7-deazapurine) (8f)



The crude product after cross-coupling was directly deprotected by refluxing in 2 ml solution of THF: dioxane: HCl (1:1:1) for 2 hours. The reaction mixture was evaporated and ethanol (2 ml) was added. The mixture was then kept in a fridge overnight to furnish **8g** (79 mg, 83 %) as white crystals.

M.p. >300 °C. ^{1}H NMR (500 MHz, DMSO-d_6): 5.69 (t, 1H, 4J = 1.7, H-5´); 5.71 (s, 2H, CH_2); 6.99 (m, 2H, H-*o*-Bn); 7.24 (m, 1H, H-*p*-Bn); 7.29 (m, 2H, H-*m*-Bn); 7.54 (s, 1H, H-5); 7.59-7.65 (m, 3H, H-*m,p*-Ph); 8.26 (m, 2H, H-*o*-Ph); 9.01 (s, 1H, H-2); 11.25 (bs, 1H, NH-3´); 11.31 (bs, 1H, NH-1´). ^{13}C NMR (125.7 MHz, DMSO-d_6): 46.29 (CH_2Ph); 101.35 (CH-5´); 105.01 (CH-5); 114.02 (C-4a); 126.63 (CH-*o*-Bn); 127.81 (CH-*p*-Bn); 128.98 (CH-*m*-Bn); 129.07 (CH-*o*-Ph); 129.25 129.07 (CH-*m*-Ph); 131.04 (CH-*p*-Ph); 133.00 (C-6); 137.19 (C-*i*-Bn and C-*i*-Ph); 143.59 (C-6´); 151.53 (C-2´); 153.08 (CH-2); 153.57 (C-7a); 157.76 (C-4); 163.71 (C-4´). IR($CHCl_3$): 3417, 3146, 3031, 2805, 1711, 1687, 1637, 1585, 1496, 1457, 1415, 1347, 1262, 1221. HRMS (ESI) calculated for $C_{23}H_{17}N_5O_2$: 396.1455; found: 396.1451.

General procedure for direct C-H arylation

DMF (3 mL) was added through a septum to an argon purged vial containing a 9-benzyl-6-phenyl-7-deazapurin **2** (143 mg, 0.5 mmol, 1 equiv.), $Pd(OAc)_2$ (5.6 mg, 0.025mmol, 5 mol %), CuI (286 mg, 1.5 mmol, 3 equiv.), Aryl halide (2 equiv.) and Cs_2CO_3 (408 mg, 1.25 mmol, 2.5 equiv.). Reaction mixture was heated to 160 °C for 60 h. The solvent was evaporated under reduced pressure. Products were isolated by flash column chromatography (gradient elution hexanes → ethyl acetate/hexanes 1:6).

7-benzyl-6-(4-methoxyphenyl)-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine
(9-benzyl-6-phenyl-8-(4-methoxyphenyl)-7-deazapurine) (8a)

Product **8a** (76 mg, 39%) was obtained as yellow solid. Crystalization in hexan/EtOAc gave yellowish crystals.

7-benzyl-4-phenyl-6-p-tolyl-7*H*-pyrrolo[2,3-*d*]pyrimidine

(7-benzyl-6-phenyl-8-p-tolyl-7-deazapurine) (8b)

Product **8b** (77 mg, 41%) was obtained as yellow solid. Crystalization in hexan/EtOAc gave yellowish crystals.

7-benzyl-4-phenyl-6-(pyren-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-6-phenyl-8-(pyren-1-yl)-7-deazapurine) (8c)

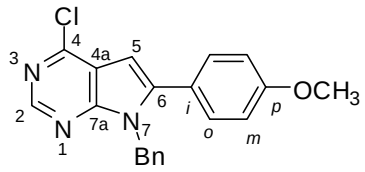
Product **8c** (85 mg, 35%) was obtained as yellow oil.

One pot C-H borylation - Suzuki coupling sequence.General procedure:

9-Benzyl-6-chloro-7-deazapurine **5** (972 mg, 4 mmol, 1 equiv.), bispinacolatodiboron (1.524 g, 6.0 mmol, 1.5 equiv.), $[Ir(COD)OMe]_2$ (218 mg, 0.32 mmol, 8 mol %) and 4,4'-di-tert-butyl-2,2'-bipyridine (172 mg, 0.64 mmol, 16 mol %) were dissolved in dry THF (30 ml). The solution was heated at 80 °C in a septum-sealed vial and stirred under argon for 20 h (NMR - full conversion of starting compound). The solvent was removed under reduced pressure and the crude boronic ester was heated at 50 °C on vacuum line for 2 h to remove organic impurities. The crude boronic ester **7** was then combined with aryl halide (4.4 mmol, 1.1 equiv.), $Pd(dppf)Cl_2$ (146 mg, 0.2 mmol, 5 mol %) and K_2CO_3 (2211 mg, 16 mmol, 4 equiv.) in DMF (30 mL) and stirred under argon at 90 °C for 1 h. The solvent was evaporated and the residue was purified by silica gel flash chromatography to give products **9a-9c**.

7-benzyl-4-chloro-6-(4-methoxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-6-chloro-8-(4-methoxyphenyl)-7-deazapurine) (9a)

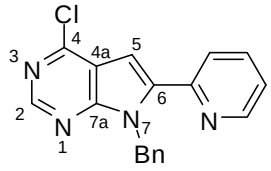


Chromatography (hexane/EtOAc 7:1) to give product **9a** (586 mg, 42%) as white solid. Crystalization in hexan/EtOAc gave white crystals.

M.p. 98-104 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.85 (s, 3H, CH_3O); 5.50 (s, 2H, CH_2); 6.61 (s, 1H, H-5); 6.938 (m, 2H, H-*m*-C_6H_4OMe); 6.942 (m, 2H, H-*o*-Bn); 7.20-7.25 (m, 3H, H-*m,p*-Bn); 7.30 (m, 2H, H-*o*-C_6H_4OMe); 8.65 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 46.48 (CH_2Ph); 55.36 (CH_3O); 98.79 (CH-5); 114.19 (CH-*m*-C_6H_4OMe); 117.68 (C-4a); 122.98 (C-*i*-C_6H_4OMe); 126.54 (CH-*o*-Bn); 127.54 (CH-*p*-Bn); 128.67 (CH-*m*-Bn); 130.68 (CH-*o*-C_6H_4OMe); 137.04 (C-*i*-Bn); 143.25 (C-6); 150.56 (CH-2); 151.13 (C-4); 152.58 (C-7a); 160.38 (C-*p*-C_6H_4OMe). IR($CHCl_3$):3005, 2944, 1615, 1587, 1574, 1542, 1497, 1463, 1442, 1351, 1252, 1176, 1031, 935, 838. HRMS (ESI) calculated for $C_{20}H_{16}ClN_3O$: 350.1066; found: 350.1055. Anal. calculated for $C_{25}H_{20}N_4$ (349.81): C 68.67%, H 4.61%, N 12.01%, Cl 10.13%; found: C 68.57%, H 4.63%, N 11.85%, Cl 10.40 %.

7-benzyl-4-chloro-6-(pyridin-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine

(9-benzyl-4-chloro-8-(pyridin-2-yl)-7-deazapurine) (9b)

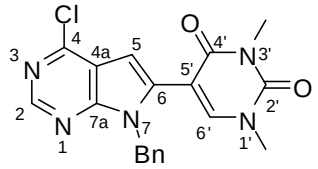


Chromatography (hexane/EtOAc 7:1) to give product **9b** (396 mg, 31%) as white solid. Crystalization in hexan/EtOAc gave white crystals.

M.p. 153-154 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.85 (s, 3H, CH_3O); 5.50 (s, 2H, CH_2); 6.61 (s, 1H, H-5); 6.938 (m, 2H, H-*m*-C_6H_4OMe); 6.942 (m, 2H, H-*o*-Bn); 7.20-7.25 (m, 3H, H-*m,p*-Bn); 7.30 (m, 2H, H-*o*-C_6H_4OMe); 8.65 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 46.48 (CH_2Ph); 55.36 (CH_3O); 98.79 (CH-5); 114.19 (CH-*m*-C_6H_4OMe); 117.68 (C-4a); 122.98 (C-*i*-C_6H_4OMe); 126.54 (CH-*o*-Bn); 127.54 (CH-*p*-Bn); 128.67 (CH-*m*-Bn); 130.68 (CH-*o*-C_6H_4OMe); 137.04 (C-*i*-Bn); 143.25 (C-6); 150.56 (CH-2); 151.13 (C-4); 152.58 (C-7a); 160.38 (C-*p*-C_6H_4OMe). IR($CHCl_3$): 3089, 3035, 3019, 3000, 1588, 1567, 1546, 1497, 1435, 1422, 1354, 1272, 1249, 1172, 937, 865. HRMS (ESI) calculated for $C_{18}H_{13}ClN_4$: 321.0902; found: 321.0903.

5-(7-benzyl-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidin-6-yl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione

(9-benzyl-6-chloro-8-(1,3-dimethyluracil-5-yl)-7-deazapurine) (9c)



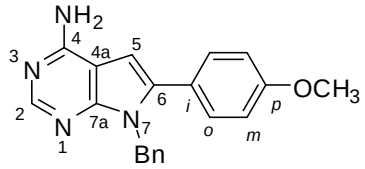
The residue was dissolved in 5 ml $CHCl_3$ and colorless crystals were formed and filtred off [excess of 5-iodo-1,3-dimethylpyrimidine-2,4(1H,3H)-dione]. The residual solution was purified by chromatography (hexane/EtOAc 7:1 to 1:1) to give product **9c** (548 mg, 36%) as white solid.

M.p. 189-192 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.25 (s, 3H, CH_3-1′); 3.41 (s, 3H, CH_3-3′); 5.53 (s, 2H, CH_2); 6.57 (s, 1H, H-5); 6.89 (m, 2H, H-*o*-Bn); 6.95 (s, 1H, H-6′); 7.17-7.21 (m, 3H, H-*m,p*-Bn); 8.66 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 28.29 (CH_3-3′); 37.10 (CH_3-1′); 46.85 (CH_2Ph); 101.39 (CH-5); 105.25 (C-5′); 116.88 (C-4a); 126.86 (CH-*o*-Bn); 127.55 (CH-*p*-Bn); 128.56 (CH-*m*-Bn); 134.61 (C-6); 137.23 (C-*i*-Bn); 143.89 (CH-6′); 150.94 (C-2′); 151.10 (CH-2); 151.70 (C-4); 152.41 (C-7a); 161.46 (C-4′). IR($CDCl_3$): 3029, 3010, 2960, 2928, 1711, 1661, 1585, 1542, 1466, 1455, 1433, 1350, 1253, 1170, 909. HRMS (ESI) calculated for $C_{19}H_{16}ClN_5O_2$: 382.1065; found: 382.1064.

Procedure for amination of 8-aryl-6-chloro-7-deazapurines

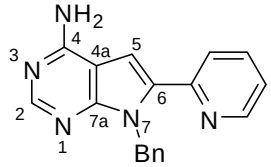
8-Aryl-9-benzyl-6-chloro-7-deazapurines **9a-9c** (0.5 mmol) were dissolved in 10-15 ml methanolic ammonia (saturated with NH_3 at 0 °C) and placed in an autoclave. The reaction mixture was heated at 120–130 °C overnight. The mixture was then cooled and the solvent was evaporated to provide the crude deaza adenines **10a-10c**. The residue was purified by silica gel flash chromatography (EtOAc/MeOH 20:1).

(4-amino-6-(4-methoxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-7-yl)(phenyl)methanone
(6-amino-9-benzyl-8-(4-methoxyphenyl)-7-deazapurine) (10aa)



Product **10aa** (143 mg, 83%) was obtained as yellow foam.
M.p. 158-162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 3.83 (s, 3H, CH_3O); 5.44 (s, 2H, CH_2); 5.47 (bs, 2H, NH_2); 6.37 (s, 1H, H-5); 6.90 (m, 2H, H-*m*-C_6H_4OMe); 7.95 (m, 2H, H-*o*-Bn); 7.18-7.24 (m, 3H, H-*m,p*-Bn); 7.25 (m, 2H, H-*o*-C_6H_4OMe); 8.34 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.05 (CH_2Ph); 55.31 (CH_3O); 97.20 (CH-5); 103.20 (C-4a); 113.97 (CH-*m*-C_6H_4OMe); 123.99 (C-*i*-C_6H_4OMe); 126.44 (CH-*o*-Bn); 127.19 (CH-*p*-Bn); 128.53 (CH-*m*-Bn); 130.54 (CH-*o*-C_6H_4OMe); 137.84 (C-*i*-Bn); 138.85 (C-6); 151.25 (CH-2); 151.67 (C-7a); 156.02 (C-4); 159.78 (C-*p*-C_6H_4OMe). IR($CHCl_3$): 3523, 3414, 3009, 2967, 2840, 1619, 1589, 1562, 1550, 1497, 1467, 1455, 1350, 1302, 1291, 1252, 1177, 1031, 838. HRMS (ESI) calculated for $C_{20}H_{18}N_4O$: 331.1553; found: 331.1553.

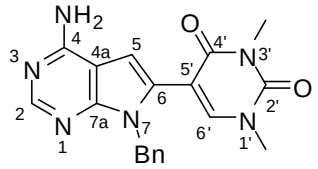
7-benzyl-6-(pyridin-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-amine
(6-amino-9-benzyl-8-(pyridin-2-yl)-7-deazapurine) (10b)



Product **10b** (128 mg, 85%) was obtained as yellowish foam.
M.p. 195-199 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 5.65 (bs, 2H, NH_2); 6.05 (s, 2H, CH_2); 6.74 (s, 1H, H-5); 7.02 (m, 2H, H-*o*-Bn); 7.03-7.15 (m, 3H, H-*m,p*-Bn); 7.18 (ddd, 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 4.9, $J_{5,3}$ = 1.2, H-5-py); 7.50 (ddd, 1H, $J_{3,4}$ = 7.9, $J_{3,5}$ = 1.2, $J_{3,6}$ = 1.0, H-3-py); 7.64 (ddd, 1H, $J_{4,3}$ = 7.9, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.8, H-4-py); 8.38 (s, 1H, H-2); 8.63 (ddd, 1H, $J_{6,5}$ = 4.9, $J_{6,4}$ = 1.8, $J_{6,3}$ = 1.0, H-6-py). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.34 (CH_2Ph); 99.70 (CH-5); 103.09 (C-4a); 122.22 (CH-5-py); 122.71 (CH-3-py); 126.87 (CH-*p*-Bn); 126.92 (CH-*o*-Bn); 128.18 (CH-*m*-Bn); 136.01 (C-6); 136.58 (CH-4-py); 138.48 (C-*i*-Bn); 149.05

(CH-6-py); 151.41 (C-2-py); 152.39 (CH-2); 152.62 (C-7a); 156.78 (C-4). IR($CHCl_3$): 3523, 3415, 3010, 2975, 2930, 2856, 1620, 1588, 1566, 1497, 1471, 1455, 1432, 1354, 1285, 1237. HRMS (ESI) calculated for $C_{18}H_{15}N_5$: 302.1400; found: 302.1401.

5-(4-amino-7-benzyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-6-yl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (6-amino-9-benzyl-8-(1,3-dimethyluracil-5-yl)-7-deazapurine) (10c)



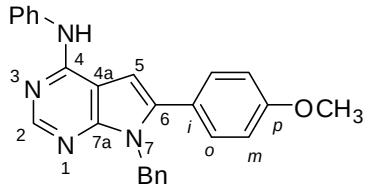
Product **10c** (143 mg, 79%) was obtained as brown foam. Crystalization in $CHCl_3$/hexane gave brownish crystals.

M.p. 222-226 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.21 (s, 3H, CH_3-1´); 3.42 (s, 3H, CH_3-3´); 5.31 (bs, 2H, NH_2); 5.45 (s, 2H, CH_2); 6.38 (s, 1H, H-5); 6.82 (s, 1H, H-6´); 6.93 (m, 2H, H-*o*-Bn); 7.17-7.24 (m, 3H, H-*m,p*-Bn); 8.37 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 28.35 (CH_3-3´); 37.04 (CH_3-1´); 46.38 (CH_2Ph); 100.15 (CH-5); 102.71 (C-4a); 105.94 (C-5´); 126.79 (CH-*o*-Bn); 127.31 (CH-*p*-Bn); 128.55 (CH-*m*-Bn); 129.53 (C-6); 138.23 (C-*i*-Bn); 143.36 (CH-6´); 151.16 (C-2´); 151.92 (C-7a); 152.36 (CH-2); 156.40 (C-4); 162.01 (C-4´). IR($CDCl_3$): 3527, 3416, 3020, 2983, 1708, 1661, 1620, 1588, 1563, 1545, 1470, 1454, 1370, 1349, 1340. HRMS (ESI) calculated for $C_{19}H_{18}N_6O_2$: 363.1564; found: 363.1563.

Procedure for introduction of aryl/alkylamino group to 8-aryl-6-chloro-7-deazapurines

9-Benzyl-6-chloro-7-deazapurine **9a** (0.5 mmol) was refluxed with an amine (1.5 mmol) in 1-butanol (6 ml) overnight. The volatiles were evaporated in vacuo. The residue was purified by silica gel flash chromatography (hexane/EtOAc 3:1).

7-benzyl-6-(4-methoxyphenyl)-*N*-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-amine (6-amino-9-benzyl-8-(4-methoxyphenyl)- *N*-phenyl-7-deazapurine) (10ab)

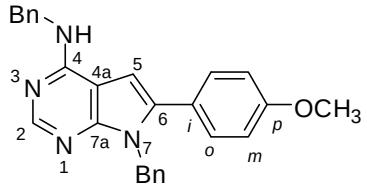


Product **10ab** (132 mg, 65%) was obtained as white foam. Crystalization in hexane/EtOAc gave white crystals.

M.p. 145-146 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 3.83 (s, 3H, CH_3O); 5.45 (s, 2H, CH_2N); 6.10 (s, 1H, H-5); 6.89 (m, 2H, H-*m*-C_6H_4OMe); 6.96 (m, 2H, H-*o*-Bn); 7.18 (m, 1H, H-*p*-Ph); 7.19-7.25 (m, 5H, H-*m,p*-Bn

and H-*o*-C_6H_4OMe); 7.40 (m, 2H, H-*m*-Ph); 7.61 (m, 2H, H-*o*-Ph); 8.48 (s, 1H, H-2). ^{13}C NMR (151 MHz, $CDCl_3$): 46.08 (CH_2N); 55.33 (CH_3O); 98.07 (CH-5); 103.65 (C-4a); 114.00 (CH-*m*-C_6H_4OMe); 122.55 (CH-*o*-Ph); 123.88 (C-*i*-C_6H_4OMe); 124.59 (CH-*p*-Ph); 126.51 (CH-*o*-Bn); 127.25 (CH-*p*-Bn); 128.57 (CH-*m*-Bn); 129.13 (CH-*m*-Ph); 130.56 (CH-*o*-C_6H_4OMe); 137.78 (C-*i*-Bn); 138.63 (C-*i*-Ph); 138.89 (C-6); 150.73 (CH-2); 152.04 (C-7a); 153.39 (C-4); 159.85 (C-*p*-C_6H_4OMe). IR($CHCl_3$):3034, 2966, 2929, 1650, 1608, 1584, 1564, 1497, 1468, 1455, 1292, 1252, 1177, 839. HRMS (ESI) calculated for $C_{26}H_{22}N_4O$: 407.1866; found: 407.1864. Anal. calculated for $C_{26}H_{22}N_4O$ (406.48): C 76.83%, H 5.46%, N 13.78%; found: C 79.50%, H 5.51%, N 13.56%.

7-benzyl-4-(benzylamino)-6-(4-methoxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine
(6-(benzylamino)-9-benzyl-8-(4-methoxyphenyl)-7-deazapurine) (10ac)



Poduct **10ac** (162 mg, 77%) was obtained as white foam. Crystalization in hexane/EtOAc gave white crystals.

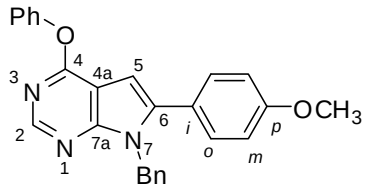
M.p. 145-149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 3.82 (s, 3H, CH_3O); 4.88 (d, 2H, J_{vic} = 5.6, C**H$_2$**NH); 5.31 (bs, 1H, NH); 5.44 (s, 2H, CH_2N); 6.33 (s, 1H, H-5); 6.88 (m, 2H, H-*m*-C_6H_4OMe); 6.95 (m, 2H, H-*o*-BnN); 7.16-7.22 (m, 3H, H-*m,p*-BnN); 7.22 (m, 2H, H-*o*-C_6H_4OMe); 7.30 (m, 1H, H-*p*-BnNH); 7.37 (m, 2H, H-*m*-BnNH); 7.42 (m, 2H, H-*o*-BnNH); 8.43 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 45.35 (CH_2NH); 46.02 (CH_2N); 55.31 (CH_3O); 97.09 (CH-5); 103.09 (C-4a); 113.98 (CH-*m*-C_6H_4OMe); 124.26 (C-*i*-C_6H_4OMe); 126.53 (CH-*o*-BnN); 127.14 (CH-*p*-BnN); 127.53 (CH-*p*-BnNH); 127.79 (CH-*o*-BnNH); 128.52 (CH-*m*-BnN); 128.76 (CH-*m*-BnNH); 130.53 (CH-*o*-C_6H_4OMe); 138.06 (C-*i*-BnN); 138.20 (C-6); 138.85 (C-*i*-BnNH); 151.42 (C-7a); 151.84 (CH-2); 155.77 (C-4); 159.73 (C-*p*-C_6H_4OMe). IR($CHCl_3$): 3010, 2966, 1654, 1601, 1564, 1497, 1467, 1454, 1343, 1291, 1251, 1177, 1030, 838. HRMS (ESI) calculated for $C_{27}H_{24}N_4O$: 421.2023; found: 421.2021. Anal. calculated for $C_{27}H_{24}N_4O$ (420.51): C 77.12%, H 5.75%, N 13.32%; found: C 76.92%, H 5.75%, N 13.23%.

Procedure for introduction phenoxy group to 8-aryl-6-chloro-7-deazapurines

A solution of phenol (57 mg, 0.6 mmol, 1.2 equiv.) in DMF (4 ml) was treated with KO*t*-Bu (67 mg, 0.6 mmol, 1.2 equiv.) and the mixture was stirred at rt for 2 h. The mixture was then treated with deazapurine **9a** (175 mg, 0.5 mmol, 1.0 equiv.) and K_2CO_3 (52 mg, 0.375 mmol, 0.75 equiv.) and heated at 110 °C for 16 h. The mixture was then cooled and the solvent was evaporated. Crude product was purified by silica gel flash chromatography (hexane/EtOAc 6:1→ 3:1) to give product **10ad** (162 mg, 77%) as white solid.

7-benzyl-6-(4-methoxyphenyl)-4-phenoxy-7H-pyrrolo[2,3-d]pyrimidine

(9-benzyl-8-(4-methoxyphenyl)-6-phenoxy-7-deazapurine) (10c)



M.p. 162-165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 3.84 (s, 3H, CH_3O); 5.52 (s, 2H, CH_2); 6.50 (s, 1H, H-5); 6.93 (m, 2H, H-*m*-C_6H_4OMe); 6.99 (m, 2H, H-*o*-Bn); 7.20-7.32 (m, 8H, H-*o,p*-PhO, H-*m,p*-Bn and H-*o*-C_6H_4OMe); 7.47 (m, 2H, H-*m*-PhO); 8.50 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 46.30 (CH_2); 55.25 (CH_3O); 97.99 (CH-5); 105.84 (C-4a); 114.04 (CH-*m*-C_6H_4OMe); 121.75 (CH-*o*-PhO); 123.70 (C-*i*-C_6H_4OMe); 125.40 (CH-*p*-PhO); 126.52 (CH-*o*-Bn); 127.28 (CH-*p*-Bn); 128.53 (CH-*m*-Bn); 129.58 (CH-*m*-PhO); 130.60 (CH-*o*-C_6H_4OMe); 137.59 (C-*i*-Bn); 140.61 (C-6); 150.78 (CH-2); 153.00 (C-*i*-PhO); 154.28 (C-7a); 159.99 (C-*p*-C_6H_4OMe); 161.87 (C-4). IR($CHCl_3$): 3067, 3011, 2929, 2840, 1613, 1591, 1558, 1497, 1491, 1467, 1454, 1446, 1317, 1252, 1200, 1177, 1035, 838. HRMS (ESI) calculated for $C_{26}H_{21}N_3O$: 408.1718; found: 408.1706.

Single crystal X-ray structure analysis

The diffraction data of single crystals of **6** (colourless, 0.24 × 0.28 × 0.45 mm) and **8b** (colourless, 0.22 × 0.27 × 0.49 mm) were collected on Xcalibur X-ray diffractometr with $Cu_{K\alpha}$ (λ=1.54180 Å) at 298 K. Both structure were solved by direct methods with SIR92 [2] and refined by full-matrix least-squares on F with CRYSTALS [1]. All hydrogen atoms were located in a difference map but later were repositioned geometrically and then refined with riding constraints, while all other atoms were refined anisotropically in both cases.

Crystal data for 6: $C_{25}H_{26}B_1N_3O_2$, triclinic, space group *P-1*, *a* = 12.0486(3) Å, *b* = 12.5522(3) Å Å, *c* = 15.7030(4) Å, α = 98.5162(18)°, β = 97.4398(18)°, γ = 103.2928(18)°, *V* = 2252.52(10) $Å^3$, *Z* = 4, *M* = 822.62, 73819 reflections measured, 9449 independent reflections. Final *R* = 0.0589, *wR* = 0.0675, *GoF* = 1.0755 for 4276 reflections with $I > 2\sigma(I)$ and 560 parameters. CCDC 703631.

Crystal data for 8b: $C_{26}H_{21}N_3$, triclinic, space group *P-1*, *a* = 9.8513(18) Å, *b* = 10.4417(18) Å, *c* = 11.565(2) Å, α = 101.076(14)°, β = 114.026(17) (6)°, γ = 104.117(15)°, *V* = 995.1(4) $Å^3$, *Z* = 2, *M* = 375.47, 31243 reflections measured, 4195 independent reflections. Final *R* = 0.0501, *wR* = 0.0610, *GoF* = 1.0007 for 2354 reflections with $I > 2\sigma(I)$ and 263 parameters. CCDC 703632.

References:

1. Altomare, A.; Cascarano, G.; Giacovazzo G.; Guagliardi A.; Burla M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994,** *27*, 435.

2. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K., Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.