An Efficient Synthesis of 2-Substituted 6-Methylpurine Bases and Nucleosides by Fe- or Pd-Catalyzed Cross-coupling Reactions of 2,6-Dichloropurines

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Supplementary Information

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9-Benzyl-2-chloro-6-methylpurine (2a). Colourless crystals from CH_2Cl_2/heptane. M.p. 103-105°C. FAB MS, *m/z* (rel. %): 259 (83), 91 (100). ^{1}H NMR ($CDCl_3$, 500 MHz): 2.84 (s, 3 H, CH_3); 5.20 (s, 2 H, CH_2Ph); 7.29-7.29 (m, 5 H, H-arom.); 7.96 (s, 1 H, H-8). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.4 (CH_3); 47.4 (CH_2); 128.0, 128.8 and 129.2 (CH-arom.); 132.0 (C-5); 134.6 (C-i-arom.); 144.1 (CH-8); 152.3 (C-4); 154.1 (C-2); 161.8 (C-6). ^{1}H-^{13}C HMBC, cross-peaks: C**H**$_3$ to C-5 and C-6. Anal. calculated for $C_{13}H_{11}ClN_4$ (258.7): C, 60.35; H, 4.29; N, 21.66; Cl, 13.70; found: C, 60.22; H, 4.18; N, 21.54; Cl, 13.63.

2-Chloro-6-methyl-9-(tetrahydropyran-2-yl)purine (2b). Colourless foam solidified on standing. M.p. 87-90°C. FAB MS, *m/z* (rel. %): 253 (35), 169 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): 1.60-1.84 and 1.95-2.20 (m, 6 H, CH_2); 2.86 (s, 3 H, CH_3); 3.81 (t, 1 H, *J* = 11.4, H-5'a); 4.20 (d, 1 H, *J* = 10.1, H-5'b); 5.78 (d, 1 H, *J* = 10.6, H-1'); 8.26 (s, 1 H, H-8). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.5 (CH_3); 22.6, 24.8 and 32.0 (CH_2); 68.9 (CH_2O); 81.9 (NCHO); 132.1 (C-5); 142.2 (CH-8); 151.3 (C-4); 153.8 (C-2); 161.7 (C-6). Exact mass (FAB HR MS): 253.0850, calculated for $C_{11}H_{14}ClN_4O$ [M+H]: 253.0856. Anal. calculated for $C_{11}H_{13}ClN_4O$ (252.7): C, 52.28; H, 5.19; N, 22.17; found: C, 52.37; H, 5.34; N, 21.86.

2-Chloro-6-methyl-9-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)purine (2c). Colourless foam solidified on standing. M.p. 71-75°C. FAB MS, *m/z* (rel. %): 613 (10), 455 (25), 105 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.81 (s, 3 H, CH_3); 4.73 (dd, 1 H, *J* = 12.2 and 4.2, H-5'b); 4.83-4.87 (m, 1 H, H-4'); 4.91 (dd, 1 H, *J* = 12.1 and 3.1, H-5'a); 6.15-6.21 (m, 2 H, H-3' and H-2'); 6.50 (d, 1 H, *J* = 5.3, H-1'); 7.35-7.62 (m, 9 H, H-arom.); 7.93-8.10 (m, 6 H, H-arom.); 8.09 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, $CDCl_3$): 19.5 (CH_3); 63.6 (CH_2-5'); 71.6 (CH-3'); 74.3 (CH-2'); 81.2 (CH-4'); 86.5 (CH-1'); 128.3 and 129.2 (C-*i*-arom.); 128.55, 128.58, 128.7, 129.7, 129.86, 129.90, 133.5, 133.8, 133.9 (CH-arom.); 132.7 (C-5); 142.4 (CH-8); 151.8 (C-4); 154.3 (C-2); 162.3 (C-6); 165.1, 165.3 and 166.1 (C=O). Exact mass (FAB HR MS): 613.1474, calculated for $C_{32}H_{26}ClN_4O_7$ [M+H]: 603.1490. Anal. calculated for $C_{32}H_{25}ClN_4O_7$ (613.0): C, 62.70; H, 4.11; N, 9.14; found: C, 62.53; H, 4.37; N, 8.88.

2-Chloro-6-methyl-9-[3,5-bis-*O*-(4-toluoyl)-2-deoxy-β-D-erythropentofuranosyl]purine (2d). Colourless foam solidified on standing. M.p. 121-124°C. FAB MS, *m/z* (rel. %): 521

(15), 353 (20), 169 (30), 81 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.39 and 2.44 (2 x s, 2 x 3 H, 2 x CH_3Ph); 2.81 (s, 3 H, CH_3Pu); 2.87-3.01 (m, 2 H, CH_2-2'); 4.64-4.69 (m, 2 H, H-4' and 5'); 4.74-4.79 (m, 1 H, H-5'); 5.77-5.80 (m, 1 H, H-3'); 6.56 (dd, 1 H, *J* = 6.0 and 8.1, H-1'); 7.21 (d, 2 H, *J* = 8.1, H-arom.); 7.28 (d, 2 H, *J* = 8.1, H-arom.); 7.87 (d, 2 H, *J* = 8.2, H-arom.); 7.97 (d, 2 H, *J* = 8.2, H-arom..); 8.20 (s, 1 H, H-8). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.5, 21.6 and 21.7 (3 x CH_3); 38.4 (CH_2-2'); 63.9 (CH_2-5'); 75.0 (CH-3'); 83.3 (CH-4'); 84.7 (CH-1'); 126.3 and 126.5 (2 x C-arom.); 129.28, 129.29, 129.5 and 129.8 (4 x CH-arom.); 132.6 (C-5); 142.2 (CH-8); 144.2 and 144.6 (C-arom.); 151.5 (C-4); 154.0 (C-2); 162.0 (C-6); 165.9 and 166.0 (CO). Exact mass (FAB HR MS): 521.1567, calculated for $C_{27}H_{26}ClN_4O_5$ [M+H]: 521.1592. Anal. calculated for $C_{27}H_{25}ClN_4O_5$ (521.0): C, 62.25; H, 4.84; N, 10.75; found: C, 62.43; H, 5.12; N, 10.38.

2-Chloro-6-methylpurine (2e). Colourless crystals. M.p. 255-258°C (lit.[1] 275°C dec.). EI MS, *m/z* (rel. %): 168 (100), 132 (15), 106 (10). ^{1}H NMR (DMSO-d_6, 400 MHz): 2.69 (s, 3 H, CH_3); 8.59 (s, 1 H, H-8). ^{13}C NMR (DMSO-d_6, 100.6 MHz): 19.4 (CH_3); 146.1 (CH-8), 152.1 (C-Pu), other quaternary carbon signals did not appear probably due to tautomerism. Exact mass (EI HR MS): 168.0208, calculated for $C_6H_5ClN_4$: 168.0203. Anal. calculated for $C_6H_5ClN_4$ (168.6): C, 42.75; H, 2.99; N, 33.23; found: C, 42.78; H, 3.00; N, 33.02.

2-Chloro-6-methyl-9-(β-D-ribofuranosyl)purine (2f). Colourless crystals. M.p. 185-187°C (lit.[2] 188-191°C). $[\alpha]_D$ –14.5 (*c* 1.9, DMF). FAB MS, *m/z* (rel. %): 301 (50), 169 (100). ^{1}H NMR (400 MHz, DMSO-d_6): 2.72 (s, 3 H, CH_3); 3.55-3.60 (m, 1 H, H-5'b); 3.66-3.72 (m, 1 H, H-5'a); 3.96-4.00 (m, 1 H, H-4'); 4.27 (dd, 1 H, *J* = 4.3, 8.3, H-3'); 4.56 (q, 1 H, *J* = 5.2, H-2'); 5.03 (t, 1 H, *J* = 5.3, 5'-OH); 5.23 (d, 1 H, *J* = 5.1, 3'-OH); 5.53 (d, 1 H, *J* = 5.8, 2'-OH); 5.96 (d, 1 H, *J* = 5.4, H-1'); 8.80 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, DMSO-d_6): 19.0 (CH_3); 61.0 (CH_2-5'); 70.1 (CH-3'); 73.8 (CH-2'); 85.7 (CH-4'); 87.6 (CH-1'); 132.2 (C-5); 144.7 (C-8); 151.8, 152.3 and 161.0 (C-2, C-4 and C-6). Exact mass (FAB HR MS): 301.0724, calculated for $C_{11}H_{14}ClN_4O_4$ [M+H]: 301.0704. Anal. calculated for $C_{11}H_{13}ClN_4O_4$ (300.7): C, 43.94; H, 4.36; N, 18.63; found: C, 43.62; H, 4.39; N, 18.29.

2-Chloro-9-(2-deoxy-β-D-erythropentofuranosyl)-6-methylpurine (2g). Colourless crystals. M.p. 159-162°C. $[\alpha]_D$ –8.3 (*c* 2.0, DMF). FAB MS, *m/z* (rel. %): 285 (50), 169 (100). ^{1}H NMR (400 MHz, DMSO-d_6): 2.36 (ddd, 1H, *J* = 13.3, 6.3, 3.8, H-2'b); 2.70 (s, 3 H, CH_3); 2.70-2.74 (m, 1H, H-2'a); 3.51-3.66 (m, 2 H, H-5'); 3.89 (dd, 1 H, *J* = 4.3 and 7.7, H-4'); 4.41-

4.46 (m, 1 H, H-3'); 4.91 (t, 1 H, *J* = 5.5, 5'-OH); 5.34 (d, 1 H, *J* = 4.3, 3'-OH); 6.38 (t, 1 H, *J* = 6.6, H-1'); 8.74 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, DMSO-d_6): 19.0 (CH_3); ≈ 39 (overlapped by DMSO, CH_2-2'); 61.3 (CH_2-5'); 70.4 (CH-3'); 83.7 (CH-1'); 88.0 (CH-4'); 132.2 (C-5); 144.6 (CH-8); 151.5, 152.1 and 160.8 (C-2, C-4 and C-6). Exact mass (FAB HR MS): 285.0825, calculated for $C_{11}H_{14}ClN_4O_3$ [M+H]: 285.0754. Anal. calculated for $C_{11}H_{13}ClN_4O_3$ (284.7): C, 46.41; H, 4.60; N, 19.68; found: C, 46.47; H, 4.72; N, 19.36.

2. Characterization data for compounds 3a-3g

9-Benzyl-2,6-dimethylpurine (3a). Colourless crystals from CH_2Cl_2/heptane. M.p. 83-85°C. EI MS, *m/z* (rel. %): 238 (70), 237 (74), 223 (12), 182 (10), 161 (23), 91 (100). ^{1}H NMR ($CDCl_3$, 500 MHz): 2.77 and 2.79 (2 x s, 2 x 3 H, 2 x CH_3); 5.37 (s, 2 H, CH_2Ph); 7.23-7.34 (m, 5 H, H-arom.); 7.86 (s, 1 H, H-8). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.3 and 26.0 (CH_3); 46.9 (CH_2); 127.8, 128.4 and 129.0 (CH-arom.); 130.6 (C-5); 135.4 (C-i-arom.); 142.8 (CH-8); 151.2 (C-4); 158.8 and 162.1 (C-2 and C-6). Exact mass (EI HR MS): 238.1207, calculated for $C_{14}H_{14}N_4$: 238.1218. Anal. calculated for $C_{14}H_{14}N_4$ (238.3): C, 70.57; H, 5.92; N, 23.51; found: C, 70.44; H, 6.00; N, 23.38.

2,6-Dimethyl-9-(tetrahydropyran-2-yl)purine (3b). Oil. FAB MS, *m/z* (rel. %): 233 (30), 149 (100). ^{1}H NMR ($CDCl_3$, 500 MHz): 1.60-1.80 and 1.97-2.10 (m, 6 H, CH_2); 2.75 and 2.78 (2 x s, 2 x 3 H, CH_3); 3.77 (dt, 1 H, *J* = 2.4 and 11.6, H-5'a); 4.12-4.16 (m, 1 H, H-5'b); 5.75 (dd, 1 H, *J* = 10.0 and 2.4, H-1'); 8.14 (s, 1 H, H-8). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.4 and 26.0 (CH_3); 22.8, 24.9 and 31.9 (CH_2); 68.7 (CH_2O); 81.4 (NCHO); 130.8 (C-5); 140.9 (CH-8); 150.4, 158.8 and 162.0 (C-2, C-4 and C-6). Exact mass (FAB HR MS): 233.1414, calculated for $C_{12}H_{17}N_4O$ [M+H]: 233.1402. Anal. calculated for $C_{12}H_{16}N_4O$ (232.3): C, 62.05; H, 6.94; N, 24.12; found: C, 62.33; H, 6.80; N, 23.88.

2,6-Dimethyl-9-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)purine (3c). Colourless foam. FAB MS, *m/z* (rel. %): 593 (7), 445 (5), 105 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.75 and 2.79 (2 x s, 2 x 3 H, 2 x CH_3); 4.72 (dd, 1 H, *J* = 11.8 and 4.4, H-5'b); 4.83-4.91 (m, 2 H, H-4' and H-5'a); 6.34-6.43 (m, 3 H, H-3', H-2' and H-1'); 7.35-7.42 (m, 7 H, H-arom.); 7.53-7.60 (m, 3 H, H-arom.); 7.93-8.02 (m, 5 H, H-arom.); 8.09 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, $CDCl_3$): 19.5 and 26.0 (CH_3); 63.6 (CH_2-5'); 71.5 (CH-3'); 74.1 (CH-2'); 80.6 (CH-4'); 87.1 (CH-1'); 128.8 and 129.3 (C-*i*-arom.); 128.5, 129.6, 129.8, 133.4, 133.7, 133.8 (CH-arom.); 131.5 (C-

5); 141.8 (CH-8); 150.7 (C-4); 159.4 and 162.5 (C-2 and C-6); 165.1, 165.3 and 166.1 (C=O). Exact mass (FAB HR MS): 593.2031, calculated for $C_{33}H_{29}N_4O_7$ [M+H]: 593.2036. Anal. calculated for $C_{33}H_{28}N_4O_7$ (592.6): C, 66.68; H, 4.76; N, 9.45; found: C, 66.89; H, 5.01; N, 9.10.

2,6-Dimethyl-9-[3,5-bis-*O*-(4-toluoyl)-2-deoxy-β-D-erythropentofuranosyl]purine (3d). Colourless foam solidified on standing. M.p. 129-134°C. FAB MS, *m/z* (rel. %): 501 (8), 149 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.43 and 2.47 (2 x s, 2 x 3 H, 2 x CH_3Ph); 2.81 and 2.82 (2 x s, 2 x 3 H, CH_3Pu); 2.82-2.90 and 3.16-3.22 (m, 2 H, CH_2-2'); 4.67-4.72 (m, 2 H, H-4' and 5'); 4.77-4.82 (m, 1 H, H-5'); 5.86-5.88 (m, 1 H, H-3'); 6.60 (dd, 1 H, *J* = 6.0 and 8.1, H-1'); 7.24 (d, 2 H, *J* = 8.1, H-arom.); 7.31 (d, 2 H, *J* = 8.1, H-arom.); 7.91 (d, 2 H, *J* = 8.2, H-arom.); 8.01 (d, 2 H, *J* = 8.2, H-arom..); 8.14 (s, 1 H, H-8). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.4, 21.6, 21.7 and 26.0 (4 x CH_3); 37.7 (CH_2-2'); 64.0 (CH_2-5'); 75.1 (CH-3'); 82.9 (CH-4'); 84.5 (CH-1'); 126.5 and 126.7 (2 x C-arom.); 129.2, 129.3, 129.6 and 129.8 (4 x CH-arom.); 131.4 (C-5); 141.2 (CH-8); 144.1 and 144.5 (C-arom.); 150.6 (C-4); 159.1 and 162.2 (C-2 and C-6); 165.9 and 166.1 (CO). Exact mass (FAB HR MS): 510.2117, calculated for $C_{28}H_{29}N_4O_5$ [M+H]: 501.2138. Anal. calculated for $C_{28}H_{28}N_4O_5$ (500.5): C, 67.19; H, 5.64; N, 11.19; found: C, 67.01; H, 5.76; N, 10.87.

2,6-Dimethylpurine (3e). Colourless crystals. M.p. 235-239°C (lit.[1] M.p. 266-268°C). EI MS, *m/z* (rel. %): 148 (100), 133 (13), 120 (8), 107 (10). ^{1}H NMR (DMSO-d_6, 400 MHz): 2.62 and 2.66 (2 x s, 2 x 3 H, 2 x CH_3); 8.44 (s, 1 H, H-8); ~13.2 (vbr, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100.6 MHz): 19.1 and 25.2 (CH_3); 144.0 (CH-8); 160.1 (C-Pu), other purine-carbon signals did not appear probably due to tautomerism. Exact mass (EI HR MS): 148.0751, calculated for $C_7H_8N_4$: 148.0749. Anal. calculated for $C_7H_8N_4$ (148.2): C, 56.74; H, 5.44; N, 37.81; found: C, 56.51; H, 5.53; N, 37.56.

2,6-Dimethyl-9-(β-D-ribofuranosyl)purine (3f). Colourless crystals. M.p. 211-212°C (lit.[3] 232-233°C). $[\alpha]_D$ -47.1 (*c* 0.7, DMF) (lit.[3] $[\alpha]_D$ -47.1). FAB MS, *m/z* (rel. %): 281 (30), 149 (100). ^{1}H NMR (400 MHz, DMSO-d_6): 2.64 and 2.67 (2 x s, 2 x 3 H, CH_3); 3.55-3.61 (m, 1 H, H-5'b); 3.67-3.73 (m, 1 H, H-5'a); 3.97-4.00 (m, 1 H, H-4'); 4.27 (dd, 1 H, *J* = 4.6, 7.7, H-3'); 4.60-4.64 (m, 1 H, H-2'); 5.18-5.22 (m, 2 H) and 5.45 (d, 1 H, *J* = 5.8, 3 x OH); 5.98 (d, 1 H, *J* = 5.8, H-1'); 8.63 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, DMSO-d_6): 19.0 and 25.4 (CH_3); 61.5 (CH_2-5'); 70.5 (CH-3'); 73.5 (CH-2'); 85.8 (CH-4'); 87.4 (CH-1'); 130.9 (C-5); 143.3 (C-

8); 150.6 (C-4); 158.0 and 160.6 (C-2 and C-6). Exact mass (FAB HR MS): 281.1266, calculated for $C_{12}H_{17}N_4O_4$ [M+H]: 281.1250. Anal. calculated for $C_{12}H_{16}N_4O_4$ (280.3): C, 51.42; H, 5.75; N, 19.99; found: C, 51.65; H, 5.80; N, 19.77.

9-(2-Deoxy-β-D-erythropentofuranosyl)-2,6-dimethylpurine (3g). Colourless crystals. M.p. 183-186°C. $[\alpha]_D$ –25.1 (*c* 0.8, DMF). FAB MS, *m/z* (rel. %): 265 (35), 149 (100). ^{1}H NMR (400 MHz, DMSO-d_6): 2.31 (ddd, 1H, *J* = 13.2, 6.0, 3.1, H-2'b); 2.63 and 2.65 (2 x s, 2 x 3 H, CH_3); 2.73 (ddd, 1H, *J* = 13.2, 7.3, 6.0, H-2'a); 3.51-3.66 (m, 2 H, H-5'); 3.88-3.93 (m, 1 H, H-4'); 4.42-4.47 (m, 1 H, H-3'); 5.07 (t, 1 H, *J* = 5.6, 5'-OH); 5.32 (d, 1 H, *J* = 4.1, 3'-OH); 6.42 (t, 1 H, *J* = 6.5, H-1'); 8.60 (s, 1 H, H-8). ^{13}C NMR (100 MHz, DMSO-d_6): 19.0 and 25.4 (CH_3); ≈ 39 (overlapped by DMSO, CH_2-2'); 61.7 (CH_2-5'); 70.8 (CH-3'); 83.6 (CH-1'); 88.0 (CH-4'); 130.8 (C-5); 143.1 (CH-8); 150.3 (C-4); 157.9 and 160.6 (C-6 and C-2). Exact mass (FAB HR MS): 265.1302, calculated for $C_{12}H_{17}N_4O_3$ [M+H]: 265.1301. Anal. calculated for $C_{12}H_{16}N_4O_3$ (264.3): C, 54.54; H, 6.10; N, 21.20; found: C, 54.34; H, 6.12; N, 20.92.

3. Characterization data for compounds 4a-4g

9-Benzyl-6-methyl-2-phenylpurine (4a). Colourless crystals from CH_2Cl_2/heptane. M.p. 126-129°C. EI MS, *m/z* (rel. %): 300 (55), 285 (9), 233 (12, 149 (18), 91 (100). ^{1}H NMR ($CDCl_3$, 500 MHz): 2.91 (s, 3 H, CH_3); 5.47 (s, 2 H, CH_2); 7.32-7.38 (m, 5 H, H-arom.); 7.45-7.52 (m, 3 H, H-arom.); 7.96 (s, 1 H, H-8); 8.55 (d, 2 H, *J* = 7.3, H-arom.). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 19.6 (CH_3); 47.0 (CH_2); 127.9, 128.1, 128.32, 128.34, 128.9 and 129.8 (CH-arom.); 131.4 (C-5); 135.4 and 138.1 (C-*i*-arom.); 143.3 (CH-8); 151.4 (C-4); 158.9 and 159.0 (C-2 and C-6). Exact mass (EI HR MS): 300.1384, calculated for $C_{19}H_{16}N_4$: 300.1375. Anal. calculated for $C_{19}H_{16}N_4$ (300.6): C, 75.98; H, 5.37; N, 18.65; found: C, 75.75; H, 5.46; N, 18.45.

6-Methyl-2-phenyl-9-(tetrahydropyran-2-yl)purine (4b). Colourless foam solidified on standing. M.p. 138-140°C. FAB MS, *m/z* (rel. %): 295 (50), 211 (100), 85 (15). ^{1}H NMR ($CDCl_3$, 500 MHz): 1.65-1.88 and 2.05-2.22 (m, 6 H, CH_2); 2.91 (s, 3 H, CH_3); 3.78-3.85 (m, 1 H, H-5'a); 4.16-4.22 (m, 1 H, H-5'b); 5.88 (dd, 1 H, *J* = 10.0 and 2.4, H-1'); 7.44-7.52 (m, 3 H, H-arom.); 8.23 (s, 1 H, H-8); 8.52 (d, 2 H, *J* = 7.1, H-arom.). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 19.8 (CH_3); 22.8, 24.9 and 31.9 (CH_2); 68.7 (CH_2O); 81.8 (NCHO); 128.3, 128.4 and

129.9 (CH-arom.); 131.6 (C-5); 138.3 (C-*i*-arom.); 141.6 (CH-8); 150.6 (C-4); 158.9 and 159.1 (C-2 and C-6). Exact mass (FAB HR MS): 295.1564, calculated for $C_{17}H_{19}N_4O$ [M+H]: 295.1559. Anal. calculated for $C_{17}H_{18}N_4O$ (294.4): C, 69.37; H, 6.16; N, 19.03; found: C, 69.14; H, 6.35; N, 18.65.

6-Methyl-2-phenyl-9-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)purine (4c). Colourless foam. FAB MS, *m/z* (rel. %): 655 (7), 455 (8), 211 (30), 105 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.90 (s, 3 H, CH_3); 4.67 (dd, 1 H, *J* = 12.0 and 4.1, H-5'b); 4.86-4.94 (m, 2 H, H-4' and H-5'a); 6.45-6.49 (m, 2 H) and 6.54-6.57 (m, 1 H, H-1', H-2' and H-3'); 7.23-7.62 (m, 13 H, H-arom.); 7.92-8.06 (m, 5 H, H-arom.); 8.15 (s, 1 H, H-8); 8.60 (d, 2 H, *J* = 6.9, H-arom.). ^{13}C NMR (100.6 MHz, $CDCl_3$): 19.8 (CH_3); 63.3 (CH_2-5'); 71.3 (CH-3'); 74.3 (CH-2'); 80.3 (CH-4'); 87.7 (CH-1'); 128.0, 128.4, 128.5, 128.6, 129.6, 129.9, 130.2, 132.6, 133.3, 133.7 and 133.8 (CH-arom.); 128.9 (C-*i*-arom.); 132.3 (C-5); 137.9 (C-*i*-arom.); 142.5 (CH-8); 150.9 (C-4); 159.5 and 159.8 (C-2 and C-6); 165.2, 165.2 and 166.1 (C=O). Exact mass (FAB HR MS): 655.2231, calculated for $C_{38}H_{31}N_4O_7$ [M+H]: 655.2192. Anal. calculated for $C_{38}H_{30}N_4O_7$ (654.7): C, 69.72; H, 4.62; N, 8.56; found: C, 69.43; H, 4.87; N, 8.18.

6-Methyl-2-phenyl-9-[3,5-bis-*O*-(4-toluoyl)-2-deoxy-β-D-erythropentofuranosyl]purine (4d). Colourless foam. FAB MS, *m/z* (rel. %): 563 (8), 211 (72), 119 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.37 and 2.45 (2 x s, 2 x 3 H, 2 x CH_3Ph); 2.88 (s, 3 H, CH_3Pu); 2.85-2.92 and 3.28-3.36 (m, 2 H, CH_2-2'); 4.61-4.68 (m, 2 H, H-4' and 5'); 4.78-4.83 (m, 1 H, H-5'); 5.92-5.94 (m, 1 H, H-3'); 6.60 (t, 1 H, *J* = 6.9, H-1'); 7.14 (d, 2 H, *J* = 8.1, H-arom.); 7.30 (d, 2 H, *J* = 7.8, H-arom.); 7.44-7.52 (m, 3 H, H-arom.); 7.84 (d, 2 H, *J* = 8.2, H-arom.); 8.00 (d, 2 H, *J* = 8.2, H-arom..); 8.16 (s, 1 H, H-8); 8.52-8.55 (m, 2 H, H-arom.). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 19.7, 21.6 and 21.7 (3 x CH_3); 37.8 (CH_2-2'); 63.9 (CH_2-5'); 75.0 (CH-3'); 82.9 (CH-4'); 84.8 (CH-1'); 126.5 and 126.6 (2 x C-arom.); 128.4, 128.5, 129.2, 129.3, 129.6, 129.9 and 130.1 (CH-arom.); 132.2 (C-5); 138.1 (C-*i*-Ph); 142.0 (CH-8); 144.1 and 144.5 (C-i-Tol); 150.9 (C-4); 159.1 and 159.4 (C-2 and C-6); 165.9 and 166.1 (CO). Exact mass (FAB HR MS): 563.2274, calculated for $C_{33}H_{31}N_4O_5$ [M+H]: 563.2294. Anal. calculated for $C_{33}H_{30}N_4O_5$ (562.6): C, 70.45; H, 5.37; N, 9.96; found: C, 70.22; H, 5.56; N, 9.61.

6-Methyl-2-phenylpurine (4e). Colourless crystals. M.p. 260-264°C. EI MS, *m/z* (rel. %): 210 (100), 195 (10), 149 (20). ^{1}H NMR (DMSO-d_6, 400 MHz): 2.79 (s, 3 H, CH_3); 7.46-7.53 (m, 3 H, H-arom.); 8.42-8.46 (m, 3 H, H-arom. + H-8); 13.38 (brs, 1 H, NH). ^{13}C NMR

(DMSO-d_6, 100.6 MHz): 19.4 (CH_3); 127.6, 128.4 and 129.7 (CH-arom.); 138.0 and 157.1 (C-Pu); 143.9 (CH-8). Exact mass (EI HR MS): 210.0903, calculated for $C_{12}H_{10}N_4$: 210.0905. Anal. calculated for $C_{12}H_{10}N_4$ (210.2): C, 68.56; H, 4.79; N, 26.65; found: C, 68.26; H, 4.80; N, 26.31.

6-Methyl-2-phenyl-9-(β-D-ribofuranosyl)purine (4f). Colourless crystals. M.p. 198-201°C. $[\alpha]_D$ +24.3 (*c* 0.6, DMF). ^{1}H NMR (400 MHz, DMSO-d_6): 2.81 (s, 3 H, CH_3); 3.58-3.64 (m, 1 H, H-5'b); 3.70-3.76 (m, 1 H, H-5'a); 3.99-4.03 (m, 1 H, H-4'); 4.27 (dd, 1 H, *J* = 5.0, 8.6, H-3'); 4.76 (ddd, 1 H, *J* = 6.0, 5.6, 5.0, H-2'); 5.02 (t, 1 H, *J* = 5.4, 5'-OH); 5.26 (d, 1 H, *J* = 5.0, 3'-OH); 5.53 (d, 1 H, *J* = 6.0, 2'-OH); 6.12 (d, 1 H, *J* = 5.6, H-1'); 7.50-7.56 (m, 3 H, H-arom.); 8.45-8.49 (m, 2 H, H-arom.); 8.75 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, DMSO-d_6): 19.4 (CH_3); 61.4 (CH_2-5'); 70.4 (CH-3'); 73.5 (CH-2'); 85.6 (CH-4'); 87.4 (CH-1'); 127.8, 128.5 and 130.1 (CH-arom.); 131.7 (C-5); 137.6 (C-*i*-arom.); 144.4 (C-8); 151.1 (C-4); 157.3 and 158.2 (C-2 and C-6). FAB MS, *m/z* (rel. %): 343 (20), 211 (25), 185 (30), 93 (100). Exact mass (FAB HR MS): 343.1415, calculated for $C_{17}H_{19}N_4O_4$ [M+H]: 343.1406. Anal. calculated for $C_{17}H_{18}N_4O_4$ (342.3): C, 59.64; H, 5.30; N, 16.37; found: C, 59.51; H, 5.34; N, 16.18.

9-(2-Deoxy-β-D-erythropentofuranosyl)-6-methyl-2-phenylpurine (4g). Colourless crystals. $[\alpha]_D$ +8.6 (*c* 0.7, DMF). FAB MS, *m/z* (rel. %): 327 (45), 211 (100). ^{1}H NMR (400 MHz, DMSO-d_6): 2.39 (ddd, 1H, *J* = 13.2, 6.3, 3.5, H-2'b); 2.79 (s, 3 H, CH_3); 2.89 (ddd, 1H, *J* = 13.2, 6.3, 6.3, H-2'a); 3.53-3.69 (m, 2 H, H-5'); 3.93 (dd, 1 H, *J* = 7.6, 4.4, H-4'); 4.50-4.54 (brm, 1 H, H-3'); 4.92 (t, 1 H, *J* = 5.3, 5'-OH); 5.39 (d, 1 H, *J* = 4.0, 3'-OH); 6.55 (t, 1 H, *J* = 6.7, H-1'); 7.48-7.54 (m, 3 H, H-arom.); 8.44-8.47 (m, 2 H, H-arom.); 8.70 (s, 1 H, H-8). ^{13}C NMR (100 MHz, DMSO-d_6): 19.4 (CH_3); ≈ 39 (overlapped by DMSO, CH_2-2'); 61.7 (CH_2-5'); 70.8 (CH-3'); 83.5 (CH-1'); 87.9 (CH-4'); 127.8, 128.5 and 130.0 (CH-arom.); 131.8 (C-5); 137.6 (C-*i*-arom.); 144.3 (CH-8); 150.8 (C-4); 157.2 and 158.1 (C-6 and C-2). Exact mass (FAB HR MS): 327.1451, calculated for $C_{17}H_{19}N_4O_3$ [M+H]: 327.1457. Anal. calculated for $C_{17}H_{18}N_4O_3$ (326.4): C, 62.57; H, 5.56; N, 17.17; found: C, 62.19; H, 5.64; N, 16.86.

4. References

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