

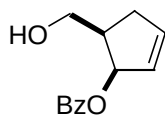
Solid Phase Synthesis of Carbocyclic Nucleosides

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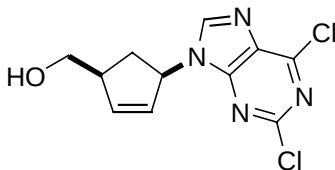
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Experimental.

General. All reactions involving air and/or water sensitive reagents were carried out under an atmosphere of N₂ using oven-dried glassware. Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Cl₂(PCy₃)₂Ru=CHPh was prepared according to a modified procedure of Grubbs and coworkers.¹ Et₂O, THF, and CH₂Cl₂ were purified according to the method of Grubbs and coworkers.² Et₃N, EtNi-Pr₂, DMSO, and pyridine were distilled from CaH₂. Purification by silica gel chromatography was performed by the method of Still and coworkers using Scientific Adsorbents Incorporated 40 micron flash silica gel.³



cis-3-Benzoyloxy-4-(hydroxymethyl)cyclopentene (3). ¹H NMR (CDCl₃, 200 MHz) δ 2.17-2.36 (m, 1), 2.40-2.54 (m, 2), 2.58-2.74 (m, 1), 3.68-3.77 (m, 2), 5.89-5.94 (m, 2), 6.14-6.19 (m, 1), 7.34-7.43 (m, 2), 7.48-7.56 (m, 1), 7.94-8.00 (m, 2); ¹³C NMR (CDCl₃, 100 MHz) δ 34.12, 43.81, 61.61, 79.92, 128.33, 129.03, 129.50, 129.99, 133.04, 137.93, 166.93; IR (film) 3460 (br), 3070, 2940, 1720, 1605, 1455, 1260 cm⁻¹; HRMS calcd for C₁₃H₁₄NaO₃ [MNa]⁺: 241.0841; found, 241.0845.

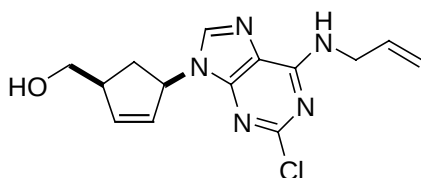


2,6-Dichloropurine derivative (7a). ¹H NMR (CDCl₃, 200 MHz) δ 1.80-1.92 (m, 1), 2.77-2.94 (m, 1), 3.02-3.14 (m, 1), 3.69 (dd, 1, *J* = 10.5, 4.1), 3.85 (dd, 1, *J* = 10.4, 3.8), 5.72-5.80 (m, 1), 5.81-5.86 (m, 1), 6.18-6.23 (m, 1), 8.43 (s, 1); ¹³C NMR (CDCl₃, 100 MHz) δ 33.88, 47.43, 60.53, 64.07, 128.92, 130.76, 140.06, 145.47, 151.31, 152.58, 152.66; IR (film) 3600-3200, 2980, 2960, 1585, 1550, 1355, 970 cm⁻¹; HRMS calcd for C₁₁H₁₀Cl₂N₄NaO [MNa]⁺: calcd, 307.0129; found, 307.0129.

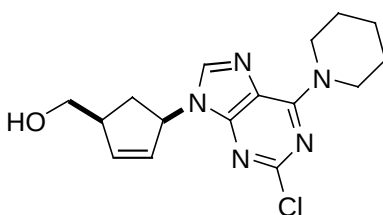
¹ Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

² Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

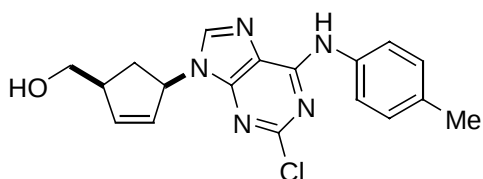
³ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.



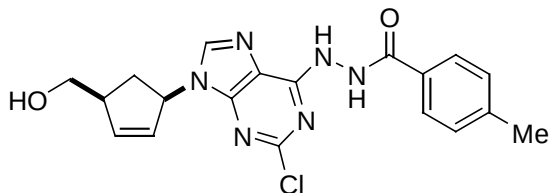
6-Allylamino-2-chloropurine Derivative (7b). ^1H NMR (CDCl_3 , 200 MHz) δ 1.84-1.97 (m, 1), 2.74-2.91 (m, 1), 3.03-3.10 (m, 1), 3.68-3.75 (m, 1), 3.79-3.87 (m, 1), 4.21-4.31 (m, 1), 5.14-5.521 (m, 1), 5.22-5.33 (m, 1), 5.58-5.67 (m, 1), 5.79-5.85 (m, 1), 5.88-6.05 (m, 1), 6.11-6.17 (m, 1), 7.81 (s, 1); ^{13}C NMR (CDCl_3 , 100 MHz) δ 33.73, 42.97, 47.55, 60.47, 64.85, 116.96, 118.94, 130.04, 133.72, 138.57, 139.15, 149.64, 154.15, 155.10; IR (film): 3500-3100, 2924, 1618, 1575, 1535, 1178 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{ClN}_5\text{NaO}$ $[\text{MNa}]^+$: 328.0941; found, 328.0924.



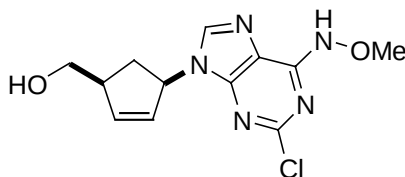
2-Chloro-6-piperidinopurine Derivative (7c). ^1H NMR (CDCl_3 , 200 MHz) δ 1.61-1.77 (m, 6), 1.83-1.96 (m, 1), 2.51-2.62 (m, 1), 2.72-2.89 (m, 1), 2.99-3.11 (m, 1), 3.69 (dd, 1, J = 10.7, 4.3), 3.83 (dd, 1, J = 10.7, 4.3), 4.07-4.26 (m, 1), 5.57-5.66 (m, 1), 5.78-5.82 (m, 1), 6.10-6.15 (m, 1), 7.76 (s, 1); ^{13}C NMR (CDCl_3 , 100 MHz) δ 24.61, 26.11, 33.56, 45.49, 47.54, 60.39, 65.03, 119.10, 130.22, 137.28, 138.26, 151.49, 153.57, 153.83; IR (film): 3500-3100, 2931, 2854, 1579, 1445, 1309, 1111; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{ClN}_5\text{O}$ $[\text{MH}]^+$: 334.1435; found, 334.1435.



2-Chloro-6-*p*-toluidinopurine Derivative (7d). ^1H NMR (CDCl_3 , 200 MHz) δ 1.82-1.94 (m, 1), 2.31 (s, 3), 2.75-2.92 (m, 1), 3.01-3.14 (m, 1), 3.70 (dd, 1, J = 10.6, 4.4), 3.83 (dd, 1, J = 10.6, 4.4), 5.61-5.69 (m, 1), 5.80-5.85 (m, 1), 6.13-6.18 (m, 1), 7.15 (d, 1, J = 8.2), 7.61 (d, 1, J = 8.6), 7.88 (s, 1), 8.22 (br s, 1). ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.87, 33.92, 47.56, 60.33, 64.61, 119.10, 120.40, 129.52, 129.76, 133.68, 135.45, 138.89, 139.59, 150.02, 152.27, 153.87; IR (film): 3500-3100, 2924, 1688, 1620, 1579, 1511, 1459, 1314, 1167, 1123; HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{ClN}_5\text{O}$ $[\text{MH}]^+$: 356.1278; found, 356.1266.



2-Chloro-6-(*p*-tolylhydrazido)purine Derivative (7e). ^1H NMR (CDCl_3 , 200 MHz) δ 1.78-1.91 (m, 1), 2.37 (s, 3), 2.71-2.87 (m, 1), 3.00-3.08 (m, 1), 3.66 (dd, $J = 10.8, 3.8$ Hz, 1), 3.80 (dd, $J = 11.0, 4.0$ Hz, 1), 5.58-5.64 (m, 1), 5.76-5.83 (m, 1), 6.09-6.16 (m, 1), 7.19 (d, $J = 8.0$, 2), 7.75 (d, $J = 8.0$, 2), 7.96 (s, 1); ^{13}C NMR (CDCl_3 , 100 MHz) δ ;IR (film): 3500-3100, 2924, 1660, 1611, 1573, 1496, 1462, 1316, 1226; HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{ClN}_6\text{NaO}$ $[\text{MH}]^+$: calcd, 421.1156, found, 421.1167.



2-Chloro-6-(methoxyamino)purine Derivative (7f). ^1H NMR (CDCl_3 , 200 MHz) δ 1.80-1.94 (m, 1), 2.75-2.91 (m, 1), 3.03-3.14 (m, 1), 3.69 (dd, 1, $J = 10.6, 4.2$), 3.83 (dd, 1, $J = 10.8, 4.2$), 3.93 s, 3), 5.63-5.73 (m, 1), 5.80-5.85 (m, 1), 6.14-6.19 (m, 1), 7.99 (s, 1) 9.38-9.48 (br m, 1); ^{13}C NMR (CDCl_3 , 100 MHz) δ 33.82, 47.52, 60.34, 64.68, 64.98, 117.27, 129.74, 138.95, 140.79, 151.35, 153.93, 155.90; IR (film); HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{ClN}_5\text{NaO}_2$ $[\text{MNa}]^+$: 318.0734; found, 318.0738.