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Supplementary Material for: Independent Generation and Reactivity of 2'-Deoxyurid-1'-yl.

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Preparation of Disiloxane of 3. Psicofuranosyluracil (2.87 g, 11.1 mmol) was dried by azeotrope from pyridine (2 x 5 mL). Dried psicofuranosyluracil was dissolved in pyridine (120 mL), and 1,3-dichloro-1,1,3,3-tetrakis(isopropyl)disiloxane (3.85 g, 12.3 mmol) in pyridine (15 mL) was added at -20°C over the course of 2.5 h. After allowing the reaction to stir and warm to room temperature overnight, it was quenched with saturated NaHCO₃. The solvents were removed in vacuo, and the residue was taken up in EtOH (100 mL). The solids were filtered, and the salts washed with EtOH (3 x 25 mL). Silica gel (30 g) was added, and after removing the solvent in vacuo it was applied to a column of silica (150 g). The column was eluted with EtOAc: Hex (1:1), which were increased to EtOAc: Hex (3:2) upon commencement of product elution. The column was washed with EtOH in order to elute polar products. Disiloxane **3** (1.43 g, 26%) was obtained as an oil. Psicofuranosyluracil could be recovered from the mixture of undesired silylated nucleosides by desilylation with NH₄F in MeOH. ¹H NMR (CDCl₃) δ 8.56 (bd s, 1H), 7.93 (d, 1H, J=8.5 Hz), 5.64 (d, 1H, J=8.5 Hz), 4.31 (m, 1H), 4.02 (m, 4H), 3.82 (dd, 1H, J=2.5, 8 Hz), 2.92 (dd, 1H, J=6.8, 13.5 Hz), 2.47 (t, 1H, J=6 Hz), 2.40 (dd, 1H, J=10.5, 13.5 Hz), 0.98 (m, 28 H). ¹³C NMR (CDCl₃) δ 164.8, 150.3, 141.9, 100.6, 97.2, 85.1, 67.9, 65.2, 60.1, 39.4, 17.4, 17.2, 17.1, 16.9, 16.8, 13.4, 13.0, 12.8, 12.4. IR (film) 3445, 2944, 2868, 1709, 1691, 1679, 1462, 1300, 1118, 1038 cm⁻¹. Anal. Calcd. for C₂₂H₄₀N₂O₇Si₂: C, 52.77; H, 8.05; N, 5.59. Found: C, 52.52; H, 7.89; N, 5.60.

Preparation of 4. DMSO (0.22 g, 2.8 mmol) in CH₂Cl₂ (9 mL) was added dropwise to oxalyl chloride (0.175 g, 1.38 mmol) in CH₂Cl₂ (7 mL) at -60°C. After stirring for 10 min, **3** (0.62 g, 1.22 mmol) was added in CH₂Cl₂ (9 mL). After stirring for 35 min at -60°C, triethylamine (0.66

g, 6.43 mmol) was added. The mixture was stirred briefly at -60°C , before warming to room temperature. The reaction mixture was quenched with H_2O (30 mL), and extracted with CH_2Cl_2 (2 x 100 mL). The organic layers were combined and washed with 1% HCl (75 mL), followed by 5% NaHCO_3 (75 mL) and brine (100 mL). After drying over MgSO_4 , the solvents were removed in vacuo to yield 0.56 g (91%) of **4**. An analytical sample could be obtained via flash chromatography ($\text{EtOAc}:\text{CH}_2\text{Cl}_2$; 1:1). However, in practice **4** was carried on without further purification. mp $148\text{--}148.5^{\circ}\text{C}$. ^1H NMR (CDCl_3) δ 9.22 (s, 1H), 8.78 (bd s, 1H), 7.90 (d, 1H, $J=8$ Hz), 5.75 (d, 1H, $J=8$ Hz), 4.39 (m, 1H), 4.13 (d, 1H, $J=14$ Hz), 3.95 (dd, 1H, $J=2.6, 14$ Hz), 3.74 (dd, 1H, $J=1.5, 9$ Hz), 3.09 (dd, 1H, $J=10.3, 13.4$ Hz), 2.33 (dd, 1H, $J=8, 13.4$ Hz), 0.91 - 1.08 (m, 28 H). ^{13}C NMR (CDCl_3) δ 187.7, 163.7, 150.4, 139.1, 102.2, 92.6, 85.2, 66.7, 58.8, 37.0, 25.4, 24.6, 17.4, 17.3, 17.2, 17.1, 17.0, 16.9, 16.7, 13.4, 12.8, 12.4. IR (film) 2946, 2894, 2868, 1745, 1700, 1464, 1386, 1301, 1276, 1118, 1077, 1056, 1038 cm^{-1} . Anal. calcd. for $\text{C}_{22}\text{H}_{38}\text{N}_2\text{O}_7\text{Si}_2$: C, 52.98; H, 7.68; N, 5.62. Found: C, 53.13; H, 7.82; N, 5.61.

Preparation of 5. To **4** (402 mg, 0.81 mmol) in THF (5 mL) at -78°C was added $t\text{-BuLi}$ (1.08 mL, 1.5 M) solution. The solution was stirred for 3 h, at which time it was quenched by the addition of 0.3 N NaOAc (1 mL), and allowed to warm to room temperature. The solution was diluted with EtOAc (45 mL), washed with H_2O (30 mL) and brine (40 mL). After drying over MgSO_4 , the secondary alcohol (243 mg, 54%) was obtained as a mixture of diastereomers by flash chromatography ($\text{EtOAc}:\text{Hexanes}$; 1:4). The alcohol was very unstable, and was typically used immediately. ^1H NMR (CDCl_3) δ 9.15 (bd s, 1H), 8.08 (d, 1H, $J=8$ Hz, minor), 8.00 (d, 1H, $J=8$ Hz, major), 5.69 (dd, 1H, $J=2.8$ Hz), 4.21 - 3.85 (m, 4H), 3.12 - 2.95 (m, 1H), 2.91 (d, 1H, $J=9$ Hz, major), 2.78 - 2.55 (m, 1H), 2.40 (d, 1H, $J=9.5$ Hz), 2.03 (d, 1H, $J=9.5$ Hz), 1.26 - 0.82 (m, 37H).

Dess-Martin periodinane (526 mg, 1.10 mmol) was added to the alcohol (243 mg, 0.44 mmol) in CH_2Cl_2 (20 mL) at 0°C . After stirring for 5 h at room temperature, additional Dess-Martin reagent (526 mg, 1.10 mmol) was added, and the reaction was stirred overnight. The mixture was diluted with EtOAc (75 mL) and washed with cold, saturated NaHCO_3 (50 mL) with 2.5 g $\text{Na}_2\text{S}_2\text{O}_3$. The organic layer was washed with brine (25 mL) and dried over MgSO_4 . The residue was purified by flash chromatography (EtOAc: Hex; 1:4) to yield 213 mg of **5** (88%). ^1H NMR (CDCl_3) δ 8.68 (bd s, 1H), 8.03 (d, 1H, $J=8$ Hz), 5.73 (dd, 1H, $J=1.8, 8.2$ Hz), 4.34 (m, 1H), 4.16 (d, 1H, $J=14$ Hz), 3.96 (dd, 1H, $J=2.6, 13.5$ Hz), 3.69 (dd, 1H, $J=1.7, 9$ Hz), 3.42 (dd, 1H, $J=11.5, 13.5$ Hz), 2.23 (dd, 1H, $J=6.7, 13.5$ Hz), 1.15 - 0.97 (m, 37 Hz). IR (soln) 3184, 3054, 2945, 2867, 1682, 1622, 1463, 1384, 1366, 1299, 1272, 1203, 1149, 1116, 1039 cm^{-1} .

Preparation of 2. NH_4F (73 mg, 1.96 mmol) and **5** (51.4 mg, 0.09 mmol) were refluxed in MeOH (4 mL) for 2 h. The reaction mixture was cooled to room temperature and quenched with saturated NaHCO_3 (1 mL). The solvents were removed in vacuo, and the salts were washed with EtOAc (25 mL), filtered and concentrated. The residue was chromatographed (MeOH: EtOAc: Hexanes; 1:4:5) to yield 28 mg of **2** (96%). MP: $195 - 196^\circ\text{C}$. ^1H NMR (CD_3CN) δ 8.09 (d, 1H, $J=8$ Hz), 5.65 (d, 1H, $J=8$ Hz), 4.25 (m, 1H), 3.84 - 3.65 (m, 3H), 3.14 (dd, 1H, $J=7, 14$ Hz), 2.25 (dd, 1H, $J=7.5, 14$ Hz), 1.15 (s, 9H). IR (film) 3390 (bd), 2962, 1684, 1457, 1419, 1365, 1299, 1227, 1091, 1042 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_6$: C, 53.84; H, 6.45; N, 8.97. Found: C, 53.71; H, 6.47; N, 8.89.