Supporting Information

Concurrent Hydrogenation of Three Functional Groups Enables Synthesis of C3´-Homologated Nucleoside Amino Acids

Venubabu Kotikam* and Eriks Rozners*

Department of Chemistry, Binghamton University, The State University of New York, Binghamton, NY 13902, USA

E-mail: erozners@binghamton.edu/ vkotikam@binghamton.edu

General procedure:

Dry methylene chloride and dry pyridine were obtained by refluxing them over CaH_2 for six hours followed by distillation. Dry DMF (DriSolv®) was purchased from Millipore Sigma. All the dry reactions were carried out under an atmosphere of nitrogen. All NMR spectra were recorded on a Bruker AM 600/300 spectrometer at ambient temperature. Silacycle 0.25 mm 60 Å silica gel F254 plates were used for TLC analysis. Column chromatography was done on SiliaFlash® P60 230-400 mesh silica gel (Silacycle). All the hydrogenation reactions were handled with additional care. In general, the reaction mixture was purged with a line of nitrogen gas followed by the addition of 10% Pd/C under inert atmosphere of nitrogen.

5'-Azido-5'-deoxy-2'-O-tert-butyldimethylsilyluridine, 3a:

5'-Azido-5'-deoxyribonucleosides (2a/2b) were obtained following reported procedures.¹ Compound 2a (7.0 g, 26.0 mmol) was co-evaporated with dry pyridine (20 mL) two times and re-suspended in dry pyridine

(50 mL), followed by the addition of TBS-Cl (4.7 g, 31.2 mmol) at room temperature. Reaction was stirred overnight at room temperature. Upon the completion of reaction (monitored by TLC), the reaction mixture was quenched with methanol (2 mL), followed by the removal of solvents under reduced pressure. The crude residue was partitioned between ethyl acetate (300 mL) and water (100 mL). Water layer was washed with another 100 mL of ethyl acetate. The combined organic layer was washed with brine solution (200 mL), dried over anhydrous Na₂SO₄ and concentrated. The crude residue was purified by silica gel column chromatography using a gradient (5 to 40 %) of EtOAc in hexanes. Yield: **3a**, 4.6 g, 47%; **3ai**, 3.9 g, 40%.



The isomerization of the undesired isomer **3ai** (3.9 g, 10.3 mmol) to the desired **3a** was effected by stirring **3ai** in pyridine:water (100 mL, 9:1) for 24 h at room temperature.² Solvents were removed and the crude residue (~50:50 of **3a:3ai** on TLC) was purified by silica gel column chromatography using the above mentioned gradient. The total amount of combined **3a** was 6.5 g, 66% yield.

3a: ¹H NMR (600 MHz, CDCl3) $\delta_{\rm H}$ 9.05 (s, 1H), 7.53 (d, J = 8.1 Hz, 1H), 5.83 – 5.79 (m, 2H), 4.27 (dd, J = 5.2, 4.1 Hz, 1H), 4.11 – 4.03 (m, 2H), 3.79 (dd, J = 13.3, 2.9 Hz, 1H), 3.65 (dd, J = 13.3, 3.6 Hz, 1H), 2.65 (bs, 1H), 0.91 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H). ¹³C NMR (151 MHz, CDCl3) $\delta_{\rm C}$ 163.0, 150.2, 140.0, 103.1, 90.2, 82.3, 75.2, 70.6, 51.9, 25.7, 18.1, -4.5, -5.0.

3ai: ¹H NMR (600 MHz, CDCl3) $\delta_{\rm H}$ 9.42 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 5.70 (dd, J = 8.1, 1.7 Hz, 1H), 5.62 (d, J = 3.7 Hz, 1H), 4.28 (t, J = 5.7 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.96 (dd, J = 3.3, 1.9 Hz, 1H), 3.65 (dd, J = 13.4, 3.1 Hz, 1H), 3.43 (dd, J = 13.4, 4.1 Hz, 1H), 2.98 (bs, 1H), 0.86 (s, 9H), 0.09 (s, 6H). ¹³C NMR (151 MHz, CDCl3) $\delta_{\rm C}$ 163.3, 150.4, 141.1, 102.9, 92.3, 82.4, 74.0, 71.4, 51.5, 25.7, 18.1, -4.6, -4.7.

5'-Azido-5'-deoxy-N6-benzoyl-2'-O-tert-butyldimethylsilyladenosine, 3b:

Compound **2b** (8.0 g, 20.18 mmol) was co-evaporated with dry DMF (30 mL) and dissolved in DMF:pyridine (2:8, 100 mL), followed by addition of imidazole (2.0 g, 30.2 mmol) and TBS-Cl (3.6 g, 24.2 mmol) at room temperature. The reaction was stirred ovrnight at room temperature. Solvents were removed under reduced pressure and the crude residue was partitioned between ethyl acetate (300 mL) and water (200 mL). Water layer was washed with another 200 mL of ethyl acetate. The organic layer was

¹ Yamamoto, I.; Sekine, M.; Hata, T. J. Chem. Soc., Perkin Trans. 1, 1980, 306-310.

² Ogilvie, K. K.; Beaucage, S. L.; Schifman, A. L.; Theriault, N. Y.; Sadana, K. L. Can. J. Chem., 1978, 56, 2768-2780.

washed with brine solution (200 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude residue was purified by silica gel column chromatography using a gradient (10 to 50%) of EtOAc in hexanes. Yield: **3bii**, 1.1 g, 9%; **3bi**, 3.7 g, 36%; **3b**, 4.1 g, 40%.

The isomerization of the undesired **3bi** (3.7 g, 7.2 mmol) to the desired **3b** was effected by stirring 3'-*O*-TBS isomer in pyridine:water (70 mL, 9:1) for 24 h at room temperature. Solvents wear removed under reduced preasure and the crude (~50:50 of **3b**:**3bi** on TLC) was purified by silica gel column chromatography using the above mentioned gradient. The total amount of combined **3b** was 5.6 g, 55% yield.

3b: ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 8.79 (s, 1H), 8.24 (s, 1H), 8.02 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 6.02 (d, J = 4.3 Hz, 1H), 4.92 (t, J = 4.7 Hz, 1H), 4.31 (t, J = 5.0 Hz, 1H), 4.22 (dd, J = 8.5, 4.4 Hz, 1H), 3.73 (qd, J = 13.3, 4.2 Hz, 2H), 0.86 (s, 9H), 0.00 (s, 3H), -0.08 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 164.7, 152.8, 151.5, 149.8, 141.9, 133.7, 132.9, 129.0, 127.9, 123.6, 89.5, 83.1, 75.1, 71.3, 52.0, 25.7, 18.0, -4.7, -5.0.



3bi: ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 9.09 (s, 1H), 8.77 (s, 1H), 8.19 (s, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 6.03 (d, J = 3.1 Hz, 1H), 4.81 – 4.69 (m, 2H), 4.18 (dd, J = 8.6, 4.4 Hz, 1H), 3.71 (dd, J = 13.3, 3.6 Hz, 1H), 3.51 (dd, J = 13.3, 4.5 Hz, 1H), 3.23 (bs, 1H), 0.96 (s, 9H), 0.19 (d, J = 1.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 164.7, 152.8, 151.5, 149.8, 142.2, 133.7, 132.9, 129.0, 128.0, 123.8, 89.9, 82.9, 74.4, 71.9, 51.4, 25.8, 18.1, -4.5, -4.6.

3bii: ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 9.10 (s, 1H), 8.79 (s, 1H), 8.28 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 5.98 (d, J = 3.9 Hz, 1H), 4.87 (t, J = 4.0 Hz, 1H), 4.31 (t, J = 4.5 Hz, 1H), 4.23 (q, J = 4.5 Hz, 1H), 3.77 (dd, J = 13.2, 4.2 Hz, 1H), 3.70 (dd, J = 13.2, 4.7 Hz, 1H), 0.93 (s, 9H), 0.84 (s, 9H), 0.11 (d, J = 9.1 Hz, 6H), 0.01 (s, 3H), -0.13 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 164.6, 152.7, 151.4, 149.7, 142.4, 133.7, 132.9, 128.9, 127.9, 123.9, 90.0, 82.8, 74.7, 72.2, 51.5, 25.9, 25.8, 18.1, 18.0, -4.2, -4.5, -4.70, -4.75.

General procedure for the synthesis of GH substrates, 4a/4b:

The silyl derivative (**3a** 2.5 g, 6.5 mmol or **3b** 2.3 g, 4.5 mmol) was dissolved in dry dichloromethane (20 mL for **3a** or 15 mL for **3b**) and added to a solution of fresh DMP (4.1 g, 9.7 mmol for **3a** or 2.8 g, 6.7 mmol for **3b**) in dichloromethane (45 mL for **3a** or 30 mL for **3b**) with continuous stirring at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and allowed to warm up to room temperature. After 2 h, a drop of water was added and the reaction mixture was stirred at room temperature for another 2 h. The reaction mixture was diluted with diethyl ether (300 mL), ice-cold solution of 1:1 of saturated aq. NaHCO₃ (50 mL) and 10% aq. Na₂S₂O₃ (50 mL) was added and the mixture was shaken for 5 min. The organic layer was separated and washed with sat. NaHCO₃ solution (100 mL), water (100 mL) and brine solution (100 mL), followed by drying over anhydrous Na₂SO₄. Solvents were removed under vacuum and the white solid (**3ak** or **3bk**, quantitative conversions in both cases) was subjected to the Wittig olefination without further purification.



To a stirred solution of benzyl(triphenylphosphoranylidine)acetate (3.2 g, 7.8 mmol for **3ak** or 2.2 g, 5.4 mmol for **3bk**) in dry dichloromethane (60 mL for **3ak** or 35 mL for **3bk**), was added a solution of keto derivatives in dry dichloromethane (15 mL for **3ak** or 10 mL for **3bk**) at 0 °C. After 15 min, the reaction mixture was warmed to room temperature and stirred for 2 h. Solvents were removed under vacuum and the crude residue was purified by silica gel column chromatography using a gradient (for **4a**, 0 to 15%; for **4b**, 0 to 25%) of EtOAc in hexanes affording the 3'-homologated nucleosides as white foam. Yield over two steps: **4a**, 2.8 g, 84 %; **4b**, 2.5 g, 87%.

4a: ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 9.04 (s, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.42 – 7.34 (m, 5H), 6.00 (d, J = 1.9 Hz, 1H), 5.88 (d, J = 7.9 Hz, 2H), 5.38 (m, 1H), 5.24 – 5.16 (m, 2H), 4.75 (d, J = 7.9 Hz, 1H), 4.06 (dd, J = 13.0, 2.5 Hz, 1H), 3.74 (dd, J = 13.0, 2.6 Hz, 1H), 0.89 (s, 9H), 0.08 (s, 3H), -0.04 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 164.9, 162.7, 158.7, 150.5, 139.4, 135.5, 128.8, 128.6, 128.5, 115.4, 104.0, 86.0, 77.4, 75.4, 66.8, 53.8, 25.6, 17.9, -4.6, -4.8.

HRMS-EI (+): Mass calc. for C24H32N5O6Si (M+H), 514.2122; found, 514.2117.

4b: ¹H NMR (600 MHz, CDCl3) $\delta_{\rm H}$ 9.10 (s, 1H), 8.83 (s, 1H), 8.28 (s, 1H), 8.03 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.40 (m, 5H), 6.04 (s, 1H), 5.87 (d, J = 7.7 Hz, 1H), 5.62 (d, J = 7.6 Hz, 1H), 5.52 (s, 1H), 5.21 (d, J = 2.4 Hz, 2H), 4.06 (dd, J = 12.8, 4.4 Hz, 1H), 3.73 (dd, J = 12.6, 1.3 Hz, 1H), 0.76 (s, 9H), -0.06 (s, 3H), -0.55 (s, 3H). ¹³C NMR (151 MHz, CDCl3) $\delta_{\rm C}$ 164.7, 164.4, 158.5, 153.1, 152.0, 149.8, 141.6, 135.4, 133.6, 132.8, 128.9, 128.7, 128.5, 128.5, 127.8, 123.2, 115.2, 87.0, 78.4, 75.7, 66.7, 53.7, 25.4, 17.7, -4.8, -5.4.

HRMS-EI (+): Mass calc. for C32H37N8O5Si (M+H), 641.2660; found, 641.2656.

4c: The original GH substrate **4b** (1.8 g, 2.85 mmol) was dissolved in dry pyridine (30 mL) followed by addition of Bz-Cl (1.0 mL, 8.56 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. Solvents were removed on rotary evaporator under vacuum. Na. (Bz)

The residue was diluted with dichloromethane (300 mL) and washed with sat. NaHCO₃ (100 mL), water (100 mL) and brine solution (100 mL). Organic layer was separated and dried over anhydrous Na₂SO₄ and concentrated. The crude residue was purified by silica gel column chromatography using a gradient (0 to 20%) of EtOAc in hexanes furnishing **4c** as white foam. Yield: 2.1 g, 99%.



¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 8.68 (s, 1H), 8.40 (s, 1H), 7.86 (d, J = 7.8 Hz, 4H), 7.48 (t, J = 7.5 Hz, 2H), 7.42 – 7.31 (m, 9H), 6.03 (s, 1H), 5.87 (d, J = 7.7 Hz, 1H), 5.55 – 5.47 (m, 2H), 5.25 – 5.18 (m, 2H), 4.04 (dd, J = 12.9, 3.9 Hz, 1H), 3.75 (dd, J = 12.6, 1.4 Hz, 1H), 0.75 (s, 9H), -0.08 (s, 3H), -0.60 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 172.2, 164.8, 158.4, 153.3, 152.7, 152.3, 143.5, 135.5, 134.1, 133.0, 130.2, 129.5, 128.8, 128.7, 128.6, 128.5, 128.0, 115.3, 87.0, 78.5, 76.2, 66.9, 53.8, 25.5, 17.8, -4.7, -5.3.

HRMS-EI (+): Mass calc. for C39H41N8O6Si (M+H), 745.2918; found, 745.2908.

5'-Amino-2'-O-tert-butyldimethylsilyl-3'-carboxymethyl-3', 5'-dideoxyuridine, 5a:

Compound 4a (100 mg, 0.19 mmol) was dissolved in tert-butanol (3 mL), followed by addition of water (3

mL). 10% Pd/C (30 mg, 30% w/W) was added and the reaction mixture was degassed by purging with nitrogen. The reaction mixture was purged with hydrogen gas from a balloon and stirred under slight positive pressure of hydrogen (balloon) at room temperature for 3.5 h. The reaction progress was monitored by the ¹H NMR analysis to avoid formation of the over-reduced (uracil C5=C6) product **7**. Reaction mixture was



filtered through celite and the solvents were removed to obtain crude 5a, which was used in the next step without further purification.

¹H NMR of crude (300 MHz, MeOD) $\delta_{\rm H}$ 7.68 (d, J = 8.1 Hz, 1H), 5.75 – 5.69 (m, 2H), 4.57 (dd, J = 5.4, 1.8 Hz, 1H), 4.17 (td, J = 8.8, 3.1 Hz, 1H), 3.35 (m, 1H), 3.19 (dd, J = 13.5, 8.5 Hz, 1H), 2.53 (dd, J = 15.6, 5.0 Hz, 1H), 2.40 (m, 1H), 2.24 (dd, J = 15.5, 8.3 Hz, 1H), 0.93 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H).

HRMS-EI (+): Mass calc. for C17H30N3O6Si (M+H), 400.1904; found, 400.1900

5'-Amino-(4-methoxytrityl)-2'-O-tert-butyldimethylsilyl-3'-carboxymethyl-3', 5'-dideoxyuridine, 1a:

Compound 5a (0.19 mmol) was co-evaporated with dry pyridine (2 x 5 mL) and re-dissolved in dry pyridine (2.0 mL) followed by the addition of MMTr-Cl (118 mg, 0.38 mmol) at room temperature. The reaction

mixture was left for stirring for 3 h, and another equivalent of MMTr-Cl (60 mg, 0.19 mmol) and catalytic DMAP (10 mg) was added. The reaction mixture was allowed to stir at room temperature overnight. Solvents were removed and the crude residue was dissolved in dichloromethane (100 mL), followed by washing with saturated aqueous NaHCO₃ (30 mL), water (30 mL) and brine (30 mL). The organic



layer was concentrated and the crude residue was purified by silica gel column chromatography using a gradient (0 to 2.0%) of MeOH in dichloromethane containing 1% NEt₃ affording **1a** as white foam (triethylammonium salt). Yield over two steps: 85 mg, 60%.

¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 9.42 (s, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.44 (m, 4H), 7.35 (d, J = 8.7 Hz, 2H), 7.27 – 7.16 (m, 6H), 6.80 (d, J = 8.7 Hz, 2H), 5.64 (s, 1H), 5.49 (d, J = 8.1 Hz, 1H), 4.36 (d, J = 3.7 Hz, 1H), 4.15 – 4.13 (m, 1H), 3.76 (d, J = 6.8 Hz, 3H), 3.54 (q, J = 7.0 Hz, NEt₃), 3.02 (q, J = 7.2 Hz, NEt₃), 2.79 (d, J = 11.9 Hz, 1H), 2.53 (dd, J = 17.0, 8.1 Hz, 1H), 2.34 (s, 1H), 2.19 – 2.09 (m, 3H), 1.38 (t, J = 7.0 Hz, NEt₃), 1.30 (t, J = 7.3 Hz, NEt₃), 0.89 (s, 9H), 0.20 (s, 3H), 0.05 (s, 3H). 13 C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 175.6, 163.9, 158.1, 150.2, 146.06, 146.00, 140.32, 137.7, 129.9, 129.1, 128.67, 128.62, 128.3, 128.0, 126.5, 125.3, 113.3, 101.3, 92.4, 84.2, 78.3, 70.4, 55.3, 53.0, 45.6 (NEt₃), 45.5 (NEt₃), 40.1, 30.1, 29.7, 25.9, 18.1, 8.6 (NEt₃), 8.1 (NEt₃), -4.3, -5.4.

MS-EI (-): Mass calc. for C37H45N3O7Si (M), 671.3027; found, 670.2954 (M-H).

5'-Amino-N6-benzoyl-3'-carboxymethyl-3', 5'-dideoxy-2'-O-tert-butyldimethylsilyladenosine, 5b:

Compound 4c (100 mg, 0.13 mmol) was dissolved in methanol (6 mL), followed by addition of water (0.7 mL, excess of water resulted in the precipitation of 4c). 10% Pd/C (100 mg, 100% w/W) **A**^{Bz} was added and the reaction mixture was degassed by purging with nitrogen. The reaction mixture was purged with hydrogen gas from a balloon and stirred under slight positive pressure of hydrogen (balloon) at room temperature for 24 h. The reaction progress was monitored by the 1H NMR analysis. Reaction mixture was filtered



¹H NMR of crude (300 MHz, MeOD) $\delta_{\rm H}$ 8.74 (s, 1H), 8.56 (s, 1H), 8.10 – 8.07 (m, 2H), 7.67-7.64 (m, 1H), 7.60-7.55 (m, 2H), 6.11 (d, J = 2.2 Hz, 1H), 5.00 (dd, J = 5.5, 2.1 Hz, 1H), 4.34 (m, 1H), 3.42-3.35 (m, 2H), 2.94-2.84 (m, 1H), 2.63 (dd, J = 16.4, 4.8 Hz, 1H), 2.36 (dd, J = 16.4, 9.1 Hz, 1H), 0.93 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H).

HRMS-EI (+): Mass calc. for C25H35N6O5Si (M+H), 527.2438; found, 527.2435.

through celite and the solvents were removed to obtain crude **5b**, which was used in the

next step without further purification.

5'-Amino-(4-methoxytrityl)-*N*6-benzoyl-2'-*O-tert*-butyldimethylsilyl-3'-carboxymethyl-3',5'-dideoxyadenosine, 1b:

Synthesis of compound **1b** followed the same procedure described above for **1a** (except that 5 equivalents of MMTr-Cl and no DMAP were used). The crude residue was purified by silica gel column chromatography using a gradient (0 to 2%) of MeOH in dichloromethane containing 1% NEt₃ affording **1b** as white foam (triethylammonium salt). Yield over two steps: 70 mg, 61%.



¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 9.55 (s, 1H), 8.51 (s, 1H), 8.09 (s, 1H), 8.01 (d, J = 7.5 Hz, 2H), 7.55 – 7.41 (m, 7H), 7.37 (d, J = 8.9 Hz, 2H), 7.25 (m, 4.8 Hz, 4H), 7.16 (t, J = 7.2 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 5.97 (d, J = 1.1 Hz, 1H), 4.87 – 4.84 (m, 1H), 4.23 – 4.18 (m, 1H), 3.75 (s, 3H), 3.01 (q, J = 7.3 Hz, NEt₃), 2.75 – 2.60 (m, 3H), 2.38 (dd, J = 13.0, 6.3 Hz, 1H), 2.27 (dd, J = 16.6, 4.6 Hz, 1H), 1.28 (t, J = 7.2 Hz, NEt₃), 0.89 (s, 9H), 0.10 (s, 3H), -0.00 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) $\delta_{\rm C}$ 175.9, 157.9, 145.9, 141.4, 137.8, 133.5, 132.7, 129.8, 129.0, 128.8 – 128.3, 128.3 – 127.9, 127.9 – 127.7, 126.4, 123.7, 113.2, 91.4, 84.2, 77.2, 77.0, 76.8, 70.3, 55.1, 46.3, 45.3 (NEt₃), 40.6, 30.4, 25.7, 17.9, 8.5 (NEt₃), -4.5, -5.3.

HRMS-EI (+): Mass calc. for C45H51N6O6Si (M+H), 799.3639; found, 799.3644.

































Copies of Mass spectra:







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