

# **A Concise and Highly Stereocontrolled Synthesis of 1- Deoxygalactonojirimycin and Its Congeners using Dioxanylpiperidene, A Promising Chiral Building Block**

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## **Supporting Information**

**(4*R*,5*R*)-5-(*tert*-Butoxycarbonylamino)-2,2-dimethyl-4-vinyl-1,3-dioxan (8) and (4*R*,1'*S*)-3-*tert*-Butoxycarbonyl-2,2-dimethyl-4-(hydroxyallyl)-1,3-oxazolidine (*syn*-6).** MeLi (1.18 M in Et<sub>2</sub>O, 6.79 mL, 8 mmol) was added to a solution of tetravinyltin (0.36 mL, 2 mmol) in Et<sub>2</sub>O (15 mL) at 0 °C and the mixture was stirred for 15 min at the same temperature. Then ZnBr<sub>2</sub> (1.82 g, 8 mmol) was added to the mixture and stirred for 1 h at room temperature. The mixture was slowly added to a suspension of **5** (458.5 mg, 2 mmol) and ZnBr<sub>2</sub> (0.45 g, 2 mmol) in Et<sub>2</sub>O (5 mL) at –78 °C. The reaction was warmed to room temperature and stirred for 2 h. Saturated NH<sub>4</sub>Cl was added to the mixture with ice cooling. Organic layer was separated and the aqueous layer was extracted with Et<sub>2</sub>O two times. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to give a mixture of *syn* and *anti* **6** (*syn:anti* = 5:1) (464 mg, 91%) as a pale yellow solid. Recrystallization of the solid from a solution of

hexane/EtOAc (5:1) gave **6** (334 mg, 72%) as a diastereomeric mixture (*syn:anti* = 24:1). 0.15N HCl gas in CHCl<sub>3</sub> (3 mL) was added to a solution of **6** (3.08 g, 12 mmol) in CHCl<sub>3</sub> (150 mL). The mixture was stirred overnight at room temperature and evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 15:1 ~ 2:1) to give **8** (2.12 g, 69%) and *syn*-**6** (0.74 g, 24%). Compound **8**: oil;  $[\alpha]_D^{23} +10.0^\circ$  (*c* 1.14, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.43 (s, 9H), 1.45 (s, 3H), 1.49 (s, 3H), 3.59 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.78 (dd, *J* = 12.0, 1.3 Hz, 1H), 4.10 (dd, *J* = 11.9, 1.5 Hz, 1H), 4.46–4.52 (m, 1H), 5.21 (d, *J* = 10.7 Hz, 1H), 5.27 (br s, 1H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.77 (ddd, *J* = 17.1, 10.7, 4.8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  18.5, 28.2, 29.5, 47.2, 64.6, 71.5, 79.2, 98.9, 116.5, 134.5, 155.4; IR (neat) 3350.0, 2982.0, 1700.2, 1498.6 cm<sup>-1</sup>; HRMS calcd for C<sub>13</sub>H<sub>23</sub>NO<sub>4</sub> (M<sup>+</sup>) 257.1670, Found 257.1613. Compound *syn*-**6**: mp 80–80.5 °C;  $[\alpha]_D^{21} +48.9^\circ$  (*c* 1.25, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.49 (s, 3H), 1.49 (s, 9H), 1.58 (s, 3H), 3.88–3.97 (m, 3H), 4.10–4.60 (m, 2H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.33 (d, *J* = 17.0 Hz, 1H), 5.54–5.92 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  24.5, 27.4, 28.6, 31.2, 62.0, 64.7, 76.5, 81.6, 94.4, 118.0, 137.8, 144.0; IR (neat) 3454.6, 1678.1, 1406.1 cm<sup>-1</sup>. Anal. calcd for C<sub>13</sub>H<sub>23</sub>NO<sub>4</sub>: C, 60.68; N, 5.44; H, 9.01. Found: C, 60.78; N, 5.34; H, 8.84.

**(4*R*,5*R*)-5-(*N*-Allyl-*N*-*tert*-butoxycarbonylamino)-2,2-dimethyl-4-vinyl-1,3-dioxan (7).** NaH (60% mineral oil dispersion, 324 mg, 8.1 mmol) was added to a solution of **8** (1.79 g, 6.96 mmol) in THF (40 mL) at 0 °C and the mixture was stirred for 1 h. Allyl iodide (0.74 mL, 8.1 mmol) was added to the mixture at 0 °C and the mixture was stirred overnight at the same temperature. The mixture was quenched with saturated NH<sub>4</sub>Cl and was extracted with EtOAc three times. The extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 15:1) to give **7** (1.57 g, 76%) as an oil:

$[\alpha]_D^{25} +57.1^\circ$  (*c* 1.14,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.41 (s, 9H), 1.42 (s, 3H), 1.44 (s, 3H), 3.86–4.34 (m, 5H), 4.57–4.68 (m, 1H), 5.01–5.39 (m, 4H), 5.72–6.04 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  19.2, 28.4, 29.1, 48.2, 49.7, 63.3, 72.2, 79.6, 98.9, 114.8, 115.8, 134.6, 136.3, 156.2; IR (neat) 2980.2, 1689.9, 1175.3  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{16}\text{H}_{27}\text{NO}_4$  ( $\text{M}^+$ ) 297.2012, Found 297.1909.

**(4aR,8aR)-5-tert-Butoxycarbonyl-2,2-dimethyl-4,4a,6,8a-tetrahydro[1,3]dioxino[5,4-**

**b]pyridine (4).** Grubbs' catalyst (5mol%, 91 mg, 0.11 mmol) was added to a solution of **7** (710 mg, 2.38 mmol) in  $\text{CH}_2\text{Cl}_2$  (105 mL) and the mixture was stirred for 2 h at room temperature. After evaporation, the residue was purified by column chromatography on silica gel (hexane/EtOAc, 15:1) to give **4** (608 mg, 95%) as an oil:  $[\alpha]_D^{24} -26.2^\circ$  (*c* 1.47,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.30 (s, 3H), 1.40 (s, 12H), 3.43 (dd,  $J = 19.1, 2.0$  Hz, 1H), 3.58 (dd,  $J = 10.8, 5.6$  Hz, 1H), 3.78 (t,  $J = 10.7$  Hz, 1H), 4.02 (br d,  $J = 18.4$  Hz, 1H), 4.44–4.49 (m, 2H), 5.87 (d,  $J = 10.7$  Hz, 1H), 5.69 (d,  $J = 10.4$  Hz, 1H), 5.76(m, 2H);  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{CDCl}_3$ )  $\delta$  23.7, 28.5, 29.6, 40.3, 45.2, 57.7, 66.6, 80.5, 98.2, 123.6, 128.4, 154.7; IR (neat) 2978.9, 1698.1, 1368.9, 1170.0  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{14}\text{H}_{23}\text{NO}_4$  ( $\text{M}^+$ ) 269.1479, Found 269.1682.

**(2R,3R)-2-Hydroxymethylpiperidin-3-ol (9).** A suspension of **4** (100 mg, 0.436 mmol) and 10% Pd-C (50%wet 10 mg) in MeOH (2 mL) was stirred at  $\text{H}_2$  atmosphere overnight. The mixture was filtered off and the filtrate was evaporated. 5N HCl (10 mL) was added to a solution of the residue in MeOH (3 mL). The mixture was heated at 60  $^\circ\text{C}$  for 2 h and evaporated. Two drops of 30% NaOH were added to the residue with ice cooling. A mixture of  $\text{CHCl}_3$ : isopropyl alcohol (4:1) (15 mL) was added to the mixture and dried over  $\text{K}_2\text{CO}_3$ . After evaporation, the residue was purified by column chromatography on silica gel ( $\text{CHCl}_3/\text{MeOH}$ ,

10:1 ~ 5:1) to afford **9** (50.3 mg, 88%) as an oil:  $[\alpha]_D^{21} -12.4^\circ$  (*c* 2.51, H<sub>2</sub>O); <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O)  $\delta$  1.42–1.77 (m, 4H), 2.56–2.61 (m, 1H), 2.71–2.78 (m, 1H), 2.94–2.97 (m, 1H), 3.48–3.59 (2H, m), 3.87 (br s, 1H); <sup>13</sup>C NMR (75MHz, D<sub>2</sub>O/ free)  $\delta$  20.6, 31.0, 45.2, 60.0, 62.7, 65.7; <sup>13</sup>C NMR (75MHz, D<sub>2</sub>O/ HCl salt)  $\delta$  17.2, 29.2, 44.9, 60.5, 61.1, 63.3; <sup>13</sup>C NMR (75MHz, D<sub>2</sub>O/ *p*-TsOH salt)  $\delta$  18.5, 21.9, 31.0, 46.0, 61.9, 62.7, 64.1, 127.2, 130.2, 142.2, 143.6; HRMS calcd for C<sub>6</sub>H<sub>13</sub>NO<sub>2</sub> (M<sup>+</sup>) 131.0879, Found 131.0956.

**(1*S*,3*aR*,7*aS*,8*S*)-3-*tert*-Butoxycarbonyl-6,6-dimethyl-1*a*,2,3*a*,4,7*a*,7*b*-hexahydro-1,5,7-trioxa-3-azacyclopropa[*a*]naphthalene (10).** To a solution of **4** (700 mg, 5.3 mmol) in CH<sub>3</sub>CN (19.6 mL) was successively added 4 x 10<sup>-4</sup> M Na<sub>2</sub>EDTA (13 mL) and CF<sub>3</sub>COCH<sub>3</sub> (2.6 mL) at 0 °C. A mixture of NaHCO<sub>3</sub> (1.6 g) and Oxone (7.95 g) was added to the reaction mixture over 1 h at 0 °C and the whole mixture was stirred at the same temperature for 30 min. H<sub>2</sub>O (15 mL) was added to the reaction mixture and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 15:1 ~ 7:1) to yield **10** (733 mg, 99%) as a white solid: mp 100–101 °C;  $[\alpha]_D^{22} -129.5^\circ$  (*c* 1.06, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.40 (s, 6H), 1.43 (s, 9H), 3.27–3.29 (m, 2H), 3.41 (br d, *J* = 14.2 Hz, 1H), 3.80–3.86 (m, 3H), 4.48 (br s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  21.3, 26.9, 28.1, 48.9, 49.6, 61.1, 63.5, 80.1, 98.7, 100.3, 154.9; IR (KBr) 2988.7, 1675.9, 1403.4 cm<sup>-1</sup>. Anal. calcd for C<sub>14</sub>H<sub>23</sub>NO<sub>5</sub>: C, 58.93 ; N, 4.91; H, 8.12. Found: C, 58.84 ; N, 4.93 ; H, 7.90.

**(2*R*,3*R*)-1-*tert*-Butoxycarbonyl-3-hydroxy-2-hydroxymethyl-3,6-dihydro-2*H*-pyridine (12).** *p*-TsOH•H<sub>2</sub>O (53.7 mg) was added to a solution of **4** (1.42 g, 5.29 mmol) in MeOH (54 mL). The mixture was stirred for 2 h at room temperature and evaporated. The residue was purified

by column chromatography on silica gel (hexane/EtOAc, 1:1) to yield **12** (1.17 g, 97%) as a white solid: mp 130.0–130.5 °C;  $[\alpha]_D^{26} +6.7^\circ$  ( $c$  0.92, MeOH);  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  3.47–3.55 (m, 1H), 3.51 (dd,  $J = 10.8, 10.1$  Hz, 1H), 3.79 (br dd,  $J = 11.2, 3.3$  Hz, 1H), 4.08–4.09 (m, 0.5H), 4.15–4.16 (m, 0.5H), 4.38–4.40 (m, 1H), 4.52 (br s, 1H), 5.48 (s, 2H), 5.61–5.68 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  27.5, 56.3, 64.6, 79.6, 123.5, 127.6; IR (neat) 3297.9, 1691.3, 1415.5, 1047.9  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{11}\text{H}_{19}\text{NO}_4$ : C, 57.62; N, 6.11; H, 8.35. Found: C, 57.71; N, 5.93; H, 8.49.

**(1R,3aR,7aS,8R)-3-tert-Butoxycarbonyl-6,6-dimethyl-1a,2,3a,4,7a,7b-hexahydro-1,5,7-**

**trioxa-3-azacyclopropa[a]naphthalene (13).** *m*-CPBA (1.04 g, 4.18 mmol) was added to a suspension of **12** (200 mg, 0.87 mmol) and  $\text{NaH}_2\text{PO}_4$  (720 mg, 6.01 mmol) in  $\text{CH}_2\text{Cl}_2$  (15.8 mL) at 0 °C. After being stirred at room temperature overnight. The insoluble materials were filtered off and the filtrate was evaporated. The residue was dissolved in acetone (6.3 mL), and then 2,2-DMP (2.1 mL) and PPTS (219 mg) were added. The mixture was stirred at room temperature overnight, and evaporated to yield an oil, which was diluted with EtOAc. Organic solvent was successively washed with 5%  $\text{Na}_2\text{CO}_3$ , water, saturated  $\text{NaHCO}_3$ , and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Evaporation yielded an oil, which was purified by column chromatography on silica gel (hexane:EtOAc, 7:1) to yield **13** (130.1 mg, 53%) as a white solid: mp 86.5–87.0 °C;  $[\alpha]_D^{25} -8.37^\circ$  ( $c$  0.43,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.41 (s, 3H), 1.44 (s, 9H), 1.64 (s, 3H), 3.46–3.53 (m, 2H), 3.61–3.76 (m, 3H), 4.07–4.23 (m, 2H), 4.40 (d,  $J = 6.3$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  23.3, 28.5, 30.1, 40.4, 47.2, 53.0, 53.5, 59.8, 68.2, 80.8, 97.7, 154.8; IR (KBr) 2939.4, 1694.1, 1371.5  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{14}\text{H}_{23}\text{NO}_5$ : C, 58.93; N, 4.91; H, 8.12. Found: C, 59.10; N, 5.20; H, 8.22.

**D-1-Deoxygalactonojirimycin (1).** A mixture of **13** (82.6 mg, 0.29 mmol), 1,4-dioxane (7.4 mL), H<sub>2</sub>O (5.0 mL), and H<sub>2</sub>SO<sub>4</sub> (876 mg) was refluxed for 3 h. After evaporation of the reaction mixture, the residue was successively treated with ion-exchange resin (Amberlite IRA-410 OH<sup>-</sup> form) using water as eluent and DOWEX-1w X 2 (OH<sup>-</sup> form) using water as eluent to yield **1** (39 mg, 83%) as an oil:  $[\alpha]_D^{24} +50.2^\circ$  (*c* 1.02, H<sub>2</sub>O) [lit.<sup>1</sup>  $[\alpha]_D^{22} +52.0^\circ$  (*c* 0.4, H<sub>2</sub>O)]; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O)  $\delta$  2.24 (dd, *J* = 12.4, 10.8 Hz, 1H), 2.62 (td, *J* = 6.6, 1.3 Hz, 1H), 2.99 (dd, *J* = 12.6, 5.2 Hz, 1H), 3.34 (dd, *J* = 9.7, 3.1 Hz, 1H), 3.43–3.50 (m, 2H), 3.66 (ddd, *J* = 10.9, 9.9, 5.3 Hz, 1H), 3.87 (dd, *J* = 3.0, 1.1 Hz, 1H); <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O)  $\delta$  49.9, 59.6, 62.2, 69.0, 70.1, 75.9 [lit.<sup>2</sup> <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  49.89, 59.67, 62.25, 69.02, 70.11, 75.91]; HRMS calcd for C<sub>6</sub>H<sub>13</sub>NO<sub>4</sub> (M<sup>+</sup>) 163.0776, Found 163.0858.

**(1S,4S,5S,8S)-6-Oxa-2-azabicyclo[3.2.1]octane-4,8-diol (14).** A mixture of **10** (285.1mg, 1.0mmol), 1,4-dioxane (6.0 mL), H<sub>2</sub>O (4.0 mL), and H<sub>2</sub>SO<sub>4</sub> (706 mg) was refluxed for 3 h. After evaporation of the reaction mixture, the residue was treated with ion-exchange resin (Amberlite IRA-410 OH<sup>-</sup> form) using water as eluent to yield **14** (120.4 mg, 83%) as a solid: mp 192-193 °C; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O)  $\delta$  2.52 (d, *J* = 14.8 Hz, 1H), 2.82 (dd, *J* = 14.8, 2.2 Hz, 1H), 3.38 (s, 1H), 3.89 (br s, 1H), 3.95 (s, 2H), 4.14 (d, *J* = 5.2 Hz, 1H), 4.29 (s, 1H); <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O)  $\delta$  43.3, 58.5, 68.5, 69.6, 72.3, 81.5. Anal. calcd for C<sub>6</sub>H<sub>11</sub>NO<sub>3</sub>: C, 49.65; N, 9.65; H, 7.64. Found: C, 49.93; N, 9.66; H, 7.82.

#### Single-Crystal X-ray Diffraction

A colorless block crystal of C<sub>5</sub>H<sub>9</sub>O<sub>3</sub>N having approximate dimensions of 0.45 x 0.35 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K $\alpha$  radiation. The structure was solved by direct method (SIR 88). Non-hydrogen atoms were refined anisotropically.

Crystal data for  $C_5H_9O_3N$ :  $M=131.13$ , orthorhombic,  $a=9.0765$  (7) Å,  $b=12.182$  (2) Å,  $c=5.8746$  (5) Å,  $V=649.54$  (9) Å<sup>3</sup>,  $T=23 \pm 1$  °C, space group  $P2_12_12_1$  (no.19),  $Z=4$ ,  $m(MoK\alpha)$   $1.11\text{cm}^{-1}$ ,  $D_c=1.341\text{g/cm}^3$ , 6456 reflections measured, 893 unique ( $R_{\text{int}}=0.018$ ). Full-matrix least-squares refinement was based on 1486 observed reflections ( $I>-10.00\sigma(I)$ ) and 102 variable parameters.  $R1=0.039$ ,  $wR2=0.132$ ,  $GOF=0.92$ .

**D-1-Deoxyidonojirimycin (2).** A mixture of **10** (390 mg, 1.36 mmol), 1,4-dioxane (33.4 mL), and 0.3 M KOH (68.4 mL) was refluxed two overnight. After evaporation, EtOAc was added to the residue. The mixture was extracted with EtOAc. The extract was washed with brine, dried over  $Na_2SO_4$ , and evaporated. The residue was purified by column chromatography on silica gel ( $CHCl_3/MeOH$ , 8:1) to give 4,6-*O*-isopropylidene-1,5-imino-D-iditol (254 mg, 92%) as a solid: mp 168-169 °C;  $[\alpha]_D^{22} -10.5^\circ$  ( $c$  0.85, MeOH);  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  1.38 (s, 3H), 1.40 (s, 3H), 2.72 (s, 1H), 2.87 (d,  $J = 4.0$  Hz, 1H), 3.10 (dd,  $J = 14.0, 1.3$  Hz, 1H), 3.40 (d,  $J = 1.4$  Hz, 1H), 3.68–3.78 (m, 5H), 3.90 (s, 1H), 4.01 (dd,  $J = 12.0, 2.2$  Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  18.2, 29.9, 46.2, 46.8, 64.5, 67.2, 68.0, 69.9, 99.3; IR (KBr) 3459.4, 1447.9, 1389.7, 1273.6  $cm^{-1}$ . Anal. calcd for  $C_9H_{17}NO_4$ : C, 53.19; N, 6.89; H, 8.43. Found : C, 53.47; N, 6.92; H, 8.33.

To a solution of the obtained solid (40 mg, 0.13 mmol) in MeOH (1.1 mL) was added 6N HCl (3.3 mL). The mixture was heated at 60 °C for 1 h and evaporated. The residue was successively treated with ion-exchange resins (DOWEX-50wX8  $H^+$  form) using a sequence of water and 1.5N  $NH_3$  as eluents and (Amberlite IRA-410  $OH^-$  form) using water as eluent to yield **2** (30.8 mg, 95%) as a solid: mp 135-135.5 °C [lit.<sup>3</sup> mp 137-139 °C];  $[\alpha]_D^{25} +27.8^\circ$  ( $c$  0.67,  $H_2O$ ) [lit.<sup>3</sup>  $[\alpha]_D^{23} +28^\circ$  ( $c$  0.5,  $H_2O$ )];  $^1H$  NMR (300 MHz,  $D_2O$ )  $\delta$  2.59–2.65 (m, 1H), 2.81–2.87 (m, 1H), 3.02–3.08 (m, 1H), 3.46–3.48 (m, 2H), 3.59–3.66 (m, 3H);  $^{13}C$  NMR (75 MHz,  $D_2O$ )  $\delta$  44.7, 57.1,

58.4, 70.9, 71.4, 73.3 [lit.<sup>4</sup>  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ )  $\delta$  44.5, 56.8, 58.3, 70.1, 70.7, 72.3]; HRMS calcd for  $\text{C}_6\text{H}_{13}\text{NO}_4$  ( $\text{M}^+$ ) 163.0855, Found 163.0843. Anal. calcd for  $\text{C}_6\text{H}_{13}\text{NO}_4$ : C, 44.16; N, 8.58; H, 8.03. Found: C, 44.31; N, 8.55; H, 7.71.

**4,6-*O*-Isopropylidene-*N*-*tert*-butyloxycarbonyl-1,5-imino-D-gulitol (15).** A solution of 50% NMO (167  $\mu\text{L}$ , 3.40 mmol) in water and a solution of  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$  (123 mg, 56.7 mmol) in water (0.5 mL) were successively added to a solution of **4** (190 mg, 0.7 mmol) in acetone (5 mL) at 0  $^\circ\text{C}$  and the mixture was stirred at room temperature overnight.  $\text{Na}_2\text{S}_2\text{O}_3$  (166 mg) was added to the mixture and the mixture was stirred for 30 min. The insoluble materials were filtered off and the filtrate was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 2:3) to yield **15** (181 mg, 85%) as an oil:  $[\alpha]_{\text{D}}^{22} -71.2^\circ$  ( $c$  1.20,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.37 (s, 3H) 1.43 (s, 12H), 3.56 (br d,  $J = 13.4$  Hz, 3H), 3.86–4.01 (m, 6H), 4.25 (br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 28.4, 28.6, 45.3, 46.5, 62.2, 65.5, 67.2, 68.3, 80.6, 98.8, 158.7; IR (neat) 3431.4, 2983.2, 1694.0, 1455.3  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{14}\text{H}_{25}\text{NO}_6$  ( $\text{M}^+$ ) 303.1738, Found 303.1658.

**D-1-Deoxygulonojirimycin (3).** To a solution of **15** (160 mg, 0.52 mmol) in MeOH (4.4 mL) was added 6N HCl (13.3 mL). The mixture was heated at 60  $^\circ\text{C}$  for 1 h and evaporated. The residue was treated with ion-exchange resin (DOWEX-50wX8  $\text{H}^+$  form) using a sequence of water and 1.5N  $\text{NH}_3$  as eluents to yield **3** (77.7 mg, 90%) as a pale yellow oil:  $[\alpha]_{\text{D}}^{24} -15.0$  ( $c$  1.55, EtOH) [lit.<sup>5</sup>  $[\alpha]_{\text{D}}^{24} -13.9^\circ$  ( $c$  0.3, EtOH)];  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ )  $\delta$  2.59 (dd,  $J = 12.3, 10.6$  Hz, 1H), 2.73–2.77 (m, 1H), 2.83 (td,  $J = 6.4, 2.1$  Hz, 1H), 3.47–3.54 (m, 2H), 3.79–3.84 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ /free)  $\delta$  45.0, 54.6, 61.9, 66.5, 70.1, 71.1 [lit.<sup>6</sup>  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ /free)  $\delta$  46.95, 56.9, 63.8, 68.3, 72.0, 73.0];  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ /HCl salt)  $\delta$  42.8, 55.9,



59.4, 63.0, 67.6, 68.9 [lit. <sup>7</sup> <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O/HCl salt) δ 42.64, 55.65, 59.01, 62.81, 67.38, 68.69]; HRMS calcd for C<sub>6</sub>H<sub>13</sub>NO<sub>4</sub> (M<sup>+</sup>) 163.0822, Found 163.0961.

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