JOC*Note*

Regioselective Reductive Cleavage of Bis-benzylidene Acetal: Stereoselective Synthesis of Anticancer Agent OGT2378 and Glycosidase Inhibitor 1,4-Dideoxy-1,4-imino-L-xylitol

Appu Aravind, Muthukumar Gomathi Sankar, Babu Varghese, and Sundarababu Baskaran*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

sbhaskar@iitm.ac.in

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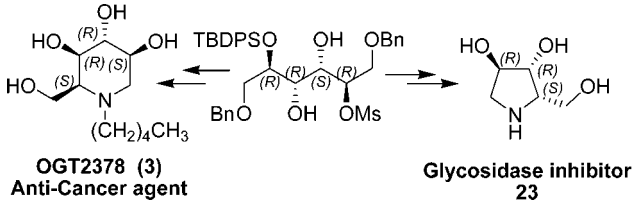

A highly regioselective reductive cleavage of the bis-benzylidene acetal of D-mannitol was performed using a $BF_3 \cdot Et_2O/Et_3SiH$ reagent system. A chiral intermediate **6** thus obtained was efficiently utilized in the stereoselective synthesis of the anticancer agent OGT2378 (**3**) and glycosidase inhibitor derivative *N*-tosyl 1,4-dideoxy-1,4-imino-L-xylitol (**22**). Chemoselective reduction of azido epoxide **10** followed by regioselective intramolecular cyclization of amino epoxide **11** resulted in the exclusive formation of deoxyidonojirimycin derivative **12**. By changing the order of deprotection, the chiral intermediate **6** was readily transformed to glycosidase inhibitor derivative **22**.

Generating a high level of skeletally and stereochemically diverse intermediates from a common substrate is an especially challenging and innovative task for synthetic organic chemists. Meeting this formidable task is the goal of diversity-oriented synthesis.[1] Many strategies have been developed for the diversity-oriented synthesis of biologically active and pharmaceutically important molecules.[2] The polyhydroxylated piperidines and pyrrolidines have been studied in the most detail,

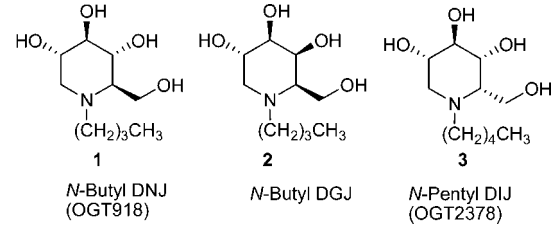

FIGURE 1. Structures of NB-DNJ (**1**), NB-DGJ (**2**), and NP-DIJ (**3**).

owing to their ability to mimic their analogous pyranoses and furanoses in interactions with carbohydrate-processing enzymes. Thus, because of their biomimetic properties, iminosugars are becoming important lead compounds for drug development in a variety of therapeutic areas, including diabetes, viral infections, and tumor metastasis.[3,4]

Butters and co-workers have shown that the hydrophobic substituent on iminosugars increases the enzyme inhibitory activities.[5] *N*-Alkylated analogues of glucose and galactose isomers have additional inhibitory activities toward ceramide glucosyltransferase, an enzyme involved in the biosynthesis of glycospingolipids (Figure 1).[6,7]

Recently, Ladisch et al. identified a new iminosugar, *N*-pentyl deoxyidonojirimycin (NP-DIJ) (**3**), also known as OGT2378, as a novel and potent anticancer agent that inhibits the synthesis of gangliosides in cancer cells with no cytotoxic or antiproliferative effects.[8]

Very recently, we reported a highly regioselective method for the reductive cleavage of bis-benzylidene acetals of D-mannitol using a $BF_3 \cdot Et_2O/Et_3SiH$ reagent system under mild conditions, which resulted in the formation of highly functionalized chiral intermediates in good yields (Scheme 1).[9]

(1) For reviews and seminal papers on diversity-oriented synthesis, see: (a) Schreiber, S. L. *Science* **2000**, *287*, 1964. (b) Burke, M. D.; Berger, E. M.; Schreiber, S. L. *Science* **2003**, *302*, 613. (c) Spring, D. R. *Org. Biomol. Chem.* **2003**, *1*, 3867. (d) Burke, M. D.; Schreiber, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 46. (e) Arya, P.; Joseph, R.; Gan, Z.; Rakic, B. *Chem. Biol.* **2005**, *12*, 163. (f) Wang, W.−W.; Ibrahem, I.; Córdova, A. *Chem. Commun.* **2006**, 674.

(2) Please see ref 1. For diversity-oriented synthesis of iminosugars see: (a) Lee, B. W.; Jeong, I.-Y.; Yang, M. S.; Choi, S. U.; Park, K. H. *Synthesis* **2000**, 1305. (b) Pandey, G.; Kapur, M. *Org. Lett.* **2002**, *4*, 3883. (c) Takahata, H.; Banba, Y.; Ouchi, H.; Nemoto, H. *Org. Lett.* **2003**, *5*, 2527. (d) Dhavale, D. D.; Kumar, K. S. A.; Chaudhari, V. D.; Sharma, T.; Sabharwal, S. G.; Reddy, J. P. *Org. Biomol. Chem.* **2005**, *3*, 3720. (e) Boucheron, C.; Compain, P.; Martin, O. R. *Tetrahedron Lett.* **2006**, *47*, 3081.

(3) (a) *Iminosugars as Glycosidase Inhibitors: Nojirimycin and Beyond*; Stutz, A. E., Ed.; Wiley-VCH: Weinheim, Germany, 1999. (b) Elbein, A. D. *FASEB J.* **1991**, *5*, 3055. (c) Look, G. C.; Fotsch, C. H.; Wong, C.-H. *Acc. Chem. Res.* **1993**, *26*, 182. (d) Bols, M. *Acc. Chem. Res.* **1998**, *31*, 1. (e) Afarinkia, K.; Bahar, A. *Tetrahedron: Asymmetry* **2005**, *16*, 1239. (f) Pearson, M. S. M.; Mathé-Allainmat, M.; Fargeas, V.; Lebreton, J. *Eur. J. Org. Chem.* **2005**, 2159, and references cited therein.

(4) (a) Gruters, R. A.; Neefjes, J. J.; Tersmette, M.; de Goede, R. E. Y.; Tulp, A.; Huisman, H. G.; Miedema, F.; Ploegh, H. L. *Nature* **1987**, *330*, 74. (b) Bollen, M.; Stalmans, W. *Eur. J. Biochem.* **1989**, *181*, 775. (c) Tsuruoka, T.; Fukuyasu, H.; Ishii, M.; Usui, T.; Shibahara, S.; Inouye, S. *J. Antibiot.* **1996**, *49*, 155. (d) Johnston, P. S.; Lebovitz, H. E.; Coniff, R. F.; Simonson, D. C.; Raskin, P.; Munera, C. L. *J. Clin. Endocrinol. Metab.* **1998**, *83*, 1515. (e) Nishimura, Y. *Curr. Top. Med. Chem.* **2003**, *3*, 575.

(5) (a) Butters, T. D.; van den Broek, L. A. G. M.; Fleet, G. W. J.; Krulle, T. M.; Wormald, M. R.; Dwek, R. A.; Platt, F. M. *Tetrahedron: Asymmetry* **2000**, *11*, 113. (b) Butters, T. D.; Dwek, R. A.; Platt, F. M. *Chem. Rev.* **2000**, *100*, 4683. (c) Boucheron, C.; Desvergnes, V.; Compain, P.; Martin, O. R.; Lavi, A.; Mackeen, M.; Wormald, M.; Dwek, R.; Butters, T. D. *Tetrahedron: Assymmetry* **2005**, *16*, 1747.

(6) For biological activity, see: (a) ref 5. (b) Fan, J. Q.; Ishii, S.; Asano, N.; Suzuki, Y. *Nat. Med.* **1999**, *5*, 112. (c) Watts, R. W. E. *Philos. Trans. R. Soc. London, Ser. B* **2003**, *358*, 975. (d) Segraves, N. L.; Crews, P. *J. Nat. Prod.* **2005**, *68*, 118.

(7) For synthesis see: (a) Weber, K. T.; Hammache, D.; Fantini, J.; Ganem, B. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1011. (b) Szczepina, M. G.; Johnston, B. D.; Yuan, Y.; Svensson, B.; Pinto, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 12458.

(8) (a) Weiss, M.; Hettmer, S.; Smith, P.; Ladisch, S. *Cancer Res.* **2003**, *63*, 3654. (b) For highlights, see: Borman, S. *Chem. Eng. News* **2005**, (Sept 26), 39.

(9) (a) Aravind, A.; Baskaran, S. *Tetrahedron Lett.* **2005**, *46*, 743. (b) Aravind, A.; Mohanty, S. K.; Pratap, T. V.; Baskaran, S. *Tetrahedron Lett.* **2005**, *46*, 2965.

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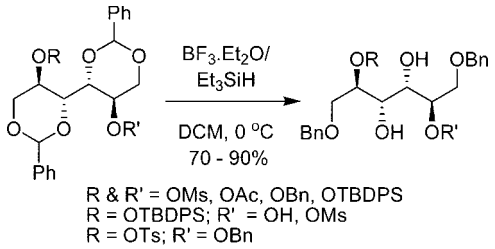
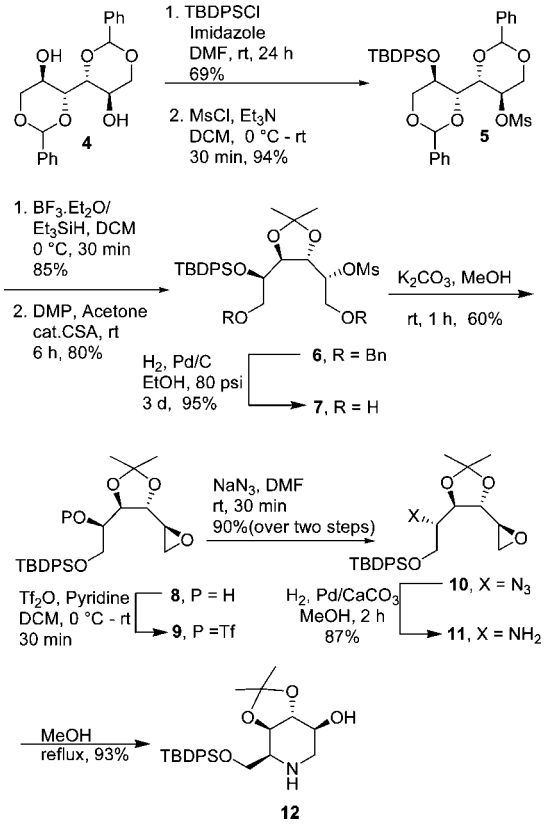
SCHEME 1. Regioselective Reductive Cleavage of Bis-benzylidene Acetals of D-Mannitol



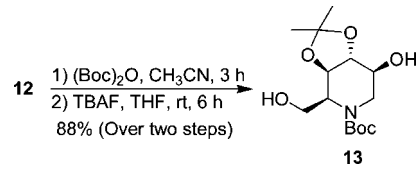
SCHEME 2. Synthesis of Deoxyidonojirimycin Derivative 12



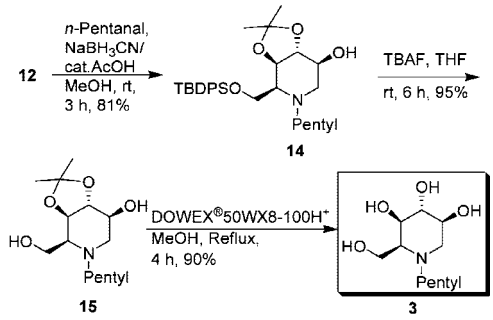
Herein we report our diversity-oriented approach for the synthesis of the anticancer agent *N*-pentyl-deoxyidonojirimycin (OGT2378) (**3**) and glycosidase inhibitor derivative *N*-tosyl 1,4-dideoxy-1,4-imino-L-xylitol (**22**) from a common chiral intermediate derived through the regioselective reductive cleavage of the bis-benzylidene acetal of D-mannitol.

Our approach toward the stereo- and regioselective synthesis of anticancer agent *N*-pentyl-deoxyidonojirimycin (OGT2378) starting from the chiral intermediate **6** is shown in Schemes 2−4.[10] Selective monoprotection of one of the hydroxy functional groups of bis-benzylidene acetal **4** was achieved using TBDPSCl in DMF, and the other hydroxy group was converted to the corresponding mesylate **5** in good yield. Regioselective reductive cleavage of bis-benzylidene acetal **5** with the $BF_3 \cdot Et_2O$ and Et_3SiH reagent system resulted in the formation in 85% yield of a diol, which was further converted to the corresponding acetonide **6** using 2,2-DMP. Debenzylation of **6** under catalytic hydrogenation conditions furnished diol **7** in very good yield. Exposure of diol derivative **7** to K_2CO_3 in MeOH resulted in a smooth S_N2 displacement of mesylate leading to an epoxide with concomitant migration of the TBDPS group from the secondary to the primary hydroxyl group.[11] Interestingly, this migration paved the way for the synthesis of deoxyidonojirimycin with the desired stereochemistry (vide infra). Chemoselective conversion of epoxy alcohol **8** to epoxy azide **10** was achieved under very mild conditions, by converting the hydroxyl group to the corresponding triflate **9** and then treating it with sodium azide at room temperature. Chemoselective reduction of azide **10** in the presence of epoxide was readily achieved under catalytic hydrogenation conditions using Lindlar's catalyst[12] to yield amino epoxide **11**, which on refluxing in methanol underwent facile regioselective cyclization via 6-*endo-tet* mode[13] to furnish deoxyidonojirimycin derivative **12** as the only product in 93% yield.

SCHEME 3. Synthesis of *N*-Boc Deoxyidonojirimycin Derivative 13



SCHEME 4. Synthesis of Anticancer Agent OGT2378 (3)



The structure and the relative stereochemistry of the cyclized product **12** was established by 2D NMR experiments and further unambiguously confirmed by single crystal X-ray analysis on the corresponding *N*-Boc deoxyidonojirimycin derivative **13** (Scheme 3 and Figure 2).

Reductive alkylation of deoxyidonojirimycin derivative **12**, with pentanal in combination with $NaBH_3CN$, yielded *N*-pentyl derivative **14**, which was desilylated using TBAF to give diol **15**. Finally, the deprotection of the acetonide in **15** was readily achieved using DOWEX50WX8-100H$^+$, which resulted in the isolation of anticancer agent OGT2378 (**3**) in 90% yield (Scheme 4).

1,4-Dideoxy-1,4-iminopentitols have been attracting the attention of synthetic chemists as a result of their potential

(10) The first and only synthesis of OGT2378 was reported in the patent literature: Butters, T. D.; Dwek, R. A.; Fleet, G.; Orchard, M. G.; Platt, F. M. *PCT Int. Appl. WO 2002055498*, 2002.

(11) Mulzer, J.; Schollhorn, B. *Angew. Chem., Int. Ed.* **1990**, *29*, 431.

(12) (a) Reddy, P. G.; Pratap, T. V.; Kumar, G. D. K.; Mohanty, S. K.; Baskaran, S. *Eur. J. Org. Chem.* **2002**, 3740. (b) Corey, E. J.; Nicolaou, K. C.; Balanson, R. D.; Machida, Y. *Synthesis* **1975**, 590.

(13) (a) Kilonda, A.; Compernolle, F.; Peeters, K.; Joly, G. J.; Toppet, S.; Hoornaert, G. J. *Tetrahedron* **2000**, *56*, 1005. (b) Somfai, P.; Marchand, P.; Torsell, S.; Lindström, U. M. *Tetrahedron* **2003**, *59*, 1293. *cis*-Acetonide as well as the corresponding *cis*- and *trans*-dibenzyl ether derivatives are known to give a mixture of regioisomers. (c) Merrer, Y. L.; Poitout, L.; Depezay, J.-C.; Dosbaa, I.; Geoffroy, S.; Foglietti, M.-J. *Bioorg. Med. Chem.* **1997**, *5*, 519. (d) Pino-González, M. S.; Assiego, C.; López-Herrera, F. J. *Tetrahedron Lett.* **2003**, *44*, 8353.

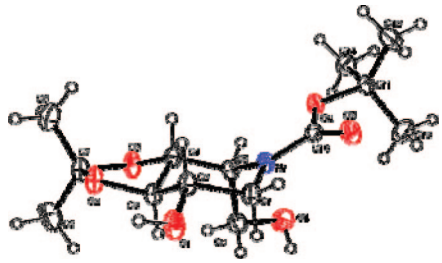
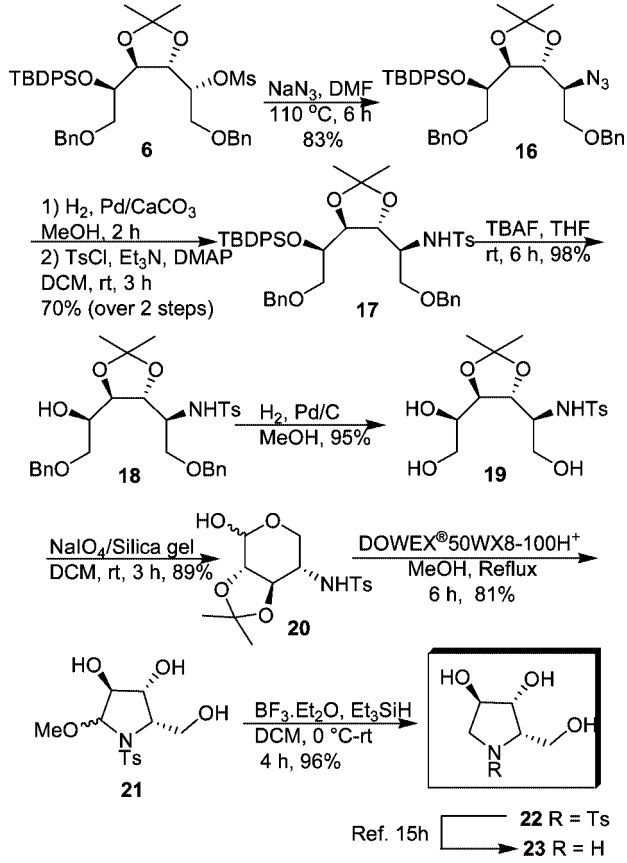


FIGURE 2. ORTEP diagram of *N*-Boc deoxyidonojirimycin derivative **13**.

SCHEME 5. Stereoselective Synthesis of 1,4-Dideoxy-1, 4-imino-L-xylitol (23)



biological activities.[14] The versatility of our chiral intermediate **6** in the diversity-oriented synthesis of iminosugars is further exemplified in the stereoselective synthesis of the glycosidase inhibitor 1,4-dideoxy-1,4-imino-L-xylitol (**23**)[15] by changing the order of deprotection as well as functional group interconversions (FGI) (Scheme 5). Thus, acetonide **6** on treatment with NaN_3 yielded azido derivative **16**, which on catalytic hydrogenation with Lindlar's catalyst and subsequent tosylation furnished *N*-tosyl derivative **17** in good yield. Deprotection of silyl ether with TBAF gave the corresponding hydroxy derivative **18**, which was debenzylated under catalytic hydrogenation conditions to yield the corresponding triol **19** in 95% yield. Oxidative cleavage of the vicinal diol under heterogeneous conditions using $NaIO_4$ supported on silica gel yielded lactol **20**, which upon refluxing in methanol with DOWEX50WX8-100H$^+$ furnished 2-methoxy-iminopentitol **21** in good yield. 2-Methoxy-iminopentitol derivative **21** upon treatment with $BF_3 \cdot Et_2O/Et_3SiH$ yielded *N*-tosyl 1,4-dideoxy-1,4-imino-L-xylitol (**22**) in good yield.

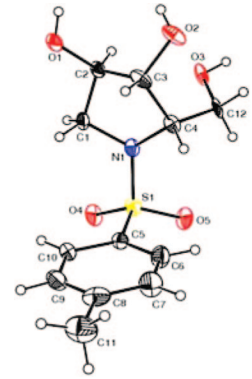


FIGURE 3. ORTEP diagram of *N*-tosyl derivative **22**.

The structure and relative stereochemistry of compound **22** was further confirmed by single crystal X-ray analysis (Figure 3). The conversion of *N*-tosyl 1,4-dideoxy-1,4-imino-L-xylitol (**22**) to 1,4-dideoxy-1,4-imino-L-xylitol (**23**) in the presence of $NaNH_2$ in liquid ammonia has already been reported in the literature.[15h]

In conclusion, the highly functionalized chiral intermediate **6** obtained through regioselective reductive cleavage of the bis-benzylidene acetal of D-mannitol was efficiently utilized in the stereoselective synthesis of the anticancer agent OGT2378 (**3**) and glycosidase inhibitor derivative *N*-tosyl 1,4-dideoxy-1,4-imino-L-xylitol (**22**) with overall yields of 12.6% and 16.5%, respectively. Salient features of our synthesis are (i) facile migration of the TBDPS group from the secondary to primary hydroxyl group, which paved the way for the stereoselective synthesis of deoxyidonojirimycin scaffold; (ii) chemoselective reduction of azido epoxide **10** to amino epoxide **11** in the presence of Lindlar's catalyst; and (iii) highly regioselective intramolecular cyclization of amino epoxide **11** to deoxyidonojirimycin scaffold (**12**), which was unambiguously established by single crystal X-ray analysis. In addition, by changing the order of deprotection and FGI, stereoselective synthesis of glycosidase inhibitor derivative **22** was readily achieved from the chiral intermediate **6**. The success of our diversity-oriented approach in the stereoselective synthesis of iminosugars underscores the power of the chiral intermediates derived through the regioselective reductive cleavage of bis-benzylidene acetal of D-mannitol.

Experimental Section

(*R*)-2-(*tert*-Butyldiphenylsilyloxy)-1-((4*R*,5*R*)-2,2-dimethyl-5-((*S*)-oxiran-2-yl)-1,3-dioxolan-4-yl)ethanol (8). To a stirred solution of compound **7** (400 mg, 0.74 mmol) in dry MeOH (10 mL) was added K_2CO_3 (112 mg, 0.81 mmol), and the resultant mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure to remove MeOH. The residue

(14) (a) Asano, N.; Oseki, K.; Kizu, H.; Matsui, K. *J. Med. Chem.* **1994**, *37*, 3701. (b) Asano, N.; Kizu, H.; Oseki, K.; Tomioka, E.; Matsui, K.; Okamoto, M.; Baba, M. *J. Med. Chem.* **1995**, *38*, 2349.

(15) (a) Hosaka, A.; Ichikawa, S.; Shindo, H.; Sato, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 797. (b) Buchanan, J. G.; Lumbard, K. W.; Sturgeon, R. J.; Thompson, D. K.; Wightman, R. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 699. (c) Meng, Q.; Hesse, M. *Helv. Chim. Acta* **1991**, *74*, 445. (d) van der Klein, P. A. M.; Filemon, W.; Broxterman, H. J. G.; vander Marel, G. A.; van Boom, J. H. *Synth. Commun.* **1992**, *22*, 1763. (e) Huang, Y.; Dalton, D. R.; Carroll, P. J. *J. Org. Chem.* **1997**, *62*, 372. (f) Kim, J. H.; Yang, M. S.; Lee, W. S.; Park, K. H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2877. (g) Wang, C.-C.; Luo, S.-Y.; Shie, C.-R.; Hung, S.-C. *Org. Lett.* **2002**, *4*, 847. (h) Lei, A.; Liu, G.; Lu, X. *J. Org. Chem.* **2002**, *67*, 974.

was diluted with water (10 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude compound was purified by column chromatography over deactivated silica gel (gradient elution with 20−30% EtOAc in hexane) to yield the pure title compound **8** (197 mg, 60%) as a viscous liquid. $[\alpha]^{30}_D$ −3.9 (*c* 1.0, $CHCl_3$); IR (neat) 3520, 3072, 2944, 2832, 1462, 1427, 1376, 1260, 1216, 1174, 1110, 1062, 739, 704, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.32 (s, 3H), 1.37 (s, 3H), 2.77−2.82 (m, 2H), 2.99−3.14 (m, 1H), 3.65 (m, 1H), 3.79 (dd, J = 10.2, 5.6 Hz, 1H), 3.84−3.91 (m, 2H), 3.96−3.99 (m, 1H), 7.37−7.45 (m, 6H), 7.65−7.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.5, 26.8, 27.0, 44.8, 52.2, 65.1, 73.1, 77.1, 80.0, 109.9, 127.8, 127.8, 129.9, 129.9, 132.8, 132.9, 135.5, 135.5; HRMS(ESI) calcd for $C_{25}H_{34}O_5SiNa$ $(M + Na)^+$ 465.2073, found 465.2085.

(3a*R*,4*S*,7*S*,7a*R*)-4-((*tert*-Butyldiphenylsilyloxy)methyl)-2,2-dimethylhexahydro-[1,3]dioxolo[4,5-*c*]pyridin-7-ol (12). A solution of compound **11** (140 mg, 0.32 mmol) in MeOH was refluxed for 4 h. The reaction mixture was then concentrated in vacuum, and the residue was purified by column chromatography over silica gel (gradient elution with 40−50% EtOAc in hexane) to yield deoxyidonojirimycin derivative **12** (130 mg, 93%) as a viscous liquid. $[\alpha]^{26}_D$ −28.5 (*c* 1, $CHCl_3$); IR (neat) 3472, 2928 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.29 (s, 3H), 1.39 (s, 3H), 2.40 (dd, J = 12.0, 9.9 Hz, 1H), 2.94 (dd, J = 12.1, 5.1 Hz, 1H), 3.37 (t, J = 9.4 Hz, 1H), 3.52−3.55 (m, 1H), 3.60 (dd, J = 9.5, 5.4 Hz, 1H), 3.76−3.83 (m, 3H), 7.36−7.43 (m, 6H), 7.65−7.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.5, 26.7, 26.8, 45.7, 56.0, 58.9, 70.7, 76.0, 79.5, 109.9, 127.7, 127.8, 129.7, 129.8, 133.2, 133.3, 135.5, 135.5; HRMS (ESI) calcd for $C_{25}H_{36}NO_4Si$ $(M + H)^+$ 442.2414, found 442.2419.

2-(Hydroxymethyl)-1-pentylpiperidine-3,4,5-triol (3). To a stirred solution of compound **15** (51 mg, 0.09 mmol) in dry MeOH (3 mL) was added DOWEX50WX8-100H^+ (51 mg), and the resultant mixture was refluxed for 2 h. The reaction mixture was treated with aqueous ammonia and filtered, and the filtrate was concentrated under reduced pressure to yield pure OGT2378 (**3**) (39 mg, 90%) as a viscous liquid. $[\alpha]^{27}_D$ +2.1 (*c* 1, CH_3OH); IR (neat) 3376, 2348, 2327, 1677, 1413, 1356, 1077 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 0.86 (t, J = 6.4 Hz, 3H), 1.25−1.33 (m, 4H), 1.48−1.55 (m, 2H), 2.59−2.78 (m, 3H), 2.92 (dd, J = 12.4, 4.8 Hz, 1H), 3.18−3.20 (m, 1H), 3.47 (t, J = 8.8 Hz, 1H), 3.63 (dt, J = 9.6, 4.4 Hz, 1H), 3.77 (dd, J = 9.4, 5.6 Hz, 1H), 3.82−3.88 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 15.9, 24.5, 28.3, 31.5, 53.8, 56.5, 58.1. 65.0, 71.7, 73.1, 76.4; HRMS (ESI) calcd for $C_{11}H_{24}NO_4$ $(M + H)^+$ 234.1705, found 234.1713.

(2*S*,3*R*,4*R*)-2-(Hydroxymethyl)-1-tosylpyrrolidine-3,4-diol (22). To a stirred solution of compound **21** (70 mg, 0.22 mmol) in dry CH_2Cl_2 (5 mL) was added Et_3SiH (52 mg, 0.44 mmol) followed by $BF_3 \cdot Et_2O$ (157 mg, 1.1 mmol). The reaction mixture was stirred for 4 h at room temperature. The reaction mass was then diluted with CH_2Cl_2 (10 mL) and water (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude compound. Column chromatographic purification of the crude compound over silica gel using gradient elution with 0−10% MeOH in EtOAc yielded the pure title compound **22** (63 mg, 96%) as a colorless solid. $[\alpha]^{26}_D$ +19.3 (*c* 1.3, EtOH); IR (neat) 3339, 2926, 1328 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3) δ 2.44 (s, 3H), 3.21 (dd, J = 11.2, 3.2 Hz, 1H), 3.60 (dd, J = 10.8, 6.4 Hz, 1H), 3.65 (dd, J = 11.0, 4.8 Hz, 1H), 3.89−3.96 (m, 2H), 4.00 (dd, J = 11.0, 4.0 Hz, 1H), 4.09−4.10 (m, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 21.3, 55.0, 61.8, 63.4, 74.4, 77.6, 128.6, 130.2, 144.1; HRMS (ESI) calcd for $C_{12}H_{17}NO_5SNa$ $(M + Na)^+$ 310.0725, found 310.0731.

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Supporting Information Available: General experimental procedures, experimental data, and ^1H and ^{13}C NMR spectra for all new compounds and X-ray crystallographic data of **13** and **22** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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