

## Supporting Information

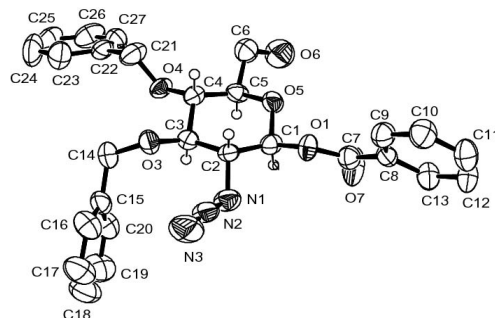
### **Metal Trifluoromethanesulfonate-catalyzed Regioselective Borane-reductive Ring Opening of Benzyldiene Acetals: A Concise Synthesis of 1,4-Dideoxy-1,4-imino-L-xylitol**

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**§ The X-ray single-crystal analysis of compound 20.** Colorless crystals from chloroform/hexane, C<sub>27</sub>H<sub>27</sub>N<sub>3</sub>O<sub>6</sub>, fw = 489.20, crystal dimensions: 0.44 x 0.31 x 0.38 mm<sup>3</sup>, crystal system: orthorhombic, space group: P212121, unit-cell dimensions: *a* = 8.8646(15), *b* = 11.5634(12), *c* = 18.468(4) Å, *V* = 1893.1(5) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.335 gcm<sup>-3</sup>, wavelength = 0.7107 Å, *F*(000) = 796, μ = 0.10 mm<sup>-1</sup>, 2θ(max) = 50.0. The ORTEP drawing is illustrated in Figure 1. The deposition number at the Cambridge Crystallographic Data Centre is CCDC 162432.



**Figure 1.** The ORTEP drawing of compound **20**.

## § Experimental Section

**General Procedures.** Dichloromethane, tetrahydrofuran, acetonitrile, and toluene were purified and dried through activated alumina under argon atmosphere.<sup>1</sup> Anhydrous *N,N*-dimethylformamide and pyridine were purchased from Aldrich company. Flash column chromatography<sup>2</sup> was carried out as recommended with Silica Gel 60 (230-400 mesh, E. Merck). TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , as well as  $\text{H}_2\text{SO}_4$  in water and subsequent heating on a hot plate. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-370 polarimeter at ~25 °C.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with Bruker AC300 and AMX400 MHz instruments. Chemical shifts are in ppm from  $\text{Me}_4\text{Si}$ , generated from the  $\text{CDCl}_3$  lock signal at  $\delta$  7.26. Mass spectra were obtained with a VG 70-250S mass spectrometer in the EI and FAB modes. IR spectra were taken with a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were measured with a Perkin-Elmer 2400CHN instrument.

**General procedure for the metal trifluoromethanesulfonate-catalyzed regioselective borane-reductive ring opening of benzylidene acetals.** To a solution of the 4,6-*O*-benzylidene-D-hexopyranoside (1 mmol) in dichloromethane (9 mL) was slowly added a 1 M solution of borane-tetrahydrofuran complex in tetrahydrofuran (5 mmol) at room

temperature under nitrogen atmosphere. After stirring for 10 min, freshly dried metal trifluoromethanesulfonate (0.15 mmol) was added to the solution, and the mixture was kept stirring for a period of time (Table 1 and 2). The reaction was quenched via sequential additions of triethylamine (1 mmol) and methanol (18 mL per mmol), and the resulting mixture was concentrated at reduced pressure followed by co-evaporation with methanol. The residue was purified by flash column chromatography on silica gel to afford the expected product. The yields are summarized in Table 1 and 2.

**Compounds 2, 6, 10, 14, 18, and 20.** Comparison of our data of compounds **2**,<sup>3</sup> **6**,<sup>4</sup> **10**,<sup>5</sup> **14**,<sup>4</sup> **18**,<sup>6</sup> and **20**<sup>7</sup> with the literature report revealed identity with respect to <sup>1</sup>H or <sup>13</sup>C spectra.

**Compound 4.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 7.2 Hz, 2H, BzH), 7.57 (t, *J* = 7.2 Hz, 1H, BzH), 7.44 (t, *J* = 7.2 Hz, 2H, BzH), 7.36-7.33 (m, 4H, PhH), 7.31-7.28 (m, 1H, PhH), 5.00 (d, *J* = 3.6 Hz, 1H, H-1), 4.89 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 4.86 (d, *J* = 11.4 Hz, 1H, PhCH<sub>2</sub>), 4.76 (d, *J* = 11.4 Hz, 1H, PhCH<sub>2</sub>), 4.27 (dt, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.86 (ddd, *J* = 11.5, 10.0, 7.7 Hz, 1H, H-6a), 3.79 (ddd, *J* = 11.5, 7.7, 3.3 Hz, 1H, H-6b), 3.72 (dt, *J* = 10.0, 3.3 Hz, 1H, H-5), 3.59 (t, *J* = 10.0, 3.6 Hz, 1H, H-4), 3.34 (s, 3H, OCH<sub>3</sub>), 2.26 (d, *J* = 3.3 Hz, 1H, 3-OH), 1.80 (t, *J* = 7.7 Hz, 1H, 6-OH) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.39 (C), 138.11 (C), 133.35 (CH), 129.89 (CH), 129.53 (C), 128.60 (CH), 128.43 (CH), 128.09 (CH), 128.04 (CH), 97.08 (CH), 77.75 (CH), 74.68 (CH<sub>2</sub>), 74.13 (CH), 72.03 (CH), 70.46 (CH), 61.82 (CH<sub>2</sub>), 55.29 (CH<sub>3</sub>) ppm; HRMS (FAB, MH<sup>+</sup>) calcd for C<sub>24</sub>H<sub>25</sub>O<sub>7</sub> 389.1601,

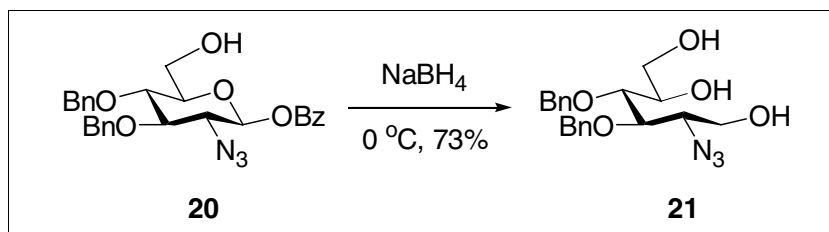
found 389.1597.

**Compound 8.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.26 (m, 15H, PhH), 4.92 (d,  $J$  = 11.2 Hz, 1H, PhCH<sub>2</sub>), 4.90 (d,  $J$  = 11.0 Hz, 1H, PhCH<sub>2</sub>), 4.85 (d,  $J$  = 11.0 Hz, 1H, PhCH<sub>2</sub>), 4.80 (d,  $J$  = 11.2 Hz, 1H, PhCH<sub>2</sub>), 4.70 (d,  $J$  = 11.0 Hz, 1H, PhCH<sub>2</sub>), 4.63 (d,  $J$  = 11.0 Hz, 1H, PhCH<sub>2</sub>), 4.35 (d,  $J$  = 7.8 Hz, 1H, H-1), 3.87 (ddd,  $J$  = 12.0, 6.4, 2.4 Hz, 1H, H-6a), 3.71 (ddd,  $J$  = 12.0, 6.4, 4.4 Hz, 1H, H-6b), 3.66 (t,  $J$  = 9.0 Hz, 1H, H-3), 3.56 (t,  $J$  = 9.0 Hz, 1H, H-4), 3.56 (s, 1H, OCH<sub>3</sub>), 3.39 (dd,  $J$  = 9.0, 7.8 Hz, 1H, H-2), 3.35 (ddd,  $J$  = 9.0, 4.4, 2.4 Hz, 1H, H-5), 1.90 (t,  $J$  = 6.4 Hz, 1H, 6-OH) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.52 (C), 138.42 (C), 137.97 (C), 128.49 (CH), 128.37 (CH), 128.06 (CH), 127.92 (CH), 127.86 (CH), 127.67 (CH), 127.63 (CH), 104.81 (CH), 84.44 (CH), 82.37 (CH), 77.55 (CH), 75.68 (CH<sub>2</sub>), 75.08 (CH<sub>2</sub>), 74.99 (CH), 74.82 (CH<sub>2</sub>), 62.05 (CH<sub>2</sub>), 57.29 (CH<sub>3</sub>) ppm; HRMS (FAB,  $\text{M}^+\text{-H}$ ) calcd for  $\text{C}_{28}\text{H}_{31}\text{O}_6$  463.2120, found 463.2116.

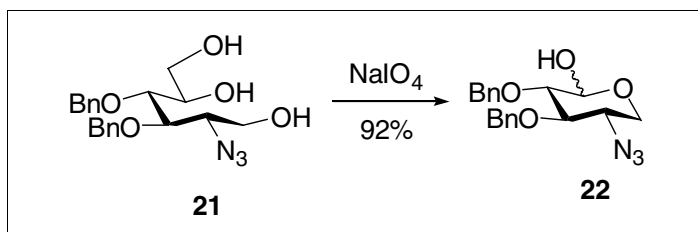
**Compound 12.**  $[\alpha]_{\text{D}}^{22}$  -7.2 (c 0.6,  $\text{CHCl}_3$ ); mp 116-117 °C; IR ( $\text{CHCl}_3$ )  $\nu$  3320, 2896, 1609, 1515, 1250, 1075, 1037, 736, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.26 (m, 10H, PhH), 7.18 (d,  $J$  = 8.6 Hz, 2H, 4-OMePhH), 6.83 (d,  $J$  = 8.6 Hz, 2H, 4-OMePhH), 4.91 (d,  $J$  = 11.0 Hz, 1H, PhCH<sub>2</sub>), 4.89 (d,  $J$  = 10.4 Hz, 1H, PhCH<sub>2</sub>), 4.86 (d,  $J$  = 11.0 Hz, 1H, PhCH<sub>2</sub>), 4.76 (d,  $J$  = 10.6 Hz, 1H, PhCH<sub>2</sub>), 4.72 (d,  $J$  = 10.4 Hz, 1H, PhCH<sub>2</sub>), 4.56 (d,  $J$  = 10.6 Hz, 1H, PhCH<sub>2</sub>), 4.47 (d,  $J$  = 9.6 Hz, 1H, H-1), 4.83 (ddd,  $J$  = 12.0, 6.0, 2.7 Hz, 1H, H-6a), 3.77 (s, 3H, ArOCH<sub>3</sub>), 3.67 (t,  $J$  = 9.6 Hz, 1H, H-3), 3.67-3.62 (m, 1H, H-6b), 3.53 (t,

$J = 9.6$  Hz, 1H, H-4), 3.38 (t,  $J = 9.6$  Hz, 1H, H-2), 3.33 (ddd,  $J = 9.6, 4.7, 2.7$  Hz, 1H, H-5), 2.73 (ddt,  $J = 14.9, 7.4, 5.2$  Hz, 2H, SEt), 1.88 (t,  $J = 6.0$  Hz, 1H, 6-OH), 1.30 (t,  $J = 7.4$  Hz, 3H, SEt) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.44 (C), 138.48 (C), 137.90 (C), 130.05 (C), 129.78 (CH), 128.45 (CH), 128.39 (CH), 128.28 (CH), 127.87 (CH), 127.72 (CH), 113.93 (CH), 86.48 (CH), 85.26 (CH), 81.77 (CH), 79.28 (CH), 77.44 (CH), 75.72 ( $\text{CH}_2$ ), 75.55 ( $\text{CH}_2$ ), 74.78 ( $\text{CH}_2$ ), 62.20 ( $\text{CH}_2$ ), 55.27 ( $\text{CH}_3$ ), 25.19 ( $\text{CH}_2$ ), 15.15 ( $\text{CH}_3$ ) ppm; HRMS (FAB,  $\text{MH}^+$ ) calcd for  $\text{C}_{30}\text{H}_{37}\text{O}_6$  525.2311, found 525.2315.

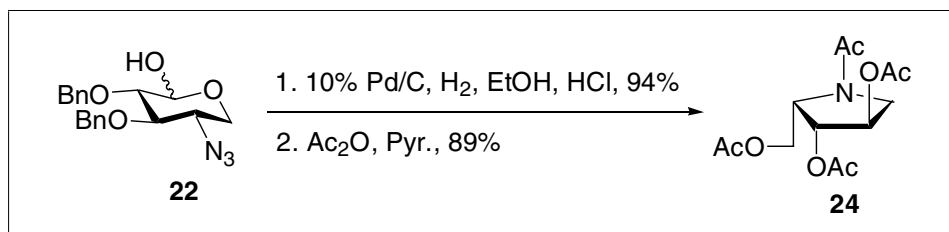
**Compound 16.**  $[\alpha]_{\text{D}}^{23} +151.5$  ( $c$  1.4,  $\text{CHCl}_3$ ); IR ( $\text{CHCl}_3$ )  $\nu$  3510, 2938, 1724, 1602, 1452, 1282, 1106, 1052, 711  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.96 (m, 4H, BzH), 7.52-7.46 (m, 2H, BzH), 7.38-7.32 (m, 4H, BzH), 7.28-7.23 (m, 5H, PhH), 5.78-5.72 (m, 2H, H-2, H-3), 5.18 (d,  $J = 2.6$  Hz, 1H, H-1), 4.79 (d,  $J = 11.5$  Hz, 1H,  $\text{PhCH}_2$ ), 4.50 (d,  $J = 11.5$  Hz, 1H,  $\text{PhCH}_2$ ), 4.21 (s, 1H, H-4), 4.04 (dd,  $J = 6.6, 5.3$  Hz, H-5), 3.83 (dd,  $J = 11.3, 6.6$  Hz, 1H, H-6a), 3.60 (dd,  $J = 11.3, 5.3$  Hz, 1H, H-6b), 3.40 (s, 3H,  $\text{OCH}_3$ ), 1.78 (bs, 1H, 6-OH) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.05 (C), 105.97 (C), 137.34 (C), 133.34 (CH), 133.16 (CH), 129.77 (CH), 129.47 (C), 129.31 (C), 128.52 (CH), 128.49 (CH), 128.36 (CH), 128.34 (CH), 128.12 (CH), 97.60 (CH), 75.04 (CH), 74.98 ( $\text{CH}_2$ ), 71.44 (CH), 70.20 (CH), 69.50 (CH), 62.02 ( $\text{CH}_2$ ), 55.48 ( $\text{CH}_3$ ) ppm; HRMS (FAB,  $\text{MH}^+$ ) calcd for  $\text{C}_{28}\text{H}_{29}\text{O}_8$  493.1862, found 493.1859.



**Compound 21.** To a solution of **20** (1.50 g, 3.07 mmol) in methanol (50 mL) was added sodium borohydride (2.30 g, 61.4 mmol) at 0 °C. After stirring for 18 h, the mixture was quenched by brine (50 mL), and the resulting solution was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexane = 2/1,  $R_f$  0.3) to give the product **21** (0.89 g, 73 %) as colorless oil.  $[\alpha]_D^{25}$  -6.1 ( $c$  0.96,  $\text{CHCl}_3$ ); IR ( $\text{CHCl}_3$ )  $\nu$  3366, 2922, 2098, 1728, 1451, 1347, 691  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.26 (m, 10H, ArH), 4.63 (s, 2H,  $\text{PhCH}_2$ ), 4.61 (d,  $J$  = 11.4 Hz, 1H,  $\text{PhCH}_2$ ), 4.55 (d,  $J$  = 11.4 Hz, 1H,  $\text{PhCH}_2$ ), 3.91-3.89 (m, 1H), 3.77-3.71 (m, 4H), 3.68-3.66 (m, 3H), 3.20 (d,  $J$  = 2.8 Hz, 1H, OH), 2.04 (s, 1H, OH), 1.96 (s, 1H, OH) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.44 (C), 137.08 (C), 128.77 (CH), 128.55 (CH), 128.48 (CH), 128.40 (CH), 78.85 (CH), 76.51 (CH), 74.50 ( $\text{CH}_2$ ), 73.97 ( $\text{CH}_2$ ), 71.95 (CH), 63.94 (CH), 63.44 ( $\text{CH}_2$ ), 62.34 ( $\text{CH}_2$ ) ppm; HRMS (FAB,  $\text{MH}^+$ ) calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}_5$  388.1872, found 388.1872.



**Compound 22.** Sodium periodate (0.94 g, 4.41 mmol) was added to a solution of compound **21** (0.57 g, 1.47 mmol) in methanol (2 mL) at room temperature. After stirring for 3 h, the mixture was filtered through celite, and the filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexane = 1/3) to give a solid, which was re-crystallized in 95% ethanol to afford the product **22** (0.48 g, 92%) as white powder.  $[\alpha]_D^{29} -72.4$  (*c* 1.0, CHCl<sub>3</sub>); mp 93–93.5 °C; IR (CHCl<sub>3</sub>)  $\nu$  3348, 2922, 2107, 1451, 1356, 1025, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31–7.19 (m, 10H, Ar-H), 5.02 (dd, *J* = 3.3, 3.1 Hz, 1H, H-1), 4.80 (d, *J* = 10.7 Hz, 1H, PhCH<sub>2</sub>), 4.73 (d, *J* = 10.7 Hz, 1H, PhCH<sub>2</sub>), 4.65 (d, *J* = 11.7 Hz, 1H, PhCH<sub>2</sub>), 4.57 (d, *J* = 11.7 Hz, 1H, PhCH<sub>2</sub>), 3.71 (t, *J* = 9.0 Hz, 1H, H-3), 3.63–3.53 (m, 2H, H-4, H-5), 3.49–3.36 (m, 2H, H-2, H-5'), 3.06 (d, *J* = 3.1 Hz 1H, OH) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.80 (C), 137.46 (C), 128.60 (CH), 128.47 (CH), 128.25 (CH), 128.17 (CH), 128.05 (CH), 127.94 (CH), 91.51 (CH), 79.67 (CH), 79.32 (CH), 75.52 (CH<sub>2</sub>), 73.37 (CH<sub>2</sub>), 60.89 (CH), 60.20 (CH<sub>2</sub>) ppm; HRMS (FAB, M<sup>+</sup>-H) calcd for C<sub>19</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub> 354.1454, found 354.1450. Anal. Calcd for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>: C, 64.21; H, 5.96; N, 11.82. Found: C, 64.59; H, 5.68; N, 11.58.



**Compound 24.** A mixture of **22** (50 mg, 0.14 mmol), 10% palladium on charcoal (50 mg), 1N HCl (3 mL), and ethanol (6 mL) was bubbled with argon for 10 min followed by equipment with a hydrogen balloon for 18 h. The mixture was filtered through celite, and the filtrate was concentrated *in vacuo* to give the crude 1,4-dideoxy-1,4-imino-L-xylitol (18.7 mg, 94%). This crude compound was dissolved in pyridine (1 mL), acetic anhydride (0.2 mL) was added to the solution, and the mixture was stirred at room temperature for 4 h. The reaction was quenched by methanol (0.1 mL), and the resulting solution was kept stirring for 30 min. The mixture was concentrated *in vacuo*, and the residue was purified by flash column chromatography (ethyl acetate) to afford the expected product **24** (34 mg, 89%). Comparison of our data with the literature report<sup>8</sup> revealed identity with respect to <sup>1</sup>H and <sup>13</sup>C spectra.

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