Asymmetric Cyclopropanation of Allylic Ethers: Cleavage and Regeneration of the Chiral Auxiliary

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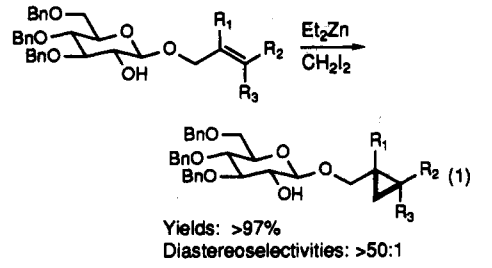
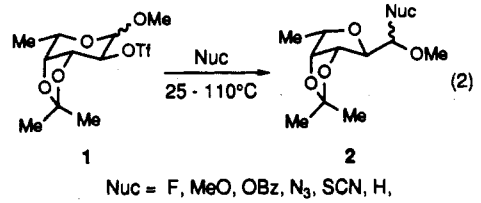
The ring contraction reaction of 2-*O*-[[(trifluoromethyl)sulfonyl]oxy]-β-D-glucopyranosides and their corresponding α-anomers is reported. The rearrangement was shown to occur under extremely mild basic conditions to allow isolation of acid-sensitive optically active substituted cyclopropylmethanols. The chiral auxiliary can be regenerated by converting the *C*-glucofuranoside, byproduct of the rearrangement, into tri-*O*-benzyl-D-glucal (two steps).

We recently reported that 2-hydroxy-β-D-glucopyranose can be used as an extremely efficient chiral auxiliary for the stereoselective cyclopropanation of allylic alcohols (eq 1).[2] These exciting results led us to develop new alternatives for the cleavage of the chiral auxiliary in order to isolate the corresponding substituted cyclopropylmethanol moiety in high yield. One key element in our system is that the C-2 hydroxy group is not protected and can be used to induce new reaction pathways. This whole strategy for the cleavage of the chiral auxiliary was based on reports in the literature involving ring contraction of methyl 3,4-*O*-isopropylidene-2-*O*-[(trifluoromethyl)sulfonyl]-α-L-fucopyranoside (1α) and its β-anomer (1β).[3] It was shown that treatment of either anomer with a number of nucleophilic reagents produced the 2,5-anhydro sugar derivatives **2** (eq 2).[4]





Two stereoelectronic requirements were thought to be mandatory for ring contraction reaction of protected glycosides.[5] First, the endocyclic C–O bond must be antiperiplanar to the C–OTf bond (Figure 1). Secondly, the anomeric exocyclic oxygen must be able to achieve the conformation in which one of its nonbonded lone pairs is antiperiplanar to the endocyclic C–O bond. Since both requirements are present in the glucopyranose series, heating of 2-*O*-[(trifluoromethyl)sulfonyl]-β-D-glucopyranoside (3β) or its α-anomer (3α) *in the presence of water as nucleophile* should produce the corresponding aldehyde **4** and liberate the cyclopropane aglycone moiety **5**.

Treatment of 2-hydroxy-β-D-glucopyranoside **6a** with triflic anhydride and pyridine in dichloromethane[6] afforded the corresponding triflate **6b** which, upon heating at 160 °C in a mixture of DMF/pyridine/H_2O for 5 min, underwent smooth ring contraction to produce, after reduction,[7] the corresponding alcohol **8** (80%, 7-12:1 mixture of epimers by ^{13}C NMR[8,9]) and cyclopropylmethanol (+)-**7** ($[\alpha]_D$ = +86° (*c* 1.31, EtOH)) in 90% yield (Scheme I). Remarkably, the cyclopropylmethanol moiety was stable for this short period at that temperature. It should be pointed out that the rearrangement can occur at lower temperature but an increase in the reaction time is required (ca. 5 min at 120 °C; >15 min at 80 °C). The rearrangement could also be done in one pot from the alcohol **6a** (Tf_2O, pyr; then DMF, H_2O, 160 °C). The overall isolated yield of the cyclopropylmethanol, however, was slightly lower (75%) to that obtained for the two steps.

Several key substrates were submitted to the rearrangement conditions as illustrated in Table I. When glycoside **9** was heated to 120 °C, cyclopropylmethanol (+)-**10**, a key intermediate in the synthesis of dictyopterenes A and C′ was produced in 73% yield ($[\alpha]_D$ + 10° (*c* 1.24, CH_2Cl_2) (lit.[10] 10.3° (*c* 0.73, CH_2Cl_2)). Similarly, the α-anomer **11** and 6-deoxy-L-glucopyranose derivative **12** reacted under the same conditions (160 °C) to afford, after reduction, the aglycon moiety (−)-**7** ($[\alpha]_D$ − 85° (*c* 1.5, EtOH)) in 88% and 86% yield, respectively. To

(1) NSERC (Canada) University Research Fellow, 1989-1994; Bio-Méga Young Investigator, 1991-1993.

(2) Charette, A. B.; Côté, B.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1991**, *113*, 8166-8167.

(3) Baer, H. H.; Hernandez, M.; Simesen, L. *Carbohydr. Res.* **1989**, *187*, 67-92.

(4) For other ring contraction reaction of glucopyranose see: Hanessian, S.; Pernet, A. G. In *Advances in Carbohydrate Chemistry and Biochemistry*; Tipson, R. S., Horton, D., Eds.; Academic Press: New York, 1976; Vol. 33, pp 111-188. Hanessian, S.; Tyler, P. C.; Demailly, G.; Chapleur, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6243-6246.

(5) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983; pp 183-190. Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer Verlag: Berlin, 1983.

(6) Binkley, R. W. *J. Org. Chem.* **1991**, *56*, 3892-3896.

(7) The crude isolated rearrangement residue was directly submitted to $NaBH_4$ in methanol to facilitate separation of the products.

(8) If the mixture was rapidly cooled to 0 °C in an ice-water bath immediately after the rearrangement the diastereomeric ratio was slightly higher (12:1).

(9) The structure of the α-*C*-glucofuranoside was unambigously established by converting alcohol 8α into known 2,5-anhydro-1,3,4,6-tetra-*O*-benzyl-D-mannitol: Kaye, A.; Neidle, S.; Reese, C. B. *Tetrahedron Lett.* **1988**, *29*, 1841-1844. The other diastereomer, 2,5-anhydro-1,3,4,6-tetra-*O*-benzyl-D-glucitol, was compared to the known 2,5-anhydro-d-glucitol derived material: Koerner, T. A. W., Jr.; Voll, R. J.; Younathan, E. S. *Carbohydr. Res.* **1977**, *59*, 403-416.

(10) Grandjean, D.; Pale, P.; Chuche, J. *Tetrahedron* **1991**, *47*, 1215-1230.

0022-3263/93/1958-0933$04.00/0

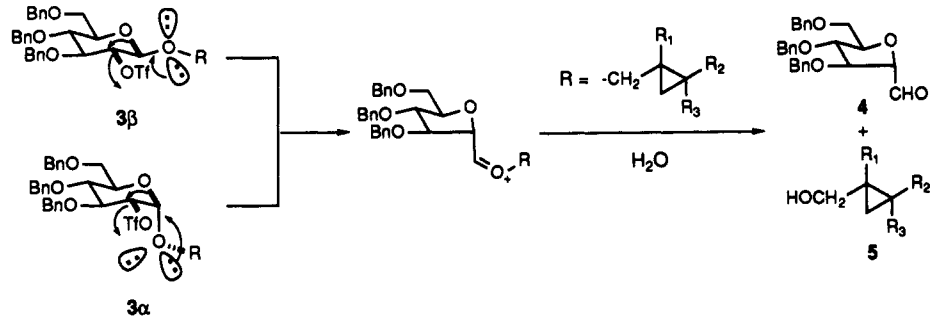
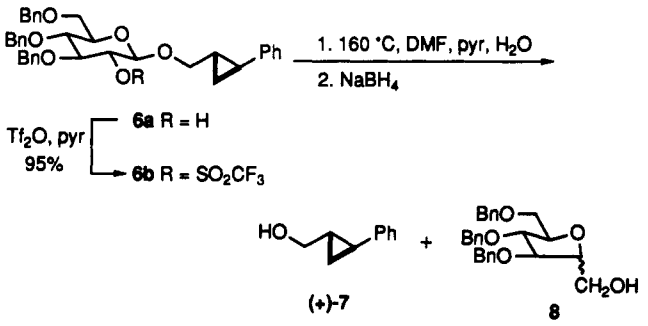


Figure 1

Scheme I



facilitate isolation of volatile cyclopropylmethanol moieties (in the presence of DMF, pyridine) an in situ protection protocol was developed. Rearrangement of glycoside **14** followed by sequential treatment with anhydrous $MgSO_4$, 3-Å molecular sieves,[11] imidazole, and *tert*-butyldiphenylsilyl chloride allowed easy isolation of the corresponding silyl ethers (+)-**15** in 60% yield.

To demonstrate the stereospecificity of the rearrangement and that epimerization of the initial aldehyde occurred under the reaction conditions, the ring contraction of methyl glycosides **16** (ca. 2:1 α/β)[12] was investigated. Treatment of **16** under the standard reaction conditions led to aldehyde **4** in 90% yield again as a ca. 7:1 mixture of epimers. If, however, the H_2O was replaced by MeOH, dimethyl acetal **17** was obtained cleanly as a *single isomer* in 97% yield confirming that the rearrangement is stereospecific. Regeneration of the chiral auxiliary from aldehyde **4** was relatively straightforward (Scheme III). Deoxygenation of the α-alkoxy aldehyde upon treatment with samarium diiodide[13] proceeded in 75% yield to produce lactol **18** as a mixture of anomers. Subsequent dehydration via the mesylate[14] regenerated tri-*O*-benzyl-D-glucal.

We have therefore demonstrated that the rearrangement of 2-*O*-[(trifluoromethyl)sulfonyl]-β-D-glucopyranosides and their corresponding α-anomers allows us to isolate the sensitive substituted cyclopropylmethanol moieties in high yields and also be generate cleanly *C*-glucofuranoside derivatives from glucopyranosides. Furthermore, the chiral auxiliary for the cyclopropanation reaction can be regenerated via a two-step sequence.

(11) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966–3968.

(12) Obtained in two steps (MeOH, HCl; Tf_2O, pyr, CH_2Cl_2) from the corresponding 3,4,6-tri-*O*-benzyl-D-glucopyranose: Charette, A. B.; Marcoux, J.-F.; Côté, B. *Tetrahedron Lett.* **1991**, *32*, 7215–7218. See also: Crich, D.; Lim, L. B. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2209–2214.

(13) Inanaga, J.; Katsuki, J.; Yamaguchi, M. *Chem. Lett.* **1991**, 1025–1026. Hanessian, S.; Girard, C.; Chiara, J. L. *Tetrahedron Lett.* **1992**, *33*, 573–576 and references cited therein.

(14) Lerous, Jacques; Perlin, A. S. *Carbohydr. Res.* **1978**, *67*, 163–178.

Experimental Section

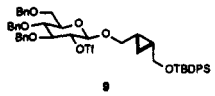
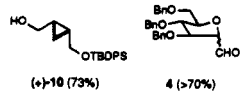
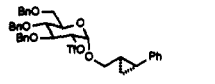
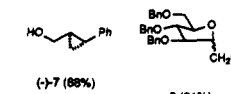
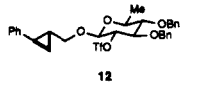
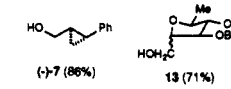
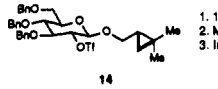
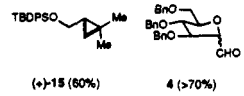
General. Unless otherwise noted, all nonaqueous reactions were performed under an oxygen-free atmosphere of nitrogen with rigid exclusion of moisture from reagents and glassware. ^1H (and ^{13}C NMR) spectra were recorded in deuteriochloroform at 200.05 or 400.13 MHz (50 or 100 MHz). When necessary, solvents and reagents were dried prior to use as follows: ether, tetrahydrofuran, benzene, and toluene were stored over and distilled from sodium benzophenone ketyl; dichloromethane, triethylamine, pyridine, and hexane were distilled over calcium hydride. Unless otherwise stated, the reagents were purchased and used as received. Trifluoromethanesulfonic anhydride was distilled three times over P_2O_5.

General Procedure for Triflate Formation. 3′-Phenyl-2′,3′-methanopropyl 2-*O*-[[(Trifluoromethyl)sulfonyl]oxy]-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (6b). To a solution of 101 mg (0.174 mmol) of 2-hydroxy-β-D-glucopyranoside **6a** in 2.0 mL of CH_2Cl_2 was added 59 μL (0.731 mmol) of pyridine. The resulting clear solution was cooled to −20 °C, and 59 μL (0.348 mmol) of trifluoromethanesulfonic anhydride was added over 15 min. The reaction was then warmed slowly to 0 °C over 1 h and stirred at that temperature until TLC analysis showed complete consumption of starting material (2 h). The mixture was quenched with saturated aqueous $NaHCO_3$ and diluted with ether. The organic layer was washed with water (4 × 5 mL) and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed through a short pad of silica gel using 12% EtOAc/hexanes as eluent to afford 117 mg (95%) of glucopyranoside **6b**. The triflates were immediately submitted to the rearrangement conditions since extensive decomposition was observed upon standing.

General Procedure for the Ring Contraction. 3,4,6-Tri-*O*-benzyl-2,5-anhydro-D-mannitol (8α). To a solution of 189 mg (0.265 mmol) of the triflate **6b** in 4 mL of DMF was added 213 μL (2.64 mmol) of pyridine and 390 μL (21.7 mmol) of H_2O. The reaction flask was placed in an oil bath that had been previously heated to 160 °C. The mixture was heated at that temperature for 5 min and then cooled to room temperature. The solution was then diluted with 50% Et_2O/EtOAc, and the organic layer was washed with 5% aqueous HCl (5 × 5 mL). The combined aqueous layer was subsequently washed with EtOAc (5 × 5 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was dissolved in 3 mL of MeOH, and 30 mg (0.795 mmol) of $NaBH_4$ was added in one portion. After 1 h of stirring at room temperature, water was added. The resulting solution was diluted with 50% Et_2O/EtOAc. The organic layer was washed with water (2 × 5 mL), and the combined aqueous layers were washed with EtOAc (5 × 5 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel using a gradient of 30–40% EtOAc/hexanes as eluent to produce 36 mg (90%) of the known substituted cyclopropylmethanol (+)-**7** and 91 mg (79%) of a 7:1 mixture of 2,5-anhydro-D-mannitol (8α) and 2,5-anhydro-D-glucitol (8β).

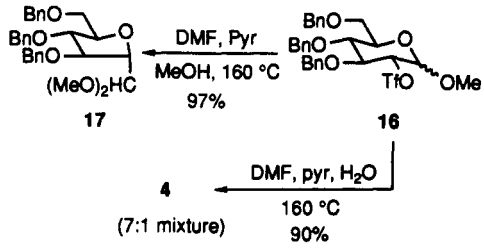
3,4,6-Tri-*O*-benzyl-2,5-anhydro-D-mannitol (8α): ^1H NMR (200 MHz, $CDCl_3$) δ 7.37–7.25 (m, 15 H, Ph), 4.56–4.53 (m, 6 H, CH_2Ph), 4.27–4.22 (m, 1 H, $CHCH_2OBn$), 4.13–4.06 (m, 3 H,

Table I. Ring Contraction Reaction of 2-[(Trifluoromethanesulfonyl)oxy]glucopyranosides

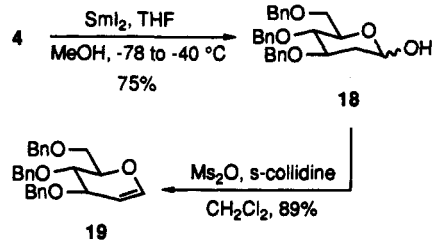
starting material[a]	condns	products (yields)[b]
 9	120 °C, DMF, pyr, H_2O	 (+)-10 (73%) 4 (>70%)
 11	1. 160 °C, DMF, pyr, H_2O 2. $NaBH_4$	 (+)-7 (68%) 8 (81%)
 12	1. 160 °C, DMF, pyr, H_2O 2. $NaBH_4$	 (+)-7 (66%) 13 (71%)
 14	1. 140 °C, DMF, pyr, H_2O 2. $MgSO_4$; 3 Å Mol. Siev. 3. Imidazole (4 eq), TBDPSCl (4 eq)	 (+)-15 (60%) 4 (>70%)

[a] The starting materials were obtained from the corresponding alcohols (Tf_2O, pyr); see ref 2. [b] The *C*-glucofuranosides were obtained as mixture of diastereomers (7–12:1 α/β).

Scheme II



Scheme III



CHOBn, $CHCH_2OH$), 3.71–3.68 (m, 2 H, CH_2OH), 3.61 (dd, J = 7, 2 Hz, 2 H, CH_2OBn), 2.1 (s(br), 1 H, CH_2OH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 138.0, 137.6, 137.5, 128.4, 128.3, 127.8, 127.8, 127.7, 127.6, 84.6, 84.1, 83.2, 81.8, 73.4, 72.0, 71.8, 70.0, 62.7.

6-Deoxy-3,4-di-*O*-benzyl-2,5-anhydro-L-mannitol (13): ^1H NMR (200 MHz, $CDCl_3$) δ 7.4–7.33 (m, 10 H, Ph), 4.56 (s(br), 4 H, CH_2Ph), 4.21–4.12 (m, 2 H, $CHCH_3$, $CHCH_2OH$), 4.01 (t, J = 4 Hz, 1 H, CHOBn), 3.80 (t, J = 4 Hz, 1 H, CHOBn), 3.70–3.67 (m, 2 H, CH_2OH), 2.15 (s(br), 1 H, CH_2OH), 1.32 (d, J = 6 Hz, 3 H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 137.6, 137.6, 128.5, 128.4, 127.8, 127.7, 127.6, 88.6, 84.5, 82.6, 78.5, 72.1, 71.8, 62.8, 19.0; HRMS (FAB) calcd for $C_{20}H_{24}O_4$ 328.1675, found 328.1648.

Stereochemistry of the Rearranged Products: Derivatization to Known Compounds. 1,3,4,6-Tetra-*O*-benzyl-2,5-anhydro-D-mannitol. To a solution of 91 mg (0.209 mmol) of 2,5-anhydro-D-mannitol (8α) in 2 mL of DMF was added 10 mg (0.251 mmol) of NaH (60% in oil) and 30 μL (0.251 (mmol) of benzyl bromide. The reaction was stirred for 2 h at room temperature after which time TLC analysis showed complete consumption of starting material. Water was slowly added, and the resulting solution was diluted with ether. The organic layer was washed with 5% aqueous HCl (4 × 5 mL), saturated aqueous $NaHCO_3$ (5 mL), brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (10% EtOAc/hexanes) to afford 103 mg (94%) of the tetra-*O*-benzyl derivative containing the analogous D-glucitol derivatives (<10%) that was identical in all respects to known material:[10] R_f 0.27 (10% EtOAc/hexanes); $[\alpha]_D$ +10.72° (*c* 3.19, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.32–7.22 (m, 20 H, Ph), 4.55 (s, 4 H, CH_2Ph), 4.49 (s, 4 H, CH_2Ph), 4.26–4.18 (m, 2 H, $CHCH_2OBn$), 4.07 (m, 2 H, CHOBn), 3.59 (d, J = 6 Hz, 4 H, CH_2OBn); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 138.1, 137.9, 128.3, 127.7, 127.5, 84.9, 81.8, 73.3, 71.8, 70.2.

1,3,4,6-Tetra-*O*-benzyl-2,5-anhydro-D-glucitol:[10] R_f 0.27 (10% EtOAc/hexanes); $[\alpha]_D$ +24.9° (*c* 4.28, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.17 (m, 20 H, Ph), 4.64–4.34 (m, 8 H, CH_2Ph), 4.29–4.22 (m, 1 H, $CHCH_2OBn$), 4.14–4.08 (m, 1 H, $CHCH_2OBn$), 3.98–3.94 (m, 2 H, CHOBn), 3.78 (dd, J = 10, 6 Hz, 1 H, CH_2OBn), 3.71 (dd, J = 10, 6 Hz, 1 H, CH_2OBn), 3.64 (dd, J = 10, 6 Hz, CH_2OBn), 3.52 (dd, J = 10, 7 Hz, 1 H, CH_2OBn); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 138.2, 137.8, 137.8, 128.3, 128.3, 127.7, 127.6, 127.5, 83.7, 82.7, 82.6, 80.1, 73.4, 73.2, 71.5, 71.4, 70.4, 68.3.

1,1-Dimethoxy-3,4,6-tri-*O*-benzyl-2,5-anhydro-D-mannitol (17). To a solution of 132.4 mg (0.222 mmol) of the triflate **16** in 3.1 mL of DMF was added 178 μL (2.21 mmol) of pyridine and 714 μL (17.6 mmol) of MEOH. The reaction flask was placed in an oil bath that had been preheated to 160 °C. The mixture was heated at that temperature for 5 min and then cooled to room temperature. The solution was then diluted with 50% Et_2O/EtOAc, the organic layer was washed with water (5 × 5 mL), and the combined aqueous layers were subsequently washed with EtOAc (5 × 5 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel using 25% EtOAc/hexanes as eluent to produce 103 mg (97%) of the desired glucofuranoside **17**: R_f 0.34 (15% EtOAc/petroleum ether 35–60 °C); $[\alpha]_D$ + 2.62° (*c* 5.58, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.36–7.21 (m, 15 H, Ph), 4.60–4.49 (m, 6 H, CH_2Ph), 4.40 (d, J = 6.2 Hz, 1 H, $CH(OMe)_2$), 4.25 (dt, J = 5.9, 4.0 Hz, 1 H, $CHCH_2OBn$), 4.16–4.05 (m, 3 H, CHOBn, $ChCH(OMe)_2$), 3.59 (d, J = 5.9 Hz, 2 H, CH_2OBn), 3.43 (s, 3 H, OCH_3), 3.40 (s, 3 H, OCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 138.2, 137.9, 137.8, 128.3, 127.8, 127.7, 127.6, 127.5, 127.2, 103.6, 84.7, 84.6, 83.0, 82.0, 73.3, 71.6, 69.8, 55.4, 53.8; HRMS (FAB) calcd for $C_{29}H_{33}O_6$ 477.2277, found 477.2325.

General Procedure for the in Situ Protection. 3,3-Dimethylcyclopropylmethanol (*tert*-Butyldiphenylsilyl)-oxy Ether (15). After the triflate **14** had been submited to ring contraction conditions (0.107 mmol scale), the reaction was cooled to room temperature and 200 mg of dry $MgSO_4$ was added. The resulting slurry was stirred for 6 h and then filtered to remove $MgSO_4$. The solution was concentrated to ca. 3 mL with a stream of dry nitrogen. Freshly activated molecular sieves (200 mg, 3 Å) were then added, and after 12 h, 30 mg (0.428 mmol) of imidazole and 112 μL (0.428 mmol) of *tert*-butyldiphenylsilyl chloride were successively added. After 3 h of stirring at room temperature, the reaction was quenched with water and diluted with 50% Et_2O/EtOAc. The aqueous layer was washed with 5 mL of EtOAc, and the combined organic layers were washed with water (4 × 5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC (1% EtOAc/hexanes) to afford 21.5 mg (60%) of cyclopropylmethanol **15**: R_f 0.14 (petroleum ether 35–60 °C); $[\alpha]_D$ +1.94° (*c* 1.75, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.71–7.67 (m, 4 H, Ph), 7.46–7.33 (m, 8 H, Ph), 3.79 (dd, J = 11, 6 Hz, 1 H, $CH_2OTBDPS$), 3.52 (dd, J = 11, 8 Hz, 1 H, $CH_2OTBDPS$), 1.05 (s, 9 H, $(CH_3)_3C$), 1.05–0.83 (m, 7 H, $(CH_3)_2C$, CH_2CH_{cyclop}), 0.37 (dd, J = 9, 4 Hz, 1 H, $CH_{2cyclopr}$), 0.00 (t, J = 5 Hz, 1 H, $CH_{2cyclopr}$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 135.6, 134.3, 129.4, 127.5, 65.1, 27.3, 26.9, 26.4, 19.9, 19.2, 18.1, 15.8; HRMS (FAB) calcd for $C_{18}H_{21}OSi$ 281.1362, found 281.1343.

2-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (18). To a solution of 34.2 mg (0.079 mmol) of aldehyde **4** in 1 mL of THF was added 500 μL of anhyd MeOH. The solution was cooled to −78 °C, and 1.58 mL of a solution of SmI_2 in THF (0.1 M) was added over 30 min. The reaction was then allowed to warm to −40 °C over 1 h and kept at that temperature for an additional 1 h, after which time TLC analysis showed the complete consumption of starting material. The blue solution was then warmed to 0 °C (turned colorless at ca. −20 °C), and H_2O was

added. The organic layer was diluted with 50% Et_2O/EtOAc. The aqueous layer was washed with EtOAc (5 mL), and the combined organic layers were washed with water (5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC (40% EtOAc/hexanes) to afford 25.6 mg (75%) of 2-deoxyglucopyranose 18 that was identical in all respects to material prepared from tri-*O*-benzyl-D-glucal (aqueous HCl).

Tri-*O*-benzyl-D-glucal (19). To a solution of 95.4 mg (0.219 mmol) of glucopyranose 18 in 2.2 mL of CH_2Cl_2 was added 434 μL (3.285 mol) of *s*-collidine. The resulting clear solution was cooled to 0 °C, and 76 mg (0.439 mmol) of methanesulfonic anhydride was added in one portion. After 6 h of stirring at 0 °C, the brown solution was quenched with 1 mL of saturated aqueous $NaHCO_3$. The mixture was diluted with water and 50% Et_2O/EtOAc. The aqueous layer was extracted with 50% Et_2O/EtOAc (3 × 5 mL). The combined organic layers were washed with water (3 × 5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was filtered through a short pad of silica gel (10% EtOAc/hexanes) to afford 81 mg (89%) of tri-*O*-benzyl-D-glucal (19) that was identical in all respects to known material.

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