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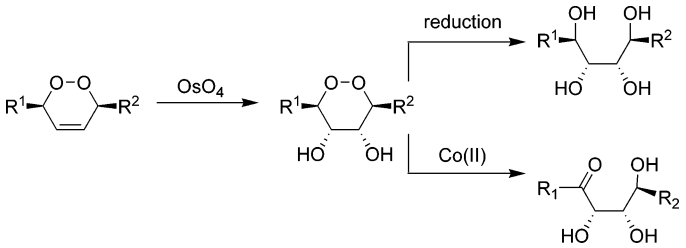
Osmium Catalyzed Dihydroxylation of 1,2-Dioxines: A New Entry for Stereoselective Sugar Synthesis

Tony V. Robinson,[†] Dennis K. Taylor,*[,†] and Edward R. T. Tiekink[‡]

Department of Chemistry, The University of Adelaide, South Australia 5005, Australia, and Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698

dennis.taylor@adelaide.edu.au

Received May 7, 2006

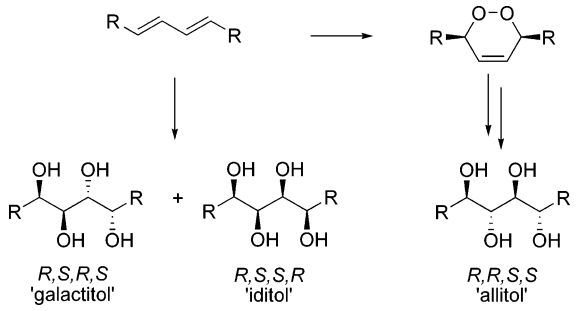


A series of 3,6-substituted 3,6-dihydro-1,2-dioxines were dihydroxylated with osmium tetroxide to furnish 1,2-dioxane-4,5-diols (peroxy diols) in yields ranging from 33% to 98% and with de values not less than 90%. The peroxy diols were then reduced to generate a stereospecific tetraol core with *R*,*R*,*S*,*S* or "allitol" stereochemistry. The peroxy diols and their acetonide derivatives were also ring-opened with Co(II) salen complexes to give novel hydroxy ketones in 77−100% yield, including the natural sugar psicose. Importantly, preliminary work on the catalytic asymmetric ring-opening of *meso*-peroxy diols using the Co(II) Jacobsens's catalyst indicates that asymmetric sugar synthesis from 1,2-dioxines is possible.

Introduction

The stereospecific synthesis of sugars and other polyhydroxylated compounds remains a challenge to the modern synthetic chemist. The Sharpless dihydroxylation of olefins has made the assembly of such compounds substantially easier, however, this method does not readily allow access to all stereoisomers because of the inherent stereochemical control defined by the Sharpless dihydroxylation procedure.[1] In a study by Sharpless, it was shown that one-pot dihydroxylation of 1,3-dienes and 1,3,5-trienes could be used to generate tetraols and hexaols with a fair degree of selectivity (Scheme 1).[2] Thus four to six contiguous stereogenic centers could be assembled in one step. Sharpless found dihydroxylation of *E*,*E* 1,3-dienes gave a tetraol core with *R*,*S*,*R*,*S* or 'galactitol' stereochemistry as the major product, with varying amounts of *R*,*S*,*S*,*R* or 'iditol' tetraol forming as the minor product depending on the R groups (Scheme 1). The preference for galactitol over iditol stereochemistry dramatically decreased when the R groups were small or when *E*,*Z* 1,3-dienes were used. This methodology has recently been extended by the stepwise asymmetric dihydroxylation of dienoates, providing a convenient route to *galacto*- and *talo*-lactones.[3,4]

SCHEME 1



Our group is largely concerned with the chemistry of 1,2-dioxines, and so it was proposed that singlet oxygen addition to 1,3-butadienes could accomplish stereoselective addition of

* To whom correspondence should be addressed. Phone: (+61) 8 8303 5494. Fax: (+61) 8 83034358.
[†] The University of Adelaide.
[‡] The University of Texas at San Antonio.

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10.1021/jo060949p CCC: $33.50
Published on Web 08/17/2006

2 hydroxyl groups, which would be masked as the cyclic peroxide. This would leave only a solitary double bond as part of a cis fused heterocycle, which if dihydroxylated would allow for improved selectivity, and also a different stereochemistry than is available from direct dihydroxylation of the precursor 1,3-dienes. Thus dihydroxylation would allow for the stereospecific generation of a tetraol core with allitol stereochemistry (Scheme 1). Moreover, 1,2-dioxines may also be homolytically cleaved by metal catalysts,[5] therefore dihydroxylation of dihydro dioxines could also be a viable route to polyhydroxylated keto compounds such as the natural sugar psicose.

Previous studies have shown that both unsaturated acyclic peroxides[6] and 1,2,4-trioxane antimalarial compounds[7] can be dihydroxylated using osmium tetroxide with no disruption to the peroxide linkage. However, osmium(II) complexes have been previously shown to homolytically ring-open 1,2-dioxines to give bisepoxides and hydroxy ketones.[8] To the best of our knowledge, there have been no previous reports of the dihydroxylation of dihydro dioxines.We therefore report herein the first examples of the osmium catalyzed *cis*-1,2-dihydroxyaltion of 3,6-dihydro-1,2-dioxines and demonstrate the utility of this transformation by the stereospecific generation of polyhydroxylated products.

Results and Discussion

3,6-Dihydro-1,2-dioxines **1a**−**k** were prepared by photooxidation of the requisite 1,3-butadienes in the presence of rose bengal bis(triethylammonium) salt or 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine as previously reported.[9] Because of convenience, dihydroxylation of the dihydro dioxines was initially carried out with commercially available AD mix (method A) which generally gave good yields; however, the reaction times were somewhat slow (Table 1). The slow dihydroxylation turnover of the cyclic cis fused olefin is consistent with the general sluggishness exhibited by cis olefins.[10,11]

When the substrate contained an additional free alcohol, it was found that protection with TBDMS prior to dihydroxylation dramatically increased the yield and aided in the ease of isolation (compare entries 1, 2 and 3, 4 in Table 1). Given that the model dihydro dioxines were either meso or racemic, employing chiral AD mixes seemed wasteful, so a mix without the chiral ligand was prepared (method B) and used on substrate **1f** (entry 7). It was found that without the chiral ligand, the reaction time slowed dramatically and did not go to completion, which is in agreement with the findings of Sharpless in regards to the rate accelerating effects of amine ligands with OsO_4 dihydroxylation.[12] With this in mind, the Upjohn process (method C) was employed;[13] however, the presence of excess NMO resulted only in the formation of diketone which occurs readily with 1,2-dioxines when exposed to amine bases via the Kornblum−De La Mare rearrangement.[14]

TABLE 1. Osmium Catalyzed Dihydroxylation of Dihydro Dioxines 1a−k

entry	dihydro dioxine	method[a]	time (d)	product (% yield)
1	**1a**	A	1	*b*
2	**1b**	A	5	**2b** (80)
3	**1c**	A	1	**2c** (33)
4	**1d**	A	6	**2d** (98)
5	**1e**	D	1	**2e** (73)
6	**1f**	A	3	**2f** (93)
7	**1f**	B	5	**2f** (65)[c]
8	**1f**	C	5	*d*
9	**1f**	D	1	**2f** (94)
10	**1g**	D	1	**2g** (95)
11	**1h**	D	1	**2h** (89)
12	**1i**	A	5	**2i** (98)
13	**1j**	D	1	**2j** (96)
14	**1k**	C	1	*d*
15	**1k**	D	1	*e*
16	**1k**	E	14	**2k** (77)

[a] See Experimental Section for reaction conditions. [b] Product decomposed during isolation. [c] Remainder of yield was recovered starting material. [d] Major product isolated was 1,4-diketone.[9] [e] Major product isolated was furan.

In a recent report, Sharpless found that the standard Upjohn conditions could be modified by buffering with citric acid, which made dihydroxylation possible under mildly acidic conditions, and was found to also dramatically increase the reaction rate for many sluggish substrates.[15] These conditions (method D) were found to work remarkably well for the dihydroxylation of most dihydro dioxines, decreasing the reaction rate over standard AD mix conditions as well as avoiding the complications of excess amine bases.

Dihydroxylation of substrate **1k** was initially complicated by diketone formation under basic conditions (entry 14) and furan formation under mildly acidic conditions (entry 15). This can be attributed to the two phenyl groups α to the peroxide linkage which dramatically increase the acidity of the protons α to the peroxide linkage, thus making decomposition of the peroxide relatively facile under acidic and basic conditions. To avoid these problems, diol **2k** was prepared using neutral conditions based upon $KClO_3$ as the reoxidant (method E);[16] the diol was unobtainable using any other method.

The addition of the *cis*-1,2-diol unit was found to occur with high diastereoselectivity. Not surprisingly the diastereomeric excess was lowest for the monosubstituted dihydro dioxine **1e** at 90%, with all other de values being greater than 95% as determined by yields and ^{1}H NMR integration. It was found in all cases that the major diastereomer occurred by anti addition of the 1,2-diol unit with respect to the substituents α to the

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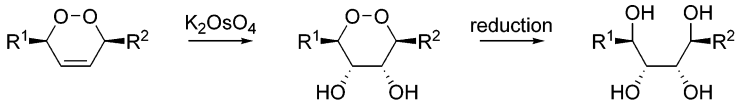
SCHEME 2



1a: R^1 = Me, R^2 = CH_2OH
1b: R^1 = Me, R^2 = $CH_2OTBDMS$
1c: R^1 = Me, R^2 = $(CH_2)_3OH$
1d: R^1 = Me, R^2 = $(CH_2)_3OTBDMS$
1e: R^1 = *c*-C_6H_{11}, R^2 = H
1f: R^1 = R^2 = *n*-Pr
1g: R^1 = R^2 = Me
1h: R^1 = R^2 = *c*-C_5H_9
1i: R^1 = R^2 = $CH_2OTBDMS$
1j: R^1 = R^2 = CH_2Br
1k: R^1 = R^2 = Ph

3b: R^1 = Me, R^2 = CH_2OH
3d: R^1 = Me, R^2 = $(CH_2)_3OH$
3e: R^1 = *c*-C_6H_{11}, R^2 = H
3f: R^1 = R^2 = *n*-Pr
3g: R^1 = R^2 = Me
3h: R^1 = R^2 = *c*-C_5H_9
3i: R^1 = R^2 = CH_2OH
3j: R^1 = R^2 = CH_2Br
3k: R^1 = R^2 = Ph

TABLE 2. Reduction of the Peroxide Bond of 2 To Give Tetraols and Polyols 3

entry	dioxane	method[a]	product (% yield)[b]
1	**2b**	A	**3b** (75)
2	**2d**	A	**3d** (69)
3	**2e**	A	**3e** (62)
4	**2f**	A	**3f** (72)
5	**2f**	B	**3f** (84)
6	**2f**	C	**3f** (69)
7	**2f**	D	**3f** (77)
8	**2f**	E	**3f** (66)
9	**2g**	A	**3g** (66)
10	**2h**	A	**3h** (73)
11	**2i**	A	**3i** (90)
12	**2j**	B	**3j** (84)
13	**2k**	B	**3k** (77)

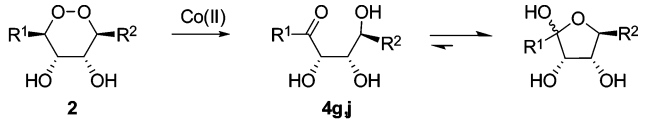
[a] See Experimental Section for reaction conditions. [b] Isolated yield after recrystallization.

TABLE 3. Ring-Opening of 1,2-Dioxanes 2 Using Co(II) Salen

entry[a]	dioxane	product, anomeric ratio[b]	isolated yield (%)
1	**2f**		*c*
2	**2g**	**4g**, 16:(45:39)	91
3	**2h**		*c*
4	**2j**	**4j**, 0:(51:49)	92
5	**2k**		*c*

[a] Reactions were performed in THF using 5 mol % of *N*,*N*′-bis(salicylidene)ethylenediaminocobalt(II). [b] Ratio was determined by ^{1}H NMR by dissolving the sample in deuterated solvent and allowing the mixture to equilibrate for 1 h before integrating the peak height. The individual anomers could not be unambiguously assigned. Furanose forms are in parentheses. [c] No isolable product was recovered.

SCHEME 3



2f: R^1 = R^2 = *n*-Pr
2g: R^1 = R^2 = Me
2h: R^1 = R^2 = *c*-C_5H_9
2j: R^1 = R^2 = CH_2Br
2k: R^1 = R^2 = Ph

peroxide linkage (Scheme 2). This is the expected stereochemistry given the preference for OsO_4 to add from the least hindered face,[17] and was verified by ^{1}H NMR coupling constants and through the synthesis of allitol and psicose. Surprisingly the peroxy diols were found to be moderately unstable at room temperature with decomposition evident after only a few days in some instances. The stability could be improved by keeping the diols in solvent or by storage below 0 °C with minimal evidence of decomposition in the neat samples after several weeks.

We next examined reduction of the peroxide linkage to generate stereospecific tetraol core structures (Table 2). There are several methods in the literature for peroxide reduction, including hydrogenation with metal catalysts,[18,19] $LiAlH_4$,[20] Zn/AcOH,[21] Mg/MeOH,[22] and thiourea. The latter has become a popular choice as a mild reductant for bicyclic peroxides.[23] Of these methods, reduction with Pd/C in the presence of H_2 (method A) proved to be the most convenient owing to the small amount of catalyst required, good yields, and ease of purification. It was also found that by using Pd/C in methanol both peroxide reduction and removal of the TBDMS group for compounds **2b**,**d**, and **i** could be accomplished in one pot, consistent with the literature.[24]

The exceptionally mild reducing conditions of zinc dust in acetic acid (method B) proved to be a useful alternative where incompatibilities with Pd/C arose, such as with the dibromo compound **2j** (entry 12). This allowed for the convenient synthesis of the previously unknown dibromo allitol, which could potentially be a potent anticancer agent, given the clinical use of the mannitol and galactitol versions.[25,26] The tetraols and polyols afforded by reduction were all crystalline and thus readily purified by recrystallization from methanol and ether

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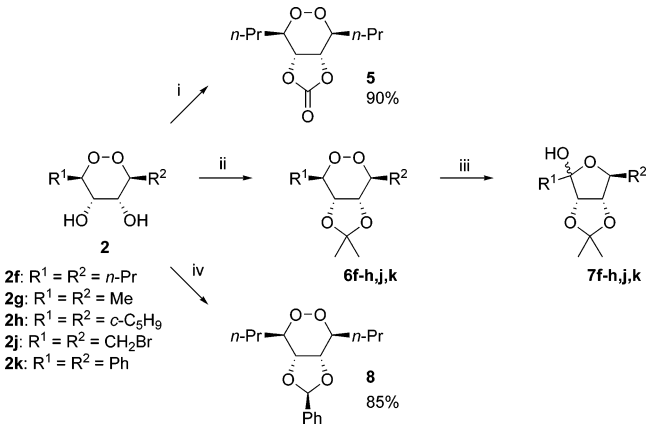
SCHEME 4[a]



[a] Reagents and conditions: (i) *N*,*N*′-carbonyldiimidazole, benzene, 1 h; (ii) $(CH_3)_2C(OCH_3)_2$, *p*-TSA, CH_2Cl_2, 1 h; (iii) Co(II)[SALEN]$_2$, THF, 3−12 h; $C_6H_6CH(OCH_3)_2$, *p*-TSA, CH_2Cl_2; 1 h.

or chloroform. The stereochemistry of the tetraol core formed by the dihydroxylation/reduction sequence was determined by assigning the structure of the meso hexitol **3i** as allitol by comparison with the ^{13}C NMR's of the hexitols and their hexaacetates.[27] Unambiguous determination was also afforded by X-ray analysis of the tetraol **3f** clearly showing the *R*,*R*,*S*,*S* stereochemistry (see Supporting Information).

A previous study by Taylor et al. showed that epoxy-1,2-dioxines can be homolytically ring-opened with Co(II) salen complexes to give stabilized 1,4-hydroxy ketones.[28] It was therefore of interest to extend this methodology to the peroxy diols described thus far. Initial attempts at ring-opening the free hydroxy compounds using 5 mol % of *N*,*N*′-bis(salicylidene)-ethylenediaminocobalt(II) gave mixed results (Table 3, Scheme 3). Compounds **2g**,**j** gave good yields of the hydroxy ketones which existed predominantly in the ring-closed furanose forms. The reactions of compounds **2f**,**h**,**k** showed complete consumption of starting material; however, no major products were recovered upon workup.

TABLE 4. Acetonide Protection of Diols 2 To Give 1,2-Dioxane Acetonides 6, Followed by Co(II) Salen Ring-Opening To Give Furanoses 7

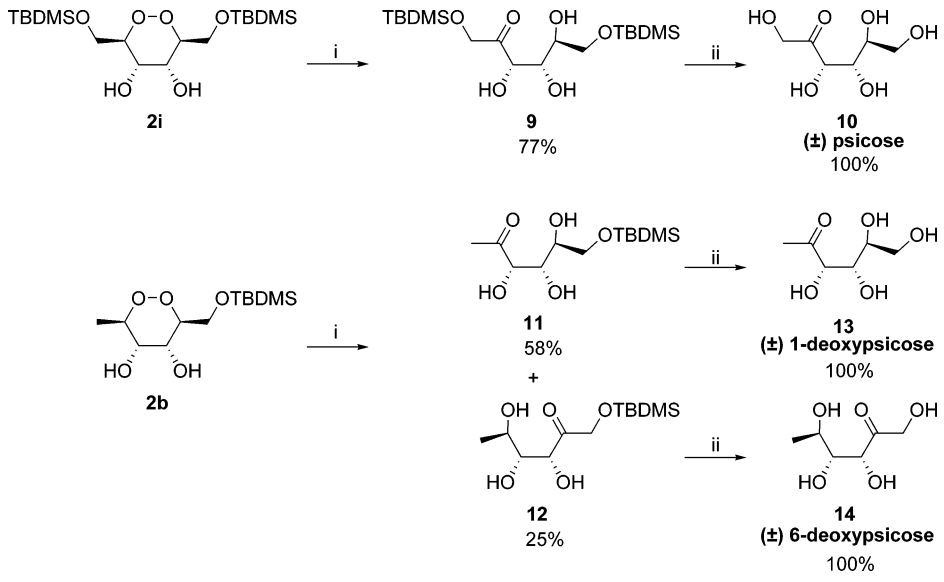
entry	1,2-dioxane[a]	product (% yield)	entry	1,2-dioxane acetonide[b]	product (% yield)	anomeric ratio[c]
1	**2f**	**6f** (91)	6	**6f**	**7f** (100)	70:30
2	**2g**	**6g** (87)	7	**6g**	**7g** (91)	53:47
3	**2h**	**6h** (98)	8	**6h**	**7h** (100)	75:25
4	**2j**	**6j** (93)	9	**6j**	**7j** (91)	95:5
5	**2k**	**6k** (94)	10	**6k**	**7k** (80)	80:20

[a] Reactions were typically performed on a 200 mg scale with 3 equiv of 2,2-DMP and 10 mol % TsOH in CH_2Cl_2. [b] Reactions were performed in THF using 5 mol % of *N*,*N*′-bis(salicylidene)ethylenediaminocobalt(II). [c] Ratio was determined by ^1H NMR by dissolving the sample in deuterated solvent and allowing the mixture to equilibrate for 1 h before integrating the peak height. The individual anomers could not be unambiguously assigned.

Given the moderate instability of the peroxy diols and the mixed results of the Co(II) ring-opening of them, it was decided to investigate whether acetal protection of the 1,2-diols would have any effect on stability (Scheme 4). Acetonide protection was found to occur rapidly and in high yield (Table 4) with no apparent decomposition of the peroxide linkage. Interestingly, the addition of the acetonide group was also found to dramatically increase stability over the free diols, with the neat protected 1,2-dioxanes being stable at room temperature for months with no evidence of decomposition. Both carbonate and benzylidene acetals were also found to form rapidly in good yield to give **5** and **8**; however, the benzylidene acetal was found to be labile over a period of days.

Co(II) ring-opening of the acetonide protected dioxanes **6** gave the desired hydroxy ketones **7** in excellent yields (Table 4). As with the 1,2-dioxanes, acetonide protection of the hydroxy ketones resulted in a dramatic increase in stability, with all of products being stable at room temperature for months with no detectable decomposition. All of the hydroxy ketones **7** formed were found to exist solely in their cyclic furanose forms, both in solution as indicated by NMR (Table 4), and in their neat form as indicated by an absence of a carbonyl stretch in the IR spectra.

SCHEME 5[a]



[a] Reagents and conditions: (i) Co(II)[SALEN]$_2$, THF, 3−12 h; (ii) 3:2 AcOH/H_2O, 16 h.

TABLE 5. Asymmetric Ring-Opening of *meso*-1,2-Dioxanes 6k and 2i

entry[a]	1,2-dioxane	ee[d]
1	**6k**[b]	20
2	**6k**[c]	20
3	**2i**[b]	26
4	**2i**[c]	26

[a] Reactions were performed in THF (2 mL) on a 30 mg scale using 5 mol % of Co(II) catalyst. [b] Catalyst used was (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II). [c] Catalyst used was (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II). [d] Ratio was determined by chiral shift NMR using europium tris[3-(heptafluoropropylhydroxymethylene)]-(+)-camphorate in $CDCl_3$.

By utilizing the osmium tetroxide catalyzed dihydroxylation of 1,2-dioxines, it was envisaged that the rare sugar psicose as well as 1-deoxypsicose could be readily made from the Co(II) ring-opening of the peroxy diols. It was initially decided to try Co(II) ring-opening on the free diols for efficiency which yielded the TBDMS protected hydroxy ketones (Scheme 5). Silyl deprotection with aqueous acetic acid afforded the racemic keto sugars in good yields which showed NMR spectra identical to those found in the literature.[29−31]

Taylor and others have previously established that 1,2-dioxines could be asymmetrically ring opened using chiral Co(II) catalysts to give optically enriched hydroxy ketones.[3,24] It therefore follows that the peroxy diols described herein should also be amenable to asymmetric ring-opening with the same catalysts. Preliminary results using the commercially available Co(II) Jacobsen catalyst are tabulated in Table 5. It was found that both acetonide protected **6k** and free diol **2i** derivatives showed moderate selectivity with the Jacobsen catalyst, which should be improved using the previously described catalysts that are customed to 1,2-dioxine ring-opening.[5,28] The ring-opening of **2i** to give optically enriched *D*- and *L*-psicose shows that the synthesis of optically enriched sugars from 1,2-dioxines is possible.

Conclusion

In summary, peroxy diols **2** can be readily prepared from 3,6-dihydro-1,2-dioxines **1** in high yield and excellent de. Facile reduction of the peroxide bond under a range of conditions allows for a synthetically viable route to stereospecific tetraols without the use of protecting groups. Ring-opening of the peroxy diols, and their considerably more stable acetonide derivatives, afforded novel hydroxy ketones in excellent yields, providing a useful pathway to keto-sugars such as psicose and its derivatives. Preliminary work applying chiral Co(II) Jacobsen complexes to the ring-opening of *meso*-peroxy diols gave some asymmetric induction, meaning with appropriate chiral Co(II) complexes highly enantioselective synthesis of sugar type hydroxy ketones is feasible.

Experimental Section

General Methods for Dihydroxylation of 1,2-Dioxines. Method A. To a stirred solution of *t*-BuOH (5 mL) and water (5 mL) was added AD mix (2.8 g) and methane sulfonamide (1 mmol), followed by 1,2-dioxine (1 mmol). The mixture was stirred rapidly until complete by TLC. The reaction mixture was extracted with CH_2Cl_2 or ethyl acetate (4 × 50 mL), dried (Na_2SO_4), concentrated in vacuo, and the product was subjected to flash chromatography to yield the product peroxy diol.

Method B. To a stirred solution of *t*-BuOH (5 mL) and water (5 mL) was added K_2OsO_4 (0.5 mol %), $K_3Fe(CN)_6$ (3 mmol), K_2CO_3 (3 mmol), and methane sulfonamide (1 mmol), followed by 1,2-dioxine (1 mmol), The mixture was stirred rapidly until complete by TLC. The workup was as per method A.

Method C. To a stirred solution of K_2OsO_4 (0.5 mol %) and NMO (1 mmol) in acetone (10 mL) was added 1,2-dioxine (1 mmol). The mixture was stirred rapidly until complete by TLC. The workup was as per method A.

Method D. To a stirred solution of 1,2-dioxine (1 mmol) in *t*-BuOH or CH_3CN (5 mL) and water (5 mL) was added K_2OsO_4 (0.5 mol %) and citric acid (2 mmol), followed by NMO (1.1 mmol). The mixture was stirred rapidly until complete by TLC. The workup was as per method A.

Method E. To a stirred solution of 1,2-dioxine (1 mmol) in CH_3CN (5 mL) and water (5 mL) was added K_2OsO_4 (0.5 mol %) and $KClO_3$ (3 mmol). The mixture was stirred rapidly until complete by TLC. The workup was as per method A.

(±)-(3*S*,4*R*,5*S*,6*R*)-3-([1-(*tert*-Butyl)-1,1-dimethylsilyl]oxymethyl)-6-methyl-1,2-dioxane-4,5-diol (2b). Colorless solid (458 mg); mp 69−70 °C; R_f = 0.25 (2:3 ethyl acetate/hexane). IR (neat): 3401, 1472, 1255, 1123, 838, 779 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.09 (s, 6H), 0.90 (s, 9H), 1.36 (d, J = 6.6 Hz, 3H), 2.53 (br s, 1H), 2.76 (br s, 1H), 3.69 (dd, J = 4.8, 4.2 Hz, 1H), 3.82 (dd, J = 11.1, 6.6 Hz, 1H), 3.95 (dd, J = 11.1, 5.4 Hz, 1H), 4.01 (dd, J = 6.0, 4.2 Hz, 1H), 4.24 (ddd, J = 6.6, 6.0, 5.4 Hz, 1H), 4.31 (dq, J = 6.6, 4.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.6, −5.5, 15.2, 18.2, 25.8, 61.6, 65.4, 69.1, 80.1, 82.9. MS *m*/*z* (+EI): 279 (M^+ + H, 100), 261 (61), 243 (12), 173 (12), 159 (14), 117 (13). HRMS calcd for (M^+ + Na) $C_{12}H_{26}O_5$-SiNa, 301.1447; found, 301.1439.

(±)-(3*S*,4*R*,5*S*,6*R*)-3-(3-Hydroxypropyl)-6-methyl-1,2-dioxane-4,5-diol (2c). Colorless solid (80 mg); mp 76.5−78.5 °C (ethyl acetate); R_f = 0.28 (19:1 ethyl acetate/methanol). IR (Nujol) 3392, 3342, 1419, 1363, 1074, 1049, 923 cm^{-1}. ^1H NMR (600 MHz, d_6 DMSO): δ 1.13 (d, J = 6.6 Hz, 3H), 1.37−1.44 (m, 1H), 1.49−1.59 (m, 2H), 1.60−1.67 (m, 1H), 3.36−3.38 (m, 2H), 3.40 (ddd, J = 6.6, 6.0, 3.6 Hz, 1H), 3.50 (ddd, J = 5.4, 4.8, 3.6 Hz, 1H), 3.96 (dddd, J = 4.8, 4.8, 4.2, 4.2 Hz, 1H), 4.14 (dq, J = 6.6, 6.6 Hz, 1H), 4.37 (t, J = 5.4 Hz, OH), 4.70 (d, J = 5.4 Hz, OH), 4.71 (d, J = 6.0 Hz, OH). ^{13}C NMR (150 MHz, d_6 DMSO): δ 15.2, 26.6, 28.8, 60.5, 67.2, 68.4, 78.8, 84.0. MS *m*/*z* (+EI): 193 (M^+ + H, 18), 175 (64), 87 (50), 71 (90), 60 (85), 43 (100). HRMS calcd for (M^+ + Na) $C_8H_{16}O_5Na$, 215.0895; found, 215.0899.

(±)-(3*S*,4*R*,5*S*,6*R*)-3-(3-[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxypropyl)-6-methyl-1,2-dioxane-4,5-diol (2d). Colorless oil (301 mg); R_f = 0.27 (2:3 ethyl acetate/hexane). IR (neat) 3401, 1472, 1256, 1100, 1061, 837, 776 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.90 (s, 9H), 1.33 (d, J = 6.6 Hz, 3H), 1.52−1.68 (m, 1H), 1.70−1.83 (m, 3H), 2.40 (br s, 2H), 3.60−3.70 (m, 3H), 3.75 (dd, J = 4.8, 3.6 Hz, 1H), 4.14 (dd, J = 11.7, 6.3 Hz, 1H), 4.27 (dq, J = 6.6, 6.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.3, 15.2, 18.3, 25.8, 25.9, 28.7, 62.6, 68.3, 69.2, 79.5, 84.3. MS *m*/*z* (+EI): 307 (M^+ + H, 82), 271 (13), 203 (7), 187 (18), 157 (14), 145 (100). HRMS calcd for (M^+ + Na) $C_{14}H_{30}O_5SiNa$, 329.1760; found, 329.1753.

(±)-(3*R*,4*S*,5*S*)-3-Cyclohexyl-1,2-dioxane-4,5-diol (2e). Colorless solid (183 mg); mp 78−80 °C; R_f = 0.27 (1:1 ethyl acetate/hexane). IR (Nujol) 3459, 3299, 1078, 1060, 1044, 988, 890 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 1.04−1.40 (m, 5H), 1.63−1.83 (m, 6H), 2.36 (br s, 2H), 3.82 (dd, J = 8.4, 3.6 Hz, 1H), 3.96 (ddd, J = 3.6, 3.6, 1.8 Hz, 1H), 4.00 (dd, J = 8.4, 3.6 Hz, 1H), 4.21 (dd, J = 13.2, 3.6 Hz, 1H), 4.36 (dd, J = 13.2, 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 26.3, 26.4, 26.5, 30.1, 37.3, 66.0, 66.3,

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75.8, 86.1. MS *m*/*z* (+EI): 202 (M^+, 2), 186 (8), 150 (7), 95 (95), 83 (100), 60 (79). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.06; H, 8.87.

(±)-(3*R*,4*S*,5*R*,6*S*)-3,6-Dipropyl-1,2-dioxane-4,5-diol (2f). Amorphous solid (223 mg); mp 76 °C; R_f = 0.28 (2:3 ethyl acetate/hexane). IR (Nujol): 3351, 1300, 1277, 1085, 1068, 1037, 1028 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.95 (t, J = 7.2 Hz, 6H), 1.36−1.45 (m, 2H), 1.51−1.60 (m, 2H), 1.62−1.72 (m, 4H), 2.19 (br s, 2H), 3.66−3.69 (m, 2H), 4.09−4.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 18.9, 31.4, 68.2, 83.8. MS *m*/*z* (+EI): 205 (M^+ + H, 2), 187 (9), 171 (7), 145 (14), 115 (42), 60 (80), 43 (100). Anal. Calcd for $C_{10}H_{20}O_4$: C, 58.80; H, 9.87. Found: C, 58.90; H, 9.88.

(±)-(3*R*,4*S*,5*R*,6*S*)-3,6-Dimethyl-1,2-dioxane-4,5-diol (2g). Colorless oil (616 mg); R_f = 0.39 (7:3 ethyl acetate/hexane). IR (neat): 3418, 1378, 1241, 1087, 1014, 972 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.37 (d, J = 6.6 Hz, 6H), 2.44 (br s, 2H), 3.67 (d, J = 5.1 Hz, 2H), 4.29 (dq, J = 6.6, 5.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.2, 69.1, 80.0. MS *m*/*z* (+EI): 149 (M^+ + H, 6), 131 (12), 117 (18), 85 (33), 60 (100). HRMS calcd for (M^+ + Na) $C_6H_{12}O_4Na$, 171.0633; found, 171.0631.

(±)-(3*R*,4*S*,5*R*,6*S*)-3,6-Dicyclopentyl-1,2-dioxane-4,5-diol (2h). White solid (616 mg); mp 117−118 °C; R_f = 0.39 (2:3 ethyl acetate/hexane). IR (Nujol): 3307, 1337, 1077, 1050, 1007 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.32−1.46 (m, 4H), 1.50−1.71 (m, 8H), 1.73−1.90 (m, 4H), 2.31 (sext, J = 8.4 Hz, 2H), 2.38 (d, J = 8.4 Hz, 2H), 3.79−3.93 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.2, 25.6, 28.3, 29.2, 39.3, 67.7, 87.3. MS *m*/*z* (+EI): 257 (M^+ + H, 2), 189 (28), 158 (23), 145 (56), 131 (50), 108 (100). Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.60; H, 9.42.

(±)-(3*R*,4*S*,5*R*,6*S*)-3,6-Di([1-(*tert*-butyl)-1,1-dimethylsilyl]oxymethyl)-1,2-dioxane-4,5-diol (2i). Colorless oil (533 mg); R_f = 0.38 (3:7 ethyl acetate/hexane). IR (neat): 3403, 1472, 1361, 1256, 1128, 1005, 838 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.079 (s, 6H), 0.082 (s, 6H), 0.90 (s, 18H), 2.45 (br s, 2H), 3.81 (dd, J = 11.0, 6.0 Hz, 2H), 3.95 (dd, J = 11.0, 5.4 Hz, 2H), 4.03−4.05 m (2H), 4.23−4.26 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.6, −5.5, 18.2, 25.8, 61.3, 65.3, 83.3. MS *m*/*z* (+EI): 409 (M^+ + H, 2), 315 (31), 299 (23), 201 (48), 117 (69), 89 (93), 73 (100). HRMS calcd for (M^+ + Na) $C_{18}H_{40}O_6Si_2Na$, 431.2261; found, 431.2254.

(±)-(3*R*,4*R*,5*S*,6*S*)-3,6-Di(bromomethyl)-1,2-dioxane-4,5-diol (2j). White solid (710 mg); mp 115−118 °C (dec); R_f = 0.33 (1:1 ethyl acetate/hexane). IR (Nujol): 3495, 3360, 1418, 1336, 1232, 1048 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/d_6 DMSO): δ 3.65 (d, J = 5.7 Hz, 4H), 3.78 (br s, 2H), 3.97−4.02 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$/d_6 DMSO): δ 28.9, 65.3, 82.7. MS *m*/*z* (+EI): 307 (M^+ + H, 3), 200 (8), 179 (27), 156 (45), 72 (100). Anal. Calcd for $C_6H_{10}O_4Br_2$: C, 23.55; H, 3.29. Found: C, 23.66; H, 3.44.

(±)-(3*R*,4*S*,5*R*,6*S*)-3,6-Diphenyl-1,2-dioxane-4,5-diol (2k). White solid (320 mg); R_f = 0.22 (2:3 ethyl acetate/hexane). IR (Nujol) 3345, 1495, 1341, 1098, 1048, 949 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.56 (br s, 2H), 4.28 (d, J = 5.4 Hz, 2H), 5.39 (d, J = 5.4 Hz, 2H), 7.34−7.44 (m, 10H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 68.5, 84.6, 127.2, 128.6, 128.7, 135.7. HRMS calcd for (M^+ + Na) $C_{16}H_{16}O_4Na$, 295.0946; found, 295.0940.

General Methods for Peroxide Reduction. Method A. To a stirred solution of 1,2-dioxine (1 mmol) in methanol (5 mL) was added 10% w/w of 5% palladium on carbon, and the mixture stirred overnight under a hydrogen atmosphere. The suspension was then filtered through kenite washing with methanol, and the solvent was removed in vacuo giving the crude polyol, which was readily recrystallized from methanol/ether or methanol/chloroform.

Method B. To a stirred solution of 1,2-dioxine (1 mmol) in acetic acid (5 mL) was added zinc dust (5 mmol), and the mixture was rapidly stirred for 24 h. The acetic acid was removed in vacuo, and the solids triturated with THF. The triturate was then recrystallized as per method A.

Method C. As per method A except 10% platinum on carbon was used.

Method D. To a stirred solution of 1,2-dioxine (1 mmol) in methanol (5 mL) was added magnesium turnings (5 mmol) and catalytic iodine. The reaction mixture was heated gently until the iodine color faded and then stirred rapidly for 24 h. The solvent was removed in vacuo, and the solids triturated with THF. The triturate was then recrystallized as per method A.

Method E. To a stirred solution of 1,2-dioxine (1 mmol) in methanol (5 mL) was added thiourea (5 mmol), and the mixture rapidly stirred until complete by TLC (ca. 3−5 days). The solvent was removed in vacuo, and the residue purified by flash chromatography to give the polyol product.

(±)-1-Deoxyallitol (3b). Colorless needles (58 mg); mp 106−108 °C; R_f = 0.40 (7:3 dichloromethane/methanol). IR (Nujol) 3306, 3188, 1333, 1118, 1068, 997 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ 1.21 (d, J = 6.3 Hz, 3H), 3.55 (dd, J = 6.6, 5.4 Hz, 1H), 3.60−3.68 (m, 2H), 3.74−3.84 (m, 2H), 3.93 (dq, J = 6.3, 5.4 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 18.4, 64.3, 69.9, 74.6, 74.6, 77.3. MS *m*/*z* (+EI): 167 (M^+ + H, 5), 131 (8), 117 (20), 103 (14), 73 (100). Anal. Calcd for $C_6H_{14}O_5$: C, 43.37; H, 8.49. Found: C, 43.07; H, 8.68.

(±)-(4*S*,5*S*,6*R*,7*R*)Octane-1,4,5,6,7-pentaol (3d). Colorless solid (80 mg); mp 108.5−109.5 °C; R_f = 0.19 (4:1 CH_2Cl_2/methanol). IR (Nujol) 3249, 1338, 1057, 1048, 998, 974 cm^{-1}. ^1H NMR (600 MHz, CD_3OD): δ 1.19 (d, J = 6.6 Hz, 3H), 1.45−1.52 (m, 1H), 1.56−1.64 (m, 1H), 1.71−1.81 (m, 2H), 3.46 (dd, J = 7.5, 5.1 Hz, 1H), 3.49 (dd, J = 7.5, 4.8 Hz, 1H), 3.59 (dd, J = 6.6, 6.0 Hz, 2H), 3.74 (ddd, J = 9.5, 5.1, 2.4 Hz, 1H), 3.93 (dq, J = 6.6, 4.8 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 18.0, 29.3, 30.1, 63.3, 70.0, 74.2, 76.7, 77.2. MS *m*/*z* (+EI): 194 (M^+, 8), 191 (11), 147 (29), 124 (15), 68 (100). Anal. Calcd for $C_8H_{18}O_5$: C, 49.47; H, 9.34. Found: C, 49.25; H, 9.27.

(±)-(1*R*,2*R*,3*S*)-1-Cyclohexylbutane-1,2,3,4-tetraol (3e). Amorphous solid (75 mg); mp 133−134 °C; R_f 0.36 (17:3 CH_2Cl_2/methanol). IR (Nujol): 3369, 3227, 1089, 1070, 1050, 1015, 947 cm^{-1}. ^1H NMR (600 MHz, CD_3OD): δ 1.12−1.38 (m, 5H), 1.54−1.58 (m, 1H), 1.64−1.72 (m, 2H), 1.74−1.81 (m, 3H), 3.40 (dd, J = 8.4, 3.6 Hz, 1H), 3.59 (dd, J 8.4, 5.4 Hz, 1H), 3.63 (dd, J = 12.6, 7.2 Hz, 1H), 3.75−3.78 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 27.0, 27.6, 27.9, 28.0, 31.6, 40.8, 64.3, 72.9, 75.3, 78.6. MS *m*/*z* (+EI): 205 (M^+ + H, 45), 187 (49), 169 (52), 151 (36), 113 (34), 95 (100). Anal. Calcd for $C_{10}H_{20}O_4$: C, 58.80; H, 9.87. Found: C, 58.85; H, 9.69.

(±)-(4*R*,5*R*,6*S*,7*S*)Decane-4,5,6,7-tetraol (3f). Colorless crystals (62 mg); mp 176 °C. IR (Nujol): 3370, 1325, 1211, 1064, 1026, 980 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ 0.94 (t, J = 7.2 Hz, 6H), 1.30−1.68 (m, 8H), 3.46−3.52 (m, 2H), 3.70−3.76 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 14.7, 20.0, 32.2, 74.0, 76.8. MS *m*/*z* (+EI): 207 (M^+ + H, 17), 189 (5), 99 (21), 70 (100), 57 (45), 44 (66). Anal. Calcd for $C_{10}H_{22}O_4$: C, 58.23; H, 10.75. Found: C, 57.94; H, 10.51.

(±)-1,6-Dideoxyallitol (3g). Colorless needles (100 mg); mp 177−178 °C (lit[32] 178 °C); R_f = 0.20 (17:3 CH_2Cl_2/methanol). IR (Nujol): 3294, 3207, 1341, 1125, 1056, 999 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ 1.19 (d, J = 6.3 Hz, 6H), 3.40−3.46 (m, 2H), 3.90−3.99 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 17.6, 69.9, 77.0. MS *m*/*z* (+EI): 155 (M^+ + H, 100), 133 (73), 115 (97), 97 (85), 57 (88).

(±)-(1R,2R,3S,4S)-1,4-Dicyclopentylbutane-1,2,3,4-tetraol (3h). Colorless flakes (110 mg); mp 203−205 °C; R_f = 0.56 (17:3 CH_2Cl_2/methanol). IR (Nujol): 3398, 3260, 1329, 1284, 1055, 1021 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ 1.38−1.80 (m, 16H), 2.19−2.32 (m, 2H), 3.61−3.71 (m, 4H). ^{13}C NMR (75 MHz, CD_3OD): δ 26.6, 26.7, 27.6, 30.1, 43.1, 76.1, 76.5. MS *m*/*z* (+EI): 259 (M+

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+ H, 20), 223 (100), 205 (57), 111 (41), 81 (40), 73 (56). Anal. Calcd for C14H26O4: C, 65.09; H, 10.14. Found: C, 65.10; H, 10.26.

(±)-Allitol (3i). Colorless crystals (78 mg); mp 149−150.5 °C (lit 150 °C[33]). ^{13}C NMR (75 MHz, D_2O): δ 65.0, 74.9, 75.0.

(±)-1,6-Dibromo-1,6-dideoxyallitol (3j). Colorless cubes (170 mg); mp 119−121 °C; R_f = 0.26 (9:1 CH_2Cl_2/methanol). IR (Nujol): 3344, 1338, 1290, 1056, 1016 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD): δ 3.55 (dd, J = 10.8, 7.2 Hz, 2H), 3.72 (dd, J = 10.8, 3.0 Hz, 2H), 3.71−3.77 (m, 2H), 3.93−4.00 (m, 2H), 4.63 (br s, 4H). ^{13}C NMR (75 MHz, CD_3OD): δ 37.7, 73.4, 75.0. MS *m*/*z* (+EI): 308 (M^+, 10), 208 (21), 123 (22), 103 (81), 73 (90), 57 (100). Anal. Calcd for $C_6H_{12}O_4Br_2$: C, 23.40; H, 3.93. Found: C, 23.60; H, 3.92.

(±)-(1*R*,2*R*,3*S*,4*S*)-1,4-Diphenylbutane-1,2,3,4-tetraol (3k). Colorless needles (96 mg); mp 175−176.5 °C. IR (Nujol): 3321, 1496, 1338, 1309, 1075, 1040 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD): δ 3.59−3.65 (m, 2H), 4.84 (dd, J = 3.3, 1.5 Hz, 2H), 7.22−7.35 (m, 6H), 7.41−7.46 (m, 4H). ^{13}C NMR (75 MHz, CD_3OD): δ 76.4, 76.8, 128.6, 129.0, 129.2, 142.6. MS *m*/*z* (+EI): no molecular ion, 150 (19), 132 (68), 131 (47), 107 (68), 79 (100), 77 (47). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.23; H, 6.57.

General Procedure for the Ring-Opening of 1,2-Dioxines using Co(II) Salen. To a stirred solution of *N*,*N*′-bis(salicylidene)-ethylenediaminocobalt(II) in THF (5 mL) at ambient temperature was added 1,2-dioxine (1 mmol), and the reaction mixture was left to stir until complete by TLC (∼16 h). All volatiles were then removed in vacuo, and the product was purified by flash chromatography.

(±)-1,6-Dideoxy psicose (4g). Keto Anomer. Colorless oil (56 mg); R_f = 0.27 (ethyl acetate). IR (neat): 3388, 1713, 1455, 1380, 1130, 1072, 921 cm^{-1}. ^{1}H NMR (600 MHz, CD_3OD): δ 1.21 (d, J = 6.6 Hz, 3H), 2.22 (s, 3H), 3.63 (dd, J = 7.2, 4.8, 1H), 3.83 (dq, J = 7.2, 6.6 Hz, 1H), 4.12 (d, J = 4.8 Hz, 1H). ^{13}C NMR (150 MHz, CD_3OD): δ 20.3, 27.6, 68.4, 78.9, 80.8, 212.3. MS *m*/*z* (+EI): 149 (M^+ + H, 11), 131 (100), 113 (15), 87 (27), 74 (36), 71 (68). HRMS calcd for (M^+ + Na) $C_6H_{12}O_4Na$, 171.0633; found, 171.0632.

Major Anomer. ^{1}H NMR (600 MHz, CD_3OD): δ 1.20 (d, J = 6.6 Hz, 3H), 1.38 (s, 3H), 3.64 (dd, J = 6.0, 4.8 Hz, 1H), 3.96 (dq, J = 6.6, 4.8 Hz, 1H), 3.74 (d, J = 6.0 Hz, 1H). ^{13}C NMR (150 MHz, CD_3OD): δ 19.8, 26.2, 76.2, 77.6, 79.9, 103.9.

Minor Anomer. ^{1}H NMR (600 MHz, CD_3OD): δ1.29 (d, J = 6.0 Hz, 1H), 1.40 (s, 3H), 3.70 (d, J = 4.8 Hz, 1H), 3.88 (dq, J = 7.8, 6.0 Hz, 1H), 4.03 (dd, J = 7.8, 4.8 Hz, 1H). ^{13}C NMR (150 MHz, CD_3OD): δ 21.2, 23.3, 78.7, 78.8, 79.9, 107.3.

(±)-1,6-Dibromo-1,6-dideoxy Psicose (4j). Major Anomer. Colorless solid (92 mg); mp 59−60 °C (dec); R_f = 0.23 (1:1 ethyl acetate/hexane). IR (Nujol): 3343, 1237, 1193, 1129, 1065, 1008 cm^{-1}. ^{1}H NMR (600 MHz, CD_3OD): δ 3.45 (d, J = 10.2 Hz, 1H), 3.49 (dd, J = 10.5, 7.2 Hz, 1H), 3.61 (dd, J = 10.5, 4.2 Hz, 1H), 3.70 (d, J = 10.2 Hz, 1H), 3.94 (d, J = 4.2 Hz, 1H), 4.08 (ddd, J = 7.2, 7.2, 4.2 Hz, 1H), 4.26 (dd, J = 7.2, 4.2 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 33.7, 35.5, 72.9, 75.7, 84.2, 106.3. MS *m*/*z* (+EI): 306 (M^+, 4), 269 (8), 254 (33), 191 (10), 149 (17), 80 (100). HRMS calcd for (M^+ + Na) $C_6H_{10}O_4Br_2Na$, 326.8844; found, 326.8836.

Minor Anomer. ^{1}H NMR (600 MHz, CD_3OD): δ 3.49 (s, 2H), 3.50 (dd, J = 10.8, 5.4 Hz, 1H), 3.58 (dd, J = 10.8, 4.8 Hz, 1H), 4.01 (dd, J = 6.0, 5.4 Hz, 1H), 4.11−4.14 (m, 2H). ^{13}C NMR (150 MHz, CD_3OD): δ 35.1, 35.8, 74.1, 76.6, 83.1, 103.2.

(±)-(3a*R*,4*S*,7*R*,7a*S*)-4,7-Dipropylperhydro[1,3]dioxolo[4,5-*d*]-[1,2]dioxin-2-one (5). To a stirred solution of **2f** (110 mg, 0.73 mmol) in dry benzene (5 mL) was added *N*,*N*-carbonyldiimidazole (175 mg, 1.08 mmol), and the mixture was stirred under a nitrogen atmosphere until complete by TLC (∼1 h). The reaction mixture was diluted with ether (50 mL), washed with water (4 × 20 mL), dried (Na_2SO_4), and concentrated in vacuo, and the product was subjected to flash chromatography to yield the title compound (112 mg) as a colorless oil; R_f = 0.22 (3:2 CH_2Cl_2/hexane). IR (neat) 1808, 1466, 1381, 1303, 1173, 1135, 1056 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 7.2 Hz, 6H), 1.38−1.78 (m, 8H), 4.24−4.30 (m, 2H), 4.48−4.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 18.4, 32.6, 74.3, 79.7, 153.7. MS *m*/*z* (+EI): 231 (M^+ + H, 69), 97 (37), 87 (59), 71 (94), 55 (100). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.65; H, 7.92.

General Procedure for the Acetonide Protection of Diols 2f−h, j,k. To a stirred solution of 1,2-dioxine (1 mmol) in dry CH_2Cl_2 (5 mL) was added 2,2-dimethoxypropane (3 mmol) followed by *p*-toluenesulfonic acid (10 mol %), and the solution was stirred under nitrogen until complete by TLC (∼1 h). The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with saturated $NaHCO_3$ (20 mL), and dried (Na_2SO_4), and the solvent was removed in vacuo. The residue was then purified by flash chromatography.

(±)-(3a*R*,4*S*,7*R*,7a*S*)-2,2-Dimethyl-4,7-dipropylperhydro[1,3]-dioxolo[4,5-*d*][1,2]dioxine (6f). Colorless oil (271 mg); R_f = 0.30 (1:1 CH_2Cl_2/hexane). IR (neat) 1460, 1382, 1247, 1220, 1066, 869 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (t, J = 7.2 Hz, 6H), 1.37 (s, 3H), 1.39−1.70 (m, 8H), 1.53 (s, 3H), 3.95−4.00 (m, 2H), 4.13−4.19 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 18.8, 26.3, 28.1, 33.1, 73.8, 81.0, 109.2. MS *m*/*z* (+EI): 245 (M^+ + H, 15), 229 (65), 143 (68), 129 (61), 101 (90), 55 (100). Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 63.61; H, 9.72.

(±)-(3a*R*,4*S*,7*R*,7a*S*)-2,2,4,7-Tetramethylperhydro[1,3]dioxolo-[4,5-*d*][1,2]dioxine (6g). Colorless solid (331 mg); mp 47−48 °C; R_f = 0.33 (CH_2Cl_2). IR (Nujol): 1248, 1220, 1153, 1069, 864 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (d, J = 6.6 Hz, 6H), 1.37 (s, 3H), 1.52 (s, 3H), 3.94−3.99 (m, 2H), 4.27−4.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.7, 26.3, 28.1, 74.5, 77.6, 109.4. MS *m*/*z* (+EI): 189 (M^+ + H, 29), 173 (68), 129 (32), 100 (31), 85 (100). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.49; H, 8.65.

(±)-(3a*R*,4*S*,7*R*,7a*S*)-4,7-Dicyclopentyl-2,2-dimethylperhydro-[1,3]dioxolo[4,5-*d*][1,2]dioxine (6h). Colorless solid (340 mg); mp 73−74 °C; R_f = 0.33 (1:1 CH_2Cl_2/hexane). IR (Nujol): 1245, 1221, 1156, 1063, 1023 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (s, 3H), 1.40−1.50 (m, 4H), 1.51−1.70 (m, 8H), 1.53 (s, 3H), 1.73−1.90 (m, 4H), 2.11 (sext, J = 8.4 Hz, 2H), 3.87−3.94 (m, 2H), 4.09−4.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.1, 25.5, 26.4, 28.1, 29.1, 29.2, 41.2, 73.2, 85.1, 109.0. MS *m*/*z* (+EI): 297 (M^+ + H, 23), 279 (39), 239 (28), 132 (60), 92 (77), 41 (100). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.88; H, 9.59.

(±)-(3a*R*,4*R*,7*S*,7a*S*)-4,7-Di(bromomethyl)-2,2-dimethyl-perhydro[1,3]dioxolo[4,5-*d*][1,2]dioxine (6j). Colorless needles (220 mg); mp 79−80 °C; R_f = 0.31 (1:1 CH_2Cl_2/hexane). IR (Nujol): 1421, 1251, 1220, 1153, 1071, 1044 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (s, 3H), 1.54 (s, 3H), 3.54−3.65 (m, 4H), 4.37−4.43 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 27.9, 29.3, 70.7, 80.8, 110.4. MS *m*/*z* (+EI): 346 (M^+, 4), 330 (17), 127 (19), 85 (46), 59 (42), 43 (100). Anal. Calcd. for $C_9H_{14}O_4Br_2$: C, 31.24; H, 4.08. Found: C, 31.45; H, 4.26.

(±)-(3a*R*,4*S*,7*R*,7a*S*)-2,2-Dimethyl-4,7-diphenylperhydro[1,3]-dioxolo[4,5-*d*][1,2]dioxine (6k). Colorless solid (113 mg); mp 126−127 °C; R_f = 0.45 (3:2 CH_2Cl_2/hexane). IR (Nujol) 1496, 1244, 1221, 1071, 880, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H), 1.69 (s, 3H), 4.57−4.62 (m, 2H), 5.34−5.39 (m, 2H), 7.31−7.47 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 28.3, 74.3, 83.1, 109.6, 127.3, 128.5, 128.6, 137.0. MS *m*/*z* (+EI): 313 (M^+ + H, 11), 296 (43), 237 (15), 219 (26), 100 (100), 85 (97). Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.27; H, 6.42.

(±)-(3a*S*,6*S*,6a*S*)-2,2-Dimethyl-4,6-dipropylperhydrofuro[3,4-*d*][1,3]dioxol-4-ol (7f). Major Anomer. White solid (75 mg); mp 57.5−58.5 °C; R_f = 0.22 (1:9 ethyl acetate/hexane). IR (neat) 3462,

(33) Coffey, S. *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Elsevier Publishing Company: Amsterdam, The Netherlands, 1967; Vol. 1F, p 19.

1463, 1374, 1210, 1072, 878 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.92 (m, 6H), 1.38 (s, 3H), 1.39−1.71 (m, 7H), 1.59 (s, 3H), 1.75 (ddd, J = 13.4, 11.4, 4.8 Hz, 1H), 3.95 (br s, 1H), 3.99 (ddd, J = 7.2, 6.6, 5.4 Hz, 1H), 4.33 (dd, J = 7.2, 5.4 Hz, 1H), 4.43 (d, J = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 14.2, 16.9, 18.7, 25.1, 26.6, 35.4, 41.3, 80.7, 83.2, 84.6, 102.1, 112.3. MS *m*/*z* (+EI): 245 (M^+ + H, 1), 227 (82), 187 (50), 141 (21), 98 (25), 86 (100). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 64.17; H, 9.90.

Minor Anomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.92−0.98 (m, 6H), 1.33 (s, 3H), 1.39−1.71 (m, 7H), 1.49 (s, 3H), 1.85 (ddd, J = 13.7, 10.5, 5.4 Hz, 1H), 2.0 (br s, 1H), 4.06 (ddd, J = 7.8, 7.2, 1.8 Hz, 1H), 4.49 (d, J = 6.0 Hz, 1H), 4.60 (dd, J = 6.0, 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.8, 14.3, 16.7, 19.3, 25.1, 26.7, 38.0, 38.4, 85.3, 85.6, 86.3, 108.3, 112.3.

(±)-1,6-Dideoxy-3,4-*O*-(1-methylethylidene) Psicose (7g).[34] **Major Anomer.** Colorless oil (91 mg); R_f = 0.34 (3:7 ethyl acetate/hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.30 (d, J = 6.6 Hz, 3H), 1.39 (s, 3H), 1.49 (s, 3H), 1.60 (s, 3H), 4.03 (br s, 1H), 4.10 (dq, J = 6.6, 4.8 Hz, 1H), 4.33 (dd, J = 7.2, 4.8 Hz, 1H), 4.46 (d, J = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.6, 25.1, 26.2, 26.7, 77.2, 85.9, 84.5, 100.7, 116.2.

Minor Anomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.33 (s, 3H), 1.36 (d, J = 6.6 Hz, 3H), 1.49 (s, 3H), 1.51 (s, 3H), 2.32 (br s, 1H), 4.27 (dq, J = 6.6, 1.2 Hz, 1H), 4.53 (d, J = 5.4 Hz, 1H), 4.60 (dd, J = 5.4, 1.2 Hz, 1H); 21.8, 23.6, 25.1, 26.6, 82.3, 86.4, 86.5, 107.1, 112.4.

(±)-(3a*S*,6*S*,6a*S*)-4,6-Dicyclopentyl-2,2-dimethylperhydrofuro-[3,4-*d*][1,3]dioxol-4-ol (7h). Major Anomer. Colorless oil (120 mg); R_f = 0.33 (1:9 ethyl acetate/hexane). IR (neat): 3506, 1455, 1372, 1210, 1078, 868 cm^{-1}. ^{1}H NMR (600 MHz, d_6-benzene): δ 1.13 (s, 3H), 1.33 (s, 3H), 1.40−1.90 (m, 16H), 1.95−2.03 (m, 1H), 2.28 (quint, J = 8.4 Hz, 1H), 4.05 (dd, J = 8.4, 5.4 Hz, 1H), 4.05 (br s, 1H), 4.14 (dd, J = 7.8, 5.4 Hz, 1H), 4.22 (d, J = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, d_6-benzene): δ 25.1, 25.8, 25.9, 26.5, 26.6, 26.7, 27.4, 27.7, 28.5, 29.6, 42.9, 47.8, 83.4, 84.2, 84.7, 103.8, 115.9. MS *m*/*z* (+EI): 297 (M^+ + H, 5), 279 (100), 239 (17), 140 (66), 124 (65), 97 (80). HRMS calcd for (M^+ + Na) $C_{17}H_{28}O_4Na$, 319.1885; found, 319.1881.

Minor Anomer. ^{1}H NMR (600 MHz, d_6-benzene): δ 0.56 (br s, 1H), 1.22 (s, 3H), 1.40−1.90 (m, 16H), 1.50 (s, 3H), 2.15−2.21 (m, 1H), 2.69 (quint, J = 8.4 Hz, 1H), 3.94 (dd, J = 11.1, 1.8 Hz, 1H), 4.57−4.60 (m, 2H). ^{13}C NMR (150 MHz, d_6-benzene): δ 25.4, 25.6, 25.6, 26.2, 26.3, 26.5, 27.0, 28.0, 29.0, 30.6, 44.6, 45.1, 85.3, 86.6, 91.6, 109.5, 112.4.

(±)-1,6-Dibromo-1,6-dideoxy-3,4-*O*-(1-methylethylidene) Psicose (7j). Major Anomer. Colorless planks (123 mg); mp 72−73 °C (dec); R_f = 0.18 (1:9 ethyl acetate/hexane). IR (Nujol): 3459, 1274, 1215, 1061, 1011, 873 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (s, 3H), 1.50 (s, 3H), 3.30 (br s, 1H), 3.45−3.54 (m, 2H), 3.62 (d, J = 10.8 Hz, 1H), 3.73 (d, J = 10.8 Hz, 1H), 4.39 (ddd, J = 90., 6.9, 1.2 Hz, 1H), 4.66 (d, J = 6.0 Hz, 1H), 4.95 (dd, J = 6.0, 1.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0, 26.4, 32.5, 37.7, 84.1, 85.1, 86.0, 104.9, 113.5. MS *m*/*z* (+EI): 347 (M^+ + H, 6), 329 (100), 289 (17), 271 (21), 251 (9). Anal. Calcd for $C_9H_{14}O_4Br_2$: C, 31.24; H, 4.08. Found: C,31.42; H, 4.19.

(±)-(3a*S*,6*S*,6a*S*)-2,2-Dimethyl-4,6-diphenylperhydrofuro[3,4-*d*][1,3]dioxol-4-ol (7k). Major Anomer. Colorless oil (59 mg); R_f = 0.19 (1:9 ethyl acetate/hexane). IR (neat) 3401, 1496, 1211, 1066, 1049, 1027 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.74 (s, 3H), 4.69 (dd, J = 7.2, 5.4 Hz, 1H), 4.71 (br s, 1H), 4.74 (d, J = 7.2 Hz, 1H), 5.23 (d, J = 5.4 Hz, 1H), 7.30−7.41 (m, 6H), 7.47−7.49 (m, 2H), 7.63−7.65 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.2, 26.7, 82.9, 86.3, 86.6, 101.5, 117.2, 125.6, 125.9, 128.0, 128.3, 128.4, 128.6, 139.0, 142.0. MS *m*/*z* (+EI): 312 (M^+, 3), 299 (67), 238 (26), 206 (100), 175 (43), 165 (85). HRMS calcd for (M^+ + Na) $C_{19}H_{20}O_4Na$, 335.1259; found, 335.1250.

(34) Suh, H.; Wilcox, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 470.

Minor Anomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.29 (s, 3H), 1.46 (s, 3H), 2.71 (br s, 1H), 4.76 (d, J = 5.4 Hz, 1H), 5.17 (dd, J = 5.4, 2.4 Hz, 1H), 5.44 (d, J = 2.4 Hz, 1H), 7.26−7.41 (m, 6H), 7.49−7.52 (m, 2H), 7.65−7.68 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.3, 26.8, 86.9, 87.3, 88.3, 108.0, 113.3, 126.0, 127.0, 127.4, 127.9, 128.4, 128.7, 139.9, 141.4.

(±)-(3a*R*,4*S*,7*R*,7a*S*)-2-Phenyl-4,7-dipropylperhydro[1,3]-dioxolo[4,5-*d*][1,2]dioxine (8). To a stirred solution of **2f** (90 mg, 0.44 mmol) in dry CH_2Cl_2 (5 mL) was added α,α-dimethoxytoluene (201 mg, 1.32 mmol) followed by *p*-toluenesulfonic acid (7 mg, 0.04 mmol), and the mixture was stirred under a nitrogen atmosphere until complete by TLC (∼1 h). The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with saturated $NaHCO_3$ (20 mL), dried (Na_2SO_4), and concentrated in vacuo, and the product was purified by flash chromatography to yield the title compound (110 mg) as a colorless oil; R_f = 0.50 (1:1 CH_2Cl_2/hexane). IR (neat) 3366, 1461, 1406, 1220, 1094, 1070, 1028 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 6H), 1.38−1.77 (m, 8H), 4.06−4.11 (m, 2H), 4.25−4.32 (m, 2H), 5.91 (s, 1H), 7.38−7.44 (m, 3H), 7.49−7.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 18.7, 33.2, 74.7, 81.2, 104.1, 126.6, 128.5, 129.5, 137.1. MS *m*/*z* (+EI): 292 (M^+, 8), 191 (9), 177 (21), 105 (100), 77 (31). HRMS calcd for (M^+ + Na) $C_{17}H_{24}O_4Na$, 315.1572; found, 315.1562.

(±)-1,6-Bis-*O*-[1,1-dimethylethyl)dimethylsilyl] Psicose (9). Major Anomer. Colorless oil (153 mg); R_f = (0.19) (3:7 ethyl acetate/hexane). IR (neat): 3391, 1472, 1362, 1256, 1104, 837 cm^{-1}. ^{13}C NMR (75 MHz, d_6-benzene): δ −5.0, −5.0, −5.0, −4.9, 18.8, 19.0, 26.4, 26.4, 64.4, 66.9, 72.9, 73.1, 84.6, 103.7. MS *m*/*z* (+EI): 409 (M^+ + H, 3), 391 (32), 315 (27), 201 (45), 159 (44), 117 (93), 75 (100). HRMS calcd for (M^+ + Na) $C_{18}H_{40}O_6Si_2Na$, 431.2261; found, 431.2259.

Minor Anomer. ^{13}C NMR (75 MHz, d_6-benzene): δ −5.3, −5.2, −5.1, −5.0, 18.8, 18.8, 26.2, 26.3, 64.2, 67.2, 73.3, 76.4, 85.7, 104.6.

(±)-Psicose (10). To a solution of acetic acid (3 mL) and water (2 mL) was added **9** (153 mg, 0.37 mmol), and the mixture was stirred overnight. The solvent was removed in vacuo, and the residue was dried at reduced pressure to give psicose (67.4 mg) as a viscous oil. ^{13}C NMR (75 MHz, D_2O): δ 60.7, 64.1, 65.1, 65.6, 65.8, 66.0, 66.7, 66.9, 67.8, 68.2, 68.6, 71.7, 73.0, 73.0, 73.1, 73.7, 74.5, 77.4, 85.4, 85.4, 100.4, 101.2, 106.0, 108.3.

(±)-1-Deoxy-6-*O*-[1,1-dimethylethyl)dimethylsilyl] Psicose (11). Colorless oil (70 mg); R_f = 0.23 (1:1 ethyl acetate/hexane). IR (neat): 3401, 1716, 1472, 1255, 1119, 837 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.7, −5.6, −5.6, −5.5, −5.5, −5.4, 18.2, 18.2, 18.3, 21.0, 24.1, 25.8, 25.8, 25.8, 26.6, 62.6, 63.4, 64.4, 70.3, 71.3, 72.5, 73.3, 75.2, 77.3, 79.0, 83.9, 83.9, 103.2, 105.7, 207.7. MS *m*/*z* (+EI): 278 (M^+, 1), 261 (41), 243 (27), 203 (17), 117 (22), 85 (100). HRMS calcd for (M^+ + Na) $C_{12}H_{26}O_5SiNa$, 301.1447; found, 301.1446.

(±)-1-*O*-[1,1-Dimethylethyl)dimethylsilyl]-6-deoxypsicose (12). Colorless oil (30 mg); R_f = 0.34 (1:1 ethyl acetate/hexane). IR (neat) 3402, 1472, 1390, 1255, 1104, 839 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 3H), 0.10 (s, 3H), 0.91 (s, 9H), 1.26 (d, J = 6.6 Hz, 3H), 2.82 (d, J = 6.9 Hz, 1H), 3.13 (d, J = 6.9 Hz, 1H), 3.65 (s, 2H), 3.71−3.78 (m, 1H), 3.97 (ddd, J = 6.9, 6.0, 5.7 Hz, 1H), 4.04 (br s, 1H), 4.11 (dq, J = 6.6, 4.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.4, 18.3, 18.9, 25.8, 65.9, 71.6, 76.0, 79.1, 102.4. MS *m*/*z* (+EI): 278 (M^+, 1), 261 (100), 243 (63), 159 (18), 131 (25), 75 (54). HRMS calcd for (M^+ + Na) $C_{12}H_{26}O_5SiNa$, 301.1447; found, 301.1446.

(±)-1-Deoxypsicose (13). Deprotection Procedure as per 10. Colorless oil (37 mg). ^{13}C NMR (75 MHz, D_2O): δ 23.9, 26.4, 26.4, 26.9, 29.1, 60.9, 64.1, 65.6, 65.6, 66.8, 67.8, 68.8, 71.2, 72.5, 73.1, 73.9, 74.1, 74.1, 74.9, 75.9, 76.9, 78.7, 81.7, 85.1, 85.9, 100.7, 101.2, 105.7, 108.7, 215.0.

(±)-6-Deoxypsicose (14). Deprotection Procedure as per 10. Colorless oil (19 mg). ^{13}C NMR (75 MHz, D_2O): δ 20.3, 22.0, 65.1, 66.1, 73.0. 77.8, 77.9, 78.7, 80.6, 81.2, 105.6, 107.9.

Acknowledgment. We thank the Australian Research Council for financial support. T. V. Robinson thanks the Commonwealth government of Australia, for support in the form of a scholarship.

Supporting Information Available: Experimental details for compounds **1a**−**k** and crystallographic data for **3f**; ^{13}C NMR spectra for compounds **1d**, **2b**−**d**,**i**,**k**, **3b**,**g**,**i**,**j**, **4 g**,**j**, **5**, **6f**,**j**, **7f**,**h**,**j**,**k**, and **9**−**14**, and ^{1}H NMR spectra for compounds **1**,**b**,**i**,**j**, **2f**,**g**,**j**, **3d**,**f**,**i**,**k**, **6k**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060949P