ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 328 (2000) 17–36

CARBOHYDRATE RESEARCH

Syntheses of four D- and L-hexoses via diastereoselective and enantioselective dihydroxylation reactions

Joel M. Harris, Mark D. Keränen, Hang Nguyen [1], Victor G. Young [2], George A. O'Doherty *

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455, USA

Received 25 October 1999; accepted 4 January 2000

Abstract

An expeditious approach to various protected hexoses has been developed by the use of the Sharpless catalytic asymmetric dihydroxylation reaction. Applying the Sharpless catalytic asymmetric dihydroxylation reaction on vinylfuran, diols with high enantioexcess are produced. The resulting diols can be stereoselectively transformed into either protected D- or L-mannose in five steps and approximately 39% yield from furfural. Similarly, both D- and L-talose and gulose have been synthesized in 19% overall yields, respectively. Using a modified strategy, both protected D- and L-gulo- and allo-sugar-δ-lactones were synthesized in eight steps and ~20% overall yield from furfural.

Keywords: Vinylfuran; Talose; Allose; Mannose; Gulose; Dihydroxylation; Sugar lactone; AD mix; Enantioselective synthesis

1. Introduction

The de novo enantioselective synthesis of the hexoses stands as a challenge to asymmetric catalysis (for a good review, see Ref. [1]). Despite some germinal efforts toward the hexoses, notably by Masamune and Sharpless (epoxidation) [2], Danishefsky (Diels–Alder) (for a review, see Ref. [3a], and for improved catalysis, see Ref. [3b]), Johnson and Hudlicky (enzymatic desymmetrization) [4] and Wong and Sharpless (osmium/enzyme) [5], there still does not exist a practical, nonenzymatic route to the hexoses [6][3]. We are particularly interested in studying oligosaccharide analogs of the all D-, all L-, and mixed D- and L-oligosugar structures, such as the D-mannose-L-gulose portion of bleomycin [7] (for a synthesis of bleomycin see Ref. [7a]). Herein, we would like to present our discovery of an expeditious

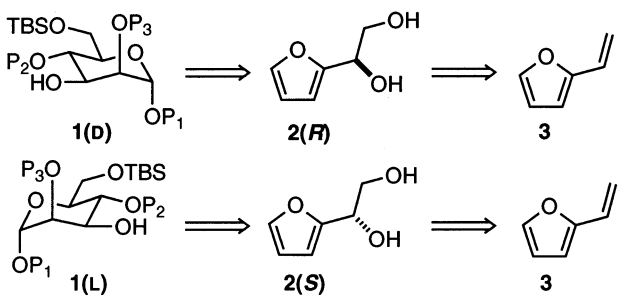


Fig. 1. Retrosynthetic scheme for protected D- and L-mannopyranose.

* Corresponding author. Tel.: +1-612-6258862; fax: +1-612-6267541.

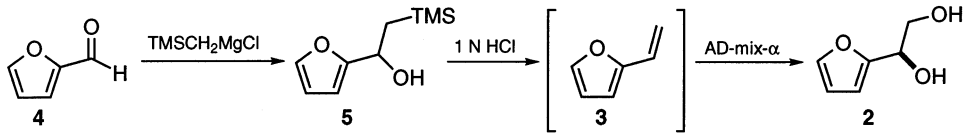
E-mail address: odoherty@chem.umn.edu (G.A. O'Doherty).

[1] University of Minnesota Undergraduate Research Opportunity Program (UROP) participant.

[2] Corresponding author for questions regarding the X-ray structure.

[3] Recently Wong has developed a route to a mixture of glucose and fructose using an enzymatic process [6].

0008-6215/00/$ - see front matter
PII: S0008-6215(00)00031-8



Scheme 1.

route to either mannose, gulose or talose using Sharpless's dihydroxylation reaction to set the D- or L-configuration depending on the ligand used.

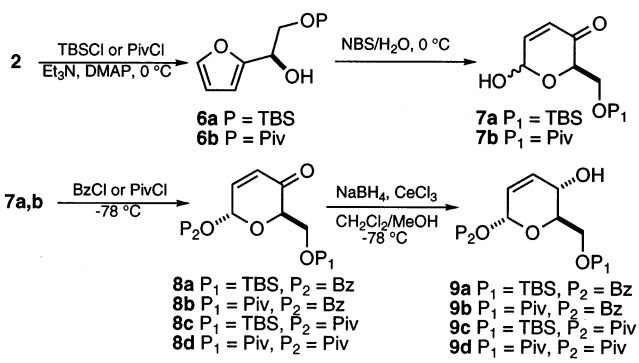
We initially targeted the differentially protected D- and L-mannose **1** as building blocks for the oligosaccharide assembly (Fig. 1). We desired a route in which the synthetic efficiency was better than traditional protection–deprotection strategies from mannose and is amenable to both D- and L-mannose. The ideal synthesis should also start from a commercially available starting material that is even cheaper than D-mannose[4,5]. The strategy outlined below has led to a highly stereocontrolled synthesis of D- or L-mannose in only five steps and in approximately 39% yield from furfural (Scheme 4) [8].

2. Results and discussion

In order to accomplish this goal we, as have others, recognized that substituted furyl carbinols possess the proper C-5 stereochemistry for the hexopyranoses (for a good review see Ref. [9]). Our approach relies upon the use of catalytic asymmetric osmium chemistry on vinylfuran **3** developed by us [10] and Ogasawara [11][6] and augments the earlier work of Achmatowicz [12]. A key part of this sequence is our ability to convert furfural into an ether solution of vinylfuran (Scheme 1) [13][7]. This one-step in situ process for the generation of vinylfuran constitutes a significant improvement in terms of overall efficiency. Crucial to our approach to the hexoses is a simple, three-step route toward pyranone **8** from diol **2** (Scheme 2). We envision **8** as the linchpin molecule that will be amenable for the synthesis of all the possible stereoisomers of the hexoses.

Furan diol.—We have found that the key furan diol **2** could be prepared from furfural **4** via an asymmetric dihydroxylation of vinylfuran. This was most easily accomplished by a one-pot Peterson olefination–Sharpless dihydroxylation procedure. This in situ use of vinylfuran allows for much higher yields of diol **2** without any loss of enantioexcess.

Preparation of the trimethylsilylmethylmagnesium chloride Grignard reagent from chloromethyltrimethylsilane and magnesium, followed by addition of furfural, gave excellent yields of β-hydroxysilane **5**. Washing a 2 M ether solution of furan **5** with 1 N HCl produces a 2 M vinylfuran solution, which can be used as is in the AD-mix reaction after washing with saturated aqueous $NaHCO_3$. The 2 M solution of vinylfuran was used directly in the *t*-BuOH/H_2O AD-mix reaction mixture developed by Sharpless [10,14]. The $(DHQ)_2PHAL$ ligand gave an 85% yield of



Scheme 2.

[4] According to the Aldrich Catalog on a per-gram basis D-mannose costs 35 times more than furfural and for L-mannose the cost ratio is 4000:1.

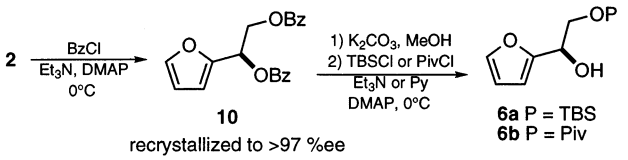
[5] Furfural is commercially produced by Great Lakes Chemical Co. [8].

[6] Ogasawara has previously demonstrated the asymmetric dihydroxylation of vinylfuran and applied it toward the synthesis of D- and L-levoglucosenone and hexoses [11].

[7] Wittig technology provides vinylfuran in yields of the order of 10%. Previous practical approaches to vinylfuran involve a four-step sequence from furfural that involves a stoichiometric Cu-promoted decarboxylation of 3-furylpropanoic acid [13].

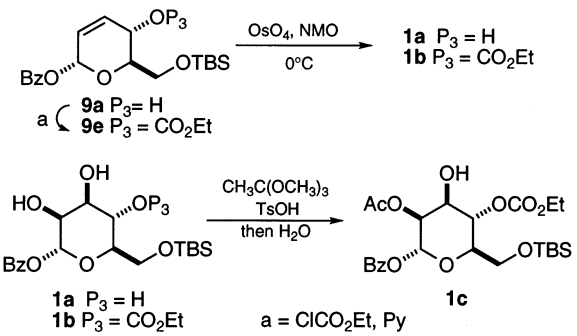
(*R*)-diol 2(*R*) from furfural in 92% ee[8,9]. The $(DHQD)_2PHAL$ ligand afforded (*S*)-diol 2(*S*) in an 85% yield with a 90% ee [15][10].

Diol **2** can be selectively protected with TBSCl (90%) or PivCl (85%) to give furan **6a** and **6b**, respectively. Both **6a** and **6b** smoothly rearrange to hemiacetal **7a** and **7b** when oxidized with NBS in aqueous THF [12b,16]. Hemiacetals **7a** and **7b** exist as an equilibrating mixture of anomers, diastereomerically enriched mixtures of **7a** equilibrate to a 1:1 mixture of anomers in deuterated chloroform. Our hopes of taking advantage of the difference in reactivities of axial versus equatorial anomeric alcohols were realized when hemiacetal **7a** and **7b** were treated with benzoyl chloride at -78 °C to produce pyranone **8a** and **8b** as the major diastereomers (>20:1). This result appears to be general for acid chlorides, as pivaloyl chloride reacts to give **8c** and **8d** (>10:1) with similar selectivity, where as TBSCl reacted with **7a** to give approximately a 1:1 mixture of anomers[11]. With the two stereocenters of **8a–d** introduced, the molecule was poised for introduction of the remaining functionality of the hexoses (Scheme 2). All four pyranones **8a–d** were stereoselectively reduced under the Luche conditions ($NaBH_4$–$CeCl_3$, -78 °C) [17] to give alcohols **9a–d**, respectively[12] as the only observable stereoisomer ($>95\%$), each in 95% yield. The relative configuration of **9a–d** was assigned based upon the ~ 10 Hz coupling constant between the protons at C-4 and C-5 (Scheme 3).



Scheme 3.

The enantioexcess of diol **2** can be improved ($>97\%$ ee) by a simple recrystallization of the dibenzoate **10** from hexanes, which can be easlily converted to **6a** or **6b** via a hydrolysis–protection sequence. The absolute configuration is based upon the Sharpless mnemonic [14] and Mosher ester analysis [15].



Scheme 4.

Mannose.—Allylic alcohol **9a** can be protected without purification to give ethyl carbonate **9e**. Two partially protected mannosugars were produced via a completely diastereoselective dihydroxylation to give **1a** and **1b** both in $\sim 90\%$ yield (Scheme 4) (for a review of diastereoselection in the osmium catalyzed dihydroxylation reaction see Ref. [18]). A differentially protected mannose was easily achieved upon treatment of diol **1b** with trimethylorthoacetate to form a cyclic orthoester in situ, which was subsequently hydrolyzed to the axial acetate **1c**. The differentially protected mannosugar **1c** was formed in a 62% yield with a regioselectivity greater than 25:1[13]. The relative configuration of **1a** was determined by examining relevant coupling constants and NOEs from a series of ^1H NMR, ^1H,^1H-COSY, and ^1H NOE experiments. Particularly telling were the coupling constants between hydrogens at C-1 and C-2 (2 Hz), C-2 and C-3 (3.5 Hz), C-3 and C-4 (9

[8] Although we were concerned about an adverse solvent effect caused by the presence of ether, Ogasawara has observed identical ee values in *t*-BuOH/H_2O [11a].

[9] The (*R*)-diol **2** has been prepared on a half-mole scale with no reduction of enantioselectivity. Similarly the (*S*)-diol **2** has been prepared on a quarter-mole scale.

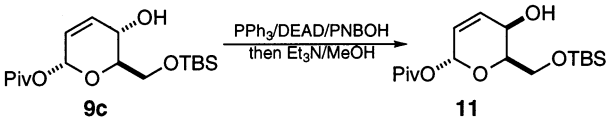
[10] The enantioexcesses were determined by examining the ^1H and ^{19}F NMR spectra of the Mosher esters of **6a** and **6b** [15].

[11] The selective benzoylation allows for the simple purification of **8a** without resorting to tedious chromatographic separation. BzCl at room temperature with excess Et_3N gave a 4:1 mixture of isomers, whereas, with 1 equivalent of Et_3N gave a 1:1 mixture. Achmatowicz has previously shown that molecules related to **7a** gave a 1:1 mixture of methoxy anomers with MeOH–acid [12a].

[12] Mosher ester analysis of **9a** showed that recrystallized enone **8a** had significantly increased enantioexcess ($>96\%$ ee).

[13] A mixture of axial and equatorial acetates was produced upon treatment of **1b** with 1 equivalent of Ac_2O, which allowed for easy detection of the >25:1 mixture by ^1H NMR spectroscopy.

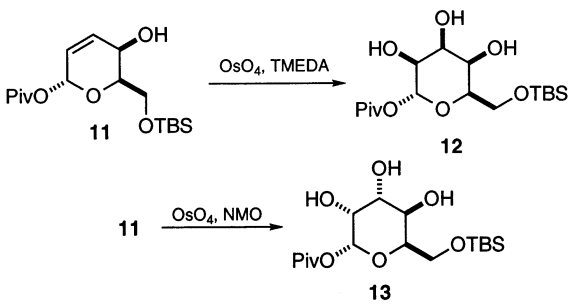
Hz), C-4 and C-5 (10 Hz), and NOEs from hydrogens C-1 and C-5 to hydrogens at C-4 and C-3, respectively.



Scheme 5.

Gulose and talose.—The rare hexose sugars, gulose and talose, can also be prepared from the diastereomeric allylic alcohol **11**. The C-4 isomer of allylic alcohol **9c** was produced by performing a Mitsunobu reaction sequence (Scheme 5). Key to this transformation is the selective hydrolysis of a *p*-nitrobenzoyl ester in the presence of the anomeric ester. Although this operation can be performed on benzoate **9a**, more reproducible results are observed when pivolate **9c** is used. Exposure of **9c** to the Mitsunobu reaction conditions (PPh_3, DEAD, *p*-nitrobenzoic acid (PNBOH)) yielded a *p*-nitrobenzoic ester (65%), which was selectively hydrolyzed with Et_3N in MeOH to yield the axial alcohol **11** (90%) [19].

Access to **11** extends this versatile synthetic strategy to other hexoses, as illustrated by the synthesis of a protected talose **12** and gulose **13** (Scheme 6). Treatment of allylic alcohol **11** with OsO_4–NMO in *t*-BuOH–H_2O afforded an 80% yield of the protected gulose isomer **13** [20][14]. Amazingly, the protected talose isomer **12** can be selectively produced upon treatment of **11** with the TMEDA adduct of OsO_4 (80%) [20][15]. Unfortunately for this system, the hydroxy-directed delivery of a cis diol seems to require an axial alcohol, since exposure of **9a** to the identical conditions only yielded the mannose isomer **1a**. The relative configurations of **12** were determined by examining relevant coupling constants and NOEs from a series of ^1H NMR, ^1H,^1H-COSY, and ^1H NOE experiments. Some representative examples are the W-coupling between hydrogens at C-2 and C-4, and NOEs between the methyls on the pivolate group and hydrogens at C-2, C-3 and C-5 of talose triol **12**. Similarly, the relative and absolute configuration of the gulose sugar **13** was confirmed by single-crystal X-ray analysis.



Scheme 6.

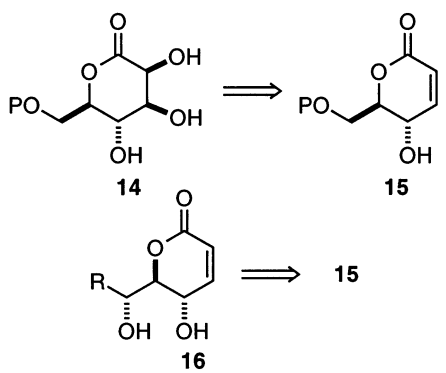


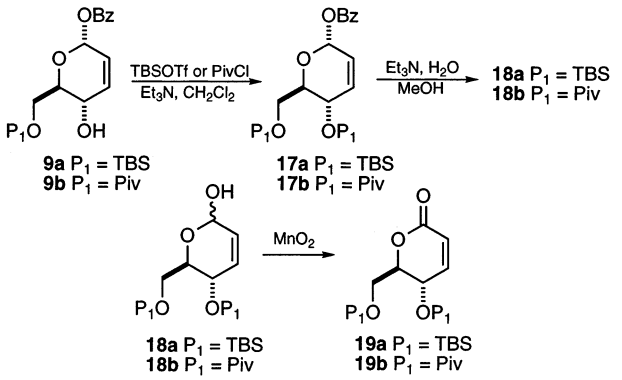
Fig. 2. Retrosynthetic scheme for a 6-protected D-mannonolactone.

Sugar lactones.—In the context of our research program aimed at the synthesis of *C*-glycoside natural products (for an application of sugar lactones toward the synthesis of a papulacandin see Ref. [21]), we were looking for an easy entry into a δ-lactone sugar with the manno stereochemistry **14** (Fig. 2). To this end we targeted the α,β-unsaturated-δ-lactone **15** as a potentially versatile entry point for the synthesis of these sugars, as well as analogs related to styryllactone **16** [22]. Our approach to synthesize sugar lactones relies upon an efficient enantioselective and diastereoselective oxidation and reduction sequence.

Substituted α,β-unsaturated δ-lactones (e.g. styryllactones) are an important class of natural products and many synthetic methodologies have been employed to synthesize this core structure [23]. One of the most useful methodologies employed is the kinetic resolu-

[14] For a recent eight-step synthesis of gulose from L-xylose. Dondoni appraises L-gulose at \$2000 g^{-1} [7d].

[15] Less than 5% of the gulose isomer was formed. These conditions were chosen for the hydroxy directed delivery of a cis diol [20].



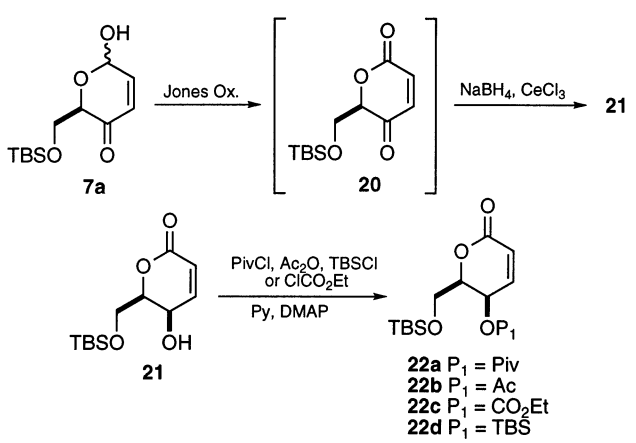
Scheme 7.

tion of 2-furylcarbinols developed by Honda [24], Sato [25], and augmented by Zhou [26]. This strategy employs the kinetic resolution of racemic 2-furylcarbinols with the Sharpless epoxidation reaction conditions to produce an optically active pyranone product resulting from the selective, fast oxidation of only one enantiomer of the racemic 2-furylcarbinols. The optically pure pyranone or 2-furylcarbinol products of the kinetic resolution can both be used in the synthesis of natural products (secondary furyl alcohols have been resolved both chemically and enzymatically, see Ref. [27a,b]; for enzymatic resolutions see Ref. [27c]).

We envisioned extending our earlier work to synthesize these useful building blocks from pyranone **8a–d** with differentiated oxygen functionality in a limited number of steps and avoiding a kinetic resolution (Scheme 7). The alcohol functionality at C-1 and C-4 needed to be differentiated. This was easily accomplished by protection of **9a** and **9b** with TBSOTf or PivCl to give **17a** and **17b**, respectively. Deprotection of the anomeric benzoyl group proved troublesome, with the best results obtained using Et_3N, MeOH, H_2O in a 1:5:1 ratio, giving lactol **18a** or **18b** in 50–60% yield. Oxidation of **18a** or **18b** with MnO_2 provided the α,β-unsaturated-δ-lactone **19a** or **19b** in 75–85% yield.

Having established the feasibility of preparing the α,β-unsaturated δ-lactone **19a** and **19b** with complete enantio- and diastereocontrol, we turned our attention to improving the efficiency of the route to the general structure of α,β-unsaturated-δ-lactones. The obvious disadvantage of the route in Scheme 7 is the requisite protection of the C-1 and C-4 hydroxyl groups. A significant reduction in steps could be achieved by oxidation of lactol **7a** to ketolactone **20**, provided the carbonyl groups could be reductively differentiated (Scheme 8). Similar approaches have been used by other groups using CrO_3 and acetic acid [28]. A potential problem of this shorter route is the possible racemization or β-elimination in the ketolactone. We envisioned using a reagent for fast oxidation of lactol **7a** to ketolactone **20** that would be immediately compatible for exposure to Luche conditions[16]. This was most easily accomplished by Jones oxidation followed by Luche reduction (Scheme 8).

Treatment of an acetone solution of **7a** with a slight excess of Jones reagent produced ketolactone **20** in ~20 min. Upon completion the reaction mixture was quenched with isopropyl alcohol, washed with a saturated $NaHCO_3$ solution, and extracted with ether. After solvent exchange (ether to MeOH), **20** was treated with $NaBH_4$ to yield differentially protected δ-lactone **21** in 60–70% yield over two steps with no loss of enantiomeric excess. The observed stereoselectivity of the reduction is explained by the apparent hydride attack on the less hindered face of the molecule [29][17]. Protection of the allylic alcohol using PivCl, Ac_2O, or $ClCO_2Et$ provided **22a**, **22b**, or **22c** in 80, 94, and 90% yields, respectively. The

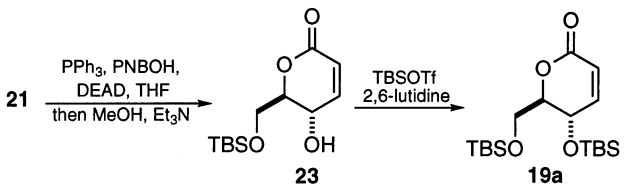


Scheme 8.

[16] Ketolactone **20** decomposed when attempting to purify by silica gel chromatography.

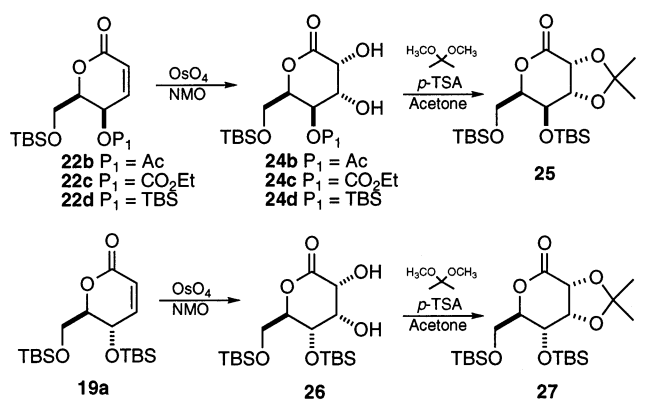
[17] Various selectivities have been observed depending on the steric bulk of the substituent at C-5 [29].

diastereomeric lactone **23** can be prepared from **21** by a Mitsunobu reaction [19], followed by hydrolysis of the *p*-nitrobenzoyl group in 70% yield over two steps (Scheme 9). The allylic alcohol **23** was also protected as a TBS ether to form **19a**, which confirms the diastereoselectivity of the reduction of ketolactone **20**. This not only provides a shorter route to lactones **21** and **23**, but also provides the δ-lactone in a higher overall yield (~ 45% to **21** and 32% **23** from diol **2** as compared to ~ 20% to **19** from diol **2**).



Scheme 9.

Finally, four sugar lactones were stereoselectively prepared by dihydroxylation of α,β-unsaturated δ-lactones **22b–d** and **19a** with OsO_4 (Scheme 10). Treatment of the protected allylic alcohols **22b–d** with a catalytic amount of OsO_4 and a 50% aqueous solution of NMO yields the gulonolactone **24b–d** in ~ 60% yields, whereas, the bis-TBS ether **19a** reacted to give the allonolactone **26** in 73% yield. The relative configurations of **24b–d** and **26** were determined by examining relevant coupling constants and NOEs from a series of ^1H NMR, ^1H,^1H-COSY, and ^1H NOE experiments. Additional support for the stereochemical assignment was realized by the conversion of **24d** and **26** into their corresponding acetonides **25** and **27**. Both lactones **25** and **27**



Scheme 10.

displayed ^1H NOE from the endo methyl of the acetonide to the hydrogen at C-5, indicating that the substituent at C-5 controls the facial selectivity of dihydroxylation as opposed to the C-4 substitution. Some representative coupling constants for the gulose sugar **24b** are the cis-axial–equatorial coupling constant between the hydrogens at C-5 and C-4 (2.5 Hz), the trans–diequatorial coupling constant between the hydrogens at C-4 and C-3 (4.5 Hz), and the lack of W-couplings and NOEs between the hydrogens at C-5 and C-3. Similarly, representative coupling constants for the allose sugar **26** were trans-diaxial coupling constant between the hydrogens at C-5 and C-4 (9 Hz), cis-axial–equatorial coupling constant between the hydrogens at C-4 and C-3 (2.1 Hz), and cis coupling constant between the hydrogens at C-3 and C-2 (2.4 Hz).

In summary, we have developed a practical, five-step synthesis of differentially protected D- and L-mannose sugars from furfural (39% yield) via highly diastereoselective and enantioselective dihydroxylation reactions. This route is amenable to multigram-scale preparation. Further study of the diastereoselection of the dihydroxylation reaction allowed for the extension of this methodology to protected D- and L-gulose and D- and L-talose sugars in comparable yields (19%). Finally, D- and L-gulono- and allonopyranolactones can also be produced with equal efficiency (in 8 steps and ~ 20% overall yield from furfural). We are currently investigating an epoxide ring opening approach to the other isomers of the hexoses as well as rare deoxy sugars. We feel this new efficient route to L-sugars will be very beneficial for the synthesis of natural and unnatural oligosaccharides.

3. Experimental

General methods.—Liquid chromatography was performed using (flash chromatography) of the indicated solvent system on ICN reagent Silica Gel 60 (60–200 mesh). Ether and tetrahydrofuran were distilled from benzophenone and sodium metal. Dichloromethane and triethylamine were distilled from calcium hydride. Hexanes refers to the

petroleum fraction bp 40–60 °C. Commercial reagents were used without purification unless otherwise noted. ^{1}H and ^{13}C spectra were recorded on Varian 200, 300 and 500 MHz spectrometers. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven-dried glassware and standard syringe–septa techniques. Melting points are uncorrected. Combustion analyses were performed by M-H-W Laboratories, Phoenix, AZ.

1-(2-Furyl)-2-trimethylsilanylethan-1-ol (**5**).—Magnesium turnings (10.1 g, 0.415 mol) were placed in a 1-L 3-neck round-bottom flask and a condenser along with a side arm addition funnel were attached. The apparatus was flame dried (3 ×), each time flushing with nitrogen. Chloromethyltrimethylsilane (42.4 g, 0.346 mol) in 200 mL of Et_2O were added slowly to the dry magnesium. After the addition, the solution was refluxed for 1 h. Freshly distilled furfural (25.0 mL, 0.302 mol) and 300 mL of Et_2O were added slowly to the Grignard reagent at 0 °C, and the solution was stirred for 3 h at 0 °C and 9 h at room temperature (rt). The reaction was quenched with 200 mL of satd aq NH_4Cl and extracted (3 × 100 mL) with Et_2O. The organic layer was washed with satd aq $NaHCO_3$ (2 × 50 mL), brine (2 × 50 mL), dried (Na_2SO_4), and concentrated under reduced pressure to give the β-hydroxy silane **5** in 90% yield (50.1 g, 0.272 mol): R_f 0.58 (3:7 Et_2O–hexanes); IR (thin film, cm^{-1}) 3390, 2950, 2895, 1655, 1505, 1250; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, *J* 1.8, 0.7 Hz, 1 H), 6.24 (dd, *J* 3.1, 1.8 Hz, 1 H), 6.13 (d, *J* 3.3 Hz, 1 H), 4.77 (dd, *J* 8.8, 6.9 Hz, 1 H), 3.13 (bs, 1 H), 1.28 (dd, *J* 14.1, 8.8 Hz, 1 H), 1.23 (dd, *J* 14.1, 6.8 Hz, 1 H), −0.10 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 141.6, 110.1, 105.5, 65.6, 24.8, −1.4; CIHRMS Calcd for $[C_9H_{16}O_2Si]^+$: 184.0920. Found: 184.0905.

(1R)-1-(2-Furyl)ethan-1,2-diol (**2**).—The β-hydroxy silane (44.2 g, 0.240 mol) and 120 mL of Et_2O were added to a 500-mL round-bottom flask, followed by addition of 120 mL of 1 M HCl, and the solution was stirred for 1 h. Phases were separated and the aq layer was extracted (2 × 50 mL) with Et_2O and combined with the organic layer. The organic layer was washed (2 × 50 mL) with satd aq $NaHCO_3$ and added to a solution of 300 mL of *t*-BuOH, 750 mL of H_2O, 50 g of AD-mix-α, 133 g of $K_3Fe(CN)_6$, and 56 g of K_2CO_3 at 0 °C. The solution was vigorously stirred with a mechanical stirrer for 12 h at 0 °C. The reaction was slowly quenched with (500 mL) satd aq Na_2SO_3. The phases were separated, and the aq layer was extracted (6 × 100 mL) with EtOAc. The organic layer was washed with satd aq $NaHCO_3$ (2 × 100 mL), brine (2 × 100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography eluting with 2:3 Et_2O–hexanes to yield 25.0 g (0.195 mol, 85%) of **2**: R_f 0.37 (1:1 Et_2O–hexanes); $[\alpha]_D^{21}$ +32.0° (*c* 2.17, CH_2Cl_2); IR (thin film, cm^{-1}) 3390, 2933, 2881, 1684, 1505, 1464, 1228; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, *J* 1.8, 0.6 Hz, 1 H), 6.27 (dd, *J* 4.0, 1.8 Hz, 1 H), 6.23 (dd, *J* 4.0, 0.6 Hz, 1 H), 4.71 (t, *J* 5.9 Hz, 1 H), 4.54 (bs, 2 H), 3.74 (d, *J* 5.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 142.3, 110.5, 107.0, 68.4, 65.0; CIHRMS Calcd for $[C_6H_8O_3 + NH_4]^+$: 146.0817. Found: 146.0822; Anal. Calcd for $C_6H_8O_3$: C, 56.23; H, 6.30. Found: C, 56.04; H, 6.20.

(1R)-1-(2-Furyl)-2-tert-butyldimethylsilanyloxyethanol (**6a**).—Diol **2** (0.986 g, 7.70 mmol), 15 mL of CH_2Cl_2, and 5.5 mL of Et_3N were added to a round-bottom flask and cooled to 0 °C. A catalytic amount (50 mg, 0.41 mmol) of DMAP was added, followed by addition of *tert*-butylchlorodimethylsilane (1.19 g, 7.89 mmol), and the solution was stirred at 0 °C for 6 h. The reaction was quenched with 1 M $NaHSO_4$ and extracted (3 × 25 mL) with Et_2O, washed with satd aq $NaHCO_3$ (2 × 20 mL), and dried (Na_2SO_4). The crude product was purified by silica gel flash chromatography eluting with 1:3 Et_2O–hexanes to yield 1.69 g (6.97 mmol, 91%) of **6a**: R_f 0.55 (3:7 Et_2O–hexanes); $[\alpha]_D^{21}$ +15.9° (*c* 1.37, CH_2Cl_2); IR (thin film, cm^{-1}) 3447, 2954, 2930, 2884, 2857, 1471, 1463, 1361; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* 1.8, 0.9 Hz, 1 H), 6.35 (dd, *J* 3.3, 1.8 Hz, 1 H),

6.33 (dd, *J* 3.3, 0.9 Hz, 1 H), 4.75 (dd, *J* 6.4, 4.6 Hz, 1 H), 3.86 (dd, *J* 10.1, 4.6 Hz, 1 H), 3.85 (dd, *J* 10.1, 6.7 Hz, 1 H), 3.04 (bs, 1 H), 0.90 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 142.0, 110.3, 107.1, 68.5, 65.9, 26.0, 18.4, −5.3; CIHRMS Calcd for $[(C_{12}H_{22}O_3Si)-H_2O]^+$: 225.1310. Found: 225.1296; Anal. Calcd for C, 59.47; H, 9.16. Found: C, 59.80; H, 9.37.

1-[(2-Furan-2-yl)-2-hydroxy]ethyl pivalate (**6b**).—Diol **2** (1.96 g, 15.3 mmol), 30 mL of CH_2Cl_2, and 1.62 mL of pyridine were added to a round-bottom flask and cooled to 0 °C. A catalytic amount (93 mg, 0.77 mmol) of DMAP was added, followed by addition of pivaloyl chloride (1.89 mL, 15.3 mL), and the solution was stirred at 0 °C for 12 h. The reaction was quenched with satd aq $NaHCO_3$ (30 mL), extracted (3×25 mL) with Et_2O, combined and dried (Na_2SO_4). The crude product was purified by silica gel flash chromatography eluting with 1:5 EtOAc–hexanes to yield 2.76 g (13.0 mmol, 85%) of **6b**: R_f 0.33 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ +15.0° (*c* 2.76, CH_2Cl_2); IR (thin film, cm^{-1}) 3448, 2973, 1731, 1481, 1462, 1285; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* 1.9, 0.9 Hz, 1 H), 6.33 (dd, *J* 3.4, 2.0 Hz, 1 H), 6.30 (dd, *J* 3.2, 0.9 Hz, 1 H), 4.94 (dd, *J* 5.3, 5.3 Hz, 1 H), 4.37 (dd, *J* 11.5, 6.5 Hz, 1 H), 4.34 (dd, *J* 11.5, 4.9 Hz, 1 H), 2.74 (bs, 1 H), 1.17 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 142.0, 110.3, 107.1, 68.5, 65.9, 26.0, 18.4, −5.3; CIHRMS Calcd for $[(C_{12}H_{22}O_3Si)-H_2O]^+$: 225.1310. Found: 225.1296. Anal. Calcd for C, 59.47; H, 9.16. Found: C, 59.80; H, 9.37.

(2R)-1,2-Di-O-benzoyl-1-(furan-2-yl)-ethane-1,2-diol (**10**).—Diol **2** (25 g, 0.20 mol) was dissolved in 400 mL of CH_2Cl_2, and 108 mL of Et_3N were added to the solution. A catalytic amount of DMAP (1.19 g, 9.7 mmol) and benzoyl chloride (68 mL, 0.59 mol) were added to solution and stirred for 12 h. The reaction was quenched with 150 mL satd aq $NaHSO_4$, and the organic layer was washed with 200 mL of satd aq $NaHCO_3$. The aq layers were extracted (5×100 mL) with Et_2O and the organic fractions were combined, dried ($MgSO_4$), and concentrated, and the products were recrystallized from hexanes to yield 53 g (0.16 mol, 80%) of dibenzoate **10**: mp 82–83 °C; R_f 0.50 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ 59.4° (*c* 2.06, CH_2Cl_2); IR (thin film, cm^{-1}) 3016, 2977, 1714, 1601, 1504, 1452, 1397, 1317, 1262; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (ddd, *J* 8.0, 2.0, 1.5 Hz, 2 H), 8.00 (ddd, *J* 7.5, 2.0, 1.5 Hz, 2 H), 7.56 (ddd, *J* 9.0, 1.5, 1.0 Hz, 1 H), 7.53 (ddd, *J* 8.0, 2.0, 1.5 Hz, 1 H), 7.43 (m, 5 H), 6.55 (d, *J* 2.5 Hz, 1 H), 6.53 (dd, *J* 7.5, 4.0 Hz, 1 H), 6.40 (dd, *J* 3.5, 2.0 Hz, 1 H), 4.90 (dd, *J* 11.5, 8.0 Hz, 1 H), 4.81 (dd, *J* 11.5, 4.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.5, 149.3, 133.2, 133.1, 129.8, 129.7, 129.6, 129.5, 128.4, (2 C), 110.5, 109.8, 66.9, 63.9; CIHRMS Calcd for $[C_{20}H_{16}O_5+NH_4]^+$: 354.1342. Found: 354.1336; Anal. Calcd for C, 71.41; H, 4.78. Found: C, 71.40; H, 4.78.

(2R)-2-tert-Butyldimethylsilanyloxymethyl-6-hydroxy-6H-pyran-3-one (**7a**).—Compound **6a** (1.69 g, 6.97 mmol), 12 mL of THF, and 3 mL of H_2O were added to a round-bottom flask and cooled to 0 °C. Solid $NaHCO_3$ (1.17 g, 13.9 mmol), $NaOAc{\cdot}3H_2O$ (0.950 g, 6.98 mmol), and NBS (1.24 g, 6.97 mmol) were added to the solution, and the mixture was stirred for 1 h at 0 °C. The reaction was quenched with satd aq $NaHCO_3$ (15 mL), extracted (3×25 mL) with Et_2O, dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel chromatography eluting with 1:4 EtOAc–hexanes to give 1.71 g (6.62 mmol, 95%) of **7a**: R_f 0.40 (2:3 Et_2O–hexanes); IR (thin film, cm^{-1}) 3388, 2951, 2929, 2884, 2858, 1699, 1464, 1256; ^{1}H NMR (300 MHz, $CDCl_3$) major isomer δ 6.93 (dd, *J* 10.3, 3.3 Hz, 1 H), 6.12 (dd, *J* 10.4, 0.6 Hz, 1 H), 5.79 (dd, *J* 5.1, 3.1 Hz, 1 H), 4.59 (dd, *J* 5.0, 2.8 Hz, 1 H), 4.02 (dd, *J* 11.2, 5 Hz, 1 H), 3.93 (dd, *J* 11.2, 2.0 Hz, 1 H), 0.87 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) major isomer δ 194.9, 145.9, 128.1, 88.1, 76.7, 63.5, 25.8, 18.5, −5.2, −5.3; CIHRMS Calcd for $[(C_{12}H_{22}O_4Si)+H]^+$: 259.1366. Found: 259.1366; Anal. Calcd for C, 55.79; H, 8.59. Found: C, 55.86; H, 8.45.

(2R)-6-Hydroxy-3-oxo-3,6-dihydro-2H-pyran-2-ylmethyl pivalate (**7b**).—Compound **6b** (2.42 g, 11.4 mmol), 30 mL of THF, and 10 mL of H_2O were added to a round-bottom flask and cooled to 0 °C. Solid $NaHCO_3$ (1.92 g, 22.8 mmol), $NaOAc{\cdot}3H_2O$ (1.55 g, 11.4

mmol), and NBS (2.23 g, 12.5 mmol) were added to the solution, and the mixture was stirred for 1 h at 0 °C. The reaction was quenched with satd aq $NaHCO_3$ (40 mL), extracted (3×50 mL) with Et_2O, dried (Na_2SO_4), concentrated under reduced pressure, and purified by silica gel chromatography eluting with 1:4 EtOAc–hexanes to give 2.47 g (10.8 mmol, 95%) of **7b**: R_f 0.24 (3:7 EtOAc–hexanes); IR (thin film, cm^{-1}) 3436, 2974, 2937, 2874, 1732, 1700, 1481, 1369, 1286; ^1H NMR (500 MHz, $CDCl_3$) major isomer δ 6.94 (dd, *J* 10.0, 3.5 Hz, 1 H), 6.13 (dd, *J* 10.0 Hz, 1 H), 5.67 (dd, *J* 3.5, 3.5 Hz, 1 H), 4.77 (dd, *J* 4.5, 3.0 Hz, 1 H), 4.50 (dd, *J* 12.0, 3.0 Hz, 1 H), 4.45 (dd, *J* 12.0, 4.5 Hz, 1 H), 4.17 (bs, 1 H), 1.13 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) major isomer δ 193.5, 178.5, 145.5, 127.4, 87.6, 72.9, 62.6, 38.8, 27.0; CIHRMS Calcd for $[(C_{11}H_{16}O_5)+H]^+$: 229.1076. Found: 229.1069.

*(2*S,*6*R*) - 6 - (*tert - *Butyldimethylsilanyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**8a**).—Compound **7a** (1.54 g, 5.96 mmol), 20 mL of CH_2Cl_2, and 5 mL of Et_3N were added to a round-bottom flask and cooled to −78 °C. A catalytic amount (75 mg, 0.61 mmol) of DMAP and benzoyl chloride (0.70 mL, 6.0 mmol) were added, and the solution was stirred for 3 h at −78 °C. The reaction was quenched with 50 mL of satd aq $NaHCO_3$, extracted (3×50 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 1:9 EtOAc–hexanes to give 1.62 g (4.47 mmol, 60%) of **8a**: mp 107–110 °C; R_f 0.43 (2:3 Et_2O–hexanes); $[\alpha]_D^{21}$ −178.75° (*c* 0.64, CH_2Cl_2); IR (thin film, cm^{-1}) 2935, 1716, 1690, 1454, 1264; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* 8.4, 1.4 Hz, 2 H), 7.58 (tt, *J* 7.5, 1.4 Hz, 1 H), 7.44 (tt, *J* 7.5, 1.5 Hz, 2 H), 7.04 (ddd, *J* 10.2, 3.5, 1.7 Hz, 1 H), 6.86 (dd, *J* 3.5, 1.7 Hz, 1 H), 6.30 (dd, *J* 10.4, 1.5 Hz, 1 H), 4.59 (dd, *J* 4.1, 2.3 Hz, 1 H), 4.10 (ddd, *J* 11.3, 4.1, 1.7 Hz, 1 H), 4.04 (ddd, *J* 11.3, 4.0, 1.7 Hz, 1 H), 0.83 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 164.8, 142.1, 133.5, 129.8, 129.2, 129.1, 128.4, 87.6, 77.9, 62.7, 25.7, 18.1, −5.5; CIHRMS Calcd for $[C_{19}H_{26}O_5Si+H]^+$: 363.1628. Found: 363.1653; Anal. Calcd for C, 62.95; H, 7.23. Found: C, 63.14; H, 7.42.

*(2*S,*6*R*)-6-(Pivaloyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**8b**).—Compound **7b** (1.10 g, 4.82 mmol), 40 mL of CH_2Cl_2, and 1.5 mL of Et_3N were added to a round-bottom flask and cooled to −78 °C. A catalytic amount (30 mg, 0.25 mmol) of DMAP and benzoyl chloride (0.84 mL, 7.2 mmol) were added, and the solution was stirred for 3 h at −78 °C. The reaction was quenched with 50 mL of satd aq $NaHCO_3$, extracted (3×50 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 1:9 EtOAc–hexanes to give 1.12 g (3.37 mmol, 70%) of **8b**: mp 87–89 °C; R_f 0.38 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −180.9° (*c* 1.59, CH_2Cl_2); IR (thin film, cm^{-1}) 2972, 1731, 1703, 1452, 1265; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* 8.0, 1.5 Hz, 2 H), 7.62 (tt, *J* 8.0, 7.0, 1.5 Hz, 1 H), 7.47 (tt, *J* 8.0, 7.0, 1.5 Hz, 2 H), 7.08 (dd, *J* 10.0, 4.0 Hz, 1 H), 6.82 (dd, *J* 3.5 Hz, 1 H), 6.30 (dd, *J* 10.5 Hz, 1 H), 4.83 (dd, *J* 5.0, 3.0 Hz, 1 H), 4.54 (ddd, *J* 12.0, 3.0 Hz, 1 H), 4.50 (dd, *J* 12.0, 5.0 Hz, 1 H), 1.14 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 177.9, 164.8, 142.2, 133.8, 129.8, 128.9, 128.8, 128.6, 87.3, 74.5, 62.2, 38.7, 26.9; CIHRMS Calcd for $[C_{18}H_{20}O_6+NH_4]^+$: 350.1604. Found: 350.1609; Anal. Calcd for C, 65.04; H, 6.07. Found: C, 65.26; H, 6.02.

*(2*S,*6*R*) - 6 - (*tert - *Butyldimethylsilanyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl pivalate* (**8c**).—Compound **7a** (2.22 g, 8.59 mmol), 30 mL of CH_2Cl_2, and 1.5 mL of Et_3N were added to a round-bottom flask and cooled to −78 °C. A catalytic amount (53 mg, 0.43 mmol) of DMAP and pivaloyl chloride (1.06 mL, 8.59 mmol) were added, and the solution was stirred for 3 h at −78 °C. The reaction was quenched with 50 mL of satd aq $NaHCO_3$, extracted (3×50 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 1:9 EtOAc–hexanes to give 2.41 g (7.04 mmol, 82%) of **8c**: mp 88–90 °C; R_f 0.45 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −92.7° (*c* 0.89,

CH_2Cl_2); IR (thin film, cm^{-1}) 2935, 2910, 2855, 1730, 1696, 1461, 1399, 1279; ^1H NMR (500 MHz, $CDCl_3$) δ 6.92 (dd, *J* 10.5, 3.5 Hz, 1 H), 6.59 (d, *J* 3.5 Hz, 1 H), 6.23 (d, *J* 10.5 Hz, 1 H), 4.48 (dd, *J* 4.5, 3.0 Hz, 1 H), 4.06 (dd, *J* 11.5, 3.0 Hz, 1 H), 4.03 (dd, *J* 11.0, 4.0 Hz, 1 H), 1.23 (s, 9 H), 0.86 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 176.9, 142.5, 129.1, 87.0, 77.9, 62.7, 39.2, 27.0, 25.8, 18.3, −5.4 (2 C); CIHRMS Calcd for $[C_{17}H_{30}O_5Si + NH_4]^+$: 360.2206. Found: 360.2209; Anal. Calcd for C, 59.62; H, 8.84. Found: C, 59.72; H, 8.59.

*(2*S,*6*R*)-6-(Pivaloyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl pivalate* (**8d**).—Compound **7b** (4.1 g, 18 mmol), 36 mL of CH_2Cl_2, and pyridine (2.9 mL, 36 mmol) were added to a round-bottom flask and cooled to −78 °C. Pivaloyl chloride (4.4 mL, 36 mmol) was added, and the solution was stirred for 4 h at −78 °C. The reaction was quenched with 50 mL of satd aq $NaHCO_3$, extracted (3 × 50 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 1:3 Et_2O–hexanes to give 3.9 (12.6 mmol, 70%) of **8d**: mp 71–73 °C; R_f 0.67 (1:1 Et_2O–hexanes); $[\alpha]_D^{21}$ 92.9° (*c* 1.52, $CHCl_3$); IR (thin film, cm^{-1}) 2976, 2936, 2874, 1732, 1704, 1480, 1462, 1280; ^1H NMR (500 MHz, $CDCl_3$) δ 6.94 (dd, *J* 10.2, 3.6 Hz, 1 H), 6.53 (d, *J* 3.9 Hz, 1 H), 6.25 (d, *J* 10.5 Hz, 1 H), 4.70 (dd, *J* 5.7, 2.7 Hz, 1 H), 4.53 (dd, *J* 12.0, 2.7 Hz, 1 H), 4.43 (dd, *J* 12.0, 5.7 Hz, 1 H), 1.22 (s, 9 H), 1.15 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 178.1, 176.8, 142.5, 128.6, 86.6, 74.4, 62.4, 39.3, 38.8, 27.1; FABHRMS Calcd for $[C_{16}H_{24}O_6 + Na]^+$: 335.1470. Found: 335.1492.

*(2*S,*5*S,*6*R*)-6-(*tert-*Butyldimethylsilanyloxymethyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**9a**).—Enone **8a** (125 mg, 0.343 mmol) was dissolved in 2 mL CH_2Cl_2 and was cooled to −78 °C in a dry ice–acetone bath under a nitrogen atmosphere. To the solution 2 mL of a 0.4 M solution of $CeCl_3$ in CH_3OH was added. $NaBH_4$ (20 mg, 0.53 mmol) was added, and the reaction was allowed to stir at −78 °C for 1.5 h. The reaction was allowed to warm to 0 °C, diluted with 20 mL of Et_2O and was quenched with 20 mL of water. The layers were separated, and the aq layer was extracted with Et_2O (5 × 20 mL) and washed with 50 mL of brine. The combined organic extracts were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel chromatography eluting with 1:4 EtOAc–hexanes to give 118 mg (0.323 mmol, 95% yield) of alcohol **9a**: R_f 0.35 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −85.9° (*c* 2.55, CH_2Cl_2); IR (thin film, cm^{-1}) 3458, 3012, 2928, 2871, 2855, 1727, 1451, 1264; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* 8.5, 1.0 Hz, 2 H), 7.58 (ddd, *J* 8.5, 7.0, 1.0 Hz, 1 H), 7.45 (ddd, *J* 8.0, 1.5 Hz, 2 H), 6.49 (dd, *J* 1.5, 1.5 Hz, 1 H), 6.14 (ddd, *J* 10.5, 1.0 Hz, 1 H), 5.87 (dddd, *J* 10.5, 2.5 Hz, 1 H), 4.33 (dddd, *J* 9.0, 2.0 Hz, 1 H), 3.98 (dd, *J* 10.0, 4.5 Hz, 1 H), 3.87 (ddd, *J* 13.0, 8.0, 5.0 Hz, 1 H), 3.77 (dd, *J* 10.0, 8.0 Hz, 1 H), 3.33 (s, 1 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 134.2, 133.3, 129.9 (2 C), 128.4, 123.8, 88.5, 71.6, 67.1, 65.6, 25.8, 18.2, −5.5, −5.6; CIHRMS Calcd for $[C_{19}H_{28}O_5Si - C_7H_5O_2]^+$: 243.1416. Found: 243.1426; Anal. Calcd for C, 62.61; H, 7.75. Found: C, 62.45; H, 7.74.

*(2*S,*5*S,*6*R*)-6-(Pivaloyloxymethyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**9b**).—Compound **8b** (125 mg, 0.376 mmol) was dissolved in 4 mL of CH_2Cl_2 and cooled to −78 °C with a dry ice–acetone bath. To the solution, 2 mL of a 0.4 M solution of $CeCl_3$ in MeOH was added, followed by $NaBH_4$ (19 mg, 0.488 mmol), and the solution was stirred for 1.5 h. The reaction was warmed to 0 °C, and 30 mL of Et_2O and 30 mL of H_2O were added to the solution. The phases were separated, and the aq layer was extracted with (5 × 20 mL) of Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and purified by silica gel chromatography eluting with 1:4 EtOAc–hexanes to yield 123 mg (0.368 mmol, 98%) of alcohol **9b**: R_f 0.29 (3:7 EtOAc–hexanes); $[\alpha]_D^{21}$ −40.2° (*c* 2.04, CH_2Cl_2); IR (thin film, cm^{-1}) 3484, 2960, 2925, 1729, 1452, 1267; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* 8.5, 1.5 Hz, 2 H), 7.57 (ddd, *J* 8.5, 7.5, 1.5 Hz, 1 H), 7.47 (ddd, *J* 8.5, 7.5, 1.5 Hz, 2 H), 6.54 (dd, *J* 2.0, 1.0 Hz, 1 H), 6.17 (d, *J* 10.5 Hz, 1 H), 5.88 (ddd, *J* 10.5, 2.5

Hz, 1 H), 4.54 (dd, *J* 12.5, 5.0 Hz, 1 H), 4.28 (dd, *J* 12.0, 2.0 Hz, 1 H), 4.09 (ddd, *J* 9.0, 6.0, 2.0 Hz, 1 H), 3.95 (dddd, *J* 9.5, 4.5, 2.0 Hz, 1 H), 2.90 (d, *J* 6.0 Hz, 1 H), 1.16 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 165.4, 134.6, 133.3, 129.8, 129.7, 128.4, 124.5, 88.9, 72.8, 63.3, 63.2, 38.9, 27.1; CIHRMS Calcd for $[C_{18}H_{22}O_6 + NH_4]^+$: 352.1760. Found: 352.1739.

*(2*S,*5*S,*6*R*)-6-(*tert-*Butyldimethylsilanyloxymethyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl pivalate* (**9c**).—Compound **8c** (85 mg, 0.25 mmol) was dissolved in 1.5 mL of CH_2Cl_2 and cooled to −78 °C with a dry ice–acetone bath. To the solution, 2 mL of a 0.4 M solution of $CeCl_3$ in MeOH was added, followed by $NaBH_4$ (12 mg, 0.30 mmol), and the solution was stirred for 1.5 h. The reaction was warmed to 0 °C, and 20 mL of Et_2O and 20 mL of H_2O were added to the solution. The phases were separated and the aq layer was extracted with (5 × 20 mL) of Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and purified by silica gel chromatography eluting with 1:9 EtOAc–hexanes to yield 82 mg (0.24 mmol, 95%) of alcohol **9c**: R_f 0.40 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −17.7° (*c* 1.42, CH_2Cl_2); IR (thin film, cm^{-1}) 3496, 2957, 2929, 2857, 1742, 1472, 1463, 1280, 1255; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (dd, *J* 3.0, 1.5 Hz, 1 H), 6.06 (dd, *J* 10.0, 1.5 Hz, 1 H), 5.74 (ddd, *J* 10.0, 3.0, 3.0 Hz, 1 H), 4.26 (dd, *J* 6.5, 2.0 Hz, 1 H), 3.94 (dd, *J* 8.0, 3.0 Hz, 1 H), 3.92 (dd, *J* 8.0, 3.0 Hz, 1 H), 3.74 (m, 2 H), 3.20 (d, *J* 2.5 Hz, 2 H), 1.22 (s, 9 H), 0.91 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 134.8, 124.0, 87.7, 71.5, 67.1, 65.7, 38.0, 25.8, 18.2, −5.5, −5.6; CIHRMS Calcd for $[C_{17}H_{32}O_5Si - C_5H_9O_2]^+$: 243.1416. Found: 243.1416.

*(2*S,*5*S,*6*R*)-6-(Pivaloyloxymethyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl pivalate* (**9d**).—Compound **8d** (31 mg, 0.10 mmol) was dissolved in 0.5 mL of CH_2Cl_2 and cooled to −78 °C with a dry ice–acetone bath. To the solution 1 mL of a 0.4 M solution of $CeCl_3$ in MeOH was added, followed by $NaBH_4$ (3.8 mg, 0.10 mmol), and the solution was stirred for 0.5 h. The reaction was warmed to 0 °C, and 20 mL of Et_2O and 20 mL of $NaHCO_3$ were added to the solution. The phases were separated and the aq layer was extracted with (5 × 20 mL) of Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and purified by silica gel chromatography eluting with 1:3 Et_2O–hexanes to yield 29 mg (0.092 mmol, 92%) of alcohol **9d**: R_f 0.25 (1:3 Et_2O–hexanes); $[\alpha]_D^{21}$ 36.1° (*c* 2.80, $CHCl_3$); IR (thin film, cm^{-1}) 3156, 2976, 2874, 1728, 1480, 1462, 1283; ^{1}H NMR (500 MHz, C_6D_6) δ 6.36 (d, *J* 2.7 Hz, 1 H), 5.76 (dt, *J* 10.2, 1.2 Hz, 1 H), 5.34 (ddd, *J* 10.0, 2.7, 1.8 Hz, 1 H), 4.38 (dd, *J* 12.3, 5.4 Hz, 1 H), 4.18 (dd, *J* 12.3, 2.1 Hz, 1 H), 3.87 (ddd, *J* 9.3, 5.3, 2.1 Hz, 1 H), 3.79 (d, *J* 9.9 Hz, 1 H), 2.39 (bs, 1 H), 1.11 (s, 9 H), 1.08 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 177.4, 134.2, 124.7, 110.4, 88.2, 72.6, 66.5, 63.3, 39.0, 27.2; FABHRMS Calcd for $[C_{16}H_{26}O_6 + Na]^+$: 337.1627. Found: 337.1634.

*(2*S,*5*S,*6*R*)-6-(*tert-*Butyldimethylsilanyloxymethyl)-5-ethoxycarbonyloxy-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**9e**).—Compound **9a** (190 mg, 0.521 mmol) was dissolved in 5 mL of CH_2Cl_2 and cooled to −78 °C. Pyridine (85 μL, 1.0 mmol) and DMAP (7 mg, 0.05 mmol) were added to the solution, followed by ethyl chloroformate (75 μL, 0.78 mmol), and the solution was stirred for 3 h. The reaction was warmed to 0 °C, and 30 mL of Et_2O and 30 mL of satd aq $NaHCO_3$ were added to the solution. The phases were separated, and the aq layer was extracted (3 × 20 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and purified by silica gel chromatography eluting with 1:4 Et_2O–hexanes to yield 185 mg (0.424 mmol, 81%) of carbonate **9e**: R_f 0.3 (1:4 Et_2O–hexanes); $[\alpha]_D^{21}$ −20.3° (*c* 2.00, CH_2Cl_2); IR (thin film, cm^{-1}) 2925, 2841, 1725, 1256; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* 8.5, 1.0 Hz, 2 H), 7.58 (tt, *J* 8.5, 7.5, 1.5 Hz, 1 H), 7.44 (tt, *J* 7.5, 1.5 Hz, 2 H), 6.57 (d, *J* 3.0 Hz, 1 H), 6.17 (d, *J* 10.0 Hz, 1 H), 5.98 (ddd, *J* 10.0, 3.0, 2.0 Hz, 1 H), 5.33 (ddd, *J* 9.5, 3.5, 2.0 Hz, 1 H), 4.24 (q, *J* 14.5, 7.0 Hz, 2 H), 4.07 (ddd, *J* 9.0, 3.5, 3.5 Hz, 1 H), 3.83 (m, 2 H), 1.33 (t, *J* 7.5 Hz, 3 H), 0.84 (s, 9 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 154.3, 133.3, 130.6, 129.8, 128.4, 126.2, 88.7, 71.6, 68.1, 64.4, 62.2, 25.8, 18.3, 14.2, −5.4, −5.5; FABHRMS Calcd

for $[C_{22}H_{32}O_7Si - C_7H_5O_2]^+$: 315.1628. Found: 315.1596; Anal. Calcd for C, 60.52; H, 7.39. Found: C, 60.80; H, 7.25.

1-O-*Benzoyl*-*6*-O-tert-*butyldimethylsilyl*-α-D-*mannopyranose* (**1a**).—A round-bottom flask containing a 0.75 M solution of compound **9a** in 1:1 *tert*-butanol–acetone was cooled to 0 °C with an ice water bath. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide in water was added to the solution. After the solution was cooled, a catalytic amount (2 mol%) of OsO_4 was added to the reaction. The reaction was allowed to stir at 0 °C for 8 h. The reaction was quenched with satd aq Na_2SO_3, and the mixture was extracted (5 × 25 mL) with Et_2O and washed with brine. The combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and purified by silica gel chromatography eluting with 3:1 Et_2O–hexanes to give triol **1a** as a white solid in 80% yield: mp 100–104 °C; R_f 0.2 (3:1 Et_2O–hexanes); $[\alpha]_D^{21}$ −198.4° (*c* 1.25, CH_2Cl_2); IR (thin film, cm^{-1}) 3461, 3024, 2963, 1715, 1272; ^1H NMR (300 MHz, DMSO) δ 7.98 (d, *J* 6.0 Hz, 2 H), 7.70 (t, *J* 6.0 Hz, 1 H), 7.56 (t, *J* 6.0 Hz, 2 H), 6.09 (d, J 2.0 Hz, 1 H), 5.19 (d, *J* 4.0 Hz, 1 H), 4.91 (d, *J* 6.0 Hz, 1 H), 4.79 (d, *J* 6.0 Hz, 1 H), 3.87 (dd, *J* 11.5, 1.5, 1.0 Hz, 1 H), 3.79 (dd, *J* 4.0, 3.5, 2.0 Hz, 1 H), 3.70 (dd, *J* 9.0, 6.0, 3.5 Hz, 1 H), 3.66 (dd, *J* 6.0, 1.5 Hz, 1 H), 3.57 (ddd, *J* 10.0, 6.0, 1.5 Hz, 1 H), 3.49 (dd, *J* 10.0, 9.0, 6.0 Hz, 1 H), 0.78 (s, 9 H), −0.01 (s, 3 H), −0.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 133.1, 129.8, 129.6, 128.4, 128.1, 127.7, 127.2, 94.6, 75.2, 72.1, 68.6, 63.9, 25.7, 18.1, −5.4; FABHRMS Calcd for $[C_{19}H_{30}O_7Si + H]^+$: 399.1839. Found: 399.1836; Anal. Calcd for C, 57.26; H, 7.59. Found: C, 57.10; H, 7.71.

1-O-*Benzoyl*-*6*-O-tert-*butyldimethylsilyl*-*3*-O-*ethoxycarbonyl*-α-D-*mannopyranose* (**1b**).—A round-bottom flask containing a 0.75 M solution of compound **9e** in 1:1 *tert*-butanol–acetone was cooled to 0 °C with an ice-water bath. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide in water was added to the solution. A catalytic amount (2 mol%) of OsO_4 was added to the reaction. The reaction was allowed to stir at 0 °C for 8 h. The reaction was quenched with satd aq Na_2SO_3, and the mixture was extracted (5 × 20 mL) with Et_2O and washed with brine. The combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and purified by silica gel chromatography eluting with 1:1 Et_2O–hexanes to give diol **1b** as a white solid in 75% yield: R_f 0.30 (3:1 Et_2O–hexanes); $[\alpha]_D^{21}$ 37.0° (*c* 2.00, CH_2Cl_2); IR (thin film, cm^{-1}) 2924, 2850, 1732 1629, 1273; ^1H NMR (200 Mhz, $CDCl_3$) δ 8.00 (dd, *J* 7.0, 1.5 Hz, 2 H), 7.56 (tt, *J* 7.0, 1.5 Hz, 1 H), 7.40 (tt, *J* 7.0, 1.5 Hz, 2 H), 6.40 (s, 1 H), 5.10 (t, *J* 10.0 Hz, 1 H), 4.20 (q, *J* 14.0, 7.0 Hz, 2 H), 4.10 (s, 1 H), 3.90 (ddd, *J* 10.0, 3.0, 3.0 Hz, 1 H), 3.84 (d, *J* 3.0 Hz, 2 H), 3.46 (s, 1 H), 1.30 (t, *J* 7.0 Hz, 3 H), 0.90 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (60 MHz, C_6D_6) δ 164.2, 155.4, 133.7, 129.8, 129.1, 128.6, 93.6, 73.0 (2 C), 70.4, 70.0, 64.8, 62.1, 25.8, 18.27, 14.1, −5.5; FABHRMS Calcd for $[C_{22}H_{34}O_9Si + H]^+$: 471.2050. Found: 471.2046.

2-O-*Acetyl*-*1*-O-*benzoyl*-*3*-O-*ethoxycarbonyl*-*6*-O-tert-*butyldimethylsilyl*-α-D-*mannopyranose* (**1d**).—To a round-bottom flask containing a 0.5 M solution of carbonate **1b** in benzene trimethylorthoacetate (5 equiv) and a catalytic amount of *p*-toluenesulfonic acid (5 mol%) was added. The reaction was allowed to stir until only the cyclic orthoester was observed via its markedly less polar spot on thin-layer chromatography (TLC) (R_f 0.7, 1:4 Et_2O–hexanes). Upon formation of the orthoester, the solvent was removed under reduced pressure and was replaced by an equal amount of THF and water to make the concentration approximately 0.4 M. The reaction was allowed to stir until hydrolysis was complete as seen by TLC (R_f 0.3, 1:4 Et_2O–hexanes) producing exclusively the C-2 axial acetate ester **1d** as a clear, light yellow oil in a 60% yield from the diol: R_f 0.30 (1:4 Et_2O–hexanes); $[\alpha]_D^{21}$ 28.6° (*c* 2.36, $CHCl_3$); IR (thin film, cm^{-1}) 3492, 3066, 2931, 1736, 1629, 1600, 1254; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* 7.0, 1.2 Hz, 2 H), 7.58 (dt, *J* 7.0, 1.2 Hz, 1 H), 7.49 (dt, *J* 7.0, 1.2 Hz, 2 H), 6.36 (d, *J* 2.0 Hz, 1 H), 5.24 (m, 2 H), 4.24 (q, *J* 14.0, 7.0 Hz, 2 H), 3.89 (dt, *J* 10.0, 2.5 Hz, 1 H), 3.79 (m, 2 H), 2.18 (s, 3 H), 1.33 (t, *J* 7.0 Hz, 3 H), 0.09 (s, 9 H), 0.04 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1,

163.6, 155.3, 133.7, 129.7, 128.5, 128.0, 90.8, 72.7, 72.2, 71.3, 68.9, 64.7, 61.3, 25.6, 20.7, 18.0, 15.1, 14.0, −5.5, −5.7; FABHRMS Calcd for $[C_{24}H_{36}O_{10}Si + NH_4]^+$: 530.2422. Found: 530.2408.

*(2*S,*6*R*) - 6 - (*tert - *Butyldimethylsilanyloxy-methyl) - 5 - (*p - *nitrobenzoyloxy) - 5,6 - dihydro - 2*H*-pyran-2-yl benzoate (not shown, Scheme 6).*—Alcohol **9c** (300 mg, 0.871 mmol) was dissolved in 3 mL of THF. The solution was cooled to 0 °C, and triphenylphosphine (456 mg, 1.74 mmol), *p*-nitrobenzoic acid (290 mg, 1.74 mmol), and diethyl azodicarboxylate (275 μL, 1.74 mmol) were added to the solution. The solution was stirred for 12 h, quenched with satd aq $NaHCO_3$ (15 mL), and extracted (5 × 20 mL) with Et_2O. The extracts were dried ($MgSO_4$), concentrated, and purified by silica gel chromatography eluting with 10% EtOAc–hexanes to yield 280 mg (0.566 mmol, 65%) of the *p*-nitrobenzoic ester: R_f 0.57 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −181.3° (*c* 1.01, CH_2Cl_2); IR (thin film, cm^{-1}) 3055, 2957, 2930, 2883, 2857, 1728, 1531, 1344, 1320, 1270; ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* 8.5 Hz, 2 H), 8.21 (d, *J* 9.0 Hz, 2 H), 6.42 (d, *J* 10.0, 5.5 Hz, 1 H), 6.41 (d, *J* 4.0 Hz, 1 H), 6.09 (dd, *J* 10.0, 3.0 Hz, 1 H), 5.38 (dd, *J* 6.0, 2.5 Hz, 1 H), 4.28 (ddd, *J* 7.0, 2.5 Hz, 1 H), 3.81 (d, *J* 7.0 Hz, 2 H), 1.24 (s, 9 H), 0.80 (s, 9 H), −0.01 (s, 3 H), −0.09 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 163.9, 150.7, 135.3, 130.8, 129.7, 126.2, 123.6, 87.7, 71.3, 63.6, 61.3, 39.1, 27.0, 25.7, 18.1, −5.49, −5.65; CIHRMS Calcd for $[C_{24}H_{35}O_8NSi + NH_4]^+$: 511.2476. Found: 511.2474; Anal. Calcd for C, 58.39; H, 7.15. Found: C, 58.36; H, 7.20.

*(2*S,*5*R,*6*R*)-6-(*tert-*Butyldimethylsilanyloxy-methyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl pivalate* (**11**).—The *p*-nitrobenzoic ester (64 mg, 0.13 mmol) was dissolved in 2 mL of CH_3OH, and Et_3N (50 μL, 0.36 mmol) was added to the solution. The solution was stirred for 12 h, and the solution was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (1:4 EtOAc–hexanes) to yield 41 mg (0.12 mmol, 92%) of alcohol **11**: R_f 0.22 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −98.9° (*c* 1.23, CH_2Cl_2); IR (thin film, cm^{-1}) 3476, 2956, 2929, 2857, 1739, 1472, 1278; ^1H NMR (500 MHz, $CDCl_3$) δ 6.33 (dd, *J* 3.0 Hz, 1 H), 6.29 (ddd, *J* 10.0, 6.0, 1.0 Hz, 1 H), 5.92 (dd, *J* 10.0, 3.0 Hz, 1 H), 4.03 (ddd, *J* 6.0, 6.0, 2.0 Hz, 1 H), 3.99 (td, *J* 7.5, 6.0, 2.0 Hz, 1 H), 3.88 (dd, *J* 16.5, 10.5 Hz, 1 H), 3.84 (dd, *J* 10.5, 6.0 Hz, 1 H), 2.05 (bs, 1 H), 1.21 (s, 9 H), 0.90 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 130.6, 126.9, 88.2, 72.8, 62.5, 61.3, 39.0, 27.0, 25.9, 18.3, −5.3, −5.4; CIHRMS Calcd for $[C_{17}H_{32}O_5Si–C_5H_9O_2]^+$: 243.1416. Found: 243.1415.

1-O-*Pivaloyl-6*-O-tert-*butyldimethylsilyl-α*-D-*talose* (**12**).—A round-bottom flask containing a 0.75 M solution of alcohol **11** in CH_2Cl_2 was cooled to −78 °C with an acetone–dry ice bath. To the stirring solution, OsO_4 (1.2 equiv) and *N*,*N*,*N*′*N*′-tetramethylethylenediamine (1.2 equiv) was added. The solution was cooled and turned a dark orange color. The reaction was allowed to stir at −78 °C for 2 h. The reaction was warmed to rt. The solvent was removed under reduced pressure and replaced with equal volumes of satd aq Na_2SO_3 and THF to make the solution 0.25 M. The mixture was heated to reflux for 3 h before the solution was poured onto brine and extracted (5 × 25 mL) EtOAc. The combined organic extracts were dried ($MgSO_4$), concentrated and purified by silica gel chromatography eluting with 1:1 Et_2O–hexanes to give protected talose **12** as a white solid in 80% yield: mp 134–135 °C; R_f 0.5 (Et_2O); $[\alpha]_D^{21}$ −53.6° (*c* 0.39, CH_2Cl_2); IR (thin film, cm^{-1}) 3475, 3250, 2956, 2936, 2856, 1737; ^1H NMR (200 MHz, $CDCl_3$) δ 6.23 (s, 1 H), 4.25 (s, 1 H), 4.00–3.96 (m, 2 H), 3.85–3.70 (m, 2 H), 1.55 (s, 3 H), 1.21 (s, 9 H), 0.88 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 94.29, 71.6, 71.4, 70.0, 66.3, 64.5, 39.0, 27.0, 25.7, 18.2, −5.5, −5.6; CIHRMS Calcd for $[C_{17}H_{34}O_7Si + NH_4]^+$: 396.2418. Found: 396.2418; Anal. Calcd for C, 53.94; H, 9.05. Found: C, 53.99; H, 8.89.

1-O-*Pivaloyl-6*-O-tert-*butyldimethylsilyl-α*-D-*gulopyranose* (**13**).—A round-bottom flask containing a 0.75 M solution of alcohol **11** in 1:1 *tert*-butanol–acetone was cooled to 0 °C with an ice-water bath. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-

oxide in H_2O was added. After cooling, a catalytic amount (2 mol%) of OsO_4 was added to the reaction, which was allowed to stir at 0 °C for 8 h. The reaction was quenched with satd aq Na_2SO_3, and the mixture was extracted (5×25 mL) with Et_2O and washed with brine. The combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and purified by silica gel chromatography eluting with 1:1 Et_2O–hexanes to give protected gulose **13** in 80% yield: mp 109–112°C; R_f 0.5 (Et_2O); $[\alpha]_D^{21}$ −42.7° (*c* 0.81, CH_2Cl_2); IR (thin film, cm^{-1}) 3440, 2957, 2933, 2852, 1724; ^1H NMR (200 MHz, $CDCl_3$) δ 6.20 (d, *J* 4.2 Hz, 1 H), 4.22 (dd, *J* 4.4, 4.2 Hz, 1 H), 4.12 (d, *J* 3.9 Hz, 1 H), 4.04 (d, *J* 3.9 Hz, 1 H), 4.02 (d, *J* 3.0 Hz, 1 H), 3.98 (d, *J* 6.0 Hz, 1 H), 3.97 (d, *J* 6.0 Hz, 1 H), 2.52 (bs, 3 H), 1.23 (s, 9 H), 0.89 (s, 9 H), 0.09 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 92.6, 71.8, 70.0, 65.9, 65.2, 64.2, 39.0, 27.1, 25.8, −5.5, −5.6; CIHRMS Calcd for $[C_{17}H_{34}O_7Si + NH_4]^+$: 396.2418. Found: 396.2399; Anal. Calcd for C, 53.94; H, 9.05. Found: C, 54.32; H, 8.83.

*(2*S,*5*S,*6*R*)-6-(*tert-*Butyldimethylsilanyloxymethyl)-5-(*tert-*butyldimethylsilanyloxy)-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**17a**).—Compound **9a** (25 mg, 0.069 mmol) was dissolved in 1 mL of CH_2Cl_2, cooled to −78 °C, and 2,6-lutidine (25 μL, 0.207 mmol) was added. The reaction was stirred for 3 h, warmed to rt, and 10 mL of Et_2O and 10 mL of satd aq $NaHCO_3$ were added to the solution. The phases were separated, and the aq layer was extracted (3×10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), and concentrated, and the crude product was purified by silica gel chromatography, eluting with 3:7 CH_2Cl_2–hexanes to give 24 mg (0.050 mmol, 73%) of pyran **17a**: R_f 0.63 (1:1 CH_2Cl_2–hexanes); $[\alpha]_D^{21}$ −21.0° (*c* 1.41, CH_2Cl_2); IR (thin film, cm^{-1}) 3062, 3021, 2955, 2929, 2857, 1730, 1602, 1472, 1260; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* 8.5, 1.5 Hz, 2 H), 7.56 (ddd, *J* 8.5, 7.0, 1.5 Hz, 1 H), 7.43 (ddd, *J* 8.0, 7.0, 2.0 Hz, 2 H), 6.53 (dd, *J* 2.5, 1.0 Hz, 1 H), 6.04 (d, *J* 10.0, 1.0 Hz, 1 H), 5.83 (dddd, *J* 10.0, 2.5, 2.0 Hz, 1 H), 4.33 (dddd, *J* 10.0, 3.5, 2.0 Hz, 1 H), 3.84 (m, 3 H), 0.93 (s, 9 H), 0.86 (s, 9 H), 0.15 (s, 3 H), 0.13 (s, 3 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 136.0, 133.1, 130.2, 129.9, 128.3, 123.8, 89.4, 75.0, 63.4, 62.1, 25.9, 25.8, 18.4, 18.0, −4.3, −4.8, −5.1, −5.2; CIHRMS Calcd for $[C_{25}H_{42}O_5Si_2 + NH_4]^+$: 496.2915. Found: 496.2914; Anal. Calcd for C, 62.73; H, 8.85. Found: C, 62.39; H, 8.71.

*(2*S,*5*S,*6*R*) - 6 - (Pivaloyloxymethyl) - 5-pivaloyloxy-5,6-dihydro-2*H*-pyran-2-yl benzoate* (**17b**).—Compound **9b** (73 mg, 0.218 mmol) was dissolved in 2 mL of CH_2Cl_2, and Et_3N (91 μL, 0.654 mmol) and DMAP (1.5 mg, 0.012 mmol) were added to the solution. Pivaloyl chloride (40 μL, 0.327 mmol) was added, and the solution was stirred at rt for 6 h. The reaction was quenched with 15 mL of satd aq $NaHCO_3$ and extracted (5×20 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), and concentrated. The product was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 75 mg (0.18 mmol, 82%) of compound **17b**: R_f 0.45 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ −3.22° (*c* 1.04, CH_2Cl_2); IR (thin film, cm^{-1}) 2973, 2873, 1733, 1480, 1265; ^1H NMR (500 MHz, C_6D_6) δ 8.07 (dt, *J* 8.0, 1.5 Hz, 2 H), 7.09 (tt, *J* 8.5, 7.0, 1.5 Hz, 1 H), 7.00 (tt, *J* 8.0, 1.5 Hz, 2 H), 6.63 (dd, *J* 1.0 Hz, 1 H), 5.77 (ddd, *J* 10.0, 1.5 Hz, 1 H), 5.48 (ddd, *J* 9.5, 3.5, 2.0 Hz, 1 H), 5.42 (ddd, *J* 10.0, 3.0, 2.5 Hz, 1 H), 4.31 (ddd, *J* 9.5, 6.0, 1.5 Hz, 1 H), 4.26 (dd, *J* 12.0, 1.5 Hz, 1 H), 4.20 (dd, *J* 12.0, 6.0 Hz, 1 H), 1.14 (s, 9 H), 1.08 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 177.6, 165.2, 133.4, 131.4, 129.8, 129.7, 128.4, 125.8, 88.7, 69.7, 64.5, 62.3, 38.9, 38.8, 27.04, 26.98; CIHRMS Calcd for $[C_{23}H_{30}O_7 + NH_4]^+$: 436.2335. Found: 436.2334.

*(2*S,*5*S,*6*R*)-6-(*tert-*Butyldimethylsilanyloxymethyl)-5-(*tert-*butyldimethylsilanyloxy)-5,6-dihydro-2*H*-pyran-2-ol* (**18a**).—Compound **17a** (20 mg, 0.042 mmol) was dissolved in 0.5 mL of MeOH, 50 μL of Et_3N, and 50 μL of H_2O and heated to reflux for 6 h. The solution was concentrated and purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 10 mg (0.025 mmol, 64%) of alcohol **18a**: mp 90–95 °C; R_f 0.21 (1:9 EtOAc–hexanes); IR (thin film, cm^{-1}) 3409, 2952, 2929, 2886, 2857, 1471, 1462, 1254; ^1H NMR (500 MHz, C_6D_6) major isomer δ 5.76

(d, *J* 10.5 Hz, 1 H), 5.55 (ddd, *J* 10.5, 2.0, 2.0 Hz, 1 H), 5.21 (dd, *J* 2.5, 1.5 Hz, 1 H), 4.38 (ddd, *J* 10.0, 3.0, 1.5 Hz, 1 H), 3.95–3.84 (3 H), 2.73 (d, *J* 5.0 Hz, 1 H), 1.03 (s, 9 H), 0.96 (s, 9 H), 0.19 (s, 3 H), 0.18 (s, 3 H), 0.10 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) major isomer δ 134.1, 127.2, 89.2, 72.7, 64.0, 62.9, 26.2, 25.9, 18.7, 18.1, −4.2, −4.7, −4.8, −5.1; CIHRMS Calcd for $[C_{18}H_{38}O_4Si_2 - H_2O + NH_4]^+$: 374.2547. Found: 374.2543.

*(2*S,*5*S,*6*R*)-6-(Pivaloyloxymethyl)-5-pivaloyloxy-5,6-dihydro-2*H*-pyran-2-ol* (**18b**).—Compound **17b** (66 mg, 0.16 mmol) was dissolved in 2 mL of MeOH, 75 μL of Et_3N, and 75 μL of H_2O and heated to reflux for 6 h. The solution was concentrated and purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 20 mg (0.093 mmol, 40%) of alcohol **18b**: R_f 0.20 (1:9 EtOAc–hexanes); IR (thin film, cm^{-1}) 3469, 2974, 2934, 2874, 1733, 1481, 1283; ^{1}H NMR (500 MHz, C_6D_6) major isomer δ 5.69 (d, *J* 10.5 Hz, 1 H), 5.54 (ddd, *J* 7.5, 3.5, 1.5 Hz, 1 H), 5.48 (dt, *J* 10.0, 2.5 Hz, 1 H), 5.05 (bs, 1 H), 4.36 (dd, *J* 12.0, 2.0 Hz, 1 H), 4.29 (dd, *J* 12.0, 4.5 Hz, 1 H), 4.19 (dddd, *J* 10.0, 4.5, 2.0 Hz, 1 H), 2.40 (t, *J* 6.0 Hz, 1 H), 1.20 (s, 9 H), 1.13 (s, 9 H).; ^{13}C NMR (125 MHz, $CDCl_3$) major isomer δ 177.7, 177.2, 129.5, 129.0, 89.2, 67.9, 64.9, 62.7, 39.0, 38.8, 27.3, 27.1; CIHRMS Calcd for $[C_{16}H_{26}O_6 + NH_4]^+$: 332.2073. Found: 332.2072.

*(5*S,*6*R*)-5-(*tert*-Butyldimethylsilanyloxy)-6-(*tert*-butyldimethylsilanyloxymethyl)-5,6-dihydropyran-2-one* (**19a**).—Compound **18a** (35 mg, 0.093 mmol) was dissolved in 3 mL of benzene, and activated MnO_2 (100 mg, 1.15 mmol) was added to the solution. The solution was heated at reflux for 12 h. The solution was cooled to rt and filtered through a pad of Celite, washing with 100 mL of Et_2O. The filtrate was concentrated and purified by silica gel chromatography eluting with 1:9 EtOAc–hexanes to yield 26 mg (0.070 mmol, 75%) of pure pyranone **19a**: R_f 0.67 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ 43.7° (*c* 1.19, CH_2Cl_2); IR (thin film, cm^{-1}) 2952, 2927, 2883, 2855, 1747, 1471, 1251, 1216; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (dd, *J* 10.0, 2.5 Hz, 1 H), 5.91 (dd, *J* 10.0, 2.0 Hz, 1 H), 4.70 (ddd, *J* 9.0, 2.0, 2.0 Hz, 1 H), 4.18 (ddd, *J* 9.0, 3.0, 2.5 Hz, 1 H), 3.89 (dd, *J* 11.5, 2.5 Hz, 1 H), 3.84 (dd, *J* 11.5, 3.0 Hz, 1 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.14 (s, 3 H), 0.13 (s, 3 H), 0.094 (s, 3 H), 0.088 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 149.8, 119.5, 83.0, 62.3, 61.0, 25.8, 25.6, 18.3, 17.9, −4.5, −5.0, −5.2, −5.4; CIHRMS Calcd for $[C_{18}H_{36}O_4Si_2 + NH_4]^+$: 390.2496. Found: 390.2462.

*(2*R,*3*S*)-2-(Pivaloyloxymethyl)-6-oxo-3,6-dihydro-2*H*-pyran-3-yl pivalate* (**19b**).—Compound **18b** (21 mg, 0.066 mmol) was dissolved in 3 mL of benzene, and activated MnO_2 (100 mg, 1.15 mmol) was added to the solution. The solution was heated at reflux for 12 h. The solution was cooled to rt and filtered through a pad of Celite, washing with 100 mL of Et_2O. The filtrate was concentrated and purified by silica gel chromatography eluting with 1:9 EtOAc–hexanes to yield 18 mg (0.058 mmol, 88%) of pure pyranone **19b**: R_f 0.41 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ 27.7° (*c* 0.84, CH_2Cl_2); IR (thin film, cm^{-1}) 2921, 2851, 1737, 1480, 1462, 1367, 1280; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (dd, *J* 10.0, 3.0 Hz, 1 H), 6.13 (dd, *J* 10.0, 2.0 Hz, 1 H), 5.52 (ddd, *J* 7.5, 3.0, 2.0 Hz, 1 H), 4.67 (ddd, *J* 7.5, 4.5, 3.0 Hz, 1 H), 4.33 (dd, *J* 12.0, 4.5 Hz, 1 H), 4.27 (dd, *J* 12.0, 3.0 Hz, 1 H), 1.22 (s, 9 H), 1.21 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) 177.9, 177.2, 161.4, 143.4, 122.4, 77.7, 63.1, 61.2, 38.9, 38.8, 27.1, 26.9; CIHRMS Calcd for $[C_{16}H_{24}O_6 + NH_4]^+$: 330.1917. Found: 330.1933.

*(6*R*)-6-*tert*-Butyldimethylsilanyloxymethyl-pyran-2,5-dione* (**20**).—Compound **7a** (460 mg, 1.79 mmol) was dissolved in 15 mL of acetone, and Jones reagent (2.5 M) was dripped in at rt until a yellow color persisted. After 15 min the starting material was no longer visible by TLC, and the solution was filtered through a pad a Celite and washed with 150 mL of Et_2O. The Et_2O filtrate was washed with satd aq $NaHCO_3$ (50 mL), and the phases were separated. The organic layer was dried ($MgSO_4$) and concentrated to yield 367 mg (1.43 mmol, 80%) of pure dione **20**: R_f 0.40 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ 55.8° (*c* 3.71, CH_2Cl_2); IR (thin film, cm^{-1}) 3949, 2928, 2892, 2856, 1719, 1697, 1461, 1360, 1306, 1261; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (d,

J 10.0 Hz, 1 H), 6.73 (d, *J* 10.0 Hz, 1 H), 4.83 (dd, *J* 2.0, 1.5 Hz, 1 H), 4.01 (dd, *J* 12.5, 1.5 Hz, 1 H), 3.97 (dd, *J* 12.5, 2.0 Hz, 1 H), 0.74 (s, 9 H), −0.04 (s, 3 H), −0.07 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 160.5, 138.8, 136.1, 84.3, 65.1, 25.4, 17.9, −5.9, −6.0; CIHRMS Calcd for $[C_{12}H_{20}O_4Si + NH_4]^+$: 274.1475. Found: 274.1484; Anal. Calcd for C, 56.23; H, 7.87. Found: C, 56.10; H, 7.68.

*(5*R,*6*R*) - 6 -* tert *- Butyldimethylsilanyloxymethyl - 5 - hydroxy - 5,6 - dihydro - pyran - 2 - one* (**21**).—Compound **20** (870 mg, 3.39 mmol) was dissolved in 10 mL of CH_2Cl_2, cooled to −78 °C with a dry ice–acetone bath, and 17 mL of a 0.4 M solution of $CeCl_3$ in MeOH was added to the solution. $NaBH_4$ (193 mg, 5.09 mmol) was added, and the solution was stirred for 1.5 h. The solution was warmed to rt, and 50 mL of Et_2O and 100 mL of H_2O were added. The phases were separated, and the aq layer was extracted (5 × 50 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), and concentrated, and the crude product was purified by silica gel chromatography eluting with (1:4 EtOAc–hexanes) to give 840 mg (3.25 mmol, 96%) of compound **21**: R_f 0.65 (3:7 EtOAc–hexanes); $[\alpha]_D^{21}$ −73.2° (*c* 0.90, CH_2Cl_2); IR (thin film, cm^{-1}) 3424, 2954, 2930, 2885, 2857, 1714, 1472, 1257; ^{1}H NMR (500 MHz, C_6D_6) δ 6.25 (dd, *J* 9.5, 6.0 Hz, 1 H), 5.73 (d, *J* 9.5 Hz, 1 H), 3.96 (dd, *J* 10.0, 7.0 Hz, 1 H), 3.87 (ddd, *J* 7.0, 5.0, 3.0 Hz, 1 H), 3.79 (dd, *J* 10.0, 5.0 Hz, 1 H), 3.76 (m, 1 H), 3.00 (bs, 1 H), 0.98 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 163.1, 144.2, 122.7, 79.9, 61.7, 60.4, 26.0, 18.4, −5.3, −5.4; CIHRMS Calcd for $[C_{12}H_{22}O_4Si + NH_4]^+$: 276.1631. Found: 276.1631; Anal. Calcd for C, 55.79; H, 8.59. Found: C, 55.63; H, 8.45.

*(2*R,*3*R*) - 2 - (*tert *- Butyldimethylsilanyloxymethyl)-6-oxo-3,6-dihydro-2*H*-pyran-3-yl pivalate* (**22a**).—Compound **21** (23 mg, 0.089 mmol) was dissolved in 1 mL of CH_2Cl_2, cooled to 0 °C, and 75 μL of pyridine was added, to the solution. Pivaloyl chloride (110 μL, 0.89 mmol) was added and the solution was stirred for 8 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated, and the aq layer was extracted (5 × 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), and concentrated, and the crude product was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 24 mg (0.07 mmol, 80%) of compound **22a**: R_f 0.29 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ −172.5° (*c* 0.53, CH_2Cl_2); IR (thin film, cm^{-1}) 2957, 2930, 2857, 1735, 1480, 1277, 1252; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, *J* 10.0, 6.0 Hz, 1 H), 6.20 (d, *J* 10.0 Hz, 1 H), 5.28 (dd, *J* 6.0, 3.0 Hz, 1 H), 4.55 (ddd, *J* 7.5, 7.5, 3.0 Hz, 1 H), 3.88 (d, *J* 7.5 Hz, 2 H), 1.19 (s, 9 H), 0.87 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 162.3, 140.7, 124.9, 78.5, 60.8, 60.0, 39.0, 27.0, 25.7, 18.1, −5.5, −5.6; CIHRMS Calcd for $[C_{17}H_{30}O_5Si + NH_4]^+$: 343.1941. Found: 343.1941; Anal. Calcd for C, 59.62; H, 8.84. Found: C, 59.80; H, 8.66.

*(2*R,*3*R*) - 2 - (*tert *- Butyldimethylsilanyloxymethyl)-6-oxo-3,6-dihydro-2*H*-pyran-3-yl acetate* (**22b**).—Compound **21** (31 mg, 0.12 mmol) was dissolved in 1.5 mL of CH_2Cl_2 and 100 μL of pyridine was added to the solution. Acetic anhydride (115 μL, 1.2 mmol) was added, and the solution was stirred at rt for 8 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated, and the aq layer was extracted (5 × 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), and concentrated, and the crude product was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 34 mg (0.11 mmol, 92%) of compound **22b**: R_f 0.33 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ −207° (*c* 2.26, CH_2Cl_2); IR (thin film, cm^{-1}) 2955, 2930, 2886, 2857, 1747, 1472, 1372, 1252; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (dd, *J* 10.0, 6.0 Hz, 1 H), 6.17 (d, *J* 10.0 Hz, 1 H), 5.28 (dd, *J* 6.0, 3.0 Hz, 1 H), 4.52 (ddd, *J* 8.0, 7.5, 3.0 Hz, 1 H), 3.86 (d, *J* 7.5 Hz, 2 H), 2.05 (s, 3 H), 0.84 (s, 9 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 162.1, 140.4, 125.0, 78.0, 61.0, 59.9, 25.6, 20.4, 18.0, −5.6, −5.8; FABHRMS Calcd for $[C_{14}H_{24}O_5Si + H]^+$: 301.1471. Found: 301.1477; Anal. Calcd for C, 55.97; H, 8.06. Found: C, 55.87; H, 7.84.

*(2*R,*3*R*) - 2 - (*tert - *Butyldimethylsilanyloxymethyl)-6-oxo-3,6-dihydro-2*H*-pyran-3-yl ethyl carbonate* (**22c**).—Compound **21** (32 mg, 0.12 mmol) was dissolved in 1.5 mL of CH_2Cl_2, and 100 μL of pyridine was added to the solution. Ethyl chloroformate (118 μL, 1.2 mmol) was added, and the solution was stirred at rt for 8 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated, and the aq layer was extracted (5×10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), and concentrated, and the crude product was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 37 mg (0.11 mmol, 92%) of compound **22c**: R_f 0.28 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ −183° (*c* 1.87, CH_2Cl_2); IR (thin film, cm^{-1}) 2956, 2931, 2886, 2857, 1745, 1472, 1372, 1341, 1260; ^1H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* 9.5, 6.0 Hz, 1 H), 6.24 (d, *J* 9.5 Hz, 1 H), 5.21 (dd, *J* 5.5, 3.0 Hz, 1 H), 4.55 (ddd, *J* 8.0, 5.5, 2.5 Hz, 1 H), 4.21 (dq, *J* 14.5, 7.5, 1.0 Hz, 2 H), 3.94 (dd, *J* 10.0, 9.0 Hz, 1 H), 3.90 (dd, *J* 10.0, 5.5 Hz, 1 H), 1.31 (t, *J* 7.5 Hz, 3 H), 0.87 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 154.2, 139.7, 125.7, 78.0, 64.8, 63.7, 59.9, 25.7, 18.1, 14.2, −5.6, −5.8; FABHRMS Calcd for $[C_{15}H_{26}O_6Si + H]^+$: 331.1577. Found: 331.1573; Anal. Calcd for C, 54.52; H, 7.94. Found: C, 54.72; H, 8.04.

*(5*R,*6*R*) - 5 -* tert *- Butyldimethylsilanyloxymethyl - 6 -* tert *- butyldimethylsilanyloxymethyl-5,6-dihydropyran-2-one* (**22d**).—Compound **21** (70 mg, 0.27 mmol) was dissolved in 1.5 mL of CH_2Cl_2, and 125 μL (1.1 mmol) of 2,6-lutidine was added to the solution. TBSOTf (125 μL, 0.54 mmol) was added and the solution was stirred at 0 °C for 0.5 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated and the aq layer was extracted (5×10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 86 mg (0.23 mmol, 85%) of compound **22d**: R_f 0.25 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ −125.4° (*c* 0.56, CH_2Cl_2); IR (thin film, cm^{-1}) 2954, 2929, 2886, 2857, 1716, 1472, 1254; ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (dd, *J* 10.0, 5.5 Hz, 1 H), 6.05 (d, *J* 9.5 Hz, 1 H), 4.30 (dd, *J* 5.0, 3.0 Hz, 1 H), 4.26 (ddd, *J* 8.0, 5.5, 3.0 Hz, 1 H), 3.94 (dd, *J* 10.5, 8.0 Hz, 1 H), 3.83 (dd, *J* 10.0, 5.0 Hz, 1 H), 0.88 (s, 9 H), 0.86 (s, 9 H), 0.10 (s, 3 H), 0.07 (s, 6 H), 0.06 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 144.5, 122.6, 80.7, 60.4, 60.2, 25.8, 25.6, 18.2, 18.0, −4.2, −4.9, −5.4, −5.5; FABHRMS Calcd for $[C_{18}H_{36}O_4Si_2 + Na]^+$: 395.2045. Found: 395.2068.

*(2*R,*3*S*) - 2 - (*tert - *Butyldimethylsilanyloxymethyl)-6-oxo-3,6-dihydro-2*H*-pyran-3-yl benzoate (not shown, Scheme 11).*—Compound **21** (34 mg, 0.13 mmol) was dissolved in 1.5 mL of THF. The solution was cooled to 0 °C, and triphenylphosphine (69 mg, 0.26 mmol), *p*-nitrobenzoic acid (44 mg, 0.26 mmol), and diethyl azodicarboxylate (42 μL, 0.26 mmol) were added to the solution. The solution was stirred for 12 h, quenched with satd aq $NaHCO_3$ (15 mL), and extracted (5×20 mL) with Et_2O. The extracts were dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 48 mg (0.12 mmol, 92%) of the *p*-nitrobenzoate ester: R_f 0.13 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ 127.8° (*c* 0.64, CH_2Cl_2); IR (thin film, cm^{-1}) 3112, 2929, 2857, 1735, 1607, 1528, 1472, 1388, 1350, 1322, 1266; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (dt, *J* 9.0, 2.0, 2.0 Hz, 2 H), 8.21 (dt, *J* 9.0, 2.0, 2.0 Hz, 2 H), 6.90 (dd, *J* 9.5, 3.5 Hz, 1 H), 6.21 (dd, *J* 10.0, 1.0 Hz, 1 H), 5.84 (ddd, *J* 5.0, 4.0, 1.0 Hz, 1 H), 4.73 (dd, *J* 9.5, 4.5 Hz, 1 H), 3.93 (dd, *J* 11.5, 3.5 Hz, 1 H), 3.88 (dd, *J* 11.5, 5.5 Hz, 1 H), 0.85 (s, 9 H), 0.043 (s, 3 H), 0.040 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 161.3, 150.9, 140.3, 134.2, 131.0, 124.0, 123.7, 80.1, 64.8, 62.5, 25.7, 18.1, −5.60, −5.63; CIHRMS Calcd for $[C_{19}H_{25}O_7NSi + NH_4]^+$: 425.1744. Found: 425.1785.

*(5*S,*6*R*) - 6 -* tert *- Butyldimethylsilanyloxymethyl - 5 - hydroxy - 5,6 - dihydro - pyran - 2 - one* (**23**).—The *p*-nitrobenzoate ester (51 mg, 0.13 mmol) was dissolved in 2.5 mL of methanol, and triethylamine (55 μL, 0.38 mmol) was added to the solution. The solution was stirred for 12 h and then concentrated under reduced pressure. The crude product was purified by

silica gel chromatography (1:4 EtOAc–hexanes) to yield 25 mg (0.10 mmol, 80%) of compound **23**: R_f 0.15 (1:4 EtOAc–hexanes); $[\alpha]_D^{21}$ −20.5° (*c* 1.11, CH_2Cl_2); IR (thin film, cm^{-1}) 3432, 2954, 2929, 2857, 1712, 1472, 1256; ^1H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* 10.0, 2.5 Hz, 1 H), 5.95 (dd, *J* 10.0, 2.0 Hz, 1 H), 4.64 (ddd, *J* 9.5, 5.5, 2.0 Hz, 1 H), 4.31 (ddd, *J* 9.5, 7.0, 4.0 Hz, 1 H), 4.04 (dd, *J* 10.5, 4.0 Hz, 1 H), 3.89 (dd, *J* 10.5, 7.0 Hz, 1 H), 3.30 (bs, 1 H), 0.90 (s, 9 H), 0.12 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 148.8, 119.6, 80.0, 65.5, 64.0, 25.7, 18.2, −5.56, −5.58; CIHRMS Calcd for $[C_{12}H_{22}O_4Si + NH_4]^+$: 276.1631. Found: 276.1626; Anal. Calcd for C, 55.79; H, 8.59. Found: C, 55.61; H, 8.59.

*(2*R*,3*R*,4*R*,5*R*)-2-(*tert-*Butyldimethylsilanyloxymethyl)-4,5-dihydroxy-6-oxotetrahydropyran-3-yl acetate* (**24b**).—Compound **22b** (34 mg, 0.113 mmol) was dissolved in 0.6 mL of *tert*-butanol and 0.6 mL of acetone. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide in water was added to the solution. After the solution was cooled to 0 °C, a catalytic amount (2 mol%) of OsO_4 was added to the reaction. The reaction was allowed to stir at 0 °C for 8 h. The reaction was quenched with satd aq Na_2SO_3 and the mixture was extracted (5 × 25 mL) with Et_2O and washed with brine. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The product was purified by silica gel chromatography eluting with (3:7 EtOAc–hexanes) to give 23 mg (0.07 mmol, 62%) of compound **24b**: R_f 0.11 (3:7 EtOAc–hexanes); $[\alpha]_D^{21}$ 28.0° (*c* 1.08, CH_2Cl_2); IR (thin film, cm^{-1}) 3433, 2955, 2930, 2885, 2857, 1752, 1374, 1227; ^1H NMR (500 MHz, C_6D_6) δ 5.43 (dd, *J* 4.5, 2.5 Hz, 1 H), 4.82 (ddd, *J* 8.0, 6.0, 2.5 Hz, 1 H), 4.07 (m, 2 H), 3.65 (dd, *J* 10.0, 6.0 Hz, 1 H), 3.59 (dd, *J* 10.0, 8.0 Hz, 1 H), 3.22 (bs, 1 H), 2.55 (bs, 1 H), 1.51 (s, 3 H), 0.86 (s, 9 H), −0.07 (s, 3 H), −0.09 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 173.3, 169.0, 78.2, 68.7, 68.6, 68.4, 60.5, 25.9, 20.2, 18.3, −5.5, −5.7; Anal. Calcd for C, 50.28; H, 7.84. Found: C, 50.44; H, 7.97.

*(2*R*,3*R*,4*R*,5*R*)-6-(*tert-*Butyldimethylsilanyloxymethyl)-4,5-dihydroxy-6-oxotetrahydropyran-3-yl ethyl carbonate* (**24c**).—Compound **22c** (80 mg, 0.24 mmol) was dissolved in 1.5 mL of dichloromethane. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide in water was added to the solution. After the solution was cooled to 0 °C, a catalytic amount (2 mol%) of OsO_4 was added to the reaction. The reaction was allowed to stir at 0 °C for 3 h. The mixture was purified directly by silica gel chromatography eluting with (3:7 EtOAc–hexanes) to give 70 mg (0.19 mmol, 79%) of compound **24c**: R_f 0.2 (1:1 EtOAc–hexanes); $[\alpha]_D^{21}$ 19.8° (*c* 0.47, CH_2Cl_2); IR (thin film, cm^{-1}) 3446, 2955, 2930, 2886, 2857, 1755, 1472, 1374, 1259, 1198, 1111, 1041; ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (dd, *J* 4.5, 2.5 Hz, 1 H), 4.89 (ddd, *J* 9.0, 6.5, 2.5 Hz, 1 H), 4.46 (ddd, *J* 4.5, 3.5, 1.5 Hz, 1 H), 4.41 (dd, *J* 3.0, 1.0 Hz, 1 H), 4.23 (dd, *J* 14.0, 7.0 Hz, 2 H), 3.87 (dd, *J* 10.0, 6.0 Hz, 1 H), 3.84 (dd, *J* 10.0, 9.0, 1 H), 3.25 (bs, 1 H), 2.88 (bs, 1 H), 1.33 (t, *J* 7.0 Hz, 3 H), 0.88 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 153.8, 77.8, 71.2, 67.9, 67.7, 64.9, 59.8, 25.6, 18.1, 14.1, −5.6, −5.8; FABHRMS Calcd for $[C_{15}H_{28}O_8Si + H]^+$: 365.1632. Found: 365.1640.

*(3*R*,4*R*,5*R*,6*R*)-5-*tert-*Butyldimethylsilanyloxy-6-*tert-*butyldimethylsilanyloxymethyl-3,4-dihydroxytetrahydropyran-2-one* (**24d**).—Compound **22d** (63 mg, 0.17 mmol) was dissolved in 0.8 mL of *tert*-butanol and 0.8 mL of acetone. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide in water was added to the solution. After the solution was cooled to 0 °C, a catalytic amount (2 mol%) of OsO_4 was added to the reaction. The reaction was allowed to stir at 0 °C for 8 h. The reaction was quenched with satd aq Na_2SO_3, and the mixture was extracted (5 × 25 mL) with Et_2O and washed with brine. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The mixture was purified by silica gel chromatography eluting with (3:7 EtOAc–hexanes) to give 45 mg (0.11 mmol, 65%) of compound **24d**: R_f 0.23 (3:7 EtOAc–hexanes); $[\alpha]_D^{21}$ 33.8° (*c* 2.42, CH_2Cl_2); IR (thin film, cm^{-1}) 3370, 2954, 2928, 2885, 2856, 1730, 1472, 1361, 1256, 1207, 1115; ^1H NMR (500 MHz, $CDCl_3$) δ 4.65 (ddd, *J* 8.0, 6.0, 1.5 Hz,

1 H), 4.48 (dd, *J* 3.0, 1.5 Hz, 1 H), 4.24 (ddd, *J* 5.5, 4.5, 1.0 Hz, 1 H), 4.22 (dd, *J* 4.5, 1.5 Hz, 1 H), 3.84 (dd, *J* 10.0, 8.0 Hz, 1 H), 3.79 (dd, *J* 10.0, 6.0 Hz, 1 H), 3.50 (bs, 1 H), 3.10 (bs, 1 H), 0.89 (s, 18 H), 0.134 (s, 3 H), 0.130 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 80.3, 70.1, 67.9, 67.6, 60.3, 25.9, 25.6, 18.3, 17.9, −4.7, −5.2, −5.3, −5.4; FABHRMS Calcd for $[C_{18}H_{38}O_6Si_2 + Na]^+$: 429.2105. Found: 429.2092.

*(4*R,*5*R,*6*R,*7*R*)-7-*tert-*Butyldimethylsilanyloxy-6-(*tert-*butyldimethylsilanyloxymethyl)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-c]pyran-4-one* (**25**).—Compound **24d** (27 mg, 0.066 mmol) was dissolved in 0.3 mL of acetone. Excess 80 μL (0.66 mmol) 2,2-dimethoxypropane was added followed by 1 mg of *p*-toluenesulfonic acid. The reaction was allowed to stir at for 8 h. The reaction was quenched with satd aq $NaHCO_3$, and the mixture was extracted (5 × 5 mL) with Et_2O. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The mixture was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 19 mg (0.043 mmol, 65%) of compound **25**: R_f 0.5 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ 10.4° (*c* 1.35, CH_2Cl_2); IR (thin film, cm^{-1}) 2931, 2858, 1763, 1472, 1257, 1120, 1066; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 (d, *J* 7.0 Hz, 1 H), 4.48 (ddd, *J* 7.5, 4.5, 1.5 Hz, 1 H), 4.37 (dd, *J* 7.0, 3.5 Hz, 1 H), 4.04 (dd, *J* 3.5, 2.0 Hz, 1 H), 3.84 (dd, *J* 10.0, 4.5 Hz, 1 H), 3.75 (dd, *J* 10.5, 8.0 Hz, 1 H), 1.51 (s, 3 H), 1.37 (s, 3 H), 0.90 (s, 9 H), 0.87 (s, 9 H), 0.13 (s, 3 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 111.2, 76.5, 72.9 (2 C), 66.7, 59.9, 26.2, 25.8, 25.6, 24.1, 18.2, 17.9, −4.6, −5.1, −5.41, −5.43; FABHRMS Calcd for $[C_{21}H_{42}O_6Si_2 + H]^+$: 447.2598. Found: 447.2600.

*(3*R,*4*R,*5*R,*6*R*)-5-(*tert-*Butyldimethylsilanyloxy)-6-(*tert-*butyldimethylsilanyloxymethyl)-3,4-dihydroxytetrahydropyran-2-one* (**26**).—Compound **19a** (34 mg, 0.091 mmol) was dissolved in 1.0 mL of dichloromethane. A molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide in water was added to the solution. After the solution was cooled to 0 °C, a catalytic amount (2 mol%) of OsO_4 was added to the reaction. The reaction was allowed to stir at 0 °C for 2 h. The mixture was purified directly by silica gel chromatography eluting with (3:7 EtOAc–hexanes) to give 27 mg (0.066 mmol, 73%) of compound **26**: R_f 0.17 (3:7 EtOAc–hexanes); $[\alpha]_D^{21}$ 30.2° (*c* 1.43, CH_2Cl_2); IR (thin film, cm^{-1}) 3449, 2954, 2929, 2857, 1750, 1472, 1463, 1254, 1124; ^{1}H NMR (300 MHz, C_6D_6) δ 4.36 (ddd, *J* 9.0, 1.8, 1.8 Hz, 1 H), 4.11 (dd, *J* 9.0, 2.1 Hz, 1 H), 4.04 (dd, *J* 2.4, 2.1 Hz, 1 H), 3.76 (d, *J* 2.1 Hz, 1 H), 3.58 (dd, *J* 1.5, 1.2 Hz, 1 H), 3.21 (bs, 1 H), 2.35 (bs, 1 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.01 (s, 3 H), 0.00 (s, 6 H), −0.04 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 81.1, 71.1, 69.2, 65.6, 60.8, 25.8, 25.6, 18.2, 17.9, −4.5, −5.0, −5.3, −5.5; FABHRMS Calcd for $[C_{18}H_{38}O_6Si_2 + H]^+$: 407.2285. Found: 407.2278.

*(4*R,*5*R,*6*R,*7*R*)-7-(*tert-*Butyldimethylsilanyloxy)-6-(*tert-*butyldimethylsilanyloxymethyl)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-c]pyran-4-one* (**27**).—Compound **26** (4 mg, 0.01 mmol) was dissolved in 0.1 mL of acetone. Excess 6 μL (0.05 mmol) 2,2-dimethoxypropane was added followed by 1 mg of *p*-toluenesulfonic acid. The reaction was allowed to stir at for 8 h. The reaction was quenched with satd aq $NaHCO_3$, and the mixture was extracted (5 × 5 mL) with Et_2O. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The mixture was purified by silica gel chromatography eluting with (1:9 EtOAc–hexanes) to give 3 mg (0.007 mmol, 70%) of compound **26**: R_f 0.5 (1:9 EtOAc–hexanes); $[\alpha]_D^{21}$ 40.4° (*c* 1.15, CH_2Cl_2); IR (thin film, cm^{-1}) 2989, 2929, 2856, 1742, 1463, 1373, 1253, 1133; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (d, *J* 7.0 Hz, 1 H), 4.52 (dd, *J* 7.0, 3.0 Hz, 1 H), 4.47 (ddd, *J* 8.5, 2.5, 2.5 Hz, 1 H), 4.16 (dd, *J* 8.0, 3.0 Hz, 1 H), 3.89 (d, *J* 2.5 Hz, 1 H), 1.50 (s, 3 H), 1.38 (s, 3 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.14 (s, 3 H), 0.12 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 111.3, 78.7, 74.8, 73.1, 65.2, 61.0, 26.4, 25.9, 25.6, 24.7, 18.3, 18.1, −4.6, −4.9, −5.2, −5.4; FABHRMS Calcd for $[C_{21}H_{42}O_6Si_2 + H]^+$: 447.2598. Found: 447.2601.

Acknowledgements

We thank the University of Minnesota (Grant-in-Aid program), the ACS for an Institutional Research Grant (IRG-58-001-40-IRG-19), the American Chemical Society–Petroleum Research Fund (ACS–PRF # 33953-G1) and the Arnald and Mabel Beckman Foundation for their generous support of our program. We would also like to thank Dr Dirk Friedrich (Hoechst Marion Roussel) for his help in the structure determination of **1a** and **13**.

References

[1] A. Zamoiski, A. Banaszek, G. Grynkiewicz, *Adv. Carbohydr. Chem. Biochem.*, 40 (1982) 1.
[2] K.B. Sharpless, S. Masamune, *Science*, 220 (1983) 949.
[3] (a) S. Danishefsky, *J. Chemtracts*, (1989) 273. (b) S.E. Schaus, J. Branalt, E.N. Jacobsen, *J. Org. Chem.*, 63 (1998) 403–405.
[4] (a) C.R. Johnson, A. Golebiowski, D.H. Steensma, M.A. Scialdone, *J. Org. Chem.*, 58 (1993) 7185–7194. (b) T. Hudlicky, K.K. Pitzer, M.R. Stabile, A.J. Thorpe, G.M. Whited, *J. Org. Chem.*, 61 (1996) 4151–4153.
[5] I. Henderson, K.B. Sharpless, C.-H. Wong, *J. Am. Chem. Soc.*, 116 (1994) 558–561.
[6] H.J.M. Gijsen, L. Qiao, W. Fitz, C.-H. Wong, *Chem. Rev.*, 96 (1996) 443–473.
[7] (a) D.L. Boger, T. Honda, *J. Am. Chem. Soc.*, 116 (1994) 5647–5656. (b) D.L. Boger, T. Honda, R.F. Menezes, S.L. Colletti, *J. Am. Chem. Soc.*, 116 (1994) 5631–5646. (c) D.L. Boger, S. Teramoto, J.C. Zhou, *J. Am. Chem. Soc.*, 117 (1995) 7344–7356. (d) A. Dondoni, A. Marra, A. Massi, *J. Org. Chem.*, 62 (1997) 6261.
[8] R. Adams, V. Voorhees, *Org. Synth. Coll.*, 1 (1921) 280–283.
[9] T. Hudlicky, D.A. Entwistle, A.J. Thorpe, *Chem. Rev.*, 96 (1996) 1195.
[10] J.M. Harris, M.D. Keranen, G.A. O'Doherty, *J. Org. Chem.*, 64 (1999) 2982.
[11] (a) T. Taniguchi, K. Nakamura, K. Ogasawara, *Synlett*, (1996) 971. (b) T. Taniguchi, H. Ohnishi, K. Ogasawara, *Chem. Commun.*, (1996) 1477–1478. (c) M. Taniguchi, T. Taniguchi, K. Ogasawara, *Synthesis*, (1999) 341.
[12] (a) O. Achmatowicz, R. Bielski, *Carbohydr. Res.*, 55 (1977) 165. (b) I.K. Grapsas, E.A. Couladouros, M.P. Georgiadis, *Pol. J. Chem.*, 64 (1990) 823.
[13] U. Schmidt, J. Werner, *Synthesis*, (1986) 986.
[14] H.C. Kolb, M.S. VanNieuwenhze, K.B. Sharpless, *Chem. Rev.*, 94 (1994) 2483–2547.
[15] (a) G.R. Sullivan, J.A. Dale, H.S. Mosher, *J. Org. Chem.*, 38 (1975) 2143. (b) S. Yamaguchi, F. Yasuhara, K.T. Kabuto, *tetrahedron*, 32 (1976) 1363. (c) A.G.M. Barrett, S.A. Lebold, *J. Org. Chem.*, 56 (1991) 4875.
[16] M.P. Georgiadis, E.A. Couladouros, *J. Org. Chem.*, 51 (1986) 2725.
[17] J.-L. Luche, *J. Am. Chem. Soc.*, 110 (1978) 2226.
[18] J.K. Cha, N.-S. Kim, *Chem. Rev.*, 95 (1995) 1761.
[19] (a) S.P. Martin, J.A. Dodge, *Tetrahedron Lett.*, 32 (1991) 3017. (b) G. Grynkiewicz, *Pol. J. Chem.*, 53 (1979) 2501. (c) O. Mitsunobu, *Synthesis*, (1981) 1.
[20] T.J. Donohoe, P.R. Moore, M.J. Waring, N.J. Newcombe, *Tetrahedron Lett.*, 38 (1997) 5027.
[21] A.G.M. Barrett, M. Pena, J.A. Willardsen, *J. Org. Chem.*, 61 (1996) 1082.
[22] J.M. Harris, G.A. O'Doherty, *Tetrahedron Lett.*, 41 (2000) 183.
[23] (a) R.H. Schlessing, K.W. Gillman, *Tetrahedron Lett.*, 40 (1999) 1257–1260. (b) M. Tsubuki, K. Kanai, H. Nagase, T. Honda, *Tetrahedron*, 55 (1999) 2493. (c) W.-P. Chen, S.M. Roberts, *J. Chem. Soc., Perkin Trans. 1*, (1999) 103–105. (d) D.J. Dixon, S.V. Ley, E.W. Tate, *J. Chem. Soc., Perkin Trans. 1*, (1998) 3125–3126. (e) Z.-C. Yang, X.-B. Jiang, Z.-M Wang, W.-S. Zhou, *J. Chem. Soc., Perkin Trans. 1*, (1997) 317–321. (f) A.M. Gomez, B. Lopez de Uralde, S. Valverde, J.C. Lopez, *J. Chem. Soc., Chem. Commun.* (*Cambridge*), (1997) 1647. (g) T. Honda, N. Sano, K. Kanai, *Heterocycles*, 41 (1995) 425–429. (h) Z.-C. Yang, W.-S. Zhou, *Tetrahedron Lett.*, 36 (1995) 5617–5618. (i) Y. Masaki, T. Imaeda, H. Oda, A. Itoh, M. Shiro, *Chem. Lett.*, (1992) 1209–1212. For a review, see (j) M.A. Ogliaruso, J.F. Wolfe, in: S. Patai, Z. Rappoport (Eds.), *Synthesis of Lactones and Lactams*, Wiley, New York, 1993, pp. 3–131, 271–396.
[24] (a) T. Kametani, M. Tsubuki, Y. Tatsuzaki, T. Honda, *Heterocycles*, 27 (1988) 2107–2110. (b) T. Kametani, M. Tsubuki, Y. Tatsuzaki, T. Honda, *J. Chem. Soc., Perkin Trans. 1*, (1990) 639–646. (c) T. Honda, T. Kametani, K. Kanai, Y. Tatsuzaki, M. Tsubuki, *J. Chem. Soc., Perkin Trans. 1*, (1990) 1733–1737.
[25] (a) Y. Kobayashi, M. Kusakabe, Y. Kitano, F. Sato, *J. Org. Chem.*, 53 (1988) 1587–1590. (b) M. Kusakabe, Y. Kitano, Y. Kobayashi, F. Sato, *J. Org. Chem.*, 54 (1989) 2085–2091.
[26] (a) Z-C. Yang, W.-S. Zhou, *Tetrahedron Lett.*, 36 (1995) 5617–5618. (b) Z.-C. Yang, X.-B. Jiang, Z.-M. Wang, W.-S. Zhou, *J. Chem. Soc., Chem. Commun.*, (1995) 2389.
[27] (a) J.C. Ruble, J. Tweddell, G.C. Fu, *J. Org. Chem.*, 63 (1998) 2794. (b) E. Vedejs, O. Daugulis, S.T. Diver, *J. Org. Chem.*, 61 (1986) 430. (c) K. Drauz, H. Waldmann, *Enzyme Catalysis in Organic Synthesis: A Comprehensive Handbook*, VCH, New York, 1995.
[28] (a) Y.-H. Kuo, K.-S. Shih, *Heterocycles*, 31 (1990) 1941–1949. (b) M. Tsubuki, K. Kanai, T. Honda, *J. Chem. Soc., Chem. Commun.*, (1992) 1640–1641. (c) W.-S. Zhou, Z.-C. Yang, *Tetrahedron Lett.*, 34 (1993) 7075–7076.
[29] (a) T. Honda, H. Takada, S. Miki, M. Tsubuki, *Tetrahedron Lett.*, 34 (1993) 8275–8278. (b) M. Tsubuki, H. Takada, T. Katoh, S. Miki, T. Honda, *Tetrahedron*, 52 (1996) 14,515–14,532.