Back to the Sugars: A New Enantio and Diastereocontrolled Route to Hexoses from Furfural

Miwako Takeuchi, Takahiko Taniguchi, Kunio Ogasawara*

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980-8578, Japan
Fax +81(22)2176845; E-mail: konol@mail.cc.tohoku.ac.jp

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Dedicated to the memory of Professor George Büchi

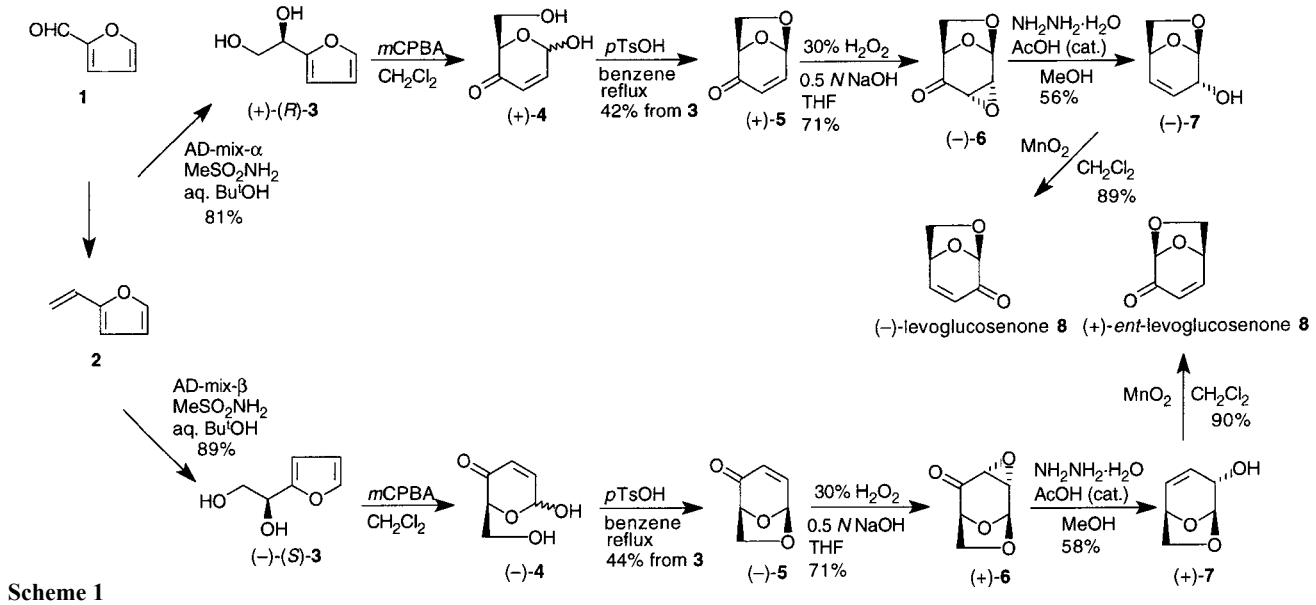
Abstract: An integrated enantio and diastereocontrolled route to both enantiomers of the eight possible hexoses has been explored starting from furfural, by employing the Sharpless asymmetric dihydroxylation as a key step. At the present, a route to six of the eight possible hexoses has been established. The present synthesis may be taken as a reversion of the sugar-originated furfural to the sugars via a levoglucosenone, a pyrolysate of cellulose, type intermediate.

Key words: asymmetric dihydroxylation, furfural, hexoses, oxidative ring expansion, enantiocontrolled synthesis

The hexoses are stereoisomers having a concatenation of four contiguous hydroxy-bearing carbogenic centers. Their enantiocontrolled synthesis, therefore, requires a procedure leading to eight pairs of stereoisomers in an enantio and diastereocontrolled manner. So far, the procedure devised by the groups of Masamune and Sharpless[1] employing the Katsuki–Sharpless asymmetric epoxidation[2] coped only with precise installation of four contiguous hydroxy functionalities to give rise to all hexoses. The Masamune–Sharpless synthesis is based on the reiterative application of the asymmetric epoxidation and stereoselective two-carbon extension starting from a glyoxyaldehyde unit. This procedure allowed the installation of the four hydroxy-bearing centers through two cycles comprising stereoselective construction of the allylic alcohol functionality and its enantiocontrolled epoxidation using an appropriate chiral tartrate followed by stereo- and regioselective opening of the oxirane ring generated. Although the procedure provides a concise and flexible way to the hexoses, we felt that it still left us the challenge to devise an alternative procedure that does not require reiteration of the two-carbon elongation and the asymmetric epoxidation. We wish to report here a new strategy capable of producing all the stereoisomers of the hexoses from a single starting material employing a single asymmetric chiral induction step.

As the basis of the present study, we established an enantiocontrolled synthesis of levoglucosenone[3] **8** of which only the (–)-enantiomer was obtained in a low yield by acid-catalyzed thermolysis[4] of cellulose, a hexose polymer. Owing to its enone functionality and masked formyl and 1,2-glycol functionalities confined in the biased bicyclic framework, levoglucosenone **8** has been expected to be a versatile chiral building block and was actually used for the enantiocontrolled production of several natural products.[5] However, its inefficient production and limited enantiomeric availability[6] restricted to the cellulose configuration prevented its use as a versatile chiral building block. We, therefore, examined the asymmetric synthesis of levoglucosenone **8** and have established its preparation in both enantiomeric forms without using carbohydrate precursors. In the synthesis, we employed the Sharpless asymmetric dihydroxylation reaction[7] to introduce the chirality of the target levoglucosenone **8**. Thus, 2-vinylfuran (**2**) generated from furfural (**1**), furnished the (+)-(*R*)-glycol **3** with AD-mix-α and the (–)-(*S*)-glycol **3** with AD-mix-β, as expected by the empirical rule, in 90 and 93% ee. Recrystallization, after converting the products into the corresponding dibenzoates, afforded the optically pure products (>99% ee). Exposure of the glycol **3** with 3-chloroperbenzoic acid (MCPBA) induced the oxidative furan-ring expansion[8,9] to give the 3-pyrone derivative **4** as a mixture at the hemiacetal center. Intramolecular acetalization of the mixture was next carried out in the presence of an acid catalyst to afford the bicyclic acetal **5** having a dioxabicyclo[3.2.1]octane framework.[10] Overall yields of (+)-**5** from (+)-**3** and (–)-**5** from (–)-**3** were 42 and 44%, respectively. Functionally, the bicyclic enone **5** is taken to be the same as levoglucosenone **8** which possesses the isomeric enone functionality on the same dioxabicyclo[3.2.1]octane framework. In order to obtain levoglucosenone **8**, the enone functionality of **5** was isomerized by employing the Wharton rearrangement.[11] Thus, **5** was treated with alkaline hydrogen peroxide to give the single *exo*-epoxide **6** in which the reaction occurred exclusively from the less hindered convex face. Thus, (+)-**5** afforded (–)-epoxide **6** and (–)-**5** afforded (+)-epoxide **6** both in 71% yields. Treatment of the epoxide **5** with hydrazine hydrate gave the single allylic alcohol **7** which yielded levoglucosenone **8** on oxidation with manganese(IV) oxide. Overall yields of (–)-levoglucosenone (**8**) via (–)-allyl alcohol **7** and (+)-*ent*-levoglucosenone (**8**) via (+)-allyl alcohol **7** were 50% (Scheme 1).

In a sense, the above synthesis of levoglucosenone **8** may be taken to be a reversion of the synthesis of furfural (**1**) as it is obtained from naturally occurring substances containing pentose fragments such as corncobs[12] and straw though levoglucosenone **8** is not pentose but hexose in origin.[4] We, therefore, envisaged that the present route could be further traced back to the pentose stage as well as

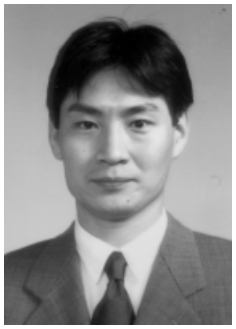


Scheme 1

Biographical Sketches

Kunio Ogasawara was born in 1938 in Kagoshima, Japan. He studied at the Pharmaceutical Institute at Tohoku University in Sendai where he received his PhD degree in 1968 under the direction of Professor Tetsuji Kametani. After postdoctoral studies with Professor George Büchi at Massachusetts Institute of Technology from 1968 to 1971, he returned to the Pharmaceutical Institute, Tohoku University where he worked with Professor Seiichi Takano for 22 years as Associate Professor. He has been Professor since 1994 at the Department of Organic Synthesis, Pharmaceutical Institute, Tohoku University. His research interests are in the field of synthetic organic chemistry in particular enantiocontrolled synthesis of natural products.

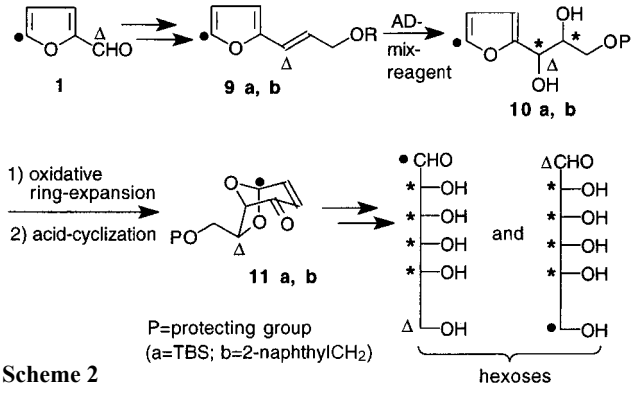
Miwako Takeuchi was born in 1976 in Ibaraki, Japan. She received her bachelor's degree in 1998 from Tohoku University in Sendai. She is currently working towards her master's degree under the direction of Professor Kunio Ogasawara at the Pharmaceutical Institute, Tohoku University in Sendai.



Takahiko Taniguchi was born in 1967 in Shiga, Japan. He received his bachelor's and master's degree from Tokyo College of Pharmacy under the direction of Professor Yasuji Yamada, and PhD degree in 1994 from Tohoku University under the direction of Professor Keiichiro Fukumoto. In 1994, he joined Professor Ogasawara's group as an Assistant Professor. His current research interests is the development of versatile chiral building blocks and their utilization in natural product synthesis.

to the hexose stage via a common levoglucosenone-type intermediate. Since the synthesis of the pentoses is less challenging, we decided to examine the synthesis of all stereoisomers of the hexoses starting from furfural (**1**) based on the levoglucosenone synthesis above.

The essential features of the present synthesis are outlined in a general way in Scheme 2. The strategy is based on the utilization of the levoglucosenone-type intermediate **11** having an extra hydroxymethyl functionality to control the regioselective cleavage of the bicyclic system and to discriminate the two terminal functionalities of the substrate (marked as • and Δ). With respect to the construction of the four contiguous hydroxy-bearing centers, as the key intermediate **11** possesses a fixed oxygen functionality fated to be one of the four contiguous hydroxy functionalities, it was planned to install the three remaining by modification of the enone functionality. The most salient feature of the strategy in the present synthesis is the use of the key intermediate **11** in two ways, namely the acetal carbon and the C_2 of the glycol carbons are placed at either the C_1 formyl functionality or the C_6 hydroxymethyl functionality of the target hexoses so as to produce the isomeric and/or the enantiomeric hexoses from the same precursor (Scheme 2).



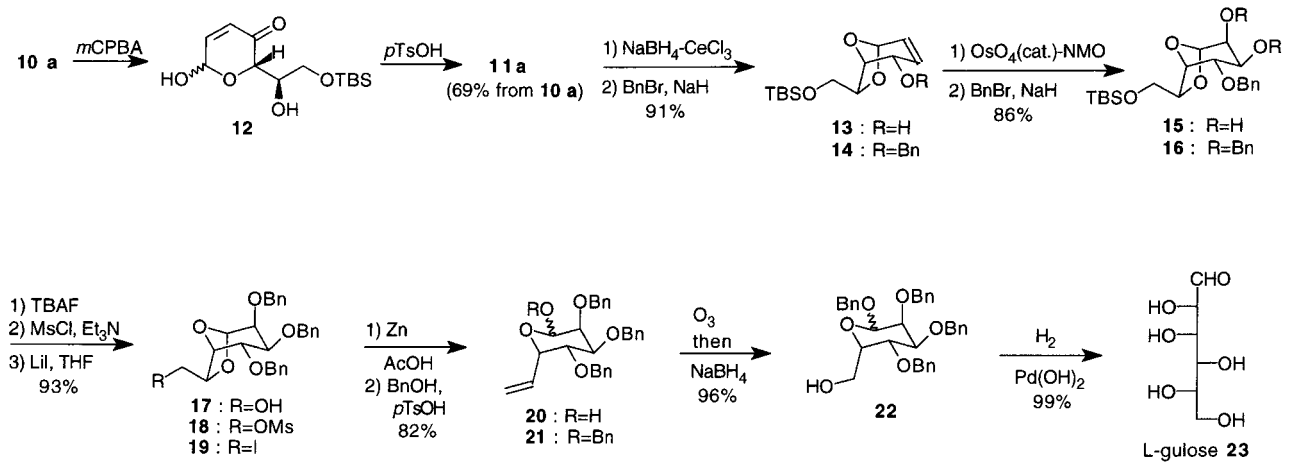
Scheme 2

The actual synthesis commenced with the asymmetric dihydroxylation of the allyl ether **9** (R=TBS) which was readily prepared in three steps from furfural (**1**) via the allyl alcohol[13] **9** (R = H). On reaction using AD-mix-α and -β, **9** afforded the chiral glycols **10** both in 90% yield with >99% ee, respectively. The observed remarkable enhancement of asymmetric induction of **9**, which possesses one extra carbon functionality on the monosubstituted alkene **2**, is worthy of note even though it was anticipated to some extent. Oxidative furan ring expansion of **10** proceeded with MCPBA[9] to give rise to the 3-pyrone **12** which afforded the key intermediate **11,** on acid treatment, having a dioxabicyclo[3.2.1]octane structure (Scheme 3).

Having obtained the key starting material, we first examined its conversion into the hexoses by stereoselective modification of the enone functionality and by regioselective cleavage of the dioxolane moiety. Reduction of **11** with sodium borohydride–Ce(III) chloride[14] proceeded stereoselectively to give the single allyl alcohol **13** excellently. After benzylation, the resulting benzyl ether **14** was dihydroxylated[15] to give the single diol **15** which was again benzylated to give the tribenzyl ether **16** having four contiguous oxygen-bearing centers. Both the reduction and the dihydroxylation occurred stereoselectively from the convex face of the molecule, which was confirmed by conversion into two hexoses, L-gulose **23** and D-glucose **27**, as described below (Schemes 3 and 4).

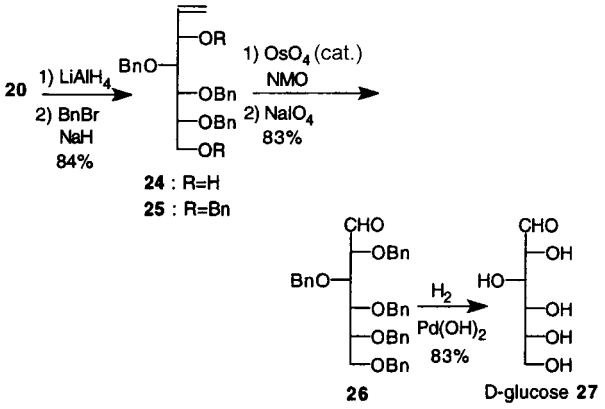
To obtain L-gulose (**23**), the tribenzyl ether **16** was desilylated to give the primary alcohol **17** which was further transformed into the iodide **19** via the mesylate **18**. On treatment with zinc in acetic acid, **19** furnished the six-membered hemiacetal **20** as an epimeric mixture by reductive cleavage of the dioxolane ring. Treatment of **20** with benzyl alcohol in the presence of an acid catalyst gave a mixture of the benzyl acetal **21** whose vinyl functionality was sequentially cleaved and reduced[16] to give the primary alcohol **22**. Finally, **22** was debenzylated under catalytic hydrogenolysis conditions to give L-gulose (**23**) (Scheme 3).

On the other hand, the hemiacetal mixture **20** was reduced with lithium aluminum hydride to give the diol **24** which was benzylated to give the pentabenzyl ether **25**. The vinyl functionality of **25** was then cleaved by sequential dihydroxylation and periodate oxidation[16] to give the al-



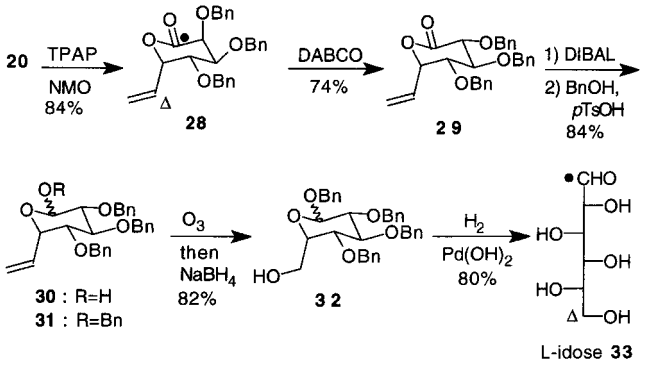
Scheme 3

dehyde **26** which was subjected to catalytic hydrogenolysis to remove the benzyl groups to give D-glucose (**27**) (Scheme 4).



Scheme 4

Moreover, the hemiacetal mixture **20** was oxidized with tetrapropylammonium perruthenate[17] (TPAP) in the presence of *N*-methylmorphorine *N*-oxide (NMO) to give the δ-lactone **28** which, on treatment with 1,4-diazabicyclo[2.2.2]octane (DABCO), induced α-epimerization to give the isomeric δ-lactone **29** as a single product in satisfactory yield after recrystallization. Reduction of **29** with diisobutylaluminum hydride (DIBAL) gave the hemiacetal **30** as a mixture of epimers at the acetal center. With the same treatment as for L-gulose **23**, **30** could be transformed into L-idose **33** via the tetrabenzyl ether **31** and the primary alcohol **32**. Although we did not carry out an alternative transformation, the same L-idose **33** may be obtained from **30** on the same treatment as for the above D-glucose **27** (Scheme 5).



Scheme 5

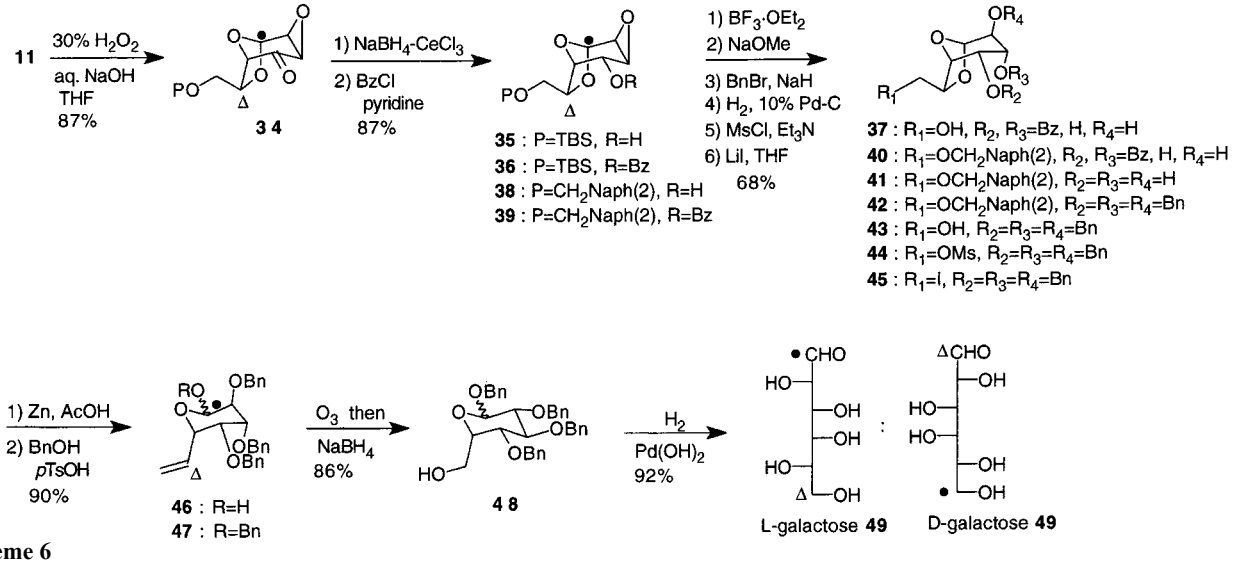
Having established the conversion of the dioxabicyclooctane framework into the hexose framework in two ways by demonstrating the route to the three hexoses, we next examined the stereocontrolled introduction of three contiguous hydroxy groups on the enone system of the key intermediate **11** to obtain the remaining five hexoses.

Treatment of **11** with alkaline hydrogen peroxide afforded the single *exo*-epoxide **34** which gave the single *endo*-alcohol **35** on reduction with sodium borohydride–Ce(III) chloride.[14] After benzoylation, the benzoate **36** obtained was treated with boron trifluoride–diethyl ether complex to cleave the epoxide bond stereoselectively by the neighboring group participation of the benzoate functionality.[18] The reaction proceeded with stereoselective cleavage of the epoxide bond, but the silyl protecting group was removed under the conditions to give a mixture of the triols **37**. Since discrimination of the primary alcohol from the secondary alcohols in **37** was found to be difficult, the epoxybenzoate **39** bearing a different protecting group[19] was prepared from the allyl alcohol **9** (R = H) via the enone **11** (P = 2-naphthylCH$_2$), the epoxide **34** (P = 2-naphthylCH$_2$) and the alcohol **38** (P = 2-naphthylCH$_2$) by employing the same procedure. Reaction of **39** with boron trifluoride–diethyl ether complex[18] afforded the single diol **40**, without affecting the protecting group, which gave the single triol **41** after removal of the benzoate group. After benzylation, the tribenzyl ether **42** obtained was hydrogenated in ethanol on palladized charcoal (10%) to allow chemoselective removal of the naphthylmethyl protecting group[19] to give the primary alcohol **43**. As above, the dioxolane ring of **43** was cleaved in a three-step sequence via the mesylate **44** and the iodide **45** to give the hemiacetal **46** without difficulty. This compound was then treated with benzyl alcohol in the presence of an acid catalyst to give the acetal mixture **47** which was transformed into the primary alcohol **48** by sequential ozonolysis and borohydride reduction in the same flask as for **22**. Hydrogenolysis of **48** furnished L-galactose **49** by removal of four benzyl groups. Although we did not carry out the further conversion, **46** may also serve as the precursor of the enantiomeric D-galactose **49** on the same treatment as for the synthesis of D-glucose **27** above (Scheme 6).

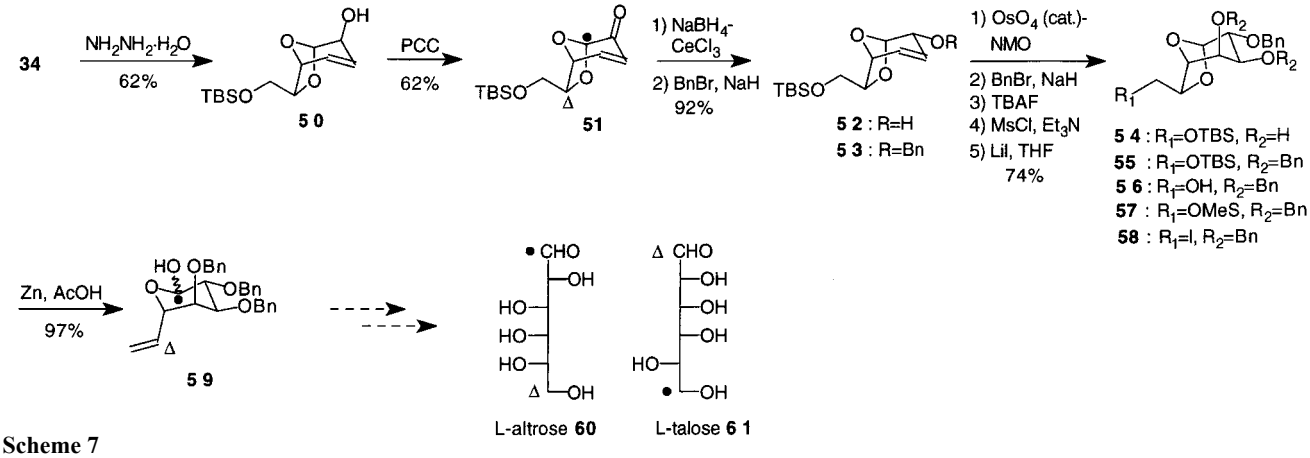
Having established the route to the four hexoses, we next examined the synthesis of the remaining four hexoses, allose, altrose, talose and mannose starting from the oxo epoxide **34**. At present, since the Wharton reaction of **34**, in particular the substrate having a 2-naphthylmethyl protecting group, was very capricious, we have just reached the common intermediate **59** of L-altrose **60** and L-talose **61**.

Thus, on treatment with hydrazine hydrate, the epoxide **34** (P = TBS) afforded the *exo*-allyl alcohol **50** which was then converted into the enone **51** on oxidation. Reduction of **51** with sodium borohydride–Ce(III) chloride[14] gave the single *endo*-allyl alcohol **52** which was converted into the benzyl ether **53**. On the same treatment for the isomeric **15**, **53** furnished the *exo*-diol **54** diastereoselectively, which was then benzylated to give the tribenzyl ether **55**. After removal of the silyl protecting group, the resulting primary alcohol **56** was transformed into the iodide **58**, via the tosylate **57**, which furnished the hemiacetal **59** expected to be served as the common precursor of L-altrose **60** and L-talose **61** on reductive treatment with zinc powder in acetic acid (Scheme 7).

Of two remaining hexoses, L-mannose **65** may be obtained from the enone **51** having a 2-naphthylmethyl protecting group by employing the same procedure for the isomeric enone **34** which gave rise to galactose **49** via the intermediates **62**, **63** and **64**, while both enantiomeric al-



Scheme 6



Scheme 7

loses **67** may be obtained from the *exo*-allyl alcohol **50** via the common intermediate **66** by application of the procedure established for the closely related system[20] (Scheme 8).

In conclusion, although the present study has not been completed, the basis of our strategy for an integrated route to both enantiomers of eight hexoses has been demonstrated. Further investigation for the completion of the present procedure is currently in progress.

Melting points are uncorrected. IR spectra were recorded on a JASCO-IR-700 spectrometer. ^{1}H NMR spectra were recorded on Gemini 2000 (300 MHz) or JEOL JMX-GX500 (500 MHz) spectrometers. Mass spectra were recorded on a JEOL JMS-DX303 instrument. Optical purities were determined on a Gilson Model-307 instrument equipped with a chiral column. Optical rotations were measured with a JASCO-DIP-370 digital polarimeter.

(*E*)-3-(2-Furyl)prop-2-en-1-ol (9: R = H)
Ethyl (*E*)-3-(2-Furfuryl)acrylate

To a stirred suspension of NaH (60% in oil, 12.5 g, 0.31 mol) in THF (450 mL) was added triethyl phosphonoacetate (72 mL, 0.36 mol) at 0 °C. After 30 min at the same temperature, furfural (**1**) (25 g, 0.26 mol) in THF (50 mL) was added dropwise at the same temperature. The mixture, after being kept stirring for 30 min at room temperature, was diluted with Et_2O (300 mL) and was treated with H_2O (100 mL). The organic layer was separated, washed with brine (50 mL) and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 500 g, elution with EtOAc–hexane 1:10 v/v) to remove a minor amount of the *Z*-olefin (0.9 g, 2%) to give the pure (*E*)-acrylate (42.1 g, 97%) as a pale yellow oil.

IR (film): ν = 1710, 1640 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48 (1 H, d, *J* = 1.6 Hz), 7.43 (1 H, d, *J* = 15.9 Hz), 6.60 (1 H, d, *J* = 3.4 Hz), 6.46 (1 H, dd, *J* = 3.4, 1.6 Hz), 6.32 (1 H, d, *J* = 15.9 Hz), 4.25 (2 H, q, *J* = 7.1 Hz), 1.32 (3 H, t, *J* = 7.1 Hz).

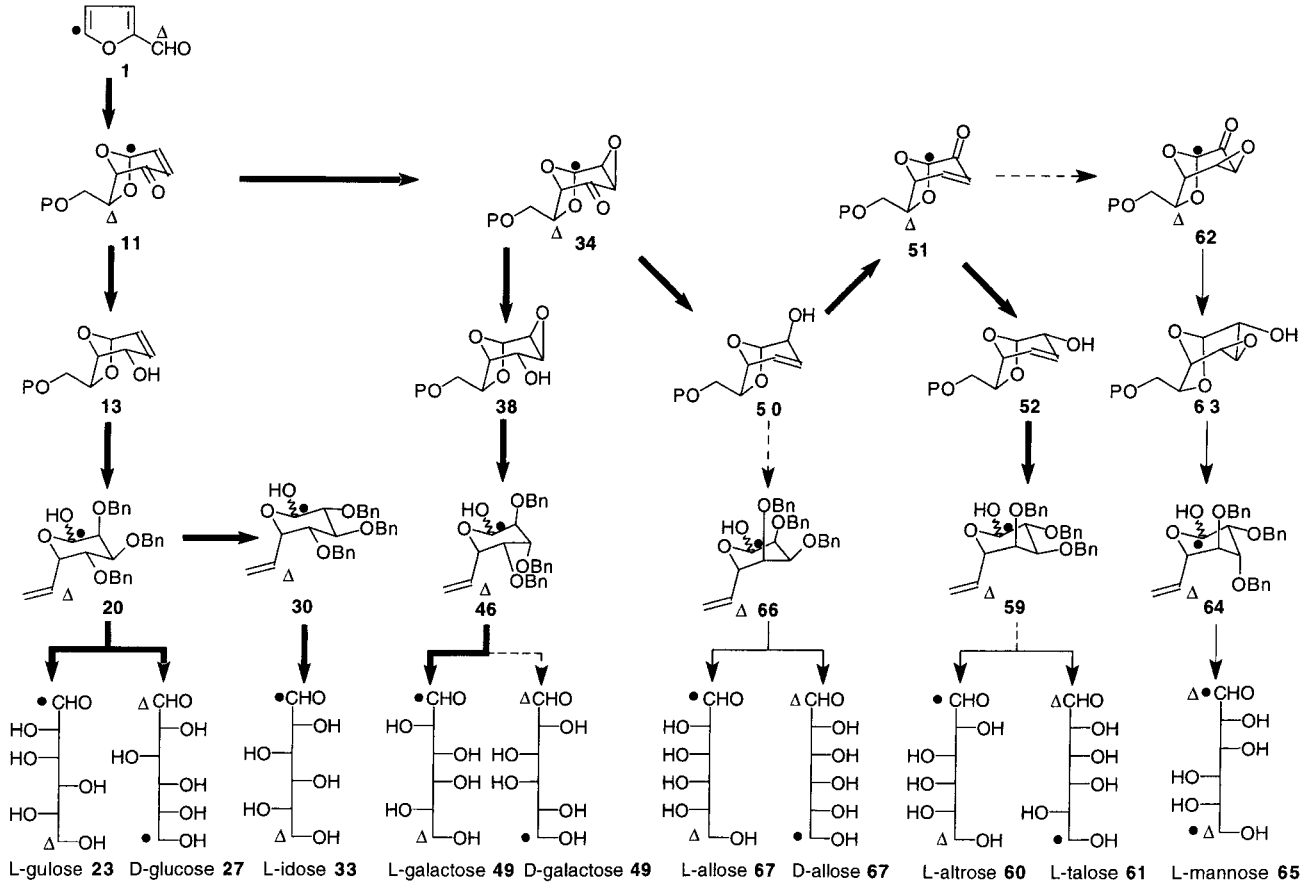
^{13}C NMR ($CDCl_3$, 75 MHz): δ=166.9, 150.9, 144.6, 130.8, 115.8, 114.5, 112.1, 60.1, 14.0.

HRMS calcd for $C_9H_{10}O_3$ (M^+) 166.0630, found 166.0610.

(*E*)-3-(2-Furfuryl)prop-2-en-1-ol (9:R = H)

To a stirred solution $LiAlH_4$ (3.7 g, 96.4 mmol) in Et_2O (400 mL) was added the above acrylate (20 g, 120.4 mmol) in Et_2O (100 mL) at 0 °C and the mixture was stirred at the same temperature for 1 h. The excess hydride was quenched by addition of 28% NH_4OH (~10 mL) and after 2 h the mixture was filtered through a Celite pad. The filtrate was evaporated under reduced pressure and the residue was chromatographed (silica gel, 400 g, elution with EtOAc–hexane, 1:2 v/v) to give **9** (R = H) (14.8 g, 97%) as a pale yellow oil.

IR (film): ν = 3328 cm^{-1}.



Scheme 8

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35 (1 H, d, *J* = 1.5 Hz), 6.45 (1 H, dt, *J* = 15.9, 1.2 Hz), 6.37 (1 H, dd, *J* = 3.3, 1.5 Hz), 6.30 (1 H, dt, *J* = 15.9, 5.7 Hz), 6.25 (1 H, d, *J* = 3.3 Hz), 4.30 (2 H, d, *J* = 5.7 Hz), 1.49 (1 H, br s).

HRMS calcd for $C_7H_8O_2$ (M^+) 124.0524, found 124.0482.

tert-Butyldimethylsilyl (*E*)-3-(2-Furyl)prop-2-enyl Ether (9: R = TBS)

A mixture of **9** (R = H) (1.03 g, 8.34 mmol), Et_3N (1.74 mL, 12.5 mmol), *tert*-butyldimethylchlorosilane (TBSCl) (1.51 g, 10.0 mmol) and 4-(*N*,*N*-dimethyl)pyridine (DMAP) (51 mg, 0.42 mmol) in CH_2Cl_2 (20 mL) was stirred at r.t. for 4 h. The mixture was washed successively with H_2O (5 mL) and brine (3 mL) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the residue was chromatographed (silica gel, 25 g, elution with EtOAc–hexane, 1:100) to give the ether **9** (R = TBS) (1.95 g, 98%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (1 H, d, *J* = 1.8 Hz), 6.43 (1 H, dt, *J* = 15.7, 1.8 Hz), 6.36 (1 H, dd, *J* = 3.2, 1.8 Hz), 6.23 (1 H, dt, *J* = 15.7, 4.6 Hz), 6.21 (1 H, d, *J* = 3.2 Hz), 4.33 (2 H, dd, *J* = 4.6, 1.8 Hz), 0.93 (9 H, s), 0.10 (6 H, s).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.1, 141.8, 128.1, 117.8, 111.3, 107.3, 63.3, 25.9, 18.4, –5.3.

HRMS calcd for $C_{13}H_{22}O_2Si$ (M^+) 238.1389, found 238.1381.

(*E*)-3-(2-Furyl)prop-2-enyl (2-Naphthylmethyl) Ether (9: R = 2-naphthylCH$_2$)

To a stirred solution of **9** (R = H) (8.74 g, 70.48 mmol) in THF (150 mL) was added NaH (60% in oil, 4.2 g, 105.72 mmol) at 0 °C and, after having ceased hydrogen gas evolution, 2-bromomethylnaphthalene (25 g, 112.77 mmol) and Bu_4NI (2.6 g, 70.48 mmol) were added. After stirring for 8 h at r.t., MeOH (2 mL, 49.34 mmol) and NaH (60% in oil, 1.97 g, 49.34 mmol) were added to the mixture. The mixture was diluted with EtOAc (200 mL) and was washed successively with H_2O (40 mL) and brine (20 mL), and the organic layer was dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 200 g, elution with EtOAc–hexane, 1:200 then 1:30) to give the ether **9** (R = 2-naphthylCH$_2$) (17.69 g, 95%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86–7.78 (4 H, m), 7.50–7.43 (3 H, m), 7.35 (1 H, br d, *J* = 1.7 Hz), 6.48 (1 H, d, *J* = 15.9 Hz), 6.36 (1 H, dd, *J* = 3.3, 1.7 Hz), 6.28 (1 H, dt, *J* = 15.9, 5.8 Hz), 6.24 (1 H, d, *J* = 3.3 Hz), 4.72 (2 H, s), 4.20 (2 H, dd, *J* = 5.8, 1.4 Hz).

HRMS calcd for $C_{18}H_{16}O_2$ (M^+) 264.1150, found 264.1132.

(–)-(1*S*,2*R*)-3-_tert_-Butyldimethylsiloxy-1-(2-furyl)propane-1,2-diol (10: P = TBS)

To a stirred solution of **9** (R=TBS) (1.70 g, 7.13 mmol) in *t*-BuOH–H_2O (1:1 v/v, 60 mL), $MeSO_2NH_2$ (678 mg, 7.13 mmol), and AD-mix-β (9.76 g) was added at 0 °C and the mixture was stirred at the same temperature for 95 h. The reaction was quenched by addition of Na_2SO_3 (2.70 g, 21.4 mmol) and the mixture was extracted with EtOAc (3 × 200 mL). The extract was washed successively with 10% aq KOH (60 mL) and brine (30 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 35 g, elution with EtOAc–hexane, 1:5 v/v) to give the glycol **10** (P = TBS) (1.83 g, 94%) as a pale yellow oil: $[\alpha]_D^{28}$ –1.70 (*c* = 1.1, $CHCl_3$). The optical purity was determined to be 99.6% ee by hplc using a chiral column (CHIRALCEL OD, elution with *i*-PrOH–hexane, 1:500 v/v) after conversion into the dibenzoate.

IR (film): ν = 3404 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40 (1 H, t, *J* = 1.4 Hz), 6.36 (2 H, d, *J* = 1.4 Hz), 4.74 (1 H, dd, *J* = 5.5, 4.1 Hz), 3.98–3.92 (1 H, m), 3.72 (1 H, dd, *J* = 10.4, 4.0 Hz), 3.61 (1 H, dd, *J* = 10.4, 4.9 Hz), 3.06 (1 H, d, *J* = 4.1 Hz), 2.72 (1 H, d, *J* = 6.3 Hz), 0.91 (9 H, s), 0.07 (6 H, s).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.9, 142.3, 128.1, 110.3, 107.6, 73.1, 68.2, 63.9, 25.7, 18.1, –5.7.

HRMS calcd for $C_{13}H_{23}O_3Si$ (M^+–OH) 255.1417, found 255.1418.

The (+)-(1*R*,2*S*)-enantiomer **10** (P = TBS) was also prepared under the same conditions using AD-mix-α in a comparable yield: $[\alpha]_D^{25}$ +1.63 (*c* = 1.1, $CHCl_3$), 99.6% ee (for dibenzoate) by hplc (CHIRALCEL OD, elution with *i*-PrOH–hexane 1:500 v/v).

(+)-(1*S*,2*R*)-1-(2-Furyl)-3-(2-naphthylmethyloxy)propane-1,2-diol (10: P = 2-naphthyl CH_2)

To a stirred solution of **9** (R = 2-naphthylCH_2) (8.05 g, 30.49 mmol) in *t*-BuOH–H_2O (1:1 v/v, 300 mL), $MeSO_2NH_2$ (2.9 g, 30.49 mmol), and AD-mix-β (39 g) was added at 0 °C and the mixture was stirred at the same temperature for 46 h. The reaction was quenched by addition of Na_2SO_3 (11.5 g, 91.47 mmol) and the mixture was extracted with EtOAc (3 × 200 mL). The combined extracts were washed successively with 10% aq KOH (60 mL) and brine (30 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel 160 g, elution with EtOAc–hexane, 1:2 v/v) to give the glycol **10** (P = 2-naphthylCH_2) (6.69 g, 74%) as colorless needles, mp 83–85 °C: $[\alpha]_D^{27}$ +24.06 (*c* = 1.0, $CHCl_3$).

IR (Nujol): ν = 3379 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85–7.81 (3 H, m), 7.75 (1 H, s), 7.52–7.43 (3 H, m), 7.36 (1 H, t, *J* = 1.1 Hz), 6.31–6.34 (2 H, m), 4.78 (1 H, d, *J* = 4.7 Hz), 4.74 (1 H, d, *J* = 11.7 Hz), 4.67 (1 H, d, *J* = 11.7 Hz), 4.16–4.09 (1 H, m), 3.62 (1 H, dd, *J* = 9.8, 3.8 Hz), 3.53 (1 H, dd, *J* = 9.8, 5.5 Hz), 2.95 (1 H, d, *J* = 4.7 Hz), 2.76 (1 H, d, *J* = 5.2 Hz).

HRMS calcd for $C_{18}H_{18}O_4$ (M^+) 298.1205, found 298.1206.

(–)-(1*S*,5*S*,7*R*)-7-*tert*-Butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]oct-3-en-2-one (11: P = TBS)

To a stirred solution of **10** (P = TBS) (3.61 g, 13.2 mmol) in CH_2Cl_2 (80 mL) was added MCPBA (70%, 3.59 g, 14.6 mmol) at 0 °C in the presence of $NaHCO_3$ (2.23 g, 26.5 mmol) and the mixture was stirred at r.t. for 3 h. The mixture was filtered through a Celile pad and evaporated under the reduced pressure to give the crude pyran-3-one **12** (P = TBS).

The crude **12**, without purification, was then refluxed in benzene (80 mL) in the presence of *p*-toluenesulfonic acid (*p*-TsOH) (25 mg, 0.13 mmol) with removal of water using a Dean–Stark apparatus. After 5 h, the mixture in EtOAc (100 mL) was washed successively with sat. aq $NaHCO_3$ (3 × 20 mL), and brine (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 75 g, elution with EtOAc–hexane, 1:20 v/v) to give the bicyclic enone **11** (P = TBS) (2.47 g, 69% from **10**) as a pale yellow oil: $[\alpha]_D^{28}$ –187.01 (*c* = 1.0, $CHCl_3$).

IR (film): ν = 1701 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.12 (1 H, dd, *J* = 9.8, 3.2 Hz), 6.08 (1 H, dd, *J* = 9.8, 1.1 Hz), 5.79 (1 H, d, *J* = 3.2 Hz), 4.61 (1 H, t, *J* = 1.1 Hz), 3.88–3.77 (2 H, m), 3.58 (1 H, dd, *J* = 9.9, 7.1 Hz), 0.90 (9 H, s), 0.08 (3 H, s), 0.07 (3 H, s).

HRMS calcd for $C_{12}H_{19}O_4Si$ (M^-CH_3) 255.1053, found 255.1008.

The (+)-(1*R*,5*R*,7*S*)-enantiomer **11** (P = TBS) was also prepared under the same conditions a comparable yield: $[\alpha]_D^{25}$ +186.10 (*c* = 1.0, $CHCl_3$).

(+)-(1*S*,5*S*,7*R*)-7-(2-Naphthylmethyloxymethyl)-6,8-dioxabicyclo[3.2.1]oct-3-en-2-one (11: P = 2-naphthylCH_2)

To a stirred solution of **10** (P = 2-naphthylCH_2) (4.61 g, 15.47 mmol) in CH_2Cl_2 (100 mL) was added MCPBA (70%, 4.19 g, 17.01 mmol) at 0 °C and the mixture was stirred at r.t. for 3 h. The mixture was filtered through a Celile pad and evaporated under reduced pressure to give the crude pyran-3-one **12** (P = 2-naphthylCH_2).

The crude **12**, without purification, was then refluxed in benzene (100 mL) in the presence of *p*-TsOH (29 mg, 0.15 mmol) for 10 h. After cooling, the mixture was diluted with EtOAc (100 mL) and the solution was washed with sat. aq $NaHCO_3$ (3 × 10 mL) and brine (10 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 100 g, elution with EtOAc–hexane, 1:8 v/v) to give the bicyclic enone **11** (P=2-naphthylCH_2) (3.11 g, 68% from **10**) as a colorless prisms, mp 80–83 °C: $[\alpha]_D^{29}$ –156.16 (*c* = 1.2, $CHCl_3$).

IR (Nujol): ν = 1700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86–7.82 (3 H, m), 7.77 (1 H, s), 7.52–7.45 (3 H, m), 7.12 (1 H, dd, *J* = 9.9, 3.2 Hz), 6.09 (1 H, d, *J* = 9.9 Hz), 5.83 (1 H, d, *J* = 3.2 Hz), 4.76 (2 H, s), 4.62 (1 H, t, *J* = 1.2 Hz), 4.04 (1 H, td, *J* = 5.5, 1.4 Hz), 3.67 (1 H, dd, *J* = 10.0, 5.6 Hz), 3.57 (1 H, dd, *J* = 10.0, 6.6 Hz).

HRMS calcd for $C_{18}H_{16}O_4$ (M^+) 296.1048, found 296.1027.

(+)-(1*R*,2*S*,5*S*,7*R*)-7-*tert*-Butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]oct-3-en-2-ol (13: P = TBS)

To a stirred mixture of **11** (P = TBS) (658 mg, 2.44 mmol) and $CeCl_3{\cdot}7H_2O$ (1.09 g, 2.92 mol) in MeOH (25 mL) was added $NaBH_4$ (411 mg, 2.92 mmol) at 0 °C. After stirring for 25 min at the same temperature, the solvent was removed under reduced pressure and the residue was dissolved in EtOAc (30 mL) and the organic layer was washed successively with H_2O (5 mL) and brine (3 mL) and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 15 g, elution with EtOAc–hexane, 1:10 v/v) to give the *endo*-alcohol **13** (P = TBS) (654 mg, 99%) as a colorless oil: $[\alpha]_D^{28}$ +1.57 (*c* = 1.0, $CHCl_3$).

IR (film): ν = 3456 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.91 (1 H, ddd, *J* = 9.7, 3.2, 1.8 Hz), 5.72 (1 H, dtd, *J* = 9.7, 2.0, 0.8 Hz), 5.49 (1 H, d, *J* = 3.2 Hz), 4.80–4.75 (1 H, m), 4.32 (1 H, ddd, *J* = 7.1, 5.2, 1.6 Hz), 4.27 (1 H, dt, *J* = 4.7, 1.6 Hz), 3.74 (1 H, dd, *J* = 10.4, 5.2 Hz), 3.58 (1 H, dd, *J* = 10.4, 7.1 Hz), 1.75 (1 H, br.d, *J* = 6.0 Hz), 0.89 (9 H, s), 0.07 (6 H, s).

HRMS calcd for $C_9H_{15}O_4Si$ ($M^-C_4H_9$) 215.0740, found 215.0713.

The (–)-(1*S*,2*R*,5*R*,7*S*)-enantiomer **13** (P = TBS) was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{24}$ –1.30 (*c* = 1.1, $CHCl_3$).

(+)-(1*R*,2*S*,5*S*,7*R*)-2-Benzyloxy-7-*tert*-butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]oct-3-ene (14: P = TBS)

To a stirred solution of **13** (P = TBS) (1.39 g, 5.09 mmol) in THF (40 mL) was added NaH (60% in oil, 265 mg, 6.62 mol) at 0 °C and, after 10 min, BnBr (848 μL, 7.13 mmol) was added and the mixture was refluxed for 12 h. The mixture was cooled to 0 °C and was again treated with NaH (60% in oil, 143 mg, 3.57 mmol) and MeOH (144 μL, 3.57 mmol) for 15 min to destroy the excess BnBr. The mixture was then treated with H_2O (10 mL) and extracted with EtOAc (100 mL). The extract was washed with brine (5 mL), dried ($MgSO_4$), evaporated, and chromatographed (silica gel 30 g, elution with EtOAc–hexane, 1:100 v/v) to give the benzyl ether **14** (P = TBS) (1.69 g, 92%) as a colorless oil: $[\alpha]_D^{28}$ +12.25 (*c* = 1.2, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36–7.29 (5 H, m). 5.92 (1 H, ddd, *J* = 9.7, 3.1, 1.6 Hz), 5.76 (1 H, dt, *J* = 9.7, 1.9 Hz), 5.47 (1 H, d, *J* = 3.1 Hz), 4.68 (1 H, d, *J* = 11.8 Hz), 4.56 (1 H, d, *J* = 11.8 Hz),

4.53–4.45 (3 H, m), 3.74 (1 H, dd, *J* = 10.2, 4.9 Hz), 3.54 (1 H, dd, *J* = 10.2, 8.2 Hz), 0.89 (9 H, s), 0.08 (3 H, s), 0.06 (3 H, s).

HRMS calcd for $C_{20}H_{30}O_4Si$ (M^+) 362.1913, found 362.1930.

The (–)-(1*S*,2*R*,5*R*,7*S*)-enantiomer **14** (P = TBS) was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{27}$ –11.58 (*c* = 1.1, $CHCl_3$).

(–)-(1*R*,2*S*,3*R*,4*S*,5*S*,7*R*)-2-Benzyloxy-7-*tert*-butyldimethylsil–oxymethyl-6,8-dioxabicyclo[3.2.1]octane-3,4-diol (15: P = TBS)
To a stirred solution of **14** (P = TBS) (2.93 g, 8.08 mmol), NMO (1.42 g, 12.1 mmol) in acetone–H_2O (1:1 v/v, 60 mL) was added OsO_4 (0.1967 M in THF, 4.09 mL, 0.81 mmol) at 0 °C and the mixture was stirred for 3 h at the r.t. The reaction was quenched by addition of sat. aq Na_2SO_3 (5 mL) and the organic layer was extracted with EtOAc (2 × 50 mL). The extract was washed with brine (5 mL), dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed (silica gel, 60 g, elution with EtOAc–hexane, 1:2 v/v) to give the glycol **15** (P = TBS) (3.02 g, 94%) as an amorphous solid: $[\alpha]_D^{26}$ –41.12 (*c* = 1.0, $CHCl_3$).

IR (film): ν = 3400 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.37–7.30 (5 H, m), 5.42 (1 H, d, *J* = 1.9 Hz), 4.73 (1 H, d, *J* = 11.7 Hz), 4.65 (1 H, d, *J* = 11.7 Hz), 4.42 (1 H, d, *J* = 4.1 Hz), 4.16 (1 H, dd, *J* = 8.6, 5.4 Hz), 3.87–3.79 (2 H, m), 3.64 (1 H, dd, *J* = 8.2, 4.1 Hz), 3.58 (1 H, dd, *J* = 9.9, 5.4 Hz), 3.39 (1 H, dd, *J* = 9.9, 8.6 Hz), 2.48 (1 H, br s), 2.20 (1 H, br s), 0.89 (9 H, s), 0.07 (3 H, s), 0.06 (3 H, s).

HRMS calcd for $C_{16}H_{23}O_6Si$ ($M^-C_4H_9$) 339.1264, found 339.1277.

The (+)-(1*S*,2*R*,3*S*,4*R*,5*R*,7*S*)-enantiomer **15** (P = TBS) was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{31}$ +41.44 (*c* = 1.0, $CHCl_3$).

(+)-(1*R*,2*S*,3*S*,4*S*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-*tert*-butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]octane (16: P = TBS)
To a stirred solution of the glycol **15** (P = TBS) (435 mg, 1.20 mmol) in THF (9 mL) was added NaH (60% in oil, 220 mg, 5.49 mmol) at 0 °C. After 10 min, BnBr (784 µL, 6.59 mmol) was added to the mixture and the mixture was refluxed for 5 h. After cooling, the mixture was treated with NaH (60% in oil, 62 mg, 1.54 mmol) and MeOH (62 µl, 1.54 mmol) for 15 min to quench the excess BnBr. The mixture was diluted with EtOAc (30 mL) and washed with H_2O (5 mL), brine (3 mL) and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure, followed by chromatography (silica gel 10 g, elution with EtOAc–hexane, 1:40 v/v) to give the trisbenzyl ether **16** (P = TBS) (581 mg, 92%) as a colorless oil: $[\alpha]_D^{28}$ +3.38 (*c* = 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.37–7.27 (15 H, m), 5.26 (1 H, d, *J* = 1.9 Hz), 4.80 (1 H, d, *J* = 12.4 Hz), 4.73 (1 H, d, *J* = 11.4 Hz), 4.72 (1 H, d, *J* = 11.8 Hz), 4.69 (1 H, d, *J* = 11.4 Hz), 4.65 (1 H, d, *J* = 11.8 Hz), 4.60 (1 H, d, *J* = 12.4 Hz), 4.36 (1 H, d, *J* = 4.1 Hz), 4.13 (1 H, dd, *J* = 8.4, 5.4 Hz), 4.00 (1 H, dd, *J* = 8.5, 4.1 Hz), 3.75–3.68 (2 H, m), 3.52 (1 H, dd, *J* = 9.8, 5.4 Hz), 3.36 (1 H, dd, *J* = 9.8, 8.4 Hz), 0.88 (9 H, s), 0.05 (3 H, s), 0.04 (3 H, s).

HRMS calcd for $C_{27}H_{37}O_6Si$ (M^+–C_7H_7) 485.2359, found 485.2329.

The (–)-(1*S*,2*R*,3*R*,4*R*,5*R*,7*S*)-enantiomer **16** (P = TBS) was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{29}$ –3.03 (*c* = 1.2, $CHCl_3$).

(+)-(1*R*,2*S*,3*S*,4*S*,5S,7*R*)-2,3,4-Trisbenzyloxy-7-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octane (17)
To a stirred solution of **16** (P = TBS) (6.53 g, 11.3 mmol) in THF (100 mL) was added tetrabutylammonium fluoride (TBAF) in THF (1.0 M, 17.0 mL, 17.0 mmol) at 0 °C and the mixture was stirred at a r.t. for 2 h. The mixture was washed successively with H_2O (20 mL) and brine (10 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 135 g, elution with EtOAc–hexane 1:2 v/v) to give the primary alcohol **17** (3.02 g, 94%) as a colorless oil: $[\alpha]_D^{31}$ +14.11 (*c* = 1.1, $CHCl_3$).

IR (film): ν = 3482 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.38–7.28 (15 H, m), 5.31 (1 H, d, *J* = 1.9 Hz), 4.81 (1 H, d, *J* = 12.4 Hz), 4.80 (1 H, d, *J* = 12.4 Hz), 4.71 (1 H, d, *J* = 12.1 Hz), 4.66 (1 H, d, *J* = 12.1 Hz), 4.64 (1 H, d, *J* = 12.4 Hz), 4.60 (1 H, d, *J* = 12.4 Hz), 4.20–4.17 (2 H, m), 4.01–3.95 (1 H, m), 3.74–3.70 (2 H, m), 3.46 (2 H, d, *J* = 5.8 Hz), 1.71 (1 H, br s).

HRMS calcd for $C_{21}H_{23}O_6$ (M^+–C_7H_7) 371.1495, found 371.1472.

The (–)-(1*S*,2*R*,3*R*,4*R*,5*R*,7*S*)-enantiomer **16** (P = TBS) was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{28}$ –14.02 (*c* = 1.0, $CHCl_3$).

(–)-(1*R*,2*S*,3*S*,4*S*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-iodomethyl-6,8-dioxabicyclo[3.2.1]octane (19)
To a stirred solution of **17** (P = TBS) (1.65 g, 3.57 mmol) and Et_3N (1.49 mL, 10.7 mmol) in CH_2Cl_2 (35 mL) was added methanesulfonyl chloride (MsCl) (414 µL, 5.35 mmol) at 0 °C and the mixture was stirred at r.t. for 3 h. The mixture was washed with H_2O (5 mL), brine (3 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude mesylate **18**. Without purification, the crude **18** was refluxed with LiI (4.77 g, 35.7 mmol) in THF (35 mL) for 6 h. After cooling, the mixture was diluted with EtOAc (50 mL) and was washed successively with 10% aq $Na_2S_2O_3$ (10 mL), sat. aq $NaHCO_3$ (10 mL) and brine (5 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 35 g, elution with EtOAc–hexane, 1:20 v/v) to give the iodide **19** (2.01 g, 99% from **16**) as a colorless oil: $[\alpha]_D^{28}$ –7.70 (*c* = 1.1, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41–7.28 (15 H, m), 5.34 (1 H, d, *J* = 1.9 Hz), 4.80 (1 H, d, *J* = 12.2 Hz), 4.75 (2 H, s), 4.71 (1 H, d, *J* = 12.1 Hz), 4.65 (1 H, d, *J* = 12.1 Hz), 4.59 (1 H, d, *J* = 12.2 Hz), 4.41 (1 H, d, *J* = 14.4 Hz), 4.38 (1 H, dd, *J* = 9.5, 5.8 Hz), 4.01–3.94 (1 H, m), 3.71–3.66 (2 H, m), 3.10 (1 H, dd, *J* = 9.5, 5.8 Hz), 3.01 (1 H, dd, *J* = 9.5 Hz).

HRMS calcd for $C_{21}H_{22}IO_5$ (M^+–C_7H_7) 481.0471, found 481.0506.

The (+)-(1*S*,2*R*,3*R*,4*R*,5*R*,7*S*)-enantiomer **19** was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{30}$ +7.56 (*c* = 1.1, $CHCl_3$).

(2*R/S*,3*S*,4*S*,5*S*,6*S*)-3,4,5-Trisbenzyloxy-6-vinyloxan-2-ol (20)
A solution of the iodide **19** (2.21 g, 3.86 mmol) in HOAc (40 mL) was stirred with activated Zn powder (12.6 g, 193 mmol) at r.t. for 3 h. The mixture was filtered and the filtrate was diluted with EtOAc (100 mL) and the mixture was washed successively with H_2O (10 mL), sat. aq $NaHCO_3$ (10 mL), brine (5 mL) and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 45 g, elution with EtOAc–hexane, 1:5 v/v) to give the hemiacetal **20** (1.67g, 97%) as a colorless oil.

IR (film): ν = 3470 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.25 (15 H, m), 5.89 (0.5 H, ddd, *J* = 17.3, 10.6, 6.2 Hz), 5.86 (0.5 H, ddd, *J* = 17.3, 10.6, 5.8 Hz), 5.37 (0.5 H, dt, *J* = 17.3, 1.5 Hz), 5.32 (0.5 H, dt, *J* = 17.3, 1.5 Hz), 5.22 (0.5 H, dt, *J* = 10.6, 1.5 Hz), 5.20 (0.5 H, dt, *J* = 10.6, 1.5 Hz), 5.18–5.14 (1.5 H, m), 4.79–4.32 (7 H, m), 3.86 (0.5 H, s), 3.85 (0.5 H, s), 3.76 (0.5 H, t, *J* = 3.3 Hz), 3.56 (0.5 H, dd, *J* = 8.0, 3.0 Hz), 3.46 (0.5 H, br.t, *J* = 1.8 Hz), 3.35 (0.5 H, dd, *J* = 3.9, 1.5 Hz), 3.11 (0.5 H, d, *J* = 6.0 Hz).

HRMS calcd for $C_{21}H_{23}O_5$ (M^+–C_7H_7) 355.1546, found 355.1527.

The (2*R*/*S*,3*R*,4*R*,5*R*,6*R*)-enantiomer **20** was also prepared under the same conditions in a comparable yield.

(2*R*/*S*,3*S*,4*S*,5*S*,6*S*)-2,3,4,5-Tetrakisbenzyloxy-6-vinyloxane (21)

A mixture of the hemiacetal **20** (505 mg, 1.13 mmol) in benzyl alcohol (1.17 mL, 11.3 mmol) in benzene (10 mL) was refluxed for 6 h in the presence of *p*-TsOH (2 mg, 0.01 mmol) using a Dean–Stark apparatus. The mixture diluted with EtOAc (20 mL) was washed with sat. aq $NaHCO_3$ (5 mL), brine (3 mL), dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed (silica gel 15 g, elution with EtOAc–hexane, 1:40 v/v) to give the tetrabenzyl ether **21** (516 mg, 85%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.25 (20 H, m), 5.90 (1 H, ddd, *J* = 17.4, 10.5, 5.9 Hz), 5.34 (1 H, dt, *J* = 17.4, 1.5 Hz), 5.20 (1 H, dt, *J* = 10.5, 1.5 Hz), 5.05–4.98 (1 H, m), 5.00 (1 H, dt, *J* = 12.2 Hz), 4.87 (1 H, d, *J* = 12.2 Hz), 4.73 (1 H, dt *J* = 12.2 Hz), 4.65 (1 H, d, *J* = 12.2 Hz), 4.62 (1 H, d, *J* = 12.2 Hz), 4.52 (1 H, d, *J* = 12.2 Hz), 4.40 (1 H, d, *J* = 12.2 Hz), 4.39–4.34 (1 H, m), 4.34 (1 H, d, *J* = 12.2 Hz), 3.77 (1 H, t, *J* = 3.4 Hz), 3.71(1 H, dd, *J* = 8.0, 3.3 Hz), 3.35 (1 H, dd, *J* = 3.8, 1.6 Hz).

FABMS: *m/z* = 535 (M^+ –1).

The (2*R*/*S*,3*R*,4*R*,5*R*,6*R*)-enantiomer was also prepared under the same conditions in a comparable yield.

(2*R*/*S*,3*S*,4*S*,5*S*,6*S*)-2,3,4,5-Tetrakisbenzyloxy-6-hydroxymethyloxane (22)

To a stirred solution of the alkene **21** (323 mg, 0.60 mmol) in MeOH–CH_2Cl_2 (1:1 v/v, 6 mL) was introduced ozone at –78 °C for 10 min. After excess ozone was removed by introduction of Ar, $NaBH_4$ (228 mg, 6.02 mmol) was added to the mixture and the mixture was stirred at r.t. for 20 min. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 10 g, elution with EtOAc–hexane, 1:4 v/v) to give the alcohol **22** (311 mg, 96%) as a colorless oil.

IR (film): ν = 3472 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.44–7.09 (20 H, m), 5.04–4.17 (9 H, m), 3.95 (1 H, ddd, *J* = 6.3, 4.7, 1.6 Hz), 3.88–3.78 (2 H, m), 3.68 (1 H, dd, *J* = 8.0, 3.3 Hz), 3.42–3.59 (1 H, m), 3.73 (1 H, dd, *J* = 3.8, 1.6 Hz), 1.76 (1 H, br.s).

HRMS calcd for $C_{27}H_{28}O_5$ (M^+–C_7H_8O) 432.1937, found 432.1905.

The (2*R*/*S*,3*S*,4*S*,5*S*,6*S*)-enantiomer **22** was also prepared under the same conditions in a comparable yield.

(+)-L-Gulose (23)

A solution of the tetrabenzyl ether **22** (311 mg, 0.58 mmol) in MeOH (6 mL) was hydrogenated on $Pd(OH)_2$ (10 mg) at r.t. for 144 h. The mixture was diluted with MeOH (20 mL) and filtered through a Celite pad to remove the catalyst. The filtrate was evaporated under reduced pressure and chromatographed (silica gel, 10 g, elution with EtOAc–MeOH–H_2O, 15:2:1 v/v) to give the L-gulose (**23**) (103 mg, 99%) as an amorphous solid: $[\alpha]_D^{31}$ +20.94 (*c* = 1.0, H_2O) [lit. $[\alpha]_D^{25}$ +16.0 (*c* = 1.28, H_2O), $[\alpha]_D$ –20 (for D-gulose)].

Spectral data (IR, ^{1}H NMR) and tlc were identical with those of an authentic material. (–)-D-Gulose (**23**) was also prepared under the same conditions in a comparable yield: $[\alpha]_D^{31}$ –21.09 (*c* = 1.1, H_2O).

(3*S*,4*R*,5*R*,6*R*)-3,7-Dihydroxy-4,5,6-tribenzyloxyhept-1-ene (24)

To a stirred solution of hemiacetal **20** (448 mg, 1.00 mmol) in THF (10 mL) was added $LiAlH_4$ (76 mg, 2.00 mmol) at r.t.. After stirring for 3 h at the same temperature, the mixture was treated with 30 % NH_4OH (2 mL) and the mixture was filtered through a Celite pad. The filtrate was dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed (silica gel, 9 g, elution with EtOAc–hexane, 1:5 v/v) to give the diol **24** (405 mg, 90%) as a colorless oil: $[\alpha]_D^{27}$ –5.23 (*c* = 1.0, $CHCl_3$).

IR (neat): ν = 3438 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37–7.25 (15 H, m). 5.93 (1 H, ddd, *J* = 17.2, 10.6, 5.8 Hz), 5.33 (1 H, d, *J* = 17.2 Hz), 5.19 (1 H, d, *J* = 10.6 Hz), 4.76–4.53 (6 H, m), 4.36–4.25 (1 H, m), 3.91–3.74 (4 H, m), 3.62 (1 H, dd, *J* = 5.2, 3.6 Hz), 2.79 (1 H, br.d, *J* = 5.2 Hz), 2.31 (1 H, br.s).

FABMS: *m/z* = 499 (M^++1).

(3*S*,4*R*,5*R*,6*R*)-3,4,5,6,7-Pentabenzyloxyhept-1-ene (25)

A diol **24** (1 g, 2.23 mmol) was treated with NaH (60% in oil, 356 mg, 8.92 mmol) and BnBr (1.3 mL, 11.15 mmol) in THF (30 mL) in the presence of Bu_4NI (82 mg, 0.22 mmol) as for the preparation of **16**. After workup and evaporating the solvent under reduced pressure the residue was chromatographed (silica gel, 20 g, elution with Et_2O–hexane, 1:10 v/v) to give **25** (1.3 g, 93%) as a colorless oil: $[\alpha]_D^{29}$ +15.66 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34–7.22 (25 H, m). 5.83 (1 H, ddd, *J* = 17.5, 10.3, 7.5 Hz), 5.26 (1 H, dd, *J* = 10.3, 1.6 Hz), 5.17 (1 H, dt, *J* = 17.5, 0.8 Hz), 4.79 (1 H, d, *J* = 11.5 Hz), 4.73 (1 H, d, *J* = 11.8 Hz), 4.64 (1 H, d, *J* = 11.8 Hz), 4.63 (1 H, d, *J* = 11.5 Hz), 4.60 (1 H, d, *J* = 11.8 Hz), 4.59 (1 H, d, *J* = 11.8 Hz), 4.50 (1 H, d, *J* = 11.8 Hz), 4.45 (1 H, d, *J* = 12.2 Hz), 4.41 (1 H, d, *J* = 12.2 Hz), 4.34 (1 H, d, *J* = 11.8 Hz), 4.09 (1 H, dd, *J* = 7.7, 6.0 Hz), 3.95 (1 H, t, *J* = 4.8 Hz), 3.88–3.82 (2 H, m), 3.75 (1 H, dd, *J* = 5.8, 4.9 Hz), 3.73–3.65 (1 H, m).

FABMS: *m/z* = 629 (M^++1).

(2*R*,3*S*,4*R*,5*R*)-2,3,4,5,6-Pentabenzyloxyhept-1-al (26)

To a stirred solution of OsO_4 (0.1967 M in THF, 324 μL, 0.06 mmol), NMO (228 mg, 1.91 mmol) in acetone–H_2O (1:1 v/v, 15 mL) was added **25** (800 mg, 1.27 mmol) at 0 °C. After 2 h at the r.t., the reaction was quenched by addition of sat. aq Na_2SO_3 (2 mL) and, after 10 min, the mixture was extracted with EtOAc (2 × 50 mL). The extract was washed successively with H_2O (10 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was then dissolved in THF–H_2O (2:1 v/v, 15 mL) and was then treated with $NaIO_4$ (834 mg, 3.81 mmol) at r.t. for 1 h with stirring. The mixture diluted in EtOAc (50 mL) was washed successively with H_2O (10 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 15 g, elution with Et_2O–hexane, 1:3 v/v) to give **26** (662 mg, 83% from **25**) as a colorless oil: $[\alpha]_D^{29}$ +8.27 (*c* = 1.0, $CHCl_3$).

IR (film): ν = 1727 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.72 (1 H, s), 7.35–7.15 (25 H, m), 4.78 (1 H, d, *J* = 12.1 Hz), 4.66 (1 H, d, *J* = 11.8 Hz), 4.59–4.39 (8 H, m), 4.12 (1 H, dd, *J* = 6.9, 3.4 Hz), 4.03 (1 H, dd, *J* = 6.7, 3.6 Hz), 3.91–3.80 (3 H, m), 3.70–3.27 (1 H, m).

HRMS calcd for $C_{34}H_{35}O_6$ (M^+–C_7H_7) 539.2432, found 539.2458.

(+)-D-Glucose (27)

A solution of the tetrabenzyl ether **26** (390 mg, 618 mmol) in MeOH (15 mL) was hydrogenated on $Pd(OH)_2$ (40 mg) at r.t. for 120 h. As treated for **23** D-glucose **27** (93 mg, 83%) was obtained after chromatography (silica gel, 8 g, elution with EtOAc–MeOH–H_2O, 15:2:1 v/v) as an amorphous solid: $[\alpha]_D^{29}$ +43.37 (*c* = 1.3, H_2O) [lit. $[\alpha]_D^{21}$ –47.2 (*c* = 0.83, H_2O), $[\alpha]_D$ –51.4 (for L-glucose)].

Spectral data (IR, ^{1}H NMR) and tlc were identical with those of an authentic material.

(3*S*,4*S*,5*S*,6*S*)-3,4,5-Trisbenzyloxy-6-vinyloxan-2-one (28)
A solution of **20** (310 mg, 0.70 mmol), NMO (163 mg, 1.40 mmol), 4 A sieves (372 mg) and TPAP (24 mg, 0.07 mmol) in CH_2Cl_2 (7.0 mL) was stirred at r.t. for 1.5 h. After filtration, the filtrate was evaporated under reduced pressure and the residue was chromatographed (silica gel, 6 g, elution with EtOAc–hexane, 1:5 v/v) to give **28** (259 mg, 84%) as a colorless oil: $[\alpha]_D^{27}$ –96.79 (*c* = 1.2, $CHCl_3$).

IR (film): ν = 1754 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.25 (15 H, m), 5.92 (1 H, ddd, *J* = 17.3, 10.5, 6.7 Hz), 5.38 (1 H, dt, *J* = 17.3, 1.1 Hz), 5.29 (1 H, dt, *J* = 10.5, 1.1 Hz), 5.13–5.09 (2 H, m), 4.89 (1 H, d, *J* = 12.1 Hz), 4.66 (1 H, d, *J* = 12.1 Hz), 4.59 (1 H, d, *J* = 12.1 Hz), 4.42 (1 H, d, *J* = 11.8 Hz), 4.40 (1 H, d, *J* = 2.7 Hz), 4.33 (1 H, d, *J* = 11.8 Hz), 3.96 (1 H, dd, *J* = 4.4, 3.0 Hz), 3.61 (1 H, dd, *J* = 4.4, 2.7 Hz).

HRMS calcd for $C_{21}H_{21}O_5$ ($M^-C_7H_7$) 353.1389, found 353.1347.

(3*R*,4*S*,5*S*,6*S*)-3,4,5-Trisbenzyloxy-6-vinyloxan-2-one (29)
A solution of **28** (338 mg, 0.76 mmol) and DABCO (128 mg, 1.14 mmol) in benzene (8 mL) was stirred at r.t. for 15 h. The mixture, after diluted with EtOAc (30 mL), was washed successively with H_2O (5 mL) and brine (3 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 6 g, elution with EtOAc–hexane, 1:2 v/v) to give a crystalline solid which was recrystallized to give **29** (249 mg, 74%) as colorless needles, mp 117–119 °C: $[\alpha]_D^{27}$ +32.02 (*c* = 1.1, $CHCl_3$).

IR (Nujol): ν = 1745 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.44–7.23 (15 H, m), 6.00 (1 H, ddd, *J* = 17.3, 10.7, 6.6 Hz), 5.41 (1 H, dt, *J* = 17.3, 1.1 Hz), 5.32 (1 H, dt, *J* = 10.7, 1.1 Hz), 5.06 (1 H, d, *J* = 11.5 Hz), 4.85 (1 H, dd, *J* = 6.6, 1.5 Hz), 4.66 (1 H, d, *J* = 11.5 Hz), 4.61 (1 H, d, *J* = 11.8 Hz), 4.57 (1 H, d, *J* = 12.1 Hz), 4.54 (1 H, d, *J* = 11.8 Hz), 4.41 (1 H, d, *J* = 12.1 Hz), 4.18 (1 H, d, *J* = 6.3 Hz), 3.87 (1 H, dd, *J* = 6.3, 1.5 Hz), 3.64 (1 H, t, *J* = 1.5 Hz).

HRMS calcd for $C_{21}H_{21}O_5$ (M^+–C_7H_7) 353.1389, found 353.1404.

(2*R*/*S*,3*R*,4*S*,5*S*,6*S*)-3,4,5-Trisbenzyloxy-6-vinyloxan-2-ol (30)
To a stirred solution of **29** (55 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was added DIBAL (1.5 M in toluene, 140 µL, 0.21 mmol), at –78 °C and the stiring was continued for 2 h at the same temperature. The mixture was diluted with Et_2O (10 mL) and the reaction was quenched by addition of H_2O (140 µL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was chromatographed (silica gel, 1 g, elution with EtOAc–hexane, 1:5 v/v) to give **30** (53 mg, 96%) as a colorless oil.

IR (film): ν = 3407 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.15 (15 H, m), 6.11 (0.7 H, ddd, *J* = 17.3, 10.7, 6.0 Hz), 6.04 (0.3 H, ddd, *J* = 17.3, 10.7, 6.9 Hz), 5.43 (0.7 H, dt, *J* = 17.3, 1.5 Hz), 5.34 (0.3 H, dt, *J* = 17.3, 1.1 Hz), 5.32 (0.7 H, dt, *J* = 10.7, 1.5 Hz), 5.21 (0.3 H, dt, *J* = 10.7, 1.1 Hz), 5.14 (0.7 H, dd, *J* = 7.4, 4.7 Hz), 4.96 (0.3 H, dd, *J* = 12.4, 2.2 Hz), 4.76–4.46 (6 H, m), 4.35 (0.7 H, d, *J* = 1.6 Hz), 4.30 (0.3 H, br d, *J* = 6.3 Hz), 3.85 (0.3 H, d, *J* = 12.1 Hz), 3.75–3.69 (1 H, m), 3.59–3.51 (1.4 H, m), 3.40–3.36 (1 H, m), 3.29–3.27 (0.3 H, m).

FABMS: *m/z* = 445 (M^+ – 1).

(2*R*/*S*,3*R*,4*S*,5*S*,6*S*)-2,3,4,5-Tetrakisbenzyloxy-6-vinyloxane (31)
A mixture of **30** (387 mg, 0.87 mmol), benzyl alcohol (449 µl, 4.35 mmol) and *p*-TsOH (2 mg, 0.01 mmol) in benzene (8 mL) was refluxed for 7 h. After dilution with EtOAc (20 mL), the mixture was washed successively with sat. aq $NaHCO_3$ (5 mL) and brine (3 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (silica gel, 8 g, elution with EtOAc–hexane, 1:10 v/v) to give **31** (410 mg, 88%) as a colorless crystalline solid, mp 44–46 °C.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.42–7.03 (20 H, m), 6.46–6.31 (0.25 H, m), 6.16–6.04 (0.75 H, m), 5.50–5.29 (2 H, m), 4.92–4.48 (9.75 H, m), 4.37–4.31 (0.25 H, m), 4.10–4.04 (0.25 H, m), 3.76–3.68 (1.5 H, m), 3.65–3.59 (0.25 H, m), 3.55–3.48 (1 H, m).

HRMS calcd for $C_{28}H_{29}O_5$ ($M^+ - C_7H_7$) 445.2014, found 445.1989.

(2*R*/*S*,3*R*,4*S*,5*S*,6*S*)-2,3,4,5-Tetrakisbenzyloxy-6-hydroxymethyloxane (32)
To a solution of **31** (500 mg, 0.93 mmol) in MeOH–CH_2Cl_2 (1:1 v/v, 30 mL) was introduced ozone at –78 °C for 10 min. After 10 min, $NaBH_4$ (353 mg, 9.33 mmol) was added at the same temperature and the mixture was warmed to r.t. After evaporation of the solvent, the residue was chromatographed (silica gel, 10 g, elution with EtOAc–hexane, 1:4 v/v) to give **32** (411 mg, 82%) as a colorless crystalline solid, mp 90–92 °C.

IR (Nujol): ν = 3344 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.26 (25 H, m), 4.97–4.49 (9 H, m), 4.14–3.47 (6 H, m), 2.05–2.02 (1 H, m).

HRMS calcd for $C_{27}H_{29}O_6$ (M^+–C_7H_7) 449.1963, found 449.1952.

(–)-L-Idose (33)
A solution of the tetrabenzyl ether **32** (400 mg, 741 mmol) in MeOH (15 mL) was hydrogenated on $Pd(OH)_2$ (40 mg) at r.t. for 144 h. As treated for **23** L-idose **33** (106 mg, 80%) was obtained after chromatographed (silica gel, 8 g, elution with EtOAc–MeOH–H_2O, 15:2:1 v/v) as an amorphous solid: $[\alpha]_D^{29}$ –12.35 (*c* = 1.0, H_2O) [lit. $[\alpha]_D^{25}$ –10.6 (*c* = 0.98, H_2O), $[\alpha]_D$ +15.8 (for D-idose)].

Spectral data (IR, ^1H NMR) and tlc were identical with those of an authentic material.

(+)-(1*S*,3*R*,4*S*,5*S*,7*R*)-3,4-Epoxy-7-(2-naphthylmethyloxymethyl)-6,8-dioxabicyclo[3.2.1]octan-2-one (34: P = 2-naphthylCH$_2$)
To a stirred solution of the enone **11** (P = 2-naphthylCH$_2$) (756 mg, 2.55 mmol) in THF (15 mL) and 0.5 N NaOH (2.6 mL, 1.28 mmol) was added 30% H_2O_2 (434 µL, 3.83 mmol) at 0 °C. After stirring for 30 min at r.t., the mixture was diluted with EtOAc (20 mL) and was washed with H_2O (5 mL) and brine (3 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, a crystalline residue was recrystallized from Et_2O to give the oxo epoxide **34** (P = 2-naphthylCH$_2$) (695 mg, 87%) as a colorless crystals, mp 136–139 °C: $[\alpha]_D^{28}$ +11.68 (*c* = 1.0, $CHCl_3$).

IR (Nujol): ν = 1738 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.86–7.83 (3 H, m), 7.75 (1 H, s), 7.51–7.43 (3 H, m), 5.89 (1 H, d, *J* = 0.5 Hz), 4.72 (2 H, s), 4.52 (1 H, t, *J* = 1.4 Hz), 4.14–4.10 (1 H, m), 3.57 (1 H, dd, *J* = 9.9, 5.8 Hz), 3.47 (1 H, dd, *J* = 3.6, 1.4 Hz), 3.45 (1 H, dd, *J* = 9.9, 6.9 Hz), 3.36–3.34 (1 H, m).

HRMS calcd for $C_{18}H_{16}O_5$ (M^+) 312.0998, found 312.1013.

(–)-(1*R*,2*S*,3*S*,4*S*,5*S*,7*R*)-3,4-Epoxy-2-hydroxy-7-(2-naphthylmethyloxymethyl)-6,8-dioxabicyclo[3.2.1]octane (38)
To a stirred solution of the oxo epoxide **34** (P = 2-naphthylCH$_2$) (558 mg, 1.79 mmol) and $CeCl_3 \cdot 7H_2O$ (800 mg, 2.15 mmol) in MeOH (10 mL) was added $NaBH_4$ (81 mg, 2.15 mmol) at 0 °C and the stirring was continued for 25 min at the same temperature. After dilution with EtOAc (20 mL) the mixture was washed successively with H_2O (5 mL) and brine (3 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 10 g, elution with EtOAc–hexane, 1:3 v/v) to give the *endo*-alcohol **38** (529 mg, 94%) as colorless needles, mp 114–116 °C: $[\alpha]_D^{27}$ –16.64 (*c* = 1.1, $CHCl_3$).

IR (Nujol): ν = 3418 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.85–7.82 (3 H, m), 7.77 (1 H, s), 7.51–7.45 (3 H, m), 5.63 (1 H, s), 4.76 (1 H, d, *J* = 12.9 Hz), 4.72 (1 H, d, *J* = 12.9 Hz), 4.54 (1 H, dt, *J* = 6.2, 1.9 Hz), 4.28 (1 H, t, *J* = 4.9 Hz), 4.18 (1 H, br d, *J* = 5.2 Hz), 3.58 (1 H, dd, *J* = 9.7, 5.8 Hz), 3.46 (1 H, dd, *J* = 9.7, 6.5 Hz), 3.07 (2 H, s), 2.15 (1 H, br d, *J* = 4.7 Hz).

HRMS calcd for $C_{18}H_{18}O_5$ (M^+) 314.1154, found 314.1158.

(+)-(1*S*,2*S*,3*S*,4*S*,5*S*,7*R*)-2-Benzoyloxy-3,4-epoxy-7-(2-naphthylmethyloxymethyl)-6,8-dioxabicyclo[3.2.1]octane (39)

To a stirred mixture of the epoxy alcohol **38** (468 mg, 1.49 mmol) and pyridine (542 μL, 6.71 mmol) in CH_2Cl_2 (10 mL) was added benzoyl chloride (606 μL, 5.23 mmol) at 0 °C and the stirring was continued for 22 h at r.t.. The mixture was diluted with EtOAc (30 mL) and was washed successively with H_2O (5 mL) and brine (3 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 10 g, elution with EtOAc–hexane, 1:30 then 1:10 v/v) to give the benzoate **39** (582 mg, 93%) as colorless needles, mp 75–77 °C: $[\alpha]_D^{27}$ +28.85 (*c* = 1.0, $CHCl_3$).

IR (Nujol): ν = 1720 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 8.00–7.96 (2 H, m), 7.82–7.67 (3 H, m), 7.64 (1 H, s), 7.56–7.41 (3 H, m), 7.37–7.30 (3 H, m), 5.71 (1 H, s), 5.41 (1 H, dd, *J* = 5.2, 0.8 Hz), 4.64 (2 H, s), 4.58 (1 H, td, *J* = 6.6, 1.6 Hz), 4.51 (1 H, dt, *J* = 5.2, 1.9 Hz), 3.61 (1 H, dd, *J* = 9.6, 5.6 Hz), 3.44 (1 H, dd, *J* = 9.6, 7.1 Hz), 3.26 (1 H, dd, *J* = 3.2, 2.1 Hz), 3.13 (1 H, d, *J* = 3.8 Hz).

HRMS calcd for $C_{29}H_{22}O_6$ (M^+) 418.1416, found 418.1417.

(+)-(1*S*,2*S*(*R*),3*S*(*R*),4*S*,5*S*,7*R*)-2(3)-Benzoyloxy-3(2),4-dihydroxy-7-(2-naphthylmethyloxymethyl)-6,8-dioxabicyclo-[3.2.1]octane (40)

To a stirred solution of the epoxybenzoate **39** (513 mg, 1.23 mmol) in benzene (10 mL) was added $BF_3{\cdot}Et_2O$ (150 μL, 1.23 mmol) at r.t. After stirring for 20 min at the same temperature, the mixture was diluted with EtOAc (20 mL) and was washed successively with H_2O (5 mL) and brine (3 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 10 g, elution with EtOAc–hexane, 1:1 v/v) to give the diol **40** (508 mg, 95%) as an amorphous solid: $[\alpha]_D^{27}$ +24.11 (*c* = 1.0, $CHCl_3$).

IR (film): ν = 3444, 1717 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 8.07–8.04 (2 H, m), 7.84–7.80 (3 H, m), 7.77 (1 H, s), 7.63–7.58 (1 H, m), 7.49–7.44 (4 H, m), 5.46 (1 H, t, *J* = 0.7 Hz), 5.40–5.38 (2 H, m), 4.79–4.67 (3 H, m), 4.41–4.34 (2 H, m), 3.88 (1 H, dt, *J* = 9.1, 1.4 Hz), 3.58 (1 H, dd, *J* = 9.6, 5.8 Hz), 3.45 (1 H, dd, *J* = 9.6, 7.1 Hz), 2.38 (1 H, d, *J* = 4.9 Hz), 2.26 (1 H, d, *J* = 9.1 Hz).

HRMS calcd for $C_{25}H_{24}O_7$ (M^+) 436.1522, found 436.1515.

(+)-(1*R*,2*S*,3*R*,4*S*,5*S*,7*R*)-2,3,4-Trihydroxy-7-(2-naphthylmethyloxymethyl)-6,8-dioxabicyclo[3.2.1]octane (41)

To a stirred solution of the benzoate **40** (460 mg, 1.06 mmol) in MeOH (9 mL) was added NaOMe (285 mg, 5.30 mmol) at r.t. and the stirring was continued for 45 min at same temperature. After evaporation of the solvent, the residue was chromatographed (silica gel, 9 g, elution with EtOAc–hexane, 5:1 v/v) to give the triol **41** (287 mg, 82%) as colorless prisms, mp 184–186 °C: $[\alpha]_D^{29}$ +7.46 (*c* = 1.0, EtOH).

IR (Nujol): ν = 3454 cm^{-1}.

^1H NMR (CD_3OD, 300 MHz): δ = 7.77–7.73 (4 H, m), 7.41–7.36 (3 H, m), 5.18 (1 H, t, *J* = 1.6 Hz), 4.69–4.58 (3 H, m), 4.06 (1 H, br d, *J* = 2.7 Hz), 3.88 (1 H, t, *J* = 4.7 Hz), 3.82–3.76 (1 H, m), 3.60–3.56 (1 H, m), 3.40 (1 H, dd, *J* = 9.6, 5.8 Hz), 3.32 (1 H, dd, *J* = 9.9, 7.1 Hz), 3.24–3.21 (3 H, m).

HRMS calcd for $C_{18}H_{20}O_6$ (M^+) 332.1260, found 332.1245.

(+)-(1*R*,2*S*,3*R*,4*S*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-(2-naphthylmethyloxymethyl)-6,8-dioxabicyclo[3.2.1]octane (42)

To a stirred solution of the triol **41** (110 mg, 0.33 mmol) in THF (3 mL) was added NaH (60% in oil, 106 mg, 2.65 mmol) at 0 °C and, after having ceased hydrogen gas evolution, BnBr (394 μL, 3.30 mmol) was added. After refluxing for 8 h, MeOH (28 μL, 0.69 mmol) followed by NaH (60% in oil, 28 mg, 0.69 mmol) was added to the mixture at r.t. and the mixture was diluted with EtOAc (20 mL). The mixture was successively washed with H_2O (5 mL) and brine (3 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 2 g, elution with EtOAc–hexane, 1:10 v/v) to give the tribenzyl ether **42** (196 mg, 98%) as a colorless oil: $[\alpha]_D^{30}$ +14.72 (*c* = 1.2, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.84–7.76 (4 H, m), 7.49–7.44 (3 H, m), 7.36–7.21 (15 H, m), 5.35 (1 H, s), 4.91 (1 H, t, *J* = 6.6 Hz), 4.74 (1 H, d, *J* = 12.2 Hz), 4.68 (1 H, d, *J* = 12.2 Hz), 4.64–4.55 (4 H, m), 4.45 (1 H, d, *J* = 12.1 Hz), 4.37–4.32 (2 H, m), 3.90–3.87 (1 H, m), 3.82–3.80 (1 H, m), 3.53–3.48 (2 H, m), 3.39 (1 H, dd, *J* = 17.0, 7.4 Hz).

HRMS calcd for $C_{32}H_{31}O_6$ ($M^+ - C_7H_7$) 511.2121, found 511.2094.

(+)-(1*R*,2*S*,3*R*,4*S*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octane (43)

To a stirred suspension of 10% Pd/C (50 mg) in EtOH (6 mL) containing 1 drop of $CHCl_3$ was added the ether **42** (302 mg, 0.50 mmol) under hydrogen at r.t. and the stirring was continued for 1.5 h at the same temperature. After filtration through a Celite pad, the filtrate was evaporated under reduced pressure and the residue was chromatographed (silica gel, 6 g, elution with EtOAc–hexane, 1:3 v/v) to give the primary alcohol **43** (223 mg, 96%) as a colorless oil: $[\alpha]_D^{27}$ +32.45 (*c* = 1.1, $CHCl_3$).

IR (film): ν = 3482 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.38–7.22 (15 H, m), 5.37 (1 H, s), 5.79 (1 H, t, *J* = 15.4 Hz), 4.62 (1 H, d, *J* = 12.1 Hz), 4.60 (1 H, d, *J* = 13.2 Hz), 4.56 (1 H, d, *J* = 13.2 Hz), 4.54 (1 H, d, *J* = 12.1 Hz), 4.46 (1 H, d, *J* = 12.2 Hz), 4.37 (1 H, d, *J* = 12.2 Hz), 4.24 (1 H, d, *J* = 3.8 Hz), 3.88 (1 H, t, *J* = 4.4 Hz), 3.82–3.80 (1 H, m), 3.55–3.52 (3 H, m), 1.76 (1 H, br.t, *J* = 5.9 Hz).

HRMS calcd for $C_{21}H_{23}O_6$ ($M^+ - C_7H_7$) 371.1497, found 371.1501.

(–)-(1*R*,2*S*,3*R*,4*S*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-iodomethyl-6,8-dioxabicyclo[3.2.1]octane (45)

To a stirred suspension of **43** (1.99 g, 4.31 mmol) and Et_3N (1.8 mL, 12.93 mmol) in CH_2Cl_2 (40 mL) was added MsCl (500 μL, 6.47 mmol) at 0 °C. After 1 h at the same temperature, the mixture was diluted with EtOAc (200 mL) and was washed successively with H_2O (40 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude mesylate **44** which was used without purification.

A solution of **44** obtained and LiI (5.76 g, 43.05 mmol) in THF (40 mL) was then refluxed for 17 h and the mixture, diluted with EtOAc (200 mL) and was washed successively with 10% aq $Na_2S_2O_3$ (40 mL), sat. aq $NaHCO_3$ (40 mL), and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (silica gel, 40 g, elution with EtOAc–hexane, 1:15 v/v) to give the iodide **45** (2.3 g, 93%) as a colorless oil: $[\alpha]_D^{27}$ –1.57 (*c* = 1.1, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.61–7.17 (15 H, m), 5.41 (1 H, s), 4.95 (1 H, dd, *J* = 9.3, 5.2 Hz), 4.69 (1 H, d, *J* = 12.1 Hz), 4.63

(1 H, d, J = 12.4 Hz), 4.59 (1 H, d, J = 12.1 Hz), 4.55 (1 H, d, J = 12.4 Hz), 4.46–4.42 (2 H, m), 4.32 (1 H, d, J = 12.4 Hz), 3.86 (1 H, t, J = 4.4 Hz), 3.82–3.09 (1 H, m), 3.47 (1 H, s), 3.18 (1 H, dd, J = 9.5, 5.5 Hz), 3.06 (1 H, dd, J = 9.5 Hz).

HRMS calcd for $C_{21}H_{22}IO_5$ (M^+–C_7H_7) 481.0513, found 481.0493.

(2*R*/*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-Trisbenzyloxy-6-vinyloxan-2-ol (46)

A solution of **45** (2.3 g, 4.02 mmol) in HOAc (50 mL) was stirred with activated Zn powder (13.1 g, 201 mmol) at r.t. for 1 h. After filtration, the filtrate was diluted EtOAc (2 × 200 mL) and was washed successively with H_2O (40 mL), sat. aq $NaHCO_3$ (40 mL), and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (silica gel, 40 g, elution with EtOAc–hexane, 1:5 v/v) to give **46** (1.75 g, 98%) as a colorless crystalline solid, mp 75–77 °C.

IR (Nujol): ν = 3396 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.24 (15 H, m), 5.89 (0.34 H, ddd, J = 17.0, 10.3, 5.8 Hz), 5.87 (0.66 H, ddd, J = 17.0, 10.4, 6.0 Hz), 5.36–5.28 (1.66 H, m), 5.19 (0.34 H, dt, J = 10.3, 1.7 Hz), 5.17 (0.66 H, dt, J = 10.4, 1.4 Hz), 4.95–4.64 (6.68 H, m), 4.45 (0.66 H, br.d, J = 5.8 Hz), 4.07 (0.66 H, dd, J = 9.6, 3.6 Hz), 3.96–3.75 (3 H, m), 3.57 (0.34 H, dd, J = 9.6, 3.0 Hz).

HRMS calcd for $C_{21}H_{23}O_5$ ($M^+ - C_7H_7$) 355.1546, found 355.1558.

(2*R*/*S*,3*S*,4*R*,5*S*,6*S*)-2,3,4,5-Tetrakisbenzyloxy-6-vinyloxane (47)

A solution of **46** (1.75 g, 3.93 mmol) and benzyl alcohol (2.03 mL, 19.65 mmol) in benzene (40 mL) was refluxed in the presence of *p*-TsOH (7 mg, 0.04 mmol) for 23 h. The mixture, after dilution with EtOAc (100 mL) was washed successively with sat. aq $NaHCO_3$ (20 mL), and brine (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (silica gel, 40 g, elution with EtOAc–hexane, 1:10 v/v) to give **47** (1.94 g, 92%) as a colorless crystalline solid, mp 74–76 °C.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41–7.19 (20 H, m), 5.89 (0.34 H, ddd, J = 16.8, 10.7, 5.8 Hz), 5.84 (0.66 H, ddd, J = 17.3, 10.6, 6.0 Hz), 5.35 (0.34 H, dt, J = 16.8, 1.4 Hz), 5.26 (0.66 H, dt, J = 17.3, 1.6 Hz), 5.20 (0.34 H, dt, J = 10.7, 1.4 Hz), 5.15 (0.66 H, dt, J = 10.6, 1.6 Hz), 5.06–4.48 (9 H, m), 4.24 (0.66 H, br d, J = 6.0 Hz), 4.10–4.00 (1.32 H, m), 3.93 (0.34 H, dd, J = 9.9, 7.7 Hz), 3.84–3.80 (1 H, m), 3.73 (0.34 H, br d, J = 2.2 Hz), 3.54 (0.34 H, dd, J = 9.9, 3.0 Hz).

HRMS calcd for $C_{28}H_{29}O_5$ (M^+–C_7H_7) 445.2014, found 445.2042.

(2*R*/*S*,3*S*,4*R*,5*S*,6*S*)-2,3,4,5-Tetrakisbenzyloxy-6-hydroxymethyloxane (48)

To a stirred solution of **47** (704 mg, 1.31 mmol) in MeOH–CH_2Cl_2 (1:1 v/v, 40 mL) was introduced ozone at –78 °C for 10 min. After excess ozone was removed by introduction of Ar, $NaBH_4$ (500 mg, 13.13 mmol) was added at the mixture and the mixture was stirred at r.t. for 20 min. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 15 g, elution with EtOAc–hexane, 1:2 v/v) to give **48** (613 mg, 86%) as a colorless crystalline solid, mp 69–72 °C.

IR (Nujol): ν = 3394 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.43–7.17 (20 H, m), 4.99–4.47 (9 H, m), 4.08–3.34 (6 H, m), 1.48–1.42 (1 H, m).

HRMS calcd for $C_{27}H_{29}O_6$ (M^+–C_7H_7) 449.1963, found 449.1945.

L-Galactose (49)

A solution of **48** (590 mg, 1.09 mmol) in MeOH (12 mL) was hydrogenated on $Pd(OH)_2$ (59 mg) at r.t. for 176 h. The mixture was diluted with MeOH (20 mL) and filtered through a Celite pad to remove the catalyst. The filtrate was evaporated under reduced pressure and chromatographed (silica gel, 12 g, elution with EtOAc–MeOH–H_2O, 15:2:1 v/v) to give the L-galactose **49** (180 mg, 92%) as an amorphous solid: $[\alpha]_D^{29}$ –77.62 (c = 0.8, H_2O) [lit. $[\alpha]_D^{23}$ –72.2 (c = 0.70, H_2O), $[\alpha]_D$ –81].

(–)-(1*S*,3*R*,4*S*,5*S*,7*R*)-7-*tert*-Butyldimethylsiloxymethyl-3,4-epoxy-6,8-dioxabicyclo[3.2.1]octan-4-one 34 (P = TBS)

To a stirred solution of **11** (P = TBS) (1.31 g, 4.84 mmol) in THF (30 mL) and 0.5 M NaOH (4.9 mL, 2.42 mmol) was added 30% H_2O_2 (823 μL, 7.26 mmol) at 0 °C. After stirring for 10 min at r.t., the mixture was diluted with EtOAc (50 mL) and was washed successively with H_2O (10 mL) and brine (5 mL), and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, 20 g, elution with EtOAc–hexane, 1:5 v/v) to give **34** (1.24 g, 90%) as a colorless oil: $[\alpha]_D^{29}$ –5.24 (c = 1.1, $CHCl_3$).

IR (film): ν = 1738 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 5.83 (1 H, s), 4.48 (1 H, s), 3.91 (1 H, ddd, J = 7.8, 5.2, 1.2 Hz), 3.65 (1 H, dd, J = 10.2, 5.2 Hz), 3.48–3.42 (2 H, m), 3.32–3.30 (1 H, m), 0.86 (9 H, s), 0.03 (6 H, s).

HRMS calcd for $C_9H_{13}O_5Si$ (M^+–C_4H_9) 229.0532, found 229.0523.

(+)-(1*R*,4*S*,5*S*,7*R*)-7-*tert*-Butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]octan-2-en-4-ol (50)

To a stirred solution of **34** (P = TBS) (102 mg, 0.36 mmol) in MeOH (2 mL) containing HOAc (2 μL, 0.04 mmol) was added hydrazine hydrate (99%, 52 μL, 1.08 mmol), at 0 °C and the stirring was continued for 3 h at r.t.. The mixture was diluted with Et_2O (3 mL) and treated with sat. aq $NaHCO_3$ (1 mL). The mixture was extracted with EtOAc (20 mL) and the extract washed successively with H_2O (5 mL) and brine (3 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 2 g, elution with EtOAc-hexane, 1:8 v/v) to give **50** (60 mg, 62%) as a pale yellow oil: $[\alpha]_D^{30}$ +34.48 (c = 1.2, $CHCl_3$).

IR (film): ν = 3428 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 6.22 (1 H, dd, J = 9.9, 4.7 Hz), 5.85–5.80 (1 H, m), 5.48 (1 H, s), 4.54 (1 H, d, J = 4.7 Hz), 3.83 (1 H, dd, J = 9.5, 4.9 Hz), 3.63–3.56 (2 H, m), 3.40 (1 H, dd, J = 9.5 Hz), 1.77 (1 H, br d, J = 10.2 Hz), 0.89 (9 H, s), 0.06 (6 H, s).

HRMS calcd for $C_9H_{15}O_4Si$ (M^+–C_4H_9) 215.0740, found 215.0696.

(+)-(1*R*,5*S*,7*R*)-7-*tert*-Butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]oct-2-en-4-one (51)

To a stirred solution of **50** (26 mg, 0.10 mmol) in CH_2Cl_2 (4 mL) and NaOAc (24 mg, 0.30 mmol) was added pyridinium chlorochromate (PCC) (41 mg, 0.20 mmol) at r.t. in the pressure of florisil (41 mg) the stirring was continued for 10 h. After filtration through a Celite pad, the filtrate was evaporated under the reduced pressure and chromatographed (silica gel, 1 g, elution with EtOAc–hexane, 1:10 v/v) to give **51** (16mg, 62%) as a pale yellow oil: $[\alpha]_D^{25}$ +266.83 (c = 1.2, $CHCl_3$).

IR (film): ν = 1711 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.32 (1 H, dd, J = 9.9, 4.7 Hz), 6.14 (1 H, dd, J = 9.9, 1.6 Hz), 5.33 (1 H, d, J = 1.6 Hz), 4.86 (1 H, d, J = 4.7 Hz), 3.92 (1 H, dd, J = 9.6, 4.9 Hz), 3.77 (1 H, dd, J = 9.6, 4.9 Hz), 3.46 (1 H, dd, J = 9.6 Hz), 0.91 (9 H, s), 0.09 (3 H, s), 0.08 (3 H, s).

HRMS calcd for $C_{13}H_{22}O_4Si$ (M^+) 270.1286, found 270.1279.

(+)-(1*R*,4*R*,5*S*,7*R*)-7-*tert*-Butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]oct-2-en-4-ol (52)

To a stirred solution of **51** (185 mg, 0.69 mmol) and $CeCl_3 \cdot 7H_2O$ (306 mg, 0.83 mmol) in MeOH (5 mL) was added $NaBH_4$ (31 mg, 0.83 mmol) at 0 °C. After 30 min at the same temperature the mixture was diluted with EtOAc (20 mL) and washed successively with

H_2O (5 mL) and brine (3 mL). The mixture was evaporated under reduced pressure and chromatographed (silica gel, 4g, elution with EtOAc–hexane, 1:10 v/v) to give **52** (186 mg, 100%) as a colorless oil: $[\alpha]_D^{29}$ +5.31 (*c* = 1.1, $CHCl_3$).

IR (film): ν = 3460 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 6.13 (1 H, ddd, *J* = 9.9, 4.4, 0.7 Hz), 5.71 (1 H, dt, *J* = 9.9, 2.3 Hz), 5.47 (1 H, t, *J* = 2.5 Hz), 4.50 (1 H, d, *J* = 4.4 Hz), 4.28 (1 H, br d, *J* = 11.4 Hz), 3.96 (1 H, dd, *J* = 9.2, 5.2 Hz), 3.56 (1 H, dd, *J* = 9.9, 5.2 Hz), 3.41 (1 H, dd, *J* = 9.9, 9.2 Hz), 2.09 (1 H, br d, *J* = 11.4, Hz), 0.88 (9 H, s), 0.06 (6 H, s).

HRMS calcd for $C_9H_{15}O_4Si$ (M^+–C_4H_9) 215.0740, found 215.0734.

(+)-(1*R*,4*R*,5*S*,7*R*)-4-Benzyloxy-7-*tert*-butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]oct-2-ene (53)

To a stirred solution of **52** (186 mg, 0.68 mmol) in THF (5 mL) was added NaH (60% in oil, 36 mg, 0.88 mmol) followed by BnBr (114 μL, 0.95 mmol) as for **14** to give **53** (227 mg, 92%) as a colorless oil after chromatography (silica gel, 4 g, elution with EtOAc–hexane, 1:20 v/v): $[\alpha]_D^{29}$ +3.94 (*c* = 1.1, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.27 (5 H, m), 6.14 (1 H, ddd, *J* = 10.0, 4.2, 1.4 Hz), 5.73 (1 H, dt, *J* = 10.0, 2.2 Hz), 5.52 (1 H, t, *J* = 2.3 Hz), 4.69 (1 H, d, *J* = 12.4 Hz), 4.64 (1 H, d, *J* = 12.4 Hz), 4.52 (1 H, d, *J* = 4.4 Hz), 4.23 (1 H, q, *J* = 2.2 Hz), 4.10 (1 H, dd, *J* = 9.7, 4.9 Hz), 3.58 (1 H, dd, *J* = 9.7, 4.9 Hz), 3.40 (1 H, dd, *J* = 9.7 Hz), 0.88 (9 H, s), 0.05 (6 H, s).

HRMS calcd for $C_{16}H_{21}O_4Si$ (M^+–C_4H_9) 305.1209, found 305.1211.

(+)-(1*R*,2*R*,3*S*,4*R*,5*S*,7*R*)-4-Benzyloxy-7-*tert*-butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]octane-2,3-diol (54)

To a stirred solution of **53** (227 mg, 0.63 mmol), NMO (110 mg, 0.95 mmol) in acetone–H_2O (1:1 v/v, 6 mL) was added OsO_4 (0.1967 M in THF, 319 μL, 0.06 mmol) at 0 °C and was treated as for **15** to give **54** (225 mg, 91%) as an amorphous solid after chromatography (silica gel, 4 g, elution with EtOAc–hexane, 1:4 v/v): $[\alpha]_D^{27}$ +70.20 (*c* = 1.0, $CHCl_3$).

IR (film): ν = 3452 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.29 (5 H, m), 5.35 (1 H, d, *J* = 1.6 Hz), 4.75 (1 H, d, *J* = 12.3 Hz), 4.71 (1 H, d, *J* = 12.3 Hz), 4.48 (1 H, d, *J* = 2.2 Hz), 3.91–3.79 (3 H, m), 3.60 (1 H, dd, *J* = 9.9, 4.7 Hz), 3.43–3.35 (2 H, m), 2.51–2.47 (2 H, m), 0.88 (9 H, s), 0.05 (6 H, s).

HRMS calcd for $C_{20}H_{33}O_6Si$ (M^++1) 397.2044, found 397.2089.

(+)-(1*R*,2*R*,3*S*,4*R*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-*tert*-butyldimethylsiloxymethyl-6,8-dioxabicyclo[3.2.1]octane (55)

To a stirred solution of **54** (256 mg, 0.65 mmol) in THF (6 mL) was added NaH (60% in oil, 129 mg, 3.25 mmol), followed by BnBr (461 μL, 3.90 mmol) as for **16** to give **55** (335 mg, 90%) as a colorless oil after chromatography (silica gel, 5 g, elution with EtOAc–hexane, 1:20 v/v): $[\alpha]_D^{26}$ +40.84 (*c* = 1.1, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.24 (15 H, m), 5.31 (1 H, d, *J* = 1.4 Hz), 4.82 (1 H, d, *J* = 11.9 Hz), 4.75 (2 H, s), 4.68 (1 H, d, *J* = 11.9 Hz), 4.65 (2 H, s), 4.44 (1 H, d, *J* = 2.5 Hz), 3.79–3.70 (2 H, m), 3.66–3.61 (2 H, m), 3.53 (1 H, dd, *J* = 9.7, 4.5 Hz), 3.30 (1 H, dd, *J* = 9.7 Hz), 0.85 (9 H, s), 0.01 (6 H, s).

HRMS calcd for $C_{27}H_{37}O_6Si$ (M^+–C_7H_7) 485.2359, found 485.2341.

(+)-(1*R*,2*R*,3*S*,4*R*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octane (56)

To a stirred solution of **55** (250 mg, 0.43 mmol) in THF (5 mL) was added TBAF (1.0 M in THF, 651 μL, 0.65 mmol) at 0 °C and was treated as for **17** to give **56** (198 mg, 99%) as a colorless oil after chromatography (silica gel, 5 g, elution with EtOAc–hexane, 1:2 v/v): $[\alpha]_D^{26}$ +60.48 (*c* = 1.1, $CHCl_3$).

IR (film): ν = 3466 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.61–7.28 (15 H, m), 5.38 (1 H, d, *J* = 1.4 Hz), 4.84 (1 H, d, *J* = 11.9 Hz), 4.74 (2 H, s), 4.70 (2 H, d, *J* = 11.9 Hz), 4.65 (1 H, d, *J* = 11.9 Hz), 4.36 (1 H, br d, *J* = 2.5 Hz), 3.81–3.67 (4 H, m), 3.57–3.44 (2 H, m), 1.75 (1 H, br t, *J* = 5.9 Hz).

HRMS calcd for $C_{21}H_{23}O_6Si$ (M^+–C_7H_7) 371.1495, found 371.1490.

(+)-(1*R*,2*R*,3*S*,4*R*,5*S*,7*R*)-2,3,4-Trisbenzyloxy-7-iodomethyl-6,8-dioxabicyclo[3.2.1]octane (58)

To a stirred solution of **56** (198 mg, 0.43 mmol) and Et_3N (179 μL, 1.29 mmol) in CH_2Cl_2 (5 mL) was added MsCl (50 μL, 0.65 mmol) at 0 °C as for **19** to give the crude mesylate **57**. The crude **57** without purification was then refluxed with LiI (573 mg, 4,30 mmol) in THF (5 mL) for 6 h and was treated as for **19** to give **58** (223 mg, 91%) as a colorless oil after chromatography (silica gel, 4 g, elution with EtOAc–hexane, 1:20 v/v): $[\alpha]_D^{29}$ +37.75 (*c* = 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.27 (15 H, m), 5.45 (1 H, s), 4.81 (1 H, d, *J* = 11.8 Hz), 4.78 (1 H, d, *J* = 12.6 Hz), 4.73 (1 H, d, *J* = 12.6 Hz), 4.68 (1 H, d, *J* = 11.8 Hz), 4.64 (1 H, s), 4.54 (1 H, d, *J* = 0.9 Hz), 3.92 (1 H, dd, *J* = 10.0, 4.4 Hz), 3.75–3.67 (3 H, m), 3.13 (1 H, dd, *J* = 10.0, 4.4 Hz), 3.01 (1 H, dd, *J* = 10.0 Hz).

HRMS calcd for $C_{21}H_{22}IO_5$ (M^+–C_7H_7) 481.0471, found 481.0520.

(2*R/S*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Trisbenzyloxy-6-vinyloxan-2-ol (59)

A solution of **58** (240 mg, 0.42 mmol) in HOAc (6 mL) was stirred with activated Zn powder (1.37 g, 21.0 mmol) at r.t. for 3 h and the mixture was treated as for **20** to give **59** (181 mg, 97%) as a colorless oil after chromatography (silica gel, 5 g, elution with EtOAc–hexane, 1:10 v/v).

IR (film): ν = 3460 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.16 (15 H, m), 6.02 (0.6 H, ddd, *J* = 17.3, 10.7, 6.3 Hz), 5.98 (0.4 H, ddd, *J* = 17.3, 10.7, 6.0 Hz), 5.51 (0.6 H, dt, *J* = 17.3, 1.4 Hz), 5.46 (0.4 H, dt, *J* = 17.3, 1.4 Hz), 5.30 (0.6 H, dt, *J* = 10.7, 1.4 Hz), 5.26 (0.4 H, dt, *J* = 10.7, 1.4 Hz), 5.10 (0.4 H, d, *J* = 1.6 Hz), 5.06 (0.6 H, s), 4.79–4.35 (7 H, m), 3.88 (0.6 H, br t, *J* = 2.7 Hz), 3.74 (0.4 H, t, *J* = 3.3 Hz), 3.64 (0.6 H, d, *J* = 2.7 Hz), 3.61–3.59 (1.2 H, m), 3.51 (0.4 H, d, *J* = 2.7 Hz), 3.49–3.47 (0.8 H, m).

HRMS calcd for $C_{21}H_{23}O_5$ (M–C_7H_7) 355.1546, found 355.1575.

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