The Stereoselective Preparation of an Enantiomerically Pure Cyclopentane Using Intramolecular Aldol Cyclopentaannulation of a Glucose Derivative

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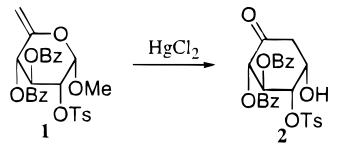
Methods for the annulation of carbohydrates have found extensive applications in organic synthesis. We report here a new protocol for the stereoselective conversion of glucose into an enantiomerically pure cyclopentane aldehyde **22**. The readily available epoxide **15** was reacted with allyl Grignard to produce alcohol **16** in 86% yield. Swern oxidation followed by epimerization using triethylamine in *N*,*N*-dimethylformamide furnished the ketone **17** also in 86% yield. Regioselective deprotonation with lithium hexamethyldisilazane in THF was followed by methylation with methyl iodide and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone as cosolvent to give 80% yield of ketone **18**. Oxidation of ketone **18** by the Wacker procedure gave the 1,4-diketone **19** in 56% yield. Intramolecular aldol condensation occurred readily on treatment of diketone **19** with potassium *tert*-butoxide in toluene to furnish a 90% yield of enone **20**. Treatment with *N*-bromosuccinimide produced the bromoester **21** in 72% yield, which was reduced to a mixture of aldehydes **22** (61%) and **23** (14%) with zinc shot in 2-propanol.

Introduction

The use of carbohydrates as chiral starting materials has been an important strategy in organic synthesis for many years.[1] Examples of this strategy for the synthesis of "carbohydrate-like" and "noncarbohydrate-like" target molecules are widespread. The extent to which a carbohydrate can be used in a route to any particular synthetic objective depends on methods which exercise control over the proportion of the original five or six carbon atoms of the sugar which ultimately end up in the target molecule. It is common for pathways using this approach to involve annulation reactions of the sugar derivatives as a means of synthesizing cyclic target molecules.[2] To elucidate more closely the type of sugar transformation process being used in any particular case, we have found it useful to define two types of carbohydrate annulation based on two landmark discoveries in this area. When all the carbon atoms of the sugar end up in the carbocycle, we call the reaction an F-type annulation, after Ferrier, who studied this process extensively. An example of an F-type annulation is the cyclization of the enol ether **1** to the "carbohydrate-like" carbocycle **2**.[3]



1 **2**

The alternative type of cyclization is called the S-type annulation, after Stork, the discoverer of several carbohydrate annulation reactions in which only some of the carbons of the sugar end up in a relatively "noncarbohydrate-like" carbocyclic product. An example of an S-type annulation is the cyclization of the protected cyanohydrin **3** to the cyclopentane derivative **4**. The

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(12) Wood, A. J.; Jenkins, P. R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1567.
(13) Pipelier, M.; Ermolenko, M. S.; Zampella, A.; Olesker, A.; Lukacs, G.; *Synlett* **1996**, 24.
(14) The epoxide **7** was prepared by first forming methyl-4,6-*O*-benzylidene-α-D-glucopyranoside according to Evans (Evans, M. E. *Carbohydr. Res.* **1972**, *21*, 473). Subsequent conversion to the corresponding bis-mesylate and cyclization to the epoxide with sodium methoxide was performed by the method of Richtmeyer and Hicks and Fraser-Reid (Richtmeyer, N. K.; Hudson, C. S. *J. Am. Chem. Soc.* **1941**, *63*, 1727. Hicks, D. R.; Fraser-Reid, B. *Can. J. Chem.* **1975**, *53*, 2017).
(15) Asano, T.; Yokota, S.; Mitsonobu, O. *Chem. Lett.* **1983**, 343. Reaction with allylmagnesium bromide gives a different product arising from the opening of the epoxide with bromide anion followed by attack on the introduced bromine by the Grignard reagent; see: Mitsonobu, O. *Organic Synthesis in Japan, Past, Present and Future*; Kagaaku Dozin Co.: Tokyo, 1992; pp 215−226.

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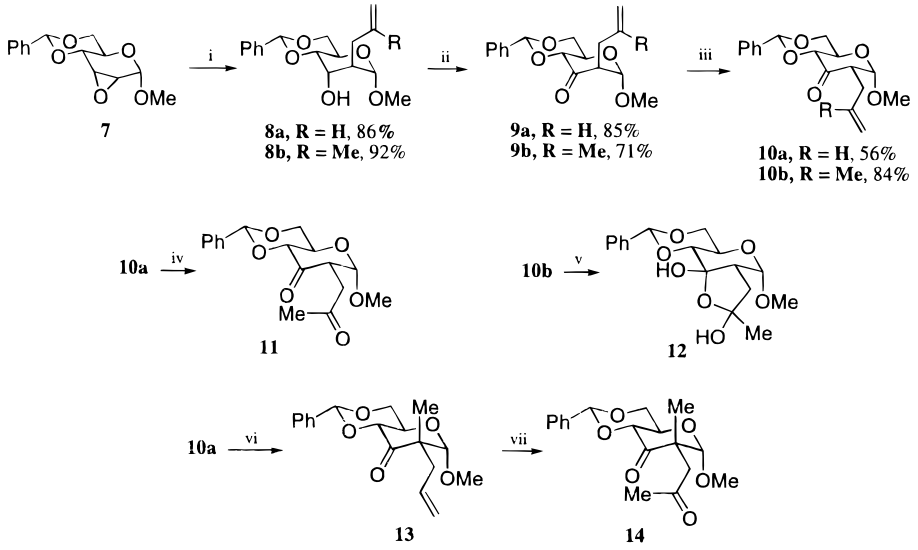
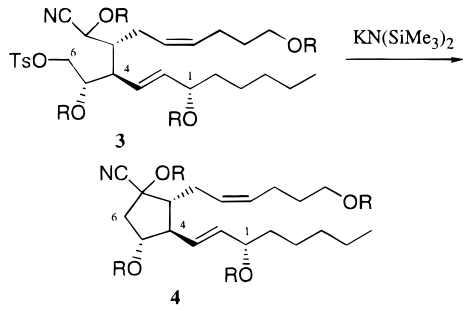
Scheme 1[a]

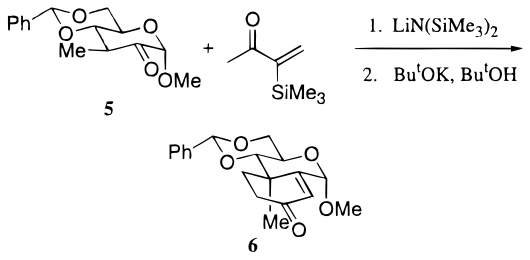


[a] Reagents and conditions: i, CH_2CRCH_2MgCl, THF, 2 h reflux; ii, DMSO, $(CF_3CO)_2O$, DCM, 1.5 h, −78 °C, Et_3N; iii, Et_3N, DMF; 48 h for **9a**, 7 days for **9b**; iv, $PdCl_2$, $CuCl_2$, O_2, DMF−H_2O (1:1), 5 h, 92%; v, O_3, DCM, 0.5 h; H_2NCSNH_2, 3 h, 36%; vi, $NaN(SiMe_3)_2$, THF, 0 °C, 1 h, then MeI, DMPU, 24 h, 42%; vii, $PdCl_2$, $CuCl_2$, O_2, DMF−H_2O (1:1), 5 h, 45%.

numbers 1−6 on structure **3** indicate the carbons from glucose; clearly only three of these are involved in the new ring.[4]



We have reported examples of the S-type annulation involving a Robinson annulation of the sugar methyl ketone **5** to give the cyclohexenone **6**,[5] radical cyclizations of cyclohexaannulated sugars,[6] and cyclopentaannulated sugars,[7] and we have used these procedures in the synthesis of a C-ring synthon of paclitaxel.[8]



There are several reports of sugar annulation methods which involve enolate cyclization reactions via alkylation,[9] aldol condensation,[10] and dithiane alkylation.[11] We report here full details of our studies on cyclopentaannulation based on the intramolecular aldol reaction[12] and the removal of the sugar component to produce stereoselectively a chiral cyclopentane derivative. Shortly after our communication of part of these results, a report on the synthesis of cyclopentaannulated sugars using an intramolecular phosphonate cyclization appeared.[13]

Results and Discussion

The objective in this project has been the cyclopentaannulation of glucose derivatives. Our first studies on this topic are summarized in Scheme 1. Epoxide **7** is a known compound,[14] and this was reacted separately with allylmagnesium chloride[15] and methallylmagnesium chloride to give the alcohols **8a** and **8b**. Oxidation to the ketones **9a** and **9b** using the Swern procedure[16] was followed by epimerization to produce the ketones **10a** and **10b** with the equatorial allyl groups, despite a previous report by Ferrier that the latter reaction was not possible.[17] The main evidence in favor of the epimerized structures **10a** and **10b** comes from the proton NMR spectra. The ketone **9a** with the axial allyl group shows a singlet for H-1 at δ 4.77 and a triplet for the equatorial proton at C-2, which is coupled only to the CH_2 of the allyl group. In the epimerized structure **10a**, H-1 now appears as a doublet at δ 4.99, J = 4.1 Hz, which is coupled to the axial proton at C-2. Similar changes were observed for the conversion of **9b** to **10b**.

Ketone **10a** was oxidized by the Wacker reaction[18] with oxygen in the presence of palladium chloride and copper(II) chloride to produce the diketone **11**, the first substrate for cyclization. Ozonolysis of **10b** occurred in a low yield and gave a poor yield of the hemiacetal **12**. Treatment of diketone **11** with sodium hydroxide in refluxing methanol gave no cyclization. To remove one position of enolization, the ketone **10a** was converted into the alkylate ketone **14**, which was subjected to three different conditions of cyclization; potassium *tert*-butoxide in toluene, sodium carbonate in methanol, and sodium

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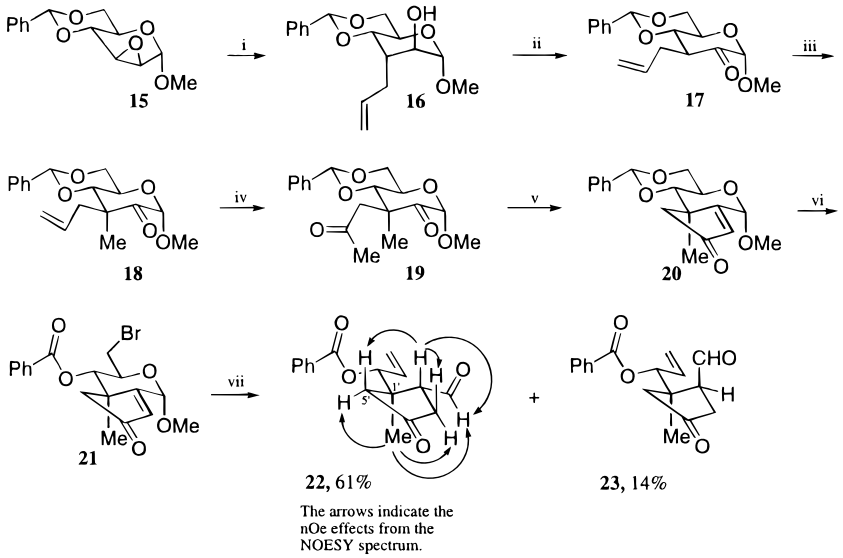
(18) Pauley, D.; Anderson, F.; Hudlicky, T. *Org. Synth.* **1989**, *67*, 121.

Scheme 2[a]



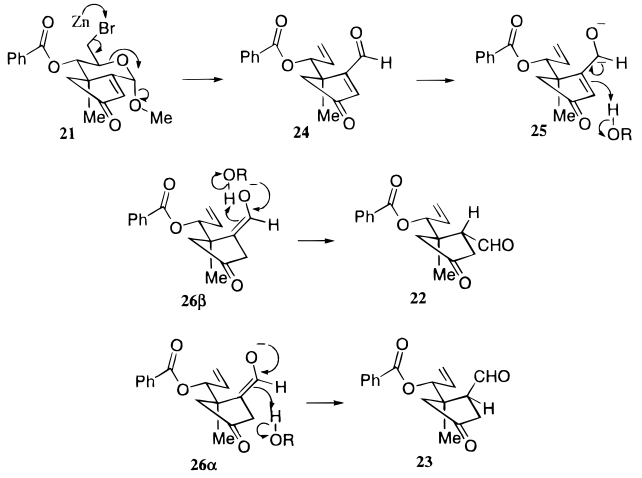
[a] Reagents and conditions: i, CH_2CHCH_2MgCl, THF, 2 h reflux, 86%; ii, DMSO, $(CF_3CO)_2O$, DCM, 1.5 h, −78 °C, then Et_3N 24 h, 86%; iii, $LiN(SiMe_3)_2$, THF, 0 °C, 1 h, then MeI, DMPU, 24 h, 80%; iv, $PdCl_2$, O_2, DMF−H_2O (1:1), 5 h, 56%; v, Bu^{t}OK, toluene, 0.5 h, 90%; vi, NBS, $BaCO_3$, CCl_4, 3 h reflux, 72%; vii, Zn shot, IPA-H_2O (10:1), 22 h reflux.

methoxide in methanol. In each case, the starting material was isolated with a trace of benzaldehyde, and no evidence in favor of cyclization was observed.

The search for a viable cyclopentaannulation method was continued using the reaction sequence described in Scheme 2. The known β-epoxide **15**[19] was reacted with allylmagnesium chloride to produce the alcohol **16**,[15] which was oxidized[16] and epimerized[17] to give the ketone **17**. Deprotonation and methylation of **17** furnished the ketone **18**, which was subsequently oxidized by the Wacker procedure[18] to furnish the diketone **19**. Successful cyclization was achieved using potassium *tert*-butoxide in toluene to give the enone **20**. The structure of **20** was confirmed by an X-ray crystal structure; full details of this were submitted with the preliminary publication of part of these results.[12] NBS bromination was surprisingly clean, leading to the expected product **21**.[20] Treatment of the bromide **21** with zinc shot gave a mixture of two aldehydes, **22** and **23**, in 61 and 14% yields, respectively. This reaction is an application of the method for carbohydrate ring cleavage by Vasella,[21] but as explained below, the form of zinc used on **21** was different from that previously reported.

The configurational assignment of the major aldehyde product **22** was determined with the aid of a NOESY spectrum. First we are sure of the configuration of the C-1′ center in **22** from the X-ray crystal structure of **20**. The assignment of the signals of the CH_2 protons at carbons 3′ and 5′ in the H^1 NMR spectrum of **22** is clear from the chemical shift expected of protons adjacent to a carbonyl group. From the NOESY spectrum we see a strong NOE between the methyl group at the quaternary center and one of the protons of each methylene group

Scheme 3



at C-3′ and C-5′. Consequently, we can assign the signals at δ 2.2 and δ 2.84 to the two α-hydrogens H-5′ and H-3′; and the signals at δ 2.37 and δ 2.70 to the β-hydrogens H-3′ and H-5′. Turning now to the hydrogen on C-2′ we see a strong NOE to the β-hydrogens, confirming that the C-2′ proton is on the β face of the molecule. This assignment is confirmed by the NOE between the aldehyde proton and the methyl group.

A possible mechanism for the zinc reduction is shown in Scheme 3. The Vasella reaction normally occurs by attack of the zinc on the bromo substituent to give the aldehyde **24**, which can be regarded as an enedione. The electron-transfer reduction of enediones using zinc is known,[22] and in Scheme 3 we adapt this mechanism to explain the formation of **22** and **23**. Transfer of two electrons from the zinc may be expected to produce the dianion **25**, which protonates on carbon to give the enolate **26**. Protonation of the enolate from the β face

(19) The epoxide **15** was prepared by first forming methyl-4,6-*O*-benzylidene-α-D-glucopyranoside according to Evans (Evans, M. E. *Carbohydr. Res.* **1972**, *21*, 473). Subsequent conversion to the corresponding mono-tosylate by the method of Hicks and Fraser-Reid (Hicks, D. R.; Fraser-Reid, B. *Synthesis* **1974**, 203) was followed by conversion to the β epoxide following the procedure of Pougny (Pougny, J. R.; Sinay, P. *J. Chem. Res.*, Miniprint **1982**, 186).

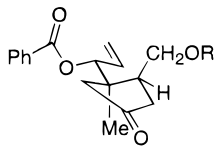
(20) Hanessian, S.; Plessas, N. R. *J. Org. Chem.* **1969**, *34*, 1035.

(21) Vasella, A., Bernet, B. *Helv. Chim. Acta* **1979**, *62*, 1990.

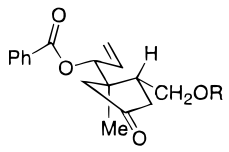
(22) (a) Windhaus, A., *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3752. (b) Elks, J.; Evans, R. M.; Long, A. G.; Thomas, G. H.; *J. Chem. Soc.* **1954**, 451. (c) Toda, M.; Hayashi, M.; Hirata, S.; Yamamura, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 264.

as shown in **26*β*** would furnish the aldehyde **22**. Protonation from the α face is shown in **26α** yielding the aldehyde **23**.

The nature of the zinc has an important effect on the reduction of **21**. Using zinc shot we obtained the aldehydes **22** and **23**. This form of zinc is different from the activated powdered zinc described by Vasella,[21] which we used in our previous work.[8] In fact, when we used activated powdered zinc in the reduction of **21**, we obtained the alcohols **27a** and **27b** as the major products. These alcohols were isolated and characterized as their *p*-nitrobenzoate esters. We believe the explanation of this is that powdered zinc prepared by the Vasella method is a more reactive reducing agent, because of its greater active surface area, than the equivalent material prepared from zinc shot.

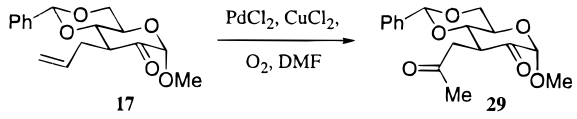


27a, R = H
27b, R = p-nitrobenzoate



28a, R = H
28b, R = p-nitrobenzoate

The structural requirements for facile cyclopentaannulation are very stringent; the only substrate we were able to cyclize was **19**. An especially important feature seems to be the quaternary center α to the carbonyl group. Wacker oxidation of **17** was used to produce the ketone **29** without the quaternary center. However, all attempts to cyclize this material failed. One possible explanation of this phenomenon is that it might be related to the Thorpe−Ingold effect[23] in which the degrees of rotational freedom of the ketone side chain of **19** are restricted so that cyclization is favored.



17 **29**

In conclusion, we have developed a procedure for the cyclopentaannulation of a glucose-derived diketone **19**, and we have used a reaction with *N*-bromosuccinimide followed by reductive elimination using activated zinc shot to stereoselectively produce an enantiomerically pure cyclopentane **22** with a quaternary stereogenic center, which we believe will find use in the synthesis of steroids and vitamin D derivatives.

Experimental Section

All reactions were performed under an atmosphere of nitrogen (unless otherwise stated in the text), and solvent extractions were dried with $MgSO_4$. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Carbon tetrachloride was distilled from phosphorus pentoxide and stored under nitrogen. Diethyl ether was distilled from lithium aluminum hydride. Dichloromethane was distilled from calcium hydride. Petroleum ether refers to the 40−60 °C boiling fraction. Flash column chromatography was performed on Sorbsil C-60 silica gel (Crosfield Chemicals), 40−60 M. Melting points are uncorrected. All chemical shifts were taken directly from the spectra, and *J* values are given in hertz.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-propenyl-α-D-altropyranoside (8a) and Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(2-methyl-2-propenyl)-α-D-altropyranoside (8b). Allylmagnesium chloride (27.0 mL, 2 M solution in THF) was added dropwise to an ice-cooled, stirred suspension of the epoxide **7** (4.75 g, 18.00 mmol) in dry THF (65.0 mL). The reaction mixture was heated to reflux for 2 h and then the reaction was quenched by the dropwise addition of water (30 mL). The mixture was extracted into diethyl ether (2 × 75 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 50 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (5:1 to 1:1) as the eluent yielded **8a** as a white solid (4.98 g, 86%): $[\alpha]^{20}_D$ +59° (*c* 1.0, $CHCl_3$); R_f 0.45, 2:1 petroleum ether−ethyl acetate; ν_{max} (CH_2Cl_2)/cm^{-1} 3575 br s, 1650 s, 1380 s; δ_H (300 MHz $CDCl_3$) 2.17−2.29 (2H, m, 7-H), 3.13 (1H, d, *J* 6.9, 2-H), 3.39 (3H, s, OMe), 3.42 (1H, t, obscured, 4-H), 3.67 (1H, dd, *J* 2.9, 9.8, 3-H), 3.79 (1H, t, *J* 10.0, 6ax-H), 4.18−4.27 (1H, m, 5-H), 4.31 (1H, dd, *J* 5.0, 9.9, 6eq-H), 4.55 (1H, s, 1-H), 5.08−5.16 (2H, m, 9-H), 5.61 (1H, s, 10-H), 5.72−5.83 (1H, m, 8-H), 7.29−7.52 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 34.1 (CH_2, C7), 44.6 (CH, C2), 55.4 (CH_3, OMe), 58.3 (CH, C5), 68.3 (CH, C3), 69.2 (CH_2, C6), 76.7 (CH, C4), 101.2 (CH, C1), 102.1 (CH, C10), 117.3 (CH_2, C9), 126.5 (CH, Ph), 128.1 (CH, Ph), 128.9 (CH, Ph), 135.3 (CH, C8), 137.2 (C, Ph); *m*/*z* (EI) 306 (M^+, 1.9) 274 (15.8), 179 (25.9), 105 ($PhCO^+$, 100) (found M^+, 306.14665; $C_{17}H_{22}O_5$ requires 306.1467).

This compound was previously communicated without full experimental and spectroscopic data.[15]

In the same way, the epoxide **7** (497 mg, 1.88 mmol) was treated with 2-methyl-2-propenylmagnesium chloride to yield **8b** as a white solid (576 mg, 92%); mp 97−99 °C (lit.[15] mp 98−100 °C); R_f 0.45, 2:1 petroleum ether−ethyl acetate; ν_{max} (CH_2Cl_2)/cm^{-1} 3510 br w, 2940 s, 1690 w; δ_H (300 MHz $CDCl_3$) 1.7 (3H, s, 11-H), 2.12−2.31 (2H, m, 7-H), 2.38−2.48 (1H, m, 2-H), 3.43 (3H, s, OMe), 3.72 (1H, dd, *J* 3.0, 9.7, 3-H), 3.83 (1H, t, *J* 9.9, 6ax-H), 3.99 (1H, br s, 4-H), 4.22−4.32 (1H, m, 5-H), 4.35 (1H, dd, *J* 4.9, 9.9, 6eq-H), 4.57 (1H, s, 1-H), 4.81 (1H, s, 9-H), 4.88 (1H, s, 9-H), 5.65 (1H, s, 10-H), 7.34−7.63 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 21.8 (CH_3, C11), 38.1 (CH_2, C7), 42.5 (CH, C3), 55.4 (CH_3, OMe), 58.3 (CH, C2), 68.7 (CH, C5), 69.3 (CH_2, C6), 76.7 (CH, C4), 101.5 (CH, C1), 102.1 (CH, C10), 113.0 (CH_2, C9), 126.1 (CH, Ph), 128.1 (CH, Ph), 128.9 (CH, Ph), 137.2 (C, Ph), 142.0 (CH, C8); *m*/*z* (EI) 320 (M^+, 29.6) 288 (110.5), 264 (14.5), 179 (29.4), 105 ($PhCO^+$, 100) (found: M^+, 320.1625; $C_{18}H_{24}O_5$ requires 320.1625).

This compound was previously communicated without full experimental and spectroscopic data.[15]

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-propenyl-α-D-*arabino*-hexopyranosid-3-ulose (9a) and Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(2-methyl-2-propenyl)-α-D-*arabino*-hexopyranosid-3-ulose (9b). Trifluoroacetic anhydride (0.96 mL, 6.80 mmol) in dry dichloromethane (1.0 mL) was added dropwise to a cooled solution (−65 °C) of dimethyl sulfoxide (0.63 mL, 6.78 mmol) in dry dichloromethane (4.0 mL) under an atmosphere of nitrogen. Once addition was complete, the mixture was stirred for 0.3 h at −65 °C, and then a solution of **8a** (1.5 g, 4.90 mmol) in dry dichloromethane (6.0 mL) was added slowly, dropwise, the temperature being kept at −65 °C. Once addition was complete, the reaction mixture was stirred for a further 1.5 h at this temperature. Triethylamine (3.67 mL, 26.30 mmol) was then added dropwise, and the solution was allowed to warm to room temperature. The reaction mixture was diluted with dichloromethane (30 mL), washed with 1 M hydrochloric acid until the aqueous layer was just acidic, and then washed with sodium hydrogen carbonate followed by saturated sodium chloride solution (20 mL). The dichloromethane layer was then dried and evapo-

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rated to dryness. Chromatography on silica gel with petroleum ether−ethyl acetate (5:1) as the eluent yielded **9a** as a white solid (1.27 g, 85%): R_f 0.8, 2:1 petroleum ether−ethyl acetate; $[\alpha]^{23}_D$ +23.9° (*c* 1.89, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 2.31−2.51 (2H, m, 7-H), 2.69 (1H, t, *J* 7.9, 2-H), 3.31 (3H, s, OMe), 3.86 (1H, t, *J* 10.1, 6ax-H), 4.10 (1H, ddd, *J* 4.4, 10.1, 5-H), 4.30 (2H, overlapping d and dd, *J* 9.8, 4-H, *J* 4.4, 10.1, 6eq-H), 4.77 (1H, s, 1-H), 5.02−5.15 (2H, m, 9-H), 5.51 (1H, s, 10-H), 5.57−5.73 (1H, m, 8-H), 7.23−7.47 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 34.0 (CH_2, C7), 54.0 (CH_3, OMe), 55.3 (CH, C2), 65.0 (CH, C5), 68.5 (CH_2, C6), 79.9 (CH, C4), 101.3 (CH, C1), 102.1 (CH, C10), 117.4 (CH_2, C9), 127.3 (CH, Ph), 128.3 (CH, Ph), 129.2 (CH, Ph), 133.9 (CH, C8), 135.6 (C, Ph), 199.5 (C, C3); *m*/*z* (EI) 304 (M^+, 4.7), 273 (8.9), 263 (6.1), 149 (40.2), 105 ($PhCO^+$, 100) (found M^+, 304.1311; $C_{17}H_{20}O_5$ requires 304.1311).

This compound was previously communicated,[17] but it was prepared by a different method.

In the same way, the alcohol **8b** (1.5 g, 4.68 mmol) was oxidized to the ketone, and the crude material was purified by chromatography on silica gel with petroleum ether−ethyl acetate (5:1) as the eluent to yield **9b** as a white solid (1.05 g, 71%): mp 115−117 °C; R_f 0.8, 2:1 petroleum ether−ethyl acetate; $[\alpha]^{23}_D$ +12.2° (*c* 1.26, $CHCl_3$); ν_{max} (CH_2Cl_2)/cm^{-1} 2915 s, 1735 s (CO), 1650 m, 1400 s; δ_H (300 MHz $CDCl_3$) 1.77 (3H, s, 11-H), 2.40 (1H, dd, *J* 7.2, 14.1, 7a-H), 2.52 (1H, dd, *J* 9.2, 14.0, 7b-H), 2.90−2.96 (1H, m, 2-H), 3.38 (3H, s, OMe), 3.96 (1H, t, *J* 10.2, 6ax-H), 4.17 (1H, dt, *J* 4.8, 10.0, 5-H), 4.39 (1H, dd, *J* 4.8, 10.1, 6eq-H), 4.45 (1H, obscured d, *J* 9.9, 4-H), 4.85 (1H, s, 1-H), 4.85−4.89 (2H, m, 9-H), 5.61 (1H, s, 10-H), 7.35−7.55 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 21.6 (CH_3, C11), 39.0 (CH_2, C7), 54.6 (CH_3, OMe), 54.9 (CH, C2), 65.1 (CH, C5), 69.4 (CH_2, C6), 80.6 (CH, C4), 102.2 (CH, C1), 103.4 (CH, C10), 113.9 (CH_2, C9), 126.3 (CH, Ph), 128.1 (CH, Ph), 129.2 (CH, Ph), 136.5 (C, Ph), 140.8 (CH, C8), 200.5 (C, C3); *m*/*z* (EI) 318 (M^+, 46.6), 287 (15.5), 183 (17.4), 149 (57.3), 105 ($PhCO^+$, 100) (found M^+, 318.1467; $C_{18}H_{22}O_5$ requires M^+, 318.1467).

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-propenyl-α-D-*erythro*-hexopyranosid-3-ulose (10a) and Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(2-methyl-2-propenyl)-α-D-*erythro*-hexopyranosid-3-ulose (10b). Ketone **9a** (1.31 g, 4.30 mmol) was dissolved in DMF−triethylamine (50.0 mL, 1:1) and stirred for 48 h. The reaction mixture was diluted with dichloromethane (75 mL), and the resulting solution was washed with saturated sodium chloride solution (3 × 25 mL). The dichloromethane layer was then dried and evaporated to dryness. Chromatography on silica gel with petroleum ether−ethyl acetate (5:1) as the eluent yielded **10a** as a white solid (0.73 g, 56%): mp 148−152 °C; R_f 0.6, 2:1 petroleum ether−ethyl acetate; $[\alpha]^{21}_D$ +75.3° (*c* 0.96, $CHCl_3$); ν_{max} (CH_2Cl_2)/cm^{-1} 2920 s, 1745 s, 1595 m, 1400 m; δ_H (250 MHz, $CDCl_3$) 2.12−2.28 (1H, m, 7a-H), 2.50−2.64 (1H, m, 7b-H), 2.75−2.86 (1H, m, 2-H), 3.35 (3H, s, OMe), 3.91 (1H, t, *J* 10.1, 6ax-H), 4.08 (1H, ddd, *J* 4.4, 9.8, 10.1, 5-H), 4.28 (1H, dd, *J* 1.3, 9.8, 4-H), 4.37 (1H, dd, *J* 4.4, 10.1, 6eq-H), 4.99 (1H, d, *J* 4.1, 1-H), 5.02−5.17 (2H, m, 9-H), 5.54 (1H, s, 10-H), 5.66−5.85 (1H, m, 8-H), 7.30−7.55 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 27.6 (CH_2, C7), 53.5 (CH, C2), 55.3 (CH_3, OMe), 66.0 (CH, C5), 69.6 (CH_2, C6), 83.1 (CH, C4), 102.0 (CH, C1), 103.2 (CH, C10), 117.3 (CH_2, C9), 126.1 (CH, Ph), 128.3 (CH, Ph), 129.3 (CH, Ph), 134.9 (CH, C8), 136.7 (C, Ph), 198.4 (C, C3); *m*/*z* (EI) 304 (M^+, 26.2), 263 (11.6), 169 (19.7), 149 (64.7), 98 (100) (found M^+, 304.1310; $C_{17}H_{20}O_5$ requires 304.1310).

In the same way, the ketone **9b** (1.27 g, 4.00 mmol) was dissolved in DMF−triethylamine (100 mL, 1:1) and was stirred for 7 days. The resulting solution was reduced in vacuo and then diluted with dichloromethane (30 mL), and this solution was washed with saturated sodium chloride solution (2 × 20 mL). The dichloromethane layer was then dried and evaporated to dryness. Chromatography on silica gel with petroleum ether−ethyl acetate (5:1) as the eluent yielded **10b** as a white solid (1.1 g, 84%); mp 135−137 °C (from petroleum ether); R_f 0.8, 2:1 petroleum ether−ethyl acetate; $[\alpha]^{17}_D$ +103.1° (*c* 0.99, $CHCl_3$); ν_{max} (CH_2Cl_2)/cm^{-1} 2940 s, 1780 s, 1650 m, 1450 m, 1410 m, 1280 m, 1210 m; δ_H (250 MHz, $CDCl_3$) 1.74 (3H, s, C8-Me), 2.26 (1H, dd, *J* 9.4, 14.8, 7a-H), 2.50 (1H, dd, *J* 5.0, 14.8, 7b-H), 2.90−3.00 (1H, m, 2-H), 3.35 (3H, s, OMe), 3.93 (1H, t, *J* 10.1, 6ax-H), 4.11 (1H, ddd, *J* 4.4, 9.8, 10.1, 5-H), 4.31 (1H, overlapping dd, *J* 1.3, 9.8, 4-H), 4.37 (1H, overlapping dd, *J* 4.4, 9.8, 6eq-H), 4.75 (1H, br s, 9a-H), 4.83 (1H, br s, 9b-H), 4.97 (1H, d, *J* 4.1, 1-H), 5.57 (1H, s, 10-H), 7.32−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 22.9 (CH_3, C11), 31.9 (CH_2, C7), 52.2 (CH, C2), 55.7 (CH_3, OMe), 66.5 (CH, C5), 70.0 (CH_2, C6), 83.6 (CH, C4), 102.4 (CH, C1), 103.6 (CH, C10), 112.9 (CH_2, C9), 126.8 (CH, Ph), 128.7 (CH, Ph), 129.6 (CH, Ph), 137.1 (C, Ph), 142.3 (C, C8), 198.9 (C, C3); *m*/*z* (EI) 318 (M^+, 9.8), 256 (6.1), 167 (5.4), 149 (52.8), 145 (20.2), 105 (100) (found, 318.1467; $C_{18}H_{22}O_5$ requires 318.1467). Anal. Found: C, 67.83; H, 6.77. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.96.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(propan-2-one)-α-D-*ribo*-hexopyranosid-3-ulose (11). Palladium(II) chloride (23.0 mg, 0.13 mmol) and copper(II) chloride (130 mg, 1.31 mmol) were added to a solution of **10a** (398 mg, 1.31 mmol) in DMF and water (42.0 mL, 1:1). The reaction mixture was stirred at room temperature while oxygen was bubbled through the solution for 5 h. The reaction mixture was extracted with dichloromethane (2 × 20 mL) and the combined organic layers were washed with saturated sodium chloride solution (2 × 25 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−ethyl acetate (5:1) as the eluent yielded **11** as a white solid (388 mg, 92); mp 180−182 °C; R_f 0.75, petroleum ether−ethyl acetate (2:1); $[\alpha]^{19}_D$ +136.8° (*c* 2.0, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3000 w, 1745 s, 1710 w, 1410 w, 1145 m, 1050 s; δ_H (300 MHz, $CDCl_3$) 2.24 (3H, s, 9-H), 2.45 (1H, dd, *J* 5.8, 18.5, 7a-H), 3.13 (1H, dd, *J* 7.1, 18.4, 7b-H), 3.36 (3H, s, OMe), 3.42−3.47 (1H, m, 2-H), 3.96 (1H, t, *J* 10.1, 6ax-H), 4.10 (1H, dt, *J* 4.5, 10.0, 5-H), 4.37−4.41 (2H, 4-H, 6eq-H), 5.09 (1H, d, *J* 4.3, 1-H), 5.60 (1H, s, 10-H), 7.35−7.54 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 30.1 (CH_3, C9), 37.4 (CH_2, C7), 49.3 (C, C2), 55.1 (CH_3, OMe), 65.6 (CH, C5), 69.3 (CH_2, C6), 82.6 (CH, C4), 101.8 (CH, C1), 102.9 (CH, C10), 126.2 (CH, Ph), 128.1 (CH, Ph), 129.1 (CH, Ph), 136.4 (C, Ph), 197.8 (C, C3), 206.1 (C, C8); *m*/*z* (EI) 319 ($[M - H]^+$, 3.0) 279 (18.1), 263 (12), 171 (12.6), 149 (100) (found $[M - H]^+$, 319.1182; $C_{17}H_{19}O_6$ requires $[M - H]^+$ 319.1182).

Ozonolysis of Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(2-methyl-2-propenyl)-α-D-*ribo*-hexopyranosid-3-ulose (10b). Olefin **10b** (0.20 g, 0.63 mmol) was dissolved in dichloromethane (25 mL), and ozone was bubbled through the solution for 0.5 h. The flask was then flushed with nitrogen for 0.3 h, and thiourea was added (48.0 mg, 0.63 mmol), and the solution was stirred for 3 h. Water (30 mL) was added portionwise, and the mixture was extracted with dichloromethane (2 × 30 mL), washed with saturated sodium chloride solution (2 × 30 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−ethyl acetate (5:1) as the eluent yielded **12** as a white solid (77 mg, 36%): δ_H (300 MHz, $CDCl_3$) 1.76 (3H, s, 9-H), 1.98−2.19 (2H, m, 7-H), 2.90−2.99 (1H, m, 2-H), 3.48 (3H, s, OMe), 3.89 (1H, t, *J* 10.0, 6ax-H), 3.92 (1H, d, *J* 9.4, 4-H), 4.14 (1H, ddd, *J* 4.4, 9.63, 5-H), 4.42 (1H, dd, *J* 4.4, 10.1, 6eq-H), 5.00 (1H, d, *J* 8.3, 1-H), 5.64 (1H, s, 10-H), 7.35−7.54 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 15.1 (CH_3, C9), 34.5 (CH_2, C7), 47.5 (CH, C2), 55.6 (CH_3, OMe), 65.4 (CH, C5), 70.1 (CH_2, C6), 76.2 (CH, C4), 102.2 (CH, C1), 103.4 (CH, C10), 106.9 (C, C8), 115.3 (C, C3), 126.3 (CH, Ph), 128.2 (CH, Ph), 129.2 (CH, Ph), 136.4 (C, Ph); *m*/*z* 338 (M^+, 7.2), 289 (56.8), 52 (100).

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-methyl-2-*C*-propenyl-α-D-*erythro*-hexopyranosid-3-ulose (13). Sodium hexamethyldisilazide (0.4 mL, 0.40 mmol, 1 M solution in THF) was cooled to 0 °C, and a solution of **10a** (136 mg, 0.40 mmol) was added dropwise in THF (15.0 mL), the temperature being maintained at 0 °C. The solution was stirred for 1 h at 0 °C, and then methyl iodide (0.2 mL, 3.20 mmol) was added, followed by DMPU (0.04 mL, 0.04 mmol). The solution was allowed to warm to room temperature and stirred overnight. Water (25 mL) was added portionwise, and the mixture was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with saturated sodium chloride solution (2 × 10 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−ethyl

acetate (5:1) as the eluent yielded **13** as a clear oil (but also containing an unidentified compound) (59 mg, 42%): δ_H (250 MHz, $CDCl_3$) 1.38 (3H, s, C2-Me), 2.33 (1H, dd, *J* 7.9, 13.5, 7a-H), 2.46 (1H, dd, *J*, 7.5, 13.8, 7b-H), 3.35 (3H, s, OMe), 3.94 (1H, t, *J* 10.1, 6ax-H), 4.12 (1H, ddd, *J* 4.4, 9.8, 10.1, 5-H), 4.36 (1H, dd, *J* 4.4, 10.1, 6eq-H), 4.55 (1H, s, 1-H), 4.59 (1H, d, *J* 9.8, 4-H), 5.07−5.21 (2H, m, 9-H), 5.57 (1H, s, 10-H), 5.60−5.82 (1H, m, 8-H), 7.30−7.56 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 21.5 (CH_3, C2-Me), 36.4 (CH_2, C7), 53.5 (C, C2), 55.2 (CH_3, OMe), 65.8 (CH, C5), 69.6 (CH_2, C6), 80.0 (CH, C4), 102.2 (CH, C1), 107.0 (CH, C10), 119.3 (CH_2, C9), 126.5 (CH, Ph), 128.3 (CH, Ph), 129.3 (CH, Ph), 133.0 (CH, C8), 136.7 (C, Ph), 202.6 (C, C3); *m*/*z* (EI) 318 (M^+, 2.8) 277 (6.1), 191 (8.9), 149 (26.6), 121 (16.4), 113 (10.6), 112 (100) (found M^+ 318.1467; $C_{18}H_{22}O_5$ requires 318.1467).

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-methyl-2-*C*-propanone-α-D-*erythro*-hexopyranosid-3-ulose (14). Palladium(II) chloride (10.0 mg, 0.05 mmol) and copper(II) chloride (73 mg, 0.54 mmol) were added to a solution of **13** (173 mg, 0.54 mmol) in DMF and water (20.0 mL, 1:1). The reaction mixture was stirred at room temperature, and oxygen was bubbled through it for 5 h. The reaction mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 25 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (10:1) as the eluent yielded **14** as a white solid (90 mg, 45%): R_f 0.5, petroleum ether−diethyl ether (1:2); $[\alpha]^{20}_D$ + 50.9 (*c* 0.95, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3045 m, 1765 s, 1755 s; δ_H (250 MHz, $CDCl_3$) 1.53 (3H, s, C2-Me), 2.14 (3H, s, 9-H), 2.74 (1H, d, *J* 18.3, 7a-H), 2.99 (1H, d, *J* 18.2, 7b-H), 3.29 (3H, s, OMe), 3.93 (1H, t, *J* 10.1, 6ax-H), 4.08 (1H, dt, *J* 4.4, 10.1, 5-H), 4.36 (1H, dd, *J* 4.4, 10.1, 6eq-H), 4.56 (1H, d, *J* 10.1, 4-H), 5.19 (1H, s, 1-H), 5.58 (1H, s, 10-H), 7.31−7.55 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 22.4 (CH_3, C2), 31.7 (CH_3, C9), 44.8 (CH_2, C7), 53.6 (C, C2), 55.8 (CH_3, OMe), 65.6 (CH, C5), 69.9 (CH_2, C6), 79.9 (CH, C4), 102.6 (CH, C1), 106.3 (CH, C10), 126.8 (CH, Ph), 128.7 (CH, Ph), 129.7 (CH, Ph), 137.0 (C, Ph), 202.7 (C, C3), 207.4 (C, C8); *m*/*z* (EI) 334 (M^+, 0.9), 276 (10.6), 149 (45.9), 129 (10.5), 128 (66.5), 121 (15.2), 105 (36.2), 97 (15.4), 91 (34.1), 85 (100) (found M^+, 334.1416; $C_{18}H_{22}O_6$ requires 334.1416).

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (16). Allylmagnesium chloride (100 mL, 2 M solution in THF, 0.20 mol) was added dropwise to an ice-cooled, stirred suspension of the epoxide **15** (17.62 g, 66.60 mmol) in dry THF (100 mL). The reaction mixture was heated under reflux for 2 h and then the reaction was quenched by the dropwise addition of water (50 mL). The reaction mixture was extracted with diethyl ether (2 × 200 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 75 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (3:1 to 1:1) as the eluent yielded **16** as a clear sticky oil (18.95 g, 86%): R_f 0.22, 1:1 petroleum ether−diethyl ether; (found: C, 65.5; H, 7.2. $C_{17}H_{22}O_5$ requires C, 66.7; H, 7.4); δ_H (250 MHz, $CDCl_3$) 2.14−2.35 (1H, m, 2-H), 2.45−2.65 (3H, 3-H and 7-H), 3.37 (3H, s, OMe), 3.78 (1H, t, *J* 10.0, 6ax-H), 3.9 (1H, br s, OH), 3.92−4.05 (1H, m, 5-H), 4.11 (1H, dd, *J* 9.7, 5.3, 4-H), 4.28 (1H, dd, *J* 10.1, 4.8, 6eq-H), 4.55 (1H, s, 1-H), 5.03−5.20 (2H, m, 9-H), 5.59 (1H, s, 10-H), 5.74−5.94 (1H, m, 8-H), 7.32−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 29.2 (CH_2, C7), 42.7 (CH, C3), 55.7 (CH_3, OMe), 55.9 (CH, C5), 69.6 (CH, C2), 70.0 (CH_2, C6), 76.4 (CH, C4), 102.5 (CH, C1), 102.8 (CH, C10), 117.2 (CH_2, C9), 126.7 (CH, Ph), 128.8 (CH, Ph), 129.6 (CH, Ph), 137.6 (CH, C8), 138.1 (C, Ph); *m*/*z* (EI) 306 (M^+, 1.9) 305 $[M - H]^+$ (3.6), 274 (2.9), 256 (3.3), 105 ($PhCO^+$, 100) (found M^+, 306.14665; $C_{17}H_{22}O_5$ requires 306.1467).

This compound was previously communicated without full experimental and spectroscopic data.[15]

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-propenyl-α-D-*arabino*-hexopyranoside-2-ulose (17). Trifluoroacetic anhydride (12.67 mL, 89.73 mmol) in dry dichloromethane (40 mL) was added dropwise to a cooled solution (−65 °C) of dimethyl sulfoxide (8.36 mL, 0.12 mol) in dry dichloromethane (130 mL) under an atmosphere of nitrogen. Once addition was complete, the mixture was stirred for 0.3 h at −65 °C, and then a solution of **16** (18.95 g, 61.90 mmol) in dry dichloromethane (20 mL) was added slowly, dropwise, the internal temperature being kept at −65 °C. Once addition was complete, the reaction mixture was stirred for a further 1.5 h at this temperature. Triethylamine (48.64 mL, 0.35 mol) was then added dropwise, and the solution was allowed to warm to room temperature. The reaction mixture was diluted with dichloromethane (200 mL), and the resulting solution was washed with 1 M hydrochloric acid until the aqueous layer remained acidic and then washed with enough sodium hydrogen carbonate to neutralize the acid, followed by saturated sodium chloride solution (200 mL). The dichloromethane layer was then dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **17** as a white solid (16.18 g, 86%), mp 99−101 °C (from petroleum ether) (lit.[17] mp 100−102 °C); R_f 0.72, 1:1 petroleum ether−diethyl ether; ν_{max} (CH_2Cl_2)/cm^{-1} 2920 s, 1740 s (CO), 1640 m; δ_H (250 MHz, $CDCl_3$) 2.33−2.56 (2H, m, 7-H), 2.97−3.10 (1H, m, 3-H), 3.46 (3H, s, OMe), 3.53 (1H, dd, *J* 10.3, 9.4, 4-H), 3.67 (1H, t, *J* 10.3, 6ax-H), 4.14 (1H, ddd, *J* 4.9, 9.7, 10.3, 5-H), 4.31 (1H, dd, *J* 4.9, 10.3, 6eq-H), 4.53 (1H, s, 1-H), 4.94−5.10 (2H, m, 9-H), 5.41 (1H, s, 10-H), 5.70−5.88 (1H, m, 8-H), 7.27−7.47 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 28.0 (CH_2, C7), 51.1 (CH, C3), 56.1 (CH_3, OMe), 64.6 (CH, C5), 69.5 (CH_2, C6), 80.4 (CH, C4), 101.3 (CH, C1), 101.6 (CH, C10), 117.8 (CH_2, C9), 126.5 (CH, Ph), 128.7 (CH, Ph), 129.6 (CH, Ph), 135.2 (CH, C8), 137.5 (C, Ph), 200.1 (C, CO); *m*/*z* (EI) 304 (M^+, 2.4), 276 ($M^+ - C_2H_4$) (5.2), 105 ($PhCO^+$, 100); (found M^+, 304.1311; $C_{17}H_{20}O_5$ requires M^+, 304.1311). Anal. Found: C, 66.83; H, 6.58. $C_{17}H_{20}O_5$ requires C, 67.14; H, 6.62%.

This compound was previously communicated,[17] but it was prepared by a different method.

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-3-*C*-propenyl-α-D-*erythro*-hexopyranoside (18). Lithium hexamethyldisilazide (18.08 mL, 18.08 mmol, 1 M solution in THF) was cooled to 0 °C, and a solution of **17** (5.0 g, 16.44 mmol) was added dropwise in THF (15 mL), the temperature being maintained at 0 °C. The solution was stirred for 1 h at 0 °C, and then methyl iodide (7.8 mL, 98.64 mmol) was added, followed by DMPU (1.0 mL, 8.22 mmol). The solution was allowed to warm to room temperature and stirred overnight. Water (200 mL) was added portionwise, the mixture was extracted with diethyl ether (2 × 200 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 25 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (10:1) as the eluent yielded **18** as a clear oil (4.19 g, 80%): R_f 0.75, 1:1 petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ −3.3° (*c* 2.07, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.26 (3H, s, C3-Me), 2.21 (1H, dd, *J* 13.8, 9.15, 7a-H), 2.59 (1H, dd, *J* 13.8, 5.5, 7b-H), 3.37 (3H, s, OMe), 3.64 (1H, t, *J* 10.1, 6ax-H), 3.73 (1H, d, *J* 10.0, 4-H), 4.23 (1H, dt, *J* 10.0, 5.16, 5-H), 4.33 (1H, dd, *J* 10.1, 5.2, 6eq-H), 4.48 (1H, s, 1-H), 4.94−5.08 (2H, m, 9-H), 5.4 (1H, s, 10-H), 5.56−5.75 (1H, m, 8-H), 7.25−7.46 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 19.3 (CH_3, C3-CH_3), 38.5 (CH_2, C7), 51.8 (C, C3), 55.6 (CH_3, OMe), 60.0 (CH, C5), 69.8 (CH_2, C6), 77.5 (CH, C4), 101.5 (CH, C1), 101.7 (CH, C10), 119.21 (CH_2, C9), 126.5 (CH, Ph), 128.7 (CH, Ph), 129.5 (CH, Ph), 134.5 (CH, C8), 137.9 (C, Ph), 203.7 (C, C2); *m*/*z* (EI) 318 (M^+, 0.9), 290 ($M^+ - CH_2CH_2$) (1.3), 174 (100) (found M^+, 318.1467; $C_{18}H_{22}O_5$ requires 318.1467). Anal. Found: C, 67.83; H, 7.21. $C_{18}H_{22}O_5$ requires C, 67.96; H 6.97).

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-3-*C*-propanone-α-D-*erythro*-hexopyranosid-2-ulose (19). Palladium(II) chloride (233 mg, 1.32 mmol) and copper(II) chloride (2.24 g, 13.16 mmol) were added to a stirred solution of **18** (4.17 g, 13.16 mmol) in DMF and water (80 mL, 1:1). The reaction was stirred at room temperature while oxygen was bubbled through the solution for 5 h. The product was extracted into dichloromethane (2 × 75 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 25 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (10:1) as the eluent yielded **19** as a white solid (2.48 g,

56%): mp 112−114 °C; R_f 0.75, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ −78° (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3940 w, 1760 m, 1730 m; δ_H (250 MHz, $CDCl_3$) 1.19 (3H, s, C3-Me), 2.01 (3H, s, 9-H), 2.77 (1H, d, *J* 18.6, 7a-H), 2.98 (1H, d, *J* 18.6, 7b-H), 3.36 (3H, s, OMe), 3.70 (1H, t, *J* 10.0, 6ax-H), 4.06 (1H, d, *J* 10.1, 4-H), 4.18 (1H, dt, *J* 10.1, 4.97, 5-H), 4.31 (1H, dd, *J* 10.1, 4.97, 6eq-H), 4.63 (1H, s, 1-H), 5.40 (1H, s, 10-H), 7.23−7.43 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 19.2 (CH_3, C3-*C*H_3), 30.4 (CH_3, C9), 48.1 (CH_2, C7), 49.0 (C, C3), 56.6 (CH_3, OMe), 60.1 (CH, C5), 69.7 (CH_2, C6), 79.5 (CH, C4), 100.7 (CH, C1), 101.7 (CH, C10), 126.7 (CH, Ph), 128.7 (CH, Ph), 129.6 (CH, Ph), 137.9 (C, Ph), 204.4 (C, C2), 206.8 (C, C8); *m*/*z* (EI) 334 (M^+, 4.8) 228 (M^+ − PhCHO) (5.8), 188 (88.7), 159 (100) (found M^+, 334.1416; $C_{18}H_{22}O_6$ requires 334.1416). Anal. Found: C, 64.83; H, 6.59. $C_{18}H_{22}O_6$ requires C, 64.70; H, 6.63).

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-propenone-α-D-*arabino*-hexopyranosid-2-ulose (29). Palladium(II) chloride (40 mg, 0.21 mmol) and copper(II) chloride (106 mg, 2.1 mmol) were added to a stirred solution of **17** (657 mg, 2.10 mmol) in DMF and water (25 mL, 1:1). The reaction mixture was stirred at room temperature while oxygen was bubbled through the solution for 0.5 h. The product was extracted into dichloromethane (2 × 25 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 15 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (2:1) as the eluent yielded **29** as a clear oil (429 mg, 62%): R_f 0.50, petroleum ether−diethyl ether (2:1); ν_{max} ($CHCl_3$)/cm^{-1} 3940 w, 1760 m, 1730 m; δ_H (250 MHz, $CDCl_3$) 2.20 (3H, s, 9-H), 2.75 (1H, dd, *J* 3.9, 17.7, 7a-H), 2.87 (1H, dd, *J* 6.9, 17.6, 7b-H), 3.44−3.55 (1H, m, 3-H), 3.50 (3H, overlapping s, OMe), 3.67 (1H, dd, *J* 9.4, 11.6, 4-H), 3.78 (1H, t, *J* 10.0, 6ax-H), 4.23 (1H, ddd, *J* 5.0, 9.4, 10.0, 5-H), 4.39 (1H, dd, *J* 5.0, 10.0, 6eq-H), 4.65 (1H, s, 1-H), 5.49 (1H, s, 10-H), 7.33−7.50 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 30.2 (CH_3, C9), 37.3 (CH_2, C7), 47.6 (CH, C3), 55.7 (CH_3, OMe), 64.4 (CH, C5), 69.0 (CH_2, C6), 79.9 (CH, C4), 100.6 (CH, C1), 101.5 (CH, C10), 126.2 (CH, Ph), 128.4 (CH, Ph), 129.3 (CH, Ph), 136.9 (C, Ph), 199.2 (C, C2), 205.8 (C, C8); *m*/*z* (EI) 320 (M^+, 2.1), 292 (15.5), 174 (30.8), 145 (100) (found M^+, 320.1260; $C_{17}H_{20}O_6$ requires 320.1260).

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-methyl-3,2-*C*-(2′-oxapropan-1′-yl-3′-ylidene)-α-D-*arabino*-hexopyranoside (20). Potassium *tert*-butoxide (91 mg, 0.86 mmol) was added to a solution of **19** (239 mg, 0.79 mmol) in dry toluene (5.0 mL). The solution was stirred at room temperature under an atmosphere of nitrogen for 0.5 h. Water (100 mL) was added portionwise. The mixture was extracted with dichloromethane (2 × 200 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 25 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (2:1) as the eluent yielded **20** as a white solid (204 mg, 90%): mp 134−136 °C (petroleum ether); R_f 0.75, petroleum ether−diethyl ether (1:2); $[\alpha]^{23}_D$ +25.5° (*c* 1.73, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3000 w, 1720 s, 1090 s; δ_H (250 MHz, $CDCl_3$) 1.42 (3H, s, C3-Me), 2.28 (1H, d, *J* 18.8, 9a-H), 2.47 (1H, d, *J* 18.8, 9b-H), 3.41 (1H, d, *J* 9.4, 4-H), 3.42 (3H, s, OMe), 3.65 (1H, t, *J* 10.2, 6ax-H), 4.12 (1H, ddd, *J* 10.0, 9.37, 5.08, 5-H), 4.27 (1H, dd, *J* 10.1, 5.06, 6eq-H), 5.29 (1H, s, 1-H), 5.48 (1H, s, 10-H), 5.96 (1H, s, 7-H), 7.27−7.46 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 20.5 (CH_3, C3-*C*H_3), 46.2 (C, C3), 50.5 (CH_2, C9), 55.9 (CH_3, OMe), 61.2 (CH, C5), 69.6 (CH_2, C6), 86.3 (CH, C4), 98.1 (CH, C1), 102.3 (CH, C10), 126.6 (CH, Ph), 128.7 (CH, Ph), 129.7 (CH, Ph), 130.2 (CH, C7), 137.7 (C, Ph), 174.0 (C, C2), 207.4 (C, C8); *m*/*z* (EI) 316 (M^+, 6.5), 273 (9.2), 167 (73.8), 138 (100), (found M^+, 316.1310. $C_{18}H_{20}O_5$ requires 316.1311). Anal. Found: C, 68.14; H, 6.24. $C_{18}H_{20}O_5$ requires C, 68.39; H, 6.37.

4-Benzoyloxy-5-bromomethyl-2,3-*C*-(2-propen-2′-one)-3-deoxy-3-*C*-methyl-α-D-*arabino*-hexopyranosid-2-ulose (21). Barium carbonate (2.6 g, 13.2 mmol) followed by *N*-bromosuccinimide (507 mg, 2.85 mmol) was added to a solution of **20** (708 mg, 2.31 mmol) in dry carbon tetrachloride (73.0 mL). This solution was stirred under an atmosphere of nitrogen at reflux for 3 h. The barium carbonate was removed by filtration and washed with diethyl ether (75 mL), and the combined organic layers were washed with water (2 × 75 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **21** as a white solid (654 mg, 72%): mp 131−132 °C (petroleum ether 40−60 °C); R_f 0.50, petroleum ether−ethyl acetate (1:1); $[\alpha]^{22}_D$ + 128.2° (*c* 2.0, $CHCl_3$); ν_{max} (CH_2Cl_2)/cm^{-1} 2960 m, 1730 s, 1710 s, 1640 w, 1600 w, 1450 m, 1260 s, 1180 m, 1110 s; δ_H (250 MHz, $CDCl_3$) 1.47 (3H, s, C3-Me), 2.18 (1H, d, *J* 18.7, 9a-H), 2.66 (1H, d, *J* 18.6, 9b-H), 3.37 (1H, dd, *J* 11.0, 7.6, 6a-H), 3.46 (1H, obscured dd, *J* 11.0, 2.5, 6b-H), 3.77 (3H, s, OMe), 4.36 (1H, dt, *J* 9.8, 7.4, 2.5, 5-H), 5.06 (1H, d, *J* 9.8, 4-H), 5.40 (1H, s, 1-H), 6.00 (1H, s, 7-H), 7.41−7.69 (3H, Ph), 8.00−8.11 (2H, Ph); δ_C (62.9 MHz, $CDCl_3$) 20.1 (CH_3, C3-*C*H_3), 31.0 (CH_2, C6), 45.7 (C, C3), 49.6 (CH_2, C9), 54.6 (CH_3, OMe), 66.8 (CH, C5), 76.1 (CH, C4), 96.1 (CH, C1), 127.7 (2CH, *m*-Ph), 127.0 (CH, C7), 128.5 (CH, *p*-Ph), 128.8 (CH, *o*-Ph), 132.9 (C, Ph), 164.2 (CO, OBz), 205.0 (C, C8); *m*/*z* (EI) 394/396 (M^+, 3), 365, 353, 315 (M^+ − Br), 105 ($PhCO^+$, 100) (found M^+, 394.0518; $C_{18}H_{19}O_5Br$ requires 394.0518).

(3*R*,1′*R*,2′*R*)-2′-Formyl-1′-methyl-3-cyclopentan-4′-one-2-propenyl-3-benzoate (22) and (3*R*,1′*R*,2′*S*)-2′-Formyl-1′-methyl-3-cyclopentan-4′-one-2-propenyl-3-benzoate (23). Zinc shot (100 g) was activated by washing with 2 M hydrochloric acid (6 × 50 mL), water (5 × 60 mL), 10% w/v aqueous potassium carbonate solution (50 mL), water (4 × 70 mL), 2-propanol (2 × 60 mL), and ether (3 × 60 mL). The bromo compound **21** (356 mg, 0.90 mmol) was heated to reflux with the activated zinc (7.66 g, 0.117 mol) in 2-propanol−water (20:2 mL) for 22 h. The zinc was removed by filtration and washed with diethyl ether (3 × 40 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 40 mL), dried, and evaporated to dryness. Separation by the chromatotron technique[24] on a 2 mm plate with petroleum ether−diethyl ether (2:1) as the eluent yielded starting material **21** (64 mg, 18%), **22** as a colorless oil (100 mg, 39%), and a 1:1 mixture of **22** and **23** (58 mg, 23%). **22**: R_f 0.47, diethyl ether−petroleum ether (2:1); $[\alpha]^{18}_D$ −80.0° (*c* 1.2, $CHCl_3$); ν_{max} (CH_2Cl_2)/cm^{-1} 3050 w, 2920 m, 2840 w, 1745 s, 1725 s, 1715 s, 1600 w, 1450 m, 1245 s, 1105 m, 1095 s; δ_H (250 MHz, $CDCl_3$) 1.17 (3H, s, C1′-Me), 2.20 (1H, d, *J* 17.6, 5′α-H), 2.37 (1H, dd, *J* 8.8, 19.5, 3′*β*-H), 2.70 (1H, d, *J* 17.6, 5′*β*-H), 2.84 (1H, ddd, *J* 1.5, 10.3, 19.5, 3′α-H), 3.32 (1H, ddd, *J* 1.4, 8.8, 10.3, 2′-H), 5.44 (1H, d, *J* 10.4, 1_{cis}-H), 5.51 (1H, d, *J* 17.0, 1_{trans}-H), 5.76 (1H, d, *J* 7.2, 3-H), 5.93 (1H, ddd, *J* 7.2, 10.4, 17.0, 2-H), 7.42−7.67 (3H, Ph), 8.00−8.09 (2H, Ph), 9.98 (1H, d, *J* 1.4, C*H*O); δ_C (62.9 MHz, $CDCl_3$) 19.9 (CH_3, C1′-*C*H_3), 36.6 (CH_2, C5′), 46.8 (C, C1′), 49.2 (CH_2, C3′), 52.3 (CH, C2′), 79.3 (CH, C3), 121.6 (CH_2, C1), 129.1 (CH, C2), 129.9 (C, Ph), 130.0 (CH, Ph), 132.4 (CH, Ph), 134.0 (CH, Ph), 165.7 (CO, OBz), 201.1 (CH, C*H*O), 213.6 (C, C4′); *m*/*z* (CI) 304 (MNH_4^+, 100) (found MNH_4^+, 304.1549; $C_{17}H_{22}NO_4$ requires 304.1549). Anal. Found: C, 70.76; H, 6.62. $C_{17}H_{18}O_4$ requires C, 71.31; H, 6.34). **23**: δ_C (62.9 MHz, $CDCl_3$) 25.8 (CH_3, C1′-*C*H_3), 38.1 (CH_2, C5′), 47.5 (C, C1′), 48.6 (CH_2, C3′), 57.9 (CH, C2′), 78.8 (CH, C3), 121.1 (CH_2, C1), 129.9 (CH, C2), 130.2 (C, Ph), 130.4 (CH, Ph), 132.7 (CH, Ph), 133.9 (CH, Ph), 165.0 (CO, OBz), 200.6 (CH, C*H*O), 214.4 (C, C4′).

(3*R*,1′*R*,2′*R*)-2′-Hydroxymethyl-1′-methyl-3-cyclopentan-4′-one-2-propenyl-3-benzoate (27a) and (3*R*,1′*R*,2′*S*)-2′-Hydroxymethyl-1′-methyl-3-cyclopentan-4′-one-2-propenyl-3-benzoate (28a). Zinc was activated by washing with 2 M hydrochloric acid (2 × 50 mL), water (50 mL), 2-propanol (75 mL), and ether (2 × 100 mL). This was left to stand open to the air for up to 1 month. The bromo compound **21** (200 mg, 0.51 mmol) was heated to reflux with the activated zinc in 2-propanol (28.0 mL) for 3 h. The zinc was removed by filtration and washed with diethyl ether (3 × 25 mL), and the combined organic layers were washed with saturated sodium chloride solution (2 × 25 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (4:6) as the eluent yielded **27a** and **28a** as a mixture of diastereoisomers (105 mg, 72%): R_f 0.26, diethyl

(24) Instruction Manual, Model 7924T, Chromatotron. Harrison Research, 840 Moana Court, Palo Alto, CA.

ether−petroleum ether (7:3); ν_{max} (Et_2O)/cm^{-1} 3440 s, 2920 w, 2890 w, 1745 s, 1720 s, 1605 w, 1270 s, 1100 w, 1110 s; δ_H (250 MHz, $CDCl_3$) 1.10 (3H, s, C1′-Me minor), 1.21 (3H, s, C1′-Me major), 1.72 (1H, br s, OH minor), 1.86 (1H, br s, OH major), 1.97−2.73 (10H, minor and major), 3.64−3.87 (4H, CH_2OH major and minor), 5.6 (2H, d, *J* 6.3, 3-H major, minor obscured), 5.74−5.91 (2H, 2-H major and minor), 7.32−7.57 (6H, Ph major and minor), 7.81−8.00 (4H, Ph major and minor). Major compound only: δ_C (62.9 MHz, $CDCl_3$) 24.0 (CH_3, C1′ Me), 40.8 (CH_2, C3′), 43.3 (C, C1′), 47.1 (CH, C2′), 47.8 (CH_2, C5′), 61.3 (CH_2, CH_2OH), 77.2 (CH, C3), 118.2 (CH_2, C1), 127.6 (2CH, Ph), 128.6 (CH, C2), 128.6 (CH, Ph), 131.6 (CH, Ph), 132.4 (C, Ph), 164.2 (CO, OBz), 217.0 (C, C4′); *m*/*z* (EI) 288 (M^+, 12), 257 ($M^+ - CH_2OH$) (4), 183 ($M^+ - PhCO^+$) (18), 166 ($M^+ - PhCO_2H$) (65), 105 ($PhCO^+$, 100) (found M^+, 288.1365; $C_{17}H_{20}O_4$ requires 288.1365).

(3*R*,1′*R*,2′*R*)-1′-Methyl-2′-*p*-nitrobenzoyloxymethylcyclopentan-4′-one-2-propenyl-3-benzoate (27b) and (3*R*,1′*R*,2′*S*)-3-1′-Methyl-2′-*p*-nitrobenzoate-methyl-cyclopentan-4′-one-2-propenyl-3-benzoate (28b). The mixture of alcohols **27a** and **28a** (57 mg, 0.20 mmol) in dry toluene (2.0 mL) was stirred magnetically at 0 °C with triethylamine (0.07 cm, 0.49 mmol). *p*-Nitrobenzyl chloride was added, and the solution was stirred until no starting material remained by TLC. Water (25 mL) was added portionwise, and the mixture was extracted with diethyl ether (2 × 10 mL), washed with saturated sodium chloride solution (2 × 5 mL), dried, and evaporated to dryness. Chromatography on silica gel with petroleum ether−diethyl ether (2:1) as the eluent yielded **27b** and **28b** (5:1) (72 mg, 96%). **27b**: R_f 0.75, petroleum ether−ethyl acetate (4:1); $[\alpha]^{22}_D$ +20.4° (*c* 3.3, $CHCl_3$); ν_{max} (CH_2Cl_2)/cm^{-1} 2960 m, 1730 s, 1710 s, 1640 w, 1600 w, 1450 m, 1260 s, 1180 m, 1110 s; δ_H (250 MHz, $CDCl_3$) 1.30 (3H, s, C1′-Me), 2.15 (1H, d, *J* 18.3, 5′a-H), 2.22 (1H, ddd, *J* 1.6, 9.8, 18.9, 3′a-H), 2.54 (1H, dd, *J* 9.44, 18.9, 3′b-H), 2.60−2.75 (1H, m, 2-H), 2.78 (1H, d, *J* 18.3, 5′b-H), 4.42 (1H, dd, *J* 11.3, 7.2, C*H*HO), 4.52 (1H, dd, *J* 11.3, 6.3, CH*H*O), 5.28 (1H, d, *J* 4.4, 1a-H), 5.33 (1H, d, *J* 11.3, 1b-H), 5.62 (1H, d, *J* 6.3, 3-H), 5.85 (1H, ddd overlapping, *J* 4.4, 6.0, 10.7, 2-H), 7.33−7.57 (3H, Ph), 7.82−7.90 (2H, Ph), 8.06 (2H, dd, *J* 6.9, 1.9, Ph), 8.18 (2H, dd, *J* 6.9, 1.9, Ph); δ_C (62.9 MHz, $CDCl_3$) 25.5 (CH_3, C1′-Me), 42.1 (CH_2, C3′), 44.9 (C, C1′), 45.9 (CH, C2′), 48.9 (CH_2, C5′), 65.6 (CH_2, CH_2O), 78.4 (CH, C3), 120.4 (CH_2, C1), 124.0 (CH, Ph), 129.1 (CH, Ph), 129.8 (C, Ph), 130.1 (CH, Ph), 131.1 (CH, Ph), 132.6 (CH, Ph), 134.0 (CH, Ph), 135.5 (C, Ph), 151.0 (C, *p*-NO_2-Ph), 164.8 (C, OBz), 165.3 (C, OBz), 214.4 (C, C4′). **28b**: R_f 0.35 petroleum ether−ethyl acetate (4:1); $[\alpha]^{22}_D$−31.3° (*c* 0.8, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.48 (3H, s, C1′-Me), 2.07−2.25 (2H, 5′a-H and 3′a-H), 2.54 (1H, dd, *J* 8.8, 18.9, 3′b-H), 2.74 (1H, d, *J* 18.3, 5′b-H), 2.80−2.93 (1H, m, 2′-H), 4.38 (1H, dd, *J* 11.3, 6.92, C*H*HO), 4.52 (1H, dd, *J* 11.3, 6.6, CH*H*O), 5.33 (2H, m, 1-H), 5.59 (1H, d, *J* 7.2, 3-H), 5.71−5.90 (1H, m, 2-H), 7.34−7.59 (3H, Ph), 7.93−8.28 (6H, Ph).

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Supporting Information Available: Spectroscopic data for **8a**,**b** **9a,b**, **10a**,, **11**−**14**, **16**, **17**, **21**−**23** and **27a,b**, **28a,b**, and **29** (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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