Stereoselective Preparation of Enantiomerically Pure Annulated Carbohydrates Using Ring-Closing Metathesis

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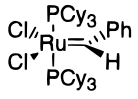
Ring-closing metathesis has been applied to a series of glucose derivatives to produce cyclopentene derivatives **5a** and **5b**, cyclohexene derivatives **8** and **9**, cycloheptene **12**, and cyclooctene **14**. Spirocyclic dihydrofurans **19**, **26a**, and **26b**, along with dihydropyran **22**, were also produced. A range of fused oxepine derivatives **29a**−**c** and one oxo-cyclononene **31** were also prepared. Cyclopentene **5b** was subjected to a sequence of hydrogenation, NBS bromination, and treatment with powdered zinc to furnish the ring-expanded product **35**. No such ring expansion occurred when the cyclohexaannulated compound **8** was treated with NBS followed by powdered zinc, leading to aldehyde **39**. The spiro dihydrofuran derivative **19** was converted to the aldehyde **42** via the same reaction sequence used to fragment cyclopentene derivative **5b**.

Introduction

Ring-closing metathesis (RCM), in which two unsubstituted olefins undergo ring closure with formal loss of ethylene, is one of the most popular synthetic methods at the present time. A very wide range of structures have been studied in the reaction, which is remarkably tolerant of other fuctional groups in the substrate.[1] The most widely used catalyst is the commercially available Grubbs catalyst **1**.[2] Oxygen and nitrogen heterocyclic derivatives of sugars have been prepared by the RCM reaction of sugars with appropriate side chains.[3] Macrocyclic lactones have also been prepared from sugar substrates using a tungsten catalyst in RCM,[4] and lactonization with the Grubbs catalyst **1** has also been reported.[5] Syntheses of tricolorin A[6] and of (+)-cyclitophellitol[7] from carbohydrate precursors have also been achieved. Recent contributions to this area have included the synthesis of racemic large and medium ring oxacycles[8] and the synthesis of (+)-valienamine from D-glucose.[9]



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"The Chiron Approach" to the synthesis of chiral target molecules involves the use of sugars as starting materials.[10] A key element in this strategy is the ability to form ring systems from carbohydrate molecules.[11] Our previous results in this area have involved carbohydrate annulation using the Robinson Annulation,[12] aldol condensation,[13] radical cyclization,[14] and the application of these methods to the synthesis of a C-ring synthon of taxol.[15] As part of this continuing program of research on carbohydrate annulation along with its application to the synthesis of chiral taxoids[16] and other structures, we have studied the application of RCM in this area. We report here full details[17] of the use of RCM in the formation of five-, six-, seven-, eight-, and nine-membered carbocyclic and oxygen-containing annulated ring fused sugars. Potentially useful examples of the formation of spiro fused oxygen rings are also reported.

(1) (a) Fürstner, A. *Top. Catal.* **1997**, *4*, 285. (b) Blechert, S.; Schuster, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036. (c) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (d) Armstrong, S. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 371. (e) Fürstner, A. *Alkene Metathesis in Organic Synthesis*; Springer-Verlag: Berlin, 1998.

(2) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) P. Schwab, P.; Grubbs, R. H.; Ziller, J. W *J. Am. Chem. Soc.* **1996**, *118*, 100.

(3) (a) Overkleeft, H. S.; Pandit, U.K. *Tetrahedron Lett.* **1996**, *37*, 547. (b) Leeuwenburgh, M. A.; Overkleeft, H. S.; van der Marel, G. A.; van Boom, J. H. *Synlett* **1997**, 1263. (c) Ovaa, H.; Leeuwenburgh, M. A.; Overkleeft, H. S.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **1998**, *39*, 3025. (d) Overkleeft, H. S.; Bruggeman, P.; Pandit, U.K. *Tetrahedron Lett.* **1998**, *39*, 3869.

(4) Descotes, G.; Ramza, J.; Basset, J.-M.; Pagano, S.; Gentil, E.; Banoub, J. *Tetrahedron* **1996**, *52*, 10903.

(5) Sukkari, H. E.; Gesson, J.-P.; Renoux, B. *Tetrahedron Lett.* **1998**, *39*, 4043.

(6) Fürstner, A.; Muller, T. *J. Org. Chem.* **1998**, *63*, 424.

(7) Ziegler, F. E.; Wang, Y. *J. Org. Chem.* **1998**, *63*, 426.

(8) Delgado, M.; Martín, J. D. *J. Org. Chem.* **1999**, *64*, 4798.

(9) Kapferer, P.; Sarabia, F., Vasella, A. *Helv. Chim. Acta* **1999**, *82*, 645.

(10) Hanessian, S. *Total Synthesis of Natural Products; The Chiron Approach*; Pergamon: Oxford, 1993.

(11) Ferrier, R. J.; Middleton, S. *Chem. Rev.* **1993**, *93*, 2779; Lopez, J. C. B.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1997**, 2251.

(12) (a) Bonnert, R. V.; Jenkins, P. R. *J. Chem. Soc., Chem. Commun.* **1987**, 6. (b) Bonnert, R. V.; Howarth, J.; Jenkins, P. R.; Lawrence, N. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1225.

(13) (a) Wood, A. J.; Jenkins, P. R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1567. (b) Wood, A. J.; Holt, D. J.; Dominguez, M.-C.; Jenkins, P. R. *J. Org. Chem.* **1998**, *63*, 8522.

(14) (a) Bonnert, R. V.; Davies, M. J.; Howarth, J.; Jenkins, P. R. *J. Chem. Soc., Chem. Commun.* **1987**, 148. (b) Bonnert, R. V.; Davies, M. J.; Howarth, J.; Jenkins, P. R.; Lawrence, N. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 27. (c) Wood, A. J.; Jenkins, P. R. *Tetrahedron Lett.* **1997**, *38*, 1853.

(15) Boa, A. N.; Clark, J.; Jenkins, P. R.; Lawrence, N. J. *J. Chem. Soc., Chem. Commun.* **1993**, 151.

(16) Jenkins, P. R. *Pure Appl. Chem.*, **1996**, *68*, 771.

(17) For a preliminary report of some of these results see Holt, D. J.; Barker, W. D.; Jenkins, P. R.; Davies, D. L.; Garratt, S.; Fawcett, J.; Russell, D. R.; Ghosh, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 3298.

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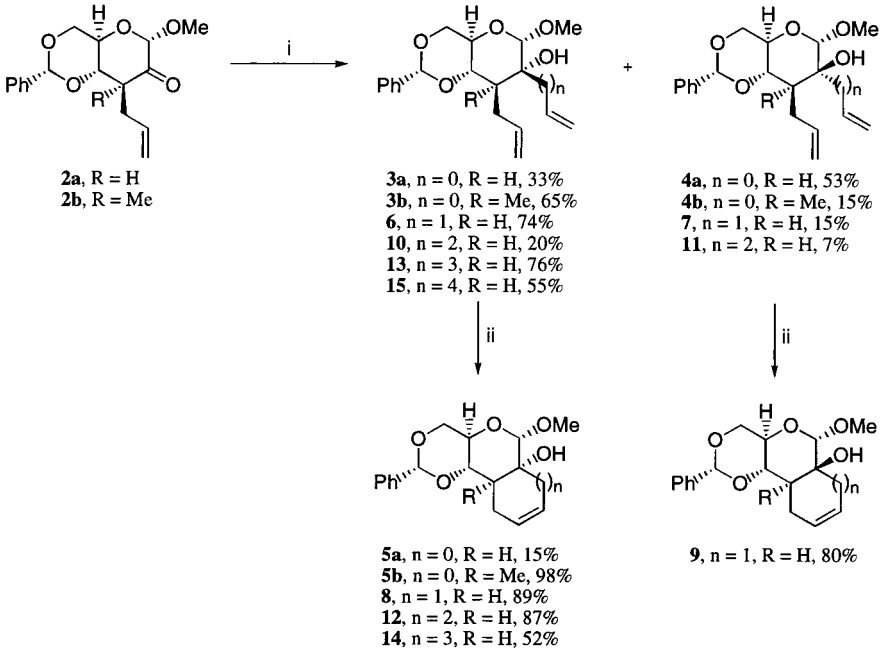
Scheme 1[a]



[a] Reagents and conditions: i, $H_2C{=}CH(CH_2)_nMgCl$, THF, reflux 2 h (for $n = 0, 1$); $H_2C{=}CH(CH_2)nMgBr{\cdot}CeCl_3$, diethyl ether, −40 °C, 1.5−2 h (for $n = 2-4$); ii, $Cl_2((C_6H_{11})_3P)_2RuCHPh$ (3−6 mol %), benzene, 60 °C, 17−65 h.

Results and Discussion

Initial studies into the potential use of RCM in carbohydrate annulation are summarized in Scheme 1. The ketone **2a**[17] was reacted with vinylmagnesium chloride to produce alcohols **3a** and **4a** in 33 and 53% yield, respectively. RCM only occurred with the cis isomer **3a** which was converted into the cyclopentene **5a** in a modest 15% yield, with 75% starting material recovered. The assignment of **5a** was confirmed by an X-ray crystal structure.[19] A much improved yield of 98% was obtained from the methylated compound **3b**. We have observed this kind of phenomenon in our previous work on the intramolecular aldol condensation, where cyclizaton was only possible when the side chain was attached to the sugar at a quaternary center.[13] We believe this result may be explained by a Thorpe−Ingold type of effect, in which the quaternary center restricts the degrees of freedom of the carbon chain, making intramolecular cyclization more efficient. The major product in the addition of allyl Grignard to ketone **2a** is the cis diene **6** as opposed to the trans diene **4a**, the major product with vinyl Grignard. This may be explained by coordination of the magnesium to the ketone and reaction via allylic rearrangement in the case of allyl Grignard, which is not possible with the equivalent vinyl reagent. Both diene isomers **6** and **7** underwent RCM to produce cyclohexene derivatives **8** and **9** in 89 and 80% yield, respectively. The structure of the cis product **8** was confirmed by an X-ray crystal structure.[19]

The addition of butenylmagnesium chloride to ketone **2a** in the presence of cerium(III) chloride gave a 20% yield of alcohol **10** along with 7% of its isomer **11**. The major product from this reaction, alcohol **27a** (50%), arises from hydride reduction from the Grignard reagent. Cycloheptaannulation of **10** by RCM occurred readily to give the cis-fused alcohol **12** in 87% yield.

The preparation of a chiral cyclooctenone from D-glucose has been reported by Thiem and Werschkun,[20] and the synthesis of carbocyclic and heterocyclic eight-membered rings using RCM has been reported by Grubbs.[21] An efficient reaction occurred in the addition of 4-pentenylmagnesium bromide to ketone **2a**, in the presence of cerium(III) chloride, to produce the alcohol **13** in 76% yield. We reported a much lower yield of this product using the Grignard reagent alone in the preliminary communication of this work.[17] RCM of **13** furnished the cis-fused cyclooctenyl alcohol **14** in 52% yield, along with 30% recovered starting material.

Addition of 5-hexenylmagnesium bromide to ketone **2a** in the presence of cerium(III) chloride gave alcohol **15** in 55% yield. When this compound was subjected to the standard RCM conditions no evidence of ring closure was obtained. However, a peak consistent with an intermolecular metathesis product was observed in the mass spectrum. When the reaction was carried out under more dilute conditions with a larger amount of catalyst, only starting material was obtained.

Spiro-fused tetrahydrofuran and pyran ring systems have been prepared by spiroether formation,[22a−d] intramolecular radical addition,[22e] and intramolecular reaction of an oxonium ion onto an allyl silane.[22f] Enantio-

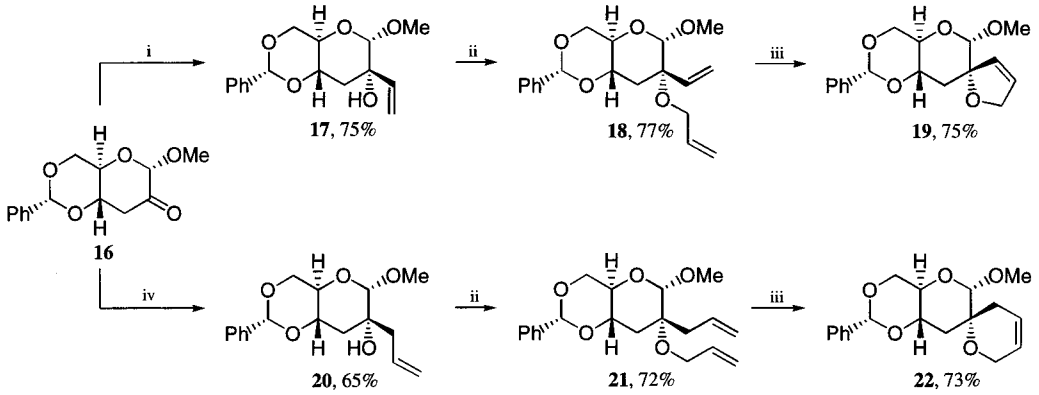
(18) Ferrier, R. J.; Lee, C.-K.; Wood, T. A. *J. Chem. Soc., Chem. Commun.* **1991**, 690.

(19) Crystallographic data for compounds **5a**, **8**, **14**, **19**, and **22** in this paper have been deposited with the Cambridge Crystallographic Data Center as deposition numbers CCDC-101536; 101537; 101538; 101539; and 1015340, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

(20) Werschkun, B.; Thiem, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2793.

(21) (a) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108. (b) Visser, M. S.; Heron, N. M.; Didiuk, M. T.; Sagal, J. F. Hoveyda, A. H. *J. Am. Chem. Soc.* **1996**, *118*, 4291. (c) Fürstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 8746. (d) Clark, J. S.; Kettle, J. G. *Tetrahedron Lett.* **1997**, *38*, 123 and 127. (e) Nicolaou, K. C.; Postema M. H. D.; Claiborne, C. F. *J. Am. Chem. Soc.* **1996**, *118*, 1565.

Scheme 2[a]

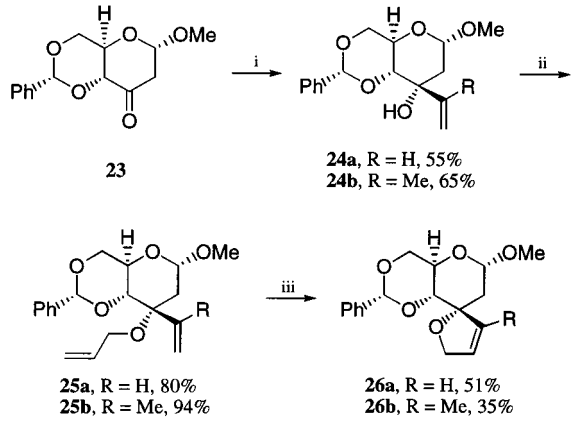


[a] Reagents and conditions: i, $H_2C{=}CHMgCl$, THF, reflux, 2h; ii, NaH, $CH_2{=}CHCH_2Br$, THF; iii, $Cl_2((C_6H_{11})_3P)_2RuCHPh$, benzene, 60 °C, 36 h; iv, $CH_2{=}CHMgCl$, THF, reflux, 2 h.

merically pure spiro products have been prepared from an enantiomerically pure ketone by addition of an organometallic and acid-catalyzed ether formation.[22g] In seeking applications for our studies on RCM in carbohydrate annulation we came upon the idea of trying the reaction on systems suitable for the formation of spiro compounds.[23] Ketone **16**[24] was reacted with vinylmagnesium chloride to provide the alcohol **17** in 75% yield (Scheme 2). Deprotonation with sodium hydride and reaction with allyl bromide produced the ether **18** in 77% yield, which was readily cyclized to the spiro product **19** in 75% yield, via RCM. A similar sequence involving addition of allylmagnesium chloride gave alcohol **20** in 65% yield, the ether **21** was obtained in 72% yield and the RCM reaction gave the spiro dihydropyran **22** in 73% yield. This sequence seems to have general applicability as shown by the results described in Scheme 3. Addition of vinylmagnesium chloride to ketone **23** gave a 55% yield of alcohol **24a**, which was converted into the ether **25a** in an 80% yield. RCM of the ether **25a** produced the spiro dihydrofuran in 51% yield. The same sequence was carried out using isopropenyl Grignard to give alcohol **24b** (65%), ether **25b** (94%), and the spiro compound **26b** in 35% yield.

Studies on the synthesis of medium rings containing oxygen are shown in Scheme 4. The addition of $LiAlH_4$ or MeLi to ketone **2a** produced alcohols **27a** and **27b** in 90 and 86% yield, respectively. Conversion to the ethers **28a**−**c** was achieved in 78−87% yield and the three RCM reactions occurred in 87% yield coincidentally. Alcohol **27a** was converted into the ether **30** in 83% yield, which gave the nine-membered ring **31** in 74% yield, as a product of RCM. The successful formation of the nine-membered heterocyclic ring **31** is in stark contrast to the failure of RCM in the case of the carbon-containing analogue, **15**. One difference between the two examples

Scheme 3[a]



[a] Reagents and conditions: i, $H_2C{=}CRMgCl$, THF, reflux, 2 h; ii, NaH, $CH_2{=}CHCH_2Br$, DMPU, THF; iii, $Cl_2((C_6H_{11})_3P)_2RuCHPh$, benzene, 60 °C, 36 h.

is that in **15** the chains are cis and in **30** they are trans, another could be due to the oxygen, although a convincing explanation does not seem possible on the basis of the available data. The result seems to be in line with literature precedent as there are far fewer examples of metathesis leading to nine-membered rather than to eight-membered rings.[1] The three reported examples of the formation of nine-membered rings all have oxygen in the ring.[25]

We will now demonstrate that the methods described so far can be used to prepare enantiomerically pure carbocyclic and heterocyclic rings with quaternary centers. The cyclopentaannulated sugar **5b** was reduced to the saturated derivative **32** in 99% yield (Scheme 5). Reaction with *N*-bromosuccinimide according to the procedure of Hanessian[26] gave the bromo ester **33** in good yield. Treatment of **33** with activated zinc in a Vasella elimination[27] did not produce the expected cyclopentane product. Instead ring-expansion occurred to produce the cyclohexanone derivative **35** in 54% yield. The configuration of the new stereogenic center in **35** is in accord

(22) (a) Reynolds, D. D.; Kenyon, W. O. *J. Am. Chem. Soc.* **1950**, *72*, 1593. (b) Picard, P.; Leclercq, D.; Moulines, J. *Tetrahedron Lett.* **1975**, 2731. (c) Canonne, P.; Foscolos, G. B.; Belanger, D. *J. Org. Chem.* **1980**, *45*, 1828. (d) Piers E.; Ashvinikumar, V. G. *J. Org. Chem.* **1990**, *55*, 2380. (e) Middleton, D. S.; Simpkins, N. S. *Tetrahedron Lett.* **1988**, *29*, 1315. (f) Paquette, L. A.; Tae, J. *J. Org. Chem.* **1996**, *61*, 7860. (g) Paquette L. A.; Negri, J. T. *J. Am. Chem. Soc.* **1991**, *113*, 5072.

(23) After submission of the preliminary communication[17] of some of the results in this paper a publication appeared on the spiroannulation of a different set of sugar derivatives using RCM.; van Hooft, P. A. V.; Leeuvwenburgh, M. A.; Overkleeft, H. S.; van der Marel, G. A.; van Boeckel, C. A. A.; van Boom, J. H. *Tetrahedron Lett.* **1998**, *39*, 6061.

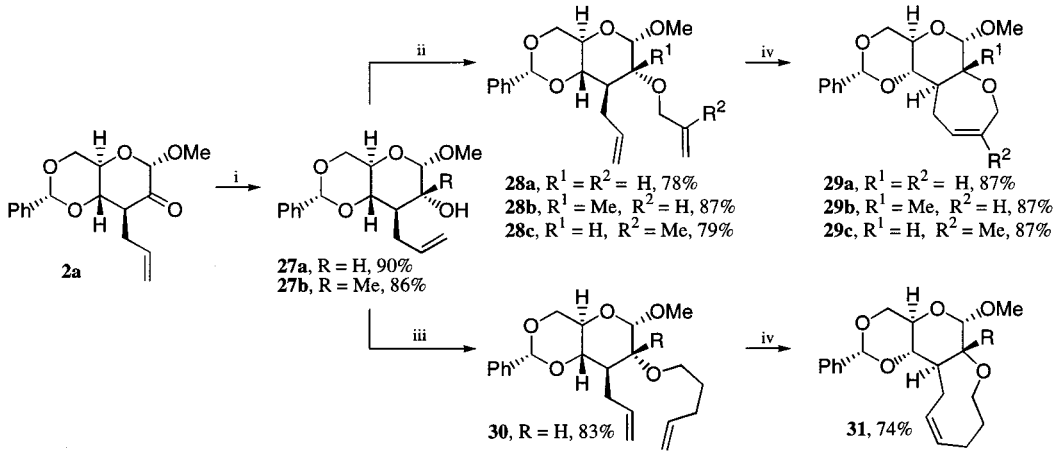
(24) Rosenthal, A.; Catsoulacos, P. *Can. J. Chem.* **1969**, *47*, 2747.

(25) (a) Barrett, A. G. M.; Baugh, S. P. D.; Gibson, V. C.; Giles, M. R.; Marshall, E. L.; Procopiou, P. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2231. (b) Crimmins, M. T.; Choy, A. L. *J. Org. Chem.* **1997**, *62*, 7548. (c) Delgado, M.; Martin, J. D. *Tetrahedron Lett.* **1997**, *38*, 6299.

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

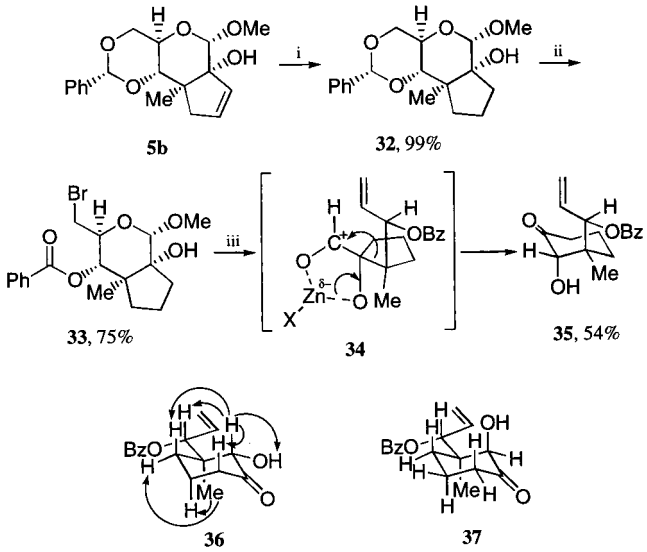
(27) Vasella, A.; Bernet, B. *Helv. Chim. Acta* **1979**, *62*, 1990; *Helv. Chim. Acta* **1984**, *67*, 1328.

Scheme 4[a]



[a] Reagents and conditions: i, **27a**/$LiAlH_4$, THF, 0 °C, then 3 h reflux; **27b**/MeLi, THF, 0 °C, then 6 h rt; ii, NaH, THF, 2 h reflux, then cool to rt, $CH_2{=}CR^2CH_2Br$, HMPA, 2 h, reflux; iii, NaH, THF, 2 h reflux, then cool to rt, $CH_2{=}CH(CH_2)_3Br$, HMPA, 2 h reflux; iv, $Cl_2((C_6H_{11})_3P)_2RuCHPh$, benzene, 60 °C, 6 h.

Scheme 5[a]



[a] Reagents and conditions: i, H_2, EtOH, 5% Pd/C; ii, NBS, $BaCO_3$, $CHCl_3$, reflux; iii, activated Zn, IPC:H_2O (10:1), reflux.

with literature precedent[28] where rearrangement occurrs via the chelated transition state **34**. Zinc bromide is produced in the Vasella reaction which is the Lewis acid for the rearrangement. We believe the major ring conformation of the product **35** is as indicated in structure **36**. In the NOESY spectrum of alcohol **35** the major NOE effects of the methyl group are across the α face of the ring to the adjacent equatorial proton, and the axial proton. The NOE effects of the proton on the carbon bearing the hydroxyl are to the two axial protons on the *β* face of the molecule, to the side chain C*H* and to the O*H*. On the assumption that the conformation of the cyclohexane ring is controlled by the largest substituent being equatorial, the other possible rearrangement product (instead of **35**) is shown in structure **37**. Here we would not expect to see an NOE between the equatorial proton on the carbon bearing the hydroxyl and the other CH_2 protons in the ring.

(28) Schor, L.; Seldes, A. M.; Gros, E. G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 163; *J. Chem. Soc., Perkin Trans. 1* **1992**, 453.

In the case of the cyclohexene derivative **8**, direct bromination was possible to furnish the bromo ester **38** in 38% yield (Scheme 6). Treatment with activated zinc gave the aldehyde **39** in 50% yield, no ring expansion was observed. The driving force for expanding a five-membered ring in **34** to a six-membered ring in **35** is clearly greater than from a six-membered ring in **39** to what would be a seven-membered ring.

The spiro compound **19** was reduced to the saturated analogue **40** in 89% yield, reacted with *N*-bromosuccinimide leading to bromo ester **41** in good yield, and subjected to Vasella elimination to give the aldehyde **42** in 59% yield.

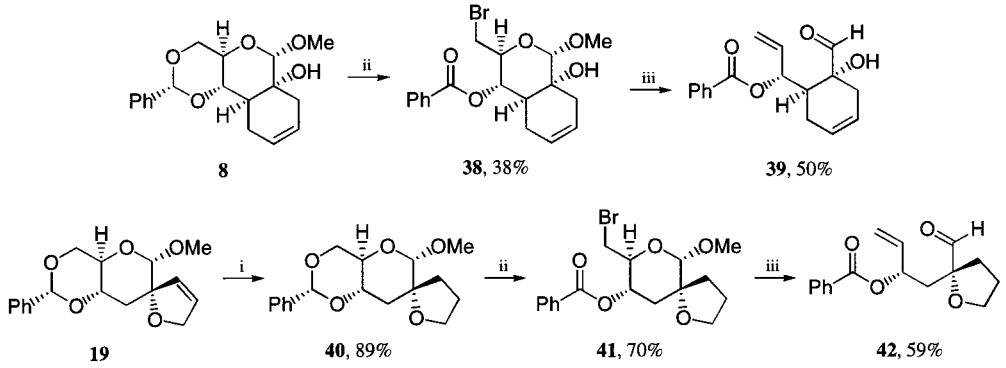
In conclusion we have demonstrated that RCM can be applied to carbohydrate substrates for the formation of five- to nine-membered rings, and that the products can be converted into highly substituted enantiomerically pure alicylic compounds. Studies on the application of these compounds in natural product synthesis are underway.

Experimental Section

All reactions were performed under an atmosphere of nitrogen (unless otherwise stated in the text) and solvent extractions dried with anhydrous magnesium sulfate. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl. Chloroform was distilled from phosphorus pentoxide and stored under nitrogen. 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 (*R*)-4,6-*O*-Benzylidene-2-*C*-ethenyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (3a) and Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-ethenyl-3-deoxy-3-*C*-propenyl-α-D-mannopyranoside (4a). Vinylmagnesium chloride (5.70 mL, 9.60 mmol, 15 wt % solution in THF) was added dropwise to an ice-cooled solution of the ketone **2a** (2.00 g, 6.58 mmol) in dry THF (7.0 mL). The solution was then heated to reflux for 2 h and allowed to cool to room temperature and then quenched by portionwise addition to ice/water (300 mL). The resulting mixture was extracted into diethyl ether (2 × 150 mL), and the combined organic layers were washed with water (2 × 150 mL), followed by saturated sodium chloride solution (150 mL), dried, and evaporated to leave a yellow oil. Chromatography

Scheme 6[a]



[a] Reagents and conditions: i, H_2, MeOH, 5% Pd/C; ii, NBS, $BaCO_3$, $CHCl_3$, reflux; iii, activated Zn, IPC:H_2O (10:1), reflux.

on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded **3a** as a colorless oil (711 mg, 33%) and **4a** as a colorless oil (1.16 g, 53%). **3a**: R_f 0.58, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +58.8° (*c* 5.9, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 2.09−2.43 (3H, 3-H and 9-H), 2.61 (1H, s, O*H*), 3.33−3.46 (1H, m, 4-H), 3.36 (3H, s, overlapping, OMe), 3.68 (1H, t, *J* 9.8, 6ax-H), 3.82 (1H, dt, *J* 4.4, 9.8, 5-H), 4.23 (1H, dd, *J* 4.4, 9.8, 6eq-H), 4.29 (1H, s, 1-H), 4.91 (1H, d, *J* 10.1, 11-H_{cis}), 5.00 (1H, dd, *J* 1.1, 17.2, 11-H_{trans}), 5.31 (1H, dd, *J* 1.6, 11.0, 8-H_{cis}), 5.45 (1H, s, 12-H), 5.56 (1H, dd, *J* 1.6, 17.2, 8-H_{trans}), 5.91−6.10 (2H, 7-H and 10-H), 7.27−7.51 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 31.4 (CH_2, C9), 46.3 (CH, C3), 55.7 (CH_3, OMe), 64.9 (CH, C5), 69.7 (CH_2, C6), 75.9 (C, C2), 80.9 (CH, C4), 101.9 (CH, C12), 103.2 (CH, C1), 115.3 (CH_2, C11), 117.4 (CH_2, C8), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.3 (CH, Ph), 136.4 (CH, C10), 138.1 (C, Ph), 139.4 (CH, C7); *m*/*z* (FAB) 333 (MH^+, 39) (found MH^+, 333.1703; $C_{19}H_{25}O_5$ requires 333.1702). **4a**: R_f 0.46, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ + 12.9° (*c* 10.35, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 2.08−2.40 (3H, 3-H and 9-H), 2.33 (1H, s, overlapping, O*H*), 3.25 (3H, s, OMe), 3.68−3.91 (3H, 4-H, 5-H and 6ax-H), 4.09 (1H, s, 1-H), 4.18 (1H, dd, *J* 4.4, 9.8, 6eq-H), 4.85−5.04 (2H, 11-H), 5.18 (1H, d, *J* 11.0, 8-H_{cis}), 5.36 (1H, d, *J* 17.3, 8-H_{trans}), 5.45 (1H, s, 12-H), 5.80−6.07 (2H, 7-H and 10-H), 7.22−7.49 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 30.6 (CH_2, C9), 42.7 (CH, C3), 55.6 (CH_3, OMe), 65.1 (CH, C5), 69.7 (CH_2, C6), 77.9 (C, C2), 79.0 (CH, C4), 102.1 (CH, C12), 104.5 (CH, C1), 115.4 (CH_2, C11), 116.3 (CH_2, C8), 126.6 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 138.4 (C, Ph), 138.8 (CH, C10), 140.7 (CH, C7); *m*/*z* (FAB) 333 (MH^+, 72) (found MH^+, 333.1701; $C_{19}H_{25}O_5$ requires 333.1702).

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-ethenyl-3-deoxy-3-*C*-methyl-3-*C*-propenyl-α-D-glucopyranoside (3b) and Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-ethenyl-3-deoxy-3-*C*-methyl-3-*C*-propenyl-α-D-mannopyranoside (4b). Vinylmagnesium chloride (2.00 mL, 3.37 mmol, 15 wt % solution in THF) was added dropwise to an ice-cooled solution of the ketone **2b** (729 mg, 2.29 mmol) in dry THF (6.0 mL). The solution was then heated to reflux for 2 h and allowed to cool to room temperature and then quenched by dropwise addition of water (20 mL). The resulting mixture was then diluted with water (50 mL) and extracted into diethyl ether (2 × 75 mL), and the combined organic layers were washed with water (50 mL), followed by saturated sodium chloride solution (50 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **3b** as a colorless oil (518 mg, 65%) and **4b** as a colorless oil (118 mg, 15%). **3b**: R_f 0.62, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +26.6° (*c* 0.7, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.23 (3H, s, C3-Me), 2.13−2.32 (2H, m, 9-H), 2.71 (1H, d, *J* 1.3, O*H*), 3.37 (3H, s, OMe), 3.55 (1H, d, *J* 9.8, 4-H), 3.71 (1H, t, *J* 10.1, 6ax-H), 3.95 (1H, ddd, *J* 5.0, 9.8, 10.1, 5-H), 4.27 (1H, s, 1-H), 4.30 (1H, dd, overlapping, *J* 5.0, 10.1, 6eq-H), 4.88−5.00 (2H, m, 11-H), 5.25 (1H, dd, *J* 1.9, 11.0, 8-H_{cis}), 5.49 (1H, s, 12-H), 5.56 (1H, dd, *J* 1.9, 17.2, 8-H_{trans}), 5.90−6.24 (2H, 7-H and 10-H), 7.28−7.53 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 14.2 (CH_3, C3-Me), 41.9 (CH_2, C9), 44.1 (C, C3), 56.3 (CH_3, OMe), 60.4 (CH, C5), 70.0 (CH_2, C6), 76.8 (C, C2), 82.9 (CH, C4), 101.9 (CH, C12), 105.0 (CH, C1), 115.5 (CH_2, C11), 116.7 (CH_2, C8), 126.6 (CH, Ph), 128.6 (CH, Ph), 129.3 (CH, Ph), 136.7 (CH, C10), 138.3 (C, Ph), 138.7 (CH, C7); *m*/*z* (FAB) 347 (MH^+, 20) (found MH^+, 347.1858; $C_{20}H_{27}O_5$ requires 347.1859). **4b:** R_f 0.38, petroleum ether−diethyl ether (1:1); δ_H (250 MHz, $CDCl_3$) 1.26 (3H, s, C3-Me), 2.12−2.48 (3H, 9-H and O*H*), 3.36 (3H, s, OMe), 3.72−3.90 (1H, m, 5-H), 3.94−4.10 (2H, 4-H and 6ax-H), 4.15 (1H, s, 1-H), 4.30 (1H, dd, *J* 5.0, 10.1, 6eq-H), 4.92−5.10 (2H, m, 11-H), 5.32 (1H, d, *J* 10.0, 8-H_{cis}), 5.44 (1H, d, *J* 17.0, 8-H_{trans}), 5.58 (1H, s, 12-H), 5.97−6.19 (1H, m, 10-H), 6.24 (1H, dd, *J* 10.0, 17.0, 7-H), 7.30−7.56 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 16.3 (CH_3, C3-Me), 40.7 (CH_2, C9), 43.3 (C, C3), 56.2 (CH_3, OMe), 60.8 (CH, C5), 69.9 (CH_2, C6), 79.0 (C, C2), 80.5 (CH, C4), 101.9 (CH, C12), 106.3 (CH, C1), 116.0 (CH_2, C11), 117.2 (CH_2, C8), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 137.6 (CH, C10), 138.0 (CH, C7), 138.4 (C, Ph); *m*/*z* (FAB) 347 (MH^+, 34) (found MH^+, 347.1859; $C_{20}H_{27}O_5$ requires 347.1859).

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(propene-1-ylidene-3-yl)-3-deoxy-α-D-glucopyranoside (5a). Nitrogen gas was bubbled through a solution of the diene **3a** (106 mg, 0.32 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (8 mg, 0.0097 mmol, 3.0 mol %) was then added and the solution heated at 60 °C for 48 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1 to 2:1) as the eluent yielded starting material **3a** as a colorless oil (79 mg, 75%) and **5a** as a white solid (15 mg, 15%): mp 148−150 °C; R_f 0.15, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +28.5° (*c* 0.9, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.35 (1H, dt, *J* 5.0, 9.8, 3-H), 2.38−2.45 (1H, m, overlapping, CH*H*, 9-H), 2.80−2.89 (1H, m, C*H*H, 9-H), 2.86 (1H, s, overlapping, O*H*), 3.12 (1H, t, *J* 9.8, 4-H), 3.53 (3H, s, OMe), 3.66 (1H, t, *J* 10.3, 6ax-H), 3.90 (1H, ddd, *J* 5.1, 9.8, 10.3, 5-H), 4.31 (1H, dd, *J* 5.1, 10.3, 6eq-H), 4.76 (1H, s, 1-H), 5.47 (1H, s, 10-H), 5.78−5.83 (1H, m, 7-H), 6.17−6.22 (1H, m, 8-H), 7.33−7.52 (5H, Ph); δ_C (100.6 MHz, $CDCl_3$) 35.2 (CH_2, C9), 48.0 (CH, C3), 55.8 (CH_3, OMe), 61.8 (CH, C5), 69.7 (CH_2, C6), 81.5 (CH, C4), 83.5 (C, C2), 100.2 (CH, C10), 102.4 (CH, C1), 126.6 (CH, Ph), 128.7 (CH, Ph), 129.5 (CH, Ph), 133.7 (CH, C8), 138.0 (C, Ph), 138.0 (CH, C7); *m*/*z* (CI) 305 (MH^+, 100) (found MH^+, 305.1388; $C_{17}H_{21}O_5$ requires 305.1389). Anal. Found: C, 64.36; H, 6.68. $C_{17}H_{20}O_5$ requires C, 67.09; H, 6.62%.

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(propene-1-ylidene-3-yl)-3-deoxy-3-*C*-methyl-α-D-glucopyranoside (5b). Nitrogen gas was bubbled through a solution of the diene **3b** (124 mg, 0.36 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (10 mg, 0.012 mmol, 3.4 mol %) was then added and the solution heated at 60 °C for 17 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (2:1) as the eluent yielded **5b** as a white solid (112 mg, 98%): mp 107−108 °C; R_f 0.21, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +39.5° (*c* 5.95, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.31 (3H, s, C3-Me), 2.38 (1H, dt, *J* 2.1, 16.8, CH*H*, 9-H), 2.52 (1H,

dd, *J* 1.6, 16.8, C*H*H, 9-H), 2.81 (1H, s, O*H*), 3.33 (1H, d, *J* 9.9, 4-H), 3.47 (3H, s, OMe), 3.69 (1H, t, *J* 10.3, 6ax-H), 3.93 (1H, ddd, *J* 5.1, 9.9, 10.3, 5-H), 4.31 (1H, dd, *J* 5.1, 10.3, 6eq-H), 4.71 (1H, s, 1-H), 5.47 (1H, s, 10-H), 5.74−5.84 (1H, m, 7-H), 6.09−6.19 (1H, m, 8-H), 7.32−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 13.4 (CH_3, C3-Me), 43.1 (CH_2, C9), 48.3 (C, C3), 56.0 (CH_3, OMe), 58.8 (CH, C5), 69.8 (CH_2, C6), 82.6 (CH, C4), 82.9 (C, C2), 101.2 (CH, C10), 102.1 (CH, C1), 126.6 (CH, Ph), 128.6 (CH, Ph), 129.4 (CH, Ph), 134.6 (CH, C8), 137.9 (CH, C7), 138.3 (C, Ph); *m*/*z* (FAB) 319 (MH^+, 26) (found MH^+, 319.1545; $C_{18}H_{23}O_5$ requires 319.1546). Anal. Found: C, 67.68; H, 6.92. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.96%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-propenyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (6) and Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-propenyl-3-deoxy-3-*C*-propenyl-α-D-mannopyranoside (7). Allylmagnesium chloride (9.94 mL, 19.88 mmol, 2 M solution in THF) was added dropwise to an ice-cooled solution of the ketone **2a** (2.00 g, 6.58 mmol) in dry THF (7.0 mL). The solution was then heated to reflux for 2 h, allowed to cool to room temperature, and then quenched by portionwise addition to ice/water (300 mL). The resulting mixture was then treated with saturated ammonium chloride solution (30 mL) and extracted into diethyl ether (2 × 150 mL), and the combined organic layers were washed with water (300 mL), followed by saturated sodium chloride solution (300 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded **6** as a colorless oil (1.68 g, 74%) and **7** as a colorless oil (344 mg, 15%). **6**: R_f 0.68, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +75.9° (*c* 4.8, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 2.32−2.78 (6H, 3-H, 7-H, 10-H and O*H*), 3.60 (3H, s, OMe), 3.64 (1H, dd, overlapping, *J* 9.1, 10.7, 4-H), 3.88−4.05 (2H, 5-H and 6ax-H), 4.40−4.49 (1H, m, 6eq-H), 4.68 (1H, s, 1-H), 5.10−5.40 (4H, 9-H and 12-H), 5.70 (1H, s, 13-H), 6.05−6.33 (2H, 8-H and 11-H), 7.53−7.69 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 31.3 (CH_2, C10), 36.6 (CH_2, C7), 46.6 (CH, C3), 55.7 (CH_3, OMe), 64.8 (CH, C5), 69.8 (CH_2, C6), 74.7 (C, C2), 81.1 (CH, C4), 101.0 (CH, C1), 101.9 (CH, C13), 115.3 (CH_2, C9), 119.0 (CH_2, C12), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 133.6 (CH, C11), 138.1 (C, Ph), 139.3 (CH, C8); *m*/*z* (FAB) 347 (MH^+, 34) (found MH^+, 347.1858; $C_{20}H_{27}O_5$ requires 347.1859). **7**: R_f 0.40, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +9.6° (*c* 5.8, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 2.00−2.16 (2H, 3-H and O*H*), 2.26−2.59 (4H, 7-H and 10-H), 3.33 (3H, s, OMe), 3.64−3.91 (3H, 4-H, 5-H and 6ax-H), 4.22 (1H, dd, *J* 4.1, 9.8, 6eq-H), 4.25 (1H, s, overlapping, 1-H), 4.92−5.22 (4H, 9-H and 12-H), 5.50 (1H, s, 13-H), 5.71−6.10 (2H, 8-H and 11-H), 7.25−7.52 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 29.4 (CH_2, C10), 41.5 (CH_2, C7), 43.6 (CH, C3), 55.3 (CH_3, OMe), 65.1 (CH, C5), 69.7 (CH_2, C6), 76.4 (C, C2), 78.7 (CH, C4), 102.1 (CH, C1), 102.9 (CH, C13), 115.9 (CH_2, C9), 119.7 (CH_2, C12), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 133.1 (CH, C11), 138.3 (C, Ph), 139.1 (CH, C8); *m*/*z* (FAB) 347 (MH^+, 60) (found MH^+, 347.1859; $C_{20}H_{27}O_5$ requires 347.1859).

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(but-2-ene-1,4-diyl)-3-deoxy-α-D-glucopyranoside (8). Nitrogen gas was bubbled through a solution of the diene **6** (101 mg, 0.29 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (8 mg, 0.0097 mmol, 3.3 mol %) was then added and the solution heated at 60 °C for 17 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1 to 2:1) as the eluent yielded **8** as a white solid (83 mg, 89%): mp 142−143 °C; R_f 0.19, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +33.6° (*c* 8.3, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.98−2.13 (1H, m, CH*H*, 7-H), 2.19−2.58 (5H, 3-H, C*H*H, 7-H, 10-H and O*H*), 3.41 (1H, dd, *J* 9.1, 10.7, 4-H), 3.50 (3H, s, OMe), 3.68−3.86 (2H, 5-H and 6ax-H), 4.27 (1H, dd, *J* 3.5, 9.1, 6eq-H), 4.32 (1H, s, 1-H), 5.51 (1H, s, 11-H), 5.61−5.79 (2H, 8-H and 9-H), 7.34−7.54 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 18.8 (CH_2, C10), 30.8 (CH_2, C7), 38.2 (CH, C3), 54.4 (CH_3, OMe), 63.7 (CH, C5), 68.3 (CH_2, C6), 69.1 (C, C2), 76.1 (CH, C4), 100.6 (CH, C11), 101.8 (CH, C1), 121.4 (CH, C8), 123.5 (CH, C9), 125.1 (CH, Ph), 127.2 (CH, Ph), 127.9 (CH, Ph), 136.6 (C, Ph); *m*/*z* (FAB) 319 (MH^+, 100) (found MH^+, 319.1547; $C_{18}H_{23}O_5$ requires 319.1546). Anal. Found: C, 67.75; H, 7.05. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.96%.

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(but-2-ene-1,4-diyl)-3-deoxy-α-D-mannopyranoside (9). Nitrogen gas was bubbled through a solution of the diene **7** (86 mg, 0.25 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (8 mg, 0.0097 mmol, 3.9 mol %) was then added and the solution heated at 60 °C for 17 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1 to 2:1) as the eluent yielded **9** as a colorless oil (63 mg, 80%): R_f 0.13, petroleum ether−diethyl ether (1:1); $[\alpha]^{18}_D$ +8.8° (*c* 6.0, $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 1.86 (1H, dd, *J* 4.4, 18.2, CH*H*, 7-H), 1.94−2.10 (1H, m, CH*H*, 10-H), 2.04 (1H, s, overlapping, O*H*), 2.16 (1H, dt, *J* 5.2, 10.6, 3-H), 2.40−2.55 (1H, m, C*H*H, 10-H), 2.51−2.67 (1H, m, overlapping, C*H*H, 7-H), 3.41 (3H, s, OMe), 3.65 (1H, t, *J* 10.6, 4-H), 3.76−3.94 (1H, t, *J* 9.0, 6ax-H; 1H, m, overlapping, 5-H), 4.25 (1H, dd, *J* 3.6, 9.0, 6eq-H), 4.39 (1H, s, 1-H), 5.53 (1H, s, 11-H), 5.54−5.68 (1H, m, 8-H), 5.70−5.82 (1H, m, 9-H), 7.30−7.53 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 24.4 (CH_2, C10), 34.3 (CH_2, C7), 37.6 (CH, C3), 55.5 (CH_3, OMe), 64.5 (CH, C5), 69.7 (CH_2, C6), 71.9 (C, C2), 80.2 (CH, C4), 102.3 (CH, C11), 103.3 (CH, C1), 123.5 (CH, C8), 126.1 (CH, C9), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.3 (CH, Ph), 138.2 (C, Ph); *m*/*z* (FAB) 319 (MH^+, 34) (found MH^+, 319.1544; $C_{18}H_{23}O_5$ requires 319.1546).

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-but-3-enyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (10) and Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-but-3-enyl-3-deoxy-3-*C*-propenyl-α-D-mannopyranoside (11). Anhydrous cerium(III) chloride (2.03 g, 8.23 mmol) in dry diethyl ether (4.0 mL) was stirred at room temperature for 1.5 h. In another flask, 4-bromo-1-butene (0.835 mL, 8.23 mmol) in dry diethyl ether (5.0 mL) was added dropwise to magnesium turnings (220 mg, 9.05 mmol) in dry diethyl ether (4.0 mL) at 0 °C. This mixture was stirred at 0 °C for 0.25 h and then at room temperature for 1 h. The cerium(III) chloride mixture was then cooled to −78 °C, the freshly prepared Grignard added dropwise via a cannula, and the resulting mixture stirred at −78 °C for 2 h. Ketone **2a** (500 mg, 1.64 mmol) in dry diethyl ether (6.0 mL) was added dropwise via a cannula to the cooled (−78 °C) reaction mixture. The mixture was then stirred at −40 °C for 1.5 h, then added portionwise to ice/water (150 mL) and saturated ammonium chloride solution (50 mL). The mixture was then extracted into dichloromethane (2 × 100 mL), and the combined organic layers were washed with saturated sodium chloride solution (200 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1 to 2:1) as the eluent yielded **10** as a colorless oil (120 mg, 20%), **11** as a colorless oil (39 mg, 7%) and the reduced product **27a** as a white solid (252 mg, 50%): **10** − R_f 0.60, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +43.1° (*c* 2.1, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.62−1.88 (2H, m, 7-H), 2.00−2.61 (5H, 3-H, 8-H and 11-H), 2.30 (1H, d, overlapping, *J* 1.6, O*H*), 3.40−3.57 (1H, m, 4-H), 3.47 (3H, s, overlapping, OMe), 3.65−3.90 (2H, 5-H and 6ax-H), 4.28 (1H, dd, *J* 3.2, 8.7, 6eq-H), 4.55 (1H, s, 1-H), 4.90−5.20 (4H, 10-H and 13-H), 5.53 (1H, s, 14-H), 5.78−6.18 (2H, 9-H and 12-H), 7.32−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 27.5 (CH_2, C11), 30.9 (CH_2, C8), 31.3 (CH_2, C7), 46.8 (CH, C3), 55.8 (CH_3, OMe), 64.9 (CH, C5), 69.8 (CH_2, C6), 74.7 (C, C2), 81.2 (CH, C4), 100.7 (CH, C14), 101.9 (CH, C1), 115.1 (CH_2, C10), 115.1 (CH_2, C13), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 138.0 (C, Ph), 139.1 (CH, C12), 139.5 (CH, C9); *m*/*z* (FAB) 361 (MH^+, 32) (found MH^+, 361.2015; $C_{21}H_{29}O_5$ requires 361.2015). **11** − R_f 0.24, petroleum ether−diethyl ether (1:1); δ_H (250 MHz, $CDCl_3$) 1.60−2.63 (7H, 3-H, 7-H, 8-H and 11-H), 1.86 (1H, s, overlapping, O*H*), 3.40 (3H, s, OMe), 3.65−3.96 (3H, 4-H, 5-H and 6ax-H), 4.25 (1H, dd, *J* 3.3, 9.3, 6eq-H), 4.38 (1H, s, 1-H), 4.90−5.20 (4H, 10-H and 13-H), 5.55 (1H, s, 14-H), 5.72−6.16 (2H, 9-H and 12-H), 7.29−7.56 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 27.2 (CH_2, C11), 29.2 (CH_2, C8), 36.2 (CH_2, C7), 43.8 (CH, C3), 55.3 (CH_3, OMe), 64.9 (CH, C5), 69.7 (CH_2, C6), 76.7 (C, C2), 78.4 (CH, C4), 102.2 (CH, C14), 102.5 (CH, C1), 115.1 (CH_2, C10), 116.2 (CH_2, C13), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 138.2 (C, Ph),

138.7 (CH, C12), 139.2 (CH, C9); *m*/*z* (FAB) 361 (MH^+, 28) (found MH^+, 361.2015; $C_{21}H_{29}O_5$ requires 361.2015).

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(pent-3-ene-1,5-diyl)-3-deoxy-α-D-glucopyranoside (12). Nitrogen gas was bubbled through a solution of the diene **10** (120 mg, 0.33 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (10 mg, 0.012 mmol, 3.6 mol %) was then added and the solution heated at 60 °C for 17 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **12** as a white solid (96 mg, 87%): mp 113−114 °C; R_f 0.32, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ − 30.0° (*c* 3.6, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.40−1.59 (1H, m, CH*H*, 7-H), 1.77−2.09 (2H, C*H*H, 7-H and CH*H*, 8-H), 2.09−2.22 (1H, m, 3-H), 2.24−2.43 (1H, m, CH*H*, 11-H), 2.49 (1H, d, *J* 2.1, O*H*), 2.54−2.83 (2H, C*H*H, 8-H and C*H*H, 11-H), 3.45 (3H, s, OMe), 3.62−3.90 (3H, 4-H, 5-H and 6ax-H), 4.13 (1H, s, 1-H), 4.27 (1H, dd, *J* 3.8, 9.3, 6eq-H), 5.48 (1H, s, 12-H), 5.68−5.85 (1H, m, 10-H), 5.93−6.10 (1H, m, 9-H), 7.31−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 21.2 (CH_2, C11), 21.5 (CH_2, C8), 31.9 (CH_2, C7), 42.8 (CH, C3), 55.7 (CH_3, OMe), 65.3 (CH, C5), 69.8 (CH_2, C6), 75.1 (C, C2), 76.7 (CH, C4), 101.9 (CH, C12), 105.6 (CH, C1), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.3 (CH, Ph), 129.8 (CH, C10), 133.7 (CH, C9), 138.2 (C, Ph); *m*/*z* (FAB) 333 (MH^+, 41) (found MH^+, 333.1703; $C_{19}H_{25}O_5$ requires 333.1702). Anal. Found: C, 68.65; H, 7.26. $C_{19}H_{24}O_5$ requires C, 68.66; H, 7.28%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-pent-4-enyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (13). Anhydrous cerium(III) chloride (2.03 g, 8.23 mmol) in dry diethyl ether (4.0 mL) was stirred at room temperature for 1.5 h. In another flask, 5-bromo-1-pentene (0.975 mL, 8.23 mmol) in dry diethyl ether (5.0 mL) was added dropwise to magnesium turnings (220 mg, 9.05 mmol) in dry diethyl ether (4.0 mL) at 0 °C. This mixture was stirred at 0 °C for 0.25 h and then at room temperature for 1 h. The cerium(III) chloride mixture was then cooled to −78 °C, the freshly prepared Grignard added dropwise via a cannula, and the resulting mixture stirred at −78 °C for 2 h. Ketone **2a** (500 mg, 1.64 mmol) in dry diethyl ether (6.0 mL) was added dropwise via a cannula to the cooled (−78 °C) reaction mixture. The mixture was then stirred at −40 °C for 2 h and then added portionwise to ice/water (150 mL) and saturated ammonium chloride solution (50 mL). The mixture was then extracted into dichloromethane (2 × 100 mL), and the combined organic layers were washed with saturated sodium chloride solution (200 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1 to 1:1) as the eluent yielded **13** as a colorless oil (465 mg, 76%) and the reduced product **27a** as a white solid (83 mg, 16%). **13**: R_f 0.56, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +47.3° (*c* 4.3, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.22−1.78 (4H, 7-H and 8-H), 2.00−2.58 (5H, 3-H, 9-H and 12-H), 2.22 (1H, s, overlapping, O*H*), 3.46 (3H, s, OMe), 3.46 (1H, t, *J* 9.9, 4-H), 3.68−3.88 (2H, 5-H and 6ax-H), 4.26 (1H, dd, *J* 3.1, 8.6, 6eq-H), 4.54 (1H, s, 1-H), 4.89−5.13 (4H, 11-H and 14-H), 5.53 (1H, s, 15-H), 5.73−6.17 (2H, 10-H and 13-H), 7.30−7.56 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 22.4 (CH_2, C8), 31.1 (CH_2, C9), 31.3 (CH_2, C12), 34.7 (CH_2, C7), 46.9 (CH, C3), 55.7 (CH_3, OMe), 64.9 (CH, C5), 69.8 (CH_2, C6), 74.9 (C, C2), 81.2 (CH, C4), 100.9 (CH, C1), 101.9 (CH, C15), 115.1 (CH_2, C14), 115.2 (CH_2, C11), 126.4 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 138.0 (C, Ph), 138.9 (CH, C13), 139.5 (CH, C10); *m*/*z* (FAB) 375 (MH^+, 19) (found MH^+, 375.2172; $C_{22}H_{31}O_5$ requires 375.2172).

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(hex-4-ene-1,6-diyl)-3-deoxy-α-D-glucopyranoside (14). Nitrogen gas was bubbled through a solution of the diene **13** (144 mg, 0.39 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (10 mg, 0.012 mmol, 3.2 mol %) was then added and the solution heated at 60 °C for 17 h. More catalyst **1** (10 mg, 0.012 mmol, 3.2 mol %) was then added and the solution heated at 60 °C for a further 48 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded starting material **13** as a colorless oil (43 mg, 30%) and **14** as a white solid (69 mg, 52%): mp 109−110 °C; R_f 0.40, petroleum ether−diethyl ether (1:1); $[\alpha]^{17}_D$ − 79.1° (*c* 2.4, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 1.39 (1H, dd, *J* 4.1, 11.0, CH*H*, 7-H), 1.44−1.56 (1H, m, CH*H*, 8-H), 1.93−2.11 (3H, C*H*H, 7-H; C*H*H, 8-H and CH*H*, 9-H), 2.19−2.33 (2H, CH*H*, 12-H and 3-H), 2.26 (1H, s, overlapping, O*H*), 2.49−2.61 (1H, m, C*H*H, 9-H), 2.65 (1H, dd, *J* 8.4, 12.5, C*H*H, 12-H), 3.42 (3H, s, OMe), 3.60 (1H, dd, *J* 9.2, 10.8, 4-H), 3.71 (1H, t, *J* 9.6, 6ax-H), 3.79 (1H, ddd, *J* 4.1, 9.2, 9.6, 5-H), 4.17 (1H, s, 1-H), 4.25 (1H, dd, *J* 4.1, 9.6, 6eq-H), 5.53 (1H, s, 13-H), 5.68−5.78 (1H, m, 10-H), 5.80−5.90 (1H, m, 11-H), 7.31−7.54 (5H, Ph); δ_C (100.6 MHz, $CDCl_3$) 20.9 (CH_2, C12), 24.4 (CH_2, C8), 26.2 (CH_2, C9), 30.8 (CH_2, C7), 46.2 (CH, C3), 55.6 (CH_3, OMe), 65.3 (CH, C5), 69.9 (CH_2, C6), 74.7 (C, C2), 78.1 (CH, C4), 102.0 (CH, C13), 107.3 (CH, C1), 126.5 (CH, Ph), 128.7 (CH, Ph), 129.2 (CH, C11), 129.3 (CH, Ph), 132.7 (CH, C10), 138.1 (C, Ph); *m*/*z* (FAB) 347 (MH^+, 10) (found MH^+, 347.1858; $C_{20}H_{27}O_5$ requires 347.1859). Anal. Found: C, 69.35; H, 7.35. $C_{20}H_{26}O_5$ requires C, 69.34; H, 7.56%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-hex-5-enyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (15). Anhydrous cerium(III) chloride (2.03 g, 8.23 mmol) in dry diethyl ether (4.0 mL) was stirred at room temperature for 1.5 h. In another flask, 6-bromo-1-hexene (1.00 g, 6.13 mmol) in dry diethyl ether (5.0 mL) was added dropwise to magnesium turnings (220 mg, 9.05 mmol) in dry diethyl ether (4.0 mL) at 0 °C. This mixture was stirred at 0 °C for 0.25 h and then at room temperature for 1 h. The cerium(III) chloride mixture was then cooled to −78 °C, the freshly prepared Grignard added dropwise via a cannula, and the resulting mixture stirred at −78 °C for 2 h. Ketone **2a** (500 mg, 1.64 mmol) in dry diethyl ether (6.0 mL) was added dropwise via a cannula to the cooled (−78 °C) reaction mixture. The mixture was then stirred at −40 °C for 2 h and then added portionwise to ice/water (150 mL) and saturated ammonium chloride solution (50 mL). The mixture was then extracted into dichloromethane (2 × 100 mL), and the combined organic layers were washed with saturated sodium chloride solution (200 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **15** as a colorless oil (350 mg, 55%) and the reduced product **27a** as a white solid (139 mg, 28%). **15**: R_f 0.65, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +35.5° (*c* 3.1, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.20−1.78 (6H, 8-H, 9-H and 10-H), 2.00−2.58 (5H, 3-H, 7-H and 13-H), 2.22 (1H, s, overlapping, O*H*), 3.46 (3H, s, OMe), 3.46 (1H, t, overlapping, *J* 9.5, 4-H), 3.68−3.88 (2H, 5-H and 6ax-H), 4.20−4.32 (1H, m, 6eq-H), 4.53 (1H, s, 1-H), 4.90−5.13 (4H, 12-H and 15-H), 5.53 (1H, s, 16-H), 5.73−6.16 (2H, 11-H and 14-H), 7.30−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 22.7 (CH_2, C8), 30.1 (CH_2, C9), 31.3 (CH_2, C10), 31.6 (CH_2, C13), 34.2 (CH_2, C7), 46.8 (CH, C3), 55.7 (CH_3, OMe), 64.9 (CH, C5), 69.8 (CH_2, C6), 74.9 (C, C2), 81.3 (CH, C4), 100.9 (CH, C1), 101.9 (CH, C16), 114.9 (CH_2, C15), 115.0 (CH_2, C12), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 138.1 (C, Ph), 139.2 (CH, C14), 139.6 (CH, C11); *m*/*z* (FAB) 389 (MH^+, 33) (found MH^+, 389.2328; $C_{23}H_{33}O_5$ requires 389.2328).

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-ethenyl-3-deoxy-α-D-glucopyranoside (17). Vinylmagnesium chloride (20.60 mL, 34.70 mmol, 15 wt % solution in THF) was added dropwise to an ice-cooled solution of the ketone **16** (1.85 g, 7.00 mmol) in dry THF (10.0 mL). The solution was then heated to reflux for 4 h, allowed to cool to room temperature, and then quenched by dropwise addition of saturated ammonium chloride solution (30 mL). The resulting mixture was extracted into diethyl ether (2 × 100 mL), and the combined organic layers were washed with saturated sodium chloride solution (100 mL), dried, and evaporated to leave a brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded **17** as a colorless oil (1.35 g, 75%): R_f 0.13, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +76.5° (*c* 3.45, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.95 (1H, t, *J* 11.5, 3ax-H), 2.09 (1H, dd, *J* 4.2, 11.5, 3eq-H), 2.63 (1H, d, *J* 0.6, O*H*), 3.39 (3H, s, OMe), 3.52−3.62 (1H, m, overlapping, 4-H), 3.68 (1H, t, overlapping, 6ax-H), 3.68−3.76 (1H, m, overlapping, 5-H), 4.20 (1H, ddd, *J* 3.5, 9.1, 6eq-H), 4.35 (1H, s, 1-H), 5.23 (1H, dd, *J* 1.3, 10.9, 8-H_{cis}), 5.43 (1H, s, 9-H), 5.47 (1H, dd, *J*

1.3, 17.4, 8-H_{trans}), 6.03 (1H, ddd, *J* 0.6, 10.9, 17.4, 7-H), 7.32−7.52 (5H, Ph); δ_C (75.8 MHz, $CDCl_3$) 39.1 (CH_2, C3), 55.8 (CH_3, OMe), 64.7 (CH, C5), 69.8 (CH_2, C6), 72.6 (C, C2), 76.0 (CH, C4), 102.2 (CH, C9), 102.3 (CH, C1), 116.5 (CH_2, C8), 126.6 (CH, Ph), 128.8 (CH, Ph), 129.6 (CH, Ph), 137.8 (C, Ph), 139.1 (CH, C7); *m*/*z* (FAB) 293 (MH^+, 52), found MH^+, 293.1389; $C_{16}H_{20}O_5$ requires 293.1389.

Methyl(*R*)-4,6-*O*-Benzylidene-2-*C*-ethenyl-2-*O*-propenyl-3-deoxy-α-D-glucopyranoside (18). Sodium hydride (169 mg, 60% dispersion in mineral oil, 4.23 mmol) was added portionwise to an ice-cooled solution of alcohol **17** (1.18 g, 4.00 mmol) in dry THF (30.0 mL). The resulting mixture was heated to reflux for 2 h and allowed to cool to room temperature. Allyl bromide (710 μL, 8.20 mmol) and DMPU (400 μL) were then added, and the mixture was heated to reflux for 4 h, allowed to cool to room temperature, and quenched by addition of water (10 mL). The resulting mixture was then extracted into diethyl ether (2 × 50 mL), and the combined organic layers were washed with saturated sodium chloride solution (50 mL), dried, and evaporated to leave a yellow solid. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **18** as a white solid (1.03 g, 77%): mp 146−147 °C; R_f 0.52, petroleum ether−diethyl ether; $[\alpha]^{20}_D$ +75.1° (*c* 2.48, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 2.16 (1H, dd, *J* 4.6, 11.5, 3eq-H), 2.25 (1H, t, *J* 11.5, 3ax-H), 3.52 (3H, s, OMe), 3.67 (1H, ddd, *J* 4.4, 4.6, 11.5, 4-H), 3.76 (1H, t, *J* 9.4, 6ax-H), 3.85 (1H, dd, *J* 4.4, 9.4, 5-H), 3.91 (1H, ddt, *J* 1.4, 5.5, 11.5, C*H*H 9-H), 4.02 (1H, ddt, *J* 1.4, 5.5, 11.5, CH*H* 9-H), 4.31 (1H, dd, *J* 4.4, 9.4, 6eq-H), 4.72 (1H, s, 1-H), 5.18 (1H, ddd, *J* 1.4, 3.6, 10.5, 11-H_{cis}), 5.32 (1H, ddd, *J* 1.4, 3.6, 16.5, 11-H_{trans}), 5.51 (1H, dd, *J* 1.7, 7.2, 8-H_{cis}), 5.53 (1H, s, 12-H), 5.54 (1H, dd, *J* 1.7, 13.7, 8-H_{trans}), 5.95 (1H, dd, overlapping, 7-H), 5.87−6.02 (1H, m, overlapping, 10-H), 7.32−7.59 (5H, Ph); δ_C (75.8 MHz, $CDCl_3$) 36.7 (CH_2, C3), 55.4 (CH_3, OMe), 64.0 (CH_2, C9), 64.8 (CH, C5), 69.8 (CH_2, C6), 76.2 (CH, C4), 77.5 (C, C2), 100.3 (CH, C1), 102.3 (CH, C12), 116.9 (CH_2, C8), 118.8 (CH_2, C11), 126.6 (CH, Ph), 128.8 (CH, Ph), 129.5 (CH, Ph), 135.5 (CH, C10), 137.8 (C, Ph), 139.1 (CH, C7); *m*/*z* (FAB) 333 (MH^+, 100). Anal. Found: C, 68.43; H, 7.08. $C_{19}H_{24}O_5$ requires C, 68.66; H, 7.28%.

Methyl (*R*)-4,6-*O*-Benzylidene-2(*S*)-spiro(2,5′-2′,5′-dihydrofuran)-2,3-dideoxy-α-D-glucopyranoside (19). Nitrogen gas was bubbled through a solution of the diene **18** (279 mg, 0.84 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (10 mg, 0.012 mmol, 1.4 mol %) was then added and the solution heated at 60 °C for 36 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded **19** as a white solid (191 mg, 75%): mp 86−87 °C; R_f 0.12, petroleum ether−diethyl ether (1:1); $[\alpha]^{14}_D$ +47.8° (*c* 5.8, $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 2.02 (1H, dd, *J* 4.1, 11.3, 3eq-H), 2.35 (1H, t, *J* 11.3, 3ax-H), 3.48 (3H, s, OMe), 3.63 (1H, ddd, *J* 4.1, 9.0, 11.3, 4-H), 3.77 (1H, t, *J* 9.4, 6ax-H), 3.86 (1H, ddd, overlapping, *J* 3.8, 9.0, 9.4, 5-H), 4.31 (1H, dd, *J* 3.8, 9.4, 6eq-H), 4.39 (1H, s, 1-H), 4.63−4.77 (2H, 7-H and 8-H), 5.54 (1H, s, 10-H), 6.02−6.15 (2H, m, 9-H), 7.30−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 36.5 (CH_2, C3), 55.5 (CH_3, OMe), 64.3 (CH, C5), 69.9 (CH_2, C6), 75.2 (CH_2, C9), 77.2 (CH, C4), 89.5 (C, C2), 102.2 (CH, C10), 102.3 (CH, C1), 126.6 (CH, Ph), 128.7 (CH, Ph), 129.2 (CH, C8), 129.5 (CH, Ph), 130.4 (CH, C7), 137.9 (C, Ph); *m*/*z* (FAB) 305 (MH^+, 47) (found MH^+, 305.1389; $C_{17}H_{21}O_5$ requires 305.1389). Anal. Found: C, 66.97; H, 6.66. $C_{17}H_{20}O_5$ requires C, 67.09; H, 6.62%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-propenyl-3-deoxy-α-D-glucopyranoside (20). Allylmagnesium chloride (0.50 mL, 1.00 mmol, 2 M solution in THF) was added dropwise to an ice-cooled solution of the ketone **16** (105 mg, 0.40 mmol) in dry THF (10.0 mL). The solution was then heated to reflux for 4 h, allowed to cool to room temperature, and then quenched by dropwise addition of saturated ammonium chloride solution (2 mL). The resulting mixture was then diluted with water (50 mL) and extracted into diethyl ether (2 × 50 mL), and the combined organic layers were washed with saturated sodium chloride solution (100 mL), dried, and evaporated to leave a brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **20** as a colorless oil (70 mg, 65%): R_f 0.16, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +51.6° (*c* 3.64, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.85 (1H, t, *J* 11.8, 3ax-H), 2.17 (1H, dd, *J* 4.3, 11.8, 3eq-H), 2.35−2.48 (2H, m, 7-H), 2.51 (1H, br s, O*H*) 3.46 (3H, s, OMe), 3.51−3.62 (1H, m, 4-H), 3.68−3.82 (2H, overlapping, 5-H and 6eq-H), 4.62 (1H, dd, *J* 10.7, 16.1, 6ax-H), 4.34 (1H, s, 1-H), 5.12−5.18 (1H, m, 9-H_{trans}), 5.21 (1H, br s, 9-H_{cis}), 5.52 (1H, s, 10-H), 5.87−6.05 (1H, m, 8-H), 7.30−7.56 (5H, Ph); δ_C (75.8 MHz, $CDCl_3$) 37.0 (CH_2, C3), 40.9 (CH_2, C7), 55.4 (CH_3, OMe), 64.3 (CH, C5), 69.4 (CH_2, C6), 72.0 (C, C2), 75.5 (CH, C4), 101.9 (CH, C1), 102.0 (CH, C9), 118.8 (CH_2, C9), 126.2 (CH, Ph), 128.3 (CH, Ph), 129.1 (CH, Ph), 132.5 (CH, C8), 137.4 (C, Ph); *m*/*z* (FAB) 347 (MH^+, 52) (found MH^+, 347.1858, $C_{17}H_{22}O_5$ requires 347.1859).

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-propenyl-2-*O*-propenyl-3-deoxy-α-D-glucopyranoside (21). Sodium hydride (65 mg, 60% dispersion in mineral oil, 1.63 mmol) was added portionwise to an ice-cooled solution of alcohol **20** (312 mg, 0.97 mmol) in dry THF (15.0 mL). The resulting mixture was heated to reflux for 2 h and allowed to cool to room temperature. Allyl bromide (200 μL, 2.30 mmol) and DMPU (200 μL) were then added, and the mixture was heated to reflux for 4 h, allowed to cool to room temperature, and quenched by addition of water (5 mL). The resulting mixture was then extracted into diethyl ether (2 × 25 mL), the combined organic layers washed with saturated sodium chloride solution (50 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **21** as a colorless oil (250 mg, 72%): R_f 0.46, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +35.4° (*c* 4.42, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 2.01−2.18 (2H, m, 3-H), 2.39−2.62 (2H, m, 7-H), 3.43 (3H, s, OMe), 3.53−3.66 (1H, m, 4-H), 3.73 (1H, t, *J* 10.4, 6ax-H) 3.78 (1H, dd, *J* 3.8, 10.4, 5-H), 3.96 (1H, ddt, *J* 1.5, 5.4, 12.1 CH*H*, 10-H), 4.10 (1H, ddt, *J* 1.5, 5.4, 12.1, C*H*H 10-H), 4.25 (1H, dd, *J* 3.8, 10.4, 6eq-H), 4.43 (1H, s, 1-H), 5.14 (1H, ddd, *J* 1.6, 3.1 9-H_{cis}), 5.14−5.22 (2H, overlapping, 9-H_{trans} and 12-H_{cis}), 5.27 (1H, ddd, *J* 1.7, 3.4, 17.2, 12-H_{trans}), 5.51 (1H, s, 13-H), 5.77−5.99 (2H, overlapping, 8-H and 11-H), 7.30−7.56 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 33.2 (CH_2, C3), 38.7 (CH_2, C7), 55.5 (CH_3, OMe), 63.8 (CH_2, C10) 64.8 (CH, C5), 69.9 (CH_2, C6), 76.1 (CH, C4), 77.0 (C, C2), 102.3 (CH, C13), 102.4 (CH, C1), 116.5 (CH_2, C12), 119.8 (CH_2, C9), 126.7 (CH, Ph), 128.7 (CH, Ph), 129.1 (CH, Ph), 132.7 (CH, C8),135.7 (CH, C11) 137.9 (C, Ph); *m*/*z* (FAB) 307 (MH^+, 28) (found 307.1545, $C_{20}H_{26}O_5$ requires 307.1546).

Methyl (*R*)-4,6-*O*-Benzylidene-2(*R*)-spiro(2,6′-5′,6′-dihydro-2′*H*-pyran)-2,3-dideoxy-α-D-glucopyranoside (22). Nitrogen gas was bubbled through a solution of the diene **21** (250 mg, 0.72 mmol) in benzene (10 mL) for 2−3 min. The catalyst **1** (10 mg, 0.012 mmol, 1.7 mol %) was then added and the solution heated at 60 °C for 36 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **22** as a white solid (186 mg, 73%): mp 69−70 °C; R_f 0.19, petroleum ether−diethyl ether (1:1); $[\alpha]^{14}_D$ +93.5° (*c* 9.2, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 2.09−2.17 (2H, m, 3-H), 2.25−2.33 (1H, m, CH*H*, 7-H), 2.37−2.45 (1H, m, C*H*H, 7-H), 3.51 (3H, s, OMe), 3.66 (1H, dt, *J* 6.3, 9.8, 4-H), 3.76 (1H, t, *J* 9.8, 6ax-H), 3.86 (1H, dt, *J* 4.4, 9.8, 5-H), 4.15−4.27 (2H, m, 10-H), 4.30 (1H, dd, *J* 4.4, 9.8, 6eq-H), 4.66 (1H, s, 1-H), 5.56 (1H, s, 11-H), 5.76−5.85 (2H, 8-H and 9-H), 7.32−7.55 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 32.6 (CH_2, C7), 36.4 (CH_2, C3), 55.6 (CH_3, OMe), 61.6 (CH_2, C10), 64.8 (CH, C5), 69.8 (CH_2, C6), 72.5 (C, C2), 76.0 (CH, C4), 100.1 (CH, C11), 102.3 (CH, C1), 122.1 (CH, C8), 126.2 (CH, C9), 126.6 (CH, Ph), 128.7 (CH, Ph), 129.5 (CH, Ph), 137.8 (C, Ph); *m*/*z* (FAB) 319 (MH^+, 88) (found MH^+, 319.1545; $C_{18}H_{23}O_5$ requires 319.1546). Anal. Found: C, 67.80; H, 6.73. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.96%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-deoxy-3-*C*-(1-methylethenyl)-α-D-allopyranoside (24b). Isopropenylmagnesium bromide (25.00 mL, 12.50 mmol, 0.5 M solution in THF) was added dropwise to a cooled (−78 °C) solution of the ketone **23** (921 mg, 3.50 mmol) in dry THF (40.0 mL). The solution was

then stirred at −50 °C for 4 h, allowed to warm to room temperature, and then quenched by dropwise addition of saturated ammonium chloride solution (40 mL). The resulting mixture was extracted into diethyl ether (2 × 100 mL), and the combined organic layers were washed with saturated sodium chloride solution (100 mL), dried, and evaporated to leave a yellow solid. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **24b** as a white solid (694 mg, 65%): R_f 0.24, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +117.2° (*c* 7.23, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.83 (3H, d, *J* 0.7, 9-H), 1.95 (1H, dd, *J* 1.3, 14.9, 2eq-H), 2.05 (1H, dd, *J* 3.9, 14.9, 2ax-H), 3.37 (1H, s, O*H*), 3.39 (3H, s, OMe), 3.78 (1H, t, *J* 10.0, 6ax-H), 3.78 (1H, dd, overlapping, 4-H), 4.21 (1H, dt, *J* 5.1, 14.8, 5-H), 4.34 (1H, dd, *J* 5.1, 10.0, 6eq-H), 4.79 (1H, dd, *J* 1.3, 3.9, 1-H), 4.97 (1H, quintet, *J* 0.7, 8-H_{trans}), 5.24 (1H, d, *J* 0.7, 8-H_{cis}), 5.58 (1H, s, 10-H), 7.32−7.55 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 19.7 (CH_3, C9), 40.2 (CH_2, C2), 55.8 (CH_3, OMe), 60.0 (CH, C5), 69.8 (CH_2, C6), 73.3 (C, C3), 80.9 (CH, C4), 99.1 (CH, C1), 102.2 (CH, C10), 113.0 (CH_2, C8), 126.6 (CH, Ph), 128.5 (CH, Ph), 129.3 (CH, Ph), 137.9 (C, Ph), 146.9 (C, C7); *m*/*z* (EI) 329 (MNa^+, 100). Anal. Found: C, 66.82; H, 7.07. $C_{17}H_{22}O_5$ requires C, 66.65; H, 7.24%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-deoxy-3-*C*-ethenyl-3-*O*-propenyl-α-D-allopyranoside (25a). Sodium hydride (250 mg, 80% dispersion in mineral oil, 8.33 mmol) was added portoinwise to an ice-cooled solution of alcohol **24a** (1.22 g, 4.18 mmol) in dry THF (25.0 mL). The resulting mixture was heated to reflux for 2 h and allowed to cool to room temperature. Allyl bromide (680 μL, 7.86 mmol) and DMPU (200 μL) were then added, and the mixture was heated to reflux for 4 h, allowed to cool to room temperature, and quenched by addition of water (15 mL). The resulting mixture was then extracted into diethyl ether (2 × 75 mL), and the combined organic layers were washed with saturated sodium chloride solution (150 mL), dried, and evaporated to leave a brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded **25a** as a colorless oil (1.11 g, 80%): R_f 0.52, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +79.9° (*c* 5.6, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.77 (1H, dd, *J* 4.6, 14.8, 2ax-H), 2.17 (1H, d, *J* 14.8, 2eq-H), 3.28 (3H, s, OMe), 3.52 (1H, d, *J* 9.2, 4-H), 3.61 (1H, t, *J* 10.3, 6ax-H), 3.89−4.05 (2H, m, 9-H), 4.22 (1H, dd, *J* 5.4, 10.3, 6eq-H), 4.34 (1H, ddd, *J* 5.4, 9.2, 10.3, 5-H), 4.64 (1H, d, *J* 4.6, 1-H), 5.00 (1H, ddd, *J* 1.9, 3.5, 8.8, 11-H_{cis}), 5.16 (1H, dd, *J* 0.9, 3.8, 8-H_{cis}), 5.21 (1H, overlapping, 8-H_{trans}), 5.25 (1H, overlapping, 11-H_{trans}), 5.41 (1H, s, 12-H), 5.79−5.97 (2H, overlapping, 7-H and 10-H), 7.30−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 36.9 (CH_2, C2), 55.7 (CH_3, OMe), 59.3 (CH, C5), 65.7 (CH_2, C9), 69.9 (CH_2, C6), 75.0 (C, C3), 83.8 (CH, C4), 98.5 (CH, C1), 102.5 (CH, C12), 115.3 (CH_2, C8), 117.0 (CH_2, C11), 126.7 (CH, Ph), 128.6 (CH, Ph), 129.3 (CH, Ph), 136.6 (C, C7), 138.3 (C, Ph), 139.0 (CH, C10); *m*/*z* (EI) 333 (MH^+, 48) (found 333.17029, $C_{19}H_{24}O_5$ requires 333.17020).

Methyl (*R*)-4,6-*O*-Benzylidene-2-deoxy-3-*C*-(1-methylethenyl)-3-*O*-propenyl-α-D-allopyranoside (25b). Sodium hydride (240 mg, 80% dispersion in mineral oil, 8.00 mmol) was added portionwise to an ice-cooled solution of alcohol **24b** (610 mg, 2.00 mmol) in dry THF (30.0 mL). The resulting mixture was heated to reflux for 2 h and allowed to cool to room temperature. Allyl bromide (344 μL, 4.00 mmol) and DMPU (200 μL) were then added, and the mixture was heated to reflux for 4 h, allowed to cool to room temperature, and quenched by addition of water (10 mL). The resulting mixture was then extracted into diethyl ether (2 × 50 mL), and the combined organic layers were washed with saturated sodium chloride solution (100 mL), dried, and evaporated to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **25b** as a colorless oil (650 mg, 94%): R_f 0.45, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +77.0° (*c* 9.64, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.80 (3H, d, *J* 0.7, 9-H), 1.86 (1H, dd, *J* 4.7, 14.8, 2ax-H), 2.23 (1H, dd, *J* 0.7, 14.8, 2eq-H), 3.37 (3H, s, OMe), 3.71 (1H, t, *J* 8.9, 6ax-H), 3.87 (1H, d, *J* 8.5, 4-H), 4.01 (1H, ddt, *J* 1.6, 5.3, 13.1, CH*H* 10-H), 4.18 (1H, ddt, *J* 1.6, 4.9, 13.1, C*H*H, 10-H), 4.31 (1H, dt, *J* 5.3, 8.9, 5-H), 4.42 (1H, dd, *J* 5.3, 8.9, 6eq-H), 4.71 (1H, d, *J* 4.7, 1-H), 5.04−5.11 (2H, overlapping, 8-H_{cis} and 12-H_{cis}), 5.13 (1H, br s, 8-H_{trans}), 5.30 (1H, ddd, *J* 1.8, 3.7, 17.2, 12-H_{trans}), 5.49 (1H, s, 13-H), 5.89−6.06 (1H, m, 11-H), 7.35−7.55 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 19.7 (CH_3, C9), 39.4 (CH_2, C2), 55.8 (CH_3, OMe), 59.4 (CH, C5), 66.9 (CH_2, C9), 70.0 (CH_2, C6), 77.7 (C, C3), 83.3 (CH, C4), 98.6 (CH, C1), 102.3 (CH, C13), 114.9 (CH_2 C8), 115.4 (CH_2, C12), 126.5 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 136.6 (CH, C11), 138.3 (C, Ph), 145.3 (C, C7); *m*/*z* (FAB) 347 (MH^+, 48) (found MH^+, 347.18585; $C_{20}H_{27}O_5$ requires 347.19592).

Methyl (*R*)-4,6-*O*-Benzylidene-3(*R*)-spiro(3,5′-2′,5′-dihydrofuran)-2,3-dideoxy-α-D-allopyranoside (26a). Nitrogen gas was bubbled through a solution of the diene **25a** (416 mg, 1.25 mmol) in benzene (20 mL) for 2−3 min. The catalyst **1** (11 mg, 0.013 mmol, 1.1 mol %) was then added and the solution heated at 60 °C for 36 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **26a** as a white solid (210 mg, 51%): mp 155−157 °C; R_f 0.32, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +202.1° (*c* 2.76, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.98 (1H, dd, *J* 1.2, 14.9, 2ax-H), 2.05 (1H, dd, *J* 4.2, 14.9, 2eq-H), 3.35 (3H, s, OMe), 3.46 (1H, dt, *J* 2.9, 9.4, 4-H), 3.57−3.69 (1H, m, 5-H), 4.18−4.30 (2H, m, H-6), 4.62−4.76 (3H, overlapping, 9-H and 1-H), 5.42 (1H, dt, *J* 2.4, 6.0, 8-H), 5.45 (1H, s, 10-H), 5.95 (1H, dt, *J* 1.5, 6.0, 7-H), 7.32−7.55 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 40.3 (CH_2, C2), 56.0 (CH_3, OMe), 60.0 (CH, C5), 69.8 (CH_2, C6), 77.4 (CH_2, C9), 81.4 (CH, C4), 87.2 (C, C3), 98.5 (CH, C1), 102.1 (CH, C10), 126.6 (CH, Ph), 128.5 (CH, Ph), 128.9 (CH, C7), 129.2 (CH, Ph), 130.3 (CH, C8), 138.3 (C, Ph); *m*/*z* (EI) 327.5 (MNa^+, 100).

Methyl (*R*)-4,6-*O*-Benzylidene-3(*R*)-spiro(3,5′-2′,5′-dihydro-4′-methyl-furan)-2,3-dideoxy-α-D-allopyranoside (26b). Nitrogen gas was bubbled through a solution of the diene **25b** (90 mg, 0.26 mmol) in benzene (8 mL) for 2−3 min. The catalyst **1** (10 mg, 0.012 mmol, 4.6 mol %) was then added and the solution heated at 60 °C for 36 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded starting material **25b** as a colorless oil (46 mg, 51%) and **26b** as a white solid (29 mg, 35%): mp 143−144 °C; R_f 0.35, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +137.9° (*c* 3.84, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.71 (3H, dd, *J* 2.2, 3.8, 10-H), 1.93 (1H, dd, *J* 0.7, 14.6, 2eq-H), 2.14 (1H, dd, *J* 4.7, 14.6, 2ax-H), 3.42 (3H, s, OMe), 3.53−3.61 (1H, m, 5-H), 4.25−4.40 (2H, m, 6-H), 4.57−4.71 (2H, m, 9-H), 4.78 (1h, d, *J* 4.7, 1-H), 5.51 (1H, s, 11-H), 5.64 (1H, dd, *J* 1.3.1, 8-H), 7.30−7.55 (5H, Ph); δ_C (100 MHz, $CDCl_3$) 12.3 (CH_3, C10), 38.2 (CH_2, C2), 56.1 (CH_3, OMe), 59.9 (CH, C5), 69.9 (CH_2, C6), 75.2 (CH_2, C9), 79.2 (CH, C4), 87.9 (C, C3), 98.8 (CH, C1), 102.2 (CH, C11), 124.4 (CH, C8), 126.6 (CH, Ph), 128.5 (CH, Ph), 129.2 (CH, Ph), 135.1 (C, C7), 138.4 (C, Ph); *m*/*z* (EI) 341 (MNa^+, 100). Anal. Found: C, 67.83; H, 7.07. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.96%.

Methyl (*R*)-4,6-*O*-Benzylidene-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (27a). To a magnetically stirred suspension of $LiAlH_4$ (8 mg, 0.21 mmol) in THF (8 mL) cooled to 0 °C was added a solution of the ketone **2a** (100 mg, 0.32 mmol) in THF (2 mL). The reaction mixture was then allowed to warm to room temperature and refluxed for 3 h. It was then cooled to 0 °C, and to it were added sequentially water (10 μL), 15% aqueous NaOH (10 μL), and water 30 μL). The resulting mixture was then stirred for 30 min. The white grannular precipitate was then filtered off, and the filtrate was dried (Na_2SO_4) and evaporated to afford the alcohol **27a** (90 mg, 90%): mp 139 °C; $[\alpha]^{20}_D$ +71.0° (*c* 0.52, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.92 (1H, d, *J* 11.0, O*H*), 2.02−2.18 (1H, m, 3-H), 2.42−2.58 (2H, m, 7-H), 3.32 (1H, dd, *J* 9.0, 10.8, 4-H), 3.46 (3H, s, OMe), 3.54 (1H, dt, *J* 3.8, 11.0, 2-H), 3.67 (1H, t, *J* 10.0, 6ax-H), 3.76 (1H, overlapping, ddd, *J* 4.0, 9.0, 10.0, 5-H), 4.27 (1H, dd, *J* 4.0, 10.0, 6eq-H), 4.68 (1H, d, *J* 3.8, 1-H), 5.05−5.23 (2H, m, 9-H), 5.48 (1H, s, 10-H), 5.84−6.06 (1H, m, 8-H), 7.29−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 30.3 (CH_2, C7), 42.5 (CH, C3), 55.7 (CH_3, OMe), 64.1 (CH, C5), 69.7 (CH_2, C6), 70.2 (CH,

C2), 78.6 (CH, C4), 99.8 (CH, C1), 101.8 (CH, C10), 118.2 (CH_2, C9), 126.5 (CH, Ph), 128.7 (CH, Ph), 129.3 (CH, Ph), 135.1 (CH, C8), 138.0 (C, Ph); *m*/*z* (FAB) 307 (MH^+, 54) (found MH^+, 307.1546; $C_{17}H_{23}O_5$ requires 307.1546). Anal. Found: C, 65.94; H, 7.12. $C_{17}H_{22}O_5$ requires C, 66.65; H, 7.24%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-methyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (27b). To an ice-cold solution of the ketone **2a** (100 mg, 0.33 mmol) in THF (5 mL) was added MeLi (500 μL, 0.66 mmol, 1.3 M in diethyl ether) with stirring. The reaction mixture was then allowed to warm to room temperature and stirred for 6 h. It was then quenched by addition of saturated aqueous ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated to yield the carbinol **27b** (90 mg, 86%): mp 143 °C; $[\alpha]^{21}_D$ +38.4° (*c* 0.29, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.25 (3H, s, C2-Me), 1.59 (1H, br s, O*H*), 2.13 (1H, m, 3-H), 2.34−2.50 (2H, m, 7-H), 3.38 (1H, dd, *J* 9.0, 12.0, 4-H), 3.44 (3H, s, OMe), 3.54−3.85 (2H, 5-H and 6ax-H), 4.25 (1H, dd, *J* 6.0, 15.0, 6eq-H), 4.29 (1H, s, 1-H), 4.94 (1H, d, *J* 9.0, 9-H_{cis}), 5.05 (1H, d, *J* 18.0, 9-H_{trans}), 5.49 (1H, s, 10-H), 6.02 (1H, m, 8-H), 7.34−7.49 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 20.2 (CH_3, C2-Me), 31.5 (CH_2, C7), 46.2 (CH, C3), 55.7 (CH_3, OMe), 65.0 (CH, C5), 69.7 (CH_2, C6), 73.5 (C, C2), 81.4 (CH, C4), 101.8 (CH, C1), 104.6 (CH, C10), 115.2 (CH_2, C9), 126.4 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 138.0 (C, Ph), 139.3 (CH, C8). Anal. Found: C, 67.68; H, 7.48. $C_{18}H_{24}O_5$ requires C, 67.48; H, 7.55%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*O*-propenyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (28a). To a suspension of NaH (40 mg, 40% suspension in mineral oil, 0.67 mmol, prewashed with petroleum ether to free it from mineral oil) in dry THF (4.0 mL) was added a solution of the alcohol **27a** (80 mg, 0.26 mmol) in dry THF (2.0 mL). The resulting mixture was refluxed for 2 h and cooled to room temperature, and then allyl bromide (63 mg, 0.52 mmol) and HMPA (150 μL) were added. The mixture was again refluxed for 2 h, cooled to room temperature, and quenched by addition of cold water. The mixture was then extracted with diethyl ether (3 × 10 mL). The combined organic extracts were then washed with saturated sodium chloride solution (30 mL), dried (Na_2SO_4), and concentrated. Chromatography on silica gel with petroleum ether−diethyl ether (4:1) as the eluent yielded ether **28a** (70 mg, 78%): mp 72 °C; $[\alpha]^{21}_D$ +31.5° (*c* 0.10, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 2.34 (1H, m), 2.48 (2H, m), 3.36 (2H, m), 3.46 (3H, s, OMe), 3.67 (1H, t, *J* 10.0, 6ax-H), 3.80 (1H, m), 4.09 (2H, m), 4.27 (1H, dd, *J* 4.5, 10.0, 6eq-H), 4.81 (1H, d, *J* 3.3, 1-H), 5.09−5.34 (4H, 9-H and 12-H), 5.49 (1H, s, 13-H), 5.91 (2H, 8-H and 11-H), 7.36−7.51 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 29.5 (CH_2, C10), 39.7 (CH, C3), 55.3 (CH_3, OMe), 63.5 (CH, C5), 69.5 (CH_2, C6), 71.5 (CH_2, C7), 76.6 (CH, C2), 78.4 (CH, C4), 97.6 (CH, C1), 101.5 (CH, C13), 117.7 (CH_2, C9), 117.8 (CH_2, C12), 126.1 (CH, Ph), 128.3 (CH, Ph), 129.0 (CH, Ph), 134.6 (CH, C8), 134.8 (CH, C11), 138.0 (C, Ph). Anal. Found: C, 69.43; H, 7.52. $C_{20}H_{26}O_5$ requires C, 69.34; H, 7.56%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*C*-methyl-2-*O*-propenyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (28b). Prepared by the procedure described for **28a**. Yield 87%: mp 125 °C; $[\alpha]^{21}_D$ +64.2° (*c* 0.22, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.28 (3H, s, C2-Me), 2.30 (1H, dd, *J* 6.4, 13.2), 2.43 (2H, m, 10-H), 3.44 (3H, s, OMe), 3.49 (1H, t, *J* 10.2, 4-H), 3.69−3.96 (3H, m), 4.16 (1H, dd, *J* 5.0, 12.5), 4.25 (1H, dd, *J* 4.3, 9.8, 6eq-H), 4.44 (1H, s, 1-H), 4.89−5.31 (4H, 9-H and 12-H), 5.52 (1H, s, 13-H), 5.95 (2H, 8-H and 11-H), 7.33−7.50 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 18.6 (CH_3, C2-Me), 31.5 (CH_2, C10), 42.5 (CH, C3), 54.9 (CH_3, OMe), 63.5 (CH_2, C7), 64.4 (CH, C5), 69.5 (CH_2, C6), 77.0 (C, C2), 81.7 (CH, C4), 101.6 (CH, C1), 103.4 (CH, C13), 114.7 (CH_2, C9), 115.7 (CH_2, C12), 126.1 (CH, Ph), 128.3 (CH, Ph), 128.9 (CH, Ph), 135.7 (CH, C8), 138.0 (C, Ph), 138.8 (CH, C11). Anal. Found: C, 69.75; H, 7.64. $C_{21}H_{28}O_5$ requires C, 69.98; H, 7.83%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*O*-(2-methylpropenyl)-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (28c). Prepared by the procedure described for **28a**. Ether **28c** was obtained using methallyl chloride as alkylating agent. Yield: 79%: mp 66 °C; $[\alpha]^{21}_D$ +40.6° (*c* 0.80, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.79 (3H, s, C8-Me), 2.34 (1H, m), 2.48 (2H, m, 10-H), 3.33 (2H, m), 3.44 (3H, s, OMe), 3.66 (1H, t, *J* 10.1, 6ax-H), 3.80 (1H, m), 3.91 (1H, d, *J* 12.0, CH*H*, H-7), 3.96 (1H, d, *J* 12.0 C*H*H, H-7), 4.26 (1H, dd, *J* 4.6, 10.1, 6eq-H), 4.80 (1H, d, *J* 3.3, 1-H), 4.91−5.14 (4H, 9-H and 12-H), 5.48 (1H, s, 13-H), 5.89 (1H, m, 11-H), 7.34−7.49 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 19.9 (CH_3, C8-Me), 29.8 (CH_2, C10), 40.0 (CH, C3), 55.5 (CH_3, OMe), 63.8 (CH, C5), 69.7 (CH_2, C6), 74.9 (CH_2, C7), 77.2 (CH, C2), 78.7 (CH, C4), 97.9 (CH, C1), 101.8 (CH, C13), 113.5 (CH_2, C9), 118.1 (CH_2, C12), 126.4 (CH, Ph), 128.6 (CH, Ph), 129.2 (CH, Ph), 134.9 (CH, C8), 138.0 (C, Ph), 142.5 (CH, C11). Anal. Found: C, 69.84; H, 7.53. $C_{21}H_{28}O_5$ requires C, 69.98; H, 7.83%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*O*-pent-4-enyl-3-deoxy-3-*C*-propenyl-α-D-glucopyranoside (30). Prepared by the procedure described for **28a**. Yield: 83%: mp 84 °C; $[\alpha]^{21}_D$ +45.0° (*c* 0.50, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.72 (1H, m), 2.16 (2H, m), 2.28 (1H, m), 2.47 (2H, m), 3.21−3.44 (4H, m), 3.45 (3H, s, OMe), 3.66 (2H, m), 3.79 (1H, dt, *J* 4.6, 10.0, 5-H), 4.26 (1H, dd, *J* 4.6, 10.0, 6eq-H), 4.81 (1H, d, *J* 3.3, 1-H), 4.95−5.13 (4H, 11-H and 14-H), 5.48 (1H, s, 15-H), 5.84 (2H, 10-H and 13-H), 7.33−7.50 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 29.2 (CH_2, C8), 29.4 (CH_2, C12), 30.2 (CH_2, C9), 39.6 (CH, C3), 55.1 (CH_3, OMe), 63.5 (CH, C5), 69.4 (CH_2, C7), 69.5 (CH_2, C6), 77.2 (CH, C2), 78.3 (CH, C4), 97.4 (CH, C1), 101.4 (CH, C15), 114.9 (CH_2, C11), 117.7 (CH_2, C14), 126.0 (CH, Ph), 128.2 (CH, Ph), 128.9 (CH, Ph), 134.5 (CH, C10), 137.6 (C, Ph), 138.1 (CH, C13). Anal. Found: C, 70.28; H, 8.91. $C_{22}H_{30}O_5$ requires C, 70.56; H, 8.07%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*O*-3-*C*-(but-2-ene-1,4-diyl)-3-deoxy-α-D-glucopyranoside (29a). Nitrogen gas was bubbled through a solution of the diene **28a** (50 mg, 0.16 mmol) in benzene (5 mL) for 2−3 min. The catalyst **1** (5 mg, 0.006 mmol, 3.9 mol %) was then added and the solution heated at 60 °C for 6 h. The solvent was then removed under reduced pressure to leave a dark brown oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **29a** as a white solid (40 mg, 87%): mp 99 °C; $[\alpha]^{21}_D$ +50.0° (*c* 0.35, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 2.06 (1H, m, CH*H*, 10-H), 2.37 (1H, dq, *J* 2.7, 10.5, 3-H), 2.83 (1H, dd, *J* 6.9, 15.0, C*H*H, 10-H), 3.22 (1H, t, *J* 9.6, 4-H), 3.46 (3H, s, OMe), 3.56 (1H, dd, *J* 3.6, 10.5, 2-H), 3.68 (1H, t, *J* 10.2, 6ax-H), 3.84 (1H, dt, *J* 4.8, 10.2, 5-H), 4.04 (1H, br d, *J* 14.0, CH*H*, 7-H), 4.27 (1H, dd, *J* 4.5, 10.2, 6eq-H), 4.46 (1H, dd, *J* 4.2, 14.0, C*H*H, 7-H), 4.73 (1H, d, *J* 3.6, 1-H), 5.49 (1H, s, 11-H), 5.88 (2H, 8-H and 9-H), 7.36−7.51 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 28.9 (CH_2, C10), 39.1 (CH, C3), 55.0 (CH_3, OMe), 63.2 (CH, C5), 66.9 (CH_2, C7), 69.3 (CH_2, C6), 80.2 (CH, C2), 83.0 (CH, C4), 99.5 (CH, C1), 101.7 (CH, C11), 126.0 (CH, Ph), 128.2 (CH, Ph), 128.9 (CH, Ph), 130.9 (CH, C8), 131.4 (CH, C9), 137.4 (C, Ph). Anal. Found: C, 67.20; H, 6.90. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.96%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-methyl-2-*O*-3-*C*-(but-2-ene-1,4-diyl)-3-deoxy-α-D-glucopyranoside (29b). Prepared by the procedure described for **29a**. Yield 87%: mp 154 °C; $[\alpha]^{21}_D$ +60.2° (*c* 0.40, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.34 (3H, s, C2-Me), 2.24 (1H, m, CH*H*, 10-H), 2.69 (1H, br d, *J* 18.0, C*H*H, 10-H), 2.90 (1H, dt, *J* 2.4, 11.7, 3-H), 3.40 (1H, t, *J* 9.0, 4-H), 3.48 (3H, s, OMe), 3.75 (1H, t, *J* 10.0, 6ax-H), 3.87 (1H, dt, *J* 4.5, 10.0, 5-H), 4.05 (1H, br d, *J* 15.6, CH*H*, 7-H), 4.29 (1H, dd, *J* 4.5, 10.0, 6eq-H), 4.39 (1H, s, 1-H), 4.74 (1H, dd, *J* 2.4, 15.6, C*H*H, 7-H), 5.52 (1H, s, 11-H), 5.68 (2H, 8-H and 9-H), 7.37−7.52 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 19.6 (CH_3, C2-Me), 25.7 (CH_2, C10), 40.7 (CH, C3), 55.1 (CH_3, OMe), 62.9 (CH_2, C7), 64.5 (CH, C5), 69.4 (CH_2, C6), 77.5 (C, C2), 79.5 (CH, C4), 101.7 (CH, C1), 105.3 (CH, C11), 126.0 (CH, Ph), 128.2 (CH, Ph), 128.9 (CH, Ph), 129.1 (CH, C8), 129.8 (CH, C9), 137.5 (C, Ph). Anal. Found: C, 68.65; H, 7.08. $C_{19}H_{24}O_5$ requires C, 68.66; H, 7.28%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*O*-3-*C*-(2-methyl-but-2-ene-1,4-diyl)-3-deoxy-α-D-glucopyranoside (29c). Prepared by the procedure described for **29a**. Yield: 87%: mp 104 °C; $[\alpha]^{21}_D$ +61.5° (*c* 1.10, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.69 (3H, s, C8-Me), 1.99 (1H, m, CH*H*, 10-H), 2.39 (1H, dq, *J* 2.2, 10.5, 3-H), 2.71 (1H, ddd, *J* 2.0, 8.0, 15.7, C*H*H, 10-H), 3.18

(1H, t, *J* 10.0, 4-H), 3.45 (3H, s, OMe), 3.53 (1H, dd, *J* 3.5, 10.5, 2-H), 3.66 (1H, t, *J* 10.5, 6ax-H), 3.82 (1H, dt, *J* 4.7, 10.5, 5-H), 4.04 (1H, d, *J* 14.8, CH*H*, 7-H), 4.23−4.33 (2H, 6eq-H and C*H*H, 7-H), 4.71 (1H, d, *J* 3.5, 1-H), 5.47 (1H, s, 11-H), 5.56−5.60 (1H, m, 9-H), 7.35−7.50 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 22.8 (CH_3, C8-Me), 28.2 (CH_2, C10), 39.3 (CH, C3), 55.0 (CH_3, OMe), 63.2 (CH, C5), 69.2 (CH_2, C6), 71.6 (CH_2, C7), 80.0 (CH, C2), 83.4 (CH, C4), 99.3 (CH, C1), 101.6 (CH, C11), 124.9 (CH, C9), 126.0 (CH, Ph), 128.1 (CH, Ph), 128.9 (CH, Ph), 137.4 (C, Ph), 138.9 (C, C8). Anal. Found: C, 68.75; H, 7.43. $C_{19}H_{24}O_5$ requires C, 68.66; H, 7.28%.

Methyl (*R*)-4,6-*O*-Benzylidene-2-*O*-3-*C*-(hex-4-ene-1,6-diyl)-3-deoxy-α-D-glucopyranoside (31). Prepared by the procedure described for **29a**. Ether **31** was obtained in 74% yield with recovery of the diene **30** (17%) after 14 h at 60 °C: mp 93 °C; $[\alpha]^{21}_D$ +49.3° (*c* 0.20, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.62 (1H, m), 1.84 (1H, m), 2.03 (1H, m), 2.35 (2H, m), 2.55 (1H, m), 2.68 (1H, m), 3.28 (2H, m), 3.43 (1H, m), 3.46 (3H, s, overlapping, OMe), 3.72 (2H, m), 4.01 (1H, quin, *J* 5.4), 4.24 (1H, dd, *J* 3.8, 9.2, 6eq-H), 4.72 (1H, d, *J* 3.0, 1-H), 5.51 (1H, s, 13-H), 5.63 (2H, 10-H and 11-H), 7.35−7.52 (5H, Ph); δ_C (75 MHz, $CDCl_3$) 21.6 (CH_2, C8), 21.9 (CH_2, C12), 27.5 (CH_2, C9), 38.9 (CH, C3), 55.2 (CH_3, OMe), 64.3 (CH, C5), 69.4 (CH_2, C7), 69.5 (CH_2, C6), 78.9 (CH, C2), 80.5 (CH, C4), 98.4 (CH, C1), 101.6 (CH, C13), 126.1 (CH, C10), 126.2 (CH, Ph), 128.2 (CH, Ph), 129.0 (CH, Ph), 132.5 (CH, C11), 137.6 (C, Ph). Anal. Found: C, 69.14; H, 7.64. $C_{20}H_{26}O_5$ requires C, 69.34; H, 7.56%.

Methyl (*R*)-4,6-*O*-Benzylidene-2,3-*C*-(propane-1,3-diyl)-3-deoxy-3-*C*-methyl-α-D-glucopyranoside (32). A solution of the olefin **5b** (100 mg, 0.31 mmol) in dry ethanol (5.0 mL) was degassed several times with nitrogen. The catalyst (palladium, 5% on carbon, 10 mg) was then added, and the mixture was degassed several times with hydrogen and then allowed to stir under a positive pressure of hydrogen (balloon) for 17 h. At this point the mixture was filtered through a plug of Celite under reduced pressure, and the residue was washed with ethanol (3 × 5 mL). The filtrate was then concentrated under reduced pressure to yield **32** as a pale yellow oil (100 mg, 99%): δ_H (250 MHz, $CDCl_3$) 1.20 (3H, s, C3-Me), 1.60−2.24 (6H, 7-H, 8-H and 9-H), 2.70 (1H, br s, O*H*), 3.37 (1H, d, *J* 9.7, 4-H), 3.43 (3H, s, OMe), 3.69 (1H, t, *J* 10.2, 6ax-H), 3.92 (1H, ddd, *J* 5.0, 9.7, 10.2, 5-H), 4.31 (1H, dd, *J* 5.0, 10.2, 6eq-H), 4.51 (1H, s, 1-H), 5.52 (1H, s, 10-H), 7.31−7.57 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 14.3 (CH_3, C3-Me), 19.9 (CH_2, C9), 35.0 (CH_2, C8), 35.9 (CH_2, C7), 49.4 (C, C3), 56.1 (CH_3, OMe), 59.6 (CH, C5), 70.0 (CH_2, C6), 80.4 (CH, C4), 81.3 (C, C2), 101.9 (CH, C10), 102.1 (CH, C1), 126.6 (CH, Ph), 128.6 (CH, Ph), 129.3 (CH, Ph), 138.3 (C, Ph); *m*/*z* (FAB) 321 (MH^+, 6) (found MH^+, 321.1702; $C_{18}H_{25}O_5$ requires 321.1702).

Methyl (*R*)-4-*O*-Benzoyl-6-*C*-bromo-2,3-*C*-(propane-1,3-diyl)-3,6-dideoxy-α-D-glucopyranoside (33). Barium carbonate (247 mg, 1.25 mmol) and *N*-bromosuccininmide (61 mg, 0.34 mmol) were added sequentially to a solution of **32** (100 mg, 0.31 mmol) in dry chloroform (10 mL). The mixture was then heated to reflux for 17 h. The mixture was allowed to cool to room temperature, barium carbonate removed by filtration, and the residue washed with dichloromethane (2 × 10 mL). The filtrate was then washed with water (2 × 30 mL), dried, and concentrated under reduced pressure to leave a yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **33** as a colorless oil (93 mg, 75%): R_f 0.32, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +78.6° (*c* 4.3, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.26 (3H, s, C3-Me), 1.53−1.97 (5H, CH*H*, 7-H, 8-H and 9-H), 2.15−2.38 (1H, m, C*H*H, 7-H), 2.64 (1H, d, *J* 2.3, O*H*), 3.33−3.49 (2H, m, 6-H), 3.52 (3H, s, OMe), 4.16 (1H, ddd, *J* 2.9, 7.8, 10.3, 5-H), 4.61 (1H, s, 1-H), 5.04 (1H, d, *J* 10.3, 4-H), 7.47 (2H, *m*-Ph), 7.61 (1H, *p*-Ph), 8.05 (2H, *o*-Ph); δ_C (62.9 MHz, $CDCl_3$) 14.6 (CH_3, C3-Me), 19.7 (CH_2, C9), 33.2 (CH_2, C6), 35.5 (CH_2, C8), 35.9 (CH_2, C7), 51.0 (C, C3), 56.3 (CH_3, OMe), 67.4 (CH, C5), 72.6 (CH, C4), 81.1 (C, C2), 101.4 (CH, C1), 129.0 (CH, Ph), 129.8 (C, Ph), 130.2 (CH, Ph), 133.9 (CH, Ph), 166.3 (CO, OBz); *m*/*z* (FAB) 398/400 (M^+, 1), 105 ($PhCO^+$, 96) (found M^+, 398.0729; $C_{18}H_{23}O_5Br$ requires 398.0729).

(1*R*,1′*R*,2′*S*)-1′-Methyl-2′-hydroxy-1-cyclohexan-3′-one-2-propenyl-1-benzoate (35). Zinc powder (60 g) was activated by washing with 2 M hydrochloric acid (6 × 30 mL), water (5 × 35 mL), 10% w/v aqueous potassium carbonate solution (30 mL), water (4 × 40 mL), 2-propanol (2 × 35 mL), and diethyl ether (3 × 35 mL). The bromo compound **33** (214 mg, 0.54 mmol) was heated to reflux with the activated zinc (4.56 g, 0.070 mol) in 2-propanol:water (16:1.6 mL) for 48 h. The zinc was removed by filtration and washed with diethyl ether (2 × 50 mL), and the combined organic layers were washed with water (100 mL) and saturated sodium chloride solution (100 mL), dried, and evaporated to leave a colorless oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **35** as a colorless oil (83 mg, 54%): R_f 0.28, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +57.3° (*c* 1.8, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.86 (3H, s, C3-Me), 1.76−1.91 (2H, 4α-H and 5α-H), 2.03−2.15 (1H, m, 5*β*-H), 2.15−2.23 (1H, m, 4*β*-H), 2.35−2.47 (1H, m, 6*β*-H), 2.52−2.60 (1H, m, 6α-H), 3.56 (1H, d, *J* 4.1, O*H*), 4.25 (1H, dd, *J* 1.2, 4.1, 2-H), 5.34 (1H, dt, *J* 1.3, 10.6, H-9_{cis}), 5.41 (1H, dt, *J* 1.4, 17.1, H-9_{trans}), 5.67 (1H, d, *J* 6.7, 7-H), 5.94 (1H, ddd, *J* 6.7, 10.6, 17.1, 8-H), 7.39 (2H, *m*-Ph), 7.61 (1H, *p*-Ph), 8.13 (2H, *o*-Ph); δ_C (100.6 MHz, $CDCl_3$) 15.3 (CH_3, C3-Me), 21.7 (CH_2, C5), 29.1 (CH_2, C4), 39.1 (CH_2, C6), 48.0 (C, C3), 77.9 (CH, C2), 78.1 (CH, C7), 119.7 (CH_2, C9), 128.9 (CH, Ph), 130.0 (CH, Ph), 130.7 (C, Ph), 132.6 (CH, C8), 133.4 (CH, Ph), 165.5 (CO, OBz), 211.6 (C, C1); *m*/*z* (FAB) 289 (MH^+, 56), 311 (MNa^+, 45) (found MH^+, 289.1440; $C_{17}H_{21}O_4$ requires 289.1440).

Methyl (*R*)-4-*O*-Benzoyl-6-*C*-bromo-2,3-*C*-(but-2-ene-1,4-diyl)-3,6-dideoxy-α-D-glucopyranoside (38). Barium carbonate (248 mg, 1.26 mmol) and *N*-bromosuccininmide (61 mg, 0.34 mmol) were added sequentially to a solution of **8** (100 mg, 0.31 mmol) in dry chloroform (10 mL). The mixture was then heated to reflux for 16 h. The mixture was allowed to cool to room temperature, barium carbonate removed by filtration, and the residue washed with diethyl ether (2 × 25 mL). The filtrate was concentrated under reduced pressure to leave a yellow oil. Chromatography on silica gel with dichloromethane-diethyl ether (97.5:2.5) as the eluent yielded starting material **8** as a white solid (21 mg, 21%) and **38** as a colorless oil (48 mg, 38%): R_f 0.50, dichloromethane-diethyl ether (9:1); $[\alpha]^{20}_D$ +66.7° (*c* 2.8, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.83−2.68 (6H, 3-H, 7-H, 10-H and O*H*), 3.39−3.52 (2H, m, 6-H), 3.57 (3H, s, OMe), 4.02 (1H, ddd, *J* 2.5, 7.9, 10.2, 5-H), 4.43 (1H, s, 1-H), 5.04 (1H, t, *J* 10.2, 4-H), 5.57−5.76 (2H, 8-H and 9-H), 7.48 (2H, *m*-Ph), 7.62 (1H, *p*-Ph), 8.05 (2H, *o*-Ph); δ_C (62.9 MHz, $CDCl_3$) 20.3 (CH_2, C10), 30.4 (CH_2, C7), 31.5 (CH_2, C6), 38.4 (CH, C3), 54.6 (CH_3, OMe), 69.0 (C, C2), 69.3 (CH, C5), 69.8 (CH, C4), 100.9 (CH, C1), 122.0 (CH, C8), 122.6 (CH, C9), 127.5 (CH, Ph), 128.2 (C, Ph), 128.8 (CH, Ph), 132.5 (CH, Ph), 164.6 (CO, OBz); *m*/*z* (EI) 396/398 (M^+, 2), 105 ($PhCO^+$, 100) (found M^+, 396.0572; $C_{18}H_{21}O_5Br$ requires 396.0572).

(1*R*,1′*S*,2′*R*)-2′-Formyl-2′-hydroxy-1-cyclohex-4′-ene-2-propenyl-1-benzoate (39). Zinc powder (60 g) was activated by washing with 2 M hydrochloric acid (6 × 30 mL), water (5 × 35 mL), 10% w/v aqueous potassium carbonate solution (30 mL), water (4 × 40 mL), 2-propanol (2 × 35 mL), and diethyl ether (3 × 35 mL). The bromo compound **38** (155 mg, 0.39 mmol) was heated to reflux with the activated zinc (3.32 g, 0.051 mol) in 2-propanol:water (10:1 mL) for 5 h. The zinc was removed by filtration and washed with diethyl ether (2 × 50 mL), and the combined organic layers were washed with water (100 mL), saturated sodium chloride solution (100 mL), dried, and evaporated to leave a colorless oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **39** as a colorless oil (56 mg, 50%): R_f 0.54, diethyl ether−petroleum ether (2:1); δ_H (250 MHz, $CDCl_3$) 2.18 (1H, dd, *J* 5.0, 17.6, CH*H*, 7-H), 2.40−2.80 (4H, 3-H, C*H*H, 7-H and 10-H), 3.95 (1H, s, O*H*), 5.19−5.33 (2H, m, 6-H), 5.66−5.97 (3H, 4-H, 5-H, 8-H) 6.06−6.16 (1H, m, 9-H), 7.43 (2H, *m*-Ph), 7.56 (1H, *p*-Ph), 7.95 (2H, *o*-Ph), 9.81 (1H, s, C*H*O); δ_C (62.9 MHz, $CDCl_3$) 24.8 (CH_2, C10), 36.7 (CH_2, C7), 47.2 (CH, C3), 71.3 (CH, C4), 76.2 (C, C2), 117.0 (CH_2, C6), 123.8 (CH, C8), 126.8 (CH, C9), 128.9 (CH, Ph), 129.9 (CH, Ph), 130.0 (C,

Ph), 133.6 (CH, Ph), 134.9 (CH, C5), 165.2 (CO, OBz), 202.2 (CH, *C*HO); *m*/*z* (FAB) 287 (MH^+, 9), 309 (MNa^+, 21) (found MH^+, 287.1281; $C_{17}H_{19}O_4$ requires 287.1283).

Methyl (*R*)-4,6-*O*-Benzylidene-2(*R*)-spiro(2,5′-2′,3′,4′,5′-tetrahydrofuran)-2,3-dideoxy-α-D-glucopyranoside (40). A solution of the olefin **19** (363 mg, 1.19 mmol) in dry methanol (25.0 mL) was degassed several times with nitrogen. The catalyst (palladium, 5% on carbon, 30 mg) was then added, and the mixture was degassed several times with hydrogen and then allowed to stir under a positive pressure of hydrogen (balloon) for 48 h. At this point the mixture was filtered through a plug of Celite under reduced pressure, and the residue was washed with methanol (3 × 5 mL). The filtrate was then concentrated under reduced pressure to yield a pale yellow oil. Chromatography on silica gel with petroleum ether−diethyl ether (2:1) as the eluent yielded **40** as a colorless oil (323 mg, 89%): R_f 0.22, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +67.8° (*c* 8.64, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.77−2.14 (5H, overlapping, 3eq-H, 8-H and 7-H), 2.26 (1H, t, *J* 11.7, 3ax-H), 3.43 (3H, s, OMe), 3.51 (1H, ddd, *J* 4.3, 8.8, 16.3, 4-H), 3.70 (1H, t, *J* 8.7, 6ax-H), 3.68−3.94 (3H, overlapping, 5-H and 9-H), 4.25 (1H, dd, *J* 4.1, 8.7, 6eq-H), 4.26 (1H, s, 1-H), 5.51 (1H, s, 10-H), 7.31−7.53 (5H, Ph); δ_C (62.9 MHz, $CDCl_3$) 26.1 (CH_2, C7), 35.8 (CH_2, C8), 36.5 (CH_2, C3), 55.5 (CH_3, OMe), 64.3 (CH, C5), 68.2 (CH_2, C9), 69.9 (CH_2, C6), 77.7 (CH, C4), 82.3 (C, C2), 102.2 (CH, C1), 102.2 (CH, C10), 126.6 (CH, Ph), 128.6 (CH, Ph), 129.5 (CH, Ph), 137.9 (C, Ph); *m*/*z* (FAB) 307 (MH^+, 11) (found MH^+ 307.15449, $C_{17}H_{23}O_5$ requires 307.15455).

Methyl (*R*)-4-*O*-Benzoyl-6-*C*-bromo-2(*R*)-spiro(2,5′-2′,3′,4′,5′-tetrahydrofuran)-2,3,6-trideoxy-α-D-glucopyranoside (41). Barium carbonate (835 mg, 4.24 mmol) and *N*-bromosuccininmide (207 mg, 1.16 mmol) were added sequentially to a solution of **40** (323 mg, 1.06 mmol) in dry chloroform (40 mL). The mixture was then heated to reflux for 4 h. The mixture was allowed to cool to room temperature, barium carbonate removed by filtration, and the residue washed with diethyl ether (2 × 50 mL). The filtrate was concentrated under reduced pressure to leave a yellow oil. Chromatography on silica gel with toluene−diethyl ether (3:1) as the eluent yielded **41** as a white solid (285 mg, 70%): R_f 0.48, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ +89.6° (*c* 2.87, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.84−2.13 (4H, overlapping, 7-H and 8-H), 2.13 (1H, dd, overlapping, *J* 5.3, 11.3, 3eq-H), 2.24 (1H, t, *J* 11.3, 3ax-H), 3.44 (1H, dd, *J* 7.1, 11.0, CH*H*, 6-H), 3.54 (3H, s, OMe), 3.59 (1H, dd, *J* 2.4, 11.0, C*H*H 6-H), 3.78−3.95 (2H, m, 9-H), 4.07 (1H, ddd, *J* 2.4, 7.1, 9.6, 5-H), 4.37 (1H, s, 1-H), 4.95 (1H, ddd, *J* 5.3, 9.6, 11.3, 4-H), 7.42−7.63 (3H, Ph), 8.00 (2H, o-Ph); δ_C (62.9 MHz, $CDCl_3$) 26.1 (CH_2, C7), 32.9 (CH_2, C8), 35.1 (CH_2, C3), 35.8 (CH_2, C6), 55.8 (CH_3, OMe), 68.5 (CH_2, C9), 69.6 (CH, C5), 70.4 (CH, C4), 81.7 (C, C2), 101.8 (CH, C1), 128.9 (CH, Ph), 129.9 (CH, Ph), 130.1 (CH, Ph), 133.8 (C, Ph), 165.7 (C, C10); *m*/*z* (EI) 407/409 (MNa^+, 100). Anal. Found: C, 52.91; H, 5.42. $C_{17}H_{21}O_5Br$ requires C, 53.00; H, 5.49%.

(2*R*,2′*S*)-2-(3′-Butenyl-2′-benzoate)tetrahydrofuran-2-carbaldehyde (42). Zinc powder (60 g) was activated by washing with 2 M hydrochloric acid (6 × 30 mL), water (5 × 35 mL), 10% w/v aqueous potassium carbonate solution (30 mL), water (4 × 40 mL), 2-propanol (2 × 35 mL), and diethyl ether (3 × 35 mL). The bromo compound **41** (233 mg, 0.59 mmol) was heated to reflux with the activated zinc (5.08 g, 0.078 mol) in 2-propanol:water (15:1.5 mL) for 3.5 h. The zinc was removed by filtration and washed with diethyl ether (2 × 50 mL), and the combined organic layers were washed with water (150 mL), saturated sodium chloride solution (150 mL), dried, and evaporated to leave a colorless oil. Chromatography on silica gel with petroleum ether−diethyl ether (3:1) as the eluent yielded **42** as a colorless oil (96 mg, 59%): R_f 0.36, petroleum ether−diethyl ether (1:1); $[\alpha]^{20}_D$ −52.9° (*c* 3.99, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 1.76−2.18 (4H, overlapping, 7-H and 8-H), 1.94 (1H, overlapping, dd, *J* 6.3, 14.5, CH*H*, 3-H) 2.50 (1H, dd, *J* 10.6, 14.5, C*H*H, 3-H), 3.83−4.06 (2H, m, 9-H), 5.18 (1H, dt, *J* 1.0, 10.4, 6-H_{cis}) 5.32 (1H, dt, *J* 1.0, 17.1, 6-H_{trans}) 5.66−5.77 (1H, m, 5-H), 5.87 (1H, ddd, *J* 6.3, 10.6, 16.7, 4-H), 7.34−7.68 (3H, Ph), 8.01 (2H, d, 0-Ph), 9.58 (1H, s, 1-H); δ_C (62.9 MHz, $CDCl_3$) 25.8 (CH_2, C7), 34.5 (CH_2, C8), 42.1 (CH_2, C3), 69.6 (CH_2, C9), 71.8 (CH, C4), 87.7 (C, C2), 117.3 (CH_2, C6), 128.8 (CH, Ph), 130.1 (CH, Ph), 130.4 (C, Ph), 133.4 (CH, Ph), 136.4 (CH, C5), 165.5 (C, C10), 205.2 (CH, C1); *m*/*z* (EI) 297 (MNa^+, 82) (found MH^+ 275.1283, $C_{16}H_{19}O_4$ requires 275.1283).

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