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Rapid Synthesis of Carbohydrate Derivatives, Including Mimetics of *C*-Linked Disaccharides and *C*-Linked Aza Disaccharides, Using the Hetero-Diels−Alder Reaction

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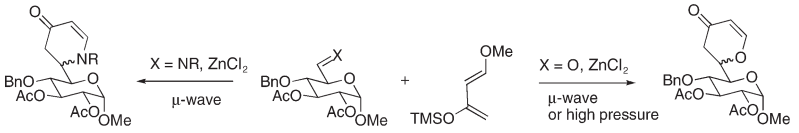

In this work we demonstrate the value of performing a hetero-Diels−Alder reaction (HDAR) between Danishefsky's diene and a range of aldehydes or imines, under microwave irradiation. By using a range of aldehydes and imines, including those derived from carbohydrates, access to functionalized 2,3-dihydro-4*H*-pyran-4-ones or 2,3-dihydro-4-pyridinones in good to excellent synthetic yields is possible. A particular strength of the methodology is its ability to access mimetics of *C*-linked disaccharides and *C*-linked aza disaccharides, targets of current therapeutic interest, in a rapid, convenient, and diastereoselective manner. The effect of high pressure on the HDARs involving carbohydrate-derived aldehydes and imines is also explored, with enhancement in yields occurring for the aldehyde substrates. Finally, HDARs using carbohydrate derived ketones, enones, and enals are described under a range of conditions. Optimum results were obtained under high-pressure conditions, with highly functionalized carbohydrate derivatives being afforded, in good yields, in this way.

Introduction

The hetero-Diels−Alder reaction (HDAR) has played a pivotal role in the development of new synthetic methodologies for access to heterocycles, often with high regio- and stereocontrol. For example, by using either a diene or a dienophile that contains a heteroatom, access to dihydropyrans or tetrahydropyridines,[1] of considerable interest within a range of biological applications,[2] is possible. In recent years the utility of microwave heating technology to enhance synthetic chemistry transformations, including cycloaddition reactions,[3−6] has received considerable attention, with shorter reaction times, less decomposition of sensitive materials, and the ability to perform multistep reactions efficiently in one pot offering advantages for such methodology. The value of using high pressure to enhance the Diels−Alder and hetero-Diels−Alder reactions has also been extensively documented in the literature with the yield and the optical purity of synthetically useful products generally being improved compared with more traditional protocols.[7]

In this program we have focused on the reaction of aldehydes, ketones, and imines with Danishefsky's diene to afford dihydropyranone and tetrahydropyridine derivatives,

(1) (a) Coisson, D.; Osborn, H. M. I. *Mini Rev. Org. Chem.* **2004**, *1*, 41. (b) Pellissier, H. *Tetrahedron* **2009**, *65*, 2839–2877.

(2) (a) Tietze, L. F.; Rackelmann, N. *Pure Appl. Chem.* **2004**, *76*, 1967–1983. (b) Chiacchio, U.; Padwa, A.; Romeo, G. *Curr. Org. Chem.* **2009**, *13*, 422–447.

(3) For recent reviews see: (a) Kappe, C. O.; Dallinger, D. *Mol. Diversity* **2009**, *13*, 71–193. (b) Polshettiwar, V.; Varma, R. S. *Chem. Soc. Rev.* **2008**, *37*, 1546–1557. (c) Kappe, C. O. *Chem. Soc. Rev.* **2008**, *37*, 1127–1139. (d) Kappe, C. O.; Dallinger, D. *Nat. Rev. Drug Discovery* **2006**, *5*, 51–63.

(4) (a) Pineiro, M.; Melo, T. M. V. D. P. E. *Eur. J. Org. Chem.* **2009**, *31*, 5287–5307. (b) de la Hoz, A.; Diaz-Ortis, A.; Moreno, A.; Langa, F. *Eur. J. Org. Chem.* **2000**, *22*, 3659–3673.

(5) (a) Caddick, S.; Fitzmaurice, R. *Tetrahedron* **2009**, *65*, 3325–3355. (b) Candeias, N. R.; Branco, L. C.; Gois, P. M.; Afonso, C. A. M.; Trindad, A. F. *Chem. Rev.* **2009**, 2703–2802. (c) Kappe, C. O. *Chem. Soc. Rev.* **2008**, *37*, 1127–1139. (d) de la Hoz, A.; Diaz-Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164–178. (e) Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250–6284.

(6) (a) Monbaliu, J. C.; Marchand-Brynaert, J. *Synthesis* **2009**, 1876–1880. (b) Nagarajan, S.; Barthes, C.; Gourdon, A. *Tetrahedron* **2009**, *65*, 3767–3772. (c) Castagnolo, D.; Botta, L.; Botta, M. *Tetrahedron Lett.* **2009**, *50*, 1526–1528. (d) Monbaliu, J.-C.; Marchand-Brynaert, J. *Tetrahedron Lett.* **2008**, *49*, 1839–1842.

(7) (a) Benito-lópez, F.; Egberink, R. J. M.; Reinhoudt, D. N.; Verboom, W. *Tetrahedron* **2008**, *64*, 10023–10040. (b) Ballerini, E.; Minuti, L.; Piermatti, O.; Pizzo, F. *J. Org. Chem.* **2009**, *74*, 4311–4317. (c) Marrero, J. G.; Harwood, L. M. *Tetrahedron Lett.* **2009**, *50*, 3574–3576.

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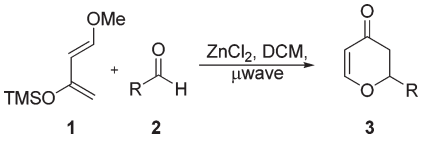
SCHEME 1. The Diels−Alder Reaction Producing Pyranone 3



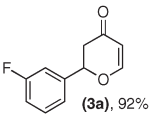
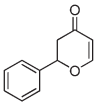
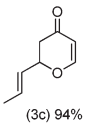
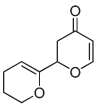
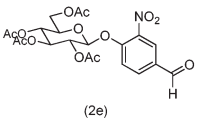
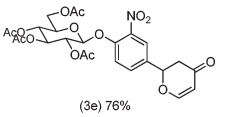
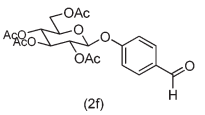
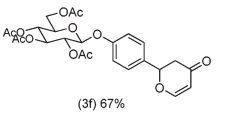
with particular emphasis on determining the value of microwave irradiation on the efficiency of the methodology. We have also applied the methodology to the synthesis of carbohydrate mimetics, by incorporating aldehydes, ketones, or imines appended to carbohydrate frameworks as the dienophile, within the HDAR. In these cases the study was extended to also examine the effect of high-pressure conditions on the efficiency of the methodology. If such methodology proved effective, access to *C*-linked disaccharide and *C*-linked aza disaccharide mimetics, of interest as inhibitors of glycosidase enzymes involved in a range of disease processes, or as ligands for carbohydrate binding processes involved in a range of diseases,[8] would be achieved.

Results and Discussion

At the initial stage of the project a range of aromatic and aliphatic aldehydes were selected as the dienophiles, for reaction with Danishefsky's diene, in order to access structurally diverse dihydropyranones. Excellent literature precedence exists for the HDAR of such systems in the absence of microwave irradiation.[4,9] The aldehydes utilized in this program were therefore selected to probe the effect of microwave irradiation on the efficiency of the reaction, as well as expand the range of dihydropyranones previously prepared with the conventional HDAR. In the experimental protocol (see the Supporting Information) the reaction mixture was heated to 30 °C under microwave irradiation for 90 s. The mixture was then quenched by the addition of trifluoroacetic acid, the solvents were removed *in vacuo*, and the residue was purified by column chromatography. Following the above procedure the compounds below were synthesized from the corresponding aldehydes in excellent synthetic yields, as summarized in Scheme 1 and Table 1.

For all substrates the reactions proceeded quickly affording the desired product in excellent yields after purification by column chromatography on silica gel. Where the same conversions had been reported using alternative reaction conditions, the advantages of applying microwave irradiation were evident. For example, for substrate **2b** that afforded dihydropyranone **3b** in 83% yield after a reaction time of 90 s, alternative reaction at −20 °C required a prolonged reaction time of 72 h to afford the product in a similar yield of 90% yield.[10] In addition, formation of dihydropyranone **3c** had previously been reported in a lower yield of 70%, with conventional conditions requiring reaction at −78 °C for 2 h without microwave irradiation.[11] Using the method described here the product was formed in 94% yield after 90 s. Substrates **2e** and **2f** were utilized in order to probe whether the chirality of the carbohydrate framework could invoke any diastereocontrol during the formation of the dihydropyran. However, ^{1}H and ^{13}C NMR spectroscopic analysis of dihydropyranone **3e** or **3f** illustrated that each dihydropyranone was formed as a 1:1 mixture of diastereoisomers at C-2. Presumably for substrates **2e** and **2f**, the chiral carbohydrate framework was insufficiently close to the aldehyde functional group involved in the HDAR to offer any stereocontrol.

TABLE 1. Oxa-HDAR with Substituted Aldehydes

Starting material	Product, Yield %
m-Fluorobenzaldehyde **(2a)**	 (3a), 92%
Benzaldehyde **(2b)**	 (3b) 83%
E-Propenylaldehyde **(2c)**	 (3c) 94%
5,6-Dihydro-4*H*-pyran-2-carbaldehyde **(2d)**	 (3d) 83%
 (2e)	 (3e) 76%
 (2f)	 (3f) 67%

In the next stage of the program the microwave-enhanced HDAR using a range of imines was investigated. If successful this would allow rapid access to tetrahydropyridinones. Imines were prepared by reaction of the corresponding aldehyde with benzylamine under anhydrous conditions and these were used in two different protocols, specifically a one-step protocol where the imine was reacted with Danishefsky's diene in situ, without any prior isolation of the imine (method A), as well as a two-step protocol where the imine was isolated and characterized first, before reaction with the diene (method B). The results of these studies are illustrated in Scheme 2 and Table 2. Substrates were again chosen that would allow results to be compared with the conventional HDAR, as well as to allow the efficiencies of the oxa- and aza-HDARs to be compared.

(8) (a) de Melo, E. B.; Gomes, A. S.; Carvalho, I. *Tetrahedron* **2006**, *62*, 10277–10302. (b) Zhou, W. *Curr. Top. Med. Chem.* **2005**, *5*, 1363–1391. (c) Compain, P.; Chagnault, V.; Martin, O. R. *Tetrahedron: Asymmetry* **2009**, *20*, 672–711.

(9) For example see: (a) Lowe, R. F.; Stoodley, R. J. *Tetrahedron Lett.* **1994**, *35*, 6351–6354. (b) Bednarski, M.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 7060–7067.

(10) Keck, G. E.; Li, Y.-X.; Krishnamurthy, D. *J. Org. Chem.* **1995**, *60*, 5995–5999.

(11) Danishefsky, S. J.; Kerwin, J. F. *J. Org. Chem.* **1982**, *47*, 3183–3184.

SCHEME 2. The Diels−Alder Reaction Producing Pyridinone 5

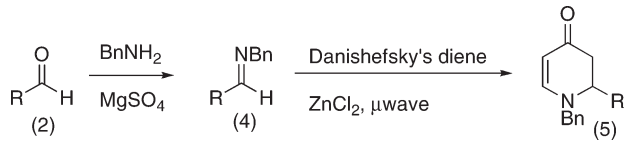
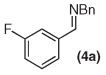
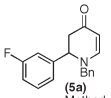
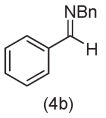
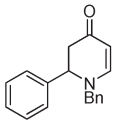
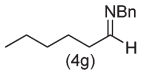
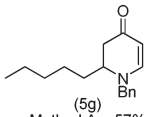
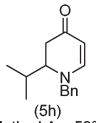


TABLE 2. Aza-HDAR with Substituted Aldehydes

Starting material	Imine	Product, Yield (%)
m- Fluorobenzaldehyde **(2a)**	 (4a)	 (5a) Method A = 86% Method B = 87%
Benzaldehyde **(2b)**	 (4b)	 (5b) Method A = 96% Method B = 98%
Hexanal **(2g)**	 (4g)	 (5g) Method A = 57% Method B = 71%
2-Methylpropanal **(2h)**	 (4h)	 (5h) Method A = 59% Method B = 64%

As can be seen from Table 2, yields were good to excellent with both the one-step and two-step approaches, but yields were generally superior when the two-step protocol was applied. For substrates **2a** and **2b**, the conventional HDAR afforded **5a** and **5b** in yields of 84% and 51%, respectively.[12] By comparing the results of the oxa- and aza-HDAR for substrates **2a** and **2b** it is evident that both HDARs occur with similar efficiency, despite the prerequisite for the formation of an imine, from aldehyde **2a** or **2b**.

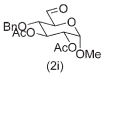
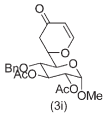
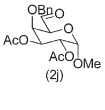
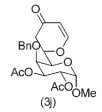
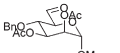
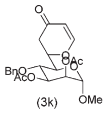
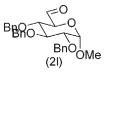
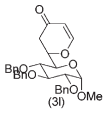
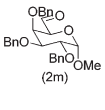
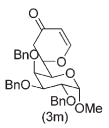
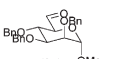
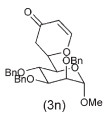
Having proved the validity of using microwave irradiation to enhance the oxa- and aza-HDARs, attention next turned to the feasibility of using more structurally complex aldehydes and imines, which incorporated carbohydrate frameworks, within the methodology. If the HDARs with these substrates were successful, facile entry to *C*-linked disaccharide mimetics, including the more synthetically elusive aza *C*-linked disaccharides, would be achieved.[8] For the carbohydrate derived aldehyde substrates **2i**−**n**, an identical procedure to that described above for the oxa-HDAR with aldehydes **2a**−**f** was utilized. Pleasingly the proof of concept results reported above proved extendable allowing entry to the desired *C*-linked dihydropyrans **3i**−**n** in generally good to very good yields (Table 3).

(12) Ali, T.; Chaunhan, K.; Frost, C. *Tetrahedron Lett.* **1999**, *40*, 5621–5624.

To determine whether high pressure could also be beneficial for optimizing the yield of the HDARs, the HDAR with substrates **2i**−**n** were also performed at pressures of 19 kBar. For comparative purposes, the HDAR was also performed with neither microwave irradiation nor high-pressure conditions. The results of this study are illustrated below in Table 3.

From Table 3 it can be seen that optimum results were generally obtained with microwave irradiation. However, reactions performed under high pressure generally afforded higher yields of the desired products than by simply treating the reactants with a Lewis acid at −78 °C to room temperature. In general, for all reactions, improved yields of the desired products were obtained when acetate groups were present at C-2 and C-3 rather than benzyl ethers. Moreover, the mannose substrates **2k** and **2n** afforded the poorest yields suggesting that the axial C-2 substituent hinders the approach of the diene onto the aldehyde. Indeed for substrate **2n** no HDAR could be effected in the absence of microwave irradiation or high-pressure conditions. The reactions summarized in Table 3 were generally highly stereoselective, with each reaction affording a single diastereoisomer, as evidenced by ^{1}H and ^{13}C NMR spectroscopic analysis of crude reaction mixtures. However, given the free rotation around the C-5,C-6 bond, it proved impossible to determine the absolute stereochemistry of the

TABLE 3. Yields of the HDARs

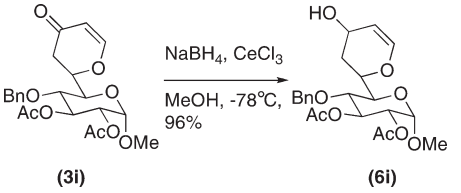
Starting material	Product	Yield (%) Lewis acid plus microwave[a]	Yield (%) High pressure[b]	Yield (%) Lewis acid[c]
 (2i)	 (3i)	75	63	52
 (2j)	 (3j)	67	55	52
 (2k)	 (3k)	66	51	44
 (2l)	 (3l)	65	40	60
 (2m)	 (3m)	62	66	42
 (2n)	 (3n)	43	22	0

[a]Addition of $ZnCl_2$ and reaction under microwave irradiation at 30 °C for 90 s. [b]High-pressure conditions involved reaction at 19 kbar using a Psika pressure system. [c]Addition of $ZnCl_2$ and reaction at −78 °C to room temperature for 7 h.

newly formed stereocenter at C-6, using NMR spectroscopic techniques. The only substrate that afforded a 1:1 epimeric mixture of products at C-6 was substrate **2j**, and this only afforded such an epimeric mixture when the reaction was performed under microwave irradiation.

To further functionalize the HDAR adducts and convert them to closer mimics of natural disaccharide systems, reduction of the ketone functionality within the dihydropyranones **3i**−**n**, to afford the corresponding alcohols **6i**−**n**, was attempted with use of Luche reduction conditions (Scheme 3).

SCHEME 3. Representative Luche Reduction of Dihydropyranone (3i) To Afford Alcohol (6i)



In all cases the reactions progressed successfully in excellent synthetic yields (92−96%) that were in line with literature precedent for similar reduction of pyranones, to afford single diastereoisomers of *C*-linked disaccharide mimetics.[13] To determine the stereochemistry of the newly formed stereogenic center at C-8, relative to that at C-6, a series of NOE experiments were performed. These suggested that the hydrogens at C-6 and C-8 were of a *syn* arrangement. The protecting groups within **6i**−**n** are currently being removed within our laboratories, affording tetrols ready for analysis of their ability to inhibit a range of glycosidase enzymes.

To fully explore the value of this HDAR methodology for preparing *C*-linked disaccharide mimetics, the utility of the imines derived from aldehydes **2i**−**n** in the one-step and two-step aza-HDARs was next probed. Pleasingly these substrates again proved effective precursors to *C*-linked disaccharide mimetics, specifically *C*-linked aza disaccharide mimetics. The best results were again obtained by using the two-step HDAR protocol as when the one-step protocol was utilized, a competing oxa-Diels−Alder reaction occurred, presumably due to the reaction of the aldehydes with Danishefsky's diene before imine formation was complete. For the two-step protocol, experimentation was required to match the reactivity of the imine with solubility in solvents appropriate for the HDAR; reaction of imines derived from aniline, in DCM, proved optimal. Yields in these cases were average to very good and products were again formed as single diastereoisomers at C-6; interestingly when these reactions were performed in the absence of microwave irradiation, or under high-pressure conditions, no HDARs could be effected with starting material being returned (Table 4).

From Table 4 it can be seen that optimum results were generally obtained by using imines derived from methyl glucopyranoside or methyl galactopyranoside rather than methyl mannopyranoside. As observed before for the oxa-HDARs (Table 3), improved yields of the desired products were generally obtained when acetate groups were present at C-2 and C-3 rather than benzyl ethers. It can be seen from Tables 3 and 4 that the dihydropyranones **3i**,**3j**,**3l** and **3n**

TABLE 4. Aza-HDAR with Carbohydrate Derived Imines under Microwave Irradiation

Starting material	Imine	Product	Yield (%)
(2i)	(4i)	(5i)	87
(2j)	(4j)	(5j)	67
(2k)	(4k)	(5k)	17
(2l)	(4l)	(5l)	67
(2m)	(4m)	(5m)	35
(2n)	(4n)	(5n)	37

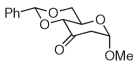
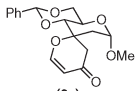
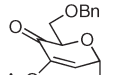
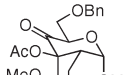
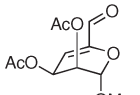
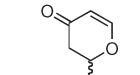
were generally formed in comparable yields to the dihydropyridinones **5i**,**5j**,**5l** and **5n**, respectively. However, the oxa-HDAR proceeded in superior yields for substrates **2k** and **2m** compared with the aza-HDAR by using imines **4k** and **4m**. This reactivity illustrates that entry to *C*-linked aza disaccharides derived from mannose is better achieved by using the tri-*O*-benzyl protected imine **4n** as opposed to the di-*O*-acetyl protected imine **4k**.

To conclude this program, a carbohydrate derived ketone **7a**, enone **7b**, and enal **7c** were next utilized within the oxa-HDARs in an attempt to prepare spiro-carbohydrate derivatives. The effectiveness of Lewis acid, high-pressure, and microwave irradiation on the reactions was again probed. Ketone **7a** was prepared according to a literature protocol,[14] while ketones **7b** and **7c** were formed with Swern oxidation protocols. Interesting reactivity profiles were observed with high-pressure conditions, as illustrated in Table 5. However, in contrast to the HDARs

(13) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226–2227.

(14) Jones, D. N.; Taylor, G. M.; Wood, W. *Tetrahedron Lett.* **1991**, *13*, 1667–1670.

TABLE 5

Ketone	Product	Yield (%) and comment,
		High pressure[1]
 (7a)	 (8a)	43%
		1:1 Mixture of epimers at C-3
 (7b)	 (8b)	69%
 (7c)	 (9c)	48% 1:1 Mixture of epimers at C-6

with aldehydes **2i**−**n**, no reactions could be effected with **7a**−**c** with either conventional heating methodologies or microwave irradiation but reactions did prove effective under high pressure protocols. This reactivity profile presumably reflects both the decreased reactivity of the ketone functional group compared with the aldehyde functional group as well as increased steric effects with ketones **7a**−**c**.

For ketone **7a** the HDAR proceeded as expected to afford the spirocyclic carbohydrate **8a** as a mixture of epimers at C-3. In contrast, for enone **7b**, a Diels−Alder reaction occurred between the electron-deficient alkene within **7b** and the electron-rich Danishefsky's diene, affording the *cis*-decalin derivated structure **8b**. The relative and absolute stereochemistry of the new structure was determined by NOE spectroscopic analysis. For enal **7c** the desired HDAR occurred affording **8c** as a mixture of epimers at C-6. The difference in reactivity profiles between **7b** and **7c** presumably reflects the enhanced reactivity of the aldehyde framework within enal **7c** over the ketone framework within enone **7b**.

Conclusion

In conclusion this study has illustrated the potential of the microwave-enhanced oxa- and aza-HDARs for rapid access to dihydropyranones and tetrahydropyridinones under mild and short reaction conditions. It has also demonstrated the value of using high pressure to enhance the oxa-HDAR, particularly where ketones or enals are used as substrates. In particular this study has allowed access to carbohydrate derivatives including mimetics of *C*-linked disaccharides and aza-*C*-linked disaccharides in synthetically useful yields with high diastereoselectivity. The elaboration of these targets to afford further mimetics of aza-*C*-disaccharides is currently under investigation within our laboratories and will be reported in due course.

Experimental Section

2-(3-Fluorophenyl)-2,3-dihydro-4*H*-pyran-4-one (3a): ν_{max} (NaCl disk/cm^{-1}) 3045 m (Ar, C—H), 1684 s (C=O, ketone stretch), 1634 m (C=C stretch); δ_H ($CDCl_3$, 250 MHz) 2.62 (1H, ddd, $J_{3a,5}$ 1.0, $J_{2,3a}$ 3.5, $J_{3a,3b}$ 17.0, C(3a)H), 2.85 (1H, dd, $J_{2,3b}$ 14.0, $J_{3a,3b}$ 17.0, C(3b)H), 5.42 (1H, dd, $J_{2,3a}$ 3.5, $J_{2,3b}$ 14.0, C(2)H), 5.53 (1H, dd, $J_{3a,5}$ 1.0, $J_{5,6}$ 6.0, C(5)H), 6.90−7.47 (4H, m, ArH), 7.55 (1H, d, $J_{5,6}$ 6.0, C(6)H); δ_c ($CDCl_3$, 62.8 MHz) 43.7 (C-3), 80.5 (d, *J* 1.8, C-2), 107.1 (C-5), 113.5 (d, *J* 22.8, C-2′), 116.2 (d, *J* 20.7, C-4′), 121.9 (d, *J* 3.1, C-6′), 130.9 (d, *J* 8.1, C-5′), 140.7 (d, *J* 7.2, C-1′), 163.3 (d, *J* 246.2, C-3′), 163.3 (C-6), 191.9 (C-4); *m*/*z* (CI) 122 (10%), 163 (15%), 193 (MH^+, 17%); $[C_{11}H_{10}FO_2]^+$ requires 193.0665, found 193.0668.

2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (3b): ν_{max} ($CHCl_3$, thin film) 3062 (C—H), 1679 (C=C), 1595, 1403 (C=C), 1271, 1228, 1038 (C−O) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) 2.60 (1H, ddd, J_{3-5} 1.5, J_{3-2} 3.5, J_{3-3} 17.0, H3), 2.85 (1H, dd, J_{3-2} 14.0, J_{3-3} 17.0, H3), 5.36 (1H, dd, J_{2-3} 3.5, J_{2-3} 14.0, H2), 5.47 (1H, dd, J_{5-3} 1.0, J_{5-6} 6.0, H5), 7.28−7.48 (6H, m, Ar−H, H6); ^{13}C NMR ($CDCl_3$, 62.8 MHz) 42.34 (C3), 80.08 (C2), 106.33 (C5), 125.08−129.11 (Ar−C), 162.26 (C6); *m*/*z* (CI) MH^+ ($C_{11}H_{11}O_2$) requires 175.0714, found 175.0754.

((*E*)-Propenyl)-2,3-dihydro-4*H*-pyran-2-one (3c): ν_{max} (NaCl disk/cm^{-1}) 1680 s (C=O, stretch), 1640 m (C=C, stretching), 1435 m (C=C, stretch); δ_H ($CDCl_3$, 250 MHz) 1.70 (3H, ddd, *J* 1, *J* 1.5, *J* 2.5, CH_3), 2.66−2.68 (2H, m, C(3)H), 4.53 (1H, dd, $J_{2,3b}$ 6.5, $J_{2,3a}$ 12.5, C(2)H), 5.50−5.59 (1H, m, RCH=$CHCH_3$), 5.56 (1H, d, $J_{5,6}$ 6.0, C(5)H), 5.70−5.72 (1H, m, RCH=$CHCH_3$), 7.62 (1H, d, $J_{5,6}$ 6.0, C(6)H); δ_C ($CDCl_3$, 62.8 MHz) 18.0 (Me), 47.3 (C-3), 69.3 (C-2), 106.4 (C-5), 127.3 (RC=CCH_3), 132.5 (RC=CCH_3), 163.9 (C-6), 199.9 (C-4); *m*/*z* (CI) 111 (14%), 129 (4%), 138 (M^+, 20%), 139 (MH^+, 72%); $[C_8H_{11}O_2]^+$ requires 139.0759, found 139.0754.

2,3,5′,6′-Tetrahydro-4′*H*-[2,2′]bipyranyl-4-one (3d): ν_{max} (NaCl disk/cm^{-1}) 1755 s (C=O, stretch), 1654 m (C=C conjugated double bond stretch), 1435 m (C=C stretch); δ_H ($CDCl_3$, 250 MHz) 2.03−2.24 (2H, m, C(5′)H), 2.48 (1H, ddd, $J_{3a,5}$ 1.0, $J_{2,3a}$ 3.5, $J_{3a,3b}$ 16.5, C(3a)H), 2.73 (1H, dd, $J_{2,3b}$ 13.5, $J_{3a,3b}$ 16.5, C(3b)H), 3.75−3.84 (2H, m, C(6′)H), 4.19−4.22 (2H, m, C(4′)H), 4.80 (1H, dd, $J_{2,3a}$ 3.5, $J_{2,3b}$ 13.5, C(2)H), 5.44 (1H, dd, $J_{3a,5}$ 1.0, $J_{5,6}$ 6.0, C(5)H), 5.94−5.97 (1H, m, C(3′)H), 7.35 (1H, $J_{5,6}$ 6.0, C(6)H); δ_C ($CDCl_3$, 62.8 MHz) 25.2 (C-5′), 40.7 (C-3), 64.4 (C-6′), 65.0 (C-4′), 80.4 (C-2′), 107.6 (C-5), 124.2 (C-3′), 134.3 (C-2′), 163.1 (C-6), 192.4 (C-4); *m*/*z* (CI) 150 (19%), 163 (21%), 181 (MH^+, 100%), $[C_{10}H_{13}O_3]^+$ requires 181.0865, found 181.0861.

Acetic acid (2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-6-acetoxymethyl-2-[2-nitro-4-(4-oxo-3,4-dihydro-2*H*-pyran-2-yl)phenoxy]tetrahydropyran-3-yl ester (3e): mp 87−88 °C; ν_{max} (NaCl disk/cm^{-1}) 3024 m (C−H), 1740 s (C=O, carbonyl ester stretch), 1734 s (C=O, ketone stretch), 1648 m (C=C stretch), 1550 s (nitro group stretch), 1145 s (R—O—CH_3 stretch); δ_H ($CDCl_3$, 400 MHz) 1.97−2.10 (12H, m, CH_3COR), 2.70 (1H, ddd, $J_{3a,5}$ 1.0, $J_{2,3a}$ 3.5, $J_{3a,3b}$ 17.0, C(3a)H), 2.85 (1H, ddd, $J_{3b,6}$ 2.0, $J_{2,3b}$ 14.0, $J_{3a,3b}$ 17.0, C(3b)H), 3.89 (1H, ddd, *J* 3.0, *J* 4.5, *J* 7.5, C(5″)H), 4.21−4.30 (2H, m, C(6″)H), 5.17 (1H, d, $J_{1'',2''}$ 2.0, C(1″)H), 5.24−5.27 (1H, m, C(4″)H), 5.30 (1H, dd, $J_{1'',2''}$ 2.0, $J_{2'',3''}$ 8.5, C(2″)H), 5.34 (1H, dd, $J_{2'',3''}$ 8.5, $J_{3'',4''}$ 9.0, C(3″)H), 5.47 (1H, dd, $J_{2,3a}$ 3.5, $J_{2,3b}$ 14.0, C(2)H), 5.57 (1H, dd, $J_{3a,5}$ 1.0, $J_{5,6}$ 6.0, C(5)H), 7.40 (1H, dd, $J_{5',6'}$ 2.0, *J* 8.5, Ar(6′)H), 7.49 (1H, d, $J_{3b,6}$ 2.0, $J_{5,6}$ 6.0, C(6)H), 7.53−757 (1H, m, Ar(3′)H), 7.90 (1H, dd, $J_{5',6'}$ 2.0, *J* 6.0, Ar(5′)H); δ_C ($CDCl_3$, 100.4 MHz) 20.6−20.7 (4×CH_3COR), 43.1 (C-3), 61.7 (C-6″), 68.0 (C-4″), 70.4 (C-2″), 72.2 (C-3″), 72.4 (C-5″), 79.1 (C-2), 100.1 (C-1″), 100.1 (C-1″), 107.9 (C-5), 120.3 (C-6′), 120.3 (C-6′), 123.0 (C-5′), 131.1 (C-3′), 131.1 (C-3′), 134.1 (C-4′), 141.4 (C-1′), 141.5 (C-1′), 149.3 (C-2′), 162.6 (C-6), 169.3 (CH_3COOR), 170.5 (CH_3COOR), 190.8 (C-4); *m*/*z* (CI) 169 (39%), 331 (100%), 332 (15%), 566 (MH^+, 42%); $[C_{25}H_{28}NO_{14}]^+$ requires 566.1510, found 566.1492.

Acetic acid (2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-6-acetoxymethyl-2-[2-nitro-4-(4-oxo-3,4-dihydro-2*H*-pyran-2-yl)phenoxy]tetrahydropyran-3-yl ester (3f): ν_{max} (NaCl disk/cm^{-1}) 3035 m

(C−H), 1745 s (C═O, carbonyl ester stretch), 1720 s (C═O, ketone stretch), 1655 m (C═C, stretch), 1140 s (R—O—CH_3, stretch); δ_H ($CDCl_3$, 250 MHz) 1.97−2.10 (12H, m, CH_3COR), 2.67 (1H, ddd, $J_{3a,5}$ 1.0, $J_{2,3a}$ 3.5, $J_{3a,3b}$ 16.5, C(3a)H), 2.90 (1H, dd, $J_{2,3b}$ 14.0, $J_{3a,3b}$ 16.5, C(3b)H), 3.91 (1H, ddd, J 3.5, J 5.0, J 7.5, C(5″)H), 4.21−4.30 (2H, m, C(6″)H), 5.14 (1H, d, $J_{1'',2''}$ 2.0, C(1″)H), 5.24−5.27 (1H, m, C(4″)H), 5.26 (1H, dd, $J_{1'',2''}$ 2.0, $J_{2'',3''}$ 7.5, C(2″)H), 5.31 (1H, dd, $J_{2'',3''}$ 7.5, $J_{3'',4''}$ 8.5, C(3″)H), 5.47 (1H, dd, $J_{2,3a}$ 3.5, $J_{2,3b}$ 14.0, C(2)H), 5.57 (1H, dd, $J_{3a,5}$ 1.0, $J_{5,6}$ 5.5, C(5)H), 7.05 (1H, d, $J_{5',6'}$ J 8.0, Ar(6′)H), 7.08 (1H, d, $J_{2',3'}$ 7.0, Ar(2′)H), 7.49 (1H, d, $J_{5,6}$ 5.5, C(6)H), 7.42 (1H, d, $J_{2',3'}$ 7.0, Ar(3′)H), 7.45 (1H, $J_{5',6'}$ 8.0, Ar(5′)H); δ_C ($CDCl_3$, 100.4 MHz) 20.6−20.7 (4×CH_3COR), 43.2 (C-3), 61.9 (C-6″), 68.2 (C-4″), 71.0 (C-2″), 72.1 (C-3″), 72.6 (C-5″), 80.5 (C-2), 80.6 (C-2), 98.9 (C-1″), 107.4 (C-5), 117.2 (C-6′ and C-2′), 127.7 (C-5′ and C-3′), 132.0 (C-4′), 140.4 (C-1′), 163.3 (C-6), 169.3−170.8 (CH_3COOR), 192.8 (C-4); m/z (CI) 553 (MH^+, 42%), 456 (M − $C_5H_5O_2$, 43%); $[C_{27}H_{37}O_{12}]^+$ requires 553.2287, found 553.2277.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-one glucopyranoside (3i): $[\alpha]^{20}_D$ +27.0 (c 1.0, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2916 (C—H), 1749 (C═C), 1678 (C═O), 1595, 1369 (C—H), 1240, 1055 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 2.02 (3H, s, $COCH_3$), 2.08 (3H, s, $COCH_3$), 2.25 (1H, ddd, J_{7-9} 1.0, J_{7-6} 3.5, J_{7-7} 17.0, H7), 3.01 (1H, dd, J_{7-6} 14.5, J_{7-7} 17.0, H7), 3.35 (3H, s, OCH_3), 3.67 (1H, d, J_{5-4} 9.5, H5), 3.90 (1H, t, J_{4-3} = J_{4-5} 9.5, H4), 4.55 (1H, d, J 11.5, 1×$BnCH_2$), 4.63−4.69 (2H, m, H6, 1×$BnCH_2$), 4.86 (1H, dd, J_{2-1} 3.5, J_{2-3} 10.0, H2), 4.93 (1H, d, J_{1-2} 3.5, H1), 5.39 (1H, dd, J_{9-7} 1.0, J_{9-10} 7.0, H9), 5.56 (1H, dd, J_{3-4} 9.5, J_{3-2} 10.0, H3), 7.21−7.36 (6H, m, Ar−H, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 20.8 ($COCH_3$), 20.9 ($COCH_3$), 37.8 (C7), 55.3 (OCH_3), 70.3 (C5), 71.0 (C2), 72.3 (C3), 74.6 (C4), 74.9 ($BnCH_2$), 75.2 (C6), 97.0 (C1), 107.2 (C9), 128.2−128.6 (Ar−C), 162.3 (C10), 169.8 ($COCH_3$), 170.4 ($COCH_3$), 192.2 (C8); m/z (CI) MNa^+ ($C_{22}H_{26}O_9Na$) requires 457.1469, found 457.1468.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-one galactopyranoside (3j): ν_{max} ($CHCl_3$, thin film) 2924 (C−H), 1744 (C═C), 1666 (C═O), 1600, 1440 (C—H), 1359, 1225, 1047 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) 2.06 (3H, s, $COCH_3$), 2.07 (3H, s, $COCH_3$), 2.56 (1H, app s, H7), 2.79 (1H, dd, J_{7-6} 5.0, J_{7-7} 7.5, H7), 3.34 (3H, s, OCH_3), 3.73 (3H, s, OCH_3), 3.95 (1H, app d, J_{5-6} 10.0, H5), 4.23 (1H, app s, H4), 4.50−4.61 (3H, m, H6, $BnCH_2$), 4.99 (1H, d, J_{1-2} 2.5, H1), 5.32−5.33 (2H, m, H2, H3), 5.41 (1H, d, J_{9-10} 5.0, H9), 5.62 (1H, d, J_{9-10} 12.5, H9), 7.13 (1H, d, J_{10-9} 5.0, H10), 7.28−7.33 (5H, m, Ar−H), 7.63 (1H, d, J_{10-9} 12.5, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 20.90 ($COCH_3$), 21.10 ($COCH_3$), 38.35 (C7), 55.50 (OCH_3), 57.53 (OCH_3), 68.61 (C2/C3), 69.87 (C5), 70.45 (C2/C3), 73.66 (C4), 75.37 ($BnCH_2$), 97.34 (C1), 106.67 (C9), 107.67 (C9), 128.11−131.02 (Ar−C), 162.16 (C10), 163.95 (C10); m/z (CI) MH^+ ($C_{22}H_{27}O_9$) requires 435.1650, found 435.1646.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-one mannopyranoside (3k): ν_{max} ($CHCl_3$, thin film) 3440, 2932 (C−H), 1750, 1678 (C═C), 1597 (C═O), 1405, 1369, 1244, 1137 (C—O—C), 1085 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) 2.00 (3H, s, $COCH_3$), 2.17 (3H, s, $COCH_3$), 2.27 (1H, ddd, J_{7-9} 1.0, J_{7-6} 3.5, J_{7-7} 17.0, H7), 3.07 (1H, dd, J_{7-6} 15.0, J_{7-7} 17.0, H7), 3.36 (3H, s, OCH_3), 3.67 (1H, dd, J_{5-6} 1.5, J_{5-4} 10.0, H5), 4.12 (1H, t, J_{4-3} = J_{4-5} 10.0, H4), 4.59 (1H, d, J 11.5, 1×$BnCH_2$), 4.72−4.76 (4H, m, H1, H6, 1×$BnCH_2$), 5.29 (1H, dd, J_{2-1} 1.5, J_{2-3} 3.5, H2), 5.34 (1H, dd, J_{3-2} 3.5, J_{3-4} 10.0, H3), 5.42 (1H, dd, J_{9-7} 1.0, J_{9-10} 6.0, H9), 7.24−7.37 (6H, m, H10, Ar−H); ^{13}C NMR ($CDCl_3$, 100.1 MHz) 20.9 ($COCH_3$), 21.0 ($COCH_3$), 37.9 (C7), 55.3 (OCH_3), 69.7 (C2), 71.3 (C5), 71.6 (C4), 72.1 (C3), 75.1 ($BnCH_2$), 75.5 (C6), 99.1 (C1), 107.4 (C9), 127.9−128.6 (Ar−C), 162.6 (C10), 169.8 ($COCH_3$), 170.0 ($COCH_3$), 192.5 (C8); m/z (CI) MNa^+ ($C_{22}H_{26}O_9Na$) requires 457.1475, found 457.1469.

Methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyran-8-one glucopyranose (3l): $[\alpha]^{20}_D$ +64.2 (c 1.01, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2916 (C—H), 2091, 1650 (C═O), 1441 (C—H), 1357, 1276, 1093 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) 2.21 (1H, ddd, J_{7-9} 1.0, J_{7-6} 3.5, J_{7-7} 17.0, H7), 2.97 (1H, dd, J_{7-6} 15.0, J_{7-7} 17.0, H7), 3.34 (3H, s, OCH_3), 3.54−3.57 (2H, m, H2, H5), 3.74 (1H, t, J_{4-3} = J_{4-5} 10.0, H4), 4.01 (1H, t, J_{3-2} = J_{3-4} 10.0, H3), 4.59−4.67 (4H, m, H1, H6, 2×$BnCH_2$), 4.80−4.91 (3H, m, 3×$BnCH_2$), 5.01 (1H, d, J 7.0, $BnCH_2$), 5.36 (1H, dd, J_{9-7} 1.0, J_{9-10} 6.0, H9), 7.15 (1H, d, J_{10-9} 6.0, H10), 7.22−7.39 (15H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 37.9 (C7), 55.3 (OCH_3), 70.3 (C5), 73.5 ($ArCH_2$), 75.1 ($ArCH_2$), 75.5 (C6), 75.8 (C4), 75.9 ($ArCH_2$), 79.6 (C2), 82.2 (C3), 98.4 (C1), 107.1 (C9), 127.8−128.5 (Ar−C), 162.6 (C10), 192.6 (C8); m/z (CI) MNa^+ ($C_{32}H_{34}O_7Na$) requires 553.2197, found 553.2197.

Methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyran-8-one galactopyranoside (3m): $[\alpha]^{20}_D$ −5.1 (c 1.0, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2916 (C—H), 1675 (C═C), 1598 (C═O), 1496, 1453 (C—H), 1402, 1353, 1272, 1096 (C—O), 1046 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) 2.45 (1H, dd, J_{7-6} 13.0, J_{7-7} 17.0, H7), 2.72 (1H, ddd, J_{7-9} 1.0, J_{7-6} 4.0, J_{7-7} 17.0, H7), 3.32 (1H, s, OCH_3), 3.77 (1H, dd, J_{5-4} 0.5, J_{5-6} 9.0, H5), 3.94 (1H, dd, J_{3-4} 3.0, J_{3-2} 10.0, H3), 4.04 (1H, dd, J_{2-1} 3.5, J_{2-3} 10.0, H2), 4.08 (1H, dd, J_{4-5} 0.5, J_{4-3} 3.0, H4), 4.53 (1H, ddd, J_{6-7} 4.0, J_{6-5} 9.0, J_{6-7} 13.0, H6), 4.62−4.70 (3H, m, H1, 2×$BnCH_2$), 4.79 (1H, d, J 12.0, 1×$BnCH_2$), 4.85 (1H, d, J 12.0, 1×$BnCH_2$), 4.91 (1H, d, J 12.0, 1×$BnCH_2$), 5.35 (1H, dd, J_{9-7} 1.0, J_{9-10} 6.0, H9), 7.01 (1H, d, J_{10-9} 6.0, H10), 7.26−7.41 (15H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 100.1 MHz) 38.6 (C7), 55.5 (OCH_3), 70.5 (C5), 73.2 (C4), 73.6 ($BnCH_2$), 73.7 ($BnCH_2$), 74.8 ($BnCH_2$), 75.6 (C6), 76.2 (C2), 78.9 (C3), 99.0 (C1), 107.6 (C9), 127.5−128.6 (Ar−C), 138.2−138.6 (Ar−C), 161.9 (C10), 191.9 (C8); m/z (CI) MH^+ ($C_{32}H_{34}O_7Na$) requires 553.2202, found 553.2203.

Methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyran-8-one mannopyranoside (3n): $[\alpha]^{20}_D$ +58.2 (c 1.0, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 3435, 2914 (C—H), 1677 (C═C), 1595 (C═O), 1453, 1403, 1361, 1276, 1124 (C—O—C), 1068 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) 2.22 (1H, ddd, J_{7-9} 1.0, J_{7-6} 3.5, J_{7-7} 15.0, H7), 3.08 (1H, dd, J_{7-7} 15.0, J_{7-6} 17.0, H7), 3.27 (3H, s, OCH_3), 3.48−3.52 (1H, m, H5), 3.80 (1H, dd, J_{2-1} 2.0, J_{2-3} 3.0, H2), 3.87 (1H, dd, J_{3-2} 3.0, J_{3-4} 9.5, H3), 4.23 (1H, t, J_{4-3} = J_{4-5} 9.5, H4), 4.61−4.66 (1H, m, 1×$BnCH_2$), 4.70−4.77 (4H, m, 2×$BnCH_2$, H1, H6), 4.96 (1H, d, J 11.0, 1×$BnCH_2$), 5.38 (1H, dd, J_{9-7} 1.0, J_{9-10} 6.0, H9), 7.24−7.37 (16H, m, Ar−H, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 38.2 (C7), 55.1 (OCH_3), 71.9 (C5), 72.4 ($BnCH_2$), 73.1 ($BnCH_2$), 73.3 (C4), 74.1 (C2), 75.5 ($BnCH_2$), 76.0 (C6), 80.8 (C3), 100.0 (C1), 107.1 (C9), 127.8−128.7 (Ar−C), 163.6 (C10), 193.5 (C8); m/z (CI) MNa^+ ($C_{32}H_{34}O_7Na$) requires 553.2202, found 553.2197.

1-Benzyl-2-(3-fluorophenyl)-2,3-dihydropyridin-4-one (5a). ν_{max} ($CHCl_3$, thin film) 3029 (C—H), 2919 (C—H), 1638 (C═O), 1594, 1486, 1449 (C—N), 1383, 1213, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 2.63 (1H, dd, J_{3-2} 7.0, J_{3-3} 16.5, H3), 2.87 (1H, dd, J_{3-2} 7.0, J_{3-3} 16.5, H3), 4.13 (1H, d, J 15.0, $BnCH_2$), 4.38 (1H, d, J 15.0, $BnCH_2$), 4.50 (1H, t, J_{2-3} = J_{2-3} 7.0, H2), 5.09 (1H, d, J_{5-6} 7.5, H5), 6.96−7.37 (9H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 100.4 MHz) 43.39 (C3), 57.54 ($BnCH_2$), 60.05 (C2), 98.96 (C5), 113.90 (d, J 22.0, C2′), 115.34 (d, J 21.0, C4′), 122.70 (d, J 2.9, C6′), 127.71−129.05 (Ar−C), 130.76 (d, J 8.2, C5′), 141.17 (d, J 6.6, C1′), 154.04 (C6), 163.06 (d, J 246.0, C3′), 189.84 (C4); m/z (CI) MH^+ ($C_{18}H_{17}FNO$) requires 282.1289, found 282.1286.

1-Benzyl-2-phenyl-2,3-dihydropyridin-4-one (5b): ν_{max} ($CHCl_3$, thin film) 3028 (C—H), 1636 (C═O), 1576, 1451 (C—N), 1381, 1357, 1204, 1158; ^1H NMR ($CDCl_3$, 250 MHz) 2.69 (1H, dd, J_{3-2}

8.0, J_{3-3} 16.5, H3), 2.86 (1H, dd, J_{3-2} 8.0, J_{3-3} 16.5, H3), 4.13 (1H, d, J 15.0, $BnCH_2$), 4.34 (1H, d, J 15.0, $BnCH_2$), 4.50 (1H, t, $J_{2-3} = J_{3-2}$ 8.0, H2), 5.10 (1H, d, J_{5-6} 7.5, H5), 7.23−7.46 (11H, m, Ar−H, H6); ^{13}C NMR ($CDCl_3$, 62.8 MHz) 29.43 (C3), 43.97 ($BnCH_2$), 61.04 (C2), 99.00 (C5), 127.52−129.48 (Ar−C), 154.87 (C6), 190.95 (C4); m/z (CI) MH^+ ($C_{18}H_{18}NO$) requires 264.1388, found 264.1378.

1-Benzyl-2-pentyl-2,3-dihydropyridin-4-one (5g): ν_{max} ($CHCl_3$, thin film) 2927 (C—H), 2857, 1697, 1616 (C=O), 1518, 1451 (C—N), 1403, 1205, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) 0.87 (3H, t, J 7.0, H11), 1.19−1.32 (5H, m, 1×H8, H9, H10), 1.35−1.44 (1H, m, H8), 1.55−1.64 (1H, m, H7), 1.77−1.87 (1H, m, H7), 2.65 (1H, dd, J_{3-2} 2.0, J_{3-3} 17.0, H3), 2.87 (1H, dd, J_{3-2} 7.5, J_{3-3} 17.0, H3), 3.47−3.51 (1H, m, H2), 4.43 (1H, d, J 15.0, $BnCH_2$), 4.53 (1H, d, J 15.0, $BnCH_2$), 5.39 (1H, d, J_{5-6} 7.0, H5), 7.33 (1H, d, J_{6-5} 7.0, H6), 7.25−7.44 (5H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 100.4 MHz) 13.98 (C11), 22.43, 25.05, 31.52 (C8, C9, C10), 28.30 (C7), 37.32 (C3), 56.15 (C2), 58.76 ($BnCH_2$), 96.45 (C5), 127.69−129.37 (Ar−C), 157.23 (C6); m/z (CI) MH^+ ($C_{17}H_{24}NO$) requires 258.1852, found 258.1848.

1-Benzyl-2-isopropyl-2,3-dihydropyridin-4-one (5h): ν_{max} ($CHCl_3$, thin film) 2963 (C—H), 2237, 1698 (C=O), 1588, 1453 (C—N), 1407, 1360, 1263, 1201, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) 0.97 (3H, d, J 3.5, $CH(CH_3)_2$), 0.98 (3H, d, J 3.0, $CH(CH_3)_2$), 2.29 (1H, m, H7), 2.69 (1H, dd, J_{3-2} 3.0, J_{3-3} 17.5, H3), 3.30 (1H, ddd, J_{2-3} 3.0, J_{2-7} 5.5, J_{2-3} 8.0, H2), 4.46 (1H, d, J 15.0, $BnCH_2$), 4.54 (1H, d, J 15.0, $BnCH_2$), 5.24 (1H, d, J_{5-6} 7.0, H5), 7.30 (1H, d, J_{6-5} 7.0, H6), 7.24−7.43 (5H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 100.4 MHz) 17.91 ($CH(CH_3)_2$), 19.46 ($CH(CH_3)_2$), 29.16 ($CH(CH_3)_2$), 35.04 (C3), 59.17 ($BnCH_2$), 61.19 (C2), 96.88 (C5), 127.42−129.27 (Ar−C), 156.77 (C6), 192.62 (C4); m/z (CI) MH^+ ($C_{15}H_{19}NO$) requires 230.1539, found 230.1533.

***N*-Phenyl methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyridin-8-one glucopyranoside (5i):** $[\alpha]^{20}_D$ +42.1 (c 1.1, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2918 (C—H), 1748 (C=C), 1683 (C=O), 1653, 1574, 1493 (C—N), 1200, 1135 (C—O—C), 1051 (C−O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) 1.88 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 2.63 (1H, dd, J_{7-6} 2.5, J_{7-7} 17.0, H7), 3.27 (1H, t, $J_{4-3} = J_{4-5}$ 9.0, H4), 3.28 (1H, dd, J_{7-6} 9.5, J_{7-7} 17.0, H7), 3.33 (1H, dd, J_{4-5} 7.5, J_{4-3} 8.5, H4), 3.36 (3H, s, OCH_3), 3.47 (1H, d, J 11.0, $BnCH_2$), 3.84 (1H, dd, J_{5-6} 2.5, J_{5-4} 9.0, H5), 4.23 (1H, d, J 11.0 $BnCH_2$), 4.69 (1H, app d, J 8.5, H6), 4.75 (1H, dd, J_{2-1} 3.5, J_{2-3} 10.5, H2), 4.83 (1H, d, J_{1-2} 3.5, H1), 5.28 (1H, d, J_{9-10} 7.5, H9), 5.43 (1H, dd, J_{3-4} 9.0, J_{3-2} 10.5, H3), 7.23−7.43 (6H, m, Ar−H, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 21.0 ($COCH_3$), 21.1 ($COCH_3$), 39.6 (C7), 56.1 (OCH_3), 56.4 (C6), 71.1 (C2), 73.1 (C3), 73.3 ($BnCH_2$), 74.6 (C5), 76.9 (C4), 96.7 (C1), 100.7 (C9), 123.0 (C10), 127.3−130.4 (Ar−C), 169.8 ($COCH_3$), 170.1 ($COCH_3$), 192.4 (C8); (MH^+ 510.2122) found 510.2138, $C_{28}H_{32}NO_8$ requires 510.2128.

***N*-Phenyl methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyridin-8-one galactopyranoside (5j):** $[\alpha]^{20}_D$ −109.0 (c 0.93, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2929 (C—H), 1744 (C=C), 1642 (C=O), 1575, 1494 (C—N), 1370, 1223, 1140 (C—O—C), 1047 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) 2.00 (1H, app d, J 17.0, H7), 2.08 (3H, s, $COCH_3$), 2.11 (3H, s, $COCH_3$), 2.73 (1H, dt, $J_{7-6} = J_{7-9}$ 2.5, J_{7-7} 17.0, H7), 3.20 (3H, s, OCH_3), 3.99 (1H, app d, J 2.5, H4), 4.46−4.49 (3H, m, H5, H6, 1×$BnCH_2$), 4.89 (1H, d, J_{1-2} 3.0, H1), 4.96 (1H, d, J 11.5, 1×$BnCH_2$), 5.24 (1H, dd, J_{9-7} 1.0, J_{9-10} 7.5, H9), 5.35 (1H, dd, J_{2-1} 3.0, J_{2-3} 11.0, H2), 5.40 (1H, dd, J_{3-4} 2.5, J_{3-2} 11.0, H3), 7.26−7.37 (10H, m, Ar−H), 7.41 (1H, d, J_{10-9} 7.5, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 20.9 ($COCH_3$), 21.1 ($COCH_3$), 37.2 (C7), 55.2 (OCH_3), 57.7 (C6), 65.1 (C5), 68.9 (C2), 70.8 (C3), 74.4 (C4), 75.1 ($BnCH_2$), 96.9 (C1), 102.8 (C9), 119.6−137.3 (Ar−C), 146.9 (C10), 169.8 ($COCH_3$), 170.6 ($COCH_3$), 190.6 (C8); m/z (CI) MH^+ ($C_{28}H_{32}NO_8$) requires 510.2122, found 510.2128.

***N*-Phenyl methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyridin-8-one mannopyranose (5k):** $[\alpha]^{20}_D$ −110.1 (c 0.68, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2921 (C—H), 1751 (C=C), 1638 (C=O), 1584, 1489 (C—N), 1363, 1220, 1134 (C—O—C), 1076 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz), 1.82 (3H, s, OCH_3), 2.16 (3H, s, OCH_3), 2.73 (1H, app d, J_{7-7} 17.0, H7), 3.20−3.37 (4H, m, OCH_3, H7), 3.49 (1H, dd, J_{4-3} 8.5, J_{4-5} 10.0, H4), 3.74 (1H, d, J 11.5, $BnCH_2$), 3.75 (1H, dd, J_{5-6} 2.0, J_{5-4} 9.5, H5), 4.34 (1H, d, J 11.5, $BnCH_2$), 4.63 (1H, app s, H1), 4.73 (1H, app d, J 9.5, H6), 5.16−5.19 (2H, m, H2, H3), 5.38 (1H, d, J_{9-10} 7.5, H9), 7.12−7.43 (11H, m, Ar−C, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 20.80 ($COCH_3$), 20.93 ($COCH_3$), 39.58 (C7), 55.78 (OCH_3), 56.83 (C6), 69.85 (C2), 72.68 (C3), 73.58 ($BnCH_2$), 73.93 (C4), 74.89 (C5), 122.92−129.91 (Ar−C), 169.52 ($COCH_3$), 169.62 ($COCH_3$); m/z (CI) MH^+ ($C_{28}H_{32}O_8N$) requires 510.2128, found 510.2119.

***N*-Phenyl methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyridin-8-one glucopyranose (5*l*):** $[\alpha]^{20}_D$ +15.3 (c 0.79, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2916 (C—H), 1651 (C=O), 1584, 1494, 1454 (C−N), 1258, 1208, 1090 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) 2.52 (1H, d, J 16.5, H7), 3.15 (1H, dd, J_{7-6} 8.5, J_{7-7} 16.5, H7), 3.21 (1H, dd, J_{4-3} 9.0, J_{4-5} 10.0, H4), 3.36 (3H, s, OCH_3), 3.41 (1H, d, J 11.5, 1×$BnCH_2$), 3.47 (1H, dd, J_{2-1} 3.5, J_{2-3} 10.0, H2), 3.77 (1H, dd, J_{5-6} 2.5, J_{5-4} 10.0, H5), 3.87 (1H, dd, J_{3-4} 9.0, J_{3-2} 10.0, H3), 4.61−4.66 (2H, m, H1, H6, 2×$BnCH_2$), 4.73 (1H, d, J 12.0, 2×$BnCH_2$), 4.91 (1H, d, J 12.0, 1×$BnCH_2$), 5.08 (1H, d, J_{9-10} 8.0, H9), 7.10−7.34 (21H, m, 20×Ar−H, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 40.2 (C7), 55.8 (OCH_3), 56.3 (C6), 73.2 ($BnCH_2$), 73.2 ($BnCH_2$), 74.5 (C5), 75.7 ($BnCH_2$), 77.7 (C4), 80.1 (C2), 82.8 (C3), 97.5 (C1), 100.8 (C9), 122.2−138.5 (Ar−C), 150.9 (C10), 191.1 (C8); m/z (CI) MH^+ ($C_{38}H_{40}O_6N$) requires 606.2856, found 606.2873.

***N*-Phenyl methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyridin-8-one galactopyranose (5m):** $[\alpha]^{20}_D$ −108.8 (c 0.9, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2915 (C—H), 2366, 1641 (C=O), 1576, 1495 (C—N), 1346, 1200, 1124 (C—O—C), 1048 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) 1.97 (1H, app d, J_{7-7} 17.5, H7), 2.71 (1H, dd, J_{7-6} 6.0, J_{7-7} 17.5, H7), 3.21 (3H, s, OCH_3), 3.97−4.04 (3H, m, H4, $BnCH_2$), 4.06 (1H, dd, J_{3-4} 3.5, J_{3-2} 10.0, H3), 4.35 (1H, d, J_{5-6} 10.0, H5), 4.46 (1H, dd, J_{6-7} 6.0, J_{6-5} 10.0, H6), 4.59−4.71 (2H, m, H1, H2), 4.81−4.90 (2H, m, $BnCH_2$), 5.09 (1H, d, J 11.5, 1×$BnCH_2$), 5.31 (1H, d, J_{9-10} 7.5, H9), 7.25−7.37 (20H, m, Ar−H), 7.42 (1H, d, J_{10-9} 7.5, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 36.4 (C7), 55.2 (OCH_3), 58.1 (C6), 65.4 (C5), 73.6 (C2), 73.7 ($BnCH_2$), 74.4 ($BnCH_2$), 76.2 (C3), 79.6 (C4), 98.6 (C1), 101.7 (C9), 120.1−138.5 (Ar−C), 148.9 (C10), 191.9 (C8); m/z (CI) MH^+ ($C_{38}H_{40}NO_6$) requires 606.2850, found 606.2854.

***N*-Phenyl methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyridin-8-one mannopyranose (5n):** $[\alpha]^{20}_D$ −2.1 (c 1.1, $CHCl_3$); ν_{max} ($CHCl_3$, thin film) 2916 (C—H), 1643 (C=O), 1584, 1493 (C—N), 1453, 1203, 1098 (C—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) 2.57 (1H, d, J_{7-7} 16.5, H7), 3.22 (1H, dd, J_{7-6} 8.0, J_{7-7} 16.5, H7), 3.27 (3H, s, OCH_3), 3.64 (1H, t, $J_{4-3} = J_{4-5}$ 10.0, H4), 3.71−3.74 (1H, m, H5), 3.80 (1H, dd, J_{3-2} 3.0, J_{3-4} 10.0, H3), 4.49−4.74 (9H, m, 3×$BnCH_2$, H1, H2, H6), 5.15 (1H, d, J_{9-10} 7.5, H9), 7.13−7.38 (20H, m, Ar−H, H10); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 40.36 (C7), 55.25 (OCH_3), 57.62 (C6), 71.83 ($BnCH_2$), 72.67 ($BnCH_2$), 73.71 ($BnCH_2$), 74.85 (C5), 74.97 (C4), 80.75 (C3), 98.50 (C1), 100.39 (C9), 122.83−129.68 (Ar−C), 151.77 (C10), 191.59 (C8); m/z (CI) MH^+ ($C_{38}H_{40}NO_6$) requires 606.2856, found 606.2855.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-ol glucopyranoside (6i): ν_{max} (NaCl disk/cm^{-1}) 3520 m (OH), 3055 m (C—H), 1753 s (C=O carbonyl ester stretch), 1665 m (C=C stretch), 1135 s (R—O—Me, stretch), 1030 (C—O stretch); $[\alpha]^{20}_D$ 111.3 (c 0.2, $CHCl_3$); δ_H ($CDCl_3$, 250 MHz) 1.23−1.28 (1H, m, C(7a)H), 1.90−1.97 (1H, m, C(7b)H), 1.95 (3H, s, Me), 2.08 (3H, s, Me), 3.37 (3H, s, OMe), 3.60 (1H, dd $J_{4,5}$ 8.5, $J_{5,6}$ 9.0,

C(5)H), 3.76 (1H, dd, $J_{3,4}$ 7.0, $J_{4,5}$ 8.5, C(4)H), 4.44−4.54 (1H, m, C(8)H), 4.59 (1H, ddd, $J_{6,7}$ 3.0, $J_{6,7}$ 8.0, $J_{5,6}$ 9.0, C(6)H), 4.76 (1H, d, J 10.0, $ArCH_2$), 4.81 (1H, d, J 10.0, $ArCH_2$), 4.81 (1H, dd, $J_{8,9}$ 4.0, $J_{9,10}$ 6.0, C(9)H), 5.04 (1H, d, $J_{1,2}$ 3.5, C(1)H), 5.31−5.35 (2H, m, C(2)H, C(3)H), 6.41 (1H, d, $J_{9,10}$ 6.0, C(10)H), 7.23−7.37 (5H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 20.8 (Me), 20.9 (Me), 34.2 (C-7), 55.2 (OMe), 63.2 (C-8), 71.1 (C-2), 71.2 ($ArCH_2$), 71.5 (C-5), 72.2 (C-6), 75.0 (C-3), 75.4 (C-4), 97.0 (C-1), 106.2 (C-9), 128.0−128.5 (Ar−C), 137.6 (iAr−C), 144.7 (C-10), 169.9−170.4 (RCOOR′); m/z (CI) 437 (MH^+, 35%), 393 (M − Ac, 34%); $[C_{22}H_{28}O_9]^+$ requires 437.1712, found 437.1708.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-ol galactopyranoside (6j). ν_{max} (NaCl disk/cm^{-1}) 3530 br (OH stretch), 3065 m (C—H), 1740 s (C=O carbonyl ester stretch), 1665 m (C=C stretch), 1130 (R—O—Me stretch); $[\alpha]^{20}_D$ 136.2 (c 1.8, $CHCl_3$); δ_H ($CDCl_3$, 400 MHz) 1.61 (1H, dddd, $J_{7a,10}$ 1.0, $J_{6,7a}$ 4.5, $J_{7a,8}$ 7.0, $J_{7a,7b}$ 11.0, C(7a)H), 1.91 (3H, s, Me), 2.01 (3H, s, Me), 2.51 (1H, ddd, $J_{6,7b}$ 7.0, $J_{7b,8}$ 7.5, $J_{7b,7a}$ 11.0, C(7b)H), 3.30 (3H, s, OMe), 3.81 (1H, dd, $J_{4,5}$ 2.5, $J_{5,6}$ 9.5, C(5)H), 4.17 (1H, ddd, $J_{6,7a}$ 4.5, $J_{6,7b}$ 7.0, $J_{5,6}$ 9.5, C(6)H), 4.20−4.23 (1H, m, C(4)H), 4.43 (1H, ddd, $J_{8,9}$ 2.0, $J_{7a,8}$ 7.0, $J_{7b,8}$ 7.5, C(8)H), 4.63 (1H, d, J 11.0, $ArCH_2$), 4.69 (1H, d, J 11.0, $ArCH_2$), 4.82 (1H, dd, $J_{8,9}$ 2.0, $J_{9,10}$ 6.0, C(9)H), 4.99 (1H, d, $J_{1,2}$ 3.0, C(1)H), 5.27−5.33 (2H, m, C(2H), C(3)H), 6.29 (1H, dd, $J_{7a,10}$ 1.0, $J_{9,10}$ 6.0, C(10)H), 7.22−7.28 (5H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 21.2 (Me), 21.3 (Me), 34.7 (C-7), 55.7 (OMe), 62.5 (C-8), 69.2 (C-2), 70.7 (C-3), 71.2 (C-5), 71.5 (C-6), 74.7 (C-4), 75.7 ($ArCH_2$), 97.6 (C-1), 106.7 (C-9), 128.2−128.7 (Ar−C), 138.3 (iAr−C), 144.4 (C-10), 170.6 (RCOOR′), 170.8 (RCOOR′); m/z (CI) 437 (MH^+, 100%), 420 (M − OMe, 32%), 419 (42%); $[C_{22}H_{28}O_9]^+$ requires 437.1712, found 437.1720.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-ol mannopyranoside (6k). ν_{max} (NaCl disk/cm^{-1}) 3540 br (OH stretch), 3055 m (C—H), 1750 s (C=O carbonyl ester stretch), 1660 m (C=C stretch), 1140 (R—O—CH_3, stretch); $[\alpha]^{20}_D$ 75.6 (c 0.80, $CHCl_3$); δ_H ($CDCl_3$, 250 MHz) 1.81−1.91 (1H, m, C(7a)H), 2.00 (3H, s, Me), 2.01 (1H, ddd, $J_{6,7b}$ 7.0, $J_{7b,8}$ 7.5, $J_{7a,7b}$ 9.0, C(7b)H), 2.23 (3H, s, Me), 3.56 (1H, dd, J 2.0, J 15.0, C(5)H), 3.97−4.01 (2H, m, C(6)H, C(4)H), 4.27 (1H, app dd, $J_{7b,8}$ 7.5, J 10.0, C(8)H), 4.72 (1H, dd, $J_{1,2}$ 2.0, $J_{2,3}$ 2.5, C(2)H), 4.77−4.79 (1H, m, C(9)H), 5.19 (1H, dd, $J_{2,3}$ 2.5, $J_{3,4}$ 8.0, C(3)H), 5.23 (1H, d, $J_{1,2}$ 2.0, C(1)H), 5.30 (1H, d, J 10.0, $ArCH_2$), 5.35 (1H, d, J 10.0, $ArCH_2$), 6.37 (1H, dd, J 1.0, $J_{9,10}$ 6.5, C(10)H), 7.17−7.39 (5H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 20.9 (Me), 21.0 (Me), 30.1 (C-7), 55.1 (OMe), 63.5 (C-8), 69.9 (C-5), 71.3 (C-6), 72.0 (C-3), 72.4 ($ArCH_2$), 72.7 (C-6), 75.1 (C-2), 77.7 (C-4), 99.0 (C-1), 106.1 (C-9), 127.7−128.5 (Ar−C), 137.9 (iAr−C), 145.1 (C-10), 169.9 (RCOOR′), 170.2 (RCOOR′); m/z (CI) 437 (MH^+, 22%), 393 (M − Ac, 32%), 351(26%); $[C_{22}H_{28}O_9]^+$ requires 437.1712, found 437.1718.

Methyl 2,3,4-tri-O-benzyl-6,7-dihydropyran-8-ol glucopyranoside (6*l*). ν_{max} (NaCl disk/cm^{-1}) 3530 br (OH), 3075 m (C—H), 1673 m (C=C, stretch), 1140 s (R—O—CH_3, stretch); $[\alpha]^{20}_D$ 11.4 (c 0.35, $CHCl_3$); δ_H ($CDCl_3$, 250 MHz) 1.39−1.49 (1H, m, C(7a)H), 1.96 (1H, ddd, $J_{6,7a}$ 7.0, $J_{7b,8}$ 8.0, $J_{7a,7b}$ 9.5, C(7b)H), 3.29 (3H, s, OMe), 3.45−3.50 (2H, m, C(2)H, C(3)H), 3.65 (1H, app t, $J_{3,4} = J_{4,5}$ 8.5, C(4)H), 3.90 (1H, dd, $J_{5,6}$ 7.5, $J_{4,5}$ 8.5, C(5)H), 4.21 (1H, dd, $J_{5,6}$ 7.5, $J_{6,7a}$ 8.0, C(6)H), 4.40 (1H, ddd, $J_{7a,8}$ 3.0, $J_{8,9}$ 3.5, $J_{7b,8}$ 8.0, C(8)H), 4.52 (1H, d, J 12.0, $ArCH_2$), 4.55 (1H, d, J 12.0, $ArCH_2$), 4.57 (1H, d, J 11.0, $ArCH_2$), 4.63 (1H, d, J 11.0, $ArCH_2$), 4.74 (1H, d, J 2.0, C(1)H), 4.78 (1H, d, J 10.0, $ArCH_2$), 4.84 (1H, d, J 10.0, $ArCH_2$), 4.92 (1H, d, $J_{8,9}$ 3.5, $J_{9,10}$ 6.5, C(9)H), 6.27 (1H, d, $J_{9,10}$ 6.5, C(10)H), 7.19−7.29 (15H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 34.9 (C-7), 55.5 (OMe), 63.6 (C-8), 71.5 ($ArCH_2$), 71.9 (C-5), 73.7 ($ArCH_2$), 75.5 ($ArCH_2$), 76.0 (C-3), 77.1 (C-6), 79.8 (C-2), 82.5 (C-4), 98.7 (C-1), 106.2 (C-9), 127.9−128.7 (Ar−C), 138.3−138.9 (iAr−C), 145.2 (C-10); m/z (CI) 533 (MH^+, 37%), 441 (M − OBn, 23%), 426 (22%); $[C_{32}H_{37}O_7]$ requires 533.2541, found 533.2534.

Methyl 2,3,4-tri-*O*-benzyl-6,7-dihydropyran-8-ol galactopyranoside (6m): ν_{max} (NaCl disk/cm^{-1}) 3530 br (OH stretching), 3365 m (C—H), 1665 m (C=C stretch), 1520 m (Ar, C—C stretch), 1130 s (R—O—Me stretch); $[\alpha]^{20}_D$ 22.2, 95.2 (c 0.5, $CHCl_3$); δ_H ($CDCl_3$, 250 MHz) 1.80 (1H, ddd, $J_{7a,8}$ 5.0, $J_{6,7a}$ 7.5, $J_{7a,7b}$ 10.0, C(7a)H), 2.43 (1H, ddd, $J_{6,7b}$ 3.0, $J_{7b,8}$ 7.0, $J_{7a,7b}$ 10.0, C(7b)H), 3.26 (3H, s, OMe), 3.85 (1H, dd, $J_{4,5}$ 2.5, $J_{5,6}$ 10.0, C(5)H), 3.96 (1H, dd, $J_{2,3}$ 3.0, $J_{3,4}$ 3.5, C(3)H), 4.04 (1H, dd, $J_{2,3}$ 3.0, $J_{1,2}$ 3.5, C(2)H), 4.05 (1H, ddd, $J_{6,7b}$ 3.0, $J_{6,7a}$ 7.5, $J_{5,6}$ 10.0, C(6)H), 4.10 (1H, dd, $J_{4,5}$ 2.5, $J_{3,4}$ 3.5, C(4)H), 4.33 (1H, ddd, $J_{8,9}$ 2.0, $J_{7a,8}$ 5.0, $J_{7b,8}$ 7.0, C(8)H), 4.56 (1H, d, J 12.0, $ArCH_2$), 4.61 (1H, J 12.0, $ArCH_2$), 4.66 (1H, d, $J_{1,2}$ 3.5, C(1)H), 4.77 (1H, d, J 10.0, $ArCH_2$), 4.81 (1H, d, J 10.0, $ArCH_2$), 4.82−4.84 (1H, m, C(9)H), 4.86 (1H, d, J 11.0, $ArCH_2$), 4.89 (1H, d, J 12.0, $ArCH_2$), 6.16 (1H, d, $J_{9,10}$ 6.0, C(10)H), 7.19−7.35 (15H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 34.8 (C-7), 55.6 (OMe), 62.7 (C-8), 69.3 ($ArCH_2$), 70.5 (C-5), 71.5 (C-4), 72.4 ($ArCH_2$), 73.4 ($ArCH_2$), 73.9 (C-4), 75.7 (C-6), 76.4 (C-2), 79.2 (C-3), 79.2 ($ArCH_2$), 99.2 (C-1), 106.5 (C-9), 127.7−128.6 (Ar−C), 138.8−139.0 (iAr−C), 144.5 (C-10); m/z (CI) 533 (MH^+, 41%), 441 (M − OBn, 15%), 426 (22%); $[C_{32}H_{37}O_7]$ requires 533.2541, found 533.2534.

Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6,7-dihydropyran-8-ol mannopyranoside (6n): ν_{max} (NaCl disk/cm^{-1}) 3560 br (OH), 3065 m (C−H), 1665 m (C=C stretch), 1525 m (Ar, C—C stretch), 1130 s (R—O—Me stretch); $[\alpha]^{20}_D$ 22.2 (c 0.75, $CHCl_3$); δ_H ($CDCl_3$, 250 MHz) 1.51−1.54 (1H, m, C(7a)H), 2.02 (1H, ddd, $J_{7b,8}$ 7.0, $J_{6,7b}$ 7.5, $J_{7a,7b}$ 9.5, C(7b)H), 3.23 (3H, s, OMe), 3.48 (1H, dd, $J_{1,2}$ 3.0, $J_{2,3}$ 3.5, C(2)H), 3.71 (1H, dd, $J_{5,6}$ 6.0, $J_{4,5}$ 8.0, C(5)H), 3.76 (1H, dd, $J_{4,5}$ 8.0, $J_{3,4}$ 9.0, C(4)H), 4.12 (1H, dd, $J_{2,3}$ 3.5, $J_{3,4}$ 9.0, C(3)H), 4.21−4.27 (1H, m, C(6)H), 4.47 (1H, app dt, $J_{8,9} = J_{7a,8}$ 3.5, $J_{7b,8}$ 7.0, C(8)H), 4.52−4.55 (1H, d, J 12.0, $ArCH_2$), 4.58 (1H, d, J 12.0, $ArCH_2$), 4.63 (1H, d, $J_{1,2}$ 3.0, C(1)H), 4.68 (1H, d, J 11.5, $ArCH_2$), 4.70 (1H, d, J 11.5, $ArCH_2$), 4.72 (1H, d, J 11.0, $ArCH_2$), 4.76 (1H, d, J 11.0, $ArCH_2$), 4.84 (1H, dd, $J_{8,9}$ 3.5, $J_{9,10}$ 6.0, C(9)H), 6.35 (1H, d, $J_{9,10}$ 6.0, C(10)H), 7.08−7.28 (15H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 34.5 (C-7), 55.0 (OMe), 63.7 (C-8), 71.7 (C-6), 72.3 (C-5), 72.9 ($ArCH_2$), 73.3 ($ArCH_2$), 73.7 ($ArCH_2$), 74.3 (C-3), 75.5 (C-2), 80.6 (C-4), 99.8 (C-1), 105.6 (C-9), 127.7−12 8.6 (Ar−C), 138.5−138.7 (iAr−C), 145.8 (C-10); m/z (CI) 533 (MH^+, 42%), 441 (M − OBn, 21%), 349 (18%); $[C_{32}H_{37}O_7]$ requires 533.2541, found 533.2546.

1-Methoxy-7,8-benzylidene spiro[5.5]undex-9-en-8-one mannopyranoside (8a): ν_{max} (NaCl disk/cm^{-1}) 3071 m (C−H), 2860 m (aliphatic C—H stretch), 1689 s (C=O, ketone stretch), 1630 m (C=C stretch), 1143 s (R—O—CH_3, stretch); $[\alpha]^{20}_D$ 91.1 (c 0.4, $CHCl_3$); δ_H ($CDCl_3$, 400 MHz) 1.71 (1H, dd $J_{1,2a}$ 4.5, $J_{2a,2b}$ 15.0, C(2a)H), 2.25 (1H, dd, $J_{7a,9}$ 1.0, $J_{7a,7b}$ 16.5, C(7a)H), 2.63 (1H, d, $J_{2a,2b}$ 15.0, C(2b)H), 3.16 (1H, d, $J_{7a,7b}$ 16.5, C(7b)H), 3.35 (3H, s, OMe), 3.53 (1H, d, $J_{4,5}$ 9.0, C(4)H), 3.75 (1H, ddd, $J_{5,6b}$ 3.0, $J_{5,6a}$ 8.0, $J_{4,5}$ 9.0, C(5)H), 4.34−4.39 (2H, m, C(6)H), 4.74 (1H, d, $J_{1,2a}$ 4.5, C(1)H), 5.41 (1H, dd, $J_{7,9}$ 1.0, $J_{9,10}$ 6.0, C(9)H), 5.58 (1H, s, ArCH), 7.26−7.47 (6H, m, ArH, C(10)H); δ_C ($CDCl_3$, 100 MHz) 36.2 (C-7), 43.1 (C-2), 55.5 (OMe), 58.2 (C-5), 69.2 (C-6), 79.0 (C-3), 81.0 (C-4), 97.4 (C-1), 102.0 (ArCH), 106.0 (C-9), 126.1−129.1 (Ar−C), 137.0 (iAr−C), 161.6 (C-10), 191.3 (C-8; m/z (CI) 349 (MH^+, 34%), 318 (M− OMe, 54%), 305 (17%); $[C_{19}H_{25}O_6]$ requires 349.1653, found 349.1646.

Methyl 3-*O*-acetyl-4-oxy-6-*O*-benzyl-8-oxy-10-methoxyoctahydroisochromen-1-ol (8b): ν_{max} (NaCl disk/cm^{-1}) 3082 m (C—H), 1752 s (C=O, carbonyl ester stretch), 1723 s (C=O, ketone stretch), 1720 s (C=O, ketone stretch), 1121 s (R—O—Me, stretch); $[\alpha]^{20}_D$ 54 (c 0.4, $CHCl_3$); δ_H ($CDCl_3$, 400 MHz) 2.04 (3H, s, OMe), 2.47 (1H, app dt, $J_{2,7a} = J_{7a,9a}$ 2.0, $J_{7a,7b}$ 15.5, C(7a)H), 2.57 (1H, dd, $J_{2,7b}$ 7.5, $J_{7a,7b}$ 15.5, C(7b)H), 2.68 (1H,

app dt, $J_{9a,10} = J_{7a,9a}$ 2.5, $J_{9a,9b}$ 15.0, C(9a)H), 2.82 (1H, dd, $J_{9b,10}$ 3.5, $J_{9a,9b}$ 15.0, C(9b)H), 3.13 (3H, s, OMe), 3.23 (1H, ddd, $J_{2,7a}$ 2.0, $J_{1,2}$ 4.0, $J_{2,7b}$ 7.5, C(2)H), 3.38 (3H, s, OMe), 3.75 (1H, dd, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 11.0, C(6a)H), 3.95 (1H, dd, $J_{5,6b}$ 3.0, $J_{6a,6b}$ 11.0, C(6b)H), 4.04 (1H, dd, $J_{9a,10}$ 2.5, $J_{9b,10}$ 3.5, C(10)H), 4.54 (2H, s, $ArCH_2$), 4.75 (1H, d, $J_{1,2}$ 4.0, C(1)H), 4.95 (1H, dd, $J_{5,6a}$ 3.0, $J_{5,6b}$ 6.5, C(5)H), 7.16−7.54 (5H, m, ArH); δ_C ($CDCl_3$, 100.0 MHz) 21.0 (Me), 38.7 (C-7), 41.9 (C-9), 42.2 (C-2), 56.0 (OMe), 58.4 (OMe′), 68.0 (C-6), 73.8 ($ArCH_2$), 74.4 (C-5), 77.1 (C-3), 83.4 (C-10), 100.7 (C-1), 127.9−129.7 (Ar−C), 138.5 (iAr−C), 169.5 (RCOOR′), 202.8 (C-4), 207.1 (C-8); *m*/*z* (CI) 407 (MH^+, 100%), 375 (M − OMe, 65%), 342 (M − $(OMe)_2$, 34%); $[C_{21}H_{27}O8]^+$ requires 407.1706, found 407.1712.

Methyl 2,3-di-*O*-acetate-4,5-ene-6,7-dihydropyran-8-one mannopyranoside (8c). ν_{max} (NaCl disk/cm^{-1}) 3047 m (C-Hing), 1759 s (C═O, carbonyl ester stretching), 1695 s (C═O carbonyl stretching), 1630 m (C═C stretching), 1125 s (R—O—Me, stretching); δ_H ($CDCl_3$, 250 MHz) 2.06 (3H, s, Me), 2.12 (3H, s, Me), 2.61 (1H, ddd, $J_{7a,9}$ 1.0, $J_{6,7a}$ 4.0, $J_{7a,7b}$ 16.5, C(7a)H), 2.85 (1H, dd, $J_{6,7b}$ 8.0, $J_{7a,7b}$ 13.5, C(7b)H), 2.89 (1H, dd, *J* 8.5, $J_{6,7b'}$ 10.5, C(7b′)H), 3.51 (3H, s, OMe), 3.52 (3H, s, OMe), 4.84 (1H, dt, $J_{6,7a}$ 3.5, $J_{6,7b}$ 13.5, C(6)H), 5.01 (1H, d, $J_{1,2}$ 4.0, C(1)H), 5.03 (1H, d, $J_{1,2}$ C(1′)H), 5.08 (1H, d, $J_{3,4}$ 3.0, C(4)H), 5.22 (1H, ddd, *J* 1.0, $J_{1,2}$ 4.0, $J_{1,2}$ 4.5, $J_{2,3}$ 5.0, C(2)H), 5.47 (1H, dd, $J_{7a,9}$ 1.0, $J_{9,10}$ 6.0, C(9)H), 5.59 (1H, dd, $J_{3,4}$ 3.5, $J_{2,3}$ 5.0, C(3)H), 7.38 (1H, d, $J_{9,10}$ 6.0, C(10)H); δ_C ($CDCl_3$, 62.8 MHz) 20.8 (Me), 21.0 (Me), 39.1 (C-7), 39.3 (C-7′), 56.5 (OMe), 56.7 (OMe), 63.4 (C-3), 65.2 (C-2), 65.5 (C-2′), 77.7 (C-6), 98.1 (C-4), 98.5 (C-4′), 98.8 (C-1), 98.9 (C-1′), 107.4 (C-9), 107.5 (C-9′), 149.0 (C-5), 149.1 (C-5′), 162.3 (C-10), 162.4 (C-10′), 170.0 (RCOOR′), 170.1 (RCOOR′), 191.1 (C-8′), 191.2 (C-8); *m*/*z* (CI) 327 (MH^+, 44%), 296 (M − OMe, 100%), 258 (M − OAc, 34%); $[C_{15}H_{18}O_8]^+$ requires 327.1032, found 327.1040.

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Supporting Information Available: Experimental procedures as well as NMR spectra and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.