A Convergent Route to Enantiomers of the Bicyclic Monosaccharide Bradyrhizose Leads to Insight into the Bioactivity of an Immunologically Silent Lipopolysaccharide

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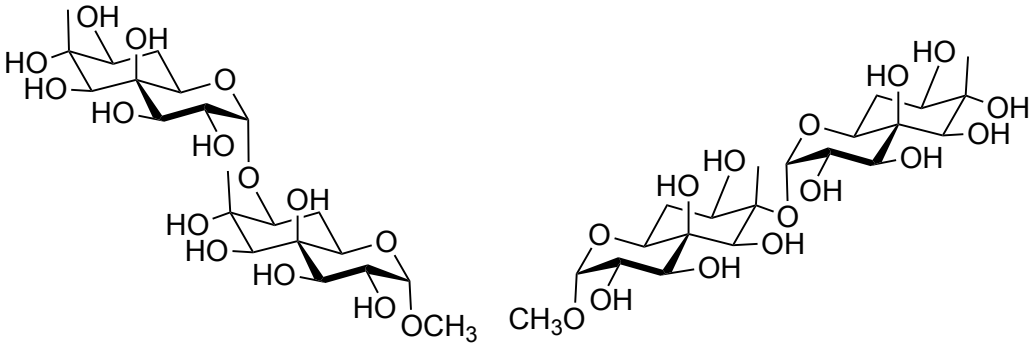
Graphical Abstract



Abstract

The synthesis of bradyrhizose, the monosaccharide component of the lipopolysaccharide O-antigen of the nitrogen-fixing bacteria *Bradyrhizobium* sp. BTAi1 and sp. ORS278, has been achieved in 25 steps in an overall yield of 6% using *myo*-inositol and ethyl propiolate as the starting materials. The route involved the late state resolution of a racemic intermediate to provide both enantiomers of this unusual bicyclic monosaccharide. Both the natural D-enantiomer, and the unnatural and heretofore unknown L-enantiomer, were converted to disaccharide derivatives containing different forms of the monosaccharide (D,D; L,L; D,L; L,D). Evaluation of the synthetic compounds for their ability to act as microbe-associated molecular patterns in plants, through induction of reactive oxygen species, was investigated. These experiments suggest that the immunologically-silent nature of the natural glycans is due to specific structural features.

Introduction

Lipopolysaccharide (LPS) is a key immunologically-active molecule produced by gram-negative bacteria.[1] Found in the outer membrane of these organisms, interaction of LPS with the immune system of a host leads to both the production of antibodies and the induction of the innate immune system.[2,3] In this context, the 2011 report by Molinaro and co-workers that LPS produced by the nitrogen-fixing bacteria *Bradyrhizobium* sp. BTAi1 and sp. ORS278, and the O-chain domain of these polysaccharides, did not activate innate immunity in their natural host (plants) was noteworthy.[4] This is the first example of an LPS that does not activate a defence response. Structural studies[4] revealed that the O-chain repeating unit of both these LPSs is composed of a single monosaccharide with an unprecedented structure: D-bradyrhizose (Figure 1a). This bicyclic monosaccharide, possessing a *cis*-decalin-like core, has to date only been identified in these LPS and is present as an α-(1→7)- or an α-(1→9)-linked homopolymer, depending upon the strain (Figures 1b and 1c) in which it is found.

Understanding the origin of the intriguing, immunologically-silent, nature of this glycoconjugate requires access to structurally defined fragments and derivatives of the larger molecule. To date, a single synthetic route to D-bradyrhizose has been reported by Yu and coworkers,[5] who have also described its oligomerization into a series of α-(1→7)-linked homo-oligosaccharides up to a pentasaccharide.[6] Similar to the polysaccharide, these oligosaccharides did not induce a defensive innate immune response in plants.[6]

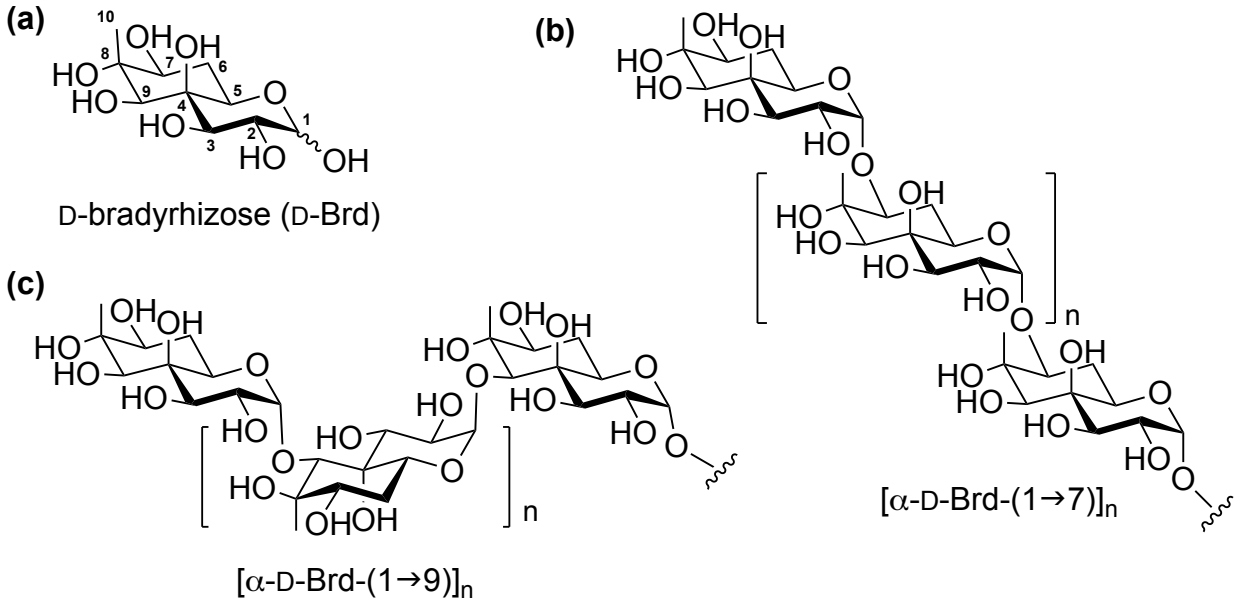


Figure 1. (a) D-Bradyrhizose (b) O-antigen in *Bradyrhizobium* sp. BTAi1 and sp. ORS278 (c) O-antigen in *Bradyrhizobium* sp. ORS278.

On the basis of this earlier work, we became interested in gaining additional insight into the potential immunological activity (or not) of bradyrhizose-containing glycoconjugates. In particular, we were curious if specific structural features in these molecules led to their immunologically silent nature. In selecting analogs to synthesized, which could then be evaluated for immunomodulatory activity as described previously,[4,6] we chose to explore a comparison of molecules containing this monosaccharide in its natural D-form and its unnatural (at least to date) L-form. Such an approach, termed stereochemical structure–activity relationships (S-SAR), has been shown to be a powerful method for probing the bioactivity of glycoconjugates[7-9] and other natural products.[10]

To this end, we describe here a convergent synthetic approach to both enantiomers of bradyrhizose and their further transformation into disaccharides containing different forms of the monosaccharide (D,D; L,L; D,L; L,D). Following their synthesis, the compounds were evaluated for

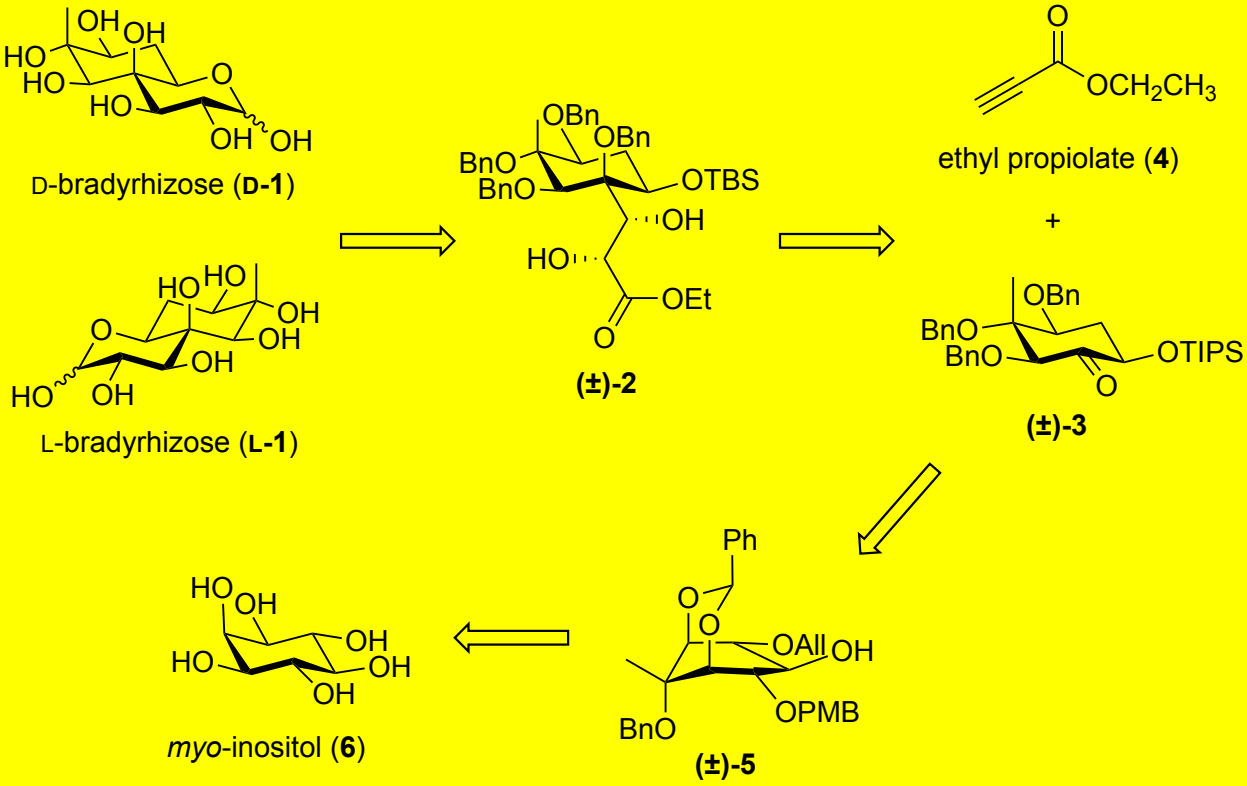
their ability to induce a defence response in plants through generation of reactive oxygen species (ROS). These experiments showed that some, but not all, of these compounds do induce ROS thus providing new insights into the immunological silence of the natural compound.

Results and discussion

Synthesis of D and L-bradyrhizose monosaccharides

Retrosynthetic analysis. The previous synthesis of D-bradyrhizose (**1**) began from 2,3,6-tri-*O*-acetyl-D-glucal, a commercially available material.[5] Given our desire to access both enantiomers of bradyrhizose, use of that route would require its application to both that substrate and 2,3,6-tri-*O*-aceyl-L-glucal, accessible from very expensive L-glucose. Instead, our strategy was to develop a route to an advanced achiral intermediate that could, at a late stage, be resolved into the enantiomers and then elaborated into oligosaccharides. We envisioned that both D-bradyrhizose (**D-1**)[†] and L-bradyrhizose (**L-1**) could be prepared from resolution of racemic ethyl ester **2** (Scheme 1), which could be produced from ketone **3** and ethyl propiolate (**4**). The former would serve as the precursor to the 'back' ring of bradyrhizose (C-4–C-9) and the latter C1–C3 (See Figure 1a for numbering scheme). Ketone **3** could be prepared from bicyclic alcohol **5**, which, in turn, could be prepared from *myo*-inositol (**6**), a readily available *meso* compound.

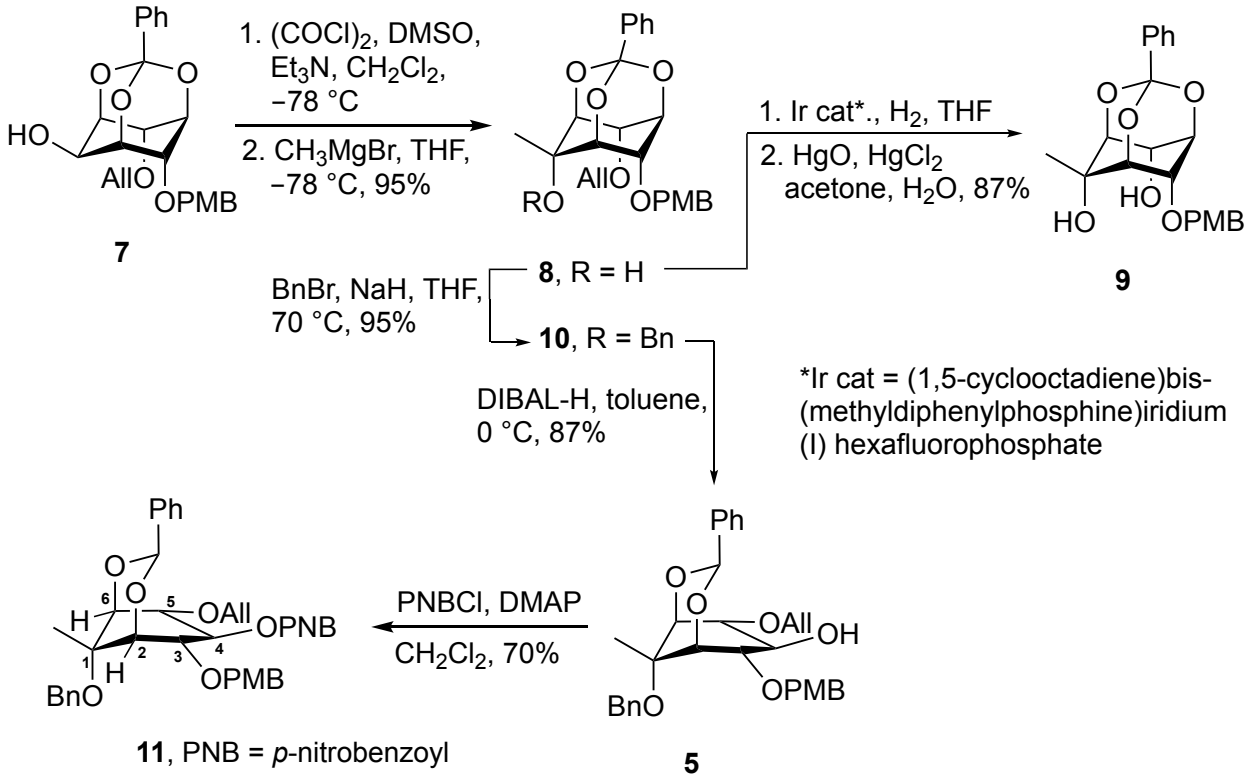
[†] Compounds lacking a D or L descriptor are racemic



Scheme 1. Retrosynthetic analysis of D- and L-bradyrhizose

Construction of bicyclic alcohol 5. The route to **5** began with inositol derivative **7** (Scheme 2), synthesized in three steps (46% yield) from *myo*-inositol (**6**).[11] Oxidation using Swern conditions converted alcohol **7** to the corresponding ketone, which was prone to hydration. All attempts to purify the ketone resulted only in isolation of the hydrate; efforts to dehydrate it for subsequent transformations failed. As such, immediately after oxidation of **7** the crude ketone was treated with methyl magnesium bromide leading to tertiary alcohol **8** in 95% yield over the two steps. Proving the stereochemistry of the new stereocentre in **8** was challenging, but was possible through removal of the allyl group leading diol **9**, which was a crystalline solid. X-ray crystallographic analysis of **9** demonstrated the *cis*-relationship between the methyl group and the orthoester (See Supporting Information. Figure S1). The free hydroxyl group in compound **8** was

then protected as a benzyl ether in 95% yield (to give **10**) and the orthoester was opened[11] using DIBAL-H, affording only bicyclic compound **5** in 87% yield.



Scheme 2. Synthesis of bicyclic alcohol **5**

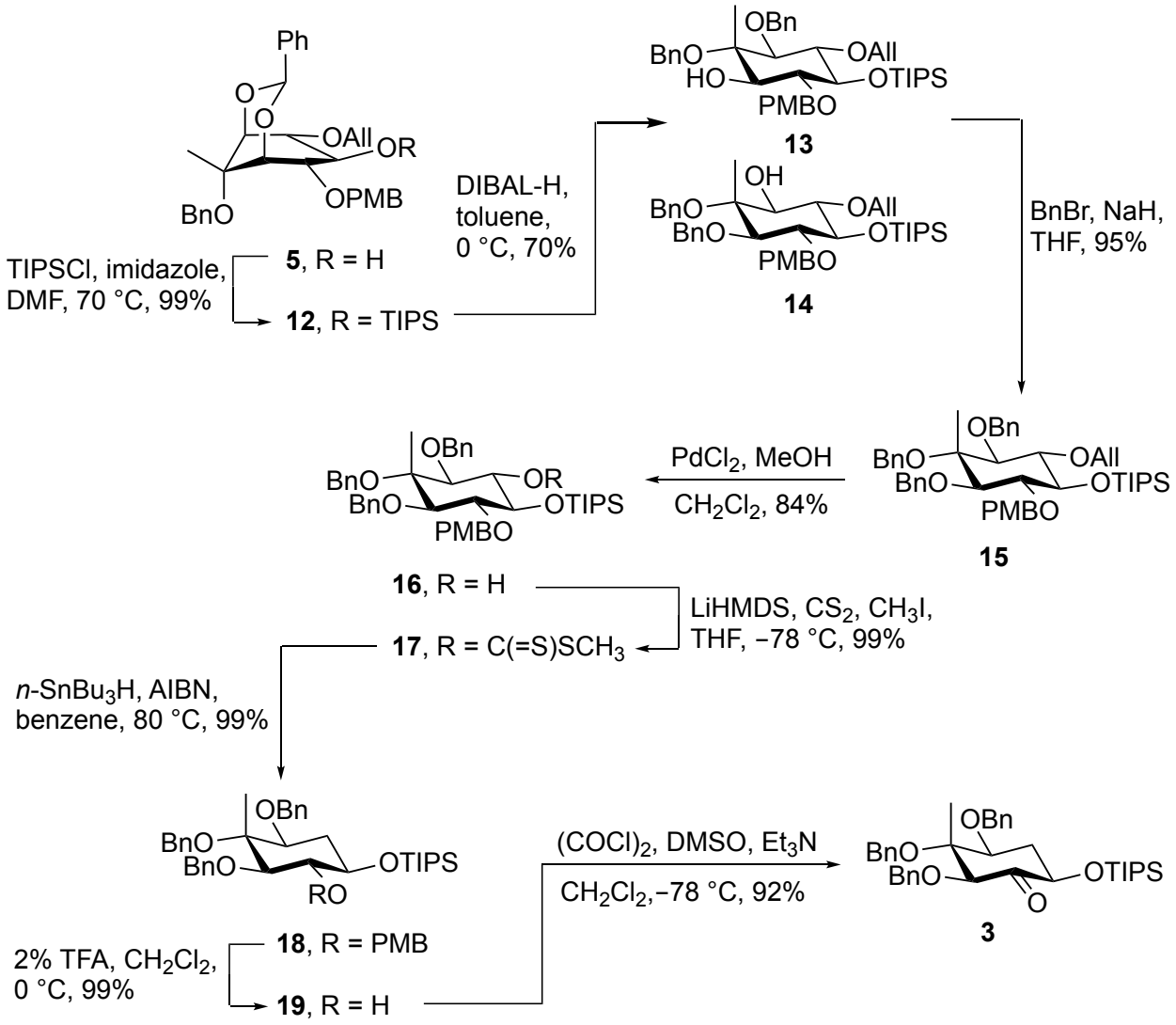
To verify the regioselectivity of this reaction, the *p*-nitrobenzoate ester **11** was synthesized from alcohol **5** (Scheme 2). Attempts to obtain a crystalline solid from this material failed. However, the ^{1}H NMR spectrum of **11** showed H-4 as a deshielded doublet of doublets (6.21 ppm), due to the anisotropic deshielding of the ester carbonyl group. Had the opening occurred at one of the other two positions possible (the oxygens attached to C-2 or C-6), a doublet for the deshielded signal would be observed because the adjacent carbon (C-1) has no attached protons. The conformation of **11** could also be determined from its ^{1}H NMR spectrum, which showed that the resonances for H-2 and H-6 are doublets with J = 2.0 Hz. The resonance for H-3 and H-5 are also doublets (J = 8.0 Hz) and that for H-4 is an apparent triplet (J = 8.0 Hz). The lack of coupling

between H-2/H-3 and H-5/H-6 suggests an angle close to 90° between them. Furthermore, the doublet seen for H-2 and H-6 appear to be the result of in a long range 'W coupling' between them. This data suggests that that the cyclohexane ring adopts a half chair conformation as drawn, not a chair. The half chair conformation is unique as it is an unsubstituted cyclohexane it is the highest energy conformation. The ^{1}H NMR spectrum for alcohol **5** also shared the same features. Finally, the ROESY spectrum of **11** supported this conformation; there is an NOE correlation between H-4 and the benzylic protons on the C-1 benzyloxy group.

Synthesis of ketone 3. With a route to **5** established, we moved towards the preparation of ketone **3** (Scheme 3). A key initial consideration was the choice of protecting group for the alcohol in **5**, which needed to be orthogonal to benzyl, allyl and *p*-methoxybenzyl ethers. We initially explored the use of a naphthylmethyl ether for this purpose, but its selective cleavage later in the synthesis was very troublesome. On the other hand, we found the triisopropylsilyl (TIPS) group more suitable. This silyl ether could be introduced onto **5** to give **12** in high yield, using TIPSCl and imidazole at 70 °C. Subsequent DIBAL-H reduction of the benzylidene acetal gave the desired alcohols **13** and **14** in 70% combined yield. Treatment of both of these intermediates with benzyl bromide and sodium hydride led to the formation of the same tribenzyl ether derivative **15** in 95% yield. The allyl group was then deprotected using palladium(II) chloride to give alcohol **16** in an 84% yield.

We next sought to reduce the alcohol through xanthate formation and Barton–McCombie deoxygenation. Attempted generation of xanthate **17** from alcohol **16** using standard conditions (NaH, CS_2 and then CH_3I) led to a mixture of two products: the starting material and the product resulting from migration of the silyl group to the adjacent free hydroxyl group. Fortunately, the use of LiHMDS, instead of NaH and carrying out the reaction at –78 °C (not room temperature) gave **17** in excellent yield. Treatment of the xanthate with AIBN tri-*n*-butyltin hydride gave a good

yield of the corresponding deoxygenated product **18**. Deprotection of the PMB group was done using 2% trifloroacetic acid in dichloromethane and oxidation of the resulting alcohol **19** using Swern conditions gave ketone **3** in 91% yield over the two steps.



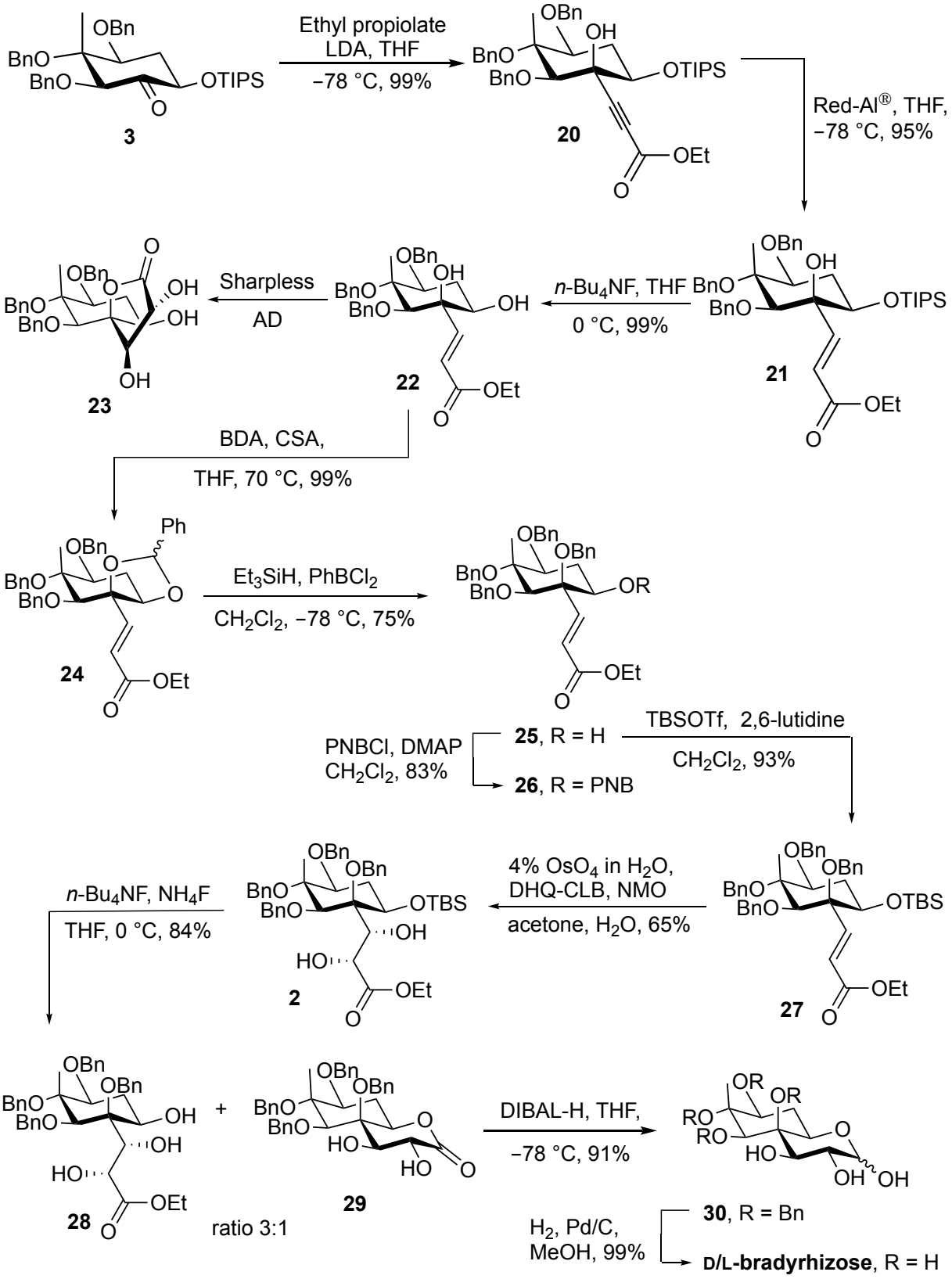
Scheme 3. Synthesis of ketone **3**.

Synthesis of diol 2 and (D/L)-bradyrhizose. Having established a robust route for the synthesis of ketone **3**, the stage was set for the critical carbon–carbon bond forming step (Scheme 4). Thus, deprototation of ethyl propiolate upon treatment with LDA and addition of **3** to the mixture provided propargylic alcohol **20** in near quantitative yield. Subsequent reduction of the

alkyne to the *E*-alkene **21** was achieved using Red-Al®.[12,13] Presumably the reduction proceeds by a hydroxyl-directed *trans*-selective Red-Al-promoted conjugated addition onto the acetylenic ester, followed by quenching water.[13] This reaction did not go to completion. However, isolation of the unreacted starting material, and subjection to the reaction again was possible. After three cycles, alkene **21** was obtained in excellent combined yield. The TIPS protecting group was then removed using TBAF to give diol **22**.

The final step in establishing the bradyrhizose skeleton was asymmetric dihydroxylation of the alkene to provide what would become the C-2 and C-3 stereocentres. The dihydroxylation was attempted first on diol **22**, but the reaction was very slow. One major compound was formed but was isolated in only 10% yield. The product was identified by NMR spectroscopic analysis to be the five-membered ring lactone **23**. The formation of this compound is perhaps not unexpected as the presence of analogous furanose forms of bradyrhizose are present in the equilibrium mixture of the reducing sugar.[5]

This result suggested that protection of the tertiary alcohol could provide a substrate that could be more easily dihydroxylated. We first explored the possibility of benzylating the alcohol in intermediate **21**, using standard conditions (NaH, BnBr or BuLi, BnBr, −78 °C) but none of the desired compound was observed, presumably due to steric hindrance arising from the tertiary centre and the adjacent silyl group. We then moved to an indirect approach in which diol **22** was converted to a benzylidene acetal and then regioselectivly opened. Thus, treatment of **22** with benzadehyde dimethylacetal and CSA led to an essentially quantitative yield of benzylidene acetal **24** as a 3:5 *exo*:*endo* mixture. In the ROESY spectrum of the minor isomer, there was an NOE correlation between the axial methylene proton of the six-membered ring and the benzylidene acetal proton, which supports its stereochemistry as *exo*.



Scheme 4. Synthesis of diol **2** and D/L-bradyrhizose.

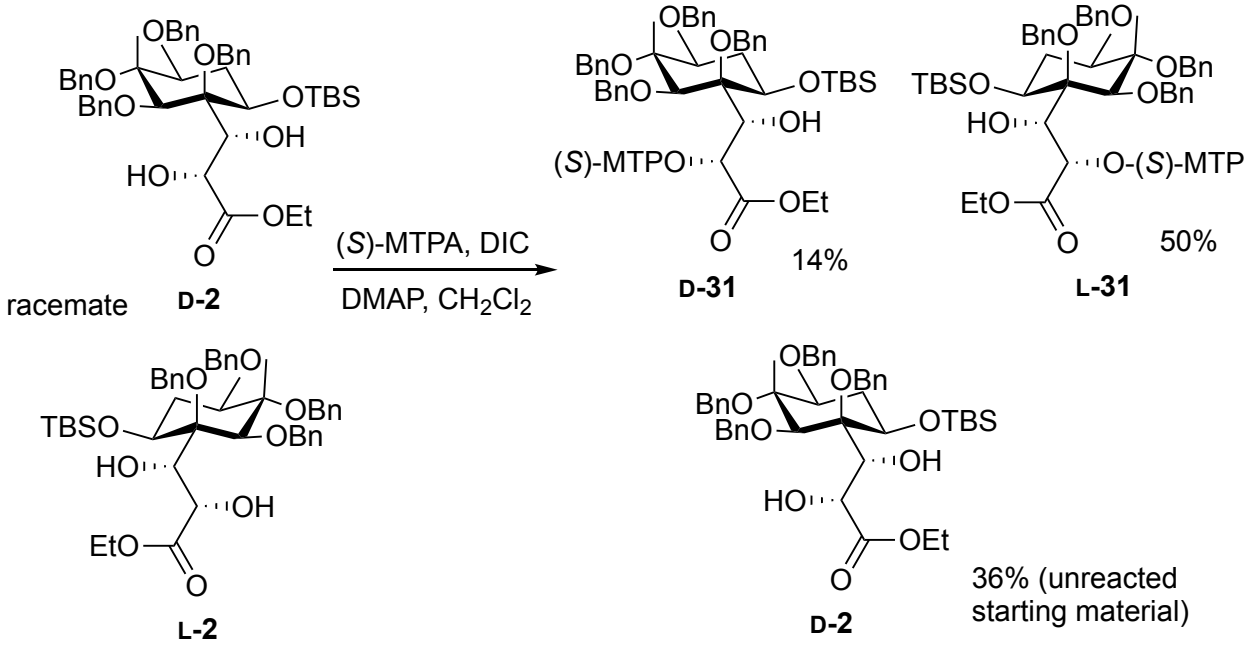
The regioselective reductive opening of the benzylidene acetal in **24** was performed using borane and copper(II) triflate at –78 °C,[14] but only 45% of desired compound **25** was obtained. Fortunately, the use of triethylsilane and dichlorophenylborane[15] gave **25** in 75% yield. The signals in the ^{1}H NMR spectrum of **25** were broad and it was not possible to determine the regiocontrol of the acetal opening. However, this could be circumvented by conversion of **25** to the corresponding *p*-nitrobenzoyl ester **26**. The signals in the ^{1}H NMR spectrum of **26** were well-resolved and the resonance for the proton on the carbon bearing the *p*-nitrobenzoyl group appeared as a deshielded doublet of doublets (5.19 ppm) indicating that the reaction had proceeded with the desired regiocontrol.

With **25** in hand, the asymmetric dihydroxylation was then attempted but only starting material was recovered after three days. To determine if the free hydroxyl group was hindering the reaction, this functionality was protected as a TBS ether upon reaction with TBSOTf and 2,6-lutidine, giving compound **27** in 93% yield. Asymmetric dihydroxylation of **27** using potassium osmate and $(DHQ)_2PHAL$ did not complete and the yield of the desired compound was low. We then moved to explore an alternate approach involving an aqueous solution of osmium tetroxide and the *O*-(4-chlorobenzoyl)hydroquinine (DHQ-CLB) ligand, which has given good results with similar compounds.[16] Under these conditions, the desired diol **2** was obtained in 65% yield.

With all of the carbon atoms and stereocentres in place, we proceeded to prepare D/L-bradyrhizose. This was achieved by removal of the TBS group, which, after some optimization, was done by buffering a solution of tetra-*n*-butylammonium fluoride with ammonium fluoride. The reaction gave a 3:1 mixture of ester **28** and lactone **29** in 84% combined yield. This mixture was then reduced using DIBAL-H at –78 °C to give the lactol **30** in 91% yield. Finally, deprotection of the benzyl groups using palladium on carbon in methanol gave D/L-bradyrhizose. The NMR spectra of this compound was identical to those published previously.[5] Overall, the

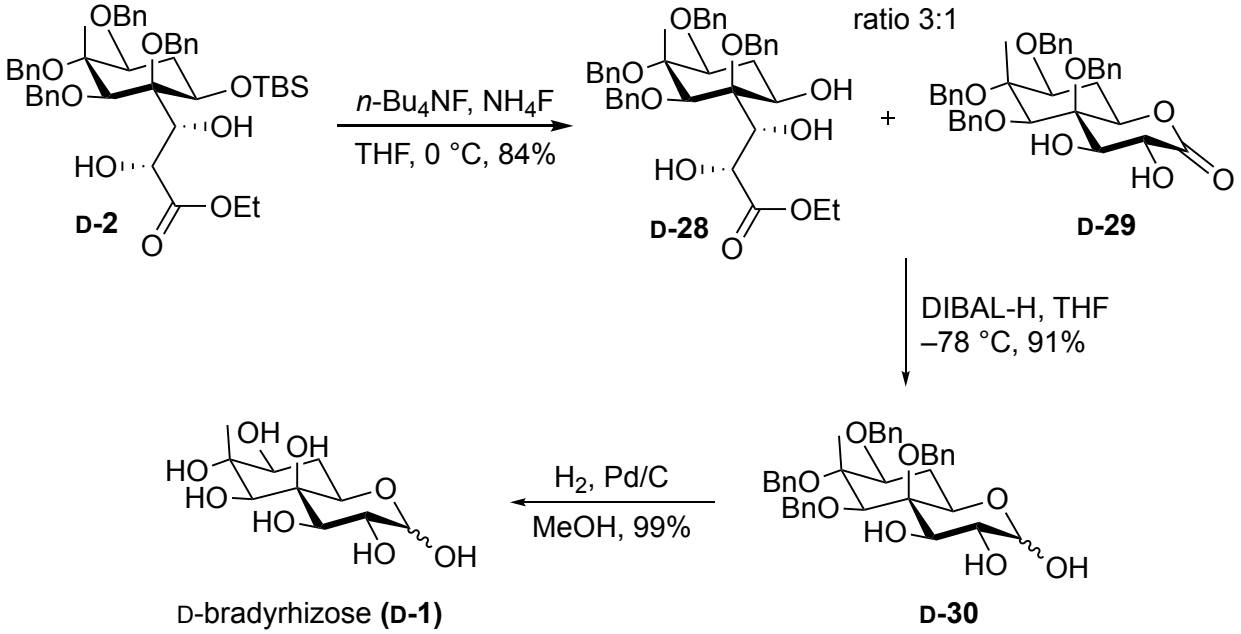
synthesis was accomplished in 25 steps from *myo*-inositol in a yield of 6%. This is comparable, both in number of steps and overall yield, to the previous synthesis of D-bradyrhizose.[5] Use of an enantiomerically-pure *myo*-inositol derivative (*e.g.,* **D-7** or **L-7**, Scheme 2) would enable the preparation of either antipode, as would resolution of an achiral intermediate in the route discussed above. This latter approach is described below.

Synthesis of D- and L-bradyrhizose. We next turned our attention to preparing the enantiomerically pure forms of bradyrhizose via resolution of an appropriate intermediate. We found that this was successful using diol **2** and (*S*)-(–)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (Scheme 5). It was discovered that (*S*)-MTPA reacted preferentially with one enantiomer to give **L-31** in 50% yield. The other enantiomer reacted with (*S*)-MTPA to give **D-31** in 14% yield. In addition, unreacted starting material was recovered. Analysis of unreacted **D-2** by chiral HPLC revealed that it was enantiomerically pure (>99% ee). Note: The assignment of D and L to these structures was achieved by conversion of each of the target monosaccharides (below) and comparison with previously reported data.[5]



Scheme 5. Resolution of enantiomers of **2** by derivatization

After the separation of the enantiomers of **2**, the unreacted stereoisomer (**D-2**) was treated with tetra-*n*-butylammonium fluoride with ammonium fluoride as described for the racemate. Under these conditions, ester **D-28** and lactone **D-29** were produced in a combined 84% yield (Scheme 6). The mixture was then treated with DIBAL-H to give the lactol **D-30** followed by hydrogenation to give D-bradyrhizose (**D-1**). The optical rotation found for this material was +20.4 (*c* 0.2, H_2O), which differed in magnitude but not in sign from that reported previously, +6.5 (*c* 0.2, H_2O).[5] The difference between these numbers could possibly arise from different ratios of the five cyclic forms of the reducing sugar[5] in the samples used for the two measurements.

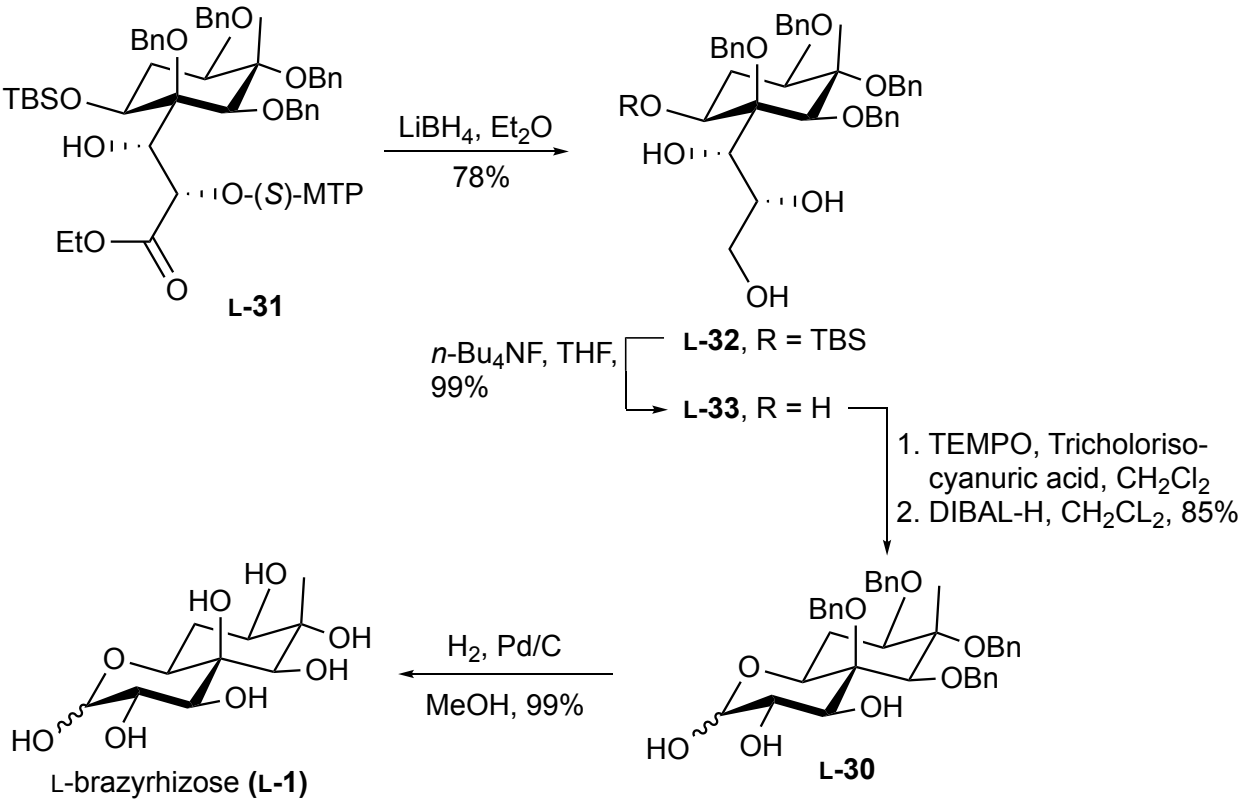


Scheme 6. Synthesis of D-bradyrhizose.

We next explored the conversion of the (*S*)-MTPA derivatized compounds, **D-31** and **L-31**, into D- and L-bradyrhizose, respectively. The same steps (shown in Scheme 6) should work for both compounds: 1) deprotection of the TBS group with ammonium fluoride buffered-tetra-*n*-butylammonium fluoride; 2) reduction and removal of the auxiliary using DIBAL-H to form the

lactol and 3) hydrogenation. The TBS deprotection was first tried with **L-31** using tetra-*n*-butylammonium fluoride and ammonium fluoride, but the yield of the desired compound was low and side products were formed. Cleavage of the silyl group with trifluoroacetic acid and acetic acid were also tried with poor results.

Faced with this challenge, we investigated removal of the auxiliary first (Scheme 7). Cleavage with sodium methoxide in methanol was performed on **L-31**, but the reaction would not complete and side products were formed. The final, ultimately successful, attempt explored was the removal of the auxiliary using a reducing agent, mindful that this approach would also reduce the ethyl ester to a primary alcohol. The first reducing agent used was $LiAlH_4$, but the yield of the desired compound was only 50–60%. DIBAL-H was then tried, but the chiral auxiliary was not cleaved. Finally, the reduction was performed using $LiBH_4$ on intermediate **L-31** and 78% of the desired compound (**L-32**) was obtained.



Scheme 7. Synthesis of L-bradyrhizose

The TBS group was then deprotected using tetra-*n*-butylammonium fluoride to yield **L-33** in 99% yield. The primary hydroxyl group of **L-33** was selectively oxidized using TEMPO to form a mixture of lactol **L-30** and the corresponding lactone (overoxidation), and the mixture was reduced back to the lactol **L-30** using DIBAL-H in 85% yield over the two steps.[5] Hydrogenation of **L-30** gave L-bradyrhizose (optical rotation −21.8, *c* 0.2, H_2O) in near quantitative yield.

Using the same approach, isomer **D-32** was transformed in D-bradyrhizose (**D-1**). All enantiomers made in this sequence had the similar specific rotation magnitudes as those in the L-series, with opposite signs.

Assembly of Glycosylation Partners

When considering to make bradyrhizose-containing oligosaccharides, we hypothesized that donors of this monosaccharide (*e.g.,* **34**, Figure 2) would provide α-glycosides with high selectivity. This is due to their structural similarity to glucopyranose donors possessing a 4,6-*O*-benzlidene acetal (*e.g.,* **35**) – both possess a '*cis*-decalin' framework – which have been shown by Crich and co-workers to be highly α-selective donors.[17-19] Indeed, in their synthesis of bradyrhizose oligosaccharides, Yu and coworkers showed that *N*-phenyl trifluoroacetimidate donors of bradyrhizose afforded α-glycoside products.[6]

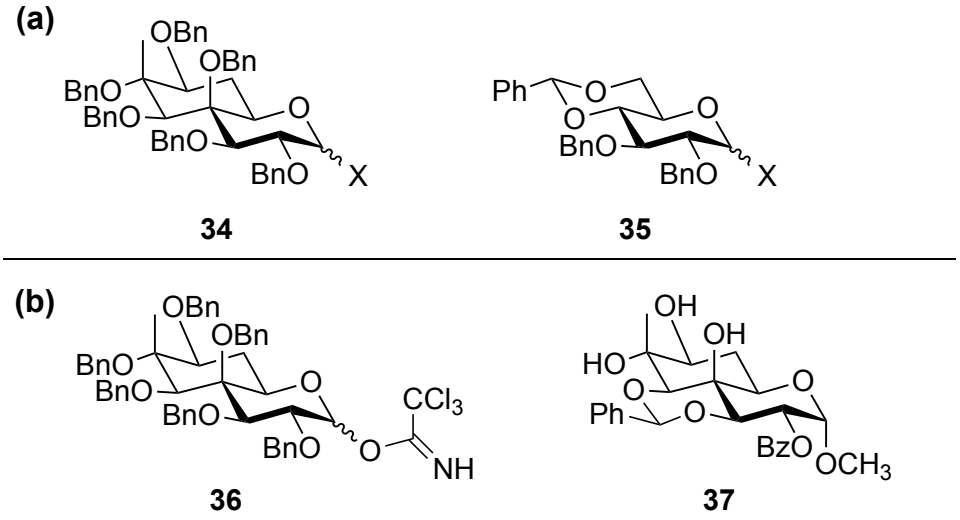


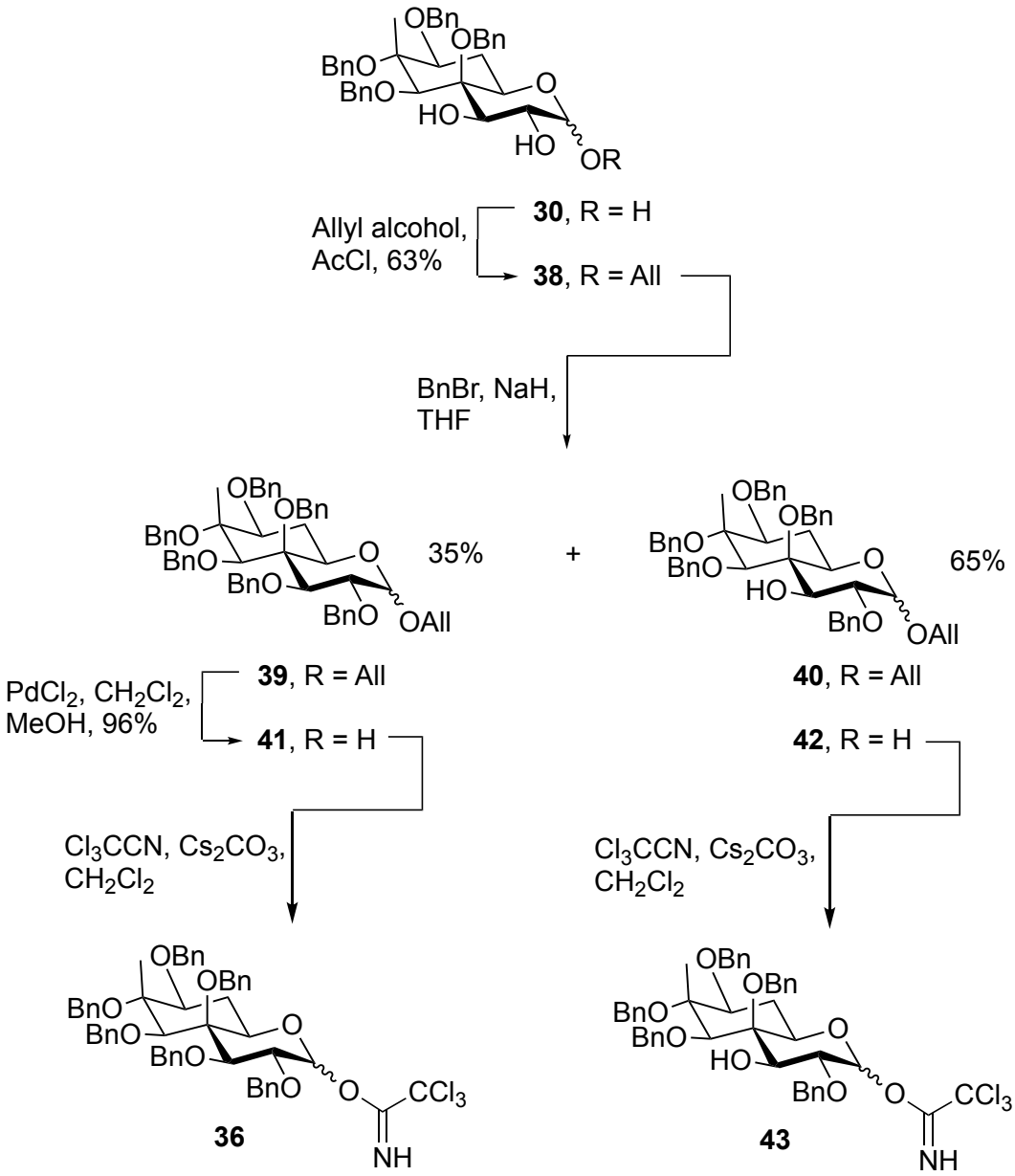
Figure 2. (a) Structural comparison of hypothetical bradyrhizose (**34**) and 4,6-*O*-benylidene-protected glucopyranose (**35**) donors (b) Bradyrhizose donor (**36**) and acceptor (**37**) targets.

We wished to expand the diversity of bradyrhizose oligosaccharide available, by synthesizing a series of α-(1→7)-linked disaccharides containing all possible D/L combinations (D,D; L,L; D,L; L,D), for subsequent immunological studies. To do this, we selected a fully-benzylated trichloroacetimidate donor (**36**, Figure 2) and a 'lightly-protected' methyl glycoside acceptor (**37**). The choice of this acceptor was made as it was anticipated that the nucleophilicity of tertiary alcohols in **37α** would be substantially reduced compared to the secondary alcohol. Hence, more complicated strategies leading to fully-protected acceptors might be unnecessary.

The preparation of **36** and **37α** was developed using racemic material and then applied to the enantiomerically-pure compounds. It should be noted that we also investigated glycosylations between the racemic donors and acceptors, but the number of stereoisomeric products possible made obtaining pure compounds, and unequivocally characterizing them, extremely difficult. Therefore, that approach was abandoned.

Synthesis of the donor. As shown in Scheme 8, the synthesis of **36** started with lactol **30**, which was subjected to a Fischer glycosylation with allyl alcohol to produce allyl glycoside **38** in

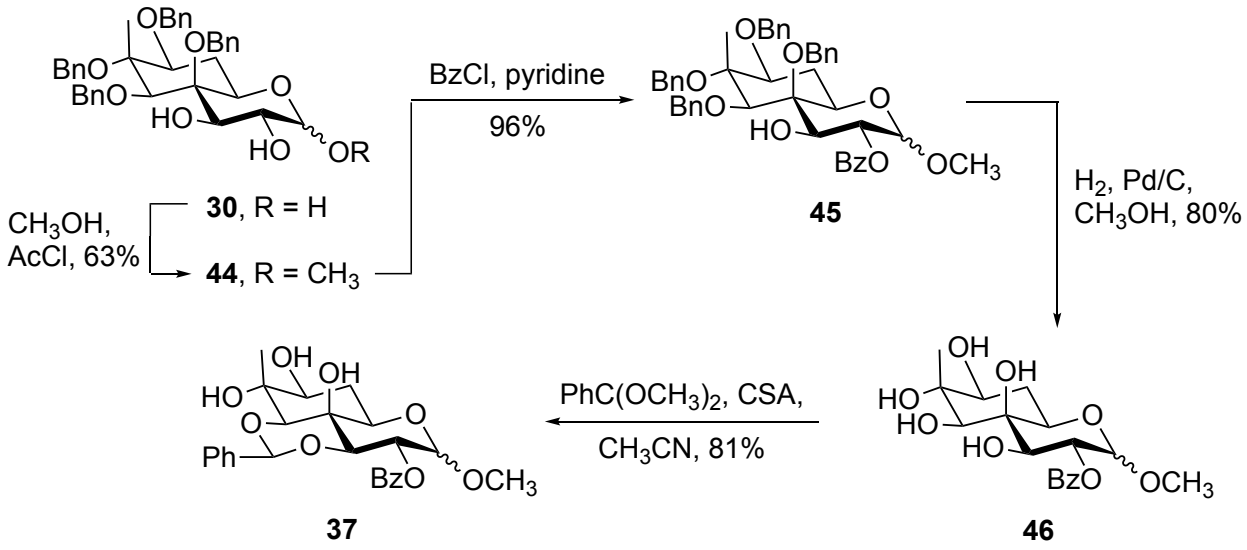
63% yield as a 1:1 α/β mixture. The next step was to protect the free hydroxyl groups as benzyl ethers. Use of standard conditions (benzyl bromide, NaH at room temperature) provided only a 35% yield of the fully protected compound **39**. The major product was **40**, in which the C-3 hydroxyl group remained unprotected. The low reactivity of this position to alkylation was also found by Yu and coworkers.[6] In their case, they were able to acetylate this hydroxyl group under forcing conditions. However, we hypothesized that the free hydroxyl group at this position would not be a problem during the glycosylations, given its poor nucleophilicity. It was then decided to explore the use of trichloroacetimidates derived from **40** as glycosyl donors and proceed with those from **39** only in case self-coupling of the donor was seen. Hence, the allyl group in **39** and **40** was removed using palladium(II) chloride to provide the corresponding reducing sugars **41** and **42** in 96% and 97% yield, respectively. The corresponding trichloacetimidate donors, **36** and **43,** were not stable and were made immediately prior to glycosylation and used without purification.



Scheme 8. Synthesis of **36** and **43**

Synthesis of the acceptor. Like the preparation the donors, the synthesis of the acceptor **37** (Scheme 9) started with lactol **30**, which was treated with methanol and acetyl chloride to give a 73% yield of methyl glycoside **44** as an inseparable 3:2 α/β mixture. Treatment of **44** with benzoyl chloride and pyridine gave a 96% yield of **45** with the benzoate ester only at C-2, pointing again to the low nucleophilicity of the bradyrhizose C-3 hydroxyl group. The benzyl ethers were cleaved

using palladium on carbon in 80% yield to give **46**, with five hydroxyl groups (two tertiary and three secondary). Two of the secondary hydroxyl groups were then regioselectively protected as a benzylidene acetal to provide **37** in 81% yield. Although the anomers of methyl glycoside **44**–**46** were inseparable, those for **37** were separable. Yields for the latter three steps in Scheme 9 are those obtained when carrying out the reaction on the mixture.



Scheme 9. Synthesis of **37**

Insight into the regioselectivity of the acetal-forming reaction came from analysis of the ^{1}H NMR spectrum of the α-isomer of **37 (37α)**. The coupling constants for the pyranose ring protons correlated to it being in a chair conformation, as would be expected for the tricyclic compound. A ^{4}J "W-coupling", with a magnitude of 1.6 Hz, was observed between the hydroxyl group at C-4 and H-5 (Figure 3a). This is at the high end of magnitudes of such *J*'s, which we attribute to the C-4 hydroxyl group hydrogen-bonding to the two oxygens of the acetal moiety, thus fixing the hydrogen atom in a W relationship with H-5.

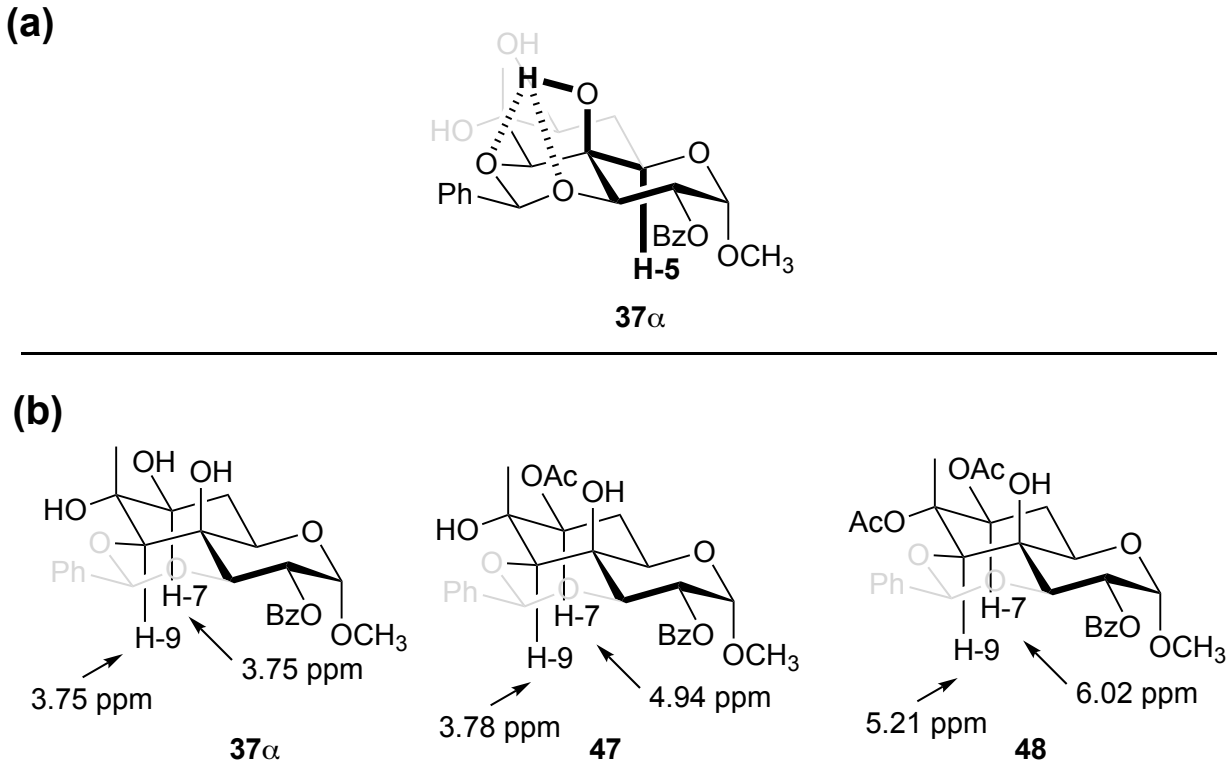


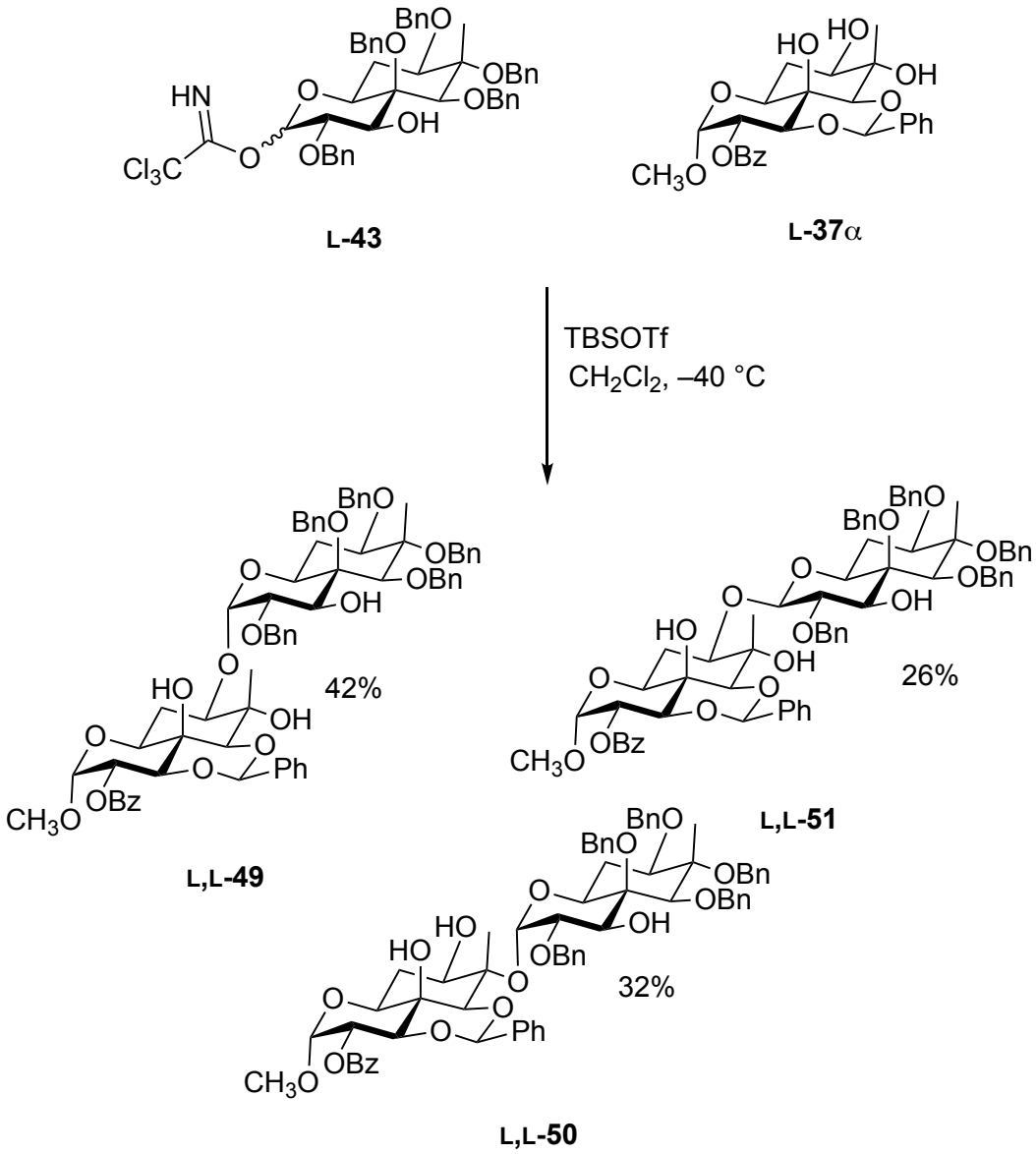
Figure 3. (a) Proposed hydrogen-bonding between C-4 OH hydrogen and acetal oxygens in **37α** leading to a "W-coupling" with H-5. (b) Chemical shift changes of resonances for H-7 and H-9 upon acetylation of OH-7 and OH-7/OH-8 in **37α** (all spectra were recorded in $CDCl_3$).

Additional confirmation of the structure came from the acetylation of **37α**, which lead to two new compounds: **47** and **48** (Figure 3b). In the ^{1}H NMR spectrum of **47**, the resonance for H-7 shifted downfield compared to **37α**, as would be expected upon acylation; the resonance for H-9 was not significantly changed. Interestingly, when both OH-7 and OH-8 were acetylated (compound **48**), significant downfield shifts in the resonances for H-7 and H-9 were seen. These data suggest not only that **37α** contains hydroxyl groups at C-7 and C-8, but also that the deshielding cone of the ester carbonyl group of the C-8 acetoxy group must be placed so that is deshields both H-7 and H-9. It should also be noted that the W-coupling between 4-OH and H-5 that was observed in **37α**, is also seen in **47** and **48**.

Taken together, the data above provides support for the structure of **37α**. Final support came from an X-ray structure of **37α** (See Supporting Information, Figure S2), which showed that the benzylidine acetal spans O-3 and C-9. This structure also provides support of the stereochemistry of the synthetic bradyrhizose prepared by the approach detailed above.

Disaccharide Assembly

Glycosylations. Optimization of the glycosylation reactions with **L-43** and **L-37α** (Scheme 10) revealed that the most effective protocol involved an 'inverse' method [20,21] in which the freshly formed trichloroacetimidate (2 equiv) was added to a solution of acceptor **L-37α** (1 equiv) and TBSOTf in dichloromethane. This glycosylation gave three products in combined near quantitative yield: the α-(1→7)-linked disaccharide (**L,L-49**), the α-(1→8)-linked disaccharide (**L,L-50**) and the β-(1→7)-linked disaccharide (**L,L-51**) in a ratio of 42:32:26. The major compound, **L,L-49**, was the desired one, having an α-(1→7)-glycosidic linkage, which is that present, albeit in the enantiomeric form, in the bradyrhizose homopolymer from *Bradyrhizobium* sp. BTAi1 and sp. ORS278. Application of the same approach to **D-43** and **D-37α** provided the same three (yet enantiomeric) products in a near identical ratio (43:32:25) although the combined yield was lower (60%) as due to limitations in sample only 1.4 equiv of the donor was used relative to the acceptor. When the protocol was used with donor and acceptor pairs differing in absolute stereochemistry (*i.e.,* **D-43** and **L-37α**; **L-43** and **D-37α**) the same three products, but in different ratios compared to when both donors had the same absolute stereochemistry. The results of these glycosylations are summarized in Table 1.



L-43 **L-37α** **L,L-49** **L,L-51** **L,L-50**

Scheme 10. Glycosylation of **L-37α** with **L-43**

Table 1. Summary of Glycosylation of **37α** with **43**.

Donor	Acceptor	Donor Equiv.	Yield (%)	Products[a] α-(1→7) (%)	α-(1→8) (%)	β-(1→7) (%)
L-43	**L-37α**	2.0	100	**L,L -49** 42	**L,L-50** 32	**L,L-51** 26
D-43	**D-37α**	1.4	60	**D,D-49** 43	**D,D-50** 32	**D,D-51** 25
D-43	**L-37α**	2.0	72	**D,L-49** 53	**D,L-50** 36	**D,L-51** 11
L-43	**D-37α**	2.2	70	**L,D-49** 54	**L,D-50** 39	**L,D-51** 7

[a]Ratio determined by separation of the products by column chromatography and identification by NMR spectroscopy.

A notable conclusion of these reactions is that the use of donors (*i.e.,* **D-43** and **L-43**) possessing a free C-3 hydroxyl group does not lead to any self-coupling products. This is in line with both the work outlined above (Scheme 7), and described before,[6] revealing that this hydroxyl group has very low nucleophilicity. This is presumably due to its location adjacent to the ring juncture (C-4), a carbon that also bears a substituent. Hence, we did not explore the fully benzylated substrates **D-36** and **L-36** in the glycosylations.

With regard to the selective glycosylation of the three hydroxyl groups (C-4, C-7 and C-8) present in acceptors **D-37α** and **L-37α**, as we hypothesized, no products arising from the glycosylation of the C-4 hydroxyl group were observed. This hydroxyl group would be expected to be the least nucleophilic of the three given that it is significantly sterically hindered by virtue of its axial orientation, its 1,3-diaxial relationship with regard to the C-8 methyl group and it being embedded in the centre of the fused tricyclic ring system. On the other hand, the regioselectivity observed between the C-7 (secondary) and C-8 (tertiary) hydroxyl groups was lower than expected (~2:1). Although products arising from reaction at the least hindered secondary C-7 hydroxyl

group were formed as the major product, glycosylation of the tertiary C-8 hydroxyl group also occurred to a significant degree.

Given the similarity between these bradyrhizose donors and 4,6-*O*-benzylidene-protected glucopyranose derivatives, we postulated (above) that they would be highly α-selective. Earlier work[6] using donors of the type **52** (Figure 4a), demonstrated that them to indeed be α-selective, which was attributed to long-range participation of the acetate ester at C-3. Donors **43** employed in this study showed lower α-selectivity, providing from 7–26% of the β-(1→7)-linked disaccharide **51**, but none of the product with a β-linkage to the C-8 hydroxyl group. Whether this reduced selectivity in reactions with **43** arises from the lack of an acetate present in the donor, or from the inherent selectivity of this particular substrate, remains to be determined. We favor the latter explanation, however, given that varying amounts of β-linked product were seen with the different combinations of donors and acceptors (Table 1). If the lack of acetate protection is the origin of the reduced selectivity, one could expect a similar ratio of β-linked product regardless of the donor and acceptor pair.

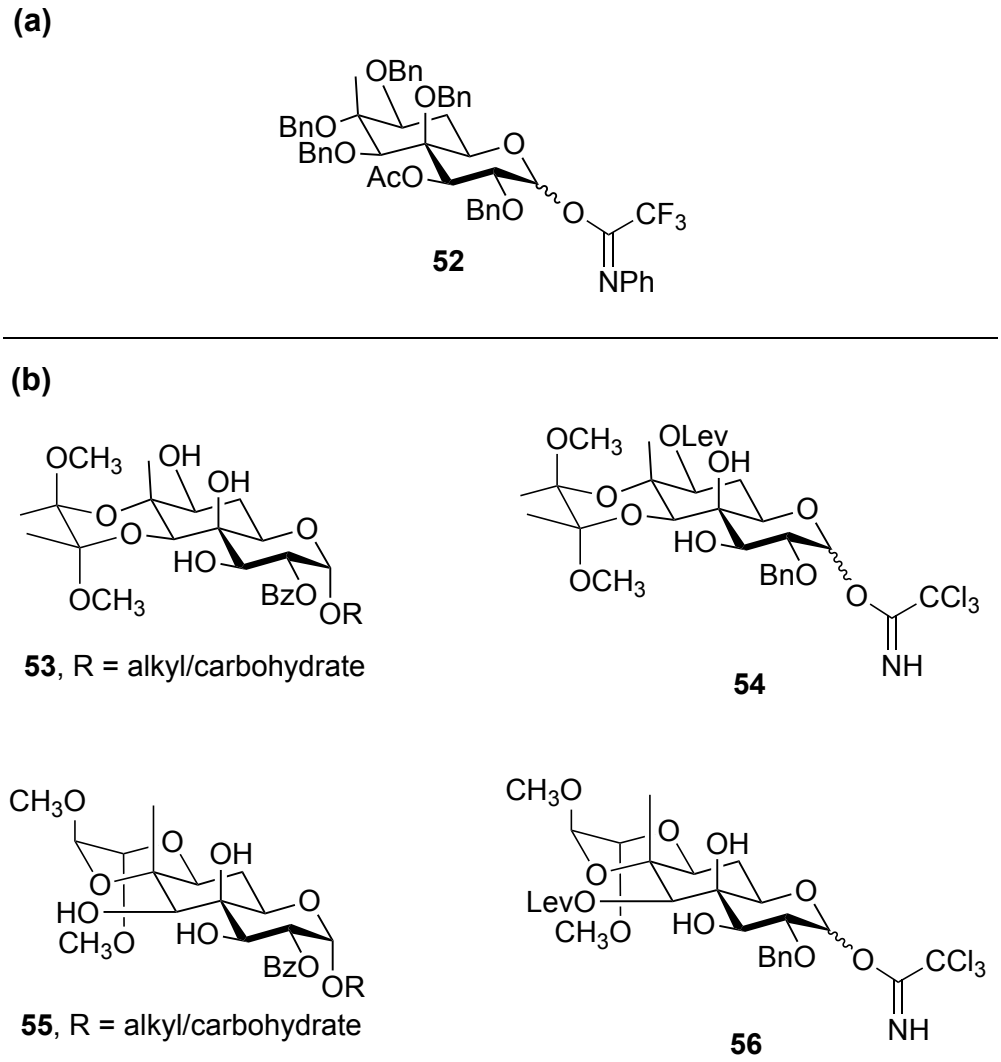
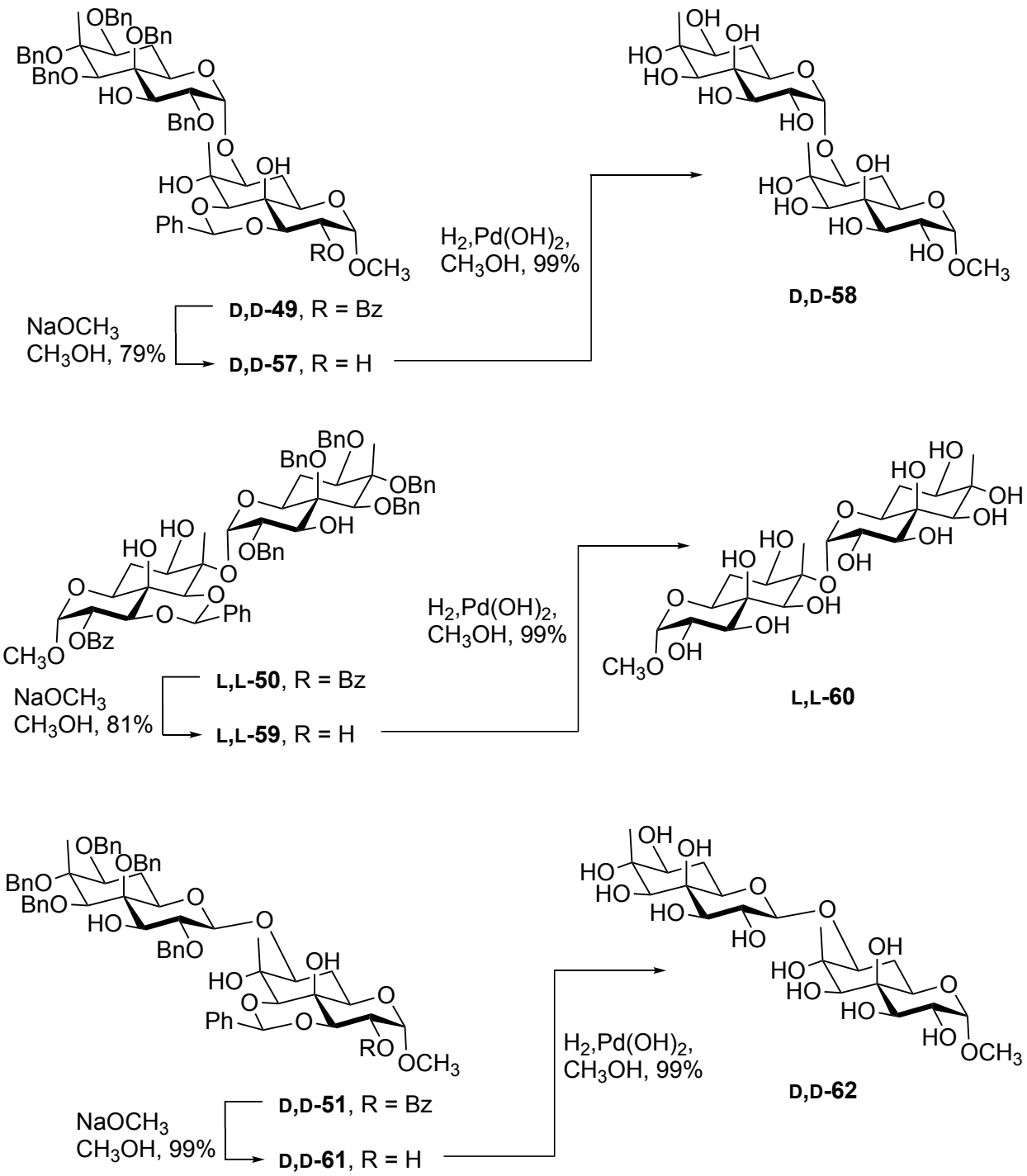


Figure 4. (a) Donor (**52**) used in bradyrhizose glycosylations by Yu and coworkers.[6] (b) Putative acceptors (**53** and **55**) and donors (**54** and **56**) that could be used to assemble α -(1→7)- or α -(1→9)-linked bradyrhizose homopolymers, respectively.

The results outlined above, in conjunction with previous work,[6] point to imidate donors of bradyrhizose bearing non-participating groups at C-2 being α-selective. Whether this arises from the 'kinetic anomeric effect',[22] remote participation,[6] or other effects needs to be examined. The small amount of β-linked product formed from **43** appears to be a function of the structure of the acceptor. This work has also shown that the use of partially-protected bradyrhizose acceptors is a productive strategy for synthesizing oligosaccharides containing this bicyclic monosaccharide. It

should be noted, however, that **37α** does not appears to be an optimized acceptor with regard to obtaining the α-(1→7)-linked homopolymers, which is one of the two structures found in nature. Although not tested here, the lack of products arising from self-coupling of **43**, or from glycosylation of the C-4 hydroxyl group in **37α**, suggest that donors and acceptors lacking protection on both the C-3 and C-4 hydroxyl groups may be viable reagents to synthesize bradyrhizose-containing oligosaccharides. Indeed, we postulate that species such as **53**–**56** (Figure 4b) may be suitable building blocks for the preparation the naturally-occurring α-(1→7)-linked and α-(1→9)-linked homopolymers. Such species are expected to be readily produced from compounds such as **46** (Scheme 9).

Deprotections. All of the disaccharides were deprotected in a two-step process. As examples, the deprotections of **D,D-49**, **L,L-50** and **D,D-51** are shown in Scheme 11. The benzoyl group was removed using sodium methoxide in methanol and then the benzyl ethers were removed by hydrogenolysis using $Pd(OH)_2$ in methanol. These transformations proceeded in generally excellent overall yield.



Scheme 11. Deprotection of **D,D-49**, **L,L-50** and **D,D-51**

Evaluation of Bradyrhizose-Containing Glycans as Inducers of the Innate Immune Response in Plants

Once deprotected, the compounds were evaluated for their ability to activate the innate immune system in *Arabidopsis thaliana* through the generation of reactive oxygen species (ROS).[23] The results of these experiments are depicted in Table 2. In some cases, too little of the material was obtained after deprotection to allow testing.

Table 2. Generation of ROS upon treatment of *Arabidopis thaliana* with synthetic glycans.

Entry	Compound[a]	Linkage	ROS Generation
1	**D-1**	NA[b]	–
2	**L-1**	NA[b]	–
3	**D,D-58**	α-(1→7)	–
4	**L,L-58**	α-(1→7)	ND[c]
5	**L,D-58**	α-(1→7)	–
6	**D,L-58**	α-(1→7)	–
7	**D,D-60**	α-(1→8)	ND[c]
8	**L,L-60**	α-(1→8)	+
9	**L,D-60**	α-(1→8)	–
10	**D,L-60**	α-(1→8)	–
11	**D,D-62**	β-(1→7)	+
12	**L,L-62**	β-(1→7)	+
13	**L,D-62**	β-(1→7)	ND[c]
14	**D,L-62**	β-(1→7)	ND[c]

[a] Stereochemical descriptors given in the order: Non-reducing end residue, reducing end residue. [b]Monosaccharide. [c]Not tested due to insufficient amount of material

Consistent with previous studies,[4,6] both the naturally-occurring monosaccharide (**D-1**, Entry 1) and disaccharide with the natural α-(1→7) linkage (**D,D-58**, Entry 3) were inactive. The other diastereomers with the α-(1→7) linkage (Entries 5 and 6) similarly failed to induce ROS in

Arabidopsis. On the other hand, some of the compounds possessing the unnatural α-(1→8) or β-(1→7) linkages (**L,L-60**, **D,D-62** and **L,L-62**, Entries 8, 13 and 14) did lead to the generation of ROS. In particular both of the β-(1→7)-linked compounds evaluated were active. Testing of the other two diastereomers with this linkage was, unfortunately, not possible given a lack of material.

These data suggest that specific molecular features in the natural polysaccharide lead to its immunologically silent nature. Furthermore, the results indicate that when connected through unnatural linkages, or when an enantiomeric form of the monosaccharide is evaluated, bradyrhizose-containing molecules can lead to activation of the innate immune response in *A. thaliana*. These studies are also consistent with a hypothesis put forward previously[4,6] that the bacteria that produce α-(1→7)-linked homopolymers of D-bradyrhizose have evolved to produce an immunologically silent LPS that facilitates symbiosis with the plant host. In this regard, the synthesis of additional analogs, containing both antipodes of the monosaccharide and through other natural (i.e., α-(1→9)-linked) and non-natural linkages would be instructive to better understand the structural features that renders this bacterial LPS unrecognizable by the host immune system.

Conclusion

We have developed a convergent approach to the enantiomeric forms of the bicyclic monosaccharide bradyrhizose starting from *myo*-inositol and ethyl propiolate. The route proceeds in 6% overall yield in 25 steps, comparable to the only other synthesis of the molecule, which starts from 2,3,6-tri-*O*-acetyl glucal.[5] Although we chose to make the racemate and separate the enantiomers by resolution, the use of a chiral inositol derivative would allow the synthesis of a desired single enantiomer. The monosaccharide was converted to a trichloroacetimidate donor and an acceptor and its use in producing disaccharides was explored. These investigations revealed

that the donor is generally α-selective and that chemoselective glycosylation of specific hydroxyl groups allows the use of partially protected donors and acceptors in these reactions. Evaluation of the ability of the synthesized molecules to induce a defence response in plants, revealed that many of the derivatives are, like the naturally occurring polysaccharide, immunologically silent. However others do lead to the generation of ROS. These results provide support for the hypothesis that specific structural motifs in D-bradyrhizose lead to its inability to activate the plant innate immune response. In sum, this work provides novel insights into both the chemical reactivity and immunological activity of this fascinating monosaccharide.

Experimental section

General experimental methods. Reactions were carried out in oven-dried glassware. All reagents used were purchased from commercial sources and were used without further purification unless noted. Solvents used in reactions were purified by successive passage through columns of alumina and copper under argon. Unless stated otherwise, all reactions were carried out at room temperature under a positive pressure of argon and were monitored by TLC on silica gel 60 F254 (0.25 mm, E. Merck). Spots were detected under UV light or by charring with a solution of ammonium molybdate (12 g) and ceric ammonium nitrate (0.42 g) in H_2O (235 mL) and concentrated sulfuric acid (15 mL). Unless otherwise indicated, all column chromatography was performed on silica gel 60 (40–60 μM). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 21 ± 2 °C at the sodium D line (589 nm) and are in units of deg·mL(dm·g)-1. ^{1}H NMR spectra were recorded at 500 MHz, and chemical shifts are referenced to either TMS (0.0 ppm, $CDCl_3$), HOD (4.78 ppm, D_2O) or DMSO-d_5 (2.50 ppm, quint, J_{HD} = 1.9 Hz, DMSO-d_6). ^{13}C NMR spectra were recorded at 125 MHz, and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (77.2 ppm, $CDCl_3$), external dioxane (67.4 ppm, D_2O) or DMSO-d_6

(39.5 ppm, DMSO-d_6). In the processing of reaction mixtures, solutions of organic solvents were washed with equal amounts of aqueous solutions. Organic solutions were concentrated under vacuum at < 40°C (bath). Electrospray mass spectra were recorded using TOF mass spectrometry on samples suspended in mixtures of THF with CH_3OH and added NaCl. The separation of the racemic mixture **2** and the determination of the enantiomeric excess for chiral compound **D-2** were done using an Agilent HPLC instrument with Chiralpak-IA (4.6 x 150 mm, inner diameter x length; particle size 5 µm) column (1:99 *i*-PrOH–hexanes) at 5 °C.

***Racemic* bradyrhizose (1)**. Palladium on carbon (70 mg, 0.0654 mmol, 10 wt. % loading) was added to a solution of **30** (82 mg, 0.131 mmol) in MeOH (5 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium on carbon was filtered through Celite® 545 and the filtrate was concentrated. The resulting crude product was purified by reversed phase column chromatography (C-18 silica gel, H_2O) to give **1** (34 mg, 99%) as a colorless oil (isomeric mixture; Figure S3 shows the strucrues of the different isomers). ^{1}H NMR (500 MHz, D_2O, δ_H) 5.27 (d, 0.05 H, J = 5.3 Hz, H-1**e**), 5.25 (br, 0.03 H), 5.23 (d, 0.24 H, J = 4.0 Hz, H-1**b**), 5.07–5.05 (m, 0.13 H, H-1**c** and H-1**d**), 4.62 (d, 0.56 H, J = 8.1 Hz, H-1**a),** 4.34–4.29 (m, 0.18 H), 4.23 (br, 0.03 H), 4.18–4.15 (m, 0.05 H), 4.04–3.86 (m, 0.81 H), 3.82–3.73 (m, 0.96 H), 3.68–3.45 (m, 3.47 H), 2.03–1.82 (m, 2.22 H), 1.76–1.67 (m, 0.14 H), 1.31–1.18 (m, 3.48 H); ^{13}C{^{1}H} NMR (125 MHz, D_2O, δ_C) 97.6 (C-1**a**), 93.3 (C-1**b**), 79.4, 79.3, 78.7, 78.4(9), 78.4(6), 75.4, 74.4, 73.9, 73.6, 73.2, 73.0, 71.5, 70.1, 66.4, 32.0 (C-6), 31.9 (C-6), 15.1 (C-10), 15.0 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{10}H_{18}NaO_8$: 289.0894. Found 289.0896.

D-Bradyrhizose (D-1). Palladium on carbon (15 mg, 0.0143 mmol, 10 wt. % loading) was added to a solution of **D-30** (18 mg, 0.0286 mmol) in MeOH (1.5 mL) under Ar. The reaction mixture

was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium on carbon was filtered through Celite® 545 and the solvent evaporated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **D-1** (8 mg, 99%) as colorless oil (isomeric mixture). The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compound **1** previously described. $[\alpha]_D$ +20.4 (*c* 0.2, H_2O).

L-Bradyrhizose (L-1). Palladium on carbon (10.4 mg, 0.00980 mmol, 10 wt. % loading) was added to a solution of **L-30** (12.3 mg, 0.0.0196 mmol) in MeOH (1 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium on carbon was filtered through Celite® 545 and the solvent evaporated. The resulting crude product did not need further purification to give **L-1** (5.2 mg, 99%) as a colorless oil (isomeric mixture). The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compound **1** previously described. $[\alpha]_D$ –21.8 (*c* 0.2, H_2O).

***Racemic* 1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-(ethoxycarbonyl-(1'*R*,2'*R*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (2).** 4-Methylmorpholine *N*-oxide (535 mg, 4.57 mmol) and DHQ-CLB (2.20 g, 4.74 mmol) were added to a solution of **27** (2.64 g, 3.51 mmol) in acetone (30 mL). Water (5 mL) was added, followed by osmium tetroxide (1.12 mL, 0.176 mmol, 4% solution in H_2O). The reaction mixture was stirred in the dark at rt overnight and then EtOAc and a saturated aqueous solution of $Na_2O_3S_2$ were added and the mixture was stirred for 2 h. The aqueous and organic layer were separated and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **2** (1.78 g, 65%) as colorless oil. R_f 0.50 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.44–7.41 (m, 2 H, Ar), 7.39–7.24 (m, 18 H,

Ar), 5.12 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 5.06 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 5.01 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.98 (d, 1 H, $J_{1',2'}$ = 8.6 Hz, H-1'), 4.86 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.81 (d, 1 H, $J_{1',2'}$ = 8.4 Hz, H-2'), 4.74 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.65 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.62 (s, 2 H, 2 x C$\underline{H}_2$Ar), 4.50 (dd, 1 H, $J_{5ax,6}$ = 12.1 Hz, $J_{5eq,6}$ = 4.0 Hz, H-6), 4.37 (d, 1 H, J = 7.2 Hz, OH), 4.30–4.17 (m, 2 H, C$\underline{H}_2$CH$_3$), 3.60 (dd, 1 H, $J_{4,5ax}$ = 12.3 Hz, $J_{4,5eq}$ = 4.6 Hz, H-4), 3.60 (s, 1 H, H-2), 3.32 (d, 1 H, J = 7.2 Hz, OH), 2.16 (ddd, 1 H, $J_{4,5ax}$ = 12.0 Hz, $J_{5eq,5ax}$ = 12.0 Hz, $J_{5ax,6}$ = 12.0 Hz, H-5$_{ax}$), 1.89 (ddd, 1 H, $J_{5eq,5ax}$ = 12.1 Hz, $J_{4,5eq}$ = 4.2 Hz, $J_{5eq,6}$ = 4.2 Hz, H-5$_{eq}$), 1.71 (s, 3 H, CH$_3$), 1.18 (t, 3 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$), 0.93 (s, 9 H, 3 x SiC(CH$_3$)$_3$), 0.15 (s, 3 H, SiCH$_3$), 0.10 (s, 3 H, SiCH$_3$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, δ_C) 173.7 (C=O), 140.0 (Ar), 139.8 (Ar), 139.0 (Ar), 138.5 (Ar), 128.5 (Ar), 128.3(2) (Ar), 128.2(5) (Ar), 127.9 (Ar), 127.7 (Ar), 127.5 (Ar), 127.3(5) (Ar), 127.3(1) (Ar), 127.2 (Ar), 127.0 (Ar), 126.8 (Ar), 84.1 (C-2), 83.9 (C-1/C-3), 81.7 (C-4), 80.2 (C-3/C-1), 75.7 (C$\underline{H}_2$Ar), 72.4 (C-6), 71.9 (C$\underline{H}_2$Ar), 71.3 (C-1'/C-2'), 71.0 (C-1'/C-2'), 67.4 (C$\underline{H}_2$Ar), 66.1 (C$\underline{H}_2$Ar), 62.3 (C$\underline{H}_2$CH$_3$), 33.2 (C-5), 25.8 (3 x SiC(C$\underline{H}_3$)$_3$), 18.1 (SiC(CH$_3$)$_3$), 14.0 (CH$_2$C$\underline{H}_3$), 11.4 (CH$_3$), –3.6 (SiCH$_3$), –4.3 (SiCH$_3$). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{46}H_{60}NaO_9Si$: 807.3899. Found 807.3894.

(–)-1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-(ethoxycarbonyl-(1'*S*,2'*S*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (D-2). For experimental, see compound **31**. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained for the racemic compound **2** previously described. $[\alpha]_D$ –57.2 (*c* 0.3, $CHCl_3$).

***Racemic* 2,3,4-tri-*O*-benzyl-5-deoxy-3-*C*-methyl-6-*O*-triisopropylsilyl-*scyllo*-inosose (3).** A solution of DMSO (877 µL, 12.3 mmol) in CH_2Cl_2 (12 mL) was added dropwise to a cooled (–

78 °C) solution of oxalyl chloride (760 µL, 8.98 mmol) in CH_2Cl_2 (24 mL). After 30 min, a solution of **19** (2.26 g, 1.63 mmol) in CH_2Cl_2 (60 mL) was added slowly to the reaction mixture. After 1 h, Et_3N (2.87 mL, 20.6 mmol) was added slowly and the reaction mixture was stirred for 4 h at –78 °C. Water was added and the reaction mixture was warmed to rt and then extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 → 9:1 hexanes–EtOAc) to give **3** (2.07 g, 92%) as as a colorless oil. R_f 0.43 (9:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38–7.28 (m, 15 H, Ar), 4.86 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 4.82 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.79 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 4.72 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.71 (d, 1 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 4.46 (d, 1 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 4.30 (ddd, 1 H, $J_{5ax,6}$ = 12.5 Hz, $J_{5eq,6}$ = 6.8 Hz, $J_{2,6}$ = 1.1 Hz, H-6), 4.07 (d, 1 H, $J_{2,6}$ = 0.9 Hz, H-2), 3.90 (dd, 1 H, $J_{4,5ax}$ = 12.1 Hz, $J_{4,5eq}$ = 4.8 Hz, H-4), 2.39 (ddd, 1 H, $J_{5ax,5eq}$ = 13.0 Hz, $J_{5eq,6}$ = 6.8 Hz, $J_{4,5eq}$ = 4.8 Hz, H-5$_{eq}$), 1.73 (ddd, 1 H, $J_{4,5ax}$ = 12.5 Hz, $J_{5eq,5ax}$ = 12.5 Hz, $J_{5ax,6}$ = 12.5 Hz, H-5$_{ax}$), 1.38 (s, 3 H, CH_3), 1.17–1.05 (m, 21 H, 3 x SiC$\underline{H}$($C\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 204.2 (C-1), 139.5 (Ar), 138.4 (Ar), 137.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.8 (Ar), 127.7(3) (Ar), 127.6(8) (Ar), 127.3 (Ar), 127.2 (Ar), 85.3 (C-6), 83.8 (C-3), 78.0 (C-4), 73.0 ($\underline{C}H_2$Ar), 72.7 ($\underline{C}H_2$Ar), 72.1 (C-2), 66.5 ($\underline{C}H_2$Ar), 36.7 (C-5), 18.0 (SiCH($\underline{C}H_3$)$_2$), 17.9 (SiCH($\underline{C}H_3$)$_2$), 12.3 (3 x Si$\underline{C}$H(CH_3)$_2$), 11.4 (CH_3). HRMS (ESI) Calcd for $[M + H]^+$ $C_{37}H_{51}O_5Si$: 603.3500. Found 603.3498.

***Racemic* 5-*O*-allyl-1-*O*-benzyl-2,6-*O*-benzylidene-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-*scyllo*-inositol (5)**. DIBAL-H (109 mL, 109 mmol, 1.0M in toluene) was added to a cooled (0 °C) solution of **10** (10.5 g, 19.8 mmol) in toluene (140 mL). The reaction mixture was stirred at 0 °C for 30 min. A saturated aqueous solution of potassium sodium tartrate and CH_2Cl_2 were added at 0 °C and the mixture was stirred overnight while warming to rt. The aqueous solution was extracted

with CH_2Cl_2 and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **5** (9.17 g, 87%) as a colourless oil. R_f 0.23 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.50–7.47 (m, 2 H, Ar), 7.43–7.35 (m, 5 H, Ar), 7.33–7.29 (m, 2 H, Ar), 7.28–7.23 (m, 3 H, Ar), 6.88–6.84 (m, 2 H, Ar), 5.93 (app ddt, 1 H, J = 17.2 Hz, J = 10.4 Hz, J = 5.7 Hz, C<u>H</u>=CH_2), 5.59 (s, 1 H, C<u>H</u>Ar), 5.30 (app dq, 1 H, J = 17.2 Hz, J = 1.7 Hz, CH=C<u>H</u>$_2$ *trans*), 5.18 (app dq, 1 H, J = 10.4 Hz, J = 1.7 Hz, CH=C<u>H</u>$_2$ *cis*), 4.76 (d, 1 H, J = 11.7 Hz, C<u>H</u>$_2$Ar), 4.63 (s, 2 H, 2 x C<u>H</u>$_2$Ar), 4.59 (d, 1 H, J = 1.7 Hz, C<u>H</u>$_2$Ar), 4.54 (ddd, 1 H, J = 7.7 Hz, J = 7.7 Hz, J = 2.8 Hz, H-4), 4.29–4.24 (m, 1 H, C<u>H</u>$_2$CH=CH_2), 4.26 (d, 1 H, J = 2.6 Hz, H-2/H-6), 4.19 (d, 1 H, J = 2.4 Hz, H-2/H-6), 4.15 (app ddt, 1 H, J = 13.2 Hz, J = 5.7 Hz, J = 1.5 Hz, C<u>H</u>$_2$CH=CH_2), 3.94 (d, 1 H, J = 7.5 Hz, H-3/H-5), 3.89 (d, 1 H, J = 7.5 Hz, H-3/H-5), 3.80 (s, 3 H, OCH_3), 2.43 (d, 1 H, J = 3.3 Hz, OH), 1.78 (s, 3 H, CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 159.3 (Ar), 138.4 (Ar), 137.5 (Ar), 134.6 (<u>C</u>H=CH_2), 130.2 (Ar), 129.4(0) (Ar), 129.3(8) (Ar), 128.5 (Ar), 128.3 (Ar), 127.5 (Ar), 127.3 (Ar), 126.4 (Ar), 117.2 (CH=<u>C</u>H_2), 113.9 (Ar), 92.7 (<u>C</u>HAr), 82.9 (C-3/C-5), 82.7 (C-3/C-5), 78.4 (C-2/C-6), 78.3 (C-2/C-6), 74.8 (C-4), 73.4 (<u>C</u>H_2CH=CH_2), 71.3 (<u>C</u>H_2Ar), 70.8 (C-1), 63.7 (<u>C</u>H_2Ar), 55.3 (OCH_3), 19.3 (CH_3). HRMS (ESI) Calcd for $[M + H]^+$ $C_{32}H_{37}O_7$: 533.2534. Found 533.2534.

***Racemic* 5-*O*-allyl-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-*scyllo*-inositol 2,4,6-orthobenzoate (8)**. A solution of DMSO (16.2 mL, 227 mmol) in CH_2Cl_2 (50 mL) was added dropwise to a cooled (–78 °C) solution of oxalyl chloride (14.0 mL, 165 mmol) in CH_2Cl_2 (50 mL). After 30 min, a solution of **7** (29.4 g, 68.9 mmol) in CH_2Cl_2 (250 mL) was added slowly to the reaction mixture. After 1 h, Et_3N (0.51 mL, 5.89 mmol) was added slowly and the reaction mixture was stirred for an additional hour at –78 °C and then warmed to rt. The solution was concentrated and the crude

compound was used without purification for the next step. THF (600 mL) was added to the crude compound and the mixture was sonicated for 15 min. The reaction mixture was then cooled (–78 °C) and methylmagnesium bromide solution (115 mL, 344 mmol) was added dropwise. After 1 h, a saturated aqueous solutiom of NH_4Cl was added slowly to the reaction mixture at –78 °C. The mixture was warmed to rt, then water and CH_2Cl_2 were added. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (9:1 → 4:1 hexanes–EtOAc) to give **8** (28.7 g, 95%) as a colorless oil. R_f 0.40 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.63–7.57 (m, 2 H, Ar), 7.38–7.34 (m, 3 H, Ar), 7.30–7.27 (m, 2 H, Ar), 6.91–6.87 (m, 2 H, Ar), 5.90 (app ddt, 1 H, J = 17.2 Hz, J = 10.4 Hz, J = 5.7 Hz, C<u>H</u>=CH$_2$), 5.27 (app dq, 1 H, J = 17.2 Hz, J = 1.5 Hz, CH=C<u>H$_2$</u> *trans*), 5.20 (app dq, 1 H, J = 10.4 Hz, J = 1.5 Hz, CH=C<u>H$_2$</u> *cis*), 4.69–4.3 (m, 4 H, C<u>H$_2$</u>Ar, OH, 2 x H_{inos}), 4.54–4.50 (m, 2 H, 2 x H_{inos}), 4.23–4.14 (m, 4 H, 2 x C<u>H$_2$</u>CH=CH$_2$, 2 x H_{inos}), 3.82 (s, 3 H, OCH_3), 1.63 (d, 3 H, $J_{CH3,OH}$ = 1.1 Hz, CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 159.4 (Ar), 136.7 (Ar), 133.6 (<u>C</u>H=CH$_2$), 129.6 (Ar), 129.1 (Ar), 128.1 (Ar), 125.3 (Ar), 117.9 (CH=<u>C</u>H$_2$), 113.9 (Ar), 107.5 (<u>C</u>Ar), 74.2(3) (C_{inos}), 74.2(0) (C_{inos}), 74.0 (C_{inos}), 73.6 (C_{inos}), 71.4 (C-1), 70.6 (<u>C</u>H$_2$Ar), 68.5 (C_{inos}), 67.7 (<u>C</u>H$_2$CH=CH$_2$), 55.3 (OCH_3), 25.0 (CH_3). HRMS (ESI) Calcd for $[M + H]^+$ $C_{25}H_{29}O_7$: 441.1908. Found 441.1900.

***Racemic* 3-*O*-(4-methoxybenzyl)-1-*C*-methyl-*scyllo*-inositol 2,4,6-orthobenzoate (9)**. To a solution of **8** (51 mg, 0.116 mmol) in THF (0.6 mL), degassed under vacuum and stirring under an Ar atmosphere, (1,5-cyclooctadiene)bis-(methyldiphenylphosphine)iridium I hexafluorophosphate catalyst (5 mg, 0.00637 mmol) was added followed by further degassing of the mixture under vacuum. The suspension was stirred for 15 min at 0 °C, and the catalyst was then activated with H_2 (2 min under a H_2 atmosphere). At this point, the solution became nearly

colorless. The excess H_2 was removed by three cycles of placing the flask under vacuum and then flushing the flask with Ar. The reaction mixture was then stirred for 3 h at rt under an Ar atmosphere. The solvent was then evaporated, and the residue was dissolved in acetone–water (10:1, 4.45 mL) before HgO (35 mg, 0.162 mmol) and $HgCl_2$ (38 mg, 0.139 mmol) were added. After 1 h, the solvent was evaporated and the residue was diluted with Et_2O and washed with a 10% aqueous solution of KI, a saturated aqueous solution of $Na_2S_2O_3$, and water. The aqueous layers were extracted with EtOAc and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **9** (40 mg, 87%) as a white solid. mp = 117−119 °C; R_f 0.28 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.62–7.58 (m, 2 H, Ar), 7.38–7.34 (m, 3 H, Ar), 7.32–7.28 (m, 2 H, Ar), 6.93–6.89 (m, 2 H, Ar), 4.72 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.72–4.68 (m, 1 H, H-5), 4.67 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.59–4.55 (m, 2 H, H-2, H-3), 4.19–4.15 (m, 2 H, H-4, H-6), 3.94 (d, 1 H, J = 0.6 Hz, OH), 3.82 (s, 3 H, OCH_3), 3.30 (d, 1 H, J = 7.9 Hz, OH), 1.66 (d, 3 H, $J_{CH3,OH}$ = 1.1 Hz, CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 159.4 (Ar), 136.4 (Ar), 129.9 (Ar), 129.6 (Ar), 128.6 (Ar), 128.1 (Ar), 125.4 (Ar), 114.1 (Ar), 107.2 (C$\underline{C}$Ar), 75.5 (C_{inos}), 74.0(1) (C_{inos}), 74.0(0) (C_{inos}), 72.1 (C$\underline{C}H_2$Ar), 69.8 (C_{inos}), 68.8 (C-1), 68.4 (C-2), 55.3 (OCH_3), 26.1 (CH_3). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{22}H_{24}NaO_7$: 423.1414. Found 423.1415.

***Racemic* 5-*O*-allyl-1-*O*-benzyl-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-*scyllo*-inositol 2,4,6-orthobenzoate (10)**. Sodium hydride (5.22 g, 130 mmol, 60% wt in mineral oil), benzyl bromide (23.2 mL, 196 mmol) and TBAI (2.41 g, 6.52 mmol) were added to a solution of **9** (28.7 g, 65.2 mmol) in THF (600 mL). The reaction mixture was heated at reflux for 2 h. Water was added and the aqueous solution was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography

(19:1 to 17:3 hexanes–EtOAc) to give **10** (32.9 g, 95%) as a yellow oil. R_f 0.60 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.66–7.62 (m, 2 H, Ar), 7.40–7.36 (m, 5 H, Ar), 7.21–7.15 (m, 5 H, Ar), 6.80–6.76 (m, 2 H, Ar), 5.87 (app ddt, 1 H, J = 17.2 Hz, J = 10.5 Hz, J = 5.9 Hz, C<u>H</u>=CH_2), 5.22 (app dq, 1 H, J = 17.2 Hz, J = 1.7 Hz, CH=C<u>H</u>$_2$ *trans*), 5.13 (app dq, 1 H, J = 10.5 Hz, J = 1.7 Hz, CH=C<u>H</u>$_2$ *cis*), 4.66–4.63 (m, 3 H, 2 x C<u>H</u>$_2$Ar, H_{inos}), 4.59 (s, 2 H, 2 x C<u>H</u>$_2$Ar), 4.52 (ddd, 1 H, J = 6.6 Hz, J = 3.3 Hz, J = 1.3 Hz, H_{inos}), 4.49 (ddd, 1 H, J = 6.6 Hz, J = 3.3 Hz, J = 1.3 Hz, H_{inos}), 4.45–4.41 (m, 2 H, 2 x H_{inos}), 4.17–4.10 (m, 2 H, 2 x C<u>H</u>$_2$CH=CH_2), 3.80 (s, 3 H, OCH_3), 1.80 (s, 3 H, CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 159.1 (Ar), 138.9 (Ar), 136.9 (Ar), 134.7 (<u>C</u>H=CH_2), 130.2 (Ar), 129.5 (Ar), 128.1 (Ar), 127.8 (Ar), 127.5 (Ar), 126.8 (Ar), 125.3 (Ar), 117.3 (CH=<u>C</u>H_2), 113.6 (Ar), 108.1 (<u>C</u>Ar), 74.1 (C_{inos}), 73.9 (C_{inos}), 73.8 (C_{inos}), 73.7 (C_{inos}), 71.4 (<u>C</u>H_2Ar), 71.1 (<u>C</u>H_2CH=CH_2), 70.9 (C-1), 69.2 (C_{inos}), 63.8 (<u>C</u>H_2Ar), 55.3 (OCH_3), 21.7 (CH_3). HRMS (ESI) Calcd for $[M + K]^+$ $C_{32}H_{34}KO_7$: 569.1936. Found 569.1932.

Racemic **5-*O*-allyl-1-*O*-benzyl-2,6-*O*-benzylidene-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-(4-nitrobenzoate)-*scyllo*-inositol (11)**. *p*-Nitrobenzoyl chloride (10 mg, 0.0518 mmol) was added to a solution of **5** (23 mg, 0.0432 mmol) and DMAP (8 mg, 0.0648 mmol) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 2 h at rt. Water was added and the mixture was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **11** (29 mg, 99%) as a yellow oil. R_f 0.44 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.27 (d, 2 H, J = 8.4 Hz, Ar), 8.09 (d, 2 H, J = 8.4 Hz, Ar), 7.56–7.37 (m, 10 H, Ar), 7.08 (d, 2 H, J = 8.1 Hz, Ar), 6.56 (d, 2 H, J = 8.1 Hz, Ar), 6.21 (dd, 1 H, $J_{3,4}$ = 8.1 Hz, $J_{4,5}$ = 8.1 Hz, H-4), 5.74 (s, 1 H, C<u>H</u>Ar), 5.74–5.64 (m, 1 H, C<u>H</u>=CH_2), 5.16 (d, 1 H, J = 17.2 Hz, CH=C<u>H</u>$_2$ *trans*), 5.04 (d, 1 H, J = 10.6 Hz, CH=C<u>H</u>$_2$ *cis*), 4.72 (s, 2 H, 2 x C<u>H</u>$_2$Ar), 4.66 (d, 1 H, J = 12.2 Hz, C<u>H</u>$_2$Ar), 4.38 (d, 1 H,

J = 12.2 Hz, C$\underline{H}_2$Ar), 4.34 (d, 1 H, J = 2.0 Hz, H-2/H-6), 4.27 (d, 1 H, J = 2.0 Hz, H-2/H-6), 4.18–4.10 (m, 3 H, H-3, H-5, C$\underline{H}_2$CH=CH$_2$), 3.96 (dd, 1 H, J = 12.5 Hz, J = 5.6 Hz, C$\underline{H}_2$CH=CH$_2$), 3.66 (s, 3 H, OCH$_3$), 1.82 (s, 3 H, CH$_3$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, δ_C) 163.8 (C=O), 159.2 (Ar), 150.5 (Ar), 138.0 (Ar), 137.3 (Ar), 135.9 (Ar), 134.0 (C$\underline{H}$=CH$_2$), 130.8 (Ar), 130.0 (Ar), 129.5 (Ar), 129.3 (Ar), 128.6 (Ar), 128.5 (Ar), 127.9 (Ar), 127.6 (Ar), 126.3 (Ar), 123.4 (Ar), 117.8 (CH=C$\underline{H}_2$), 113.6 (Ar), 92.6 (C$\underline{H}$Ar), 79.7 (C$_{inos}$), 78.8 (C$_{inos}$), 78.6 (C$_{inos}$), 78.1 (C$_{inos}$), 77.7 (C$_{inos}$), 73.3 (C$\underline{H}_2$CH=CH$_2$), 70.4 (C$\underline{H}_2$Ar/C-1), 70.3 (C$\underline{H}_2$Ar/C-1), 64.3 (C$\underline{H}_2$Ar), 55.1 (OCH$_3$), 19.2 (CH$_3$). HRMS (ESI) Calcd for [M + NH$_4$]$^+$ $C_{39}H_{43}N_2O_{10}$: 699.2912. Found 699.2906.

Racemic **5-*O*-allyl-1-*O*-benzyl-2,6-*O*-benzylidene-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (12)**. Imidazole (1.05 g, 15.5 mmol) and TIPSCl (6.61 mL, 30.9 mmol) were added to a solution of **5** (5.50 g, 10.3 mmol) in DMF (90 mL). The reaction mixture was heated at 70 °C overnight. Water was added and the aqueous solution was extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **12** (7.03 g, 99%) as a yellow oil. R_f 0.68 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$, δ_H) 7.59–7.56 (m, 2 H, Ar), 7.46–7.40 (m, 3 H, Ar), 7.37–7.34 (m, 2 H, Ar), 7.32–7.22 (m, 5 H, Ar), 6.87–6.84 (m, 2 H, Ar), 5.95 (app ddt, 1 H, J = 17.2 Hz, J = 10.5 Hz, J = 5.1 Hz, C$\underline{H}$=CH$_2$), 5.67 (s, 1 H, C$\underline{H}$Ar), 5.28 (app dq, 1 H, J = 17.2 Hz, J = 1.8 Hz, CH=C$\underline{H}_2$ *trans*), 5.15 (app dq, 1 H, J = 10.5 Hz, J = 1.8 Hz, CH=C$\underline{H}_2$ *cis*), 4.73 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.65–4.61 (m, 3 H, 2 x C$\underline{H}_2$Ar, H-4), 4.54 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.29–4.24 (m, 2 H, C$\underline{H}_2$CH=CH$_2$, H-2/H-6), 4.19 (d, 1 H, J = 2.2 Hz, H-2/H-6), 4.05 (app ddt, 1 H, J = 12.8 Hz, J = 5.3 Hz, J = 1.7 Hz, C$\underline{H}_2$CH=CH$_2$), 3.94 (d, 1 H, J = 6.8 Hz, H-3/H-5), 3.85–3.82 (m, 4 H, H-3/H-5, OCH$_3$), 1.80 (s, 3 H, CH$_3$), 1.17–1.08 (m, 3 H, 3 x SiCH), 1.17–1.08 (m, 18 H, 3 x SiCH(C$\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, δ_C) 158.8

(Ar), 138.5 (Ar), 137.7 (Ar), 134.7 (C$\underline{H}$=CH_2), 130.7 (Ar), 129.4 (Ar), 128.6 (Ar), 128.5 (Ar), 128.0 (Ar), 127.1 (Ar), 127.0 (Ar), 126.4 (Ar), 116.0 (CH=C$\underline{H}_2$), 113.5 (Ar), 92.8 (C$\underline{H}$Ar), 85.7 (C-3/C-5), 85.5 (C-3/C-5), 77.5 (C-2/C-6), 77.4 (C-2/C-6), 75.7 (C-4), 72.9 (C-1), 70.7 (C$\underline{H}_2$Ar), 70.2 (C$\underline{H}_2$CH=CH_2), 63.4 (C$\underline{H}_2$Ar), 55.3 (OCH_3), 19.3 (CH_3), 18.2 (3 x SiCH(C$\underline{H}_3$)$_2$), 12.6 (3 x Si$\underline{C}$H(CH_3)$_2$). HRMS (ESI) Calcd for $[M + H]^+$ $C_{41}H_{57}O_7Si$: 689.3868. Found 689.3872.

***Racemic* 3-*O*-Allyl-1,2-di-*O*-benzyl-5-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (13)** and ***racemic* 5-*O*-Allyl-1,2-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (14)**. DIBAL-H (72 mL, 72.0 mmol, 1.0M in toluene), was added to a cooled (0 °C) solution of **12** (3.21 g, 4.66 mmol) in toluene (86 mL). The reaction mixture was stirred overnight at 0 °C. A saturated aqueous solution of potassium sodium tartrate and CH_2Cl_2 were added and the mixture was stirred at rt overnight. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 to 17:3 hexanes–EtOAc) to give **13** and **14** (2.25 g, 70%) as a colorless oil (isomeric mixture 4:1). R_f 0.58 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.34–7.18 (m, 12 H, Ar), 6.92–6.89 (m, 0.4 H, Ar), 6.85–6.82 (m, 1.6 H, Ar), 5.99 (app ddt, 0.8 H, J = 17.2 Hz, J = 10.6 Hz, J = 5.3 Hz, C$\underline{H}$=CH_2), 5.92 (app ddt, 0.2 H, J = 17.2 Hz, J = 10.6 Hz, J = 5.1 Hz, C$\underline{H}$=CH_2), 5.31 (app dq, 0.8 H, J = 17.2 Hz, J = 1.8 Hz, CH=C$\underline{H}_2$ *trans*), 5.23 (app dq, 0.2 H, J = 17.2 Hz, J = 1.8 Hz, CH=C$\underline{H}_2$ *trans*), 5.18 (app dq, 0.8 H, J = 10.5 Hz, J = 1.7 Hz, CH=C$\underline{H}_2$ *cis*), 5.12 (app dq, 0.20 H, J = 10.5 Hz, J = 1.7 Hz, CH=C$\underline{H}_2$ *cis*), 4.94 (d, 0.8 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.86–4.67 (m, 5.8 H, C$\underline{H}_2$Ar), 4.47–4.27 (m, 1.8 H, C$\underline{H}_2$CH=CH_2), 4.22 (app ddt, 0.2 H, J = 12.5 Hz, J = 5.1 Hz, J = 1.5 Hz, C$\underline{H}_2$CH=CH_2), 3.85–3.81 (m, 4 H, H_{inos}, OCH_3), 3.74–3.57 (m, 2 H, 2 x H_{inos}), 3.40 (dd, 0.8 H, J = 9.2 Hz, J = 9.2 Hz, H_{inos}), 3.27 (dd, 0.4 H, J = 9.4 Hz, J = 9.4 Hz, H_{inos}), 3.19 (dd, 0.8 H, J = 9.4 Hz, J = 9.4 Hz, H_{inos}), 2.40 (d, 0.8 H, J =

2.2 Hz, OH), 2.26 (d, 0.2 H, J = 1.8 Hz, OH), 1.45 (s, 2.4 H, CH_3), 1.41 (s, 0.6 H, CH_3), 1.24–1.06 (m, 21 H, $SiCH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 159.1 (Ar), 158.6 (Ar), 139.5 (Ar), 139.4 (Ar), 138.9 (Ar), 138.8 (Ar), 135.3 ($\underline{C}H=CH_2$), 131.3 (Ar), 131.2 (Ar), 129.0 (Ar), 128.4 (Ar), 128.3(3) (Ar), 128.2(5) (Ar), 128.2 (Ar), 128.0 (Ar), 127.5 (Ar), 127.4(3) (Ar), 127.4(0) (Ar), 127.3(4) (Ar), 127.2(7) (Ar), 127.2 (Ar), 116.3 ($CH=\underline{C}H_2$), 115.4 (Ar), 113.8 (Ar), 113.4 (Ar), 84.7(1) (C_{inos}), 84.6(7) (C_{inos}), 83.7 (C_{inos}), 83.2 (C_{inos}), 83.0 (C_{inos}), 82.6 (C_{inos}), 79.8 (C-1), 79.7 (C-1), 76.1(3) (C_{inos}), 76.1(0) (C_{inos}), 75.6 ($\underline{C}H_2Ar$), 75.1 ($\underline{C}H_2Ar$), 75.0 ($\underline{C}H_2Ar$), 74.5 ($\underline{C}H_2Ar$), 73.9 (2 x $\underline{C}H_2CH=CH_2$), 65.4 ($\underline{C}H_2Ar$), 65.3 ($\underline{C}H_2Ar$), 55.3 (OCH_3), 18.4 ($SiCH(CH_3)_2$), 18.3(5) ($SiCH(CH_3)_2$), 18.3(3) ($SiCH(CH_3)_2$), 13.6 ($SiCH(CH_3)_2$), 13.4 (CH_3), 13.3 (CH_3). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{41}H_{58}NaO_7Si$: 713.3844. Found 713.3838.

***Racemic* 5-*O*-Allyl-1,2,6-tri-*O*-benzyl-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (15)**. Sodium hydride (484 mg, 12.1 mmol, 60% wt in mineral oil) was added to a solution of **13** and **14** (4.18 g, 6.05 mmol) in THF (65 mL). After 30 min, benzyl bromide (3.60 mL, 30.2 mmol) was added and the reaction mixture was stirred at rt overnight. Water was added and the aqueous solution was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **15** (4.48 g, 95%) as a yellow oil. R_f 0.49 (9:1 hexanes–EtOAc); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.19 (m, 17 H, Ar), 6.87–6.84 (m, 2 H, Ar), 5.95 (app ddt, 1 H, J = 17.2 Hz, J = 10.6 Hz, J = 5.1 Hz, $C\underline{H}=CH_2$), 5.25 (app dq, 1 H, J = 17.2 Hz, J = 1.8 Hz, $CH=C\underline{H}_2$ *trans*), 5.13 (app dq, 1 H, J = 10.6 Hz, J = 1.8 Hz, $CH=C\underline{H}_2$ *cis*), 4.97 (d, 1 H, J = 11.0 Hz, $C\underline{H}_2Ar$), 4.93 (d, 1 H, J = 11.0 Hz, $C\underline{H}_2Ar$), 4.88–4.80 (m, 5 H, 5 x $C\underline{H}_2Ar$), 4.47 (d, 1 H, J = 11.0 Hz, $C\underline{H}_2Ar$), 4.47 (app ddt, 1 H, J = 12.5 Hz, J = 5.3 Hz, J = 1.7 Hz, $C\underline{H}_2CH=CH_2$), 4.24 (app ddt, 1 H, J = 12.5 Hz, J = 5.0 Hz, J = 1.7 Hz, $C\underline{H}_2CH=CH_2$), 3.86–3.82 (m, 1 H, H_{inos}), 3.84 (s, 3 H, OCH_3), 3.64 (d, 1 H, J = 9.7 Hz, H-2/H-6), 3.60 (d, 1 H, J = 9.9 Hz,

H-2/H-6), 3.39 (dd, 1 H, J = 9.4 Hz, J = 9.4 Hz, H_{inos}), 3.28 (dd, 1 H, J = 9.5 Hz, J = 9.4 Hz, H_{inos}), 1.57 (s, 3 H, CH_3), 1.22–1.09 (m, 21 H, 3 x SiC<u>H</u>(C<u>H</u>$_3$)$_2$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 158.6 (Ar), 139.6 (Ar), 139.0 (Ar), 138.9 (Ar), 135.4 (<u>C</u>H=CH_2), 131.5 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.3(8) (Ar), 127.3(5) (Ar), 127.3 (Ar), 127.1 (Ar), 115.4 (CH=<u>C</u>H_2), 113.4 (Ar), 86.1(3) (C-2/C-6), 86.0(7) (C2/C6), 83.2 (C_{inos}), 82.8 (C_{inos}), 80.5 (C-1), 75.3(9) (C_{inos}), 75.3(8) (<u>C</u>H_2Ar), 75.3 (<u>C</u>H_2Ar), 74.5 (<u>C</u>H_2Ar), 73.9 (<u>C</u>H_2CH=CH_2), 66.1 (<u>C</u>H_2Ar), 55.3 (OCH_3), 18.4(1) (SiCH(<u>C</u>H_3)$_2$), 18.4(0) (SiCH(<u>C</u>H_3)$_2$), 13.6 (3 x Si<u>C</u>H(CH_3)$_2$), 13.2 (CH_3). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{48}H_{68}NO_7Si$: 798.4760. Found 798.4750.

Racemic **1,2,6-tri-*O*-benzyl-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (16)**. Palladium(II) chloride (477 mg, 2.69 mmol) was added to a solution of **15** (21.0 g, 26.9 mmol) in CH_2Cl_2 (300 mL) and MeOH (300 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through silica and the silica was rinsed with EtOAc. The solvent was then evaporated and the crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **16** (17.1 g, 86%) as a colourless oil. R_f 0.37 (9:1 hexanes–EtOAc); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.19 (m, 17 H, Ar), 6.85–6.81 (m, 2 H, Ar), 4.97 (d, 1 H, J = 11.2 Hz, C<u>H</u>$_2$Ar), 4.91(d, 1 H, J = 11.2 Hz, C<u>H</u>$_2$Ar), 4.86 (d, 1 H, J = 10.6 Hz, C<u>H</u>$_2$Ar), 4.83–4.77 (m, 5 H, 5 x C<u>H</u>$_2$Ar), 3.82 (s, 3 H, OCH_3), 3.81 (dd, 1 H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 8.8 Hz, H-4), 3.65 (d, 1 H, $J_{2,3}$ = 9.7, H-2), 3.53 (ddd, 1 H, $J_{5,6}$ = 9.9 Hz, $J_{4,5}$ = 8.8 Hz, $J_{5,OH}$ = 2.0 Hz, H-5), 3.47 (d, 1 H, $J_{5,6}$ = 9.9, H-6), 3.42 (dd, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 2.44 (d, 1 H, $J_{5,OH}$ = 2.0, OH), 1.55 (s, 3 H, CH_3) 1.26–1.17 (m, 3 H, 3 x SiC<u>H</u>(CH_3)$_2$), 1.14–1.09 (m, 18 H, 3 x SiCH(C<u>H</u>$_3$)$_2$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 158.7 (Ar), 139.4 (Ar), 138.9 (Ar), 138.8 (Ar), 131.3 (Ar), 128.4(8) (Ar), 128.4(6) (Ar), 128.3 (Ar), 128.2 (Ar), 127.6(8) (Ar), 127.6(6) (Ar), 127.3(0) (Ar), 127.2(6) (Ar), 127.2(0) (Ar), 127.1(6) (Ar), 113.5 (Ar), 86.0 (C-2), 85.0 (C-6), 83.4

(C-3), 80.7 (C-1), 76.1(C-4), 75.6 ($\underline{C}H_2Ar$), 75.3 ($\underline{C}H_2Ar$), 74.9 ($\underline{C}H_2Ar$), 74.9 (C-5), 66.0 ($\underline{C}H_2Ar$), 55.3 (OCH_3), 18.4 (2C x SiCH($\underline{C}H_3$)$_2$), 13.4 (Si$\underline{C}$H(CH_3)$_2$/CH_3), 13.3 (CH_3/Si$\underline{C}$H(CH_3)$_2$). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{45}H_{64}NO_7Si$: 758.4447. Found 758.4437.

Racemic **1,2,6-tri-*O*-benzyl-5-*O*-(4-methoxybenzyl)-1-*C*-methyl-3-*O*-(*S*-methylxanthate)-4-*O*-triisopropylsilyl-*scyllo*-inositol (17)**. LiHMDS (5.66 mL, 5.66 mmol, 1.0M in THF) was added to a cooled (–78 °C) solution of **16** (3.75 g, 5.06 mmol) and CS_2 (3.04 mL, 50.6 mmol) in THF (300 mL). After 30 min, methyl iodide (1.58 mL, 25.3 mmol) was added and the reaction mixture was stirred at –78 °C for 1 h. Water was added and the aqueous solution was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 → 9:1 hexanes–EtOAc) to give **17** (4.19 g, 99%) as a yellow oil. R_f 0.47 (9:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.33–7.19 (m, 17 H, Ar), 6.88–6.84 (m, 2 H, Ar), 6.18 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 5.00 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.91 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.84 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.80–4.74 (m, 3 H, 3 x C$\underline{H}_2$Ar), 4.71 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.67 (d, 1 H, J = 10.6 Hz, C$\underline{H}_2$Ar), 4.15 (dd, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 3.84 (s, 3 H, OCH_3), 3.71 (d, 1 H, $J_{5,6}$ = 9.5, H-6), 3.69 (d, 1 H, J = 9.7, H-2), 3.52 (dd, 1 H, $J_{5,6}$ = 9.4 Hz, $J_{4,5}$ = 9.2 Hz, H-5), 2.57 (s, 3H, SCH_3), 1.61 (s, 3 H, CH_3), 1.15–1.02 (m, 21 H, 3 x SiC$\underline{H}$(C$\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 215.7 (C=S), 158.7 (Ar), 139.4 (Ar), 138.7 (Ar), 138.4 (Ar), 131.2 (Ar), 128.3(0) (Ar), 128.2(5) (Ar), 128.1(3) (Ar), 128.0(6) (Ar), 127.7 (Ar), 127.4 (Ar), 127.3 (Ar), 127.2(4) (Ar), 127.2(0) (Ar), 113.5 (Ar), 86.3 (C-6), 84.3 (C-2), 83.8 (C-3), 82.9 (C-5), 80.2 (C-1), 75.7 ($\underline{C}H_2Ar$), 75.5 ($\underline{C}H_2Ar$), 74.7 ($\underline{C}H_2Ar$), 73.8 (C-4), 66.2 ($\underline{C}H_2Ar$), 55.3 (OCH_3), 19.5 (SCH_3), 18.4(0) (SiCH($\underline{C}H_3$)$_2$), 18.3(9) (SiCH($\underline{C}H_3$)$_2$), 13.7 (3 x Si$\underline{C}$H(CH_3)$_2$), 13.0 (CH_3). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{47}H_{62}NaO_7S_2Si$: 853.3598. Found 853.3597.

Racemic **1,2,6-tri-*O*-benzyl-5-deoxy-3-*O*-(4-methoxybenzyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (18)**. A solution of *n*-Bu_3SnH (4.95 mL, 18.4 mmol) and AIBN (377 mg, 2.30 mmol) in degassed benzene (75 mL) was added to a solution of **17** (3.82 g, 4.60 mmol) in degassed benzene (155 mL) at 80 °C over a period of 60 min. The reaction mixture was heated at reflux for 2 h, then cooled, and the solvent evaporated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **18** (3.32 g, 99%) as a colourless oil. R_f 0.40 (9:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.21 (m, 17 H, Ar), 6.84–6.80 (m, 2 H, Ar), 488–4.82 (m, 4 H, 4 x C$\underline{H}_2$Ar), 4.79 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.76 (d, 1 H, J = 10.6 Hz, C$\underline{H}_2$Ar), 4.70 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 4.64 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 3.85–3.79 (m, 1 H, H-4), 3.82 (s, 3 H, OCH_3), 3.55 (dd, 1 H, $J_{5ax,6}$ = 12.3 Hz, $J_{5eq,6}$ = 4.4 Hz, H-6), 3.49 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-2), 3.39 (dd, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 2.17 (ddd, 1 H, $J_{5eq,5ax}$ = 13.0 Hz, $J_{4,5eq}$ = 4.8 Hz, $J_{5eq,6}$ = 4.8 Hz, H-5_{eq}), 1.62–1.54 (m, 1 H, H-5_{ax}), 1.56 (s, 3 H, CH_3), 1.14–1.06 (m, 21 H, 3 x SiC$\underline{H}$($C\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 158.8 (Ar), 140.0 (Ar), 139.4 (Ar), 138.7 (Ar), 131.4 (Ar), 129.1 (Ar), 128.4 (Ar), 128.2(3) (Ar), 128.1(6) (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 127.3 (Ar), 127.2 (Ar), 127.0 (Ar), 113.5 (Ar), 85.8 (C-3), 85.5 (C-2), 82.1 (C-1), 79.6 (C-6), 75.6 ($\underline{C}H_2$Ar), 75.2 ($\underline{C}H_2$Ar), 72.5 ($\underline{C}H_2$Ar), 71.1 (C-4), 66.1 ($\underline{C}H_2$Ar), 55.3 (OCH_3), 36.1 (C-5), 18.2(5) (SiCH($\underline{C}H_3$)$_2$), 18.2(0) (SiCH($\underline{C}H_3$)$_2$), 12.7 (3 x Si$\underline{C}$H(CH_3)$_2$), 11.9 (CH_3). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{45}H_{60}NaO_6Si$: 747.4051. Found 747.4047.

Racemic **1,2,6-tri-*O*-benzyl-5-deoxy-1-*C*-methyl-4-*O*-triisopropylsilyl-*scyllo*-inositol (19)**. TFA (8 mL) was added to a cooled (0 °C) solution of **18** (2.85 g, 3.94 mmol) in CH_2Cl_2 (400 mL). The reaction mixture was stirred at 0 °C for 2 h. A saturated aqueous solution of $NaHCO_3$ was

added and the reaction mixture was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 to 9:1 hexanes–EtOAc) to give **19** (2.36 g, 99%) as as a colorless oil. R_f 0.45 (9:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.26 (m, 15 H, Ar), 4.92 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.86 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.85 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.79 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.68 (d, 1 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 4.65 (d, 1 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 3.69–3.63 (m, 1 H, H-4), 3.59 (dd, 1 H, $J_{5ax,6}$ = 12.3 Hz, $J_{5eq,6}$ = 4.4 Hz, H-6), 3.55–3.49 (m, 1 H, H-3), 3.40 (d, 1 H, $J_{2,3}$ = 9.7 Hz, H-2), 2.55 (d, 1 H, $J_{3,OH}$ = 1.3 Hz, OH), 2.17 (ddd, 1 H, $J_{5ax,5eq}$ = 13.0 Hz, $J_{4,5eq}$ = 4.8 Hz, $J_{5eq,6}$ = 4.8 Hz, H-5$_{eq}$), 1.59–1.50 (m, 1 H, H-5$_{ax}$), 1.52 (s, 3 H, CH_3), 1.12–1.09 (m, 21 H, SiCH(CH_3)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 139.9 (Ar), 139.1 (Ar), 138.6 (Ar), 128.4 (Ar), 128.3(2) (Ar), 128.2(6) (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 127.3 (Ar), 127.1 (Ar), 85.3 (C-2), 82.1 (C-1), 80.0 (C-6), 77.4 (C-3), 75.5 (C$\underline{H}_2$Ar), 72.4 (C$\underline{H}_2$Ar), 70.8 (C-4), 66.1 (C$\underline{H}_2$Ar), 35.5 (C-5), 18.1 (SiCH(C$\underline{H}_3$)$_2$), 12.6 (SiC$\underline{H}$(CH$_3$)$_2$), 11.9 (CH_3). HRMS (ESI) Calcd for $[M + H]^+$ $C_{37}H_{53}O_5Si$: 605.3657. Found 605.3658.

***Racemic* 1,2,6-tri-*O*-benzyl-5-deoxy-3-(ethoxycarbonylethynyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-3-*myo*-inositol (20)**. *n*-BuLi (23.3 mL, 37.3 mmol, 1.6M in hexanes) was added dropwise to a cooled (–78 °C) solution of (*i*-Pr)$_2$NH (5.51 mL, 39.3 mmol) in THF (146 mL). After 30 min, ethyl propiolate (3.88 mL, 38.3 mmol) was added to the mixture. After another 30 min, a solution of **3** (12.47 g, 20.7 mmol) in THF (181 mL) was added slowly to the reaction mixture. After 3 h, a saturated aqueous solution of NH_4Cl was added and the reaction mixture was warmed to rt then extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (49:1 → 19:1 hexanes–EtOAc) to give **20** (14.5 g, 99%) as a colorless oil. R_f 0.27 (9:1 hexanes–EtOAc); ^{1}H

NMR (500 MHz, $CDCl_3$, δ_H) 7.43–7.40 (m, 2 H, Ar), 7.35–7.26 (m, 13 H, Ar), 4.99 (d, 1 H, J = 10.6 Hz, C$\underline{H}_2$Ar), 4.90 (d, 1 H, J = 10.6 Hz, C$\underline{H}_2$Ar), 4.84 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.79 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.68 (d, 1 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 4.62 (d, 1 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 4.23 (q, 2 H, J = 7.2 Hz, C$\underline{H}_2$CH$_3$), 3.97 (dd, 1 H, $J_{4,5ax}$ = 11.7 Hz, $J_{4,5eq}$ = 4.6 Hz, H-4), 3.62 (s, 1 H, H-2), 3.52 (dd, 1 H, $J_{5ax,6}$ = 12.3 Hz, $J_{5eq,6}$ = 4.2 Hz, H-6), 2.99 (br, 1 H, OH), 1.97 (ddd, 1 H, $J_{5eq,5ax}$ = 12.8 Hz, $J_{4,5eq}$ = 4.4 Hz, $J_{5eq,6}$ = 4.4 Hz, H-5$_{eq}$), 1.86 (ddd, 1 H, $J_{4,5ax}$ = 12.1 Hz, $J_{5eq,5ax}$ = 12.1 Hz, $J_{5ax,6}$ = 12.1 Hz, H-5$_{ax}$), 1.63 (s, 3 H, CH$_3$), 1.29 (t, 3 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$), 1.16–1.06 (m, 21 H, 3 x SiC$\underline{H}$(C$\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 153.1 (C=O), 139.8 (Ar), 138.4 (Ar), 138.2 (Ar), 128.4 (Ar), 128.3 (2 x Ar), 128.2 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 127.1 (Ar), 88.9 (C$\underline{\equiv}$C–C=O), 85.1 (C-2), 82.3 (C-1), 80.2 (C-4), 76.7 (C-3), 75.2 (C$\underline{H}_2$Ar), 74.5 (C$\equiv\underline{C}$–C=O), 72.5 (C$\underline{H}_2$Ar), 71.7 (C-6), 66.2 (C$\underline{H}_2$Ar), 61.8 (C$\underline{H}_2$CH$_3$), 33.0 (C-5), 18.2 (SiCH(C$\underline{H}_3$)$_2$), 18.1 (SiCH(C$\underline{H}_3$)$_2$), 14.0 (CH$_2$C$\underline{H}_3$), 12.6 (3 x SiC$\underline{H}$(CH$_3$)$_2$), 11.9 (CH$_3$). HRMS (ESI) Calcd for [M + NH$_4$]$^+$ $C_{42}H_{60}NO_7Si$: 718.4134. Found 718.4130.

Racemic **1,2,6-tri-*O*-benzyl-5-deoxy-3-((*E*)-ethoxycarbonylethenyl)-1-*C*-methyl-4-*O*-triisopropylsilyl-3-*myo*-inositol (21)**. Red-Al® (13.5 mL, 40.0 mmol, 60% wt in toluene) was added to a cooled (–78 °C) solution of **20** (14.0 g, 20.0 mmol) in THF (300 mL). The reaction mixture was stirred at –78 °C for 30 min. A saturated aqueous solution of potassium sodium tartrate and CH_2Cl_2 were added at –78 °C and the mixture was stirred at rt overnight. The aqueous solution was extracted with CH_2Cl_2 and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **21** (9.10 g, 65%) as a colourless oil. Alkyne **20** was recovered and the reaction was done again twice to give **21** in 95% yield (combined). R_f 0.26 (9:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.18 (m, 15 H, Ar), 6.81 (d, 1 H, J = 15.2 Hz, C$\underline{H}$=CH–C=O), 6.22

(d, 1 H, J = 15.4 Hz, CH=C<u>H</u>–C=O), 4.86 (d, 1 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 4.79 (d, 1 H, J = 11.6 Hz, C<u>H</u>$_2$Ar), 4.76 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.69 (d, 1 H, J = 11.7 Hz, C<u>H</u>$_2$Ar), 4.63 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 4.57 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.26–4.16 (m, 2 H, C<u>H</u>$_2$CH$_3$), 3.81 (dd, 1 H, $J_{4,5ax}$ = 11.4 Hz, $J_{4,5eq}$ = 4.4 Hz, H-4), 3.53 (dd, 1 H, $J_{5ax,6}$ = 12.3 Hz, $J_{5eq,6}$ = 4.2 Hz, H-6), 3.40 (s, 1 H, H-2), 2.53 (s, 1 H, OH), 1.99 (ddd, 1 H, $J_{5ax,5eq}$ = 12.7 Hz, $J_{4,5eq}$ = 4.4 Hz, $J_{5eq,6}$ = 4.4 Hz, H-5$_{eq}$), 1.91 (ddd, 1 H, $J_{4,5ax}$ = 11.9 Hz, $J_{5ax,5eq}$ = 11.9 Hz, $J_{5ax,6}$ = 11.9 Hz, H-5$_{ax}$), 1.70 (s, 3 H, CH$_3$), 1.28 (t, 3 H, J = 7.0 Hz, CH$_2$C<u>H</u>$_3$), 1.11–0.93 (m, 21 H, 3 x SiC<u>H</u>(C<u>H</u>$_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, δ_C) 166.0 (C=O), 151.6 (<u>C</u>=C–C=O), 139.9 (Ar), 138.5 (Ar), 138.0 (Ar), 128.4 (Ar), 128.3(5) (Ar), 128.2(8) (Ar), 128.1 (Ar), 127.7 (Ar), 127.6(5) (Ar), 127.5(6) (Ar), 127.4 (Ar), 127.1 (Ar), 123.5 (C=<u>C</u>–C=O), 83.5 (C-2), 82.6 (C-1), 80.8 (C-6), 79.2 (C-3), 75.8 (<u>C</u>H$_2$Ar), 72.3 (<u>C</u>H$_2$Ar), 71.0 (C-4), 66.2 (<u>C</u>H$_2$Ar), 60.2 (<u>C</u>H$_2$CH$_3$), 33.5 (C-5), 18.0(9) (SiCH(<u>C</u>H$_3$)$_2$), 18.0(7) (SiCH(<u>C</u>H$_3$)$_2$), 14.3 (CH$_2$<u>C</u>H$_3$), 12.6 (3 x Si<u>C</u>H(CH$_3$)$_2$), 11.7 (CH$_3$). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{42}H_{58}NaO_7Si$: 725.3844. Found 725.3852.

Racemic **1,2,6-tri-*O*-benzyl-5-deoxy-3-((*E*)-ethoxycarbonylethenyl)-1-*C*-methyl-3-*myo*-inositol (22)**. TBAF (2.10 mL, 2.10 mmol, 1.0M in THF) was added to a cooled (0 °C) solution of **21** (985 mg, 1.40 mmol) in THF (35 mL). The reaction mixture was stirred for 15 min at 0 °C, then a saturated aqueous solution of $NaHCO_3$ was added and the reaction mixture was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (4:1 → 1:1 hexanes–EtOAc) to give **22** (760 mg, 99%) as a white solid. mp = 107–108 °C; R_f 0.17 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$, δ_H) 7.37–7.27 (m, 13 H, Ar), 7.24–7.19 (m, 2 H, Ar), 6.95 (d, 1 H, J = 15.6 Hz, C<u>H</u>=CH–C=O), 6.21 (d, 1 H, J = 15.4 Hz, CH=C<u>H</u>–C=O), 4.81 (d, 1 H, J = 11.2 Hz, C<u>H</u>$_2$Ar), 4.80 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.74 (d, 1 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 4.73 (d, 1 H, J = 11.2 Hz, C<u>H</u>$_2$Ar),

4.63 (d, 1 H, J = 10.6 Hz, C$\underline{H}_2$Ar), 4.56 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.26–4.18 (m, 2 H, C$\underline{H}_2$CH$_3$), 3.65–3.59 (m, 2 H, H-4, H-6), 3.53 (s, 1 H, H-2), 2.89 (br, 1 H, OH), 2.27 (ddd, 1 H, $J_{5ax,5eq}$ = 13.0 Hz, $J_{4,5eq}$ = 4.0 Hz, $J_{5eq,6}$ = 4.0 Hz, H-5$_{eq}$), 1.96 (br s, 1 H, H-5$_{ax}$), 1.63 (s, 3 H, CH$_3$), 1.31 (t, 3 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, δ_C) 166.0 (C=O), 150.4 ($\underline{C}$=C–C=O), 139.5 (Ar), 138.2 (Ar), 137.8 (Ar), 128.4 (Ar), 128.3(4) (Ar), 128.3(2) (Ar), 128.1 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 127.3 (Ar), 123.0 (C=$\underline{C}$–C=O), 84.2 (C-2), 81.9 (C-1), 80.3 (2C, C-4, C-6), 76.3 (C-3), 76.0 ($\underline{C}$H$_2$Ar), 71.8 ($\underline{C}$H$_2$Ar), 65.9 ($\underline{C}$H$_2$Ar), 60.5 ($\underline{C}$H$_2$CH$_3$), 29.7 (C-5), 14.3 (2C, CH$_2\underline{C}$H$_3$, $\underline{C}$H$_3$). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{33}H_{38}NaO_7$: 569.2510. Found 569.2506.

***Racemic* 7,8,9-tri-*O*-benzyl-bradyrhizose-1,4-lactone (23)**. Potassium osmate(VI) dihydrate (2 mg, 0.00410 mmol) was added to a cooled (0 °C) solution of **22** (112 mg, 0.205 mmol), (DHQ)$_2$PHAL (7 mg, 0.00820 mmol), K$_3$Fe(CN)$_6$ (202 mg, 0.615 mmol), potassium carbonate (85 mg, 0.615 mmol), sodium bicarbonate (52 mg, 0.615 mmol) and MeSO$_2$NH$_2$ (20 mg, 0.205 mmol) in *t*-BuOH (0.5 mL) and water (0.5 mL). The reaction mixture was stirred for 2 h at 0 °C, then overnight at rt. A saturated aqueous solution of sodium thiosulfate was added and the reaction mixture was extracted with EtOAc. The organic extract was dried (Na$_2$SO$_4$), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (49:1 CH$_2$Cl$_2$–MeOH) to give **23** (11 mg, 10%) as a colorless oil. The starting material could be recovered. R_f 0.31 (24:1 CH$_2$Cl$_2$–MeOH); ^{1}H NMR (500 MHz, CDCl$_3$, δ_H) 7.35–7.15 (m, 15 H, Ar), 4.99 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.85 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.83 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.72–4.51 (m, 7 H, 3 x C$\underline{H}_2$Ar, H-2, H-3, 2 x OH), 4.08 (d, 1 H, J = 9.2 Hz, OH), 3.87 (s, 1 H, H-9), 3.63–3.55 (m, 2 H, H-5, H-7), 2.30 (ddd, 1 H, $J_{5ax,5eq}$ = 12.7 Hz, $J_{4,5eq}$ = 4.4 Hz, $J_{5eq,6}$ = 4.4 Hz, H-6$_{eq}$), 1.96 (ddd, 1 H, $J_{4,5ax}$ = 12.5 Hz, $J_{5eq,5ax}$ = 12.5 Hz, $J_{5ax,6}$ = 12.5 Hz, H-6$_{ax}$),

1.58 (s, 3 H, H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 175.1 (C-1), 139.5 (Ar), 138.6 (Ar), 138.2 (Ar), 128.4 (Ar), 128.3 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4(4) (Ar), 127.3(8) (Ar), 127.3 (Ar), 127.2 (Ar), 88.6 (C-4), 83.2 (C-8), 80.2 (C-5/C-7), 78.7 (C-9), 74.5 (C-3/C-2), 74.4 ($\underline{C}H_2Ar$), 74.0 (C-3/C-2), 71.6 ($\underline{C}H_2Ar$), 66.3 ($\underline{C}H_2Ar$), 65.2 (C-5/C-7), 32.6 (C-6), 11.7 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{31}H_{34}NaO_8$: 557.2146. Found 557.2136.

***Racemic exo*-2,3,4-tri-*O*-benzyl-1,6-benzylidene-5-deoxy-1-((*E*)-ethoxycarbonylethenyl)-3-*C*-methyl-1-*myo*-inositol (24a)** and ***racemic endo*-2,3,4-tri-*O*-benzyl-1,6-benzylidene-5-deoxy-1-((*E*)-ethoxycarbonylethenyl)-3-*C*-methyl-1-*myo*-inositol (24b)**. Benzaldehyde dimethyl acetal (1.18 mL, 8.11 mmol) and CSA (75 mg, 0.324 mmol) were added to a solution of **22** (887 mg, 1.62 mmol) in THF (10 mL). The reaction mixture was heated at reflux overnight. After cooling, a saturated aqueous solution of $NaHCO_3$ was added and the reaction mixture was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **24a** and **24b** (1.01 g, 99%) as as a colorless oil (inseparable diastereomeric mixture, 3:7). R_f 0.42 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.53–7.50 (m, 2 H, Ar), 7.45–7.25 (m, 18 H, Ar), 7.12 (d, 0.3 H, J = 15.4 Hz, C$\underline{H}$=CH–C=O), 7.05 (d, 0.7 H, J = 15.6 Hz, C$\underline{H}$=CH–C=O), 6.30 (d, 0.7 H, J = 15.8 Hz, CH=C$\underline{H}$–C=O), 6.21 (s, 0.3 H, C$\underline{H}$Ar), 6.08 (d, 0.3 H, J = 15.8 Hz, CH=C$\underline{H}$–C=O), 5.89 (s, 0.7 H, C$\underline{H}$Ar), 4.85–4.58 (m, 5.7 H, C$\underline{H}_2$Ar), 4.41 (dd, 0.3 H, $J_{5ax,6}$ = 9.9 Hz, $J_{5eq,6}$ = 6.4 Hz, H-6), 4.29–4.10 (m, 3 H, H_{inos}, C$\underline{H}_2$CH$_3$), 3.70–3.61 (m, 2 H, H-2, H_{inos}), 2.36–2.19 (m, 1.3 H, H-5_{eq}, H-5_{ax}), 2.04 (app q, 0.7 H, J = 12.7 Hz, H-5_{ax}), 1.62 (s, 0.9 H, CH_3), 1.60 (s, 2.1 H, CH_3), 1.29 (t, 2.1 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$), 1.23 (t, 0.9 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.3 (C=O), 166.1 (C=O), 149.2 ($\underline{C}$=C–C=O), 147.9 ($\underline{C}$=C–C=O), 139.0 (Ar), 138.9 (Ar), 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 138.0 (Ar), 137.6 (Ar),

137.3 (Ar), 129.3 (Ar), 129.1 (Ar), 128.4 (Ar), 128.3(5) (Ar), 128.3(1) (Ar), 128.2(4) (Ar), 128.1(9) (Ar), 128.1(3) (Ar), 128.0(9) (Ar), 127.6 (Ar), 127.5(1) (Ar), 127.4(7) (Ar), 127.3(3) (Ar), 127.2(8) (Ar), 127.0 (Ar), 126.8 (Ar), 121.6 (C=C–C=O), 104.3 (CHPhCHAr), 103.0 (CHAr), 84.9 (C-1/C-3), 84.8 (C-1/C-3), 84.3 (C-2), 83.2 (C-2), 82.1 (C-1/C-3), 81.7 (C-1/C-3), 79.5 (C-6), 78.7 (C_{inos}), 78.3 (C_{inos}), 77.5 (C_{inos}), 76.6 (CH_2Ar), 76.3 (CH_2Ar), 71.9(3) (CH_2Ar), 71.8(9) (CH_2Ar), 65.3 (CH_2Ar), 60.6 (CH_2CH_3), 60.3 (CH_2CH_3), 31.2 (C-5), 29.7 (C-5), 14.8 (CH_3), 14.5 (CH_3), 14.2 (CH_2CH_3). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{40}H_{46}NO_7$: 652.3269. Found 652.3269.

Racemic **1,2,3,4-tetra-*O*-benzyl-5-deoxy-1-((*E*)-ethoxycarbonylethenyl)-3-*C*-methyl-1-*myo*-inositol (25)**. Copper(II) triflate (6 mg, 0.0161 mmol) was added to a cooled (– 15 °C) solution of **24** (102 mg, 0.161 mmol) and borane–tetrahydrofuran complex solution (805 μL, 0.805 mmol, 1.0M in THF) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred at – 15 °C for 2 h, and Et_3N and MeOH were added. The mixture was then concentrated and the resulting crude product was purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **25** (43 mg, 43%) as a colorless oil. R_f 0.44 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.27 (m, 20 H, Ar), 7.14 (d, 1 H, J = 16.1 Hz, CH=CH–C=O), 6.17 (d, 1 H, J = 16.3 Hz, CH=CH–C=O), 5.04–4.91 (m, 2 H, 2 x CH_2Ar), 4.87–4.70 (m, 5 H, 5 x CH_2Ar), 4.58 (d, 1 H, J = 11.6 Hz, CH_2Ar), 4.28–4.18 (m, 2 H, CH_2CH_3), 3.71–3.62 (m, 3 H, H-2, H-4, H-6), 2.27 (ddd, 1 H, $J_{5ax,5eq}$ = 13.0 Hz, $J_{4,5eq}$ = 4.2 Hz, $J_{5eq,6}$ = 4.2 Hz, H-5_{eq}), 2.03 (br s, 1 H, H-5_{ax}), 1.73 (s, 3 H, CH_3), 1.31 (t, 3 H, J = 7.2 Hz, CH_2CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 146.9 (C=C–C=O), 139.6 (Ar), 139.0 (Ar), 138.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 127.6 (Ar), 127.4(3) (Ar), 127.4(1) (Ar), 127.3(9) (Ar), 127.2 (Ar), 123.6 (C=C–C=O), 87.5 (C-2), 82.0 (C-1/C-3), 81.9 (C-1/C-3), 80.7 (C-4/C-6), 76.7 (CH_2Ar), 76.6 (CH_2Ar), 71.7 (CH_2Ar), 70.2 (C-4/C-6), 66.0 (CH_2Ar),

60.6 ($\underline{C}H_2CH_3$), 29.7 (C-5), 14.3 (2C, $CH_2\underline{C}H_3$, $\underline{C}H_3$). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{40}H_{44}NaO_7$: 659.2979. Found 659.2978.

Racemic **1,2,3,4-tetra-*O*-benzyl-5-deoxy-1-((*E*)-ethoxycarbonylethenyl)-3-*C*-methyl-6-*O*-(4-nitrobenzoate)-1-*myo*-inositol (26)**. *p*-Nitrobenzoyl chloride (23 mg, 0.125 mmol) was added to a solution of **25** (53 mg, 0.0832 mmol) and DMAP (12 mg, 0.0998 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 2 h at rt. Water was added and the mixture was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (9:1 → 17:3 hexanes–EtOAc) to give **26** (54 mg, 83%) as a yellow oil. R_f 0.35 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.28 (d, 2 H, J = 8.4 Hz, Ar), 8.16 (d, 2 H, J = 9.0 Hz, Ar), 7.47–7.28 (m, 20 H, Ar), 7.04 (d, 1 H, J = 16.1 Hz, C$\underline{H}$=CH–C=O), 6.03 (d, 1 H, J = 16.3 Hz, CH=C$\underline{H}$–C=O), 5.19 (dd, 1 H, $J_{5ax,6}$ = 11.4 Hz, $J_{5eq,6}$ = 4.4 Hz, H-6), 5.02–4.97 (m, 2 H, 2 x C$\underline{H}_2$Ar), 4.90 (d, 1 H, J = 12.8 Hz, C$\underline{H}_2$Ar), 4.87 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.80 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.73 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.70 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.62 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.12 (q, 2 H, J = 7.0 Hz, C$\underline{H}_2$CH$_3$), 3.84 (dd, 1 H, $J_{4,5ax}$ = 11.2 Hz, $J_{4,5eq}$ = 4.8 Hz, H-4), 3.71 (s, 1 H, H-2), 2.43–2.30 (m, 2 H, H-5$_{eq}$, H-5$_{ax}$), 1.79 (s, 3 H, CH$_3$), 1.20 (t, 3 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 165.4 (C=O), 164.0 (Ar), 150.7 (Ar), 145.8 ($\underline{C}$=C–C=O), 139.7 (Ar), 139.5 (Ar), 138.4 (Ar), 138.2 (Ar), 135.1 (Ar), 130.8 (Ar), 128.4(2) (Ar), 128.4(0) (Ar), 128.3(3) (Ar), 128.3(2) (Ar), 127.6(4) (Ar), 127.5(8) (Ar), 127.5 (Ar), 127.4(2) (Ar), 127.3(6) (Ar), 127.2 (Ar), 126.6 (Ar), 124.3 (C=$\underline{C}$–C=O), 123.7 (Ar), 87.2 (C-2), 83.1 (C-1/C-3), 81.9 (C-1/C-3), 80.9 (C-4), 76.6 ($\underline{C}H_2$Ar), 72.9 (C-6), 71.9 ($\underline{C}H_2$Ar), 68.0 ($\underline{C}H_2$Ar), 66.2 ($\underline{C}H_2$Ar), 60.7 ($\underline{C}H_2CH_3$), 29.2 (C-5), 14.2 ($CH_2\underline{C}H_3$), 11.9 ($\underline{C}H_3$). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{47}H_{47}NNaO_{10}$: 808.3092. Found 808.3091.

Racemic **1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-((*E*)-ethoxycarbonylethenyl)-3-*C*-methyl-1-*myo*-inositol (27)**. 2,6-Lutidine (183 μL, 1.58 mmol) followed by TBSOTf (181 μL, 0.787 mmol) were added to a cooled (0 °C) solution of **25** (334 mg, 0.525 mmol) in CH_2Cl_2 (4 mL). The ice bath was removed and the mixture was stirred for 30 min. Methanol was added, then water, and the mixture was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **27** (366 mg, 93%) as a colorless oil. R_f 0.68 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.47–7.44 (m, 2 H, Ar), 7.41–7.26 (m, 18 H, Ar), 7.02 (d, 1 H, J = 16.1 Hz, C<u>H</u>=CH–C=O), 6.10 (d, 1 H, J = 16.1 Hz, CH=C<u>H</u>–C=O), 4.94–4.88 (m, 5 H, 5 x C<u>H</u>$_2$Ar), 4.70 (s, 2 H, 2 x C<u>H</u>$_2$Ar), 4.61 (d, 1 H, J = 11.2 Hz, C<u>H</u>$_2$Ar), 4.25–4.15 (m, 2 H, C<u>H</u>$_2$CH$_3$), 3.78 (dd, 1 H, $J_{5ax,6}$ = 11.9 Hz, $J_{5eq,6}$ = 3.7 Hz, H-6), 3.65 (dd, 1 H, $J_{4,5ax}$ = 12.1 Hz, $J_{4,5eq}$ = 4.4 Hz, H-4), 3.49 (s, 1 H, H-2), 2.15 (ddd, 1 H, $J_{4,5ax}$ = 12.0 Hz, $J_{5eq,5ax}$ = 12.0 Hz, $J_{5ax,6}$ = 12.0 Hz, H-5$_{ax}$), 2.00 (ddd, 1 H, $J_{5eq,5ax}$ = 12.0 Hz, = 12.5 Hz, $J_{4,5eq}$ = 4.2 Hz, $J_{5eq,6}$ = 4.2 Hz, H-5$_{eq}$), 1.74 (s, 3 H, CH$_3$), 1.27 (t, 3 H, J = 7.2 Hz, CH$_2$C<u>H</u>$_3$), 0.94 (s, 9 H, 3 x SiC(CH$_3$)$_3$), 0.10 (s, 3 H, SiCH$_3$), 0.09 (s, 3 H, SiCH$_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 165.9 (C=O), 147.8 (<u>C</u>=C–C=O), 140.5 (Ar), 140.1 (Ar), 138.8 (Ar), 138.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 127.1 (Ar), 126.7 (Ar), 126.3 (Ar), 124.0 (C=<u>C</u>–C=O), 86.3 (C-2), 83.6 (C-1/C-3), 83.4 (C-1/C-3), 81.4 (C-4), 76.2 (<u>C</u>H$_2$Ar), 72.9 (C-6), 72.1 (<u>C</u>H$_2$Ar), 67.7 (<u>C</u>H$_2$Ar), 66.1 (<u>C</u>H$_2$Ar), 60.3 (<u>C</u>H$_2$CH$_3$), 33.6 (C-5), 25.8 (SiC(<u>C</u>H$_3$)$_3$), 18.0 (Si<u>C</u>(CH$_3$)$_3$), 14.3 (CH$_2$<u>C</u>H$_3$), 12.1(CH$_3$), –4.1 (SiCH$_3$), –4.9 (SiCH$_3$). HRMS (ESI) Calcd for [M + NH$_4$]$^+$ $C_{46}H_{62}NO_7Si$: 768.4290. Found 768.4285.

Racemic **1,2,3,4-tetra-*O*-benzyl-5-deoxy-1-(ethoxycarbonyl-(1'*R*,2'*R*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (28)** and ***racemic*** **4,7,8,9-tetra-*O*-benzyl-bradyrhizose-1,5-lactone (29)**. Ammonium fluoride (77 mg, 2.07 mmol) followed by TBAF (2.07 mL, 2.07 mmol, 1.0M in THF) were added to a cooled (0 °C) solution of **2** (1.25 g, 1.59 mmol) in THF (80 mL). After 5 min, brine and EtOAc were added and the mixture was separated. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (7:3 → 2:3 hexanes–EtOAc) to give **28** and **29** (1.78 g, 84%) as a colorless oil (ratio 3:1). (**28**): R_f 0.33 (24:1 CH_2Cl_2–MeOH); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.42–7.40 (m, 2 H, Ar), 7.39–7.26 (m, 18 H, Ar), 5.12 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 5.08 (d, 1 H, J = 10.3 Hz, C$\underline{H}_2$Ar), 5.03–4.98 (m, 2 H, C$\underline{H}_2$Ar, H-1'), 4.86 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.76 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.69 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.65 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.54 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.46–4.39 (m, 2 H, H-2', H-6), 4.35–4.18 (m, 3 H, OH, C$\underline{H}_2$CH$_3$), 3.64 (dd, 1 H, $J_{4,5ax}$ = 12.3 Hz, $J_{4,5eq}$ = 4.6 Hz, H-4), 3.62 (s, 1 H, H-2), 3.52 (d, 1 H, J = 6.4 Hz, OH), 2.55 (d, 1 H, J = 10.5 Hz, OH), 2.12 (ddd, 1 H, $J_{5ax,5eq}$ = 12.1 Hz, $J_{4,5eq}$ = 4.4 Hz, $J_{5eq,6}$ = 4.4 Hz, H-5$_{eq}$), 1.93 (ddd, Hz, $J_{4,5ax}$ = 12.0 Hz, $J_{5eq,5ax}$ = 12.0 Hz, $J_{5ax,6}$ = 12.0 Hz, H-5$_{ax}$), 1.76 (s, 3 H, CH$_3$), 1.18 (t, 3 H, J = 7.2 Hz, CH$_2$C$\underline{H}_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 173.5 (C=O), 139.7 (Ar), 139.1 (Ar), 138.9 (Ar), 138.3 (Ar), 128.4(2) (Ar), 128.3(5) (Ar), 128.3(3) (Ar), 128.2(8) (Ar), 128.2(5) (Ar), 127.6(3) (Ar), 127.6(0) (Ar), 127.5 (Ar), 127.4 (Ar), 127.2 (Ar), 126.9 (Ar), 84.4 (C-2), 83.5 (C-1/C-3), 81.2 (C-4), 80.5 (C-1/C-3), 76.1 (C$\underline{H}_2$Ar), 71.4 (C$\underline{H}_2$Ar), 71.1 (C-2'/C-6), 71.0 (C-2'/C-6), 69.9 (C-1'), 67.2 (C$\underline{H}_2$Ar), 66.2 (C$\underline{H}_2$Ar), 62.6 (C$\underline{H}_2$CH$_3$), 33.8 (C-5), 14.0 (CH$_2$C$\underline{H}_3$), 11.3 (CH$_3$). HRMS (ESI) Calcd for $[M + H]^+$ $C_{40}H_{47}O_9$: 671.3215. Found 671.3215.

(**29**): R_f 0.30 (24:1 CH_2Cl_2–MeOH); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.26 (m, 20 H, Ar), 5.53 (d, 1 H, J = 12.1 Hz, C$\underline{H}_2$Ar), 5.30 (d, 1 H, J = 12.1 Hz, C$\underline{H}_2$Ar), 5.17 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.88 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.78 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.76 (d, 1 H, J

= 11.2 Hz, C$\underline{H}_2$Ar), 4.71 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.56 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.46 (d, 1 H, $J_{2,3}$ = 9.7 Hz, H-2), 4.44 (s, 1 H, OH), 4.29 (d, 1 H, $J_{2,3}$ = 9.7 Hz, H-3), 4.05 (dd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{5,6eq}$ = 4.2 Hz, H-5), 3.85 (s, 1 H, H-9), 3.68 (dd, 1 H, $J_{6eq,7}$ = 11.9 Hz, $J_{6eq,7}$ = 4.8 Hz, H-7), 3.16 (s, 1 H, OH), 2.31 (ddd, 1 H, $J_{6eq,6ax}$ = 12.3 Hz, $J_{5,6eq}$ = 4.6 Hz, $J_{6eq,7}$ = 4.6 Hz, H-6_{eq}), 2.23 (ddd, 1 H, $J_{5,6ax}$ = 12.0 Hz, $J_{6ax,6eq}$ = 12.0 Hz, $J_{6ax,7}$ = 12.0 Hz, H-6_{ax}), 1.74 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 171.8 (C=O), 139.1 (Ar), 137.7 (Ar), 128.9 (Ar), 128.5(4) (Ar), 128.4(5) (Ar), 128.4(2) (Ar), 128.3(8) (Ar), 128.1 (Ar), 127.9 (Ar), 127.7(4) (Ar), 127.6(6) (Ar), 127.5 (Ar), 127.4 (Ar), 126.7 (Ar), 88.3 (C-9), 83.2 (C-8), 81.0 (C-7), 79.1 (C-3), 76.6 (C-4), 76.6 (C-5), 75.4 (C$\underline{H}_2$Ar), 71.6 (C$\underline{H}_2$Ar), 70.8 (C-2), 69.4 (C$\underline{H}_2$Ar), 66.4 (C$\underline{H}_2$Ar), 28.9 (C-6), 11.3 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{38}H_{40}NaO_8$: 647.2615. Found 647.2621.

(–)-1,2,3,4-tetra-*O*-benzyl-5-deoxy-1-(ethoxycarbonyl-(1'*R*,2'*R*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (D-28) and **D-4,7,8,9-tetra-*O*-benzyl-bradyrhizose-1,5-lactone (D-29)**. Ammonium fluoride (23 mg, 0.627 mmol) followed by TBAF (627 µL, 0.627 mmol, 1.0M in THF) were added to a cooled (0 °C) solution of **D-2** (3.78 mg, 0.482 mmol) in THF (80 mL). After 5 min, brine and EtOAc were added and the mixture was separated. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (7:3 to 2:3 hexanes–EtOAc) to give **D-28** and **D-29** (270 mg, 84%) as a colorless oil (mixture). The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compounds **28** and **29** previously described. (D-28): $[\alpha]_D$ –40.7 (*c* 0.1, $CHCl_3$). (D-29): $[\alpha]_D$ +5.3 (*c* 0.3, $CHCl_3$).

***Racemic* 4,7,8,9-tetra-*O*-benzyl-1,5-α-bradyrhizose (30α)** and ***racemic* 4,7,8,9-tetra-*O*-benzyl-1,5-β-bradyrhizose (30β)**. DIBAL-H (10 mL, 10.0 mmol, 1.0M in THF) was added to a cooled (–78 °C) solution of a mixture of **28** and **29** (667 g, 0.994 mmol) in THF (60 mL). The reaction

mixture was stirred for 90 min then MeOH (3 mL) and a 10% aqueous solution of HCl and CH_2Cl_2 were added at –78 °C. The mixture was warmed to rt and extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (49:1 CH_2Cl_2–MeOH) to give **30α** and **30β** (567 mg, 91%) as a colorless oil (diastereomeric ratio 0.55:0.45). R_f 0.23 (24:1 CH_2Cl_2–MeOH); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.23 (m, 20 H, Ar), 5.50 (d, 0.55 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 5.45 (d, 0.45 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 5.33 (app t, 0.55 H, J = 2.8 Hz, H-1α), 5.23–5.12 (m, 2 H, C$\underline{H}_2$Ar), 4.86–4.83 (m, 1 H, C$\underline{H}_2$Ar), 4.75 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.72–4.67 (m, 2 H, 2 x C$\underline{H}_2$Ar), 4.60 (app t, 0.45 H, J = 6.2 Hz, H-1β), 4.51 (d, 0.55 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.50 (d, 0.45 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.30 (s, 0.45 H, OH), 4.27 (s, 0.55 H, OH), 4.13 (d, 0.55 H, $J_{2,3}$ = 9.9 Hz, H-3α), 4.07–4.01 (m, 0.55 H, H-2α), 3.93 (br, 0.45, C-1-OHβ), 3.89–3.75 (m, 2 H, H-2β, H-9α, H-3β, H-5/H-7α), 3.71–3.62 (m, 1.45 H, H-9β, H-5, H-7), 3.37 (br, 0.55 H, C-1-OHα), 3.25 (dd, 0.45 H, J = 11.4 Hz, J = 4.4 Hz, H-5/H-7β), 3.01 (br, 0.45 H, C-2-OHβ), 2.69 (d, 0.55 H, $J_{2,OH}$ = 5.0 Hz, C-2-OHα), 2.20–2.05 (m, 2 H, 2 x H-6), 1.67 (s, 1.65 H, H-10), 1.66 (s, 1.35 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 139.5(4) (Ar), 139.4(8) (Ar), 139.4 (Ar), 138.2 (Ar), 138.0 (Ar), 137.8 (Ar), 137.7 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4(2) (Ar), 128.3(7) (Ar), 128.3 (Ar), 128.2(3) (Ar), 128.2(0) (Ar), 128.1(5) (Ar), 128.1 (Ar), 128.0 (Ar), 127.7 (Ar), 127.6(5) (Ar), 127.6(1) (Ar), 127.5(7) (Ar), 127.3(1) (Ar), 127.2(6) (Ar), 127.1 (Ar), 127.0(1) (Ar), 127.9(6) (Ar), 126.8 (Ar), 97.6 (C-1β), 92.6 (C-1α), 89.6 (C-9α), 89.4 (C-9β), 83.5 (C-8), 83.4 (C-8), 82.0(7) (C_{brady}), 81.9(6) (C_{brady}), 80.0 (C_{brady}), 76.4 (C-4), 76.3 (C$\underline{H}_2$Ar), 76.2 (C$\underline{H}_2$Ar), 75.9 (C-4), 73.4 (C_{brady}), 72.7 (C_{brady}), 71.4 (C$\underline{H}_2$Ar), 71.3 (C$\underline{H}_2$Ar), 69.7 (C_{brady}), 68.9(2) (C$\underline{H}_2$Ar), 68.8(8) (C$\underline{H}_2$Ar), 67.7 (C_{brady}), 66.1 (C$\underline{H}_2$Ar), 66.0 (C$\underline{H}_2$Ar), 28.9 (C-6), 28.7 (C-6), 11.5 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{38}H_{42}NaO_8$: 649.2772. Found 649.2779.

4,7,8,9-tetra-*O*-benzyl-1,5-α-D-bradyrhizose (D-30α) and **4,7,8,9-tetra-*O*-benzyl-1,5-β-D-bradyrhizose (D-30β)**. Trichloroisocyanuric acid (45 mg, 0.191 mmol), followed by TEMPO (0.5 mg, 0.00355 mmol) were added to a cooled (0 °C) solution of **D-33** (45 mg, 0.0709 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at 0 °C for 30 min and a saturated aqueous solution of $Na_2S_2O_3$ was added, followed by an extraction with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. The resulting crude product was used without further purification. DIBAL-H (354 µL, 0.354 mmol, 1.0M in cyclohexane) was added to a cooled (–78 °C) solution of the crude product in CH_2Cl_2 (2.5 mL). The reaction mixture was stirred for 90 min before MeOH (1 mL) and a 10% aqueous solution of HCl (1 mL) were added at –78 °C. The mixture was warmed to rt and extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product were purified by silica gel column chromatography (49:1 CH_2Cl_2–MeOH) to give **D-30α** and **D-30β** (41 mg, 91%) as a colorless oil (diastereomeric mixture, 0.45:0.55). The R_f, ^{1}H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to the that of the racemic compounds **30α** and **30β** previously described. $[\alpha]_D$ +9.1 (*c* 0.2, $CHCl_3$).

4,7,8,9-tetra-*O*-benzyl-1,5-α-L-bradyrhizose (L-30α) and **4,7,8,9-tetra-*O*-benzyl-1,5-β-L-bradyrhizose (L-30β)**. Trichloroisocyanuric acid (255 mg, 1.10 mmol), followed by TEMPO (2 mg, 0.0122 mmol) were added to a cooled (0 °C) solution of **L-33** (256 mg, 0.407 mmol) in CH_2Cl_2 (11.5 mL). The mixture was stirred at 0 °C for 30 min and a saturated aqueous solution of $Na_2S_2O_3$ was added, followed by an extraction with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. The resulting crude product was used without further purification. DIBAL-H (1.77 mL, 1.77 mmol, 1.0M in cyclohexane) was added to a cooled (–78 °C) solution of the crude in CH_2Cl_2 (12.5 mL). The reaction mixture was stirred for 90 min then MeOH (3 mL) and a 10% aqueous solution of HCl were added at –78 °C. The mixture was warmed

to rt and extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (49:1 CH_2Cl_2–MeOH) to give **L-30α** and **L-30β** (216 mg, 85%) as a colorless oil (diastereomeric mixture, 0.45:0.55). The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained on the racemic compounds **30α** and **30β** previously described. $[\alpha]_D$ –9.6 (*c* 0.2, $CHCl_3$).

(–)-1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-(ethoxycarbonyl-2'-*O*-((2'*S*)-2-phenyl-2-methoxy-3,3,3-trifluoropropionoyl)-(1'*S*,2'*S*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (L-31), **(–)-1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-(ethoxycarbonyl-2'-*O*-((2'*S*)-2-phenyl-2-methoxy-3,3,3-trifluoropropionoyl)-(1'*R*,2'*R*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (D-31)** and **(–)-1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-(ethoxycarbonyl-(1'*S*,2'*S*)-ethanediol)-3-*C*-methyl-1-*myo*-inositol (D-2)**. *N,N*-Diisopropylcarbodiimide (362 µL, 2.34 mmol) was added to a solution of **2** (914 mg, 1.16 mmol), (*S*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetic acid (547 mg, 2.34 mmol) and DMAP (72 mg, 0.592 mmol) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 2 h and then water was added. The aqueous and organic layer were separated and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **L-31** (583 mg, 50%), **D-31** (170 mg, 14%) as colorless oils and unreacted **D-2** (329 mg, 36%). (**L-31**): R_f 0.45 (9:1 hexanes–EtOAc); $[\alpha]_D$ –9.7 (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.67 (d, 2 H, J = 7.5 Hz, Ar), 7.44–7.22 (m, 23 H, Ar), 5.62 (d, 1 H, J = 8.3 Hz, OH), 5.26–5.20 (m, 3 H, C$\underline{H}_2$Ar, H-1', H-2'), 4.94 (d, 1 H, J = 10.5 Hz, C$\underline{H}_2$Ar), 4.91 (d, 1 H, J = 10.5 Hz, C$\underline{H}_2$Ar), 4.73 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.69 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.48 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 4.39 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.34–4.19 (m, 3 H, C$\underline{H}_2$Ar, C$\underline{H}_2$CH$_3$), 3.98 (s, 3 H, OCH_3), 3.70 (dd, 1 H, $J_{5ax,6}$

= 12.1 Hz, $J_{5eq,6}$ = 3.9 Hz, H-6), 2.84 (s, 1 H, H-2), 2.48 (dd, 1 H, $J_{4,5ax}$ = 12.3 Hz, $J_{4,5eq}$ = 4.6 Hz, H-4), 1.88 (ddd, 1 H, $J_{4,5ax}$ = 12.1 Hz, $J_{5eq,5ax}$ = 12.1 Hz, $J_{5ax,6}$ = 12.1 Hz, H-5_{ax}), 1.54 (s, 3 H, CH_3), 1.47 (ddd, 1 H, $J_{5eq,5ax}$ 11.7 Hz, $J_{4,5eq}$ = 4.2 Hz, $J_{5eq,6}$ = 4.2 Hz, H-5_{eq}), 1.24 (t, 3 H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 0.89 (s, 9 H, $SiC(CH_3)_3$), 0.10 (s, 3 H, $SiCH_3$), –0.03 (s, 3 H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 167.0 (2 x C=O), 139.7 (Ar), 139.2 (Ar), 138.6 (Ar), 132.9 (Ar), 129.9 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 127.9(5) (Ar), 127.9(0) (Ar), 127.6 (Ar), 127.5 (Ar), 127.3(5) (Ar), 127.3(0) (Ar), 127.1(3) (Ar), 127.0(6) (Ar), 126.8 (Ar), 123.1 (q, 1 C, J = 294.5, CF_3), 84.8 (C-2), 84.2 (q, 1 C, J = 27.7, $\underline{C}CF_3$), 83.2 (C-3), 81.5 (C-4), 79.5 (C-1), 76.5 (C-2'), 76.1 ($\underline{C}H_2Ar$), 73.0 (C-1') 71.2 ($\underline{C}H_2Ar$), 70.2 (C-6), 66.9 ($\underline{C}H_2Ar$), 65.8 ($\underline{C}H_2Ar$), 62.0 ($\underline{C}H_2CH_3$), 56.7 (OCH_3) 33.7 (C-5), 25.8 ($SiC(\underline{C}H_3)_3$), 18.0 ($Si\underline{C}(CH_3)_3$), 14.0 ($CH_2\underline{C}H_3$), 11.2 (CH_3), –3.0 ($SiCH_3$), –3.9 ($SiCH_3$). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{56}H_{67}F_3NaO_{11}Si$: 1023.4297. Found 1023.4294.

(**D-31**): R_f 0.43 (9:1 hexanes–EtOAc); $[\alpha]_D$ –31.1 (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.74–7.69 (m, 2 H, Ar), 7.47–7.43 (m, 3 H, Ar), 7.41–7.38 (m, 2 H, Ar), 7.36–7.24 (m, 18 H, Ar), 5.46–5.42 (m, 2 H, OH, H-2'), 5.28 (dd, 1 H, J = 7.7 Hz, J = 2.9 Hz, H-1'), 5.15 (d, 1 H, J = 11.7 Hz, $C\underline{H}_2Ar$), 5.03 (d, 1 H, J = 10.5 Hz, $C\underline{H}_2Ar$), 4.97 (d, 1 H, J = 10.5 Hz, $C\underline{H}_2Ar$), 4.83 (d, 1 H, J = 11.6 Hz, $C\underline{H}_2Ar$), 4.69 (d, 1 H, J = 11.4 Hz, $C\underline{H}_2Ar$), 4.54 (s, 2 H, 2 x $C\underline{H}_2Ar$), 4.50 (d, 1 H, J = 11.9 Hz, $C\underline{H}_2Ar$), 4.47 (dd, 1 H, $J_{5ax,6}$ = 12.1 Hz, $J_{5eq,6}$ = 4.0 Hz, H-6), 4.28–4.13 (m, 2 H, $C\underline{H}_2CH_3$), 3.48 (s, 3 H, OCH_3), 3.42 (dd, 1 H, $J_{4,5ax}$ = 12.3 Hz, $J_{4,5eq}$ = 4.4 Hz, H-4), 3.28 (s, 1 H, H-2), 2.11 (ddd, 1 H, $J_{4,5ax}$ = 12.1 Hz, $J_{5eq,5ax}$ = 12.1 Hz, $J_{5ax,6}$ = 12.1 Hz, H-5_{ax}), 1.84 (ddd, 1 H, $J_{5eq,5ax}$ = 11.9 Hz, $J_{4,5eq}$ = 4.2 Hz, $J_{5eq,6}$ = 4.2 Hz, H-5_{eq}), 1.66 (s, 3 H, CH_3), 1.20 (t, 3 H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 0.85 (s, 9 H, $SiC(CH_3)_3$), 0.05 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 167.1 (2 x C=O), 139.7 (Ar), 139.4 (Ar), 138.8 (Ar), 138.2 (Ar), 131.1 (Ar), 129.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2(7) (Ar), 128.2(5) (Ar), 128.0 (Ar), 127.9 (Ar),

127.8 (Ar), 127.4 (Ar), 127.2 (Ar), 127.1(3) (Ar), 127.0(5) (Ar), 124.5 (q, 1 C, J = 289.1, CF_3), 84.2 (C-2), 85.4 (q, 1 C, J = 27.6, $\underline{C}CF_3$), 83.3 (C-3), 80.7 (C-4), 79.9 (C-1), 76.7 (C-2'), 75.8 ($\underline{C}H_2Ar$), 72.7 (C-1'), 71.8 ($\underline{C}H_2Ar$), 70.4 (C-6), 67.1 ($\underline{C}H_2Ar$), 65.4 ($\underline{C}H_2Ar$), 62.0 ($\underline{C}H_2CH_3$), 55.5 (OCH_3), 33.0 (C-5), 25.8 ($SiC(\underline{C}H_3)_3$), 18.0 ($Si\underline{C}(CH_3)_3$), 14.0 ($CH_2\underline{C}H_3$), 11.8 (CH_3), –3.0 ($SiCH_3$), –4.1 ($SiCH_3$). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{56}H_{67}F_3NaO_{11}Si$: 1023.4297. Found 1023.4312.

(D-2): The Rf, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained for the racemic compound 2 previously described. [α]D –57.2 (c 0.3, CHCl3).

(+)-1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-((1'*S*,2'*R*)-propane-1,2,3-triol)-3-*C*-methyl-1-*myo*-inositol (L-32). Lithium borohydride solution (1.32 mL, 2.65 mmol, 2.0M in THF) was added to a solution of **L-31** (530 mg, 0.529 mmol) in Et_2O (28 mL). After 1 h, additional lithium borohydride solution (660 μL, 1.32 mmol, 2.0M in THF) was added. The mixture was stirred for 2 h and a saturated aqueous solution of ammonium chloride was added. The aqueous layer was extracted with EtOAc and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **L-32** (307 mg, 78%) as a yellow oil. R_f 0.27 (7:3 hexanes–EtOAc); $[\alpha]_D$ +29.2 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.45–7.25 (m, 20 H, Ar), 5.11 (d, 1 H, J = 11.9 Hz, $C\underline{H}_2Ar$), 5.03 (d, 1 H, J = 11.6 Hz, $C\underline{H}_2Ar$), 4.97 (d, 1 H, J = 11.4 Hz, $C\underline{H}_2Ar$), 4.88 (d, 1 H, J = 11.2 Hz, $C\underline{H}_2Ar$), 4.74 (d, 1 H, J = 11.2 Hz, $C\underline{H}_2Ar$), 4.64 (d, 1 H, J = 7.0 Hz, C1'-OH), 4.63 (s, 2 H, 2 x $C\underline{H}_2Ar$), 4.56 (d, 1 H, J = 7.0 Hz, H-1'), 4.52 (d, 1 H, J = 11.9 Hz, $C\underline{H}_2Ar$), 4.46 (dd, 1 H, $J_{5ax,6}$ = 12.1 Hz, $J_{5eq,6}$ = 3.9 Hz, H-6), 3.74–3.57 (m, 4 H, H-2, H-4, H-2',H-3'), 3.56–3.47 (m, 1 H, H-3'), 2.92 (d, 1 H, J = 8.4 Hz, C-2'-OH), 2.64 (br s, 1 H, C3'-OH), 2.15 (ddd, 1 H, $J_{4,5ax}$ = 12.3 Hz, $J_{5ax,5eq}$ = 12.3 Hz, $J_{5ax,6}$ = 12.3 Hz, H-5_{ax}), 1.92 (ddd, 1 H, $J_{5ax,5eq}$ = 11.9 Hz, $J_{4,5eq}$

= 4.2 Hz, $J_{5eq,6}$ = 4.2 Hz, H-5_{eq}), 1.72 (s, 3 H, CH_3), 0.93 (s, 9 H, $SiC(CH_3)_3$), 0.14 (s, 3 H, $SiCH_3$), 0.10 (s, 3 H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 139.9 (Ar), 139.7 (Ar), 138.8 (Ar), 138.4 (Ar), 128.5(0) (Ar), 128.4(9) (Ar), 128.3 (Ar), 128.1 (Ar), 127.8 (Ar), 127.6 (Ar), 127.4 (Ar), 127.2 (Ar), 127.1 (Ar), 127.0 (Ar), 126.9 (Ar), 83.8 (C-2), 83.8 (C-3), 81.6 (C-4), 80.3 (C-1), 75.7 ($\underline{C}H_2Ar$), 72.3 (C-6), 72.0 ($\underline{C}H_2Ar$), 71.5 (C-1'), 69.5 (C-2'), 66.6 ($\underline{C}H_2Ar$), 66.2 ($\underline{C}H_2Ar$), 66.0 (C-3'), 33.2 (C-5), 25.9 ($SiC(\underline{C}H_3)_3$), 18.0 ($Si\underline{C}(CH_3)_3$), 11.5 (CH_3), –3.5 ($SiCH_3$), –4.3 ($SiCH_3$). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{44}H_{58}NaO_8Si$: 765.3793. Found 765.3799.

(–)-1,2,3,4-tetra-*O*-benzyl-6-*O*-(*t*-butyldimethyl)silyl-5-deoxy-1-((1'*R*,2'*S*)-propane-1,2,3-triol)-3-*C*-methyl-1-*myo*-inositol (D-32). Lithium borohydride solution (237 µL, 0.474 mmol, 2.0M in THF) was added to a solution of **D-31** (95 mg, 0.0948 mmol) in Et_2O (5 mL). After 1 h, additional lithium borohydride solution (118 µL, 0.237 mmol, 2.0M in THF) was added. The mixture was stirred for 2 h and a saturated aqueous solution of ammonium chloride was added. The aqueous layer was extracted with EtOAc and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **D-32** (52 mg, 75%) as a yellow oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the **L-32** enantiomer previously described. $[\alpha]_D$ –30.4 (*c* 0.1, $CHCl_3$).

(+)-1,2,3,4-tetra-*O*-benzyl-5-deoxy-1-((1'*S*,2'*R*)-propane-1,2,3-triol)-3-*C*-methyl-1-*myo*-inositol (L-33). A solution of TBAF (569 µL, 0.100 mmol, 1.0M in THF) was added to a solution of **L-32** (313 mg, 0.422 mmol) in THF (16.5 mL). The reaction mixture was stirred for 30 min and brine was added. The aqueous layer was extracted with EtOAc and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column

chromatography (1:1 hexanes–EtOAc, then 19:1 CH_2Cl_2–MeOH) to give **L-33** (264 mg, 99%) as a colorless oil. R_f 0.28 (24:1 CH_2Cl_2:MeOH); $[\alpha]_D$ +11.8 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.21 (m, 20 H, Ar), 5.05 (d, 1 H, *J* = 10.5 Hz, C$\underline{H}_2$Ar), 5.04 (d, 1 H, *J* = 11.8 Hz, C$\underline{H}_2$Ar), 4.93 (d, 1 H, *J* = 10.6 Hz, C$\underline{H}_2$Ar), 4.83 (d, 1 H, *J* = 11.2 Hz, C$\underline{H}_2$Ar), 4.72 (d, 1 H, *J* = 11.0 Hz, C$\underline{H}_2$Ar), 4.65 (d, 1 H, *J* = 11.5 Hz, C$\underline{H}_2$Ar), 4.54 (d, 1 H, $J_{1',2'}$ = 7.4 Hz, H-1'), 4.50 (d, 1 H, *J* = 11.4 Hz, C$\underline{H}_2$Ar), 4.46 (d, 1 H, *J* = 11.8 Hz, C$\underline{H}_2$Ar), 4.40–4.33 (m, 2 H, OH, H-6), 3.73–3.68 (m, 1 H, H-2'), 3.64 (dd, 1 H, *J* = 11.1 Hz, *J* = 5.1 Hz, H-3'), 3.60 (dd, 1 H, $J_{4,5ax}$ = 12.0 Hz, $J_{4,5eq}$ = 4.5 Hz, H-4), 3.56 (s, 1 H, H-2), 3.53–3.47 (m, 1 H, H-3'), 3.19 (br, 1 H, OH), 2.81–2.69 (m, 2 H, C-6-OH, OH), 2.07 (ddd, 1 H, $J_{5ax,5eq}$ = 12.2 Hz, $J_{4,5eq}$ = 4.4 Hz, $J_{5eq,6}$ = 4.4 Hz, H-5_{eq}), 1.92 (ddd, 1 H, $J_{4,5ax}$ = 12.2 Hz, $J_{5ax,5eq}$ = 12.2 Hz, $J_{5ax,6}$ = 12.2 Hz, H-5_{ax}), 1.73 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 139.6 (Ar), 139.1 (Ar), 138.8 (Ar), 138.3 (Ar), 128.5 (Ar), 128.4(0) (Ar), 128.3(8) (Ar), 128.3 (Ar), 128.0 (Ar), 127.6(1) (Ar), 127.5(6) (Ar), 127.5(3) (Ar), 127.5(0) (Ar), 127.2 (Ar), 127.1 (Ar), 84.3 (C-2), 83.5 (C-3), 81.1 (C-4), 80.2 (C-1), 76.1 (C$\underline{H}_2$Ar), 71.4 (C$\underline{H}_2$Ar), 71.3 (C-1'), 70.0 (C-6), 69.7 (C-2'), 67.0 (C$\underline{H}_2$Ar), 66.5 (C$\underline{H}_2$Ar), 66.2 (C-3'), 33.7 (C-5), 11.4 (CH_3). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{38}H_{44}NaO_8$: 651.2928. Found 651.2936.

(–)-1,2,3,4-tetra-*O*-benzyl-5-deoxy-1-((1'*R*,2'*S*)-propane-1,2,3-triol)-3-*C*-methyl-1-*myo*-inositol (D-33). A solution of TBAF (100 µL, 0.100 mmol, 1.0M in THF) was added to a solution of **D-32** (57 mg, 0.0767 mmol) in THF (3 mL). The reaction mixture was stirred for 30 min and brine was added. The aqueous layer was extracted with EtOAc and the organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (1:1 hexanes–EtOAc then 19:1 CH_2Cl_2–MeOH) to give **D-33** (47 mg, 98%) as a colorless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the **L-33** enantiomer previously described. $[\alpha]_D$ –11.2 (*c* 0.1, $CHCl_3$).

Racemic **methyl 2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-bradyrhizopyranoside (37α)** and ***racemic*** **methyl 2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-β-bradyrhizopyranoside (37β)**. Benzaldehyde dimethyl acetal (120 μL, 0.798 mmol) and CSA (6 mg, 0.0266 mmol) were added to a solution of **46** (51 mg, 0.133 mmol) in MeCN (5 mL). The reaction mixture was placed on the rotary evaporator to remove the MeOH formed. Et_3N was added and the mixture was concentrated. The resulting crude product was purified by silica gel column chromatography (1:0 → 19:1 CH_2Cl_2–MeOH) to give **37α** and **37β** as separable products (51 mg, 81%, diastereomeric mixture 7:3) as a white solid. (**37α**): mp = 194–196 ˚C; R_f 0.34 (19:1 CH_2Cl_2–MeOH); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09–8.04 (m, 2 H, Ar), 7.60–7.55 (m, 1 H, Ar), 7.54–7.48 (m, 2 H, Ar), 7.48–7.42 (m, 2 H, Ar), 7.40–7.34 (m, 3 H, Ar), 5.80 (s, 1 H, C<u>H</u>Ar), 5.54 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 5.19 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.36 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3), 3.86 (ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{5,6eq}$ = 4.0 Hz, $J_{4OH,5}$ = 1.5 Hz, H-5), 3.75 (dd, 1 H, $J_{6ax,7}$ = 11.9 Hz, $J_{6eq,7}$ = 4.2 Hz, H-7), 3.69 (s, 1 H, H-9), 3.44 (s, 3 H, OCH_3), 2.95 (d, 1 H, $J_{4OH,5}$ = 1.5 Hz, 4-OH), 2.27 (br s, 1H, OH), 2.20 (br, 1H, OH), 2.16 (ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{6ax,6eq}$ = 11.9 Hz, $J_{6ax,7}$ = 11.9 Hz, H-6_{ax}), 2.09 (ddd, 1 H, $J_{6ax,6eq}$ = 11.9 Hz, $J_{5,6eq}$ = 4.4 Hz, $J_{6eq,7}$ = 4.4 Hz, H-6_{eq}), 1.46 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 136.6 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 129.3(8) (Ar), 128.3(7) (Ar), 128.3 (Ar), 126.1 (Ar), 102.7 (<u>C</u>HAr), 98.5 (C-1), 83.2 (C-9), 78.0 (C-3), 76.1 (C-8), 73.4 (C-7), 69.9 (C-2), 67.7 (C-4), 64.8 (C-5), 55.9 (OCH_3), 30.6 (C-6), 16.8 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{25}H_{28}NaO_9$: 495.1626. Found 495.1624.

(**37β**): mp = 261–264 ˚C; R_f 0.29 (19:1 CH_2Cl_2–MeOH);); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 8.02–7.97 (m, 2 H, Ar), 7.61–7.50 (m, 3 H, Ar), 7.48–7.42 (m, 2 H, Ar), 7.30–7.25 (m, 3 H, Ar), 5.73 (s, 1 H, C<u>H</u>Ar), 5.51 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 7.9 Hz, H-2), 4.67 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1), 4.10 (d, 1 H, $J_{2,3}$ = 9.7 Hz, H-3), 3.67 (dd, 1 H, $J_{5,6ax}$ = 11.7 Hz, $J_{5,6eq}$ = 4.4 Hz, H-5),

3.62 (s, 1 H, H-9), 3.61 (dd, 1 H, $J_{6ax,7}$ = 12.1 Hz, $J_{6eq,7}$ = 4.4 Hz, H-7), 3.47 (s, 3 H, OCH_3), 2.09 (ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{6eq,6ax}$ = 11.9 Hz, $J_{6ax,7}$ = 11.9 Hz, H-6_{ax}), 1.98 (ddd, 1 H, $J_{6ax,6eq}$ = 11.9 Hz, $J_{5,6eq}$ = 4.2 Hz, $J_{6eq,7}$ = 4.2 Hz, H-6_{eq}), 1.36 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, δ_C) 167.1 (C=O), 138.9 (Ar), 134.4 (Ar), 131.2 (Ar), 130.6 (Ar), 129.9 (Ar), 129.6 (Ar), 128.9 (Ar), 127.6 (Ar), 104.3 (C-1), 104.2 (CHAr), 84.6 (C-9), 82.6 (C-3), 76.7 (C-8), 74.7 (C-7), 72.2 (C-2), 71.1 (C-5), 68.3 (C-4), 57.3 (OCH_3), 32.7 (C-6), 16.4 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{25}H_{28}NaO_9$: 495.1626. Found 495.1626.

Methyl 2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (D-37α) and **methyl 2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-β-D-bradyrhizopyranoside (D-37β)**. Benzaldehyde dimethyl acetal (17 μL, 0.115 mmol) and CSA (1.7 mg, 0.00764 mmol) were added to a solution of **D-46** (15 mg, 0.0382 mmol) in MeCN (5 mL). The reaction mixture was placed on the rotary evaporator to remove the MeOH formed. Et_3N was added and the mixture was concentrated. The resulting crude product was purified by silica gel column chromatography (1:0 to 19:1 CH_2Cl_2–MeOH) to give **D-37α** and **D-37β** (14.4 mg, 80%, inseparable diastereomeric mixture 22:3) as a white solid. The mp, R_f, ^1H NMR, ^{13}C NMR and MS data correspond to that obtained from the racemic compounds **37α** and **37β** previously described. The mp, R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **37α** and **37β** previously described.

Methyl 2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (L-37α) and **methyl 2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-β-L-bradyrhizopyranoside (L-37β)**. Benzaldehyde dimethyl acetal (26 μL, 0.176 mmol) and CSA (2.7 mg, 0.0118 mmol) were added to a solution of **L-46** (23 mg, 0.0588 mmol) in MeCN (5 mL). The reaction mixture was placed on the rotary evaporator to

remove the MeOH formed. Et_3N was added and the mixture was concentrated. The resulting crude product was purified by silica gel column chromatography (1:0 → 19:1 CH_2Cl_2–MeOH) to give **L-37α** and **L-37β** (23 mg, 83%, diastereomeric mixture 7:3) as a white solid. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **37α** and **37β** previously described. (**L-37α**): $[\alpha]_D$ –154.0 (*c* 0.1, $CHCl_3$). (**L-37β**): $[\alpha]_D$ –23.4 (*c* 0.1, $CHCl_3$).

***Racemic* allyl 4,7,8,9-tetra-*O*-benzyl-1,5-α-bradyrhizopyranoside (38α)** and ***racemic* allyl 4,7,8,9-tetra-*O*-benzyl-1,5-β-bradyrhizopyranoside (38β)**. To a stirred solution of **30** (131 mg, 0.209 mmol) in AllOH (5 mL), HCl (250 μL of a solution of AcCl (0.1 mL) in AllOH (2.5 mL)) was added and the mixture was stirred at 65 °C for 2 days. After cooling to rt, water was added and the aqueous layer was extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **38α** and **38β** (88 mg, 63%) as a colorless oil (inseparable diastereomeric mixture 1:1). The starting material 30 can be recovered by silica gel column chromatography (97:3 CH_2Cl_2–MeOH) and the reaction can be done again to yield more product **38α** and **38β**. R_f 0.34 (3:2 hexanes–EtOAc); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.24 (m, 20 H, Ar), 6.04–5.91 (m, 1 H, C<u>H</u>=CH_2), 5.56 (d, 0.5 H, *J* = 12.1 Hz, C<u>H</u>$_2$Ar), 5.43 (d, 0.5 H, *J* = 11.4 Hz, C<u>H</u>$_2$Ar), 5.37 (app dq, 0.5 H, *J* = 17.2 Hz, *J* = 1.7 Hz, CH=C<u>H</u>$_2$ *trans*), 5.35 (app dq, 0.5 H, *J* = 17.2 Hz, *J* = 1.7 Hz, CH=C<u>H</u>$_2$ *trans*), 5.29–5.24 (m, 1 H, CH=C<u>H</u>$_2$ *cis*), 5.22 (d, 0.5 H, *J* = 12.1 Hz, C<u>H</u>$_2$Ar), 5.17–5.11 (m, 1.5 H, C<u>H</u>$_2$Ar), 5.01 (d, 0.5 H, *J* = 4.0 Hz, H-1α), 4.86 (d, 0.5 H, *J* = 11.0 Hz, C<u>H</u>$_2$Ar), 4.84 (d, 0.5 H, *J* = 11.0 Hz, C<u>H</u>$_2$Ar), 4.79–4.67 (m, 3 H, C<u>H</u>$_2$Ar), 4.56 (d, 0.5 H, *J* = 11.4 Hz, C<u>H</u>$_2$Ar), 4.53 (d, 0.5 H, *J* = 11.4 Hz, C<u>H</u>$_2$Ar), 4.45 (app ddt, 0.5 H, *J* = 12.5 Hz, *J* = 5.1 Hz, *J* = 1.5 Hz, C<u>H</u>$_2$CH=CH_2), 4.38 (d, 0.5 H, $J_{1,2}$ = 7.3 Hz, H-1β), 4.28–4.22 (m, 1 H, C<u>H</u>$_2$CH=CH_2 and OH), 4.17 (app ddt, 0.5 H, *J* = 12.7 Hz, *J* = 6.2 Hz, *J* = 1.3 Hz, C<u>H</u>$_2$CH=CH_2),

4.15–4.02 (m, 2 H, H-2α, H-3α, OH, C$\underline{H}_2$CH=CH$_2$), 3.93 (dd, 0.5 H, $J_{1,2}$ = 7.3 Hz, $J_{2,3}$ = 9.5 Hz, H-2β), 3.88 (d, 0.5 H, $J_{2,3}$ = 9.5 Hz, H-3β), 3.77 (s, 0.5 H, H-9), 3.72–3.63 (m, 2 H, H-9, H-7, H-5), 3.27 (dd, 0.5 H, $J_{5,6ax}$ = 11.2 Hz, $J_{5,6eq}$ = 4.6 Hz, H-5), 2.51 (br, 0.5 H, C-2-OHβ), 2.22–2.01 (m, 2.5 H, H-6, OH), 1.68 (s, 1.5 H, H-10), 1.66 (s, 1.5 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 139.5 (Ar), 139.5 (Ar), 139.4 (Ar), 138.2(1) (Ar), 138.1(7) (Ar), 137.9 (Ar), 137.7 (Ar), 133.9 (C$\underline{H}$=CH$_2$), 133.7 (C$\underline{H}$=CH$_2$), 128.7 (Ar), 128.4(4) (Ar), 128.3(6) (Ar), 128.2 (Ar), 128.1(3) (Ar), 128.0(5) (Ar), 127.9 (Ar), 127.6(4) (Ar), 127.5(7) (Ar), 127.3(0) (Ar), 127.2(7) (Ar), 127.2 (Ar), 127.0 (Ar), 126.9 (Ar), 126.8 (Ar), 117.9 (CH=C$\underline{H}_2$), 102.7 (C-1β), 97.8 (C-1α), 89.7 (C-9), 89.6 (C-9), 83.7 (C-8), 83.5 (C-8), 82.3 (C-7), 82.2 (C-7), 80.0 (C-3β), 77.6 (C-3α), 77.0 (C-4), 76.5 (C$\underline{H}_2$Ar), 76.3 (C$\underline{H}_2$Ar), 76.2 (C$\underline{H}_2$Ar), 76.0 (C$\underline{H}_2$Ar), 72.5 (C-5), 72.0 (C-2β), 71.5 (C$\underline{H}_2$Ar), 71.4 (C$\underline{H}_2$Ar), 70.3 (C$\underline{H}_2$CH=CH$_2$), 70.3 (C$\underline{H}_2$CH=CH$_2$), 69.6 (C-2α), 69.0(0) (C$\underline{H}_2$Ar), 68.9(6) (C$\underline{H}_2$Ar), 68.9 (C$\underline{H}_2$Ar), 67.8 (C-5), 66.1 (C$\underline{H}_2$Ar), 28.9 (C-6), 28.8 (C-6), 11.6 (C-10), 11.4 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{41}H_{46}NaO_8$: 689.3085. Found 689.3086.

Allyl 4,7,8,9-tetra-*O*-benzyl-1,5-α-D-bradyrhizopyranoside (D-38α) and **allyl 4,7,8,9-tetra-*O*-benzyl-1,5-β-D-bradyrhizopyranoside (D-38β)**. To a stirred solution of **D-30** (115 mg, 0.183 mmol) in AllOH (5 mL), HCl (213 µL of a solution of AcCl (0.1 mL) in AllOH (2.5 mL)) was added and the mixture was stirred at 65 °C for 2 days. After cooling to rt, water was added and the aqueous layer was extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **D-38α** and **D-38β** (77 mg, 63%, inseparable diastereomeric mixture 11:9) as a colorless oil . The starting material **D-30** can be recovered by silica gel column chromatography (97:3 CH_2Cl_2–MeOH) and the reaction can be done again to yield more product

D-38α and **D-38β**. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compounds **38α** and **38β** previously described.

Allyl 4,7,8,9-tetra-*O*-benzyl-1,5- α -L-bradyrhizopyranoside (L-38α) and **allyl 4,7,8,9-tetra-*O*-benzyl-1,5- β -L-bradyrhizopyranoside (L-38β)**. To a stirred solution of **L-30** (90 mg, 0.145 mmol) in AllOH (4 mL), HCl (160 µL of a solution of AcCl (0.1 mL) in AllOH (2.5 mL)) was added and the mixture was stirred at 65 °C for 2 days. After cooling to rt, water was added and the aqueous layer was extracted with EtOAc. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude products were purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **L-38α** and **L-38β** (61 mg, 63%, inseparable diastereomeric mixture 1:1) as a colorless oil. The starting material **L-30** can be recovered by silica gel column chromatography (97:3 CH_2Cl_2–MeOH) and the reaction can be done again to yield more product **L-38α** and **L-38β**. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compounds **38α** and **38β** previously described.

***Racemic* allyl 2,3,4,7,8,9-hexa-*O*-benzyl-1,5-α-bradyrhizopyranoside (39α)**, ***racemic* allyl 2,3,4,7,8,9-hexa-*O*-benzyl-1,5-β-bradyrhizopyranoside (39β)**, ***racemic* allyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-bradyrhizopyranoside (40α)** and ***racemic* allyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-bradyrhizopyranoside (40β)**. Sodium hydride (18 mg, 0.453 mmol, 60% wt in mineral oil) was added to a solution of **38** (100 mg, 0.151 mmol) in THF (3.5 mL). After 30 min, benzyl bromide (90 µL, 0.755 mmol) was added and the reaction mixture was stirred at rt overnight. Water was added and the aqueous solution was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 → 9:1 hexanes–EtOAc) to give **39α** and **39β** (40 mg, 31%, inseparable

diastereomeric mixture 36:64) and **40α** and **40β** (76 mg, 67%, separable diastereomeric mixture 65:35) as yellow oils. **40α** and **40β** were separated for characterization. (**39α**) and (**39β**): R_f 0.58 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.46–7.41 (m, 1 H, Ar), 7.39–7.04 (m, 29 H, Ar), 6.06–5.92 (m, 1 H, C<u>H</u>=CH$_2$), 5.70 (d, 0.36 H, J = 12.7 Hz, C<u>H</u>$_2$Ar), 5.65 (d, 0.64 H, J = 12.5 Hz, C<u>H</u>$_2$Ar), 5.51 (d, 0.64 H, J = 12.5 Hz, C<u>H</u>$_2$Ar), 5.45 (d, 0.36 H, J = 12.7 Hz, C<u>H</u>$_2$Ar), 5.42–5.30 (m, 1 H, CH=C<u>H</u>$_2$ *trans*), 5.29–5.21 (m, 1.36 H, CH=C<u>H</u>$_2$ *cis*, C<u>H</u>$_2$Ar), 5.18 (d, 0.64 H, J = 11.7 Hz, C<u>H</u>$_2$Ar), 5.06 (d, 0.64 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 5.01 (d, 0.36 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 4.88–4.41 (m, 9.72 H, C<u>H</u>$_2$Ar, C<u>H</u>$_2$CH=CH$_2$, H-1α and H-1β), 4.23–4.07 (m, 1.64 H, H-3α, C<u>H</u>$_2$Ar and C<u>H</u>$_2$CH=CH$_2$), 4.03 (dd, 0.36 H, J = 9.9 Hz, J = 3.5 Hz, H-2α), 3.86 (dd, 0.64 H, J = 9.5 Hz, J = 7.5 Hz, H-2β), 3.76–3.62 (m, 3 H, H-3β, H-9, H-7 and H-5α), 3.23 (dd, 0.64 H, $J_{5,6ax}$ = 11.4 Hz, $J_{5,6eq}$ = 4.0 Hz, H-5β), 2.22–2.09 (m, 1.28 H, H-6β$_{ax}$), 2.06 (ddd, 0.36 H, $J_{5,6ax}$ = 12.3 Hz, $J_{6eq,6ax}$ = 12.3 Hz, $J_{6ax,7}$ = 12.3 Hz, H-6α$_{ax}$), 1.95 (ddd, 0.36 H, $J_{6eq,6ax}$ = 12.1 Hz, $J_{5,6eq}$ = 3.5 Hz, $J_{6eq,7}$ = 3.5 Hz, H-6α$_{eq}$), 1.72 (s, 1.08 H, H-10), 1.70 (s, 1.92 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 140.4 (Ar), 139.7 (Ar), 139.3 (Ar), 139.2 (Ar), 138.9 (Ar), 138.7 (Ar), 138.5 (Ar), 138.1 (Ar), 137.8 (Ar), 134.3 (<u>C</u>H=CH$_2$), 134.1 (<u>C</u>H=CH$_2$), 128.5 (Ar), 128.3 (Ar), 128.1 (Ar), 127.8 (Ar), 127.5 (Ar), 127.3 (Ar), 127.1 (Ar), 126.8 (Ar), 126.6(5) (Ar), 126.5(5) (Ar), 126.3 (Ar), 126.2 (Ar), 118.4 (CH=<u>C</u>H$_2$), 117.3 (CH=<u>C</u>H$_2$), 103.3 (C-1β), 96.1 (C-1α), 88.8 (C-9), 88.7 (C-9), 87.7 (C-3β), 84.3 (C-8), 84.2 (C-8), 84.0 (C-3α), 82.0 (C-7), 81.9 (C-2β), 81.3 (C-7), 78.8 (C-4), 77.9 (C-2α), 77.7 (<u>C</u>H$_2$Ar), 76.1(3) (<u>C</u>H$_2$Ar), 76.0(6) (<u>C</u>H$_2$Ar), 75.6 (<u>C</u>H$_2$Ar), 75.4 (<u>C</u>H$_2$Ar), 73.6 (<u>C</u>H$_2$Ar), 72.9 (C-5β), 71.6 (<u>C</u>H$_2$Ar), 71.5 (<u>C</u>H$_2$CH=CH$_2$), 70.3 (<u>C</u>H$_2$CH=CH$_2$), 69.3 (<u>C</u>H$_2$Ar), 69.2 (<u>C</u>H$_2$Ar), 68.5(3) (<u>C</u>H$_2$Ar), 68.5(1) (C-5α), 66.3(4) (<u>C</u>H$_2$Ar), 66.2(9) (<u>C</u>H$_2$Ar), 29.1 (C-6β), 28.8 (C-6α), 11.7(4) (C-10), 11.6(8) (C-10). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{55}H_{62}NO_8$: 864.4470. Found 864.4471.

(40α): R_f 0.45 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δH) 7.39−7.22 (m, 25 H, Ar), 5.93 (dddd, 1 H, J = 16.7 Hz, J = 10.5 Hz, J = 6.2 Hz, J = 5.3 Hz, C<u>H</u>=CH$_2$), 5.56 (d, 1 H, J = 12.3 Hz, C<u>H</u>$_2$Ar), 5.34 (app dq, 1 H, J = 6.2 Hz, J = 5.3 Hz, CH=C<u>H</u>$_2$ *trans*), 5.25–5.19 (m, 2 H, CH=C<u>H</u>$_2$ *cis*, C<u>H</u>$_2$Ar), 5.01 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.84–4.79 (m, 3 H, 2 x C<u>H</u>$_2$Ar, H-1), 4.76–4.67 (m, 3 H, 3 x C<u>H</u>$_2$Ar), 4.60 (d, 1 H, J = 12.1 Hz, C<u>H</u>$_2$Ar), 4.56 (d, 1 H, J = 11.6 Hz, C<u>H</u>$_2$Ar), 4.34 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3), 4.14 (app ddt, 1 H, J = 13.2 Hz, J = 5.3 Hz, J = 1.5 Hz, C<u>H</u>$_2$CH=CH$_2$), 3.99 (app ddt, 1 H, J = 13.0 Hz, J = 6.4 Hz, J = 1.1 Hz, C<u>H</u>$_2$CH=CH$_2$), 3.87 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 3.76 (s, 1 H, OH), 3.71 (s, 1 H, H-9), 3.68–3.61 (m, 2 H, H-5, H-7), 2.05 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6$_{ax}$), 1.95 (ddd, 1 H, $J_{6eq,6ax}$ = 12.1 Hz, $J_{5,6eq}$ = 4.0 Hz, $J_{6eq,7}$ = 4.0 Hz, H-6$_{eq}$), 1.65 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 140.0 (Ar), 139.7 (Ar), 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 134.0 (<u>C</u>H=CH$_2$), 128.5 (Ar), 128.4(0) (Ar), 128.3(8) (Ar), 128.3 (Ar), 128.1(9) (Ar), 128.1(5) (Ar), 127.8 (Ar), 127.7(2) (Ar), 127.7(0) (Ar), 127.5(8) (Ar), 127.5(6) (Ar), 127.5 (Ar), 127.2 (Ar), 127.0 (Ar), 126.8 (Ar), 117.8 (CH=<u>C</u>H$_2$), 96.3 (C-1), 89.7 (C-9), 83.5 (C-8), 82.0 (C-5), 76.9 (C-4), 76.2 (C-2/C-3), 76.1 (C-2/C-3), 76.0 (<u>C</u>H$_2$Ar), 73.2 (<u>C</u>H$_2$Ar), 71.7 (<u>C</u>H$_2$Ar), 68.9 (<u>C</u>H$_2$Ar), 68.7 (<u>C</u>H$_2$CH=CH$_2$), 67.4 (C-7), 66.2 (<u>C</u>H$_2$Ar), 29.4 (C-6), 11.5 (C-10). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{48}H_{52}NaO_8$: 779.3554. Found 779.3563.

(40β): R_f 0.52 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δH) 7.41−7.22 (m, 25 H, Ar), 5.97 (app ddt, 1 H, J = 16.9 Hz, J = 10.8 Hz, J = 5.7 Hz, <u>C</u>H=CH$_2$), 5.41–5.32 (m, 2 H, CH=C<u>H</u>$_2$ *trans*, C<u>H</u>$_2$Ar), 5.22 (d, 1 H, J = 10.3 Hz, CH=C<u>H</u>$_2$ *cis*), 5.15 (d, 1 H, J = 11.6 Hz, C<u>H</u>$_2$Ar), 5.04 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.90 (d, 1 H, J = 11.2 Hz, C<u>H</u>$_2$Ar), 4.81–4.68 (m, 5 H, 5 x C<u>H</u>$_2$Ar), 4.53 (d, 1 H, J = 11.6 Hz, C<u>H</u>$_2$Ar), 4.47 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1), 4.44 (app dd, 1 H, J = 13.0 Hz, J = 5.5 Hz, C<u>H</u>$_2$CH=CH$_2$), 4.15 (app dd, 1 H, J = 12.7 Hz, J = 6.1 Hz, C<u>H</u>$_2$CH=CH$_2$), 3.93 (d, 1 H, $J_{2,3}$ = 9.4 Hz, H-3), 3.89 (s, 1 H, OH), 3.74 (app t, 1 H, J = 8.8 Hz, H-2), 3.64 (dd, 1

H, $J_{6ax,7}$ = 11.0 Hz, $J_{6eq,7}$ = 5.7 Hz, H-7), 3.58 (s, 1 H, H-9), 3.22 (dd, 1 H, $J_{5,6ax}$= 13.0 Hz, $J_{5,6eq}$ = 5.5 Hz, H-5), 2.20–2.09 (m, 2 H, 2 x H-6), 1.63 (s, 3 H, H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 139.7 (Ar), 139.6 (Ar), 138.2(1) (Ar), 138.5 (Ar), 138.3 (Ar), 138.2 (Ar), 134.1 (CH=CH_2), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1(2) (Ar), 128.1(1) (Ar), 127.7 (Ar), 127.6(2) (Ar), 127.5(9) (Ar), 127.5 (Ar), 127.2 (Ar), 126.9 (Ar), 126.8 (Ar), 117.3 (CH=CH_2), 103.4 (C-1), 89.4 (C-9), 83.7 (C-8), 82.2 (C-7), 80.0 (C-2), 79.8 (C-3), 76.4 (C-4), 75.8 (CH_2Ar), 75.0 (CH_2Ar), 72.3 (C-5), 71.5 (CH_2Ar), 70.4 (CH_2CH=CH_2), 68.9 (CH_2Ar), 66.2 (CH_2Ar), 29.0 (C-6), 11.6 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{48}H_{52}NaO_8$: 779.3554. Found 779.3560.

Allyl 2,3,4,7,8,9-hexa-*O*-benzyl-1,5-α-D-bradyrhizopyranoside (D-39α), **allyl 2,3,4,7,8,9-hexa-*O*-benzyl-1,5-β-D-bradyrhizopyranoside (D-39β)**, **allyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranoside (D-40α)** and **allyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-D-bradyrhizopyranoside (D-40β)**. Sodium hydride (16 mg, 0.390 mmol, 60% wt in mineral oil) was added to a solution of **D-38** (87 mg, 0.130 mmol) in THF (2 mL). After 30 min, benzyl bromide (77 μL, 0.652 mmol) was added and the reaction mixture was stirred at rt overnight. Water was added and the aqueous solution was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 → 9:1 hexanes–EtOAc) to give **D-39α** and **D-39β** (34 mg, 31%, inseparable diastereomeric mixture 1:3) and **D-40α** and **D-40β** (66 mg, 67%, separable diastereomeric mixture 65:35) as a yellow oils. **D-40α** and **D-40β** were separated for characterization. The R_f, ^1H NMR, $^{13}C\{^{1}H\}$ NMR and MS data correspond to that obtained from the racemic compounds **39α**, **39β**, **40α** and **40β** previously described. (**D-40α**): $[\alpha]_D$ +13.8 (*c* 0.1, $CHCl_3$). (**D-40β**): $[\alpha]_D$ –3.8 (*c* 0.1, $CHCl_3$).

Allyl 2,3,4,7,8,9-hexa-*O*-benzyl-1,5-α-L-bradyrhizopyranoside (L-39α), **allyl 2,3,4,7,8,9-hexa-*O*-benzyl-1,5-β-L-bradyrhizopyranoside (L-39β)**, **allyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranoside (L-40α)** and **allyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-L-bradyrhizopyranoside (L-40β)**. Sodium hydride (14 mg, 0.0.353 mmol, 60% wt in mineral oil) was added to a solution of **L-38** (78 mg, 0.118 mmol) in THF (2 mL). After 30 min, benzyl bromide (70 μL, 0.590 mmol) was added and the reaction mixture was stirred at rt overnight. Water was added and the aqueous solution was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 → 9:1 hexanes–EtOAc) to give **L-39α** and **L-39β** (31 mg, 31%, inseparable diastereomeric mixture 1:3) and **L-40α** and **L-40β** (60 mg, 67%, separable diastereomeric mixture 65:35) as yellow oils. **L-40α** and **L-40β** were separated for characterization.The R_f, ^{1}H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **39α**, **39β**, **40α** and **40β** previously described. (**L-40α**): $[\alpha]_D$ –11.6 (*c* 0.1, $CHCl_3$). (**L-40β**): $[\alpha]_D$ +2.0 (*c* 0.1, $CHCl_3$).

***Racemic* 2,3,4,7,8,9-hexa-*O*-benzyl-1,5- α -bradyrhizopyranose (41α)** and ***racemic* 2,3,4,7,8,9-hexa-*O*-benzyl-1,5- β -bradyrhizopyranose (41β)**. Palladium(II) chloride (1 mg, 0.00543 mmol) was added to a solution of **39** (46 mg, 0.0543 mmol) in CH_2Cl_2 (0.6 mL) and MeOH (0.6 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through Celite® 545 and the Celite was rinsed with EtOAc. The filtrate was then concentrated and the crude product was purified by silica gel column chromatography (17:3 hexanes–EtOAc) to give **41α** and **41β** (41 mg, 96%, inseparable diastereomeric mixture 7:3) as a colourless oil. R_f 0.55 and 0.42 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.43–7.04 (m, 30 H, Ar), 5.70 (d, 0.3 H, J = 12.5 Hz, C$\underline{H}_2$Ar), 5.68 (d, 0.7 H, J = 12.8 Hz, C$\underline{H}_2$Ar), 5.49 (d, 0.3 H, J = 12.5 Hz, C$\underline{H}_2$Ar), 5.46 (d, 0.7 H,

J = 12.8 Hz, C$\underline{H}_2$Ar), 5.20–5.11 (m, 1.7 H, C$\underline{H}_2$Ar), 5.09–5.02 (m, 1 H, C$\underline{H}_2$Ar), 4.84–4.45 (m, 8.3 H, C$\underline{H}_2$Ar, H-1α, H-1β), 4.08 (d, 0.7 H, *J* = 9.9 Hz, H-3α), 4.01 (dd, 0.7 H, *J* = 9.9 Hz, *J* = 3.5 Hz, H-2α), 3.90 (dd, 0.7 H, *J* = 11.4 Hz, *J* = 4.8 Hz, H-5α), 3.75–3.63 (m, 2.6 H, H-2β, H-3β, H-9, H-7), 3.30 (dd, 0.3 H, *J* = 11.0 Hz, *J* = 5.1 Hz, H-5β), 3.00–2.91 (m, 1 H, OH), 2.17–2.10 (m, 2 H, H-6), 1.71 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 140.4 (Ar), 139.7 (Ar), 139.6 (Ar), 139.3 (Ar), 139.2 (Ar), 138.7 (Ar), 138.5 (Ar), 137.9 (Ar), 137.3 (Ar), 128.5 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.5 (Ar), 127.3 (Ar), 127.1 (Ar), 126.9 (Ar), 126.8 (Ar), 126.6 (Ar), 126.4 (Ar), 126.3 (Ar), 98.0 (C-1β), 91.6 (C-1α), 88.6 (C-9β), 88.5 (C-9α), 87.7 (C-3β), 84.2(2) (C-8β), 84.1(9) (C-8α), 83.9 (C-3α), 82.4 (C-7/ C-2β), 81.7(3) (C-7/C-2β), 81.6(9) (C-7/C-2β), 78.8 (C-4), 78.4 (C-2α), 77.7 (C-4), 76.2 (C$\underline{H}_2$Ar), 76.1 (C$\underline{H}_2$Ar), 75.6(3) (C$\underline{H}_2$Ar), 75.5(8) (C$\underline{H}_2$Ar), 75.2 (C$\underline{H}_2$Ar), 73.7 (C$\underline{H}_2$Ar), 73.1 (C-5β), 71.5 (C$\underline{H}_2$Ar), 71.4 (C$\underline{H}_2$Ar), 69.2(1) (C$\underline{H}_2$Ar), 69.1(6) (C$\underline{H}_2$Ar), 69.0 (C-5α), 66.3 (C$\underline{H}_2$Ar), 66.2 (C$\underline{H}_2$Ar), 29.1 (C-6β), 28.9 (C-6α), 11.7 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{52}H_{54}NaO_8$: 829.3711. Found 829.3712.

2,3,4,7,8,9-Hexa-*O*-benzyl-1,5-α-D-bradyrhizopyranose (D-41α) and **2,3,4,7,8,9-hexa-*O*-benzyl-1,5-β-D-bradyrhizopyranose (D-41β)**. Palladium(II) chloride (0.7 mg, 0.00398 mmol) was added to a solution of **D-39** (34 mg, 0.0398 mmol) in CH_2Cl_2 (0.4 mL) and MeOH (0.4 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through Celite® 545 and the Celite was rinsed with EtOAc. The filtrate was then concentrated and the crude product was purified by silica gel column chromatography (17:3 hexanes–EtOAc) to give **D-41α** and **D-41β** (31 mg, 96%, inseparable diastereomeric mixture 7:3) as a colourless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **41α** and **41β** previously described.

2,3,4,7,8,9-Hexa-*O*-benzyl-1,5-α-L-bradyrhizopyranose (L-41α) and **2,3,4,7,8,9-hexa-*O*-benzyl-1,5-β-L-bradyrhizopyranose (L-41β)**. Palladium(II) chloride (0.5 mg, 0.00297 mmol) was added to a solution of **L-39** (25 mg, 0.0297 mmol) in CH_2Cl_2 (0.3 mL) and MeOH (0.3 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through Celite® 545 and the Celite was rinsed with EtOAc. The filtrate was then concentrated and the crude product was purified by silica gel column chromatography (17:3 hexanes–EtOAc) to give **L-41α** and **L-41β** (23 mg, 96%, inseparable diastereomeric mixture 65:35) as a colourless oil. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic **41α** and **41β** previously described.

***Racemic* 2,4,7,8,9-penta-*O*-benzyl-1,5-α-bradyrhizopyranose (42α)** and ***racemic* 2,4,7,8,9-penta-*O*-benzyl-1,5-β-bradyrhizopyranose (42β)**. Palladium(II) chloride (2.2 mg, 0.0126 mmol) was added to a solution of **40** (95 mg, 0.126 mmol) in CH_2Cl_2 (1.2 mL) and MeOH (1.2 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through Celite® 545 and the Celite was rinsed with EtOAc. The filtrate was then concentrated and the crude product was purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **42α** and **42β** (87 mg, 97%, inseparable diastereomeric mixture 60:40) as a colourless oil. R_f 0.48 and 0.30 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.43–7.26 (m, 25 H, Ar), 5.53 (d, 0.6 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 5.47 (d, 0.4 H, J = 11.7 Hz, C$\underline{H}_2$Ar), 5.28–5.19 (m, 1.6 H, C$\underline{H}_2$Ar, H-1α), 5.16 (d, 0.6 H, J = 10.8 Hz, C$\underline{H}_2$Ar), 5.10 (d, 0.4 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.91 (d, 0.4 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.88–4.67 (m, 6 H, C$\underline{H}_2$Ar, H-2α, H-1β), 4.55 (d, 0.4 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.52 (d, 0.6H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.32 (d, 0.6, J = 9.7 Hz, H-3α), 4.13 (s, 0.6 H, OHα), 4.03 (s, 0.4 H, OHβ), 3.98 (d, 0.4 H, J = 9.4 Hz, H-3β), 3.92–3.86 (m, 1.2 H, H-2α, H-5α), 3.78 (s, 0.6 H, H-9α), 3.72–3.62 (m, 1.8 H, H-2β, H-9β, H-7), 3.31–3.24 (m, 0.8 H, H-5β, C-1OHβ), 3.17 (br, 0.6 H, OH), 2.20–2.04 (m, 2 H, H-6), 1.70 (s, 1.8 H, H-10), 1.68 (s, 1.2 H, H-10); ^{13}C{^{1}H} NMR (125

MHz, $CDCl_3$, δ_C) 139.7 (Ar), 139.6 (Ar), 138.3(3) (Ar), 138.2(5) (Ar), 138.2 (Ar), 138.1 (Ar), 137.7 (Ar), 128.6(3) (Ar), 128.5(8) (Ar), 128.4 (Ar), 128.3(4) (Ar), 128.2(8) (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6(2) (Ar), 127.5(8) (Ar), 127.2 (Ar), 127.1 (Ar), 127.0 (Ar), 97.9 (C-1β), 91.7 (C-1α), 89.6 (C-9α), 89.4 (C-9β), 83.7 (C-8β), 83.5 (C-8α), 82.0(0) (C-2β/C-7), 81.9(7) (C-2β/C-7), 81.1 (C-2β/C-7), 80.1 (C-3β), 76.8 (C-4), 76.7 (C-2α/C-3α), 76.6 (C-2α/C-3α), 76.3 (C-4), 76.1 ($\underline{C}H_2Ar$), 75.9 ($\underline{C}H_2Ar$), 74.9 ($\underline{C}H_2Ar$), 73.7 ($\underline{C}H_2Ar$), 72.6 (C-5β), 71.5 ($\underline{C}H_2Ar$), 71.4 ($\underline{C}H_2Ar$), 69.0(2) ($\underline{C}H_2Ar$), 68.9(5) ($\underline{C}H_2Ar$), 67.5 (C-5α), 66.2 ($\underline{C}H_2Ar$), 66.1 ($\underline{C}H_2Ar$), 29.1 (C-6), 28.7 (C-6), 11.6 (C-10). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{45}H_{48}NaO_8$: 739.3241. Found 739.3239.

2,4,7,8,9-Penta-*O*-benzyl-1,5-α-D-bradyrhizopyranose (D-42α) and **2,4,7,8,9-penta-*O*-benzyl-1,5-β-D-bradyrhizopyranose (D-42β)**. Palladium(II) chloride (1.5 mg, 0.00871 mmol) was added to a solution of **D-40** (66 mg, 0.0871 mmol) in CH_2Cl_2 (0.9 mL) and MeOH (0.9 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through Celite® 545 and the Celite was rinsed with EtOAc. The filtrate was then concentrated and the crude product was purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **D-42α** and **D-42β** (61 mg, 97%, inseparable diastereomeric mixture 6:4) as a colourless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **42α** and **42β** previously described.

2,4,7,8,9-Penta-*O*-benzyl-1,5-α-L-bradyrhizopyranose (L-42α) and **2,4,7,8,9-penta-*O*-benzyl-1,5-β-L-bradyrhizopyranose (L-42β)**. Palladium(II) chloride (1.3 mg, 0.00727 mmol) was added to a solution of **L-40** (55 mg, 0.727 mmol) in CH_2Cl_2 (1 mL) and MeOH (1 mL). The reaction mixture was stirred at rt overnight. The solution was filtered through Celite® 545 and the Celite

was rinsed with EtOAc. The filtrate was then and the crude product was purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **L-42α** and **L-42β** (47 mg, 91%, inseparable diastereomeric mixture 6:4) as a colourless oil. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compounds **42α** and **42β** previously described.

***Racemic* methyl 4,7,8,9-tetra-*O*-benzyl-1,5- α -bradyrhizopyranoside (44α)** and ***racemic* methyl 4,7,8,9-tetra-*O*-benzyl-1,5- β -bradyrhizopyranoside (44β)**. To a stirred solution of **30** (76 mg, 0.121 mmol) in MeOH (5 mL), HCl (45 μL of a solution of AcCl (0.5 mL) in MeOH (3 mL)) was added and the mixture was stirred at 60 °C for 2 days. After cooling to rt, the solvent was evaporated and the resulting crude product was purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **44α** and **44β** (56 mg, 73%, inseparable diastereomeric mixture 6:4) as a colorless oil. The starting material **30** can be recovered by silica gel column chromatography (97:3 CH_2Cl_2–MeOH) and the reaction can be done again to yield more product **44α** and **44β**. R_f 0.54 (1:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.24 (m, 20 H, Ar), 5.55 (d, 0.6 H, J = 12.1 Hz, C$\underline{H}_2$Ar), 5.43 (d, 0.4 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 5.22 (d, 0.6 H, J = 12.1 Hz, C$\underline{H}_2$Ar), 5.18–5.11 (m, 1.4 H, C$\underline{H}_2$Ar), 4.89–4.83 (m, 1.6 H, C$\underline{H}_2$Ar, H-1α), 4.80–4.67 (m, 3 H, C$\underline{H}_2$Ar), 4.58–4.52 (m, 1 H, C$\underline{H}_2$Ar), 4.29–4.25 (m, 0.8 H, OH, H-1β), 4.15 (s, 0.6 H, OH), 4.11–4.02 (m, 1.2 H, H-3α, H-2α), 3.92–3.86 (m, 0.8 H, H-2β, H-3β), 3.77 (s, 0.6 H, H-9α), 3.74–3.66 (m, 1.4 H, H-9β, H-7), 3.65–3.60 (m, 1.8 H, OCH_3β, H-5α), 3.48 (s, 1.8 H, OCH_3α), 3.28 (dd, 0.4 H, J = 11.7 Hz, J = 4.0 Hz, H-5β), 2.60 (br, 0.4 H, OHβ), 2.27–2.04 (m, 2.6 H, H-6, OH), 1.68 (s, 1.8 H, H-10), 1.67 (s, 1.2 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 139.6 (Ar), 139.5 (Ar), 139.4 (Ar), 138.2(2) (Ar), 138.1(6) (Ar), 137.9 (Ar), 137.7 (Ar), 128.7 (Ar), 128.4(3) (Ar), 128.3(8) (Ar), 128.3 (Ar), 128.2 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.7 (Ar), 127.5 (Ar), 127.3 (Ar), 127.1 (Ar), 127.0 (Ar), 126.9 (Ar), 126.8 (Ar), 104.7 (C-1β), 99.6 (C-1α), 89.6(1) (C-9α), 89.5(8)

(C-9β), 83.7 (C-8β), 83.5 (C-8α), 82.3 (C-7), 82.2 (C-7), 80.0 (C-2/C-3β), 77.5 (C-2/C-3α), 76.5 (C-4), 76.3 (C-4), 76.2 ($\underline{C}H_2Ar$), 76.0 ($\underline{C}H_2Ar$), 72.5 (C-5β), 72.0 (C-2/C-3β), 71.5 ($\underline{C}H_2Ar$), 71.4 ($\underline{C}H_2Ar$), 69.6 (C-2/C-3α), 69.0 ($\underline{C}H_2Ar$), 68.9 ($\underline{C}H_2Ar$), 67.5 (C-5α), 66.2 ($\underline{C}H_2Ar$), 66.1 ($\underline{C}H_2Ar$), 57.3 (OCH_3β), 55.7 (OCH_3α), 28.9 (C-6), 28.8 (C-6), 11.6 (C-10), 11.5 (C-10). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{39}H_{48}NO_8$: 658.3374. Found 658.3365.

Methyl 4,7,8,9-tetra-*O*-benzyl-1,5- α -D-bradyrhizopyranoside (D-44α) and **methyl 4,7,8,9-tetra-*O*-benzyl-1,5- β -D-bradyrhizopyranoside (D-44β)**. To a stirred solution of **D-30** (76 mg, 0.121 mmol) in MeOH (5 mL), HCl (45 μL of a solution f AcCl (0.5 mL) in MeOH (3 mL)) was added and the mixture was stirred at 60 °C for 2 days. After cooling to rt, the solvent was evaporated and the resulting crude product was purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **D-44α** and **D-44β** (56 mg, 73%, inseparable diastereomeric mixture 53:47) as a colorless oil. The starting material **D-30** can be recovered by silica gel column chromatography (97:3 CH_2Cl_2–MeOH) and the reaction can be done again to yield more product **D-44α** and **D-44β**. The R_f, ^{1}H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **44α** and **44β** previously described.

Methyl 4,7,8,9-tetra-*O*-benzyl-1,5- α -L-bradyrhizopyranoside (L-44α) and **methyl 4,7,8,9-tetra-*O*-benzyl-1,5- β -L-bradyrhizopyranoside (L-44β)**. To a stirred solution of **L-30** (76 mg, 0.121 mmol) in MeOH (5 mL), HCl (45 μL of a solution of AcCl (0.5 mL) in MeOH (3 mL)) was added and the mixture was stirred at 60 °C for 2 days. After cooling to rt, the solvent was evaporated and the resulting crude product was purified by silica gel column chromatography (7:3 hexanes–EtOAc) to give **L-44α** and **L-44β** (56 mg, 73%, inseparable diastereomeric mixture 57:43) as a colorless oil. The starting material **L-30** can be recovered by silica gel column chromatography

(97:3 CH_2Cl_2–MeOH) and the reaction can be done again to yield more product **L-44α** and **L-44β**. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **44α** and **44β** previously described.

***Racemic* methyl 2-*O*-benzoyl-4,7,8,9-tetra-*O*-benzyl-1,5-α-bradyrhizopyranoside (45α)** and ***racemic* methyl 2-*O*-benzoyl-4,7,8,9-tetra-*O*-benzyl-1,5-β-bradyrhizopyranoside (45β)**. To a stirred solution of **44** (37 mg, 0.0577 mmol) in CH_2Cl_2 (0.5 mL) and pyridine (0.5 mL), benzoyl chloride (20 µL, 0.173 mmol) was added at 0 °C. The mixture was stirred at rt for 2 h. A saturated aqueous solution of $CuSO_4$ was added and the aqueous layer was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **45α** and **45β** as separable compounds (total: 41 mg, 96%, diastereomeric mixture 3:2) as colourless oils. (**45α**): R_f 0.33 (4:1 hexanes–EtOAc); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.15–8.11 (m, 2 H, Ar), 7.61–7.56 (m, 1 H, Ar), 7.50–7.43 (m, 4 H, Ar), 7.40–7.26 (m, 18 H, Ar), 5.60 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 5.53 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, $J_{1,2}$ = 4.0 Hz, H-2), 5.28 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 5.22 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 5.12 (d, 1 H, J = 4.0 Hz, H-1), 4.88 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.77 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.75 (d, 1 H, J = 11.4 Hz, C$\underline{H}_2$Ar), 4.72 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.57 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.52 (d, 1 H, J = 10.3 Hz, H-3), 4.23 (s, 1 H, OH), 3.85 (s, 1 H, H-9), 3.78–3.72 (m, 2 H, H-5, H-7), 3.44 (s, 3 H, OCH_3), 2.23–2.09 (m, 2 H, 2 x H-6), 1.71 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.4 (C=O), 139.5 (Ar), 139.4 (Ar), 138.2 (Ar), 137.7 (Ar), 133.1 (Ar), 130.0 (Ar), 128.7 (Ar), 128.4(5) (Ar), 128.3(6) (Ar), 128.3(4) (Ar), 128.2(6) (Ar), 128.0 (Ar), 127.7(2) (Ar), 127.6(8) (Ar), 127.6 (Ar), 127.3 (Ar), 127.2 (Ar), 127.1 (Ar), 97.8 (C-1), 89.6 (C-9), 83.6 (C-8), 82.4 (C-5/C-7), 77.0 (C-4), 76.1 (C$\underline{H}_2$Ar), 74.8 (C-3), 71.7 (C-2),

71.5 (CH$_2$Ar), 69.3 (CH$_2$Ar), 67.1 (C-5/C-7), 66.1 (CH$_2$Ar), 55.8 (OCH$_3$), 28.7 (C-6), 11.6 (C-10). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{46}H_{48}NaO_9$: 767.3191. Found 767.3190.

(**45β**): R_f 0.25 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.13–8.18 (m, 2 H, Ar), 7.61–7.56 (m, 1 H, Ar), 7.49–7.44 (m, 4 H, Ar), 7.39–7.26 (m, 18 H, Ar), 5.63 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 7.9 Hz, H-2), 5.52 (d, 1 H, J = 11.0 Hz, CH$_2$Ar), 5.24 (d, 1 H, J = 11.2 Hz, CH$_2$Ar), 5.18 (d, 1 H, J = 11.2 Hz, CH$_2$Ar), 4.85 (d, 1 H, J = 11.2 Hz, CH$_2$Ar), 4.75 (d, 1 H, J = 11.0 Hz, CH$_2$Ar), 4.74 (d, 1 H, J = 11.4 Hz, CH$_2$Ar), 4.67 (d, 1 H, J = 11.2 Hz, CH$_2$Ar), 4.56 (d, 1 H, J = 7.9 Hz, H-1), 4.54 (d, 1 H, J = 11.2 Hz, CH$_2$Ar), 4.25 (s, 1 H, OH), 4.12 (d, 1 H, J = 4.0 Hz, H-3), 3.73–3.68 (m, 2 H, H-7, H-9), 3.36 (s, 3 H, OCH$_3$), 3.36 (dd, 1 H, J = 11.5 Hz, J = 4.0 Hz, H-5), 2.28–2.15 (m, 2 H, 2 x H-6), 1.69 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 165.8 (C=O), 139.5 (Ar), 139.1 (Ar), 138.1 (Ar), 137.5 (Ar), 133.0 (Ar), 130.1 (Ar), 129.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6(4) (Ar), 127.6(0) (Ar), 127.5(7) (Ar), 127.3 (Ar), 127.1 (Ar), 102.5 (C-1), 89.1 (C-9), 83.8 (C-8), 82.3 (C-7), 78.5 (C-3), 76.3 (C-4), 75.8 (CH$_2$Ar), 72.6 (C-5), 72.4 (C-2), 71.4 (CH$_2$Ar), 69.4 (CH$_2$Ar), 66.2 (CH$_2$Ar), 56.5 (OCH$_3$), 28.8 (C-6), 11.6 (C-10). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{46}H_{48}NaO_9$: 767.3191. Found 767.3188.

Methyl 2-*O*-benzoyl-4,7,8,9-tetra-*O*-benzyl-1,5- α -D-bradyrhizopyranoside (D-45α) and **methyl 2-*O*-benzoyl-4,7,8,9-tetra-*O*-benzyl-1,5- β -D-bradyrhizopyranoside (D-45β)**. To a stirred solution of **D-44** (77 mg, 0.120 mmol) in CH_2Cl_2 (1.5 mL) and pyridine (1.5 mL), benzoyl chloride (70 µL, 0.600 mmol) was added at 0 °C. The mixture was stirred at rt for 2 h. A saturated aqueous solution of $CuSO_4$ was added and the aqueous layer was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (3 x) (19:1 hexanes–EtOAc) to give **D-45α** and **D-**

45β (86 mg, 96%, diastereomeric mixture 3:1) as colourless oils. The R_f, ^{1}H NMR, ^{13}C{^{1}H}NMR and MS data correspond to that obtained from the racemic compounds **45α** and **45β** previously described. (**D-45α**): $[\alpha]_D$ +65.2 (*c* 0.1, $CHCl_3$). (**D-45β**): $[\alpha]_D$ +18.0 (*c* 0.1, $CHCl_3$).

Methyl 2-*O*-benzoyl-4,7,8,9-tetra-*O*-benzyl-1,5- α -L-bradyrhizopyranoside (L-45α) and **methyl 2-*O*-benzoyl-4,7,8,9-tetra-*O*-benzyl-1,5- β -L-bradyrhizopyranoside (L-45β)**. To a stirred solution of **L-44** (67 mg, 0.104 mmol) in CH_2Cl_2 (1.3 mL) and pyridine (1.3 mL), benzoyl chloride (61 μL, 0.522 mmol) was added at 0 °C. The mixture was stirred at rt for 2 h. A saturated aqueous solution of $CuSO_4$ was added and the aqueous layer was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **L-45α** and **L-45β** (74 mg, 96%, diastereomeric mixture 57:43) as colourless oils diastereomeric mixture 57:43. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compounds **45α** and **45β** previously described. (**L-45α**): $[\alpha]_D$ –69.6 (*c* 0.1, $CHCl_3$). (**L-45β**): $[\alpha]_D$ –11.8 (*c* 0.2, $CHCl_3$).

***Racemic* methyl 2-*O*-benzoyl-1,5-α-bradyrhizopyranoside (46α)** and ***racemic* methyl 2-*O*-benzoyl-1,5-β-bradyrhizopyranoside (46β)**. Palladium on carbon (90 mg, 0.0876 mmol, 10 wt. % loading) was added to a solution of **45** (130 mg, 0.175 mmol) in MeOH (10 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium on carbon was filtered and the solvent concentrated. The resulting crude product was purified by column chromatography (19:1 → 9:1 CH_2Cl_2–MeOH) to give **46α** and **46β** (54 mg, 80%, inseparable diastereomeric mixture 7:3) as a colorless oil. R_f 0.38 (9:1 CH_2Cl_2–MeOH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 8.06–7.99 (m, 2 H, Ar), 7.61–7.56 (m, 1 H, Ar), 7.48–7.43 (m, 2 H,

Ar), 5.23 (dd, 0.3 H, $J_{2,3}$ = 9.2 Hz, $J_{1,2}$ = 8.3 Hz, H-2β), 5.18 (dd, 0.7 H, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 3.9 Hz, H-2α), 4.98 (d, 0.7 H, J = 4.0 Hz, H-1α), 4.51 (d, 0.3 H, J = 8.1 Hz, H-1β), 4.19 (d, 0.7 H, J = 9.9 Hz, H-3α), 3.96 (d, 0.3 H, J = 9.4 Hz, H-3β), 3.75 (dd, 0.7 H, $J_{5,6ax}$ = 12.5 Hz, $J_{5,6eq}$ = 4.0 Hz, H-5α), 3.58–3.51 (m, 2 H, H-5β, H-7α, H-9), 3.49 (dd, 0.3 H, $J_{6ax,7}$ = 12.1 Hz, $J_{6eq,7}$ = 4.2 Hz, H-7β), 3.43 (s, 0.9 H, OCH_3β), 3.33 (s, 2.1 H, OCH_3α), 2.04–1.86 (m, 1.3 H, H-6), 1.79 (ddd, 0.7 H, $J_{6ax,6eq}$ = 11.9 Hz, $J_{5,6eq}$ = 4.0 Hz, $J_{6eq,7}$ = 4.0 Hz, H-6_{eq}), 1.29 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, δ_C) 167.9 (C=Oα), 167.5 (C=Oβ), 134.4 (Ar), 134.3 (Ar), 131.6 (Ar), 131.3 (Ar), 130.8 (Ar), 130.7 (Ar), 129.5 (Ar), 103.7 (C-1β), 98.8 (C-1α), 80.7 (C-9α), 80.5 (C-9β), 78.5(5) (C-8), 78.5(2) (C-8), 78.3 (C-3β), 74.9 (C-3α), 74.6(1) (C-4), 74.5(6) (C-2β), 74.1(5) (C-2α), 74.1(2) (C-4), 74.0 (C-5β/C-7), 73.9 (C-5β/C-7), 72.4 (C-5β/C-7), 67.2 (C-5α), 57.1 (OCH_3β), 55.8 (OCH_3α), 32.8 (C-6β), 32.7 (C-6α), 15.5(0) (C-10α), 15.4(5) (C-10β). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{18}H_{24}NaO_9$: 407.1313. Found 407.1316.

Methyl 2-*O*-benzoyl-1,5-α-D-bradyrhizopyranoside (D-46α) and **methyl 2-*O*-benzoyl-1,5-β-D-bradyrhizopyranoside (D-46β)**. Palladium on carbon (36.5 mg, 0.344 mmol, 10 wt. % loading) was added to a solution of **D-45** (51 mg, 0.0687 mmol) in MeOH (10 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred for 3 days. The palladium on carbon was filtered and the filtrate was concentrated. The resulting crude product was purified by column chromatography (19:1 → 9:1 CH_2Cl_2–MeOH) to give **D-46α** and **D-46β** (21 mg, 80%, inseparable diastereomeric mixture 22:3) as a colorless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained from the racemic compounds **46α** and **46β** previously described.

Methyl 2-*O*-benzoyl-1,5-α-L-bradyrhizopyranoside (L-46α) and **methyl 2-*O*-benzoyl-1,5-β-L-bradyrhizopyranoside (L-46β)**. Palladium on carbon (36.5 mg, 0.344 mmol, 10 wt. % loading) was added to a solution of **L-45** (51 mg, 0.0687 mmol) in MeOH (10 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred for 3 days. The palladium on carbon was filtered and the filtrate was concentrated. The resulting crude product was purified by column chromatography (19:1 → 9:1 CH_2Cl_2–MeOH) to give **L-46** and **L-46β** (21 mg, 80%, inseparable diastereomeric mixture 7:3) as a colorless oil. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained from the racemic compounds **46α** and **46β** previously described.

***Racemic* methyl α-7-*O*-acetyl-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-bradyrhizopyranoside (47α)** and ***racemic* methyl α-2-7,8-di-*O*-acetyl-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-bradyrhizopyranoside (48α)**. To a stirred solution of **37α** (5 mg, 0.0.0106 mmol) in pyridine (0.5 mL), acetic anhydride (10 µL, 0.105 mmol) and DMAP (1 mg) were added at rt and the mixture was stirred overnight. A saturated aqueous solution of $CuSO_4$ was added and the aqueous layer was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by silica gel column chromatography (19:1 hexanes–EtOAc) to give **47α** (3.5 mg, 63%) and **48α** (2 mg, 33%) as colourless oils. (**47α**): R_f 0.12 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.06 (m, 2 H, Ar), 7.61–7.57 (m, 1 H, Ar), 7.55–7.50 (m, 2 H, Ar), 7.49–7.44 (m, 2 H, Ar), 7.42–7.36 (m, 3 H, Ar), 5.84 (s, 1 H, CHAr), 5.54 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 5.19 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.94 (dd, 1 H, $J_{6ax,7}$ = 11.9 Hz, $J_{6eq,7}$ = 4.8 Hz, H-7), 4.40 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3), 3.93 (ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{5,6eq}$ = 4.8 Hz, $J_{4OH,5}$ = 1.5 Hz, H-5), 3.78 (s, 1 H, H-9), 3.45 (s, 3 H, OCH_3), 2.47 (d, 1 H, J = 1.7 Hz, 4-OH), 2.24–2.09 (m, 5 H, 2 x H-6, (C=O)CH_3), 1.53 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz,

$CDCl_3$, δ_C) 170.7 (C=O), 166.0 (C=O), 136.6 (Ar), 133.2 (Ar), 129.9 (Ar), 129.7 (Ar), 129.4 (Ar), 128.4(0) (Ar), 128.3(9) (Ar), 128.3 (Ar), 126.1 (Ar), 102.8 (CHAr), 98.6 (C-1), 83.0 (C-9), 77.9 (C-3), 74.6(8) (C-7), 74.6(5) (C-8), 69.8 (C-2), 67.4 (C-4), 66.4 (C-5), 56.0 (OCH_3), 28.7 (C-6), 21.2 ((C=O)CH_3), 11.6 (C-10). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{27}H_{34}NO_{10}$: 532.2177. Found 532.2172.

(**48α**): R_f 0.43 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.07 (m, 2 H, Ar), 7.62–7.57 (m, 1 H, Ar), 7.53–7.45 (m, 4 H, Ar), 7.41–7.35 (m, 3 H, Ar), 6.02 (dd, 1 H, $J_{6ax,7}$ = 11.9 Hz, $J_{6eq,7}$ = 5.0 Hz, H-7), 5.83 (s, 1 H, CHAr), 5.52 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 5.21 (s, 1 H, H-9), 5.18 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.45 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3), 4.01 (ddd, 1 H, $J_{5,6ax}$ = 12.5 Hz, $J_{5,6eq}$ = 4.4 Hz, $J_{4OH,5}$ = 1.5 Hz, H-5), 3.45 (s, 3 H, OCH_3), 3.03 (d, 1 H, J = 1.8 Hz, 4-OH), 2.29 (ddd, 1H, $J_{5,6ax}$ = 11.9, $J_{6eq,6ax}$ = 11.9, $J_{6ax,7}$ = 11.9, H-6_{ax}), 2.15 (s, 3H, (C=O)CH_3), 2.10–2.04 (m, 1 H, H-6_{eq}), 2.01 (s, 3H, (C=O)CH_3), 1.59 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ_C) 171.3 (C=O), 170.0 (C=O), 166.1 (C=O), 136.6 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 129.3 (Ar), 128.4 (Ar), 128.3 (Ar), 126.1 (Ar), 102.4 (CHAr), 98.5 (C-1), 85.5 (C-8), 78.7 (C-3), 78.0 (C-9), 69.7 (C-2), 69.0 (C-7), 67.9 (C-4), 63.9 (C-5), 55.9 (OCH_3), 29.2 (C-6), 22.8 ((C=O)CH_3), 20.9 ((C=O)CH_3), 16.4 (C-10). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{29}H_{36}NO_{11}$: 574.2283. Found 574.2274.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (D,D-49), **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→8)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-D-bradyrhizopyranoside (D,D-50)** and **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-D-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (D,D-51)**. Cesium carbonate (2 mg, 0.00675 mmol) was added to a cooled (0 °C) solution of **D-43** (18 mg, 0.0247 mmol) and

trichloroacetonitrile (13 μL, 0.124 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at rt overnight then filtered through Celite® 545. The filtrate was concentrated and the crude trichloroacetimidate was used for the next step without further purification.

Molecular sieves (~20 mg, activated powder 4 Å) were added to a solution of **D-37α** (8.5 mg, 0.0180 mmol) in CH_2Cl_2 (0.5 mL) at rt. The mixture was stirred for 1 h then cooled to –40 °C and stirred for 15 min. TBSOTf (42 μL of a solution of TBSOTf (20 μL) in CH_2Cl_2 (2 mL)) was added followed by a solution of the crude trichloroacetimidate in CH_2Cl_2 (0.4 mL). The mixture was stirred at –40 °C for 30 min and Et_3N (50 μL) was added. The reaction mixture was warmed to rt and the solvent was evaporated. The resulting crude products were purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **D,D-49** (5.5 mg, 26%) and **D,D-50** and **D,D-51** (7.1 mg, 34%) as colorless oils. Another silica gel column chromatography (9:1 hexanes–acetone) was necessary to purify **D,D-49**. Compounds **D,D-50** and **D,D-51** were separated by preparative TLC (9:1 toluene–EtOAc) to give **D,D-50** (1.6 mg, 8%) and **D,D-51** (3.4 mg, 16%). (**D,D-49**): R_f 0.37 (3:2 hexanes–EtOAc); $[\alpha]_D$ +82.6 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.05 (m, 2 H, Ar), 7.61–7.52 (m, 3 H, Ar), 7.48–7.43 (m, 2 H, Ar), 7.41–7.23 (m, 28 H, Ar), 5.84 (s, 1 H, C<u>H</u>Ar), 5.58 (d, 1 H, J = 12.3 Hz, C<u>H</u>$_2$Ar), 5.54 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 5.23 (d, 1 H, J = 12.3 Hz, C<u>H</u>$_2$Ar), 5.21 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 5.06 (d, 1 H, J = 10.6 Hz, C<u>H</u>$_2$Ar), 4.91 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1'), 4.81 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 4.80 (d, 1 H, J = 10.6 Hz, C<u>H</u>$_2$Ar), 4.75 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 4.73 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 4.68 (d, 1 H, J = 11.6 Hz, C<u>H</u>$_2$Ar), 4.56 (d, 1 H, J = 11.7 Hz, C<u>H</u>$_2$Ar), 4.54 (d, 1 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 4.36 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3), 4.33 (d, 1 H, $J_{2',3'}$ = 10.1 Hz, H-3'), 3.94 (dd, 1 H, $J_{5',6'ax}$ = 12.1 Hz, $J_{5',6'eq}$ = 3.9 Hz, H-5'), 3.90 (dd, 1 H, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 3.9 Hz, H-2'), 3.86 (s, 1 H, C-3'-OH), 3.76 (dd, 1 H, $J_{5,6ax}$ = 11.4 Hz, $J_{5,6eq}$ = 4.6 Hz, H-5), 3.74 (s, 1 H, H-9'), 3.67 (s, 1 H, H-9), 3.61 (dd, 1 H, $J_{6'ax,7'}$ = 11.9 Hz, $J_{6'eq,7'}$ = 4.8 Hz, H-7'), 3.48–3.43 (m, 4 H, H-7, CH_3O), 2.95 (d, 1 H, $J_{4OH,5}$ =

1.7 Hz, C-4-OH), 2.72 (br s, 1H, C-8-OH), 2.17 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6_{ax}), 2.08–2.00 (m, 2 H, H-6_{eq}, H-6'$_{ax}$), 1.97 (ddd, 1 H, $J_{6ax,6eq}$ = 11.9 Hz, $J_{5,6eq}$ = 4.4 Hz, $J_{6eq,7}$ = 4.4 Hz, H-6'$_{eq}$), 1.68 (s, 3 H, H-10'), 1.45 (s, 3 H, H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 140.0 (Ar), 139.5 (Ar), 138.3 (Ar), 138.1 (Ar), 136.7 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 129.4 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 126.9 (Ar), 126.2 (Ar), 102.8 (CHAr), 98.6 (C-1), 97.5 (C-1'), 89.8 (C-9), 83.4 (C-8'), 82.9 (C-9'), 81.7 (C-7'), 81.2 (C-7), 78.0 (C-3), 76.4 (C-2'), 76.2(3) (C-3'), 76.2(2) (CH_2Ar), 75.2 (C-8), 73.4 (CH_2Ar), 71.6 (CH_2Ar), 69.9 (C-2), 69.5 (C-4), 69.0 (CH_2Ar), 68.1 (C-5'), 67.4 (C-4'), 66.3 (CH_2Ar), 64.3 (C-5), 56.0 (OCH_3), 28.9 (C-6/C-6'), 28.7 (C-6/C-6'), 18.0 (C-10), 11.6 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{70}H_{74}NaO_{16}$: 1193.4869. Found 1193.4887.

(**D,D-50**): R_f 0.35 (1:1 hexanes–EtOAc); $[\alpha]_D$ +47.6 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–8.04 (m, 2 H, Ar), 7.61–7.56 (m, 1 H, Ar), 7.55–7.51 (m, 2 H, Ar), 7.49–7.44 (m, 2 H, Ar), 7.42–7.22 (m, 26 H, Ar), 7.10–7.05 (m, 2 H, Ar), 5.79 (s, 1 H, CHAr), 5.56 (d, 1 H, *J* = 12.1 Hz, CH_2Ar), 5.42 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 5.21 (d, 1 H, *J* = 11.0 Hz, CH_2Ar), 5.18 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 5.15 (d, 1 H, *J* = 11.9 Hz, CH_2Ar), 5.10 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1'), 4.86 (d, 1 H, *J* = 11.7 Hz, CH_2Ar), 4.71–4.64 (m, 4 H, 4 x CH_2Ar), 4.52 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3'), 4.34 (d, 2 H, *J* = 9.9 Hz, H-3), 4.33 (s, 1H, OH), 3.93 (dd, 1 H, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 4.0 Hz, H-2'), 3.85 (dd, 1 H, $J_{5',6'ax}$ = 12.5 Hz, $J_{5',6'eq}$ = 3.7 Hz, H-5'), 3.83 (s, 1 H, H-9'), 3.81 (s, 1 H, H-9), 3.75–3.69 (m, 3 H, H-5, H-7, CH_2Ar), 3.64 (d, 1 H, *J* = 11.4 Hz, CH_2Ar), 3.52 (br d, *J* = 1.1 Hz, OH), 3.43 (s, 3H, OCH_3), 3.41 (dd, 1 H, $J_{6'ax,7'}$ = 11.9 Hz, $J_{6'eq,7'}$ = 5.1 Hz, H-7'), 2.96 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.23 (ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{6eq,6ax}$ = 11.9 Hz, $J_{6ax,7}$ = 11.9 Hz, H-6_{ax}), 2.09 (ddd, 1 H, $J_{6eq,6ax}$ = 11.9 Hz, $J_{5,6eq}$ = 4.0 Hz, $J_{6eq,7}$ = 4.0 Hz, H-6_{eq}), 1.83 (ddd, 1 H, $J_{5',6'ax}$ = 12.3 Hz, $J_{6'eq,6'ax}$ = 12.3 Hz, $J_{6'ax,7'}$ = 12.3 Hz, H-6'$_{ax}$), 1.60 (s, 3 H, H-10'),

1.55–1.51 (m, 1 H, H-6'$_{eq}$), 1.51 (s, 3 H, H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 139.6 (Ar), 139.7 (Ar), 138.3 (Ar), 137.8 (Ar), 137.4 (Ar), 137.1 (Ar), 133.1 (Ar), 129.8 (Ar), 129.4 (Ar), 128.9 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.2(4) (Ar), 128.1(9) (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.3 (Ar), 127.1 (Ar), 127.0 (Ar), 126.9 (Ar), 125.8 (Ar), 101.6 (CHAr), 98.5 (C-1), 90.5 (C-1'), 89.9 (C-9'), 83.5 (C-8'), 82.2 (C-7'), 81.9 (C-8), 78.9 (C-9), 78.0 (C-3), 77.6 (C-3')76.9 (CH_2Ar), 74.9 (C-2'), 74.7 (CH_2Ar), 70.4 (CH_2Ar), 70.0 (C-2, C-5/C-7), 69.0 (CH_2Ar), 68.2 (C-4/C-4'), 68.1 (C-4/C-4'), 67.9 (C-5'), 66.1 (CH_2Ar), 64.9 (C-5/C-7), 55.9 (OCH_3), 29.9 (C-6), 28.6 (C-6'), 15.4 (C-10), 11.4 (C-10'). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{70}H_{78}NO_{16}$: 1188.5315. Found 1188.5343.

(**D,D-51**): R_f 0.36 (1:1 hexanes–EtOAc); $[\alpha]_D$ +46.8 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09–8.05 (m, 2 H, Ar), 7.60–7.55 (m, 1 H, Ar), 7.52–7.22 (m, 32 H, Ar), 5.79 (s, 1 H, CHAr), 5.52 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 5.38 (d, 1 H, J = 11.4 Hz, CH_2Ar), 5.20 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 5.13 (d, 1 H, J = 11.6 Hz, CH_2Ar), 5.08 (d, 1 H, J = 11.0 Hz, CH_2Ar), 4.93 (d, 1 H, J = 11.0 Hz, CH_2Ar), 4.83 (d, 1 H, J = 11.0 Hz, CH_2Ar), 4.79 (d, 1 H, J = 11.0 Hz, CH_2Ar), 4.75–4.70 (m, 4 H, 3 x CH_2Ar, H-1'), 4.52 (d, 1 H, J = 11.4 Hz, CH_2Ar), 4.33 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3), 4.08 (s, 1 H, OH), 3.97 (d, 1 H, $J_{2',3'}$ = 9.2 Hz, H-3'), 3.86–3.79 (m, 2 H, H-2', H-5), 3.71 (dd, 1 H, $J_{6ax,7}$ = 11.9 Hz, $J_{6eq,7}$ = 4.8 Hz, H-7), 3.67 (s, 1 H, H-9), 3.64 (dd, 1 H, $J_{6'ax,7'}$ = 11.6 Hz, $J_{6'eq7'}$ = 5.1 Hz, H-7'), 3.60 (s, 1 H, H-9'), 3.46 (s, 3H, OCH_3), 3.26 (dd, 1 H, $J_{5',6'ax}$ = 11.6 Hz, $J_{5',6'eq}$ = 4.0 Hz, H-5'), 2.92 (d, 1 H, $J_{4OH,5}$ = 1.5 Hz, C-4-OH), 2.75 (br s, 1H, OH), 2.30–2.12 (m, 4 H, 2 x H-6, 2 x H-6'), 1.63 (s, 3 H, H-10'), 1.42 (s, 3 H, H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 139.5(4) (Ar), 139.5(0) (Ar), 138.2 (Ar), 138.0 (Ar), 137.8 (Ar), 136.7 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 129.3 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4(1) (Ar), 128.3(6) (Ar), 128.3 (Ar), 128.2(4) (Ar), 128.1(6) (Ar), 128.0 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 127.1 (Ar), 127.0 (Ar), 126.2 (Ar), 105.4 (C-1'), 102.7 (CHAr), 98.6 (C-1), 89.2

(C-9'), 83.8 (C-8'), 82.6 (C-9/C-7/C-7'), 82.4(4) (C-9/C-7/C-7'), 82.4(0) (C-9/C-7/C-7'), 80.6 (C-3'), 80.3 (C-2'), 78.0 (C-3), 76.5 (C-4/C-4'), 76.1 (C-8), 75.8 ($\underline{C}H_2Ar$), 74.9 ($\underline{C}H_2Ar$), 72.4 (C-5'), 71.5 ($\underline{C}H_2Ar$), 70.0 (C-2), 68.9 ($\underline{C}H_2Ar$), 67.4 (C-4/C-4'), 66.2 ($\underline{C}H_2Ar$), 64.9 (C-5), 56.1 (OCH_3), 30.9 (C-6/C-6'), 29.1 (C-6/C-6'), 17.6 (C-10), 11.7 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{70}H_{74}NaO_{16}$: 1193.4869. Found 1193.4897.

Methyl 2,4,7,8,9-enta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1-*O*-methyl-1,5-α-L-bradyrhizopyranoside (L,L-49), **methyl 2,4,7,8,9-Penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→8)-2-*O*-benzoyl-3,9-*O*-benzylidene-1-*O*-methyl-1,5-α-L-bradyrhizopyranoside (L,L-50)** and **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-L-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1-*O*-methyl-1,5-α-L-bradyrhizopyranoside (L,L-51)**. Cesium carbonate (3 mg, 0.00921 mmol) was added to a cooled (0 °C) solution of **L-43** (16.3 mg, 0.0190 mmol) and trichloroacetonitrile (10 μL, 0.0949 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at rt overnight then filtered through Celite® 545. The filtrate was concentrated and the crude trichloroacetimidate was used in the next step without further purification.

Molecular sieves (~20 mg, activated powder 4 Å) were added to a solution of **L-37α** (5.4 mg, 0.0114 mmol) in CH_2Cl_2 (0.5 mL) at rt. The mixture was stirred for 1 h then cooled to –40 °C and stirred for 15 min. TBSOTf (52 μL of a solution of TBSOTf (20 μL) in CH_2Cl_2 (2 mL)) was added followed by a solution of the crude trichloroacetimidate in CH_2Cl_2 (0.4 mL). The mixture was stirred at –40 °C for 30 min and Et_3N (50 μL) was added. The reaction mixture was warmed to rt and the solvent was evaporated. The resulting crude products were purified by silica gel column chromatography (9:1 hexanes–EtOAc and 9:1 hexanes–acetone) to give **L,L-49** (5.5 mg, 42%) and **L,L-50** and **L,L-51** (7.5 mg, 58%) as colorless oils. Another silica gel column (9:1 hexanes–acetone)

was necessary to purify **L,L-49**. Disaccharides **L,L-50** and **L,L-51** were separated by preparative TLC (9:1 toluene–EtOAc) to give **L,L-50** (2.3 mg, 18%) and **L,L-51** (1.8 mg, 14%). The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS correspond to that obtained for compounds **D,D-49**, **D,D-50** and **D,D-51** previously described. (**L,L-49**): $[\alpha]_D$ –91.0 (*c* 0.1, $CHCl_3$). (**L,L-50**): $[\alpha]_D$ –58.8 (*c* 0.1, $CHCl_3$). (**L,L-51**): $[\alpha]_D$ –61.6 (*c* 0.1, $CHCl_3$).

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (D,L-49), **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→8)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (D,L-50)** and **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-D-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (D,L-51)**. Cesium carbonate (3 mg, 0.00921 mmol) was added to a cooled (0 °C) solution of **D-43** (23.9 mg, 0.0333 mmol) and trichloroacetonitrile (17 µL, 0.167 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at rt overnight then filtered through Celite® 545. The filtrate was concentrated and the crude trichloroacetimidate was used in the next step without further purification.

Molecular sieves (~20 mg, activated powder 4 Å) were added to a solution of **L-37α** (8.1 mg, 0.0171 mmol) in CH_2Cl_2 (0.5 mL) at rt. The mixture was stirred for 1 h and then cooled to –40 °C and stirred for 15 min. TBSOTf (67 µL of a solution of TBSOTf (10 µL) in CH_2Cl_2 (1 mL)) was added followed by a solution of the crude trichloroacetimidate in CH_2Cl_2 (0.4 mL). The mixture was stirred at –40 °C for 30 min and Et_3N (50 µL) was added. The reaction mixture was warmed to rt and the solvent was evaporated. The resulting crude products were purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **D,L-49** and **D,L-50** and **D,L-51** (6.8 mg, 34%) as colorless oils. Another silica gel column (9:1 hexanes–acetone) was necessary to purify **D,L-49** (7.6 mg, 38%). Disaccharides **D,L-50** and **D,L-51** were separated by preparative TLC (1:1

hexanes–EtOAc) to give **D,L-50** (5.2 mg, 26%) and **D,L-51** (1.1 mg, 6%). (**D,L-49**): R_f 0.36 (3:2 hexanes–EtOAc); $[\alpha]_D$ –25.8 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.06 (m, 2 H, Ar), 7.61–7.52 (m, 3 H, Ar), 7.48–7.44 (m, 2 H, Ar), 7.41–7.22 (m, 28 H, Ar), 5.86 (s, 1 H, C<u>H</u>Ar), 5.53 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 5.51 (d, 1 H, J = 10.6 Hz, C<u>H</u>$_2$Ar), 5.22 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 5.20 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 5.17 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 4.85 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1'), 4.83 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 4.82 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 4.75–4.68 (m, 4 H, 4 x C<u>H</u>$_2$Ar), 4.54 (d, 1 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 4.42 (d, 1 H, $J_{2',3'}$ = 10.1 Hz, H-3'), 4.38 (d, 1 H, $J_{2,3}$ = 10.1 Hz, H-3), 4.27 (s, 1 H, OH), 3.88 (dd, 1 H, $J_{2',3'}$ = 9.9 Hz, $J_{1',2'}$ = 3.9 Hz, H-2'), 3.86–3.81 (m, 2 H, H-5, H-9'), 3.78 (s, 1 H, H-9), 3.76 (dd, 1 H, $J_{5',6'ax}$ = 11.9 Hz, $J_{5',6'eq}$ = 3.9 Hz, H-5'), 3.68 (dd, 1 H, $J_{6'ax,7'}$ = 11.9 Hz, $J_{6'eq,7'}$ = 4.8 Hz, H-7'), 3.56 (br, 1 H, OH), 3.47 (dd, 1 H, $J_{6ax,7}$ = 12.3 Hz, $J_{6eq,7}$ = 4.2 Hz, H-7), 3.45 (s, 3 H, CH_3O), 3.01 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.24 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6$_{ax}$), 2.11 (ddd, 1 H, $J_{6eq,6ax}$ = 11.7 Hz, $J_{5,6ax}$ = 4.4 Hz, $J_{6ax,7}$ = 4.4 Hz, H-6$_{eq}$), 2.02 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6'$_{ax}$), 1.99–1.92 (m, 1 H, H-6'$_{eq}$), 1.67 (s, 3 H, H-10'), 1.50 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.1 (C=O), 139.6 (Ar), 139.4 (Ar), 138.1 (Ar), 137.9 (Ar), 137.5 (Ar), 136.7 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 129.2 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 127.0 (Ar), 126.9 (Ar), 126.2 (Ar), 102.6 (<u>C</u>HAr), 102.2 (C-1'), 98.6 (C-1), 89.7 (C-9'), 85.8 (C-7), 83.4 (C-8'), 82.1 (C-7'), 82.0 (C-9), 77.9 (C-3), 77.5 (C-3'), 76.9 (C-4/C-4'), 76.3 (<u>C</u>H$_2$Ar), 75.7 (C-8), 75.4 (C-2'), 74.1 (<u>C</u>H$_2$Ar), 71.7 (<u>C</u>H$_2$Ar), 70.0 (C-2), 69.0 (<u>C</u>H$_2$Ar), 68.1 (C-5'), 67.6 (C-4/C-4'), 66.2 (<u>C</u>H$_2$Ar), 64.9 (C-5), 56.0 (OCH_3), 29.4 (C-6), 28.7 (C-6'), 17.6 (C-10), 11.5 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{70}H_{74}NaO_{16}$: 1193.4869. Found 1193.4888.

(**D,L-50**): R_f 0.23 (1:1 hexanes–EtOAc); $[\alpha]_D$ –32.2 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.09 (m, 2 H, Ar), 7.62–7.57 (m, 1 H, Ar), 7.56–7.52 (m, 2 H, Ar), 7.50–7.45 (m,

2 H, Ar), 7.42–7.24 (m, 26 H, Ar), 7.17–7.12 (m, 2 H, Ar), 5.70 (s, 1 H, CHAr), 5.53 (d, 1 H, J = 11.9 Hz, CH_2Ar), 5.53 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 5.22 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.21 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1), 5.19–5.14 (m, 2 H, 2 x CH_2Ar), 4.79 (d, 1 H, J = 11.7 Hz, CH_2Ar), 4.78 (d, 1 H, J = 11.0 Hz, CH_2Ar), 4.72 (d, 1 H, J = 10.8 Hz, CH_2Ar), 4.70 (d, 1 H, J = 11.0 Hz, CH_2Ar), 4.67 (d, 1 H, J = 11.6 Hz, CH_2Ar), 4.40 (d, 1 H, $J_{2',3'}$ = 10.1 Hz, H-3'), 4.37 (d, 1 H, $J_{2,3}$ = 10.1 Hz, H-3), 4.17 (s, 1 H, OH), 4.13 (d, 1 H, J = 11.7 Hz, CH_2Ar), 4.10 (d, 1 H, J = 11.4 Hz, CH_2Ar), 3.92 (dd, 1 H, $J_{2',3'}$ = 9.9 Hz, $J_{1',2'}$ = 3.9 Hz, H-2'), 3.87 (br ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{5,6eq}$ = 4.0 Hz, $J_{5,OH}$ = 1.3 Hz, H-5), 3.78–3.70 (m, 3 H, H-7, H-5', H-9'), 3.62 (s, 1 H, H-9), 3.46 (s, 3 H, CH_3O), 3.45 (dd, 1 H, $J_{6'ax,7'}$ = 11.7 Hz, $J_{6'eq,7'}$ = 4.8 Hz, H-7'), 3.40 (br, 1 H, OH), 2.96 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.18 (ddd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{6eq,6ax}$ = 12.3 Hz, $J_{6ax,7}$ = 12.3 Hz, H-6_{ax}), 2.06 (ddd, 1 H, $J_{6eq,6ax}$ = 12.1 Hz, $J_{5,6ax}$ = 4.0 Hz, $J_{6ax,7}$ = 4.0 Hz, H-6_{eq}), 1.94 (ddd, 1 H, $J_{5',6'ax}$ = 12.1 Hz, $J_{6'eq,6'ax}$ = 12.1 Hz, $J_{6'ax,7'}$ = 12.1 Hz, H-6'$_{ax}$), 1.74 (ddd, 1 H, $J_{6'eq,6'ax}$ = 12.5 Hz, $J_{5',6'eq}$ = 4.4 Hz, $J_{6'eq,7}$ = 4.4 Hz, H-6'$_{eq}$), 1.63 (s, 3 H, H-10'), 1.51 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 139.7 (Ar), 139.5 (Ar), 138.2 (Ar), 137.9 (Ar), 137.4 (Ar), 136.8 (Ar), 133.2 (Ar), 129.9 (Ar), 129.2 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3(2) (Ar), 128.2(8) (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 127.0 (Ar), 126.9 (Ar), 125.9 (Ar), 102.0 (CHAr), 98.5 (C-1), 92.0 (C-1'), 90.0 (C-9'), 83.6 (C-8'), 83.3 (C-9), 82.6 (C-7'), 82.2 (C-8), 78.1 (C-3), 77.2 (C-3'), 76.8 (C-4/C-4'), 76.3 (CH_2Ar), 75.8 (C-2'), 74.4 (CH_2Ar), 74.2 (C-7), 71.3 (CH_2Ar), 70.0 (C-2), 69.0 (CH_2Ar), 68.1 (C-4/C-4'), 67.6 (C-5'), 66.2 (CH_2Ar), 65.0 (C-5), 55.9 (OCH_3), 29.7 (C-6), 29.0 (C-6'), 11.6 (C-10), 11.4 (C-10'). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{70}H_{78}NO_{16}$: 1188.5315. Found 1188.5341.

(**D,L-51**): R_f 0.33 (1:1 hexanes–EtOAc); $[\alpha]_D$ –44.8 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.05 (m, 2 H, Ar), 7.60–7.52 (m, 3 H, Ar), 7.48–7.44 (m, 2 H, Ar), 7.40–7.23 (m, 28 H, Ar), 5.86 (s, 1 H, CHAr), 5.53 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 5.43 (d, 1 H, J =

11.9 Hz, C$\underline{H}_2$Ar), 5.21 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 5.14 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 5.07 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.85 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.80–4.73 (m, 3 H, C$\underline{H}_2$Ar), 4.70 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.66 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.52 (d, 1 H, $J_{1',2'}$ = 7.5 Hz, H-1'), 4.43 (d, 1 H, J = 11.9 Hz, C$\underline{H}_2$Ar), 4.41 (s, 1 H, OH), 4.37 (d, 1 H, $J_{2,3}$ = 10.1 Hz, H-3), 3.98 (s, 1 H, OH), 4.94 (d, 1 H, $J_{2',3'}$ = 9.5 Hz, H-3'), 3.81 (br ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{5,6eq}$ = 3.9 Hz, $J_{5,OH}$ = 1.3 Hz, H-5), 3.75 (s, 1 H, H-9), 3.75 (dd, 1 H, $J_{2',3'}$ = 9.4 Hz, $J_{1',2'}$ = 7.5 Hz, H-2'), 3.66 (dd, 1 H, $J_{6ax,7}$ = 12.3 Hz, $J_{6eq,7}$ = 4.4 Hz, H-7), 3.61 (dd, 1 H, $J_{6'ax,7'}$ = 11.6 Hz, $J_{6'eq,7'}$ = 5.1 Hz, H-7'), 3.61 (s, 1 H, H-9'), 3.43 (s, 3 H, CH_3O), 3.32 (dd, 1 H, $J_{5',6'ax}$ = 11.6 Hz, $J_{5',6'eq}$ = 4.2 Hz, H-5'), 3.00 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.34 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6_{ax}), 2.21–2.09 (m, 3 H, H-6_{eq}, 2 x H-6'), 1.61 (s, 3 H, H-10'), 1.49 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 139.6 (Ar), 139.4 (Ar), 137.9(9) (Ar), 137.9(5) (Ar), 136.7 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 129.2 (Ar), 128.6 (Ar), 128.4(1) (Ar), 128.3(8) (Ar), 128.3 (Ar), 128.2(5) (Ar), 128.2(0) (Ar), 127.9 (Ar), 127.8 (Ar), 127.6(5) (Ar), 127.5(7) (Ar), 127.3 (Ar), 127.0 (Ar), 126.8 (Ar), 126.2 (Ar), 104.6 (C-1'), 102.6 (C$\underline{H}$Ar), 98.5 (C-1), 89.0 (C-9'), 86.0 (C-7), 83.5 (C-8'), 82.6 (C-9), 81.8 (C-7'), 80.0 (C-3'), 79.5 (C-2'), 77.9 (C-3), 75.9(4) (C$\underline{H}_2$Ar), 75.8(7) (C$\underline{H}_2$Ar), 75.3 (C-4/C-4'), 74.5 (C-8), 72.6 (C-5'), 71.3 (C$\underline{H}_2$Ar), 69.9(2) (C-2), 68.8(6) (C$\underline{H}_2$Ar), 67.3 (C-4/C-4'), 66.3 (C$\underline{H}_2$Ar), 64.7 (C-5), 55.9 (OCH_3), 30.3 (C-6), 28.8 (C-6'), 14.1 (C-10), 11.4 (C-10'). HRMS (ESI) Calcd for $[M + NH_4]^+$ $C_{70}H_{78}NO_{16}$: 1188.5315. Found 1188.5337.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (L,D-49), **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→8)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (L,D-50)** and **methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-L-**

bradyrhizopyranosyl-(1→7)-2-*O*-benzoyl-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (L,D-51). Cesium carbonate (3 mg, 0.00921 mmol) was added to a cooled (0 °C) solution of **L-43** (19 mg, 0.0275 mmol) and trichloroacetonitrile (14 µL, 0.138 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at rt overnight then filtered through Celite® 545. The filtrate was concentrated and the crude trichloroacetimidate was used for the next step without further purification. Molecular sieves (~20 mg, activated powder 4 Å) were added to a solution of **D-37α** (5.8 mg, 0.0123 mmol) in CH_2Cl_2 (0.5 mL) at rt. The mixture was stirred for 1 h then cooled to –40 °C and stirred for 15 min. TBSOTf (56 µL of a solution of TBSOTf (10 µL) in CH_2Cl_2 (1 mL)) was added followed by a solution of the crude trichloroacetimidate in CH_2Cl_2 (0.4 mL). The mixture was stirred at –40 °C for 30 min and Et_3N (50 µL) was added. The reaction mixture was warmed to rt and the solvent was evaporated. The resulting crude products were purified by silica gel column chromatography (9:1 hexanes–EtOAc) to give **L,D-49** and **L,D-50** and **L,D-51** (4.6 mg, 32%) as colorless oils. Another silica gel column (9:1 hexanes–acetone) was necessary to purify **L,D-49** (5.5 mg, 38%). Disaccharides **L,D-50** and **L,D-51** were separated by preparative TLC (1:1 hexanes–EtOAc) to give **L,D-50** (3.8 mg, 26%) and **L,D-51** (0.8 mg, 5%). The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained for compounds **D,L-49**, **D,L-50** and **D,L-51** previously described. (**L,D-49**): $[\alpha]_D$ +22.0 (*c* 0.1, $CHCl_3$). (**L,D-50**): $[\alpha]_D$ +40.4 (*c* 0.1, $CHCl_3$). (**L,D-51**): $[\alpha]_D$ +34.6 (*c* 0.1, $CHCl_3$).

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→7)-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (D,D-57). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **D,D-49** (5.5 mg, 0.00470 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until neutral pH and the mixture was filtered. The filtrate was evaporated and the resulting crude product was purified by silica gel

column chromatography (3:2 hexanes–EtOAc) to give **D,D-57** (3.9 mg, 78%) as a colorless oil. R_f 0.27 (2:3 hexanes–EtOAc); $[\alpha]_D$ +46.7 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.61–7.56 (m, 2 H, Ar), 7.45–7.22 (m, 28 H, Ar), 5.79 (s, 1 H, C<u>H</u>Ar), 5.57 (d, 1 H, *J* = 12.3 Hz, C<u>H</u>$_2$Ar), 5.23 (d, 1 H, *J* = 12.1 Hz, C<u>H</u>$_2$Ar), 5.05 (d, 1 H, *J* = 10.8 Hz, C<u>H</u>$_2$Ar), 4.91 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1'), 4.90 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.80 (d, 1 H, *J* = 10.5 Hz, C<u>H</u>$_2$Ar), 4.78 (d, 1 H, *J* = 10.1 Hz, C<u>H</u>$_2$Ar), 4.73 (d, 1 H, *J* = 11.7 Hz, C<u>H</u>$_2$Ar), 4.73 (d, 1 H, *J* = 10.8 Hz, C<u>H</u>$_2$Ar), 4.67 (d, 1 H, *J* = 11.4 Hz, C<u>H</u>$_2$Ar), 4.56 (d, 1 H, *J* = 11.9 Hz, C<u>H</u>$_2$Ar), 4.53 (d, 1 H, *J* = 11.4 Hz, C<u>H</u>$_2$Ar), 4.32 (d, 1 H, $J_{2',3'}$ = 10.1 Hz, H-3'), 4.18 (ddd, 1 H, $J_{2,3}$ = 9.7 Hz, $J_{2,OH}$ = 9.7 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 3.93 (dd, 1 H, $J_{5',6'ax}$ = 12.3 Hz, $J_{5',6'eq}$ = 3.9 Hz, H-5'), 3.93 (d, 1 H, $J_{2,3}$ = 9.5 Hz, H-3), 3.89 (dd, 1 H, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 3.9 Hz, H-2'), 3.86 (s, 1 H, C-3'-OH), 3.73 (s, 1 H, H-9'), 3.68 (dd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{5,6eq}$ = 4.4 Hz, H-5), 3.60 (s, 1 H, H-9), 3.59 (dd, 1 H, $J_{6'ax,7'}$ = 11.9 Hz, $J_{6'eq,7'}$ = 4.8 Hz, H-7'), 3.52 (s, 3 H, CH_3O), 3.44 (dd, 1 H, $J_{6ax,7}$ = 11.9 Hz, $J_{6eq,7}$ = 4.8 Hz, H-7), 2.83 (d, 1 H, $J_{4OH,5}$ = 1.5 Hz, C-4-OH), 2.68 (br s, 1H, C-8-OH), 2.15–1.92 (m, 5 H, 2 x H-6, 2 x H-6', C-2-OH), 1.67 (s, 3 H, H-10'), 1.43 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 140.0 (Ar), 139.5 (Ar), 138.3 (Ar), 138.1 (Ar), 136.7 (Ar), 129.5 (Ar), 128.5(4) (Ar), 128.5(0) (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 126.9 (Ar), 126.3 (Ar), 103.2 (<u>C</u>HAr), 100.7 (C-1), 97.4 (C-1'), 89.8 (C-9'), 83.4 (C-8'), 82.9 (C-9), 81.8 (C-7'), 81.3 (C-3), 81.1 (C-7), 76.8 (C-4'), 76.3(4) (C-3'/C-2'), 76.2(5) (C-2'/C-3'), 76.2 (<u>C</u>H$_2$Ar), 75.1 (C-8), 73.4 (<u>C</u>H$_2$Ar), 71.6 (<u>C</u>H$_2$Ar), 68.9 (<u>C</u>H$_2$Ar), 68.1 (C-5'), 67.6 (C-2), 67.2 (C-4), 66.3 (<u>C</u>H$_2$Ar), 65.0 (C-5), 56.0 (OCH_3), 28.9 (C-6/C-6'), 28.7 (C-6/C-6'), 17.9 (C-10), 11.4 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{63}H_{70}NaO_{15}$: 1089.4607. Found 1089.4617.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→7)-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (L,L-57). A solution of MeONa in MeOH (0.15 mL, 0.5 M in

MeOH) was added to **L,L-49** (5.5 mg, 0.00470 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until the pH of the solution was neutral. The resin was filtered off, and the filtrate was concentrated. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **L,L-57** (4.2 mg, 84%) as a colorless oil. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS correspond to that obtained for compound **D,D-57** previously described. $[\alpha]_D$ –70.0 (*c* 0.1, $CHCl_3$).

Methyl 2,4,7,8,9-Penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→7)-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (D,L-57). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **D,L-49** (8.0 mg, 0.00683 mmol) in MeOH (3 mL) The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until neutral pH and the mixture was filtered. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **D,L-57** (7.3 mg, 93%) as a colorless oil. R_f 0.36 (2:3 hexanes–EtOAc); $[\alpha]_D$ –21.2 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.61–7.57 (m, 2 H, Ar), 7.43–7.22 (m, 28 H, Ar), 5.81 (s, 1 H, C<u>H</u>Ar), 5.51 (d, 1 H, *J* = 12.1 Hz, C<u>H</u>$_2$Ar), 5.19 (d, 1 H, *J* = 11.2 Hz, C<u>H</u>$_2$Ar), 5.16 (d, 1 H, *J* = 11.5 Hz, C<u>H</u>$_2$Ar), 4.90 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1), 4.86–4.78 (m, 3 H, 2 x C<u>H</u>$_2$Ar, H-1'), 4.75–4.67 (m, 4 H, C<u>H</u>$_2$Ar), 4.54 (d, 1 H, *J* = 11.4 Hz, C<u>H</u>$_2$Ar), 4.40 (d, 1 H, $J_{2,3}$ = 10.1 Hz, H-3'), 4.25 (s, 1 H, OH), 4.18 (br ddd, 1 H, $J_{2,3}$ = 9.0 Hz, $J_{2,OH}$ = 9.0 Hz, $J_{1,2}$ = 3.5 Hz, H-2), 3.95 (d, 1 H, $J_{2',3'}$ = 9.4 Hz, H-3), 3.87 (dd, 1 H, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 3.9 Hz, H-2'), 3.82 (s, 1 H, H-9'), 3.77–3.71 (m, 2 H, H-5, H-5'), 3.70 (s, 1 H, H-9), 3.67 (dd, 1 H, $J_{5,6ax}$ = 11.7 Hz, $J_{5,6eq}$ = 5.0 Hz, H-7'), 3.53 (br, 1 H, OH), 3.51 (s, 3 H, CH_3O), 3.44 (dd, 1 H, $J_{6'ax,7'}$ = 12.3 Hz, $J_{6'eq,7'}$ = 4.4 Hz, H-7), 2.90 (d, 1 H, $J_{4OH,5}$ = 1.1 Hz, C-4-OH), 2.19 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6$_{ax}$), 2.12–2.05 (m, 1 H, H-6$_{eq}$), 2.01 (ddd, 1 H, $J_{5',6'ax}$ = 11.9 Hz, $J_{6'eq,6'ax}$ = 11.9 Hz, $J_{6'ax,7'}$ = 11.9 Hz, H-6'$_{ax}$), 1.98–1.91 (m, 1 H, H-

6'$_{eq}$), 1.67 (s, 3 H, H-10'), 1.48 (s, 3 H, H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 139.5 (Ar), 138.1 (Ar), 137.9 (Ar), 137.5 (Ar), 136.7 (Ar), 129.3 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2(4) (Ar), 128.2(0) (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 127.0 (Ar), 126.9 (Ar), 126.4 (Ar), 103.0 (CHAr), 102.2 (C-1'), 100.8 (C-1), 89.7 (C-9'), 85.8 (C-7), 83.4 (C-8'), 82.2 (C-7'), 82.0 (C-9), 81.2 (C-3), 77.5 (C-3'), 76.9 (C-4/C-4'), 76.3 (CH_2Ar), 75.6 (C-8), 75.3 (C-2'), 74.0 (CH_2Ar), 71.7 (CH_2Ar), 69.0 (CH_2Ar), 68.0 (C-5'), 67.6 (C-2), 67.4 (C-4/C-4'), 66.2 (CH_2Ar), 65.2 (C-5), 56.0 (OCH_3), 30.7 (C-6), 28.7 (C-6'), 17.6 (C-10), 11.4 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{63}H_{70}NaO_{15}$: 1089.4607. Found 1089.4630.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→7)-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (L,D-57). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **L,D-49** (5.5 mg, 0.00470 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until the pH of the solution was neutral and the mixture was filtered. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **L,D-57** (2.9 mg, 58%) as a colorless oil. The R_f, ^1H NMR, $^{13}C\{^{1}H\}$ NMR and MS data correspond to that obtained for compound **D,L-57** previously described. $[\alpha]_D$ +8.0 (*c* 0.1, $CHCl_3$).

Methyl 1,5-α-D-bradyrhizopyranosyl-(1→7)-1,5-α-D-bradyrhizopyranoside (D,D-58). Palladium hydroxide on carbon (7.0 mg, 0.00997 mmol, 20 wt. % loading) was added to a solution of **D,D-57** (3.9 mg, 0.00365 mmol) in MeOH (4 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium hydroxide on carbon was filtered through Celite® and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **D,D-58** in

quantitative yield and as a colorless oil. $[\alpha]_D$ +103.6 (*c* 0.1, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 4.89 (d, 1 H, $J_{1',2'}$ = 4.1 Hz, H-1'), 4.66 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1), 4.10 (dd, 1 H, $J_{5,6ax}$ = 12.0 Hz, $J_{5,6eq}$ = 4.4 Hz, H-5/H-5'), 3.87 (d, 1 H, $J_{2,3}$ = 9.7 Hz, H-3), 3.80 (d, 1 H, $J_{2',3'}$ = 9.5 Hz, H-3'), 3.77 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 4.1 Hz, H-2), 3.76 (dd, 1 H, $J_{2',3'}$ = 9.5 Hz, $J_{1',2'}$ = 3.8 Hz, H-2'), 3.64–3.59 (m, 1 H, H-5/H-5'), 3.55–3.49 (m, 4 H, H-7, H-7', H-9, H-9'), 3.39 (s, 3 H, OCH_3), 1.94–1.79 (m, 4 H, H-6, H-6'), 1.35 (s, 3 H, H-10'/H-10), 1.28 (s, 3 H, H-10'/H-10); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, δ_C) 101.6 (C-1), 98.2 (C-1'), 80.8 (C-9/C-9'), 79.5 (C-7/C-7'), 79.4 (C-9/C-9'), 78.6 (C-4/C-8), 77.7 (C-8/C-8'/C-4/C-4'), 77.0 (C-3/C-3'), 76.9 (C-3/C-3'), 74.4 (C-8/C-8'/C-4/C-4'), 74.2 (C-8/C-8'/C-4/C-4'), 74.1 (C-8/C-8'/C-4/C-4'), 70.9 (C-2, C-2'), 67.4 (C-5/C-5'), 67.1 (C-5/C-5'), 55.8 (OCH_3), 32.5 (C-6/C-6'), 29.3 (C-6/C-6'), 16.2 (C-10/C-10'), 15.5 (C-10/C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{21}H_{36}NaO_{15}$: 551.1946. Found 551.1941.

Methyl 1,5-α-D-bradyrhizopyranosyl-(1→7)-1,5-α-L-bradyrhizopyranoside (D,L-58). Palladium hydroxide on carbon (6.8 mg, 0.00637 mmol, 20 wt. % loading) was added to a solution of **D,L-57** (12.4 mg, 0.0116 mmol) in MeOH (7 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladum hydroxide on carbon was filtered through Celite® and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **D,L-58** (in quantitative yield and as a colorless oil. $[\alpha]_D$ +10.0 (*c* 0.1, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 4.99 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1'), 4.64 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1), 3.83–3.71 (m, 5 H, H-2, H-2', H-3, H-3', H-5/H-5'), 3.67–3.62 (m, 1 H, H-5/H-5'), 3.52–3.46 (m, 4 H, 2 x H-7,H-7', H-9, H-9'), 3.37 (s, 3 H, OCH_3), 2.00–1.93 (m, 2 H, 2 x H-6/H-6'), 1.89 (ddd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{6eq,6ax}$ = 12.3 Hz, $J_{6ax,7}$ = 12.3 Hz, H-6ax/H-6'$_{ax}$), 1.71 (ddd, 1 H, $J_{6eq,6ax}$ = 11.9 Hz, $J_{5,6ax}$ = 4.2 Hz, $J_{6ax,7}$ = 4.2 Hz, H-6$_{eq}$/H-6'$_{eq}$), 1.34 (s, 3 H, H-10/H-10'), 1.26 (s, 3 H, H-10/H-10); $^{13}C\{^1H\}$ NMR

(125 MHz, CD_3OD, δ_C) 102.8 (C-1'), 101.6 (C-1'), 84.4 (C-7/C-7'), 80.8 (C-9/C-9'), 80.1 (C-9/C-9'), 78.5 (C-8/C-4/C-8'/C-4'), 78.4 (C-8/C-4/C-8'/C-4'), 77.2 (C-3/C-3'), 76.9 (C-3/C-3'), 74.3(1) (C-8/C-4/C-8'/C-4'), 74.2(6) (C-7/C-7''), 74.0 (C-8/C-4/C-8'/C-4'), 71.5 (C-2/C-2'), 70.9 (C-2/C-2'), 68.0 (C-5/C-5'), 67.0 (C-5/C-5'/), 55.9 (OCH_3), 32.7 (C-6/C-6'), 31.9 (C-6/C-6'), 16.4 (C-10/C-10'), 15.4 (C-10/C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{21}H_{36}NaO_{15}$: 551.1946. Found 551.1938.

Methyl 1,5-α-L-bradyrhizopyranosyl-(1→7)-1,5-α-D-bradyrhizopyranoside (L,D-58). Palladium hydroxide on carbon (5.3 mg, 0.00499 mmol, 20 wt. % loading) was added to a solution of **L,D-57** (2.9 mg, 0.0.0272 mmol) in MeOH (3 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium hydroxide on carbon was filtered and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **L,D-58** in quantitative yield and as a colorless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained for compound **D,L-58** previously described. $[\alpha]_D$ –14.2 (*c* 0.1, $CHCl_3$).

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→8)-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (L,L-59). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **L,L-50** (2.3 mg, 0.00196 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until the pH of the solution was neutral and then the mixture was filtered. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **L,L-59** (1.7 mg, 81%) as a colorless oil. R_f 0.21 (2:3 hexanes–EtOAc); $[\alpha]_D$ –26.4 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.57–7.55 (m, 2 H, Ar), 7.38–7.31 (m, 7 H, Ar), 7.30–7.19 (m, 19 H, Ar), 7.08–

7.05 (m, 2 H, Ar), 5.71 (s, 1 H, C<u>H</u>Ar), 5.51 (d, 1 H, J = 12.0 Hz, C<u>H</u>$_2$Ar), 5.17 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 5.11 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 5.04 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1'), 4.84 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.83 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 4.67–4.61 (m, 4 H, 4 x C<u>H</u>$_2$Ar), 4.48 (d, 1 H, $J_{2',3'}$ = 10.0 Hz, H-3'), 4.30 (s, 1 H, OH), 4.06 (ddd, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{2,OH}$ = 9.4 Hz, $J_{1,2}$ = 3.8 Hz, H-2), 3.89 (dd, 1 H, $J_{2',3'}$ = 10.0 Hz, $J_{1',2'}$ = 3.8 Hz, H-2'), 3.87 (d, 1 H, $J_{2,3}$ = 9.5 Hz, H-3), 3.80 (dd, 1 H, $J_{5',6'ax}$ = 12.4 Hz, $J_{5',6'eq}$ = 3.6 Hz, H-5'), 3.79 (s, 1 H, H-9'), 3.69 (s, 1 H, H-9), 3.66 (d, 1 H, $J_{2,3}$ = 11.4 Hz, C<u>H</u>$_2$Ar), 3.65 (br dd, 1 H, $J_{5,6ax}$ = 11.4 Hz, $J_{5,6eq}$ = 3.7 Hz, H-7), 3.61 (d, 1 H, $J_{2,3}$ = 11.4 Hz, C<u>H</u>$_2$Ar), 3.61–3.57 (m, 1 H, H-5), 3.51 (br d, 1 H, J = 1.2 Hz, OH), 3.48 (s, 3 H, CH$_3$O), 3.36 (dd, 1 H, $J_{6'ax,7'}$ = 11.9 Hz, $J_{6'eq,7'}$ = 4.7 Hz, H-7'), 2.82 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.16 (ddd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{6eq,6ax}$ = 11.9 Hz, $J_{6ax,7}$ = 11.9 Hz, H-6$_{ax}$), 2.04 (ddd, 1 H, $J_{6eq,6ax}$ = 11.9 Hz, $J_{5,6eq}$ = 4.1 Hz, $J_{6eq,7}$ = 4.1 Hz, H-6$_{eq}$), 2.00 (br d, 1 H, $J_{2,OH}$ = 9.7 Hz, C-2-OH), 1.78 (ddd, 1 H, $J_{5',6'ax}$ = 12.0 Hz, $J_{6'eq,6'ax}$ = 12.0 Hz, $J_{6'ax,7'}$ = 12.0 Hz, H-6'$_{ax}$), 1.56 (s, 3 H, H-10'), 1.50–1.46 (m, 1 H, H-6'$_{eq}$), 1.46 (s, 3 H, H-10); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, δ_C) 139.6 (Ar), 139.4 (Ar), 138.3 (Ar), 137.8 (Ar), 137.4 (Ar), 137.2 (Ar), 129.4 (Ar), 128.9 (Ar), 128.7 (Ar), 128.6(4) (Ar), 128.5(9) (Ar), 128.4 (Ar), 128.2(3) (Ar), 128.2(0) (Ar), 128.1 (Ar), 127.9 (Ar), 127.7 (Ar), 127.3 (Ar), 127.2 (Ar), 127.0 (Ar), 126.9 (Ar), 126.0 (Ar), 101.9 (<u>C</u>HAr), 100.7 (C-1), 90.4 (C-1'), 89.8 (C-9'), 83.5 (C-8'), 82.3 (C-7'), 81.8 (C-8), 81.4 (C-3), 78.8 (C-9), 77.4 (C-3'), 76.9 (<u>C</u>H$_2$Ar), 76.4 (C-4/C-4'), 74.9 (C-2'), 74.7 (<u>C</u>H$_2$Ar), 70.4 (<u>C</u>H$_2$Ar), 68.9 (<u>C</u>H$_2$Ar), 68.0(4) (C-5'), 68.0(0) (C-4/C-4'), 67.8 (C-2), 67.6 (C-7), 66.1 (<u>C</u>H$_2$Ar), 65.2 (C-5), 55.9 (OCH$_3$), 29.4 (C-6), 28.6 (C-6'), 15.4 (C-10), 11.4 (C-10'). HRMS (ESI) Calcd for [M + Na]$^+$ $C_{63}H_{70}NaO_{15}$: 1089.4607. Found 1089.4606.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-D-bradyrhizopyranosyl-(1→8)-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (D,L-59). A solution of MeONa in MeOH (0.15 mL, 0.5 M in

MeOH) was added to **D,L-50** (5.2 mg, 0.00444 mmol) in MeOH (3 mL) The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until neutral pH and the mixture was filtered. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **D,L-59** (4.7 mg, 99%) as a colorless oil. R_f 0.22 (3:7 hexanes–EtOAc); $[\alpha]_D$ –16.2 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.64–7.60 (m, 2 H, Ar), 7.42–7.20 (m, 26 H, Ar), 7.13–7.08 (m, 2 H, Ar), 5.72 (s, 1 H, C<u>H</u>Ar), 5.52 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 5.19 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.17 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 5.16 (d, 1 H, J = 11.9 Hz, C<u>H</u>$_2$Ar), 4.89 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1), 4.81 (d, 1 H, J = 11.6 Hz, C<u>H</u>$_2$Ar), 4.75 (d, 1 H, J = 11.0 Hz, C<u>H</u>$_2$Ar), 4.69 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.68 (d, 1 H, J = 10.8 Hz, C<u>H</u>$_2$Ar), 4.66 (d, 1 H, J = 11.7 Hz, C<u>H</u>$_2$Ar), 4.40 (d, 1 H, $J_{2,3}$ = 9.9 Hz, H-3'), 4.19 (s, 1 H, OH), 4.19–4.12 (m, 1 H, H-2), 4.03 (d, 1 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 3.98 (d, 1 H, J = 11.4 Hz, C<u>H</u>$_2$Ar), 3.94 (d, 1 H, $J_{2,3}$ = 9.4 Hz, H-3), 3.92 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{1,2}$ = 4.0 Hz, H-2'), 3.78 (br ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{5,6eq}$ = 4.4 Hz, $J_{5,OH}$ = 1.3 Hz, H-5), 3.74 (s, 1 H, H-9'), 3.71 (dd, 1 H, $J_{6ax,7}$ = 11.9 Hz, $J_{6eq,7}$ = 4.2 Hz, H-7), 3.70 (dd, 1 H, $J_{5',6'ax}$ = 12.5 Hz, $J_{5',6'eq}$ = 3.9 Hz, H-5'), 3.56 (s, 1 H, H-9), 3.52 (s, 3 H, CH_3O), 3.49 (br, 1 H, OH), 3.39 (dd, 1 H, $J_{5,6ax}$ = 11.9 Hz, $J_{5,6eq}$ = 4.8 Hz, H-7'), 2.84 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.12 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6$_{ax}$), 2.03 (ddd, 1 H, $J_{6eq,6ax}$ = 12.1 Hz, $J_{5,6ax}$ = 4.4 Hz, $J_{6ax,7}$ = 4.4 Hz, H-6$_{eq}$), 1.90 (ddd, 1 H, $J_{5',6'ax}$ = 12.1 Hz, $J_{6'eq,6'ax}$ = 12.1 Hz, $J_{6'ax,7'}$ = 12.1 Hz, H-6'$_{ax}$), 1.76–1.70 (m, 1 H, H-6'$_{eq}$), 1.61 (s, 3 H, H-10'), 1.50 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 139.4 (Ar), 138.1 (Ar), 137.9 (Ar), 137.4 (Ar), 136.9 (Ar), 129.3 (Ar), 128.7 (Ar), 128.6 (Ar), 128.3(7) (Ar), 128.3(6) (Ar), 128.3 (Ar), 128.2(2) (Ar), 128.1(7) (Ar), 128.0 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 127.0 (Ar), 126.0 (Ar), 102.2 (<u>C</u>HAr), 100.6 (C-1), 91.9 (C-1'), 90.0 (C-9'), 83.5 (C-8'), 83.2 (C-9), 82.6 (C-7'), 82.2 (C-8), 81.5 (C-3), 77.4 (C-3'), 77.0 (C-4/C-4'), 76.3 (<u>C</u>H$_2$Ar), 75.8 (C-2'), 74.5 (<u>C</u>H$_2$Ar), 74.3 (C-7), 71.0 (<u>C</u>H$_2$Ar), 69.0 (<u>C</u>H$_2$Ar), 67.9 (C-4/C-

4'), 67.7 (C-5'), 67.6 (C-2), 66.2 ($\underline{C}H_2Ar$), 65.3 (C-5), 56.0 (OCH_3), 30.2 (C-6), 28.7 (C-6'), 11.4 (C-10), 11.3 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{63}H_{70}NaO_{15}$: 1089.4607. Found 1089.4635.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-α-L-bradyrhizopyranosyl-(1→8)-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (L,D-59). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **L,D-50** (3.8 mg, 0.00470 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until the pH of the solution was neutral and the mixture was filtered. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **L,D-59** (3.5 mg, 99%) as a colorless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained for compound **D,L-59** previously described. $[\alpha]_D$ +4.4 (*c* 0.1, $CHCl_3$).

Methyl 1,5-α-L-bradyrhizopyranosyl-(1→8)-1,5-α-L-bradyrhizopyranoside (L,L-60). Palladium on carbon (3.4 mg, 0.00327 mmol, 10 wt. % loading) was added to a solution of **L,L-59** (1.7 mg, 0.00159 mmol) in MeOH (2 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium on carbon was filtered and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **L,L-60** in quantitative yield and as a colorless oil. $[\alpha]_D$ –97.1 (*c* 0.07, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 5.35 (d, 1 H, $J_{1',2'}$ = 4.1 Hz, H-1'), 4.66 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1), 3.99 (dd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{5,6eq}$ = 4.1 Hz, H-5/H-5'), 3.84 (d, 1 H, $J_{2,3}$ = 9.7 Hz, H-3/H-3'), 3.82 (d, 1 H, $J_{2,3}$ = 9.5 Hz, H-3/H-3'), 3.79–3.73 (m, 3 H, H-2, H-2', H-9/H-9'), 3.73–3.69 (m, 2 H, H-7/H-7', H-5/H-5'), 3.55 (dd, 1 H, $J_{5,6ax}$ = 12.0 Hz, $J_{5,6eq}$ = 4.4 Hz, H-7/H-7'), 3.52 (s, 1 H, H-9/H-9'), 3.39 (s, 3 H, OCH_3), 1.95 (ddd, 1 H, $J_{5,6ax}$ = 12.0 Hz, $J_{6eq,6ax}$

= 12.0 Hz, $J_{6ax,7}$ = 12.0 Hz, H-6_{ax}/H-6'$_{ax}$), 1.87 (ddd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{6eq,6ax}$ = 12.3 Hz, $J_{6ax,7}$ = 12.3 Hz, H-6_{ax}/H-6'$_{ax}$), 1.78 (ddd, 1 H, $J_{6eq,6ax}$ = 12.0 Hz, $J_{5,6eq}$ = 4.1 Hz, $J_{6eq,7}$ = 4.1 Hz, H-6_{eq}/H-6'$_{eq}$), 1.75 (ddd, 1 H, $J_{6eq,6ax}$ = 11.8 Hz, $J_{5,6eq}$ = 4.1 Hz, $J_{6eq,7}$ = 4.1 Hz, H-6_{eq}/H-6'$_{eq}$), 1.39 (s, 3 H, H-10'/H-10), 1.29 (s, 3 H, H-10'/H-10); $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3OD, δ_C) 101.6 (C-1), 94.2 (C-1'), 85.7 (C-8/C-4/C-4'/C-8'), 80.8 (C-9/C-9'), 79.8 (C-9/C-9'), 78.5 (C-8/C-4/C-4'/C-8'), 77.0 (C-3/C-3'), 76.9 (C-3/C-3'), 74.4 (C-8/C-4/C-4'/C-8'), 74.3 (C-8/C-4/C-4'/C-8'), 74.2 (C-7/C-7'), 72.1 (C-7/C-7'), 71.1 (C-2/C-2'), 70.9 (C-2/C-2'), 67.7 (C-5/C-5'), 66.7 (C-5/C-5'), 55.8 (OCH_3), 32.7 (C-6/C-6'), 32.4 (C-6/C-6'), 15.5 (C-10/C-10'), 12.4 (C-10/C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{21}H_{36}NaO_{15}$: 551.1946. Found 551.1944.

Methyl 1,5-α-D-bradyrhizopyranosyl-(1→8)-1,5-α-L-bradyrhizopyranoside (D,L-60). Palladium hydroxide on carbon (4.9 mg, 0.00459 mmol, 20 wt. % loading) was added to a solution of **D,L-59** (8.8 mg, 0.0116 mmol) in MeOH (5 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium hydroxide on carbon was filtered through Celite® and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **D,L-60** in quantitative yield and as a colorless oil. $[\alpha]_D$ +4.0 (*c* 0.1, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 5.27 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1'), 4.63 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1), 3.96 (dd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{5,6eq}$ = 4.2 Hz, H-5/H-5'), 3.83–3.66 (m, 7 H, 2 x H-2, 2 x H-3, H-5/H-5', H-7/H-7', H-9/H-9'), 3.53 (dd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{5,6eq}$ = 4.4 Hz, H-7/H-7'), 3.50 (s, 1 H, H-9/H-9'), 3.37 (s, 3 H, OCH_3), 1.95 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6_{ax}/H-6'$_{ax}$), 1.87 (ddd, 1 H, $J_{5,6ax}$ = 12.1 Hz, $J_{6eq,6ax}$ = 12.1 Hz, $J_{6ax,7}$ = 12.1 Hz, H-6_{ax}/H-6'$_{ax}$), 1.77 (ddd, 1 H, $J_{6eq,6ax}$ = 11.9 Hz, $J_{5,6ax}$ = 4.4 Hz, $J_{6ax,7}$ = 4.4 Hz, H-6_{eq}/H-6'$_{eq}$), 1.74 (ddd, 1 H, $J_{6eq,6ax}$ = 11.9 Hz, $J_{5,6ax}$ = 4.4 Hz, $J_{6ax,7}$ = 4.4 Hz, H-6_{eq}/H-6'$_{ax}$), 1.35 (s, 3 H, H-10/H-10'), 1.26 (s, 3 H, H-10 /H-10'); $^{13}C\{^{1}H\}$ NMR (125

MHz, CD_3OD, δ_C) 101.5 (C-1), 94.4 (C-1'), 85.9 (C-8/C-8'/C-4/C-4'), 80.7 (C-9/C-9'), 78.7 (C-9/C-9'), 78.5 (C-8/C-8'/C-4/C-4'), 76.8(2) (C-3/C-3'), 76.8(1) (C-3/C-3'), 74.3(4) (C-8/C-8'/C-4/C-4'), 74.3(2) (C-8/C-8'/C-4/C-4'), 74.1 (C-7/C-7'), 72.5 (C-2'), 71.0 (C-7/C-7'), 70.9 (C-2), 68.0 (C-5/C-5'), 66.7 (C-5/C-5'), 55.8 (OCH_3), 32.8 (C-6/C-6'), 32.6 (C-6/C-6'), 15.5 (C-10/C-10'), 13.3 (C-10/C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{21}H_{36}NaO_{15}$: 551.1946. Found 551.1938.

Methyl 1,5-α-L-bradyrhizopyranosyl-(1→8)-1,5-α-D-bradyrhizopyranoside (L,D-60). Palladium hydroxide on carbon (7.0 mg, 0.00660 mmol, 20 wt. % loading) was added to a solution of **L,D-59** (3.7 mg, 0.0.0347 mmol) in MeOH (4 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2 (g) and stirred overnight. The palladium hydroxide on carbon was filtered and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **L,D-60** in quantitative yield and as a colorless oil. The R_f, ^1H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained for compound **D,L-60** previously described. $[\alpha]_D$ –5.0 (*c* 0.1, $CHCl_3$).

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-D-bradyrhizopyranosyl-(1→7)-3,9-*O*-benzylidene-1,5-α-D-bradyrhizopyranoside (D,D-61). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **D,D-51** (3.0 mg, 0.00256 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until the pH of the solution was neutral and then the mixture was filtered. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **D,D-61** (2.7 mg, 99%) as a colorless oil. R_f 0.23 (2:3 hexanes–EtOAc); $[\alpha]_D$ +24.8 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.57–7.53 (m, 2 H, Ar), 7.43–7.23 (m, 28 H, Ar), 5.75 (s, 1 H, C<u>H</u>Ar), 5.37 (d,

1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 5.13 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 5.08 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.92 (d, 1 H, J = 11.2 Hz, C$\underline{H}_2$Ar), 4.89 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1), 4.82 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 4.79 (d, 1 H, J = 11.0 Hz, C$\underline{H}_2$Ar), 7.43–7.23 (m, 4 H, 3 x C$\underline{H}_2$Ar, H-1'), 4.52 (d, 1 H, J = 11.6 Hz, C$\underline{H}_2$Ar), 4.17 (ddd, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{2,OH}$ = 9.4 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 4.07 (s, 1 H, OH), 3.96 (d, 1 H, $J_{2',3'}$ = 9.0 Hz, H-3'), 3.90 (d, 1 H, $J_{2,3}$ = 9.4 Hz, H-3), 3.80 (dd, 1 H, $J_{2',3'}$ = 9.0 Hz, $J_{1',2'}$ = 7.7 Hz, H-2'), 3.74 (br dd, 1 H, $J_{5',6'ax}$ = 10.8 Hz, $J_{5',6'eq}$ = 5.9 Hz, H-5), 3.68 (dd, 1 H, $J_{5,6ax}$ = 10.8 Hz, $J_{5,6eq}$ = 5.7 Hz, H-7), 3.64 (dd, 1 H, $J_{6'ax,7'}$ = 11.4 Hz, $J_{6'eq,7'}$ = 5.3 Hz, H-7'), 3.60–3.57 (m, 2 H, H-9, H-9'), 3.52 (s, 3 H, CH_3O), 3.25 (dd, 1 H, $J_{6ax,7}$ = 11.6 Hz, $J_{6eq,7}$ = 4.2 Hz, H-5'), 2.80 (d, 1 H, $J_{4OH,5}$ = 1.7 Hz, C-4-OH), 2.25–2.11 (m, 4 H, 2 x H-6, 2 x H-6'), 2.72 (br s, 1H, C-2-OH), 1.63 (s, 3 H, H-10'), 1.39 (s, 3 H, H-10); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ_C) 139.5(2) (Ar), 139.5(1) (Ar), 138.2 (Ar), 138.0 (Ar), 137.8 (Ar), 136.7 (Ar), 129.4 (Ar), 128.6 (Ar), 128.4(4) (Ar), 128.4(2) (Ar), 128.3(4) (Ar), 128.2(8) (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 127.1 (Ar), 127.0 (Ar), 126.3 (Ar), 105.3 (C-1'), 103.1 (C$\underline{H}$Ar), 100.8 (C-1), 89.1 (C-9'), 83.8 (C-8'), 82.5 (C-9), 82.4(3) (C-7/C-7'), 82.3(9) (C-7/C-7'), 81.3 (C-3), 80.5 (C-3'), 80.2 (C-2'), 76.5 (C-4/C-4'), 76.0 (C-8), 75.8 (C$\underline{H}_2$Ar), 74.9 (C$\underline{H}_2$Ar), 72.4 (C-5'), 71.5 (C$\underline{H}_2$Ar), 68.9 (C$\underline{H}_2$Ar), 67.6 (C-2), 67.2 (C-4/C-4'), 66.2 (C$\underline{H}_2$Ar), 65.2 (C-5), 56.1 (OCH_3), 31.0 (C-6/C-6'), 29.1 (C-6/C-6'), 17.5 (C-10), 11.6 (C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{63}H_{70}NaO_{15}$: 1089.4607. Found 1089.4628.

Methyl 2,4,7,8,9-penta-*O*-benzyl-1,5-β-L-bradyrhizopyranosyl-(1→7)-3,9-*O*-benzylidene-1,5-α-L-bradyrhizopyranoside (L,L-61). A solution of MeONa in MeOH (0.15 mL, 0.5 M in MeOH) was added to **L,L-51** (1.8 mg, 0.00154 mmol) in MeOH (3 mL). The mixture was stirred for 3 h at rt. Amberlite® IR120 H^+ form resin was added until the pH of the solution was neutral and the mixture was filtered. The filtrate was concentrated and the resulting crude product was

purified by silica gel column chromatography (3:2 hexanes–EtOAc) to give **L,L-61** (1.4 mg, 88%) as a colorless oil. The R_f, ^{1}H NMR, ^{13}C{^{1}H} NMR and MS data correspond to that obtained for compound **D,D-61** previously described. $[\alpha]_D$ –23.6 (*c* 0.1, $CHCl_3$).

Methyl 1,5-β-D-bradyrhizopyranosyl-(1→7)-1,5-α-D-bradyrhizopyranoside (D,D-62). Palladium hydroxide on carbon (5.3 mg, 0.00752 mmol, 20 wt. % loading) was added to a solution of **D,D-61** (2.8 mg, 0.00262 mmol) in MeOH (3 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2 (g) and stirred overnight. The palladium hydroxide on carbon was filtered through Celite® and the filtrate concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **D,D-62** in quantitative yield and as a colorless oil. $[\alpha]_D$ +24.0 (*c* 0.1, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 4.66 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.53 (d, 1 H, $J_{1',2'}$ = 7.9 Hz, H-1'), 3.79 (d, 1 H, $J_{2,3}$ = 9.5 Hz, H-3), 3.75 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 4.1 Hz, H-2), 3.66 (dd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{5,6ax}$ = 4.4 Hz, H-5/H-5'), 3.62–3.58 (m, 2 H, H-3', H-7/H-7'), 3.54 (dd, 1 H, $J_{2',3'}$ = 9.2 Hz, $J_{1',2'}$ = 7.9 Hz, H-2'), 3.52 (s, 1 H, H-9/H-9'), 3.51 (dd, 1 H, $J_{6ax,7}$ = 12.3 Hz, $J_{6eq,7}$ = 4.1 Hz, H-7/H-7'), 3.47 (s, 1 H, H-9/H-9'), 3.40 (s, 3 H, OCH_3), 3.38 (dd, 1 H, $J_{5,6ax}$ = 11.6 Hz, $J_{5,6ax}$ = 4.0 Hz, H-5/H-5'), 2.03 (ddd, 1 H, $J_{6eq,6ax}$ = 12.3 Hz, $J_{5,6eq}$ = 4.6 Hz, $J_{6eq,7}$ = 4.6 Hz, H-6_{eq}/H-$6'_{eq}$), 1.97 (ddd, 1 H, $J_{5,6ax}$ = 12.3 Hz, $J_{6eq,6ax}$ = 12.3 Hz, $J_{6ax,7}$ = 12.3 Hz, H-6_{ax}/H-$6'_{ax}$), 1.96 (ddd, 1 H, $J_{5,6ax}$ = 12.0 Hz, $J_{6eq,6ax}$ = 12.0 Hz, $J_{6ax,7}$ = 12.0 Hz, H-6_{ax}/H-$6'_{ax}$), 1.85 (ddd, 1 H, $J_{6eq,6ax}$ = 12.0 Hz, $J_{5,6eq}$ = 4.4 Hz, $J_{6eq,7}$ = 4.4 Hz, H-6_{eq}/H-$6'_{eq}$), 1.36 (s, 3 H, H-10/H-10'), 1.28 (s, 3 H, H-10/H-10'); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD, δ_C) 106.7 (C-1'), 101.6 (C-1), 84.3 (C-3'/C-7/C-7'), 80.7 (C-9'/C-9), 80.2 (C-9'/C-9), 80.1 (C-3'/C-7/C-7'), 78.6 (C-8/C-8'/C-4/C-4'), 78.5 (C-8/C-8'/C-4/C-4'), 77.0 (C-3), 74.0(3) (C-3'/C-7/C-7'), 73.9(8) (C-8/C-8'/C-4/C-4'), 73.8 (C-2'), 73.6 (C-8/C-8'/C-4/C-4'), 72.2 (C-2), 70.9 (C-5/C-5'), 67.1 (C-5/C-5'), 55.9 (OCH_3), 33.1 (C-6/C-6'), 32.3 (C-6/C-6'), 16.4 (C-

10/C-10'), 15.4 (C-10/C-10'). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{21}H_{36}NaO_{15}$: 551.1946. Found 551.1942.

Methyl 1,5-β-L-bradyrhizopyranosyl-(1→7)-1,5-α-L-bradyrhizopyranoside (L,L-62). Palladium on carbon (2.6 mg, 0.00245 mmol, 10 wt. % loading) was added to a solution of **L,L-61** (1.4 mg, 0.00131 mmol) in MeOH (1.5 mL) under Ar. The reaction mixture was then placed under a positive pressure of H_2(g) and stirred overnight. The palladium on carbon was filtered and the filtrate was concentrated. The resulting crude product was purified by reverse phase column chromatography (C-18 silica gel, H_2O) to give **L,L-62** in quantitative yield and as a colorless oil. The R_f, ^{1}H NMR, $^{13}C\{^1H\}$ NMR and MS data correspond to that obtained for compound **D,D-62** previously described. $[\alpha]_D$ –17.1 (*c* 0.07, CH_3OH).

Test of reactive oxygen species (ROS)

The generation of ROS was measured as peroxide with a luminol assay as described Erbs et al. *Chem. Biol.* 2008, *15*, 438–448) with a few adaptations. Leaf strips of 6 weeks old *A. thaliana* (cv. Columbia) were cut and left overnight in water (pH 5.5). The next day 240 U of horseradish peroxidase, 20µM luminol, together with the synthetic glycan (100 µg/mL H_2O) to be tested, *Xanthomonas campestris* pv campestris LPS (100 µg/mL H_2O, acting as a positive control) or equivalent volume of water controls were added. Luminescence was measured every 5 second in a Sirius Single Tube Luminometer (Berthold Detection Systems GmbH) for 30 min after the addition of the elicitor.

Supporting Information

NMR data for all new compounds and details on X-ray crystal structures of 9 and 37α. This material is available free of charge via the Internet at http://pubs.acs.org.

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