Reactivity and selectivity in glycosylation reactions

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Chapter 7

Synthesis of C-2- and C-5-modified furanosides

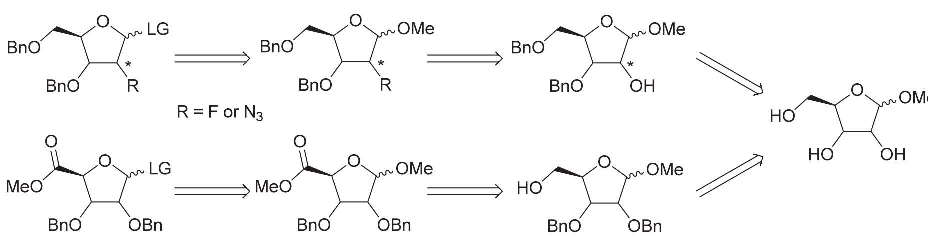
Introduction

Furanosides are key structural components in a variety of bacterial and plant oligosaccharides.[1–3] In this framework, the glycosylation of furanosides has been studied to obtain specific target oligosaccharides with the required anomeric configuration. Furanosylation is more extensively investigated for the synthesis of modified nucleosides and oligonucleotides.[4–6] Besides structural variants, in which the ring oxygen is replaced by sulfur, selenium, nitrogen, or carbon, furanosides with differently configured amino or fluoro substituents have been studied.[7–9] Uronic acid furanosides occur in natural compounds and have attracted attention as biomimics. Modified (oligo)nucleotides are studied as potential therapeutics and as radio-tracer compounds (primarily ^{18}F, but also ^{11}C, ^{13}N) in Positron Emission Tomography (PET).[10–13] Despite their biological relevance, the synthesis of the differently substituted furanosides and their glycosylating properties are scarcely investigated.[5] The development of effective routes of synthesis for these compounds and insight in their reactivity will contribute to the application of these saccharides.[14] For instance, oligosaccharides containing furanosyl moieties can be relevant for the development of carbohydrate based vaccines.[4,7,15] Furthermore, insight in the reactivity of differently substituted furanosides will be a valuable asset to understand the mechanisms of the glycosylation reaction of both furanosides and pyranosides. This chapter describes the synthesis of all four diastereoisomers of the D-pentofuranosides as their 2-fluoro, 2-azido, and 5-uronic acid derivatives. The influence of these functional groups in glycosylation reactions is the subject of Chapter 8, where they are studied using experimental and computational means.

Results and discussion

The strategy to obtain the three modifications on all four diastereoisomers is shown in Scheme 1. The C-2-modified furanoside donors were obtained by inversion of the 2-hydroxy group in otherwise protected methyl furanosides. The C-5-methyl esters were generated from their suitably protected 5-hydroxy methyl furanosides. Subsequent anomeric hydrolysis and installation of the anomeric leaving group (LG), will then give all twelve D-pentofuranoside donors, four configurations for each functional group.

Scheme 1. Retrosynthesis of C-2- and C-5-modified furanosides.

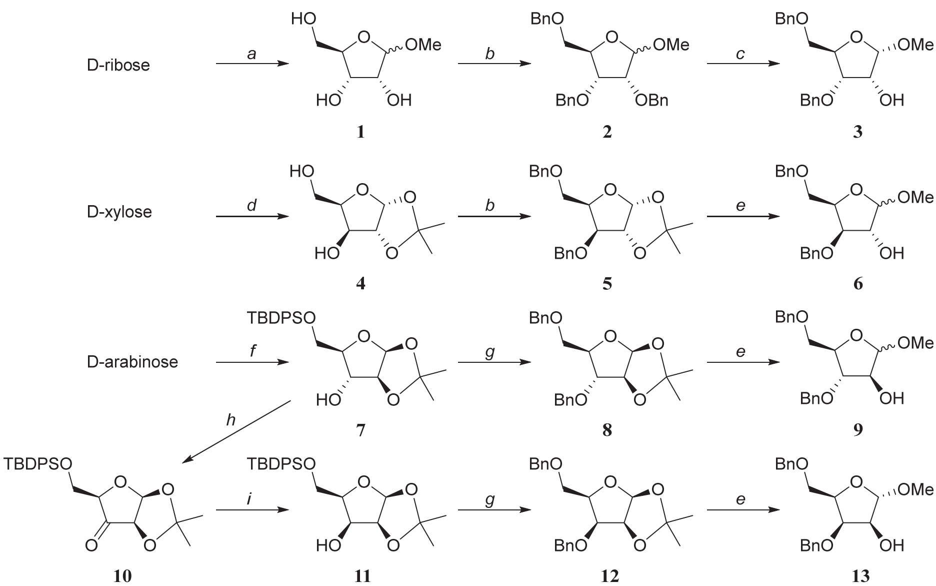


*Center of inversion. LG = leaving group.

The syntheses of the protected 2-hydroxy pentofuranoses is outlined in Scheme 2. Adapting literature procedures, the 2-hydroxy pentofuranoses could be obtained on large scale (10-150 mmol). *Ribo*-configured structure **3** was prepared by treatment of fully protected **2** with $SnCl_4$, inducing both anomerization and regioselective benzyl cleavage.[16] Similarly protected *xylo*se derivative **6** was obtained from 1,2-isopropylidene-xylofuranose **4** in high yield (97%) by benzylation and CSA mediated acetal exchange.

The syntheses of *arabino*- and *lyxo*-derivatives **9** and **13** required more steps, as di-isopropylidenation of arabinose yields the pyranoside and regioselective removal of the C-2–*O*-benzyl, as reported for ribose derivative **3**, is unknown for these epimers.[17] First, the primary alcohol of arabinose was protected with a bulky TBDPS group to force the carbohydrate in the furanose form. Subsequent isopropylidene protection gave **7**. Conveniently, the epimeric lyxose compound could be easily obtained from **7** by an oxidation-reduction sequence.[18] Dess-Martin oxidation proved superior over the Sarett (CrO_3, pyridine in DCM)[19] and Moffat (DMSO, Ac_2O)[20] oxidations both in yield and ease of purification.[21] Reduction of ulose **10** with $NaBH_4$ gave optically pure *lyxo*-configured **11**. Both **7** and **11** were silyl-deprotected and benzylated in a one-pot procedure using KOH and BnCl in THF.[22] An alternative two-step reaction sequence of removing the TBDPS (with TBAF, AcOH in THF) and subsequent benzylation (NaH, BnBr in DMF) was less efficient. Finally, acetal exchange yielded both the *arabino*-configured **9** and *lyxo*-configured **13**.

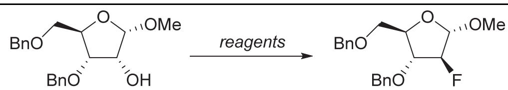
Scheme 2. Synthesis of 2-hydroxy pentofuranosides **3**, **6**, **9**, and **13**.



Reagents and conditions: (a) AcCl, MeOH; (b) BnBr, NaH, DMF, **2**: 89% (two steps); (c) $SnCl_4$, DCM, 92%; (d) *i*. H_2SO_4, acetone; *ii*. HCl, H_2O, aceton, 90% (two steps); (e) CSA, MeOH, **6**: 97% (two steps), **9**: 91%, **13**: 84%; (f) *i*. TBDPSCl, imidazole, DMF; *ii*. dimethoxypropane, CSA, DCM, 53% (two steps); (g) BnCl, KOH, THF, **8**: 71%, **12**: 99%; (h) Dess-Martin periodinane, DCM, 77%; (i) $NaBH_4$, DCM, MeOH, 73%.

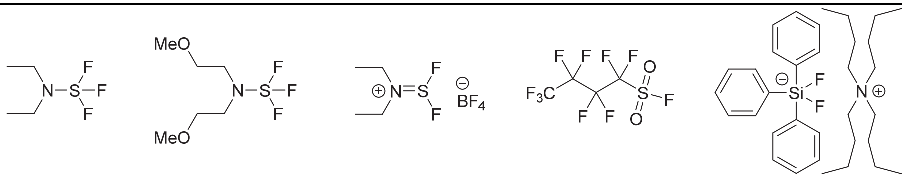
Having synthesized all 2-hydroxy pentofuranosides (**3**, **6**, **9**, **13**), the inversion procedures were investigated. Fluoride substitutions were considered first, since a range of fluorination reagents are commercially available. Table 1 summarizes the results of the direct substitution reactions on ribose derivative **3**. Unfortunately, none of the reagents was successful in substituting the 2-hydroxy group to provide 2-fluoroarabinoside **18** in decent yield.

Table 1. Inversion of riboside **3** with different fluorination reagents.



3 → **18**

Entry	Scale (mmol)	Reagents[a] (eq.)	Temperature (°C)	Time (h)	Yield (%)
1	0.5	DAST (1.8)	-60 to 20	72	12
2	2.0	DAST (4)	-60 to 45	24	13
3	0.5	Deoxo-Fluor® (1.2)	0 to 20	72	15
4	0.5	PFBS-F (2.2), TBAT (0.8), DiPEA (2.5)	0 to 20	30	< 25
5	0.5	XtalFluor-E® (1.5), $3HF{\cdot}Et_3N$ (1.5)	0 to 20	30	-



DAST Deoxo-Fluor XtalFluor-E PFBS-F TBAT

[a]Concentration for all reactions was 0.2 M in DCM.

Therefore, the 2-hydroxy groups in the projected furanoses were converted into the corresponding triflates followed by substitution with fluoride or azide anions, respectively.[23] Figure 1 provides an overview of the triflates, readily prepared from the alcohols, the targeted substitution products as well as the side products obtained in the reactions (deviations colored red).

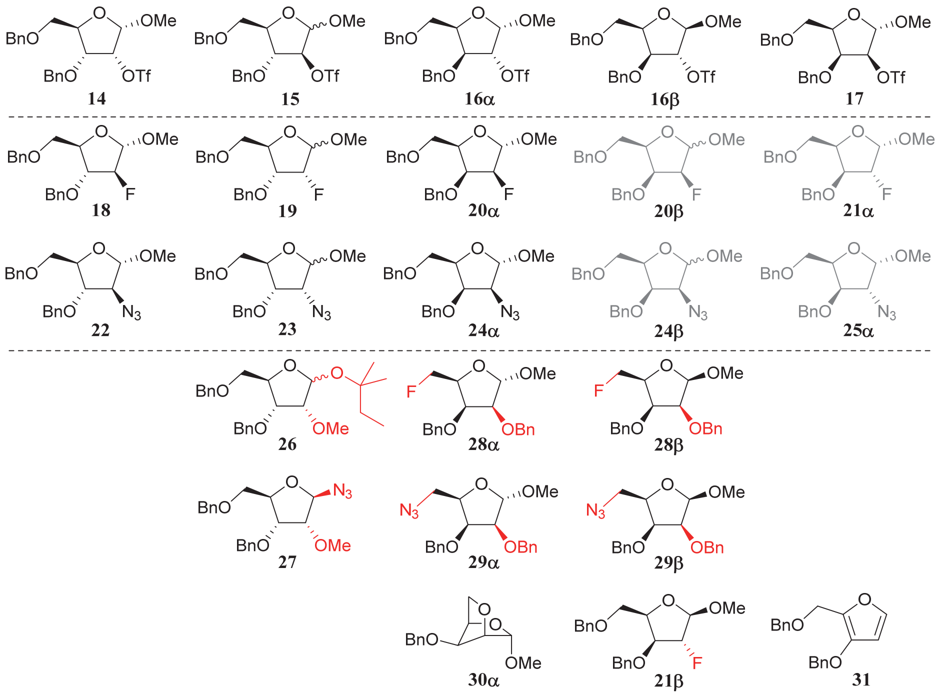
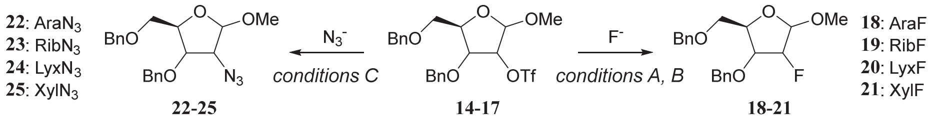


Figure 1. Furanosyl C-2–*O*-triflates (**14-17**) and their substitution products by fluoride inversion (**18-21**), and azide inversion (**22-25**). Major side products isolated from the reaction mixture (**26-31**), red color indicates the deviations from the expected products. Formation of the structures in grey was not observed.

Table 2 reports the outcome of all substitution reactions. Entries 1-3 show that *ribo*-configured triflate **14** is readily substituted with the fluoride (TBAF, or CsF) and azide anions (NaN_3), respectively. The yield of the fluoride substitution on triflate **14** with TBAF in THF (71%) was increased to 86% when CsF was used in a polar protic solvent (*tert*-amyl alcohol, entry 2).[24] Azide **22** was obtained in 93% yield. Substitution of the arabinotriflate **15** (a mixture of anomers), with fluorine and azide nucleophiles gave **19** and **23**, respectively in reasonable to good yields. As reported by the group of Woerpel,[22] only the β-anomer of **15** reacted with TBAF (entry 4), and the triflate of the α-anomer could be recovered.

Under conditions B (entry 5) both anomers of **15** reacted and despite the generation of side product **26**, the yield was increased to 63%. Azide **23** was obtained in high yield, although a similar migration to side product **27** occurred during the azide substitution (entry 6).[25] The possible reaction pathways for the formation of these side products are displayed in Figure 2. The anomeric methoxy substituent can substitute the neighboring triflate and form a highly reactive methyl oxiranium ion, which is attacked with inversion at the anomeric center, explaining the stereochemistry of the anomeric azide side product found (**27**). Alternatively, an S_N1 reaction on the oxocarbenium ion, formed upon opening of the oxiranium ion, happens in entry 4 with the solvent, explaining the mixture of anomers found in product **26**.

Table 2. Results of substitution reactions on triflates **14-17**.



Entry	Triflate[b]	Conditions[a]	Substitution product	Yield (%)	Side product 1	Side product 2
1	**14**	A (TBAF)	**18**	71	-	-
2	**14**	B (CsF)	**18**	86	-	-
3	**14**	C (N_3)	**22**	93	-	-
4	**15**	A	**19**, β only	42	**15α**, 17%	-
5	**15**	B	**19**	63	**26**[g], 17%	-
6	**15**	C	**23**	86[c]	**27**[c]	-
7	**16α**	A[d]	**20α**	44	**6**, 17%	**16α**, 3%
8	**16α**	B[e]	**20α**	-	**28α**, 57%	**30α**, 21%
9	**16α**	C[f]	**24α**	67	**29α**, 12%	**30α**, 7%
10	**16β**	A[d]	**20β**	-	**28β**, 18%	**31**[h]
11	**16β**	B	**20β**	-	**28β**, 47%	**21β**, 10%
12	**16β**	C[f]	**24β**	-	**29β**, 30%	-
13	**17**	A,B,C	**21 / 25**	-	**31**[h]	-

[a]*Reagents and conditions*: (A) 0.2 M solution in THF, 2.5 eq. TBAF, 0°C to 20°C, overnight; (B) 0.35 M solution in *tert*-amyl alcohol, 4 eq. CsF, 90°C, overnight; (C) 0.2 M solution in DMF, 5 eq. NaN_3, 80°C, 2 h. [b]See experimental section for the general procedure of the triflate formation. [c]Combined yield of **23** and **27**, as a 4:1 mixture. [d]70°C, 5 h for entry 7, overnight for entry 10. [e]110°C overnight. [f]overnight. [g]α : β = 88 : 12. . [h]Yield not determined.

Both anomers of xyloside **6** were obtained, therefore both triflates **16α** and **16β** could be independently studied. Substitution of **16α**, using CsF in *tert*-amyl alcohol at 90°C, only gave the side products 5-fluorolyxoside **28α** and the bicycle **30α** (entry 8). The formation of these products can be explained by participation of the C-5–*O*-benzyl group followed by substitution from the least hindered sites (path A and B, Figure 2B), to yield 5-fluorolyxoside **28α** and the bicycle **30α**, respectively. No products arising from double inversion (path C) or elimination were detected. Fortunately, heating **16α** in a

THF solution with TBAF for 5 hours did give the desired fluoride inversion and product **20α** was isolated in 44% yield (entry 7). Interestingly, the only observed side products were unreacted and hydrolysed triflate and no products derived from C-5–*O*-benzyl participation were found. Subjection of **16α** to conditions C led to effective azide substitution to give the desired product **24α** (entry 9) together with small amounts of bicycle **30α** and 5-azidolyxoside **29α** originating from pathways A and B, respectively (Figure 2B).

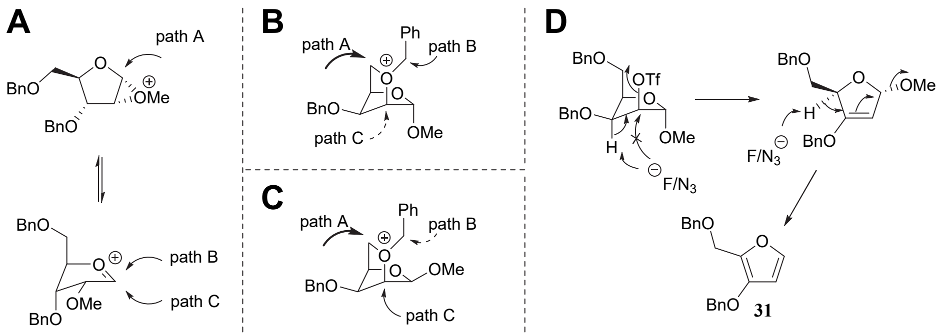


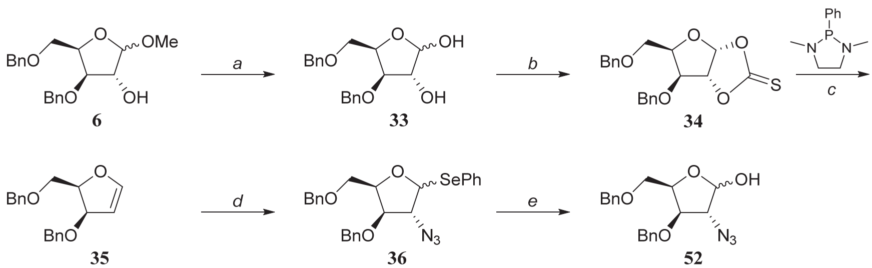
Figure 2. Mechanistic pathways underlying the formation of side products **26**-**31**.

Similar reactions with β-xylotriflate **16β** did not lead to the required substitutions (entries 10-12, Table 2). Both conditions A and B gave 5-fluoroxyloside **28β**, and condition A led to elimination product **31**, while condition B gave **21β**. The more nucleophilic and basic fluoride ion in condition A resulted in substitution on triflate **16α**, but elimination to furan **31** for **16β**. The formation of 2-fluoroxyloside **21β** with net retention of configuration can be explained by a double inversion mechanism as shown in Figure 2C (path C). Since **21β** is one of the target compounds and its formation from lyxotriflate **17** was ineffective, generation of **21β** through this route proved advantageous. Azide substitution at the C-5-position (path A) resulted in the formation of the 5-azidolyxoside side product **29α**.

All substitutions with lyxotriflate **17** to attain the target C-2-substituted xylofuranosides were ineffective and resulted in the elimination product **31**. The fast elimination of triflate **17** into furan **31** can be explained by the steric hindrance that is experienced during nucleophilic attack and the favorable H-OTf alignment for elimination (Figure 2D).[26]

An alternative approach towards the missing C-2-substituted xylofuranosides **21** and **25** was devised (Scheme 3). This synthetic route started with the preparation of glycal **35**. Among the various procedures to generate glycals,[27–31] two methods, using relatively neutral conditions, were examined. Direct conversion of diol **33** by the Garegg olefination conditions (I_2, Ph_3P, imidazole) led to the glycal but it could only be isolated in low yield.[32–34] A two-step procedure via thionocarbonate **34** proved more effective and this method was reproducible and scalable.[35,36] This Corey-Winter olefination method cleanly converted **34** into glycal **35** when 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine was used as desulfurization agent.[37]

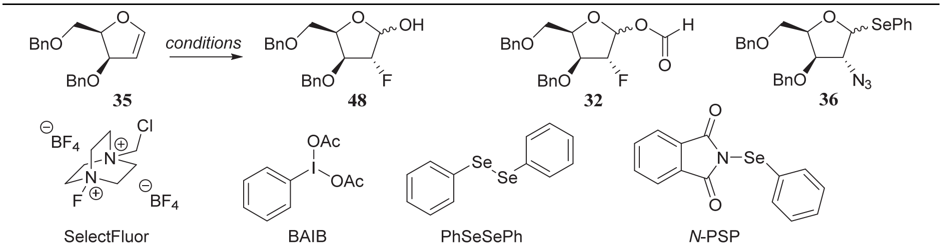
Scheme 3. Synthetic route towards 2-azidoxylose **52** via azidophenylselenation of glycal **35**.



Reagents and conditions: (a) TFA, THF, H_2O, 84%; (b) DMAP, DiPEA, thiophosgene, DCM, 78%; (c) 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine, toluene, 76%; (d) *N*-(phenylseleno)phthalimide, $TMSN_3$, TBAF, DCM, 65%; (e) NIS, H_2O, acetone, THF, 87%.

The glycal **35** can be transformed to 2-fluoroxyloside **48** by electrophilic fluorination or to 2-azidoselenoxyloside **36** by azidophenylselenation respectively, see Table 3. Although the diastereoselectivity of the addition with SelectFluor in 4:1 DMF/H_2O was good (9:1, *xylo*:*lyxo*),[38] the yield was low (**48**, 36%) and a 2-fluoro-1-*O*-formyl (**32**) side product was isolated in 18%, resulting from reaction with DMF. Standard azidophenylselenation conditions (entry 2) delivered **36** as a 9:1 *xylo*:*lyxo* product mixture, which proved difficult to purify. The incompatibility of this reagent system with *O*-benzyl groups has been noted before[39,40] and a switch to an alternative reagent proved beneficial. The *N*-(phenylseleno)phthalimide (*N*-PSP) mediated azidophenylselenation proceeded much cleaner and with equally good regio- and diastereoselectivity to give product **36** (entry 3).[41–46]

Table 3. Conversion of glycal **35** to 2-fluoro- and 2-azidoxylosides **48** and **36**.

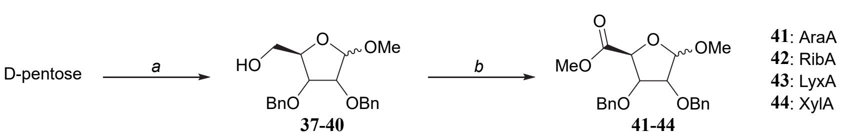


Entry	Conditions[a]	Product, yield[c]	*xylo*:*lyxo*[c]
1	SelectFluor, DMF, H_2O	**48**, 36% **32**, 18%	9 : 1
2	$TMSN_3$, BAIB, PhSeSePh, DCM	**36**, 50%	9 : 1
3	$TMSN_3$, TBAF, *N*-PSP, DCM	**36**, 65%	9 : 1

[a]Reaction time was 20 h, stirred from 0°C to 20°C. [b]Yield of the isolated *xylo*-configuration. [c]Ratio obtained by crude ^{1}H-NMR.

With the critical functionalizations at C-2 completed, the attention was turned to modification of the C-5-position. The general synthetic route towards the uronic acid esters is presented in Scheme 4. The intermediates **37-40** are synthesized from the D-aldopentose by a straightforward four-step procedure giving roughly the same yield for all the diastereoisomers (41%-50%). The subsequent oxidation reaction was carried out in a biphasic system of DCM and H_2O with catalytic TEMPO as the oxidating agent and BAIB as co-oxidant. Yields of the oxidation were high but loss of product was observed in the subsequent methylation step to give **41-44**. Shorter reaction times and aqueous work up, without concentration of the reaction mixture, were crucial to a higher isolated yield. Quenching with acetic acid instead of water or methanol also helped to increase the yield.

Scheme 4. Synthesis of 5-uronic acid functionalized methyl glycosides **41**-**44**.

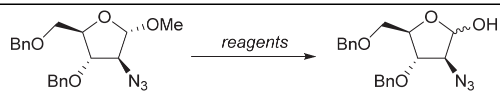


Reagents and conditions: (a) *i*. AcCl, MeOH; *ii*. TrtCl, Et_3N, DMF; *iii*. BnBr, NaH, DMF; *iv*. pTsOH·H_2O, MeOH, **37**: 41%, **38**: 43%, **39**: 46%, **40**: 50%, (all over four steps); (b) *i*. TEMPO, BAIB, DCM, H_2O; *ii*. MeI, K_2CO_3, DMF, **41**: 70%, **42**: 87%, **43**: 89%, **44**: 88%, (all over two steps).

With all methyl furanosides **18**-**24** and **41**-**44** available, the conversion of these furanosides into suitable glycosyl donors was undertaken. The first step comprises the hydrolysis of the methyl acetals to give lactols **45**-**56**. Because of the electron-withdrawing nature of the azido, fluoro, and uronic acid ester substituents in the furanosides, the anomeric acetals proved relatively stable and optimization of the acidic hydrolysis was required to prevent concomitant C-5–*O*-benzyl cleavage. The results of the optimization studies are summarized in Table 4.

In an attempt to obtain the acetyl donor **57**, methyl furanoside **22** was treated with H_2SO_4 in acetic anhydride, but this led to formation of diacetyl compound **61** instead (entry 1, see experimental section). Heating an 80% aq. AcOH solution of **22** overnight (entry 2) gave no conversion, and upon HCl addition decomposition occurred (entry 3).[47] Aqueous 70-90% TFA at room temperature (entries 5-7) gave **49** in low yield with significant concurrent decomposition.[48] Fortunately, using 50% aqueous TFA at 75°C significantly improved the outcome (entry 10), and also the use of 80% aqueous formic acid at this temperature provided the target compound. The best results were obtained with formic acid at a temperature of 60°C (entries 10 and 11).[24]

Table 4. Evaluation of acidic hydrolysis conditions.



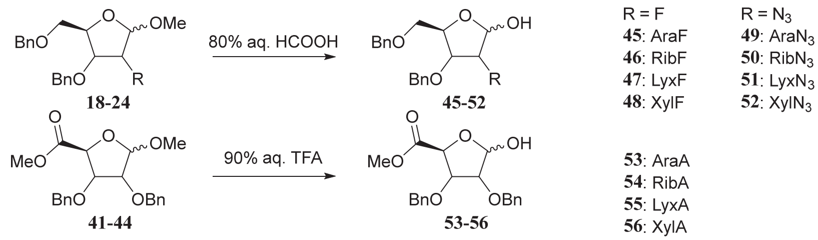
22 → **49**

Entry	Conc.[a]	Conditions	Temperature (°C)	Time (h)	Yield (%)
1	0.3 M	1.5% H_2SO_4 in Ac_2O	0	0.3	[b]
2	0.1 M	80% aq. AcOH	115	24	-
3	0.2 M	20% 5M HCl in AcOH	85	16	-
4	0.3 M	Ph_3C-BF_4 in DCM	20	70	-
5	0.2 M	90% aq. TFA	20	40	17
6	0.2 M	80% aq. TFA	20	300	23
7	0.2 M	70% aq. TFA	20	300	50
8	0.1 M	50% aq. TFA	75	24	50
9	0.05 M	80 aq. formic acid	75	24	51
10	0.1 M	50% aq. TFA	60	80	73
11	0.05 M	80 aq. formic acid	60	80	76

[a]Concentration. Scale is 0.4 mmol except entry 1 (1.0 mmol) and entries 10 and 11 (1.5 mmol). [b]Yield of 1,5-di-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α/β-D-arabinofuranoside **61** was 85%.

The hydrolysis of all other furanosides are listed in Table 5. The formic acid conditions proved effective for the 2-fluoro (entries 1-4), and 2-azido (entries 5-7) series, to give the corresponding lactols in good yield. The reactivity of the different substrates varied greatly, and changing the temperature and reaction time was needed to push the reactions to completion. The uronic acids (entries 8-11) were hydrolysed with 90% aqueous TFA to give the lactol products in good yield.

Table 5. Hydrolysis reaction results for methyl glycosides **18-24**, and **41-44**.



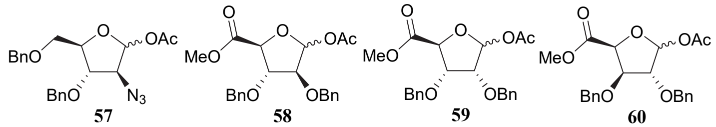
Entry	Substrate	Configuration	Product	Conditions	Temperature (°C)	Time (h)	Yield (%)
1	**18**	AraF	**45**	A	65	64	63
2	**19**	RibF	**46**	A	60	18	78
3	**20**	LyxF	**47**	A	65	6	75
4	**21**	XylF	**48**	A	60	6	75
5	**22**	$AraN_3$	**49**	A	60	80	76
6	**23**	$RibN_3$	**50**	A	65	6	70[a]
7	**24**	$LyxN_3$	**51**	A	60	18	62
8	**41**	AraA	**53**	B	0 to 20	8	60
9	**42**	RibA	**54**	B	0 to 20	7.5	73
10	**43**	LyxA	**55**	B	0 to 20	6	85
11	**44**	XylA	**56**	B	0 to 20	4	90

Reagents and conditions: (A) HCOOH/H_2O (4/1 v/v, 0.05 M); (B) TFA/H_2O (9/1 v/v, 0.2 M). [a]Yield over two steps (including inversion), the combined yield of the 4:1 mixture of **23** and **27** was 89%.

The acetyl donors were prepared by treatment of the lactol precursors with acetic anhydride in pyridine (Table 6). But as a pilot study revealed that TMSOTf catalyzed glycosylations with allyl-trimethylsilane and deuterated triethylsilane were not productive using the acetyl donors even at room temperature, it was decided to generate the trifluoro-*N*-phenylimidate donors (Table 7, **62-73**), as these are more reactive and can be activated under catalytical conditions.[49]

The majority of the imidates were synthesized using an acetone/H_2O mixture and Cs_2CO_3 as a base. However, since some of the reactions were slow and purification

Table 6. Conversion of lactols to acetyl donors **57**-**60**.

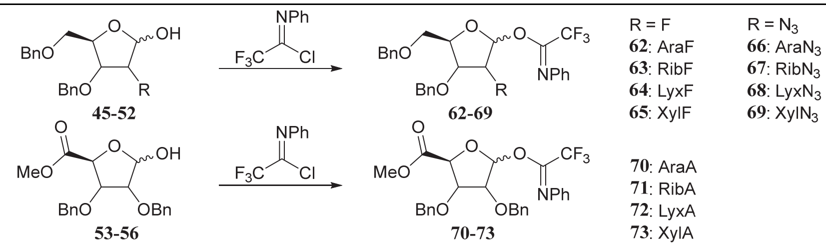


Entry	Substrate	Configuration	Product	α : β	Yield (%)
1	**49**	AraN_3	**57**	2.3 : 1	90
2	**53**	AraA	**58**	5.7 : 1	90
3	**54**	RibA	**59**	0 : 1	91
4	**56**	XylA	**60**	1.2 : 1	98

Reagents and conditions: Ac_2O (1.25 eq.) in pyridine (0.25 M), 0°C to r.t.

issues occurred, separating the target compounds from the hydrolyzed or unreacted 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride, an anhydrous DCM/DBU procedure was explored. These reactions were complete within minutes, successfully generating the target compounds, even though work up and purification led to some degradation.

Table 7. Conversion of lactols **45**-**56** to imidate donors **62**-**73**.



Entry	Substrate	Configuration	Product	Conditions	α : β	Yield (%)
1	**45**	AraF	**62**	A	5 : 1	85 (69 + 16)
2	**46**	RibF	**63**	A	0 : 1	98
3	**47**	LyxF	**64**	A	1 : 0	82
4	**48**	XylF	**65**	A	1 : 2	91
5	**49**	AraN_3	**66**	B	1.6 : 1	71 (44 + 27)
6	**50**	RibN_3	**67**	A	1 : 8	77 (8 + 69)
7	**51**	LyxN_3	**68**	B	1 : 1.2	67 (30 + 37)
8	**52**	XylN_3	**69**	A	1 : 1	100
9	**53**	AraA	**70**	A	1 : 1	97
10	**54**	RibA	**71**	A	0 : 1	85
11	**55**	LyxA	**72**	A	5 : 1	85 (70 + 15)
12	**56**	XylA	**73**	A	0 : 1	81

Reagents and conditions: (A) 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.95 eq.), Cs_2CO_3 (1.1 eq.) in acetone/H_2O (9/1 v/v, 0.2 M), 0°C to r.t. (B) 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.95 eq.), DBU (1 eq.) in DCM (0.25 M), 0°C.

Conclusions

This chapter presents the synthesis of C-2- (2-fluoro, 2-azido) and C-5- (5-methyl uronates) modified furanosides of all four diastereoisomers. While the synthesis of the C-5-modified furanosides was relatively straightforward, the inversion reactions of the C-2-alcohols to provide the azides and fluorides, proved challenging. Eventually all synthetic pitfalls were overcome, leading to the successful synthesis of all twelve pentofuranoside imidate donors. The stereoelectronic effects originating from the newly introduced functional groups on C-2 and C-5 in glycosylation reactions will be discussed in Chapter 8.

Experimental section

General procedure for the formation of 2-*O*-trifluoromethanesulfonyl-furanosides (14-17). A 0.2 M solution of the alcohol (1 eq.) in DCM was cooled to 0°C followed by the addition of pyridine (2 eq.) and Tf_2O (1.2 eq.). After stirring for 40 min the reaction mixture was poured into cold 1 M aq. HCl and extracted twice with DCM. The combined organic layers were washed with cold H_2O, cold sat. aq. $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. After coevaporated with toluene the crude triflated furanoside was dissolved in the solvent required for the next synthetic step.

General procedure for the inversion of 2-*O*-trifluoromethanesulfonyl-furanosides (18-24). Conditions A: The triflate (1 eq.) was dissolved in *tert*-amyl alcohol (0.35 M) and CsF (4 eq.) was added. The reaction mixture was heated overnight at 90°C, followed by aqueous work up. Conditions B: The triflate (1 eq.) was dissolved in THF (0.2 M) and TBAF (1 M in THF, 2.5 eq.) was added at 0°C. The reaction mixture was allowed to reach room temperature and stirred overnight, followed by aqueous work up. Conditions C: The triflate (1 eq.) was dissolved in DMF (0.2 M) and NaN_3 (5 eq.) was added. The reaction mixture was heated for 2 h at 80°C, followed by aqueous work up. Work up conditons: the reaction mixture was diluted with H_2O (volume×10) and extracted with Et_2O three times. The combined organic layers were washed with H_2O, sat .aq. $NaHCO_3$, and brine. The organic layer was dried (MgSO4), filtered and concentrated *in vacuo*. Flash column chromatography (1/0 to 9/1 pentane/EtOAc) provided the target inverted furanosides as colourless oils.

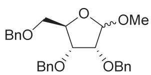
General procedure for the synthesis of primary furanoside alcohols (37-40). To a suspension of D-pentose in MeOH (0.2 M) was added AcCl (0.3-0.9 eq) and the reaction was stirred until complete conversion to the methyl furanoside was observed (TLC). $NaHCO_3$ (s) was added to the reaction mixture until neutral. The slurry was filtered and concentrated under reduced pressure, followed by coevaporated with toluene. The residue was dissolved in DMF (0.2 M) and Et_3N (2.0 eq.), TrtCl (1.5 eq.), and DMAP (0.05 eq.) were successively added. After stirring for 1-2 days the mixture was diluted with H_2O and extracted twice with DCM. The combined DCM fractions were washed with H_2O and brine, then dried with $MgSO_4$, filtered and concentrated in vacuo followed by coevaporation with toluene. The crude tritylated product was redissolved in DMF (0.2 M) and cooled to 0°C. NaH (60% dispersion in mineral oil, 2.5 eq.) and TBAI (0.05 eq.) were added, followed by drop wise addition of BnBr (2.5 eq.). After stirring overnight at room temperature, the reaction was quenched by the addition of H_2O and extracted three times with Et_2O. The combined organic layers were washed with H_2O and brine, dried ($MgSO_4$), filtered over a short plug of silica gel, and concentrated under reduced pressure. The crude material was dissolved in MeOH/DCM (1/1, v/v, 0.2 M) and pTsOH·H_2O (0.1 eq.) was added and the reaction stirred at room temperature overnight and then quenched with Et_3N (0.15 eq.) The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (19/1 to 6/4 pentane/EtOAc) to yield the primary furanoside alcohols as yellow oils.

General procedure for the synthesis furanosyl methyl uronates by TEMPO/BAIB oxidation and methylation (41-44). The primary alcohol was dissolved in DCM/H_2O (2/1, v/v, 0.17 M) and the mixture was cooled to 0°C. TEMPO (0.2 eq.) and BAIB (2.5 eq.) were added and the reaction mixture was stirred vigorously overnight. A 10 % aq. NaS_2O_3 solution was added and the mixture stirred for 15 min at room temperature. The mixture was diluted with 0.01 M aq. HCl and DCM and phase separated and the aqueous layer extracted three times with DCM. The combined DCM layers were washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude carboxylic acid was dissolved in DMF (0.2 M) and K_2CO_3 (3 eq.) and MeI (3 eq.) were added at 0°C. The reaction was stirred for 3 h and then quenched with AcOH (5 eq). The solution was diluted with H_2O and extracted three times with Et_2O. The combined organic layers were washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (19/1 to 7/3) to give the uronic acid methyl ester.

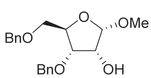
General procedure for the hydrolysis of methyl furanosides (49-64). Conditions A: The methyl glycoside was mixed with 80% aq. formic acid to a concentration of 0.05 M and stirred at 60-65°C for 6-64 h as mentioned for each experiment. After the reaction mixture was cooled to room temperature and transferred to a seperatory funnel, it was diluted 5× with H_2O and extracted three times with DCM. The combined DCM layers were washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (pentane/EtOAc mixtures) to provide the target lactol as a mixture of anomers. Conditions B: The methyl glycoside was dissolved in 90% aq. TFA at 0°C and stirred for 4-8 h. The reaction was diluted with DCM and washed with H_2O three times. The aqueous layers were extracted twice with DCM and the combined organic layers were washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residu was purified by flash column chromatography (19/1 to 6/4 pentane/EtOAc) to provide the target lactol as a mixture of anomers.

General procedure for the synthesis of acetyl donors from lactols (65-69). The furanose lactol was dissolved in pyridine (0.25 M) and cooled to 0°C. Ac_2O (1.3 eq.) was added and the reaction mixture was stirred overnight at room temperature. The solution was diluted with 0.1 M aq. HCl and extracted three times with Et_2O. The combined organic layers were washed with 0.1 M HCl, H_2O, sat. aq. $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by flash column chromatography (1/0 to 8/2 pentane/EtOAc) gave the acetylated compound as a light yellow oil.

General procedure for the installation of the trifluoro-*N*-phenylacetimidoyl group (71-86). Conditions A: The furanose lactol was dissolved in acetone/H_2O (0.2 M, 9/1 v,v) and cooled to 0°C. Cs_2CO_3 (1.1 eq.) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.95 eq.) were added and the reaction mixture stirred until TLC-analysis showed complete conversion (1-4 days). The reaction mixture was reduced in volume under reduced pressure and H_2O was added. The aqueous phase was extracted twice with DCM and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Flash column chromatography (0-15% Et_2O/pentane) of the residue provided the target imidate donors. Conditions B: The furanose lactol was dissolved in DCM (0.25 M) and cooled to 0°C. 2,2,2-Trifluoro-*N*-phenylacetimidoyl chloride (0.95 eq.) was added followed bu DBU (1 eq.). The reaction mixture was stirred for 1 h and then concentrated under reduced pressure. Flash column chromatography (1/0 to 85/15 pentane/Et_2O) of the residue provided the target imidate donors.

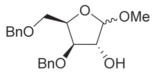


Methyl 2,3,5-tri-*O*-benzyl-α/β-D-ribofuranoside (2). D-Ribose (25 g, 167 mmol, 1 eq.) was dissolved in 600 mL MeOH and AcCl (4 mL, 56 mmol, 0.3 eq.) was added. The reaction mixture was stirred for 5 h and then quenched by the addition of solid $NaHCO_3$ (30 g). The mixture was filtered and concentrated under reduced pressure. The crude product **1** was coevaporated with toluene and then dissolved in 800 mL DMF and cooled to 0°C. NaH (60% dispersion in mineral oil, 26.7 g, 668 mmol, 4 eq.) was added in four portion while BnBr (80 mL, 668 mmol, 4 eq.) was slowly added over the course of 1 h. After stirring overnight the reaction was quenched by the addition of 75 mL MeOH and the reaction mixture was concentrated under reduced pressure. The crude mixture was taken up in H_2O and extracted twice with Et_2O. The combined Et_2O layers were washed with brine, dried with $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash column chromatography (19/1 to 2/1 pentane/EtOAc) gave compound **2** as a colourless oil (65 g, 150 mmol, 89%). Spectroscopic data were in accord with those previously reported.[50] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.36 – 7.25 (m, 13H, CH_{arom}), 7.23 – 7.19 (m, 2H, CH_{arom}), 4.88 (d, 1H, *J* = 4.2 Hz, H-1), 4.68 (d, 1H, *J* = 12.8 Hz, C*H*H Bn), 4.64 (d, 1H, *J* = 12.3 Hz, C*H*H Bn), 4.61 – 4.56 (m, 2H, 2xCH*H* Bn), 4.49 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.42 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.25 (td, 1H, *J* = 4.1, 2.9 Hz, H-4), 3.82 (dd, 1H, *J* = 6.8, 3.0 Hz, H-3), 3.77 (dd, 1H, *J* = 6.8, 4.2 Hz, H-2), 3.46 (s, 3H, CH_3 OMe), 3.41 (dd, 1H, *J* = 10.4, 4.1 Hz, H-5), 3.35 (dd, 1H, *J* = 10.4, 4.2 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.6, 138.0, 137.9 (C_q), 128.5, 128.5, 128.4, 128.4, 128.2, 127.9, 127.8, 127.8 (CH_{arom}), 102.6 (C-1), 82.3 (C-4), 77.9 (C-2), 75.1 (C-3), 73.6, 72.6, 72.5 (CH_2 Bn), 70.3 (C-5), 55.7 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.25 (m, 15H, CH_{arom}), 4.92 (d, 1H, *J* = 1.0 Hz, H-1), 4.67 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.59 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.45 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.34 (ddd, 1H, *J* = 7.1, 5.8, 3.7 Hz, H-4), 4.01 (dd, 1H, *J* = 7.1, 4.7 Hz, H-3), 3.84 (dd, 1H, *J* = 4.6, 1.0 Hz, H-2), 3.61 (dd, 1H, *J* = 10.6, 3.7 Hz, H-5), 3.51 (dd, 1H, *J* = 10.6, 5.8 Hz, H-5), 3.31 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3, 137.8, 137.8 (C_q), 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.6, 127.5 (CH_{arom}), 106.3 (C-1), 80.5 (C-4), 79.6 (C-2), 78.3 (C-3), 73.2, 72.4, 72.3 (CH_2 Bn), 71.3 (C-5), 55.1 (OMe).

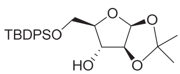


Methyl 3,5-di-*O*-benzyl-α-D-ribofuranoside (3). Compound **2** (4.35 g, 10 mmol, 1 eq.) was coevaporated with toluene twice and then was dissolved in 50 mL DCM at 0°C, followed by the addition of a 1 M $SnCl_4$ solution in DCM (10 mL, 10 mmol, 1 eq.). The reaction mixture was stirred overnight at 4°C and then quenched by the addition of sat. aq. $NaHCO_3$. The organic layer was washed with H_2O and brine, then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield the title compound as a colourless oil (3.19 g, 9.26 mmol, 93%). Spectroscopic data were in accord with those previously reported.[17] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.36 – 7.22 (m, 10H, CHarom), 4.88 (d, 1H, *J* = 4.6 Hz, H-1), 4.72 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.44 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.16 (td, 1H, *J* = 4.1, 3.1 Hz, H-4), 4.14 –

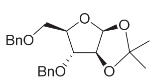
4.06 (m, 1H, H-2), 3.78 (dd, 1H, *J* = 7.1, 3.2 Hz, H-3), 3.47 (s, 3H, CH_3 OMe), 3.43 (dd, 1H, *J* = 10.4, 4.1 Hz, H-5), 3.35 (dd, 1H, *J* = 10.4, 4.3 Hz, H-5), 2.96 (bd, 1H, *J* = 10.1 Hz, 2-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.9 (C_q), 128.5, 128.5, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 103.0 (C-1), 82.0 (C-4), 76.4 (C-3), 73.5, 73.0 (CH_2 Bn), 71.9 (C-2), 70.1 (C-5), 55.7 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{24}O_5Na$ 367.15160, found 367.15139.



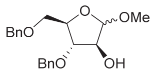
Methyl 3,5-di-*O*-benzyl-α/β-D-xylofuranoside (6). 1,2-*O*-Isopropylidene-α-D-xylofuranoside **4**[51] (28.6 g, 150 mmol, 1 eq.) was dissolved in 750 mL DMF and cooled to 0°C. NaH (60% dispersion in mineral oil, 15 g, 375 mmol, 2.5 eq.) was added followed by the slow addition of BnBr (45 mL, 375 mmol, 2.5 eq.). After 4 h the reaction was quenched by the addition of 50 mL MeOH and the reaction mixture was concentrated under reduced pressure. The crude mixture was taken up in H_2O and extracted twice with Et_2O. The combined Et_2O layers were washed with brine and dried with $MgSO_4$. After filtration and concentration, the crude product **5** was dissolved in 750 mL MeOH and CSA (3.5 g, 15 mmol, 0.1 eq.) was added and the reaction mixture was refluxed for 4 h. The reaction was quenched by addition of solid $NaHCO_3$, which after stirring for 15 min, was removed by filtration followed by concentration on the reaction mixture *in vacuo*. The residue was redissolved in EtOAc and was washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (9/1 to 1/1 pentane/EtOAc) yielded compound **6** as a light yellow oils in three fractions (1: α only, 21.8 g, 63.4 mmol, 2: α/β mixture, 7.6 g, 22.2 mmol, 3: β only, 20.8 g, 60.5 mmol) combined yield: 146.1 mmol, 97%. Spectroscopic data were in accord with those previously reported.[52] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.24 (m, 10H, CH_{arom}), 4.99 (d, 1H, *J* = 4.7 Hz, H-1), 4.73 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.39 (td, 1H, *J* = 6.4, 4.2 Hz, H-4), 4.26 (dt, 1H, *J* = 7.5, 4.4 Hz, H-2), 4.00 (dd, 1H, *J* = 6.0, 4.1 Hz, H-3), 3.72 (dd, 1H, *J* = 10.5, 4.2 Hz, H-5), 3.65 (dd, 1H, *J* = 10.5, 6.7 Hz, H-5), 3.49 (s, 3H, CH_3 OMe), 2.71 (d, 1H, *J* = 7.6 Hz, 2-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.4, 138.1 (C_q), 128.5, 128.5, 127.9, 127.8, 127.7, 127.7 (CH_{arom}), 101.9 (C-1), 83.7 (C-3), 77.5 (C-4), 77.1 (C-2), 73.6, 72.0 (CH_2 Bn), 69.2 (C-5), 55.9 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.25 (m, 10H, CH_{arom}), 4.80 (d, 1H, *J* = 1.7 Hz, H-1), 4.66 – 4.58 (m, 2H, 2xC*H*H Bn), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.47 (ddd, 1H, *J* = 7.2, 6.1, 4.6 Hz, H-4), 4.21 (ddd, 1H, *J* = 4.7, 2.9, 1.7 Hz, H-2), 3.95 (dd, 1H, *J* = 6.1, 2.9 Hz, H-3), 3.77 (dd, 1H, *J* = 10.3, 4.7 Hz, H-5), 3.70 (dd, 1H, *J* = 10.3, 7.3 Hz, H-5), 3.40 (s, 3H, CH_3 OMe), 1.95 (d, 1H, *J* = 4.8 Hz, 2-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.4, 137.9 (C_q), 128.6, 128.5, 128.0, 127.9, 127.9, 127.7 (CH_{arom}), 109.6 (C-1), 83.5 (C-3), 80.1 (C-4), 79.8 (C-2), 73.6, 72.5 (CH_2 Bn), 70.0 (C-5), 55.9 (OMe).



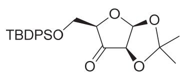
1,2-*O*-Isopropylidene-5-*O*-(*tert*-butyldiphenylsilyl)-β-D-arabinofuranoside (7). D-Arabinose (30 g, 200 mmol, 1 eq.) was dissolved in 1 L DMF and imidazole (27.2 g, 400 mmol, 2 eq.) and TBDPSCl (52 mL, 200 mmol, 1 eq.) were added sequentially. The reaction mixture was heated to 60°C for 3 h and then two thirds of the DMF was removed under reduced pressure. The remaining solution was mixed with H_2O (1.5 L) and conc. HCl (15 mL) and the aqueous phase extracted four times with EtOAc. The organic layers were combined and washed with sat. aq. $NaHCO_3$ and brine. The organic phase was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was coevaporated with toluene and then dissolved in DCM (1.1 L) and cooled to 0°C. CSA (2.5 g, 10.8 mmol, 0.05 eq.) was added followed by dropwise addition of 2,2-dimethoxypropane (44 mL, 360 mmol, 1.8 eq.). After 4 h, the reaction was quenched with Et_3N (2.8 mL) and concentrated under reduced pressure. Flash column chromatography (19/1 to 8/2 pentane/EtOAc) yielded compound 7 as a colourless oil (43.7 g, 102 mmol, 51%). Spectroscopic data were in accord with those previously reported.[53] ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.73 – 7.61 (m, 4H, CH_{arom}), 7.46 – 7.33 (m, 6H, CH_{arom}), 5.88 (d, 1H, *J* = 4.0 Hz, H-1), 4.54 (d, 1H, *J* = 4.0 Hz, H-2), 4.43 (t, 1H, *J* = 3.1 Hz, H-3), 4.05 (ddd, 1H, *J* = 7.9, 5.7, 2.6 Hz, H-4), 3.86 – 3.78 (m, 2H, H-5), 2.00 (d, 1H, *J* = 4.3 Hz, 3-OH), 1.32 (s, 3H, CH_3 Me), 1.28 (s, 3H, CH_3 Me), 1.06 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 135.7, 135.7 (CH_{arom}), 133.3, 133.2 (C_q Ph), 129.9, 129.9, 127.9, 127.9 (CH_{arom}), 112.6 (C_q), 105.7 (C-1), 87.5 (C-4), 87.1 (C-2), 76.5 (C-3), 63.8 (C-5), 27.0, 27.0 (^{t}Bu), 26.2 (Me), 19.3 (C_q ^{t}Bu).



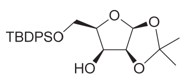
Methyl 3,5-di-*O*-benzyl-1,2-*O*-isopropylidene-β-D-arabinofuranoside (8). Compound **7** (14.1 g, 32.8 mmol, 1 eq.) and BnCl (22.6 mL, 197 mmol, 6 eq.) were dissolved in 140 mL THF. Freshly crushed KOH pellets (35 g, 623 mmol, 19 eq.) were added and the reaction mixture was stirred under a N_2 atmosphere at reflux overnight. Once the mixture was cooled to room temperature, it was filtered through glass wool and concentrated *in vacuo*. Flash column chromatography (1/0 to 9/1 pentane/EtOAc) afforded the title compound as a yellow oil (9.0 g, 24.3 mmol, 74%). Spectroscopic data were in accord with those previously reported.[22] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.34 – 7.26 (m, 10H, CH_{arom}), 5.90 (d, 1H, *J* = 4.0 Hz, H-1), 4.64 (d, 1H, *J* = 4.1 Hz, H-2), 4.62 – 4.57 (m, 2H, CH_2 Bn), 4.57 – 4.51 (m, 2H, CH_2 Bn), 4.27 (td, 1H, *J* = 6.3, 3.0 Hz, H-4), 4.02 (d, 1H, *J* = 2.7 Hz, H-3), 3.63 (d, 2H, *J* = 6.2 Hz, H-5), 1.44 (s, 3H, CH_3 Me), 1.32 (s, 3H, CH_3 Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.4 (C_q Bn), 128.6, 128.5, 128.0, 127.9, 127.8, 127.8 (CH_{arom}), 112.8 (C_q), 105.8 (C-1), 85.3 (C-2), 83.7 (C-4), 83.2 (C-3), 73.5, 71.8 (CH_2 Bn), 70.1 (C-5), 27.2, 26.4 (Me).



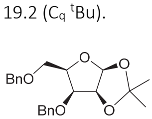
Methyl 3,5-di-*O*-benzyl-α/β-D-arabinofuranoside (9). Fully protected compound **8** (11 g, 30 mmol, 1 eq.) and CSA (0.7 g, 3.0 mmol, 0.1 eq.) were dissolved in 150 mL MeOH and brought to reflux. After stirring for 5 h, the reaction mixture was cooled down and solid $NaHCO_3$ was added. The reaction mixture was concentrated and then H_2O was added. Extraction with EtOAc twice and those combined organic layers were washed with brine, then dried with $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (19/1 to 8/2 pentane/EtOAc) afforded the title compound (9.4 g, 27 mmol, 91%) as a colourless oil. Spectroscopic data were in accord with those previously reported.[22] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 10H, CH_{arom}), 4.89 (s, 1H, H-1), 4.68 (d, 1H, *J* = 12.3 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 4.46 (d, 1H, *J* = 11.9 Hz, CH*H* Bn),4.26 (s, 1H, H-4), 4.12 (d, 1H, *J* = 10.9 Hz, H-2), 3.84 (s, 1H, H-3), 3.64 (dd, 1H, *J* = 10.4, 2.4 Hz, H-5), 3.43 (dd, 1H, *J* = 10.4, 2.5 Hz, H-5), 3.40 (s, 3H, CH_3 OMe), 3.34 (d, 1H, *J* = 10.8 Hz, OH); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.22 (m, 10H, CH_{arom}), 4.84 (d, 1H, *J* = 4.7 Hz, H-1), 4.74 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.57 (s, 2H, CH_2 Bn), 4.31 – 4.21 (m, 1H, H-2), 4.19 – 4.09 (m, 1H, H-4), 3.84 (t, 1H, *J* = 5.8 Hz, H-3), 3.53 (d, 2H, *J* = 5.6 Hz, H-5), 3.41 (s, 3H, CH_3 OMe), 2.57 (d, 1H, *J* = 9.4 Hz, OH); Data for the both anomers: ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 138.0, 137.8, 137.1 (C_q), 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7 (CH_{arom}), 110.5 (C-1$_\alpha$), 102.8 (C-1$_\beta$), 85.0 (C-3$_\alpha$), 84.7 (C-3$_\beta$), 83.5 (C-4$_\alpha$), 80.8 (C-4$_\beta$), 78.1 (C-2$_\alpha$), 78.0 (C-2$_\beta$), 73.8, 73.4, 72.2 (CH_2 Bn), 72.1 (C-5$_\beta$), 71.9 (CH_2 Bn), 69.8 (C-5$_\alpha$), 55.4, 55.3 (OMe).



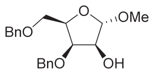
1,2-O-Isopropylidene 5-O-(*tert*-butyldiphenylsilyl)-β-D-arabinofuran-3-uloside (10). Compound **7** (9.95 g, 23.2 mmol, 1 eq.) was dissolved in 230 mL DCM and Dess-Martin periodinane (13.4 g, 31 mmol, 1.36 eq.) was added. After stirring 4 h, $Na_2S_2O_3$ (20 g) was added and the reaction mixture was poured into sat. aq. $NaHCO_3$. The mixture was extracted with DCM three times and the combined organic layers were washed with H_2O and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. Flash column chromatography (1/0 to 8/2 pentane/EtOAc) afforded the title compound as a colourless oil (7.65 g, 17.9 mmol, 77%). Spectroscopic data were in accord with those previously reported.[18] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.75 – 7.63 (m, 4H, CH_{arom}), 7.45 – 7.33 (m, 6H, CH_{arom}), 6.03 (d, 1H, *J* = 4.3 Hz, H-1), 4.39 (d, 1H, *J* = 4.3 Hz, H-2), 4.29 (dd, 1H, *J* = 6.3, 4.2 Hz, H-4), 3.99 – 3.87 (m, 2H, H-5), 1.37 (s, 3H, CH_3 Me), 1.35 (s, 3H, CH_3 Me), 1.05 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 207.3 (C=O), 135.9, 135.7 (CH_{arom}), 133.2, 132.9 (C_q Ph), 129.9, 127.9 (CH_{arom}), 114.9 (C_q), 102.7 (C-1), 82.5 (C-4), 76.9 (C-2), 64.6 (C-5), 27.6 (Me), 26.9 (^{t}Bu), 19.4 (C_q ^{t}Bu);



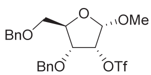
1,2-*O*-Isopropylidene-5-*O*-(*tert*-butyldiphenylsilyl)-β-D-lyxofuranoside (11). Ketone **9** (6.9 g, 16.2 mmol, 1 eq.) was dissolved in DCM/MeOH (100 mL, 1/1) and cooled to 0C. $NaBH_4$ (1.8 g, 48 mmol, 3 eq.) was added in three equal portions and the reaction mixture was stirred for 30 min after each addition. After 1.5 h sat. aq. NH_4Cl was added and the mixture was extracted three times with DCM. The combined organic layers were washed with sat. aq. NH_4Cl, H_2O, and brine. The organic layer was then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash column chromatography (2% to 14% EtOAc/pentane) afforded the title compound as a yellow oil (5.2 g, 13.1 mmol, 75%). Spectroscopic data were in accord with those previously reported.[54] ^{1}H NMR ($CDCl_3$, HH-COSY, HSQC): δ 7.78 – 7.62 (m, 4H, CH_{arom}), 7.48 – 7.31 (m, 6H, CH_{arom}), 5.71 (d, 1H, *J* = 4.1 Hz, H-1), 4.60 (dd, 1H, *J* = 5.8, 4.1 Hz, H-2), 4.33 (q, 1H, *J* = 5.9 Hz, H-3), 4.20 – 4.11 (m, 2H, H-4, H-5), 3.93 – 3.84 (m, 1H, H-5), 3.10 (d, 1H, *J* = 6.4 Hz, 3-OH), 1.42 (s, 3H, CH_3 Me), 1.34 (s, 3H, CH_3 Me), 1.06 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 135.7, 135.7 (CH_{arom}), 133.2, 133 (C_q Ph).1, 129.8, 127.8, 127.8 (CH_{arom}), 114.1 (C_q), 105.0 (C-1), 81.4 (C-4), 79.9 (C-2), 71.0 (C-3), 63.3 (C-5), 26.9 (CH_3 ^{t}Bu), 26.8, 26.6 (Me), 19.2 (C_q ^{t}Bu).



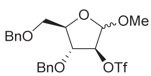
Methyl 3,5-di-*O*-benzyl-1,2-*O*-isopropylidene-β-D-lyxofuranoside (12). Compound **11** (9.0 g, 21 mmol, 1 eq.) and BnCl (14 mL, 123 mmol, 5.9 eq.) were dissolved in 90 mL THF. Freshly crushed KOH pellets (19.7 g, 351 mmol, 16.7 eq.) were added and the reaction mixture was stirred under a N_2 atmosphere at reflux overnight. Once the mixture was cooled to room temperature, it was filtered through glass wool and concentrated *in vacuo*. Flash column chromatography (1/0 to 8/2 pentane/EtOAc) afforded the title compound as a colourless oil (7.9 g, 21 mmol, 100%). Spectroscopic data were in accord with those previously reported for the L-enantiomer.[55] R*f*: 0.16 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +15° (*c* = 0.44, $CHCl_3$). IR (thin film): 698, 737, 1026, 1097, 1152, 1209, 1255, 1454, 2868, 2946, 2986; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.41 – 7.18 (m, 10H, CH_{arom}), 5.70 (d, 1H, *J* = 4.0 Hz, H-1), 4.67 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.63 – 4.57 (m, 3H, CH_2 Bn, CH*H* Bn), 4.55 (dd, 1H, *J* = 5.1, 4.0 Hz, H-2), 4.32 (dt, 1H, *J* = 7.2, 5.8 Hz, H-4), 4.05 (dd, 1H, *J* = 7.3, 5.1 Hz, H-3), 3.88 (d, 2H, *J* = 5.9 Hz, 2xH-5), 1.48 (s, 3H, CH_3 Me), 1.30 (s, 3H, CH_3 Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.4, 137.5 (C_q Bn), 128.5, 128.3, 128.0, 127.9, 127.8, 127.5 (CH_{arom}), 113.5 (C_q), 104.7 (C-1), 80.0 (C-4), 78.4 (C-2), 77.2 (C-3), 73.3, 72.6 (CH_2 Bn), 69.9 (C-5), 26.6, 26.1 (Me); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{30}NO_5$ 388.21185, found 388.21226.



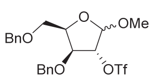
Methyl 3,5-di-*O*-benzyl-α-D-lyxofuranoside (13). Fully protected compound **12** (7.8 g, 21 mmol, 1 eq.) and CSA (0.46 g, 2.0 mmol, 0.1 eq.) were dissolved in 100 mL MeOH and brought to reflux. After stirring for 5 h, the reaction mixture was cooled down and solid $NaHCO_3$ was added. The reaction mixture was concentrated and then H_2O was added. Extraction with EtOAc twice and those combined organic layers were washed with brine, then dried with $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (19/1 to 8/2 pentane/EtOAc) afforded the title compound (6.1 g, 17.7 mmol, 84%) as a colourless oil and a single anomer. Spectroscopic data were in accord with those previously reported.[56] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.24 (m, 10H, CH_{arom}), 4.86 (s, 1H, H-1), 4.72 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.64 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.48 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.40 (dd, 1H, *J* = 8.0, 4.9 Hz, H-3), 4.35 – 4.28 (m, 2H, H-4, 2-OH), 4.05 (dd, 1H, *J* = 10.2, 4.9 Hz, H-2), 3.67 (dd, 1H, *J* = 10.5, 3.3 Hz, H-5), 3.61 (dd, 1H, *J* = 10.5, 2.3 Hz, H-5), 3.34 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.3 (C_q), 128.6, 128.5, 128.0, 128.0, 127.9 (CH_{arom}), 108.6 (C-1), 77.8 (C-3), 77.5 (C-4), 74.0, 72.6 (CH_2 Bn), 72.2 (C-2), 68.0 (C-5), 55.2 (OMe).



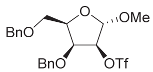
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α-D-ribofuranoside (14). The title compound was generated by the general procedure for triflate formation and used crude. Spectroscopic data were in accord with those previously reported.[57] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 10H, CH_{arom}), 5.09 (d, 1H, *J* = 4.3 Hz, H-1), 5.01 (dd, 1H, *J* = 6.5, 4.3 Hz, H-2), 4.75 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.53 – 4.44 (m, 2H, CH*H* Bn, C*H*H Bn), 4.40 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.19 (dt, 1H, *J* = 5.8, 3.1 Hz, H-4), 4.07 (dd, 1H, *J* = 6.5, 5.0 Hz, H-3), 3.53 (dd, 1H, *J* = 10.9, 2.9 Hzm H-5), 3.51 (s, 3H, CH_3 OMe), 3.33 (dd, 1H, *J* = 10.8, 3.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.7, 137.1 (C_q), 128.7, 128.6, 128.4, 128.3, 128.0, 127.9 (CH_{arom}), 118.7 (d, *J* = 319.6 Hz), 101.1 (C-1), 81.4 (C-2), 81.1 (C-4), 74.6 (C-3), 73.7, 73.5 (CH_2 Bn), 68.5 (C-5), 56.4 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{27}F_3NO_7S$ 494.14548, found 494.14526.



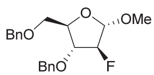
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α/β-D-arabinofuranoside (15). The title compound was generated by the general procedure for triflate formation and used crude. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CH_{arom}), 5.20 (s, 1H, H-2), 5.10 (s, 1H, H-1), 4.70 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.52 – 4.45 (m, 2H, 2x CH*H* Bn), 4.22 – 4.18 (m, 1H, H-4), 4.13 (ddd, 1H, *J* = 5.9, 1.7, 0.9 Hz, H-3), 3.61 (dd, 1H, *J* = 10.9, 3.6 Hz, H-5), 3.54 (dd, 1H, *J* = 10.9, 4.6 Hz, H-5), 3.42 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 136.7 (C_q), 128.7, 128.5, 128.3, 128.1, 127.9, 127.9 (CH_{arom}), 118.5 (q, *J* = 319.8 Hz), 105.9 (C-1), 92.7 (C-2), 82.6 (C-3), 81.8 (C-4), 73.7, 72.8 (CH_2 Bn), 68.6 (C-5), 55.2 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.11 – 5.07 (m, 1H, H-1), 5.00 (d, 1H, *J* = 4.4 Hz, H-2), 4.62 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.55 – 4.48 (m, 2H, CH_2 Bn), 4.29 (dd, 1H, *J* = 6.5, 5.4 Hz, H-3), 4.17 – 4.12 (m, 1H, H-4), 3.57 – 3.53 (m, 1H, H-5), 3.47 (dd, 1H, *J* = 9.9, 6.2 Hz, H-5), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 100.4 (C-1), 88.3 (C-2), 80.9 (C-3), 79.8 (C-4), 73.5, 72.6 (CH_2 Bn), 71.4 (C-5), 55.5 (OMe).



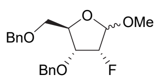
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α/β-D-xylofuranoside (16). The title compound was generated by the general procedure for triflate formation (anomers were treated separately) and used crude. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 10H, CH_{arom}), 5.18 (t, 1H, *J* = 5.1 Hz, H-2), 5.06 (d, 1H, *J* = 4.4 Hz, H-1), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.55 – 4.50 (m, 2H, 2xCH*H* Bn), 4.44 (dd, 1H, *J* = 6.9, 5.8 Hz, H-3), 4.33 (dt, 1H, *J* = 7.0, 4.6 Hz, H-4), 3.67 (dd, 1H, *J* = 10.5, 4.2 Hz, H-5), 3.59 (dd, 1H, *J* = 10.5, 5.1 Hz, H-5), 3.44 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 136.9 (C_q), 128.7, 128.5, 128.3, 127.9, 127.8, 127.8 (CH_{arom}), 118.6 (q, *J* = 319.6 Hz), 99.6 (C-1), 87.9 (C-2), 79.3 (C-3), 75.7 (C-4), 73.7, 73.3 (CH_2 Bn), 68.4 (C-5), 56.0 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.42 – 7.23 (m, 10H, CH_{arom}), 5.17 (s, 1H, H-2), 5.05 (s, 1H, H-1), 4.71 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.48 (dt, 1H, *J* = 6.7, 5.5 Hz, H-4), 4.21 (dd, 1H, *J* = 5.9, 1.8 Hz, H-3), 3.74 (dd, 1H, *J* = 10.3, 5.1 Hz, H-5), 3.69 (dd, 1H, *J* = 10.3, 7.0 Hz, H-5), 3.42 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 136.6, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 106.4, 91.2, 80.6, 80.4, 73.7, 72.8, 69.2, 56.1; HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{27}F_3NO_7S$ 494.14548, found 494.14515.



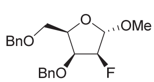
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α-D-lyxofuranoside (17). The title compound was generated by the general procedure for triflate formation and used crude. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.43 – 7.13 (m, 10H, CH_{arom}), 5.08 (s, 1H, H-1), 5.05 (d, 1H, *J* = 4.3 Hz, H-2), 4.73 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.46 – 4.37 (m, 2H, H-3, H-4), 3.74 (dd, 1H, *J* = 10.5, 4.1 Hz, H-5), 3.64 (dd, 1H, *J* = 10.5, 7.3 Hz, H-5), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 136.9 (C_q), 128.7, 128.5, 128.3, 128.0, 128.0, 127.8 (CH_{arom}), 118.6 (q, *J* = 319.6 Hz, CF_3), 104.0 (C-1), 86.2 (C-2), 77.5 (C-4), 76.4 (C-3), 73.9, 73.7 (CH_2 Bn), 69.6 (C-5), 55.7 (OMe).



Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-arabinofuranoside (18). Employing conditions **A** of the general experimental for inversion of furanosyl triflates gave **18** in 86% yield (0.95 mmol) from triflate **14**. Spectroscopic data were in accord with those previously reported.[24] IR (thin film): 696, 737, 947, 988, 1039, 1055, 1098, 1193, 1364, 1454, 2862, 2922; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.25 (m, 10H, CH_{arom}), 5.06 (d, 1H, *J* = 12.0 Hz, H-1), 4.94 (dd, 1H, *J* = 51.3, 1.8 Hz, H-2), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.56 – 4.51 (m, 2H, 2xCH*H* Bn), 4.21 (ddd, 1H, *J* = 6.4, 5.2, 3.8 Hz, H-4), 3.99 (dddd, 1H, *J* = 24.7, 6.4, 1.9, 1.0 Hz, H-3), 3.63 (dd, 1H, *J* = 10.8, 3.8 Hz, H-5), 3.58 (dd, 1H, *J* = 10.8, 5.1 Hz, H-5), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.0, 137.2 (C_q), 128.5, 128.4, 128.0, 127.7, 127.7 (CH_{arom}), 106.5 (d, *J* = 36.0 Hz, C-1), 99.6 (d, *J* = 181.3 Hz, C-2), 83.0 (d, *J* = 25.6 Hz, C-3), 81.3 (d, *J* = 4.0 Hz, C-4), 73.4, 72.5 (CH_2 Bn), 69.3 (C-5), 54.9 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -188.39 (ddd, *J* = 51.3, 24.6, 12.0 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$ = -0.7 Hz, $^2J_{C2\text{-}H1}$ = -2.0 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}NFO_4$ 364.19186, found 364.19196.

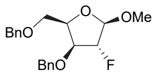


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-ribofuranoside (19). Employing conditions **A** of the general experimental for inversion of furanosyl triflates gave **19** in 63% yield (3.2 mmol), as two anomers (R*f*: 0.47, and Rf: 0.15, 9/1 pentane/EtOAc) and two anomers of **26**. Spectroscopic data were in accord with those previously reported for the β-anomer.[22] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.41 – 7.27 (m, 10H, CH_{arom}), 5.09 (dd, 1H, *J* = 4.1, 3.5 Hz, H-1), 4.88 (ddd, 1H, *J* = 51.1, 6.1, 4.2 Hz), 4.82 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 4.58 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.49 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.30 (dt, 1H, *J* = 5.3, 3.4 Hz, H-4), 4.00 (ddd, 1H, *J* = 7.6, 6.0, 5.2 Hz, H-3), 3.63 (dd, 1H, *J* = 10.9, 2.9 Hz, H-5), 3.56 (s, 3H, CH3 OMe), 3.49 (dd, 1H, *J* = 10.8, 3.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.8 (C_q), 128.5, 128.5, 128.0, 128.0, 127.8, 127.7 (CH_{arom}), 101.8 (d, *J* = 15.9 Hz, C-1), 88.2 (d, *J* = 202.7 Hz, C-2), 80.9 (d, *J* = 2.1 Hz, C-4), 74.6 (d, *J* = 14.8 Hz, C-3), 73.6 (CH_2 5-OBn), 72.9 (d, *J* = 2.2 Hz, CH_2 3-OBn), 69.1 (C-5), 56.1 (OMe); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -216.73 (ddd, *J* = 51.2, 7.6, 3.3 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$: +2.4 Hz, $^2J_{C2\text{-}H1}$: -+3.2 Hz; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.35 – 7.26 (m, 10H, CH_{arom}), 5.00 (d, 1H, *J* = 10.6 Hz, H-1), 4.76 (dd, 1H, *J* = 53.2, 3.7 Hz, H-2), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.30 (ddd, 1H, *J* = 8.0, 5.7, 3.4 Hz, H-4), 4.07 (ddd, 1H, *J* = 24.6, 7.7, 3.7 Hz, H-3), 3.64 (dd, 1H, *J* = 10.6, 3.4 Hz, H-5), 3.53 (dd, 1H, *J* = 10.6, 5.7 Hz, H-5), 3.32 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3, 137.4 (C_q), 128.6, 128.4, 128.1, 128.0, 127.7 (CH_{arom}), 105.7 (d, *J* = 29.3 Hz, C-1), 91.2 (d, *J* = 185.1 Hz, C-2), 80.1 (C-4), 77.8 (d, *J* = 15.6 Hz, C-3), 73.3, 72.8 (CH_2 Bn), 71.0 (C-5), 55.1 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -209.71 (ddd, *J* = 53.2, 24.6, 10.6 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$: +1.6 Hz, $^2J_{C2\text{-}H1}$: -1.6 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{24}FNO_4$ 364.19186, found 364.19205.

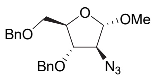


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-lyxofuranoside (20). Employing conditions **B** of the general experimental for inversion of furanosyl triflates, with an additional 70°C reflux for 7 h, gave **20** in 44% yield (2.19 mmol) from triflate **16α**. Conditions **A** yielded 57% **28** and 21% **30**. IR (thin film): 698, 739, 1056, 1452, 2932; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.40 – 7.24 (m, 10H, CH_{arom}), 5.08 (dd, 1H, *J* = 10.0, 1.0 Hz, H-1), 4.80 (ddd, 1H, *J* = 52.8, 4.1, 1.0 Hz, H-2), 4.68 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.65 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.53 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.42 (ddd, 1H, *J* = 8.0, 7.1, 3.8 Hz, H-4), 4.30 (ddd, 1H, *J* = 20.9, 7.1, 4.1 Hz, H-3), 3.77 (dd, 1H, *J* = 10.5, 3.8 Hz, H-5), 3.67 (ddd, 1H, *J* = 10.5, 8.0, 1.4 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.4, 137.5 (C_q), 128.6, 128.5, 128.1, 128.0, 127.8, 127.7 (CH_{arom}), 105.0 (d, *J* = 29.8 Hz, C-1), 92.4 (d, *J* = 187.9 Hz, C-2), 77.7 (C-4), 77.1 (d, *J* = 14.9 Hz, C-3), 73.6, 73.3 (CH_2 Bn), 70.3 (C-5), 55.5 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz, HH-COSY, HSQC): δ -207.58 (dddd, *J* = 52.8, 20.9, 10.0, 1.0 Hz); ^{13}C

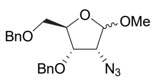
HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C2,H1}$ = -2.5 Hz; HRMS: $[M+Na]^+$ calcd for $C_{20}H_{23}FO_4Na$ 369.14726, found 369.14734.



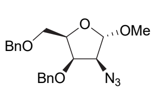
Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-xylofuranoside (21). Employing conditions **A** of the general experimental for inversion of furanosyl triflates gave **21** in 10% yield (0.52 mmol) as the minor product from triflate **16β**. IR (thin film): 698, 712, 978, 1068, 1107, 2929; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.26 (m, 10H, CH_{arom}), 5.02 (d, 1H, *J* = 14.8 Hz, H-1), 4.93 (d, 1H, *J* = 50.6 Hz, H-2), 4.68 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.52 – 4.48 (m, 1H, H-4), 4.15 (ddd, 1H, *J* = 18.2, 6.1, 1.7 Hz, H-3), 3.76 (dd, 1H, *J* = 10.3, 4.9 Hz, H-5), 3.70 (dd, 1H, *J* = 10.3, 7.3 Hz, H-5), 3.41 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.3, 137.4 (C_q), 128.6, 128.5, 128.1, 127.9, 127.9, 127.8 (CH_{arom}), 107.1 (d, *J* = 35.2 Hz, C-1), 98.4 (d, *J* = 181.0 Hz, C-2), 80.9 (d, *J* = 25.9 Hz, C-3), 80.7 (d, *J* = 1.9 Hz, C-4), 73.6, 72.7 (CH_2 Bn), 69.7 (C-5), 55.8 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -192.85 (ddd, *J* = 50.6, 18.1, 14.9 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = -2.6 Hz, $^2J_{C2,H1}$ = -0.2 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}FNO_4$ 364.19186, found 364.19192.



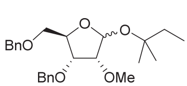
Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-arabinofuranoside (22). Employing conditions **C** of the general experimental for inversion of furanosyl triflates gave **22** in 93% yield (5.37 mmol) from triflate **14**. $[\alpha]_D^{20}$ = +76.4° (*c* = 1.0, $CHCl_3$). IR (thin film): 698, 714, 1026, 1070, 1097, 1107, 1271, 1452, 2104, 2932; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.35 – 7.23 (m, 10H, CH_{arom}), 4.88 (d, 1H, *J* = 1.5 Hz, H-1), 4.61 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.49 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.23 – 4.15 (m, 1H, H-4), 3.92 – 3.85 (m, 2H, H-2, H-3), 3.60 (dd, 1H, *J* = 10.8, 3.6 Hz, H-5), 3.54 (dd, 1H, *J* = 10.8, 4.8 Hz, H-5), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.2 (C_q), 128.5, 128.4, 128.0, 128.0, 127.8, 127.7 (CH_{arom}), 107.0 (C-1), 83.1 (C-3), 81.2 (C-4), 73.5, 72.6 (CH_2 Bn), 70.8 (C-2), 69.0 (C-5), 55.3 (OMe); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = -2.1 Hz, $^2J_{C2,H1}$ = -0.3 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}N_4O_4$ 387.20268, found 387.20271.



Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-ribofuranoside (23). Employing conditions **C** of the general experimental for inversion of furanosyl triflates gave **23** as an α:β = 1:2 mixture from triflate **15**, and as a 4:1 mixture of **23** and **27**, combined yield 86% (4.3 mmol). IR (thin film): 698, 740, 1028, 1066, 1107, 1271, 1452, 2108, 2918; Data for the α-anomer (intermixed with **27**, *vide infra*): ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.35 – 7.20 (m, 10H, CH_{arom}), 5.03 (d, 1H, *J* = 4.6 Hz, H-1), 4.76 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 12.5 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.40 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.30 – 4.22 (m, 1H, H-4), 3.99 (dd, 1H, *J* = 7.2, 3.7 Hz, H-3), 3.49 (s, 3H, OMe), 3.45 (dd, 1H, *J* = 10.5, 3.7 Hz, H-5), 3.36 – 3.28 (m, 2H, H-2, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.6 (C_q), 128.4, 128.4, 128.0, 128.0, 127.7 (CH_{arom}), 104.5 (C-1), 82.5 (C-4), 77.8 (C-3), 73.5, 72.9 (CH_2 Bn), 69.5 (C-5), 61.0 (C-2), 55.7 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CH_{arom}), 4.83 (s, 1H, H-1), 4.63 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.51 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.28 – 4.21 (m, 2H, H-3, H-4), 3.80 (d, 1H, *J* = 3.8 Hz, H-2), 3.59 – 3.54 (m, 1H, H-5), 3.52 – 3.47 (m, 1H, H-5), 3.29 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.3 (C_q), 128.5, 128.4, 128.1, 127.9, 127.6 (CH_{arom}), 106.6 (C-1), 80.7 (C-4), 79.8 (C-3), 73.2, 73.0 (CH_2 Bn), 71.2 (C-5), 64.6 (C-2), 55.0 (OMe); HRMS: $[M-N_2+H]^+$ calcd for $C_{20}H_{24}NO_4$ 387.20268, found 387.20275.

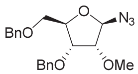


Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-lyxofuranoside (24). Employing conditions **C** of the general experimental for inversion of furanosyl triflates, with additional 16 h stirring, gave **24** in 67% yield (3.36 mmol) from triflate **16α**, and side products **29α** (12%) and **30** (7%). Spectroscopic data were in accord with those previously reported.[58] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.34 – 7.27 (m, 10H, CH_{arom}), 4.95 (d, 1H, *J* = 2.1 Hz, H-1), 4.69 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.52 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.38 – 4.31 (m, 2H, H-3, H-4), 3.79 – 3.66 (m, 3H, H-2, H-5, H-5), 3.36 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.4 (C_q), 128.5, 128.4, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 105.9 (C-1), 79.0 (C-3), 78.2 (C-4), 73.9, 73.6 (CH_2 Bn), 69.2 (C-5), 65.9 (C-2), 55.6 (OMe); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = -3.2 Hz, $^2J_{C2,H1}$ = -0.1 Hz, $^3J_{C1,H3}$ = +2.3 Hz, $^3J_{C3,H1}$ = +2.4 Hz; HRMS: $[M+Na]^+$ calcd for $C_{20}H_{23}N_3O_4$ 392.15808, found 392.15787.

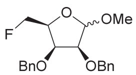


(2-Methyl-2-butyl) 3,5-di-*O*-benzyl-2-methyl-α/β-D-ribofuranoside (26). Formed as an 88:12 α:β anomeric mixture. Data for the isolated α-anomer: $[\alpha]_D^{20}$ = +86.3° (*c* = 0.35, $CHCl_3$).IR (thin film): 698, 739, 1026, 1042, 1109, 1211, 1454, 2928, 2970; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC, HMBC): δ 7.37 – 7.20 (m, 10H, CH_{arom}), 5.34 (d, 1H, *J* = 4.1 Hz, H-1), 4.70 (d, 1H, *J* = 12.6

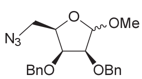
Hz, C*H*H Bn), 4.55 – 4.49 (m, 2H, C*H*H Bn, CH*H* Bn), 4.42 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.22 (q, 1H, *J* = 3.9 Hz, H-4), 3.91 (dd, 1H, *J* = 6.5, 4.5 Hz, H-3), 3.57 (dd, 1H, *J* = 6.5, 4.2 Hz, H-2), 3.50 – 3.44 (m, 4H, CH_3 OMe, H-5), 3.36 (dd, 1H, *J* = 10.6, 3.9 Hz, H-5), 1.60 (q, 2H, *J* = 7.5 Hz, CH_2CH_3 *t*-amyl), 1.26 (s, 3H, CH_3 *t*-amyl), 1.24 (s, 3H, CH_3 *t*-amyl), 0.93 (t, 3H, *J* = 7.5 Hz, CH_2CH_3 *t*-amyl); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.5, 138.2 (C_q), 128.3, 128.2, 128.0, 127.6, 127.5, 127.5 (CH_{arom}), 95.9 (C-1), 80.6, 80.5 (C-2, C-4), 77.0 (C_q t-amylOH)75.7 (C-3), 73.3, 72.2 (CH_2 Bn), 70.0 (C-5), 58.8 (OMe), 34.5 (CH_2 *t*-amyl), 26.1, 25.9 (C_qCH_3 *t*-amyl), 8.6 (CH_2CH_3 *t*-amyl); HRMS: $[M+Na]^+$ calcd for $C_{25}H_{34}O_5Na$ 437.22985, found 437.22953.



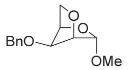
1-Azido 3,5-di-*O*-benzyl-1-deoxy-2-methyl-β-D-ribofuranoside (27). Intermixed with **24**. (*vide supra).* ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.34 – 7.20 (m, 10H, CH_{arom}), 5.32 (d, 1H, *J* = 1.9 Hz, H-1), 4.60 – 4.56 (m, 2H, 2xC*H*H Bn), 4.53 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.51 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.29 – 4.22 (m, 1H, H-4), 4.08 (dd, 1H, *J* = 6.9, 4.6 Hz, H-3), 3.64 (dd, 1H, *J* = 10.8, 3.3 Hz, H-5), 3.52 (dd, 1H, *J* = 10.9, 4.6 Hz, H-5), 3.50 – 3.47 (m, 1H, H-2), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.5 (C_q), 128.4, 128.4, 128.0, 127.9, 127.8, 127.6 (CH_{arom}), 92.2 (C-1), 82.5 (C-2), 81.3 (C-4), 77.1 (C-3), 73.4, 72.7 (CH_2 Bn), 69.8 (C-5), 58.3 (OMe); After hydrolysis of the mixture of **24** an **27**, **3,5-di-*O*-benzyl-2-*O*-methyl-α/β-D-ribofuranose** could be isolated as a α:β = 1:0.7 anomeric mixture. Spectroscopic data were in accord with those previously reported.[59] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.22 (m, 17H), 5.32 (dd, 1H, *J* = 11.2, 4.1 Hz, H-1α), 5.28 (d, 0.7H, *J* = 6.4 Hz, H-1β), 4.68 (d, 1H, *J* = 11.9 Hz, C*H*H Bnα), 4.63 (d, 0.7H, *J* = 12.0 Hz, C*H*H Bnβ), 4.61 (d, 1H, *J* = 11.9 Hz, CH*H* Bnα), 4.59 – 4.42 (m, 4.1H, CH_2 Bnα,β, CH*H* Bnβ), 4.35 (td, 1H, *J* = 4.2, 2.4 Hz, H-4α), 4.27 – 4.17 (m, 1.4H, H-3β, H-4β), 4.12 (d, 1H, *J* = 11.2 Hz, 1-OHα), 4.01 (dd, 1H, *J* = 5.0, 2.4 Hz, H-3α), 3.78 (dd, 1H, *J* = 4.9, 4.3 Hz, H-2α), 3.67 – 3.59 (m, 2.1H, H-2β, H-5β, 1-OHβ), 3.52 – 3.43 (m, 7.8H, CH_3 OMeα,β, H-5β, 2xH-5α); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.8, 137.5, 137.4 (C_q), 128.6, 128.6, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 99.7 (C-1β), 96.1 (C-1α), 83.4 (C-2β), 81.0 (C-4α), 80.7 (C-3β), 80.2 (C-2β), 77.4 (C-3α), 77.2 (C-4β), 73.6, 73.5, 72.8, 72.7 (CH_2 Bn), 70.0 (C-5α), 69.6 (C-5β), 58.6, 58.4 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{24}O_5Na$ 367.15160, found 367.15164.



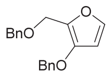
Methyl 2,5-di-*O*-benzyl-5-deoxy-5-fluoro-α/β-D-lyxofuranoside (28). Data for the α-anomer: m.p. 62-64 °C. $[\alpha]_D^{20}$ = +16.6° (*c* = 0.62, $CHCl_3$); IR (thin film): 698, 737, 1009, 1026, 1069, 1107, 1150, 1454, 2922, 3032; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.36 – 7.28 (m, 10H, CH_{arom}), 5.00 (d, 1H, *J* = 1.6 Hz, H-1), 4.74 – 4.62 (m, 4H, 2xC*H*H Bn, H-5, H-5), 4.60 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.44 (dtd, 1H, *J* = 15.6, 6.8, 4.4 Hz, H-4), 4.30 (dd, 1H, *J* = 6.6, 4.6 Hz, H-3), 3.88 (dt, 1H, *J* = 4.6, 1.6 Hz, H-2), 3.36 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.8, 137.7 (C_q), 128.5, 128.5, 128.0, 127.9, 127.8, 127.8 (CH_{arom}), 106.2 (C-1), 84.0 (d, *J* = 164.8 Hz, C-5), 81.1 (C-2), 77.8 (d, *J* = 7.1 Hz, C-3), 77.3 (d, *J* = 20.2 Hz, C-4), 73.2, 72.7 (CH_2 Bn), 55.5 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -228.75 (td, *J* = 47.6, 15.7 Hz); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -0.8 Hz, $^2J_{C2,H1}$ = -0.8 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}NFO_4$ 364.19186, found 364.19199. Data for the β-anomer: $[\alpha]_D^{20}$ = -100.5° (*c* = 0.95, $CHCl_3$); IR (thin film): 698, 737, 1003, 1066, 1109, 1163, 1348, 1454, 2910, 2924; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.37 – 7.27 (m, 10H, CH_{arom}), 4.84 (dd, 1H, *J* = 4.5, 1.2 Hz, H-1), 4.82 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.70 – 4.64 (m, 2H, C*H*H Bn, H-5), 4.63 – 4.59 (m, 2H, 2xCH*H* Bn), 4.59 – 4.52 (m, 1H, H-5), 4.28 (dddd, 1H, *J* = 14.4, 7.0, 6.0, 5.1 Hz, H-4), 4.11 (t, 1H, *J* = 6.0 Hz, H-3), 3.80 (dd, 1H, *J* = 5.9, 4.5 Hz, H-2), 3.46 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.2, 137.7 (C_q), 128.6, 128.5, 128.3, 128.1, 128.0, 127.9 (CH_{arom}), 101.7 (C-1), 83.8 (d, *J* = 165.6 Hz, C-5), 79.1 (d, *J* = 0.9 Hz, C-2), 78.5 (d, *J* = 21.4 Hz, C-4), 74.7 (d, *J* = 6.0 Hz, C-3), 73.9, 72.7 (CH_2 Bn), 55.8 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -227.76 (td, *J* = 47.5, 14.4 Hz); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}NFO_4$ 364.19186, found 364.19178.



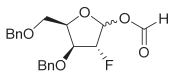
Methyl 5-azido-2,5-di-*O*-benzyl-5-deoxy-α/β-D-lyxofuranoside (29). Data for the α-anomer: IR (thin film):695, 734, 923, 1047, 1101, 1145, 1270, 1454, 2095; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.38 – 7.24 (m, 10H, CH_{arom}), 4.98 (d, 1H, *J* = 1.6 Hz, H-1), 4.71 – 4.63 (m, 2H, 2xC*H*H Bn), 4.59 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.29 – 4.19 (m, 2H, H-3, H-4), 3.88 (dd, 1H, *J* = 4.3, 1.7 Hz, H-2), 3.62 (dd, 1H, *J* = 12.8, 7.6 Hz, H-5), 3.45 (dd, 1H, *J* = 12.9, 3.8 Hz, H-5), 3.34 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 137.8 (C_q), 128.5, 128.0, 127.9, 127.9, 127.8 (CH_{arom}), 106.1 (C-1), 81.5 (C-2), 77.9, 77.8 (C-3, C-4), 73.2, 72.8 (CH_2 Bn), 55.5 (OMe), 52.1 (C-5); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -0.9 Hz, $^2J_{C2,H1}$ = -1.0 Hz, $^2J_{C3,H2}$ = +0.7 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}N_4O_4$ 387.20268, found 387.20275. Data for the β-anomer: $[\alpha]_D^{20}$ = -58.5° (*c* = 0.48, $CHCl_3$); IR (thin film): 698, 737, 999, 1053, 1105, 1157, 1454, 2096, 2874, 2914, 3030; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.41 – 7.27 (m, 10H, CH_{arom}), 4.89 – 4.83 (m, 2H, C*H*H Bn, H-1), 4.72 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.62 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.58 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.13 (ddd, 1H, *J* = 8.7, 5.9, 4.3 Hz, H-4), 4.05 (t, 1H, *J* = 5.9 Hz, H-3), 3.83 (dd, 1H, *J* = 5.8, 4.5 Hz, H-2), 3.66 (dd, 1H, *J* = 13.0, 8.7 Hz, H-5), 3.47 (s, 3H, CH_3 OMe), 3.29 (dd, 1H, *J* = 13.0, 4.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.7 (C_q), 128.6, 128.5, 128.3, 128.1, 128.0, 127.9 (CH_{arom}), 102.0 (C-1), 79.3 (C-4), 79.0 (C-2), 75.0 (C-3), 73.8, 72.8 (CH_2 Bn), 55.9 (OMe), 52.8 (C-5); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +1.0 Hz, $^2J_{C2,H1}$ = +2.5 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}N_4O_4$ 387.20268, found 387.20272.



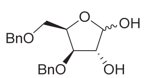
Methyl 2,5-anhydro-3-*O*-benzyl-α-D-lyxofuranoside (30). $[\alpha]_D^{20}$ = +88.3° (*c* = 0.41, $CHCl_3$); IR (thin film): 698, 741, 880, 989, 1028, 1051, 1107, 11998, 1454, 2882, 2940; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.28 (m, 5H, CH_{arom}), 4.74 (s, 1H, H-1), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.25 (d, 1H, *J* = 2.7 Hz, H-4), 4.23 (d, 1H, *J* = 2.6 Hz, H-3), 4.10 (s, 1H, H-2), 3.99 (d, 1H, *J* = 7.8 Hz, H-5), 3.70 (d, 1H, *J* = 7.8 Hz, H-5), 3.36 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.7 (C_q), 128.6, 128.1, 127.9 (CH_{arom}), 106.2 (C-1), 78.6 (C-3), 76.7 (C-2), 75.0 (C-4), 72.5, 70.9 (CH_2 Bn), 55.5 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{13}H_{20}NO_4$ 254.13868, found 254.13878.



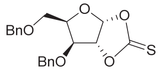
3-benzyloxy-2-(benzyloxy)methyl-furan (31). Spectroscopic data were in accord with those previously reported.[57] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.21 (m, 10H), 7.20 (d, 1H, *J* = 2.1 Hz), 6.25 (d, 1H, *J* = 2.1 Hz), 4.95 (s, 2H), 4.47 (s, 2H), 4.46 (s, 2H).



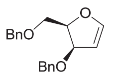
Formyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-xylofuranoside (32). Data for the α-anomer: IR (thin film):698, 737, 1026, 1088, 1271, 1454, 1732, 2868, 2926; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 8.09 (d, 1H, *J* = 0.5 Hz, *H*C=O), 7.37 – 7.26 (m, 10H, CH_{arom}), 6.45 (dd, 1H, *J* = 4.2, 1.9 Hz, H-1), 5.23 (dt, 1H, *J* = 52.7, 4.7 Hz, H-2), 4.73 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.59 – 4.54 (m, 3H, CH_2 Bn, CH*H* Bn), 4.53 – 4.50 (m, 1H, H-4), 4.39 (ddd, 1H, *J* = 15.9, 6.7, 5.0 Hz, H-3), 3.70 (ddd, 1H, *J* = 10.6, 4.1, 0.8 Hz, H-5), 3.64 (dd, 1H, *J* = 10.6, 5.1 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 159.5 (HC=O), 138.0, 137.2 (C_q), 128.7, 128.2, 127.8 (CH_{arom}), 93.7 (d, *J* = 199.3 Hz, C-1), 93.4 (d, *J* = 17.4 Hz, C-2), 79.4 (d, *J* = 22.4 Hz, C-3), 78.7 (d, *J* = 7.1 Hz, C-4), 73.7, 72.7 (CH_{arom}), 68.1 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): -202.33 (dd, 0.3F *J* = 52.6, 15.9 Hz, F-2α); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = +2.8 Hz, $^2J_{C2,H1}$ = +3.3 Hz; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 8.03 (dd, 1H, *J* = 2.2, 0.9 Hz, *H*C=O), 7.40 – 7.25 (m, 10H, CH_{arom}), 6.33 (d, 1H, *J* = 13.3 Hz, H-1), 5.07 (dd, 1H, *J* = 49.5, 1.4 Hz, H-2), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.60 – 4.53 (m, 4H, CH*H* Bn, CH_2 Bn, H-4), 4.22 (ddd, 1H, *J* = 14.9, 5.6, 1.3 Hz, H-3), 3.80 (dd, 1H, *J* = 10.3, 5.4 Hz, H-5), 3.72 (dd, 1H, *J* = 10.3, 6.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 159.5 (HC=O), 138.0, 137.0 (C_q), 128.7, 128.5, 128.3, 127.9, 127.8 (CH_{arom}), 98.8 (d, *J* = 37.3 Hz, C-1), 96.8 (d, *J* = 184.2 Hz, C-2), 82.7 (C-4), 79.7 (d, *J* = 25.7 Hz, C-3), 73.6, 73.0 (CH_2 Bn), 68.4 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -193.49 – -193.70 (m, 1F, F-2β); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +0.3 Hz, $^2J_{C2,H1}$ = -1.7 Hz; HRMS: $[M+Na]^+$ calcd for $C_{20}H_{21}FO_5Na$ 383.1271, found 383.1276.



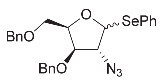
3,5-di-*O*-benzyl-α/β-D-xylofuranose (33). Xyloside **6** (7.6 g, 22 mmol) was dissolved in 20 mL THF and 40 mL H_2O and cooled to 0°C, followed by the slow addition of 100 mL TFA. After stirring overnight, the reaction mixture was partitioned between DCM and H_2O, and the aqueous layer was extracted three times with DCM. The combined DCM layers were washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$, filtered and concentrated *in vacuo*. Flash column chromatography (9/1 to 1/1 pentane/EtOAc) afforded the title compound (6.1 g, 18.5 mmol, 84%) as a waxy material of a α:β = 70:30 anomeric composition. Spectroscopic data were in accord with those previously reported.[60] ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.34 – 7.23 (m, 10H, CH_{arom}), 5.44 (t, 0.7H, *J* = 4.8 Hz, H-1α), 5.11 (d, 0.3H, *J* = 10.9 Hz, H-1β), 4.87 (d, 0.7H, *J* = 5.5 Hz, 1-OHα), 4.66 – 4.53 (m, 2H, 2xC*H*H Bnα, 2xC*H*H Bnβ), 4.52 – 4.43 (m, 2.7H, 2xCH*H* Bnα, 2xCH*H* Bnβ, H-4α), 4.40 (q, 0.3H, *J* = 5.2 Hz, H-4β), 4.19 (t, 0.3H, *J* = 2.9 Hz, H-2β), 4.13 – 4.08 (m, 1H, H-2α, 1-OHβ), 3.98 – 3.93 (m, 1H, H-3α, H-3β), 3.77 – 3.70 (m, 0.6H, H-5β, H-5β), 3.66 – 3.64 (m, 1.4H, H-5α, H-5α), 3.30 (d, 0.7H, *J* = 5.8 Hz, 2-OHα), 3.14 (d, 0.3H, *J* = 4.3 Hz, 2-OHβ); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.9, 137.7, 137.4 (C_q), 128.6, 128.5, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.6 (CH_{arom}), 103.5 (C-1β), 96.1 (C-1α), 83.6 (C-3α), 82.9 (C-3β), 80.0 (C-4β), 79.2 (C-2β), 77.5 (C-4α), 75.6 (C-2α), 73.7 (CH_2 Bnα), 73.6 (CH_2 Bnβ), 72.7 (CH_2 Bnα), 72.0 (CH_2 Bnβ), 69.2 (C-5), 69.1 (C-5α); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{22}O_5Na$ 353.13594, found 353.13594.



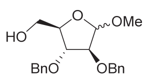
1,2-*O*-thiocarbonate-3,5-di-*O*-benzyl-α/β-D-xylofuranose (34). Diol **33** (1.65 g, 5 mmol, 1 eq.) was dissolved in 25 mL DCM and cooled to 0°C. DiPEA (7 ml, 40 mmol, 8 eq.) and DMAP (122 mg, 1 mmol, 0.2 eq.) were added, followed by the addition of thiophosgene (0.5 mL, 6.25 mmol, 1.25 eq., dissolved in 25 mL DCM). After 15 min the reaction was complete as concluded from TLC analysis. The reaction mixture was diluted with DCM and washed with 1 M aq. HCl, sat. aq. NH_4Cl, sat. aq. $NaHCO_3$, and brine. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. Flash column chromatography (19/1 to 8/2 pentane/EtOAc) afforded the title compound (1.45 g, 3.9 mmol, 78%) as a light orange oil. Spectroscopic data were in accord with those previously reported.[61,62] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.25 (m, 10H, CH_{arom}), 6.40 (d, 1H, *J* = 4.7 Hz, H-1), 5.08 (d, 1H, *J* = 4.7 Hz, H-2), 4.65 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.35 (td, 1H, *J* = 5.8, 3.5 Hz, H-4), 4.20 (d, 1H, *J* = 3.5 Hz, H-3), 3.78 (d, 2H, *J* = 5.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 189.8 (C=S), 137.6, 136.3 (C_q), 128.9, 128.7, 128.6, 128.1, 128.1, 127.9 (CH_{arom}), 107.8 (C-1), 86.0 (C-2), 80.7 (C-4), 79.4 (C-3), 73.8, 73.0 (CH_2 Bn), 66.5 (C-5).



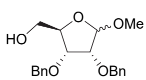
3-benzyloxy-2-(benzyloxy)methyl-2,3-dihydrofuran (35). Thionocarbonate **34** (330 mg, 0.89 mmol, 1 eq.) was dissolved in toluene (1.8 mL) and heated to 70°C. When the target temperature was reached 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (0.18 mL, 0.98 mmol, 1.1 eq.) was added, and the reaction was continued to stir for 20 min. The reaction mixture was concentrated in vacuo and flash column chromatography (1/0 to 85/15 pentane/Et_2O) afforded the title compound (191 mg, 0.68 mmol, 76%) as a colourless oil. Spectroscopic data were in accord with those previously reported.[36] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CHarom), 6.61 (d, 1H, *J* = 2.8 Hz, H-1), 5.24 (t, 1H, *J* = 2.6 Hz, H-2), 4.64 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.61 (ddd, 2H, *J* = 7.1, 2.5, 0.7 Hz, H-3), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.50 – 4.44 (m, 2H, C*H*H Bn, H-4), 4.42 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 3.96 (dd, 1H, *J* = 10.6, 4.6 Hz, H-5), 3.85 (dd, 1H, *J* = 10.6, 7.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 150.6 (C-1), 138.5, 138.1 (C_q), 128.4, 128.4, 127.8, 127.7, 127.6, 127.5 (CH_{arom}), 101.4 (C-2), 83.3 (C-4), 79.5 (C-3), 73.6, 70.7 (CH_2 Bn), 67.8 (C-5).



Phenyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-1-seleno-α/β-D-xylofuranoside (36). Glycal **35** (314 mg, 1.11 mmol, 1 eq.) was dissolved in DCM (5.5 mL) followed by the subsequent addition of $TMSN_3$ (295 µL, 2.22 mmol, 2 eq.), TBAF (1M solution in THF, 220 µL, 0.22 mmol, 0.2 eq.), and *N*-(phenylseleno)phthalimide (671 mg, 2.22 mmol, 2 eq.). The reaction was stirred overnight, diluted with DCM and washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residu was purified by flash column chromatography (1/0 to 85/15 pentane/Et_2O) to give the still impure title compound (360 mg, 0.72 mmol, <65%) and was used direct in the subsequent hydrolysis (*vide infra*, **52**). The major product was confirmed as the trans-*xylo* isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, NOESY, HSQC): δ 7.66 – 7.59 (m, 2H, CH_{arom}), 7.36 – 7.27 (m, 13H, CH_{arom}), 5.46 (d, 1H, *J* = 3.7 Hz, H-1), 4.66 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.62 – 4.53 (m, 3H, CH*H* Bn, CH_2 Bn), 4.34 (q, 1H, *J* = 5.4 Hz, H-4), 4.27 (t, 1H, *J* = 3.4 Hz, H-2), 4.01 (dd, 1H, *J* = 5.4, 3.2 Hz, H-3), 3.78 (dd, 1H, *J* = 10.2, 5.2 Hz, H-5), 3.73 (dd, 1H, *J* = 10.2, 6.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.1 (C_q), 134.3 (CH_{arom}), 130.0 (C_q), 129.2, 128.7, 128.6, 128.4, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7 (CH_{arom}), 85.7 (C-1), 81.6 (C-3), 81.1 (C-4), 73.6, 72.7 (CH_2 Bn), 70.1 (C-2), 68.6 (C-5); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -1.1 Hz, $^2J_{C2,H1}$ = -3.1 Hz, $^2J_{C2,H1}$ = -4.0 Hz. And minor products are identified as cis-xylo (^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +0.9 Hz, $^2J_{C2,H1}$ = +1.3 Hz), and trans-lyxo (^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz):$^2J_{C1,H2}$ = -0.7 Hz, $^2J_{C2,H1}$ = -3.0 Hz).

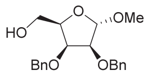


Methyl 2,3-di-*O*-benzyl-α/β-D-arabinofuranoside (37). The title compound was prepared by the general procedure for the synthesis of primary furanoside alcohols from D-arabinose (200 mmol) in 41% as a yellow oil (28.2 g, 82 mmol). Spectroscopic data were in accord with those previously reported.[63] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.26 (m, 10H, CH_{arom}), 4.94 (s, 1H, H-1), 4.69 – 4.41 (m, 4H, CH_2Bn), 4.19 – 4.11 (m, 1H, H-3), 4.03 – 3.93 (m, 2H, H-2, H-4), 3.83 (ddd, 1H, *J* = 12.1, 4.2, 2.8 Hz, H-5), 3.64 (ddd, 1H, *J* = 12.0, 7.9, 4.1 Hz, H-5), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.4 (C_q), 128.6, 128.6, 128.1, 128.1, 128.0, 128.0 (CH_{arom}), 107.6 (C-1), 87.8 (C-2), 82.6 (C-4), 82.5 (C-3), 72.5, 72.0 (CH_2Bn), 62.4 (C-5), 55.1 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.42 – 7.27 (m, 10H, CH_{arom}), 4.73 – 4.56 (m, 5H, H-1, 2xCH_2Bn), 4.27 (dd, 1H, *J* = 6.9, 6.1 Hz, H-3), 4.07 (m, 2H, *J* = 9.4, 6.4, 3.8 Hz, H-2, H-3), 3.69 (d, 1H, *J* = 11.8 Hz, H-5), 3.57 (dt, 1H, *J* = 11.6, 5.6 Hz, H-5), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 137.6 (C_q), 128.6, 128.6, 128.3, 128.2, 128.0, 127.9 (CH_{arom}), 101.9 (C-1), 84.4 (C-2), 82.4 (C-4), 81.1 (C-3), 72.8, 72.7 (CH_2 Bn), 64.1 (C-5), 55.9 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{28}NO_5$ 362.19620, found 362.19611.

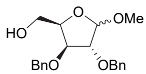


Methyl 2,3-di-*O*-benzyl-α/β-D-ribofuranoside (38). The title compound was prepared by the general procedure for the synthesis of primary furanoside alcohols from D-ribose (100 mmol) in 43% as a yellow oil (14.8 g, 43 mmol). Spectroscopic data were in accord with those previously reported.[64] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.27 (m, 10H, CH_{arom}), 4.87 (d, 1H, *J* = 4.3 Hz, H-1), 4.74 (d, *J* = 12.7 Hz, C*H*H Bn), 4.65 (d, *J* = 12.3 Hz, C*H*H Bn), 4.61 (d, *J* = 12.3 Hz, CH*H* Bn), 4.58

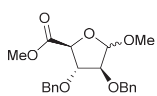
(d, *J* = 12.7 Hz, CH*H* Bn), 4.17 (q, 1H, *J* = 3.5 Hz, H-3), 3.84 (dd, 1H, *J* = 6.9, 3.6 Hz, H-4), 3.73 (dd, 1H, *J* = 6.9, 4.3 Hz, H-2), 3.66 (dd, 1H, *J* = 12.0, 3.2 Hz, H-5), 3.46 (s, 3H, CH_3OMe), 3.44 – 3.37 (m, 1H, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3, 137.9 (C_q), 128.5, 128.5, 128.3, 128.1, 128. 0, 127.9 (CH_{arom}), 102.8 (C-1), 83.2 (C-3), 78.3 (C-2), 74.8 (C-4), 72.8, 72.7 (CH_2Bn), 62.9 (C-5), 55.7 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.44 – 7.25 (m, 10H, CH_{arom}), 4.89 (s, 1H, H-1), 4.65 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.48 (d, 1H, *J* = 11.7 Hz, CHH Bn), 4.27 (dt, 1H, *J* = 6.8, 3.4 Hz, H-4), 4.11 (dd, 1H, *J* = 7.0, 4.7 Hz, H-3), 3.86 (d, 1H, *J* = 4.7 Hz, H-2), 3.79 (dt, 1H, *J* = 12.0, 3.4 Hz, H-5), 3.56 (ddd, 1H, *J* = 12.1, 8.5, 3.8 Hz, H-5), 3.35 (s, 3H, CH_3 OMe), 2.06 (dd, 1H, *J* = 8.5, 4.1 Hz, OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.7 (C_q), 128.5, 128.1, 128.0, 127.9 (CH_{arom}), 106.9 (C-1), 82.4 (C-4), 80.2 (C-2), 77.3 (C-3), 72.7, 72.5 (CH_2 Bn), 62.8 (C-5), 55.7 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{24}O_5Na$ 367.15160, found 367.15159.



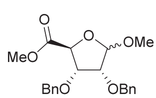
Methyl 2,3-di-*O*-benzyl-α-D-lyxofuranoside (39). The title compound was prepared by the general procedure for the synthesis of primary furanoside alcohols from D-lyxose (160 mmol) in 42% as a yellow oil (23.1 g, 67.2 mmol). Spectroscopic data were in accord with those previously reported.[65] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.26 (m, 10H, CH_{arom}), 5.00 (s, 1H, H-1), 4.72 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.64 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.46 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.36 (dd, 1H, *J* = 7.3, 4.9 Hz, H-3), 4.26 (dt, 1H, *J* = 7.5, 4.2 Hz, H-4), 3.88 (dd, 1H, *J* = 4.8, 0.8 Hz, H-2), 3.85 – 3.80 (m, 2H, H-5), 3.34 (s, 3H, CH_3 OMe), 2.68 (t, 1H, *J* = 6.1 Hz, OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.7, 137.4 (C_q), 128.6, 128.6, 128.1, 128.0, 128.0, 127.7 (CH_{arom}), 105.5 (C-1), 80.0 (C-2), 78.4 (C-4), 78.3 (C-3), 73.0, 72.8 (CH_2 Bn), 62.0 (C-5), 55.3 (OMe); HRMS: $[M+H]^+$ calcd for $C_{20}H_{25}O_5$ 345.16965, found 345.16967.



Methyl 2,3-di-*O*-benzyl-α/β-D-xylofuranoside (40). The title compound was prepared by the general procedure for the synthesis of primary furanoside alcohols from D-xylose (200 mmol) in 50% as a yellow oil (34.4 g, 100 mmol). Spectroscopic data were in accord with those previously reported.[66] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.25 (m, 18H, CH_{arom}), 4.90 (d, 1H, *J* = 1.9 Hz, H-1β), 4.80 (d, 0.8H, *J* = 4.2 Hz, H-1α), 4.73 (d, 0.8H, *J* = 11.8 Hz, C*H*H Bnα), 4.67 – 4.47 (m, 6.4H, CH*H* Bnα, CH_2 Bnα, 2xCH_2 Bnβ), 4.43 (dd, 0.8H, *J* = 7.8, 6.5 Hz, H-3α), 4.31 (dt, 1H, *J* = 6.8, 4.8 Hz, H-4β), 4.22 (dd, 0.8H, *J* = 7.7, 3.9 Hz, H-4α), 4.18 (dd, 1H, *J* = 6.8, 3.8 Hz, H-3β), 4.10 (dd, 1H, *J* = 3.9, 1.9 Hz, H-2β), 4.05 (dd, 0.8H, *J* = 6.5, 4.2 Hz, H-2α), 3.83 – 3.70 (m, 3.6H, 2xH-5α, 2xH-5β), 3.40 (s, 3H, CH_3 OMeβ), 3.38 (s, 2.4H, CH_3 OMeα), 2.58 (t, 1H, *J* = 6.6 Hz, 5-OHβ), 2.43 (dd, 0.8H, *J* = 8.7, 5.0 Hz, 5-OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.6, 137.5 (C_q), 128.6, 128.6, 128.6, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8 (CH_{arom}), 108.0 (C-1β), 100.2 (C-1α), 87.2 (C-2β), 84.6 (C-2α), 82.9 (C-3β), 82.3 (C-3α), 80.6 (C-4β), 76.3 (C-4α), 72.8, 72.7, 72.5, 72.3 (CH_2 Bn), 62.3, 62.3 (C-5α,β), 55.7 (OMeβ), 55.2 (OMeα); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{24}O_5Na$ 367.15160, found 367.15152.

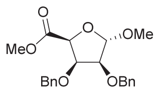


Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (41). The title compound was generated from **37** (28.2 g, 78.8 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 70% (20.6 g, 55.3 mmol) as a yellow oil. R*f*: 0.75 (7/3 pentane/EtOAc). IR (thin film): 698, 737, 1028, 1059, 1099, 1207, 1360, 1454, 1734, 1755, 2874, 2916, 2949, 3030. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.44 – 7.21 (m, 10H, CH_{arom}), 5.09 (s, 1H, H-1), 4.63 (d, 1H, *J* = 4.8 Hz, H-4), 4.67 – 4.54 (m, 2H, CH_2 Bn), 4.47 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.41 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.15 (dd, 1H, *J* = 4.8, 1.8 Hz, H-3), 3.96 (dd, 1H, *J* = 1.8, 0.8 Hz, H-2), 3.73 (s, 3H, CH_3 CO_2Me), 3.41 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.6 (C=O), 137.2, 137.2 (C_q), 128.4, 128.2, 128.0, 127.9, 127.9, 127.9 (CH_{arom}), 108.0 (C-1), 86.5 (C-2), 84.9 (C-3), 80.9 (C-4), 72.1, 71.7 (CH_2 Bn), 55.5 (CH_3 OMe), 52.4 (CH_3 CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.22 (m, 10H, CH_{arom}), 4.76 (d, 1H, *J* = 4.2 Hz, H-1), 4.73 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.67 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.64 – 4.58 (m, 2H, CH_2 Bn), 4.53 (dd, 1H, *J* = 6.6, 4.9 Hz, H-3), 4.42 (d, 1H, *J* = 4.9 Hz, H-4), 4.01 (dd, 1H, *J* = 6.6, 4.2 Hz, H-2), 3.73 (s, 3H, CH_3 CO_2Me), 3.42 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.5 (C=O), 137.7, 137.4 (C_q), 128.4, 128.4, 128.3, 128.1, 127.9, 127.7 (CH_{arom}), 102.3 (C-1), 83.8, 83.8 (C-2, C-3), 79.4 (C-4), 72.5, 72.5 (CH_2 Bn), 55.5 (CH_3 OMe), 52.2 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{28}NO_6$ 390.19111, found 390.19094.

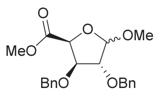


Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-ribofuranosyl uronate) (42). The title compound was generated from **38** (13.3 g, 38.7 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 87% (12.5 g, 33.7 mmol) as a yellow oil. R*f*: 0.73 (7/3 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[67] Data for the β-anomer: IR (thin film): 698, 739, 957, 1026, 1063, 1111, 1136, 1205, 1358, 1454, 1738, 1753, 2930, 3030; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.38 – 7.26 (m, 10H, CH_{arom}), 4.97 (s, 1H, H-1), 4.68 – 4.62 (m, 3H, CH_2 Bn, H-4), 4.61 (d, 1H, *J* = 12.0

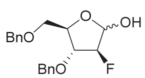
Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.35 (dd, 1H, *J* = 6.4, 4.7 Hz, H-3), 3.85 (d, 1H, *J* = 4.6 Hz, H-2), 3.74 (s, 3H, CH_3 CO_2Me), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 172.0 (C=O), 137.6, 137.5 (C_q), 128.5, 128.4, 128.0, 127.9, 127.9 (CH_{arom}), 107.1 (C-1), 80.6 (C-3), 79.8 (C-2), 79.6 (C-4), 72.8, 72.7 (CH_2 Bn), 55.3 (CH_3 OMe), 52.3 (CH_3 CO_2Me); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$: +0.3 Hz, $^2J_{C2,H1}$: -0.6 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{28}NO_6$ 390.19111, found 390.19105.



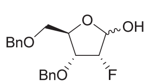
Methyl (methyl 2,3-di-*O*-benzyl-α-D-lyxofuranosyl uronate) (43). The title compound was generated from 39 (9.91 g, 28.8 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 89% (9.5 g, 25.5 mmol) as a white solid. R*f*: 0.70 (7/3 pentane/EtOAc). m.p. 76-80 °C. $[\alpha]_D^{20}$ = +29.7° (*c* = 0.92, $CHCl_3$); IR (thin film): 698, 739, 1028, 1065, 1145, 1211, 1454, 1734, 1767, 2949; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CH_{arom}), 5.23 (d, 1H, *J* = 3.6 Hz, H-1), 4.76 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.72 (d, 1H, *J* = 4.7 Hz, H-4), 4.69 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.59 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.35 (t, 1H, *J* = 4.7 Hz, H-3), 3.93 (dd, 1H, *J* = 4.6, 3.6 Hz, H-2), 3.72 (s, 3H, CH_3 CO_2Me), 3.43 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 169.1 (C=O), 138.0, 137.8 (C_q), 128.5, 128.4, 127.9, 127.9, 127.8, 127.8 (CH_{arom}), 108.0 (C-1), 83.3 (C-2), 79.0 (C-3), 78.5 (C-4), 73.9, 72.8 (CH_2 Bn), 56.5 (CH_3 OMe), 52.3 (CH_3 CO_2Me); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = -2.8 Hz, $^2J_{C2,H1}$ = -1.6 Hz; HRMS: $[M+H]^+$ calcd for $C_{21}H_{25}O_6$ 373.16456, found 373.16471.



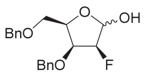
Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (44). The title compound was generated from 40 (34.4 g, 100 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 88% (30.8 g, 88.2 mmol) as a yellow oil. R*f*: 0.65 (7/3 pentane/EtOAc). IR (thin film): 698, 739, 1063, 1119, 1207, 1454, 1738, 1765, 2916, 2949, 3030. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.21 (m, 10H, CH_{arom}), 4.94 (d, 1H, *J* = 4.3 Hz, H-1), 4.79 (d, 1H, *J* = 7.4 Hz, H-4), 4.64 – 4.57 (m, 4H, 2xCH_2 Bn), 4.47 (dd, 1H, *J* = 7.4, 6.2 Hz, H-3), 4.11 (dd, 1H, *J* = 6.2, 4.3 Hz, H-2), 3.73 (s, 3H, CH_3 CO_2Me), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (C=O), 137.6, 137.4 (C_q), 128.5, 128.4, 128.2, 128.1, 127.7, 127.5 (CH_{arom}), 101.6 (C-1), 82.5 (C-2), 81.8 (C-3), 76.5 (C-4), 73.0, 72.9 (CH_2 Bn), 55.7 (OMe), 52.2 (CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.23 (m, 10H, CH_{arom}), 5.04 (s, 1H, H-1), 4.90 (d, 1H, *J* = 6.2 Hz, H-4), 4.61 – 4.56 (m, 1H, C*H*H Bn) 4.53 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.43 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.39 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.23 (dd, 1H, *J* = 6.2, 1.4 Hz, H-2), 3.98 – 3.97 (m, 1H, H-2), 3.77 (s, 3H, CH_3 CO_2Me), 3.53 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (C=O), 137.2, 137.2 (C_q), 128.5, 128.5, 128.1, 128.0, 127.7, 127.5 (CH_{arom}), 108.8 (C-1), 85.1 (C-2), 81.2 (C-3), 81.1 (C-4), 72.7, 71.9 (CH_2 Bn), 56.0 (OMe), 52.1 (CO_2Me); HRMS: $[M+H]^+$ calcd for $C_{21}H_{25}O_6$ 373.16456, found 373.16448.



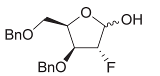
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-arabinofuranose (45). The title compound was generated from 18 (470 mg, 1.36 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (65°C, 64 h). Yield: 63% α:β = 70:30 (0.85 mmol) as a colourless oil. Spectroscopic data were in accord with those previously reported.[24] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.23 (m, 10H, CH_{arom}), 5.45 (dd, 1H, *J* = 10.7, 2.9 Hz, H-1), 4.93 (d, 1H, *J* = 50.2 Hz, H-2), 4.62 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.57 – 4.47 (m, 3H, CH_2 Bn, CH*H* Bn), 4.43 (q, 1H, *J* = 5.2 Hz, H-4), 3.98 (dd, 1H, *J* = 21.0, 4.8 Hz, H-3), 3.76 (d, 1H, *J* = 4.1 Hz, OH), 3.58 – 3.54 (m, 1H, H-5), 3.51 (dd, 1H, *J* = 10.3, 5.1 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.9, 137.0 (C_q), 128.6, 128.4, 128.1, 128.0, 127.8, 127.8 (CH_{arom}), 100.4 (d, *J* = 34.5 Hz, C-2), 98.4 (d, *J* = 182.7 Hz, C-1), 82.6 (d, *J* = 25.6 Hz, C-3), 81.9 (d, *J* = 2.0 Hz, C-4), 73.5, 72.4 (CH_2 Bn), 69.7 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -189.12 (ddd, *J* = 50.7, 21.0, 10.8 Hz); ^{13}C HSQC-HECADE NMR: $^2J_{C1\text{-}H2}$ = +1.8 Hz, $^2J_{C2\text{-}H1}$ = +3.9 Hz; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.23 (m, 10H, CH_{arom}), 5.32 – 5.24 (m, 1H, H-1), 5.00 – 4.85 (m, 1H, H-2), 4.66 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.57 – 4.47 (m, 3H, CH*H* Bn, CH_2 Bn), 4.28 (dt, 1H, *J* = 17.8, 4.9 Hz, H-3), 4.22 (d, 1H, *J* = 9.5 Hz, OH), 4.09 (q, 1H, *J* = 3.8 Hz, H-4), 3.58 – 3.54 (m, 1H, H-5), 3.47 (dd, 1H, *J* = 10.3, 3.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.3, 137.1 (C_q), 128.6, 128.6, 128.1, 128.1, 128.0, 127.9 (CH_{arom}), 95.8 (d, *J* = 194.1 Hz, C-2), 95.4 (d, *J* = 18.8 Hz, C-1), 80.6 (d, *J* = 22.8 Hz, C-3), 80.1 (d, *J* = 8.2 Hz, C-4), 73.7, 72.2 (CH_2 Bn), 70.0 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -202.72 (dd, *J* = 52.7, 17.8 Hz); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}FO_4Na$ 355.13161, found 355.13160.



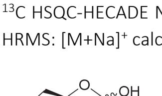
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-ribofuranose (46). The title compound was generated from 19 (205 mg, 0.59 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 18 h). Yield: 78% α:β = 25:75 (0.46 mmol). Spectroscopic data were in accord with those previously reported.[22] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.21 (m, 10H, CH_{arom}), 5.35 (dd, 0.75H, *J* = 8.5, 6.7 Hz, H-1β), 5.33 (dt, 0.25H, *J* = 11.7, 3.6 Hz, H-1α), 4.91 (dt, 0.25H, *J* = 51.8, 4.3 Hz, H-2α), 4.76 (dd, 0.75H, *J* = 53.3, 3.4 Hz, H-2$_{\beta}$), 4.72 (d, 0.25H, *J* = 11.8 Hz, C*H*H Bn$_{\alpha}$), 4.66 (d, 0.75H, *J* = 11.7 Hz, C*H*H Bn$_{\beta}$), 4.60 – 4.42 (m, 3H, CH*H* Bn$_{\alpha}$, CH*H* Bn$_{\beta}$, CH$_2$ Bn$_{\alpha}$, CH$_2$ Bn$_{\beta}$), 4.34 (qd, 0.25H, *J* = 3.4, 1.0 Hz, H-4$_{\alpha}$), 4.31 – 4.21 (m, 1.5H, H-3$_{\beta}$, H-4$_{\beta}$), 4.09 – 4.01 (m, 0.5H, H-3$_{\alpha}$, 1-OH$_{\alpha}$), 3.89 (dd, 0.75H, *J* = 6.7, 0.9 Hz, 1-OH$_{\beta}$), 3.66 (dd, 0.75H, *J* = 10.4, 2.4 Hz, H-5$_{\beta}$), 3.54 (dd, 0.25H, *J* = 10.7, 3.3 Hz, H-5$_{\alpha}$), 3.51 – 3.45 (m, 1H, H-5$_{\alpha}$, H-5$_{\beta}$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 137.8, 137.3, 137.1 (C$_q$), 128.6, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.7 (CH$_{arom}$), 99.8 (d, *J* = 29.2 Hz, C-1$_{\beta}$), 95.9 (d, *J* = 18.5 Hz, C-1$_{\alpha}$), 91.9 (d, *J* = 187.5 Hz, C-2$_{\beta}$), 88.8 (d, *J* = 197.2 Hz, C-2$_{\alpha}$), 80.7 (d, *J* = 3.5 Hz, C-4$_{\alpha}$), 76.8 (C-4$_{\beta}$), 76.8 (d, *J* = 14.7 Hz, C-3$_{\alpha}$), 76.5 (d, *J* = 15.5 Hz, C-3$_{\beta}$), 73.6 (CH$_2$ Bn$_{\alpha}$), 73.6 (CH$_2$ Bn$_{\beta}$), 73.2 (d, *J* = 2.2 Hz, CH$_2$ Bn$_{\alpha}$), 72.8 (CH$_2$ Bn$_{\beta}$), 69.4 (C-5$_{\alpha}$), 69.1 (C-5$_{\beta}$); ^{13}C HSQC-HECADE NMR (CDCl$_3$, 126 MHz): α-anomer: $^2J_{C1-H2}$: +1.8 Hz, $^2J_{C2-H1}$: -+2.0 Hz, β-anomer: $^2J_{C2-H1}$: -0.3 Hz; HRMS: [M+Na]$^+$ calcd for C$_{19}$H$_{21}$FO$_4$Na 355.13161, found 355.13147.



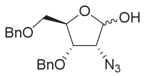
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-lyxofuranose (47). The title compound was generated from 20 (340 mg, 0.98 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (65°C, 6 h). Yield: 75% α:β = 1:1 (0.73 mmol). IR (thin film): 696, 735, 1027, 1045, 1454, 2864, 2926, 3410; ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC): δ 7.42 – 7.29 (m, 20H, CH$_{arom}$), 5.58 (dd, 1H, *J* = 9.8, 2.6 Hz, H-1$_{\alpha}$), 5.28 (dd, 1H, *J* = 12.5, 4.5 Hz, H-1$_{\beta}$), 4.94 (dt, 1H, *J* = 50.3, 4.4 Hz, H-2$_{\alpha}$), 4.87 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.87 (ddd, 1H, *J* = 52.6, 4.1, 1.0 Hz, H-2$_{\beta}$), 4.73 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.68 – 4.61 (m, 3H, CH*H* Bn 2xC*H*H Bn), 4.60 – 4.53 (m, 4H, 3xCH*H* Bn, H-4$_{\alpha}$), 4.40 (ddd, 1H, *J* = 20.3, 7.1, 4.1 Hz, H-3$_{\alpha}$), 4.25 (td, 1H, *J* = 4.2, 1.8 Hz, H-3$_{\beta}$), 4.23 – 4.18 (m, 1H, H-4$_{\beta}$), 4.17 (dd, 1H, *J* = 12.6, 1.0 Hz, 1-OH$_{\beta}$), 3.85 (dd, 1H, *J* = 9.7, 6.6 Hz, H-5$_{\beta}$), 3.79 (dd, 1H, *J* = 10.5, 3.6 Hz, H-5$_{\alpha}$), 3.76 – 3.67 (m, 2H, H-5$_{\alpha}$, H-5$_{\beta}$), 3.43 (t, 1H, *J* = 2.9 Hz, 1-OH$_{\alpha}$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 138.1, 137.8, 137.4, 137.0 (C$_q$), 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7 (CH$_{arom}$), 99.0 (d, *J* = 30.5 Hz, C-1$_{\alpha}$), 95.1 (d, *J* = 19.2 Hz, C-1$_{\beta}$), 92.9 (d, *J* = 187.9 Hz, C-2$_{\alpha}$), 89.5 (d, *J* = 202.2 Hz, C-2$_{\beta}$), 77.7 (C-4$_{\alpha}$), 77.4 (d, *J* = 5.9 Hz, C-4$_{\beta}$), 76.9 (d, *J* = 15.0 Hz, C-3$_{\alpha}$), 76.3 (d, *J* = 14.6 Hz, C-3$_{\beta}$), 74.5 (d, *J* = 3.1 Hz, CH$_2$ Bn), 73.8, 73.6 (CH$_2$ Bn), 73.2 (d, *J* = 1.3 Hz, CH$_2$ Bn), 70.3 (d, *J* = 1.2 Hz, C-5$_{\alpha}$), 68.9 (C-5$_{\beta)}$; ^{19}F NMR (CDCl$_3$, 471 MHz): δ -207.67 (ddd, *J* = 52.6, 20.1, 9.3 Hz, C2-F$_{\alpha}$), -214.36 (d, *J* = 50.4 Hz, C2-F$_{\beta}$); HRMS: [M+Na]$^+$ calcd for C$_{19}$H$_{21}$FO$_4$Na 355.13161, found 355.13164.



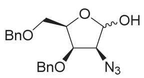
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-xylofuranose (48). The title compound was generated from 21 (181 mg, 0.52 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 6 h). Yield: 75% α:β = 30:70 (0.40 mmol) as a colourless oil. Spectroscopic data were in accord with those previously reported for the L-enantiomer.[68] IR (thin film): 696, 735, 1026, 1047, 1454, 2868, 2924, 3400; ^{1}H NMR (CDCl$_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.24 (m, 10H), 5.48 (td, 0.3H, *J* = 8.3, 3.7 Hz, H-1$_{\alpha}$), 5.29 (dd, 0.7H, *J* = 13.9, 11.6 Hz, H-1$_{\beta}$), 4.95 (ddd, 0.7H, *J* = 52.2, 3.2, 0.8 Hz, H-2$_{\beta}$), 4.90 (dt, 0.3H, *J* = 52.1, 3.4 Hz, H-2$_{\alpha}$), 4.68 (d, 0.7H, *J* = 11.7 Hz, C*H*H Bn$_{\beta}$), 4.65 (d, 0.3H, *J* = 11.9 Hz, C*H*H Bn$_{\alpha}$), 4.60 – 4.50 (m, 3H, CH*H* Bn$_{\alpha}$, CH*H* Bn$_{\beta}$, CH$_2$ Bn$_{\alpha}$, CH$_2$ Bn$_{\beta}$), 4.50 – 4.46 (m, 0.3H, H-4$_{\alpha}$), 4.39 (dt, 0.7H, *J* = 6.1, 4.2 Hz, H-4$_{\beta}$), 4.27 (ddd, 0.3H, *J* = 13.2, 5.3, 3.1 Hz, H-3$_{\alpha}$), 4.23 (dddd, 0.7H, *J* = 17.8, 6.1, 3.0, 0.7 Hz, H-3$_{\beta}$), 4.14 (d, 0.7H, *J* = 11.6 Hz, 1-OH$_{\beta}$), 3.73 (ddd, 0.7H, *J* = 10.1, 4.6, 1.2 Hz, H-5$_{\beta}$), 3.71 – 3.67 (m, 1H, H-5$_{\alpha}$, H-5$_{\beta}$), 3.64 (dd, 0.3H, *J* = 10.2, 5.9 Hz, H-5$_{\alpha}$), 3.57 (dd, 0.3H, *J* = 8.5, 3.2 Hz, 1-OH$_{\alpha}$); ^{13}C-APT NMR (CDCl$_3$, 126 MHz, HSQC): δ 138.1, 137.4, 137.3, 137.0 (C$_q$), 128.7, 128.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (CH$_{arom}$), 101.0 (d, *J* = 34.4 Hz, C-1$_{\beta}$), 99.1 (d, *J* = 185.0 Hz, C-2$_{\beta}$), 95.6 (d, *J* = 17.1 Hz, C-1$_{\alpha}$), 93.8 (d, *J* = 191.1 Hz, C-2$_{\alpha}$), 80.9 (d, *J* = 24.6 Hz, C-3$_{\beta}$), 80.3 (d, *J* = 24.1 Hz, C-3$_{\alpha}$), 80.0 (d, *J* = 3.4 Hz, C-4$_{\beta}$), 77.2 (d, *J* = 4.1 Hz, C-4$_{\alpha}$), 73.9 (CH$_2$ Bn$_{\beta}$), 73.6 (CH$_2$ Bn$_{\alpha}$), 73.0 (CH$_2$ Bn$_{\beta}$), 72.7 (CH$_2$ Bn$_{\alpha}$), 68.4 (C-5$_{\alpha}$), 68.4 (C-5$_{\beta}$); ^{19}F NMR (CDCl$_3$, 471 MHz): δ -189.88 (ddd, 0.7F, *J* = 52.2, 17.7, 14.1 Hz, F-2$_{\beta}$), -204.74 (dt, 0.3F, *J* = 52.2, 9.7 Hz, F-2$_{\alpha}$); ^{13}C HSQC-HECADE NMR (CDCl$_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = +3.1 Hz, $^2J_{C2,H1}$ = +5.6 Hz, β-anomer: $^2J_{C2,H1}$ = -2.3 Hz; HRMS: [M+Na]$^+$ calcd for C$_{19}$H$_{21}$FO$_4$Na 355.1322, found 355.1326.



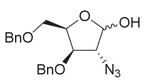
2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-arabinofuranose (49). The title compound was generated from 22 (554 mg, 1.50 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 64 h). Yield: 76% α:β = 1:1 (1.1 mmol) as a colourless oil. IR (thin film): 696, 735, 1070, 1454, 2108, 3320; ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.10 (m, 20H), 5.33 (d, 1H, *J* = 7.0 Hz, H-1$_{\alpha}$), 5.30 (dd, 1H, *J* = 9.1, 4.6 Hz, H-1$_{\beta}$), 4.68 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.62 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.58 – 4.54 (m, 4H, 2x CH$_2$ Bn), 4.52 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.45 – 4.38 (m, 1H, H-4$_{\alpha}$), 4.24 (dd, 1H, *J* = 7.0, 5.2 Hz, H-3$_{\beta}$), 4.16 (dt, 1H, *J* = 5.2, 3.0 Hz, H-4$_{\beta}$), 3.98 – 3.94 (m, 2H, H-2$_{\alpha}$, OH$_{\beta}$), 3.91 (ddd, 1H, *J* = 4.3, 2.6, 0.6 Hz, H-3$_{\alpha}$), 3.80 (dd, 1H, *J* = 6.9, 4.5 Hz, H-2$_{\beta}$), 3.59 (dd, 1H, *J* = 10.3, 3.2 Hz, H-5$_{\beta}$), 3.60 – 3.50 (m, 2H, 2xH-5$_{\alpha}$), 3.41 (dd, 1H, *J* = 10.3, 3.0 Hz, H-5$_{\beta}$), 3.30 (d, 1H, *J* = 6.9 Hz, OH$_{\alpha}$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 137.9, 137.4, 136.9, 136.8 (C$_q$), 128.8, 128.7, 128.7, 128.6, 128.4, 128.3, 128.3, 128.1, 128.1, 128.1, 127.9 (CH$_{arom}$), 101.0 (C-1$_{\alpha}$), 97.4 (C-1$_{\beta}$), 82.9 (C-3$_{\alpha}$), 82.2 (C-4$_{\alpha}$), 81.8 (C-4$_{\beta}$), 80.3 (C-3$_{\beta}$), 73.9, 73.6, 72.7, 72.6 (CH$_2$ Bn), 70.2 (C-2$_{\alpha}$), 69.9 (C-5β), 69.6 (C-5α), 68.7 (C-2β); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1\text{-}H2}$ = -2.2 Hz, $^2J_{C2\text{-}H1}$ = -0.1 Hz. β-anomer: $^2J_{C1\text{-}H2}$ = -2.1 Hz, $^2J_{C2\text{-}H1}$ = +2.2 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{26}N_3O_4Na$ 378.14243, found 378.14248.



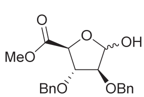
2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-ribofuranose (50). The title compound was generated from a 4:1 mixture of **23** and **27** by the general procedure for methyl furanoside hydrolysis, conditions A (65°C, 6 h). Combined yield: 89%, Yield of **42** was 70% over two steps (from **15**), α:β = 33:67 (0.29 mmol) as a colourless oil. IR (thin film): 696, 741, 1094, 1454, 2105, 2866, 3330; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.22 (m, 15H, CH_{arom}), 5.35 (bs, 0.5H, H-1α), 5.23 (s, 1H, H-1β), 4.68 – 4.58 (m, 2H, CH2 Bnα, C*H*H Bnβ), 4.53 (d, 1H, *J* = 11.8 Hz, C*H*H Bnβ), 4.49 – 4.35 (m, 4.5H, 2xCH*H* Bnβ, CH_2 Bnα, H-3β, H-4α), 4.21 (dt, 1H, *J* = 6.4, 3.1 Hz, H-4β), 4.13 (bs, 1H, 1-OHβ), 4.09 (dd, 0.5H, *J* = 5.4, 2.7 Hz, H-3α), 3.96 (bs, 0.5H, 1-OHα), 3.78 (d, 1H, *J* = 5.1 Hz, H-2β), 3.66 (dd, 0.5H, *J* = 5.4, 4.4 Hz, H-2α), 3.62 (dd, 1H, *J* = 10.4, 2.9 Hz, H-5β), 3.49 – 3.40 (m, 1.5H, H-5β, 2xH-5α); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.6, 137.2, 137.0, 136.8 (C_q), 128.6, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.7 (CH_{arom}), 100.8 (C-1β), 97.6 (C-1α), 81.6 (C-4α), 80.9 (C-4β), 78.8 (C-3α), 78.4 (C-3β), 73.6, 73.6, 73.1, 73.0 (CH_2 Bn), 69.6 (C-5α), 69.3 (C-5β), 65.9 (C-2β), 62.1 (C-2α); HRMS: $[M+NH_4]^+$ calcd for $C_{19}H_{25}N_4O_4$ 373.18703, found 373.18699.



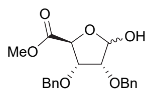
2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-lyxofuranose (51). The title compound was generated from **24** (620 mg, 1.68 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 18 h). Yield: 62% α:β = 60:40 (1.04 mmol) as a colourless oil. IR (thin film): 696, 734, 1026, 1070, 1269, 1454, 2110, 2868, 2924, 3400; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.28 (m, 10H, CH_{arom}), 5.45 (t, 0.6H, *J* = 2.7 Hz, H-1α), 5.28 (dd, 0.4H, *J* = 12.2, 4.6 Hz, H-1β), 4.80 (d, 0.4H, *J* = 11.0 Hz, C*H*H Bnβ), 4.72 (d, 0.6H, *J* = 11.7 Hz, C*H*H Bnα), 4.65 (d, 0.4H, *J* = 11.0 Hz, CH*H* Bnβ), 4.62 – 4.47 (m, 3.2H, CH_2 Bnα, CH_2 Bnβ, CH*H* Bnα, H-4α), 4.41 (t, 0.6H, *J* = 5.5 Hz, H-3α), 4.22 (t, 0.4H, *J* = 4.0 Hz, H-3β), 4.17 (ddd, 0.4H, *J* = 7.2, 5.5, 3.8 Hz, H-4β), 3.84 – 3.76 (m, 1.4H, H-2α, H-5β, OHβ), 3.74 – 3.67 (m, 1.6H, H-5β, H-5α, H-5α), 3.63 (t, 0.4H, *J* = 4.4 Hz, H-2β), 3.06 (d, 0.6H, *J* = 3.1 Hz, OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.8 (CH_{arom}), 99.8 (C-1α), 97.3 (C-1β), 79.6 (C-4α), 79.0 (C-3), 78.5, 78.4 (C-3β, C-4β), 75.0, 74.0, 73.9, 73.7 (CH_2 Bn), 69.4 (C-5α), 68.8 (C-5β), 66.6 (C-2α), 63.0 (C-2β); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.14243, found 378.14233.



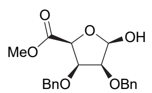
2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-xylofuranose (52). Selenoglycoside **36** (360 mg, 0.72 mmol, 1 eq.) was dissolved in THF/H_2O/acetone (3/2/3 v/v/v, 8 mL) and cooled to 0°C, followed by addition of NIS (180 mg, 0.8 mmol, 1.1 eq.). After 1 h the reaction mixture was quenched by addition of 10% $Na_2S_2O_3$, diluted with H_2O and extracted with DCM three times. The combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (19/1 to 8/2 pentane/EtOAc) gave the title compound as a colourless oil (222 mg, 0.62 mmol, 87%). IR (thin film): 696, 737, 1053, 1255, 1454, 2102, 2866, 2924, 3390; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, NOESY, HSQC): δ 7.37 – 7.25 (m, 20H, CH_{arom}), 5.48 (dd, 1H, *J* = 5.4, 4.6 Hz, H-1α), 5.15 (dd, 1H, *J* = 11.4, 1.7 Hz, H-1β), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.65 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.59 – 4.54 (m, 4H, C*H*H Bn, 3xCH*H* Bn), 4.52 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.47 (td, 1H, *J* = 6.1, 4.5 Hz, H-4α), 4.29 (dt, 1H, *J* = 5.6, 4.5 Hz, H-4β), 4.23 (dd, 1H, *J* = 5.9, 5.2 Hz, H-3α), 4.15 (d, 1H, *J* = 11.4 Hz, 1-OHβ), 4.03 (dd, 1H, *J* = 5.6, 3.7 Hz, H-3β), 3.99 (dd, 1H, *J* = 4.1, 1.7 Hz, H-2β), 3.89 – 3.85 (m, 1H, H-2α), 3.73 (dd, 1H, *J* = 10.1, 4.7 Hz, H-5β), 3.70 (dd, 1H, *J* = 10.1, 4.3 Hz, H-5β), 3.68 (dd, 1H, *J* = 10.3, 4.6 Hz, H-5α), 3.61 (dd, 1H, *J* = 10.3, 6.2 Hz, H-5α), 3.61 (d, 1H, *J* = 5.6 Hz, 1-OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.3, 136.9 (C_q), 128.7, 128.6, 128.5, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8 (CH_{arom}), 101.2 (C-1β), 96.2 (C-1α), 81.6 (C-3β), 80.8 (C-3α), 79.5 (C-4β), 77.1 (C-4α), 73.9, 73.6, 73.2, 73.0 (CH_2 Bn), 70.5 (C-2β), 68.8 (C-5α), 68.5 (C-5β), 66.9 (C-2α); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = -0.5 Hz, $^2J_{C2,H1}$ = +3.9 Hz, β-anomer: $^2J_{C1,H2}$ = -2.4 Hz, $^2J_{C2,H1}$ = -0.2 Hz; As additional confirmation of the xylo-configuration: α -anomer: $^2J_{C2,H3}$ = -2.8 Hz, $^2J_{C3,H2}$ = -5.0 Hz, β -anomer: $^2J_{C2,H3}$ = -3.3 Hz, $^2J_{C3,H2}$ = -4.6 Hz). HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.14243, found 378.14235.



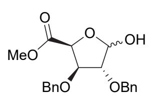
Methyl (2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (53). The title compound was generated from **41** (11.9 g, 32 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (8 h). Yield: 60% α:β = 2:1 (6.87 g, 19.2 mmol) as a yellow oil. R*f*: 0.38 (7/3 pentane/EtOAc). IR (thin film): 698, 739, 1028, 1076, 1090, 1207, 1454, 1740. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.22 (m, 10H, CH_{arom}), 5.51 (d, 1H, *J* = 10.2 Hz, H-1), 4.86 (d, 1H, *J* = 1.7 Hz, H-4), 4.70 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.53 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.46 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.38 – 4.34 (m, 1H, H-3), 3.94 (d, 1H, *J* = 0.9 Hz, H-2), 3.69 (s, 3H, CH_3 CO_2Me), 3.41 (d, 1H, *J* = 10.3 Hz, OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.5 (C=O), 137.1, 136.7 (C_q), 128.6, 128.5, 128.4, 128.0, 128.0, 127.7 (CH_{arom}), 102.1 (C-1), 84.6 (C-2), 84.1 (C-3), 81.1 (C-4), 72.3, 71.6 (CH_2 Bn), 52.4 (CH_3 CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.22 (m, 10H, CH_{arom}), 5.55 (dd, 1H, *J* = 10.0, 3.9 Hz, H-1), 4.66 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.57 – 4.54 (m, 1H, CH*H* Bn), 4.53 (d, 1H, *J* = 2.2 Hz, H-4), 4.38 – 4.34 (m, 1H, H-3), 3.91 (dd, 1H, *J* = 3.9, 2.7 Hz, H-2), 3.85 (d, 1H, *J* = 10.0 Hz, OH), 3.72 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.8 (C=O), 137.2, 136.9 (C_q), 128.5, 128.2, 128.2, 128.0, 127.9, 127.8 (CH_{arom}), 98.2 (C-1), 84.2 (C-3), 81.5 (C-2), 79.7 (C-4), 72.7, 72.1 (CH_2 Bn), 52.5 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{26}NO_6$ 376.17546, found 376.17566.



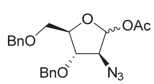
Methyl (2,3-di-*O*-benzyl-α/β-D-ribofuranosyl uronate) (54). The title compound was generated from **42** (8.33 g, 22.38 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (7.5 h). Yield: 73% α:β = 1.1:1 (5.87 g, 16.4) as a colourless oil. R*f*: 0.54 (7/3 pentane/EtOAc). IR (thin film): 698, 739, 1026, 1070, 1209, 1358, 1454, 1740, 2870, 2951, 3030, 3441; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.25 (m, 10H, CH_{arom}), 5.45 (dd, 1H, *J* = 11.1, 4.3 Hz, H-1), 4.82 – 4.44 (m, 5H, 2xCH_2Bn, H-4), 4.19 (d, 1H, *J* = 11.5 Hz, OH), 4.16 – 4.06 (m, 1H, H-3), 3.89 (d, 1H, *J* = 4.5 Hz, H-2), 3.71 (d, 3H, *J* = 4.2 Hz, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.6 (C=O), 137.11, 136.74 (C_q), 128.5 – 127.9 (CH_{arom}), 96.8 (C-1), 80.2 (C-2), 79.1 (C-4), 77.5 (C-3), 72.5, 72.4 (CH_2Bn), 52.6 (CH_3 CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.25 (m, 10H, CH_{arom}), 5.55 (s, 1H, H-1), 5.07 – 4.88 (m, 1H, OH), 4.78, (d, *J* = 1.4 Hz, H-4), 4.82 – 4.44 (m, 4H, 2xCH_2Bn), 4.38 (dd, 1H, *J* = 6.5, 4.5 Hz, H-3), 3.93 (t, 1H, *J* = 4.6 Hz, H-2), 3.71 (d, 3H, *J* = 4.2 Hz, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.3 (C=O), 137.6, 137.4 (C_q), 128.5 – 127.9 (CH_{arom}), 101.1 (C-1), 80.4 (C-3), 80.2 (C-2), 79.7 (C-4), 73.0, 72.7 (CH_2Bn), 52.6 (CH_3 CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{22}O_6Na$ 381.13086, found 381.13084.



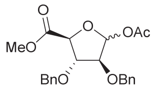
Methyl (2,3-di-*O*-benzyl-β-D-lyxofuranosyl uronate) (55). The title compound was generated from **43** (1.0 g, 2.7 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (6 h). Yield: 85% β only (818 mg, 2.28 mmol) as a white solid. R*f*: 0.35 (1/1 pentane/EtOAc). IR (thin film): 698, 739, 1026, 1065, 1141, 1211, 1360, 1437, 1454, 1738, 1763, 2874, 2951, 3466. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.43 – 7.22 (m, 10H, CH_{arom}), 5.40 (dd, 1H, *J* = 12.6, 4.3 Hz, H-1), 4.85 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.80 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.63 – 4.59 (m, 3H, 2xCH*H* Bn, H-4), 4.37 (t, 1H, *J* = 4.4 Hz, H-3), 4.33 (d, 1H, *J* = 12.6 Hz, OH), 3.91 (t, 1H, *J* = 4.2 Hz, H-2), 3.73 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.5 (C=O), 137.3, 137.2 (C_q), 128.7, 128.5, 128.2, 128.2, 128.1, 127.9 (CH_{arom}), 97.0 (C-1), 78.8 (C-4), 78.5, 78.4 (C-2, C-3), 74.8, 72.2 (CH_2 Bn), 52.4 (CH_3 CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{22}O_6Na$ 376.17546, found 376.17580.



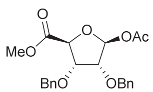
Methyl (2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (56). The title compound was generated from **44** (17.7 g, 47.6 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (4 h). Yield: 90% α:β = 1:1.3 (15.3 mg, 42.7 mmol) as a light yellow oil. R*f*: 0.2 (8/2 pentane/EtOAc). IR (thin film): 698, 739, 1028, 1061, 1072, 1209, 1366, 1437, 1454, 1738, 1759, 2951, 3030, 3430; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.21 (m, 17.5H, CH_{arom}), 5.65 (dd, 0.75H, *J* = 10.1, 4.0 Hz, H-1α), 5.39 (d, 1H, *J* = 11.3 Hz, H-1β), 4.90 (d, 1H, *J* = 5.9 Hz, H-4β), 4.83 (d, 0.75H, *J* = 5.2 Hz, H-4α), 4.61 – 4.49 (m, 7H, CH_2 Bn), 4.28 (ddd, 1H, *J* = 5.9, 2.4, 0.8 Hz, H-3β), 4.25 (ddd, 1H, *J* = 5.2, 2.5, 0.4 Hz, H-3α), 4.00 (d, 1H, *J* = 11.6 Hz, 1-OHβ), 4.00 (dt, 1H, *J* = 2.4, 0.8 Hz, H-2β), 3.94 (dd, 0.75H, *J* = 3.9, 2.6 Hz, H-2α), 3.84 (d, 0.75H, *J* = 10.1 Hz, 1-OHα), 3.77 (s, 3H, CH_3 CO_2Meβ), 3.74 (s, 2.25H, CH_3 CO_2Meα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.2, 169.7 (C=O), 137.1, 136.7 (C_q), 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.1, 127.9, 127.8 (CH_{arom}), 102.8 (C-1β), 97.4 (C-1α), 85.2 (C-2β), 82.1 (C-3β), 81.7 (C-3α), 80.8 (C-4β), 80.4 (C-2α), 77.9 (C-4α), 73.2, 73.0, 72.8, 72.1 (CH_2 Bn), 52.5 (CO_2Meβ), 52.1 (CO_2Meα); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{26}NO_6$ 376.17546, found 376.17564.



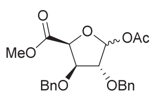
Acetyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-arabinofuranoside (57). The title compound was generated from **49** (107 mg, 0.3 mmol) by the general procedure for acetyl donor synthesis. Yield: 90% α:β = 2.3:1 ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.41 – 7.22 (m, 10H, CH_{arom}), 6.24 (d, 0.3H, *J* = 4.6 Hz, H-1β), 6.11 (d, 0.7H, *J* = 1.0 Hz, H-1α), 4.71 – 4.47 (m, 4H, 4xCH_2 Bnα,β), 4.33 (dt, 0.7H, *J* = 5.8, 4.5 Hz, H-4α), 4.25 – 4.15 (m, 0.6H, H-3β, H-4β), 4.05 (dd, 0.7H, *J* = 3.1, 1.3 Hz, H-2α), 3.95 (ddd, 1H, *J* = 10.3, 6.8, 3.9 Hz, H-2β, H-3α), 3.63 – 3.55 (m, 1.4H, H-5α), 3.53 (dd, 0.6H, *J* = 4.7, 1.9 Hz, H-5β); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.8, 169.4 (C=O), 137.8, 137.7, 137.3, 137.1 (C_q), 128.5, 128.5, 128.4, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6 (CH_{arom}), 100.4 (C-1$_{\beta}$), 95.2 (C-1$_{\alpha}$), 83.4 (C-4$_{\beta}$), 83.0 (C-3$_{\beta}$), 82.1 (C-4$_{\alpha}$), 80.4 (C-3$_{\alpha}$), 73.5, 73.3, 72.8, 72.6 (CH_2 Bn), 70.5 (C-2$_{\beta}$), 70.3 (C-5$_{\alpha}$), 68.7 (C-5$_{\beta}$), 66.4 (C-2$_{\alpha}$), 21.1, 21.0 (CH_3 OAc); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.1424, found 378.1425.



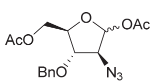
Methyl (acetyl 2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (58). The title compound was generated from **53** (5.20 g, 14.5 mmol) by the general procedure for acetyl donor synthesis. Yield: 91% α:β = 6.7:1 (5.29 g, 13.2 mmol) as a light yellow oil. R*f*: 0.80 (7/3 pentane/EtOAc). IR (thin film): 698, 1011, 1223, 1371, 1454, 1734, 1749, 2872, 2951, 3030. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.26 (m, 8.5H, CH_{arom}), 6.36 (s, 0.85H, H-1), 4.76 (d, 0.85H, *J* = 3.9 Hz, H-4), 4.62 (d, 0.85H, *J* = 12.0 Hz, C*H*H Bn), 4.62 (d, 0.85H, *J* = 12.0 Hz, C*H*H Bn), 4.54 (d, 0.85H, *J* = 12.0 Hz, CH*H* Bn), 4.49 (d, 0.85H, *J* = 12.1 Hz, CH*H* Bn), 4.25 (ddd, 0.85H, *J* = 3.9, 1.4, 0.7 Hz, H-3), 4.04 (dd, 0.85H, *J* = 1.4, 0.5 Hz, H-2), 3.74 (s, 2.55H, CH_3 CO_2Me), 2.08 (s, 2.55H, CH_3 OAc); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.8, 169.7 (C=O), 137.2, 137.0 (C_q), 128.5, 128.1, 127.9, 127.9 (CH_{arom}), 100.7 (C-1), 85.3 (C-2), 85.0 (C-3), 82.8 (C-4), 72.2, 72.0 (CH_2 Bn), 52.6 (CH_3 CO_2Me), 21.2 (OAc); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.26 (m, 1.5H, CH_{arom}), 6.24 (d, 0.15H, *J* = 4.3 Hz, H-1), 4.75 (d, 0.15H, *J* = 11.7 Hz, C*H*H Bn), 4.68 (d, 0.15, *J* = 11.8 Hz, CH*H* Bn), 4.57 – 4.46 (m, 0.6H, CH2 Bn, H-3, H-4), 4.18 (dd, 0.15H, *J* = 6.4, 4.2 Hz, H-2), 3.76 (s, 0.45H, CH_3 CO_2Me), 2.07 (s, 0.45H, CH_3 OAc); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.9, 170.0 (C=O), 137.5, 137.1 (C_q), 128.6, 128.5, 128.5, 128.2, 128.0, 128.0 (CH_{arom}), 94.5 (C-1), 83.4 (C-3), 83.2 (C-2), 80.4 (C-4), 73.1, 72.8 (CH_2 Bn), 52.6 (CO_2Me), 21.2 (OAc); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{28}NO_7$ 418.18603, found 418.18598.



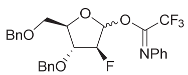
Methyl (acetyl 2,3-di-*O*-benzyl-β-D-ribofuranosyl uronate) (59). The title compound was generated from **54** (5.9 g, 16.4 mmol) by the general procedure for acetyl donor synthesis. Yield: 90% β only (5.9 g, 14.7 mmol) as a light yellow oil. R*f*: 0.67 (7/3 pentane/EtOAc). IR (thin film): 698, 738, 959, 1013, 1094, 1138, 1209, 1371, 1454, 1749, 2870, 2951; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.30 (m, 10H, CH_{arom}), 6.24 (s, 1H, H-1), 4.73 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.69 (d, 1H, *J* = 6.7 Hz, H-4), 4.64 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.60 (d, *J* = 12.0 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.32 (dd, 1H, *J* = 6.7, 4.7 Hz, H-3), 3.94 (d, 1H, *J* = 4.6 Hz, H-2), 3.76 (s, 3H, CH_3 CO_2Me), 2.05 (s, 3H, CH_3 OAc); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.3 (C=O CO_2Me), 169.7 (C=O OAc), 137.3, 137.2 (C_q), 128.6, 128.6, 128.2, 128.1, 127.9 (CH_{arom}), 99.4 (C-1), 80.4 (C-4), 79.7 (C-3), 79.0 (C-2), 72.8, 72.6 (CH_2 Bn), 52.7 (CH_3 CO_2Me), 21.3 (CH_3 OAc); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{28}NO_7$ 418.18603, found 418.18605.



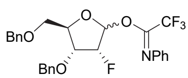
Methyl (acetyl 2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (60). The title compound was generated from **56** (15.3 g, 42.7 mmol) by the general procedure for acetyl donor synthesis. Yield: 89% α:β = 1.3:1 (15.2 g, 38.1 mmol) as a light yellow oil. R*f*: 0.60 and 0.73 (8/2 pentane/EtOAc). IR (thin film): 698, 739, 1016, 1026, 1098, 1211, 1369, 1454, 1748, 2872, 2951, 3030. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.21 (m, 17.5H), 6.42 (d, 1H, *J* = 4.4 Hz, H-1$_{\alpha}$), 6.24 (s, 0.75H, H-1$_{\beta}$), 4.95 (d, 0.75H, *J* = 5.8 Hz, H-4$_{\beta}$), 4.87 (d, 1H, *J* = 7.3 Hz, H-4$_{\alpha}$), 4.66 – 4.48 (m, 7H, 2xCH_2 Bn$_{\alpha}$, 2x CH_2 Bn$_{\beta}$), 4.47 – 4.43 (m, 1H, H-3$_{\alpha}$), 4.30 (dd, 1H, *J* = 6.6, 4.4 Hz, H-2$_{\alpha}$), 4.27 (ddd, 0.75H, *J* = 5.8, 1.5, 0.6 Hz, H-3$_{\beta}$), 4.08 (dt, 0.75H, *J* = 1.4, 0.7 Hz, H-2$_{\beta}$), 3.74 (s, 2.25H, CH_3 CO_2Me_{α}), 3.73 (s, 3H, CH_3 CO_2Me_{β}), 2.09 (s, 2.25H, CH_3 OAc$_{\alpha}$), 2.07 (s, 3H, CH_3 OAc$_{\beta}$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.3, 169.7, 169.2, 168.8 (C=O), 137.4, 137.2, 137.2, 137.0 (C_q), 128.6, 128.6, 128.5, 128.5, 128.2, 128.2, 128.0, 128.0, 127.9, 127.8, 127.6, 127.5 (CH_{arom}), 100.7 (C-1$_{\beta}$), 94.4 (C-1$_{\alpha}$), 83.9 (C-2$_{\beta}$), 82.2 (C-4$_{\beta}$), 81.8 (C-2$_{\alpha}$), 81.6 (C-3$_{\beta}$), 81.0 (C-3$_{\alpha}$), 77.7 (C-4$_{\alpha}$), 73.6, 73.1, 72.6, 72.2 (CH_2 Bn), 52.3 (C-5$_{\alpha}$), 52.2 (C-5$_{\beta}$), 21.3 (OAc$_{\beta}$), 21.2 (OAc$_{\alpha}$); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{28}NO_7$ 418.18603, found 418.18599.



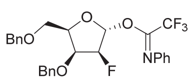
1,5-Di-*O*-acetyl 2-azido-3-*O*-benzyl-2-deoxy-α/β-D-arabinofuranoside. (61). ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.39 – 7.29 (m, 7.9H, CH_{arom}), 6.29 (d, 0.58H, *J* = 4.5 Hz, H-1$_{\beta}$), 6.11 (d, 1H, *J* = 1.2 Hz, H-1$_{\alpha}$), 4.73 (d, 0.58H, *J* = 11.7 Hz, C*H*H Bn$_{\beta}$), 4.69 – 4.61 (m, 1.58H, C*H*H Bn$_{\alpha}$, CH*H* Bn$_{\beta}$), 4.57 (d, 1H, *J* = 11.8 Hz, CH*H* Bn$_{\alpha}$), 4.36 (td, 1H, *J* = 5.6, 3.4 Hz, H-4$_{\alpha}$), 4.26 (dd, 1H, *J* = 12.2, 3.5 Hz, H-5$_{\alpha}$), 4.23 – 4.19 (m, 0.58H, H-4$_{\beta}$), 4.17 – 4.04 (m, 3.74H, H-2$_{\alpha}$, H-3$_{\beta}$, H-5$_{\alpha}$, H-5$_{\beta}$, H-5$_{\beta}$), 3.99 (dd, 0.58H, *J* = 7.8, 4.6 Hz, H-2$_{\beta}$), 3.86 (dd, 1H, *J* = 6.2, 3.1 Hz, H-3$_{\alpha}$), 2.09 (s, 1.74H, CH_3 OAc$_{\beta}$), 2.09 (s, 3H, CH_3 OAc$_{\alpha}$), 2.05 (s, 1.74H, CH_3 OAc$_{\beta}$), 2.02 (s, 3H, CH_3 OAc$_{\alpha}$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.4, 170.3, 169.6, 169.1 (C=O, Ac), 136.8, 136.7 (C_q Bn), 128.6, 128.2, 128.2, 127.8, 127.8 (CH_{arom}), 100.4 (C-1$_{\alpha}$), 95.2 (C-1$_{\beta}$), 82.7 (C-3$_{\alpha}$), 81.8 (C-4$_{\alpha}$), 80.6 (C-4$_{\beta}$), 80.1 (C-3$_{\beta}$), 72.9 (CH_2 Bn$_{\beta}$), 72.7 (CH_2 Bn$_{\alpha}$), 70.2 (C-2$_{\alpha}$), 66.3 (C-2$_{\beta}$), 64.6 (C-5$_{\beta}$), 62.8 (C-5$_{\alpha}$), 21.0, 21.0, 20.6, 20.6 (CH_3 OAc); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = -3.5 Hz, $^2J_{C2,H1}$ = -0.5 Hz, β-anomer: $^2J_{C1,H2}$ = -0.6 Hz, $^2J_{C2,H1}$ = +1.9 Hz; HRMS: $[M+Na]^+$ calcd for $C_{16}H_{19}N_3O_6Na$ 372.11661, found 372.11646.



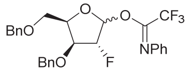
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranoside (62). The title compound was generated from **45** by the general procedure for imidate donor synthesis, conditions A. Yield: 85% α:β = 5:1 as separate anomers (0.14 mmol and 0.60 mmol respectively) as colourless oils. Data for the α-anomer: $[\alpha]_D^{20}$ = +67.7° (*c* = 1.39, $CHCl_3$); IR (thin film): 696, 933, 1101, 1153, 1159, 1207, 1327, 1454, 1714, 2866, 3032; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.24 (m, 12H, CH_{arom}), 7.11 – 7.06 (m, 1H, NPh), 6.83 (d, 2H, *J* = 7.5 Hz, NPh), 6.37 (d, 1H, *J* = 8.3 Hz, H-1), 5.17 (dd, 1H, *J* = 50.5, 1.6 Hz, H-2), 4.65 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.61 – 4.55 (m, 2H, CH*H* Bn, C*H*H Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.44 (q, 1H, *J* = 4.9 Hz, H-4), 4.16 (dddd, 1H, *J* = 23.1, 5.8, 1.8, 0.9 Hz, H-3), 3.64 (d, 2H, *J* = 4.7 Hz, H-5, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8 (C_q NPh), 138.1, 137.4 (C_q Bn), 128.9, 128.7, 128.6, 128.2, 127.9, 127.9, 124.6, 119.8 (CH_{arom}), 116.2 (q, *J* = 286.8 Hz, CF_3), 102.7 (d, *J* = 38.8 Hz, C-1), 98.9 (d, *J* = 184.9 Hz, C-2), 84.3 (d, *J* = 3.4 Hz, C-4), 82.9 (d, *J* = 25.7 Hz, C-3), 73.8, 72.8 (CH_2 Bn), 69.2 (C-5); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz, HH-COSY, HSQC): δ -66.34 (bs, 3F, CF_3), -188.59 (ddd, 1F, *J* = 50.5, 23.1, 11.0 Hz, F-2); Data for the β-anomer: $[\alpha]_D^{20}$ = -43.0° (*c* = 0.6, $CHCl_3$); IR (thin film): 696, 1026, 1072, 1092, 1153, 1159, 1207, 1319, 1717, 2864; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.24 (m, 12H, CH_{arom}), 7.10 – 7.05 (m, 1H, NPh), 6.80 (dd, 2H, *J* = 8.4, 1.1 Hz, NPh), 6.46 (bs, 1H, H-1), 5.17 (ddd, 1H, *J* = 52.0, 5.8, 4.5 Hz, H-2), 4.69 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.57 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.32 (dt, 1H, *J* = 16.7, 5.9 Hz, H-3), 4.25 (q, 1H, *J* = 5.7 Hz, H-4), 3.63 (dd, 1H, *J* = 10.4, 5.6 Hz, H-5), 3.60 (dd, 1H, *J* = 10.5, 5.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8 (C_q NPh), 138.1, 137.5 (C_q Bn), 128.9, 128.6, 128.6, 128.1, 127.9, 127.9, 127.9, 124.4, 119.7 (CH_{arom}), 116.1 (q, *J* = 285.9 Hz, CF_3), 96.9 (d, *J* = 18.1 Hz, C-1), 95.1 (d, *J* = 201.9 Hz, C-2), 81.9 (d, *J* = 9.0 Hz, C-4), 81.2 (d, *J* = 21.4 Hz, C-3), 73.7, 72.7 (CH_2 Bn), 70.9 (C-5); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz, HH-COSY, HSQC): δ -66.45 (bs, 3F, CF_3), -203.20 (dd, 1F, *J* = 52.1, 16.7 Hz, F-2); HRMS: $[M+H]^+$ calcd for $C_{27}H_{26}F_4NO_4$ 504.17925, found 504.17933.



3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-ribofuranoside (63). The title compound was generated from **46** by the general procedure for imidate donor synthesis, conditions A. Yield: 98% β only (0.45 mmol) as a white solid, includes ~10% acetamide. IR (thin film): 694, 1092, 1151, 1207, 1712, 2869; ^1H NMR ($CDCl_3$, *T* = 328 K, 400 MHz, HH-COSY, HSQC): δ 7.36 – 7.21 (m, 12H, CH_{arom}), 7.11 – 7.04 (m, 1H, NPh), 6.79 (d, 2H, *J* = 8.2 Hz, NPh), 6.36 (d, 1H, *J* = 9.1 Hz, H-1), 4.95 (dd, 1H, *J* = 52.3, 3.5 Hz, H-2), 4.66 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.60 – 4.49 (m, 3H, CH_2 Bn, CH*H* Bn), 4.38 (dt, 1H, *J* = 7.6, 3.9 Hz, H-4), 4.24 (ddd, 1H, *J* = 23.6, 7.6, 3.6 Hz, H-3), 3.69 (dd, 1H, *J* = 11.1, 3.1 Hz, H-5), 3.58 (dd, 1H, *J* = 11.1, 4.4 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 328 K, 101 MHz, HSQC): δ 143.6 (C_q NPh), 138.2, 137.3 (C_q Bn), 129.4, 128.8, 128.6, 128.5, 128.2, 128.0, 127.8, 127.7, 124.6, 119.6 (CH_{arom}), 116.0 (q, *J* = 286.1 Hz, CF_3), 101.2 (d, *J* = 32.4 Hz, C-1), 91.0 (d, *J* = 188.6 Hz, C-2), 82.0 (C-4), 77.0 (d, *J* = 15.7 Hz, C-3), 73.5, 73.2 (CH_2 Bn), 69.7 (C-5); ^{19}F NMR ($CDCl_3$, *T* =298 K, 471 MHz): δ -65.81 (bs, 3F, CF_3), -209.42 (ddd, 1F, *J* = 52.3, 23.9, 9.4 Hz); HRMS: $[M+H]^+$ calcd for $C_{27}H_{26}F_4NO_4$ 504.17925, found 504.17889.

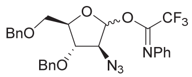


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-lyxofuranoside (64). The title compound was generated from **47** by the general procedure for imidate donor synthesis, conditions A. Yield: 82% α only (0.54 mmol) as a colourless oil. $[\alpha]_D^{20}$ = +50.2° (*c* = 1.30, $CHCl_3$); IR (thin film): 694, 737, 931, 1086, 1097, 1150, 1207, 1321, 1715, 2872, 3032; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.22 (m, 12H, CH_{arom}), 7.11 – 7.04 (m, 1H, NPh), 6.82 (d, 2H, *J* = 7.5 Hz, NPh), 6.41 (bs, 1H, H-1), 5.02 (dd, 1H, *J* = 51.7, 3.8 Hz, H-2), 4.69 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.60 – 4.53 (m, 3H, C*H*H Bn, CH*H* Bn, H-4), 4.50 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.34 (ddd, 1H, *J* = 17.6, 6.4, 4.3 Hz, H-3), 3.83 (dd, 1H, *J* = 10.7, 4.5 Hz, H-5), 3.68 (dd, 1H, *J* = 9.8, 7.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 143.6 (C_q NPh), 142.9 (q, *J* = 36.4 Hz, F_3CC=N), 138.3, 137.4 (C_q Bn), 128.9, 128.6, 128.5, 128.2, 127.9, 127.7, 124.6, 119.7 (CH_{arom}), 116.2 (q, *J* = 285.9 Hz, CF_3), 101.3 (d, *J* = 33.4 Hz, C-1), 92.6 (d, *J* = 192.3 Hz, C-2), 80.2 (C-4), 76.6 (d, *J* = 15.0 Hz, C-3), 73.7, 73.7 (CH_2 Bn), 69.5 (C-5); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz): δ -66.49 (bs, 3F, CF_3), -207.43 (ddd, 1F *J* = 51.8, 17.6, 9.5 Hz, C2-F); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_8N_3O_8$ 1024.37777, found 1024.37849.

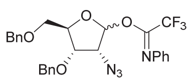


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-xylofuranoside (65). The title compound was generated from **48** by the general procedure for imidate donor synthesis, conditions A. Yield: 91% α:β = 37:63 (0.36 mmol) as a colourless oil. IR (thin film): 694, 1086, 1153, 1207, 1323, 1715; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.22 (m, 12H, CH_{arom}), 7.11 – 7.04 (m, 1H, NPh), 6.84 – 6.78 (m, 2H, NPh), 6.46 (bs, 0.37H, H-1_α), 6.34 (d, 0.63H, *J* = 12.5 Hz, H-1_β), 5.23 (dt, 0.37H, *J* = 51.9, 4.0 Hz, H-2_α), 5.18 (dd, 0.63H, *J* = 49.8, 1.6 Hz, H-2_β), 4.71 (d, 0.37H, *J* = 11.8 Hz, C*H*H Bn_α), 4.68 – 4.50 (m, 3.63H, CH*H* Bn_α, CH_2 Bn_α, 2xCH_2 Bn_β, H-4_α, H-4_β), 4.41 (ddd, 0.37H, *J* = 15.7, 6.5, 4.8 Hz, H-3_α), 4.26

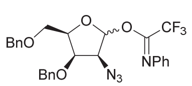
(ddd, 0.63H, *J* = 16.2, 5.8, 1.6 Hz, H-3$_{\beta}$), 3.85 (dd, 0.63H, *J* = 10.5, 5.4 Hz, H-5$_{\beta}$), 3.75 (dd, 0.63H, *J* = 10.4, 6.6 Hz, H-5$_{\beta}$), 3.72 (dd, 0.37H, *J* = 10.7, 4.5 Hz, H-5$_{\alpha}$), 3.65 (dd, 0.37H, *J* = 10.6, 5.0 Hz, H-5$_{\alpha}$); ^{13}C-APT NMR ($CDCl_3$, *T* = 323K, 126 MHz, HSQC): δ 143.9, 143.8 (C_q NPh), 138.4, 138.2, 137.4, 137.4 (C_q Bn), 128.9, 128.9, 128.7, 128.5, 128.5, 128.2, 128.1, 127.8, 127.8, 127.8, 127.6, 124.5, 124.4, 119.7 (CH_{arom}), 116.1 (q, *J* = 286.3 Hz, CF_3), 102.1 (d, *J* = 37.5 Hz, H-1$_{\beta}$), 97.0 (d, *J* = 16.8 Hz, H-1$_{\alpha}$), 97.0 (d, *J* = 184.5 Hz, H-2$_{\beta}$), 94.1 (d, *J* = 200.0 Hz, H-2$_{\alpha}$), 83.1 (C-4$_{\beta}$), 80.5 (d, *J* = 25.6 Hz, C-3$_{\beta}$), 79.9 (d, *J* = 22.9 Hz, C-3$_{\alpha}$), 79.0 (d, *J* = 6.8 Hz, C-4$_{\alpha}$), 73.8 (CH_2 Bn$_{\alpha}$), 73.7, 73.2 (CH_2 Bn$_{\beta}$), 72.9 (CH_2 Bn$_{\alpha}$), 68.9 (C-5$_{\beta}$), 68.2 (C-5$_{\alpha}$); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz): δ -66.32 (s, 3F, CF_3), -193.57 (dt, 0.63F, *J* = 49.8, 14.1 Hz, F-2$_{\beta}$), -202.33 (dd, 0.37F, *J* = 52.1, 15.6 Hz, F-2$_{\alpha}$); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_8N_3O_8$ 1024.37777, found 1024.37842.



2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranoside (66). The title compound was generated from **49** by the general procedure for imidate donor synthesis, conditions B. Yield: 71% α:β = 1.6:1 as separate anomers (0.31 mmol and 0.19 mmol respectively) as colourless oils. Data for the α-anomer: $[\alpha]_D^{20}$ = +5.4° (*c* = 0.50, $CHCl_3$); IR (thin film): 696, 929, 1103, 1161, 1207, 1329, 1456, 1700, 1717, 2106, 2866, 3032; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.22 (m, 12H, CH_{arom}), 7.08 (t, 1H, *J* = 7.5 Hz, NPh), 6.82 (d, 2H, *J* = 7.7 Hz, NPh), 6.18 (bs, 1H, H-1), 4.63 – 4.56 (m, 2H, CH_2 Bn), 4.56 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.42 (q, 1H, *J* = 4.6 Hz, H-4), 4.17 (d, 1H, *J* = 2.2 Hz, H-2), 4.00 (dd, 1H, *J* = 6.0, 3.1 Hz, H-3), 3.64 (dd, 1H, *J* = 11.0, 4.2 Hz, H-5), 3.61 (dd, 1H, *J* = 11.0, 4.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.7 (C_q NPh), 138.0, 137.4 (C_q Bn), 128.9, 128.7, 128.5, 128.2, 127.9, 127.9, 127.9, 124.6, 119.8 (CH_{arom}), 116.1 (q, *J* = 286.7 Hz, CF_3), 104.0 (C-1), 84.2 (C-4), 83.4 (C-3), 73.7, 73.0 (CH_2 Bn), 70.8 (C-5), 68.9 (C-2); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_6N_9O_8$ 1070.39941, found 1070.40019. Data for the β-anomer: $[\alpha]_D^{20}$ = -56.1° (*c* = 1.30, $CHCl_3$); IR (thin film): 696, 1024, 1094, 1144, 1161, 1207, 1317, 1713, 2110, 2864; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.22 (m, 12H, CH_{arom}), 7.12 – 7.03 (m, 1H, NPh), 6.81 (d, 2H, *J* = 7.5 Hz, NPh), 6.43 (bs, 1H, H-1), 4.67 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.59 – 4.52 (m, 2H, CH_2 Bn), 4.26 (q, 1H, *J* = 5.6 Hz, H-4), 4.21 (dd, 1H, *J* = 7.5, 6.0 Hz, H-3), 4.04 (dd, 1H, *J* = 7.5, 4.5 Hz, H-2), 3.63 – 3.53 (m, 2H, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8 (C_q NPh), 138.0, 137.5 (C_q Bn), 128.9, 128.7, 128.6, 128.2, 128.0, 127.9, 127.9, 124.5, 119.6 (CH_{arom}), 116.1 (d, *J* = 286.6 Hz, CF_3), 98.6 (C-1), 82.9 (C-4), 81.5 (C-3), 73.7, 73.1 (CH_2 Bn), 70.9 (C-5), 67.4 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{29}F_3N_5O_4$ 544.21662, found 544.21623.

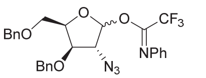


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-ribofuranoside (67). The title compound was generated from **50** by the general procedure for imidate donor synthesis, conditions A. Yield: 77% α:β = 1:8 as separate anomers (0.085 mmol and 0.69 mmol respectively) as a white soild. Data for the α-anomer: $[\alpha]_D^{20}$ = +52.4° (*c* = 0.46, $CHCl_3$); IR (thin film): 696, 1101, 1144, 1161, 1207, 1319, 1713, 2114, 2864; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.25 (m, 10H, CH_{arom}), 7.25 – 7.21 (m, 2H, CH_{arom}), 7.11 – 7.05 (m, 1H, NPh), 6.87 (d, 2H, *J* = 7.7 Hz, NPh), 6.45 (bs, 1H, H-1), 4.74 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.45 – 4.40 (m, 2H, CH*H* Bn, H-4), 4.18 (dd, 1H, *J* = 6.6, 3.1 Hz, H-3), 3.63 – 3.58 (m, 1H, H-2), 3.51 (dd, 1H, *J* = 10.8, 3.7 Hz, H-5), 3.45 (dd, 1H, *J* = 10.7, 3.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 144.0 (C_q NPh), 137.8, 137.7 (C_q Bn), 128.9, 128.6, 128.6, 128.0, 127.8, 124.5, 119.9 (CH_{arom}), 99.9 (C-1), 84.8 (C-4), 78.3 (C-3), 73.9, 73.1 (CH_2 Bn), 69.6 (C-5), 61.4 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{25}F_3N_4O_4Na$ 549.17201, found 549.17174. Data for the β-anomer: $[\alpha]_D^{20}$ = -1.6° (*c* = 0.70, $CHCl_3$); IR (thin film): 696, 1090, 1144, 1159, 1207, 1331, 1715, 2108, 2862; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.24 (m, 12H, CH_{arom}), 7.08 (t, 1H, *J* = 7.4 Hz, NPh), 6.80 (d, 2H, *J* = 7.7 Hz, NPh), 6.18 (bs, 1H, H-1), 4.64 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.39 (dd, 1H, *J* = 7.0, 5.0 Hz, H-3), 4.33 (dt, 1H, *J* = 7.0, 4.3 Hz, H-4), 4.03 (d, 1H, *J* = 5.0 Hz, H-2), 3.64 (dd, 1H, *J* = 10.9, 4.0 Hz, H-5), 3.57 (dd, 1H, *J* = 10.9, 4.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 143.7 (C_q NPh), 138.1, 137.2 (C_q Bn), 128.9, 128.7, 128.5, 128.3, 128.1, 127.8, 127.8, 124.6, 119.7 (CH_{arom}), 116.06 (q, *J* = 286.0 Hz, CF_3), 102.5 (C-1), 82.6 (C-4), 79.0 (C-3), 73.6, 73.6 (CH_2 Bn), 70.0 (C-5), 64.8 (C-2); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_6N_9O_8$ 1070.39941, found 1070.40023.

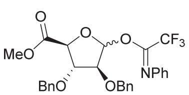


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-lyxofuranoside (68). The title compound was generated from **51** by the general procedure for imidate donor synthesis, conditions B. Yield: 67% α:β = 1:1.2 (0.30 mmol and 0.37 mmol respectively) as colourless oils. Data for the α-anomer: $[\alpha]_D^{20}$ = -57.5° (*c* = 0.69, $CHCl_3$); IR (thin film): 696, 1045, 1098, 1144, 1207, 1323, 1714, 2112, 2866, 2926; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.22 (m, 12H, CH_{arom}), 7.11 – 7.03 (m, 1H, NPh), 6.82 (d, 2H, *J* = 7.5 Hz, NPh), 6.27 (bs, 1H, H-1), 4.71 (d, 1H, *J* = 11.5 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.53 – 4.47 (m, 2H, CH*H* Bn, H-4), 4.41 (t, 1H,

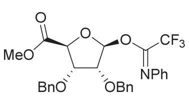
J = 5.5 Hz, H-3), 4.02 (dd, 1H, J = 5.1, 1.9 Hz, H-1), 3.81 (dd, 1H, J = 10.4, 5.4 Hz, H-5), 3.71 (dd, 1H, J = 10.4, 6.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, T = 323 K, 126 MHz, HSQC): δ 143.7 (C_q NPh), 138.2, 137.2 (C_q Bn), 128.9, 128.7, 128.5, 128.2, 127.9, 127.9, 127.8, 124.6, 119.7 (CH_{arom}), 116.2 (q, J = 286.9 Hz, CF_3), 102.3 (C-1), 80.7 (C-4), 78.6 (C-3), 74.4, 73.7 (CH_2 Bn), 68.7 (C-5), 66.2 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{29}F_3N_5O_4$ 544.21662, found 544.21667. Data for the β-anomer: $[\alpha]_D^{20}$ = +24.9° (c = 0.68, $CHCl_3$); IR (thin film): 696, 1094, 1144, 1153, 1207, 1319, 1717, 2110, 2926; ^{1}H NMR ($CDCl_3$, T = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 12H, CH_{arom}), 7.10 – 7.02 (m, 1H, NPh), 6.84 (d, 2H, J = 7.5 Hz, NPh), 6.41 (bs, 1H, H-1), 4.83 (d, 1H, J = 11.7 Hz, C*H*H Bn), 4.66 (d, 1H, J = 11.7 Hz, CH*H* Bn), 4.51 (d, 1H, J = 11.8 Hz, C*H*H Bn), 4.46 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.36 (q, 1H, J = 6.3 Hz, H-4), 4.26 (t, 1H, J = 5.4 Hz, H-3), 3.82 (dd, 1H, J = 9.9, 6.7 Hz, H-5), 3.70 (dd, 1H, J = 9.9, 6.2 Hz, H-5), 3.51 (t, 1H, J = 4.9 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, T = 323 K, 126 MHz, HSQC): δ 143.9 (C_q NPh), 138.1, 137.6 (C_q Bn), 128.8, 128.5, 128.5, 127.9, 127.8, 127.5, 124.4, 119.7 (CH_{arom}), 116.2 (q, J = 286.3 Hz, CF_3), 98.5 (C-1), 82.2 (C-4), 77.7 (C-3), 74.7, 73.8 (CH_2 Bn), 69.0 (C-5), 62.2 (C-2); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_6N_9O_8$ 1070.39941, found 1070.39931.



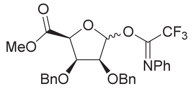
2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-xylofuranoside (69). The title compound was generated from **52** by the general procedure for imidate donor synthesis, conditions A. Yield: 100% α:β = 1:1 (0.33 mmol) as a colourless oil. IR (thin film): 696, 1044, 1099, 1143, 1207, 1321, 1712, 2114; ^{1}H NMR ($CDCl_3$, T = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.23 (m, 24H, CH_{arom}), 7.10 – 7.06 (m, 2H, NPh), 6.84 (d, 2H, J = 7.7 Hz, NPh), 6.80 (d, 2H, J = 7.6 Hz, NPh), 6.43 (bs, 1H, H-1$_{\alpha}$), 6.15 (bs, 1H, H-1$_{\beta}$), 4.69 (d, 1H, J = 11.7 Hz, C*H*H Bn), 4.64 – 4.57 (m, 4H, CH_2 Bn, CH*H* Bn, C*H*H Bn), 4.56 – 4.50 (m, 4H, CH_2 Bn, CH*H* Bn, H-4$_{\beta}$), 4.50 – 4.45 (m, 1H, H-4$_{\alpha}$), 4.32 (t, 1H, J = 6.7 Hz, H-3$_{\alpha}$), 4.22 (bs, 1H, H-2$_{\beta}$), 4.17 – 4.11 (m, 1H, H-2$_{\alpha}$), 4.08 (dd, 1H, J = 5.8, 2.8 Hz, H-3$_{\beta}$), 3.85 (dd, 1H, J = 10.5, 5.3 Hz, H-5$_{\beta}$), 3.76 (dd, 1H, J = 10.5, 6.5 Hz, H-5$_{\beta}$), 3.71 (dd, 1H, J = 10.7, 4.4 Hz, H-5$_{\alpha}$), 3.61 (dd, 1H, J = 10.7, 4.9 Hz, H-5$_{\alpha}$); ^{13}C-APT NMR ($CDCl_3$, T = 323 K, 126 MHz, HSQC): δ 143.8, 143.8 (C_q NPh), 138.3, 138.2, 137.4, 137.4 (C_q Bn), 128.9, 128.9, 128.7, 128.5, 128.5, 128.3, 128.3, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 124.5, 119.8, 119.7 (CH_{arom}), 103.2 (C-1$_{\beta}$), 98.4 (C-1$_{\alpha}$), 82.7 (C-4$_{\beta}$), 81.6 (C-3$_{\beta}$), 79.1 (C-3$_{\alpha}$), 73.8 (C-4$_{\alpha}$), 73.8, 73.6, 73.3 (CH_2 Bn), 69.1 (C-2$_{\beta}$), 69.0 (C-5$_{\beta}$), 68.5 (C-5$_{\alpha}$), 66.7 (C-2$_{\alpha}$); HRMS: only mass of hydrolysis found $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.1430, found 378.1433.



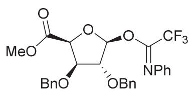
Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranosyl uronate) (70). The title compound was generated from **53** (466 mg, 1.3 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 97%, α:β = 1:1.2 (670 mg, 1.27 mmol) as a white solid. R*f*: 0.51 (8/2 pentane/Et_2O). IR (thin film): 696, 1074, 1105, 1318, 1712, 1769; ^{1}H NMR ($CDCl_3$, T = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.20 (m, 24H, CH_{arom}), 7.10 – 7.02 (m, 2H, NPh), 6.79 (d, 2H, J = 7.7 Hz, NPh), 6.77 – 6.74 (m, 2H, NPh), 6.41 (bs, 1H, H-1$_{\beta}$), 6.29 (bs, 1H, H-1$_{\alpha}$), 4.82 (d, 1H, J = 3.8 Hz, H-4$_{\beta}$), 4.76 (d, 1H, J = 11.8 Hz, C*H*H Bn), 4.72 – 4.61 (m, 4H, CH_2 Bn, CH*H* Bn, C*H*H Bn), 4.60 – 4.53 (m, 4H, CH_2 Bn, H-3$_{\alpha}$, H-4$_{\alpha}$), 4.50 (d, 1H, J = 12.0 Hz, CH*H* Bn), 4.29 (d, 1H, J = 3.1 Hz, H-3$_{\beta}$), 4.24 – 4.18 (m, 2H, H-2$_{\alpha}$, H-2$_{\beta}$), 3.74 (s, 3H, CH_3 CO_2Me), 3.73 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, T = 323 K, 126 MHz, HSQC): δ 170.7, 169.6 (C=O), 144.0, 143.8, 137.8, 137.5, 137.4, 137.1 (C_q), 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 124.5, 124.2, 119.8, 119.6 (CH_{arom}), 116.1 (q, J = 286.7 Hz, CF_3), 116.1 (q, J = 286.5 Hz, CF_3), 104.0 (C-1$_{\alpha}$), 97.3 (C-1$_{\beta}$), 85.2, 85.2 (C-2$_{\beta}$, C-3$_{\alpha}$), 84.0 (C-2$_{\alpha}$), 83.7 (C-3$_{\beta}$), 83.3 (C-4$_{\alpha}$), 80.9 (C-4$_{\beta}$), 73.4, 73.0, 72.4, 72.2 (CH_2 Bn), 52.5 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -66.18; HRMS: $[M+Na]^+$ calcd for $C_{28}H_{26}F_3NO_6Na$ 552.16044, found 552.16010.



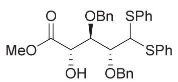
Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-ribofuranosyl uronate) (71). The title compound was generated from **54** (1.0 g, 2.8 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 85% β only (1.26 g, 2.38 mmol) as a white solid. R*f*: 0.54 (7/3 pentane/Et_2O). $[\alpha]_D^{20}$ = +18.6° (c = 0.90, $CHCl_3$); IR (thin film): 696, 1090, 1146, 1206, 1456, 1717, 1740; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.25 (m, 12H, CH_{arom}), 7.08 (t, 1H, J = 7.5 Hz, NPh), 6.81 (d, 2H, J = 7.5 Hz, NPh), 6.29 (bs, 1H, H-1), 4.72 (d, 1H, J = 6.4 Hz, H-4), 4.68 – 4.63 (m, 3H, CH_2 Bn, C*H*H Bn), 4.62 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.43 (dd, 1H, J = 6.3, 4.7 Hz, H-3), 4.09 (d, 1H, J = 4.5 Hz, H-2), 3.76 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 170.9 (C=O), 143.9 (C_q NPh), 137.5, 137.4 (C_q Bn), 128.9, 128.7, 128.6, 128.2, 128.2, 128.1, 128.1, 124.5, 119.7 (CH_{arom}), 116.11 (q, J = 285.8 Hz, CF_3), 102.6 (C-1), 81.2 (C-4), 80.3 (C-3), 79.7 (C-2), 73.3, 73.0 (CH_2 Bn), 52.5 (CH_3 CO_2Me); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -66.62; HRMS: $[M+H]^+$ calcd for $C_{28}H_{27}F_3NO_6$ 530.17850, found 530.17802.



Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-lyxofuranosyl uronate) (72). The title compound was generated from **55** (1.05 g, 2.90 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 85% as two separate anomers (487 mg, 0.92 mmol α and 105 mg, 0.20 mmol β respectively) as colourless oils. R*f*: 0.24 and 0.69 (8/2 pentane/Et_2O). Data for the α-anomer: $[\alpha]_D^{20}$ = -5.5° (*c* = 1.23, $CHCl_3$); IR (thin film): 696, 1026, 1101, 1159, 1207, 1327, 1707, 1734, 1770; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.33 – 7.22 (m, 12H, CH_{arom}), 7.10 – 7.02 (m, 1H, NPh), 6.80 (d, 2H, *J* = 7.5 Hz, NPh), 6.49 (bs, 1H, H-1), 4.81 (d, 1H, *J* = 5.3 Hz, H-4), 4.71 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.66 (s, 2H, CH_2 Bn), 4.61 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.43 (t, 1H, *J* = 5.1 Hz, H-3), 4.20 (dd, 1H, *J* = 4.6, 2.7 Hz, H-2), 3.68 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 167.9 (C=O), 143.7 (C_q NPh), 143.1 (q, *J* = 36.2 Hz, CF_3-*C*=N), 137.7, 137.3 (C_q Bn), 128.8, 128.5, 128.4, 128.1, 127.9, 127.8, 124.5, 119.7, (CH_{arom}), 116.1 (q, *J* = 285.8 Hz, CF_3), 103.5 (C-1), 82.0 (C-2), 79.7 (C-4), 78.4 (C-3), 73.9, 73.0 (CH_2 Bn), 52.1 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{30}F_3N_2O_6$ 547.20505, found 547.20459. Data for the β-anomer: $[\alpha]_D^{20}$ = -66.4° (*c* = 0.70, $CHCl_3$); IR (thin film): 696, 1074, 1086, 1144, 1327, 1715, 1769; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.25 (m, 10H, CH_{arom}), 7.25 – 7.19 (m, 3H, NPh), 7.09 – 6.99 (m, 1H, NPh), 6.79 (d, 2H, *J* = 7.7 Hz, NPh), 6.40 (bs, 1H, H-1), 4.89 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 5.5 Hz, H-4), 4.69 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.66 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.62 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.39 (t, 1H, *J* = 5.3 Hz, H-3), 3.98 (t, 1H, *J* = 4.6 Hz, H-2), 3.64 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 168.3 (C=O), 144.4 (C_q NPh), 138.4, 137.4 (C_q Bn), 128.7, 128.7, 128.2, 128.2, 127.7, 127.4, 127.3, 124.0, 119.8 (CH_{arom}), 116.3 (q, *J* = 286.8 Hz, CF_3), 96.4 (C-1), 81.1 (C-4), 79.9 (C-2), 76.4 (C-3), 74.2, 73.3 (CH_2 Bn), 52.0 (CH_3 CO_2Me); HRMS: $[M+H]^+$ calcd for $C_{28}H_{27}F_3NO_6$ 530.17850, found 530.17835.



Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-xylofuranosyl uronate) (73). The title compound was generated from **56** (1.20 g, 3.0 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 81% β only (561 mg, 1.06 mmol) as a colourless oil. R*f*: 0.28 (8/2 pentane/Et_2O). $[\alpha]_D^{20}$ = +10.2° (*c* = 0.55, $CHCl_3$); IR (thin film): 696, 1105, 1159, 1207, 1325, 1717, 1732, 1771; ^1H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.34 – 7.22 (m, 12H, CH_{arom}), 7.15 – 7.02 (m, 1H, NPh), 6.82 (d, 1H, *J* = 7.5 Hz, NPh), 6.32 (bs, 1H, H-1), 5.00 (d, 1H, *J* = 6.0 Hz, H-4), 4.57 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.55 – 4.50 (m, 3H, CH_2 Bn, CH*H* Bn), 4.32 (dd, 1H, *J* = 6.0, 1.2 Hz, H-3), 4.23 (s, 1H, H-2), 3.72 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 168.6 (C=O), 144.1 (C_q NPh), 137.5, 137.1 (C_q Bn), 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 127.6, 124.2, 119.8 (CH_{arom}), 116.1 (q, *J* = 286.8 Hz, CF_3), 103.3 (C-1), 84.0 (C-2), 82.9 (C-4), 82.0 (C-3), 73.1, 72.5 (CH_2 Bn), 52.0 (CH_3 CO_2 Me); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{26}F_3NO_6Na$ 552.16044, found 552.15999.



Methyl (2,3-di-*O*-benzyl-D-ribosyl uronate) diphenyl mercaptal (74). Compound **59** (200 mg, 0.5 mmol) was dissolved in 2 mL DCM and cooled to 0°C. Thiophenol (90 µL, 0.88 mmol, 1.75 eq.) and $BF_3 \cdot OEt_2$ (105 µL, 0.85 mmol, 1.7 eq.) were added and the reaction stirred for 4 h. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ and the mixture was extracted with DCM three times. The combined organic layers were washed with H_2O and brine, then dried ($MgSO_4$), filtered and concentrated in vacuo. Purfication by flash column chromatography (1/0 to 8/2 pentane/EtOAc) gave the dithioacetal as a colourless oil (156, 0.28 mmol, 56%). IR (thin film): 696, 737, 1026, 1101, 1217, 1230, 1267, 1439, 1454, 1481, 1581, 1734, 2873, 2922, 2949, 3030, 3059, 3466; ^1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.50 – 7.11 (m, 20H, CH_{arom}), 5.19 (d, 1H, *J* = 10.5 Hz, C*H*H Bn), 5.05 (s, 1H, H-1), 4.76 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 10.5 Hz, CH*H* Bn), 4.53 (bs, 1H, H-4), 4.48 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.39 – 4.30 (m, 2H, H-2, H-3), 3.42 (s, 3H, CH_3 CO_2Me), 3.02 (bs, 1H, OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.8 (C=O), 137.9, 137.5, 136.0, 135.1 (C_q), 131.3, 130.7, 129.2, 129.1, 128.5, 128.4, 128.3, 127.9, 127.8, 127.3, 127.0 (CH_{arom}), 81.4, 78.8 (C-2, C-3), 74.8, 73.4 (CH_2 Bn), 69.8 (C-4), 60.4 (C-1), 52.6 (CH_3 CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{32}H_{32}O_5S_2Na$ 583.158.34, found 583.15803.

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