Sigmatropic Rearrangement of Uronic Acid Derived Saccharide Allyl Ketene Acetals. A Study of Stereochemistry and Structural Limitations

Barbara Werschkun, Joachim Thiem*

Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany
Fax: +49(40)41234325; E-mail: thiem@chemie.uni-hamburg.de

Received 4 May 1998; revised 30 June 1998

Abstract: Allyl ketene acetal Claisen rearrangement of uronic acid derivatives with furanoside structure was studied. Reproducibility of the observed stereodiscrimination was confirmed in the conversion of enantiomeric starting materials. From X-ray structural data of the major reaction product obtained from a *cis*-pentenyl uronate, the transition state was proven to preferentially adopt a chair-like geometry. Alterations in the protecting group pattern led to a significant decrease in total yields. Use of β-deoxygenated starting material allowed a greater extent of variation, but was accompanied by the total loss of stereodiscrimination. For the first time, the reaction was applied to pyranoid starting material structures. The conversion of a *gluco*-configurated compound remaining unsuccessful, with the corresponding *galacto* and 4-deoxy derivatives an interesting stereoselectivity could be observed. This was lost by further structural simplification to a 1,4-dideoxypyranoid ring. This way, however, a substantial improvement in yield could be achieved.

Key words: Claisen rearrangements, allyl ketene acetals, furanosiduronates, pyranosiduronates

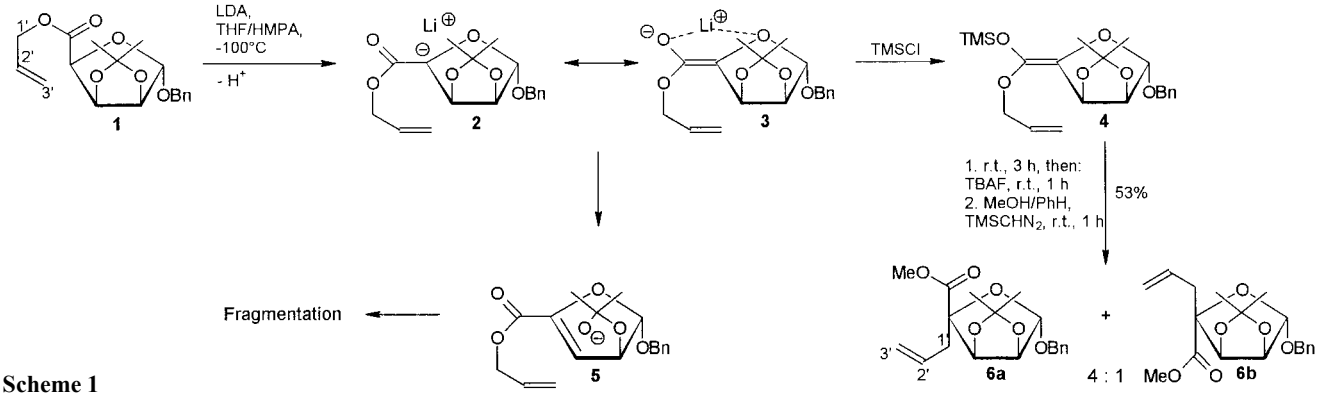
Modified carbohydrate derivatives frequently receive attention as interesting synthetic targets from several aspects. The constantly increasing knowledge concerning the outstanding relevance of carbohydrates in biological processes[1] has generated substantial demands for potent artificial mimetics of naturally occurring glyco structures. Additionally, carbohydrate derived building blocks have been successfully employed for a long time as chiral starting materials in many natural product syntheses.[2] Particularly for this latter purpose, often fundamental changes in the molecular frame are required, above all the substitution of oxygen functionalities by carbon–carbon bonds. Due to their complex structures, however, carbohydrate derivatives have often proved to cause unexpected difficulties even in well-established synthetic transformations.

With respect to C–C bond formation, an especially valuable method for the manipulation of sensitive starting material is provided by application of sigmatropic rearrangements. Among these, easy preparative access to compounds bearing an oxygen functionality has rendered the Claisen rearrangement, in particular, a powerful synthetic tool, which is frequently employed even in the most delicate problems of natural product chemistry.[3] Substantial benefits in terms of availability of starting materials, as well as influence on the stereochemically crucial matter of double bond geometry, have been derived from the extensive work of Ireland et al., who established the synthetic variant of silylketene acetal Claisen rearrangement.[4]

Profitable use of this reaction in carbohydrate chemistry has been made employing glycal starting material as allylic component and generating a ketene acetal function from an external, non-carbohydrate acyl residue.[5] The reverse combination of placing the ketene acetal structural unit within the carbohydrate moiety, as can be achieved by enolization of allyl uronates, has received much less attention, so far. The first example of uronic acid derived ketene acetals was introduced by Ireland et al. in the course of polyether-type natural product synthesis in the mid-eighties.[6] Since then, repetition of the reaction has been performed only once by Rizzacasa et al. employing virtually the same furanoid starting material.[7] Apart from these two instances, however, the formation and sigmatropic rearrangement of saccharide ketene acetals has not been investigated. With regard to conceptional applications for future synthetic purposes, several basic reaction features had to be elucidated. The investigations presented in this study covered subjects such as the stereochemistry of the newly generated quarternary carbon atom, the transition state geometry, the effect of the number and the nature of ring substituents, and studies on the feasability to extend the reaction to pyranoid starting material.

For the initial experiments, allyl D-lyxofuranosiduronate **(1)** was prepared from D-mannose according to literature procedures.[6–8] Successful transformation of the same starting material in a ketene acetal Claisen rearrangement has already been reported by Rizzacasa et al.,[7] following the results obtained earlier by Ireland et al. with the analogous crotyl ester.[6] The fundamental problem that is encountered during enolate formation from esters containing a suitable leaving group in the β-position is illustrated in Scheme 1. Subsequent to deprotonation adjacent to the carbonyl carbon atom, two competing reaction pathways can originate from the enolate anion which is represented by the mesomeric structures **2** and **3**. If the desired ketene acetal formation by *O*-silylation to **4** cannot be achieved in time, β-elimination will occur to generate the conjugated intermediate **5**, from which further fragmentation can emerge. To suppress the latter unwanted process, Ireland et al. developed a strategy of in situ trapping, which should secure that any amount of enolate formed is instantly reacted to the silyl ketene acetal before elimination can occur.[6]

According to the published experimental protocol, a solution of lithium diisopropylamide in tetrahydrofuran and hexamethylphosphoramide is premixed with chlorotrimethylsilane at –100 °C before the respective allyl ester is



Scheme 1

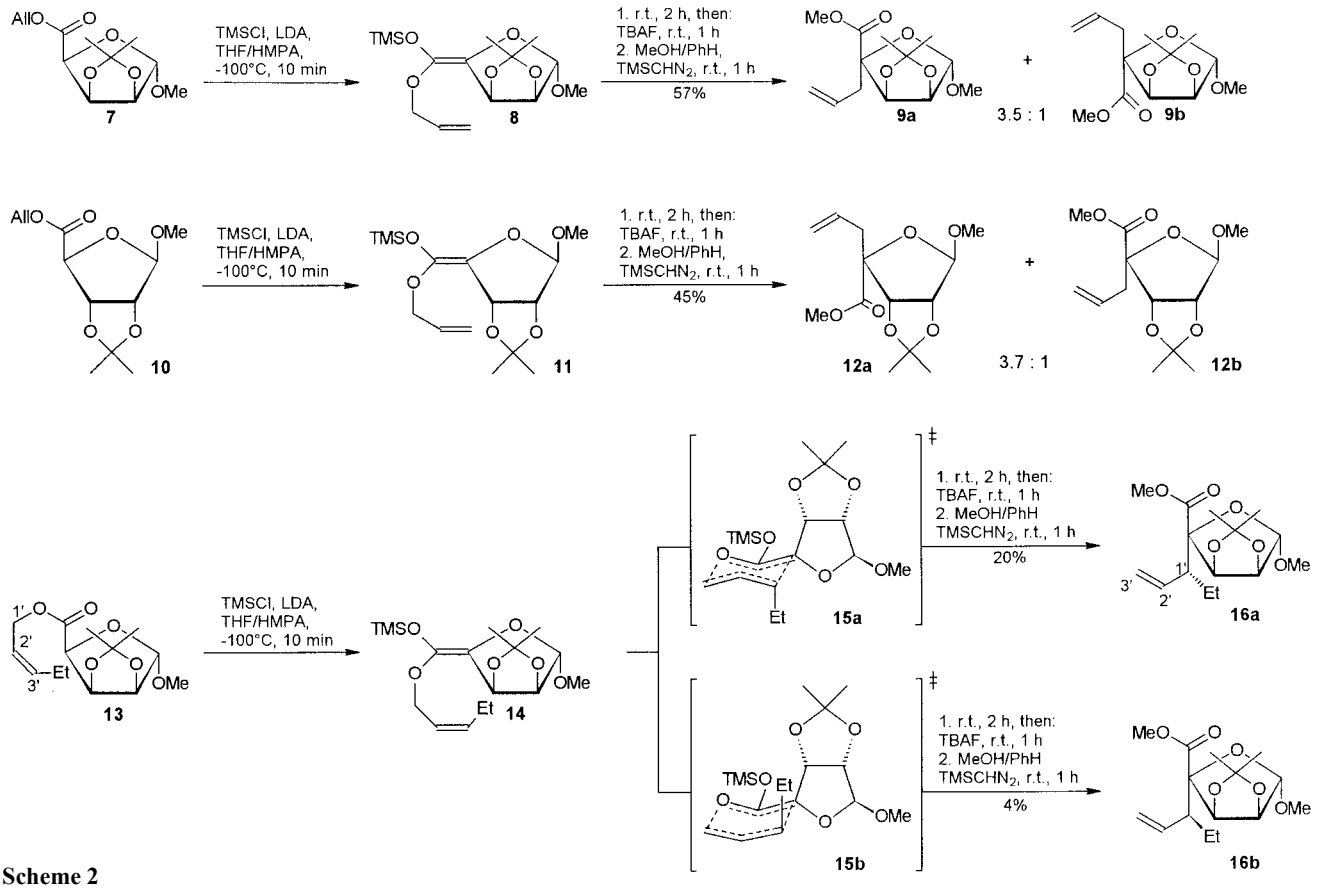
added at the same temperature. The rearrangement products from the crotyl uronate analogous to **1** were reported to be obtained in 80% yield, this way. Our attempts, though, to transform allyl ester **1** in the same manner, remained unsuccessful. Instead of the fragmentation reactions which could have been expected, however, in all cases ester **1** was isolated almost quantitatively. This was considered to be unchanged starting material, since hydrolysis of unreacted silyl ketene acetal **5** should additionally produce the C-4 epimer, which was in no case detected. Therefore, and in accordance with observations reported earlier by others,[9] our assumption was that in the premixed reagent solution, the alkylamide base might have been consumed in a reaction with the chlorosilane before the ester starting material ever entered the reaction mixture. Since under such circumstances the order in which the respective compounds are added seemed to be a crucial point, several variations were tested. Fairly good results of up to 70% of rearrangement products **6a** and **6b** could be obtained by simultanously adding chlorosilane and ester to the cooled base solution.

Unfortunately, this method turned out to be extremely difficult to reproduce and was therefore considered too unreliable for further systematic investigations or preparative purposes. The reverse procedure of adding the base to a cooled solution of both silylating agent and ester starting material, which had already been described by Rizzacasa et al.,[7] resulted in our hands in only moderate yields of around 50%. Losses of yield in all cases originated from the competing *N*-silylation of diisopropylamide, as could be concluded from the amount of unchanged **1** recovered. Variations using lithium or sodium hexamethyldisilazide as the base and chloro-*tert*-butyldimethylsilane or chloro-*tert*-butyldiphenylsilane as the silylating agent did not result in any improvement. Nevertheless, in terms of reproducibility, this method still proved to be the best. Taking into account how difficult the same quarternary allyl branched product might be to prepare by other means from notoriously delicate carbohydrate starting material, the obtained result still renders ketene acetal Claisen rearrangement in this class of compounds worthwhile for further systematic investigations and preparative purposes possibly originating therefrom.

In the course of the Claisen rearrangement of ketene acetal **4**, the *C*-allyl branched diastereomers **6a** and **6b** were formed in a ratio of 4 to 1 in favour of the D-*lyxo* configurated product, resulting from C–C bond formation predominantly taking place *trans* to the isopropylidenedioxy moiety. This finding was largely in accordance with the results published by Rizzacasa et al. who could also determine the absolute configuration at C-4 by X-ray crystallography of a derivative of **6a**.[7] With regard to the above mentioned difficulties to exactly reproduce the rearrangement reaction, however, additional evidence for the observed stereodiscrimination being displayed independently from the somewhat varying total reaction outcome was thought to be desirable. For this purpose, comparison of two separately transformed enantiomeric ketene acetals was considered particularly instructive, since apart from the respective absolute configurations, these should give entirely identical results.

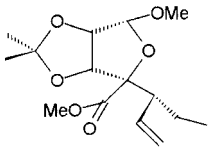
Thus, the diastereomeric allyl esters **7** and **10** were synthesized from the corresponding D-lyxo- and D-ribofuranosiduronic acids,[10] respectively. Due to the chelating effect of the ring oxygen atom, during enolate formation the (*E*)-isomer should be strongly favoured, as had been demonstrated before.[11] Assuming that silylation is taking place under retention of configuration,[12] it should lead to the enantiomeric (*Z*)-ketene acetals **8** and **11** (Scheme 2). Following sigmatropic rearrangement, the mixtures of C-4 diastereomers **9a**,**b** and **12a**,**b**, respectively, were isolated. The absolute configurations of the generated quarternary stereocentres were assigned by comparison of NMR data with compounds **6a** and **6b**. The difference in total yields may be attributed to different deprotonation rates of the diastereomeric esters **7** and **10**. Apparently, this does not influence the stereochemical behaviour of the ketene acetals **8** and **11**, once they are formed, since the diastereomeric ratios within the respective product mixtures turned out to be virtually the same. Thus, for further investigations, the stereochemical course could be considered independent from possibly slightly varying reaction conditions and total yields.

Regarding stereochemistry, a feature of general interest in sigmatropic reactions has always been the transition state geometry.[5c,5e,13] This can be investigated, if in the course of rearrangement a new chiral centre is generated from the



Scheme 2

terminal position of a stereochemically unequivocally substituted allyl double bond. For this purpose, the (*Z*)-pent-2-enyl ester **13** was prepared from commercially available (*Z*)-pent-2-en-1-ol and the above mentioned D-lyxofuranosiduronic acid.[10a] Ireland–Claisen rearrangement resulted in the formation of all four possible stereoisomers. Apart from the predominating D-*lyxo* products **16a** and **16b**, which are shown in Scheme 2, the corresponding L-*ribo* isomers were formed in 4% total yield, but due to this small amount they will be neglected in the following discussion. From the product fraction **16**, the side chain epimers **a** and **b** were separated by chromatography and obtained in a 5:1 ratio. Fortunately, the major component **16a** formed crystals suitable for X-ray structural analysis, the ORTEP projection of which is shown in the Figure. The absolute configuration of the newly formed chiral centre could thus be assigned as *R*, allowing the conclusion, that in the reaction pathway the chair-like structure **15a** for the transition state is predominating. Since the strong general preference of sigmatropic rearrangements to proceed via chair-like transition state structures has long been established, this result is scarcely surprising for a comparatively unhindered structure such as **14**. The contribution of the alternative boat-like structure **15b**, however, although minor, can still be counted as substantial, indicating the difference in energy levels being rather small. It can be well imagined, that in the case of a sterically more biased system the reaction might easily take a different course.



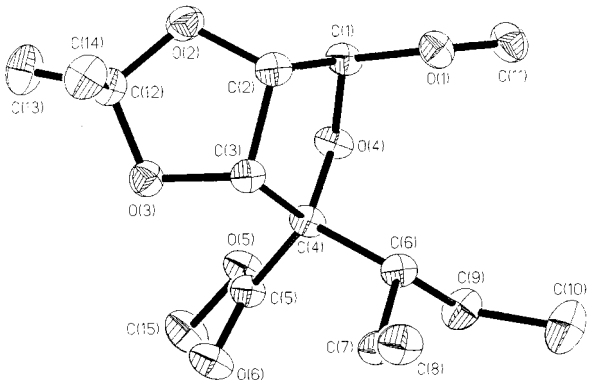
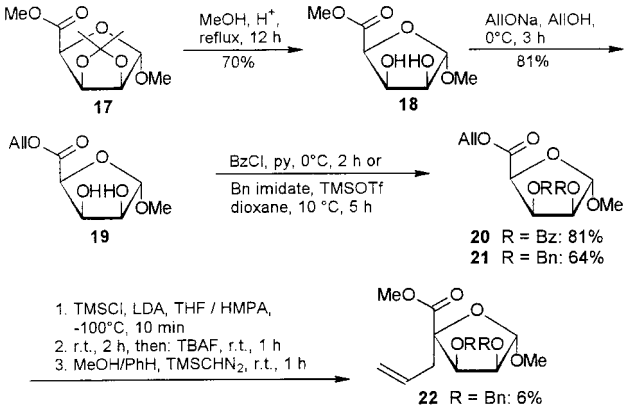


Figure ORTEP Diagram of **16a**

Subsequent to these findings of a more basic nature, the effect of starting material structure variations should be investigated. Retaining the same D-*lyxo* molecular backbone which had been employed before, the diolic allyl ester **19** was prepared by standard synthetic steps from the isopropylidene precursor **17**[14] and transformed into the protected derivatives **20** and **21** (Scheme 3). The benzoyl

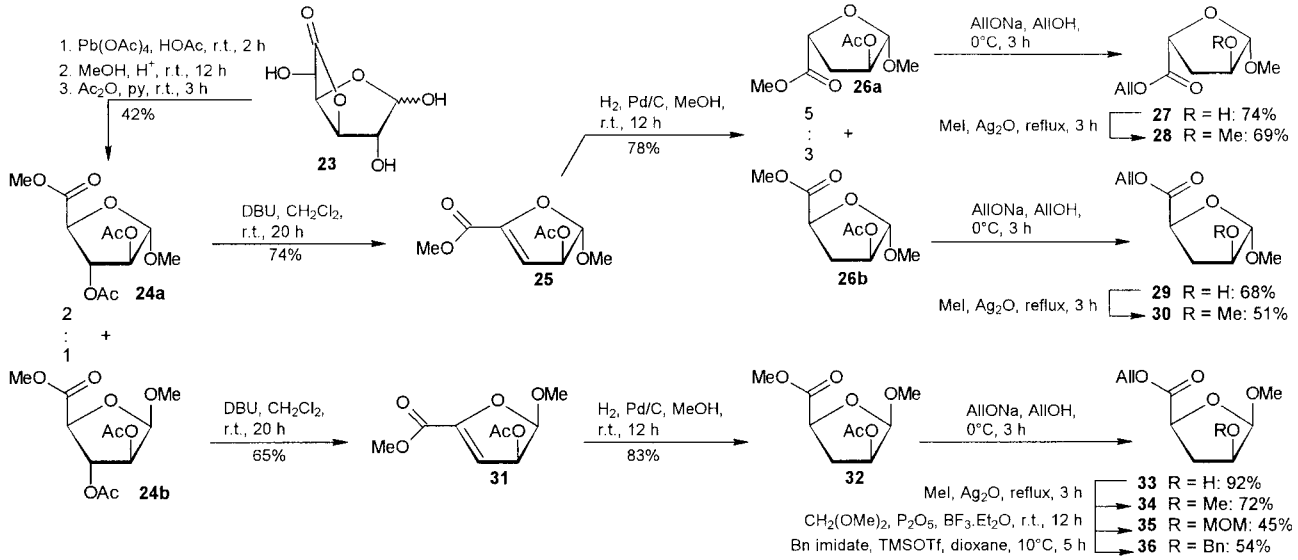


Scheme 3

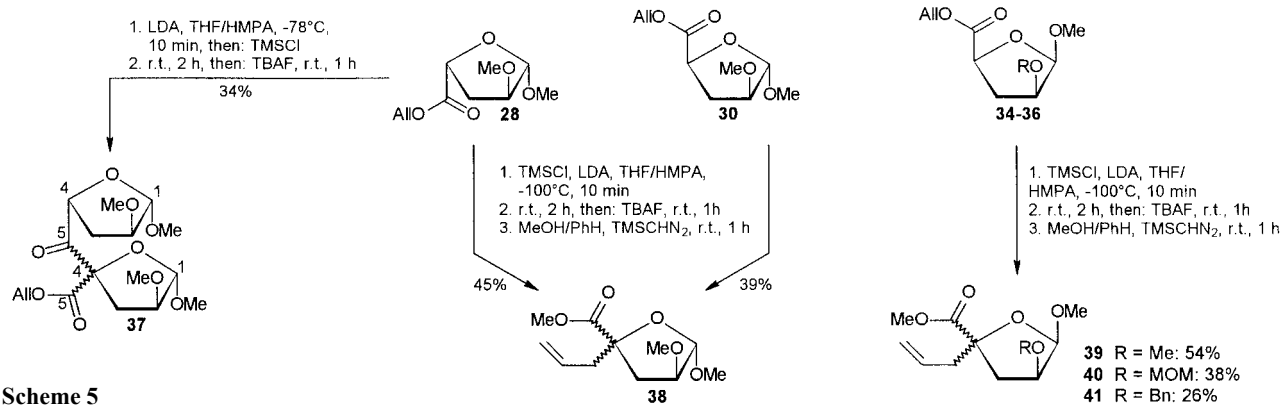
ester **20** was chosen as an example for an ester protecting group which cannot be enolized itself, and the benzyl ether **21** as a representative for any ether-type substituent. Following the Ireland–Claisen reaction of dibenzoate **20**, no product could be isolated. Instead, a substantial amount of fragmentation was observed, which can be rationalized by a destabilising effect of the electron-withdrawing ester functions on the initially formed carbanion. In such terms, benzyl ether **21** could be expected to provide less difficulties. However, although the rearrangement product **22** was indeed obtained, the minor yield and the loss of material by decomposition indicated again that this structure was unsuitable for ketene acetal Claisen rearrangement. In view of these scarcely encouraging results, no further experiments with fully oxygenated furanosides were performed. Instead, improvement was sought to be achieved by simplification of starting material structures, namely deoxygenation in the crucial 3-position.

Easy access to a variety of differently configurated 3-deoxy uronates is provided by the divergent synthetic pathway illustrated in Scheme 4. The glycol cleavage of glucuronolactone **23** and subsequent acid-catalyzed esterification and Fischer glycosylation to a mixture of the anomeric arabinofuranosiduronates has already been reported.[15] Final acetylation enabled chromatographic separation of the product mixture into the pure anomers **24a** and **24b**. According to a common procedure,[16] deoxygenation was accomplished in two steps by β-elimination followed by catalytic hydrogenation of the obtained unsaturated esters. In the course of the latter, an interesting difference in the stereochemical behaviour of both anomers was observed. Whereas the 1,2-*trans* substituted **25** gave a mixture of both C-4 epimers **26a** and **26b**, from the 1,2-*cis* isomer **31,** the D-*threo* compound **32** was obtained as the single product. All three diastereomers were transformed into suitable precursors for ketene acetal formation by transesterification to allyl esters **27**, **29** and **33** followed by silver(I)-catalyzed methylation of the free hydroxy groups to give **28**, **30** and **34**.

Since there is no potential leaving group in the crucial 3-position, the procedure of in situ silylation from the first sight did not seem to be necessary, and hence for the reaction of compound **28**, the generally more common protocol of separate enolization prior to addition of the silylating agent was employed (Scheme 5). Unexpectedly, however, a new source of complication arose from a carbonyl addition reaction of the initially formed carbanion with a second ester molecule to give the dimeric structure **37** as the sole product to be isolated. This compound was obtained as a single stereoisomer, but due to its pronounced instability, the absolute configuration of the quarternary carbon atom could not be assigned. Thus, even in the case of β-deoxy uronates, the modified procedure of in situ silylation had to be used. Application to **28** gave the diastereomeric rearrangement products **38** as an inseparable 1:1 mixture, the total yield of 48% was as before within the range observed for fully oxygenated derivatives. As expected, the same product mixture was obtained from the C-4-epimeric starting material **30**, thereby demonstrating that the configuration at the site of deprotonation does not significantly affect the reaction outcome. Remembering the stereochemical course during



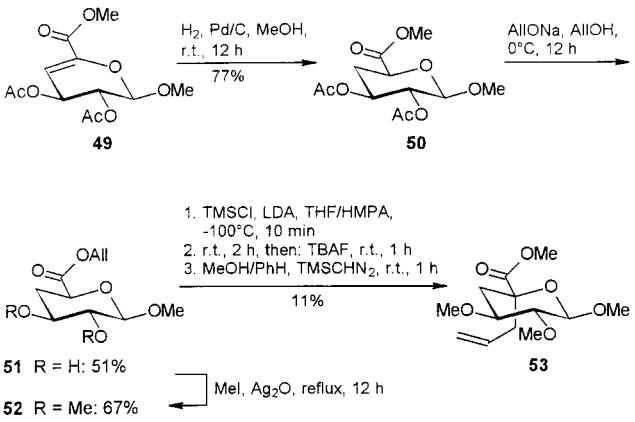
Scheme 4



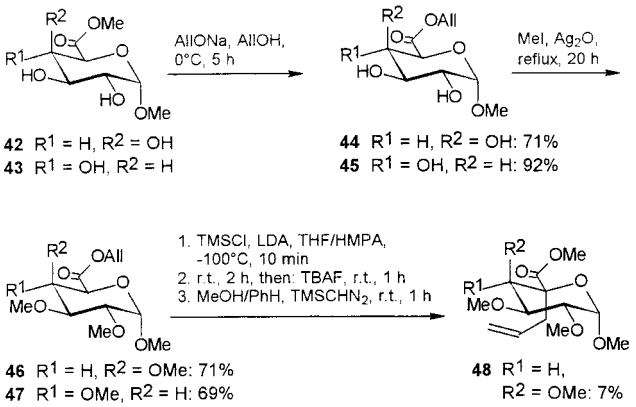
Scheme 5

the hydrogenation reaction of **31** to **32**, a similar directing influence of the 1,2-*cis*-substitution pattern could be expected for the ketene acetal rearrangement of the corresponding allyl ester **34**. The diastereomeric rearrangement products **39**, however, again were formed in equal amounts. Changing the substitution at 2-position to larger residues such as in methoxymethyl and benzyl derivatives **35** and **36**, respectively, did not alter the diastereomeric ratio. However, the yields decreased significantly, and the benzyl ether **36** gave the poorest result in accordance with the observations made in the D-*lyxo* series. Although β-deoxygenation proved to allow a greater extent of protecting group variation, acceptable yields could only be obtained with acetal and methyl ether derivatives. In addition, regarding the total loss of stereoselectivity, the use of deoxygenated starting material in the furanoside series did not lead to a substantial synthetic benefit.

Although the first instance of ketene acetal rearrangement employing uronate-type starting material is now more than twelve years ago, to our knowledge, no efforts to apply this reaction to any of the far more common pyranoid carbohydrate structures have been published, so far. Suitable precursor molecules were easily prepared from the methyl galacto- and glucopyranosiduronates **42**[17] and **43**,[18] respectively, by transesterification and *O*-methylation to give the protected allyl esters **46** and **47** (Scheme 6). Application of the Ireland–Claisen reaction, however, only in the case of *galacto* compound **46** led to the isolation of the rearrangement product **48** in very small amounts, whereas with the analogous *gluco* derivative **47** no transformation could be achieved at all. Taking into account that loss of material by 4,5-elimination should be strongly favored by the *trans*-diaxial arrangement given in the case of *galacto* configuration, it appears even more surprising that the *gluco* isomer did not prove to give better results. The configuration of the newly formed quarternary stereocentre in **48**, which was assigned by means of NOE-NMR spectral data, reveals that during the rearrangement process bond forming exclusively occurs *trans* to the C-4 methoxy substituent.



Scheme 7



Scheme 6

For further elucidation of the influence of substitution adjacent to the ketene acetal moiety on the course of the rearrangement reaction, a C-4 deoxygenated derivative was employed. Its preparation could be easily achieved from the unsaturated uronate **49**[19] in analogy to the synthetic sequence used before in the furanoside series (Scheme 7). The methylated allyl ester **52** was obtained as a suitable starting material via the sole product **50** from the catalytic hydrogenation of **49**. The Ireland–Claisen reaction of **52** led to the isolation of **53** as the single rearrangement product. Again, the configuration at C-5 could be assigned by NOE-NMR spectroscopy and turned out to be the same as in the *galacto* compound obtained before. Since in this case, no directing substituent in the neighbouring C-4 position is present, the observed stereoselectivity seems as-

tonishing. As a possible reason the conformation of the pyranoside ring should be considered, in particular the folding of the C-1 to C-3 moiety, which might hinder bond formation from above the ring surface. From this aspect, the above observed failure of the *gluco* derivative to undergo any rearrangement reaction would become somewhat comprehensive. In that case, in addition to the assumed hindrance on the top side, also the bottom face is shielded by the equatorial methoxy group in position 4, and thus there is no possible reaction pathway remaining. With respect to the yield, β-deoxygenation gave a small, but scarcely significant improvement compared to the *galacto* compound, the values obtained so far in the hexopyranoside series altogether turned out to be rather poor. As a crucial factor, the chair-like ring conformation could be responsible, because compared to the furanoid derivatives rehybridization subsequent to deprotonation should be more difficult.

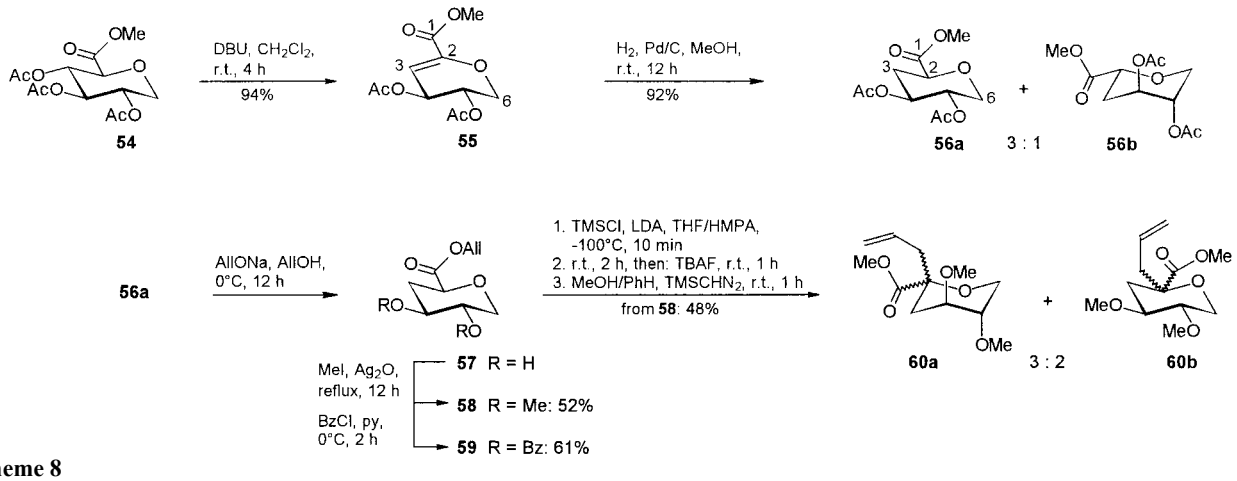
As conformational rigidity to a substantial part is supported by stereoelectronic influence of the ring substituents, simplification of the molecular backbone by further deoxygenation could be expected to be an effective way to facilitate the Ireland–Claisen rearrangement with pyranoid starting material. For this purpose, 2,6-anhydrohexonate **54**,[20] prepared by radical reduction of the corresponding glucuronyl bromide as described in the literature,[21] was manipulated in the common β-elimination-hydrogenation sequence, which resulted in the isolation of the epimeric dideoxygenated pyranoid esters **56a** and **56b**. The major component **56a** was transformed into the *O*-methylated allyl ester **58**, which, upon ketene acetal formation, gave a mixture of the diastereomeric rearrangement products **60a** and **60b** (Scheme 8). The total yield of 48% corresponds to the results obtained in the furanoid series and within the pyranoid class of compounds represents a substantial improvement. The aforementioned assumption that a decreased extent of ring substitution will enhance conformational flexibility is confirmed not only by this increase in yield, but also by the observed loss of stereoselectivity. The diastereomeric products are formed to almost equal parts and obviously adopt opposite chair-like conformations. The absolute configurations of the generated quarternary stereocentres, however, could not be assigned. In both NOESY-NMR spectra, no distinct interactions could be recognized, and due to their sirupy nature neither of the isomers enabled X-ray structural resolvement. An attempt to repeat the reaction with the dibenzoylated derivative **59** in order to possibly obtain crystalline rearrangement products failed as before in the lyxofuranoside series.

The material presented in this study certainly shows the formation and reaction of saccharide ketene acetals to be of a rather delicate nature. To obtain satisfying results, several structural restrictions have to be taken into account. Nevertheless, upon appropriate adjustments, preparative purposes may still be realized. Efforts in this direction are under current investigation in our laboratories and will be reported in due course.

Solvents were purified and dried according to standard procedures. Petroleum ether used refers to bp 50–70 °C. TLC was performed on silica gel 60-coated aluminum sheets (Merck or Macherey-Nagel), with detection by UV at 254 nm and by heating with H_2SO_4 (5% in EtOH). Flash chromatography was carried out on silica gel 60 (0.04–0.063 mm) (Merck, Macherey-Nagel or ICN). NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz) with TMS as internal standard. Melting points were determined on a Leitz apparatus and are uncorrected. The optical rotations were measured on a Perkin-Elmer 243 or 341 polarimeter at 20 °C. Due to inherent impurities in the case of all Claisen rearrangement products, correct elemental analysis results could only be obtained for crystalline derivatives. ^{1}H and ^{13}C NMR data of the products are listed in Tables 1–12.

Ketene Acetal Formation and Sigmatropic Rearrangement; General Procedure A

To a solution of the allyl uronate in anhyd THF (4 mL/mmol) and HMPA (1 mL/mmol) under argon was added chlorotrimethylsilane (3.4 equiv) at –100 °C. Then, a freshly prepared 1 M solution of LDA in anhyd THF (2 equiv) was added dropwise maintaining the same temperature. When addition was complete, the reaction mixture was allowed to warm up to r.t. over a period of 40 min and stirred for additional 2 or 3 h. After that time, a 1 M solution of TBAF in THF (4 equiv) was added and the mixture was further stirred at r.t. for 1 h. The solution was diluted with Et_2O (10 mL/mmol) and extracted with 1 M NaOH (3 × 20 mL/mmol). The combined aqueous extracts were acidified with 10 M HCl to pH 1 or be-



Scheme 8

low and quickly extracted with CH_2Cl_2 (3 × 50 mL/mmol). The organic extracts were dried ($MgSO_4$) and concentrated in vacuo. A solution of the residual brown oil in benzene (6 mL/mmol) and MeOH (2 mL/mmol) was treated with a 2 M solution of $TMSCHN_2$[22] in hexane (1.2 equiv) for 1 h under vigorous stirring at r.t. After removal of the solvents in vacuo, the resulting viscous solid was purified by flash chromatography.

Esterification of Uronic Acids via the Acid Chlorides; General Procedure B

To a solution of the uronic acid and a few drops of anhyd DMF in benzene (2.5 mL/mmol) was added oxalyl chloride (2 equiv) at 0 °C. The mixture was stirred under warming to r.t. until no further gas formation could be observed (approximately 1 to 3 h). After concentration in vacuo, the residue was taken up in Et_2O (5 mL/mmol), the solution was filtered through Celite, and the filtrate was evaporated in vacuo. To a solution of the resulting crude acid chloride in anhyd CH_2Cl_2 (5 mL/mmol) the respective alcohol (1.5 equiv) and DMAP (1.5 equiv) were added at 0 °C, and the mixture was stirred under warming to r.t. Upon completion of conversion as monitored by TLC (petroleum ether/EtOAc, 3:1), the solution was diluted with Et_2O (10 mL/mmol), washed with sat. aq $NaHCO_3$ (10 mL/mmol), and dried ($MgSO_4$). The solvents were removed in vacuo, and the crude ester was purified by flash chromatography.

Transesterification with AllONa; General Procedure C

To a solution of the methyl uronate in anhyd allyl alcohol (AllOH, 10 mL/mmol) was added a freshly prepared 1 M solution of AllONa in AllOH (0.25 equiv) at 0 °C. The solution was allowed to slowly warm up to r.t. and upon completion of conversion (TLC monitoring: petroleum ether/EtOAc/MeOH, 10:10:1) was neutralized by stirring with ion exchange resin Amberlite IR 120 H^+. The solution was filtered, the filtrate was evaporated in vacuo, and the crude allyl uronate was purified by flash chromatography.

Elimination to α,β-Unsaturated Uronates with DBU; General Procedure D

A solution of the β-acetoxyuronate in anhyd CH_2Cl_2 (10 mL/mmol) was stirred with DBU (2 equiv) at r.t. until conversion was complete (TLC monitoring: petroleum ether/EtOAc, 2:1), washed with 4 M HCl (5 mL/mmol), and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the crude unsaturated uronate was purified by flash chromatography.

Hydrogenation of Unsaturated Uronates; General Procedure E

A solution of the unsaturated uronate in MeOH (10 mL/mmol) containing 10% Pd on activated charcoal (40 mg/mmol) was stirred under H_2 at r.t. until conversion was complete (TLC monitoring: petroleum ether/EtOAc, 2:1). The catalyst was filtered off, the filtrate was evaporated in vacuo, and the crude hydrogenation product was purified by flash chromatography.

Methylation of Hydroxyl Groups with MeI/Ag_2O; General Procedure F

A solution of the free alcohol in MeI (5 mL/mmol) containing Ag_2O (3 equiv/OH group) was heated under reflux until conversion was complete (TLC monitoring: petroleum ether/EtOAc, 2:1). The silver salts were filtered off and extracted with CH_2Cl_2 (3 × 10 mL/mmol), the combined filtrates were evaporated in vacuo, and the crude methyl ether was purified by flash chromatography.

Methyl (Benzyl 2,3-*O*-isopropylidene-4-C-(prop-2-enyl)-α-D-lyxofuranosid)uronate (6a) and Methyl (Benzyl 2,3-*O*-isopropylidene-4-C-(prop-2-enyl)-β-L-ribofuranosid)uronate (6b)

Prepared according to General Procedure A, from allyl (benzyl 2,3-*O*-isopropylidene-α-D-lyxofuranosid)uronate (**1**;[7] 167 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (10:1).

Table 1 ^{1}H NMR Data of Pentofuranosiduronates **7**, **10**, **13**, **18–21**, and **24**

Product	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)										
	H-1	H-2	H-3	H-4	H-1'	H-2'	H-3'	Others	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
7	5.01	4.51/4.53	4.94	4.51/4.53	4.62, 4.71	5.83–5.94	5.19, 5.31	1.23, 1.36 (CH_3), 3.29 (OCH_3)	0	4.1[a]	5.6[a]
10	5.00	4.52	5.20	4.59–4.62		5.85–5.95	5.22–5.34	1.30, 1.45 (CH_3), 3.35 (OCH_3)	0	5.6	0
13	5.01	4.50	4.92	4.51	4.66, 4.77	5.44–5.50	5.56–5.62	0.93 (CH_3CH_2), 1.23, 1.36 (CH_3), 2.07 (CH_2), 3.29 (OCH_3)	0	5.9	3.6
18	4.96	4.02	4.53	4.59	–	–	–	3.31, 3.73 (OCH_3), 3.69, 3.80 (OH)	1.4	4.9	5.6
19[b]	5.05	4.65–4.77		4.06	4.65–4.77	5.90–5.99	5.28–5.41	2.95 (OH), 3.39 (OCH_3)	–	–	–
20	5.38	5.63	6.12	5.05	4.48, 4.59	5.61–5.71	5.00, 5.12	3.50 (OCH_3), 7.27–7.36, 7.52, 7.84, 7.95 (Ar)	1.3	5.4	6.4
21	5.23	3.93, 4.38		4.54–4.77		5.79–5.89	5.18, 5.29	3.43 (OCH_3), 4.54–4.77 (OCH_2), 7.26–7.35 (Ar)	3.9	4.4	4.9
24a	4.99	4.96	5.23	4.49	–	–	–	2.03, 2.06 ($OCOCH_3$), 3.37, 3.75 (OCH_3)	0	1.5	5.1
24b	5.09	4.94	5.75	4.33	–	–	–	2.04 ($OCOCH_3$), 3.36, 3.72 (OCH_3)	4.4	6.4	4.9

[a] May be interchanged.
[b] Coupling constants of **19** are insufficiently resolved.

Table 2 ^{13}C NMR Data of Pentofuranosiduronates **7**, **10**, **13**, **18–21**, and **24**

Product	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ						
	C-1	C-2, C-3, C-4	C-5	C-1'	C-2'	C-3'	Others
7	107.44	79.44, 80.53, 83.99	167.09	65.73	131.69	118.63	25.05, 25.89 (CH_3), 55.01 (OCH_3), 113.32 (OCO)
10	109.32	82.11, 83.60, 84.30	169.80	66.01	131.51	119.04	24.98, 26.33 (CH_3), 55.45 (OCH_3), 112.69 (OCO)
13	107.53	79.58, 80.65, 84.08	167.41	61.04	122.38	137.32	14.04 (CH_3CH_2), 20.91 (CH_2), 25.16, 26.00 (CH_3), 55.09 (OCH_3), 113.39 (OCO)
18	107.94	70.69, 74.23, 77.83	170.19	–	–	–	51.60, 54.60 (OCH_3)
19	108.95	71.73, 75.27, 78.91	170.49	66.36	131.35	119.31	55.63 (OCH_3)
20	106.82	72.02, 75.21, 76.72	–[a]	66.22	–[b]	119.45	55.93 (OCH_3), 128.37–134.54 (C-2', Ar), 164.82, 165.19, 167.51 (CO_2)
21	107.79	78.29, 78.85, 82.96	168.33	65.88	–[b]	118.92	56.29 (OCH_3), 72.69, 73.72 (OCH_2), 127.69–137.77 (C–2', AR)
24a	106.59	77.39, 78.87, 79.69	–[a]	–	–	–	19.68 (CH_3), 51.72, 54.44 (OCH_3), 168.28, 168.65, 168.80 (CO_2)
24b	100.73	75.46, 76.01, 76.95	–[a]	–	–	–	19.59, 19.73 (CH_3), 51.52, 54.64 (OCH_3), 168.82, 168.99, 169.33 (CO_2)

[a] Not distinguishable from other carboxyl signals.
[b] Not distinguishable from aromatic signals.

Table 3 ^{1}H NMR Data of *C*-Branched Pentofuranosiduronates **6**, **9**, **12**, **16**, and **22**

Product	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)								
	H-1	H-2	H-3	H-1'	H-2'	H-3'	Others	$J_{1,2}$	$J_{2,3}$
6a	5.38	4.71, 4.78		2.67, 2.82	5.80–5.87	5.12	1.30, 1.42 (CH_3), 3.79 (OCH_3), 4.53, 4.82 (OCH_2), 7.27–7.36 (Ar)	0	6.1
6b	5.03	4.60	5.23	2.56, 2.71	5.65–5.73	5.03	1.27, 1.41 (CH_3), 3.48 (OCH_3), 4.41, 4.67 (OCH_2), 7.17–7.27 (Ar)	0	6.1
9a	4.68 (2 H), 5.16			2.58, 2.79	5.74–5.84	5.13	1.30, 1.42 (CH_3), 3.42, 3.78 (OCH_3)	–[a]	–[a]
9b	4.90	4.58	5.27	2.61, 2.75	5.69–5.80	5.10	1.33, 1.49 (CH_3), 3.32, 3.71 (OCH_3)	0	6.1
12a	4.61 (2 H), 5.09			2.50, 2.72	5.66–5.75	5.06	1.23, 1.35 (CH_3), 3.35, 3.71 (OCH_3)	–[a]	–[a]
12b	4.83	4.50	5.19	2.54, 2.67	5.63–5.73	5.06	1.27, 1.42 (CH_3), 3.26, 3.64 (OCH_3)	0	5.9
16a	5.08	4.57, 4.89		2.27	5.79–5.88	5.00, 5.14	0.78 (CH_3CH_2), 1.00, 1.76 (CH_2), 1.22, 1.33 (CH_3), 3.34, 3.71 (OCH_3)	0	5.9
16b	5.10	4.42	4.66	2.53	5.55–5.64	5.10, 5.16	0.76 (CH_3CH_2), 1.33 (CH_2), 1.21, 1.34 (CH_3), 3.37, 3.72 (OCH_3)	1.5	6.1
22	5.19	3.94	4.04	2.45, 2.76	5.74–5.84	5.08, 5.11	3.44, 3.67 (OCH_3), 4.59–4.73 (OCH_2), 7.26–7.33 (Ar)	3.1	4.9

[a] Not identified due to overlapping signals.

6a; yield: 75 mg (43%); colourless crystals; mp 91 °C (petroleum ether); $[\alpha]_D^{20}$ +5.3 (*c* = 1, $CHCl_3$); {Lit.[7] mp 91–92 °C; $[\alpha]_D^{20}$ +4.2 (*c* = 1, $CHCl_3$)}.

6b; yield: 18 mg (10%); yellow syrup; $[\alpha]_D^{20}$ +75.8 (*c* = 2, $CHCl_3$); {Lit.[7] $[\alpha]_D^{20}$ +63.8 (*c* = 1.5, $CHCl_3$)}.

Allyl (Methyl 2,3-*O*-isopropylidene-α-D-lyxofuranosid)uronate (7)
Prepared according to General Procedure B, from methyl 2,3-*O*-isopropylidene-α-D-lyxofuranosiduronic acid[10a] (1.73 g, 8 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 1.84 g (90%); colourless syrup; $[\alpha]_{578}^{20}$ +28.3 (*c* = 2, $CHCl_3$).

Anal. $C_{12}H_{18}O_6$ (258.3): calc. C 55.81, H 7.03; found C 55.56, H 7.16.

Methyl (Methyl 2,3-*O*-isopropylidene-4-*C*-(prop-2-enyl)-α-D-lyxofuranosid)uronate (9a) and Methyl (Methyl 2,3-*O*-isopropylidene-4-*C*-(prop-2-enyl)-β-L-ribofuranosid)uronate (9b)
Prepared according to General Procedure A, from **7** (129 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (10:1).

9a; yield: 60 mg (44%); colourless crystals; mp 66 °C (petroleum ether); $[\alpha]_D^{20}$ –11.6 (*c* = 0.5, $CHCl_3$).

Anal. $C_{13}H_{20}O_6$ (272.3): calc. C 57.34, H 7.40; found C 57.28; H 7.49.

9b; yield: 17 mg (13%); yellow syrup; $[\alpha]_D^{20}$ +1.3 (*c* = 0.1, $CHCl_3$).

Table 4 ^{13}C NMR Chemical Data of *C*-Branched Pentofuranosiduronates **6**, **9**, **12**, **16**, and **22**

Product	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ							
	C-1	C-2, C-3	C-4	C-5	C-1'	C-2'	C-3'	Others
6a	106.97	84.33, 84.67	91.79	168.81	40.87	–[a]	117.81	23.96, 24.95 (CH_3), 51.21 (OCH_3) 69.09 (OCH_2), 112.24 (OCO), 126.80–136.10 (C-2', Ar)
6b	105.04	80.11, 84.07	88.01	171.44	37.04	–[a]	117.82	23.85, 25.07 (CH_3), 51.03 (OCH_3), 68.16 (OCH_2), 111.49 (OCO), 126.64–136.18 (C-2', Ar)
9a	109.37	84.76, 85.15	92.13	169.41	41.47	131.72	118.30	24.54, 25.51 (CH_3), 51.75, 55.39 (OCH_3), 112.76 (OCO)
9b	108.42	81.04, 84.96	88.73	172.57	37.86	131.54	118.86	24.92, 26.12 (CH_3), 51.96, 55.36 (OCH_3), 112.52 (OCO)
12a	109.39	84.77, 85.17	92.15	169.40	41.50	131.74	118.31	24.56, 25.53 (CH_3), 51.76, 55.42 (OCH_3), 112.76 (OCO)
12b	107.37	80.00, 83.91	87.70	171.55	36.83	130.51	117.85	23.88, 25.09 (CH_3), 50.95, 54.34 (OCH_3), 111.49 (OCO)
16a	108.86	82.56, 84.46	93.52	168.51	52.99	136.89	117.94	11.02 (CH_3CH_2), 20.90 (CH_2), 24.06, 25.12 (CH_3), 50.87, 54.36 (OCH_3), 111.90 (OCO)
16b	109.86	83.36, 84.68	93.92	170.09	51.63	135.73	118.37	11.01 (CH_3CH_2), 21.83 (CH_2), 24.15, 25.29 (CH_3), 51.19, 55.04 (OCH_3), 112.36 (OCO)
22	107.80	82.13, 82.85	88.59	170.99	42.32	–[a]	119.03	52.15, 56.23 (OCH_3), 72.59, 73.83 (OCH_2), 127.64–137.88 (C-2', Ar)

[a] Not distinguishable from aromatic signals.

Table 5 ^{1}H NMR Data of Deoxy Pentofuranosiduronates **25–36**[a]

Product	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)											
	H-1	H-2	H-3a	H-3b	H-4	Others	$J_{1,2}$	$J_{2,3a}$	$J_{2,3b}$	$J_{3a,3b}$	$J_{3a,4}$	$J_{3b,4}$
25	5.31	5.47	5.96		–	2.01 ($OCOCH_3$), 3.49, 3.78 (OCH_3)	1.5	3.1		–	–	–
26a	4.90	5.03	2.24	2.41	4.69	2.01 ($OCOCH_3$), 3.36, 3.70 (OCH_3)	0	0	5.1	14.0	7.9	7.9
26b	5.02	4.96	2.12	2.62	4.60	1.96 ($OCOCH_3$), 3.32, 3.73 (OCH_3)	0	1.3	5.9	14.0	9.7	4.1
27	4.84	4.21	2.19	2.30	4.76	3.35 (OCH_3), 4.58 (H-1'), 5.19, 5.27 (H-3'), 5.81–5.91 (H-2')	0	0	4.6	13.7	8.4	8.4
28	4.93	3.74	2.17–2.30		4.69	3.29, 3.37 (OCH_3), 4.59 (H-1'), 5.19, 5.27 (H-3'), 5.81–5.91 (H-2')	0	0	4.6	–[a]	8.4	8.4
29	4.97	4.08	1.93	2.50	4.56	3.30 (OCH_3), 4.62 (H-1'), 5.21, 5.28 (H-3'), 5.82–5.90 (H-2')	0	0	5.1	14.0	2.3	10.0
30	5.02	4.56	2.15	2.42	3.69	3.23, 3.32 (OCH_3), 4.61 (H-1'), 5.18, 5.27 (H-3'), 5.81–5.91 (H-2')	0	4.6	9.2	13.2	1.8	5.4
31	5.54	5.76	5.94		–	2.13 ($OCOCH_3$), 3.52, 3.80 (OCH_3)	6.1	2.5		–	–	
32	5.09	4.90	2.31	2.67	4.56	2.10 ($OCOCH_3$), 3.47, 3.78 (OCH_3)	4.1	10.0	8.4	–	8.4	8.4
33	4.86	4.24	2.04	2.62	4.53	2.37 (OH), 3.53 (OCH_3), 4.66 (H-1'), 5.25–5.38 (H-3'), 5.88–5.98 (H-2')	4.4	8.4	8.4	12.5	8.7	8.4
34	4.95	3.87	2.19	2.63	4.56	3.42, 3.51 (OCH_3), 4.65 (H-1'), 5.25, 5.34 (H-3'), 5.88–5.98 (H-2')	4.1	10.2	8.1	12.5	8.7	8.4
35	4.91	4.06	2.26	2.62	4.54	3.40, 3.51 (COH_3), 4.63–4.72 (H-1', OCH_2O), 5.24–5.37 (H-3'), 5.88–5.98 (H-2')	4.1	12.2	8.1	11.7	8.6	8.6
36	4.81	3.95	2.24	2.53	4.49	3.48 (OCH_3), 4.60–4.64 (H-1', OCH_2), 5.25, 5.33 (H-3'), 5.87–5.96 (H-2'), 7.28–7.37 (Ar)	4.1	10.7	8.1	12.2	9.0	8.4

[a] Not identified due to overlapping signals.

Table 6 ^{13}C NMR Chemical Data of Deoxy Pentofuranosiduronates **25–36**

Product	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ					
	C-1	C-3	C-2	C-4	C-5	Others
25	106.90	108.92	79.43	150.56	159.05	19.78 (CH_3), 51.49, 55.91 (OCH_3), 168.93 (CO_2)
26a	107.74	33.62	76.78, 77.12		–[a]	21.33 (CH_3), 52.61, 55.23 (OCH_3), 170.51, 172.92 (CO_2)
26b	108.02	34.24	76.01, 76.71		–[a]	21.26 (CH_3), 55.78, 55.47 (OCH_3), 170.53, 172.36 (CO_2)
27	108.72	35.12	74.28, 75.27		171.26	53.79 (OCH_3), 64.67 (C-1'), 117.71 (C-3'), 130.72 (C-2')
28	106.02	32.23	75.68, 83.21		171.30	53.75, 55.98 (OCH_3), 64.62 (C-1'), 117.65 (C-3'), 130.76 (C-2')
29	110.58	36.16	74.69, 75.82		173.94	54.96 (OCH_3), 66.36 (C-1'), 119.41 (C-3'), 131.26 (C-2')
30	107.57	33.73	75.84, 83.62		171.58	55.07, 56.92 (OCH_3), 65.73 (C-1'), 118.61 (C-3'), 131.84 (C-2')
31	105.01	108.0	73.85	–[b]	–[b]	20.52 (CH_3), 52.54, 57.92 (OCH_3)
32	101.48	30.89	73.04, 73.88		–[a]	21.14 (CH_3), 52.66, 55.63 (OCH_3), 170.91, 172.60 (CO_2)
33	102.39	35.04	72.07, 74.64		171.84	55.33 (OCH_3), 65.73 (C-1'), 118.77 (C-3'), 131.72 (C-2')
34	101.40	31.29	74.21, 80.38		171.69	55.16, 58.14 (OCH_3), 65.73 (C-1'), 118.82 (C-3'), 131.72 (C-2')
35	102.01	31.67	73.87, 77.06		171.71	55.09, 55.78 (OCH_3), 65.72 (C-1'), 96.80 (OCH_2O), 118.78 (C-3'), 131.78 (C-2')
36	101.50	31.55	73.96, 77.88		171.71	55.10 (OCH_3), 65.71, 72.54 (C-1', OCH_2), 118.79 (C-3'), 126.99–137.51 (C-2', Ar)

[a] Not distinguishable from other carboxyl signals.
[b] Signals of quaternary carbon atoms of **31** not detected.

Table 7 ^1H NMR Data of *C*-Branched Deoxy Pentofuranosiduronates **38–41**

Product[a]	^1H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)											
	H-1	H-2	H-3a	H-3b	H-1'	H-2'	H-3'	Others	$J_{1,2}$	$J_{2,3a}$	$J_{2,3b}$	$J_{3a,3b}$
38	4.94	3.66	1.92	2.50	2.43, 2.57	5.67–5.77	5.04	3.20, 3.29, 3.34 (6 H), 3.67, 3.68 (OCH_3)	0	1.5,	0,	13.7
	4.95	3.73	2.00	2.51–2.65	2.51–2.65		5.06			4.6	6.1	
39	4.88	3.73	1.99, 2.24, 2.35 (2 H), 2.58 (4 H)			5.64–5.73	5.03–5.11	3.31, 3.33, 3.40, 3.41, 3.67, 3.68 (OCH_3)	4.1	–[b]	–[b]	–[b]
	4.94	3.83										
40	4.92	3.99	2.15	2.32	2.40–2.70	5.70–5.83	5.11–5.18	3.39 (6 H), 3.47, 3.48, 3.75 (6 H, OCH_3), 4.64–4.71 (OCH_2O)	4.1,	8.6,	8.4,	12.7
	4.97	4.11	2.40–2.70	2.40–2.70					4.4	11.2	9.7	
41	4.81	3.89	2.14	2.37	2.49, 2.61	5.65–5.80	5.11	3.43, 3.44, 3.72, 3.73 (OCH_3), 4.53–4.60 (OCH_2), 7.26–7.37 (Ar)	4.0,	8.4,	7.8,	12.6,
	4.87	4.01	2.22	2.16	2.61				4.3	11.0	9.8	13.1

[a] Data given for a 1:1 mixture of C-4 diastereoisomers.
[b] Not resolved.

Allyl (Methyl 2,3-*O*-isopropylidene-β-D-ribofuranosid)uronate (10)

Prepared according to General Procedure B, from methyl 2,3-*O*-isopropylidene-β-D-ribofuranosiduronic acid[10b] (654 mg, 3 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 679 mg (88%); colourless syrup; $[\alpha]_D^{20}$ –47.6 (*c* = 1, $CHCl_3$).

Anal. $C_{12}H_{18}O_6$ (258.3): calc. C 55.81, H 7.03; found C 55.52, H 6.91.

Methyl (Methyl 2,3-*O*-isopropylidene-4-*C*-(prop-2-enyl)-β-L-lyxofuranosid)uronate (12a) and Methyl (Methyl 2,3-*O*-isopropylidene-4-*C*-(prop-2-enyl)-β-D-ribofuranosid)uronate (12b)

Prepared according to General Procedure A, from **10** (129 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (10:1).

12a; yield: 48 mg (35%); colourless crystals; mp 67 °C (petroleum ether); $[\alpha]_D^{20}$ +12.1 (*c* = 0.5, $CHCl_3$).

Anal. $C_{13}H_{20}O_6$ (272.3): calc. C 57.35, H 7.40; found C 57.31, H 7.51.

12b; yield: 13 mg (10%); yellow syrup; $[\alpha]_D^{20}$ –0.9 (*c* = 0.1, $CHCl_3$).

***cis*-Pent-2-enyl (Methyl 2,3-*O*-isopropylidene-α-D-lyxofuranosid)uronate (13)**

Prepared according to General Procedure B, from methyl 2,3-*O*-isopropylidene-α-D-lyxofuranosiduronic acid[10a] (397 mg, 1.82 mmol); flash chromatography: petroleum ether/EtOAc (10:1); yield: 430 mg (83%); colourless oil; $[\alpha]_D^{20}$ +16.5 (*c* = 1.5, $CHCl_3$).

Anal. $C_{14}H_{22}O_6$ (286.3): calc. C 58.73, H 7.75; found C 58.90, H 7.66.

Methyl {Methyl 2,3-*O*-isopropylidene-4-*C*-[(1*R*)-1-ethylprop-2-enyl]-α-D-lyxofuranosid}uronate (16a) and Methyl {Methyl 2,3-*O*-isopropylidene-4-*C*-[(1*S*)-1-ethylprop-2-enyl]-α-D-lyxofuranosid}uronate (16b)

Prepared according to General Procedure A, from **13** (1.46 g, 5 mmol); flash chromatography: petroleum ether/EtOAc (10:1).

16a; yield: 298 mg (20%); colourless crystals; mp 65 °C (EtOH); $[\alpha]_D^{20}$ +4.6 (*c* = 1, $CHCl_3$).

Anal. $C_{15}H_{24}O_6$ (300.4): calc. C 59.98, H 8.05; found C 60.07; H 8.07.

16b; yield: 57 mg (4%); yellow syrup; $[\alpha]_D^{20}$ +7.5 (*c* = 1, $CHCl_3$).

Table 8 ^{13}C NMR Chemical Data of *C*-Branched Deoxy Pentofuranosiduronates **38–41**

Product[a]	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ								
	C-1	C-2	C-3	C-4	C-5	C-1'	C-2'	C-3'	Others
38	106.52	83.04	36.31	85.56	173.12	42.87	131.31	117.63	51.10, 51.37, 53.87, 53.93, 55.53, 56.00 (OCH_3)
	106.68	83.89	36.43	86.23	173.24	43.10	131.39	117.76	
39	100.89	78.78	34.10	82.72	172.44	42.40	130.57	118.02	51.24, 51.51, 54.10, 54.21, 56.94, 57.06 (OCH_3)
	101.31	79.04	35.59	83.72	173.16	43.30	131.09	118.60	
40	102.53	76.47	35.42	83.33	173.43	43.38	131.54	119.03	52.26, 52.55, 55.06, 55.18, 55.78 (OCH_3), 96.77
	103.03	76.85	37.11	84.36	174.24	44.37	132.16	119.68	96.82 (OCH_2O)
41	102.03	78.03	35.38	83.47	173.45	43.42	–[b]	118.98	52.24, 52.49, 55.06, 55.18 (OCH_3), 72.49, 72.58
	102.49	78.05	36.98	84.46	174.22	44.42		119.54	(OCH_2), 126.98–137.54 (C-2', Ar)

[a] Data given for a 1:1 mixture of C-4 diastereoisomers.
[b] Not distinguishable from aromatic signals.

Methyl (Methyl α-D-lyxofuranosid)uronate (18)
A solution of methyl (methyl 2,3-*O*-isopropylidene-α-D-lyxofuranosid)uronate (**17**;[14] 1.42 g, 6.1 mmol) in anhyd MeOH (130 mL) containing ion exchange resin Amberlite IR 120 H^+ was heated under reflux overnight. The mixture was filtered, the filtrate was evaporated in vacuo, and the residue was purified by flash chromatography (petroleum ether/EtOAc, 1:1) to yield 820 mg (70%) **18** as a colourless amorphous solid; $[\alpha]_D^{20}$ +50.1 (*c* = 0.7, $CHCl_3$).

Anal. $C_7H_{12}O_6$ (192.2): calc. C 43.75, H 6.29; found C 43.62, H 6.58.

Allyl (Methyl α-D-lyxofuranosid)uronate (19)
Prepared according to General Procedure C, from **18** (820 mg, 4.3 mmol); flash chromatography: petroleum ether/EtOAc (1:1); yield: 756 mg (81%); colourless syrup; $[\alpha]_D^{20}$ +101.4 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{14}O_6$ (218.2): calc. C 49.54, H 6.47; found C 49.03, H 6.66.

Allyl (Methyl 2,3-di-*O*-benzoyl-α-D-lyxofuranosid)uronate (20)
To a solution of **19** (179 mg, 0.8 mmol) in anhyd pyridine and CH_2Cl_2 (8 mL each) was added benzoyl chloride (0.24 ml, 2 mmol) at 0 °C. The mixture was allowed to warm up to r.t. and stirred until conversion was complete (TLC monitoring: petroleum ether/EtOAc, 5:1). The solvents were evaporated by codistillation with toluene in vacuo and the residue was purified by flash chromatography (petroleum ether/EtOAc 15:1) to yield 284 mg (81%) **20** as a colourless syrup; $[\alpha]_D^{20}$ +12.0 (*c* = 1, $CHCl_3$).

Anal. $C_{23}H_{22}O_8$ (426.4): calc. C 64.78, H 5.20; found C 64.53, H 5.22.

Allyl (Methyl 2,3-di-*O*-benzyl-α-D-lyxofuranosid)uronate (21)
To a solution of **19** (153 mg, 0.7 mmol) in anhyd dioxane (14 mL) was added benzyl trichloroacetimidate (1 mL, 5.4 mmol) and trimethylsilyl trifluoromethanesulfonate (1 drop) at 10°C. The mixture was allowed to warm up to r.t. and upon completion of conversion (TLC monitoring: petroleum ether/EtOAc, 5:1) was stirred with pyridine (3 mL) for a few min. The solution was diluted with EtOAc (30 mL), washed with H_2O (2 × 40 mL), dried ($MgSO_4$), and evaporated in vacuo. The residue after purification by flash chromatography (petroleum ether/EtOAc, 10:1) yielded 180 mg (64%) **21** as a colourless amorphous solid; $[\alpha]_D^{20}$ +17.5 (*c* = 1, $CHCl_3$).

Anal. $C_{23}H_{26}O_6$ (398.5): calc. C 69.33, H 6.58; found C 69.48, H 6.30.

Methyl (Methyl 2,3-di-*O*-benzyl-4-*C*-(2-propenyl)-α-D-lyxofuranosid)uronate (22)
Prepared according to General Procedure A, from **21** (178 mg, 0.45 mmol); flash chromatography: petroleum ether/EtOAc (10:1); yield: 11 mg (6%) **22**; yellow syrup; $[\alpha]_D^{20}$ +3.2 (*c* = 0.5, $CHCl_3$).

Methyl (Methyl 2,3-di-*O*-acetyl-α-D-arabinofuranosid)uronate (24a) and Methyl (Methyl 2,3-di-*O*-acetyl-β-D-arabinofuranosid)uronate (24b)
D-Glucuronolactone **23** (3.52 g, 20 mmol) was added to a solution of $Pb(OAc)_4$ (12.6 g, 28.4 mmol) in AcOH (350 mL) at r.t. and stirred for 2 h. The resulting clear solution was treated with a solution of oxalic acid in HOAc (10% m/v, 30 mL) for 0.5 h, filtered, and the filtrate was coevaporated with toluene in vacuo. The residue was taken up in H_2O (50 mL), stirred with ion exchange resin Amberlite IR 120 H^+ for a few min, filtered, and the filtrate was again codistilled with toluene in vacuo. A solution of the residual solid in anhyd MeOH (50 mL) containing Amberlite IR 120 H^+ was heated under reflux overnight. After removal of the ion exchange resin by filtration, the filtrate was concentrated in vacuo, the residue was dissolved in pyridine (100 mL) and Ac_2O (50 mL), and stirred under warming from 0 °C to r.t. overnight. Coevaporation with toluene in vacuo and flash chromatography (petroleum ether/Et_2O, 2:1) of the remaining crude product yielded the separated anomeric glycosides **24a** and **24 b**.

24a; yield: 1.53 g (28%); viscous oil; $[\alpha]_D^{20}$ +56.0 (*c* = 1, $CHCl_3$).

Anal. $C_{11}H_{16}O_8$ (276.2): calc. C 47.83, H 5.84; found C 47.87, H 5.92.

24b; yield: 752 mg (14%); amorphous solid; $[\alpha]_D^{20}$ –73.7 (*c* = 1, $CHCl_3$).

Anal. $C_{11}H_{16}O_8$ (276.2): calc. C 47.83, H 5.84; found C 48.34, H 6.22.

Methyl (Methyl 2-*O*-acetyl-3-deoxy-β-L-glycero-pent-3-enofuranosid)uronate (25)
Prepared according to General Procedure D, from **24a** (3.33 g, 12.1 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 1.94 g (74%); colourless syrup;$[\alpha]_D^{20}$ +107.0 (*c* = 0.5, $CHCl_3$).

Anal. $C_9H_{12}O_6$ (216.2): calc. C 47.79, H 5.35; found C 47.31, H 5.28.

Methyl (Methyl 2-*O*-acetyl-3-deoxy-β-L-erythro-pentofuranosid)uronate (26a) and Methyl (Methyl 2-*O*-acetyl-3-deoxy-α-D-threo-pentofuranosid)uronate (26b)
Prepared according to General Procedure E, from **25** (1.94 g, 9.0 mmol); flash chromatography: petroleum ether/EtOAc (10:1).

Table 9 ^{1}H NMR Data of Hexopyranosiduronates **44–48** and **50–53**

Product	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)																
	H-1	H-2	H-3	H-4$_{eq}$	H-4$_{ax}$	H-5	H-1'	H-2'	H-3'	Others	$J_{1,2}$	$J_{2,3}$	$J_{3,4eq}$	$J_{3,4ax}$	$J_{4eq,4ax}$	$J_{4eq,5}$	$J_{4ax,5}$
44[a]	4.91		4.14, 4.47 (2 H)		–	4.00	4.72, 4.84	5.89–5.99	5.30, 5.40	3.33 (3 OH), 3.36 (OCH_3)	–	–	–	–	–	–	–
45	4.83	3.61	3.72/3.80	–	3.72/3.80	4.13	4.72	5.90–6.00	5.26–5.39	3.46 (OCH_3), 3.93 (3 OH)	3.6	9.7	–	9.2	–	4.1	9.7
46	4.90	3.69	3.82	4.24	–	3.96	4.64–4.75	5.89–5.99	5.25, 5.36	3.36, 3.40, 3.42, 3.52 (OCH_3)	0.5	2.8	6.6	–	–	–	–
47	4.86	3.26	3.38/3.52	–	3.38/3.52	4.07	4.71	5.90–6.00	5.27–5.40	3.45, 3.50, 3.52, 3.62 (OCH_3)	3.5	9.5	–	9.1	–	–	9.8
48	4.85	4.10	3.85	3.57	–	–	2.60, 2.76	5.81	5.04–5.13	3.31 (6 H), 3.32, 3.39, 3.66 (OCH_3)	0	6.4	1.5	–	–	–	–
50	4.31	4.85	4.96	1.77	2.39	4.08	–	–	–	1.96, 1.99 ($OCOCH_3$), 3.46, 3.72 (OCH_3)	7.6	9.2	0	5.1	12.5	0	2.0
51	4.60	3.24	3.67	1.66	2.24	4.60	4.02–4.10	5.80–5.90	5.18–5.30	3.49 (OCH_3)	7.6	8.6	0	2.0	11.7	0	4.6
52	4.12	2.92	3.24	1.55	2.34	3.95	4.61	5.81–5.89	5.20, 5.26	3.38, 3.49, 3.51 (OCH_3)	7.4	8.7	5.4	11.5	13.9	2.3	12.2
53	4.55	3.10	3.43	2.18	1.98	–	2.51–2.64	5.68–5.78	5.11–5.15	3.41, 3.48, 3.50, 3.74 (OCH_3)	4.6	7.1	4.6	11.2	13.7	–	–

[a] Coupling constants of **44** were insufficiently resolved.

Table 10 ^{13}C NMR Chemical Data of Hexopyranosiduronates **44–48** and **50–53**

Product	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ									
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	Others
44	109.68	78.05, 79.98, 87.00			70.22	171.70	66.79	131.12	118.96	55.03 (OCH_3)
45	99.93	70.75, 71.49, 71.58, 73.56				169.86	66.30	131.40	119.12	55.85 (OCH_3)
46	106.72	79.91, 81.39, 84.59, 89.48				169.54	65.77	131.71	118.74	54.89, 57.55, 58.12, 59.95 (OCH_3)
47	98.52	70.52, 81.68, 83.37				169.80	66.47	131.84	119.34	56.04, 59.60, 60.94, 61.40 (OCH_3)
48	105.73	83.52, 83.94, 87.87			81.10	170.41	35.21	131.57	117.54	51.07, 51.87, 53.77, 56.17, 56.86 (OCH_3)
50	101.02	69.34, 70.91		31.93	69.34	–[a]	–	–	–	19.78, 19.85 (CH_3), 51.40, 56.03 (OCH_3), 168.19, 168.61, 169.25 (CO_2)
51	102.77	69.47, 69.86		34.00	74.58	168.06	64.91	130.44	117.97	56.39 (OCH_3)
52	104.56	79.74, 83.36		32.88	70.54	169.34	65.89	131.53	118.96	57.12, 57.54, 60.66 (OCH_3)
53	101.04	75.72, 82.96		31.06	76.32	172.20	39.96	130.67	118.02	51.20, 55.84, 56.13, 58.02 (OCH_3)

[a] Not distinguishable from other carboxyl signals.

26a; yield: 961 mg (49%), colourless syrup; $[\alpha]_D^{20}$ +77.8 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{18}O_6$ (218.2): calc. C 49.54, H 6.47; found C 49.21, H 6.55.

26b; yield: 561 mg (29%); colourless syrup; $[\alpha]_D^{20}$ +54.5 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{18}O_6$ (218.2): calc. C 49.54, H 6.47; found C 49.40, H 6.46.

Allyl (Methyl 3-deoxy-β-L-erythro-pentofuranosid)uronate (27)
Prepared according to General Procedure C, from **26a** (1.05 g, 4.8 mmol); flash chromatography: petroleum ether/EtOAc (2:1); yield: 715 mg (74%); colourless syrup; $[\alpha]_{578}$ +96.5 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{14}O_5$ (202.2): calc. C 53.46, H 6.98; found C 53.21, H 6.98.

Allyl (Methyl 3-deoxy-2-*O*-methyl-β-L-erythro-pentofuranosid)uronate (28)
Prepared according to General Procedure F, from **27** (182 mg, 0.9 mmol); flash chromatography: petroleum ether/EtOAc (3:1); yield: 133 mg (69%); colourless oil; $[\alpha]_{578}^{20}$ +13.5 (*c* = 0.2, $CHCl_3$).

Anal. $C_{10}H_{16}O_5$ (216.2): calc. C 55.55, H 7.46; found C 55.22, H 7.41.

Allyl (Methyl 3-deoxy-α-D-threo-pentofuranosid)uronate (29)
Prepared according to the General Procedure C, from **26b** (200 mg, 0.9 mmol); flash chromatography: petroleum ether/EtOAc/MeOH (10:10:1); yield: 127 mg (68%); colourless syrup; $[\alpha]_D^{20}$ +94.9 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{14}O_5$ (202.2): calc. C 53.46, H 6.98; found C 53.23, H 6.93.

Allyl (Methyl 3-deoxy-2-*O*-methyl-α-D-threo-pentofuranosid)uronate (30)
Prepared according to General Procedure F, from **29** (202 mg, 1.1 mmol); flash chromatography: petroleum ether/EtOAc (3:1); yield: 121 mg (51%); colourless syrup; $[\alpha]_D^{20}$ +53.0 (*c* = 1, $CHCl_3$).

Anal. $C_{10}H_{16}O_5$ (216.2): calc. C 55.55, H 7.46; found C 55.43, H 7.40.

Methyl (Methyl 2-*O*-acetyl-3-deoxy-α-L-glycero-pent-3-enofuranosid)uronate (31)
Prepared according to General Procedure D, from **24b** (2.06 g, 7.5 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 1.08 g (65%) **31**; colourless syrup; $[\alpha]_D^{20}$ –120.0 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{12}O_6$ (216.2): calc. C 47.79, H 5.35; found C 47.52, H 5.33.

Methyl (Methyl 2-*O*-acetyl-3-deoxy-β-D-threo-pentofuranosid)uronate (32)
Prepared according to General Procedure E, from **31** (1.08 g, 5 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 899 mg (83%); colourless syrup;$[\alpha]_D^{20}$ –145.0 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{14}O_6$ (218.2): calc. C 49.54, H 6.47; found C 49.60, H 6.57.

Allyl (Methyl 3-deoxy-β-D-threo-pentofuranosid)uronate (33)
Prepared according to General Procedure C, from **32** (899 mg, 4.1 mmol); flash chromatography: petroleum ether/EtOAc/MeOH (10:10:1); yield: 770 mg (92%); colourless syrup; $[\alpha]_D^{20}$ –129.4 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{14}O_5$ (202.2): calc. C 53.46, H 6.98; found C 52.94, H 7.27.

Allyl (Methyl 3-deoxy-2-*O*-methyl-β-D-threo-pentofuranosid)uronate (34)
Prepared according to General Procedure F, from **33** (162 mg, 0.8 mmol); flash chromatography: petroleum ether/EtOAc (3:1); yield: 124 mg (72%); colourless syrup; $[\alpha]_D^{20}$ –224.0 (*c* = 1, $CHCl_3$).

Anal. $C_{10}H_{16}O_5$ (216.2): calc. C 55.55, H 7.46; found C 55.27, H 7.70.

Allyl (Methyl 3-deoxy-2-*O*-methoxymethyl-β-D-*threo*-pentofuranosid)uronate (35)
A solution of **33** (162 mg, 0.8 mmol) in dimethoxymethane (8 mL) containing P_4O_{10} (170 mg, 1.2 mmol) and $BF_3 \cdot OEt_2$ (2 drops) was stirred at r.t. overnight. The mixture was diluted with EtOAc

Table 11 ^{1}H NMR Data of 2,6-Anhydrohexonates **55–60**

Product	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, J (Hz)																			
	H-2	H-3$_{ex}$	H-3$_{aq}$	H-4	H-5	H-6$_{eq}$	H-6$_{ax}$	H-1'	H-2'	H-3'	Others	$J_{2,3ax}$	$J_{2,3eq}$	$J_{3ax,3eq}$	$J_{3ax,4}$	$J_{3eq,4}$	$J_{4,5}$	$J_{5,6ax}$	$J_{5,6eq}$	$J_{6ax,6eq}$
55	–	6.08		5.07	4.92	3.98	4.34	–	–	–	2.01, 2.02 ($OCOCH_3$), 3.77 (OCH_3)	–	–	–	5.1		2.0	3.1	1.5	12.2
56a	4.07	1.81	2.43	4.95	4.85	4.18	3.31	–	–	–	1.98, 1.99 ($OCOCH_3$), 3.71 (OCH_3)	10.2	3.1	13.2	10.2	5.1	8.7	8.7	5.1	11.7
56b	4.31	2.07	2.16	5.07	4.69	4.07	3.89	–	–	–	2.11, 2.13 ($OCOCH_3$), 3.80 (OCH_3)	11.0	3.0	11.2	6.9	3.2	2.9	2.2	0	13.0
57	3.99	1.64	2.31	3.61	3.52	4.07	3.16	4.61	5.81–5.90	5.19–5.30	–	11.7	2.5	13.0	11.0	5.1	8.4	9.7	4.6	11.5
58	4.04	1.67	2.44	3.20–3.35			4.22	4.67	5.88–5.98	5.27–5.35	3.44, 3.48 (OCH_3)	10.5	3.4	13.2	10.2	4.4	–[a]	9.0	–[a]	15.7
59	4.32	2.16	2.72	5.47	5.21–5.36	3.65	4.50–4.66		5.81–5.91	5.21–5.36	7.43, 7.54, 7.98 (Ar)	9.7	3.6	13.2	9.7	4.6	–[b]	–[a]	2.1	11.7
60a	–	1.83	2.28–2.39	3.43	3.06	3.76	4.09	2.28–2.39	5.72–5.77	4.96–5.02	3.24, 3.35, 3.65 (OCH_3)	–	–	14.2	2.7	0	0	1.6	0	12.9
60b	–	1.25–1.33	2.57	3.11–3.17			3.94	2.38	5.63–5.70	4.99–5.05	3.38, 3.39, 3.69 (OCH_3)	–	–	13.2	–[b]	4.1	–[a]	3.7	–[a]	10.9

[a] Not identified due to overlapping signals.
[b] Not resolved

Table 12. ^{13}C NMR Chemical Data of 2,6-Anhydrohexonates **55–60**

Product	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ									
	C-1	C-3	C-2	C-4	C-5	C-6	C-1'	C-2'	C-3'	Others
55	161.24	103.91	145.71	62.39, 65.43		63.76	–	–	–	19.83, 19.88 (CH_3), 51.61 (OCH_3), 168.41, 168.71 (CO_2)
56a	–[a]	32.11	68.71, 69.97, 73.51			66.11	–	–	–	20.83, 20.93 (CH_3), 52.46 (OCH_3), 169.93, 170.07, 170.11 (CO_2)
56b	–[a]	29.76	67.00, 71.57, 76.72			66.15	–	–	–	21.06, 21.41 (CH_3), 52.80 (OCH_3), 169.69, 170.29, 171.33 (CO_2)
57	170.10	35.53	71.24, 72.50, 74.82			69.41, 66.05		131.36	119.27	–
58	170.24	31.86	74.03, 78.47, 79.44			65.88, 66.59		131.57	119.11	57.08, 58.50 (OCH_3)
59	–[a]	32.01	69.19, 70.23, 73.28			65.99, 66.07		–[b]	119.31	128.47–133.62 (C-2', Ar), 165.55, 165.59, 169.52 (CO_2)
60a	172.64	30.23	75.76	72.60, 74.09		60.50	43.81	131.08	117.39	50.68, 55.55, 55.98 (OCH_3)
60b	172.80	34.99	79.86	77.87, 78.35		63.93	43.41	130.40	118.15	51.23, 56.21, 57.56 (OCH_3)

[a] Not distinguishable from other carboxyl signals.
[b] Not distinguishable from aromatic signals.

(20 mL), washed with satd aq $NaHCO_3$ solution (50 mL), and dried ($MgSO_4$). After evaporation in vacuo, the crude product was purified by flash chromatography (petroleum ether/EtOAc, 4:1) to afford **35** (89 mg, 45%); colourless syrup; $[\alpha]_D^{20}$ –78.7 (c = 1, $CHCl_3$); and its α-anomer (35 mg, 17%), which was not fully characterized.

Anal. $C_{11}H_{18}O_6$ (246.3): calc. C 53.65, H 7.37; found C 53.46, H 7.45.

Allyl (Methyl 2-*O*-benzyl-3-deoxy-β-D-threo-pentofuranosid)uronate (36)
Prepared from **33** in analogy to **21** (340 mg, 1.7 mmol); flash chromatography: petroleum ether/EtOAc (10:1); yield: 263 mg (54%) **36**; colourless syrup; $[\alpha]_D^{20}$ –58.2 (c = 1, $CHCl_3$).

Anal. $C_{16}H_{20}O_5$ (292.3): calc. C 65.75, H 6.90; found C 65.60, H 6.79.

Allyl (Methyl 3-deoxy-2-*O*-methyl-4-*C*-(methyl 3-deoxy-2-*O*-methyl-β-L-*erythro*-pentodialdofuranosid-5-yl)-β-L-*erythro*- or -α-D-*threo*-pentofuranosid)uronate (37)
A solution of diisopropylamine (100 μL, 0.8 mmol) in anhyd THF (2 mL) and HMPA (0.5 mL) under argon was mixed with a 1.6 M solution of BuLi in hexane (0.5 mL) and stirred for 10 min at r.t. A solution of **28** (108 mg, 0.5 mmol) in THF (1 mL) and HMPA (0.25 mL) was added dropwise at –78 °C. After stirring for 10 min at –78 °C, chlorotrimethylsilane (125 μL, 1 mmol) was added, and the mixture was allowed to warm up to r.t. and stirred for another 2 h. Following the addition of a 1 M solution of TBAF in THF (1.2 mL) and further stirring at r.t. for 1 h, the mixture was diluted with Et_2O (20 mL) and washed with 1 M NaOH (20 mL). The ethereal layer was dried ($MgSO_4$) and evaporated in vacuo. Purification of the remaining crude product by flash chromatography (petroleum ether/EtOAc, 5:1) yielded **37** (34 mg, 36%) as a yellow syrup.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.13 (m, 1 H, H-3), 2.50 (m, 1 H, H-3), 2.59 (m, 1 H, H-3), 2.72 (m, 1 H, H-3), 3.25, 3.38, 3.39, 3.46 (4 s, 4 × 3 H, 4 OMe), 3.76 (m, 2 H, 2 H-2), 4.59–4.70 (m, 2 H, H-1'), 4.93, 5.05 (2 s, 2 × 1 H, 2 H-1), 5.22–5.35 (m, 2 H, H-3'), 5.30 (s, 1 H, H-4), 5.89–5.91 (m, 1 H, H-2').

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.92, 37.95 (C-3), 55.19, 55.39, 56.99, 57.42 (OCH_3), 66.80 (C-1'), 81.26 (C-4), 83.70, 84.66 (C-2), 91.17 (C-4 quart.), 107.19, 108.97 (C-1), 119.13 (C-3'), 131.65 (C-2'), 171.30, 205.53 (C-5).

Due to its apparent instability, the compound could not be obtained spectroscopically pure, and no other physical data were collected. Efforts of further purification resulted in decomposition.

Methyl (Methyl 3-deoxy-2-*O*-methyl-4-*C*-(prop-2-enyl)-α-D-threo- and -β-L-erythro-pentofuranosid)uronate (38)
Prepared according to General Procedure A, from **28** and **30**, respectively (108 mg, 0.5 mmol each); flash chromatography: petroleum ether/EtOAc (5:1); yield: 52 mg (45%) **38** from **28**; 45 mg (39%) **38** from **30**; yellow syrup; 1:1 mixture of C-4 diastereomers.

Methyl (Methyl 3-deoxy-2-*O*-methyl-4-*C*-(prop-2-enyl)-β-D-threo- and -α-L-erythro-pentofuranosid)uronate (39)
Prepared according to General Procedure A, from **34** (106 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 62 mg (54%); yellow syrup; 1:1 mixture of C-4 diastereomers.

Methyl (Methyl 3-deoxy-2-*O*-methoxymethyl-4-*C*-(prop-2-enyl)-β-D-threo- and -α-L-erythro-pentofuranosid)uronate (40)
Prepared according to General Procedure A, from **35** (75 mg, 0.3 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 30 mg (38%); yellow syrup; 1:1 mixture of C-4 diastereomers.

Methyl (Methyl 2-*O*-benzyl-3-deoxy-4-*C*-(prop-2-enyl)-β-D-threo- and -α-L-erythro-pentofuranosid)uronate (41)
Prepared according to General Procedure A, from **36** (150 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 40 mg (26%); yellow syrup; 1:1 mixture of C-4 diastereomers.

Allyl (Methyl α-D-galactopyranosid)uronate (44)
Prepared according to General Procedure C, from **42**[17] (2.14 g, 9.6 mmol); flash chromatography: petroleum ether/EtOAc/MeOH (10:10:1); yield: 1.82 g (71%); colourless syrup; $[\alpha]_D^{20}$ –102.1 (c = 1, $CHCl_3$).

Anal. $C_{10}H_{16}O_7$ (248.2): calc. C 48.39, H 6.50; found C 48.80, H 6.68.

Allyl (Methyl α-D-glucopyranosid)uronate (45)
Prepared according to General Procedure C, from **43**[18] (1.35 g, 6 mmol); flash chromatography: petroleum ether/EtOAc (3:1); yield: 1.37 g (92%) **45**; colourless crystals; mp 60 °C (EtOAc/petroleum ether); $[\alpha]_D^{20}$ +25.5 (*c* = 0.3, $CHCl_3$).

Anal. $C_{10}H_{16}O_7$ (248.2): calc. C 48.39, H 6.50; found C 48.06, H 6.49.

Allyl (Methyl 2,3,4-tri-*O*-methyl-α-D-galactopyranosid)uronate (46)
Prepared according to General Procedure F, from **44** (500 mg, 2 mmol); flash chromatography: petroleum ether/EtOAc (4:1); yield: 414 mg (71%); slightly yellow syrup; $[\alpha]_D^{20}$ –118.5 (*c* = 1, $CHCl_3$).

Anal. $C_{13}H_{22}O_7$ (290.3): calc. C 53.79, H 7.64; found C 53.41, H 7.63.

Allyl (Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranosid)uronate (47)
Prepared according to General Procedure F, from **45** (248 mg, 1 mmol); flash chromatography: petroleum ether/EtOAc (10:1 to 8:1); yield: 200 mg (69%); colourless syrup; $[\alpha]_D^{20}$ +51.7 (*c* = 0.5, $CHCl_3$).

Anal. $C_{13}H_{22}O_7$ (290.3): calc. C 53.79, H 7.64; found C 53.35, H 7.61.

Methyl (Methyl 2,3,4-tri-*O*-methyl-5-*C*-(prop-2-enyl)-α-D-galactopyranosid)uronate (48)
Prepared according to General Procedure A, from **46** (169 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (10:1); yield: 13 mg (7%) **48**; yellow syrup; $[\alpha]_{578}^{20}$ –45.8 (*c* = 1, $CHCl_3$).

Methyl (Methyl 2,3-di-*O*-acetyl-4-deoxy-β-D-xylo-hexopyranosid)uronate (50)
Prepared according to General Procedure E, from **49**[19] (1.09 g, 3.8 mmol); flash chromatography: petroleum ether/EtOAc (4:1 to 2:1); yield: 843 mg (77%); colourless syrup; $[\alpha]_D^{20}$ –14.3 (*c* = 0.5, $CHCl_3$).

Anal. $C_{12}H_{20}O_6$ (260.3): calc. C 55.37, H 7.75; found C 55.03, H 7.69.

Allyl (Methyl 4-deoxy-β-D-xylo-hexopyranosid)uronate (51)
Prepared according to General Procedure C, from **50** (1.19 g, 4.1 mmol); flash chromatography: petroleum ether/EtOAc/MeOH (10:10:1); yield: 485 mg (51%); colourless syrup; $[\alpha]_D^{20}$ –76.3 (*c* = 1, $CHCl_3$).

Anal. $C_{10}H_{16}O_6$ (232.2): calc. C 51.72, H 6.94; found C 51.51, H 7.03.

Allyl (Methyl 4-deoxy-2,3-di-*O*-methyl-β-D-xylo-hexopyranosid)uronate (52)
Prepared according to General Procedure F, from **51** (142 mg, 0.6 mmol); flash chromatography: petroleum ether/EtOAc (4:1); yield: 106 mg (67%); colourless syrup; $[\alpha]_D^{20}$ –36.1 (*c* = 1, $CHCl_3$).

Anal. $C_{12}H_{20}O_6$ (260.3): calc. C 55.37, H 7.75; found C 55.29, H 7.81.

Methyl (Methyl 4-deoxy-2,3-di-*O*-methyl-5-*C*-(prop-2-enyl)-β-D-xylo-hexopyranosid)uronate (53)
Prepared according to General Procedure A, from **52** (89 mg, 0.34 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 10 mg (11%); yellow syrup; $[\alpha]_{578}^{20}$ –13.3 (*c* = 0.5, $CHCl_3$).

Methyl 4,5-Di-*O*-acetyl-2,6-anhydro-3-deoxy-L-threo-hex-2-enonate (55)
Prepared according to General Procedure D, from **54**[20] (4.05 g, 12.7 mmol); flash chromatography: petroleum ether/EtOAc (2:1); yield: 3.08 g (94%); colourless syrup; $[\alpha]_D^{20}$ +225.5 (*c* = 1, $CHCl_3$).

Anal. $C_{11}H_{14}O_7$ (258.2): calc. C 51.16, H 5.46; found C 50.65, H 5.58.

Methyl 4,5-Di-*O*-acetyl-2,6-anhydro-3-deoxy-L-xylo-hexonate (56a) and Methyl 4,5-Di-*O*-acetyl-2,6-anhydro-3-deoxy-L-lyxo-hexonate (56b)
Prepared according to General Procedure E, from **55** (2.69 g, 10.4 mmol); flash chromatography: petroleum ether/EtOAc (5:1).

56a; yield: 1.87 g (69%); colourless syrup; $[\alpha]_D^{20}$ +57.2 (*c* = 1, $CHCl_3$).

Anal. $C_{11}H_{16}O_7$ (260.2): calc. C 50.77, H 6.20; found C 50.77, H 6.40.

56b; yield: 622 mg (23%); colourless crystals; mp 107–108 °C (EtOH); $[\alpha]_D^{20}$ +57.5 (*c* = 1, $CHCl_3$).

Anal. $C_{11}H_{16}O_7$ (260.2): calc. C 50.77, H 6.20; found C 50.82, H 6.27.

Allyl 2,6-Anhydro-3-deoxy-L-xylo-hexonate (57)
Prepared according to General Procedure C, from **56a** (2.60 g, 10 mmol); flash chromatography: petroleum ether/EtOAc/MeOH (10:10:1); yield: 1.72 g (85%); colourless syrup; $[\alpha]_D^{20}$ –4.0 (*c* = 1, $CHCl_3$).

Anal. $C_9H_{14}O_5$ (202.2): calc. C 53.46, H 7.88; found C 53.30, H 7.79.

Allyl 2,6-Anhydro-3-deoxy-4,5-di-*O*-methyl-L-xylo-hexonate (58)
Prepared according to General Procedure F, from **57** (263 mg, 1.3 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 156 mg (52%); colourless syrup; $[\alpha]_D^{20}$ +44.1 (*c* = 1, $CHCl_3$).

Anal. $C_{11}H_{18}O_5$ (230.3): calc. C 57.38, H 7.88; found C 57.38, H 7.81.

Allyl 2,6-Anhydro-4,5-di-*O*-benzoyl-3-deoxy-L-*xylo*-hexonate (59)
Prepared in analogy to **20** from **57** (404 mg, 2 mmol); flash chromatography: petroleum ether/EtOAc (5:1); yield: 501 mg (61%); colourless syrup; $[\alpha]_D^{20}$ +103.0 (*c* = 1, $CHCl_3$).

Anal. $C_{23}H_{22}O_7$ (410.4): calc. C 67.31, H 5.40; found C 66.94, H 5.47.

Methyl 2,6-Anhydro-3-deoxy-4,5-di-*O*-methyl-2-C-(2-propenyl)-L-xylo- and -lyxo-hexonate (60a and 60b):
Prepared according to General Procedure A, from **58** (115 mg, 0.5 mmol); flash chromatography: petroleum ether/EtOAc (15:1).

60a; yield: 35 mg (28%); yellow syrup; $[\alpha]_{578}^{20}$ +37.5 (*c* = 1, $CHCl_3$).

60b; yield: 25 mg (20%); yellow syrup; $[\alpha]_D^{20}$ +0.2 (*c* = 0.2, $CHCl_3$).

Crystallographic Data for Compound 16a
$C_{15}H_{24}O_6$ (300.3): monoclinic; $P2_1$: a = 8.222(2), b = 10.229(2), c = 10.271(2) Å; α = 90, β = 112.10(2), γ = 90°; V = 800.35(5) Å^3; Z = 2; d_c = 1.246 g cm^{-3}; F(000) = 324. Data were collected with an Enraf Nonius CAD 4 diffractometer at 153(2) K using graphite monochromated Cu-Kα radiation, λ = 1.54178 Å, μ = 0.797 mm^{-1}; scan range 4.65 < Θ < 76.62 °. 2021 Independent reflections were used in the analysis. The structure was solved with SHELXS-97, refinement was done with SHELXL-97 based on 198 parameters. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, UK. The deposition number is 101441.

References

(1) Varki, A. *Glycobiology* **1993**, *3*, 97.
(2) (a) Fraser-Reid, B.; Tsang, R. In *Strategies and Tactics in Organic Synthesis*; Lindberg, T., Ed.; Academic: Orlando, FL, 1989; Vol. 2, pp 123–162.
(b) Kunz, H.; Rück, K. *Angew. Chem.* **1993**, *105*, 355; *Angew. Chem., Int. Ed.* Engl. **1993**, *32*, 336.
(3) (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.
(b) Bennett, G. B. *Synthesis* **1977**, 589.
(c) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.
(d) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3.
(e) Hill, R. K. In *Asymmetric Synthesis*, Vol. 3; Morrison, J. D., Ed.; Academic: Orlando, FL, 1984; p 503.
(f) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423.
(g) Wipf, P. In *Comprehensive Organic Synthesis*, Vol.5; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; p 827.
(4) (a) Ireland, R. E.; Mueller, R. H.; Willard, A.K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
(b) Pereira, S.; Srebnik, M. *Aldrichim. Acta* **1993**, *26*, 17.
(5) (a) Ireland, R. E.; Wilcox, C. S.; Thaisrivongs, S.; Vanier, N. R. *Can. J. Chem.* **1979**, *57*, 1743.
(b) Ireland, R. E., Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *J. Org. Chem.* **1980**, *45*, 48.
(c) Ireland, R. E.; Vevert, J.-P. *J. Org. Chem.* **1980**, *45*, 4259.
(d) Ireland, R. E.; Vevert, J.-P. *Can. J. Chem.* **1981**, *59*, 572.
(e) Ireland, R. E.; Daub, J. P. *J. Org. Chem.* **1981**, *46*, 479.
(f) Ireland, R. E.; Wuts, P. G.; Ernst, B. *J. Am. Chem. Soc.* **1981**, *103*, 3205.
(g) Curran, D. P.; Suh, Y.-G. *Carbohydr. Res.* **1987**, *171*, 161.
(6) (a) Ireland, R. E.; Norbeck, D. W. *J. Am. Chem. Soc.* **1985**, *107*, 3279.
(b) Ireland, R. E.; Norbeck, D. W.; Mandel, G. S.; Mandel, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 3285.
(7) Gable, R. W.; McVinish, L. M.; Rizzacasa, M. A. *Aust. J. Chem.* **1994**, *47*, 1537.
(8) Brimacombe, J. S.; Hunedy, F.; Tucker, L. C. N. *J. Chem. Soc. (C)* **1968**, 1381.
(9) Corey, E. J.; Gross, A. *Tetrahedron Lett.* **1984**, 495.
(10) (a) Barton, D. H. R.; Géro, S. D.; Quiclet-Sire, B.; Samadi, M. *Tetrahedron Asym.* **1994**, *5*, 2123.
(b) Walton, E.; Rodin, J. O.; Stammer, C. H.; Holly, F. W.; Folkers. K. *J. Am. Chem. Soc.* **1958**, *80*, 5168.
(11) (a) Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *J. Org. Chem.* **1982**, *47*, 3941.
(b) Kallmerten, J.; Gould, T. J. *Tetrahedron Lett.* **1983**, *24*, 5177.
(c) Burke, S. D.; Fobare, W. F.; Pacofsky, G. J. *J. Org. Chem.* **1983**, *48*, 5221.
(12) Wilcox, C. S.; Babston, R. E.; Lynch, V. *Tetrahedron Lett.* **1989**, *30*, 447.
(13) (a) Vittorelli, P.; Winkler, T.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1968**, *51*, 1457.
(b) Büchi, G.; Powell, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 3126.
(c) Hansen, H.-J., Schmid, H. *Tetrahedron* **1974**, *30*, 1959.
(d) Vittorelli, P.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1975**, *58*, 1293.
(e) Chapleo, C. B.; Hallett, P.; Lythgoe, B.; Waterhouse, I.; Wright, P. W. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1211.
(f) Cave, R. J.; Lythgoe, B.; Metcalfe, D. A.; Waterhouse, I. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1218.
(14) Schmidt, R. R.; Hermentin, P. *Chem. Ber.* **1979**, *112*, 3616.
(15) Gorin, P. A.; Perlin, A. S. *Can. J. Chem.* **1956**, *34*, 693.
(16) Kiss, J. *Adv. Carbohydr. Chem. Biochem.* **1974**, *29*, 229.
(17) (a) Ehrlich, F.; Guttmann, R. *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 220.
(b) Jones, J. K. N.; Stacey, M. *J. Chem. Soc.* **1947**, 1340.
(18) Owen, L. N.; Peat, S.; Jones, W. J. G. *J. Chem. Soc.* **1941**, 339.
(19) Schmidt, H. W. H.; Neukom, H. *Tetrahedron Lett.* **1969**, 2011.
(20) Ferrier, R. J.; Furneaux, R. H. *J. Chem. Soc., Chem. Commun.* **1977**, 332.
(21) (a) Augé, J.; David, S. *Carbohydr. Res.* **1977**, *59*, 255.
(b) Kocienski, P.; Pant, C. *Carbohydr. Res.* **1982**, *110*, 330.
(22) Hashimoto, N.; Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1981**, *29*, 1475.