Synthesis of Methoxy-Substituted Exocyclic (*E*)- and (*Z*)-Unsaturated Methyl Pyranosides and a Study of Their Reactivity towards Lewis Acids

Aurélie Deleuze,[a] Matthieu Sollogoub,[a] Yves Blériot,[a] Jérôme Marrot,[b] and Pierre Sinaÿ*[a]

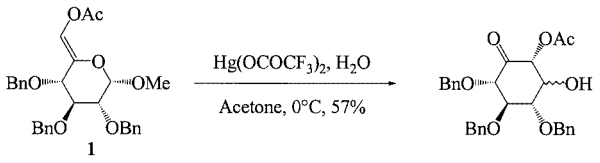
Dedicated to Gérard Descotes in appreciation of his remarkable contribution to the organic chemistry of carbohydrates

Keywords: Carbohydrates / Aluminum / Lewis acids / Carbocycles

The first synthesis of methoxy-substituted exocyclic (*E*)- and (*Z*)-unsaturated methyl pyranosides is reported involving the *syn* elimination of a selenoxide derivative as a key step. The rearrangement of these exocyclic enol ethers in the presence of TIBAL and DIBAL-H is also described.

Introduction

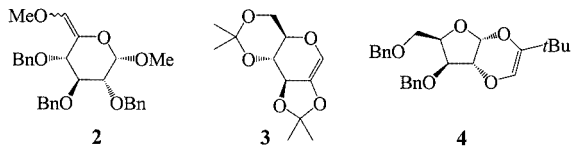
The conversion of carbohydrates into carbocycles is an attractive route for the synthesis of polyfunctionalised carbocyclic derivatives from readily available sugar precursors.[1] We have recently developed triisobutylaluminium-(TIBAL-)[2] and $TiCl_3OiPr$[3]-mediated carbocyclisations which, in contrast with the classical Ferrier-II reaction,[4] retain the anomeric substituent. This methodology has been successfully applied to the synthesis of carbasugar analogues of L-idose,[5] *S*-, *Se*-, and *C*-arylglycosides,[6] and di-[7] and trisaccharides.[8] As depicted in Scheme 1, the Ferrier-II reaction has previously been extended to the conversion, in acceptable yield, of the easily preparable acetylated enol ether **1** into a fully oxygenated cyclohexane derivative.[9] This is a useful transformation, inasmuch as inositols constitute a family of natural products involved in many biological processes.[10] We thus logically decided to investigate the possible mode of action of TIBAL on oxy-substituted enol ethers. As may be anticipated, the acetate **1** is not compatible with TIBAL and the putative rearrangement failed.[11]



1

Scheme 1. Access to inositols from an acetylated enol ether by a Ferrier-II reaction

Compound **2** should be more suitable for the TIBAL rearrangement. To the best of our knowledge, this kind of methoxy-substituted exocyclic (*E*)- and (*Z*)-unsaturated methyl pyranosides has not been reported in the literature so far, and we have only found two examples, **3**[12] and **4**[13] (Figure 1), of endocyclic unsaturated derivatives in carbohydrate chemistry combining these features.



2 3 4

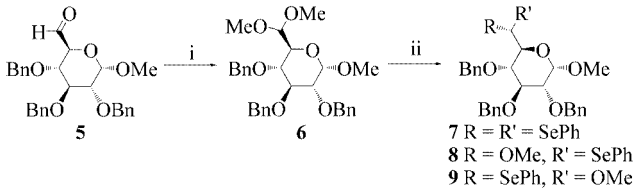
Figure 1. Structure of the alkoxy derivatives **2**−**4**

The difficulty associated with the synthesis of such compounds has already been underlined by Jones and Scott in their synthesis of **3**:[12] "The oxyglycal **3** ... represents a new class of acetal-protected oxyglycals, which is unavailable by classic methods." In carbohydrate chemistry, mixed O,Se-acetals have previously been utilized to synthesise endo-[14] and exocyclic unsaturated derivatives[15] as well as oxy-substituted endocyclic unsaturated derivatives.[16] We therefore explored this option to provide an entry, so far unknown, to alkoxy-substituted exocyclic unsaturated derivatives.

[a] Ecole Normale Supérieure, Département de Chimie, UMR 8642,
24 rue Lhomond, 75231 Paris, Cedex 05, France
Fax: (internat.) + 33-1/44323397
E-mail: Pierre.Sinay@chimie.ens.fr
[b] Institut Lavoisier, Université de Versailles-Saint-Quentin
45, avenue des Etats-Unis, 78035 Versailles Cedex, France

Results and Discussion

The known aldehyde **5**[17] was first easily converted into the dimethyl acetal **6** as shown in Scheme 2.



Scheme 2. Synthesis of mixed O,Se-acetals **8** and **9**; reagents and conditions: i) CSA, MeOH, 50 °C, 76%; ii) $BF_3{\cdot}OEt_2$, PhSeH, −10 °C (**7**/**8**/**9** = 1:5:5, 96%)

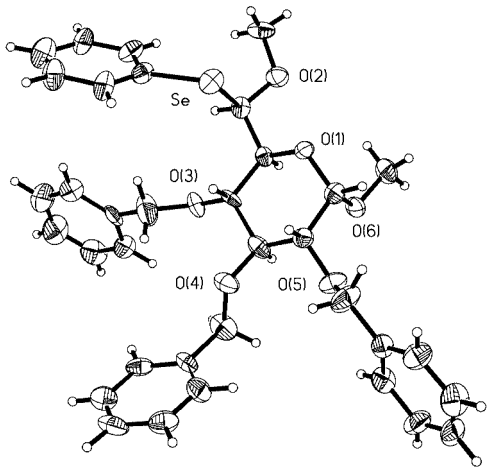
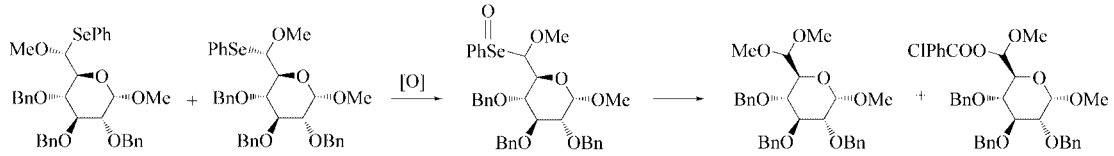


Figure 2. X-ray crystallographic structure of mixed O,Se-acetal **8**

Aluminium selenolates, such as iBu$_2$AlSePh[18] or Et$_2$AlSePh,[19] have been shown to convert symmetric O,O-acetals into monoselenoacetals in good yield. In our case, these reagents led only to undesired reactions. Such a transformation has also been reported through the use of selenophenol in the presence of Lewis acids. While the use of $SnCl_4$ [20] as a Lewis acid gave only the bis(selenophenyl) acetal derivative **7**, $BF_3{\cdot}OEt_2$[21] allowed access to the desired mixed O,Se-acetals **8** and **9** in a gratifying 86% yield, as a 1:1 easily separable diastereoisomeric mixture. It is noteworthy that the Lewis acid had to be added first, followed, after 10 min of stirring, by the selenophenol. The stereochemistry of the new stereogenic centre was elucidated by solving the crystal structure[22] of the mixed acetal **8** (Figure 2).

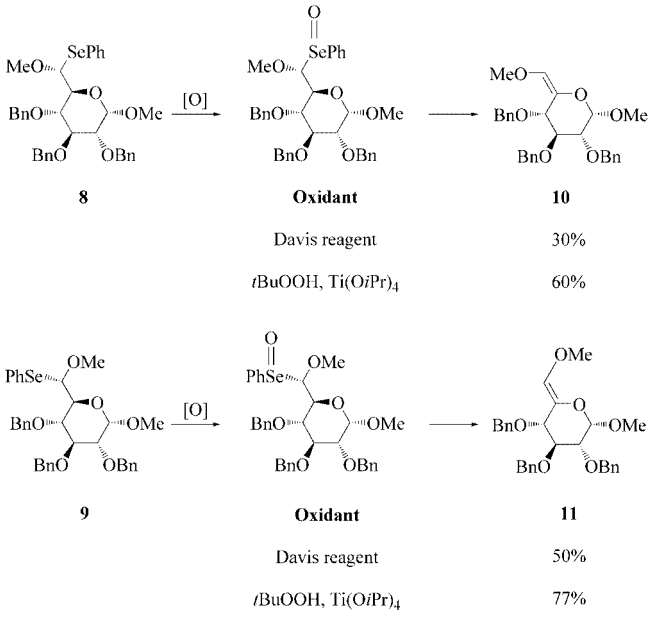
The following key step consisted of the oxidation of the selenium atom of the mixed O,Se-acetals to afford the selenoxide, which should easily eliminate to provide the corresponding enol ether. A similar strategy has been reported to synthesise a fluoro-substituted exocyclic unsaturated furanose derivative.[23] Preliminary studies demonstrated that the presence of a nucleophile in the reaction mixture is highly detrimental, affording only unwanted asymmetric O,O-acetals, resulting from a nucleophilic substitution of the selenoxide. Thus, the use of various standard oxidation conditions such as $NaIO_4$ in methanol or mCPBA only afforded the O,O-acetals **6** and **12** in moderate yields without traces of the expected exocyclic unsaturated derivatives (Scheme 3). Such a behaviour has previously been observed.[24]

Davis' reagent,[25] known to perform an oxidation without the release of a nucleophile, was then used[26] in the presence of vinyl acetate to trap the released PhSeOH,[15] thus affording the methoxy-substituted exocyclic derivatives **10** and **11** in 30 and 50% yield, from the acetals **8** and **9**, respectively (Scheme 4). Finally, the use of Ti(OiPr)$_4$ and tBuOOH[24,27] in the presence of anhydrous triethylamine, proved to be the best conditions and gave the methoxy-substituted exocyclic derivatives **10** and **11** in 60 and 77% yield from **8** and **9**, respectively (Scheme 4). The expected *syn* elimination of the selenoxide was confirmed by determination of the stereochemistry of the newly formed double bond. Compound **11** showed an NOE between 1-H and C=COCH_3 and between 6-H and CH_2Ph at the C-4 position, demonstrating a (*Z*) geometry for the double bond. Furthermore, the observation of an NOE between 6-H and the



Oxidant	6	12
$NaIO_4$, CH_3OH	50%	-
mCPBA, CH_2Cl_2	-	31%

Scheme 3. Compounds obtained from mixed O,Se-acetals **8** and **9** under various oxidation conditions



Scheme 4. Compounds obtained from pure mixed O,Se-acetals **8** and **9** under various oxidation conditions

anomeric OCH_3 for compound **10** confirmed the (*E*) geometry for this compound (Figure 3).

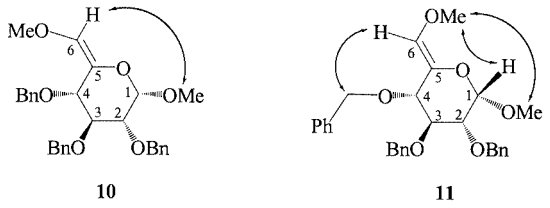


Figure 3. NOEs observed for enol ethers **10** and **11**

In conclusion, we have developed in this work a selective entry into the methoxy-substituted exocyclic unsaturated derivatives **10** and **11** from the easily available aldehyde **5**. These compounds are now available for a study of reactions, such as the Ferrier-II reaction, similar to the transformation depicted in Scheme 1. At this stage, the TIBAL- or DIBAL-H-mediated potential rearrangement was investigated (Scheme 5).

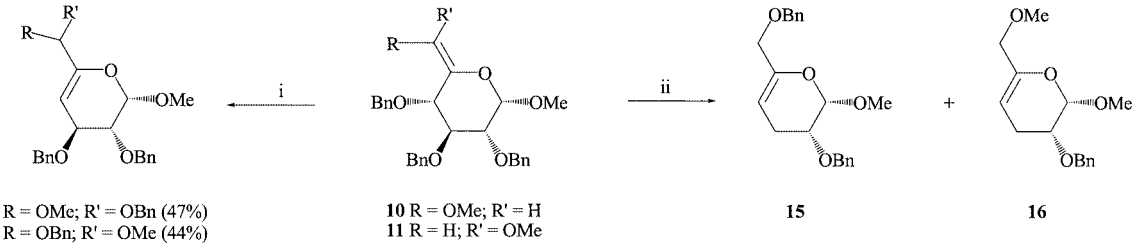
Treatment of oxyglycals **10** or **11** with TIBAL in toluene at 50 °C afforded the derivatives **13** or **14** in 47 and 44% yield, respectively. These compounds are formed by an allylic rearrangement, which is thus favoured over the desired conversion into a carbocycle. The reaction is stereospecific, but the absolute configuration of the created stereogenic centre was not determined in this work. This is an exocyclic variation of the isomerisation of a benzylated glycal described by Descotes and Martin.[28] The (*Z*) isomer **11** was next treated with diisobutylaluminium hydride (DIBAL-H) in toluene at 50 °C to give, after careful chromatography, pure compounds **15**[29] and **16** in low yields. We propose that the (*Z*) isomer **11** is first converted into **14**, as in the case of TIBAL. This asymmetric acetal thus generated at C-6 is then nonselectively reduced, via an alkoxycarbenium ion, to afford a mixture of 6-*O*-benzyl and -methyl ethers. Likewise, the conjugation of the ring oxygen lone pairs with the endocyclic double bond allows another reduction at C-3. Treatment of the exocyclic unsaturated derivative **11** with other Lewis acids such as $TiCl_4$, $SnCl_4$, $AlBr_3$, $BF_3.OEt_2$, TMSOTf, $Cu(SO_3CF_3)_2$ or $Hg(OAc)_2$ only afforded rearranged compounds and complex mixtures of products.

Conclusion

In this work, we have developed a synthetic strategy to obtain a so-far unknown category of sugar derivatives, that is to say methoxy-substituted exocyclic (*E*)- and (*Z*)-unsaturated methyl pyranosides. This is a very rare assembly of functions, whose chemistry can now be explored. For example, we have shown that the presence of a methoxy group on the exocyclic unsaturated derivative completely turns off the carbohydrate-carbocycle conversion and drives an allylic rearrangement.

Experimental Section

General Methods: Melting points were recorded with a Büchi model 535 m.p. apparatus and are uncorrected. ^{1}H NMR spectra (δ_H) were recorded with a Bruker AC 250 (250 MHz) or a Bruker DRX 500 (500 MHz) spectrometer. ^{13}C NMR spectra (δ_C) were recorded with a Bruker AC 250 (62.9 MHz) or a Bruker DRX 500 (100.6 MHz) spectrometer and multiplicities were assigned using the DEPT sequence. All chemical shifts are quoted on the δ scale. Mass spectra were recorded with a JMS-700 spectrometer using fast atom bombardment (FAB-MS) or chemical ionisation (CI, NH_3) as stated. Optical rotations were measured with a Perkin−Elmer 241 polarimeter with a path length of 1 dm. Concentrations are given in g/100 mL. Microanalyses were performed by the microanalysis service of the Université Pierre et Marie Curie,



Scheme 5. Reactivity of enol ethers towards TIBAL and DIBAL-H; reagents and conditions: i) TIBAL, toluene, 50 °C; ii) DIBAL-H, toluene, −78 °C, 20%

Paris. Thin layer chromatography (TLC) was carried out on aluminium sheets coated with $60F_{254}$ silica, and plates were developed using a spray of 0.2% w/v cerium(IV) sulfate and 5% ammonium molybdate in 2 M sulfuric acid. Flash chromatography was carried out using Merck silica gel 60 (230−400 mesh). Solvents and commercially available reagents were dried and purified before use according to standard procedures.

Methyl 2,3,4-Tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside Dimethyl Acetal (6): Aldehyde **5** (7 g, 15.2 mmol) was dissolved in dry methanol (200 mL) and camphorsulfonic acid (3.86 g, 15.2 mmol) was added. The reaction mixture was stirred at 50 °C under argon overnight and TLC (cyclohexane/ethyl acetate, 1:1) showed the absence of starting material (R_f = 0.38) and formation of a new product (R_f = 0.7). The reaction mixture was neutralised with aq. Na_2CO_3 (100 mL), washed with water and the aqueous layer was extracted with ethyl acetate. The organic extracts were combined, dried with $MgSO_4$ and concentrated to afford an oil which was purified by flash chromatography (cyclohexane/ethyl acetate, 5:1 then 3:1 then 1:1) to afford acetal **6** (5.84 g, 11.5 mmol, 76% yield) as a colourless oil. $[\alpha]_D^{20}$ = +17 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39−7.30 (m, 15 H, aromatic H), 5.02 (d, ^3J = 11.0 Hz, 1 H, CHPh), 4.91 (d, ^3J = 11.0 Hz, 1 H, CHPh), 4.85 (d, ^3J = 11.0 Hz, 1 H, CHPh), 4.82 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.68 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.68 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.64 (d, ^3J = 11.0 Hz, 1 H, CHPh), 4.53 (d, $^3J_{5,6}$ = 1.7 Hz, 1 H, 6-H), 4.02 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.82 (dd, $^3J_{4,5}$ = 10.0, $^3J_{5,6}$ = 1.7 Hz, 1 H, 5-H), 3.63 (dd, $^3J_{3,4}$ = 9.3, $^3J_{4,5}$ = 10.0 Hz, 1 H, 4-H), 3.59 (dd, $^3J_{1,2}$ = 3.5, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.48, 3.44, 3.41 (3 × s, 3 × 3 H, 3 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.75, 138.25, 138.07 (3 × C_{ipso}), 127.57−128.44 (aromatic C), 102.56 (C-6), 98.20 (C-1), 82.10 (C-3), 79.66 (C-2), 78.13 (C-4), 75.73, 74.91, 73.40 (3 × CH_2Ph), 70.16 (C-5), 56.12, 55.53, 55.29 (3 × CH_3O) ppm. MS (CI; NH_3): *m*/*z* = 526 $[M + NH_4]^+$. $C_{30}H_{36}O_7$ (508.6): calcd. C 70.85, H 7.13; found C 70.76, H 7.32.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6,6-di-*C*-phenylseleno-α-D-glucopyranoside (7), Methyl (6*R*)-2,3,4-Tri-*O*-benzyl-6-*O*-methyl-6-*C*-phenylseleno-α-D-glucopyranoside (8) and Methyl (6*S*)-2,3,4-Tri-*O*-benzyl-6-*O*-methyl-6-*C*-phenylseleno-α-D-glucopyranoside (9): Acetal **6** (7.2 g, 14.17 mmol) was dissolved in CH_2Cl_2 (40 mL) under argon and the reaction mixture was cooled to −20 °C. $BF_3{\cdot}Et_2O$ (1.44 mL, 11.34 mmol) was then added and the reaction mixture was stirred at −20 °C for 10 min. Selenophenol (1.65 mL, 15.59 mmol) was then added and the reaction mixture stirred for 15 min at −20 °C and then left to warm to room temperature and stirred overnight. TLC monitoring (cyclohexane/ethyl acetate, 2:1) showed the absence of starting material (R_f = 0.37) and three new spots (R_f = 0.68, 0.71, 0.74). The reaction mixture was then diluted with CH_2Cl_2 (60 mL), cooled to 0 °C, neutralised with aq. $NaHCO_3$ (100 mL), and washed with water (100 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. Purification by careful flash chromatography (cyclohexane/ethyl acetate, 20:1 then 3:1) afforded Se,Se-acetal **7** (1.25 g, 1.64 mmol) as a yellow solid. $[\alpha]_D^{20}$ = −133 (*c* = 1.0, $CHCl_3$); m.p. 80−81 °C (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52−7.02 (m, 25 H, aromatic H), 5.02 (d, ^3J = 10.7 Hz, 1 H, CHPh), 4.93 (d, ^3J = 11.1 Hz, 1 H, CHPh), 4.87 (br. s, 1 H, 6-H), 4.86 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.80 (d, ^3J = 10.8 Hz, 1 H, CHPh), 4.73 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.72 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.41 (d, ^3J = 11.2 Hz, 1 H, CHPh), 4.11 (dd, $^3J_{4,5}$ = 9.3, $^3J_{5,6}$ = 0.9 Hz, 1 H, 5-H), 4.01 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 3.93 (dd, $^3J_{3,4}$ = 9.1, $^3J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.63 (dd, $^3J_{1,2}$ = 3.6, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.50 (s, 3 H, CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.55, 138.24, 138.05 (3 × C_{ipso}), 133.64, 133.27 (2 × aromatic C), 131.82, 130.12 (2 × aromatic C), 129.14−127.31 (aromatic C), 98.01 (C-1), 81.68 (C-3), 80.36 (C-4), 80.04 (C-2), 74.25 (C-5), 75.72, 75.00, 73.39 (3 × CH_2Ph), 55.48 (CH_3O) 46.47 (C-6) ppm. MS (CI; NH_3): *m*/*z* = 778 $[M + NH_4]^+$. $C_{40}H_{40}O_5Se_2$ (758.66): calcd. C 63.33, H 5.31; found C 63.77, H 5.67.

Further elution afforded the mixed O,Se-acetal **8** (3.8 g, 6 mmol, 43% yield) as a solid. $[\alpha]_D^{20}$ = −9 (*c* = 1.0, $CHCl_3$); m.p. 118−119 °C (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66−7.19 (m, 20 H, aromatic H), 5.35 (d, $^3J_{5,6}$ = 0.9 Hz, 1 H, 6-H), 5.08 (d, ^3J = 10.8 Hz, 1 H, CHPh), 4.98 (d, ^3J = 11.0 Hz, 1 H, CHPh), 4.86 (d, ^3J = 12.4 Hz, 1 H, CHPh), 4.85 (d, ^3J = 10.4 Hz, 1 H, CHPh), 4.74 (d, ^3J = 11.1 Hz, 1 H, CHPh), 4.72 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.72 (d, ^3J = 11.0 Hz, 1 H, CHPh), 4.18 (dd, $^3J_{4,5}$ = 9.3, $^3J_{5,6}$ = 0.9 Hz, 1 H, 5-H), 4.15 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 3.92 (t, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.67 (dd, $^3J_{1,2}$ = 3.5, $^3J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 3.48, 3.47 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.51, 138.15, 138.00 (3 × C_{ipso}), 134.17 (aromatic C), 134.12 (aromatic C), 130.95−127.35 (aromatic C), 97.97 (C-1), 92.23 (C-6), 81.91 (C-3), 80.07 (C-2), 79.09 (C-4), 75.69, 74.82, 73.37 (3 × CH_2Ph), 74.06 (C-5), 57.81, 55.34 (2 × CH_3O) ppm. MS (CI; NH_3): *m*/*z* = 652 $[M + NH_4]^+$. $C_{35}H_{38}O_6Se$ (633.63): calcd. C 66.34, H 6.04; found C 66.14, H 6.20.

Further elution afforded the mixed O,Se-acetal **9** (3.8 g, 6 mmol, 43% yield) as a solid. $[\alpha]_D^{20}$ = −6 (*c* = 1.2, $CHCl_3$); m.p. 76−77 °C (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64−7.26 (m, 20 H, aromatic H), 5.28 (d, $^3J_{5,6}$ = 1.8 Hz, 1 H, 6-H), 5.03 (d, ^3J = 10.9 Hz, 1 H, CHPh), 4.91 (d, ^3J = 11.3 Hz, 1 H, CHPh), 4.86 (d, ^3J = 10.9 Hz, 1 H, CHPh), 4.85 (d, ^3J = 12.2 Hz, 1 H, CHPh), 4.70 (d, ^3J = 12.2 Hz, 1 H, CHPh), 4.69 (d, $^3J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 4.57 (d, ^3J = 11.3 Hz, 1 H, CHPh), 4.21 (dd, $^3J_{4,5}$ = 9.5, $^3J_{5,6}$ = 1.8 Hz, 1 H, 5-H), 4.04 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.77 (dd, $^3J_{3,4}$ = 9.3, $^3J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.61 (dd, $^3J_{1,2}$ = 3.7, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.56, 3.23 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.67, 138.24, 137.99 (3 × C_{ipso}), 134.68 (aromatic C), 134.20 (aromatic C), 130.94−127.44 (aromatic C), 98.50 (C-1), 89.84 (C-6), 81.92 (C-3), 79.53 (C-2), 78.20 (C-4), 75.26 (C-5), 75.81, 75.00, 73.45 (3 × CH_2Ph), 57.84, 55.79 (2 × CH_3O) ppm. MS (CI; NH_3): *m*/*z* = 652 $[M + NH_4]^+$. $C_{35}H_{38}O_6Se$ (633.63): calcd. C 66.34, H 6.04; found C 66.67, H 6.30.

Methyl (5*E*)-2,3,4-Tri-*O*-benzyl-6-*C*-methoxy-α-D-*xylo*-hex-5-enopyranoside (10). Method 1: Acetal **8** (1.0 g, 1.58 mmol) was dissolved in dry dichloromethane (20 mL) under argon, and pyridine (0.65 mL, 7.89 mmol) and vinyl acetate (15 mL, 167.4 mmol) were added consecutively. The reaction mixture was cooled to 0 °C and a solution of Davis' reagent (580 mg, 1.89 mmol) in dry dichloromethane (5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred for 2 h and concentrated under reduced pressure. Purification by flash chromatography (cyclohexane/ethyl acetate, 10:1) afforded enediol **10** (225 mg, 0.47 mmol, 30% yield) as an oil. **Method 2:** Acetal **8** (200 mg, 0.316 mmol) was dissolved in dry dichloromethane (2 mL) under argon and the solution cooled to 0 °C. Anhydrous triethylamine (75 μL, 0.536 mmol) was then added, followed by dropwise addition of *t*BuOOH (5.5 M in decane, 132 μL, 0.726 mmol) and $Ti(OiPr)_4$ (94 μL, 0.316 mmol). The reaction mixture was stirred at 0 °C for 45 min. TLC monitoring (cyclohexane/ethyl acetate, 2:1) showed a new product (R_f = 0.54) and some remaining starting material (R_f = 0.64). The reaction mixture was allowed to warm to room

temperature and was concentrated under reduced pressure. Purification by flash chromatography (cyclohexane/ethyl acetate, 7:1) afforded enediol **10** (90 mg, 0.189 mmol, 60% yield) as an oil. $[\alpha]_D^{20}$ = +5 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42−7.30 (m, 15 H, aromatic H), 6.25 (d, $^4J_{4,6}$ = 1.4 Hz, 1 H, 6-H), 4.85 (d, ^3J = 10.9 Hz, 1 H, CHPh), 4.84 (d, 2 H, 2 × CHPh), 4.76 (d, ^3J = 11.1 Hz, 1 H, CHPh), 4.72 (d, ^3J = 12.3 Hz, 1 H, CHPh), 4.64 (d, $^3J_{1,2}$ = 3.1 Hz, 1 H, 1-H), 4.55 (d, ^3J = 11.2 Hz, 1 H, CHPh), 4.27 (dd, $^3J_{3,4}$ = 6.5, $^4J_{4,6}$ = 1.4 Hz, 1 H, 4-H), 4.06 (dd, $^3J_{2,3}$ = 8.4, $^3J_{3,4}$ = 6.5 Hz, 1 H, 3-H), 3.57 (dd, $^3J_{1,2}$ = 3.1, $^3J_{2,3}$ = 8.4 Hz, 1 H, 2-H), 3.63, 3.47 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 139.14 (C-6), 138.57, 138.53, 138.31 (3 × C_{ipso}), 131.83 (C-5), 128.43−127.43 (aromatic C), 99.72 (C-1), 79.91 (C-3), 78.13 (C-2), 76.84 (C-4), 74.60, 73.40, 72.82 (3 × CH_2Ph), 60.59, 55.73 (2 × CH_3O) ppm. MS (CI; NH_3): m/z = 494 [M + NH_4]$^+$. HRMS: $C_{29}H_{36}O_6N$: calcd. 494.2543; found 494.2547.

Methyl (5*Z*)-2,3,4-Tri-*O*-benzyl-6-*C*-methoxy-α-D-*xylo*-hex-5-enopyranoside (11). Method 1: Acetal **9** (1.1 g, 1.735 mmol) was dissolved in dry dichloromethane (33 mL) under argon, and pyridine (0.7 mL, 8.68 mmol) and vinyl acetate (8 mL, 86.75 mmol) were then added consecutively. The reaction mixture was cooled to 0 °C and a solution of Davis' reagent (700 mg, 2.29 mmol) in dry dichloromethane (4 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred for 2 h and concentrated under reduced pressure. Purification by flash chromatography (cyclohexane/ethyl acetate, 10:1) afforded enediol **11** (406 mg, 0.85 mmol, 50% yield) as an oil. **Method 2:** Acetal **9** (500 mg, 0.789 mmol) was dissolved in dry dichloromethane (4 mL) under argon and the solution cooled to 0 °C. Anhydrous triethylamine (188 μL, 1.34 mmol) was added, followed by dropwise addition of *t*BuOOH (5.5 M in decane, 330 μL, 1.81 mmol) and Ti(O*i*Pr)$_4$ (236 μL, 0.789 mmol). The reaction mixture was stirred at 0 °C for 45 min. TLC monitoring (cyclohexane/ethyl acetate, 2:1) showed a new product (R_f = 0.72) and some remaining starting material (R_f = 0.82). The reaction mixture was allowed to warm to room temperature and was concentrated under reduced pressure. Purification by flash chromatography (cyclohexane/ethyl acetate, 7:1) afforded enediol **11** (289 mg, 0.607 mmol, 77% yield) as an oil. $[\alpha]_D^{20}$ = −131 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41−7.30 (m, 15 H, aromatic H), 5.95 (d, $^4J_{4,6}$ = 1.8 Hz, 1 H, 6-H), 4.95 (d, ^3J = 10.9 Hz, 1 H, CHPh), 4.87 (d, ^3J = 10.9 Hz, 1 H, CHPh), 4.85 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.84 (d, ^3J = 11.4 Hz, 1 H, CHPh), 4.74 (d, ^3J = 11.4 Hz, 1 H, CHPh), 4.74 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.72 (d, ^3J = 12.9 Hz, 1 H, CHPh), 4.00 (dd, $^3J_{3,4}$ = 8.6, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-H), 3.96 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 8.6 Hz, 1 H, 3-H), 3.62 (dd, $^3J_{1,2}$ = 3.5, $^3J_{2,3}$ = 8.6 Hz, 1 H, 2-H), 3.65, 3.51 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.65, 138.07, 138.01 (3 × C_{ipso}), 134.65 (C-6), 128.67 (C-5), 128.42−127.60 (aromatic C), 99.20 (C-1), 81.81 (C-3), 79.47 (C-2), 78.21 (C-4), 75.58, 74.37, 73.53 (3 × CH_2Ph), 60.41, 56.03 (2 × CH_3O) ppm. MS (CI; NH_3): m/z = 494 [M + NH_4]$^+$. $C_{29}H_{32}O_6$ (476.56): calcd. C 73.09, H 6.77; found C 73.16, H 6.95.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-methyl-6-*C*-(4-chlorobenzoyl)-α-D-glucopyranoside (12): A 1:1 mixture of acetals **8** and **9** (100 mg, 0.158 mmol), dissolved in dry dichloromethane (2 mL), was cooled to −60 °C and a solution of *m*CPBA (28 mg, 0.166 mmol) in dry dichloromethane (2 mL) was added. After 1 h, TLC monitoring (cyclohexane/ethyl acetate, 2:1) showed a new spot. The reaction mixture was diluted with dichloromethane (10 mL), neutralised with aq. $NaHCO_3$ (10 mL), and then washed with aq. NaCl (10 mL) and water (10 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated. Purification by flash chromatography (cyclohexane/ethyl acetate, 5:1 then 2:1 then 1:1) afforded an inseparable diastereoisomeric mixture of acetals **12** (30 mg, 0.047 mmol, 31% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.12−8.10 (m, 6 H, PhCl), 7.58 (m, 2 H, PhCl), 7.43−7.30 (m, 30 H, aromatic H), 6.34 (d, $^3J_{5,6}$ = 1.4 Hz, 1 H, 6-H), 4.59 (d, $^3J_{5,6}$ = 1.5 Hz, 1 H, 6-H′), 5.05 (d, ^3J = 10.9 Hz, 1 H, CHPh′), 5.00 (d, ^3J = 10.7 Hz, 1 H, CHPh), 4.98 (d, ^3J = 11.3 Hz, 1 H, CHPh′), 4.91−4.85 (m, 5 H, 3 × CHPh, 2 × CHPh′), 4.75 (d, $^3J_{1,2}$ = 1.6 Hz, 1 H, 1-H′), 4.72 (d, 2 H, CHPh, CHPh′), 4.70 (d, ^3J = 11.1 Hz, 1 H, CHPh′), 4.61 (d, ^3J = 10.3 Hz, 1 H, CHPh), 4.09 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1 H, 3-H′), 4.06 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.02 (dd, $^3J_{4,5}$ = 10.1, $^4J_{5,6}$ = 1.4 Hz, 1 H, 5-H′), 3.93 (dd, $^3J_{4,5}$ = 10.0, $^4J_{5,6}$ = 1.5 Hz, 1 H, 5-H), 3.73 (t, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.62 (dd, $^3J_{1,2}$ = 4.5, $^3J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.62 (dd, $^3J_{1,2}$ = 1.5, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H′), 3.55 (dd, $^3J_{3,4}$ = 9.2, $^3J_{4,5}$ = 10.1 Hz, 1 H, 4-H′), 3.59, 3.48 (2 × s, 2 × 3 H, 2 × CH_3O'), 3.39, 3.36 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 165.10 (C=O), 164.68 (C=O′), 138.56, 138.40, 137.58, 137.52, 134.67, 134.62 (6 × C_{ipso}), 133.50−127.65 (aromatic C), 98.26 (C-1), 97.93 (C-1′), 97.26 (C-6′), 97.09 (C-6), 82.00 (C-3′), 81.99 (C-3), 79.87 (C-2′), 79.44 (C-2), 77.54 (C-4′), 77.51 (C-4), 75.90, 75.78, 75.04, 74.83, 73.50, 73.42 (6 × CH_2Ph), 70.52 (C-5′), 70.45 (C-5), 57.86, 55.24 (2 × CH_3O'), 55.66, 55.09 (2 × CH_3O') ppm. MS (CI; NH_3): m/z = 650 [M + NH_4]$^+$. $C_{36}H_{37}O_8Cl$ (633.13): calcd. C 68.29, H 5.89; found C 68.65, H 6.23.

Methyl (6*R* or 6*S*)-2,3-Di-*O*-benzyl-6-*C*-benzyloxy-4,5-didehydro-4-deoxy-6-*O*-methyl-α-D-glucopyranoside (13): TIBAL (1.3 mL, 1.26 mmol) was added to a solution of enediol **10** (86 mg, 0.181 mmol), dissolved in dry toluene (1 mL) under argon. The reaction mixture was heated up to 50 °C for 1 h. TLC monitoring (cyclohexane/ethyl acetate, 3:1) showed conversion of the starting material (R_f = 0.4) into three new products (R_f = 0.40, 0.50, 0.55). The reaction mixture was then cooled and hydrolised with water (20 mL). The aqueous layer was extracted with ethyl acetate and the organic phase was washed with water, dried with $MgSO_4$, filtered and concentrated. Purification by flash chromatography (cyclohexane/ethyl acetate, 10:1) afforded **13** (40 mg, 0.084 mmol, 47% yield) as an oil. $[\alpha]_D^{20}$ = −12 (c = 1.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40−7.30 (m, 15 H, aromatic H), 5.36 (dd, $^3J_{3,4}$ = 2.8, $^4J_{4,6}$ = 0.6 Hz, 1 H, 4-H), 4.93 (d, $^3J_{1,2}$ = 2.5 Hz, 1 H, 1-H), 4.89 (d, $^4J_{4,6}$ = 0.6 Hz, 1 H, 6-H), 4.86 (d, ^3J = 12.2 Hz, 1 H, CHPh), 4.79 (d, ^3J = 12.2 Hz, 1 H, CHPh), 4.73 (d, ^3J = 11.8 Hz, 1 H, CHPh), 4.69 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.68 (d, ^3J = 12.0 Hz, 1 H, CHPh), 4.60 (d, ^3J = 11.9 Hz, 1 H, CHPh), 4.35 (dd, $^3J_{2,3}$ = 7.3, $^3J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 3.84 (dd, $^3J_{1,2}$ = 2.6, $^3J_{2,3}$ = 7.3 Hz, 1 H, 2-H), 3.52, 3.39 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 146.60 (C-5), 138.39, 138.12, 137.61 (3 × C_{ipso}), 128.39−127.59 (aromatic C), 100.58 (C-4), 99.65 (C-1), 98.50 (C-6), 76.40 (C-2), 73.28 (C-3), 73.12, 71.44, 67.44 (3 × CH_2Ph), 56.72, 52.93 (2 × CH_3O) ppm. MS (CI; NH_3): m/z = 494 [M + NH_4]$^+$. HRMS: $C_{29}H_{36}O_6N$: calcd. 494.2543; found 494.2539.

Methyl (6*S* or 6*R*)-2,3-Di-*O*-benzyl-6-*C*-benzyloxy-4,5-didehydro-4-deoxy-6-*O*-methyl-α-D-glucopyranoside (14): TIBAL (1.9 mL, 1.89 mmol) was added to a solution of enediol **11** (128 mg, 0.267 mmol), dissolved in dry toluene (1 mL) under argon. The reaction mixture was heated up to 50 °C for 1 h. TLC monitoring (cyclohexane/ethyl acetate, 3:1) showed conversion of the starting material (R_f = 0.4) into two new products (R_f = 0.50, 0.55). The reaction mixture was then cooled and hydrolysed with water (20 mL). The aqueous layer was extracted with ethyl acetate and

the organic phase was washed with water, dried with $MgSO_4$, filtered and concentrated. Purification by flash chromatography (cyclohexane/ethyl acetate, 10:1) afforded **14** (56 mg, 0.117 mmol, 44% yield) as an oil. $[\alpha]_D^{20} = -150$ (c = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43−7.30 (m, 15 H, aromatic H), 5.37 (dd, $^3J_{3,4}$ = 2.9, $^4J_{4,6} < 0.5$ Hz, 1 H, 4-H), 4.91 (d, $^3J_{1,2}$ = 2.5 Hz, 1 H, 1-H), 4.90 (d, $^4J_{4,6} < 0.5$ Hz, 1 H, 6-H), 4.86 (d, ^3J = 12.2 Hz, 1 H, CHPh), 4.80 (d, ^3J = 12.2 Hz, 1 H, CHPh), 4.70 (d, ^3J = 12.8 Hz, 1 H, CHPh), 4.69 (d, ^3J = 11.8 Hz, 1 H, CHPh), 4.68 (d, ^3J = 12.0 Hz, 1 H, CHPh), 4.61 (d, ^3J = 12.0 Hz, 1 H, CHPh), 4.36 (dd, $^3J_{2,3}$ = 7.3, $^3J_{3,4}$ = 2.9 Hz, 1 H, 3-H), 3.83 (dd, $^3J_{1,2}$ = 2.5, $^3J_{2,3}$ = 7.3 Hz, 1 H, 2-H), 3.54, 3.41 (2 × s, 2 × 3 H, 2 × CH_3O) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 146.69 (C-5), 138.35, 138.09, 137.62 (3 × C_{ipso}), 128.36−127.56 (aromatic C), 100.00 (C-4), 99.58 (C-1), 98.37 (C-6), 76.28 (C-2), 73.17 (C-3), 73.07, 71.36, 67.34 (3 × CH_2Ph), 56.66, 52.89 (2 × CH_3O) ppm. MS (CI; NH_3): m/z = 494 $[M + NH_4]^+$. HRMS: $C_{29}H_{36}O_6N$: calcd. 494.2543; found 494.2539.

Methyl 2,6-Di-*O*-benzyl-4,5-didehydro-3,4-dideoxy-α-D-glucopyranoside (15) and Methyl 2-*O*-Benzyl-4,5-didehydro-3,4-dideoxy-6-*O*-methyl-α-D-glucopyranoside (16): A solution of enediol **11** (160 mg, 0.336 mmol) in dry toluene (2 mL) under argon was cooled to −78 °C. DIBAL-H (1.57 mL, 2.35 mmol) was then added and the reaction mixture was stirred at −78 °C for 3 h, by which time TLC monitoring (cyclohexane/ethyl acetate, 2:1) showed conversion of the starting material (R_f = 0.5) into two new products (R_f = 0.30, 0.45). The reaction mixture was warmed to room temperature and then hydrolysed with water (20 mL). The aqueous layer was extracted with ethyl acetate, the organic extracts were combined, dried with $MgSO_4$, filtered and concentrated. Purification by flash chromatography (cyclohexane/ethyl acetate, 10:1) afforded compound **15** (17 mg, 15%) as an oil. $[\alpha]_D^{20} = +75$ (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40−7.31 (m, 10 H, aromatic H), 5.01 (d, $^3J_{1,2}$ = 2.5 Hz, 1 H, 1-H), 4.89 (dd, $^3J_{3,4}$ = 2.4, $^3J_{3',4}$ = 5.3, $^4J_{4,6} < 0.5$ Hz, 1 H, 4-H), 4.72 (d, ^3J = 12.5 Hz, 1 H, CHPh), 4.64 (d, ^3J = 12.5 Hz, 1 H, CHPh), 4.60 (d, ^3J = 12.1 Hz, 1 H, CHPh), 4.54 (d, ^3J = 12.0 Hz, 1 H, CHPh), 3.87 (br. s, 2 H, 6-H, 6-H′), 3.75 (ddd, $^3J_{1,2}$ = 2.5, $^3J_{2,3}$ = 10.1, $^3J_{2,3'}$ = 6.7 Hz, 1 H, 2-H), 3.54 (s, 3 H, CH_3O), 2.28−2.23 (m, $^3J_{2,3}$ = 10.1, $^3J_{2,3'}$ = 6.7, $^3J_{3,4}$ = 2.4 Hz, 2 H, 3-H, 3-H′) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 146.10 (C-5), 138.02, 138.00 (2 × C_{ipso}), 128.44−127.58 (aromatic C), 99.09 (C-4), 97.34 (C-1), 72.11 (C-2), 72.10, 71.29(2 × CH_2Ph), 69.57 (C-6), 55.97 (CH_3O), 29.69 (C-3) ppm. MS (CI; NH_3): m/z = 358 $[M + NH_4]^+$. HRMS: $C_{21}H_{28}O_4N$: calcd. 358.2018; found 358.2016. Ref.[29] ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.98 (d, $^3J_{1,2}$ = 2.2 Hz, 1 H, 1-H), 4.86 (dd, $^3J_{3,4}$ = 2.6, $^3J_{3',4}$ = 5.1 Hz, 1 H, 4-H).

Further elution afforded compound **16** (5 mg, 5%) as an oil. $[\alpha]_D^{20} = +35$ (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42−7.32 (m, 5 H, aromatic H), 5.00 (d, $^3J_{1,2}$ = 2.5 Hz, 1 H, 1-H), 4.89 (ddd, $^3J_{3,4}$ = 2.4, $^3J_{3',4}$ = 5.1, $^4J_{4,6} < 0.5$ Hz, 1 H, 4-H), 4.72 (d, ^3J = 12.4 Hz, 1 H, CHPh), 4.63 (d, ^3J = 12.4 Hz, 1 H, CHPh), 3.83 (br. s, 2 H, 6-H, 6-H′), 3.75 (ddd, $^3J_{1,2}$ = 2.5, $^3J_{2,3}$ = 10.5, $^3J_{2,3'}$ = 6.8 Hz, 1 H, 2-H), 3.55, 3.38 (2 × s, 2 × 3 H, 2 × CH_3O), 2.40−2.21 (m, $^3J_{2,3}$ = 10.5, $^3J_{2,3'}$ = 6.8, $^3J_{3,4}$ = 2.5 Hz, 2 H, 3-H, 3-H′) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 145.95 (C-5), 138.00 (C_{ipso}), 128.49−127.55 (aromatic C), 99.21 (C-4), 99.37 (C-1), 72.14 (C-6), 72.10 (C-2), 71.29 (CH_2Ph), 57.92, 55.95 (2 × CH_3O), 29.60 (C-3) ppm. MS (CI; NH_3): m/z = 282 $[M + NH_4]^+$. HRMS: $C_{15}H_{21}O_4$: calcd. 265.1440; found 265.1429.

[1] [1a] R. J. Ferrier, *Top. Curr. Chem.* **2001**, *215*, 277. [1b] P. I. Dalko, P. Sinaÿ, *Angew. Chem.* **1999**, *111*, 819; *Angew. Chem. Int. Ed.* **1999**, *38*, 773.
[2] S. K. Das, J.-M. Mallet, P. Sinaÿ, *Angew. Chem.* **1997**, *109*, 513; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 493.
[3] M. Sollogoub, J.-M. Mallet, P. Sinaÿ, *Tetrahedron Lett.* **1998**, *39*, 4871.
[4] R. J. Ferrier, *J. Chem. Soc., Perkin Trans. 1* **1979**, 1455.
[5] M. Sollogoub, A. J. Pearce, A. Hérault, P. Sinaÿ, *Tetrahedron: Asymmetry* **2000**, *11*, 283.
[6] M. Sollogoub, J.-M. Mallet, P. Sinaÿ, *Angew. Chem.* **2000**, *112*, 370; *Angew. Chem. Int. Ed.* **2000**, *35*, 362.
[7] A. J. Pearce, M. Sollogoub, J.-M. Mallet, P. Sinaÿ, *Eur. J. Org. Chem.* **1999**, 2103.
[8] A. J. Pearce, R. Chevalier, J.-M. Mallet, P. Sinaÿ, *Eur. J. Org. Chem.* **2000**, 2203.
[9] S. L. Bender, R. J. Budhu, *J. Am. Chem. Soc.* **1991**, *113*, 9883.
[10] B. V. L. Potter, D. Lampe, *Angew. Chem.* **1995**, *107*, 2085; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1933.
[11] P. Jenkins, personal communication.
[12] G. S. Jones, W. J. Scott, *J. Am. Chem. Soc.* **1992**, *114*, 1491.
[13] D. Craig, J. P. Tierney, C. Williamson, *Tetrahedron Lett.* **1997**, *38*, 4153.
[14] [14a] D. J. Goldsmith, D. C. Liotta, M. Volmer, W. Hoekstra, L. Waykole, *Tetrahedron* **1985**, *41*, 4873. [14b] M. Kassou, S. Castillón, *Tetrahedron Lett.* **1994**, *35*, 5513.
[15] J.-M. Lancelin, J.-R. Pougny, P. Sinaÿ, *Carbohydr. Res.* **1985**, *136*, 369.
[16] G. Jaurand, J.-M. Beau, P. Sinaÿ, *J. Chem. Soc., Chem. Commun.* **1982**, 701.
[17] H. Hashimoto, K. Asano, F. Fuji, J. Yoshimura, *Carbohydr. Res.* **1982**, *104*, 87.
[18] Y. Nishiyama, S. Nakata, S. Hamanaka, *Chem. Lett.* **1991**, 1775.
[19] R. Hoffmann, R. Brückner, *Chem. Ber.* **1992**, *125*, 1957.
[20] B. Hermans, L. Hevesi, *J. Org. Chem.* **1995**, *60*, 6141.
[21] A. Krief, M. Hobe, E. Badaoui, J. Bousbaa, W. Dumont, A. Nazih, *Synlett* **1993**, 707.
[22] Selected crystal structure data for **8**: crystal system orthorhombic; space group $P2_12_12_1$; Z = 4; cell parameters a = 5.6945(6), b = 22.663(2), c = 24.575(2); radiation (Mo-K_α) λ = 0.71073 Å; 382 variables for 4573 reflections; final R = 0.0723, R_w = 0.0683; CCDC-203167 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
[23] M. J. Robins, S. F. Wnuk, K. B. Mullah, N. K. Dalley, *J. Org. Chem.* **1994**, *59*, 544.
[24] A. P. Brunetière, J. Y. Lallemand, *Tetrahedron Lett.* **1988**, *29*, 2179.
[25] F. A. Davis, O. D. Stringer, *J. Org. Chem.* **1982**, *47*, 1774.
[26] J. C. Anderson, S. V. Ley, D. Santafianos, R. N. Sheppard, *Tetrahedron.* **1991**, *47*, 6813.
[27] Y. Díaz, A. El-Laghdach, M. I. Matheu, S. Castillón, *J. Org. Chem.* **1997**, *62*, 1501.
[28] G. Descotes, J.-C. Martin, *Carbohydr. Res.* **1977**, *56*, 168.
[29] Y. Shibata, Y. Kosuge, S. Ogawa, *Carbohydr. Res.* **1990**, *199*, 37.

Received February 18, 2003

