Elaboration of Monoarabinofuranosidic Building Blocks[‡]

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Keywords: Arabinofuranosides / Carbohydrates / Mycobacteria / Orthoesters

Nucleophilic opening of 1,2,5-orthoesters **1**, **2** and **6** of D-arabinose with alcohols, ethanethiol and selenophenol was carried out under very mild conditions with Lewis acid catalysis. The reaction is stereoselective and gave α-D-arabinofuranosides in high yields. Various monoarabinofuranosides, thio- and selenoglycoside donors as well as acceptors were obtained in few steps from the opening products. These building blocks define a comprehensive system of glycosylation for the synthesis of any glycosidic linkage between arabinofuranosides.

Introduction

The mycobacterium genus includes two human pathogens, *Mycobacterium leprae*, responsible for leprosy, and *M. tuberculosis*, the causative agent of tuberculosis, a major worldwide health problem taking millions of lives annually. The development of new drugs against mycobacterial infections requires a better understanding of their pathogenicity and the identification of new therapeutic targets.[1] One such is the arabinan biosynthetic pathway,[2] already identified as the site of action of ethambutol, a first-line anti-tuberculosis drug.[3−5] Mycobacteria make large use of D-arabinose for the construction of their cell walls, where it is to be found in arabinogalactan (AG) and lipoglycans: lipoarabinomannan (LAM) and arabinomannan (AM).[6,7] AG is the major component of the cell wall by weight, is covalently linked to the peptidoglycan and carries mycolic acids at its ends. LAM is a major antigen with various biological properties, depending on the mycobacterial species.[8,9] Although the structural models for AG and LAM show small differences, D-arabinose occurs in all these compounds as furanoside oligomers. The core of this arabinan domain is a chain with α-(1→5)-linked units (■, see Figure 1); branching is found when some of these units (◆ are also α-glycosylated with another arabinofuranosyl residue at the 3-position. At the end of the domain, β-arabinofuranosides (▲ are found, linked on the 2-position of the preceding residue. In AG, only Ara$_6$ motifs were found, while both Ara$_4$ and Ara$_6$ have been identified in LAM (Figure 1). In LAM, these terminal units are substituted on the 5-position by small motifs called caps, while in AG both terminal units (▲ and ●) may be esterified with mycolic acids on their 5-positions.[5] Renewed interest in oligoarabinofuranoside construction[10−17] has arisen from the isolation of a mycobacterial arabinose donor[18] and the development of an arabinosyl transferase assay that allows in vitro testing of inhibitors with synthetic oligoarabinofuranosidic acceptors.[4,11,19]

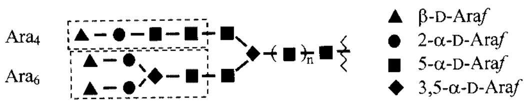

Figure 1. Schematic structural model of mycobacterial arabinans; ▲: attachment points for caps in LAMs; ▲, ●: attachment points for mycolic acids in AG

Although the glycosylation reaction, involving coupling of a glycosyl donor with an acceptor to give a disaccharide (Figure 2), is simple in principle, the synthesis of complex oligosaccharides is still a long and complicated task, owing to the variety of the linkages between sugar units involved. Control over the stereochemical outcome of the glycosylation can be obtained by an appropriate choice of substituent on the hydroxy group in position 2 in the donor: ester or similar groups give α-glycosides, while β-glycosides are obtained by use of the internal aglycon delivery (IAD) approach[20−26] (see Figure 2). Major simplification can be achieved if all the sugar units involved in the synthesis of an oligosaccharide − both donors and acceptors − can be obtained by the minimum number of steps from a common advanced synthetic precursor (divergent/convergent approach) and if some disaccharide blocks obtained from the first glycosylation, and usually used as acceptors for further elongation (plain arrow, Figure 2) can also play a donor role (broken arrow).

[‡] Synthesis of Oligoarabinofuranosides from the Mycobacterial Cell Wall, I

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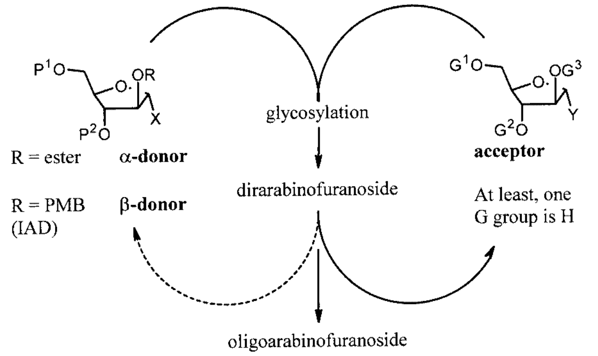


Figure 2. Schematic representation of a comprehensive system for the synthesis of oligoarabinofuranosides

We now report the implementation of a strategy based on this analysis and describe a comprehensive system for the elaboration of oligoarabinofuranosides capitalizing on the reactivity of 1,2,5-orthoesters of arabinose towards various nucleophiles (see Figure 3).

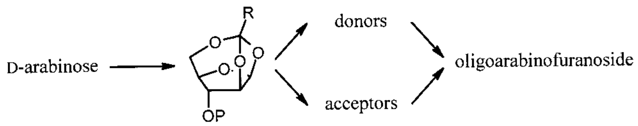


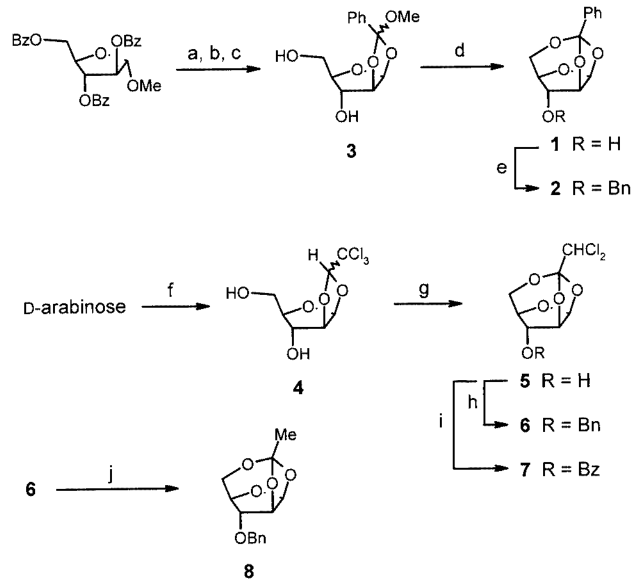
Figure 3. Divergent/convergent approach to oligoarabinofuranosides from 1,2,5-orthoesters of arabinose

It has been known for over 30 years that oligomerization of the 1,2,5-orthobenzoate of L-arabinose (the enantiomer of **1**, Scheme 1) can be initiated by treatment with a catalytic amount of an alcohol under acidic conditions.[27] High regio- and stereoselectivities have been observed for the opening reaction of the orthoester, and stereoregular arabinans with high proportions of α-(1→5)- and α-(1→3)-glycosidic linkages have been obtained.

We have now shown that: 1) oligomerization of the orthoester **1** can be avoided under suitable conditions, 2) the opening reaction is not restricted to alcohols and can be extended to sulfur and selenium nucleophiles, 3) other orthoesters of arabinose can be used, and 4) monoarabinofuranoside building blocks, ideally suited for construction of any possible oligoarabinofuranoside, are efficiently obtained from the products.

Among the numerous methods available for IAD, the procedure described by Ogawa,[25,26] which uses the 4-methoxybenzaldehyde acetal as a temporary tether, seemed to us to be the most convenient: products are easily prepared, they are stable, and this methodology has been shown to work for furanoside synthesis.[12,28,29]

This first paper deals with the preparation of arabinofuranoside building blocks from orthoesters of arabinose, while applications to the synthesis of various structural motifs of mycobacterial arabinans, including the terminal pentasaccharide of arabinogalactan and the caps of the LAM of *M. tuberculosis*, will be reported in the near future.[13,14]



Scheme 1. a: 10.5 equiv. CH_3OCHCl_2, 0.8 equiv. $SnCl_4$, CH_2Cl_2, room temp., 8 h; b: 2.0 equiv. NEt_3, 1.5 equiv. MeOH, 1.0 equiv. nBu$_4$NBr, 3 Å MS, CH_2Cl_2, room temp., 16 h, 86%, 2 steps; c: 0.01 M MeONa, MeOH, room temp., overnight, 92%; d: 0.03 equiv. camphorsulfonic acid, 4 Å MS, CH_2Cl_2, room temp., 0.5 h, 86%; e: 1.5 equiv. BnBr, 2 equiv. NaH, DMF, room temp., 1 h, 95%; f: chloral, H_2SO_4, reflux, 2 h, 43%; g: 2.0 equiv. *t*BuOK, *t*BuOH, 90 °C, 2 h, 78%; h: same as e, 90%; i: 1.5 equiv. BzCl, pyridine, room temp., 4 h, 86%; j: 5.0 equiv. Bu_3SnH, AIBN, toluene, reflux, 7 h, 84%

Synthesis of Orthoesters

Orthoester **1** was obtained from methyl tri-*O*-benzoyl-α-D-arabinofuranoside[30] in four steps (Scheme 1), by applying (with slight modifications) the procedure described by Kochetkov for L-arabinose.[31−34] It was found that, to ensure good and reproducible yields for the final step, the very acid-sensitive intermediate 1,2-orthoester **3** had to be purified on triethylamine-deactivated silica before use. The closing reaction had to be performed in the presence of large quantities of 4 Å molecular sieves to trap the released methanol efficiently. With these precautions, an overall yield of 66% for the four steps could routinely be obtained on a multigram scale.

Benzylation of **1** with benzyl bromide and sodium hydride in DMF gave the protected orthoester **2** in high yield.

Although orthodichloroacetate **5** has been mentioned in the literature,[35] no preparation was available. The procedure described for the preparation of the corresponding galactofuranose derivative[36] was thus investigated and adapted. Arabinose was treated with a large excess of anhydrous chloral in acidic medium to give 1,2-trichloroethylidene acetal **4** in 43% isolated yield after crystallization. Treatment of this acetal with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol gave the crystalline orthoester **5** in 78% yield. Protection of the 3-hydroxy group was then effected either with benzyl bromide and NaH to give the benzyl ether **6** (90%), or with benzoyl chloride and pyridine to afford the benzoate **7**, isolated in 86% yield.

Finally, the 1,2,5-orthoacetate of arabinose **8** could be obtained in 84% yield by radical reduction of the orthodichloroacetate **6** with tributyltin hydride and AIBN in refluxing toluene.[37]

Opening of Orthoesters of D-Arabinose

Opening with Alcohols

The opening reactions of orthoesters **1**, **2**, and **6** with alcohols under Lewis acid catalysis conditions were then investigated. The conditions described in ref.[27] for the oligomerization of the enantiomer of **1** are very drastic: the orthoester was heated under reflux in nitromethane with catalytic amounts of mercuric bromide as Lewis acid for 22 h. As we wanted to isolate monoarabinofuranosides (rather than to oligomerize the orthoester) and to use much milder conditions, we looked for different opening conditions.

For **1** and **2**, opening reactions were found to be very fast at 0 °C in acetonitrile or dichloromethane in the presence of 5−10% of Lewis acid. α-Glycosides were obtained in high yields and with complete regiocontrol: only products with the benzoate group on the 2-position of the ring were observed (see Figure 4), as determined from the NMR spectroscopic data. In the ^{13}C NMR spectra of compounds **9−16**, the observed chemical shifts for C-1 were found between δ = 104 and 108 ppm, typical values for α-arabinofuranosides.[38] Signals for 2-H in the ^{1}H NMR were found as broad doublets between δ = 5.0 and 5.5 ppm, indicating that this position was benzoylated, with the observed small coupling constant to 1-H ($J_{H1,H2} \leq 1.5$ Hz) confirming the α configuration of the anomeric center.[39]

A fivefold excess of alcohol was enough to suppress oligomerization of the orthoester, whereas treatment with only 1 equiv. of alcohol gave 25% of monoarabinofuranoside together with oligomers. No significant influence of the Lewis acid was noted: good to excellent yields of α-glycosides were obtained with 5−10% of tin tetrachloride, boron trifluoride−diethyl ether, or trimethylsilyl trifluoromethanesulfonate in dichloromethane (results are summarized in Table 1). Opening of **6** was more difficult, and the reactions had to be run at room temperature, for a longer period of time and with significantly larger quantities of acidic promoter. In this case the major 2-*O*-dichloroacetate derivative was always contaminated with a variable amount of the 5-*O*-dichloroacetate. The crude reaction mixture from the opening reactions was treated with catalytic sodium methoxide and the 2,5-diols were isolated.

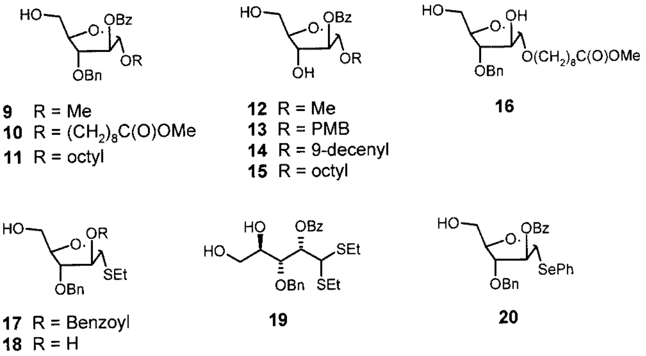


Figure 4. Products of opening of orthoesters **1**, **2**, and **6**

Opening with other Nucleophiles

The opening reactions of **2** and **6** with ethanethiol and selenophenol, intended to provide glycosyl donors, were then investigated. These reactions were found to be more sensitive to the reaction conditions than their alcohol-based counterparts, with mixtures of 5-*O*- and 2-*O*-benzoylated compounds being observed when **2** was treated with EtSH and $BF_3·OEt_2$ in dichloromethane. Tin tetrachloride and 1.2 equiv. of EtSH in dichloromethane were found to be superior for the synthesis of thioglycosides from **2** and **6**. The amounts of thiol and acidic promoter had to be controlled carefully, the use of a threefold excess of ethanethiol and a stoichiometric amount of $SnCl_4$ in the opening of **2** giving the diethyl dithioacetal derivative **19** in 62% yield. Opening of **2** was complete in 1.5 h at −15 °C with 0.08

Table 1. Nucleophilic opening of orthoesters

Orthoester	Nucleophile (equiv.)	Promoter (equiv.)	Product[a]	Yield (%)[b]
1	methanol (5.0)	$SnCl_4$ (0.1)	**12**	72
1	4-$MeOC_6H_4CH_2OH$ (5.0)	$SnCl_4$ (0.1)	**13**	77
1	9-decen-1-ol (5.0)	$SnCl_4$ (0.1)	**14**	81
1	octanol (5.0)	$SnCl_4$ (0.1)	**15**	95
2	methanol (5.0)	$SnCl_4$ (0.1)	**9**	86
2	$MeOC(O)[CH_2]_8OH$ (5.0)	$SnCl_4$ (0.1)	**10**	76
2	octanol (5.0)	$BF_3·OEt_2$ (0.1)	**11**	89
2	octanol (5.0)	TMSOTf (0.1)	**11**	90
6	$MeOC(O)[CH_2]_8OH$ (5.0)	$SnCl_4$ (2.0)	**16**	60
2	EtSH (1.2)	$SnCl_4$ (0.1)	**17**	77
2	EtSH (3.0)	$SnCl_4$ (2.1)	**19**	62
6	EtSH (1.2)	$SnCl_4$ (0.2)	**18**	64
2	PhSeH (1.0)	$SnCl_4$ (0.1)	**20**	61
2	PhSeH (1.0)	$HgBr_2$ (0.1)[c]	**20**	78

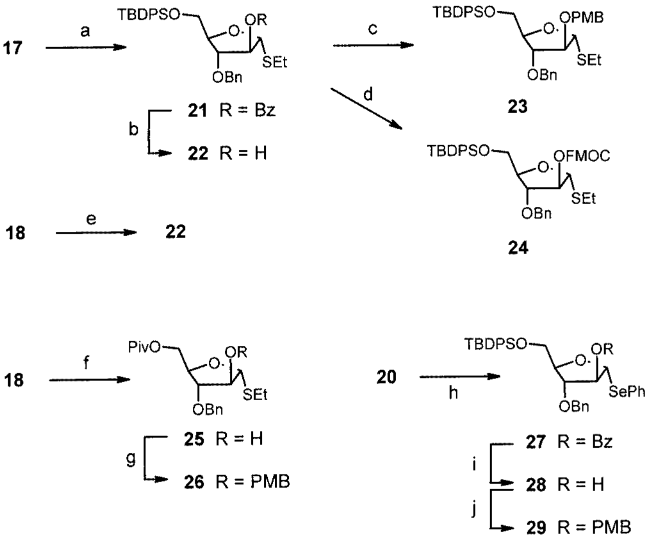
[a] For structural formulas, see Figure 4. [b] Isolated yields of homogeneous, analytically pure products. [c] Reaction performed in acetonitrile.

equiv. of $SnCl_4$, while opening of **6** required more acid promoter (0.2 equiv.) and a reaction time of 2 h at 0 °C. In this case, small amounts (4%) of the β-anomer of **18** were also isolated from the reaction mixture. For unclear reasons and despite numerous experiments, opening of **1** with ethanethiol was sluggish under any conditions tried (best yields 25%); this is in sharp contrast with the troublefree reaction between **1** and alcohols.

Phenyl selenoglycoside **20** has been obtained in 61% yield by treatment of **2** with phenylselenophenol[40] and 10% $SnCl_4$ in dichloromethane.[14] However, the best results (78%) were obtained with a combination of 1.0 equiv. of PhSeH and catalytic quantities of mercuric bromide in acetonitrile, the only case in which acetonitrile proved to be superior to dichloromethane for opening of the orthoesters. Selenoglycosides are of particular interest, as they might be selectively activatable in the presence of thioglycosides[41,42] to yield oligosaccharide glycosyl donors (X = SePh, Y = SEt; Figure 2).

Elaboration of Donors

The opening products of the orthoesters were then transformed into the required glycosyl donors. As compounds deriving from the opening of **2** already have a participating ester group on the 2-position of the ring, silylation of the 5-position with *tert*-butylchlorodiphenylsilane (TBDPSCl) was enough to provide α-donors. Thioglycoside **21** and selenoglycoside **27** were thus obtained in 93% and 86% yields, respectively, from **17** and **20** (Scheme 2). The synthesis of the β-donor **23** began with the removal of the 2-*O*-benzoyl group of **21** with catalytic sodium methoxide in methanol and afforded alcohol **22**, ready for the attachment of the temporary tether required for the IAD procedure.[25,26] A much better precursor to glycosyl donors (α and β), however, was compound **18**, obtained in 64% yield from orthoester **6**. Monoprotection of the primary position of the ring was easily accomplished with TBDPSCl, to give **22** in 80% yield, or with pivaloyl chloride in pyridine, to give **25** (65%).



Scheme 2. a :1.5 equiv. tBu(Ph)$_2$SiCl, imidazole, DMF, room temp., 1 h, 93%; b: 0.01 M MeONa, MeOH, room temp., overnight, 80%; c: 2.5 equiv. 4-MeOBnBr, 2.5 equiv. BEMP, CH_3CN, 0 °C to room temp., 3 h, 67%; d: 1.5 equiv. FMOC-Cl, pyridine, CH_2Cl_2, room temp., 1 h, 82%; e: same as a, 80%; f: 1.3 equiv. PivCl, 0.1 equiv. DMAP, pyridine, 0 °C to room temp., 2.5 h, 65%; g: same as c, 67%; h: same as a, 86%; i: same as b, room temp., overnight, 84%; j: same as c, 1 h, 75%

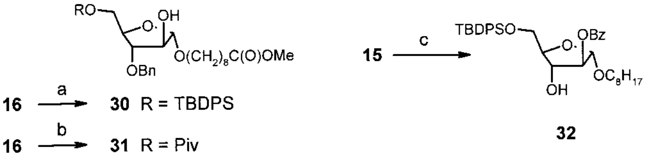
This left the introduction of the controlling element for the glycosylation on the 2-hydroxy group of the arabinose ring at the very last stage of the synthesis of the donors. Introduction of the 4-methoxybenzyl ether[25,26] was found to be difficult. Under standard benzylation conditions (NaH, 4-MeOBnCl, DMF) or with use of phase-transfer catalysis (4-MeOBnCl, Bu_4NHSO_4, aqueous NaOH)[43] almost complete degradation of starting material was observed, and compound **23** was only isolated in very low yields. This problem was eventually solved by use of the hindered strong base 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP)[44−46] and 4-methoxybenzyl bromide[47] in acetonitrile, β-donor **23** being obtained in 70% yield from **22** under these conditions.

From **22**, a wide range of α-donors is accessible. The α-donor **24**, for example, was easily obtained in 82% yield by treatment of **22** with 9-fluorenylmethyl chloroformate (FMOC-Cl) and pyridine in CH_2Cl_2. The choice of the FMOC group as participating group for glycosylation was based on its easy removal in the presence of other ester groups (benzoate or pivalate). In an analogous manner, β-donor **26** was obtained in 67% yield from **25**. The use of **18** as a pivotal point to α- and β-donors gives maximum flexibility for the introduction of various protecting group on position 5 and of different control elements for glycosylation on position 2. This opens the way to the synthesis of a wide range of tailor-made thioglycoside donors in only three steps from orthoester **6**.

Another class of α- and β-donors was obtained from selenoglycoside **20**. Protection of the primary hydroxy group of **20** was achieved with TBDPSCl by the use of the same chemistry as above, and gave α-donor **27** in 86% yield. Basic removal of the benzoyl group (84%) and introduction of the *p*-methoxybenzyl ether with BEMP gave the corresponding β-donor **29** in 75%.

Elaboration of Acceptors

One major feature of our system is that many of the acceptors are the products of opening of the orthoesters and might be usable directly for elaboration of oligoarabinofuranosides. Compounds **12−15** (Figure 4) are acceptors on positions 3 and 5, compounds **9−11** are 5-acceptors. Acceptors on position 2 were available in a single step from opening product **16** (Scheme 3), monoprotection of the primary hydroxy group, as described above for the preparation of donors, was performed with TBDPSCl to give **30** (69%) and with PivCl to give **31** (80%). The last acceptor on position 3, although not relevant to the synthesis of mycobacterial arabinan fragments, was obtained by monosilylation of the primary hydroxy group of **15**, and gave **32** in 77% isolated yield. Finally, thioglycosides **21**, **22**, and **25**, which are synthetic intermediates for the preparation of α- and β-donors (Scheme 2), are also acceptors for selenoglycosides donors **27** or **29**.



Scheme 3. a: 1.4 equiv. *t*Bu(Ph)$_2$SiCl, imidazole, DMF, room temp., 1 h, 69%; b: 1.5 equiv. PivCl, 0.1 equiv. DMAP, pyridine, 0 °C, 1.5 h, 80%; c: same as a, 77%

Conclusion

We have shown that nucleophilic opening of various 1,2,5-orthoesters of D-arabinose with alcohols, ethanethiol, and selenophenol under Lewis acid catalysis conditions occurred with complete regio- and stereoselectivities. α-D-Arabinofuranosides were obtained in every case, in good to excellent yields. These compounds were then elaborated to provide a wide range of arabinofuranosidic donors and acceptors in a very efficient way. From the orthoesters, a maximum of two steps was enough to provide any acceptor, while the longest sequence to donors was only four steps. Our results on the use of these blocks for the construction of fragments of mycobacterial arabinans[13,14] will be reported in the near future.

Experimental Section

General: All reactions were performed under argon in oven-dried glassware. Anhydrous solvents were distilled before use. Commercial reagents were used as received. Published procedures were applied for preparation of methyl 9-hydroxynonanoate,[48] selenophenol,[40] and 4-methoxybenzyl bromide.[47] Chromatographic separations were performed on silica gel (35−70 µm) obtained from SDS (Peypin, France). NMR spectra were recorded with a Bruker AM 250 spectrometer, working at 250 MHz for ^{1}H and 62.89 MHz for ^{13}C. All chemical shifts are expressed in ppm from internal tetramethylsilane. Optical rotations were measured at 25 °C with a Perkin−Elmer 41 polarimeter. Elemental analyses were obtained from the Laboratoire de Chimie de Coordination du CNRS at Toulouse (France).

β-D-Arabinofuranose 1,2,5-Orthobenzoate (1): $[\alpha]_D^{25} = -28$ (c = 0.94 in chloroform) {ref.[31] $[\alpha]_D^{25} = +28$ (c = 1 in chloroform) for the enantiomer}. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.97 (d, $^3J_{OH,3}$ = 7.5 Hz, 1 H, 3-OH), 4.06 (dd, $^2J_{5',5}$ = 13.0, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.14 (dd, $^2J_{5,5'}$ = 13.0, $^3J_{5,4}$ = 1.0 Hz, 1 H, 5-H), 4.42 (m, 1 H, 4-H), 4.52 (br. d, $^3J_{3,OH}$ = 7.5 Hz, 1 H, 3-H), 4.72 (dd, $^3J_{2,H}$ = 3.5, $^3J_{2,3}$ = 1.5 Hz, 1 H, 2-H), 6.13 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 7.20−7.70 (2 m, 5 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 69.3 (C-5), 83.6 (2), 83.7 (C-2, C-3, C-4), 103.7 (C-1), 121.8, 125.8, 128.1, 129.6, 135.8 (Ar) ppm.

3-*O*-Benzyl-β-D-arabinofuranose 1,2,5-Orthobenzoate (2): Compound **1** (414 mg, 1.69 mmol) in DMF (3 mL) was benzylated with benzyl bromide (302 µL, 2.54 mmol) and NaH (135 mg of a 60% suspension in mineral oil, washed twice with petroleum ether, 3.38 mmol) for 30 min at room temperature before quenching with a few drops of MeOH. CH$_2$Cl$_2$/water extraction and chromatography (petroleum ether/ethyl acetate, 4:1) gave **2** (543 mg, 95%). $[\alpha]_D^{25} = -52$ (c = 1.1 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 3.98 (dd, $^2J_{5,5'}$ = 12.5, $^3J_{5,4}$ = 3.5 Hz, 1 H, 5-H), 4.12 (dd, $^2J_{5',5}$ = 12.5, $^3J_{5',4}$ = 1.5 Hz, 1 H, 5-H), 4.24 (s, 1 H, 3-H), 4.51 (m, 1 H, 4-H), 4.67 and 4.60 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 4.82 (dd, $^3J_{2,1}$ = 4.0, $^4J_{2,4}$ = 1.5 Hz, 1 H, 2-H), 6.12 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 68.9 (C-5), 71.6 (CH$_2$-benzyl), 81.2 (2), 83.5 (C-2, C-3, C-4), 104.0 (C-1), 121.0, 125.8, 127.8, 128.0, 128.1, 128.6, 129.5, 135.8, 137.0 ppm. C$_{19}$H$_{18}$O$_5$ (326.3): calcd. C 69.93, H 5.56; found C 70.31, H 5.79.

1,2-*O*-(2,2,2-Trichloroethylidene)-β-D-arabinofuranose (4): A suspension of D-arabinose (100 g, 0.67 mol) in anhydrous chloral (250 mL) was treated with concentrated H$_2$SO$_4$ (6 mL, 67 mmol) at reflux for 2 h. Chloroform was added in two portions: one of 130 mL to the hot solution (***CAUTION!***) and one of 600 mL after cooling to room temp. The mixture was stirred overnight and the resulting black solid was filtered and rinsed with CHCl$_3$. This solid was deposited on Celite and washed with methanol, and the washings were concentrated. The brown residue was recrystallized from boiling methanol, filtered and washed with CH$_2$Cl$_2$ to give a light brown solid (56 g, 30%). A further crop (24 g, 13%) was obtained from similar treatment of the mother liquor. M.p. 184 °C (ref.[35] 184−186 °C). $[\alpha]_D^{25} = +25$ (c = 1.06 in methanol) {ref.[35] $[\alpha]_D^{25}$ = +30.2 (c = 1.7 in methanol)}. ^{1}H NMR (250 MHz, CD$_3$OD, 25 °C): δ = 3.67 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 6.5 Hz, 1 H, 5-H), 3.72 (dd, $^2J_{5',5}$ = 11.0, $^3J_{5',4}$ = 6.5 Hz, 1 H, 5-H), 4.16 (dt, $^3J_{4,5}$ = 6.5, $^3J_{4,5}$ = 6.5, $^3J_{4,3}$ = 1.5 Hz, 1 H, 4-H), 4.33 (d, $^3J_{3,4}$ = 1.5 Hz, 1 H, 3-H), 4.92 (d, $^3J_{2,1}$ = 4.0 Hz, 1 H, 2-H), 5.77 (s, 1 H, CHCCl$_3$), 6.33 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CD$_3$OD, 25 °C): δ = 63.3 (C-5), 76.6 (C-3), 90.8, 90.9, 101.4, 109.2 (C-1), 110.7 (C-acetal) ppm. C$_7$H$_9$Cl$_3$O$_5$ (279.5): calcd. C 30.08, H 3.24; found C 30.17, H 2.89.

β-D-Arabinofuranose 1,2,5-Orthodichloroacetate (5): Compound **4** (1.33 g, 4.77 mmol) was dissolved in *tert*-butyl alcohol (48 mL), and potassium *tert*-butoxide (1.10 g, 9.80 mmol) was added. The mixture was heated under reflux for 2 h before cooling and addition of NH$_4$Cl (300 mg, 5.60 mmol). The solvent was evaporated and the residue was extracted with EtOAc/water to yield a white solid, which was recrystallized from EtOAc/petroleum ether (902 mg, 78%). M.p. 123 °C (ref.[35] 117−119 °C). $[\alpha]_D^{25} = -37$ (c = 1.00 in methanol) {ref.[35] $[\alpha]_D^{25} = -41.0$ (c = 1.26 in methanol)}. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 4.04 (m, 2 H, 5-H), 4.39 (m, 2 H, 3-H, 4-H), 4.66 (dd, $^3J_{2,1}$ = 4.0, $^3J_{2,3}$ = 1.5 Hz, 1 H, 2-H), 5.76 (s, 1 H, CHCl$_2$), 6.08 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H) ppm.^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 68.9, 69.2 (C-5, CHCl$_2$), 76.0 (C-3), 83.6, 83.9 (C-2, C-4), 104.2 (C-1), 119.3 (C-orthoester) ppm. C$_7$H$_8$Cl$_2$O$_5$ (243.0): calcd. C 34.59, H 3.32; found C 34.82, H 3.04.

3-*O*-Benzyl-β-D-arabinofuranose 1,2,5-Orthodichloroacetate (6): Compound **5** (902 mg, 3.71 mmol) was dissolved in DMF (12 mL) and treated with benzyl bromide (530 µL, 4.45 mmol) and NaH (297 mg of a 60% suspension in mineral oil, washed twice with petroleum ether, 7.42 mmol). After 1 h at room temp, the reaction mixture was treated with ethanol and water and extracted with CH$_2$Cl$_2$. Recrystallization of the residue from EtOAc/petroleum ether gave **6** as a white solid (1.11 g, 90%). m.p. 107 °C. $[\alpha]_D^{25}$ =

−23 (c = 1.04 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 3.99 (dd, $^2J_{5,5'}$ = 13.0, $^3J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 4.06 (dd, $^2J_{5',5}$ = 13.0, $^3J_{5',4}$ = 1.5 Hz, 1 H, 5-H), 4.19 (s, 1 H, 3-H), 4.51 (dd, $^3J_{4,5}$ = 3.0, $^3J_{4,5}$ = 1.5 Hz, 1 H, 4-H), 4.59 and 4.65 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 4.81 (dd, $^3J_{2,1}$ = 4.0, $^3J_{2,3}$ = 1.5 Hz, 1 H, 2-H), 5.74 (s, 1 H, C*H*Cl$_2$), 6.09 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 7.30−7.40 (m, 5 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 69.3, 69.4 (C-5, CHCl$_2$), 71.7 (CH$_2$-benzyl),. 81.3, 81.7, 83.0 (C-2, C-3, C-4), 104.5 (C-1), 119.5 (C-orthoester), 127.7, 128.2, 128.6, 136.7 (Ar) ppm. C$_{14}$H$_{14}$Cl$_2$O$_5$ (333.2): calcd. C 50.47, H 4.23; found C 50.32, H 4.06.

3-*O*-Benzoyl-β-D-arabinofuranose 1,2,5-Orthodichloroacetate (7): Compound **5** (1.31 g, 5.39 mmol) was dissolved at 0 °C in pyridine (15 mL) and treated by dropwise addition of benzoyl chloride (0.94 mL, 8.09 mmol). The mixture was left at room temperature for 4 h, hydrolyzed with water, and extracted with CH$_2$Cl$_2$. The organic phase was washed once with water and dried, and the solvent was evaporated. The resulting solid was washed three times with petroleum ether to give **7** as a white solid (1.37 g, 73%). A further crop of product (0.24 g, 13%) was obtained from chromatography (petroleum ether/dichloromethane, 1:1) of the petroleum ether washings. $[\alpha]_D^{25}$ = −76 (c = 1.40 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 4.12 (dd, $^2J_{5,5'}$ = 13.0, $^3J_{5,4}$ = 1.5 Hz, 5-H), 4.22 (dd, $^2J_{5',5}$ = 13.0, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.66 (m, 1 H, 4-H), 4.95 (dd, $^3J_{2,1}$ = 3.5, $^3J_{2,4}$ = 2.0 Hz, 1 H, 2-H), 5.50 (s, 1 H, 3-H), 5.81 (s, 1 H, CHCl$_2$), 6.17 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 7.46 (td, $^3J_{ortho}$ = 7.5, $^3J_{meta}$ = 1.0 Hz, 2 H, Ar-H), 7.61 (td, $^3J_{ortho}$ = 7.5, $^3J_{meta}$ = 1.0 Hz, 1 H, Ar-H), 8.30 (d, $^3J_{ortho}$ = 7.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 68.9, 69.1 (C-5, CHCl$_2$), 76.7 (*C*H$_2$-benzyl), 78.1, 82.1 (2), 84.1, 104.3 (C-1), 119.9 (C-orthoester), 128.8, 129.8, 133.7 (Ar), 165.4 (CO-benzoyl) ppm. C$_{14}$H$_{12}$Cl$_2$O$_6$ (347.1): calcd. C 48.44, H 3.48; found C 48.50, H 3.10.

3-*O*-Benzyl-β-D-arabinofuranose 1,2,5-Orthoacetate (8): Compound **6** (200 mg, 0.60 mmol) and tributyltin hydride (0.81 mL, 3.00 mmol) were dissolved in toluene (6 mL). The mixture was brought to reflux and AIBN (1.75 mL of a 0.24 M solution in toluene, 0.42 mmol) was added over 7 h by syringe pump. Evaporation of solvent and chromatography (petroleum ether/ethyl acetate, 8:1 to 6:1) gave **8** as a white solid (134 mg, 84%). $[\alpha]_D^{25}$ = −38 (c = 1.10 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.64 (s, 3 H, CH$_3$), 3.77 (dd, $^2J_{5,5'}$ = 13.0, $^3J_{5,4}$ = 3.0 Hz, 5-H), 3.91 (dd, $^2J_{5',5}$ = 13.0, $^3J_{5',4}$ = 1.0 Hz, 1 H, 5-H), 4.08 (br. s, 1 H, 3-H), 4.41 (ddd, $^3J_{4,5}$ = 3.0, $^3J_{4,5'}$ = 1.0, $^3J_{4,3}$ = 1.0 Hz, 1 H, 4-H), 4.63 (dd, $^3J_{2,1}$ = 4.0, $^3J_{2,3}$ = 1.5 Hz, 1 H, 2-H), 4.58 and 4.64 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.95 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 7.30−7.40 (m, 5 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C, TMS): δ = 22.5 (CH$_3$), 68.2 (C-5), 71.6 (CH$_2$-benzyl), 81.2 (2), 83.4 (C-2, C-3, C-4), 103.9 (C-1), 122.1 (C-orthoester), 127.8, 128.6, 128.9, 137.0 (Ar) ppm. C$_{14}$H$_{16}$O$_5$ (264.3): calcd. C 63.63, H 6.10; found C 63.40, H 5.82.

General Procedure for the Opening of Orthoesters 1 and 2 with Alcohols: The orthoester was stirred in CH$_2$Cl$_2$ (0.2 M solution) with the alcohol (5 equiv.) and 4 Å molecular sieves for 15 min. The mixture was cooled to 0 °C before addition of the Lewis acid (0.1 equiv. as a 1 M solution in toluene). After completion of the reaction, the mixture was hydrolyzed with 5% NaHCO$_3$ and extracted with CH$_2$Cl$_2$. Chromatographic purification gave the glycoside.

General Procedure for the Opening of Orthoester 6 with Alcohols: Compound **6** (0.3 M solution) was stirred in CH$_2$Cl$_2$ with the alcohol (5 equiv.) and 4 Å molecular sieves for 15 min. The mixture was cooled to 0 °C before addition of the Lewis acid (1 equiv. as a 1 M solution in toluene). After completion of the reaction, the mixture was hydrolyzed with 5% NaHCO$_3$ and filtered through Celite. The filtrate was diluted with EtOAc, the organic phase was washed with saturated NaHCO$_3$ and dried, and the solvent was evaporated. The residue was treated for 1 h at room temp with NaOMe (0.01 M solution in MeOH). Neutralization with an H$^+$ resin, filtration, concentration, and chromatographic purification gave the glycoside.

Methyl 2-*O*-Benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (9): This compound was prepared from **2** (43 mg, 0.13 mmol), petroleum ether/ethyl acetate (2:1), 46 mg, 96%. $[\alpha]_D^{25}$ = +19 (c = 1.60 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.91 (dd, $^3J_{\mathrm{OH},5}$ = 8.0, $^3J_{\mathrm{OH},5'}$ = 4.0 Hz, 1 H, 5-OH), 3.45 (s, 3 H, OCH$_3$), 3.64 (m, $^2J_{5,5'}$ = 12.0, $^3J_{5,\mathrm{OH}}$ = 8.0, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.87 (m, $^2J_{5',5}$ = 12.0, $^3J_{5',4}$ ≈ $^3J_{5',\mathrm{OH}}$ ≈ 3.5 Hz, 1 H, 5-H), 4.07 (m, 1 H, 3-H), 4.24 (m, 1 H, 4-H), 4.63 and 4.83 (2 d, ^2J = 13.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.06 (br. s, 1 H, 1-H), 5.36 (d, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 54.9 (OMe), 61.9 (C-5), 72.5 (CH$_2$-benzyl), 81.9, 82.6, 83.1 (C-2, C-3, C-4), 107.3 (C-1), 127.9, 128.0, 128.4, 128.5, 129.7, 133.4, 137.4, 165.4 (CO-benzoyl) ppm. C$_{20}$H$_{22}$O$_6$ (358.4): calcd. C 67.02, H 6.18; found C 67.28, H 5.93.

8-Methoxycarbonyloctyl 2-*O*-Benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (10): This compound was prepared from **2** (214 mg, 0.65 mmol), toluene/ethyl acetate (4:1), 256 mg, 76%. $[\alpha]_D^{25}$ = +101 (c = 1.60 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.26−1.41 and 1.55−1.69 (2 m, 4H and 8 H, CH$_2$-octyl), 1.89 (dd, $^3J_{\mathrm{OH},5}$ = 8.5, $^3J_{\mathrm{OH},5'}$ = 4.5 Hz, 1 H, 5-OH), 2.30 (t, ^3J = 6.5 Hz, 2 H, CH$_2$CO), 3.48 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH$_2$-octyl), 3.67 (s, 3 H, OMe), 3.67 (m, $^2J_{5,5'}$ = 12.0, $^3J_{5,\mathrm{OH}}$ = 8.5, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.75 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH$_2$-octyl), 3.88 (m, $^2J_{5',5}$ = 12.0, $^3J_{5',\mathrm{OH}}$ = 4.5, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.06 (m, $^3J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.24 (m, 1 H, 4-H), 4.60 and 4.83 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.14 (br. s, 1 H, 1-H), 5.37 (d, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 24.9, 26.0, 29.0, 29.1, 29.3, 34.1 (CH$_2$-octyl), 51.5 (CH$_3$), 62.0 (OCH$_2$-octyl), 67.6 (C-5), 72.4 (CH$_2$-benzyl), 82.1, 82.9 (2) (C-2, C-3, C-4), 106.1 (C-1), 127.8, 128.4, 128.5, 128.5, 129.4, 129.7, 133.4, 137.6, 165.4 (CO-benzoyl), 174.4 (CO-methyl ester) ppm. C$_{29}$H$_{38}$O$_8$ (514.6): calcd. C 67.68, H 7.44; found C 67.37, H 7.55.

Octyl 2-*O*-Benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (11): This compound was prepared from **2** (29 mg, 0.09 mmol), petroleum ether/ethyl acetate (3:1), 38 mg, 90%. $[\alpha]_D^{25}$ = +88 (c = 1.05 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.88 (m, 3 H, CH$_3$-octyl), 1.22−1.41 and 1.53−1.69 (2 m, 4 H and 8 H, CH$_2$-octyl), 1.90 (m, 1 H, 5-OH), 3.48 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH$_2$-octyl), 3.66 (m, $^2J_{5,5'}$ = 12.0, $^3J_{5,\mathrm{OH}}$ = 8.5, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.73 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH$_2$-octyl), 3.88 (m, $^2J_{5',5}$ = 12.0, $^3J_{5',\mathrm{OH}}$ = 4.5, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.06 (m, $^3J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.24 (m, $^3J_{4,3}$ = 5.5, $^3J_{4,5}$ = 4.0, $^3J_{4,5}$ = 3.0 Hz, 1 H, 4-H), 4.60 and 4.83 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.14 (br. s, 1 H, 1-H), 5.38 (d, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ =14.1, 22.7, 29.2, 29.36, 29.40, 31.8 (CH$_2$-octyl), 62.0 (OCH$_2$-octyl), 67.7 (C-5), 72.4 (CH$_2$-benzyl), 82.1, 82.9 (2) (C-2, C-3, C-4), 106.1 (C-1), 127.8, 127.8, 128.4, 128.5, 129.4, 129.8, 133.4, 137.6 (Ar), 165.4 (CO-benzoyl) ppm. C$_{27}$H$_{36}$O$_6$ (456.6): calcd. C 71.03, H 7.95; found C 71.00, H 7.94.

Methyl 2-*O*-Benzoyl-α-D-arabinofuranoside (12): This compound was prepared from **1** (50 mg, 0.21 mmol), petroleum ether/ethyl acetate (1:1), 40 mg, 72%. $[\alpha]_D^{25}$ = +88 (c = 0.97 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 3.40 (m, 1 H, 3-H), 3.46 (s, 3 H, OMe), 3.79 (br. d, $^3J_{5,5'}$ = 12.0 Hz, 1 H, 5-H), 3.95 (br. d, $^3J_{5,5'}$ = 12.0 Hz, 1 H, 5-H), 4.20 (m, 1 H, 4-H), 5.08 (br. d, $^3J_{2,3}$ = 1.5 Hz, 1 H, 2-H), 5.16 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 55.0 (OMe), 61.8 (C-5), 76.3, 84.0, 85.9 (C-2, C-3, C-4), 106.4 (C-1), 128.5, 128.9, 129.7, 133.6, 166.6 (CO-benzoyl) ppm. $C_{13}H_{16}O_6$ (268.3): calcd. C 58.20, H 6.01; found C 58.49, H 6.14.

4-Methoxybenzyl 2-*O*-Benzoyl-α-D-arabinofuranoside (13): This compound was prepared from **1** (30 mg, 0.13 mmol), petroleum ether/ethyl acetate (3:2), 36 mg, 76%. $[\alpha]_D^{25}$ = +121 (c = 0.95 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.10 (br, 1 H, 5-OH), 3.39 (d, $^3J_{OH,3}$ = 5.5 Hz, 1 H, 3-OH), 3.80 (ddd, $^2J_{5,5'}$ = 12.0, $^3J_{5,OH}$ = 7.5, $^3J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 3.80 (s, 3 H, OMe), 3.95 (ddd, $^2J_{5',5}$ = 12.0, $^3J_{5',4}$ = 4.5, $^3J_{5',OH}$ = 3.0 Hz, 1 H, 5-H), 4.18 (m, $^3J_{3,4}$ = 6.0, $^3J_{3,OH}$ = 5.5, $^3J_{3,2}$ = 2.5 Hz, 1 H, 3-H), 4.24 (ddd, $^3J_{4,3}$ = 6.0, $^3J_{4,5}$ = 4.5, $^3J_{4,5}$ = 3.0 Hz, 1 H, 4-H), 4.53 and 4.77 (2 d, ^2J = 11.5 Hz, 2 × 1 H, CH_2-benzyl), 5.14 (dd, $^3J_{2,3}$ = 2.5, $^3J_{2,1}$ = 1.0 Hz, 1 H, 2-H), 5.31 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 55.2 (OMe), 61.9 (C-5), 68.7, 76.4 (CH_2-benzyl), 84.1, 86.0, 104.0 (C-1), 113.9, 128.5, 128.9, 129.7, 133.6, 159.3, 166.6 (CO-benzoyl) ppm. $C_{20}H_{22}O_7$ (374.4): calcd. C 64.16, H 5.92; found C 64.33, H 6.04.

9-Decenyl 2-*O*-Benzoyl-α-D-arabinofuranoside (14): This compound was prepared from **1** (200 mg, 0.85 mmol), petroleum ether/ethyl acetate (2:1), 270 mg, 81%. $[\alpha]_D^{25}$ = +84 (c = 1.10 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.25−1.42 and 1.56−1.67 (2 m, 2H and 12 H, CH_2-decenyl), 1.88 [m, 1 H, 5-OH), 2.09−1.99 (m, 2 H, $CH_2{-}CH{=}CH_2$), 3.26 (m, 1 H, 3-OH), 3.49 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-decenyl), 3.78 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-decenyl), 3.80 (m, $^2J_{5,5'}$ = 12.5, $^3J_{5,OH}$ = 7.5, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.95 (ddd, $^2J_{5',5}$ = 12.5, $^3J_{5',OH}$ = 5.0, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.14−4.24 (m, 2 H, 3-H, 4-H), 4.90−5.04 (m, 2 H, $CH_2{=}CH$-decenyl), 5.08 (dd, $^3J_{2,3}$ = 2.5, $^3J_{2,1}$ = 1.0 Hz, 1 H, 2-H), 5.25 (br. s, 1 H, 1-H), 5.81 (m, $^3J_{9',10'}$ = 16.5, $^3J_{9',10'}$ = 10.0, $^3J_{9',8'}$ = 6.5, $^3J_{9',8'}$ = 6.5 Hz, 1 H, $CH_2{=}CH$-decenyl) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 26.0, 28.8, 29.0, 29.3, 29.4, 29.4, 33.7 (CH_2-decenyl), 61.9 (C-5) 67.9 (OCH_2-decenyl), 76.4 (C-3), 84.0, 86.0 (C-2, C-4), 105.2 (C-1), 114.1, 128.5, 129.0, 129.7, 133.6, 139.2, 166.7 (CO-benzoyl) ppm. $C_{22}H_{32}O_6$ (392.5): calcd. C 67.32, H 8.22; found C 67.10, H 7.86.

Octyl 2-*O*-Benzoyl-α-D-arabinofuranoside (15): This compound was prepared from **1** (142 mg, 0.60 mmol), petroleum ether/ethyl acetate (2:1 then 3:2), 211 mg (95%). $[\alpha]_D^{25}$ = +89 (c = 1.10 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 0.88 (m, 3 H, CH_3-octyl), 1.20−1.40 and 1.55−1.70 (2 m, 4 H and 8 H, CH_2-octyl), 1.82 (dd, $^3J_{OH,5}$ = 7.5, $^3J_{OH,5}$ = 5.0 Hz, 1 H, 5-OH), 3.24 (d, $^3J_{OH,3}$ = 5.5 Hz, 3-OH), 3.49 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.78 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.80 (ddd, $^2J_{5,5}$ = 12.0, $^3J_{5,OH}$ = 7.5, $^3J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 3.94 (ddd, $^2J_{5',5}$ = 12.0, $^3J_{5',OH}$ = 5.0, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.14−4.24 (m, 2 H, 3-H, 4-H), 5.08 (dd, $^3J_{2,3}$ = 2.5, $^3J_{2,1}$ = 1.0 Hz, 1 H, 2-H), 5.26 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 25.9, 29.1, 29.3, 29.4, 31.7 (CH2-octyl), 61.8 (C-5), 67.8 (OCH_2-octyl), 76.2 (C-3), 83.9, 85.9 (C-2, C-4), 105.2 (C-1), 128.4, 128.9, 129.7, 133.5, 166.6 (CO-benzoyl) ppm. $C_{20}H_{30}O_6$ (366.4): calcd. C 65.55, H 8.25; found C 65.46, H 7.99.

8-Methoxycarbonyloctyl 3-*O*-Benzyl-α-D-arabinofuranoside (16): This compound was prepared from **6** (107 mg, 0.32 mmol), toluene/ethyl acetate (2:1), 79 mg, 60%. $[\alpha]_D^{25}$ = +97 (c = 1.21 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.25−1.40 and 1.50−1.65 (2 m, octyl), 2.06 (dd, $^3J_{OH,5}$ = 6.5, $^3J_{OH,5}$ = 4.5 Hz, 1 H, 5-OH), 2.30 [t, ^3J = 7.5 Hz, 2 H, $C(O)CH_2$-octyl], 2.77 (d, $^3J_{OH,2}$ = 8.0 Hz, 1 H, 2-OH), 3.42 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.63 (ddd, $^2J_{5,5}$ = 12.0, $^3J_{5,OH}$ = 6.5, $^3J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 3.66 (s, 3 H, OMe), 3.70 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.86 (dd, $^3J_{3,4}$ = 4.5, $^3J_{3,2}$ = 2.0 Hz, 1 H, 3-H), 3.87 (ddd, $^2J_{5,5}$ = 12.0, $^3J_{5,OH}$ = 4.0, $^3J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 4.19 (m, 2 H, 2-H, 4-H), 4.58 and 4.71 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 4.97 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.8, 25.9, 28.9, 29.0, 29.3, 33.9 (CH_2-octyl), 51.4 (OMe), 61.8 (C-5), 67.4 (OCH_2-octyl), 71.9 (CH_2-benzyl), 78.8, 83.4, 84.9 (C-2, C-3, C-4), 108.6 (C-1), 127.6, 127.6, 128.3, 137.8, 174.4 (CO-ester) ppm. $C_{22}H_{34}O_7$ (410.5): calcd. C 64.37, H 8.35; found C 64.03, H 8.40.

Ethyl 2-*O*-Benzoyl-3-*O*-benzyl-1-thio-α-D-arabinofuranoside (17): Orthoester **2** (4.04 g, 12.38 mmol) was dissolved in CH_2Cl_2 (100 mL), powdered 3 Å molecular sieves were added, and the mixture was stirred for 1.5 h at room temperature. The temperature was brought to −15 °C, and EtSH (1.12 mL, 15.12 mmol) and $SnCl_4$ (62 μL of a 1 M solution in toluene, 0.06 mmol) were added. After 1 h at −15 °C, another portion of $SnCl_4$ (37 μL of a 1 M solution in toluene, 0.04 mmol) was added and the reaction mixture was left for 30 min before quenching with a few drops of satd. $NaHCO_3$ and filtration through Celite. Workup of the filtrate (H_2O/CH_2Cl_2) and chromatography (petroleum ether/ethyl acetate, 4:1 then 3:1) gave **17** as a colorless oil (3.72 g 77%). $[\alpha]_D^{25}$ = +178 (c = 1.10 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.33 (t, ^3J = 7.5 Hz, 3 H, S CH_2CH_3), 1.79 (dd, $^3J_{OH,5}$ = 8.0, $^3J_{OH,5'}$ = 4.0 Hz, 1 H, 5-OH), 2.60−2.83 (m, ^3J = 7.5 Hz, 2 H, SCH_2CH_3), 3.70 (ddd, $^2J_{5,5'}$ = 12.0, $^3J_{5,OH}$ = 8.0, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.90 (ddd, $^2J_{5',5}$ = 12.0, $^3J_{5',OH}$ = 4.0, $^3J_{5',4}$ = 3.0 Hz, 1 H, 5-H), 4.12 (m, $^3J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.39 (m, 1 H, 4-H), 4.61 and 4.82 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 5.40 (dd, $^3J_{2,3}$ = 1.5, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 5.48 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 14.7 (SCH_2CH_3), 25.2 (SCH_2CH_3), 61.6 (C-5), 72.4 (CH_2-benzyl), 82.6, 82.7 (2) (C-2, C-3, C-4), 88.1 (C-1), 127.9, 128.4, 128.5, 129.2, 129.7, 133.5, 137.4, 165.4 (CO-benzoyl) ppm. $C_{21}H_{24}O_5S$ (388.5): calcd. C 64.92, H 6.23; found C 64.99, H 6.47.

Ethyl 3-*O*-Benzyl-1-thio-α-D-arabinofuranoside (18): Compound **6** (1.38 g, 4.14 mmol) was dissolved in CH_2Cl_2 (20 mL) and treated at 0 °C with $SnCl_4$ (0.41 mL of a 1 M solution in toluene, 0.41 mmol) and ethanethiol (0.37 mL, 4.97 mmol). After 15 min, a further portion of $SnCl_4$ (0.41 mL of a 1 M solution in toluene, 0.41 mmol) was added and the mixture was stirred for 2 h at 0 °C. The reaction was quenched with cold satd. $NaHCO_3$ and the mixture filtered through Celite. The filtrate was washed with water and dried, and the solvent was evaporated. The residue was treated for 1 h at room temp with NaOMe (0.01 M solution in MeOH). Neutralization with IR 120 H^+ resin, filtration, concentration, and chromatographic purification with toluene/ethyl acetate (2:1) gave thioglycoside **18** (748 mg, 64%). $[\alpha]_D^{25}$ = +115 (c = 1.10 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.31 (t, ^3J = 7.5 Hz, 3 H, SCH_2CH_3), 2.65 and 2.72 (2 dq, ^2J = 13.0, ^3J = 7.5 Hz, 2 H, SCH_2CH_3), 3.67 (dd, $^2J_{5,5}$ = 12, $^3J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 3.86 (dd, $^2J_{5',5}$ = 12, $^3J_{5',4}$ = 2.5 Hz, 1 H, 5-H), 3.92 (dd, $^3J_{3,4}$ = 4.5 Hz $^3J_{3,2}$ = 2.0 Hz, 1 H, 3-H), 4.23 (dd, $^3J_{2,3}$ = 2.0, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 4.28 (ddd, $^3J_{4,3}$ = 4.5, $^3J_{4,5}$ = 3.0, $^3J_{4,5}$ = 2.5 Hz, 1 H, 4-H), 4.57 and 4.72 (2 d, ^3J = 12.0 Hz, 2 × H, CH_2-benzyl), 5.26 (d, $^3J_{1,2}$ = 1.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 15.0 (SCH_2CH_3), 25.7

($\mathrm{S}C\mathrm{H_2CH_3}$), 62.1 (C-5), 72.3 ($CH_2$-benzyl), 80.0, 82.9, 84.7 (C-2, C-3, C-4), 91.1 (C-1), 127.8, 127.9, 128.5, 137.6 ppm. $C_{14}H_{20}O_4S$ (284.4): calcd. C 59.13, H 7.59; found C 58.79, H 7.17.

2-*O*-Benzoyl-3-*O*-benzyl-D-arabinose Diethyl Dithioacetal (19): Orthoester **2** (63 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (2 mL) and treated at −18 °C with 4 Å molecular sieves, EtSH (43 µL, 0.58 mmol), and $SnCl_4$ (0.21 mL of a 1 M solution in toluene, 0.21 mmol). The reaction was quenched after 20 min with a few drops of NEt_3, the mixture was filtered, and the solvent was evaporated. Chromatography (petroleum ether/ethyl acetate, 2:1) gave **19** as a colorless oil (54 mg, 62%). $[\alpha]_D^{25}$ = +105 (*c* = 0.69 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.20 and 1.26 (2 t, ^3J = 7.5 Hz, 2 × 3 H, $\mathrm{SCH_2C}H_3$), 2.04 (br, 1 H, 5-OH), 2.58−2.79 (2 dq, ^2J = 13.0, ^3J = 7.5 Hz, 2 × 2 H, $\mathrm{SC}H_2\mathrm{CH_3}$), 3.33 (d, $^3J_{OH,4}$ = 7.5 Hz, 1 H, 4-OH), 3.63 (m, $^2J_{5,5}$ = 11.5, $^3J_{5,OH}$ = 5, $^3J_{5,4}$ = 3.5 Hz, 1 H, 5-H), 3.73 (m, 1 H, 4-H), 3.83 (ddd, $^2J_{5,5}$ = 11.5, $^3J_{5,OH}$ = 6, $^3J_{5,4}$ = 3.5 Hz, 1 H, 5-H), 4.27 (dd, $^3J_{3,4}$ = 8.0, $^3J_{3,2}$ = 3.5 Hz, 1 H, 3-H), 4.32 (d, $^3J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 4.73 and 4.83 (2 d, ^2J = 11.5 Hz, 2 × 1 H, CH_2Ph), 5.54 (dd, $^3J_{2,1}$ = 8.5, $^3J_{2,3}$ = 3.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 14.3 ($\mathrm{SCH_2}C\mathrm{H_3}$), 24.3, 24.6 ($\mathrm{S}C\mathrm{H_2CH_3}$), 52.0 (C-1), 63.3 (C-5), 74.7 (CH_2-benzyl), 75.1, 78.1, 127.6, 127.8, 128.5, 130.2, 133.5 ppm. $C_{23}H_{30}O_5S_2$ (450.6): calcd. C 61.30, H 6.31; found C 61.43, H 6.59.

Phenyl 2-*O*-Benzoyl-3-*O*-benzyl-1-seleno-α-D-arabinofuranoside (20): A solution of compound **2** (100 mg, 0.30 mmol) in acetonitrile containing 4 Å MS was stirred for 15 min at room temp. After this mixture had been cooled to 0 °C, selenophenol (2.5 mL of a 0.12 M solution in CH_2Cl_2, 0.30 mmol) and mercuric bromide were added. After 30 min and warming to room temp, the reaction mixture was filtered through Celite. Concentration and chromatography (petroleum ether/ethyl acetate, 4:1) gave **20** (116 mg, 78%). $[\alpha]_D^{25}$ = +146 (*c* = 0.99 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.77 (dd, $^3J_{OH,5}$ = 8.5, $^3J_{OH,5}$ = 4.5 Hz, 1 H, 5-OH), 3.73 (ddd, $^2J_{5,5}$ = 12.0, $^3J_{5,OH}$ = 8.5, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.92 (ddd, $^2J_{5,5}$ = 12.0, $^3J_{5,OH}$ = 4.5, $^3J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 4.16 (br. d, $^3J_{3,4}$ = 5.0 Hz, 1 H, 3-H), 4.53 (m, 1 H, 4-H), 4.65 and 4.88 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 5.68 (br. s, 1 H, 2-H), 5.97 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 61.6 (C-5), 72.4 (CH_2-benzyl), 82.6 (2), 84.1 (C-2, C-3, C-4), 87.7 (C-1), 127.8, 128.5, 129.1, 129.7, 133.5, 134.1, 137.3, 165.3 (CO-benzoyl) ppm. $C_{25}H_{24}O_5Se$ (483.4): calcd. C 62.11, H 5.00; found C 62.30, H 5.12.

Ethyl 2-*O*-Benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-arabinofuranoside (21): Compound **17** (332 mg, 0.85 mmol) in DMF (1.5 mL) was treated at 0 °C with imidazole (87 mg, 1.28 mmol) and *tert*-butyldiphenylchlorosilane (328 µL, 1.28 mmol) and then allowed to warm to room temperature. After 1 h, the reaction mixture was quenched with methanol (a few drops) and the DMF was evaporated under vacuum. CH_2Cl_2/water extraction and chromatography (petroleum ether/ethyl acetate, 8:1) gave **21** as a colorless oil (496 mg, 93%). $[\alpha]_D^{25}$ = +69 (*c* = 0.8 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.32 (t, ^3J = 7.5 Hz, 3 H, $\mathrm{SCH_2C}H_3$), 2.59−2.83 (m, ^3J = 7.5 Hz, 2 H, $\mathrm{SC}H_2\mathrm{CH_3}$), 3.86 (m, 2 H, 5-H), 4.21 (m, $^3J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.40 (m, 1 H, 4-H), 4.78 and 4.58 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 5.43 (dd, $^3J_{2,3}$ = 1.5, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 5.48 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 14.8 ($\mathrm{SCH_2}C\mathrm{H_3}$), 19.2 [$\mathrm{Si}C\mathrm{(CH_3)_3}$], 25.2 ($\mathrm{S}C\mathrm{H_2CH_3}$), 26.7 [$\mathrm{SiC(}C\mathrm{H_3)_3}$], 62.9 (C-5), 72.2 ($CH_2$-benzyl), 82.9 (2), 83.0 (C-2, C-3, C-4), 87.9 (C-1), 127.6, 127.7, 127.9, 128.4, 129.3, 129.7, 129.8, 133.2, 133.3, 135.6, 137.5, 165.4 (CO-benzoyl) ppm. $C_{37}H_{42}O_5SSi$ (626.9): calcd. C 70.89, H 6.75; found C 70.55, H 6.38.

Ethyl 3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-arabinofuranoside (22). From 18: Compound **18** (118 mg, 0.41 mmol) was silylated with imidazole (42 mg, 0.62 mmol) and *tert*-butyldiphenylsilyl chloride (160 µL, 0.62 mmol) for 3 h at room temperature as described for the preparation of **21**. Chromatography (petroleum ether/ethyl acetate, 6:1) gave **22** as a colorless oil (174 mg, 80%). **From 21:** Compound **21** (145 mg, 0.24 mmol) was dissolved in methanol (1.5 mL) and treated overnight at room temperature with sodium methoxide (2.42 mL of a 0.01 M solution in methanol, 24 µmol). Neutralization (IR 120, H^+ resin) filtration and chromatography gave **22** (96 mg, 80%). $[\alpha]_D^{25}$ = +54 (*c* = 1.05 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.03 (s, 9 H, *t*BuSi), 1.33 (t, ^3J = 7.5 Hz, 3 H, $\mathrm{SCH_2C}H_3$), 2.79−2.64 (m, ^3J = 7.5 Hz, 2 H, $\mathrm{SC}H_2\mathrm{CH_3}$), 3.50 (d, $^3J_{OH,2}$ = 9.5 Hz, 1 H, 2-OH), 3.64 (dd, $^2J_{5,5}$ = 11.5, $^3J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 3.85 (dd, $^2J_{5,5}$ = 11.5, $^3J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 4.05 (m, 1 H, 3-H), 4.23−4.30 (m, 2 H, 2-H, 4-H), 4.54 and 4.73 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 5.32 (d, $^3J_{1,2}$ = 2.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ =18.1 ($\mathrm{SCH_2}C\mathrm{H_3}$), 19.1 [$\mathrm{Si}C\mathrm{(CH_3)_3}$], 26.0 ($\mathrm{S}C\mathrm{H_2CH_3}$), 26.7 [$\mathrm{SiC(}C\mathrm{H_3)_3}$], 63.9 (C-5), 72.0 ($CH_2$-benzyl), 79.2, 83.7, 84.5 (C-2, C-3, C-4), 91.5 (C-1), 127.8, 127.8, 127.9, 128.5, 129.9, 130.0, 132.2, 132.3, 135.5, 135.6, 137.6 ppm. $C_{30}H_{38}O_4SSi$ (522.8): calcd. C 68.92, H 7.32; found C 68.62, H 7.47.

Ethyl 3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-2-*O*-(4-methoxybenzyl)-1-thio-α-D-arabinofuranoside (23): Compound **22** (326 mg, 0.62 mmol), dissolved in acetonitrile (3 mL), was treated at 0 °C with BEMP (452 µL, 1.56 mmol) and 4-methoxybenzyl bromide (313 mg, 1.56 mmol). The mixture was allowed to warm to room temperature and stirred for 1 h before quenching with saturated $NaHCO_3$ solution (3 mL) and further stirring for 3 h until complete hydrolysis of the excess of 4-methoxybenzyl bromide. CH_2Cl_2/water extraction and chromatography (petroleum ether/ethyl acetate, 12:1) gave **23** (280 mg, 70%). $[\alpha]_D^{25}$ = +76 (*c* = 0.74 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.04 (s, 9 H, *t*BuSi), 1.31 (t, ^3J = 7.5 Hz, 3 H, $\mathrm{SCH_2C}H_3$), 2.56−2.81 (m, ^3J = 7.5 Hz, 2 H, $\mathrm{SC}H_2\mathrm{CH_3}$), 3.78 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 6.5 Hz, 1 H, 5-H), 3.80 (s, 3 H, OCH_3), 3.84 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 3.98 (dd, $^3J_{2,1}$ = 3.0, $^3J_{2,3}$ = 3.0 Hz, 1 H, 2-H), 4.05 (dd, $^3J_{3,4}$ = 6.5, $^3J_{3,2}$ = 3.0 Hz, 1 H, 3-H), 4.23 (m, 1 H, 4-H), 4.47 and 4.53 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-methoxybenzyl), 4.42 and 4.55 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 5.32 (d, $^3J_{1,2}$ = 3.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 15.0 ($\mathrm{SCH_2}C\mathrm{H_3}$), 19.3 [$\mathrm{Si}C\mathrm{(CH_3)_3}$], 25.3 ($\mathrm{S}C\mathrm{H_2CH_3}$), 26.7 [$\mathrm{SiC(}C\mathrm{H_3)_3}$], 55.3 (OMe), 63.5 (C-5), 71.6, 72.0 (CH_2-benzyl), 81.7, 83.4, 87.2 (C-2, C-3, C-4), 88.3 (C-1), 113.8, 127.6, 127.6, 128.3, 129.6, 129.6, 133.4, 135.6, 135.7, 137.8, 159.3 ppm. $C_{38}H_{46}O_5SSi$ (642.9): calcd. C 70.99, H 7.21; found C 70.96, H 7.20.

Ethyl 3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-2-*O*-(9-fluorenylmethoxycarbonyl)-1-thio-α-D-arabinofuranoside (24): Compound **22** (563 mg, 1.08 mmol), dissolved in CH_2Cl_2 (2 mL), was treated at room temperature with pyridine (175 µL) and 9-fluorenylmethyl chloroformate (418 mg, 1.61 mmol) for 1 h. Water/CH_2Cl_2 workup and chromatography (toluene/petroleum ether, 4:1) gave **24** as a colorless oil (658 mg, 82%). $[\alpha]_D^{25}$ = +84.7 (*c* = 0.90 in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.04 (s, 9 H, *t*BuSi), 1.31 (t, ^3J = 7.5 Hz, 3 H, $\mathrm{SCH_2C}H_3$), 2.65 and 2.74 (2 dq, ^2J = 13.0, ^3J = 7.5 Hz, 2 H, $\mathrm{SC}H_2\mathrm{CH_3}$), 3.79 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 3.86 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 3.5 Hz, 1 H, 5-H), 4.14 (dd, $^3J_{3,4}$ = 5.0, $^3J_{3,2}$ = 2.0 Hz, 1 H, 3-H), 4.32 (ddd, $^3J_{4,3}$ = 5.0, $^3J_{4,5} \approx {}^3J_{4,5}$ = 4.0 Hz, 1 H, 4-H), 4.45 (d, ^3J = 1.5 Hz, 2 H, OCH_2-

fmoc), 4.52 and 4.69 (2 d, ^{2}J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.07 (dd, $^{3}J_{2,3}$ = 2.0, $^{3}J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 5.42 (d, $^{3}J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 7.17−7.47, 7.57−7.77 and 7.74−7.80 (3 m, 23 H, Ar-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 14.8 (SCH$_2$*C*H$_3$), 19.2 [Si*C*(CH$_3$)$_3$], 25.1 (S*C*H$_2$CH$_3$), 26.7 [C(*C*H$_3$)$_3$], 46.6 (*C*H-FMOC), 62.8 (C-5), 70.0 (*C*H$_2$-FMOC), 72.0 (*C*H$_2$-benzyl), 82.5, 82.8 (C-3, C-4), 85.9 (C-2), 87.3 (C-1), 120.0, 125.1, 127.1, 127.6, 127.6, 127.7, 127.8, 127.9, 128.3, 129.6, 133.2, 133.2, 135.5, 137.3, 141.2, 143.1, 154.3 (CO-FMOC) ppm. $C_{45}H_{48}O_6SSi$ (745.0): calcd. C 72.55, H 6.49; found C 72.85, H 6.26.

Ethyl 3-*O*-Benzyl-5-*O*-pivaloyl-1-thio-α-D-arabinofuranoside (25): Thioglycoside **18** (748 mg, 2.63 mmol) was dissolved in pyridine (5 mL) at 0 °C. DMAP (32 mg, 0.26 mmol) and pivaloyl chloride (0.42 mL, 3.42 mmol) were then added, and the mixture was left at 0 °C for 1.5 h. Workup and chromatography with petroleum ether/ethyl acetate (4:1) gave the 2,5-dipivaloylated compound (206 mg, 17%), together with **25** (635 mg, 65%) as a colorless oil. $[\alpha]_D^{25}$ = +158 (*c* = 1.23 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.31 (t, ^{3}J = 7.5 Hz, 3 H, SCH$_2$C*H*$_3$), 2.63 and 2.71 (2 dq, ^{2}J = 13.0, ^{3}J = 7.5 Hz, 2 H, SC*H*$_2$CH$_3$), 3.83 (dd, $^{2}J_{3,4}$ = 6.0, $^{3}J_{3,2}$ = 3.5 Hz, 1 H, 3-H), 4.18 (ddd, $^{3}J_{2,\mathrm{OH}}$ = 6.0, $^{3}J_{2,3}$ = 3.5, $^{3}J_{2,1}$ = 3.5 Hz, 1 H, 2-H), 4.19 (dd, $^{2}J_{5,5}$ = 12.0, $^{3}J_{5,4}$ = 5.0 Hz, 1 H, 5-H), 4.28 (dd, $^{2}J_{5,5}$ = 12.0, $^{3}J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 4.34 (ddd, $^{3}J_{4,3}$ = 6.0, $^{3}J_{4,5}$ = 5.0, $^{3}J_{4,5}$ = 3.0 Hz, 1 H, 4-H), 4.61 and 4.71 (2 d, ^{3}J = 12.0 Hz, 2 × H, CH$_2$-benzyl), 5.14 (d, $^{3}J_{1,2}$ = 3.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 15.1 (SCH$_2$*C*H$_3$), 25.4 (S*C*H$_2$CH$_3$), 27.1 [C(*C*H$_3$)$_3$], 39.0 [*C*(CH$_3$)$_3$], 63.4 (C-5), 72.4 (CH$_2$-benzyl), 79.3, 81.0, 84.5 (C-2, C-3, C-4), 89.8 (C-1), 127.8, 128.0, 128.5, 137.4, 178.1 (CO-ester) ppm. $C_{19}H_{28}O_5S$ (368.5): calcd. C 61.93, H 7.66; found C 61.64, H 7.91.

Ethyl 3-*O*-Benzyl-2-*O*-(4-methoxybenzyl)-5-*O*-pivaloyl-1-thio-α-D-arabinofuranoside (26): Compound **25** (475 mg, 1.29 mmol) in acetonitrile (3.5 mL) was treated at 0 °C with BEMP (0.93 mL, 3.22 mmol) and a solution of 4-methoxybenzyl bromide (648 mg, 3.22 mmol) in acetonitrile (3 mL). After 2 h, the mixture was diluted with CH$_2$Cl$_2$, hydrolyzed with satd. NaHCO$_3$ solution (6 mL), and vigorously stirred for 1.5 h. CH$_2$Cl$_2$ extraction and chromatography (petroleum ether/ethyl acetate, 10:1) gave **26** as a colorless oil (427 mg, 67%). $[\alpha]_D^{25}$ = +110 (*c* = 1.07 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.17 [s, 9 H, C(C*H*$_3$)$_3$], 1.31 (t, ^{3}J = 7.5 Hz, 3 H, SCH$_2$C*H*$_3$), 2.62 and 2.72 (2 dq, ^{2}J = 13.0, ^{3}J = 7.5 Hz, 2 H, SC*H*$_2$CH$_3$), 3.81 (s, 3 H, OMe), 3.85 (dd, $^{3}J_{3,4}$ = 7.0, $^{3}J_{3,2}$ = 3.0 Hz, 1 H, 3-H), 3.94 (dd, $^{3}J_{2,3}$ = 3.0, $^{3}J_{2,1}$ = 2.5 Hz, 1 H, 2-H), 4.18 (dd, $^{2}J_{5,5}$ = 12.0, $^{3}J_{5,4}$ = 6.0 Hz, 1 H, 5-H), 4.28 (dd, $^{2}J_{5,5}$ = 12.0, $^{3}J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 4.32 (ddd, $^{3}J_{4,3}$ = 7.0, $^{3}J_{4,5}$ = 6.0, $^{3}J_{4,5}$ = 3.0 Hz, 1 H, 4-H), 4.46 and 4.54 (2 d, ^{3}J = 12.0 Hz, 2 × H, OC*H*$_2$C$_6$H$_4$OCH$_3$), 4.41 and 4.56 (2 d, ^{3}J = 11.5 Hz, 2 × H, CH$_2$-benzyl), 5.34 (d, $^{3}J_{1,2}$ = 2.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 14.9 (SCH$_2$*C*H$_3$), 25.2 (S*C*H$_2$CH$_3$), 27.0 [C(*C*H$_3$)$_3$], 38.7 [*C*(CH$_3$)$_3$], 55.1 (OMe), 63.0 (C-5), 71.6, 72.1 (CH$_2$-benzyl), 78.5, 83.6, 87.2 (C-2, C-3, C-4), 88.0 (C-1), 113.7, 127.7, 127.8, 128.3, 129.2, 129.6, 137.3, 159.3, 178.0 ppm. $C_{27}H_{36}O_6S$ (488.6): calcd. C 66.37, H 7.43; found C 66.26, H 7.30.

Phenyl 2-*O*-Benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-1-seleno-α-D-arabinofuranoside (27): Compound **20** (260 mg, 0.54 mmol) was silylated by the procedure described for the preparation of **22**. After chromatography with toluene/ethyl acetate (12:1), **27** was obtained as a colorless oil (334 mg, 86%). $[\alpha]_D^{25}$ = +108 (*c* = 0.92 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.98 (s, 9 H, *t*BuSi), 3.82 (dd, $^{2}J_{5,5}$ = 12.0, $^{3}J_{5,4}$ = 5.5 Hz, 1 H, 5-H), 3.89 (dd, $^{2}J_{5,5}$ = 11.0, $^{3}J_{5,4}$ = 5.0 Hz, 1 H, 5-H), 4.21 (dt, $^{3}J_{3,4}$ = 4.5, $^{3}J_{3,2}$ = 1.0, $^{4}J_{3,1}$ = 1.0 Hz, 1 H, 3-H), 4.53 (m, 1 H, 4-H), 4.64 and 4.82 (2 d, ^{2}J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.70 (t, $^{3}J_{2,3}$ = 1.0, $^{3}J_{2,1}$ = 1.0 Hz, 1 H, 2-H), 5.96 (m, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 19.2 [*C*(CH$_3$)$_3$], 26.7 [C(*C*H$_3$)$_3$], 62.8 (C-5), 72.2 (CH$_2$-benzyl), 82.8, 82.8, 84.2 (C-2, C-3, C-4), 87.6 (C-1), 127.6, 127.7, 127.8, 128.4, 129.0, 129.7, 133.1, 134.0, 135.5, 135.6 ppm. $C_{41}H_{42}O_5SeSi$ (721.8): calcd. C 68.22, H 5.86; found C 68.24, H 5.97.

Phenyl 3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-1-seleno-α-D-arabinofuranoside (28): Compound **27** (271 mg, 0.37 mmol) was debenzoylated by the procedure described for the preparation of **22**. Chromatography (petroleum ether/ethyl acetate, 8:1) gave **28** as a colorless oil (194 mg, 84%). $[\alpha]_D^{25}$ = +188 (*c* = 1.27 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.02 (s, 9 H, *t*Bu), 3.67 (dd, $^{2}J_{5,5}$ = 11.5, $^{3}J_{5,4}$ = 2.0 Hz, 1 H, 5-H), 3.88 (dd, $^{2}J_{5,5}$ = 11.5, $^{3}J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 4.04 (d, $^{3}J_{\mathrm{OH},2}$ = 11.0 Hz, 1 H, 2-OH), 4.06 (m, 1 H, 3-H), 4.41 (m, 1 H, 4-H), 4.56 and 4.74 (2 d, ^{2}J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 4.60 (d, $^{3}J_{2,\mathrm{OH}}$ = 11.0 Hz, 1 H, 1 H, 2-H), 5.87 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 19.0 [*C*(CH$_3$)$_3$], 26.7 [C(*C*H$_3$)$_3$], 63.7 (C-5), 72.0 (CH$_2$-benzyl), 79.1, 84.5, 84.9 (C-2, C-3, C-4), 92.2 (C-1), 127.2, 127.8, 127.9, 128.5, 129.1, 130.0, 133.6, 135.5, 135.6, 137.3 ppm. $C_{34}H_{38}O_4SeSi$ (617.7): calcd. C 66.11, H 6.20; found C 66.15, H 6.15.

Phenyl 3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-2-*O*-(4-methoxybenzyl)-1-seleno-α-D-arabinofuranoside (29): Treatment of **28** (250 mg, 0.40 mmol) with BEMP (293 μL, 1.01 mmol) and 4-methoxybenzyl bromide (203 mg, 1.01 mmol) by the procedure described for the preparation of **23** gave **29** as a colorless oil (224 mg, 75%) after chromatography (petroleum ether/ethyl acetate, 14:1). $[\alpha]_D^{25}$ = +66 (*c* = 0.98 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.01 (s, 9 H, Si*t*Bu), 3.79 (s, 3 H, OCH$_3$), 3.83 (d, $^{3}J_{5,4}$ = 5.0 Hz, 2 H, 5-H), 4.05 (dd, $^{3}J_{3,4}$ = 5.5, $^{3}J_{3,2}$ = 2.5 Hz, 1 H, 3-H), 4.24 (m, $^{3}J_{2,3}$ = 2.5, $^{3}J_{2,1}$ = 2.0 Hz, 1 H, 2-H), 4.38 and 4.51 (2 d, ^{2}J = 11.5 Hz, 2 × 1 H, CH$_2$-benzyl), 4.40 (m, 1 H, 4-H), 4.52 (s, 2 H, CH$_2$-methoxybenzyl), 5.87 (d, $^{3}J_{1,2}$ = 2.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 19.2 [*C*(CH$_3$)$_3$], 26.7 [C(*C*H$_3$)$_3$], 55.2 (CH$_3$O), 63.2 (C-5), 71.4 and 72.0 (CH$_2$-benzyl), 83.0, 83.3, 87.2 (C-2, C-3, C-4), 88.2 (C-1), 113.8, 127.3, 127.6, 128.4, 128.9, 129.4, 129.6, 130.7, 133.3, 133.6, 135.6, 137.7, 159.3 ppm.

8-Methoxycarbonyloctyl 3-*O*-Benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (30): Silylation of **16** (103 mg, 0.25 mmol) was accomplished by the procedure described for the preparation of **21**. Chromatography (petroleum ether/ethyl acetate, 6:1) gave **30** as a colorless oil (113 mg, 69%). $[\alpha]_D^{25}$ = +60 (*c* = 1.24 in chloroform). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.02 [s, 9 H, SiC(CH$_3$)$_3$], 1.24−1.40 and 1.52−1.66 (2 m, octyl), 2.29 (t, ^{3}J = 7.5 Hz, 2 H, CH$_2$CO-octyl), 3.26 (d, $^{3}J_{\mathrm{OH},2}$ = 10.5 Hz, 1 H, 2-OH), 3.46 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, OCH$_2$-octyl), 3.57 (dd, $^{2}J_{5,5}$ = 11.0, $^{3}J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 3.66 (s, 3 H, OMe), 3.71 (dt, ^{2}J = 9.5, ^{3}J = 6.5 Hz, 1 H, OCH$_2$-octyl), 3.81 (dd, $^{2}J_{5,5}$ = 11.0, $^{3}J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 3.98 (dd, $^{3}J_{4,3}$ = 3.0, $^{3}J_{4,5}$ = 2.5 Hz, 1 H, 4-H), 4.17 (dd, $^{3}J_{3,4}$ = 3.0, $^{3}J_{3,2}$ = 2.0 Hz, 1 H, 3-H), 4.18 (dd, $^{3}J_{2,\mathrm{OH}}$ = 10.5, $^{3}J_{2,3}$ = 2.0 Hz, 1 H, 2-H), 4.52 and 4.70 (2 d, ^{2}J = 12.0 Hz, 2 × 1 H, CH$_2$-benzyl), 5.06 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 25 °C): δ = 19.1, 24.9, 26.0, 26.7, 29.1, 29.2, 29.6, 34.1 (CH$_2$-octyl), 51.5 (OMe), 64.4 (C-5), 67.6 (OCH$_2$-octyl), 71.9 (CH$_2$-benzyl), 77.9, 84.1, 84.7 (C-2, C-3, C-4), 108.7 (C-1), 127.7, 127.8, 127.8, 127.9, 128.4, 129.9, 130.0, 132.3, 132.4, 135.6, 135.7, 138.0, 174.4 (CO-ester) ppm. $C_{38}H_{52}O_7Si$ (648.9): calcd. C 70.33, H 8.08; found C 70.45, H 7.80.

8-Methoxycarbonyloctyl 3-*O*-Benzyl-5-*O*-pivaloyl-α-D-arabinofuranoside (31): Compound **16** (251 mg, 0.61 mmol) was pivaloated according to the procedure described for the preparation of **25** to give **31** as a colorless oil (241 mg, 80%) after chromatography (petroleum ether/ethyl acetate, 3:1). $[\alpha]_D^{25} = +74$ ($c = 1.18$ in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.18 [s, 9 H, $C(CH_3)_3$], 1.27−1.35 and 1.50−1.65 (2 m, octyl), 1.92 (d, $^3J_{OH,2}$ = 6.5 Hz, 1 H, 2-OH), 2.30 (t, ^3J = 7.5 Hz, 2 H, CH_2CO-octyl), 3.42 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.66 (s, 3 H, OMe), 3.67 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.75 (dd, $^3J_{3,4}$ = 6.0, $^3J_{3,2}$ = 3.0 Hz, 1 H, 3-H), 4.14 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 4.0 Hz, 1 H, 5-H), 4.22 (ddd, $^3J_{4,3}$ = 6.0, $^3J_{4,5}$ = 4.0, $^3J_{4,5}$ = 2.5 Hz, 1 H, 4-H), 4.23 (dd, $^3J_{2,OH}$ = 6.5, $^3J_{2,3}$ = 3.0 Hz, 1 H, 2-H), 4.29 (dd, $^2J_{5,5}$ = 11.0, $^3J_{5,4}$ = 2.5 Hz, 1 H, 5-H), 4.60 and 4.69 (2 d, ^2J = 12.0 Hz, 2 × 1 H, CH_2-benzyl), 4.92 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 24.8, 25.9, 27.1, 29.1, 29.4, 34.0, 38.8 (CH_2-octyl), 51.5 (OMe), 63.6 (C-5), 67.7 (OCH_2-octyl), 72.4 (CH_2-benzyl), 79.7, 80.6, 85.0 (C-2, C-3, C-4), 108.0 (C-1), 127.8, 128.0, 128.5, 137.6, 174.4, 178.1 (CO-esters) ppm. $C_{27}H_{42}O_8$ (494.6): calcd. C 65.56, H 8.56; found C 65.40, H 8.91.

Octyl 2-*O*-Benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (32): Compound **15** (140 mg, 0.38 mmol) was silylated as described for the preparation of **21**. Chromatography (toluene/acetone, 100:3) gave **32** as a colorless oil (211 mg, 77%). $[\alpha]_D^{25} = +33$ ($c = 1.19$ in chloroform). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 0.88 (m, 3 H, CH_3-octyl), 1.04 (s, 9 H, *t*BuSi), 1.24−1.40 and 1.56−1.68 (2 m, 2H and 10 H, CH_2-octyl), 3.08 (m, ^3J = 6.0 Hz, 1 H, 3-OH), 3.48 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.74 (dt, ^2J = 9.5, ^3J = 6.5 Hz, 1 H, OCH_2-octyl), 3.83−3.90 (m, 2 H, 5-H), 4.18−4.23 (m, 2 H, 3-H, 4-H), 5.10 (br. d, $^3J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 5.22 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 25 °C): δ = 14.1, 19.3, 22.7, 26.1, 26.7, 26.7, 26.8, 29.2, 29.3, 29.5, 31.8 (CH_2-octyl), 63.6 (C-5), 67.9 (OCH_2-octyl), 76.8, 84.7, 85.2 (C-2, C-3, C-4), 105.1 (C-1), 127.7, 128.5, 129.7, 129.8, 133.3, 133.5, 135.6, 166.5 (CO-benzoyl) ppm. $C_{36}H_{48}O_6Si$ (604.9): calcd. C 71.49, H 8.00; found C 71.40, H 8.37.

Acknowledgments

Support of this work by the Comité Mixte Inter Universitaire Franco-Marocain (AI, 00/235/SVS) is gratefully acknowledged.

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Received June 5, 2002
[O02305]