Total Synthesis of Everninomicin 13,384-1—Part 4: Explorations of Methodology; Stereocontrolled Synthesis of 1,1′-Disaccharides, 1,2-Seleno Migrations in Carbohydrates, and Solution- and Solid-Phase Synthesis of 2-Deoxy Glycosides and Orthoesters

K. C. Nicolaou,* Konstantina C. Fylaktakidou, Helen J. Mitchell, Floris L. van Delft, Rosa Maria Rodríguez, Scott R. Conley, and Zhendong Jin[a]

Abstract: Methods for the stereocontrolled construction of 1,1′-disaccharides, 2-deoxy glycosides, and orthoesters are reported. Specifically, a tin-acetal moiety was utilized to fix the anomeric stereochemistry of a carbohydrate acceptor leading to an efficient and stereoselective synthesis of 1,1′-disaccharides, while a newly discovered 1,2-phenylseleno migration reaction in carbohydrates opened entries to 2-deoxy glycosides and orthoesters. Thus, reaction of 2-hydroxy phenylselenoglycosides with DAST led to 2-phenylselenoglycosyl fluorides which reacted with carbohydrate acceptors to afford, stereoselectively, 2-phenylselenoglycosides. The latter compounds could be reductively deselenated to 2-deoxy glycosides or oxidatively converted to orthoesters via the corresponding ketene acetals.

Keywords: carbohydrates · everninomicin · orthoester formation · phenylseleno glycoside · stereocontrolled glycosidation

Introduction

In the preceding articles,[1–3] we described investigations which led to the eventual total synthesis[4] of the powerful antibiotic everninomicin 13,384-1 (**1**) (Ziracin). The success of this program had as a prerequisite the discovery and development of a number of synthetic methods. Most notable among these new technologies were a) the use of tin-acetals for the stereocontrolled construction of the 1,1′-disaccharide linkage[5] and b) the discovery and application of the 1,2-phenylseleno migration reaction to form 2-deoxy glycosides and orthoesters (see Figure 1 for these functionalities within the everninomicin structure). The latter methodology was also demonstrated on solid phase[6] using a newly developed resin containing an arylselenyl bromide moiety.[7] Realizing the importance of these new methods in organic synthesis and their potential applications in other fields of investigation including combinatorial chemistry, we proceeded to explore their generality and scope. In this article, we describe our investigations including stereochemical aspects of these reactions particularly with regards to orthoester and allylic orthoester formation.

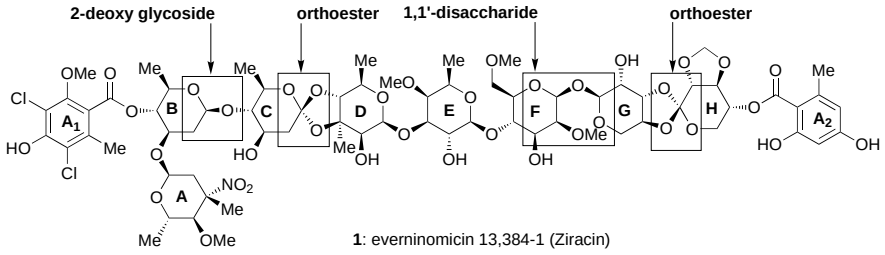


Figure 1. Structure of everninomicin 13,384-1 (**1**, Ziracin) and challenging carbohydrate linkages.

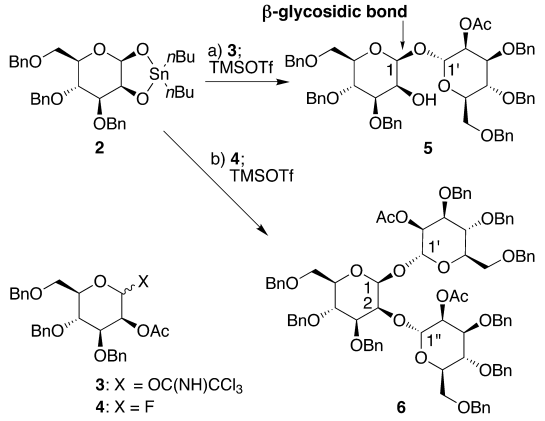
Results and Discussion

Stereocontrolled construction of 1,1′-disaccharides: In Part 2 of this series,[2] we described initial results which led to the development of a new synthetic technology for the stereo-

[a] Prof. Dr. K. C. Nicolaou, Dr. K. C. Fylaktakidou, H. J. Mitchell, Dr. F. L. van Delft, Dr. R. M. Rodríguez, Dr. S. R. Conley, Dr. Z. Jin
Department of Chemistry and The Skaggs Institute for Chemical Biology
The Scripps Research Institute
10550 North Torrey Pines Road, La Jolla, California 92037 (USA)
and
Department of Chemistry and Biochemistry
University of California San Diego
9500 Gilman Drive, La Jolla, California 92093 (USA)
Fax: (+1) 858-784-2469
E-mail: kcn@scripps.edu

0947-6539/00/0617-3166 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

selective construction of 1,1′-disaccharides and its application to the synthesis of the ring FG system of everninomicin 13,384-1 (**1**). Further exploration[5] of this chemistry has also led to the construction of 1,1′:1″,2-trisaccharides. As described previously, in order to address the problem of simultaneously controlling the stereochemistry at two anomeric centers while forming the necessary 1,1′-glycosidic linkage, a five-membered ring tin-acetal[8] was used to generate the desired β-mannoside bond present in ring F, while using a participating group to direct glycosidation of the ring G anomeric center. Other attempts to address the issue of the FG linkage include the reaction of a suitable α-chloro mannose donor and lactol under silver salt containing conditions, furnishing the β-1,1′-linked glycoside in 32% yield.[9] As illustrated in Scheme 1,



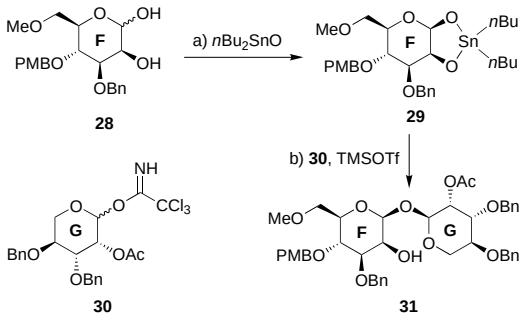
Scheme 1. Synthesis of model 1,1′-disaccharide **5** and 1,1′;1″,2-trisaccharide **6**. a) 0.6 equiv **3**, 0.5 equiv TMSOTf, Et_2O, $0 \rightarrow 25\,^{\circ}C$, 35 h, 66%; b) 2.0 equiv **4**, 1.1 equiv TMSOTf, Et_2O, $0 \rightarrow 25\,^{\circ}C$, 24 h, 84%. Tf = trifluoromethanesulfonyl; TMS = trimethylsilyl; Ac = acetyl; Bn = benzyl.

reaction of ring F model tin-acetal **2** with 0.6 equivalents of trichloroacetimidate **3** in ether in the presence of TMSOTf furnished the desired 1,1′-disaccharide **5** in 66% yield as a single stereoisomer. In this reaction we also observed the formation of a small amount (9%) of a trisaccharide-like compound assigned as **6**, resulting from the reaction of **2** with 2 equivalents of the donor **3**. In addition, when fluoride donor **4** was used in excess (i.e., 2 equivalents) an 84% yield of trisaccharide **6** was obtained in which all three glycosidic bonds were formed stereoselectively.

Abstract in Greek: Παρουσιάζονται μέθοδοι για τη στερεοεκλεκτική σύνθεση 1,1'-δισακχαριτών, 2-δεσοξυγλυκοζιτών και ορθοεστέρων. Ειδικότερα, η κασσιτερική ακετάλη χρησιμοποιήθηκε για να καθορίσει τη στερεοχημεία του ανωμερούς κέντρου του σακχάρου "δέκτη", οδηγώντας έτσι στην αποτελεσματική και στερεοεκλεκτική σύνθεση 1,1'-δισακχαριτών, ενώ η νέα αντίδραση της 1,2-σεληνιοφαινυλο-μετάθεσης στα σάκχαρα άνοιξε νέες οδούς σύνθεσης 2-δεσοξυγλυκοζιτών και ορθοεστέρων. Έτσι, η αντίδραση 2-υδροξυ-σεληνιοφαινυλο-γλυκοζιτών με DAST οδήγησε σε 2-σεληνιοφαινυλο-γλυκοσυλο-φθορίδια τα οποία αντέδρασαν στη συνέχεια με σάκχαρα "δέκτες" για να δώσουν στερεοεκλεκτικά 2-σεληνιοφαινυλο-γλυκοζίτες. Οι τελευταίες ενώσεις είναι δυνατόν να αποσεληνιωθούν αναγωγικά προς 2-δεσοξυγλυκοζίτες ή να μετατραπούν οξειδωτικά σε ορθοεστέρες, μέσω των αντίστοιχων κετενο-ακεταλών.

The generality of these glycosidation reactions was explored and selected results are shown in Table 1. A variety of carbohydrate scaffolds were tested as tin-acetal acceptors (i.e., mannose unit **2**, 6-deoxymannose unit **22**, rhammnose unit **19**, and lyxose unit **25**) in combination with a number of different donor types. It was found that while thioglycosides and glycosylphosphates were modestly successful, trichloroacetimidate donors and glycosyl fluorides gave the highest yields and cleanest reactions. In general, it was observed that under the correct stoichiometry, trichloroacetimidate[10] donors lead to good yields of disaccharides (entries 1, 5, 9, 13, 15, 19, 21), and the use of excess glycosyl fluorides[11] favored trisaccharide formation (entries 4, 8, 12, 18, and 20). As expected, disaccharide formation results from glycosidation at the equatorial oxygen (C-1) (over axial) for mannose-type units (all entries, Table 1), whereas the coupling of a tin-acetal derived glucose-type unit (not shown) produces the corresponding 2-*O*-linked disaccharide and the 1α,1′α-disaccharide in a ratio of ca. 2:1.

The stereochemistry of the newly formed glycoside bonds was assigned on the basis of $^{13}C-{}^{1}H$ spin-coupling constants[12] measuring 156.9 and 151.2 Hz for compounds **5** and **6** (Scheme 1), respectively (as compared with 174.1 Hz for compound **15** in Part 2[2] of this series (α,α'-linked)). The anomeric configuration may also be assigned on the basis of the chemical shift for the mannose H-5 proton ($\delta \approx 3.4$ for β-linked mannosides, e.g. entries 1–14, Table 1). Before application of this technology to the total synthesis of everninomicin 13,384-1, FG model system **31** was constructed as illustrated in Scheme 2. Thus, conversion of ring F unit **28** to

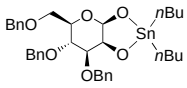
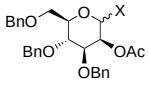
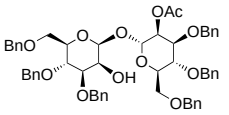
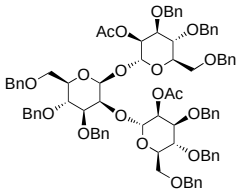
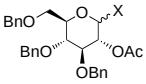
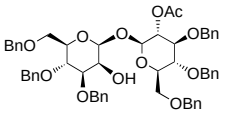
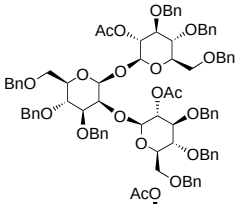
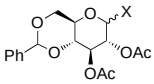
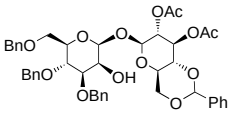
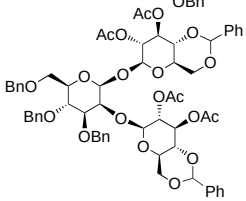
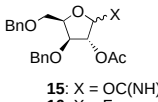
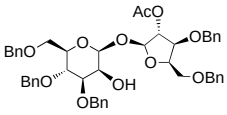
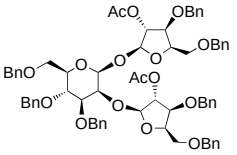
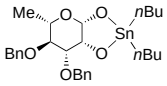
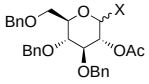
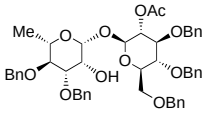
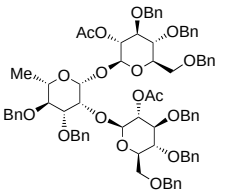
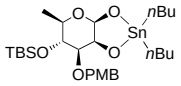
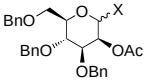
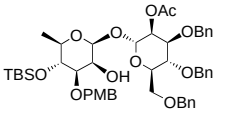
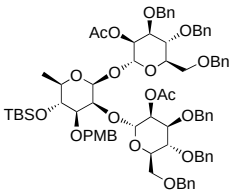
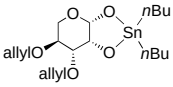
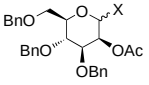
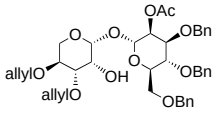
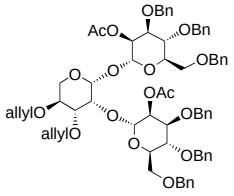


Scheme 2. Stereocontrolled synthesis of ring FG system **31** of everninomicin 13,384-1. a) 1.1 equiv nBu$_2$SnO, MeOH, $90\,^{\circ}C$, 3 h, 100%; b) 0.7 equiv **30**, 0.5 equiv TMSOTf, CH_2Cl_2, $0 \rightarrow 25\,^{\circ}C$, 48 h, 67%.

its tin-acetal **29** under standard conditions, followed by reaction with 0.7 equivalents of ring G trichloroacetimidate donor **30** in the presence of TMSOTf, furnished the desired 1β,1′α-disaccharide **31** in 67% yield as a single stereoisomer. When applied to the real system (Part 2 in this series),[2] this reaction proceeded in 74% yield and proved essential for the total synthesis of **1**.

1,2-Phenylseleno migrations in carbohydrates and their application to the synthesis of 2-deoxy glycosides, orthoesters and allylic orthoesters: Our previous observation of the 1,2-phenylthio migration in carbohydrate systems[13] and its application to the construction of 2-deoxy glycosides, includ-

Table 1. Synthesis of β-linked 1,1′-disaccharides and 1,1′;1″,2-trisaccharides.[a]

Entry	Acceptor [equiv]	Donor	Donor/ Solvent[b]	Cat [equiv][c]	Time [h]	Disaccharide [% yield][d]		Trisaccharide [% yield]	
									
1	**2** (1.5)	 **3**: X = $OC(NH)CCl_3$ **4**: X = F	**3**/A	0.5	35		**5** (66)		**6** (9)
2	**2** (0.45)		**3**/A	0.5	72		**5** (-)		**6** (-)
3	**2** (1.5)		**4**/A	1.1	24		**5** (10)		**6** (70)
4	**2** (0.45)		**4**/A	0.6	24		**5** (-)		**6** (84)
5	**2** (1.5)	 **7**: X = $OC(NH)CCl_3$ **8**: X = F	**7**/A	0.4	48		**9** (68)		**10** (-)
6	**2** (0.45)		**7**/A	0.3	96		**9** (22)		**10** (47)
7	**2** (1.5)		**8**/A	1.2	48		**9** (64)		**10** (-)
8	**2** (0.45)		**8**/A	0.5	72		**9** (23)		**10** (32)
9	**2** (1.5)	 **11**: X = $OC(NH)CCl_3$ **12**: X = F	**11**/B	0.8	72		**13** (57)		**14** (22)
10	**2** (0.45)		**11**/B	0.3	72		**13** (58)		**14** (14)
11	**2** (1.5)		**12**/B	1.2	0.5		**13** (59)		**14** (5)
12	**2** (0.45)		**12**/B	0.5	48		**13** (-)		**14** (33)
13	**2** (1.5)	 **15**: X = $OC(NH)CCl_3$ **16**: X = F	**15**/A	0.5	0.5		**17** (72)		**18** (8)
14	**2** (1.5)		**16**/A	1.1	0.5		**17** (70)		**18** (12)
									
15	**19** (1.5)	 **7**: X = $OC(NH)CCl_3$ **8**: X = F	**7**/B	0.5	40		**20** (58)		**21** (-)
16	**19** (0.45)		**7**/B	0.5	72		**20** (-)		**21** (-)
17	**19** (1.5)		**8**/B	1.1	2		**20** (52)		**21** (9)
18	**19** (0.45)		**8**/B	0.5	48		**20** (7)		**21** (11)
									
19	**22** (1.5)	**3**: X = $OC(NH)CCl_3$ **4**: X = F	**3**/C	0.5	40		**23** (85)		**24** (3)
20	**22** (0.45)		**4**/C	0.6	40		**23** (-)		**24** (10)
									
21	**25** (1.5)	**3**: X = $OC(NH)CCl_3$ **4**: X = F	**3**/C	0.5	22		**26** (82)		**27** (-)
22	**25** (0.45)		**4**/C	0.5	22		**26** (38)		**27** (30)

[a] All reactions were started at 0 °C and then allowed to proceed at ambient temperature for the indicated time; [b] solvent system A = ether; B = ether/CH_2Cl_2 3:1, C = ether/CH_2Cl_2 1:1; [c] based on donor; [d] combined yield of disaccharide and its TMS derivative; removal of the TMS group was effected with PPTS in MeOH. PMB = *p*-methoxybenzyl; TBS = *tert*-butyldimethylsilyl.

ing an everninomicin BC model system[2, 4a] prompted us to investigate a possible extension of this methodology to include the corresponding selenium chemistry. Such 1,2-migrations would provide substantial advantages among which milder reaction conditions, higher efficiency and versatility and possibly solid-phase applications. We have already described specific applications of this new selenium-based chemistry in Parts 2[2] and 3[3] in this series as well as in a preliminary communication.[6] Herein, we describe full details of our explorations in this field. Figure 2 depicts the plans for

0947-6539/00/0617-3168 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

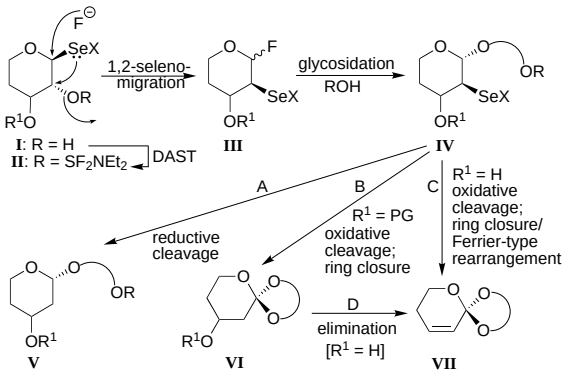
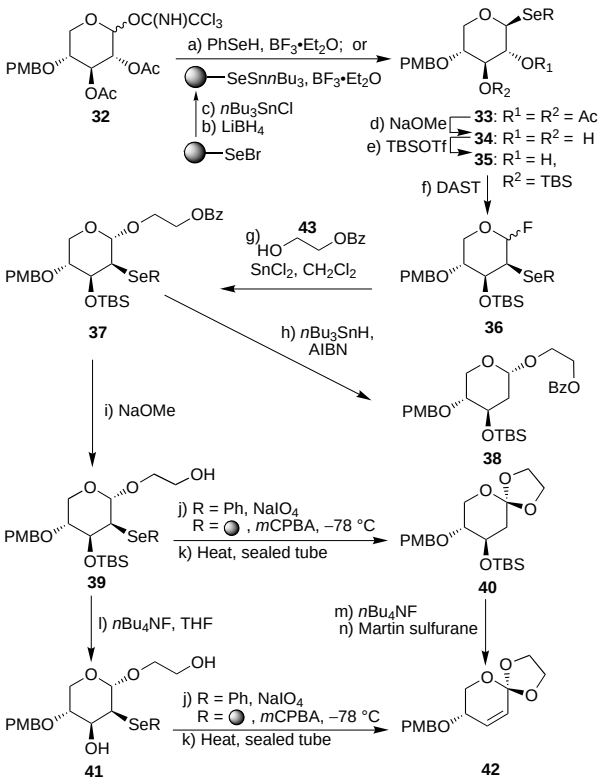


Figure 2. General concept for the solid-phase stereoselective synthesis of 2-deoxy glycosides (**V**), orthoesters (**VI**), and allylic orthoesters (**VII**) via 1,2-selenium migrations. PG = protecting group; X = Ph or polystyrene.

this chemistry. Thus, we envisioned a general method starting with readily available 2-hydroxy phenylselenoglycosides (**I**) and proceeding to provide, through a 1,2-migration reaction, 2-phenylseleno glycosyl fluorides (**III**) whose glycosidation with hydroxy components would provide 2-phenylseleno glycosides (**IV**). Manipulation of the latter intermediates (**IV**) either reductively or oxidatively was expected to provide access to 2-deoxy glycosides (**V**) or orthoesters (**VI** or **VII**), respectively. Thus, treatment of the readily available 2-hydroxy-1-selenoglycoside (**I**) with diethylaminosulfur trifluoride (DAST) should result in a stereospecific 1,2-migration of the selenium group, with simultaneous installation of a fluoride group at C-1, furnishing (**III**). The desired α-glycosides (**IV**) should result from participation of the seleno group, upon exposure of these reactive donor (**III**) to various alcohols in the presence of Lewis acids especially in a non-coordinating solvent such as CH_2Cl_2. From **IV**, one of the following three paths may be followed: radical deselenation facilitated with nBu$_3$SnH should furnish the 2-deoxy glycosides (**V**) via path A. 2-Deoxy orthoesters (**VI**) should be obtained from path B, requiring first removal of the protecting group R, followed by oxidation of the selenium to the selenoxide and heating to promote the required *syn*-elimination and cyclization. Path C would require that both protecting groups (R and R^1) be removed before subsequent oxidation and heating, and should afford the 2,3-allylic orthoesters (**VII**) via a Ferrier-type rearrangement.[14] And, path D would involve elimination of the hydroxy group of **VI**, again furnishing **VII**, allowing for expansion of the process and for comparison of the stereochemistries of the orthoester moieties generated by paths B and C.

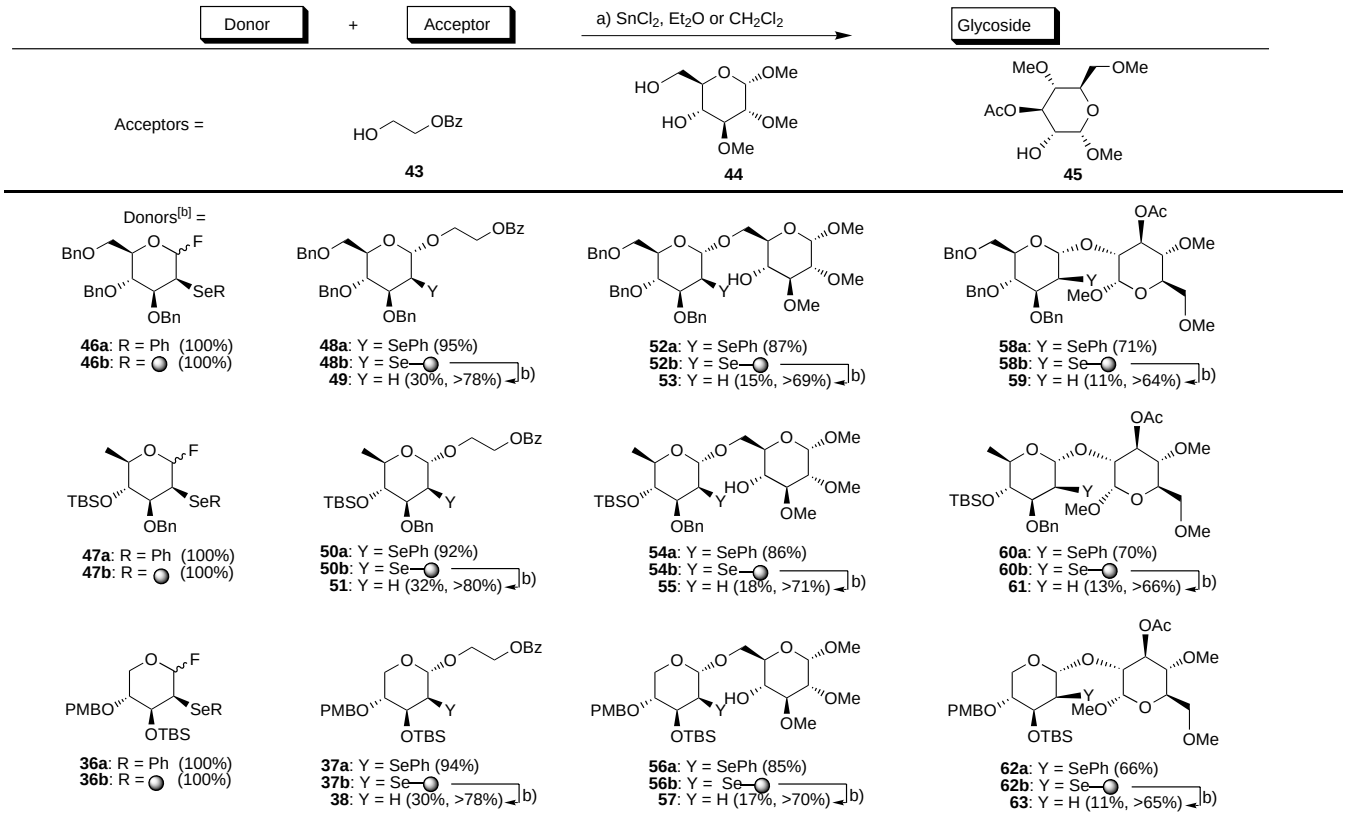
As a demonstration of the efficiency and utility of the 1,2-seleno-migration chemistry, we employed three different carbohydrate donors which were coupled with three alcohols of varying complexity, to afford a small library of 2-deoxy glycosides and orthoesters, followed by the formation of three allylic orthoesters. Scheme 3 illustrates the method and conditions used for one example, while Tables 2 and 3 provide data for all cases studied. Scheme 3 exemplifies the chemistry both in solution (R = Ph) and on solid phase (R = ● = polystyrene) for the synthesis of 2-deoxy glycoside **38** and orthoesters **40** and **42**. Thus, for the solution-phase chemistry,



Scheme 3. Solution- and solid-phase synthesis of 2-deoxy glycosides (**38**), 2-deoxy orthoesters (**40**), and 2,3-allylic orthoesters (**42**). R = Ph: a) 2.0 equiv PhSeH (0.5 M solution in CH_2Cl_2), 1.5 equiv $BF_3 \cdot Et_2O$, CH_2Cl_2, $-78\,^\circ$C, 2 h, 90%; d) 2.5 equiv NaOMe, MeOH, 25 °C, 3 h, 95%; e) 1.1 equiv TBSOTf, 1.3 equiv 2,6-lutidine, CH_2Cl_2, $-78\,^\circ$C, 1 h, 90%; f) 1.5 equiv DAST, CH_2Cl_2, 0 °C, 0.5 h, 100%; g) 1.5 equiv $HOCH_2CH_2OBz$, 1.5 equiv $SnCl_2$, CH_2Cl_2, 0 °C, 3 h, 94%; h) 10 equiv nBu$_3$SnH, 0.1 equiv AIBN, benzene, 80 °C, 1 h, 90%; i) 1.5 equiv NaOMe, MeOH, 25 °C, 3 h, 95%; j) 10.0 equiv $NaIO_4$, MeOH/CH_2Cl_2/H_2O 3:2:1, 25 °C, 1 h; k) vinyl acetate/toluene/diisopropylamine 2:2:1, sealed tube, 140 °C, 12 h, 82% for **40**, 79% for **42;** l) 1.5 equiv nBu$_4$NF, THF, 25 °C, 1 h, 95%; m) 1.5 equiv nBu$_4$NF, THF, 25 °C, 1 h, 95%; n) 4.0 equiv Martin sulfurane, 0.5 equiv Et_3N, $CHCl_3$, 50 °C, 2 h, 87%. R = polystyrene: a) 3.0 equiv **2**, 1.5 equiv $BF_3 \cdot Et_2O$, CH_2Cl_2, $-78\,^\circ$C, 2 h, >90%; b) 1.5 equiv $LiBH_4$, THF, 25 °C, 2 h, 100%; c) 20 equiv nBu$_3$SnCl, THF, 25 °C, 2 h, 100%; d) 5.0 equiv NaOMe, THF/MeOH, 25 °C, 3 h, >95%; e) 1.1 equiv TBSOTf, 1.3 equiv 2,6-lutidine, CH_2Cl_2, $-78\,^\circ$C, 1 h, >80%; f) 3.0 equiv DAST, CH_2Cl_2, 0 °C, 0.5 h, 100%; g) 10.0 equiv $HOCH_2CH_2OBz$, 3.0 equiv $SnCl_2$, CH_2Cl_2, 0 °C, 3 h, >89%; h) 10.0 equiv nBu$_3$SnH, 0.1 equiv AIBN, benzene, 80 °C, 1 h, 95%; i) 5.0 equiv NaOMe, THF/MeOH, 25 °C, 3 h, >95%; j) 3.0 equiv mCPBA, CH_2Cl_2, $-78\,^\circ$C, 10 min; k) vinyl acetate/toluene/diisopropylamine 2:2:1, sealed tube, 140 °C, 12 h, >85% for **40**, >81% for **42;** l) 5.0 equiv nBu$_4$NF, THF, 25 °C, 1 h, >95%. Yields of solid-phase chemistry reported here were determined by NMR spectroscopy after cleavage, see Tables 1 and 2 for overall yields determined by weight after cleavage. AIBN = 2,2′-azobisisobutyronitrile; DAST = diethyl(aminosulfur) trifluoride; mCPBA = m-chloroperoxybenzoic acid; THF = tetrahydrofuran; Bz = benzoyl; ● = polystyrene.

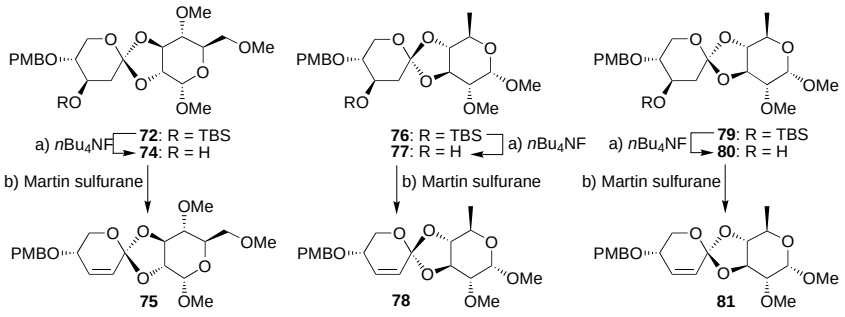
trichloroacetimidate **32** was treated with freshly prepared PhSeH[15] in the presence of $BF_3 \cdot Et_2O$ to afford stereoselectively (by virtue of the 2-acetoxy group exerting its directing effect) glycoside **33** (90% yield). Both acetates were removed from **33** (NaOMe, MeOH, 95% yield) leading to **34** from which monosilyl ether **35** was generated (TBSOTf, 2,6-lutidine, THF, $-78\,^\circ$C, 90% yield) stereoselectively. Treatment of **35** with DAST facilitated the 1,2-phenylseleno

Table 2. Solution- and solid-phase synthesis of 2-phenylselenoglycosides and 2-deoxy glycosides.[a]



[a] Glycosides were prepared by: a) R = Ph: 1.5 equiv acceptor, 1.5 equiv $SnCl_2$, Et_2O, 0 °C, 3 h; R = polystyrene: 10.0 equiv acceptor, 3.0 equiv $SnCl_2$, CH_2Cl_2, 0 °C, 3 h; yields of 2-deoxy glycosides from solid-phase chemistry were determined by weight after cleavage and include the glycosidation step: (overall yield, average yield for each step (e.g. for **49**: 0.785 = 0.30)). b) nBu$_3$SnH, AIBN, benzene, 80 °C, 1 h; ● = polystyrene. [b] Donors were prepared by DAST-induced 1,2-migration from the corresponding 2-hydroxy-β-phenylseleno glycosides.

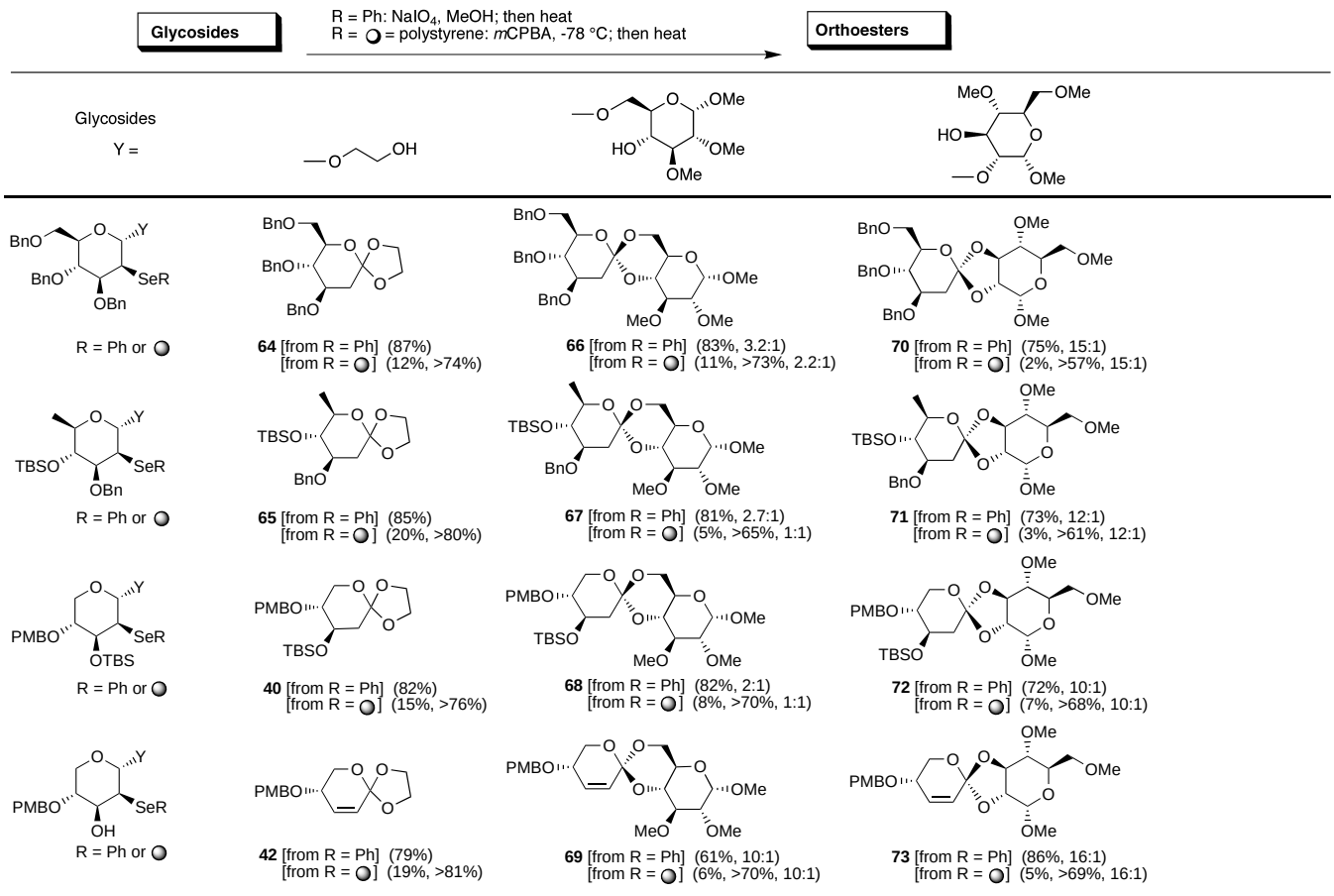
migration affording the 2-phenylseleno-1-fluoro donor **36** in essentially quantitative yield. This donor (**36**) was coupled with alcohol **43** in the presence of $SnCl_2$ and in CH_2Cl_2 leading to the selective formation of α-glycoside **37** (94% yield). Upon exposure of the latter compound (**37**) to nBu$_3$SnH/AIBN cat., formation of the 2-deoxy glycoside **38** (90% yield) was observed via radical cleavage of the C–Se bond. Removal of the benzoate group from **37** (NaOMe, MeOH, 95% yield) afforded **39** and was followed by oxidation of the selenium moiety to the selenoxide ($NaIO_4$, 95% yield). Heating of this selenoxide in a sealed tube (vinyl acetate/toluene/diisopropylamine 2:2:1, 140 °C, 12 h)[16] led to the formation of the 2-deoxy orthoester **40** in 82% yield. On the other hand, removal of the silyl group from **39** (nBu$_4$NF, THF, 95% yield) led to diol **41** and this was followed by oxidation to the corresponding selenoxide and heating in a sealed tube as described above, furnishing, via *syn*-elimination, ring closure and expulsion of the C-3 hydroxyl group, the 2,3-allylic orthoester **42** in 79% overall yield. Orthoester **40** was converted to allylic orthoester **42** by treatment with nBu$_4$NF to remove the TBS group (95% yield), followed by elimination of H_2O facilitated by exposure to Martin sulfurane[17] in the presence of a catalytic amount of Et_3N (87% yield). The samples of **42** obtained by the two routes were identical. Table 2 provides a variety of examples demonstrating the generality and scope of these reactions. Thus, donors **46**, **47**, and **36** coupled with acceptors **43**, **44**, and **45** to afford the respective 2-phenylseleno glycosides in good



Scheme 4. Synthesis of allylic orthoesters **75**, **78**, and **81** from 2-deoxy orthoesters **72**, **76**, and **79**, respectively. a) 1.5 equiv nBu$_4$NF, THF, 25 °C, 1 h, **74**: 95%, **77**: 95%, **80**: 93%; b) 4.0 equiv Martin sulfurane, 0.5 equiv Et_3N, $CHCl_3$, 50 °C, 2 h, **75**: 87%, **78**: 95%, **81**: 87%.

0947-6539/00/0617-3170 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

Table 3. Solution- and solid-phase synthesis of 2-deoxy orthoesters and 2,3-allylic orthoesters.[a]

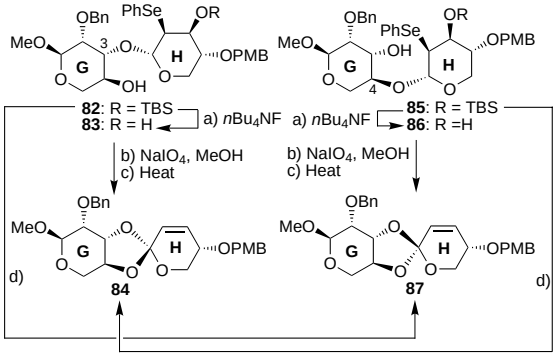


[a] Selenoxides were heated in a sealed tube at 140 °C in vinyl acetate/toluene/diisopropylamine 1:1:2 for 12 h. Yields of orthoesters from solution-phase chemistry: (combined yield for deprotection, oxidation and orthoester formation, ratio of orthoester diastereoisomers). Yields of orthoesters from solid-phase chemistry: (overall yield for sequence from arylselenium bromide resin determined by weight of released product, average yield for each step, (e.g. for **64**: 0.746 = 0.12), ratio of orthoester diastereoisomers). (● = polystyrene).

to excellent yields (66–95%). Table 3 catalogs a number of examples of orthoester formation as well as of 2,3-allylic orthoesters.

In order to compare the stereochemistries of orthoesters **72** and **73** (Table 3), **72** was transferred to its respective 2,3-allylic orthoester as shown in Scheme 4. Thus, liberation of the silicon protected hydroxyl group of **72** (nBu$_4$NF, THF, 95% yield) followed by dehydration of the resulting alcohol **74** with Martin sulfurane ($CHCl_3$, 50 °C, 87% yield) furnished orthoester **75**. This orthoester (**75**) obtained by the three-step sequence proved, by NMR spectroscopy, to possess the opposite stereochemistry to that obtained directly via the one-step Ferrier-type procedure (**73**, Table 3). Thus it appears, that while the stereochemistry during the formation of 2-deoxy orthoesters (e.g. **72**, Table 2) is controlled by the anomeric effect[18] [the incoming hydroxyl group approaches the intermediate ketene acetal from an axial direction so as to maximize the anomeric effect], the Ferrier-type orthoester formation (e.g. **73**, Table 3) must involve attack from the top (same side as the leaving hydroxyl group) face of the molecule. The latter mechanism may require initial departure of the leaving group with concomitant double bond migration and oxonium species formation followed by ring closure. Further examples of these modes of action are found in Part 2 of this series (GH and FGH model systems)[2] and in Scheme 5.

The latter Scheme shows the fate of the G-3 and G-4 linked disaccharides **82** and **85** when subjected to the Ferrier-type allylic orthoester formation versus their processing through

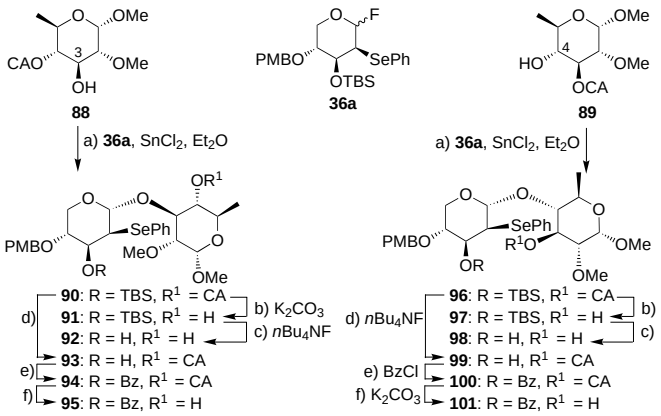


Scheme 5. Solution-phase synthesis of 2,3-allylic orthoesters **84** and **87**. a) 1.5 equiv nBu$_4$NF, THF, 25 °C, 1 h, **83**: 94%, **86**: 90%; b) 10.0 equiv $NaIO_4$, MeOH/CH_2Cl_2/H_2O 7:3:1, 25 °C, 1 h, 95%; c) vinyl acetate/toluene/diisopropylamine 2:2:1, sealed tube, 140 °C, 12 h, **84**: 70%, **87**: 75%; d) oxidation, heat, desilylation, mesylation, elimination, see Part 2 in this series.[2]

  0947-6539/00/0617-3171 $ 17.50+.50/0

the multi-step sequence to the same products. Thus, when **82** and **85** were desilylated (nBu$_4$NF, THF) led to hydroxy compounds **83** (94% yield) and **86** (90% yield), respectively. Oxidation of these substances ($NaIO_4$, MeOH) followed by heating (vinyl acetate/toluene/diisopropylamine 2:2:1, 140 °C) furnished allylic orthoesters **84** (70% yield) and **87** (75% yield). In contrast and as already described in Part 2 of this series,[2] the normal orthoester conditions starting with **82** and **85** led to the isomeric allylic orthoesters **87** and **84**, respectively, underscoring the mechanistic differences of the two processes.

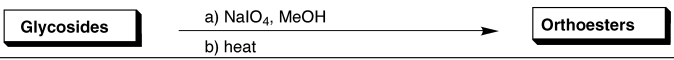
Intrigued by these results and in order to explore the generality of these phenomena we prepare, according to Scheme 6, further substrates (**91**, **92**, **95**, **97**, **98**, **101**) for orthoester formation. Thus, the C-3 and C-4 hydroxy compounds **88** and **89** were coupled with glycosyl fluoride **36a** ($SnCl_2$, Et_2O) furnishing the C-3 and C-4 linked disaccharides **90** and **96** in 45 and 52% yield, respectively. These disaccharides were modified to produce three orthoester precursors each. Thus, removal of the chloroacetate groups (K_2CO_3, MeOH) led to alcohols **91** (98% yield) and **97** (99% yield) ready for normal orthoester formation. Subsequent cleavage (nBu$_4$NF, THF) of the TBS groups from **91** and **97** furnished diols **92** (86% yield) and **98** (90% yield) ready for allylic orthoester formation. In order to probe the effect of esterifying the C-3 hydroxyl group on orthoester formation, we proceeded to prepare, via a three-step procedure, benzoates **95** and **101**. Desilylation of **90** and **96** (nBu$_4$NF, AcOH, THF) gave hydroxy compounds **93** (90% yield) and **99** (93% yield) onto which the benzoate group was installed (BzCl, Et_3N, 4-DMAP cat.) leading to **94** (92% yield) and **100** (93% yield) respectively. Finally, selective removal of the chloroacetate group (K_2CO_3, MeOH) from **94** and **100** led to the desired compounds **95** (75% yield) and **101** (93% yield), respectively.



Scheme 6. Solution-phase synthesis of 2-phenylselenoglycosides for stereochemical studies. a) 2.5 equiv **36a**, 2.5 equiv $SnCl_2$, Et_2O, 0 → 25 °C, 12 h, **90**: 45%, **96**: 45%; b) 0.5 equiv K_2CO_3, MeOH, 25 °C, 1 h, **91**: 98%, **97**: 99%; c) 1.2 equiv nBu$_4$NF, THF, 25 °C, 4 h, **92**: 86%, **98**: 90%; d) 1.1 equiv nBu$_4$NF, 0.2 equiv AcOH, THF, 25 °C, 3 h, **93**: 90%, **99**: 93%; e) 2.0 equiv BzCl, 3.0 equiv Et_3N, 0.5 equiv 4-DMAP, CH_2Cl_2, 0 → 25 °C, 3 h, **94**: 92%, **100**: 93%; f) 0.2 equiv K_2CO_3, MeOH, 25 °C, 1 h, **95**: 75%, **101**: 93%. CA = chloroacetyl.

Table 4 illustrates the results of the orthoester forming reactions with these phenylseleno substrates. Thus, beginning with alcohols **91** and **97**, orthoesters **79** and **76** were obtained as the major products [3.2:1 (92% total yield) and 3.5:1 ratios (89% total yield), respectively]. These results were in line with our previous experience with orthoester formation reactions. However, when the C-3 linked diol **92** was subjected to the allylic orthoester conditions, allylic orthoester **81** was obtained as the major product (ca. 30:1 ratio, 86% combined yield) instead of the predicted **78**. This reversal in selectivity was also observed when the C-4 linked diol **98** was similarly processed leading to allylic orthoester **78** as the major product (ca. 20:1 selectivity, 87% combined yield) instead of the expected **81**. The corresponding benzoates **95** and **101** followed the same pattern, leading to the same allylic orthoesters **81** (ca. 15:1 ratio, 80% combined yield) and **78** (ca. 15:1 ratio, 82% combined yield), respectively, when subjected to the same orthoester forming conditions and indicating that either a C-3 alcohol or its benzoate could be used for the same orthoester construction. These results were inconsistent with our previous observations in that in these latter cases the anomeric effect seemed to control both types of orthoester formation, suggesting that other factors, including precise substitution and sterics play important roles.

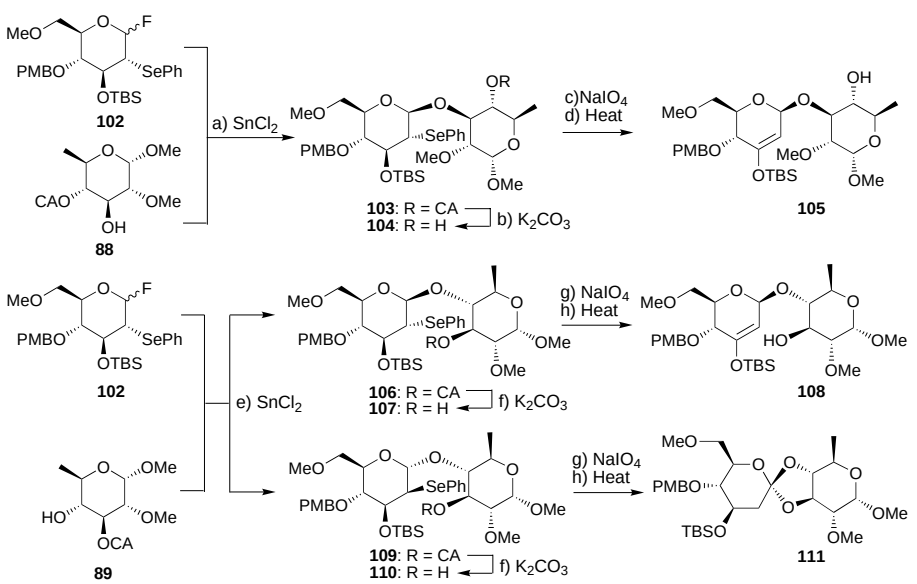
Table 4. Solution-phase synthesis of 2-deoxy orthoesters and 2,3-allylic orthoesters.[a]



Glycoside	Combined yield (%) of orthoesters	Ratio of orthoesters: 81	78	76	79
91	92	-	-	1	3.2
92	86	30	1	-	-
95	80	15	1	-	-
97	89	-	-	3.5	1
98	87	1	20	-	-
101	82	1	15	-	-

[a] Orthoesters were prepared by: a) 10.0 equiv $NaIO_4$, MeOH/CH_2Cl_2/H_2O 7:3:1, 25 °C, 1 h, 95%; b) vinyl acetate/toluene/diisopropylamine 2:2:1, sealed tube, 140 °C, 12 h.

0947-6539/00/0617-3172 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17



Scheme 7. Solution-phase synthesis of 2-phenylselenoglycosides and orthoesters from mannose donor **102**. a) 2.5 equiv **102**, 2.5 equiv $SnCl_2$, Et_2O, $0 \rightarrow 25\,^{\circ}C$, 12 h, 42 %; b) 0.5 equiv K_2CO_3, MeOH, 25 °C, 1 h, 93 %; c) 10.0 equiv $NaIO_4$, $MeOH/CH_2Cl_2/H_2O$ 7:3:1, 25 °C, 1 h; d) vinyl acetate/toluene/diisopropylamine 2:2:1, sealed tube, 140 °C, 12 h, 70 %; e) 2.5 equiv **102**, 2.5 equiv $SnCl_2$, Et_2O, $0 \rightarrow 25\,^{\circ}C$, 12 h, 50 % as 1:2 ratio of inseparable isomers **106** and **109;** f) 0.5 equiv K_2CO_3, MeOH, 25 °C, 1 h, **107**:**110** ca. 1:2 ratio, 90 % combined yield; g) 10.0 equiv $NaIO_4$, $MeOH/CH_2Cl_2/H_2O$ 7:3:1, 25 °C, 1 h; h) vinyl acetate/toluene/diisopropylamine 2:2:1, sealed tube, 140 °C, 12 h, 65 % of **108** from **107**, 70 % of **111** as a 2:1 ratio of diastereoisomers from **110**.

As a final application of this methodology, we chose to study the chemistry of the mannose-type substrate **102** (Scheme 7). The couplings of carbohydrate donor **102** with the C-3 and C-4 hydroxy components **88** and **89** were first investigated. With alcohol **88**, the glycosidation proceeded under the influence of $SnCl_2$ in ether and, through the directing effect of the 2-phenylseleno group, afforded the expected β-disaccharide **103**, albeit sluggishly and in only 42 % yield. In an attempt to produce the corresponding orthoester, the chloroacetate group was removed from **103** by the action of K_2CO_3 in MeOH (93 % yield) and the resulting alcohol **104** was subjected to the normal oxidative/thermolysis conditions. Purification followed by spectroscopic analysis, however, revealed that enol ether **105** had been formed (70 % yield) instead of the desired orthoester, indicating that the *syn*-elimination had occurred away from the anomeric center. In the case of alcohol **89**, the coupling reaction with **102** furnished both isomers **106** and **109** in 50 % combined yield (**106**:**109** ca. 1:2 ratio). An explanation for the origin of this unexpected observation may be that the reaction proceeded so sluggishly that the 2-phenylseleno-1-fluoro derivative **102** suffered loss of PhSeF under the Lewis acid conditions, which re-added back to the generated glycal from both faces, forming a mixture of the 2α- and 2β-phenylseleno fluorides whose combination with **89** led to the observed products **106** and **109**. Removal of the chloroacetate group from **106** and **109** (K_2CO_3, MeOH) provided **107** and **110** (90 % combined yield, ca. 1:2 ratio), respectively. Processing **107** under the orthoester forming protocol, again furnished the unexpected enol ether **108** (65 % yield), whereas the isomeric hydroxy selenide **110** led to the anticipated orthoester **111** in 70 % yield and as a mixture of diastereoisomers (ca. 2:1, **111** major). The stereochemical outcome of this orthoester formation was in line with expectation (control by the anomeric effect) although the selectivity was rather low.

Our next objective was to develop a solid-phase version of this selenium-based chemistry that may aid combinatorial chemistry efforts. To describe our initial studies in this context, we must return to Scheme 3. In the solution-phase chemistry, we utilized a solution of PhSeH generated from PhSeSePh by reduction under argon (PhSeH undergoes rapid oxidative dimerization in air) to form the phenylseleno glycosides. For the purposes of the solid-phase version of this chemistry, we required a suitable resin-bound selenol that could be manipulated in air. To this end, the previously reported polystyrene selenium bromide resin[7] (●-SeBr) was reduced ($LiBH_4$, THF) and the resulting lithioselenide resin (●-SeLi) was quenched with excess $n$$Bu_3SnCl$ furnishing a colorless, odorless resin (●-SeSn$n$$Bu_3$) which could be quickly filtered in air and immediately used. Thus treatment of this seleno-tin resin with three equivalents of trichloroacetimidate **32** (Scheme 3) in the presence of $BF_3 \cdot Et_2O$ led to excellent loading (> 90 %, as determined by IR spectroscopy and cleavage with $n$$Bu_3SnH$/AIBN cat.) of the sugar, furnishing **33** (R = ●). Of particular interest was the fact that cleavage of the resin-bound 1- or 2-seleno glycosides with $n$$Bu_3SnH$/AIBN cat. regenerated the $n$$Bu_3SnSe$-resin, which could be filtered off and re-used in coupling reactions. Proceeding with resin-bound selenoglycoside **33** (R = ●), its acetate groups were cleaved (NaOMe, MeOH, > 95 % yield) to afford diol **34** (R = ●), which was monoprotected (TBSOTf, 2,6-lutidine, > 80 % yield) furnishing the 2-hydroxyseleno glycoside **35** (R = ●). Exposure of the latter resin (**35**) to DAST in CH_2Cl_2 led, in quantitative yield, to glycosyl fluoride **36** (R = ●) in which the carbohydrate moiety was attached to the seleno polymer at the C-2 position. Coupling of **36** with the monobenzoate of ethylene glycol (**43**) (10 equivalents) under the influence of $SnCl_2$ furnished, stereoselectively, resin **37** (R = ●) in > 89 % yield. The 2-deoxy glycoside **38** was then released from **37** (R = ●) by reductive cleavage of the C–Se bond ($n$$Bu_3SnH$/AIBN cat., benzene, 80 °C, 95 % yield). In order to set the stage for orthoester formation, the benzoate group was removed from **37** (R = ● by exposure to NaOMe in THF/MeOH (> 95 % yield) leading to **39** (R = ●) which underwent smooth desilylation upon treatment with $n$$Bu_4NF$ to afford dihydroxy selenide **41** (R = ●) (> 95 % yield). Oxidation of the resin-bound selenium to the selenoxide was found to be delicate and, therefore, several methods were explored, including mCPBA in CH_2Cl_2 at $-78\,^{\circ}C$, H_2O_2 in

  0947-6539/00/0617-3173 $ 17.50+.50/0

THF at 0 °C, and O_3 in toluene at −78 °C. Unlike the solution-phase selenoxides, it was observed that the resin-bound selenoxides were more prone to *syn*-elimination at room temperature and, therefore, necessitated the employment of lower temperatures for the oxidation step and the *m*CPBA method was proven to be the preferred procedure for this task. Thus, treating selenide resin **39** (R = ●) with *m*CPBA in CH_2Cl_2 at > −78 °C, followed by rapid filtration and transfer to a sealed tube was found to give the cleanest results. The orthoester **40** was obtained after heating the selenoxide in vinyl acetate/toluene/diisopropylamine 2:2:1 at 140 °C for 12 h in a sealed tube, filtering, concentrating the obtained solution and finally chromatography (>85% yield). Diol **41** (R = ●) yielded **42** on similar treatment (81% yield) as expected. The generality and scope of the solid-phase synthesis of 2-deoxy sugars, orthoesters, and 2,3-allylic orthoesters were examined and the results are tabulated in Tables 2 and 3. The selectivities and yields in these reactions were found to be identical or similar to those observed for the solution-phase chemistry (see Tables 2 and 3).

Conclusion

The described chemistry lays the foundation for reliable, practical and stereocontrolled constructions of 1,1′-disaccharides and higher oligosaccharides on one hand, and 2-deoxy glycosides and orthoesters on the other. The first method relies on tin-acetal, trichloroacetimidate, and glycosyl fluoride technologies while the second objective requires 1,2-phenylseleno migrations followed by oxidative or reductive processing of the 2-phenylseleno glycosides obtained. A solid-phase version of the latter, selenium-based methodology was also developed. Both technologies found admirable applications in, and were crucial for the success of the total synthesis of everninomicin 13,384-1 (**1**) described in the preceding articles.[1–3] Further applications of these methods in organic synthesis in general and combinatorial chemistry in particular are envisioned.

Experimental Section

General: For general techniques and procedures, see paper 1 in this series.[1]

Typical procedure for the synthesis of disaccharides Preparation of disaccharide 5: In a 50 mL Schlenk-tube were added diol **2** (91 mg, 0.20 mmole), nBu$_2$SnO (60 mg, 0.24 mmol), and anhydrous methanol (5 mL) and the mixture was brought to a gentle reflux under argon. After the solution turned clear, refluxing was continued for an additional 2 h, before cooling to ambient temperature and concentration under reduced pressure. The residue was azeotroped with benzene (2 mL) before addition of imidate **3** (85 mg, 0.13 mmol) in benzene (2 mL). Removal of the solvent under reduced pressure followed by further drying by azeotroping with benzene (3 × 2 mL) and finally applying high vacuum (1 mbar, 0.5 h) gave an amorphous residue which was dissolved in anhydrous Et_2O (1.0 mL). The solution was cooled (0 °C) and TMSOTf in Et_2O (0.13 mL, 0.5 M) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred until TLC analysis indicated complete disappearance of imidate **3** (ca 48 h). Triethylamine (0.2 mL) was added, followed by a saturated aqueous solution of $NaHCO_3$ (10 mL) and EtOAc (30 mL). The layers were separated and the organic phase was extracted with brine (5 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residual oil on silica gel (30 → 100% Et_2O in hexanes) afforded compounds **5** (81 mg, 66%) and **6** (17 mg, 9%).

Disaccharide 5: The data for disaccharide **5** was given in Part 2[1] of this series.

Typical procedure for the synthesis of trisaccharides Preparation of trisaccharide 6: The procedure as described above for the synthesis of disaccharides was followed, except for the use of 2.2 equiv of glycosyl fluoride **4** instead of trichloroacetimidate **3**. Yield of **6** (84%).

Trisaccharide 6: R_f = 0.11 (60% Et_2O in hexanes); $[\alpha]_D^{22}$ = +21.8 (c = 1.71, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3031, 2864, 1743, 1496, 1454, 1368, 1236, 1110, 912, 739, 698 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 – 7.02 (m, 45H, ArH), 5.69 (dd, J = 3.3, 1.8 Hz, 1H, H2′), 5.43 (s, 1H, H2″), 5.38 (s, 1H, H1′), 5.12 (s, 1H, H1″), 4.92 – 4.27 (m, 18H, CH_2Ar), 4.64 (s, 1H, H1), 4.35 (d, J = 1.6 Hz, 1H, H2), 4.32 (br d, J = 10.4 Hz, 1H, H5′), 4.22 – 4.20 (m, 1H, H5″), 4.16 (dd, J = 9.6, 3.4 Hz, 1H, H3′), 4.00 (dd, J = 9.7, 9.4 Hz, 1H, H4″), 3.93 (dd, J = 10.0, 9.9 Hz, 1H, H4′), 3.89 – 3.82 (m, 3H, H3″, H4, H6′), 3.73 – 3.66 (m, 6H, H3, H6, H6, H6′, H6″, H6″), 3.49 (ddd, J = 9.9, 5.6, 1.9 Hz, 1H, H5), 2.17 (s, 3H, OAc), 2.13 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 170.1, 138.5, 138.4, 138.2, 138.2, 138.0, 138.0, 137.9, 137.6, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.4, 127.1, 127.0, 98.9, 98.7, 98.2, 82.4, 78.6, 78.6, 75.7, 75.1, 75.0, 74.8, 74.2, 73.8, 73.8, 73.3, 73.1, 72.1, 72.0, 71.8, 71.8, 71.5, 71.5, 69.3, 68.6, 68.5, 68.2, 68.1, 21.1, 21.0; ^{13}C NMR (150 MHz, $CDCl_3$; proton coupled): δ = 98.9 ($J_{C,H}$ = 177.5 Hz), 98.7 ($J_{C,H}$ = 151.2 Hz), 98.2 ($J_{C,H}$ = 170.5 Hz); HRMS (FAB): calcd for $C_{85}H_{90}O_{18}Cs$ [M+Cs$^+$]: 1532.5182, found 1532.5122.

Diol 2: See ref. [19].

Imidate 3: See ref. [20].

Fluoride 4: See ref. [21].

Imidate 7: See ref. [22].

Fluoride 8α: R_f = 0.54 (50% Et_2O in hexanes); $[\alpha]_D^{22}$ = +50.6 (c = 1.47, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 2923, 1746, 1454, 1366, 1231, 1162, 1060 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 – 7.14 (m, 15H, ArH), 5.71 (dd, J = 53.9, 2.7 Hz, 1H, H1), 4.90 (ddd, J = 24.9, 9.9, 2.7 Hz, 1H, H2), 4.84 – 4.50 (m, 6H, CH_2Ar), 3.98 (dd, J = 9.6, 9.6 Hz, 1H, H3), 3.96 (ddd, J = 10.0, 3.5, 1.9 Hz, 1H, H5), 3.81 (dd, J = 9.6, 9.6 Hz, 1H, H4), 3.77 (dd, J = 11.0, 3.5 Hz, 1H, H6), 3.68 (dd, J = 11.0, 1.9 Hz, 1H, H6), 2.03 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 138.2, 137.8, 137.7, 128.4, 128.4, 127.9, 127.9, 127.8, 127.8, 127.6, 105.4, 103.9, 79.4, 76.7, 75.5, 75.3, 73.5, 72.9, 72.9, 72.8, 67.7, 20.7; HRMS (FAB): calcd for $C_{29}H_{31}O_6FNa$ [M+Na]$^+$: 517.2002, found 517.2018.

Fluoride 8β: m.p. 49 – 50 °C (Et_2O/hexanes); R_f = 0.52 (50% Et_2O in hexanes); $[\alpha]_D^{22}$ = +15.5 (c = 2.19, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3025, 2873, 1750, 1454, 1368, 1228, 1106 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 – 7.16 (m, 15H, ArH), 5.26 (dd, J = 54.0, 6.3 Hz, 1H, H1), 5.11 (ddd, J = 11.0, 8.2, 6.5 Hz, 1H, H2), 4.78 – 4.53 (m, 6H, CH_2Ar), 3.85 (dd, J = 9.3, 9.2 Hz, 1H, H3), 3.77 – 3.66 (m, 4H, H4, H5, H6, H6), 2.02 (s, 3H, OAc); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 137.7, 137.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.6, 107.5, 105.8, 81.5, 81.5, 76.6, 74.8, 74.3, 73.5, 72.5, 72.3, 68.3, 20.7; HRMS (FAB): calcd for $C_{29}H_{31}O_6FNa$ [M+Na]$^+$: 517.2002, found 517.2014.

Disaccharide 9: R_f = 0.24 (70% Et_2O in hexanes); $[\alpha]_D^{22}$ = −2.1 (c = 1.1, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3025, 2868, 1746, 1366, 1234, 1066 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 – 7.19 (m, 30H, ArH), 5.05 (dd, J = 9.2, 7.9 Hz, 1H, H2′), 4.84 (d, J = 7.8 Hz, 1H, H1′), 4.84 – 4.53 (m, 12H, CH_2Ar), 4.78 (s, 1H, H1), 4.17 (d, J = 3.0 Hz, 1H, H2), 3.96 (dd, J = 9.5, 9.4 Hz, 1H, H4), 3.78 (dd, J = 11.0, 1.9 Hz, 1H, H6′), 3.75 – 3.73 (m, 5H, H3′, H4′, H6, H6, H6′), 3.57 (dd, J = 9.1, 3.1 Hz, 1H, H3), 3.53 (m, 1H, H5′), 3.44 (ddd, J = 9.7, 4.9, 1.8 Hz, 1H, H5), 2.48 (s, 1H, OH), 1.96 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 138.2, 138.1, 138.0, 137.8, 137.7, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 96.6, 95.4, 82.4, 80.8, 77.4, 75.2, 75.2, 75.0, 74.9, 74.9, 73.9, 73.4, 73.2, 73.1, 70.9, 68.9, 68.4, 67.7, 20.9; HRMS (FAB): calcd for $C_{56}H_{60}O_{12}Cs$ [M+Cs]$^+$: 1057.3139, found 1057.3108.

Trisaccharide 10: R_f = 0.49 (70% Et_2O in hexane); $[\alpha]_D^{22}$ = −19.0 (c = 0.3, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3029, 2920, 1746, 1454, 1365, 1233, 1058, 739, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 – 7.14 (m, 45H, ArH), 5.09 (dd, J = 8.0, 3.3 Hz, 1H, H2′ or H2″), 5.07 (dd, J = 8.0, 2.9 Hz, 1H, H2′ or H2″), 4.94 – 4.45 (m, 18H, CH_2Ar), 4.85 (d, J = 7.8 Hz, 1H, H1′ or H1″),

0947-6539/00/0617-3174 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

4.78 (d, $J = 7.9$ Hz, 1H, H1′ or H1″), 4.59 (s, 1H, H1), 4.40 (d, $J = 2.7$ Hz, 1H, H2), 3.87 (dd, $J = 9.6$, 8.9 Hz, 1H, H3′ or H3″), 3.77–3.52 (m, 11H, H3′ or H3″, H4, H4′, H4″, H5′ or H5″, H6, H6, H6′, H6′, H6″, H6″), 3.48 (dd, $J = 9.4$, 2.9 Hz, 1H, H3), 3.44 (ddd, $J = 9.9$, 3.7, 2.3 Hz, 1H, H5), 3.41 (ddd, $J = 9.8$, 7.2, 2.2 Hz, 1H, H5′ or H5″), 1.9 (s, 3H, OAc), 1.89 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.7$, 169.4, 138.9, 138.6, 138.3, 138.2, 138.2, 137.9, 137.7, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.4, 127.4, 127.3, 99.6, 95.5, 95.1, 93.6, 83.1, 82.4, 80.0, 78.6, 77.6, 75.7, 75.1, 75.1, 74.9, 74.7, 74.7, 74.4, 74.3, 73.8, 73.5, 73.4, 72.9, 70.2, 69.6, 69.4, 68.1, 21.3, 21.2; HRMS (FAB): calcd for $C_{85}H_{90}O_{18}Cs$ $[M+Cs]^+$: 1531.5182, found 1531.5254.

Imidate 11: See ref. [23].

Fluoride 12: See ref. [24].

Disaccharide 13: m.p. 74–75 °C (Et_2O/hexanes); $R_f = 0.13$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = -25.7$ ($c = 0.43$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3541$, 3032, 2868, 1750, 1496, 1454, 1372, 1239, 1073, 911, 800, 735, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.43-7.24$ (m, 20H, ArH), 5.50 (s, 1H, ArCH), 5.40 (dd, $J = 9.5$, 9.4 Hz, 1H, H3′), 5.03 (dd, $J = 9.2$, 8.0 Hz, 1H, H2′), 5.00 (d, $J = 7.9$ Hz, 1H, H1′), 4.91, 4.57 (AB, $J = 11.1$ Hz, 2H, CH_2Ar), 4.77, 4.65 (AB, $J = 12.3$ Hz, 2H, CH_2Ar), 4.73 (d, $J = 0.6$ Hz, 1H, H1), 4.61, 4.55 (AB, $J = 12.3$ Hz, 2H, CH_2Ar), 4.35 (dd, $J = 10.5$, 5.0 Hz, 1H, H6′), 4.11 (d, $J = 2.8$ Hz, 1H, H2), 3.95 (dd, $J = 9.4$, 9.4 Hz, 1H, H4), 3.78 (dd, $J = 10.8$, 2.1 Hz, 1H, H6), 3.77 (dd, $J = 10.3$, 10.2 Hz, 1H, H6′), 3.73 (dd, $J = 10.9$, 4.9 Hz, 1H, H6), 3.69 (dd, $J = 9.6$, 9.5 Hz, 1H, H4′), 3.56 (dd, $J = 9.2$, 3.0 Hz, 1H, H3), 3.53 (ddd, $J = 9.8$, 9.8, 4.9 Hz, 1H, H5′), 3.46 (ddd, $J = 9.5$, 4.9, 2.0 Hz, 1H, H5), 2.36 (s, 1H, OH), 2.07, 2.00 (2 × s, 2 × 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.7$, 169.9, 138.2, 138.1, 137.8, 136.7, 129.1, 128.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 126.1, 101.5, 97.2, 95.9, 80.9, 78.3, 75.4, 75.2, 73.8, 73.8, 73.4, 71.9, 71.2, 71.1, 68.9, 68.4, 67.8, 66.4, 20.7; HRMS (FAB): calcd for $C_{44}H_{48}O_{13}Cs$ $[M+Cs]^+$: 917.2149, found 917.2170.

Trisaccharide 14: m.p. 97–98 °C (Et_2O/hexanes); $R_f = 0.36$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = -70.0$ ($c = 1.2$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3033$, 2871, 1751, 1497, 1454, 1372, 1316, 1236, 1068, 912, 802, 739, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.44-7.26$ (m, 25H, ArH), 5.50 (s, 2H, ArCH), 5.50 (t, $J = 9.8$, 9.2 Hz, 1H, H3″), 5.40 (t, $J = 9.9$, 9.8 Hz, 1H, H3′), 5.15 (dd, $J = 9.8$, 8.1 Hz, 1H, H2′), 5.14 (dd, $J = 9.2$, 8.3 Hz, 1H, H2″), 5.11 (d, $J = 8.0$ Hz, 1H, H1″), 5.01 (d, $J = 8.2$ Hz, 1H, H1′), 4.92, 4.49 (AB, $J = 11.2$ Hz, 2H, CH_2Ar), 4.80 (s, 1H, H1), 4.75, 4.58 (AB, $J = 12.2$ Hz, 2H, CH_2Ar), 4.55, 4.50 (AB, $J = 12.5$ Hz, 2H, CH_2Ar), 4.41 (dd, $J = 10.5$, 5.0 Hz, 1H, H6′), 4.37 (dd, $J = 10.8$, 5.1 Hz, 1H, H6″), 4.30 (d, $J = 2.9$ Hz, 1H, H2), 3.83 (dd, $J = 10.5$, 10.4 Hz, 1H, H4″), 3.75 (dd, $J = 10.5$, 10.4 Hz, 1H, H4′), 3.74–3.68 (m, 4H, H6, H6, H6′, H6″), 3.61 (dd, $J = 9.6$, 9.6 Hz, 1H, H4), 3.56–3.53 (m, 2H, H5′, H5″), 3.52 (dd, $J = 9.3$, 2.8 Hz, 1H, H3), 3.47 (ddd, $J = 9.6$, 5.5, 1.9 Hz, 1H, H5), 2.22, 2.08, 2.05, 1.94 (4 × s, 4 × 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.4$, 169.9, 169.9, 169.6, 138.2, 137.9, 137.8, 136.9, 136.6, 129.1, 129.0, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 126.2, 126.1, 101.5, 99.7, 95.5, 94.8, 80.4, 78.9, 78.3, 75.7, 75.2, 74.3, 73.1, 72.4, 71.7, 71.3, 71.1, 71.1, 70.7, 69.7, 68.6, 68.3, 66.2, 65.7, 20.9, 20.7; HRMS (FAB): calcd for $C_{61}H_{66}O_{20}Cs$ $[M+Cs]^+$: 1251.3202, found 1251.3258.

Imidate 15*α*: $R_f = 0.49$ (60% Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 3031$, 2868, 1747, 1620, 1452, 1369, 1299, 1228, 1066, 884, 832, 797, 739, 698, 645 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 8.41$ (s, 1H, NH), 7.22–7.06 (m, 10H, ArH), 6.97 (d, $J = 4.6$ Hz, 1H, H1), 5.52 (dd, $J = 5.1$, 4.6 Hz, 1H, H2), 4.53 (ddd, $J = 5.6$, 5.6, 5.1 Hz, 1H, H4), 4.41, 4.29 (AB, $J = 11.5$ Hz, 2H, CH_2Ar), 4.28 (s, 2H, CH_2Ar), 4.25 (dd, $J = 6.0$, 5.1 Hz, 1H, H3), 3.72 (dd, $J = 10.3$, 5.2 Hz, 1H, H5), 3.61 (dd, $J = 10.3$, 5.1 Hz, 1H, H5), 1.63 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.5$, 161.8, 139.0, 138.4, 129.3, 129.2, 128.8, 128.6, 128.5, 128.5, 98.2, 80.6, 79.3, 78.0, 74.4, 73.5, 68.8, 30.6, 21.4.

Imidate 15*β*: $R_f = 0.27$ (60% Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 3031$, 2868, 1747, 1670, 1452, 1369, 1299, 1228, 1066, 843, 832, 797, 739, 698, 645 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 8.41$ (s, 1H, NH), 7.30–7.05 (m, 10H, ArH), 6.59 (s, 1H, H1), 5.57 (s, 1H, H2), 4.67, 4.42 (AB, $J = 12.0$ Hz, 2H, CH_2Ar), 4.60 (ddd, $J = 6.0$, 6.0, 5.6 Hz, 1H, H4), 4.40, 4.33 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 3.98 (dd, $J = 10.0$, 5.6 Hz, 1H, H5), 3.91 (dd, $J = 10.0$, 5.5 Hz, 1H, H5), 3.84 (d, $J = 5.3$ Hz, 1H, H3), 1.46 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 161.8$, 129.2, 129.2, 129.2, 128.6, 128.5, 128.5, 128.4, 104.1, 84.0, 80.9, 79.6, 74.3, 72.8, 69.6, 21.7.

Disaccharide 17: $R_f = 0.16$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = -54.9$ ($c = 0.8$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3495$, 3029, 2866, 2359, 1742, 1496, 1453, 1369, 1233, 1097, 1046, 739, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.37-7.19$ (m, 25H, ArH), 5.52 (s, 1H, H1′), 5.35 (s, 1H, H2′), 4.90–4.51 (m, 10H, CH_2Ar), 4.81 (d, $J = 0.7$ Hz, 1H, H1), 4.45 (dt, $J = 7.4$, 4.9 Hz, 1H, H4′), 4.06 (br s, 1H, H2), 3.95 (d, $J = 5.1$ Hz, 1H, H3′), 3.93 (dd, $J = 9.3$, 9.0 Hz, 1H, H4), 3.77–3.70 (m, 4H, H5′, H5′, H6, H6), 3.57 (dd, $J = 9.0$, 3.1 Hz, 1H, H3), 3.47 (ddd, $J = 9.4$, 3.3, 2.9 Hz, 1H, H5), 2.46 (s, 1H, OH), 2.06 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.5$, 138.2, 138.2, 138.0, 137.9, 137.6, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.5, 102.6, 95.3, 81.6, 81.2, 80.4, 79.7, 75.2, 75.0, 73.9, 73.4, 73.3, 71.6, 71.3, 69.2, 68.9, 68.2, 65.8, 20.8; HRMS (FAB): calcd for $C_{48}H_{52}O_{11}Cs$ $[M+Cs]^+$: 937.2564, found 937.2597.

Trisaccharide 18: $R_f = 0.48$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = -104.2$ ($c = 0.9$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3030$, 2865, 1742, 1496, 1453, 1369, 1234, 1050, 738, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.39-7.11$ (m, 35H, ArH), 5.65 (s, 1H, H1′ or H1″), 5.52 (s, 1H, H1′ or H1″), 5.40 (s, 1H, H2′ or H2″), 5.31 (s, 1H, H2′ or H2″), 4.91–4.78 (m, 14H, CH_2Ar), 4.79 (s, 1H, H1), 4.45 (ddd, $J = 7.5$, 7.5, 5.4 Hz, 1H, H4′ or H4″), 4.36 (m, 1H, H4′ or H4″), 4.23 (d, $J = 3.0$ Hz, 1H, H2), 3.91 (d, $J = 5.1$ Hz, 2H, H3′, H3″), 3.79–3.67 (m, 7H, H4, H6, H6, H5′, H5′, H5″, H5″), 3.51 (dd, $J = 9.3$, 2.9 Hz, 1H, H3), 3.45 (ddd, $J = 9.7$, 5.3, 1.8 Hz, 1H, H5), 2.07, 1.99 (2 × s, 2 × 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.7$, 169.7, 138.7, 138.5, 138.4, 138.4, 138.3, 138.0, 137.5, 128.4, 128.4, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.7, 127.7, 127.6, 127.5, 127.4, 127.4, 127.4, 127.3, 127.2, 127.1, 106.4, 102.0, 99.5, 95.9, 81.7, 81.2, 80.8, 80.6, 80.1, 79.8, 79.8, 75.5, 75.0, 74.3, 73.3, 73.2, 73.0, 72.4, 71.3, 71.2, 70.1, 69.5, 69.2, 20.9, 20.8; HRMS (FAB): calcd for $C_{69}H_{74}O_{16}Cs$ $[M+Cs]^+$: 1291.4031, found 1291.4135.

Disaccharide 20: m.p. 165–166 °C (Et_2O/hexanes); $R_f = 0.21$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = +19.9$ ($c = 0.56$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3546$, 3031, 2903, 1744, 1452, 1365, 1231, 1071, 740, 695 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.34-7.26$ (m, 25H, ArH), 5.05 (dd, $J = 9.3$, 8.0 Hz, 1H, H2′), 4.96–4.54 (m, 10H, CH_2Ar), 4.81 (d, $J = 8.0$ Hz, 1H, H1′), 4.60 (s, 1H, H1), 4.05 (d, $J = 2.7$ Hz, 1H, H2), 3.74 (dd, $J = 10.8$, 1.9 Hz, 1H, H6′), 3.68–3.64 (m, 3H, H3′, H4′, H6′), 3.57 (m, 1H, H5′), 3.56 (dd, $J = 9.2$, 9.2 Hz, 1H, H4), 3.49 (dd, $J = 9.1$, 3.0 Hz, 1H, H3), 3.34 (dq, $J = 9.2$, 6.2 Hz, 1H, H5), 2.90 (br s, 1H, OH), 1.95 (s, 3H, OAc), 1.34 (d, $J = 6.1$ Hz, 3H, H6); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.4$, 138.3, 138.0, 137.9, 137.8, 137.7, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 98.1, 97.8, 82.9, 81.0, 79.2, 77.8, 75.4, 75.4, 75.1, 75.0, 73.4, 72.9, 71.2, 68.6, 68.4, 20.9, 17.9; HRMS (FAB): calcd for $C_{49}H_{54}O_{11}Cs$ $[M+Cs]^+$: 951.2735, found 951.2720.

Trisaccharide 21: $R_f = 0.2$ (60% Et_2O in hexanes); $[\alpha]_D^{22} = +9.2$ ($c = 0.4$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3029$, 2866, 1741, 1453, 1365, 1235, 1064, 826, 739, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CHCl_3$): $\delta = 7.34-7.16$ (m, 40H, ArH), 5.03 (dd, $J = 9.1$, 7.9 Hz, 1H, H2′ or H2″), 5.01 (dd, $J = 9.0$, 8.1 Hz, 1H, H2′ or H2″), 4.80 (d, $J = 7.8$ Hz, 1H, H1′ or H1″), 4.79–4.45 (m, 16H, CH_2Ar), 4.75 (d, $J = 8.9$ Hz, 1H, H1′ or H1″), 4.59 (s, 1H, H1), 4.16 (br s, 1H, H2), 3.74 (br d, $J = 11.5$ Hz, 1H, H6′ or H6″), 3.70 (dd, $J = 11.5$, 5.2 Hz, 1H, H6′ or H6″), 3.66–3.61 (m, 5H, H3′ or H3″, H4′, H4″, H6′, H6″), 3.58 (dd, $J = 9.3$, 9.3 Hz, 1H, H3′ or H3″), 3.47–3.43 (m, 3H, H3, H5′, H5″), 3.37 (dd, $J = 9.0$, 9.0 Hz, 1H, H4), 3.31 (dq, $J = 8.9$, 2.7 Hz, 1H, H5), 1.96, 1.86 (2 × s, 2 × 3H, OAc), 1.59 (d, $J = 2.4$ Hz, 3H, H6); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 169.6$, 169.3, 138.6, 138.3, 138.2, 138.1, 138.0, 137.9, 128.4, 128.4, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 101.0, 98.0, 95.6, 83.1, 83.0, 82.6, 80.0, 78.0, 77.8, 76.8, 75.5, 75.3, 75.0, 74.9, 74.2, 73.8, 73.5, 73.2, 72.5, 72.3, 72.3, 69.1, 68.7, 21.1, 21.0, 17.9; HRMS (FAB): calcd for $C_{78}H_{84}O_{17}Cs$ $[M+Cs]^+$: 1425.4763, found 1425.4860.

Diol 22: $R_f = 0.30$ (50% Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 3411$, 2954, 2927, 2853, 1612, 1514, 1358, 1300, 1250, 1180, 1096, 837 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, α:β ratio ca. 1.5:1): $\delta = 7.24$ (d, $J = 8.8$ Hz, 4H, PMB), 6.88 (d, $J = 8.8$ Hz, 4H, PMB), 5.21 (s, 1H, H1), 4.67 (s, 1H, H1), 4.58, 4.48 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.57, 4.48 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 3.94 (dd, $J = 3.5$, 1.8 Hz, 1H, H2), 3.91 (dq, $J = 8.8$ Hz, 1H, H5), 3.87 (dd, $J = 3.5$, 1.5 Hz, 1H, H2), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.63 (dd, $J = 8.8$, 3.5 Hz, 1H, H3), 3.53 (t, $J = 8.8$ Hz, 1H, H4), 3.46 (t, $J = 8.8$ Hz, 1H, H4), 3.33 (dd, $J = 8.8$, 3.5 Hz, 1H, H3), 3.27 (dq, $J = 8.8$, 6.1 Hz, 1H, H5), 1.29 (d, $J = 6.1$ Hz, 3H, H6), 1.25 (d, $J = 6.1$ Hz, 3H, H6), 0.88 (s, 18H, *t*BuSi), 0.07 (s, 3H, MeSi), 0.06 (s, 6H, MeSi), 0.05 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 129.6$, 129.5, 114.0, 113.9, 93.8, 81.6, 79.6, 77.1, 72.6, 72.3, 71.5, 71.4, 68.8, 68.7, 68.3, 55.2; HRMS (FAB): calcd for $C_{20}H_{34}O_6SiNa$ $[M+Na]^+$: 421.2017, found 421.2037.

Disaccharide 23: $R_f = 0.41$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = +9.1$ ($c = 0.23$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3064, 3031, 2931, 2858, 1736, 1613, 1514, 1456, 1369, 1248, 1104, 1050, 836, 735\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.35–7.15 (m, 17H, ArH), 6.88 (d, $J = 8.8$ Hz, 2H, PMB), 5.40 (brs, 1H, H2′), 5.14 (s, 1H, H1′), 4.86, 4.48 (AB, $J = 11.0$ Hz, 2H, CH_2Ar), 4.69, 4.46 (AB, $J = 10.9$ Hz, 2H, CH_2Ar), 4.66, 4.54 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.60 (s, 1H, H1), 4.54 (brs, 2H, CH_2Ar), 4.13 (brd, $J = 8.3$ Hz, 1H, H5′), 4.06 (dd, $J = 9.7$, 3.5 Hz, 1H, H3′), 4.04 (brs, 1H, H2), 3.94 (t, $J = 9.7$ Hz, 1H, H4′), 3.81 (s, 3H, OMe), 3.78 (dd, $J = 9.4$, 4.0 Hz, 1H, H6′), 3.66 (brd, $J = 9.3$ Hz, 1H, H6′), 3.55 (t, $J = 8.8$ Hz, 1H, H4), 3.27 (dd, $J = 9.7$, 7.0 Hz, 1H, H3), 3.24 (dq, $J = 8.8$, 6.1 Hz, 1H, H5), 2.51 (d, $J = 2.2$ Hz, 1H, OH), 2.15 (s, 3H, OAc), 1.24 (d, $J = 6.1$ Hz, 3H, H6), 0.89 (s, 9H, *t*BuSi), 0.13, 0.07 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.5$, 163.6, 159.3, 138.4, 138.0, 137.8, 129.7, 129.6, 128.3, 128.3, 128.2, 128.0, 127.7, 127.7, 127.6, 127.5, 127.4, 113.8, 99.1, 97.8, 80.9, 77.8, 74.9, 74.0, 73.4, 73.3, 72.2, 72.0, 70.9, 68.6, 68.4, 67.9, 55.2, 25.9, 21.0, 18.2, 18.0, −3.7, −4.6; HRMS (FAB): calcd for $C_{49}H_{64}O_{12}Na$ $[M+Na]^+$: 895.4059, found 895.4037.

Trisaccharide 24: $R_f = 0.62$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = +14.5$ ($c = 2.94$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3031, 2929, 2858, 1746, 1512, 1455, 1369, 1237, 1107, 1054, 837\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.36–7.00 (m, 32H, ArH), 6.84 (d, $J = 8.3$ Hz, 2H, PMB), 5.61 (brs, 1H, H2″), 5.39 (brs, 1H, H2′), 5.20 (s, 1H, H1″), 5.08 (s, 1H, H1′), 4.80–4.25 (m, 15H, 7 × CH_2Ar, H1), 4.26–4.25 (m, 2H, H5′, H5″), 4.20 (brd, $J = 9.7$ Hz, 1H, H2), 4.14 (dd, $J = 9.7$, 3.1 Hz, 1H, H3″), 3.99 (dd, $J = 9.7$, 3.1 Hz, 1H, H3′), 3.94 (t, $J =$ 9.7 Hz, 1H, H4″), 3.89 (t, $J = 10.1$ Hz, 1H, H4′), 3.84–3.77 (m, 3H, H6′, H6′, H6″), 3.80 (s, 3H, OMe), 3.64 (d, $J = 9.6$ Hz, 1H, H6″), 3.62 (t, $J =$ 9.2 Hz, 1H, H4), 3.28–3.22 (m, 2H, H3, H5), 2.15, 2.10 (2 × s, 2 × 3H, OAc), 1.26 (d, $J = 6.2$ Hz, 3H, H6), 0.89 (s, 9H, *t*BuSi), 0.14, 0.06 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.3$, 170.1, 158.9, 138.5, 138.3, 138.1, 137.9, 128.4, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 129.9, 127.9, 127.8, 127.8, 127.6, 125.6, 100.7, 98.7, 98.7, 98.7, 98.4, 82.3, 78.6, 78.5, 75.1, 74.9, 74.2, 74.0, 73.9, 73.7, 73.3, 72.5, 72.2, 71.9, 71.6, 71.5, 71.1, 68.7, 68.5, 68.4, 68.3, 55.2, 30.3, 29.7, 21.2, 21.1, 18.4, 18.1, −3.8, −4.5; HRMS (FAB): calcd for $C_{79}H_{94}O_{18}SiNa$ $[M+Na]^+$: 1369.6102, found 1369.6088.

Diol 25: $R_f = 0.32$ (100% Et_2O); IR (thin film): $\tilde{\nu} = 3401, 2919, 2927, 1643, 1455, 1419, 1355, 1255, 1091, 1002, 920, 844, 761\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$, α:β ratio ca. 3:1): $\delta =$ 5.93–5.82 (m, 8H, C*H*CH_2), 5.29–5.23 (m, 8H, CH_2-*E*), 5.18–5.13 (m, 8H, CH_2-*Z*), 5.00 (t, $J = 4.3$ Hz, 3H, H1), 4.87 (dd, $J = 10.5$, 2.6 Hz, 1H, H1), 4.48 (d, $J = 10.6$ Hz, 1H, OH), 4.17–4.12 (m, 8H, OCH_2), 4.09–4.05 (m, 8H, OCH_2), 3.96–3.93 (m, 2H, H2, H5), 3.83 (ddd, $J = 4.0$, 4.0, 3.7 Hz, 3H, H2), 3.79 (d, $J = 4.8$ Hz, 3H, OH), 3.74 (d, $J =$ 5.6 Hz, 6H, H5), 3.71 (dd, $J = 6.9$, 3.4 Hz, 3H, H3), 3.65–3.60 (m, 5H, H4, H4, H5), 3.42 (dd, $J = 12.6$, 5.0 Hz, 1H, H3), 2.79 (d, $J = 7.5$ Hz, 1H, OH), 2.75 (d, $J = 4.0$ Hz, 3H, OH); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 134.6$, 134.5, 134.4, 133.9, 118.3, 117.4, 117.3, 117.2, 94.4, 94.3, 78.5, 77.5, 73.7, 73.4, 72.3, 71.6, 71.4, 71.0, 69.6, 66.8, 61.5, 59.2; HRMS (MALDI): calcd for $C_{11}H_{18}O_5Na$ $[M+Na]^+$: 253.1046, found 253.1041.

Disaccharide 26: $R_f = 0.33$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = +36.7$ ($c = 0.21$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3459, 2908, 1736, 1592, 1448, 1364, 1232, 1082, 927, 795, 729\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.35–7.12 (m, 15H, ArH), 5.92–5.80 (m, 2H, C*H*CH_2), 5.42 (dd, $J = 3.0$, 2.0 Hz, 1H, H2′), 5.29 (ddm, $J = 17.2$, 1.6 Hz, 1H, CH_2-*E*), 5.27 (ddm, $J = 17.2$, 1.6 Hz, 1H, CH_2-*E*), 5.19 (s, 1H, H1′), 5.18 (ddm, $J = 10.4$, 1.2 Hz, 1H, CH_2-*Z*), 5.11 (ddm, $J = 10.4$, 1.3 Hz, 1H, CH_2-*Z*), 4.97 (d, $J = 3.5$ Hz, 1H, H1), 4.82, 4.46 (AB, $J = 10.6$ Hz, 2H, CH_2Ar), 4.69, 4.49 (AB, $J = 11.0$ Hz, 2H, CH_2Ar), 4.68, 4.48 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 4.12–4.00 (m, 4H, OCH_2), 3.97 (dd, $J = 9.3$, 3.2 Hz, 1H, H3′), 3.93 (t, $J = 9.6$ Hz, 2H, H4′, H5), 3.91 (brs, 1H, H2), 3.87 (brdd, $J = 9.6$, 2.2 Hz, 1H, H5′), 3.80 (dd, $J = 10.9$, 3.9 Hz, 1H, H6′), 3.68 (dd, $J = 10.8$, 1.6 Hz, 1H, H6′), 3.59 (brs, 2H, H3, H5), 3.44 (ddd, $J = 12.1$, 2.4, 2.4 Hz, 1H, H4), 2.14 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.4$, 138.1, 138.0, 137.8, 134.5, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 117.4, 117.0, 94.0, 93.6, 78.2, 76.5, 75.3, 74.1, 73.4, 73.0, 71.8, 71.6, 70.8, 68.6, 68.5, 65.5, 58.8, 30.3, 21.1; HRMS (MALDI): calcd for $C_{40}H_{48}O_{11}Na$ $[M+Na]^+$: 727.3089, found 727.3063.

Trisaccharide 27: $R_f = 0.42$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = +46.0$ ($c = 0.48$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2919, 2860, 1741, 1598, 1448, 1364, 1232, 1095, 1053, 735, 693\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.35–7.12 (m, 30H, ArH), 5.89–5.76 (m, 2H, C*H*CH_2), 5.59 (brs, 1H, H2″), 5.25 (brs, 1H, H2′), 5.25 (d, $J = 1.4$ Hz, 1H, H1″), 5.23 (dd, $J = 17.2$, 1.5 Hz, 1H, CH_2-*E*), 5.22 (dd, $J = 17.2$, 1.6 Hz, 1H, CH_2-*E*), 5.13 (brs, 1H, H1′), 5.13 (dd, $J =$ 10.2, 1.2 Hz, 1H, CH_2-*Z*), 5.07 (dd, $J = 10.4$, 1.3 Hz, 1H, CH_2-*Z*), 4.83 (d, $J = 10.9$ Hz, 1H, CH_2Ar), 4.82 (d, $J = 10.8$ Hz, 1H, CH_2Ar), 4.75 (d, $J =$ 10.7 Hz, 1H, CH_2Ar), 4.74 (brs, 1H, H1), 4.71–4.62 (m, 4H, CH_2Ar), 4.51–4.41 (m, 5H, CH_2Ar), 4.20 (brs, 1H, H5′), 4.12 (dd, $J = 13.0$, 5.3 Hz, 2H, OCH_2), 4.07 (t, $J = 1.6$ Hz, 1H, H2), 4.05–3.98 (m, 3H, OCH_2, H5), 3.97–3.93 (m, 2H, H3′, H4′), 3.90 (dd, $J = 8.9$, 3.6 Hz, 1H, H3″), 3.84 (t, $J =$ 9.5 Hz, 1H, H4″), 3.78 (dd, $J = 10.7$, 3.6 Hz, 1H, H6′), 3.77–3.67 (m, 3H, H5″, H6″, H6″), 3.61 (dd, $J = 10.5$, 1.1 Hz, 1H, H6′), 3.58 (ddd, $J = 8.2$, 8.2, 4.8 Hz, 1H, H4), 3.37 (brs, 1H, H3), 3.18 (dd, $J = 10.5$, 9.1 Hz, 1H, H5), 2.11, 1.96 (2 × s, 2 × 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.0$, 169.9, 138.6, 138.4, 138.3, 138.2, 138.2, 138.0, 134.8, 134.7, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.4, 116.9, 116.5, 98.6, 98.5, 94.4, 91.8, 78.7, 77.7, 75.1, 75.0, 74.2, 74.1, 74.0, 73.5, 73.4, 72.1, 71.9, 71.6, 71.5, 71.2, 68.9, 68.8, 68.8, 68.4, 29.7, 21.0, 20.9; HRMS (MALDI): calcd for $C_{69}H_{78}O_{17}Na$ $[M+Na]^+$: 1201.5131, found 1201.5166.

Ring F diol 28: See Part 2[2] in this series.

Imidate 30: $R_f = 0.55$ (70% Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 3336, 3032, 2921, 1746, 1672, 1496, 1367, 1231, 1069, 795, 737\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$, α:β ca. 9:1): $\delta = 8.69$ (s, 0.9H, NHα), 8.60 (s, 0.1H, NHβ), 7.37–7.30 (m, 10H, ArH), 7.26 (s, 0.1H, H1β), 6.17 (d, $J = 3.3$ Hz, 0.9H, H1α), 5.60 (dd, $J = 3.1$, 3.1 Hz, 0.9H, H2α), 5.55 (d, $J = 3.0$ Hz, 0.1H, H2β), 4.83, 4.66 (AB, $J = 11.5$ Hz, 2H, CH_2Ar), 4.75, 4.64 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 3.99–3.93 (m, 3H, H3, H4, H5), 3.75 (m, 1H, H5), 2.17, 2.13 (2 × s, 2 × 3H, OAc); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 169.9$, 160.1, 138.1, 137.5, 128.4, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 95.1, 77.3, 77.0, 76.7, 76.4, 73.7, 73.4, 72.6, 72.3, 67.7, 67.3, 63.4, 20.9.

Ring FG system 31: $R_f = 0.14$ (70% Et_2O in hexanes); $[\alpha]_D^{22} = -32.2$ ($c =$ 0.7, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3477, 3031, 2922, 1746, 1613, 1513, 1456, 1371, 1304, 1242, 1105, 1048, 924, 820, 738, 699\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.39–7.26 (m, 15H, ArH), 7.25 (d, $J = 8.9$ Hz, 2H, PMB), 6.88 (d, $J = 8.8$ Hz, 2H, PMB), 5.52 (dd, $J = 2.8$, 2.7 Hz, 1H, H2′), 5.19 (d, $J =$ 2.2 Hz, 1H, H1′), 4.84–4.53 (m, 8H, CH_2Ar), 4.67 (s, 1H, H1), 4.06 (d, $J =$ 3.7 Hz, 1H, H2), 3.92 (dd, $J = 9.3$, 3.3 Hz, 1H, H3′), 3.90 (dd, $J = 9.4$, 9.4 Hz, 1H, H4), 3.86 (ddd, $J = 9.6$, 3.8, 2.8 Hz, 1H, H4′), 3.81 (s, 3H, OMe), 3.79 (dd, $J = 11.1$, 5.5 Hz, 1H, H6), 3.63 (dd, $J = 11.1$, 2.5 Hz, 1H, H5′), 3.60 (dd, $J = 11.1$, 4.3 Hz, 1H, H5′), 3.56 (dd, $J = 9.2$, 3.1 Hz, 1H, H3), 3.52 (dd, $J =$ 10.8, 10.5 Hz, 1H, H6), 3.38 (s, 3H, OMe), 3.35 (ddd, $J = 9.9$, 4.3, 2.5 Hz, 1H, H5), 2.12 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.8$, 159.3, 138.3, 137.9, 137.7, 130.3, 129.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 113.8, 101.6, 94.8, 94.5, 81.2, 77.2, 77.0, 76.9, 76.8, 75.3, 74.8, 73.7, 73.7, 73.4, 71.9, 71.4, 71.1, 68.3, 68.1, 61.7, 59.3, 56.7, 55.2, 33.4, 29.6, 20.9; ^{13}C NMR (150 MHz, $CDCl_3$; proton coupled): δ 94.9 ($J_{C,H} = 168.8$ Hz), 94.6 ($J_{C,H} = 159.1$ Hz); HRMS (FAB): calcd for $C_{43}H_{50}O_{12}Cs$ $[M+Cs]^+$: 891.2357, found 891.2379.

General procedure for the formation of resin bound seleno-glycosides: $LiBH_4$ (1.5 equiv) was added to a solution of the selenium bromide resin[7] (1.0 equiv) in THF (0.1 M) at 25 °C and the reaction mixture was stirred until the resin turned completely colorless. The solvents were removed by cannula and the resin was rinsed with THF under an atmosphere of argon. The colorless lithio-selenium resin was redissolved in THF (0.1 M) and nBu$_3$SnCl (20 equiv) was added. The reaction mixture was stirred for 2 h and then filtered through a sintered glass frit. The resin was rinsed with THF, CH_2Cl_2, and Et_2O and then dried under argon for 30 min. The resin was dissolved in CH_2Cl_2 containing the trichloroacetimidate (2.0 equiv, 0.1 M) and 4 Å MS were added. After stirring for 10 min, the reaction mixture was cooled to −78 °C and $BF_3 \cdot Et_2O$ (1.5 equiv) was added dropwise. The reaction mixture was stirred at −78 °C for 3–12 h and then filtered through a sintered glass frit. The resin was rinsed with CH_2Cl_2, MeOH, CH_2Cl_2, and finally Et_2O. The resin was then air dried for 2 h.

General procedure for the preparation of glycosyl fluorides: *Solid phase*: DAST (3.0 equiv) was added to a solution of the resin-bound alcohol (1.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C and the resulting mixture was stirred for 0.5 h. The reaction mixture was filtered through a glass frit and dried under argon for 30 min.

Solution phase: DAST (1.5 equiv) was added to a solution of the alcohol (1.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C and the resulting mixture was stirred for 0.5 h. The reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$, diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4) and the solvents

0947-6539/00/0617-3176 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

were removed under reduced pressure. The residue was used crude. This procedure is further illustrated by the following example:

Fluoride 36: DAST (0.08 mL, 0.60 mmol) was added to a solution of alcohol **35**[2] (0.210 g, 0.40 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C and the resulting mixture stirred for 0.5 h. The reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ (5 mL), diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was used crude.

Fluoride 46 was prepared from the corresponding 2-hydroxy-1-selenophenyl glycoside. **Alcohol**: $R_f = 0.35$ (40 % Et_2O in hexanes); $[\alpha]_D^{22} = -1.41$ ($c = 0.92$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3442$, 3030, 2867, 1580, 1360, 1210, 1116, 1073, 910, 738, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J =$ 7.7 Hz, 2H, ArH), 7.39–7.23 (m, 18H, ArH), 4.94–4.87 (m, 6H, CH_2Ar), 4.76 (d, $J = 9.7$ Hz, 1H, H1), 3.82 (dd, $J = 11.0$, 1.8 Hz, 1H, H6), 3.78 (dd, $J = 11.0$, 4.2 Hz, 1H, H6), 3.66–3.59 (m, 2H), 3.56–3.49 (m, 2H), 2.48 (d, $J = 1.9$ Hz, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.4$, 138.2, 138.0, 135.0, 129.0, 128.5, 128.4, 128.3, 128.3, 127.9, 127.9, 127.7, 127.5, 126.9, 126.6, 85.6, 84.6, 80.4, 77.2, 75.3, 75.0, 73.3, 73.4, 68.8; HRMS (MALDI): calcd for $C_{33}H_{34}O_5SeNa$ $[M+Na]^+$: 613.1463, found 613.1473.

Fluoride 47 was prepared from the corresponding 2-hydroxy-1-selenophenyl glycoside. **Alcohol**: $R_f = 0.38$ (50 % Et_2O in hexanes); $[\alpha]_D^{22} = -13.2$ ($c = 0.65$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3496$, 2930, 2857, 1580, 1474, 1381, 1252, 1120, 1074, 1037, 858, 837, 779, 736, 694 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 6.9$ Hz, 2H, ArH), 7.39–7.27 (m, 8H, ArH), 4.94, 4.78 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.76 (d, $J = 9.8$ Hz, 1H, H1), 3.50 (ddd, $J = 10.1$, 10.1, 1.9 Hz, 1H, H2), 3.37 (dq, $J = 8.9$, 6.2 Hz, 1H, H5), 3.35 (t, $J = 8.5$ Hz, 1H, H3), 3.29 (t, $J = 8.7$ Hz, 1H, H4), 2.38 (d, $J = 2.0$ Hz, 1H, OH), 1.33 (d, $J = 6.2$ Hz, 3H, H6), 0.92 (s, 9H, *t*BuSi), 0.08 (s, 3H, MeSi), 0.06 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.7$, 124.7, 129.0, 128.3, 128.1, 127.7, 127.5, 127.1, 85.7, 85.4, 78.2, 75.6, 74.9, 73.9, 25.9, 18.7, 18.0, −3.7, −4.3; HRMS (MALDI): calcd for $C_{25}H_{36}O_4SeSiNa$ $[M+Na]^+$: 531.1548, found 531.1523.

Fluoride 102 was prepared from the corresponding 2-hydroxy-1-selenophenyl glycoside. **Alcohol**: $R_f = 0.38$ (70 % Et_2O in hexanes); $[\alpha]_D^{22} = +164.9$ ($c = 2.66$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3467$, 2929, 2861, 1612, 1580, 1513, 1472, 1302, 1250, 1088, 869, 837 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.57–7.55$ (m, 2H, ArH), 7.26–7.22 (m, 5H, ArH), 6.88 (d, $J = 8.3$ Hz, 2H, PMB), 5.87 (d, $J = 1.3$ Hz, 1H, H1), 4.75, 4.51 (AB, $J = 10.8$ Hz, 2H, CH_2Ar), 4.13 (dd, $J = 3.1$, 1.3 Hz, 1H, H2), 4.05 (ddd, $J = 9.8$, 3.6, 1.9 Hz, 1H, H5), 4.02 (dd, $J = 8.8$, 3.5 Hz, 1H, H3), 3.84 (t, $J = 9.4$, Hz, 1H, H4), 3.79 (s, 3H, OMe), 3.65 (dd, $J = 10.8$, 3.7 Hz, 1H, H6), 3.50 (dd, $J = 10.8$, 2.0 Hz, 1H, H6), 3.32 (s, 3H, OMe), 2.80 (br s, 1H, OH), 0.95 (s, 9H, *t*BuSi), 0.16, 0.15 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.2$, 133.7, 130.4, 129.3, 129.2, 129.1, 127.6, 113.7, 85.3, 75.1, 74.8, 73.9, 73.8, 70.9, 59.0, 55.2, 25.8, 17.9, −4.6, −4.7; HRMS (MALDI): calcd for $C_{27}H_{40}O_6SeSiNa$ $[M+Na]^+$: 591.1656, found 591.1658.

Alcohols used in coupling reactions:

Alcohol 44: See ref. [26].

Alcohol 45: $R_f = 0.21$ (100 % Et_2O); $[\alpha]_D^{22} = +136.4$ ($c = 0.89$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3035$, 2975, 2945, 2885, 1725, 1205, 1105, 1000, 960, 736 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 5.12$ (t, $J = 9.7$ Hz, 1H, H3), 4.72 (d, $J =$ 3.8 Hz, 1H, H1), 3.61–3.59 (m, 1H, H5), 3.57–3.52 (m, 3H, H2, H6, H6), 3.31 (t, $J = 9.7$ Hz, 1H, H4), 3.40 (s, 3H, OMe), 3.37 (s, 6H, OMe), 2.25 (d, $J = 9.4$ Hz, 1H, OH), 2.10 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 171.2, 99.4, 76.7, 75.5, 71.2, 70.5, 69.8, 60.0, 59.1, 55.3, 21.0; HRMS (MALDI): calcd for $C_{11}H_{20}O_7Na$ $[M+Na]^+$: 287.1101, found 287.1099.

Alcohol 88: $R_f = 0.28$ (100 % Et_2O); $[\alpha]_D^{22} = +107.3$ ($c = 0.79$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3449$, 2928, 1765, 1743, 1451, 1303, 1248, 1160, 1094, 1044, 1028, 962, 791 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 4.81$ (d, $J = 3.5$ Hz, 1H, H1), 4.69 (d, $J = 9.7$ Hz, 1H, H4), 4.09, 4.07 (AB, $J = 14.5$ Hz, 2H, CH_2Cl), 3.89 (t, $J = 9.5$ Hz, 1H, H3), 3.76 (dq, $J = 9.7$, 6.2 Hz, 1H, H5), 3.46 (s, 3H, OMe), 3.38 (s, 3H, OMe), 3.21 (dd, $J = 9.2$, 3.5 Hz, 1H, H2), 2.73 (br s, 1H, OH), 1.15 (d, $J = 6.1$ Hz, 3H, H6); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 166.9$, 96.5, 81.5, 77.1, 70.4, 64.7, 58.5, 55.3, 40.7, 17.2; HRMS (MALDI): calcd for $C_{10}H_{17}ClO_6Na$ $[M+Na]^+$: 291.0611, found 291.0608.

Alcohol 89: $R_f = 0.45$ (100 % Et_2O); $[\alpha]_D^{22} = +148.4$ ($c = 0.42$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3456$, 2917, 1754, 1451, 1308, 1248, 1193, 1160, 1099, 1050, 967, 912, 835, 791 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 5.14$ (t, $J = 9.7$ Hz, 1H, H3), 4.78 (d, $J = 3.5$ Hz, 1H, H1), 4.11, 4.09 (AB, $J = 14.9$ Hz, 2H, CH_2Cl), 3.64 (dq, $J = 9.6$, 6.2 Hz, 1H, H5), 3.39 (s, 3H, OMe), 3.37 (s, 3H, OMe), 3.30 (dd, $J = 9.8$, 3.7 Hz, 1H, H2), 3.22–3.17 (m, 1H, H4), 2.62 (d, $J = 6.6$ Hz, 1H, OH), 1.24 (d, $J = 6.1$ Hz, 3H, H6); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 167.9$, 96.9, 79.0, 76.9, 74.7, 67.3, 58.8, 55.1, 40.8, 17.3; HRMS (MALDI): calcd for $C_{10}H_{17}ClO_6Na$ $[M+Na]^+$: 291.0611, found 291.0601.

General procedure for the coupling of glycosyl fluorides and alcohols:

Solid phase: The resin was diluted with CH_2Cl_2 (1.0 M), 4 Å MS (spheres) were added and the reaction mixture was stirred for 10 min. The alcohol (10 equiv) was added, followed by the addition of $SnCl_2$ (3.0 equiv) in one portion, and the resulting mixture was warmed to 25 °C and stirred for 2–12 h. The reaction mixture was filtered through a sintered glass frit and washed with CH_2Cl_2, MeOH, CH_2Cl_2, and finally Et_2O. The resin was then air dried for 2 h.

Solution phase: The crude glycosyl fluoride (1.5–2.5 equiv) and the alcohol (1.0 equiv) were azeotroped with benzene (3 × 10 mL) and then dried under high vacuum for 1 h. Et_2O (0.2 M) and 4 Å MS were added, and the mixture was stirred for 5 min. $SnCl_2$ (1.5–2.5 equiv) was added in one portion and the resulting mixture was warmed to 25 °C and stirred for 2–12 h. The reaction mixture was quenched by the addition of Et_3N (5 mL), diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4), the solvents were removed under reduced pressure, and the residue was purified by flash column chromatography. This procedure is further illustrated by the following example:

Glycoside 37a: Glycosyl fluoride **36a** (0.20 g, 0.40 mmol) and alcohol **43** (0.10 g, 0.60 mmol) were azeotroped with benzene (3 × 10 mL) and then dried under high vacuum for 1 h. Et_2O (2.0 mL) and 4 Å MS were added, the mixture was stirred for 5 min, and then cooled to 0 °C. $SnCl_2$ (0.114 g, 0.60 mmol) was added in one portion and the resulting mixture was warmed to 25 °C and stirred for 3 h. The reaction mixture was quenched by the addition of Et_3N (5 mL), diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4), and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, 50 % Et_2O in hexanes) to afford glycoside **37a** (0.253 g, 94 %) as a white foam. **37a**: $R_f = 0.38$ (50 % Et_2O in hexanes); $[\alpha]_D^{22} = +20.0$ ($c = 0.2$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2929$, 2856, 1724, 1672, 1513, 1453, 1359, 1274, 1175, 1110, 943, 838, 778, 713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.08$ (d, $J =$ 8.0 Hz, 2H, ArH), 7.71–7.68 (m, 2H, ArH), 7.60 (t, $J = 7.4$ Hz, 1H, ArH), 7.46 (t, $J = 7.7$ Hz, 2H, ArH), 7.34 (d, $J = 8.3$ Hz, 2H, ArH), 7.23–7.10 (m, 3H, ArH), 6.95 (d, $J = 8.3$ Hz, 2H, ArH), 4.93 (d, $J = 7.4$ Hz, 1H, H1), 4.77, 4.60 (AB, $J = 12.0$ Hz, 2H, CH_2Ar), 4.53–4.46 (m, 2H, CH_2OBz), 4.38 (t, $J = 3.9$ Hz, 1H, H3), 4.20–4.16 (m, 1H, CH_2O), 3.95–3.89 (m, 3H, CH_2O, H5), 3.87 (s, 3H, OMe), 3.68 (dd, $J = 7.3$, 3.3 Hz, 1H, H2), 3.39 (m, 1H, H4), 0.99 (s, 9H, *t*BuSi), 0.22 (s, 3H, MeSi), 0.05 (s, 3H, MeSi); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.4$, 159.3, 133.0, 132.7, 130.9, 130.1, 129.6, 129.3, 128.6, 128.1, 126.4, 113.8, 101.9, 75.1, 72.5, 71.2, 66.8, 63.9, 62.4, 55.2, 49.7, 25.8, 18.0, −4.5, −4.8; HRMS (FAB): calcd for $C_{34}H_{44}O_7SeSiNa$ $[M+Na]^+$: 695.1914, found 695.1900.

Glycoside 48a: $R_f = 0.42$ (50 % Et_2O in hexanes); $[\alpha]_D^{22} = +37.5$ ($c = 0.20$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3062$, 3030, 2918, 1724, 1602, 1453, 1363, 1273, 1110, 1026, 909, 739, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 8.14$ (d, $J = 9.6$ Hz, 2H, ArH), 7.74 (d, $J = 10.0$ Hz, 2H, ArH), 7.63 (t, $J = 7.5$ Hz, 1H, ArH), 7.49–7.26 (m, 20H, ArH), 5.32 (d, $J = 1.7$, 1H, H1), 5.01–4.55 (m, 6H, CH_2Ar), 4.54–4.52 (m, 2H, CH_2OBz), 4.35 (dd, $J = 10.1$, 5.5 Hz, 1H, H3), 4.07–3.96 (m, 4H), 3.88–3.86 (m, 2H), 3.81 (dd, $J = 13.0$, 2.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 166.3$, 138.4, 138.3, 138.0, 134.6, 132.9, 129.9, 129.6, 129.0, 128.3, 128.2, 128.2, 127.9, 127.9, 127.6, 127.5, 127.4, 100.5, 78.8, 75.6, 74.8, 73.3, 71.9, 71.5, 69.6, 65.1, 63.6, 49.2; HRMS (MALDI): calcd for $C_{42}H_{42}O_7SeNa$ $[M+Na]^+$: 761.1988, found 761.2001.

Glycoside 50a: $R_f = 0.63$ (50 % Et_2O in hexanes); $[\alpha]_D^{22} = +78.0$ ($c = 0.23$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2929$, 2856, 1727, 1454, 1383, 1273, 1116, 1025, 877, 835, 779, 740 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 8.04$ (d, $J = 7.8$ Hz, 2H, ArH), 7.59–7.53 (m, 2H, ArH), 7.45 (t, $J = 7.8$ Hz, 2H, ArH), 7.35–7.18 (m, 9H, ArH), 4.98 (s, 1H, H1), 4.65, 4.38 (AB, $J = 11.6$ Hz, 2H, CH_2Ar), 4.47–4.39 (m, 2H), 3.95–3.88 (m, 3H), 3.77 (dq, $J = 8.9$, 6.3 Hz, 1H), 3.71–3.68 (m, 1H), 3.54 (t, $J = 8.3$ Hz, 1H), 1.29 (d, $J = 6.3$ Hz, 3H, H6), 0.84 (s, 9H, *t*BuSi), 0.07, 0.03 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 166.4$, 159.1, 137.9, 134.5, 133.0, 130.0, 130.0, 129.6, 129.3, 129.1, 128.4, 128.1, 128.0, 127.6, 100.2, 78.4, 74.3, 70.7, 69.4, 65.1, 63.7, 48.6, 30.3,

29.7, 25.9, 18.5, 18.2, 15.2, −3.5, −4.7; HRMS (MALDI): calcd for $C_{34}H_{44}O_6SeSiNa$ $[M+Na]^+$: 679.1969, found 679.1972.

Disaccharide 52a: $R_f = 0.35$ (100% Et_2O); $[\alpha]_D^{22} = +47.5$ ($c = 0.72$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3441$, 3030, 2920, 1453, 1362, 1070, 910, 737, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.64$ (d, $J = 8.2$ Hz, 2H, ArH), 7.40–7.14 (m, 18H, ArH), 5.14 (s, 1H, H1), 4.86, 4.47 (AB, $J = 10.8$ Hz, 2H, CH_2Ar), 4.79 (d, $J = 3.5$ Hz, 1H, H1′), 4.66, 4.51 (AB, $J = 11.3$ Hz, 2H, CH_2Ar), 4.62, 4.58 (AB, $J = 12.2$ Hz, 2H, CH_2Ar), 4.17 (dd, $J = 7.5$, 4.6 Hz, 1H), 3.98 (dd, $J = 11.1$, 3.6 Hz, 1H), 3.93–3.90 (m, 2H), 3.76 (t, $J = 9.1$ Hz, 1H), 3.71–3.63 (m, 2H), 3.62–3.59 (m, 1H), 3.61 (s, 3H, OMe), 3.54 (dt, $J = 11.0$, 2.2 Hz, 1H), 3.50 (s, 3H, OMe), 3.47 (t, $J = 9.1$ Hz, 1H), 3.36 (s, 3H, OMe), 3.21 (br s, 1H), 3.18 (dd, $J = 9.6$, 3.7 Hz, 1H), 1.85 (br s, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.0$, 138.0, 137.9, 135.0, 129.0, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 100.4, 97.5, 82.9, 81.6, 78.9, 75.6, 75.0, 73.2, 71.8, 71.3, 70.0, 69.4, 68.9, 65.5, 61.2, 58.6, 57.4, 55.1, 49.1, 30.0; HRMS (MALDI): calcd for $C_{42}H_{50}O_{10}SeNa$ $[M+Na]^+$: 817.2466, found 817.2428.

Disaccharide 54a: $R_f = 0.41$ (100% Et_2O); $[\alpha]_D^{22} = +26.2$ ($c = 0.42$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3442$, 2930, 1455, 1384, 1254, 1113, 878, 837, 779, 740 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.57–7.19$ (m, 10H, ArH), 4.97 (s, 1H, H1), 4.72 (d, $J = 3.6$ Hz, 1H, H1′), 4.66, 4.36 (AB, $J = 11.0$ Hz, 2H, CH_2Ar), 3.86 (dd, $J = 4.5$, 1.3 Hz, 1H), 3.76 (dq, $J = 8.9$, 6.3 Hz, 1H), 3.62–3.57 (m, 2H), 3.83–3.80 (m, 2H), 3.64 (s, 3H, OMe), 3.51 (t, $J = 8.8$ Hz, 1H), 3.49 (s, 3H, OMe), 3.48–3.44 (m, 2H), 3.41 (t, $J = 9.1$ Hz, 1H), 3.34 (s, 3H, OMe), 3.14 (dd, $J = 9.4$, 3.7 Hz, 1H), 1.28 (d, $J = 6.2$ Hz, 3H, H6), 0.84 (s, 9H, *t*BuSi), 0.05, −0.04 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 137.9$, 135.1, 129.0, 128.1, 128.0, 127.7, 127.4, 100.0, 97.3, 82.9, 81.7, 78.2, 74.3, 70.6, 69.9, 69.8, 69.3, 65.4, 61.3, 58.4, 55.1, 48.8, 30.3, 18.5, 18.2, −3.8, −4.7; HRMS (MALDI): calcd for $C_{34}H_{52}O_9SeSiNa$ $[M+Na]^+$: 735.2443, found 735.2412.

Disaccharide 56a: $R_f = 0.28$ (100% Et_2O); $[\alpha]_D^{22} = +67.3$ ($c = 0.92$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3441$, 3063, 2931, 1613, 1515, 1470, 1359, 1302, 1250, 1046, 908, 835, 778, 735 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.61–7.59$ (m, 2H, ArH), 7.23–7.17 (m, 5H, ArH), 6.84 (d, $J = 8.6$ Hz, 2H, PMB), 4.82 (d, $J = 7.0$ Hz, 1H, H1), 4.71 (d, $J = 3.5$ Hz, 1H, H1′), 4.55, 4.47 (AB, $J = 12.0$ Hz, 2H, CH_2Ar), 4.23 (t, $J = 4.2$ Hz, 1H), 3.93 (dd, $J = 10.9$, 4.3 Hz, 1H), 3.83–3.71 (m, 2H), 3.76 (s, 3H, OMe), 3.60–3.54 (m, 2H), 3.60 (s, 3H, OMe), 3.50–3.46 (m, 2H), 3.46 (s, 3H, OMe), 3.40 (t, $J = 9.3$ Hz, 1H), 3.30 (s, 3H, OMe), 3.11 (dd, $J = 9.4$, 3.5 Hz, 1H), 3.00 (br s, 1H, H4), 2.25 (br s, 1H, OH), 0.88 (s, 9H, *t*BuSi), 0.09, −0.08 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.1$, 133.2, 129.9, 129.2, 128.5, 126.7, 113.7, 101.0, 97.1, 82.5, 81.1, 75.2, 72.3, 71.2, 70.1, 70.0, 67.1, 62.4, 60.9, 58.3, 55.1, 54.9, 30.1, 25.7, 17.9, −4.6, −4.9; HRMS (FAB): calcd for $C_{34}H_{52}O_{10}SeSiNa$ $[M+Na]^+$: 751.2392, found 751.2405.

Disaccharide 58a: $R_f = 0.19$ (50% Et_2O in hexanes); $[\alpha]_D^{22} = +52.9$ ($c = 0.17$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3037$, 2926, 1749, 1453, 1368, 1231, 1196, 1072, 989, 909, 737, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.72–7.23$ (m, 20H, ArH), 5.47 (t, $J = 9.8$ Hz, 1H), 5.19 (s, 1H, H1), 5.02–4.56 (m, 6H, CH_2Ar), 4.81 (d, $J = 4.1$ Hz, 1H), 4.20 (dd, $J = 8.7$, 4.8 Hz, 1H), 4.08 (dd, $J = 4.8$, 1.2 Hz, 1H), 3.97 (t, $J = 9.5$ Hz, 1H), 3.93–3.81 (m, 4H), 3.77–3.75 (m, 1H), 3.71 (dd, $J = 10.6$, 3.7 Hz, 1H), 3.67 (dd, $J = 10.6$, 2.1 Hz, 1H), 3.51 (s, 6H, OMe), 3.44 (t, $J = 9.8$ Hz, 1H), 3.37 (s, 3H, OMe), 2.11 (s, 3H, OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.9$, 138.6, 138.4, 137.9, 134.5, 129.2, 129.0, 128.2, 128.0, 127.6, 127.5, 127.3, 127.2, 96.3, 95.9, 78.6, 77.2, 74.8, 74.7, 73.2, 72.4, 71.9, 71.8, 71.1, 70.6, 69.5, 68.9, 59.8, 59.1, 55.0, 48.0, 30.2, 20.9; HRMS (MALDI): calcd for $C_{44}H_{52}O_{11}SeNa$ $[M+Na]^+$: 859.2567, found 859.2603.

Disaccharide 60a: $R_f = 0.38$ (50% Et_2O in hexanes); $[\alpha]_D^{22} = +37.3$ ($c = 0.44$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2930$, 2856, 1752, 1554, 1370, 1231, 1121, 1073, 989, 837 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.54–7.20$ (m, 10H, ArH), 5.32 (t, $J = 9.7$ Hz, 1H, H3′), 4.84 (s, 1H, H1), 4.73, 4.29 (AB, $J = 10.7$ Hz, 2H, CH_2Ar), 4.57 (d, $J = 3.4$ Hz, 1H, H1′), 4.01 (d, $J = 5.0$ Hz, 1H), 3.72 (dd, $J = 8.8$, 5.0 Hz, 1H), 3.67 (dd, $J = 10.1$, 3.3 Hz, 1H), 3.66–3.63 (m, 2H), 3.60 (dd, $J = 10.6$, 3.5 Hz, 1H), 3.56 (br d, $J = 10.6$ Hz, 1H), 3.49 (t, $J = 6.1$ Hz, 1H), 3.43 (s, 3H, OMe), 3.41 (s, 3H, OMe), 3.37 (t, $J = 9.3$ Hz, 1H), 3.19 (s, 3H, OMe), 2.12 (s, 3H, OAc), 1.30 (d, $J = 6.2$ Hz, 3H, H6), 0.80 (s, 9H, *t*BuSi), 0.02, −0.11 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.9$, 137.8, 134.5, 129.1, 128.9, 128.2, 128.0, 127.6, 127.3, 96.0, 95.9, 78.0, 77.1, 73.8, 72.5, 71.7, 70.6, 70.3, 69.5, 69.1, 59.9, 59.2, 55.2, 47.4, 30.3, 25.8, 21.0, 18.4, 18.1, −3.9, −4.8; HRMS (MALDI): calcd for $C_{36}H_{54}O_{10}SeSiNa$ $[M+Na]^+$: 777.2548, found 777.2561.

Disaccharide 62a: $R_f = 0.15$ (50% Et_2O in hexanes); $[\alpha]_D^{22} = +27.5$ ($c = 0.12$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2931$, 2856, 1751, 1612, 1513, 1468, 1369, 1249, 1195, 1046, 907, 837, 779, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 8.6$ Hz, 2H, ArH), 7.31–7.27 (m, 5H, ArH), 6.93 (d, $J = 8.6$ Hz, 2H, PMB), 5.46 (t, $J = 9.7$ Hz, 1H, H3′), 4.78 (d, $J = 5.1$ Hz, 1H, H1′), 4.72 (d, $J = 3.0$ Hz, 1H, H1), 4.60 (s, 2H, CH_2Ar), 4.24 (dd, $J = 5.8$, 4.0 Hz, 1H), 3.87 (s, 3H, OMe), 3.72–3.71 (m, 1H), 3.79 (dd, $J = 10.3$, 3.6 Hz, 1H), 3.73 (dd, $J = 10.3$, 3.3 Hz, 1H), 3.68 (t, $J = 4.3$ Hz, 1H), 3.66 (dd, $J = 10.5$, 3.5 Hz, 1H), 3.61 (dd, $J = 10.5$, 2.1 Hz, 1H), 3.49 (s, 3H, OMe), 3.48–3.46 (m, 1H), 3.46 (s, 3H, OMe), 3.45 (t, $J = 9.8$ Hz, 1H), 3.44–3.40 (m, 1H), 3.18 (s, 3H, OMe), 2.18 (s, 3H, OAc), 0.98 (s, 9H, *t*BuSi), 0.19, 0.09 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 169.8$, 159.1, 130.4, 129.1, 128.8, 126.8, 113.7, 75.4, 72.6, 70.7, 69.5, 59.6, 59.1, 55.2, 55.0, 25.8, 21.6, 18.0, −4.5, −4.8; HRMS (FAB): calcd for $C_{36}H_{54}O_{11}SeSiNa$ $[M+Na]^+$: 793.2493, found 793.2502.

Disaccharide 90: $R_f = 0.42$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +72.9$ ($c = 0.41$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2930$, 1771, 1611, 1512, 1462, 1248, 1165, 1105, 1039, 835, 780 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.53$ (dd, $J = 7.8$, 1.9 Hz, 2H, ArH), 7.23–7.18 (m, 5H, ArH), 6.83 (d, $J = 8.7$ Hz, 2H, PMB), 4.86 (d, $J = 7.4$ Hz, 1H, H1), 4.70 (d, $J = 3.6$ Hz, 1H, H1′), 4.66 (t, $J = 9.7$ Hz, 1H, H4′), 4.55, 4.43 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 4.23 (t, $J = 3.6$ Hz, 1H, H3), 4.10 (t, $J = 9.6$ Hz, 1H, H3′), 3.96 (br d, $J = 9.6$ Hz, 1H, H5), 3.89 (br s, 2H, CH_2Cl), 3.77 (s, 3H, OMe), 3.74–3.68 (m, 2H, H5, H5′), 3.43 (s, 3H, OMe), 3.42 (dd, $J = 7.0$, 3.3 Hz, 1H, H2), 3.36 (s, 3H, OMe), 3.26 (br s, 1H, H4), 3.06 (dd, $J = 9.5$, 3.5 Hz, 1H, H2′), 1.11 (d, $J = 6.3$ Hz, 3H, H6′), 0.87 (s, 9H, *t*BuSi), 0.10, 0.05 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 166.4$, 159.2, 133.2, 130.2, 129.2, 128.7, 126.8, 113.8, 101.9, 97.9, 80.3, 77.5, 75.9, 75.4, 65.1, 61.9, 60.2, 55.2, 55.1, 41.2, 25.8, 18.1, 17.3, −4.5, −4.8; HRMS (MALDI): calcd for $C_{35}H_{51}ClO_{10}SeSiNa$ $[M+Na]^+$: 797.2002, found 797.2000.

Disaccharide 96: $R_f = 0.46$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +55.0$ ($c = 0.32$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2931$, 1774, 1605, 1514, 1468, 1308, 1252, 1138, 1088, 1036, 834, 775, 736 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.56$ (dd, $J = 6.7$, 1.5 Hz, 2H, ArH), 7.23 (d, $J = 8.6$ Hz, 2H, PMB), 7.20–7.17 (m, 3H, ArH), 6.85 (d, $J = 8.6$ Hz, 2H, PMB), 5.32 (t, $J = 9.5$ Hz, 1H, H3′), 4.85 (d, $J = 8.4$ Hz, 1H, H1), 4.76 (d, $J = 3.4$ Hz, 1H, H1′), 4.56, 4.46 (AB, $J = 12.1$ Hz, 2H, CH_2Ar), 4.24 (br s, 1H, H3), 4.06 (br s, 2H, CH_2Cl), 3.85, 3.76 (AB, $J = 12.0$ Hz, 2H, H5, H5), 3.78 (s, 3H, OMe), 3.46–3.43 (m, 2H, H4′, H5′), 3.37 (s, 3H, OMe), 3.36 (s, 3H, OMe), 3.32 (dd, $J = 8.3$, 2.9 Hz, 1H, H2), 3.21 (dd, $J = 10.0$, 3.4 Hz, 1H, H2′), 3.20 (br s, 1H, H4), 1.23 (d, $J = 5.5$ Hz, 3H, H6′), 0.87 (s, 9H, *t*BuSi), 0.10, −0.07 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 165.8$, 159.3, 133.9, 129.9, 129.5, 129.2, 128.5, 126.8, 113.8, 102.2, 96.6, 80.2, 75.3, 75.3, 66.2, 62.6, 58.5, 55.2, 55.1, 41.4, 25.8, 18.0, 17.9, −4.5, −4.8; HRMS (MALDI): calcd for $C_{35}H_{52}ClO_{10}SeSiNa$ $[M+Na]^+$: 797.2002, found 797.2036.

Disaccharide 103: $R_f = 0.56$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +26.30$ ($c = 0.46$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2917$, 1770, 1748, 1611, 1578, 1512, 1462, 1369, 1303, 1248, 1165, 1132, 1105, 1039, 835, 775 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.50$ (dd, $J = 8.4$, 1.1 Hz, 2H, ArH), 7.24–7.11 (m, 5H, ArH), 6.83 (d, $J = 8.6$ Hz, 2H, PMB), 4.73 (d, $J = 9.1$ Hz, 1H, H1), 4.70, 4.48 (AB, $J = 16.9$ Hz, 2H, CH_2Cl), 4.70 (d, $J = 3.6$ Hz, 1H, H1′), 4.48 (t, $J = 9.2$ Hz, 1H, H4′), 4.39, 4.14 (AB, $J = 15.1$ Hz, 2H, CH_2Ar), 3.90 (t, $J = 9.3$ Hz, 1H, H3′), 3.80–3.72 (m, 1H, H5′), 3.76 (s, 3H, OMe), 3.59 (dd, $J = 10.0$, 8.0 Hz, 1H, H3), 3.57 (dd, $J = 10.2$, 2.7 Hz, 1H, H6), 3.49 (dd, $J = 10.2$, 2.0 Hz, 1H, H6), 3.44 (t, $J = 7.8$ Hz, 1H, H4), 3.40 (s, 3H, OMe), 3.38 (s, 3H, OMe), 3.29 (s, 3H, OMe), 3.25–3.21 (m, 1H, H5), 3.04 (t, $J = 10.0$ Hz, 1H, H2), 3.01 (dd, $J = 9.6$, 3.4 Hz, 1H, H2′), 1.14 (d, $J = 6.3$ Hz, 3H, H6′), 0.84 (s, 9H, *t*BuSi), 0.14, 0.01 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 167.0$, 158.9, 133.1, 132.2, 131.2, 130.7, 129.0, 128.6, 128.5, 125.8, 113.6, 103.4, 96.5, 81.5, 79.6, 75.6, 75.3, 74.8, 73.7, 73.5, 70.9, 64.3, 58.4, 58.2, 55.2, 55.2, 52.3, 40.9, 26.2, 18.2, 17.3, −3.2, −3.3; HRMS (MALDI): calcd for $C_{37}H_{55}ClO_{11}SeSiNa$ $[M+Na]^+$: 841.2264, found 841.2248.

General procedure for the formation of 2-deoxyglycosides: *Solid phase*: AIBN (0.1 equiv) was added to a solution of the resin bound glycoside (1.0 equiv) and nBu$_3$SnH (10 equiv) in benzene (0.1 M) at 25 °C and the resulting mixture was refluxed for 1 h. The reaction mixture cooled and the reaction mixture was filtered. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography.

Solution phase: AIBN (0.1 equiv) was added to a solution of the glycoside (1.0 equiv) and nBu$_3$SnH (10 equiv) in benzene (0.2 M) at 25 °C and the

0947-6539/00/0617-3178 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

resulting mixture was refluxed for 1 h. The reaction mixture cooled, the solvents were removed under reduced pressure, and the residue was purified by flash column chromatography. This procedure is further illustrated by the following example:

Glycoside 38: AIBN (0.002 g, 0.007 mmol) was added to a solution of the glycoside (0.05 g, 0.074 mmol) and nBu$_3$SnH (0.20 mL, 0.74 mmol) in benzene (3.0 mL) at 25 °C and the resulting mixture was refluxed for 1 h. The reaction mixture cooled, the solvents were removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, 50 % Et$_2$O in hexanes) to afford glycoside **38** (0.034 g, 90 %) as a white foam. **38**: $R_f = 0.45$ (50 % Et$_2$O in hexanes); $[\alpha]_D^{22} = +28.4$ ($c = 1.25$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2954$, 2932, 2897, 2856, 1723, 1611, 1513, 1460, 1380, 1273, 1250, 1109, 1043, 1006, 902, 837, 778, 712 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.12$ (d, $J = 8.0$ Hz, 2H, ArH), 7.62 (t, $J = 8.0$ Hz, 1H, ArH), 7.49 (t, $J = 8.0$ Hz, 2H, ArH), 7.30 (d, $J = 8.8$ Hz, 2H, PMB), 6.92 (d, $J = 8.8$ Hz, 2H, PMB), 4.90 (t, $J = 3.3$ Hz, 1H, H1), 4.69, 4.59 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 4.56 (ddd, $J = 11.8$, 6.3, 3.7 Hz, 1H, CH_2OBz), 4.51 (ddd, $J = 11.8$, 6.3, 3.7 Hz, 1H, CH_2OBz), 4.08 (ddd, $J = 9.5$, 7.7, 4.8 Hz, 1H, H3), 4.02 (ddd, $J = 11.4$, 6.6, 4.1 Hz, 1H, OCH$_2$), 3.87 (s, 3H, OMe), 3.80 (ddd, $J = 11.4$, 6.6, 4.1 Hz, 1H, OCH$_2$), 3.70 (dd, $J = 11.8$, 5.2 Hz, 1H, H5), 3.64 (dd, $J = 11.4$, 8.5 Hz, 1H, H5), 3.32 (dt, $J = 8.1$, 4.8 Hz, 1H, H4), 2.08 (ddd, $J = 13.4$, 4.4, 3.3 Hz, 1H, H2), 1.71 (ddd, $J = 12.9$, 9.2, 3.3 Hz, 1H, H2), 0.95 (s, 9H, tBuSi), 0.12 (s, 6H, MeSi); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 166.5, 159.1, 132.9, 130.8, 130.1, 129.6, 129.3, 128.3, 113.7, 97.8, 77.8, 72.4, 69.0, 65.1, 63.9, 61.3, 55.3, 38.1, 25.8, 18.0, −4.6, −4.8; HRMS (FAB): calcd for $C_{28}H_{40}O_7SiNa$ $[M+Na]^+$: 539.2441, found 539.2426.

Glycoside 49 (from solid phase): $R_f = 0.31$ (50 % Et$_2$O in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.02$ (d, $J = 7.4$ Hz, 2H, ArH), 7.53 (t, $J = 7.5$ Hz, 1H, ArH), 7.48 (t, $J = 7.4$ Hz, 2H, ArH), 7.14 (m, 15H, ArH), 5.04 (brs, 1H, H1), 4.88–4.45 (m, 6H, CH_2Ar), 4.45–4.42 (m, 2H, CH_2OBz), 4.00 (ddd, $J = 13.6$, 8.9, 5.2 Hz, 1H, H3), 3.92 (ddd, $J = 11.4$, 6.2, 3.5 Hz, 1H, CH_2O), 3.82–3.80 (m, 1H), 3.77–3.71 (m, 2H), 3.64–3.58 (m, 2H), 2.30–2.28 (m, 1H), 2.00–1.98 (m, 1H); HRMS (MALDI): calcd for $C_{36}H_{38}O_7Na$ $[M+Na]^+$: 605.2515, found 605.2537.

Disaccharide 51 (from solid phase): $R_f = 0.21$ (70 % Et$_2$O in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.57$–7.14 (m, 10H, ArH), 4.73 (brs, 1H, H1), 4.67, 4.41 (AB, $J = 11.0$ Hz, 2H, CH_2Ar), 4.53–4.51 (m, 1H), 3.83 (dq, $J = 8.6$, 6.4 Hz, 1H), 3.74–3.62 (m, 2H), 3.62 (dd, $J = 8.6$, 4.7 Hz, 1H), 3.56 (t, $J = 8.0$ Hz, 1H), 3.53–3.47 (m, 1H), 3.33–3.27 (m, 1H), 3.17 (brs, 1H), 1.29 (d, $J = 6.2$ Hz, 3H, H6), 0.81 (s, 9H, tBuSi), 0.09, 0.04 (2 × s, 2 × 3H, MeSi); HRMS (MALDI): calcd for $C_{28}H_{40}O_6SiNa$ $[M+Na]^+$: 500.2594, found 500.2578.

Disaccharide 53 (from solid phase): $R_f = 0.15$ (100 % Et$_2$O); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.36$–7.14 (m, 15H, ArH), 4.98 (brd, $J = 3.1$ Hz, 1H, H1), 4.86–4.47 (m, 6H, CH_2Ar), 4.87 (d, $J = 4.0$ Hz, 1H, H1′), 4.01 (dd, $J = 10.9$, 3.1 Hz, 1H), 3.94 (ddd, $J = 11.0$, 8.8, 4.8 Hz, 1H), 3.84 (dd, $J = 9.7$, 3.5 Hz, 1H), 3.71–3.54 (m, 5H), 3.63 (s, 3H, OMe), 3.51 (s, 3H, OMe), 3.48 (t, $J = 9.2$ Hz, 1H), 3.43 (t, $J = 9.2$ Hz, 1H), 3.40 (s, 3H, OMe), 3.25 (dd, $J =$ 9.2, 3.5 Hz, 1H), 3.12 (brs, 1H, OH), 2.38 (dd, $J = 12.7$, 4.4 Hz, 1H), 1.76 (ddd, $J = 12.8$, 12.8, 4.0 Hz, 1H); HRMS (MALDI): calcd for $C_{36}H_{46}O_{10}Na$ $[M+Na]^+$: 661.2989, found 661.2964.

Disaccharide 55 (from solid phase): $R_f = 0.20$ (100 % Et$_2$O); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.31$–7.28 (m, 5H, ArH), 4.88 (d, $J = 3.1$ Hz, 1H, H1), 4.86 (d, $J = 3.5$ Hz, 1H, H1′), 4.55, 4.49 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 3.90 (dd, $J = 10.9$, 4.4 Hz, 1H), 3.71–3.49 (m, 5H), 3.66 (s, 3H, OMe), 3.51 (s, 3H, OMe), 3.46 (t, $J = 9.2$ Hz, 1H), 3.42 (s, 3H, OMe), 3.28–3.22 (m, 2H), 2.51 (brs, 1H, OH), 2.29 (dd, $J = 13.1$, 4.8 Hz, 1H), 1.71–1.69 (m, 1H), 1.28 (d, $J = 6.2$ Hz, 3H, H6), 0.87 (s, 9H, tBuSi), 0.05, −0.01 (2 × s, 2 × 3H, MeSi); HRMS (MALDI): calcd for $C_{28}H_{48}O_9SiNa$ $[M+Na]^+$: 579.2965, found 579.2977.

Disaccharide 57 (from solid phase): $R_f = 0.14$ (100 % Et$_2$O); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.29$–7.22 (m, 2H, PMB), 6.87 (d, $J = 8.6$ Hz, 2H, PMB), 4.84 (d, $J = 3.5$ Hz, 1H, H1′), 4.78 (t, $J = 3.1$ Hz, 1H, H1), 4.60, 4.53 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.00–3.97 (m, 1H), 3.91 (dd, $J = 10.9$, 4.4 Hz, 1H), 3.80 (s, 3H, OMe), 3.68–3.60 (m, 2H), 3.64 (s, 3H, OMe), 3.58–3.48 (m, 2H), 3.50 (s, 3H, OMe), 3.40 (t, $J = 9.2$ Hz, 1H), 3.34 (s, 3H, OMe), 3.25–3.19 (m, 2H), 2.75 (d, $J = 2.6$ Hz, 1H, OH), 2.04–2.00 (m, 1H), 1.65–1.63 (m, 1H), 0.88 (s, 9H, tBuSi), 0.09, −0.08 (2 × s, 2 × 3H, MeSi); HRMS (MALDI): calcd for $C_{28}H_{48}O_{10}SiNa$ $[M+Na]^+$: 595.2914, found 595.2930.

Disaccharide 59 (from solid phase): $R_f = 0.10$ (70 % Et$_2$O in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.72$–7.23 (m, 15H, ArH), 5.38 (t, $J =$ 10.0 Hz, 1H), 5.07 (s, 1H, H1), 4.91–4.40 (m, 6H, CH_2Ar), 4.91 (d, $J =$ 4.1 Hz, 1H), 3.90–3.52 (m, 9H), 3.42 (s, 3H, OMe), 3.41 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.36 (t, $J = 9.2$ Hz, 1H), 2.36–2.28 (m, 1H), 2.10 (s, 3H, OAc), 1.89–1.79 (m, 1H); HRMS (MALDI): calcd for $C_{38}H_{48}O_{11}Na$ $[M+Na]^+$: 703.3094, found 703.3104.

Disaccharide 61 (from solid phase): $R_f = 0.18$ (50 % Et$_2$O in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.37$–7.20 (m, 5H, ArH), 5.39 (t, $J =$ 10.1 Hz, 1H, H3′), 4.95 (d, $J = 3.1$ Hz, 1H, H1), 4.55, 4.41 (AB, $J =$ 11.4 Hz, 2H, CH_2Ar), 3.92–3.84 (m, 4H), 3.66–3.63 (m, 2H), 3.60 (dd, $J = 10.6$, 3.5 Hz, 1H), 3.56 (brd, $J = 10.6$ Hz, 1H), 3.45 (s, 3H, OMe), 3.43 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.28 (t, $J = 9.3$ Hz, 1H), 2.36–2.24 (m, 1H), 2.12 (s, 3H, OAc), 1.79–1.64 (m, 1H), 1.30 (d, $J = 6.2$ Hz, 3H, H6), 0.83 (s, 9H, tBuSi), 0.04, −0.03 (2 × s, 2 × 3H, MeSi); HRMS (MALDI): calcd for $C_{30}H_{50}O_{10}SiNa$ $[M+Na]^+$: 621.3071, found 621.3094.

Disaccharide 63 (from solid phase): $R_f = 0.10$ (70 % Et$_2$O in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.23$ (d, $J = 8.6$ Hz, 2H, PMB), 6.86 (d, $J =$ 8.6 Hz, 2H, PMB), 5.37 (t, $J = 9.7$ Hz, 1H, H3′), 4.86 (d, $J = 5.3$ Hz, 1H, H1), 4.84 (d, $J = 3.0$ Hz, 1H, H1′), 4.62, 4.50 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 3.90–3.86 (m, 1H), 3.88 (s, 3H, OMe), 3.72–3.56 (m, 5H), 3.49–3.44 (m, 2H), 3.43 (s, 3H, OMe), 3.42 (s, 3H, OMe), 3.38 (s, 3H, OMe), 3.25–3.22 (m, 1H), 2.20–2.07 (m, 1H), 2.18 (s, 3H, OAc), 1.99–1.97 (m, 1H), 0.87 (s, 9H, tBuSi), 0.06 (s, 3H, MeSi), 0.05 (s, 3H, MeSi); HRMS (MALDI): calcd for $C_{30}H_{50}O_{11}SiNa$ $[M+Na]^+$: 637.3020, found 637.3015.

General procedure for the removal of esters (chloroacetates, acetates, benzoates): *Solid phase*: NaOMe (5.0 equiv) was added to a solution of the resin bound ester (1.0 equiv) in THF/MeOH (2:1, 0.1 M) at 25 °C and the resulting mixture was stirred for 6–12 h. The reaction mixture was filtered through a sintered glass frit and washed thoroughly with MeOH, CH_2Cl_2, and Et$_2$O. The resin was then air dried for 2 h.

Solution phase: K_2CO_3 or NaOMe (0.2–2.0 equiv) was added to a solution of the ester (1.0 equiv) in MeOH (0.2 M) at 25 °C and the resulting mixture was stirred for 1–3 h. The reaction mixture quenched by the addition of saturated aqueous NH_4Cl, diluted with Et$_2$O or CH_2Cl_2 and washed with brine. The organic layer was dried (Na_2SO_4), the solvents were removed under reduced pressure, and the residue was purified by flash column chromatography. This procedure is further illustrated by the following example:

Alcohol 39: NaOMe (0.051 g, 0.95 mmol) was added to a solution of benzoate **37a** (0.253 g, 0.38 mmol) in MeOH (2.0 mL) at 25 °C and the resulting mixture was stirred for 1 h. The reaction mixture quenched by the addition of saturated aqueous NH_4Cl (5 mL), diluted with Et$_2$O (200 mL) and washed with brine (2 × 10 mL). The organic layer was dried (Na_2SO_4), and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 → 50 % Et$_2$O in hexanes) to afford alcohol **39** (0.191 g, 95 %) as a white foam. **39**: $R_f = 0.18$ (50 % Et$_2$O in hexanes); $[\alpha]_D^{22} = +38.2$ ($c = 0.33$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3454$, 2929, 1612, 1514, 1469, 1351, 1303, 1250, 1033, 942, 834, 777, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 7.7$ Hz, 2H, ArH), 7.35–7.27 (m, 5H, ArH), 6.95 (d, $J = 8.6$ Hz, 2H, PMB), 4.86 (d, $J = 8.5$ Hz, 1H, H1), 4.71, 4.56 (AB, $J = 12.1$ Hz, 2H, CH_2Ar), 4.38 (brt, $J = 2.8$ Hz, 1H, H3), 3.96–3.90 (m, 3H, H5, H5, CH_2O), 3.87 (s, 3H, OMe), 3.76–3.73 (m, 1H, CH_2O), 3.71 (dd, $J = 8.7$, 3.1 Hz, 1H, H2), 3.70–3.65 (m, 2H, CH_2O), 3.32 (m, 1H, H4), 2.47 (brt, $J = 6.4$ Hz, 1H, OH), 0.99 (s, 9H, tBuSi), 0.23, 0.03 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 132.4, 130.8, 129.8, 129.3, 128.7, 126.7, 102.5, 74.8, 72.7, 71.8, 70.8, 66.7, 62.8, 61.8, 55.1, 49.3, 30.2, 25.7, 17.9, 15.1, −4.5, −4.8; HRMS (FAB): calcd for $C_{27}H_{40}O_6SeSiNa$ $[M+Na]^+$: 591.1651, found 591.1642.

Alcohol 91: $R_f = 0.33$ (60 % Et$_2$O in hexanes); $[\alpha]_D^{22} = +69.8$ ($c = 0.63$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3456$, 2929, 1612, 1513, 1459, 1358, 1297, 1250, 1103, 1053, 956, 906, 834, 777 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.62$ (dd, $J = 7.5$, 1.2 Hz, 2H, ArH), 7.27–7.21 (m, 5H, ArH), 6.84 (d, $J = 8.6$ Hz, 2H, PMB), 4.99 (d, $J = 9.1$ Hz, 1H, H1), 4.75 (d, $J = 3.6$ Hz, 1H, H1′), 4.60, 4.45 (AB, $J = 12.1$ Hz, 2H, CH_2Ar), 4.30 (brs, 1H, H3), 3.97, 3.81 (AB, $J =$ 12.3 Hz, 2H, H5, H5), 3.84 (t, $J = 9.1$ Hz, 1H, H3′), 3.79 (s, 3H, OMe), 3.69–3.63 (m, 1H, H5′), 3.64 (dd, $J = 9.1$, 2.8 Hz, 1H, H2), 3.56 (brs, 1H, OH), 3.52 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.19 (t, $J = 1.6$ Hz, 1H, H4), 3.17 (dd, $J = 9.6$, 3.7 Hz, 1H, H2′), 3.11 (dt, $J = 9.3$, 2.2 Hz, 1H, H4′), 1.22 (d, $J = 6.2$ Hz, 3H, H6′), 0.87 (s, 9H, tBuSi), 0.13, −0.07 (2 × s, 2 × 3H, MeSi);

^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 131.8, 130.8, 130.0, 129.3, 129.0, 126.8, 113.9, 103.0, 97.8, 83.9, 79.9, 76.3, 75.1, 73.7, 70.5, 66.3, 63.0, 59.4, 55.3, 54.9, 51.2, 25.8, 17.7, −4.4, −4.7; HRMS (MALDI): calcd for $C_{33}H_{50}O_9SeSiNa$ $[M+Na]^+$: 721.2286, found 721.2264.

Alcohol 95: R_f = 0.37 (100% Et_2O); $[\alpha]_D^{22}$ = +72.8 (c = 0.67, $CHCl_3$); IR (neat): $\tilde{\nu}$ = 3478, 2917, 1721, 1599, 1578, 1506, 1446, 1369, 1253, 1171, 1105, 1050 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.3 Hz, 2H, ArH), 7.57 (t, J = 8.7 Hz, 1H, ArH), 7.57 (t, J = 8.7 Hz, 1H, ArH), 7.54–7.50 (m, 2H, ArH), 7.43 (t, J = 8.0 Hz, 2H, ArH), 7.23 (d, J = 8.6 Hz, 2H, PMB), 7.18–7.13 (m, 3H, ArH), 6.81 (d, J = 8.6 Hz, 2H, PMB), 5.61 (t, J = 4.2 Hz, 1H, H3), 5.23 (d, J = 7.0 Hz, 1H, H1), 4.78 (d, J = 3.6 Hz, 1H, H1′), 4.61, 4.59 (AB, J = 11.9 Hz, 2H, CH_2Ar), 3.97 (dd, J = 12.5, 4.3 Hz, 1H, H5), 3.89 (dd, J = 6.9, 3.5 Hz, 1H, H2), 3.88 (t, J = 9.1 Hz, 1H, H3′), 3.79 (dd, J = 12.5, 2.9 Hz, 1H, H5), 3.76 (s, 3H, OMe), 3.69–3.64 (m, 2H, H4, H5′), 3.50 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.24 (t, J = 9.5 Hz, 1H, H4′), 3.22 (dd, J = 9.4, 3.7 Hz, 1H, H2′), 3.18 (br s, 1H, OH), 1.25 (d, J = 6.3 Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.4, 159.3, 133.4, 133.2, 129.8, 129.5, 129.2, 128.5, 127.5, 125.5, 113.8, 102.6, 97.5, 80.4, 76.2, 77.7, 72.6, 71.6, 66.5, 65.8, 59.2, 55.2, 55.1, 48.1, 29.7, 17.6; HRMS (MALDI): calcd for $C_{34}H_{40}O_{10}SeNa$ $[M+Na]^+$: 711.1684, found 711.1677.

Alcohol 97: R_f = 0.26 (60% Et_2O in hexanes); $[\alpha]_D^{22}$ = +90.5 (c = 0.55, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3456, 2929, 1612, 1513, 1459, 1358, 1297, 1250, 1103, 1053, 956, 907, 834, 771 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (dd, J = 7.8, 1.5 Hz, 2H, ArH), 7.24–7.16 (m, 5H, ArH), 6.83 (d, J = 8.6 Hz, 2H, PMB), 5.04 (d, J = 8.8 Hz, 1H, H1), 4.74 (d, J = 3.6 Hz, 1H, H1′), 4.58, 4.45 (AB, J = 12.2 Hz, 2H, CH_2Ar), 4.27 (br s, 1H, H3), 3.88, 3.80 (AB, J = 12.4 Hz, 2H, H5, H5), 3.85 (dt, J = 9.8, 2.3 Hz, 1H, H3′), 3.77 (s, 3H, OMe), 3.54 (dq, J = 9.7, 6.2 Hz, 1H, H5′), 3.52 (dd, J = 8.6, 2.9 Hz, 1H, H2), 3.49 (s, 3H, OMe), 3.35 (s, 3H, OMe), 3.22 (dd, J = 9.9, 3.8 Hz, 1H, H2′), 3.19 (t, J = 9.6 Hz, 1H, H4′), 3.17 (br s, 1H, H4), 1.29 (d, J = 6.2 Hz, 3H, H6′), 0.85 (s, 9H, tBuSi), 0.10, −0.06 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.4, 132.3, 130.5, 129.4, 128.9, 126.8, 113.9, 102.9, 96.9, 85.3, 80.5, 75.0, 73.3, 73.2, 70.9, 65.5, 63.3, 58.6, 55.3, 55.1, 50.9, 25.8, 18.1, 17.9, −4.3, −4.8; HRMS (MALDI): calcd for $C_{33}H_{50}O_9SeSiNa$ $[M+Na]^+$: 721.2286, found 721.2318.

Alcohol 101: R_f = 0.37 (100% Et_2O); $[\alpha]_D^{22}$ = +91.3 (c = 0.12, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3478, 2917, 1721, 1611, 1512, 1451, 1369, 1248, 1094, 1039, 901, 813 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.3 Hz, 2H, ArH), 7.57 (t, J = 7.4 Hz, 1H, ArH), 7.51 (dd, J = 7.7, 1.4 Hz, 2H, ArH), 7.44 (t, J = 7.8 Hz, 2H, ArH), 7.25 (d, J = 8.6 Hz, 2H, PMB), 7.18–7.12 (m, 3H, ArH), 6.82 (d, J = 8.6 Hz, 2H, PMB), 5.58 (t, J = 4.3 Hz, 1H, H3), 5.37 (d, J = 6.9 Hz, 1H, H1), 4.79 (d, J = 3.5 Hz, 1H, H1′), 4.63, 4.59 (AB, J = 11.9 Hz, 2H, CH_2Ar), 3.96 (dt, J = 9.5, 2.0 Hz, 1H, H3′), 3.87 (dd, J = 12.5, 4.4 Hz, 1H, H5), 3.83 (dd, J = 6.8, 3.7 Hz, 1H, H2), 3.79 (dd, J = 12.4, 3.1 Hz, 1H, H5), 3.76 (s, 3H, OMe), 3.70–3.67 (m, 1H, H4), 3.63 (dq, J = 9.6, 6.3 Hz, 1H, H5′), 3.50 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.32 (br s, 1H, OH), 3.29 (t, J = 9.2 Hz, 1H, H4′), 3.21 (dd, J = 9.7, 3.6 Hz, 1H, H2′), 1.31 (d, J = 6.3 Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.3, 159.4, 133.6, 133.4, 129.9, 129.8, 129.5, 129.4, 129.1, 128.5, 127.5, 102.5, 96.7, 83.6, 81.0, 73.4, 72.6, 71.8, 65.8, 65.6, 63.8, 58.6, 55.2, 55.1, 18.0; HRMS (MALDI): calcd for $C_{34}H_{40}O_{10}SeNa$ $[M+Na]^+$: 711.1684, found 711.1695.

Alcohol 104: R_f = 0.35 (80% Et_2O in hexanes); $[\alpha]_D^{22}$ = +56.8 (c = 0.5, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3467, 2917, 1611, 1572, 1512, 1462, 1363, 1297, 1248, 1198, 1110, 1055, 835, 775 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (dd, J = 6.4, 1.2 Hz, 2H, ArH), 7.24–7.16 (m, 5H, ArH), 6.85 (d, J = 8.5 Hz, 2H, PMB), 4.77 (d, J = 8.2 Hz, 1H, H1), 4.73 (d, J = 3.6 Hz, 1H, H1′), 4.70, 4.48 (AB, J = 11.1 Hz, 2H, CH_2Ar), 3.80–3.76 (m, 4H, OMe, H3), 3.70 (t, J = 9.1 Hz, 1H, H3′), 3.64–3.57 (m, 1H, H5′), 3.58 (dd, J = 10.2, 3.6 Hz, 1H, H6), 3.56 (t, J = 8.2 Hz, 1H, H4), 3.50 (dd, J = 10.5, 2.4 Hz, 1H, H6), 3.46 (dt, J = 8.9, 3.2 Hz, 1H, H5), 3.37 (s, 3H, OMe), 3.33 (s, 3H, OMe), 3.31 (s, 3H, OMe), 3.18 (t, J = 8.1 Hz, 1H, H2), 3.10 (dd, J = 9.4, 3.7 Hz, 1H, H2′), 3.05 (t, J = 9.0 Hz, 1H, H4′), 1.26 (d, J = 6.3 Hz, 3H, H6′), 0.86 (s, 9H, tBuSi), 0.13 (s, 3H, MeSi), 0.04 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.0, 132.5, 131.4, 130.4, 128.9, 128.8, 126.6, 113.7, 103.5, 96.7, 81.8, 80.7, 79.1, 75.3, 74.3, 74.1, 73.6, 71.2, 66.9, 59.1, 58.4, 55.3, 54.9, 52.1, 26.2, 18.2, 17.8, −3.4, −3.5; HRMS (MALDI): calcd for $C_{35}H_{54}O_{10}SeSiNa$ $[M+Na]^+$: 765.2548, found 765.2565.

Alcohol 107: R_f = 0.09 (80% Et_2O in hexanes); $[\alpha]_D^{22}$ = +59.11 (c = 0.516, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3476, 2919, 1608, 1580, 1513, 1458, 1369, 1302, 1246, 1107, 1046, 840, 779, 734 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (dd, J = 7.9, 1.6, 2H, ArH), 7.25–7.16 (m, 5H, ArH), 6.86 (d, J = 8.7 Hz, 2H, PMB), 4.70, 4.48 (AB, J = 11.2 Hz, 2H, CH_2Ar), 4.70 (d, J = 3.3 Hz, 1H, H1′), 4.58 (d, J = 8.3 Hz, 1H, H1), 3.81–3.77 (m, 4H, OMe, H3), 3.73 (t, J = 8.9 Hz, 1H, H3′), 3.57–3.47 (m, 7H, OMe, H6, H6, H5, H4), 3.40–3.36 (m, 1H, H5′), 3.32 (s, 3H, OMe), 3.31 (s, 3H, OMe), 3.23 (t, J = 8.6 Hz, 1H, H2), 3.19 (dd, J = 9.5, 3.6 Hz, 1H, H2′), 3.05 (t, J = 8.9 Hz, 1H, H4′), 2.24 (s, 1H, OH), 1.28 (d, J = 6.2 Hz, 3H, H6′), 0.86 (s, 9H, tBuSi), 0.15, 0.04 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.1, 132.2, 131.1, 130.1, 128.9, 128.8, 126.7, 125.5, 113.8, 103.8, 96.8, 87.0, 80.8, 79.1, 74.9, 74.6, 73.7, 71.5, 71.4, 65.1, 59.2, 58.7, 55.2, 55.0, 52.7, 30.3, 26.1, 18.1, 18.1, ×3.4, ×3.4; HRMS (MALDI): calcd for $C_{35}H_{54}O_{10}SeSiNa$ $[M+Na]^+$: 765.2548, found 765.2543.

Alcohol 110: R_f = 0.21 (80% Et_2O in hexanes); $[\alpha]_D^{22}$ = +68.4 (c = 0.5, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3456, 2917, 1611, 1578, 1512, 1462, 1380, 1297, 1248, 1094, 1051, 985, 868, 834, 773 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6, 340 K): δ = 7.71 (dd, J = 8.1, 1.3, 2H, ArH), 7.28 (d, J = 8.6 Hz, 2H, PMB), 7.02–6.93 (m, 3H, ArH), 6.80 (d, J = 8.6 Hz, 2H, PMB), 5.65 (d, J = 2.3 Hz, 1H, H1), 4.88, 4.60 (AB, J = 11.2 Hz, 2H, CH_2Ar), 4.62 (dd, J = 8.0, 4.4, 2H, H3), 4.54 (d, J = 3.5 Hz, 1H, H1′), 4.23 (ddd, J = 8.8, 5.9, 2.5 Hz, 1H, H5), 4.14 (dd, J = 4.3, 2.4 Hz, 1H, H2), 4.09 (t, J = 9.2 Hz, 1H, H3′), 3.92 (t, J = 8.7 Hz, 1H, H4), 3.70–3.65 (m, 1H, H5′), 3.68 (dd, J = 10.7, 5.4 Hz, 1H, H6), 3.61 (dd, J = 10.7, 2.3 Hz, 1H, H6), 3.36 (s, 3H, OMe), 3.32 (t, J = 9.3 Hz, 1H, H4′), 3.26 (s, 3H, OMe), 3.09 (s, 3H, OMe), 3.06 (s, 3H, OMe), 2.90 (dd, J = 9.5, 3.5 Hz, 1H, H2′), 2.48 (br s, 1H, OH), 1.36 (d, J = 6.2 Hz, 3H, H6′), 1.03 (s, 9H, tBuSi), 0.19 (s, 3H, MeSi), 0.17 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.2, 134.0, 130.4, 129.8, 129.4, 128.9, 127.2, 113.7, 100.6, 96.5, 82.7, 81.3, 74.1, 72.4, 72.2, 72.1, 71.7, 65.1, 59.2, 58.4, 55.2, 55.1, 30.3, 29.6, 25.9, 18.0, 17.9, −4.5; HRMS (MALDI): calcd for $C_{35}H_{54}O_{10}SeSiNa$ $[M+Na]^+$: 765.2548, found 765.2556.

General procedure for the removal of TBS groups: *Solid phase*: nBu$_4$NF (5.0 equiv) was added to a solution of the resin bound TBS ether (0.43 g, 0.36 mmol) in THF (0.1 M) at 25 °C and the resulting mixture was stirred for 1–3 h. The reaction mixture filtered through a sintered glass frit and the resin was washed with MeOH, CH_2Cl_2, and Et_2O. The resin was then air dried for 2 h.

Solution phase: nBu$_4$NF (1.5 equiv) was added to a solution of the TBS ether (1.0 equiv) in THF (0.2 M) at 25 °C and the resulting mixture was stirred for 1–3 h. The reaction mixture quenched by the addition of saturated aqueous NH_4Cl (5 mL), diluted with CH_2Cl_2 (100 mL) and washed with brine (2 × 5 mL). The organic layer was dried (Na_2SO_4), and the solvents were removed under reduced pressure. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography. This procedure is further illustrated by the following example:

Diol 41: nBu$_4$NF (0.50 mL, 1.0 M solution in THF, 0.50 mmol) was added to a solution of alcohol **39** (0.19 g, 0.34 mmol) in THF (1.7 mL) at 25 °C and the resulting mixture was stirred for 1 h. The reaction mixture quenched by the addition of saturated aqueous NH_4Cl (5 mL), diluted with CH_2Cl_2 (100 mL) and washed with brine (2 × 5 mL). The organic layer was dried (Na_2SO_4), and the solvents were removed under reduced pressure. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, 0 → 100% EtOAc in hexanes) to afford diol **41** (0.144 g, 95%) as a white foam. **41**: R_f = 0.30 (100% Et_2O); $[\alpha]_D^{22}$ = +14.4 (c = 0.16, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3417, 2932, 2873, 1605, 1512, 1248, 1077, 1033, 830, 736 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60–7.59 (m, 2H, ArH), 7.28–7.25 (m, 3H, ArH), 7.24 (d, J = 8.4, 2H, PMB), 6.85 (d, J = 8.4, 2H, PMB), 4.93 (d, J = 5.2, 1H, H1), 4.54, 4.52 (AB, J = 11.0 Hz, 2H, CH_2Ar), 4.11 (br t, J = 4.3 Hz, 1H), 3.82 (dd, J = 11.8, 3.5 Hz, 1H), 3.78 (s, 3H, OMe), 3.76–3.61 (m, 6H), 3.47–3.45 (m, 1H), 2.86 (br s, 1H, OH), 2.46 (br s, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 133.7, 129.9, 129.4, 129.2, 128.9, 127.7, 113.8, 101.2, 75.8, 71.8, 70.7, 69.5, 62.1, 61.8, 55.2, 51.6; HRMS (MALDI): calcd for $C_{21}H_{26}O_6SeSiNa$ $[M+Na]^+$: 477.0792, found 477.0790.

Alcohol 74: R_f = 0.20 (70% Et_2O in hexanes); $[\alpha]_D^{22}$ = +7.2 (c = 0.43, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3501, 2932, 1614, 1515, 1456, 1368, 1248, 1203, 1083, 918, 746 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.5 Hz, 2H, PMB), 6.88 (d, J = 8.5 Hz, 2H, PMB), 5.08 (d, J = 3.0 Hz, 1H, H1′), 4.58, 4.52 (AB, J = 11.4 Hz, 2H, CH_2Ar), 4.06 (t, J = 9.6 Hz, 1H, H3′), 4.02–3.99 (m, 1H, H3), 3.96 (dd, J = 11.8, 3.9 Hz, 1H, H5), 3.83 (dd, J = 10.2, 3.1 Hz, 1H, H2′), 3.80 (s, 3H, OMe), 3.62 (br s, 2H, H6′, H6′), 3.53–

0947-6539/00/0617-3180 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

3.48 (m, 3H, H4′, H5, H5′), 3.50 (s, 3H, OMe), 3.44 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.37 (ddd, J = 9.1, 9.1, 4.1 Hz, 1H, H4), 2.63 (d, J = 4.5 Hz, 1H, OH), 2.33 (dd, J = 13.2, 4.7 Hz, 1H, H2), 1.93 (dd, J = 13.2, 8.5 Hz, 1H, H2); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.4, 130.0, 129.5, 120.3, 113.9, 97.4, 78.8, 78.5, 76.3, 75.2, 71.9, 71.4, 70.7, 68.8, 62.6, 59.4, 58.8, 55.6, 55.5, 37.6, 30.3; HRMS (MALDI): calcd for $C_{22}H_{32}O_{10}Na$ $[M+Na]^+$: 479.2001, found 479.1987.

Alcohol 77: R_f = 0.26 (100% Et_2O); $[\alpha]_D^{22}$ = +41.1 (c = 0.75, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3445, 2917, 1611, 1512, 1451, 1369, 1330, 1297, 1242, 1088, 1028, 967, 824 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.23 (d, J = 8.6 Hz, 2H, PMB), 6.86 (d, J = 8.6 Hz, 2H, PMB), 4.82 (d, J = 3.7 Hz, 1H, H1′), 4.56, 4.51 (AB, J = 11.4 Hz, 2H, CH_2Ar), 3.94–3.85 (m, 4H, H3, H5, H3′, H5′), 3.78 (s, 3H, OMe), 3.59 (dd, J = 11.4, 8.6 Hz, 1H, H5), 3.53 (dd, J = 10.2, 3.7 Hz, 1H, H2′), 3.49 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.38 (ddd, J = 8.2, 8.2, 4.5 Hz, 1H, H4), 3.29 (t, J = 9.6 Hz, 1H, H4′), 2.64 (d, J = 3.9 Hz, 1H, OH), 2.25 (dd, J = 13.1, 4.7 Hz, 1H, H2), 1.91 (dd, J = 13.1, 10.0 Hz, 1H, H2), 1.29 (d, J = 6.2 Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 130.0, 129.5, 120.4, 114.0, 98.5, 80.5, 79.5, 78.4, 77.3, 72.2, 68.8, 66.7, 62.9, 58.4, 55.5, 55.3, 38.2, 17.6; HRMS (ESI): calcd for $C_{21}H_{30}O_9Na$ $[M+Na]^+$: 449, found 449.

Alcohol 80: R_f = 0.31 (100% Et_2O); $[\alpha]_D^{22}$ = +28.7 (c = 0.38, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3379, 2917, 1605, 1506, 1451, 1369, 1242, 1209, 1165, 1094, 1028, 967, 824 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.23 (d, J = 8.7 Hz, 2H, PMB), 6.85 (d, J = 8.6 Hz, 2H, PMB), 4.83 (d, J = 3.9 Hz, 1H, H1′), 4.55, 4.50 (AB, J = 11.4 Hz, 2H, CH_2Ar), 4.12 (t, J = 9.9 Hz, 1H, H3′), 3.92 (ddd, J = 10.7, 8.1, 5.0 Hz, 1H, H3), 3.91–3.86 (m, 1H, H5′), 3.83 (dd, J = 11.4, 4.8 Hz, 1H, H5), 3.78 (s, 3H, OMe), 3.54 (dd, J = 11.4, 9.7 Hz, 1H, H5), 3.52 (dd, J = 10.3, 3.7 Hz, 1H, H2′), 3.49 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.36 (dt, J = 9.2, 4.8 Hz, 1H, H4), 3.06 (t, J = 9.7 Hz, 1H, H4′), 2.55 (d, J = 3.1 Hz, 1H, OH), 2.25 (dd, J = 12.9, 4.9 Hz, 1H, H2), 1.92 (dd, J = 12.9, 11.1 Hz, 1H, H2), 1.28 (d, J = 6.2 Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 129.5, 128.8, 120.3, 114.0, 98.5, 80.8, 79.8, 77.9, 72.3, 69.1, 67.4, 62.8, 58.3, 55.4, 55.3, 45.8, 38.6, 17.7; HRMS (ESI): calcd for $C_{21}H_{30}O_9Na$ $[M+Na]^+$: 449, found 449.

Diol 83: (from **82**, see ref. 2) R_f = 0.36 (100% Et_2O); $[\alpha]_D^{22}$ = −5.98 (c = 0.18, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3425, 2919, 1508, 1455, 1243, 1126, 1055, 1026, 814, 732 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.1 Hz, 2H, ArH), 7.42–7.20 (m, 8H, ArH), 7.17 (d, J = 8.6 Hz, 2H, PMB), 6.82 (d, J = 8.6 Hz, 2H, PMB), 4.91 (d, J = 7.0 Hz, 1H, H1), 4.72, 4.60 (AB, J = 12.0 Hz, 2H, CH_2Ar), 4.56 (d, J = 1.6, 1H, G1), 4.51, 4.45 (AB, J = 11.7 Hz, 2H, CH_2Ar), 4.07 (ddd, J = 9.7, 9.7, 5.7 Hz, 1H, G4), 3.97 (t, J = 3.9 Hz, 1H, H3), 3.93–3.90 (m, 2H, H5, H5), 3.83 (s, 1H, OH), 3.82 (dd, J = 11.0, 5.5 Hz, 1H, G5), 3.78 (s, 3H, OMe), 3.75 (dd, J = 7.1, 3.2 Hz, 1H, H2), 3.72 (t, J = 3.0 Hz, 1H, G2), 3.71 (dd, J = 7.4, 3.2 Hz, 1H, G3), 3.46 (br s, 1H, H4), 3.38 (t, J = 10.5 Hz, 1H, G5), 3.30 (s, 3H, OMe), 2.64 (br s, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.4, 138.3, 134.1, 129.7, 129.4, 129.4, 128.2, 127.9, 127.8, 127.5, 82.8, 76.5, 74.8, 73.7, 71.5, 68.9, 65.8, 63.3, 62.4, 55.3, 54.8, 50.9, 30.3, 29.7; HRMS (MALDI): calcd for $C_{32}H_{38}O_9SeNa$ $[M+Na]^+$: 669.1578, found 669.1547.

Diol 86: (from **85**, see ref. 2) R_f = 0.16 (60% Et_2O in hexanes); $[\alpha]_D^{22}$ = −3.80 (c = 0.26, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3413, 2919, 1613, 1508, 1443, 1378, 1302, 1249, 1108, 1067, 1026, 808, 738, cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (dd, J = 5.2, 1.6 Hz, 2H, ArH), 7.37–7.25 (m, 8H, ArH), 7.22 (d, J = 8.6 Hz, 2H, PMB), 6.85 (d, J = 8.6 Hz, 2H, PMB), 4.93 (d, J = 6.0 Hz, 1H, H1), 4.78, 4.69 (AB, J = 12.0 Hz, 2H, CH_2Ar), 4.58 (d, J = 2.6 Hz, 1H, G1), 4.55, 4.50 (AB, J = 11.7 Hz, 2H, CH_2Ar), 4.06–4.03 (m, 1H, H3), 3.95–3.84 (m, 4H, G3, G4, H5, H5), 3.80 (s, 3H, OMe), 3.71 (t, J = 2.8 Hz, 1H, G2), 3.70–3.59 (m, 2H, G5, H2), 3.49–3.46 (m, 1H, H4), 3.43–3.37 (m, 2H, G5, OH), 3.32 (s, 3H, OMe), 2.52 (d, J = 4.2, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.1, 132.9, 130.4. 130.0, 129.8, 129.2, 128.3, 128.2, 127.5, 127.5, 127.4, 113.7, 82.6, 77.5, 76.5, 73.4, 71.8, 70.6, 67.9, 59.0, 55.3, 30.3, 29.7; HRMS (MALDI): calcd for $C_{32}H_{38}O_9SeNa$ $[M+Na]^+$: 669.1578, found 669.1556.

Diol 92: R_f = 0.50 (100% Et_2O); $[\alpha]_D^{22}$ = +50.5 (c = 0.94, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3449, 2917, 1611, 1583, 1506, 1446, 1369, 1303, 1242, 1094, 1039, 896, 819, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 2H, Ar), 7.29–7.26 (m, 3H, Ar), 7.21 (d, J = 8.6 Hz, 2H, PMB), 6.84 (d, J = 8.6 Hz, 2H, PMB), 5.25 (d, J = 6.2 Hz, 1H, H1), 4.78 (d, J = 3.6 Hz, 1H, H1′), 4.55, 4.50 (AB, J = 11.7 Hz, 2H, CH_2Ar), 4.11 (dd, J = 9.1, 4.2 Hz, 1H, H3), 3.92 (dd, J = 12.2, 5.2 Hz, 1H, H5), 3.84 (t, J = 9.2 Hz, 1H, H3′), 3.82 (dd, J = 11.3, 8.8 Hz, 1H, H5), 3.79 (s, 3H, OMe), 3.73 (dd, J = 6.2, 3.6 Hz, 1H, H2), 3.64 (dq, J = 9.5, 6.2 Hz, 1H, H5′), 3.49 (s, 3H, OMe), 3.46–3.42 (m, 1H, H4), 3.40 (s, 3H, OMe), 3.21 (dt, J = 9.3, 3.7 Hz, 1H, H4′), 3.20 (dd, J = 9.6, 3.6 Hz, 1H, H2′), 2.50 (d, J = 4.5 Hz, 1H, OH), 1.25 (d, J = 6.2 Hz, 3H, H6′); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 133.7, 130.1, 129.3, 128.9, 127.7, 113.8, 101.1, 97.4, 80.3, 76.4, 75.7, 71.3, 70.1, 66.6, 62.4, 59.0, 55.3, 55.1, 52.8, 30.3, 17.6; HRMS (MALDI): calcd for $C_{27}H_{36}O_9SeNa$ $[M+Na]^+$: 607.1422, found 607.1426.

Alcohol 93: R_f = 0.28 (80% Et_2O in hexanes); $[\alpha]_D^{22}$ = +55.6 (c = 0.5, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3456, 2917, 1765, 1605, 1506, 1451, 1297, 1248, 1165, 1099, 1039, 967, 831 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59–7.54 (m, 2H, ArH), 7.27–7.25 (m, 3H, ArH), 7.21 (d, J = 8.5 Hz, 2H, PMB), 6.84 (d, J = 8.6 Hz, 2H, PMB), 5.15 (d, J = 3.0 Hz, 1H, H1), 4.79 (d, J = 3.4 Hz, 1H, H1′), 4.73 (t, J = 9.6 Hz, 1H, H4′), 4.55, 4.53 (AB, J = 11.5 Hz, 2H, CH_2Ar), 4.02 (dd, J = 7.7, 4.1 Hz, 1H, H3), 3.97 (t, J = 9.5 Hz, 1H, H3′), 3.83 (dd, J = 11.5, 8.8 Hz, 1H, H5), 3.78 (s, 3H, OMe), 3.74 (dq, J = 9.9, 6.3 Hz, 1H, H5′), 3.68 (dd, J = 11.6, 4.7 Hz, 1H, H5), 3.63, 3.60 (AB, J = 14.6 Hz, 2H, CH_2Cl), 3.55 (t, J = 3.5 Hz, 1H, H2), 3.46–3.42 (m, 4H, OMe, H4), 3.38 (s, 3H, OMe), 3.21 (dd, J = 9.6, 3.6 Hz, 1H, H2′), 1.10 (d, J = 6.3 Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 133.7, 131.3, 130.2, 129.4, 127.7, 113.9, 101.6, 97.1, 80.4, 77.7, 75.7, 72.1, 69.3, 65.9, 64.8, 61.6, 59.0, 55.3, 53.4, 48.6, 40.3, 30.3, 29.7, 17.2; HRMS (MALDI): calcd for $C_{29}H_{37}ClO_{10}SeNa$ $[M+Na]^+$: 683.1132, found 683.1157.

Diol 98: R_f = 0.14 (90% Et_2O in hexanes); $[\alpha]_D^{22}$ = +56.7 (c = 0.62, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3445, 2917, 1611, 1583, 1506, 1446, 1369, 1303, 1242, 1094, 1038, 896, 819, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 2H, ArH), 7.29–7.24 (m, 3H, ArH), 7.21 (d, J = 8.6 Hz, 2H, PMB), 6.85 (d, J = 8.6 Hz, 2H, PMB), 5.38 (d, J = 5.5 Hz, 1H, H1), 4.79 (d, J = 3.5 Hz, 1H, H1′), 4.55 (s, 2H, CH_2Ar), 4.06 (dd, J = 5.8, 3.6 Hz, 1H, H3), 3.90 (t, J = 9.4 Hz, 1H, H3′), 3.81 (dd, J = 11.9, 3.6 Hz, 1H, H5), 3.80 (s, 3H, OMe), 3.76 (dd, J = 11.9, 5.9 Hz, 1H, H5), 3.72 (dd, J = 5.4, 3.7 Hz, 1H, H2), 3.64 (dq, J = 9.6, 6.2 Hz, 1H, H5′), 3.54–3.44 (m, 1H, H4), 3.49 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.26 (t, J = 9.9 Hz, 1H, H4′), 3.15 (dd, J = 9.6, 3.5 Hz, 1H, H2′), 1.31 (d, J = 6.2 Hz, 3H, H6′); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4, 133.8, 130.1, 129.4, 129.2, 128.9, 127.7, 113.9, 101.4, 96.5, 94.4, 82.4, 81.3, 73.2, 71.8, 69.7, 65.6, 62.5, 58.5, 55.3, 55.1, 38.1, 30.3, 18.1; HRMS (MALDI): calcd for $C_{27}H_{36}O_9SeNa$ $[M+Na]^+$: 607.1422, found 607.1405.

Alcohol 99: R_f = 0.36 (80% Et_2O in hexanes); $[\alpha]_D^{22}$ = +14.3 (c = 3.48, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 3445, 2927, 1770, 1611, 1578, 1506, 1457, 1369, 1303, 1248, 1165, 1132, 1088, 1039, 912, 819, 742 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2H, ArH), 7.28–7.24 (m, 3H, ArH), 7.20 (d, J = 8.6 Hz, 2H, PMB), 6.84 (d, J = 8.6 Hz, 2H, PMB), 5.37 (t, J = 9.6 Hz, 1H, H3′), 5.08 (d, J = 5.1 Hz, 1H, H1), 4.78 (d, J = 3.4 Hz, 1H, H1′), 4.51, 4.51 (AB, J = 12.2 Hz, 2H, CH_2Ar), 3.93 (dd, J = 6.2, 3.6 Hz, 1H, H3), 3.81, 3.80 (AB, J = 14.7 Hz, 2H, CH_2Cl), 3.78 (s, 3H, OMe), 3.78–3.72 (m, 2H, H5, H5), 3.69 (dq, J = 9.5, 6.2 Hz, 1H, H5′), 3.51 (dd, J = 5.0, 3.7 Hz, 1H, H2), 3.47–3.42 (m, 1H, H4), 3.40 (t, J = 9.8 Hz, 1H, H4′), 3.39 (s, 3H, OMe), 3.36 (s, 3H, OMe), 3.23 (dd, J = 10.1, 3.5 Hz, 1H, H2′), 1.29 (d, J = 6.2 Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.0, 134.0, 130.0, 129.3, 127.8, 125.5, 113.9, 101.8, 96.6, 79.9, 75.7, 75.6, 71.8, 68.9, 66.0, 62.6, 58.6, 55.2, 55.1, 51.7, 40.7, 30.3, 29.7, 17.9; HRMS (MALDI): calcd for $C_{29}H_{37}ClO_{10}SeNa$ $[M+Na]^+$: 683.1132, found 683.1105.

General procedure for the formation of orthoesters: *Solid phase*: *m*CPBA (3.0 equiv) was added to a solution of the resin bound glycoside (1.0 equiv) in CH_2Cl_2 (0.1 M) at −78 °C. After stirring for 10 min at −78 °C, the resulting mixture was quickly filtered through a cold sintered glass frit and washed with CH_2Cl_2. The resin was then transferred to a sealed tube and diluted with diisopropylamine/vinyl acetate/toluene 1:2:2. The tube was sealed and heated to 140 °C for 12 h. After cooling, the reaction mixture was filtered, and concentrated, and the residue was purified by flash column chromatography.

Solution phase: $NaIO_4$ (10 equiv) and $NaHCO_3$ (8.0 equiv) were added to a solution of the glycoside (1.0 equiv) in MeOH/CH_2Cl_2/H_2O 3:2:1 (0.2 M) and the resulting mixture was stirred at 25 °C for 1–6 h. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous NH_4Cl and brine. The organic layer was dried (Na_2SO_4), and the solvents were removed under reduced pressure. The crude selenoxide was dissolved in toluene and transferred by cannula to a sealed tube. The flask was washed with toluene and the organics were transferred to the cannula. Diisopropylamine and vinyl acetate were added so that the final ratio was

2:2:1 toluene/vinyl acetate/diisopropylamine, and the tube was sealed and heated to 140 °C for 12 h. After cooling, the reaction mixture was concentrated and the residue was purified by flash column chromatography. This procedure is further illustrated by the following example:

Orthoester 40: $NaIO_4$ (305 mg, 1.43 mmol) and $NaHCO_3$ (96 mg, 1.14 mmol) were added to a solution of alcohol **39** (81 mg, 0.14 mmol) in $MeOH/CH_2Cl_2/H_2O$ (3:2:1, 2.1 mL) and the resulting mixture was stirred at 25 °C for 1 h. The reaction mixture was diluted with CH_2Cl_2 (150 mL) and washed with saturated aqueous NH_4Cl (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and the solvents were removed under reduced pressure. The crude selenoxide was dissolved in toluene (2 mL) and transferred by cannula to a sealed tube. The flask was washed with toluene (2 × 2 mL) and the organics were transferred to the tube. Diisopropylamine (3 mL) and vinyl acetate (6 mL) were added, and the tube was sealed and heated to 140 °C for 12 h. After cooling, the reaction mixture was concentrated and the residue was purified by flash column chromatography (silica gel, 0 → 80 % Et_2O in hexanes) to afford the orthoester **40** (49 mg, 82 % over two steps) as a colorless oil. **40**: $R_f = 0.33$ (70 % Et_2O in hexanes); $[\alpha]_D^{22} = +10.9$ ($c = 0.23$, $CHCl_3$); IR (neat): $\tilde{\nu} =$ 2929, 1688, 1512, 1462, 1253, 1099, 1044, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.24$ (d, $J = 8.4$ Hz, 2H, PMB), 6.85 (d, $J = 8.5$, 2H, PMB), 4.66, 4.50 (AB, $J = 11.5$ Hz, 2H, CH_2Ar), 4.08 (ddd, $J = 11.9$, 11.9, 5.3 Hz, 1H, CH_2O), 3.98 (m, 2H, CH_2O), 3.94 – 3.92 (m, 2H, H3, CH_2O), 3.79 (s, 3H, OMe), 3.66 (dd, $J = 11.2$, 5.0 Hz, 1H, H5), 3.40 (t, $J = 11.2$ Hz, 1H, H5), 3.34 – 3.30 (m, 1H, H4), 2.09 (dd, $J = 12.9$, 5.1, 1H, H2), 1.93 (t, $J = 12.6$ Hz, 1H, H2), 0.90 (s, 9H, *t*BuSi), 0.08, 0.06 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.1$, 134.5, 133.6, 132.5, 130.6, 128.6, 119.0, 113.7, 78.1, 72.8, 70.8, 64.4, 63.5, 62.7, 55.2, 39.5, 25.8, 18.0, −4.5, −4.8; HRMS (MALDI): calcd for $C_{21}H_{34}O_6SiNa$ $[M+Na]^+$: 433.2115, found 433.2132.

Orthoester 42: $R_f = 0.16$ (70 % Et_2O in hexanes); $[\alpha]_D^{22} = +29.2$ ($c = 0.12$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2903$, 1738, 1612, 1513, 1450, 1401, 1248, 1183, 1071, 1017, 950, 821 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.26$ (d, $J = 8.1$ Hz, 2H, PMB), 6.87 (d, $J = 8.1$ Hz, 2H, PMB), 6.18 (dd, $J = 12.2$, 3.1 Hz, 1H, H3), 5.74 (dd, $J = 11.9$, 1.4 Hz, 1H, H2), 4.53 (s, 2H, CH_2Ar), 4.06 – 3.92 (m, 7H, H4, H5, H5, CH_2O, CH_2O), 3.78 (s, 3H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.3$, 132.9, 130.1, 129.4, 127.0, 113.8, 70.4, 67.7, 65.3, 64.6, 55.3; HRMS (MALDI): calcd for $C_{15}H_{18}O_5Na$ $[M+Na]^+$: 301.1154, found 301.1123.

Orthoester 64: $R_f = 0.44$ (70 % Et_2O in hexanes); $[\alpha]_D^{22} = +43.5$ ($c = 0.20$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3016$, 2895, 1539, 1451, 1358, 1236, 1203, 1099, 1022, 742, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.36 – 7.19$ (m, 15H, ArH), 4.91, 4.55 (AB, $J = 10.9$ Hz, 2H, CH_2Ar), 4.69, 4.65 (AB, $J = 11.5$ Hz, 2H, CH_2Ar), 4.63, 4.52 (AB, $J = 12.2$ Hz, 2H, CH_2Ar), 4.19 – 4.16 (m, 1H), 4.03 – 3.93 (m, 4H), 3.76 – 3.68 (m, 3H), 3.62 (t, $J = 9.2$ Hz, 1H), 2.36 (dd, $J = 12.6$, 5.1 Hz, 1H, H2), 2.05 (t, $J = 12.6$ Hz, 1H, H2); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.4$, 138.4, 138.3, 128.5, 128.4, 127.8, 127.7, 127.6, 127.5, 118.8, 79.0, 77.8, 74.8, 73.4, 73.3, 71.8, 69.0, 64.6, 63.6, 36.6, 30.3, 29.6; HRMS (MALDI): calcd for $C_{29}H_{32}O_6Na$ $[M+Na]^+$: 499.2097, found 499.2099.

Orthoester 65: $R_f = 0.58$ (50 % Et_2O in hexanes); $[\alpha]_D^{22} = +8.5$ ($c = 0.68$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2930$, 2856, 1473, 1368, 1250, 1114, 1050, 876, 836, 778, 738 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.33 – 7.26$ (m, 5H, ArH), 4.57, 4.52 (AB, $J = 11.6$ Hz, 2H, CH_2Ar), 4.15 (dt, $J = 6.4$, 6.4 Hz, 1H), 3.95 (t, $J = 7.5$ Hz, 1H), 3.66 – 3.58 (m, 2H), 3.54 – 3.53 (m, 2H), 3.27 (t, $J = 8.9$ Hz, 1H), 2.30 (dd, $J = 12.6$, 5.0 Hz, 1H, H2), 1.96 (t, $J = 12.6$ Hz, 1H, H2), 1.25 (t, $J = 6.3$ Hz, 3H, H6), 0.88 (s, 9H, *t*BuSi), 0.05, 0.03 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.4$, 134.6, 133.6, 129.4, 128.2, 127.7, 127.4, 118.6, 78.7, 76.5, 71.3, 71.2, 64.5, 63.6, 36.8, 36.5, 30.3, 25.9, 18.6, −3.7, −4.6; HRMS (MALDI): calcd for $C_{21}H_{34}O_5SiNa$ $[M+Na]^+$: 417.2073, found 417.2075.

Orthoester 66: $R_f = 0.49$ (100 % Et_2O); IR (thin film): $\tilde{\nu} = 3030$, 2920, 1453, 1367, 1298, 1196, 1055, 913, 737, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major isomer): $\delta = 7.37 – 7.17$ (m, 15H, ArH), 4.88, 4.51 (AB, $J = 10.8$ Hz, 2H, CH_2Ar), 4.79 (d, $J = 3.7$ Hz, 1H, H1′), 4.65, 4.56 (AB, $J = 11.3$ Hz, 2H, CH_2Ar), 4.65, 4.56 (AB, $J = 12.2$ Hz, 2H, CH_2Ar), 4.26 (dd, $J = 10.2$, 7.2 Hz, 1H), 4.07 – 4.05 (m, 1H), 3.88 – 3.83 (m, 2H), 3.73 – 3.71 (m, 2H), 3.67 (dd, $J = 10.9$, 1.9 Hz, 1H), 3.62 – 3.59 (m, 2H), 3.54 (s, 3H, OMe), 3.53 – 3.50 (m, 1H), 3.49 (s, 3H, OMe), 3.34 (s, 3H, OMe), 3.21 – 3.20 (m, 1H), 2.55 (dd, $J = 12.2$, 4.9 Hz, 1H, H2), 1.69 (t, $J = 12.2$ Hz, 1H, H2); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.4$, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 111.2, 98.3, 80.7, 80.5, 78.3, 75.0, 74.1, 73.2, 68.7, 63.2, 62.5, 59.3, 55.2, 49.2, 37.1; HRMS (MALDI): calcd for $C_{36}H_{44}O_{10}Na$ $[M+Na]^+$: 659.2832, found 659.2851.

Orthoester 67: $R_f = 0.27$ (50 % Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 2931$, 1455, 1383, 1252, 1112, 1056, 875, 836, 778, 737 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major isomer): $\delta = 7.33 – 7.26$ (m, 5H, ArH), 4.79 (d, $J = 3.7$ Hz, 1H, H1′), 4.79 (s, 2H, CH_2Ar), 4.15 (dd, $J = 10.3$, 6.8 Hz, 1H), 3.98 – 3.96 (m, 1H), 3.76 – 3.73 (m, 1H), 3.60 – 3.51 (m, 2H), 3.58 (s, 3H, OMe), 3.54 (s, 3H, OMe), 3.49 (t, $J = 7.7$ Hz, 1H), 3.42 – 3.40 (m, 1H), 3.40 (s, 3H, OMe), 3.27 (t, $J = 8.8$ Hz, 1H), 3.21 (dd, $J = 9.2$, 3.8 Hz, 1H), 2.54 (dd, $J = 12.2$, 4.7 Hz, 1H, H2), 1.51 (t, $J = 12.2$ Hz, 1H, H2), 1.27 (d, $J = 6.2$ Hz, 3H, H6), 0.88 (s, 9H, *t*BuSi), 0.06 (s, 3H, MeSi), 0.04 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.3$, 128.3, 128.2, 128.0, 127.8, 127.6, 127.4, 111.0, 98.4, 80.8, 80.4, 77.6, 76.5, 74.7, 71.6, 71.5, 63.3, 62.5, 60.8, 59.4, 55.3, 35.8, 25.9, 18.6, 18.2, −3.7, −4.6; HRMS (MALDI): calcd for $C_{28}H_{46}O_9SiNa$ $[M+Na]^+$: 577.2809, found 577.2796.

Orthoester 68: $R_f = 0.5$ (100 % Et_2O); IR (thin film): $\tilde{\nu} = 2931$, 2856, 1613, 1514, 1466 1383, 1250, 1101, 1055, 914, 864, 837, 779, 733 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major isomer): $\delta = 7.23$ (d, $J = 8.5$ Hz, 2H, PMB), 6.86 (d, $J = 8.5$ Hz, 2H, PMB), 4.79 (d, $J = 3.7$ Hz, 1H, H1′), 4.78, 4.66 (AB, $J =$ 11.5 Hz, 2H, CH_2Ar), 3.92 – 3.89 (m, 1H), 3.86 – 3.84 (m, 1H), 3.80 (s, 3H, OMe), 3.72 – 3.67 (m, 3H), 3.56 (s, 3H, OMe), 3.53 – 3.50 (m, 1H), 3.51 (s, 3H, OMe), 3.49 (t, $J = 9.3$ Hz 1H), 3.40 (s, 3H, OMe), 3.35 – 3.33 (m, 1H), 3.28 (t, $J = 10.7$ Hz, 1H), 3.21 (dd, $J = 9.1$, 3.6 Hz, 1H, H2′), 2.12 (dd, $J =$ 13.1, 5.3 Hz, 1H, H2), 1.67 (dd, $J = 12.8$, 10.2 Hz, 1H, H2), 0.89 (s, 9H, *t*BuSi), 0.08 (s, 3H, MeSi), 0.07 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.2$, 129.5 113.9, 111.4, 110.3, 98.4, 81.6, 79.4, 77.9, 73.6, 73.0, 70.1, 62.5, 62.0, 60.7, 55.4, 41.3, 25.8, 18.0, −4.6, −4.8; HRMS (FAB): calcd for $C_{28}H_{46}O_{10}SiNa$ $[M+Na]^+$: 593.2758, found 593.2741.

Orthoester 69: $R_f = 0.33$ (100 % Et_2O); IR (thin film): $\tilde{\nu} = 2920$, 2840, 1611, 1517, 1303, 1242 1182, 1099, 1050, 1000 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major isomer): $\delta = 7.26$ (d, $J = 8.6$ Hz, 2H, PMB), 6.87 (d, $J = 8.6$ Hz, 2H, PMB), 6.04 (dd, $J = 10.6$, 3.8 Hz, 1H, H3), 5.80 (dd, $J = 10.1$, 1.3 Hz, 1H, H2), 4.81 (d, $J = 3.7$ Hz, 1H, H1′), 4.53 (br s, 2H, CH_2Ar), 4.04 – 3.98 (m, 3H, H6′, H6′, H5), 3.89 – 3.87 (m, 1H, H5′), 3.86 – 3.81 (m, 2H, H4′, H5), 3.80 (s, 3H, OMe), 3.74 (dd, $J = 10.4$, 5.0 Hz, 1H, H4), 3.54 – 3.42 (m, 4H, OMe, H3′), 3.51 (s, 3H, OMe), 3.23 (dd, $J = 9.2$, 3.6 Hz, 1H, H2′), 3.16 (s, 3H, OMe); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.3$, 130.1, 129.9, 129.4, 128.7, 113.8, 98.4, 81.6, 79.5, 73.5, 70.3, 67.2, 64.4, 62.4, 62.0, 60.7, 59.3, 55.2, 49.3; HRMS (FAB): calcd for $C_{22}H_{30}O_9Na$ $[M+Na]^+$: 461.1787, found 461.1789.

Orthoester 70: $R_f = 0.32$ (70 % Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 3010$, 2919, 1496, 1454, 1366, 1313, 1203, 1073, 916, 805, 737, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major isomer): $\delta = 7.38 – 7.17$ (m, 15H, ArH), 5.13 (d, $J = 3.0$ Hz, 1H, H1′), 4.92, 4.56 (AB, $J = 10.7$ Hz, 2H, CH_2Ar), 4.71, 4.65 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.67, 4.53 (AB, $J = 12.2$ Hz, 2H, CH_2Ar), 4.10 (ddd, $J = 9.6$, 4.2, 4.2 Hz, 1H), 4.00 (ddd, $J = 11.7$, 9.1, 5.1 Hz, 1H), 3.95 (dd, $J = 10.1$, 2.7 Hz, 1H), 3.92 – 3.89 (m, 1H), 3.82 (dd, $J = 10.9$, 3.9 Hz, 1H), 3.73 (t, $J = 10.2$ Hz, 2H), 3.65 – 3.52 (m, 3H), 3.51 – 3.48 (m, 1H), 3.50 (s, 3H, OMe), 3.48 (s, 3H, OMe), 3.43 (s, 3H, OMe), 2.45 (dd, $J = 12.2$, 5.0 Hz, 1H, H2), 2.05 (t, $J = 12.2$ Hz, 1H, H2); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 120.0, 97.1, 79.2, 78.8, 77.3, 75.3, 75.0, 73.5, 73.4, 71.6, 71.3, 70.6, 68.6, 65.7, 59.3, 58.7, 55.5, 37.7; HRMS (MALDI): calcd for $C_{36}H_{44}O_{10}Na$ $[M+Na]^+$: 659.2832, found 659.2809.

Orthoester 71: $R_f = 0.35$ (100 % Et_2O); IR (thin film): $\tilde{\nu} = 2928$, 2862, 1451, 1253, 1204, 1116, 1077, 1017, 918, 879, 841, 775 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major isomer): $\delta = 7.32 – 7.26$ (m, 5H, ArH), 5.08 (d, $J = 3.7$ Hz, 1H, H1′), 4.57, 4.48 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.04 (t, $J = 9.9$ Hz, 1H, H3′), 3.88 (dd, $J = 10.1$, 3.1 Hz, 1H, H2′), 3.72 (dq, $J = 9.1$, 6.2 Hz, 1H, H5), 3.66 – 3.61 (m, 3H, H3, H6′, H6′), 3.64 (s, 3H, OMe), 3.55 – 3.48 (m, 2H, H4′, H5′), 3.54 (s, 3H, OMe), 3.42 (s, 3H, OMe), 3.27 (t, $J = 9.9$ Hz, 1H, H4), 2.37 (dd, $J = 12.2$, 4.9 Hz, 1H, H2), 1.88 (t, $J = 12.2$ Hz, 1H, H2), 1.26 (d, $J = 6.2$ Hz, 3H, H6), 0.87 (s, 9H, *t*BuSi), 0.05 (s, 3H, MeSi), 0.02 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.2$, 128.2, 127.8, 127.5, 119.9, 97.1, 78.7, 78.6, 78.5, 76.4, 75.3, 71.5, 71.3, 71.1, 70.7, 59.4, 58.9, 55.5, 37.6, 26.0, 18.6, 18.2, −3.7, −4.6; HRMS (MALDI): calcd for $C_{28}H_{46}O_9SiNa$ $[M+Na]^+$: 577.2809, found 577.2807.

Orthoester 72: $R_f = 0.35$ (50 % Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 2931$, 2856, 1613, 1514, 1468, 1383, 1320, 1250, 1203, 1104, 963, 920, 838, 778 cm^{-1};

0947-6539/00/0617-3182 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

^{1}H NMR (600 MHz, $CDCl_3$, 10:1 ratio, major isomer): $\delta = 7.24$ (d, $J =$ 8.5 Hz, 2H, PMB), 6.85 (d, $J = 8.5$ Hz, 2H, PMB), 5.07 (d, $J = 3.0$ Hz, 1H, H1′), 4.65, 4.51 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.03 (t, $J = 9.6$ Hz, 1H, H3′), 3.98–3.92 (m, 1H, H3), 3.82 (dd, $J = 10.1$, 3.1 Hz, 1H, H2′), 3.78 (s, 3H, OMe), 3.77 (dd, $J = 11.2$, 4.8 Hz, 1H, H5), 3.61 (br s, 2H, H6′, H6′), 3.55 (t, $J = 11.4$ Hz, 1H, H5), 3.52–3.48 (m, 2H, H4′, H5′), 3.49 (s, 3H, OMe), 3.41 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.33 (ddd, $J = 9.1$, 9.1, 4.1 Hz, 1H, H4), 2.13 (dd, $J = 13.0$, 5.0 Hz, 1H, H2), 1.91 (dd, $J = 13.0$, 10.0 Hz, 1H, H2), 0.86 (s, 9H, *t*BuSi), 0.08 (s, 3H, MeSi), 0.07 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.2$, 130.6, 129.4, 120.3, 113.7, 97.2, 78.7, 78.5, 75.2, 72.9, 71.4, 70.7, 70.6, 62.9, 59.3, 58.7, 55.5, 55.2, 40.5, 30.3, 25.7, 18.0, −4.6, −4.8; HRMS (MALDI): calcd for $C_{28}H_{46}O_{10}SiNa$ $[M+Na]^+$: 593.2758, found 593.2755.

Orthoester 73: $R_f = 0.32$ (100% Et_2O); IR (thin film): $\tilde{\nu} = 2983$, 2922, 2862, 1617, 1512, 1451, 1384, 1248, 1182, 1077, 1017, 918, 819 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 10:1 ratio, major isomer): $\delta = 7.25$ (d, $J = 8.6$ Hz, 2H, PMB), 6.86 (d, $J = 8.6$ Hz, 2H, PMB), 6.15 (dd, $J = 10.0$, 4.1 Hz, 1H, H3), 5.77 (dd, $J = 10.0$, 1.1 Hz, 1H, H2), 5.06 (d, $J = 3.0$ Hz, 1H, H1′), 4.59, 4.51 (AB, $J = 11.7$ Hz, 2H, CH_2Ar), 4.31 (t, $J = 9.5$ Hz, 1H, H3′), 4.14–4.11 (m, 2H, H3, H5), 3.88–3.85 (m, 1H, H4), 3.81 (s, 3H, OMe), 3.65–3.63 (m, 2H, H6′), 3.61–3.53 (m, 2H, H4′, H5′), 3.59 (dd, $J = 10.1$, 3.0 Hz, 1H, H2′), 3.50 (s, 3H, OMe), 3.46 (s, 3H, OMe), 3.41 (s, 3H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.2$, 130.5, 130.2, 129.3, 128.4, 125.5, 116.6, 113.8, 97.4, 77.7, 76.2, 71.3, 70.7, 69.9, 66.8, 65.7, 59.3, 58.8, 55.7, 55.2, 30.3, 20.6; HRMS (MALDI): calcd for $C_{22}H_{30}O_9Na$ $[M+Na]^+$: 461.1787, found 461.1789.

Orthoester 76: $R_f = 0.44$ (80% Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 2928$, 1611, 1512, 1462, 1380, 1319, 1248, 1165, 1094, 1033, 972, 835, 774 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.22$ (d, $J = 8.6$ Hz, 2H, PMB), 6.83 (d, $J =$ 8.6 Hz, 2H, PMB), 4.80 (d, $J = 3.7$ Hz, 1H, H1′), 4.64, 4.47 (AB, $J = 11.3$ Hz, 2H, CH_2Ar), 3.94–3.86 (m, 2H, H3, H5′), 3.83 (t, $J = 9.9$ Hz, 1H, H3′), 3.77 (s, 3H, OMe), 3.70 (dd, $J = 11.3$, 5.2 Hz, 1H, H5), 3.55–3.45 (m, 5H, OMe, H2′, H5), 3.39 (s, 3H, OMe), 3.33 (ddd, $J = 10.1$, 8.2, 5.2 Hz, 1H, H4), 3.24 (t, $J = 9.6$ Hz, 1H, H4′), 2.08–2.04 (m, 1H, H2), 1.94–1.89 (m, 1H, H2), 1.28 (d, $J = 6.1$ Hz, 3H, H6′), 0.87 (s, 9H, *t*BuSi), 0.07, 0.06 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.2$ 130.5, 129.4, 120.3, 113.7, 98.6, 80.6, 79.4, 78.2, 77.8, 73.0, 70.4, 66.7, 63.4, 58.4, 55.5, 55.2, 29.7, 25.7, 23.9, 20.9, 20.6, 17.9, 17.6, −4.6, −4.7; HRMS (MALDI): calcd for $C_{27}H_{45}O_9Si$ $[M+H]^+$: 541.2833, found 541.2847.

Orthoester 78: $R_f = 0.28$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +4.04$ ($c = 0.99$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2917$, 1727, 1605, 1506, 1457, 1374, 1253, 1171, 1132, 1088, 1033, 978, 797 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.21$ (d, $J = 8.8$ Hz, 2H, PMB), 6.83 (d, $J = 8.8$ Hz, 2H, PMB), 6.12 (dt, $J = 10.1$, 1.3 Hz, 1H, H3), 5.62 (dd, $J = 10.1$, 1.3 Hz, 1H, H2), 4.82 (d, $J = 3.5$ Hz, 1H, H1′), 4.51, 4.47 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.07–4.04 (m, 1H, H4), 4.02 (dd, $J = 11.0$, 5.3 Hz, 1H, H5), 3.91–3.86 (m, 3H, H3′, H5′, H5), 3.77 (s, 3H, OMe), 3.55 (dd, $J = 10.3$, 3.7 Hz, 1H, H2′), 3.48 (s, 3H, OMe), 3.37 (s, 3H, OMe), 3.29 (t, $J = 9.6$ Hz, 1H, H4′); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 159.4, 132.8, 129.8, 129.4, 113.9, 98.5, 88.3, 80.5, 79.7, 78.4, 70.9, 66.9, 58.4, 55.5, 55.3, 17.7; HRMS (ESI): calcd for $C_{21}H_{28}O_8Na$ $[M+Na]^+$: 431, found 431.

Orthoester 79: $R_f = 0.44$ (80% Et_2O in hexanes); IR (thin film): $\tilde{\nu} = 2930$, 1612, 1513, 1464, 1380, 1320, 1250, 1170, 1099, 1035, 972 864, 835, 779 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.21$ (d, $J = 8.2$ Hz, 2H, PMB), 6.83 (d, $J =$ 8.6 Hz, 2H, PMB), 4.83 (d, $J = 3.6$ Hz, 1H, H1′), 4.63, 4.47 (AB, $J = 11.2$ Hz, 2H, CH_2Ar), 4.09 (t, $J = 10.0$ Hz, 1H, H3′), 3.93 (ddd, $J = 9.5$, 8.6, 5.2 Hz, 1H, H3), 3.89 (dq, $J = 9.4$, 6.4 Hz, 1H, H5′), 3.78 (s, 3H, OMe), 3.65 (dd, $J = 11.3$, 5.2 Hz, 1H, H5), 3.54 (dd, $J = 10.4$, 3.7 Hz, 1H, H2′), 3.49 (s, 3H, OMe), 3.45 (t, $J = 10.7$ Hz, 1H, H5), 3.39 (s, 3H, OMe), 3.33 (ddd, $J = 13.5$, 10.3, 5.2 Hz, 1H, H4), 3.04 (t, $J = 9.6$ Hz, 1H, H4′), 2.09 (dd, $J = 13.2$, 5.2 Hz, 1H, H2), 1.92 (t, $J = 12.0$ Hz, 1H, H2), 1.26 (d, $J = 6.1$ Hz, 3H, H6′), 0.88 (s, 9H, *t*BuSi), 0.07 (s, 3H, MeSi), 0.06 (s, 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.2$, 130.5, 129.4, 120.3, 113.7, 98.4, 80.6, 79.7, 78.0, 73.0, 70.5, 67.4, 63.2, 58.1, 55.4, 55.2, 45.9, 41.1, 30.3, 29.6, 25.7, 17.9, 17.6, 10.7, −4.5, −4.8; HRMS (ESI): calcd for $C_{27}H_{45}O_9Si$ $[M+H]^+$: 541, found 541.

Orthoester 81: $R_f = 0.28$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +41.6$ ($c = 0.67$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2917$, 1726, 1605, 1506, 1457, 1374, 1253, 1171, 1088, 1028, 973, 797 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.22$ (d, $J =$ 8.6 Hz, 2H, PMB), 6.85 (d, $J = 8.6$ Hz, 2H, PMB), 6.15 (dd, $J = 10.1$, 1.3 Hz, 1H, H3), 5.64 (dd, $J = 10.1$, 1.9 Hz, 1H, H2), 4.83 (d, $J = 3.7$ Hz, 1H, H1′), 4.50, 4.48 (AB, $J = 11.4$ Hz, 2H, CH_2Ar), 4.14 (t, $J = 9.9$ Hz, 1H, H3′), 4.13–4.11 (m, 1H, H4), 3.99 (ddd, $J = 11.1$, 5.3, 1.0 Hz, 1H, H5), 3.92 (dq, $J = 9.6$, 6.3 Hz, 1H, H5′), 3.87 (dd, $J = 11.1$, 9.1 Hz, 1H, H5), 3.78 (s, 3H, OMe), 3.53 (dd, $J = 10.3$, 3.7 Hz, 1H, H2′), 3.50 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.08 (t, $J = 9.6$ Hz, 1H, H4′), 1.29 (d, $J = 6.2$ Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 145.6$, 133.9, 129.4, 126.2, 124.8, 113.9, 98.5, 81.1, 79.9, 70.9, 68.4, 67.4, 66.1, 58.3, 55.4, 55.3, 17.7; HRMS (ESI): calcd for $C_{21}H_{28}O_8Na$ $[M+Na]^+$: 431, found 431.

Orthoester 84: See Part 2[2] of this series.

Orthoester 87: See Part 2[2] of this series.

Enol ether 105: $R_f = 0.36$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +68.8$ ($c = 0.49$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3459$, 2928, 1677, 1611, 1550, 1511, 1462, 1363, 1303, 1242, 1083, 1033, 967, 840 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6, 340 K): $\delta = 7.23$ (d, $J = 8.5$, 2H, ArH PMB), 6.78 (d, $J = 8.6$ Hz, 2H, PMB), 5.46 (s, 1H, H2), 5.23 (d, $J = 2.0$ Hz, 1H, H1), 4.69, 4.50 (AB, $J = 11.2$ Hz, 2H, CH_2Ar), 4.68 (d, $J = 3.5$ Hz, 1H, H1′), 4.11 (t, $J = 9.1$ Hz, 1H, H3′), 4.04 (ddd, $J = 6.3$, 5.0, 4.1 Hz, 1H, H5), 3.92 (d, $J = 5.0$ Hz, 1H, H4), 3.90 (dq, $J = 9.3$, 6.1 Hz, 1H, H5′), 3.63 (dd, $J = 10.4$, 6.5 Hz, 1H, H6), 3.38 (t, $J =$ 9.0 Hz, 1H, H4′), 3.35 (s, 3H, OMe), 3.31 (dd, $J = 10.4$, 4.0 Hz, 1H, H6), 3.25 (s, 3H, OMe), 3.22 (dd, $J = 9.5$, 3.6 Hz, 1H, H2′), 3.16 (s, 3H, OMe), 3.11 (s, 3H, OMe), 1.50 (d, $J = 6.2$ Hz, 3H, H6′), 0.95 (s, 9H, *t*BuSi), 0.16, 0.15 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.2$, 151.7, 130.0, 129.6, 113.7, 104.8, 99.2, 97.4, 84.4, 80.6, 74.6, 74.5, 72.6, 72.2, 71.8, 67.2, 59.4, 58.6, 55.2, 54.9, 25.6, 17.8, −4.4, −4.5; HRMS (ESI): calcd for $C_{29}H_{48}O_{10}SiNa$ $[M+Na]^+$: 607, found 607.

Enol ether 108: $R_f = 0.09$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +57.0$ ($c = 0.43$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3456$, 2917, 1732, 1672, 1611, 1550, 1506, 1462, 1363, 1297, 1248, 1094, 982, 837, 775 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.22 (d, $J = 8.5$, 2H, PMB), 6.83 (d, $J = 8.6$ Hz, 2H, PMB), 5.19 (s, 1H, H2), 4.87 (d, $J = 2.0$ Hz, 1H, H1), 4.75 (d, $J = 3.5$ Hz, 1H, H1′), 4.65, 4.50 (AB, $J = 11.1$ Hz, 2H, CH_2Ar), 4.06 (ddd, $J = 7.7$, 4.3, 4.3 Hz, 1H, H5), 3.79 (t, $J =$ 9.1 Hz, 1H, H3′), 3.77 (s, 3H, OMe), 3.71 (d, $J = 4.3$ Hz, 1H, H4), 3.64 (dq, $J = 9.5$, 6.1 Hz, 1H, H5′), 3.55 (t, $J = 9.0$ Hz, 1H, H6), 3.54 (s, 3H, OMe), 3.39 (dd, $J = 9.1$, 4.8 Hz, 1H, H6), 3.37 (s, 3H, OMe), 3.30 (s, 3H, OMe), 3.23 (dd, $J = 9.7$, 3.4 Hz, 1H, H2′), 3.08 (t, $J = 9.0$ Hz, 1H, H4′), 1.20 (d, $J =$ 6.2 Hz, 3H, H6′), 0.92 (s, 9H, *t*BuSi), 0.19, 0.18 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.3$, 151.9, 130.0, 129.7, 129.6, 113.7, 104.2, 98.9, 97.2, 88.0, 80.9, 74.8, 72.4, 72.2, 71.9, 71.5, 65.2, 59.1, 59.0, 55.2, 55.0, 30.3, 29.7, 25.6, 17.6, −4.4, −4.5; HRMS (ESI): calcd for $C_{29}H_{48}O_{10}$-SiNa $[M+Na]^+$: 607, found 607.

Orthoester 111 (major): $R_f = 0.4$ (90% Et_2O in hexanes); $[\alpha]_D^{22} = +68.2$ ($c = 0.20$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2919$, 1608, 1514, 1461, 1378, 1308, 1250, 1207, 1087, 1033, 971, 955, 836, 778 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.22$ (d, $J = 8.6$, 2H, PMB), 6.85 (d, $J = 8.6$, 2H, PMB), 4.83 (d, $J = 3.7$, 1H, H1′), 4.79, 4.50 (AB, $J = 10.6$ Hz, 2H, CH_2Ar), 4.11 (t, $J = 9.9$, 1H, H3′), 4.03 (ddd, $J = 11.3$, 8.7, 5.3 Hz, 1H, H3), 3.94 (dq, $J = 9.7$, 6.1 Hz, 1H, H5′), 3.77 (s, 3H, OMe), 3.69 (ddd, $J = 10.0$, 2.6, 2.6 Hz, 1H, H5), 3.57 (dd, $J = 10.5$, 3.2 Hz, 1H, H6), 3.52 (dd, $J = 10.4$, 3.6 Hz, 1H, H2′), 3.49 (t, $J =$ 9.8 Hz, 1H, H4), 3.47 (s, 3H, OMe), 3.46 (dd, $J = 10.0$, 1.9 Hz, 1H, H6), 3.40 (s, 3H, OMe), 3.29 (s, 3H, OMe), 3.05 (t, $J = 9.6$ Hz, 1H, H4′), 2.07 (dd, $J =$ 12.7, 5.3 Hz, 1H, H2), 2.01 (t, $J = 12.6$ Hz, 1H, H2), 1.27 (d, $J = 6.1$ Hz, 3H, H6′), 0.87 (s, 9H, *t*BuSi), 0.09, 0.07 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.1$, 130.7, 129.5, 119.9, 113.8, 98.4, 80.8, 79.8, 78.4, 76.7, 74.7, 73.7, 71.5, 70.8, 59.0, 58.3, 55.4, 55.3, 41.7, 17.9, 17.7, −4.4, −4.5; HRMS (MALDI): calcd for $C_{29}H_{48}O_{10}SiNa$ $[M+Na]^+$: 607.2909, found 607.2898.

Orthoester 111 (minor): $R_f = 0.33$ (90% Et_2O in hexanes); $[\alpha]_D^{22} = +71.2$ ($c = 0.24$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2919$, 1608, 1508, 1461, 1378, 1308, 1243, 1202, 1090, 1049, 967, 832, 773 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta =$ 7.23 (d, $J = 8.6$, 2H, PMB), 6.85 (d, $J = 8.6$, 2H, PMB), 4.81 (d, $J = 3.7$, 1H, H1′), 4.81, 4.49 (AB, $J = 10.6$ Hz, 2H, CH_2Ar), 4.00 (ddd, $J = 11.4$, 8.6, 5.3 Hz, 1H, H3), 3.87 (dq, $J = 9.6$, 6.2 Hz, 1H, H5′), 3.82 (t, $J = 9.9$ Hz, 1H, H3′), 3.78 (s, 3H, OMe), 3.71 (ddd, $J = 10.0$, 4.0, 2.0 Hz, 1H, H5), 3.57 (dd, $J = 10.2$, 3.6 Hz, 1H, H2′), 3.57 (dd, $J = 10.5$, 4.2 Hz, 1H, H6), 3.52 (dd, $J =$ 10.6, 2.0 Hz, 1H, H6), 3.48 (s, 3H, OMe), 3.43 (dd, $J = 9.9$, 8.7 Hz, 1H, H4), 3.39 (s, 3H, OMe), 3.31 (s, 3H, OMe), 3.26 (t, $J = 9.6$ Hz, 1H, H4′), 2.05 (dd, $J = 12.8$, 5.3 Hz, 1H, H2), 1.99 (dd, $J = 12.7$, 11.5 Hz, 1H, H2), 1.25 (d, $J =$ 6.2 Hz, 3H, H6′), 0.89 (s, 9H, *t*BuSi), 0.09, 0.07 (2 × s, 2 × 3H, MeSi); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.2$, 130.7, 129.5, 120.1, 113.8, 98.5, 80.1, 79.5, 78.5, 78.0, 74.7, 73.8, 71.6, 71.2, 66.7, 59.0, 58.4, 55.5, 55.3, 41.7, 25.8, 17.9,

17.7, −4.4, −4.5; HRMS (MALDI): calcd for $C_{29}H_{48}O_{10}SiNa$ $[M+Na]^+$: 607.2909, found 607.2898.

General procedure for the dehydration of alcohols with Martin sulfurane: Martin sulfurane dehydrating agent (4.0 equiv) was added to a solution of alcohol (1.0 equiv) and Et_3N (0.1 equiv) in $CHCl_3$ (1.5 mL) at 25 °C and the resulting mixture was heated to 50 °C and stirred for 2 h. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography.

Orthoester 75: $R_f = 0.43$ (100% Et_2O); $[\alpha]_D^{22} = +16.3$ ($c = 0.23$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2919, 1698, 1649, 1514, 1249, 1184, 1074, 823\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.26$ (d, $J = 8.6$ Hz, 2H, PMB), 6.86 (d, $J = 8.6$ Hz, 2H, PMB), 6.14 (dd, $J = 10.0$, 4.4 Hz, 1H, H3), 5.77 (dd, $J = 10.0$, 0.8 Hz, 1H, H2), 5.09 (d, $J = 3.1$ Hz, 1H, H1′), 4.56, 4.51 (AB, $J = 11.6$ Hz, 2H, CH_2Ar), 4.14–4.11 (m, 1H, H5), 4.09 (t, $J = 9.7$ Hz, 1H, H3′), 3.81–3.77 (m, 2H, H6′, H6′), 3.80 (s, 3H, OMe), 3.79 (dd, $J = 10.1$, 3.0 Hz, 1H, H2′), 3.61–3.53 (m, 2H, H4′, H5′), 3.59 (t, $J = 9.3$ Hz, 1H, H4), 3.54–3.52 (m, 1H, H5), 3.53 (s, 3H, OMe), 3.46 (s, 3H, OMe), 3.41 (s, 3H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.3, 131.0, 130.1, 129.7, 129.4, 129.4, 129.3, 128.5, 124.8, 116.6, 113.8, 97.2, 79.2, 78.4, 74.3, 71.5, 70.9, 70.2, 66.5, 65.9, 59.4, 58.9, 55.5, 55.3$; HRMS (MALDI), cald for $C_{22}H_{30}O_9Na$ $[M+Na]^+$: 461.1787, found 461.1789.

General procedure for benzoylation: BzCl (2 equiv) was added to a solution of alcohol (1 equiv), Et_3N (3 equiv), and 4-DMAP (0.5 equiv) in CH_2Cl_2 (0.1M) at 0 °C. The resulting mixture was warmed to 25 °C and stirred for 3 h. The reaction mixture was quenched by the addition of MeOH, diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4), and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography. This procedure is further illustrated by the following example:

Benzoate 94: BzCl (3.5 μL, 0.030 mmol) was added to a solution of alcohol **93** (10 mg, 0.015 mmol), Et_3N (6.4 μL, 0.045 mmol) and 4-DMAP (0.92 mg, 0.008 mmol) in CH_2Cl_2 (0.15 mL) at 0 °C. The resulting mixture was warmed to 25 °C and stirred for 2 h. The reaction mixture was quenched by the addition of MeOH (0.1 mL), diluted with CH_2Cl_2 (60 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 → 100% Et_2O in hexanes) to afford benzoate **94** (10.6 mg, 92%) as a white foam. **94**: $R_f = 0.33$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +139.2$ ($c = 0.24$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2917, 1765, 1721, 1605, 1512, 1451, 1363, 1253, 1165, 1105, 1039, 813, 709\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 8.0$ Hz, 2H, ArH), 7.54 (t, $J = 7.4$ Hz, 1H, ArH), 7.45 (t, $J = 7.5$ Hz, 2H, ArH), 7.42–7.35 (m, 2H, ArH), 7.17 (d, $J = 8.5$ Hz, 2H, PMB), 7.12–7.04 (m, 3H, ArH), 6.77 (d, $J = 8.5$ Hz, 2H, PMB), 5.48 (dd, $J = 7.0$, 4.2 Hz, 1H, H3), 5.18 (d, $J = 4.1$ Hz, 1H, H1), 4.82 (t, $J = 9.5$ Hz, 1H, H4′), 4.80 (d, $J = 2.2$ Hz, 1H, H1′), 4.56, 4.54 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 4.08 (t, $J = 9.5$ Hz, 1H, H3′), 3.99 (dd, $J = 11.8$, 7.5 Hz, 1H, H5), 3.85, 3.84 (AB, $J = 14.6$ Hz, 2H, CH_2Cl), 3.84–3.80 (m, 2H, H2, H4), 3.79–3.70 (m, 5H, OMe, H5, H5′), 3.49 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.28 (dd, $J = 9.5$, 3.6 Hz, 1H, H2′), 1.14 (d, $J = 6.3$ Hz, 3H, H6′); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 166.4, 165.4, 159.2, 133.7, 133.5, 133.1, 130.2, 129.7, 129.3, 129.1, 129.0, 128.9, 128.4, 128.4\ 128.3, 127.5, 126.3, 113.8, 97.2, 80.6, 77.6, 75.8, 73.0, 64.9, 59.4, 55.3, 55.2, 17.3$; HRMS (MALDI): calcd for $C_{36}H_{41}ClO_{11}SeNa$ $[M+Na]^+$: 787.1400, found 787.1368.

Benzoate 100: $R_f = 0.35$ (80% Et_2O in hexanes); $[\alpha]_D^{22} = +96.6$ ($c = 0.96$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2917, 1765, 1743, 1721, 1506, 1451, 1253, 1094, 1039, 918, 818, 714\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 7.1$ Hz, 2H, ArH), 7.57 (t, $J = 7.4$ Hz, 1H, ArH), 7.46 (dd, $J = 6.8$, 1.5 Hz, 2H, ArH), 7.44 (t, $J = 7.8$ Hz, 2H, ArH), 7.23 (d, $J = 8.6$ Hz, 2H, PMB), 7.17–7.10 (m, 3H, ArH), 6.82 (d, $J = 8.6$ Hz, 2H, PMB), 5.47 (t, $J = 3.6$ Hz, 1H, H3), 5.45 (t, $J = 9.6$ Hz, 1H, H3′), 5.12 (d, $J = 6.8$ Hz, 1H, H1), 4.80 (d, $J = 3.4$ Hz, 1H, H1′), 4.61, 4.57 (AB, $J = 11.8$ Hz, 2H, CH_2Ar), 4.11, 4.08 (AB, $J = 14.8$ Hz, 2H, CH_2Cl), 3.86 (dd, $J = 12.4$, 4.7 Hz, 1H, H5), 3.78 (dd, $J = 12.4$, 3.4 Hz, 1H, H5), 3.77 (s, 3H, OMe), 3.69–3.66 (m, 2H, H2, H4), 3.66 (dq, $J = 9.5$, 6.2 Hz, 1H, H5′), 3.54 (t, $J = 9.4$ Hz, 1H, H4′), 3.40 (s, 6H, OMe), 3.29 (dd, $J = 10.0$, 3.5 Hz, 1H, H2′), 1.30 (d, $J = 6.3$ Hz, 3H, H6′); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.8, 165.1, 159.3, 134.4, 133.3, 129.9, 129.6, 129.5, 129.4, 128.9, 128.7, 128.4, 127.6, 113.8, 102.1, 96.7, 80.1, 78.9, 75.5, 72.8, 72.7, 71.7, 66.2, 63.5, 58.6, 55.3, 55.2, 41.1, 30.3, 17.9$; HRMS (MALDI): calcd for $C_{36}H_{41}ClO_{11}SeNa$ $[M+Na]^+$: 787.1400, found 787.1374.

Acknowledgements

We thank Dr. A. K. Ganguly for helpful discussions and a generous gift of everninomicin 13,384-1 and Drs. D. H. Huang, G. Siuzdak, and R. Chadha for NMR spectroscopic, mass spectroscopic and X-ray crystallographic assistance, respectively. This work was financially supported by the National Institutes of Health (USA), the Skaggs Institute for Chemical Biology, postdoctoral fellowships from M.E.C., Spain (R.M.R., Fullbright), the Japan Society for the Promotion of Science (H.S.) and the George Hewitt Foundation (K.C.F.), and grants from Schering–Plough, Pfizer, Glaxo, Merck, Hoffmann–LaRoche, DuPont, Bayer, Boehringer Ingelheim, and Abbott Laboratories.

[1] K. C. Nicolaou, R. M. Rodríguez, H. J. Mitchell, H. Suzuki, K. C. Fylaktakidou, O. Baudoin, F. L. van Delft, *Chem. Eur. J.* **2000**, *6*, ■■, Part 1 in this series of four papers.
[2] K. C. Nicolaou, H. J. Mitchell, K. C. Fylaktakidou, R. M. Rodríguez, H. Suzuki, *Chem. Eur. J.* **2000**, *6*, ■■, Part 2 in this series of four papers.
[3] K. C. Nicolaou, H. J. Mitchell, R. M. Rodríguez, K. C. Fylaktakidou, H. Suzuki, S. R. Conley, *Chem. Eur. J.* **2000**, *6*, ■■, Part 3 in this series of four papers.
[4] a) K. C. Nicolaou, H. J. Mitchell, H. Suzuki, R. M. Rodriguez, O. Baudoin, K. C. Fylaktakidou, *Angew. Chem.* **1999**, *111*, 3523–3528; *Angew. Chem. Int. Ed.* **1999**, *38*, 3334–3339; b) K. C. Nicolaou, R. M. Rodriguez, K. C. Fylaktakidou, H. Suzuki, H. J. Mitchell, *Angew. Chem.* **1999**, *111*, 3529–3534; *Angew. Chem. Int. Ed.* **1999**, *38*, 3340–3345; c) K. C. Nicolaou, H. J. Mitchell, R. M. Rodriguez, K. C. Fylaktakidou, H. Suzuki, *Angew. Chem.* **1999**, *111*, 3535–3540; *Angew. Chem. Int. Ed.* **1999**, *38*, 3345–3350.
[5] K. C. Nicolaou, F. L. van Delft, S. C. Conley, H. J. Mitchell, J. Jin, M. Rodríguez, *J. Am. Chem. Soc.* **1997**, *119*, 9057–9058.
[6] K. C. Nicolaou, H. J. Mitchell, K. C. Fylaktakidou, H. Suzuki, R. M. Rodríguez, *Angew. Chem.* **2000**, *112*, 1131–1135; *Angew. Chem. Int. Ed.* **2000**, *39*, 1089–1093.
[7] K. C. Nicolaou, J. Pastor, S. Barluenga, N. Winssinger, *Chem. Commun.* **1998**, 1947–1948; For the preparation of a related selenium resin see: T. Ruhland, K. Anderson, H. Pedersen, *J. Org. Chem.* **1998**, *63*, 9204–9211.
[8] a) V. K. Srivastava, C. Schuerch, *Tetrahedron Lett.* **1979**, *35*, 3269–3272; b) T. L. Su, R. S. Klein, J. J. Fox, *J. Org. Chem.* **1982**, *47*, 1506–1509; c) G. Hodosi, P. Kovác, *J. Am. Chem. Soc.* **1997**, *119*, 2335–2336; d) For a review of tin-containing intermediates in carbohydrate chemistry, see: T. B. Grindley, *Adv. Carbohydr. Chem. Biochem.* **1998**, *53*, 17–142.
[9] V. A. Olah, J. Harangi, A. Liptak, *Carbohydr. Res.* **1988**, *174*, 113–120.
[10] R. R. Schmidt, J. Michel, *Angew. Chem.* **1980**, *92*, 763–765; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 731–733.
[11] a) T. Mukaiyama, Y. Murai, S. Shoda, *Chem. Lett.* **1981**, 431–433; b) W. Rosenbrook, Jr., D. A. Riley, P. A. Lartey, *Tetrahedron Lett.* **1985**, *26*, 3–4, c) G. H. Posner, S. R. Haines, *Tetrahedron Lett.* **1985**, *26*, 5–8.
[12] C. A. Podlasek, J. Wu, W. A. Stripe, P. B. Bondo, A. S. Serianni, *J. Am. Chem. Soc.* **1995**, *117*, 8635–8644.
[13] K. C. Nicolaou, T. Ladduwahetty, J. L. Randall, A. Chucholowski, *J. Am. Chem. Soc.* **1986**, *108*, 2466–2467.
[14] P. Bhate, D. Horton, W. Priebe, *Carbohydr. Res.* **1985**, *144*, 325–331.
[15] S. Mehta, B. M. Pinto, *J. Org. Chem.* **1993**, *58*, 3269–3276.
[16] G. Jaurand, J.-M. Beau, P. Sinaÿ, *J. Chem. Soc. Chem. Commun.* **1982**, 701–703; J.-M. Beau, G. Jaurand, J. Esnault, P. Sinaÿ, *Tetrahedron Lett.* **1987**, *28*, 1105–1108.
[17] J. C. Martin, R. J. Arhart, *J. Am. Chem. Soc.* **1971**, *93*, 4327–4329.
[18] a) P. Deslongschamps, R. Chênevert, R. J. Taillefer, C. Moreau, J. K. Saunders, *Can. J. Chem.* **1975**, *53*, 1601–1615; b) P. Deslongschamps, *Stereoelectronic Effects in Organic Chemistry*, Pergamon Press, New York, **1983**.
[19] V. Srivastava, C. Schuerch, *J. Org. Chem.* **1981**, *46*, 1121–1126.
[20] H. Paulsen, *Carbohydr. Res.* **1991**, *216*, 289–313.

  0947-6539/00/0617-3184 $ 17.50+.50/0

[21] Y. O. Ito, *Angew. Chem.* **1994**, *106*, 1843–1845; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1765–1767.
[22] A. B. Charette, N. Turcotte, B. Cote, *J. Carbohydr. Chem.* **1994**, *13*, 421–432.
[23] D. P. Larson, C. H. Heathcock, *J. Org. Chem.* **1996**, *61*, 5208–5209.
[24] R. Miethchem, G. Kolp, D. Peters, J. Holz, *Z. Chem.* **1990**, *30*, 56–57.
[25] Q. Chen, K. Kong, *Carbohydr. Res.* **1993**, *240*, 107–117.
[26] T. Miyake, T. Tsuchiya, S, Umezawa, S. Saito, H. Umezawa, *Bull. Chem. Soc. Jap.* **1986**, *59*, 1387–1397.

Received: February 11, 2000 [F2297]

  0947-6539/00/0617-3185 $ 17.50+.50/0