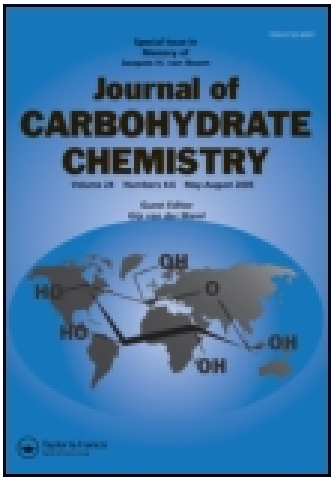

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Approach Towards Highly Oxygenated *cis*-Decalins from Sugar Allyltins

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A convenient method for the preparation of sugar allyltin derivatives and their application in stereocontrolled synthesis of highly oxygenated, optically pure carbobicyclic derivatives is presented. Special attention is focused on stereoselective transformations of the precursors obtained directly from sugar allyltins.

Keywords Sugars, Allyltin derivatives, Carbocyclic derivatives, Rearrangement, Mechanism

INTRODUCTION: FROM HIGHER CARBON SUGARS TO CARBOBICYCLIC SYNTHONS

Higher carbon sugars apart from *C*-disaccharides are attractive targets, and their synthesis has gained considerable attention in the past two decades. A number of methods leading to such complicated molecules have been developed.[1,2] In the past several years, we proposed a general methodology for the preparation of higher carbon sugars by coupling of two sugar subunits. The precursor **5** is readily obtained from sugar phosphoranes **1**, phosphonates **2**, or vinyltin derivatives of monosaccharides **4** (Fig. 1).[2] Higher carbon sugars can be, eventually, obtained also from homoallylic alcohols **6**, which can be prepared directly from sugar allyltin derivatives **3**.[3–5]

However, the latter process is not trivial. In the typical reaction of the D-*gluco*-configurated allyltin **7** with the aldehyde **8**, the expected homoallylic alcohol **9** was formed as a *minor* product; the main turned out to be dienoaldehyde **10**, resulting from a controlled fragmentation of **7** (Sch. 1).[3]

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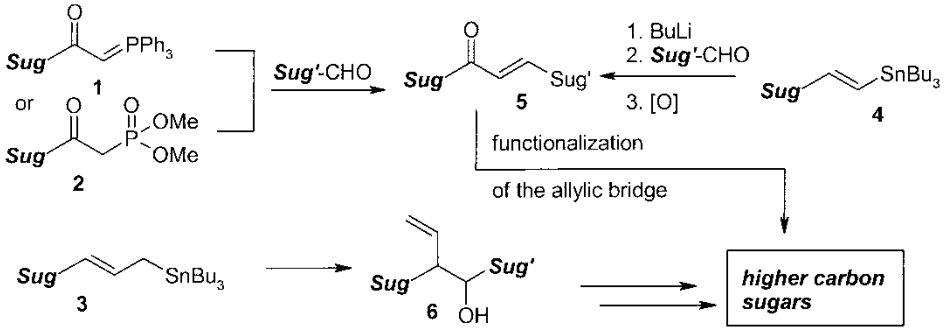
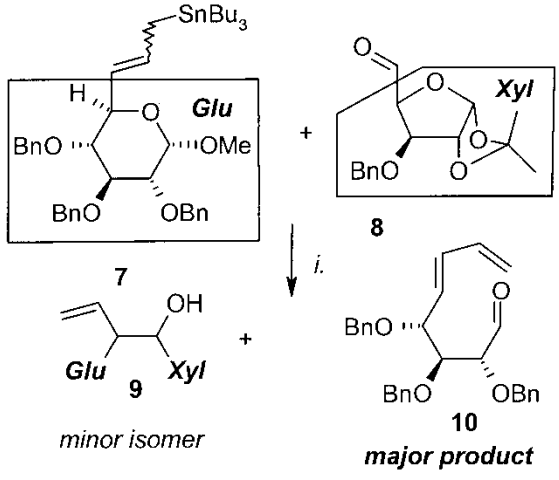


Figure 1: Methods for the preparation of higher carbon sugars.

This result opened a new, very interesting possibility for stereocontrolled synthesis of highly functionalized enantiomerically pure carbocyclic compounds (see "Synthesis of carbobicylic highly oxygenated derivatives from sugar allytins").

SYNTHESIS OF SUGAR ALLYLTIN DERIVATIVES

Organotin derivatives are, nowadays, useful reagents in modern organic chemistry.[6–9] Although known for more than 150 years,[9] they became useful synthons only since mid-1960s when Kuivila et al.[10] discovered that trialkyltin hydrides react with alkyl halides according to a radical-chain mechanism involving short-lived trialkyltin radicals. This led to elaboration of one of the



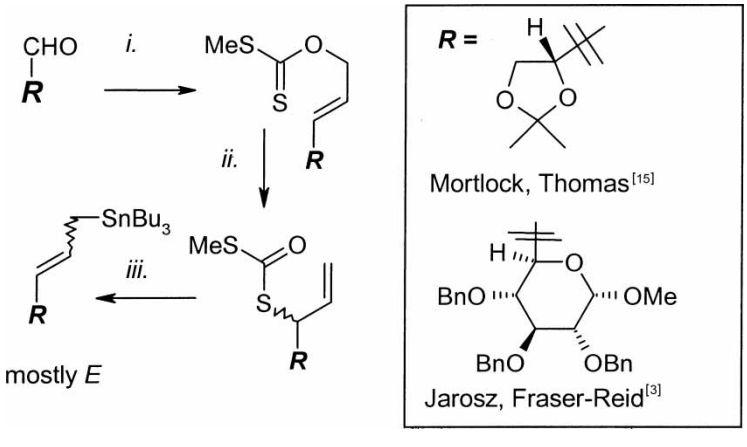
Scheme 1: *i.* $TiCl_4$, CH_2Cl_2, − 78°C.

most convenient methods for deoxygenation of secondary alcohols—the Barton-McCombie reaction.[11] Special attention is directed to the preparation and application of allyltin derivatives, useful precursors of homoallylic alcohols.[12] Very interesting are sugar allyltins, which may be prepared most conveniently by a C(3) + C(0) strategy, that is, reaction of properly activated allyl derivative (a C3 fragment) with tin electrophile, nucleophile, or radical (a C0 fragment).[13]

The 'Xanthate' Method of the Preparation of Sugar Allyltins

One of the most convenient methods consists of conversion of allylic alcohols into xanthates followed by sigmatropic thermal [3,3] rearrangement into dithiocarbonates and reaction with Bu_3SnH, leading finally to allyltins usually as a mixture of geometrical isomers.[14] This method is most suitable for the preparation of sugar allyltin derivatives. First such derivative was prepared by Mortlock and Thomas from D-glyceraldehyde.[15]

Soon after this we reported on the synthesis of the more complicated derivative **7** using the same methodology[3] (Sch. 2). By this method a number of sugar organometallics, derivatives of pyranoses and furanoses, were prepared in good yields.[16,17] The important feature of this methodology was formation of a mixture of sugar allyltins with the *E*-isomer highly predominating regardless of the geometry across the double bond in starting allylic alcohol. As we proved, a mixture of the same composition of the *E*/*Z* isomers was obtained either from the pure *E* or pure *Z* or a 1:1 mixture of both isomers.[18]



Scheme 2: *i.* 1. $Ph_3P{=}CHCO_2Me$; 2. DIBAL-H; 3. $NaH/CS_2/MeI$; *ii.* 80°C (ref. 15) or 110°C (ref. 3); *iii.* Bu_3SnH.

Tin Nucleophiles in the Preparation of Sugar Allyltins

Although the 'xanthate' method is highly reproducible and provides sugar allyltins in good yields, it has one main limitation. The allyltin derivatives obtained by this method are always mixtures of geometrical isomers with the *E* isomers strongly predominating; availability of the *Z*-isomers is very limited by this method. However, for many synthetic purposes (e.g., for reaction with aldehydes under high pressure or at high temperature directed to homoallylic alcohols[12]) such pure isomers are needed. Pure geometrical isomers of sugar allyltins may be, eventually, prepared by reaction of the properly activated allylic derivatives with tin nucleophiles, particularly with soft tributyltin cuprate ('Bu_3SnCu').[19]

It was found that reaction of sterically hindered D-*galacto*-configurated primary allylic bromides with Bu_3SnCu indeed proceeded with the retention of the configuration across the double bond.[18,20] However, less sterically hindered sugar electrophiles (derived from D-glucose, or D-mannose) reacted preferentially in an S_N2' mode leading to secondary sugar allyltins in reasonable yields[21] (Fig. 2). We observed that only one secondary isomer was formed regardless of the configuration across the double bond in starting allylic derivative **11**.[21]

CONTROLLED FRAGMENTATION OF SUGAR ALLYLTINS

Upon treatment with a Lewis acid (preferably $ZnCl_2$), both the primary[16] and the secondary[21] sugar allyltin derivatives undergo facile fragmentation to the dienoaldehydes **12** with the *E*-geometry across the internal double bond. Thermal stability of both isomers, however, is different. Primary sugar allyltins are stable up to 214°C (boiling trichlorobenzene), while the secondary isomers decompose already at 140°C (boiling benzene). From the *S*-isomers, the main or exclusive products of the reaction of Bu_3SnCu with allylic sugar electrophiles, the *Z*-dienoaldehydes **13** are formed (Fig. 3).[21]

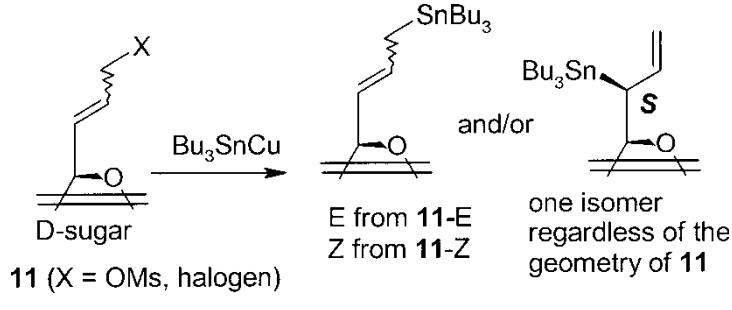


Figure 2: Regioselectivity of formation of sugar allyltins.

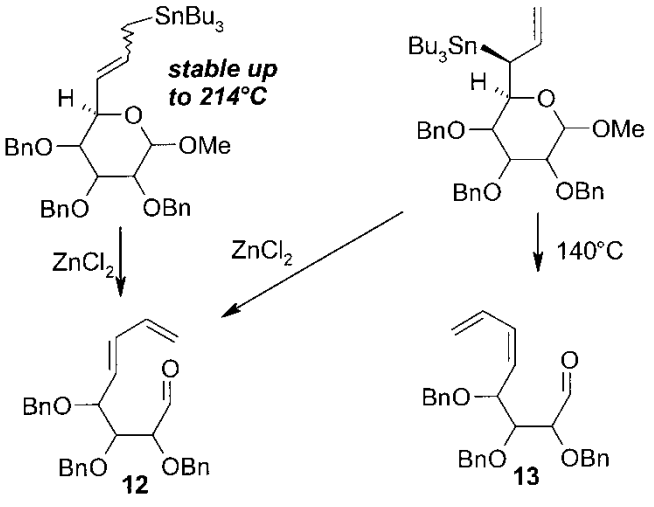


Figure 3: Fragmentation of sugar allyltins.

This fact opened a convenient route to carbobicyclic derivatives with the desired geometry of the ring junction.

SYNTHESIS OF CARBOBICYLIC HIGHLY OXYGENATED DERIVATIVES FROM SUGAR ALLYLTINS

The idea of the stereoselective preparation of enantiomerically pure bicyclo[4.3.0]nonene (**14**) derivative is shown in Figure 4. Reaction of the *E*-diene **12** with the simplest stabilized Wittig reagent afforded the corresponding triene, cyclization of which under high pressure (10 kbar) led to the *trans* derivative **14-***trans*. Alternatively, the same sequence performed for the *Z*-diene **13** provided the *cis* bicycle **14-***cis*. Such stereochemistry resulted from the *endo*-transition state of this intramolecular Diels-Alder reaction (IMDA).[13]

Compounds **14** prepared above from sugar allyltins (via dienoaldehydes **12** and **13**) can, eventually, serve as precursors in the stereoselective synthesis of highly oxygenated, optically pure derivatives of perhydroindane **15**, which might possess interesting biological properties.[22]

Also, more highly oxygenated decalins might be prepared from the same dienoaldehydes as shown in Scheme 3.

Conversion of the aldehyde **10** into the methyl ester **16** followed by reaction with dimethyl methylphosphonate anion afforded the phosphonate **17** in good yield. Further reaction with 2,3-isopropylidene-D-glyceraldehyde (**18**) under mild phase transfer conditions furnished the triene **19**, which cyclized spontaneously to the bicyclic synthon **20**.[23] The *cis*-configuration at the ring junction was secured by the *endo*-transition state of this IMDA reaction.

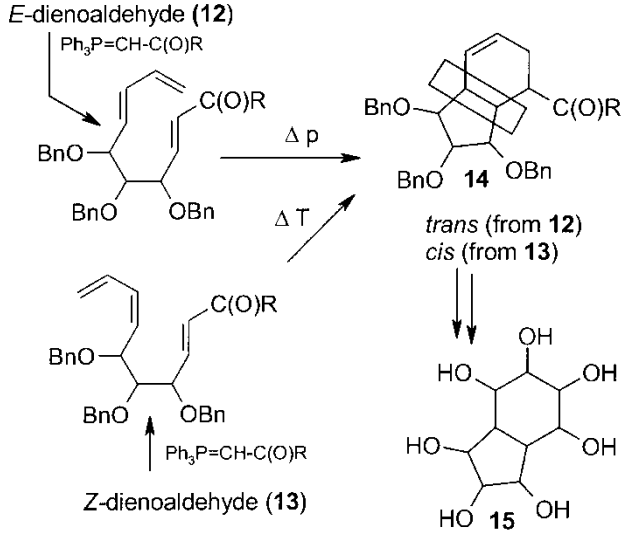
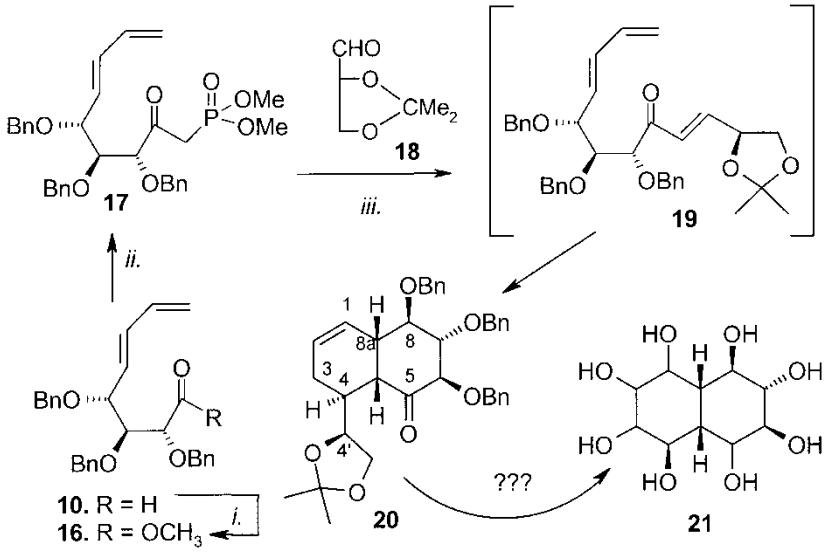


Figure 4: Preparation of highly oxygenated bicyclo(4.3.0)nonanes from dienoaldehydes derived from sugar allyltins.

Functionalization of the double bond in **20** was performed using standard methodology: *cis*- or *trans*-dihydroxylation; the results are shown in Figure 5.

First, reduction of the carbonyl group at the C-5 position was performed highly stereoselectively with sodium borohydride, and the resulting alcohol



Scheme 3: *i.* Jones' oxidation, then CH_2N_2; *ii.* MeP(O)(OMe)$_2$, BuLi THF, 15 min, 86%, *iii.* K_2CO_3, toluene, rt, 18-crown-6, 75%.

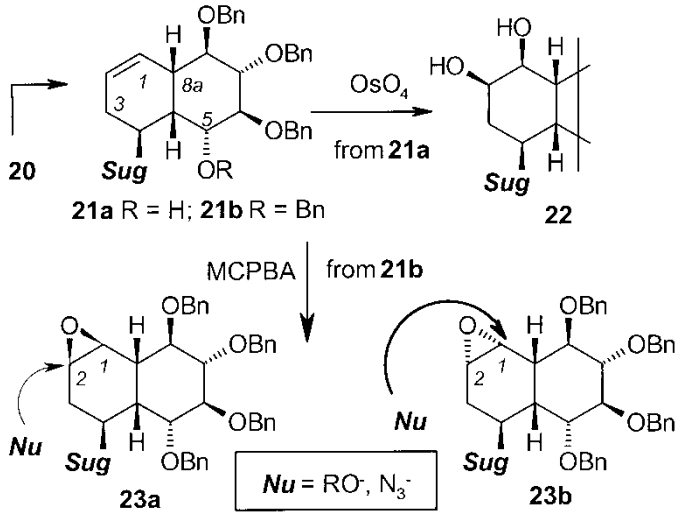
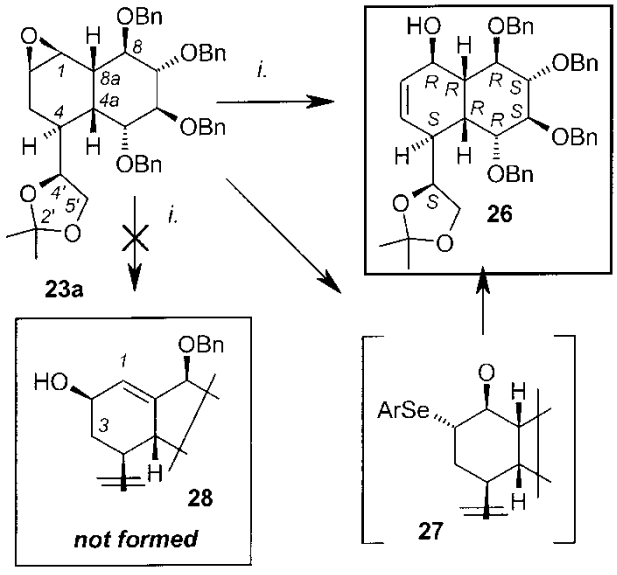


Figure 5: Partial functionalization of decalin precursor 20.

21a was osmylated with very high selectivity to compound **22** (Fig. 5).[24] Epoxidation of the double bond in **21b**, the benzyl protected form of alcohol **21a**, was done conveniently with MCPBA, although selectivity of this process was low; oxiranes **23a** and **23b** were formed in comparable amounts.[24] Opening, however, of the three-membered ring with nucleophiles (AcO^-, or N_3^-) was highly regioselective and occurred at the C2 position in **23a** and at the C1 position in **23b**.[24]

To finish the synthesis of fully oxygenated decalin (e.g., **21**) two important problems had to be solved: oxidation of the allylic position (in **20**) and the cleavage of the C4–C4′ bond with insertion of the heteroatom. Functionalization of the C8 position can be done eventually on two routes: direct allylic oxidation[25] or isomerization of the C1-C2 epoxide under basic conditions.[26] However, as we observed, both these convenient methods could not be applied for functionalization of the allylic position in our bicyclic systems.[27] We decided, therefore, to take advantage of this highly regioselective opening of the oxirane ring and use the selenium chemistry[28] for functionalization of the C3 position. For the model study, epoxide **23a**[24] was selected, which should be opened by a nucleophile at the desired C2 position (Sch. 4).

The reaction proceeded as expected. Indeed, the opening of the three-membered ring occurred at the C2 position to give selenium intermediate **27**, which decomposed under oxidative conditions to the allylic alcohol **26**. No formation of the alternative isomer **28** resulting from the opening of the oxirane ring at the C1 position was noted. Its eventual presence was excluded on the basis of the ^{13}C NMR data, in which no signal of the aliphatic CH_2 group (at the C3 position of **28**) was seen.



Scheme 4: *i.* 1.$NaBH_4$, EtOH, $(PhSe)_2$, 5 min, then **23a** reflux 2 h; *ii.* THF, H_2O_2, 0°C to rt, overnight; 93% overall.

Compound **26** is a powerful synthon for the stereoselective preparation of different analogs of highly oxygenated decalins. Inversion of the configuration at the C1 position can be performed with either oxygen or other nucleophile. Functionalization of the C2═C3 double bond can be achieved either by *cis*- or *trans*-dihydroxylation, aminohydroxylation, etc. Also, various heteroatoms such as N, P, or S can be placed at either position from C1 to C3 of the skeleton of **26**. This will be a subject of further studies.

CONCLUSION

The efficient method for the preparation of highly oxygenated, optically pure bicyclo[4.3.0]nonenes (e.g., **14**) and bicyclo[4.4.0]decenes (e.g., **20**) from sugar allyltin derivatives were reviewed. The allylic fragment in **20** was conveniently functionalized by epoxidation of the double bond followed by highly regioselective opening of the oxirane ring and subsequent elimination of selenoxide. The resulting allylic alcohol **26** will be extremely useful in the preparation of various stereoisomeric, highly oxygenated decalins.

EXPERIMENTAL

General: NMR spectra were recorded with a Bruker AM 500 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). All resonances were assigned by COSY (^1H-^1H), HETCOR, and DEPT correlations. The ^1H and ^{13}C aromatic

resonances occurring at the typical δ values were omitted for simplicity. Mass spectra were recorded with an ESI/MS Mariner (PerSeptive Biosystem) mass spectrometer. Optical rotations were measured with a Jasco P-1020 polarimeter at rt. IR spectra (film) were recorded with a Perkin Elmer Spectrum 2000 apparatus. THF was distilled from potassium prior to use. Column chromatography was performed on silica gel (Merck, 70-230). For chromatography purposes a fraction of mineral oil with a boiling point in the range of 70 to 90°C was used as mixture of hexanes. Acetylation reaction was performed under standard conditions: acetic anhydride, triethylamine, and DMAP as a catalyst in dry methylene chloride.

Synthesis of 1(R),4(S),4a(R),5(R),6(S),7(S),8(R),8a(R),4′(S)-4-(2′, 2′-Dimethyl-[1′,3′]dioxolan-4′-yl)-5,6,7,8-tetrabenzyloxy-1,4,4a,5,6,7,8,8a-octa-hydro-naphthalen-1-ol (26): To a solution of diphenyl diselenide (32 mg, 0.1 mmol) in anhydrous ethanol (5 mL), sodium borohydride (15 mg, 0.4 mmol) was added in portions under an argon atmosphere until disappearance of the yellow color of the solution. After 5 min, a solution of epoxide **23a**[24] (101.2 mg, 0.15 mmol) in a mixture of anhydrous ethanol and THF (6 mL; 1:1 v/v) was added, and the mixture was boiled under reflux for 2 h. It was then diluted with THF (10 mL) and cooled to 0°C on an ice bath. Hydrogen peroxide (0.5 mL of a 30% solution in water, 4.4 mmol) was added dropwise, and the mixture was allowed to warm to rt and then kept at this temperature overnight. A saturated aqueous solution of sodium carbonate in water (100 mL) was added, and the aqueous phase extracted with diethyl ether (4 × 20 mL) and ethyl acetate (15 mL). The combined organic layers were washed with concentrated aqueous sodium carbonate in water (50 mL), dried over anhyd Na_2SO_4, and concentrated, and the crude product was isolated by column chromatography on silica gel (Merck, 70-230 mesh) with 4:1 to 3:1 hexane/ethyl acetate to give **26** (94.7 mg, 0.14 mmol, 93%); ESI HRMS: Calcd [$C_{43}H_{48}O_7Na$]: 669.3292. Found: 669.3260. This compound was characterized as its acetate **26-Ac**. Data for the acetate: $[\alpha]_D^{24} = -8.7$ ($c = 0.5$, $CHCl_3$); IR (CH_2Cl_2, cm^{-1}) 3031, 2916, 1737, 1454, 1368, 1239, 1070, 799, 736, 698. ^{1}H NMR δ 6.08 (dd, $J_{3,2} = 10.1$, $J_{3,4} = 2.7$ Hz, 1H, H-3), 5.88–5.84 (m, 1H, H-2), 5.40 (dd, $J = 5.5$, 1.9 Hz, 1H, H-1), 5.06–5.00 (m, 1H, H-1′), 4.96–4.90 (m, 2H, CH_2OPh), 4.83–4.77 (m, 4H, CH_2OPh), 4.62 (d, $J = 11.3$ Hz, 1H, part of AB), 4.50 (d, $J = 10.9$ Hz, 1H, part of AB), 3.85–3.78 (m, 2H, H-6, H-5′), 3.59–3.53 (m, 3H, H-1, H-5′, H-7), 3.36 (dd, $J = 11.4$, 9.2, 1H, H-8), 2.77–2.72 (m, 1H, H-4), 2.06–2.01 (m, 1H, H-4a), 2.01 (s, 3H, OAc), 1.88–1.82 (m, 1H, H-8a), 1.41 and 1.21 (2 × s, 6H, CMe_2). ^{13}C NMR δ 169.9 (C=O), 138.6, 138.5, 138.1, and 137.8 (4xC_{IV} in Bn), 131.4 (C-4), 124.7 (C-2), 108.6 (*C*Me$_2$), 86.3 (C-7 or C-5), 83.6 (C-5 or C-7), 82.6 (C-6), 78.1 (C-8), 76.0, 75.8, 75.2 and 73.9 (4xO*C*CH_2Ph), 75.6 (C-4′), 66.3 (C-1), 64.7 (C-5′), 41.4 (C-8a), 36.9 (C-4), 32.6 (C-4a), 26.0 and 24.5 (C*Me*$_2$), 21.1 (*Me*CO).

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