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Note

Anchimeric assistance by the anomeric phenylthio group in the nucleophilic substitution of a 6-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside

Muriel Compain-Batissou, Lamya Mesrari, Daniel Anker, Alain Doutheau *

Laboratoire de Chimie Organique, EA 1844, Institut National des Sciences Appliquées, 20 avenue Albert Einstein, F-69621 Villeurbanne, France

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Abstract

Nucleophilic displacement by the cyanide anion of the 6-*O*-triflyl group in phenyl 6-*O*-triflyl-2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-1-thio-β-D-galactopyranoside takes place via an intermediate 1,6-sulfonium salt resulting from the anchimeric assistance of the C-1 phenylthio group.

Keywords: D-Galactose; Thioglycoside; Anchimeric assistance; C-6 substitution; Cyanide

1. Introduction

Pectin, a constituent of plant cell walls, is mainly composed of partially methyl esterified oligomers of D-galacturonic acid units joined together by α-(1→4) glycosidic linkages. These polysaccharides can be degraded by enzymes from phytopathogenic fungi or bacteria that cause damage to plants. Among them are lyases that catalyse a β-elimination reaction involving the glycosidic linkage and the C-5 proton of D-galacturonic acid residues. With the aim of preparing potential inhibitors for these enzymes, we recently became interested in the synthesis of the D-*galacto*-heptopyranuronic acid derivatives **1a** and **1b** and planned to obtain these compounds from the corresponding cyano derivatives **2** that could result from the displacement by the cyanide anion of the 6-*O*-triflyl group of the D-*galacto* derivatives **3**.

Starting alcohols **4a** and **4b** were prepared respectively from phenyl 2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside **5a** obtained from the corresponding 4,6-*O*-benzylidene derivative [1], and benzyl 2,3-di-*O*-benzyl-β-D-galactopyranoside **5b** [2], by a three-step sequence involving selective tritylation at O-6, *p*-methoxybenzylation at O-4 and detritylation. When **4a** was reacted with triflic anhydride and then tetrabutylammonium cyanide [3], the expected phenyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-*p*-methoxybenzyl-1-thio-β-D-*galacto*-heptopyranosiduronononitrile **2a** was obtained in 66% yield. In contrast, when the benzyl glycoside **4b** was treated under the same conditions, the expected benzyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-*p*-methoxybenzyl-β-D-*galacto*-heptopyran-

* Corresponding author. Tel.: +33-4-72438221; fax: +33-4-72438896.

E-mail address: doutheau@insa.insa-lyon.fr (A. Doutheau)

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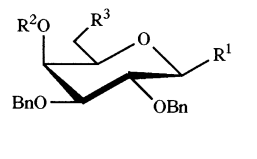
osidurononitrile **2b** was obtained in only 16% yield. The major product was benzyl 3,6-anhydro-2-*O*-benzyl-4-*O*-*p*-methoxybenzyl-β-D-galactopyranoside **6** obtained in 68% yield.

From a literature survey, it appeared that nucleophilic substitution reactions at the 6-position of galactopyranoside derivatives carrying a 3-benzyloxy or a 3-methoxy group often led to the exclusive or partial formation of 3,6-anhydro-derivatives [4–6]. These compounds are assumed to result from the competitive internal nucleophilic displacement of the sulfonyl group by the C-3 oxygen atom, after a conformational change from $^4C_1$ to $^1C_4$ chair conformation, leading to an intermediate cyclic oxonium ion which subsequently suffers nucleophilic attack at the benzyl or methyl group.

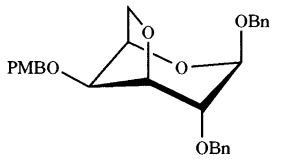
Considering these literature data, an explanation had to be found for the successful formation of the C-6 substituted compound **2a** from **3a** instead of an internal displacement involving the 3-*O*-benzyloxy group to give a 3,6-anhydro analog of **6**. Two hypotheses could be proposed: (i) due to the presence of the thiophenyl group, the transition state leading to the anhydro compound is energetically disfavoured, or (ii) the nitrile **2a** is formed via the sulfonium cation **7** resulting from the internal nucleophilic displacement of the triflyl group by the sulfur atom. Since nucleophilic cleavage of the S–phenyl bond is most unlikely, sulfonium cation **7** would subsequently be further attacked by a cyanide anion at the C-6 position to give **2a**. It seemed to us that the second hypothesis was more likely, since the formation of intermediate cyclic sulfonium ions during nucleophilic displacement reactions performed on carbohydrates containing an alkylthio group has often been put forward. Though these species were not isolated, their intermediate formation was necessary to explain the migration of a thio group from C-1 to C-6 and/or the formation of 1,6 thioanhydrosugars [7]. Furthermore, the reaction of the sulfonium salt **8** with various nucleophiles had been investigated by Lundt and Skelbaek-Pedersen [8]. Depending of the nature of the nucleophilic reagents, different compounds were formed. With cyanide anion a mixture of the 1,6-thioanhydro compound, the substitution product at C-6 and an orthoacid cyanide involving the O-2 acyl group participation, was obtained. With sodium methoxide, only the C-1 position was involved. These authors rationalized their results on the basis of the hard and soft acid and bases (HSAB) principle. In our case, the absence of both an alkyl substituent on the sulfur atom and of a participating group at C-2 ruled out the formation of the anhydro and the orthoacid derivatives. Consequently, the exclusive attack at C-6 was consistent with the results of Lundt and Skelbaek-Pedersen.

The hypothesis that neighbouring-group participation by the 1-phenylthio group of **3a** accounted for the formation of **2a** was confirmed by the following result. When the alcohol **4a** was reacted with triflic anhydride, followed by sodium methoxide, methyl 2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-deoxy-6-thiophenyl-α-D-galactopyranoside (**9α**) was formed in 68% yield beside a small amount (10%) of **9β**. Thus, in full agreement with Lundt and Skelbaek-Pedersen's observation [8], the hard nucleophilic methoxide anion attacked the intermediate sulfonium compound **7** at C-1, mainly in an S_N2-type substitution reaction, to give **9α** as the major anomer.

In conclusion, we report here that when a phenyl 1-thio-6-*O*-triflyl-β-D-galactopyranoside bearing a benzyloxy group at C-3 was reacted with cyanide anion, it led to the C-6 substituted compound. The reaction proceeds via the formation of an intermediate 1,6-sulfonium salt resulting from the anchimeric assistance of the anomeric phenylthio group. This result contrasts with the behaviour of its *O*-glycoside analogues which lead predominantly, or exclusively, to 3,6-anhydro compounds when reacted with nucleophiles. To our knowledge, such an observation has not yet been reported in the literature. Since the anomeric thio group can be further easily substituted by water or alcohols, it turns out that thioglycosides could be valuable intermediates for the preparation of some C-6 functionalized *O*-glycoside derivatives of hexoses otherwise susceptible to resulting in 3,6-anhydro compounds, such as in the galactose, glucose, mannose or talose series. However, the functionalization at C-6 may be restricted to soft nucleophilic species.



	R^1	R^2	R^3
1a	SPh	PMB	CO_2Bn
1b	OBn	PMB	CO_2Bn
2a	SPh	PMB	CN
2b	OBn	PMB	CN
3a	SPh	PMB	OSO_2CF_3
3b	OBn	PMB	OSO_2CF_3
4a	SPh	PMB	OH
4b	OBn	PMB	OH
5a	SPh	H	OH
5b	OBn	H	OH



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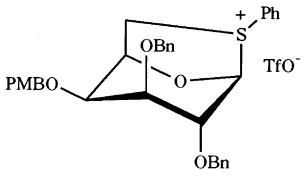

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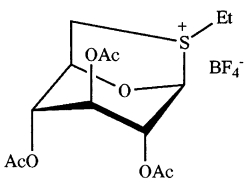

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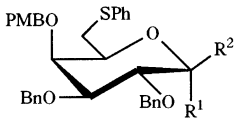

	R^1	R^2
9α	OMe	H
9β	H	OMe

2. Experimental

General methods.—Solvents were distilled and dried before use. Reaction mixtures were magnetically stirred. The reactions were monitored by TLC on silica gel (60 F_{254}, E. Merck) and detection was carried out by UV examination and then charring with a 5% phosphomolybdic acid solution in ethanol containing 10% H_2SO_4. Column chromatography was performed on silica gel (Kieselgel 60, 0.04–0.06 mm, E. Merck). The following solvent-systems (v/v) were used: (A_1) 3:1, (A_2) 4:1, (A_3) 5:1 pentane–acetone; (*B*) 5:1 pentane–EtOAc; (*C*) CH_2Cl_2; (*D*) 5:1 CH_2Cl_2–Et_2O. Organic solutions were dried using $MgSO_4$. Melting points were determined with a Kofler hot-stage melting-point apparatus. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. ^1H NMR and ^{13}C NMR spectra were recorded, in $CDCl_3$, using a Bruker AM 200 spectrometer. Chemical shifts are given in ppm downfield from internal Me_4Si. Splitting patterns abbreviations are: s, singlet; d, doublet; t, triplet; m, multiplet; p, pseudo. Elemental analyses were performed by the 'Service Central de Microanalyses du CNRS' Solaize (France).

*Phenyl 2,3-di-*O*-benzyl-1-thio-β-*D*-galactopyranoside* (**5a**).—To a solution of phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside [1] (7 g, 13.0 mmol) in acetone (80 mL) was added water (18 mL) and HCl 1 N (5.2 mL). The reaction mixture was refluxed for 4 h and $BaCO_3$ (2 g, 10.4 mmol) and water (40 mL) were added. After stirring for 10 min, acetone was evaporated under reduced pressure and the aq phase extracted with CH_2Cl_2 (3 × 40 mL). Organic layers were pooled and dried and, after solvent evaporation under reduced pressure, the solid residue was washed with pentane (2 × 20 mL) and then dissolved in hot EtOH (50 mL). Compound **5a** (5.58 g, 95%) was precipited by addition of water (100 mL) filtered and dried (P_2O_5); mp (from cyclohexane) 120–122 °C; $[\alpha]_D^{25}$ −4.7° (*c* 1.0, $CHCl_3$); ^1H NMR: δ 7.57–7.52 (m, 2 H, H aromatic), 7.41–7.20 (m, 13 H, H aromatic), 4.82, 4.73 (2d, 2 H, *J* 11.2 Hz, C*H*$_2$Ph), 4.70 (brs, 2 H, C*H*$_2$Ph), 4.64 (d, 1 H, $J_{1,2}$ 9.6 Hz, H-1), 4.05 (pt, 1 H, *J* 3 Hz, H-4), 3.95 (ddd, 1 H, $J_{6,OH}$ 4.4, $J_{6,6'}$ 11.7, $J_{6,5}$ 6.7 Hz, H-6), 3.8 (ddd, 1 H, $J_{6'OH}$ 8.3, $J_{6',5}$ 4.5 Hz, H-6′), 3.75 (dd, 1 H, $J_{2,1}$ 9.6, $J_{2,3}$ 9.0 Hz, H-2), 3.56 (dd, 1 H, $J_{3,2}$ 9.0, $J_{3,4}$ 3.2 Hz, H-3), 3.46 (brpt, 1 H, H-5), 2.74 (brs, 1 H, CHO*H*), 2.4 (dd, 1 H, CH_2O*H*). Anal. Calcd for $C_{26}H_{28}O_5S$: C, 69.03; H, 6.24. Found: C, 69.13; H, 6.11.

*Phenyl 2,3,-di-*O*-benzyl-4-*O*-p-methoxybenzyl-1-thio-β-*D*-galactopyranoside* (**4a**).—To a solution of **5a** (1.5 g, 3.3 mmol) in pyridine (24 mL), were added trityl chloride (1.57 g, 5.65 mmol) and a catalytic amount of 4-dimethylaminopyridine. The reaction mixture was stirred at room temperature for 3 days (TLC, solvent A_1). The reaction mixture was concentrated under reduced pressure and Et_2O (200 mL) was added to the residue. The solution was washed with a saturated aq $NaHCO_3$ solution (2 × 30 mL), dried and concentrated under reduced pressure to give a solid residue which was dried (P_2O_5) and then dissolved in 10 mL of dry DMF. The resulting solution was added to NaH (0.27 g of a 60% suspension in oil, ~6.6 mmol, and washed three times with pentane) in 10 mL of dry DMF. A catalytic amount of imidazole was added to the reaction mixture stirred at 20 °C. After the

evolution of H_2 ceased, *p*-methoxybenzyl bromide (0.614 mL, 4.53 mmol) and a catalytic amount of Bu_4NI were added. After 4 h, the starting material had disappeared (TLC, solvent *B*). The solvent was evaporated under reduced pressure and Et_2O (100 mL) was added to the residue. The excess of NaH was destroyed by careful addition of water (5 mL). The mixture was washed with aq 3 N HCl (2×20 mL) dried, concentrated and the residue was dissolved in 1:1 MeOH–$CHCl_3$ (40 mL). To this solution was added Amberlyst 15 (H^+, 1.5 g) and the reaction mixture was gently stirred (rotatory evaporator) and heated at 60 °C. After 1 h, the reaction was complete (TLC, solvent A_1). The resin was removed by filtration and washed with MeOH (3×30 mL). The filtrate was concentrated under reduced pressure in the presence of a small amount of triethylamine at 40 °C giving a residue that was dissolved in Et_2O (100 mL). To this solution was added water (50 mL) and the organic phase was separated, washed with water (3×10 mL) dried and concentrated under reduced pressure. Column chromatography of the crude product (solvent A_1) gave **4a** (1.62 g, 85% from **5a**) as a colourless solid; mp (cyclohexane) 109–111 °C; $[\alpha]_D^{25}$ −11.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 7.60–7.21 (m, 17 H, H aromatic), 6.94–6.88 (m, 2 H, H aromatic), 4.79 (s, 2 H, CH_2Ph), 4.93–4.61 (m, 4 H, 2 CH_2Ph), 4.68 (d, 1 H, $J_{1,2}$ 9.6 Hz, H-1), 3.98 (pt, 1 H, H-2), 3.87 (brd, 1 H, $J_{4,3}$ 2.8 Hz, H-4), 3.84 (s, 3 H, OCH_3), 3.85–3.74 (m, 1 H, H-6), 3.62 (dd, 1 H, $J_{3,2}$ 9.2 Hz, H-3), 3.52–3.39 (m, 2 H, H-6′, H-5). Anal. Calcd for $C_{34}H_{36}O_6S$: C, 71.30; H, 6.34. Found: C, 71.54; H, 6.31.

Benzyl 2,3-di-O-*benzyl-4*-O-p-*methoxybenzyl-β*-D-*galactopyranoside* (**4b**).—This compound was prepared from **5b** [2] (2 g, 4.4 mmol) as described for **4a**. After column chromatography (solvent A_3), **4b** (1.23 g, 49%) was obtained as a colourless solid; mp 109–110 °C (from cyclohexane); $[\alpha]_D^{25} = -48.8°$ (*c* 0.93, $CHCl_3$); ^{1}H NMR: δ 7.37–7.23 (m, 17 H, H aromatic), 6.85 (brd, 2 H, *J* 8.7 Hz, H aromatic), 4.98–4.58 (4d, 8 H, 4 CH_2Ph), 4.47 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.90 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.79 (s, 3 H, OCH_3), 3.76 (brd, 1 H, $J_{4,3}$ 2.4 Hz, H-4), 3.70 (m, 1 H, H-6), 3.52 (dd, 1 H, H-3), 3.45 (m, 1 H, H-6′), 3.36 (m, 1 H, H-5). Anal. Calcd for $C_{35}H_{38}O_7$: C, 73.66; H, 6.71. Found: C, 73.43; H, 6.50.

Phenyl 2,3-di-O-*benzyl-6-deoxy-4*-O-p-*methoxybenzyl-1-thio-β*-D-galacto-*heptopyranosidurononitrile* (**2a**).—To a stirred solution of **4a** (1.0 g, 1.75 mmol) in CH_2Cl_2 (25 mL) at −78 °C, under a dry nitrogen atmosphere, were added 2,6-di-*tert*-butylpyridine (1 mL, 3.68 mmol) and, dropwise (syringe), triflic anhydride (0.50 mL, 3 mmol). The reaction mixture was warmed to −25 °C for 30 min allowing the reaction to be complete (TLC, solvent A_1). After cooling to −78 °C, a solution of dried (P_2O_5; 24 h) tetrabutylammonium cyanide (2.35 g, 8.75 mmol) in dry CH_2Cl_2 (15 mL) was added and the reaction mixture was allowed to warm to room temperature. After 3 h, the reaction was complete (TLC, solvent A_2). After concentration under reduced pressure, the residue was purified by column chromatography (solvent A_2) to give **2a** (0.672 g, 66%) as a solid; mp 112–114 °C (from cyclohexane). $[\alpha]_D^{25}$ −3.9° (*c* 1.1, $CHCl_3$); ^{1}H NMR: δ 7.58–7.53 (m, 2 H, Ar), 7.37–7.22 (m, 15 H, Ar) 6.88 (pd, 2 H, Ar), 4.99 (d, 1 H, *J* 11.1 Hz, CH_2Ph), 4.86–4.73 (m, 4 H, 2 CH_2Ph), 4.61 (d, 1 H, $J_{1,2}$ 9.3 Hz, H-1), 4.56 (d, 1 H, *J* 11.1 Hz, CH_2Ph), 3.88 (pt, 1 H, $J_{2,3}$ 9.3 Hz, H-2), 3.82 (brd, 1 H, $J_{4,3}$ 3.2 Hz, H-4), 3.81 (s, 3 H, OCH_3), 3.66 (pt, 1 H, $J_{5,6} = J_{5,6'}$ 6.9 Hz, H-5), 3.61 (dd, 1 H, H-3), 2.69 (dd, 1 H, $J_{6,6'}$ 16.7, $J_{6,5}$ 7.0 Hz, H-6), 2.46 (dd, 1 H, $J_{6',5}$ 7 Hz, H-6′); ^{13}C NMR: δ 159.3, 138.1, 137.8, 133.6, 129.9, 129.8, 129.1, 128.8, 128.4, 128.3, 128.2, 127.8, 127.7, 127.5, 127.4 (C Ar), 117.1 (CN), 113.8 (C Ar), 87.8 (C-1), 83.5, 76.8, 73.6, 73.5 (C-2,3,4,5) 75.5, 74.2, 73.0 (3 CH_2Ph), 55.2 (OCH_3), 20.0 (C-6). Anal. Calcd for $C_{35}H_{35}O_5NS$: C, 72.27; H, 6.06. Found: C, 72.01; H, 6.20.

Benzyl 2,3-di-O-*benzyl-6-deoxy-4*-O-p-*methoxybenzyl-β*-D-galacto-*heptopyranosidurononitrile* (**2b**) *and benzyl 3,6-anhydro-2*-O-*benzyl-4*-O-p-*methoxybenzyl-β*-D-*galactopyranoside* (**6**).—A solution of **4b** (0.5 g, 0.88 mmol) in 20 mL of dry CH_2Cl_2 was treated according to the above mentionned conditions, using 0.50 mL of 2,6-di-*tert*-butylpyridine, 0.25 mL of triflic anhydride and

1.2 g of tetrabutylammonium cyanide. After solvent evaporation under reduced pressure, the residue was chromatographed on a column (solvent A_2) to afford sequentially **6** (0.270 g, 68%) and **2b** (0.08 g, 16%). **2b**: Syrup; ^{1}H NMR: δ 7.34–7.30 (m, 17 H, H Ar), 6.86 (pd, 2 H, J 8.5 Hz, H Ar), 5.0–4.54 (4d, 8 H, 4 CH_2Ph), 4.45 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.86 (dd, 1 H, $J_{2,3}$ 9.5, H-2), 3.81 (s, 3 H, OCH_3), 3.73 (brd, 1 H, $J_{4,3}$ 2.5 Hz, H-4), 3.61 (brt, 1 H, H-5), 3.53 (dd, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 2.70 (dd, 1 H, $J_{6,5}$ 7.8, $J_{6,6'}$ 16.7 Hz, H-6), 2.32 (dd, 1 H, $J_{6',5}$ 6.0 Hz, H-6′). **6**: Syrup; ^{1}H NMR: δ 7.32–7.12 (m, 12 H, H Ar), 6.8 (brd, 2 H, J 8.7 Hz, H Ar), 4.80–4.40 (6d, 6 H, 3 CH_2Ph), 4.71 (s, 1 H, H-1), 4.39 (brd, 1 H, H-3), 4.32 (brs, 1 H, H-5), 4.24 (d, 1 H, $J_{6,6'}$ 8.9 Hz, H-6), 4.23 (d, 1 H, $J_{4,5}$ 1.9 Hz, H-4), 3.94 (dd, 1 H, $J_{6',5}$ 3.1 Hz, H-6′), 3.85 (d, 1 H, $J_{2,3}$ 4.7 Hz, H-2), 3.81 (s, 3 H, OCH_3); ^{13}C NMR: δ 160.0, 138.2, 138.0, 130.6, 130.2, 129.1, 128.6, 128.5, 128.4, 128.3, 114.5 (C Ar), 99.0 (C-1), 80.1, 78.2, 77.9, 76.8 (C-2,3,4,5), 73.0, 71.4, 71.3, 70.0 (3 CH_2Ph, C-6), 55.9 (OCH_3). This compound was not pure enough for elemental analysis but its NMR data are closely related to those of the 4-*O*-benzyl analogue [6].

Methyl 2,3,-di-O-*benzyl-6-deoxy-4*-O-p-*methoxybenzyl-6-phenylthio-α-*D-*galactopyranoside* (**9α**) *and methyl 2,3,-di*-O-*benzyl-6-deoxy-4*-O-p-*methoxybenzyl-6-phenylthio-β-*D-*galactopyranoside* (**9β**).—To a solution of **4a** (0.2 g, 0.36 mmol) at −78 °C were added a solution of di-*tert*-butylpyridine (0.2 mL, 0.73 mmol) in anhyd CH_2Cl_2 (10 mL) and triflic anhydride (0.1 mL, 0.6 mmol) and the reaction mixture was allowed to warm to −50 °C. At this temperature were added a solution of NaOMe (0.162 g, 3 mmol) in 10 mL of a 1:1 mixture of anhyd MeOH–MeCN. After stirring at room temperature for 3 h, Et_2O (50 mL) and pentane (5 mL) were added and the organic phase was washed with water until neutrality and dried. After concentration to dryness under reduced pressure, the residue was chromatographed (solvent *C*, then *D*) to give sequentially pure **9α** (0.040 g), a mixture of **9α** and **9β** (0.110 g), pure **9β** (0.010 g) and recovered starting material (0.040 g) (overall yield: 78%; α/β 7/1). **9α**: Syrup; $[\alpha]_D^{25}$ −27° (*c* 2, $CHCl_3$); ^{1}H NMR: δ 7.5–6.8 (m, 19 H, H Ar), 5.0–4.4 (6d, 6 H, 3 CH_2Ph), 4.64 (partially hidden d, 1 H, H-1), 4.02 (dd, 1 H, $J_{2,3}$ 10.0 $J_{2,1}$ 3.5 Hz, H-2), 3.93 (brd, 1 H, H-4), 3.90 (dd, 1 H, $J_{3,4}$ 2.6 Hz, H-3), 3.78 (s, 3 H, OCH_3), 3.75 (partially hidden brpt, 1 H, H-5), 3.31 (s, 3 H, OCH_3), 3.09 (dd, 1 H, $J_{6,5}$ 6.6, $J_{6,6'}$ 13.4 Hz, H-6), 2.85 (dd, 1 H, $J_{6',5}$ 6.9 Hz, H-6′). Anal. Calcd for $C_{35}H_{38}O_6S$: C, 71.65; H, 6.53; S, 5.46. Found: C, 71.65; H, 6.57; S, 5.49. **9β**: Syrup; ^{1}H NMR δ 7.5–6.8 (m, 19 H, H Ar), 5.0–4.5 (6d, 6 H, 3 CH_2Ph), 4.20 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.91 (brd, 1 H, H-4), 3.79 (s, 3 H, OCH_3), 3.78 (partially hidden dd, 1 H, $J_{2,1}+J_{2,3}$ 17.3 Hz, H-2), 3.50 (s, 3 H, OCH_3), 3.48 (partially hidden dd, 1 H, $J_{3,4}$ 2.9 Hz, H-3), 3.38 (brpt, 1 H, H-5), 3.17 (dd, 1 H, $J_{6,5}$ 6.0 Hz, H-6), 2.94 (dd, 1 H, $J_{6',5}$ 7.3 Hz, H-6′). This compound was not obtained in a sufficient amount for further analysis.

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