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Note

Synthesis of 1-thioglycosides

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Impressive progress has been made in the construction of *O*-glycosides from 1-thioglycosides [1], and methods have been developed for the preparation of 1-thioglycosides (**5–8**) from acetylated glycosyl halides (**1**) (Scheme 1) [2–3], acetylated glycosides (**2**) [4–7], and methyl glycosides (**3**) [8]. However, because of neighboring-group participation, the resultant thioglycosides (**5–6**) are usually of the 1,2-*trans*-configuration, whether derived from the reaction of an anomeric-stabilized α-bromide (**1**) with thiols [3] or from the Lewis acid-catalyzed coupling of peracylated sugars (**2**) with thiols [4]. These reactions occasionally provide both anomeric thioglycosides under conditions of strong acid-catalysis [5] [1] or high temperature [6], but yields are variable. For the conversion of methyl glycosides (**3**) into the corresponding thioglycosides (**7–8**), Hanessian's procedures or modifications are very suitable [8].

We envisioned that the use of protected sugar lactols **4** [9] would allow the conversion of either acetyl- or alkyl-protected glycopyranoses (**4**), into a variety of thioglycosides (**5–8**) under a single set of conditions. The reaction of such pyranose derivatives (**4**) with diaryl disulfides in the presence of trialkylphosphine yields the corresponding aryl thioglycosides [7b,10]. However, we found that alkyl thioglycosides could not be obtained by this method using either tributylphosphine or triphenylphosphine. Assuming that the likely mechanism of this reaction involves a rate-limiting attack of trialkylphosphine on disulfide, we reasoned that Lewis acids could provide effective catalysis for this attack. In fact, the addition of boron trifluoride etherate [2] to

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[1] Reaction of glycosides and thiols in the presence of a strong acid is generally an unsatisfactory procedure for the synthesis of 1-thioglycosides due to facile formation of dithioacetals, see ref. [2].

[2] The use of *n*-butylthiol to react directly with galactopyranose **4c** by the boron trifluoride etherate-catalyzed procedure [4b] gives thioglycoside **8d** (57%) and the corresponding thioacetal (19%) as well.

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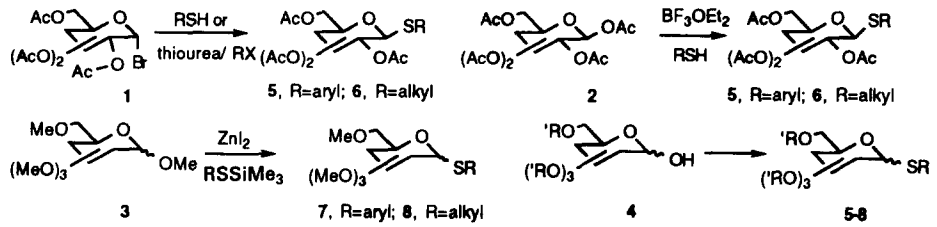
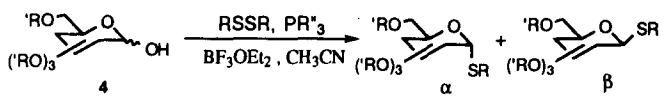
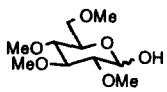
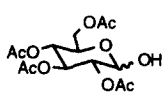
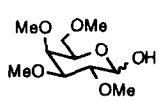
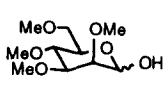


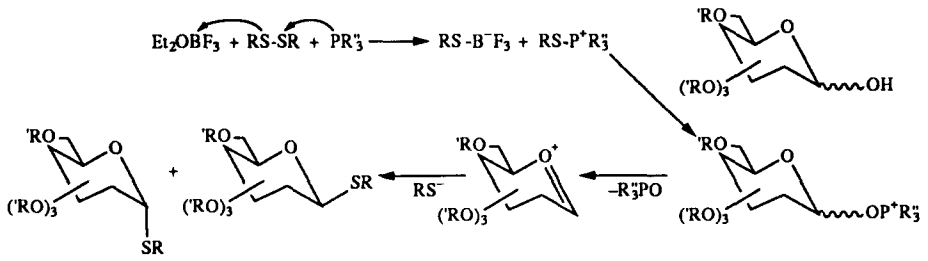
Scheme 1.

Table 1
Preparation of 1-thioglycosides from glycopyranoses



Entry	Substrate [a]	Reagent	Conditions [b]	Product (α : β) [c]	Yield [d] (%)	$[\alpha]_D$ (°) ($c = 1$, $CHCl_3$) α, β
1		$(n\text{-BuS})_2$, PPh_3	A	**8a** (3:1)	75	+226, −22
2		$(n\text{-BuS})_2$, PBu_3	B	**8a** (1:1)	92	
3		$(s\text{-BuS})_2$, PPh_3	B	**8b** (1:2)	91	+204, −46
4		$(t\text{-BuS})_2$, PPh_3	B	**8c** (1:1)	70	[f] −120
5	**4 a**	$(PhS)_2$, PBu_3	A	**7a** (1:1)	89	+261, −40
6		$(PhS)_2$, PPh_3	B	**7a** (1:1)	80	
7		$(ArS)_2$ [e], PBu_3	A	**7b** (3:2)	89	+247, −116
8		$(ArS)_2$ [e], PPh_3	B	**7b** (2:1)	65	
9		$(n\text{-BuS})_2$, PBu_3	A	**6a** (1:12)	73	+194, −22
10		$(n\text{-BuS})_2$, PPh_3	A	**6a** (1:12)	75	
11		$(n\text{-BuS})_2$, PPh_3	B	**6a** (1:3)	47	
12		$(PhS)_2$, PBu_3	A	**5a** (1:10)	51	+225, −14
13	**4 b**	$(PhS)_2$, PBu_3	B	**5a** (1:2)	35	
14		$(n\text{-BuS})_2$, PPh_3	B	**8d** (5:1)	77	+227, −13
15		$(n\text{-BuS})_2$, PBu_3	A	**8d** (7:1)	83	
16		$(PhS)_2$, PBu_3	A	**7c** (1:2)	85	+295, −19
	4 c					
17		$(n\text{-BuS})_2$, PPh_3	B	**8e** (4:1)	70	+146, −64
18		$(n\text{-BuS})_2$, PBu_3	A	**8e** (5:1)	94	
	4 d					

[a] Ref. [9].
[b] See section of experimental.
[c] The ratios were measured by ^{1}H-NMR and/or GC-MS.
[d] Isolated yield.
[e] Ar = *o*-Methoxycarbonylphenyl.
[f] The α anomer slowly decomposed at room temperature.



Scheme 2.

this reaction mixture promoted the formation of 1-thioglycosides (**5–8**) in good yields (Table 1). In all the cases shown in Table 1, both α and β anomers are produced and can be separated by silica gel chromatography.

The reaction described herein is general and applicable to the synthesis of aryl and alkyl thioglycosides with alkyl- or acetyl-protected hydroxyl groups. Therefore, eight types of thioglycosides (**5–8**, α and β) may be readily obtained by this combination of reagents. The reaction of acetylated glucopyranoses at room temperature (condition A) gives mainly β-thioglucosides (entries 10 and 12, Table 1). By increasing the reaction temperature (condition B), the ratio of α anomers increases and despite the lower overall yields, the α anomers can be isolated in appreciable amounts (entries 11 and 13). Although the ratio of α, β anomers formed depends unpredictably on the nature of the solvent (acetonitrile was the most suitable), and the use of others solvents such as benzene or dichloromethane produced the desired products in much lower yields ($< 30\%$). The detailed mechanism whereby boron trifluoride etherate promotes the formation of alkyl thioglycosides remains to be elucidated. It is likely to resemble the well-known Mitsunobu-type reactions [11] in which the key step is the boron trifluoride etherate-facilitated reduction of dialkyl disulfides by trialkylphosphines (Scheme 2). We have no concrete evidence to support this mechanism, except that we have identified the stoichiometric formation of trialkylphosphine oxide, the expected byproduct of the corresponding Mitsunobu reaction.

1. Experimental

General methods.—^{1}H-NMR spectra were recorded with Varian Gemini-200 instruments. GC-MS results were obtained on Hewlett–Packard 5890 Series II(GC) and 5971 Series(MS). Optical rotations were determined with a Perkin–Elmer 141 polarimeter at 25°C. Column chromatography was performed on "Baker" Silica Gel 40 μm with elution by petroleum ether–EtOAc. Solutions were concentrated in vacuo at 40°C.

Preparation of 1-thioglycosides — Condition A.—A suspension of activated 4 Å molecular sieves (100 mg/mmol **4**), glycopyranose (**4**, 1.0 mol equiv) [9], and anhydrous MeCN (0.2 M) was stirred for 15 min at room temperature. Disulfide (1.5 mol equiv) was then added, followed by the addition of tributylphosphine (1.5 mol equiv) and $BF_3 \cdot OEt_2$ (5.0 mol equiv). The progress of the reaction was monitored by TLC.

After the starting materials had been consumed (~ 5 h), the solution was washed with saturated $NaHCO_3$ and extracted three times with CH_2Cl_2. The combined organic solution was then washed with water, dried, and evaporated. The residue was purified by column chromatography.

Preparation of 1-thioglycosides — Condition B.—To a suspension of activated 4 Å molecular sieves (100 mg/mmol **4**), glycopyranose **4** (1.0 mol equiv), and anhydrous acetonitrile (0.2 M) were subsequently added to disulfide (2.2 mol equiv), triphenylphosphine (2.2 mol equiv), and $BF_3 \cdot OEt_2$ (8.0 mol equiv) at 70°C. After 20 min, the mixture was washed with saturated $NaHCO_3$ and purification was conducted as before.

*Phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-*D*-glucopyranoside* (**7a**). — The solvent for column chromatography was 4 : 1 petroleum ether–EtOAc. ^{1}H NMR ($CDCl_3$) for **7a**α: δ 7.51–7.46 (m, 2 H, Ar), 7.28–7.24 (m, 3 H, Ar), 5.71 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 4.14 (dt, $J_{4,5}$ 9.7, $J_{5,6}$ 2.2, $J_{5,6'}$ 3.2 Hz, H-5), 3.64, 3.55, 3.49, 3.37 (4s, 12 H, OCH_3), 3.62–3.28 (m, 5 H, H-2,3,4,6,6′) and data for **7a**β: mp 72–73°C; ^{1}H NMR ($CDCl_3$): δ 7.55–7.50 (m, 2 H, Ar), 7.30–7.22 (m, 3 H, Ar), 4.48 (d, 1 H, $J_{1,2}$ 9.6 Hz, H-1), 3.64, 3.59, 3.52, 3.38 (4s, 12 H, OCH_3), 3.60–3.00 (m, 6 H, H-2,3,4,5,6,6′).

o-*Methoxycarbonylphenyl 2,3,4,6-tetra-*O*-methyl-1-thio-*D*-glucopyranoside* (**7b**).— Solvent for column chromatography was 4 : 1 petroleum ether–EtOAc. **7b**α (solid) mp 89–91°C; ^{1}H-NMR ($CDCl_3$): δ 7.87 (dd, 1 H, J_o 7.7, J_m 1.6 Hz, Ar), 7.76 (dd, 1 H, J_o 8.1, J_m 1.1 Hz, Ar), 7.42 (ddd, 1 H, J_o 7.4, 8.1, J_m 1.6 Hz, Ar), 7.21 (ddd, 1 H, J_o 7.7, 7.4, J_m 1.1 Hz, Ar), 5.87 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 4.06 (dt, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 2.3, $J_{5,6'}$ 2.7 Hz, H-5), 3.91 (s, 3 H, $COOCH_3$), 3.65, 3.54, 3.47, 3.36 (4s, 12 H, OCH_3), 3.66–3.27 (m, 5 H, H-2,3,4,6,6′); and **7b**β (solid), mp 110–111°C; ^{1}H-NMR ($CDCl_3$): δ 7.91 (dd, 1 H, J_o 7.9, J_m 1.6 Hz, Ar), 7.57 (dd, 1 H, J_o 8.1, J_m 1.1 Hz, Ar, 7.44 (ddd, 1H, J_o 7.2, 8.1, J_m 1.6 Hz, Ar), 7.19 (ddd, 1 H, J_o 7.9, 7.2, J_m 1.1 Hz, Ar), 4.66 (d, 1 H, $J_{1,2}$ 9.3 Hz, H-1), 3.90 (s, 3 H, $-COOCH_3$), 3.67, 3.63, 3.55, 3.36 (4s, 12 H, OCH_3), 3.68–3.13 (m, 6 H, H-2, 3, 4,5, 6, 6′).

*Phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-*D*-galactopyranoside* (**7c**).—The solvent for column chromatography was 3 : 1 : 6 petroleum ether–EtOAc–methylene chloride. ^{1}H-NMR ($CDCl_3$) for **7c**α (syrup): δ 7.54–7.49 (m, 2 H, Ar), 7.29–7.25 (m, 3 H, Ar), 5.78 (d, 1 H, $J_{1,2}$ 5.5 Hz, H-1), 4.40 (t, 1 H, $J_{5,6} = J_{5,6} = 6.8$ Hz, H-5), 3.97 (dd, 1 H, $J_{1,2}$ 5.5 $J_{2,3}$ 10.2 Hz H-2), 3.77 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4), 3.59, 3.55, 3.52, 3.36 (4s, 12 H, OCH_3), 3.64–3.38 (m, 3 H, H-3,6,6′); and data for **7c**β (solid): mp 91–92°C; ^{1}H-NMR ($CDCl_3$): δ 7.55–7.51 (m, 2 H, Ar), 7.27–7.24 (m, 3 H, Ar), 4.50 (d, 1 H, $J_{1,2}$ 9.7 Hz, H-1), 3.69 (d, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 3.59, 3.56, 3.53, 3.37 (4s, 12 H, OCH_3), 3.63–3.45 (m, 4 H, H-2,5,6,6′), 3.20 (dd, 1 H, $J_{2,3}$ 9.2, $J_{3,4}$ 3.0 Hz, H-3).

n-*Butyl 2,3,4,6-tetra-*O*-methyl-l-thio-*D*-glucopyranoside* (**8a**).—The solvent for column chromatography was 4 : 1 petroleum ether – EtOAc. ^{1}H-NMR ($CDCl_3$) for **8a**α (syrup): δ 5.43 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 4.00 (DT, 1H, $J_{4,5}$ 9.8, $J_{5,6}$ 2.0, $J_{5,6}$, 3.0 Hz, H-5), 3.59, 3.52, 3.46, 3.39 (4s, 12 H, OCH_3), 3.65–3.15 (m, 5 H, H-2,3,4,6,6′), 2.58–2.49 (m, 2 H, $-SCH_2-$), 1.67–1.35 (m, 4 H, $-CH_2CH_2-$), 0.89 (t, 3 H, J 7.3 Hz, $-CH_3$); and data for **8a**β (syrup): δ 4.25 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 3.64, 3.59, 3.53, 3.38 (4s, 12 H, OCH_3), 3.60–2.91 (m, 6 H, H-2,3,4,5,6,6′), 2.69 (t, 2 H, J 7.4 Hz, $-SCH_2-$), 1.70–1.35 (m, 4 H, $-CH_2CH_2-$), 0.90 (t, J 7.3 Hz, $-CH_3$).

s-*Butyl 2,3,4,6-tetra-*O*-methyl-l-thio-*D*-glucopyranoside* (**8b**).— The solvent for col-

umn chromatography was 5:1 petroleum ether–EtOAc. ^{1}H-NMR ($CDCl_3$) for **8b**α (syrup): δ 5.49 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 4.03 (dt, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 2.3, $J_{5,6'}$ 3.4 Hz, H-5), 3.58, 3.52, 3.44, 3.38 (4s, 12 H, OCH_3), 3.66–3.15 (m, 5 H, H-2,3,4,6,6'), 2.83–2.72 (m, 1 H, –SCH–), 1.69–1.50 (m, 2 H, $-CH_2-$), 1.29, 1.26 (2d, 3 H, J 6.7 Hz, $-SCHCH_3$), 0.96, 0.95 (2t, 3 H, J 7.4 Hz, $-CH_2CH_3$); and data for **8b**β (syrup): δ 4.33, 4.31 (2d, 1 H, $J_{1,2}$ 9.7 Hz, H-1), 3.64, 3.59, 3.52, 3.38 (4s, 12 H, OCH_3), 3.55–2.87 (m, 7 H, H-2,3,4,5,6,6', –SCH–), 1.72–1.52 (m, 2 H, $-CH_2-$), 1.31, 1.30 (2d, 3 H, J 6.8 Hz, $-SCHCH_3$), 0.97 (t, J 7.3 Hz, $-CH_2CH_3$).

t-*Butyl 2,3,4,6-tetra*-O-*methyl-1-thio*-D-*glucopyranoside* (**8c**).—The solvent for column chromatography was 9:1 petroleum ether–EtOAc. **8c**α (syrup, unstable at room temperature); and ^{1}H-NMR ($CDCl_3$) for **8c**β (syrup): δ 4.15 (d, 1 H, $J_{1,2}$ 9.4 Hz, H-1), 3.63, 3.60, 351, 3.36 (4s, 12 H, OCH_3), 3.58–3.02 (m, 6 H, H-2,3,4,5,6,6'), 1.34 (s, 9 H, *t*-Bu).

n-*Butyl 2,3,4,6-tetra*-O-*methyl-1-thio*-D-*galactopyranoside* (**8d**).—The solvent for column chromatography was 3:1:6 petroleum ether–EtOAc–methylene chloride). ^{1}H-NMR ($CDCl_3$) for **8d**α (syrup): δ 5.52 (d, 1 H, $J_{1,2}$ 5.4 Hz, H-1), 4.25 (t, 1 H, $J_{5,6} = J_{5,6'} = 6.9$ Hz, H-5), 3.88 (dd, 1 H, $J_{1,2}$ 5.5, $J_{2,3}$ 10.0 Hz, H-2), 3.69 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4), 3.57, 3.51, 3.48, 3.39 (4s, 12 H, OCH_3), 3.62–3.38 (m, 3 H, H-3,6,6') 2.62–2.46 (m, 2 H, $-SCH_2-$), 1.65–1.36 (m, 4 H, $-CH_2CH_2-$), 0.91 (t, 3 H, J 7.2 Hz, $-CH_3$); and data for **8d**β (syrup): δ 4.26 (d, 1 H, $J_{1,2}$ 9.4 Hz, H-1), 3.68 (d, 1 H, $J_{3,4}$ 3.1 Hz, H-4), 3.60, 3.55, 3.53, 3.39 (4s, 12 H, OCH_3), 3.59–3.26 (m, 4 H, H-2,5,6,6'), 3.17 (dd, 1 H, $J_{2,3}$ 9.2, $J_{3,4}$ 3.1 Hz, H-3), 2.73–2.65 (m, 2 H, $-SCH_2-$), 1.65–1.36 (m, 4 H, $-CH_2CH_2-$), 0.90 (t, 3 H, J 7.2 Hz, $-CH_3$).

n-*Butyl 2,3,4,6-tetra*-O-*methyl-1-thio*-D-*mannopyranoside* (**8e**).—The solvent for column chromatography was 6:1 petroleum ether–EtOAc. ^{1}H-NMR ($CDCl_3$) for **8e**α (syrup): δ 5.41 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 3.99–3.92 (m, 1 H, H-5), 3.68–3.42 (m, 5 H, H-2, 3,4,6,6'), 3.52, 3.47, 3.45, 3.39 (4s, 12 H, OCH_3), 2.67–2.58 (m, 2 H, $-SCH_2-$), 1.65–1.34 (m, 4 H, $-CH_2CH_2-$), 0.91 (t, 3 H, J 7.2 Hz, $-CH_3$); and data for **8e**β (syrup): δ 4.47 (d, 1 H, $J_{1,2}$ 0.9 Hz, H-1), 3.72–3.19 (m, 6 H, H-2,3,4,5,6,6'), 3.63, 3.52, 3.51, 3.39 (4s, 12 H, OCH_3), 2.70 (t, 2 H, J 7.2 Hz, $-SCH_2-$), 1.66–1.36 (m, 4 H, $-CH_2CH_2-$), 0.91 (t, 3 H, J 7.2 Hz, $-CH_3$).

n-*Butyl 2,3,4,6-tetra*-O-*acetyl-1-thio*-D-*glucopyranoside* (**6a**).—The solvent for column chromatography was 3:1 petroleum ether–EtOAc. **6a**α (solid) mp 71–73°C; ^{1}H-NMR ($CDCl_3$): δ 5.64 (d, 1 H, $J_{1,2}$ 5.7 Hz, H-1), 5.35 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 9.4 Hz, H-3), 5.07–4.96 (m, 2 H, H-2, 4), 4.41 (ddd, 1 H, $J_{4,5}$ 10.1, $J_{5,6}$ 4.6, $J_{5,6'}$ 2.2 Hz, H-5), 4.28 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6,6'}$ 12.2 Hz, H-6), 4.05 (dd, 1 H, $J_{5,6'}$ 2.2, $J_{6,6'}$ 12.2 Hz, H-6'), 2.57–2.47 (m, 2 H, $-SCH_2-$), 2.67, 2.05, 2.02, 2.00 (4s, 12 H, $-COCH_3$), 1.60–1.31 (m, 4 H, $-CH_2CH_2-$), 0.89 (t, 3 H, J 7.2 Hz, $-CH_3$); and **6a**β (solid) mp 69–70°C; ^{1}H-NMR ($CDCl_3$): δ 5.27–4.98 (m, 3 H, H-2,3,4), 4.47 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1), 4.23 (dd, 1 H, $J_{6,6'}$ 12.3, $J_{5,6}$ 4.8 Hz, H-6), 4.12 (dd, 1 H, $J_{5,6'}$ 2.5, $J_{6,6'}$ 12.3 Hz, H-6'), 3.70 (ddd, 1 H, $J_{4,5}$ 9.8, $J_{5,6}$ 4.8, $J_{5,6'}$ 2.5 Hz, H-5), 2.72–2.63 (m, 2 H, $-SCH_2-$), 2.08, 2.06, 2.03, 2.01 (4s, 12 H, $-COCH_3$), 1.63–1.35 (m, 4 H, $-CH_2CH_2-$), 0.91 (t, 3 H, J 7.1 Hz, $-CH_3$).

Phenyl 2,3,4,6-tetra-O-*acetyl-1-thio*-D-*glucopyranoside* (**5a**).—The solvent for column chromatography was 3:1 petroleum ether–EtOAc. **5a**α (solid) mp 89–90°C;

^{1}H-NMR ($CDCl_3$): δ 7.48–7.42 (m, 2 H, Ar), 7.31–7.27 (m, 3 H, Ar), 5.92 (d, 1 H, $J_{1,2}$ 5.8 Hz, H-1), 5.44 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 9.3 Hz, H-3), 5.14–5.03 (m, 2 H, H-2, 4), 5.57 (ddd, $J_{4,5}$ 10.0, $J_{5,6}$ 5.1, $J_{5,6'}$ 2.3 Hz, H-5), 4.28 (dd, 1 H, $J_{5,6}$ 5.1, $J_{6,6'}$ 12.3 Hz, H-6), 4.03 (dd, 1 H, $J_{5,6'}$ 2.3, $J_{6,6'}$ 12.3 Hz, H-6'), 2.11, 2.06, 2.04, 2.03 (4s, 12 H, $-COCH_3$); and **5a**β (solid), mp 116–117°C; ^{1}H-NMR ($CDCl_3$): δ 5.22 (t, 1 H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 5.08–4.92 (m, 2 H, H-2,4), 4.70 (d, 1 H, $J_{1,2}$ 10.1 Hz, H-1), 4.21–4.18 (m, 2 H, H-6, 6'), 3.76–3.66 (m, 1 H, H-5), 2.08, 2.07, 2.01, 1.99 (4s, 12 H, $-COCH_3$).

Acknowledgments

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