Regioselective Benzoylation of 4,6-O-Benzylidene Acetals of Glycopyranosides in the Presence of Transition Metals

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GRAPHICAL ABSTRACT

Benzoylation of 4,6-O-benzylidene acetals of glycopyranosides by benzoic anhydride in acetonitrile in the presence of Cu(CF₃COO)₂ as a promoter gave 2-benzoates for α-D-glucopyranosides and α-D-mannopyranosides and 3-benzoates for β-D-galactopyranosides in good yields with high regioselectivity. Benzoylation of 4, 6-O-benzylidene acetals of glycopyranosides of D-galactose and D-mannose by benzoyl chloride in the presence of MoO₂(acac)₆ as a catalyst in all studied cases led to regioselective 3-O-substitution.

Keywords 4,6-O-benzylidene acetals; Copper (II) trifluoroacetate; Molybdenum (VI) dioxide bis(acetylacetonate); Regioselective benzoylation
INTRODUCTION

Currently, the rapid development of glycobiology requires the creation of convenient and efficient methods for the synthesis of complex carbohydrates and oligosaccharides. Since carbohydrates are multifunctional molecules, it is necessary to use temporary protections in their synthesis, which requires multiple steps and considerable time. Regioselective introduction of protecting groups in carbohydrates is an alternative approach to obtain intermediates in oligosaccharide synthesis.[1,2] The ready availability of 4,6-O-benzylidene acetals of sugars also simplifies the task of functionalization of sugar molecules, such as monoacylation, to conveniently obtain intermediates that often are acceptors in the synthesis of oligosaccharides containing 1→2 and 1→3 linkages. For monoacylation of 4,6-O-benzylidene acetals of carbohydrates, metal chelates,[3–8] organotin intermediates,[9–20] organoboron[21] and organosilicon[22] compounds, amines,[23–27] organocatalysts,[28–29] TMS ethers,[30–32] and enzymes[33] have been used. However, despite some progress in this area, the regioselective protection of hydroxyl groups in sugars can still benefit from improvements in methodology.

RESULTS AND DISCUSSION

Earlier we found that regioselective acylation of glycopyranosides could be obtained by use of the salts of transition metals. In this case, molybdenum (V, VI) compounds[34,35] oriented substitution on 3-OH in 2,3- and 3,4-cis-vicinal diols, but regioselectivity of acylation in the presence of copper (II) salts depended both on the configurations of the hydroxyl groups and on the configuration of the aglycone probably due to formation of intermediate complex glycosides with copper (II) ions.[36] In general, the causes that determine the differences in reactivity of the hydroxyl groups of carbohydrates in the acylation reactions are varied and may be because of steric and stereoelectronic effects,[37] as well as intramolecular hydrogen bonds.[38–42] In addition, regioselectivity may also be obtained by rearrangement of initially formed products to the most stable products.[43] The complexation of carbohydrates can change the ratio of these factors and, as a consequence, the reactivity of the hydroxyl groups.

In the present work we wanted to study the influence of Cu(CF₃COO)₂ and MoO₂(acac)₂ on regioselective benzoylation of 4,6-O-benzylidene acetals of glycopyranosides. The results of benzoylation of 4,6-O-benzylidene acetals of glycopyranosides in the presence of Cu(CF₃COO)₂ are presented in Table 1.

As seen from Table 1, the use of Cu(CF₃COO)₂ as the promoter in the benzoylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside 1 is preferable from the viewpoint of regioselectivity (entry 1). From Table 1, it can also be seen that benzoylation of 4,6-O-benzylidene acetals of methyl α-D-galactopyranosides 3 and 4 (entries 10 and 12, respectively) in the presence
Table 1: Regioselective benzoylation of 4,6-O-benzylidene acetics of glycopyranosides by benzoic anhydride in acetonitrile in the presence of Cu(CF$_3$COO)$_2$

| Entry | Glycoside | Catalyst | Glycoside | HO-2  | HO-3  | Di-
|--------|-----------|----------|-----------|-------|-------|-------|
| 1      | ![Glycoside Image](image1.png) | Cu(CF$_3$COO)$_2$ | 7         | 82 (76) | 4     | 7     |
| 2      | ![Glycoside Image](image2.png) | Zn(CF$_3$COO)$_2$ | 18        | 68     | 11    | 3     |
| 3      | ![Glycoside Image](image3.png) | Ni(CF$_3$COO)$_2$ | 61        | 22     | 17    | 3     |
| 4      | ![Glycoside Image](image4.png) | Co(CF$_3$COO)$_2$ | 37        | 41     | 19    | 3     |
| 5      | ![Glycoside Image](image5.png) | Gd(CF$_3$COO)$_3$ | 13        | 74     | 7     | 6     |
| 6      | ![Glycoside Image](image6.png) | no        | 62        | 25     | 8     | 5     |
| 7      | ![Glycoside Image](image7.png) | no*       | 32        | 37     | 18    | 13    |
| 8      | ![Glycoside Image](image8.png) | Cu(CF$_3$COO)$_2$ | 6         | 79 (72) | 3     | 12    |
| 9      | ![Glycoside Image](image9.png) | no        | 68        | 22     | 7     | 3     |
| 10     | ![Glycoside Image](image10.png) | Cu(CF$_3$COO)$_2$ | 4         | 26     | 61    | 9     |
| 11     | ![Glycoside Image](image11.png) | no        | 64        | 7      | 27    | 2     |

(Continued on next page)
Table 1: Regioselective benzoylation of 4,6-O-benzylidene acetals of glycopyranosides by benzoic anhydride in acetonitrile in the presence of Cu(CF₃COO)₂ (Continued)

| Entry | Glycoside | Catalyst       | Glycoside | HO-2 | HO-3 | DI- |
|-------|-----------|----------------|-----------|------|------|-----|
| 12    | 4         | Cu(CF₃COO)₂     | 6         | 24   | 64   | 6   |
| 13    | no        |                | 61        | 6    | 30   | 3   |
| 14    | 5         | Cu(CF₃COO)₂     | 5         | 5    | 80 (73) | 10 |
| 15    | no        |                | 74        | 4    | 22   |     |
| 16    | 5         | Cu(CF₃COO)₂     | 3         | 2    | 86 (79) | 9  |
| 17    | no        |                | 76        | 3    | 21   |     |
| 18    | 6         | Cu(CF₃COO)₂     | 3         | 2    | 84 (77) | 11 |
| 19    | 7         | no             | 74        | 3    | 23   |     |
| No. | Structure | Reagent | Yield % | Isolated Yields |
|-----|-----------|---------|---------|-----------------|
| 20  | ![Structure 1](image1.png) | Cu(CF$_3$COO)$_2$ | 88 | 7 | 5 |
| 21  | ![Structure 2](image2.png) | Cu(CF$_3$COO)$_2$ | 4 | 70 | 26 |
| 22  | ![Structure 3](image3.png) | Cu(CF$_3$COO)$_2$ | 7 | 77 (70) | 5 | 11 |
| 23  | ![Structure 4](image4.png) | no | 72 | 11 | 11 | 6 |
| 24  | ![Structure 5](image5.png) | Cu(CF$_3$COO)$_2$ | 4 | 78 (72) | 6 | 12 |
| 25  | ![Structure 6](image6.png) | no | 69 | 13 | 14 | 4 |

*a Determined by $^1$H NMR, isolated yields in brackets.

*1 (20 mg), Bz$_2$O (20 mg, 1.25 eq), pyr (0.2 mL), rt, 16h.
of copper (II) trifluoroacetate formed significant amounts of both 2-O- and 3-O-benzoates. It is possible to assume that it was the result of benzylation of the complexes of copper (II) atoms with the participation of adjacent atoms O-1, O-2, O-3, and O-4 of α-D-galactopyranoside (Sch 1). It is interesting that the benzylation of methyl 6-O-trityl-α-D-galactopyranoside[36] under the same conditions gave mainly the 2-O-benzoate, perhaps as a result of interference from the bulky trityl group at C-6 to form an intermediate complex of ion Cu(II) with 3-OH and 4-OH.

At the same time, the benzylation of methyl and benzyl 4,6-O-benzylidene-β-D-galactopyranosides 5, 6, and 7 (entries 14, 16, and 18, respectively), which could possibly form only one complex of copper (II) with O-3 and O-4 (Fig 1a), gave practically only 3-O-benzoate with 73% to 79% yields and high regioselectivity. Similar results were observed in the benzylation of 4, 6-O-benzylidene-β-D-galactopyranoside by N-benzyloximidazole[27] and by benzyol chloride with the use of copper (II) chelates[6] and silver (I) oxide.[44] The benzylation of methyl 4,6-O-benzylidene- and 4,6-O-p-methoxybenzylidene-α-D-glucopyranosides 1 and 2 (entries 1 and 8, respectively) resulted in selective formation of 2-benzoates that was possibly determined by the formation of an intermediate complex of copper (II) atoms with O-2 and O-1 (Fig 1b). The benzylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside 1 by benzyol chloride in the presence of organotin compounds,[11] by 1-(benzoyloxy)benzotriazole,[45] or under the conditions of phase-transfer catalysis[46] earlier also demonstrated the highest reactivity of 2-OH, although the

**Scheme 1:** Proposed mechanism of regioselective benzylation of methyl α-D-galactopyranoside in the presence of Cu(CF₃COO)₂.

**Figure 1:** The proposed coordination of methyl 4,6-O-benzylidene-β-D-galactopyranoside (a) and methyl 4,6-O-benzylidene-α-D-glucopyranoside (b) with Cu⁺(CF₃COO).
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Figure 2: The proposed coordination of methyl 4,6-O-benzylidene-α-D-mannopyranoside with Cu⁺(CF₃COO).

benzoylation of 1 by benzoyl chloride in the presence of silver (I) oxide basically resulted in the substitution of 3-OH.[44]

Treatment of 2-O and 3-O-benzoates of methyl 4,6-O-benzylidene-α-D-glucopyranoside 8 and 9 with benzoyl anhydride in the presence of Cu(CF₃COO)₂ (entries 20 and 21) showed little migration of the benzoyl group, indicating that the products’ distribution is determined by the kinetic control. The benzoylation of methyl 4,6-O-benzylidene- and methyl 4,6-O-p-methoxybenzylidene-α-D-mannopyranosides 10 and 11 (entries 22 and 24, respectively) also gave 2-O-benzoates in good yields with high selectivity. In the latter case, it was possible to assume the formation of two intermediate complexes of copper (II) atoms with O-2, O-3, and O-5 (Fig 2a, 2b).

It is known[47,48] that the benzoylation of methyl 4,6-O-benzylidene-2,3-O-dibutylstannylene-α-D-mannopyranoside by benzoyl chloride in dioxane gave 2-O and 3-O-benzoates in roughly equal amounts, but replacing the solvent with benzene gave mainly 2-O-benzoate.[12] At the same time, benzoylation of this acetal in the presence of N-methylimidazole[12] as well as the benzoylation of methyl 4,6-O-benzylidene-α-D-mannopyranoside in pyridine[49] resulted mainly in a 3-O-benzoate.

Next, we explored the benzoylation of 4,6-O-benzylidene acetals of glycopyranosides in the presence of MoO₂(acac)₂. The results are presented in Table 2.

As can be seen from this table, using acetonitrile as solvent (entry 1 vs. 2 and 3) was preferable in the reaction. Table 2 also shows that 4,6-O-benzylidene derivatives of α- and β-D-galactopyranoside and α-D-mannopyranoside demonstrated preferable reactivity for 3-OH in comparison with 2-OH in the benzoylation by benzoyl chloride even without a catalyst, but the reactions gave only moderate yields of 3-benzoate in the reaction mixture (entries 4, 6, 8, 10, and 12). The use of MoO₂(acac)₂ as the catalyst in these cases greatly increased the yields of 3-O-benzoates in the reaction mixture along with increased regioselectivity. Similar results were obtained earlier[35] on the benzoylation of pyranosides by benzoyl chloride in the presence MoO₂(acac)₂. This was probably determined by the increase of the nucleophilicity of 3-OH after complexation with Mo(VI). Table 2 also shows that the benzoylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside 1 both with and
**Table 2:** Regioselective benzoylation of 4,6-O-benzylidene acetals of glycopyranosides by benzoyl chloride in acetonitrile in the presence of MoO$_2$(acac)$_2$.

| Entry | Substrate Glycoside | Catalyst | Recovered Glycoside (%) | Benzoate yields (%)$^a$ | HO-2 | HO-3 | Di- |
|-------|----------------------|----------|-------------------------|-------------------------|------|------|-----|
| 1     | ![Structure 1](image1) | MoO$_2$(acac)$_2$ | 16                      | 10 71 (64)              | 3    |      |     |
| 2     | ![Structure 2](image2) | MoO$_2$(acac)$_2$ | 15                      | 13 69 3                |      |      |     |
| 3     | ![Structure 3](image3) | MoO$_2$(acac)$_2$ | 14                      | 14 67 5                |      |      |     |
| 4     | ![Structure 4](image4) | no       | 29                      | 7 48 16                |      |      |     |
| 5     | ![Structure 5](image5) | MoO$_2$(acac)$_2$ | 11                      | 7 82 (76)              |      |      |     |
| 6     | ![Structure 6](image6) | no       | 40                      | 6 46 8                |      |      |     |
| 7     | ![Structure 7](image7) | MoO$_2$(acac)$_2$ | 10                      | 7 83 (75)              |      |      |     |
| 8     | ![Structure 8](image8) | no       | 35                      | 7 48 10               |      |      |     |
| 9     | ![Structure 9](image9) | MoO$_2$(acac)$_2$ | 8                       | 5 85 (77) 2            |      |      |     |
| 10    | ![Structure 10](image10) | no       | 23                      | 22 43 12              |      |      |     |
| 11    | ![Structure 11](image11) | MoO$_2$(acac)$_2$ | 5                       | 4 88 (82) 3            |      |      |     |
| 12    | ![Structure 12](image12) | no       | 27                      | 19 43 11              |      |      |     |
| 13    | ![Structure 13](image13) | MoO$_2$(acac)$_2$ | 42                      | 50 6 2                |      |      |     |
| 14    | ![Structure 14](image14) | no       | 45                      | 48 5 2                |      |      |     |

$^a$Determined by $^1$H NMR, and isolated yields are in brackets.

$^b$Dioxane was used as solvent.

$^c$EtAc was used as solvent.

without a catalyst (entries 13 and 14, respectively) gave the same result with preferable formation of 2-O-benzoate. It indicates the absence of an intermediate complex of this acetal with molybdenum (VI).

In conclusion, we have found that using transition metal salts, Cu(CF$_3$COO)$_2$ and MoO$_2$(acac)$_2$ in particular, allowed the manipulation of reactivities of hydroxyl groups in 4,6-O-benzylidene acetals of glycopyranosides
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in their benzoylation with benzoyl anhydride or chloride. This has provided an efficient method for monobenzoylation of these compounds in one step in good to excellent yields and high regioselectivity.

EXPERIMENTAL

General Methods

Melting points were determined on a Boethius micro hot-stage apparatus and were uncorrected. Optical rotations were measured with a Perkin–Elmer model 141. Spectra $^1$H and $^{13}$C NMR were registered on a Bruker DPX-300 ($^1$H at 300 MHz and $^{13}$C at 75 MHz). Chemical shifts ($\delta$) are reported in ppm related to Me$_4$Si. Positive mode HR LSI mass spectra were obtained on an Agilent Technology 6510 Q TOF LC/MS mass spectrometer (USA). The samples were dissolved in methanol (c 0.01 mg/mL). TLC was performed on silica gel L (5–40 $\mu$m; Chemapol) with hexane–acetone 7:3 as eluent. For detection, 10% sulfuric acid in ethanol at 130ºC was used. Column chromatography was performed on silica gel (100–160 $\mu$m; Chemapol).

General Procedure for the Monobenzoylation of 4,6-O-benzylidene Acetals of Glycopyranosides by Benzoic Anhydride using Cu(CF$_3$COO)$_2$ as Promoter

A solution of acetal (0.25 mmol), benzoic anhydride (0.32 mmol), Cu(CF$_3$COO)$_2$ (0.32 mmol), and 2,4,6-collidine (0.32 mmol) in acetonitrile (2 mL) was stirred at rt for 6 h. The reaction was monitored by TLC. Chloroform (20 mL) was added to the reaction mixture. The organic layer was washed with 2 N HCl, aq. NaHCO$_3$, and water and was then concentrated to a small volume under reduced pressure at rt. The products were finally purified by flash chromatography on a column of silica gel using gradient acetone in hexane as eluents.

Methyl 2-O-benzoyl-4,6-O-benzylidene-$\alpha$-D-glucopyranoside (1a)

It (73 mg) was obtained in a 76% yield from 1. R$_f$ 0.50. m.p. 169–170ºC (recrystallized from EtOAc-hexane). [$\alpha$]$_D^{20}$ +108.9 (c 0.6, CHCl$_3$). Lit. data:$^{[50]}$ m.p. 169–170ºC; [$\alpha$]$_D^{20}$ +111.

Methyl 2-O-benzoyl-p-methoxy-4,6-O-benzylidene-$\alpha$-D-glucopyranoside (2a)

It (75 mg) was obtained in a 72% yield from 2. R$_f$ 0.44. m.p. 153.5–154.5ºC (recrystallized from EtOAc-hexane). [$\alpha$]$_D^{20}$ +88.5 (c 0.4, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.13–8.07 (m, 2H, PhH), 7.62–7.55 (m, 1H, PhH), 7.50–7.40 (m, 4 H, PhH), 6.93–6.88 (m, 2H, PhH), 5.53 (s, 1H, PhCH), 5.09–5.01 (m, 2H, H-1, H-2), 4.38–4.28 (m, 2H, H-3, H-6a), 3.95–3.85 (m, 1H,
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H-5), 3.80 (s, 3H, OCH₃), 3.78 (t, 1H, J = 10.1 Hz, H-6b), 3.62 (t, 1H, J = 9.3 Hz, H-4), 3.39 (s, 3H, OCH₃). ¹³C NMR (75 MHz, CDCl₃): δ 166.2, 160.2, 133.3, 129.9, 129.4, 128.3, 127.6, 113.6, 101.9, 97.7, 81.4, 74.0, 68.8, 68.7, 62.0, 55.4, 55.2. HRMS (ESI) calcd for C₂₂H₂₄O₈Na m/z (M+Na)⁺: 439.1363. Found: 439.1353.

**Methyl 3-O-benzoyl-4,6-O-benzylidene-β-D-galactopyranoside (5a)**

It (70 mg) was obtained in a 73% yield from 5. Rf 0.31. m.p. 165–166°C (recrystallized from EtOAc-hexane). [α]D²⁰ +91.3 (c 0.4, CHCl₃). Lit. data: [⁵¹] m.p. 165°C; [α]D²⁰ +94.4.

**Benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-galactopyranoside (6a)**

It (91 mg) was obtained in a 79% yield from 6. Rf 0.40. m.p. 177–179°C (recrystallized from EtOAc-hexane). [α]D²⁰ +61.7 (c 0.6, CHCl₃). Lit. data: [²⁷] m.p. 178–179°C; [α]D²⁰ +64.4.

**Benzyl 3-O-benzoyl-p-methoxy-4,6-O-benzylidene-β-D-galactopyranoside (7a)**

It (95 mg) was obtained in a 77% yield from 7. Rf 0.34. m.p. 62–63°C (recrystallized from EtOAc-hexane). [α]D²⁰ +46.8 (c 0.4, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 8.11–8.04 (m, 2H, PhH), 7.60–7.51 (m, 1H, PhH), 7.45–7.28 (m, 9H, PhH), 6.88–6.83 (m, 2H, PhH) 5.47 (s, 1H, PhC₆H₅), 5.12 (dd, 1H, J = 3.6 Hz, J = 10.1 Hz, H-3), 5.03 (d, 1H, J = 11.8 Hz, CH₂), 4.66 (d, 1H, J = 11.8 Hz, CH₂), 4.52 (d, 1H, J = 7.7 Hz, H-1), 4.47 (m, 1H, H-4), 4.38 (dd, 1H, J = 12.5 Hz, H-6a), 4.24 (dd, 1H, J = 7.8 Hz, J = 10.0 Hz, H-2), 4.09 (dd, 1H, J = 12.5 Hz, H-6b), 3.78 (s, 3H, OCH₃), 3.55 (m, 1H, H-5). ¹³C NMR (75 MHz, CDCl₃): δ 166.4, 159.9, 137.0, 133.1, 129.9, 128.4, 128.3, 128.1, 128.0, 127.4, 113.4, 101.9, 100.7, 74.0, 73.6, 70.9, 68.9, 68.7, 66.5, 55.2. HRMS (ESI) calcd for C₂₈H₂₈O₈Na m/z (M+Na)⁺: 515.1676. Found: 515.1673.

**Methyl 2-O-benzoyl-4,6-O-benzylidene-α-D-mannopyranoside (10a)**

It (68 mg) was obtained in a 70% yield from 10. Rf 0.50. [α]D²⁰ −42.7 (c 0.5, CHCl₃). Lit. data: [α]D²⁰ −44[³⁹] or [α]D²¹ −39[¹²].

**Methyl 2-O-benzoyl-p-methoxy-4,6-O-benzylidene-α-D-mannopyranoside (11a)**

It (75 mg) was obtained in a 72% yield from 11. Rf 0.44. [α]D²⁰ −45.2 (c 0.4, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 8.13–8.06 (m, 2H, PhH), 7.63–7.57 (m, 1H, PhH), 7.50–7.42 (m, 4H, PhH), 6.92–6.88 (m, 2H, PhH) 5.61 (s, 1H, PhCH), 5.45 (dd, 1H, J = 1.4 Hz, J = 3.6 Hz, H-2), 4.83 (d, 1H, J = 1.2 Hz, H-1), 4.35–4.28 (m, 2H, H-3, H-6a), 4.05–3.98 (m, 1H, H-5), 3.80 (s, 3H, OCH₃), 3.43 (s, 3H, OCH₃). ¹³C NMR (75 MHz, CDCl₃): δ 166.0, 160.2, 133.4, 130.0, 129.9, 129.6, 129.5, 128.4, 128.3, 127.6, 113.7, 102.2,
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99.6, 79.3, 72.5, 68.8, 67.4, 63.3, 55.3, 55.2. HRMS (ESI) calcd for C_{22}H_{24}O_{8}Na
m/z (M+Na)^+: 439.1363. Found: 439.1354.

**General Procedure for the Monobenzoylation of 4,6-O-benzylidene Acetals of Glycopyranosides by Benzoyl Chloride with MoO_2(acac)_2 as a Catalysis**

A solution of acetal (0.25 mmol), 2,4,6-collidine (0.5 mmol), and MoO_2(acac)_2 (0.005 mmol) in acetonitrile (2 mL) was allowed to stir at rt for 6 h. BzCl (0.37 mmol) was added to the solution in three portions. The reaction was monitored by TLC. Chloroform (20 mL) was added to the solution. The organic layer was washed with 2 N HCl, aq. NaHCO_3, and water and then concentrated to a small volume under reduced pressure at rt. The product was purified by flash chromatography on a column of silica gel using gradient acetone in hexane as eluents.

**Methyl 3-O-benzoyl-4,6-O-benzylidene-α-D-galactopyranoside (3a)**

It (62 mg) was obtained in a 64% yield from 3. R_f 0.36. m.p. 136.5–138.5°C (recrystallized from EtOAc-hexane). [α]_D^{20} +227.0 (c 0.4, CHCl_3). Lit. data: [51] m.p. 139°C; [α]_D^{20} +235.7.

**Methyl 3-O-benzoyl-4,6-O-benzylidene-β-D-galactopyranoside (5a)**

It (73 mg) was obtained in a 76% yield from 5. Its properties were the same as mentioned above.

**Benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-galactopyranoside (6a)**

It (87 mg) was obtained in a 75% yield from 6. Its properties were the same as mentioned above.

**Methyl 3-O-benzoyl-4,6-O-benzylidene-α-D-mannopyranoside (10b)**

It (74 mg) was obtained in a 77% yield from 10. R_f 0.41. m.p. 128–130°C (recrystallized from EtOAc-hexane). [α]_D^{20} –23.5 (c 0.4, CHCl_3). Lit. data: [49] m.p. 131–132°C; [α]_D^{20} –24.

**Methyl 3-O-benzoyl-p-methoxy-4,6-O-benzylidene-α-D-mannopyranoside (11b)**

It (85 mg) was obtained in a 82% yield from 11. R_f 0.38. [α]_D^{20} –33.1 (c 0.3, CHCl_3). 1H NMR (300 MHz, CDCl_3): δ 8.09–8.02 (m, 2H, PhH), 7.59–7.31 (m, 5H, PhH), 6.85–6.80 (m, 2H, PhH), 5.56 (s, 1H, PhCH), 5.53 (dd, 1H, J = 3.3 Hz, J = 10.2 Hz, H-3), 4.79 (d, 1H, J = 1.4 Hz, H-1), 4.33–4.18 (m, 3H, H-2, H-4, H-6a), 4.03–3.84 (m, 2H, H-5, H-6b), 3.76 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3). 13C NMR (75 MHz, CDCl_3): δ 165.4, 159.9, 133.2, 129.7, 129.6, 128.3,
127.3, 113.5, 101.7, 101.4, 76.0, 71.4, 69.7, 68.7, 63.7, 55.2, 55.0. HRMS (ESI) calcd for C_{22}H_{24}O_{8}Na m/z (M+Na)^+: 439.1363. Found: 439.1350.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

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