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Efficient route to orthogonally protected precursors of 2-acylamino-2-deoxy-3-O-substituted-β-D-glucopyranose derivatives and use thereof

Julien Boutet [a,b], Tae Hee Kim [a,†], Catherine Guerreiro [a], Laurence A. Mulard [a,*]

[a] Institut Pasteur, Unité de Chimie des Biomolécules (CNRS URA 2128), 28 rue du Dr Roux, F-75015 Paris, France
[b] Université Paris Descartes, 12, rue de l'École de Médecine, F-75006 Paris, France

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ABSTRACT

An efficient route to two 3-*O*-acyl-2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-D-glucopyranosyl trichloroacetimidate donors is reported. As demonstrated for the 3-*O*-acetyl derivative, these building blocks are exquisite β-D-glucosamine donors when reacted either with simple alcohols or with complex oligosaccharides. Besides, their protection pattern is compatible with selective deprotection and subsequent chain elongation at O-3 of the newly incorporated glucosamine residue.

Carbohydrates are involved in a wide range of biological processes, including intercellular recognition events[1] and host-pathogen interactions.[2] Access to relevant oligosaccharides and glycoconjugates in pure form and sufficient amounts may open the way to efficient glycotherapeutics, along with an improved understanding of carbohydrate-mediated interactions. Along this line, this study reports on the preparation and use of yet undisclosed precursors to the N-substituted →3)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→moiety. On one hand, *N*-acyl-β-D-glucosamine derivatives substituted at O-3 are major components of cell wall peptidoglycan[3] and bacterial lipid A.[4] On the other hand, *N*-acetyl-β-D-glucosamine is an important glycan constituent,[5] frequently encountered in its 3-O-glycosylated form. As such, it was identified in structures of highly diverse origins, including hyaluronan,[6] glycolipids, and glycoproteins from human,[7] insects,[8] parasites,[9] or bacteria including *Shigella*.[10] *N*-Acetyl-β-D-glucosamine residues are involved in 1,2-*trans* glycosidic linkages whose construction from readily available *N*-acetyl-D-glucosamine is, despite recent progress in the field,[11,12] often impaired by the harsh conditions required due to the weak glycosyl donor properties of the intermediate oxazoline. When complex acceptors are involved, such glycosidations are best performed by use of donors bearing temporary N-protecting groups which are able to direct the stereochemical outcome of the condensation.[13] N-Protection removal followed by in situ acetylation then provides the most common access to the N-acetylated targets. Following the early disclosure of the *N*-phthaloyl group,[13] a number of additional cyclic *N*,*N*-diacyl protecting groups were investigated.[13–15] Alternatively, the convenient use of strongly electron-withdrawing N-protecting groups, such as the trifluoroacetyl,[16] trichloroacetyl,[17] or trichloroethoxycarbonyl[18] was reported. In the course of our investigation on *Shigella flexneri* oligosaccharides, various glucosamine donors differing in their N-protecting group pattern were evaluated.[19] Over the years, the N-trichloroacetyl derivative **1** (Fig. 1) was adopted for its efficiency as a glycosyl donor,[20] combined to the various conditions allowing *N*-trichloroacetyl conversion into acetamide. Those include basic trichloroacetyl removal and subsequent N-acetylation of the resulting amine,[21,22] or direct transformation under neutral conditions such as stannan-mediated radical hydrodechlorination[17,23] or palladium-mediated reductive hydrodechlorination.[20] Alternative methodologies involve conversion into readily deprotectable carbamates,[24] or microwave-assisted zinc reduction.[25]

Within our program on the synthesis of *S. flexneri* oligosaccharides, readily accessible orthogonally protected precursors to the →3)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→moiety, acting

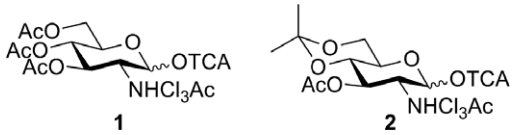

Figure 1. Structure of trichloroacetimidate donors **1** and **2**.

* Corresponding author. Tel.: +33 (0) 1 40 61 38 20; fax: +33 (0) 1 45 68 84 04.
E-mail address: lmulard@pasteur.fr (L. A. Mulard).
† Present address: Department of Bioengineering, University of Washington, 1705 NE Pacific Street, Seattle, WA 98195, USA.

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as donors and potential acceptors, were needed. Relying on our previous work on *S. flexneri* serotypes 2a and 5a O-antigen fragments, our investigation was restricted to building blocks bearing a 4,6-*O*-isopropylidene group.

Indeed, we showed early on that although used successfully in the synthesis of linear oligosaccharide fragments of *S. flexneri* serotype Y O-antigen, the more common 4,6-*O*-benzylidene glucosamine derivatives did not match the synthetic requirements associated to the serotype-specific branching pattern of *S. flexneri* 2a oligosaccharides.[26] Despite its higher sensitivity to acid hydrolysis, the 4,6-*O*-isopropylidene acetal was found as a suitable alternative and was adopted since then, including in the synthesis of a pentadecasaccharide.[23]

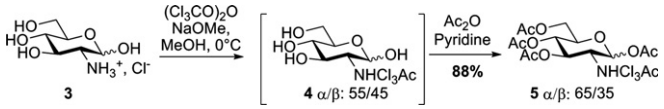
To our knowledge, 4,6-*O*-isopropylidene glucosamine acceptors, and occasionally donors,[27] have found applications in the synthesis of lipid A[28] and peptidoglycan[29] analogues or biosynthesis inhibitors.[30] Interestingly, they have scarcely been used as synthetic intermediates to complex oligosaccharides.[23,31] Overall, only two 2-azido-2-deoxy-4,6-*O*-isopropylidene glucopyranosyl trichloroacetimidate donors[27,32] and more recently a 2-*N*-trichloroethoxycarbonyl analogue[33] have been disclosed. The synthesis of derivative **2**, whose 3-*O*-acetyl moiety is selectively cleavable in the presence of a number of protecting groups, was therefore investigated. In the course of the study, an alternative to the standard N-trichloroacetylation procedure[17] was developed. Indeed, use of NaOMe/$(Cl_3CO)_2O$[34] ensured efficient conversion of **3** into trichloroacetamide **4**, as confirmed from the isolation of fully protected **5** (88%) as a 65/35 α/β mixture, following peracetylation of the crude material (Scheme 1).

Alternatively, crude **4** was advantageously reacted with 2-methoxypropene[35] and excess CSA to give hemiacetal **6** issued from the regioselective acetalation at O-4 and O-6 (Scheme 2). Conventional peracetylation of the crude material gave the fully protected intermediate **7** (70%, 3 steps). Interestingly, under these conditions, formation of the furanose derivative **8**, identified from the characteristic coupling constant of H-1 (6.26 ppm, $J_{1,2}$ = 4.9 Hz),[36] could not be totally avoided. Nevertheless, it was reduced to an acceptable 10% isolated yield over 3 steps, which compared favorably with the 30% yield obtained when using 1,2-dimethoxypropane. Turning **7** into trichloroacetimidate **2** first required selective anomeric de-O-acetylation. Use of hydrazine acetate in DMF[17] gave hemiacetal **9** in 78% only. Noteworthy, the isolated yield of **9** was brought up to 87% upon treatment of diacetate **7** with ethylenediamine/AcOH in THF.[37] Trichloroacetonitrile-mediated conversion of **9** into the target donor **2** (87%) was best performed by use of DBU as catalyst.[38] In the presence of weaker bases such as Cs_2CO_3 or K_2CO_3,[38] the reaction did not go to completion resulting in lower yields. Besides, formation of oxazoline **10** ($\delta_{H\text{-}1}$ = 7.18 ppm) was observed when Cs_2CO_3 served as base. However, due to the instability of hemiacetal **9** during column chromatography, a side-product, whose structure was tentatively assigned based on NMR data, to the unstable ketoaldehyde **11** derived from base-mediated H-2/3-acetate elimination and subsequent imine/enamine hydrolysis, was isolated. To our satisfaction, this side reaction was easily overcome upon direct conversion of crude hemiacetal **9** into trichloroacetimidate **2**[39] (80% from **7**). Taking advantage of this optimization process, large amounts of donor **2** can now be conveniently prepared in good overall yield from commercially available **3** (56% over 5 steps involving two purifications). Peracetylated donor **1** was easily prepared accordingly (76%, 4 steps).

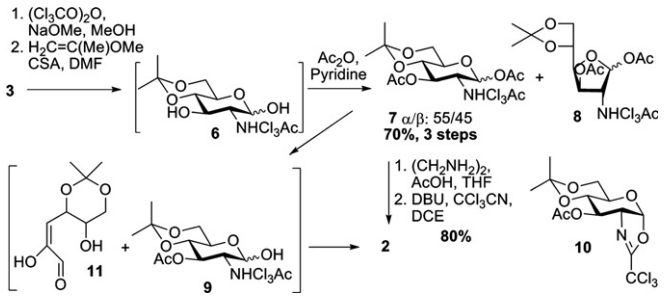
Assessing the donor properties of trichloroacetimidate **2** was next. In a preliminary investigation, allyl alcohol was used as a model acceptor. Conventional TMSOTf-mediated condensation of **2** with allyl alcohol (2 equiv) afforded as expected the novel β-allyl derivative **12**. The corresponding tri-*O*-acetyl donor **1**[17] provided **13** in a similar 83% yield (Scheme 3). To confirm that donor **2** was indeed suitable for efficient elongation at O-3 of the newly incorporated glucosamine residue, **12** served as a model to attempt deacetylation. Thus, saponification, allowing concomitant O-3/N-2 deprotection, followed by *in situ* selective N-acetylation, provided acceptor **14** (71%) otherwise obtained by isopropylidenation of the triol precursor.[29] Needless to say that the acetyl moiety could be replaced by a number of acyl groups if required.[28] Alternatively, aware of the well-known propensity of the acetamido group of glucosamine to interfere with glycosylation outcome,[40] we investigated the selective 3-O-deacetylation of **12**. Owing to possible trichloroacetyl loss during cleavage of an isolated ester,[20] reagents ensuring chemoselectivity were investigated. Optimized conditions involved K_2CO_3, readily eliminated upon filtration, to provide the trichloroacetamide acceptor **15** (94%). Interestingly in our hands, the overall yield of **15** from **3** according to this route (43%, 7 steps), was comparable to that involving donor **1** (49%, 7 steps).

Having demonstrated that the 4,6-*O*-isopropylidene acetal had no negative influence on the condensation outcome when using simple primary alcohols, and that it was fully compatible with both selective O-deacetylation or concomitant O,N-deacylation, we next turned to more complex acceptors (Scheme 4). Pentasaccharide **17**, compatible with chain elongation at O-3 of the glucosamine residue, was of interest in our ongoing study on *S. flexneri* 2a. The tetrasaccharide acceptor **16**,[20] reacted smoothly with donor **2** in the presence of catalytic TMSOTf to give pentasaccharide **17**[41] (96%). There again, the efficiency of **2** as donor matched that of the simpler analogue **1** providing **18** (98%) as reported previously.[20]

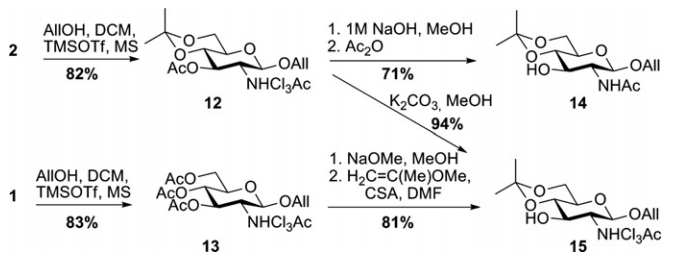
The use of donor **2** for the synthesis of *S. flexneri* 3a building blocks was thought more challenging, since the glucosamine residue is in that case part of a 2,3-*cis*-di-O-glycosylated branching



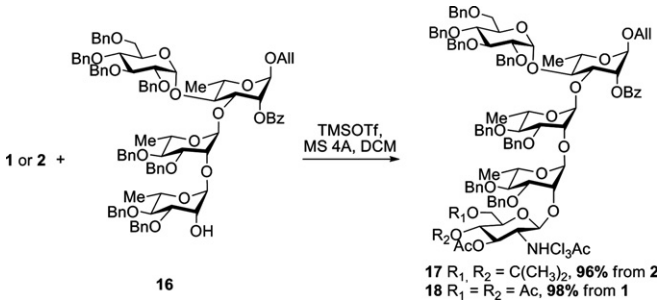
Scheme 1. Alternative synthesis of known intermediate **5**.



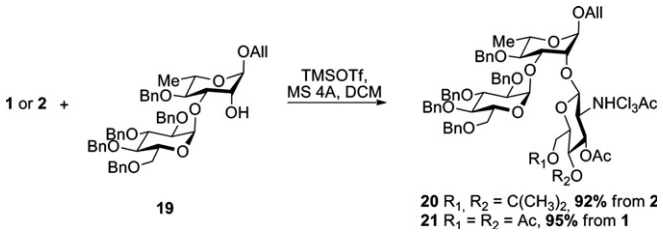
Scheme 2. Efficient synthesis of new trichloroacetimidate **2**.



Scheme 3. Readily access to acceptors **14** and **15** from donor **2**.



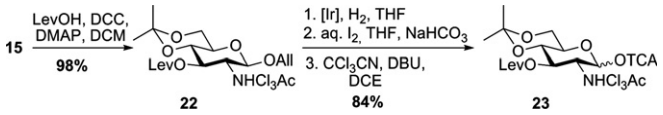
Scheme 4. Donor **2**: an efficient precursor to pentasaccharide **17**.



Scheme 5. Donor **2** as precursor to branched trisaccharide **20**.

pattern (Scheme 5). Nevertheless, coupling of donor **2** (1.4 equiv) with the known disaccharide acceptor[19] **19** gave the branched trisaccharide **20**[42] (90%). The measured $^{1}J_{C,H}$ constant at the glucosamine anomeric carbon ($^{1}J_{C,H}$ = 164 Hz) ascertained the β-stereoselectivity of the condensation.[43] For comparison, TMSOTf-mediated glycosylation of acceptor **19** and donor **1** (1.2 equiv) gave tri-*O*-acetyl **21** (92%). Possibly due to steric hindrance at the acceptor site, oxazoline **10** was identified as a side-product when using 0.2 equiv of TMSOTf to catalyze glycosylation of **19** and **2**. Fortunately, changing to 0.3 equiv allowed reopening of **10**.

Although the latter example tends to suggest that, in comparison to triacetate **1**, slightly higher amounts of both TMSOTf and donor **2** may be needed for successful introduction of an orthogonally protected glucosamine residue at sterically hindered positions, we are confident that the newly disclosed **2** has a broad potential as donor. However, we reasoned that the 3-*O*-acetyl moiety might be a limitation. In anticipation to possible orthogonality requirements with O-acetyl groups present on the target molecules, as, for example in *S. flexneri* 3a O-antigen,[10] the 3-*O*-levulinoyl analogue **23** was synthesized (Scheme 6). The β-allyl glycoside **22**, readily obtained from **15** (98%), served as the key intermediate. Conversion of **22** into **23** involved hemiacetal **24** issued from anomeric deallylation. The sensitivity of the isopropylidene group to acidic hydrolysis, added to the high propensity of hemiacetal **24** to form **11** following base-catalyzed elimination of the 3-O-acyl protection, implied careful deprotection monitoring. Thus, following conventional iridium(I)-catalyzed allyl isomerization,[44] the propenyl was cleaved in the presence of aqueous iodine and $NaHCO_3$ to avoid isopropylidene loss.[45] Direct activation of the crude material gave the target trichloroacetimidate donor **23**[46] (84%, 2 steps). Noteworthy, the strategy is applicable to other 3-O-protecting groups, including chloroacetyl. Indeed, we would like to



Scheme 6. Efficient synthesis of donor **23** from **15**.

emphasize that the acid-sensitivity of the 4,6-*O*-isopropylidene acetal prevented any transfer of the efficient methodology used to prepare 4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-2-trichloroacetamido-α-D-glucopyranosyl trichloroacetimidate.[47]

In summary, two new 2-deoxy-2-trichloroacetamido-D-glucopyranosyl trichloroacetimidate donors bearing a 4,6-*O*-isopropylidene protecting pattern are disclosed. Most interestingly, the synthesis of 3-O-acetylated **2** (56% on a 10 g scale) proceeded through an easily scalable five-step process. The high β-D-glucosamine donor potency and compatibility of **2** with possibly sterically hindered acceptors were demonstrated for simple primary alcohols as well as for a di- and a tetrasaccharide. Analogue **23**, protected at O-3 with a levulinoyl group, is proposed as a suitable alternative to **2** to answer the need for acetyl orthogonality as frequently encountered when dealing with bacterial polysaccharides. Trichloroacetimidate **23** is readily accessible from **2** (63%) via allyl glycoside **15**.

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42. Selected data for trisaccharide **20**: ^{13}C NMR ($CDCl_3$, 100 MHz) δ 101.8 ($C\text{-}1_D$, $^1J_{C,H}$ = 164.4 Hz), 100.1 (C_{iPr}), 98.7 ($C\text{-}1_A$, $^1J_{C,H}$ = 173.7 Hz), 94.9 ($C\text{-}1_E$, $^1J_{C,H}$ = 168.6 Hz), 93.1 (CCl_3), HRMS (ESI) for $C_{63}H_{72}Cl_3NO_{16}$ ($[M+Na]^+$, 1226.3814) *m*/*z* 1226.3860.
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46. Compound **23** (α anomer) had R_f = 0.55 (Tol/EtOAC), ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (s, 1H, =NH), 7.09 (d, 1H, $J_{NH,2}$ = 8.3 Hz, NH_{NTCA}), 6.42 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.33 (pt, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 4.36 (m, 1H, H-2), 3.92 (dd, 1H, $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = 9.2 Hz, H-6a), 3.90-3.84 (m, 2H, H-4, H-5), 3.81 (m, 1H, H-6b), 2.72 (m, 2H, CH_{2Lev}), 2.61 (m, 2H, CH_{2Lev}), 2.15 (s, 3H, CH_{3Lev}), 1.51 (s, 3H, H_{iPr}), 1.39 (s, 3H, H_{iPr}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.8 (C_{Lev}), 173.6 (C_{Lev}), 162.1 (C_{NTCA}), 160.2 (C=NH), 100.2 (C_{iPr}), 94.2 (C-1, $^1J_{C,H}$ = 180.9 Hz), 91.7 (CCl_3), 90.5 (CCl_3), 71.0 (C-4), 69.7 (C-3), 66.5 (C-5), 61.8 (C-6), 54.6 (C-2), 37.8 (CH_{2Lev}), 29.7 (CH_{3Lev}), 28.8 (C_{iPr}), 27.9 (CH_{2Lev}), 19.0 (C_{iPr}).
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