Tunable Activation of Glycosyl Trichloro- and (*N*-phenyl)trifluoroacetimidates with Ytterbium(III) Triflate: One-Pot Synthesis of Trisaccharides under Catalytic Conditions

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Abstract: A mild promoter such as $Yb(OTf)_3$ allows selective activation of glycosyl trichloroacetimidate building blocks in the presence of glycosyl (*N*-phenyl)trifluoroacetimidates with a similar pattern of protecting groups. This selectivity has been exploited in the one-pot assembly of two different trisaccharides in good overall yields. In contrast to other reported procedures, a catalytic amount of promoter is sufficient to trigger both glycosidation steps of the sequential process.

Key words: carbohydrates, glycosidations, ytterbium(III) triflate, solvent effects, stereoselectivity

One of most important recent advances in oligosaccharide synthesis is represented by the development of synthetic procedures enabling the construction of multiple glycosidic bonds in a one-pot fashion. These advances were strongly elicited by the recognition of the dramatic influence exerted by protecting groups on the reactivity of the glycosyl donors, an observation that has been elaborated in the 'armed' and 'disarmed' concept.[1] This tunable reactivity may be exploited in the sequential connection of several building blocks all bearing an identical leaving group.[2,3] Recently, this approach culminated in the development of a computer-assisted planning of oligosaccharide synthesis based on the preliminary assessment of the relative reactivity for a great number of protected or partially protected thioglycoside donors.[2]

In an alternative conceptual approach, the one-pot sequential multiglycosidation process can also take advantage of an available set of glycosyl donors activated under orthogonal conditions.[4] A further option is represented by the preactivation of a thioglycoside building block (donor) with a stoichiometric promoter and the subsequent addition of a partially protected thioglycoside which is intended to act at this stage as the acceptor, and the iteration of the sequence until the desired elongation is achieved.[5] This approach allows one to circumvent the normal reactivity of the building blocks, i.e. a disarmed thioglycoside can be selectively activated in the coupling with an armed thioglycoside. A less common approach contemplates the use of residues equipped with analogous but differentiated leaving groups (for example thioaryl and thioethyl glycosides) whose selective activation can be tuned by the proper choice of the experimental conditions.[3c,6]

The one-pot multiglycosidation procedures are more commonly accomplished with thioglycosides.[7] This is not surprising if one considers that partially non-protected thioglycosides, the necessary building blocks for this purpose, can be routinely prepared. Glycosyl fluorides, bromides,[8] selenides, sulfoxides[9] and underivatized hemiacetals[10] have also been used, especially in synthetic schemes relying on orthogonal activation.[4] These mentioned methodologies are all based on activation systems entailing at least a stoichiometric reagent (NIS, triflic anhydride, phenyl sulfoxide, silver triflate, Cp_2HfCl_2, $BF_3{\cdot}OEt_2$, etc). In contrast, use of glycosyl trichloroacetimidates[11] in multiglycosidation approaches is seriously restricted by the difficult preparation of saccharidic derivatives equipped with the trichloroacetimidate leaving group at the anomeric position while bearing a free accepting hydroxyl functionality. Indeed, the installation of the trichloroacetimidate leaving group is commonly carried out by reacting the sugar hemiacetal with trichloroacetonitrile in the presence of a catalytic amount of a base. Under similar conditions non-anomeric hydroxyl groups of sugars are also known to react, so that the trichloroacetimidate functionality may also be exploited for protection of non-anomeric alcohols.[12] As a matter of fact, use of glycosyl trichloroacetimidates in multiglycosidation approaches has been limited to the attachment of fragments at the non-reducing terminus of the targets and in combination with donors orthogonally activated under stoichiometric conditions, such as thio- and pentenyl glycosides.[13]

Recently, Yu and co-workers have introduced glycosyl (*N*-phenyl)trifluoracetimidates as a class of analogues of trichloroacetimidate donors.[14] On the other hand, in the course of our investigation aimed at establishing the development of glycosidation procedures relying on moisture stable promoters such as ytterbium(III) triflate,[15] we have realized that the activation of these novel donors is entailing relatively more forced conditions than their trichloroacetimidate analogues with a similar protection pattern. For example, the coupling in nitrile solvents between the trichloro donor **2** (1.4 equiv) and acceptor **1** (1 equiv) proceeds at –30 °C and requires a very low amount of catalyst (3%) whereas higher temperatures and

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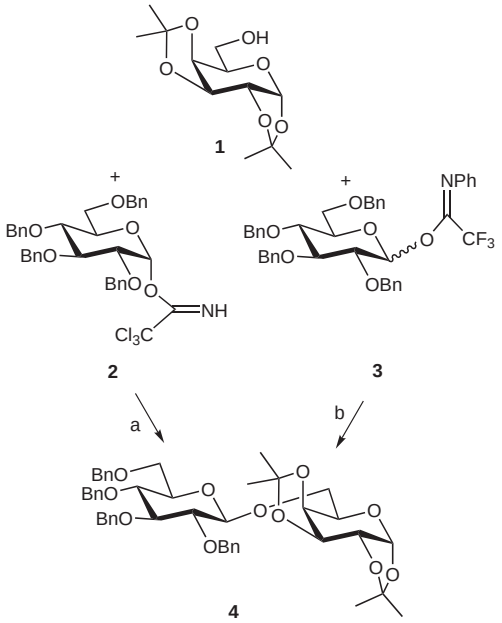
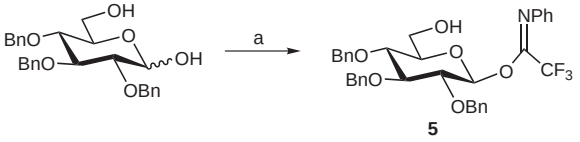
amounts of promoter (10%) are needed with the fluorinated donor **3** (Scheme 1).

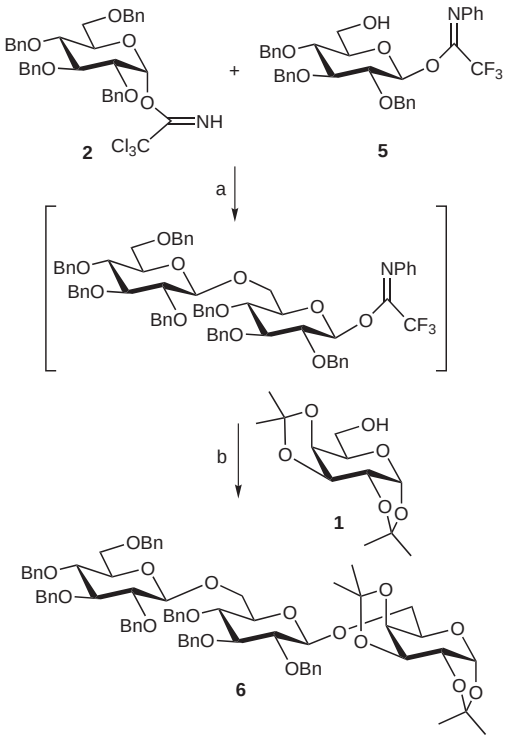


Scheme 1 *Reagents and conditions*: a) $Yb(OTf)_3$ (0.03 equiv), MeCN–*t*-BuCN 19:1, –30 °C, 1 h, 86% yield, a:b 9:8; b) $Yb(OTf)_3$ (0.10 equiv), MeCN–*t*-BuCN 6:1, from –25 °C to r.t., 5 h, 95% yield, a:b >10.

In both these experiments the lanthanide salt was added as a solution in pivalonitrile, the beneficial effect of such a cosolvent on both rate and β-selectivity having been recently disclosed.[16] This different behavior suggested the feasible development of a one-pot multiglycosidation procedure based on: *i*) selective activation of a trichloroacetimidate donor in the presence of a (*N*-phenyl)trifluoroacetimidate derivative bearing a free hydroxyl functionality (acting as the acceptor in the first glycosidation step), and *ii*) the subsequent addition of a further new acceptor and the adjustment of the conditions to achieve the activation of the less-reactive trifluoroacetimidate leaving group. For the accomplishment of this scheme the synthetic access to a partially protected glycosyl (*N*-phenyl)trifluoroacetimidate is necessary. In contrast to trichloroacetimidates, these derivatives appear less difficult to be prepared. Indeed, the installation of (*N*-phenyl)trifluoroacetimidate group entails a substitution reaction with (*N*-phenyl)trifluoroacetimidoyl chloride in the presence of a stoichiometric amount of a mild base (for instance K_2CO_3). Use of one equivalent of the base should allow the selective functionalization of the hemiacetal hydroxyl group in the presence of a second alcoholic function owing to the higher acidity of the former. Actually, in a recent report Yu and co-workers have attained this kind of selective functionalization on a disaccharide substrate.[17] However, in that example the non-anomeric hydroxyl was barely accessible so that the high selectivity observed may be ascribed to steric crowding. To demonstrate the generality of this selectivity the readily accessible 2,3,4-tri-*O*-benzyl glucopyranose[18] was reacted with (*N*-phenyl)trifluoroacetimidoyl chloride in the presence of a slight excess of K_2CO_3 in acetone to yield the desired derivative **5** in a satisfying isolated yield (Scheme 2).[19]



Scheme 2 *Reagents and conditions*: a) (*N*-phenyl)trifluoroacetimidoyl chloride (2 equiv), K_2CO_3 (1.1 equiv), acetone, r.t., 66% yield.

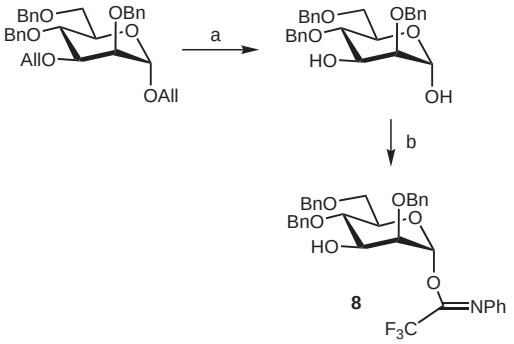


Scheme 3 *Reagents and conditions*: a) MeCN, $Yb(OTf)_3$ (0.03 equiv) in *t*-BuCN, –30 °C, 30 min; b) **1** in MeCN, $Yb(OTf)_3$ (0.07 equiv) in *t*-BuCN, from –30 °C to r.t., 5 h.

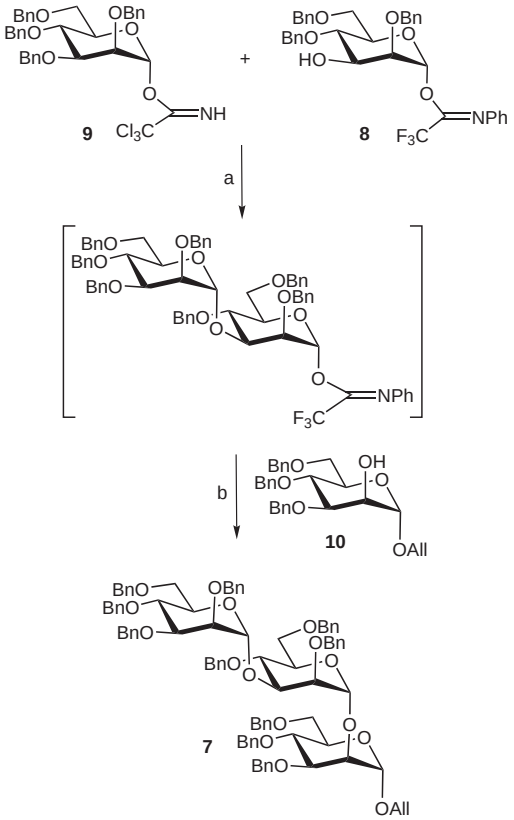
The successful access to this building block prompted us to test the 'one-pot' synthesis of the model trisaccharide **6** (Scheme 3). Initial mixing of **2** (1.4 equiv) and **5** (1 equiv) in acetonitrile at –30 °C in the presence of a low amount of $Yb(OTf)_3$ (0.03 equiv) led to the consumption of the more reactive compound **2** in less than one hour (TLC). Then acceptor **1** (1.4 equiv) was added together with a further amount of lanthanide triflate (0.07 equiv) and the mixture was allowed to slowly warm to room temperature. The desired trisaccharide was thus obtained in 55% yield slightly contaminated by anomeric by-products containing α-glycosidic bonds.[20]

To demonstrate the applicability of the approach also in ether solvents, generally adopted for obtaining the preferential generation of α-glycosides in the absence of a

participating effect on the donor, the protocol was examined for the synthesis of the mannan trisaccharide **7** (Scheme 5) representing the protected form of an important epitope of mannans from *Saccharomyces cerevisiae*.[21] To this aim, trifluoroacetimidate derivative **8**, with the free 3-OH, was readily prepared according to the sequence illustrated in Scheme 4. Known allyl 3-*O*-allyl-2,3,6-tri-*O*-benzyl-α-mannopyranoside[22] was submitted to a sequence of double deallylation and regioselective anomeric installation of the trifluoroacetimidate group that afforded the desired building block **8**.[19]



Scheme 4 *Reagents and conditions*: a) $PdCl_2$ (cat.) in MeOH, filtration; b) (*N*-phenyl)trifluoroacetimidoyl chloride (2 equiv), K_2CO_3 (1.1 equiv), acetone, r.t.; 38% yield over two steps.



Scheme 5 *Reagents and conditions*: a) 4:1 toluene–Et_2O, $Yb(OTf)_3$ (0.03 equiv) in dioxane, –10 °C, 1 h; b) **10** in 4:1 toluene–Et_2O, $Yb(OTf)_3$ (0.07 equiv) in dioxane from –10 °C to r.t., 3 h.

In this case the one-pot synthesis was performed in a solvent mixture containing dioxane and diethyl ether to maximize the α-selectivity of the $Yb(OTf)_3$-promoted glycosidation steps as suggested by our previous observations.[15] The initial coupling between **8** (1 equiv) and **9** (1.4 equiv) was performed at –10 °C under the agency of catalytic $Yb(OTf)_3$ (0.03 equiv, Scheme 5). After one hour, acceptor **10** (1.4 equiv) was added to the mixture together with an additional amount of promoter (0.07 equiv) and the temperature was allowed to rise. Chromatographic purification of the mixture afforded **7** as the only detectable trisaccharide in a good 40% overall yield.[23]

It should be noted that this result is comparable with the overall glycosidation yields reported in a recent synthesis of the analogous sequence by a conventional stepwise approach,[24] and with the results obtained in the one-pot synthesis of similar mannan sequences.[4d] On the other hand, to the best of our knowledge, the here-reported syntheses are representing the first examples of one-pot preparation of trisaccharides under catalytic activation (an overall 10% amount of promoter is sufficient for both glycosidation steps).

In conclusion, we have reported that the different reactivity of glycosyl trichloro- and (*N*-phenyl)trifluoroacetimidates can be suitably exploited for the one-pot assembly of trisaccharides without using the stoichiometric activation of the donors. In addition, a good stereocontrol was achieved without resorting to donors equipped with 'disarming' participating groups. In perspective, the inclusion of electronically disarmed building blocks in the proposed approach would offer a further element of flexibility, which can be useful for the one-pot assembly of even longer sequences.

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(19) **Procedure for the Synthesis of Glycosyl (*N*-Phenyl)trifluoroacetimidates from Diols.**
(*N*-Phenyl)trifluoroacetimidoyl chloride (55 mL, 0.45 mmol) was added at r.t. to a mixture of 2,3,4-tri-*O*-benzyl-glucopyranose (100 mg, 0.22 mmol) and K_2CO_3 (37 mg, 0.26 mmol) in acetone (2 mL). After ca. 2 h, a few drops of pyridine were added and the mixture was filtered on a short pad of neutral alumina (eluent: CH_2Cl_2). The residue was chromatographed on neutral aluminum oxide I (eluent: PE–EtOAc from 85:15 to 7:3) to yield **5** (91 mg, yield 66%) as an oil. An analogous procedure was adopted for the synthesis of **8** (38% over two steps).
Spectroscopic data of **5** (β-anomer): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–6.80 (aromatic protons), 5.75 (1 H, br s, H-1), 5.00–4.40 (benzyl CH_2), 4.00–3.20 (6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.3, 138.3, 137.8, 137.6, 129.3–127.8, 126.2, 124.4, 120.6, 119.3, 97.0 (C-1), 84.3, 81.0, 76.7, 76.0, 75.6, 75.2, 75.1, 61.4.
Spectroscopic data of **8** (α-anomer): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–6.80 (aromatic protons), 6.42 (1 H, br s, H-1), 4.95–4.55 (benzyl CH_2), 4.08 (1 H, td, $J_{2,3}$ = 3.3 Hz, $J_{3,OH} = J_{3,4}$ = 9.3 Hz, H-3), 4.00–3.70 (5 H), 2.45 (d, 3-OH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.4, 138.1, 138.0, 137.1, 128.7–127.5, 124.4, 120.6, 119.4, 94.7 (C-1), 76.0, 75.6, 75.1, 73.8, 73.4, 72.8, 71.3, 68.6.

(20) **Procedure for the One-Pot Synthesis of 6.**
Trichloroacetimidate **2** (38 mg, 56 mmol) and trifluoroacetimidate **5** (25 mg, 40 mmol) were co-evaporated three times in anhyd toluene and then, after the addition of freshly activated acid-washed molecular sieves, dissolved in MeCN (0.5 mL). The mixture was cooled at –30 °C and then a solution of $Yb(OTf)_3$ (0.7 mg, 1.2 mmol) in pivalonitrile (30 mL) was added. After consumption of the trichloroacetimidate donor (1 h), a solution of acceptor **1** (13 mg, 56 mmol) in MeCN (0.9 mL) and a further aliquot of $Yb(OTf)_3$ (1.6 mg, 2.8 mmol) in pivalonitrile (70 mL) were added and the mixture was allowed to warm spontaneously to r.t. A few drops of pyridine were added and the mixture was filtered on a short pad of silica gel. The residue was chromatographed on a silica gel column eluted with PE–EtOAc mixtures to yield trisaccharide **6** (27 mg, 55% yield) slightly contaminated by minor amounts of anomers.
Spectroscopic data of **6**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.22 (aromatic protons), 5.75 (1 H, d, $J_{1,2}$ = 4.8 Hz, H-1 Gal), 5.10–4.40 (16 H), 4.43 and 4.41 (2 H, 2 × d, $J_{1,2}$ = 7.2 Hz, 2 × H-1 Glc), 4.28 (1 H, dd, $J_{2,3}$ = 2.4 Hz, H-2 Gal), 4.25–3.40 (15 H), 1.50, 1.38, 1.30, 1.22 (12 H, 4 × s, acetonides CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.7, 138.6, 138.5, 138.2, 128.3–127.7, 109.3, 108.5, 104.4, 104.0, 96.3, 84.8, 84.5, 81.8, 81.5, 78.0, 77.8, 77.3, 77.1, 76.5, 75.7, 75.6, 75.0, 74.8, 74.7, 74.6, 74.2, 73.5, 71.3, 70.7, 70.5, 70.0, 68.9, 68.6, 67.4, 26.1, 25.9, 25.0, 24.4.

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(23) **Procedure for the One-Pot Synthesis of 7.**
Trichloroacetimidate **9** (58 mg, 85 mmol) and trifluoroacetimidate **8** (37 mg, 60 mmol) were coevaporated three times in anhyd toluene and then, after the addition of freshly activated acid washed molecular sieves, dissolved in 4:1 toluene–Et_2O (0.5 mL). The mixture was cooled at –10 °C and then a solution of $Yb(OTf)_3$ (1.2 mg, 1.7 mmol) in dioxane (100 mL) was added. After consumption of the trichloroacetimidate donor (ca. 30 min), a solution of acceptor **10** (41 mg, 84 mmol) in 4:1 toluene–Et_2O (1.2 mL) and a further aliquot of $Yb(OTf)_3$ (2.8 mg, 4.0 mmol) in dioxane (230 mL) were added and the mixture was allowed to warm spontaneously to r.t. After ca. 3 h, a few drops of pyridine were added and the mixture was filtered on a short pad of silica gel. The residue was chromatographed on a silica gel column eluted with PE–EtOAc mixtures to yield trisaccharide **7** (34 mg, 40% yield) as an oil.
Spectroscopic data of **7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–6.90 (aromatic protons), 5.83 (1H, m, $-CH_2CH{=}CH_2$), 5.25–5.22 (2 H, H-1 and $-CH_2CH{=}CH_{trans}$), 5.20 (1 H, d, $J_{1,2}$ = 1.2 Hz, H-1), 5.13 (1 H, br d, $J_{1,2}$ = 10.4 Hz, $-CH_2CH{=}CH_{cis}$), 4.97 (1 H, d, $J_{1,2}$ = 1.2 Hz, H-1), 4.90–4.30 (20 H), 4.21 (1 H, dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 8.4 Hz, H-3), 4.15–3.55 (19 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.9, 138.6, 138.5, 138.4, 138.3, 13.9, 128.3–127.0, 117.1, 99.5, 99.4, 98.2, 80.1, 79.9, 75.5, 75.3, 75.2, 75.0, 74.8, 73.3, 72.6, 72.3, 72.1, 71.8, 69.4, 68.9, 67.8.

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