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Total Synthesis

First Total Synthesis of Trehalose-Containing Branched Oligosaccharide OSE-1 of *Mycobacterium gordonae* (Strain 990)

Manishkumar A. Chaube and Suvarn S. Kulkarni*[a]

Abstract: The first total synthesis of the branched oligosaccharide OSE-1 of *Mycobacterium gordonae* (strain 990) is reported. An intramolecular aglycon delivery approach was used for constructing the desymmetrized 1,1′-α,α-linked trehalose moiety. A [3+2] glycosylation of the trisaccharide donor and trehalose acceptor furnished the right hand side pentasaccharide. Regioselective O3 glycosylation of L-rhamnosyl 2,3-diol allowed expedient synthesis of the left hand side tetrasaccharide. The nonasaccharide was assembled in a highly convergent fashion through a [4+5] glycosylation.

Despite many decades of intense research, tuberculosis (Tb) remains one of the deadliest infectious diseases.[1] Emergence of multi-drug-resistant strains[2] and its co-infection with HIV[3] has further complicated the Tb prognosis and treatment, making it a leading public health risk worldwide. Moreover, during last few years, it is being observed that diseases due to non-tubercular mycobacteria (NTM) are on the rise.[4] Especially in AIDS patients, infections due to NTM are causing serious problems, which are incurable.[5] Among various kinds of NTM isolated from soil and water, *Mycobacterium gordonae* is an important one. Initially, *M. gordonae* was considered to be a friendly bacterium but, due to the observed infections in patients with prosthetic devices, compromised immunity, chronic pulmonary disease, or a history of trauma, it is considered as a potential opportunistic respiratory tract pathogen.[6] In addition, a number of infections involving skin, soft tissues, liver, respiratory tract, and underlying immuno-suppression have been reported. In particular, in the case of individuals with advanced immunodeficiency (such as AIDS) and who are susceptible to a wide variety of microorganisms of low pathogenicity, these infections cause pulmonary diseases virtually indistinguishable from Tb. Such patients are often started on antituberculosis drugs such as isoniazid, pyrazinamide, ethambutol, and cycloserine, to which *M. gordonae* is resistant.[6,7] To avoid this confusion, the diagnosis of atypical mycobacteria is important. The highly antigenic cell-wall components of the mycobacteria are potential candidates for serodiagnosis.

Over the past few years there have been remarkable advances in the identification of bacterial glycans.[8] In a recent study, Seeberger and co-workers presented a comparative bioinformatics analysis of the mammalian and bacterial glycomes in which the most abundant bacterial monosaccharides and linkages were statistically evaluated.[9]

In 1993, Besra et al.[10] demonstrated that the basis of serореactivity and diversity in *M. gordonae* is a novel series of alkali-labile trehalose containing lipooligosaccharides (LOS). The structure of the major branched oligosaccharide of *M. gordonae* strain 990 was established as α-L-Rha*p*-(1→2)-3-*O*-CH_3-α-L-Rha*p*-(1→3)-[β-D-Xyl*p*-(1→2)-]-α-L-Rha*p*-(1→3)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-α-L-Rha*p*-(1→3)-6-*O*-CH_3-α-D-Glc*p*-(1↔1)-α-D-Glc*p* and referred to as OSE-1 (Figure 1). The branched oligosaccharide OSE-1 **1** being antigenic can produce a specific immune response in the host by developing specific antigens and thereby allow a rapid serodiagnosis of the mycobacterial infection. Thus, procurement of OSE-1 through chemical synthesis is highly warranted.

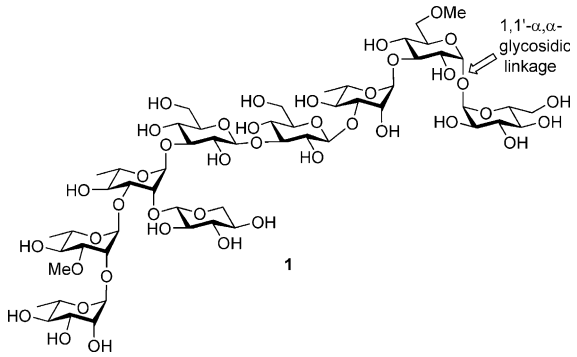

Figure 1. Structure of OSE-1 **1** from *Mycobacterium gordonae* strain 990.

Total synthesis of OSE-1 has not been reported to date, although there are some advances towards this goal. Gurjar et al. reported the synthesis of the terminal, branched tetrasaccharide of OSE-1.[11] Misra and co-workers reported a linear synthesis of the heptasaccharide.[12] However, these fragments lack the biologically important 6′-OMe 1,1′-α,α-trehalose moiety. In continuation of our studies towards the synthesis of trehalose glycoconjugates,[13] herein we report the first total synthesis of OSE-1.

A major challenge involved in the synthesis of OSE-1 is the construction of the unsymmetrically substituted 1,1′-α,α-treha-

[a] *M. A. Chaube, Prof. Dr. S. S. Kulkarni*
Department of Chemistry
Indian Institute of Technology Bombay
Powai, Mumbai, 400076 (India)
E-mail: suvarn@chem.iitb.ac.in

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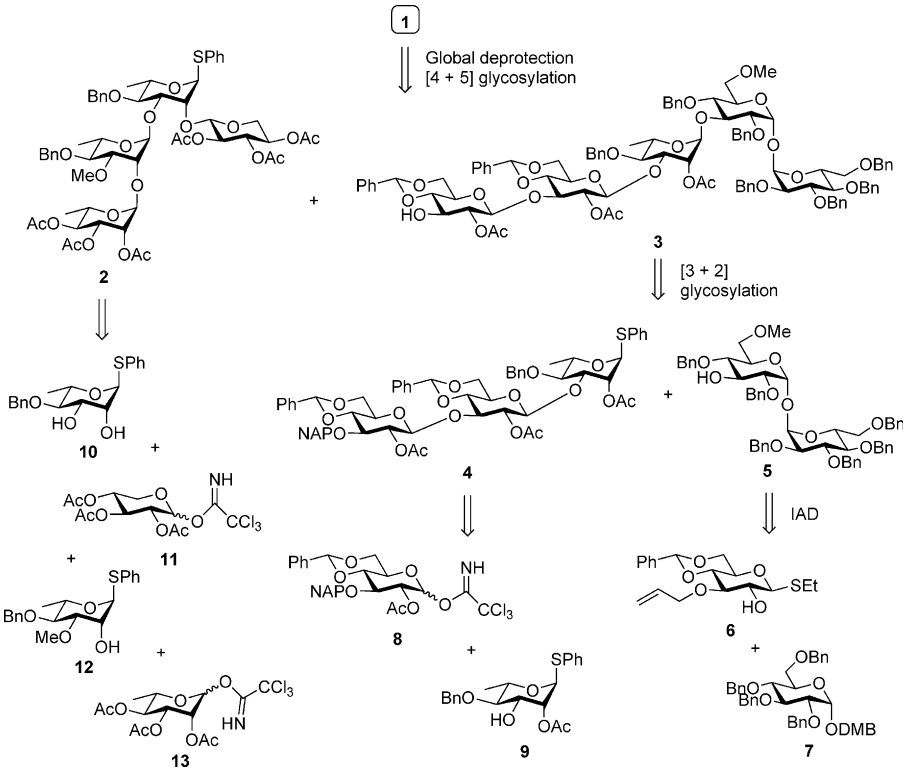
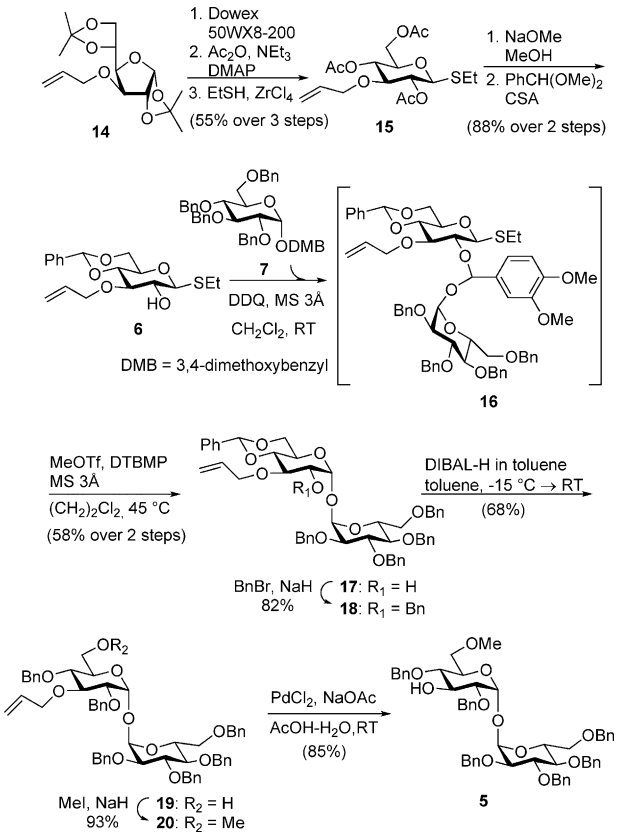
lose disaccharide bearing a methyl group at one of the termini. Moreover, the methyl group bearing a D-glucopyranoside unit should also be equipped with a temporary protecting group at the O3′ position so that it can be selectively removed prior to attachment with the L-rhamnose end of the oligosaccharide. There are a few methods reported in the literature for constructing the 1,1′-α,α-glycosidic bond.[14–16] However, most of the methods are limited by poor anomeric selectivity of the glycosylation step, as not one but two anomeric linkages are formed simultaneously and four products are possible in the case of unsymmetrical derivatives. To tackle this problem, Bertozzi and co-workers reported for the first time a methodology for the synthesis of 1,1′-α,α-trehalose derivatives, using Ito's variant[17] of intramolecular aglycon delivery (IAD).[16] In this method, the glucosyl donor and acceptor molecules are oxidatively tethered and oriented prior to activation in such a way that only the desired 1,1′-α,α-stereoisomer can be formed. This elegant method is so far the best among all the existing methods for the formation of unsymmetrically substituted 1,1′-α,α-trehalose derivatives. Alternatively, one can use commercially available trehalose. However, regioselective differentiation of chemically similar, six secondary hydroxyl groups, in the C_2 symmetrical, non-reducing disaccharide is again a challenge.[18] Owing to its convergent nature and exclusive stereoselectivity, the IAD method[16] seemed more appropriate for our purpose.

Our retrosynthetic strategy entailed a convergent assembly of the nonasaccharide, as shown in Scheme 1. It was envisaged that the target molecule **1** could be obtained upon global deprotection from its fully protected precursor, which could be constructed by a [4+5] glycosylation between the tetrasaccharide thioglycoside donor **2** and the pentasaccharide acceptor **3**. The pentasaccharide could be synthesized by a [3+2] glycosylation between the trisaccharide thioglycoside donor **4** and the 6′-OMe trehalose acceptor **5**, which in turn could be synthesized from D-glucose-derived building blocks **6** and **7** employing the IAD reaction. The trisaccharide donor **4** could be obtained by glycosylation of monosaccharide building blocks **8** and **9**. The terminal tetrasaccharide donor **2** could be assembled starting from the monosaccharide building blocks **10**, **11**, **12**, and **13** through sequential couplings.

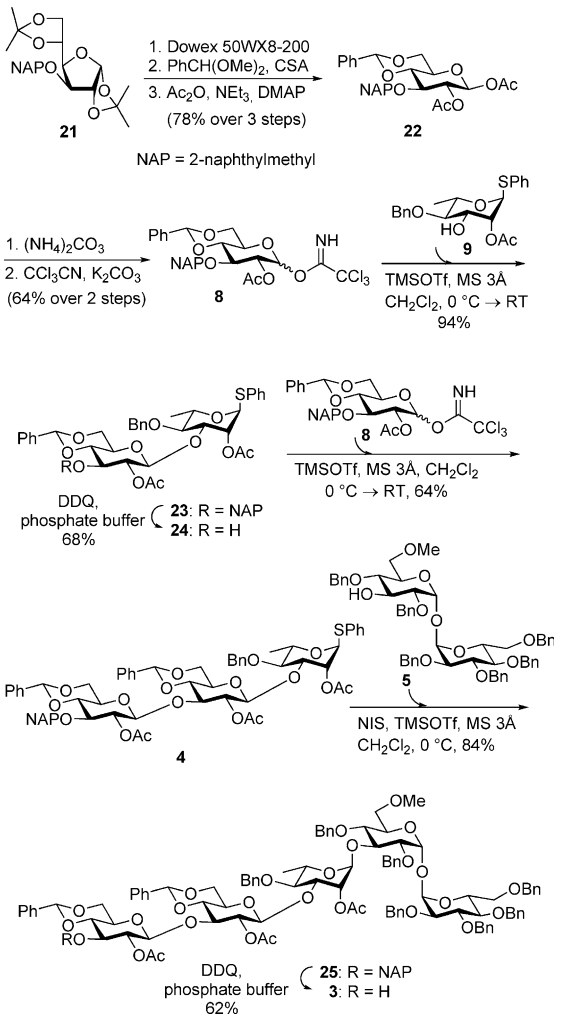
Our synthesis began with the construction of the unique 1,1′-α,α-trehalose acceptor **5** through the IAD route (Scheme 2). For this purpose, the known 3-*O*-allyl diacetone glucose **14**,[19] obtained by allylation of diacetone glucose, was converted into its pyranose form thioglycoside **15** in three steps (55% overall) through acid hydrolysis of the acetonides, per-*O*-acetylation, and concomitant nucleophilic displacement of the anomeric acetate by ethanethiol. Removal of acetates in **15** using NaOMe in MeOH and benzylidene protection of the 4,6-diol furnished the suitably protected 2-OH derivative **6** in 88% yield over two steps. The key IAD reaction of **6** and easily accessible α-linked dimethoxybenzyl (DMB) glycoside **7**[16a] was conducted next. Compound **6** was first linked with **7** by oxidation of the DMB ether using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to form the mixed acetal **16**, which upon aqueous work up was subsequently activated using methyl trifluoromethanesulfonate[16b] to afford the unsymmetrically substituted 1,1′-α,α-trehalose derivative **17** exclusively in 58% yield over two steps. The stereochemistry of the newly installed glycosidic linkage in **17** was assigned through ^{1}H, ^{13}C, and 2D NMR. The ^{1}H NMR spectrum of **17** showed two overlapping doublets for 1H each at $\delta = 5.19$ ($J = 2.8$ Hz) and 5.18 ppm ($J = 3.1$ Hz) corresponding to the H-1 and H-1′ of trehalose. ^{13}C NMR spectrum of **17** showed two separate peaks for the 1,1′-linked glucosides at $\delta = 95.3$ and 93.8 ppm with characteristic $^1J_{CH}$ coupling constants of 170 and 169 Hz, respectively, confirming the α,α-linkage (see the Supporting Information).[20] The free hydroxyl group in **17** was protected as benzyl ether to afford the fully protected trehalose building block **18** (benzyl bromide, NaH, 82%). A regioselective reductive ring opening of the 4,6-*O*-benzylidene acetal in **18** using DIBAL-H[13b,21] in toluene furnished the primary alcohol **19** (68%), as a major isomer



Scheme 1. Retrosynthetic analysis of OSE-1 **1**.



Scheme 2. Synthesis of unsymmetrically substituted 1,1′-α,α-trehalose using IAD reaction.



Scheme 3. Synthesis of pentasaccharide acceptor **3**.

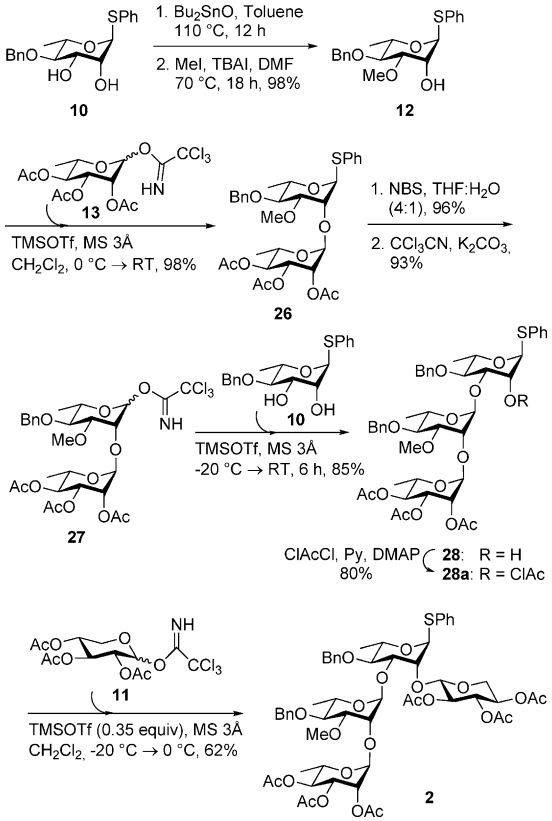
along with a minor 4-OH isomer (13%) and recovered starting material **18** (17%), which was recycled. Compound **19** was subsequently methylated using methyl iodide and NaH as a base to afford 6′-OMe derivative **20** (93%). The *O*-allyl group in **20** was selectively cleaved with palladium chloride[22] and sodium acetate to furnish the desired 3′-OH trehalose acceptor **5** in 85% yield.

With the requisite right hand side trehalose unit in hand, we proceeded further to assemble the pentasaccharide fragment (Scheme 3). For this, the trisaccharide skeleton was first constructed starting from the known 3-*O*-naphthylmethyl diacetone glucose **21**.[23] Acid hydrolysis of both the isopropylidene groups in **21**, to switch from furanose to pyranose form,[16b] followed by benzylidene protection of 4,6-diol and 1,2-di-*O*-acetylation, afforded compound **22** in 78% yield over three steps. The anomeric acetate in **22** was selectively removed by ammonium carbonate[24] in 64% yield, with recovery of the starting material to the extent of 30%. The resulting hemiacetal was converted quantitatively into the trichloroacetimidate (TCA) donor **8** using trichloroacetonitrile and potassium carbonate.[25]

Glycosylation of TCA donor **8** with the known L-rhamnose acceptor **9**[26] using 0.1 equiv of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as a promoter resulted in the formation of 1:1 mixture of the desired product **23** and the corresponding orthoester, which could be rearranged to the product **23** upon adding extra 0.15 equiv TMSOTf to the mixture. Alternatively, the use of 0.25 equiv of TMSOTf smoothly delivered β-linked disaccharide **23** in 94% yield. The characteristic NMR signals [^{1}H NMR $\delta = 4.73$ ppm (d, 1H, $J = 7.8$ Hz, H-1β), ^{13}C NMR $\delta = 101.4$ ppm] confirmed the β-linkage of the newly formed glycosidic bond in **23**. Next, the 2-naphthylmethyl group in **23** was selectively cleaved using DDQ to afford the disaccharide acceptor **24** in 68% yield, which was again coupled with the donor **8** using TMSOTf (0.35 equiv) as a promoter to furnish the β-linked trisaccharide donor **4** in 64% yield. Here, the yield could not be further improved because of the competing formation of the corresponding orthoester, which could not be rearranged even after adding 0.5 equiv of TMSOTf. The structure of trisaccharide **4** was confirmed by NMR analysis [^{1}H $\delta =$ 4.75 (d, 1H, $J = 7.7$ Hz, H-1β), 4.66 (d, 1H, $J = 7.2$ Hz, H-1β), 5.41 ppm (s, 1H, H-1α), ^{13}C NMR $\delta = 101.1$, 100.9, 85.6 ppm]. Next, the thioglycoside donor **4** and the trehalose acceptor **5** were glycosylated under NIS and TMSOTf conditions to furnish the pentasaccharide **25** in 84% yield. The 1,2-*trans* selectivity in these three consecutive glycosylations was assured by neighboring group participation of the C2-acetate groups. The structure was assigned by ^{1}H NMR, ^{13}C NMR and calculation of $^1J_{CH}$ through a partially decoupled ^{13}C NMR experiment and HSQC correlation. We observed six peaks in ^{13}C NMR in the

range $\delta = 101.4–94.0$ ppm, which included a tall peak corresponding to two benzylidenes ($\delta = 101.2$ ppm, $^1J_{CH} = 158$) and five anomeric carbons at $\delta = 101.4$ ($^1J_{CH} = 160$, β), 100.9 ($^1J_{CH} = 155$, β), 97.6 ($^1J_{CH} = 171$, α), 94.8 ($^1J_{CH} = 171$, α), and 94.0 ppm ($^1J_{CH} = 168$, α). The 2-naphthylmethyl group in **25** was selectively removed using DDQ at pH 7[27] to afford the pentasaccharide acceptor **3** in 62% yield. It should be mentioned that the use of phosphate buffer was essential, without which the yield of **3** dropped to 25%.

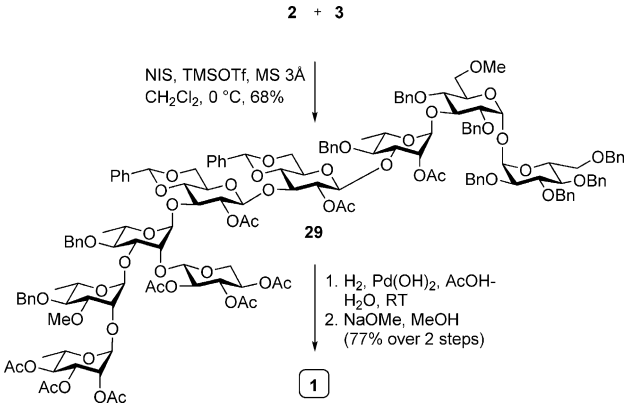
After successfully synthesizing the pentasaccharide fragment, we proceeded further to assemble the left-hand tetrasaccharide part, starting from the nonreducing end to the reducing end. As shown in Scheme 4, the known L-rhamnosyl 2,3-diol **10**[28] was converted into its tin acetal by using dibutyltin oxide in toluene at 110 °C, which was further reacted with



Scheme 4. Synthesis of tetrasaccharide donor **2**.

methyl iodide and catalytic tetrabutylammonium iodide in DMF to afford the 3-*O*-methylated compound **12** in excellent yield and regioselectivity (98%).[29] The O3 regioselectivity was confirmed by carrying out acetylation of **12** and observing a downfield shift of the H2 proton in the ^{1}H NMR spectrum ($\delta = 5.44$ ppm, dd, $J = 1.6$ and 3.2 Hz), assigned through ^{1}H-^{1}H COSY analysis. The known TCA donor **13**[30] and the 2-OH acceptor **12** were orthogonally glycosylated using TMSOTf as a promoter to afford the α-linked disaccharide **26** in 98% yield. The ^{1}H NMR of **26** displayed two downfield doublets at $\delta = 5.47$ and 5.01 ppm with $J = 1.5$ Hz each, indicating α-glycosidic linkages. In its ^{13}C NMR spectrum, two peaks were observed in the anomeric region at $\delta = 101.4$ and 85.7 ppm with characteristic coupling constants $^1J_{CH} = 174$ and 165 Hz, respectively confirming α-configurations for C1′ and C1.[11,31] The disaccharide thioglycoside **26** was then treated with NBS[32] in THF:H_2O to yield the corresponding disaccharide hemiacetal (96%), which was converted to the TCA donor **27** (93%, $\alpha/\beta = 1:0.8$). A highly regioselective orthogonal glycosylation of TCA donor **27** with the known 2,3-diol **10**[28] under controlled conditions (0.1 equiv TMSOTf and addition at −20 °C) afforded the desired 3-*O*-linked trisaccharide **28** in 85% yield as a single product. The regioselectivity of the glycosylation step was confirmed by capping the free 2-OH by chloroacetate group and observing the downfield shift of the characteristic H-2 peak ($\delta = 5.46$ ppm, dd, $J = 1.6$ and 2.8 Hz) in the ^{1}H NMR of **28a**, assigned through ^{1}H-^{1}H COSY analysis. The H-3 proton gave an upfield dd at $\delta = 4.10$ ppm with $J = 3.0$ and 9.6 Hz. The α-stereoselectivity was further confirmed by recording a partially decoupled ^{13}C NMR spectrum of **28** and calculating the CH coupling constant of the newly formed glycosidic bond. The ^{13}C NMR spectrum of **28** showed peaks at $\delta = 101.0$, 99.2, and 87.4 ppm with $^1J_{CH}$ coupling constants of 168, 168, and 166 Hz, respectively, confirming three consecutive α-linkages.[11,31] The branching unit D-xylose was then introduced at the O2 position of L-rhamnose by glycosylation of the known 2,3,4-tri-*O*-acetyl-D-xylose TCA donor **11**[33] with the trisaccharide acceptor **28** using 0.35 equiv TMSOTf to afford the desired β-xylose linked tetrasaccharide **2** (62%). Peaks in ^{1}H NMR at $\delta = 4.76$ ppm(d, 1H, $J = 7.5$ Hz, H-1β) and ^{13}C NMR peak at $\delta = 102.4$ ppm confirmed the β-glycosidic linkage of the newly formed bond.

The assembly of nonasaccharide OSE-1 and final deprotection was carried out as shown in Scheme 5. The tetrasaccharide thioglycoside donor **2** was glycosylated with the pentasaccharide acceptor **3** under NIS and TMSOTf conditions to afford the fully protected nonasaccharide **29** in 68% yield. The structure of nonasaccharide was assigned by ^{1}H NMR, ^{13}C NMR, and calculation of $^1J_{CH}$ through a ^{13}C–^{1}H coupled HSQC experiment on a 750 MHz machine, which showed a total of eleven carbon in the $\delta = 94–103$ ppm range, including nine anomeric carbons (3β and 6α) and two benzylidene carbons at $\delta = 94.0$ ($^1J_{CH} =$



Scheme 5. Synthesis of target molecule OSE-1 **1**.

174 Hz, α), 94.7($^1J_{CH}$ = 173 Hz, α), 97.6 ($^1J_{CH}$ = 179 Hz, α), 99.2 ($^1J_{CH}$ = 178 Hz, α), 100.0 ($^1J_{CH}$ = 167 Hz, β), 101.0 ($^1J_{CH}$ = 166 Hz, *PhCH*), 101.3 ($^1J_{CH}$ = 176 Hz, α), 101.2 ($^1J_{CH}$ = 173 Hz, α), 101.7 ($^1J_{CH}$ = 164 Hz, β), 102.0 ($^1J_{CH}$ = 167 Hz, *PhCH*), and 102.4 ppm ($^1J_{CH}$ = 167 Hz, β). The ^{1}H detected ^{13}C–^{1}H coupled HSQC experiment (see the Supporting Information) allowed us to calculate the C–H coupling constants at a lower concentration and in much lesser time which was not possible with a standard one dimensional ^{13}C-detected partial decoupling experiment due to significant overlapping of peaks. Using this technique, slightly higher values of $^1J_{CH}$ coupling constants (approx. 4 Hz) were observed, which were consistent.

Global deprotection of nonasaccharide **29** was carried out in two steps; hydrogenation in the presence of palladium hydroxide in 50% acetic acid removed the benzyls and benzylidene protecting groups,[34] whereas the acetates were removed using sodium methoxide. Subsequent chromatographic purification using a Sephadex G-25 column in MeOH/water system afforded the target molecule OSE-1 **1** (77% over two steps).

In conclusion, we have reported the first total synthesis of oligosaccharide OSE-1 of *M. gordonae* (strain 990) in a highly convergent manner. The potent desymmetrized trehalose moiety with 6′-OMe functionality was prepared using intramolecular aglycon delivery method. In the course of our studies, we also explored a highly O3 regioselective glycosylation of L-rhamnosyl 2,3-diol. The target molecule can be used for the speedy serodiagnosis of the infection and for the development of the vaccine candidate against *M. gordonae*.

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Keywords: 1,1′-α,α-glycosylation · total synthesis · *Mycobacterium gordonae* · regioselective glycosylation · trehalose oligosaccharides

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