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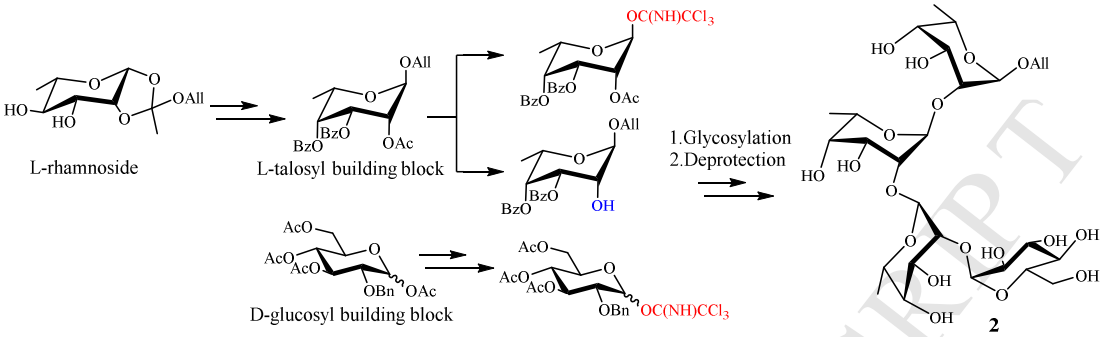

Efficient synthesis of a 6-deoxy-talose containing tetrasccharide found in *Franconibacter helveticus* LMG23732^{T}

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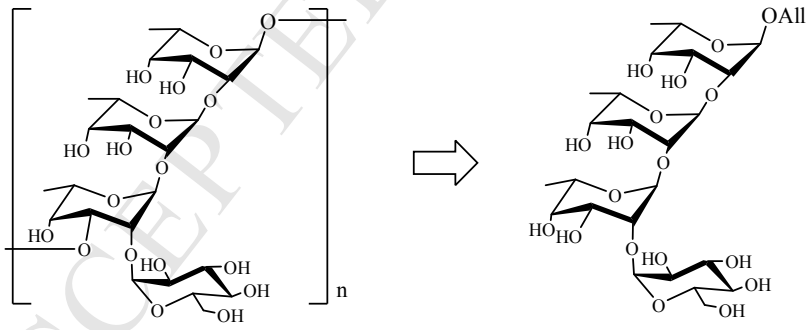
Abstract

Synthesis of the 6-deoxy-talose (6-dTal) containing tetrasaccharide, naturally found in *Franconibacter helveticus* LMG23732T, has been described. The synthetic method utilized an allyloxyethylidene group for protecting the 1-OH and 2-OH groups of rhamnopyranose and a redox reaction for synthesizing 6-deoxy talose, which eventually formed a disaccharide containing α-Glc*p*-(1→2)-6dTal*p* configured glycosidic bonds using a [2+2] synthetic strategy.

Keywords: *Franconibacter helveticus*; Lipopolysaccharides; O-specific polysaccharide; Tetrasaccharide; Synthesis

1. Introduction

Lipopolysaccharides (LPSs) are the structural components of the outer cell membranes of Gram-negative bacteria. The chemical structure of LPS is comprised of three distinct domains: lipid A, a core oligosaccharide, and the O-polysaccharide (O-PS) [1-4]. Among these domains, the O-PS, which is exposed to the external environment, is significantly involved in host-pathogen cross-talk[5-7]. The inner structure of the O-PS typically consisted of multiple repeating units of 1-4 monosaccharide residues. The antigenic nature of these glycans renders them suitable as targets for vaccine development [8-11]. Recent reports showed that the repeating units of the O-chain polysaccharide (OPS) of the lipopolysaccharides of *Franconibacter* LMG23732^T possess an unusual structural feature that consists of three 6-deoxy sugars [6-deoxy-talose (6-dTal)] in the main chain and one D-Glc*p* as the terminal branch [12] (scheme 1):

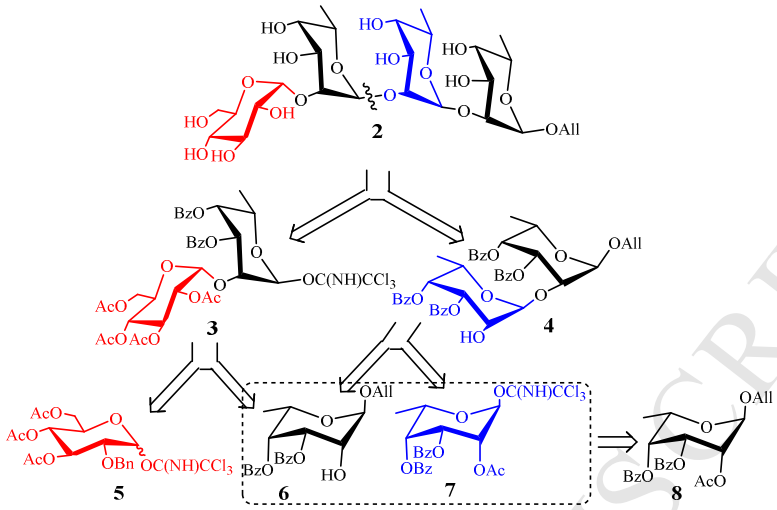


1 **2**

Scheme **1**. The repeating unit of LPSs from the bacterium *Franconibacter helveticus* LMG23732^T (**1**) and the synthesized oligosaccharide (**2**).

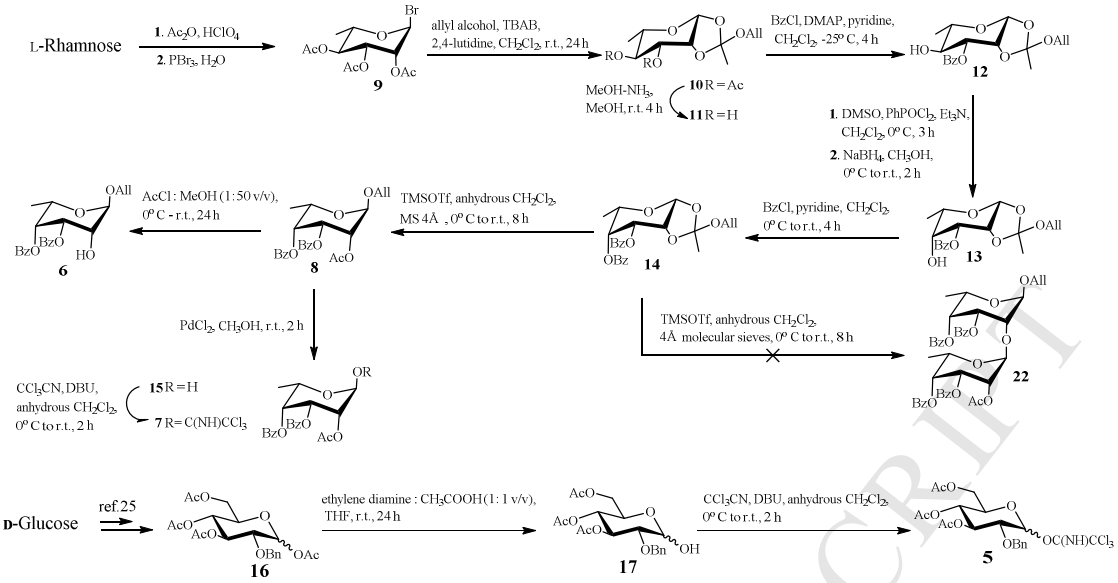
6-Deoxy-L-talose is present in many biologically important glycopeptidolipids (GPLs)[13-17] and antigenic bacterial lipopolysaccharides (LPSs) [18-23], where the O-2 or O-3 is glycosylated by other sugar units. The active involvement of these carbohydrates in bacterial physiology and pathogenesis inspired many scientists to synthesize LPS oligosaccharides and study their structure-bioactivity relationships. The present investigation was aimed at synthesizing a well-defined tetrasaccharide repeating unit (scheme 1) of LPSs present in the outer cell membrane of the bacterium *Franconibacter helveticus* LMG23732T.

2. Results and discussion



Scheme **2**. The retrosynthesis strategy for synthesizing target tetrasaccharide (2)

The synthesis strategy of tetrasaccharide **2** is outlined in Scheme 2. Since Fraser-Reid and co-workers observed that O-allyl substitution could be selectively deprotected by N-bromosuccinimide[24], the amount of glycoside synthesis were involved in allyl group as a protection strategy[25-28]. The allyl glycoside was stable and easily prepared [29-32]; moreover, it could be selectively oxidized to O-formylmethyl glycoside, which was an important intermediate in the synthesis of many activite molecules [33-35]. Therefore, we selected the allyl moiety as the anomeric protected group and the allyl glycoside as the end of the target oligosaccharide in this study, which might also be used in future investigations on this tetrasaccharide. The retrosynthetic analysis indicates that tetrasaccharide **2** can be prepared through a convergent strategy involving [2+2] glycosylation of two disaccharides: the disaccharide donor **3** and the disaccharide acceptor **4**. These two disaccharides **3** and **4** can be synthesized from glucose- or talose-derived building blocks (**5**, **6**, **7** and **8)**. The compound **8** can be transformed to **6** or **7** by suitable modifications, and utilized for synthesizing the disaccharides **3** and **4**.



Scheme **3**. The synthesis of glucose- or talose-derived monosaccharide building blocks

L-talosyl acceptor **6** and L-talosyl donor **7** were prepared from the same intermediate **9** following the synthetic strategy as described in the scheme 3. The intermediate **3** was synthesized following seven steps from the commercially available L-rhamnose[36]. The compound **9** was treated with allyl alcohol in the presence of 2,4-lutidine and tetrabutylammonium bromide (TBAB) to obtain **10**. The crude product was deacetylated using MeOH-NH_3, and the reaction mixture was concentrated and co-evaporated with toluene to obtain **11**. The C-3 hydroxyl group of **11** was selectively acylated with benzoyl chloride in dichloromethane at −25^o C, in the presence of pyridine and catalytic amounts of 4-dimethylaminopyridine(DMAP) to obtain 3-*O*-benzoyl-1,2-*O*-allyloxyethylidene-β-L-talopyranose (**12**) (yield: 72%). The regioselectivity was not surprising since the equatorially oriented 3-OH is more reactive than the axial 2-OH or 4-OH. Similar regioselective protection was observed for rhamno- and taloside derivatives.[17, 20] The equatorial 4-OH of the compound **12** was oxidized to ketone using dimethyl sulfoxide (DMSO), triethylamine, and phenylphosphonic dichloride, and the ketone was subsequently reduced to axial 4-OH by treating with $NaBH_4$ in the presence of MeOH (one-pot-reaction method)[17] to obtain compound **13** (yield: 54%). These structural modifications were confirmed by the ^{1}H NMR spectrum: the H-3 coupling constants of compound **12** (dd, *J* 4.1 Hz and 9.6 Hz at *δ* 5.16−5.21) were compared to that of the compound **13** (t, *J* 2.5 Hz at *δ* 5.63−5.64) for confirming the correct relative configuration. Benzoylation of the 4-OH of compound **13** yielded the 3,4-di-*O*-benzoyl-1,2-*O*-allyloxyethylidene-*β*-L-talopyranoside **14**. A previous study of orthoester rearrangement reaction showed that 1,2-*O*-allyloxyethylidene-β-L-rhamnopyranose can be intermolecularly rearranged to produce a disaccharide with α-L-Rha*p*-(1→2)-L-Rha*p* configured glycosidic bonds when treated with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in anhydrous CH_2Cl_2 (Shown in Figure **1**)[37, 38].

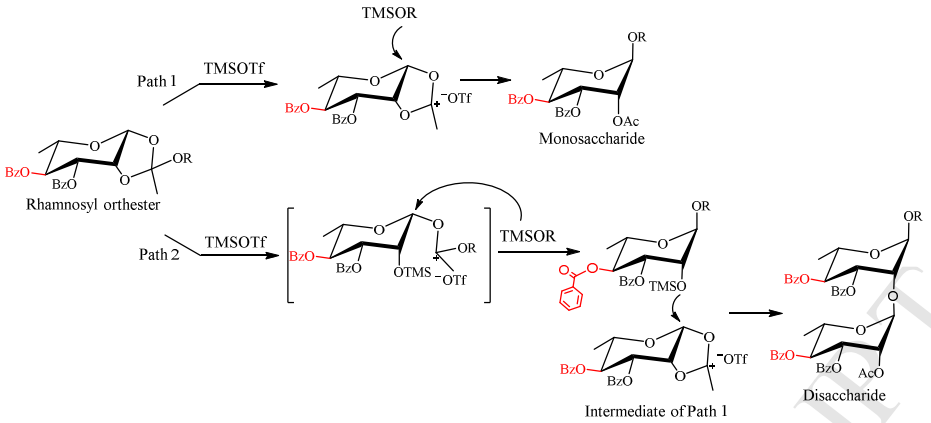


Figure **1**. Possible mechanism of TMSOTfpromoted transformation of rhamnosyl orthoester[38]

In this study, we hope to replicate a similar reaction with orthoester **14** and expected to obtain taloside disaccharide **22** (scheme 3 and scheme 4); however, the objective was not achieved as we received monosaccharide **8** as the main reaction product. The possible mechanism is shown in Figure **2**. There were two paths for the TMSOTf-catalyzed transformation of talopranosyl orthoester; path 1 was the normal rearrangement generating the corresponding monosaccharide, which yielded the same result as rhamnosyl orthoester. In path 2, the larger steric effect of the axial 4-OBz in talosyl orthoester compared to equatorial 4-OBz in rhamnosyl orthoester hindered the reaction between the axial 2-OTMS and the anomeric carbon of intermediate, because of which, the talosyl orthoester rearrangement could not form the disaccharide.

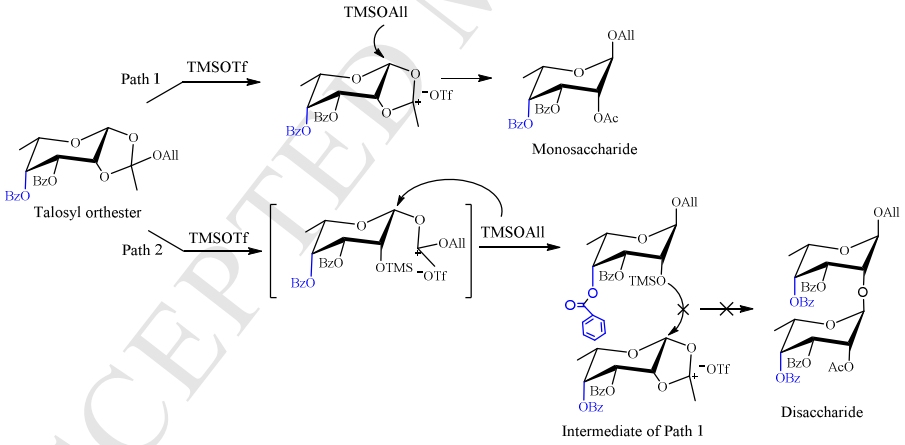
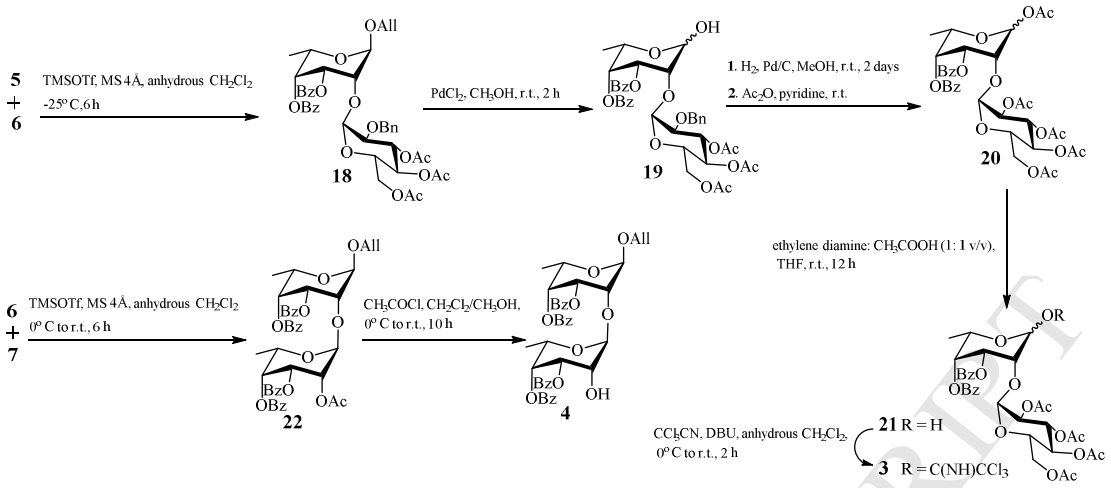


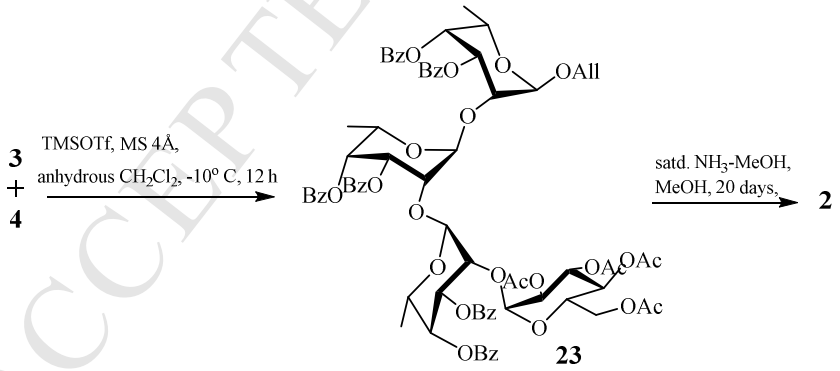
Figure **2**. Possible mechanism of TMSOTf-promoted transformation of talosyl orthoester

Using compound **8**, the 2-OH L-talosyl acceptor **6** was obtained conveniently in a solution containing AcCl-methanol (1: 50 v/v) [39] ; in addition, the $PdCl_2$-catalyzed removal of the allyl group in compound **8,** followed by anomeric trichloroacetimidation, yielded 72% donor **7** in two-steps[40]. The glucosyl donor **5** was synthesized via a two-stepped reaction from the reported product **16**[41]. The anomeric acetate was selectively removed by treating with ethylene diamine: AcOH (1: 1) in THF to obtain **17** with 77% yield. Trichloroacetimidation of **17** with CCl_3CN in the presence of 1,5-diazabicyclo(5,4,0)undec-5-ene (DBU) produced the trichloroacetimidate **5** with satisfactory yield.



Scheme **4**. The synthesis of disaccharide building blocks

The disaccharide acceptor **4** and disaccharide donor **3** were synthesized conveniently using monosaccharide building blocks **5**, **6** and **7** (Scheme 4). The compound **5** was glycosylated with the compound **6** in TMSOTf to obtain the corresponding α-(1→2)-linked disaccharide **18** with 74% yield. The 1,2-cis configuration was confirmed by analyzing the ^{1}H NMR signal of H-1-Glc*p* at 4.94 ppm (d, 1H, *J* 3.6 Hz). The allyl group in **18** was cleaved with palladium chloride ($PdCl_2$), debenzylated with Pd/C under H_2 in MeOH, and then acetylated with acetic anhydride in pyridine to produce the compound **20** with 79% yield. The disaccharide donor **3** was synthesized from **20** with 73% yield using a two-stepped reaction involving selective de-1-O-aetylation, followed by trichloroacetimidate formation. The acetyl (Ac) group at the C-2 in L-talosyl donor **7** activated the α-(1→2)-linkage to glycosylate L-talosyl acceptor **6** and finally produce disaccharide **22** with 75% yield. Further, treating **22** with acetyl chloride in MeOH/CH_2Cl_2 (1: 1 v/v) at 0°C[42] to remove the acetyl group produced disaccharide acceptor **4** with 83% yield.



Scheme 5. The synthesis of target tetrasccharide **2**

Finally, tetrasccharide **2** was synthesized following Scheme 5. The disaccharide acceptor **4** and the disaccharide donor **3** underwent Schmidt glycosylation to produce the completely protected tetrasccharide **23**, and the success of the reaction was confirmed by ^{1}H NMR signals at δ 5.24 (H_1-Tal*p*$_1$), 5.13 (H_1-Tal*p*$_2$), 4.75 (H_1-Tal*p*$_3$), and 4.68 (H_1-Glc*p*), and ^{13}C NMR signals at δ 97.2 (C_1-Tal*p*$_3$), 97.5 (C_1-Tal*p*$_2$), 100.4 (C_1-Tal*p*$_1$), and 100.7 (C_1-Glc*p*), which indicated the presence of four anomeric carbons. Complete removal of the protecting groups in **23** was achieved by hydrolyzing the compound with saturated NH_3–MeOH to obtain the desired tetrasaccharide **2**

with 70% yield. The structures were confirmed by the ^{1}H NMR signals at δ 5.06 (H_1-Tla*p*$_1$), 5.06 (H_1-Tal*p*$_2$), 4.94 (H_1-Glc*p*), and 4.87 (H_1-Tal*p*$_3$) which were the characteristic peaks of anomeric protons. The signals at *δ* 5.93−5.81 (m, 1H, $OCH_2C\boldsymbol{H}CH_2$) and 5.31−5.22 (m, 2H, $OCH_2CHC\boldsymbol{H}_2$) were the characteristic peaks of the allyl group; In ^{13}C NMR, the signals at δ 100.7 (C_1-Tal*p*$_1$), 100.4 (C_1-Tal*p*$_2$), 97.5 (C_1-Glc*p*), and 97.2 (C_1-Tal*p*$_3$) were the characteristic peaks of anomeric carbons, and the signals at *δ* 132.9 ($OCH_2\boldsymbol{C}HCH_2$) and 118.6 ($OCH_2CH\boldsymbol{C}H_2$) were the characteristic peaks of the allyl group, as was evident from the ^{13}C-^{1}H HSQC spectrum. Although one of the characteristic peaks of the allyl group was sheltered by other peaks in ^{1}H NMR with signals at *δ 3.8*−4.2, the high resolution mass spectrometry report yielded the precise molecular mass of **2** (676.3035), which was indicative of anomeric integrity.

3. Conclusion

In summary, we reported a convergent total synthesis of a tetrasccharide analogue **2,** which is related to the repeating unit of O-specific polysaccharide present in the outer cell membrane of *Franconibacter helveticus* LMG23732^{T}. This efficient synthesis features the preparation of a key monosaccharide intermediate, L-taloside **8** from 1,2-*O*-allyloxyethylidene-L-rhamnose derivative via orthoester rearrangement, and the monosaccharide can be easily converted to the monosaccharide donor **7** or acceptor **6**. The 1,2-cis glycosidic bonds, α-Glc*p*-(1-2)-6dTal*p* of the disaccharide **18** was formed by glycosylating the monosaccharide donor **5** with monosaccharide acceptor **6** at low temperature. The three-stepped reaction from **18** to **20** was followed by a two-stepped reaction to finally generate the disaccharide donor **3** with good yield. This study will enrich the O-specific polysaccharide library and contribute towards future studies in the area of carbohydrate chemistry.

4. Experimental

4.1 Materials and methods

^{1}H and ^{13}C NMR spectra were recorded using the Bruker AVANCE600 spectrometers (^{1}H NMR-300 MHz; ^{13}C NMR-75 MHz) with $CDCl_3$ or D_2O as solvents. TMS (δ 0.000 ppm for 1H) and $CDCl_3$ (δ 77.00 ppm for 13C) were the internal references. The ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (app = apparent, parobsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m= multiplet) and coupling constants in Hertz. All ^{13}C NMR spectra were recorded with complete proton decoupling. The high-resolution mass spectra (HRMS) were recorded using the Bruker Daltonics Bio-TOF-Q III (ESIMS) spectrometer. Thin layer chromatography (TLC) was performed on silica gel HF254 plates, and detected by an UV detector or by charring with 15% (v/v) H_2SO_4 in methanol. All commercially available reagents were purchased from Sinopharm, Shanghai, China, and used without further purification. All reactions were monitored by TLC. Column chromatography was conducted using a silica gel plug (200-300 mesh), and a mixture of ethyl acetate (EtOAc), and petroleum ether (bp 60-90 °C) was used as the eluent.

*4.2. 3-O-benzoyl-1,2-O-allyloxyethylidene-β-L-rhamnopyranoside (**12**)*

A solution of **11** (5.00 g, 20.35 mmol) in CH_2Cl_2 (250 mL) was mixed with pyridine (20 ml) and DMAP (0.05 g, 0.41 mmol) at −25°C in a N_2 environment. The reaction mixture was stirred for 30 min, and BzCl (2.34 ml, 20.32 mmol) in CH_2Cl_2 (50 ml) was added dropwise. The resultant mixture was stirred for another 3 h, and the completion of the reaction was confirmed by TLC (petroleum ether/ethyl acetate 1:1) analysis. The reaction was then quenched with chilled H_2O (300 mL), and extracted with CH_2Cl_2 (3 × 150 mL). The organic phases were combined, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 2.5:1) to yield **11** (4.93 g, 72%) as a colorless syrup. $[\alpha]_D^{22}$ −14.5° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61−7.36 (m, 5H, Ar*H*), 5.92−5.79 (m, 1H, OCH_2CHCH_2), 5.47 (d, 1H, *J* = 2.3 Hz, H-1), 5.26−5.07 (m, 2H, OCH_2CHCH_2), 5.21−5.16 (dd, 1H, *J* = 4.1 Hz, 9.6 Hz, H-3), 4.70 (dd, 1H, *J* = 2.3 Hz, 4.1Hz, H-2), 4.09−3.96 (m, 2H, OCH_2CHCH_2), 3.82 (t, 1H, *J* = 9.4 Hz, H-4), 3.45−3.53 (m, 1H, H-5), 1.76 (s, 3H, CH_3), 1.40−1.38 (d, 3H, *J* = 6.1 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 166.4 (*C*OPh), 133.8, 133.2, 132.9, 129.7, 128.1, 128.0, 123.7, 116.2, 97.0 (C-1), 74.1, 70.7, 69.9, 63.2, 24.8, 17.3 (C-6). ESI-HRMS $[M + NH_4]^+$ calculated for $C_{18}H_{26}NO_7$ 368.1709 found 368.1704.

*4.3. 3-O-benzoyl-1,2-O-allyloxyethylidene-β-L-talopyranoside (**13**)*

A solution of **12** (4.00 g, 11.42 mmol) in CH_2Cl_2 (150 mL) was mixed with DMSO (3.2 ml, 40.96 mmol) and Et_3N (8 ml, 78.50 mmol) at 0°C. The reaction mixture was stirred for 30 min, and phenylphosphonic dichloride (3.44 mL, 22.83 mmol) in CH_2Cl_2 (25 ml) was added dropwise. The resultant mixture was stirred for 2.5 h at room temperature, and the completion of the reaction was confirmed by TLC (petroleum ether/ethyl acetate 4:1) analysis. Methanol (100 ml) and $NaBH_4$ (1.20 g, 31.72 mmol) at 0°C was added to the reaction mixture. The resultant mixture was stirred with continuous addition of water (250 mL); the mixture was extracted with CH_2Cl_2 (3 × 100 mL); the organic layer was sequentially washed with saturated aqueous $NaHCO_3$ solution (250 mL) and brine (2 × 200 mL), and then dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 6:1) to obtain **13** (2.10 g, 54%) as a colorless syrup. $[\alpha]_D^{22}$ −25.6° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04−8.01 (m, 2H, Ar*H*), 7.65−7.60 (m, 1H, Ar*H*), 7.56−7.46 (m, 2H, Ar*H*), 5.97−5.84 (m, 1H, OCH_2CHCH_2), 5.64−5.63 (t, 1H, *J* = 2.5 Hz, H-3), 5.54 (d, 1H, *J* = 2.3 Hz, H-1), 5.31−5.15 (m, 2H, OCH_2CHCH_2), 4.21 (dd, 1H, J_1 = 2.0 Hz, J_2 = 2.5 Hz, H-2), 4.14−4.08 (m, 2H, OCH_2CHCH_2), 4.01−3.97 (m, 1H, H-4), 3.57−3.52 (m, 1H, H-5), 2.46 (d, 1H, *J* = 12.7 Hz, O*H*), 1.81 (s, 3H, CH_3), 1.36 (d, 3H, *J* = 6.5 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 164.1 (*C*OPh), 133.5, 133.4, 129.4, 128.3, 122.7, 96.36 (C-1), 74.1, 68.2, 67.9, 67.7, 67.6, 24.5, 16.1 (C-6). ESI-HRMS $[M + NH_4]^+$ calculated for $C_{18}H_{26}NO_7$ 368.1709 found 368.1704.

*4.4. 3,4-di-O-benzoyl-1,2-O-allyloxyethylidene-β-L-talopyranoside (**14**)*

A solution of **13** (2.00 g, 5.71 mmol) in CH_2Cl_2 (50 mL) was mixed with pyridine (10 mL) at 0°C in a nitrogenous environment. The reaction mixture was stirred for 5 min, and benzoyl chloride (0.79 mL, 6.90 mmol) in CH_2Cl_2 (5 ml) was added dropwise. The resultant mixture was stirred for another 4 h, and the completion of the reaction was confirmed by TLC (petroleum ether/ethyl acetate 4:1) analysis. The reaction was then quenched with chilled H_2O (200 mL), and the reaction mixture was extracted with CH_2Cl_2 (3 × 150 mL). The organic phases were combined,

dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to obtain **14** (2.28 g, 88%) as a colorless syrup. $[\alpha]_D^{22}$ −37.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16−8.05 (m, 4H, Ar*H*), 7.64−7.45 (m, 6H, Ar*H*), 5.98−5.85 (m, 1H, OCH_2CHCH_2), 5.72 (t, 1H, *J* = 2.3 Hz, H-3), 5.63 (d, 1H, *J* = 2.6 Hz, H-1), 5.31, 5.26, 5.18, 5.14, (m, 2H, OCH_2CHCH_2), 5.10 (t, 1H, *J* = 1.2 Hz, H-4), 4.22−4.17 (m, 2H, H-2, H-5), 4.12−4.09 (m, 2H, OCH_2CHCH_2), 1.90 (s, 3H, CH_3), 1.35 (d, 3H, *J* = 6.5 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 165.5 (*C*OPh), 163.9 (*C*OPh), 133.7, 133.5, 133.1, 129.7, 129.5, 129.1, 128.7, 128.3, 128.1, 123.5, 116.5, 96.2 (C-1), 67.9, 67.4, 66.7, 63.1, 25.2, 16.4 (C-6). ESI-HRMS $[M + NH_4]^+$ calculated for $C_{25}H_{30}NO_8$ 472.1971 found 472.1966.

*4.5. Allyl 2-O-acetyl-3,4-di-O-benzoyl-α-L-talopyranoside (**8**)*

A solution of **14** (2.00 g, 4.4 mmol) in anhydrous CH_2Cl_2 (50 ml) was mixed with 4 Å molecular sieves (0.5 g) at 0°C under N_2. The reaction mixture was stirred for 30 min, TMSOTf (10 μL) was added and the mixture was stirred for another 2 h until TLC analysis (petroleum ether-ethyl acetate 5:1) showed that the reaction was complete. The reaction was quenched with Et_3N (0.6 ml) at 0°C and the reaction mixture was diluted with CH_2Cl_2. Molecular sieves were filtered off and the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 12:1) to obtain **8** (1.32 g, 66%) as a colorless syrup. $[\alpha]_D^{22}$ −96.9° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20−8.17 (m, 2H, Ar*H*), 8.11−8.08 (m, 2H, Ar*H*), 7.64−7.57 (m, 2H, Ar*H*), 7.50−7.43 (m, 4H, Ar*H*), 6.02−5.89 (m, 1H, OCH_2CHCH_2), 5.41 (t, 1H, *J* = 2.7 Hz, H-3), 5.37−5.21 (m, 2H, OCH_2CHCH_2), 5.17 (t, 1H, *J* = 2.2 Hz, H-4), 5.03 (m, 1H, H-2), 4.98 (s, 1H, H-1), 4.63−4.57 (m, 1H, H-5), 4.15−4.06 (m, 1H, OCH_2CHCH_2), 4.34−4.28 (m, 1H, OCH_2CHCH_2), 2.01 (s, 3H, $OCOCH_3$), 1.32 (d, 3H, *J* = 6.7 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 169.0 (*C*OMe), 165.1 (*C*OPh), 164.4 (*C*OPh), 133.4, 133.1, 129.7, 129.6, 129.3, 129.1, 128.1, 117.1, 96.7 (C-1), 68.7, 68.3, 67.2, 66.9, 62.1, 20.4, 15.7 (C-6). ESI-HRMS $[M + Na]^+$ calculated for $C_{25}H_{26}NaO_8$ 477.1525 found 477.1521.

*4.6. Allyl 3,4-di-O-benzoyl-α-L-talopyranoside (**6**)*

A solution of **8** (1.20 g, 2.64 mmol) in methanol (50 mL) was mixed with acetyl chloride (1.00 mL, 14.06 mmol) at 0°C in a nitrogenous environment. The reaction mixture was stirred for 10 h, and the completion of the reaction was confirmed by TLC (petroleum ether/ethyl acetate 6:1) analysis. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (50 mL), diluted with CH_2Cl_2 and extracted with CH_2Cl_2 (3 × 150 mL). The organic phases were combined, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 8:1) to obtain **8** (0.76 g, 71%) as a colorless syrup. $[\alpha]_D^{22}$ −99.56° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05−8.02 (m, 2H, Ar*H*), 7.92−7.89 (m, 2H, Ar*H*), 7.62−7.56 (m, 1H, Ar*H*), 7.50−7.34 (m, 3H, Ar*H*), 7.33−7.28 (m, 2H, Ar*H*), 6.00−5.87 (m, 1H, OCH_2CHCH_2), 5.66 (t, 1H, *J* = 1.9 Hz, H-3), 5.54 (t, 1H, *J* = 3.5 Hz, H-4), 5.37−5.22 (4m, 2H, OCH_2CHCH_2), 5.05 (d, 1H, *J* = 1.5 Hz, H-1), 4.34 (m, 1H, H-2), 4.29−4.21 (m, 1H, H-5), 4.11−4.02 (m, 2H, OCH_2CHCH_2), 2.95 (d, 1H, *J* = 10.4 Hz, OH), 1.27 (d, 3H, *J* = 6.5 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 165.3 (*C*OPh), 165.0 (*C*OPh), 133.2, 132.8, 129.5, 129.3, 129.2, 129.1, 128.4, 127.9, 117.5, 99.0 (C-1), 77.2, 76.8, 76.3, 71.6, 68.3, 68.0, 67.9, 64.7, 16.0 (C-6). ESI-HRMS $[M + Na]^+$ calculated for $C_{23}H_{24}NaO_7$ 435.1420 found 435.1414.

*4.7. 2-O-acetyl-3,4-di-O-benzoyl-L-trichloroacetimidate (**7**)*

A solution of **8** (700 mg, 1.56 mmol) in methanol (20 mL) was mixed with $PdCl_2$ (100 mg).

The reaction mixture was stirred for 2 h at room temperature, and TLC analysis (petroleum ether/ethyl acetate 4:1) was performed to identify the completion of the reaction. The residue was filtered through a pad of Celite, and the filtrate was concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to acquire intermediate compound **15** (600 mg, 80%). A solution of **15** in CH_2Cl_2 (20 mL) at 0°C under nitrogenous environment was mixed with trichloroacetonitrile (0.40 mL, 3.91 mmol) and DBU (0.05 mL). The reaction mixture was stirred for 1 h, and the TLC analysis (petroleum ether/ethyl acetate 6:1) indicated the completion of the reaction; the reaction mixture was then concentrated. The residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 10:1) to obtain **7** (0.70 g, 90%) as a colorless syrup. $[\alpha]_D^{22}$ −20.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 1H, ON*H*CCl_3), 8.21−8.16 (m, 2H, Ar*H*), 7.80−7.77 (m, 2H, Ar*H*), 7.64−7.59 (m, 1H, Ar*H*), 7.51−7.46 (m, 3H, Ar*H*), 7.34−7.28 (m, 2H, Ar*H*), 6.45 (d, 1H, *J* = 1.5 Hz, H-1), 5.72−5.68 (m, 2H, H-3, H-4), 5.54−5.52 (m, 1H, H-2), 4.59−4.53 (m, 1H, H-5), 2.07 (s, 3H, $COCH_3$), 1.33 (d, 3H, *J* = 6.5 Hz, H-6);^{13}C NMR (75 MHz, $CDCl_3$) : δ 169.4 (*C*OMe), 165.4 (*C*OPh), 164.8 (*C*OPh), 159.7, 133.1, 132.9, 129.7, 129.3, 128.9, 128.1, 128.0, 95.5 (C-1), 90.5(O*C*NHCCl_3), 68.5, 67.9, 66.2, 65.3, 20.4, 16.0 (C-6). ESI-HRMS $[M + Na]^+$ calculated for $C_{24}H_2Cl_3NNaO_8$ 580.0309 found 580.0313.

*4.8. 2-O-benzyl-3,4,6-tri-O-acetyl-D-trichloroacetimidate (**5**)*

A solution of ethylene diamine: CH_3COOH (0.85 mL: 0.85mL v/v) in THF (250 mL) at 0°C was prepared and a solution of the compound **16** (5.00 g, 11.42 mmol) in THF (50 mL) was added dropwise to the previous solution. The resultant mixture was stirred for 24 h at room temperature, and the TLC analysis (petroleum ether/ethyl acetate 2:1) indicated the completion of the reaction. The reaction was then quenched with 1M HCl (200 mL), and the reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution (200 mL), and brine (2 × 200 mL), then dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to obtain **17** (3.42 g, 77%) as a colorless syrup. Subsequently, the solution of **17** (3.42 g, 8.62 mmol) in CH_2Cl_2 (50 mL) at 0°C was mixed with trichloroacetonitrile (1.26 mL, 12.60 mmol) and DBU (0.1 mL) under a nitrogenous environment. The reaction mixture was stirred for 1 h and the completion of the reaction was confirmed by TLC (petroleum ether/ethyl acetate 3:1) analysis. The reaction mixture was concentrated, and the residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 4:1) to obtain **5** (4.19 g, 90%) as a colorless syrup. $[\alpha]_D^{22}$ 10.2° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (s, 1H, OCN*H*CCl_3), 7.37−7.27 (m, 5H, Bn*H*), 6.50 (d, 1H, *J* = 3.6 Hz, H-1), 5.51 (t, 1H, *J* = 9.7 Hz, H-3), 5.09 (t, 1H, *J* = 10.0 Hz, H-4), 4.65 (d, 2H, *J* = 12.3 Hz, CH_2Ph), 4.31−4.25 (m, 1H, H-6), 4.23−4.17 (m, 1H, H-5), 4.11−4.06 (m, 1H, H-6), 3.79 (dd, 1H, J_1 = 3.6 Hz, J_2 = 9.9 Hz, H-2), 2.06, 2.05, 2.02 (3s, 9H, OCOCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 170.5, 169.9, 169.7, 161.0, 137.3, 128.5, 128.0, 127.7, 93.34 (C-1), 90.9, 75.8, 72.9, 71.5, 69.9, 68.0, 61.6, 20.7, 20.6, 20.6. ESI-HRMS $[M + NH_4]^+$ calculated for $C_{21}H_{28}Cl_3N_2O_9$ 557.0860 found 557.0851.

*4.9. Allyl 2-O-benzyl-3,4,6-tri-O-acetyl-α-D-glucopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-talopranoside (**18**)*

A mixture of **5** (1.00 g, 2.43 mmol), **6** (1.35 g, 2.50 mmol), and 4 Å MS (0.4 g) in anhydrous

CH_2Cl_2 (30 mL) was stirred at room temperature for 30 min under a N_2 atmosphere. The mixture was cooled to −25°C, and then TMSOTf (10 μL) was added. Again, the mixture was stirred at the same temperature for 8 h. The completion of the reaction was identified by TLC analysis (petroleum ether/ethyl acetate 3:1). The reaction was quenched with Et_3N, and the mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of celite, and the filtrate was concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to yield **18** (1.93 g, 74%) as a colorless syrup. $[\alpha]_D^{22}$ 8.2° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.24−8.21 (m, 2H, Ar*H*), 7.95−7.92 (m, 2H, Ar*H*), 7.52−7.46 (m, 2H, Ar*H*), 7.39−7.27 (m, 9H, Ar*H*), 5.95−5.82 (m, 1H, OCH_2CHCH_2), 5.60−5.57 (m, 2H, H-3, H-4), 5.37 (t, 1H, *J* = 9.7 Hz, H-3), 5.28−5.18, (m, 2H, OCH_2CHCH_2), 5.09 (s, 1H, H-1-Tal*p*), 4.94 (d, 1H, *J* = 3.7 Hz, H-1), 4.80 (t, 1H, *J* = 10.2 Hz, H-4), 4.66 (dd, 2H, J_1 = 11.7 Hz, J_2 = 11.7 Hz, CH_2Ph), 4.32−4.25 (m, 1H, H-5), 4.22−4.16 (m, 1H, OCH_2CHCH_2), 4.09−4.03 (m, 1H, H-2), 3.99−3.93 (m, 1H, OCH_2CHCH_2), 3.88−3.85 (m, 1H, H-5), 3.65−3.54 (m, 2H, H-6), 3.17 (dd, 1H, J_1 = 2.0 Hz, J_2 = 12.5 Hz, H-2), 1.98, 1.86, 1.78, (3s, 9H, $OCOCH_3$), 1.28 (d, 3H, *J* = 6.5 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : *δ* 169.9 (*C*OMe), 169.3 (*C*OMe), 169.2 (*C*OMe), 166.2 (*C*OPh), 166.1 (*C*OPh), 137.4, 133.3, 132.9, 132.5, 129.9, 129.5, 129.2, 129.2, 128.3, 128.2, 128.1, 127.7, 127.7, 117.3, 96.98 (C-1), 96.72 (C-1), 72.9, 72.9, 71.9, 68.3, 68.0, 67.9, 67.5, 67.2, 64.9, 60.7, 20.5 (CO*Me*), 20.3 (CO*Me*), 20.1 (CO*Me*), 16.0 (C-6). ESI-HRMS $[M + NH_4]^+$ calculated for $C_{42}H_{50}NO_{15}$ 808.3180 found 808.3170.

*4.10. 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→2)-3,4-di-O-benzoyl-α/β-L-talopranoside (**20**)*

A solution of **18** (1.60 g, 2.02 mmol) in methanol (25 mL) was mixed with $PdCl_2$ (180 mg). The reaction mixture was stirred for 2 h at room temperature. The completion of the reaction was identified by TLC analysis (petroleum ether/ethyl acetate 2:1). The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to obtain **19** (1.31 g, 86%). The resultant compound **19** was dissolved in methanol (75 ml), and mixed with 10% Pd/C (0.4 g). Hydrogen gas was passed through the mixture and the reaction was continued for 48 h. The completion of the reaction was identified by TLC analysis (petroleum ether/ethyl acetate 1:2). The reaction mixture was filtered through a pad of celite, and the filtrate was concentrated to obtain a yellow syrup. The resultant syrup was subsequently dissolved in pyridine (20 mL) at 0°C in a N_2 environment. The reaction mixture was stirred for 5 min, and acetyl chloride (0.59 mL, 8.35 mmol) in CH_2Cl_2 (5 ml) was added dropwise. The resultant mixture was stirred for another 4 h at room temperature, and TLC analysis (petroleum ether/ethyl acetate 2:1) was performed to identify the completion of the reaction. The reaction was then quenched with chilled H_2O (50 mL), and extracted with CH_2Cl_2 (3 ×25 mL). The organic phases were combined, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 3:1) to obtain **20** (1.13 g, 70% from **18**) as a colorless syrup. $[\alpha]_D^{22}$ 14.1° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.29−8.21 (m, 2H, Ar*H*), 7.90−7.82 (m, 2H, Ar*H*), 7.58−7.25 (m, 6H, Ar*H*), 6.19 (d, 0.5 H, *J* = 1.0 Hz, H_β-1-Tal*p*), 5.77 (s, 0.5H, H_α-1-Tal*p*)，5.65 (d, 0.5 H, *J* = 4.0Hz, H-1-Glc*p*), 5.24 (d, 0.5 H, *J* = 4.0 Hz, H-1-Glc*p*), 2.15−1.73 (m, 15H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 96.25 (C-1-Tal*p*), 94.68 (C-1-Tal*p*), 92.33 (C-1-Glc*p*), 91.64 (C-1-Glc*p*). ESI-HRMS $[M + NH_4]^+$ calculated for $C_{36}H_{44}NO_{17}$ 762.2609 found 762.2611.

4.11. 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-

*trichloroacetimidate (**3**)*

A solution of ethylene diamine: CH_3COOH (0.17 mL: 0.17 mL v/v) in THF (40 mL) was prepared and a solution of compound **20** (0.70 g, 0.99 mmol) in THF (10 ml) was added dropwise at 0°C to the previous solution. The resultant mixture was stirred for 12 h at room temperature. The completion of the reaction was identified by TLC analysis (petroleum ether/ethyl acetate 5:1). The reaction was then quenched with 1M HCl (200 mL), and the reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL). The organic phases were washed with saturated aqueous solution of $NaHCO_3$ (200 mL), and brine (2 × 200 mL), then dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 8:1) to obtain compound **21** (0.60 g, 87%). Subsequently, a solution of **21** (0.55 g, 0.78 mmol) in CH_2Cl_2 (10 mL) at 0°C in a N_2 environment was mixed with trichloroacetonitrile (0.195 mL, 1.95 mmol) and DBU (10 µL). The reaction mixture was stirred for 1 h and then concentrated. The residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 4:1) to obtain **3** (0.55 g, 95%) as a colorless syrup. $[\alpha]_D^{22}$ 16.6° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (s, 1H, OCN*H*CCl$_3$), 8.30−8.28 (m, 2H, Ar*H*), 7.93−7.90 (m, 2H, Ar*H*), 7.62−7.50 (m, 4H, Ar*H*), 7.38−7.33-7.38 (m, 2H, Ar*H*), 6.38 (s, 1H, H-1-Tal*p*), 5.69 (m, 1H, H-4), 5.64 (t, 1H, *J* = 4.1 Hz, H-3), 5.46 (t, 1H, *J* = 9.7 Hz, H-3), 5.37 (d, 1H, *J* = 4.1 Hz, H-1-Glc*p*), 4.95−4.88 (m, 2H, H-6), 4.54 (dd, 1H, J_1 = 5.9 Hz, J_2 = 13.7 Hz, H-2), 4.30 (d, 1H, J = 4.5 Hz, H-5), 3.92−3.86 (m, 1H, H-5), 3.52 (dd, 1H, J_1 = 3.7 Hz, J_2 = 12.6 Hz, H-2), 3.12 (dd, 1H, J_1 = 2.1 Hz, J_2 = 12.6 Hz, H-2), 2.18, 2.02, 1.86, 1.79 (4s, 12H, OCOC*H*$_3$), 1.31 (d, 3H, *J* = 6.5 Hz, H-6);^{13}C NMR (75 MHz, $CDCl_3$) : δ 170.0 (*C*OMe), 169.9 (*C*OMe), 169.4 (*C*OMe), 168.9 (*C*OMe), 166.0 (*C*OPh), 164.9 (*C*OPh), 133.3, 132.9, 129.7, 129.5, 129.0, 129.8, 128.6, 128.3, 96.11 (C-1-Tal*p*)), 96.07 (C-1-Glc*p*), 90.37 (OCNH*C*Cl$_3$), 71.1, 70.6, 70.2, 68.3, 68.2, 67.7, 67.1, 66.8, 60.3, 20.38 (2×CO*Me*), 20.12 (CO*Me*), 20.09 (CO*Me*), 16.05 (C-6). ESI-HRMS $[M + NH_4]^+$ calculated for $C_{36}H_{42}Cl_3N_2O_{16}$ 863.1600 found 863.1591.

*4.12. Allyl 2-O-acetyl-3,4-di-O-benzoyl-α-L-talopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-talopyranoside (**22**)*

A mixture of **6** (0.50 g, 1.21 mmol), **7** (0.71 g, 1.25 mmol), and 4 Å MS (0.2 g) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature for 30 min in a N_2 atmosphere. The mixture was cooled to 0°C, followed by addition of TMSOTf (2 µL). The resultant mixture was stirred at 0°C for 3 h. The completion of the reaction was monitored by TLC analysis (petroleum ether/ethyl acetate 5:1). The reaction was then quenched by adding Et_3N. The reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of celite, and the filtrate was concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 7:1) to obtain **22** (0.76 g, 75%) as a colorless syrup. $[\alpha]_D^{22}$ −51.0° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09−8.05 (m, 4H, Ar*H*), 7.88−7.86 (m, 2H, Ar*H*), 7.77−7.74 (m, 2H, Ar*H*), 7.57−7.47 (m, 4H, Ar*H*), 7.42−7.26 (m, 8H, Ar*H*), 6.02−5.89 (m, 1H, OCH$_2$C*H*CH$_2$), 5.66−5.63 (m, 2H, H-3, H-4), 5.60−5.58 (m, 2H, H-3, H-4), 5.41−5.27 (m, 2H, OC*H*$_2$CHCH$_2$), 5.15 (d, 1H, *J* = 3.7 Hz, H-2), 5.08 (s, H, H-1), 5.09 (s, 2H, H-1), 4.55−4.48 (m, 1H, H-5), 4.38−4.26 (m, 2H, H-2, H-5), 4.16−4.10 (m, 2H, OCH$_2$CHC*H*$_2$), 1.88 (s, 3H, OCOC*H*$_3$), 1.32,1.27 (2d, 6H, *J* = 6.5 Hz, H-6, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 169.0 (*C*OMe), 166.1(*C*OPh), 165.5 (*C*OPh), 165.1 (*C*OPh), 164.8 (*C*OPh), 133.05, 133.0, 132.9, 132.8, 132.7, 129.6, 129.6, 129.4, 129.3, 129.2, 129.2, 129.0, 128.2, 128.1, 128.0, 128.0, 117.65, 100.14 (C-1), 98.05 (C-1), 73.3, 69.1, 68.9, 67.9, 67.8, 66.7, 66.5, 64.8, 20.4, 16.0 (C-6, C-6). ESI-HRMS $[M + Na]^+$ calculated for $C_{45}H_{45}NaO_{14}$ 831.2629 found 831.2633.

*4.13. Allyl 3,4-di-O-benzoyl-α-L-talopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-talopyranoside (**4**)*

A solution of **22** (600 mg, 0.78 mmol) in anhydrous CH_2Cl_2/MeOH (30 mL) was mixed with acetyl chloride (1.0 mL) portion-wise at 0°C. The mixture was stirred at room temperature for 10 h, until the TLC analysis (petroleum ether/ethyl acetate 4:1) showed that the reaction was complete. The solution was neutralized with saturated aqueous $NaHCO_3$ solution and extracted with dichloromethane (2 × 30 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to dryness. The residue was subjected to column chromatography (petroleum ether/ethyl acetate 6:1) to obtain **4** (0.50 g, 83%) as a colorless syrup. $[\alpha]_D^{22}$ −13.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04−8.02 (m, 2H, Ar*H*), 7.96−7.89 (m, 6H, Ar*H*), 7.60−7.49 (m, 3H, Ar*H*), 7.45−7.34 (m, 6H, Ar*H*), 7.30−7.23 (m, 3H, Ar*H*), 7.17−7.12 (m, 1H, Ar*H*), 6.03−5.90 (m, 1H, OCH_2CHCH_2), 5.72 (d, 1H, *J* = 3.2 Hz, H-4), 5.65 (t, 1H, *J* = 3.7 Hz, H-3), 5.59 (m, 1H, H-4), 5.50 (t, 1H, *J* = 3.5 Hz, H-3), 5.41−5.27 (m, 2H, OCH_2CHCH_2), 5.19 (s, 1H, H-1), 5.10 (s, 1H, H-1), 4.55−4.51 (m, 1H, H-5), 4.37−4.26 (m, 2H, H-2, H-5), 4.16−4.07 (m, 2H, OCH_2CHCH_2), 3.75 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.4 Hz, H-2), 2.75 (d, 1H, *J* = 10.4 Hz, O*H*), 1.31, 1.27, (2d, 6H, *J* = 6.5 Hz, H-6, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 165.9 (*C*OPh), 165.2 (*C*OPh), 165.1 (*C*OPh), 164.9 (*C*OPh), 133.2 (OCH_2CHCH_2), 133.1, 132.9, 132.7, 129.5, 129.4, 129.3, 129.2, 129.2, 129.1, 128.9, 128.7, 128.4, 128.2, 128.1, 128.0, 117.6 (OCH_2CHCH_2), 102.63 (C-1), 98.17 (C-1), 73.4, 71.3, 69.2 (OCH_2CHCH_2), 68.2, 67.9, 65.2, 64.8, 16.0, 15.9. ESI-HRMS $[M + NH_4]^+$ calculated for $C_{43}H_{46}NO_{13}$ 784.2969 found 784.2974.

*4.14. Allyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-talopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-talopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-talopyranoside (**23**)*

A mixture of **3** (0.50 g, 0.59 mmol), **4** (0.44 g, 0.58 mmol), and 4 Å MS (0.2 g) in anhydrous CH_2Cl_2 (20 mL) was stirred at 25°Cfor 30 min under a N_2 atmosphere and cooled to −10°C, followed by addition of TMSOTf (5 μL) to the mixture. The mixture was stirred at −10°C for 12 h until the TLC analysis (petroleum ether/ethyl acetate 5:1) indicated completion of the reaction. The reaction mixture was neutralized with Et_3N, diluted with CH_2Cl_2 (10 mL), filtered through a pad of celite, and the filtrate was concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 3:1) to obtain **23** (0.54 g, 66%) as a colorless syrup. $[\alpha]_D^{22}$ −86.4° (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08−7.95 (m, 5H, Ar*H*), 7.92−7.83 (m, 5H, Ar*H*), 7.57−7.48 (m, 5H, Ar*H*), 7.48−7.42 (m, 5H, Ar*H*), 7.39−7.27 (m, 10H, Ar*H*), 6.02−5.89 (m, 1H, OCH_2CHCH_2), 5.64−5.61 (m, 4H, H-3, H-3, H-4, H-4), 5.54−5.49 (m, 1H, H-3), 5.50−5.32 (m, 2H, OCH_2CHCH_2), 5.39−5.36 (t, 1H, *J* = 4.2 Hz, H-3), 5.34−5.27 (m, 2H, H-4, H-4), 5.24 (s, 1H, H-1-Tal*p*$_1$), 5.13 (s, 1H, H-1-Tal*p*$_2$), 4.87−4.81 (t, 1H, *J* = 10.0 Hz, H-2), 4.75 (s, 1H, H-1-Tal*p*$_3$), 4.68 (d, 1H, *J* = 3.9 Hz, H-1-Glc*p*), 4.63−4.54 (m, 2H, H-2, H-2), 4.42−4.27 (m, 3H, H-2, H-5, H-5), 4.17−4.15 (m, 2H, OCH_2CHCH_2), 3.89−3.88 (m, 1H, H-5), 3.82−3.81 (m,1H, H-5), 3.72−3.68, 3.48−3.43 (2m, 2H, H-6), 1.94, 1.83, 1.72, 1.61, (4s, 12H, $OCOCH_3$)，1.31 (d, 3H, *J* = 6.5 Hz, H-6), 1.32 (d, 3H, *J* = 6.4 Hz, H-6), 0.73 (d, 3H, *J* = 6.5 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 167.8 (*C*OMe), 169.2 (*C*OMe), 169.1 (*C*OMe), 168.9 (*C*OMe), 165.9 (*C*OPh), 165.8 (*C*OPh), 165.7 (*C*OPh), 165.5 (*C*OPh), 165.0 (*C*OPh), 164.7 (*C*OPh), 133.1 (OCH_2CHCH_2), 133.0, 129.7, 129.4, 129.3, 129.2, 128.3, 128.3, 117.8 (OCH_2CHCH_2), 101.6 (C-1-Tal*p*$_1$), 99.7 (C-1-Tal*p*$_2$), 97.9 (C-1-Tal*p*$_3$), 95.1 (C-1-Glc*p*), 76.9,

74.8, 74.6, 72.3, 70.0 (O*C*H_2CHCH_2), 69.4, 68.9, 68.5, 68.2, 67.9, 67.7, 67.3, 67.2, 66.7, 65.4, 65.3, 64.9, 60.2, 20.3, 20.2, 20.1, 20.0, 19.8, 16.0, 15.5. ESI-HRMS $[M + NH_4]^+$ calculated for $C_{77}H_{82}NO_{28}$ 1468.5023 found 1468.5074.

*4.15. Ally α-D-glucopyranosyl-(1→2)-α-L-talopyranosyl-(1→2)-α-L-talopyranosyl-(1→2)-α-L-talopyranoside (**2**)*

A solution of **23** (400 mg, 0.28 mmol) in methanol (10 mL) was mixed with 40 mLsaturated MeOH-NH_3 solution. The resultant mixture was stirred for 14 days and the solvent was removed under reduced pressure to obtain **2** (127 mg, 70%) as a yellow syrup. $[\alpha]_D^{22}$ −20.5° (*c* 1.0, MeOH). ^{1}H NMR (300 MHz, D_2O): *δ* 5.93−5.81 (m, 1H, OCH$_2$C*H*CH$_2$), 5.31−5.22 (m, 2H, OCH$_2$CHC*H*$_2$), 5.06 (s, 2H, H-1-Tal*p*$_1$, H-1-Tal*p*$_2$), 4.94 (d, 1H, *J* = 3.7 Hz, H-1-Glc*p*), 4.87 (s, 1H, H-1-Tal*p*$_3$), 4.17−3.32 (m, 19H), 1.20−1.16 (m, 9H, H-6); ^{13}C NMR (75 MHz, D_2O) : *δ* 132.9 (OCH$_2$*C*HCH$_2$), 118.6 (OCH$_2$CH*C*H$_2$), 101.7 (C-1-Tal*p*$_1$), 100.4 (C-1-Tal*p*$_2$), 97.5 (C-1-Glc*p*), 97.2 (C-1-Tal*p*$_3$), 76.8, 76.7, 73.6, 72.4, 71.8, 71.2, 71.0, 70.8, 70.7, 69.3, 67.9, 67.6, 67.3, 66.8, 65.6, 65.2, 65.1, 60.2, 15.24, 15.19. ESI-HRMS $[M + NH_4]^+$calculated for $C_{27}H_{50}NO_{18}$ 676.3028 found676.3035.

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Supplementary Data

Supplementary data associated with this article can be found, in the online version, at http://~~.

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Highlights:

1. we have reported a convergent total synthesis of a tetrasccharide analogue

2. Stereo- and regio-specific synthesis was achieved in Schmidt glycosylation employing appropriately protected L-talopyranosyl and D-glucopyranosyl building blocks to build a disaccharide containing α-Glc*p*-(1→2)-6dTal*p* configured glycosidic bonds.

3. The synthesis involves an allyloxyethylidene group for protecting rhamnopyranose 1-OH and 2-OH at the same time, a redox reaction of rhamnopyranoside derivative for the synthesis of 6-deoxy talopyranoside.