Supporting Information

Glycosylation of N-Acetyl Glycosamine Using Catalytic Iron(III) Triflate: from a Microwave Batch Chemistry to a Scalable Continuous-Flow Process


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Experimental procedures for compounds 1β, 1α, 4, 6β, 8, 10, 12-24, 29, 30, 32, 34-49 and 55
Characterization data and NMR spectra (1H, 13C) of compounds 8, 10, 13, 16-18, 21-24, 34-38 and 40.
Commercial chemicals were obtained from Aldrich, Acros Organics, Alfa Aesar or Carbosynth and were used without further purification. All non-aqueous reactions were run under inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. All the glassware was stored in the oven or was flame-dried before using. Anhydrous solvents were obtained by filtration through drying columns. Dichloromethane and chloroform were stabilized under amylene.

Batch reactions were generally monitored by analytical thin-layer chromatography performed on silica gel 60 F254 precoated plates and were visualised under UV (254 nm) and with Vanillin as revelator. Microwave irradiation experiments were carried out in a CEM Discover instrument or in an Anton Paar Monowave 300 instrument with internal fiber-optic or IR temperature control. The vials used are in Pyrex and were sealed with Teflon-coated septums. With the Anton Paar instrument, the homogeneity and the good magnetic stirring of the reaction were controlled with a camera which directly focuses on the reaction vial.

Flow reactions were performed in a Vapourtec R-series system which is a high-temperature (up to 250 °C), high-pressure (up to 42 bar) instrument for performing homogeneous reactions. This R-series system is constituted by a R2C+ pump module (module with acid-resistant pumps and injection loops), a R4 reactor module and a fraction collector. The reaction mixture was pumped into the system with one HPLC pump, passed through a stainless steel 1 mm i.d. reactor, through a back-pressure regulator (which controls the pressure into the whole system) and was finally collected in the fraction collector. Perfluoroalkoxy (PFA) polymer tubing (1 mm i.d.) was used for interconnecting lines. Reaction parameters like temperature, residence time (or flow rate) and collection volume were monitored by using the instrument interface and the Flow Commander software.

Flash chromatography was performed on an Isco Combiflash Companion instrument using 50 µm silica columns. Preparative thin-layer chromatography was performed on silica gel 60 F254 0.5 mm 20×20 cm plates and visualised under UV (254 nm). Semi-preparative HPLC was performed using a Waters 600 instrument, combined with a 2424 Evaporating Light Scattering Detector (ELSD), a 2996 Photodiode Array Detector (PDA) and a 2767 sample manager. The column used was a Waters Sunfire C18, 19×150 mm, 5 µm.

Deuterated chloroform used for NMR analyses was neutralised by addition of anhydrous and granular K2CO3. 1H NMR spectra were recorded on Bruker 300 or 500 MHz instruments. 13C NMR spectra were recorded on the same instruments at 75 or 125 MHz. Chemical shifts δ are expressed in parts per million relative to residual chloroform as an internal standard (δ = 7.26 ppm for 1H NMR and 77.4 ppm for 13C NMR). For 1H NMR spectra, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, brs = broad singulet, dt = doublet of triplets), coupling constant (in Hz) and integration. Interpretations were obtained using DEPT 135, 1H-1H COSY, 1H-13C HMQC and HMBC experiments. Low-resolution mass spectra were obtained on a Waters Acquity UPLC system by electrospray ionization (ESI), combined to a Photodiode Array Detector (PDA), an Evaporating Light Scattering Detector (ELSD) and a Tandem Quadrupole Detector (TQD). High-resolution mass spectra were obtained with a Waters Acquity UPLC (by direct injection or with a BEH C18 2.1×50 mm, 1.7 µm column) combined with a Diode Array Detector (DAD) and a Waters LCT Premier XE mass instrument (electrospray ionization with a time-of-flight (ToF) analyzer). IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in reciprocal centimeters (cm⁻¹). Melting points were determined using a Büchi
B-540 apparatus. Optical rotations were determined using an Anton Paar MCP 300 polarimeter with a 1 dm-long cell and data are reported as follows: \([\alpha]_D\) \text{temperature} \ (\text{in} \ 10^{-1} \ \text{deg.cm}^2/\text{g}), \ \text{concentration} \ (c \ \text{in g/100 mL}) \ \text{and} \ \text{solvent}. \ \text{Elemental analyses were performed with a CHNOS Perkin-Elmer analyser (Gif-sur-Yvette, ICSN).}

**General procedures**

**A. General procedure for microwave-assisted glycosylation**

The peracetylated glycosamine (2 eq.), TTBP (2 eq.) and the iron triflate catalyst (15 mol-%) are added to the acceptor (1 eq.) in an oven-dried, argon-purged, 4, 10 or 30 mL (filling volume) microwave vial equipped with a magnetic stirring bar. Everything is flushed under argon and dry CH\(_2\)Cl\(_2\) is added ([acceptor] = 0.065 M). Liquid acceptor (benzyl alcohol) is placed into the tube after the solvent.

**Anton Paar Monowave 300 instrument:** after sealing the vial, the reaction mixture is heated to 110 °C under microwave irradiation for 30 minutes to 3 hours (1 minute ramp time from room temperature to 110 °C and 30 minutes to 3 hours hold time at 110 °C, stirring set at 800 rpm).

**CEM Discover instrument:** after sealing the vial, the reaction mixture is heated to 80 °C under microwave irradiation for 30 minutes to 3 hours.

The reaction mixture is then diluted in CH\(_2\)Cl\(_2\) and washed with a saturated aqueous solution of NaHCO\(_3\). The aqueous layer is extracted with CH\(_2\)Cl\(_2\) (×4) and the combined organic layers are washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The crude product is purified by flash chromatography on silica gel (heptane/EtOAc 5:5 to 0:1) to afford the pure product.

**B. General procedure for setting up and cleaning up the flow system**

Before each experiment, the desired assembly (including sample loop for small-scale reactions) is purged by pumping dichloromethane or chloroform (depending on the reaction solvent) at a flow rate of 5 mL/min, through both solvent and reagent needles for 10 min. Then, the needles are inserted through a septum-sealed, argon-overpressured flask (using the built-in gas manifold) of dry reaction solvent mixture (dichloromethane/acetonitrile 7:3 or chloroform/acetonitrile 7:3). The whole system is then dried by pumping this mixture at a flow rate of 5 mL/min for 10 minutes.

After each experiment, the whole system is washed with the reaction solvent mixture at a flow rate of 5 mL/min for 10 minutes and then with isopropanol with the same flow rate for another 10 minutes.

**C. General procedure for glycosylation under continuous flow conditions**

**C1: small-scale reactions**

As the glycosylation reaction is slow at room temperature, all the reagents and the catalyst are mixed together before injection into the flow system. The N-acetyl-D-glucosamine \(1\beta\) (0.300 mmol, 2 eq.) and the iron triflate catalyst (0.023 mmol, 15 mol-%) are added to the acceptor (0.150 mmol, 1 eq.) in an oven-dried, argon-purged vial equipped with a magnetic stirring bar. Dry mixture of dichloromethane/acetonitrile 7:3 (2 mL, [acceptor] = 0.075 M) is added and the reaction mixture is stirred and sonicated for a few minutes (until complete homogenisation). Liquid acceptor (benzyl alcohol) is placed into the tube after the solvent.
The variation between the solvent volume and the reaction mixture volume was controlled and was not significant.

After setting up and drying the whole flow system (Figure 1) with dry dichloromethane/acetonitrile 7:3 (procedure B), the pump is primed and the reaction mixture is injected with a syringe into the system via a 2 mL-sample loop. The reaction is then fully automated and the reaction parameters (temperature, residence time, collection volume) are controlled using Flow Commander software. The dry solvent mixture (dichloromethane/acetonitrile 7:3) is pumped and pushes the reaction mixture, which is in the sample loop, into the 10mL-stainless steel reactor heated at 110 °C with a fixed flow rate (corresponding to the desired residence time, 45 or 70 min depending on the acceptor). The system pressure (33 bar) is controlled with a back pressure regulator and the reaction mixture is finally collected into a fraction collector.

At the end of the reaction, the reaction mixture is diluted with 20 mL of dichloromethane and washed with a saturated aqueous solution of NaHCO₃ (20 mL). The aqueous layer is extracted with CH₂Cl₂ (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product is purified by flash chromatography on silica gel (heptane/EtOAc 5:5 to 0:1) to give the pure product.

C2: scale-up

As the glycosylation reaction is slow at room temperature, all the reagents and catalyst are mixed together before injection into the flow system. The N-acetyl-d-glucosamine 1β (6.50 mmol, 2 eq.) and the iron triflate catalyst (0.49 mmol, 15 mol-%) are added to the acceptor (3.25 mmol, 1 eq.) in an oven-dried, argon-purged vial equipped with a magnetic stirring bar. Dry mixture of chloroform/acetonitrile 7:3 (45 mL, [acceptor] = 0.072 M) is added and the reaction mixture is stirred and sonicated for a few minutes (until complete homogenisation).

After setting up and drying the whole flow system (Figure 2) with dry mixture of chloroform/acetonitrile 7:3 (procedure B), the reagent needle is transferred into the septum-sealed, argon-overpressured vial containing the reaction mixture. This solution is maintained under argon atmosphere during the whole reaction. The pump is then primed to bring the reaction mixture to the solvent/reagent switch valve. The reaction is fully automated and the reaction parameters (temperature, residence time, collection volume) are controlled using Flow Commander software. The reaction mixture is pumped into two 10 mL-stainless steel reactors in series, heated at 110 °C with a fixed flow rate (corresponding to the desired residence time of 70 min). Once all the reaction mixture is loaded into the reactor, the liquid stream is changed back to solvent (mixture of dry chloroform/acetonitrile 7:3) with the same flow rate and temperature until the end of the reaction. The system pressure (33 bar) is controlled with a back pressure regulator and the reaction mixture is finally collected into a single receptor.
At the end of the reaction, the reaction mixture is diluted with CH$_2$Cl$_2$ (50 mL) and washed with a saturated aqueous solution of NaHCO$_3$ (50 mL). The aqueous layer is extracted with CH$_2$Cl$_2$ (4×50 mL) and the combined organic layers are washed with brine (100 mL), dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The crude product is purified by flash chromatography on silica gel (heptane/EtOAc 5:5 to 0:1) to give the pure product.

**Products description**

Donor 2$^1$ and acceptors 3, 7, 11, 25$^5$ and 27$^6$ were prepared according to known procedures. Donor 33 and acceptor 5 are commercially available.

**Iron triflate catalysts**

Fe(OTf)$_3$·6.2DMSO and Fe(NTf)$_2$·6.3DMSO were prepared according to the procedure of Antoniotti *et al.*$^7$

Fe(OTf)$_3$·6.2DMSO: Elemental analysis: calculated %C = 18.73, %H = 3.80, %F = 17.32, %Fe = 5.66 and %S = 29.87 and experimental found %C = 18.61, %H = 3.77, %F = 16.97, %Fe = 5.22 and %S = 30.09.

Fe(NTf)$_2$·6.3DMSO: Elemental analysis: calculated %C = 16.09, %H = 2.74, %F = 24.63, %Fe = 4.02 and %S = 28.40 and experimental found %C = 16.00, %H = 2.69, %F = 24.97, %Fe = 3.72 and %S = 29.05.

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2-Azetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-ß-D-glucopyranose 1\( \beta \)

\[
\begin{align*}
\text{OAc} & \quad \text{OAc} \\
\text{AcO} & \quad \text{O} \\
\text{NHAc} & \quad \text{OAc}
\end{align*}
\]

Mol. Wt.: 389.35

1,3,4,6-Tetra-O-acetyl-2-amino-2-deoxy-ß-D-glucopyranose hydrochloride\(^6\) (5 g, 13.02 mmol, 1 eq.), acetic anhydride (7.3 mL, 78.17 mmol, 6 eq.) and pyridine (50 mL) were stirred at room temperature for 5 hours under argon. The volatiles were evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (heptane/EtOAc 3:7 to 0:1) to afford 1\( \beta \)\(^5\) (4.40 g, 87 %, white amorphous solid). 1\( \beta \) is also commercially available.

2-Azetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-ß-D-glucopyranose 1\( \alpha \)

\[
\begin{align*}
\text{OAc} & \quad \text{OAc} \\
\text{AcO} & \quad \text{O} \\
\text{NHAc} & \quad \text{OAc}
\end{align*}
\]

Mol. Wt.: 793.85

N-Acetyl-D-glucosamine (1 g, 4.52 mmol) and sodium acetate (990 mg, 12.07 mmol, 2.7 eq.) in acetic anhydride (14 mL) were stirred at 150 °C for 8 hours under argon. The reaction mixture was poured into ice and water, extracted with CH\(_2\)Cl\(_2\) (3×50 mL), washed with water (20 mL), brine (10 mL), dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 1:1 to 3:7) to give the desired product 1\( \alpha \)\(^{10}\) (1.4 g, 80 %, white amorphous solid). 1\( \alpha \) is also commercially available.

Methyl (2-azetamido-3,4,6-tri-O-acetyl-2-deoxy-ß-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-ß-D-glucopyranoside 4

\[
\begin{align*}
\text{OAc} & \quad \text{OAc} \\
\text{AcO} & \quad \text{O} \\
\text{NHAc} & \quad \text{OAc}
\end{align*}
\]

Mol. Wt.: 793.85

Microwave conditions: 4\(^{11}\) was obtained under microwave conditions using donor 1\( \beta \) (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OtF)\(_3\)·6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and acceptor 3\(^\circ\) (30 mg, 0.065 mmol, 1 eq.) in dry CH\(_2\)Cl\(_2\) (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 45 min) (46 mg, 89 %, white amorphous solid). Flow conditions: 4 was also obtained under flow conditions from donor 1\( \beta \) (2.53 g, 6.50 mmol, 2 eq.), Fe(OtF)\(_3\)·6.2DMSO (484 mg, 0.49 mmol, 15 mol-%) and acceptor 3 (1.51 g, 3.25 mmol, 1 eq.) in a mixture of dry CHCl\(_3\)/CH\(_3\)CN 7:3 (45 mL) using general procedure C2 (Vapourtec instrument, 110 °C, 33 bar, 70 min) (2.00 g, 78 %, white amorphous solid).

Benzyl 2-azetamido-3,4,6-tri-O-acetyl-2-deoxy-ß-D-glucopyranoside 6\( \beta \)

\[
\begin{align*}
\text{OAc} & \quad \text{OAc} \\
\text{AcO} & \quad \text{O} \\
\text{NHAc} & \quad \text{OAc}
\end{align*}
\]

Mol. Wt.: 437.44

Microwave conditions: 6\( \beta \)\(^{12}\) was obtained under microwave conditions using donor 1\( \beta \) (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OtF)\(_3\)·6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and benzyl alcohol 5 (7 \( \mu \)L, 0.068 mmol, 1 eq.) in dry CH\(_2\)Cl\(_2\) (1 mL) according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 45 min) (28 mg, 95 %, white amorphous solid). Flow conditions: 6\( \beta \) was also obtained under flow conditions from donor 1\( \beta \) (117 mg, 0.301 mmol, 2 eq.), Fe(OtF)\(_3\)·6.2DMSO (23 mg, 0.023 mmol, 15 mol-%) and benzyl alcohol 5 (16 \( \mu \)L, 8 \( \mu \)L.

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\(^{9}\) US Pat., 281395 A1, 2013.


0.150 mmol, 1 eq.) in a mixture of dry CH₂Cl₂/CH₃CN 7:3 (2 mL), using general procedure C1 (Vapourtec instrument, 110 °C, 33 bar, 45 min) (51 mg, 77 %, white amorphous solid).

4-(Chloromethyl)benzyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside 8

![Chemical Structure](image)

Microwave conditions: 8 was obtained under microwave conditions using donor 1β (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OTf)₃·6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and 4-(chloromethyl)benzyl alcohol 7 (10 mg, 0.064 mmol, 1 eq.) in dry CH₂Cl₂ (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 30 min) (30 mg, 95 %, white amorphous solid). Flow conditions: 8 was also obtained under flow conditions using donor 1β (117 mg, 0.300 mmol, 2 eq.), Fe(OTf)₃·6.2DMSO (23 mg, 0.023 mmol, 15 mol-%) and 4-(chloromethyl)benzyl alcohol 7 (24 mg, 0.153 mmol, 1 eq.) in a mixture of dry CH₂Cl₂/CH₃CN 7:3 (2 mL), according to general procedure C1 (Vapourtec instrument, 110 °C, 33 bar, 45 min) (56 mg, 75 %, white amorphous solid). [α]D²¹: -36.0 (c 1.0 in CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ: 7.36 (d, J = 8.0 Hz, 2H, Ar), 7.29 (d, J = 8.0 Hz, 2H, Ar), 5.48 (d, J₉H₂ = 9.0 Hz, 1H, NH), 5.21 (dd, J₂₂ = 10.5 Hz and J₅,₆ = 9.5 Hz, 1H, H3), 5.09 (t, J₆₂ = 9.5 Hz, 1H, H4), 4.88 (d, J = 12.0 Hz, 1H, OCH₂Ar), 4.65 (d, J = 9.0 Hz, 1H, H1), 4.61-4.58 (m, 3H, OCH₂Ar and ArCH₂Cl), 4.27 (dd, J₆₆ = 12.5 Hz and J₆₅ = 4.5 Hz, 1H, H6), 4.16 (dd, J₆₆ = 12.5 Hz and J₆₅ = 2.5 Hz, 1H, H6'), 3.96 (dt, J₂₃ = 10.5 Hz and J₂₁ = J₂₄ = 9.0 Hz, 1H, H2), 3.67 (ddd, J₅₄ = 9.5 Hz, J₅₆ = 4.5 Hz and J₃₄ = 2.5 Hz, 1H, H5), 2.10 (s, 3H, OCOCH₃), 2.02 (s, 3H, OCOCH₃), 1.91 (s, 3H, NHCOCH₃). ¹³C NMR (75 MHz, CDCl₃) δ: 171.3 (C, COCH₃), 171.1 (C, COCH₃), 170.5 (C, COCH₃), 169.8 (C, COCH₃), 137.7 (C, OCH₂Ar), 137.6 (C, ArCH₂Cl), 129.1 (2CH, Ar), 128.6 (2CH, Ar), 100.0 (CH, C1), 72.7 (CH, C3), 72.3 (CH, C5), 70.6 (CH₂, OCH₂Ar), 68.9 (CH, C4) 62.5 (CH₂, C6), 54.9 (CH, C2), 46.2 (CH₂, ArCH₂Cl), 23.7 (CH₃, NHCOCH₃), 21.2 (CH₃, OCOCH₃), 21.1 (CH₃, OCOCH₃), 21.0 (CH₃, OCOCH₃). IR ν (film, cm⁻¹): 3278 (N-H), 3103 (C-H), 2954 and 2877 (C-H), 1738 (C=O), 1661 (NH-C=O). MS (ESI): m/z = 486 ([M+H]⁺, 100 %), 508 ([M+Na]⁺, 40 %), 971 ([2M+H]²⁺, 15 %), 993 ([2M+Na]²⁺, 50 %). HRMS (ESI): Calcd for C₂₃H₂₉ClNO₉ [M+H]⁺: 486.1531. Found: 486.1531.

2-Chloroacetyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α/β-D-glucopyranose 10

![Chemical Structure](image)

2-chloroacetic acid 9 (0.6 g, 6.42 mmol, 2.5 eq.) and commercial Fe(OTf)₃ (260 mg, 0.51 mmol, 20 mol-%) are added to donor 1β (1 g, 2.57 mmol, 1 eq.) in an oven-dried, argon-purged microwave vial equipped with a magnetic stirring bar. Everything is flushed under argon and dry CH₂Cl₂ is added (1 mL). After sealing the vial, the reaction mixture is heated to 80 °C under microwave irradiation for 45 minutes (CEM Discover instrument). Then, the reaction mixture is diluted in CH₂Cl₂ (20 mL) and washed with a saturated aqueous solution of NaHCO₃ (20 mL). The aqueous layer is extracted with CH₂Cl₂ (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product is purified by flash chromatography on silica gel (heptane/EtOAc 5:5 to 0:1) to afford pure product 10 (230 mg, α/β mixture 8/2, 21 %, colorless oil). ¹H NMR (300 MHz, CDCl₃) δ: 6.22 (d, J₁₆₂₉ = 3.5 Hz, 0.8H, H1α), 5.92 (d, J₆₉ₓ₂₉ = 9.5 Hz, 0.2H, NH), 5.75 (d, J₉ₓ₂₉ = 9.0 Hz, 0.8H, NH), 5.74 (d, J₁₆₂₉ = 9.0 Hz, 0.2H, H1β), 5.25-5.12 (m, 1.2H), 4.50-4.43 (ddd, J₉ₓ₂₉ = 10.5 Hz, J₉ₓ₂₉ = 9.0 Hz and J₁₆₂₉ = 3.5 Hz, 0.8H, H2α), 4.28-4.18 (m, 1H), 4.13 (d, J = 1.0 Hz, 1.6H, CH₂Clα), 4.11-3.98 (m, 3.2H), 3.85-3.79 (ddd, J = 9.5 Hz, J = 7.0 Hz, J = 5.0 Hz and J = 2.5 Hz).
Hz, 0.2H, H5β), 2.05 (s, 3H, Me), 2.02, 2.01, 2.006, 2.00 (4s, 6H, Me), 1.90 (s, 3H, Me). 13C NMR (75 MHz, CDCl3) α isomer δ: 171.8 (C, CO), 170.8 (C, CO), 170.3 (C, CO), 169.3 (C, CO), 165.5 (C, CO), 92.4 (CH, C1), 70.5, 70.4, 67.4 (3CH, C3, C4, C5), 61.5 (CH2, C6), 51.5 (CH, C2), 40.8 (CH2Cl2), 23.1 (CH3), 20.9 (CH3) 20.8 (CH3), 20.7 (CH3). MS (ESI): m/z = 330 ([M-CO2HCH2Cl]̈, 100%), 441 ([M+NH4]⁺, 50%). HRMS (ESI): Calcd for C18H26ClN2O10 [M+NH4]⁺: 441.1276. Found: 441.1296.

Methyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-d-glucopyranosyl) (1→6)-4-O-benzoyl-3-O-(tert-butylidiphenylsilyloxy)-2-deoxy-2-phthalimido-β-d-glucopyranoside 12

was obtained under microwave conditions using donor 1β (33 mg, 0.084 mmol, 2 eq.), TTBP (21 mg, 0.084 mmol, 2 eq.), Fe(OTf)3·6.2DMSO (6 mg, 0.006 mmol, 15 mol-%) and acceptor 11 (28 mg, 0.042 mmol, 1 eq.) in dry CH2Cl2 (1 mL), according to general procedure A with a lower concentration (CEM Discover instrument, 80 °C, 45 min) (32 mg, 76 %, white amorphous solid).

Methyl 3-O-benzyl-4,6-O-benzylidene-α-d-glucopyranoside 15
Methyl 2,4-di-O-benzyl-6-O-tert-butylidiphenylsilyl-α-d-glucopyranoside 13
Methyl 3,4-di-O-benzyl-6-O-tert-butylidiphenylsilyl-α-d-glucopyranoside 17
Methyl 2,3,6-tri-O-benzyl-α-d-glucopyranoside 19

Scheme 1. Synthesis of acceptors 15, 13, 17 and 19

To a mixture of methyl 4,6-O-benzylidene-α-d-glucopyranoside (600 mg, 2.13 mmol, 1 eq.) in CH2Cl2 (20 mL), was added tetrabutylammonium hydrogensulfate (144 mg, 0.43 mmol, 20 mol-%) and benzyl bromide (0.30 mL, 2.55 mmol, 1.2 eq.). 1 M aqueous NaOH (7 mL) is added and the reaction mixture is stirred under reflux for 22 hours. Then, the reaction mixture is diluted with CH2Cl2, the organic layer is separated and the water phase is extracted twice with CH2Cl2. The combined organic layers are washed with aqueous saturated NaHCO3, brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude product is purified by chromatography on silica gel (heptane/EtOAc 7:3 to 5:5) to afford pure methyl 2-O-benzyl-4,6-O-benzylidene-α-d-
glucopyranoside \textsuperscript{14} (21 \%, 166 mg) and methyl 3-O-benzyl-4,6-O-benzylidene-\alpha-d-
glucopyranoside \textsuperscript{15} (48 \%, 380 mg).

Methyl 3-O-benzyl-4,6-O-benzylidene-\alpha-d-
glucopyranoside \textsuperscript{15} (169 mg, 0.45 mmol, 1 eq.) is concentrated twice from toluene in a round-bottom flask. Under argon and with magnetic stirring, the flask is almost entirely submerged in an ice-water bath for 10 min and a solution of borane·THF (3.2 mL, 1 M in THF, 3.2 mmol, 7.1 eq.) is added slowly with a syringe along the sides of the flask. After stirring for 15 minutes, a 1 M solution of dibutylboron triflate in CH\textsubscript{2}Cl\textsubscript{2} (0.45 mL, 0.45 mmol, 1.0 equiv) is added dropwise and the resulting solution is stirred for 3.5 hours at 0 °C under argon. \textsuperscript{15} Then, triethylamine (0.25 mL) is added, methanol (20 mL) is added slowly and the mixture is concentrated under reduced pressure. The mixture is coevaporated three more times with methanol (3×20 mL) and the crude product is purified by column chromatography on silica gel (heptane/\text{EtOAc} 7:3 to 4:6) to afford pure methyl 3,4-di-O-benzyl-\alpha-d-
glucopyranoside \textsuperscript{16} (57\%, 97 mg).

Methyl 3,4-di-O-benzyl-\alpha-d-
glucopyranoside (97 mg, 0.26 mmol, 1 eq.), imidazole (44 mg, 0.65 mmol, 2.5 eq.) and tert-butyl(chloro)diphenylsilane (9.5 \textmu L, 0.36 mmol, 1.4 eq.) in dry DMF (1.2 mL) were stirred at room temperature for 2 hours under argon. The reaction mixture was poured into a saturated aqueous solution of NaHCO\textsubscript{3} (20 mL), extracted with Et\textsubscript{2}O (3×10 mL), washed with brine (20 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/\text{EtOAc} 9:1 to 6:4) to give the desired product 17 (125 mg, 78 \%, colorless oil). [\alpha]_D \textsuperscript{20} \textsuperscript{a} +41.8 (c 0.9 in CHCl\textsubscript{3}). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta: 7.74-7.68 (m, 4H, Ph), 7.45-7.26 (m, 14H, Ph), 7.19-7.16 (m, 2H, Ph), 4.92 (d, J = 11.0 Hz, 1H, CH\textsubscript{2}Ph), 4.90-4.85 (m, 2H, CH\textsubscript{2}Ph), 4.79 (d, J\textsubscript{1,2} = 3.5 Hz, 1H, H1), 4.64 (d, J = 10.5 Hz, 1H, CH\textsubscript{2}Ph), 3.91 (m, 2H, H6 and H6'), 3.78 (t, J\textsubscript{3,2} = J\textsubscript{3,4} = 9.2 Hz, 1H, H3), 3.77-3.62 (m, 3H, H2, H4 and H5), 3.40 (s, 3H, OCH\textsubscript{3}), 2.14 (brs, 1H, OH), 1.06 (s, 9H, C(CH\textsubscript{3})\textsubscript{3}). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \delta: 139.0 (C, Ph), 138.6 (C, Ph), 136.2 (CH, Ph), 136.0 (CH, Ph), 134.0 (C, Ph), 133.6 (C, Ph), 130.0 (CH, Ph), 128.9 (CH, Ph), 128.8 (CH, Ph), 128.4 (CH, Ph), 128.2 (CH, Ph), 128.1 (CH, Ph), 128.1 (CH, Ph), 127.9 (CH, Ph), 99.5 (CH, C1), 83.8 (CH, C3), 78.0 (CH, C4), 75.9 (CH\textsubscript{2}, CH\textsubscript{2}Ph), 75.4 (CH\textsubscript{2}, CH\textsubscript{2}Ph), 73.6 (CH, C2), 72.1 (CH, C5), 63.2 (CH\textsubscript{2}, C6), 55.3 (CH\textsubscript{3}, OCH\textsubscript{3}), 27.2 (3CH\textsubscript{3}, C(CH\textsubscript{3})\textsubscript{3}), 19.7 (C, C(CH\textsubscript{3})\textsubscript{3}). IR \nu (film, cm\textsuperscript{-1}): 3465 (O-H), 3068 (=C-H), 2931 and 2857 (C-H). MS (ESI): m/z = 630 ([M+Na]+\textsuperscript{b}%, 5%), 635 ([M+Na]+, 100%), 1248 ([2M+Na]+, 20%). HRMS (ESI): Calcd for C\textsubscript{37}H\textsubscript{44}NaO\textsubscript{6}Si [M+Na]+: 635.2805. Found: 635.2814.

Methyl 2-O-benzyl-4,6-O-benzylidene-\alpha-d-
glucopyranoside (282 mg, 0.76 mmol, 1 eq.) is concentrated twice by coevaporation with toluene in a round-bottom flask. Under argon and with magnetic stirring, the flask is almost entirely submerged in an ice-water bath for 10 min and a solution of borane·THF (5.5 mL, 1 M in THF, 5.5 mmol, 7.1 eq.) is added slowly with a syringe along the sides of the flask. After stirring for 15 minutes, a solution of dibutylboron triflate (0.76 mL, 1 M in CH\textsubscript{2}Cl\textsubscript{2}, 0.76 mmol, 1.0 equiv) is added dropwise and the resulting solution is stirred for 2.5 hours at 0 °C under argon. \textsuperscript{15} Then, triethylamine (0.4 mL) is added, methanol (35 mL) is added slowly and the mixture is concentrated under reduced pressure. The mixture is coevaporated three more times with methanol (3×35 mL) and the crude product is purified by column chromatography on


silica gel (heptane/EtOAc 7:3 to 4:6) to afford pure methyl 2,4-di-O-benzyl-α-D-glucopyranoside\(^\text{17}\) (88%, 250 mg).

Methyl 2,4-di-O-benzyl-α-D-glucopyranoside (250 mg, 0.67 mmol, 1 eq.), imidazole (113 mg, 1.66 mmol, 2.5 eq.) and tert-butyl(chloro)diphenylsilane (240 µL, 0.93 mmol, 1.4 eq.) in dry DMF (3 mL) were stirred at room temperature for 2 hours under argon. The reaction mixture was poured into a saturated aqueous solution of NaHCO\(_3\) (30 mL), extracted with Et\(_2\)O (3×20 mL), washed with brine (30 mL), dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 9:1 to 7:3 to 4:6) to afford methyl 2,4-di-O-benzyl-α-D-glucopyranoside (96%, 250 mg).

The combined organic layers are washed with NaCl sat. (2×3 mL), cooled to 0 °C and is stirred at this temperature for 20 minutes until complete evolution of HCN! The solution is poured into a saturated aqueous solution of NaHCO\(_3\) (30 mL), washed with brine (6×20 mL), dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product is purified by chromatography on silica gel (heptane/EtOAc 9:1 to 7:3) to give the desired product 13 (390 mg, 96%, colorless oil). \([\alpha]_D^{20\circ} +47.1 (c 1.0 \text{ in CHCl}_3)\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.72-7.67 (m, 4H, Ph), 7.45-7.25 (m, 14H, Ph), 7.24-7.20 (m, 2H, Ph), 4.89 (d, \(J = 11.0 \text{ Hz}, 1H, CH_2Ph\)), 4.73 (s, 2H, \(CH_2Ph\)), 4.69 (d, \(J_{1,2} = 3.5 \text{ Hz}, 1H, H1\)), 4.63 (d, \(J = 11.0 \text{ Hz}, 1H, CH_2Ph\)), 4.11 (t, \(J_{3,2} = J_{3,4} = 9.5 \text{ Hz}, 1H, H3\)), 3.92 (dd, \(J_{6,5} = 11.0 \text{ Hz} \text{ and } J_{6,5} = 2.5 \text{ Hz}, 1H, H6\)), 3.87 (dd, \(J_{5,6} = 11.0 \text{ Hz} \text{ and } J_{6,5} = 4.0 \text{ Hz}, 1H, H6\')), 3.69 (ddd, \(J_{5,4} = 9.5 \text{ Hz}, J_{5,6} = 4.0 \text{ Hz} \text{ and } J_{3,6} = 2.5 \text{ Hz}, 1H, H5\)), 3.54 (t, \(J_{4,3} = J_{4,5} = 9.5 \text{ Hz}, 1H, H4\)), 3.42 (dd, \(J_{2,3} = 9.5 \text{ Hz} \text{ and } J_{2,1} = 3.5 \text{ Hz}, 1H, H2\)), 3.34 (s, 3H, OCH\(_3\)), 2.37 (brs, 1H, OH), 1.06 (s, 9H, C(CH\(_3\))\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 138.8 (C, Ph), 138.5 (C, Ph), 136.2 (CH, Ph), 136.0 (CH, Ph), 134.0 (C, Ph), 133.7 (C, Ph), 130.0 (CH, Ph), 129.9 (CH, Ph), 128.9 (CH, Ph), 128.7 (CH, Ph), 128.4 (CH, Ph), 128.2 (CH, Ph), 128.0 (CH, Ph), 128.0 (CH, Ph), 127.9 (CH, Ph), 97.6 (CH, C1), 80.3 (CH, C2), 78.1 (CH, C4), 75.0 (CH\(_2\), CH\(_2Ph\)), 74.0 (CH, C3), 73.4 (CH\(_2\), CH\(_2Ph\)), 71.5 (CH, C5), 63.5 (CH\(_2\), C6), 55.2 (CH\(_3\), OCH\(_3\)), 27.2 (3CH\(_3\), C(CH\(_3\))\(_3\)), 19.7 (C, C(CH\(_3\))\(_3\)). IR ν (film, cm\(^{-1}\)): 3461 (O-H), 3068 (=C-H), 2930 and 2857 (C-H). MS (ESI): \(m/z = 630 ([M+NH\(_4\)]^+, 10\%), 635 ([M+Na]^+, 100\%), 1248 ([2M+Na]^+, 85\%). HRMS (ESI): Calcd for C\(_{37}\)H\(_{44}\)NaO\(_8\)Si [M+Na]^+: 635.2805. Found: 635.2808.

Methyl 4,6-O-benzylidene-α-D-glucopyranoside (3.00 g, 10.63 mmol, 1 eq.) in dry DMF (35 mL) is cooled to 0 °C under argon. NaH (60% dispersion in mineral oil, 960 mg, 31.88 mmol, 3 eq.), is added by portion and the reaction mixture is stirred at 0 °C for 15 minutes under argon. BNBr (3.8 mL, 31.88 mmol, 3 eq.) is added slowly and the reaction mixture is allowed to warm to room temperature and is stirred at this temperature for 19 hours. MeOH (3 mL) and water (20 mL) are successively added and the reaction mixture is extracted with EtOAc (3×10 mL). The combined organic layers are washed with NaCl sat. (30 mL), dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product is purified by chromatography on silica gel (heptane/EtOAc 90:10 to 5:5) to afford methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside\(^\text{14}\) (3.05 g, 62%).

To a solution of methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (1.50 g, 3.24 mmol, 1 eq.) in dry THF (35 mL) is added powered molecular sieves (4 Å, 1.70 g), methyl orange (5 mg) and NaBH\(_4\)CN (1.70 g, 27.57 mmol, 8.5 eq.) under argon. After 15 minutes at room temperature, the yellow solution is cooled to 0 °C and HCl in Et\(_2\)O (1 M) is added slowly until the solution turns pink and gas evolution ceased completely (danger, release of HCN!).\(^\text{18}\) The solution is then warmed to room temperature and stirred at this temperature for 20 hours under argon. The reaction mixture is poured into a cold saturated aqueous solution of NaHCO\(_3\) (60 mL) and the aqueous layer is extracted with EtOAc (3×60 mL). The combined organic layers are washed with water (3×20 mL), brine (60 mL), dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product is purified by


chromatography on silica gel (heptane/EtOAc 9:1 to 6:4) to give the desired product 19 (830 mg, 55 %, white amorphous solid).

Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-α-D-glucopyranoside 14

was obtained under microwave conditions using donor 1β (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OTf)3 · 6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and acceptor 13 (42 mg, 0.068 mmol, 1 eq.) in dry CH2Cl2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 45 min) (47 mg, 74 %, white amorphous solid).

Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside 16

16 was obtained under microwave conditions using donor 1β (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OTf)3 · 6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and acceptor 15 (23 mg, 0.062 mmol, 1 eq.) in dry CH2Cl2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 60 min) (27 mg, 61 %, white amorphous solid). \([\alpha]_D^{22} +15.9 (c 0.9 \text{ in CHCl}_3)\). 1H NMR (300 MHz, CDCl3) δ: 7.44-7.40 (m, 2H, Ph), 7.36-7.24 (m, 8H, Ph), 5.53 (s, 1H, CHPh), 5.23 (dd, \(J_{B3,B2} = 10.5 \text{ Hz} \) and \(J_{B3,B4} = 9.5 \text{ Hz} \), 1H, HB-3), 5.16 (d, \(J_{NH,B2} = 8.5 \text{ Hz} \), 1H, NH), 5.01 (t, \(J_{B4,B3} = J_{B4,B5} = 9.5 \text{ Hz} \), 1H, HB-4), 4.92 (d, \(J = 12.0 \text{ Hz} \), 1H, CH3Ph), 4.90 (d, \(J_{B1,B2} = 8.5 \text{ Hz} \), 1H, HB-1), 4.85 (d, \(J_{A1,A2} = 3.5 \text{ Hz} \), 1H, HA-1), 4.63 (d, \(J = 12.0 \text{ Hz} \), 1H, CH2Ph), 4.27 (dd, \(J_{A6,A5} = 10.0 \text{ Hz} \) and \(J_{A6,A5} = 4.5 \text{ Hz} \), 1H, HA-6), 4.17 (d, \(J_{B6,B5} = J_{B6,B5} = 4.0 \text{ Hz} \), 2H, HB-6 and HB-6'), 3.99 (t, \(J_{A3,A2} = J_{A3,A4} = 9.5 \text{ Hz} \), 1H, HA-3), 3.88-3.79 (m, 2H, HB-2 and HA-5), 3.75-3.62 (m, 3H, HB-5, HA-2 and HA-6'), 3.59 (t, \(J_{AA,A6} = J_{AA,A5} = 9.5 \text{ Hz} \), 1H, HA-4), 3.40 (s, 3H, OCH3), 2.07 (s, 3H, OCOCH3), 2.00 (s, 3H, OCOCH3), 1.97 (s, 3H, OCOCH3), 1.51 (s, 3H, NHCOCH3). 13C NMR (75 MHz, CDCl3) δ: 171.0 (C, COCH3), 171.0 (C, COCH3), 170.7 (C, COCH3), 169.8 (C, COCH3), 139.3 (C, Ph), 137.6 (C, Ph), 129.4 (CH, Ph), 128.9 (CH, Ph), 128.6 (CH, Ph), 128.1 (CH, Ph), 127.4 (CH, Ph), 126.4 (CH, Ph), 102.4 (CH, CB-1), 101.8 (CH, CHPh), 100.4 (CH, CA-1), 82.8 (CH, CA-4), 81.0 (CH, CA-2), 78.0 (CH, CA-3), 75.1 (CH2, CH2Ph), 72.8 (CH, CB-3), 72.2 (CH, CB-5), 69.5 (CH3, CA-6), 69.0 (CH, CB-4), 62.6 (CH2, CB-6), 62.5 (CH, CA-5), 55.9 (CH3, OCH3), 55.3 (CH, CB-2), 23.3 (CH3, NHCOCH3), 21.2 (CH3, OCOCH3), 21.0 (CH3, OCOCH3). IR ν (film, cm⁻¹): 3280 (N-H), 3092, 3062 and 3030 (C-H), 2920 and 2871 (C-H), 1744 (C=O), 1666 (NH-C=O). MS (ESI): \(m/z = 702 ([M+H]^+, 100\%)\), 724 ([M+Na]^+, 55%), 1404 ([2M+H]^+, 10%), 1426 ([2M+Na]^+, 75%). HRMS (ESI): Calcld for C53H44NO14 [M+H]^+: 702.2762. Found: 702.2766.

Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-α-D-glucopyranoside 18

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Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside 20

\[
\begin{align*}
\text{AcO} & \quad \text{BnO} \\
\text{AcO} & \quad \text{NHAc} \\
\text{BnO} & \quad \text{OMe} \\
\text{C}_{42}H_{51}NO_{14} & \text{Mol. Wt.: 793.85}
\end{align*}
\]

20 was obtained under microwave conditions using donor 1β (500 mg, 0.128 mmol, 2 eq.), TTBP (320 mg, 1.288 mmol, 2 eq.), Fe(OTf)_3·6DMSO (96 mg, 0.097 mmol, 15 mol-%) and acceptor 19 (300 mg, 0.646 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A with a higher concentration (Anton Paar Monowave 300 instrument, 110 °C, 3 hours) (191 mg, 37 %, white amorphous solid).

(2-Methyl-5-tert-butylphenyl) 3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 21

(2-Methyl-5-tert-butylphenyl) 3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 21 (1.4 g, 2.33 mmol, 1 eq.) and trifluoroacetic acid (864 μL, 11.63 mmol, 5 eq.) in dry CH₂Cl₂ (25 mL) were cooled to 0 °C under argon. Et₃SiH (1.85 mL, 11.63, 5 eq.) was added dropwise to the reaction mixture which was then warmed to room temperature and stirred for 8 hours under argon. The reaction mixture was poured into a saturated aqueous solution of NaHCO₃ (30 mL), extracted with CH₂Cl₂ (3×40 mL), dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 8:2 to 6:4) to give the desired product 21 (1.07 g, 76 %, white amorphous solid). [α]D 25°: +32.3 (c 1.0, CHCl₃). Mp: 68.2-73.5 °C (from heptane/EtOAc). 1H NMR (500 MHz, CDCl₃) δ: 7.87-7.80 (m, 2H, NPhth), 7.75-7.69 (m, 2H, NPhth), 7.46 (d, J = 1.5 Hz, 1H, Ph), 7.36-7.27 (m, 5H, Ph), 7.16 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, Ph), 7.01 (d, J = 8.0 Hz, 1H, Ph), 5.66 (dd, J₁,₂ = 10.0 Hz, J₃,₄ = 9.0 Hz, 1H, H₃), 5.62 (d, J₁,₂ = 10.0 Hz, 1H, H₁), 4.58 (AB system, J = 12.0 Hz, 2H, CH₂Ph), 4.34 (t, J₂,₃ = J₃,₄ = 10.0 Hz, 1H, H₂), 3.88-3.81 (m, 2H, H₄ and H₅), 3.77 (dd, J₆,₇ = 10.0 Hz, J₇,₈ = 5.0 Hz, 1H, H₆), 3.71 (dd, J₅,₆ = 9.5 Hz, J₆,₇ = 5.0 Hz, 1H, H₅), 2.91 (d, J₉,H₄ = 3.5 Hz, 1H, OH), 2.13 (s, 3H, Me), 1.90 (s, 3H, Ac), 1.22 (s, 9H, t-Bu). 13C NMR (75 MHz, CDCl₃) δ: 171.2 (C, CO), 168.0 (C, NCO), 167.5 (C, NCO), 149.7 (C, Ph), 137.7 (C, Ph), 137.4 (C, Ph), 134.6 (CH, NPhth), 134.4 (CH, NPhth), 131.9 (C, NPhth), 131.5 (C, NPhth), 131.3 (C, Ph), 130.9 (CH, Ph), 130.1 (CH, Ph), 128.7 (2CH, Ph), 128.1 (3CH, Ph), 125.6 (CH, Ph), 123.8 (2CH, NPhth), 84.4 (CH, C₁), 78.1 (CH, C₅), 74.5 (CH, C₃), 74.0 (CH₂, CH₂Ph), 71.7 (CH, C₄), 70.5 (CH₂, C₆), 54.0 (CH, C₂), 34.6 (C, t-Bu), 31.4 (CH₀H, t-Bu), 20.9 (CH₃, Ac), 20.5 (CH₃, Me). IR ν (film, cm⁻¹): 3472 (O-H), 3063 and 3036 (≡C-H), 2964, 2908 and 2865 (C-H), 1776 (N-C=O), 1742 (C=O), 1715 (N-C=O). MS (ESI): m/z = 621 ([M+NH₄]⁺, 60%). HRMS (ESI): Calcd for C₄₄H₄₃N₂O₄S [M+NH₄]⁺: 621.2634. Found: 621.2618.

(2-Methyl-5-tert-butylphenyl) 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 22

Acceptor 21 (155 mg, 0.257 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.) and Fe(OTf)₃·6.2DMSO (19 mg, 0.019 mmol, 15 mol%-%) are added to donor 1β (50 mg, 0.128 mmol, 1 eq.) in an oven-dried, argon-purged microwave vial equipped with a magnetic stirring bar. Everything is flushed under argon and dry CH₂Cl₂ is added (1 mL). After sealing the vial, the reaction mixture is heated to 70 °C under microwave irradiation for 11 hours (CEM Discover instrument). Then, the reaction mixture is diluted in CH₂Cl₂ (20 mL) and washed with a saturated aqueous solution of NaHCO₃ (20 mL). The aqueous layer is extracted with CH₂Cl₂ (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 5:5 to 0:1) to afford pure product 22 (28 mg, 23 %, white amorphous solid). [α]D 25°: +42.4 (c 0.5, CHCl₃). 1H NMR (500 MHz, CDCl₃) δ: 7.85-7.78 (m, 2H, NPhth), 7.74-7.67 (m, 2H, NPhth), 7.49-7.39 (m, 6H, Ph), 7.16 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H, Ph), 7.03 (d, J = 8.0 Hz, 1H, Ph), 5.68 (t, J₃,A₃⁺A₄ = 9.5 Hz, 1H, HA-3), 5.58 (d, J₃,A₂ = 10.5 Hz, 1H, HA-1), 5.05 (t, J₈A₃⁺B₂ = J₈B₃⁺B₄ = 9.5 Hz, 1H, HB-3), 4.9 (t, J₂,B₃⁺B₃)
= \text{J}_{B4,B5} = 9.5 \text{ Hz}, 1H, HB-4), 4.83 (d, J = 12.0 \text{ Hz}, 1H, CH_2Ph), 4.77 (d, J_{\text{NH,B2}} = 9.0 \text{ Hz}, 1H, NH), 4.57 (d, J_{B1,B2} = 8.5 \text{ Hz}, 1H, HB-1), 4.45 (d, J = 12.0 \text{ Hz}, 1H, CH_2Ph), 4.37-4.27 (m, 2H, HB-6 and HA-2), 4.03 (t, J_\text{AA,AS} = J_{\text{AA,AS}} = 9.5 \text{ Hz}, 1H, HA-4), 3.95 (d, J_{BS,BS} = 12.0 \text{ Hz}, 1H, HB-6'), 3.69-3.57 (m, 4H, HB-2, HA-5, HA-6 and HA-6'), 3.52-3.44 (m, 1H, HB-5), 2.15 (s, 3H, Me), 2.01 (s, 3H, Ac), 1.99 (s, 3H, Ac), 1.96 (s, 3H, Ac), 1.83 (s, 3H, Ac), 1.72 (s, 3H, Ac), 1.25 (s, 9H, t-Bu). ^{13}C \text{ NMR (75 MHz, CDCl}_3\): 170.8 (2C, CO), 170.3 (C, CO), 170.0 (C, CO), 169.6 (C, CO), 167.8 (C, NCO), 167.4 (C, NCO), 149.6 (C, Ph), 138.0 (C, Ph), 137.6 (C, Ph), 134.5 (CH, NPhth), 134.3 (CH, NPhth), 131.9 (C, NPhth), 131.5 (C, NPhth), 131.2 (C, Ph), 131.1 (C, Ph), 130.1 (C, Ph), 129.1 (2C, Ph), 129.0 (2C, Ph), 128.8 (CH, Ph), 125.7 (CH, Ph), 123.8 (CH, NPhth), 123.7 (CH, NPhth), 100.0 (CH, CB-1), 84.4 (CH, CA-1), 78.5 (CH, CA-5), 75.3 (CH, CA-4), 73.9 (CH_2, CH_2Ph), 72.6 (CH, CB-3), 71.8 (CH, CA-3), 71.7 (CH, CB-5), 68.6 (CH, CB-4), 67.8 (CH_2, CA-6), 62.0 (CH_2, CB-6), 55.0 (CH, CB-2), 54.4 (CH, CA-2), 34.6 (C, t-Bu), 31.4 (3CH_3, t-Bu), 23.3 (CH_3, Ac), 20.8 (3CH_3, 2Ac and Me), 20.6 (CH_3, Ac), 20.5 (CH_3, Ac). IR \nu (film, cm^{-1}): 3024 (N-H), 2964 (C-H), 1745 (C=O), 1719 (N=C=O). MS (ESI): m/z = 955 ([M+Na]^+, 100%). HRMS (ESI): Calcd for C_{48}H_{56}N_2NaO_{15}S [M+Na]^+: 955.3299. Found: 955.3287.

(2-Methyl-5-tert-butylphenyl) 3,6-di-O-benzyl-2-deoxy-2-phthalamido-1-thio-β-d-glucopyranoside 23

To a suspension of (2-Methyl-5-tert-butylphenyl) 4,6-O-benzylidene-2-deoxy-2-phthalamido-1-thio-β-d-glucopyranoside\textsuperscript{23} (4.09 g, 7.31 mmol) and NaH (60 % dispersion in mineral oil, 366 mg, 9.14 mmol, 1.25 eq.) in dry DMF (40 mL), was added dropwise BnBr (1.31 mL, 10.96 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature for 4 hours under argon. MeOH (6 mL) and water (100 mL) were successively added and the reaction mixture was extracted with EtOAc (3×50 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 1:0 to 7:3) to give (2-methyl-5-tert-butylphenyl) 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalamido-1-thio-β-d-glucopyranoside (3 g, 63 %, white amorphous solid). 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalamido-1-thio-β-d-glucopyranoside (1.5 g, 2.31 mmol) and NaBH_3CN (1.99 g, 31.63 mmol, 13.7 eq.) in dry CH_2Cl_2 (23 mL) were cooled to 0 °C under argon. A solution of HCl in Et_2O (2 M, 23 mL) was added dropwise to the reaction mixture (danger, release of HCN!). It was then warmed to room temperature and stirred at this temperature for 8 hours under argon. The reaction mixture was poured into a saturated aqueous solution of NaHCO_3 (50 mL), extracted with CH_2Cl_2 (3×70 mL), washed with a saturated aqueous solution of NaHCO_3 (40 mL), a 1 M aqueous solution of HCl (40 mL), brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 8:2 to 6:4) to give the desired product 23 (1.24 g, 82 %, white amorphous solid). [α]_D\textsuperscript{25}: +81.2 (c 1.0, CHCl_3). ^{1}H NMR (500 MHz, CDCl_3): δ: 7.82 (d, J = 6.5 Hz, 1H, NPhth), 7.73-7.61 (m, 3H, NPhth), 7.41 (d, J = 1.5 Hz, 1H, Ph), 7.36-7.27 (m, 5H, Ph), 7.12 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H, Ph), 7.05-7.01 (m, 2H, Ph), 6.98 (d, J = 8.0 Hz, 1H, Ph), 6.96-6.90 (m, 3H, Ph), 5.44 (d, J_{j2} = 10.0 Hz, 1H, H1), 4.72 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.63-4.49 (m, 3H, CH_2Ph), 4.32-4.22 (m, 2H, H2 and H3), 3.88-3.79 (m, 2H, H4 and H6), 3.75 (dd, J_{j,4} = 10.0 Hz, J_{j,6} = 5.5 Hz, 1H, H6'), 3.67-3.60 (m, 1H, H5), 2.88 (d, J_{jOH} = 2.0 Hz, 1H, OH), 2.09 (s, 3H, Me), 1.2 (s, 9H, t-Bu). ^{13}C NMR (75 MHz, CDCl_3): δ: 168.2 (C, NCO), 167.5 (C, NCO), 149.6 (2C, NPhth), 138.3 (C, Ph), 137.7 (C, Ph), 137.1 (C, Ph), 134.2 (CH, NPhth), 134.0 (CH, NPhth), 131.9 (2C, Ph), 130.4 (CH, Ph), 130.0 (CH, Ph), 128.7 (2CH, Ph), 128.4 (2CH, Ph), 128.2 (3CH, Ph), 128.1 (2CH, Ph), 127.7 (CH, Ph), 125.3 (CH, Ph), 123.7 (CH, NPhth), 123.4 (CH, NPhth), 84.7 (CH, C1), 79.8 (CH, C3), 77.7 (CH, C5),
74.6 (CH and CH2, C4 and CH3Ph), 74.0 (CH2, CH3Ph), 71.0 (CH2, C6), 54.8 (CH, C2), 34.6 (C, t-Bu), 31.4 (3CH3, t-Bu), 20.4 (CH3, Me). IR ν (film, cm⁻¹): 3476 (O-H), 3059 and 3028 (=C-H), 2956, 2909 and 2865 (C-H), 1774 (N=C=O), 1713 (N=C=O). MS (ESI): m/z = 674 ([M+Na]+, 100%). HRMS (ESI): Caled for C39H41NNaO6S [M+Na]+: 674.2553. Found: 674.2576. Elementary Analysis: Caled for C39H41NO6S: C, 71.86; H, 6.34; N, 2.15; S, 4.92. Found: C, 71.45; H, 6.49; N, 2.22; S, 4.87.

(2-Methyl-5-tert-butylphenyl) (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 24

Acceptor 23 (417 mg, 0.640 mmol, 5 eq.) and Fe(OTf)3·6.2DMSO (62 mg, 0.063 mmol, 50 mol%) were added to donor 1β (50 mg, 0.128 mmol, 1 eq.) in an oven-dried, argon-purged, microwave vial equipped with a magnetic stirring bar. Everything is flushed under argon and dry CH2Cl2 is added (1 mL). After sealing the vial, the reaction mixture is heated to 70 °C under microwave irradiation for 3 hours (CEM Discover instrument). Then, the reaction mixture is diluted in CH2Cl2 (20 mL) and washed with a saturated aqueous solution of NaHCO3 (20 mL). The aqueous layer is extracted with CH2Cl2 (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na2SO4, filtered and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 5:5 to 0:1) to afford pure product 24 (30 mg, 25 %, white amorphous solid). [α]D: +44.1 (c 0.5, CHCl3). 1H NMR (500 MHz, CDCl3) δ: 7.78-7.70 (d, J = 7.0 Hz, 1H, NPhth), 7.68-7.57 (m, 2H, NPhth and Ph), 7.12 (d, J = 7.5 Hz, 1H, Ph), 6.99 (d, J = 7.5 Hz, 1H, Ph), 6.94 (d, J = 7.5 Hz, 2H, Ph), 6.80-6.68 (m, 3H, Ph), 5.35 (d, Jα,α′ = 10.0 Hz, 1H, HA-1), 4.96 (t, Jβ,B3 = JB4,B5 = 9.5 Hz, 1H, HB-4), 4.92-4.82 (m, 2H, CH2Ph and HB-3), 4.75 (d, J = 12.5 Hz, 1H, CH2Ph), 4.68 (d, JNHB2 = 9.5 Hz, 1H, NH), 4.47 (d, JBB2 = 8.5 Hz, 1H, HB-1), 4.38 (d, J = 12.0 Hz, 1H, CH2Ph), 4.35 (d, J = 12.5 Hz, 1H, CH2Ph), 4.25-4.18 (m, 3H, HB-6, HA-2 and HA-3), 4.04-3.92 (m, 3H, HB-2, HB-6' and HA-4), 3.67 (dd, Jα6,α′6 = 10.5 Hz, Jα6,α′5 = 2.0 Hz, 1H, HA-6), 3.59 (d, Jα6,α′5 = 10.5 Hz, Jα6,α′5 = 1.0 Hz, 1H, HA-6'), 3.56-3.46 (m, 2H, HB-5 and HA-5), 2.10 (s, 3H, Me), 2.00 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.94 (s, 3H, Ac), 1.70 (s, 3H, Ac), 1.23 (s, 9H, t-Bu). 13C NMR (75 MHz, CDCl3) δ: 171.0 (C, CO), 170.9 (C, CO), 169.9 (C, CO), 169.5 (C, CO), 167.9 (C, NCO), 167.4 (C, NCO), 149.5 (C, Ph), 138.8 (C, Ph), 137.8 (C, Ph), 137.2 (C, Ph), 133.9 (C, NPhth), 133.7 (C, NPhth), 131.9 (C, Ph), 131.8 (2C, NPhth), 130.6 (CH, CO), 129.3 (2CH, Ph), 129.2 (2CH, Ph), 129.1 (CH, Ph), 128.1 (2CH, Ph), 128.0 (2CH, Ph), 127.1 (CH, Ph), 125.3 (CH, Ph), 123.5 (CH, NPhth), 123.4 (CH, NPhth), 101.0 (CH, CB-1), 84.6 (CH, CA-1), 78.9 (CH, CA-4), 78.5 (CH, CA-5), 78.2 (CH, CA-3), 75.0 (CH2, CH2Ph), 74.2 (CH2, CH2Ph), 73.3 (CH, CB-3), 71.6 (CH, CB-5), 68.8 (CH, CB-4), 68.0 (CH2, CA-6), 62.1 (CH2, CB-6), 55.2 (CH, CA-2), 54.4 (CH, CB-2), 34.6 (C, t-Bu), 31.4 (3CH3, t-Bu), 23.3 (CH3, Ac), 20.8 (3CH3, 2Ac and Me), 20.4 (3CH3, Ac). IR ν (film, cm⁻¹): 3288 (N-H), 2944, 2927 and 2861 (C-H), 1778 (N=C=O), 1746 (C=O), 1714 (N=C=O), 1663 (NH=C=O). MS (ESI): m/z = 1003 ([M+Na]+, 100%). HRMS (ESI): Caled for C33H55O12N3NaS [M+Na]+: 1003.3663. Found: 1003.3691. Elementary Analysis: Caled for C33H55O12N3S: C, 64.88; H, 6.16; N, 2.86; S, 3.27. Found: C, 65.27; H, 6.56; N, 2.51; S, 2.89.

2-Acetamido-1-O-acetyl-3,4,6-tri-O-benzyl-2-deoxy-α/β-D-glucopyranose 29
2-acetamido-3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranose\(^{22}\) (510 mg, 1.03 mmol, 1 eq.) and pyridine hydrochloride (153 mg, 1.32 mmol, 1.3 eq.) in pyridine (5 mL) are stirred at 100 °C for 1 hour under argon. To this solution, acetic anhydride (255 µL, 2.70 mmol, 2.6 eq.) is added and the reaction mixture is stirred at room temperature for 8 hours. The volatiles are evaporated under reduced pressure and the crude product is purified by chromatography on silica gel (heptane/EtOAc 6:4 to 0:1) to afford pure product 29\(^{23}\) as a mixture of two anomers (470 mg, 88 %, \(\alpha/\beta: 1:2\), white amorphous solid).

**Methyl (2-acetamido-3,4,6-tri-O-benzyl-2-deoxy-\(\beta\)-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside 30**

\[
\text{BnO} \quad \text{O} \quad \text{AcO} \\
\alpha/\beta: 1:2 \quad \text{NHAc}
\]

30\(^{24}\) was obtained under microwave conditions using donor 29 (69 mg, 0.129 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OTf)\(_3\)-6.2DMSO (9 mg, 0.010 mmol, 15 mol-%) and acceptor 32 (30 mg, 0.065 mmol, 1 eq.) in dry CH\(_2\)Cl\(_2\) (1 mL), according to general procedure A (CEM Discover instrument, 80 °C, 45 min) (62 mg, 86 %, white amorphous solid).

2-Acetamido-1,3-di-O-acetyl-4,6-O-benzylidene-2-deoxy-\(\alpha\)-D-glucopyranose 32

\[
\text{Ph} \quad \text{O} \quad \text{NHAc} \\
\alpha/\beta: 1:1 \quad \text{NHAc}
\]

N-acetyl-D-glucosamine (5 g, 22.6 mmol, 1 eq.), benzaldehyde (13.7 mL, 135.6 mmol, 6 eq.) and ZnCl\(_2\) (3.1 g, 22.6 mmol, 1 eq.) were stirred at room temperature for 12 hours under argon. The precipitate was filtered off, washed with petroleum ether (2×40 mL), washed with water (2×40 mL) and dried over reduced pressure. The crude 4,6-O-benzylidene-D-glucosamine (6.99 g, quant.) was used in the next step without further purification. This intermediate (500 mg, 1.62 mmol, 1 eq.) and pyridine hydrochloride (243 mg, 2.10 mmol, 1.3 eq.) in pyridine (5 mL) were stirred at 100 °C for 1 hour. To this solution, acetic anhydride (772 µL, 8.24 mmol, 5.1 eq.) was added and the reaction mixture was stirred at room temperature for 8 hours.\(^{25}\) The volatiles were evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (heptane/EtOAc 6:4 to 0:1) to afford pure product 32\(^{26}\) (374 mg, 59 %, \(\alpha/\beta: 1:1\), white amorphous solid).

**Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-\(\beta\)-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside 34**

\[
\text{AcO} \quad \text{O} \quad \text{BnO} \\
\text{AcO} \quad \text{O} \quad \text{Me}
\]

34 was obtained under microwave conditions using donor 33 (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.128 mmol, 2 eq.), Fe(OTf)\(_3\)-6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and acceptor 3\(^{2}\) (30 mg, 0.065 mmol, 1 eq.) in dry CH\(_2\)Cl\(_2\) (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 30 min) (49 mg, 95 %, amorphous white solid). \([\alpha]_D^{20} +1.70 (c 1.0 \text{ in CHCl}_3)\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.38-7.28 (m, 15H, 3Ph), 5.33 (dd, \(J_{B4,B5} = 3.5 \text{ Hz and } J_{B4,B5} = 1.0 \text{ Hz, H1, HB-4}\), 5.28 (d, \(J_{NH,B2} =

\[\ldots\]

\[\ldots\]

Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→3)-2,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-α-D-glucopyranoside 35

was obtained under microwave conditions using donor 33 (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(Ot),[6]-2DMSO (10 mg, 0.010 mmol, 15 mol%) and acceptor 13 (40 mg, 0.065 mmol, 1 eq.) in dry CH₂Cl₂ (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 30 min) (46 mg, 75 %, white amorphous solid). \([\alpha]_D^{20}\): +16.1 (c 1.0 in CHCl₃). ¹H NMR (300 MHz, CDCl₃) \(\delta\): 7.72-7.68 (m, 4H, Ph), 7.48-7.33 (m, 13H, Ph), 7.28-7.26 (m, 3H, Ph), 5.30 (br d, \(J_{B1,B2} = 3.0\) Hz, 1H, HB-4), 5.06 (d, \(J = 10.5\) Hz, 1H, CH₂Ph), 5.02 (d, \(J_{NH,B2} = 9.5\) Hz, 1H, NH), 4.94 (d, \(J_{B1,B2} = 8.5\) Hz, 1H, HB-1), 4.93 (dd, \(J_{B2,B3} = 11.0\) Hz and \(J_{B3,B4} = 3.0\) Hz, 1H, HB-3), 4.80 (d, \(J = 12.0\) Hz, 1H, CH₂Ph), 4.75 (d, \(J_{A1,A2} = 3.5\) Hz, 1H, HA-1), 4.58 (d, \(J = 12.0\) Hz, 1H, CH₂Ph), 4.48 (d, \(J = 10.5\) Hz, 1H, CH₂Ph), 4.26 (t, \(J_{A3,A2} = J_{A3,A4} = 9.0\) Hz, 1H, HA-3), 4.22-4.09 (m, 2H, HB-6 and HB-2), 3.94 (dd, \(J_{B6',B6} = 11.0\) Hz and \(J_{B6',B5} = 6.0\) Hz, 1H, HB-6'), 3.87-3.82 (m, 3H, HA-6 and HB-5), 3.71-3.65 (m, 1H, HA-5), 3.57-3.50 (m, 2H, HA-2 and HA-4), 3.35 (s, 3H, OCH₃), 2.11 (s, 3H, OCOCH₃), 1.99 (s, 3H, OCOCH₃), 1.96 (s, 3H, OCOCH₃), 1.71 (s, 3H, NHCOCH₃), 1.07 (s, 9H, C(CH₃)₃). ¹³C NMR (75 MHz, CDCl₃) \(\delta\): 171.0 (C, COCH₃), 170.7 (C, COCH₃), 170.7 (C, COCH₃), 170.4 (C, COCH₃), 138.8 (C, Ph), 138.4 (C, Ph), 136.1 (CH, Ph), 136.0 (CH, Ph), 133.9 (C, Ph), 133.7 (C, Ph), 130.0 (CH, Ph), 129.9 (CH, Ph), 129.4 (CH, Ph), 128.8 (CH, Ph), 128.5 (CH, Ph), 128.0 (CH, Ph), 127.9 (CH, Ph), 127.5 (CH, Ph), 102.2 (CH, CB-1), 97.1 (CH, CA-1), 81.7 (CH, CA-2), 79.8 (CH, CA-3), 76.1 (CH, CA-4), 75.2 (CH₂, CH₂Ph), 72.7 (CH₂, CH₂Ph), 71.8 (CH, CA-5), 71.5 (CH, CB-3), 70.9 (CH, CB-5), 66.9 (CH, CB-4), 63.4 (CH₂, CA-6), 61.4 (CH₂, CB-6), 55.2 (CH₃, OCH₃), 51.6 (CH, CB-2), 27.2 (3CH₃, C(CH₃)₃), 23.6 (CH₃, NHCOCH₃), 21.1 (CH₃, OCOCH₃), 21.1 (CH₃, OCOCH₃), 19.7 (C, C(CH₃)₃). IR v (film, cm⁻¹): 3285 (N-H), 2958, 2929, 2999 and 2861 (C-H), 1750 (C=O), 1661 (NH-C=O). MS (ESI): \(m/z\) = 942 ([M+H]⁺, 35%), 964 ([M+Na]⁺, 100%). HRMS (ESI): Calcd for C₅₁H₆₃NO₄Si [M+Na]⁺: 964.3916. Found: 964.3917.
Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside 36

36 was obtained under microwave conditions using donor 33 (46 mg, 0.118 mmol, 2 eq.), TTBP (29 mg, 0.117 mmol, 2 eq.), Fe(OtBu)3·6.2DMSO (9 mg, 0.009 mmol, 15 mol-%) and acceptor 15 (22 mg, 0.059 mmol, 1 eq.) in dry CH2Cl2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 60 min) (26 mg, 63 %, amorphous white solid). [α]D20: +5.43 (c 0.7 in CHCl3). 1H NMR (300 MHz, CDCl3) δ: 7.47-7.44 (m, 2H, Ph), 7.38-7.29 (m, 8H, Ph), 5.56 (s, 1H, CHPh), 5.36-5.29 (m, 2H, HB-3 and HB-4), 5.06 (d, JNH,B2 = 8.5 Hz, 1H, NH), 5.00 (d, JB1,B2 = 8.5 Hz, 1H, HB-1), 4.96 (d, J = 12.0 Hz, 1H, CH2Ph), 4.87 (d, JA1,A2 = 3.5 Hz, 1H, HA-1), 4.67 (d, J = 12.0 Hz, 1H, CH2Ph), 4.30 (dd, JAB6,A6 = 10.0 Hz and JAB6,A5 = 4.5 Hz, 1H, HA-5), 4.14 (d, JB6,B5 = JB6′,B5 = 6.5 Hz, 2H, HB-6 and HB-6′), 4.04 (t, JA3,A2 = JA3,A4 = 9.5 Hz, 1H, HA-3), 3.96-3.83 (m, 3H, HB-2, HB-5, HA-5), 3.78-3.71 (m, 1H, HA-6), 3.71-3.66 (dd, JA2,A3 = 9.5 Hz and JA2,A1 = 3.5 Hz, 1H, HA-2), 3.62 (t, JA4,A3 = JA4,A5 = 9.5 Hz, 1H, HA-4), 3.43 (s, 3H, OCH3), 2.15 (s, 3H, COCH3), 2.06 (s, 3H, COCH3), 1.97 (s, 3H, COCH3), 1.49 (s, 3H, COCH3). 13C NMR (75 MHz, CDCl3) δ: 170.9 (C, COCH3), 170.8 (C, COCH3), 170.5 (C, COCH3), 137.7 (C, Ph), 129.4 (CH, Ph), 128.9 (CH, Ph), 128.1 (CH, Ph), 127.6 (CH, Ph), 126.4 (CH, Ph), 102.5 (CH, CHPh), 101.8 (CH, CB-1), 100.4 (CH, CA-1), 82.9 (CH, CA-4), 84.1 (CH, CA-2), 78.0 (CH, CA-3), 75.2 (CH2, CH2Ph), 71.3 (CH, CB-5), 70.2 (CH, CB-3), 69.5 (CH2, CA-6), 67.2 (CH, CB-4), 62.6 (CH, CA-5), 62.2 (CH2, CB-6), 55.8 (CH3, OCH3), 52.5 (CH, CB-2), 23.4 (COCH3), 21.1 (COCH3), 21.0 (COCH3). IR ν (film, cm−1): 3288 (N≡H), 3095, 3071 and 3033 (C=H), 2921 and 2851 (C=O), 1745 (C=O), 1661 (NH=C=O). MS (ESI): m/z = 702 [(M+H)+], 100%, 724 [(M+Na)+], 85%, 1425 [(2M+Na)+], 90%. HRMS (ESI): Calcd for C35H44NO14·[M+H]+: 702.2762. Found: 702.2774.

Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→2)-3,4-di-O-benzyl-6-O-tert-butylidiphenylsilyl-α-D-glucopyranoside 37

37 was obtained under microwave conditions using donor 33 (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OtBu)3·6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and acceptor 17 (40 mg, 0.065 mmol, 1 eq.) in dry CH2Cl2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 45 min) (34 mg, 55 %, amorphous white solid). [α]D20: +18.8 (c 1.0 in CHCl3). 1H NMR (300 MHz, CDCl3) δ: 7.73-7.68 (m, 4H, Ph), 7.43-7.27 (m, 11H, Ph), 7.23-7.19 (m, 3H, Ph), 7.07-7.04 (m, 2H, Ph), 5.42 (dd, JB3,B2 = 10.5 Hz and JB3,B4 = 3.5 Hz, 1H, HB-3), 5.37 (dd, JB4,B3 = 3.5 Hz and JB4,B5 = 1.0 Hz, 1H, HB-4), 5.12 (d, JNH,B2 = 8.0 Hz, 1H, NH), 5.06 (d, JB1,B2 = 8.5 Hz, 1H, HB-1), 4.91 (d, JA1,A2 = 3.5 Hz, 1H, HA-1), 4.86 (d, J = 2.0 Hz, 2H, CH2Ph), 4.79 (d, J = 10.5 Hz, 1H, CH2Ph), 4.59 (d, J = 10.5 Hz, 1H, CH2Ph), 4.18-4.16 (m, 2H, HB-6 and HB-6′), 4.02-3.97 (m, 2H, HB-5, HA-3), 3.93-3.84 (m, 3H, HB-2, HB-6 and HA-6′), 3.73-3.62 (m, 3H, HA-2, HA-4 and HA-5), 3.38 (s, 3H, OCH3), 2.13 (s, 3H, COCH3), 2.07 (s, 3H, COCH3), 1.97 (s, 3H, COCH3), 1.42 (s, 3H, COCH3), 1.07 (s, 9H, C(CH3)3). 13C NMR (75 MHz, CDCl3) δ: 170.9 (C, COCH3), 170.8 (C, COCH3), 170.7 (C, COCH3), 170.5 (C, COCH3), 139.5 (C, Ph), 138.4 (C, Ph), 136.2 (CH, Ph), 136.0 (CH, Ph), 133.9 (C, Ph), 133.6 (C, Ph), 130.0 (CH, Ph), 130.0 (CH, Ph), 128.9 (CH, Ph), 128.7 (CH, Ph), 128.3 (CH, Ph), 128.1 (CH, Ph), 128.0 (CH, Ph), 127.9 (CH, Ph), 127.1 (CH, Ph), 102.2 (CH, CB-1), 99.3 (CH, CA-1), 82.9 (CH, CA-2), 81.3 (CA-3), 78.4 (CH, CA-4), 75.5 (CH2, CH2Ph), 75.5 (CH2, CH2Ph), 75.3 (CH2, CH2Ph), 75.1 (CH2, CH2Ph), 51.1 (CH2).
under reduced pressure. The crude product was purified by chromatography on si

71.6 (CH, CA-5), 71.2 (CH, CB-5), 69.9 (CH, CB-3), 67.2 (CH, CB-4), 63.1 (CH2, CA-6), 62.3 (CH2, CB-6), 55.2 (CH4, OCH3), 52.7 (CH, CB-2), 27.2 (CH3, C(CH3)3), 23.3 (CH3, COCH3), 21.1 (CH3, COCH3), 21.0 (CH3, COCH3), 19.7 (C, C(CH3)3).


Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-a-D-glucopyranoside 38

38 was obtained under microwave conditions using donor 33 (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), Fe(OTf)3: 6.2DMSO (10 mg, 0.010 mmol, 15 mol-%) and acceptor 19 (29 mg, 0.064 mmol, 1 eq.) in dry CH2Cl2 (1 mL), according to general procedure A (Anton Parr Monowave 300 instrument, 110 °C, 3 hours) (13 mg, 26 %, amorphous white solid). [δ]20: -27.2 (c 0.7 in CHCl3).

1H NMR (500 MHz, CDC13) δ: 7.48-7.24 (m, 15H, Ph), 5.21 (dd, J = 3.0 Hz, 1H, HB-4), 4.97 (d, J = 11.0 Hz, 1H, CH2Ph), 4.84 (d, J = 12.0 Hz, 1H, CH2Ph), 4.81-4.76 (m, 3H, CH2Ph, HB-3), 4.63 (d, J = 12.0 Hz, 1H, CH2Ph), 4.57 (d, J1A2 = 4.0 Hz, 1H, HA-1), 4.40 (d, JB1,B2 = 8.5 Hz, 1H, HB-1), 4.38 (d, JNH,B2 = 10.0 Hz, 1H, NH), 4.36 (d, J = 12.0 Hz, 1H, CH2Ph), 3.97 (dt, JBB1,JB2 = 10.0 Hz and JB2,B3 = 8.5 Hz, 1H, HB-2), 3.91-3.81 (m, 4H, HA-3, HA-4, HB-6, HB-6'), 3.66-3.58 (m, 3H, HA-6, HA-5, HB-5), 3.50 (dd, JAB1,AB2 = 10.5 Hz and JAB1,AB3 = 2.0 Hz, 1H, HA-6'), 3.49-3.47 (m, 1H, HA-2), 3.37 (s, 3H, OCH3), 2.06 (s, 3H, OCOCH3), 2.00 (s, 3H, OCOCH3), 1.96 (s, 3H, OCOCH3), 1.74 (s, 3H, NHCOCH3). 13C NMR (125 MHz, CDC13) δ: 170.8 (C, COCH3), 170.6 (C, COCH3), 170.1 (C, COCH3), 139.9 (C, Ph), 138.7 (C, Ph), 138.2 (C, Ph), 129.5 (CH, Ph), 129.3 (CH, Ph), 129.2 (CH, Ph), 128.8 (CH, Ph), 128.5 (CH, Ph), 128.2 (CH, Ph), 127.7 (CH, Ph), 127.6 (CH, Ph), 101.0 (CH, CB-1), 98.9 (CH, CA-1), 80.2 (CH, CA-3), 79.2 (CH, CA-2), 77.1 (CH, CA-4), 75.4 (CH2, CH2Ph), 74.2 (CH2, CH2Ph), 74.0 (CH2, CH2Ph), 70.8 (CH, CB-3), 70.6 (CH, CB-5), 69.8 (CH, CA-5), 67.9 (CH2, CA-6), 66.5 (CH, CB-4), 61.2 (CH2, CB-6), 55.7 (CH3, OCH3), 51.6 (CH, CB-2), 23.7 (CH3, NHCOCH3), 21.1 (CH3, OCOCH3), 21.0 (CH3, OCOCH3). IR υ (film, cm⁻¹): 3326 (N-H), 3089, 3062 and 3030 (=C-H), 2918 (C-H), 1749 (C=O), 1670 (NH-C=O). MS (ESI): m/z = 794 ([M+H]+, 100%), 816 ([M+Na]+, 50%). HRMS (ESI): Calcd for C42H52NO14 [M+H]+: 794.3388. Found: 794.3399.

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-formamido-β-D-glucopyranoside 39

To a solution of 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride8 (1 g, 2.61 mmol) in a 1:1 CH2Cl2-saturated aqueous solution of NaHCO3 (40 mL) was added dropwise acetoformic anhydride27 (495 µL, 7.82 mmol, 3 eq.) at 0 °C. The reaction was then warmed to room temperature and stirred at this temperature for 3 hours and then the organic layer was separated and the aqueous layer was extracted with CH2Cl2. The combined organic layers were dried over Na2SO4 and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel

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(heptane/EtOAc 1:1 to 0:1) to give the desired product 39\(^{28}\) (912 mg, 93 \%, white amorphous solid).

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-(4-methylbenzamido)-β-D-glucopyranose 40

To a solution of 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride\(^6\) (1 g, 2.61 mmol) in pyridine (11 mL) was added dropwise 4-methylbenzoyl chloride (2.1 mL, 15.6 mmol, 6 eq.) at 0 °C under argon. The reaction was warmed to room temperature and stirred at this temperature for 8 hours. Then, the reaction mixture was poured into water (30 mL), extracted with CH\(_2\)Cl\(_2\) (3×40 mL) and the combined organic layers were washed with brine (10 mL), dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 1:1 to 0:1) to afford pure product 40 (910 mg, 75 \%, white solid). Mp: 205.4-210.3 °C (from EtOAc). [\(\alpha\)]\(_D\)\(^{22}\): +42.8 (c 1.0, CHCl\(_3\)). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.56 (d, \(J = 8.0\) Hz, 2H, Ph), 7.20 (d, \(J = 8.0\) Hz, 2H, Ph), 6.11 (br d, \(J_{NH,2} = 9.5\) Hz, 1H, NH), 5.78 (d, \(J_{1,2} = 8.5\) Hz, 1H, H1), 5.27-5.17 (m, 2H, H3 and H4), 4.59-4.48 (m, 1H, H2), 4.28 (d, \(J_{6,5} = 12.0\) Hz, \(J_{6,6} = 4.5\) Hz, 1H, H6), 4.14 (d, \(J_{6',6} = 12.0\) Hz, \(J_{6',5} = 2.0\) Hz, 1H, H6'), 3.83 (ddd, \(J_{5,5} = 9.5\) Hz, \(J_{5,6} = 4.5\) Hz, \(J_{5,6'} = 2.0\) Hz, 1H, H5), 2.37 (s, 3H, Me), 2.09 (s, 3H, Ac), 2.05 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.96 (s, 3H, Ac). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 171.8 (C, CO), 170.9 (C, CO), 169.8 (C, CO), 169.5 (C, CO), 167.4 (C, CO), 130.9 (C, Ph), 129.6 (2CHI, Ph), 127.1 (2CH, Ph), 93.1 (CH, C1), 73.4 (CH, C5), 73.0 (CH, C3), 68.0 (CH, C4), 62.0 (CH\(_2\), C6), 53.4 (CH, C2), 21.6 (CH\(_3\), Ac), 21.1 (CH\(_3\), Ac), 21.0 (CH\(_3\), Ac), 20.8 (2CH\(_3\), 2Ac). IR ν (film, cm\(^{-1}\)) : 3027 (N-H), 2952 (C-H), 1750 (C=O), 1647 (NH-C=O). MS (ESI): \(m/z = 406\) ([M+Ac]\(^+\), 100\%), 488 ([M+Na]\(^+\), 25\%). HRMS (ESI): Caled for C\(_{22}\)H\(_{27}\)N\(_4\)O\(_{10}\) [M+Na]\(^+\): 488.1533. Found: 488.1529.

1,3,4,6-Tetra-O-acetyl-2-benzoylcarbonylamino-2-deoxy-β-D-glucopyranose 41

To a solution 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose (1 g, 2.61 mmol) in pyridine (11 mL) was added dropwise CbzCl (4.1 mL, 6 eq.) at 0 °C under argon. The reaction was stirred at room temperature for 2 hours and then the organic layer was separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 1:1 to 0:1) to give the desired product 41\(^{29}\) (10.5 g, 84 \%, white amorphous solid).

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1,3,4,6-Tetra-O-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranose 42

\[
\begin{align*}
\text{AcO} & \quad \text{OAc} \\
\text{AcO} & \quad \text{OAc} \\
\text{NHCOCocl} &
\end{align*}
\]

1,3,4,6-Tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride\(^8\) (10 g, 26.06 mmol) and trichloroacetic anhydride (14.3 mL, 78.2 mmol, 3 eq.) in pyridine (11 mL) were stirred at room temperature for 5 hours under argon. The volatiles were evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (heptane/EtOAc 9:1 to 1:1) to afford pure product 42\(^{30}\) (12 g, 93 %, white amorphous solid).

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranose 43

To a solution 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride\(^8\) (1 g, 2.61 mmol) and pyridine (425 µL, 5.21 mmol, 2 eq.) in dry CH\(_2\)Cl\(_2\) (10 mL) was added dropwise trifluoroacetic anhydride (753 µL, 3.91 mmol, 1.5 eq.) at 0 °C under argon. The reaction was then warmed to room temperature and stirred at this temperature for 5 hours. The volatiles were evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (heptane/EtOAc 8:2 to 7:3) to give the desired product 43\(^{31}\) (1.11 g, 96 %, white amorphous solid).

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-chloroacetamido-β-D-glucopyranose 44

To a solution of 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride\(^8\) (1 g, 2.61 mmol), DMAP (382 mg, 3.13 mmol, 1.2 eq.) and pyridine (850 µL, 10.4 mmol, 4 eq.) in dry CH\(_2\)Cl\(_2\) (10 mL) was added dropwise chloroacetyl chloride (415 µL, 5.22 mmol, 2 eq.) at 0 °C under argon. The reaction was then warmed to room temperature and stirred at this temperature for 8 hours. The volatiles were evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (heptane/EtOAc 8:2 to 7:3) to give the desired product 44\(^{26}\) (1.06 g, 96 %, white amorphous solid).

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-pivalamido-α/β-D-glucopyranose 45

To a solution of 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride\(^8\) (1 g, 2.61 mmol), DMAP (382 mg, 3.13 mmol, 1.2 eq.) and pyridine (850 µL, 10.42 mmol, 4 eq.) in dry CH\(_2\)Cl\(_2\) (10 mL) was added dropwise pivalic anhydride (1.06 mL, 5.21 mmol, 2 eq.) at 0 °C under argon. The reaction was then warmed to room temperature and stirred at this temperature for 2 days. The volatiles were evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (heptane/EtOAc 1:1 to 0:1) to give the product 454 (392 mg, 35 %, α/β 1.5/1, white amorphous solid).

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose 46

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To a solution of d-glucosamine hydrochloride (40 g, 185.6 mmol, 1 eq.) in water (300 mL) are successively added phthalic anhydride (55 g, 372 mmol, 2 eq.) and NaHCO₃ (46 g, 548 mmol, 2.95 eq.). Then, the reaction mixture is stirred at 40 °C for 12 hours. The volatiles are evaporated under reduced pressure by coevaporation with toluene and the residue obtained was used without any further purification. Acetic anhydride (229 mL, 2445 mmol, 13.2 eq.) was added to a solution of crude intermediate in pyridine (350 mL) and the reaction mixture was stirred at 40 °C for 10 hours. The volatiles were evaporated under reduced pressure by coevaporation with toluene. The residue was diluted with CH₂Cl₂ (600 mL), washed with water (3×120 mL), brine (100 mL), dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 7:3 to 3:7) to give the desired product as a mixture of two anomers (83 g, 93%, α/β: 1/2.3, white amorphous solid). This mixture was separated by chromatography on silica gel (toluene/acetone 95:05) to afford pure β-product 46 (1.12 g, 84 %, white amorphous solid).

1,3,4,6-Tetra-O-acetyl-2-acetylatedamido-2-deoxy-β-d-glucopyranose 47

Methyl (3,4,6-tri-O-acetyl-2-deoxy-2-formamido-β-d-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-d-glucopyranoside 48

Methyl (3,4,6-tri-O-acetyl-2-deoxy-2-(4-methylbenzamido)-β-d-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-d-glucopyranoside 49

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2-(4-Methylphenyl) (3,4,6-tri-O-acetyl-1,2-di-deoxy-α-D-glucopyranosyl)-[2,1-d]-2-oxazoline 55

TTBP (53 mg, 0.215 mmol, 2 eq.) and Fe(OTf)₃·6.2DMSO (16 mg, 0.016 mmol, 15 mol%) are added donor 40 (50 mg, 0.107 mmol, 1 eq.), in an oven-dried, argon-purged microwave vial equipped with a magnetic stirring bar. Everything is flushed under argon and dry CH₂Cl₂ is added (1 mL). After sealing the vial, the reaction mixture is heated to 80 °C under microwave irradiation for 45 minutes (CEM Discover instrument). Then, the reaction mixture is diluted in CH₂Cl₂ (20 mL) and washed with a saturated aqueous solution of NaHCO₃ (20 mL). The aqueous layer is extracted with CH₂Cl₂ (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product is purified by chromatography on silica gel (heptane/EtOAc 8:2 to 4:6) to give the oxazoline 554 (27 mg, 62 %, white amorphous solid).

References


Compound 8
Compound 8

![Compound 8 molecule structure](image)
Compound 10
Compound 10

fdb2678 3 (1D 13C) CDCl3 300MHz

-20 0 20 40 60 80 100 120 140 160 180 200 220 ppm

0 20 40 60 80 100 120 140 160 180 200 ppm
AX_198_F2 1 (1D 1H) CDCl3 300MHz

Compound 13

TBDPSO

BnO

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BnO

OMe
Compound 16

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**Compound 17**
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Compound 18

OTBDPS

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AcO

NHAc

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O

OMe

ppm

Compound 18
Compound 18

AX_202_F2 3 (1D 13C) CDCl3 300MHz
Compound 21
Compound 21

41astasaroac-c13 1 (1D 13C) CDCl3 300MHz
Compound 22

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**Compound 24**

![Compound 24 Structure](image)
Compound 24

Chemical Structure:

![Chemical Structure Image]
AX_201 F2 1 (1D 1H) CDCl3 300MHz

Compound 35

ppm %
Compound 35

AX_201_F2 2 (1D 13C) CDCl3 300MHz
AX 304 F2P 2 (13C) CDCl3 300MHz

Compound 36

ppm
Compound 37

AX_268_F2 2 (1D 13C) CDCl3 300MHz
Compound 40

\[
\text{OAc} \\
\text{AcO} \\
\text{OAc} \\
\text{NHCO\textit{ToI}}
\]
Compound 40

\[ \text{OAc} \]

\[ \text{AcO} \]

\[ \text{AcO} \]

\[ \text{NHCO} \text{Tol} \]