Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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 (^{1}H, ^{13}C) of compounds **8**, **10**, **13**, **16-18**, **21-24**, **34-38** and **40.**

General considerations

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 into 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 F_{254} 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. Perfluroalkoxy (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 F_{254} 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 K_2CO_3. ^{1}H NMR spectra were recorded on Bruker 300 or 500 MHz instruments. ^{13}C 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 ^{1}H NMR and 77.4 ppm for ^{13}C NMR). For ^{1}H 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, ^{1}H-^{1}H COSY, ^{1}H-^{13}C 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: $[\alpha]_D^{temperature}$ (in 10^{-1} deg.cm^2/g), concentration (*c* in g/100 mL) and solvent. 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_2Cl_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_2Cl_2 and washed with a saturated aqueous solution of $NaHCO_3$. The aqueous layer is extracted with CH_2Cl_2 (×4) and the combined organic layers are washed with brine, dried over Na_2SO_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 **1β** (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.

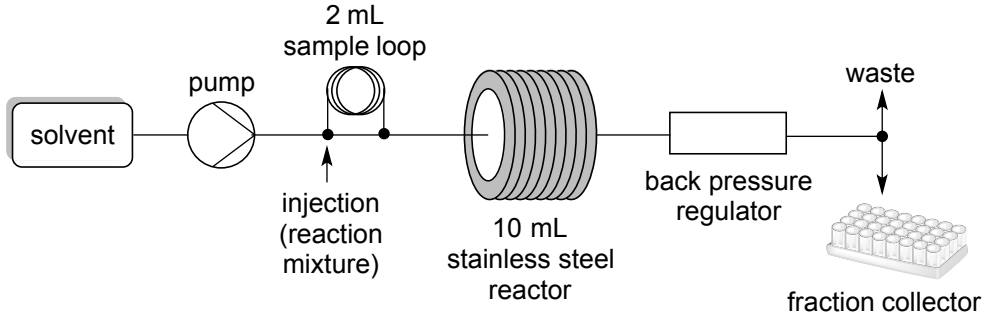

Figure 1

At the end of the reaction, the reaction mixture is diluted with 20 mL of dichloromethane and washed with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer is extracted with CH_2Cl_2 (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na_2SO_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.

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 chloroforme/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.

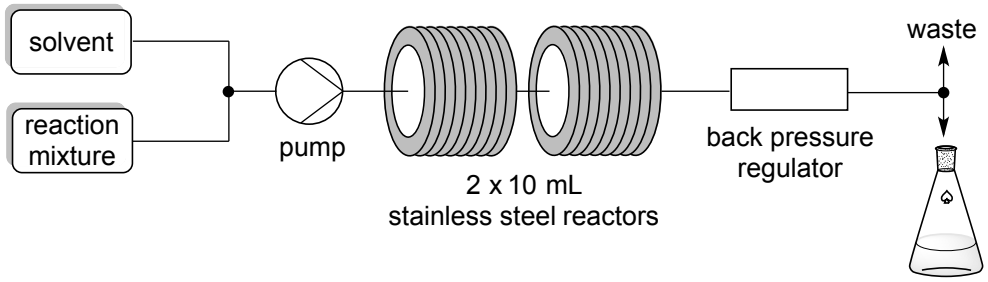

Figure 2

At the end of the reaction, the reaction mixture is diluted with CH_2Cl_2 (50 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (50 mL). The aqueous layer is extracted with CH_2Cl_2 (4×50 mL) and the combined organic layers are washed with brine (100 mL), dried over Na_2SO_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**,[2] **7**,[3] **11**,[4] **25**[5] and **27**[6] were prepared according to known procedures. Donor **33** and acceptor **5** are commercially available.

Iron triflate catalysts

$Fe(OTf)_3 \cdot 6.2DMSO$ and **$Fe(NTf_2)_3 \cdot 6.3DMSO$** were prepared according to the procedure of Antoniotti *et al.*[7]

$Fe(OTf)_3 \cdot 6.2DMSO$: 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.

$Fe(NTf_2)_3 \cdot 6.3DMSO$: 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] T. Ishikawa, Y. Shimizu, T. Kudoh, S. Saito, *Org. Lett.* **2003**, *5*, 3879-3882.
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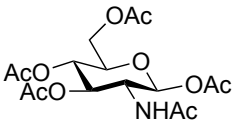
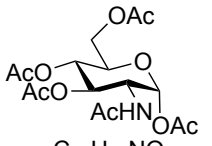
2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose 1β



$C_{16}H_{23}NO_{10}$
Mol. Wt.: 389.35

1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride[8] (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 **1β**[9] (4.40 g, 87 %, white amorphous solid). **1β** is also commercially available.

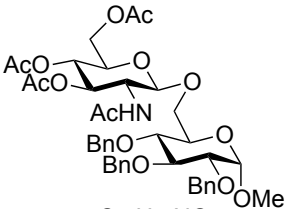
2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose 1α



$C_{16}H_{23}NO_{10}$
Mol. Wt.: 389.35

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_2Cl_2 (3×50 mL), washed with water (20 mL), brine (10 mL), dried over Na_2SO_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 **1α**[10] (1.4 g, 80 %, white amorphous solid). **1α** is also commercially available.

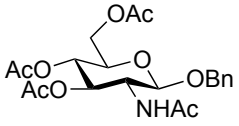
Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 4



$C_{42}H_{51}NO_{14}$
Mol. Wt.: 793.85

Microwave conditions: **4**[11] was obtained under microwave conditions using donor **1β** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **3**[2] (30 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_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 **1β** (2.53 g, 6.50 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (484 mg, 0.49 mmol, 15 mol-%) and acceptor **3** (1.51 g, 3.25 mmol, 1 eq.) in a mixture of dry $CHCl_3/CH_3CN$ 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-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 6β



$C_{21}H_{27}NO_9$
Mol. Wt.: 437.44

Microwave conditions: **6β**[12] was obtained under microwave conditions using donor **1β** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and benzyl alcohol **5** (7 µL, 0.068 mmol, 1 eq.) in dry CH_2Cl_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: **6β** was also obtained under flow conditions from donor **1β** (117 mg, 0.301 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (23 mg, 0.023 mmol, 15 mol-%) and benzyl alcohol **5** (16 µL,

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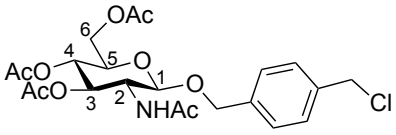
0.150 mmol, 1 eq.) in a mixture of dry CH_2Cl_2/CH_3CN 7:3 (2 mL), using general procedure C1 (Vapourtec instrument, 110 °C, 33 bar, 45 min) (51 mg, 77 %, white amorphous solid).

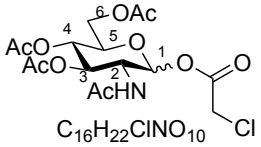
4-(Chloromethyl)benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 8



$C_{22}H_{28}ClNO_9$
Mol. Wt.: 485.91

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.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and 4-(chloromethyl)benzyl alcohol **7**[3] (10 mg, 0.064 mmol, 1 eq.) in dry CH_2Cl_2 (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.), $Fe(OTf)_3 \cdot 6.2DMSO$ (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 CH_2Cl_2/CH_3CN 7:3 (2 mL), according to general procedure C1 (Vapourtec instrument, 110 °C, 33 bar, 45 min) (56 mg, 75 %, white amorphous solid). $[\alpha]_D^{21}$: -36.0 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.36 (d, J = 8.0 Hz, 2H, Ar), 7.29 (d, J = 8.0 Hz, 2H, Ar), 5.48 (d, $J_{NH,2}$ = 9.0 Hz, 1H, NH), 5.21 (dd, $J_{3,2}$ = 10.5 Hz and $J_{3,4}$ = 9.5 Hz, 1H, H3), 5.09 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H4), 4.88 (d, J = 12.0 Hz, 1H, OCH_2Ar), 4.65 (d, $J_{1,2}$ = 9.0 Hz, 1H, H1), 4.61-4.58 (m, 3H, OCH_2Ar and ArCH_2Cl), 4.27 (dd, $J_{6,6'}$ = 12.5 Hz and $J_{6,5}$ = 4.5 Hz, 1H, H6), 4.16 (dd, $J_{6',6}$ = 12.5 Hz and $J_{6',5}$ = 2.5 Hz, 1H, H6'), 3.96 (dt, $J_{2,3}$ = 10.5 Hz and $J_{2,1} = J_{2,NH}$ = 9.0 Hz, 1H, H2), 3.67 (ddd, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 4.5 Hz and $J_{5,6'}$ = 2.5 Hz, 1H, H5), 2.10 (s, 3H, $OCOCH_3$), 2.02 (s, 3H, $OCOCH_3$), 2.01 (s, 3H, $OCOCH_3$), 1.91 (s, 3H, NHCOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.3 (C, *C*OCH_3), 171.1 (C, *C*OCH_3), 170.5 (C, *C*OCH_3), 169.8 (C, *C*OCH_3), 137.7 (C, OCH_2*Ar*), 137.6 (C, *Ar*CH_2Cl), 129.1 (2CH, Ar), 128.6 (2CH, Ar), 100.0 (CH, C1), 72.7 (CH, C3), 72.3 (CH, C5), 70.6 (CH_2, O*C*H_2Ar), 68.9 (CH, C4) 62.5 (CH_2, C6), 54.9 (CH, C2), 46.2 (CH_2, Ar*C*H_2Cl), 23.7 (CH_3, NHCO*C*H_3), 21.2 (CH_3, OCO*C*H_3), 21.1 (CH_3, OCO*C*H_3), 21.0 (CH_3, OCO*C*H_3). 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 ($[2M+H]^+$, 15%), 993 ($[2M+Na]^+$, 50%). HRMS (ESI): Calcd for $C_{22}H_{29}ClNO_9$ $[M+H]^+$: 486.1531. Found: 486.1531.

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

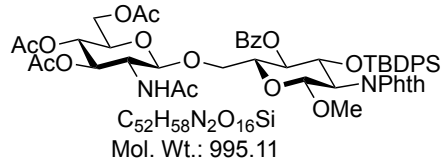


$C_{16}H_{22}ClNO_{10}$
Mol. Wt.: 423.80

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 CH_2Cl_2 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 CH_2Cl_2 (20 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer is extracted with CH_2Cl_2 (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na_2SO_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 pure product **10** (230 mg, α/β mixture 8/2, 21 %, colorless oil). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.22 (d, $J_{1\alpha,2\alpha}$ = 3.5 Hz, 0.8H, H1α), 5.92 (d, $J_{NH\beta,2\beta}$ = 9.5 Hz, 0.2H, NH), 5.75 (d, $J_{NH\alpha,2\alpha}$ = 9.0 Hz, 0.8H, NH), 5.74 (d, $J_{1\beta,2\beta}$ = 9.0 Hz, 0.2H, H1β), 5.25-5.12 (m, 1.2H), 4.50-4.43 (ddd, $J_{2\alpha,3\alpha}$ = 10.5 Hz, $J_{NH\alpha,2\alpha}$ = 9.0 Hz and $J_{1\alpha,2\alpha}$ = 3.5 Hz, 0.8H, H2α), 4.28-4.18 (m, 1H), 4.13 (d, J = 1.0 Hz, 1.6H, $CH_2Cl\alpha$), 4.11-3.98 (m, 3.2H), 3.85-3.79 (dddd, J = 9.5 Hz, J = 7.0 Hz, J = 5.0 Hz and J = 2.5

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). ^{13}C NMR (75 MHz, $CDCl_3$) 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 (CH_2, C6), 51.5 (CH, C2), 40.8 (CH_2Cl), 23.1 (CH_3), 20.9 (CH_3) 20.8 (CH_3), 20.7 (CH_3). MS (ESI): *m/z* = 330 ($[M\text{-}CO_2HCH_2Cl]^+$, 100%), 441 ($[M+NH_4]^+$, 50%). HRMS (ESI): Calcd for $C_{16}H_{26}ClN_2O_{10}$ $[M+NH_4]^+$: 441.1276. Found: 441.1296.

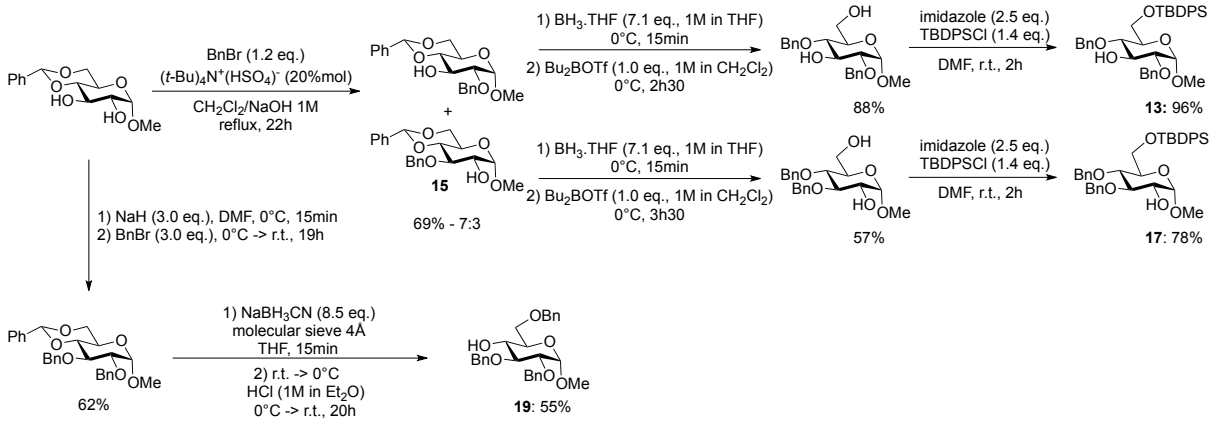
Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)-4-*O*-benzoyl-3-*O*-(*tert*-butyldiphenylsilyloxy)-2-deoxy-2-phthalimido-β-D-glucopyranoside 12



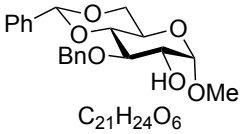
$C_{52}H_{58}N_2O_{16}Si$
Mol. Wt.: 995.11

12[4] was obtained under microwave conditions using donor **1β** (33 mg, 0.084 mmol, 2 eq.), TTBP (21 mg, 0.084 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (6 mg, 0.006 mmol, 15 mol-%) and acceptor **11**[4] (28 mg, 0.042 mmol, 1 eq.) in dry CH_2Cl_2 (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*-butyldiphenylsilyl-α-D-glucopyranoside 13
Methyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside 17
Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside 19



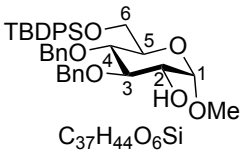
Scheme 1. Synthesis of acceptors 15, 13, 17 and 19


$C_{21}H_{24}O_6$
Mol. Wt.: 372.41

To a mixture of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (600 mg, 2.13 mmol, 1 eq.) in CH_2Cl_2 (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.[13] Then, the reaction mixture is diluted with CH_2Cl_2, the organic layer is separated and the water phase is extracted twice with CH_2Cl_2. The combined organic layers are washed with aqueous saturated $NaHCO_3$, brine, dried over Na_2SO_4, 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-

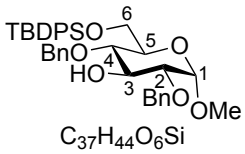
[13] D. Crich, W. Li, H. Li *J. Am. Chem. Soc.* **2004**, *126*, 15081-15086.

glucopyranoside[14] (21 %, 166 mg) and methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside **15**[14] (48 %, 380 mg).



$C_{37}H_{44}O_6Si$
Mol. Wt.: 612.83

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside **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_2Cl_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.[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/EtOAc 7:3 to 4:6) to afford pure methyl 3,4-di-*O*-benzyl-α-D-glucopyranoside[16] (57%, 97 mg).
Methyl 3,4-di-*O*-benzyl-α-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 µL, 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 $NaHCO_3$ (20 mL), extracted with Et_2O (3×10 mL), washed with 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 9:1 to 6:4) to give the desired product **17** (125 mg, 78 %, colorless oil). $[\alpha]_D^{20}$: +41.8 (*c* 0.9 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 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_2Ph), 4.90-4.85 (m, 2H, CH_2Ph), 4.79 (d, $J_{1,2}$ = 3.5 Hz, 1H, H1), 4.64 (d, J = 10.5 Hz, 1H, CH_2Ph), 3.91 (m, 2H, H6 and H6'), 3,78 (t, $J_{3,2} = J_{3,4}$ = 9.0 Hz, 1H, H3), 3.77-3.62 (m, 3H, H2, H4 and H5), 3.40 (s, 3H, OCH_3), 2.14 (brs, 1H, OH), 1.06 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 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), 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_2, *C*H_2Ph), 75.4 (CH_2, *C*H_2Ph), 73.6 (CH, C2), 72.1 (CH, C5), 63.2 (CH_2, C6), 55.3 (CH_3, OCH_3), 27.2 ($3CH_3$, C(*C*H_3)$_3$), 19.7 (C, *C*$(CH_3)_3$). IR ν (film, cm^{-1}): 3465 (O-H), 3068 (=C-H), 2931 and 2857 (C-H). MS (ESI): *m/z* = 630 ([M+NH_4]$^+$, 5%), 635 ([M+Na]$^+$, 100%), 1248 ([2M+Na]$^+$, 20%). HRMS (ESI): Calcd for $C_{37}H_{44}NaO_6Si$ [M+Na]$^+$: 635.2805. Found: 635.2814.



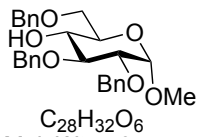
$C_{37}H_{44}O_6Si$
Mol. Wt.: 612.83

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-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_2Cl_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.[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

[14] A. G. M. Barrett, R. W. Read, D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1* **1980**, 2184-2190.
[15] V. Y. Dudkin, J. S. Miller, A. S. Dudkina, C. Antczak, D. A. Scheinberg, S. J. Danishefsky, *J. Am. Chem. Soc.* **2008**, *130*, 13598-13607.
[16] A. Français, D. Urban, J.-M. Beau, *Angew. Chem., Int. Ed.* **2007**, *46*, 8662-8665.

silica gel (heptane/EtOAc 7:3 to 4:6) to afford pure methyl 2,4-di-*O*-benzyl-α-D-glucopyranoside[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_2O (3×20 mL), washed with brine (30 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 9:1 to 7:3) to give the desired product **13** (390 mg, 96 %, colorless oil). $[\alpha]_D^{20}$: +47.1 (*c* 1.0 in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 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 Hz, 1H, CH_2Ph), 4.73 (s, 2H, CH_2Ph), 4.69 (d, $J_{1,2}$ = 3.5 Hz, 1H, H1), 4.63 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.11 (t, $J_{3,2} = J_{3,4}$ = 9.5 Hz, 1H, H3), 3.92 (dd, $J_{6,6'}$ = 11.0 Hz and $J_{6,5}$ = 2.5 Hz, 1H, H6), 3.87 (dd, $J_{6',6}$ = 11.0 Hz and $J_{6',5}$ = 4.0 Hz, 1H, H6'), 3.69 (ddd, $J_{5,4}$ = 9.5 Hz, $J_{5,6'}$ = 4.0 Hz and $J_{5,6}$ = 2.5 Hz, 1H, H5), 3.54 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H4), 3.42 (dd, $J_{2,3}$ = 9.5 Hz and $J_{2,1}$ = 3.5 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, $CDCl_3$) δ: 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, *C*H_2Ph), 74.0 (CH, C3), 73.4 (CH_2, *C*H_2Ph), 71.5 (CH, C5), 63.5 (CH_2, C6), 55.2 (CH_3, OCH_3), 27.2 ($3CH_3$, C(*C*H_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 $C_{37}H_{44}NaO_6Si$ $[M+Na]^+$: 635.2805. Found: 635.2808.



$C_{28}H_{32}O_6$
Mol. Wt.: 464.55

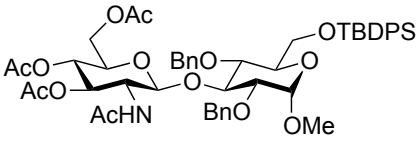
Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (3.00 g, 10.63 mmol, 1 eq.) in dry DMF (35 mL) is cooled to 0 °C under argon. NaH (60% dispersion in mineral oil, 960 mg, 31.88 mmol, 3 eq.), is added by portion and the reaction mixture is stirred at 0 °C for 15 minutes under argon. BnBr (3.8 mL, 31.88 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_2SO_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[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 (3 mg) and $NaBH_3CN$ (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_2O (1 M) is added slowly until the solution turns pink and gas evolution ceased completely (danger, release of HCN!).[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_2SO_4 and evaporated under reduced pressure. The crude product is purified by

[17] T. Ogawa, T. Kaburagi, *Carbohydr. Res.* **1982**, *103*, 53-64.
[18] S. Norsikian, A. Lubineau, *Org. Biomol. Chem.* **2005**, *3*, 4089-4094.

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

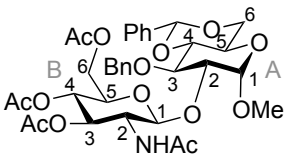
Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside 14



$C_{51}H_{63}NO_{14}Si$
Mol. Wt.: 942.13

14[4] was obtained under microwave conditions using donor **1β** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **13** (42 mg, 0.068 mmol, 1 eq.) in dry CH_2Cl_2 (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

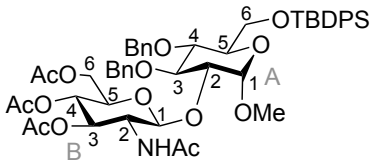


$C_{35}H_{43}NO_{14}$
Mol. Wt.: 701.71

16 was obtained under microwave conditions using donor **1β** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **15** (23 mg, 0.062 mmol, 1 eq.) in dry CH_2Cl_2 (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 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44-7.40 (m, 2H, Ph), 7.36-7.24 (m, 8H, Ph), 5.53 (s, 1H, C*H*Ph), 5.23 (dd, $J_{B3,B2}$ = 10.5 Hz and $J_{B3,B4}$ = 9.5 Hz, 1H, HB-3), 5.16 (d, $J_{NH,B2}$ = 8.5 Hz, 1H, NH), 5.01 (t, $J_{B4,B3} = J_{B4,B5}$ = 9.5 Hz, 1H, HB-4), 4.92 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.90 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.85 (d, $J_{A1,A2}$ = 3.5 Hz, 1H, HA-1), 4.63 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.27 (dd, $J_{A6,A6'}$ = 10.0 Hz and $J_{A6,A5}$ = 4.5 Hz, 1H, HA-6), 4.17 (d, $J_{B6,B5} = J_{B6',B5}$ = 4.0 Hz, 2H, HB-6 and HB-6'), 3.99 (t, $J_{A3,A2} = J_{A3,A4}$ = 9.5 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, $J_{A4,A3} = J_{A4,A5}$ = 9.5 Hz, 1H, HA-4), 3.40 (s, 3H, OCH_3), 2.07 (s, 3H, $OCOCH_3$), 2.00 (s, 3H, $OCOCH_3$), 1.97 (s, 3H, $OCOCH_3$), 1.51 (s, 3H, $NHCOCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.0 (C, *C*OCH_3), 171.0 (C, *C*OCH_3), 170.7 (C, *C*OCH_3), 169.8 (C, *C*OCH_3), 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, *C*HPh), 100.4 (CH, CA-1), 82.8 (CH, CA-4), 81.0 (CH, CA-2), 78.0 (CH, CA-3), 75.1 (CH_2, *C*H_2Ph), 72.8 (CH, CB-3), 72.2 (CH, CB-5), 69.5 (CH_2, CA-6), 69.0 (CH, CB-4), 62.6 (CH_2, CB-6), 62.5 (CH, CA-5), 55.9 (CH_3, OCH_3), 55.3 (CH, CB-2), 23.3 (CH_3, $NHCOCH_3$), 21.2 (CH_3, $OCOCH_3$), 21.0 (CH_3, $OCOCH_3$). 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): Calcd for $C_{35}H_{44}NO_{14}$ [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

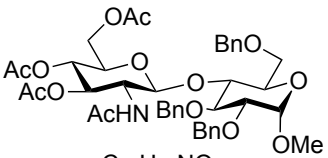
[19] C.-R. Shie, Z.-H. Tzeng, S. S. Kulkarni, B.-J. Uang, C.-Y. Hsu, S.-C. Hung *Angew. Chem., Int. Ed*. **2005**, *44*, 1665-1668.



$C_{51}H_{63}NO_{14}Si$
Mol. Wt.: 942.13

18 was obtained under microwave conditions using donor **1β** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **17** (42 mg, 0.068 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 60 min) (34 mg, 53 %, white amorphous solid). $[\alpha]_D^{20}$: +24.2 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.73-7.67 (m, 4H, Ph), 7.43-7.27 (m, 12H, Ph), 7.22-7.20 (m, 2H, Ph), 7.06-7.03 (m, 2H, Ph), 5.35 (dd, $J_{B3,B2}$ = 10.5 Hz and $J_{B3,B4}$ = 9.5 Hz, 1H, HB-3), 5.20 (d, $J_{NH,B2}$ = 8.5 Hz, 1H, NH), 5.03 (t, $J_{B4,B3} = J_{B4,B5}$ = 9.5 Hz, 1H, HB-4), 4.99 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.91 (d, $J_{A1,A2}$ = 3.5 Hz, 1H, HA-1), 4.83 (s, 2H, CH_2Ph), 4.76 (d, *J* = 10.5 Hz, 1H, CH_2Ph), 4.58 (d, *J* = 10.5 Hz, 1H, CH_2Ph), 4.23-4.21 (m, 2H, HB-6 and HB-6'), 3.97 (dd, *J* = 9.5 Hz and *J* = 8.5 Hz, 1H, HA-3), 3.88 (d, $J_{A6,A5} = J_{A6',A5}$ = 2.5 Hz, 2H, HA-6 and HA-6'), 3.84-3.61 (m, 5H, HB-2, HB-5, HA-2, HA-5 and HA-4), 3.37 (s, 3H, OCH_3), 2.09 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 1.99 (s, 3H, $OCOCH_3$), 1.45 (s, 3H, NHCO*C*H_3), 1.07 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.0 (C, *C*OCH_3), 171.0 (C, *C*OCH_3), 170.7 (C, *C*OCH_3), 169.9 (C, *C*OCH_3), 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), 128.2 (CH, Ph), 128.1 (CH, Ph), 128.0 (CH, Ph), 128.0 (CH, Ph), 127.9 (CH, Ph), 127.0 (CH, Ph), 102.2 (CB-1), 99.4 (CH, CA-1), 82.5 (CH, CA-2), 81.4 (CH, CA-3), 78.4 (CH, CA-4), 75.4 (CH_2, *C*H_2Ph), 75.4 (CH_2, *C*H_2Ph), 72.7 (CH, CB-3), 72.1 (CH, CB-5), 71.5 (CH, CA-5), 69.2 (CB-4), 63.1 (CH_2, CA-6), 62.8 (CH_2, CB-6), 55.7 (CH, CB-2), 55.3 (CH_3, OCH_3), 27.2 (CH_3, C(*C*H_3)$_3$), 23.2 (CH_3, NHCOC*H*$_3$), 21.1 (CH_3, OCO*C*H_3), 21.0 (CH_3, OCO*C*H_3), 19.7 (C, *C*$(CH_3)_3$). IR *v* (film, cm^{-1}): 3265 (N-H), 3071 and 3032 (=C-H), 2959, 2931 and 2857 (C-H), 1745 (C=O), 1656 (NH-C=O). MS (ESI): *m/z* = 964 ($[M+Na]^+$, 100%). HRMS (ESI): Calcd for $C_{51}H_{63}NNaO_{14}Si$ $[M+Na]^+$: 964.3916. Found: 964.3923.

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

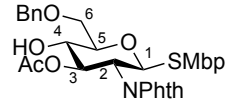


$C_{42}H_{51}NO_{14}$
Mol. Wt.: 793.85

20[20] was obtained under microwave conditions using donor **1β** (500 mg, 1.284 mmol, 2 eq.), TTBP (320 mg, 1.288 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (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).

[20] H. Christensen, M. S. Christiansen, J. Petersen, H. H. Jensen, *Org. Biomol. Chem.* **2008**, *6*, 3276-3283.

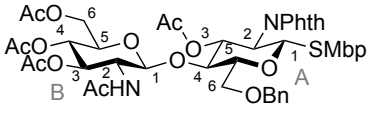
(2-Methyl-5-*tert*-butylphenyl) 3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 21



$C_{34}H_{37}NO_7S$
Mol. Wt.: 603.73

(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 CH_2Cl_2 (23 mL) were cooled to 0 °C under argon. Et_3SiH (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 $NaHCO_3$ (30 mL), extracted with CH_2Cl_2 (3×40 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 **21** (1.07 g, 76 %, white amorphous solid). $[\alpha]_D^{25}$: +32.3 (*c* 1.0, $CHCl_3$). Mp: 68.2-73.5 °C (from heptane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) 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, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H3), 5.62 (d, $J_{1,2}$ = 10.0 Hz, 1H, H1), 4.58 (AB system, J = 12.0 Hz, 2H, CH_2Ph), 4.34 (t, $J_{2,1} = J_{2,3}$ = 10.0 Hz, 1H, H2), 3.88-3.81 (m, 2H, H4 and H6), 3.77 (dd, $J_{6',6}$ = 10.0 Hz, $J_{6',5}$ = 5.0 Hz, 1H, H6'), 3.71 (dd, $J_{5,4}$ = 9.5 Hz, $J_{5,6'}$ = 5.0 Hz, 1H, H5), 2.91 (d, $J_{OH,4}$ = 3.5 Hz, 1H, OH), 2.13 (s, 3H, Me), 1.90 (s, 3H, Ac), 1.22 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$) 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 (CH_2, CH_2Ph), 71.7 (CH, C4), 70.5 (CH_2, C6), 54.0 (CH, C2), 34.6 (C, *t*-Bu), 31.4 ($3CH_3$, *t*-Bu), 20.9 (CH_3, Ac), 20.5 (CH_3, 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 ($[M+NH_4]^+$, 60%). HRMS (ESI): Calcd for $C_{34}H_{41}N_2O_7S$ $[M+NH_4]^+$: 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



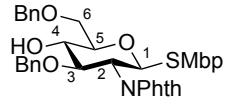
$C_{48}H_{56}N_2O_{15}S$
Mol. Wt.: 933.03

Acceptor **21** (155 mg, 0.257 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.) and $Fe(OTf)_3 \cdot 6.2DMSO$ (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 CH_2Cl_2 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 CH_2Cl_2 (20 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer is extracted with CH_2Cl_2 (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na_2SO_4, 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). $[\alpha]_D^{25}$: +42.4 (*c* 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) 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, $J_{A3,A2} = J_{A3,A4}$ = 9.5 Hz, 1H, HA-3), 5.58 (d, $J_{A1,A2}$ = 10.5 Hz, 1H, HA-1), 5.05 (t, $J_{B3,B2} = J_{B3,B4}$ = 9.5 Hz, 1H, HB-3), 4.90 (t, $J_{B4,B3}$

[21] M. Collot, J. Savreux, J.-M. Mallet, *Tetrahedron* **2008**, *64*, 1523-1535.

= $J_{B4,B5}$ = 9.5 Hz, 1H, HB-4), 4.83 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.77 (d, $J_{NH,B2}$ = 9.0 Hz, 1H, NH), 4.57 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.45 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.37-4.27 (m, 2H, HB-6 and HA-2), 4.03 (t, $J_{A4,A3}$ = $J_{A4,A5}$ = 9.5 Hz, 1H, HA-4), 3.95 (d, $J_{B6',B6}$ = 12.0 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 NMR (75 MHz, $CDCl_3$) δ: 170.8 (2C, 2CO), 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 (CH, Ph), 131.1 (CH, Ph), 130.1 (CH, Ph), 129.1 (2CH, Ph), 129.0 (2CH, 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 ν (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-phthalimido-1-thio-β-D-glucopyranoside 23

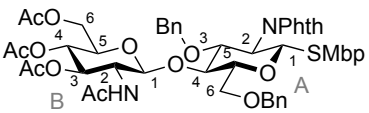


$C_{39}H_{41}NO_6S$
Mol. Wt.: 651.81

To a suspension of (2-Methyl-5-*tert*-butylphenyl) 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[21] (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-phthalimido-1-thio-β-D-glucopyranoside (3 g, 63 %, white amorphous solid). 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-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). $[\alpha]_D^{25}$: +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, $J_{1,2}$ = 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, $J_{6',6}$ = 10.0 Hz, $J_{6',5}$ = 5.5 Hz, 1H, H6'), 3.67-3.60 (m, 1H, H5), 2.88 (d, $J_{OH,4}$ = 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 CH_2Ph), 74.0 (CH_2, CH_2Ph), 71.0 (CH_2, C6), 54.8 (CH, C2), 34.6 (C, *t*-Bu), 31.4 ($3CH_3$, *t*-Bu), 20.4 (CH_3, Me). IR *v* (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): Calcd for $C_{39}H_{41}NNaO_6S$ $[M+Na]^+$: 674.2553. Found: 674.2576. Elementary Analysis: Calcd for $C_{39}H_{41}NO_6S$: 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.

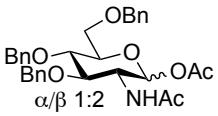
(2-Methyl-5-*tert*-butylphenyl) (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 24



$C_{53}H_{60}N_2O_{14}S$
Mol. Wt.: 981.38

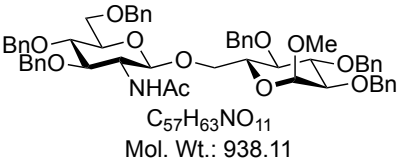
Acceptor **23** (417 mg, 0.640 mmol, 5 eq.) and $Fe(OTf)_3 \cdot 6.2DMSO$ (62 mg, 0.063 mmol, 50 mol%) were added to donor **1β** (50 mg, 0.128 mmol, 1 eq.) in an oven-dried, argon-purged, microwave vial equipped with a magnetic stirring bar. Everything is flushed under argon and dry CH_2Cl_2 is added (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 CH_2Cl_2 (20 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer is extracted with CH_2Cl_2 (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na_2SO_4, 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). $[\alpha]_D^{25}$: +44.1 (*c* 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.78-7.70 (d, *J* = 7.0 Hz, 1H, NPhth), 7.68-7.57 (m, 2H, NPhth), 7.55-7.38 (m, 7H, 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, $J_{A1,A2}$ = 10.0 Hz, 1H, HA-1), 4.96 (t, $J_{B4,B3} = J_{B4,B5}$ = 9.5 Hz, 1H, HB-4), 4.92-4.82 (m, 2H, CH_2Ph and HB-3), 4.75 (d, *J* = 12.5 Hz, 1H, CH_2Ph), 4.68 (d, $J_{NH,B2}$ = 9.5 Hz, 1H, NH), 4.47 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.38 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.35 (d, *J* = 12.5 Hz, 1H, CH_2Ph), 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, $J_{A6,A6'}$ = 10.5 Hz, $J_{A6,A5}$ = 2.0 Hz, 1H, HA-6), 3.59 (d, $J_{A6',A6}$ = 10.5 Hz, $J_{A6',A5}$ = 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). ^{13}C NMR (75 MHz, $CDCl_3$) *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 (CH, NPhth), 133.7 (CH, NPhth), 131.9 (C, Ph), 131.8 (2C, NPhth), 130.6 (CH, Ph), 130.0 (CH, Ph), 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 (CH_2, CH_2Ph), 74.2 (CH_2, CH_2Ph), 73.3 (CH, CB-3), 71.6 (CH, CB-5), 68.8 (CH, CB-4), 68.0 (CH_2, CA-6), 62.1 (CH_2, CB-6), 55.2 (CH, CA-2), 54.4 (CH, CB-2), 34.6 (C, *t*-Bu), 31.4 ($3CH_3$, *t*-Bu), 23.3 (CH_3, Ac), 20.8 ($3CH_3$, 2Ac and Me), 20.4 (CH_3, Ac). IR *v* (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): Calcd for $C_{53}H_{60}N_2NaO_{14}S$ $[M+Na]^+$: 1003.3663. Found: 1003.3691. Elementary Analysis: Calcd for $C_{53}H_{60}N_2O_{14}S$: 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



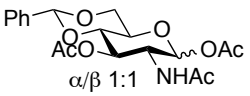
2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose[22] (510 mg, 1.03 mmol, 1 eq.) and pyridine hydrochloride (153 mg, 1.32 mmol, 1.3 eq.) in pyridine (5 mL) are stirred at 100 °C for 1 hour under argon. To this solution, acetic anhydride (255 µL, 2.70 mmol, 2.6 eq.) is added and the reaction mixture 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 %, α/β 1:2, white amorphous solid).

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

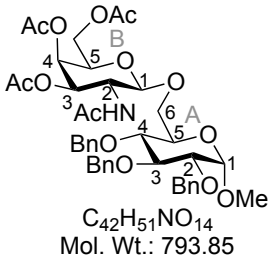


30[24] was obtained under microwave conditions using donor **29** (69 mg, 0.129 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (9 mg, 0.010 mmol, 15 mol-%) and acceptor **3**2 (30 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (CEM Discover instrument, 80 °C, 45 min) (62 mg, 86 %, white amorphous solid).

2-Acetamido-1,3-di-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranose 32



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 %, α/β 1:1, white amorphous solid).



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

34 was obtained under microwave conditions using donor **33** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **3**[2] (30 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_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 in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.38-7.28 (m, 15H, 3Ph), 5.33 (dd, $J_{B4,B3}$ = 3.5 Hz and $J_{B4,B5}$ = 1.0 Hz, 1H, HB-4), 5.28 (d, $J_{NH,B2}$ =

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[23] (a) T. D. Inch, H. G. Fletcher, *J. Org. Chem.* **1966**, *31*, 1810-1815; (b) M. Kiso, L. Anderson, *Carbohydr. Res.* **1985**, *136*, 309-323.
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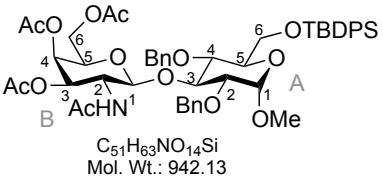
[26] F. Dasgupta, L. Anderson, *Carbohydr. Res.* **1990**, *202*, 239-255.

9.0 Hz, 1H, NH), 5.26 (dd, $J_{B3,B2}$ = 11.0 Hz and $J_{B3,B4}$ = 3.5 Hz, 1H, HB-3), 4.99 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.85 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.80 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.79 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.67 (d, $J_{B1,\ B2}$ = 8.5 Hz, 1H, HB-1), 4.65 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.60 (d, $J_{A1,A2}$ = 3.5 Hz, 1H, HA-1), 4.57 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.11-4.06 (m, 3H, HB-6, HB-6' and HA-6), 4.04-3.94 (m, 2H, HA-3 and HB-2), 3.87 (dt, $J_{B5,B6}$ = $J_{B5,B6'}$ = 6.5 Hz and $J_{B5,B4}$ = 1.0 Hz, 1H, HB-5), 3.80-3.75 (m, 1H, HA-5), 3.72 (dd, $J_{A6',A6}$ = 10.5 Hz and $J_{A6',A5}$ = 4.0 Hz, 1H, HA-6'), 3.53 (dd, $J_{A2,A3}$ = 9.5 Hz and $J_{A2,A1}$ = 3.5 Hz, 1H, HA-2), 3.48 (t, $J_{A4,A3}$ = $J_{A4,A5}$ = 9.5 Hz, 1H, HA-4), 3.37 (s, 3H, OCH_3), 2.10 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 1.83 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.8 (C, *C*OCH_3), 170.8 (C, *C*OCH_3), 170.6 (C, *C*OCH_3), 170.4 (C, *C*OCH_3), 139.1 (C, Ph), 138.7 (C, Ph), 138.5 (C, Ph), 128.9 (CH, Ph), 128.8 (CH, Ph), 128.8 (CH, Ph), 128.5 (CH, Ph), 128.3 (CH, Ph), 128.3 (CH, Ph), 128.3 (CH, Ph), 128.1 (CH, Ph), 128.0 (CH, Ph), 101.3 (CH, CB-1), 98.4 (CH, CA-1), 82.4 (CH, CA-3), 80.1 (CH, CA-2), 77.8 (CH, CA-4), 76.1 (CH_2, *C*H_2Ph), 75.0 (CH_2, *C*H_2Ph), 73.7 (CH_2, *C*H_2Ph), 71.1 (CH, CB-5), 70.2 (CH, CB-3), 69.9 (CH, CA-5), 68.1 (CH_2, CA-6), 67.1 (CH, CB-4), 61.7 (CH_2, CB-6), 55.6 (CH_3, OCH_3), 51.8 (CH, CB-2), 23.8 (CH_3, CO*C*H_3), 21.1 (CH_3, CO*C*H_3), 21.0 (CH_3, CO*C*H_3). IR ν (film, cm^{-1}): 3286 (N-H), 3092, 3065 and 3031 (=C-H), 2921 (C-H), 1743 (C=O), 1661 (NH-C=O). MS (ESI): m/z = 794 ($[M+H]^+$, 85%), 816 ($[M+Na]^+$, 100%). HRMS (ESI): Calcd for $C_{42}H_{52}NO_{14}$ $[M+H]^+$: 794.3388. Found: 794.3381.

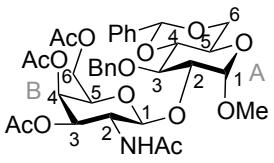
Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside 35



$C_{51}H_{63}NO_{14}Si$
Mol. Wt.: 942.13

35 was obtained under microwave conditions using donor **33** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **13** (40 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_2 (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 $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 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, $J_{B4,B3}$ = 3.0 Hz, 1H, HB-4), 5.06 (d, J = 10.5 Hz, 1H, CH_2Ph), 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, $J_{B3,B2}$ = 11.0 Hz and $J_{B3,B4}$ = 3.0 Hz, 1H, HB-3), 4.80 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.75 (d, $J_{A1,A2}$ = 3.5 Hz, 1H, HA-1), 4.58 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.48 (d, J = 10.5 Hz, 1H, CH_2Ph), 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, 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, OCH_3), 2.11 (s, 3H, $OCOCH_3$), 1.99 (s, 3H, $OCOCH_3$), 1.96 (s, 3H, $OCOCH_3$), 1.71 (s, 3H, NHCO*C*H_3), 1.07 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.0 (C, *C*OCH_3), 170.7 (C, *C*OCH_3), 170.7 (C, *C*OCH_3), 170.4 (C, *C*OCH_3), 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 (CH_2, *C*H_2Ph), 72.7 (CH_2, *C*H_2Ph), 71.8 (CH, CA-5), 71.5 (CH, CB-3), 70.9 (CH, CB-5), 66.9 (CH, CB-4), 63.4 (CH_2, CA-6), 61.4 (CH_2, CB-6), 55.2 (CH_3, OCH_3), 51.6 (CH, CB-2), 27.2 ($3CH_3$, $C(CH_3)_3$), 23.6 (CH_3, NHCO*C*H_3), 21.1 (CH_3, OCO*C*H_3), 21.1 (CH_3, OCO*C*H_3), 19.7 (C, *C*$(CH_3)_3$). IR ν (film, cm^{-1}): 3285 (N-H), 2958, 2929, 2899 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 $C_{51}H_{63}NNaO_{14}Si$ $[M+Na]^+$: 964.3916. Found: 964.3917.

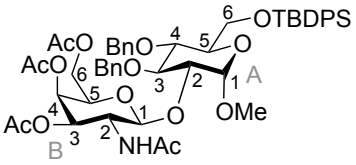
Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside 36



$C_{35}H_{43}NO_{14}$
Mol. Wt.: 701.71

36 was obtained under microwave conditions using donor **33** (46 mg, 0.118 mmol, 2 eq.), TTBP (29 mg, 0.117 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (9 mg, 0.009 mmol, 15 mol-%) and acceptor **15** (22 mg, 0.059 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 60 min) (26 mg, 63 %, amorphous white solid). $[\alpha]_D^{20}$: +5.43 (*c* 0.7 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47-7.44 (m, 2H, Ph), 7.38-7.29 (m, 8H, Ph), 5.56 (s, 1H, C*H*Ph), 5.36-5.29 (m, 2H, HB-3 and HB-4), 5.06 (d, $J_{NH,B2}$ = 8.5 Hz, 1H, NH), 5.00 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.96 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.87 (d, $J_{A1,A2}$ = 3.5 Hz, 1H, HA-1), 4.67 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.30 (dd, $J_{A6,A6'}$ = 10.0 Hz and $J_{A6,A5}$ = 4.5 Hz, 1H, HA-6), 4.14 (d, $J_{B6,B5} = J_{B6',B5}$ = 6.5 Hz, 2H, HB-6 and HB-6'), 4.04 (t, $J_{A3,A2} = J_{A3,A4}$ = 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, $J_{A2,A3}$ = 9.5 Hz and $J_{A2,A1}$ = 3.5 Hz, 1H, HA-2), 3.62 (t, $J_{A4,A3} = J_{A4,A5}$ = 9.5 Hz, 1H, HA-4), 3.43 (s, 3H, OCH_3), 2.15 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$), 1.49 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.9 (C, *C*OCH_3), 170.8 (C, *C*OCH_3), 170.5 (C, *C*OCH_3), 137.7 (C, Ph), 129.4 (CH, Ph), 128.9 (CH, Ph), 128.6 (CH, Ph), 128.1 (CH, Ph), 127.6 (CH, Ph), 126.4 (CH, Ph), 102.5 (CH, *C*HPh), 101.8 (CH, CB-1), 100.4 (CH, CA-1), 82.9 (CH, CA-4), 81.4 (CH, CA-2), 78.0 (CH, CA-3), 75.2 (CH_2, *C*H_2Ph), 71.3 (CH, CB-5), 70.2 (CH, CB-3), 69.5 (CH_2, CA-6), 67.2 (CH, CB-4), 62.6 (CH, CA-5), 62.2 (CH_2, CB-6), 55.8 (CH_3, OCH_3), 52.5 (CH, CB-2), 23.4 (CO*C*H_3), 21.1 (CO*C*H_3), 21.0 (CO*C*H_3). IR ν (film, cm^{-1}): 3288 (N-H), 3095, 3071 and 3033 (=C-H), 2921 and 2851 (C-H), 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 $C_{35}H_{44}NO_{14}$ $[M+H]^+$: 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*-butyldiphenylsilyl-α-D-glucopyranoside 37

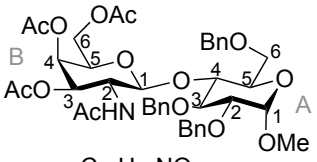


$C_{51}H_{63}NO_{14}Si$
Mol. Wt.: 942.13

37 was obtained under microwave conditions using donor **33** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **17** (40 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 45 min) (34 mg, 55 %, amorphous white solid). $[\alpha]_D^{20}$: +18.8 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) 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, $J_{B3,B2}$ = 10.5 Hz and $J_{B3,B4}$ = 3.5 Hz, 1H, HB-3), 5.37 (dd, $J_{B4,B3}$ = 3.5 Hz and $J_{B4,B5}$ = 1.0 Hz, 1H, HB-4), 5.12 (d, $J_{NH,B2}$ = 8.0 Hz, 1H, NH), 5.06 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.91 (d, $J_{A1,A2}$ = 3.5 Hz, 1H, HA-1), 4.86 (d, J = 2.0 Hz, 2H, CH_2Ph), 4.79 (d, J = 10.5 Hz, 1H, CH_2Ph), 4.59 (d, J = 10.5 Hz, 1H, CH_2Ph), 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, HA-6 and HA-6'), 3.73-3.62 (m, 3H, HA-2, HA-4 and HA-5), 3.38 (s, 3H, OCH_3), 2.15 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$), 1.42 (s, 3H, $COCH_3$), 1.07 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.9 (C, *C*OCH_3), 170.8 (C, *C*OCH_3), 170.7 (C, *C*OCH_3), 170.5 (C, *C*OCH_3), 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 (CH_2, *C*H_2Ph), 75.5 (CH_2, *C*H_2Ph),

71.6 (CH, CA-5), 71.2 (CH, CB-5), 69.9 (CH, CB-3), 67.2 (CH, CB-4), 63.1 (CH_2, CA-6), 62.3 (CH_2, CB-6), 55.2 (CH_3, OCH_3), 52.7 (CH, CB-2), 27.2 (CH_3, $C(CH_3)_3$), 23.3 (CH_3, $COCH_3$), 21.1 (CH_3, $COCH_3$), 21.1 (CH_3, $COCH_3$), 21.0 (CH_3, $COCH_3$), 19.7 (C, $C(CH_3)_3$). IR *v* (film, cm^{-1}): 3280 (N-H), 3068 and 3029 (=C-H), 2931 and 2858 (C-H), 1747 (C=O), 1656 (NH-C=O). MS (ESI): *m/z* = 964 ($[M+Na]^+$, 100%). HRMS (ESI): Calcd for $C_{51}H_{63}NNaO_{14}Si$ $[M+Na]^+$: 964.3916. Found: 964.3915.

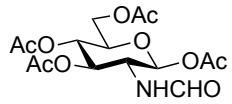
Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside 38



$C_{42}H_{51}NO_{14}$
Mol. Wt.: 793.85

38 was obtained under microwave conditions using donor **33** (50 mg, 0.128 mmol, 2 eq.), TTBP (32 mg, 0.129 mmol, 2 eq.), $Fe(OTf)_3 \cdot 6.2DMSO$ (10 mg, 0.010 mmol, 15 mol-%) and acceptor **19** (29 mg, 0.064 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (Anton Paar Monowave 300 instrument, 110 °C, 3 hours) (13 mg, 26 %, amorphous white solid). $[\alpha]_D^{20}$: -27.2 (*c* 0.7 in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) 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, CH_2Ph), 4.84 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.81-4.76 (m, 3H, CH_2Ph, HB-3), 4.63 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.57 (d, $J_{A1,A2}$ = 4.0 Hz, 1H, HA-1), 4.40 (d, $J_{B1,B2}$ = 8.5 Hz, 1H, HB-1), 4.38 (d, $J_{NH,B2}$ = 10.0 Hz, 1H, NH), 4.36 (d, J = 12.0 Hz, 1H, CH_2Ph), 3.97 (dt, $J_{B2,NH}$ = 10.0 Hz and $J_{B2,B1}$ = $J_{B2,B3}$ = 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, $J_{A6',A6}$ = 10.5 Hz and $J_{A6',A5}$ = 2.0 Hz, 1H, HA-6'), 3.49-3.47 (m, 1H, HA-2), 3.37 (s, 3H, OCH_3), 2.06 (s, 3H, $OCOCH_3$), 2.00 (s, 3H, $OCOCH_3$), 1.96 (s, 3H, $OCOCH_3$), 1.74 (s, 3H, $NHCOCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.8 (C, $COCH_3$), 170.6 (C, $COCH_3$), 170.6 (C, $COCH_3$), 170.1 (C, $COCH_3$), 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), 128.5 (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 (CH_2, CH_2Ph), 74.2 (CH_2, CH_2Ph), 74.0 (CH_2, CH_2Ph), 70.8 (CH, CB-3), 70.6 (CH, CB-5), 69.8 (CH, CA-5), 67.9 (CH_2, CA-6), 66.5 (CH, CB-4), 61.2 (CH_2, CB-6), 55.7 (CH_3, OCH_3), 51.6 (CH, CB-2), 23.7 (CH_3, $NHCOCH_3$), 21.1 (CH_3, $OCOCH_3$), 21.0 (CH_3, $OCOCH_3$), 21.0 (CH_3, $OCOCH_3$). IR *v* (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 $C_{42}H_{52}NO_{14}$ $[M+H]^+$: 794.3388. Found: 794.3399.

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



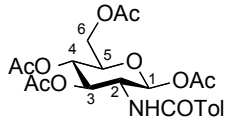
$C_{15}H_{21}NO_{10}$
Mol. Wt.: 375.33

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) in a 1:1 CH_2Cl_2-saturated aqueous solution of $NaHCO_3$ (40 mL) was added dropwise acetoformic anhydride[27] (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 CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel

[27] L. I. Krimen, J. Savage, P. Yates, *Org. Synth.* **1970**, *50*, 1-1.

(heptane/EtOAc 1:1 to 0:1) to give the desired product **39**[28] (912 mg, 93 %, white amorphous solid).

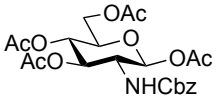
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(4-methylbenzamido)-β-D-glucopyranose 40



$C_{22}H_{27}NO_{10}$
Mol. Wt.: 465.45

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) 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_2Cl_2 (3×40 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_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, $CDCl_3$) δ: 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, $J_{6,6'}$ = 12.0 Hz, $J_{6,5}$ = 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, $J_{5,4}$ = 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, $CDCl_3$) δ: 171.8 (C, CO), 170.9 (C, CO), 169.8 (C, CO), 169.5 (C, CO), 167.4 (C, CO), 142.7 (C, Ph), 130.9 (C, Ph), 129.6 (2CH, 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): Calcd for $C_{22}H_{27}NNaO_{10}$ $[M+Na]^+$: 488.1533. Found: 488.1529.

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



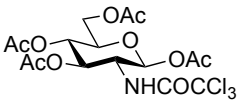
$C_{22}H_{27}NO_{11}$
Mol. Wt.: 481.45

To a solution 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride[8] (10 g, 26.1 mmol) in a 1:2 CH_2Cl_2-saturated aqueous solution of $NaHCO_3$ (380 mL) was added dropwise CbzCl (4.1 mL, 28.6 mmol, 1.1 eq.). 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_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_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).

[28] (a) C. G. Greig, D. H. Leaback, P. G. Walker, *J. Chem. Soc.* **1961**, 879-883; (b) D. H. R. Barton, G. Bringmann, G. Lamotte, W. B. Motherwell, R. S. Hay Motherwell, A. E. A. Porter, *J. Chem. Soc., Perkin Trans. 1* **1980**, 2657-2664.

[29] (a) P. Boullanger, M. Jouineau, B. Bouammali, D. Lafont, G. Descotes, *Carbohydr. Res.* **1990**, *202*, 151-164; (b) N. S. Simpkins, S. Stokes, A. J. Whittle, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 2471-2478.

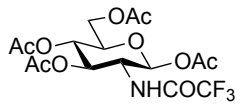
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranose 42



$C_{16}H_{20}Cl_3NO_{10}$
Mol. Wt.: 492.69

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).

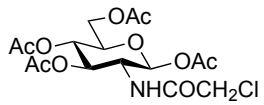
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranose 43



$C_{16}H_{20}F_3NO_{10}$
Mol. Wt.: 443.33

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_2Cl_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).

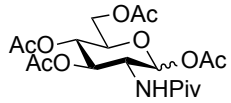
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-chloroacetamido-β-D-glucopyranose 44



$C_{16}H_{22}ClNO_{10}$
Mol. Wt.: 423.80

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_2Cl_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

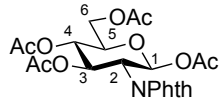


$C_{19}H_{29}NO_{10}$
Mol. Wt.: 431.43

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_2Cl_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 **45**4 (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

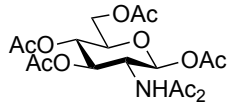
[30] G. Blatter, J.-M. Beau, J.-C. Jacquinet, *Carbohydr. Res.* **1994**, *260*, 189-202.
[31] (a) M. L. Wolfrom, H. B. Bhat, *J. Org. Chem.* **1967**, *32*, 1821-1823; (b) I. R. Greig, M. S. Macauley, I. H. Williams, D. J. Vocadlo, *J. Am. Chem. Soc.* **2009**, *131*, 13415-13422.



$C_{22}H_{23}NO_{11}$
Mol. Wt.: 477.42

To a solution of D-glucosamine hydrochloride (40 g, 185.6 mmol, 1 eq.) in water (300 mL) are successively added phtalic anhydride (55 g, 372 mmol, 2 eq.) and $NaHCO_3$ (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 CH_2Cl_2 (600 mL), washed with water (3×120 mL), brine (100 mL), dried over Na_2SO_4, 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**[32] (white amorphous solid).

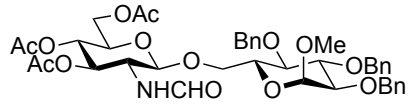
1,3,4,6-Tetra-*O*-acetyl-2-acetylacetamido-2-deoxy-β-D-glucopyranose 47



$C_{18}H_{26}NO_{11}$
Mol. Wt.: 432.40

1β (1.2 g, 3.08 mmol) and TsOH monohydrate (276 mg, 1.45 mmol, 0.47 eq.) in isopropenylacetate (35 mL) were stirred at 65 °C for 4.5 hours under argon. Et_3N (8 mL) was added and the volatiles were evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (heptane/EtOAc 8:2 to 1:1) to afford pure product **47**[33] (1.12 g, 84 %, white amorphous solid).

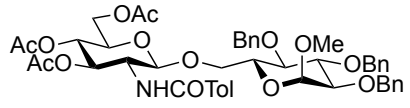
Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-formamido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 48



$C_{41}H_{49}NO_{14}$
Mol. Wt.: 779.83

48[34] was obtained under microwave conditions using donor **39** (48 mg, 0.129 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** (30 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (CEM Discover instrument, 80 °C, 45 min) (25 mg, 50 %, white amorphous solid).

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



$C_{48}H_{55}NO_{14}$
Mol. Wt.: 869.95

49[4] was obtained under microwave conditions using donor **40** (60 mg, 0.129 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**2 (30 mg, 0.065 mmol, 1 eq.) in dry CH_2Cl_2 (1 mL), according to general procedure A (CEM Discover instrument, 80 °C, 45 min) (46 mg, 82 %, white amorphous solid).

[32] D. Macmillan, A. M. Daines, M. Bayrhuber, S. L. Flitsch, *Org. Lett.* **2002**, *4*, 1467-1470.
[33] M. Suihko, M. Ahlgrén, P. Aulaskari, J. Rouvinen, *Carbohydr. Res.* **2001**, *334*, 337-341.
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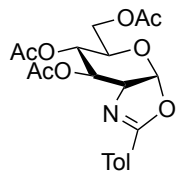
2-(4-Methylphenyl) (3,4,6-tri-*O*-acetyl-1,2-di-deoxy-α-D-glucopyrano)-[2,1-d]-2-oxazoline 55



$C_{20}H_{23}NO_8$
Mol. Wt.: 405.40

TTBP (53 mg, 0.215 mmol, 2 eq.) and $Fe(OTf)_3 \cdot 6.2DMSO$ (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 CH_2Cl_2 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 CH_2Cl_2 (20 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer is extracted with CH_2Cl_2 (4×20 mL) and the combined organic layers are washed with brine (20 mL), dried over Na_2SO_4, 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 **55**4 (27 mg, 62 %, white amorphous solid).

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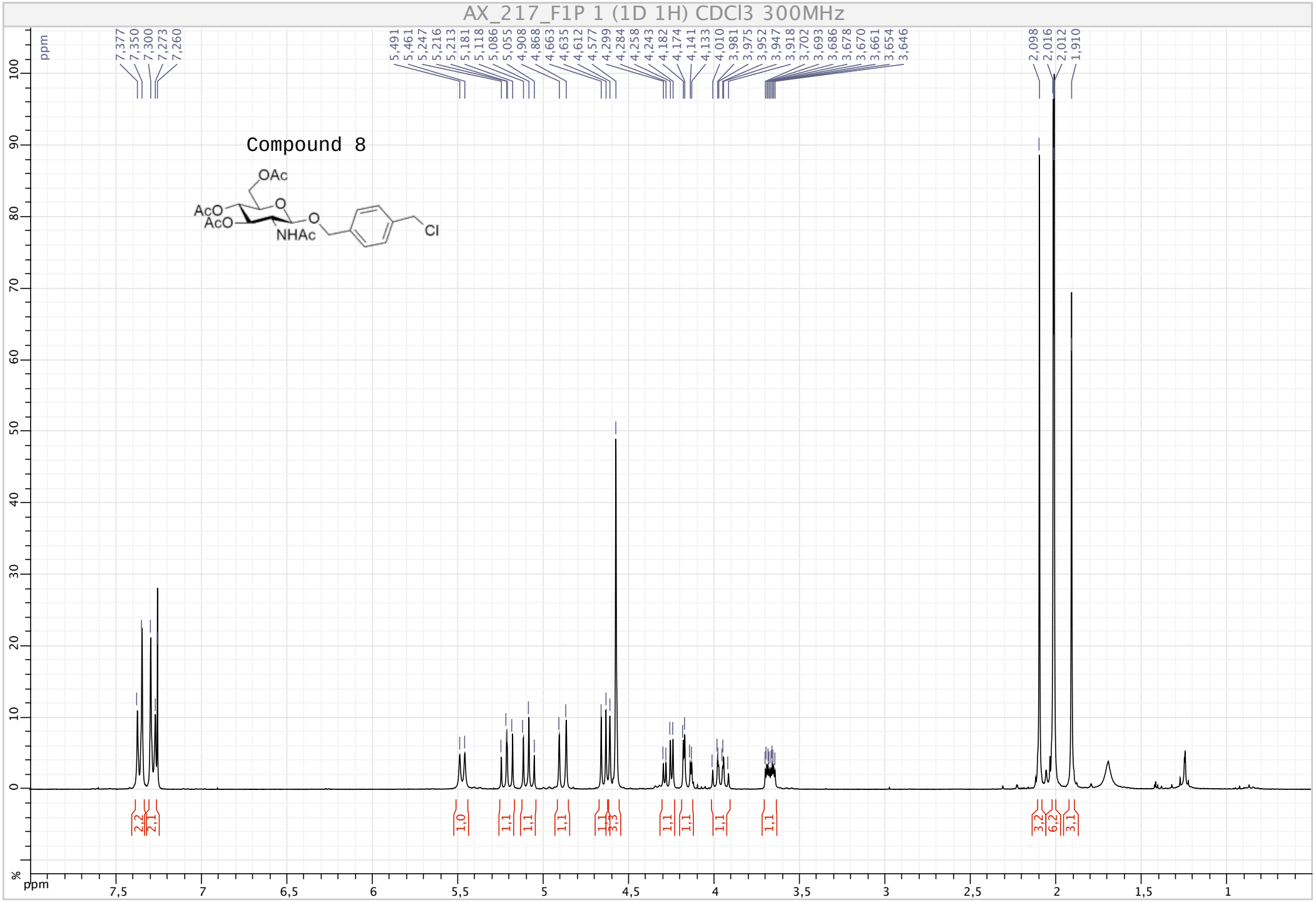
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AcO
AcO
O
O
NHAc
Cl
ppm
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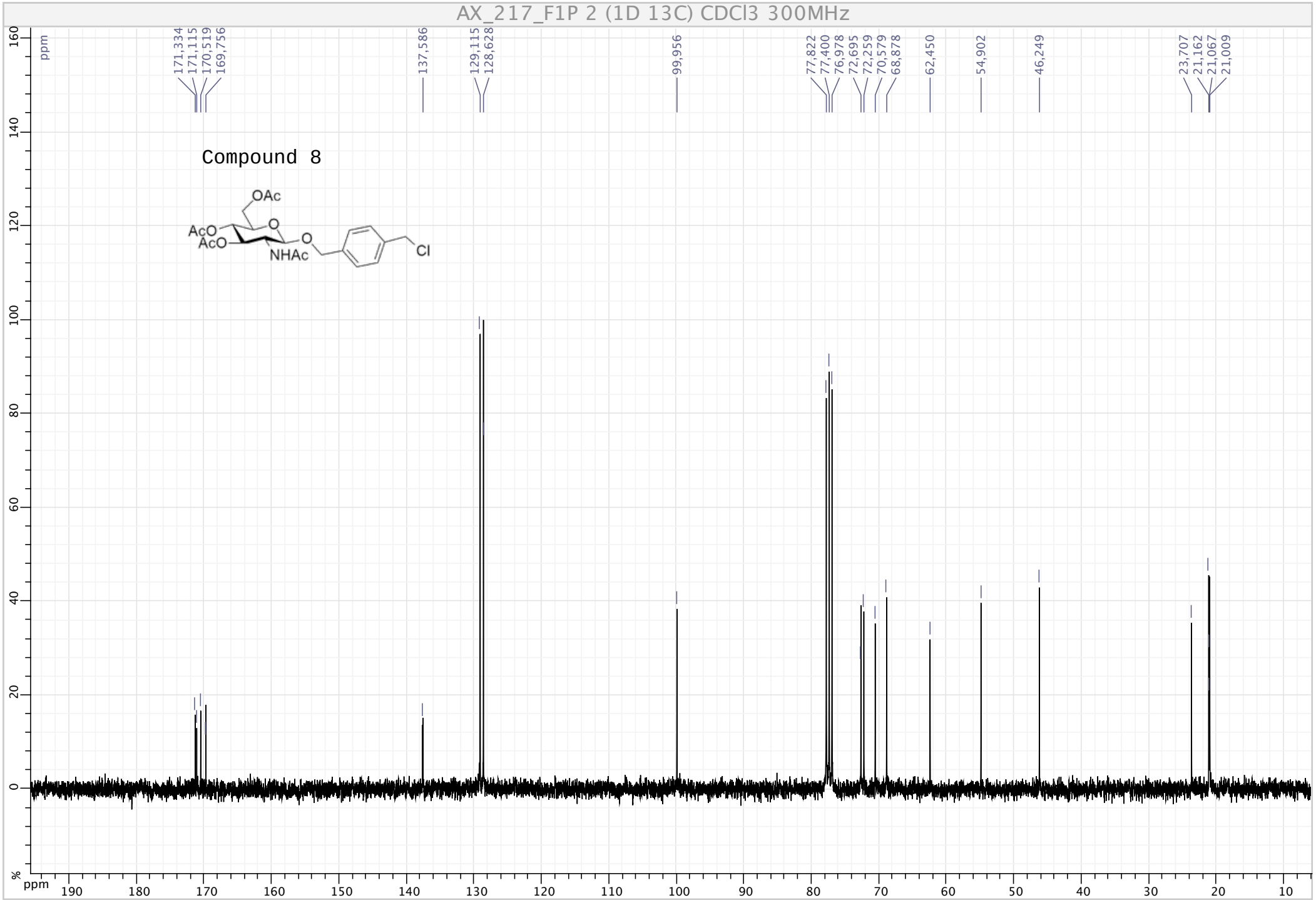
7,350
7,300
7,273
7,260
5,491
5,461
5,247
5,216
5,213
5,181
5,118
5,086
5,055
4,908
4,868
4,663
4,635
4,612
4,577
4,299
4,284
4,258
4,243
4,182
4,174
4,141
4,133
4,010
3,981
3,975
3,952
3,947
3,918
3,702
3,693
3,686
3,678
3,670
3,661
3,654
3,646
2,098
2,016
2,012
1,910
2,2
2,1
1,0
1,1
1,1
1,1
1,1
3,3
1,1
1,1
1,1
1,1
3,2
6,2
3,1
%
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1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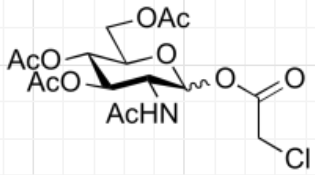
ppm
171,334
171,115
170,519
169,756
137,586
129,115
128,628
99,956
77,822
77,400
76,978
72,695
72,259
70,579
68,878
62,450
54,902
46,249
23,707
21,162
21,067
21,009
Compound 8
OAc
AcO
AcO
O
O
NHAc
Cl
%
ppm

fdb2678 1 (1D 1H) CDCl3 300MHz

Compound 10



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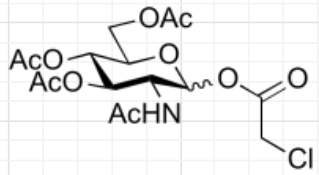
Compound 10



171,847
171,222
170,822
170,807
170,531
170,342
169,411
169,273
166,379
165,550

92,449

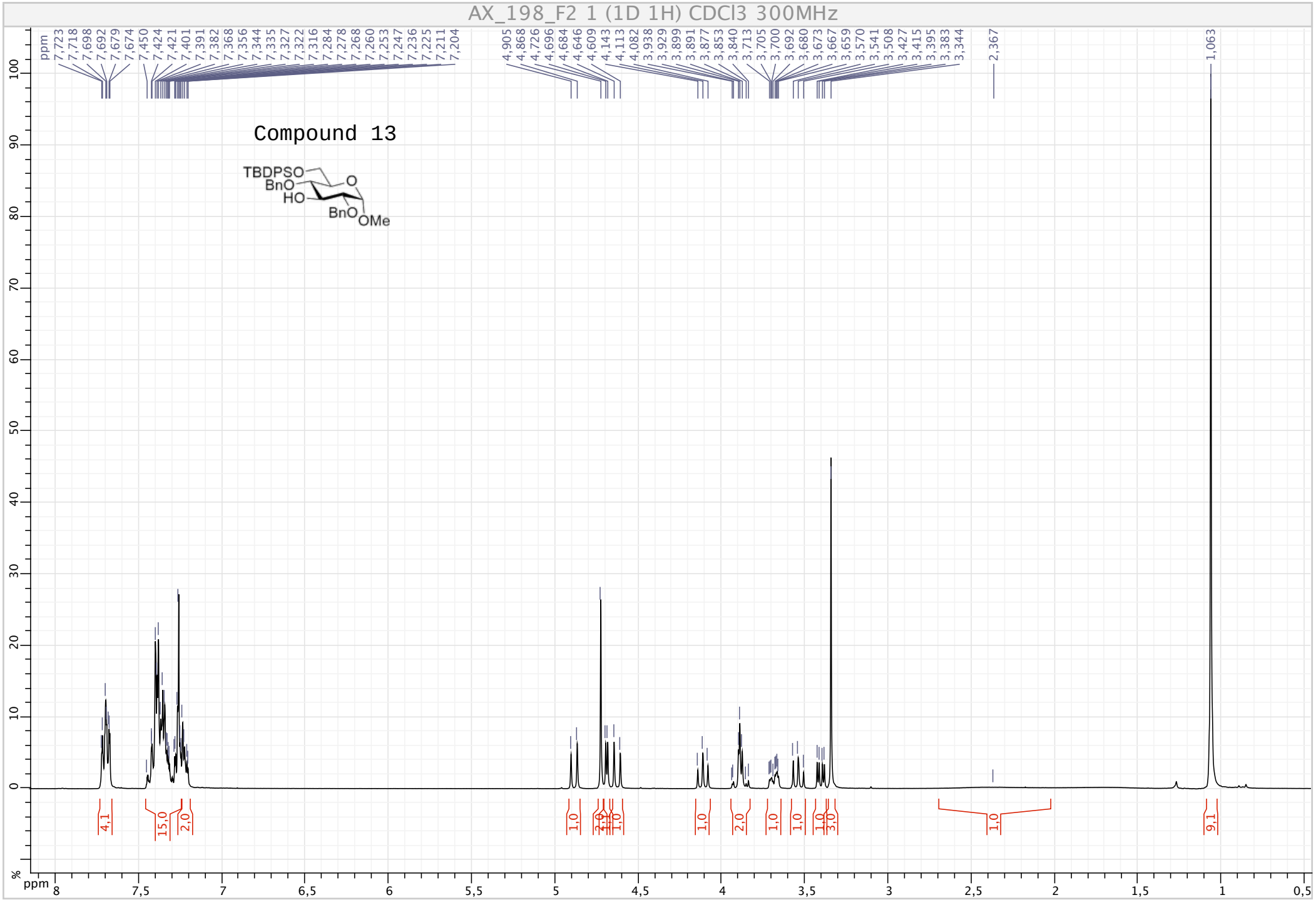
77,659
77,230
76,808
73,158
72,358
70,533
70,373
67,443
61,553

53,081
51,474

40,785

23,144
21,225
20,876
20,854
20,796
20,730
14,368

ppm
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
200
180
160
140
120
100
80
60
40
20
0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Compound 13
TBDPSO
BnO
HO
O
BnO
OMe
ppm
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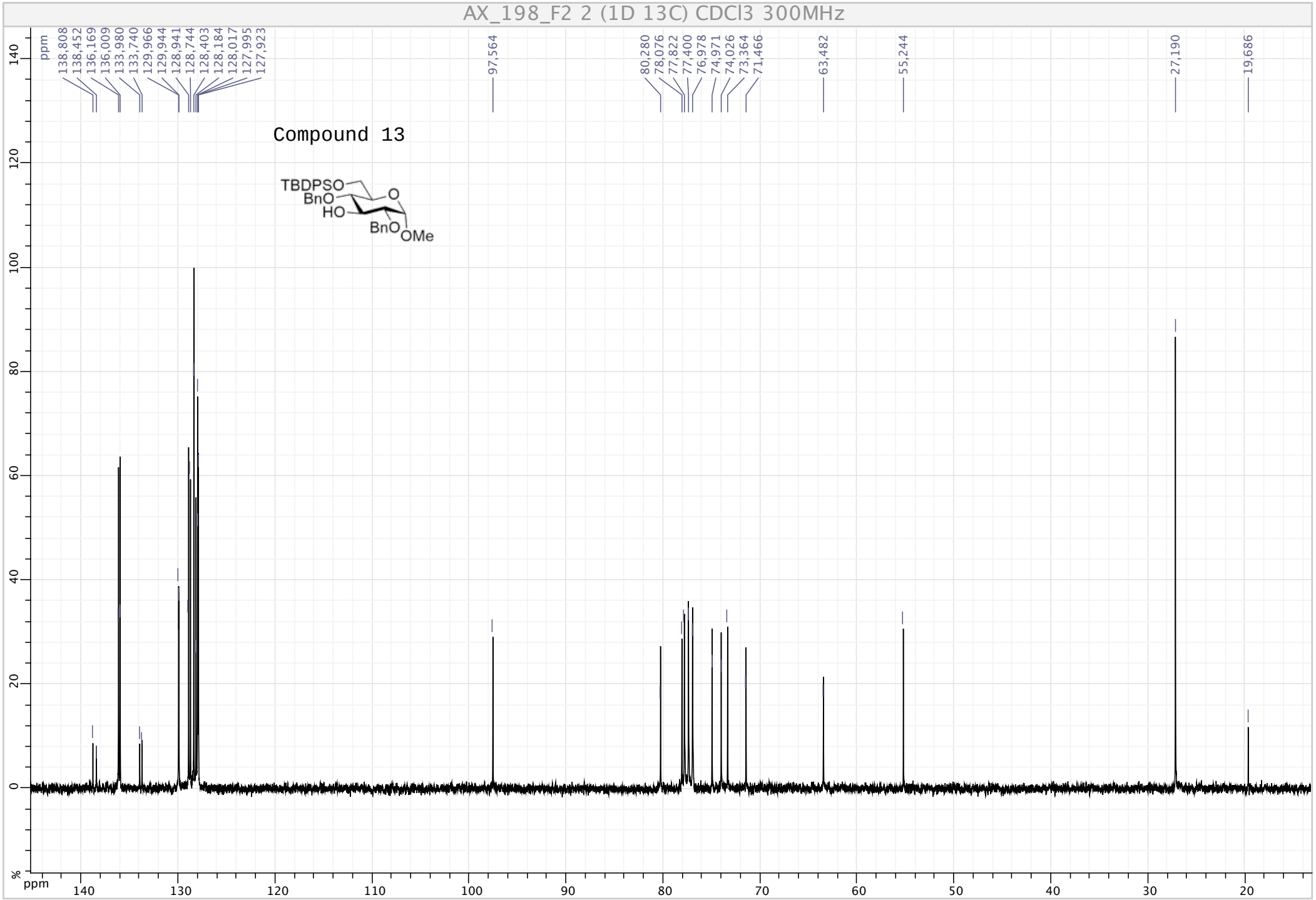
4,905 4,868 4,726 4,696 4,684 4,646 4,609 4,143 4,113 4,082 3,938 3,929 3,899 3,891 3,877 3,853 3,840 3,713 3,705 3,700 3,692 3,680 3,673 3,667 3,659 3,570 3,541 3,508 3,427 3,415 3,395 3,383 3,344
2,367
1,063
4,1
15,0
2,0
1,0
2,0
1,0
1,0
2,0
1,0
1,0
1,0
3,0
1,0
9,1
%
ppm
8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5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133,740
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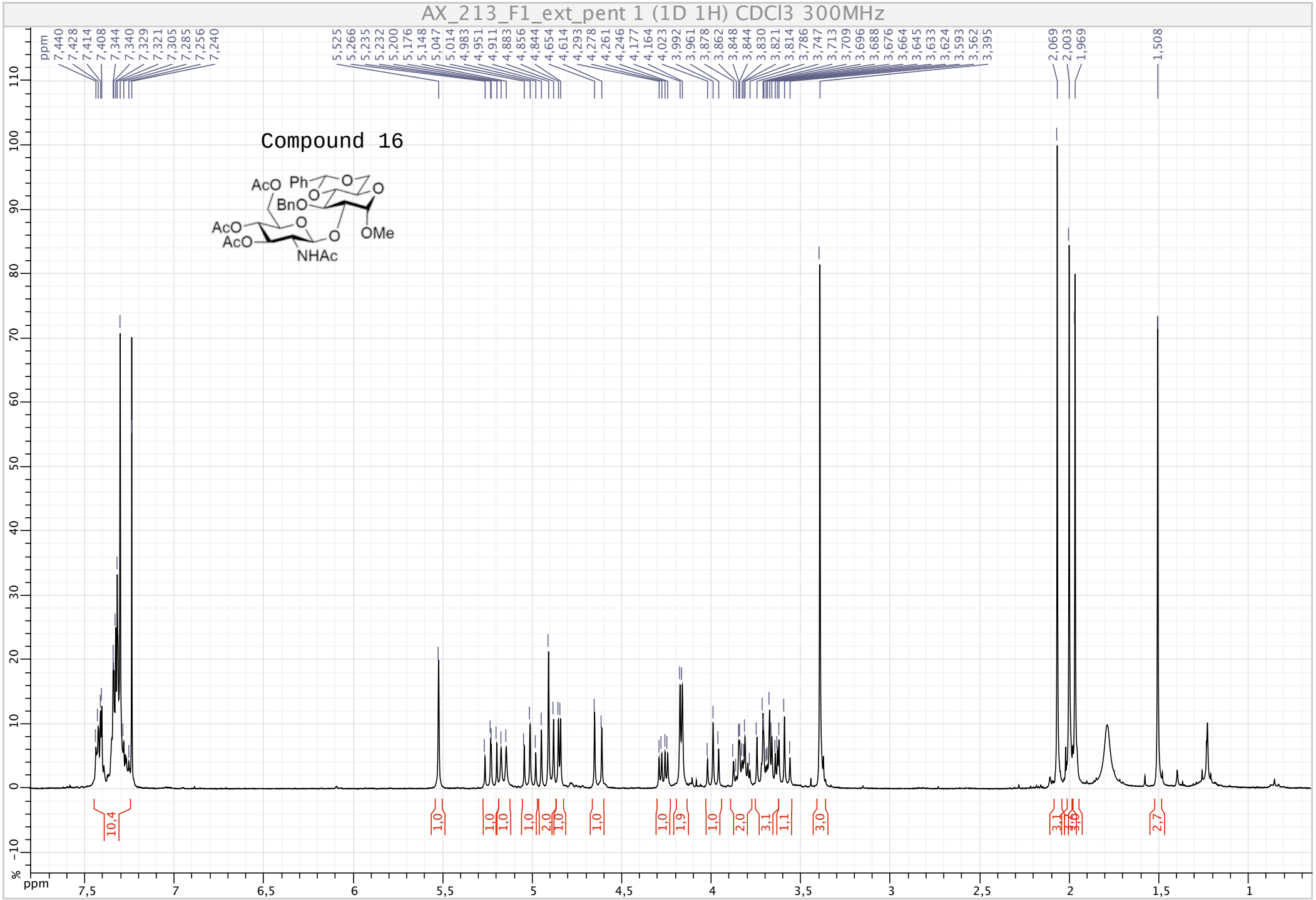
129,944
128,941
128,744
128,403
128,184
128,017
127,995
127,923
97,564
80,280
78,076
77,822
77,400
76,978
74,971
74,026
73,364
71,466
63,482
55,244
27,190
19,686
Compound 13
TBDPSO
BnO
HO
O
BnO
OMe
%
ppm


AX_213_F1_ext_pent 1 (1D 1H) CDCl3 300MHz
Compound 16
AcO
Ph
O
BnO
AcO
AcO
NHAc
OMe
ppm
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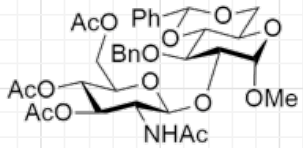
7,428
7,414
7,408
7,344
7,340
7,329
7,321
7,305
7,285
7,256
7,240
5,525
5,266
5,235
5,232
5,200
5,176
5,148
5,047
5,014
4,983
4,951
4,911
4,883
4,856
4,844
4,654
4,614
4,293
4,278
4,261
4,246
4,177
4,164
4,023
3,992
3,961
3,878
3,862
3,848
3,844
3,830
3,821
3,814
3,786
3,747
3,713
3,709
3,696
3,688
3,676
3,664
3,645
3,633
3,624
3,593
3,562
3,395
2,069
2,003
1,969
1,508
10,4
1,0
1,0
1,0
1,0
2,0
1,0
1,0
1,0
1,9
1,0
2,0
3,1
1,1
3,0
3,1
2,7
%
ppm

AX_213_F1_ext_pent 3 (1D 13C) CDCl3 300MHz

ppm

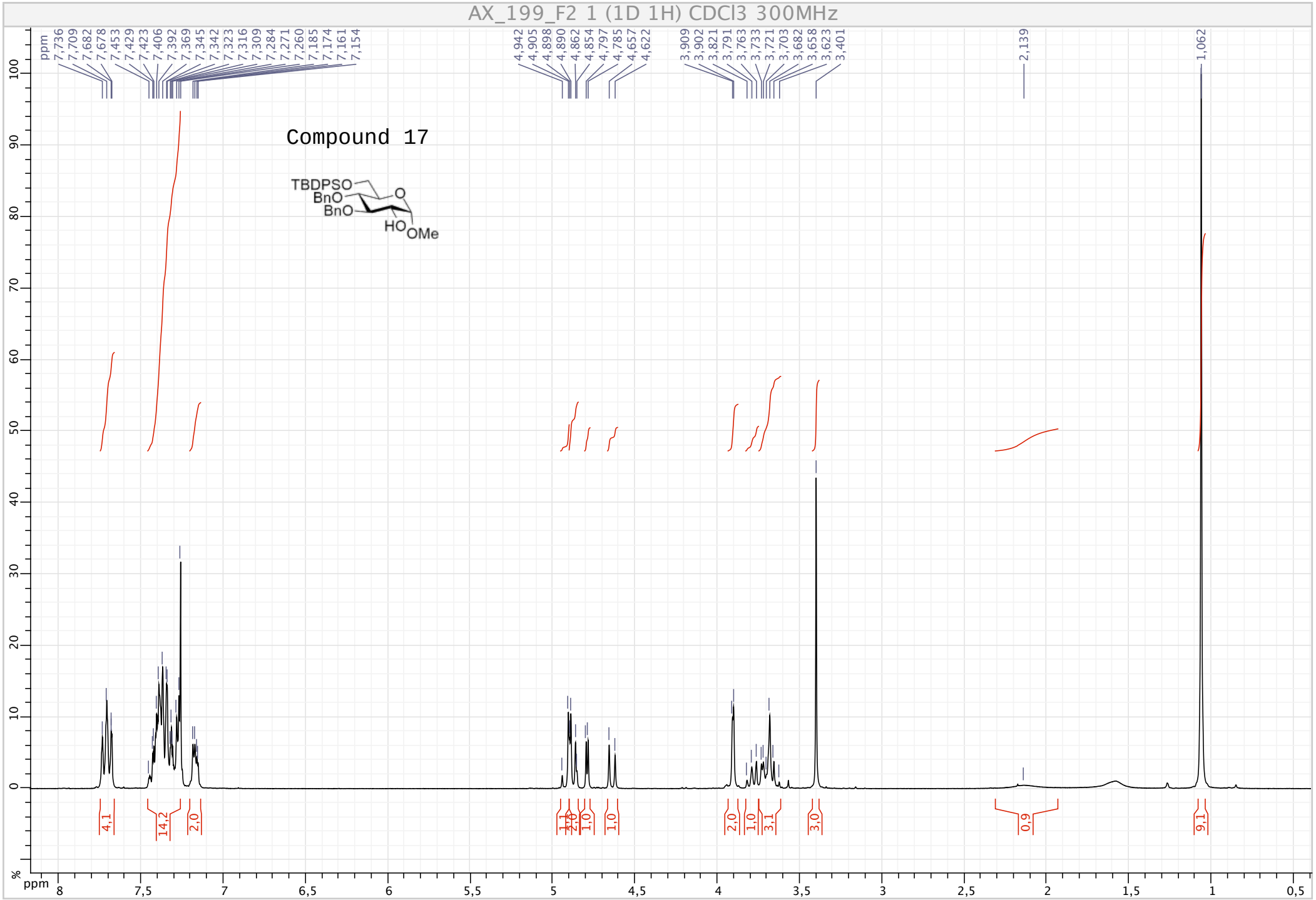
171,035
170,977
170,694
169,814
139,288
137,594
129,355
128,912
128,599
128,097
127,370
126,410
102,363
101,760
100,393
82,817
81,021
78,040
77,822
77,400
76,971
75,080
72,812
72,244
69,474
69,016
62,595
62,522
55,862
55,309
23,271
21,162
21,031

Compound 16



%

ppm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Compound 17
TBDPSO
BnO
BnO
O
HO
OMe
ppm
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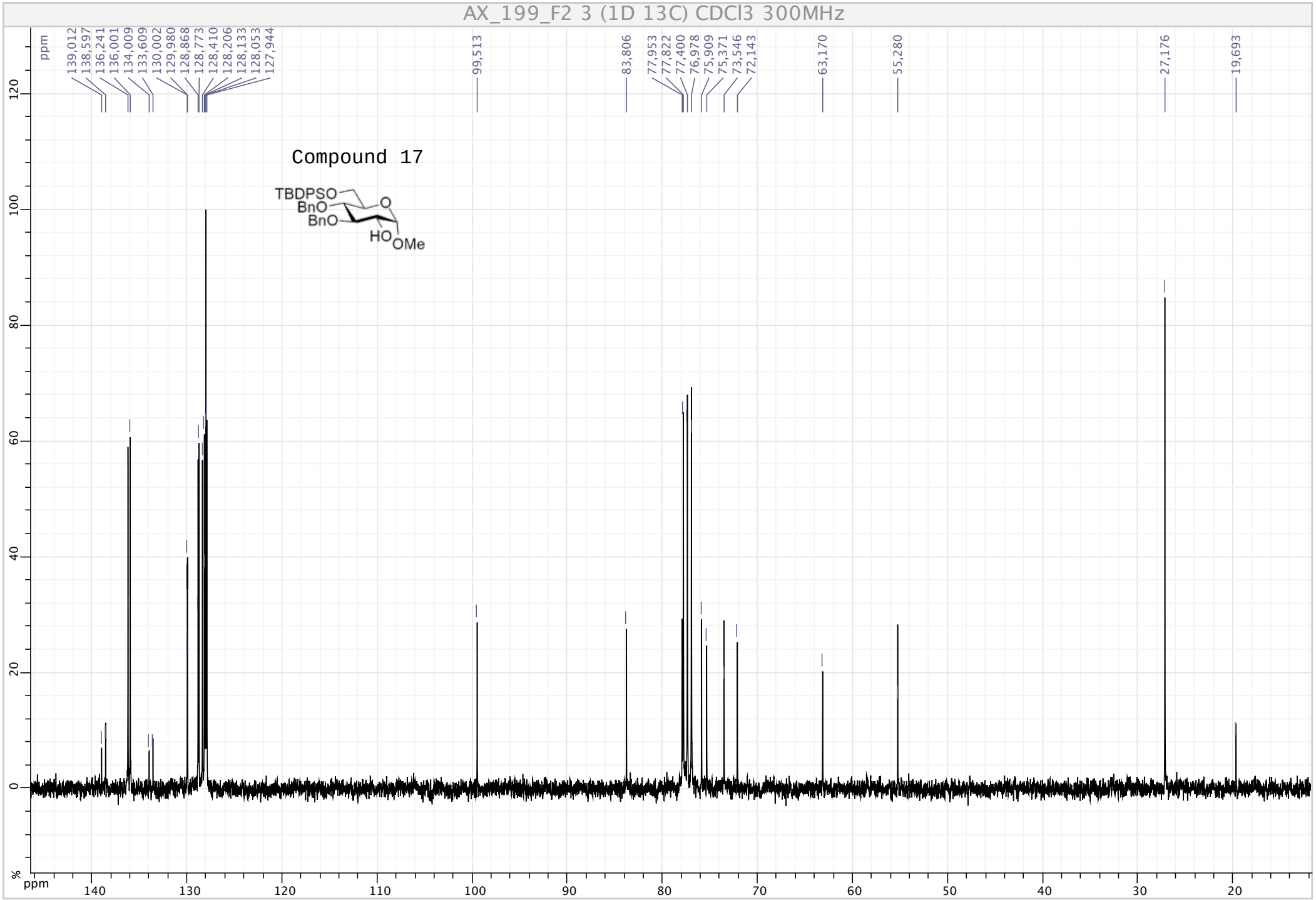
7,709
7,682
7,678
7,453
7,429
7,423
7,406
7,392
7,369
7,345
7,342
7,323
7,316
7,309
7,284
7,271
7,260
7,185
7,174
7,161
7,154
4,942
4,905
4,898
4,890
4,862
4,854
4,797
4,785
4,657
4,622
3,909
3,902
3,821
3,791
3,763
3,733
3,721
3,703
3,682
3,658
3,623
3,401
2,139
1,062
4,1
14,2
2,0
1,0
2,0
1,0
1,0
2,0
1,0
3,1
3,0
0,9
9,1
%
ppm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ppm
139,012
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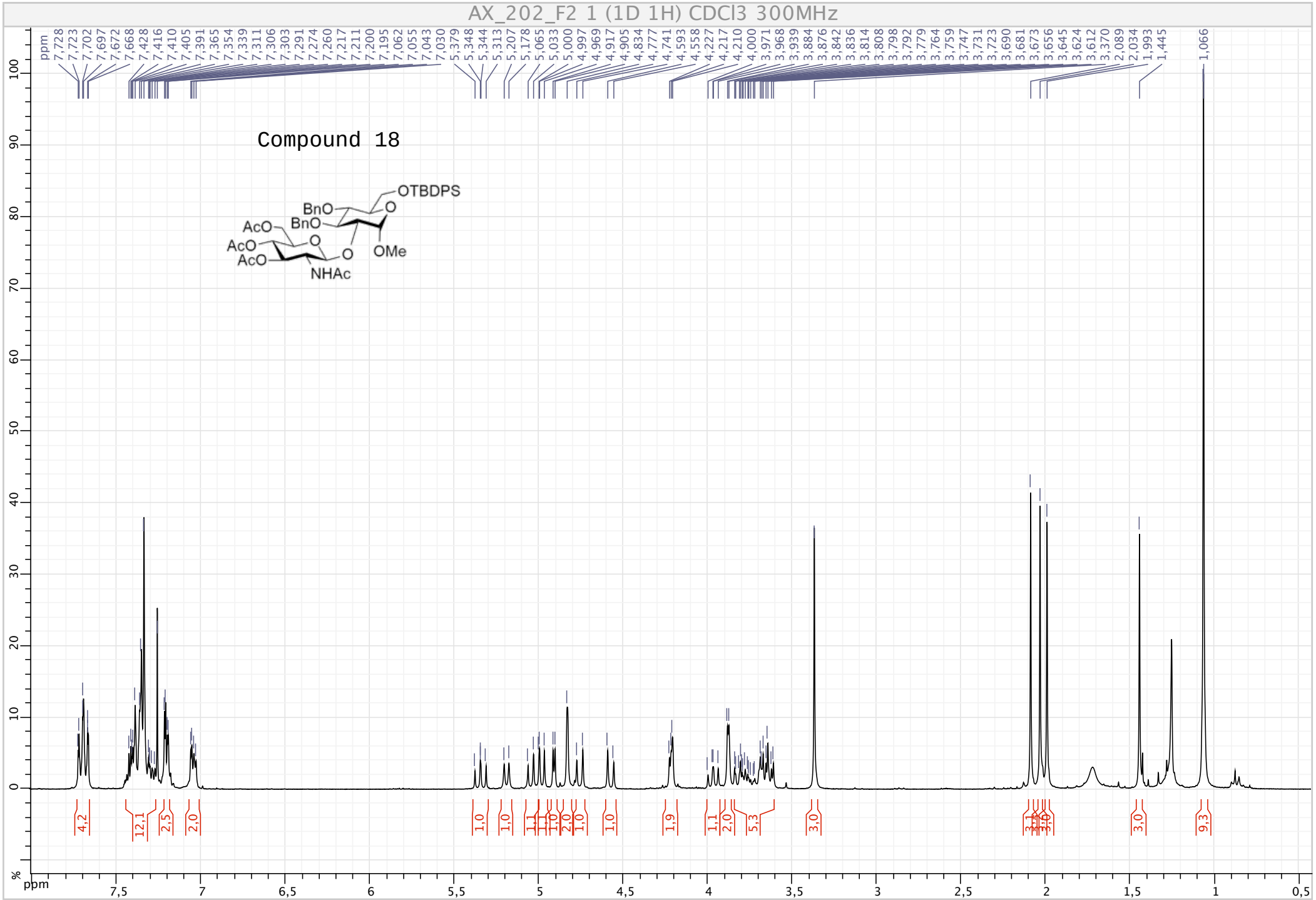
136,241
136,001
134,009
133,609
130,002
129,980
128,868
128,773
128,410
128,206
128,133
128,053
127,944
99,513
83,806
77,953
77,822
77,400
76,978
75,909
75,371
73,546
72,143
63,170
55,280
27,176
19,693
Compound 17
TBDPSO
BnO
BnO
O
HO
OMe
%
ppm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Compound 18
OTBDPS
BnO
BnO
AcO
AcO
AcO
O
O
O
OMe
NHAc
ppm
7,728
7,723
7,702
7,697
7,672
7,668
7,428
7,416
7,410
7,405
7,391
7,365
7,354
7,339
7,311
7,306
7,303
7,291
7,274
7,260
7,217
7,211
7,200
7,195
7,062
7,055
7,043
7,030
5,379
5,348
5,344
5,313
5,207
5,178
5,065
5,033
5,000
4,997
4,969
4,917
4,905
4,834
4,777
4,741
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4,558
4,227
4,217
4,210
4,000
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3,968
3,939
3,884
3,876
3,842
3,836
3,814
3,808
3,798
3,792
3,779
3,764
3,759
3,747
3,731
3,723
3,690
3,681
3,673
3,656
3,645
3,624
3,612
3,370
2,089
2,034
1,993
1,445
1,066
4,2
12,1
2,5
2,0
1,0
1,0
1,1
1,0
1,0
2,0
1,0
1,0
1,9
1,1
2,0
5,3
3,0
3,1
3,0
3,0
9,3
%
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5

AX_202_F2 3 (1D 13C) CDCl3 300MHz

ppm

171,028 170,970 170,716 169,872

139,499 136,161 135,987 133,594 130,024 129,980 128,904 128,693 128,199 128,053 128,024 127,952 127,886 126,955

102,181 99,425

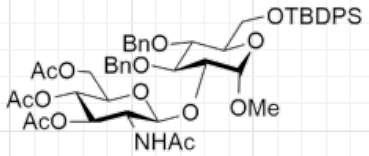
82,512 81,414 78,418 77,822 77,400 76,971 75,422 75,386 72,703 72,143 71,546 69,176 63,082 62,828

55,716 55,258

30,070 30,033 27,190

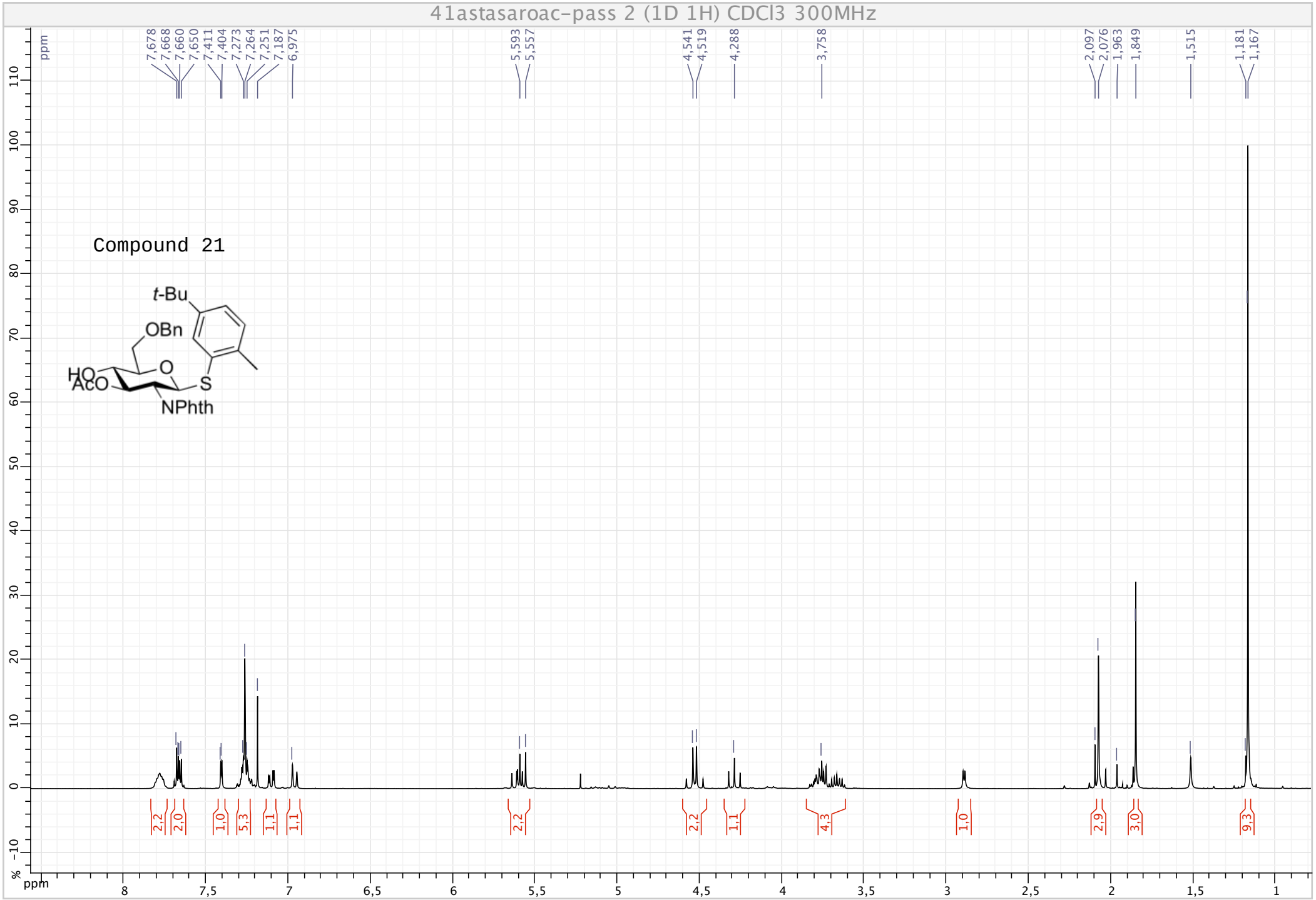
23,183 21,126 21,038 19,671

Compound 18



%

ppm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ppm
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7,660
7,650
7,411
7,404
7,273
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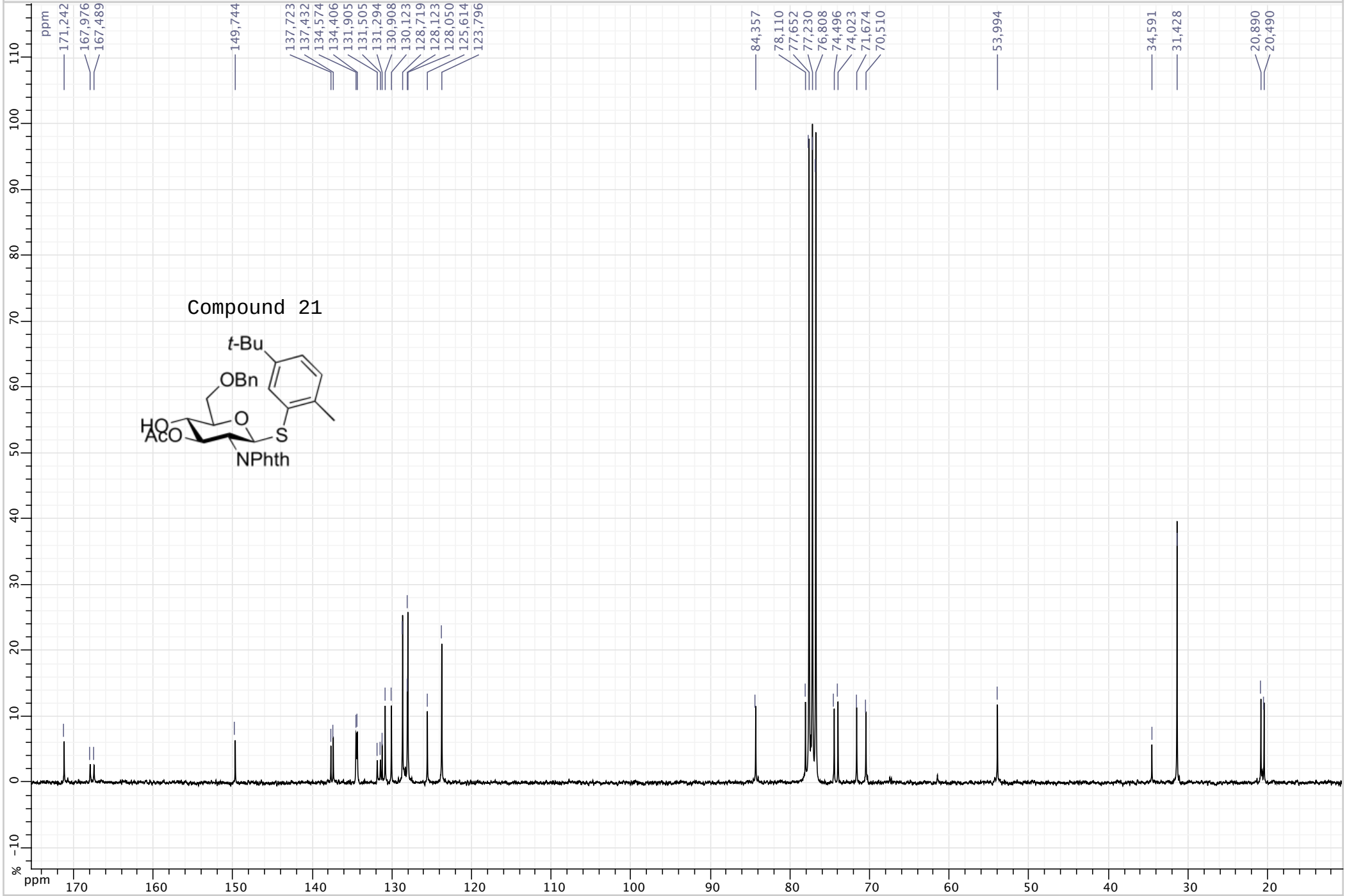
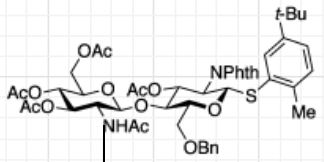
7,187
6,975
5,593
5,557
4,541
4,519
4,288
3,758
2,097
2,076
1,963
1,849
1,515
1,181
1,167
Compound 21
t-Bu
OBn
HO
AcO
O
S
NPhth
2,2
2,0
1,0
5,3
1,1
1,1
2,2
2,2
1,1
4,3
1,0
2,9
3,0
9,3
%
ppm

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



41ast548 1 (1D 1H) CDCl3 500MHz

Compound 22



41ast-548-pass2 3 (1D 13C) CDCl3 300MHz

ppm

170,771
170,277
169,986
169,586
167,804
167,433
149,633
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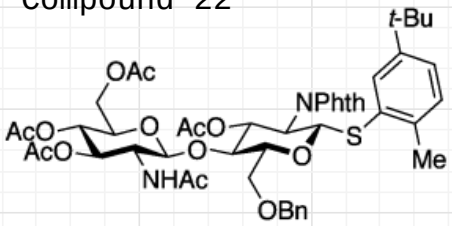
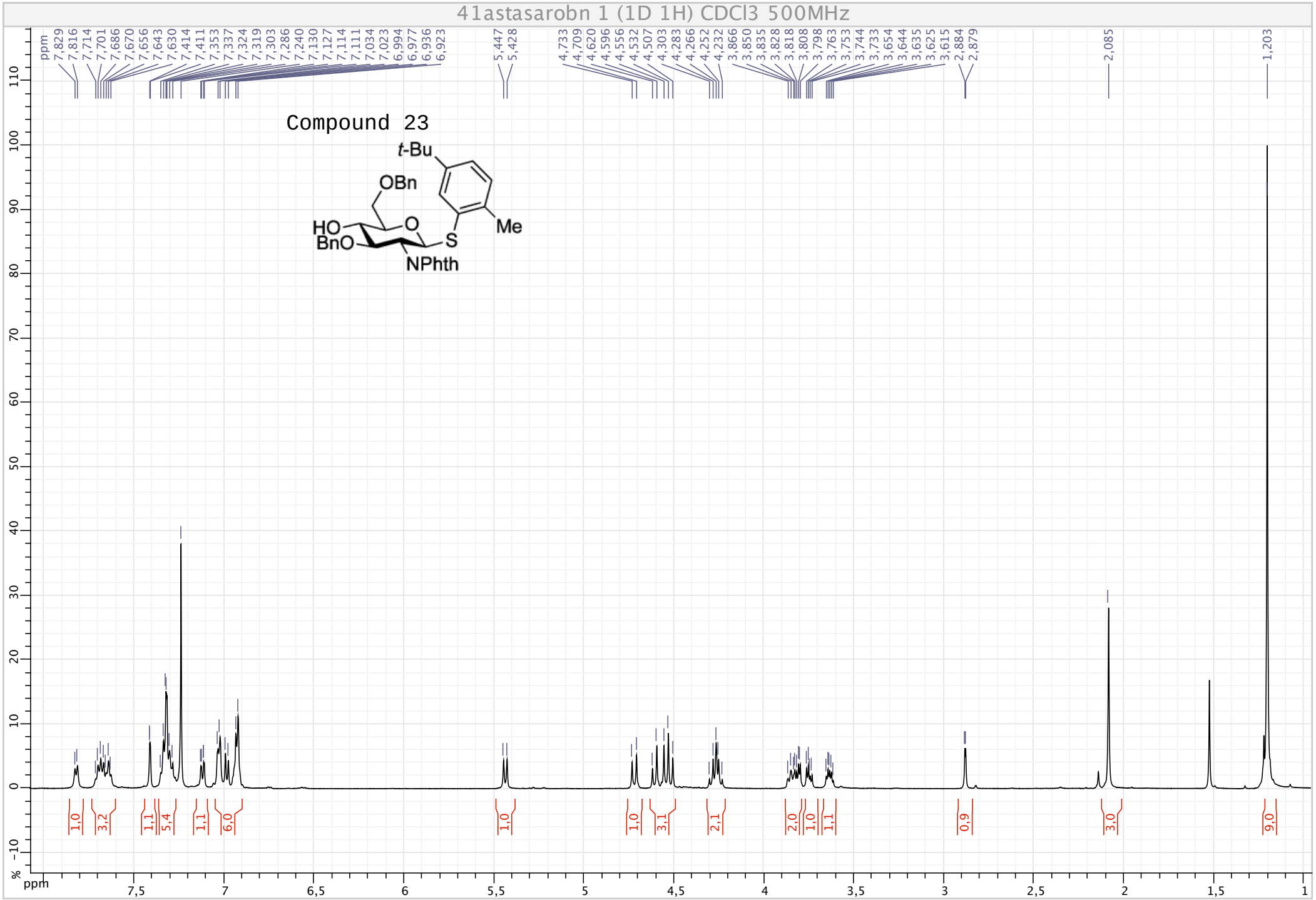
137,598
134,530
134,326
131,868
131,461
131,214
131,127
130,123
129,069
128,967
128,807
125,651
123,804
123,717
100,048
84,378
78,539
77,637
77,230
76,801
75,274
73,892
72,649
71,820
71,682
68,621
67,792
62,011
54,972
54,405
34,575
31,419
23,341
20,817
20,796
20,578
20,483

Compound 22

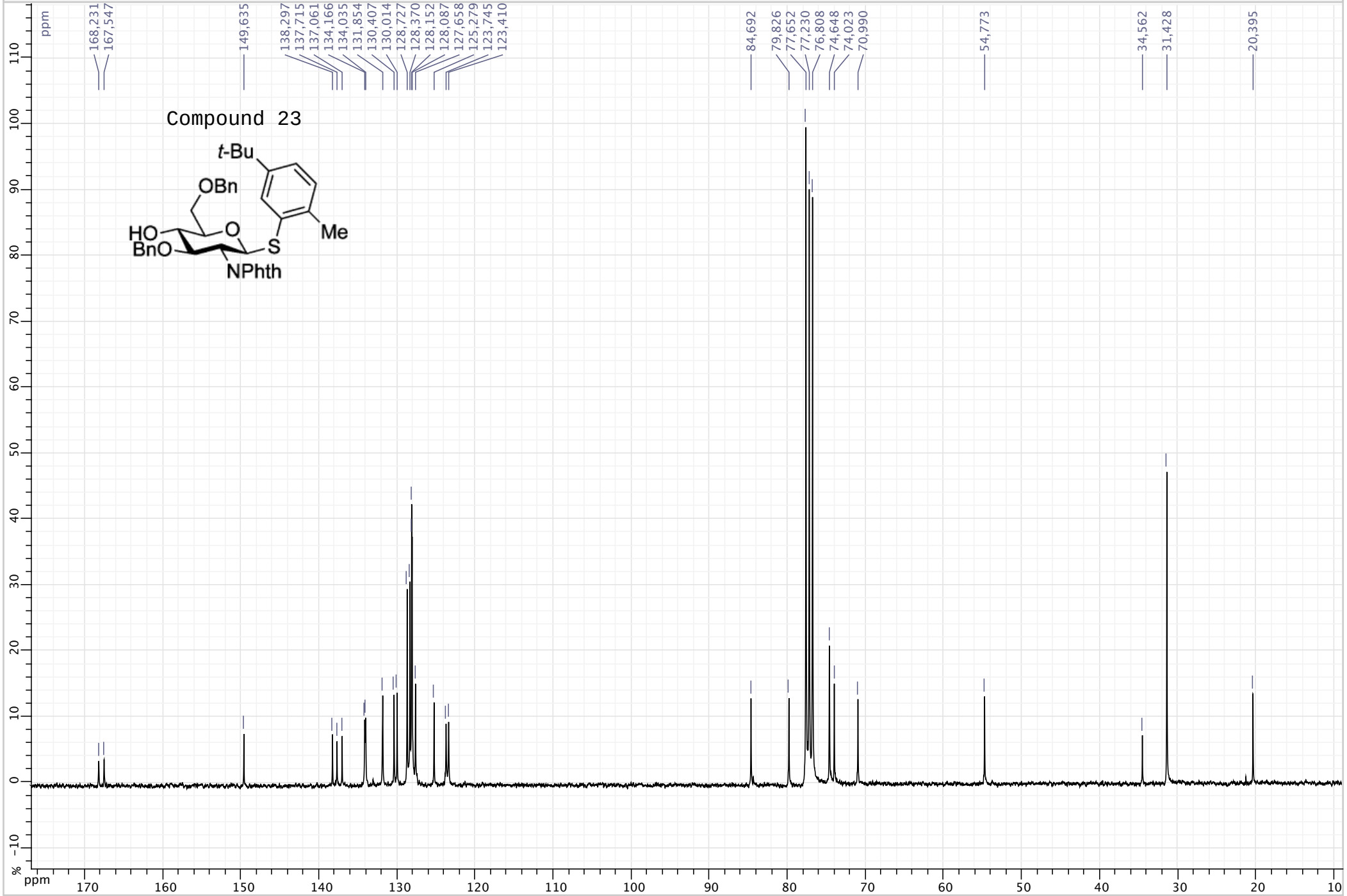


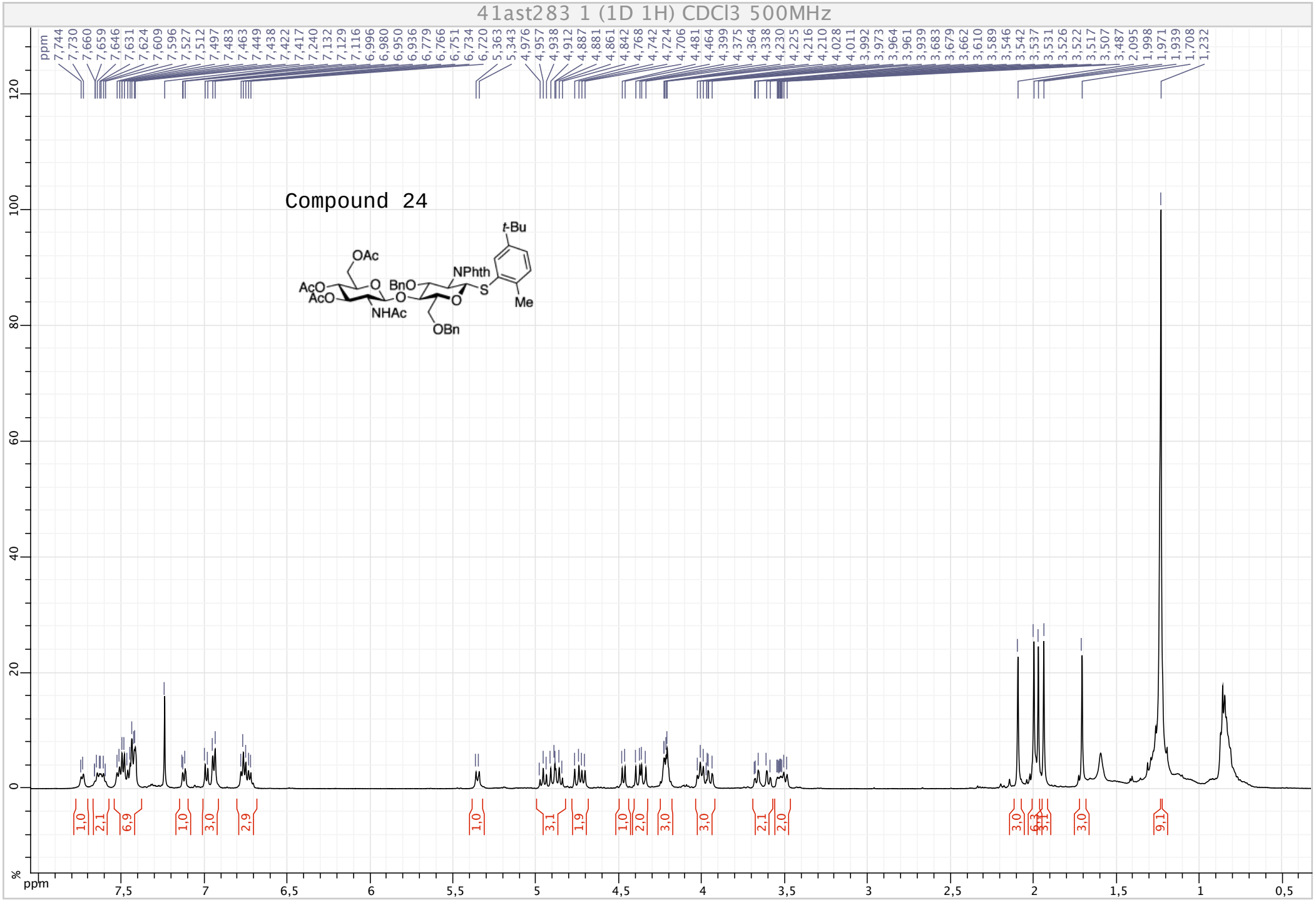
%
110
100
90
80
70
60
50
40
30
20
10
0
-10

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


41astasarobn 1 (1D 1H) CDCl3 500MHz
Compound 23
t-Bu
OBn
HO
BnO
O
S
Me
NPhth
ppm
7,829
7,816
7,714
7,701
7,686
7,670
7,656
7,643
7,630
7,414
7,411
7,353
7,337
7,324
7,319
7,303
7,286
7,240
7,130
7,127
7,114
7,111
7,034
7,023
6,994
6,977
6,936
6,923
5,447
5,428
4,733
4,709
4,620
4,596
4,556
4,532
4,507
4,303
4,283
4,266
4,252
4,232
3,866
3,850
3,835
3,828
3,818
3,808
3,798
3,763
3,753
3,744
3,733
3,654
3,644
3,635
3,625
3,615
2,884
2,879
2,085
1,203
1,0
3,2
1,1
5,4
1,1
6,0
1,0
1,0
3,1
2,1
2,0
1,0
1,1
0,9
3,0
9,0
%
ppm

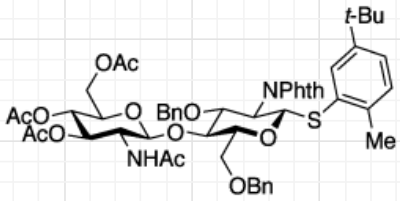
41astasarobnc13 1 (1D 13C) CDCl3 300MHz




41ast283 1 (1D 1H) CDCl3 500MHz
Compound 24
OAc
AcO
AcO
O
BnO
O
NPhth
S
t-Bu
Me
NHAc
OBn
ppm
7,744 7,730 7,660 7,659 7,646 7,631 7,624 7,609 7,596 7,527 7,512 7,497 7,483 7,463 7,449 7,438 7,422 7,417 7,240 7,132 7,129 7,116 6,996 6,980 6,950 6,936 6,779 6,766 6,751 6,734 6,720 5,363 5,343 4,976 4,957 4,938 4,912 4,887 4,881 4,861 4,842 4,768 4,742 4,724 4,706 4,481 4,464 4,399 4,375 4,364 4,338 4,230 4,225 4,216 4,210 4,028 4,011 3,992 3,973 3,964 3,961 3,939 3,683 3,679 3,662 3,610 3,589 3,546 3,542 3,537 3,531 3,526 3,522 3,517 3,507 3,487 2,095 1,998 1,971 1,939 1,708 1,232
1,0 2,1 6,9 1,0 3,0 2,9 1,0 3,1 1,9 1,0 2,0 3,0 3,0 2,1 2,0 3,0 6,3 3,1 3,0 9,1
%
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5

41ast550-pass 3 (1D 13C) CDCl3 300MHz

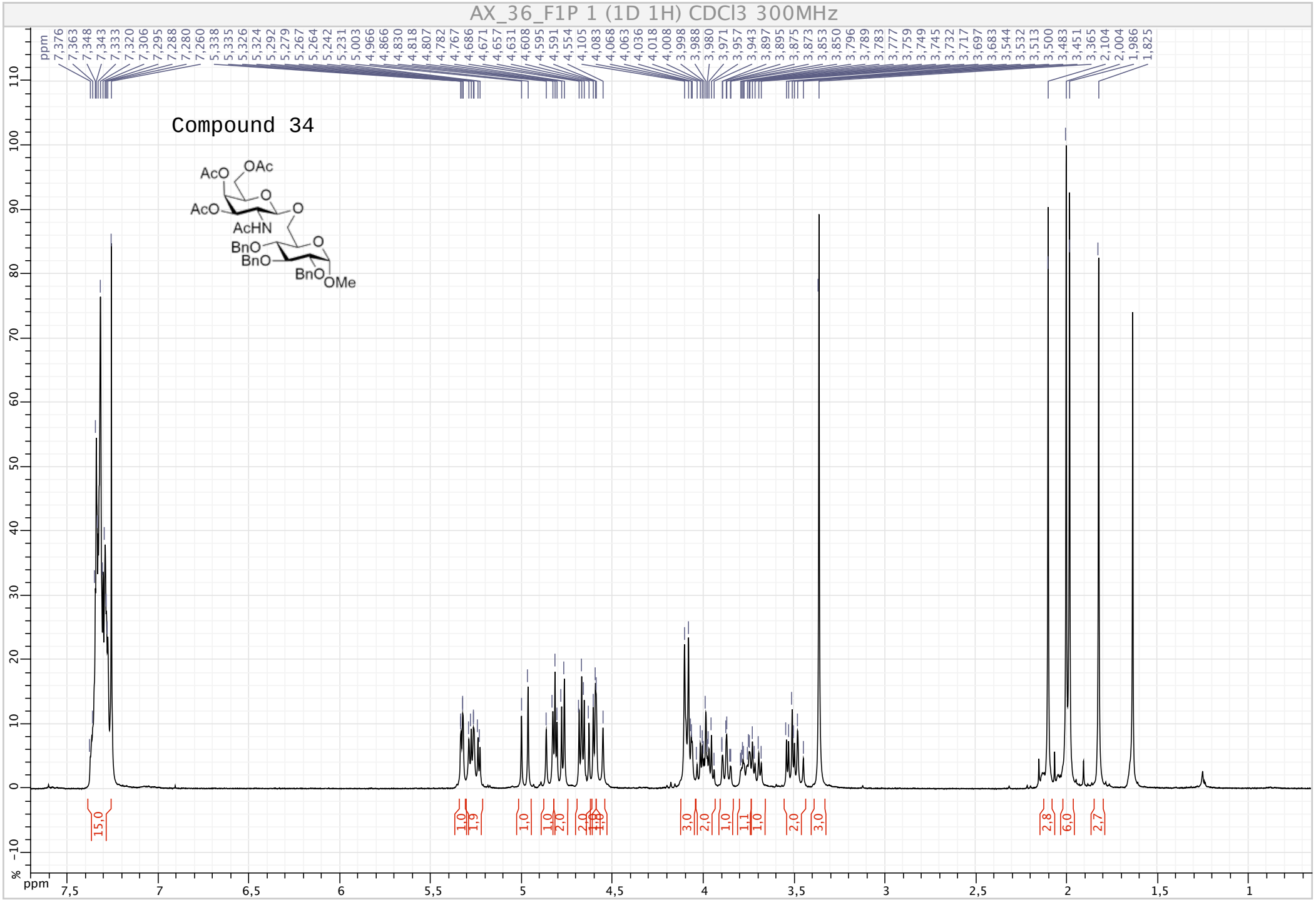
Compound 24



ppm 170,982 170,916 169,942 169,520 167,862 167,441 149,487 138,754 137,824 137,220 133,875 133,744 131,861 131,781 130,639 130,007 129,345 129,236 129,098 128,116 128,014 127,113 125,288 123,455 123,390 101,037 84,640 78,910 78,481 78,204 77,659 77,230 76,808 75,049 74,227 73,318 71,602 68,766 68,002 62,054 55,248 54,376 34,568 31,441 23,304 20,817 20,388

% 110 100 90 80 70 60 50 40 30 20 10 0 -10

ppm 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

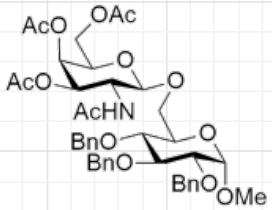

AX_36_F1P 1 (1D 1H) CDCl3 300MHz
Compound 34
AcO
OAc
AcO
O
O
AcHN
BnO
O
BnO
BnO
OMe
ppm
7,376
7,363
7,348
7,343
7,333
7,320
7,306
7,295
7,288
7,280
7,260
5,338
5,335
5,326
5,324
5,292
5,279
5,267
5,264
5,242
5,231
5,003
4,966
4,866
4,830
4,818
4,807
4,782
4,767
4,686
4,671
4,657
4,631
4,608
4,595
4,591
4,554
4,105
4,083
4,068
4,063
4,036
4,018
4,008
3,998
3,988
3,980
3,971
3,957
3,943
3,897
3,895
3,875
3,873
3,853
3,850
3,796
3,789
3,783
3,777
3,759
3,749
3,745
3,732
3,717
3,697
3,683
3,544
3,532
3,513
3,500
3,483
3,451
3,365
2,104
2,004
1,986
1,825
15,0
1,0
1,9
1,0
1,0
2,0
2,0
1,0
3,0
2,0
1,0
1,1
1,0
2,0
3,0
2,8
6,0
2,7
%
ppm

AX_36_F1P 3 (1D 13C) CDCl3 300MHz

ppm

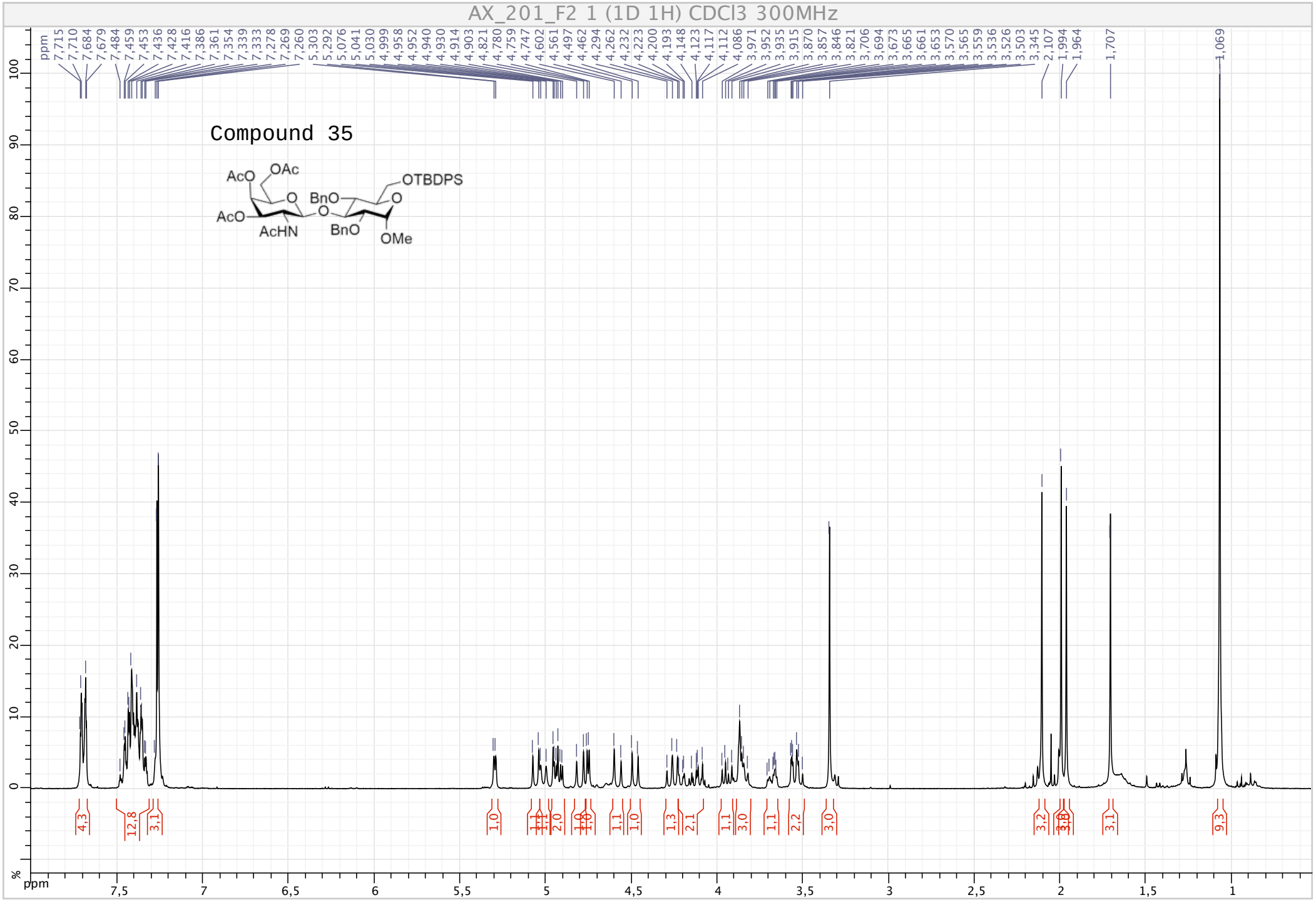
170,810 170,781 170,577 170,410 139,084 138,655 138,481 128,875 128,839 128,773 128,526 128,337 128,308 128,250 128,104 128,003 101,316 98,429 82,396 80,134 77,822 77,778 77,400 76,971 76,127 74,957 73,742 71,096 70,158 69,874 68,078 67,104 61,715 55,578 51,855 23,823 21,060 21,038

Compound 34



%

ppm

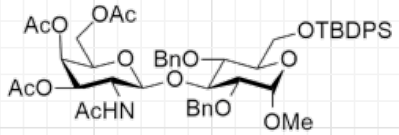

AX_201_F2 1 (1D 1H) CDCl3 300MHz
Compound 35
AcO
OAc
O
BnO
O
OTBDPS
AcO
AcHN
BnO
OMe
ppm
7,715 7,710 7,684 7,679 7,484 7,459 7,453 7,436 7,428 7,416 7,386 7,361 7,354 7,339 7,333 7,278 7,269 7,260 5,303 5,292 5,076 5,041 5,030 4,999 4,958 4,952 4,940 4,930 4,914 4,903 4,821 4,780 4,759 4,747 4,602 4,561 4,497 4,462 4,294 4,262 4,232 4,223 4,200 4,193 4,148 4,123 4,117 4,112 4,086 3,971 3,952 3,935 3,915 3,870 3,857 3,846 3,821 3,706 3,694 3,673 3,665 3,661 3,653 3,570 3,565 3,559 3,536 3,526 3,503 3,345 2,107 1,994 1,964 1,707 1,069
4,3
12,8
3,1
1,0
1,1
1,1
2,0
1,0
1,0
1,1
1,0
1,3
2,1
1,1
3,0
1,1
2,2
3,0
3,2
3,1
9,3
%
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1

AX_201_F2 2 (1D 13C) CDCl3 300MHz

ppm

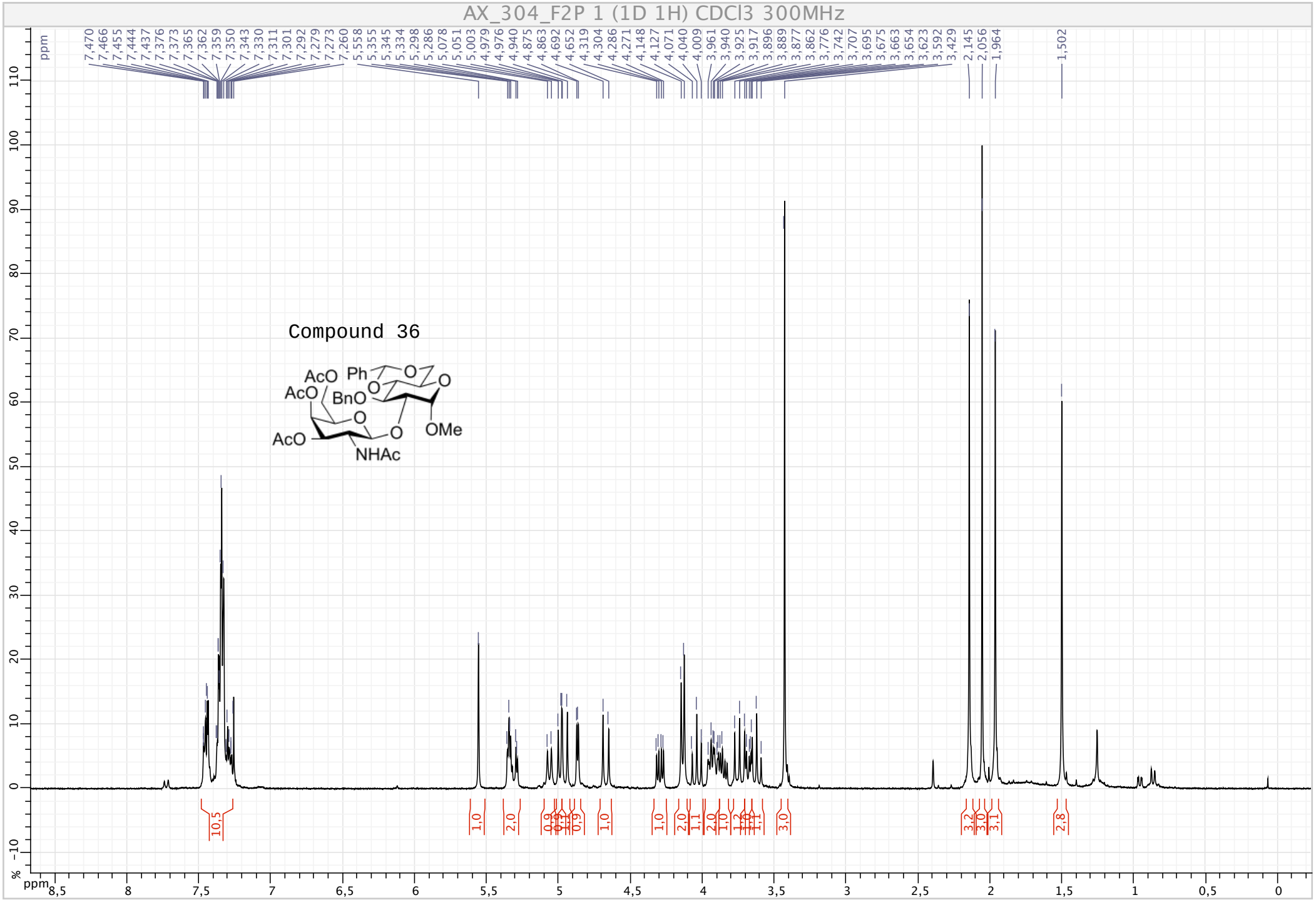
170,948 170,723 170,694 170,396 138,823 138,372 136,139 136,016 133,885 133,747 129,988 129,937 129,348 128,795 128,504 128,032 127,944 127,515 102,225 97,106 81,647 79,771 77,822 77,734 77,400 77,305 76,978 76,091 75,226 72,652 71,779 71,517 70,892 66,900 63,380 61,388 55,149 51,586 27,197 23,620 21,111 21,046 19,679

Compound 35



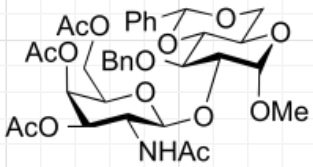
%

ppm


AX_304_F2P 1 (1D 1H) CDCl3 300MHz
Compound 36
AcO
Ph
O
AcO
BnO
O
O
O
AcO
O
OMe
NHAc
ppm
%

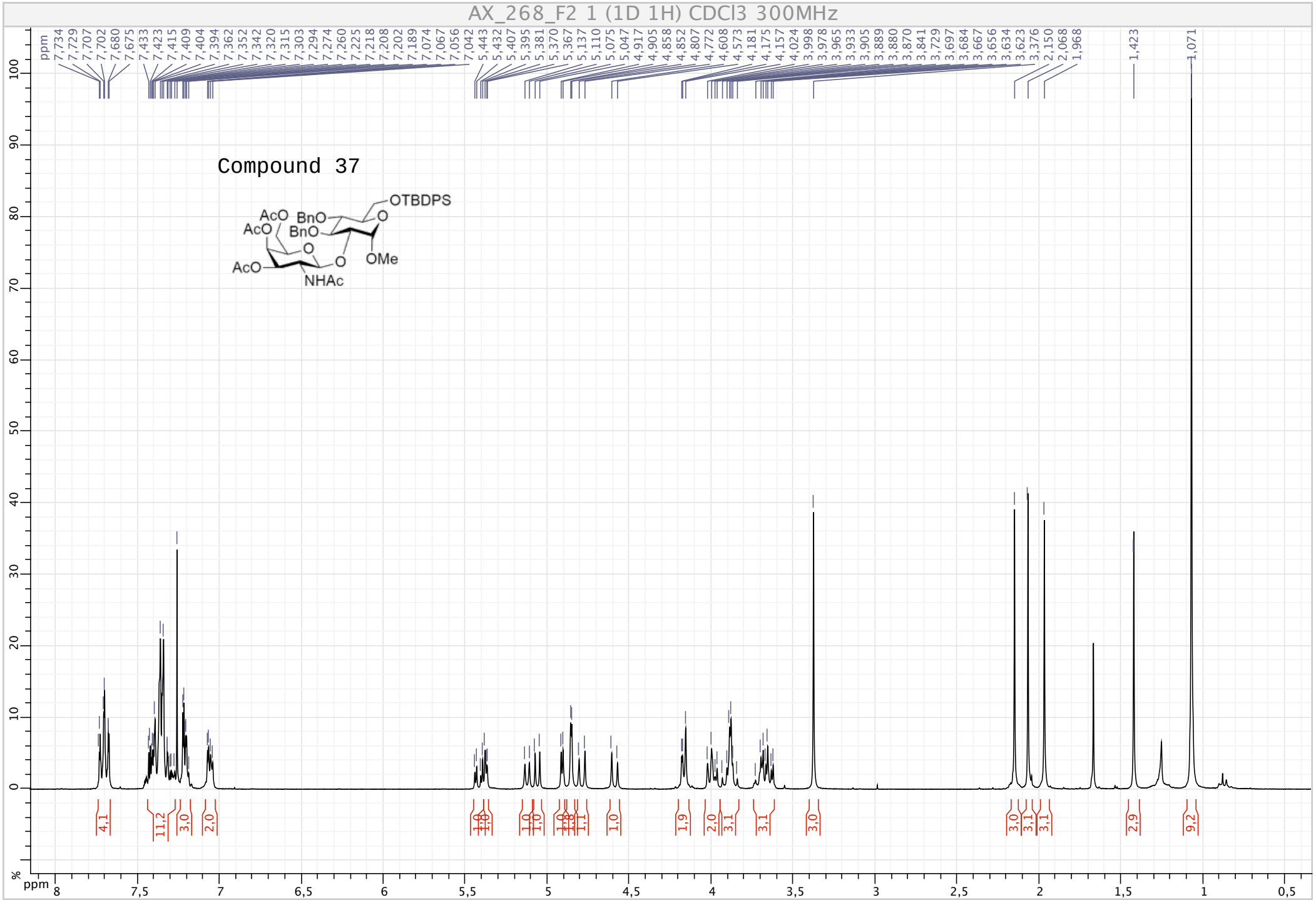
AX_304_F2P 2 (13C) CDCl3 300MHz

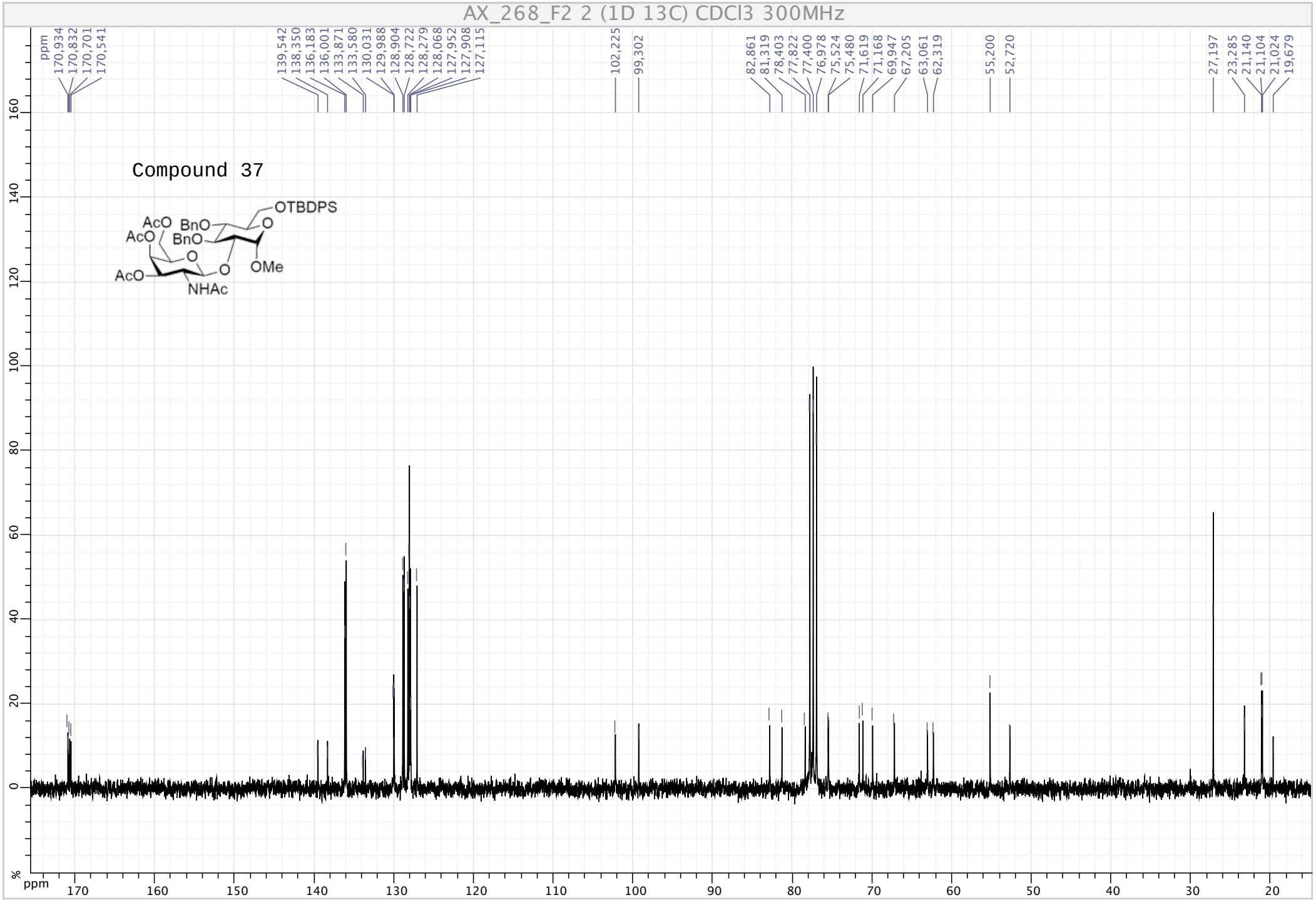
Compound 36

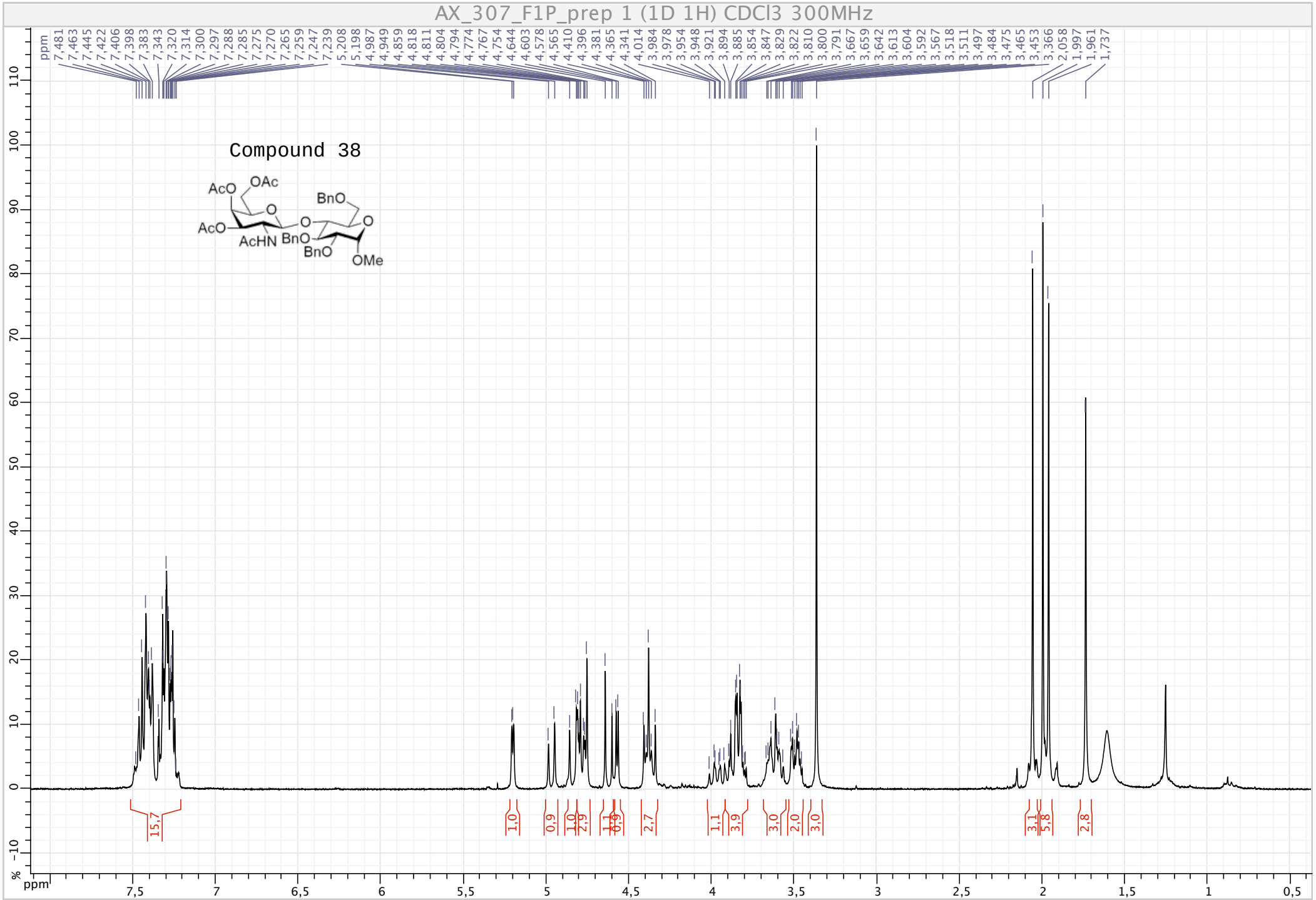


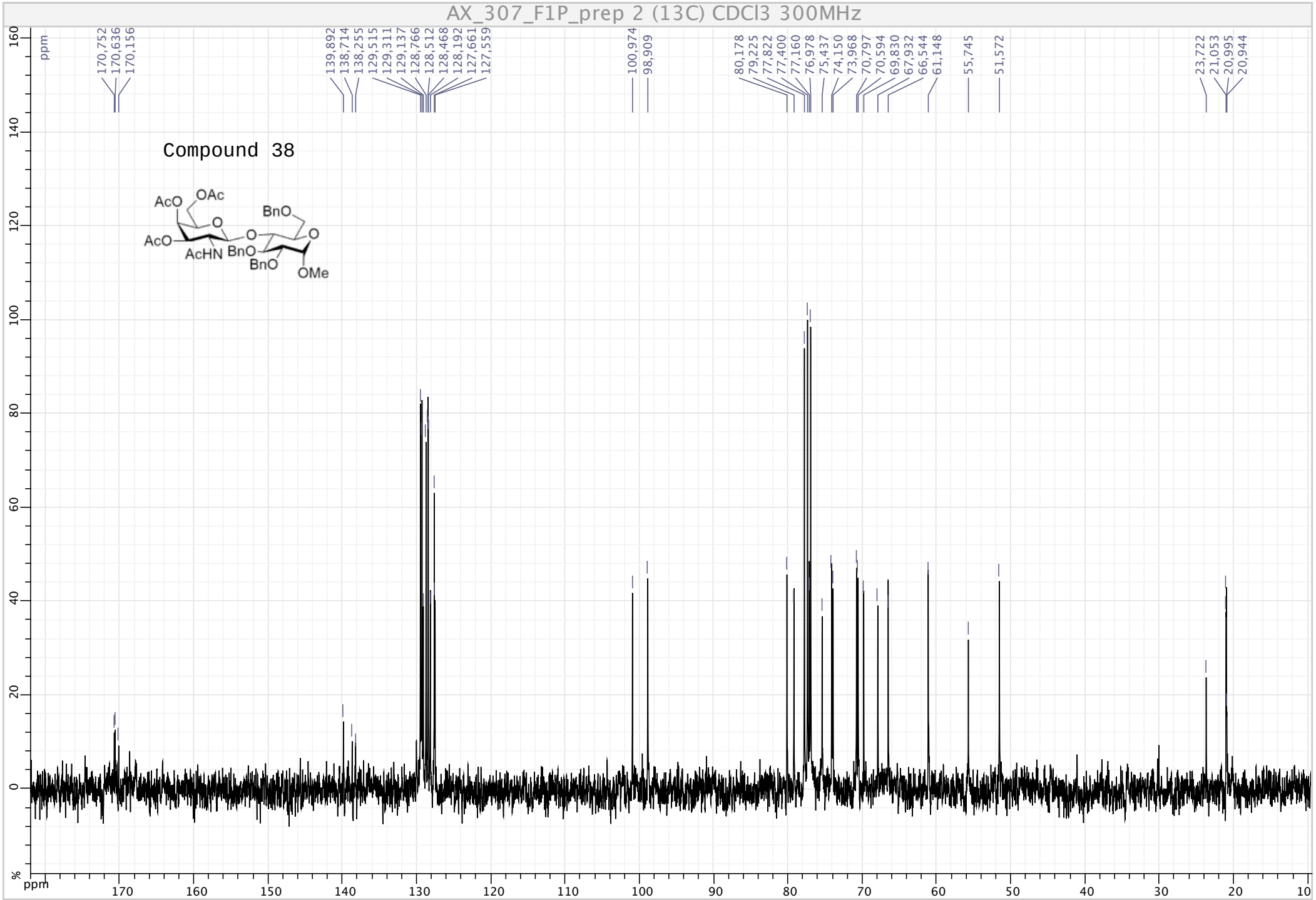
170,897
170,774
170,548
137,666
129,355
128,904
128,824
128,613
128,133
127,624
126,425
102,538
101,781
100,363
82,919
81,378
78,054
77,822
77,400
76,978
75,197
71,306
70,223
69,510
67,213
62,639
62,203
55,847
52,430
23,373
21,097
20,995

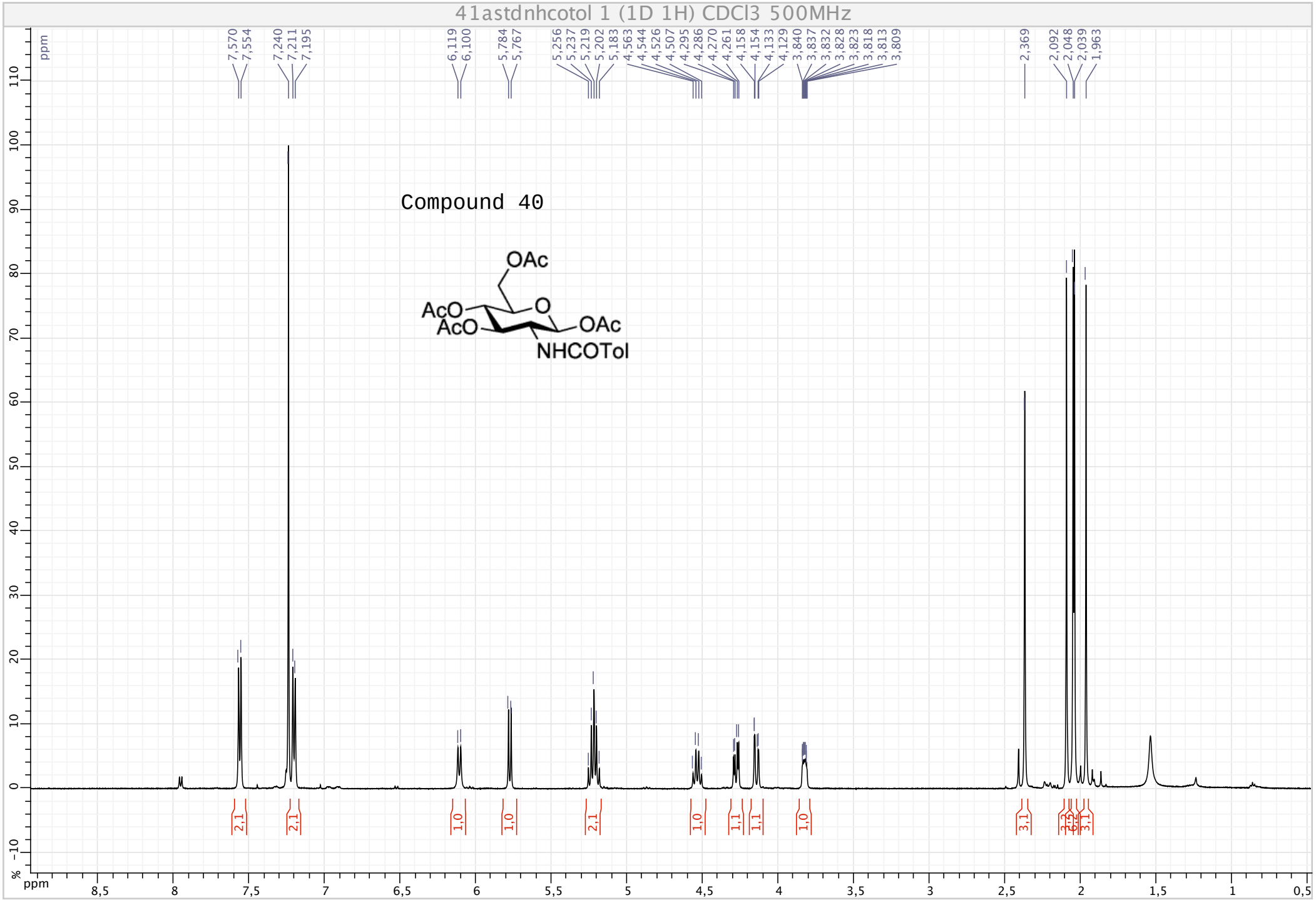
ppm
450
400
350
300
250
200
150
100
50
0
%
ppm
200
180
160
140
120
100
80
60
40
20
0

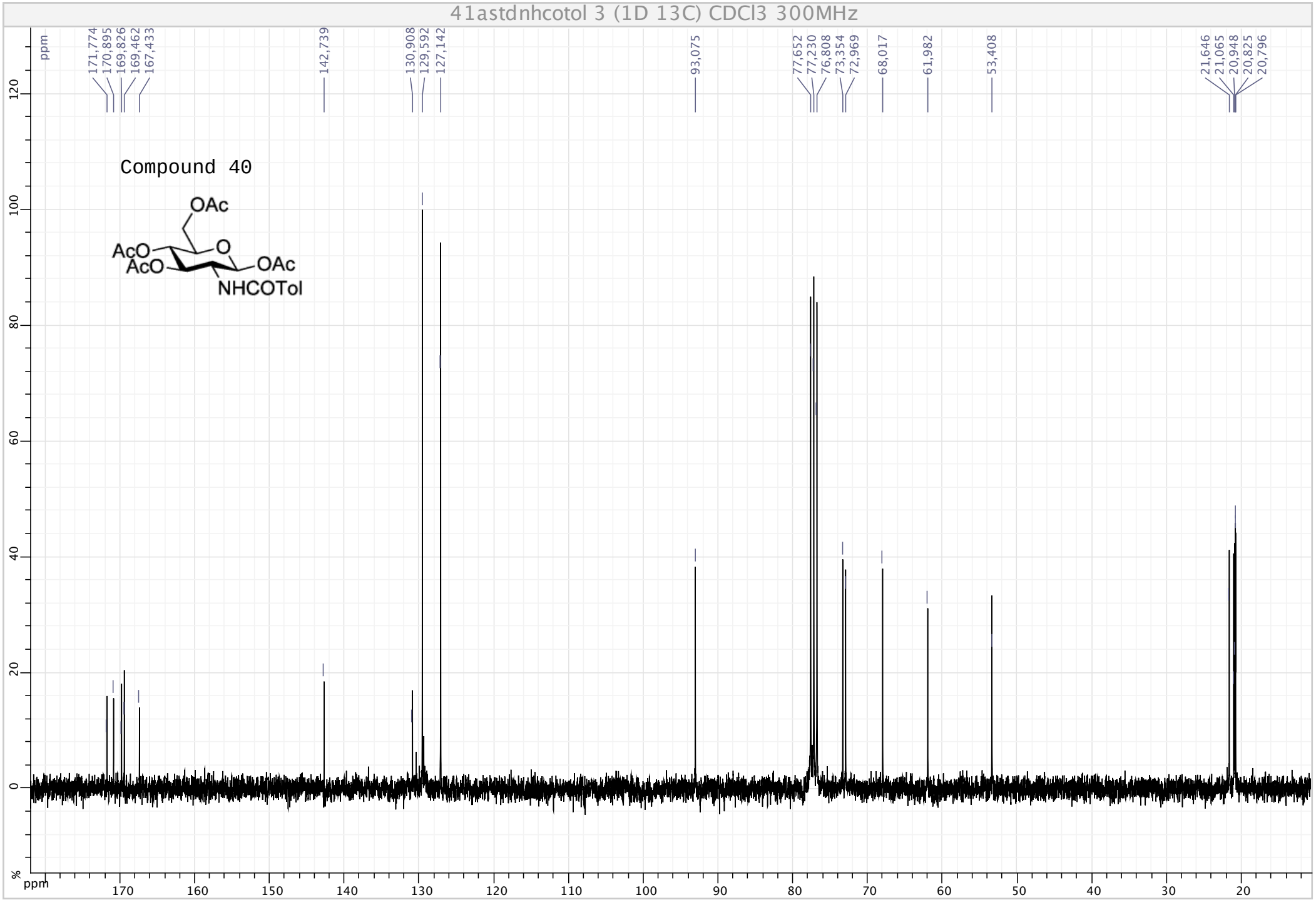

AX_268_F2 1 (1D 1H) CDCl3 300MHz
Compound 37
OTBDPS
AcO
BnO
AcO
BnO
O
O
AcO
O
OMe
NHAc
ppm
7,734 7,729 7,707 7,702 7,680 7,675 7,433 7,423 7,415 7,409 7,404 7,394 7,362 7,352 7,342 7,320 7,315 7,303 7,294 7,274 7,260 7,225 7,218 7,208 7,202 7,189 7,074 7,067 7,056 7,042 5,443 5,432 5,407 5,395 5,381 5,370 5,367 5,137 5,110 5,075 5,047 4,917 4,905 4,858 4,852 4,807 4,772 4,608 4,573 4,181 4,175 4,157 4,024 3,998 3,978 3,965 3,933 3,905 3,889 3,880 3,870 3,841 3,729 3,697 3,684 3,667 3,656 3,634 3,623 3,376 2,150 2,068 1,968 1,423 1,071
4,1
11,2
3,0
2,0
1,0
1,0
1,0
1,0
1,0
1,8
1,1
1,0
1,9
2,0
3,1
3,1
3,0
3,0
3,1
3,1
2,9
9,2
%
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5


AX_268_F2 2 (1D 13C) CDCl3 300MHz
ppm
170,934
170,832
170,701
170,541
139,542
138,350
136,183
136,001
133,871
133,580
130,031
129,988
128,904
128,722
128,279
128,068
127,952
127,908
127,115
102,225
99,302
82,861
81,319
78,403
77,822
77,400
76,978
75,524
75,480
71,619
71,168
69,947
67,205
63,061
62,319
55,200
52,720
27,197
23,285
21,140
21,104
21,024
19,679
Compound 37
OTBDPS
AcO
BnO
AcO
BnO
O
O
OMe
AcO
O
NHAc
%
ppm


AX_307_F1P_prep 1 (1D 1H) CDCl3 300MHz
Compound 38
AcO
OAc
AcO
AcHN
BnO
BnO
BnO
OMe
ppm
7,481 7,463 7,445 7,422 7,406 7,398 7,383 7,343 7,320 7,314 7,300 7,297 7,288 7,285 7,275 7,270 7,265 7,259 7,247 7,239 5,208 5,198 4,987 4,949 4,859 4,818 4,811 4,804 4,794 4,774 4,767 4,754 4,644 4,603 4,578 4,565 4,410 4,396 4,381 4,365 4,341 4,014 3,984 3,978 3,954 3,948 3,921 3,894 3,885 3,854 3,847 3,829 3,822 3,810 3,800 3,791 3,667 3,659 3,642 3,613 3,604 3,592 3,567 3,518 3,511 3,497 3,484 3,475 3,465 3,453 3,366 2,058 1,997 1,961 1,737
15,7
1,0
0,9
1,0
2,9
1,1
0,9
2,7
1,1
3,9
3,0
2,0
3,0
3,1
5,8
2,8
%
ppm


AX_307_F1P_prep 2 (13C) CDCl3 300MHz
ppm
170,752
170,636
170,156
139,892
138,714
138,255
129,515
129,311
129,137
128,766
128,512
128,468
128,192
127,661
127,559
100,974
98,909
80,178
79,225
77,822
77,400
77,160
76,978
75,437
74,150
73,968
70,797
70,594
69,830
67,932
66,544
61,148
55,745
51,572
23,722
21,053
20,995
20,944
Compound 38
AcO
OAc
AcO
AcHN
BnO
BnO
BnO
OMe
%
ppm


41astdnhcotol 1 (1D 1H) CDCl3 500MHz
Compound 40
OAc
AcO
O
AcO
OAc
NHCOTol
7,570
7,554
7,240
7,211
7,195
6,119
6,100
5,784
5,767
5,256
5,237
5,219
5,202
5,183
4,563
4,544
4,526
4,507
4,295
4,286
4,270
4,261
4,158
4,154
4,133
4,129
3,840
3,837
3,832
3,828
3,823
3,818
3,813
3,809
2,369
2,092
2,048
2,039
1,963
2,1
2,1
1,0
1,0
2,1
1,0
1,1
1,1
1,0
3,1
3,1
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
%
110
100
90
80
70
60
50
40
30
20
10
0
-10


41astdnhcotol 3 (1D 13C) CDCl3 300MHz
ppm
171,774
170,895
169,826
169,462
167,433
142,739
130,908
129,592
127,142
93,075
77,652
77,230
76,808
73,354
72,969
68,017
61,982
53,408
21,646
21,065
20,948
20,825
20,796
Compound 40
OAc
AcO
AcO
O
OAc
NHCOTol
%
120
100
80
60
40
20
0
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20