Programmed chemo-enzymatic synthesis of the oligosaccharide component of a synthetic carbohydrate-based antibacterial vaccine candidate

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Figure S1: HPLC analysis with UV detection ($\lambda = 220$ nm) of CD' glucosylation reactions catalyzed by GH13 glucansucrases (panel A) and GH70 glucansucrases (panel B). Panel C: CD' conversion degree in reactions catalyzed by GH70 glucansucrases (reaction conditions: 30 °C, 146 mM Sucrose, 146 mM CD', 24 h, 1U/mL of enzyme). DSR-S: *Leuconostoc mesenteroides* NRRL B-512F dextransucrase ; ASR : *L. mesenteroides* NRRL B-1355 alternansucrase ; DSR-E: *L. mesenteroides* NRRL B-1299 dextransucrase; GBD-CD2: N(123)-glucan-binding domain-catalytic domain 2 (Δ N(123)-GBD-CD2) is a truncated form of the bifunctional glucansucrase DSR-E from *L. mesenteroides* NRRL B-1299



Figure S2: HPLC-MS analysis ($\lambda = 220$ nm) of the CD' glucosylation reaction catalyzed by GBD-CD2.



Figure S3: Conversion rate of CD' (2) into ECD' (3) using GBD-CD2 at different [Sucrose]/[CD'] ratios and initial total dry mass.



Scheme S1 Preparation of disaccharide acceptor **2**. *Reagents and conditions:* a) TMSOTf, DCM, -15°C, 93%; b) MeONa, MeOH, 86%; c) TFA 50% aq., DCM, 95%

Experimental data

Enzymatic glucosylation

• General methods

Enzymes. Glucansucrases from families 13 and 70 were tested in acceptor reactions with sucrose as donor and CD' (2) as acceptor. The selected enzymes from the Glycoside-Hydrolase (GH) family 13 include the amylosucrases of *Neisseria polysaccharea* $(NpAS)^1$ and *Deinococcus geothermalis* $(DgAS)^2$ and the sucrose hydrolase from *Xanthomonas campestris* pv. *campestris* (XcSH).³ In the GH family 70, the native dextransucrase from *L. mesenteroides* NRRL B-512F (DSR-S),⁴ one of its truncated recombinant form (DSR-S vardel Δ 4N),⁵ the recombinant form of the alternansucrase from *L. mesenteroides* NRRL B-1355 (ASR),⁶ the native dextransucrase from *L. mesenteroides* NRRL B-1299 (DSR-E), which possesses two catalytic domains (CD1 and CD2 showing α -1,6 linkage and α -1,2 specificity, respectively⁷ and the α -1,2-branching sucrase, a transglucosylase engineered from DSR-E (GBD-CD2)⁸ that catalyzes exclusively the α -1,2 transfer of the glucosyl moiety from sucrose onto α -1,6 dextran chains were assayed.

Acceptor reaction assay. Acceptor reactions were performed in 1 mL of mixture containing equimolar amounts of sucrose and CD' (146 mM) in Tris-HCl 50 mM pH 7.5 for *Np*AS and *Xc*SH assays, Tris-HCl 50 mM pH 8 for *Dg*AS, sodium acetate buffer (AcONa) (20 mM, pH 5.4) for ASR assays, in AcONa (50 mM, [CaCl₂] = 0.5 g/L, pH 5.2) for DSR-S assays, in AcONa (20 mM, [CaCl₂] = 0.5 g/L, pH 5.4) for DSR-E and GBD-CD2 assays using 1 U/mL of enzyme at 30 °C for 24 h. One unit is defined as the amount of enzyme that catalyzes the release of 1 µmol of fructose/min at 30 °C from 146 mM sucrose (for *Np*AS, *Dg*AS and *Xc*SH) or 292 mM sucrose for DSR-S, GBD-CD2, DSR-E and ASR. All reactions were stopped by heating at 95 °C for 5 min. The final mixture was centrifuged at 18000 g for 10 min, filtered on a 0.22 µm membrane and diluted by 10 fold before HPLC analysis. To optimize the glucosylation reaction catalyzed by GBD-CD2, different initial molar sucrose/CD' ratios varying from 1 to 15 and initial sugar dry mass values (DM) varying from 75 to 425 g/L were assayed (Figure S2).

HPLC analysis of the enzymatic reactions. The HPLC analysis device consisted of a Dionex P680 series pump, a shodex RI 101 series refractometer, a Dionex UVD 340 UV/Vis detector, and an autosampler HTC-PAL. An Aminex HPX-87K column ($300 \times 7.8 \text{ mm}$) was employed at 65 °C eluting with CH₃CN/ultra-pure water (10:90, v/v). Glucose and fructose production and sucrose depletion were followed by RI detection. The conversion of CD' (**2**) and the formation of ECD' (**3**) were determined from their UV responses measured at $\lambda = 220 \text{ nm}$. Sensitivity was identical in the 205-220 nm wavelength range.

Semi-preparative HPLC. ECD' (3) was isolated by semi-preparative octadecyl reverse-phase chromatography column ($250 \times 10 \text{ mm}$, 4 µm) with MeOH:ultrapure water (30:70, v/v) at a constant rate of 2 mL/min. Detection was carried out with UV. The purity of the isolated compound was checked by analytical RP-HPLC.

LC-MS analyses. ESI-MS used a $MSQ^{\text{(B)}}$ Plus Mass Spectrometer (Dionex - Thermoscientific) equipped with a source at 450 °C. Separation was achieved with a quadrupole and detection was in the positive mode.

NMR analysis. Heteronuclear multiple bond correlation spectroscopy (HMBC) experiments were recorded on a Bruker Avance 400 spectrometer (proton frequency of 400.13 MHz and ¹³C frequency of 100.62 MHz) using the Bruker standard pulses program. The delay time for evolution of long-range ¹³C-¹H couplings was set to 120 ms. Typical used parameters were 1200 Hz spectral width for ¹H and 22,130 Hz for ¹³C, 16 scans and 196 experiments were accumulated. Samples were analyzed at 300.3 K in 5 mm o.d. tubes. Chemical shifts are given using an external reference (d6-trimethylsilylpropionic acid, sodium salt).

• Synthesis and characterization of ECD' (3)

Selecting a glucansucrase for CD' glucosylation: Acceptor reactions were first carried out with an equimolar ratio of sucrose and CD' (146 mM). Among the substrates, only CD' absorbs in UV. After 24 h, the UV-HPLC profiles of the reaction mixtures obtained with GH family 13 enzymes (*NpAS*, *DgAS* and *XcSH*) showed only one single peak corresponding to CD', indicating that none of these enzymes could glucosylate CD'(Figure S1-A). In contrast, an additional peak was observed on the profiles issued from the reactions catalyzed by the GH 70 family enzymes (Figure S1-B). LC-MS analysis of CD' glucosylation product synthesized by ASR, DSR-E and GBD-CD2 revealed a molecular weight of either 695.8 or 709.3 Da, corresponding to the ECD' sodium and potassium adducts, respectively (Figure 3). Identical MS and NMR spectra were observed for the glucosylation product isolated from the three reactions indicating that the same compound was produced irrespective of the enzyme used.

Optimization of ECD' (3) *production with GBD-CD2:* The best conversion was obtained with GBD-CD2 (Figure S1-C), which was selected to further optimize ECD' production by acting on temperature (20, 25 and 30 °C), reaction time (24 h and 48 h), total dry mass values from 75 to 425 g/L), and [Suc]/[CD'] molar ratios (from 1 to 15). Preliminary experiments served to identify 30 °C as the best performing temperature and showed the absence of evolution post 24 h (data not shown). Adopting these conditions, we showed that CD' conversion increased with the initial sucrose/CD' ratio regardless of total dry mass values (Figure S2). Furthermore, for a given [Suc]/[CD'] ratio, the increase of total dry mass value up to 350 g/L always favoured CD' conversion. Overall, the highest CD' conversion (94%) was obtained at initial [Suc]/[CD'] ratio of 12 and 350 g/L total dry mass. Preparative RP-HPLC of the crude material provided pure glucosylated CD' (ECD', **3**) and unreacted CD' (**2**).

Gram synthesis and structural characterization of ECD'(3)

Allyl α-D-glucopyranosyl- $(1\rightarrow 4)$ -α-L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-deoxy-2trichloroacetamido-β-D-glucopyranoside (ECD', 3). Sucrose (15.65 g, 45.7 mmol) was added to a solution of acceptor CD' (1.94 g, 3.8 mmol) in sodium acetate buffer (AcONa, 20 mM; [CaCl₂] = 0.5 g/L, pH 5.4, 50 mL) containing GBD-CD2 (1 U/mL). The mixture was gently stirred at 30 °C for 24 h. At this time, HPLC analysis indicated that conversion had reached 94%. Preparative HLPC of the crude mixture (H₂O/MeOH, 100:0 \rightarrow 70:30) furnished a mixture of disaccharide CD' and glucosylation product. The mixture was purified by column chromatography (DCM/MeOH 100:0 \rightarrow 70:30) to give first the unreacted acceptor CD' (140 mg, 0.27 mmol), then the enzymatic glucosylation product (2.22 g, 3.30 mmol, 87%, corrected yield 94%) both as white amorphous solids. The product of enzymatic glucosylation, identified as being the ECD' trisaccharide, was isolated as a white amorphous solid. Compound **3** had $R_f = 0.51$ (DCM/MeOH 70:30). $[\alpha]^{24}{}_D = +8.7^{\circ}$ (*c* 1.0, H₂O). ¹H NMR $(D_2O) \delta 5.98-5.88$ (m, 1H, CH=CH₂), 5.37-5.31 (m, $J_{trans} = 17.3$ Hz, 1H, CH=CH₂), 5.29-5.26 $(m, J_{cis} = 10.4 \text{ Hz}, 1\text{H}, \text{CH}=\text{CH}_2), 5.05 \text{ (d}, J_{1,2} = 3.9 \text{ Hz}, 1\text{H}, \text{H}-1_{\text{E}}), 4.91 \text{ (br s, 1H, H}-1_{\text{C}}), 4.78$ (overlapped with D₂O, 1H, H-1_D), 4.40-4.35 (m, 1H, -OCH_{2All}), 4.24-4.18 (m, 1H, -OCH_{2All}), 4.13 (dq, $J_{4.5} = 9.6$ Hz, 1H, H-5_C), 4.03-3.95 (m, 2H, H-6a_D, H-5_E), 3.90-3.77 (m, 7H, H-2_D, H-6b_D, H-3_D, H-6a_E, H-6b_E, H-2_C, H-3_C), 3.71 (pt, J = 9.3 Hz, 1H, H-3_E), 3.61-3.56 (m, 2H, H-2_E, H-4_D), 3.54-3.45 (m, 3H, H-4_E, H-4_C, H-5_D), 1.33 (d, $J_{5,6} = 6.3$ Hz, 3H, H-6_C). ¹³C NMR $(D_2O) \delta 167.4 (C_{NTCA}), 135.6 (CH=CH_2), 121.3 (CH=CH_2), 103.7 (C-1_C, {}^1J_{CH} = 170.3 Hz),$ 102.3 (C-1_E, ${}^{1}J_{CH} = 170.6$ Hz), 101.6 (C-1_D, ${}^{1}J_{CH} = 163.5$ Hz), 94.2 (CCl₃), 83.7 (2C, C-4_C, C-3_D), 78.7 (C-5_D), 75.3 (C-3_E), 74.4 (C-5_E), 74.1 (C-2_E), 73.5 (C-2_C), 73.4 (OCH_{2All}), 71.9 (C-4_E), 71.6 (C-3_C), 71.3 (C-4_D), 70.7 (C-5_C), 63.3 (C-6_D), 62.7 (C-6_E), 59.9 (C-2_D), 19.3 (C-6_C). HRMS (ESI⁺) m/z calcd for C₂₃H₃₆Cl₃NO₁₅Na [M+Na]⁺: 694.1048. Found: 694.1044.

- Chemical synthesis

Abbreviations. Ac: acetyl; anhydr.: Anhydrous; All: Allyl; Ar: Argon; CSA: Camphorsulfonic 1,8-Diazabicyclo[5.4.0]undec-7-ene; DCE: 1,2-Dichloroethane; acid; DBU: DCM: Dichloromethane; DMF: N,N-Dimethylformamide; DMP: 2,2-Dimethoxypropane; HR-ESI-TOF-MS: High Resolution Electrospray Ionisation/Time-Of-Flight Mass Spectra; HR-MALDI-TOF-MS: High Resolution Matrix-Assisted Laser Desorption-Ionisation/Time-Of-Flight Spectra; iPr: isopropylidene; 1,5-Cyclooctadiene-Mass [Ir]: bis(methyldiphenylphosphine)-iridium hexafluorophosphate; MS: Molecular sieves; NMR: Nuclear Magnetic Resonance; NTCA: trichloroacetamide; RP-HPLC: Reverse Phase High Performance Liquid Chromatography; pTSA: p-Toluenesulfonic acid; TFA: Trifluoroacetic acid; THF: Tetrahydrofuran; TLC: Thin-Layer Chromatography; TMSOTf: Trimethylsilyl trifluoromethanesulfonate.

General. Reagents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar or TCI Europe and were used as received. Solvents were obtained from VWR International and Carlo Erba and were used as received. Air and water sensitive reactions were performed in dried glassware under Ar. Anhydr. toluene, Et₂O, DCE, THF, DMF, CH₃CN, MeOH and pyridine were delivered on MS and were used as received. Sodium hydride (60% dispersion in mineral oil) was washed with anhydr. pentane under a stream of Ar before use. 4Å MS were activated before use by heating at 250°C under vacuum. Analytical TLC was performed with silica gel 60 F254, 0.25 mm pre-coated TLC plates (Merck). Compounds were visualized using UV254 and/or orcinol (1 mg·mL⁻¹) in 10% aq. H₂SO₄ with charring. Flash column chromatography was carried out using silica gel (Merck, particle size 40-63 µm or 15-40 µm). NMR spectra were recorded at 303 K on a Bruker Avance spectrometer at 400 MHz (¹H) and 100 MHz (¹³C) equipped with a BBO probe. Elucidations of chemical structures were based on ¹H, COSY, DEPT-135, HSQC, ¹³C, ¹³C gated decoupling and HMBC experiments. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), pt (pseudo triplet), dd (doublet of

doublet), dq (doublet of quadruplet), br s (broad singlet), and coupling constants are reported in hertz (Hz). Spectra were recorded in CDCl₃, CD₃OD and D₂O. Chemical shifts are reported in ppm (δ) relative to residual solvent peak, CHCl₃ in the case of CDCl₃, MeOH in the case of CD₃OD, HOD and 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) in the case of D₂O, at 7.26/77.16, 3.31/49.0, and 4.79/0.0 ppm for the ¹H and ¹³C spectra, respectively. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field is denoted H-6a, and the one at higher field is denoted H-6b. Sugar residues are serially lettered according to the lettering of the repeating unit of the S. flexneri 2a O-specific polysaccharide and identified by a subscript in the listing of signal assignments. HR-ESI-TOF-MS were recorded on a WATERS QTOF Micromass instrument in the positive-ion electrospray ionisation (ESI⁺) mode. Solutions were prepared using 1:1 CH₃CN/H₂O containing 0.1% formic acid or MeOH/water containing 10 mM ammonium acetate in the case of sensitive compounds. HR-MALDI-TOF-MS were recorded on a 4800 MALDI TOF/TOF AB SCIEX instrument in the positive-ion reflector mode using 2,5-dihydroxybenzoic acid (DHB) in CH₃CN/TFA (0.1%) as the matrix. Optical rotations were obtained using the sodium D line at ambient temperature on a Bellingham + Stanley Ltd. ADP220 polarimeter. Analytical RP-HPLC ($\lambda = 215$ nm) of the final product was carried out using an Aeris Peptide 3.6 µm C_{18} 100 Å 2.1 × 100 mm analytical column, eluting with a 0-20% linear gradient of CH₃CN in 0.08% aq. TFA over 20 min at a flow rate of 0.3 mL·min⁻¹.

Allyl (2,3,4-tri-O-acetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-2-deoxy-4,6-O-isopropylidene-2trichloroacetamido- β -D-glucopyranoside (S3). To a solution of the known acceptor⁹ S1 (489 mg, 1.21 mmol) and the known donor¹⁰ S2 (665 mg, 1.53 mmol, 1.3 equiv.) in anhydr. DCM (12 mL) containing 4Å MS (530 mg), under Ar atmosphere and cooled to -15°C, was added TMSOTf (13 µL, 72 µmol, 0.06 equiv.). The reaction mixture was stirred 30 min then Et₃N (50 µL) was added and the mixture was filtered over a pad of Celite and concentrated to dryness. Chromatography of the residue (cyclohexane-EtOAc, $90:10 \rightarrow 80:20$) afforded fully protected disaccharide S3 (760 mg, 1.12 mmol, 93%) as a white amorphous solid. $R_f = 0.27$ (cyclohexane-EtOAc 70:30). $[\alpha]_{D}^{24} = -30.9^{\circ}$ (c 1.0; CHCl₃). ¹H NMR (CDCl₃) δ 7.00 (d, $J_{\rm NH,2} = 7.2$ Hz, 1H, NH), 5.88-5.78 (m, 1H, CH=CH₂), 5.28-5.16 (m, 4H, CH=CH₂, H-2_C, H- $3_{\rm C}$), 5.02 (pt, J = 9.7 Hz, 1H, H- $4_{\rm C}$), 5.01 (d, $J_{1,2} = 8.3$ Hz, 1H, H- $1_{\rm D}$), 4.79 (d, $J_{1,2} = 1.5$ Hz, 1H, H-1_C), 4.39 (pt, J = 9.4 Hz, 1H, H-3_D), 4.33-4.28 (m, 1H, -OCH_{2All}), 4.18 (dq, 1H, H-5_C), 4.08-4.03 (m, 1H, -OCH_{2All}), 3.96 (dd, $J_{6a,6b} = 10.8$ Hz, $J_{5,6a} = 5.4$ Hz, 1H, H-6a_D), 3.80 (pt, $J_{5,6b} = 10.8$ Hz, 1H, H-6b_D), 3.64 (pt, J = 9.4 Hz, 1H, H-4_D), 3.40-3.34 (m, 2H, H-2_D, H-5_D), 2.08 (s, 3H, H_{Ac}), 2.03 (s, 3H, H_{Ac}), 1.96 (s, 3H, H_{Ac}), 1.52 (s, 3H, H_{iPr}), 1.41 (s, 3H, H_{iPr}), 1.17 (d, $J_{5.6} = 6.3$ Hz, 3H, H-6_C). ¹³C NMR (CDCl₃) δ 170.3, 170.0, 169.9 (3C, C_{Ac}), 162.2 (C_{NTCA}), 133.3 (CH=CH₂), 118.3 (CH=CH₂), 99.6 (C_{iPr}), 98.3 (C-1_C, ¹J_{CH} = 173.1 Hz), 98.2 $(C-1_D, {}^{1}J_{CH} = 165.2 \text{ Hz}), 92.3 (CCl_3), 75.2 (C-3_D), 73.1 (C-4_D), 71.0 (C-4_C), 70.8 (-OCH_{2All}),$ 69.6 (C-3_C), 69.4 (C-2_C), 67.2 (C-5_D), 66.6 (C-5_C), 62.2 (C-6_D), 60.0 (C-2_D), 29.2 (C_{iPr}), 20.9, 20.8, 20.7 (3C, C_{Ac}), 19.3 (C_{iPr}), 17.4 (C-6_C). HRMS (ESI⁺) m/z calcd for C₂₆H₃₆Cl₃NO₁₃Na [M+Na]⁺: 698.1150. Found: 698.1158.

Allyl $(\alpha$ -L-rhamnopyranosyl)- $(1\rightarrow 3)$ -2-deoxy-4,6-O-isopropylidene-2-

trichloroacetamido-β-D-glucopyranoside (S4). To a solution of protected disaccharide S3 (128 mg, 189 µmol) in anhydr. MeOH (3 mL) and under Ar atmosphere, was added MeONa (0.5 M, 115 µL, 58 µmol, 0.3 equiv.). The reaction mixture was stirred for 2 h, then guenched by addition of Dowex 50Wx8-200 and filtered over a pad of Celite. The solvent was removed under vacuum and the residue was purified by column chromatography (EtOAc) to give triol **S4** (90 mg, 163 µmol, 86%) as a white amorphous solid. $R_f = 0.45$ (EtOAc). $[\alpha]_{D}^{24} = -64.5^{\circ}$ (c 1.0; CHCl₃). ¹H NMR (MeOD) δ 5.86-5.77 (m, 1H, CH=CH₂), 5.25-5.19 (m, J_{trans} = 17.3) Hz, 1H, CH=CH₂), 5.11-5.07 (m, J_{cis} = 10.5 Hz, 1H, CH=CH₂), 4.79 (d, J_{1,2} = 1.5 Hz, 1H, H-1_C), 4.64-4.58 (m, 1H, H-1_D), 4.26-4.21 (m, 1H, -OCH_{2All}), 4.04-3.99 (m, 1H, -OCH_{2All}), 3.93 $(dq, J_{4.5} = 9.6 \text{ Hz}, 1\text{H}, \text{H}-5_{\text{C}}), 3.88-3.82 \text{ (m, 3H, H}-2_{\text{D}}, \text{H}-3_{\text{D}}, \text{H}-6a_{\text{D}}), 3.78 \text{ (pt, } J = 10.3 \text{ Hz},$ 1H, H-6b_D), 3.72 (dd, $J_{2,3} = 3.3$ Hz, 1H, H-2_C), 3.64-3.60 (m, $J_{4,5} = 9.4$ Hz, 1H, H-4_D), 3.58-3.54 (m, 1H, H-3_C), 3.29-3.24 (m, 2H, H-4_C, H-5_D), 1.49 (s, 3H, H_{iPr}), 1.35 (s, 3H, H_{iPr}), 1.17 (d, $J_{5.6} = 6.2$ Hz, 3H, H-6_C). ¹³C NMR (MeOD) δ 164.3 (C_{NTCA}), 135.0 (CH=CH₂), 117.5 (CH=CH₂), 102.5 (C-1_C), 101.7 (C-1_D), 100.8 (C_{iPr}), 94.0 (CCl₃), 78.2 (C-3_D), 74.2 (C-4_D), 73.8 (C-4_C), 72.3 (2C, C-2_C, C-3_C), 71.3 (-OCH_{2All}), 69.7 (C-5_C), 68.6 (C-5_D), 63.1 (C-6_D), 59.4 (C-2_D), 29.5 (C_{iPr}), 19.3 (C_{iPr}), 18.1 (C-6_C). HRMS (ESI⁺) m/z calcd for $C_{20}H_{30}Cl_3NO_{10}Na [M+Na]^+: 572.0833$. Found: 572.0805.

Allyl (α -L-rhamnopyranosyl)-(1 \rightarrow 3)-2-deoxy-2-trichloroacetamido- β -D-glucopyranoside (2). To a solution of triol S4 (239 mg, 0.43 mmol) in DCM (10 mL) was added TFA (50% aq., 5 mL). The biphasic mixture was vigorously stirred for 30 min then repeatedly coevaporated with toluene. The residue was purified by column chromatography (EtOAc/MeOH, 98:2) to give pentaol 2 (208 mg, 0.41 mmol, 95%) as a white amorphous solid. $R_f = 0.60$ (DCM/MeOH 84:16). $[\alpha]_{D}^{23} = -55.2^{\circ}$ (c 1.0; H₂O). ¹H NMR (D₂O) δ 6.03-5.94 (m, 1H, CH=CH₂), 5.42-5.36 (m, $J_{\text{trans}} = 17.3$ Hz, 1H, CH=CH₂), 5.35-5.31 (m, $J_{\text{cis}} =$ 10.4 Hz, 1H, CH=CH₂), 4.96 (d, $J_{1,2} = 1.6$ Hz, 1H, H-1_C), 4.84 (d, $J_{1,2} = 8.3$ Hz, 1H, H-1_D), 4.46-4.40 (m, 1H, -OCH_{2All}), 4.29-4.24 (m, 1H, -OCH_{2All}), 4.07 (dq, $J_{4,5} = 9.8$ Hz, 1H, H-5_C), 4.02 (dd, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 2.0$ Hz, 1H, H-6a_D), 3.96-3.83 (m, 4H, H-2_D, H-2_C, H-6b_D, H-3_D), 3.80 (dd, $J_{3,4} = 9.9$ Hz, $J_{2,3} = 3.4$ Hz, 1H, H-3_C), 3.66-3.54 (m, 2H, H-4_D, H-5_D), 3.51 (pt, 1H, H-4_C), 1.30 (d, $J_{5.6} = 6.3$ Hz, 3H, H-6_C). ¹³C NMR (D₂O) δ 167.4 (C_{NTCA}), 135.7 (CH=CH₂), 121.4 (CH=CH₂), 103.9 (C-1_C), 101.7 (C-1_D), 94.2 (CCl₃), 83.4 (C-3_D), 78.7 (C-5_D), 74.5 (C-4_C), 73.4 (-OCH_{2All}), 73.3 (C-2_C), 73.0 (C-3_C), 71.6 (C-5_C), 71.3 (C-4_D), 63.4 (C- 6_D), 60.0 (C-2_D), 19.1 (C-6_C). HRMS (ESI⁺) m/z calcd for $C_{17}H_{26}Cl_3NO_{10}Na$ [M+Na]⁺: 532.0520. Found: 532.0511.

$\label{eq:allyl} Allyl (2,3,4,6-tetra-O-benzyl-\alpha-D-glucopyranosyl)-(1 \rightarrow 4)-(2-O-acetyl-\alpha-L-rhamnopyranosyl)-(-(1 \rightarrow 3)-4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-\beta-D-$

glucopyranoside (5). To a solution of diol 4^* (826 mg, 0.68 mmol) in anhydr. CH₃CN (680 μ L) and under Ar, were added trimethyl orthoacetate (260 μ L, 2.04 mmol, 3.0 equiv.) and *p*-TSA (5 mg, 0.03 mmol, 0.04 equiv.). The reaction mixture was stirred for 35 min then 80% aq. AcOH (0.7 mL) was added. The reaction mixture was stirred for another 25 min then it

^{*} To be described elsewhere

was diluted with DCM (60 mL) and rapidly washed with cold water $(1 \times 10 \text{ mL})$ and brine (1 \times 10 mL). The aqueous phase was extracted with DCM (1 \times 10 mL) and the combined organics were dried (Na₂SO₄), filtered and co-evaporated with toluene to give crude alcohol 5 (802 mg, 0.64 mmol, 94%) as a white amorphous solid. $R_f = 0.20$ (cyclohexane/EtOAc 70:30). $\left[\alpha\right]^{24}_{D} = +7.8^{\circ}$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.40-7.23 (m, 29H, Ph, NH), 7.19-7.16 (m, 2H, Ph), 5.97-5.88 (m, 1H, CH=CH₂), 5.35-5.29 (m, $J_{\text{trans}} = 17.2$ Hz, 1H, CH=CH₂), 5.26-5.20 (m, $J_{cis} = 10.3$ Hz, 1H, CH=CH₂), 5.24 (bs, 1H, H-2_C), 5.11 (bs, 1H, H-1_C), 5.00 (d, $J_{1,2} = 3.6$ Hz, 1H, H-1_E), 4.93 (d, J = 11.0 Hz, 1H, H_{Bn}), 4.86 (d, J = 10.9 Hz, 1H, H_{Bn}), 4.84-4.48 (m, 11H, 10H_{Bn}, H-1_D), 4.41-4.36 (m, 1H, -OCH_{2All}), 4.22 (pt, J = 7.0 Hz, 1H, H-3_D), 4.13-4.05 (m, 3H, H-5_E, OH, -OCH_{2All}), 4.00-3.75 (m, 8H, H-4_D, H-5_D, H-6a_D, H-6b_D, H-2_D, $H-3_E$, $H-3_C$, $H-5_C$), 3.70-3.56 (m, 4H, $H-4_E$, $H-2_E$, $H-6a_E$, $H-6b_E$), 3.40 (pt, J = 9.0 Hz, 1H, H- $4_{\rm C}$), 2.15 (s, 3H, H_{Ac}), 1.36 (d, $J_{5.6} = 6.2$ Hz, H-6_C). ¹³C NMR (CDCl₃) δ 170.3 (C_{Ac}), 161.8 (C_{NTCA}), 138.7, 138.1, 138.0, 137.9, 137.6, 137.4 (6C_{quat}, Ph), 133.6 (CH=CH₂), 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7 (30C, Ph), 117.7 (CH=CH₂), 99.2 (C-1_E), 98.1 (C-1_D), 97.0 (C-1_C), 92.4 (CCl₃), 85.4 (C-4_C), 81.7 (C-3_E), 79.9 (C-2_E), 77.8 (C-4_E), 76.5 (C-4_D), 75.6 (C_{Bn}), 75.2 (C-3_D), 75.1 (C_{Bn}), 74.3 (C-5_D), 74.0, 73.6 (4C, C_{Bn}), 71.9 (C-2_C), 71.4 (C- $5_{\rm E}$), 70.0 (OCH_{2All}), 69.2 (C-6_E), 68.6 (C-6_D), 68.3 (C-3_C), 67.6 (C-5_C), 55.4 (C-2_D), 21.1 (C_{Ac}), 17.8 (C-6_C). HRMS (ESI⁺) m/z calcd for C₆₇H₇₄Cl₃NO₁₆Na [M+Na]⁺: 1276.3971. Found: 1276.4047.

 $(3,4-di-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl-2-O-levulinoyl-a-benzyl-2-O-levulinoyl-2-O$ Allyl benzyl- α -D-glucopyranosyl)- $(1\rightarrow 4)$]-(2-O-acetyl- α -L-rhamnopyranosyl)- $(1\rightarrow 3)$ -4,6-di-Obenzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (7). To a solution of the crude acceptor 5 (505 mg, 402 μ mol, 1.0 equiv.) and of the known rhamnosyl donor¹¹ 6 (280 mg. 477 µmol, 1.2 equiv.) in anhydr. Et₂O (8 mL) containing 4Å MS (500 mg), under Ar and cooled to -15 °C, was added TMSOTf (4 µL, 22 µmol, 0.05 equiv.). The reaction mixture was stirred for 40 min. Et₃N (10 μ L) was added and the mixture was filtered over a pad of Celite and concentrated to dryness. The residue was purified by column chromatography (Toluene/EtOAc, 90:10 \rightarrow 80:20) to give tetrasaccharide 7 (580 mg, 345 µmol, 86%) as a white amorphous solid. $R_f = 0.27$ (Toluene/EtOAc 86:14). $[\alpha]_{D}^{24} = +9.8^{\circ}$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.39-7.16 (m, 41H, Ph, NH), 5.95-5.85 (m, 1H, CH=CH₂), 5.68 (bs, 1H, H- $2_{\rm B}$), 5.31-5.26 (m, $J_{\rm trans} = 17.3$ Hz, 1H, CH=CH₂), 5.21-5.17 (m, $J_{\rm cis} = 10.3$ Hz, 1H, CH=CH₂), 5.14 (bs, 1H, H-2_C), 5.07 (d, $J_{1,2} = 2.4$ Hz, 1H, H-1_C), 4.97-4.40 (m, 19H, 16H_{Bn}, H-1_D, H-1_B, H-1_E), 4.38-4.32 (m, 1H, -OCH_{2All}), 4.26 (bt, 1H, H-3_D), 4.10-4.05 (m, 1H, -OCH_{2All}), 3.99-3.69 (m, 14H, H-3_C, H-3_E, H-5_E, H-5_D, H-5_C, H-4_E, H-5_B, H-3_B, H-6a_E, H-6b_E, H-6a_D, H-6b_D, H-2_D, H-4_D), 3.48-3.43 (m, 2H, H-2_E, H-4_C), 3.38 (pt, J = 9.4 Hz, 1H, H-4_B), 2.77-2.68 (m, 4H, 2×CH_{2Lev}), 2.18 (s, 3H, CH_{3Lev}), 2.10 (s, 3H, H_{Ac}), 1.24 (d, J_{5,6} = 6.3 Hz, 3H, H-6_B), 1.16 (d, $J_{5.6} = 6.2$ Hz, 3H, H-6_C). ¹³C NMR (partial, CDCl₃) δ 206.5 (C_{Lev}), 171.9 (C_{Lev}), 170.0 (CAc), 161.8 (CNTCA), 138.8, 138.6, 138.5, 138.4, 138.3, 138.0, 137.5 (8C_{quat}, Ph), 133.7 (CH=CH₂), 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (40C, Ph), 117.8 (CH=CH₂), 98.6 (C-1_E), 97.9 (C-1_D), 96.5 (C-1_C), 92.4 (CCl₃), 81.7 (C-3_E), 81.6 (C-2_E), 79.9 (C-4_B), 77.7 (C-4_E), 77.0 (C-3_B), 76.4 (C-4_D), 75.6 (2C, C_{Bn}), 75.2 (C-3_D), 75.0 (C_{Bn}), 74.3 (C-5_D), 73.9, 73.8, 73.5 (3C, C_{Bn}), 72.9 (C_{Bn}), 71.8 (C-5_E), 71.6 (C-

 $2_{\rm C}$), 70.1 (2C, C_{Bn}, OCH_{2All}), 69.2 (C-6_D), 68.8 (C-5_B), 68.6 (C-2_B), 68.3 (C-6_E), 68.0 (C-5_C), 56.3 (C-2_D), 38.1 (CH_{2Lev}), 30.0 (CH_{3Lev}), 28.3 (CH_{2Lev}), 21.2 (C_{Ac}), 18.5 (C-6_C), 18.1 (C-6_B). HRMS (ESI⁺) *m*/*z* calcd for C₉₂H₁₀₂Cl₃NO₂₂Na [M+Na]⁺: 1700.5857. Found: 1700.5919.

Allyl $(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-\alpha-D-benzyl-a-be$ glucopyranosyl)- $(1\rightarrow 4)$]-(2-O-acetyl- α -L-rhamnopyranosyl)- $(1\rightarrow 3)$ -4,6-di-O-benzyl-2deoxy-2-trichloroacetamido- β -D-glucopyranoside (8). To a solution of tetrasaccharide 7 (489 mg, 291 µmol) in anhydr. pyridine (3.6 mL), cooled to 0 °C and under Ar, were added AcOH (2.4 mL) and hydrazine hydrate (71 µL, 1.46 mmol, 5.0 equiv.), then the reaction mixture was allowed to warm to room temperature. After 70 min, cold water (15 mL) was added to the reaction mixture, which was then extracted with DCM (4 \times 20 mL). The combined organics were dried (Na₂SO₄), filtered, evaporated and co-evaporated twice with toluene. The residue was purified by column chromatography (Toluene/EtOAc, 95:5 \rightarrow 85:15) to give alcohol 8 (423 mg, 267 μ mol, 92%) as a white foam. R_f = 0.22 (Toluene/EtOAc 86:14). $[\alpha]_{D}^{24} = -6.1^{\circ}$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.39-7.13 (m, 41H, Ph, NH), 5.94-5.84 (m, 1H, CH=CH₂), 5.30-5.24 (m, J_{trans} = 17.2 Hz, 1H, CH=CH₂), 5.19-5.16 (m, $J_{cis} = 10.5$ Hz, 1H, CH=C H_2), 5.12 (bdd, $J_{2,3} = 3.2$ Hz, 1H, H-2_C), 5.07 (d, $J_{1,2} =$ 2.0 Hz, 1H, H-1_c), 5.00 (d, $J_{1,2} = 3.0$ Hz, 1H, H-1_E), 4.96 (d, $J_{1,2} = 1.7$ Hz, 1H, H-1_B), 4.89 (d, 12.1 Hz, 1H, H_{Bn}), 4.35-4.30 (m, 1H, -OCH_{2All}), 4.28-4.24 (m, 2H, H-3_D, H-2_B), 4.09-4.03 (m, 1H, -OCH_{2All}), 3.97 (bdd, 1H, H-3_C), 3.92-3.73 (m, 8H, H-4_D, H-6a_D, H-6b_D, H-5_D, H-5_C, H-2_D, H-3_E, H-5_E), 3.69-3.60 (m, 5H, H-4_E, H-6a_E, H-6b_E, H-5_B, H-3_B), 3.56 (pt, J = 9.1 Hz, 1H, H-4_C), 3.51-3.44 (m, 2H, H-4_B, H-2_E), 2.73 (bs, 1H, OH), 2.07 (s, 3H, H_{Ac}), 1.26 (d, $J_{5.6} =$ 6.2 Hz, 3H, H-6_B), 1.22 (d, $J_{5.6} = 6.2$ Hz, 3H, H-6_C). ¹³C NMR (CDCl₃) δ 169.9 (C_{Ac}), 161.6 (C_{NTCA}), 138.7, 138.6, 138.4, 138.2, 138.1, 137.9, 137.4 (8C_{quat}, Ph), 133.7 (CH=CH₂), 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6 (40C, Ph), 117.8 (CH=CH₂), 102.6 (C-1_B), 98.7 (C-1_E), 97.7 (C-1_D), 95.6 (C-1_C), 92.4 (CCl₃), 81.6 (C-3_E), 81.2 (C-2_E), 80.0 (C-4_B), 79.6 (C-4_C), 79.2 (C-3_B), 78.5 (C-3_C), 77.7 (C-4_E), 75.9 (C-4_D), 75.6, 75.1, 74.9 (3C, C_{Bn}), 74.0 (C-5_D), 73.8, 73.7, 73.5 (3C, C_{Bn}), 73.2 (2C, C-3_D, C_{Bn}), 72.5 (C-2_C), 71.6 (C_{Bn}), 71.5 (C-5_E), 70.0 (OCH_{2All}), 69.5 (C-6_D), 68.6 (C-6_E), 68.4 (C-5_B), 68.3 (C-5_C), 68.2 (C-2_B), 54.9 (C- $2_{\rm D}$), 21.0 (C_{Ac}), 18.6 (C-6_C), 18.1 (C-6_B). HRMS (ESI⁺) m/z calcd for C₈₇H₉₆Cl₃NO₂₀Na [M+Na]⁺: 1602.5490. Found: 1602.5555.

Allyl (3,4-di-*O*-benzyl-2-*O*-levulinoyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]-(2-*O*-acetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-4,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranoside (9). To a solution of the acceptor 8 (400 mg, 253 µmol, 1.0 equiv.) and the known rhamnosyl donor¹¹ 6 (191 mg, 325 µmol, 1.3 equiv.) in anhydr. Et₂O (5 mL) containing 4Å MS (680 mg), under Ar and cooled to -15 °C, was added TMSOTf (3 µL, 17 µmol, 0.07 equiv.). The reaction mixture was stirred for 1.5 h then allowed to warm to room temperature for 30 min, then Et₃N (10 µL) was added and the mixture was filtered over a pad of Celite and concentrated to dryness. The residue was purified by column chromatography (Toluene/EtOAc, 95:5 \rightarrow 85:15) to give pentasaccharide 9 (437 mg, 218 µmol, 86%) as a

white amorphous solid. $R_f = 0.50$ (Toluene/EtOAc 80:20). $[\alpha]^{24}_D = + 2.9^{\circ}$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.36-7.13 (m, 51H, Ph, NH), 5.94-5.84 (m, 1H, CH=CH₂), 5.56 (dd, $J_{2,3} = 3.0$ Hz, $J_{1,2} = 1.9$ Hz, 1H, H-2_A), 5.31-5.25 (m, $J_{trans} = 17.2$ Hz, 1H, CH=CH₂), 5.19-5.16 (m, $J_{cis} = 10.5$ Hz, 1H, CH=CH₂), 5.14 (bs, 1H, H-2_C), 5.08 (d, $J_{1,2} = 2.4$ Hz, H-1_C), 5.06 (bs, 1H, H-1_A), 4.94-4.78 (m, 8H, 5H_{Bn}, H-1_B, H-1_D, H-1_E), 4.75-4.47 (m, 14H, H_{Bn}), 4.40-4.30 (m, 4H, H-2_B, H-3_D, 1H_{Bn}, -OCH_{2All}), 4.10-4.04 (m, 1H, -OCH_{2All}), 3.97-3.37 (m, 20H, H-2_D, H-2_E, H-3_A, H-3_B, H-3_C, H-3_E, H-4_A, H-4_B, H-4_C, H-4_D, H-4_E, H-5_A, H-5_B, H-5_C, H-5_D, H-5_E, H-6a_D, H-6b_D, H-6a_E, H-6b_E), 2.68-2.47 (m, 4H, 2×CH_{2Lev}), 2.09, 2.08 (s, 6H, CH_{3Lev}, H_{Ac}), 1.30, 1.19, 1.15 (d, $J_{5,6} = 6.2$ Hz, 9H, H-6_A, H-6_B, H-6_C). ¹³C NMR (partial, CDCl₃) δ 206.1 (C_{Lev}), 171.8 (C_{Lev}), 170.1 (C_{Ac}), 161.8 (C_{NTCA}), 138.9, 138.8, 138.7, 138.6, 138.3, 138.2, 138.1, 137.5 (10C_{quat}, Ph), 133.7 (CH=CH₂), 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4 (50C, Ph), 117.9 (CH=CH₂), 99.4 (C-1_A), 97.9 (C-1_E), 96.2 (C-1_C), 92.4 (CCl₃), 56.6 (C-2_D), 38.1 (CH_{2Lev}), 29.8 (CH_{3Lev}), 28.2 (CH_{2Lev}), 21.2 (C_{Ac}), 18.7, 18.4, 18.1 (3C, C-6_A, C-6_B, C-6_C). HRMS (ESI⁺) *m*/*z* calcd for C₁₁₂H₁₂₄Cl₃NO₂₆Na [M+Na]⁺: 2026.7374. Found: 2026.7920.

$(3,4-Di-O-benzyl-2-O-levulinoyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 2)-(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-tetra-O-benzyl-\alpha-D-glucopyranosyl)-(1\rightarrow 4)]-(2-O-benzyl-\alpha-D-glucopyranosyl)-(1\rightarrow 4)]-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(1\rightarrow 4)]-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)-(2-O-benzyl-\alpha-D-glucopyranosyl)$

acetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-4,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido- α/β -1,5-Cyclooctadiene-bis(methyldiphenylphosphine)-iridium **D**-glucopyranose (10). hexafluorophosphate (3 mg, 3.5 µmol, 0.03 equiv.) was dissolved in anhydr. THF (2 mL) under Ar. Hydrogen was bubbled through the solution for 15 min, causing the color to change from red to yellow. The solution was degassed by complete evaporation of the solvent under vacuum. The activated iridium complex was dissolved under Ar in anhydr. THF (2 mL) then a solution pentasaccharide 9 (248 mg, 124 µmol) in anhydr. THF (3 mL) was added. The reaction mixture was stirred for 2.5 h at room temperature then a solution of iodine (98 mg, 386 µmol, 3.1 equiv.) in THF/water (4.5 mL, 2:1) was added. After 4h20, the excess iodine was quenched by addition of a 10% sodium bisulphite aqueous solution (15 mL). The reaction mixture was partially concentrated under reduced pressure to remove the THF then the aqueous layer was extracted with DCM (3 \times 20 mL). The combined organics were dried (Na₂SO₄), filtered and concentrated. Column chromatography of the residue (Toluene/EtOAc, $85:15 \rightarrow 80:20$) gave hemiacetal 10 (227 mg, 115 µmol, 93%) as a white foam. R_f = 0.43 (Toluene/EtOAc 75:25). β anomer: $R_f = 0.26$ (Toluene/EtOAc 75:25). ¹H NMR (CDCl₃) δ 7.41-6.99 (m, 51H, Ph, NH), 5.60 (bs, 1H, H-2_A), 5.25-4.37 (m, 26H, 20H_{Bn}, H-1_A, H-1_B, H-1_C, H-1_D, H-1_E, H-2_C), 4.29-3.40 (m, 22H, H-2_B, H-2_D, H-2_E, H-3_A, H-3_B, H-3_C, H-3_D, H-3_E, H-4_A, H-4_B, H-4_C, H-4_D, H-4_E, H-5_A, H-5_B, H-5_C, H-5_D, H-5_E, H-6a_D, H-6b_D, H-6a_E, H-6b_E), 2.72-2.57 (m, 4H, 2×CH_{2Lev}), 2.13, 2.12 (bs, 6H, CH_{3Lev}, H_{Ac}), 1.36-1.19 (m, 9H, H-6_A, H-6_B, H-6_C). ¹³C NMR (partial, CDCl₃) δ 206.2 (C_{Lev}), 171.8 (C_{Lev}), 170.1, 170.0 (C_{Ac}), 162.6, 161.7 (C_{NTCA}), 138.8-127.3 (Ph), 99.3 (C-1_A), 97.4 (C-1_E), 96.5 (C-1_C), 94.6, 91.3 (C-1_D), 92.5, 92.3 (CCl₃), 58.2, 55.4 (C-2_D), 38.1, 38.0 (CH_{2Lev}), 29.8, 29.7 (CH_{3Lev}), 28.2, 28.1 (CH_{2Lev}), 21.0 (C_{Ac}), 18.8, 18.7, 18.3, 18.2, 18.1, 18.0 (3C, C-6_A, C-6_B, C-6_C). HRMS (ESI⁺) m/z calcd for C₁₀₉H₁₂₀Cl₃NO₂₆Na [M+Na]⁺: 1986.7062. Found: 1986.7177.

 $(3,4-\text{Di-}O-\text{benzyl-}2-O-\text{levulinoyl}-\alpha-\text{L-rhamnopyranosyl})-(1\rightarrow 2)-(3,4-\text{di-}O-\text{benzyl}-\alpha-\text{L-rhamnopyranosyl})-(1\rightarrow 2)-(3,4-\text{di-}O$ rhamnopyranosyl)- $(1\rightarrow 3)$ -[2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)- $(1\rightarrow 4)$]-(2-Oacetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido- α/β -D-glucopyranosyl N-(phenyl)trifluoroacetimidate (11). To a solution of hemiacetal 10 (352 mg, 179 µmol) in acetone (4.5 mL) and under Ar were added first cesium carbonate (68 mg, 209 µmol, 1.2 equiv.), then 2,2,2-trifluoro-N-(phenyl)acetimidoyl chloride (74 mg, 357 µmol, 2.0 equiv.). After 2 h, volatiles were evaporated and the residue was purified by flash chromatography (Toluene/EtOAc, 98:2 \rightarrow 85:15) to give imidate 11 (316 mg, 148 µmol, 83%) as a white foam. NMR data indicated that donor 11 was present as a 1:0.3 mix with the corresponding oxazoline. Compound **11** had $R_f = 0.63$ (Toluene/EtOAc 85:15). ¹H NMR $(CDCl_3) \delta$ 7.36-7.10 (m, 53H, Ph), 6.88 (d, $J_{NH,2} = 8.5$ Hz, 1H, NH), 6.77 (d, J = 7.4 Hz, 2H, Ph), 6.41 (br s, 1H, H-1_D), 5.54 (dd, $J_{1,2} = 1.8$ Hz, $J_{2,3} = 3.0$ Hz, 1H, H-2_A), 5.17 (bs, 1H, H-1_C), 5.12 (m, 1H, H-2_C), 5.05 (d, 1H, H-1_A), 4.95-4.34 (m, 24H, 20H_{Bn}, H-1_B, H-1_E, H-2_B, H- $2_{\rm D}$), 4.16 (pt, $J_{2,3} = J_{3,4} = 9.3$ Hz, 1H, H- $3_{\rm D}$), 4.00-3.27 (m, 19H, H- $2_{\rm E}$, H- $3_{\rm A}$, H- $3_{\rm B}$, H- $3_{\rm C}$, H-3_E, H-4_A, H-4_B, H-4_C, H-4_D, H-4_E, H-5_A, H-5_B, H-5_C, H-5_D, H-5_E, H-6a_D, H-6b_D, H-6a_E, H-6b_E), 2.67-2.51 (m, 4H, 2×CH_{2Lev}), 2.10 (bs 3H, CH_{3Lev}), 2.08 (s, 3H, H_{Ac}), 1.30-1.18 (m, 9H, H-6_A, H-6_B, H-6_C). ¹³C NMR (partial, CDCl₃) δ 206.2 (C_{Lev}), 171.8 (C_{Lev}), 170.1 (C_{Ac}), 163.0 (C=NPh), 161.9 (C_{NTCA}), 143.1, 138.9-127.5, 119.4 (Ph), 99.5 (C-1_A), 97.2 (C-1_C), 92.3 (CCl₃), 81.7 (C-3_E), 76.0 (C-3_D), 72.0 (C-2_C), 69.5 (C-2_A), 54.5 (C-2_D), 38.2 (CH_{2Lev}), 29.9 (CH_{3Lev}) , 28.3 (CH_{2Lev}) , 21.1 (C_{Ac}) , 18.4, 18.3, 18.1 $(3C, C-6_A, C-6_B, C-6_C)$. HRMS (ESI^+) 2152.7803. calcd for $C_{117}H_{128}Cl_3F_3N_3O_{26}$ [M+NH₄]⁺: Found: 2152.4663, m/z $[M-HOC(NPh)CF_3+NH_4]^+$: $C_{109}H_{122}Cl_3N_2O_{25}$ 1963.7402. Found: 1963.6669, $C_{110}H_{126}Cl_3N_2O_{26}$ [M-OC(NPh)CF₃+OMe+NH₄]⁺: 1995.7665. Found: 1995.6724.

2-Azidoethyl (3,4-di-*O*-benzyl-2-*O*-levulinoyl– α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]-(2-*O*-acetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-4,6-di-*O*-benzyl-2-deoxy-2-

trichloroacetamido-β-D-glucopyranoside (12). A solution of donor 11 (53 mg, 27 μmol) and azidoethanol (100 µL, 121 mg, 1.39 mmol) in anhydr. toluene (4 mL) containing 4Å MS (140 mg) was stirred under Ar for 30 min. After cooling to -10 °C, TMSOTf (0.3 µL, 0.05 equiv.) was added. The reaction mixture was stirred for 1h at this temperature, then Et₃N (10 µL) was added and the mixture was filtered over a pad of Celite and concentrated to dryness. The residue was purified by column chromatography (Toluene/EtOAc, $100:0 \rightarrow 85:15$) to give azide 12 (41 mg, 20 μ mol, 81%) as a white foam. R_f = 0.41 (Toluene/EtOAc 80:20). $[\alpha]_{D}^{24} = +3.0^{\circ} (c \ 1.0, \text{CHCl}_3)$. ¹H NMR (CDCl₃) δ 7.38-7.15 (m, 51H, Ph, NH), 5.58 (dd, $J_{2,3}$ = 2.8 Hz, $J_{1,2}$ = 1.9 Hz, 1H, H-2_A), 5.17 (bs, 1H, H-2_C), 5.11 (d, $J_{1,2}$ = 2.3 Hz, 1H, H-1_C), 5.09 (bs, 1H, H-1_A), 4.97-4.91 (m, 5H, 2H_{Bn}, H-1_B, H-1_D, H-1_E), 4.85-4.35 (m, 20H, 18H_{Bn}, H-2_B, H-3_D), 4.04-3.34 (m, 24H, H-2_D, H-2_E, H-3_A, H-3_B, H-3_C, H-3_E, H-4_A, H-4_B, H-4_C, H-4_D, H-4_E, H-5_A, H-5_B, H-5_C, H-5_D, H-5_E, H-6a_D, H-6b_D, H-6a_E, H-6b_E, -OCH₂CH₂N₃), 2.70-2.52 (m, 4H, 2×CH_{2Lev}), 2.11 (bs, 6H, CH_{3Lev}, H_{Ac}), 1.33, 1.22, 1.18 (d, $J_{5.6} = 6.2$ Hz, 9H, H-6_A, H-6_B, H-6_C). ¹³C NMR (partial, CDCl₃) δ 206.1 (C_{Lev}), 171.7 (C_{Lev}), 170.0 (C_{Ac}), 161.9 (C_{NTCA}), 138.8-127.3 (Ph), 99.3 (C-1_A), 98.8, 98.4 (2C, C-1_D, C-1_E), 96.1 (C-1_C), 92.3 (CCl₃), 56.7 (C-2_D), 50.7 (CH₂N₃), 38.1 (CH_{2Lev}), 29.8 (CH_{3Lev}), 28.1 (CH_{2Lev}), 21.1 (C_{Ac}), 18.6, 18.3, 18.1

(3C, C-6_A, C-6_B, C-6_C). HRMS (ESI⁺) m/z calcd for C₁₁₁H₁₂₃Cl₃N₄O₂₆Na [M+Na]⁺: 2055.7338. Found: 2055.7261.

2-Azidoethyl (3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-Lrhamnopyranosyl)- $(1\rightarrow 3)$ -[2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)- $(1\rightarrow 4)$]-(2-Oacetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido- β -Dglucopyranoside (13). To a solution of pentasaccharide 12 (1.36 g, 0.67 mmol) in anhydr. pyridine (8.0 mL), cooled to 0 °C and under Ar, were added acetic acid (5.3 mL) and hydrazine hydrate (160 µL, 3.29 mmol, 4.9 equiv.), then the reaction mixture was allowed to warm to room temperature. After 1h30, cold water (25 mL) was added to the reaction mixture, which was then extracted with DCM (3×60 mL). The combined organics were dried (Na₂SO₄), filtered, evaporated and co-evaporated twice with Toluene. The residue was purified by column chromatography (Toluene/EtOAc, $92:8 \rightarrow 85:15$) to give alcohol **13** (1.16) g, 0.60 mmol, 90%) as a white foam. $R_f = 0.35$ (Toluene/EtOAc 80:20). $[\alpha]_{D}^{24} = -0.9^{\circ}$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.42-7.18 (m, 51H, Ph, NH), 5.19 (bs, 1H, H-2_C), 5.15-5.13 (m, 2H, H-1_A, H-1_C), 5.01 (bs, 1H, H-1_B), 4.98-4.43 (m, 23H, 20H_{Bn}, H-1_D, H-1_E, H-2_B), 4.37 (bt, 1H, H-3_D), 4.17 (dd, $J_{2,3} = 3.0$, $J_{1,2} = 1.7$ Hz, H-2_A), 4.05-3.35 (m, 24H, H-2_D, H-2_E, H-3_A, H-3_B, H-3_C, H-3_E, H-4_A, H-4_B, H-4_C, H-4_D, H-4_E, H-5_A, H-5_B, H-5_C, H-5_D, H-5_E, H-6a_D, H-6b_D, H-6a_E, H-6b_E, -OCH₂CH₂N₃), 2.34 (bs, 1H, OH), 2.12 (s, 3H, H_{Ac}), 1.33, 1.26, 1.21 (d, $J_{5.6}$ = 6.2 Hz, 9H, H-6_A, H-6_B, H-6_C). ¹³C NMR (partial, CDCl₃) δ 170.1 (C_{Ac}), 161.9 (C_{NTCA}), 138.9-127.4 (Ph), 101.1 (2C, C-1_A, C-1_B), 98.9, 98.4 (2C, C-1_D, C-1_E), 96.1 (C-1_C), 92.4 (CCl₃), 56.5 (C-2_D), 50.8 (CH₂N₃), 21.1 (C_{Ac}), 18.7, 18.3, 18.2 (3C, C-6_A, C-6_B, C-6_C). HRMS (ESI⁺) m/z calcd for C₁₀₆H₁₁₇Cl₃N₄O₂₄Na [M+Na]⁺: 1957.7021. Found: 1957.7002.

2-Azidoethyl (3,4-di-*O*-benzyl-2-*O*-levulinoyl– α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]-(2-*O*-acetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-(4,6-di-*O*-benzyl-2-deoxy-2-

rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-(2-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(4,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (14). A solution of acceptor 13 (81 mg, 42 µmol, 1.2 equiv.) and donor 11 (74 mg, 35µmol, 1.0 equiv.) in anhydr. toluene (2 mL) containing 4Å MS (100 mg), under Ar was stirred at room temperature for 15 min. After cooling to -10 °C for 15 min, TMSOTf (1.3 µL, 0.2 equiv.) was added. The reaction mixture was stirred at 0 °C for 1 h. Et₃N (10 µL) was added and the mixture was filtered over a pad of Celite and concentrated to dryness. The residue was purified by column chromatography (Toluene/EtOAc, 100:0 → 85:15) to give the expected decasaccharide 14 (111 mg, 29 µmol, 82%) as a white foam. R_f = 0.27 (Toluene/EtOAc 86:14). [α]²⁴_D = + 4.9° (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.35-6.95 (m, 102H, Ph, NH), 5.56 (bs, 1H, H-2_A), 5.12-5.07 (m, 5H, H-1_{A'}, H-1_C, H-1_{C'}, H-2_C, H-2_{C'}), 5.03 (br s, 1H, H-1_A), 4.96-4.17 (m, 51H, 40H_{Bn}, H-1_B, H-1_{B'}, H-1_D, H-1_{D'}, H-1_E, H-1_{E'}, H-2_{A'}, H-2_B, H-3_D, H-3_D), 4.00-3.31 (m, 44H, H-2_D, H-2_{D'}, H-2_E, H-2_{E'}, H-3_A, H-3_{A'}, H-3_B, H-3_{B'}, H-3_C, H-5_{A'}, H-5_B, H-5_{B'}, H-5_B, H-5_{B'}, H-5_C, H- $5_{C'}$, H- 5_{D} , H- $5_{D'}$, H- $5_{E'}$, H- $6a_{D}$, H- $6a_{D'}$, H- $6b_{D}$, H- $6b_{D'}$, H- $6a_{E}$, H- $6a_{E'}$, H- $6b_{E'}$, H- $6b_{E'}$, OCH₂CH₂N₃), 2.66-2.50 (m, 4H, 2×CH_{2Lev}), 2.09 (s 3H, CH_{3Lev}), 2.07 (s, 6H, H_{Ac}), 1.32-1.11 (m, 18H, H- 6_{A} , H- 6_{B} , H- 6_{C} , H- $6_{A'}$, H- $6_{B'}$, H- $6_{C'}$). ¹³C NMR (partial, CDCl₃) δ 206.1 (C_{Lev}), 171.8 (C_{Lev}), 170.1 (2C, C_{Ac}), 161.9 (C_{NTCA}), 161.4 (C_{NTCA}), 139.1-127.2 (Ph), 100.2 (2C, C- 1_{B} , C- $1_{B'}$), 99.5 (C- 1_{A}), 96.3 (2C, C- 1_{C} , C- $1_{C'}$), 92.7 (CCl₃), 92.4 (CCl₃), 58.7 (C- 2_{D}), 56.9 (C- $2_{D'}$), 50.8 (CH₂N₃), 38.2 (CH_{2Lev}), 29.8 (CH_{3Lev}), 28.2 (CH_{2Lev}), 21.1 (2C, C_{Ac}), 18.8-18.1 (6C, C- 6_{A} , C- 6_{B} , C- 6_{C} , C- $6_{A'}$, C- $6_{B'}$, C- $6_{C'}$). HRMS (MALDI⁺) *m*/*z* calcd for C₂₁₅H₂₃₅Cl₆N₅O₄₉Na [M+Na]⁺: 3903.4080. Found: 3803.3596, C₂₁₅H₂₃₅Cl₆N₅O₄₉K [M+K]⁺: 3919.5012. Found: 3919.4165.

2-Azidoethyl $(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 2)-(3,4-di-O-benzyl-\alpha-L$ rhamnopyranosyl)- $(1\rightarrow 3)$ -[2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)- $(1\rightarrow 4)$]-(2-Oacetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranosyl)- $(1\rightarrow 2)$ - $(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)-<math>(1\rightarrow 2)$ - $(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)$ - $(1\rightarrow 2)$ - $(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)$ -(3,4-di-Obenzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)- $(1\rightarrow 4)$]- $(2-O-acetyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-(4,6-di-O-benzyl-2-deoxy-2$ trichloroacetamido-β-D-glucopyranoside (15). The fully protected 14 (94 mg, 24 μmol, 1.0 equiv.) was dissolved under Ar in anhydr. pyridine (1.0 mL), cooled to 0 °C, and acetic acid (260 µL) followed by hydrazine hydrate (9.2 mg, 7.0 equiv.) were added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Cold water (10 mL) was added to the reaction mixture, which was then extracted with DCM (3×10 mL). The combined organics were dried (Na₂SO₄), filtered, evaporated and co-evaporated twice with toluene. The residue was purified by column chromatography (Toluene/EtOAc, 100:0 \rightarrow 85:15) to give alcohol 15 (81 mg, 22 μ mol, 89%) as a white foam. R_f = 0.39 (Toluene/EtOAc 82:18). $[\alpha]_{D}^{24} = +4.0^{\circ}$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.44-7.01 (m, 102H, Ph, NH), 5.21-5.16 (m, 6H, H-1_A, H-1_{A'}, H-1_C, H-1_{C'}, H-2_C, H-2_{C'}), 5.07-4.21 (m, 52H, 40H_{Bn}, H-1_B, H-1_{B'}, H-1_D, H-1_{D'}, H-1_E, H-1_{E'}, H-2_A, H-2_{A'}, H-2_B, H-2_{B'}, H-3_D, H-3_{D'}), 4.07-3.38 (m, 44H, H-2_D, H-2_{D'}, H-2_E, H-2_{E'}, H-3_A, H-3_{A'}, H-3_B, H-3_{B'}, H-3_C, H-3_{C'}, H-3_E, H-3_{E'}, H-4_A, H-4_{A'}, H-4_B, H-4_{B'}, H-4_C, H-4_{C'}, H-4_D, H-4_{D'}, H-4_E, H-4_{E'}, H-5_A, H-5_{A'}, H-5_B, H-5_{B'}, H-5_C, H-5_{C'}, H-5_D, H-5_D', H-5_E', H-6a_D', H-6a_D', H-6b_D', H-6b_D', H-6a_E', H-6b_E', H-6b_E', -OCH₂CH₂N₃), 2.15 (s, 6H, H_{Ac}), 1.40-1.20 (m, 18H, H-6_A, H-6_B, H-6_C, H-6_{A'}, H-6_{B'}, H-6_{C'}). ¹³C NMR (partial, CDCl₃) δ 170.0 (2C, C_{Ac}), 161.9 (C_{NTCA}), 161.3 (C_{NTCA}), 139.1-127.2 (Ph), 101.1 (2C, C-1_A, C-1_{A'}), 96.3 (2C, C-1_C, C-1_{C'}), 100.2 (2C, C-1_B, C-1_{B'}), 98.9, 98.5 (4C, C-1_D, C-1_{D'}, C-1_E, C-1_{E'}), 92.7 (CCl₃), 92.4 (CCl₃), 58.7 (C-2_D), 56.8 (C-2_{D'}), 50.7 (CH₂N₃), 21.1 (2C, C_{Ac}), 18.8-18.1 (6C, C-6_A, C-6_B, C-6_C, C-6_{A'}, C-6_{B'}, C-6_{C'}). HRMS (MALDI⁺) m/zcalcd for C₂₁₀H₂₂₉Cl₆N₅O₄₇Na [M+Na]⁺: 3806.3745. Found: 3806.0535, C₂₁₀H₂₂₉Cl₆N₅O₄₇K [M+K]⁺: 3822.3484. Found: 3822.0601.

 $\label{eq:2-Azidoethyl} \begin{array}{l} (3,4-di\ensuremath{\cdot}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensuremath{o}\ensuremath{o}\ensuremath{o}\ensuremath{\cdot}\ensuremath{o}\ensur$

 $O-benzyl-\alpha-D-glucopyranosyl)-(1\rightarrow 4)]-(2-O-acetyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-\beta-D-glucopyranosyl)-(1\rightarrow 2)-(3,4-di-O-benzyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-di-O-benzyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,4,6-di-O-benzyl-\alpha-L-rhamnopyranosyl-\alpha-L-rhamnopyranosyl-\alpha-L-rhamnopyranosyl)-(1\rightarrow 3)-[2,3,6-di-O-benzyl-\alpha-L-rhamnopyranosyl-\alpha-L-rh$

tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]-(2-*O*-acetyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-**4,6-di-***O***-benzyl-2-deoxy-2-trichloroacetamido-**β**-***D***-glucopyranoside** (16). To a solution of acceptor 15 (103 mg, 27 µmol, 1.0 equiv.) and donor 11 (87 mg, 41 µmol, 1.5 equiv.) in anhydr. toluene (1.5 mL) containing 4Å MS (160 mg), under Ar at -30 °C, was added TMSOTf (1.0 µL, 5.5 µmol, 0.2 equiv.). The reaction mixture was stirred at -30 °C for 1 h, then at room temperature for 15 min. Et₃N was added and the mixture was filtered over a pad of Celite and concentrated to dryness. The residue was purified by flash chromatography (Toluene/EtOAc, $100:0 \rightarrow 85:15$) to give pentadecasaccharide **16** (121 mg, 21 µmol, 78%) as a white foam. $R_f = 0.51$ (Toluene/EtOAc 85:15). $[\alpha]_{D}^{24} = +3.5^{\circ}$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.40-7.04 (m, 153H, Ph, NH), 5.54 (bs, 1H, H-2_A), 5.14-5.00 (m, 9H, H-1_A, H-1_{A'}, H-1_{A"}, H-1_C, H-1_C, H-1_{C"}, H-2_C, H-2_{C'}, H-2_{C'}), 4.93-4.12 (m, 75H, 60H_{Bn}, H-1_B, H-1_{B'}, H-1_{B"}, H-1_D, H-1_D', H-1_D", H-1_E, H-1_E", H-1_E", H-2_B, H-2_B", H-3_D, H-3_D", H-3_D"), 4.00-3.27 (m, 64H, H-2_D, H-2_D', H-2_D', H-2_E, H-2_E', H-2_E'', H-3_A, H-3_A'', H-3_A'', H-3_B, H-3_B'', H-3_B'', H-3_C, H-3_{C'}, H-3_{C'}, H-3_E, H-3_{E'}, H-3_{E'}, H-4_A, H-4_{A'}, H-4_{A'}, H-4_B, H-4_{B'}, H-4_{B'}, H-4_C, H-4_{C'}, H-4_{C"}, H-4_D, H-4_D, H-4_D, H-4_E, H-4_E, H-4_E, H-5_A, H-5_A, H-5_A, H-5_A, H-5_B, H-5_B, H-5_B, H-5_B, H-5_C, H-5_{C'}, H-5_{C''}, H-5_D, H-5_{D'}, H-5_{D'}, H-5_E, H-5_{E'}, H-5_{E''}, H-6a_D, H-6a_{D'}, H-6a_{D'}, H-6b_D, H-6b_{D'}, H-6b_D", H-6a_E, H-6a_E", H-6a_E", H-6b_E, H-6b_E", H-6b_E", -OCH₂CH₂N₃), 2.65-2.50 (m, 4H, 2×CH_{2Lev}), 2.06 (s, 6H, H_{Ac}), 2.04 (s, 3H, H_{Ac}), 1.33-1.16 (m, 27H, H-6_A, H-6_B, H-6_C, H-6_{A'}, H-6_{B'}, H-6_{C'}, H-6_{A''}, H-6_{B''}, H-6_{C'}). ¹³C NMR (partial, CDCl₃) δ 206.1 (C_{Lev}), 171.8 (C_{Lev}), 170.1 (3C, CAC), 161.9 (CNTCA), 161.4 (CNTCA), 161.3 (CNTCA), 139.1-127.3 (Ph), 92.7 (2C, CCl₃), 92.4 (CCl₃), 69.5 (C-2_A), 58.7 (2C, C-2_D, C-2_{D'}), 56.8 (C-2_{D'}), 50.7 (CH₂N₃), 38.2 (CH_{2Lev}), 29.9 (CH_{3Lev}), 28.2 (CH_{2Lev}), 21.1 (3C, C_{Ac}), 18.8-18.1 (9C, C-6_A, C-6_B, C-6_C, C- $6_{A'}$, C- $6_{B'}$, C- $6_{C'}$, C- $6_{A''}$, C- $6_{B''}$, C- $6_{C''}$). HRMS (MALDI⁺) m/z calcd for C₃₁₉H₃₄₇Cl₉N₆O₇₂Na $[M+Na]^+$: 5752.0806. Found: 5752.4351, $C_{319}H_{347}Cl_9N_6O_{72}K$ $[M+K]^+$: 5767.0508. Found: 5767.5322.

2-Azidoethyl (3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 3)-[2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 \rightarrow 4)]- α -L-rhamnopyranosyl-(1 \rightarrow 3)-4,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranoside (17). To a solution of the fully protected pentadecasaccharide 16 (105 mg, 18 µmol, 1.0 equiv.) in MeOH/DCM (4:3, 7 mL) was added methanolic sodium methoxide (25% w/w, 200 µL) and the mixture was stirred at 60 °C for 3 h, and then at room temperature overnight. Dowex 50Wx8-200 (H⁺ form) was added. The suspension was filtered over a pad of Celite, and the filtrate was concentrated to dryness. The residue was purified by flash

chromatography (Toluene/EtOAc 100:0 \rightarrow 81:15) to give tetraol **17** (73 mg, 13.3 µmol, 74%) as a white foam. $R_f = 0.34$ (Toluene/EtOAc 85:15). $[\alpha]^{24}{}_D = -7.2^{\circ}$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃) δ 7.43-6.92 (m, 153H, Ph, NH), 5.54 (bs, 1H, H-2_A), 5.19-4.12 (m, 81H, 60H_{Bn}, H-1_A, H-1_A', H-1_B', H-1_B', H-1_C, H-1_C', H-1_C'', H-1_D', H-1_D'', H-1_E'', H-1_E'', H-2_C', H-2_C'', H-3_D, H-3_D'', H-3_D''), 4.00-3.27 (m, 67H, H-2_B, H-2_B'', H-2_B'', H-2_B'', H-2_D'', H-2_E'', H-2_E'', H-3_A, H-3_A', H-3_A'', H-3_B'', H-3_B'', H-3_B'', H-3_C', H-3_C'', H-3_C'', H-3_E'', H-4_A', H-4_A'', H-4_B'', H-4_B'', H-4_B'', H-4_C', H-4_C'', H-4_C'', H-4_D'', H-4_D'', H-4_E'', H-4_E'', H-5_A', H-5_A'', H-5_B'', H-5_B'', H-5_C'', H-5_C'', H-5_C'', H-5_D', H-5_D'', H-6a_E'', H-6a_E'', H-6b_E'', H-6b_E'', H-6a_D'', H-6a_D'', H-6a_D'', H-6b_D'', H-6b_D'', H-6a_E, H-6a_E'', H-6a_E'', H-6b_E'', H-6b_E'', H-6b_E'', H-6b_E'', H-6b_E'', H-6b_E'', H-6b_E'', H-6a_D'', H-6a_D'', H-6b_D'', H-6b_D'', H-6a_B, H-6a_C, H-6a_C', H-6a_C'', H-6a_C'''

2-Aminoethyl α -L-rhamnopyranosyl- $(1\rightarrow 2)-\alpha$ -L-rhamnopyranosyl- $(1\rightarrow 3)-[\alpha$ -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 2)-\alpha$ -L-rhamnopyranosyl- $(1\rightarrow 2)-\alpha$ -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 2)-\alpha$ -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 3)$ -2-acetamido-2-deoxy- β -D-glucopyranosyl- $(1\rightarrow 4)$]- α -L-rhamnopyranosyl- $(1\rightarrow 4)$ -2- α -L-rhamnopyranosyl- $(1\rightarrow 4)$ -

glucopyranoside (1). To a degassed solution of pentadecasaccharide 17 (53 mg, 9.6 µmol) in tBuOH/DCM/water (7/1/1, 5.0 mL), was added Pd/C (52 mg) and the suspension was stirred for 4 days under a hydrogen atmosphere. After this time, RP-HPLC analysis of the reaction mixture revealed a peak with a retention time corresponding to that of the target pentadecasaccharide 1, albeit as a minor peak. The suspension was filtered and the crude material was dissolved in tBuOH/water (1/1, 5.0 mL). Pd/C (23 mg) was added and the suspension was stirred for a day under a hydrogen atmosphere. After this time, RP-HPLC analysis of the reaction mixture revealed the absence of any major progress. Pd(OH)₂/C (25 mg) was added and the suspension was stirred for 3 more days, at which time RP-HPLC analysis of the reaction mixture indicated that most of the intermediates had been converted into the target pentadecasaccharide 1, an observation that was supported by MS analysis. The suspension was filtered over a 0.2 µm filter. Evaporation of the volatiles, freeze-drying and purification of the residue by RP-HPLC ($\lambda = 215$ nm) using a Kromasil 5 μ m C18 100 Å 10 \times 250 mm semi-preparative column eluting with a 0-20% linear gradient of CH₃CN in 0.08% aq. TFA over 20 min at a flow rate of 5.5 mL•min⁻¹, gave the known pentadecasaccharide 1 (12.6 mg, 5.1 µmol, 52%) as a white powder following repeated freeze-drying. NMR data obtained for the fully deprotected aminoethyl glycoside 1 were identical to those of a reference compound prepared by chemical synthesis.¹² In addition, compound **1** had $\left[\alpha\right]^{24}_{D} = -$ 10.0° (c 1.0, water). HRMS (MALDI⁺) m/z calcd for C₉₈H₁₆₆N₄O₆₇Na [M+Na]⁺: 2493.9602. Found: 2493.8005, $C_{98}H_{166}N_4O_{67}K [M+K]^+$: 2509.9343. Found: 2509.7732. RP-HPLC ($\lambda =$ 215 nm): $t_R = 6.40$ min.

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F2 - Acq	uis	ition	Pa	ramet	ers
Date		2	012	1015	
Time			1	8.05	
INSTRUM			S	pect	
PROBHD	5 1	mm PAE	BBO	BB/	
PULPROG				zq30	
TD			6	5536	
SOLVENT			С	DC13	
NS				16	
DS				2	
SWH		4	006	.410	Hz
FIDRES		0	.06	1133	Hz
AQ		8.	178	8931	sec
RG				57	
DW			124	.800	usec
DE				6.00	usec
TE			3	03.0	Κ
D1		1.0	000	0000	sec
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NUC1				1H	
P1				6.75	usec
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Compound S3 OAII NHCl₃Ac AcO-AcO OAc

F2 - Acquisition Parameters Date_ 20121015 12.46 Time INSTRUM spect 5 mm PABBO BB/ PROBHD cosygpppqf 2048 PULPROG TD SOLVENT CDC13 NS 1 DS 8 3063.726 Hz SWH 1.495960 Hz FIDRES 0.3342336 sec AQ RG 64 163.200 usec  $\mathsf{DW}$ DE 6.50 usec 303.0 K ΤE 0.00000300 sec DO 1.34557998 sec D1 D11 0.03000000 sec D12 0.00002000 sec 0.00000400 sec D13 D16 0.00020000 sec INO 0.00032640 sec ====== CHANNEL fl ======= NUC1 1H ΡO 6.75 usec 6.75 usec Pl 2500.00 usec P17 -6.00 dB PL1 6.57 dB PL10 400.1316532 MHz SF01 ===== GRADIENT CHANNEL ===== GPNAM[1] SINE.100 GPZ1 10.00 % P16 1000.00 usec F1 - Acquisition parameters TD 512 SF01 400.1317 MHz 5.983839 Hz FIDRES SW 7.657 ppm QF FnMODE





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F2 - Acqu Date_ Time INSTRUM	isition Paramet 20121015 13.26 spect	ers.
PROBHD PULPROG TD SOLVENT NS DS	5 mm PABBO BB/ deptsp135 65536 CDC13 256 4	
SWH FIDRES AQ RG	23980.814 0.365918 1.3664256 16384	Hz Hz sec
DW DE TE CNST2	20.850 6.00 303.0 145.0000000	usec usec K
D1 D2 D12 TD0	2.00000000 0.00344828 0.00002000 1	sec sec sec
======= NUC1 P1 P12 PL0 PL1 SF01 SP01 SP0AL2 SP0FFS2	CHANNEL f1 ==== 13C 5.90 2000.00 120.00 -6.00 100.6228298 6.74 Crp60comp.4 0.500 0 Hz	usec usec dB dB MHz dB
====== CPDPRG[2 NUC2 P3 P4 PCPD2 PL2 PL12 SF02	CHANNEL f2 ==== waltz16 1H 6.75 13.50 80.00 -6.00 20.00 400.1316005	usec usec usec dB dB MHz

400.1316005 MHz





F2 - Acqu	uisition Parameters
Date	20121015
Time	13.29
TNSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	hsacetannd
	2048
SOLVENI	CDCIS
NS	4
DS	
SWH	3019.324 Hz
FIDRES	1.474279 Hz
AQ	0.3391488 sec
RG	5160.6
DW	165.600 usec
DE	6.00 usec
ΤE	303.0 K
CNST2	145.0000000
DO	0.00000300 sec
D1	1.47951996 sec
D4	0.00172414 sec
D11	
D13	0.0000000 500
D16	0.00000400 sec
TNO	0.00020000 sec
INU	0.00002760 sec
ZGOPTNS	
	CHANNEL fl ======
NUC1	1H
P1	6.75 usec
P2	13.50 usec
P28	1000.00 usec
PL1	-6.00 dB
SF01	400.1316387 MHz
	CHANNEL f2 ======
NUC2	1.3C
P3	5.90 USEC
PΔ	11 80 usec
PT 2	-6 00 dB
	23 00 dB
CEOS	100 6209190 MU-
SEUZ	100.6208180 MHZ
01	
===== GI	RADIENT CHANNEL =====
GPNAM [ I ]	SINE.100
GPNAM[2]	SINE.100
GPZ1	80.00 %
GPZ2	20.10 %
P16	1000.00 usec
F1 - Acqu	isition parameters
TD	256
SF01	100.6208 MHz
FIDRES	70.749016 Hz
SW	180.000 ppm

SW 180.000 ppm FnMODE Echo-Antiecho 170.25 170.06 169.91 162.20

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F2 - Acquisition Parameters 20121015 Date_ Time 18.50 INSTRUM spect 5 mm PABBO BB/ PROBHD PULPROG zgpg30 TD 65536 CDC13 SOLVENT NS 1408 DS 4 SWH 26178.010 Hz FIDRES 0.399445 Hz AQ 1.2517376 sec RG 13004  $\mathsf{DW}$ 19.100 usec DE 6.50 usec 303.0 K ΤE D1 2.00000000 sec D11 0.03000000 sec TDO ====== CHANNEL fl ======= NUC1 13C 5.90 usec Ρ1 -6.00 dB PL1 100.6248425 MHz SF01 ====== CHANNEL f2 ======= CPDPRG[2 waltz16 NUC2 1H 80.00 usec PCPD2 -6.00 dB PL2 PL12 20.00 dB PL13 20.00 dB SFO2 400.1316005 MHz F2 – Processing parameters SI 32768 SF 100.6127547 MHz WDW ΕM SSB 0 LB1.00 Hz GΒ 0 PC 1.40





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F2 -	Acquisition Pa	aramet	cers
Date_	2010	01013	
Time		11.57	
INSTR	UM s	spect	
PROBH	D 5 mm PABBC	) BB/	
PULPR	OG	zg30	
TD	- (	65536	
SOLVE	NT	MeOD	
NS		16	
DS		2	
SWH	8278	8.146	Ηz
FIDRE	S 0.12	26314	Ηz
AQ	3.958	83745	sec
RG		45.3	
DW	60	0.400	usec
DE		6.00	usec
TE		303.0	K
D1	1.0000	00000	sec
TDO		1	
	=== CHANNEL fl	1 ===:	====
NUC1		1H	
P1		6.75	usec
PL1		-6.00	dB
SE'O1	400.132	24710	MHz
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GB DC	U	1 00	
ЕС		Τ•ΟΟ	





F2 - Acquisition Parameters Date_ 20101013 Time 11.59 INSTRUM spect 5 mm PABBO BB/ PROBHD PULPROG cosygpppqf 2048 TD SOLVENT MeOD NS DS 8 SWH 2380.952 Hz FIDRES 1.162574 Hz 0.4300800 sec AQ 35.9 RG  $\mathsf{DW}$ 210.000 usec DE TE d0 D1 6.50 usec 303.0 K 0.00000300 sec 1.24932396 sec d11 0.03000000 sec d12 0.00002000 sec d13 0.00000400 sec D16 0.00020000 sec INO 0.00042000 sec ====== CHANNEL fl ======= NUC1 1H 6.75 usec ΡO Ρ1 6.75 usec P17 2500.00 usec PL1-6.00 dB 6.57 dB PL10 SF01 400.1313327 MHz ===== GRADIENT CHANNEL ===== GPNAM[1] SINE.100 GPZ1 10.00 % P16 1000.00 usec F1 - Acquisition parameters TD 128 SF01 400.1313 MHz FIDRES 18.601191 Hz SW 5.950 ppm FnMODE QF

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F2 - Acquisition Parameters 20101013 Date_ Time 23.25 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG deptsp135 TD 65536 SOLVENT MeOD 512 NS DS 4 SWH 23980.814 Hz FIDRES 0.365918 Hz AQ 1.3664256 sec RG 16384  $\mathsf{DW}$ 20.850 usec DE 6.00 usec ΤE 303.0 K CNST2 145.0000000 D1 2.00000000 sec d2 0.00344828 sec d12 0.00002000 sec DELTA 0.00000751 sec TDO ====== CHANNEL fl ======= NUC1 13C P1 5.90 usec P12 2000.00 usec PLO 120.00 dB -6.00 dB PL1 100.6228298 MHz SF01 6.74 dB SP2 SPNAM[2] Crp60comp.4 SPOAL2 0.500 SPOFFS2 0 Hz ====== CHANNEL f2 ======= CPDPRG[2 waltz16 NUC2 1H P3 6.75 usec 13.50 usec p4 80.00 usec PCPD2 PL2 -6.00 dB 20.00 dB PL12SF02 400.1316005 MHz F1 - Acquisition parameters TD 128 SF01 400.1316 MHz FIDRES 7.812500 Hz SW 2.499 ppm

QF

FnMODE



![](_page_25_Figure_1.jpeg)

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فيرالشوا بمجدول فوالعبالغان فاستجدون فلوصيتها بالباتي مخالبه بماليه ويتلوجوه المالة التقاليا والانتها والمتعا	الاست المجاد ويا البطار المتجلي فسيلط الألم فيداد الجميد الألاب أسراعها	

![](_page_26_Figure_7.jpeg)

100

80

60

20

ppm

![](_page_26_Picture_13.jpeg)

F2 - Acquisition Parameters 20101014 Date_ 3.23 Time INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT MeOD NS 4096 DS 4 SWH 26178.010 Hz 0.399445 Hz FIDRES 1.2517376 sec AQ RG 456.1  $\mathsf{DW}$ 19.100 usec DE 6.50 usec ΤE 303.0 K D1 2.00000000 sec d11 0.03000000 sec DELTA 1.89999998 sec TDO 1 ====== CHANNEL fl ======= NUC1 13C P1 5.90 usec PL1 -6.00 dB SF01 100.6248425 MHz ====== CHANNEL f2 ======= CPDPRG[2 waltz16 NUC2 1H PCPD2 80.00 usec PL2 -6.00 dB PL12 20.00 dB 20.00 dB PL13 SFO2 400.1316005 MHz F2 - Processing parameters SI 32768 SF 100.6126340 MHz WDW ΕM SSB 0 LΒ 1.00 Hz GB 0 PC 1.40

![](_page_27_Figure_0.jpeg)

![](_page_27_Figure_1.jpeg)

![](_page_27_Figure_2.jpeg)

![](_page_27_Figure_3.jpeg)

![](_page_27_Figure_5.jpeg)

F2 - Acqu	lisi	tion	Par	amet	ers
Date		2	0101	L127	
Time			7	7.54	
INSTRUM			sp	ect	
PROBHD	5 m	m PAI	BBO	BB/	
PULPROG			Z	2q30	
TD			65	5536	
SOLVENT				D20	
NS				16	
DS				2	
SWH		8	278.	.146	Hz
FIDRES		0	.126	5314	Hz
AQ		З.	9583	3745	sec
RG				181	
DW			60.	.400	usec
DE			(	5.00	usec
TE			30	0.2.0	K
D1		1.0	0000	0000	sec
TDO				1	
	CHA	NNEL	f1		
NUC1				1H	
P1			E	5.75	usec
PLI		100	- (	5.00	dB
SFOT		400.	1324	ŧ/ΙΟ	MHz
					10.0
FZ = Proc	less	Ing	para	umete Daco	ers
ST ST		100	1200	2700	MIT
		400.	1291	204Z	MHZ
N D N S S B	Ο			Ľ1°1	
JGG T.R	U		C	U 2 U	Цч
GR	Ω		(		112
PC	0		1		
T 🔿			9 <del>9</del>		

![](_page_28_Picture_0.jpeg)

![](_page_28_Figure_2.jpeg)

F2 - Acquisit:	on Pa	aramet	ers
Date	201	01127	
Time		7.55	
INSTRUM	ç	spect	
PROBHD 5 mm	PABBO	D BB/	
PULPROG	osvar	jpadc	
TD	1 71	2048	
SOLVENT		D2.0	
NS		1	
DS		8	
SWH	231	4 815	Hу
FIDRES	1 1	30281	H7
	$\cap \Delta \Delta$	23680	112 900
RC RC	0.11	23000 64	500
	21	6 000	11000
		6 50	usec
		202 0	usec v
1년 20		00200	N A a a
	0000	00300	sec
UL .		03399	sec
	1.030		sec
	.000	02000	sec
als (	.000	00400	sec
D16 (	.000	20000	sec
INO (	.000	43200	sec
CIIANI	id t	1	
HANI	ILL I.	⊥ ==== 1 TT	
NUCL			
PU D1		6.75	usec
P1	<u>с</u> г	6.75	usec
PI/	25	00.00	usec
РЫТ	2	-6.00	dB
PL10		6.57	dB
SF01 40	0.13	13888	MHz
CDADIE		א אזאזבי ד	
CDNAM[1]			
GPNAM[1]	SINE	10 00	0
GPZI D1C	1 0		5
PT0	TO	00.00	usec
F1 - Acquieit	on na	aramet	era
TD TROYULDICI	on po	128	OT D
- ビ SFO1	100	121 <i>/</i>	MU 7
DI VI DI VI	10 0	• 1 J 1 4 Q / / Q 0	MITZ Urz
E LURES	TO . U	0449U 5 705	ПZ DDD
		CQ1.C	Pbu
FUMODE		QE'	

![](_page_29_Figure_0.jpeg)

![](_page_29_Figure_2.jpeg)

F2 - Acquisition Parameters Date_ 20101127 9.57 Time INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG deptsp135 TD 65536 D20 SOLVENT NS 2048 DS 4 23980.814 Hz SWH FIDRES 0.365918 Hz 1.3664256 sec AQ RG 16384  $\mathsf{DW}$ 20.850 usec 6.00 usec DE ΤE 303.0 K CNST2 145.0000000 D1 2.00000000 sec d2 0.00344828 sec d12 0.00002000 sec 0.00000751 sec DELTA TDO ====== CHANNEL fl ======= NUC1 13C 5.90 usec P1 P12 2000.00 usec 120.00 dB PLO -6.00 dB PL1SF01 100.6228298 MHz SP2 6.74 dB SPNAM[2] Crp60comp.4 SPOAL2 0.500 SPOFFS2 0 Hz ====== CHANNEL f2 ======= CPDPRG[2 waltz16 NUC2 1H РЗ 6.75 usec p4 13.50 usec PCPD2 80.00 usec PL2 -6.00 dB 20.00 dB PL12 SFO2 400.1316005 MHz F1 - Acquisition parameters TD 128 400.1316 MHz SF01 FIDRES 7.812500 Hz 2.499 ppm SW FnMODE QF

![](_page_30_Figure_0.jpeg)

![](_page_30_Figure_1.jpeg)

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2

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200

![](_page_31_Picture_8.jpeg)

100

![](_page_31_Picture_12.jpeg)

0

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Compound 2

![](_page_31_Figure_15.jpeg)

F2 - Acqu	lisi	t	io	n	F	'a	ra	ame	et	ers
Date				2	01	10	1	12	7	
Time						1	4	• 4	6	
INSTRUM						S	pe	ect	t	
PROBHD	5 m	m	Ρ.	AI	BE	30	Ē	ЗB	/	
PULPROG					7	a	$\mathbf{p}_{\mathbf{q}}$	π3	0	
TD					10	5	5	53	6	
SOLVENT						v		D2	$\hat{\circ}$	
NG							Λ	n a	6	
NG							Ţ		Л	
			0	C	1 -	70		01	4	TT 🛶
SWH			Z	0	T ,	10	•	UТ	U E	HZ II-
FIDRES			4	U	•	59 - 1	9.0	44	5	ΗZ
AQ			1		23	ЪТ	1.	31	6	sec
RG								36	2	
DW					07 0 <del>1</del>	19	•	10	0	usec
DE							6	• 5	0	usec
TE						3	0	3.	0	K
D1			2.	0	0(	00	0	00	0	sec
d11			0.	0	30	)0	0	00	0	sec
DELTA			1.	8	99	99	9	99	8	sec
TDO									1	
	CHA	łΝ	NE	L	ſ	51		==	==	
NUC1							83 10	13	С	
P1							5	. 9	0	usec
PL1						-	6	.0	0	dB
SF01		1	00		62	24	8	42	5	MHz
=======	CHA	łΝ	NE	L	ſ	52		==	==	====
CPDPRG[2				5	wa	1l	t:	z1	6	
NUC2								1	Η	
PCPD2						8	0	.0	0	usec
PL2						_	6	.0	0	dB
PT.12						2	Õ	. 0	õ	dB
PT.13						2	ñ	0	ñ	dR
SEUS		Λ	00		1 1	ے 1	6	00	5	MH 7
DI UZ		Т	00		1、	) <u> </u>	0	00	9	1-1112
$F_2 - Proc$	7099	: 1 1	പഷ	1	na	r	ar	ne	tρ	rs
ST IIO		, – 1	.19	2008	ρc	۲ ۲	2	пс 7 б	8	тр
CL DT		1	00		61	12	乙 万1	10	3	MU 7
		Т	00	•	0_	LZ	0	U U T	M	1.1117
CCD	$\cap$							Ľ	1,1	
DGG D	U						1	$\cap$	$\cap$	U 🖙
	$\cap$						1000	• 0	U	ΠΖ
GD	U						1	л	0	
PC								• 4	U	

![](_page_31_Picture_17.jpeg)

![](_page_32_Figure_0.jpeg)

![](_page_32_Figure_2.jpeg)

![](_page_33_Figure_0.jpeg)

![](_page_33_Figure_1.jpeg)

![](_page_33_Figure_2.jpeg)

F2 - Acquisition Parameters 20110829 Date_ Time 22.28 INSTRUM spect 5 mm PABBO BB/ PROBHD PULPROG zg30 TD 65536 D20 SOLVENT NS 16 2 DS SWH 8278.146 Hz 0.126314 Hz FIDRES AQ 3.9583745 sec RG 128 DW 60.400 usec DE 6.00 usec 999.9 K ΤE D1 1.00000000 sec TDO ====== CHANNEL f1 ======= NUC1 1H 6.75 usec Ρ1 -6.00 dB PL1 SF01 400.1324708 MHz F2 - Processing parameters 32768 SI SF 400.1299637 MHz WDW ΕM SSB 0 LB 0.30 Hz GB 0 1.00 ΡC

![](_page_34_Figure_0.jpeg)

![](_page_34_Figure_1.jpeg)

F2 - Acquis	ition Parameters
Date_	20110829
Time	22.30
INSTRUM	spect
PROBHD 5 r	nm PABBO BB/
PULPROG	cosvapppaf
TD	2048
SOLVENT	D20
NS	1
DS	8
SWH	2281 022 Hz
FIDEES	1 113780 Uz
A O	0 1189216 cod
AV PC	61
NG	
	ZI9.ZUU USEC
15	999.9 K
	0.00000300 sec
DI	1.23089194 sec
dII	0.03000000 sec
d12	0.00002000 sec
d13	0.00000400 sec
D16	0.00020000 sec
INO	0.00043840 sec
===== CHA	ANNEL II =======
NUCL	
PO	6.75 usec
P1	6.75 usec
P17	2500.00 usec
PL1	-6.00 dB
PL10	6.57 dB
SF01	400.1313857 MHz
===== GRAD:	IENT CHANNEL =====
GPNAM [1]	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
	1 <u>5 55</u>
Fl - Acquis	ition parameters
TD	100 1011 m
SFOl	400.1314 MHz
FIDRES	17.820484 Hz
SW	5.701 ppm
FnMODE.	OF

FnMODE

![](_page_35_Figure_0.jpeg)

![](_page_35_Picture_1.jpeg)

F2 - Acqu	isition Paramet	ers
Date	20110829	
Time	23.33	
TNSTRUM	spect	
PROBHD	5  mm  PABBO BB/	
DITT DROG	denten135	
TOTEVOG	CEE2C	
	65536	
SOLVENT	D20	
NS	1024	
DS	4	
SWH	23980.814	Ηz
FIDRES	0.365918	Hz
AQ	1.3664256	sec
RG	16384	
กพ	20,850	usec
DF	6 00	11960
TE	0.00	v
IE ONOTO	145 0000000	Г
CNSIZ	145.0000000	
DI	2.00000000	sec
d2	0.00344828	sec
d12	0.00002000	sec
DELTA	0.00000751	sec
TDO	1	
=======	CHANNEL fl ====	====
NUC1	13C	
P1	5,90	usec
D12	2000 00	11900
	120.00	AD AD
	120.00	dD dD
PLI apol	-6.00	aв
SFOL	100.6228298	MHZ
SP2	6./4	dB
SPNAM[2]	Crp60comp.4	
SPOAL2	0.500	
SPOFFS2	0 Hz	
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
NUC2	1H	
P3	6.75	usec
 n4	13.50	usec
PCPD2	80.00	11980
DIO	-6.00	dD dD
PLZ DI10	-0.00	
PLIZ	20.00	ав
SFOZ	400.1316005	MHZ
232 R		
Fl - Acqu	usition paramet	ers
TD	128	
SF01	400.1316	MHz
FIDRES	7.812500	Ηz
SW	2.499	ppm






-	1.1	-	
- 0	34		1
	4	12	

Time

INSTRUM PROBHD

PULPROG TD

SOLVENT

FIDRES

NS DS

SWH

NUC1

P1

1H 6.75 usec 13.50 usec p2 1000.00 usec -6.00 dB 400.1313857 MHz P28 PL1SF01 ====== CHANNEL f2 ======= CPDPRG [2 garp 13C 5.90 usec NUC2 PЗ P14 P24 500.00 usec PCPI PLO PL2 PL12 SFO2 SP3 SP7 SPNA SPNA SPOA SPOA SPOE SPOF ____ GPNA GPNZ GPZ1 GPZ2 P16 F1 TD SF01

P24	2000.00	usec
PCPD2	75.00	usec
PLO	120.00	dB
PL2	-6.00	dB
PL12	23.00	dB
SFO2	100.6208180	MHz
SP3	6.74	dB
SP7	6.74	dB
SPNAM[3]	Crp60,0.5,20.1	
SPNAM[7]	Crp60comp.4	
SPOAL3	0,500	
SPOAL7	0.500	
SPOFFS3	0 Hz	
SPOFFS7	O Hz	
===== GI	RADIENT CHANNEL	1 <b></b>
GPNAM[1]	SINE.100	
GPNAM[2]	SINE.100	
GPZ1	80,00	oto
GPZ2	20.10	olo
P16	1000.00	usec
Fl - Acq	uisition paramet	lers
TD	128	
SF01	100,6208	MHz
FIDRES	141.530792	Hz
SW	180,042	ppm
FnMODE	Echo-Antiecho	1346

4 16 2281.022 Hz 1.113780 Hz 0.4489216 sec 18390.4 219.200 usec 6.00 usec 999 9 12 AQ RG  $\mathsf{DW}$ DE 6.00 usec 999.9 K 145.0000000 0.00000300 sec 1.24318099 sec 0.00172414 sec 0.03000000 sec 0.00020000 sec 0.00121950 sec 0.00147414 sec 0.0002760 sec 0 ΤE CNST2 d0D1 d4 d11 D16 DELTA DELTA1 DELTA2 INO ST1CNT ZGOPTNS ====== CHANNEL fl =======

F2 - Acquisition Parameters Date_____20110829

spect 5 mm PABBO BB/

hsqcetgpsp.2 2048

23.35

D20

	20 L	100	
200	18	0	160

120

65

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20





F2 - Acquisition Parameters 20110830 Date_ 2.42 Time INSTRUM spect 5 mm PABBO BB/ PROBHD PULPROG zgpg30 TD 65536 D20 SOLVENT NS 3072 DS SWH 26178.010 Hz FIDRES 0.399445 Hz 1.2517376 sec AQ RG 13004  $\mathsf{DW}$ 19.100 usec DE 6.50 usec ΤE 999.9 K D1 2.00000000 sec d11 0.03000000 sec DELTA 1.89999998 sec TD0 ====== CHANNEL f1 _____ NUC1 13C P1 5.90 usec PL1 -6.00 dB 100.6248425 MHz SF01 ====== CHANNEL f2 ======= CPDPRG[2 waltz16 NUC2 1H PCPD2 80.00 usec -6.00 dB PL2 20.00 dB PL1220.00 dB PL13 SFO2 400.1316005 MHz F2 SI SF Processing parameters 32768 100.6125063 MHz WDW ΕM SSB 0 LB 1.00 Hz GB 0 PC 1.40



Compound 4



F2 - Acq	uis	ition Parameters
Date_		20120222
Time		22.03
INSTRUM		spect
PROBHD	5 r	mm PABBO BB/
PULPROG		zq30
TD		65536
SOLVENT		CDC13
NS		16
DS		2
SWH		8278.146 Hz
FIDRES		0.126314 Hz
AQ		3.9583745 sec
RG		35.9
DW		60.400 usec
DE		6.00 used
TE		999.9 K
D1		1.00000000 sec
TDO		1
	сu	אאדד בו
NUC1	СП.	ANNEL II 1U
D1		6 75 usec
т т рт.1		-600 dB
SEU1		400 1324708 MH7
DECT		400.1024700 MHZ
F2 - Pro	ces	sing parameters
SI		32768
SF		400.1300000 MHz
WDW		EM
SSB	0	
LB		0.30 Hz
GB	0	
PC		1.00



Date	20120222	
Time	22.05	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	cosvapabat	
TD	2048	
SOLVENT	CDC13	
NS	1	
DS	8	
SWH	3378.378	Hz
FIDRES	1.649599	Hz
AQ	0.3031040	sec
RG	16	
DW	148.000	usec
DE	6.50	usec
TE	999.9	K
DO	0.00000300	sec
D1	1.37629998	sec
D11	0.03000000	sec
D12	0.00002000	sec
D13	0.00000400	sec
D16	0.00020000	sec
INO	0.00029600	sec
=======	CHANNEL II ====	
NUCL		
PU	6.75	usec
PI D17	6./J	usec
PI/ DII	2500.00	usec
	-6.00	dB JD
PLIV CDO1	100 1017000	ав MU-
SFOL	400.131/932	MHZ
GR	ADIENT CHANNEL	
GPNAM[1]	SINE.100	
GPZ1	10.00	20
P16	1000.00	usec
F1 - Acqu	isition paramet	cers
TD	- 128	
SF01	400.1318	MHz
FIDRES	26.393581	Hz
SW	8.443	maa







F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT	isition Paramet 20120222 22.57 spect 5 mm PABBO BB/ deptsp135 65536 CDC13	ers
NS DS SWH FIDRES AQ RG DW DE TE CNST2 D1 D2	800 4 23980.814 0.365918 1.3664256 16384 20.850 6.00 999.9 145.0000000 2.0000000 0.00344828	Hz Hz sec usec usec K sec sec
D12 TD0 ======= NUC1 P1 P12 PL0 PL1 SF01 SF01 SP2 SPNAM[2] SP0AL2 SP0FFS2	0.00002000 1 CHANNEL f1 ==== 13C 5.90 2000.00 120.00 -6.00 100.6228298 6.74 Crp60comp.4 0.500 0 Hz	sec usec usec dB dB MHz dB
EEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE	CHANNEL f2 ==== waltz16 1H 6.75 13.50 80.00 -6.00 20.00 400.1316005	usec usec usec dB dB MHz
F2 - Proc SI SF WDW SSB	essing paramete 32768 100.6127655 EM 0	ers MHz
LB GB PC	0 1.40	Ηz



Compound 4			
	_OBn	√OBn	
BnO	20	Bno	-OAII
BnO-	BnO 7	NH	ICI ₃ Ac
	0	7	
		' OH	
ppn	1		
	F2 - Acqı Date_	uisition Parame 20120222	ters
- 55	Time INSTRUM	22.59 spect	
	PROBHD PULPROG	5 mm PABBO BB/	
	TD	3000 apgl2	
	NS	CDC13 4	
<b>60</b>	DS SWH	16 3378.378	Hz
	FIDRES AO	1.126126 0.4440000	Hz sec
-	RG	6502	
05	DE	148.000	usec
- 03	TE CNST2	999.9 145.0000000	K
-	D0 D1	0.00000300 1.33679998	sec sec
	D4 D11	0.00172414	sec
- 70	D16	0.00020000	sec
	INU ZGOPTNS	0.00002/60	sec
		CHANNEL fl ====	
	NUC1 P1	1H 6.75	usec
- 75	P2 P28	13.50 1000.00	usec
	PL1	-6.00	dB MU-
3	SEOT	400.1317932	MULZ
00	CPDPRG[2	GHANNEL IZ ==== garp	
F 00	NUC2 P3	13C 5.90	usec
-	P14 P24	500.00 2000.00	usec usec
	PCPD2 PLO	75.00	usec dB
- 85	PL2	-6.00	dB
	SFO2	23.00 100.6208180	ав MHz
	SP3 SP7	6.74 6.74	dB dB
-	SPNAM [ 3 ] SPNAM [ 7 ]	Crp60,0.5,20.1 Crp60comp.4	
<b>90</b>	SPOAL3	0.500	
[	SPOFFS3	0 Hz	
-	SPUFFS/	0 п2	
L 05	===== GP GPNAM[1]	RADIENT CHANNEL SINE.100	
- 35	GPNAM[2] GPZ1	SINE.100 80.00	00
-	GPZ2 P16	20.10 1000.00	% usec
[	F1 - According	ujsition narame	tera
- 100	TD	128	MU-
	FIDRES	141.498032	Hz
	SW FnMODE	180.000 Echo-Antiecho	ppm













Acquis	ition Parameters
	20111207
	7.04
JM _	spect
) 5	mm PABBO BB/
)G	zgpg30
	65536
N.T.	CDC13
	2048
	4
~	26178.010 Hz
5	0.399445 Hz
	1.251/3/6 sec
	23170.5
	I9.100 used
	6.50 Usec
	999.9 K
	2.00000000 sec
	0.03000000 sec
	2 <del>4.</del>
=== СН	ANNEL f1 ======
855.77.47 1	13C
	5.90 usec
	-6.00 dB
	100.6248425 MHz
=== CH	ANNEL f2 ======
G[2	waltz16
	1H
	80.00 usec
	-6.00 dB
	20.00 dB
	20.00 dB
	400.1316005 MHz
rodoa	aina naramatara
rioces	32768
	100 6127592 MHz
	FM
Ω	
V	1.00 Hz
0	1.00 112
0	
	Acquis JM DG JG NT S S S S S S S S S S S S S S S S S S







F2 - Acquisition Parameters Date_ 20111208 16.13 Time INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zg30 65536 TD CDC13 SOLVENT NS 32 2 DS 8278.146 Hz SWH 0.126314 Hz FIDRES AQ 3.9583745 sec RG 114  $\mathsf{DW}$ 60.400 usec DE 6.00 usec ΤE 999.9 K D1 1.00000000 sec TDO 1 ====== CHANNEL fl ======= NUC1 1H 6.75 usec P1 PL1 -6.00 dB SF01 400.1324708 MHz F2 - Processing parameters SI 32768 SF 400.1300096 MHz ΕM WDWSSB 0 0.30 Hz LB GB 0 PC 1.00



F2 - Acqu	isition Paramet	cers
Date_	20111208	
Time	16.15	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	cosygpppqf	
TD	2048	
SOLVENT	CDC13	
NS	1	
DS	8	
SWH	3188.775	Hz
FIDRES	1.557019	Hz
AQ	0.3211264	sec
RG	64	
DW	156.800	usec
DE	6.50	usec
TE	999.9	K
DO	0.00000300	sec
D1	1.35786796	sec
D11	0.03000000	sec
D12	0.00002000	sec
D13	0.00000400	sec
D16	0.00020000	sec
INO	0.00031360	sec
	QUANNET 61	
NUC1	CHANNEL II =====	
DO	6 75	11000
ГО D1	6.75	usec
ГТ Р17	2500.00	usec
DT.1	-6.00	AB
PT.10	6.57	dB
2501	100 1317330	MH-7
SFOT	400.131/330	MILZ
===== GF	ADIENT CHANNEL	
GPNAM[1]	SINE.100	
GPZ1	10.00	00
P16	1000.00	usec
F1 - Acqu	isition paramet	lers
TD	128	
SF01	400.1317	MHz
FIDRES	24.912308	Hz
SW	7.969	ppm





F2 - Acqu	isition Paramet	ers
Date_	20111209	
Time	7.07	
TNSTRUM	spect	
DRODUD	5 mm DADDO DD/	
PROBID		
PULPROG	deptsp135	
TD	65536	
SOLVENT	CDC13	
NS	512	
DS	1	
CTUI CTUI	22000 014	II
SWH	23980.814	ΗZ
FIDRES	0.365918	Hz
AQ	1.3664256	sec
RG	16384	
DW	20.850	11960
	20:000	upee
	8.00	usec
ΤE	999.9	К
CNST2	145.0000000	
D1	2.00000000	sec
D2	0.00344828	Sec
D12	0 00002000	roa
	0.00002000	Sec
TDU	<u>1</u>	
	CHANNEL fl ====	
NUC1	13C	
P1	5 90	11560
D10	2000.00	usee
PIZ	2000.00	usec
ЪГO	120.00	aB
PL1	-6.00	dB
SF01	100.6228298	MHz
SP2	6.74	dB
SDNAM[2]	Crn60comp 4	OLD .
SENAR[2]	CIPOUCOMP.4	
SPOALZ	0.500	
SPOFFS2	0 Hz	
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
NUC2	10	
NOCZ		
P3	6.75	usec
P4	13.50	usec
PCPD2	80.00	usec
PL2	-6.00	dB
DT 12	20 00	AD
E DIZ	100 101 000	
SFOZ	400.1316005	MHZ
F2 - Proc	cessing paramete	ers
SI	32768	
SF	100.6127690	MHZ
	100.0127020 TM	11112
	EM	
SSB	U	
LB	1.00	Hz
GB	0	
PC	1.40	
2 <b>-</b>	T • 10	





 4.4
 4.2
 4.0
 3.8
 3.6
 3.4

	Cor	mpound 5		
	OPn		_OBr	1
3			2-0	
BnO	$\sum_{i=1}^{i}$	BUO	N	_OAII
BnO-		mad	Ň	
	BnO	-07		1013/10
	- Th	OAc		
ppm			_	
	F2 - Acqu Date	uisition . 201	Parame ¹ 111209	ters
- 55	Time	201	7.10	
- 55	INSTRUM		spect	
	PROBHD	5 mm PABI	30 BB/	
	TD	insqueuq	2048	
	SOLVENT		CDC13	
i passar	NS		2	
<b>⊢60</b>	SWH	337	18.378	Hz
	FIDRES	1.	649599	Hz
-	AQ	0.30	)31040	sec
-	RG DW	5 1 2	18.000	11900
-	DE	5 <del>4</del> 30	6.00	usec
- 65	TE		999.9	K
0.5	CNST2	145.00	000000	cod
	D0 D1	1.38	858902	sec
[	D4	0.00	172414	sec
	D11	0.03	000000	sec
	INO	0.00	002760	sec
- 70	ZGOPTNS	1908 B.190		
-		0113311111		
-	======== NUC1	CHANNEL I	1 ==== 1 H	
-	P1		6.75	usec
-	P2		13.50	usec
- 75	P28 P1.1	Τ	-6.00	usec dB
	SF01	400.1	318230	MHz
		0113337777		
	CPDPRG[2	CHANNEL 1	garp	
	NUC2		13C	
00	P3	ŕ	5.90	usec
00	P14 P24	20	>00.00	usec
ſ	PCPD2	2.	75.00	usec
	PLO	1	L20.00	dB
	PL2 PL12		-6.00	dB
	SFO2	100.62	208180	MHz
<b>⊢85</b>	SP3		6.74	dB
	SP7 SDNAMI31	Cr060 0	6.74 5.20 1	dB
-	SPNAM[3] SPNAM[7]	Crp60,0.	comp.4	
4	SPOAL3		0.500	
-	SPOAL7	0.47	0.500	
- 90	SPOFFS5 SPOFFS7	0 HZ 0 Hz		
		110 11-1-0		
	===== G]	RADIENT CI	HANNEL	
	GPNAM[1] GPNAM[2]	ST. STI	NE.100	
	GPZ1	511	80.00	olo
OF	GPZ2		20.10	010
<b>- 92</b>	ЧТЮ	1(	100.00	usec
	F1 - Acqu	uisition :	parame [.]	ters
	TD		128	N # T T
	FIDRES	141.	498032	mnz Hz
1	SW	18	30.000	ppm
	FnMODE	Echo-An	tiecho	

1 200	180	<b>160</b>	••••••••••••••••••••••••••••••••••••••	120





F2 – Acqu	isition Parame	ters
Date_	20111209	
Time	8.29	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zapa30	
ТD	65536	
SOLVENT	CDC13	
NS	1246	
ns	1210	
SWH	26178 010	Н⁊
FIDEES	0 399445	11Z U 7
T TOKES	1 2517276	11Z
AQ	1.231/3/0	sec
KG DM	20642.5	
	19.100	usec
DE	6.50	usec
TE	999.9	K
Dl	2.00000000	sec
D11	0.03000000	sec
TDO	1	
	CHANNEL 11 ====	
NUCI	_13C	
Pl	5.90	usec
PL1	-6.00	dB
SF01	100.6248425	MHz
	CUANNEL 60	
	CHANNEL IZ	
CEDERG[Z	Waltzio 111	
NUCZ		
PCPDZ	80.00	usec
PLZ DIJO	-6.00	aB
PL12	20.00	dB
PL13	20.00	dB
SFO2	400.1316005	MHz
E2 Date:		
FZ = Proc	cessing paramete	ers
SI	32/68	
SE	IUU.612/663	MHZ
WDW	EM	
SSB	0	5
LB	1.00	Hz
GB	0	
PC	1.40	





ÓLev

BnO

F2 - Acqu	isition Paramet	cers
Date_	20120821	
Time	10.04	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zg30	
TD	65536	
SOLVENT	CDC13	
NS	16	
DS	2	
SWH	8278.146	Hz
FIDRES	0.126314	Hz
AQ	3.9583745	sec
RG	161.3	
DW	60.400	usec
DE	6.00	usec
TE	303.0	K
D1	1.0000000	sec
TDO	1	
	CHANNEL fl ====	
NUC1	1H	
P1	6.75	usec
PL1	-6.00	dB
SF01	400.1324708	MHz
	2 17	
F2 - Proc	essing paramete	ers
SI	32768	<b>N</b> <i>A</i> T T
SE	400.1300000	MHZ
WDW	EM	
SSB	U a aa	ТТ
СР ГВ	0.30	ΗZ
GB	1 00	
РС	T•00	





Doto	20111210
Dace_ Time	20111210
тыстрим	20.02
INSIKUM DDODUD	spect
PROBED 5 N	NM PABBO BB/
PULPROG	cosygpppqI
TD	2048
SOLVENT	CDC13
NS	1
DS	8
SWH	3289.474 Hz
FIDRES	1.606188 Hz
AQ	0.3112960 sec
RG	14.3
DW	152.000 usec
DE	6.50 usec
TE	999.9 K
DO	0.00000300 sec
D1	1.36810803 sec
D11	0.03000000 sec
D12	0.00002000 sec
D13	0.00000400 sec
D16	0.00020000 sec
TNO	0 00030400 800
THO	0.00000000 500
CH7	NNFT f1 ======
NUCI	18
PO	6 75 11880
D1	6.75 usec
D17	2500 00 yang
	2300.00 usec
	-0.00 dB
PLIU	6.5/ QB
SFOL	400.131/424 MHz
CDAD	
GRAD	LENI CHANNEL ====
GPNAM[I]	SINE.IUU
GPZI	10.00 %
P16	1000.00 usec
Fl - Acquis:	ition parameters
TD	128
SF01	400.1317 MHz
FIDRES	25.699013 Hz
SW	8.221 ppm
FnMODE	QF





F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD	isition Parar 201112 21. 5 mm PABBO BI deptsp13 655	net 10 07 3/ 35 36	ers
NS DS SWH FIDRES AQ RG DW DE TE CNST2	23980.8 0.3659 1.36642 163 20.8 6. 999	13 24 14 18 56 84 50 00 .9	Hz Hz sec usec usec K
D1 D2 D12 TD0	2.000000 0.003448 0.000020	00 28 00 1	sec sec sec
======== NUC1 P1 P12 PL0 PL1 SF01 SF01 SP2 SPNAM[2] SP0AL2 SP0FFS2	CHANNEL f1 = 1 5. 2000. 120. -6. 100.62282 6. Crp60comp 0.5 0 Hz	=== 3C 90 00 00 98 74 .4 00	==== usec dB dB MHz dB
EEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE	CHANNEL f2 = waltz 6. 13. 80. -6. 20. 400.13160	=== 16 1H 75 50 00 00 00 05	usec usec usec dB dB MHz
F2 - Proc SI SF WDW SSB	cessing parame 327 100.61276 0	ete 68 90 EM	rs MHz
LB GB PC	1. 0 1.	00 40	Hz





	Co	mpound <b>7</b>	
	-OBn	Г	OBn
BnO-	NO	BnO	
BnO	-	Tod	NHCl ₂ Ac
	Buo,		
		Ó ÓAc	
Br	0.70	1	
nnm	BnO		
	F2 - Acqu	ISLLION Para	meters
-	Date_	201112	10
1	INSTRUM	spe	ct
-	PROBHD PULPROG	5 mm PABBO B hsqcetqpsp	B/ •2
60	TD SOLVENT	20 CDC	48
- 00	NS	CDC	2
-	DS SWH	3289.4	16 74 Hz
e e	FIDRES	1,6061 0,31129	88 Hz 60 sec
CE	RG	2298	.8
<b>C 00</b>	DW DE	152.U 6.	00 usec 00 usec
3	TE CNST2	999 145.00000	.9 K 00
-	D0 D1	0.000003	00 sec
-	D1 D4	0.001724	14 sec
- 70	D11 D16	0.030000 0.000200	000 sec 000 sec
	INO ZGOPTNS	0.000027	60 sec
-			
-3 19 <u>-191-</u> 91	======= NUC1	CHANNEL II =	====== 1H
- 75	P1 P2	6. 13.	75 usec 50 usec
[	P28 PL1	1000. -6.	00 usec 00 dB
-	SF01	400.13174	24 MHz
		CHANNEL f2 =	
- 80	CPDPRG[2 NUC2	ga 1:	rp 3C
	P3 P14	5.9 500.	90 usec 00 usec
-	P24 PCPD2	2000.	00 usec
-	PLO	120.	00 dB
- 85	PL2 PL12	-6.0	00 dB
	SFO2 SP3	100.62081 6.	80 MHz 74 dB
	SP7 SPNAM[3]	6. Crp60 0.5 20	74 dB .1
-	SPNAM[7]	Crp60comp	.4
<b>- 90</b>	SPOALS SPOAL7	0.5	00
	SPOFFS3 SPOFFS7	0 Hz 0 Hz	
-	===== GR	ADIENT CHANN	EL =====
	GPNAM[1]	SINE.1	00
<b>⊢ 95</b>	GENAM [2] GPZ1	SINE.1 80.	00 %
	GPZ2 P16	20. 1000.	10 % 00 usec
-	F1 – Acau	isition para	meters
	TD SFO1	1	28 08 MH7
<b>⊢100</b>	FIDRES	141.4980	32 Hz
1 C	SW FnMODE	180.0 Echo-Antiec	uu ppm ho





Compound 7



F2 - Acqu	isition Parame [.]	ters
Date_	20111211	
Time	0.09	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDC13	
NS	3072	
DS	4	
SWH	26178.010	Hz
FIDRES	0.399445	Hz
AO	1.2517376	sec
RG	6502	200
DW	19,100	115eC
DE	£ 50	USAC
TE TE	999 9	K
т <u>ы</u> П1	2 0000000	R
D11	0.03000000	Sec cod
	0.03000000	sec
IDO	Cartor S	
	CHANNEL f1 ====	
NIIC1	13C	
	5 90	11000
	-6.00	do do
CEO1	100 6249425	UD MUz
SEOL	100.0240425	МПД
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
NIIC2	ицтодто 1 Н	
PCPD2	80 00	11500
PL2	-6.00	dR
PT.12	20.00	dB
	20.00	dB dB
SEUS	400 1316005	MH7
DI UZ	100.1010000	1.11.1.2
F2 - Proc	ressing paramete	ers
ST	32768	
SF	100.6127664	MHZ
WDW	EM	11116
SSR	0	
LR	1 00	Нz
GR	0	114
PC	1 40	
L C	T • IO	



		Con	npound 7	
	5	OBn	50	DBn
	BnO	-Q	BnO	
	BnO-	Bnol -7	-07	NHCI ₃ Ac
		0.4	~	
<u> </u>	ppm	C	) ÓAc	
	BnO~	In		
	В	nÓ ol	ev	
	-64	01		
	-66	F2 - Acc	uisition Pa 2011	rameters
		Time	2011	0.12
		PROBHD	s 5 mm PABBO	BB/
۸.	-68	PULPROG TD	hmbcgplp	ndqf 2048
ŷ		SOLVENT	С	DC13 16
		DS	2000	16
	- 70	SWH FIDRES	3289	.4/4 Hz 6188 Hz
	600000	AQ RG	0.311 1	2960 sec 6384
		DW DF	152	.000 usec
	-72	TE	9	99.9 K
		CNS12 CNST13	145.000	0000
		D0 D1	0.0000 1.0081	0300 sec 9194 sec
	-74	D2 D6	0.0034 0.0500	4828 sec 0000 sec
		D16	0.0002	0000 sec
A		INO	0.0000	2240 Sec
1)	-76	======= NUC1	ECHANNEL fl	======= 1H
1		P1 P2	1.	6.75 usec 3.50 usec
ş		PL1	400 121	6.00 dB
	-78	SFOL	400.131	)424 Mn2
	Court of grants C	======= NUC2	ECHANNEL 12	======= 13C
		P3 PL2	—1	5.90 usec 6.00 dB
	- 80	SFO2	100.622	8138 MHz
		===== (	RADIENT CHA	NNEL =====
		GPNAM[1] GPNAM[2]	J SINE	.100
	- 82	GPNAM[3] GPZ1	] SINE 5	.100 0.00 %
		GPZ2 GPZ3	3	0.00 % 0.10 %
		P16	100	0.00 usec
	- 84	F1 - Acc	quisition pa	rameters
		.121)		178
	-86			





F2 – .	Acquisi	tion Para	met	ers
Date_		201209	906	
Time		22.	13	
INSTRU	JM	spe	ct	
PROBHI	D 5 n	um PABBO B	B/	
PULPR	CG	ZQ	ſ30	
TD		1000	000	
SOLVE	NT	CDC	:13	
NS			16	
DS			2	
SWH		8278.1	46	Ηz
FIDRE	S	0.0827	'81	Ηz
AQ		6.04000	000	sec
RG		22	2.6	
DW		60.4	100	usec
DE		6.	00	usec
TE		303	3.0	K
D1		1.000000	000	sec
TDO			1	
	=== CH2	ANNEL fl =		
NUC1			1H	
P1		6.	75	usec
PL1		-6.	00	dB
SF01		400.13247	08	MHz
F2 – 1	Process	sing param	iete	ers
SI		327	68	
SF		400.13000	00	MHz
WDW			ΕM	
SSB	0			
LB		Ο.	30	Ηz
GB	0			
PC		1.	00	



5	2	2		
4	9	J		







F2 - Acqu	isition Paramet	ers
Date_	20120907	
Time	0.42	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
DITIDROC	dopt op 125	
FOLFROG	depuspiss	
	65536	
SOLVENT	CDC13	
NS	2000	
DS	4	
SWH	23980.814	Ηz
FIDRES	0.365918	Ηz
AO	1.3664256	Sec
PC	16384	000
NG	20.0504	
DW	20.030	usec
DE	6.00	usec
TE	303.0	K
CNST2	145.0000000	
D1	2.00000000	sec
D2	0.00344828	sec
D12	0,00002000	sec
	0.00002000	Sec
IDU		
	CHANNEL 11 ====	
NUC1	13C	
P1	5.90	usec
P12	2000.00	usec
PT.0	120.00	dB
PT.1	-6.00	dB
	100 6220200	MUZ
SPOL	100.0220290	MIL Z
SPZ	6.74	aB
SPNAM[2]	Crp60comp.4	
SPOAL2	0.500	
SPOFFS2	0 Hz	
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
MUC2	Narczio 1u	
NOCZ		
P3	6.75	usec
P4	13.50	usec
PCPD2	80.00	usec
PL2	-6.00	dB
PL12	20.00	dB
SEO2	400.1316005	MHZ
0102	100.1010000	11112
<b>D</b> 2 <b>D</b> 200		
rz - Proc	essing paramete	:15
ST	32768	
SF	100.6127690	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	nor and a second
DC	1 10	
FU	I.40	





	Co	mpound <b>8</b>
	OBn	<u>∽</u> OBn
D		BnO O
BnO ⁻	L-1	
	BnO	NHCI3AC
	04	
	-	O OAc
Bn	0	
ppm	BnÓ d	Н
	U	
66	F2 - Acqu	isition Parameters
- 33	Time	0.44
-	INSTRUM	spect 5 mm PABBO BB/
-	PULPROG	hsqcetgpsp.2
-	TD Solvent	2048 CDC13
- 60	NS	4
	DS SWH	16 3205.128 Hz
-	FIDRES	1.565004 Hz
	AQ RG	0.3194880 sec 2298.8
- 65	DW	156.000 usec
	DE TE	6.00 usec 303.0 K
	CNST2	145.000000
-	DU D1	1.37220502 sec
- 70	D4	0.00172414 sec
-	D11 D16	0.03000000 sec 0.00020000 sec
	IN0 RCODTNC	0.00002760 sec
	ZGUPINS	
- 75	======= NUC1	CHANNEL fl ===================================
	P1	6.75 usec
-	P2 P28	13.50 usec
-	PL1	-6.00 dB
L 00	SFOI	400.131/466 MHz
00		CHANNEL f2 ======
-	CPDPRG[2 NUC2	garp 13C
	P3	5.90 usec
05	P14 P24	2000.00 usec
- 85	PCPD2 PLO	75.00 usec
	PL2	-6.00 dB
	PL12 SFO2	23.00 dB 100.6208180 MHz
-	SP3	6.74 dB
- 90	SP/ SPNAM[3]	6./4 dB Crp60,0.5,20.1
	SPNAM[7]	Crp60comp.4
	SPOAL3 SPOAL7	0.500
	SPOFFS3	0 Hz
- 95	SECEESI	0 HZ
	===== GR GPNAM[1]	ADIENT CHANNEL ===== SINE 100
	GPNAM [2]	SINE.100
-	GPZ1 GPZ2	80.00 % 20.10 %
-100	P16	1000.00 usec
	F1 - Acqu	isition parameters
	TD	512
	FIDRES	35.374508 Hz
	SW Frmode	180.000 ppm Echo-Antiecho
ppm	T IIIIODE	TOUC INCLECITO





Compound 8 OBn BnO Bn⊖ BnO→ NHCl₃Ac Br OAc BnO_ BnÓ

OH

F2 - Acqu	isition Paramet	ters
Date_	20120907	
Time	6.22	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	0Epqpz	
TD	65536	
SOLVENT	CDC13	
NS	5000	
DS	4	
SWH	26178.010	Hz
FIDRES	0.399445	Hz
AO	1.2517376	Sec
RG	9195.2	000
	19 100	11900
	£ 50	usee
	303 0	K K
т <u>ы</u> П1	2 0000000	R
D11	2.00000000	sec
	0.03000000	sec
IDO	<u>1</u> 2	
	CUNNET f1	
NUC1	13C	
D1	5 90	11000
	-6.00	usec Jp
CEO1	100 6249425	UD MUr
SPOT	100.0240425	ΜΠΖ
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
NUC2	14	
PCPD2	80 00	11500
PT.2	-6.00	dR
PT.12	20.00	dB
DT 13	20.00	dB dB
SEUS	400 1316005	MU-7
DF OZ	400.1310003	14112
$F^2 - Proc$	ressing paramete	ers
ст <u>гго</u> (	32768	- L O
2F	100 6127690	MHマ
ស្មាស		1-11-1 25
C C D	∩ EM	
TR	1_00	Ц <i>-</i> 7
	D	ΠΖ
UD DC	1 10	
FC	L.40	







	Compound 8				
	BnO- BnC	OBn DO BnO BnO	OBn OODOAII NHCI ₃ Ac		
	ppm	0 0	Ac		
	- <b>55</b>	BnO OH			
	- 60	F2 - Acquisition	n Parameters		
	- 65	Time INSTRUM PROBHD 5 mm PA PULPROG hmbco TD SOLVENT NS	6.24 spect ABBO BB/ gplpndqf 2048 CDC13 16		
	- 70	DS SWH 3 FIDRES 3 AQ 0. RG DW DE	16 3205.128 Hz 1.565004 Hz .3194880 sec 16384 156.000 usec 6.00 usec		
	- 75	TE CNST2 145 CNST13 10 D0 0.0 D1 1.0 D2 0.0	303.0 K .0000000 .0000000 00000300 sec 00000000 sec 00344828 sec		
0	- 80	D16 0.0 INO 0.0	00020000 sec 00020000 sec 00002240 sec		
	- 85	===== CHANNEI NUC1 P1 P2 PL1 SF01 400	1H 6.75 usec 13.50 usec -6.00 dB .1317466 MHz		
	- 90	====== CHANNEI NUC2 P3 PL2 SFO2 100	」f2 ======= 13C 5.90 usec −6.00 dB .6228138 MHz		
	- <b>95</b>	===== GRADIENT GPNAM[1] : GPNAM[2] : GPNAM[3] : GPZ1 GPZ2 GPZ3 P16	CHANNEL ===== SINE.100 SINE.100 50.00 % 30.00 % 40.10 % 1000.00 usec		
	- 100	F1 - Acquisitio: TD	n parameters 512		
	- 105				



## Compound 9



F2 - Acc	quis.	ition Parameters
Date_	2 <b></b>	20111214
Time		17.51
INSTRUM		spect
PROBHD	5 I	mm PABBO BB/
PULPROG		zg30
TD		65536
SOLVENT		CDC13
NS		32
DS		2
SWH		8278.146 Hz
FIDRES		0.126314 Hz
AQ		3.9583745 sec
RG		90.5
DW		60.400 used
DE		6.00 used
TE		999.9 K
D1		1.00000000 sec
TDO		1
	- 011	אזאזדיד ב1
	- Сп.	ANNEL II 1u
D1		6 75 used
рт.1		-6 00 dB
SEO1		400 1324708 MH7
DEOL		400.1024700 miz
F2 - Pro	oces	sing parameters
SI		32768
SF		400.1300000 MHz
WDW		ΕM
SSB	0	
LB		0.30 Hz
GB	0	
PC		1.00







F2 - Acquis	ition Paramet	ers
Date_	20111214	
Time	17.52	
INSTRUM	spect	
PROBHD 5 r	mm PABBO BB/	
PULPROG	cosvapppaf	
TD	2048	
SOLVENT	CDC13	
NG	1	
	A A	
SMH	3188 775	비 7
UNII UTDDDC	1 557019	
A DRES	1.JJ/01J	п <i>2</i>
AV DC	0.5211204	sec
NG Du	156 000	11000
	136.000	usec
UL TR	0.30	usec
1E DO	999.9	r
	1.00000300	sec
DI	1.35/86/96	sec
DII	0.03000000	sec
DIZ	0.00002000	sec
D13	0.00000400	sec
D16	0.00020000	sec
INO	0.00031360	sec
2003		
===== CH	ANNEL 11 ====	
NUC1	1H	
PO	6.75	usec
P1	6.75	usec
P17	2500.00	usec
PL1	-6.00	dB
PL10	6.57	dB
SF01	400.1316912	MHz
===== GRAD	IENT CHANNEL	
GPNAM[1]	SINE.100	
GPZ1	10.00	olo
P16	1000.00	usec
Fl - Acquis	ition paramet	ers
TD	128	
SF01	400.1317	MHz
FIDRES	24.912308	Ηz
SW	7.969	ppm
FnMODE	QF	42 4 <del>37</del> 0







DS 4 SWH 23980.814 Hz FIDRES 0.365918 Hz AQ 1.3664256 sec RG 16384 DW 20.850 used DE 6.00 used TE 999.9 K CNST2 145.0000000 sec D2 0.00344828 sec D12 0.00002000 sec TD0 1 ======= CHANNEL f1 ======= NUC1 13C P1 5.90 used P12 2000.00 used P12 2000.00 used P10 120.00 dB P11 -6.00 dB SF01 100.6228298 MHz SP2 6.74 dB SPNAM[2] Crp60comp.4 SPOAL2 0.500 SPOFFS2 0 Hz ====== CHANNEL f2 ====== CPDPRG[2 waltz16 NUC2 1H P3 6.75 used P4 13.50 used PL2 -6.00 dB PL1 20.00 dB PL2 -6.00 dB PL2 -6.00 dB SF02 400.1316005 MHz F2 - Processing parameters SI 32768 SF 100.6127690 MHz WDW EM	F2 - Acc Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS	uisition Parameters 20111215 13.46 spect 5 mm PABBO BB/ deptsp135 65536 CDC13 1500
======       CHANNEL f1 =====         NUC1       13C         P1       5.90 used         P12       2000.00 used         PL0       120.00 dB         PL1       -6.00 dB         SF01       100.6228298 MHz         SP2       6.74 dB         SPNAM[2]       Crp60comp.4         SPOAL2       0.500         SPOFFS2       0 Hz         =====       CHANNEL f2 ======         CPDPRG[2       waltz16         NUC2       1H         P3       6.75 used         P4       13.50 used         PL2       -6.00 dB         PL12       20.00 dB         SFO2       400.1316005 MHz         F2       Processing parameters         SI       32768         SF       100.6127690 MHz         WDW       EM	DS SWH FIDRES AQ RG DW DE TE CNST2 D1 D2 D12 TD0	4 23980.814 Hz 0.365918 Hz 1.3664256 sec 16384 20.850 usec 6.00 usec 999.9 K 145.0000000 2.00000000 sec 0.00344828 sec 0.00002000 sec 1
======       CHANNEL f2 ======         CPDPRG[2       waltz16         NUC2       1H         P3       6.75 used         P4       13.50 used         PCPD2       80.00 used         PL2       -6.00 dB         PL12       20.00 dB         SF02       400.1316005 MHz         F2       Processing parameters         SI       32768         SF       100.6127690 MHz         WDW       EM	====== NUC1 P12 PL0 PL1 SF01 SP2 SPNAM[2] SPOAL2 SPOFFS2	= CHANNEL f1 ======= 13C 5.90 usec 2000.00 usec 120.00 dB -6.00 dB 100.6228298 MHz 6.74 dB Crp60comp.4 0.500 0 Hz
F2 - Processing parameters SI 32768 SF 100.6127690 MHz WDW EM	======= CPDPRG[2 NUC2 P3 P4 PCPD2 PL2 PL12 SFO2	= CHANNEL f2 ======= waltz16 1H 6.75 usec 13.50 usec 80.00 usec -6.00 dB 20.00 dB 400.1316005 MHz
LB 1.00 Hz GB 0 PC 1.40	F2 - Pro SI SF WDW SSB LB GB PC	0 0 0 0 0 1.00 Hz 0 1.00 Hz 0 1.40









F2 - Acqu	isition Parame	ters
Date	20111216	
Time	0.34	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	20Epq30	
TD	65536	
SOLVENT	CDC13	
NS	6000	
DS	4	
SWH	26178.010	Hz
FIDRES	0.399445	Hz
AO	1.2517376	sec
RĜ	9195.2	
DW	19.100	usec
DE	6.50	usec
TE	999.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TDO	1	
	CHANNEL fl ====	
NUC1	13C	
P1	5.90	usec
PL1	-6.00	dB
SF01	100.6248425	MHz
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	-6.00	dB
PL12	20.00	dB
PL13	20.00	dB
SFO2	400.1316005	MHz









F2 – Acqu	isition Paramet	ters
Date_	20111216	
Time	0.37	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	hmbcaplppdaf	
TD	2048	
COLVENT	2040	
NOLVENI	CDCI3	
NS	16	
DS	16	ACARCEST ME
SWH	3140.704	Hz
FIDRES	1.533547	Hz
AQ	0.3260416	sec
RG	16384	
DW	159.200	usec
DE	6.00	115eC
ΥΓ ΥΓ	999 9	K
CNCTO	145 000000	K
CNSIZ	145.0000000	
CNST13	10.000000	
DO	0.00000300	sec
D1	0.99385601	sec
D2	0.00344828	sec
D6	0.05000000	sec
D16	0.00020000	sec
TNO	0 00002240	Sec
THO	0.00002240	500
	CHANNET fl	
	CHANNEL II	0
NUCI		
P1	6.75	usec
P2	13.50	usec
PL1	-6.00	dB
SF01	400.1316999	MHz
	CHANNEL f2 ====	
NUC2	130	
PS	5 90	11900
	5.90	USEC AD
E LIZ	-0.00	UD MII-
SFOZ	100.6228138	MHZ
===== GI	RADIENT CHANNEL	
GPNAM[1]	SINE.100	
GPNAM[2]	SINE.100	
GPNAM[3]	SINE.100	
GPZ1	50.00	00
GP72	30.00	2
CD73	40.10	9
GE 45 D1C	40.10	0
P10	1000.00	usec
F,1 – Ycdi	uisition parame	ters
TD	128	
SF01	100.6228	MHz
FIDRES	174.386154	Hz
SW	221.833	mag
FnMODF	0F	T. T. Sat
T TILINI I I I		





F2 - A	Acquisi	ltion	Parame	eters
Date_		2	0120419	9
Time			3.39	)
INSTRU	Μ		spect	
PROBHD	) 5 m	nm PAI	BBO BB/	
PULPRO	G		zg30	)
TD			65536	5
SOLVEN	ΙT		CDCl3	3
NS			10	5
DS			2	2
SWH		8	278.140	5 Hz
FIDRES	1	0	.126314	l Hz
AQ		3.	9583745	5 sec
RG			28.5	5
DW			60.400	) usec
DE			6.00	) usec
TE			300.0	) K
D1		1.0	0000000	) sec
TDO			-	1
	0117		<b>C</b> 4	
	=== CH <i>A</i>	ANNEL	±_ ===	
NUCL D1				1
PL DT 1			6.73	) usec
PLL CRO1		100	- 6.Ul	
SEUL		400.	1324700	5 MHZ
F2 - F	rocess	ina 1	paramet	ers
ST I	TOCCDE	, Euro	32768	3
SF		400.	1300000	) MHz
WDW		100.	, 5 5 5 5 5 5 ± 1 도	V V
SSB	0			
LB			0.30	) Hz
GB	0		C 816877 (	998 - 1979-748 T.C. (1)
PC	1045401		1.00	)





F2 - Acqu	isition Parame [.]	ters
Date_	20120419	
Time	3.41	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	cosygpppqf	
TD	2048	
SOLVENT	CDC13	
NS	1	
DS	8	
SWH	3324.468	Hz
FIDRES	1.623275	Hz
AO	0.3080192	sec
RG	12.7	
DW	150,400	usec
DE	6.50	usec
TE	300.0	K
00	0.00000300	Sec
до 1 П	1.37220395	Sec
D11	0.03000000	Sec
D12	0.00002000	Sec
D13	0.00000400	SPC
	0.00000100	cod
DI6 TNO	0.00020000	Sec
INO	0.00020000	sec
DI6 IN0	0.00020000 0.00030080 CHANNEL fl ====	sec sec
INO =======	0.00020000 0.00030080 CHANNEL f1 ==== 1H	sec sec
INO ======= v NUC1 PO	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75	sec sec =====
D16 IN0 ======= ' NUC1 P0 P1	0.00020000 0.00030080 CHANNEL fl ==== 1H 6.75 6.75	sec sec usec usec
D16 IN0 ======== ' NUC1 P0 P1 P17	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00	sec sec usec usec usec usec
D16 IN0 ======= ' NUC1 P0 P1 P17 PL1	0.00020000 0.00030080 1H 6.75 6.75 2500.00 -6.00	sec sec usec usec usec dB
D16 IN0 ======== ' NUC1 P0 P1 P17 PL1 PL10	0.00020000 0.00030080 1H 6.75 6.75 2500.00 -6.00 6.57	sec sec usec usec usec dB dB
D16 IN0 ======= NUC1 P0 P1 P17 PL1 PL10 SF01	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012	sec sec usec usec usec dB dB MHz
D16 IN0 ========= NUC1 P0 P1 P17 P17 PL1 PL10 SF01	0.00020000 0.00030080 CHANNEL fl ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012	sec sec usec usec usec dB dB dB MHz
DI6 IN0 ====== 0 NUC1 P0 P1 P17 PL1 PL10 SF01 ===== GR.	0.00020000 0.00030080 CHANNEL fl ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL	sec sec usec usec usec dB dB dB MHz
D16 IN0 ====== NUC1 P0 P1 P17 PL1 PL10 SF01 ===== GR. GPNAM[1]	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100	sec sec usec usec usec dB dB MHz =====
D16 IN0 ====== NUC1 P0 P1 P17 PL1 PL10 SF01 ===== GR. GPNAM[1] GPZ1	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00	sec sec usec usec dB dB MHz =====
D16 IN0 ======= 0 NUC1 P0 P1 P17 P17 P17 PL1 PL10 SF01 ===== GR. GPNAM[1] GPZ1 P16	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00	sec sec usec usec usec dB dB MHz ===== % usec
D16 IN0 ====== NUC1 P0 P1 P17 P17 PL1 PL10 SF01 ===== GR. GPNAM[1] GPZ1 P16	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00	sec sec usec usec usec dB dB MHz =====
D16 IN0 ====== NUC1 P0 P1 P17 P17 P17 PL1 PL10 SF01 ===== GR. GPNAM[1] GPZ1 P16 F1 - Acqu	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00	sec sec usec usec usec dB dB MHz ===== % usec ters
DI6 INO ====== NUC1 P0 P1 P17 P17 P17 PL1 PL10 SFO1 ===== GR. GPNAM[1] GPZ1 P16 F1 - Acqu TD	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00 isition parame 128	sec sec usec usec usec dB dB MHz ===== % usec ters
DI6 INO ====== NUC1 P0 P1 P17 P17 P17 PL1 PL10 SF01 ===== GR. GPNAM[1] GPZ1 P16 F1 - Acqu TD SF01	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00 isition parame 128 400.1318	sec sec usec usec usec dB dB MHz ===== % usec ters MHz
DI6 INO ====== NUC1 P0 P1 P17 P17 P17 P17 P11 P10 SF01 F1 - Acqu TD SF01 F1DRES	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00 isition parame 128 400.1318 25.972406	sec sec usec usec usec dB dB MHz ===== % usec ters Hz Hz
DI6 INO ====== NUC1 P0 P1 P17 P17 PL1 PL10 SFO1 ===== GR. GPNAM[1] GPZ1 P16 F1 - Acqu TD SFO1 F1 DRES SW	0.00020000 0.00030080 CHANNEL f1 ==== 1H 6.75 6.75 2500.00 -6.00 6.57 400.1318012 ADIENT CHANNEL SINE.100 10.00 1000.00 isition parame 128 400.1318 25.972406 8.308	sec sec usec usec usec dB dB MHz ===== % usec ters ters MHz Hz ppm









F2 - Acqu	isition Paramet	ers
Time	4.39	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	deptsp135	
TD	65536	
SOLVENT	CDC13	
NS	900	
DS	4	
SWH	23980.814	Hz
FIDRES	0.365918	Hz
AQ	1.3664256	sec
RG	16384	
DW	20.850	usec
DE	6.00	usec
TE	300.0	K
CNST2	145.0000000	
D1	2.0000000	sec
D2	0.00344828	sec
D12	0.00002000	sec
TDO	1	
	CUNNET 61	
NUC1	CHANNEL II	
NUCI D1	E 90	11000
F1 D12	2000 00	usec
PIZ DI A	2000.00	dB
PT.1	-6.00	dB
SFOL	100.6228298	MH7
SP2	6.74	dB
SPNAM[2]	Crp60comp.4	
SPOAL2	0,500	
SPOFFS2	0 Hz	
	CHANNEL f2 ====	
CPDPRG[Z	Waltzio	
NUCZ D2		
P3 D4	0./D 12 E0	usec
P4 DCDD2	20.00	usec
DT 2	-6.00	dB
	20.00	dB
SFO2	400.1316005	MHz
	2007 - 2008/03/000-2007-03 100 2 - 2008/05/07	
F2 - Proc	cessing paramete	ers
SI	32768	
SF	100.6127690	MHz
WDW	EM	
SSB	0	17 <u>171</u> 1500
LB	1.00	ΗZ
The SEA ST	Control (Control (Contro) (Control (Contro) (Control (Contro) (Con	
BC	1 10	









F2 - A	Acquis	ition	Par	amet	cers
Date_		20	0120	419	
Time			8	.44	
INSTRU	JM		sp	ect	
PROBHI	) 5 :	mm PAE	зво	BB/	
PULPRO	)G		zap	q30	
TD			65	536	
SOLVEN	TΓ		CD	C13	
NS	66.70		4	200	
DS				4	
SWH		26	178.	010	Нz
FIDRES	3	20. 0	299	445	н <u>г</u> Н 7
	,	1 1	2517	376	500
PC		2• ⊥ 7	1720 1720	570	sec
NG		2	10 10	100	11000
			13.	100 50	usec
			20	.50	usec
		0.00	0.0	0.0	ĸ
		2.00	0000	000	sec
DII		0.0.	3000	000	sec
TDO				1	
	au	* * * * * * *	<b>C1</b>		
======	=== CH.	ANNEL	ΪĹ	====	====
NUCI			2	13C	
Pl.			5	.90	usec
PLl		120202	-6	.00	dB
SF01		100.	6248	425	MHz
			60		
	=== CH.	ANNEL	t2 :		
CPDPRC	3 L Z	-V	valt	Z16	
NUC2				1H	
PCPD2			80	.00	usec
PL2			-6	.00	dB
PL12			20	.00	dB
PL13			20	.00	dB
SFO2		400.1	1316	005	MHz
F2 - E	'roces	sing p	para	mete	ers
SI			32	768	
SF		100.0	6127	690	MHz
WDW				ΕM	
SSB	0				
LB			1	.00	Hz
GB	0				
PC			1	.40	





F2 – Acqu	lisiti	lon Pa	aramet	lers
Date_		201	40729	
ſime			12.56	
INSTRUM		2	spect	
PROBHD	5 mm	PABBO	) BB/	
PULPROG			zg30	
ſD			65536	
SOLVENT		(	CDC13	
JS			16	
DS			2	
SWH		827	8.146	Ηz
FIDRES		0.12	26314	Ηz
ΑQ		3.95	83745	sec
RG			114	
W		6	0.400	usec
ЭE			6.00	usec
ſΕ		10	303.0	K
01	Ĩ	L.000	00000	sec
ed0			1	
		61	-	
========	CHANN	VEL I.	1 ====	
NUCI			1H 7 10	
21 57 1			7.10	usec
ГЦЦ 7 ПО 1	Λ (	· • • • • •	-6.00	QB MII-
SEOI	4(	10.13.	Z4708	MHZ
$r^2 - Drow$	rocair	a nai	ramoto	NY C
	-Cooti	iy pai	22768	210
기 국 규	Дſ	10 13		MH7
JT NDM	ЧV		00000 ТМ	1.111 2
ICN ICR	$\cap$		1.1	
R	0		0 30	Нァ
 FR	0		0.00	112
	U		1.00	
			T.00	


Compound	11			_							
√OBn SnO BnO	-1	2	- C	)Br O	ו		~~	76.0		~-	
	)- ]			N	м Н(	) v Cla	Ac	;(NI ;	2n)	CF	3
BnO	0						8 - 7				
	Ac										
BnO											
BUO O											
10-2-07											
BnO ÓLev		are n	-					#2017-0200			
2 – Acquisiti ate_	.or 2	р 20	P; 1,	ar 40	a: 7	m∈ 2 9	et 9	er	S		
ime			4	23		30	5				
ROBHD 5 mm	PÆ	AB.	ہ B	sp D	e Bi	ct B/	-				
ULPROG C	205	sy	g]	pp	p	qı	Ē				
D Olvent			(	2 CD		48 12	3				
S			1		Ŭ	- 1	L				
S Wh	-	31	4 (	Ο.	7	۶ ۵ ۷	3 1	Ηz			
IDRES	, , , , , , , ,	L .	5	33	5	47	7	Ηz			
Q	0.	.3	2	60	4	10	5 1	se	С		
W		1	5	9.	2	0(	т С	us	ec		
E			23	0 ۶ م		50	) 1	us v	ec		
0 0	.(	00	0	00	3	00	)	r se	C		
1 1		35	3	77	2	04	1	se	C		
12 0	•••	) 3 ) 0	0	00 02	0	00	)	se se	C C		
13 0	.(	00	0	00	4	00	)	se	С		
16 U NO O			0:	20 31	8	4 (	)	se se	C		
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—————— Снами UC1	L	_	<u> </u>		—	 1 F	 -				
0				7		1(	) )	us	ec		
_ 17		2	5	, 00	•	0(	)	us us	ec		
L1 T10			8	-6	•	0(	)	dB dB	,		
F01 40	0.	. 1	3:	0 16	4	1× 52	2	ав MH	, Z		
GRADIEN	T.	C	U :	ע ע	'NT	F T	. 8			_	
PNAM[1]		SI	NI	Ξ.	1	00	)				
PZ1 16		শ		10	٠	00	) 1	२ २	~~		
ΤO		<u></u>	0	00	3 <b>9</b> 39	00	)	us	ec		
1 - Acquisiti D	or	ר	p	ar	a: 5	m∈ 1 ≤	et	er	S		
F01	Z	10	0	.1	3	10	5	MH	Z		
IDRES	(	5.	1;	34	1	8 7 6	7 2	Hz	~		
nMODE				1.	0	ч : QE	י ד	Ъb	ΊLL		





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•		•	$\infty$	9	0	$\infty$	[	ഗ	ഹ	$\sim$	$\infty$	$\infty$	$\infty$	$\infty$	0	$\mathcal{O}$	$\sim$	$\infty$	$\sim$	5	$\mathcal{O}$	5
	4	0		٠	•	•			•	•	•	•	٠	•	•	•	•	•	•	•	٠	j
$\sim$	$\sim$	$\vdash$	5	Ч	5	$\sigma$	8	$\sim$	$\sim$	$\sim$	ഹ	$\infty$		5	$\infty$	$\infty$	$\infty$	4	0	$\bigcirc$	$\infty$	$\infty$
-	-	-	0	$\infty$	$\sim$	$\sim$	[	[	$\sim$	$\[ \]$	$\sim$	[	[	6	6	9	6	ഹ	$\sim$	$\sim$	-	<del>ر</del>
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## Compound 11



Compound 11 OBn -OBn BnO ∽ OC(NPh)CF₃ NHCl₃Ac Bn( ÓAc BnO BnO BnO TO BnO OLev F2 - Acquisition Parameters Date_ 20140730 Time 1.22 INSTRUM spect PROBHD 5 mm PABBO BB/ hsqcetgpsp.2 PULPROG TD 2048 SOLVENT CDC13 NS 4 DS 16 SWH 3140.704 Hz FIDRES 1.533547 Hz AQ 0.3260416 sec RG 18390.4  $\mathsf{DW}$ 159.200 usec DE 6.00 usec ΤE 303.0 K CNST2 145.0000000 D0 D1 D4 0.00000300 sec 1.36606097 sec 0.00172414 sec D11 0.03000000 sec D16 0.00020000 sec 0.00002760 sec INO ZGOPTNS ====== CHANNEL fl ======= NUC1 1H P1 7.10 usec Ρ2 14.20 usec P28 1000.00 usec PL1 -6.00 dB 400.1316452 MHz SF01 ====== CHANNEL f2 ======= CPDPRG[2 garp NUC2 13C РЗ 6.25 usec P14 500.00 usec P24 2000.00 usec PCPD2 75.00 usec PL0 120.00 dB

					12 18 18 18













F2 - Acqu	isition Paramet	cers
Date_	20120619	
Time	17.49	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zg30	
TD	65536	
SOLVENT	CDC13	
NS	32	
DS	2	
SWH	8278.146	Ηz
FIDRES	0.126314	Hz
AQ	3.9583745	sec
RG	35.9	
DW	60.400	usec
DE	6.00	usec
TE	299.3	K
Dl	1.00000000	sec
TDO	1	
	CHANNEL fl ====	
NUCL	1H	
PL	6.75	usec
PLL	-6.00	dB
SFOL	400.1324708	MHZ
	accing normation	
ez - Ploc	essing paramete	er S
сг	100 1300000	MU7
	400.1300000 FM	P111 Z
SSB	0	
LR	0 30	Hz
GR	0	
PC	1.00	
13411305345120	+.00	

ppm





F2 - Acquis	ition Parameters
Date_	20120619
Time	17.51
INSTRUM	spect
PROBHD 5 1	nm PABBO BB/
PULPROG	cosvapppaf
ТО	2048
SOLVENT	CDC13
NS	1
ns	4 8
SMH	3289 171 47
UNII VIII VIII	1 606188 Hz
	0 3112960 000
AQ DC	0.5112900 Sec
NG	152 000 1000
	152.000 USEC
	0.50 USEC
1E DO	299.3 K
	1.200100300 sec
	1.36810803 Sec
DII	0.03000000 sec
D12	0.00002000 sec
D13	0.00000400 sec
D16	0.00020000 sec
INO	0.00030400 sec
===== CH/	ANNEL II ======
NUCI	1H
PU	6./5 usec
P1	6.75 usec
P17	2500.00 usec
PL1	-6.00 dB
PL10	6.57 dB
SF01	400.1317587 MHz
===== GRAD	IENT CHANNEL =====
GPNAM[1]	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
<b>m</b> a a 1	
FI - Acquis	ition parameters
	128
SFOI	400.1318 MHZ
FIDRES	25.699013 Hz
SW	8.221 ppm
f'nMODE	QF







1.40



3.8 3.6 4.6 4.4 4.2 4.0



Compound 12 BnO₂ BnO BnO 12)2N3 NHCl₃Ac OAc BnO BnO BnO~ BnÓ

OLev

F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS	isition Parame 20120620 5.52 spect 5 mm PABBO BB/ zgpg30 65536 CDC13 4500	ters
DS SWH FIDRES AQ	4 26178.010 0.399445 1.2517376	Hz Hz sec
RG DW DE TE D1 D11 TD0	16384 19,100 6.50 300.0 2.00000000 0.03000000 1	usec usec K sec sec
======= NUC1 P1 PL1 SFO1	CHANNEL f1 ==== 13C 5.90 -6.00 100.6248425	usec dB MHz
CPDPRG[2 NUC2 PCPD2 PL2 PL12 PL13 SFO2	CHANNEL f2 ==== waltz16 1H 80.00 -6.00 20.00 20.00 400.1316005	usec dB dB dB dB MHz
F2 - Prod SI SF WDW SSB LB GB	cessing paramet 32768 100.6127690 EM 0 1.00	ers MHz Hz
PC	1.40	



	(	Compound 12
	_OBn	OBn
	Bno-10	BnO
	BnO	NHCl ₃ Ac
	Buo	
		Ý ÓAc
	BnO.	27
	BnO	
_ ppm	Dilo	0
-	BnO	1
	BnÓ	l Dlev
		ugition Doro
	Date	201206
- 55	Time	5.
	INSTRUM	spe
5	PROBHD	5 mm PABBO B. hmbcaplond
60	TD	20
- 00	SOLVENT	CDC
2	NS	
	SWH	3360.2
- 65	FIDRES	1.6407
	AQ	0.30474
5	RG	163 178 8
	DE	140.0 6.
- 70	TE	299
	CNST2	145.00000
	DO	LO.00000
·	D1	1.014335
- 75	D2	0.003448
	D6 D16	0.050000
-	INO	0.000022
- 80		
	======= NUC1	CHANNEL 11 =
	P1	6.
	P2	13.
- 85	PL1 SFO1	-6.
	SEUL	400.13179
		CHANNEL f2 =
1	NUC2	1
- 90	PJ2	-6.
-	SFO2	100.62281
-	<b>AT</b>	
- 05	===== GF GPNAM[1]	STNE.1
	GPNAM[2]	SINE.1
-	GPNAM[3]	SINE.1
	GPZ1 GPZ2	5U. RA
-100	GPZ3	40.
	P16	1000.
ppm		



F2 – Acqu	uisit	ion Pa	ramet	ers
Date		2012	20822	
Time		1	.8.51	
INSTRUM		S	spect	
PROBHD	5 mm	PABBC	BB/	
PULPROG			zq30	
TD		ę	55536	
SOLVENT		C	CDC13	
NS			16	
DS			2	
SWH		8278	8.146	Hz
FIDRES		0.12	26314	Hz
AQ		3.958	33745	sec
RG			35.9	
DW		6(	0.400	usec
DE			6.00	usec
TE		ĺ.	303.0	Κ
D1		1.0000	00000	sec
TDO			1	
	01133			
	CHAN	NEL IJ	==== ۱ TT	
NUCL D1				11000
			6.75	usec ap
CRO1	1	- 100 100	-0.00	UB MII-
SEUL	<u>.</u>	100.132	24708	MHZ
F2 - Prod	cessi	ng par	amete	ers
SI			32768	
SF	4	100.130	0586	MHz
WDW			ΕM	
SSB	0			
LB			0.30	Hz
GB	0			
DO			1 0 0	





F2 - Acquisi	ltion Parameters
Date_	20120822
Time	18.53
INSTRUM	spect
PROBHD 5 m	m PABBO BB/
PIILPROC	cosycoport
	COSYGPPPQI
	2048
SOLVENT	CDC13
NS	.1
DS	8
SWH	3360.215 Hz
FIDRES	1.640730 Hz
AO	0.3047424 sec
RG	16
DW	148 800 11990
ม ม	140.000 usee
	0.50 usec
I E	303.0 K
DO	0.00000300 sec
D1	1.37425196 sec
D11	0.03000000 sec
D12	0.00002000 sec
D13	0.00000400 sec
D16	0.00020000 sec
TNO	0.00029760 sec
СНД	NNFT. f1 =======
NEIC1	14
DO	£ 75 NGCC
FU D1	6.75 usec
PI D17	6./5 usec
P1/	2500.00 usec
PL1	-6.00 dB
PL10	6.57 dB
SF01	400.1317973 MHz
===== GRAD]	ENT CHANNEL =====
GPNAM[1]	CINE 100
GP7.1	SINE.IUU
P16	10.00 %
TTA	10.00 %
	10.00 % 1000.00 usec
TI Decester	10.00 % 1000.00 usec
F1 - Acquis:	10.00 % 1000.00 usec ition parameters
F1 - Acquis: TD	10.00 % 1000.00 usec ition parameters 128
F1 - Acquis: TD SF01	10.00 % 1000.00 usec Ltion parameters 128 400.1318 MHz
F1 - Acquis: TD SF01 FIDRES	10.00 % 1000.00 usec 1100 parameters 128 400.1318 MHz 26.251680 Hz
F1 - Acquis: TD SF01 FIDRES SW	10.00 % 1000.00 usec ition parameters 128 400.1318 MHz 26.251680 Hz 8.398 ppm



140 130 120 110 100





	Compound 13	
BnO BnO BnO BnO	$ \begin{array}{cccc}  & OBn \\  & O \\  & $	۷ ₃
BnO BnO BnO BnO	OH	
F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE CNST2 D1 D2 D12 TD0	nisition Parameters 20120823 6.21 spect 5 mm PABBO BB/ deptsp135 65536 CDC13 800 4 23980.814 Hz 0.365918 Hz 1.3664256 sec 16384 20.850 usec 6.00 usec 303.0 K 145.0000000 2.00000000 sec 0.00344828 sec 0.00002000 sec 1	
<pre>====================================</pre>	CHANNEL f1 ======= 13C 5.90 usec 2000.00 usec 120.00 dB -6.00 dB 100.6228298 MHz 6.74 dB Crp60comp.4 0.500 0 Hz CHANNEL f2 ====== waltz16 1H 6.75 usec 13.50 usec 80.00 usec -6.00 dB 20.00 dB	
SFO2 F2 - Prod SI SF WDW SSB LB GB PC	400.1316005 MHz cessing parameters 32768 100.6127690 MHz EM 0 1.00 Hz 0 1.40	

**10 ppm** 





Compound 13 OBn DBn BnO BnO⁻ BnO- $O(CH_2)_2N_3$ NHCl₃Ac OAc BnO BnO BnO BnO

OH

F2 - Acqu	isition Parame	ters
Date_	20120823	
Time	9.23	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	0Epqpz	
TD	65536	
SOLVENT	CDC13	
NS	3072	
DS	4	
SWH	26178.010	Hz
FIDRES	0 399445	н <u>л</u> Цл
NO	1 2517276	112 COC
AQ DC	11505 C	sec
KG DH	10 100	
	19.100	usec
DE	6.50	usec
TE	303.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TDO	1	
=======	CHANNEL fl ====	====
NUC1	13C	
P1	5.90	usec
PL1	-6.00	dB
SF01	100.6248425	MHz
	CHANNEL f2 ====	
CPDPRG[2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	-6.00	dB
PL12	20.00	dB
PT.13	20.00	dB
SFO2	400.1316005	MHZ
01 02	100.1010000	11112
F2 - Proc	ressing paramete	ars
GT LTO	32768	ST D
сг СГ	100 6127617	MH 7
MDM	ICC:CIZ/CI/	1.111.1.2
CCD		
םמט חד	1 .00	Цæ
ПО	T.00	ΠΖ
GB	U 1 10	
PC	1.40	











Compound 14 OBn OBn BnO  $O(CH_2)_2N_3$ AcCl₃HN Bn( OAc BnO BnÖ BnO-BnÓ ___2 Lev F2 - Acquisition Parameters 20141021 20.56 INSTRUM spect 5 mm PABBO BB/ PULPROG cosygpppqf 2048 SOLVENT CDC13 8 3324.468 Hz 1.623275 Hz 0.3080192 sec 20.2 150.400 usec 6.50 usec 303.0 K 0.00000300 sec 1.37220395 sec 0.03000000 sec 0.00002000 sec 0.00000400 sec 0.00020000 sec 0.00030080 sec ====== CHANNEL fl ======= 1H 7.10 usec 7.10 usec 2500.00 usec -6.00 dB 6.13 dB 400.1317800 MHz ===== GRADIENT CHANNEL ===== GPNAM[1] SINE.100 10.00 % 1000.00 usec F1 - Acquisition parameters 512 400.1318 MHz 6.493102 Hz 8.308 ppm QF









1				
				h
			1	11
				n
	10			11
1				f I
		ř		
	t v		ſ	1 T
ويقرب فالدوقة إحمدهم ورجع فاقر فسرائل	والموالية ومرالية والمحرول والمحالي والفالي والمتعالي والمتعالي والمحالية والمح	A IL IN COLORAD, AND A LAND	فساد ودغسهن والألب الاختفية الأحجاز وألداه	مالارة سردر أقاداناتها فلا
al al al a state and a state a state a	را <b>ر ما هار. ما همرا م</b> . ما منه. ار مع رب ما اهر را ماه از .	and the second se	ويشارها أولان الهجاة ببلات وفاديده	ر. <b>افراد بادر جدا</b> ل. او ه
			352 -	
000	100	400	440	400
200	180	160	140	120



$m \bowtie H$	Co	ompound 14	12	
18. 18.	BnO BnO BnO Bn	Bn O BnOO		-O(CH ₂ ) ₂ N ₃
	BnO BnO BnO		0	
	BnO E2 Dom	7 O Lev		2
	FZ - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS	201 5 mm PABB z	41022 4.01 spect 0 BB/ gpg30 65536 CDC13 4096 4	ers
	SWH FIDRES AQ RG DW DE TE D1 D11 TD0	2617 0.3 1.25 1 2.000 0.030	78.010 399445 517376 13004 9.100 6.50 303.0 000000 000000 1	Hz sec usec usec K sec sec
	======= NUC1 P1 PL1 SF01	CHANNEL f	1 ==== 13C 6.25 -6.00 48425	usec dB MHz
	======= CPDPRG[2 NUC2 PCPD2 PL2 PL12 PL13 SF02	CHANNEL f wa 400.13	2 ==== 1tz16 1H 80.00 -6.00 15.04 20.00 316005	usec dB dB dB dB MHz
	F2 - Prod SI SF WDW SSB LB GB PC	cessing pa 100.61 0	ramete 32768 27600 EM 1.00 1.40	rs MHz Hz
<b>hhin</b>				



	Cc	mpound 14	
			3n
	BnO	O Bno	O(CH ₂ ) ₂ N ₃
	Brid	AcCl ₃ HI	N
		O OAC	
	B=0 7	207	
m	BnC	7	
	BnO	4	
	BnO	<b></b>	2
		Lev	
	F2 - Acqui	sition Paramet	ters
	Date_ Time	20141022	
	INSTRUM	spect	
	PROBHD 5 PULPROG	hmbcaplpndaf	
	TD	2048	
	SOLVENT NS	CDC13 8	
	DS	16	2-20
	SWH FIDRES	3324.468	Hz Hz
	AQ	0.3080192	sec
	rg dw	16384	USEC
	DE	6.00	usec
	TE CNST2	303.0 145 000000	K
	CNST13	10.0000000	
	D0 D1	0.00000300	sec
	D2	0.00344828	sec
	D6 D16	0.05000000	sec
	INO	0.00002240	sec
	(	ЧЛ NNFT. f1 ———-	
	NUC1	1H	
	P1 P2	7.10	USEC
	PL1	-6.00	dB
	SF01	400.1317800	MHz
	====== (	CHANNEL f2 ====	=====
	NUC2 P3	13C 6 25	11900
	PL2	-6.00	dB
	SFO2	100.6228138	MHz
	===== GRA	ADIENT CHANNEL	=====
	GPNAM[1] GPNAM[2]	SINE.100 SINE 100	
	GPNAM[3]	SINE.100	
	GPZ1 GPZ2	50.00 30.00	olo ol
n	GPZ3	40.10	0-0-0
	P16	1000.00	usec







F2 - Acqu	isi	tion	Par	amet	ers
Date_		2	0120	907	
Time			23	.38	
INSTRUM			spe	ect	
PROBHD	5 mi	n PAE	BBO I	BB/	
PULPROG			Z	q30	
TD			100	000	
SOLVENT			CD	C13	
NS				256	
DS				2	
SWH		8.	278.	146	Hz
FIDRES		0	.082	781	Hz
AQ		6.	0400	000	sec
RĜ			2	0.2	
DW			60.	400	usec
DE			6	.00	usec
TE			30	3.0	Κ
D1		1.00	0000	000	sec
TDO				1	
=======	CHA	NNEL	f1	====	====
NUC1				1H	
P1			6	.75	usec
PL1			-6	.00	dB
SF01		400.	1324	708	MHz
F2 - Proc	cess	ing p	para	mete	ers
SI			32	768	
SF		400.	1300	000	MHz
WDW				ΕM	
SSB	0		42	120022	
LB	-		0	.30	Ηz
GB	0		102	~ ~	
PC			1	.00	

1.00





F2 - Acquisi	tion Parameters
Date_	20120907
Time	23.40
INSTRUM	spect
PROBHD 5 m	m PABBO BB/
PULPROG	cosyqpppqf
TD	2048
SOLVENT	CDC13
NS	8
DS	8
SWH	3396.739 Hz
FIDRES	1.658564 Hz
AO	0.3014656 sec
RG	10.1
DW	147.200 usec
DE	6.50 usec
TE	303.0 K
DO	0.00000300 sec
D1	1.37834799 sec
D11	0.03000000 sec
D12	0.00002000 sec
D13	0.00000400 sec
D16	0.00020000 sec
TNO	0.00029440 sec
2799-80-80-80-80-80-80-80-80-80-80-80-80-80-	ವನ್ನು ಮುಂದಿ ಮನ್ನು ಮುಂದಿ ಮಾಡಿದ್ದಾರೆ. ಇದು ಮನ್ನು ಮನ್ನು
===== CHA	NNEL fl =======
NUC1	1H
PO	6.75 usec
P1	6.75 usec
P17	2500.00 usec
PL1	-6.00 dB
PL10	6.57 dB
SF01	400.1317802 MHz
===== GRAD]	ENT CHANNEL =====
GPNAM [1]	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
The state of the s	CE PRESSE CONTRACTOR AND A CONTRACTOR
rı – Acquisi	Lion parameters
	51Z
SEVI	4UU.IJI8 MHZ
FIDRES	6.634256 Hz
SW	8.489 ppm
FINMODE	OF.









WM VWV  $\bigcirc$ 4.2 3.8 3.6 4.0 3.4 ppm





$F_2 - A_1$	cquisition	Pat	rame	ters
Date_	20	)120	909	
Time		5	5.52	
INSTRU.	М	sr	pect	
PROBHD	5 mm PAE	BBO	BB/	
PULPRO	G	zar	05pc	
TD		65	536	
SOLVEN	Т	CI	DC13	
NS		2.0	0000	
DS			4	
SWH	261	78	.010	Hz
FIDRES	0	390	9445	HZ
AO	1 2	, 0 5 1 7	7376	500
RG	±.• 2	91 (	15 2	000
DM		19	100	11900
		± 2 .	5 50	usec
		30	13 0	v
1 <u>5</u> D1	2.00	000	0.00	R COC
	2.00			sec
	0.03	3000	1000	sec
IDU			10	
		<del>-</del> 1		
NTTC 1	CHANNEL	Т.Т.	120	
NUCI D1		Ē	TSC S 00	
		-	5.90	usec
PLL CRO1	100 /		0.00 0405	aB MII-
SFOL	100.K	0248	3420	MHZ
<u></u>	CUANNET	fo	<u></u>	
CDDDDC	CHANNEL	上乙 70.1+	16	
NUCO	[Z V	varu	111	
NUCZ		00	) 00	
PCPDZ		80	.00	usec
PLZ DI10		- 6	.00	aB
PLIZ DI 10			.00	aB
PLI3	100 1			aB
SFOZ	400.1	L310	0005	MHZ
<b>T</b> O D				
FZ - P	rocessing p	bara	amet	ers
SI	100 /	52	2/68	D G T T
SE	TOO . 6	στΖ	1090	MHZ
WDW	0		ΕM	
SSB	U	3		T T





Compound 16 OBn BnO BnC  $O(CH_2)_2N_3$ BnO Cl₃AcHN OAc BnO BnO BnO BnO ____3 Lev F2 - Acquisition Parameters Date_ 20140802 16.13 Time INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zg30 65536 TD CDC13 SOLVENT 128 NS 2 DS SWH 8278.146 Hz 0.126314 Hz FIDRES 3.9583745 sec AQ 57 RG  $\mathsf{D}\mathsf{W}$ 60.400 usec DE TE 6.00 usec

D1 1.00000000 sec TDO ====== CHANNEL fl _____ NUC1 1H P1 7.10 usec PL1 -6.00 dB 400.1324708 MHz SF01 F2 - Processing parameters SI SF 32768 400.1300096 MHz WDW ΕM SSB LB GB PC 0 0.30 Hz 0 1.00

303.0 K





ppm





i	Con	npound	16		
	-OB	n	7	OBn	
	BnO-DO	Br	1002		$D(CH_2)_2N_3$
	BnO-			ACHN	( 2)2 3
27.	BnO	0 L	4		
 		ó	0Ac		
・・ かす	1	-07	0/10		
	BnO	$\leq$			
	BnÓ	d			
		1			
	BnO	4			
	BnÓ	ò			5
					)
		Ĺev			
	F2 - Acq	uisit	ion P	aramet	lers
	Date_		201	40802	
	Time			22.10	
	INSTRUM	E mm		spect	
	PROBHD	5 mm	PABB	OBB/	
	TD		uepu	65536	
	SOLVENT			CDC13	
	NS			5120	
	DS			4	
	SWH		2398	0.814	Hz
	FIDRES		0.3	65918	Hz
	AQ		1.36	64256	sec
	RG		-	16384	
	DW		2	0.850	usec
	DE			6.00	usec v
	LE CNST2	1.	15 00	00000	V
	D1	- <u>-</u>	2.000	00000	Sec
	D2	0.4	0.003	44828	sec
	D12		0.000	02000	sec
	TDO			1	
		CHAN	NEL f	1 ====	
	NUC1			13C	
بالمالية مع	PL D10		20	6.25	usec
HAR	PIZ DI N		∠∪ 1	20.00	dB dB
	PT.1		ción.	-6.00	dB
	SF01	1	00.62	28298	MHz
	SP2			12.00	dB
	SPNAM[2]	Cu	cp60c	omp.4	
	SPOAL2			0.500	
	SPOFFS2	0 Hz			
		11 T T T T	NIDT -	0	
		CHAN.	NEL L Wo	Z ==== 1+16	
	NUC2		Wa	1UZI0	
	P3			7.10	usec
	P4			14.20	usec
	PCPD2			80.00	usec
	PL2			-6.00	dB
	PL12			15.04	dB
	SFO2	4	00.13	16005	MHz
		a		<b>7</b>	- <b>F</b> -
	ez - Pro- gt	cessii	ig pa	ramete 30760	ers
	SF SF	ê <b>-1</b>	00.61	27690	MHァ
	WDW	ويلدو	00.01	EM	т тт т Ст
тт	SSB	0			
om	LB			1.00	Hz
	GB	0			
	PC			1.40	

 $\bigcirc$ 00 00 DOO( N Ę 63 0 5.2 5.0 4.8 4.6 4.4



Compound 16







Compound 16						
	BnO BnO BnO BnC	n Bno		3n D IN	O(CH ₂ ) ₂ N ₃	
pm 65	BnO BnO BnO BnO		T DAc		3	
70	F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS	isition 2 5 mm PA hmbcg	Parame 0140803 15.24 spect BBO BB/ plpndqf 2048 CDC13 32	ters	3	
75	DS SWH FIDRES AQ RG DW DE	3 1 0.	16 787.879 .849550 2703360 16384 132.000 6.00	) Hz )Hz sec use )use	ec ec	
80	TE CNST2 D0 D1 D2 D6 D16 IN0	145. 5. 0.0 2.0 0.1 0.1	303.0 0000000 0000000 0000300 4915190 0344828 00344828 0000000 0020000	) K ) sec ) sec ) sec ) sec ) sec		
85	======= NUC1 P1 P2 PL1 SF01	CHANNEL 400.	f1 === 1H 7.10 14.20 -6.00 1315756	use use dB MHz	== ec ec	
90	====== NUC2 P3 PL2 SF02	CHANNEL 100.	f2 === 130 6.25 -6.00 6228138	use dB MHz	== EC	
95	===== GR GPNAM[1] GPNAM[2] GPZ1 GPZ2 GPZ3 P16	ADIENT S	CHANNEL SINE.100 SINE.100 SINE.100 30.00 40.10 1000.00	, === ) ) 왕 ) 왕 ) 김동(	ec	
00 pm	F1 - Acqu TD SF01 FIDRES SW FnMODE	isition. 1 43	parame 512 00.6228 .596539 221.833 QF	ters MHz Hz ppr	3 Z N	



Compound 17 OBn OBn BnO BnO BnO  $O(CH_2)_2N_3$ Cl₃AcHN BnC OH BnO BnO BnO_ BnO ____3 п F2 - Acquisition Parameters Date_ 20140819 Time 13.17 INSTRUM spect PROBHD 5 mm PABBO BB/ zg30 65536 PULPROG TD SOLVENT CDC13 16 NS DS 2 SWH 8278.146 Hz 0.126314 Hz FIDRES 3.9583745 sec AQ RG 90.5  $\mathsf{DW}$ 60.400 usec DE 6.00 usec TE D1 303.0 K 1.00000000 sec TDO ====== CHANNEL f1 ======= NUC1 1H 7.10 usec P1 -6.00 dB PL1 SF01 400.1324708 MHz F2 - Processing parameters SI 32768 SF 400.1300437 MHz 400.1300437 MHz WDW ΕM SSB 0 LB0.30 Hz GB PC 0 1.00


	Com	pound <b>17</b>		
	BnO OBn	BnO		D(CH ₂ ) ₂ N ₃
pm	BnO BnO	O OH	CHN	
.4	BnO BnO		3	
.6	F2 - Acqu Date_ Time	H H 2014083 13.3	meters 19 19	
.8	PROBHD PULPROG TD SOLVENT NS	5 mm PABBO BI cosygppp 204 CDC	30 9/ 9f 18 13 1	
.0	DS SWH FIDRES AQ RG DW	3140.70 1.5335 0.326041 6 159.20	8 04 Hz 47 Hz 16 sec 54 00 usec	4
.2	DE TE D0 D1 D11 D12	6.5 303 0.0000030 1.3537720 0.0300000 0.0000200	50 usec .0 K )0 sec )4 sec )0 sec )0 sec	
.4	D13 D16 IN0	0.0000040 0.0002000 0.0003184 CHANNEL f1 ==	)0 sec )0 sec 40 sec	=
.6	NUC1 P0 P1 P17 PL1 PL10 SF01	7.2 7.2 2500.0 -6.0 6.2 400.13166	lH LO usec DO usec DO dB L3 dB 88 MHz	
.8	===== GF GPNAM[1] GPZ1 P16	RADIENT CHANNE SINE.1 10.0 1000.0	EL ==== 00 00 % 00 usec	
.0	F1 - Acqu TD SF01 FIDRES SW	uisition para 12 400.13 24.5367 7.84	meters 28 17 MHz 47 Hz 49 ppm	
.2	FUMODE	ç	2E	



140 130 120 110 100 90

72	• 65	. 50	• 25	.46	. 66	.44	.10	.15	.97	.57	• 08	.02	. 82	. 69	.57	.22	.73	.12	.95	.07	•54	.72	. 63	.48	.14	• 82	.29	• 00	•71	• 81	• 05	.48	.40	• 30	.24	• 18	
თ თ	99	99	99	98	81	81	81	80	96	96	979	78	LL	66	66		76	76	<u>1</u>	75	74	71	71	71	70	68	68	68	67	57	50	$1^{3}$	$1^{3}$	$1^{3}$	$1^{3}$	$1^{0}$	$1^{3}$
J									<u>ل</u>	<u>ل</u>	1			<u>_</u>	4		4										4		T		لہ ⁄/	/	1		_	<u>_</u> _	لہ
Π	m		111		F	TI					<u>ارمانی</u> ۲	Т				_			di.										1								

	Com	pound <b>17</b>	
18.11 18.11 18.12 18.12 18.11 18.11	BnO BnO BnO		O(CH ₂ ) ₂ N ₃
	BnO BnO		
	BnO BnO		3
	F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE CNST2 D1 D2 D12 TD0 ==================================	<pre>Idisition Parameter 20140819 22.18 spect 5 mm PABBO BB/ deptsp135 65536 CDC13 4096 4 23980.814 Hz 0.365918 Hz 1.3664256 se 16384 20.850 us 6.00 us 303.0 K 145.0000000 se 0.00344828 se 0.00002000 se 1 1 CHANNEL f1 ===== 13C 6.25 us 2000.00 us 120.00 dE -6.00 dE 100.6228298 MI 12.00 dE 0.500 0 Hz</pre>	z z z ec sec sec sec sec sec sec sec sec sec
	CPDPRG[2 NUC2 P3 P4 PCPD2 PL2 PL12 SF02	waltz16 1H 7.10 us 14.20 us 80.00 us -6.00 dE 15.04 dE 400.1316005 MF	sec sec sec 3 3 Hz
10 ppm	F2 - Proc SI SF WDW SSB LB GB PC	cessing parameters 32768 100.6127690 MH EM 0 1.00 Hz 0 1.40	∃ ∃z



50 50 19 1	- 138.75	<b>-</b> 138.65	- 138.51	-138.40	- 138.25	-138.01	<b>7</b> 137.96	<b>r</b> 137.85	- 137.76	- 137.51 - 137.51	- 129.19	-129.10	- 128.90	128.75	- 128.62	- 128.60	- 128.56	- 128.49	- 128.47	<b>7</b> 128.42	- 128.38	<b>7</b> 128.26	//~ 128.18	128.15		128.01	-127.95	-127.92



Compound 17