Supporting information

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1. General

All purchased chemicals were used without further purification unless stated otherwise. Solvents were dried over activated 4 Å (CH_2Cl_2, DMF, pyridine, cyclohexane) molecular sieves. 2-Propanol for glycosylation was dried over 5 Å molecular sieves for 24 h. THF was directly distilled on 4 Å molecular sieves shortly before use. Dry MeOH (secco solv) was purchased from Merck. Cation exchange resin DOWEX 50 H^+ was regenerated by consecutive washing with HCl (3 M), water and dry MeOH. Aqueous solutions of salts were saturated unless stated otherwise. Concentration of organic solutions was performed under reduced pressure < 40 °C. Optical rotations were measured with a Perkin-Elmer 243 B Polarimeter. $[\alpha]_D^{20}$ values are given in units of 10^{-1}deg cm^2g^{-1}. Thin layer chromatography was performed on Merck precoated plates: generally on 5 x 10 cm, layer thickness 0.25 mm, Silica Gel $60F_{254}$; alternatively on HP-TLC plates with 2.5 cm concentration zone (Merck). Spots were detected by dipping reagent (anisaldehyde-H_2SO_4). For column chromatography silica gel (0.040 – 0.063 mm) was used. HP-column chromatography was performed on pre-packed columns (YMC-Pack SIL-06, 0.005 mm, 250x10 mm and 250x20 mm). Size exclusion chromatography was performed on Bio-Gel® P-2 Gel extra fine < 45 µm (wet) (1 x 30 cm) or on pre-packed PD-10 columns (GE Healthcare, Sephadex^{TM} G-25 M). NMR spectra were recorded with a Bruker Avance III 600 instrument (600.22 MHz for ^1H, 150.93 MHz for ^{13}C and 564.77 MHz for ^{19}F) using standard Bruker NMR software. ^1H NMR spectra were referenced to 7.26 ($CDCl_3$) and 0.00 (D_2O, external calibration to 2,2-dimethyl-2-silapentane-5-sulfonic acid) ppm unless stated otherwise. ^{13}C NMR spectra were referenced to 77.00 ($CDCl_3$) and 67.40 (D_2O, external calibration to 1,4-dioxane) ppm. ^{19}F NMR spectra were indirectly referenced according to IUPAC recommendations[S1]. ESI-MS data were obtained on a Waters Micromass Q-TOF Ultima Global instrument.

2. Assignment of NMR signals

The ^1H and ^{13}C signals were assigned with the aid of COSY, HSQC and HMBC spectra and compared to published data for known compounds. The monosaccharides were numbered along the carbohydrate backbone according to IUPAC. The branched trisaccharides have been labeled according to Fig.S1.

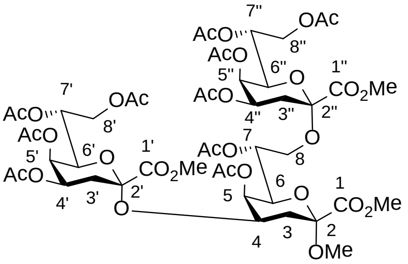
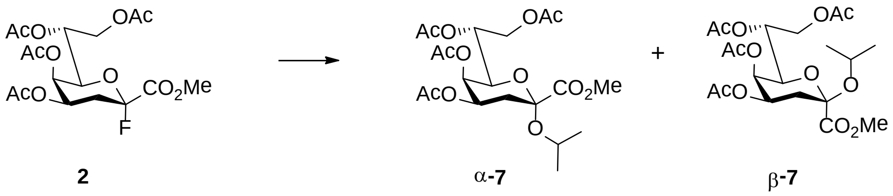


Figure S1: NMR-signal assignment of a branched trisaccharide

3. Synthesis and characterization of compounds

3.1 Model glycosylations

3.1.1 Model glycosylation without directing group



2 α-**7** β-**7**

Under an atmosphere of argon a solution of **2**[S2] (33.3 mg, 0.079 mmol) and dry 2-propanol (12.1 µL, 0.158 mmol) in dry CH_2Cl_2 (1.0 mL) was stirred for 1 h at ambient temperature in the presence of ground 3 Å molecular sieves (50 mg). At 0 °C $BF_3.Et_2O$ (32.4 µL, 0.158 mmol) was added dropwise and after stirring for 6 h at 0 °C the mixture was diluted with CH_2Cl_2 and aq $NaHCO_3$. The phases were separated and the organic extract was dried ($MgSO_4$), filtered and concentrated. HP-column chromatography (n-hexane/EtOAc 3:1→1:1) provided a mixture of **α/β-7** (17.5 mg, 48%, α/β 4.8:1) and the slower migrating glycal **3**[S3] (9.7 mg, 31%).

Methyl (2-propyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-β-D-*manno*-oct-2-ulopyranosid)onate (β-7)

Colorless oil; $[\alpha]_D^{20}$ + 53.8 (*c* 0.58, $CHCl_3$); R_f 0.75 (*n*-hexane/EtOAc 1:1, HP-TLC); ^1H NMR ($CDCl_3$): δ 5.28 - 5.27 (m, 1H, H-5), 5.16 (ddd, 1H, $J_{7,6}$ 9.4, $J_{7,8b}$ 4.3, $J_{7,8a}$ 2.5 Hz, H-7), 4.85 (ddd, 1H, $J_{4,3ax}$ 13.3, $J_{4,3eq}$ 4.5, $J_{4,5}$ 3.1 Hz, H-4), 4.38 (dd, 1H, $J_{8a,8b}$ 12.3 Hz, H-8a), 4.35 (dd, 1H, H-8b), 4.15 (dd, 1H, $J_{6,5}$ 1.4 Hz, H-6), 4.06 [m, 1H, *J* 6.2 Hz, C*H*(CH_3)$_2$], 3.80 (s, 3H, CO_2CH_3), 2.35 (ddd, 1H, $J_{3eq,3ax}$ 12.5, $J_{3eq,5}$ 1.0 Hz, H-3*eq*), 2.12 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.09 (app t, 1H, H-3*ax*), 2.01 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.23 [d, 3H, *J* 6.2 Hz, CH(C*H*$_3$)], 1.09 [d, 3H, *J* 6.2 Hz, CH(C*H*$_3$)]; ^{13}C NMR ($CDCl_3$): δ 170.73, 170.51, 169.95 and 169.85 (4 x s, *C*OCH$_3$), 168.81 (s, C-1), 99.61 (s, C-2), 70.54 (d, C-6), 68.67 [d, *C*H(CH_3)$_2$], 68.16 (d, C-7), 67.14 (d, C-4), 64.06 (d, C-5), 62.50 (t, C-8), 52.57 (q, CO_2CH_3), 32.81 (t, C-3), 24.46 [q, 1C, CH(*C*H$_3$)], 23.19 [q, 1C, CH(*C*H$_3$)], 20.79, 20.73, 20.70 and 20.66 (4 x q, CO*C*H$_3$); ESI-TOF HRMS: *m/z* = 485.1624; calcd for $C_{20}H_{30}O_{12}Na^+$: 485.1629.

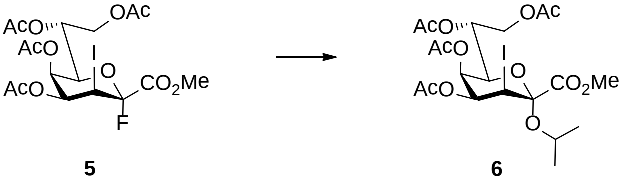
Methyl (2-propyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (α-7)

Colorless oil; $[\alpha]_D^{20}$ + 94.3 (*c* 0.93, $CHCl_3$); R_f 0.72 (*n*-hexane/EtOAc 1:1, HP-TLC); ^1H NMR ($CDCl_3$): δ 5.36 - 5.34 (m, 1H, H-5), 5.31 (ddd, 1H, $J_{4,3ax}$ 12.4, $J_{4,3eq}$ 4.9, $J_{4,5}$ 3.0 Hz, H-4), 5.20 (ddd, 1H, $J_{7,6}$ 9.8, $J_{7,8b}$ 3.6, $J_{7,8a}$ 2.6 Hz, H-7), 4.62 (dd, 1H, $J_{8a,8b}$ 12.3 Hz, H-8a), 4.18 (dd, 1H, $J_{6,5}$ 1.7 Hz, H-6), 4.16 (dd, 1H, H-8b), 4.01 [m, 1H, *J* 6.1 Hz, C*H*(CH_3)$_2$], 3.79 (s, 3H, CO_2CH_3), 2.22 (ddd, 1H, $J_{3eq,3ax}$ 12.8, $J_{3eq,5}$ 1.0 Hz, H-3*eq*), 2.05 (s, 6H, 2 x $COCH_3$), 1.99 (app t, 1H, H-3*ax*), 1.98 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.21 [d, 3H, *J* 6.1 Hz, CH(C*H*$_3$)], 1.04 [d, 3H, *J* 6.1 Hz, CH(C*H*$_3$)]; ^{13}C NMR ($CDCl_3$): δ 170.47, 170.38, 169.96 and 169.65 (4 x s, *C*OCH$_3$), 168.34 (s, C-1), 97.96 (s, C-2), 68.40 (d, C-6), 67.86 (d, C-7), 67.08 [d, *C*H(CH_3)$_2$], 66.55 (d, C-4), 64.50 (d, C-

5), 61.96 (t, C-8), 52.49 (q, CO$_2$*C*H$_3$), 32.65 (t, C-3), 23.80 [q, 1C, CH(*C*H$_3$)], 22.46 [q, 1C, CH(*C*H$_3$)], 20.75, 20.73 and 20.62 (3 x q, 4C, CO*C*H$_3$); ESI-TOF HRMS: *m/z* = 485.1628; calcd for $C_{20}H_{30}O_{12}Na^+$: 485.1629.

The anomeric configuration was assigned by comparison with published data[S4].

3.1.2 Model glycosylation with directing 3-iodo-group



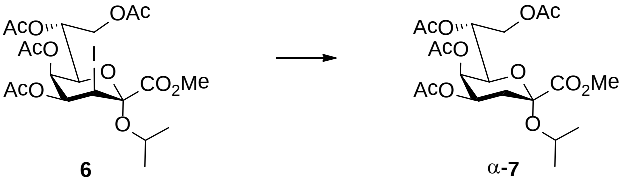
5 **6**

Glycosyl donor **5** (274 mg, 0.500 mmol) and dry 2-propanol (77 µL, 1.000 mmol) were treated with BF$_3$.Et$_2$O (205 µL, 1.000 mmol) in dry CH$_2$Cl$_2$ (8.0 mL) for 1 h according to the general procedure for glycosylation (see main paper). After aqueous work-up column chromatography (*n*-hexane/EtOAc 2:1) afforded **6** (244 mg, 83%) and the slower migrating glycal **3**[S3] (13.3 mg, 7%).

Methyl (2-propyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-*glycero*-α-D-*talo*-oct-2-ulopyranosid)onate (6)

Colorless oil; $[\alpha]_D^{20}$ + 41.8 (*c* 0.55, CHCl$_3$); R$_f$ 0.32 (*n*-hexane/EtOAc 2:1, HP-TLC); ^{1}H NMR (CDCl$_3$): δ 5.42 - 5.41 (m, 1H, H-5), 5.36 (ddd, 1H, $J_{7,6}$ 9.7, $J_{7,8b}$ 3.6, $J_{7,8a}$ 2.5 Hz, H-7), 5.04 (dd, 1H, $J_{4,3}$ 4.7, $J_{4,5}$ 3.8 Hz, H-4), 4.70 (dd, 1H, $J_{8a,8b}$ 12.5 Hz, H-8a), 4.47 (dd, 1H, $J_{3,5}$ 0.9 Hz, H-3), 4.32 (dd, 1H, $J_{6,5}$ 2.2 Hz, H-6), 4.20 (dd, 1H, H-8b), 3.95 [m, 1H, *J* 6.2 Hz, C*H*(CH$_3$)$_2$], 3.83 (s, 3H, CO$_2$C*H*$_3$), 2.10 (s, 3H, COC*H*$_3$), 2.05 (s, 6H, 2 x COC*H*$_3$), 1.96 (s, 3H, COC*H*$_3$), 1.27 [d, 3H, *J* 6.2 Hz, CH(C*H*$_3$)], 1.06 [d, 3H, *J* 6.1 Hz, CH(C*H*$_3$)]; ^{13}C NMR (CDCl$_3$): δ 170.35, 170.16, 169.44 and 169.41 (4 x s, *C*OCH$_3$), 166.66 (s, C-1), 101.09 (s, C-2), 69.67 [d, *C*H(CH$_3$)$_2$], 68.22 (d, C-6), 67.84 (d, C-7), 65.46 (d, C-4), 63.37 (d, C-5), 61.67 (t, C-8), 52.63 (q, CO$_2$C*H*$_3$), 23.88, 23.81 [2d/q, 2C, C-3, CH(*C*H$_3$)], 22.27 [q, 1C, CH(*C*H$_3$)], 20.93, 20.82, 20.73 and 20.55 (4 x q, CO*C*H$_3$); ESI-TOF HRMS: *m/z* = 606.1044; calcd for $C_{20}H_{29}IO_{12}NH_4^+$: 606.1042.

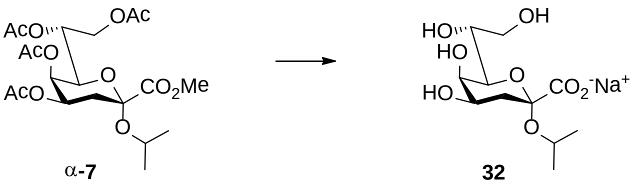
3.1.3. Dehalogenation



6 α-**7**

Dehalogenation of **6**: A solution of **6** (24.8 mg, 0.042 mmol) in dry cyclohexane (2.0 mL) was treated with lauroyl peroxide (5.0 mg, 0.013 mmol) for 2 h according to the general procedure for dehalogenation (see main paper). Pure **α-7** (17.7 mg, 91%) was isolated by column chromatography (toluene/EtOAc 4:1).

3.1.4. Global deprotection



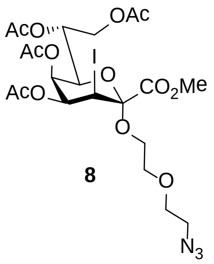
α-**7** → **32**

Sodium (2-propyl 3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (32)

According to the general procedure for global deprotection (see main paper): A solution of **α-7** (12.8 mg, 0.0228 mmol) in dry MeOH (2.0 mL) was treated with NaOMe (0.1 M in MeOH, 22.4 µL, 0.002 mmol) for 19 h at rt. After isolation of the crude product the residue was dissolved in water (2 mL) and treated with aq NaOH (0.1 M, 1.0 mL) for 3 h. The crude product was desalted on a PD10-column and lyophilisation of pooled fractions provided **32** (8.3 mg, 99%) as a colorless amorphous solid; $[\alpha]_D^{20}$ + 50.9 (*c* 0.83, D_2O); ^1H NMR (D_2O, pH ~ 6.0): δ 4.02 – 3.97 (m, 2H, H-4, H-5), 3.96 – 3.89 [m, 3H, H-7, H-8a, C*H*(CH_3)$_2$], 3.66 – 3.60 (m, 2H, H-6, H-8b), 2.09 – 2.04 (m, 1H, H-3*eq*), 1.71 (dd, 1H, $J_{3ax,3eq}$ 13.1, $J_{3ax,4}$ 11.5 Hz, H-3*ax*), 1.13 [d, 3H, *J* 6.3 Hz, CH(C*H*$_3$)], 1.10 [d, 3H, *J* 6.3 Hz, CH(C*H*$_3$)]; ^{13}C NMR (D_2O, pH ~ 6.0): δ 176.45 (s, C-1), 100.00 (s, C-2), 72.68 (d, C-6), 70.66 (d, C-7), 68.07 [d, *C*H(CH_3)$_2$], 67.09 (d, C-5), 66.89 (d, C-4), 63.93 (t, C-8), 35.61 (t, C-3), 24.03 [q, 1C, CH(*C*H$_3$)$_2$], 22.57 [q, 1C, CH(*C*H$_3$)$_2$]; ESI-TOF HRMS: *m/z* = 303.1048; calcd for $C_{11}H_{20}O_8Na^+$: 303.1050.

3.2. Synthesis of Kdo spacer-glycosides

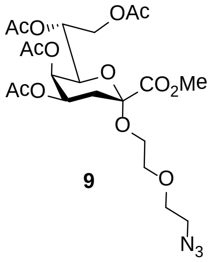
3.2.1. Methyl [2-(2-azidoethoxy)ethan-1-yl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-*glycero*-α-D-*talo*-oct-2-ulopyranosyl]onate (8)



8

Glycosyl donor **5** (25.5 mg, 0.047 mmol) and 2-(2-azidoethoxy)ethanol (7.3 mg, 0.056 mmol) were treated with $BF_3.Et_2O$ (19.1 µL, 0.093 mmol) in dry CH_2Cl_2 (1.0 mL) for 1 h according to the general procedure for glycosylation. After aqueous work-up column chromatography (*n*-hexane/EtOAc 2:1) afforded a mixture of **8** and remaining 2-(2-azidoethoxy)ethanol, which was further purified by column chromatography (toluene/EtOAc 2:1) yielding pure **8** (24.5 mg, 80%) as a colorless oil; $[\alpha]_D^{20}$ + 43.3 (*c* 0.68, $CHCl_3$); R_f 0.42 (*n*-hexane/EtOAc 1:1); ^1H NMR ($CDCl_3$): δ 5.41 - 5.37 (m, 2H, H-5, H-7), 5.07 (dd, 1H, $J_{4,3}$ 4.9, $J_{4,5}$ 3.5 Hz, H-4), 4.63 (dd, 1H, $J_{8a,8b}$ 12.4, $J_{8a,7}$ 2.3 Hz, H-8a), 4.52 (dd, 1H, $J_{3,5}$ 0.8 Hz, H-3), 4.41 (dd, 1H, $J_{6,7}$ 9.7, $J_{6,5}$ 1.8 Hz, H-6), 4.23 (dd, 1H, $J_{8b,7}$ 4.6 Hz, H-8b), 3.84 (s, 3H, CO_2C*H*$_3$), 3.75 (ddd, 1H, *J* 10.4, *J* 7.3, *J* 3.3 Hz, OC*H*$_2$), 3.70 - 3.60 (m, 4H, 2 x OC*H₂*), 3.46 - 3.35 (m, 3H, OC*H*$_2$, NC*H₂*), 2.11, 2.06, 2.05 and 1.97 (4s, each 3H, 4 x COC*H₃*); ^{13}C NMR (CDCl$_3$): δ 170.45, 170.14, 169.55 and 169.32 (4 x s, *C*OCH$_3$), 166.08 (s, C-1), 101.40 (s, C-2), 70.22 (t, 1C, O*C*H$_2$), 69.48 (t, 1C, O*C*H$_2$), 68.07 (d, C-6), 67.51 (d, C-7), 65.39 (d, C-4), 65.08 (t, 1C, O*C*H$_2$), 63.33 (d, C-5), 62.22 (t, C-8), 53.00 (q, CO$_2$*C*H$_3$), 50.81 (t, 1C, NCH$_2$), 22.24 (d, C-3), 20.91, 20.79, 20.62 and 20.56 (4 x s, CO*C*H$_3$); ESI-TOF HRMS: *m/z* = 682.0719; calcd for $C_{21}H_{30}IN_3O_{13}Na^+$: 682.0716.

3.2.2. Methyl [2-(2-azidoethoxy)ethan-1-yl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosyl]onate (9)

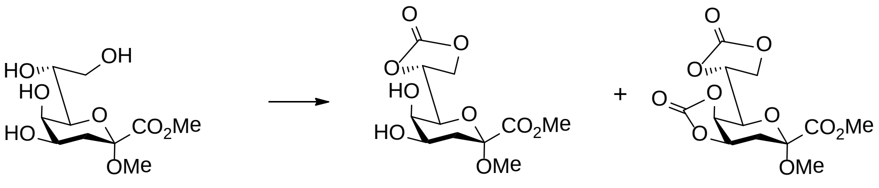


9

A suspension[S5] of **8** (16.6 mg, 0.025 mmol) in dry cyclohexane (3.0 mL) was treated with lauroyl peroxide (6.0 mg, 0.015 mmol) for 3 h according to the general procedure for dehalogenation. Pure **9** (11.2 mg, 83%) was obtained by column chromatography (*n*-hexane/EtOAc 1:1) as a colorless oil; $[\alpha]_D^{20}$ + 73.3 (*c* 1.06, CHCl$_3$); R$_f$ 0.40 (*n*-hexane/EtOAc 1:1); ^{1}H NMR (CDCl$_3$): 5.39 - 5.35 (m, 2H, H-4, H-5), 5.25 (ddd, 1H, $J_{7,6}$ 9.8, $J_{7,8b}$ 4.7, $J_{7,8a}$ 2.4 Hz, H-7), 4.57 (dd, 1H, $J_{8a,8b}$ 12.3 Hz, H-8a), 4.25 (dd, 1H, $J_{6,5}$ 1.0 Hz, H-6), 4.17 (dd, 1H, H-8b), 3.81 (s, 3H, CO$_2$C*H₃*), 3.71 - 3.63 (m, 5H, OC*H₂*), 3.57 - 3.53 (m, 1H, OC*H₂*), 3.46 - 3.39 (m, 2H, NC*H₂*), 2.20 - 2.16 (m, 1H, H-3*eq*), 2.12 - 2.07 (m, 1H, H-3*ax*), 2.09, 2.06, 2.00 and 1.97 (4 x s, each 3H, COC*H₃*); ^{13}C NMR (CDCl$_3$): δ 170.55, 170.42, 169.89 and 169.77 (4 x s, *C*OCH$_3$), 167.56 (s, C-1), 98.64 (s, C-2), 70.14, 69.84 (2t, 2C, O*C*H$_2$), 68.41 (d, C-6), 67.63 (d, C-7), 66.38 (d, C-4), 64.44 (d, C-5), 63.29 (t, 1C, O*C*H$_2$), 62.43 (t, C-8), 52.72 (q, CO$_2$*C*H$_3$), 50.84 (t, 1C, N*C*H$_2$), 31.94 (t, C-3), 20.76 and 20.65 (2 x q, 4C, CO*C*H$_3$); ESI-TOF HRMS: *m/z* = 556.1740; calcd for $C_{21}H_{31}N_3O_{13}Na^+$: 556.1749.

3.3. Synthesis of glycosyl acceptors

3.3.1. Methyl (methyl 7,8-*O*-carbonyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (10) and methyl (methyl 4,5;7,8-di-*O*-carbonyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (33)



19 **10** **33**

Carefully pre-dried **19**[S6] (294 mg, 1.104 mmol) was dissolved in dry THF under an atmosphere of argon. Freshly distilled *sym*-collidine (732 µL, 5.521 mmol) was added and the solution was cooled to -25 °C. To this mixture a separately prepared solution of diphosgene (133 µL, 1.104 mmol) in dry THF (1.5 mL) was added dropwise and the reaction mixture was stirred at -20 °C for 30 min. The reaction was stopped by dropwise addition of dry MeOH (1.0 mL) at -20 °C. After concentration the residual colorless solid was partitionated between EtOAc and aq HCl (1 M). The aqueous phase was reextracted with EtOAc 5-times and the combined organic phases were dried ($MgSO_4$), filtered and concentrated. The crude mixture was separated by column chromatography (EtOAc/MeOH 1:0 → 9:1) yielding **10** (215 mg, 67%) and **33** (106 mg, 30%).

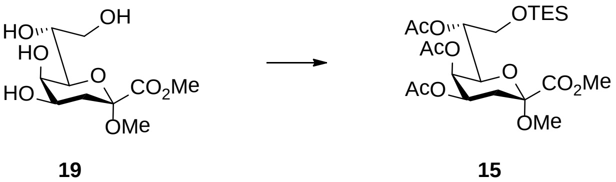
33: Colorless amorphous solid; $[\alpha]_D^{20}$ + 43.6 (*c* 0.24, $CHCl_3$); R_f 0.65 (EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.06 (app td, 1H, $J_{4,5}$ 8.4, H-4), 5.01 (ddd, 1H, $J_{7,8a}$ 8.1, $J_{7,8b}$ 6.3, $J_{7,6}$ 5.1 Hz, H-7), 4.85 (dd, 1H, $J_{5,6}$ 1.8 Hz, H-5), 4.67 (app t, H-8a), 4.63 (dd, 1H, $J_{8b,8a}$ 9.0, H-8b), 4.12 (dd, 1H, H-6), 3.85 (s, 3H, $CO_2C\mathit{H_3}$), 3.29 (s, 3H, $OC\mathit{H_3}$), 2.83 (dd, 1H, $J_{3a,3b}$ 16.3, $J_{3a,4}$ 4.0 Hz, H-3a), 2.10 (dd, 1H, $J_{3b,4}$ 3.5 Hz, H-3b); ^{13}C NMR ($CDCl_3$): δ 167.79 (s, C-1), 153.82 [s, O*C*(=O)O], 152.52 [s, O*C*(=O)O], 98.03 (s, C-2), 73.63 (d, C-7), 71.82 (d, C-5), 71.07 (d, C-4), 68.75 (d, C-6), 65.89 (t, C-8), 53.32 (q, $CO_2\mathit{C}H_3$), 51.60 (q, $O\mathit{C}H_3$), 32.71 (t, C-3); ESI-TOF HRMS: *m/z* = 336.0925; calcd for $C_{12}H_{14}O_{10}NH_4^+$: 336.0925.

10: Colorless foam; $[\alpha]_D^{20}$ + 65.6 (*c* 0.74, $CHCl_3$); R_f 0.36 (EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.00 (ddd, 1H, $J_{7,8b}$ 8.3, $J_{7,8a}$ 6.7, $J_{7,6}$ 4.3 Hz, H-7), 4.73 (dd, 1H, $J_{8a,8b}$ 8.9 Hz, H-8a), 4.59 (app t, 1H, H-8b), 4.13 (ddd, 1H, $J_{4,3ax}$ 11.6, $J_{4,3eq}$ 5.0, $J_{4,5}$ 3.2 Hz, H-4), 3.93 - 3.90 (m, 2H, H-5, H-6), 3.81 (s, 3H, $CO_2C\mathit{H_3}$), 3.23 (s, 3H, $OC\mathit{H_3}$), 2.10 (dd, 1H, $J_{3eq,3ax}$ 12.8 Hz, H-3*eq*), 1.90 (dd, 1H, H-3*ax*); ^{13}C NMR ($CDCl_3$): δ 168.42 (s, C-1), 155.08 [s, O*C*(=O)O], 99.36 (s, C-2), 75.89 (d, C-7), 71.13 (d, C-6), 66.80 (d, C-5), 66.53 (t, C-8), 65.02 (d, C-4), 52.88 (q, $CO_2\mathit{C}H_3$), 51.34 (q, $O\mathit{C}H_3$), 34.23 (t, C-3); ESI-TOF HRMS: *m/z* = 310.1140; calcd for $C_{11}H_{16}O_9NH_4^+$: 310.1133.

Recycling of starting material from 33:

A suspension of dicarbonate **33** (89 mg, 0.280 mmol) in dry MeOH (2 mL) was treated with NaOMe (0.1 M in MeOH, 112 µL, 0.011 mmol) for 18 h at ambient temperature. Another portion of NaOMe (0.1 M in MeOH, 112 µL, 0.0111 mmol) was added and after 5 h the solution was neutralized by addition of ion exchange resin DOWEX 50 (H^+). Filtration and concentration of the filtrate afforded **19** in quantitative yield in sufficient purity.

3.3.2. Methyl (methyl 4,5,7-tri-*O*-acetyl-3-deoxy-8-*O*-triethylsilyl-α-D-*manno*-oct-2-ulopyranosid)onate (15)

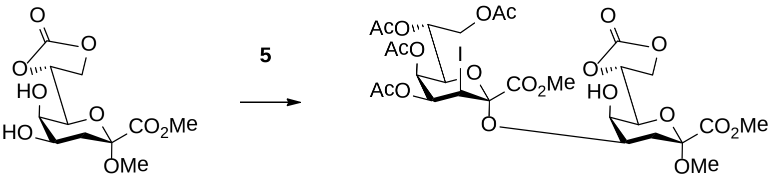


19 **15**

Dried **19**[S6] (89 mg, 0.334 mmol) and dried diazabicyclo[2.2.2]octane (64 mg, 0.567 mmol) were dissolved in dry MeCN. Chlorotriethylsilane (59 µL, 0.350 mmol) was added and the mixture was stirred at ambient temperature for 2 h. After concentration of the mixture the residue was dried under high vacuum, dissolved in dry pyridine (6.0 mL) and treated with acetic anhydride (0.2 mL) and 4-(*N*,*N*-dimethylamino)-pyridine (2 mg, 0.017 mmol) at ambient temperature for 4 h. Excessive reagent was destroyed at 0 °C by slow addition of dry MeOH (1 mL) and after stirring for 10 min the solvent was coevaporated with toluene (3 x). Column chromatography of the residue (toluene/EtOAc 9:1) provided **15** (107 mg, 60%, 2 steps) as a colorless oil; $[\alpha]_D^{20}$ + 57.4 (*c* 1.07, $\mathrm{CHCl_3}$); R_f 0.60 (toluene/EtOAc 2:1); ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.37 - 5.33 (m, 2H, H-4, H-5), 5.02 (app td, 1H, $J_{7,6}$ 9.8 Hz, H-7), 4.24 (dd, 1H, $J_{6,5}$ 1.0 Hz, H-6), 3.96 (dd, 1H, $J_{8a,8b}$ 11.7, $J_{8a,7}$ 2.7 Hz, H-8a), 3.81 (s, 3H, $\mathrm{CO_2C}\mathit{H}_3$), 3.78 (dd, 1H, $J_{8b,7}$ 2.0 Hz, H-8b), 3.28 (s, 3H, $\mathrm{OC}\mathit{H}_3$), 2.15 - 2.11 (m, 1H, H-3*eq*), 2.07 (s, 3H, $\mathrm{COC}\mathit{H}_3$), 2.07 - 2.01 (m, 1H, H-3*ax*), 2.00 and 1.96 (2 x s, each 3H, $\mathrm{COC}\mathit{H}_3$), 0.92 [t, 9H, *J* 8.0 Hz, $\mathrm{Si(CH_2C}\mathit{H}_3)_3$], 0.55 [q, 6H, *J* 8.0 Hz, $\mathrm{Si(C}\mathit{H}_2\mathrm{CH_3)_3}$]; ^{13}C NMR ($\mathrm{CDCl_3}$): δ 170.50, 169.98 and 169.88 (3 x s, $\mathit{C}\mathrm{OCH_3}$), 167.93 (s, C-1), 98.90 (s, C-2), 70.31 (d, C-7), 67.15 (d, C-6), 66.56 (d, C-4), 64.83 (d, C-5), 60.83 (t, C-8), 52.60 (q, $\mathrm{CO_2}\mathit{C}\mathrm{H_3}$), 51.23 (q, $\mathrm{O}\mathit{C}\mathrm{H_3}$), 32.09 (t, C-3), 20.80, 20.78 and 20.70 (3 x s, $\mathrm{CO}\mathit{C}\mathrm{H_3}$), 6.60 [q, 3C, $\mathrm{Si(CH_2}\mathit{C}\mathrm{H_3)_3}$], 4.28 (t, 3C, $\mathrm{Si(}\mathit{C}\mathrm{H_2CH_3)_3}$]; ESI-TOF HRMS: *m/z* = 529.2072; calcd for $\mathrm{C_{22}H_{38}O_{11}SiNa^+}$: 529.2076.

3.4. α-Kdo disaccharides

3.4.1. Methyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-*glycero*-α-D-*talo*-oct-2-ulopyranosyl)onate-(2→4)-methyl (methyl 7,8-*O*-carbonyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (11)

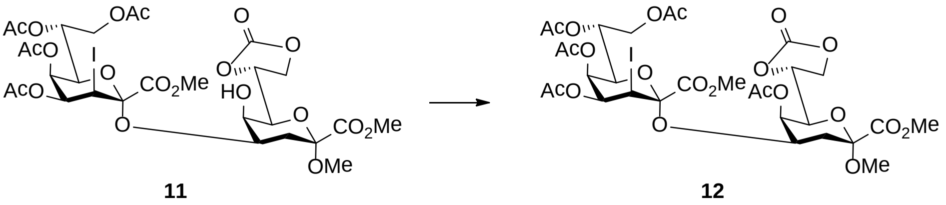


10 **11**

A mixture of **10** (105 mg, 0.359 mmol) and **5** (197 mg, 0.359 mmol) in dry $\mathrm{CH_2Cl_2}$ (8.0 mL) was treated with $\mathrm{BF_3.Et_2O}$ (148 µL, 0.719 mmol) according to the general procedure for glycosylation. After 1 h complete conversion was detected by TLC and the reaction mixture was subjected to aqueous work-up. The crude product was purified by column chromatography (toluene/EtOAC 2:1 → 1:1) affording glycal **3**[S3] (5.9 mg, 4%) and the slower migrating disaccharide **11** (229 mg, 78%).

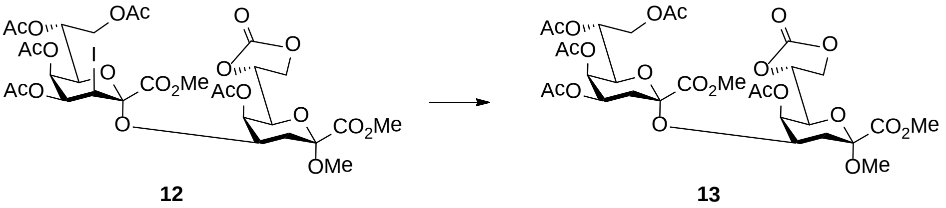
11: colorless amorphous solid; $[\alpha]_D^{20}$ + 70.9 (*c* 0.61, $\mathrm{CHCl_3}$); R_f 0.30 (toluene/EtOAc 1:1); ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.45 - 5.43 (m, 1H, H-5′), 5.33 (app td, 1H, $J_{7',6'}$ 9.3, H-7′), 4.91 (dd, 1H, $J_{4',3'}$ 5.0, $J_{4',5'}$ 3.5 Hz, H-4′), 4.90 (ddd, 1H, $J_{7,8b}$ 8.4, $J_{7,8a}$ 6.7, $J_{7,6}$ 4.1 Hz, H-7), 4.73 (dd, 1H, $J_{8'a,8'b}$ 12.2, $J_{8'a,7'}$ 3.0 Hz, H-8′a), 4.71 (dd, 1H, $J_{8a,8b}$ 9.0 Hz, H-8a), 4.54 (app t, 1H, H-8b), 4.51 (dd, 1H, $J_{3',5'}$ 0.9 Hz, H-3′), 4.22 - 4.18 (m, 2H, H-4, H-6′), 4.10 (dd, 1H, $J_{8'b,7'}$ 3.4 Hz, H-8′b), 3.88 (s, 3H, $\mathrm{CO_2C}\mathit{H}_3$), 3.88 - 3.86 (dd, 1H, $J_{6,5}$ 2.0 Hz, H-6), 3.80 (s, 3H, $\mathrm{CO_2C}\mathit{H}_3$), 3.58 - 3.55 (m, 1H, H-5), 3.21 (s, 3H, $\mathrm{OC}\mathit{H}_3$), 2.47 (b s, 1H, O*H*), 2.16 - 2.12 (m, 2H, H-3*ax*, H-3*eq*), 2.11, 2.09, 2.06 and 1.97 (4 x s, each 3H, $\mathrm{COC}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CDCl_3}$): δ 170.91, 169.92, 169.38 and 169.36 (4 x s, $\mathit{C}\mathrm{OCH_3}$), 167.40 (s, 2C, C-1, C-1′), 154.55 [s, O*C*(=O)O], 100.60 (s, C-2′), 98.99 (s, C-2), 75.76 (d, C-7), 70.28 (d, C-6), 69.46, 69.18 (2d, 2C, C-4, C-6′), 67.58 (d, C-7′), 66.10 (t, C-8), 64.96 (d, C-4′), 64.11 (d, C-5), 63.09 (d, C-5′), 61.32 (t, C-8′), 53.51 and 52.77 (2 x q, $\mathrm{CO_2}\mathit{C}\mathrm{H_3}$), 51.13 (q, $\mathrm{O}\mathit{C}\mathrm{H_3}$), 32.85 (t, C-3), 21.97 (d, C-3′), 20.88, 20.75, 20.51 and 20.48 (4 x q, $\mathrm{CO}\mathit{C}\mathrm{H_3}$); ESI-TOF HRMS: *m/z* = 838.1258; calcd for $\mathrm{C_{28}H_{37}IO_{20}NH_4^+}$: 838.1261.

3.4.2. Methyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-*glycero*-α-D-*talo*-oct-2-ulopyranosyl)onate-(2→4)-methyl (methyl 5-*O*-acetyl-7,8-*O*-carbonyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (12)



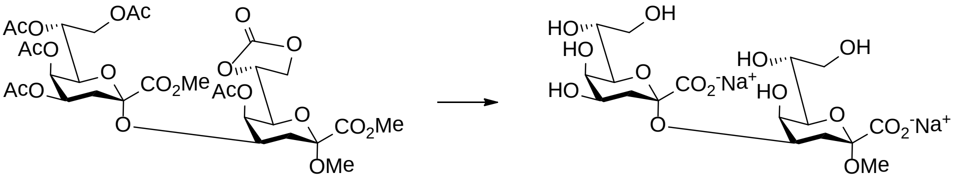
A solution of **11** (32.1 mg, 0.039 mmol) in dry pyridine (2.0 mL) was treated with acetic anhydride (0.1 mL) and 4-(*N,N*-dimethylamino)pyridine (0.5 mg, 0.004 mmol) at 0 °C for 2 h. Excessive reagent was destroyed by slow addition of dry MeOH (1 mL) at 0 °C and after 10 min the solvent was removed by coevaporation with toluene (3 x). The residue was purified by column chromatography (toluene/EtOAc 1:1) yielding **12** (32.9 mg, 98%) as a colorless amorphous solid; $[\alpha]_D^{20}$ + 68.5 (*c* 0.55, $CHCl_3$); R_f 0.34 (toluene/EtOAc 1:1); ^{1}H NMR ($CDCl_3$): δ 5.42 - 5.40 (m, 1H, H-5′), 5.34 (ddd, 1H, $J_{7',6'}$ 9.2, $J_{7',8'b}$ 3.8, $J_{7',8'a}$ 3.0 Hz, H-7′), 5.03 - 5.01 (m, 1H, H-5), 4.92 (dd, 1H, $J_{4',3'}$ 4.4, $J_{4',5'}$ 3.8 Hz, H-4′), 4.81 (ddd, 1H, $J_{7,8b}$ 8.4, $J_{7,8a}$ 6.1, $J_{7,6}$ 3.4 Hz, H-7), 4.75 (dd, 1H, $J_{8'a,8'b}$ 12.5 Hz, H-8′a), 4.57 (dd, 1H, $J_{8a,8b}$ 8.4 Hz, H-8a), 4.39 (dd, 1H, $J_{3',5'}$ 0.6 Hz, H-3′), 4.34 (app t, 1H, H-8b), 4.25 (ddd, 1H, $J_{4,3ax}$ 11.6, $J_{4,3eq}$ 5.2, $J_{4,5}$ 3.2 Hz, H-4), 4.21 (dd, 1H, $J_{6',5'}$ 2.1 Hz, H-6′), 4.12 (dd, 1H, H-8′b), 3.99 (dd, 1H, $J_{6,5}$ 0.9 Hz, H-6), 3.86 and 3.82 (2 x s, each 3H, CO_2CH_3), 3.24 (s, 3H, OCH_3), 2.24 (dd, 1H, $J_{3eq,3ax}$ 12.8 Hz, H-3*eq*), 2.17 (s, 3H, $COCH_3$), 2.15 (app t, 1H, H-3*ax*), 2.11, 2.10, 2.06 and 1.97 (4 x s, each 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.72, 170.10, 170.01, 169.44 and 169.38 (5 x s, $COCH_3$), 167.15 and 165.68 (2 x s, C-1, C-1′), 154.04 [s, OC(=O)O], 101.26 (s, C-2′), 98.97 (s, C-2), 75.07 (d, C-7), 70.38 (d, C-6), 69.46 (d, C-6′), 68.63 (d, C-4), 67.79 (d, C-7′), 66.39 (d, C-5), 64.95 (d, C-4′), 64.55 (t, C-8), 63.14 (d, C-5′), 61.45 (t, C-8′), 53.38 and 52.85 (2 x q, CO_2CH_3), 51.46 (q, OCH_3), 34.01 (t, C-3), 22.08 (d, C-3′), 20.92, 20.78, 20.76, 20.58 and 20.50 (5 x q, $COCH_3$); ESI-TOF HRMS: *m/z* = 880.1362; calcd for $C_{30}H_{39}IO_{21}NH_4^+$: 880.1367.

3.4.3. Methyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosyl)onate-(2→4)-methyl (methyl 5-*O*-acetyl-7,8-*O*-carbonyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (13)



A solution of **12** (27.3 mg, 0.032 mmol) and lauroyl peroxide (7.6 mg, 0.019 mmol) in dry cyclohexane (4 mL) was treated according to the general procedure for dehalogenation. After 4 h another portion of lauroyl peroxide (7.6 mg, 0.019 mmol) was added and after 24 h at reflux temperature full conversion was detected by TLC. After removal of the solvent, column chromatography (toluene/EtOAc 1:1) provided **13** (22.6 mg, 97%) as a colorless oil; $[\alpha]_D^{20}$ + 89.6 (*c* 0.80, $CHCl_3$); R_f 0.30 (toluene/EtOAc 1:1, HP-TLC); ^{1}H NMR ($CDCl_3$): δ 5.36 - 5.34 (m, 1H, H-5′), 5.22 - 5.20 (m, 1H, H-5), 5.20 - 5.15 (m, 2H, H-4′, H-7′), 4.75 (ddd, 1H, $J_{7,8b}$ 8.3, $J_{7,8a}$ 6.5, $J_{7,6}$ 4.1 Hz, H-7), 4.66 - 4.60 (m, 3H, H-4, H-8a, H-8′a), 4.38 (app t, 1H, $J_{8b,8a}$ 8.5 Hz, H-8b), 4.11 (dd, 1H, $J_{6',7'}$ 9.4, $J_{6',5'}$ 1.4 Hz, H-6’), 4.09 (dd, 1H, $J_{8'b,8'a}$ 12.5, $J_{8'b,7'}$ 3.6 Hz, H-8′b), 4.03 (dd, 1H, $J_{6,5}$ 1.2 Hz, H-6), 3.85 and 3.83 (2 x s, each 3H, $CO_2C\mathit{H}_3$), 3.24 (s, 3H, $OC\mathit{H}_3$), 2.17 (app t, 1H, $J_{3'ax,3'eq} = J_{3'ax,4'}$ 12.8 Hz, H-3′*ax*), 2.15 - 2.11 (m, 7H, H-3*eq*, 2 x $COC\mathit{H}_3$), 2.08 - 2.01 (m, 5H, H-3*ax*, H-3′*eq*, $COC\mathit{H}_3$), 1.99 (s, 3H, $COC\mathit{H}_3$), 1.98 (s, 3H, $COC\mathit{H}_3$); ^{13}C NMR ($CDCl_3$): δ 170.92, 170.27, 170.08, 169.97 and 169.57 (5 x s, *C*OCH$_3$), 167.38 and 167.11 (2 x s, C-1, C-1′), 154.07 [s, O*C*(=O)O], 99.20 and 97.63 (2 x s, C-2, C-2′), 74.97 (d, C-7), 70.31 (d, C-6), 69.56 (d, C-6′), 67.69 (d, C-7′), 66.57 (d, C-5), 66.24 (d, C-4′), 65.79 (d, C-4), 65.12 (t, C-8), 64.26 (d, C-5′), 61.71 (t, C-8′), 53.12 and 52.76 (2 x q, $CO_2\mathit{C}H_3$), 51.38 (q, O*C*H$_3$), 34.23 (t, C-3′), 31.46 (t, C-3), 20.77, 20.62 and 20.59 (3 x s, 5C, CO*C*H$_3$); ESI-TOF HRMS: *m/z* = 759.1993; calcd for $C_{30}H_{40}O_{21}Na^+$: 759.1954.

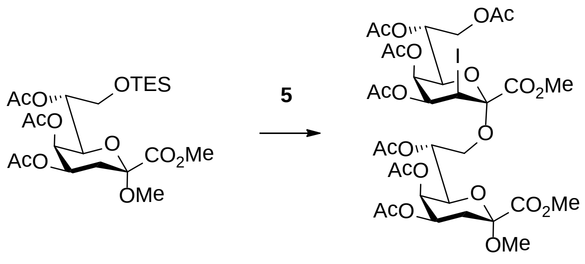
3.4.4. Sodium (3-deoxy-α-D-*manno*-oct-2-ulopyranosyl)onate-(2→4)-sodium (methyl α-D-*manno*-oct-2-ulopyranosid)onate (14)



13 **14**

According to the general procedure for global deprotection: A solution of **13** (10.6 mg, 0.014 mmol) in dry MeOH (1.0 mL) was treated with NaOMe (0.1 M in MeOH; 20 µL, 0.002 mmol) for 8 h and after addition of further NaOMe (0.1 M in MeOH; 20 µL, 0.002 mmol) stirring was continued for 14 h. After the described work-up the residue was dissolved in water (2.0 mL) and treated with aq NaOH (0.1 M, 1.0 mL). After 3 h it was subjected to standard work-up und the crude product was desalted by successive purification on a PD10 (H_2O) and BioGel-P2 column (H_2O/EtOH 19:1) followed by lyophilisation of pooled fractions affording **14** (6.2 mg, 83%) as an amorphous colorless solid. $[\alpha]_D^{20}$ + 80.2 (*c* 0.51, D_2O); ^1H NMR (D_2O, pH ~ 6.5)[S7]: δ 4.00 - 3.96 (m, 3H, H-4, H-4′, H-5), 3.93 - 3.92 (m, 1H, H-5′), 3.89 - 3.80 (m, 4H, H-7, H-7′, H-8a, H-8′a), 3.64 - 3.60 (m, 1H, H-8′b), 3.55 - 3.50 (m, 2H, H-6′, H-8b), 3.41 (dd, 1H, $J_{6,7}$ 8.6, $J_{6,5}$ 0.8 Hz, H-6), 3.03 (s, 3H, $OC\mathit{H}_3$), 2.03 (ddd, 1H, $J_{3'eq,3'ax}$ 13.2, $J_{3'eq,4'}$ 5.0, $J_{3'eq,5'}$ 0.8 Hz, H-3′*eq*), 1.88 - 1.84 (m, 1H, H-3*eq*), 1.82 - 1.76 (app t, 1H, H-3*ax*), 1.67 (dd, 1H, $J_{3'ax,4'}$ 12.1 Hz, H-3′*ax*); ^{13}C NMR (D_2O, pH ~ 6.5): δ 176.67 and 176.07 (2 x s, C-1′, C-1), 101.34 and 100.36 (2 x s, C-2, C-2′), 73.09 (d, C-6′), 72.15 (d, C-6), 70.76 (d, C-7′), 70.24 (d, C-7), 69.64 (d, C-4), 67.17 (d, C-5′), 66.72 (d, C-4′), 65.17 (d, C-5), 63.91 and 63.86 (2 x t, C-8, C-8′), 51.41 (q, O*C*H$_3$), 35.38 (t, C-3′), 34.05 (t, C-3); ESI-TOF HRMS: *m/z* = 495.1327; calcd for $C_{17}H_{28}O_{15}Na^+$: 495.1320.

3.4.5. Methyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-*glycero*-α-D-*talo*-oct-2-ulopyranosyl)onate-(2→8)-methyl (methyl 4,5,7-tri-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (16)

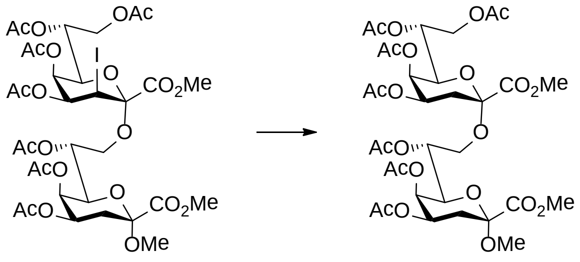


15 **16**

A suspension of **15** (27.1 mg, 0.053 mmol) and **5** (35.2 mg, 0.064 mmol) in dry CH_2Cl_2 (2.0 mL) was treated with $BF_3.Et_2O$ (22.0 µL, 0.107 mmol) according to the general procedure for glycosylation. After 2 h complete conversion was determined by TLC and the mixture was subjected to aqueous work-up. Subsequent HP-column chromatography (toluene/EtOAc 3:1 → 1:1) afforded glycal **3**[S3] (1.8 mg, 7%) and the slower migrating disaccharide **16** (30.3 mg, 62%).

16: colorless oil; $[\alpha]_D^{20}$ + 48.8 (*c* 0.46, $CHCl_3$); R_f 0.22 (toluene/EtOAc 1:1); ^{1}H NMR ($CDCl_3$): δ 5.38 - 5.33 (m, 3H, H-5, H-5′, H-7′), 5.31 (ddd, 1H, $J_{4,3ax}$ 12.3, $J_{4,3eq}$ 5.0, $J_{4,5}$ 3.1 Hz, H-4), 5.11 (ddd, 1H, $J_{7,6}$ 9.6, $J_{7,8a}$ 4.8, $J_{7,8b}$ 2.4 Hz, H-7), 4.92 (dd, 1H, $J_{4',3'}$ 4.7, $J_{4',5'}$ 3.8 Hz, H-4′), 4.64 (dd, 1H, $J_{8'a,8'b}$ 12.4, $J_{8'a,7'}$ 2.3 Hz, H-8′a), 4.52 (d, 1H, H-3′), 4.23 (dd, 1H, $J_{8'b,7'}$ 3.6 Hz, H-8′b), 4.17 (dd, 1H, $J_{6',7'}$ 9.7, $J_{6',5'}$ 2.0 Hz, H-6′), 4.12 (dd, 1H, $J_{6,5}$ 1.3 Hz, H-6), 3.87 (dd, 1H, $J_{8a,8b}$ 11.6 Hz, H-8a), 3.84 (s, 3H, CO_2CH_3), 3.81 (s, 3H, CO_2CH_3), 3.67 (dd, 1H, H-8b), 3.31 (s, 3H, OCH_3), 2.20 - 2.17 (m, 1H, H-3*eq*), 2.11 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.09 - 2.04 (m, 10H, 3 x $COCH_3$, H-3*ax*), 1.98 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.40, 170.35, 170.11, 169.85, 169.68, 169.43 and 169.24 (7 x s, $COCH_3$), 167.35 and 165.92 (2 x s, C-1, C-1’), 101.89 (s, C-2′), 99.10 (s, C-2), 68.50 (d, C-6′), 68.36 and 68.35 (2 x d, C-6, C-7), 67.58 (d, C-7′), 66.30 (d, C-4), 65.16 (d, C-4′), 64.44 (d, C-5), 64.40 (t, C-8), 63.09 (d, C-5′), 61.82 (t, C-8′), 53.05 and 52.63 (2 x q, CO_2CH_3), 51.48 (q, OCH_3), 31.55 (t, C-3), 21.38 (d, C-3′), 20.88, 20.74, 20.71, 20.67, 20.65 and 20.58 (6 x q, 7C, $COCH_3$); ESI-TOF HRMS: *m/z* = 938.1783; calcd for $C_{33}H_{45}IO_{22}NH_4^+$: 938.1785.

3.4.6. Methyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosyl)onate]-(2→8)-methyl (methyl 4,5,7-tri-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosid)onate (17)

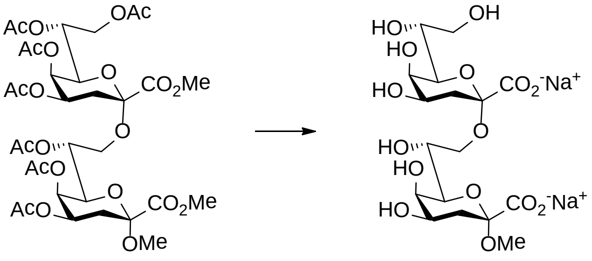


16 **17**

Following the general procedure for dehalogenation: **16** (29.0 mg, 0.032 mmol) was treated with lauroyl peroxide (3.8 mg, 0.009 mmol) in dry cyclohexane (2.0 mL) for 2 h. Evaporation of the solvent and purification by column chromatography (toluene/EtOAc 2:1) provided **17** (23.7 mg, 95%) as a colorless oil; $[\alpha]_D^{20}$ + 68.8 (*c* 0.88, $CHCl_3$); R_f 0.38 (toluene/EtOAc 1:1, HP-TLC); ^{1}H NMR ($CDCl_3$): δ 5.36 - 5.34 (m, 1H, H-5), 5.33 - 5.28

(m, 2H, H-4, H-5′), 5.22 - 5.15 (m, 2H, H-4′, H-7′), 5.13 (ddd, 1H, $J_{7,6}$ 9.7, $J_{7,8b}$ 4.5, $J_{7,8a}$ 2.4 Hz, H-7), 4.56 (dd, 1H, $J_{8'a,8'b}$ 12.4, $J_{8'a,7'}$ 2.3 Hz, H-8′a), 4.16 (dd, 1H, $J_{8'b,7'}$ 4.0 Hz, H-8′b), 4.14 (dd, 1H, $J_{6,5}$ 1.6 Hz, H-6), 4.04 (dd, 1H, $J_{6',7'}$ 9.7, $J_{6',5'}$ 1.4 Hz, H-6′), 3.85 (dd, 1H, $J_{8a,8b}$ 11.5, H-8a), 3.81 (s, 3H, CO_2CH_3), 3.79 (s, 3H, CO_2CH_3), 3.75 (dd, 1H, H-8b), 3.33 (s, 3H, OCH_3), 2.23 - 2.15 (m, 2H, H-3*eq*, H-3′*eq*), 2.11 - 2.03 (m, 14H, 4 x $COCH_3$, H-3*ax*, H-3′*ax*), 2.00, 1.96 and 1.95 (3 x s, each 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.49, 170.41, 170.35, 169.88, 169.81, 169.75 and 169.65 (7 x s, $COCH_3$), 167.47 and 167.20 (2 x s, C-1, C-1′), 99.07 and 98.96 (2 x s, C-2, C-2′), 68.85 (d, C-6′), 68.36 and 68.32 (2 x d, C-6, C-7), 67.63 (d, C-7′), 66.37 and 66.12 (2 x d, C-4, C-4′), 64.51 (d, C-5), 64.16 (d, C-5′), 62.47 (t, C-8), 62.02 (t, C-8′), 52.73 and 52.61 (2 x q, CO_2CH_3), 51.43 (q, OCH_3), 31.66 and 31.48 (2 x t, C-3, C-3′), 20.74, 20.73, 20.67 and 20.61 (4 x q, 7C, $COCH_3$); ESI-TOF HRMS: *m/z* = 812.2819; calcd for $C_{33}H_{46}O_{22}NH_4^+$: 812.2819.

3.4.7. Sodium (3-deoxy-α-D-*manno*-oct-2-ulopyranosyl)onate]-(2→8)-sodium (methyl α-D-*manno*-oct-2-ulopyranosid)onate (18)



17 **18**

According to the general procedure for global deprotection: a solution of **17** (23.0 mg, 0.029 mmol) in dry MeOH (4.0 mL) was treated with NaOMe (0.1 M in MeOH; 41 µL, 0.004 mmol) for 24 h. After the described work-up the residue was dissolved in water (2.0 mL) and treated with aq NaOH (0.1 M, 2.0 mL). After 2 h it was subjected to standard work-up and the crude product was desalted by successive purification on a PD10 (H_2O) and BioGel-P2 (H_2O/EtOH 19:1) column followed by lyophilisation of pooled fractions affording **18** (12.7 mg, 85%) as an amorphous colorless solid; $[\alpha]_D^{20}$ + 80.9 (*c* 0.73, D_2O); ^{1}H NMR (D_2O, pH ~ 6.5): δ 3.98 - 3.89 (m, 5H, H-4, H-4′, H-5, H-5′, H-7), 3.84 - 3.78 (m, 2H, H-7′, H-8′a), 3.58 - 3.48 (m, 5H, H-6, H-6′, H-8a, H-8b, H-8′b), 3.06 (s, 3H, OCH_3), 1.96 (ddd, 1H, $J_{3eq,3ax}$ 13.2, $J_{3eq,4}$ 5.4, $J_{3eq,5}$ 0.7 Hz, H-3*eq*), 1.93 - 1.88 (m, 1H, H-3′*eq*), 1.74 - 1.65 (m, 2H, H-3*ax*, H-3′*ax*); ^{13}C NMR (D_2O, pH ~ 6.5): δ 176.62 and 176.10 (2 x s, C-1, C-1′), 101.36 and 101.34 (2 x s, C-2, C-2′), 72.46 and 72.21 (2 x d, C-6, C-6′), 70.12 (d, C-7′), 68.80 (d, C-7), 67.19 and 67.13 (2 x d, C-5, C-5′), 66.94 and 66.85 (2 x d, C-4, C-4′), 65.89 (t, C-8), 63.88 (t, C-8′), 51.47 (q, OCH_3), 34.89 (t, 2C, C-3, C-3′) ; ESI-TOF HRMS: *m/z* = 495.1336; calcd for $C_{17}H_{28}O_{15}Na^+$: 495.1320.

3.5. ^{1}H-NMR for calculation of molecular ratio of compound 25 and hydroylsed donor

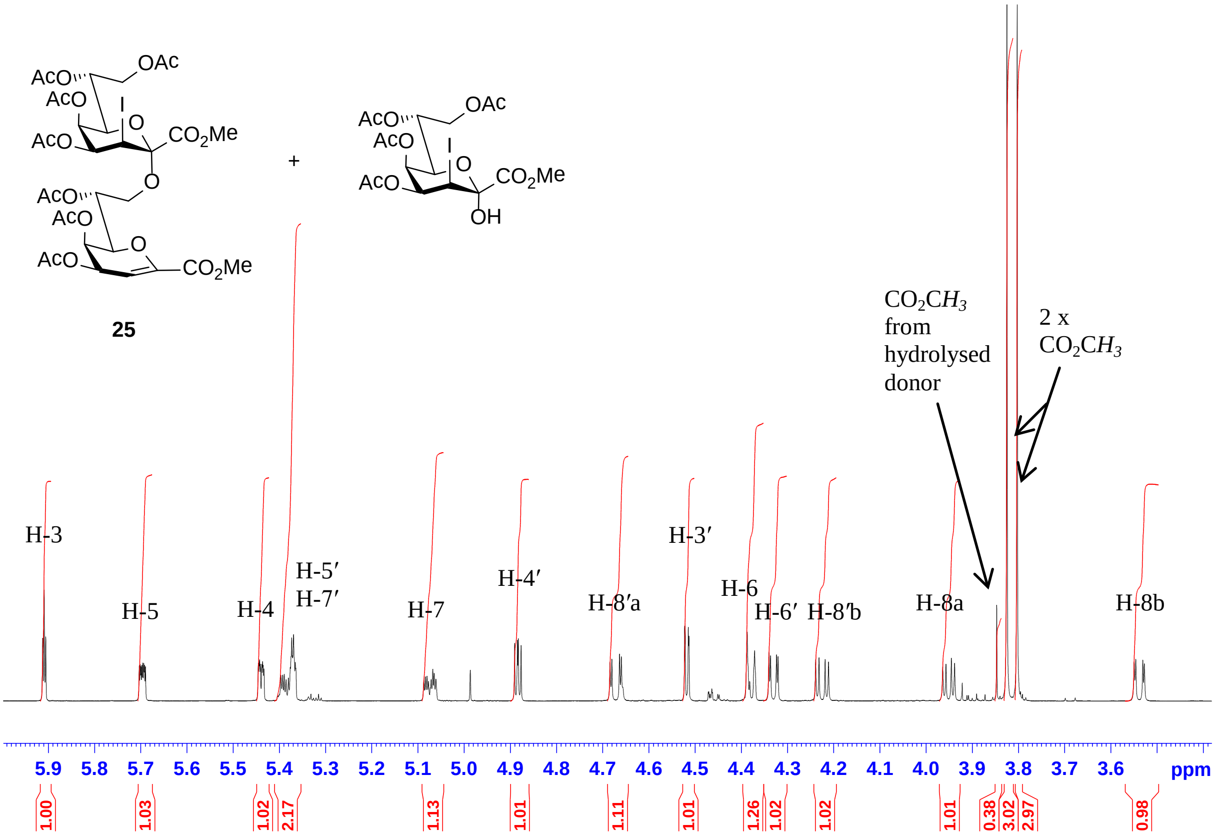


Figure S2: ^{1}H-NMR of **25** containing hydrolysed donor as minor impurity: The yield was calculated using the $CO_2C\mathit{H}_3$-signals to determine the molecular ratio

4. References for SI

[S1] R. K. Harris, E. D. Becker, S. M. C. De Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795-1818.

[S2] D. Solomon, M. Fridman, J. Zhang, T. Baasov, *Org. Lett.* **2001**, *3*, 4311-4314.

[S3] A. Claesson, K. Luthman, *Acta Chem. Scand. B* **1982**, *36*, 719-720.

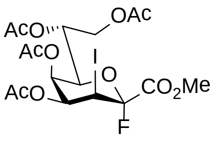
[S4] F. M. Unger, D. Stix, G. Schulz, *Carbohydr. Res.* **1980**, *80*, 191-195; P. Kosma, M. Strobl, G. Allmaier, E. Schmid, H. Brade, *Carbohydr. Res.* **1994**, 254, 105-132.

[S5] Dissolves in boiling cyclohexane.

[S6] Tetraol **19** was prepared from Kdo-peracetate **1** by standard transesterification catalyzed by sodium methoxide and was used without purification after neutralization and solvent evaporation.

[S7] Spectroscopic data is in accordance with published data: H. Brade, U. Zähringer, E. T. Rietschel, R. Christian, G. Schulz, F. M. Unger, *Carbohydr. Res.* **1984**, *134*, 157-166.

5. NMR spectra of compounds 5 - 18, 20 - 24 and 26 - 33



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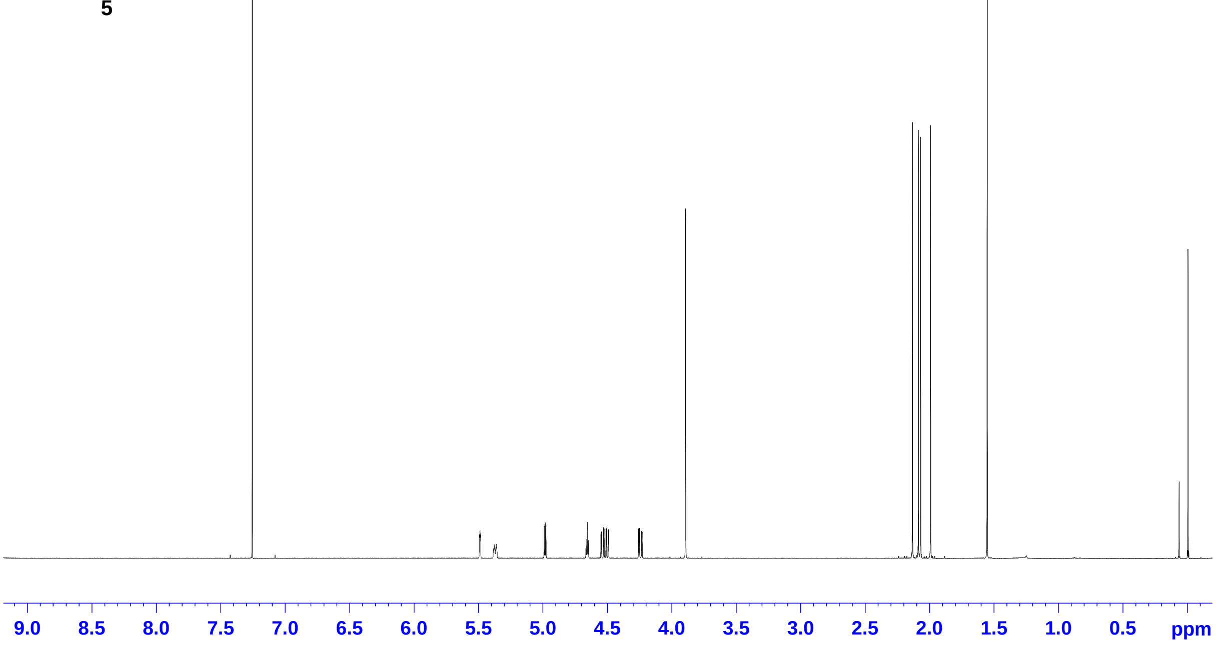
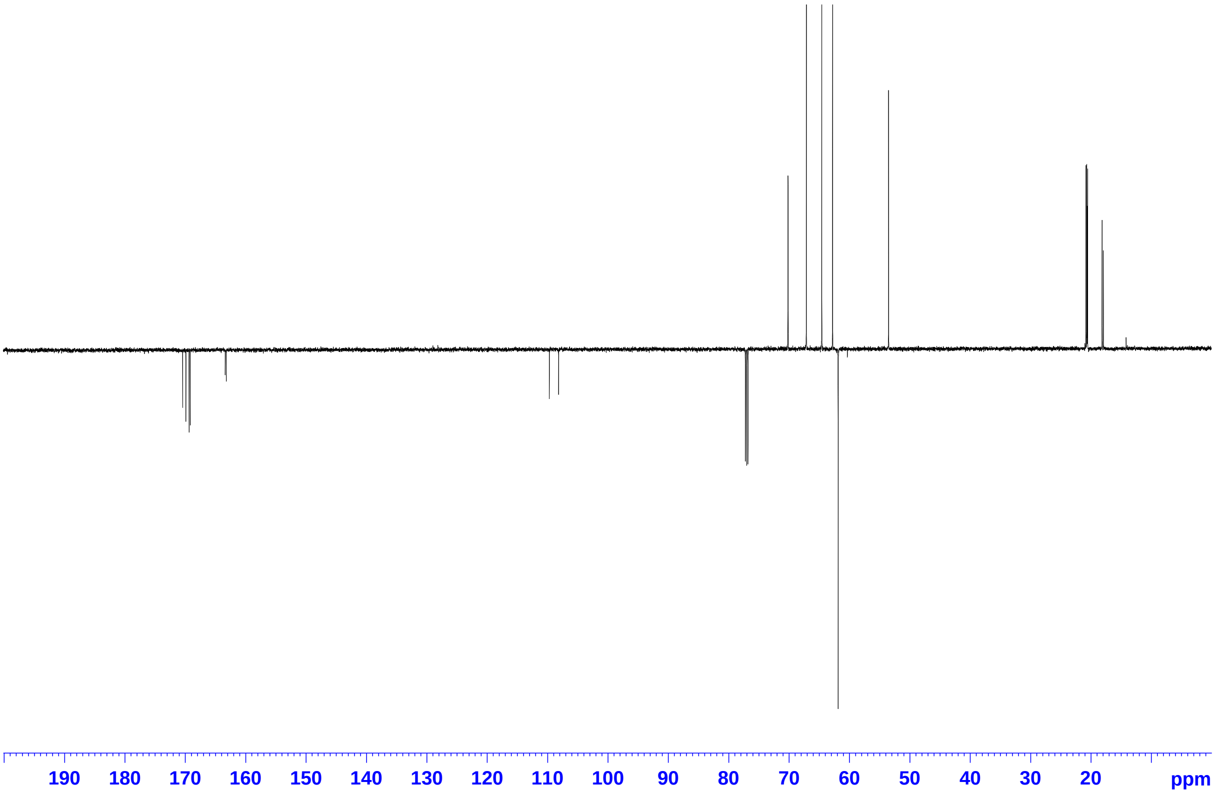
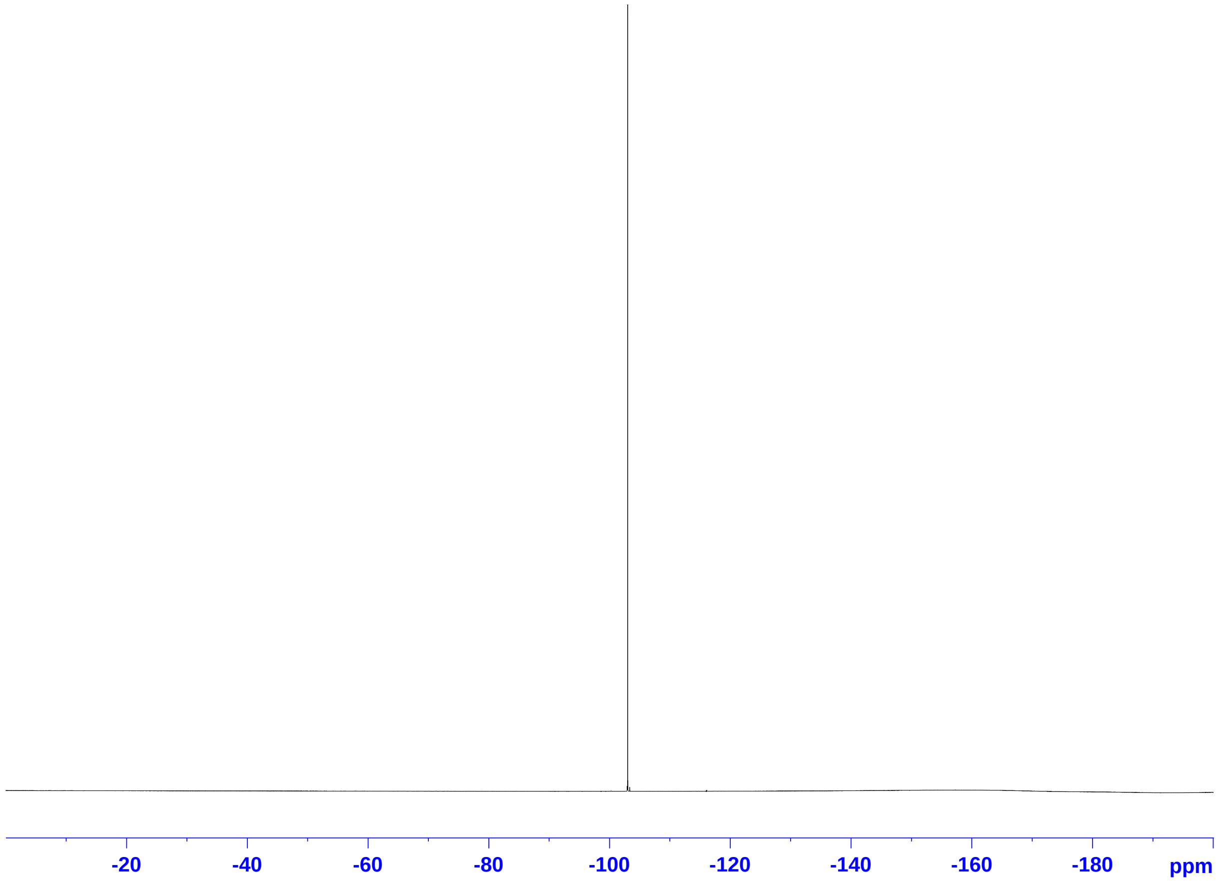


^{1}H-NMR (600 MHz, $CDCl_3$)

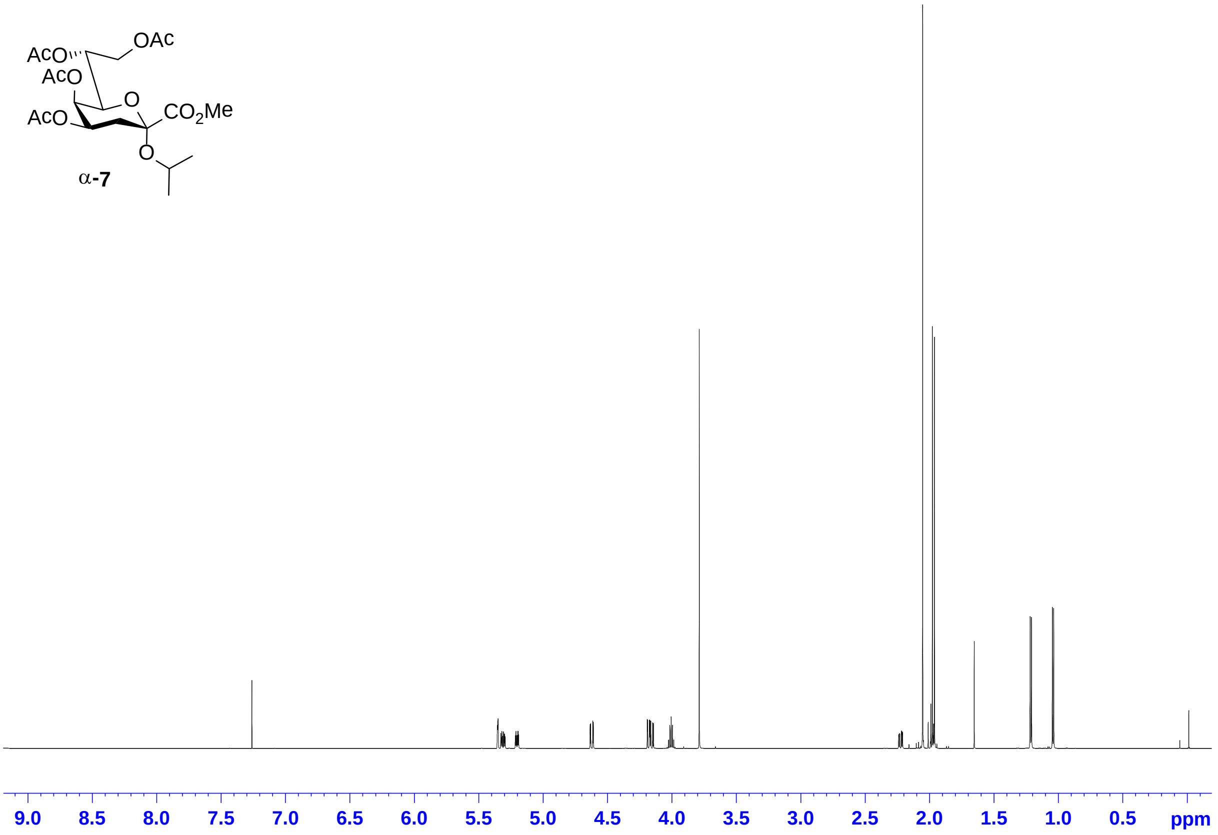


^{13}C-NMR (150 MHz, $CDCl_3$)



^{19}F-NMR (565 MHz, $CDCl_3$)

α-**7**



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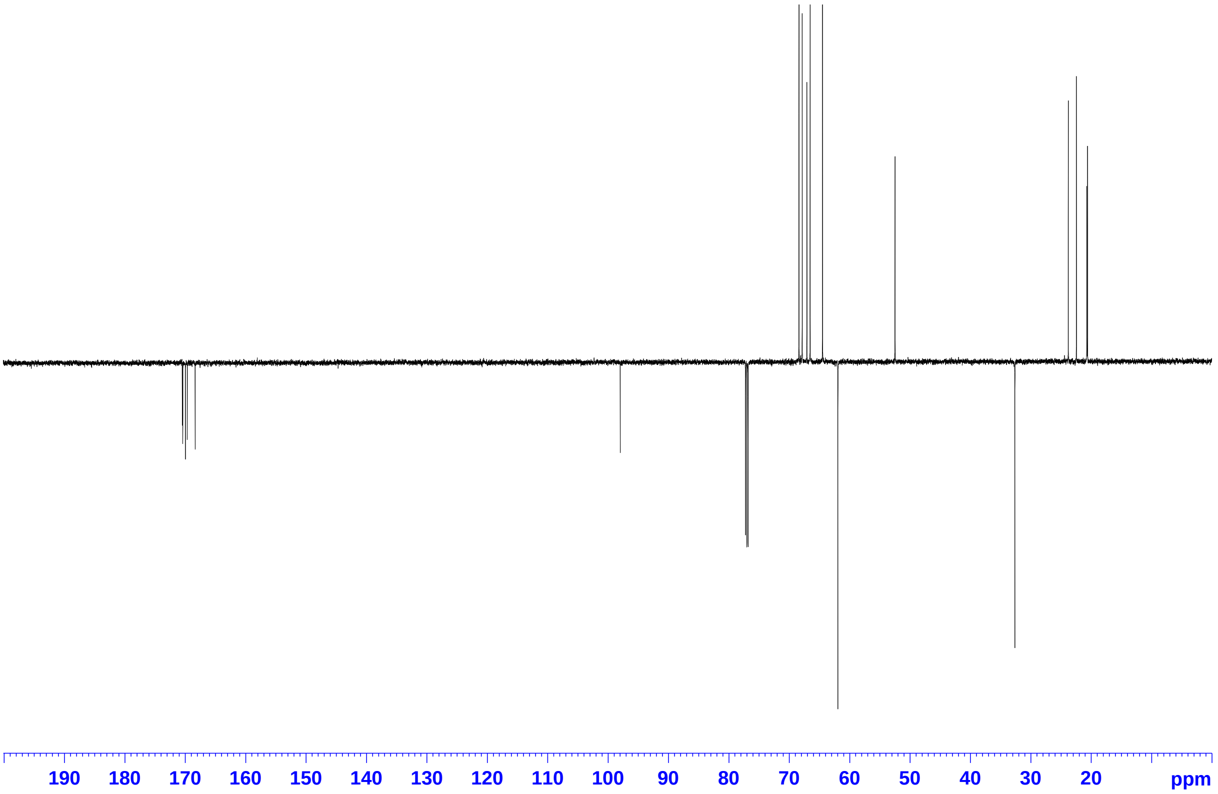
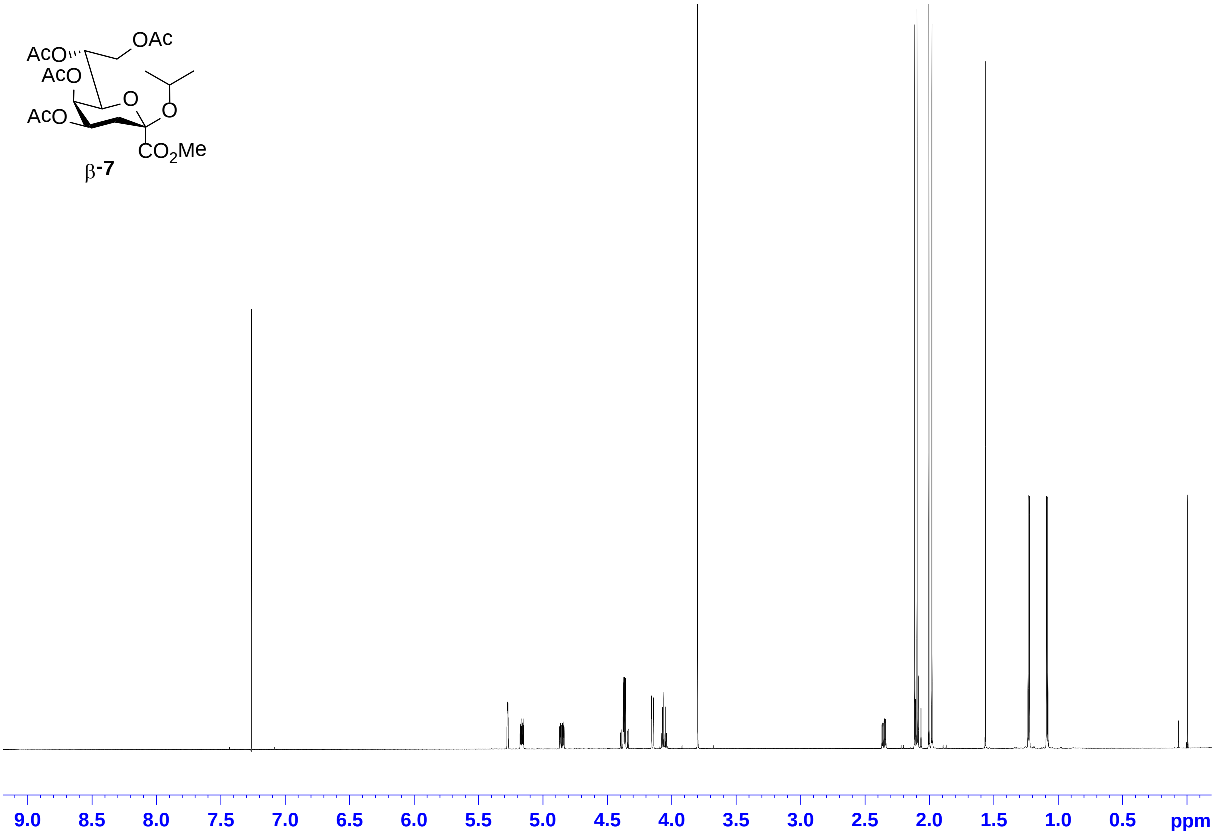
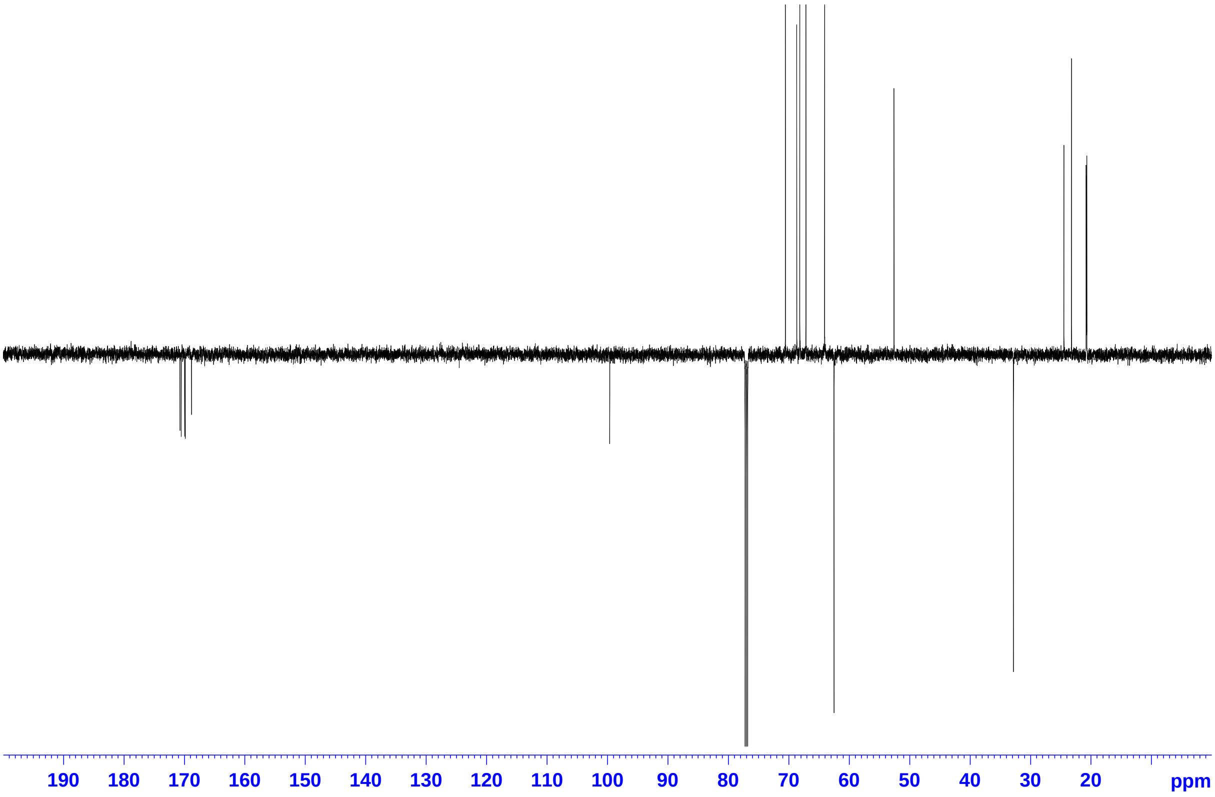


^{13}C-NMR (150 MHz, $CDCl_3$)

β-**7**



^{1}H-NMR (600 MHz, CDCl$_3$)



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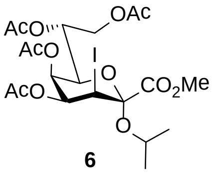

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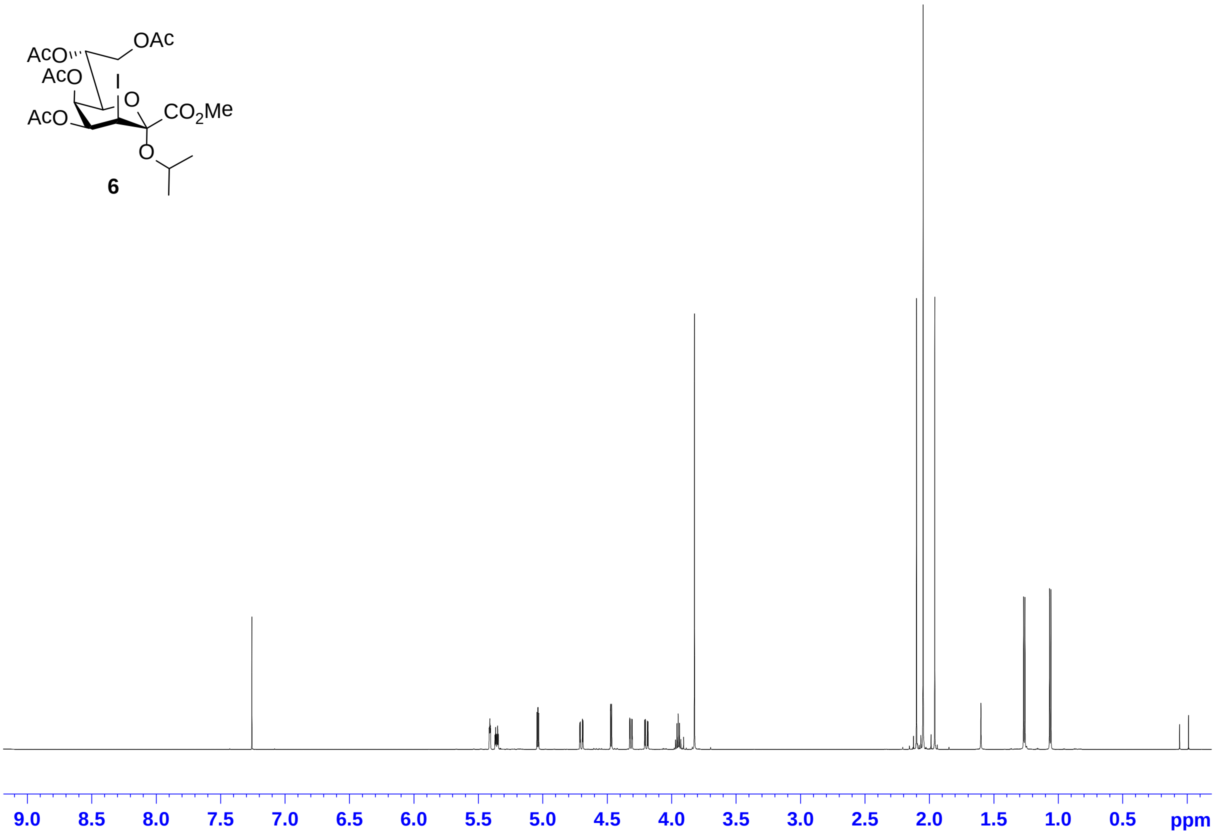

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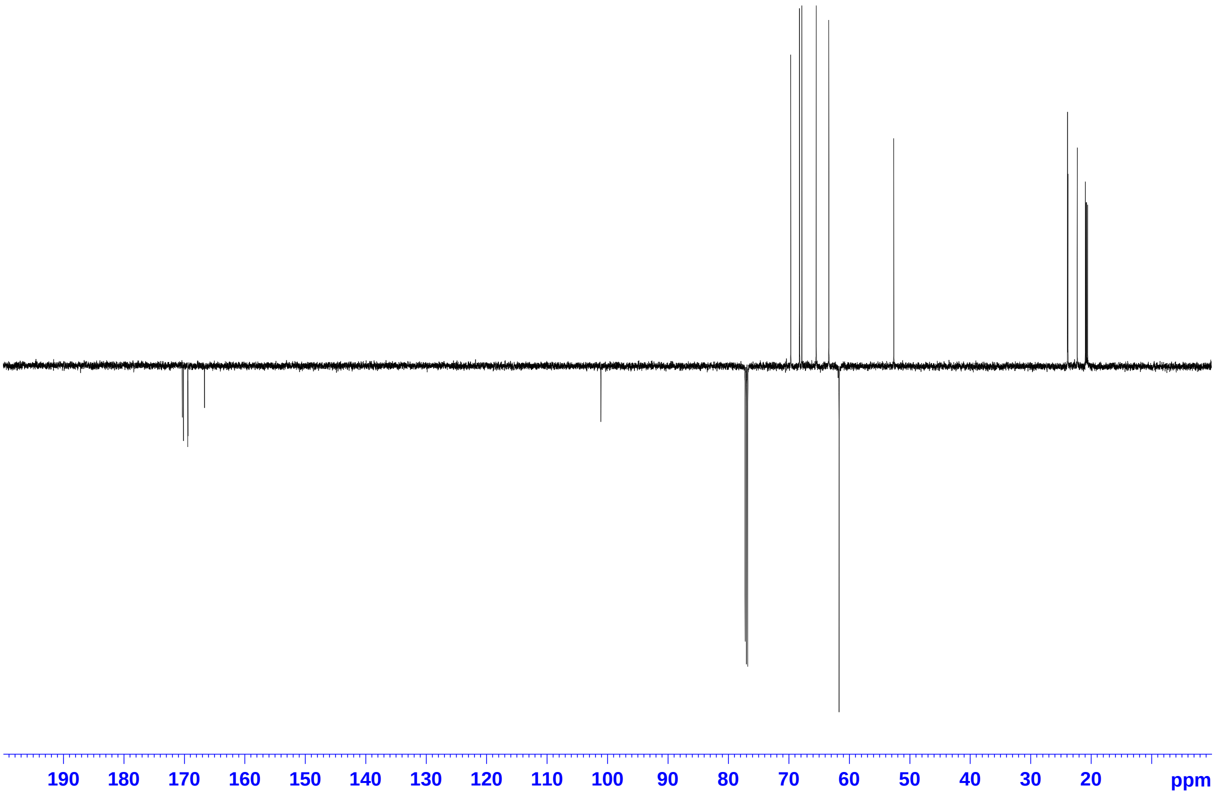

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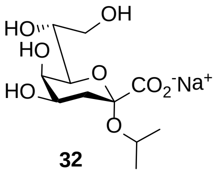

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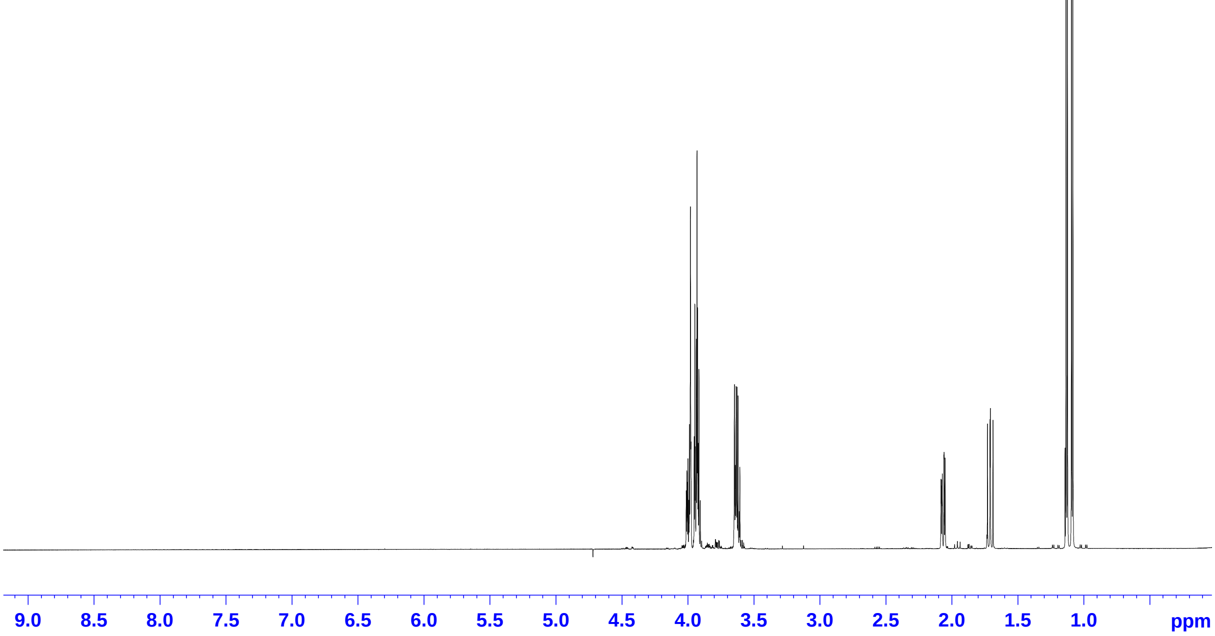

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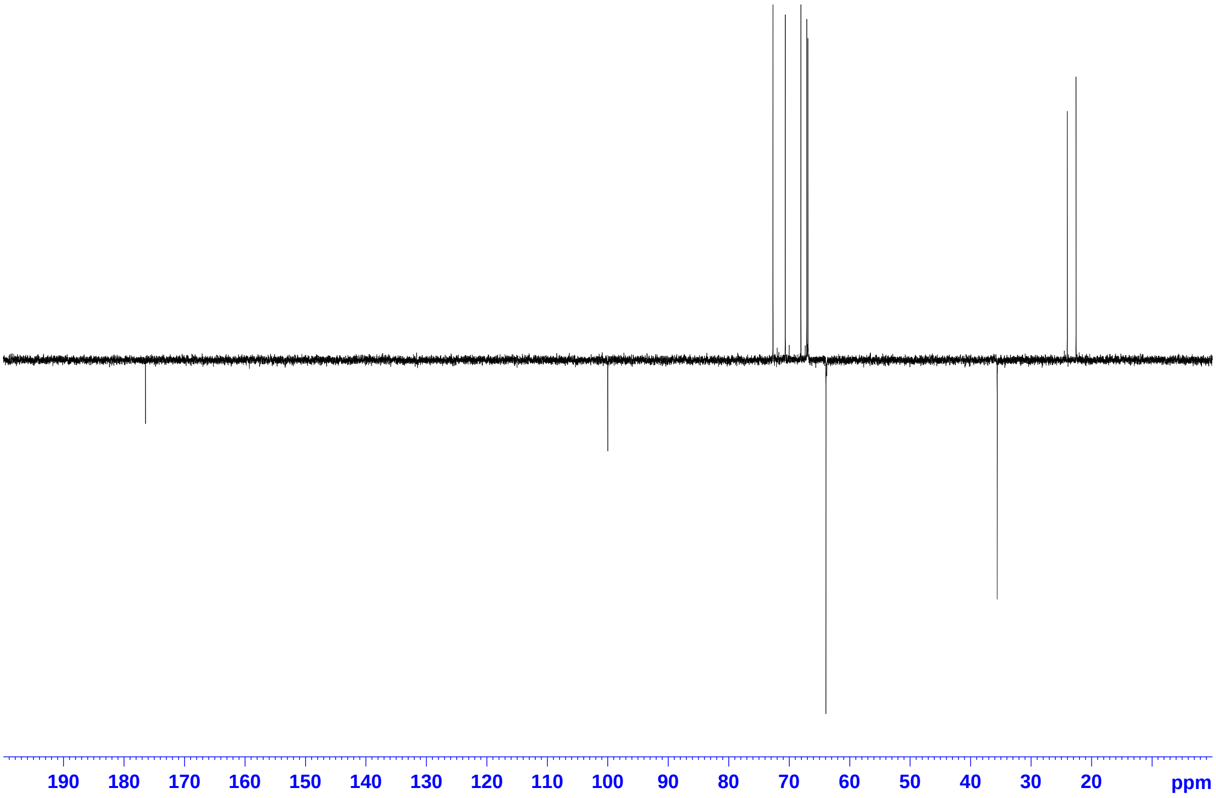

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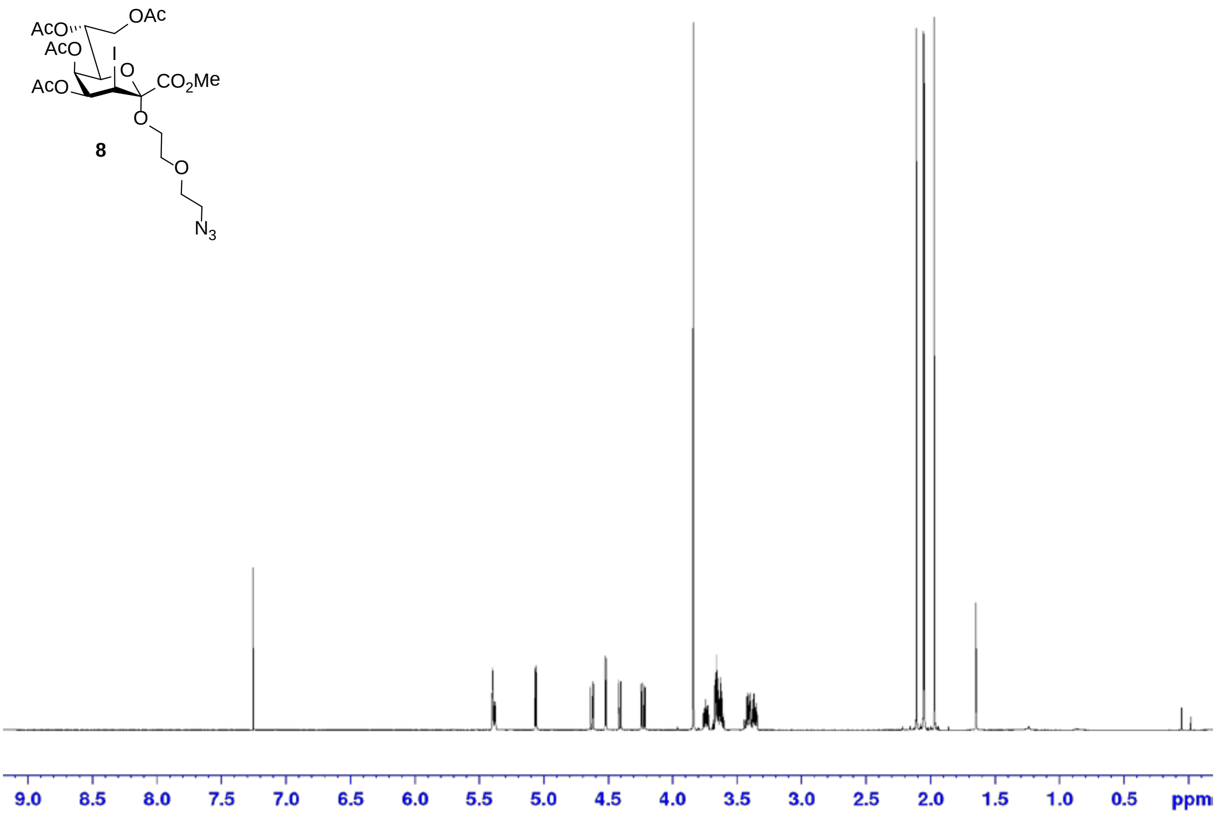

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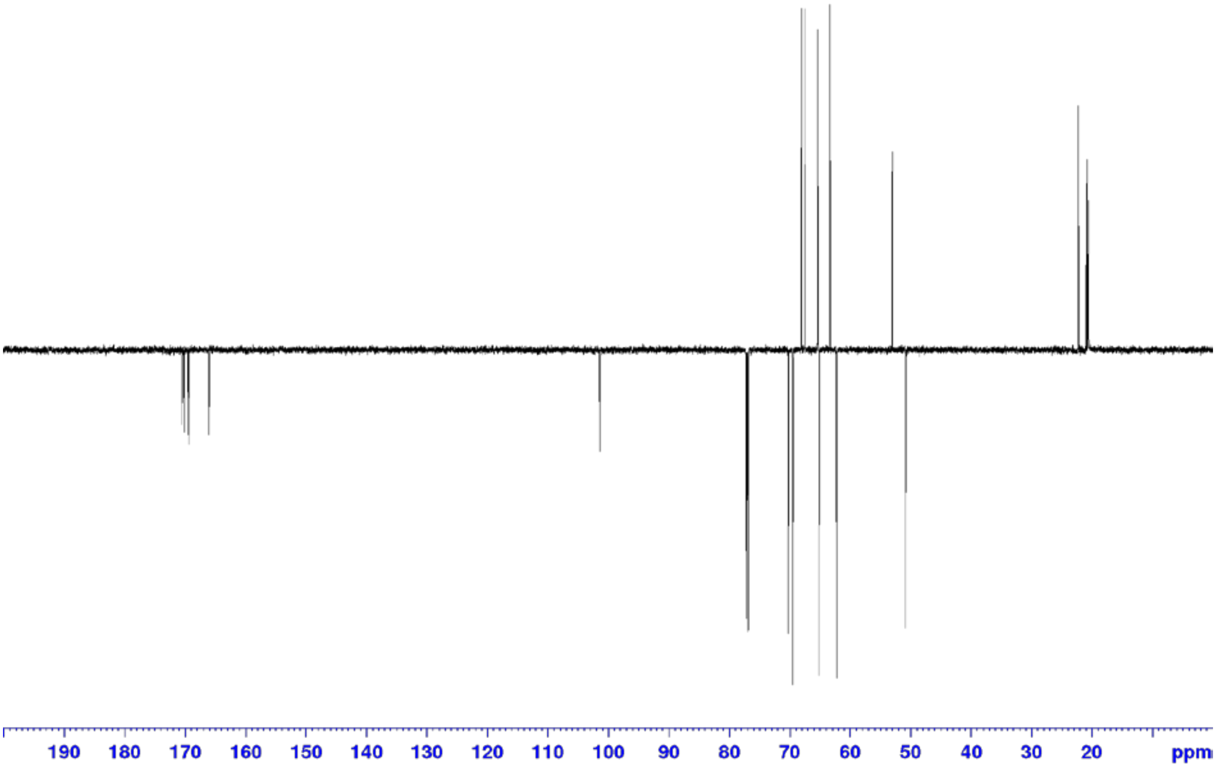
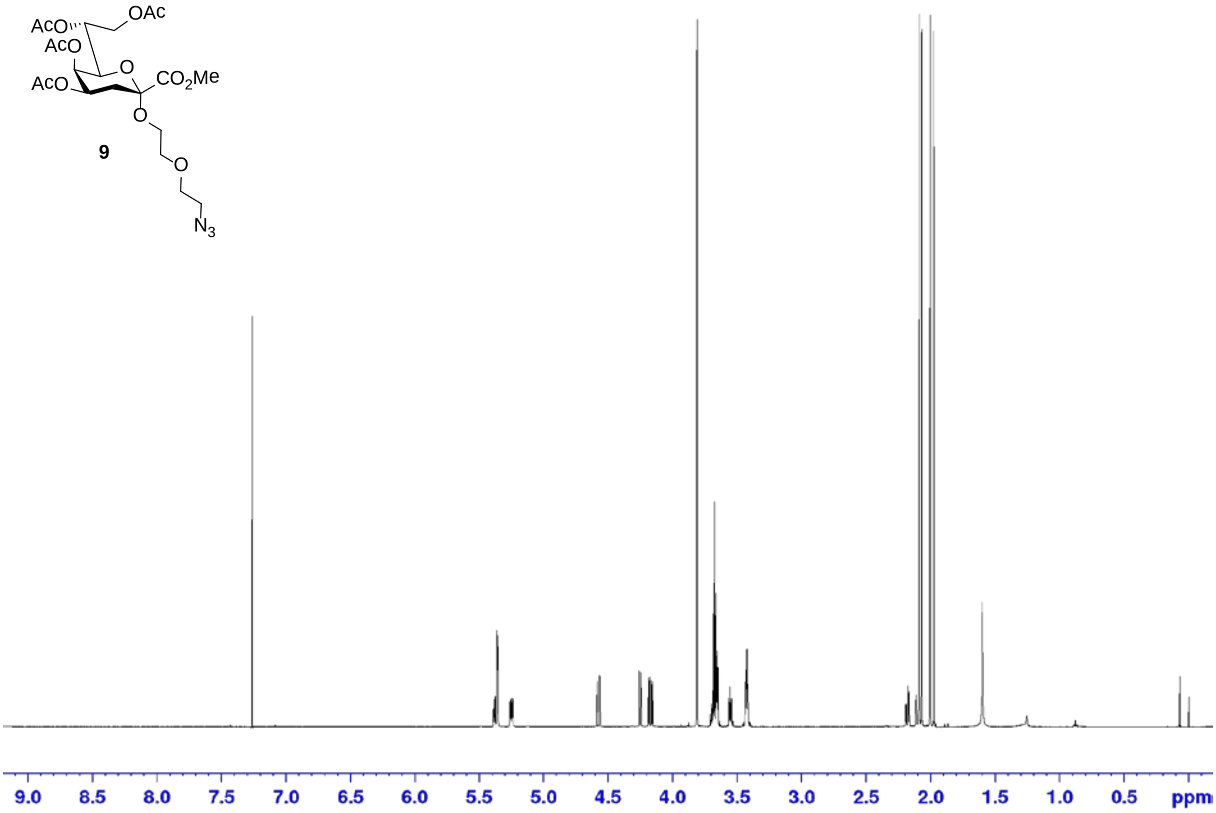


^{13}C-NMR (150 MHz, CDCl$_3$)

9



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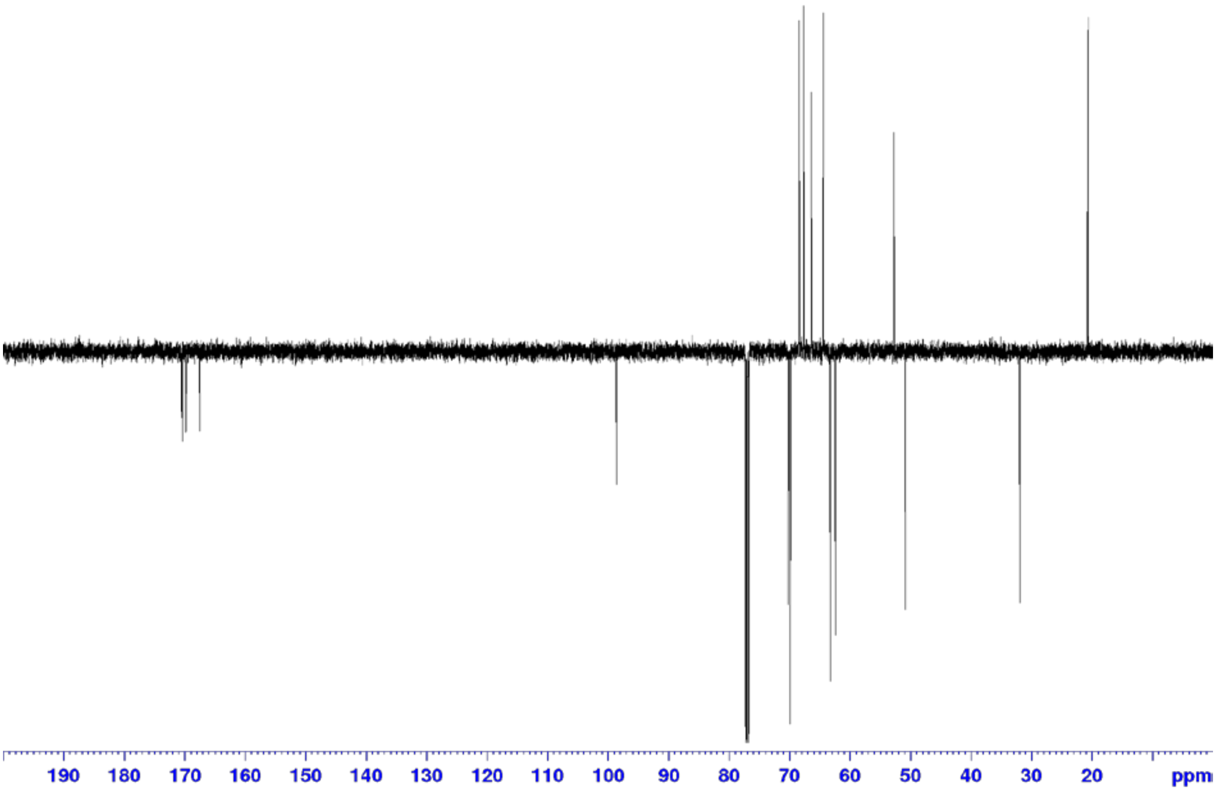

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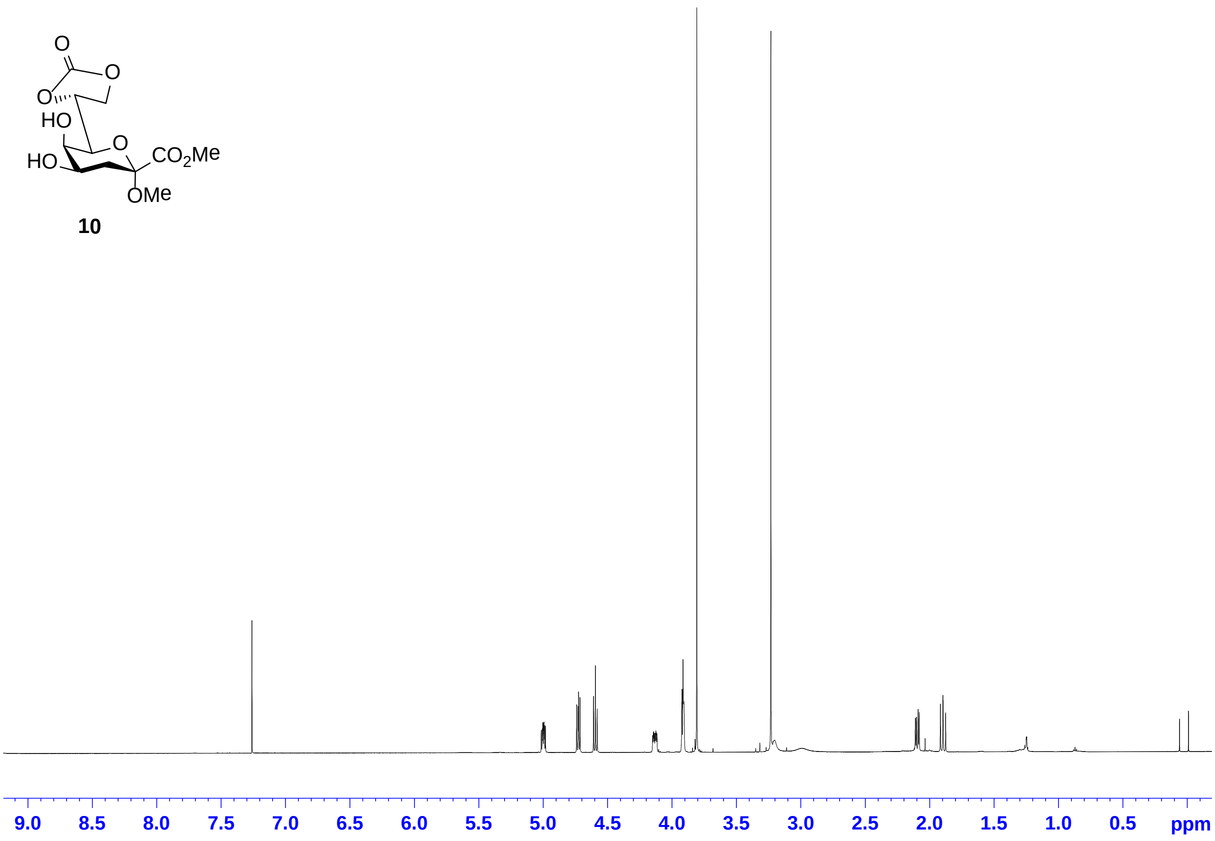

10

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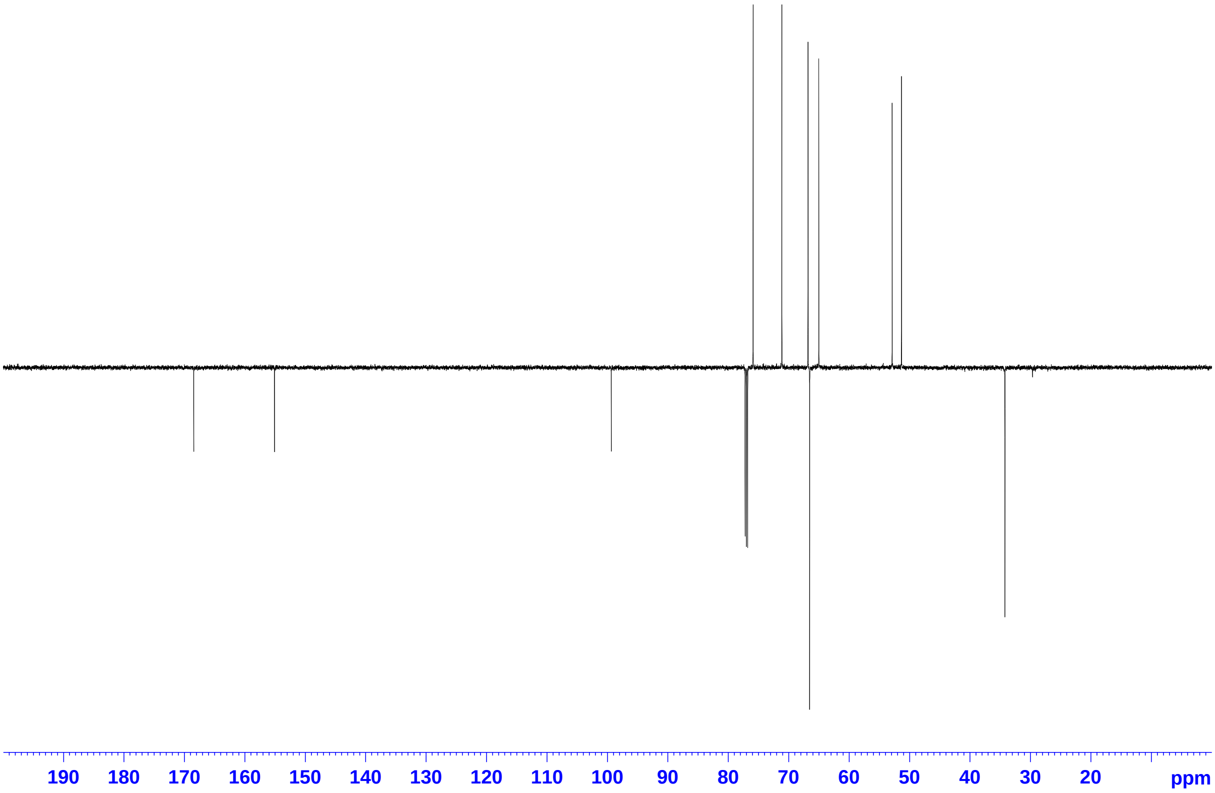

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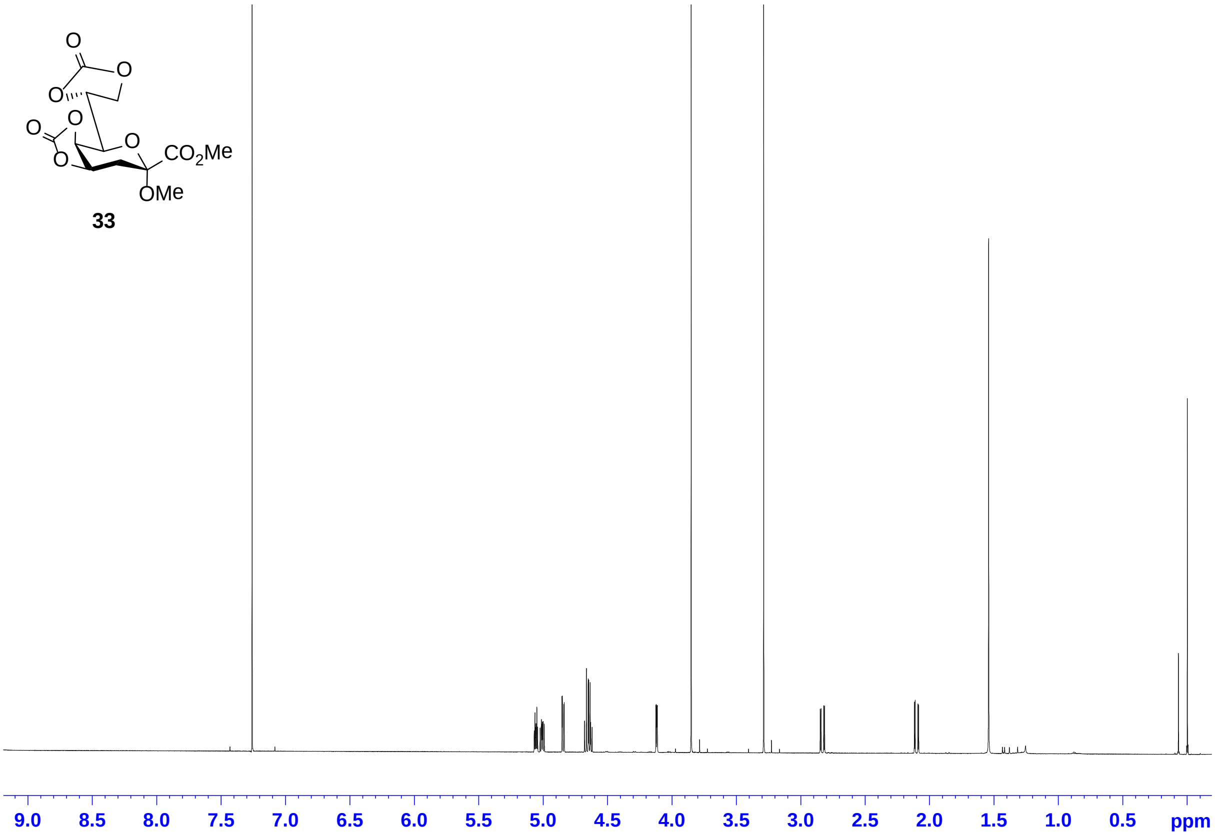

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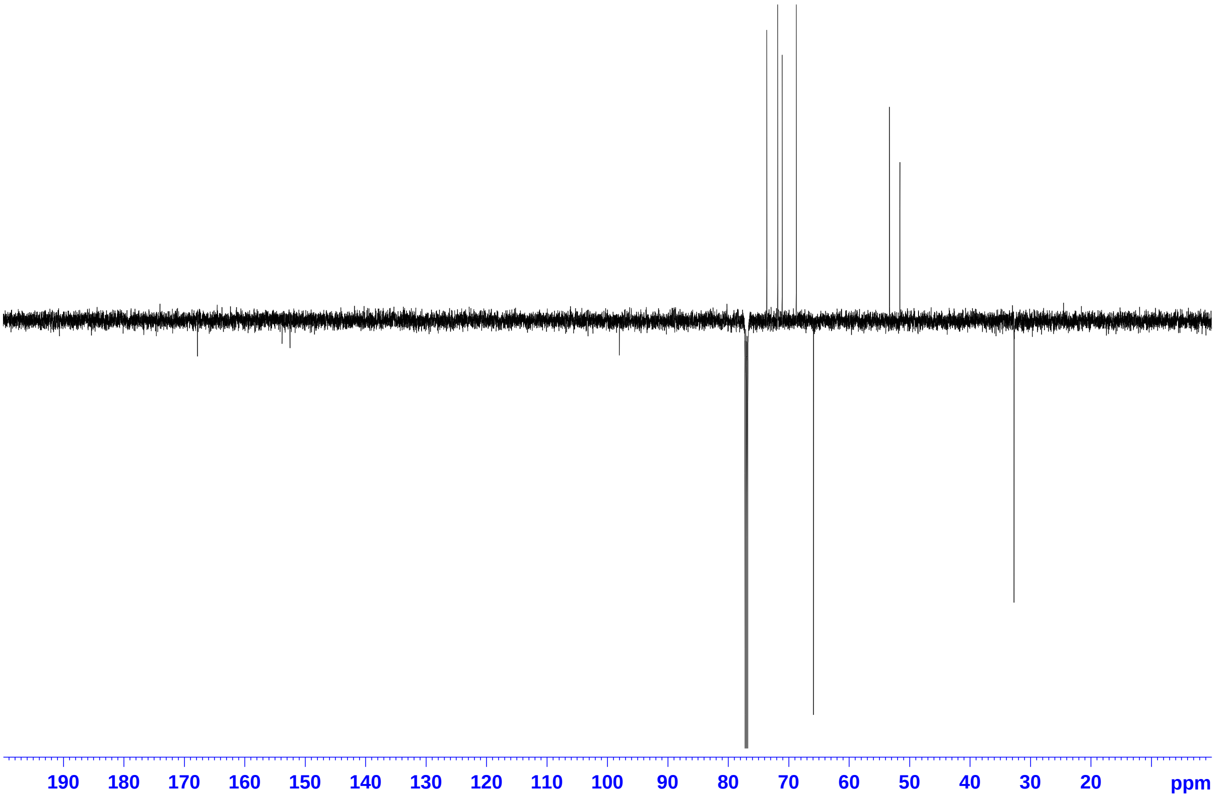

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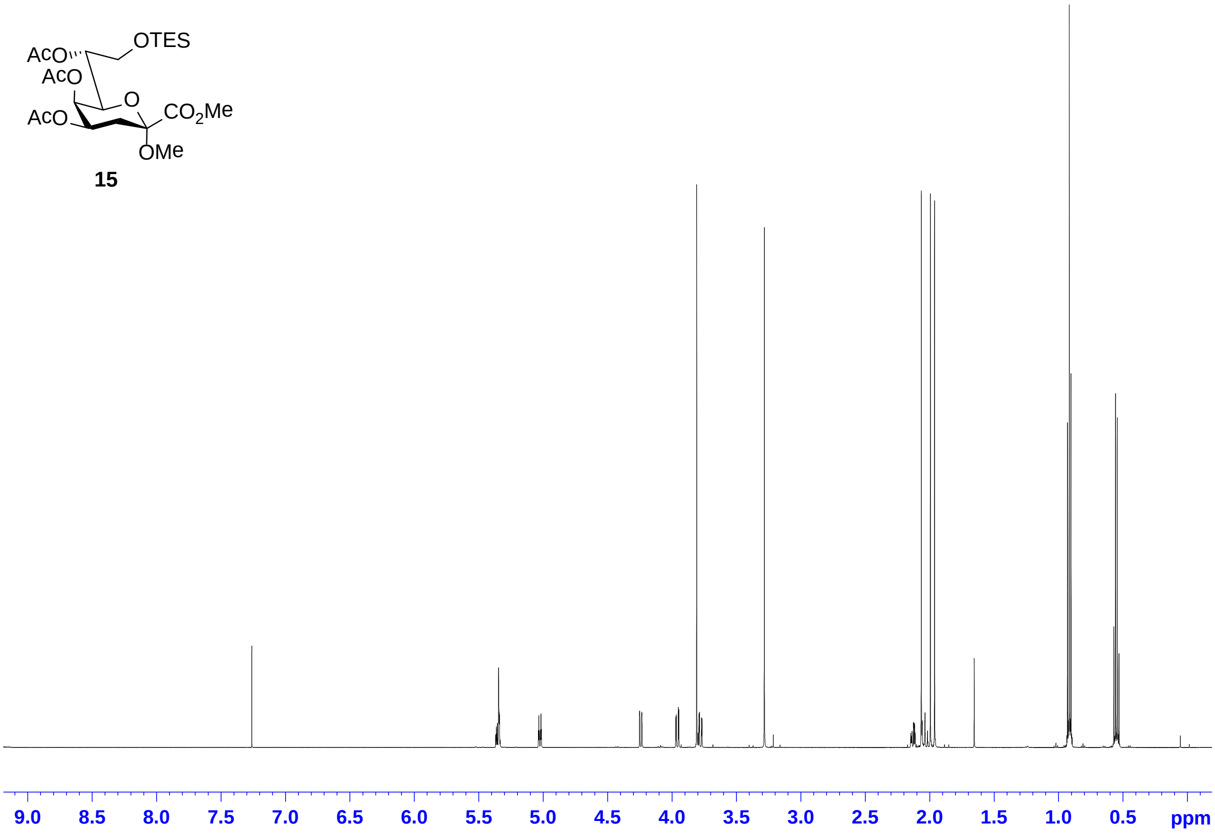

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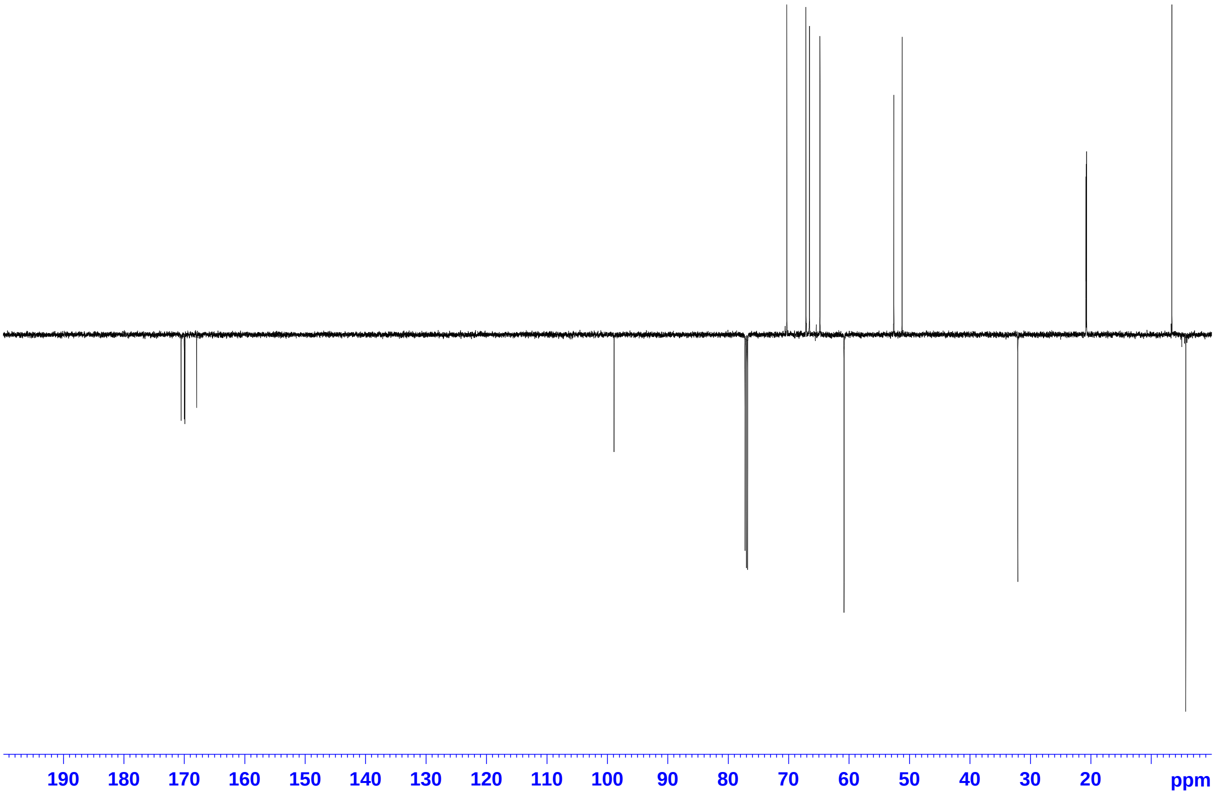

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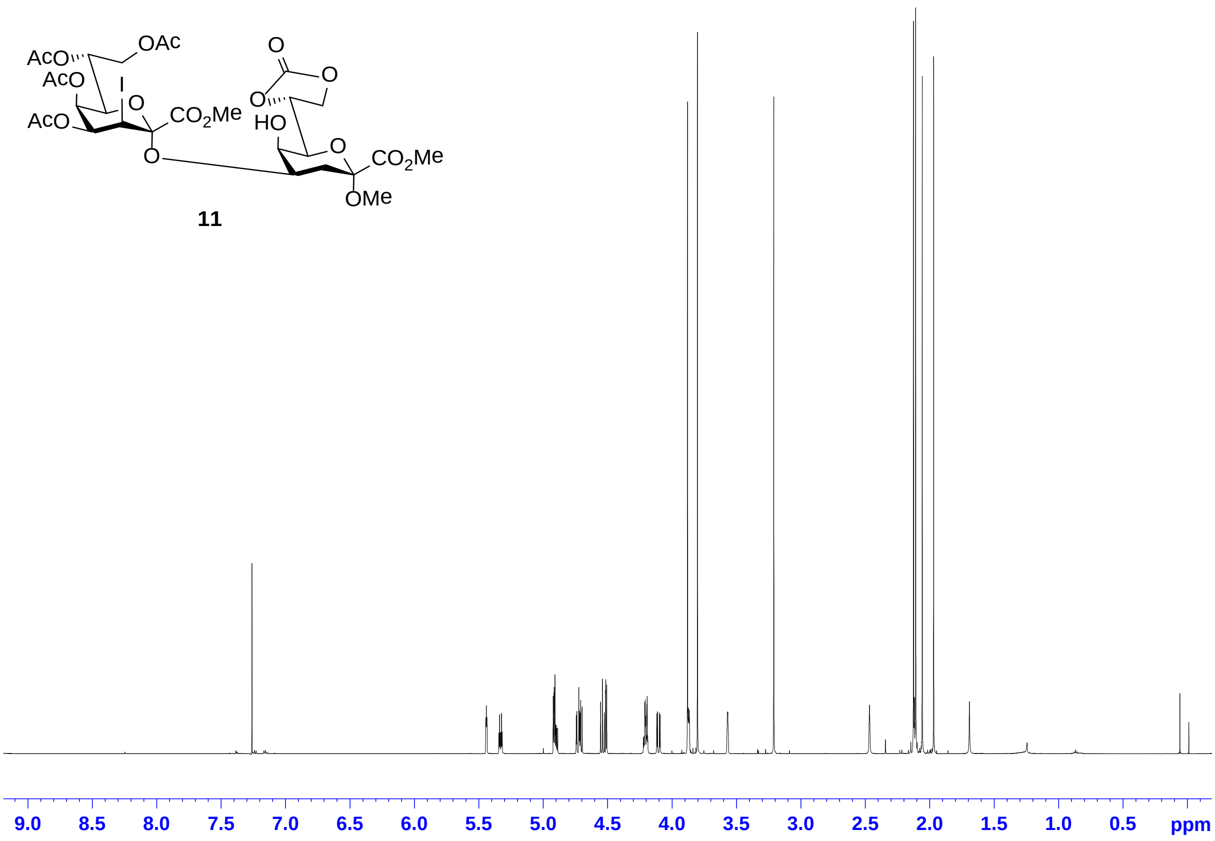

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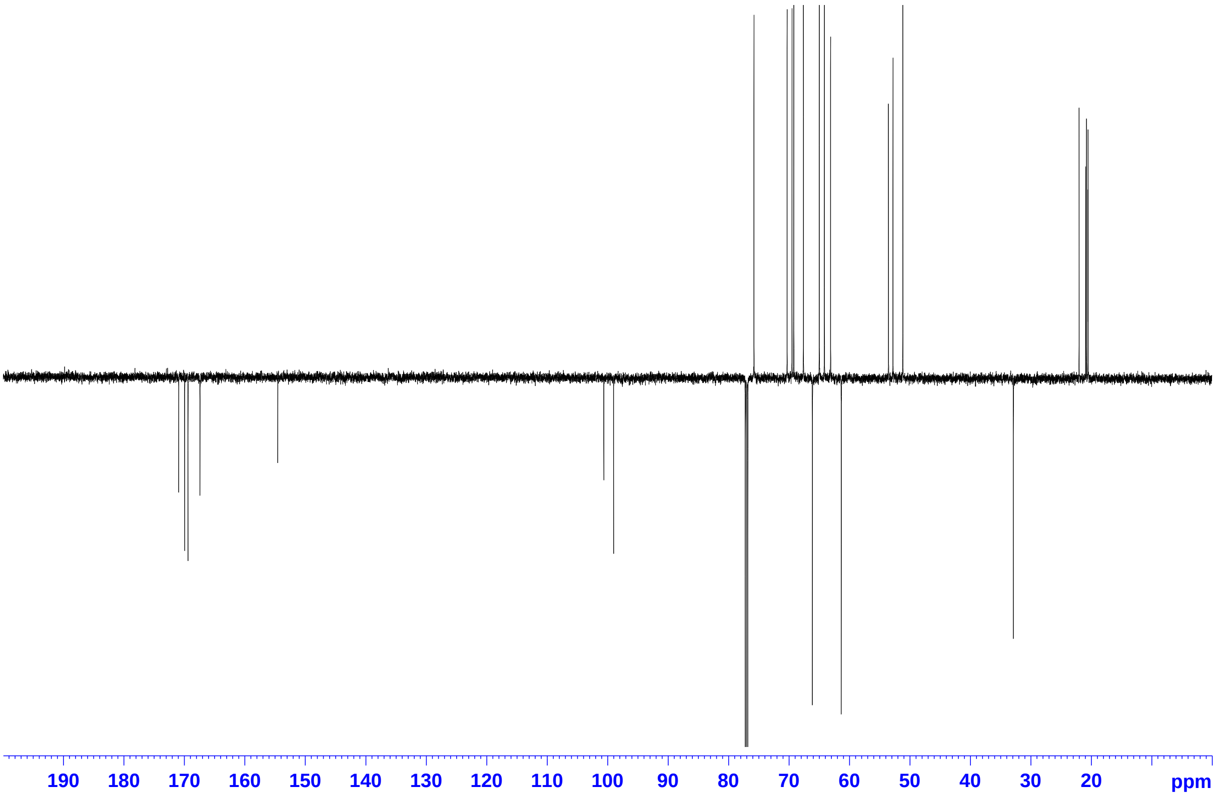

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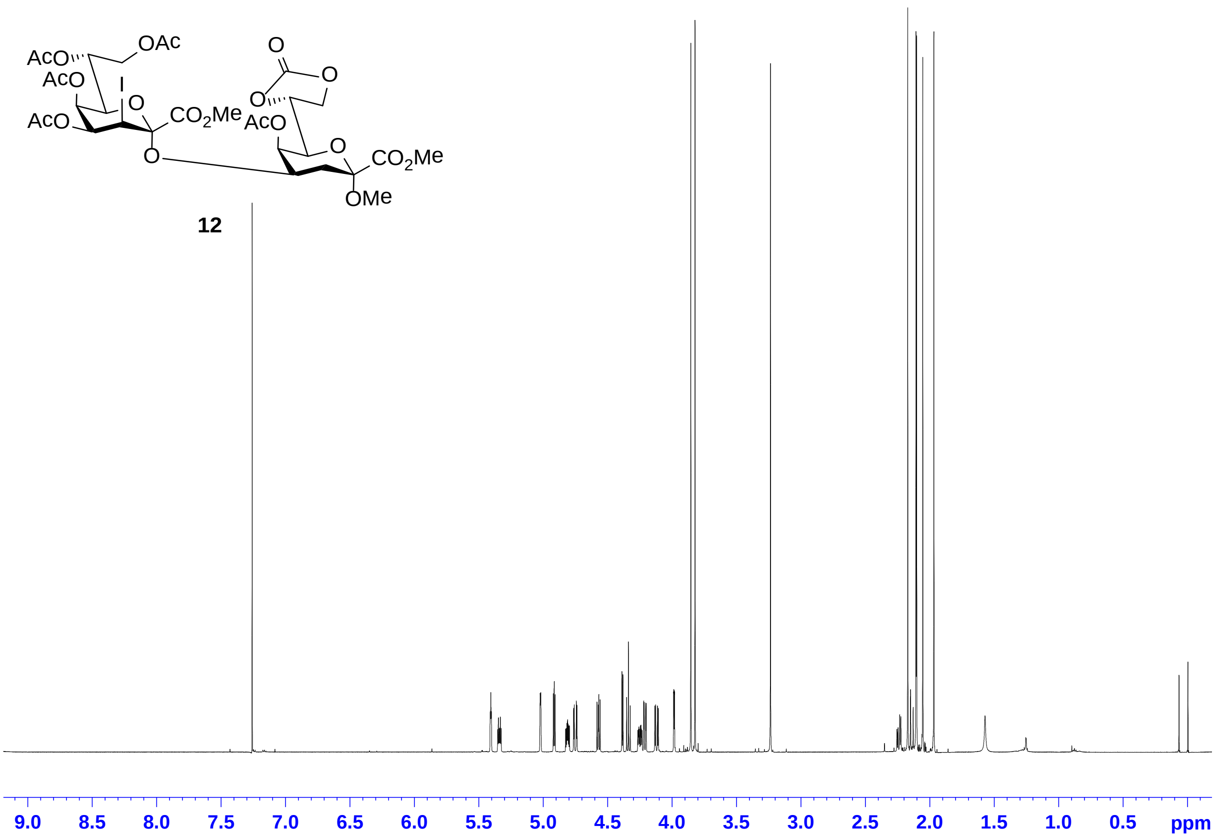

12

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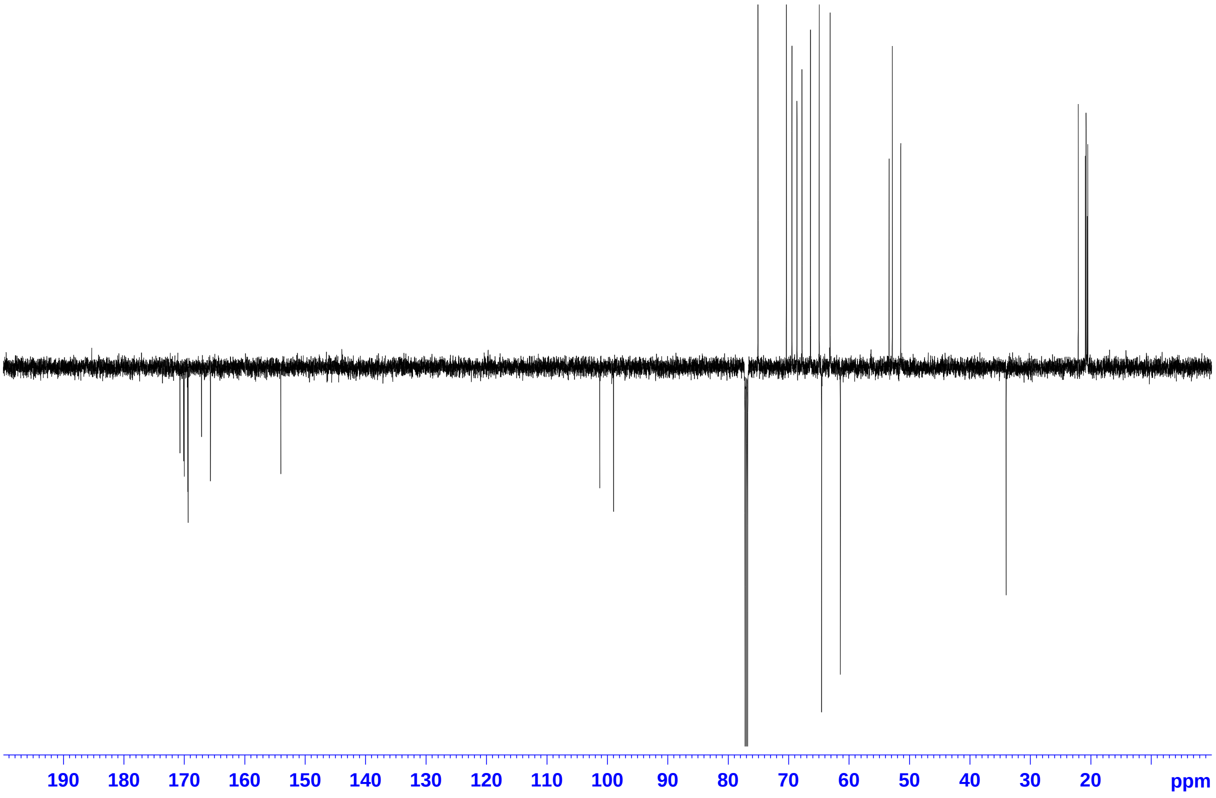

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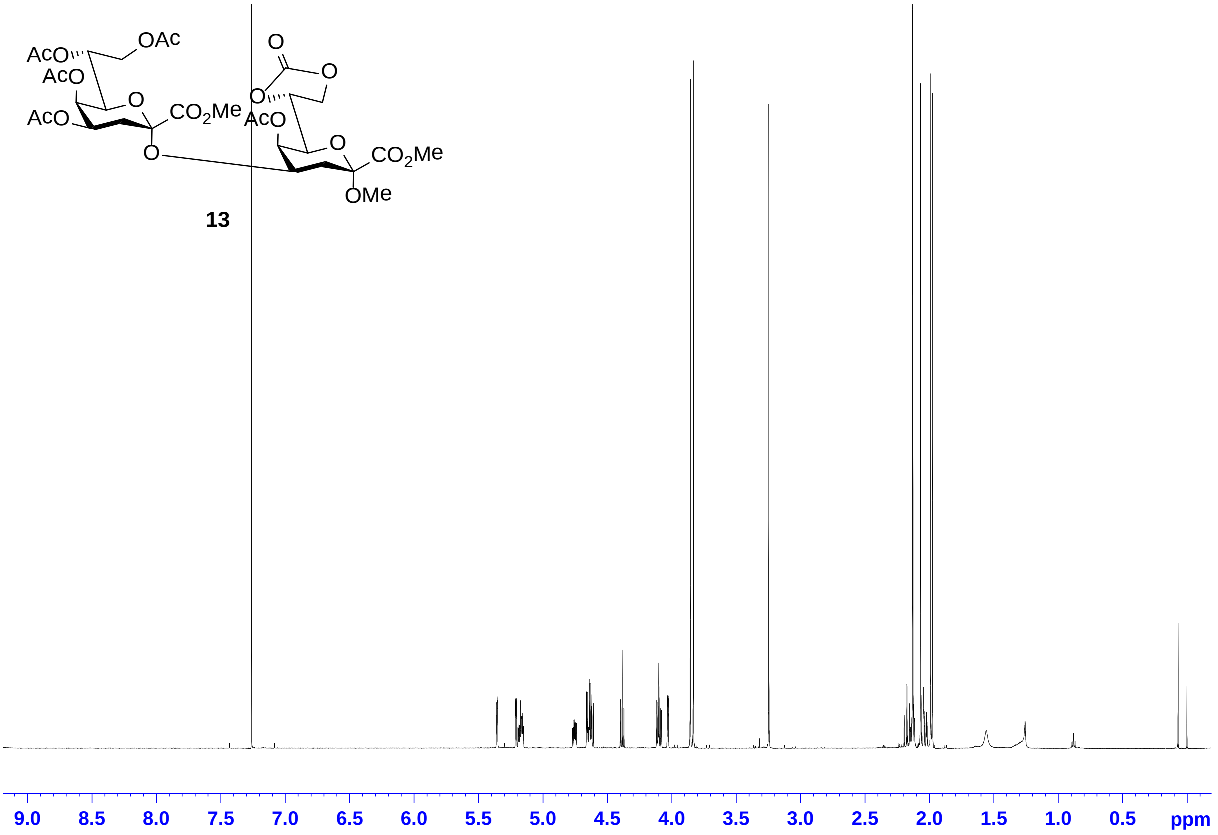

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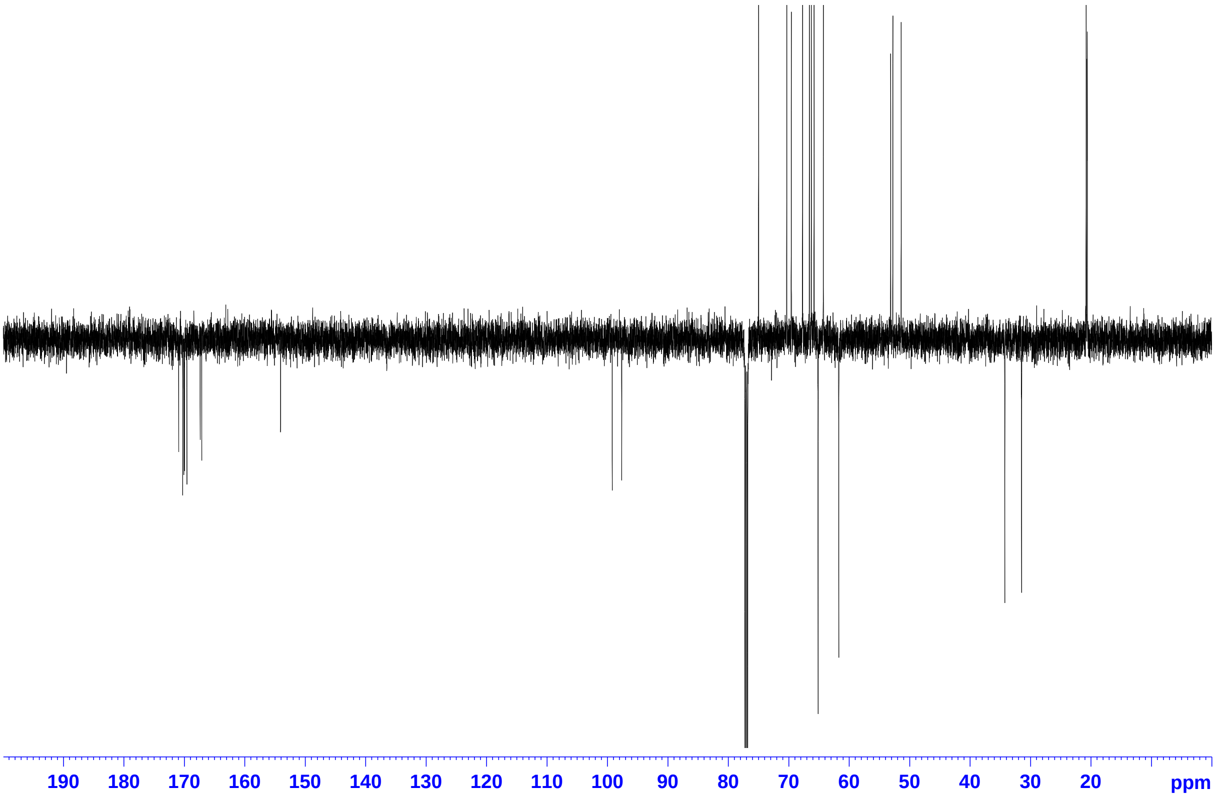

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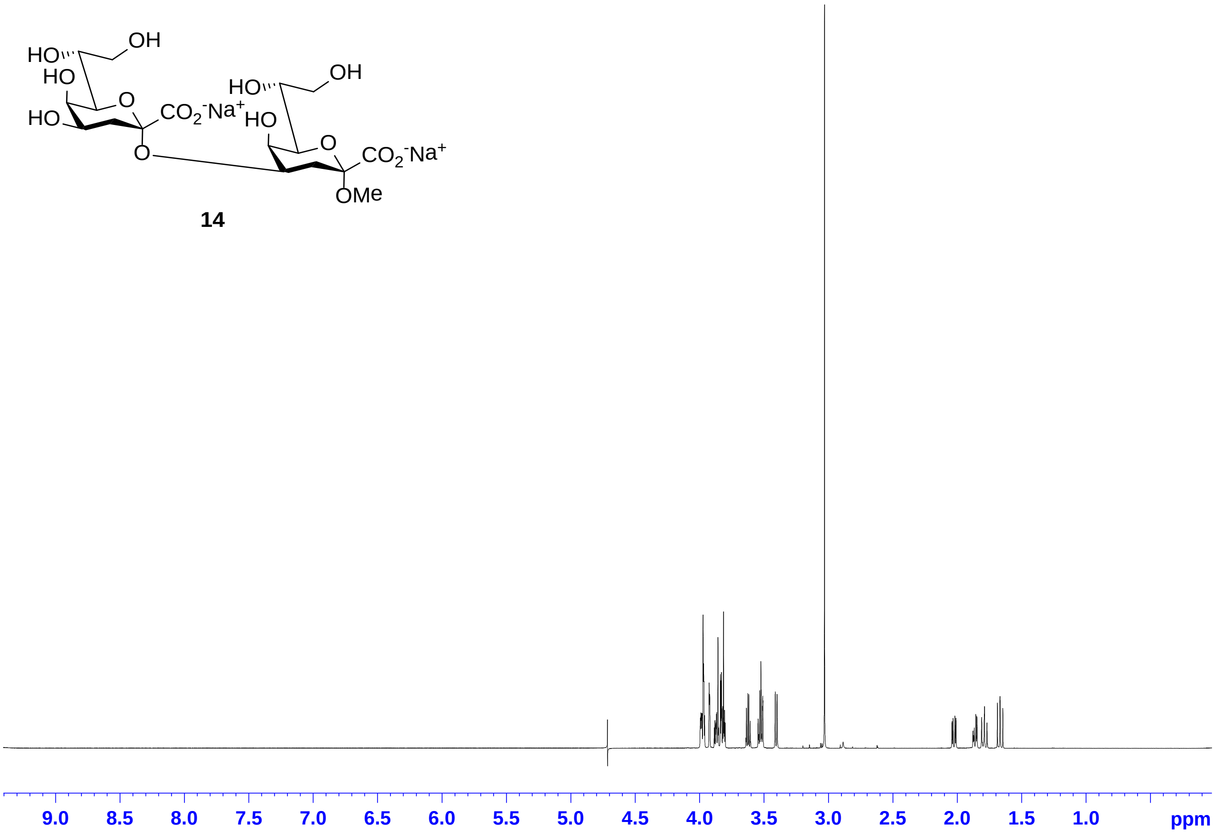

14

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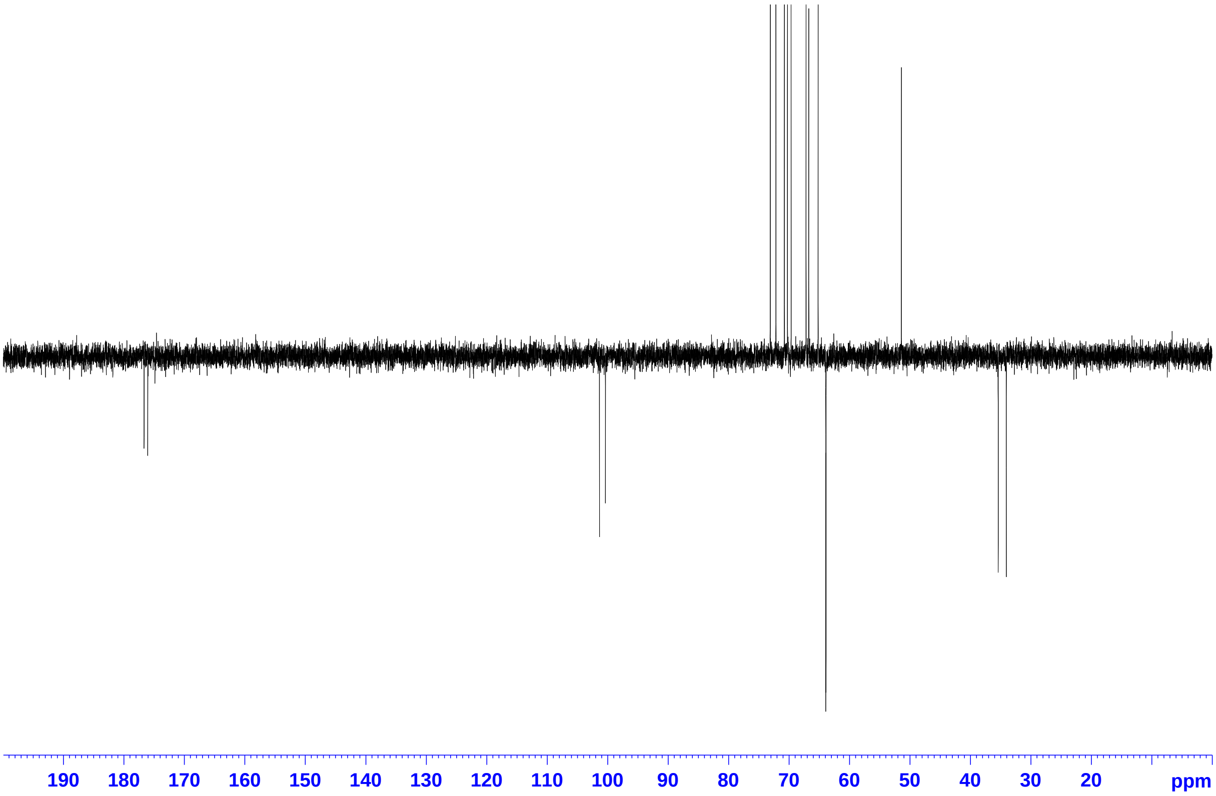
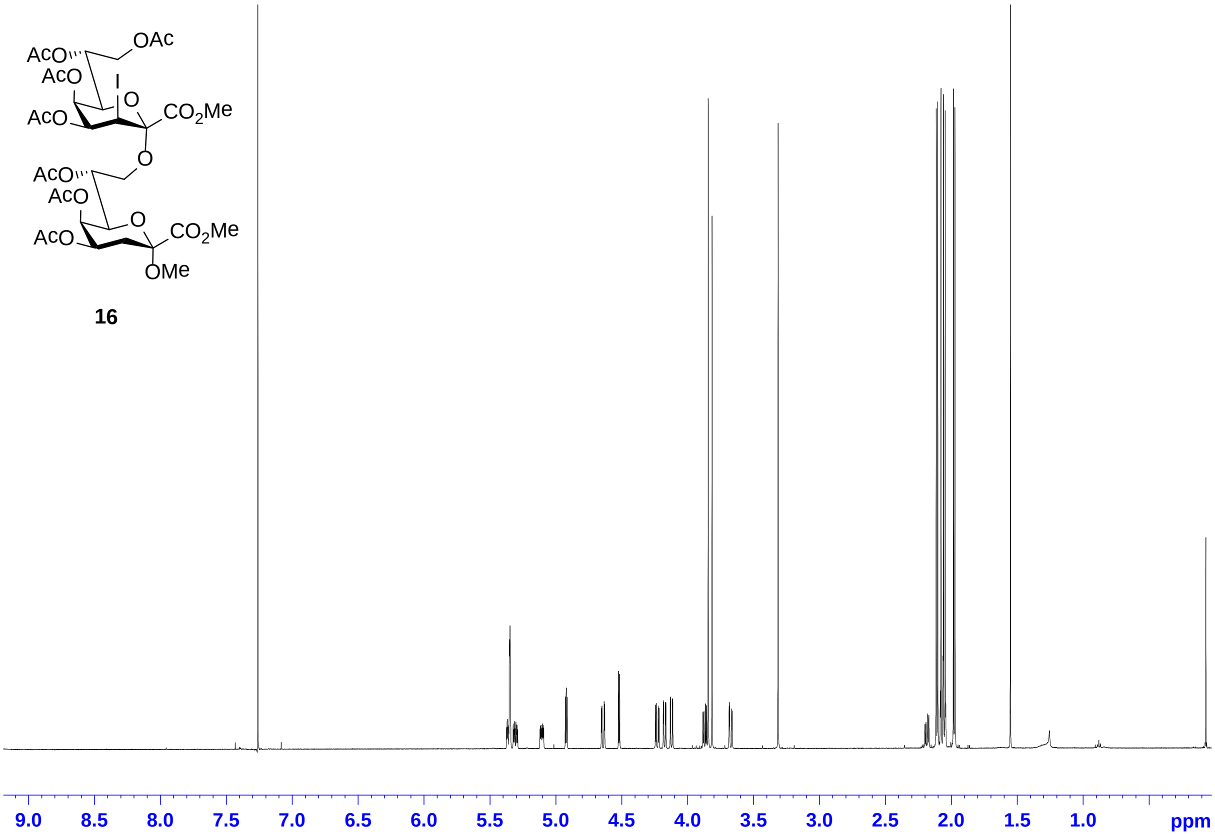


^{13}C-NMR (150 MHz, D_2O)



16

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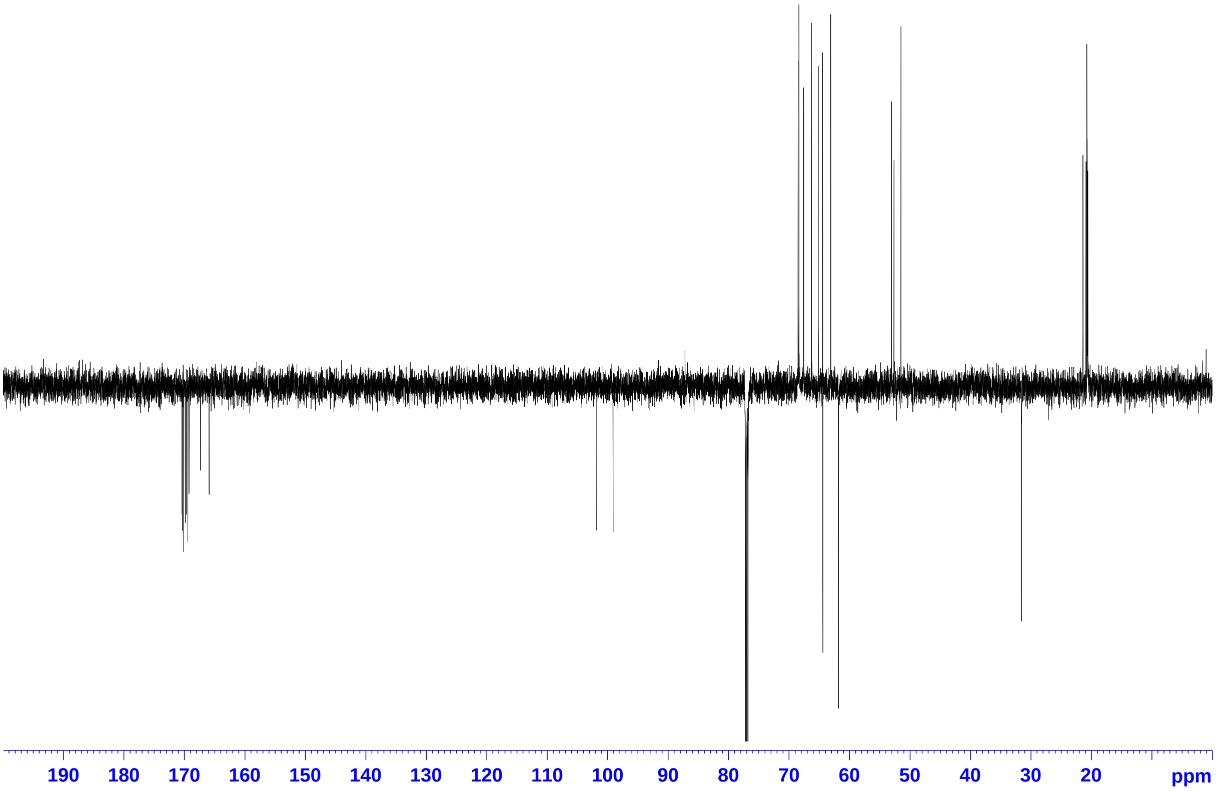
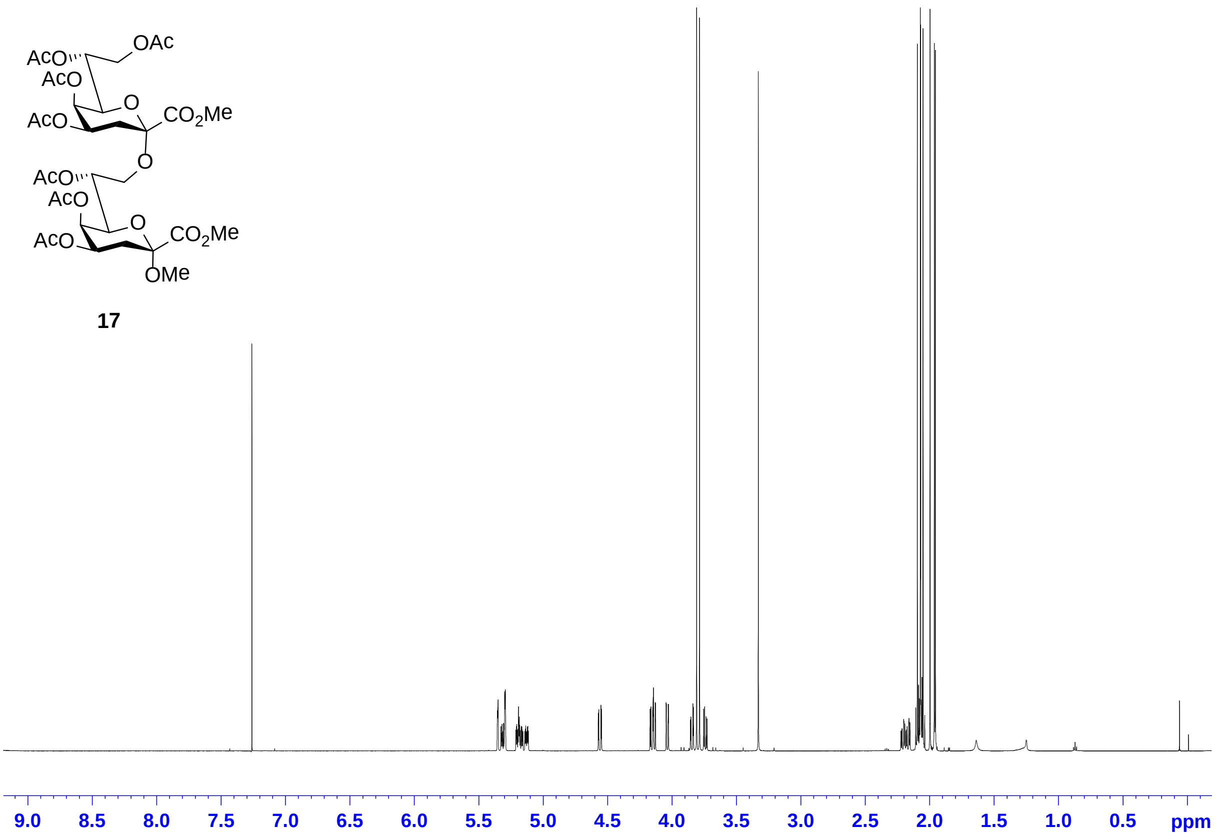


^{13}C-NMR (150 MHz, $CDCl_3$)



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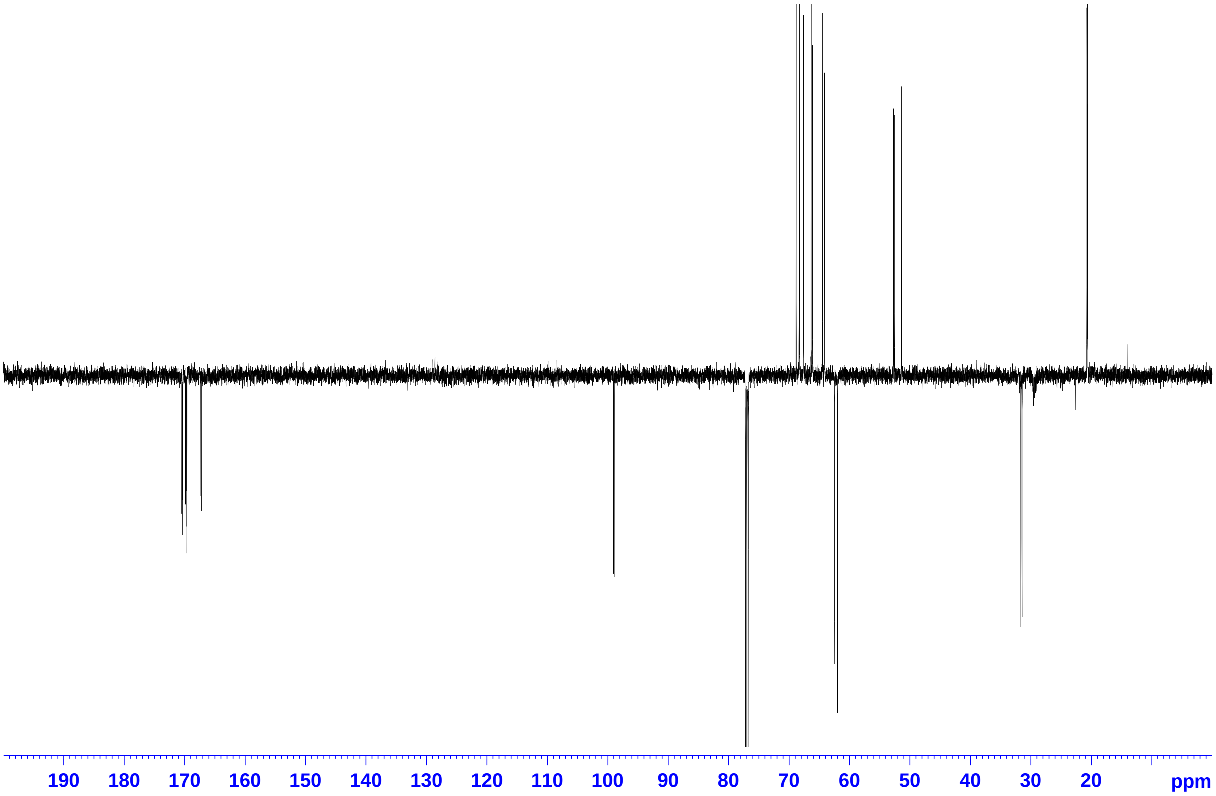
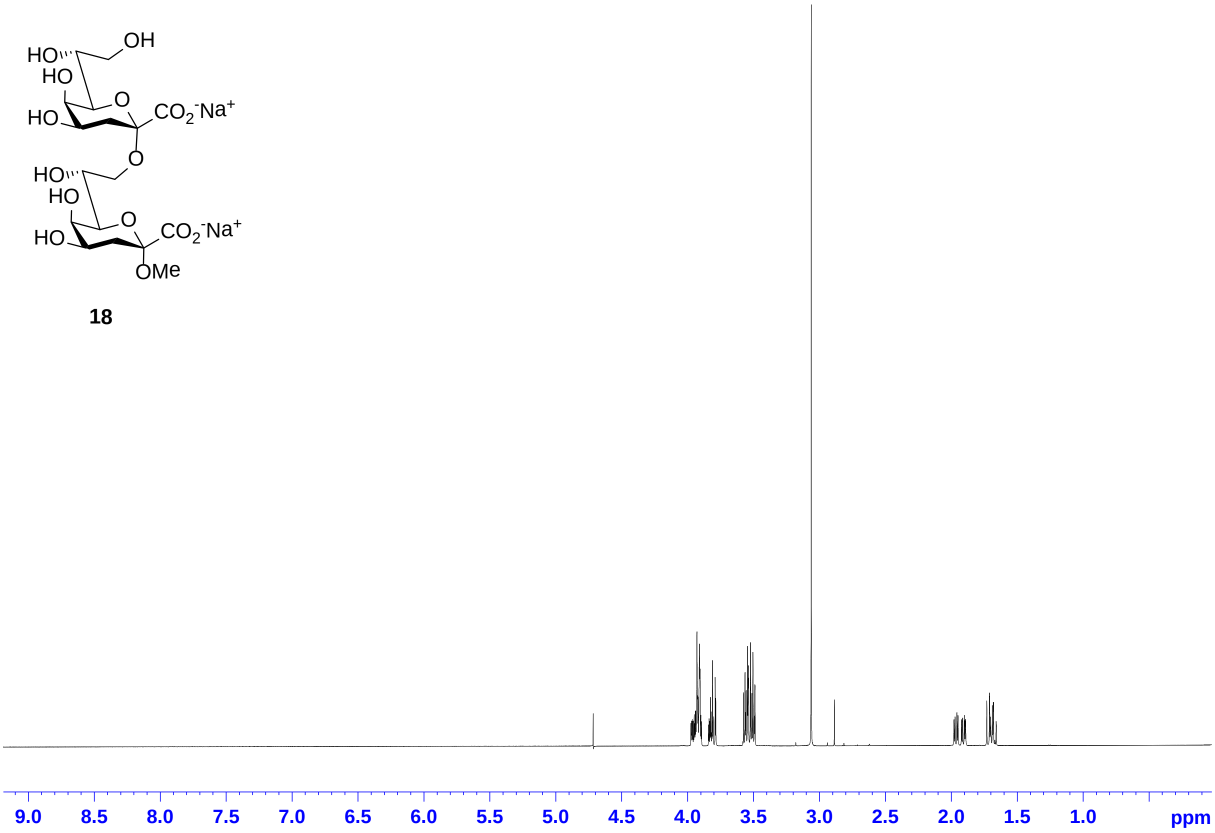
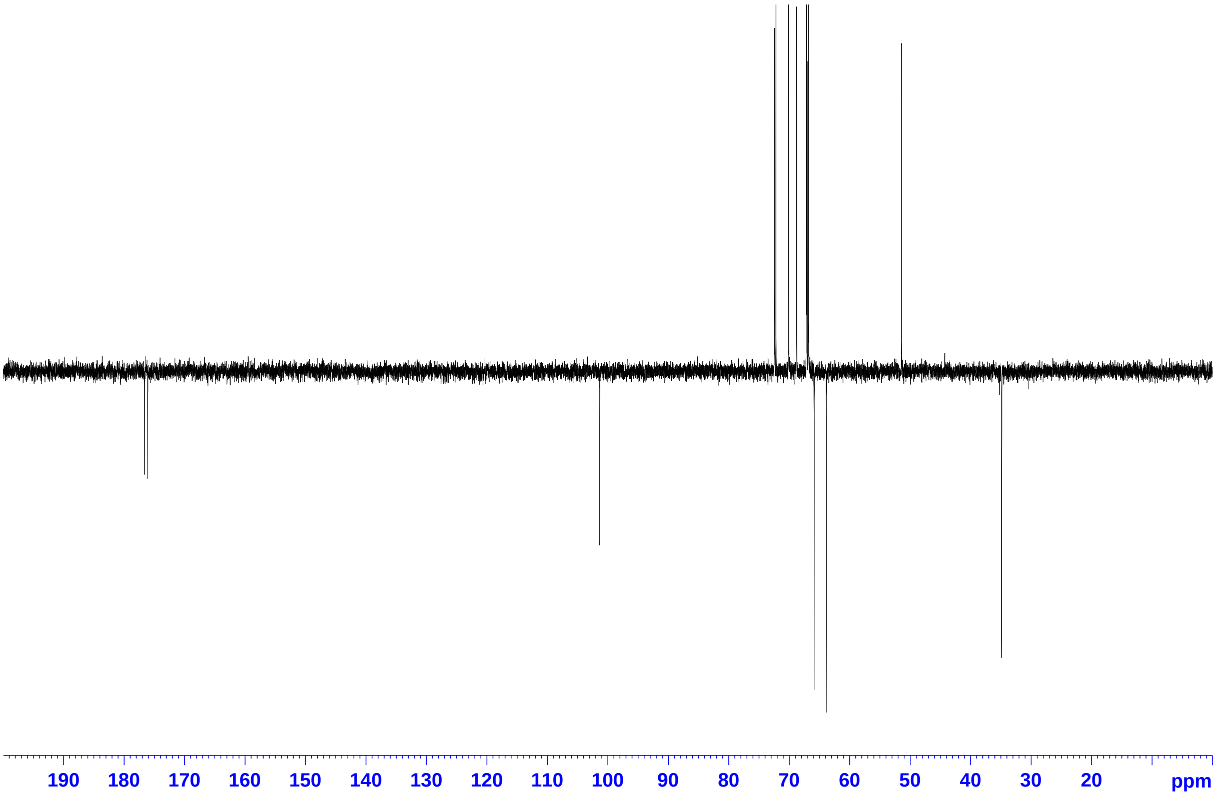


^{13}C-NMR (150 MHz, CDCl$_3$)

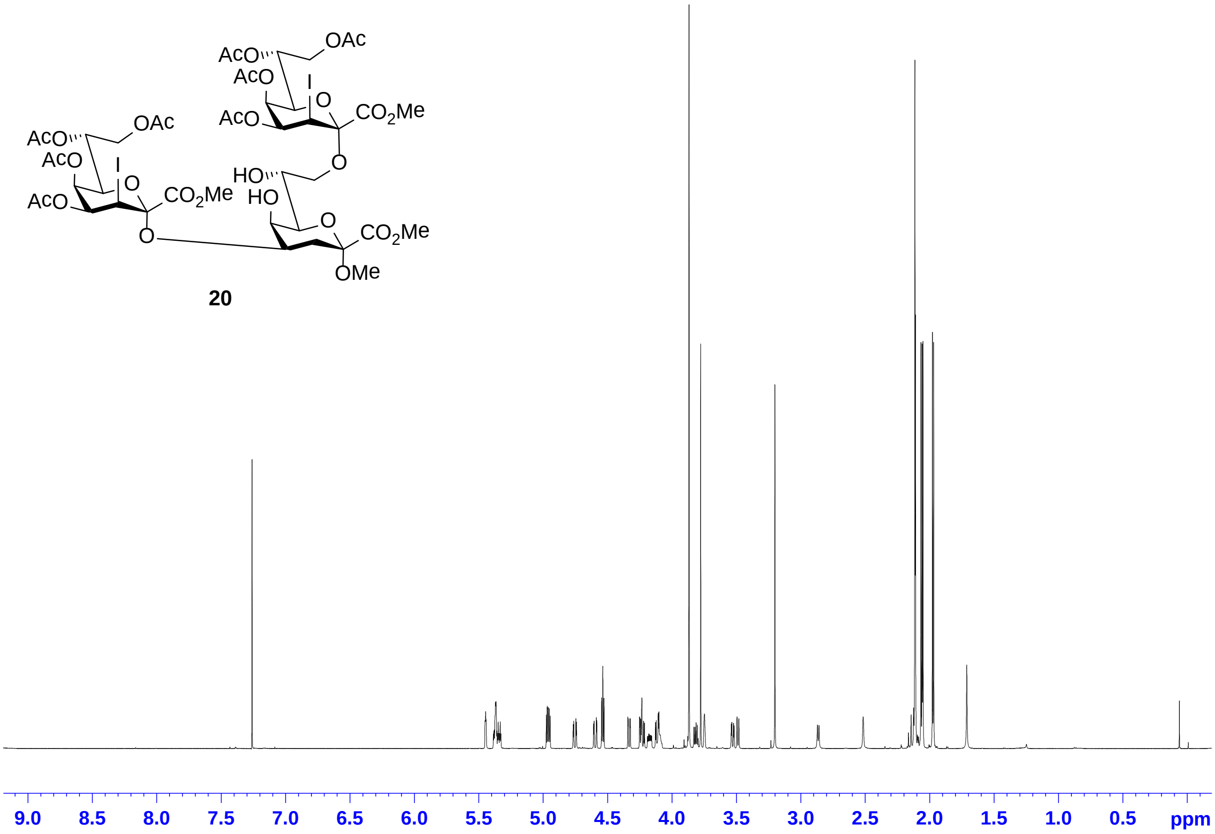
18



^{1}H-NMR (600 MHz, D_2O)



^{13}C-NMR (150 MHz, D_2O)



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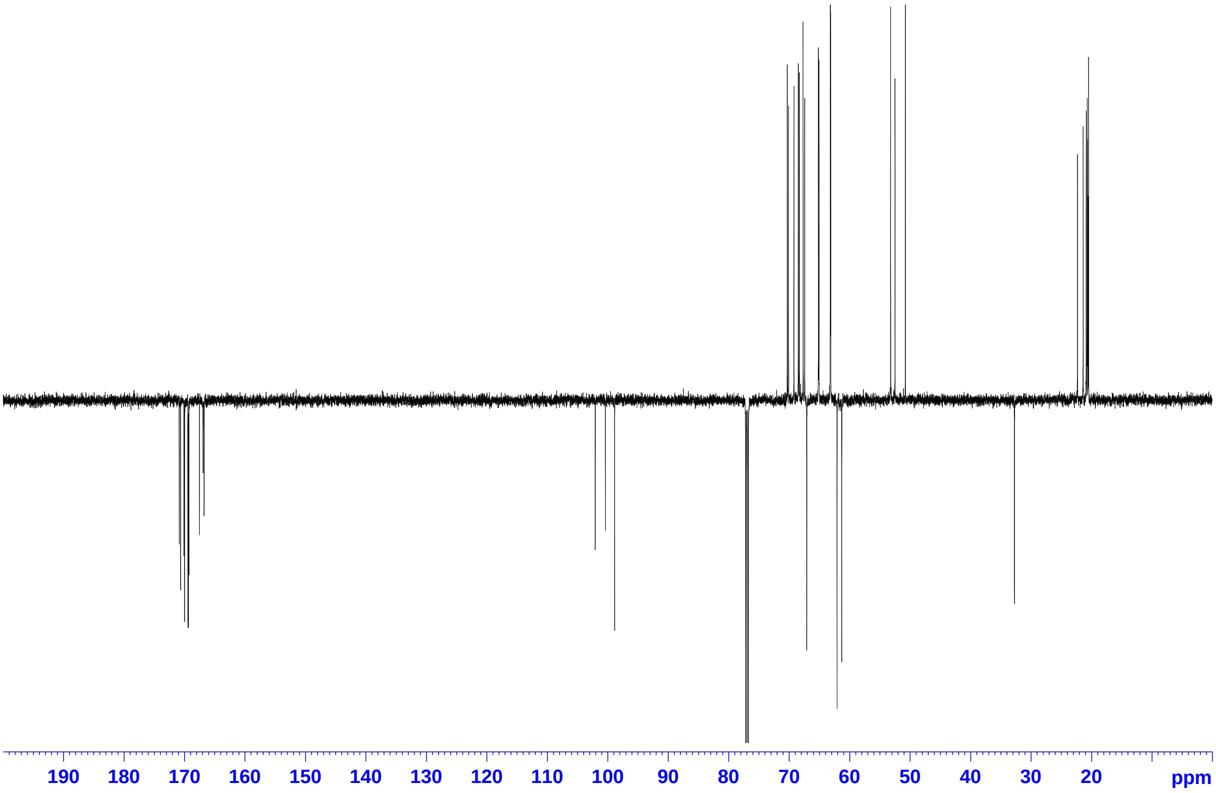
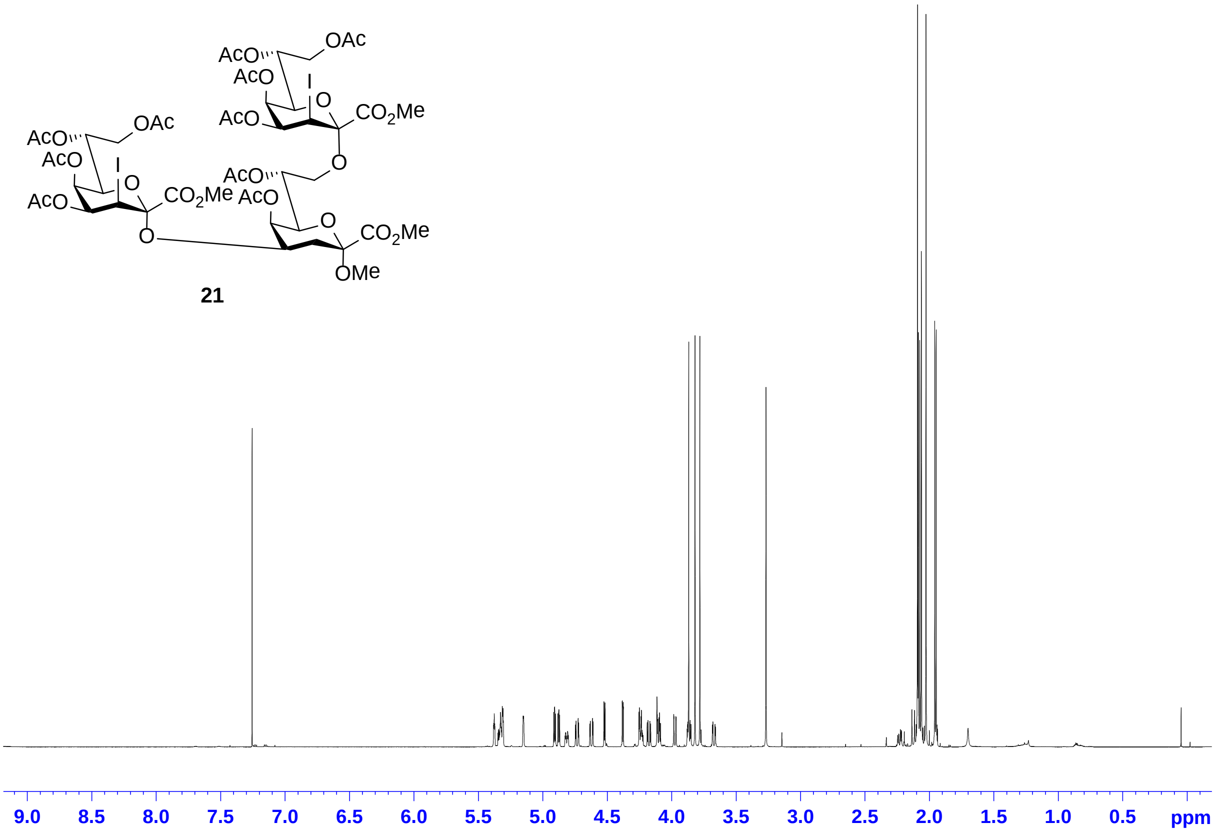
^{1}H-NMR (600 MHz, CDCl$_3$)



^{13}C-NMR (150 MHz, CDCl$_3$)



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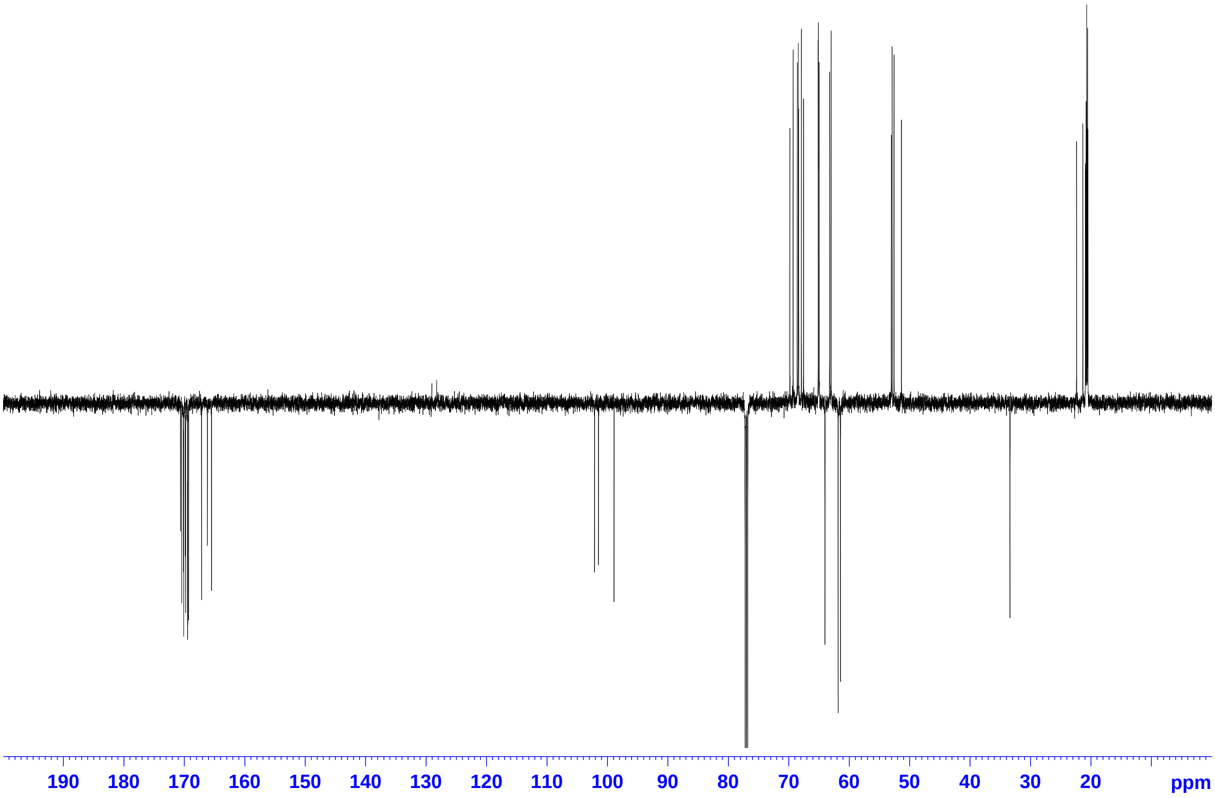
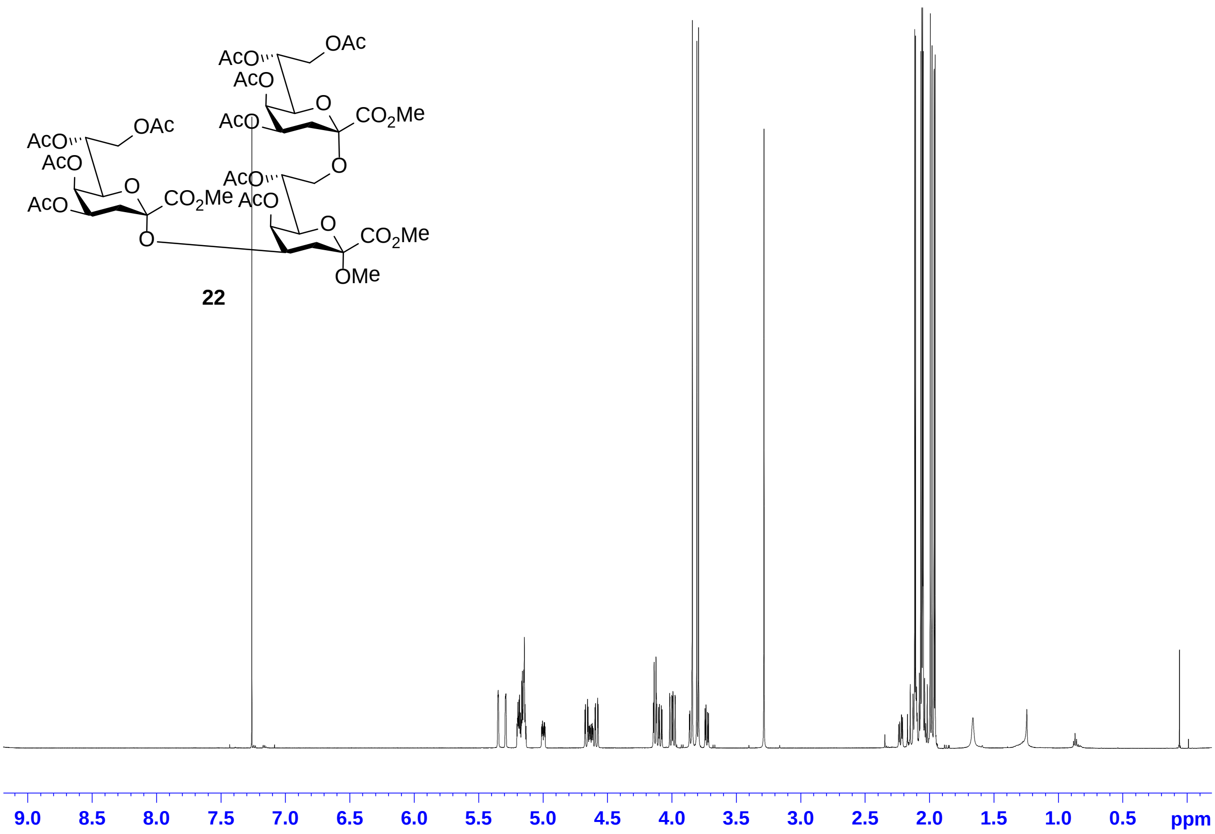
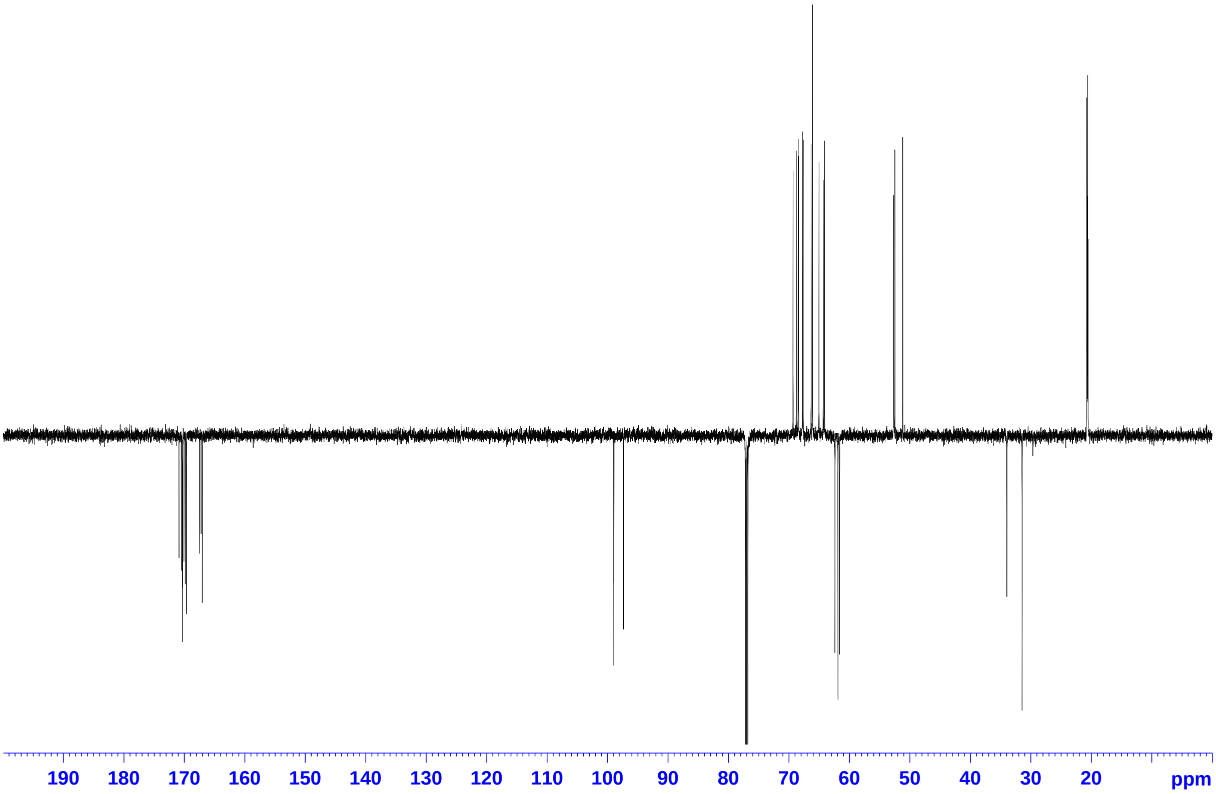
^{1}H-NMR (600 MHz, $CDCl_3$)



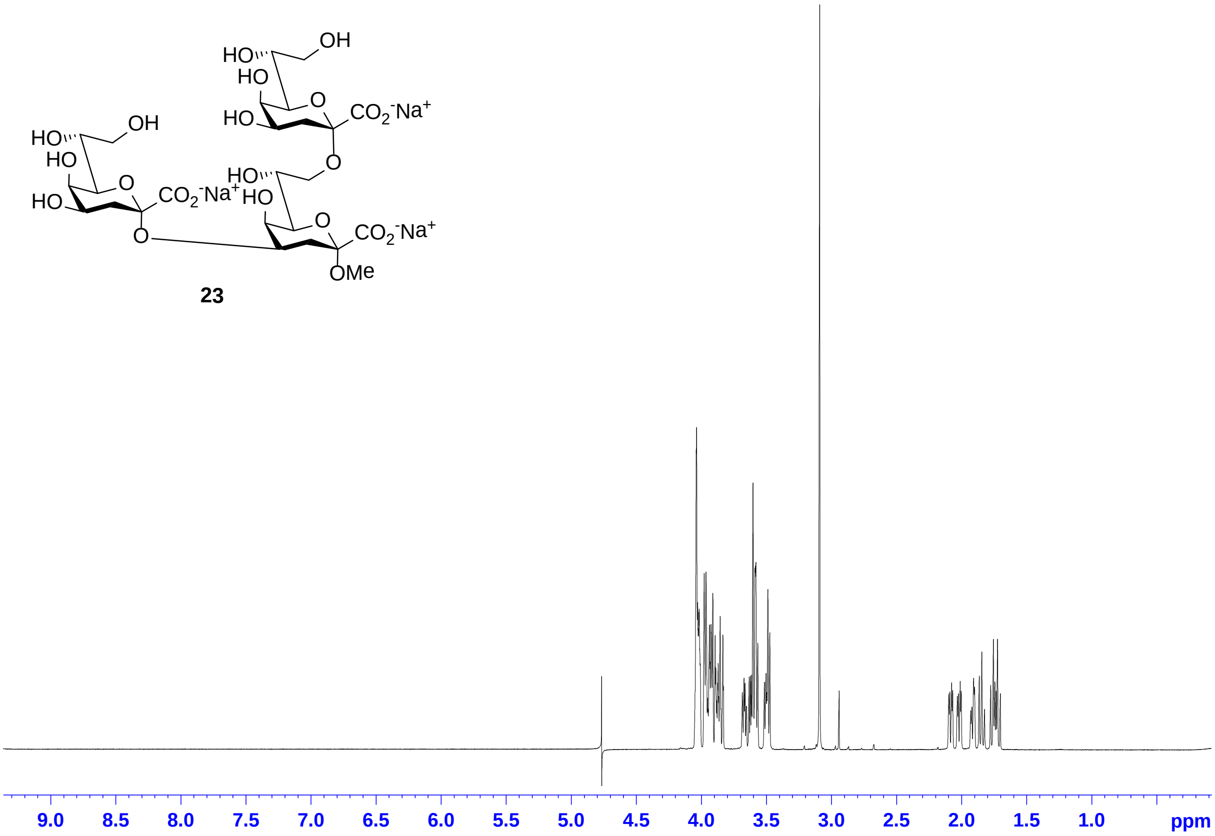
^{13}C-NMR (150 MHz, $CDCl_3$)



^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (150 MHz, $CDCl_3$)



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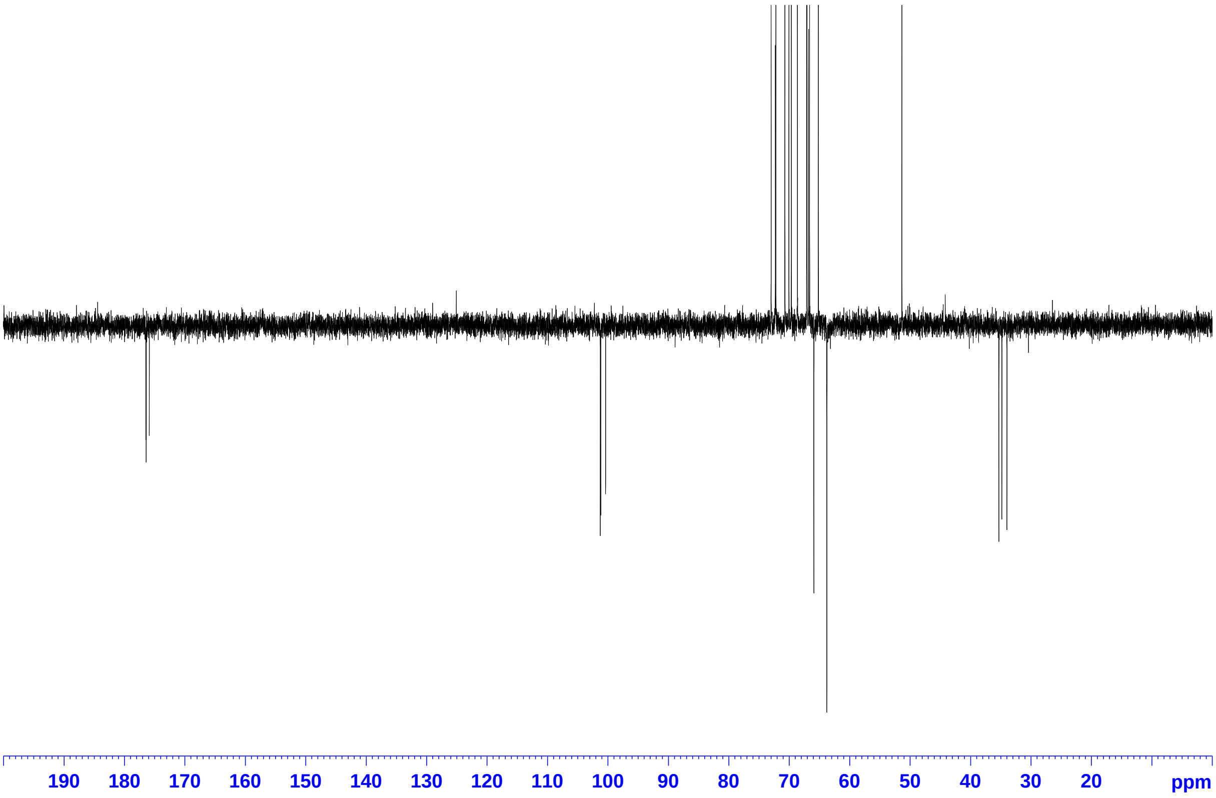
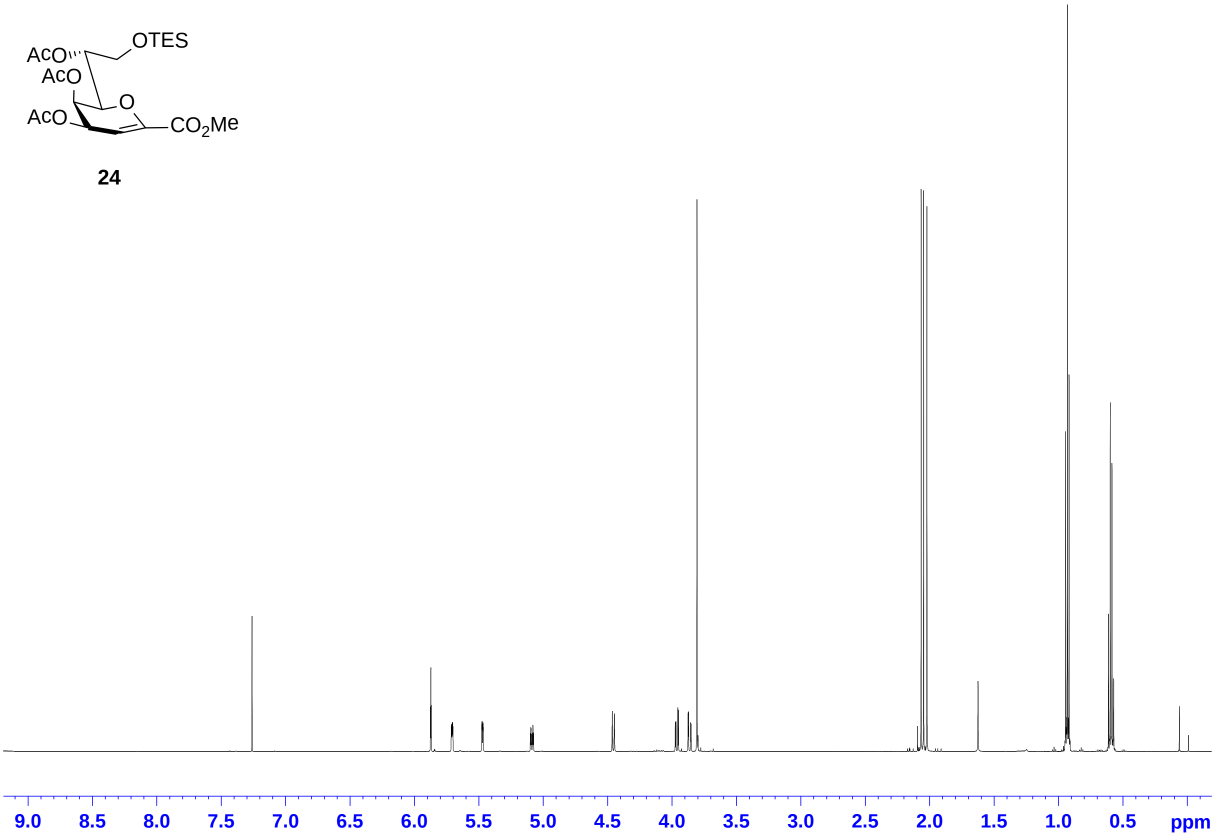
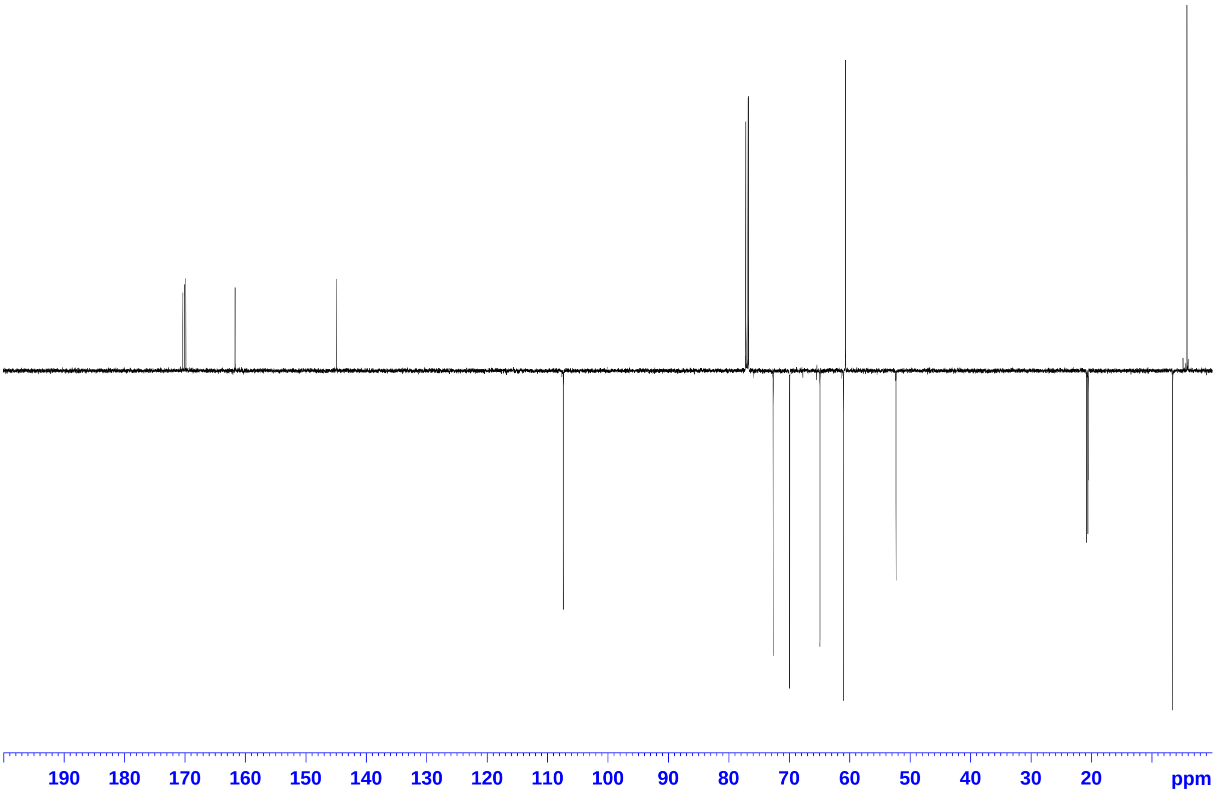
^{1}H-NMR (600 MHz, D_2O)



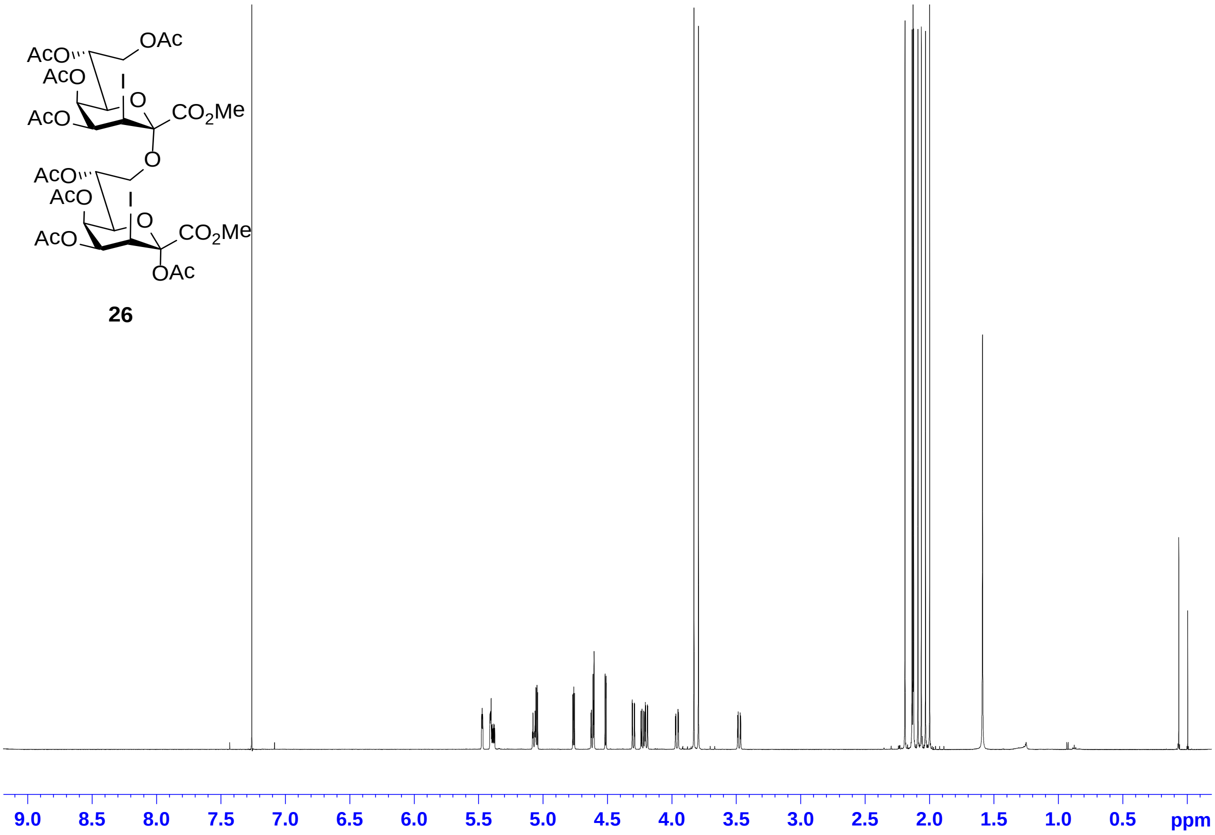
^{13}C-NMR (150 MHz, D_2O)



^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (150 MHz, $CDCl_3$)



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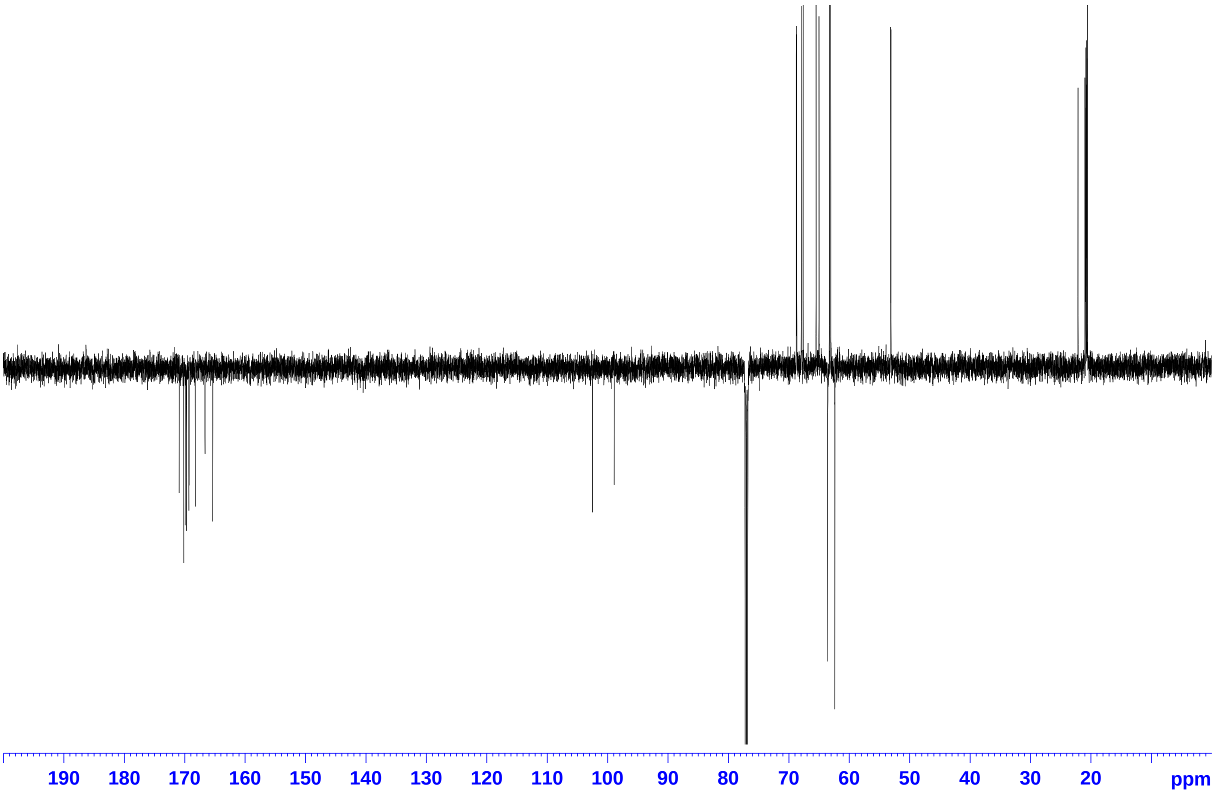
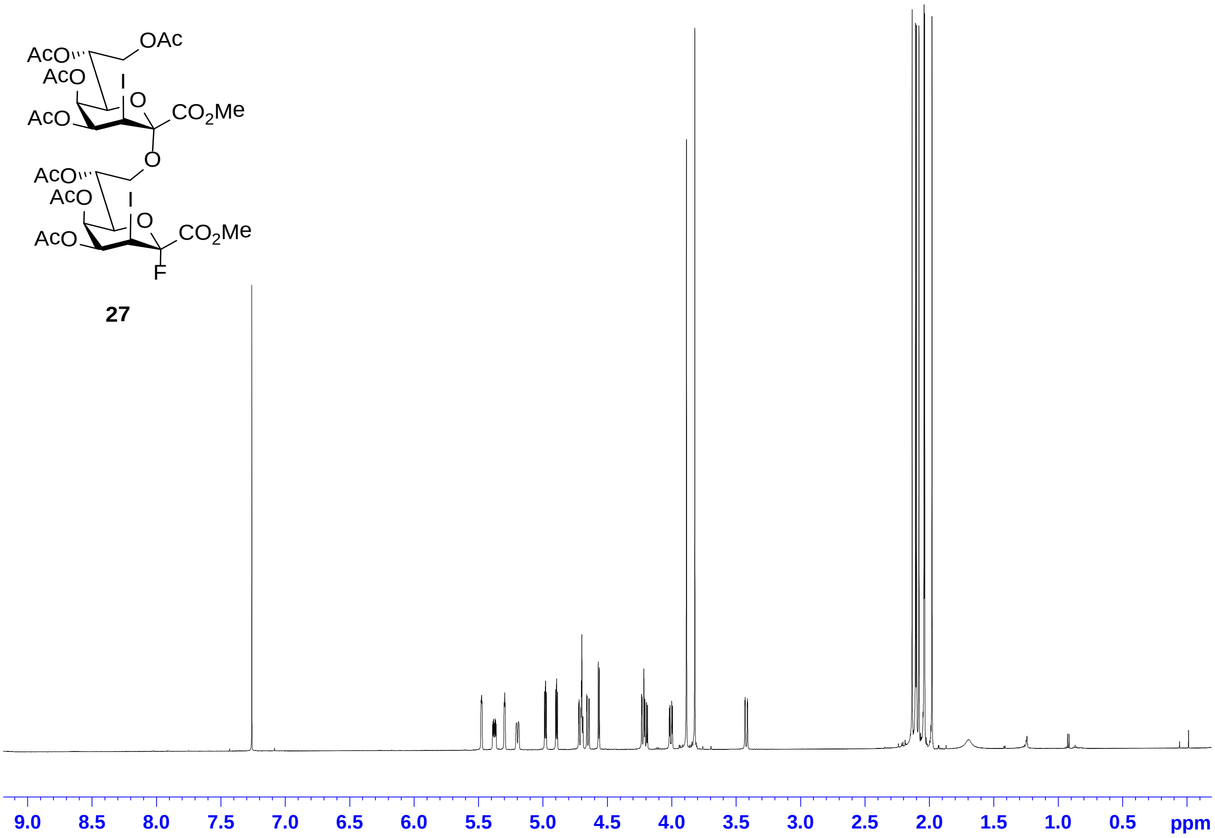
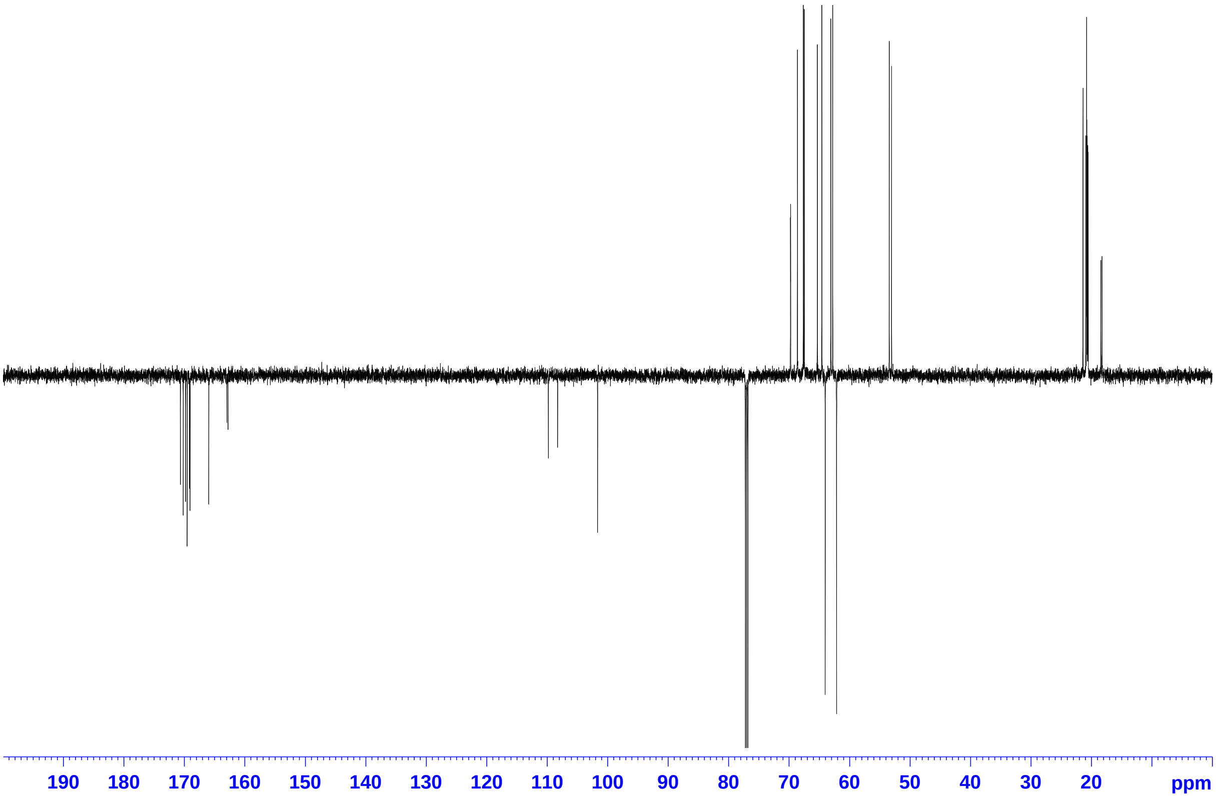
^{1}H-NMR (600 MHz, CDCl$_3$)



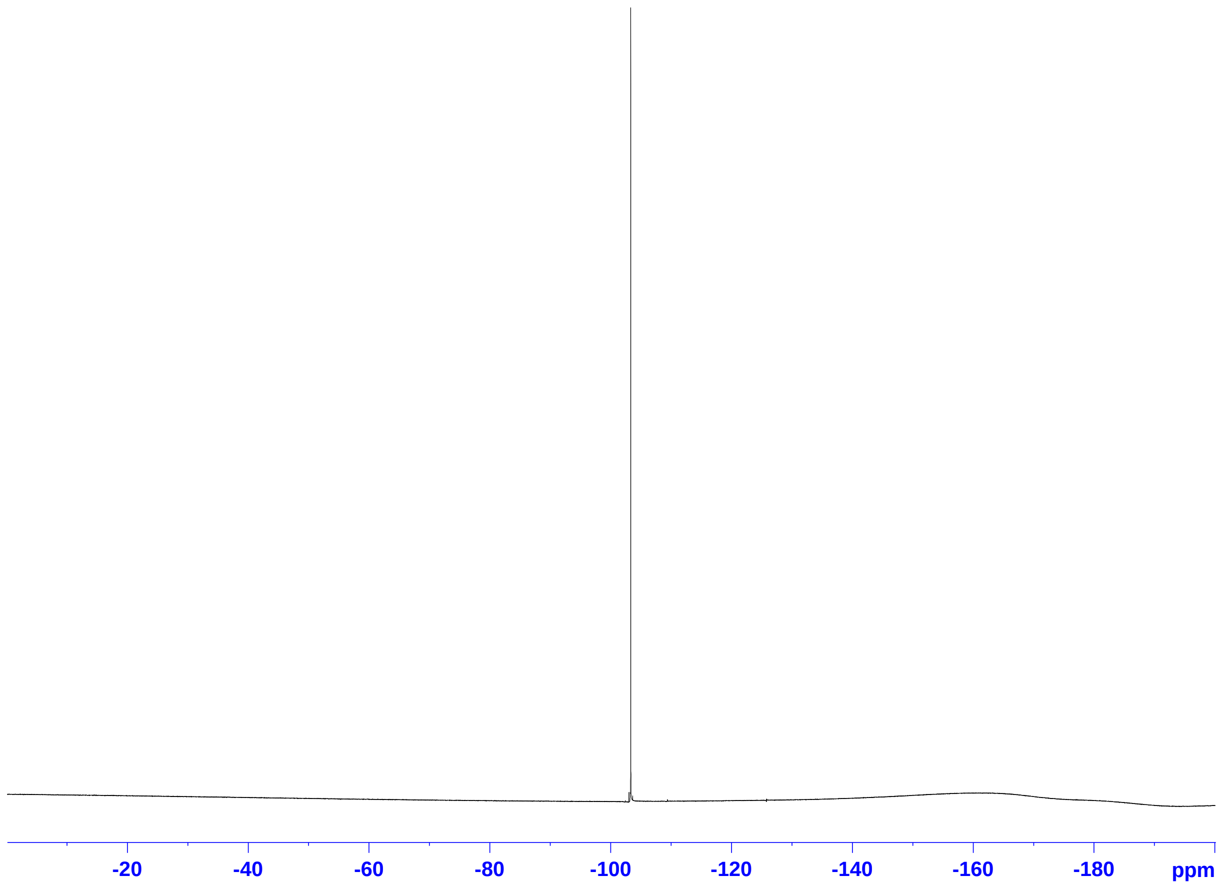
^{13}C-NMR (150 MHz, CDCl$_3$)



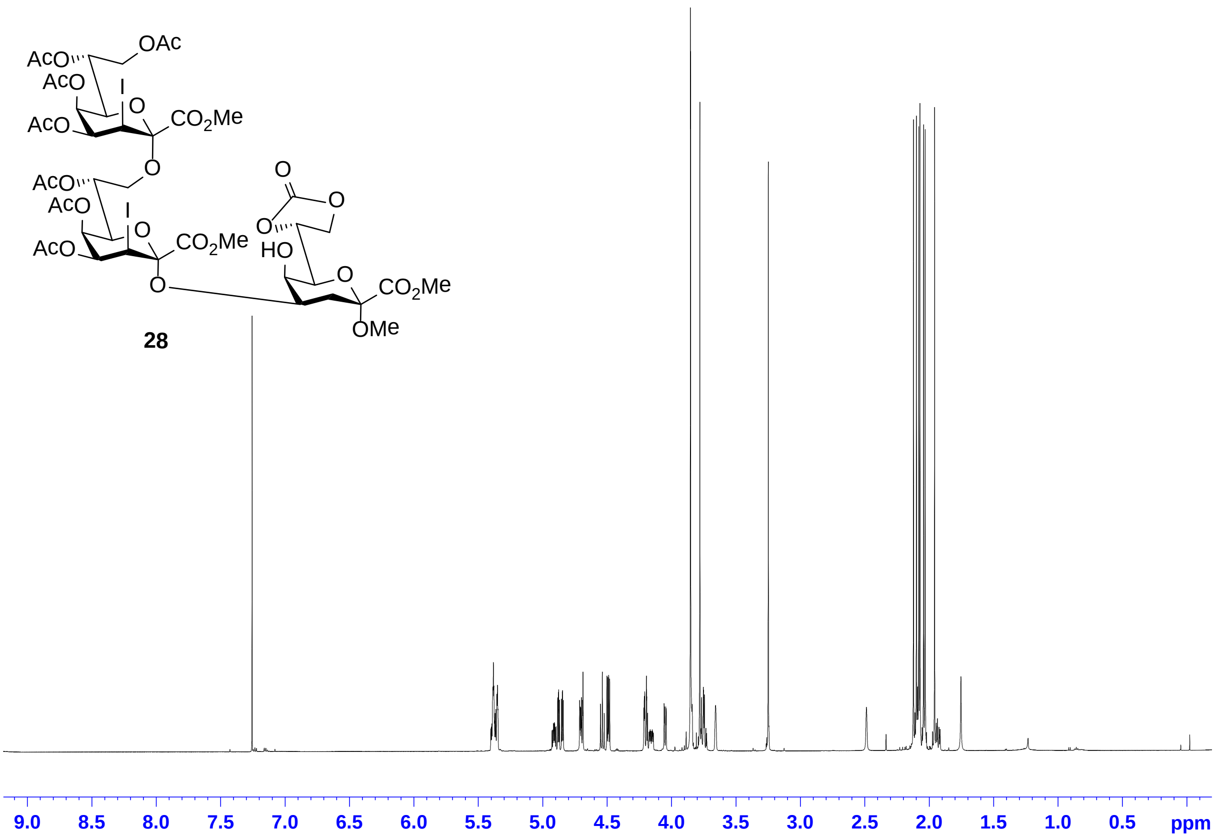
^{1}H-NMR (600 MHz, CDCl$_3$)



^{13}C-NMR (150 MHz, CDCl$_3$)



^{19}F-NMR (565 MHz, $CDCl_3$)



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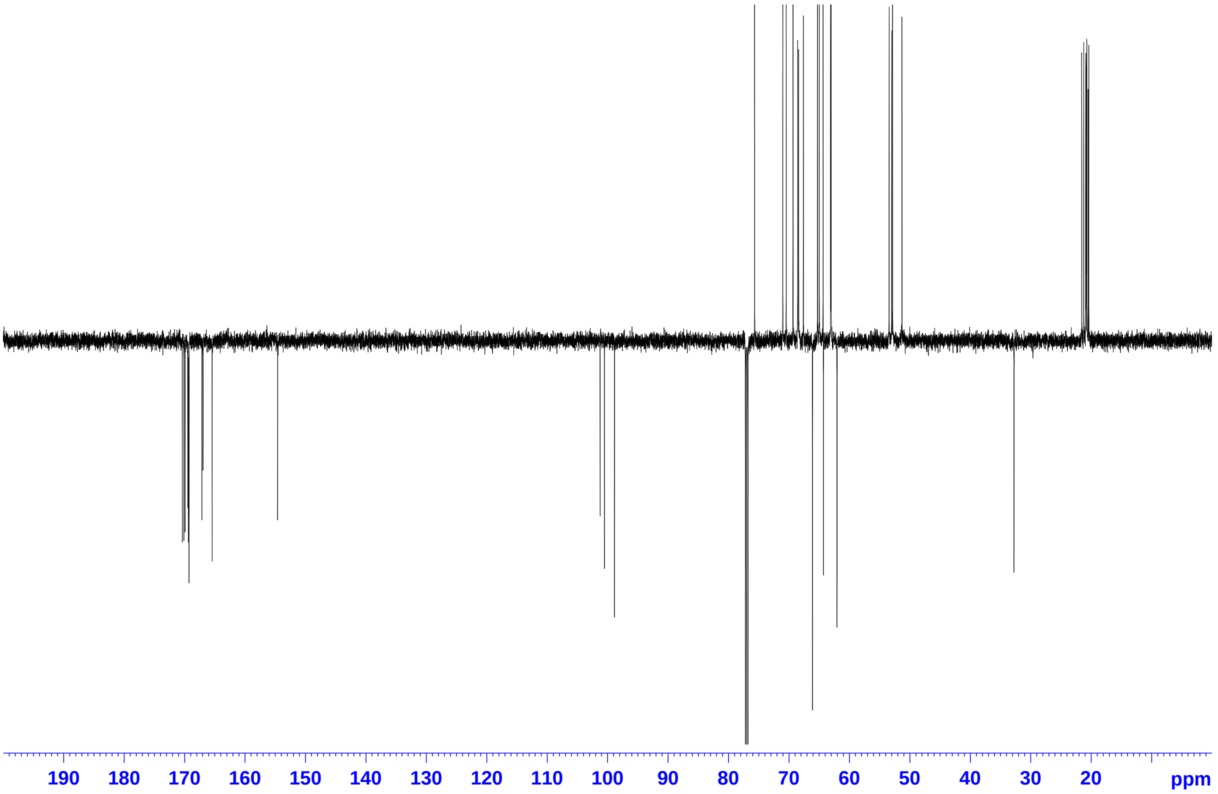
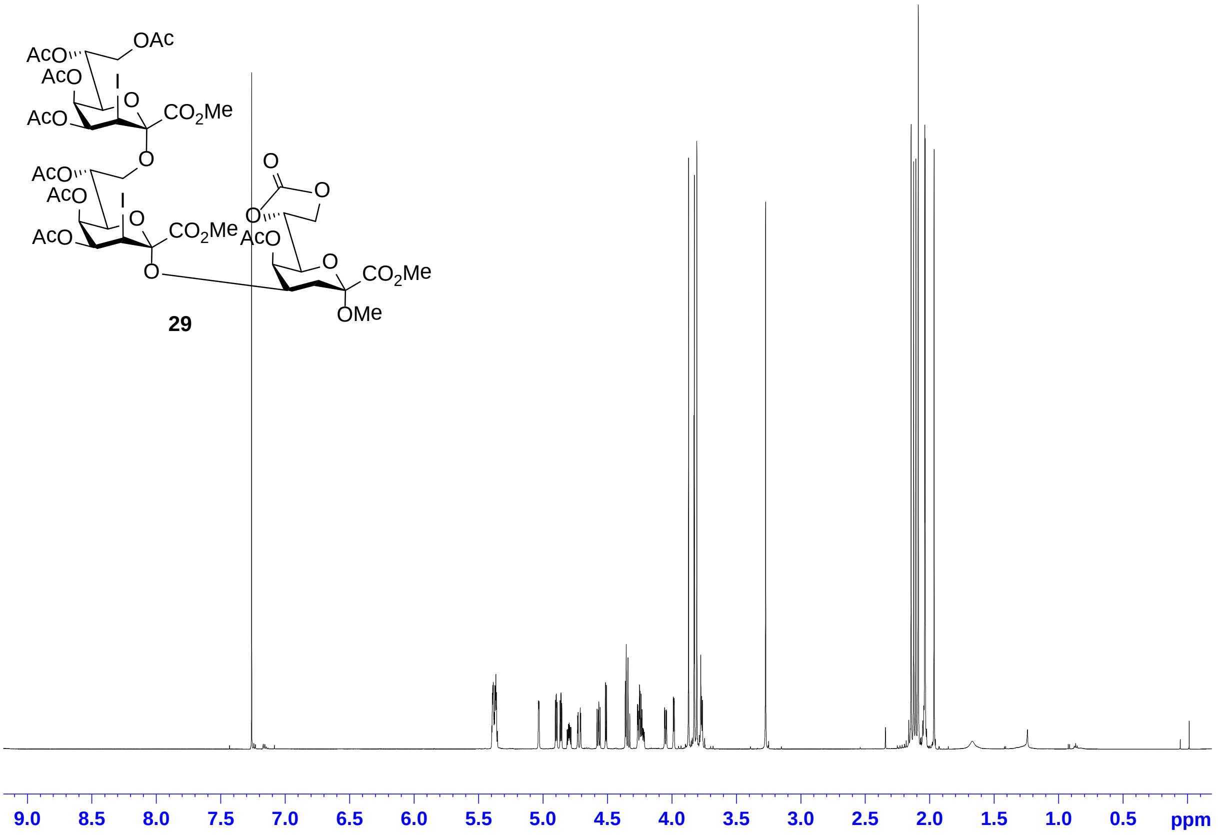
^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (150 MHz, $CDCl_3$)



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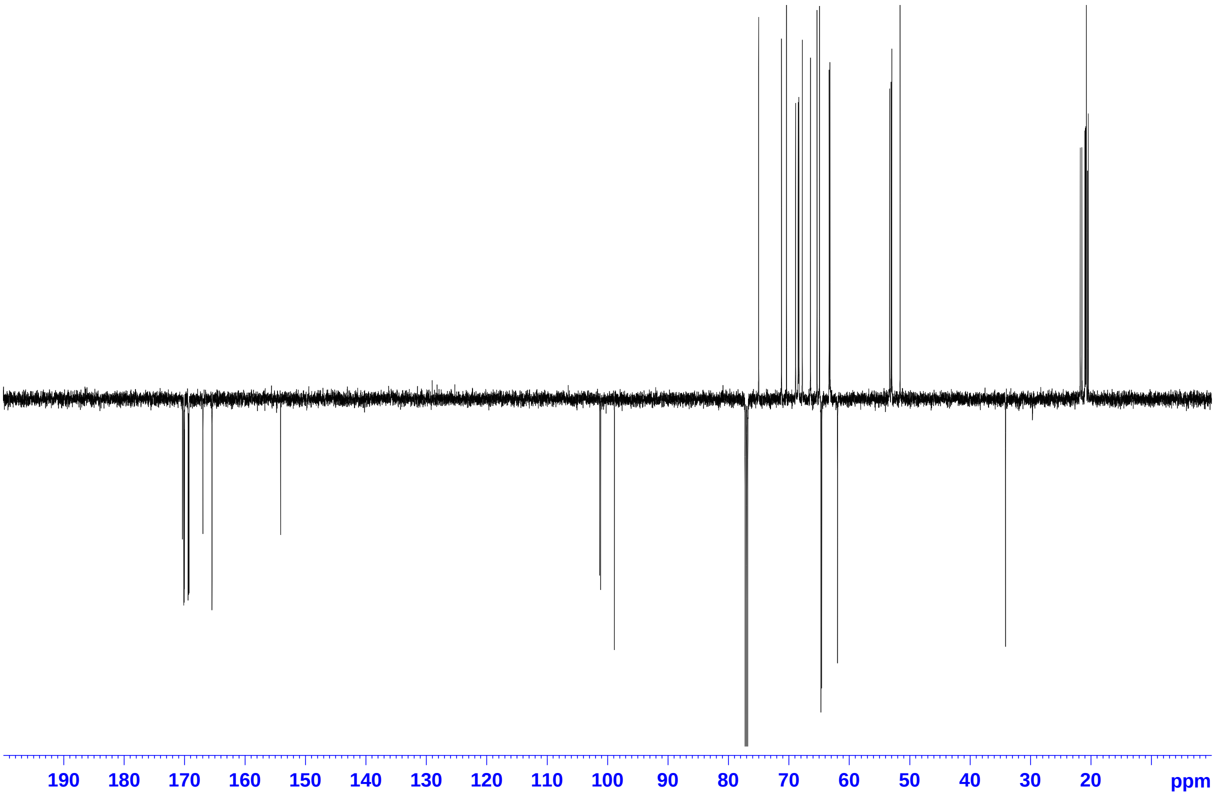
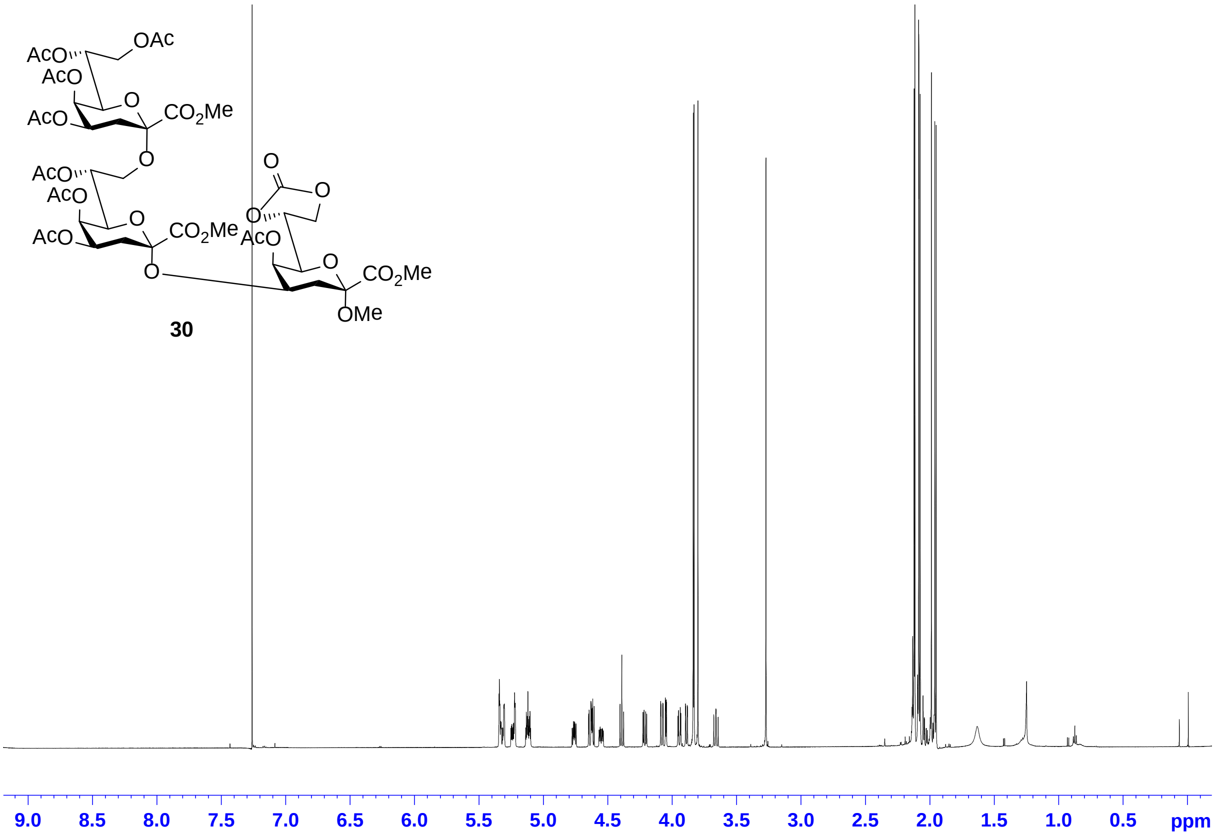
^{1}H-NMR (600 MHz, CDCl$_3$)



^{13}C-NMR (150 MHz, CDCl$_3$)



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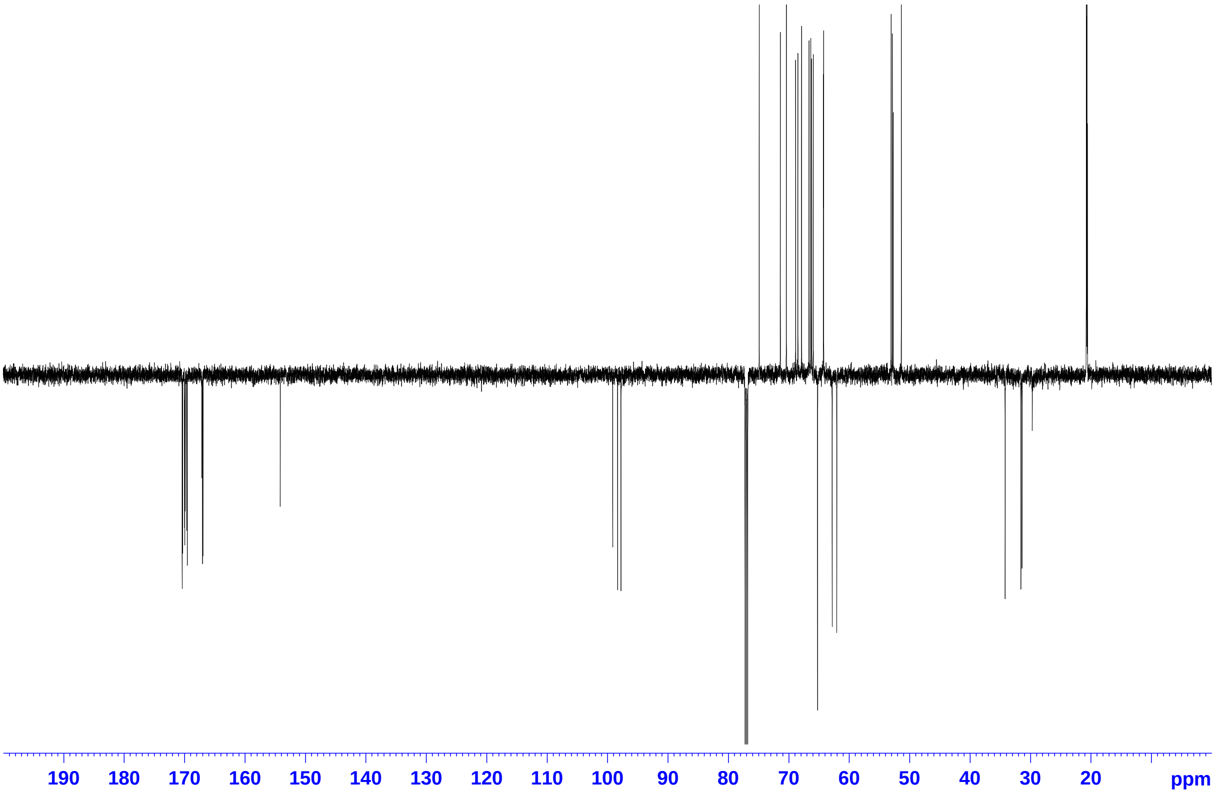
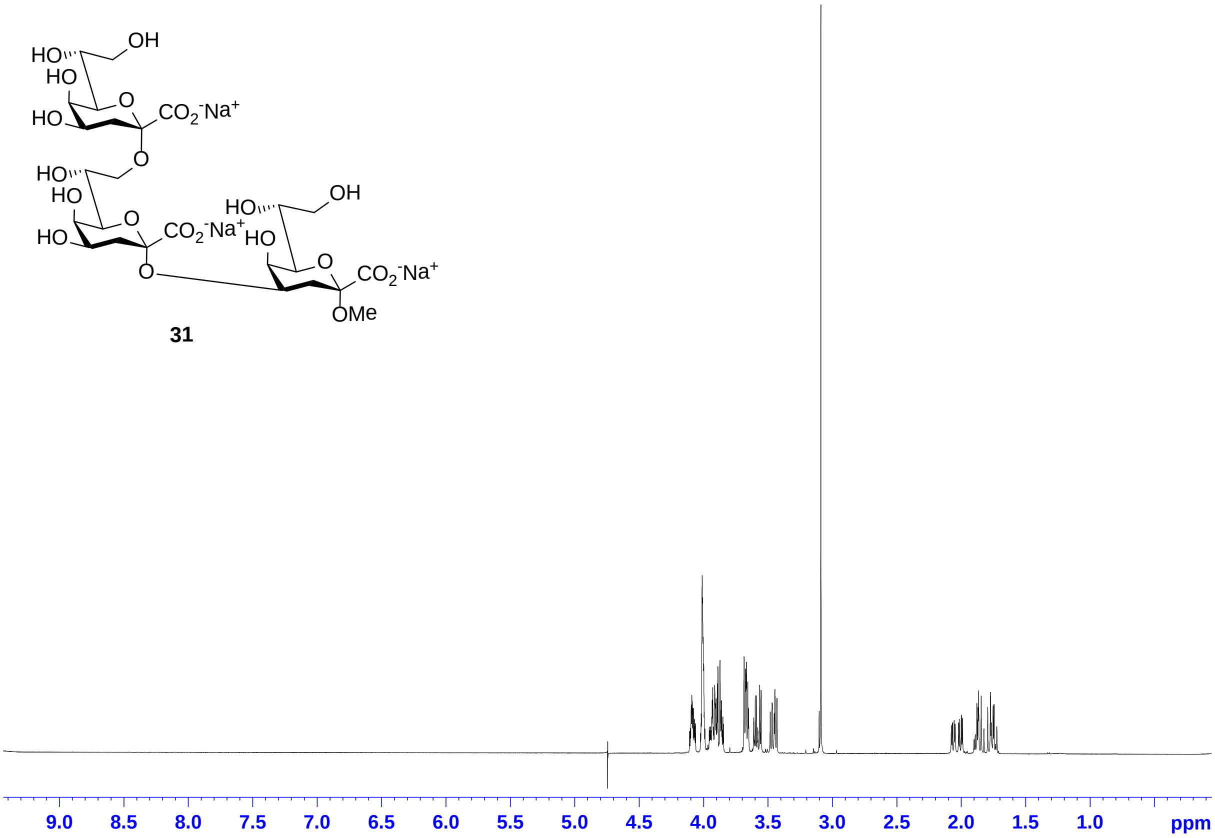
^{1}H-NMR (600 MHz, CDCl$_3$)



^{13}C-NMR (150 MHz, CDCl$_3$)



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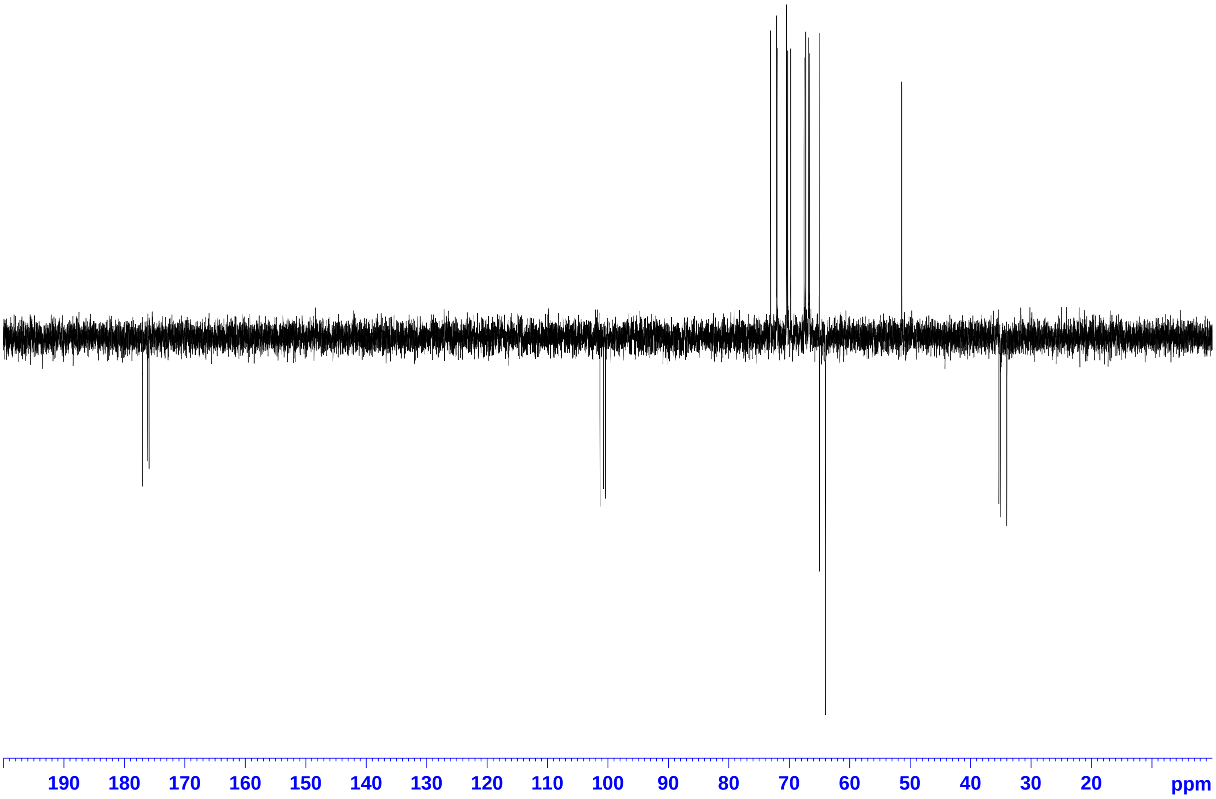
^{1}H-NMR (600 MHz, D_2O)



^{13}C-NMR (150 MHz, D_2O)