Supporting information

One-pot synthesis of Oligosaccharides by Combining Reductive Openings of Benzylidene Acetals and Glycosylations

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General remarks: Column chromatography was performed on silica gel G60 (SiliCycle, 60-200µm 60 Å), reactions were monitored by TLC on Silicagel 60 F_{254} (EMD Chemicals Inc.). The compounds were detected by examination under the UV light, by charring with 10% sulfuric acid in methanol and Cerium ammonium molybdate in 20% sulfuric acid in water. Solvents were removed under reduced pressure at < 35 °C. CH_2Cl_2 were distilled from CaH_2 prior to use in reactions. All the starting materials were kept *in vacuo* with P_2O_5 prior to use. ^{1}H-NMR spectra were recorded in $CDCl_3$ at 500 MHz (Varian), ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75 MHz (Varian). High-resolution mass spectra were obtained by using MALDI-ToF (Applied Biosystems 4700 Proteomics Analyzer) with 2,5-dihydroxybenzoic acid as an internal standard matrix.

General procedure for the synthesis of 8, 9 and 10: A mixture of glycosyl acceptor (0.13 mmol) and trichloroacetimidate donor (0.2 mmol) in CH_2Cl_2 (1 ml) was placed under an atmosphere of Ar and cooled to 0 °C. TfOH (0.013 mmol, 0.13M solution in DCM) was added and stirring at 0 ^{o}C was continued for 30 min. The reaction mixture was then cooled to -78 ^{o}C followed by addition of TfOH (0.23 mmol) and triethylsilane (0.26 mmol). The reaction mixture was then stirred at -78 ^{o}C for 30 min to 1 hr. The progress of each reaction was monitored by TLC and MALDI-ToF MS. The reaction was quenched by the addition of triethylamine (25 μL) and methanol (0.2 ml), diluted with CH_2Cl_2 (20 ml), and washed with sat. aq. $NaHCO_3$ solution (10 ml), water (10 ml) and brine (10 ml). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo.* The residue was purified by silica gel column chromatography.

Methyl 3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (**8**) was obtained from **1** and **4**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→35%) to afford compound **8** in 70% yield. Analytical data for **8**: R_f = 0.30 (ethyl acetate – hexanes, 1/2, v/v); ^{1}H-n.m.r: δ, 7.63-6.59 (m, 13H, aromatic), 5.39-5.35 (m, 2H, H-2', H-4'), 5.10 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, $J_{3',4'}$ = 10.4 Hz, H-3'), 4.94-4.91 (m, 2H, H-1, H-2), 4.72 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.56 (s, 2H, CH_2, Bn), 4.16-4.08 (m, 2H, H-6'a, H-6'b), 4.04-3.98 (m, 2H, H-5', H-3), 3.77-3.66 (m, 4H, H-6a, H-5, H-4, H-6b), 3.57 (s, 1H, O*H*), 3.23 (s, 3H, OCH_3), 2.10 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 1.81 (s, 3H, COCH_3) ppm; ^{13}C-n.m.r.: δ, 169.45, 169.09, 168.93, 164.12, 160.88, 158.17, 158.04, 154.96, 154.64, 137.25, 132.07, 128.35, 127.32, 127.18, 126.53, 100.75 (C-1'), 95.65 (C-1), 81.70, 72.56, 71.35, 70.15, 69.57, 69.48, 68.76, 68.17, 67.68, 65.88, 60.30, 54.20, 19.59, 19.58, 19.30 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{40}H_{42}F_2O_{16}$ $[M+Na]^+$ calcd 839.2339; found 839.2341.

Methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (**9**) was obtained from **2** and **4**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 5→25%) to afford compound **9** in 74% yield. Analytical data for **9**: R_f = 0.35 (ethyl acetate – hexanes, 1/2, v/v); ^{1}H-n.m.r: δ, 7.98-6.92 (m, 15H, aromatic), 5.22-5.20 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 10.5 Hz, H-3), 5.16 (bd, 1H, H-4'), 5.11 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1'), 5.09-5.07 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 4.99 (d, 1H, $J_{1,2}$ = 3.8 Hz H-1), 4.61-4.53 (q, 2H, CH_2, Bn), 4.41-4.38 (q, 1H, H-5'), 4.24-4.21(d, 1H, C*H*H, Bn), 4.14-4.10 (m, 2H, C*H*H, Bn, H-3), 3.78-3.69(m, 4H, H-4, H-5, H-6a, H-6b), 3.68-3.65 (dd, 1H, $J_{1',2'}$ = 3.6 Hz, $J_{2',3'}$ = 10.4 Hz, H-2'), 3.52 (d, 1H, O*H*), 3.31 (s, 3H, OCH_3), 1.99 (s, 3H, COCH_3), 1.82 (s, 3H, COCH_3), 0.89 (d, 3H, C$H_{3\text{fucose}}$) ppm. ^{13}C-n.m.r.: δ, 169.38, 168.91, 164.55, 136.94, 136.64, 132.09, 128.80, 127.43, 127.34, 127.22, 126.72, 126.68, 126.64, 126.46, 96.04 (C-1, C-1'), 78.16, 72.69, 71.57, 71.55, 71.38, 70.49, 69.06, 68.89, 68.80, 68.71, 64.26, 54.28, 19.72, 19.57, 14.67 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{38}H_{44}O_{13}$ $[M+Na]^+$ calcd 731.2680; found 731.2683.

Thexyldimethylsilyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**10**) was obtained from **2** and **7**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 5→40%) to afford compound **10** in 72% yield. Analytical data for **10**: R_f = 0.35 (ethyl acetate – hexanes, 1/2, v/v); ^{1}H-n.m.r: δ, = 7.17-7.06 (m, 10H, aromatic), 5.14-5.11 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, $J_{3'4'}$ = 3.0 Hz, H-3'), 5.10-4.98 (bd, 1H, H-4'), 4.57-4.25 (m, 6H, 2 x CH_2, Bn, H-1, H-5'), 3.70-3.67 (dd, 1H, $J_{1'2'}$ = 3.5

Hz, $J_{2',3'}$ = 10.5 Hz, H-2'), 3.56-3.49 (m, 2H, H-6a,b), 3.40-3.36 (m, 1H, H-4), 3.22-3.09 (m, 3H, H-5, H-3, H-2), 1.92 (s, 3H, COCH_3), 1.79 (s, 3H, COCH_3), 1.50-1.40 (m, 1H, SiC(CH_3)$_2$CH(CH_3)$_2$), 0.90 (d, 3H, OC$H_{3\text{fucose}}$), 0.70-0.69 (m, 12H, SiC(CH_3)$_2$CH(CH_3)$_2$), 0.00 (s, 6H, Si(CH_3)$_2$) ppm. ^{13}C-n.m.r.: δ, 173.71, 173.31, 141.25, 141.07, 131.67, 131.32, 131.12, 131.00, 130.84, 100.73 (C-1'), 100.49 (C-1), 86.40, 77.71, 77.57, 76.91, 76.16, 76.10, 74.72, 74.29, 73.95, 73.32, 73.25, 73.05, 72.54, 70.59, 69.80, 68.73, 37.16, 28.04, 24.09, 23.90, 23.23, 23.09, 21.76, 21.63, 19.16, 1.18, 0.00 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{38}H_{55}N_3O_{11}Si$ $[M+Na]^+$ calcd 780.3504; found 780.3501.

Methyl 3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-D-glucopyranoside (11): Premixed galactosyl donor **1** (115 mg, 0.20 mmol) and glucosyl acceptor **4** (50 mg, 0.13 mmol) were dissolved in CH_2Cl_2 (2 ml) and placed under an atmosphere of Ar at room temperature. Copper triflate (7.0 mg, 0.02 mmol) was added to the mixture and stirring was continued for 2 hr. Borane in tetrahydrofuran (0.26 ml, 0.26 mmol) was added and the resulting mixture was stirred at room temperature for 4 hr. The progress of the reaction was monitored by TLC and MALDI-ToF MS. The reaction was quenched by the addition of triethylamine (25 μL) and methanol (0.2 ml), diluted with CH_2Cl_2 (20 ml), and washed with sat. aq. $NaHCO_3$ solution (10 ml), water (10 ml) and brine (10 ml). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→45%) to afford compound **11** (48 mg, 45%). Analytical data for **11**: R_f = 0.50 (ethyl acetate – hexanes, 1/1, v/v); ^{1}H-n.m.r.: δ, 7.92-6.85 (m, 13H, aromatic), 5.42-5.38 (m, 2H, H-2', H-4'), 5.12 (bd, 1H, CH*H*, Bn), 5.00-4.98 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, $J_{2',3'}$ = 10.5 Hz, H-3'), 4.96 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.90-4.88 (m, 2H, H-1, H-2), 4.64 (d, 1H, CH*H*, Bn), 4.50-4.46 (m, 1H, H-3), 4.11-4.09 (m, 2H, H-6'a, H-6'b), 3.98-3.95 (m, 1H, H-5'), 3.83-3.74 (m, 2H, H-6a, H-6b), 3.71-3.63 (m, 2H, H-5, H-4), 3.28 (s, 3H, OCH_3), 2.08 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 1.85 (s, 3H, $COCH_3$) ppm. ^{13}C-n.m.r.: δ, 170.75, 170.59, 170.54, 170.42, 170.39, 170.26, 170.23, 170.18, 169.63, 165.55, 162.18, 162.13, 162.10, 159.60, 159.56, 159.50, 156.36, 156.32, 156.14, 156.10, 138.50, 133.74, 129.71, 129.11, 128.75, 128.54, 128.51, 128.11, 121.57, 121.45, 121.25, 121.13, 118.52, 118.41, 118.18, 118.08, 117.97, 117.63, 101.37 (C-1'), 96.98 (C-1), 78.12, 75.65, 75.33, 74.42, 70.99, 70.87, 70.80, 70.64, 67.07, 62.05, 60.91, 55.38, 20.91, 20.81, 20.61 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{40}H_{42}F_2O_{16}$ $[M+Na]^+$ calcd 839.2339; found 839.2335.

General procedure for the synthesis of 12 and 13: Compound **5** (0.11 mmol) was dissolved in CH_2Cl_2 (1 ml), placed under an atmosphere of Ar and cooled to -78 ^{o}C. TfOH (0.20 mmol) and triethylsilane (0.22 mmol) were added to the mixture followed by stirring at -78 ^{o}C for 30 min. The trichloroacetimidate donor (0.20 mmol) in CH_2Cl_2 (1 ml) was added and the temperature was increased to 0 ^{o}C and stirring was continued for 30 min. The progress of the reaction was monitored by TLC and MALDI-ToF MS. The reaction was quenched by the addition of triethylamine (25 μL) and methanol (0.2 ml), diluted with CH_2Cl_2 (20 ml), and washed with sat. aq. $NaHCO_3$ solution (10 ml), water (10 ml) and brine (10 ml). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo.* The residue was purified using silica gel column chromatography.

Methyl 3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-*O*-benzyl-α-D-glucopyranoside (**12**) was obtained from **1** and **5**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→55%) to afford compound **12** in 72% yield. Analytical data for **12**: R_f = 0.55 (ethyl acetate – Hexanes, 1/1, v/v); ^{1}H-n.m.r: δ, 7.53-7.11 (m, 18H, aromatic), 5.38-5.35 (dd, 1H, $J_{1'2'}$ = 8.1 Hz, $J_{2'3'}$ = 10.4 Hz, H-2'), 5.30 (d, 1H, $J_{3',4'}$ = 3.1 Hz, H-4'), 5.00 (d, 1H, C*H*H, Bn), 4.90-4.87 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, $J_{2',3'}$ = 10.4 Hz, H-3'), 4.87 (d, 1H, C*H*H, Bn), 4.81 (d, 1H, C*H*H, Bn), 4.69 (d, 1H, C*H*H, Bn), 4.65 (d, 1H, C*H*H, Bn), 4.58-4.56 (m, 2H, H-1, H-1'), 4.33 (d, 1H, C*H*H, Bn), 4.05-4.01(dd, 1H, $J_{5',6'}$ = 8.2 Hz, $J_{6'b,6'a}$ = 11.1 Hz, H-6'a), 3.97-3.86 (m, 3H, H-4, H-6'b, H-3), 3.68 (dd, 1H, $J_{5,6}$ = 2.9 Hz, $J_{6b,6a}$ = 10.7 Hz, H-6a), 3.59-3.49 (m, 4H, H-5, H-5', H-2, H-6b), 3.34 (s, 3H, OCH_3), 2.13 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 1.93 (s, 3H, $COCH_3$) ppm. ^{13}C-n.m.r.: δ, 170.44, 170.40, 170.21, 162.08, 162.05, 162.03, 161.99, 159.92, 159.88, 159.78, 159.74, 156.67, 156.64, 156.37, 156.33, 139.50, 138.52, 137.98, 128.86, 128.60, 128.38, 128.36, 128.34, 128.29, 128.03, 127.73, 127.53, 122.18, 122.06, 121.86, 121.74, 119.33, 119.23, 119.17, 119.07, 119.03, 118.92, 118.69, 118.58, 118.52, 118.18, 99.97 (C-1'), 98.64 (C-1), 79.96, 79.15, 76.39, 75.38, 73.73, 73.65, 71.24, 71.05, 70.62, 69.76, 67.84, 67.10, 60.85, 55.59, 20.88, 20.83, 20.73 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{47}H_{50}F_2O_{15}$ $[M+Na]^+$ calcd 915.3015; found 915.3010.

Methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**13**) was obtained from **2** and **5**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 5→45%) to afford compound **13** in 70% yield. Analytical data for **13**: R_f = 0.50 (ethyl acetate – Hexanes, 1/1, v/v); ^{1}H-n.m.r: δ, 7.31-7.14 (m, 20H, aromatic), 5.23-5.20 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, $J_{3'4'}$ = 3.5 Hz, H-3'), 5.06-5.03 (d, 1H, C*H*H, Bn), 5.01 (d, 1H, H-1'), 4.94-4.93 (bd, 1H, H-4'), 4.68-4.54 (m, 3H, 3 x C*H*H, Bn), 4.52 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.44-4.35 (m, 3H, 3 x C*H*H, Bn), 4.29-2.26 (d, 1H, C*H*H, Bn), 4.21-4.17 (m, 1H, H-5'), 3.85 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, H-3), 3.74 (t, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.70-3.64 (m, 3H, H-5, H-2', H-6a), 3.54-3.50 (m, 2H, H-6b, H-2), 3.27 (s, 3H, OCH_3), 2.00 (s, 3H, COCH_3), 1.87 (s, 3H, COCH_3), 0.53 (d, 3H, C$H_{3\text{fucose}}$) ppm. ^{13}C-n.m.r.: δ, 170.73, 170.13, 138.96, 138.31, 138.22, 138.17, 128.71, 128.62, 128.60, 128.52, 128.45, 128.27, 128.19, 128.16, 128.14, 128.07, 128.00, 127.92, 127.76, 98.02 (C-1), 97.65 (C-1'), 80.92, 80.33, 80.28, 75.97, 74.73, 74.27, 74.05, 73.57, 73.47, 72.04, 70.54, 70.44, 68.61, 64.95, 55.35, 21.09, 20.91, 15.60 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{45}H_{52}O_{12}$ $[M+Na]^+$ calcd 807.3356; found 807.3358.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-glucopyranoside -(1→4)-2,3,6-tri-*O*-benzyl- α-D-glucopyranoside (14): Compound **5** (50 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (1 ml), placed under an atmosphere of Ar and cooled to -78 °C. TfOH (17.2 μL, 0.20 mmol) and triethylsilane (2.0 eq., 0.22 mM) were added to the mixture followed by stirring at -78 °C for 30 min. The trichloroacetimidate donor **3** (137 mg, 0.20 mmol) dissolved in CH_2Cl_2 (1 ml) was added and the temperature was increased to -30 °C over a period of 15 min. followed by the addition of 2,6-di-*t*-butyl-4-methyl pyridine (66 mg, 0.33 mmol). The reaction mixture was allowed to warm to room temperature and stirring was continued for 18 hrs.

The reaction was quenched by the addition of triethylamine (25 μL) and methanol (0.2 ml), diluted with CH_2Cl_2 (20 ml), and washed with sat. aq. $NaHCO_3$ solution (10 ml), water (10 ml) and brine (10 ml). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate – hexanes gradient elution 10→55%) to afford compound **14** (61 mg, 55%). Analytical data for **14**: R_f = 0.40 (ethyl acetate – hexanes, 1/1, v/v); ^{1}H-n.m.r.: δ, 7.32-6.91 (m, 30H, aromatic), 5.57 (d, 1H, $J_{1',2'}$ = 3.4 Hz, H-1'), 5.38 (t, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 9.3 Hz, H-3'), 5.01-4.89 (q, 2H, CH_2, Bn), 4.66 (d, 1H, CH*H*, Bn), 4.55 (d, 1H, CH*H*, Bn), 4.54 (m, 1H, $J_{1,2}$ = 1.2 Hz, H-1), 4.45 (bd, 2H, CH_2, Bn), 4.41-4.30 (q, 2H, CH_2, Bn), 4.27 (t, 1H, $J_{7',8a'}$ = $J_{7',8b'}$ = 6.6 Hz, H-7'), 4.08 (t, 1H, $J_{3,2}$ = $J_{3,4}$ = 9.2 Hz, H-3), 4.01-3.95 (m, 2H, H-6'a, H-4), 3.92-3.86 (m, 2H, H-6'b, H-5'), 3.84-3.82 (dd, 1H, $J_{5,6}$ = 3.4 Hz, $J_{6b,6a}$ = 11.0 Hz, H-6a), 3.64-3.62 (m, 1H, H-5), 3.56-3.54 (m, 1H, H-6b), 3.53-3.50 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.27 (s, 3H, OCH_3), 3.27-3.22 (m, 2H, H-8'a, H-4'), 3.16-3.14 (dd, 1H, $J_{1',2'}$ = 3.4 Hz, $J_{2',3'}$ = 9.9 Hz, H-2'), 2.82-2.78 (dd, 1H, $J_{7',8'b}$ = 6.6 Hz, $J_{8'b,8'a}$ = 13.6 Hz, H-8'b), 1.89 (s, 3H, COCH_3), 1.74 (s, 3H, COCH_3) ppm. ^{13}C-n.m.r.: δ, 170.73, 169.89, 140.29, 139.66, 138.34, 138.24, 137.78, 136.92, 129.04, 128.68, 128.65, 128.54, 128.47, 128.43, 128.38, 128.13, 127.63, 127.36, 127.23, 127.16, 125.78, 98.13 (C-1), 95.17 (C-1'), 81.76, 81.12, 80.22, 77.44, 76.32, 74.57, 74.45, 73.49, 73.08, 69.87, 68.96, 63.04, 55.50, 40.75, 21.26, 21.08 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{59}H_{64}O_{13}S$ $[M+Na]^+$ calcd 1035.3965; found 1035.3961.

General procedure for the synthesis of trisaccharides 15, 16, 17 and 18: A mixture of glycosyl acceptor (0.13 mmol) and trichloroacetimidate donor (0.19 mmol) in CH_2Cl_2 (1 ml) was placed under an atmosphere of Ar and cooled to 0 ^{o}C. TfOH (0.013 mmol, 0.13M solution in DCM) was added and stirring at 0 ^{o}C was continued for 30 min. The reaction mixture was then cooled to -78 ^{o}C followed by addition of TfOH (0.23 mmol) and triethylsilane (0.26 mmol). The reaction mixture was then stirred at -78 ^{o}C for 30 min to 1 hr. The second trichloroacetimidate donor (0.23 mmol) dissolved in CH_2Cl_2 (1 ml) was added and the mixture was allowed to warm to 0 ^{o}C. The progress of the reactions was monitored by TLC and MALDI-ToF MS. The reaction was quenched by the addition of triethylamine (25 μL) and methanol (0.2 ml), diluted with CH_2Cl_2 (30 ml), and washed with sat. aq. $NaHCO_3$ solution (20 ml), water (20 ml) and brine (20 ml). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo.* The residue was purified by silica gel column chromatography.

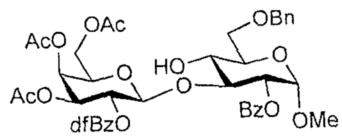
Methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-[3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→4)]-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (**15**) was obtained from **1**, **2** and **4**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→55%) to afford compound **15** in 63% yield. Analytical data for **15**: R_f = 0.30 (ethyl acetate – hexanes, 1/1, v/v); ^{1}H-n.m.r: δ, 8.02-6.81 (m, 18H, aromatic), 5.52 (d, 1H, H-1', $J_{1'2'}$ = 3.9 Hz), 5.39-5.38 (bd, 1H, H-4'), 5.34-5.33 (bd, 1H-H-4''), 5.27-5.23 (dd, 1H, $J_{1'',2''}$ = $J_{2'',3''}$ = 8.3 Hz, H-2''), 5.20-5.17 (m, 2H, H-2, H-3'), 5.10(d, 1H, H-1, $J_{1,2}$ = 3.9 Hz), 5.08-5.07 (m, 1H, H-5'), 4.89 (d, 1H, C*H*H, Bn), 4.82-4.79 (dd, $J_{2'',3''}$ = $J_{3'',4''}$ = 10.3 Hz, 1H, H-3''), (d, 1H, $J_{1'',2''}$ = 8.3 Hz, H-1''), 4.49-4.47 (dd, 1H, $J_{5'',6''a}$ = 6.4 Hz, $J_{6''b,6''a}$ = 11.5 Hz, H-6''a), 4.42-4.32 (m, 3H, C*H*H, Bn, H-3, H-6''b), 4.24 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4), 4.20-4.02 (dd, 2H, C*H*$_2$,Bn), 3.86-3.84 (dd, 1H, $J_{5,6}$ = 9.0 Hz, $J_{6b,6a}$ = 10.8 Hz, H-6a), 3.65-

3.59 (m, 2H, H-5, H-6b), 3.54 (t, 1H, $J_{4'',5''}$ = 7.0 Hz, $J_{5'',6''a}$ = 6.8 Hz, H-5''), 3.29 (s, 3H, OCH_3), 2.20 (s, 3H, $COCH_3$), 2.08 (s, 6H, 2 x $COCH_3$), 1.93 (s, 3H, $COCH_3$), 1.89 (s, 3H, $COCH_3$), 1.31 (d, 3H, $CH_{3fucose}$) ppm. ^{13}C-n.m.r.: δ, 170.92, 170.77, 170.68, 170.51, 170.08, 169.88, 165.42, 161.88, 161.86, 161.83, 161.80, 159.98, 159.94, 159.82, 159.80, 156.74, 156.70, 156.42, 156.39, 137.90, 137.63, 133.61, 129.99, 129.84, 129.26, 129.15, 128.91, 128.81, 128.75, 128.65, 128.60, 128.54, 128.44, 128.39, 128.16, 127.50, 127.42, 125.52, 122.32, 122.19, 121.99, 121.88, 119.12, 119.02, 118.95, 118.86, 118.79, 118.68, 118.62, 118.29, 99.55 (C-1''), 97.29 (C-1), 96.97 (C-1'), 75.68, 73.99, 73.05, 72.84, 72.42, 72.25, 71.88, 71.22, 71.06, 70.57, 70.31, 70.10, 67.46, 67.15, 64.29, 61.13, 55.70, 29.91, 21.04, 20.99, 20.88, 20.85, 20.73, 16.18 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{57}H_{62}F_2O_{22}$ $[M+Na]^+$ calcd 1159.3598; found 1159.3593.

Methyl 3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→3)-[3,4-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→4)]2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (16) was obtained from **1**, **2** and **4**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→55%) to afford compound **16** in 67% yield. Analytical data for **16**: R_f = 0.30 (ethyl acetate – hexanes, 1/1, v/v); ^{1}H-n.m.r: δ, 7.84-6.89 (m, 18H, aromatic), 5.46 (bd, 1H, H-4'), 5.42 (bd, 1H, H-4''), 5.33-5.29 (m, 2H, H-2', H-3''), 5.20-5.17 (m, 2H, H-1, H-5''), 5.06 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.03-5.00 (dd, 1H, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 4.97 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 4.95-4.93 (m, 1H, H-3'), 4.62- 4.43 (m, H-6'a, 2 x CH_2, Bn, H-3), 4.39-4.35 (dd, 1H, $J_{5',6'}$ = 8.5 Hz, $J_{6'b,6'a}$ = 11.0 Hz, H-6'b), 4.09 (t, 1H, H-4), 4.03-3.99 (m, 1H, H-5'), 3.95-3.92 (m, 2H, H-6a, H-2''), 3.84-3.82 (m, 1H, H-5), 3.61-3.59 (d, 1H, H-5), 3.30 (s, 3H, OCH_3), 2.38 (s, 3H, $COCH_3$), 2.21 (s, 3H, $COCH_3$), 2.19 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 1.97 (s, 3H, COCH_3), 1.88 (s, 3H, COCH_3), 1.35 (d, 3H, OC$H_{3fucose}$) ppm. ^{13}C-n.m.r.: δ, 170.97, 170.91, 170.58, 170.15, 169.91, 165.41, 161.92, 159.58, 159.46, 156.34, 156.03, 138.18, 138.09, 133.74, 129.74, 129.26, 129.12, 128.77, 128.66, 128.48, 128.45, 128.20, 128.01, 127.92, 125.52, 121.45, 121.33, 121.12, 121.01, 119.43, 119.34, 119.26, 119.17, 118.46, 118.35, 118.13, 118.02, 117.92, 117.93, 117.59, 101.53 (C-1'), 97.36 (C-1''), 96.84 (C-1), 75.52, 74.75, 74.41, 73.96, 73.70, 72.47, 72.16, 71.17, 71.00, 70.94, 70.87, 70.15, 67.70, 67.04, 64.61, 61.00, 55.22, 21.68, 21.11, 21.08, 20.96, 20.90, 20.59, 16.13 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{57}H_{62}F_2O_{22}$ $[M+Na]^+$ calcd 1159.3598; found 1159.3596.

Thexyldimethylsilyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-[3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**17**) was obtained from **1**, **2** and **7**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→55%) to afford compound **17** in 67% yield. Analytical data for **17**: R_f = 0.35 (ethyl acetate – hexanes, 1/1, v/v); ^{1}H-n.m.r: δ, 7.35-6.95 (m, 13H, aromatic), 5.44 (d, 1H, $J_{1'2'}$ = 3.8 Hz, H-1'), 5.21 (d, 1H, H-4'), 5.19 (d, 1H, H-4), 5.10-5.04 (m, 2H, H-2, H-3'), 4.86-4.82 (m, 1H, H-5'), 4.78-4.76 (dd, 1H, H-3), 4.65-4.48 (m, 4H, 3 x C*H*H, Bn, H-1), 4.33 (d, 1H, $J_{1'',2''}$ = 7.6 Hz, H-1''), 4.29-4.26 (m, 2H, C*H*H, Bn, H-6a), 4.19-4.16 (dd, 1H, $J_{5,6b}$ = 8.0 Hz, $J_{6b,6a}$ = 11.5 Hz , H-6b), 3.94 (t, 1H, H-4''), 3.73-3.71 (dd, 1H, $J_{1'2'}$ = 3.8 Hz, $J_{2',3'}$ = 10.5 Hz, H-2'), 3.57-3.48 (dd, 1H, $J_{5'',6''}$ = 9.0 Hz, $J_{6''a, 6''b}$ = 11.5 Hz, H-6''a), 3.48 (t, 1H, H-5), 3.40-3.36 (m, 2H, H-3'', H-6''b), 3.29-3.26 (dd, 1H, $J_{1'',2''}$ = 7.6 Hz, $J_{2'',3''}$ = 10.2 Hz, H-2''), 3.03-3.01 (m, 1H, H-5''), 2.02 (s, 3H, COCH_3), 1.94 (s, 3H, COCH_3), 1.90 (s, 3H, COCH_3), 1.88 (s, 3H, COCH_3), 1.82 (s, 3H, COCH_3), 1.79 (s, 3H, COCH_3), 1.74 (s, 3H, $COCH_3$), 1.52-1.48 (m, 1H, $SiC(CH_3)_2CH(CH_3)_2$), 1.09 (d, 3H, $OCH_{3fucose}$), 0.73-0.69 (m, 12H, $SiC(CH_3)_2CH(CH_3)_2$), 0.00 (s, 6H, $Si(CH_3)_2$) ppm. ^{13}C-n.m.r.: δ, 173.84, 173.58, 173.49, 172.97, 172.82, 164.67, 162.77, 162.60, 159.55, 159.23, 141.15, 140.74, 131.76, 131.35, 131.24, 130.97, 130.83, 130.74, 125.05, 124.85, 124.73, 121.96, 121.86, 121.62, 121.52, 121.41, 121.07, 121.08, 102.48 (C-1), 100.32 (C-1’’), 99.90 (C-1’), 77.96, 77.59, 76.70, 75.94, 75.87, 75.46, 75.12, 74.07, 73.41, 73.39, 71.98, 70.47, 70.06, 67.17, 64.00, 36.91, 27.86, 23.91, 23.90, 23.73, 23.56, 23.04, 22.86, 21.57, 21.41, 19.00, 0.86, 0.00 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{57}H_{73}F_2N_3O_{20}Si$ $[M+Na]^+$ calcd 1208.4422; found 1208.4425.

Methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-diflurobenzoyl-β-D-galactopyranosyl-(1→4)]-3,6-*O*-benzyl-α-D-glucopyranoside (**18**) was obtained from **1**, **2** and **6**, and purified by silica gel column chromatography (ethyl acetate - hexanes gradient elution 10→50%) to afford compound **18** in 60% yield. Analytical data for **18**: R_f = 0.35 (ethyl acetate – Hexanes, 1/1, v/v); ^{1}H-n.m.r: δ, 7.44-6.96 (m, 18H, aromatic), 5.32-5.29 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, $J_{3'4'}$ = 3.0 Hz, H-3’), 5.26-5.20 (m, 2H, H-3’’, H-4’), 5.16-5.15 (bd, 1H, H-4’’), 5.02-4.99 (d, 1H, C*H*H, Bn), 4.95 (d, 1H, $J_{1'2'}$ = 4.0 Hz, H-1’), 4.76-4.73 (m, 3H, C*H*H, Bn, H-3’’, H-1), 4.58-4.54 (m, 2H, C*H*H, Bn, H-1’’), 4.36-4.20 (m, 4H, 3 x C*H*H, Bn, H-5’), 3.29-3.72 (m, 4H, H-4’, H-6’’a,b, H-3), 3.68-3.66 (dd, 1H, $J_{1'2'}$ = 3.5 Hz, $J_{2',3'}$ = 10.5 Hz , H-2’), (dd, 1H, $J_{5,6a}$ = 8.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6a), 3.55-3.51 (m, 2H, H-5, H-2), 3.46-3.43 (m, 1H, H-6b), 3.36-3.33 (m, 1H, H-5), 3.24 (s, 3H, OCH_3), 2.01 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$), 1.93 (s, 3H, $COCH_3$), 1.88 (s, 3H, $COCH_3$), 1.82 (s, 3H, $COCH_3$), 1.00 (d, 3H, $OCH_{3fucose}$) ppm. ^{13}C-n.m.r.: δ, 170.73, 170.46, 170.35, 170.21, 139.81, 138.22, 138.04, 128.81, 128.37, 128.27, 128.22, 128.07, 127.70, 126.96, 126.88, 122.13, 122.01, 121.81, 121.69, 119.37, 119.28, 119.21, 119.11, 119.02, 118.89, 118.66, 118.55, 118.21, 100.43 (C-1'), 99.93 (C-1''), 99.21 (C-1), 81.72, 78.46, 76.35, 74.65, 73.64, 73.09, 72.63, 71.78, 71.24, 71.09, 70.59, 70.21, 69.50, 67.98, 67.01, 64.93, 60.82, 55.11, 29.91, 21.07, 20.89, 20.85, 20.78, 20.72, 16.27 ppm. HR-MALDI-ToF/MS: *m/z*: for $C_{57}H_{64}F_2O_{21}$ $[M+Na]^+$ calcd 1145.3806; found 1145.3799.



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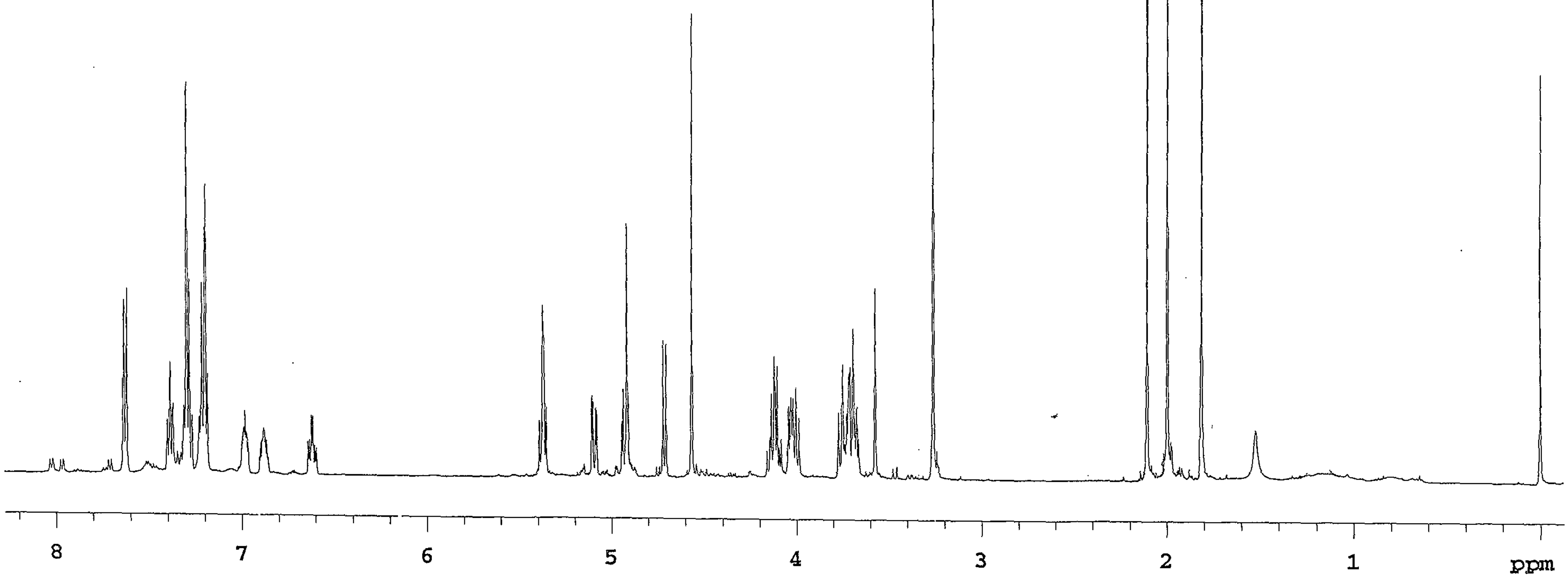

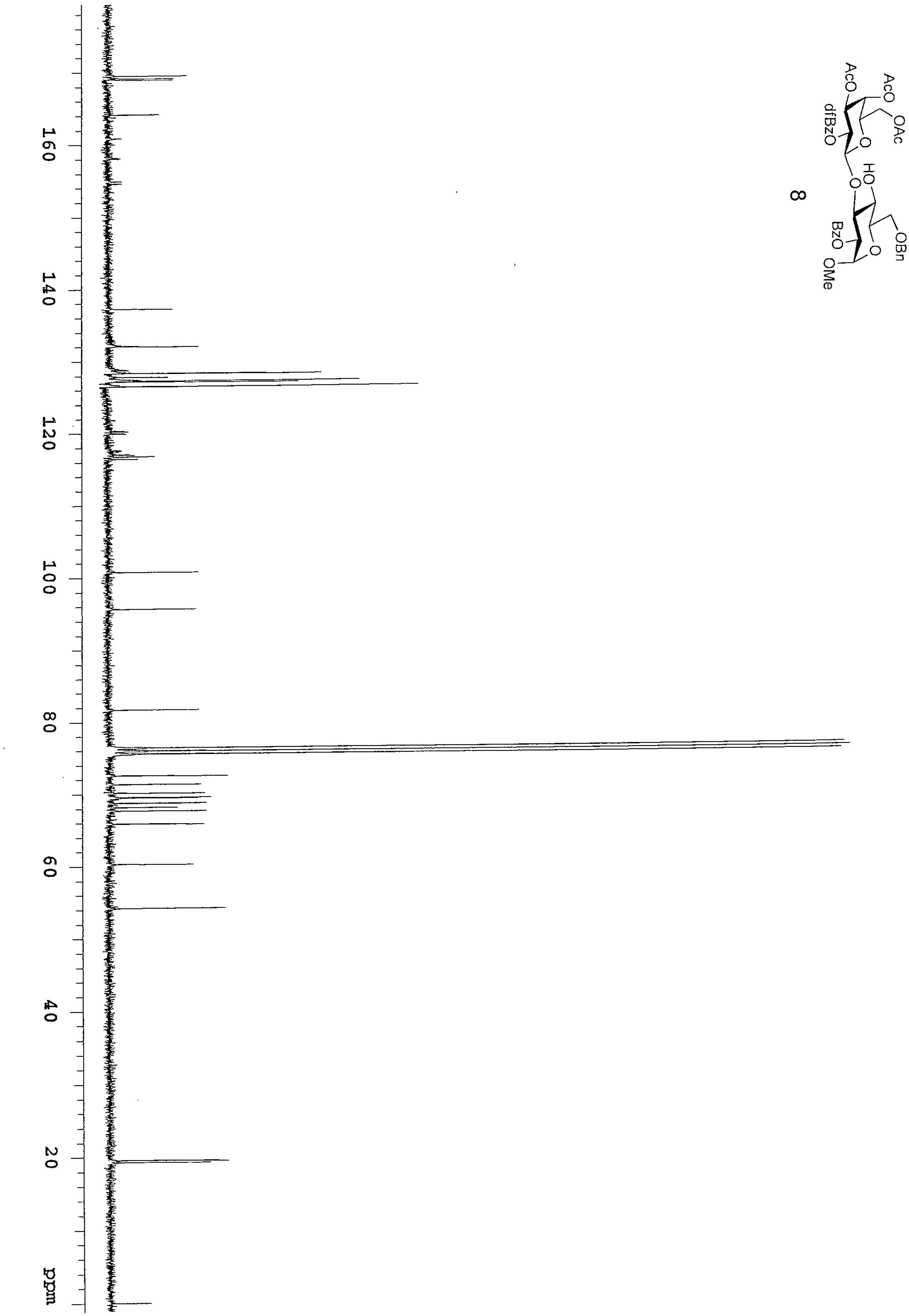
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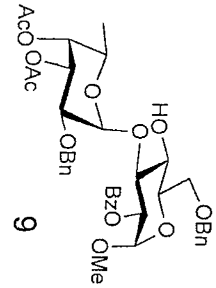

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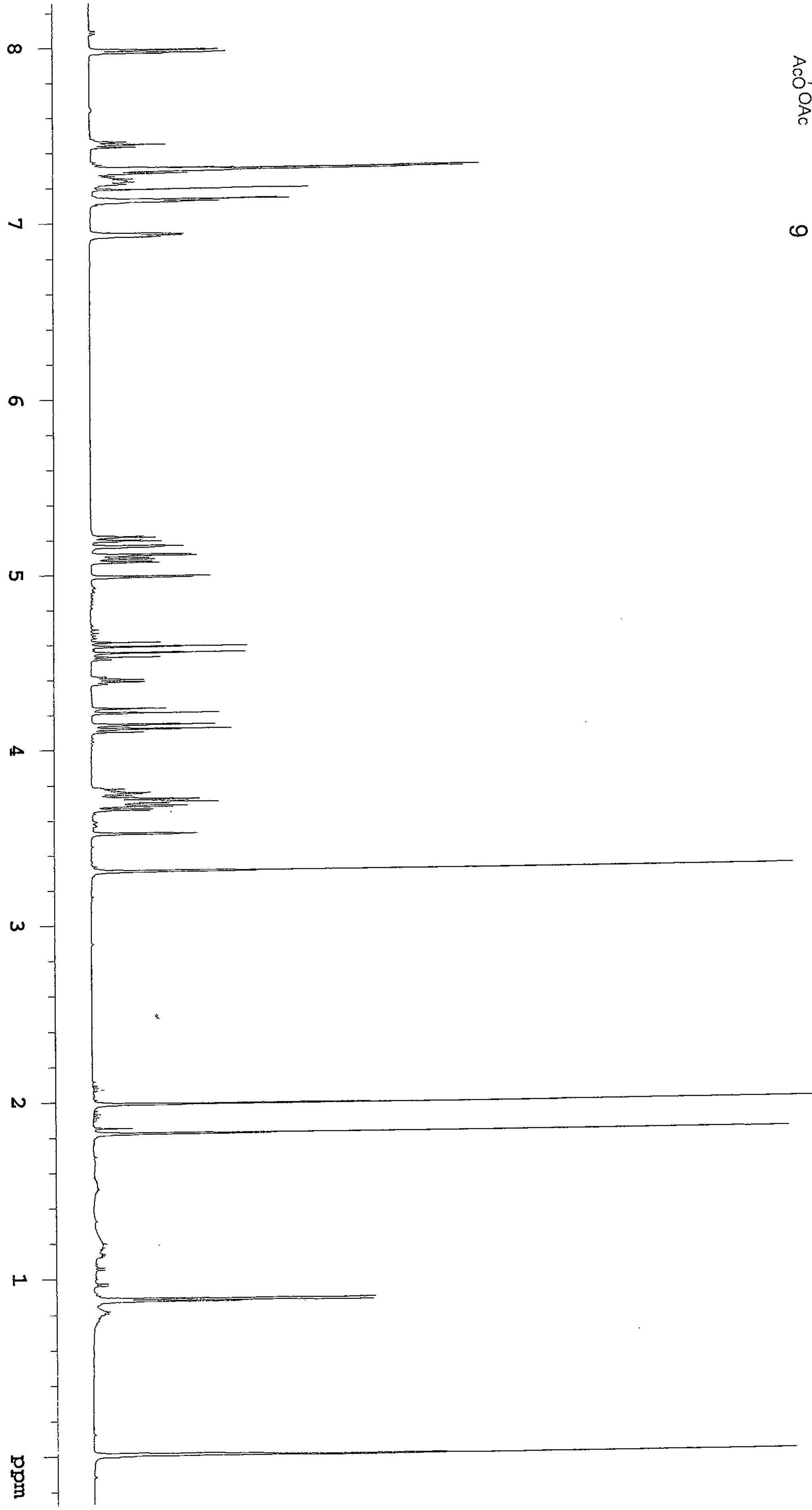

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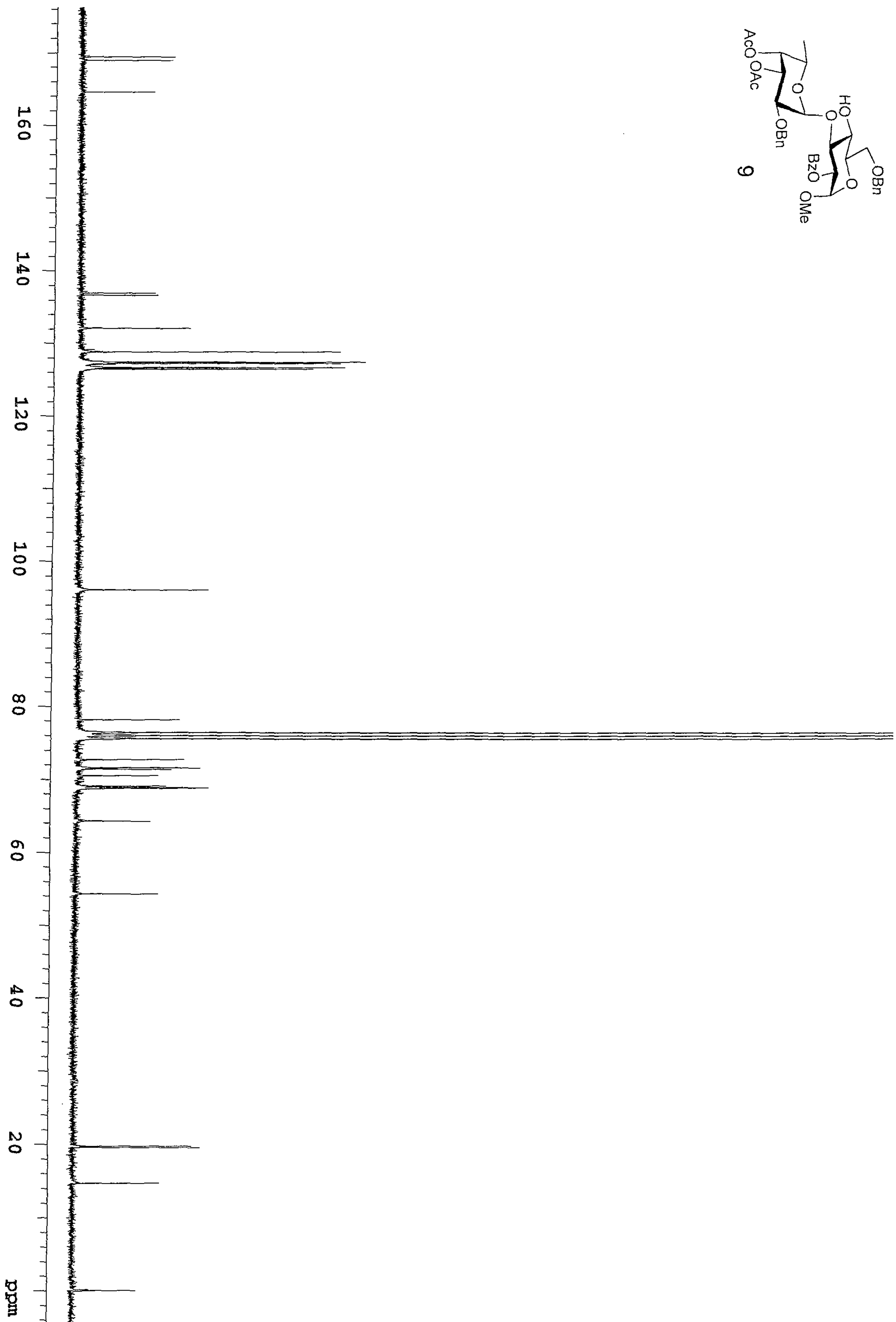

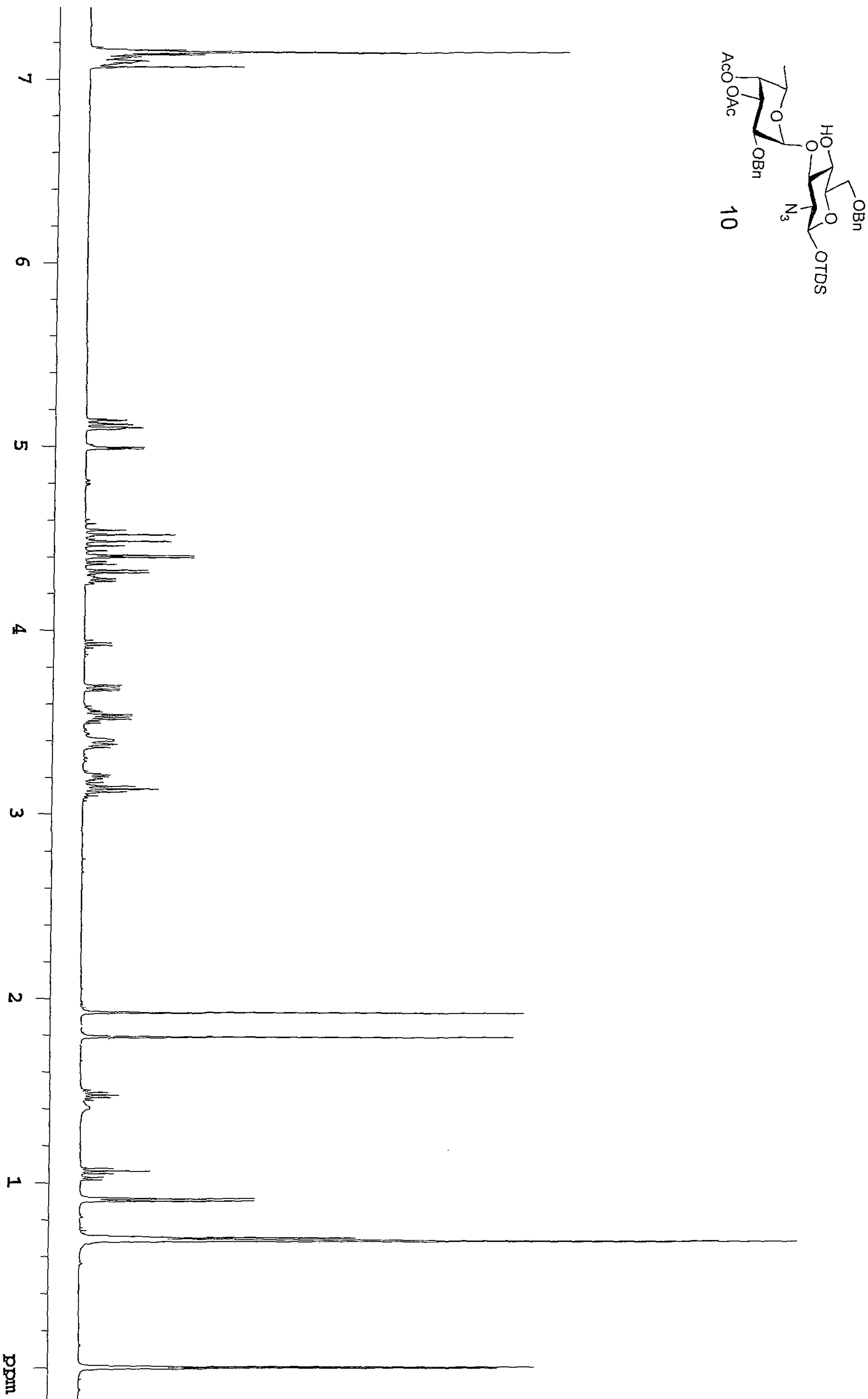
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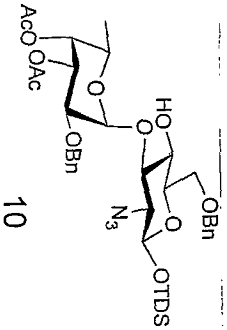

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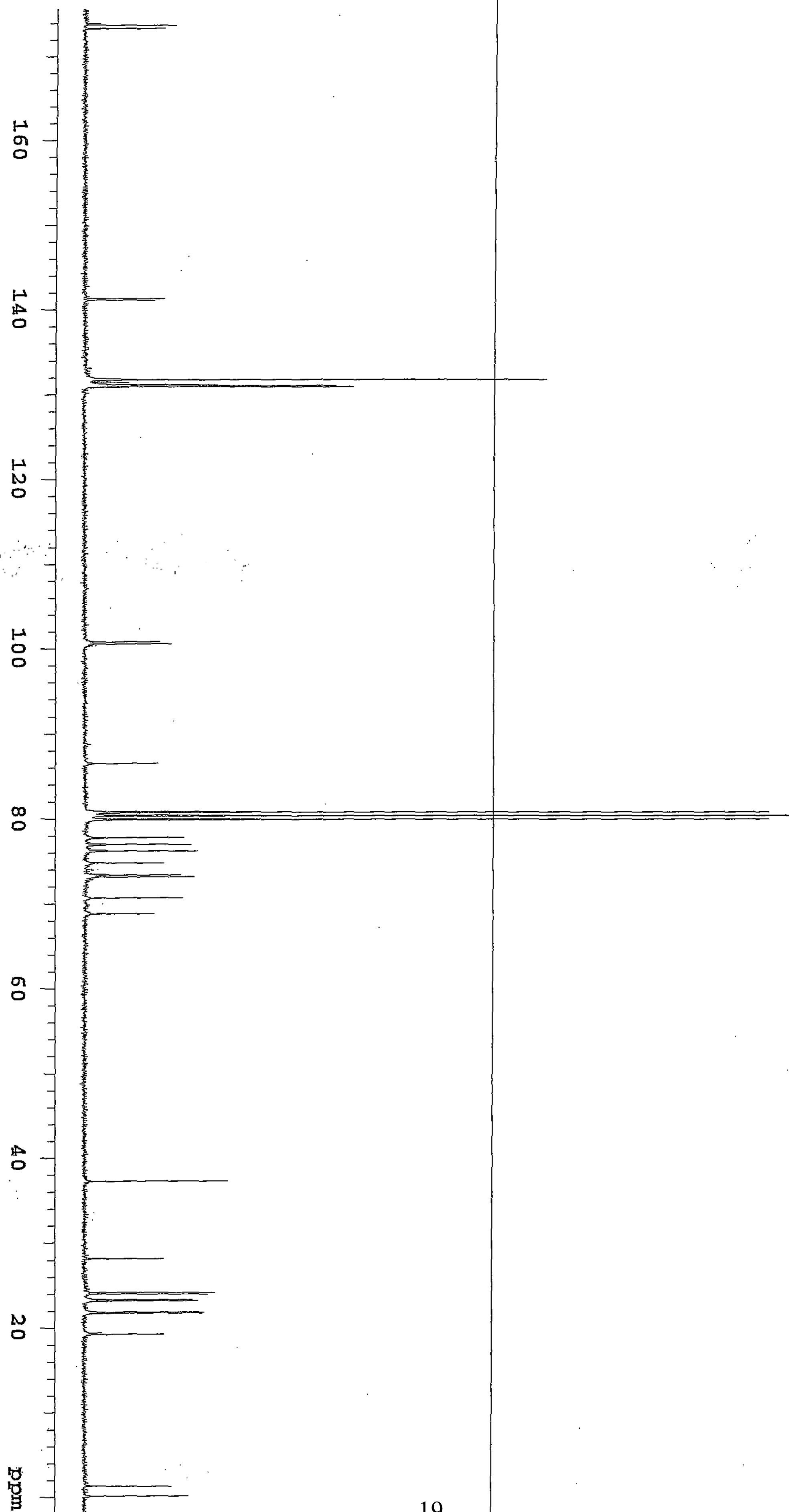

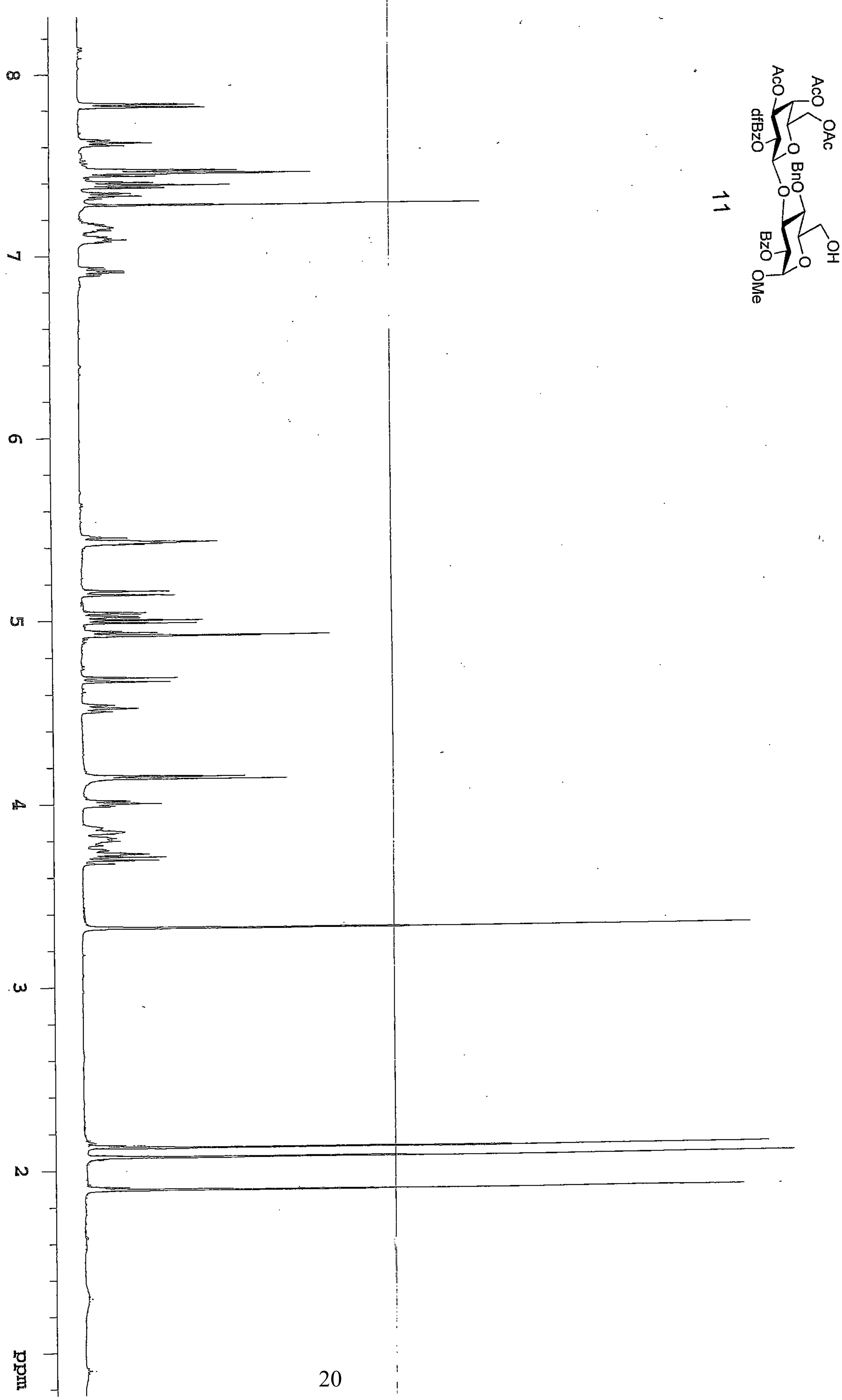
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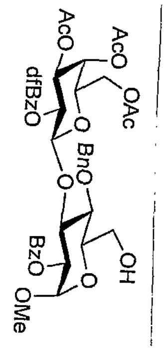

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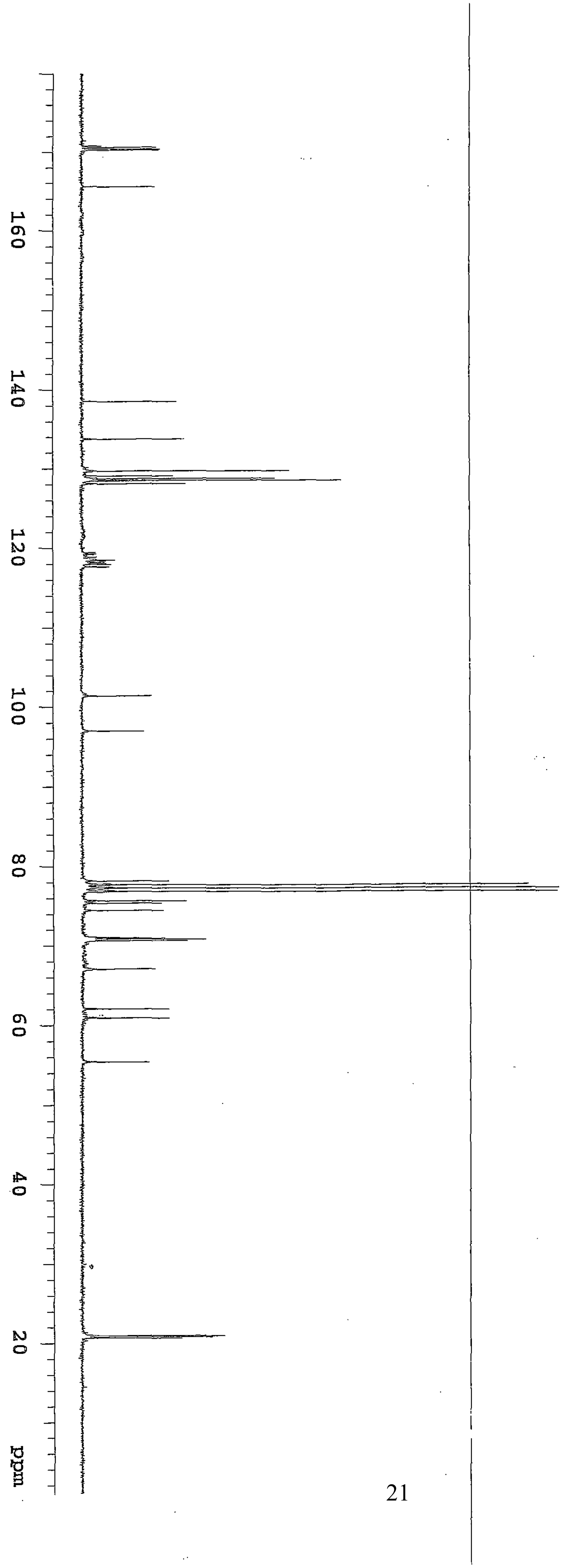

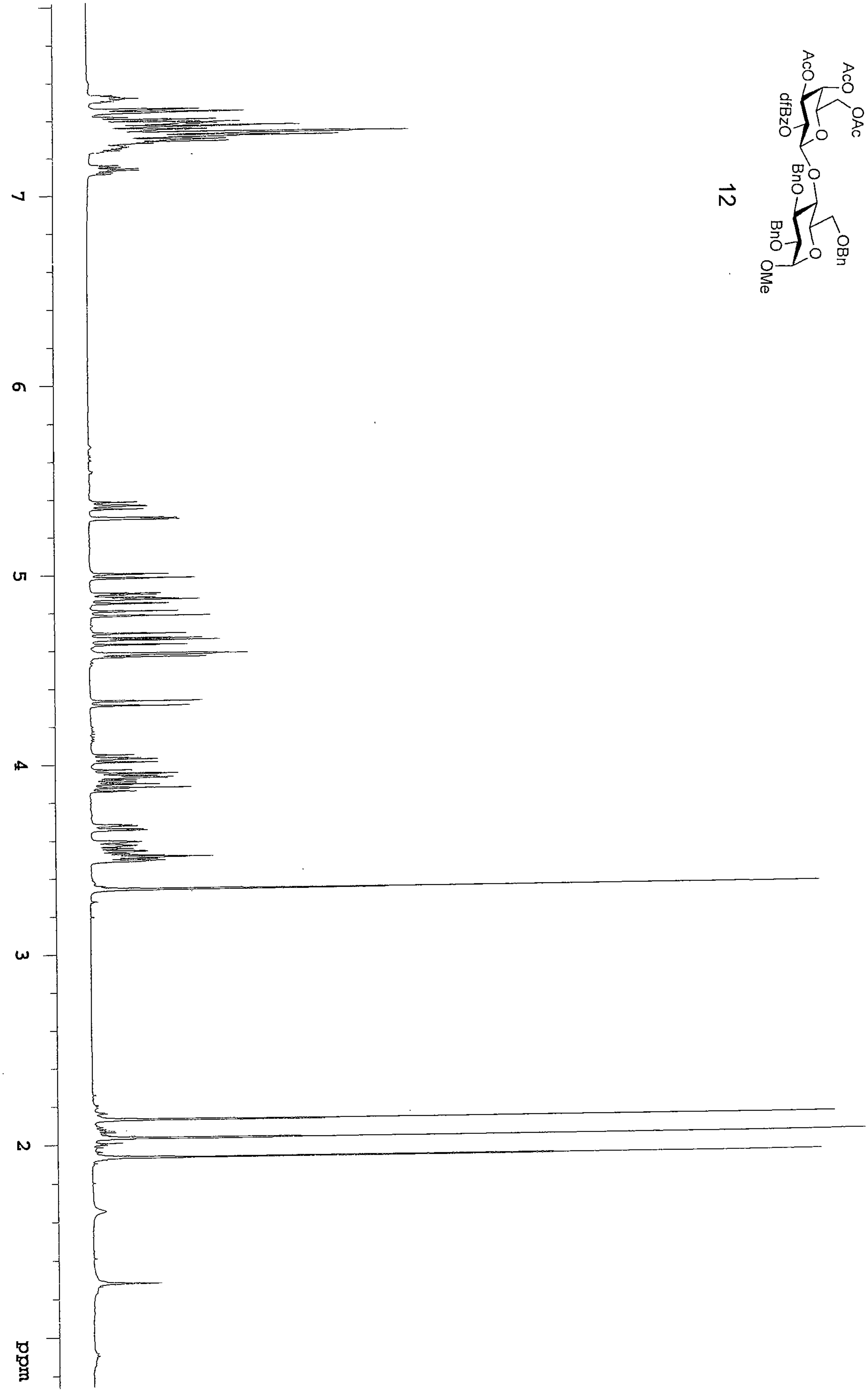
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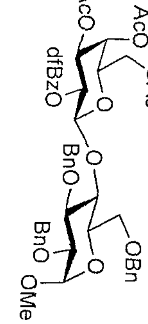
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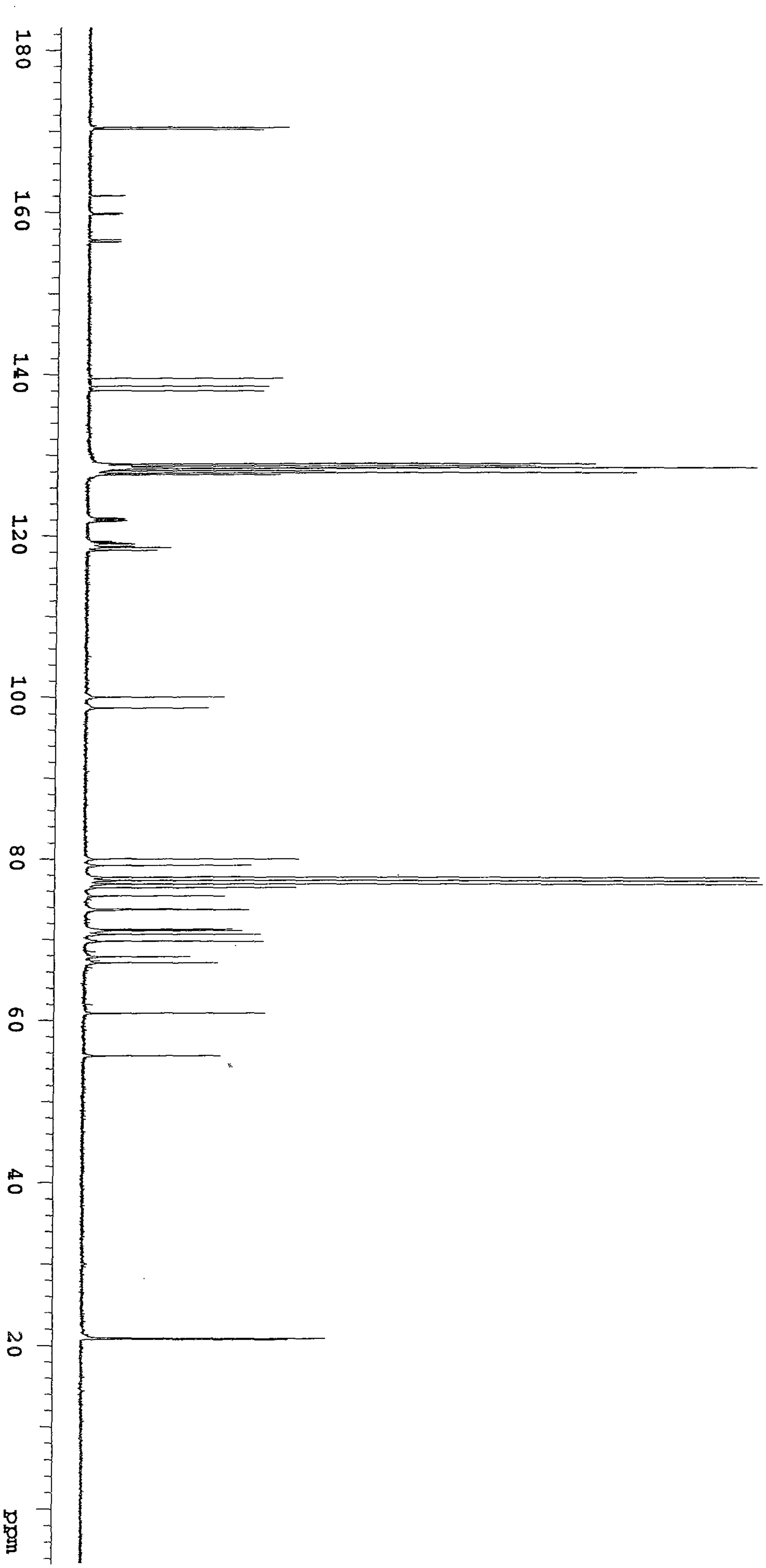
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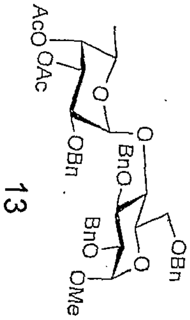

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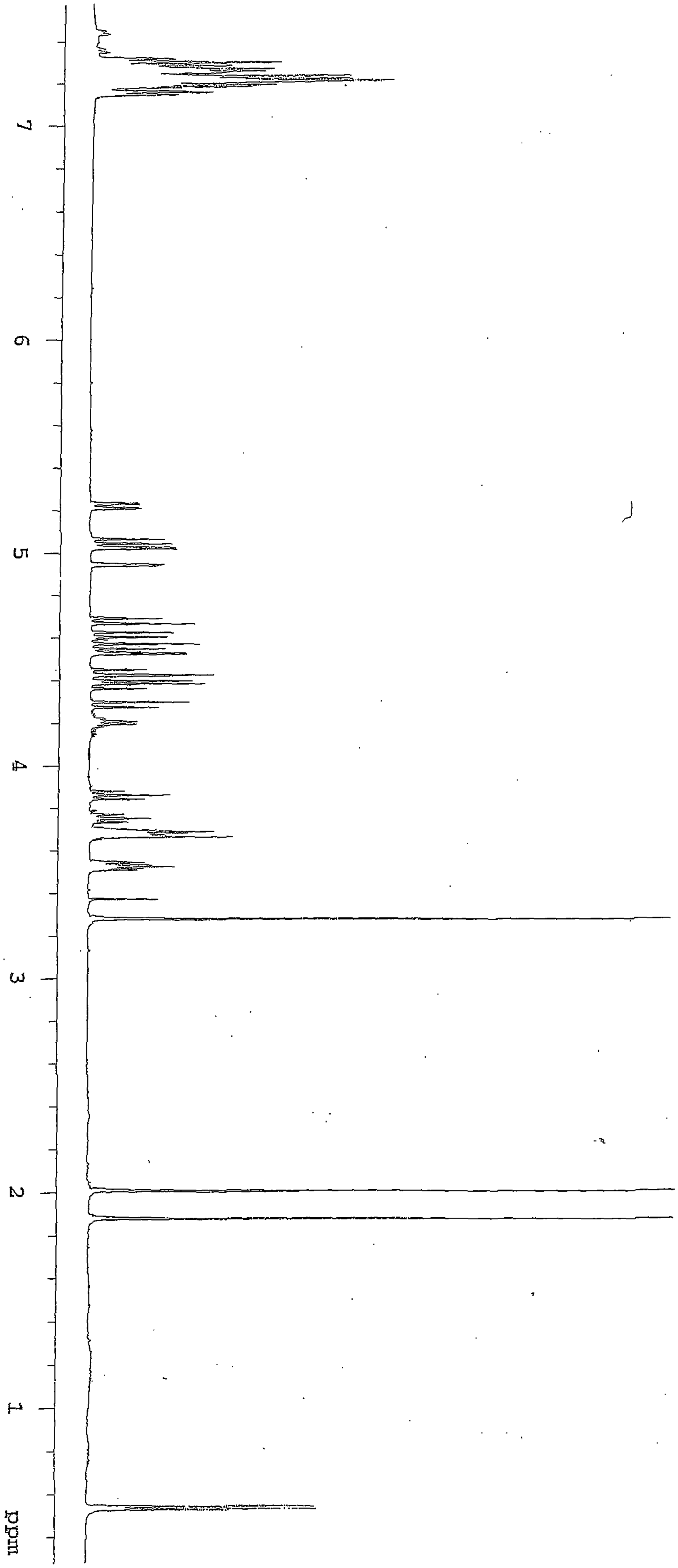

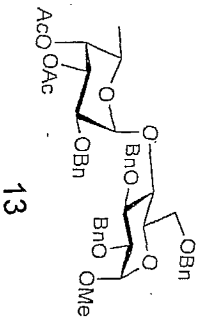

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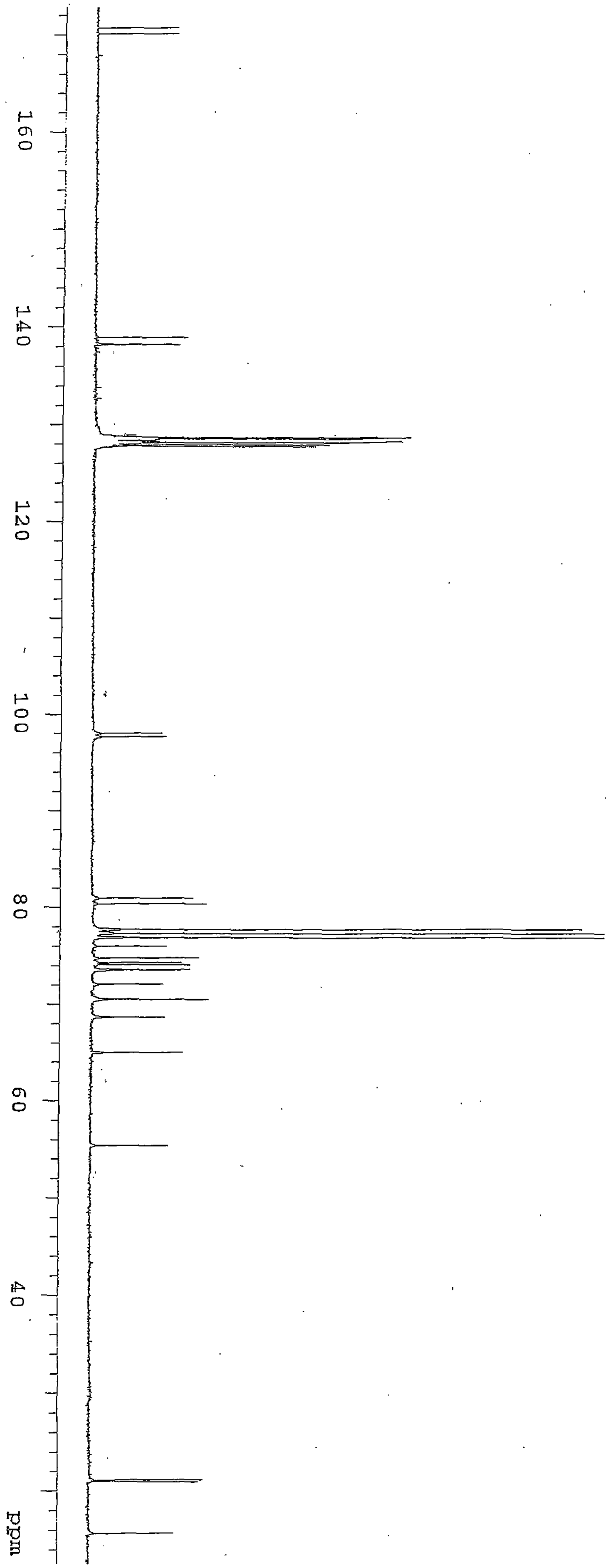

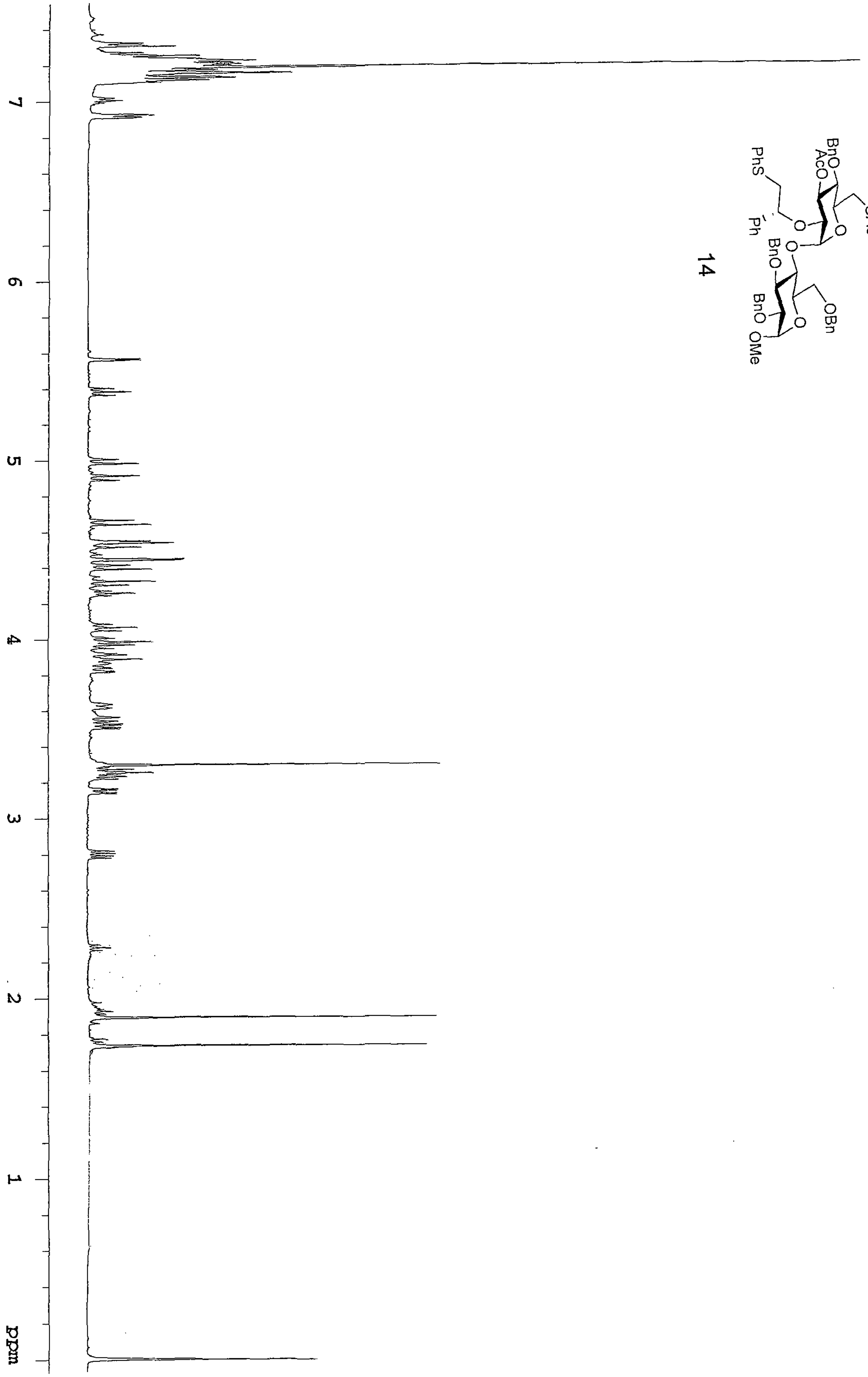
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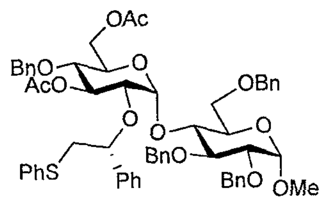
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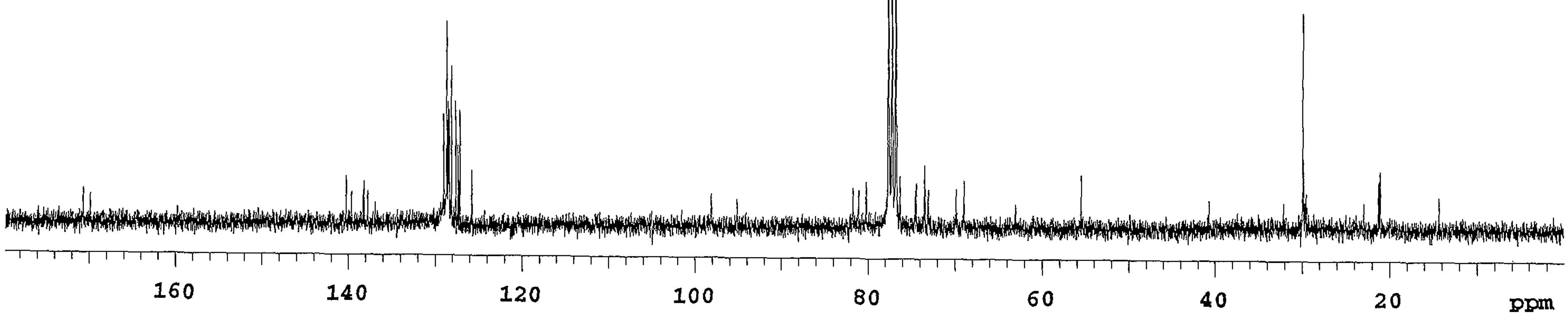
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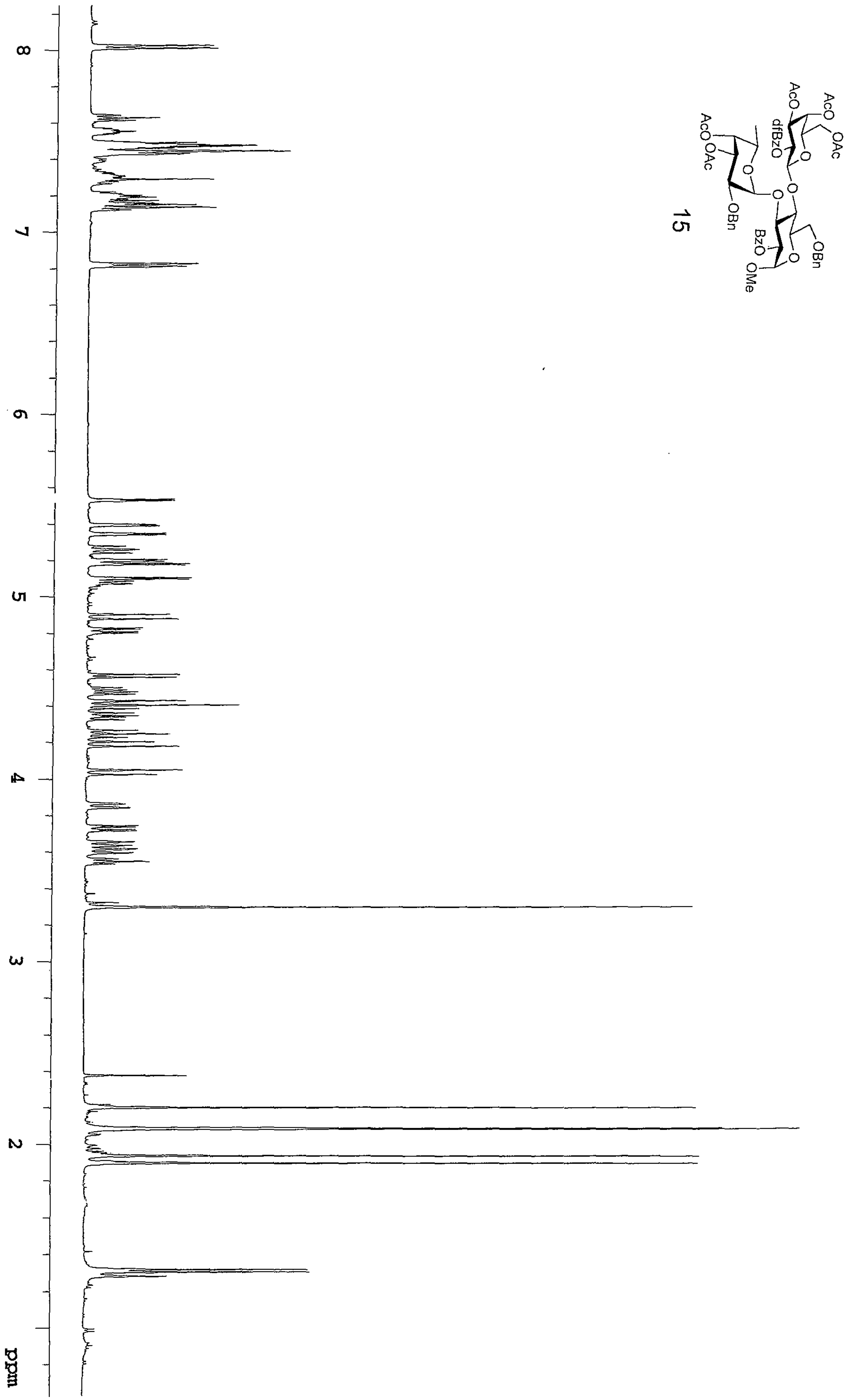
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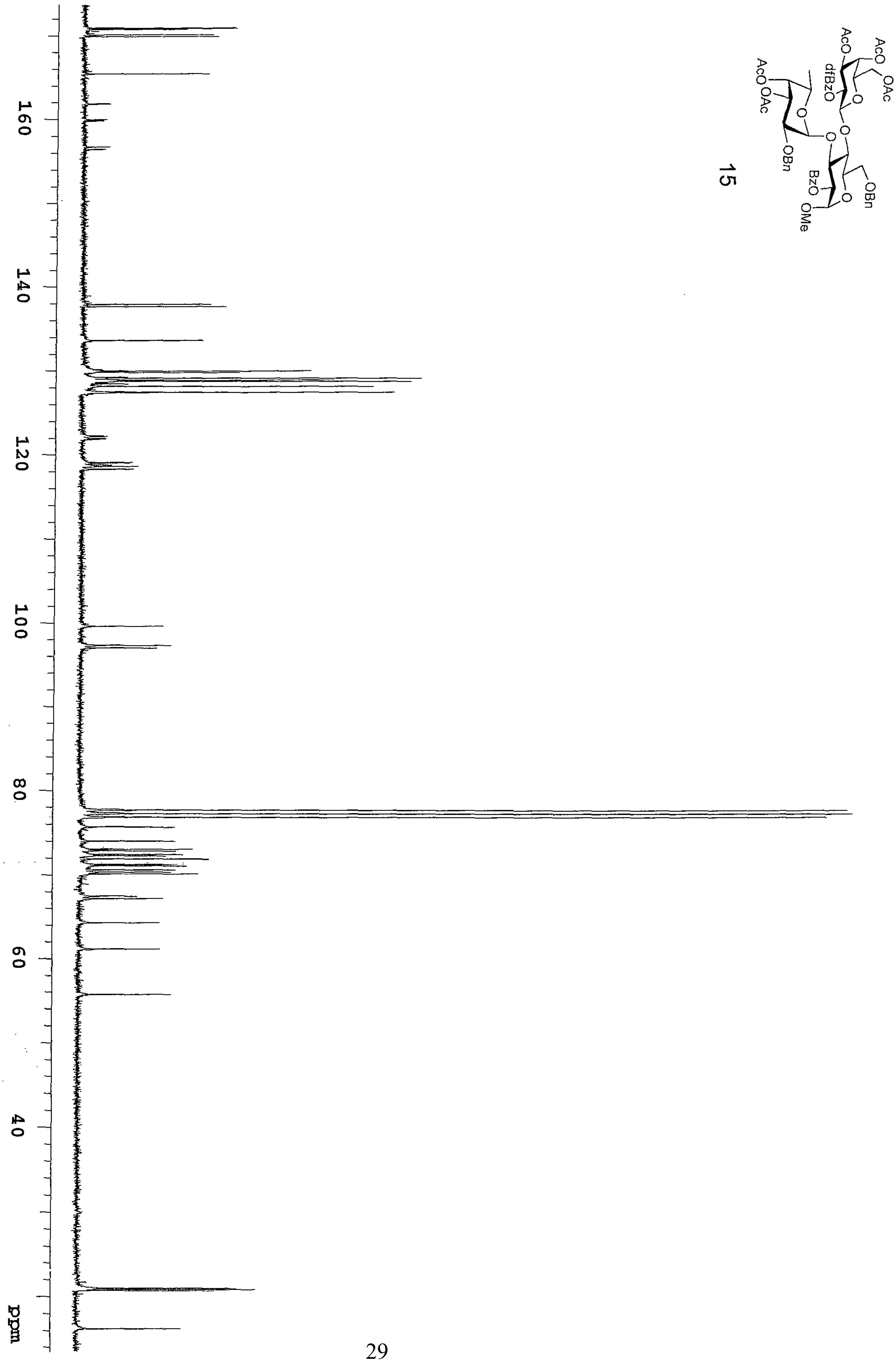
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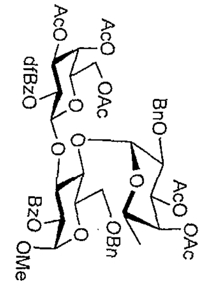

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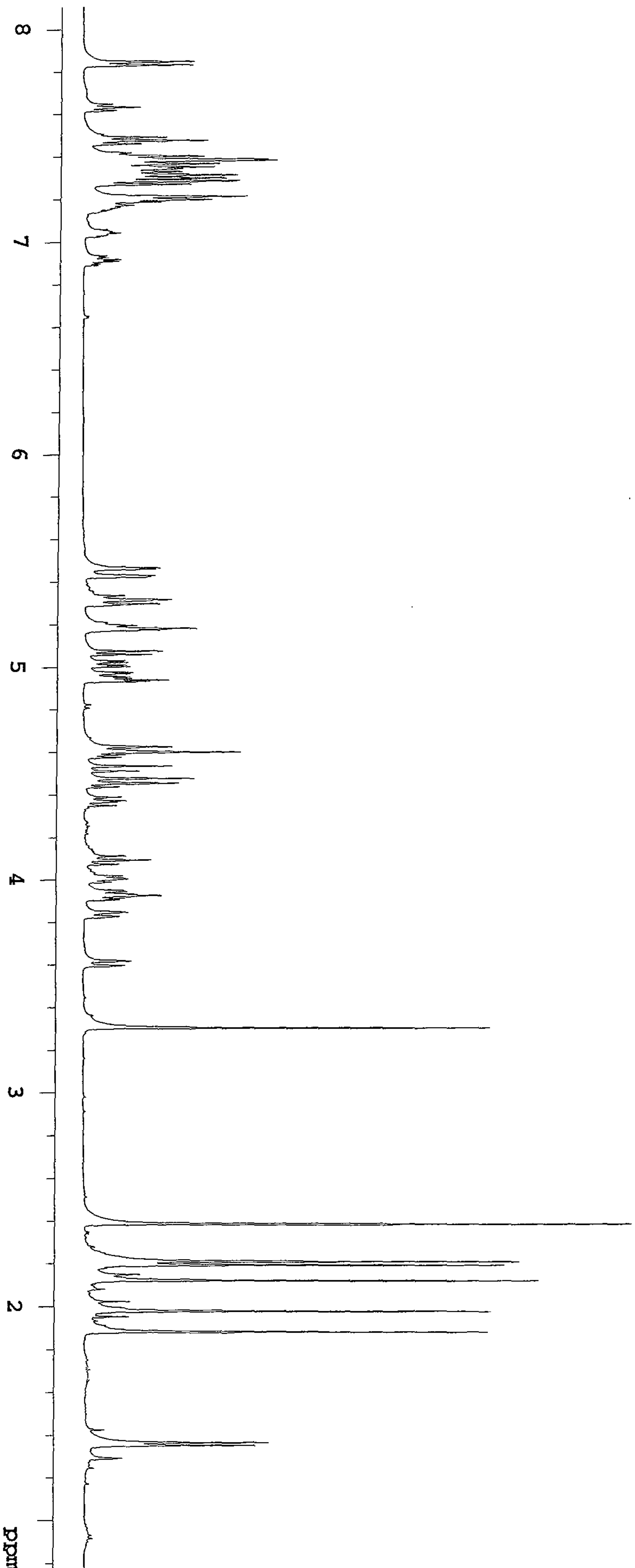

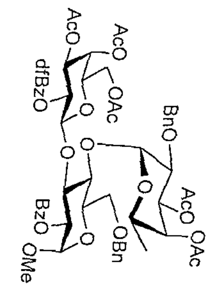
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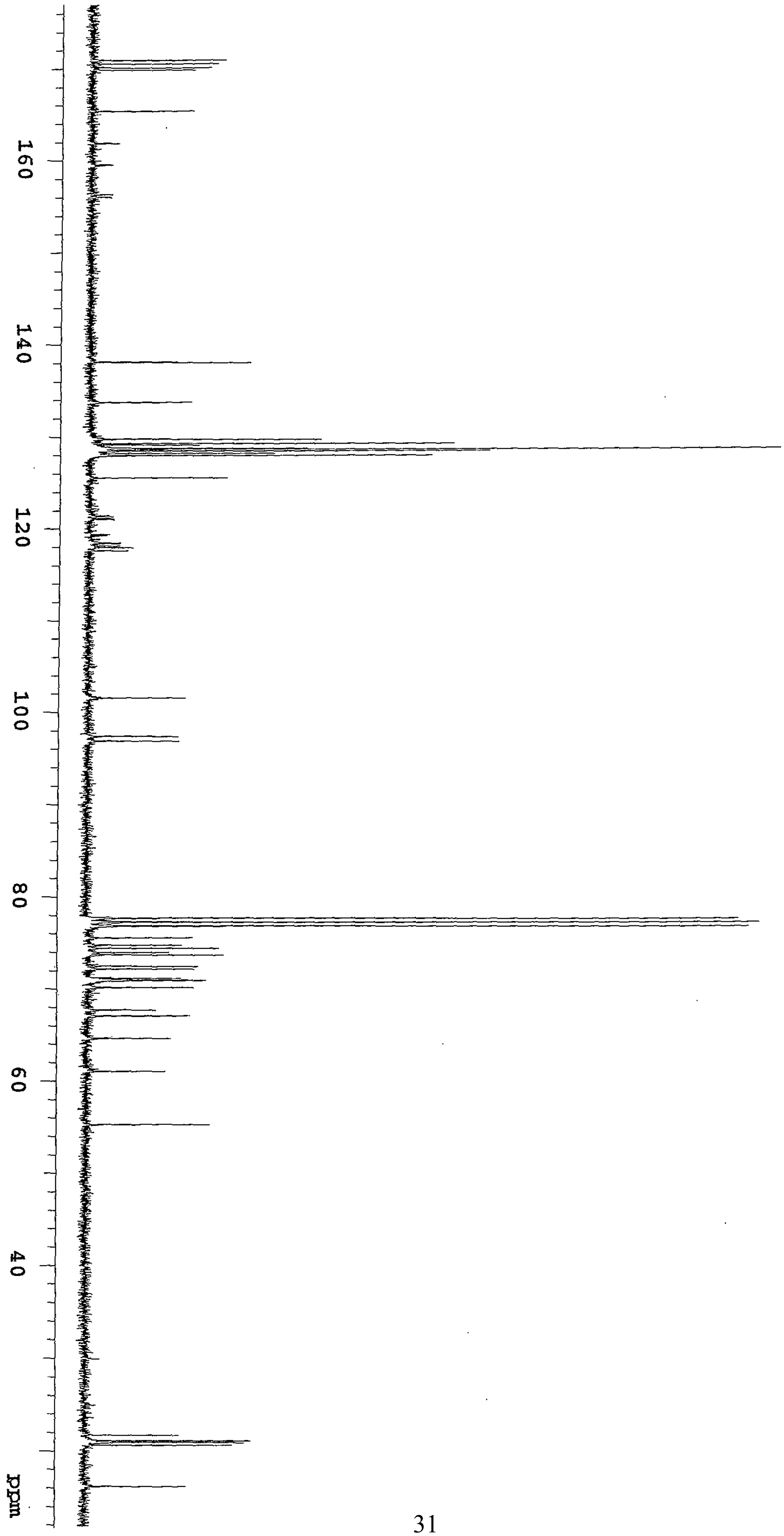
OAc
OBn
BzO
OMe

16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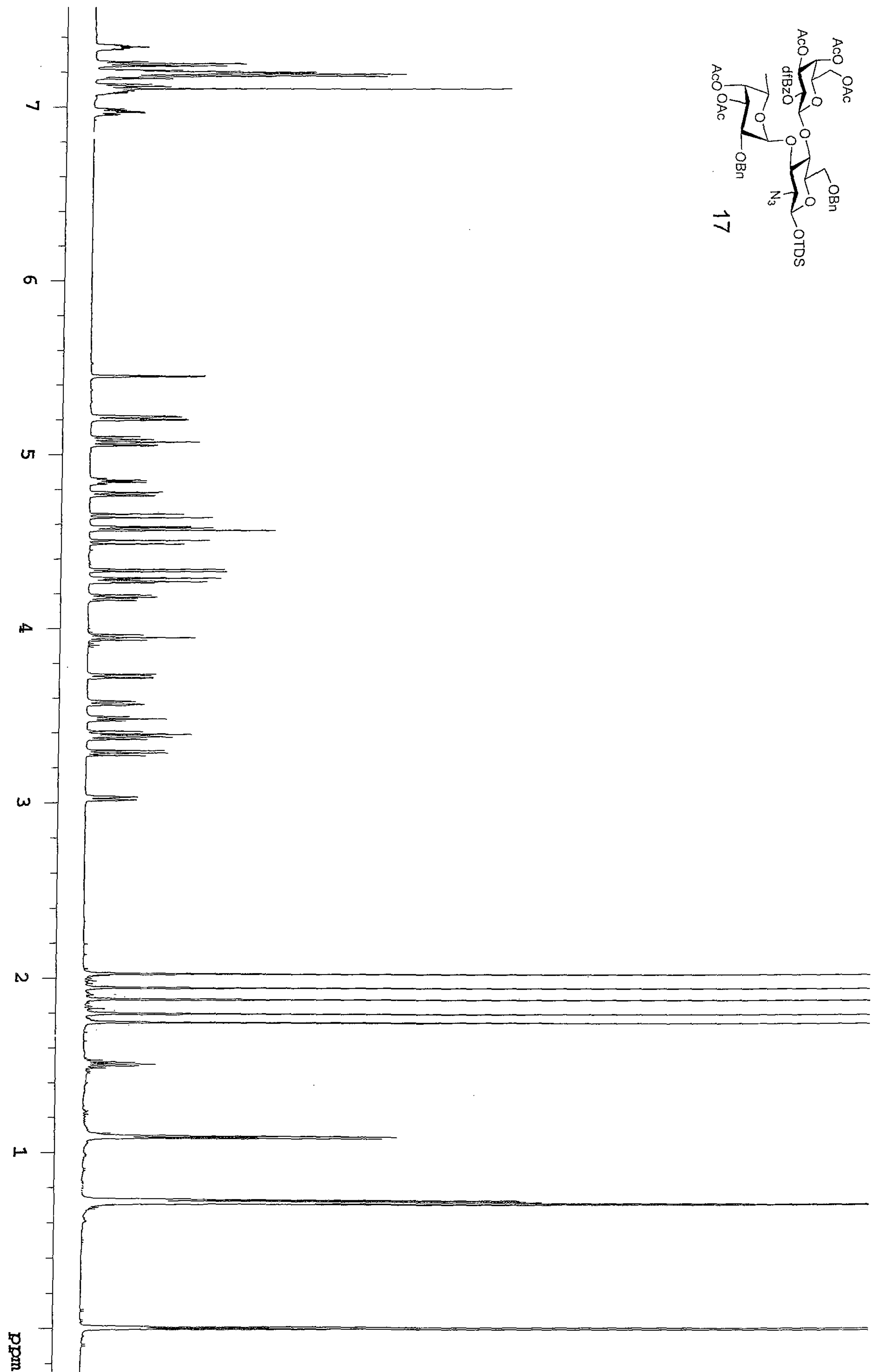

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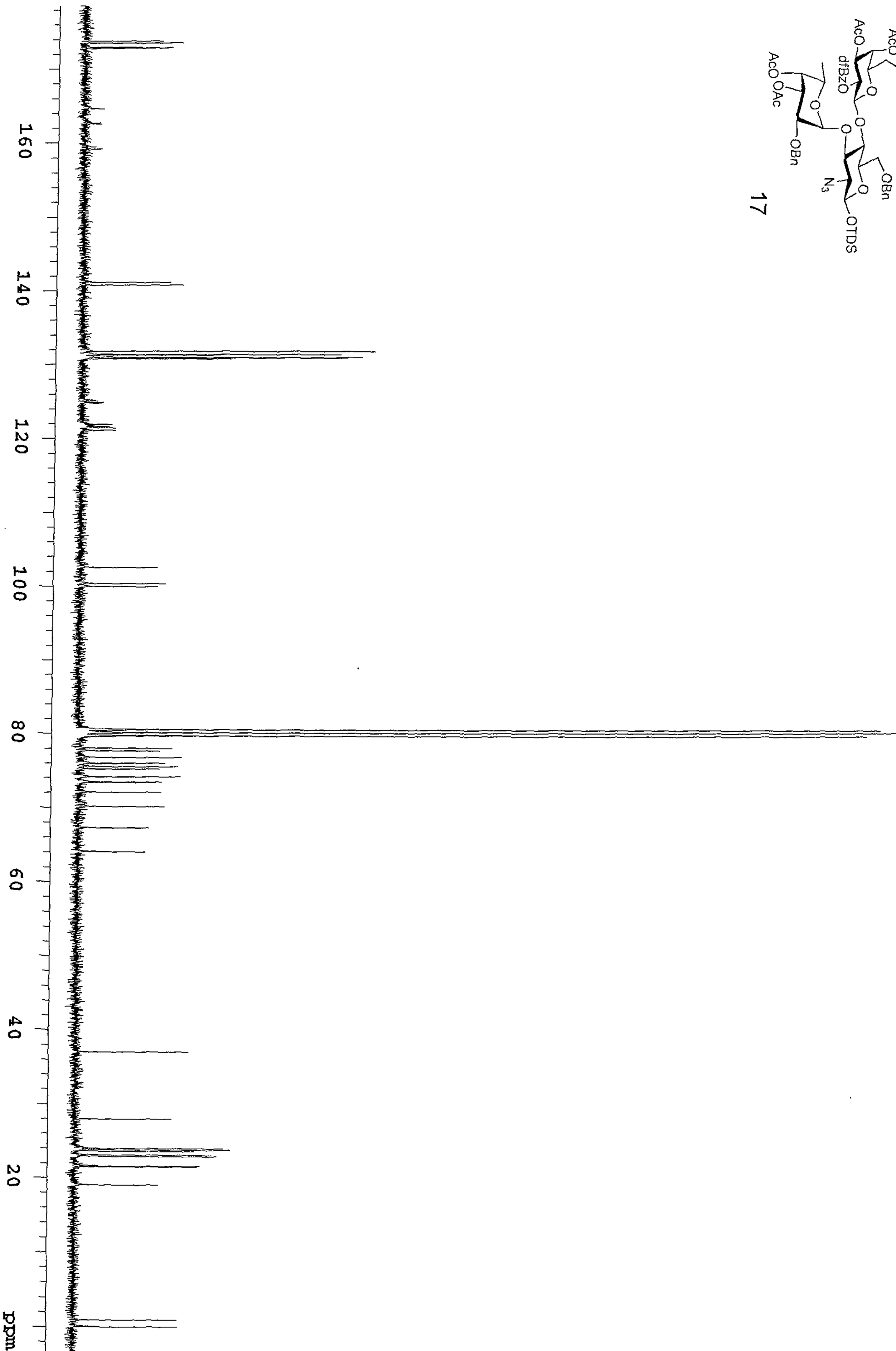
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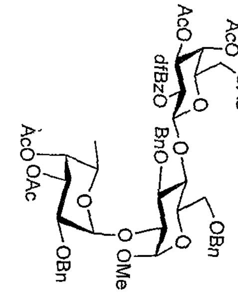

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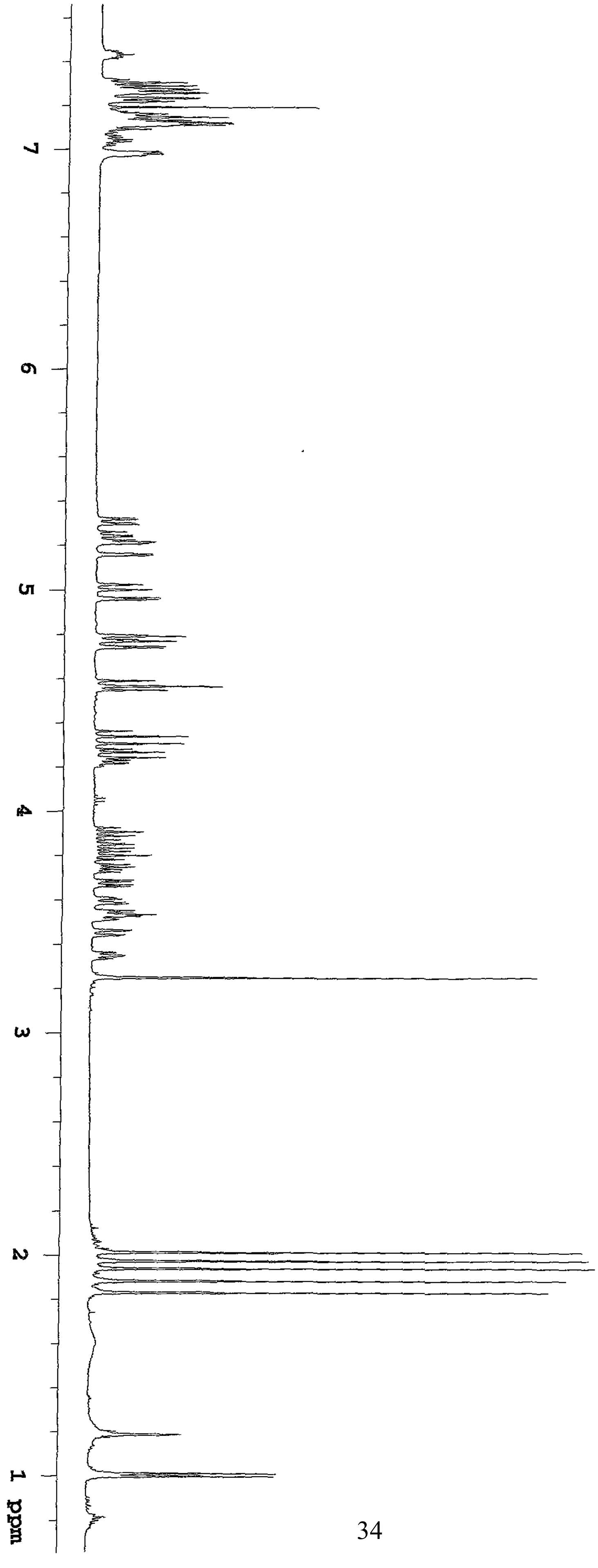

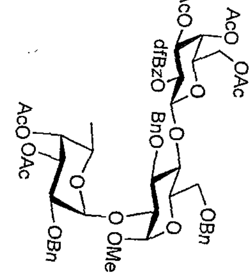
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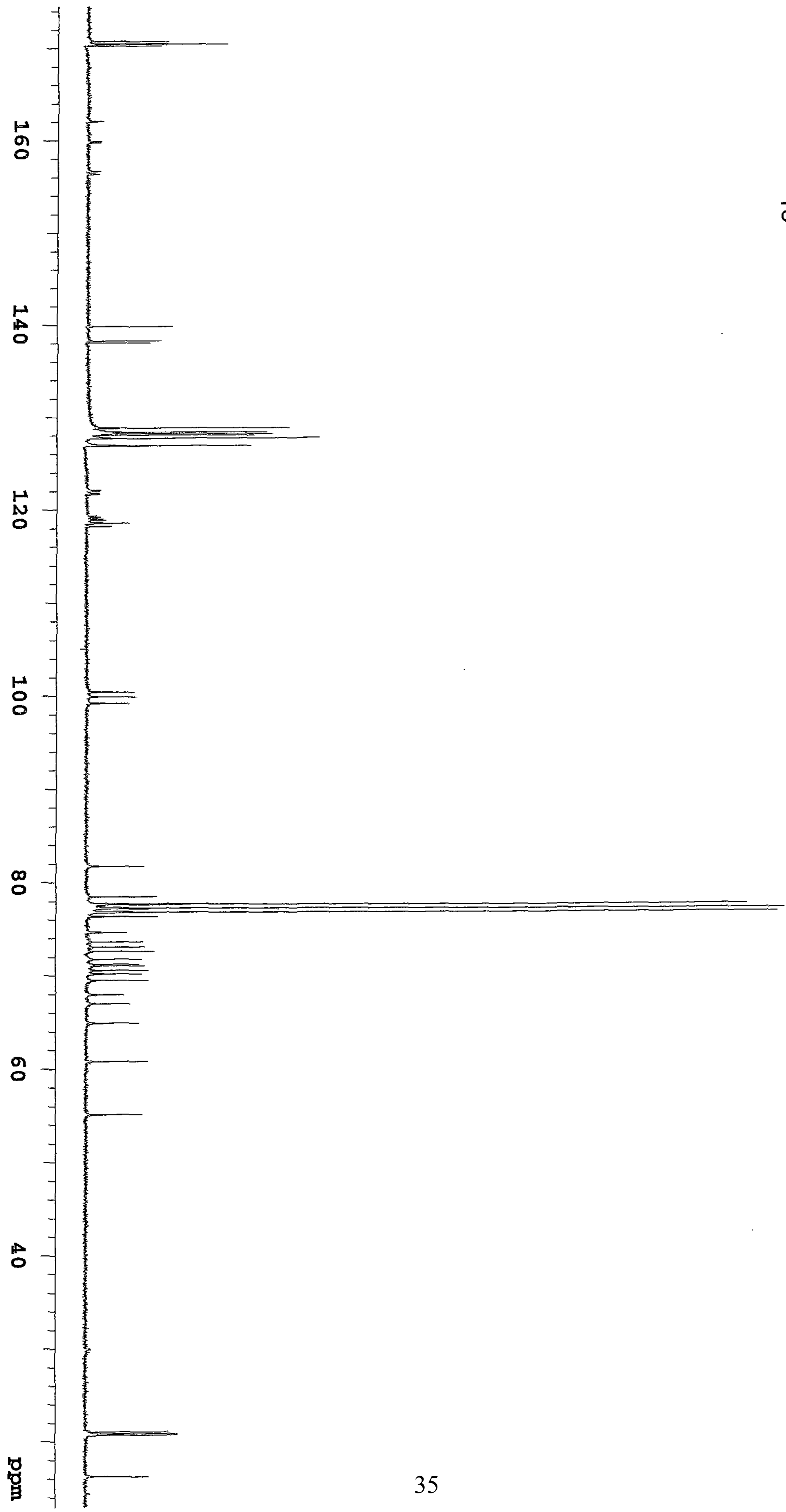
18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