Convergent synthesis and inclusion properties of novel C_n-symmetric triazole-linked cycloglucopyranosides

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Supporting Information

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General Experimental Section. All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. Anhydrous solvents were dried over standard drying agents[19] and freshly distilled prior to use. Reactions were monitored by TLC on silica gel 60 F_{254} with detection by charring with sulfuric acid. Flash column chromatography[20] was performed on silica gel 60 (40-63 μm). Optical rotations were measured at 20 ± 2 °C in the stated solvent; $[\alpha]_D$ values are given in $deg \cdot mL \cdot g^{-1} \cdot dm^{-1}$. ^1H NMR (300 and 400 MHz) and ^{13}C NMR spectra (75 MHz) were recorded from $CDCl_3$ solutions at room temperature unless otherwise specified. Peak assignments were aided by ^1H-^1H COSY and gradient-HMQC experiments. In the ^1H NMR spectra reported below, the *n* and *m* values quoted in geminal or vicinal proton-proton coupling constants $J_{n,m}$ refer to the number of the corresponding sugar protons. The closed vessel MW experiments were performed using a single-mode cavity Biotage Initiator microwave reactor; the temperature was measured externally on the outside vessel wall by an IR sensor; the reaction time was counted when the reaction mixture reached the preset temperature. For accurate mass measurements the compounds were analyzed in positive ion mode by electrospray hybrid quadrupole orthogonal acceleration time-of-flight mass spectrometer (Q-TOF) fitted with a Z-spray electrospray ion source. The capillary source voltage and the cone voltage were set at 3500 V and 35 V, respectively; the source temperature was kept at 80 °C; nitrogen was used as a drying gas at a flow rate of ca. 50 L/h. The time-of-flight analyzer was externally calibrated with NaI from *m/z* 300 to 2000 to yield an accuracy near to 5 ppm. When necessary an internal lock mass was used to further increase the mass accuracy. Accurate mass data were collected by directly infusing samples (10 pmol/μL in 1:1 CH_3CN-H_2O containing 10 mM ammonium formate) into the system at a flow rate of 5 μL/min. The monoisotopic masses were calculated according to the reported[21] atomic weights of the elements.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-8-*O*-(1-trimethylsilyloxy-vinyl)-D-*glycero*-D-*gulo*-oct-1-ynitol (2). To a stirred solution of known[22] **1** (4.77 g, 8.98 mmol) and $Bu_3SnC{\equiv}CSiMe_3$ (6.08 g, 17.96 mmol) in anhydrous CH_2Cl_2 (35 mL) was added dorpwise trimethylsilyl triflate (3.2 mL, 18.0 mmol). The solution was kept at r.t. for 2 h, then diluted with Et_3N (5 mL) and concentrated. The residue was eluted from a column of silica gel with 7:1 cyclohexane-AcOEt to give **2** (3.28 g, 57%), as a syrup; $[\alpha]_D$ = +43.7 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz): δ 7.41-7.25 (m, 15H, Ar), 4.99 and 4.84 (2 d, 2H, J =10.8 Hz, PhCH_2), 4.90 and 4.59 (2 d, 2H, J =10.7 Hz, PhCH_2), 4.78 (d, 1H, $J_{3,4}$= 5.8 Hz, H-3), 4.72 and 4.68 (2 d, 2H, J =11.5 Hz, PhCH_2), 4.37 (dd, 1H, $J_{7,8a}$= 2.3 Hz $J_{8a,8b}$ = 12.2 Hz, H-8a), 4.22 (dd, 1H, $J_{7,8b}$ = 5.0 Hz, H-8b), 4.04 (ddd, 1H, $J_{6,7}$ = 10.0 Hz, H-7), 3.96 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 9.0 Hz, H-5), 3.60 (dd, 1H, H-4), 3.42 (dd, 1H, H-6), 1.94 and 1.90 (2 d, 2H, *J* = 11.5 Hz, C=CH$_2$), 0.22 and 0.14 (2 s, 18H, 6 CH$_3$). ^{13}C NMR: δ 172.7 (C), 138.6 (C), 138.1 (C), 137.9 (C), 128.5 (CH), 128.40 (CH), 128.37 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.73 (CH), 127.67 (CH), 99.7 (C), 95.1 (C), 82.6 (CH), 79.1 (CH), 77.7 (CH), 75.5 (CH$_2$), 75.3 (CH$_2$), 72.4 (CH$_2$), 72.2 (CH), 66.7 (CH), 62.7 (CH$_2$), 26.9 (CH$_2$), -0.1 (CH$_3$), -1.3 (CH$_3$). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{37}H_{52}NO_6Si$ (M+NH$_4$)$^+$ 662.3333, found 662.3358.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*gulo*-oct-1-ynitol (3). To a solution of **2** (3.28 g, 5.08 mmol) in 5:1 CH$_3$OH-CH$_2$Cl$_2$ (250 mL) was added 1 M NaOH (4.3 mL). The solution was kept at r.t. for 1 h, then neutralized with AcOH and concentrated. A solution of the residue in AcOEt (200 mL) was washed with H$_2$O (2 x 50 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was eluted from a column of silica gel with 5:1 cyclohexane-AcOEt to give **3** (1.75 g, 75%) as a syrup; [α]$_D$ = +31.5 (*c* 0.9, CHCl$_3$). ^{1}H NMR (400 MHz): δ 7.40-7.25 (m, 15H, Ar), 5.01 and 4.86 (2 d, 2H, *J* =10.9 Hz, PhC*H$_2$*), 4.89 and 4.65 (2 d, 2H, *J* =11.0 Hz, PhC*H$_2$*), 4.76 and 4.71 (2 d, 2H, *J* =11.8 Hz, PhC*H$_2$*), 4.68 (dd, 1H, $J_{1,3}$ = 2.3 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 3.99 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 10.1 Hz, H-5), 3.90 (ddd, 1H, $J_{6,7}$ = 10.0 Hz, $J_{7,8a}$ = 2.5 Hz, $J_{7,8b}$ = 4.2 Hz, H-7), 3.82 (ddd, 1H, $J_{8a,8b}$ = 12.1 Hz, $J_{8a,OH}$ = 5.5 Hz, H-8a), 3.71 (ddd, 1H, $J_{8b,OH}$ = 7.5 Hz, H-8b), 3.60 (dd, 1H, H-4), 3.52 (dd, 1H, H-6), 2.62 (d, 1H, H-1), 1.67 (dd, 1H, OH). ^{13}C NMR: δ 138.6 (C), 138.0 (C), 137.7 (C), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 82.9 (CH), 78.8 (CH), 78.3 (C), 77.7 (CH), 75.7 (CH$_2$), 75.2 (CH$_2$), 74.2 (CH), 73.2 (CH$_2$), 66.5 (CH), 61.9 (CH$_2$). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{29}H_{30}NaO_5$ (M+Na)$^+$ 481.1991, found 481.1992.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-8-*O*-tosyl-D-*glycero*-D-*gulo*-oct-1-ynitol (4). A solution of **3** (739 mg, 1.61 mmol), *p*-toluensulfonyl chloride (470 mg, 2.42 mmol), and Et$_3$N (330 μL, 2.42 mmol) in anhydrous CH$_2$Cl$_2$ (3 mL) was kept at r.t. for 14 h, then diluted with CH$_2$Cl$_2$ (150 mL), washed with H$_2$O (2 x 100 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was eluted from a column of silica gel with toluene-Et$_2$O (from 120:1 to 60:1) to give **4** (630 mg, 64%) as a syrup; [α]$_D$ = +35.1 (*c* 1.1, CHCl$_3$). ^{1}H NMR (400 MHz): δ 7.78–7.76 (m, 2H, Ar), 7.38-7.26 (m, 15H, Ar), 7.19–7.16 (m, 2H, Ar), 5.00 and 4.82 (2 d, 2H, *J* =10.8 Hz, PhC*H$_2$*), 4.85 and 4.49 (2 d, 2H, *J* =10.6 Hz, PhC*H$_2$*), 4.73 and 4.67 (2 d, 2H, *J* =12.0 Hz, PhC*H$_2$*), 4.63 (dd, 1H, $J_{1,3}$ = 2.3 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 4.30 (dd, 1H, $J_{7,8a}$= 3.5 Hz $J_{8a,8b}$ = 10.7 Hz, H-8a), 4.18 (dd, 1H, $J_{7,8b}$ = 2.0 Hz, H-8b), 3.99 (ddd, 1H, $J_{6,7}$ = 10.0 Hz, H-7), 3.94 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 9.2 Hz, H-5), 3.56 (dd, 1H, H-4), 3.49 (dd, 1H, H-6), 2.58 (d, 1H, H-1), 2.41 (s, 3H, CH$_3$). ^{13}C NMR: δ 144.9 (C), 138.5 (C), 137.7 (C), 137.6 (C), 132.7 (C), 129.8 (CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 128.0

(CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 82.8 (CH), 78.5 (CH), 78.0 (C), 76.5 (CH), 75.7 (CH_2), 75.2 (CH_2), 73.2 (CH_2), 71.8 (CH), 68.4 (CH_2), 66.4 (CH), 21.6 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{36}H_{36}NaO_7S$ $(M+Na)^+$ 635.2079, found 635.2117.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(*t*-butyldimethylsilyl)-D-*glycero*-D-*gulo*-oct-1-ynitol (5). To a cooled (-30 °C), stirred solution of **3** (700 mg, 1.52 mmol) in anhydrous THF (11 mL) was added a 1 M solution of sodium bis(trimethylsilyl)amide in THF (3.1 mL, 3.10 mmol) and, after 10 min, a solution of *t*-butyldimethylsilyl chloride (460 mg, 3.06 mmol) in anhydrous THF (2 mL). The reaction mixture was allowed to reach -10 °C in 2 h, then was diluted with H_2O (1 mL) and concentrated. A solution of the residue in CH_2Cl_2 (150 mL) was washed with H_2O (100 mL) and concentrated. A solution of the residue in 1% HCl in methanol (4 mL) was kept at r. t. for 15 min, then neutralized with Et_3N, diluted with CH_2Cl_2 (120 mL), washed with H_2O (100 mL), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 4:1 to 2:1) to give **5** (556 mg, 64%) as a syrup; $[\alpha]_D = +92.5$ (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz): δ 7.40-7.25 (m, 15H, Ar), 4.96 and 4.66 (2 d, 2H, J =11.2 Hz, PhCH_2), 4.90 and 4.81 (2 d, 2H, J =11.2 Hz, PhCH_2), 4.78 (dd, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 4.70 (s, 2H, PhCH_2), 3.97 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.0 Hz, H-5), 3.89 (ddd, 1H, $J_{6,7}$ = 9.8 Hz, $J_{7,8a}$ = 2.6 Hz, $J_{7,8b}$ = 4.2 Hz, H-7), 3.82 (ddd, 1H, $J_{8a,8b}$ = 12.0 Hz, $J_{8a,OH}$ = 5.5 Hz, H-8a), 3.70 (ddd, 1H, $J_{8b,OH}$ = 7.5 Hz, H-8b), 3.59 (dd, 1H, H-4), 3.49 (dd, 1H, H-6), 1.67 (dd, 1H, OH), 0.98 (s, 9H, 3 CH_3), 0.19 (s, 6H, 2 CH_3). ^{13}C NMR: δ 138.6 (C), 138.2 (C), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 100.4 (C), 93.4 (C), 82.7 (CH), 79.4 (CH), 77.0 (CH), 75.6 (CH_2), 75.0 (CH_2), 74.2 (CH), 72.5 (CH_2), 66.9 (CH), 62.1 (CH_2), 26.1 (CH_3), -4.7 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{35}H_{44}NaO_5Si$ $(M+Na)^+$ 595.2856, found 595.2881.

3,7-Anhydro-8-azido-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-1-*C*-(*t*-butyldimethylsilyl)-D-*glycero*-D-*gulo*-oct-1-ynitol (6). A solution of **5** (1.01 g, 1.80 mmol), *p*-toluensulfonyl chloride (684 mg, 3.60 mmol), and Et_3N (0.50 mL, 3.60 mmol) in anhydrous CH_2Cl_2 (5.5 mL) was kept at r.t. for 14 h, then diluted with CH_2Cl_2 (150 mL), washed with H_2O (100 mL), dried (Na_2SO_4) and concentrated to give crude 3,7-anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(*t*-butyldimethylsilyl)-8-*O*-tosyl-D-*glycero*-D-*gulo*-oct-1-ynitol. A mixture of this product, NaN_3 (570 mg, 9.00 mmol), and anhydrous DMF (7 mL) was stirred at 55 °C for 16 h, then cooled to r. t., diluted with Et_2O (200 mL), washed with H_2O (100 mL), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 10:1 cyclohexane-AcOEt to give **6** (770 mg, 84%) as a syrup; $[\alpha]_D = +100.2$ (*c* 1.1, $CHCl_3$). ^1H NMR (400 MHz): δ 7.40-7.26 (m, 15H, Ar), 4.96 and 4.78 (2 d, 2H, J =10.8 Hz, Ph*CH$_2$*), 4.91 and 4.59 (2 d, 2H, *J* =11.0 Hz, Ph*CH$_2$*), 4.82 (d, 1H, $J_{3,4}$ = 5.9 Hz, H-3), 4.69 (s, 2H, Ph*CH$_2$*), 4.00 (ddd, 1H, $J_{6,7}$ = 10.0 Hz, $J_{7,8a}$ = 2.5 Hz, $J_{7,8b}$ = 4.7 Hz, H-7), 3.94 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 9.0 Hz, H-5), 3.62 (dd, 1H, H-4), 3.54 (dd, 1H, $J_{8a,8b}$ = 13.3 Hz, H-8a), 3.44 (dd, 1H, H-6), 3.35 (dd, 1H, H-8b), 0.99 (s, 9H, 3 CH_3), 0.18 (s, 6H, 2 CH_3). ^{13}C NMR: δ 138.5 (C), 138.1 (C), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 100.2 (C), 93.7 (C), 82.6 (CH), 79.3 (CH), 77.8 (CH), 75.6 (CH_2), 75.1 (CH_2), 73.1 (CH), 72.5 (CH_2), 66.9 (CH), 51.3 (CH_2), 26.1 (CH_3), -4.7 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{35}H_{43}N_3NaO_4Si$ $(M+Na)^+$ 620.2921, found 620.2890.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-1-*C*-(*t*-butyldimethylsilyl)-8-[4-(2',3',4'-tri-*O*-benzyl-6'-*O*-tosyl-α-D-glucopyranosyl)-1*H*-1,2,3-triazol-1-yl]-D-*glycero*-D-*gulo*-oct-1-ynitol (7). A mixture of alkyne **4** (471 mg, 0.77 mmol), azide **6** (458 mg, 0.77 mmol), *N,N*-diisopropylethylamine (260 µL, 1.50 mmol), CuI (30 mg, 0.15 mmol), and anhydrous DMF (3 mL) in a vial sealed with a Teflon septum and aluminum crimp was subjected to microwave irradiation for 15 min at 80 °C, then cooled to room temperature, diluted with CH_2Cl_2 (150 mL), washed with an aqueous solution of EDTA disodium salt (0.01 M, 2 x 30 mL), dried (Na_2SO_4), and concentrated to give crude **7**. ^{1}H NMR (300 MHz) selected data: δ 7.66 (s, 1H, H-5 Tr), 5.14 (d, 1H, $J_{1',2'}$ = 6.0 Hz, H-1'), 2.40 (s, 3H, CH_3).

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-1-*C*-(*t*-butyldimethylsilyl)-8-[4-(6'-azido-2',3',4'-tri-*O*-benzyl-6'-deoxy-α-D-glucopyranosyl)-1*H*-1,2,3-triazol-1-yl]-D-*glycero*-D-*gulo*-oct-1-ynitol (8). A mixture of crude **7**, NaN_3 (250 mg, 3.85 mmol), and DMF (15 mL) was stirred at 80 °C for 14 h, then cooled to r. t., diluted with Et_2O (150 mL), washed with H_2O (2 x 50 mL), dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with 3:1 cyclohexane-AcOEt to give **8** (458 mg, 55% from **4**) as a foam; $[\alpha]_D$ = +78.5 (*c* 0.9, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.68 (s, 1H, H-5 Tr), 7.42-7.20 (m, 30H, Ar), 5.24 (d, 1H, $J_{1',2'}$ = 6.0 Hz, H-1'), 4.96 and 4.79 (2 d, 2H, *J* =10.8 Hz, Ph*CH$_2$*), 4.94 and 4.81 (2 d, 2H, *J* =11.0 Hz, Ph*CH$_2$*), 4.94 and 4.78 (2 d, 2H, *J* =10.8 Hz, Ph*CH$_2$*), 4.90 and 4.62 (2 d, 2H, *J* =11.3 Hz, Ph*CH$_2$*), 4.68 (d, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 4.67 and 4.59 (2 d, 2H, *J* =11.5 Hz, Ph*CH$_2$*), 4.58 (s, 2H, Ph*CH$_2$*), 4.57 (d, 2H, $J_{7,8}$ = 4.1 Hz, 2 H-8), 4.26 (dd, 1H, $J_{2',3'}$ = 9.0 Hz, $J_{3',4'}$ = 8.5 Hz, H-3'), 4.16 (dt, 1H, $J_{6,7}$ = 10.0 Hz, H-7), 3.98 (dd, 1H, H-2'), 3.96 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 9.0 Hz, H-5), 3.83 (ddd, 1H, $J_{4',5'}$ = 9.7 Hz, $J_{5',6'a}$ = 2.5 Hz, $J_{5',6'b}$ = 4.5 Hz, H-5'), 3.62 (dd, 1H, H-4'), 3.51 (dd, 1H, $J_{6'a,6'b}$ = 13.3 Hz, H-6'a), 3.42 (dd, 1H, H-4), 3.34 (dd, 1H, H-6'b), 3.14 (dd, 1H, H-6), 0.95 (s, 9H, 3 CH_3), 0.12 (s, 6H, 2 CH_3). ^{13}C NMR: δ 143.3 (C-4 Tr), 138.6 (C), 138.3 (C), 138.2 (C), 138.1 (C), 137.9 (C), 128.5

(CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 125.9 (C-5 Tr), 99.8 (C), 94.2 (C), 82.7 (CH), 82.2 (CH), 79.8 (CH), 79.2 (CH), 78.4 (CH), 77.3 (CH), 75.7 (CH_2), 75.2 (CH_2), 75.0 (CH_2), 74.8 (CH_2), 73.1 (CH_2), 72.6 (CH_2), 72.4 (CH), 72.3 (CH), 69.0 (CH), 66.9 (CH), 51.3 (CH_2), 50.4 (CH_2), 26.0 (CH_3), -4.8 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{64}H_{72}N_6NaO_8Si$ $(M+Na)^+$ 1103.5079, found 1103.5045.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-8-[4-(6'-azido-2',3',4'-tri-*O*-benzyl-6'-deoxy-α-D-glucopyranosyl)-1*H*-1,2,3-triazol-1-yl]-D-*glycero*-D-*gulo*-oct-1-ynitol (9). A solution of **7** (120 mg, 0.10 mmol) and tetrabutylammonium fluoride trihydrate (63 mg, 0.20 mmol) in THF (2 mL) was kept at r. t. for 16 h, then diluted with CH_2Cl_2 (100 mL), washed with H_2O (20 mL), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 3:1 cyclohexane-AcOEt to give **9** (87 mg, 90%) as a syrup; $[\alpha]_D = +67.3$ (*c* 0.5, $CHCl_3$). ^1H NMR (400 MHz): δ 7.67 (s, 1H, H-5 Tr), 7.40-7.20 (m, 30H, Ar), 5.25 (d, 1H, $J_{1',2'} = 6.0$ Hz, H-1'), 4.99 and 4.82 (2 d, 2H, $J = 10.8$ Hz, $PhCH_2$), 4.95 and 4.79 (2 d, 2H, $J = 11.0$ Hz, $PhCH_2$), 4.94 and 4.79 (2 d, 2H, $J = 10.7$ Hz, $PhCH_2$), 4.89 and 4.59 (2 d, 2H, $J = 11.2$ Hz, $PhCH_2$), 4.66 and 4.60 (2 d, 2H, $J = 11.8$ Hz, $PhCH_2$), 4.64 and 4.59 (2 d, 2H, $J = 12.0$ Hz, $PhCH_2$), 4.60 (dd, 1H, $J_{1,3} = 2.3$ Hz $J_{3,4} = 5.8$ Hz, H-3), 4.58 (dd, 1H, $J_{7,8a} = 2.8$ Hz, $J_{8a,8b} = 14.3$ Hz, H-8a), 4.51 (dd, 1H, $J_{7,8b} = 6.0$ Hz, H-8b), 4.20 (dd, 1H, $J_{2',3'} = 9.2$ Hz, $J_{3',4'} = 8.6$ Hz, H-3'), 4.17 (ddd, 1H, $J_{6,7} = 10.0$ Hz, H-7), 3.97 (dd, 1H, H-2'), 3.97 (dd, 1H, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 9.0$ Hz, H-5), 3.76 (ddd, 1H, $J_{4',5'} = 9.7$ Hz, $J_{5',6'a} = 2.5$ Hz, $J_{5',6'b} = 4.5$ Hz, H-5'), 3.60 (dd, 1H, H-4'), 3.49 (dd, 1H, $J_{6'a,6'b} = 13.3$ Hz, H-6'a), 3.46 (dd, 1H, H-4), 3.33 (dd, 1H, H-6'b), 3.19 (dd, 1H, H-6), 2.49 (d, 1H, H-1). ^{13}C NMR: δ 143.3 (C-4 Tr), 138.5 (C), 138.3 (C), 138.0 (C), 137.8 (C), 137.5 (C), 128.6 (CH), 128.52 (CH), 128.48 (CH), 128.4 (CH), 128.3 (CH), 128.09 (CH), 128.05 (CH), 128.0 (CH), 127.9 (CH), 127.6 (CH), 125.4 (C-5 Tr), 82.8 (CH), 82.1 (CH), 79.7 (CH), 78.7 (CH), 78.4 (CH), 78.3 (C), 77.6 (CH), 75.8 (CH_2), 75.2 (CH_2), 74.9 (CH_2), 73.1 (CH_2), 72.3 (CH), 69.1 (CH), 66.5 (CH), 51.3 (CH_2), 50.4 (CH_2). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{58}H_{58}N_6NaO_8$ $(M+Na)^+$ 989.4214, found 989.4214.

Benzylated Cyclic Diglucoside (10). A mixture of **9** (48 mg, 0.05 mmol), *N,N*-diisopropylethylamine (45 μL, 0.25 mmol), CuI (9.5 mg, 0.05 mmol), and anhydrous toluene (8 mL) was stirred in the dark at r. t. for 24 h, then cooled to room temperature, diluted with CH_2Cl_2 (50 mL), washed with an aqueous solution of EDTA disodium salt (0.01 M, 3 x 10 mL), dried (Na_2SO_4), and concentrated. The residue was triturated with boiling cyclohexane to give **10** (39 mg, 82%) as a white solid; $[\alpha]_D = +47.4$ (*c* 0.6, $CHCl_3$). ^1H NMR (400 MHz): δ 7.40–7.15 (m, 32H, Ar, 2 H-5 Tr), 5.04 (d, 2H, $J_{1,2} = 6.4$ Hz, 2 H-1), 4.94 and 4.76 (2 d, 4H, $J = 11.3$ Hz, 2 $PhCH_2$), 4.80

and 4.56 (2 d, 4H, J =11.7 Hz, 2 PhCH_2), 4.68 (dd, 2H, $J_{5,6a}$= 1.4 Hz $J_{6a,6b}$ = 13.8 Hz, 2 H-6a), 4.62 and 4.50 (2 d, 4H, J =12.2 Hz, 2 PhCH_2), 4.45 (dd, 2H, $J_{2,3}$ = 7.2 Hz, $J_{3,4}$ = 6.1 Hz, 2 H-3), 3.98 (dd, 2H, 2 H-2), 3.92 (dd, 2H, $J_{5,6b}$ = 10.3 Hz, 2 H-6b), 3.42 (dd, 2H, $J_{4,5}$ = 10.0 Hz, 2 H-4), 3.24 (ddd, 2H, 2 H-5). ^{13}C NMR: δ 144.4 (C-4 Tr), 138.3 (C), 137.8 (C), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 124.7 (C-5 Tr), 81.1 (CH), 78.7 (CH), 77.9 (CH), 74.7 (CH_2), 73.5 (CH_2), 73.4 (CH_2), 72.7 (CH), 69.7 (CH), 51.2 (CH_2). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{58}H_{58}N_6NaO_8$ $(M+Na)^+$ 989.4214, found 989.4213.

Cyclic Diglucoside (11). To a solution of **10** (39 mg, 0.04 mmol) and ammonium formate (121 mg, 1.92 mmol) in CH_3OH (4 mL), THF (2 mL) and H_2O (1 mL) was added 10% palladium on carbon (255 mg, 0.24 mmol). The mixture was stirred in a closed vial at 50 °C for 16 h, then cooled to r. t., filtered through a pad of Celite, and concentrated. The residue was eluted from a column of Sephadex LH20 (1 x 60 cm) with 1:1 H_2O-CH_3OH to give **11** (13 mg, 76%) as a syrup; $[\alpha]_D$ = +86.4 (*c* 0.3, H_2O). ^{1}H NMR (D_2O, 300 MHz): δ 7.98 (s, 2H, 2 H-5 Tr), 5.32 (d, 2H, $J_{1,2}$ = 6.6 Hz, 2 H-1), 4.81 (dd, 2H, $J_{5,6a}$= 0.8 Hz, $J_{6a,6b}$ = 14.5 Hz, 2 H-6a), 4.18 (dd, 2H, $J_{5,6b}$ = 9.4 Hz, 2 H-6b), 4.08 (dd, 2H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 8.5 Hz, 2 H-3), 4.01 (dd, 2H, 2 H-2), 3.40 (dd, 2H, $J_{4,5}$ = 9.8 Hz, 2 H-4), 2.44 (ddd, 2H, 2 H-5). ^{13}C NMR (D_2O): δ 144.1 (C-4 Tr), 128.2 (C-5 Tr), 75.6 (CH), 74.8 (CH), 70.9 (CH), 70.8 (CH), 70.3 (CH), 51.0 (CH_2). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{16}H_{23}N_6O_8$ $(M+H)^+$ 427.1577, found 427.1575.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-8-[4-(2',3',4'-tri-*O*-benzyl-6'-*O*-tosyl-α-D-glucopyranosyl)-1*H*-1,2,3-triazol-1-yl]-D-*glycero*-D-*gulo*-oct-1-ynitol (12). A solution of **7** (400 mg, 0.33 mmol) and tetrabutylammonium fluoride trihydrate (208 mg, 0.66 mmol) in THF (5 mL) was kept at r. t. for 16 h, then diluted with CH_2Cl_2 (200 mL), washed with H_2O (50 mL), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 4:1 cyclohexane-AcOEt to give **12** (280 mg, 74%) as a syrup; $[\alpha]_D$ = +39.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.79–7.76 (m, 2H, Ar), 7.65 (s, 1H, H-5 Tr), 7.40-7.25 (m, 30H, Ar), 7.22–7.18 (m, 2H, Ar), 5.16 (d, 1H, $J_{1',2'}$ = 6.0 Hz, H-1'), 5.01 and 4.84 (2 d, 2H, J =11.0 Hz, PhCH_2), 4.95 and 4.79 (2 d, 2H, J =10.8 Hz, PhCH_2), 4.95 and 4.79 (2 d, 2H, J =11.0 Hz, PhCH_2), 4.85 and 4.55 (2 d, 2H, J =10.7 Hz, PhCH_2), 4.65 and 4.57 (2 d, 2H, J =11.5 Hz, PhCH_2), 4.65 and 4.61 (2 d, 2H, J =11.0 Hz, PhCH_2), 4.63 (dd, 1H, $J_{1,3}$ = 2.3 Hz, $J_{3,4}$ = 5.8 Hz, H-3), 4.58 (dd, 1H, $J_{7,8a}$= 2.8 Hz $J_{8a,8b}$ = 14.5 Hz, H-8a), 4.50 (dd, 1H, $J_{7,8b}$ = 6.1 Hz, H-8b), 4.29 (dd, 1H, $J_{5',6'a}$ = 3.5 Hz, $J_{6'a,6'b}$ = 10.5 Hz, H-6'a), 4.18 (dd, 1H, $J_{2',3'}$ = 9.2 Hz, $J_{3',4'}$ = 8.5 Hz, H-3'), 4.18 (ddd, 1H, $J_{6,7}$ = 9.8 Hz, H-7), 4.14 (dd, 1H, $J_{5',6'b}$ = 2.0 Hz, H-6'b), 3.99 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 8.7 Hz, H-5), 3.92 (dd,1H, H-2'), 3.80 (ddd, 1H, $J_{4',5'}$ = 10.0 Hz, H-5’), 3.65 (dd, 1H, H-4’), 3.48 (dd, 1H, H-4), 3.22 (dd, 1H, H-6), 2.51 (d, 1H, H-1), 2.40 (s, 3H, CH_3). ^{13}C NMR: δ 144.7 (C), 143.1 (C-4 Tr), 138.5 (C), 138.2 (C), 137.9 (C), 137.7 (C), 137.5 (C), 132.7 (C), 129.7 (CH), 128.5 (CH), 128.42 (CH), 128.36 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 125.4 (C-5 Tr), 82.8 (CH), 81.9 (CH), 79.3 (CH), 78.7 (CH), 78.3 (CH), 77.6 (CH), 75.7 (CH_2), 75.2 (CH_2), 74.7 (CH_2), 73.1 (CH_2), 72.3 (CH), 71.1 (CH), 69.0 (CH), 68.7 (CH_2), 66.4 (CH), 50.4 (CH_2), 21.6 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{65}H_{65}N_3NaO_{11}S$ $(M+Na)^+$ 1118.4238, found 1118.4230.

Tosylated Tetraglucoside (13). The coupling of alkyne **12** (289 mg, 0.26 mmol) with azide **8** (285 mg, 0.26 mmol) was performed as described for the synthesis of **7** to give, after column chromatography on silica gel (3:1 cyclohexane-AcOEt), **13** (453 mg, 79%) as a foam; $[\alpha]_D$ = +64.5 (*c* 0.6, $CHCl_3$). ^{1}H NMR (400 MHz) selected data: δ 7.83, 7.76, and 7.65 (3 s, 3H, 3 H-5 Tr), 7.76-7.73 (m, 2H, Ar), 5.20, 5.18, and 5.09 (3 d, 3H, J = 6.3 Hz, H-1’, H-1’’, H-1’’’), 4.62 (d, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 3.94 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 8.6 Hz, H-5), 3.87, 3.73, and 3.72 (3 dd, 3H, J = 6.3, 9.5 Hz, H-2’, H-2’’, H-2’’’), 3.40 (dd, 1H, H-4), 2.38 (s, 3H, CH_3). ^{13}C NMR selected data: δ 144.7 (C), 143.1 (C-4 Tr), 142.6 (C-4 Tr), 142.5 (C-4 Tr), 126.3 (C-5 Tr), 126.1 (C-5 Tr), 125.9 (C-5 Tr), 99.8 (C), 94.2 (C), 50.4 (CH_2), 50.3 (CH_2), 26.0 (CH_3), -4.7 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $(C_{129}H_{139}N_9O_{19}SSi)/2$ $(M+2H)^{2+}$ 1088.9839, found 1088.9791.

Azidated Tetraglucoside (14). The tosylated tetraglucoside **13** (218 mg, 0.10 mmol) was azidated as described for the synthesis of **8** to give, after column chromatography on silica gel (3:1 cyclohexane-AcOEt), **14** (143 mg, 70%) as a syrup; $[\alpha]_D$ = +36.5 (*c* 0.6, $CHCl_3$). ^{1}H NMR (400 MHz) selected data: δ 7.83, 7.81, and 7.65 (3 s, 3H, 3 H-5 Tr), 7.40-7.10 (m, 60H, Ar), 5.21 and 5.19 (2 d, 3H, J = 6.3 Hz, H-1’, H-1’’, H-1’’’), 4.62 (d, 1H, $J_{3,4}$ = 6.0 Hz, H-3), 4.33 (dd, 1H, $J_{2''',3'''}$ = $J_{3''',4'''}$ = 8.7 Hz, H-3’’’), 3.86 (ddd, 1H, $J_{4''',5'''}$ = 9.6 Hz, $J_{5''',6'''a}$ = 2.4 Hz, $J_{5''',6'''b}$ = 4.5 Hz, H-5’’’), 3.60 (dd, 1H, H-4’’’), 3.47 (dd, 1H, $J_{6'''a,6'''b}$ = 13.2 Hz, H-6’’’a), 3.40 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.33 (dd, 1H, H-6’’’b), 0.92 (s, 9H, 3 CH_3), 0.09 (s, 6H, 2 CH_3). ^{13}C NMR selected data: δ 143.3 (C-4 Tr), 142.6 (C-4 Tr), 142.5 (C-4 Tr), 126.3 (C-5 Tr), 126.1 (C-5 Tr), 125.9 (C-5 Tr), 99.8 (C), 94.2 (C), 51.4 (CH_2), 50.3 (CH_2), 26.0 (CH_3), -4.8 (CH_3). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{122}H_{130}N_{12}NaO_{16}Si$ $(M+Na)^+$ 2069.9395, found 2069.9248.

Azidated Tetraglucoside Alkyne (15). The azidated tetraglucoside **14** (184 mg, 0.09 mmol) was desilylated as described for the synthesis of **12** to give, after column chromatography on silica gel (1.5:1 cyclohexane-AcOEt), **15** (130 mg, 75%) as a foam; $[\alpha]_D$ = +63.7 (*c* 0.6, $CHCl_3$). ^{1}H NMR

(400 MHz) selected data: δ 7.84, 7.82, and 7.64 (3 s, 3H, 3 H-5 Tr), 7.40-7.11 (m, 60H, Ar), 5.22, 5.21, and 5.20 (2 d, 3H, J = 6.3 Hz, H-1’, H-1’’, H-1’’’), 3.86 (ddd, 1H, $J_{4''',5'''}$ = 9.7 Hz, $J_{5''',6'''a}$ = 2.5 Hz, $J_{5''',6'''b}$ = 4.5 Hz, H-5’’’), 3.60 (dd, 1H, $J_{3''',4'''}$ = 8.7 Hz, H-4’’’), 3.47 (dd, 1H, $J_{6'''a,6'''b}$ = 13.4 Hz, H-6’’a), 3.46 (dd, 1H, $J_{3,4}$ = 6.0 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.33 (dd, 1H, H-6’’b), 2.42 (d, 1H, $J_{1,3}$ = 2.3 Hz, H-1). ^{13}C NMR selected data: δ 143.3 (C-4 Tr), 142.66 (C-4 Tr), 142.60 (C-4 Tr), 126.3 (C-5 Tr), 126.0 (C-5 Tr), 125.2 (C-5 Tr), 51.4 (CH_2), 50.5 (CH_2), 50.3 (CH_2). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{116}H_{116}N_{12}NaO_{16}$ $(M+Na)^+$ 1955.8530, found 1955.8368.

Cyclic Tetraglucoside (16). The tetraglucoside **15** (135 mg, 0.07 mmol) was submitted to the cycloaddition as described for the synthesis of **10** to give the corresponding benzylated cyclotetramer as a yellow syrup (140 mg). ^{1}H NMR (300 MHz) selected data: δ 7.55 (s, 4H, 4 H-5 Tr), 5.16 (d, 4H, $J_{1,2}$ = 6.0 Hz, 4 H-1), 4.93 and 4.69 (2 d, 8H, J =11.3 Hz, 4 PhCH_2), 4.90 and 4.76 (2 d, 8H, J =10.8 Hz, 4 PhCH_2), 4.60 (s, 8H, 4 PhCH_2), 4.60 (dd, 4H, $J_{5,6a}$= 2.2 Hz $J_{6a,6b}$ = 14.2 Hz, 4 H-6a), 4.32 (dd, 4H, $J_{5,6b}$ = 7.3 Hz, 4 H-6b), 4.18 (dd, 4H, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 8.1 Hz, 4 H-3), 4.02 (ddd, 4H, $J_{4,5}$ = 9.5 Hz, 4 H-5), 3.90 (dd, 4H, 4 H-2), 3.36 (dd, 4H, 4 H-4). To a solution of the crude product and ammonium formate (424 mg, 6.72 mmol) in CH_3OH (12 mL), THF (6 mL) and H_2O (3 mL) was added 10% palladium on carbon (90 mg, 0.84 mmol). The mixture was stirred in a closed vial at 50 °C for 16 h, then cooled to r. t., filtered through a pad of Celite, and concentrated. The residue was eluted from a column of Sephadex LH20 (1 x 60 cm) with 1:1 H_2O-CH_3OH to give **16** (45 mg, 74%) as a syrup; $[\alpha]_D$ = +9.1 (*c* 0.5, DMF). ^{1}H NMR (D_2O, 400 MHz): δ 7.68 (s, 4H, 4 H-5 Tr), 5.04 (d, 4H, $J_{1,2}$ = 6.1 Hz, 4 H-1), 4.62 (dd, 4H, $J_{5,6a}$= 2.0 Hz, $J_{6a,6b}$ = 14.6 Hz, 4 H-6a), 4.33 (dd, 4H, $J_{5,6b}$ = 10.0 Hz, 4 H-6b), 3.88 (dd, 4H, $J_{2,3}$ = 9.5 Hz, 4 H-2), 3.82 (dd, 4H, $J_{3,4}$ = 8.8 Hz, 4 H-3), 3.56 (ddd, 4H, $J_{4,5}$ = 9.7 Hz, 4 H-5), 3.32 (dd, 4H, 4 H-4). ^{13}C NMR (D_2O): δ 142.0 (C-4 Tr), 126.1 (C-5 Tr), 73.7 (CH), 72.7 (CH), 71.8 (CH), 70.5 (CH), 70.2 (CH), 51.3 (CH_2). HRMS (ESI/Q-TOF) *m/z* calcd for $C_{32}H_{44}N_{12}NaO_{16}$ $(M+Na)^+$ 875.2896, found 875.2853.

Tosylated Hexaglucoside (17). The coupling of alkyne **12** (120 mg, 0.11 mmol) with azide **14** (224 mg, 0.11 mmol) was performed as described for the synthesis of **7** to give, after column chromatography on silica gel (3:1 cyclohexane-AcOEt), **17** (240 mg, 70%) as a syrup; $[\alpha]_D$ = +54.3 (*c* 0.7, $CHCl_3$). ^{1}H NMR (400 MHz) selected data: δ 7.83, 7.80, 7.78, 7.74, and 7.64 (5 s, 5H, 5 H-5 Tr), 5.18, 5.16, 5.14, 5.13, and 5.07 (5 d, 5H, J = 6.2 Hz, 5 anom. H), 3.39 (dd, 1H, $J_{3,4}$ = 5.8 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.12 (dd, 1H, $J_{5,6}$ = 8.7 Hz, $J_{6,7}$ = 10.0 Hz, H-6), 2.36 (s, 3H, CH_3), 0.98 (s, 9H, 3 CH_3), 0.08 (s, 6H, 2 CH_3). ^{13}C NMR selected data: δ 142.5 (C-4 Tr), 138.2 (C), 138.1 (C), 137.9

(C), 126.1 (C-5 Tr), 50.4 (CH$_2$), 26.0 (CH$_3$). ESI/Q-TOF MS *m/z* calcd for (C$_{187}$H$_{197}$N$_{15}$O$_{27}$SSi)/2 (M+2H)$^{2+}$ 1573.429, found 1573.429.

Azidated Hexaglucoside Alkyne (18). The tosylated hexaglucoside **17** (189 mg, 0.06 mmol) was azidated as described for the synthesis of **8** and desilylated as described for the synthesis of **9** to give, after column chromatography on silica gel (1.5:1 cyclohexane-AcOEt), **18** (103 mg, 59%) as a syrup; $[\alpha]_D$ = +101.7 (*c* 0.6, CHCl$_3$). ^{1}H NMR (400 MHz) selected data: δ 7.86, 7.81, 7.79, 7.63 (4 s, 5H, 5 H-5 Tr), 3.45 (dd, 1H, $J_{3,4}$ = 5.8 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 2.40 (d, 1H, $J_{1,3}$ = 2.3 Hz, H-1). ^{13}C NMR selected data: δ 142.5 (C-4 Tr), 138.2 (C), 137.9 (C), 137.7 (C), 137.5 (C), 126.1 (C-5 Tr), 50.4 (CH$_2$). ESI/Q-TOF MS *m/z* calcd for (C$_{174}$H$_{176}$N$_{18}$O$_{24}$)/2 (M+2H)$^{2+}$ 1451.709, found 1451.712.

Cyclic Hexaglucoside (19). The hexaglucoside **18** (87 mg, 0.03 mmol) was submitted to the cycloaddition as described for the synthesis of **11** to give the corresponding benzylated cyclohexamer as a yellow syrup (88 mg). To a solution of the crude product and ammonium formate (272 mg, 4.32 mmol) in CH$_3$OH (8 mL), THF (4 mL) and H$_2$O (2 mL) was added 10% palladium on carbon (575 mg, 0.54 mmol). The mixture was stirred in a closed vial at 50 °C for 16 h, then cooled to r. t., filtered through a pad of Celite, and concentrated. The residue was eluted from a column of Sephadex LH20 (1 x 60 cm) with 1:1 H$_2$O-CH$_3$OH to give **19** (27 mg, 71%) as a foam; $[\alpha]_D$ = +26.5 (*c* 0.5, DMF). ^{1}H NMR (D$_2$O, 400 MHz): δ 7.78 (s, 6H, 6 H-5 Tr), 5.05 (d, 6H, $J_{1,2}$ = 6.3 Hz, 6 H-1), 4.53 (dd, 6H, $J_{5,6a}$= 2.3 Hz, $J_{6a,6b}$ = 14.5 Hz, 6 H-6a), 4.40 (dd, 6H, $J_{5,6b}$ = 8.2 Hz, 6 H-6b), 3.81 (dd, 6H, $J_{2,3}$ = 10.0 Hz, 6 H-2), 3.75 (dd, 6H, $J_{3,4}$ = 8.3 Hz, 6 H-3), 3.53 (ddd, 6H, $J_{4,5}$ = 10.2 Hz, 6 H-5), 3.12 (dd, 6H, 6 H-4). ^{13}C NMR (D$_2$O): δ 142.4 (C-4 Tr), 126.7 (C-5 Tr), 74.0 (CH), 72.5 (CH), 71.5 (CH), 70.7 (CH), 51.2 (CH$_2$). HRMS (ESI/Q-TOF) *m/z* calcd for C$_{48}$H$_{66}$N$_{18}$NaO$_{24}$ (M+Na)$^+$ 1301.4395, found 1301.4296.

Fluorescence measurements. The solutions of ammonium 8-anilino-1-naphthalenesulfonate (ANS) (0.30 mM), **11** (42.0 mM), **16** (42.0 mM), **19** (42.0 mM), and commercially available β-cyclodextrin (42.0 mM) were prepared in 20 mM phosphate buffer at pH 7.22. The test solutions were then obtained by combining the same volume (60 μL) of the stock solutions of ANS and cyclic oligosaccharides. The fluorescence emission spectra were recorded by scanning the emission monochromator in 1 nm steps (1 s integration time) from 400 to 700 nm while exciting at a fixed wavelength of 365 nm (1.0 mm optical path length quartz cell).

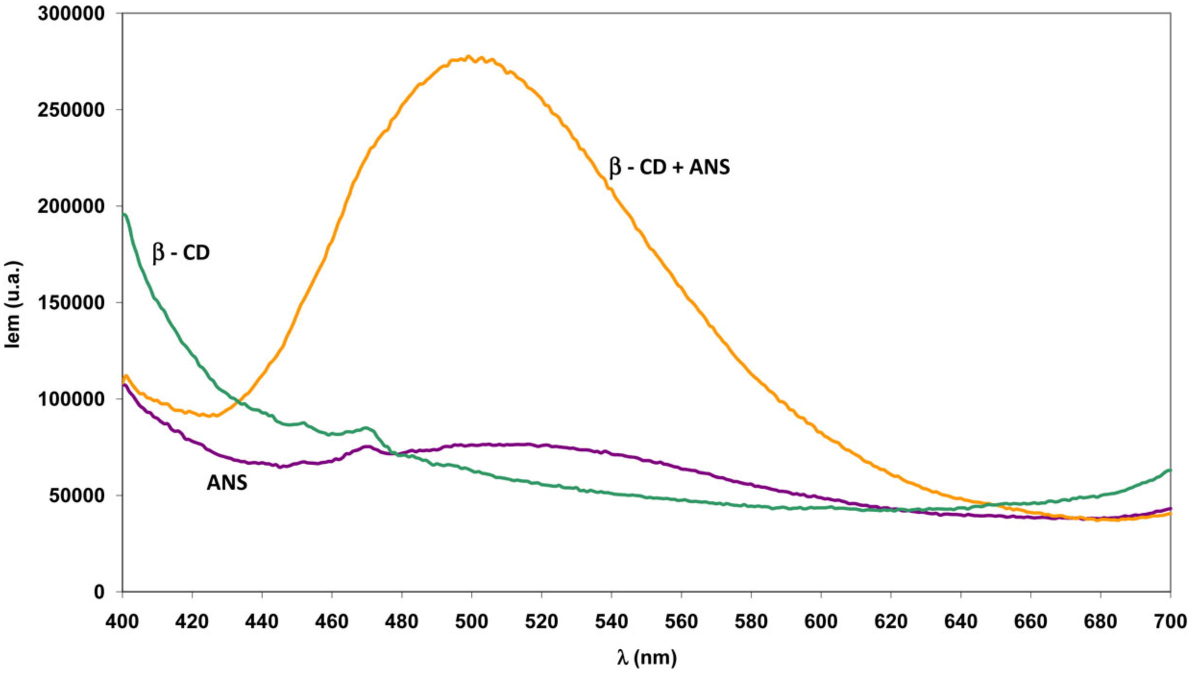

Figure S1 Fluorescence emission spectra (λ_{ex} = 365 nm) of phosphate buffer solutions (pH 7.22) of ammonium 8-anilino-1-naphthalenesulfonate (ANS), β-cyclodextrin (β-CD), and a mixture of ANS and β-CD.

Determination of the association constant. The association constant between ammonium 8-anilino-1-naphthalenesulfonate (ANS) and cyclohexaglucoside **19** was determined by fluorescence spectroscopy as described by K. L. Bodine *et al.*[13a] Fluorescence spectra were recorded at host-guest ratios of 10:1, 30:1, 80:1, 110:1, 125:1, and 138:1. The plot of F/F_0 (F_0 = fluorescence intensity of ANS solution at λ_{max} = 540 nm; F = fluorescence intensity of the host-guest mixture at λ_{max}) versus host concentration showed the rectangular hyperbolic shape expected for 1:1 complex formation (Figure S2). Using the equations derived by Conners,[23] an association constant of $22.5 \pm 1.3\ M^{-1}$ was obtained.

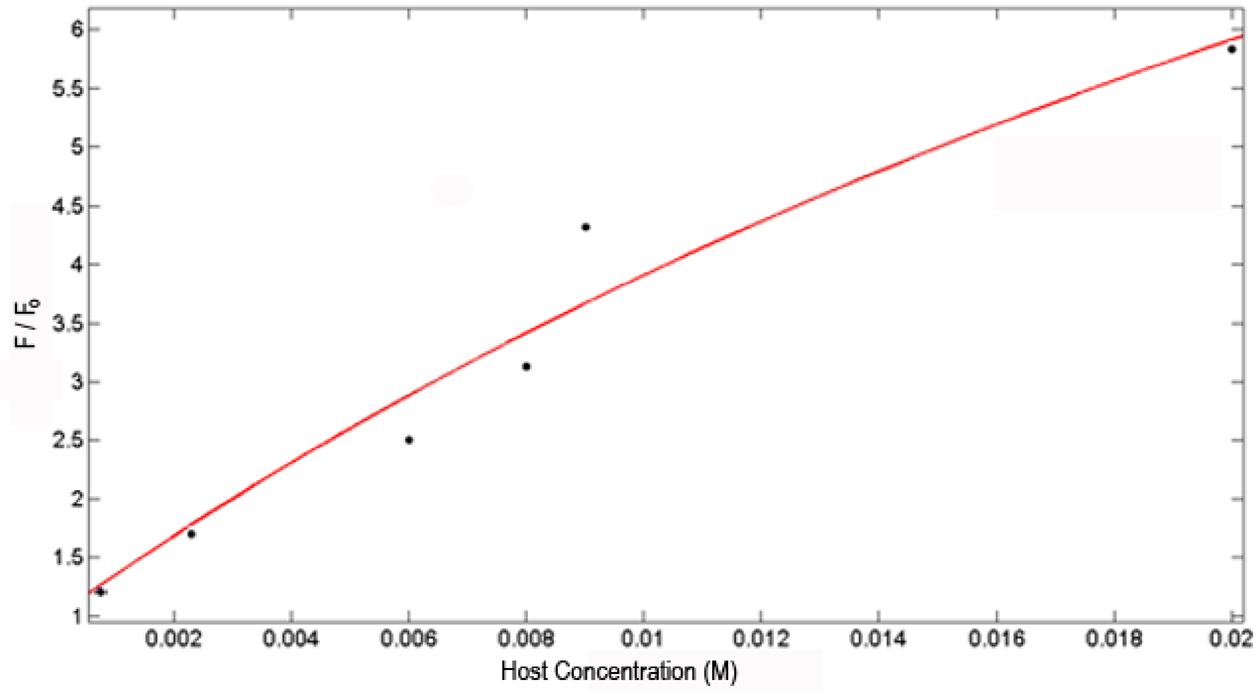

Figure S2 Plot of F/F$_0$ versus concentration of **19** with non-linear regression curve (R: 0.9538).

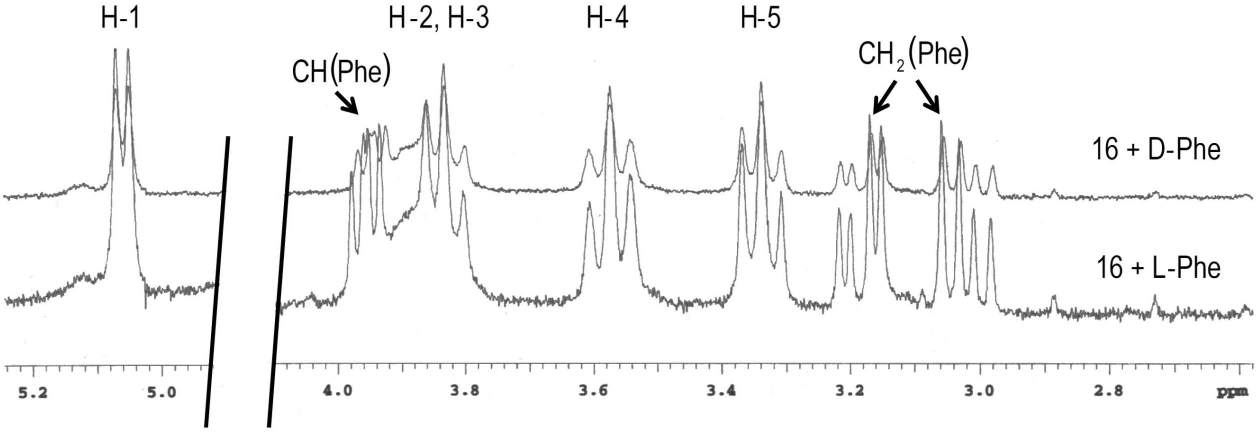

Figure S3 Comparison of the ^{1}H NMR spectra (D_2O, 300 MHz) of cyclotetraglucoside **16** and L-phenylalanine hydrochloride (L-Phe) or D-phenylalanine hydrochloride (D-Phe).

References

19 W. L. F. Armarego and C. L. L. Chai *Purification of Laboratory Chemicals,* 5th ed., Butterworth-Heinemann, Amsterdam, 2003.
20 W. C. Still, M. Kahn and A. Mitra *J. Org. Chem.*, 1978, **43**, 2923-2925.
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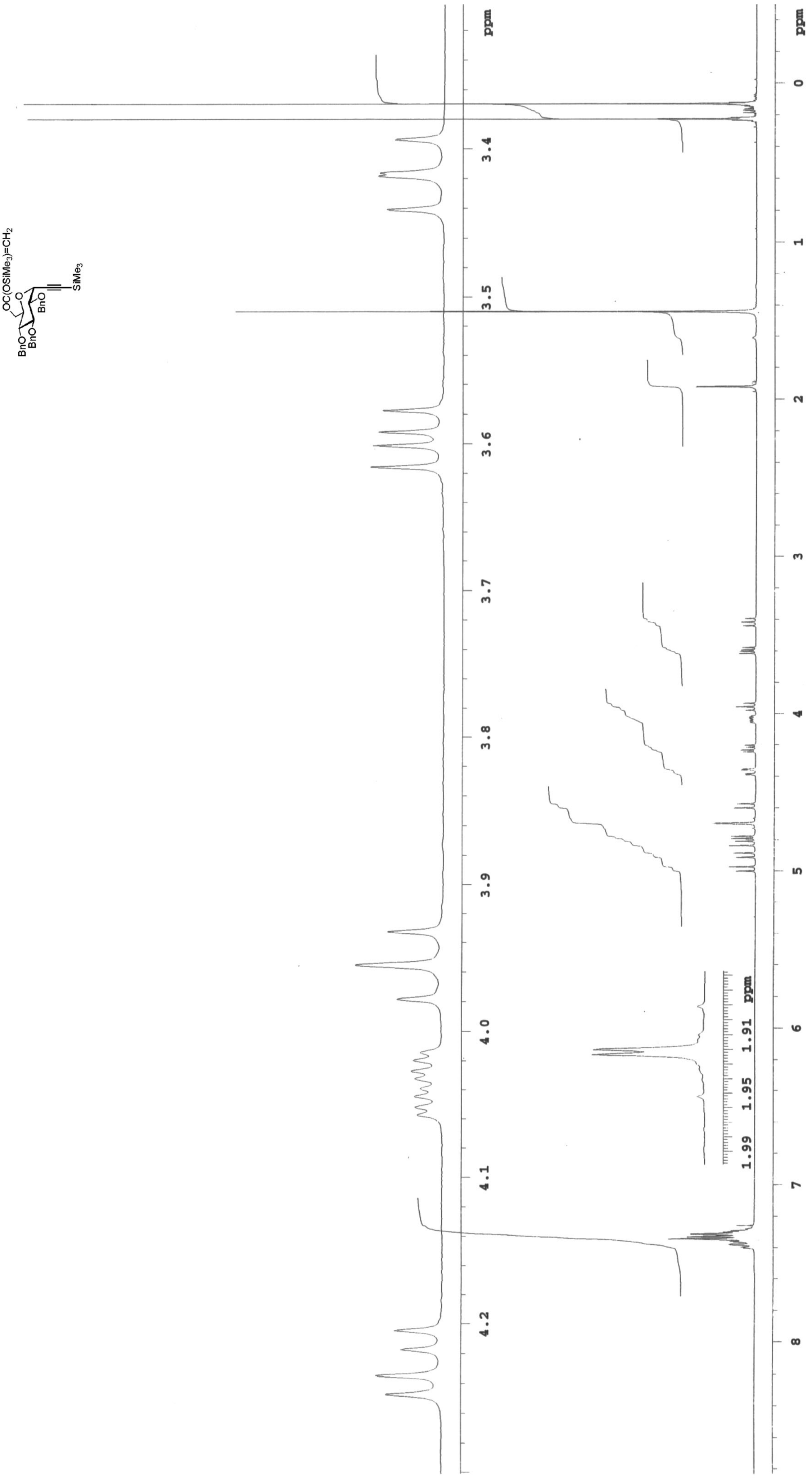
22 Y. Cao and H. Yamada *Carbohydr. Res*., 2006, **341**, 909-911.
23 K. A. Connners, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley, New York, 1987, 339-343.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BnO
O
SiMe3
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3.6
3.7
3.8
3.9
4.0
4.1
4.2
ppm
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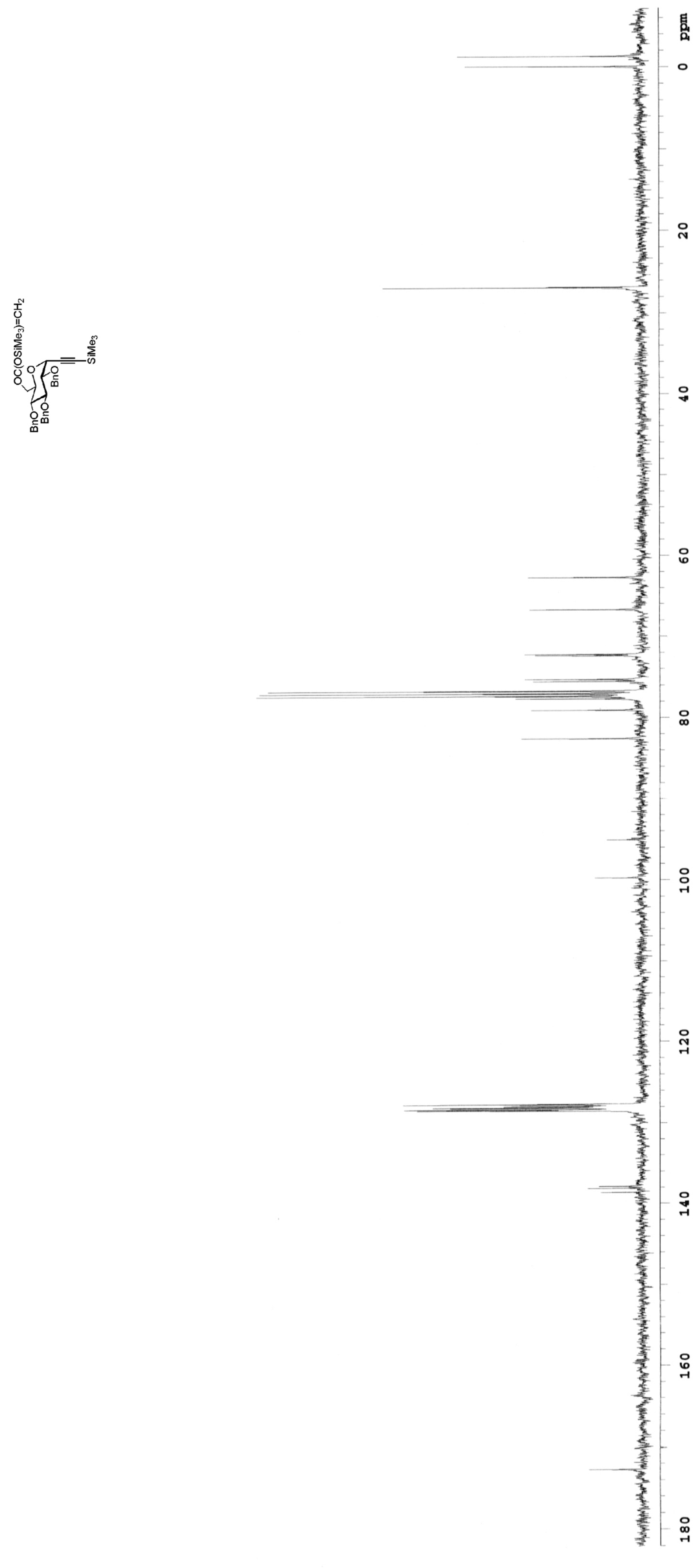
1.95
1.91
ppm
0
1
2
3
4
5
6
7
8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SiMe3
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160
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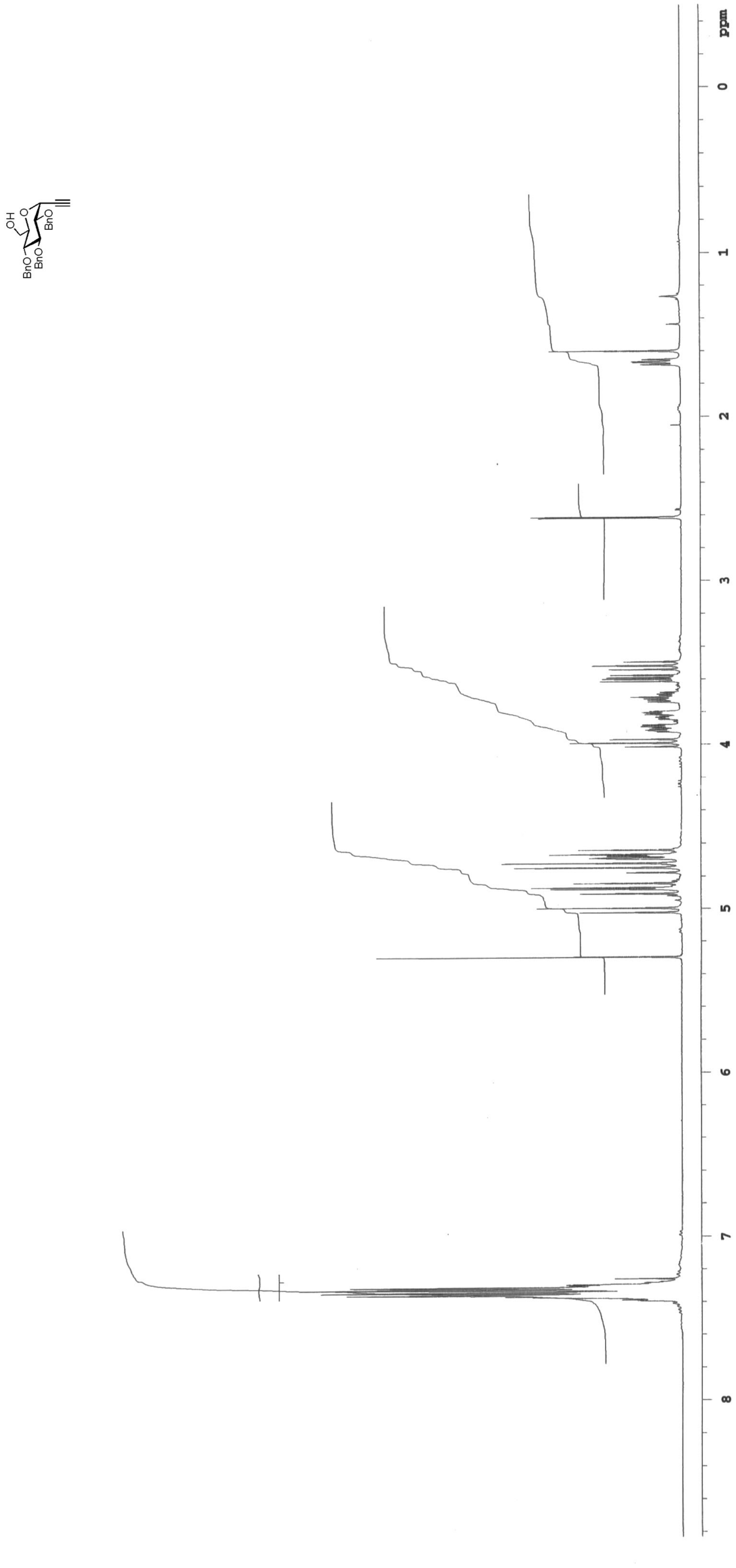
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ppm
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5
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7
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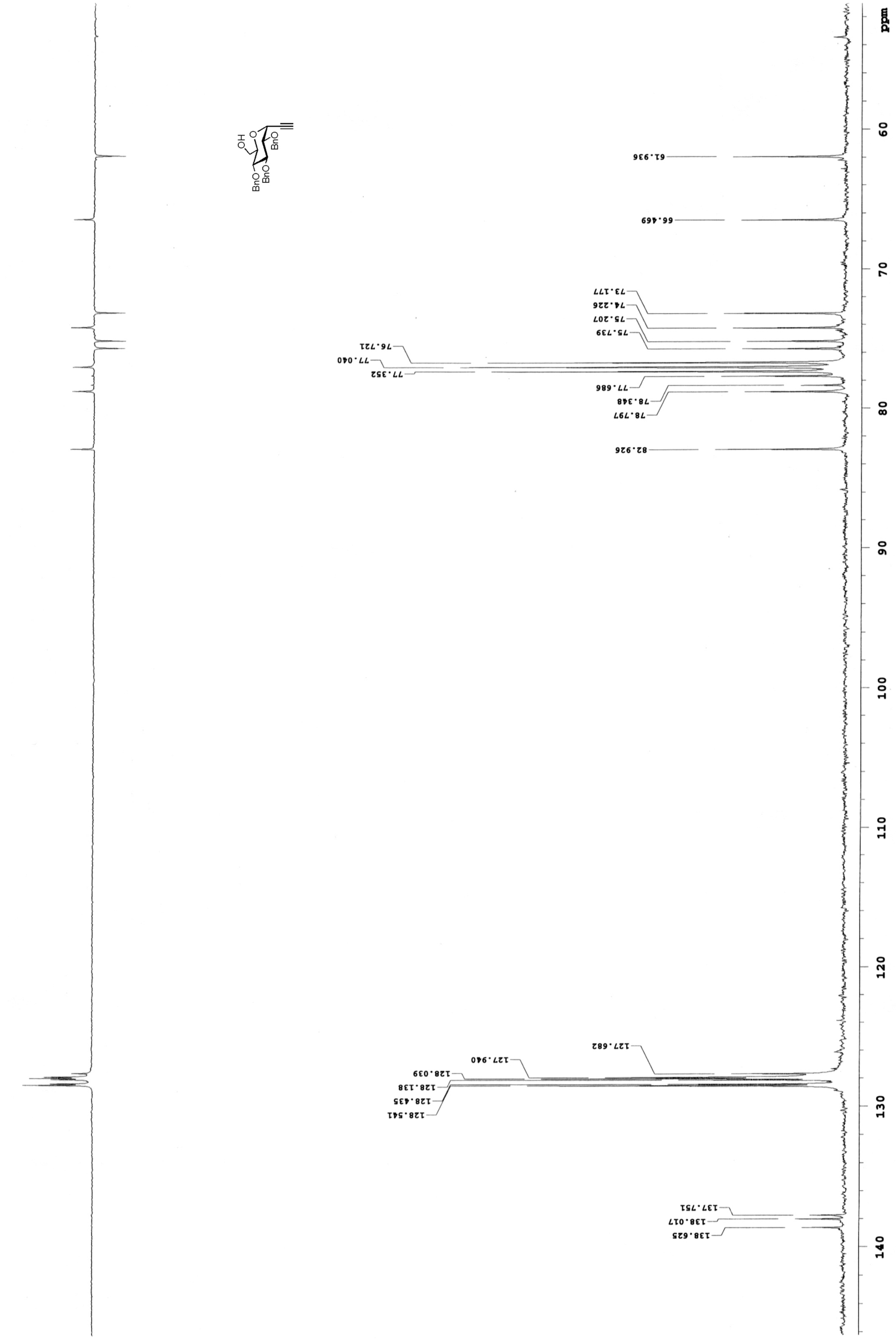
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82.926
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128.039
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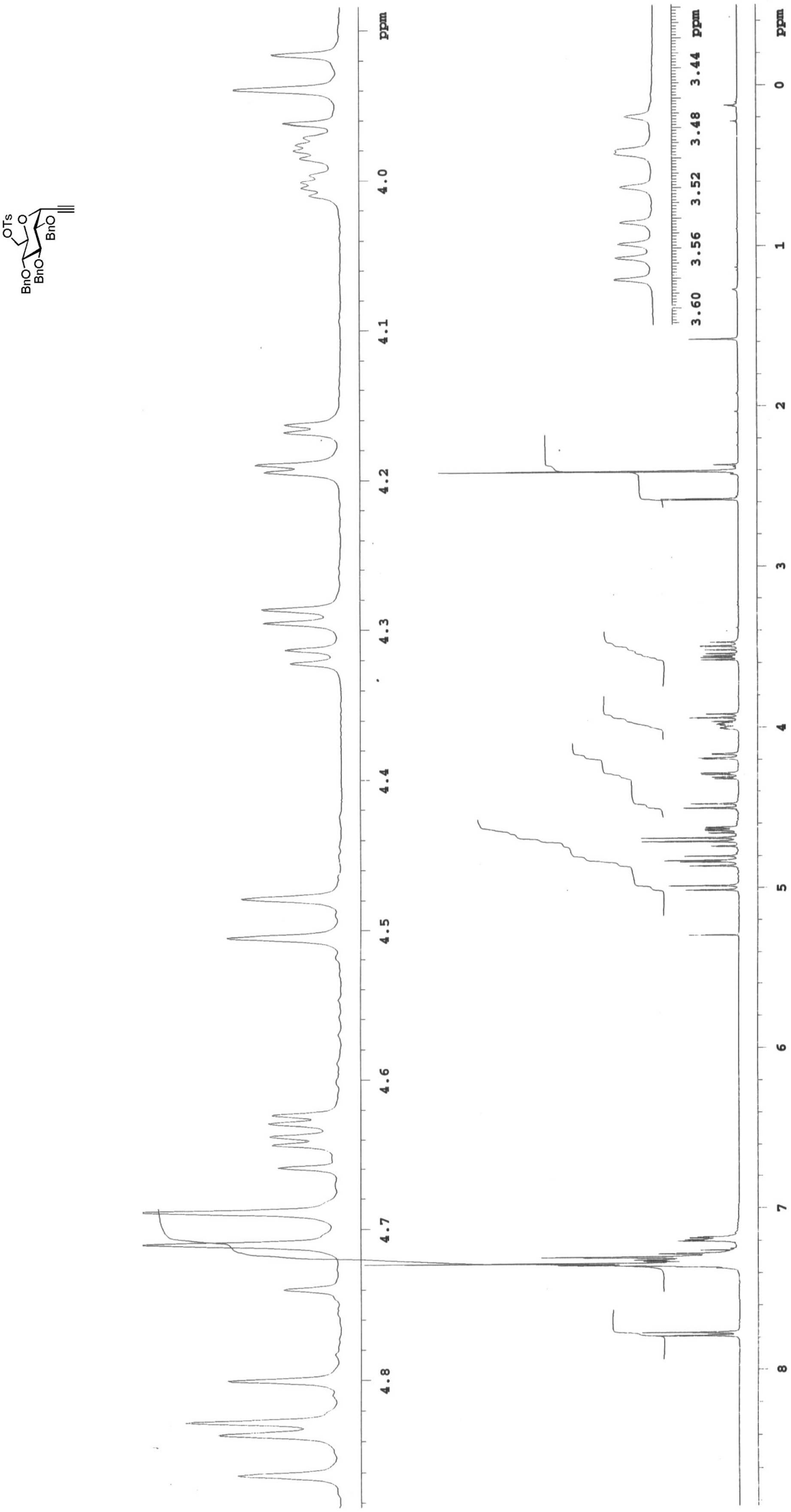
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BnO
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4
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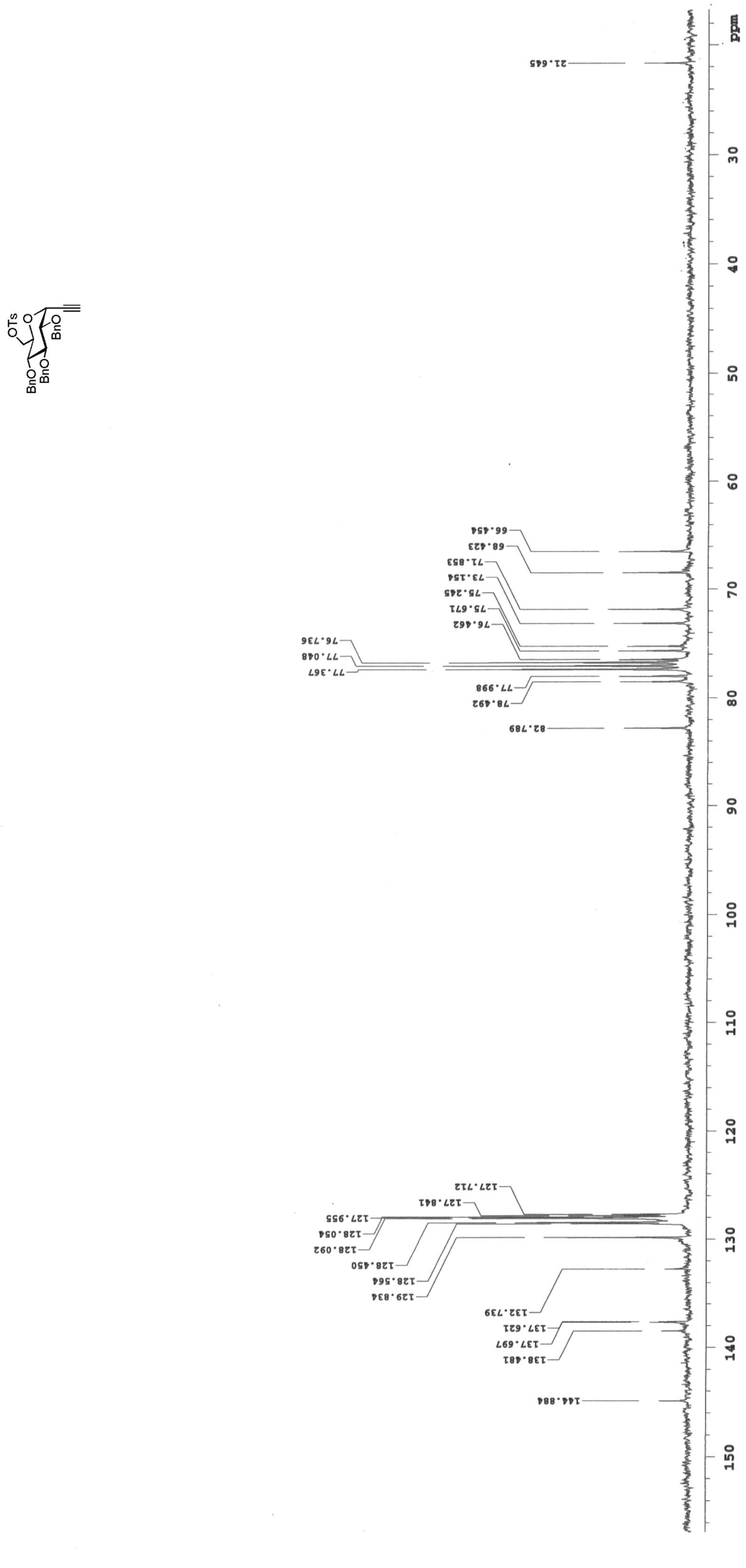
6
7
8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BnO
BnO
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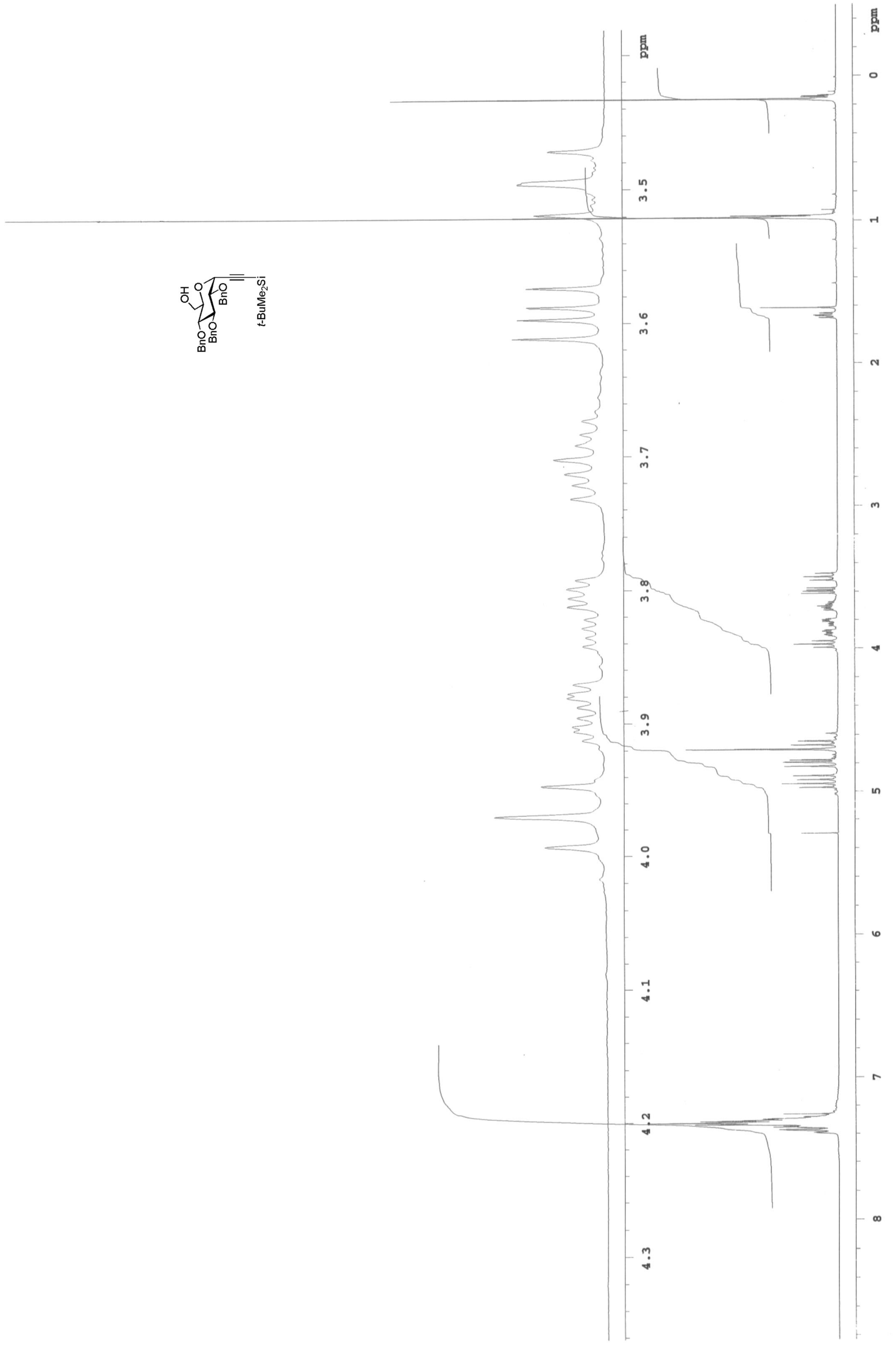
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4.3
ppm
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2
3
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5
6
7
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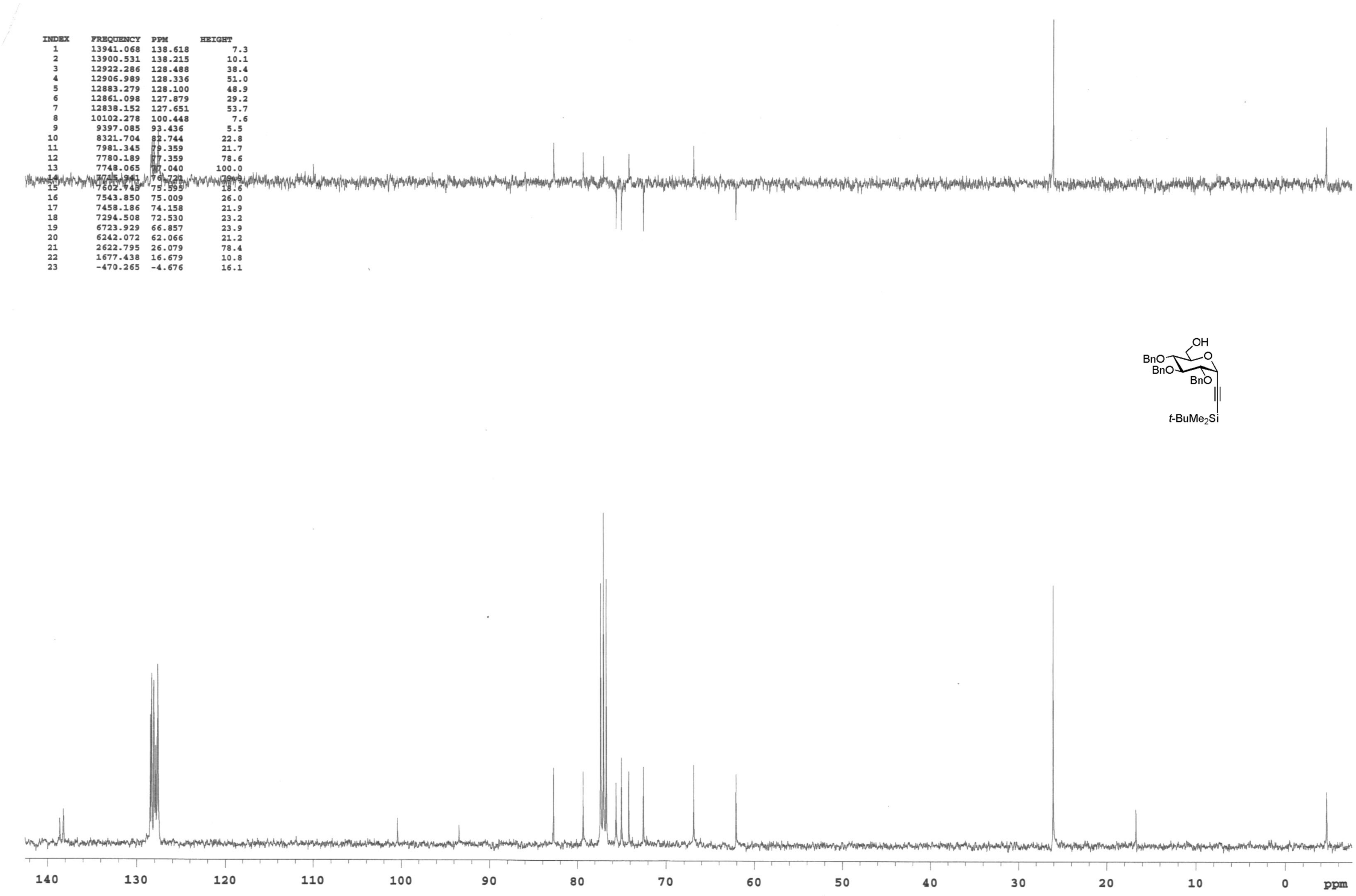

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6	12861.098	127.879	29.2
7	12838.152	127.651	53.7
8	10102.278	100.448	7.6
9	9397.085	93.436	5.5
10	8321.704	82.744	22.8
11	7981.345	79.359	21.7
12	7780.189	77.359	78.6
13	7748.065	77.040	100.0
14	7715.941	76.721	79.9
15	7602.743	75.595	18.6
16	7543.850	75.009	26.0
17	7458.186	74.158	21.9
18	7294.508	72.530	23.2
19	6723.929	66.857	23.9
20	6242.072	62.066	21.2
21	2622.795	26.079	78.4
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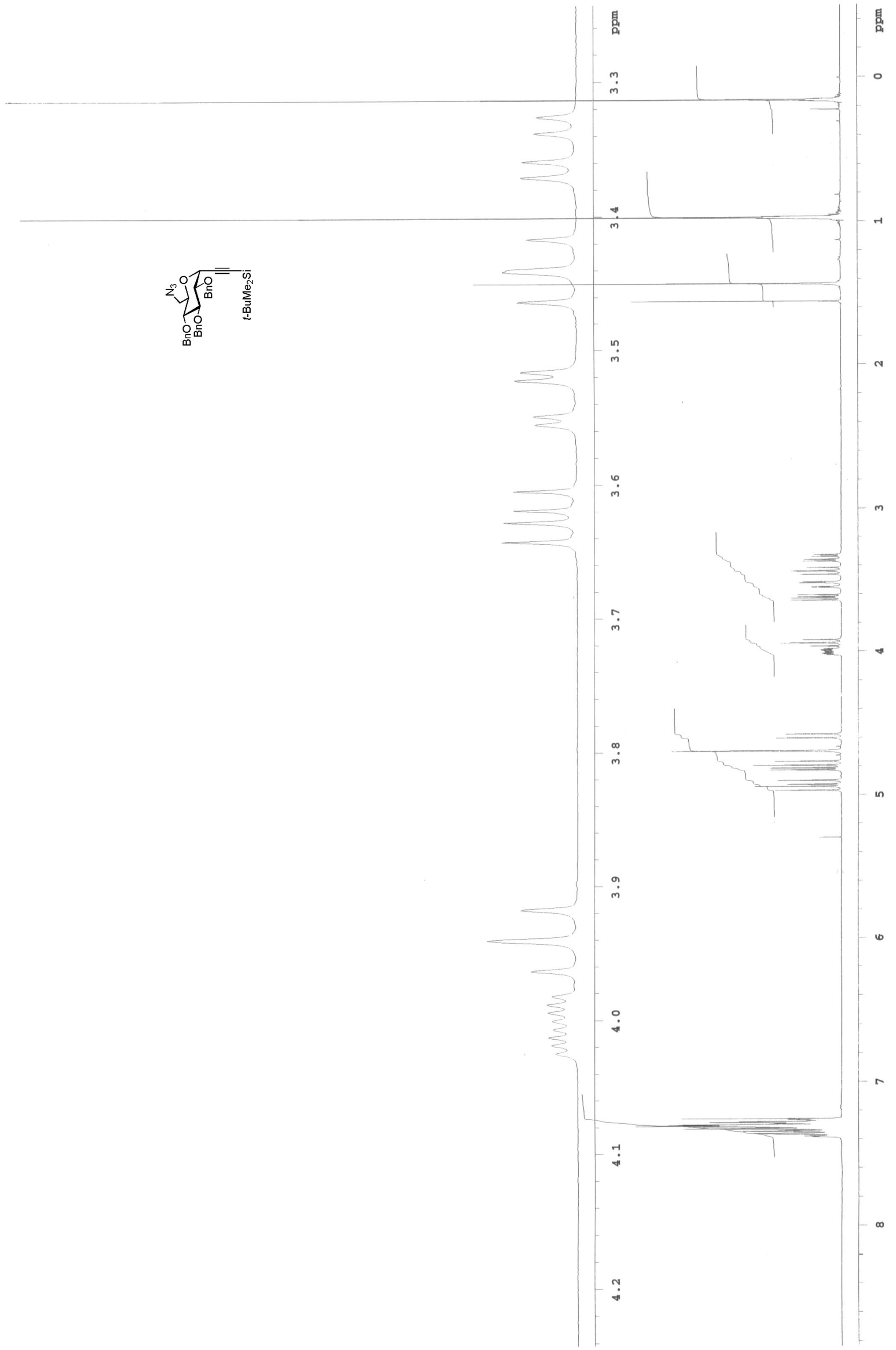
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t-BuMe$_2$Si
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3.5
3.6
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4.2
ppm
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4
5
6
7
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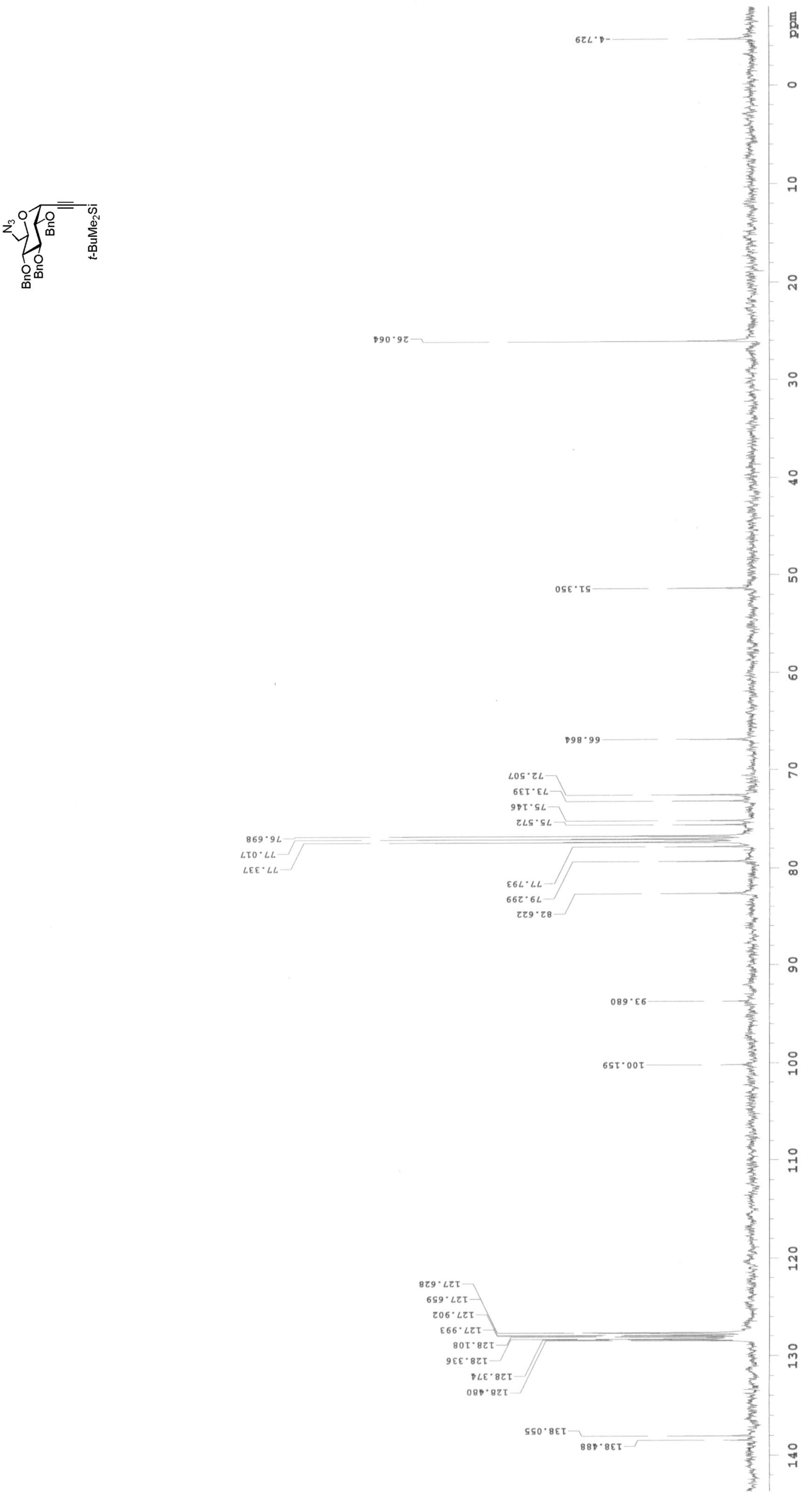
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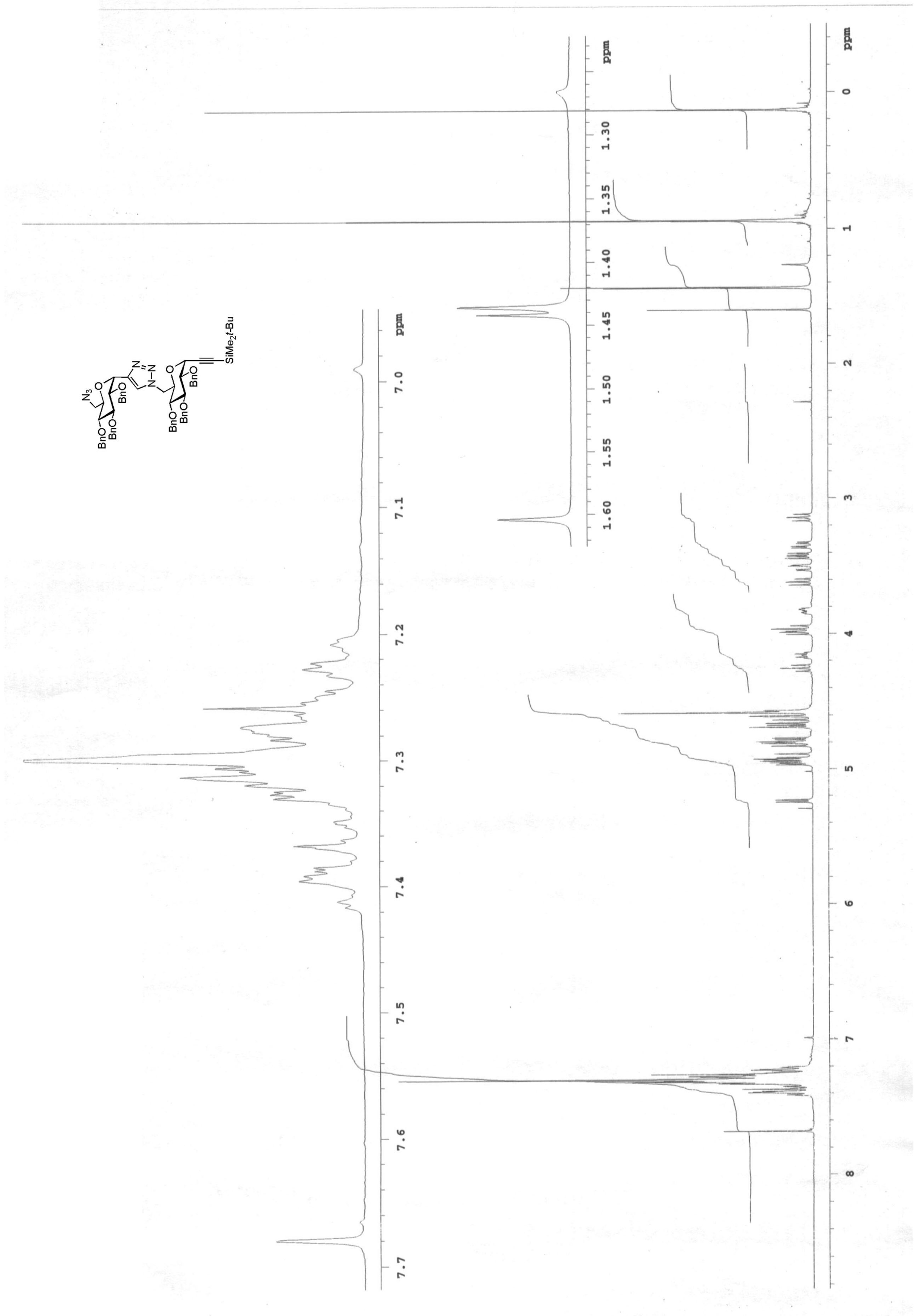
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7.6
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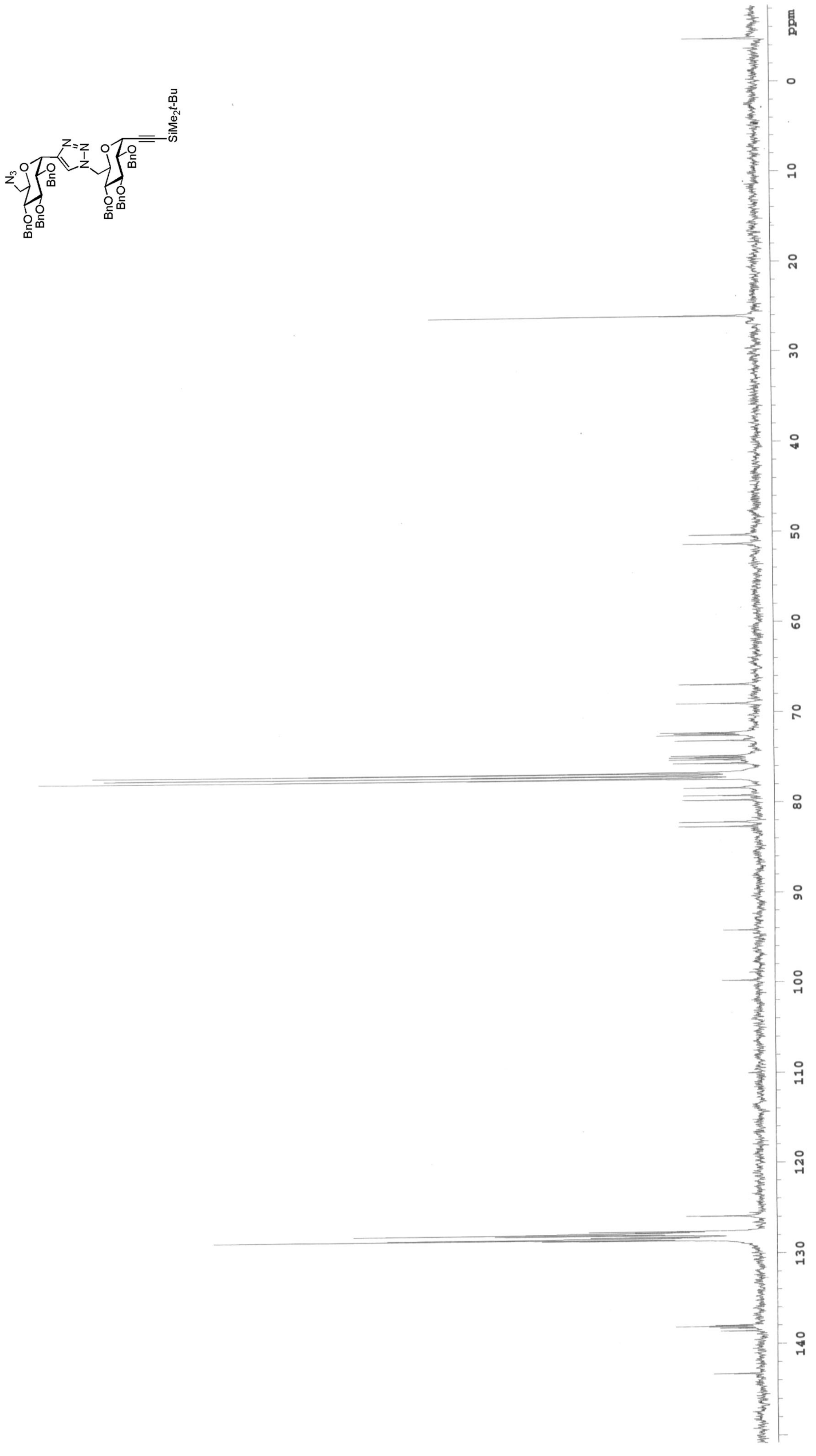
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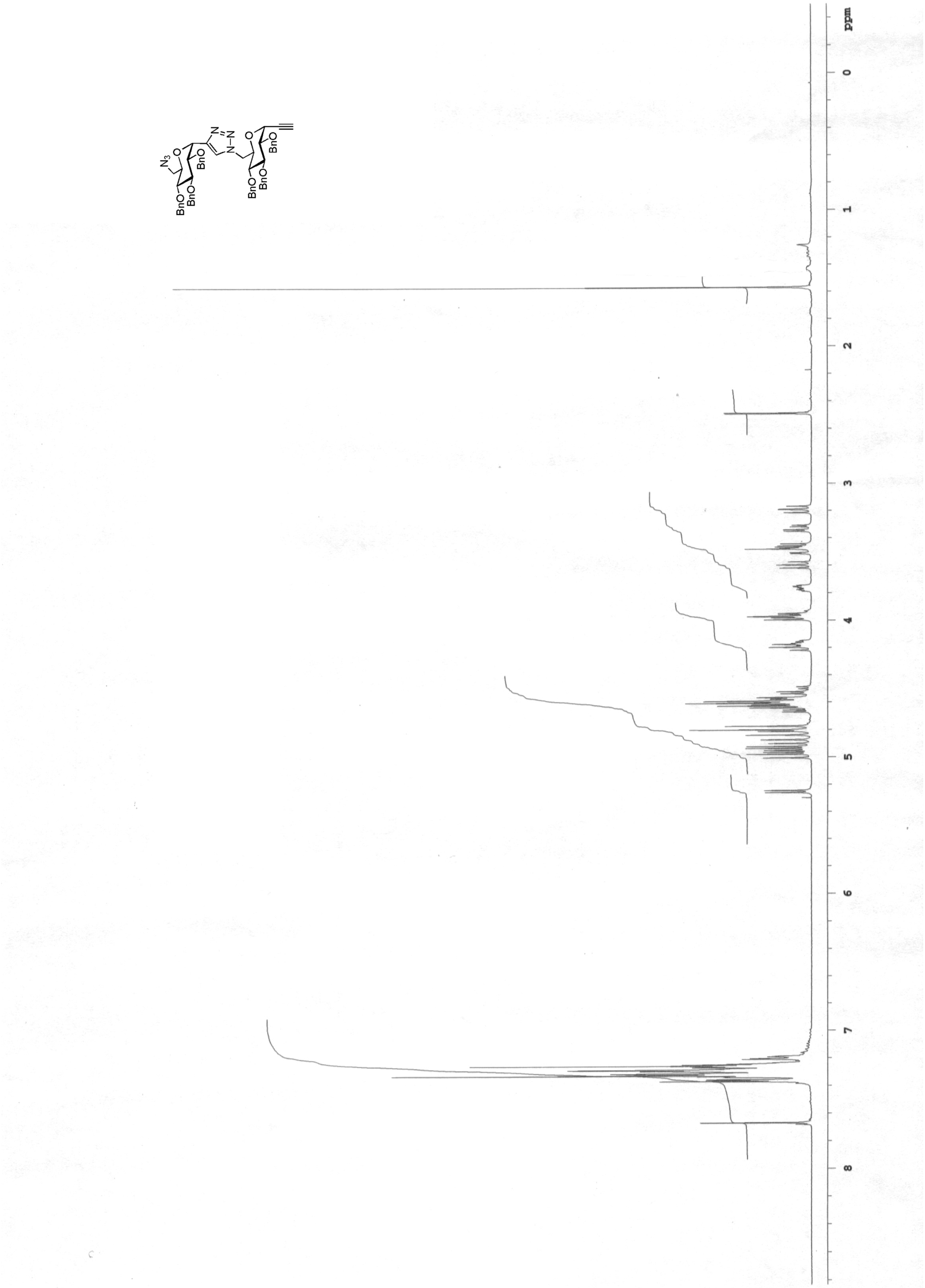
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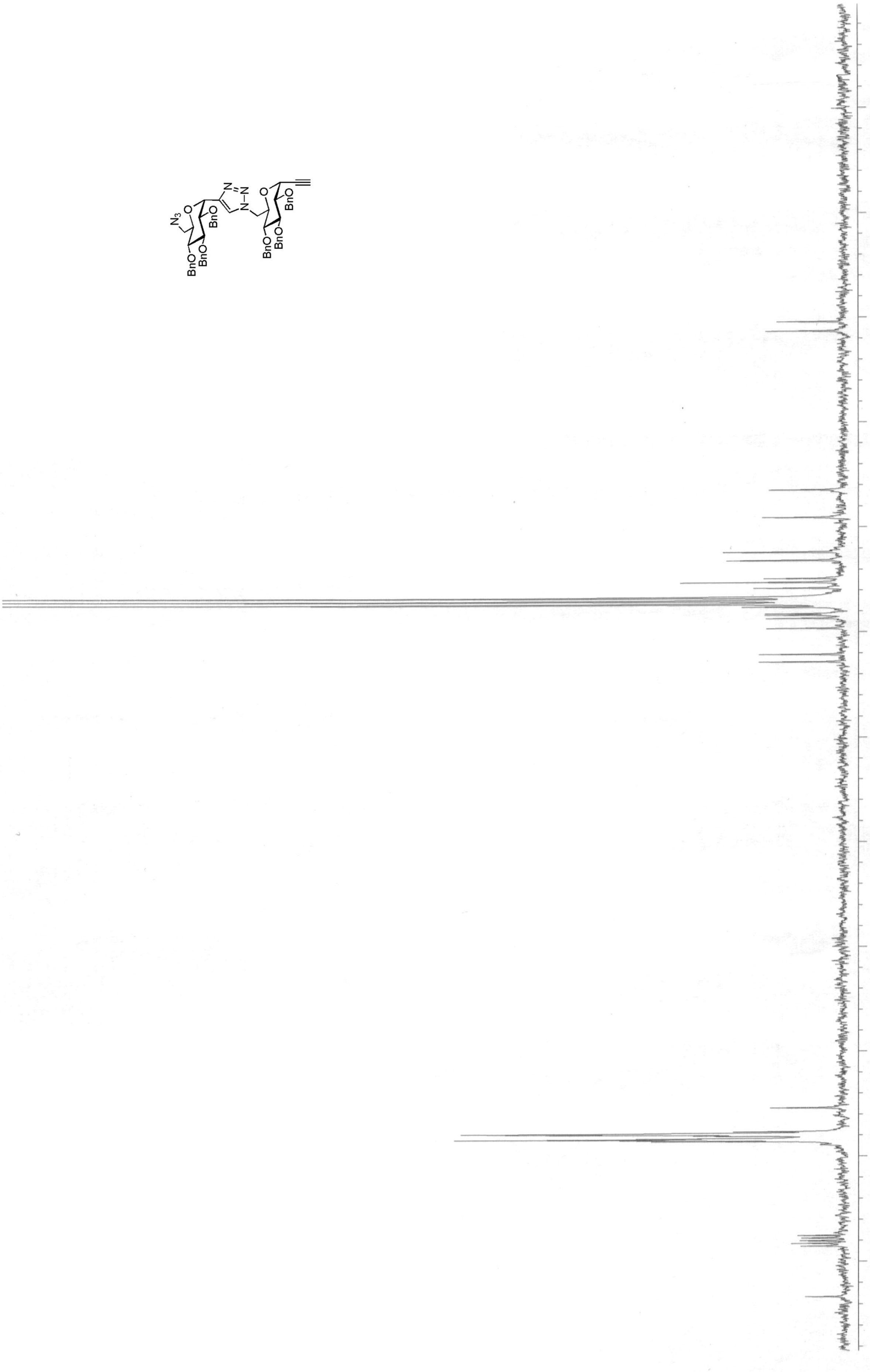
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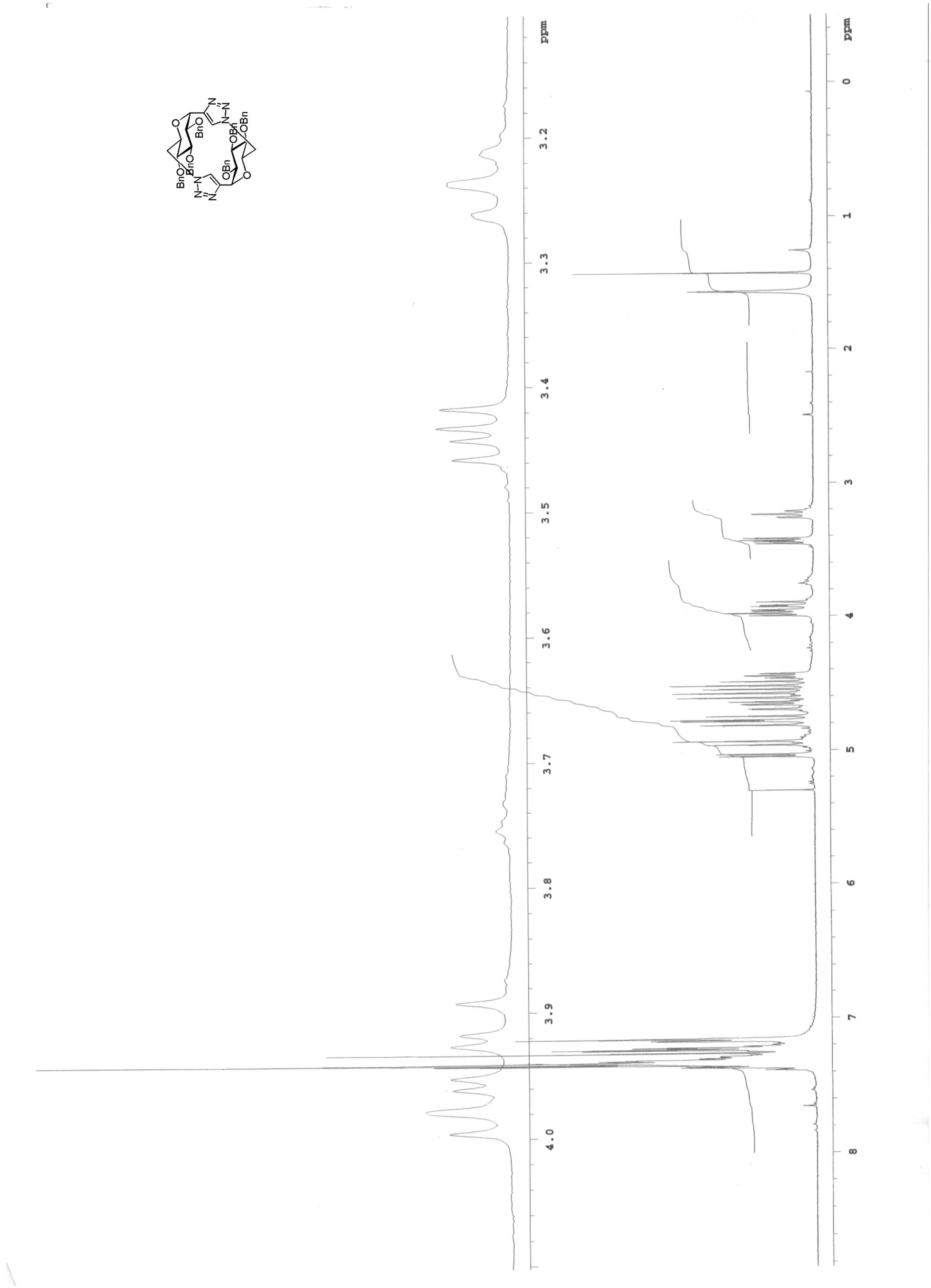
BnO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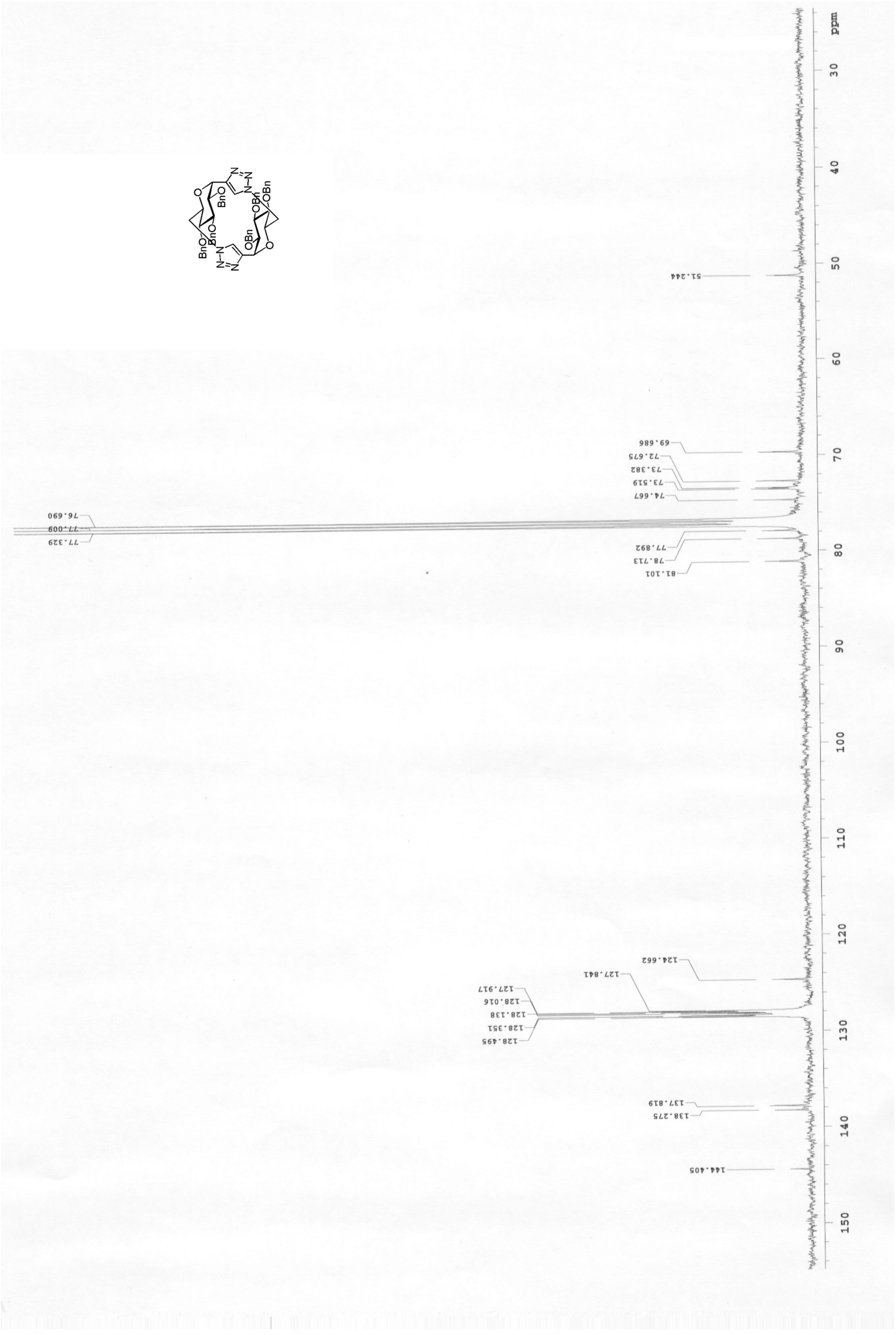
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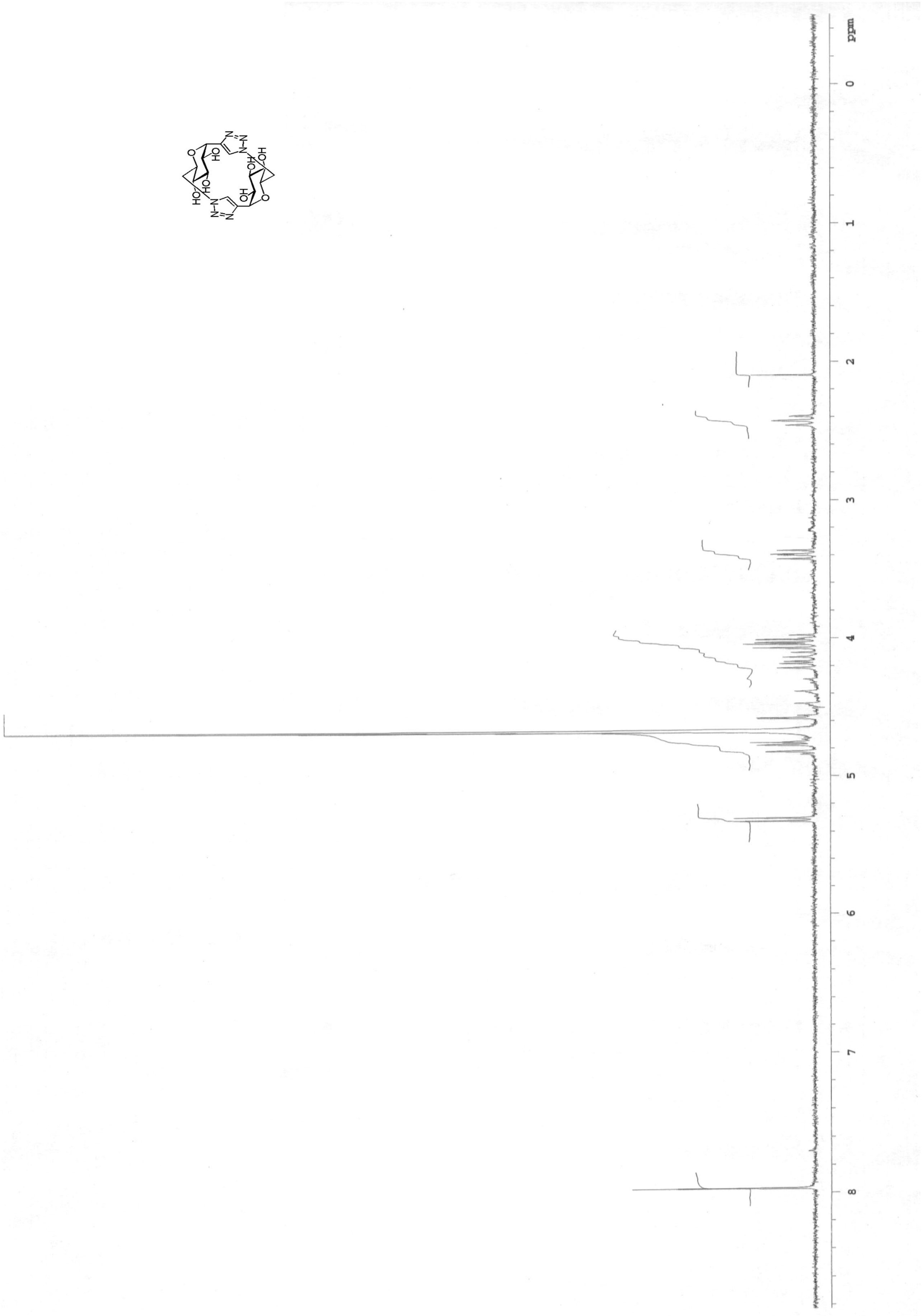
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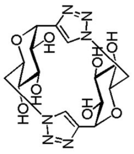
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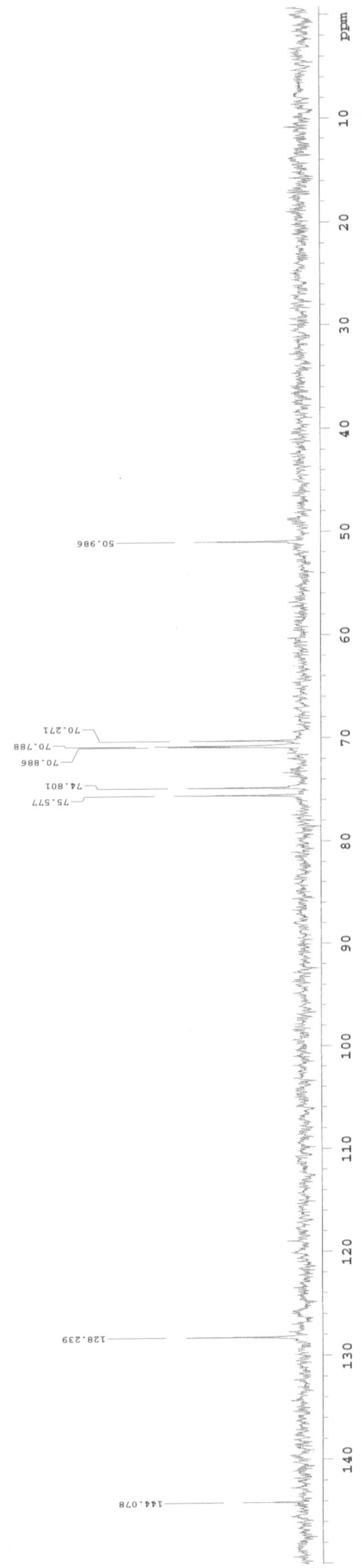
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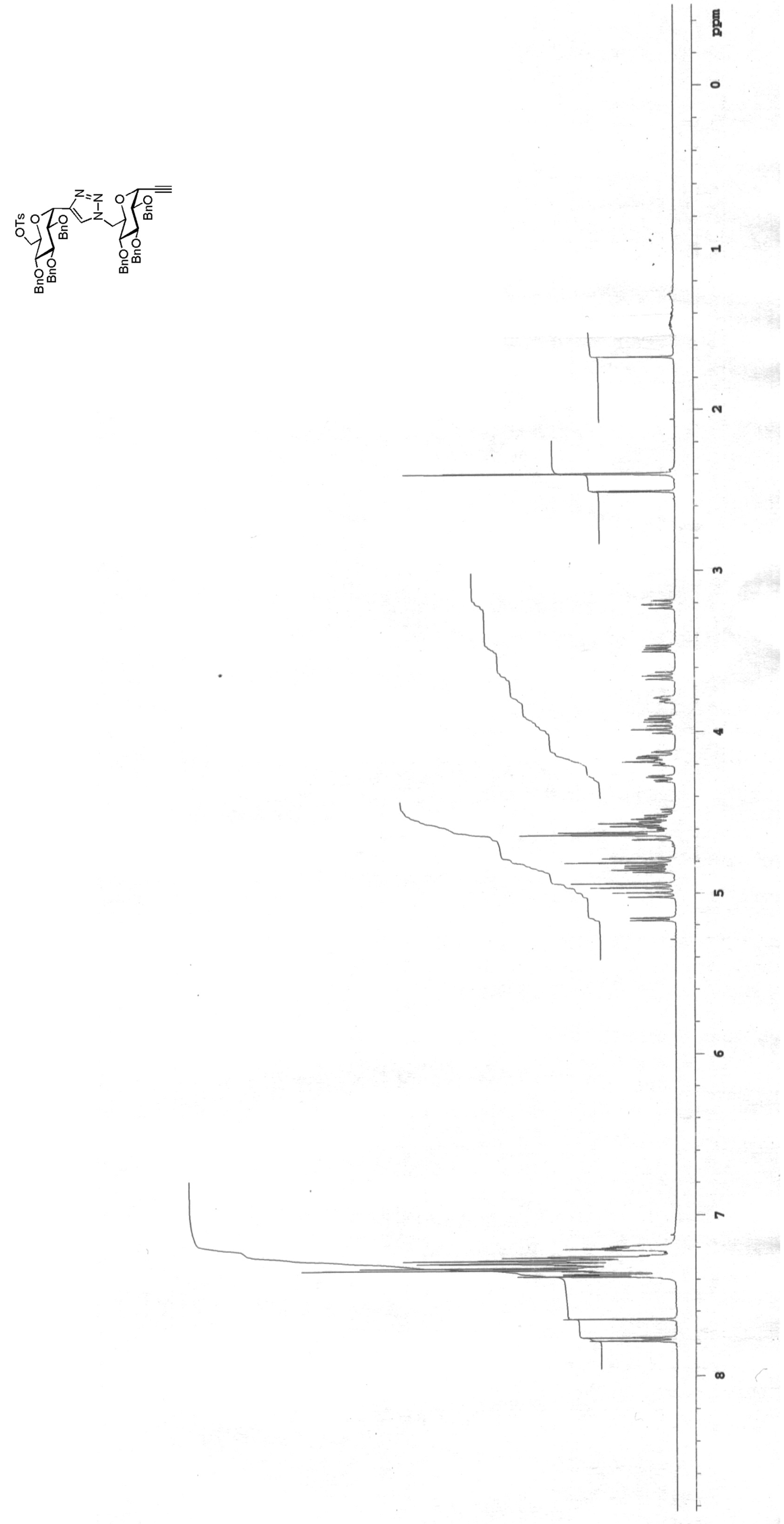
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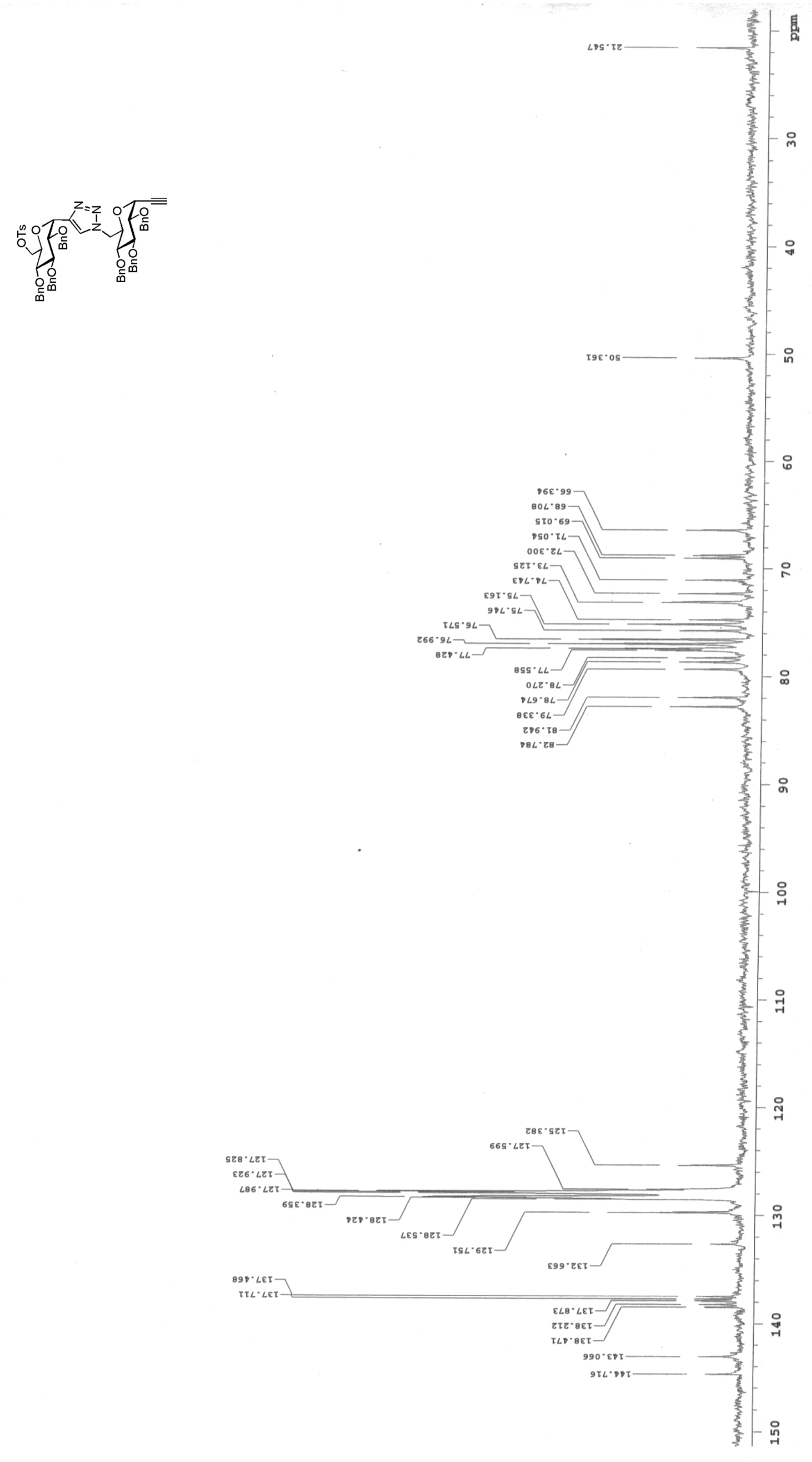
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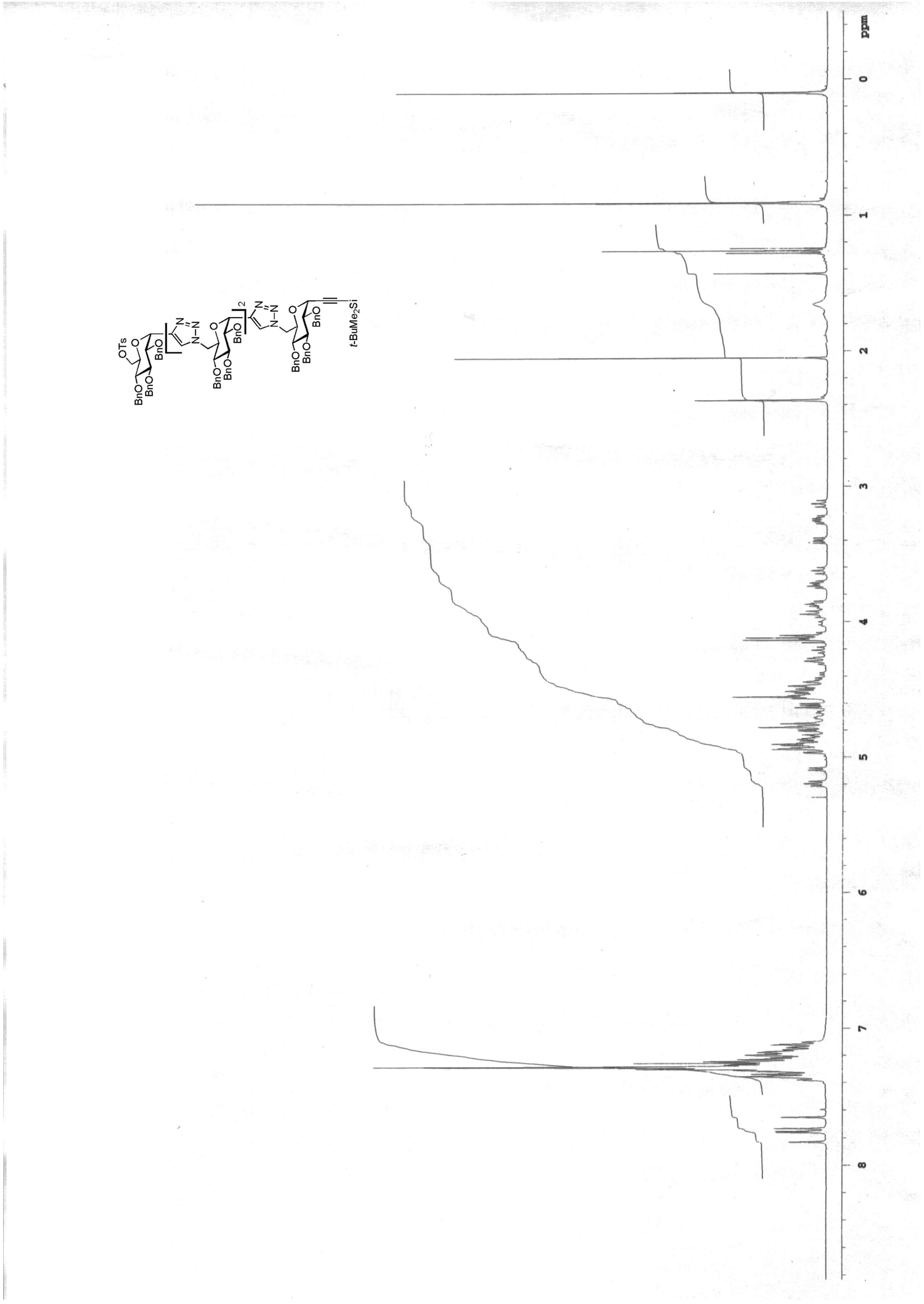
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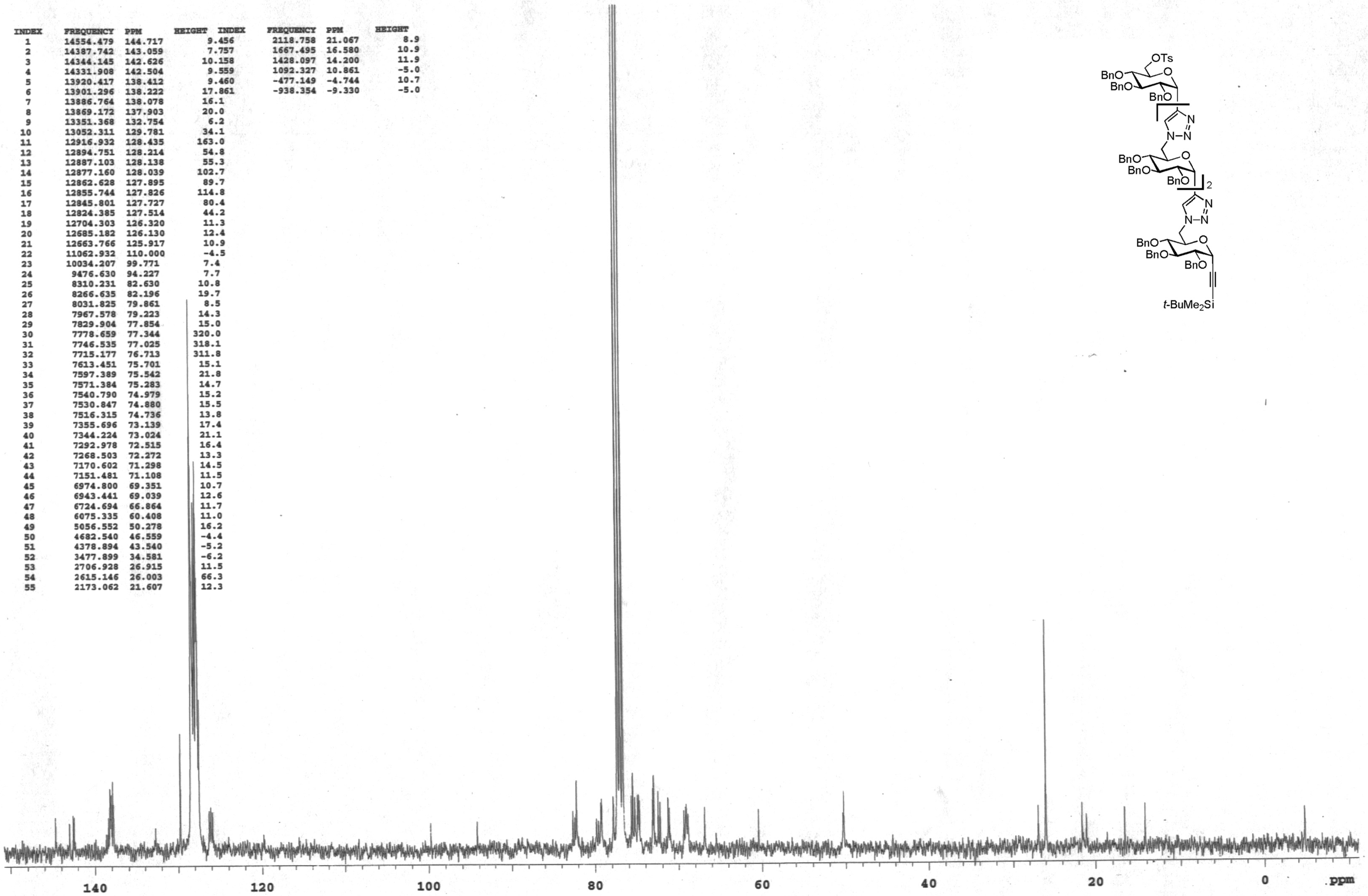
t-BuMe2Si



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3	14344.145	142.626	10.158		1428.097	14.200	11.9
4	14331.908	142.504	9.559		1092.327	10.861	-5.0
5	13920.417	138.412	9.460		-477.149	-4.744	10.7
6	13901.296	138.222	17.861		-938.354	-9.330	-5.0
7	13886.764	138.078	16.1				
8	13869.172	137.903	20.0				
9	13351.368	132.754	6.2				
10	13052.311	129.781	34.1				
11	12916.932	128.435	163.0				
12	12894.751	128.214	54.8				
13	12887.103	128.138	55.3				
14	12877.160	128.039	102.7				
15	12862.628	127.895	89.7				
16	12855.744	127.826	114.8				
17	12845.801	127.727	80.4				
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19	12704.303	126.320	11.3				
20	12685.182	126.130	12.4				
21	12663.766	125.917	10.9				
22	11062.932	110.000	-4.5				
23	10034.207	99.771	7.4				
24	9476.630	94.227	7.7				
25	8310.231	82.630	10.8				
26	8266.635	82.196	19.7				
27	8031.825	79.861	8.5				
28	7967.578	79.223	14.3				
29	7829.904	77.854	15.0				
30	7778.659	77.344	320.0				
31	7746.535	77.025	318.1				
32	7715.177	76.713	311.8				
33	7613.451	75.701	15.1				
34	7597.389	75.542	21.8				
35	7571.384	75.283	14.7				
36	7540.790	74.979	15.2				
37	7530.847	74.880	15.5				
38	7516.315	74.736	13.8				
39	7355.696	73.139	17.4				
40	7344.224	73.024	21.1				
41	7292.978	72.515	16.4				
42	7268.503	72.272	13.3				
43	7170.602	71.298	14.5				
44	7151.481	71.108	11.5				
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46	6943.441	69.039	12.6				
47	6724.694	66.864	11.7				
48	6075.335	60.408	11.0				
49	5056.552	50.278	16.2				
50	4682.540	46.559	-4.4				
51	4378.894	43.540	-5.2				
52	3477.899	34.581	-6.2				
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54	2615.146	26.003	66.3				
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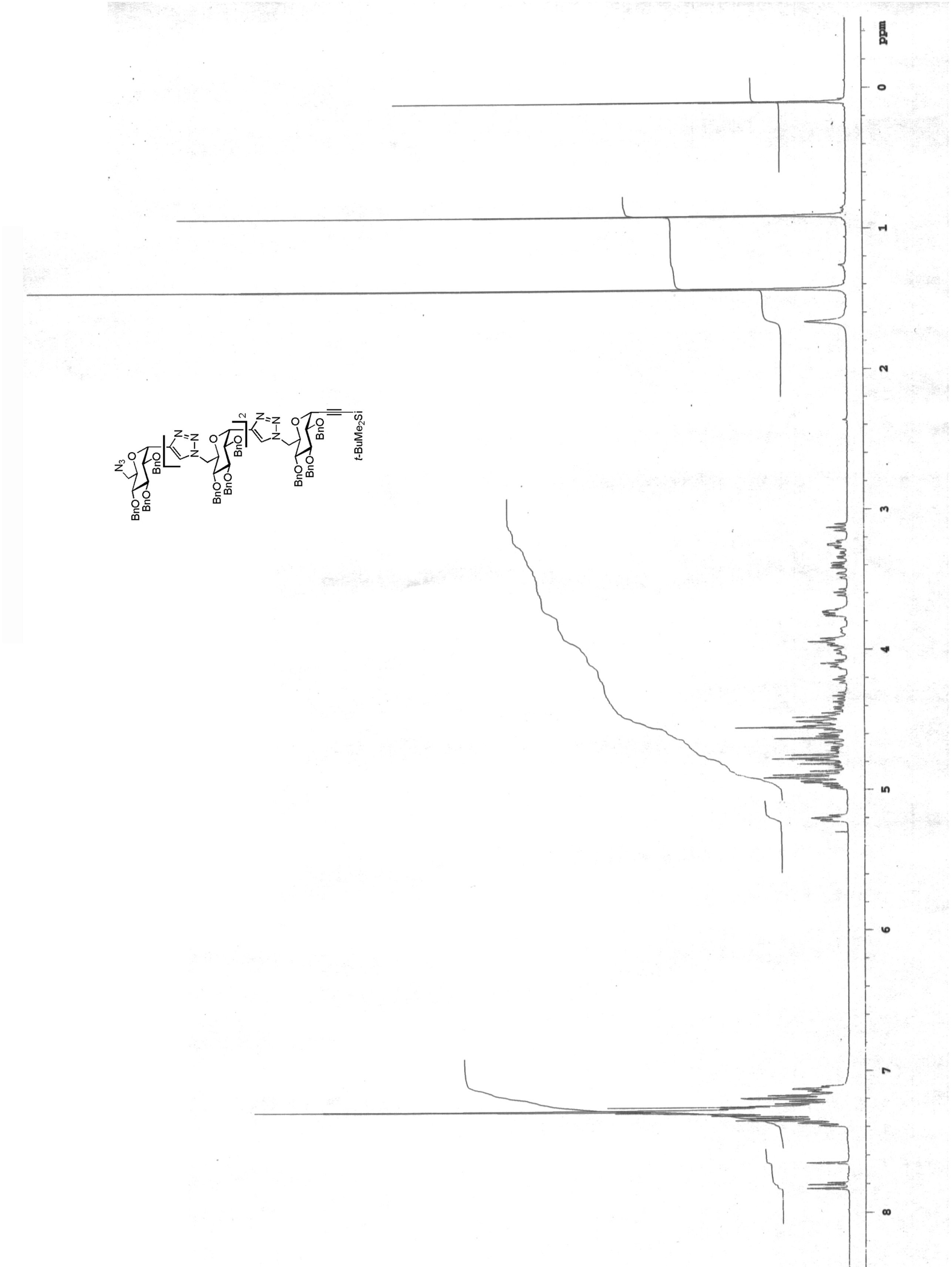
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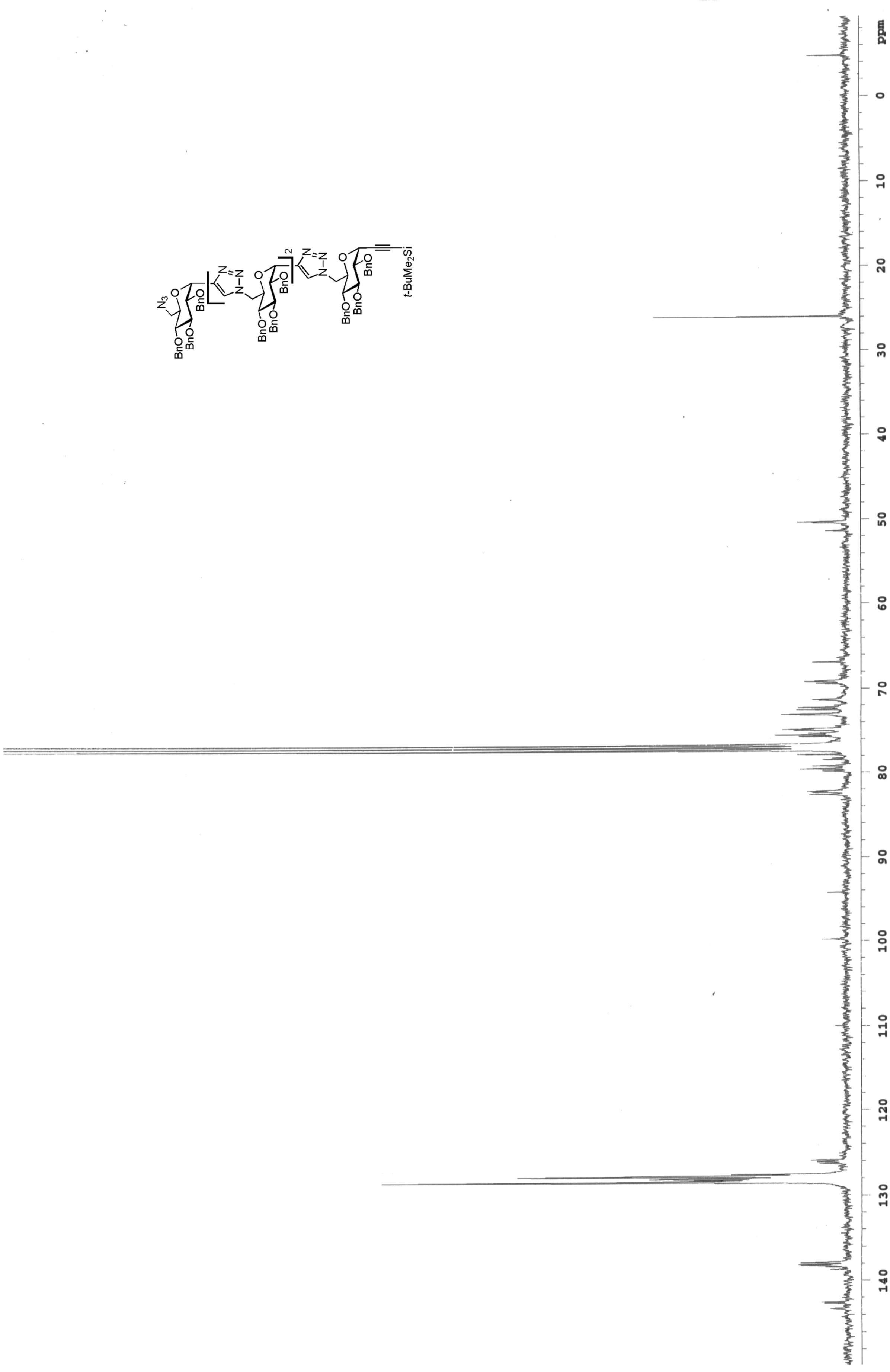
BnO
BnO
t-BuMe2Si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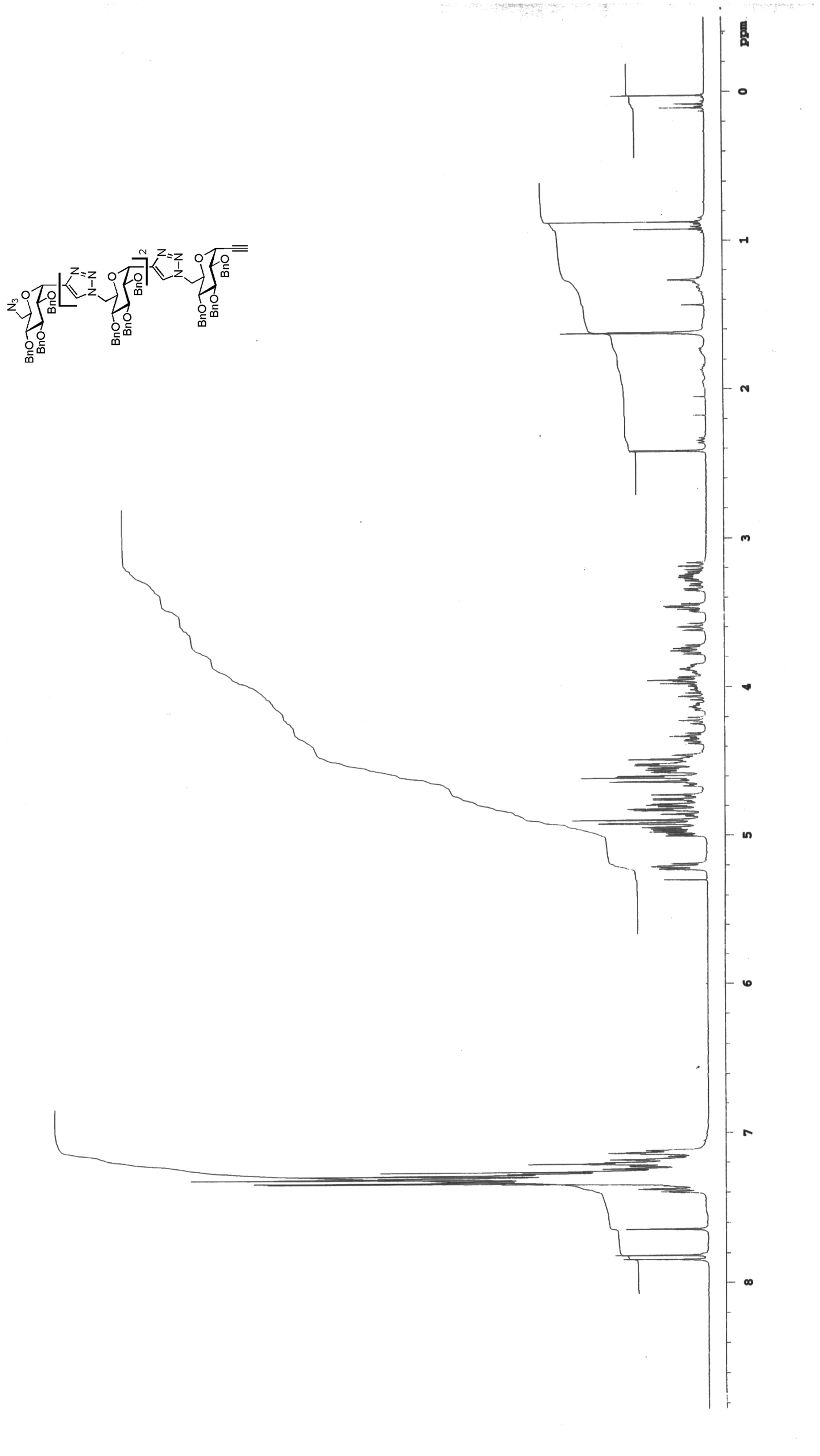
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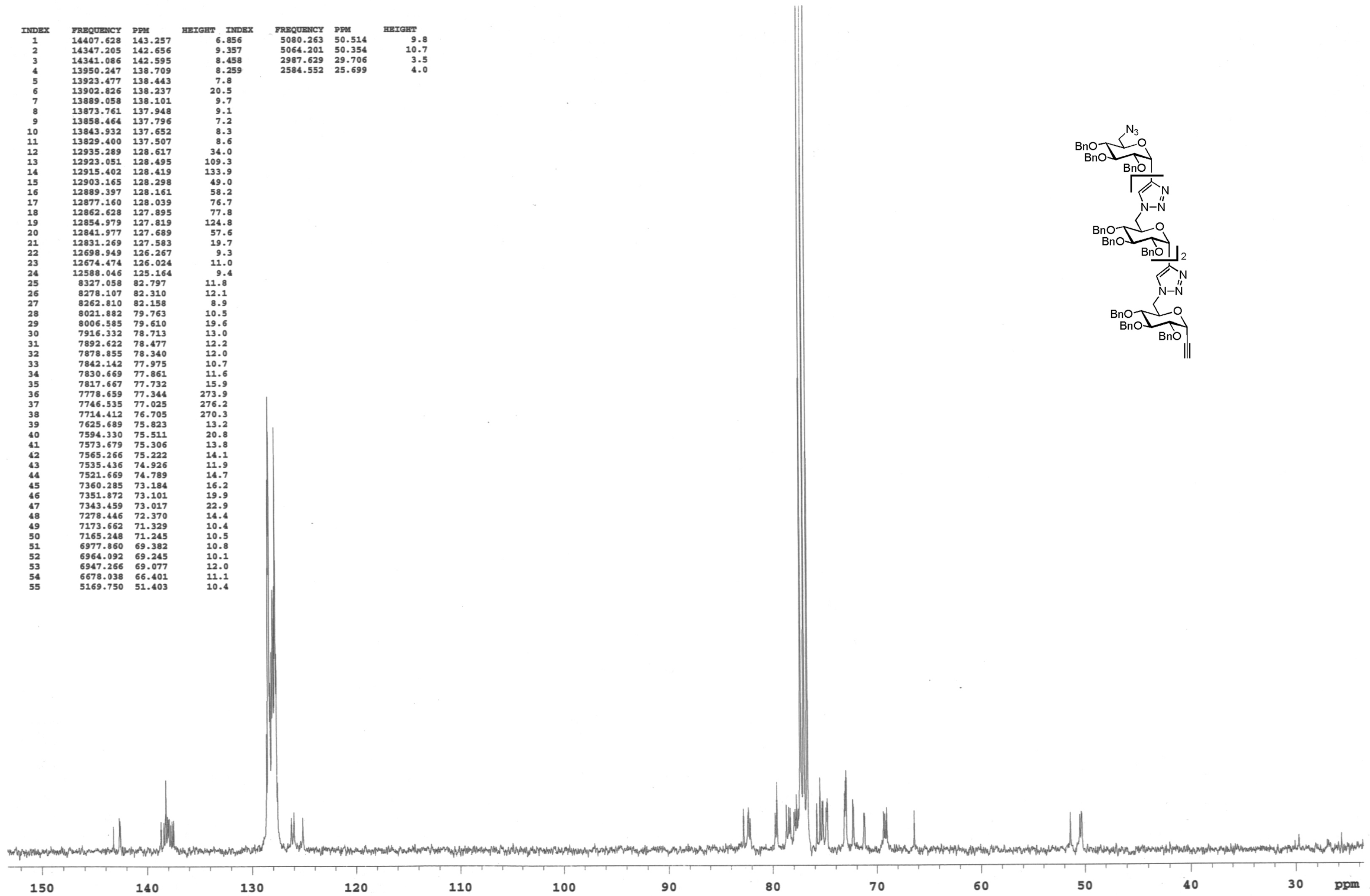

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  3       14341.086  142.595     8.458          2987.629  29.706      3.5
  4       13950.247  138.709     8.259          2584.552  25.699      4.0
  5       13923.477  138.443     7.8
  6       13902.826  138.237    20.5
  7       13889.058  138.101     9.7
  8       13873.761  137.948     9.1
  9       13858.464  137.796     7.2
 10       13843.932  137.652     8.3
 11       13829.400  137.507     8.6
 12       12935.289  128.617    34.0
 13       12923.051  128.495   109.3
 14       12915.402  128.419   133.9
 15       12903.165  128.298    49.0
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 17       12877.160  128.039    76.7
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 19       12854.979  127.819   124.8
 20       12841.977  127.689    57.6
 21       12831.269  127.583    19.7
 22       12698.949  126.267     9.3
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 36        7778.659  77.344   273.9
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 38        7714.412  76.705   270.3
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 42        7565.266  75.222    14.1
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 44        7521.669  74.789    14.7
 45        7360.285  73.184    16.2
 46        7351.872  73.101    19.9
 47        7343.459  73.017    22.9
 48        7278.446  72.370    14.4
 49        7173.662  71.329    10.4
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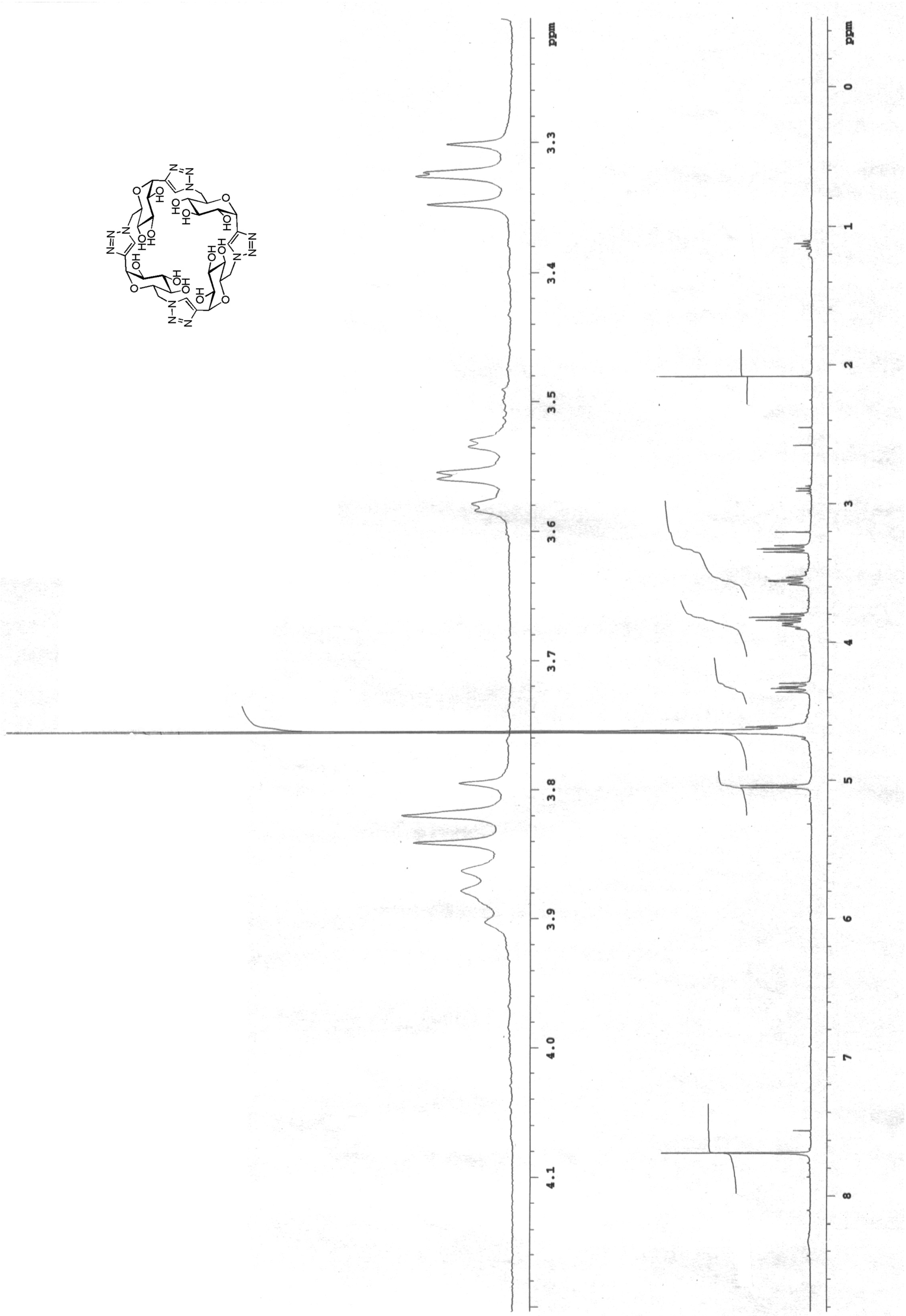
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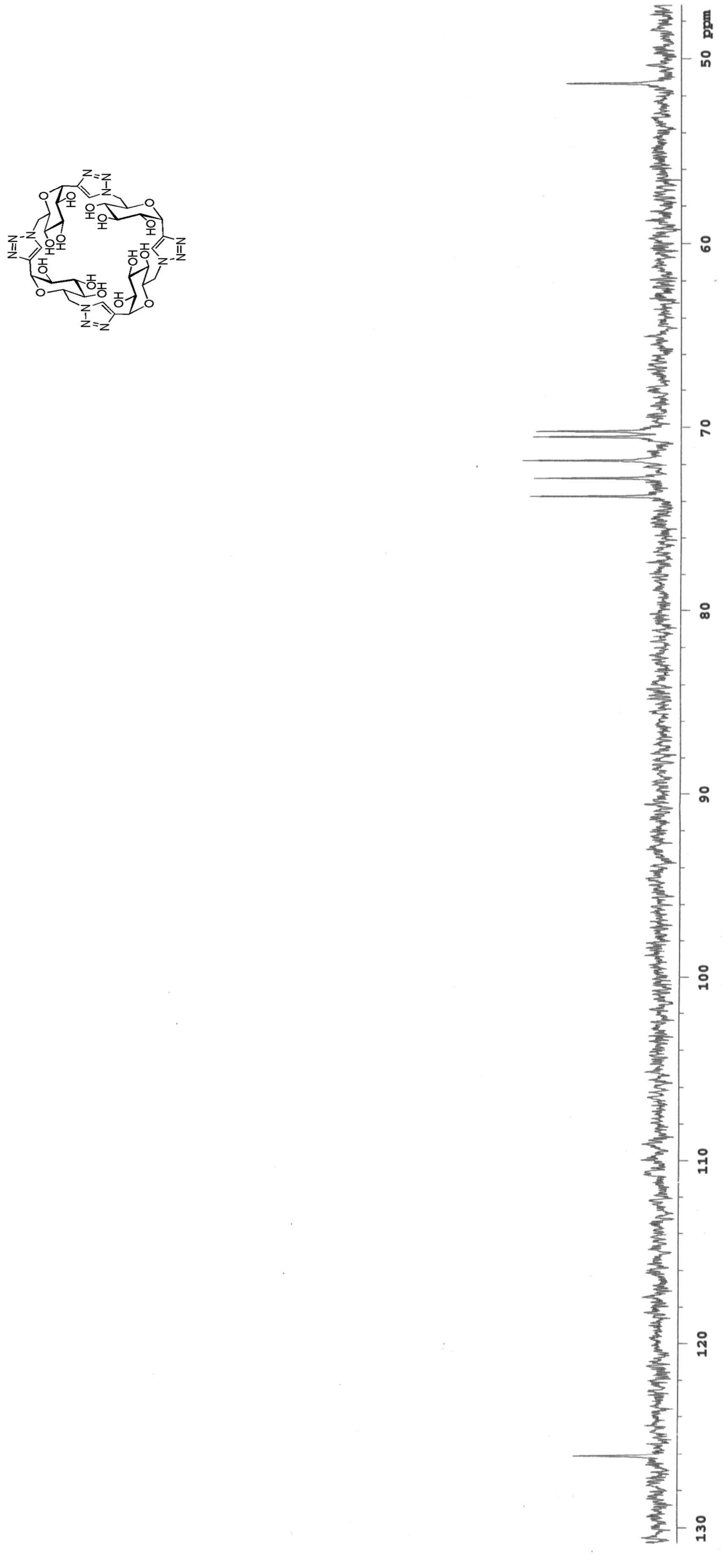
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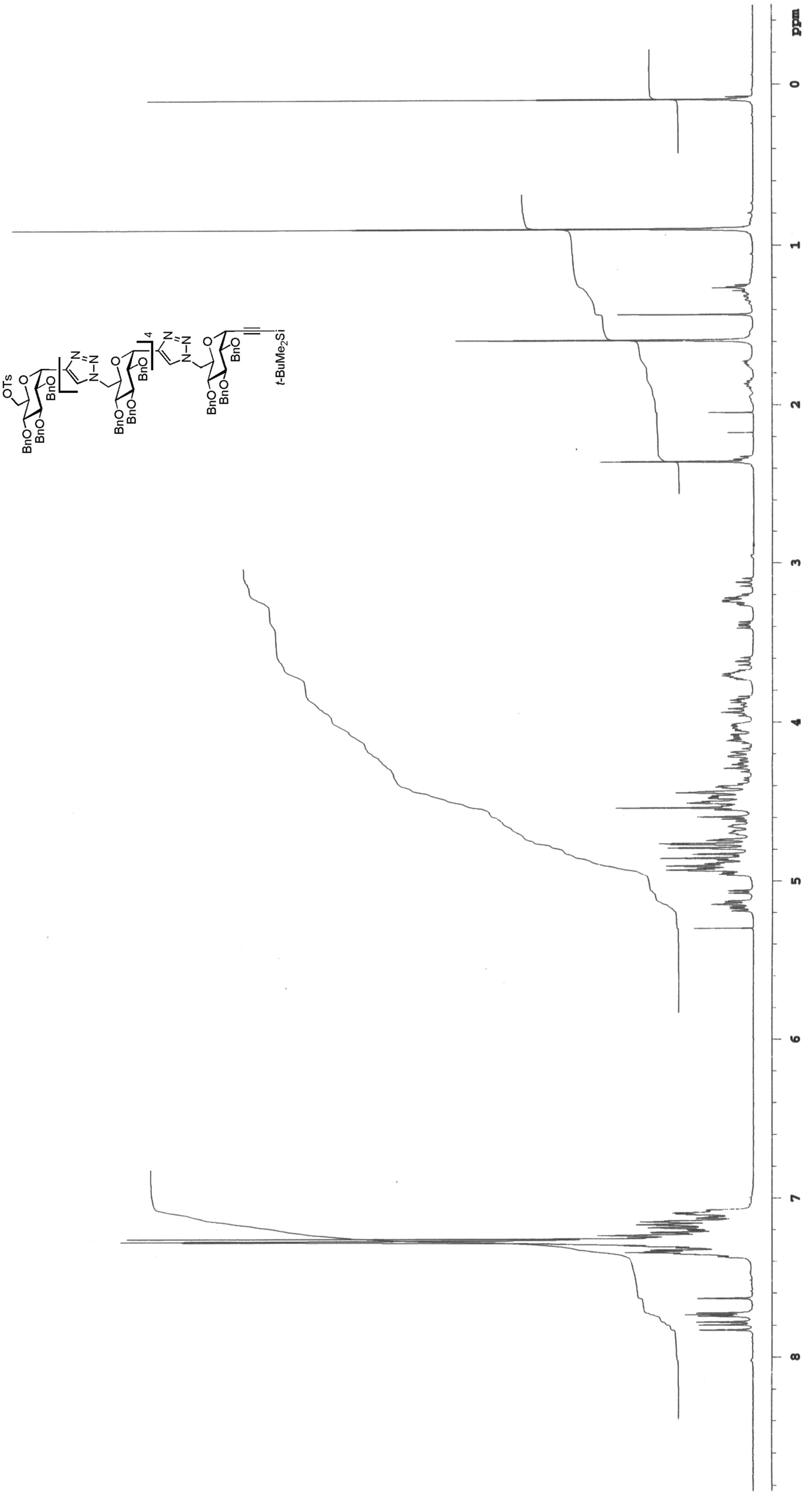
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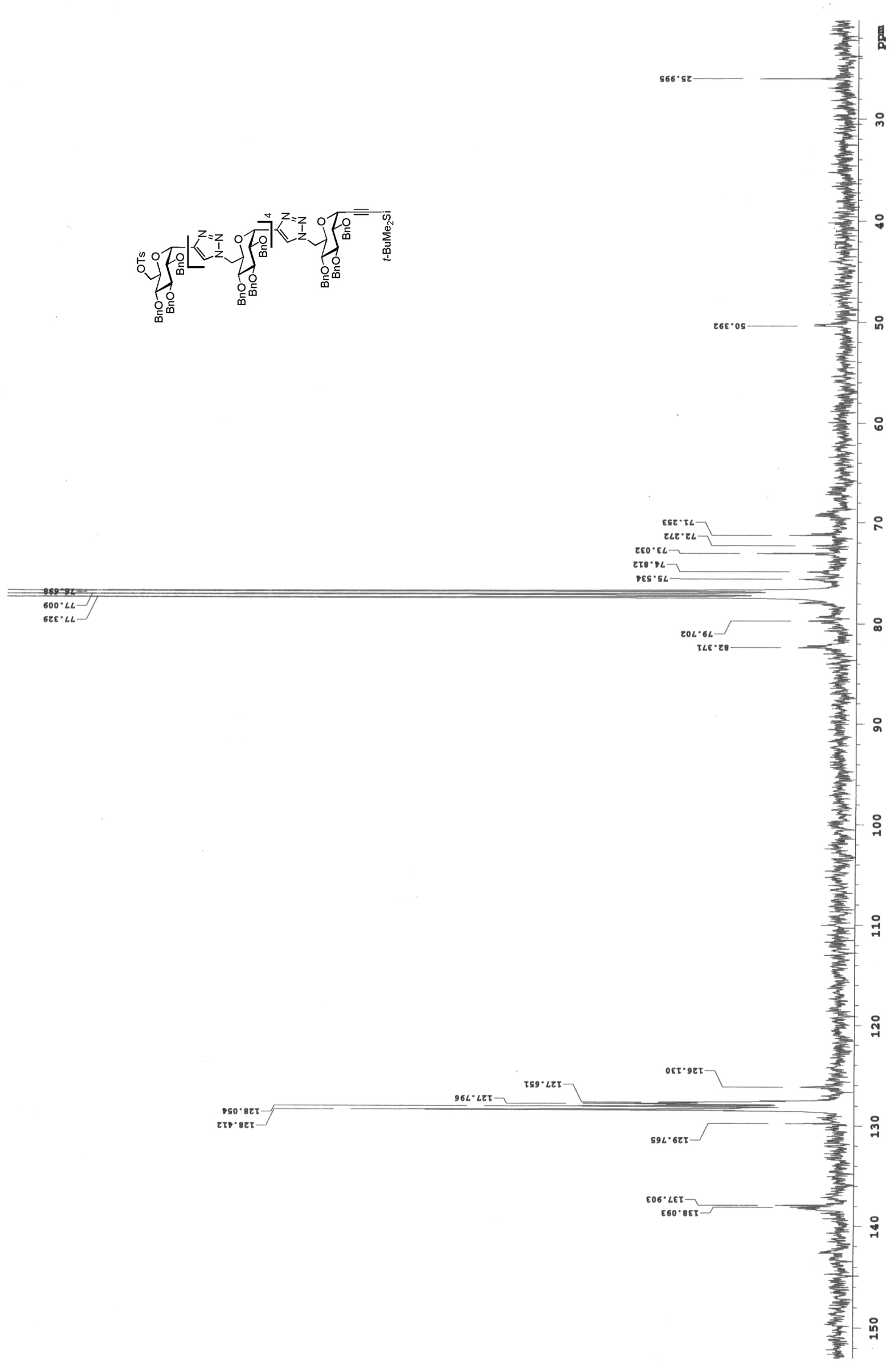
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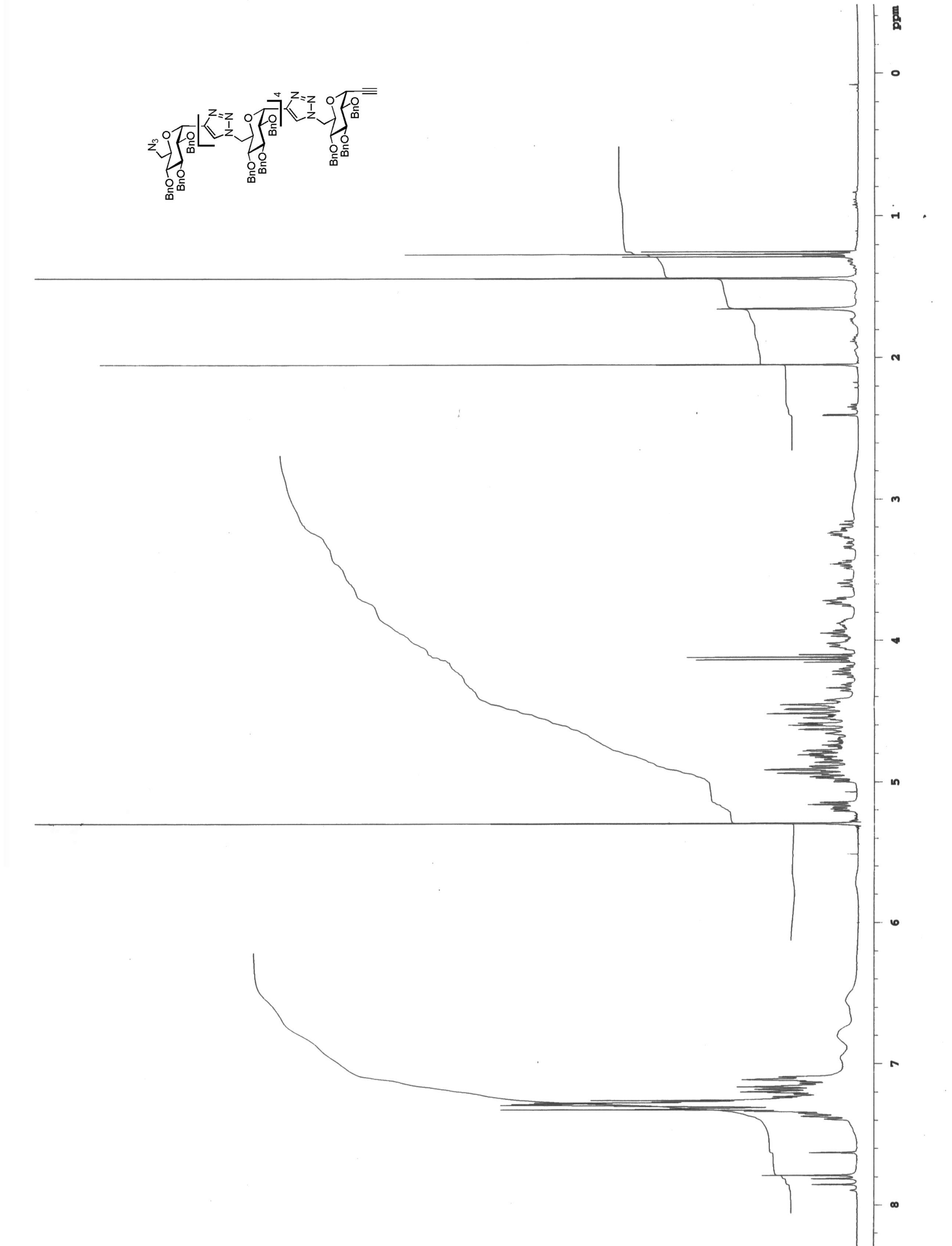
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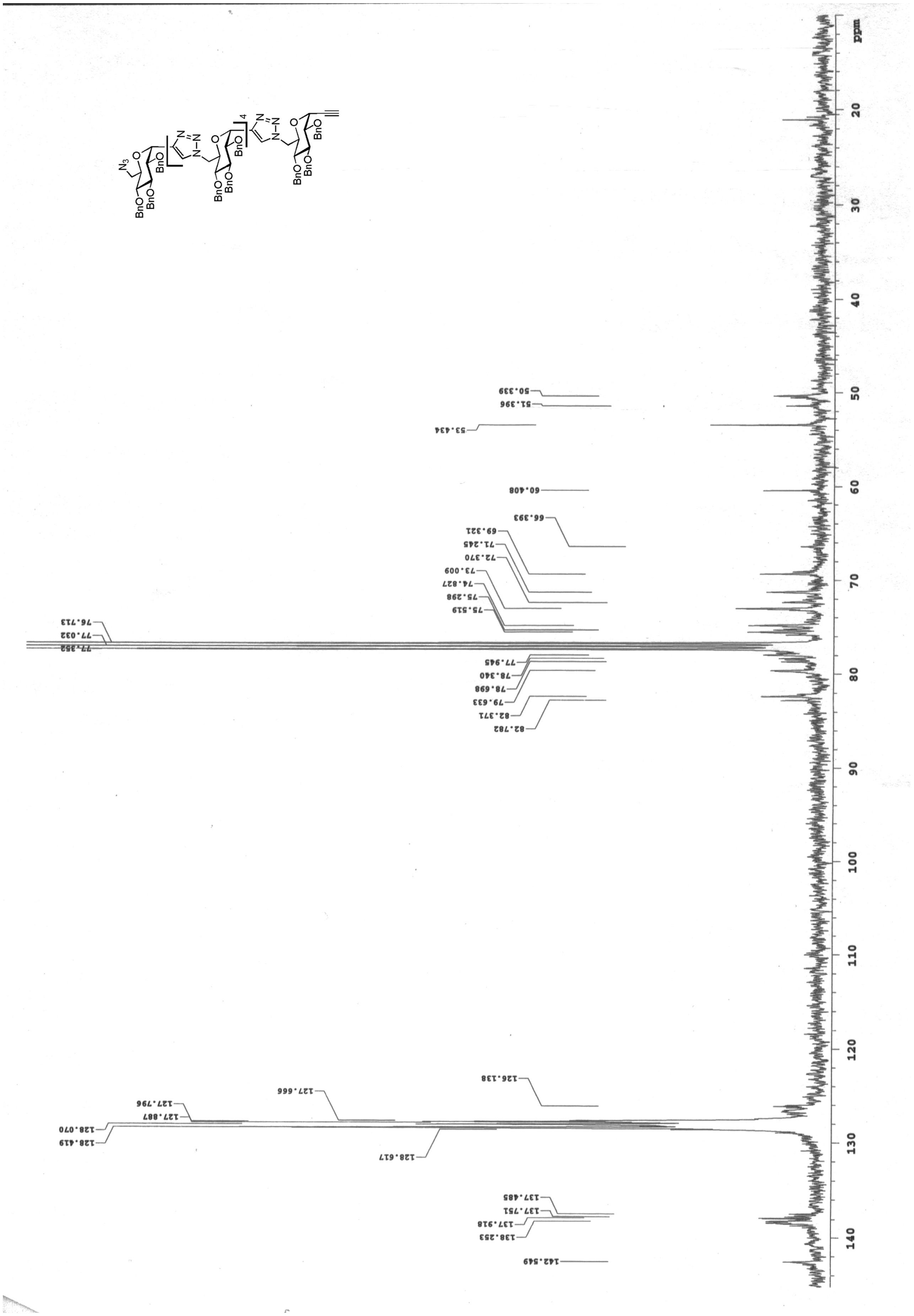
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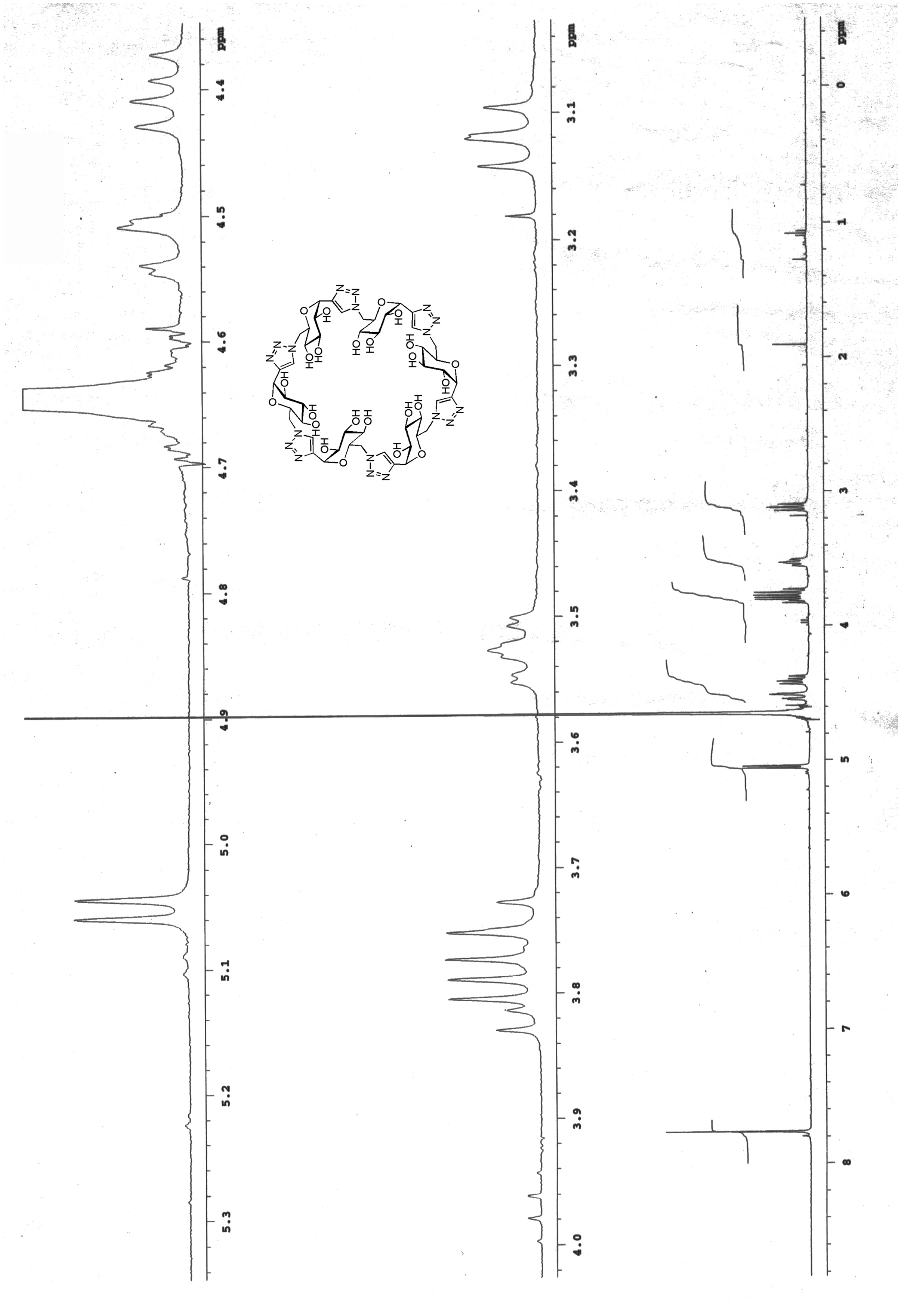
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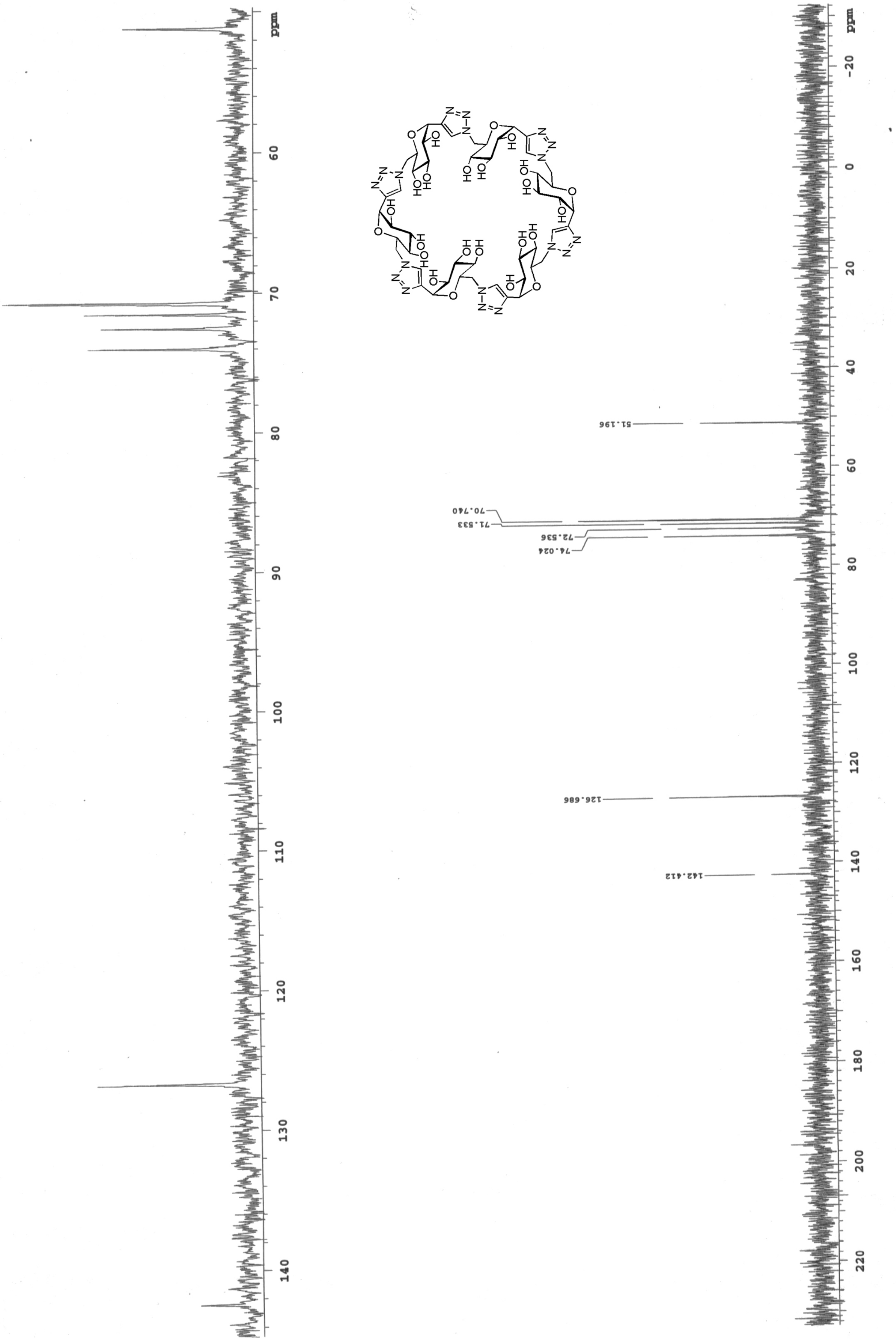
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