Stereoselective Glycosylations of 2-Azido-2-Deoxy-Glucosides Using Intermediate Sulfonium Ions

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Supporting Information

Experimental Data for Compounds

General Procedures. All reactions were carried out under a positive pressure of argon, unless otherwise noted. All chemicals were purchased from commercial suppliers and used without further purification. Dichloromethane was distilled from calcium hydride under N_2. Column chromatography was performed on silica gel 60 (EM Science, 70-230 mesh). Reactions were monitored by TLC on Kieselgel 60 F_{254} (EM Science) and the compounds were detected by examination under UV light and visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution followed by heating. Organic solutions were concentrated by rotary evaporation below 40 ^{o}C under reduced pressure. Molecular sieves (4Å), used for reactions, were crushed and activated *in vacuo* at 390 °C during 8 h and then for 2-3 h at 390 °C directly prior to application. Optical rotations were measured with a 'Jasco P-1020' polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Inova 300 spectrometer and a Varian Inova 500 spectrometer equipped with Sun workstations. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Data are presented as follow: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = double of doublet, m = multiplet and/or multiple resonances), integration, coupling constant in Hertz (Hz). High-resolution mass spectra were run in a JMS SX/SX102A tandem mass spectrometer, equipped with FAB source. The matrix used was DHB and the internal standards ultramark 1621 and PEG.

General procedure for the glycosylation reaction employing glycosyl donor 1a and 1b.

Protocol A. A mixture of glycosyl donor **1a** or **1b** (0.042 mmol), glycosyl acceptor (0.063 mmol) and activated molecular sieves (4Å) in DCM (2 mL) was stirred for 20 min under an atmosphere of argon at rt, then cooled to -78 ^{o}C or 0 ^{o}C. After the addition of trimethylsilyl trifluoromethanesulfonate (0.76 μL, 0.0042 mmol), the reaction mixture was stirred at -78 ^{o}C or 0 ^{o}C. When the donor was consumed as detected by TLC analysis, the reaction mixture was quenched with aq. $NaHCO_3$ (5 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by size exclusion LH-20 column (eluent MeOH/DCM = 1/1, v/v) to determine the α/β ratio. Then further purification was completed by silicagel column chromatography (n-hexane/ethyl acetate = 2/1).

Protocol B. A mixture of glycosyl donor **1a** or **1b** (0.042 mmol), glycosyl acceptor (0.063 mmol), activated molecular sieves (4Å) and thioether (0.42 mmol) in DCM (2 mL) was stirred for 20 min under an atmosphere of argon at rt, then cooled to -78 ^{o}C or 0 ^{o}C. After the addition of trimethylsilyl trifluoromethanesulfonate (0.76 μL, 0.0042 mmol), the reaction mixture was stirred at -78 ^{o}C or 0 ^{o}C. When the donor was consumed as detected by TLC analysis, the reaction mixture was quenched with aq. $NaHCO_3$ (5 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by size exclusion LH-20 column (eluent MeOH/DCM = 1/1, v/v) to determine the α/β ratio. Then further purification was completed by silicagel column chromatography (n-hexane/ethyl acetate = 2/1).

Methyl (3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside(7a, α); $[\alpha]^{20}_{D}$ = +82.0° (*c* = 5.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.98-7.95 (m, 4H, aromatic), 7.88-7.86 (m, 2H, aromatic), 7.54-7.25 (m, 9H, aromatic), 6.18 (t, 1H, *J* = 9.0 Hz, H-3'), 5.54 (t, 1H, *J* = 10.0 Hz, H-3), 5.54 (t, 1H, *J* = 9.0 Hz, H-4'), 5.26-5.23 (m, 2H, H-1', H-2'), 5.04 (t, 1H, *J* = 10.0 Hz, H-4), 5.01 (d, 1H, *J* = 3.0 Hz, H-1), 4.33-4.30 (m, 1H, H-5'), 4.21 (dd, 1H, *J* = 5.0, 12.0 Hz, H-6a), 4.18-4.15 (m, 1H, H-5), 4.07-4.00 (m, 1H, H-6b), 3.92 (dd, 1H, *J* = 3.5, 11.0 Hz, H-6a'), 3.69-3.67 (m, 1H, H-6b'), 3.51 (s, 3H, OCH_3), 3.32 (dd, 1H, *J* = 3.0, 10.0 Hz, H-2), 2.09 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.57, 169.91, 169.74,165.81(2), 165.37, 133.56, 133.37, 133.15, 129.94, 129.89, 129.71, 129.18, 129.06, 128.77, 128.52, 128.43, 128.29, 128.01, 97.83, 96.91, 72.09, 70.34, 70.30, 69.48, 68.41, 68.33, 67.76, 66.87, 61.77, 60.96, 55.69, 20.71, 20.67(2). HRMS (FAB) *m/z* calcd for $C_{40}H_{41}N_3O_{16}$ $(M+Na)^+$: 842.2385; found: 842.2382

Methyl (3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (8a, α); $[\alpha]^{20}_{D} = -2.76^{\circ}$ (c = 5.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-7.80 (m, 6H, aromatic), 7.51-7.23 (m, 9H, aromatic), 5.90 (dd, 1H, J = 3.5, 10.0 Hz, H-3'), 5.85 (t, 1H, J = 10.0 Hz, H-4'), 5.68-5.67 (m, 1H, H-2'), 5.53 (t, 1H, J = 10.0 Hz, H-3), 5.05-4.99 (m, 3H, H-1, H-1', H-4), 4.37-4.34 (m, 1H, H-5'), 4.18-4.09 (m, 2H, H-5, H-6b), 4.01-3.97 (m, 2H, H-6a', H-6a), 3.73-3.71 (m, 1H, H-6b'), 3.57 (s, 3H, OCH_3), 3.35 (dd, 1H, J = 3.5, 10.0 Hz, H-2), 2.09 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.51, 169.83, 169.71,165.62(2), 165.38, 133.60, 133.53, 133.15, 129.94, 129.84, 129.72, 129.30, 129.06, 128.86, 128.63, 128.53, 128.28, 98.63, 97.62, 70.63, 70.38, 69.97, 69.40, 68.41, 67.75, 67.25, 67.10, 61.74, 60.95, 55.54, 20.71, 20.65, 20.58. HRMS (FAB) *m/z* calcd for $C_{40}H_{41}N_3O_{16}$ $(M+Na)^+$: 842.2385; found: 842.2388

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (9a, α); $[\alpha]^{20}_{D} = +58.8^{\circ}$ (c = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52 (d, 1H, J = 5.0 Hz, H-1'), 5.47 (t, 1H, J = 10.0 Hz, H-3), 5.06 (t, 1H, J = 10.0 Hz, H-4), 5.04 (d, 1H, J = 3.0 Hz, H-1), 4.63 (dd, 1H, J = 2.0, 7.5 Hz, H-3'), 4.33-4.30 (m, 2H, H-2', H-4'), 4.16-4.03 (m, 4H, H-5, H-5', H-6a, H-6b), 3.85-3.77 (m, 2H, H-6a', H-6b'), 3.30 (dd, 1H, J = 3.0, 10.0 Hz, H-2), 2.09 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 1.56 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.33 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.67, 170.01, 169.73, 109.38, 108.78, 98.18, 96.25, 70.86, 70.59(2), 70.35, 68.40, 67.76, 67.61, 66.50, 61.79, 60.99, 26.09, 25.97, 24.97, 24.36, 20.73, 20.73, 20.64. HRMS (FAB) *m/z* calcd for $C_{24}H_{35}N_3O_{13}$ $(M+Na)^+$: 596.2068; found: 596.2066

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose (9a, β); $[\alpha]^{20}_{D}$ = -15.7° (*c* = 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 5.34 (d, 1H, *J* = 5.0 Hz, H-1'), 4.99 (t, 1H, *J* = 9.0 Hz, H-3), 4.98 (t, 1H, *J* = 9.0 Hz, H-4), 4.62-4.60 (m, 1H, H-6b), 4.57 (d, 1H, *J* = 9.0 Hz, H-1), 4.32-4.25 (m, 3H, H-2', H-3', H-6a), 4.13-4.04 (m, 3H, H-4', H-5', H-6a'), 3.85-3.81 (m, 1H, H-6b'), 3.66-3.65 (m, 1H, H-5), 3.50 (t, 1H, *J* = 9.0 Hz, H-2), 2.08 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 1.53 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.35 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.65, 169.97, 169.66, 109.43, 108.74, 102.27, 96.23, 72.53, 71.75, 71.24, 70.71, 70.39, 69.12, 68.49, 67.63, 63.73, 61.92, 25.98, 25.97, 24.94, 24.38, 20.71, 20.70, 20.60. HRMS (FAB) *m/z* calcd for $C_{24}H_{35}N_3O_{13}$ $(M+Na)^+$: 596.2068; found: 596.2068

Methyl (3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside(10a, α); $[\alpha]^{20}_{D}$ = +91.1° (*c* = 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.46-7.35 (m, 10H, aromatic), 5.56 (s, 1H, C*H*Ph), 5.52 (d, 1H, *J* = 4.0 Hz, H-1), 5.50 (t, 1H, *J* = 10.0 Hz, H-3), 4.99 (t, 1H, *J* = 10.0 Hz, H-4), 4.74 (d, 1H, *J* = 3.5 Hz, H-1'), 4.67 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.62 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.40-4.38 (m, 1H, H-5), 4.29-4.23 (m, 2H, H-3', H-4'), 4.14-4.10 (m, 1H, H-6a'), 3.86-3.74 (m, 4H, H-6a, H-6b, H-6b', H-5'), 3.61 (dd, 1H, *J* = 3.0, 10.0 Hz, H-2'), 3.41(s, 3H, OCH_3), 3.12 (dd, 1H, *J* = 4.0, 10.0 Hz, H-2), 2.09 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.66, 170.18, 169.55, 137.30, 137.09, 129.52, 128.72, 128.64, 128.54, 128.48, 128.40, 128.32, 128.04, 127.95, 127.84, 127.03, 128.64, 128.43, 128.28, 125.99, 101.49, 98.19, 97.80, 82.25, 77.76, 74.15, 72.70, 70.23, 68.94, 68.09, 67.40, 61.96, 61.18, 60.64, 55.33, 20.77, 20.69, 20.53; HRMS (FAB) *m/z* calcd for $C_{33}H_{39}N_3O_{13}$ $(M+Na)^+$: 708.2381; found: 708.2381

Methyl (3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside(10a, β); $[\alpha]^{20}_{D}$ = +8.8° (*c* = 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.48-7.32 (m, 10H, aromatic), 5.50 (s, 1H, C*H*Ph), 5.00 (t, 1H, *J* = 9.0 Hz, H-3), 4.95 (t, 1H, *J* = 9.0 Hz, H-4), 4.89 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.83 (d, 1H, *J* = 9.0 Hz, H-1), 4.56 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.49 (d, 1H, *J* = 3.5 Hz, H-1'), 4.29-4.16 (m, 3H, H-3', H-6a, H-6b), 3.99-3.96 (m, 1H, H-4'), 3.82-3.67 (m, 3H, H-6a', H-5', H-2'), 3.62-3.52 (m, 3H, H-2, H-6b', H-5'), 3.12(s, 3H, OCH_3), 2.08 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.70, 170.01, 169.66, 137.34, 128.99, 128.66, 128.52, 128.30, 128.13, 126.05, 101.84, 101.05, 98.45, 80.23, 79.28, 77.22, 73.75, 72.73, 71.50, 68.89, 68.42, 63.91, 62.32, 62.08, 55.32, 20.74, 20.68, 20.60; HRMS (FAB) *m/z* calcd for $C_{33}H_{39}N_3O_{13}$ $(M+Na)^+$: 708.2381; found: 708.2387

Methyl (3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (11a, α); $[\alpha]^{20}_{D}$ = +14.2° (*c* = 5.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.36-7.27 (m, 15H, aromatic), 5.81 (d, 1H, *J* = 4.0 Hz, H-1), 5.40 (t, 1H, *J* = 10.0 Hz, H-3), 5.14 (d, 1H, *J* = 10.0 Hz, C*H*HPh), 4.99 (t, 1H, *J* = 10.0 Hz, H-4), 4.80 (d, 1H, *J* = 10.0 Hz, C*H*HPh), 4.74 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.63 (d, 1H, *J* = 3.0 Hz, H-1'), 4.61 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.58 (s, 2H, C*H*HPh), 4.13-4.08 (m, 2H, H-3', H-6a), 3.95-3.91 (m, 2H, H-5, H-6a'), 3.83-3.66 (m, 4H, H-6b, H-5', H-4', H-6b'), 3.58 (dd, 1H, *J* = 3.0, 10.0 Hz, H-2'), 3.39(s, 3H, OCH_3), 3.23 (dd, 1H, *J* = 4.0, 10.0 Hz, H-2), 2.07 (s, 3H, $COCH_3$), 2.01 (s, 3H,

$COCH_3$), 1.98 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.42, 169.96, 169.46, 138.56, 137.86, 137.81, 131.03, 129.30, 128.50, 128.42, 128.35, 128.13, 128.01, 127.69, 127.47, 127.37, 124.75, 97.60, 97.35, 81.76, 80.52, 74.86, 73.54, 73.53, 73.20, 70.32, 69.30, 69.13, 68.18, 67.98, 61.44, 60.87, 55.35, 20.67, 20.66, 20.59; HRMS (FAB) *m/z* calcd for $C_{40}H_{47}N_3O_{13}$ $(M+Na)^+$: 800.3007; found: 800.3001

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (7b, α); $[\alpha]^{20}_{D}$ = +137.8° (*c* = 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.98-7.96 (m, 4H, aromatic), 7.88-7.86 (m, 2H, aromatic), 7.52-7.27 (m, 14H, aromatic), 6.17 (t, 1H, *J* = 10.0 Hz, H-3'), 5.64 (t, 1H, *J* = 9.0 Hz, H-3), 5.20 (t, 1H, *J* = 10.0 Hz, H-4'), 5.26-5.23 (m, 2H, H-1', H-2'), 4.96 (d, 1H, *J* = 3.0 Hz, H-1), 4.63 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.57 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.33-4.16 (m, 3H, H-5', H-6a, H-6b), 4.10-4.07 (m, 1H, H-5), 3.92-3.89 (m, 1H, H-6a'), 3.64-3.62 (m, 1H, H-6b'), 3.58 (t, 1H, *J* = 9.0 Hz, H-4), 3.50 (s, 3H, OCH_3), 3.12 (dd, 1H, *J* = 3.0, 9.0 Hz, H-2), 2.07 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.54, 169.73, 165.79,165.77, 165.33, 137.35, 133.49, 133.30, 133.05, 129.94, 129.71, 129.21, 129.11, 128.80, 128.55, 128.45, 128.39, 128.26, 128.08, 127.98, 98.07, 96.86, 75.95, 74.34, 72.09, 71.95, 70.35, 69.53, 68.79, 68.36, 66.84, 62.59, 61.33, 55.72, 20.93, 20.79. HRMS (FAB) *m/z* calcd for $C_{45}H_{45}N_3O_{15}$ $(M+Na)^+$: 890.2748; found: 890.2748

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (8b, α); $[\alpha]^{20}_{D}$ = +38.6° (*c* = 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.11-8.09 (m, 2H, aromatic), 7.96-7.94 (m, 2H, aromatic), 7.91-7.81 (m, 2H, aromatic), 7.61-7.22 (m, 14H, aromatic), 5.88 (dd, 1H, *J* = 3.0, 10.0 Hz, H-3'), 5.80 (t, 1H, *J* = 10.0 Hz, H-4'), 5.67 (dd, 1H, *J* = 2.0, 3.0 Hz, H-2'), 5.64 (dd, 1H, *J* = 10.0, 11.0 Hz, H-3), 4.96 (d, 1H, *J* = 2.0, Hz, H-1'), 4.96 (d, 1H, *J* = 3.0, Hz, H-1), 4.62 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.55 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.36-4.33 (m, 1H, H-5'), 4.25-4.23 (m, 1H, H-6a), 4.14-4.05 (m, 2H, H-6b, H-5), 3.99-3.95 (m, 1H, H-6b'), 3.68-3.66 (m, 1H, H-6a'), 3.57 (t, 1H, *J* = 11.0 Hz, H-4), 3.55 (s, 3H, OCH_3), 3.14 (dd, 1H, *J* = 3.0, 10.0 Hz, H-2), 2.07 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.50, 169.66, 165.61(2), 165.39, 137.31, 133.51, 133.48, 133.10, 129.96, 129.88, 129.73, 129.34, 129.11, 128.89, 128.62, 128.56, 128.47, 128.26, 128.12, 128.02, 98.60, 97.85, 75.93, 74.45, 72.04, 70.62, 69.99, 69.40, 68.84, 67.33, 67.07, 62.56, 61.33, 55.58, 20.94, 20.73. HRMS (FAB) *m/z* calcd for $C_{45}H_{45}N_3O_{15}$ $(M+Na)^+$: 890.2748; found: 890.2748

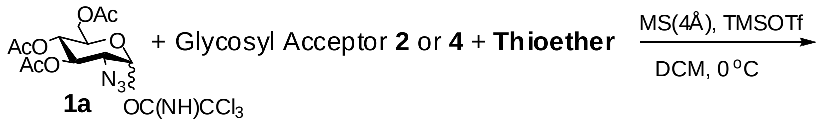
3,6-Di-*O*-acetyl-4-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (9b, α); $[\alpha]^{20}_{D}$ = +104.8° (*c* = 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.22 (m, 5H, aromatic), 5.57 (dd, 1H, *J* = 9.0, 11.0 Hz, H-3), 5.50 (d, 1H, *J* = 5.0 Hz, H-1'), 5.00 (d, 1H, *J* = 3.0 Hz, H-1), 4.62-4.55 (m, 3H, H-3', H-4', C*H*HPh), 4.33-4.26 (m, 4H, H-2', H-6b', H-6a, C*H*HPh), 4.09-4.06 (m, 1H, H-5), 4.02-4.00 (m, 1H, H-5'), 3.82-3.80 (m, 1H, H-6a'), 3.75-3.73 (m, 1H, H-6b), 3.59 (t, 1H, *J* = 9.0 Hz, H-4), 3.12 (dd, 1H, *J* = 3.0, 11.0 Hz, H-2), 2.12 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 1.64 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.64, 169.82, 137.34, 128.55, 128.08, 127.95, 109.27, 108.76, 98.29, 96.22, 75.94, 74.17, 71.84, 70.77, 70.63, 70.57, 68.63, 67.23, 66.32, 62.70, 61.39, 26.11, 25.97, 24.97, 24.33, 20.94, 20.88; HRMS (FAB) *m/z* calcd for $C_{29}H_{39}N_3O_{12}$ $(M+Na)^+$: 644.2431; found: 644.2439

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside(10b, α); $[\alpha]^{20}_D$ = +173.6° (*c* = 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.47-7.22 (m, 15H, aromatic), 5.60 (dd, 1H, *J* = 9.0, 11.0 Hz, H-3), 5.56 (s, 1H, C*H*Ph), 5.48 (d, 1H, *J* = 3.5 Hz, H-1), 4.70 (d, 1H, *J* = 3.5 Hz, H-1'), 4.62 (s, 2H, C*H*HPh), 4.55 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.49 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.35-4.26 (m, 2H, H-5, H-5'), 4.22 (t, 1H, *J* = 9.0 Hz H-3'), 4.08-4.06 (m, 1H, H-6a), 3.99 (dd, 1H, *J* = 3.5, 12.0 Hz, H-6b), 3.79-3.72 (m, 3H, H-4', H-6a', H-6b'), 3.59 (dd, 1H, *J* = 3.5, 9.0 Hz, H-2'), 3.55(t, 1H, *J* = 11.0 Hz, H-4), 3.88(s, 3H, OCH_3), 2.98 (dd, 1H, *J* = 3.5, 9.0 Hz, H-2), 2.06 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.74, 170.24, 137.89, 137.41, 129.17, 128.83, 128.65, 128.45, 128.13, 128.07, 126.21, 101.64, 98.53, 98.41, 82.46, 78.07, 75.92, 74.61, 74.56, 73.24, 72.36, 69.17, 68.75, 62.44, 62.16, 61.22, 55.53, 21.20, 21.05; HRMS (FAB) *m/z* calcd for $C_{38}H_{43}N_3O_{12}$ $(M+Na)^+$: 756.2744; found: 756.2740

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (11b, α); $[\alpha]^{20}_D$ = +79.6° (*c* = 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.34-7.20 (m, 20H, aromatic), 5.76 (d, 1H, *J* = 4.0 Hz, H-1), 5.47 (t, 1H, *J* = 10.0 Hz, H-3), 5.11 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.78 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.71 (d, 1H, *J* =

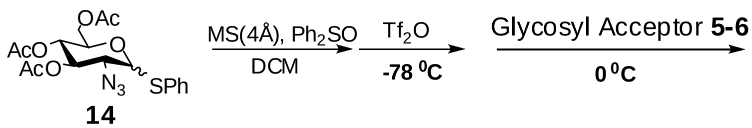
12.0 Hz, C*H*HPh), 4.61 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.62-4.47 (m, 5H, H-1', C*H*HPh), 4.11 (t, 1H, *J* = 10.0 Hz, H-3'), 4.07-3.99 (m, 2H, H-6a, H-5'), 3.89-3.79 (m, 3H, H-6b, H-4', H-5), 3.72 (dd, 1H, *J* = 3.5, 11.0 Hz, H-6a'), 3.64-3.54 (m, 2H, H-6b', H-2'), 3.49 (t, 1H, *J* = 10.0 Hz, H-4), 3.38 (s, 3H, OCH_3), 3.04 (dd, 1H, *J* = 4.0, 10.0 Hz, H-2), 2.06 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.37, 169.79, 138.71, 137.88, 137.85, 137.33, 129.45, 129.21, 128.99, 128.83, 128.63, 128.54, 128.51, 128.39, 128.32, 128.17, 128.12, 128.03, 127.74, 127.56, 127.42, 126.23, 124.27, 97.60, 97.59, 81.84, 80.55, 77.22, 75.70, 74.81, 74.65, 73.49, 73.23(2), 72.14, 69.28, 69.12, 62.43, 61.25, 55.32, 20.93, 20.81; HRMS (FAB) *m/z* calcd for $C_{45}H_{51}N_3O_{12}$ $(M+Na)^+$: 848.3370; found: 848.3377

Table 3. Glycosylation of acceptors **2** and **4** in the presence of various thioethers.



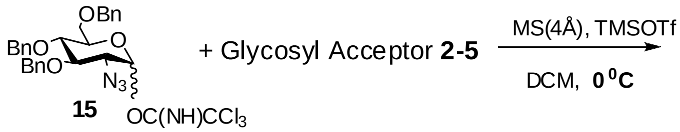
Thioether	Glycosyl Acceptor **2** product, α/β (yield)	Glycosyl Acceptor **4** product, α/β (yield)
PhSEt	**7a**, 20/1 (94%)	**9a**, 5/1 (92%)
PhSPh	**7a**, 12/1 (97%)	**9a**, 3/1 (95%)
$PhSCH_2Cl$	**7a**, 9/1 (92%)	**9a**, 5/1 (97%)
Thiophene	**7a**, α-only (91%)	**9a**, 14/1 (95%)
Selenophene	**7a**, 15/1 (94%)	**9a**, 4/1 (93%)
$PhSPh\text{-}NO_2$	**7a**, 10/1 (77%)	**9a**, 3/1 (85%)
CH_3SCH_3	Donor decomposition only	Donor decomposition only

Table 4. Glycosylations of thioglycosyl donor **14** with secondary glycosyl acceptors **5** and **6** in the presence or absence of thioethers.

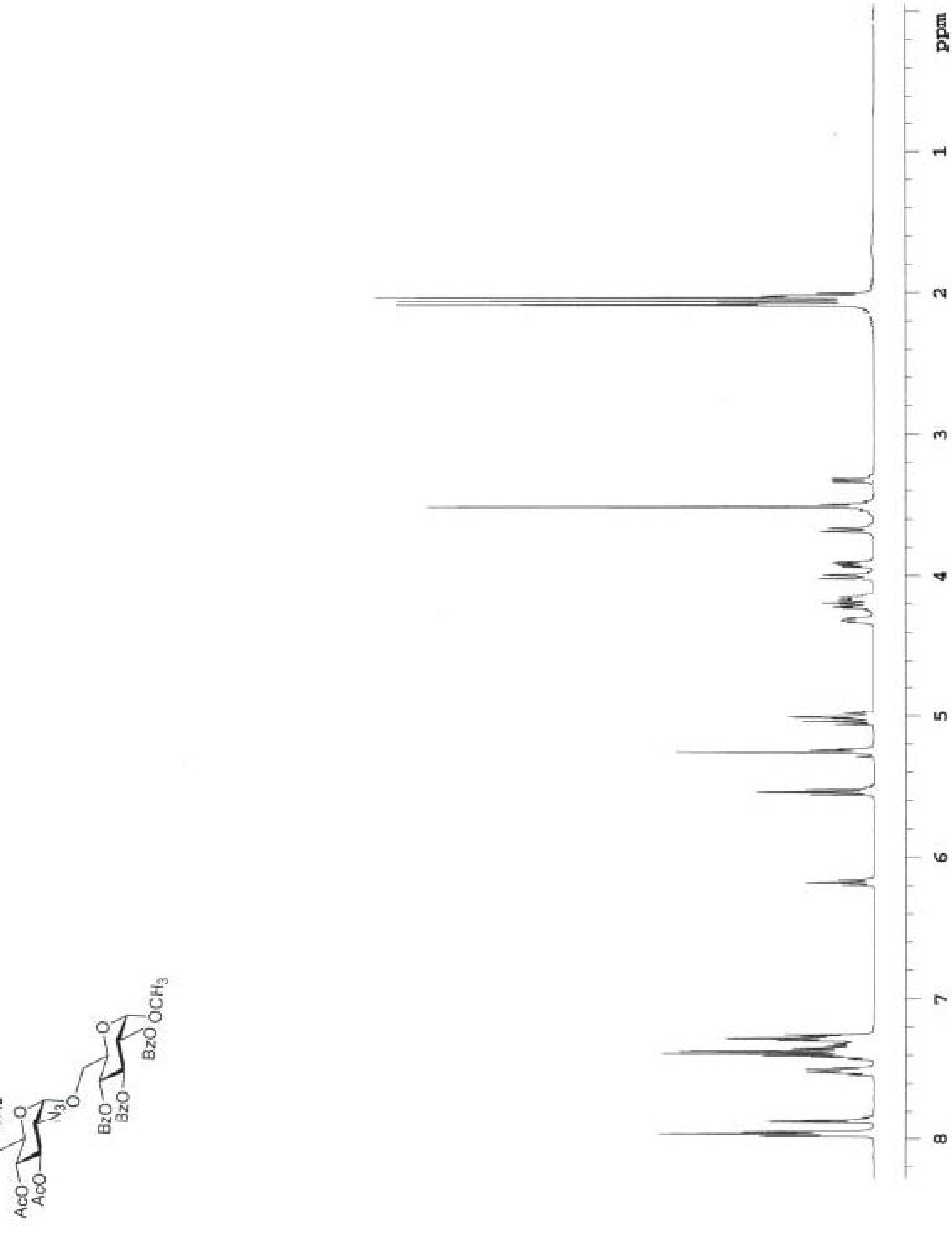


Accept.	Thioether	product, α/β (yield)
5	none	**10a**, 2/1 (60%)
5	PhSET	**10a**, 14/1 (76%)
5	thiophene	**10a**, 17/1 (74%)
6	none	**11a**, α only (40%)
6	PhSEt	**11a**, α only (45%)
6	thiophene	**11a**, α only (40%)

Table 5. Glycosylations of 2-deoxy-2-azido-3,4,6-*O*-tri-benzyl-D-glucopyranose trichloroacetimidate **15** with glycosyl acceptors **2**-**5** in the presence or absence of thiophene



Accept.	Temp.	Thioether	product, α/β (yield)
2	0 °C	none	3/1 (80%)
2	0 °C	thiophene	3/1 (82%)
3	0 °C	none	3/1 (83%)
3	0 °C	thiophene	4/1 (81%)
4	0 °C	none	1/2 (95%)
4	0 °C	thiophene	1/2 (96%)
5	0 °C	none	1/2 (45%)
5	0 °C	thiophene	1/1 (48%)



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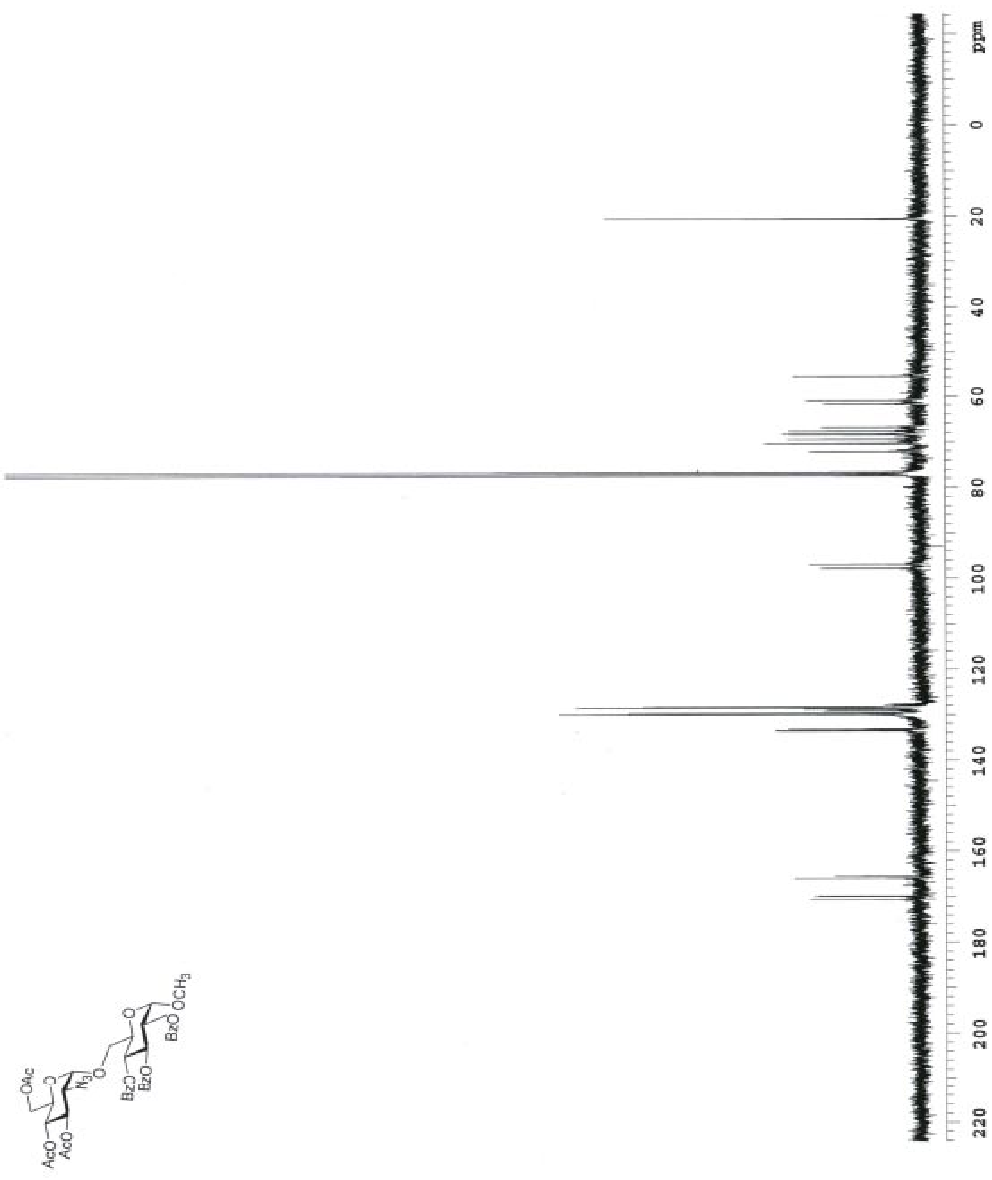

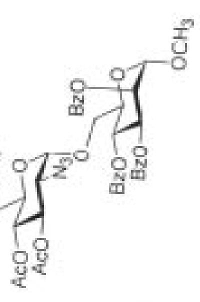
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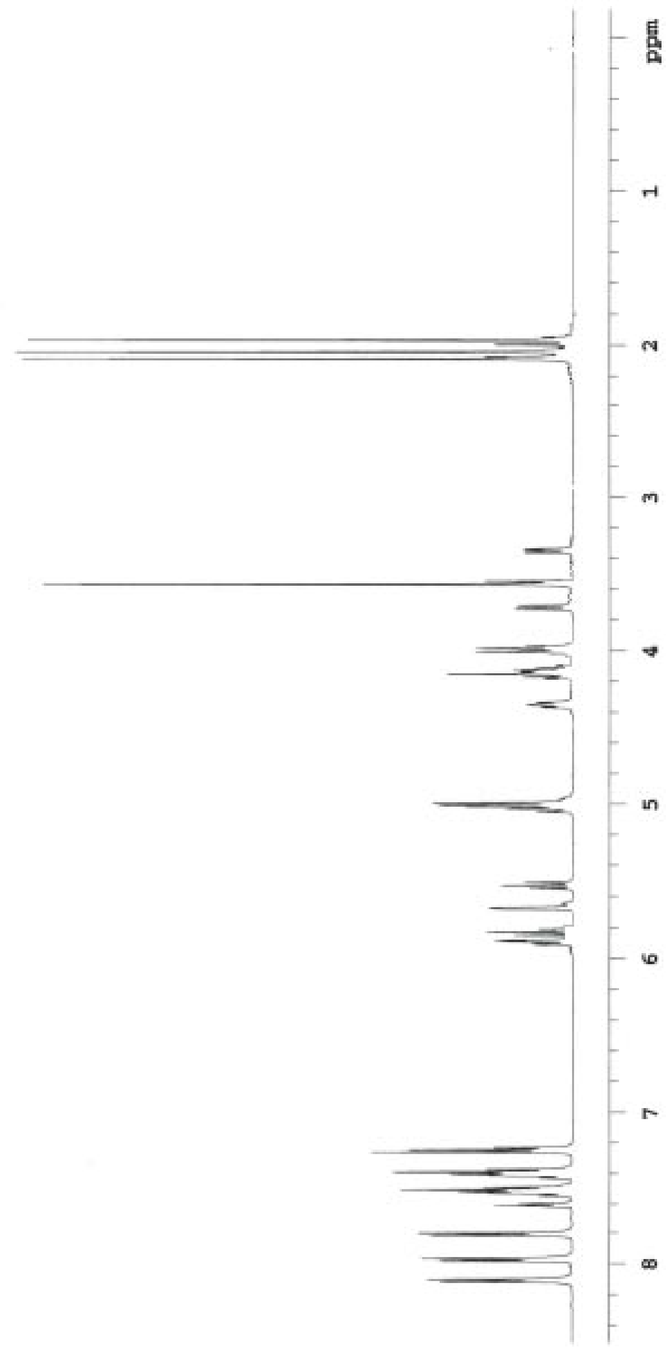
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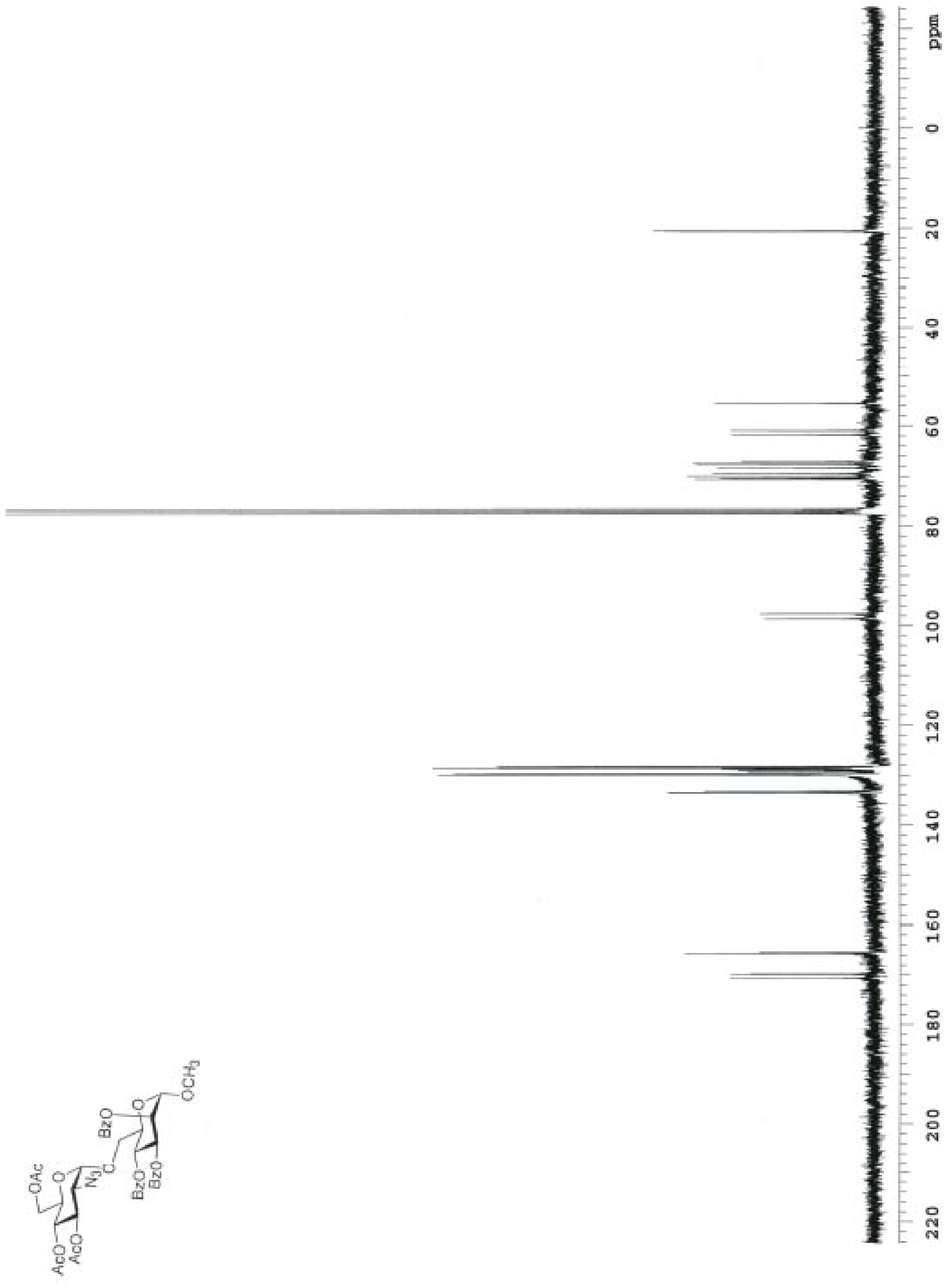

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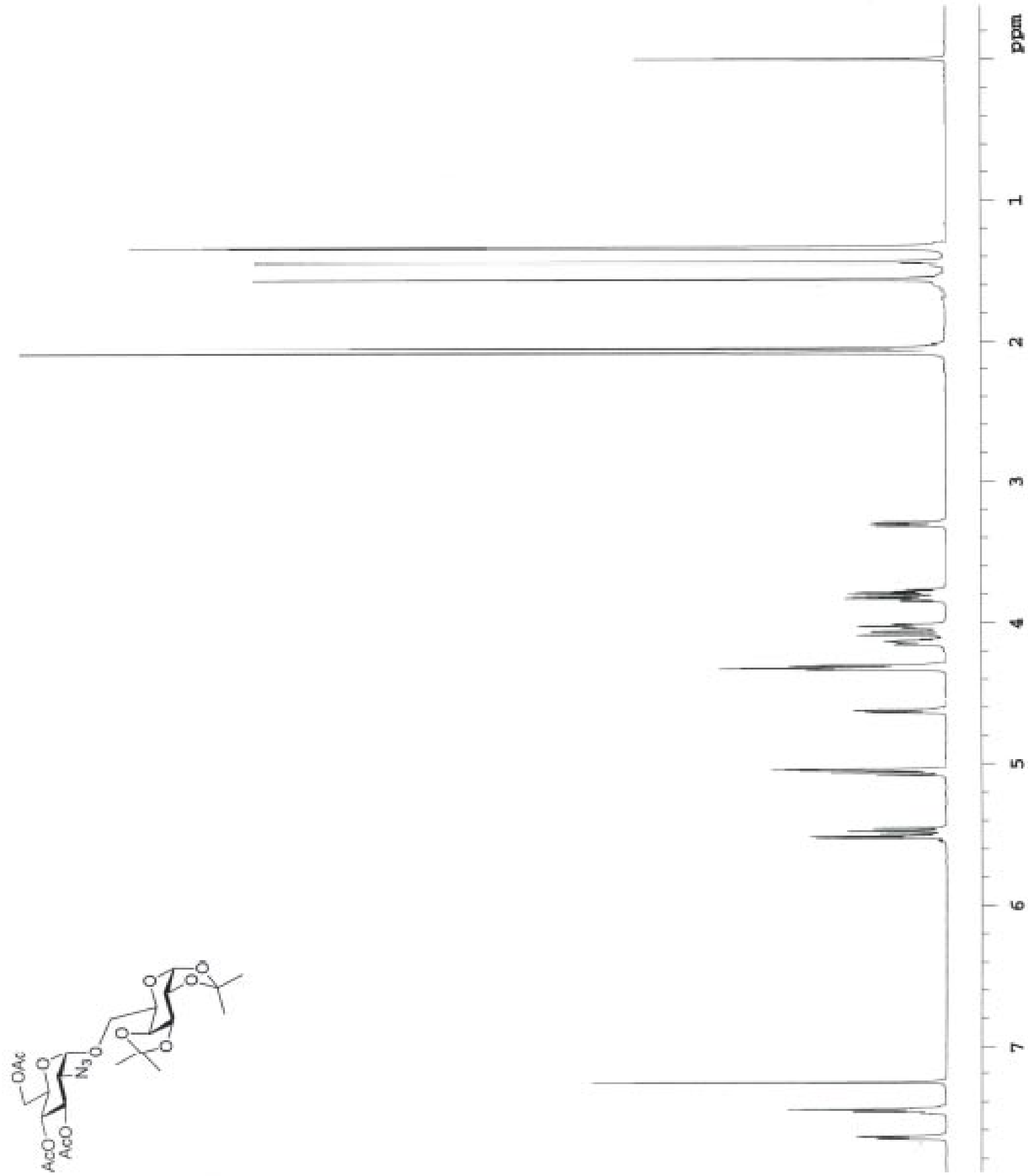

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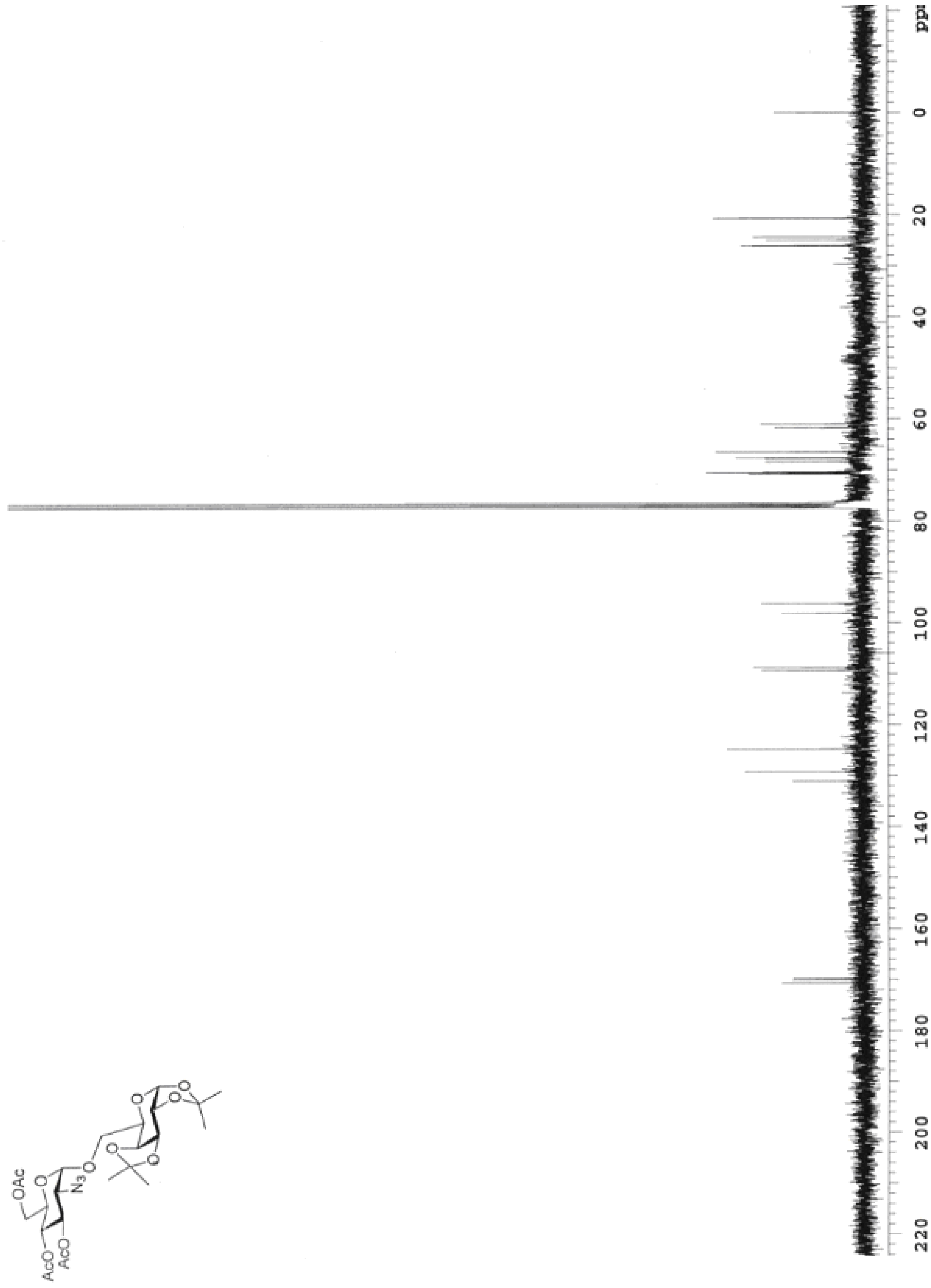
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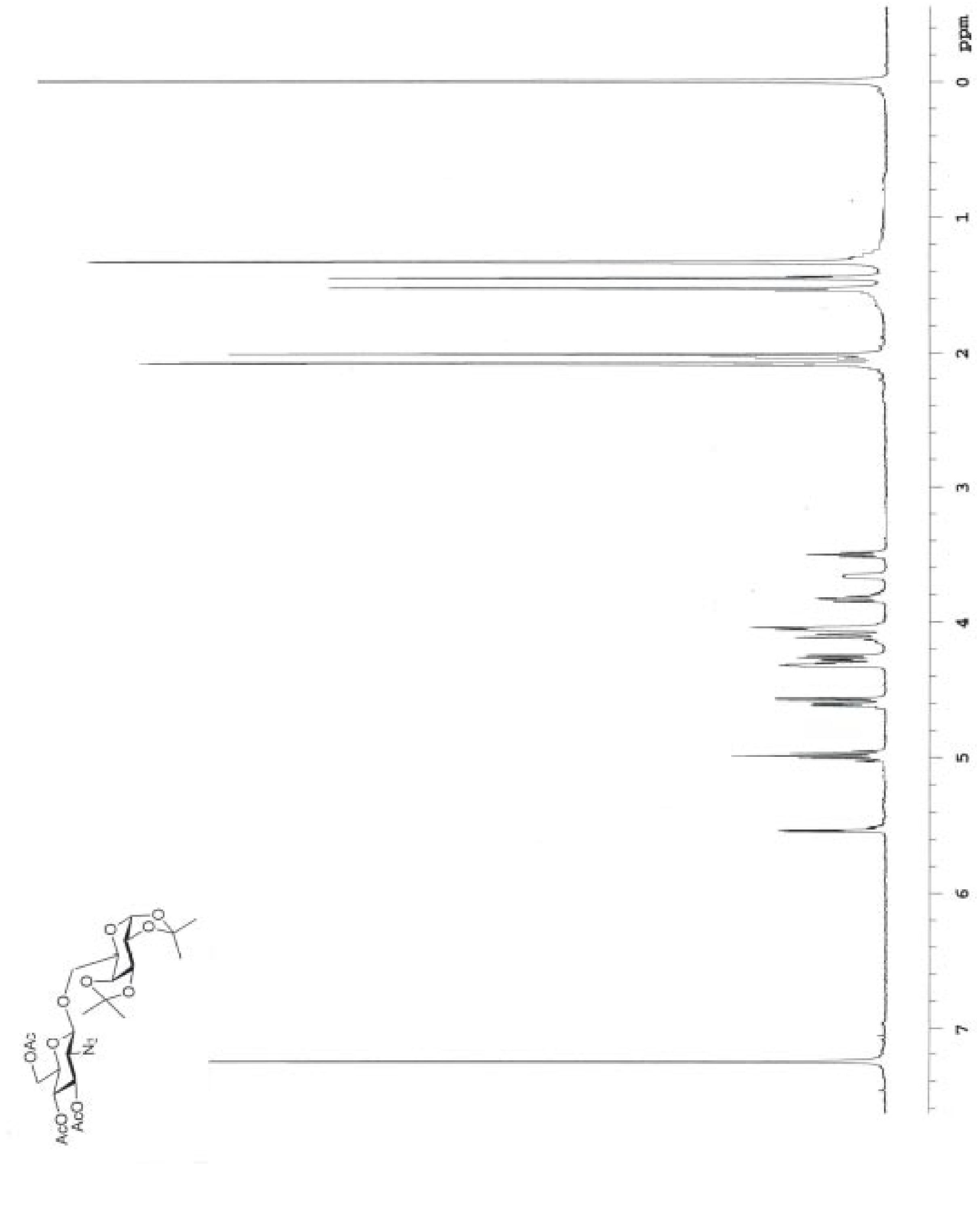

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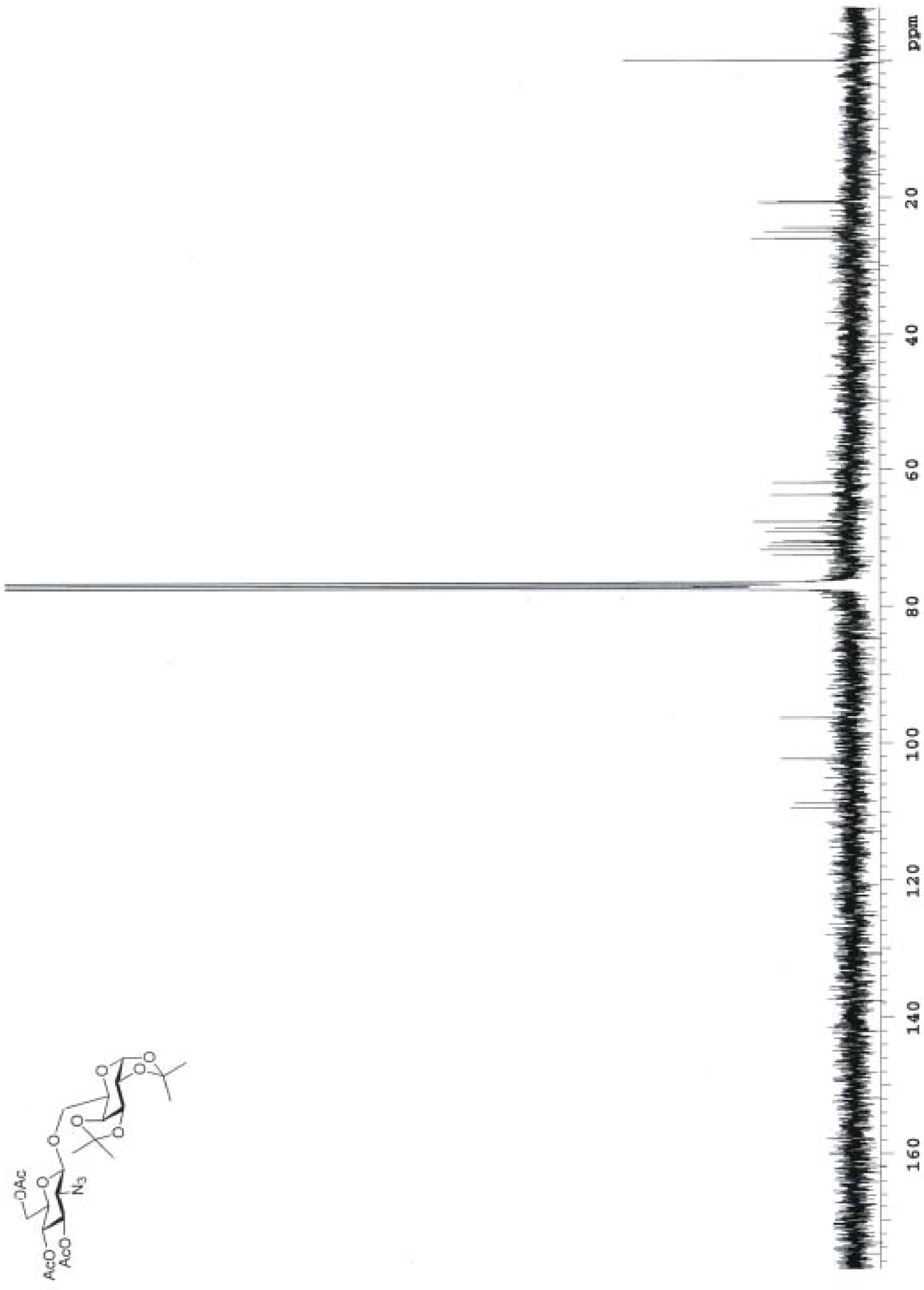
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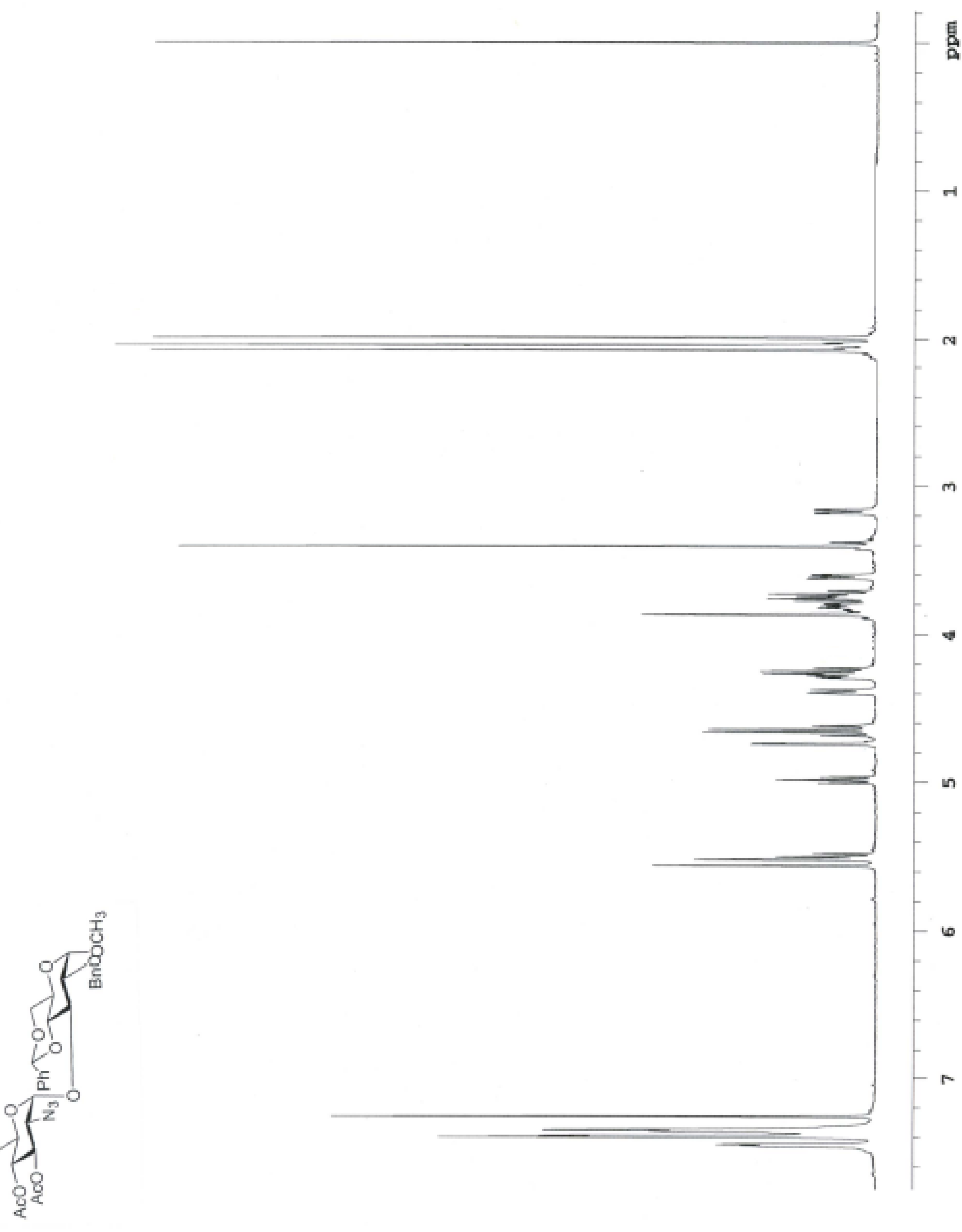

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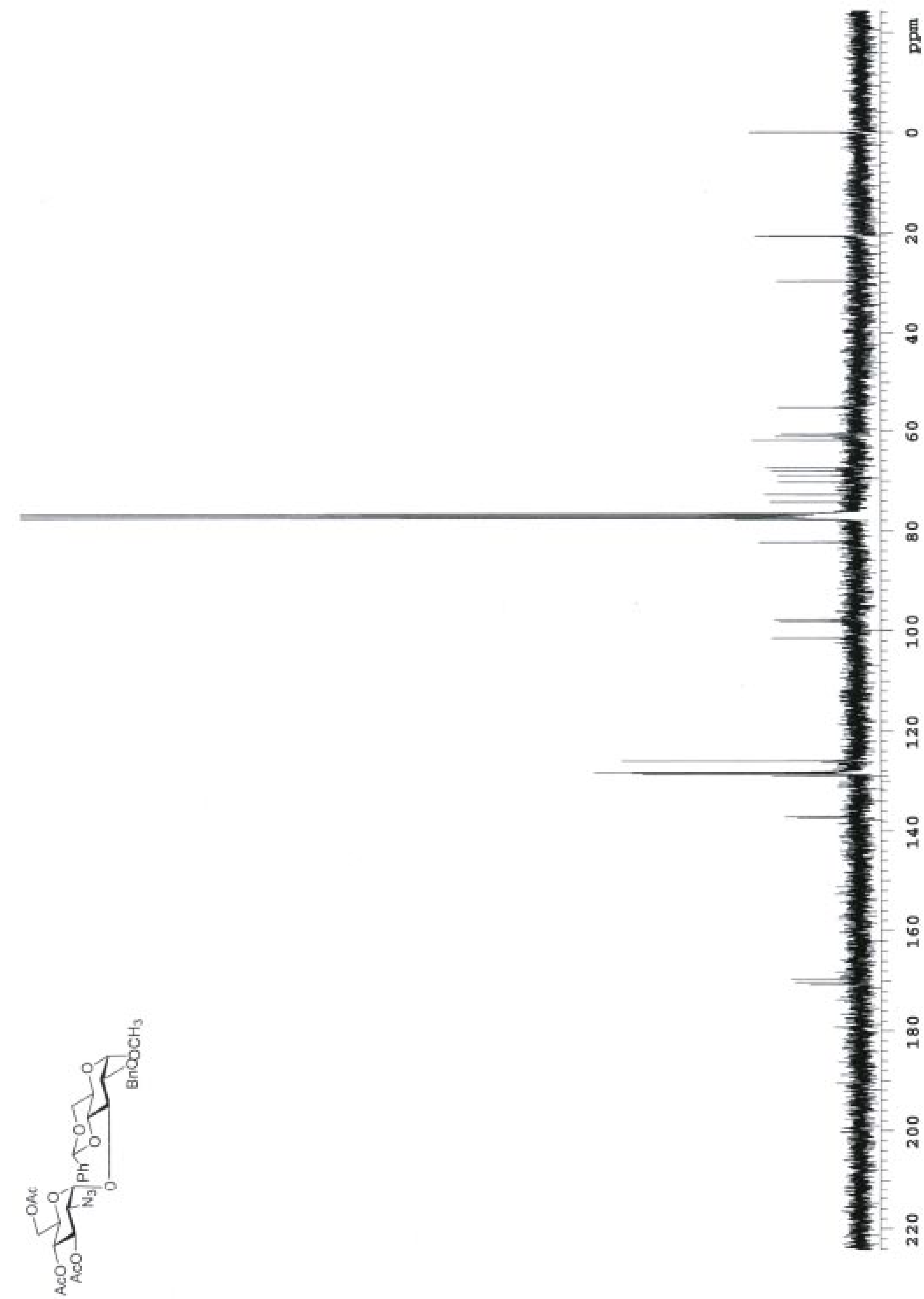
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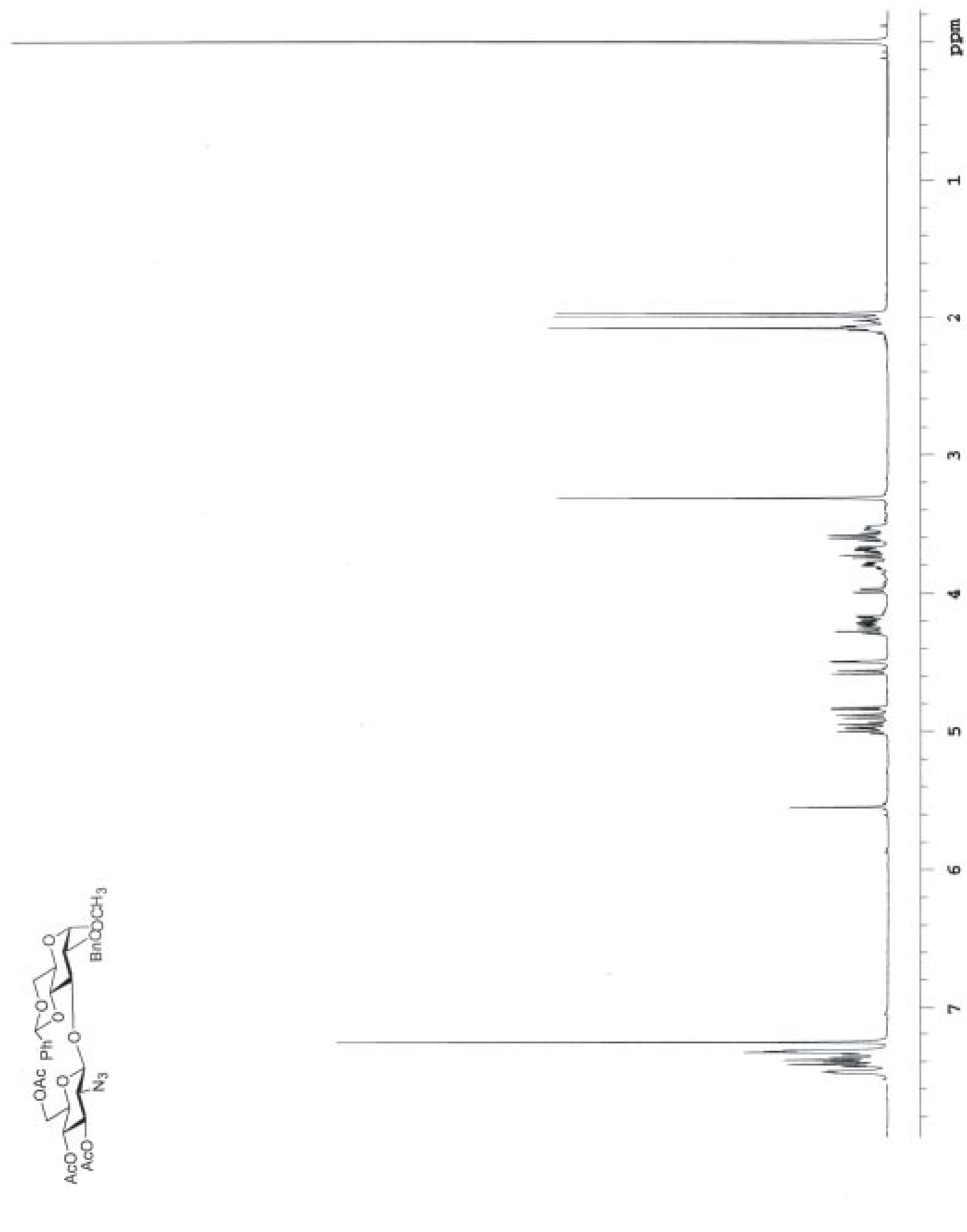
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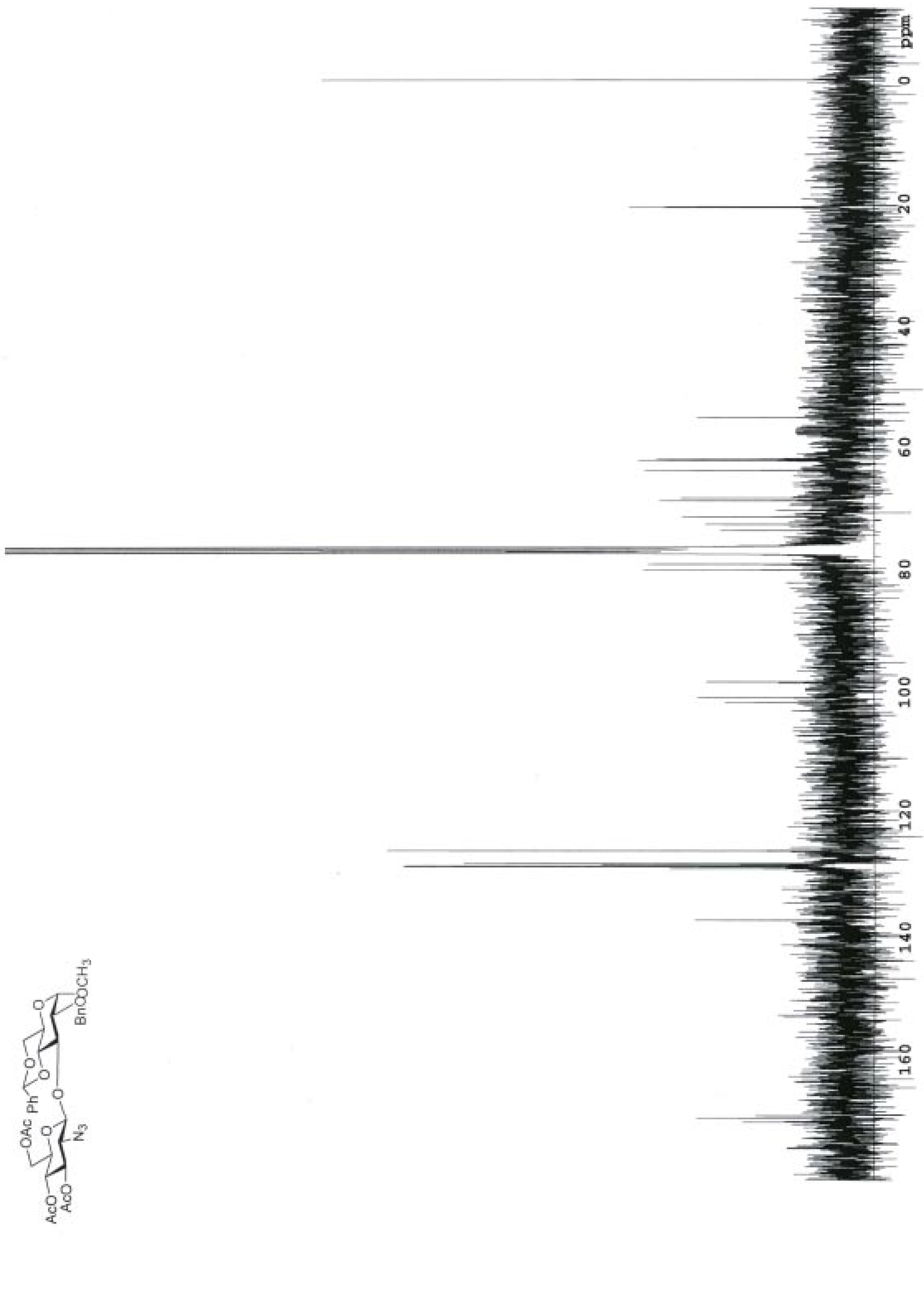
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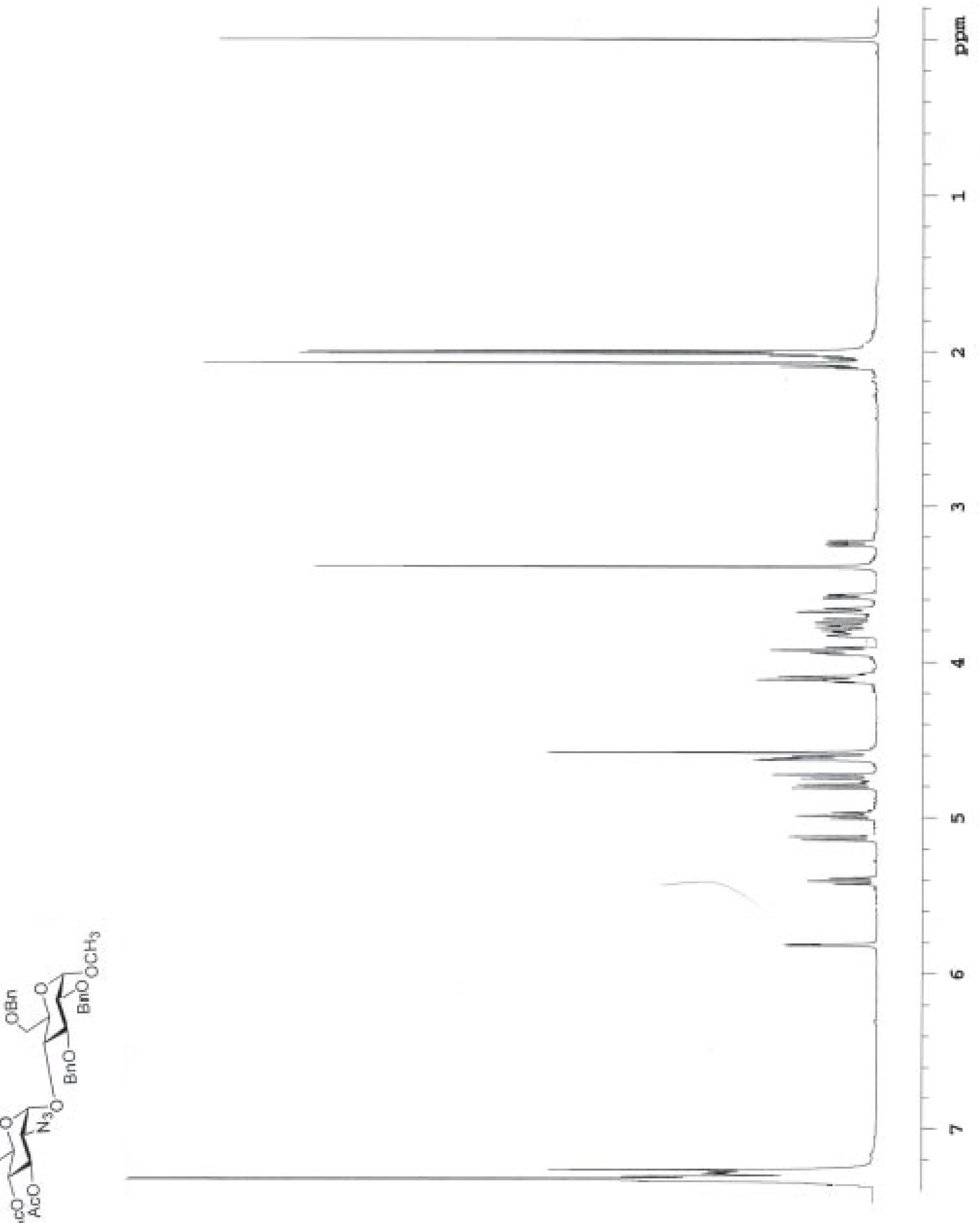
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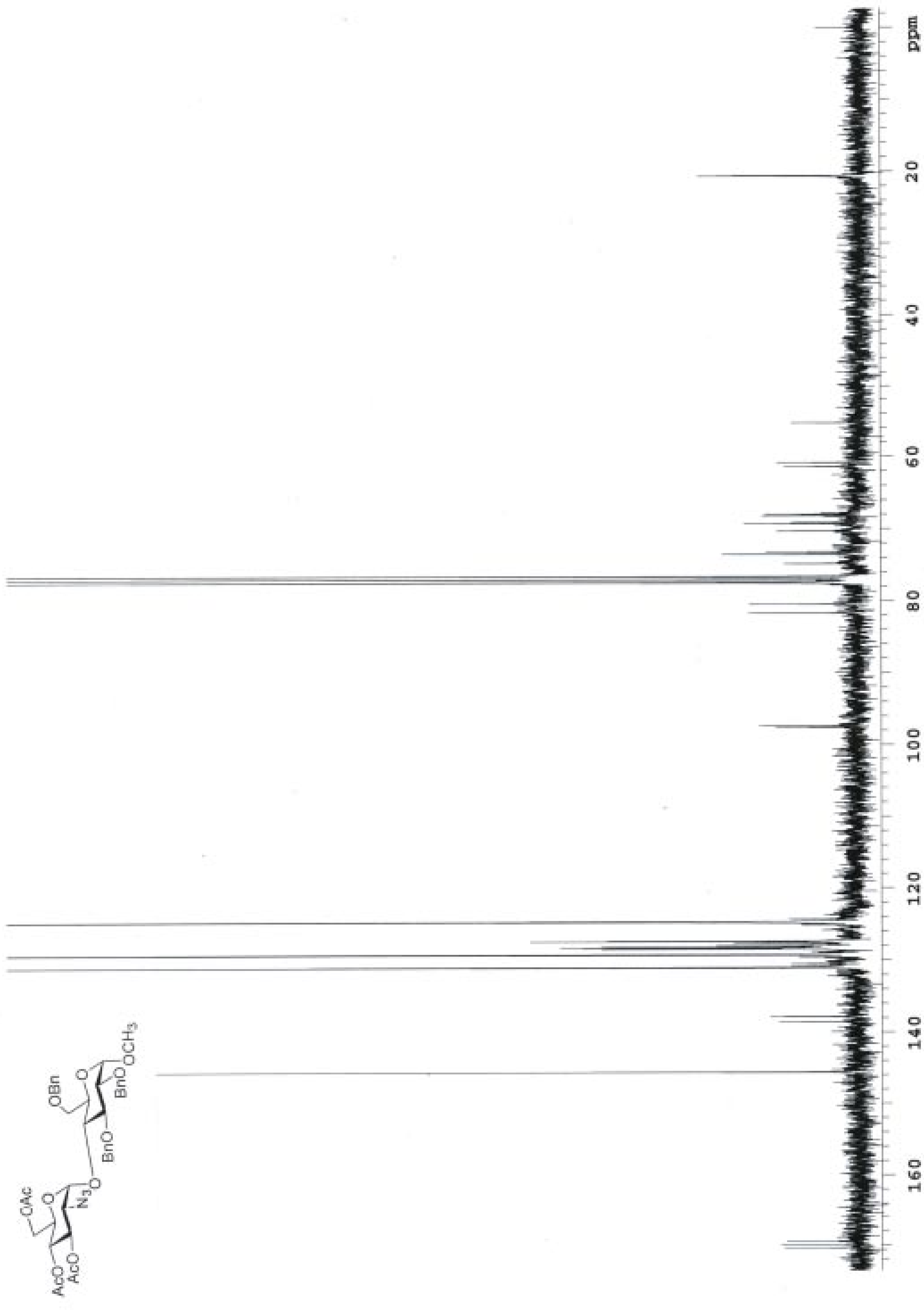
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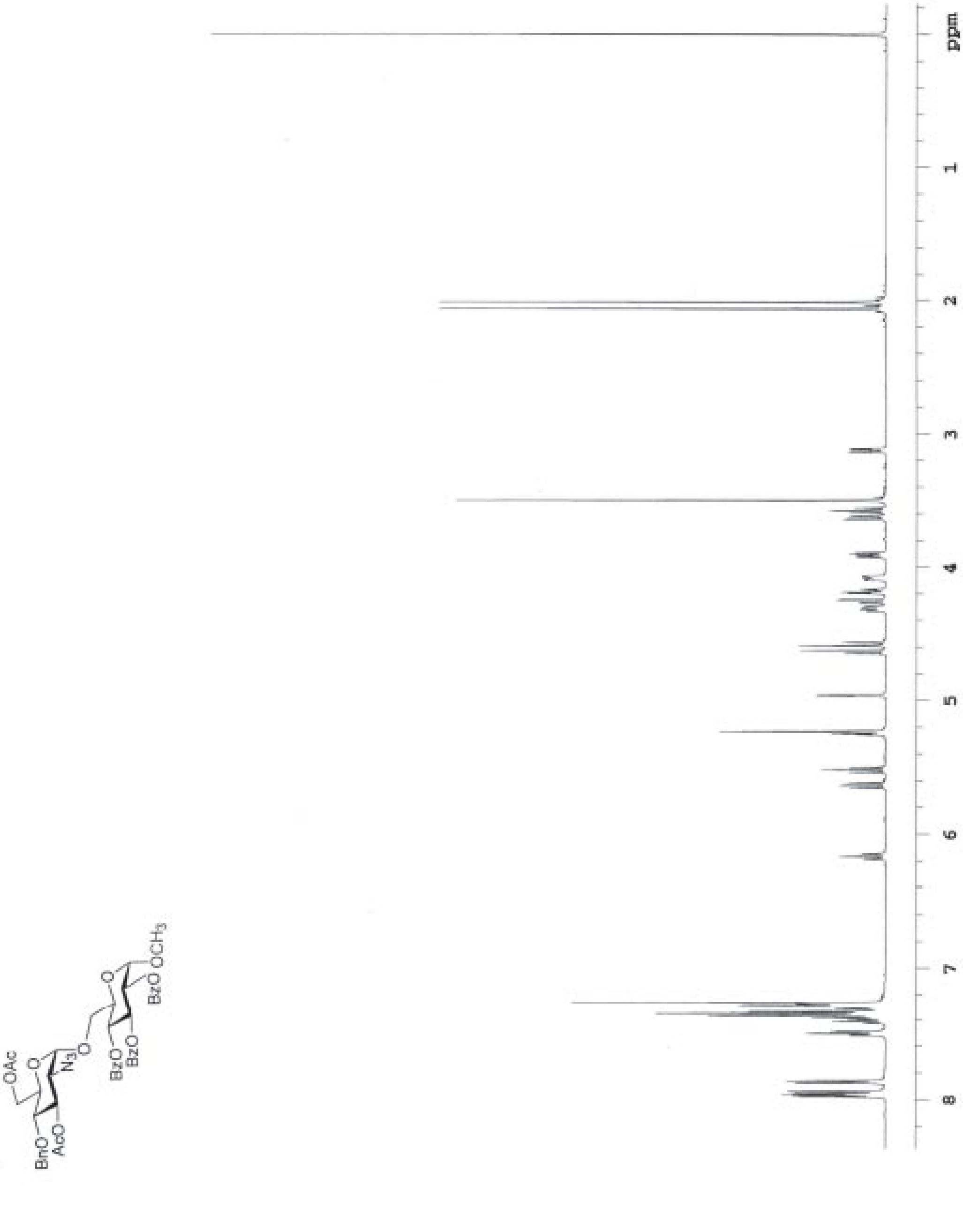

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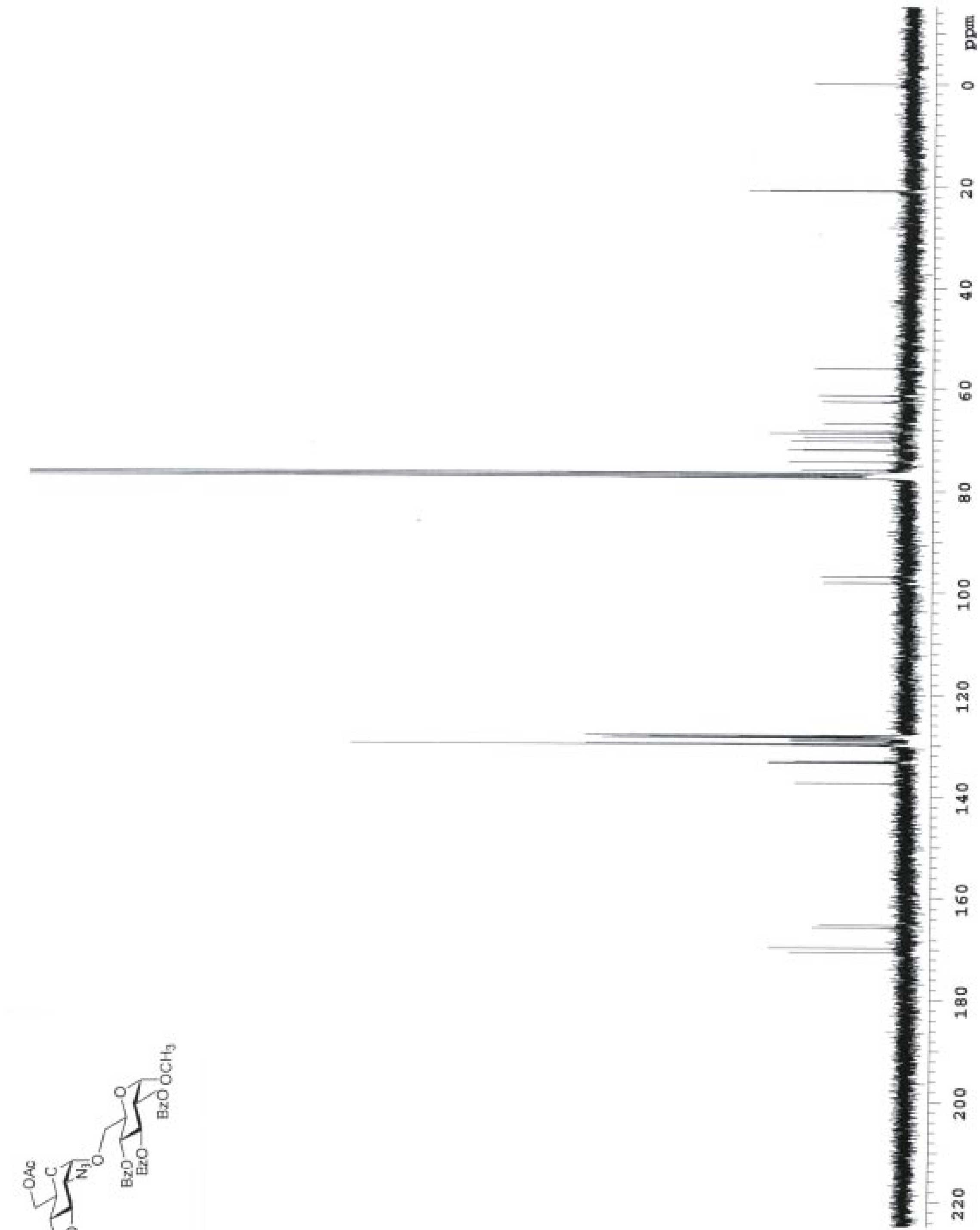
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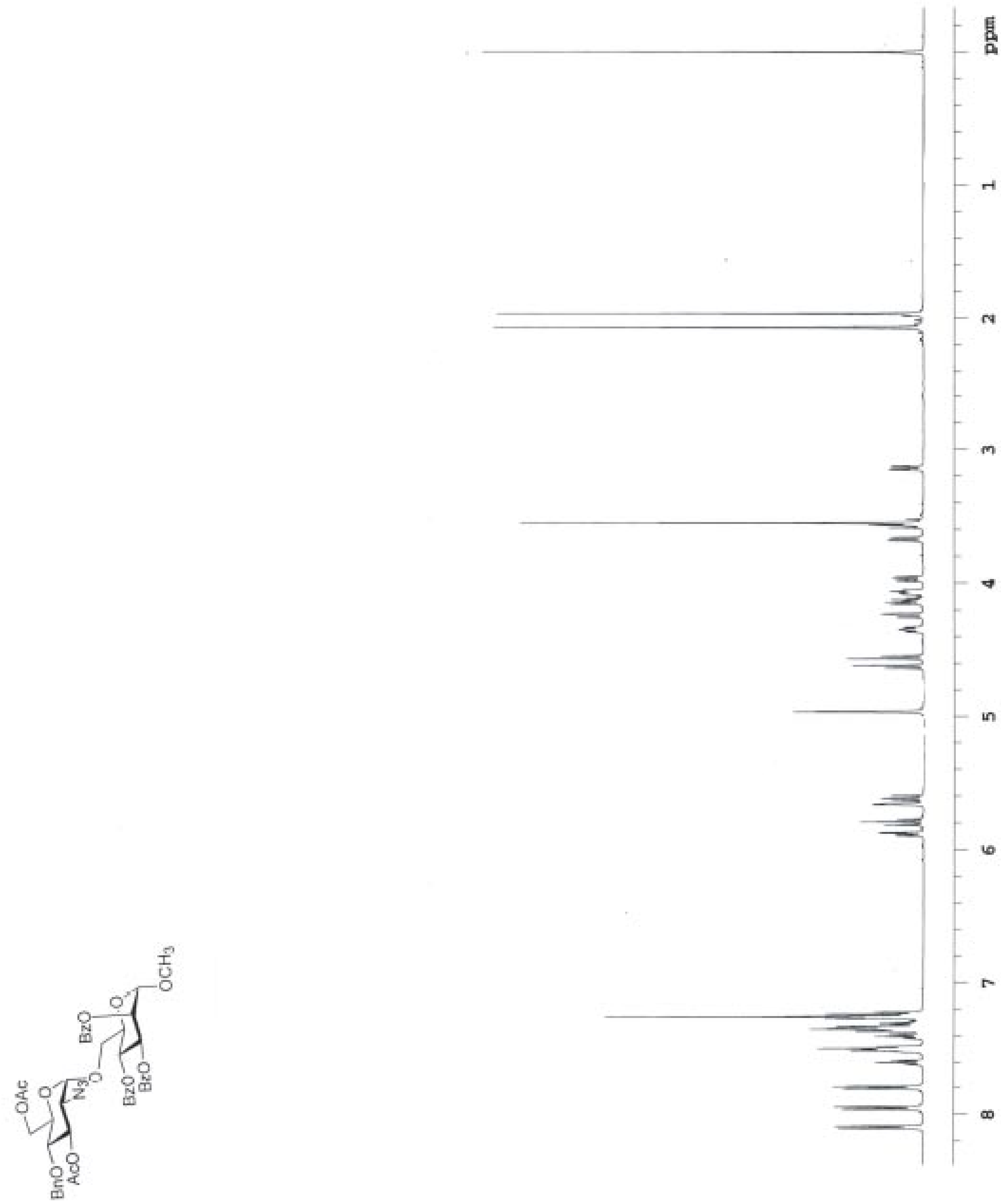
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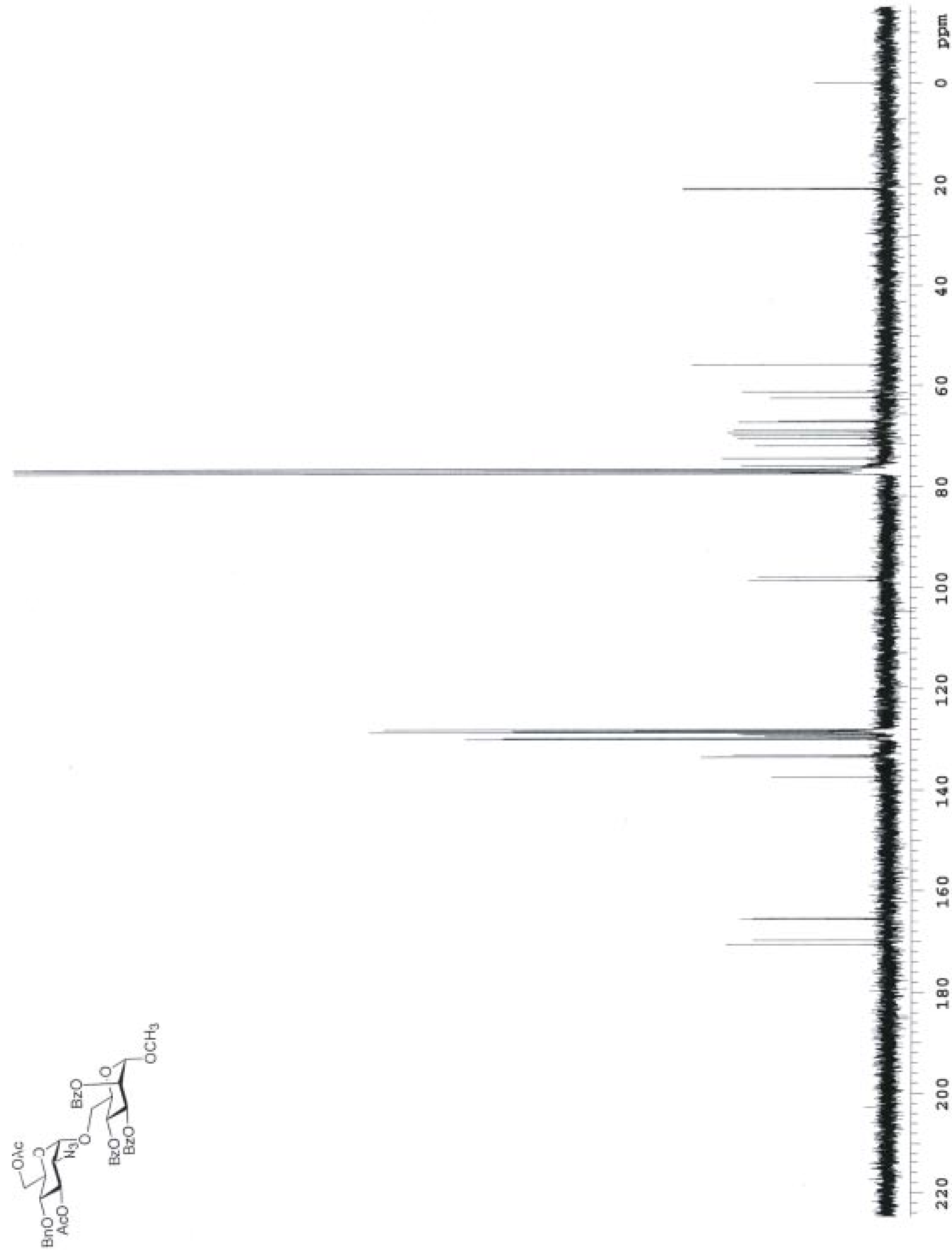
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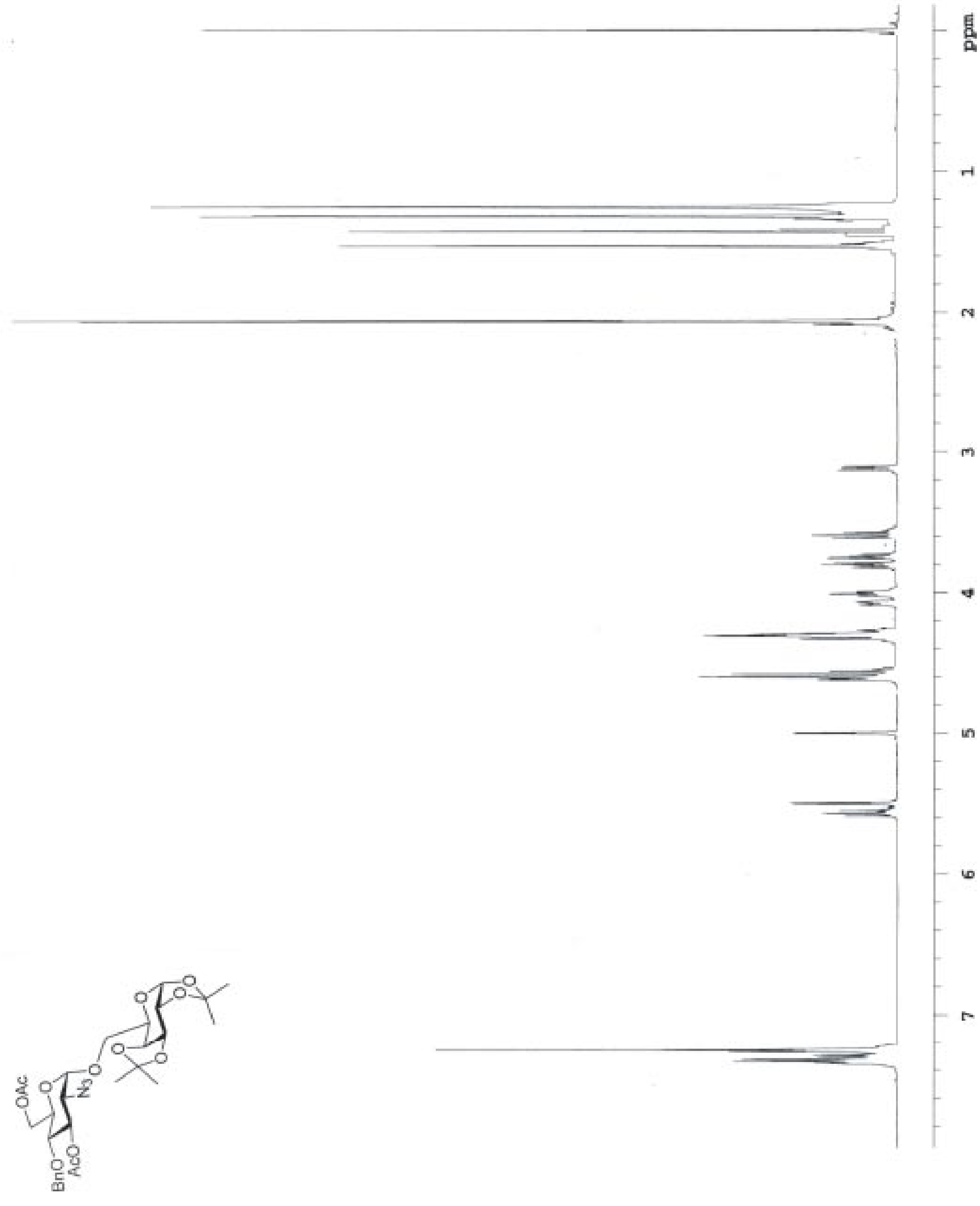
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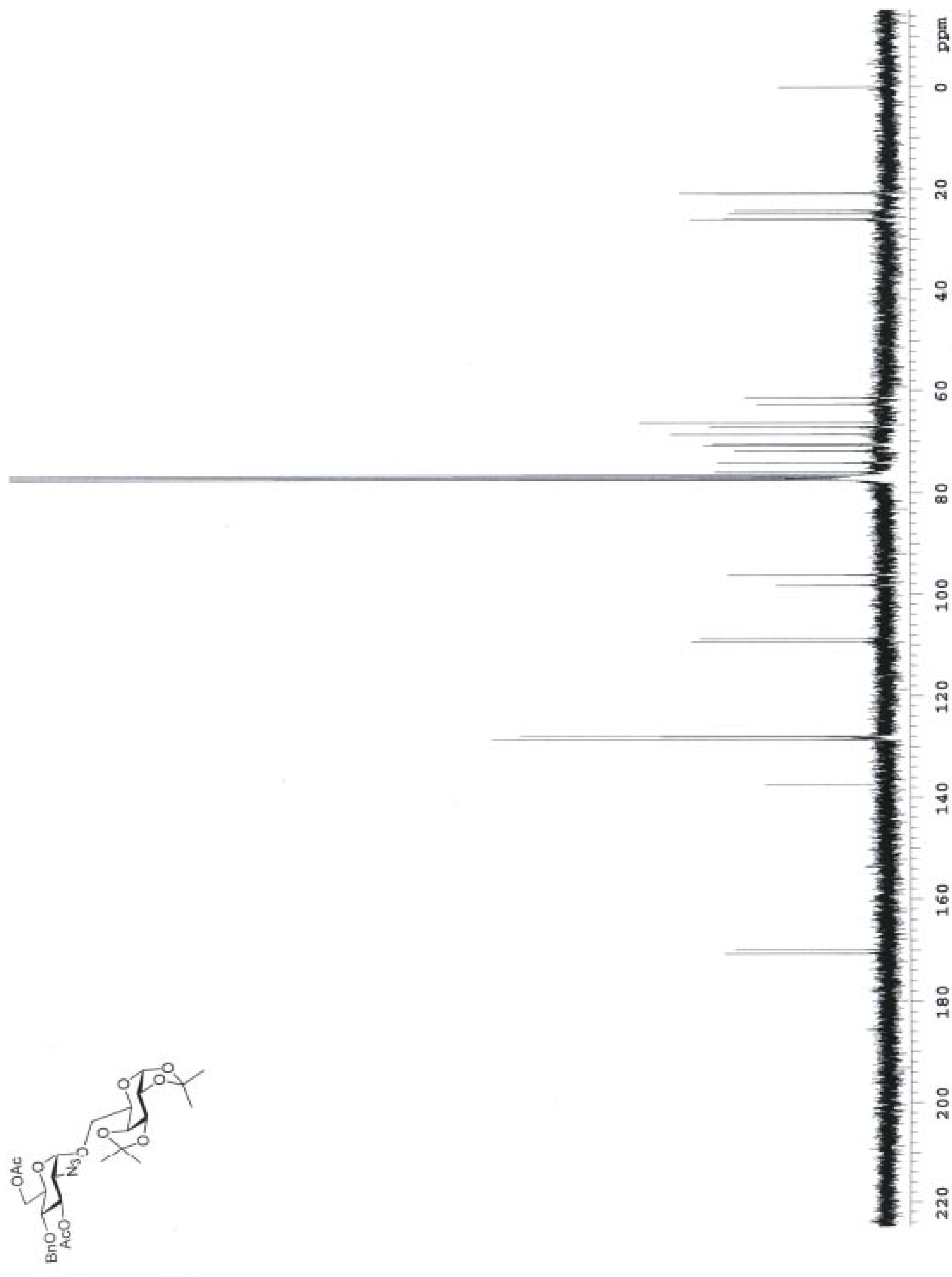
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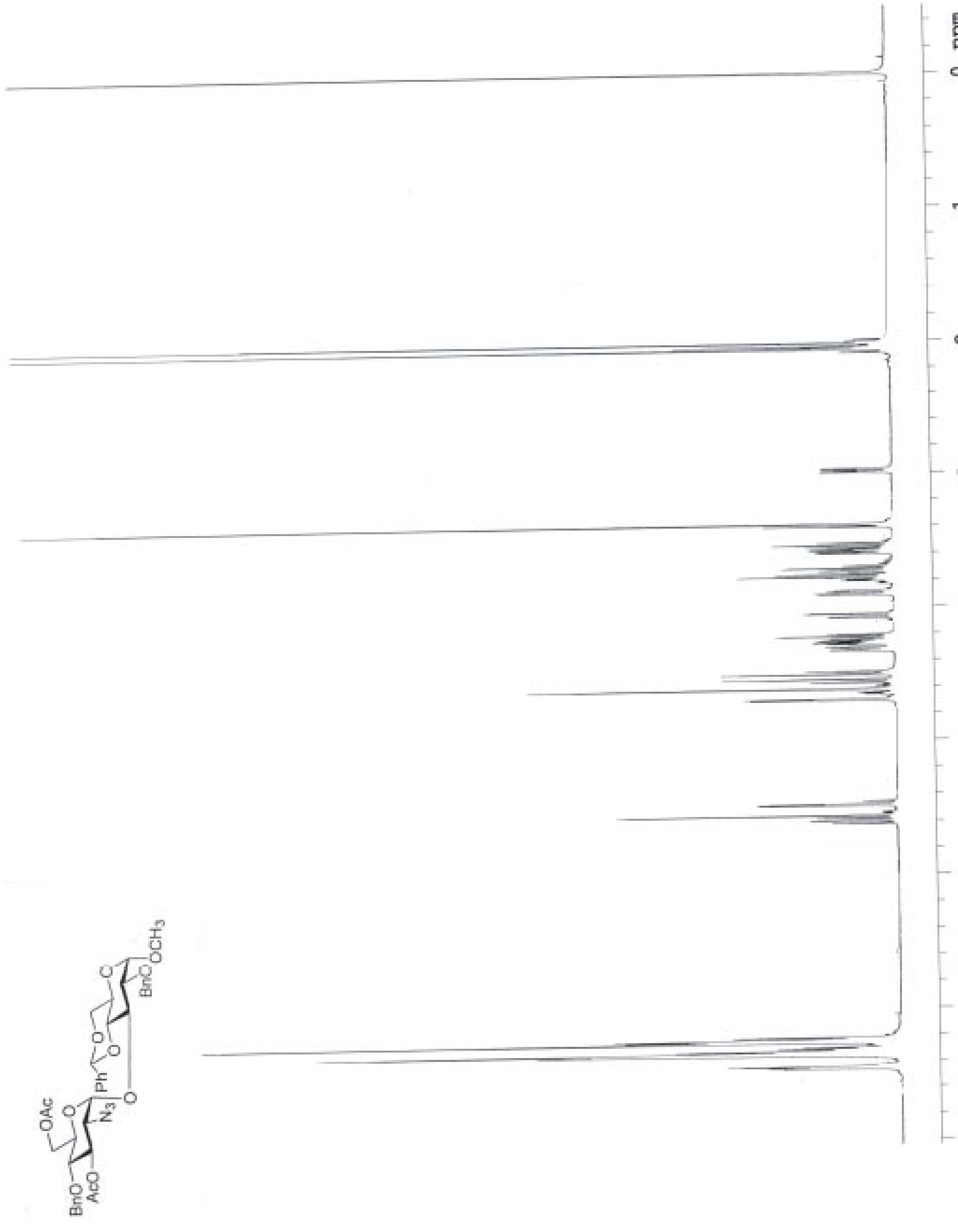
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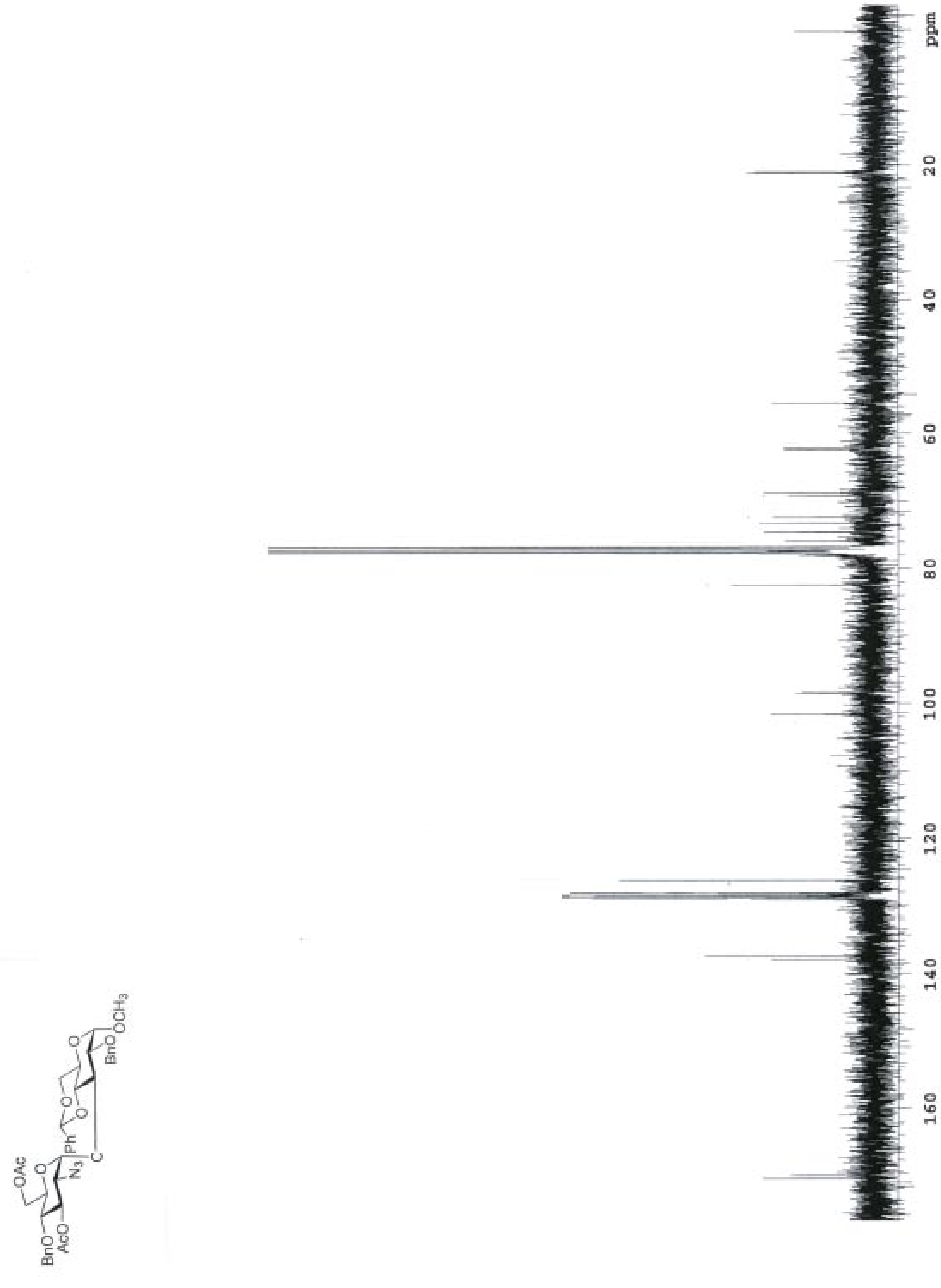

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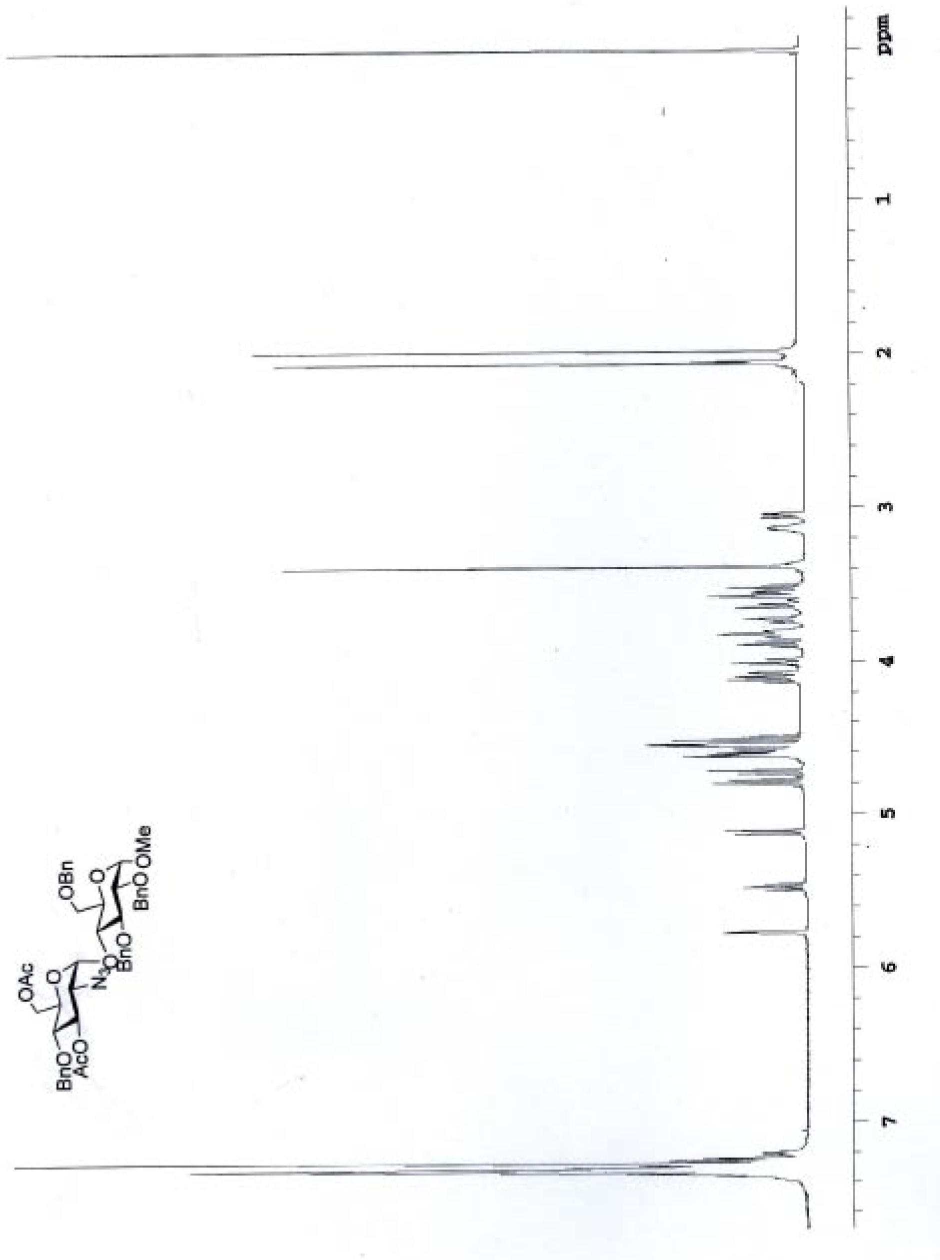
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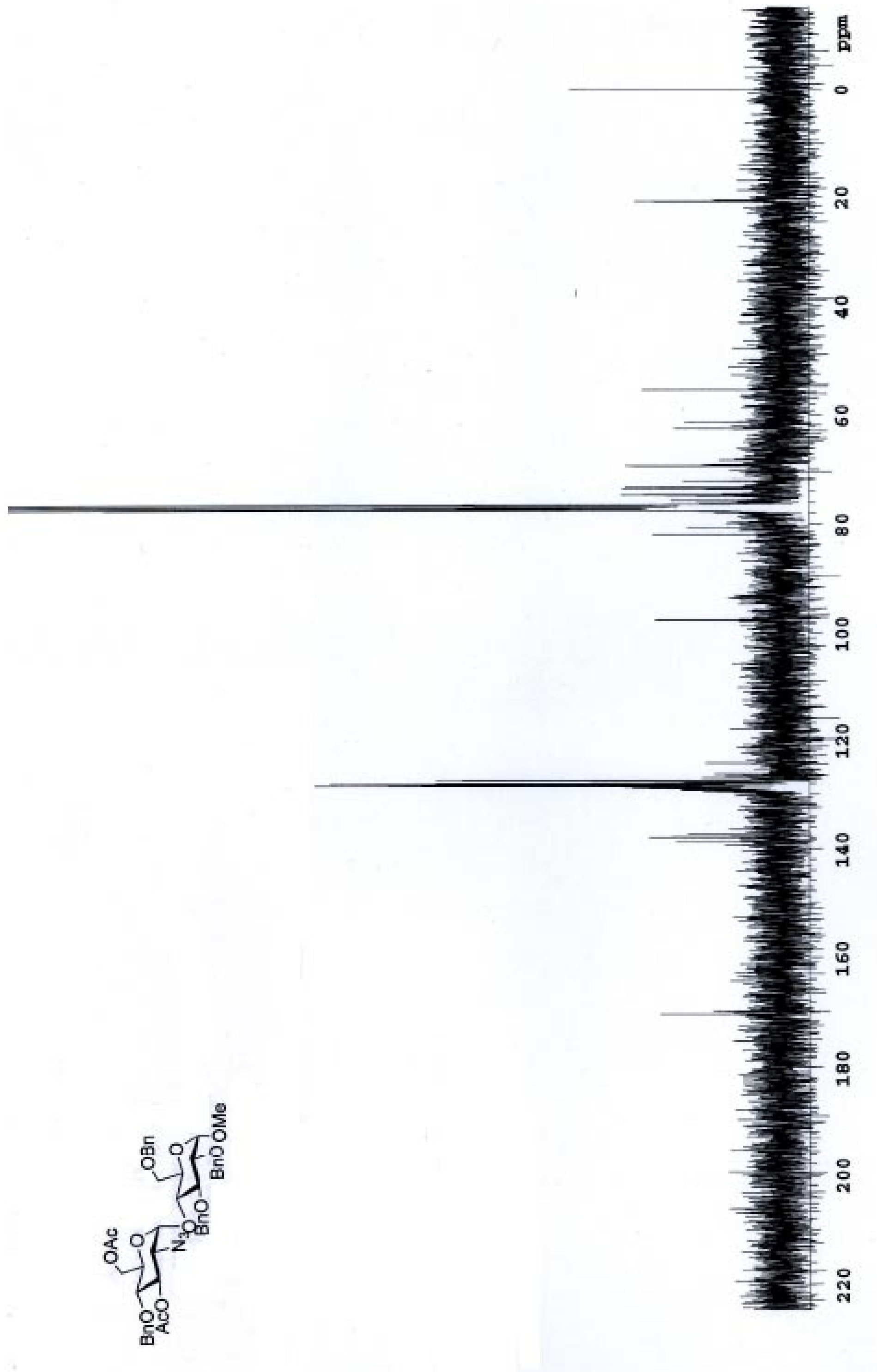
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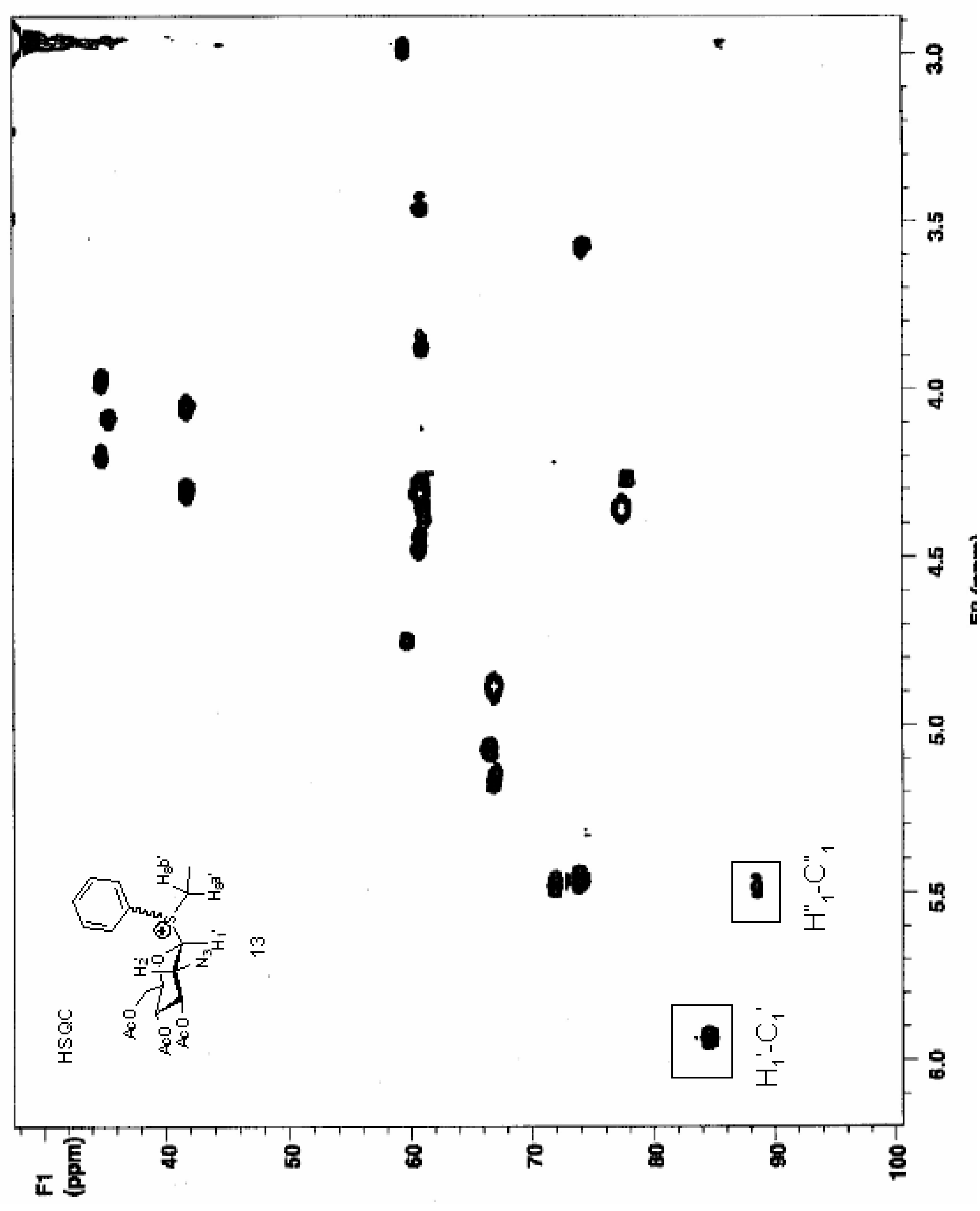
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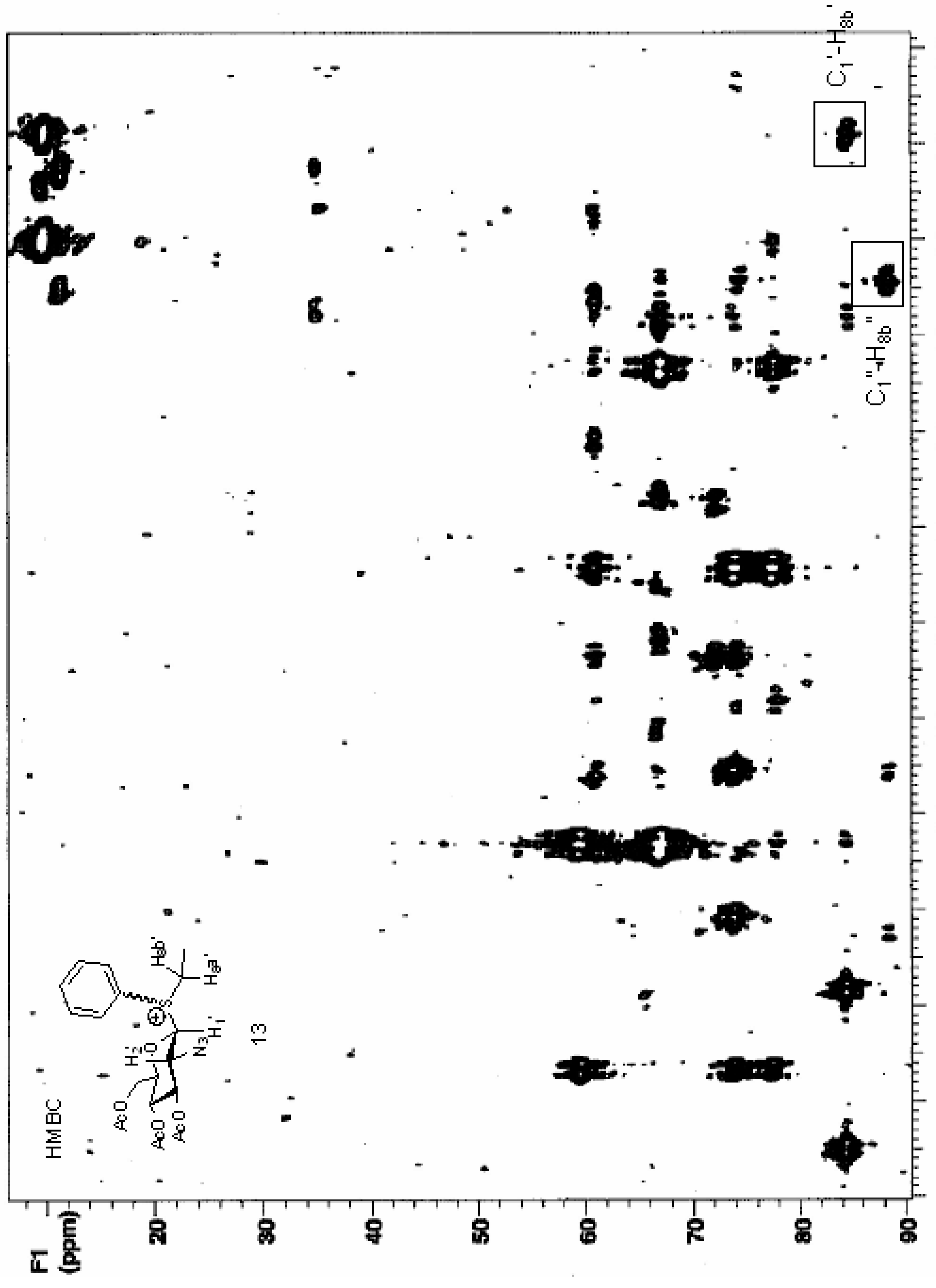
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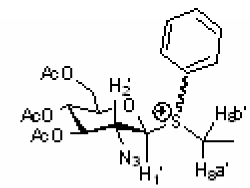
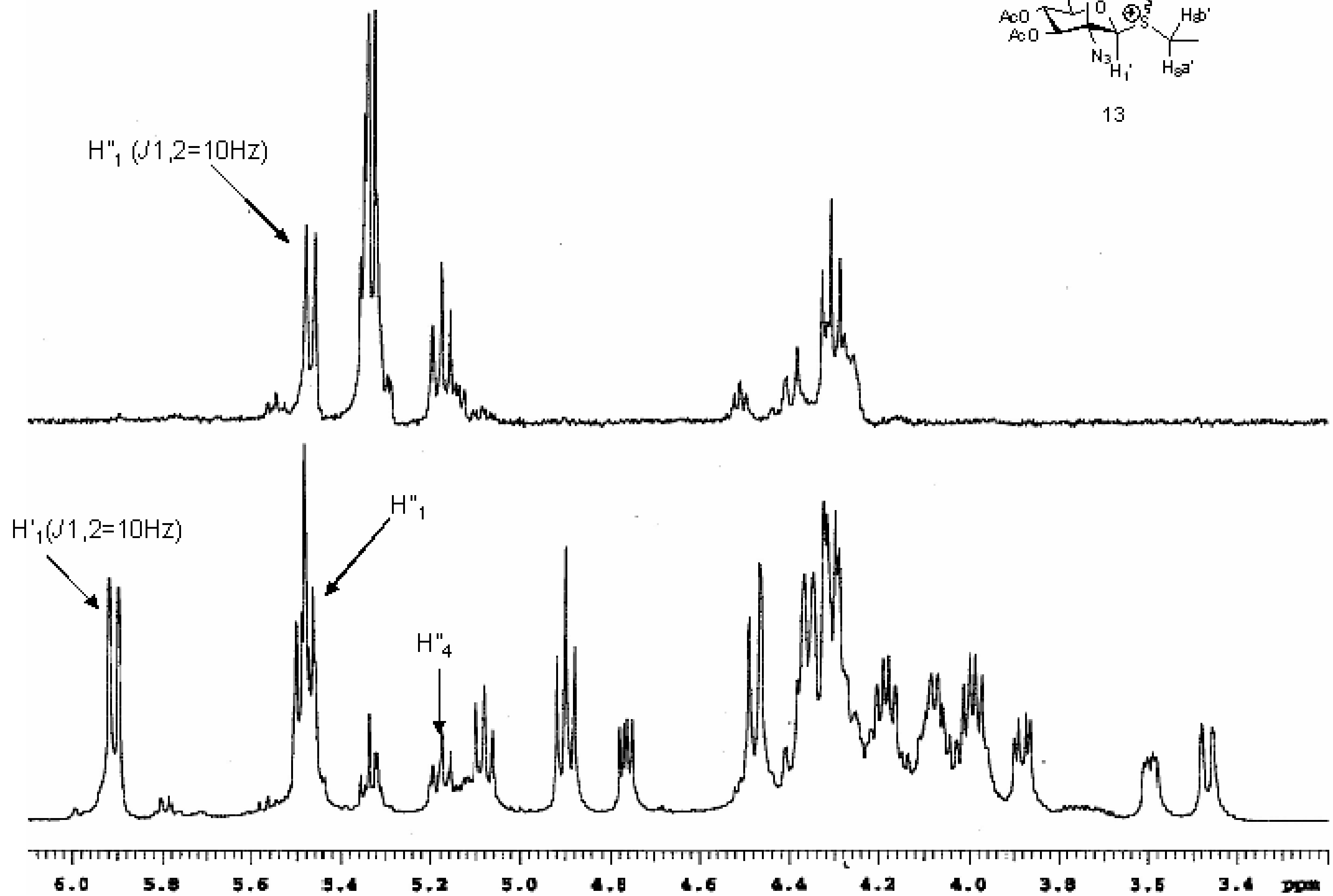
C_1''-H_{8b}''

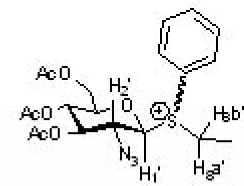
1H TOCSY 1D spectrum of irradiation on H_4'' of sulfonium ion 13



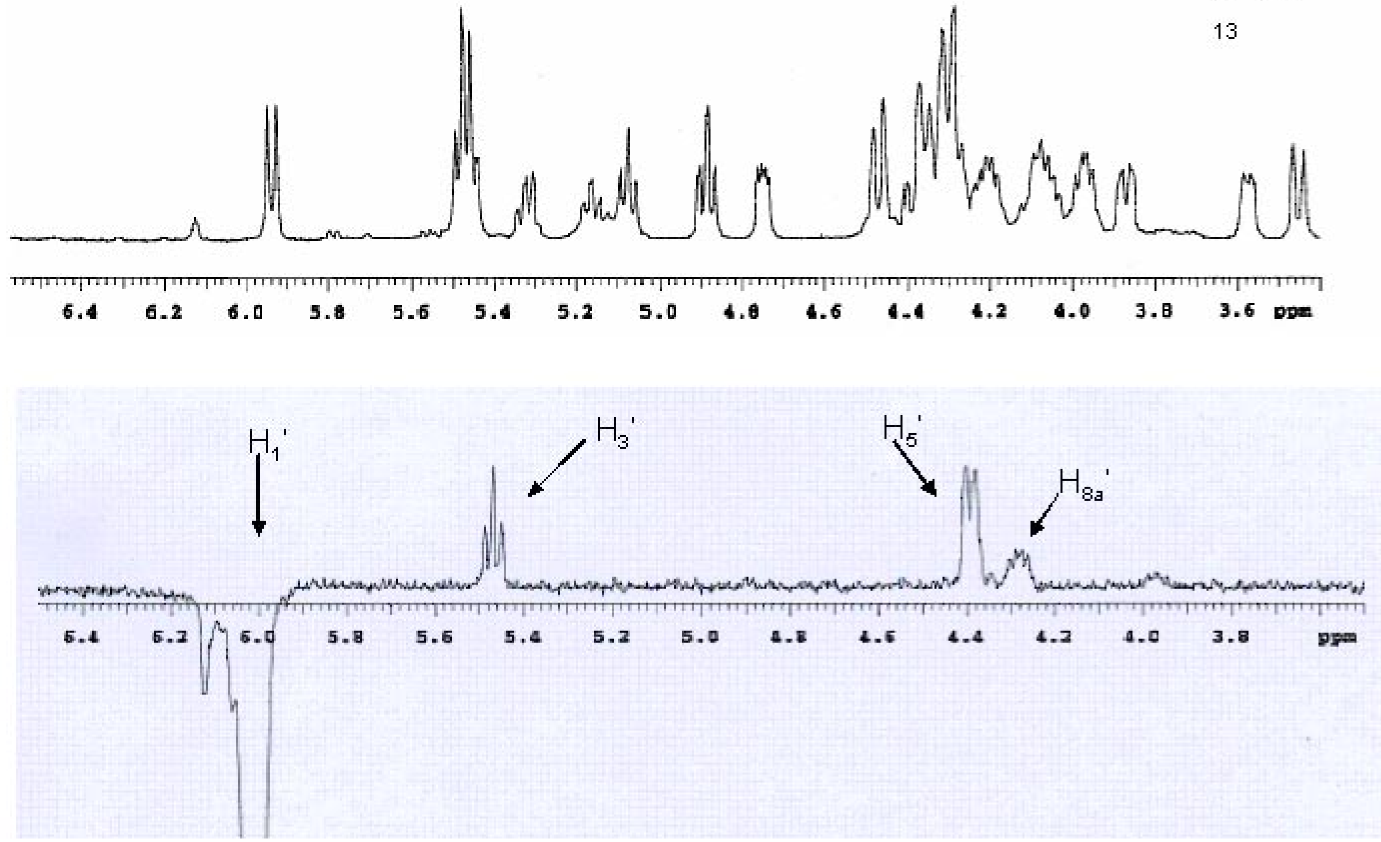
13



1H-NOESY 1D Spectrum of irradiation on H_1' of sulfonium ion **13**



13



Transformation of α-triflate **12** to the β-sulfonium ion **13**