Supporting Information

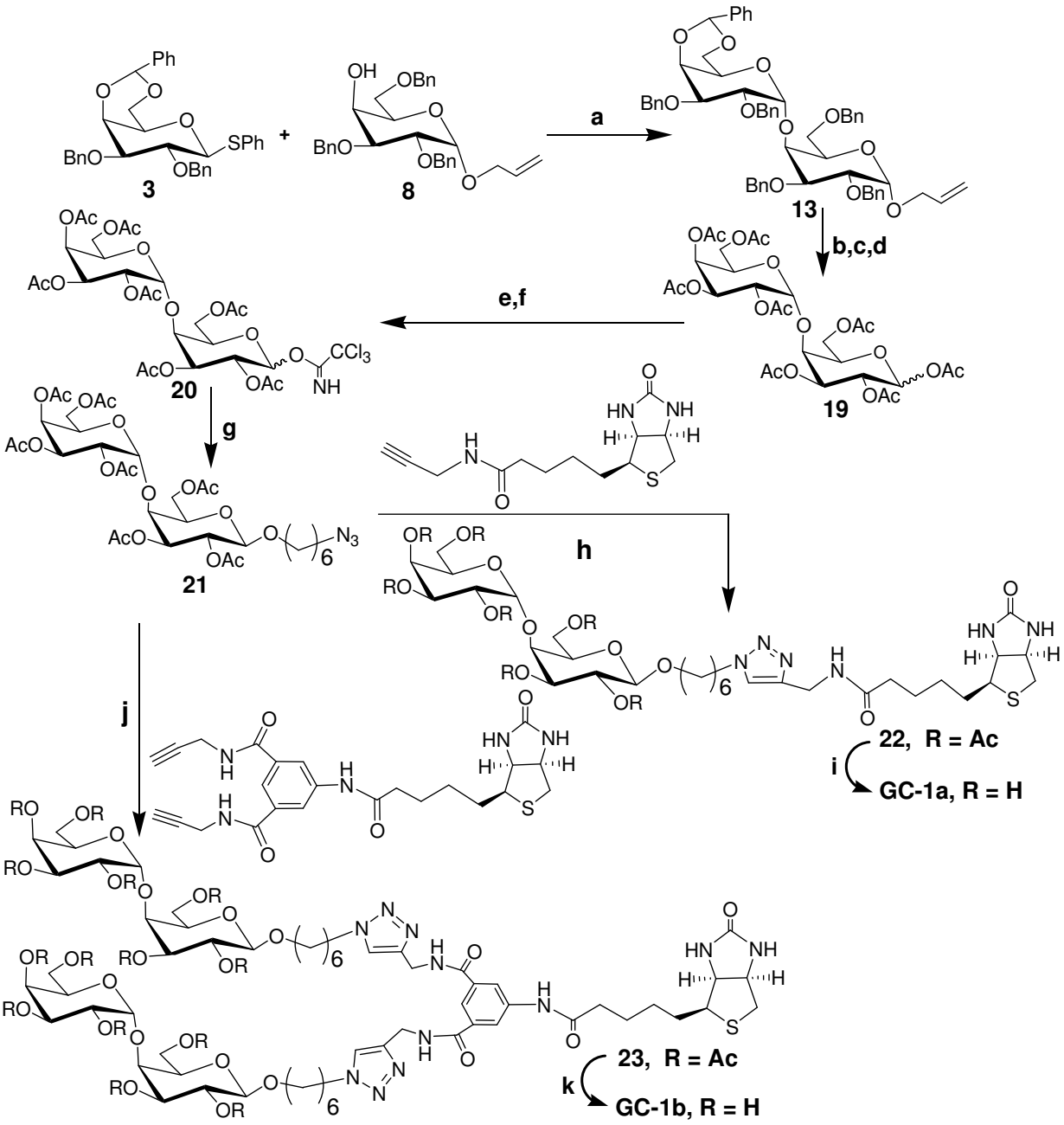
Chemical Synthesis:

General:

All chemical reagents were of analytical grade, used as supplied without further purification unless indicated. Glycosylation reactions were performed under argon with solvents dried using a solvent purification system. The acidic ion exchange resin used was Dowex-50 ion-exchange resin (H^+ form). Analytical thin layer chromatography (TLC) was conducted on silica gel 60-F254 (Merck). Plates were visualized under UV light, and/or by staining with acidic cerium ammonium molybdate followed by heating. Column chromatography was performed on silica gel (230-400 mesh) from Qualigens. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX 400MHz spectrometer. Chemical shifts are reported in δ (ppm) units using ^{13}C and residual ^1H signals from deuterated solvents as references. Spectra were analyzed with Mest-Re-C Lite and MestreNova (Mestrelab Research). The stereochemistry of the newly formed glycosidic linkages were determined by coupling constants of H1 and H2 ($J_{1,2}$) through ^1H NMR, ^1H-^1H gCOSY and ^1H-^{13}C gHMQC 2-D NMR. Smaller coupling constants (around 3 Hz) indicate α-linkages and larger coupling constants (7.2 Hz or larger) indicate β-linkages for glucosides and galactosides. Electrospray ionization mass spectra were recorded on a Micromass Q T of 2 (Waters) and data were analyzed with MassLynx 4.0 (Waters) software.

Abbreviations: 2-chloro-4,6-dimethoxy-1,3,5-triazine, CDMT; *N*–methyl morpholine, NMM; 1,8 Diazabicylo[5.4.0]undec-7-ene, DBU; Trimethylsilyl trifloromethanesulfonate, TMSOTf; Tetrahydrofuran, THF; N,N Dimethylformamide, DMF; Ethyl acetate, EtOAc; Triisopropylsilane, TIPS, Trifluroacetic acid, TFA; Acetonitrile, CH_3CN; Methylene Chloride, CH_2Cl_2; Methanol, CH_3OH; Sodium hydride, NaH; Benzyl bromide, BnBr; Sodium

cyanoborohydride, $NaBH_3CN$; Hydrazine acetate, $NH_2NH_2.HOAc$, Copper sulfate pentahydrate, $CuSO_4.5H_2O$; para-nitrobenzenesulfonyl chloride, p-NO_2PhSCl; 2, 4, 6-tri-tert-butylpyrimidine (TTBP), Silver triflate, AgOTf; 4-Dimethylaminopridine, DMAP; p-Toluenesulfonic acid, p-TsOH; Acetic acid, CH_3COOH; Acetic anhydride, Ac_2O; Thioacetic acid, AcSH; Sodium azide, NaN_3.



Scheme 1: *Synthesis of **GC-1a** and **GC-1b**. Reagents and conditions.* a) CH_2Cl_2, AgOTf, p-NO_2PhSCl, TTBP, -78 ^{0}C, 60% b) $PdCl_2$, NaOAc, AcOH, H_2O, rt, 54% c) $Pd(OH)_2$, H_2, EtOAc / EtOH, rt , 67%, d) Ac_2O, pyridine, DMAP, 0 ^{0}C to rt , 57% e) H_2NNH_2.HOAc, THF, rt, 63% f) K_2CO_3, CH_2Cl_2, Cl_3CCN, rt, 77% g) CH_2Cl_2, $HO(CH_2)_6Cl$, TMSOTf, -30 ^{0}C to rt, 55% h) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 70% i) MeOH, NaOMe, rt, quantitative j) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 70% k) MeOH, NaOMe, rt quantitative.

Allyl-(4, 5-O-benzylidene, 2, 3-di-O-benzyl-α-D-galactopyranosyl)(1→4)2, 3, 4-O-benzyl- α-D-galactopyranoside (13): A suspension of compound **3**[1] (0.66 g, 1.22 mmol), TTBP(0.36g, 1.46 mmol) and AgOTf (0.78g, 3.05 mmol) in anhydrous CH_2Cl_2 was stirred at rt for 10 min, under argon in dark. The suspension was stirred and cooled to -78 ^{0}C. After 5 min, a solution of p-NO_2PhSCl (0.28g, 1.46 mmol) in CH_2Cl_2 was added drop wise to the above suspension. Next, CH_2Cl_2 solution of compound **8**[2] (0.4g, 0.81 mmol) was added into the mixture. The reaction mixture was stirred for 3 hr at -78 ^{o}C. When TLC analysis indicated formation of the product, the reaction mixture was quenched with saturated $NaHCO_3$ and diluted with CH_2Cl_2 giving a yellow looking suspension which was filtered through a celite pad. The celite pad was washed with CH_2Cl_2 and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc: Hex 3:7, Rf 0.5) to afford 65% of the title compound. ^{1}HNMR ($CDCl_3$): δ 8.13-8.10(d, 1H, *J* = 9.6 Hz), 7.53- 7.51(d, 1H, *J* = 8.4 Hz), 7.48-7.46(dd, 2H, *J* = 1.6 and 7.2 Hz), 7.40- 7.32(m, 12H), 7.29-7.17(m, 14H), 5.97-5.87(s, 1H), 5.33(s, 1H), 5.31(d, 1H, *J* = 17.2 Hz), 5.20(d, 1H, *J* = 10.4 Hz), 5.09 (d, 1H, $J_{1,2}$ = 3.2 Hz), 5.01(s, 1H), 4.92(d, 1H, *J* = 11.6 Hz), 4.76(t, 3H, *J* = 5.8 Hz), 4.70-4.66(m, 4H), 4.29-4.24(d, 1H, *J* = 9.2 Hz), 4.21(s, 1H), 4.18-4.11(m, 3H), 4.06-3.90(m, 8H), 3.54(t, 1H, *J* = 11.8 Hz), 3.49-3.45(dd, 1H, *J* = 5.6 and 8.8 Hz), 3.40(d, 1H, *J* = 12.4 Hz). ^{13}CNMR($CDCl_3$): δ 138.9, 138.8, 138.7, 138.6, 138.2, , 138.1, 134.1, 128.9, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.3, 127.2, 126.4, 124.5 , 118.1, 100.8, 100.5, 95.9, 75.7, 75.2, 74.5, 74.4, 73.1, 72.7, 72.7, 71.5, 69.5, 69.3, 68.4, 67.6, 62.8. LRMS calculated for $[C_{57}H_{60}O_{11}Na]^+$ 943.4125 Found 943.4033.

O-(2, 3, 4, 6-tetra-O-acetyl-α-D-galactopyranosyl) (1→4) 2, 3, 6-tri-O-acetyl-α-D-galactopyranosyl trichloroacetonitrile (20): To a stirred solution of **13** (0.4g, 0.43mmol) in

CH_3COOH (4ml) and water (0.3ml) were added $PdCl_2$ (0.15g, 0.87 mmol) and NaOAc (0.15g, 1.1 mmol).The reaction mixture was stirred for 12 h at rt. After TLC analysis indicated product formation, the reaction mixture was diluted with EtOAc and passed through celite pad. The filtrate was washed with saturated $NaHCO_3$ and brine consecutively. The organic layer was dried over Na_2SO_4 and removed *in vacuo*. The dried crude residue (0.25g) was subjected for hydrogenation reaction. The crude residue was dissolved in EtOAc/EtOH 3ml/1ml and treated with 100mg of Pd/C. The reaction mixture was stirred under continuous flow of hydrogen gas at 1 atm. After 48 h, the reaction mixture was diluted with EtOH and filtered through celite. EtOH was removed *in vacuo* and a white product was obtained. This crude product was once again used for subsequent reaction (acetylation reaction) without further purification. The crude product was dissolved in anhydrous pyridine and catalytic amount of DMAP was added to the solution. The reaction mixture was cooled to 0 ^{0}C and Ac_2O was added drop wise. The reaction mixture was stirred for 12 h while the temperature rose to rt. When TLC confirmed formation of the product, pyridine was removed *in vacuo* as an azeotropic mixture with toluene. The residue was diluted with EtOAc and washed with 0.1 M HCl. The organic layer was dried over Na_2SO_4 and removed *in vacuo* and the residue was purified using flash chromatography (EtOAc:Hex 8:2) to give **19** with the overall yield of 57% over two steps. Next, hydrazine acetate (0.02g, 0.23 mmol) was added to a THF solution (2.5ml) of **19** (0.12g, 0.18 mmol). The reaction was stirred for 18 h at rt under argon. When TLC indicated completion of the reaction, the solvent was removed *in vacuo* and the crude product was washed with water and EtOAc. The organic solvent was dried over Na_2SO_4 and removed *in vacuo*. The crude product was purified with flash chromatography (EtOAc:Hexane 7:3, Rf 0.42) giving 64% of the disaccharide hemiacetal. CH_2Cl_2 solution (2ml) of the hemiacetal (0.07g, 0.11 mmol,) was added to the dried and

activated K_2CO_3 (0.38g, 2.75 mM) followed by the addition of the Cl_3CCN. The reaction mixture was stirred for 12 h at rt under argon. When TLC analysis indicated completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 and K_2CO_3 was filtered. CH_2Cl_2 was evaporated and the dried crude product was purified with flash chromatography (EtOAc: Hex 6:4, Rf 0.40) giving 77% of the title compound. ^{1}HNMR($CDCl_3$): δ 8.69 (s, 1H), 6.61(d, 1H, $J_{1.2}$ = 3.6 Hz), 5.57(d, 1H, *J* = 2.0 Hz), 5.44-5.36(m, 2H), 5.32-5.29(dd, 1H, *J* = 2.4 and 11.2 Hz), 5.26-5.23(dd, 1H, *J* = 3.6 and 11.2 Hz), 5.03(d, 1H, $J_{1,2}$ = 3.6 Hz), 4.53(t, 1H, *J* = 6.8 Hz), 4.37-4.32 (m, 2H), 4.29(d, 1H, *J* = 2.4 Hz), 4.15-4.09(m, 2H), 2.15 (s, 3H), 2.12(s, 6H), 2.04(s, 9H), 2.00(s, 3H) ^{13}CNMR ($CDCl_3$): δ 170.5, 170.5, 170.3, 170.1, 169.9, 169.7, 160.8, 99.0, 93.6, 70.6, 69.4, 68.2, 67.8, 67.3, 67.2, 67.1, 66.8, 61.9, 60.7, 21.0, 20.8, 20.7, 20.6, 20.5.

6-Azido-hexyl (2, 3, 4, 6-tetra-O-acety-α-D-galactopyranosyl) (1→4) 2, 3, 6-tri-O-acetyl-α-D-galactopyranoside (21): Compound **20** (84.60 μmol, 66 mg) was dissolved in anhydrous CH_2Cl_2 and 6-azido hexanol (0.13mmol, 18 mg) was added to the solution. The reaction mixture was cooled to -25 ^{0}C and treated with TMSOTf (21.1μmol, 20μl). The reaction mixture was stirred for 4 h while letting the temperature increase to 0 ^{0}C. The reaction mixture was then diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$. The organic solvent was dried over Na_2SO_4 and removed *in vacuo*. The crude product was purified with flash chromatography (EtOAc: Hex 6:4, Rf 0.40) giving 55% of the title compound **21**. ^{1}HNMR($CDCl_3$): δ 5.57(d, 1H, *J* = 2.8 Hz), 5.41-5.37(dd, 1H, *J* = 3.2 and 10.8 Hz), 5.21-5.15(m, 2H), 5.01(d, 1H, $J_{1,2}$ = 3.6 Hz), 4.83-4.79 (dd,1H, *J* = 2.8 and 10.8 Hz), 4.53(t, 1H, *J* = 6.8 Hz), 4.48-4.44 (m, 2H, $J_{1,2}$ = 8.0 Hz), 4.20-4.06(m, 4H), 3.91-3.86(m, 1H), 3.78 (t, 1H, *J* = 6.4 Hz), 3.51-3.46(m, 1H), 3.27(t, 2H, *J* = 7.0 Hz), 2.13(s, 3H), 2.10(s, 3H), 2.08(bs, 6H), 2.05(bs, 6H), 1.99(s, 3H), 1.61-1.59(m, 4H), 1.39(s, 4H). ^{13}CNMR ($CDCl_3$): δ 170.8, 170.6, 170.5, 170.5, 170.2, 169.8, 169.1, 101.2, 99.4, 72.8, 71.8,

69.7, 68.8, 68.6, 67.9, 67.4, 67.0, 62.0, 60.5, 51.4, 29.3, 28.8, 26.4, 25.5, 21.0, 20.8, 20.7, 20.7. HRMS Calculated for $[C_{32}H_{47}N_3O_{18}Na]+$ 784.2752 Found 784.2735.

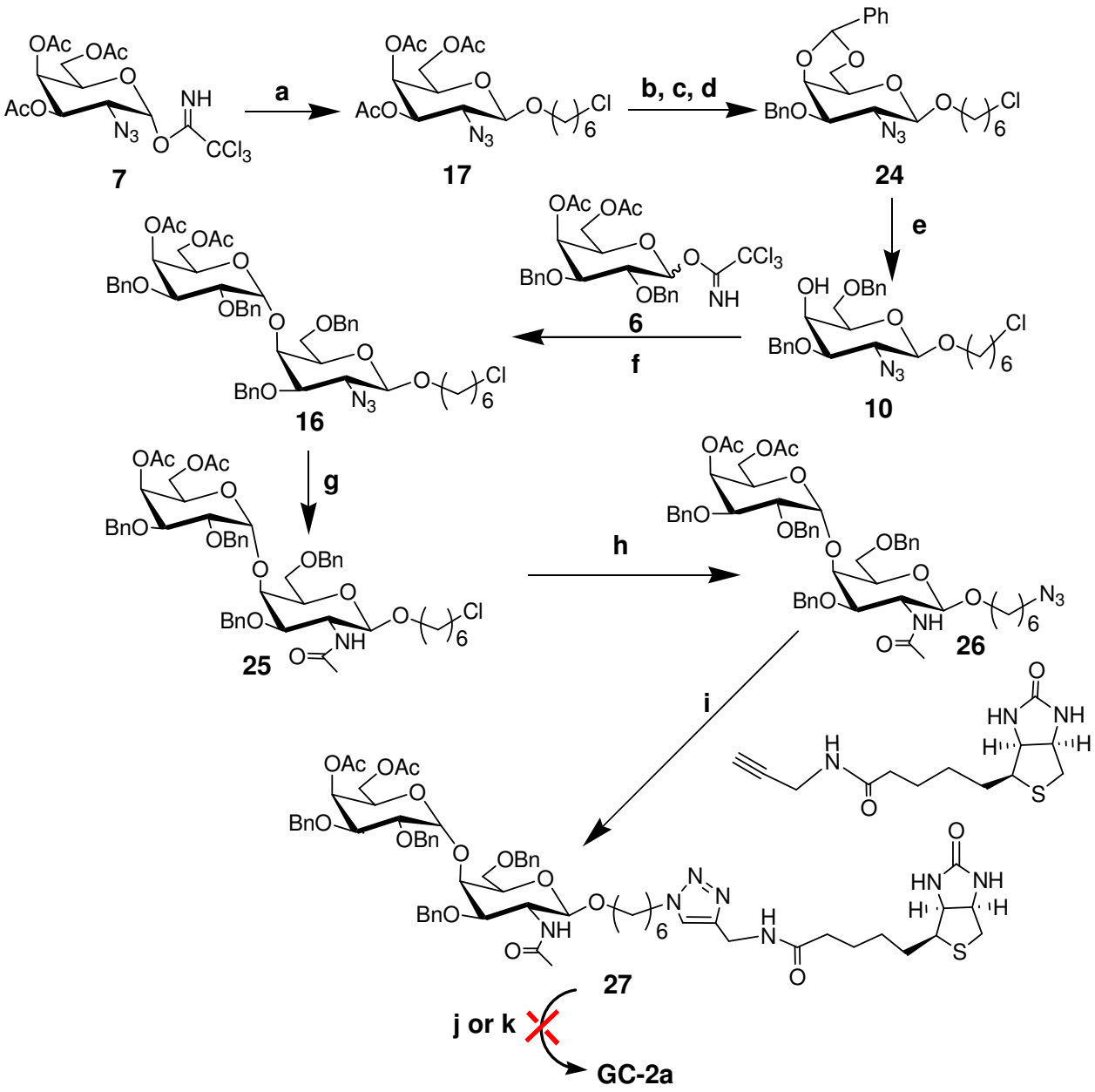
Compound 22: Biotinylated monomeric scaffold[3-5] (0.184 µmol, 5.2 mg) was added to the THF/ H_2O (1ml /1ml) solution of compound **21** (0.184 µmol, 14.0 mg) followed by the addition of $CuSO_4.5H_2O$ (0.276 umol, 6.9 mg) and sodium ascorbate (0.368umol, 7.3 mg). The reaction mixture was stirred for 24 h at rt. When TLC analysis indicated formation of the product, the reaction mixture was dried *in vacuo* and purified using flash chromatograpy (CH_2Cl_2: MeOH 8:2, Rf 0.56) to afford 79% of the title compound. ^{1}HNMR(MeOH-d_4): δ 7.88 (s, 1H), 5.54(s, 1H), 5.39-5.35(dd, 1H, *J* = 3.0 and 11.0 Hz), 5.23-5.14(m, 2H), 5.06-4.99(m, 2H), 4.64(d, 1H, $J_{1,2}$ = 7.6Hz), 4.58-4.54 (m, 1H), 4.49(bs, 2H), 4.43(bs, 2H), 4.41-3.78(m, 2H), 4.32-4.29(m, 2H), 4.21-4.13(m, 4H), 4.11-4.05(m, 1H), 4.00-3.97(m, 1H), 3.90-3.85(m, 1H), 3.58-3.54(m, 1H), 2.97-2.92(dd, 1H, *J* = 4.6 and 12.6 Hz), 2.74(d, 1H, *J* = 12.8 Hz), 2.22(t, 2H, *J* = 7.2 Hz), 2.12(s, 6H), 2.08(s, 3H), 2.05-2.02(m, 9H), 1.96(s, 3H), 1.92-1.88(m, 2H), 1.75-1.57(m, 7H), 1.44-1.29(m, 7H).^{13}CNMR(MeOH-d_4): δ 170.9, 170.6, 170.6, 170.6, 170.2, 170.0, 100.9, 99.1, 88.1, 87.8, 77.2, 75.6, 73.4, 72.4, 72.2, 69.4, 69.2, 68.2, 68.0, 67.6, 67.1, 62.7, 61.9, 60.6, 60.2, 55.7, 50.0, 39.8, 29.8, 29.0, 28.3, 28.0, 25.7, 25.3, 25.0, 19.6, 19.4, 19.4, 19.3, 19.2, 19.1.HRMS calculated for $[C_{45}H_{66}N_6O_{20}SNa]^+$ 1065.3950 Found 1065.3984.

GC-1a: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of **22** (0.145 umol, 15 mg). The reaction mixture was stirred for 5 h. The reaction solution was neutralized slowly using Dowex (H^+) resin. The resin was filtered and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as the eluant to afford 90% of the title compound. ^{1}HNMR(MeOH-d_4): δ 7.84 (s, 1H), 4.95 (s, 1H), 4.48(bs, 1H), 4.41-4.37(m,

3H), 4.28-4.25(s, 1H), 3.98(s, 1H), 3.91-3.79(m, 3H), 3.77-3.68(m, 6H), 3.60-3.52(m, 4H), 3.47-3.43(m, 1H), 3.33 (d, 1H, *J* = 1.6 Hz), 3.17(s, 2H), 3.02(s, 1H), 2.92-2.84(m, 2H), 2.71-2.51(m, 5H), 2.35-2.23(m, 3H), 1.96-1.87(m, 2H), 1.60(bs, 6H), 1.42(bs, 4H), 1.31-1.19(m, 4H). ^{13}CNMR(MeOH-d_4): δ 174.6, 164.7, 144.9, 122.8, 103.7, 101.1, 77.6, 74.7, 73.3, 71.5, 71.2, 70.0, 69.7, 69.6, 69.4, 61.9, 61.2, 60.2, 59.6, 55.6, 49.9, 47.6, 47.4, 47.2, 39.7, 35.2, 34.2, 29.8, 29.2, 28.3, 28.1, 25.8, 25.3, 25.0. HRMS Calculated for $[C_{31}H_{52}N_6O_{13}SNa]^+$ 771.3205 Found 771.3207.

Compound 23: Biotinylated dimeric scaffold[3-5] (19.30umol, 9.30mg) was added to the THF/H_2O (1m/1ml) solution of compound **21** (38.60umol, 7.65mg) followed by the addition of CuSO4.5H_2O (25.10umol, 6.27mg) and sodium ascorbate (38.60umol, 7.65mg).The reaction mixture was stirred for 24h at rt. After doing TLC analysis, the reaction mixture was dried *in vacuo* and the crude product was purified with flash chromatography (MeOH: CH_2Cl_2 1:9, Rf 0.62) to afford 40% of the title compound. ^{1}HNMR(MeOH-d_4): δ 8.17(s, 2H), 8.02-7.99(m, 2H), 5.53(s, 2H), 5.41-5.38(dd, 2H, *J* = 3.0 and 11.0 Hz), 5.22-5.13(m, 5H), 5.05(d, 2H, $J_{1,2}$ = 3.2 Hz), 5.01-4.98(dd, 2H, *J* = 2.0 and 10.8 Hz), 4.61-4.54(m, 6H), 4.51-4.49(m, 2H), 4.44-4.40(m, 7H), 4.33- 4.30(m, 1H), 4.20-4.10(m, 9H), 3.97(t, 2H, *J* = 8.0 Hz), 3.88-3.82(m, 2H), 3.55-3.50(m, 2H), 3.35(s, 1H), 3.24-3.21(m, 1H), 2.96-2.91(dd, 1H, *J* = 4.8 and 12.8 Hz), 2.74(d, 1H, *J* = 12.4 Hz), 2.44(t, 2H, *J* = 6.4 Hz), 2.13(s, 6H), 2.11(s, 6H), 2.07(s, 6H), 2.04(s, 6H), 2.00(bs, 12H), 1.95(s, 6H), 1.90(bs, 4H), 1.79-1.73(m, 3H), 1.66-1.49(m, 8H), 1.40-1.29(m, 10H). ^{13}CNMR($CDCl_3$): δ 170.9, 170.6, 170.6, 170.2, 170.0, 123.0, 121.6, 100.9, 99.0, 77.1, 72.4, 72.1, 69.2, 68.2, 67.6, 67.1, 62.6, 60.6, 29.8, 29.3, 28.9, 28.4, 28.1, 25.7, 25.2, 25.0, 19.6, 19.4, 19.4, 19.3, 19.2, 19.1. HRMS calculated for $[C_{88}H_{121}N_{11}O_{40}SNa]^{2+}$ 1025.3655 Found 1025.3909.

GC-1b: Compound **23** was dissolved in CH_3OH and NaOMe was added to the solution. The reaction was stirred for 5 h at rt. The reaction mixture was neutralized with Dowex (H^+) resin. The resin was filtered and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as the eluant to give 78% of the title compound. ^{1}HNMR(D_2O): δ 8.05- 7.99(m, 5H), 5.02(d, 2H, $J_{1,2}$ = 3.6Hz), 4.67-4.61(m, 6H), 4.39(bs, 9H), 4.08(bs, 4H), 3.95(d, 2H, J = 10.8 Hz), 3.88(m, 9H), 3.76-3.73(m, 10H), 3.59-3.55(m, 5H), 3.42(bs, 2H), 3.26-3.24(m, 3H), 3.04-2.95(m, 3H), 2.79-2.75(m, 2H), 2.47-2.39(m, 3H), 1.85(bs, 4H), 1.70-1.67(m, 4H), 1.56(bs, 6H), 1.39-1.24(m, 14H). ^{13}CNMR(D_2O): δ 175.0, 168.2, 165.2, 138.4, 134.6, 122.4, 102.8, 100.2, 77.1, 74.9, 72.5, 71.0, 70.8, 70.2, 69.2, 69.0, 68.7, 62.0, 60.5, 60.2, 60.0, 55.4, 50.4, 48.9, 39.8, 36.2, 35.1, 35.0, 29.2, 28.6, 28.0, 27.8, 25.3, 24.4. HRMS calculated for $[C_{60}H_{93}N_{11}O_{26}SNa]^+$ 1438.5928 Found 1438.5912.



Scheme 2. *Attempted synthesis of* ***GC-2a*** *and* ***GC-2b****. Reagents and conditions.* a) CH_2Cl_2, TMSOTf, -30°C to rt, 90% b)NaOMe, MeOH, rt, 93% c) $PhCH(OMe)_2$, p-TsOH, THF, 76% d) NaH, BnBr, THF, reflux, 62% e) $NaCNBH_3$, $HCl.Et_2O$, THF, 73% f) CH_2Cl_2, TMSOTf, -30°C, 62% g) AcSH, 46% h) DMF, NaN_3, 90% l) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 70% j) i.MeOH, NaOMe, rt ii. Pd $(OH)_2$, H_2, EtOH/EtOAc, k) Na, NH_3

6-Chlorohexyl-2-azido-2-deoxy-3, 4, 6-tri-O-acetyl-α-D-β-galactopyranoside (17): 6-Chlorohexanol (3.53 mmol, 0.48g) was added to a CH_2Cl_2 solution of compound **7**[6] (2.93 mmol, 1.4g). The reaction mixture was cooled down to -30 ^{0}C followed by the addition of TMSOTf (0.73 mmol, 0.73 µl). The reaction mixture was stirred until the temperature increased to 0 ^{0}C. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$. The organic solvent was collected and dried over Na_2SO_4. After removing the solvent *in vacuo*, the crude product was purified using flash chromatography (EtOAc: Hex 3:7, Rf 0.44) to afford 91% of the title compound. ^{1}HNMR ($CDCl_3$): δ 5.34(d, 1H, J = 2.8 Hz), 4.79-4.76 (dd, 1H, J = 3.6 and 11.3 Hz), 4.39(d, 1H, $J_{1,2}$ = 8.0 Hz), 4.20-4.14(m, 2H), 4.00-3.95 (m, 1H), 3.88-3.85(m, 1H), 3.70-3.66(dd, 1H, J = 8.0 and 10.8 Hz), 3.62-3.54(m, 3H), 2.16(s, 3H), 2.06(bs, 6H), 1.83-1.76(m, 2H), 1.72-1.67(m, 2H), 1.50-1.44(m, 4H). ^{13}CNMR ($CDCl_3$): δ 170.8, 170.5, 170.0, 102.3, 70.9, 70.5, 70.1, 66.6, 61.0, 60.9, 44.7, 32.1, 29.4, 26.7, 24.9, 20.8. HRMS calculated for $[C_{18}H_{28}N_3O_8Na]^+$ 472.1463 Found 472.1453.

6-Chlorohexyl-2-azido-2-deoxy-3-O-benzyl-4,6-O-benzylidene-α-D-β-galactopyranoside (24): Compound **17** (2.67 mmol, 1.2g) was dissolved in MeOH (15ml) and treated with NaOMe (10ml) to remove the ester protecting groups. The deprotected product (1.73 mmol, 0.56g) was dissolved in THF (10ml) and treated with benzaldehyde dimethylacetal (5.19 mmol, 0.8g) and catalytic amount of p-TsOH. The reaction mixture was refluxed for 12 h. After TLC analysis, the reaction mixture was cooled down to rt and the solvent was removed *in vacuo*. The crude product was washed with saturated $NaHCO_3$ and EtOAc. The organic solvent was dried over Na_2SO_4 and removed *in vacuo*. The crude product was further purified with flash chromatography (EtOAc: Hex 3:7) to give 76 % of the benzylidene acetal protected compound.

THF solution of this compound (1.32mmol, 0.54g) was treated with hexane washed NaH (6.60mmol, 0.16g) and BnBr (3.90 mmol, 0.67g). The reaction mixture was refluxed for 12 h. Once the reaction mixture was cooled to rt; the excess NaH was neutralized with CH_3OH. The reaction mixture was dried *in vacuo* and the crude product was diluted with EtOAc and washed with saturated $NaHCO_3$. The organic solvent was dried over Na_2SO_4 and removed *in vacuo*. The crude product was further purified with flash chromatography (EtOAc: Hex 2:8, Rf 0.32) to give 62% of the title compound as a white solid. ^{1}HNMR($CDCl_3$): δ 7.54-7.52 (dd, 2H, J = 2.0 and 7.2 Hz), 7.41-7.28(m, 8H), 5.47(s, 1H), 4.73(s, 2H), 4.29 (d, 1H, J = 12.4 Hz), 4.24(d, 1H, $J_{1,2}$ = 8.0Hz)**,** 4.06(d, 1H, J = 3.6 Hz), 4.02-3.93(m, 2H), 3.87-3.82(dd, 1H, J = 8.0 and 10.0 Hz), 3.54-3.47(m, 3H), 3.36-3.32(dd, 1H, J = 3.4 and 10 Hz), 3.27(s, 1H), 1.81-1.74(m, 2H), 1.70-1.63(m, 2H), 1.47-1.41(m, 4H). ^{13}CNMR ($CDCl_3$): δ 137.8, 137.7, 129.0, 128.5, 128.2, 128.0, 127.9, 126.4, 102.2, 101.1, 72.5, 71.5, 69.8, 69.2, 66.5, 62.1, 45.1, 32.5, 29.3, 26.6, 25.3. HRMS calculated for $[C_{26}H_{32}N_3O_5ClNa]^+$ 524.1923 Found 524.1922.

6-Chlorohexyl-2-azido-2-deoxy-4, 3-di-O-benzyl-β-D-galactopyranoside (10): $NaCNBH_3$ in THF (4.9mmol, 4.9 ml) was added to a THF solution of compound **24**. HCl in Et_2O was added to the stirring reaction mixture until evolution of H_2 gas ceased. After 40 min, the reaction mixture was dried *in vacuo* and the crude product was washed with saturated $NaHCO_3$ and EtOAc. The organic solvent was dried over Na_2SO_4 and removed *in vacuo*. The crude product was further purified with flash chromatography (EtOAc: Hex 3:7, Rf 0.36) to give 72% of the title compound. ^{1}HNMR($CDCl_3$): δ 7.38-7.28(m, 10H), 4.70(s, 2H), 4.57(s, 2H), 4.21(d, 1H, $J_{1,2}$ = 8.0Hz), 3.99(bs, 1H), 3.95-3.85(m, 1H), 3.80-3.76(dd, 1H, J = 6 and 9.6 Hz), 3.73-3.69(dd, 1H, J = 5.8 and 9.8 Hz), 3.66-3.61(dd, 1H, J = 8.0 and 10.0 Hz), 3.54-3.49(m, 4H), 3.29-3.26(dd, 1H, J = 3.2 and 10.0 Hz), 2.48(s, 1H), 1.81-1.74(m, 2H), 1.66-1.60(m, 2H), 1.46-1.40(m, 4H).

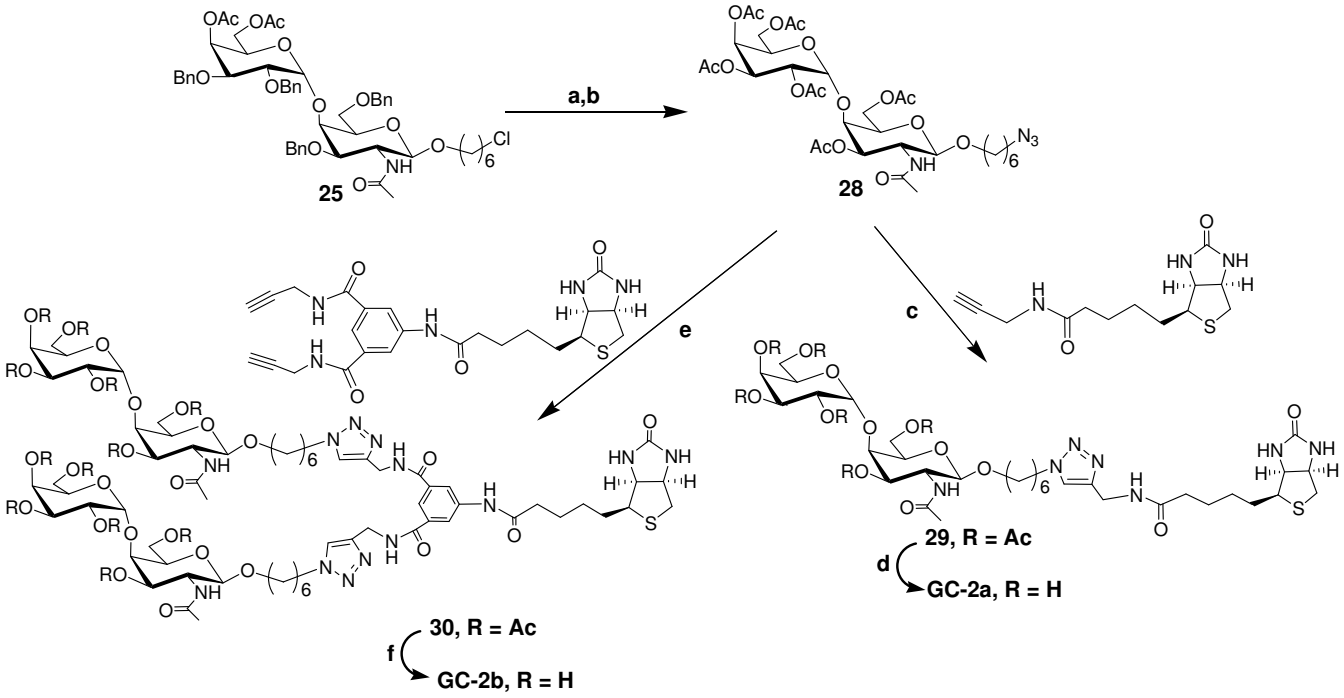
^{13}CNMR ($CDCl_3$): δ 137.8, 137.2, 128.6, 128.5, 128.2, 128.0, 127.9, 102.2, 79.1, 73.8, 73.2, 72.1, 69.9, 69.0, 65.7, 62.8, 45.1, 32.5, 29.4, 26.6, 25.3. HRMS calculated for $[C_{26}H_{34}N_3O_5ClNa]^+$ 526.2078 Found 526.2079.

6-Chloro-hexyl (4, 5-di-O-acetyl, 3-di-O-benzyl-α-D-galactopyranoside)(1→4) 2-acetamido-2-deoxy-3, 4-dibenzyl-β-D-galactopyranoside (25). 1ml CH_2Cl_2 solution of Compound **6**[6] (0.22 mmol, 0.13g) and compound **10** (0.18 mM, 0.09g) were mixed and cooled to -25^{o}C. After 5 min, TMSOTf (44.70mmol, 44.70ul) was added drop wise to the mixture. The reaction mixture was stirred for 4 h at -25^{o}C. Upon TLC analysis, the reaction was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$. The dried product was purified with flash chromatography (EtOAc: Hex 3:7, Rf 0.42) to give 62% of **27**. Thioacetic acid (3ml) was added to **27** (0.10mmol, 0.10g) and the reaction solution was stirred for 48 h excluded from light. After TLC analysis, AcSH was removed under reduced pressure, and the crude product was diluted with EtOAc and washed with saturated $NaHCO_3$. The dried product was purified with flash chromatography (EtOAc: Hex 7:3, Rf 0.36) to give 40% of the title compound. ^{1}HNMR($CDCl_3$): δ 7.33-7.30(m, 13H), 7.27-7.25(m, 5H), 7.20(d, 2H, 6.8 Hz), 5.58(d, 1H, J = 2.0 Hz), 5.53(d, 1H, 7.6 Hz), 5.06(d, 1H, $J_{1,2}$ = 3.6Hz), 4.88-4.82(m, 2H, 4.76 (bs, 1H), 4.73(bs, 1H), 4.62-4.56(m, 2H), 4.53(d, 1H, J = 10.4Hz), 4.43(d, 1H, $J_{1,2}$ = 12.0 Hz), 4.31-4.23(m, 2H), 4.16-4.11(m, 2H), 4.02-3.94(m, 3H), 3.88-3.75(m, 3H), 3.63-3.45(m, 6H), 2.08(s, 3H), 1.93(s, 3H), 1.91(s, 3H), 1.78-1.71(m, 2H), 1.61-1.56(m, 2H), 1.45-1.31(m, 4H). ^{13}CNMR($CDCl_3$): δ 170.5, 170.4, 170.3, 138.7, 138.1, 138.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 100.3, 100.2, 75.7, 74.1, 73.7, 73.5, 73.0, 71.8, 69.5, 67.8, 67.4, 66.5, 61.4, 54.5, 45.1, 32.5, 29.4, 26.6, 25.2, 23.7, 20.9, 20.8. LRMS Calculated for $[C_{52}H_{64}ClN_1O_{13}Na]^+$ 968.3879 **Found** 968.3964.

6-Azido-hexyl (4, 5-di-O-acetyl, 3-di-O-benzyl-α-D-galactopyranoside)(1→4) 2-acetamido-2-deoxy-3, 4-dibenzyl-β-D-galactopyranoside (26). NaN_3 (11.3 mg, 0.17 mmol) was added to the DMF solution of compound **25** (110mg, 0.116 mmol). The reaction was refluxed for 5 hr and DMF was removed under pressure. The dried product was washed with water and EtOAc. The organic solvent was dried over Na_2SO_4 and removed *in vacuo*. The crude product was purified with flash chromatography (EtOAc: Hex 7:3, Rf 0.36) giving 90 % of the title compound. ^{1}HNMR($CDCl_3$): δ 7.31-7.26(m, 17H), 7.20-718(m, 3H), 5.59(d, 1H, *J* = 2.0 Hz), 5.54(d, 1H, *J* = 7.8 Hz), 5.07(d, 1H, $J_{1,2}$ = 3.6 Hz), 4.88(d, 1H, *J* = 11.6 Hz), 4.82(d, 1H, $J_{1,2}$ = 8.4 Hz), 4.77(s, 1H), 4.74(d, 1H, *J* = 2.4 Hz), 4.62-4.55(m, 2H), 4.52(d, 1H, *J* = 10.4 Hz), 4.46(d, 1H, $J_{1,2}$ = 12.0 Hz), 4.30-4.23(m, 2H), 4.16-4.11(m, 2H), 4.01-3.94(m, 3H), 3.88-3.75(m, 3H), 3.63-3.43(m, 4H), 3.23(t, 2H, *J* = 7.2 Hz), 2.08(s, 3H), 1.93(s, 3H), 1.91(s, 3H), 1.59-1.56(m, 4H), 1.36-1.34(m, 4H). ^{13}CNMR($CDCl_3$): δ 170.5, 170.5, 170.3, 138.7, 138.1, 138.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 100.4, 100.2, 75.8, 74.1, 73.6, 73.5, 73.0, 72.0, 71.8, 69.4, 67.8, 67.4, 66.5, 61.4, 54.5, 51.4, 29.4, 28.8, 26.5, 25.5, 23.7, 20.9, 20.8. HRMS calculated for $[C_{52}H_{64}N_4O_{13}Na]^+$ 975.4361 **Found** 975.4362.

Compound 27. The biotinylated monomeric scaffold[3-5] (22.0umol, 6.2mg) was added to the H_2O / THF (1.5ml/1.5ml) solution of compound **26** (22umol, 21mg) followed by the addition of copper sulfate (33.0umol, 8.26mg) and sodium ascorbate (44.00umol, 8.74mg).The reaction mixture was stirred for 24 hrs at room temperature. After TLC analysis, the reaction mixture was dried under pressure and the crude product was directly dumped in to the column and purified with flash chromatography (DCM: MeOH:9:1, Rf 0.62) giving 70% the title compound.^{1}HNMR(MeOH-d_4): δ 7.82(s, 1H), 7.32-7.21(m, 19H), 5.59(s, 1H), 5.07(d, 1H, $J_{1,2}$ = 2.8 Hz), 4.81- 4.74(m, 3H), 4.71-4.65(m, 1H), 4.65(d, 1H, *J* = 11.2 Hz) , 4.54-4.45(m, 3H),

4.43-4.39(m, 3H), 4.36-4.33(m, 2H), 4.29-4.24(m, 3H), 4.17-4.13(m, 2H), 3.99-3.95(m, 2H), 3.88-3.79(m, 2H), 3.66(bs, 2H), 3.60-3.55(m, 1H), 3.48-3.44(m, 2H), 3.33(bs, 4H), 3.17-3.13(m, 1H), 2.94-2.89(dd, 1H, *J* = 4.8 and 12.8 Hz,), 2.74(d, 1H, *J* = 12.8 Hz), 2.26-2.22(t, 2H, *J* = 7.2 Hz), 2.04(s, 3H), 1.94(s, 3H),1.87(s, 5H), 1.67-1.54(m, 7H),1.40-1.28 (m, 7H). ^{13}CNMR(MeOH-d_4): δ 174.5, 172.1, 170.8, 170.6, 138.7, 138.4, 138.3, 138.2, 128.0, 120.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 126.8, 101.7, 99.9, 87.9, 79.2, 76.1, 75.8, 75.6, 73.7, 73.5, 73.4, 73.2, 72.8, 71.9, 71.5, 69.0, 68.1, 67.7, 66.4, 60.7, 60.2, 55.6, 52.0, 39.8, 35.2, 34.2, 29.8, 29.0, 28.3, 28.1, 25.7, 25.3, 25.1, 21.8, 19.5, 19.3. HRMS calculated for $[C_{65}H_{83}N_7O_5SNa]^+$1256.5559 **Found** 1256.5560.



Scheme 3: *Synthesis of **GC-2a** and **GC-2b**. Reagents and conditions:* a) i. NaOMe, MeOH, rt ii. $Pd(OH)_2$, EtOH, H_2, over two steps 75% b) i. Ac_2O, Pyridine, DMAP, 78% ii. DMF, NaN_3, 90% c) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, t-BuOH/H_2O, 70% d) MeOH, NaOMe, rt ,90% e) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, t-BuOH/H_2O, 70% f) MeOH, NaOMe, rt, 90%

GC-2a: Our attempt to remove the benzyl protecting groups from compound **27** using reductive hydrogenation reaction and birch reduction did not work. The desired product was not obtained through this synthetic route. Instead Scheme 3 was used to obtain the final product.

6-Azido-hexyl (2, 3, 4, 5-tetr-O-acetyl-α-D-galactopyranoside)(1→4) 2-acetamido-2-deoxy-3, 5-di-acetyl-β-D-galactopyranoside (28): NaOMe (3 ml of 1M solution in MeOH,) was added to CH_3OH solution (4 ml) of compound **25** (0.32 mmol, 300 mg) to remove the acetate protecting groups. The product was purified and subjected to subsequent hydrogenation reaction to remove the benzyl protecting groups giving a white powder (75% y over two steps). This product (0.16 mmol, 120 mg) was further subjected to global acetylation reaction. The acetylated product was dissolved in DMF and sodium azide (0.26mmol, 17mg) was added to the solution. The reaction mixture was stirred for 5h at 100^{o}C. DMF was removed *in vacuo* and the crude product was purified with flash chromatography (EtOAc, Rf 0.38) giving 90% of the title compound. ^{1}HNMR($CDCl_3$): δ 5.96 (d, 1H, *J* = 7.6 Hz), 5.52(s, 1H), 5.36(d, 1H, *J* = 10.8 Hz), 5.29(d, 1H, 11.2 Hz), 5.21-5.17(dd, 1H, *J* = 2.8 and 11.2 Hz), 5.03(s, 1H), 4.87(d, 1H, $J_{1,2}$ = 8.00 Hz), 4.50 (bs, 1H), 4.45-4.40(dd, 1H, *J* = 6.8 and 10.8 Hz), 4.24-4.20(dd, 1H, *J* = 5.4 and 10.6 Hz), 4.15-4.07(m, 3H), 3.90-3.72(m, 3H), 3.53-3.48(m, 1H), 3.27(t, 2H, *J* = 6.4 Hz), 2.15(s, 3H), 2.11(bs, 6), 2.07(s, 6H),1.99(s, 3H), 1.96(s, 3H), 1.61(s, 4H), 1.39(s, 4H). ^{13}CNMR($CDCl_3$): δ 170.8, 170.7, 170.6, 170.5, 170.3, 170.2, 169.9, 100.4, 99.0, 77.1, 76.8, 71.8, 71.3, 69.5, 68.5, 67.7, 67.5, 66.5, 62.2, 60.6, 52.4, 51.3, 29.3, 28.7, 26.4, 25.5, 23.4, 21.0, 20.8, 20.8, 20.7, 20.6. HRMS calculated for $[C_{32}H_{48}N_4O_{17}Na]^+$ 783.2907 **Found** 783.2908.

Compound 29. The biotinylated monomeric scaffold [3-5] (18.40umol, 5.17mg) was added to the H_2O / tert-butanol (1m/0.75ml) solution of compound **28** (18.4umol, 14m) followed by the addition of $CuSO_4.5H_2O$ (27.6umol, 6.89mg) and sodium ascorbate (55.2umol, 10.9mg).The

reaction mixture was stirred for 24 h at rt. After doing TLC analysis, the reaction mixture was dried *in vacuo* and the crude product was directly dumped in to the column and flashed with MeOH: CH_2Cl_2 (2:8, Rf 0.56) giving 52.6% yield of the title compound. ^{1}HNMR(MeOH-d_4): δ 7.82 (s, 1H), 5.50(s, 1H), 5.42-5.38(m, 2H), 5.19-5.16(m, 2H), 5.03(s, 2H), 4.52-4.46(m, 3H), 4.40-4.32(m, 4H), 4.28- 4.25(m, 1H), 4.21-4.01(m, 5H), 3.91-3.81(m, 3H), 3.50-3.46(m, 1H), 3.18-3.16(m, 2H), 2.92-2.87(m, 1H), 2.70-2.66(m, 1H), 2.10-1.85(m, 22H), 1.70(m, 8H), 1.40-1.26(m, 8H).^{13}CNMR(MeOH-d_4): δ 174.6, 172.1, 171.0, 170.9, 170.8, 170.7, 170.2, 164.7, 101.4, 98.9, 76.3, 72.3, 72.1, 70.7, 69.3, 68.2, 68.1, 67.6, 66.8, 62.6, 63.0, 60.6, 60.2, 55.6, 50.4, 49.9, 39.7, 35.2, 35.1, 34.2, 29.8, 29.0, 28.3, 28.1, 25.7, 25.3, 25.0, 21.5, 19.7, 19.5, 19.3, 19.2, 19.2.HRMS calculated $[C_{45}H_{67}N_7O_{19}SNa]^+$ 1064.4105 **Found** 1064.4108.

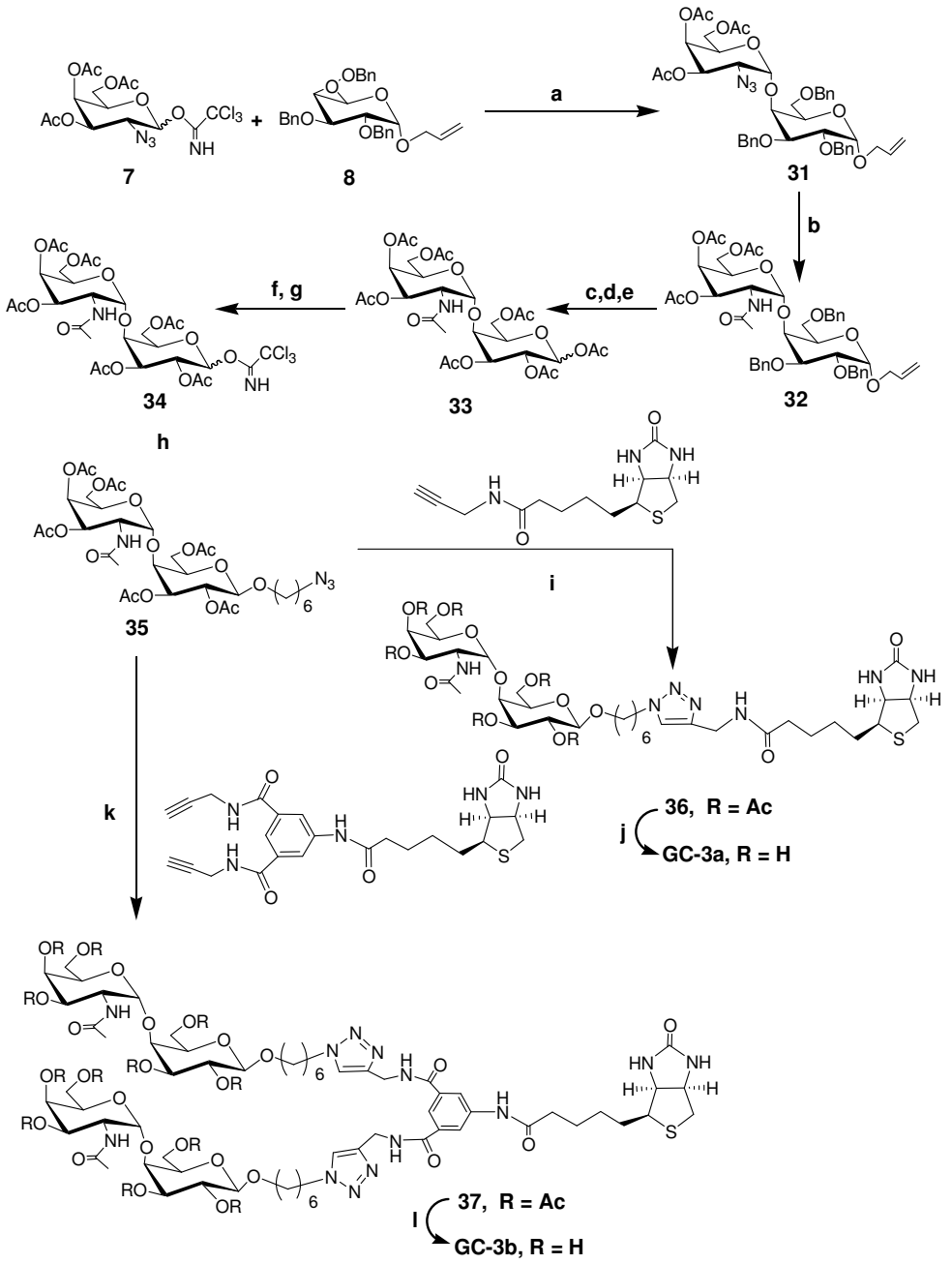
GC-2a: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **29** (0.192 umol, 20 mg). The reaction mixture was stirred for 5h and was neutralized slowly using ion exchange resin**.** The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant giving 90% of the title compound**.** ^{1}HNMR(D_2O): δ 7.96(s, 1H), 5.05(s, 1H), 4.67(bs, 1H), 4.50-4.44(m, 6H), 4.10-3.91(m, 8H), 3.77-3.62(m, 9H), 3.39-3.30(m, 2H), 3.03-2.97(m, 3H), 2.84-2.66(m, 3H), 2.35(bs, 2H), 2.06(s, 3H), 1.94(bs, 2H), 1.71-1.58(d, 7H), 1.37-1.29(m, 7H). ^{13}CNMR(D_2O): δ 176.7, 174.6, 165.2, 124.0, 101.6, 100.4, 76.9, 74.9, 71.7, 70.8, 70.6, 70.1, 69.7, 69.6, 69.4, 69.1, 69.0, 68.7, 62.5, 62.0, 60.5, 60.2, 60.2, 55.4, 52.7, 50.4, 39.7, 35.2, 34.3, 29.3, 28.4, 27.7, 27.6, 25.2, 25.1, 24.4, 22.2.HRMS calculated $[C_{32}H_{53}N_7O_{13}S+Na]^+$ 812.3471 Found 812.3471.

Compound 30: The biotinylated dimeric scaffold[3-5](24.50umol, 11.7mg) was added to the H_2O / tert-butanol (1.5ml / 1ml) solution of compound **28** (40.7umol, 31mg) followed by the addition of $CuSO_4.5H_2O$ (53.0umol, 13.2mg) and sodium ascorbate (81.5umol, 16mg).The reaction

mixture was stirred for 48 h at rt. After doing TLC analysis, the reaction mixture was dried *in vacuo* and the crude product was directly dumped in to the column and purified with flash chromatography (MeOH: CH_2Cl_2 2:8, Rf 0.58) giving 32.6% yield of the title compound. ^{1}HNMR(MeOH-d_4): δ 8.15(s, 2H), 8.03-7.92(m, 3H), 5.51(s, 2H), 5.43-5.39 (dd, 2H, *J* = 3.0 and 10.6 Hz), 5.20-5.17(m, 3H), 5.04(bs, 3H), 4.96- 4.93(m, 3H), 4.62-4.59(m, 13H), 4.49(d, 3H, *J* = 8.0 Hz), 4.41-4.37(m, 6H), 4.32-4.29(m, 1H), 4.22-4.07(m, 9H), 3.97-3.80(m, 4H), 3.49-3.48(m, 2H), 3.22-3.19(m, 1H), 2.94-2.89(dd, 1H, *J* = 4.6 and 12.6 Hz), 2.71(d, 1H, *J* = 12.8 Hz), 2.42(bs, 2H), 2.12-2.09(m, 11H), 2.06(s, 5H), 2.03(s, 5H) 1.99(s, 7H), 1.93(s, 6H), 1.89(s, 8H), 1.80-1.73(m, 3H), 1.64-1.49(m, 7H), 1.38-1.30(d, 10H). ^{13}CNMR(MeOH-d_4): δ 173.3, 172.0, 171.0, 170.8, 170.8, 170.7, 170.7, 170.1, 167.7, 164.7, 139.2, 135.3, 121.6, 121.1, 101.4, 98.9, 76.3, 72.2, 72.1, 69.2, 68.2, 68.1, 67.6, 66.8, 62.6, 62.0, 60.6, 60.2, 55.6, 50.4, 50.0, 39.7, 36.2 34.9, 29.8, 29.0, 28.4, 28.1, 25.7, 25.2, 25.0, 21.5, 19.7, 19.5, 19.3, 19.3, 19.2 $[C_{88}H_{123}N_{13}O_{38}SNa_2]^{2+}$ 1023.8798 Found 1023.8802.

GC-2b: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **30** (7.99 umol, 16.00 mg). The reaction mixture was stirred for 5 h and was neutralized slowly using ion exchange resin**.** The resin was filtered out and washed with CH_3OH. The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant giving quantitative yield of the title compound**.** ^{1}HNMR(D_2O): δ 8.51(s, 1H), 8.02-7.94(m, 5H), 5.03(s, 2H), 4.65-4.59(m, 5H), 4.43-4.38(m, 8H), 4.08-4.01(m, 6H), 3.98-3.88(m, 8H), 3.82-3.69(m, 13H), 3.63-3.60(m, 2H), 3.49(d, 2H, *J* = 6.4 Hz), 3.41(m, 2H), 3.22-3.21(m, 1H), 3.02-2.97(m, 3H), 2.76(d, 1H, *J* = 13.2 Hz), 2.42-2.37(s, 2H), 2.02(s, 7H), 1.82(m, 4H), 1.67-1.63(m, 4H), 1.47(bs, 5H), 1.37-1.20(m, 13H). ^{13}CNMR(D_2O): δ 174.9, 174.5, 170.9, 168.0, 165.1, 138.4, 134.5, 123.8, 122.3, 101.6, 100.4, 76.7, 74.8, 72.0, 70.8, 70.6,

70.0, 69.1, 69.0, 68.7, 62.5, 62.0, 60.5, 60.2, 60.1, 55.3, 52.7, 50.3, 43.4, 39.7, 36.2, 35.0, 29.4, 28.4, 28.0, 27.7, 25.2, 24.4, 22.2. HRMS calculated for $[C_{64}H_{99}N_{13}O_{26}S+2Na]^{2+}$ 771.8356 Found 771.8370.



Scheme 4. *Synthesis of **GC-3a** and **GC-3b**. Reagents and conditions.* a) CH_2Cl_2, TMSOTf, -30°C to rt, 60% b) CH_3COSH, rt, 61% c) $PdCl_2$, NaOAc, AcOH, H_2O, rt, 54% d) $Pd(OH)_2$, H_2, EtOAc/ EtOH, rt yield e) Ac_2O, pyridine, DMAP, 0°C to rt , 57% f) H_2NNH_2.HOAc, THF, rt, 63% g) K_2CO_3, CH_2Cl_2, Cl_3CCN, rt, 77% h) CH_2Cl_2,TMSOTf, $HO(CH_2)_6Cl$, -25 0°C to rt, 54.6% i)$CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H2O, 70% j) MeOH, NaOMe, rt, quantitative k)$CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 40% l) MeOH, NaOMe, rt, quantitative.

Allyl (2-N-acetamido-2-deoxy-3, 4, 6-tri-O-acetyl-α-D-galactopyranosyl) -(1→4)2, 3, 6-tri-O-benzyl-β-D-galactopyranoside (32). Compound **7**[6] (0.70g, 1.47 mmol) and **8**[2] (0.87g, 1.76 mmol) were mixed in 10 ml of anhydrous CH_2Cl_2.The reaction mixture was cooled down to -30 ^oC and treated with TMSOTf (0.37mmol, 1.60ml).The reaction was stirred until the temperature reached 0^oC. When TLC analysis indicated completion of the donor (limiting reagent), the reaction mixture was diluted with CH_2Cl_2 (10ml) and quenched with saturated $NaHCO_3$. The organic layer was separated, and after drying over $NaSO_4$, the solvent was removed *in vacuo* and the residue was then purified by flash chromatography (EtOAc: Hex 4:6, Rf 0.50) to give the coupled product (0.60g, 72%) as a colorless syrup. AcSH (10ml) was added to compound **31** (0.60 g, 0.75 mmol) and the solution was stirred for 48 h excluded from light. Excess AcSH was removed *in vacuo* and the dried product was diluted with EtOAc and washed with saturated $NaHCO_3$. The organic layer was collected, dried over Na_2SO_4 and removed *in vacuo*. The residue was purified with flash chromatography (EtOAc: Hex 8:2, Rf 0.32) to give the title compound (0.37g, 61%) as a colorless syrup. ^{1}HNMR ($CDCl_3$): δ 7.43-7.41(m, 2H), 7.38-7.29 (m, 12H), 7.26-7.22(m, 1H), 5.94-5.75(m, 1H), 5.77(d, 1H, J = 9.6 Hz), 5.33-5.26(m, 2H), 5.21-5.14(m, 2H), 5.02(d, 1H, $J_{1,2}$ = 3.6 Hz), 4.88(d, 1H, $J_{1,2}$ = 3.6Hz), 4.83-4.79(m, 2H), 4.76-4.71(m, 2H), 4.68-4.64(m, 1H), 4.62-4.56(m, 1H), 4.53(d, 1H, J = 11.6 Hz), 4.41(d, 1H, J = 11.6 Hz), 4.22(d, 1H, J = 2.4 Hz), 4.14-4.09(m, 1H), 4.02-3.84(m, 5H), 3.54-3.51(dd, 1H, J = 5.6 and 10.6 Hz), 3.45(d, 2H, J = 7.6 Hz), 2.12(s, 3H), 2.01(s, 3H), 1.91(s, 3H), 1.86(s, 3H). ^{13}CNMR ($CDCl_3$): δ 171.0, 170.4, 170.0, 169.9, 138.3, 138.2, 137.3, 133.8, 128.5, 128.4, 128.4, 128.2, 128.0, 127.8, 127.5, 127.4, 118.1, 98.1, 96.1, 76.0, 74.0, 73.6, 73.4, 73.1, 68.8, 68.5, 68.2, 67.1, 67.0, 66.3, 60.8, 48.1, 23.4, 20.9, 20.8, 20.6 HRMS: Calculated for $[C_{44}H_{53}NO_{14}+Na]^+$ 842.3364 Found 842.3362.

O-(2-N-acetamido-2-deoxy-3, 4, 6-triacetyl-α-D-galactopyronosyl)-(1→4) 2, 3, 6-tri-O-acetyl-β-D- galactopyranosyl trichloroacetonitrile (34). Compound **32** (0.11 g) was dissolved in 3 ml of AcOH and 300 µl of water. $PdCl_2$ (0.046g, 0.26 mmol) and NaOAc (0.041g, 0.29 mmol) was added to the solution and the reaction mixture was stirred for 12 h under argon. Upon TLC analysis, the reaction mixture was diluted with EtOAc and passed through celite pad. The filtrate was washed with saturated $NaHCO_3$ and brine consecutively. The organic layer was dried over Na_2SO_4 and removed *in vacuo*. The dried residue was subjective to reductive hydrogenation reaction to remove the benzyl protecting groups. The dried product was dissolved in ethanol and treated with Pd $(OH)_2$. The reaction mixture was stirred under hydrogen gas positive pressure for 48 h. The reaction mixture was diluted with EtOH and the solution was passed through celite pad. The solvent was removed *in vacuo* and the deprotected compound was obtained as a white solid. This crude product was further subjected to acetylation reaction to obtain **33** (67% over three steps) as a white powder. To the THF solution of **33** (0.13g, 0.19mmol) was added hydrazine acetate (23 mg, 0.25mmol) and the reaction was stirred at rt for 18 h. The reaction solvent was removed *in vacuo*. The dried product was diluted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and removed *in vacuo*. The dried residue was purified with flash chromatography (100% EtOAc, Rf 0.46) to get the hemiacetal product of compound **33** (55mg, 60%) as a white powder. CH_2Cl_2 solution of the hemiacetal (55mg, 86.60mmol) was added to the dried and activated K_2CO_3 (0.30g, 2.16mmol) followed by the addition of trichloroacetonitrile (0.13g, 0.87mmol). The reaction was stirred for 12 h at rt. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and removed *in vacuo*. The crude product was purified with flash chromatography

(EtOAc: Hex 7:3, Rf 0.32) to afford 77% of the title compound. ^{1}HNMR($CDCl_3$): δ 8.69(s, 1H, NH), 6.64(d, 1H, $J_{1,2}$ = 3.6 Hz), 5.86(d, 1H, *J* = 9.2 Hz), 5.47-5.44(dd, 2H, *J* = 2.6 and 6.6 Hz), 5.35-5.31(dd, 1H, *J* = 3.4 and 11.0 Hz), 5.23-5.19(dd, 1H, *J* = 2.8 and 7.6 Hz), 5.00(d, 1H, $J_{1,2}$ = 3.2 Hz), 4.69-4.63(m, 1H), 4.53(t, 1H, *J* = 6.4 Hz), 4.38-4.33(m, 3H), 4.14-3.95(m, 3H), 2.16(s, 3H), 2.12(s, 3H), 2.05-2.03(m, 15H) . ^{13}CNMR ($CDCl_3$): δ 171.0, 170.5, 170.3, 170.2, 170.1, 169.9, 160.9, 98.6, 93.3, 73.7, 70.7, 68.8, 67.8, 67.2, 67.1, 66.8, 61.1, 48.0, 23.3, 20.9, 20.8, 20.7, 20.6, 20.6, 20.5.

6-Azido-hexyl (2-N-acetamido-2-deoxy-3, 4, 6 tri-O-acetyl- α-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-acetyl- β-D-galactopyranoside (35). Compound **34** (44mg, 56.30umol)) was dissolved in distilled CH_2Cl_2 and 6-azidohexanol linker was added into the solution. The reaction mixture was cooled to -30^{o}C followed by the addition of TMSOTf (28.10umol, 28µl).The reaction mixture was stirred until the temperature reached 0^{o}C. Up on TLC analysis, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$.The organic layer was dried over Na_2SO_4 and removed *in vacuo*. The crude product was purified with flash chromatography (EtOAc: Hex 8:2, Rf 0.40) to give the title compound. ^{1}HNMR ($CDCl_3$): δ 5.99(d, 1H, *J* = 9.2 Hz), 5.46(d, 1H, *J* = 2.4 Hz), 5.22-5.14(m, 2H), 5.01(d, 2H, $J_{1,2}$ = 2.8 Hz), 4.66-4.60(m, 1H), 4.52-4.44(m, 3H, *J* = 7.6Hz), 4.15-4.10(m, 2H), 4.05-3.95(m, 2H), 3.91-3.86(m, 1H), 3.78(t, 1H, *J* = 7.0 Hz), 3.50-3.45(m, 1H), 3.27 (t, 2H, *J* = 7.2 Hz), 2.15(s, 3H), 2.09(s, 3H), 2.08(s, 3H), 2.06(s, 3H), 2.04(s, 3H), 2.01(s, 3H), 2.00(s, 3H), 1.62-1.59(m, 4H), 1.39-1.37 (m, 4H). ^{13}CNMR ($CDCl_3$): δ 170.8, 170.4, 170.3, 170.2, 169.1 100.4, 98.8, 73.6, 72.0, 72.0, 70.0, 69.2, 69.9, 67.0, 66.9, 61.2, 61.0, 51.4, 48.1, 29.3, 28.8, 26.4, 25.5, 23.2, 20.8, 20.7, 20.7, 20.7 HRMS calculated for $[C_{32}H_{48}N_4O_{17}+Na]^{+}$ 783.2907 Found 783.2907.

Compound 36: Biotinylated monomeric scaffold [3-5] was added (0.20 umol, 5.50mg) to the THF/ H_2O (1ml /1ml) solution of compound **35** (0.197umol, 15.00 mg) followed by the addition of $CuSO_4.5H_2O$ (0.296umol, 7.40mg) and sodium ascorbate (0.395umol, 7.80mg). The reaction mixture was stirred for 48 h at rt. After TLC analysis, the product was dried *in vacuo* and purified using flash chromatography (CH_2Cl_2: MeOH 8:2, Rf 0.62) to give 70% of the title compound. ^{1}HNMR(MeOH-d_4): δ 8.41 (d, 1H, *J* = 8.4 Hz), 7.84(s, 1H), 5.50 (s, 1H), 5.26-5.11(m, 3H), 4.97(d, 1H, $J_{1,2}$ = 3.6 Hz), 4.65-4.60(m, 2H), 4.51-4.45(m, 2H), 4.42-4.36(m, 5H), 4.31-4.28(m, 1H), 4.21-4.15(m, 2H), 4.10-4.06(m, 1H), 4.02-3.94(m, 2H), 3.89-3.84(m, 1H), 3.58-3.53(m, 1H), 3.35 (s, 1H), 3.22-3.17(m, 1H), 2.95-2.91(dd, 1H, *J* = 4.8 Hz and 12.8 Hz), 2.72(d, 1H, *J* = 12.4 Hz), 2.24(t, 2H, *J* = 7.4 Hz), 2.13(s, 3H), 2.09(s, 3H), 2.04(bs, 6H), 2.01(s, 3H), 1.99(s, 3H), 1.97(s, 3H), 1.89(t, 2H, *J* = 7.2 Hz), 1.71-1.58(m, 7H), 1.46-1.31(m, 7H). ^{13}CNMR (MeOH-d_4): δ 174.6, 172.7, 170.7, 170.5, 170.5, 170.2, 170.0, 122.8, 101.1, 98.8, 74.4, 72.4, 72.0, 69.8, 69.5, 67.5, 67.0, 66.7, 61.9, 61.4, 60.7, 60.2, 55.6, 49.9, 39.7, 35.2, 34.2, 29.9, 29.0, 28.3, 28.1, 25.7, 25.3, 25.0,21.2, 19.6, 19.4, 19.3, 19.2, 19.2, 19.1. HRMS calculated for $[C_{45}H_{67}N_7O_{19}S+Na]^+$ 1064.4110 Found 1064.4098.

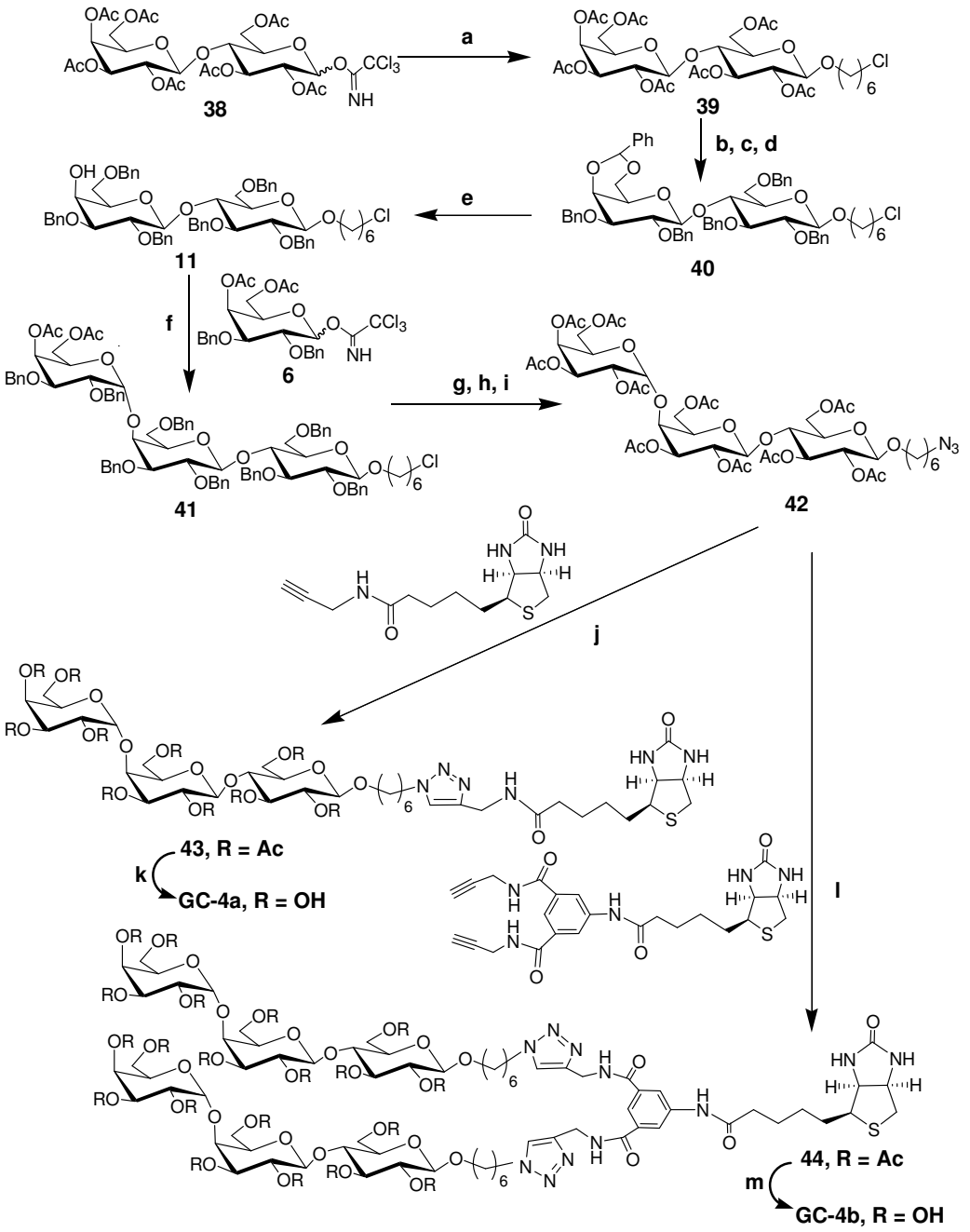
GC-3a: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **36** (0.136 umol, 14.00 mg). The reaction mixture was stirred for 5h. The reaction solution was neutralized slowly using Dowex (H^+) resin. The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant giving quantitative yield of the title compound. ^{1}HNMR(MeOH-d_4): δ 7.84(s, 1H), 4.48(bs, 1H), 4.41-4.32(m, 5H), 4.28(d, 2H, *J* = 6.8 Hz), 3.96-3.86(m, 3H), 3.77(d, 1H, *J* = 10.0 Hz), 3.71-3.66(m, 3H), 3.63-3.53(m, 4H), 3.49-3.45(m, 1H), 3.18(bs, 1H), 2.94-2.90(dd, 1H, *J* = 3.8 and *J* = 12.0 and 12.4 Hz), 2.71 (d, 1H, *J* = 12.8 Hz), 2.59-2.57(m, 1H), 2.25-2.21(m, 2H), 2.01(s, 3H), 1.94-

1.88(m, 2H), 1.66-1.62(m, 6H), 1.45-1.41(m, 4H), 1.34-1.19(m, 4H) ^{13}CNMR (MeOH-d_4): δ 174.6, 172.6, 144.9, 122.8, 103.9, 99.1, 76.2, 75.2, 73.2, 71.3, 70.8, 69.8, 68.7, 68.3, 62.0, 61.2, 60.2, 59.5, 55.6, 50.1, 49.9, 39.7, 35.2, 29.8, 29.2, 28.3, 28.1, 25.8, 25.3, 25.0, 21.4.HRMS calculated for $[C_{33}H_{53}N_7O_{13}S+Na]^+$ 812.3477 Found 812.3477

Compound 37: Biotinylated dimeric scaffold[3-5] (0.13umol, 6.00 mg) was added to the THF/ H_2O (1ml /1ml) solution of compound **35** (0.21umol, 16.00 mg) followed by the addition of $CuSO_4.5H_2O$ (0.27umol, 6.80mg) and sodium ascorbate (0.26umol, 8.30mg). The reaction mixture was stirred for 48 h at rt. After TLC analysis, the reaction mixture was dried *in vacuo* and purified using flash chromatography (CH_2Cl_2: MeOH 9:1, Rf 0.52) giving 40% yield of the title compound. ^{1}HNMR(MeOH-d_4): δ 8.17 (bs, 2H), 8.03-7.96(m, 3H), 5.49(s, 2H), 5.26-5.10(m, 6H), 4.97(d, 2H, $J_{1,2}$ = 3.2 Hz), 4.62-4.60(m, 6H), 4.48-4.38(m, 9H), 4.33-4.29(m, 3H), 4.20-4.16(m, 6H), 4.09-4.05(dd, 2H, *J* = 6.0 and 10.8 Hz), 3.97(bs, 3H), 3.87-3.82(m, 2H), 3.56-3.51(m, 2H), 3.22-3.18(m, 3H), 2.95-2.91(dd, 3H, *J* = 6.0 and 12.8 Hz), 2.72(d, 3H, *J* = 12.8 Hz), 2.63(bs, 1H), 2.43(m, 3H), 2.33(bs, 2H), 2.13(s, 4H), 2.08(s, 4H), 2.03-1.95(m, 23H), 1.89(m, 4H), 1.75(m, 6H), 1.65-1.44(m, 12H), 1.38-1.29(m, 7H). ^{13}CNMR (MeOH-d_4): δ 173.3, 173.2, 172.6, 170.7, 170.5, 170.4, 170.3, 170.0, 167.3, 164.7, 139.2, 135.1, 121.6, 121.0, 101.1, 98.7, 74.4, 72.4, 72.0, 70.9, 69.8, 69.5, 67.5, 67.0, 66.7, 62.0, 61.4, 60.7, 60.7, 60.2, 55.6, 39.7, 36.2, 29.8, 29.0, 28.7, 28.4, 28.1, 25.7, 25.2, 25.0, 21.23, 19.7, 19.4, 19.3, 19.3, 19.2, 19.2. HRMS calculated for $[C_{88}H_{123}N_{13}O_{38}S+2Na]^{2+}$ 1023.8798 Found 1023.8800.

GC-3b: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **37** (0.136 umol, 17.00 mg). The reaction mixture was stirred for 5 hr and it was neutralized slowly using Dowex (H^+) resin. The resin was filtered out and washed with CH_3OH. The product

was dried *in vacuo* and purified with Biogel P-2 using water as an eluant giving quantitative yield of the title compound. ^{1}HNMR(MeOH-d_4): δ 8.17(s, 2H), 7.99-7.93(m, 3H), 4.64(s, 2H), 4.48- 4.47(m, 3H), 4.41-4.37(m, 4H), 4.35- 4.28(m, 4H), 4.24(d, 1H, *J* = 7.6 Hz), 4.15(d, 3H, *J* = 2.0 Hz), 3.95-3.86(m, 4H), 3.80-3.77(dd, 2H, *J* = 2.6 and 9.0 Hz), 3.74-3.65(m, 6H), 3.62-3.52(m, 7H), 3.49-3.43(m, 2H), 3.25-3.18(m, 3H), 2.94-2.90(m, 3H), 2.82(d, 1H, *J* = 7.6 Hz), 2.71(d, 3H, *J* = 12.8 Hz), 2.62-2.58(m, 4H), 2.43(t, 2H, *J* = 8.2 Hz), 2.75(t, 3H, *J* = 7.2 Hz), 2.00(s, 4H), 1.92-1.88(m, 2H), 1.76-1.71(m, 5H), 1.63-1.56(m, 8H), 1.56-1.43(m, 7H), 1.37-1.30(m, 11H). ^{13}CNMR (MeOH-d_4): δ 173.3, 172.6, 167.9, 164.6, 163.7, 139.4, 139.2, 135.1, 123.0, 121.6, 103.8, 99.1, 79.2, 76.2, 75.2, 73.2, 71.3, 70.9, 70.8, 69.7, 69.0, 68.3, 62.9, 62.0, 61.2, 60.2, 59.5, 55.6, 55.5, 54.4, 50.1, 49.9, 43.1, 42.4,39.7, 36.2, 34.9, 29.8, 29.1, 28.7, 28.4, 28.4, 28.1, 25.8, 24.9, 21.4, 17.9. HRMS calculated for $[C_{64}H_{99}N_3O_{26}S+2Na]^{2+}$ 771.8356 Found 771.8370.



Scheme 5. *Synthesis of* ***GC-4a*** *and* ***GC-4b***. Reagents and conditions. a)CH_2Cl_2, 6-chlorohexanol, TMSOTf, -30^{o}C to 0^{o}C, 84% b) NaOMe, MeOH, rt c)$PhCH(OMe)_2$, p-TsOH, THF, 40% d) BnBr, NaH, THF, 50% e) $NaCNBH_3$, THF, $HCl.Et_2O$, rt , 60% f) CH_2Cl_2, TMSOTf, -30^{o}C 71% g) $Pd(OH)_2$, H_2, EtOH/EtOAc, rt h) Ac_2O, Pyridine, rt 70% over two steps i) DMF, NaN_3, 70% j) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 63% k) MeOH, NaOMe, rt, 76% l) $CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 25% l) MeOH, NaOMe, rt 79%.

6-Chloro-hexyl (2, 3, 4, 6 tetra-O-acetyl- β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-acetyl- β-D-glucopyranoside (39): 6-Chloro-hexanol (0.55g, 3.85mmol) was added to the CH_2Cl_2 solution of Compound **38**[5] (2g, 2.57mmol). The reaction mixture was cooled down to 0°C followed by the addition of TMSOTf (0.64mmol, 0.64ml). The reaction mixture was stirred for 4 h at rt. After TLC analysis the reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$. The organic solvent was dried over Na_2SO_4 and removed under pressure. The crude product was purified with flash chromatography (EtOAc: Hex 6:4, Rf 0.46) to give 84% of the title compound**.** ^{1}HNMR ($CDCl_3$): δ 5.47 (t, 1H, *J* = 14.4 Hz), 5.35(d, 1H, *J* = 2.8 Hz), 5.15-5.10(dd, 1H, *J* = 8.0 and 10.4 Hz), 4.97(d, 1H, *J* = 3.2 Hz), 4.79-4.76(dd, 1H, *J* = 3.8 and 10.2 Hz), 4.49-4.43(m, 2H), 4.18-4.06(m, 4H), 3.93-3.85(m, 2H), 3.75-3.64(m, 2H), 3.55(t, 2H, *J* = 7.2 Hz), 3.42-3.36(m, 1H), 2.16(s, 3H), 2.13(s, 3H), 2.06(m, 12H), 1.97(s, 3H), 1.82-1.75(m, 2H), 1.65-1.60(m, 2H), 1.50-1.35(m, 4H). ^{13}CNMR ($CDCl_3$): δ 170.4, 170.4, 170.2, 170.0, 169.8, 169.6, 169.1, 100.9, 100.5, 76.2, 72.8, 72.5, 71.7, 70.9, 70.6, 69.8, 69.1, 66.6, 62.0, 60.8, 44.9, 32.4, 32.4, 29.1, 26.4, 25.0, 20.8, 20.7, 20.6, 20.6, 20.4. HRMS calculated for [$C_{32}H_{47}O_{18}Cl$+Na] 777.2343 Found 777.2343.

6-Chloro-hexyl (4, 6 benzylidene, 2, 3-di-O-benzyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-benzyl-β-D-glucopyranoside (40): 5 ml of 0.5 M NaOMe was added to the CH_3OH solution (10ml) of compound **49** (2g, 2.65mmol) to remove the acetates. The purified and deprotected compound (1.2 g, 2.53 mmol) was dissolved in 15 ml of acetonitrile followed by the addition of catalytic amount of p-TsOH and benzaldehyde dimethyl acetal (0.79g, 5.21mmol). After refluxing for 12 h, the reaction mixture was cooled down to room temperature and concentrated under pressure. The concentrated product was dissolved in 12 ml THF and transferred to the hexane washed NaH (0.7g, 0.292mmol) containing flask via cannula. Benzyl bromide (1.96g,

11.45mmol) was added under argon to the mixture. The reaction mixture was refluxed for 12h. The excess sodium hydride was neutralized with CH_3OH and the reaction mixture was concentrated under pressure, diluted with EtOAc and washed with saturated $NaHCO_3$. The crude product was purified with flash chromatography (EtOAc: Hex 2:8, Rf 0.34) to afford the title compound as a white powder (0.8g, 44%) ^{1}HNMR ($CDCl_3$): δ 7.52-7.45(m, 4H), 7.38-7.26(m, 22H), 7.19-7.16(m, 4H), 5.45(s, 1H), 5.19(d, 1H, *J* = 10.8 Hz), 4.92-4.71(m, 7H), 4.56(d, 1H, $J_{1,2}$ = 12.0 Hz), 4.46(d, 1H, $J_{1,2}$ = 8.0Hz), 4.38(d, 1H, *J* = 12.0), 4.34 (d, 1H, *J* = 12.4 Hz), 4.21(d, 1H, *J* = 12.4 Hz), 4.01-3.71(m, 8H), 3.62(t, 1H, *J* = 9.0 Hz), 3.54-3.43(m, 4H), 3.41-3.36(m, 2H), 1.73-1.62(m, 4H), 1.42(bs, 4H).^{13}CNMR ($CDCl_3$): δ 139.0, 138.9, 138.8, 138.6, 138.4, 138.1, 128.9, 128.6, 128.42, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.8, 127.6, 127.6, 127.5, 127.4, 127.3, 103.7, 102.9, 101.4, 83.1, 81.9, 79.7, 78.9, 75.8, 75.3, 75.1, 75.0, 73.7, 73.0, 71.7, 69.9, 69.0, 68.4, 66.4, 45.1, 32.6, 29.6, 26.7, 25.5. HRMS calculated for [$C_{60}H_{67}O_{11}Cl$+Na] 1021.4269 **Found** 1021.4268.

6-Chloro-hexyl (2, 3, 6-di-O-benzyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-benzyl-β-D-glucopyranoside (11): $NaCNBH_3$ in THF (2.1ml, 2.1mmol,) was added to the THF solution of compound **40** (0.35g, 0.35mmol). Hydrogen chloride in diethyl ether was then added to the stirring reaction mixture until bubble formation stopped. After stirring for 40 mi, the reaction mixture was dried under pressure and the crude product was washed with saturated $NaHCO_3$ and EtOAc. The organic solvent was dried over Na_2SO_4 and removed under pressure. The crude product was further purified with flash chromatography (EtOAc: Hex 2:8, Rf 0.36) to give 71% of the title compound. ^{1}HNMR ($CDCl_3$): δ 7.39-7.37(m, 2H), 7.32-7.27(m, 24H), 7.22(bs, 4H), 4.98-4.86(dd, 2H, *J* = 10.8 and 36.0 Hz), 4.76-4.72(m, 4H), 4.71(d, 1H, *J* = 4.4 Hz), 4.67(d, 1H, *J* = 11.6 Hz), 4.53(d, 1H, $J_{1,2}$ = 12.0 Hz), 4.45-4.41(m, 2H), 4.40(bs, 1H) 4.37(d, 2H, *J* = 6.4

Hz), 4.01(d, 1H, *J* = 3.2 Hz), 3.97-3.89(m, 2H), 3.81-3.77(dd, 1H, *J* = 4.2 and 11.0 Hz), 3.72 (d, 1H, *J* = 10.4 Hz), 3.67-3.63(dd, 1H, *J* = 7.2 and 9.6 Hz), 3.60-3.52(m, 3H), 3.50-3.47 (t, 4H, *J* = 7.2 Hz), 3.39-3.34(m, 3H), 3.31(t, 1H, *J* = 6.0 Hz), 1.74-1.71(m, 2H), 1.66-1.63(m, 2H), 1.44-1.39(m, 4H). ^{13}CNMR ($CDCl_3$): δ 139.1, 138.7, 138.6, 138.3, 138.16, 137.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.3, 103.7, 102.6, 82.9, 81.8, 81.1, 79.4, 75.4, 75.3, 75.1, 74.9, 73.5, 73.2, 72.8, 72.1, 69.8, 68.5, 68.3, 66.2, 45.1, 32.6, 29.6, 26.7, 25.5.HRMS calculated for [$C_{60}H_{69}O_{11}Cl$+Na] 1023.4421 Found 1023.4420.

6-Chloro-hexyl (4, 6-di-O-acetyl, 2, 3-di-O-benzyl-α-galactopyranosyl(1→4)-2, 3, 6-di-O-benzyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-benzyl-β-D-glucopyranoside (41): Compound **11** (0.180 g, 1.79mmol) and compound **6** (0.16g, 2.70mmol) were dissolved in 10 ml anhydrous CH_2Cl_2.The reaction mixture was cooled down to -30^{o}C followed by the addition of TMSOTf (0.18mmol, 0.2ml). The reaction was stirred until the temperature rose to 0^{o}C. When TLC indicated completion of the acceptor (limiting reagent), the reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$. After drying over Na_2SO_4, the solvent was removed *in vacuo* and the residue was purified by flash chromatography (EtOAc:Hex 3:7, Rf 0.38) to give the title compound (0.18g,70%) as a colorless syrup.^{1}HNMR ($CDCl_3$): δ 7.40-7.39(d, 2H, *J* = 7.2 Hz), 7.33-7.30(m, 16H), 7.25-7.19(m, 19H), 7.16- 7.13(m, 3H), 5.52(bs, 1H), 5.08(d, 1H, $J_{1,2}$ = 3.2Hz), 5.04(d, 1H, 11.2 Hz), 4.86(s, 1H), 4.83(d, 1H, *J* = 3.2 Hz), 4.77-4.72(m, 4H), 4.70-4.64(t, 3H, *J* = 10.6 Hz), 4.61-4.56(t, 3H, *J* = 9.6 Hz), 4.53(s, 1H), 4.47(d, 1H, $J_{1,2}$ = 8.0 Hz), 4.38(d, 1H, J = 5.2 Hz), 4.34(s, 1H), 4.26(d, 2H, *J* = 6.8Hz), 4.21(d, 1H, *J* = 10.0 Hz), 4.12(t, 1H, *J* = 8.8 Hz), 4.03(d, 1H, *J* = 2.0 Hz), 4.01-3.93(m, 4H), 3.84-3.77(m, 1H), 3.74 (d, 1H, *J* = 10.8 Hz), 3.65-3.55(m, 3H), 3.49-3.46(m, 4H), 3.39-3.35(t, 2H, *J* = 8.4 Hz), 3.28(d, 2H, *J* = 7.6 Hz), 2.04(s, 3H), 1.91(s, 3H), 1.74-1.63(m, 4H), 1.43-1.41(m, 4H). ^{13}CNMR

($CDCl_3$): δ 170.4, 170.3, 139.2, 138.7, 138.6, 138.5, 138.4, 138.4, 138.2, 138.1, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.6, 127.6, 127.5, 103.6, 103.0, 100.4, 82.6, 81.7, 80.9, 79.3, 75.7, 75.3, 75.2, 75.1, 75.1, 75.0, 73.9, 73.1, 73.1, 72.4, 71.9, 69.8, 68.3, 67.6, 67.5, 66.8, 61.5, 45.1, 32.6, 29.7, 26.7, 25.7, 25.5 20.9, 20.8. LRMS calculated for [$C_{84}H_{95}O_{18}Cl$+Na] 1449.6099 Found 1449.6101.

6-Azido-hexyl (2, 3, 4, 6-tetra-O-acetyl-α-galactopyranosyl (1→4)-2, 3, 6-tri-O-acetyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-acetyl-β-D-glucopyranoside (42): $Pd(OH)_2$ (400mg, 2.85mmol) was added to the EtOAc/ EtOH(1ml/2ml) solution of compound **41**. The reaction solution was stirred for 48 h under continuous flow of hydrogen gas. The reaction mixture was washed with MeOH and passed through celite. The filtrate was dried and a white powder product was obtained. This product was subjected to acetylation reaction to obtain the acetylated trisaccharide (0.1g, 71% over two steps). The acetylated trisaccharide was dissolved in DMF and NaN_3 (0.1g, 96umol) was added to the solution. The reaction mixture was stirred for 5 h at 100^{o}C. DMF was removed *in vacuo* and the crude product was purified with flash chromatography (EtOAc, Rf 0.28) giving 70% of the title compound**.** Spectroscopic data matched with the literature values[3].

Compound 43: The biotinylated monomeric scaffold[3-5] (21.4umol, 6mg) was added to the H_2O / THF (0.5ml/0.5ml) solution of compound **42** (14.3umol, 15mg) followed by the addition of $CuSO_4.H_2O$ (28.5umol, 7mg) and sodium ascorbate (71.5umol, 14mg).The reaction mixture was stirred for 24 h at rt. After TLC analysis, the reaction mixture was dried under pressure and the crude product was directly dumped in to the column and purified with flash chromatography (EtOAc: MeOH 8:2, Rf 0.58) to get the title compound(12mg, 63%). ^{1}HNMR (MeOH-d_4): δ 7.90(s, 1H), 5.55(bs, 1H), 5.40-5.37(m, 1H), 5.21(d, 2H, J = 10.0 Hz), 5.13-5.05(m, 2H), 4.98-

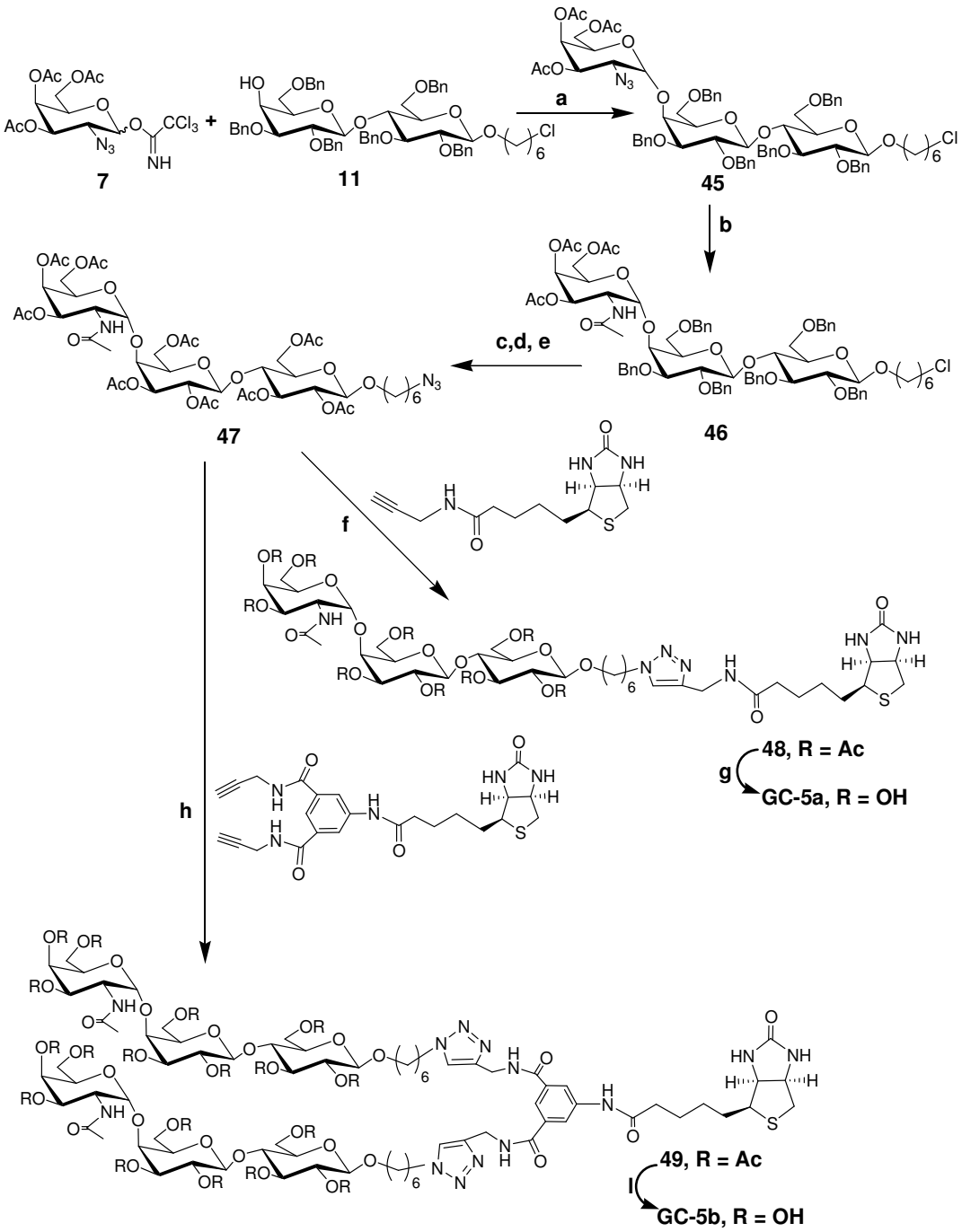
4.95(m, 2H), 4.69(d, 1H, $J_{1,2}$ = 6.4 Hz), 4.59(d, 1H, *J* = 6.4 Hz), 4.51-4.37(m, 8H), 4.30(d, 1H, *J* = 4.0 Hz), 4.20-4.13(m, 5H), 4.01(d, 1H, *J* = 5.2 Hz), 3.87-3.76(m, 3H), 3.56-3.44(m, 2H), 3.35(d, 2H, 5.6 Hz), 3.21-3.20(m, 1H), 2.96-2.93(m, 1H), 2.74-2.70(m, 1H), 2.25(d, 2H, *J* = 5.2 Hz), 2.13-1.97(m, 27H), 1.89-1.88(m, 3H), 1.72-1.55(m, 7H), 1.44-1.32(m, 7H). ^{13}CNMR (MeOH-d_4): δ 170.9, 170.9, 170.7, 170.5, 170.5, 170.0, 169.9, 169.8, 100.7, 100.4, 99.3, 77.4, 76.2, 73.0, 72.6, 72.6, 72.1, 71.7, 69.5, 69.4, 68.4, 68.1, 67.5, 67.1, 62.3, 62.2, 61.9, 60.4, 60.2, 55.7, 39.7, 29.7, 28.9, 28.3, 28.0, 25.7, 25.3, 25.0, 19.8, 19.6, 19.4, 19.4, 19.3, 19.1 HRMS calculated for [$C_{57}H_{82}$ N_6O_{28}S+Na] 1353.4795 **Found** 1353.4740.

GC-4a: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **43** (8.27umol, 11 mg). The reaction mixture was stirred for 5 h and was neutralized slowly using Dowex (H^+) resin**.** The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant to afford the title compound (5.7mg, 76%). ^{1}HNMR (D_2O): δ 7.79(s, 1H), 4.84(s, 1H), 4.50-4.26(m, 9H), 3.93-3.46(m, 24H), 3.16(bs, 3H), 2.86-2.85(m, 2H), 2.68-2.60(m, 2H), 2.17(bs, 3H), 1.78(bs, 2H), 1.55-1.47(m, 6H), 1.23-1.15(m, 9H). ^{13}CNMR (D_2O): δ 176.7, 165.3, 123.8, 103.3, 102.0, 100.3, 78.7, 77.4, 75.4, 74.8, 74.5, 72.9, 72.2, 72.1, 70.9, 70.8, 70.4, 69.1, 68.9, 68.6, 62.5, 62.0, 60.5, 60.4, 60.2, 60.1, 55.4, 50.4, 39.7, 35.2, 34.3, 29.2, 28.5, 27.6, 25.2, 25.0, 24.4. HRMS calculated for [$C3_7H_{62}$ N_6O_{18}S+Na] 933.3739 Found 933.3740.

Compound 44: The biotinylated dimeric scaffold[3,4] (12umol, 6mg) was added to the H_2O / THF (1.5ml / 1ml) solution of compound **42** (20umol, 21mg) followed by the addition of $CuSO_4.H_2O$ (5umol, 12.5mg) and sodium ascorbate (10umol, 19.8mg).The reaction mixture was stirred for 48h at rt. After TLC analysis, the reaction mixture was dried under pressure and the crude

product was purified with flash chromatography (MeOH:CH_2Cl_2 2:8, Rf 0.52) giving 25% yield of the title compound. Spectroscopic data matched with the literature values[3].

GC-4b: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **44** (4.37umol, 12.00 mg). The reaction mixture was stirred for 5h and was neutralized slowly using Dowex (H^+) resin**.** The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant to afford the title compound (6mg, 79%). Spectroscopic data matched with the literature values[3].



Scheme 6. *Synthesis of **GC-5a** and **GC-5b**. Reagents and conditions* a) **1,** CH_2Cl_2, TMSOTf, -30°C , 77% b) Zn, AcOH, Ac_2O, THF, 60% c) $Pd(OH)_2$, H_2, EtOH/EtOAc, rt d) Ac_2O, Pyridine, rt 70% over two steps e) DMF, NaN_3, 71% over three steps f)$CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 56% g) MeOH, NaOMe, rt, 93% h)$CuSO_4.5H_2O$, $C_6H_7O_6Na$, THF/H_2O, 28% l) MeOH, NaOMe, rt, 82%

6-Chloro-hexyl (2-azido-2-deoxy 3, 4, 6-tri-O-acetyl-α-galactopyranosyl (1→4)-2, 3, 6-tri-O-benzyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-benzyl-β-D-glucopyranoside (45): Compound **11** (0.2g, 0.2mmol) and compound **24**[6] (0.14g, 0.3mmol) were dissolved in 5ml of anhydrous CH_2Cl_2.The reaction mixture was cooled down to -30°C followed by the addition of TMSOTf (0.18mmol, 0.2ml).The reaction was stirred until the temperature rose to 0°C. When TLC indicated completion of the acceptor (limiting reagent), the reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$. After drying over Na_2SO_4, the solvent was removed *in vacuo* and the residue was purified by flash chromatography (EtOAc: Hex 3:7, Rf 0.46) to give the title compound (0.2g, 77%) as a colorless syrup. ^{1}HNMR ($CDCl_3$): δ 7.15-7.00(m, 30H), 5.14(s, 1H), 5.07(d, 1H, *J* = 9.2 Hz), 4.84(d, 1H, *J* = 10.8Hz), 4.79(s, 1H), 4.61(d, 2H, *J* = 13.2 Hz), 4.48-4.39(m, 5H), 4.29(d, 1H, *J* = 11.6 Hz), 4.19(d, 1H, *J* = 6.4 Hz), 4.14(m, 3H), 3.83 (s, 1H), 3.71- 3.50(m, 6H), 3.43-3.35(m, 3H), 3.33-3.23(m, 6H), 3.19-3.01(m, 3H), 3.06-3.00(t, 2H, *J* = 10.0 and 19.6 Hz), 1.86(s, 3H), 1.75(s, 3H), 1.61(s, 2H), 1.51-1.48(m, 5H), 1.20(bs, 4H). ^{13}CNMR ($CDCl_3$): δ 170.2, 170.1, 169.8, 139.4, 138.6, 138.5, 138.4, 138.0, 137.6, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.6, 127.5, 127.3, 127.1, 103.5, 103.4, 98.2, 83.0, 81.7, 80.2, 79.3, 78.0, 77.4, 77.1, 76.8, 75.5, 75.2, 75.0, 73.4, 73.2, 73.1, 73.0, 72.4, 69.8, 68.9, 68.1, 67.3, 66.6, 66.0, 60.6, 58.2, 45.2, 32.5, 29.6, 26.7, 25.5, 20.7, 20.7, 20.6**.** HRMS calculated for [$C_{72}H_{84}ClN_3O_{18}$+Na] 1336.5336 Found 1352.5356.

6-Chloro-hexyl (2-N-acetamido-2-deoxy 3, 4, 6-tri-O-acetyl-α-galactopyranosyl (1→4)-2, 3, 6-tri-O-benzyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-benzyl-β-D-glucopyranoside (46): Zinc powder (2.3g, 19.8mmol) was added to the THF solution of compound **45** (0.2g, 15.2mmol) followed by the addition of AcOH (3ml) and Ac_2O (4ml). The reaction mixture was stirred for 12 hrs. After TLC analysis the reaction mixture was passed through celite and washed with

MeOH. Then the product was dried under pressure and the dried product was diluted with EtOAc and washed with saturated $NaHCO_3$. The crude product was further purified with flash chromatography (EtOAc: Hex 5:5, Rf 0.30) to afford the title compound (120mg, 60%).^{1}HNMR ($CDCl_3$): δ 7.39-7.30(m, 13H), 7.25-7.22(m, 17H), 5.63(d, 1H, *J* = 10.0 Hz), 5.33(bs, 1H), 5.20-5.16(dd, 1H, *J* = 3.2 and 11.6 Hz), 5.06(d, 1H, $J_{1,2}$ = 3.6Hz), 5.02(d, 1H, J = 12.8 Hz), 4.90-4.85(dd, 2H, *J* = 9.4 and 11.0 Hz), 4.81(s, 1H), 4.78(d, 1H, *J* = 4.8 Hz), 4.74(s, 1H), 4.70(s, 1H), 4.67-4.61(m, 3H), 4.57(d, 2H, *J* = 11.2 Hz), 4.47-4.42(m, 2H), 4.35(d, 1H, *J* = 2.8 Hz), 4.31(d, 2H, *J* = 12.8 Hz), 4.13(d, 1H, *J* = 2.8 Hz), 3.98-3.87(m, 3H), 3.85-3.81(dd, 1H, *J* = 3.8 and 11.0 Hz), 3.68-3.57(m, 3H), 3.55-3.52(m, 1H), 3.49-3.46(t, 4H, *J* = 6.6 and 13.2 Hz), 3.42-3.37(m, 2H), 3.32-3.22(m, 3H), 2.11(s, 3H), 1.99(s, 3H), 1.85(s, 3H), 1.73-1.70(m, 2H), 1.63-1.61(m, 2H), 1.41(bs, 7H). ^{13}CNMR ($CDCl_3$): δ 170.9, 170.5, 170.1, 170.0, 139.4, 138.5, 138.3, 137.9, 137.3, 128.6, 128.5, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 127.3, 126.9, 103.5, 103.2, 98.2, 82.0, 81.9, 80.3, 79.4, 75.2, 74.9, 74.8, 73.9, 73.4, 73.1, 73.0, 72.5, 72.1, 69.8, 68.3, 67.1, 66.6, 66.3, 61.0, 47.7, 45.1, 32.5, 29.6, 26.7, 25.5, 22.7, 20.9, 20.8, 20.7. HRMS calculated for [$C_{74}H_{88}ClNO_{19}$+Na] 1352.5537 Found 1352.5544.

6-Azido-hexyl (2-N-acetamido-2-deoxy 3, 4, 6-tri-O-acetyl-α-galactopyranosyl (1→4)-2, 3, 6-tri-O-Acetyl-β-galactopyranosyl)-(1→4)-2, 3, 6-tri-O-acetyl-β-D-glucopyranoside (47): Palladium hydroxide (300mg, 2.22mmol) was added to the EtOAc / EtOH(1.5ml/2ml) solution of compound **46** (90.2umol, 120mg). The reaction solution was stirred for 48h under continuous flow of hydrogen gas. The reaction mixture was washed with MeOH and passed through celite. The filtrate was dried and a white powder product was obtained. This product was subjected to acetylation reaction followed by the nucleophilic substitution of the chlorine with azide using DMF as a solvent. DMF was removed *in vacuo* and the crude product was purified with flash

chromatography (EtOAc, Rf 0.26) to obtain the title compound (50mg, 71%). Spectroscopic data matched with the literature value.[3]

Compound 48: The biotinylated monomeric scaffold[3-5] (26.7umol, 7.5mg) was added to the H_2O / THF (0.5ml/0.5ml) solution of compound **47** (13.4umol, 14mg) followed by the addition of copper sulfate (26.7umol, 6.7mg) and sodium ascorbate (66.7umol, 13.2mg).The reaction mixture was stirred for 24 hrs at room temperature. After TLC analysis, the reaction mixture was dried under pressure and purified with flash chromatography (CH_2Cl_2: MeOH 8:2, Rf 0.62) to get the title compound (11mg, 56%). ^{1}HNMR (MeOH-d_4): δ 8.35-8.33(d, 1H, *J* = 7.6 Hz), 7.85(d, 1H,), 5.49(d, 1H, *J* = 2.4 Hz), 5.24-5.10(m, 4H), 5.03(s, 1H), 4.59(bs, 4H), 4.51-4.46(m, 3H), 4.42(bs, 2H), 4.39-4.36(m, 3H), 4.31-4.25(m, 1H), 4.19-4.15(m, 3H), 4.09-4.05(m, 1H), 3.99(bs, 1H), 3.92-3.87(m, 1H), 3.80-3.72(m, 2H), 3.53-3.48(m, 1H), 3.20-3.19(m, 1H). 2.96-2.91(m, 1H), 2.73-2.69(dd, 1H, *J* = 1.4 and 12.6 Hz), 2.26(t, 2H, *J* = 6.4 and 12.8 Hz), 2.14(s, 3H), 2.11(s, 3H), 2.09-2.08(m, 12H), 2.03-1.98(m, 13H), 1.94-1.88(m, 2H), 1.74-1.56(m, 7H), 1.45-1.33(m, 8H). ^{13}CNMR (MeOH-d_4): δ 174.6, 172.5, 171.0, 170.7, 170.6, 170.5, 170.4, 170.2, 170.0, 164.7, 101.3, 100.0, 98.6, 77.3, 74.0, 73.7, 72.4, 72.3, 72.2, 72.1, 69.6, 69.4, 67.4, 66.9, 66.7, 62.4, 61.9, 61.1, 60.6, 60.2, 55.6, 49.9, 39.7, 35.2, 34.2, 29.8, 28.9, 28.3, 28.0, 25.7, 25.3, 25.0, 21.3, 20.0, 19.6, 19.4, 19.3, 19.3, 19.2, 19.1. HRMS calculated for [$C_{57}H_{83}$ $N_7O_{27}S$+Na] 1352.4955 Found 1352.4945.

Compound 5a: NaOMe (1M, 0.5ml) was added to the anhydrous CH_3OH (1ml) solution of compound **48** (4.5umol, 6mg). The reaction mixture was stirred for 5 hrs and was neutralized slowly using Dowex (H^+) resin**.** The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant to afford the title compound (4mg, 93%). ^{1}HNMR (D_2O): δ: 7.97(s, 1H), 4.97(bs, 1H), 4.67(s, 1H), 4.59(d,

1H, *J* = 7.2 Hz), 4.54-4.44(m, 7H), 4.28(d, 1H, *J* = 10.8 Hz), 4.12-4.01(m, 4H), 3.97-3.90(m, 2H), 3.85-3.80(m, 8H), 3.73-3.60(m, 11H), 3.47-3.35(m, 3H), 3.07-3.03(dd, 1H, *J* = 3.2 and 12.8 Hz), 2.86-2.79(m, 1H), 2.37(t, 2H, *J* = 6.2 and 12.4 Hz), 2.15(bs, 3H), 1.97(t, 2H, *J* = 6.6 and 13.2 Hz), 1.56-1.43(m, 7H), 1.26-1.159(m, 8H). ^{13}CNMR (D_2O): δ 176.7, 174.5, 103.2, 102.0, 98.3, 78.6, 76.6, 75.7, 74.8, 74.5, 73.0, 72.1, 72.0, 70.9, 70.7, 70.4, 68.2, 67.2, 62.5, 62.0, 60.5, 60.2, 55.3, 50.4, 50.1, 39.7, 35.2, 34.3, 29.2, 28.5, 27.6, 27.6, 25.2, 25.0, 24.4, 21.9. HRMS calculated for [$C_{39}H_{65}N_7O_{18}S$+Na] 974.4005 **Found** 974.4016.

Compound 49 : The biotinylated dimeric scaffold[3-5] (14.3umol, 15mg) was added to the H_2O / THF (1ml / 1ml) solution of compound **47** (8.58 umol, 4.1 mg) followed by the addition of copper sulfate (35.7 umol, 8.9mg) and sodium ascorbate (70.7umol, 14mg).The reaction mixture was stirred for 48h at room temperature. After TLC analysis, the reaction mixture was dried under pressure and purified with flash chromatography (MeOH:CH_2Cl_2 2:8, Rf 0.58) to get the title compound(11mg, 28%). Spectroscopic data matched with the literature value[3].

GC-5b: NaOMe (1M, 0.5ml) was added to an anhydrous CH3OH (1ml) solution of compound **49** (7.99 µmol, 16 mg). The reaction mixture was stirred for 5h and was neutralized slowly using Dowex (H^+) resin**.** The resin was filtered out and washed with CH_3OH. The product was dried *in vacuo* and purified with Biogel P-2 using water as an eluant to afford the title compound (6 mg, 82%). Spectroscopic data matched with the literature value[3].

References:

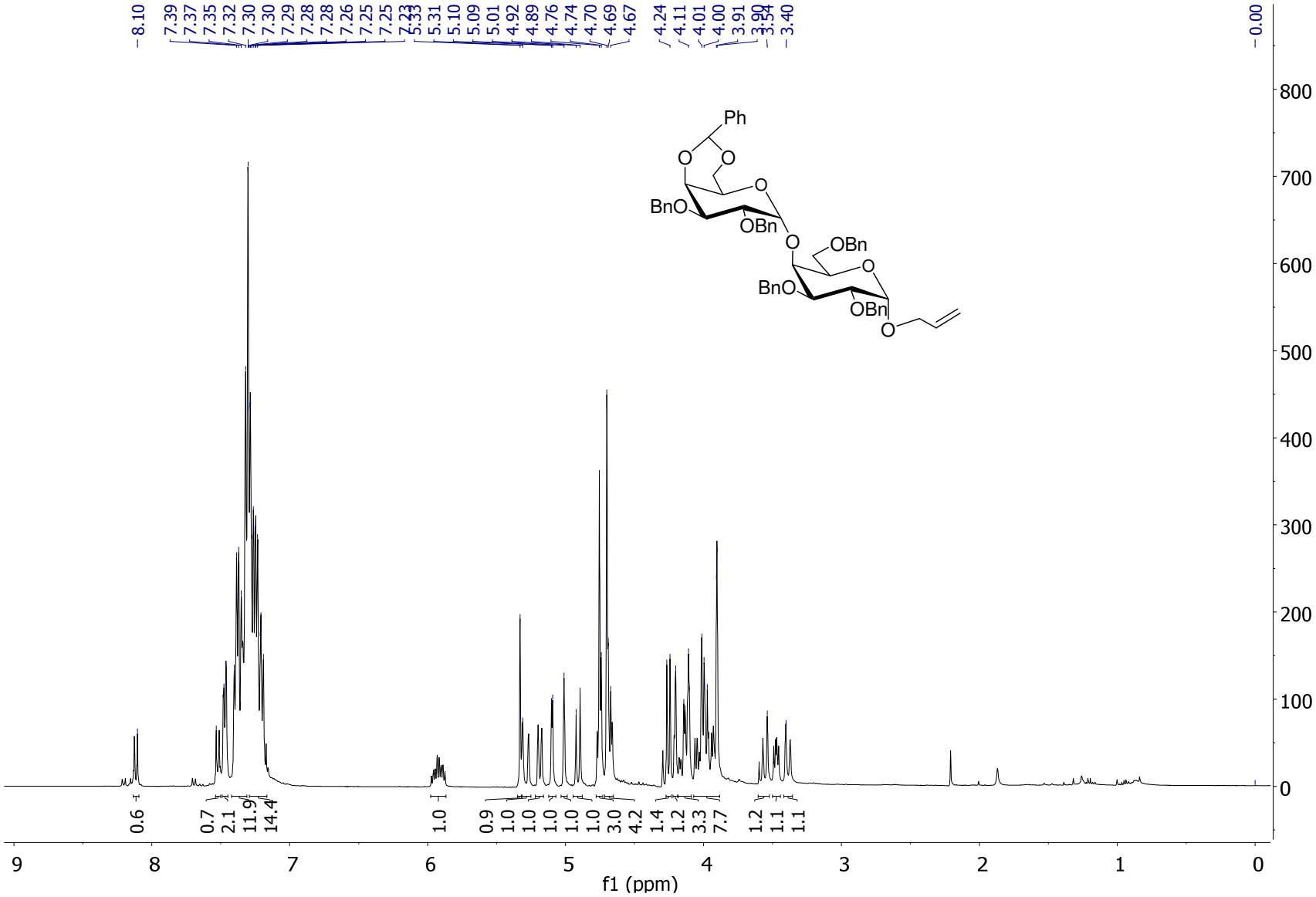
(1) Deng, S.; Gangadharmath, U.; Tom Chang, C. W. *J. Org. Chem* **2006**, *71*, 5179-5185.
(2) Dasguptat, F.; Anderson, L. *Carb. Res.* **1990**, *202*, 239-255.
(3) Kale, R. R.; McGannon, C. M.; Fuller-Schaefer, C.; Hatch, D. M.; Flagler, M. J.; Gamage, S. D.; Weiss, A. A.; Iyer, S. S. *Angew.Chem. Int. Ed.* **2008**, *47*, 1265-8.
(4) Kale, R. R.; Clancy, C. M.; Vermillion, R. M.; Johnson, E. A.; Iyer, S. S. *Bioorg Med Chem Lett* **2007**, *17*, 2459-64.

(5) Kale, R. R.; Mukundan, H.; Price, D. N.; Harris, J. F.; Lewallen, D. M.; Swanson, B. I.; Schmidt, J. G.; Iyer, S. S. *J.Am. Chem.Soc.* **2008**, *130*, 8169-71.

(6) Koeller, K. M.; Smith, M. E.; Wong, C. H. *Bioorg.Med.Chem.* **2000**, *8*, 1017-25.

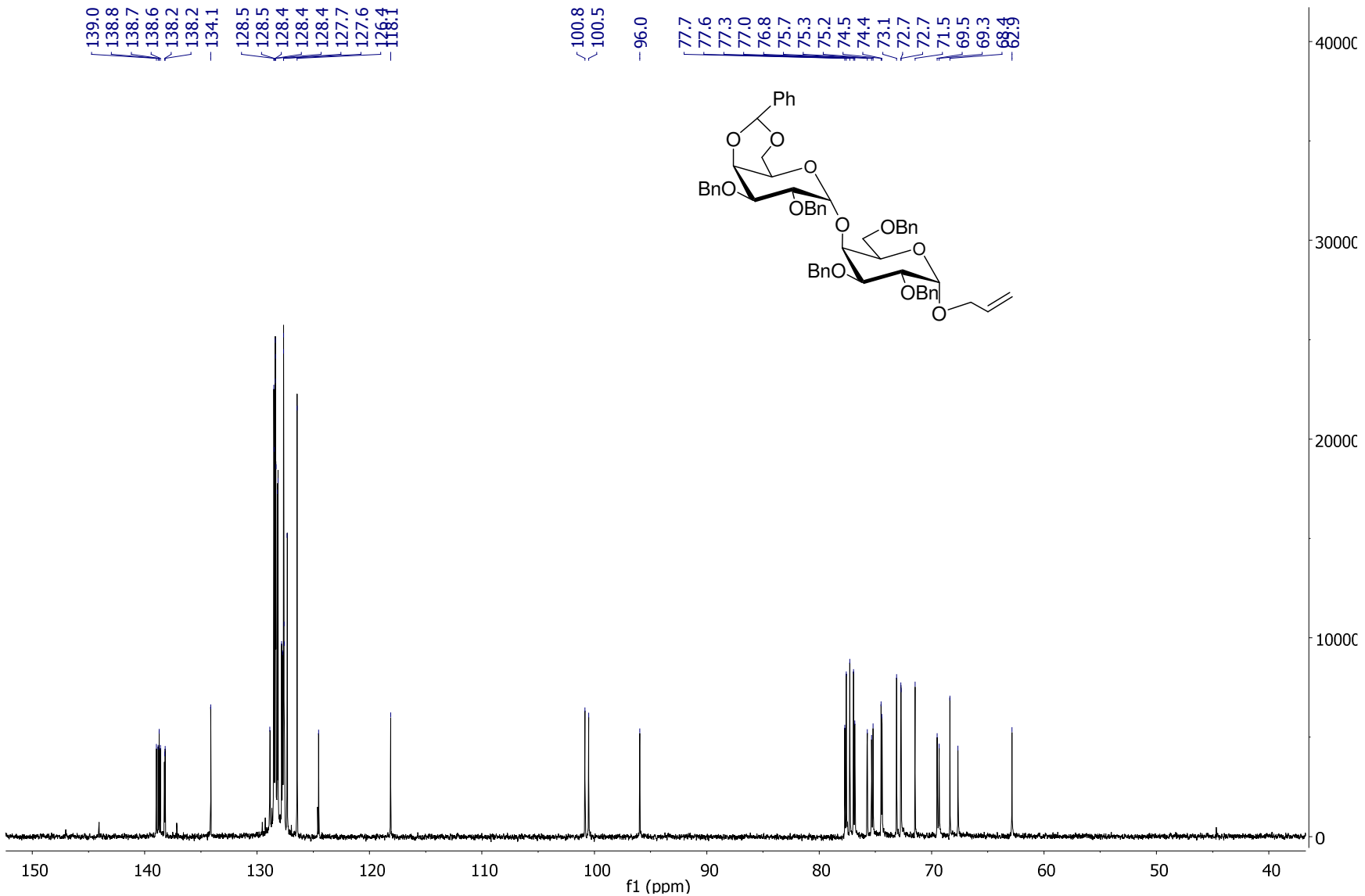
^{1}HNMR of Compound **13**.

^{1}HNMR (400 MHz, $CDCl_3$)



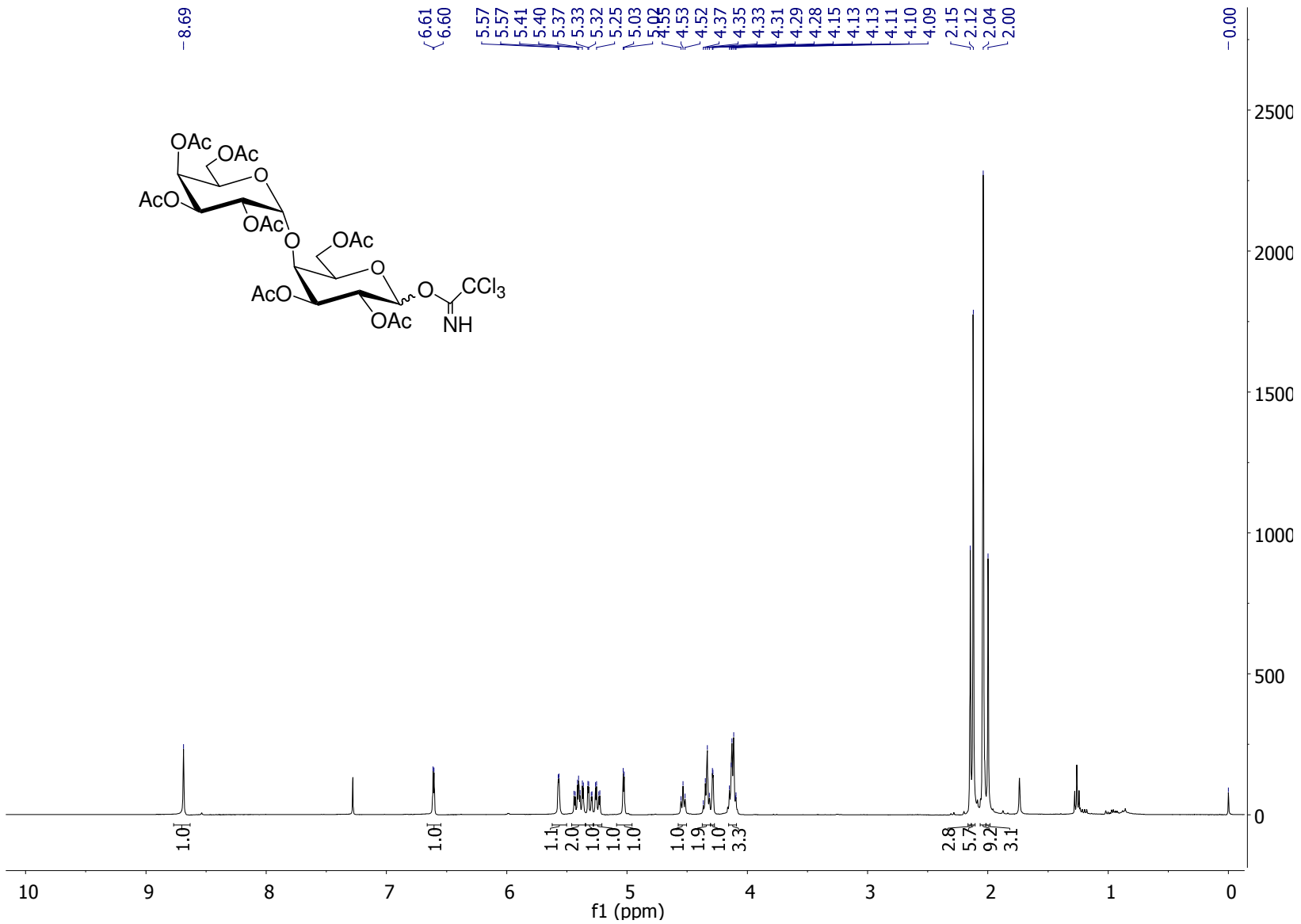
^{13}C NMR of Compound **13**.

^{13}C NMR (400 MHz, CDCl3)



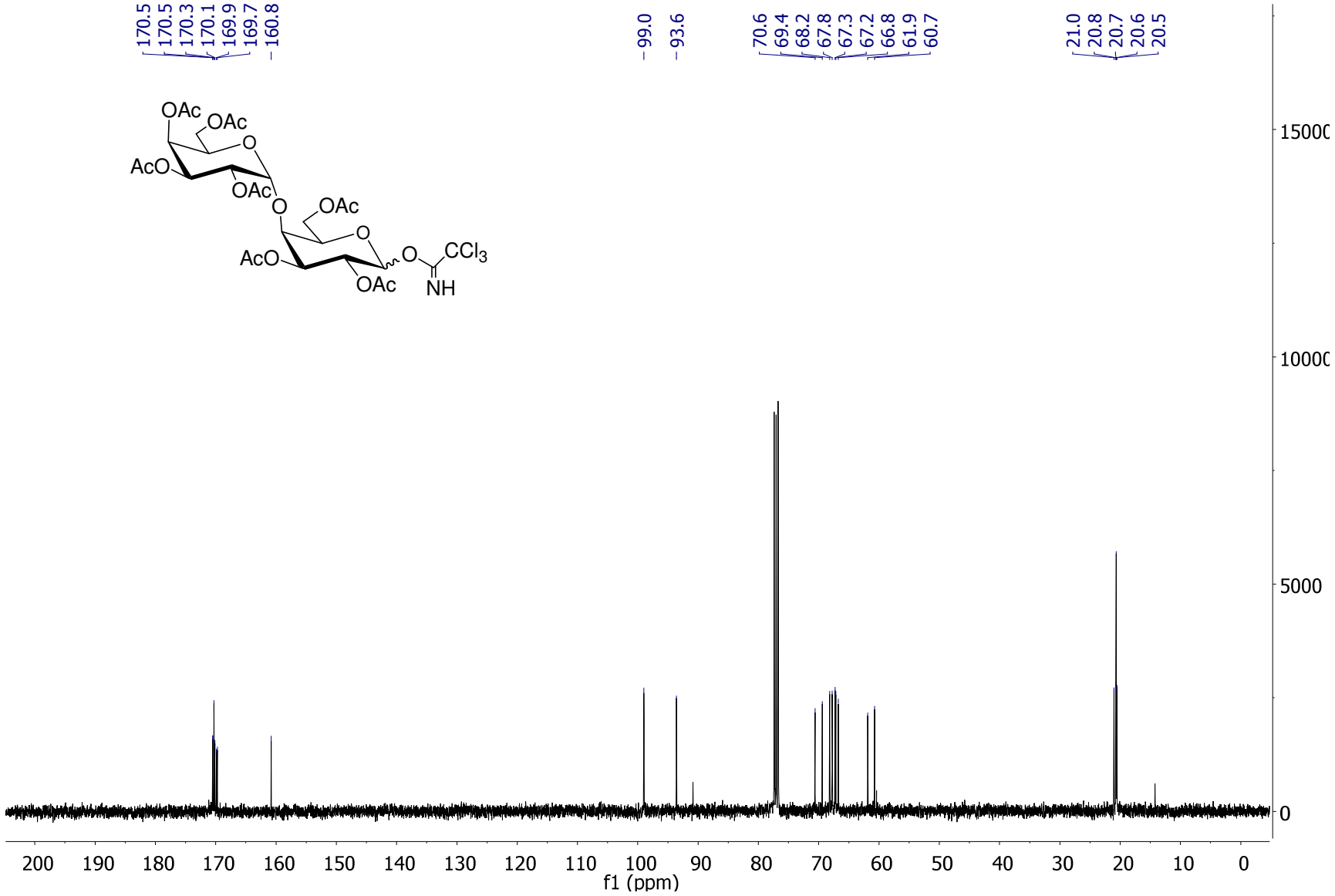
^{1}HNMR of Compound **20.**

^{1}HNMR (400 MHz, $CDCl_3$)



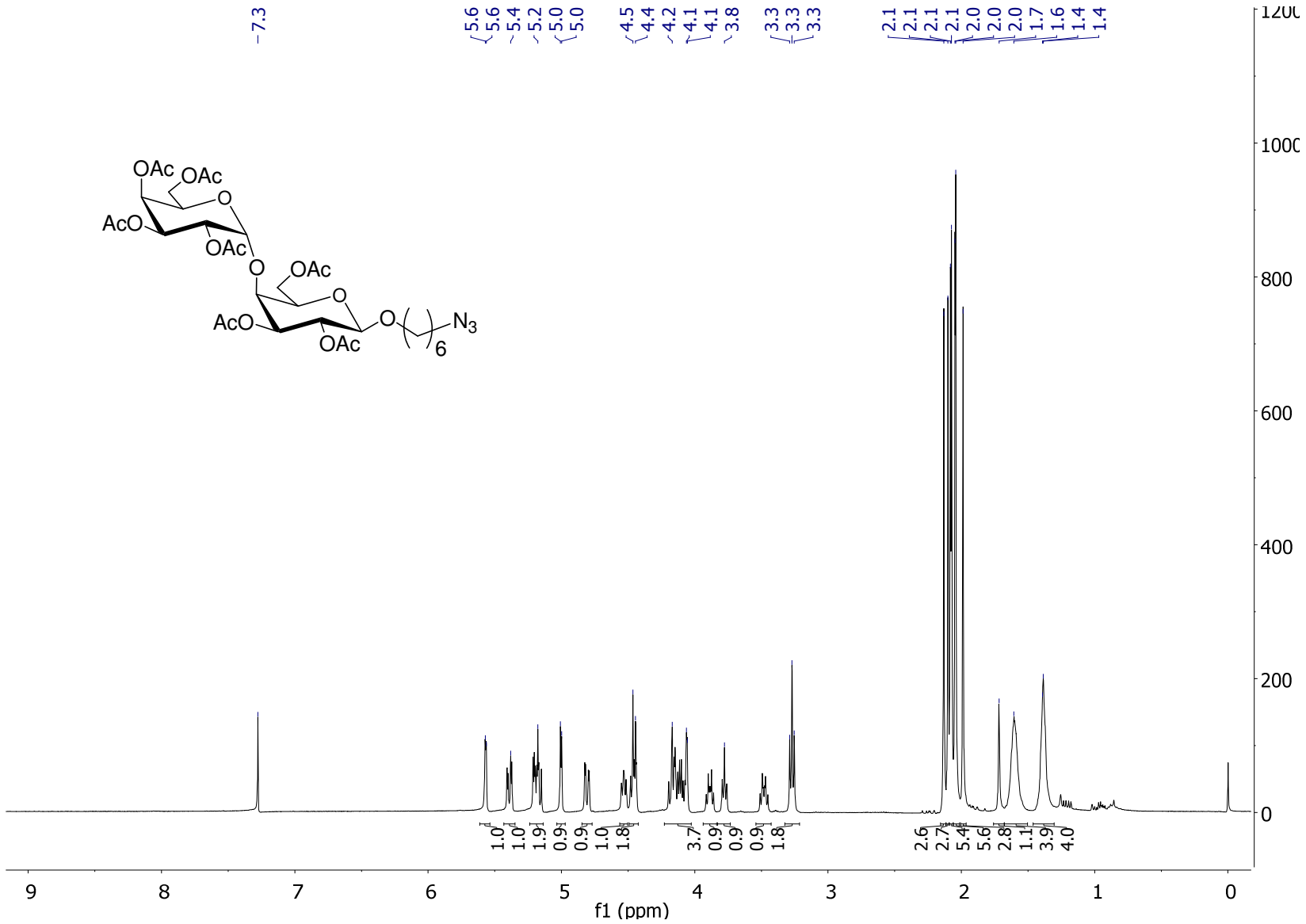
^{13}C NMR of Compound **20**.

^{13}C NMR (400 MHz, $CDCl_3$)



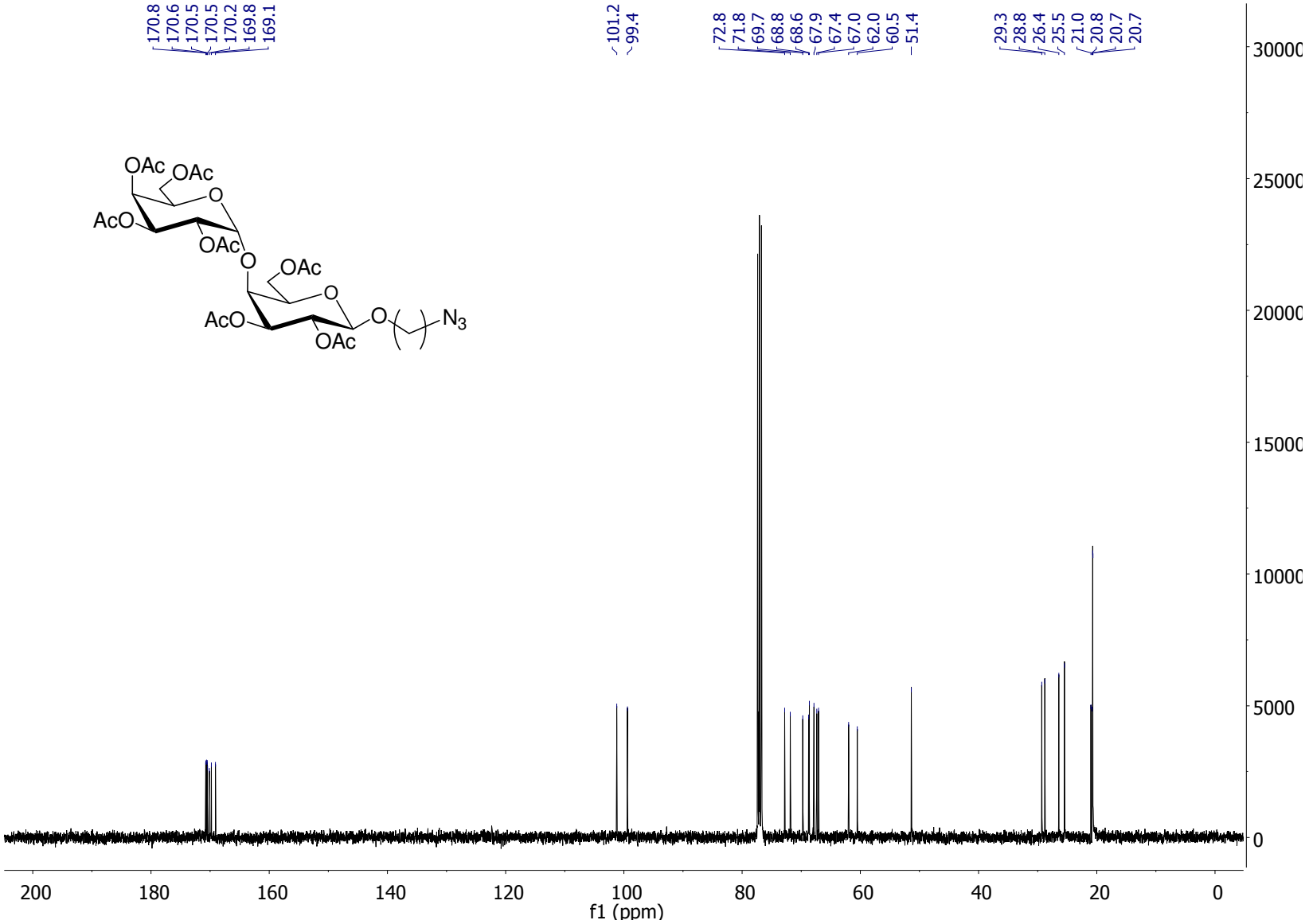
^{1}HNMR of compound **21.**

^{1}HNMR (400 MHz, $CDCl_3$)



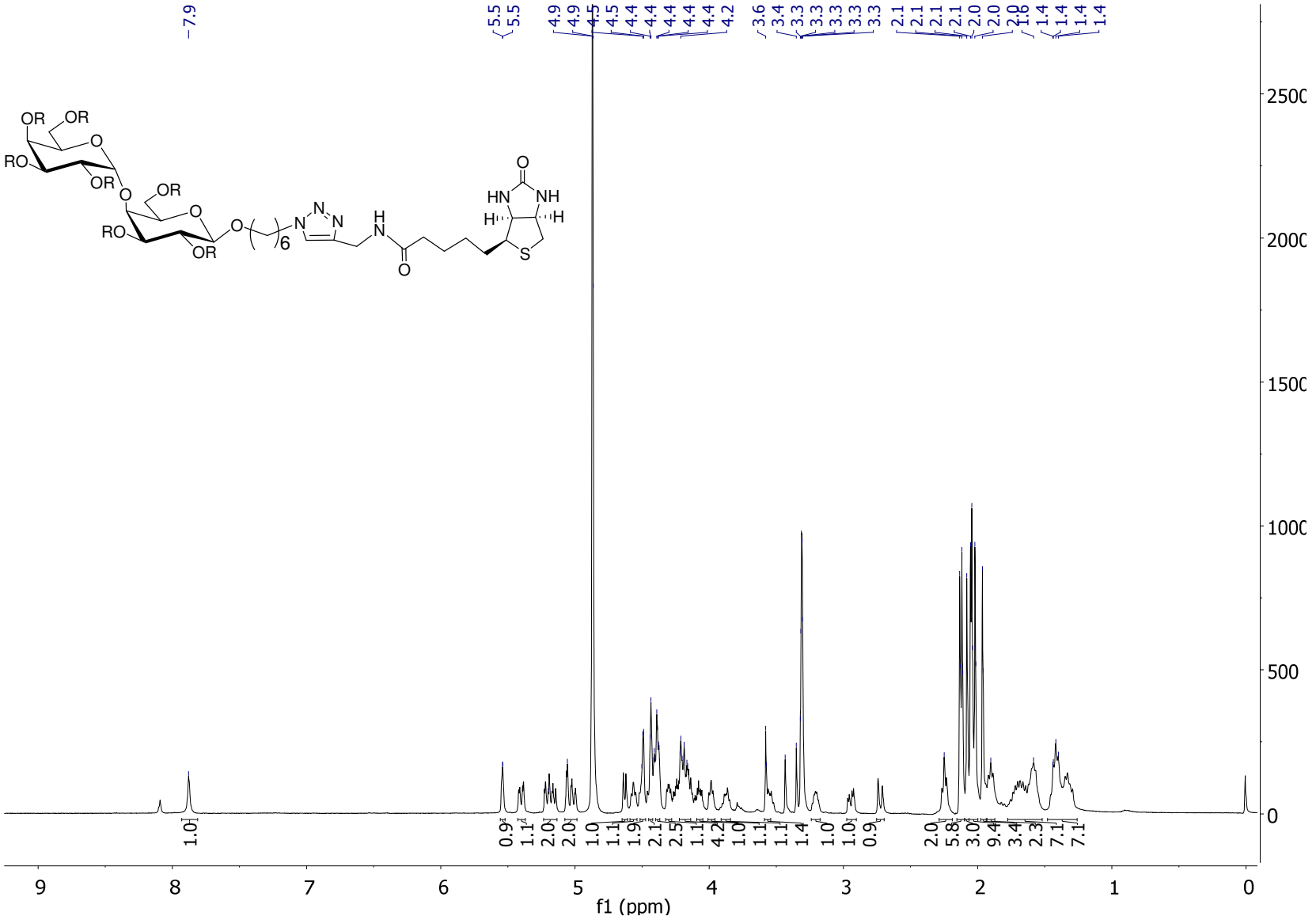
^{13}C NMR of Compound **21**.

^{13}C NMR (400 MHz, $CDCl_3$)



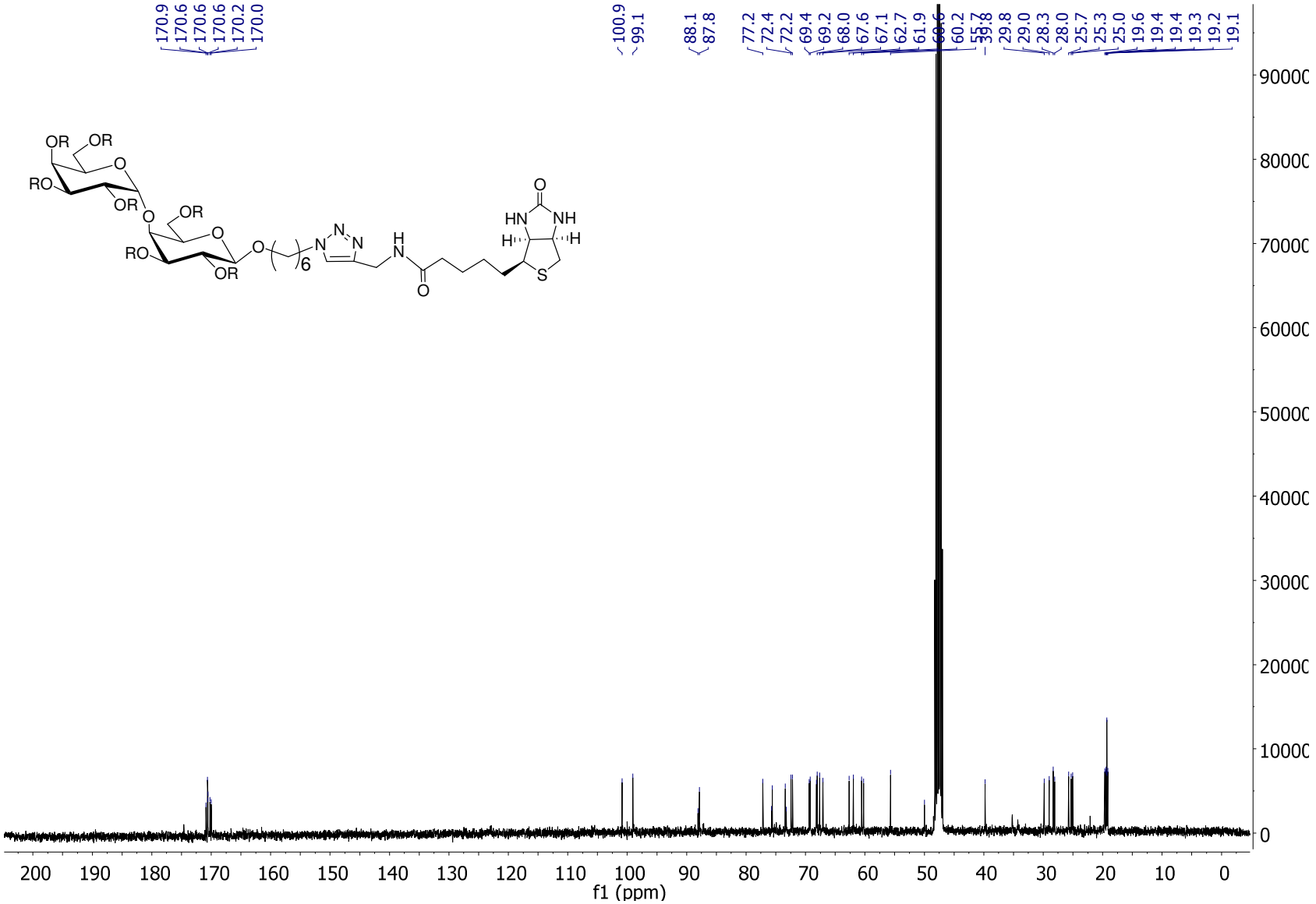
^{1}HNMR of Compound **22**.

^{1}HNMR (400 MHz, MeOH-D_4)



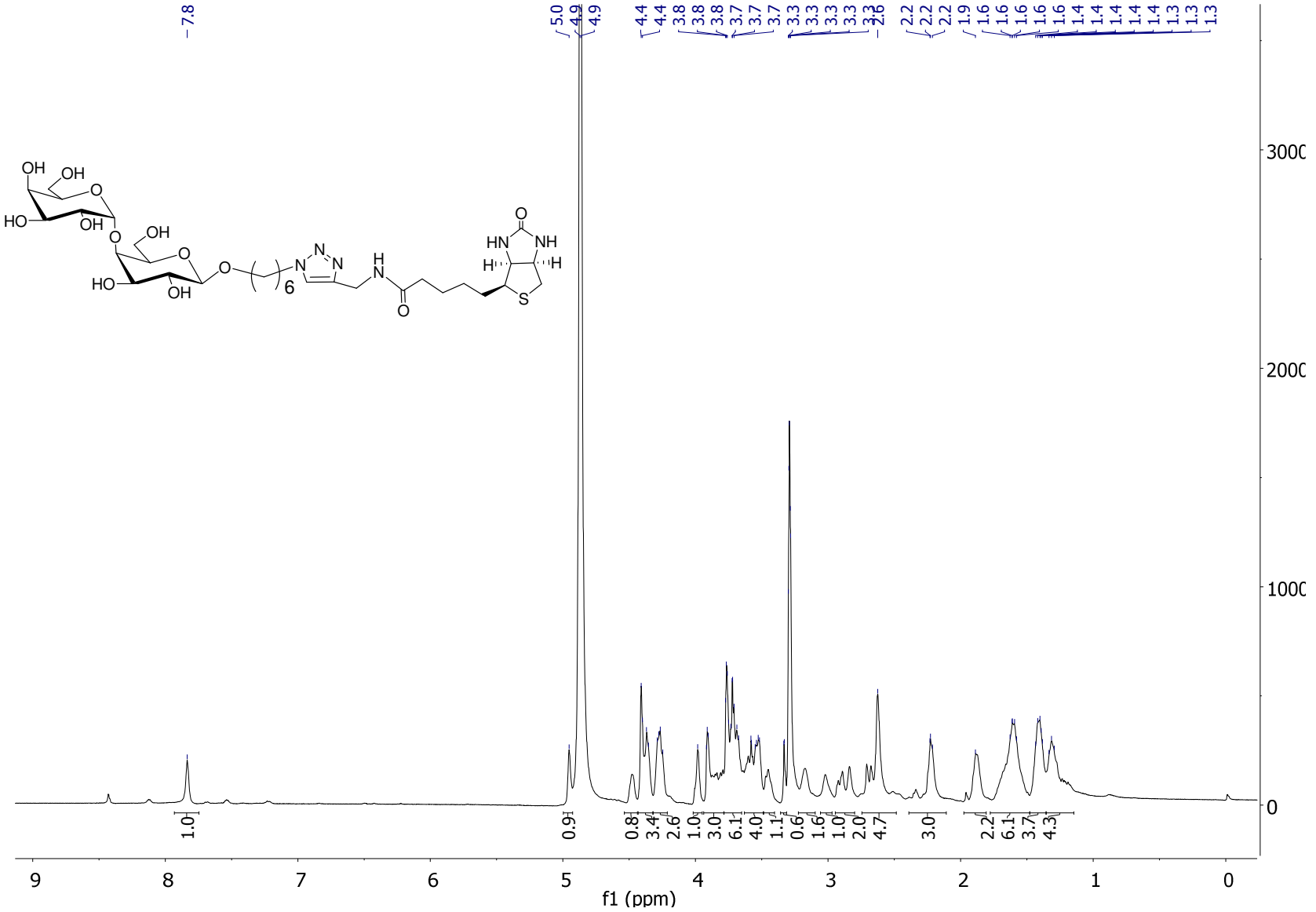
^{13}C NMR of Compound **22**.

^{13}C NMR (400 MHz, MeOH-d_4)



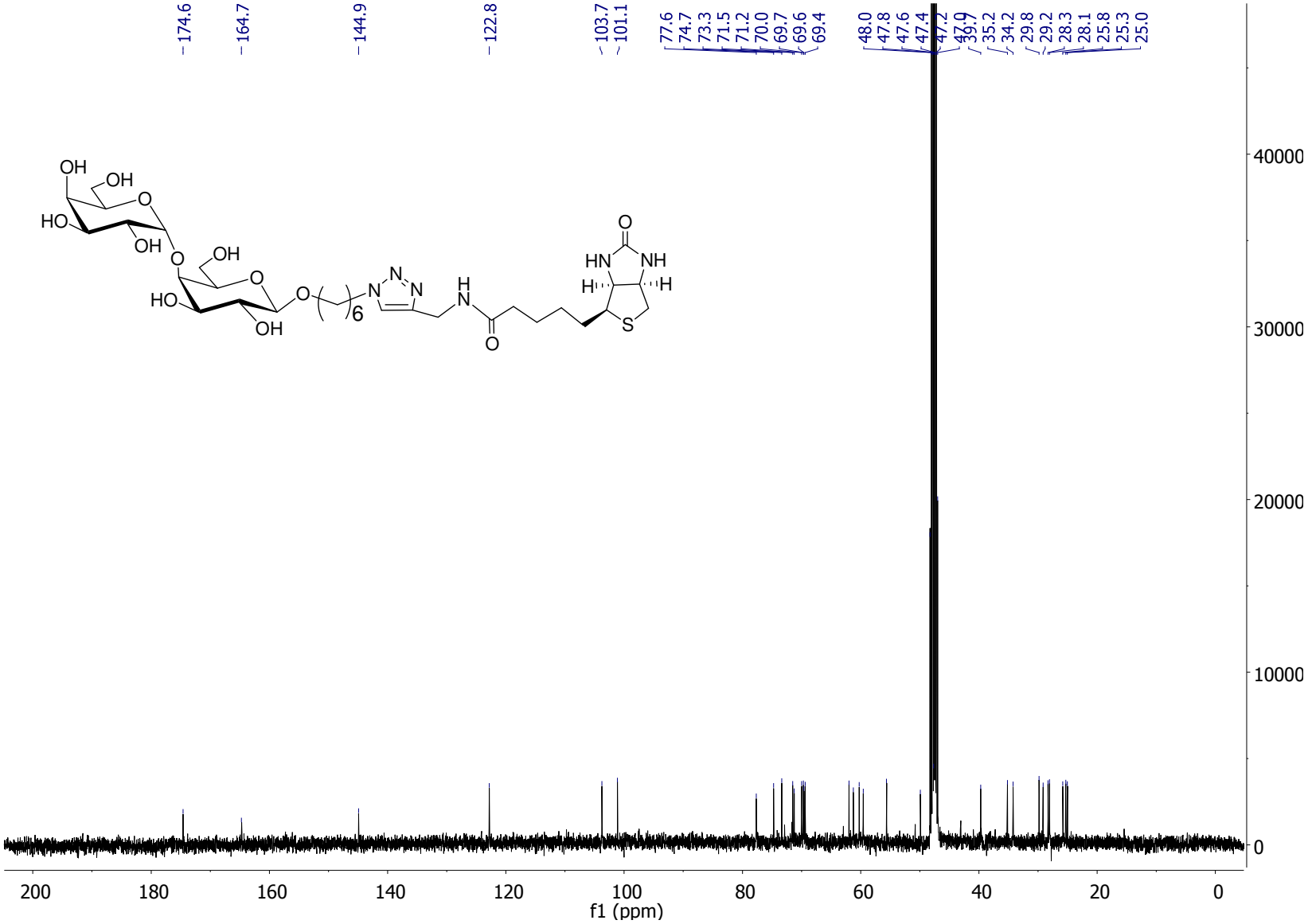
^{1}HNMR of Compound **1a**.

^{1}HNMR (400 MHz, MeOH-D_4)



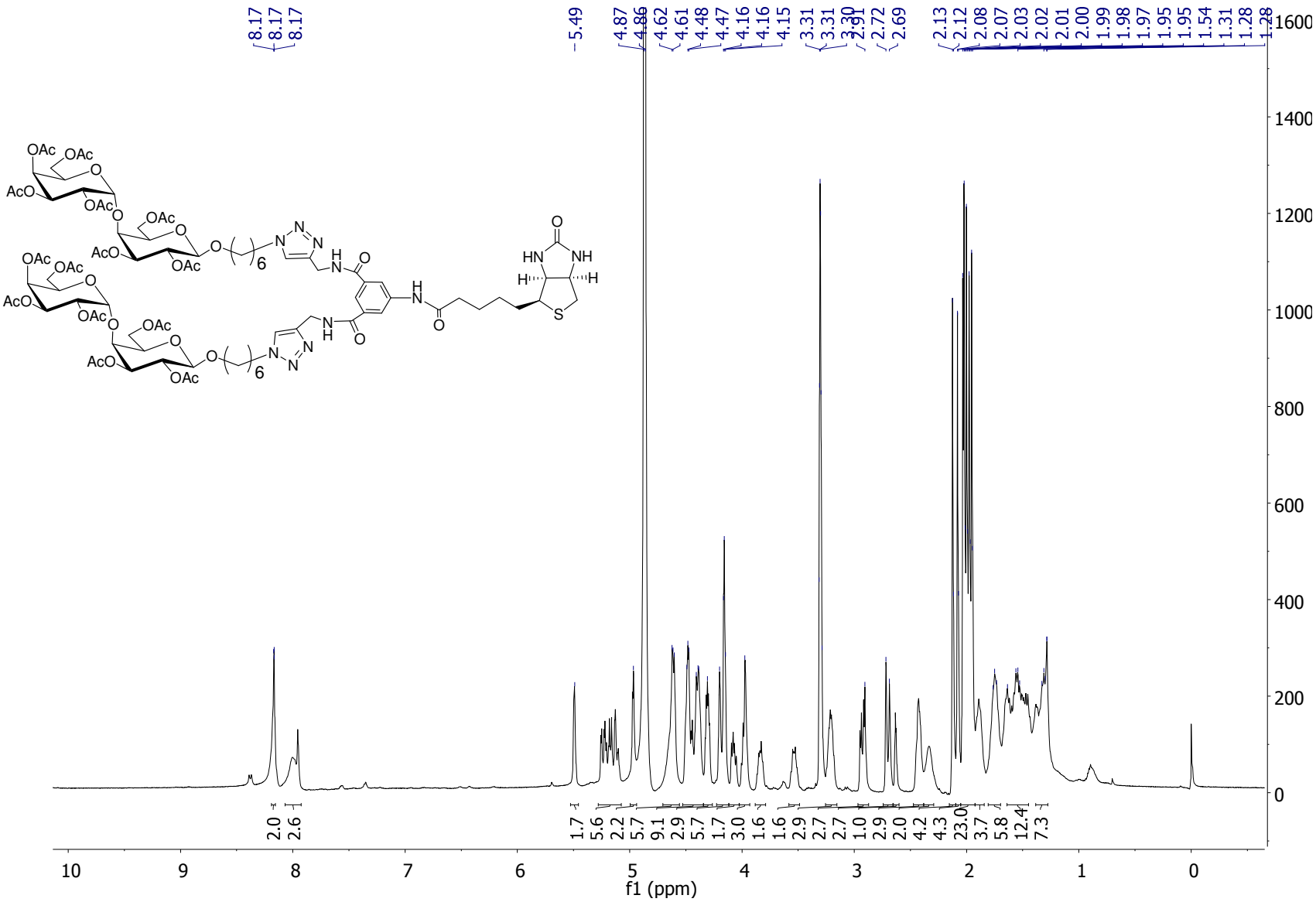
^{13}C NMR of Compound **1a**.

^{13}C NMR (400 MHz, MeOH-d_4)



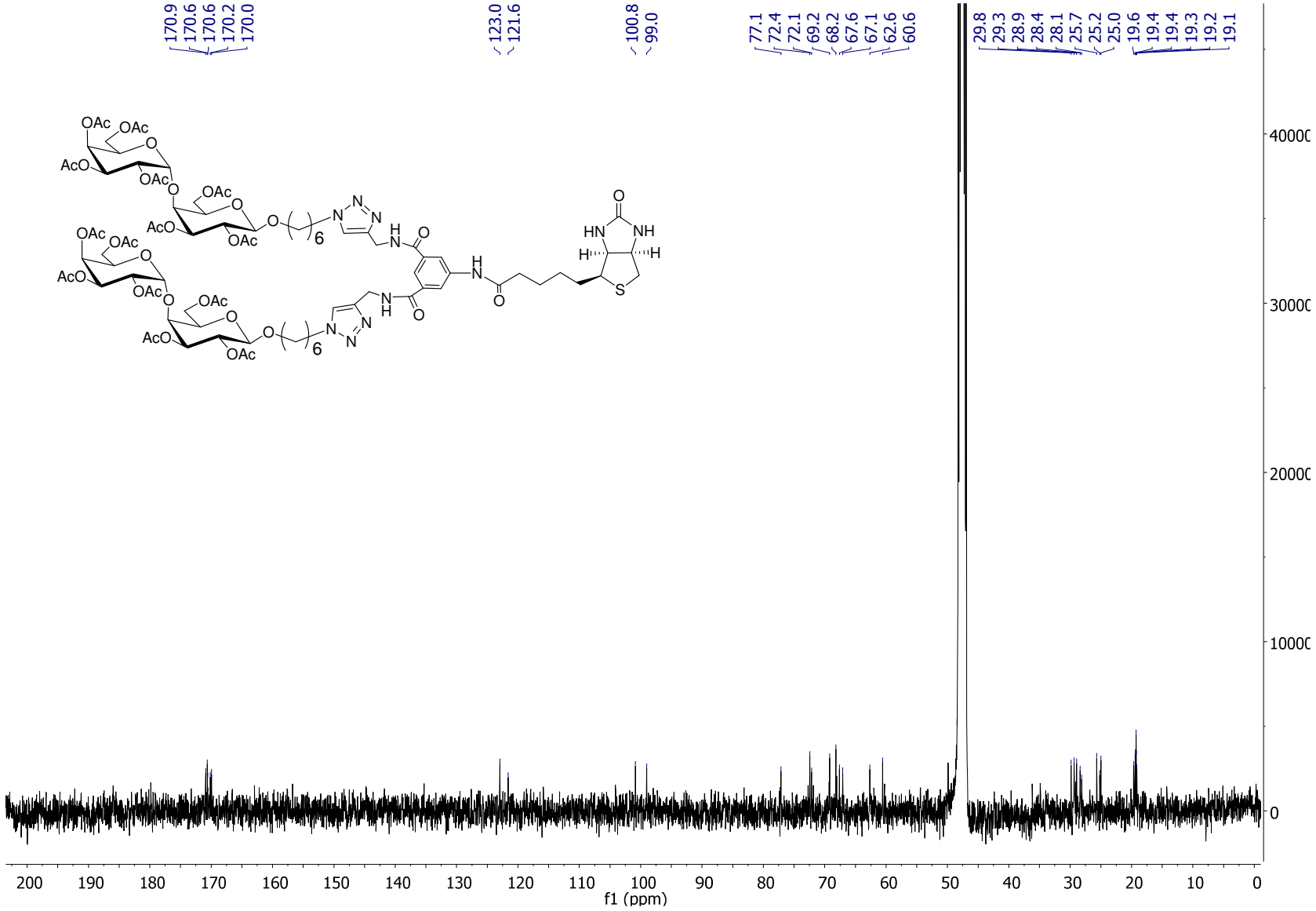
^{1}HNMR of Compound **23.**

^{1}HNMR (400 MHz, MeOH-D_4)



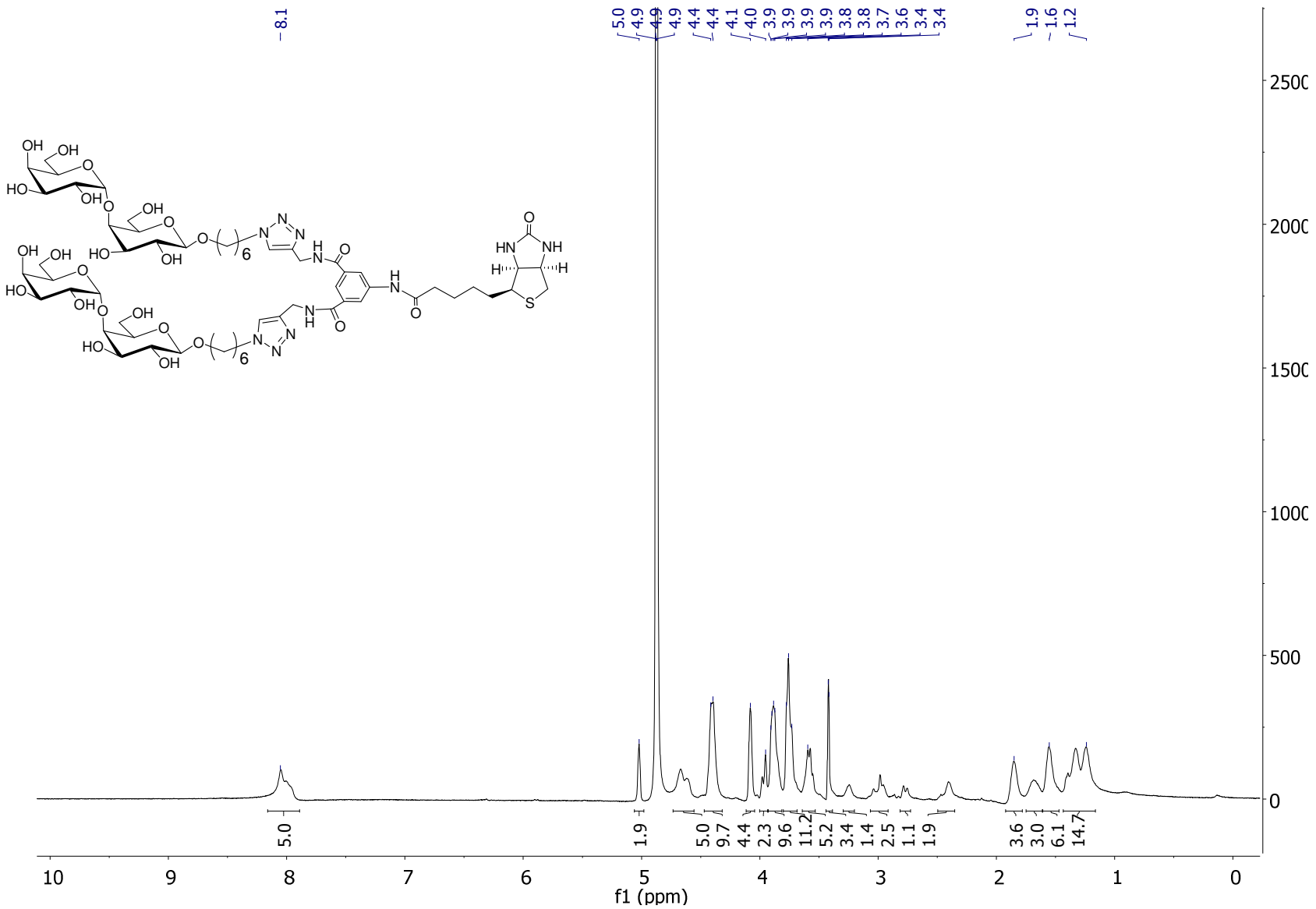
^{13}C NMR of Compound **23**.

^{13}C NMR (400 MHz, MeOH-d_4)



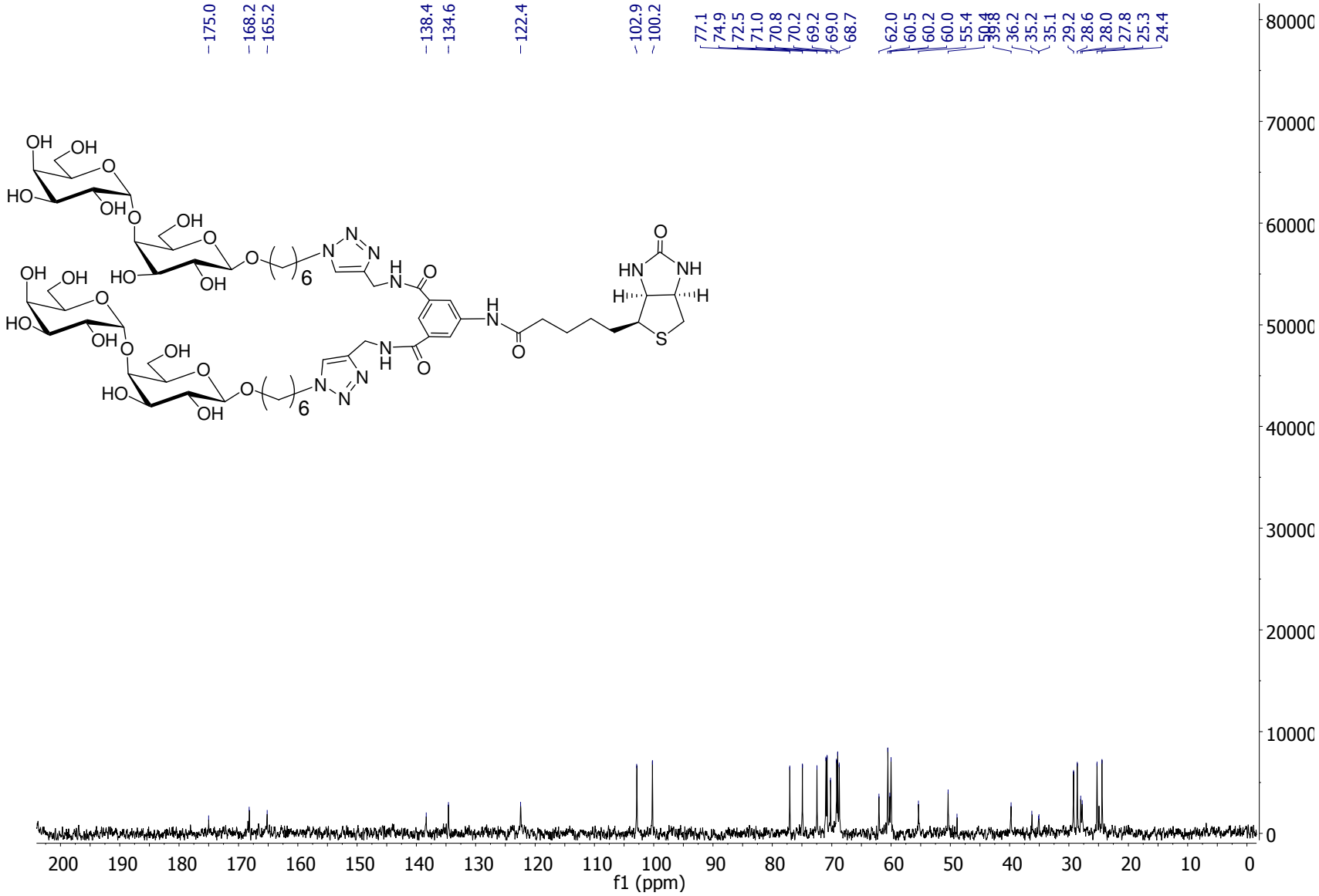
^{1}HNMR of Compound **1b.**

^{1}HNMR (400 MHz, D_2O)



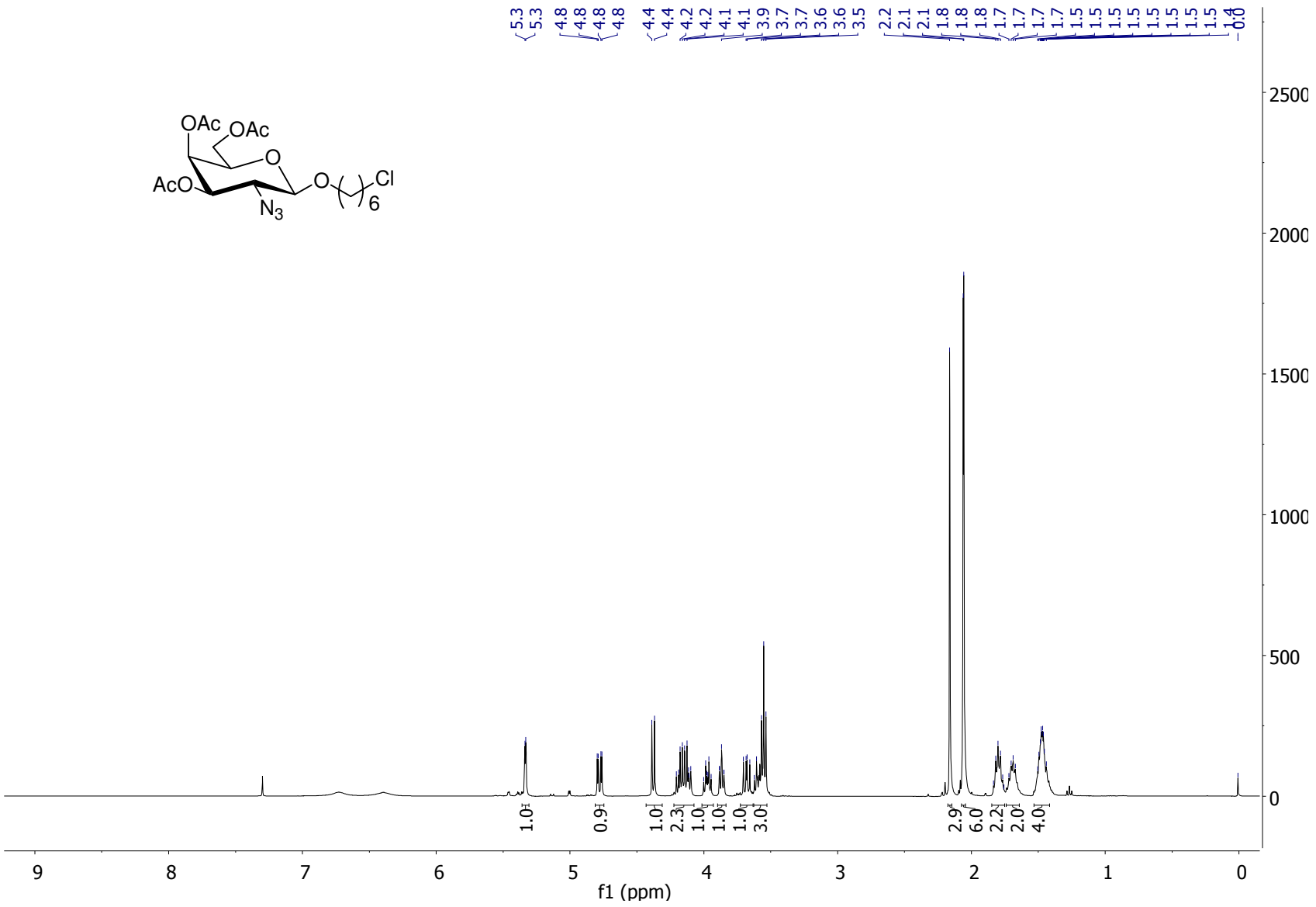
^{13}C NMR of Compound **1b.**

^{13}C NMR (400 MHz, D_2O)



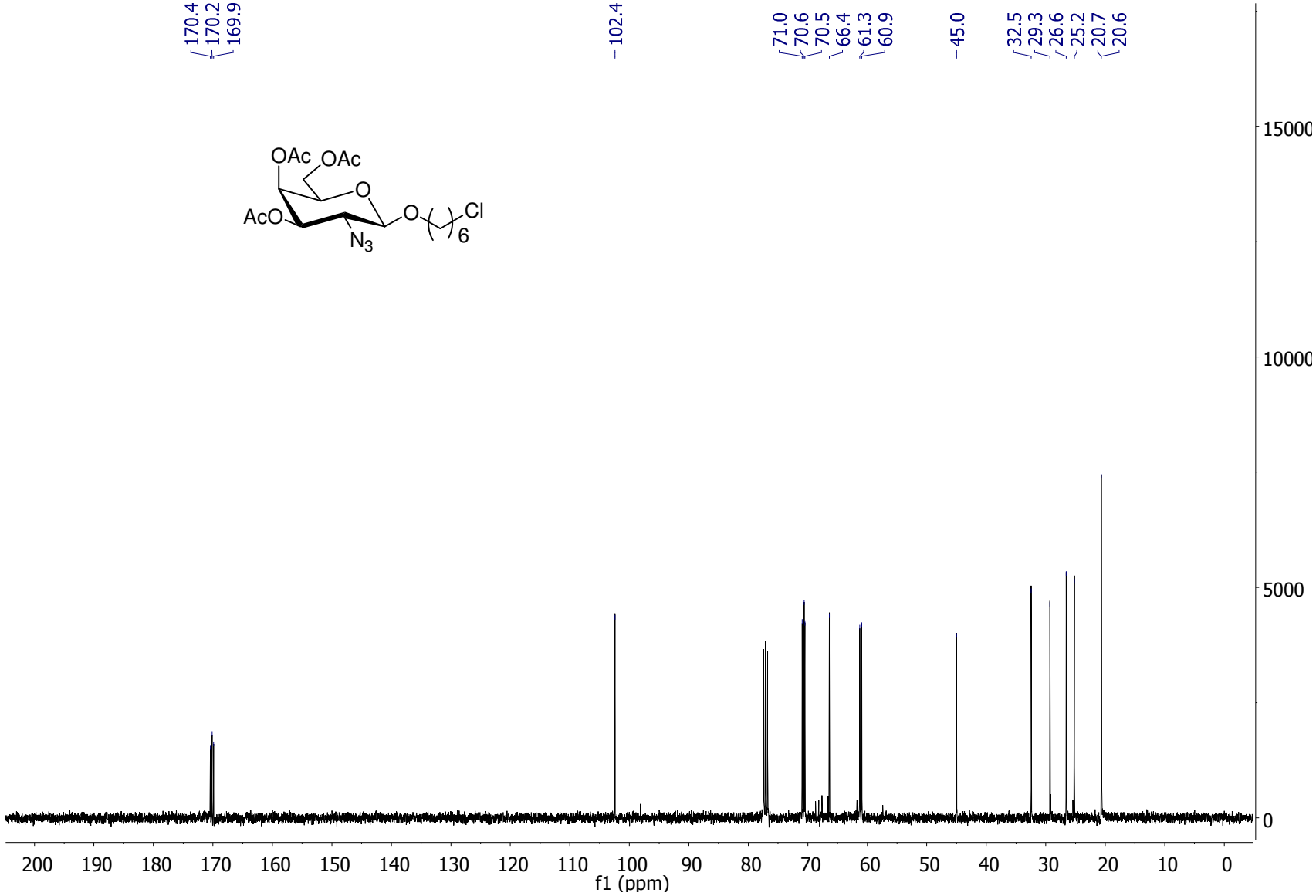
^{1}HNMR of Compound **17.**

^{1}HNMR (400 MHz, $CDCl_3$)



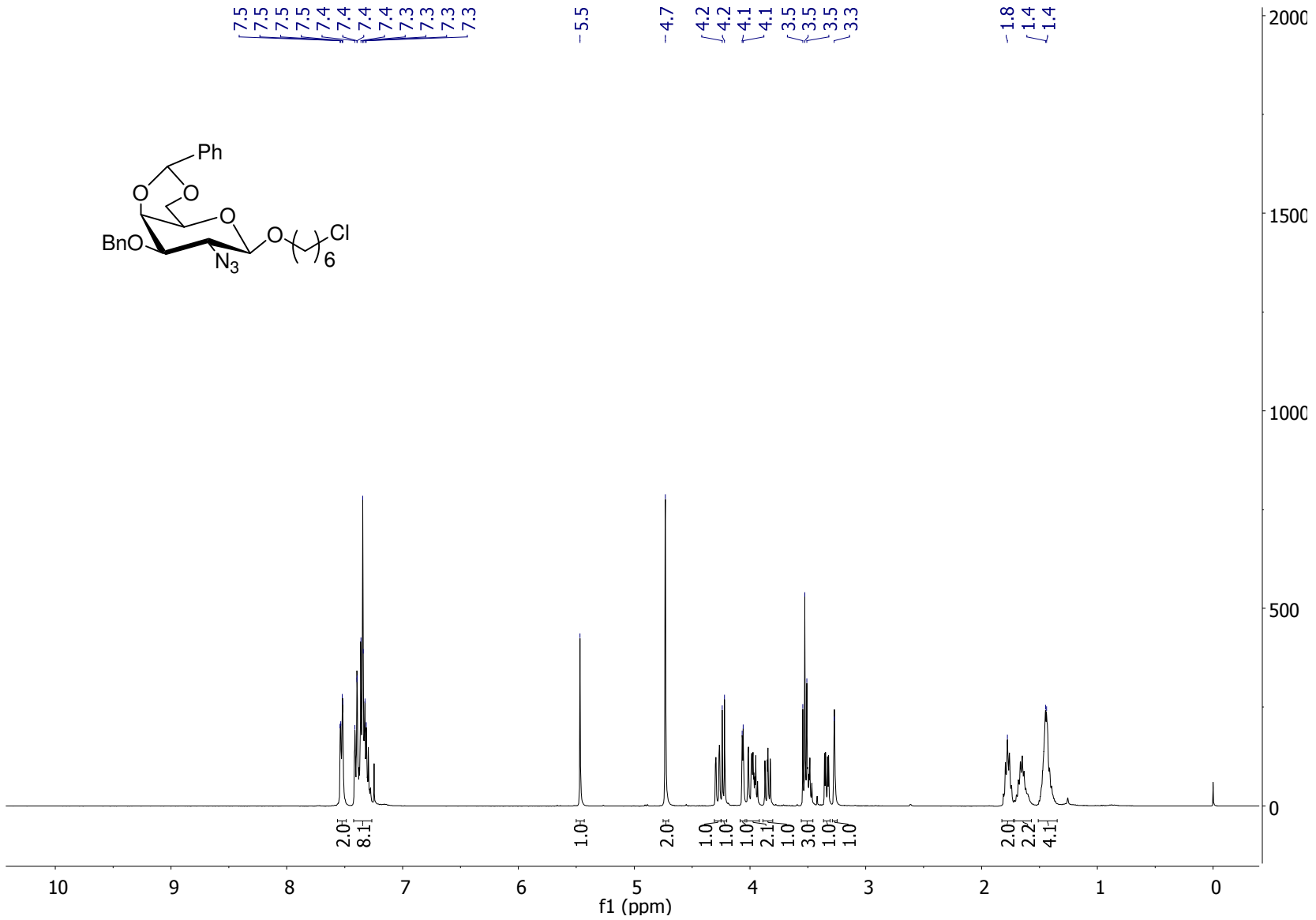
^{13}C NMR of Compound **17.**

^{13}C NMR (400 MHz, $CDCl_3$)



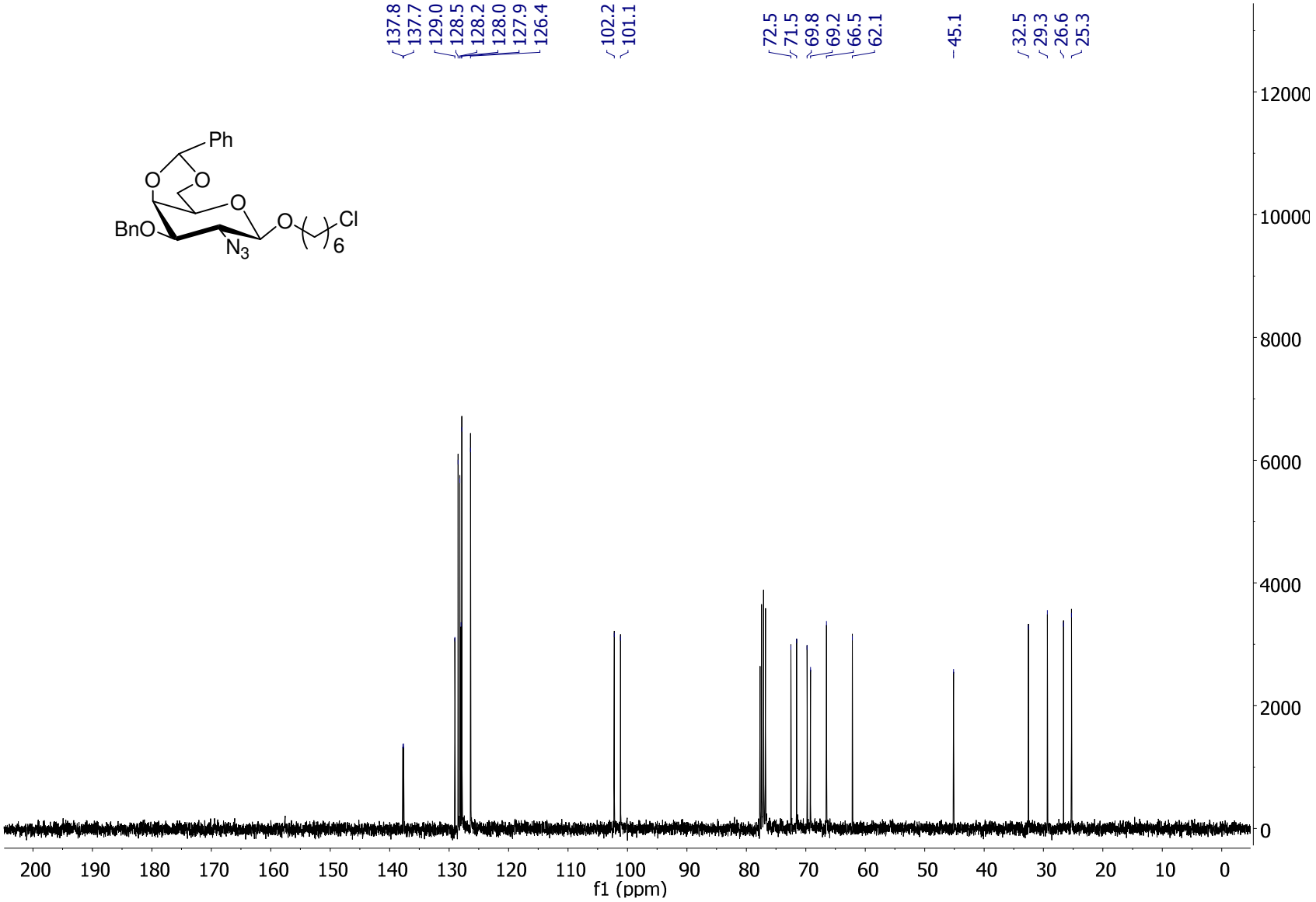
^{1}HNMR of Compound **24.**

^{1}HNMR (400 MHz, $CDCl_3$)



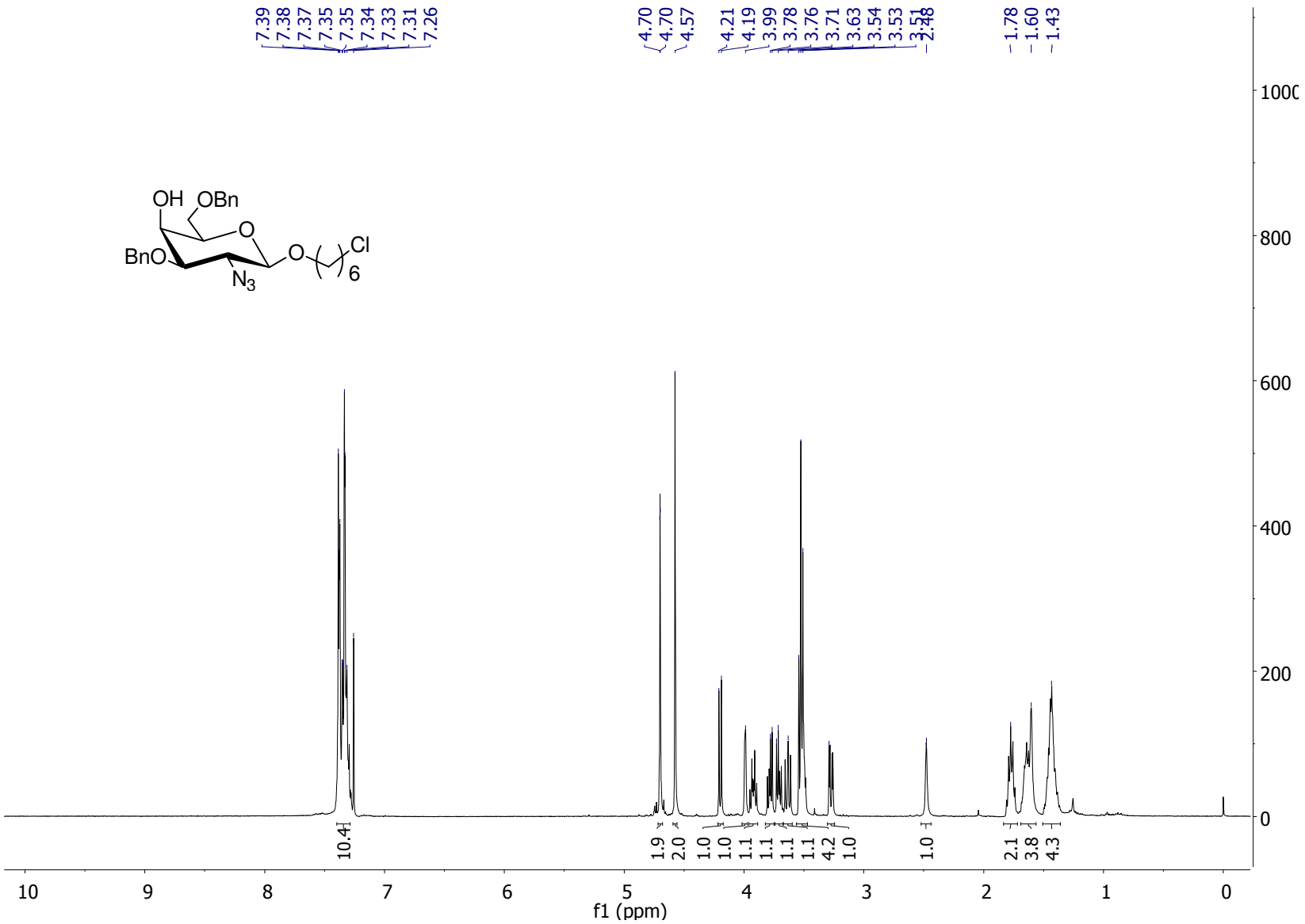
^{13}C NMR of Compound **24.**

^{13}C NMR (400 MHz, $CDCl_3$)



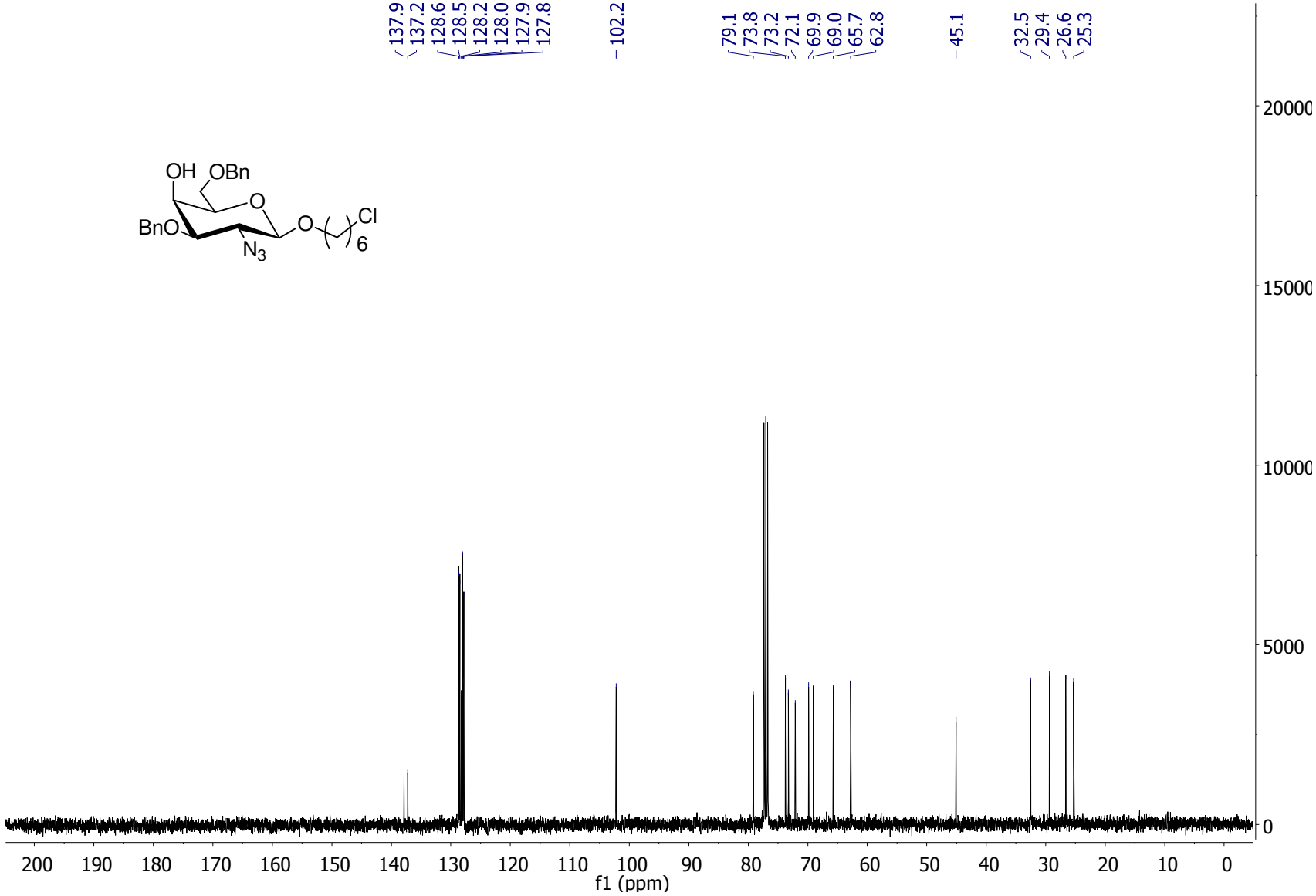
^{1}HNMR of Compound **10.**

^{1}HNMR (400 MHz, $CDCl_3$)



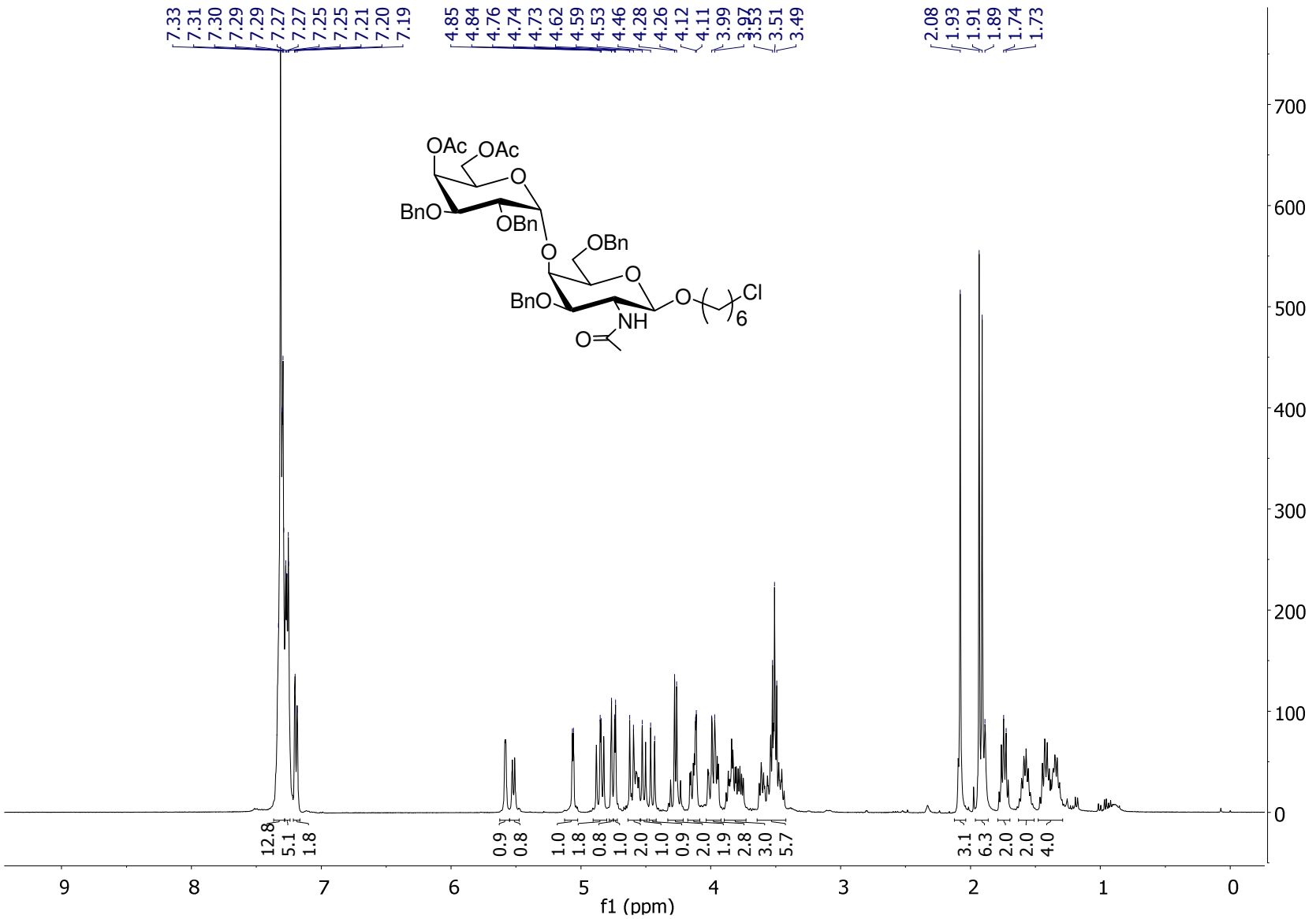
^{13}C NMR of Compound **10.**

^{13}C NMR (400 MHz, $CDCl_3$)



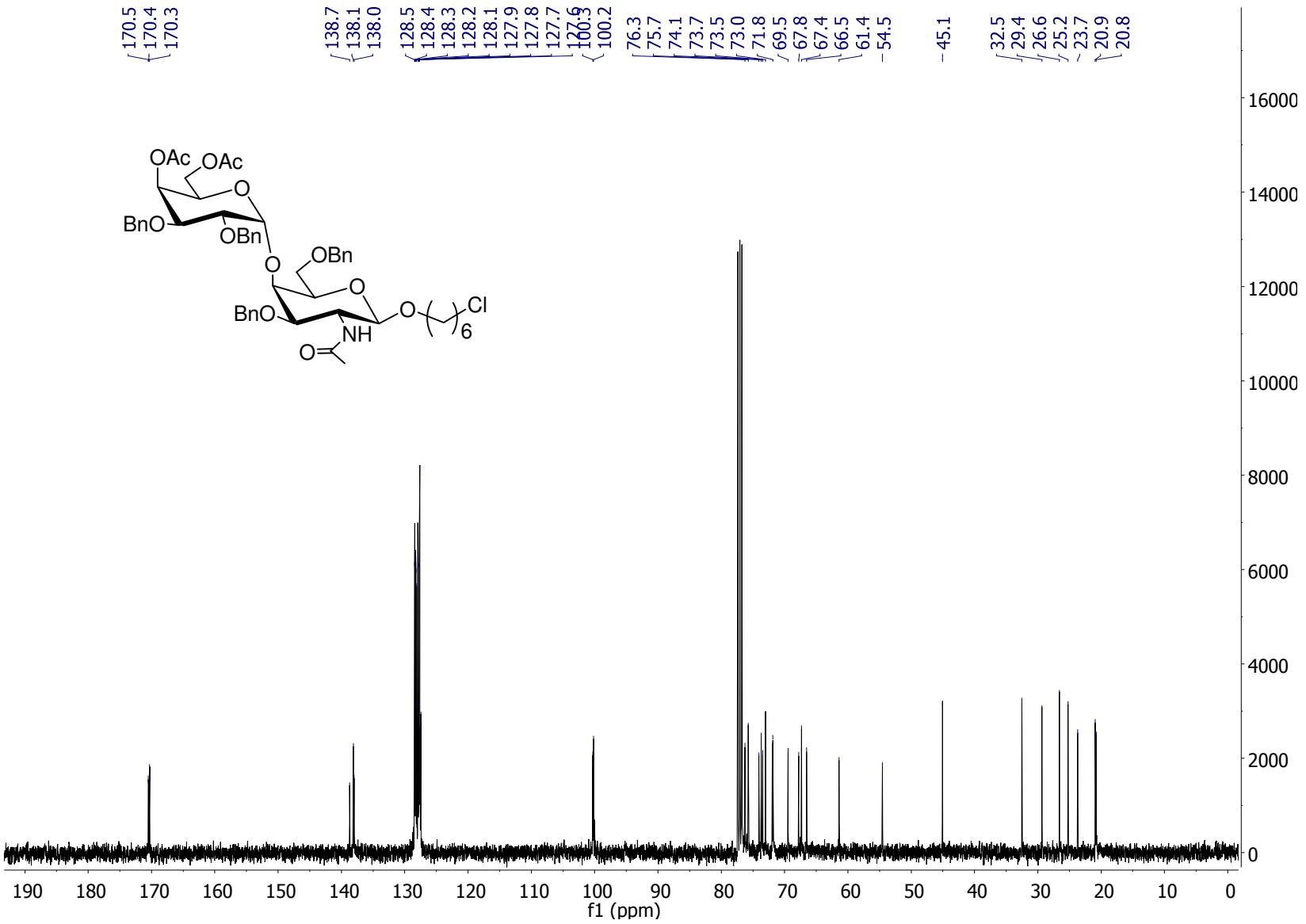
^{1}HNMR of Compound **25.**

^{1}HNMR (400 MHz, $CDCl_3$)



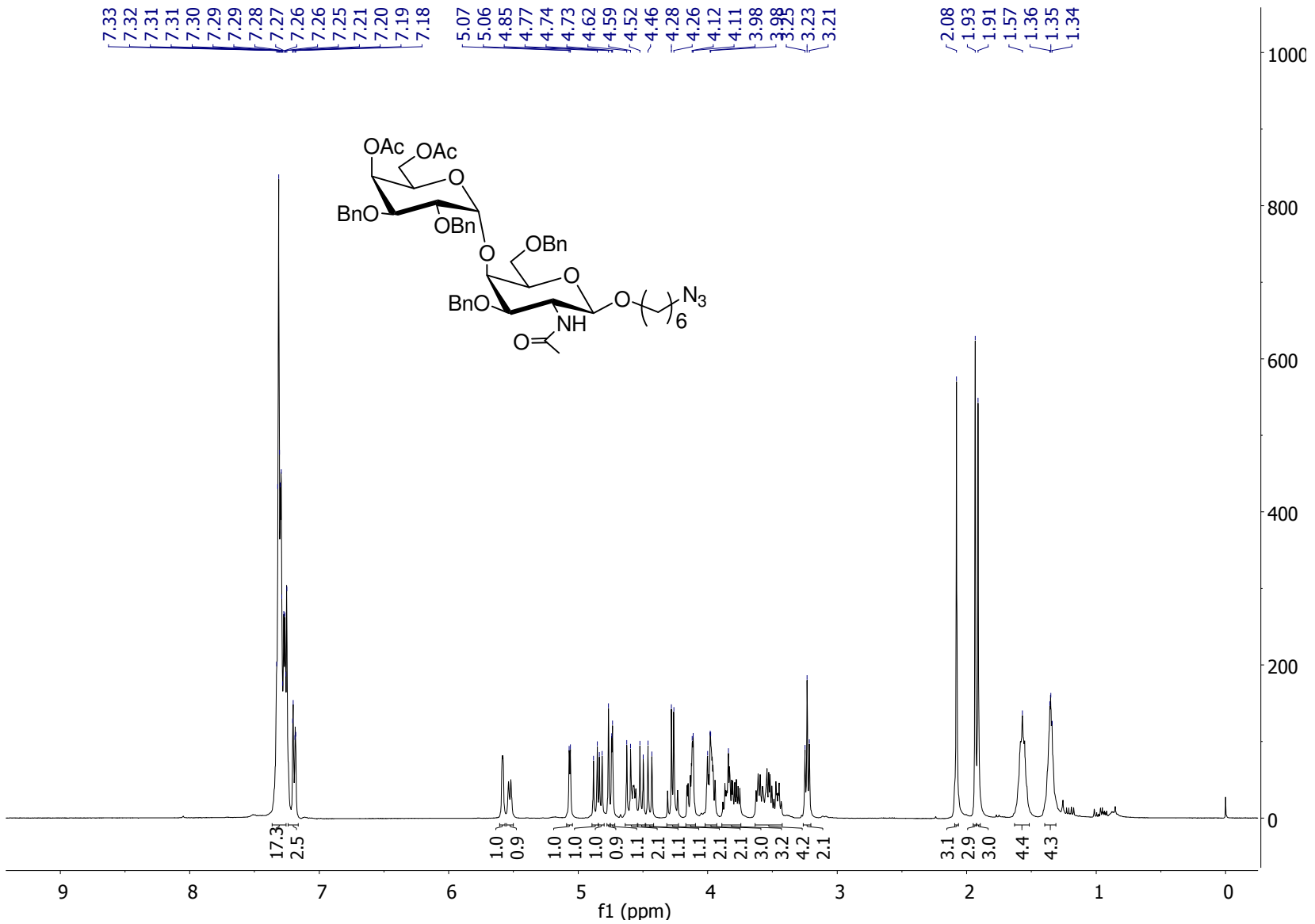
^{13}C NMR of Compound **28.**

^{13}C NMR (400 MHz, $CDCl_3$)



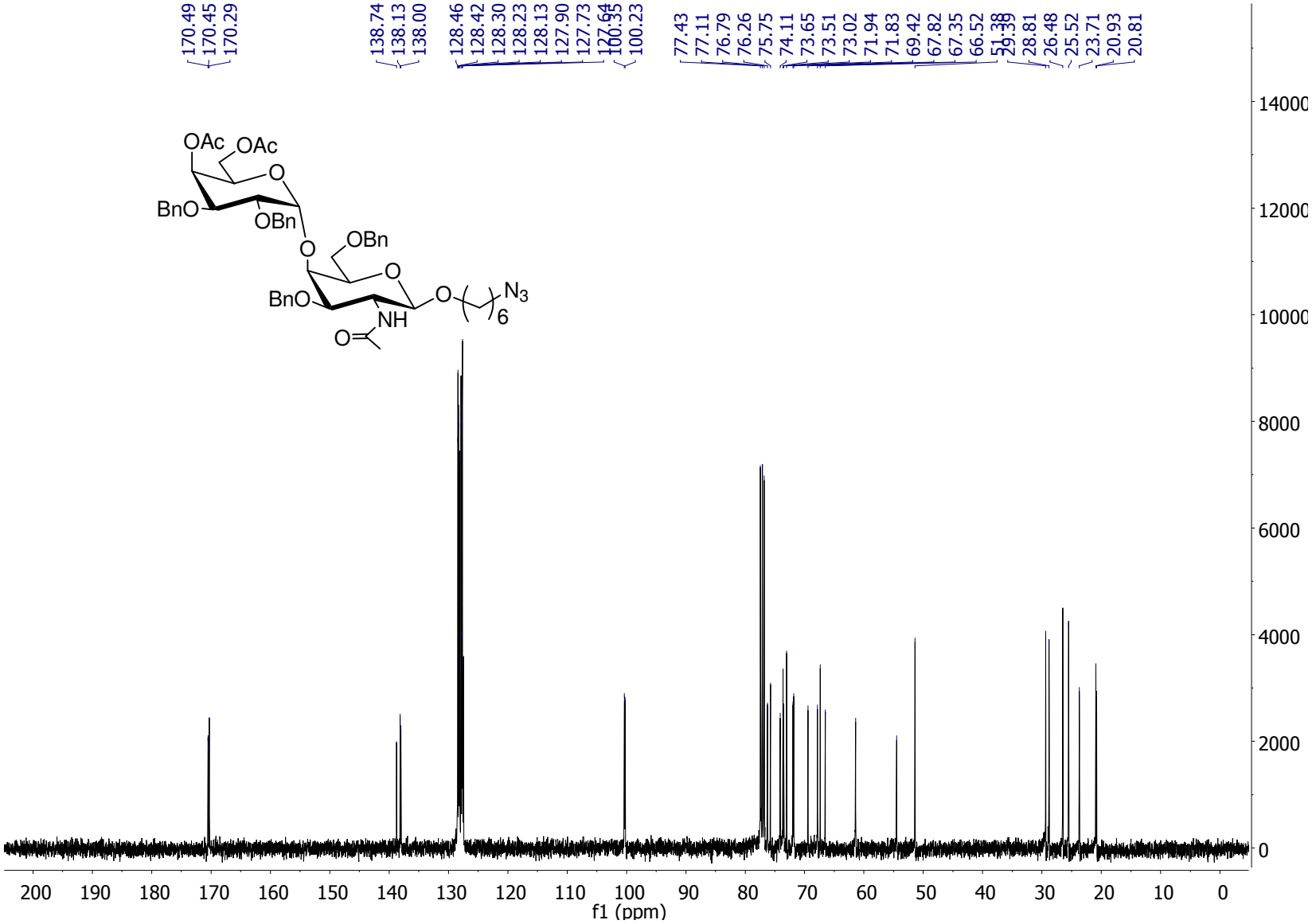
^{1}HNMR of Compound **26.**

^{1}HNMR (400 MHz, $CDCl_3$)



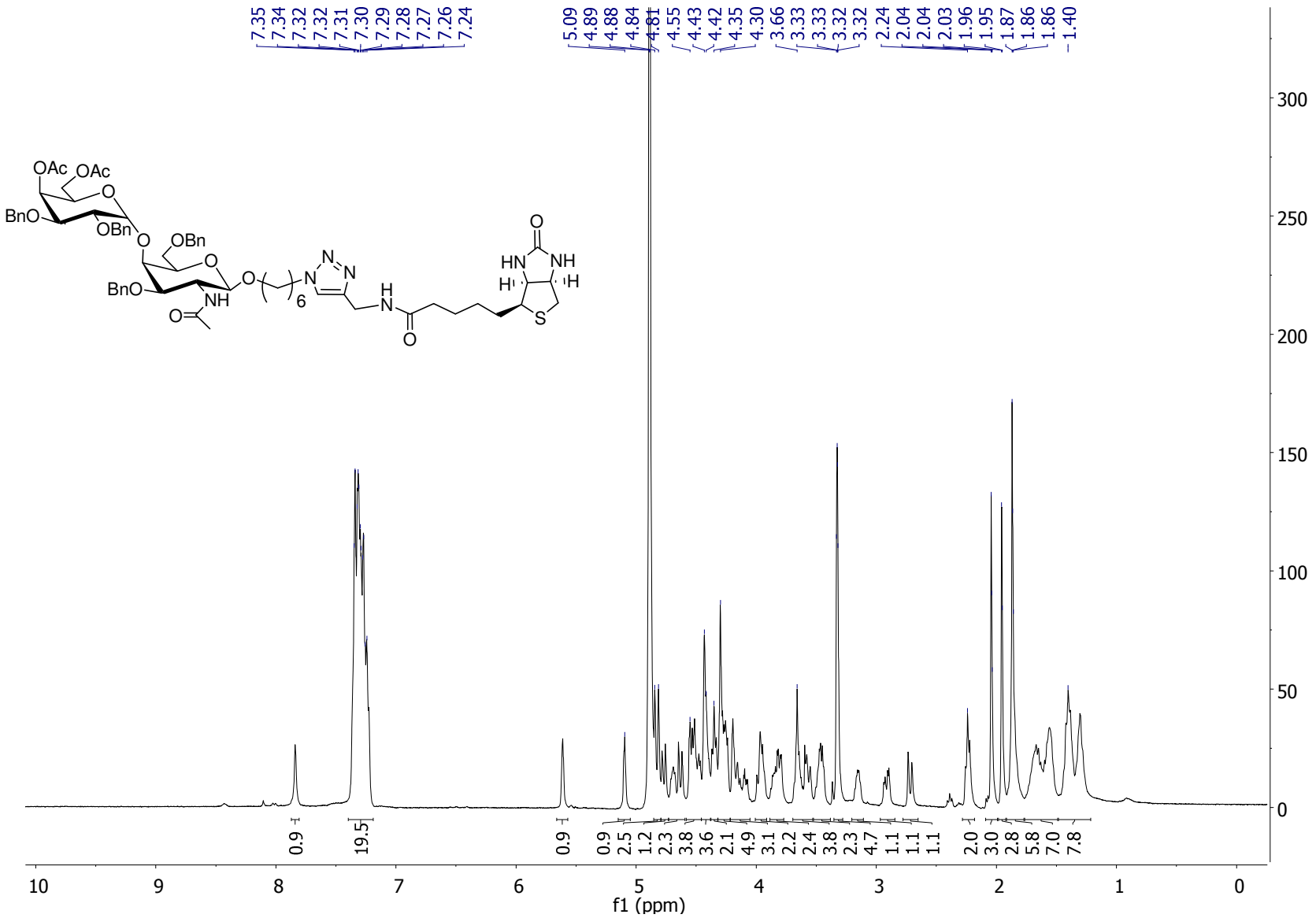
^{13}C NMR of Compound **26.**

^{13}C NMR (400 MHz, $CDCl_3$)



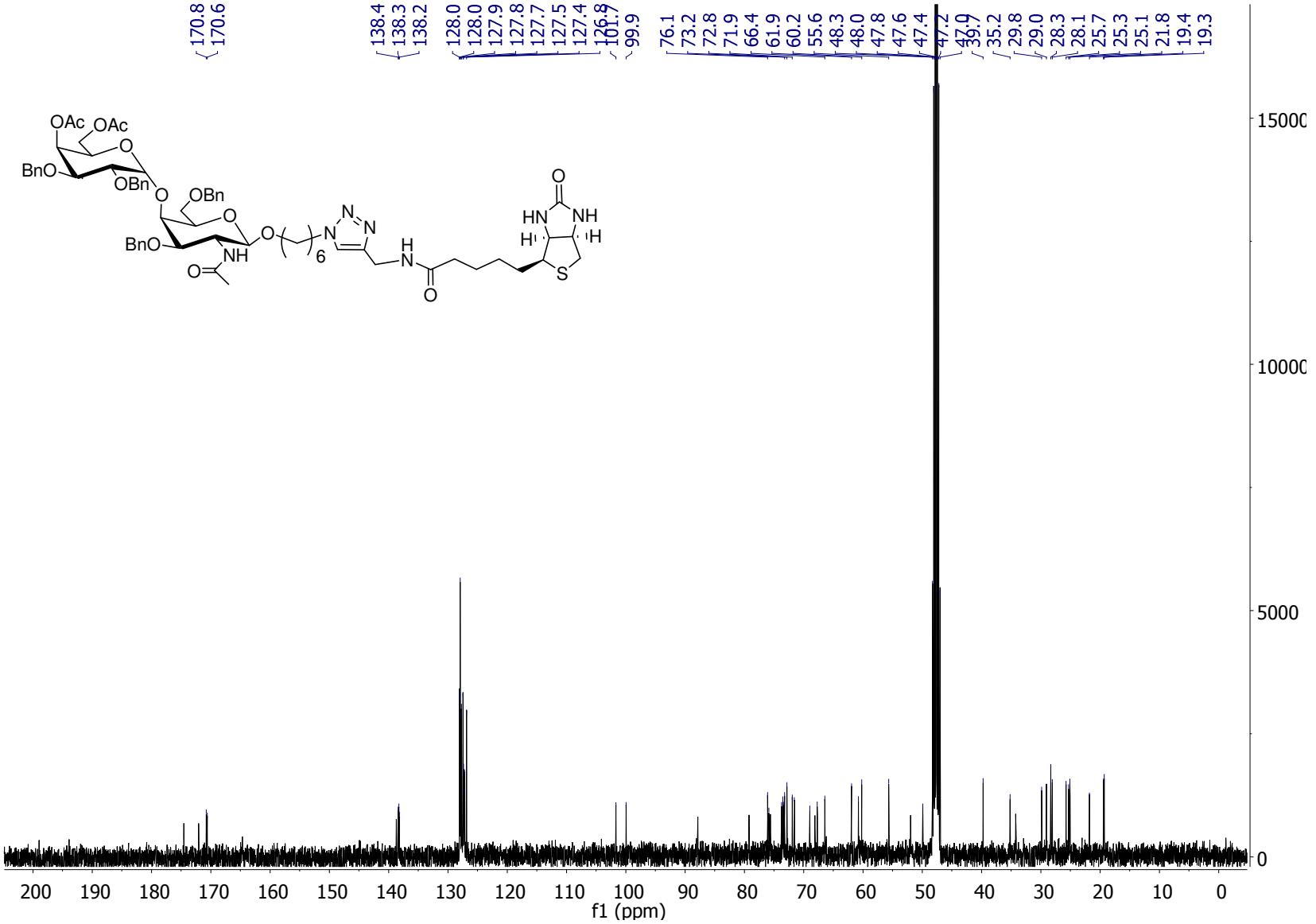
^{1}HNMR of Compound **27.**

^{1}HNMR (400 MHz, MeOH-d_4)



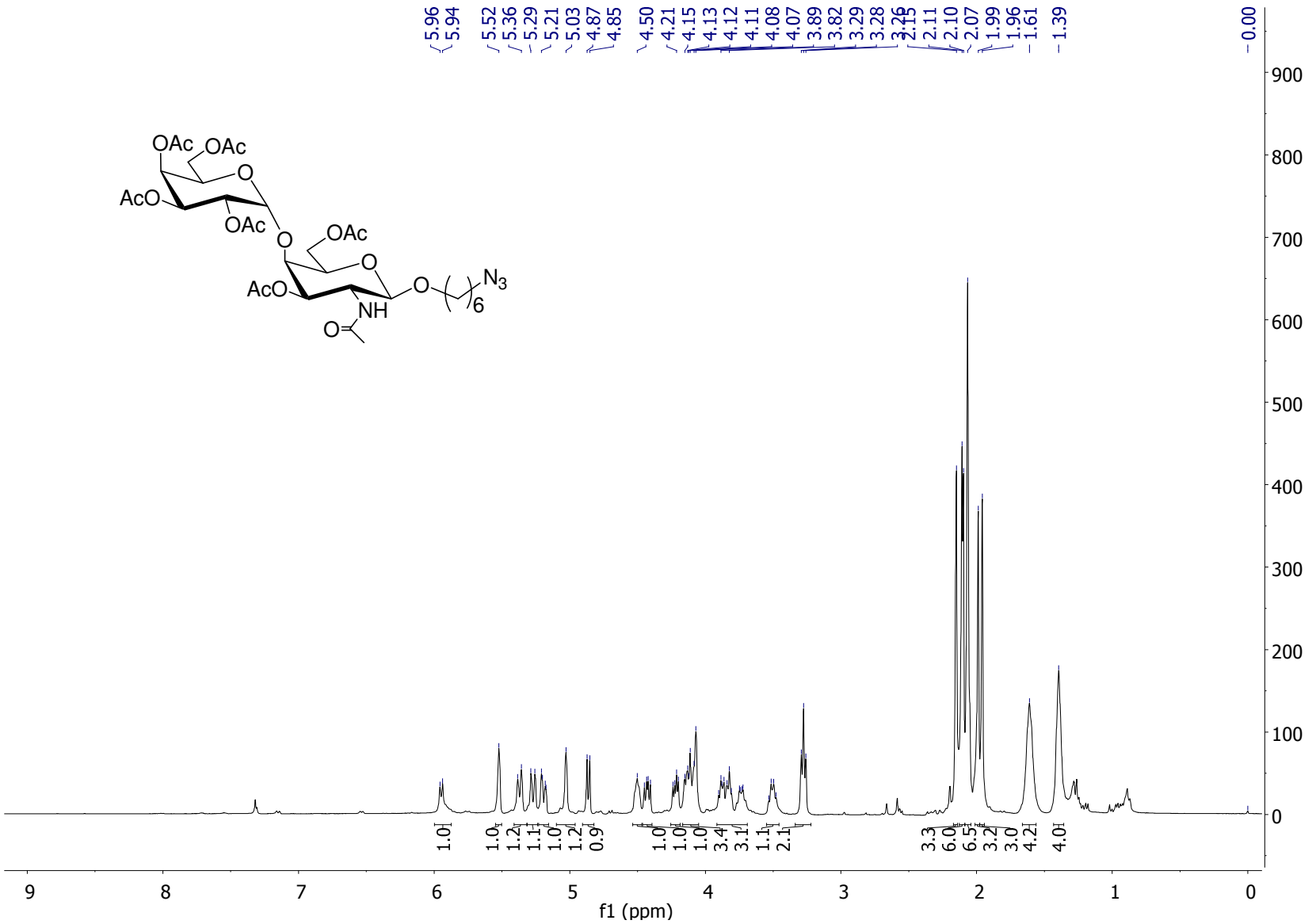
^{13}C NMR of Compound **27.**

^{13}C NMR (400 MHz, MeOH-d_4)



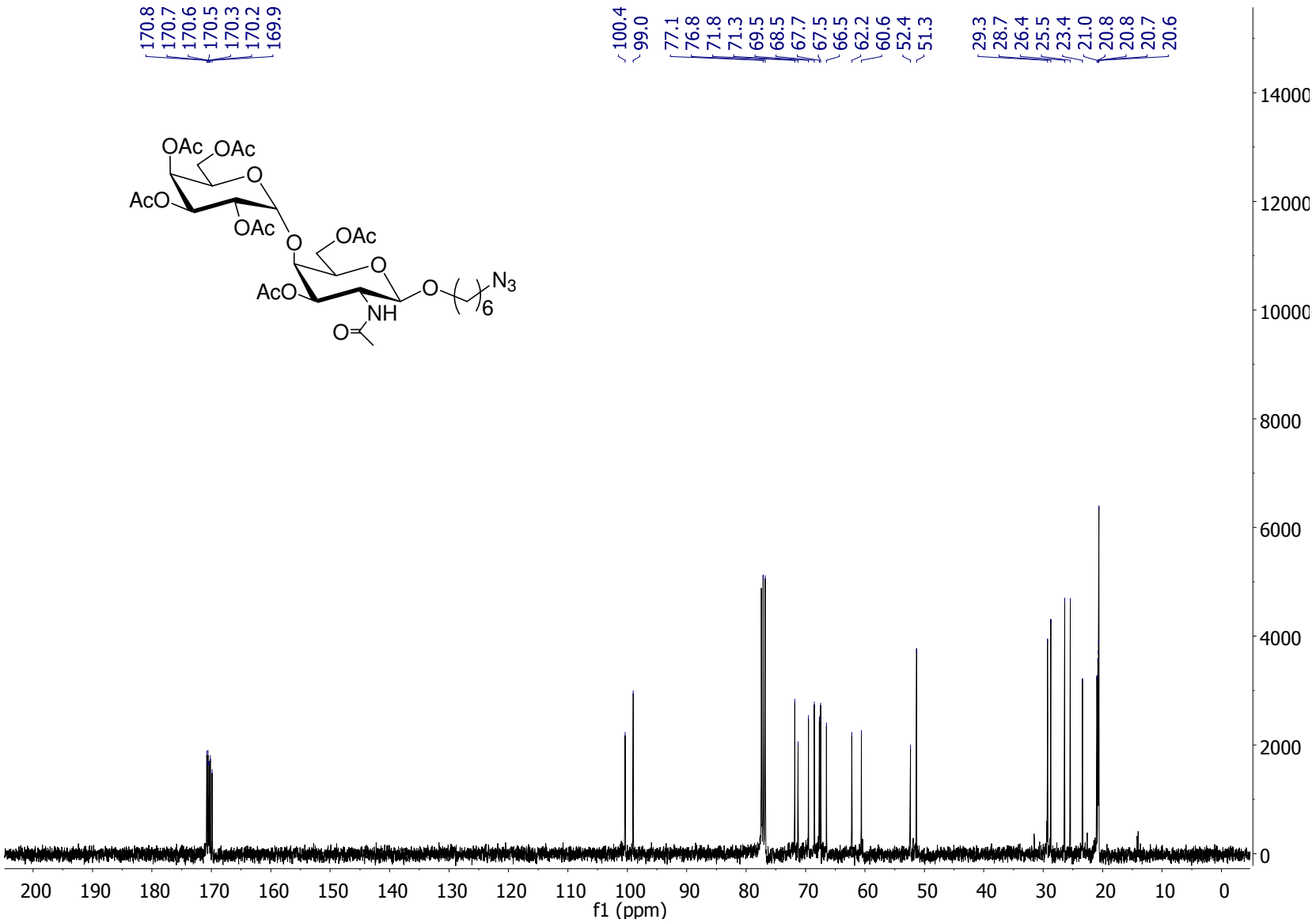
^{1}HNMR of Compound **28.**

^{1}HNMR (400 MHz, $CDCl_3$)



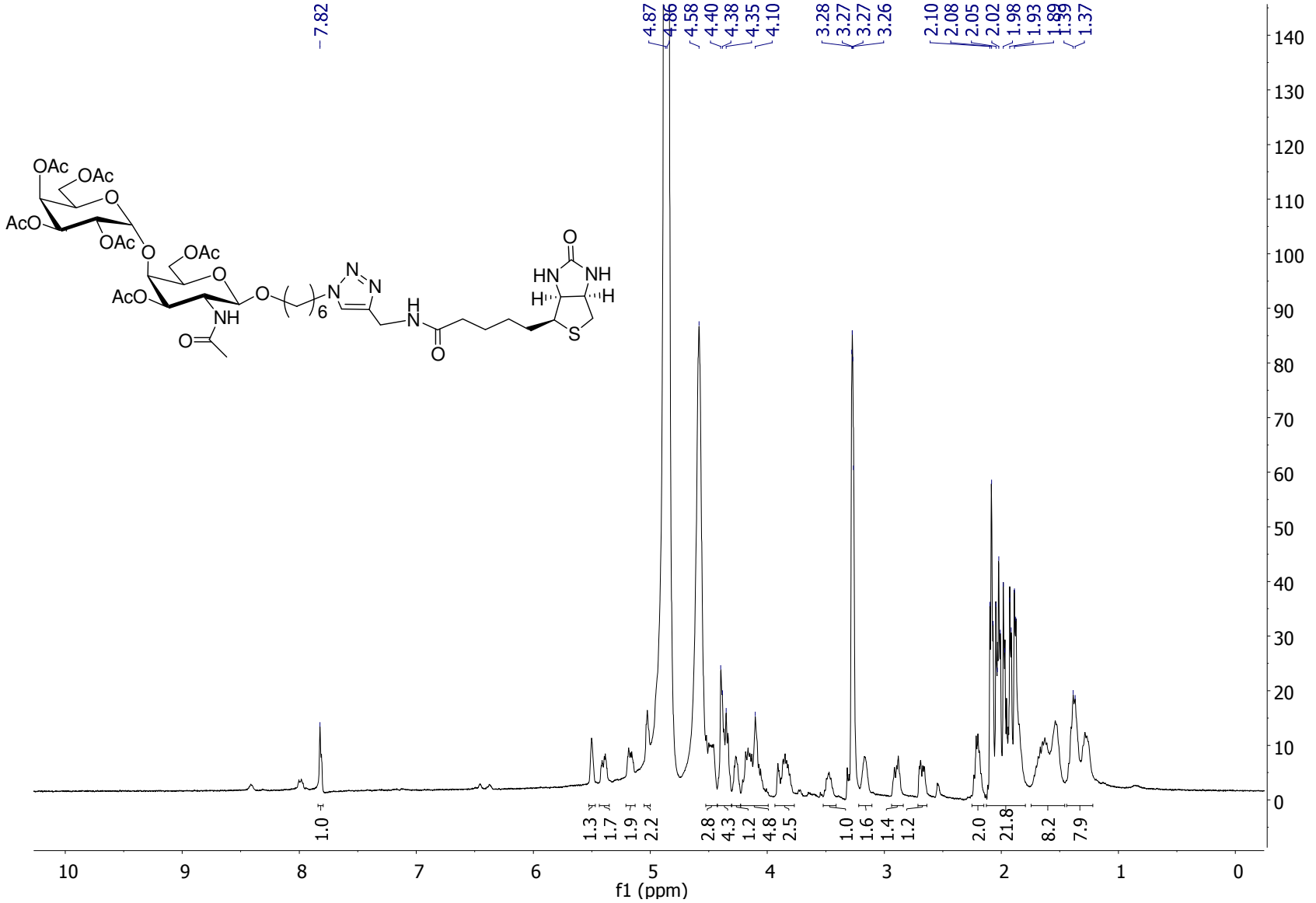
^{13}C NMR of Compound **28.**

^{13}C NMR (400 MHz, $CDCl_3$)



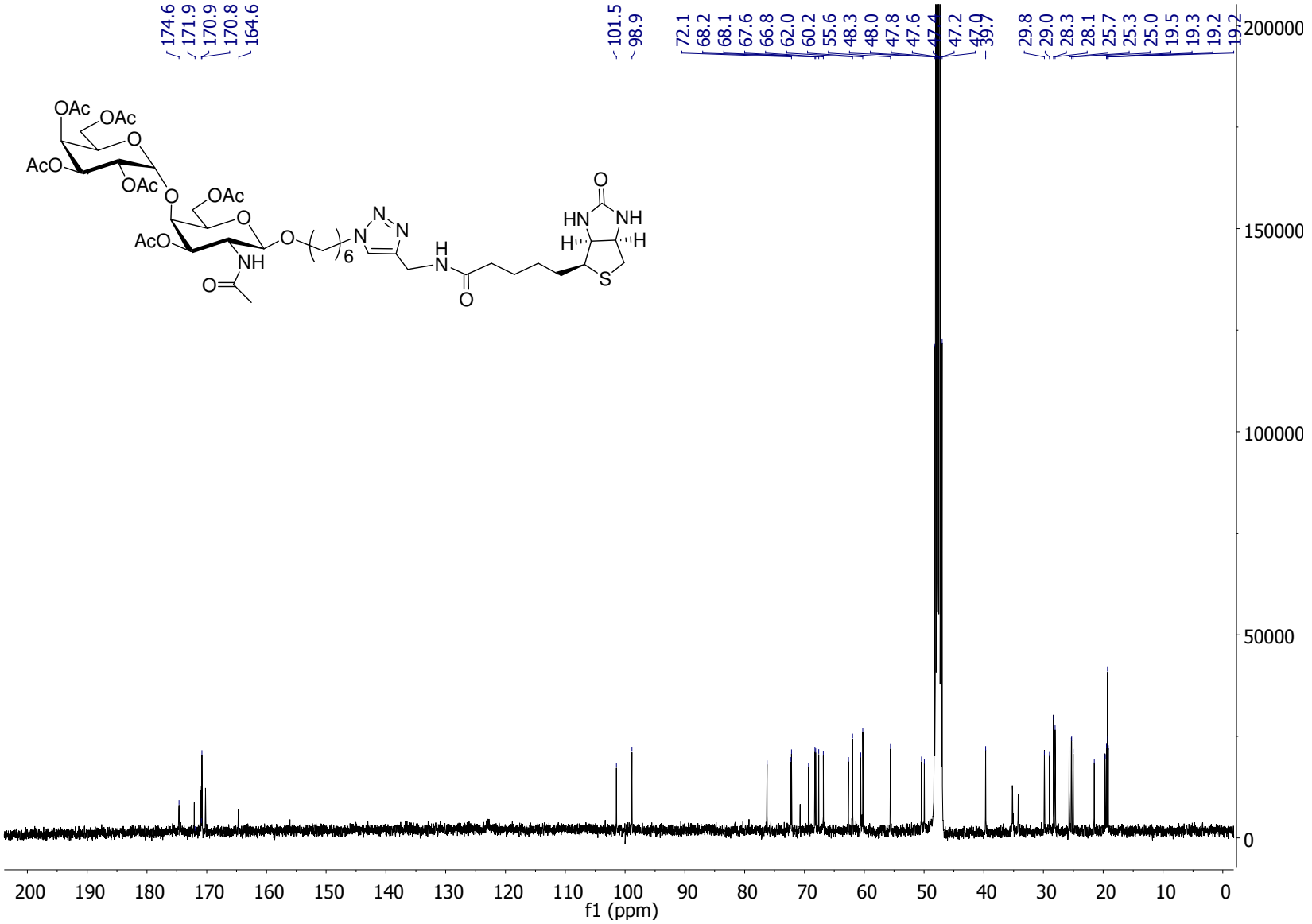
^{1}HNMR of Compound **29.**

^{1}HNMR (400 MHz, MeOH-d_4)



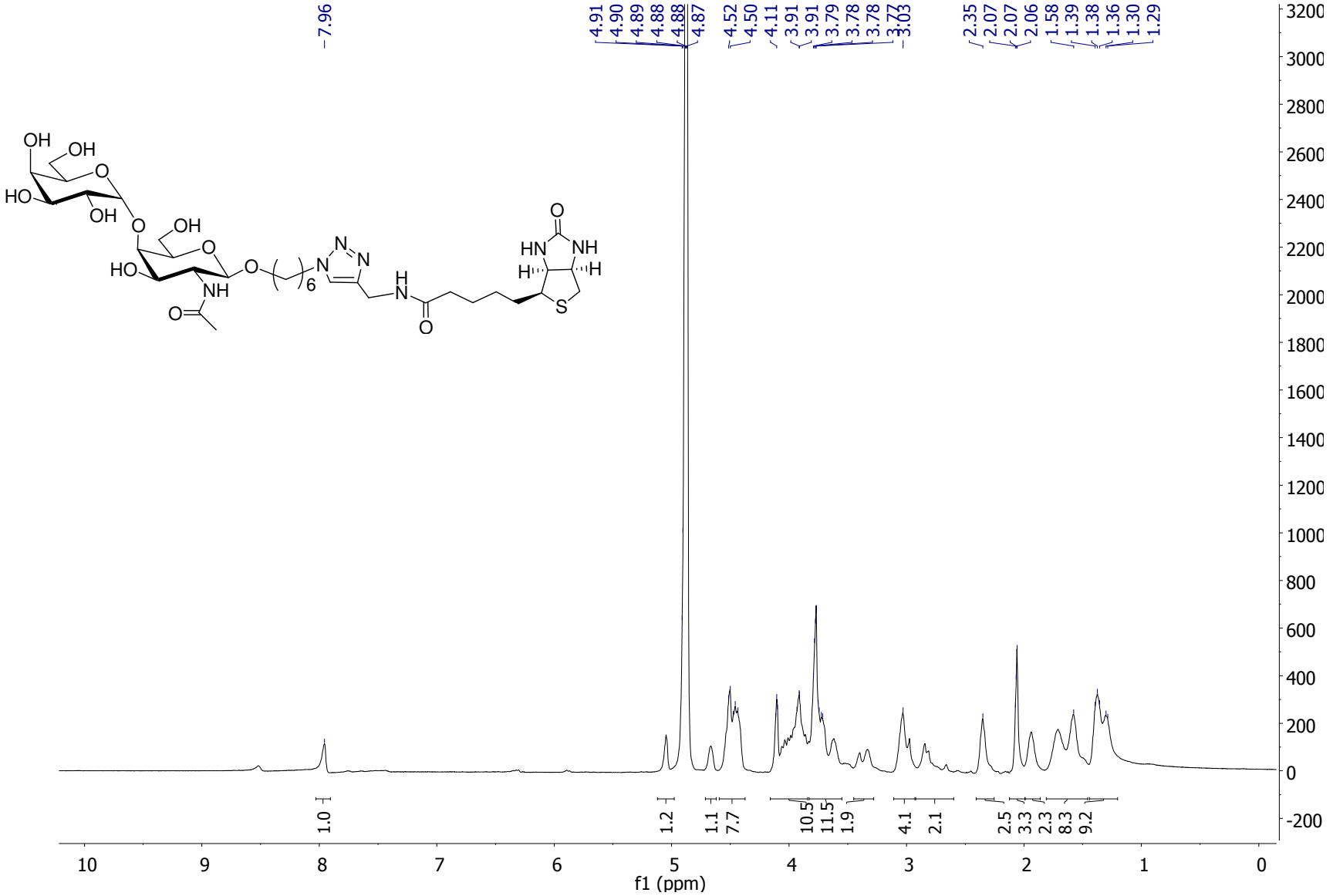
^{13}C NMR of Compound **29.**

^{13}C NMR (400 MHz, MeOH-d_4)



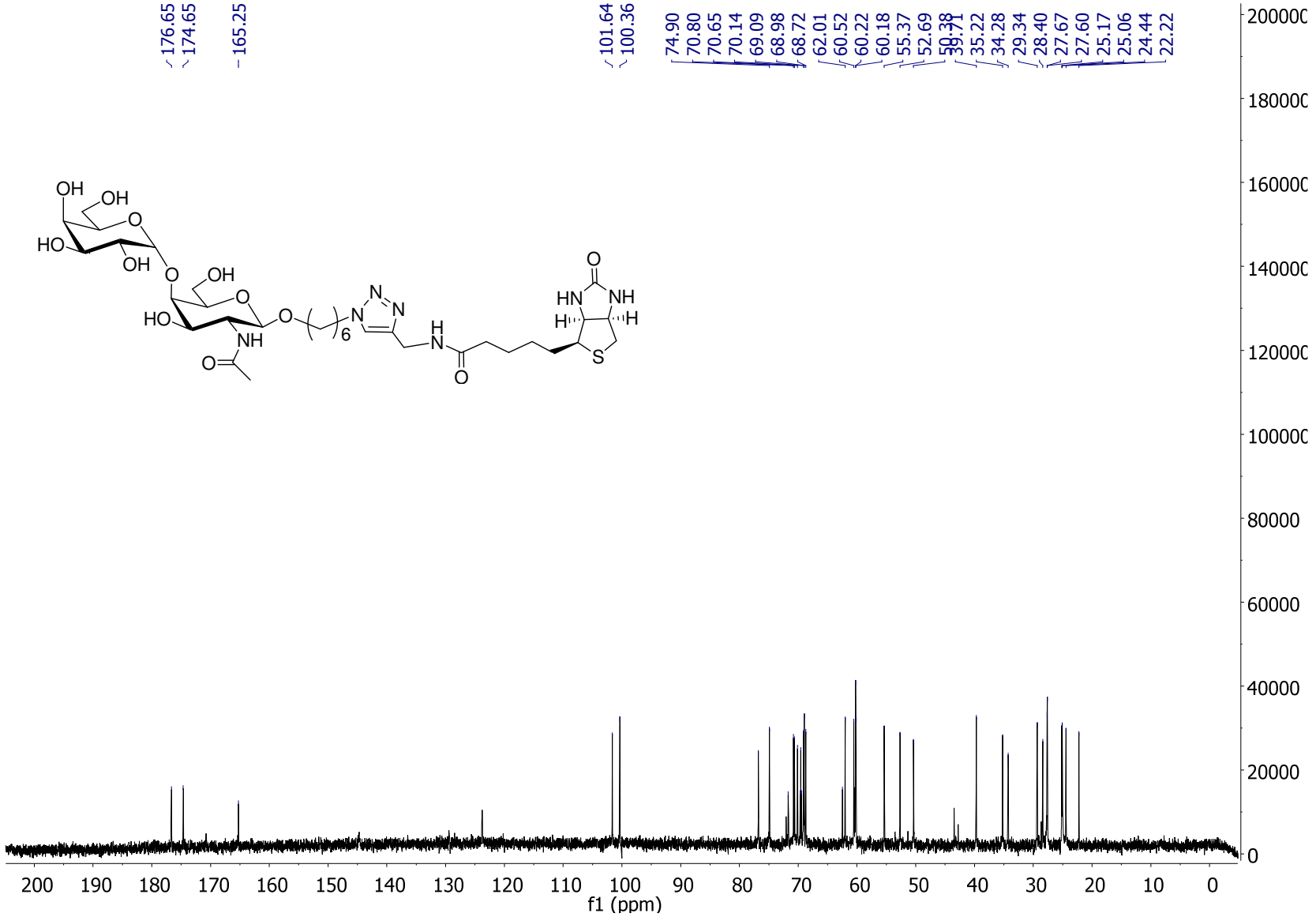
^{1}HNMR of Compound **2a.**

^{1}HNMR (400 MHz, D_2O)



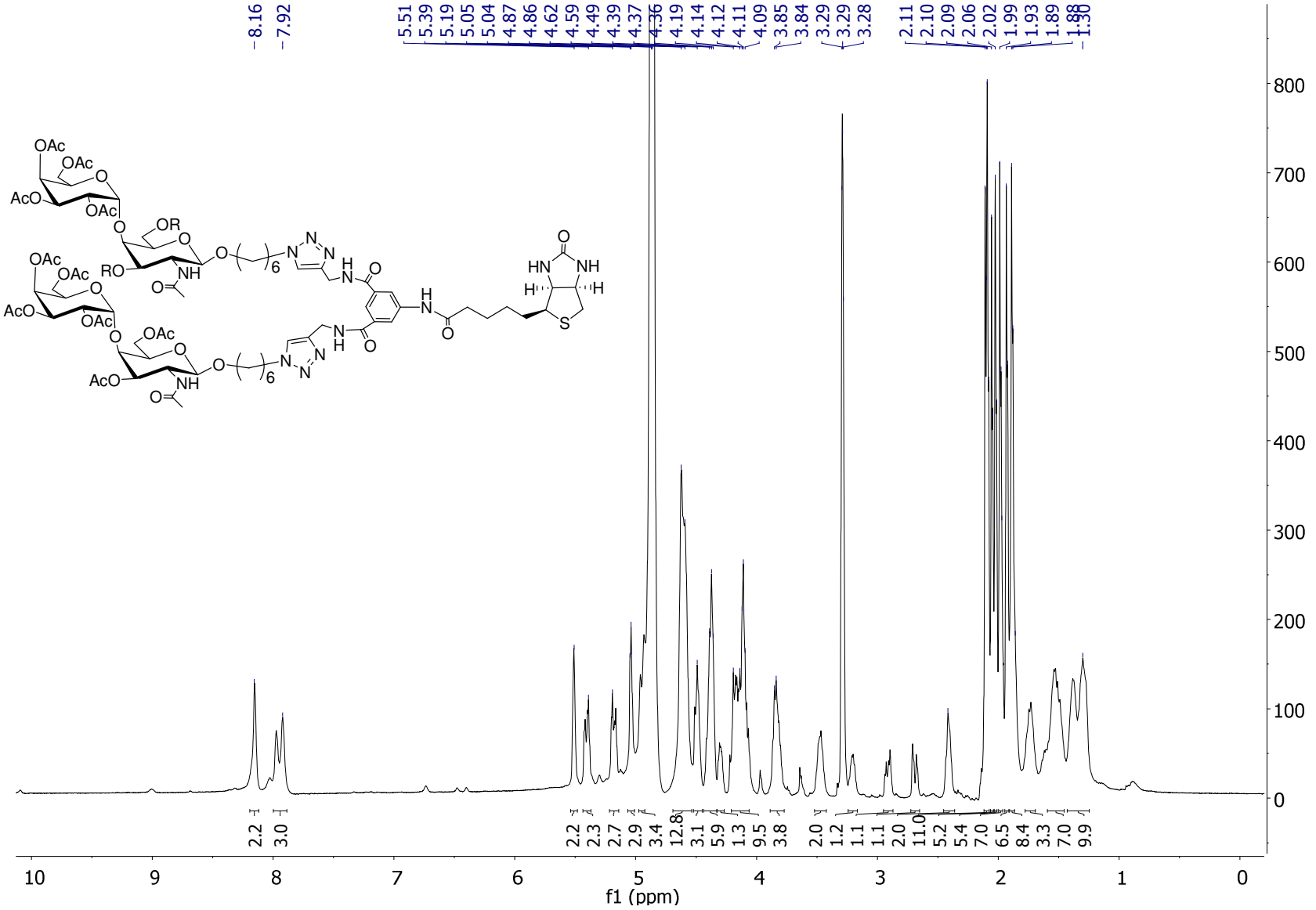
^{13}C NMR of Compound **2a.**

^{13}C NMR (400 MHz, D_2O)



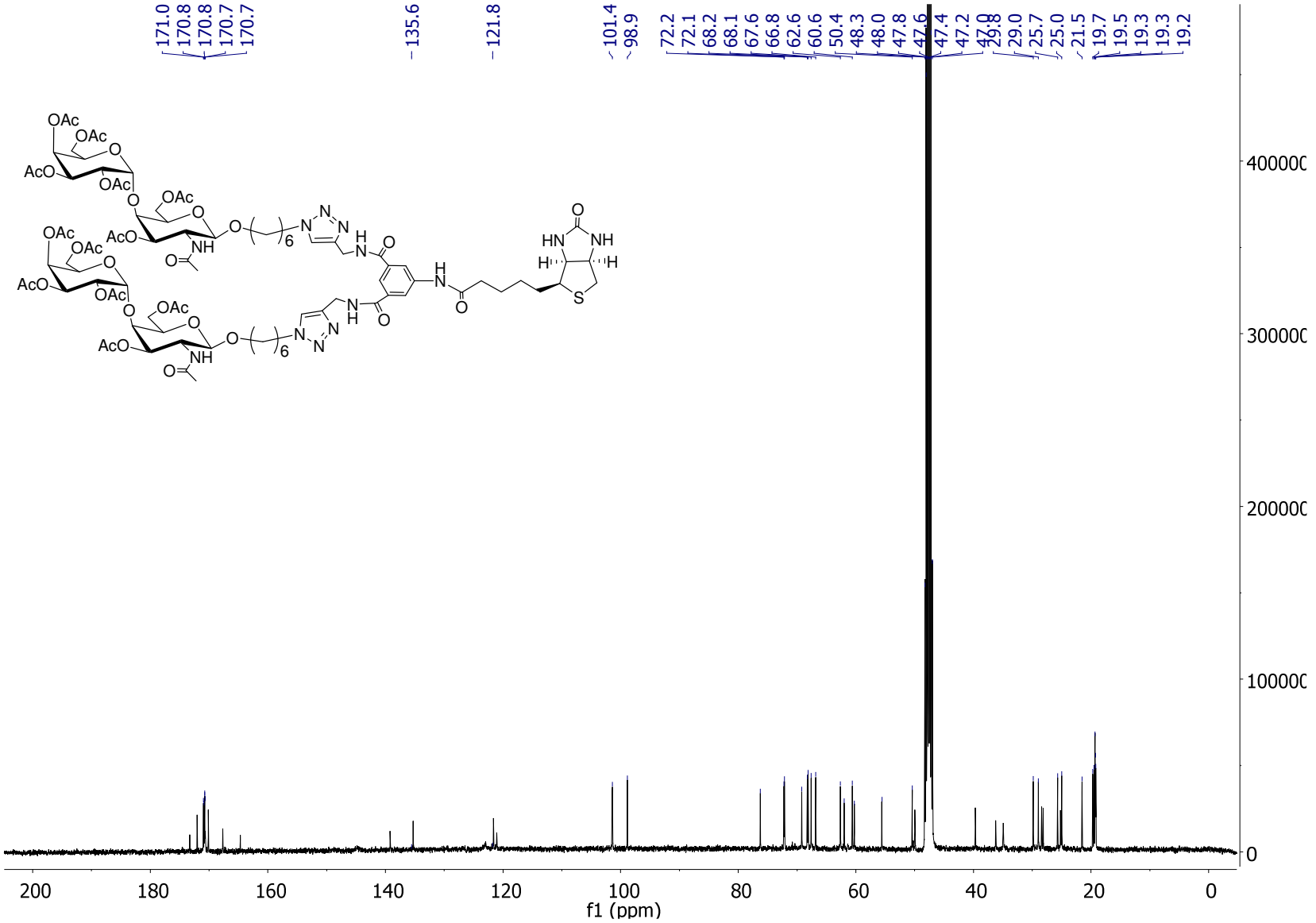
^{1}HNMR of Compound **30.**

^{1}HNMR (400 MHz, MeOH-d_4)



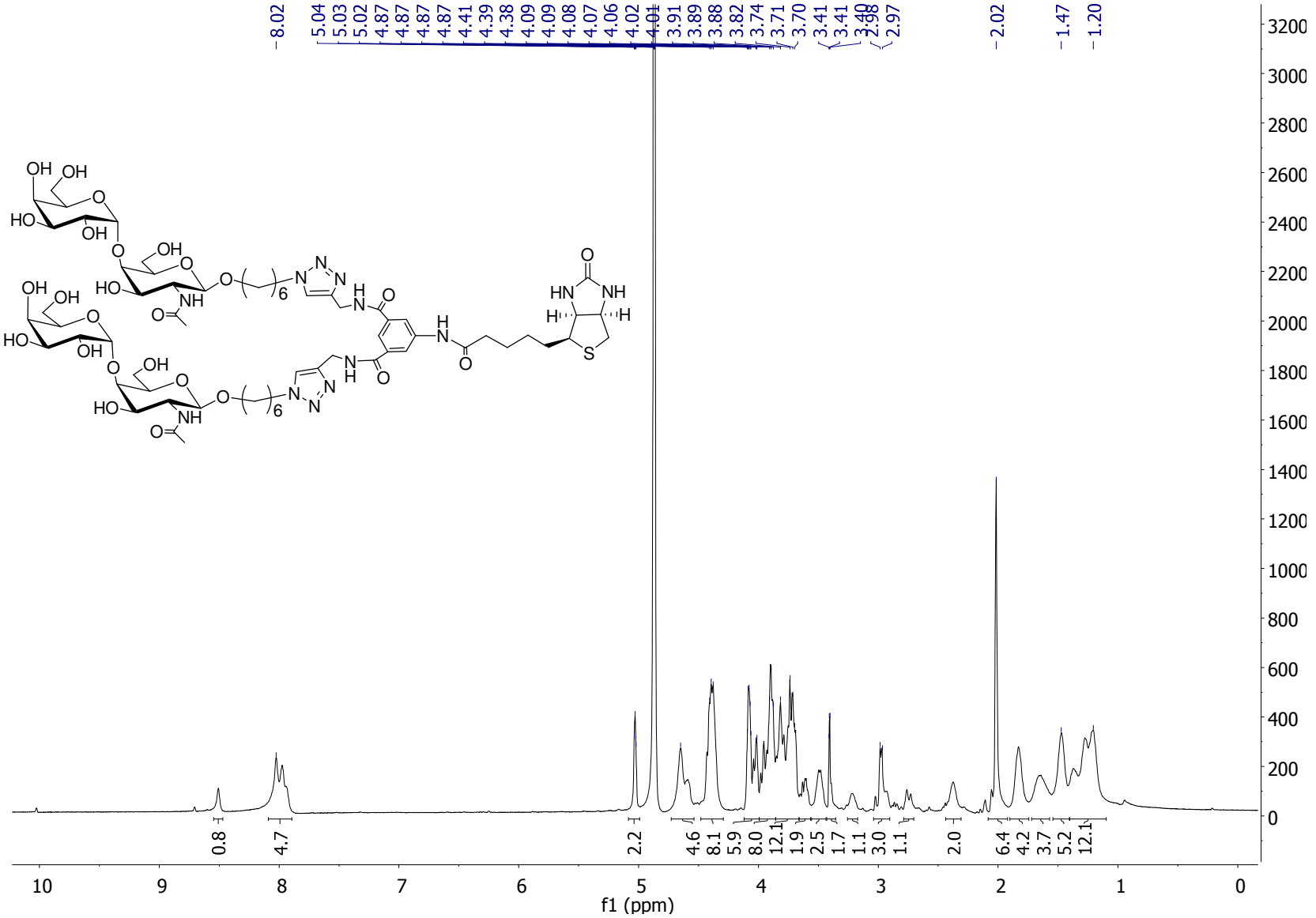
^{13}CNMR of Compound **30.**

^{13}CNMR (400 MHz, MeOH-d_4)



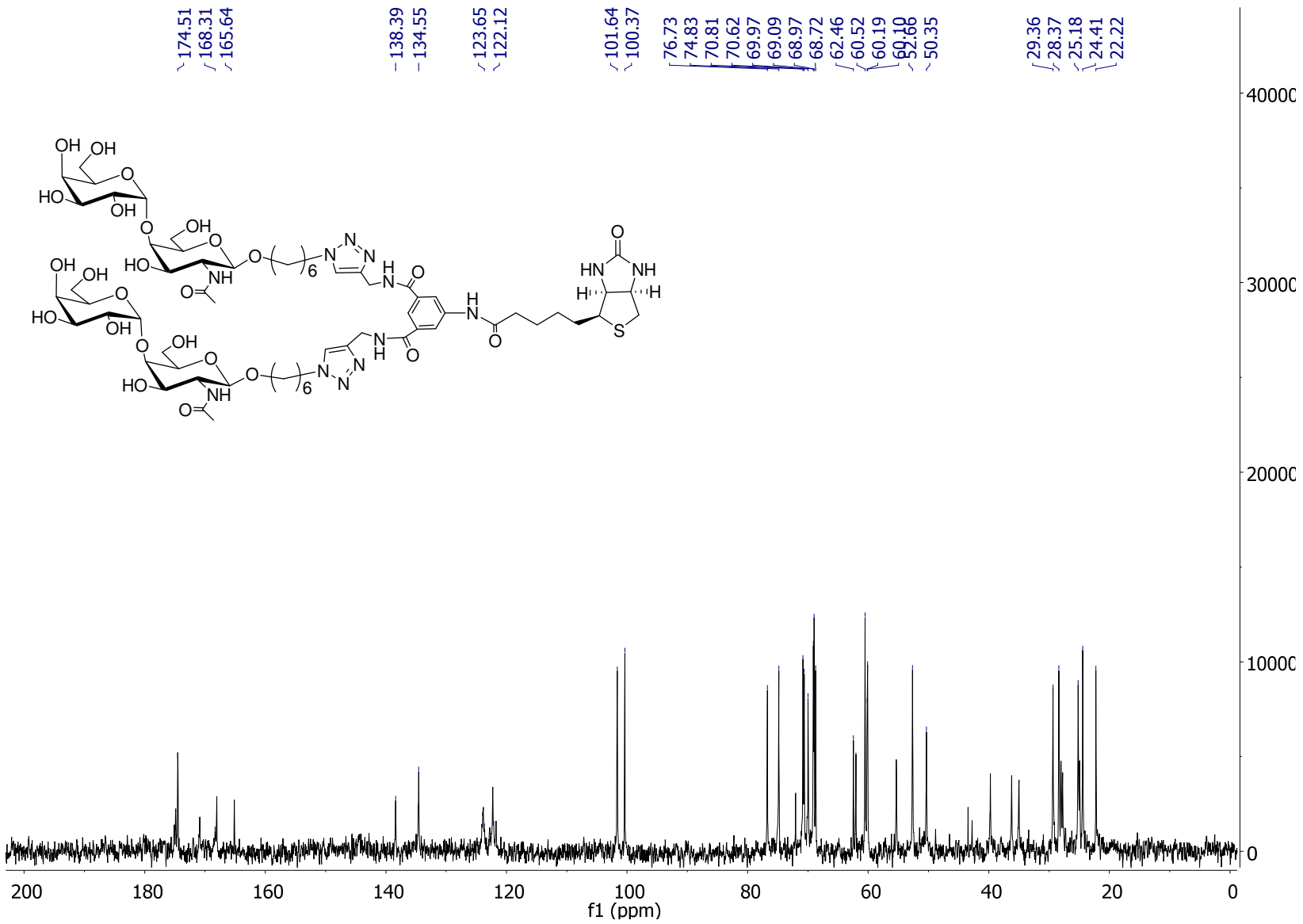
^{1}HNMR of Compound **2b.**

^{1}HNMR (400 MHz, D_2O)



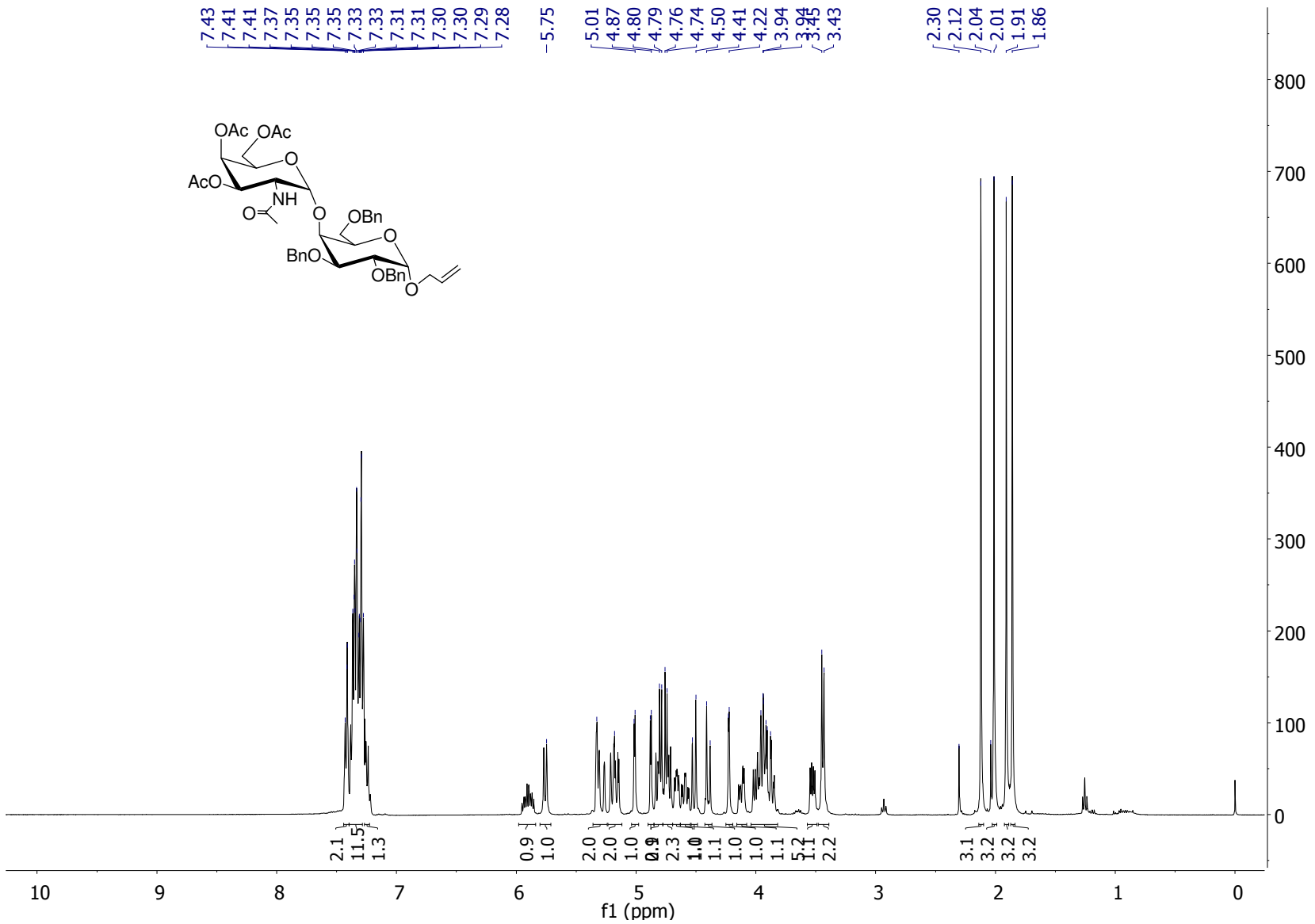
^{13}CNMR of Compound **2b.**

^{13}CNMR (400 MHz, D_2O)



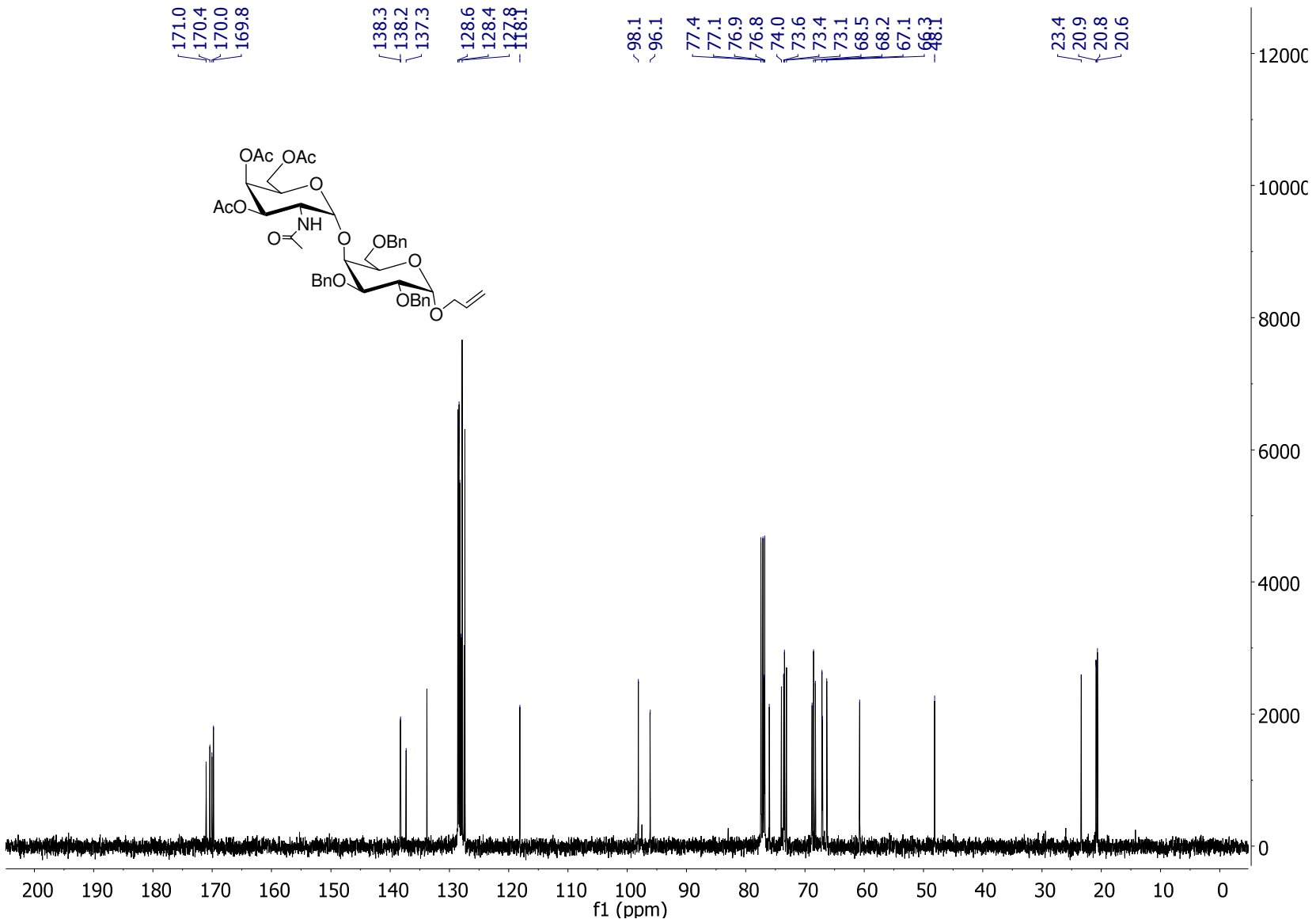
^{1}HNMR of Compound **32.**

^{1}HNMR (400 MHz, $CDCl_3$)



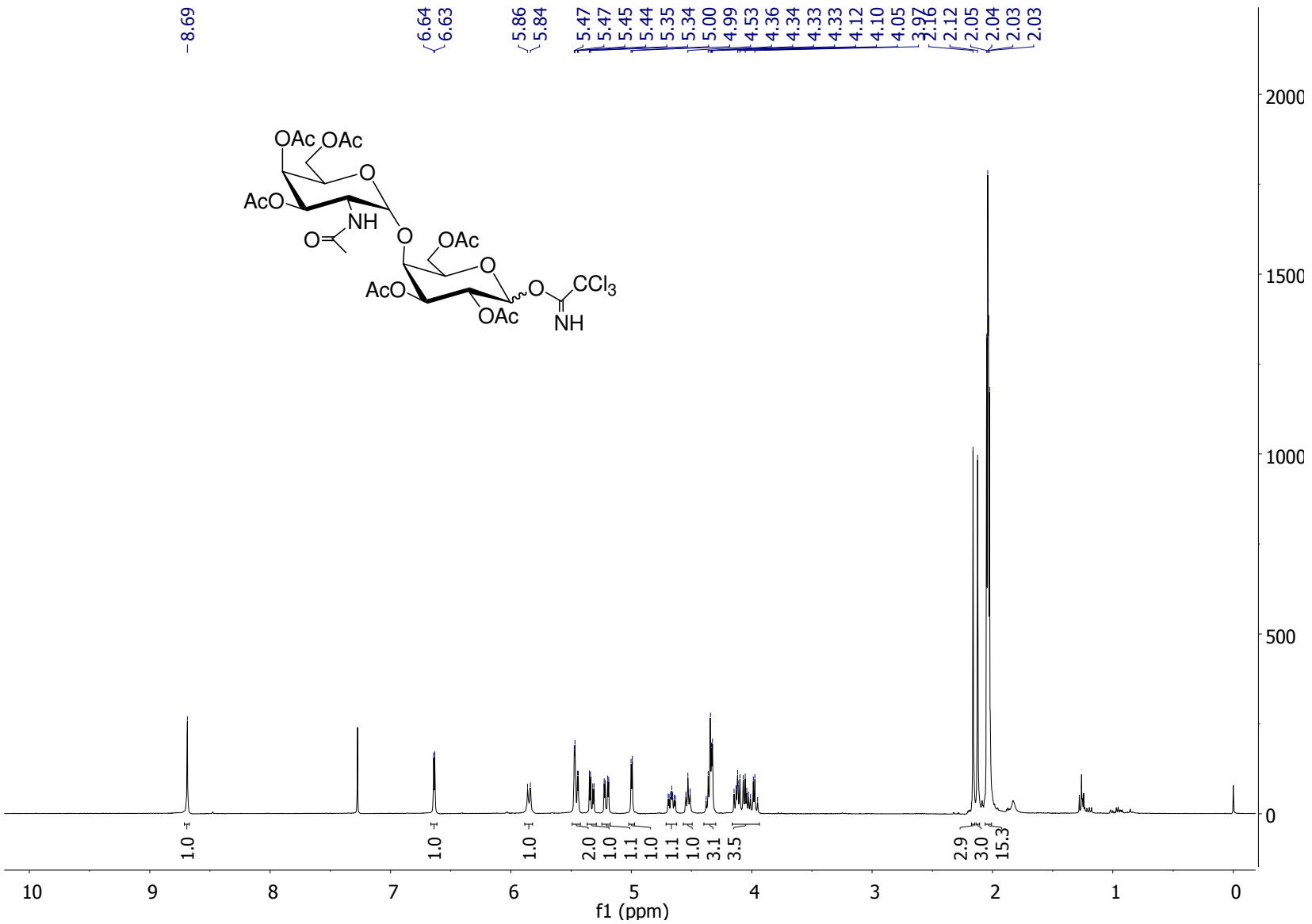
^{13}CNMR of Compound **32.**

^{13}CNMR (400 MHz, $CDCl_3$)



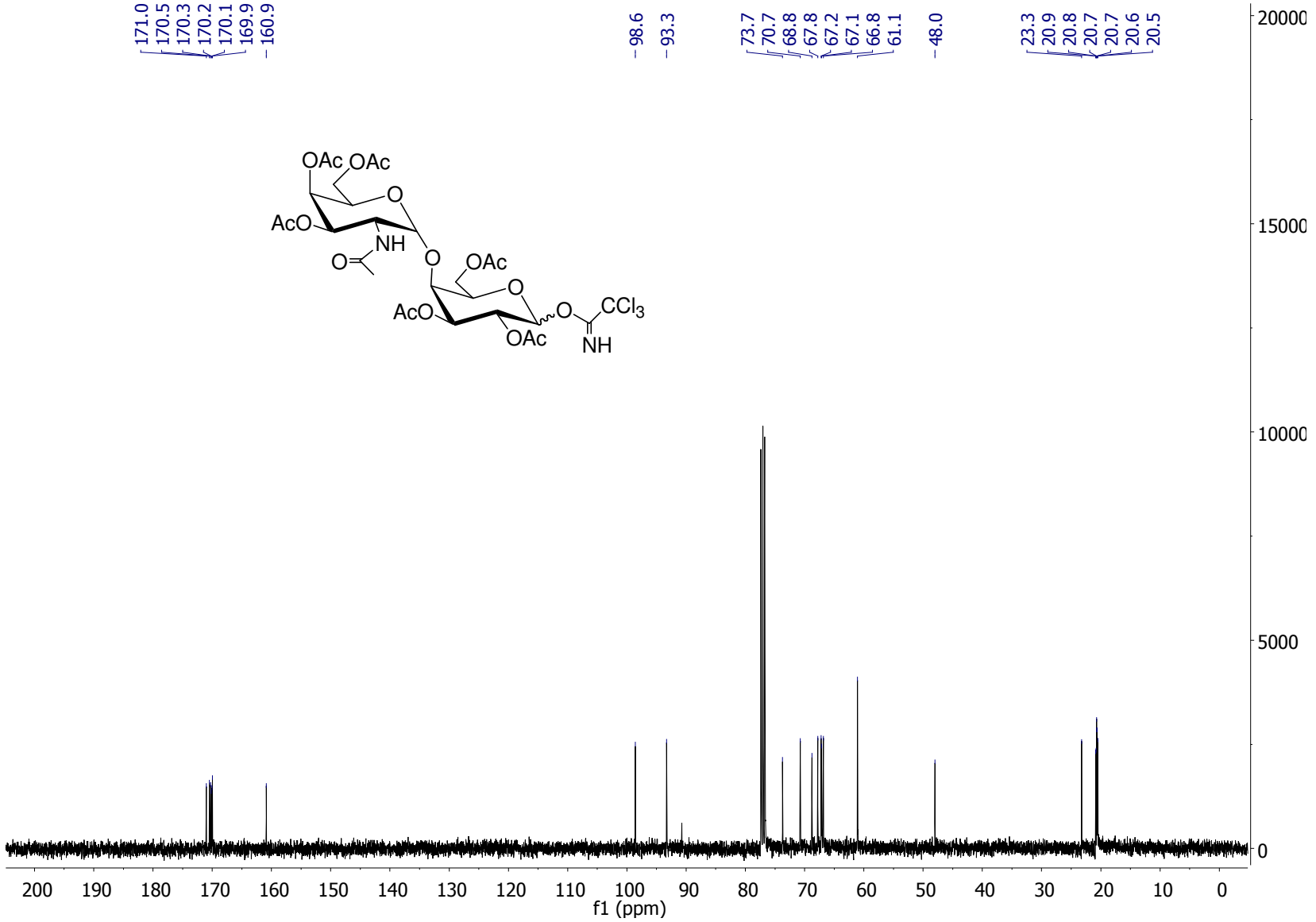
^{1}HNMR of Compound **34.**

^{1}HNMR (400 MHz, $CDCl_3$)



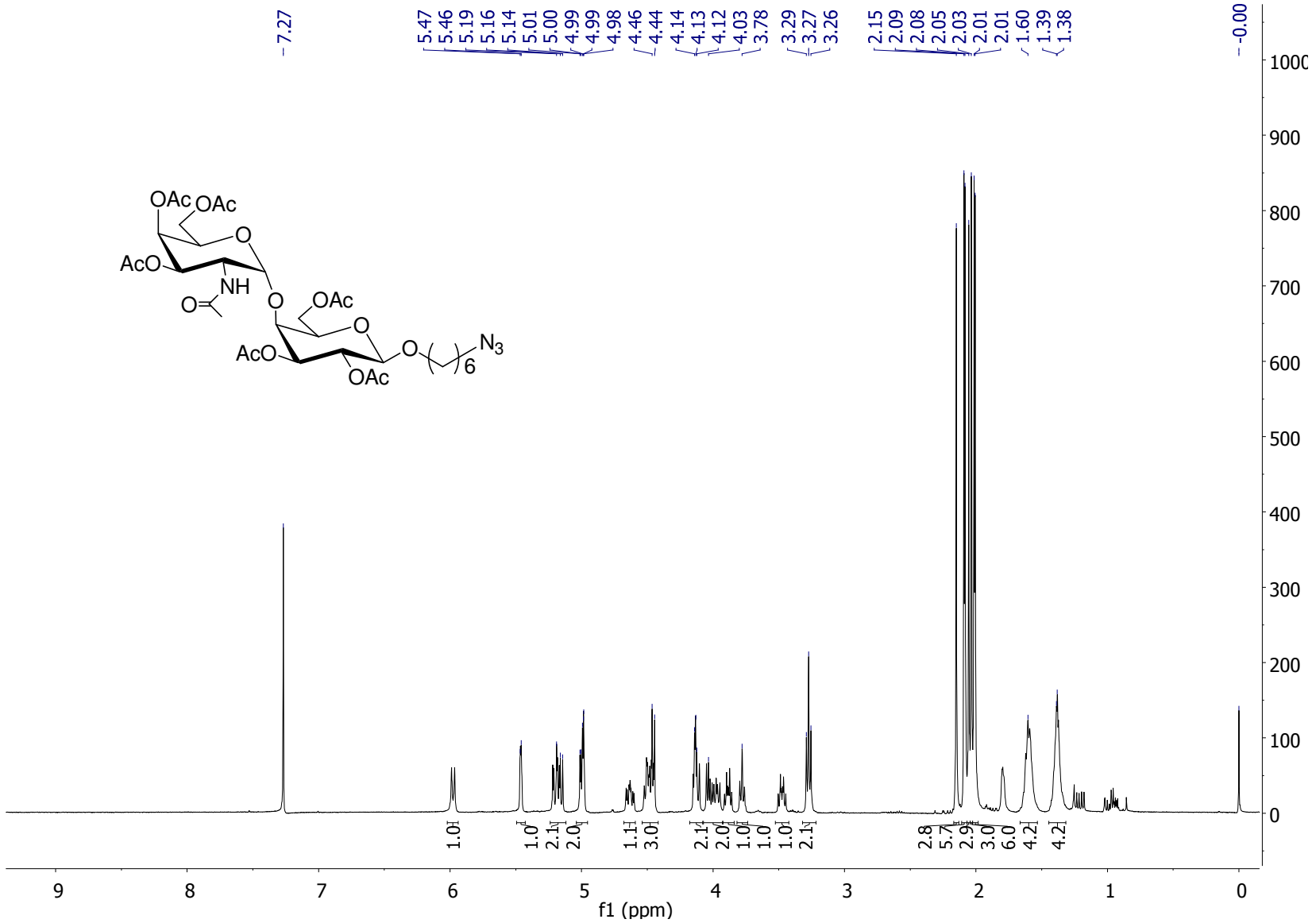
^{13}CNMR of Compound **34.**

^{13}CNMR (400 MHz, $CDCl_3$)



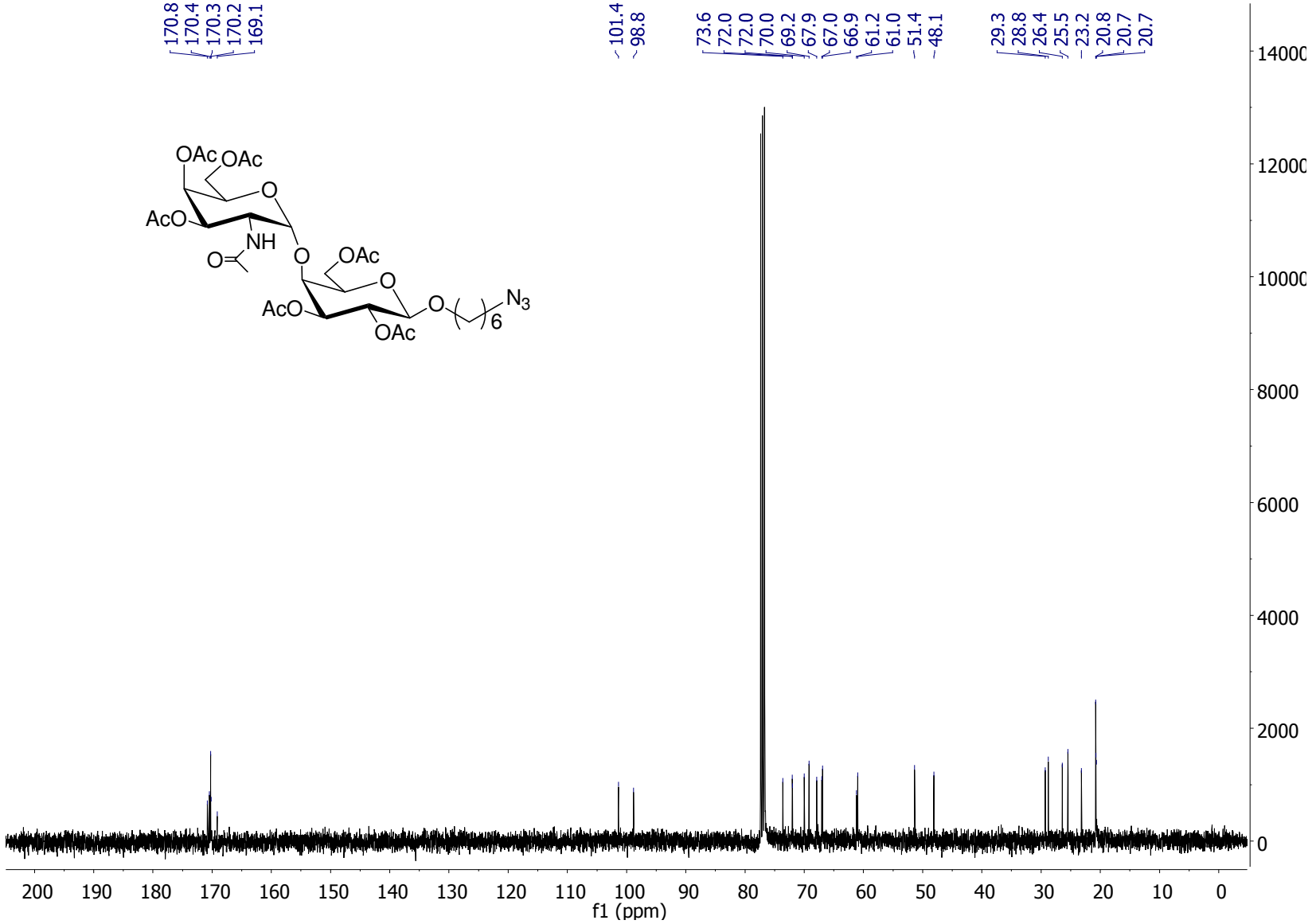
^{1}HNMR of Compound **35.**

^{1}HNMR (400 MHz, $CDCl_3$)



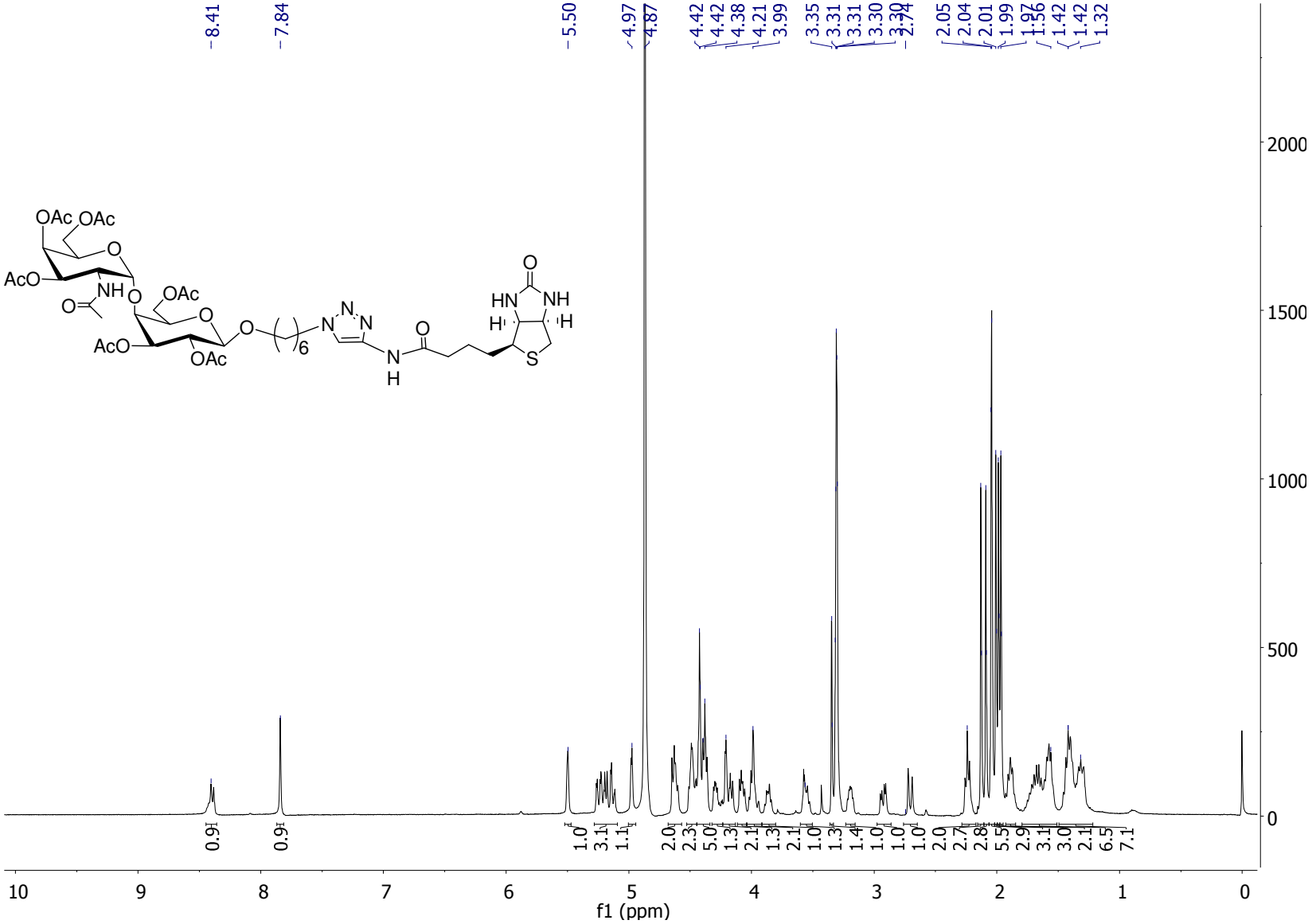
^{13}CNMR of Compound **35.**

^{13}CNMR (400 MHz, $CDCl_3$)



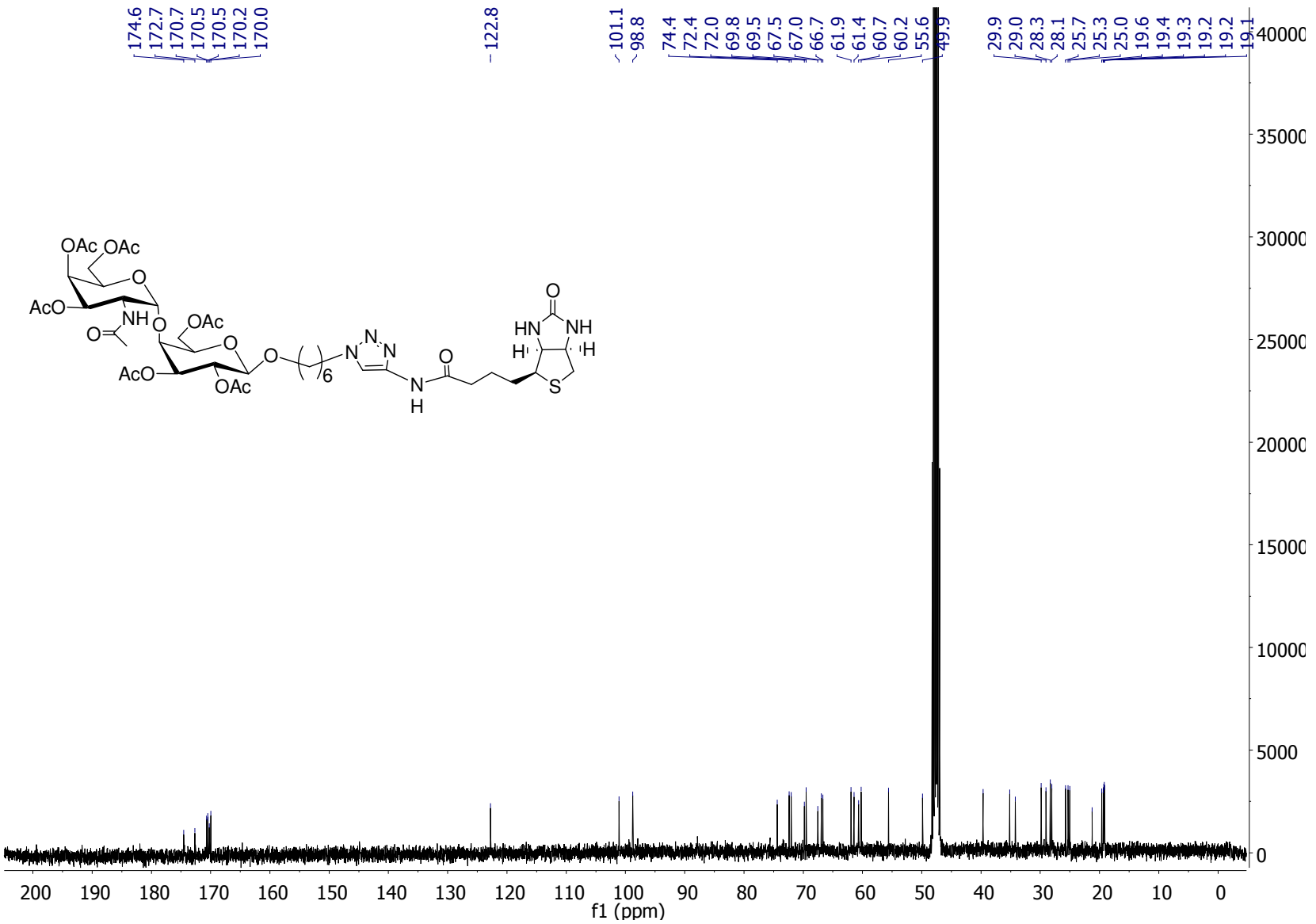
^{1}HNMR of Compound **36.**

^{1}HNMR (400 MHz, MeOH-d_4)



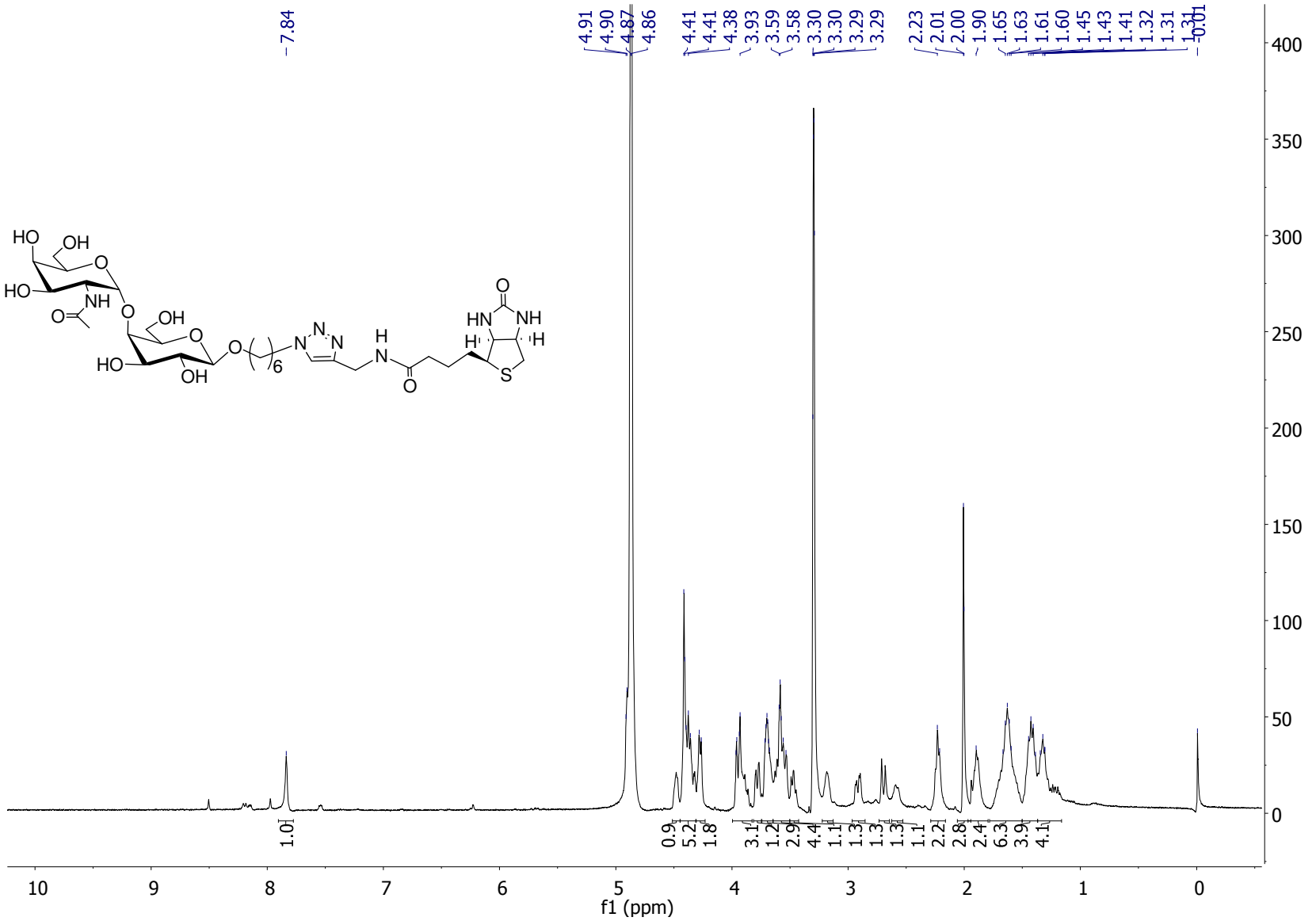
^{13}CNMR of Compound **36.**

^{13}CNMR (400 MHz, $CDCl_3$)



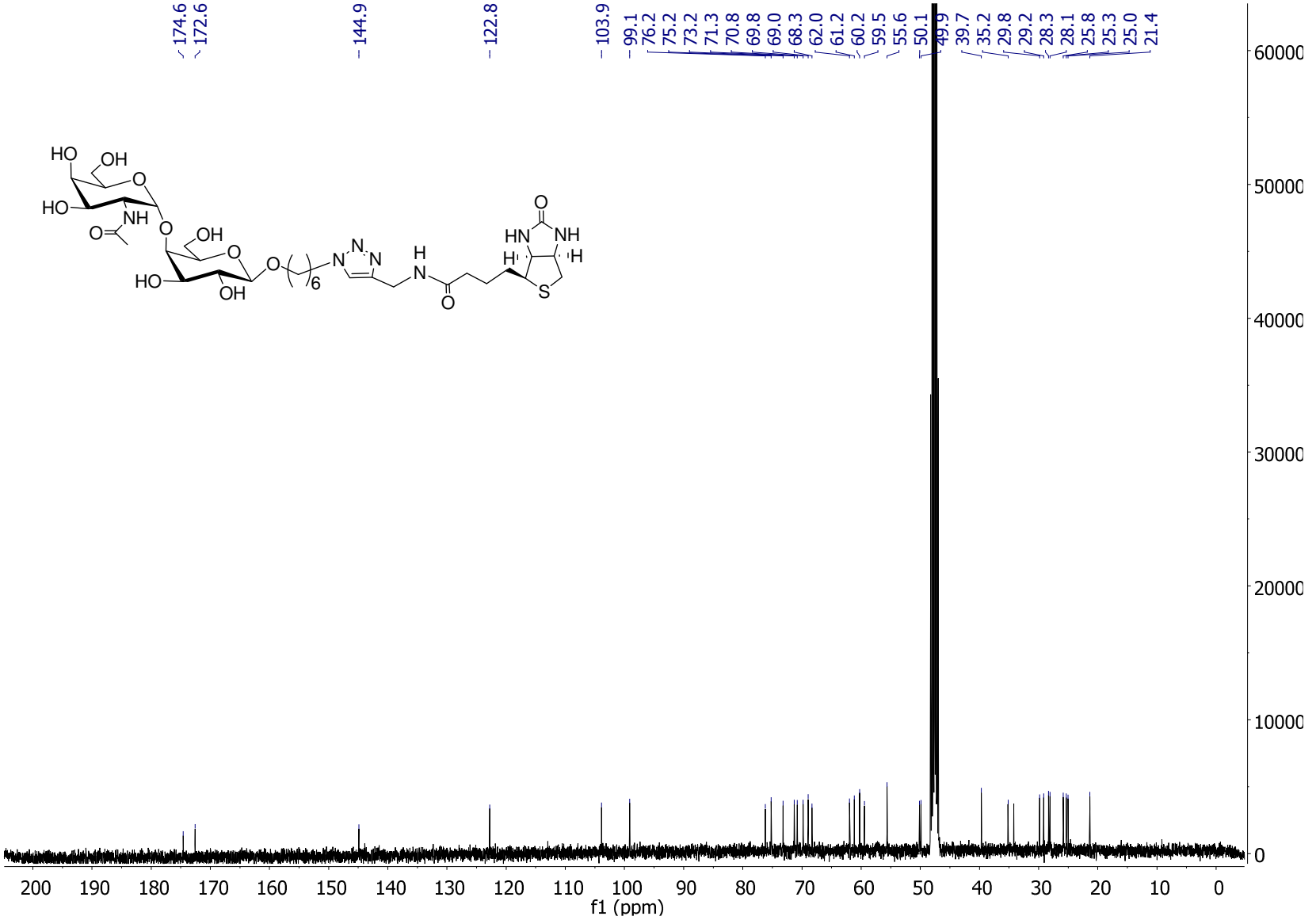
^{1}HNMR of Compound **3a.**

^{1}HNMR (400 MHz, MeOH-d_4)



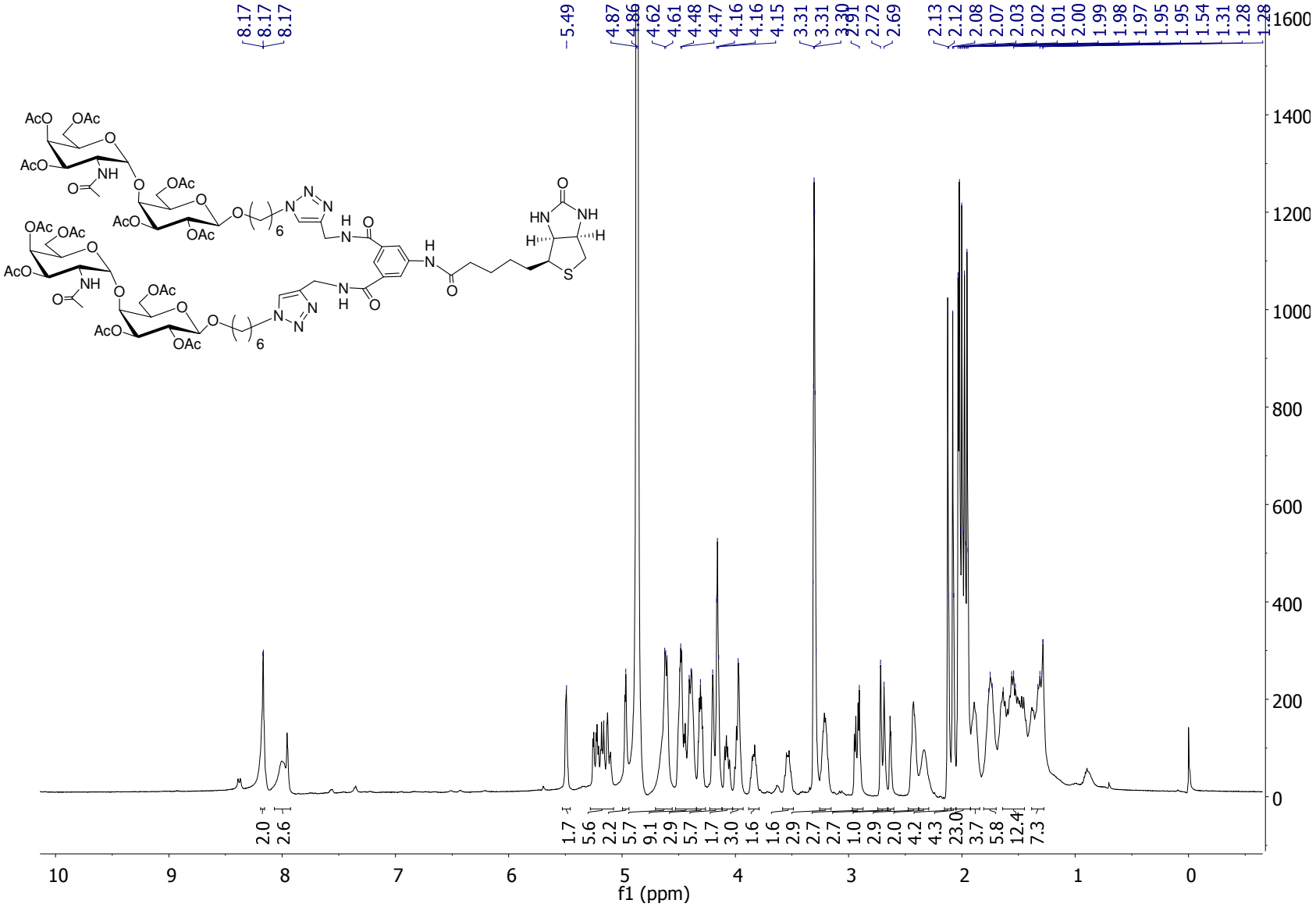
^{13}CNMR of Compound **3a.**

^{13}CNMR (400 MHz, MeOH-d_4)



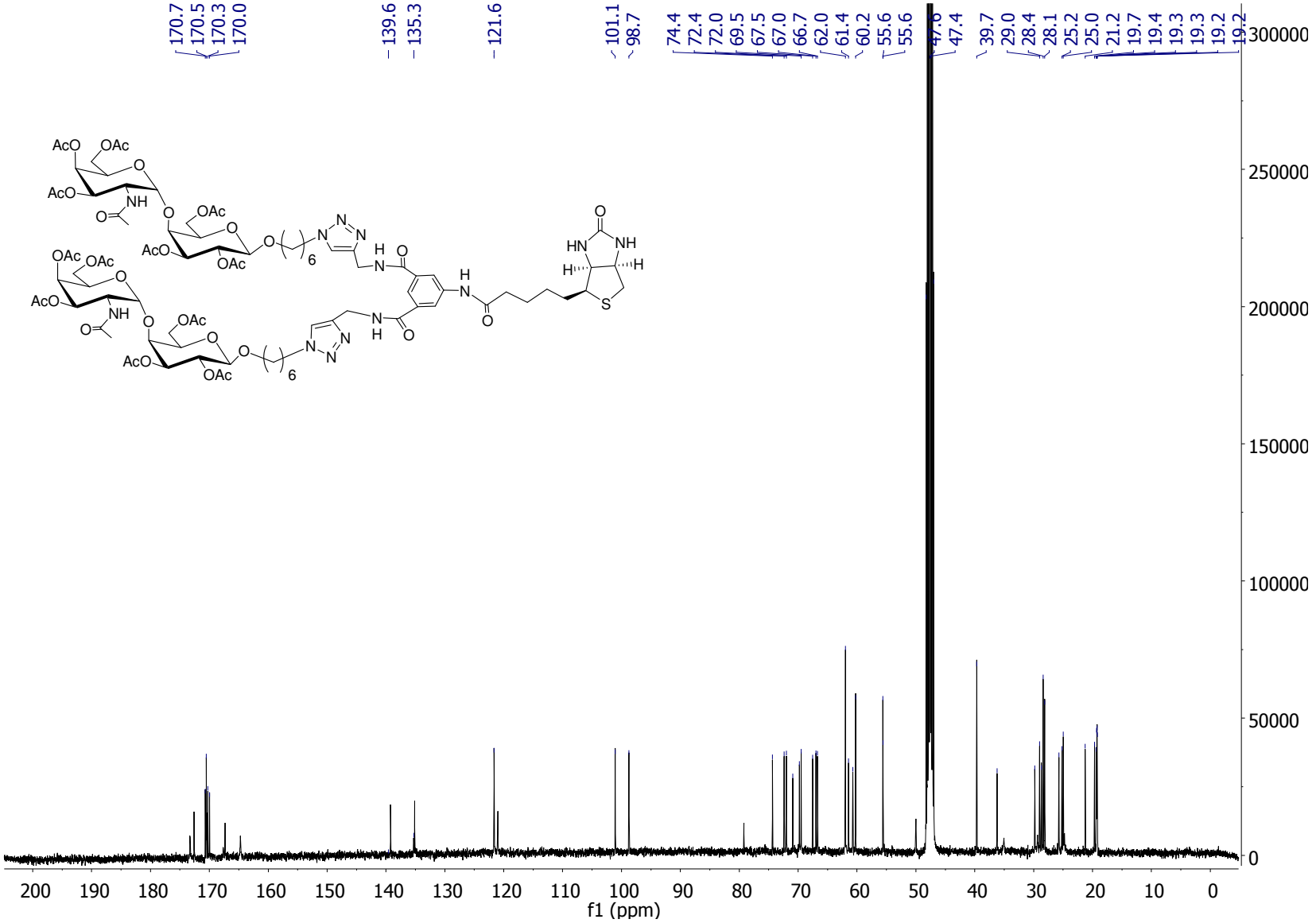
^{1}HNMR of Compound **37.**

^{1}HNMR (400 MHz, MeOH-d_4)



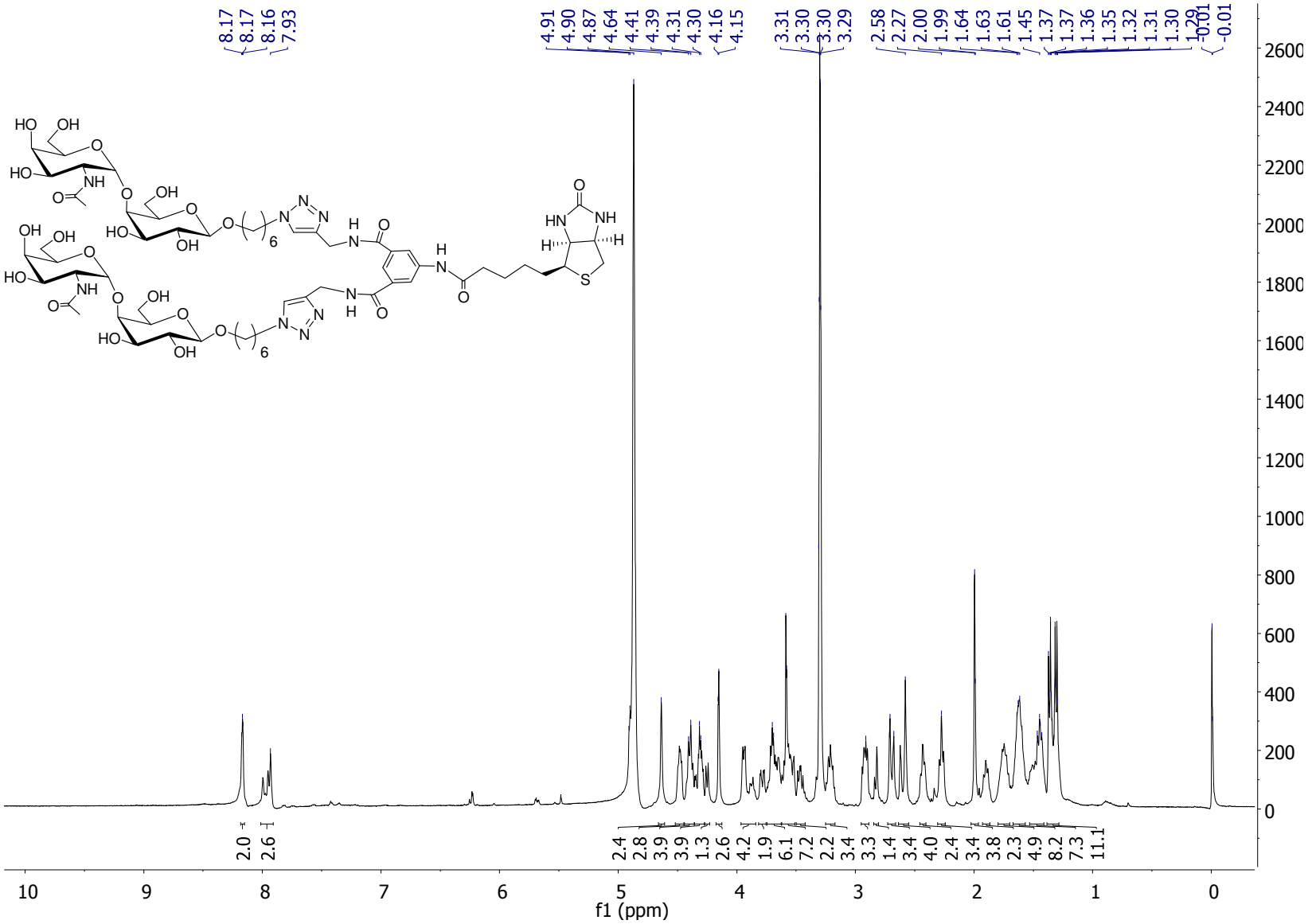
^{13}CNMR of Compound **37.**

^{13}CNMR (400 MHz, MeOH-d_4)



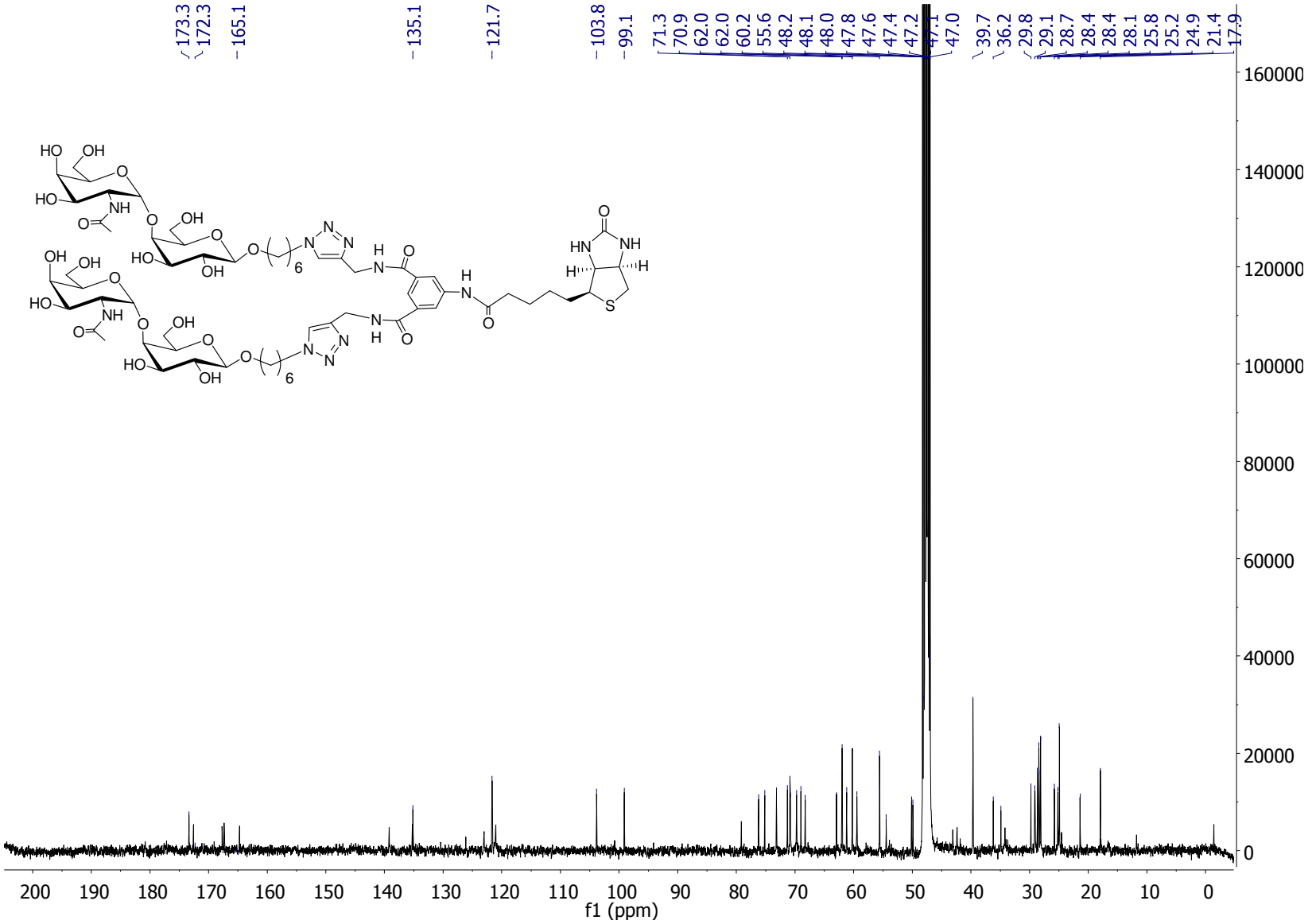
^{1}HNMR of Compound **3b.**

^{1}HNMR (400 MHz, MeOH-d_4)



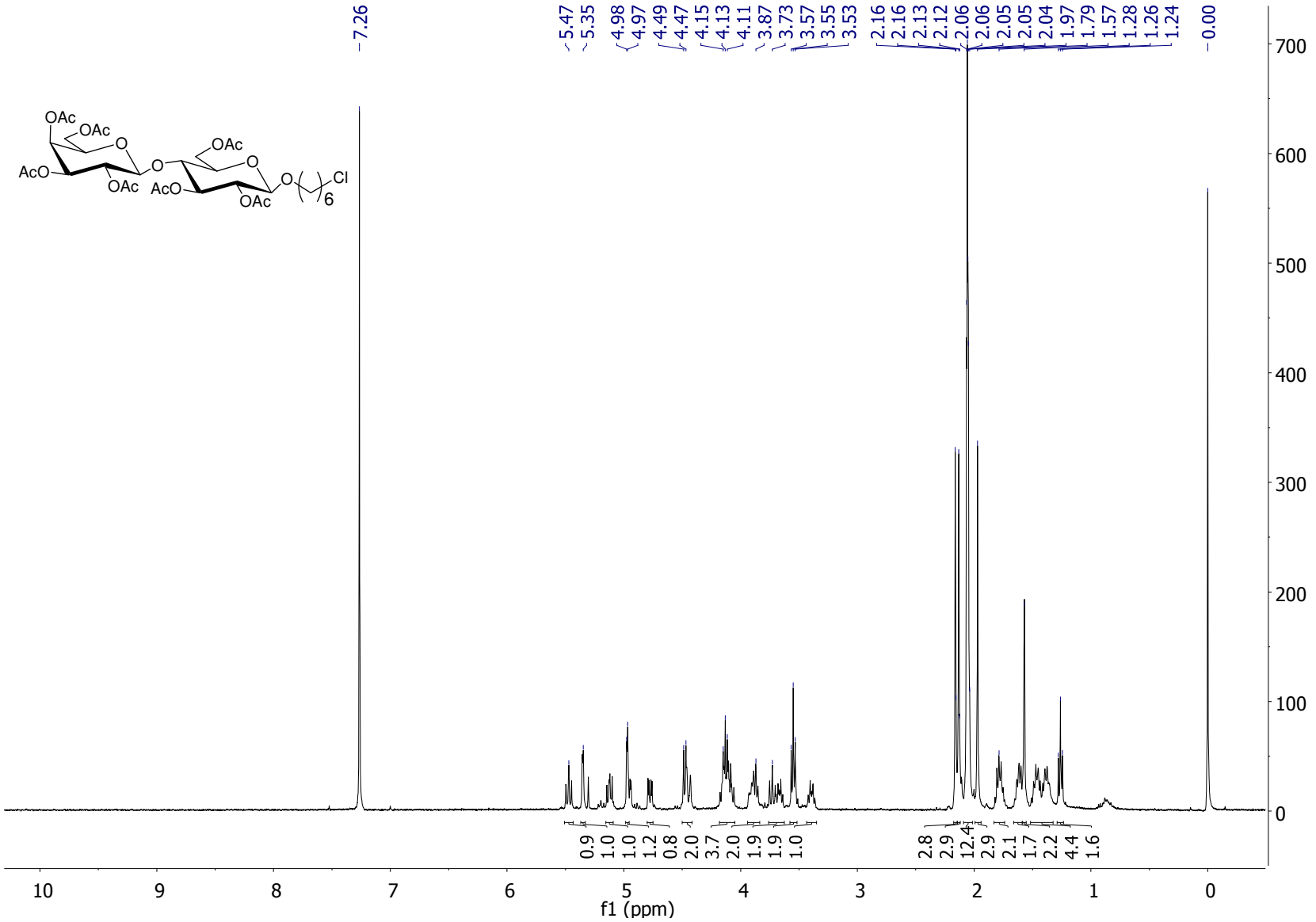
^{13}CNMR of Compound **3b.**

^{13}CNMR (400 MHz, MeOH-d_4)



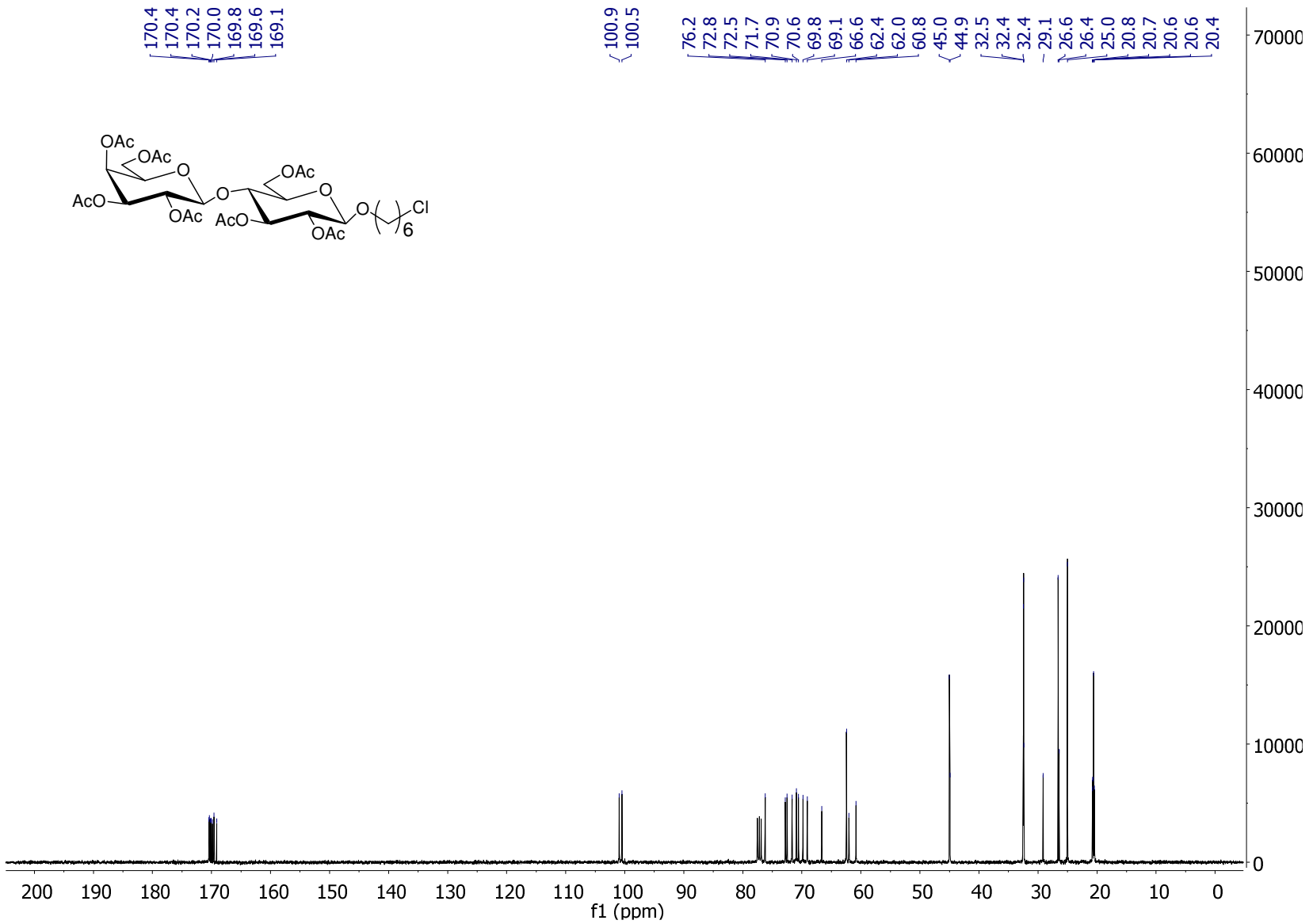
^{1}HNMR of Compound **39.**

^{1}HNMR (400 MHz, $CDCl_3$)



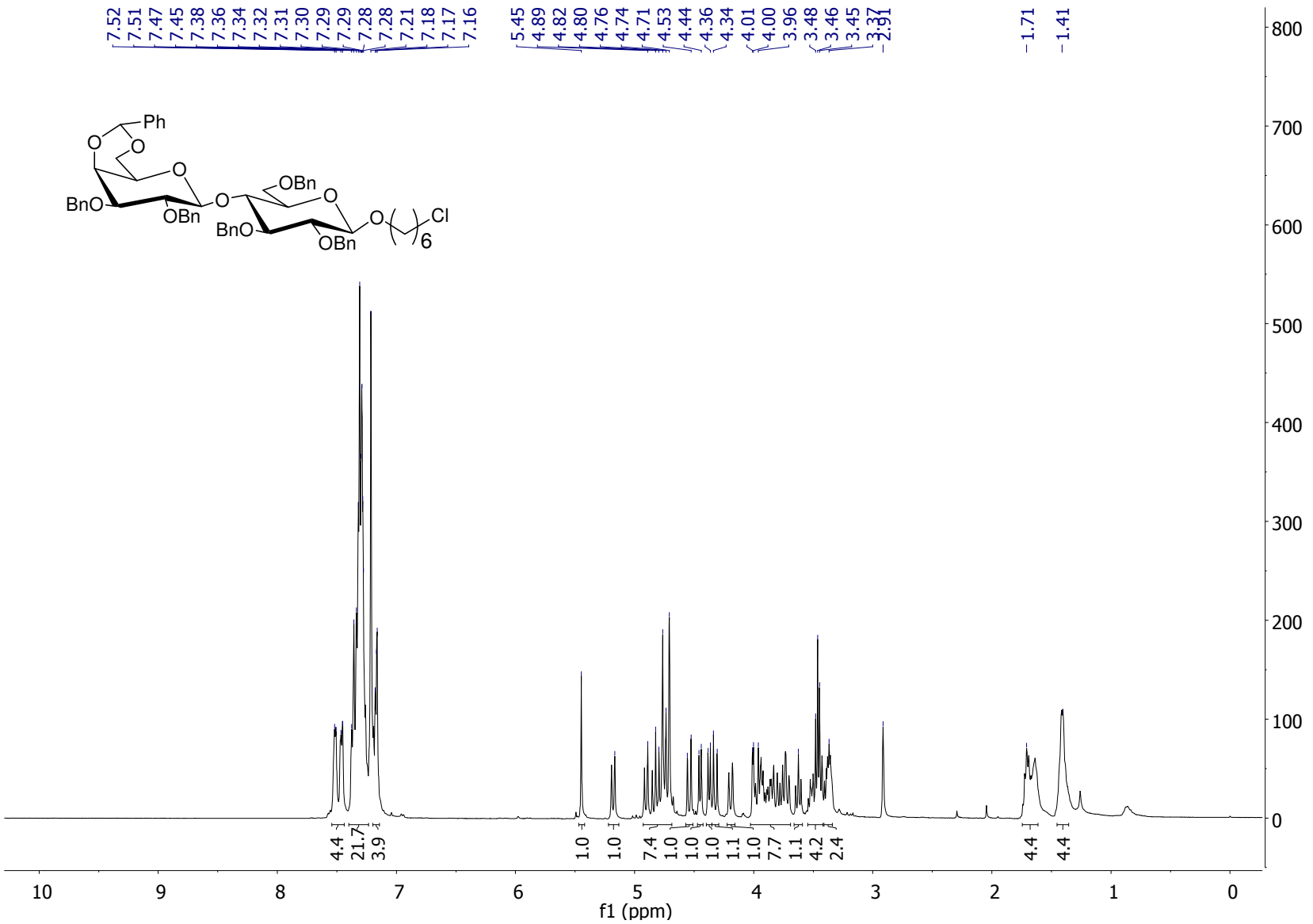
^{13}CNMR of Compound **39.**

^{13}CNMR (400 MHz, $CDCl_3$)



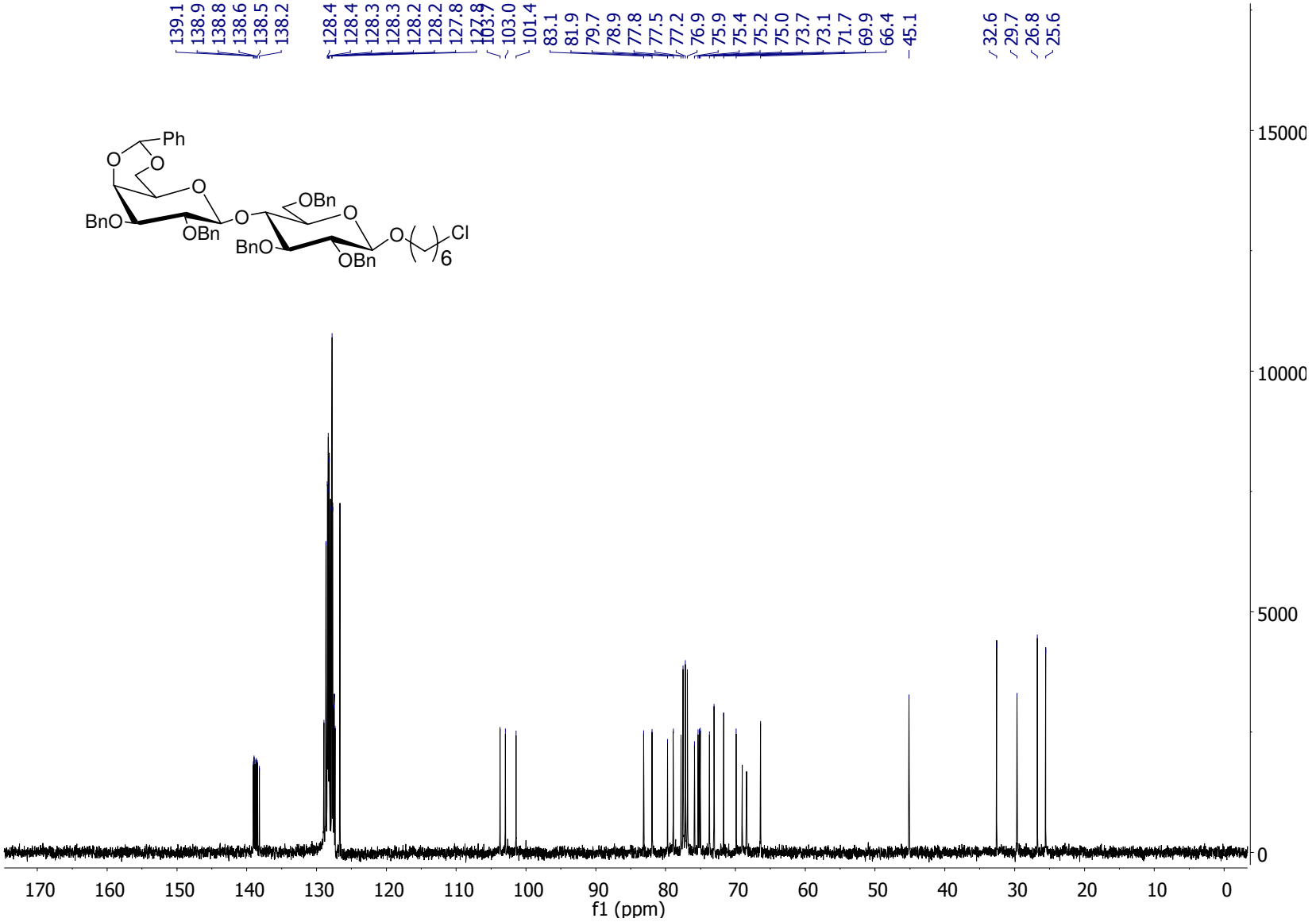
^{1}HNMR of Compound **40.**

^{1}HNMR (400 MHz, $CDCl_3$)



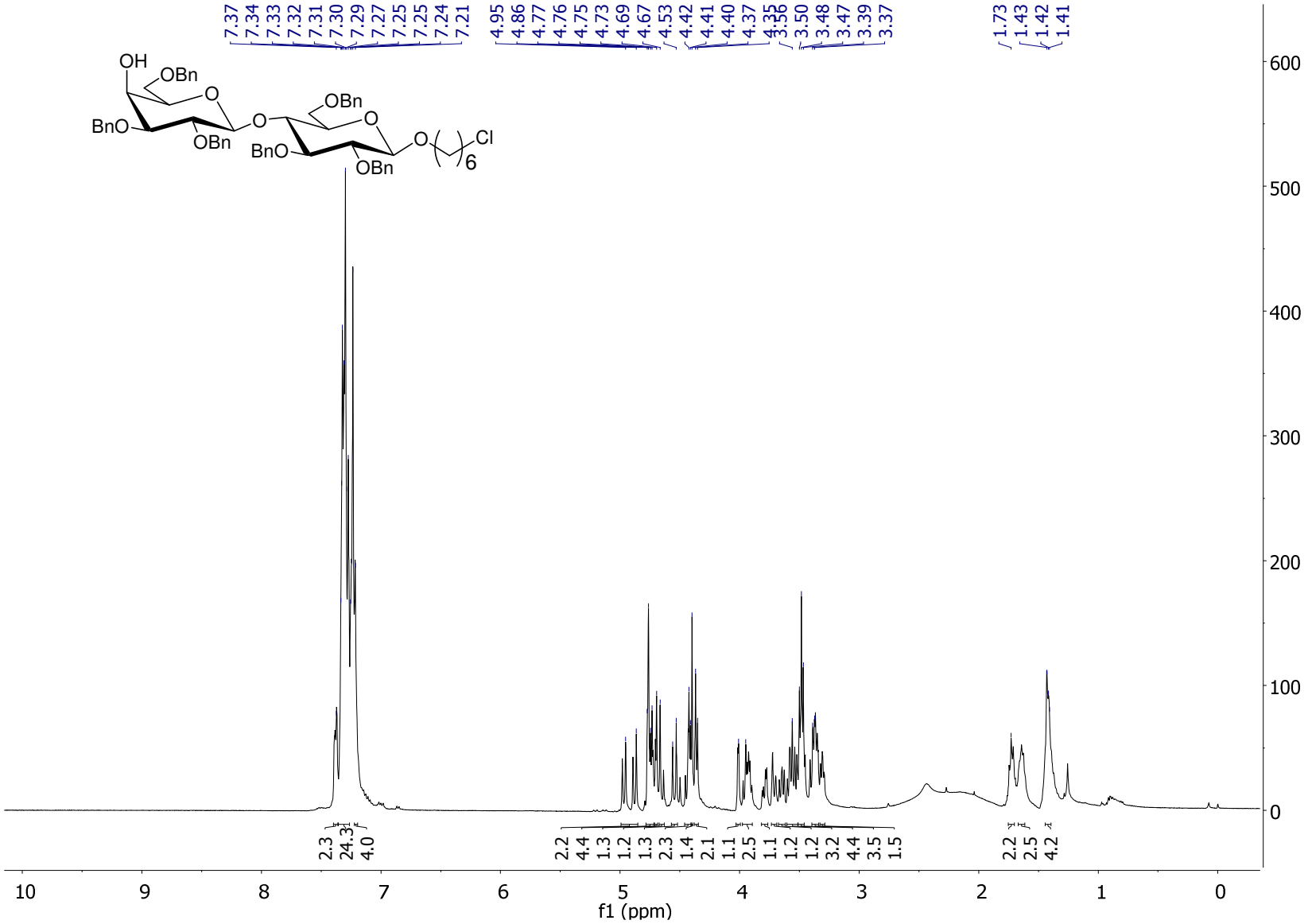
^{13}CNMR of Compound **40.**

^{13}CNMR (400 MHz, $CDCl_3$)



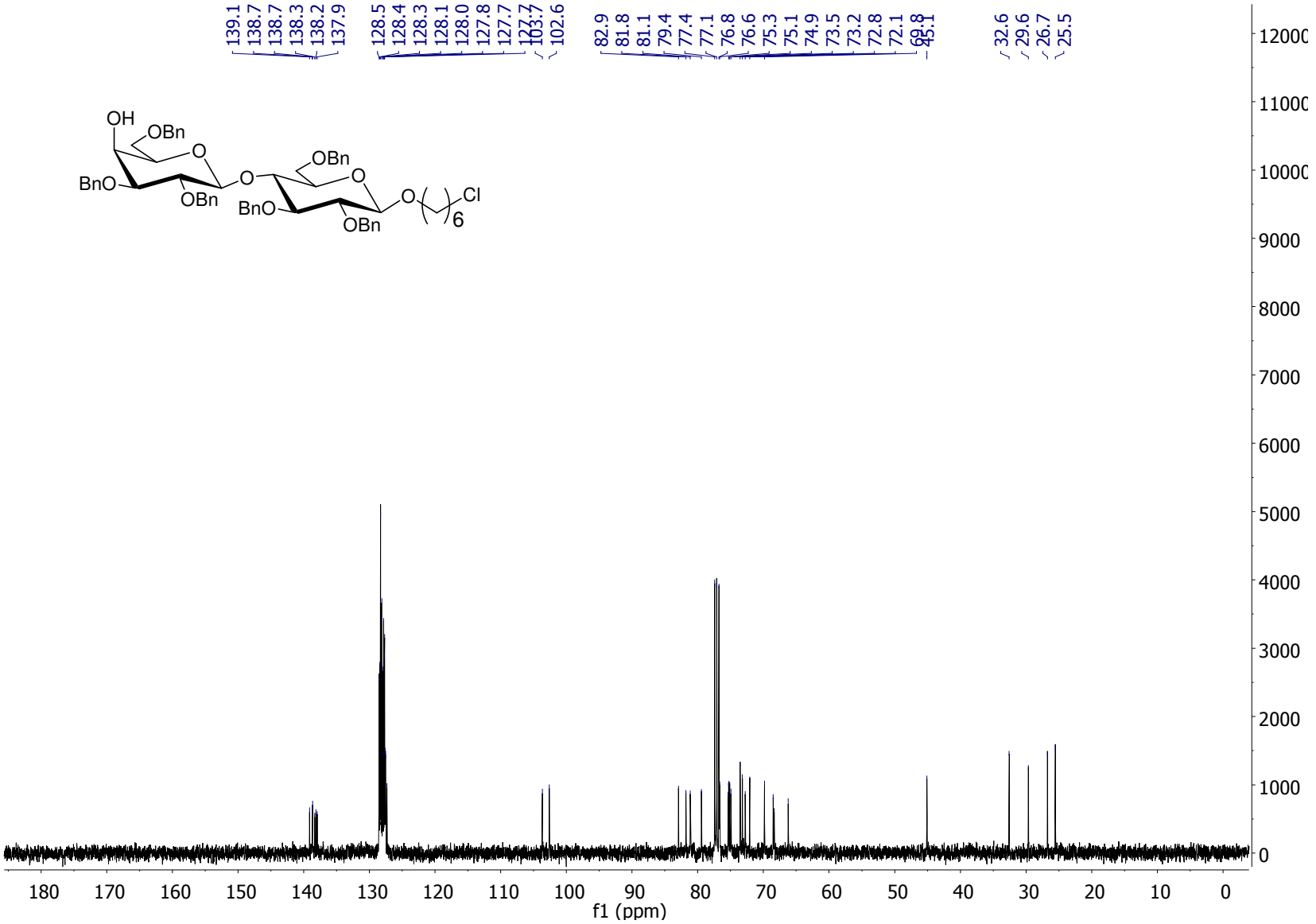
^{1}HNMR of Compound **11**

^{1}HNMR (400 MHz, $CDCl_3$)



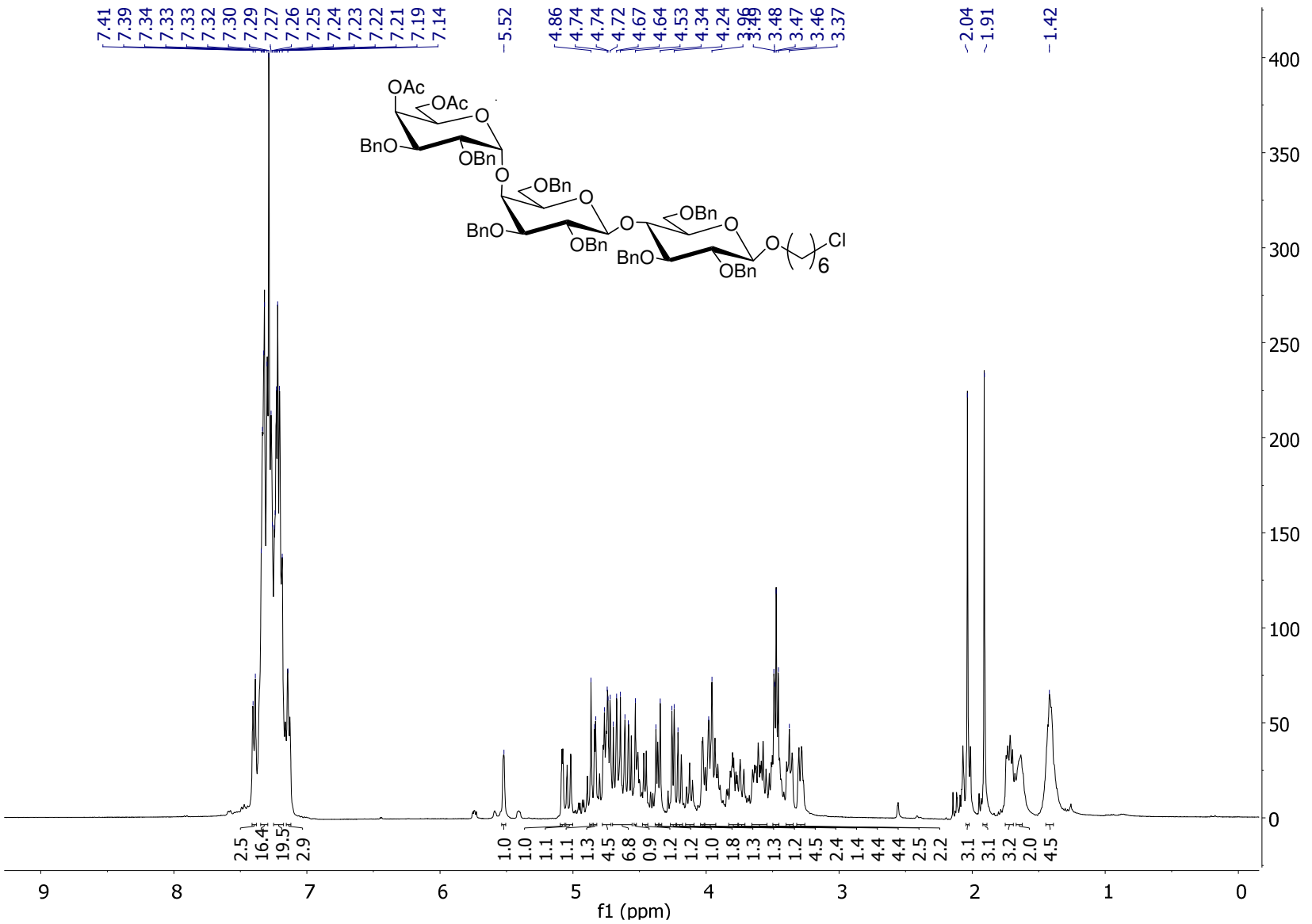
^{13}CNMR of Compound **11.**

^{13}CNMR (400 MHz, $CDCl_3$)



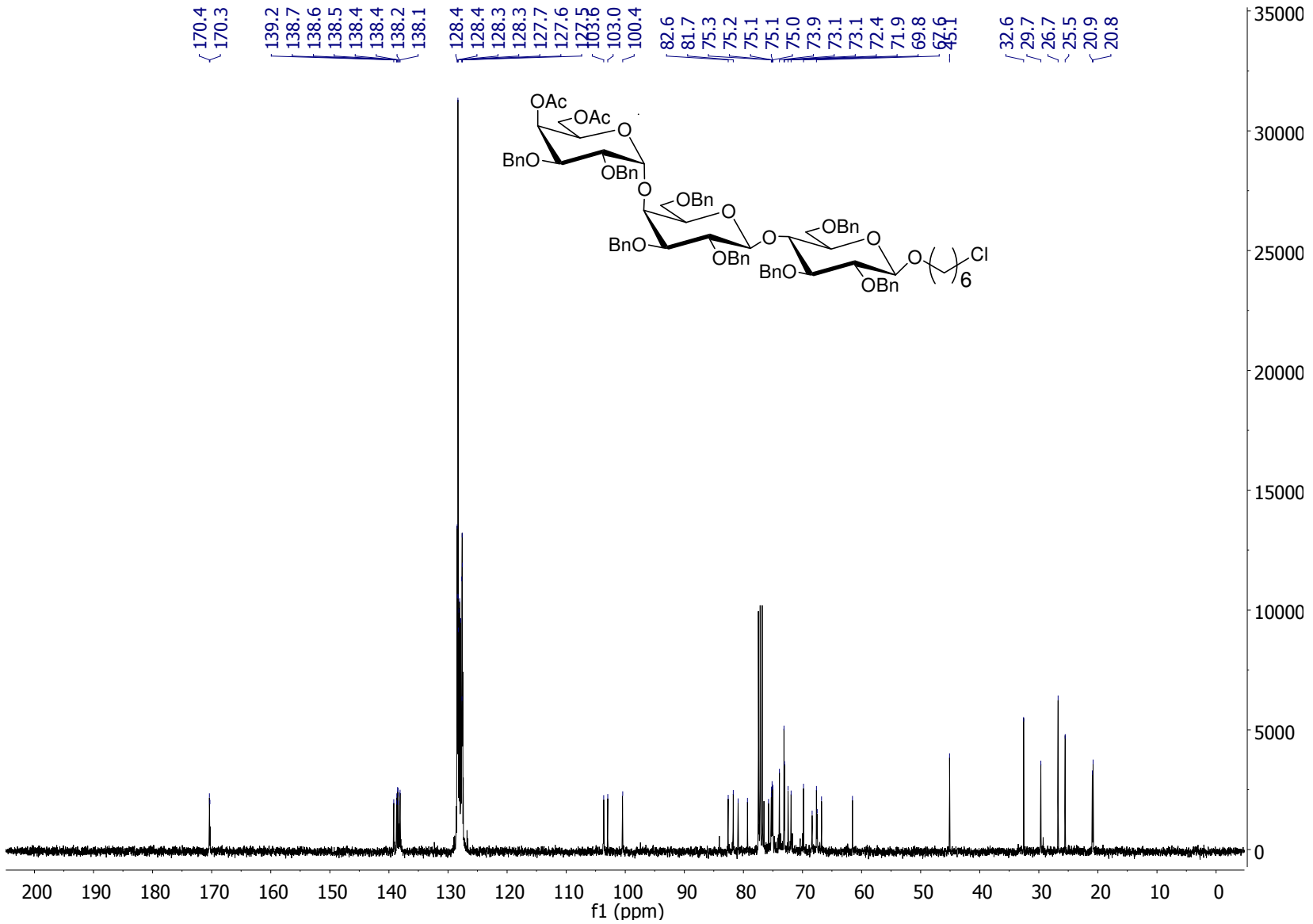
^{1}HNMR of Compound **41.**

^{1}HNMR (400 MHz, $CDCl_3$)



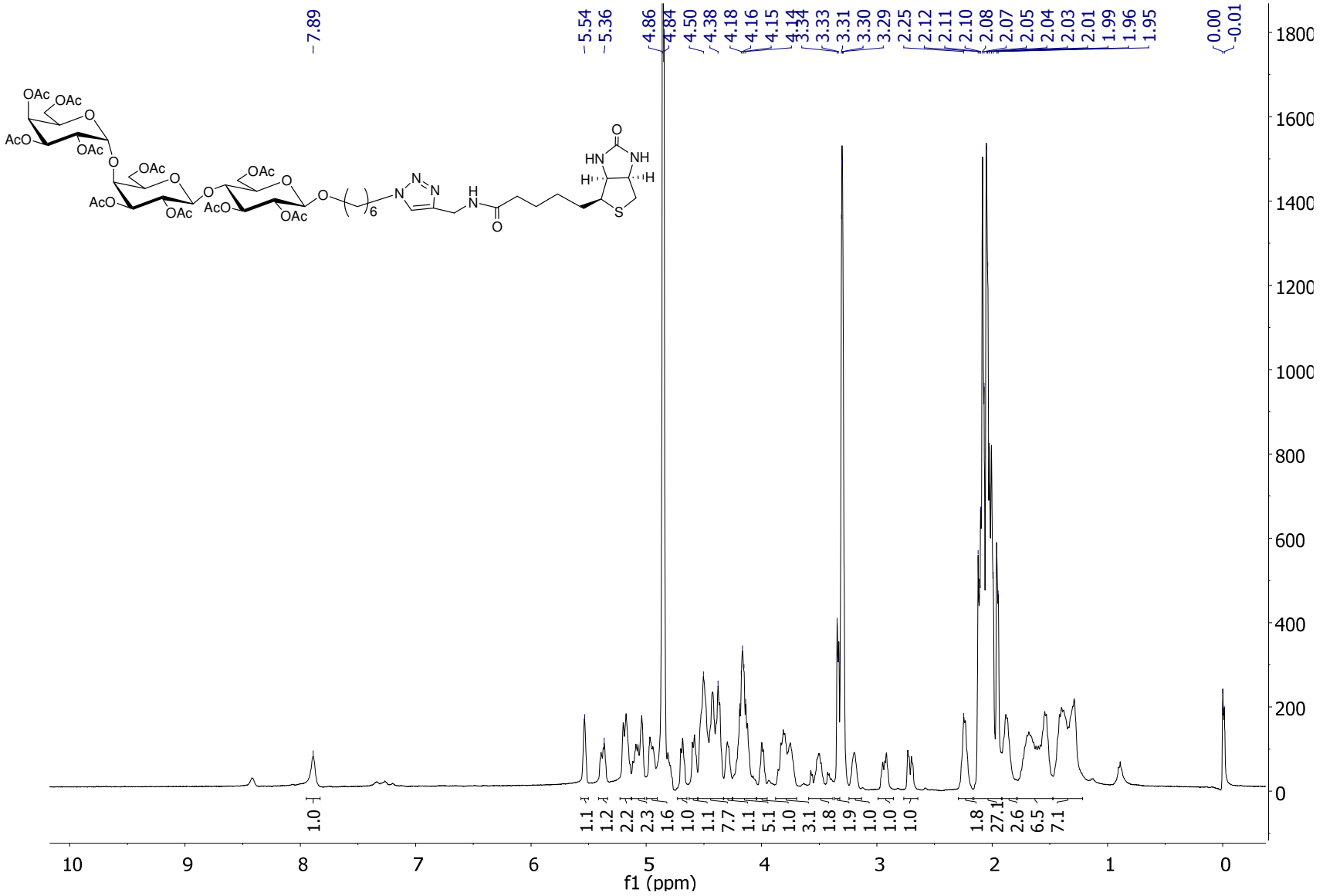
^{13}CNMR of Compound **41.**

^{13}CNMR (400 MHz, $CDCl_3$)



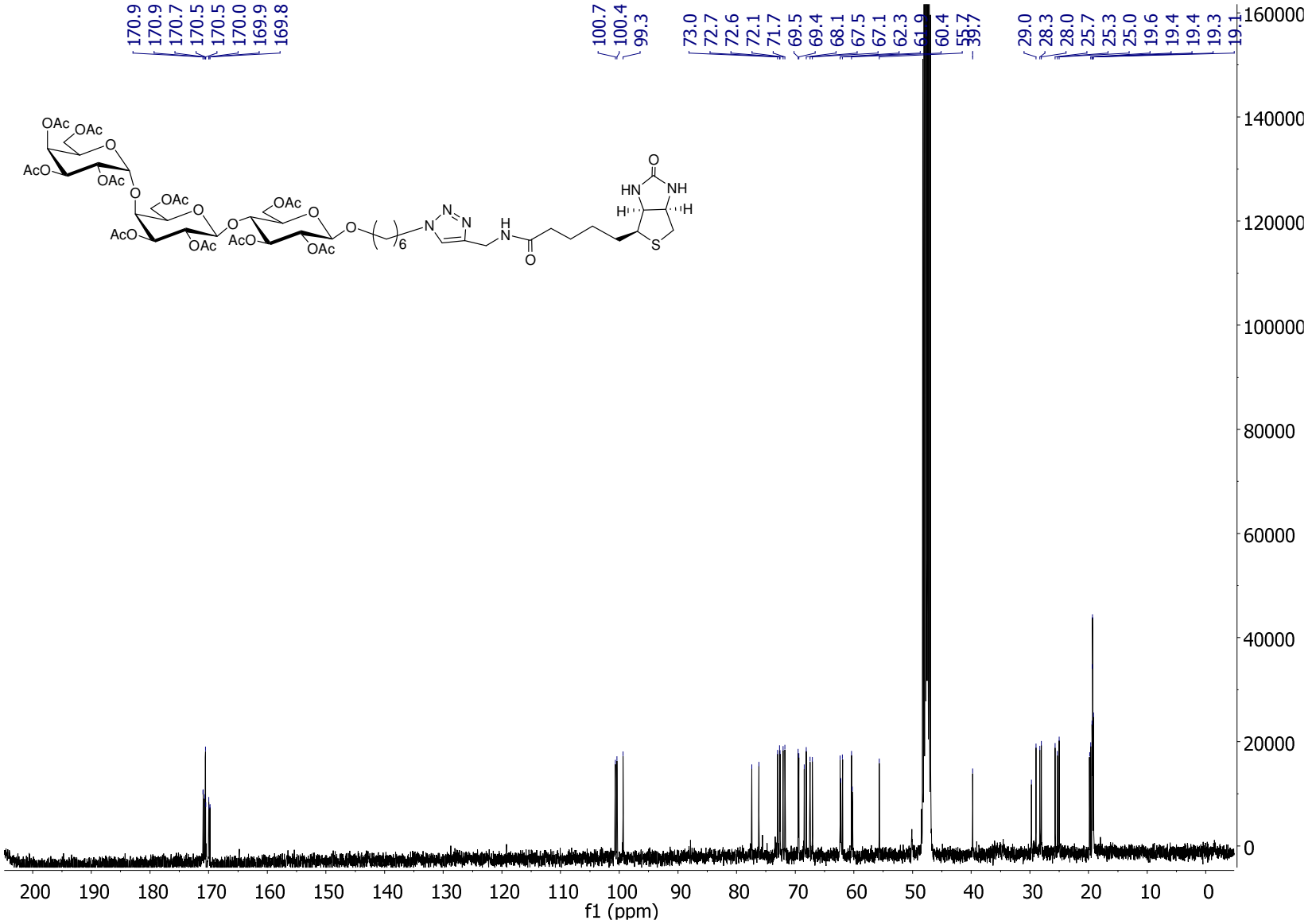
^{1}HNMR of Compound **43.**

^{1}HNMR (400 MHz, MeOH-d_4)



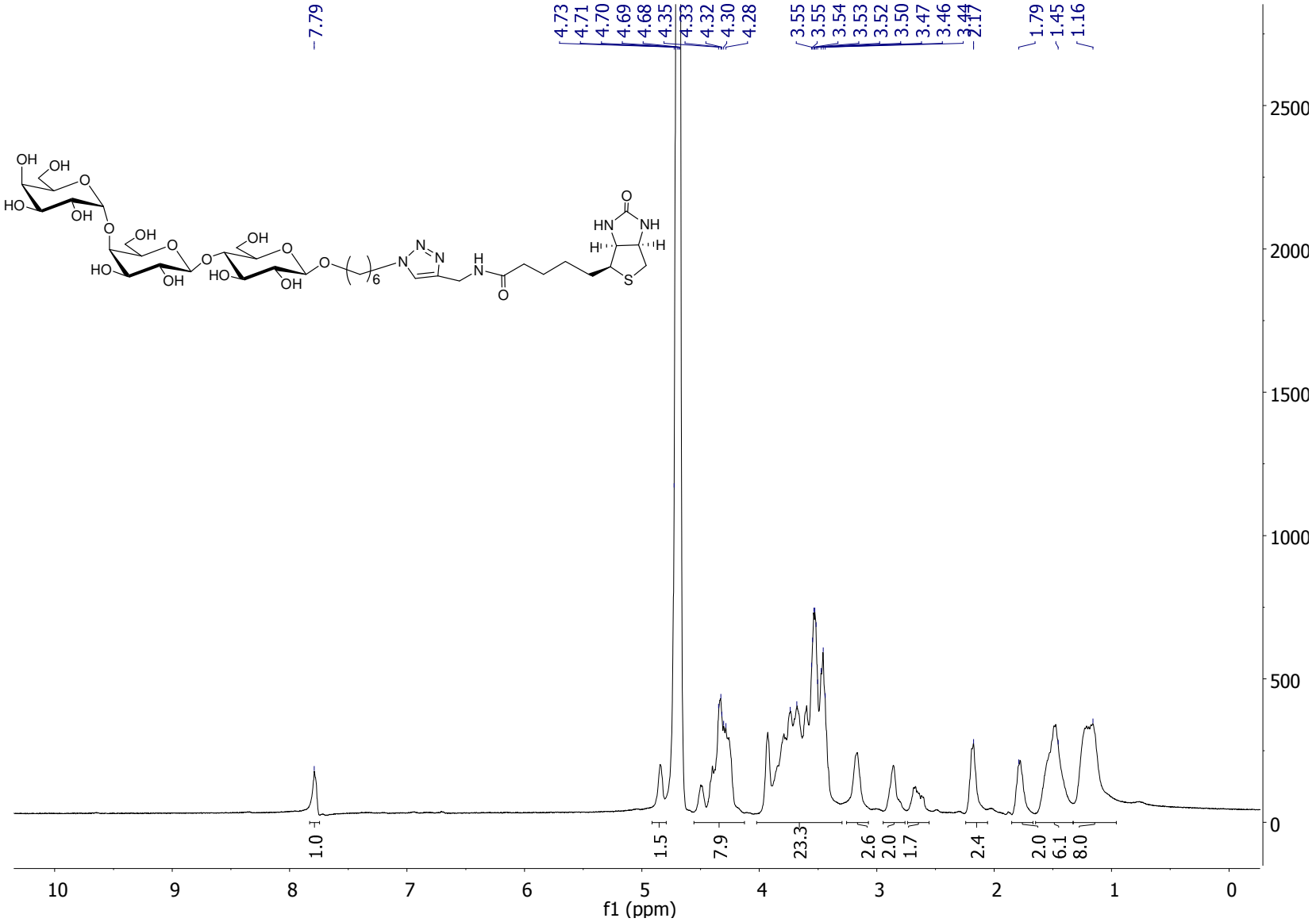
^{13}CNMR of Compound **43.**

^{13}CNMR (400 MHz, MeOH-d_4)



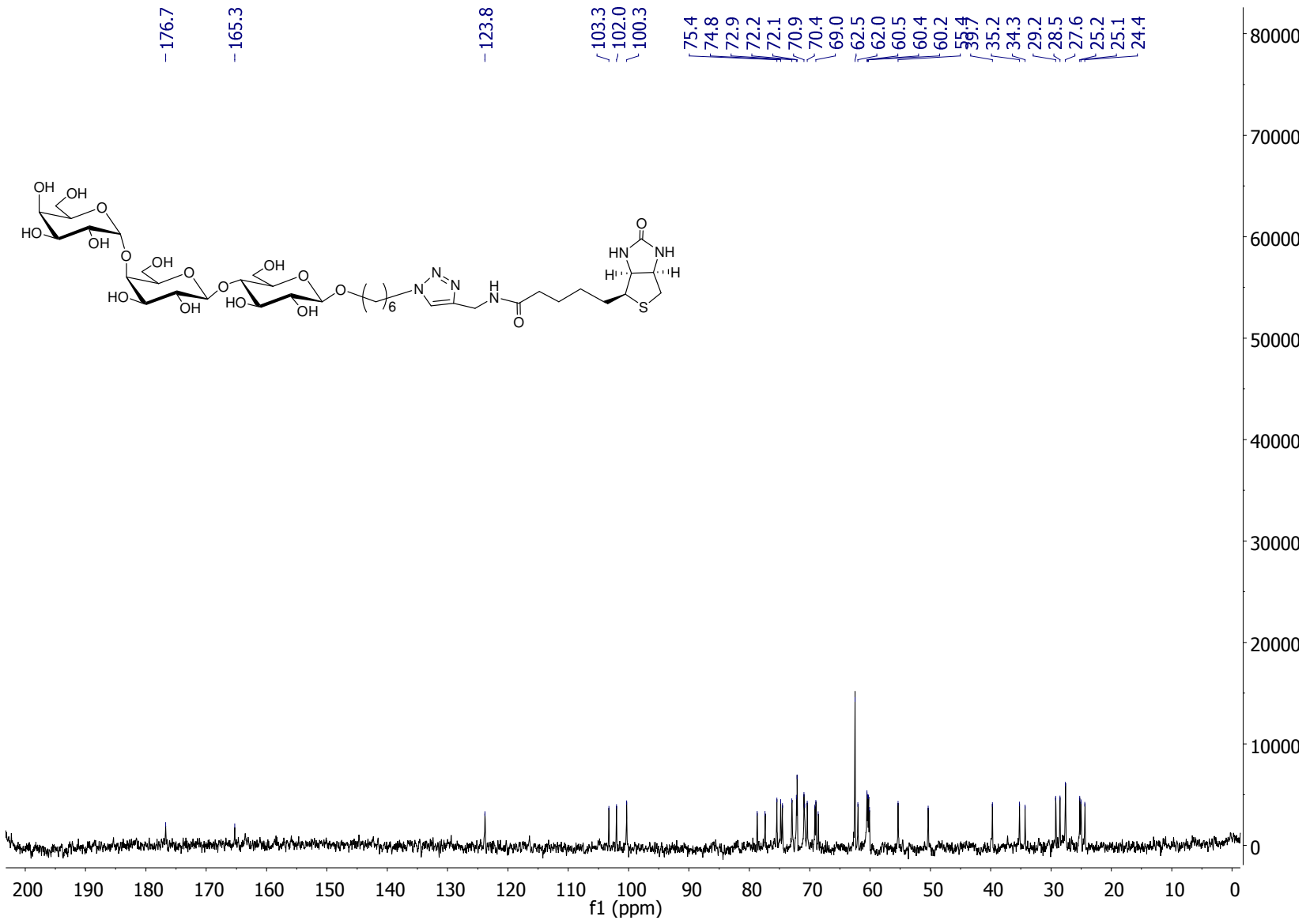
^{1}HNMR of Compound **4a.**

^{1}HNMR (400 MHz, D_2O)



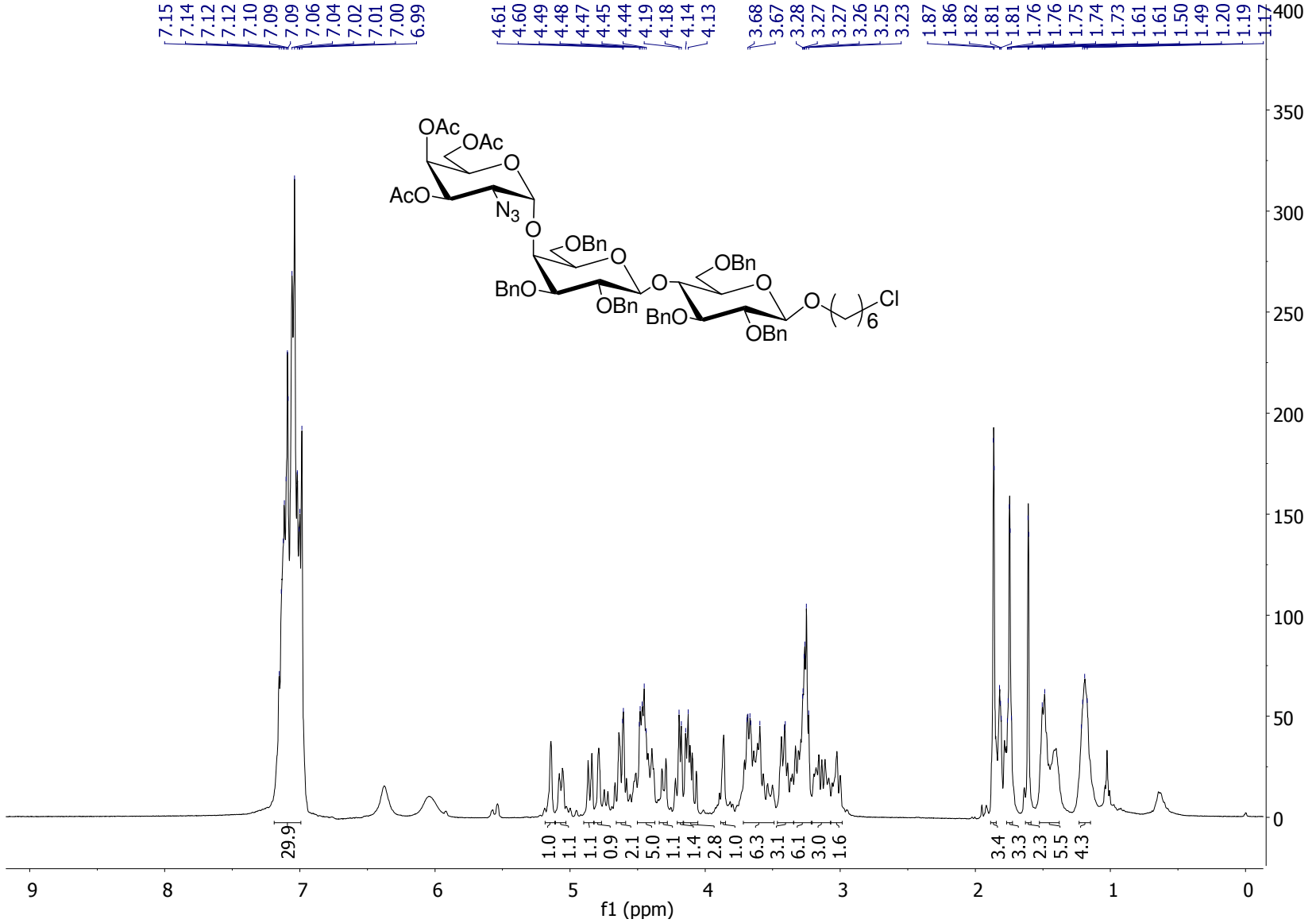
^{13}CNMR of Compound **4a.**

^{13}CNMR (400 MHz, D_2O)



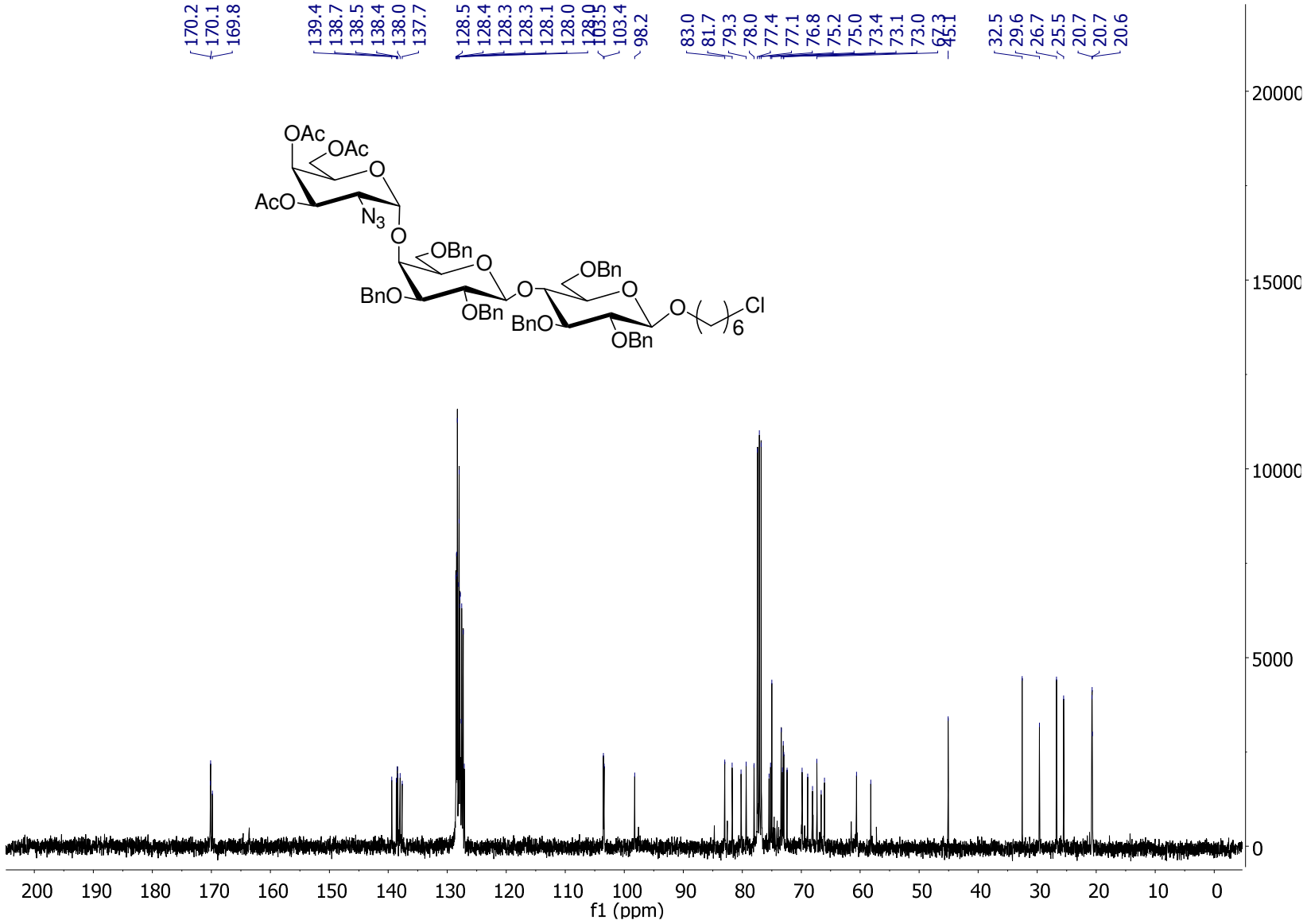
^{1}HNMR of Compound **45.**

^{1}HNMR (400 MHz, $CDCl_3$)



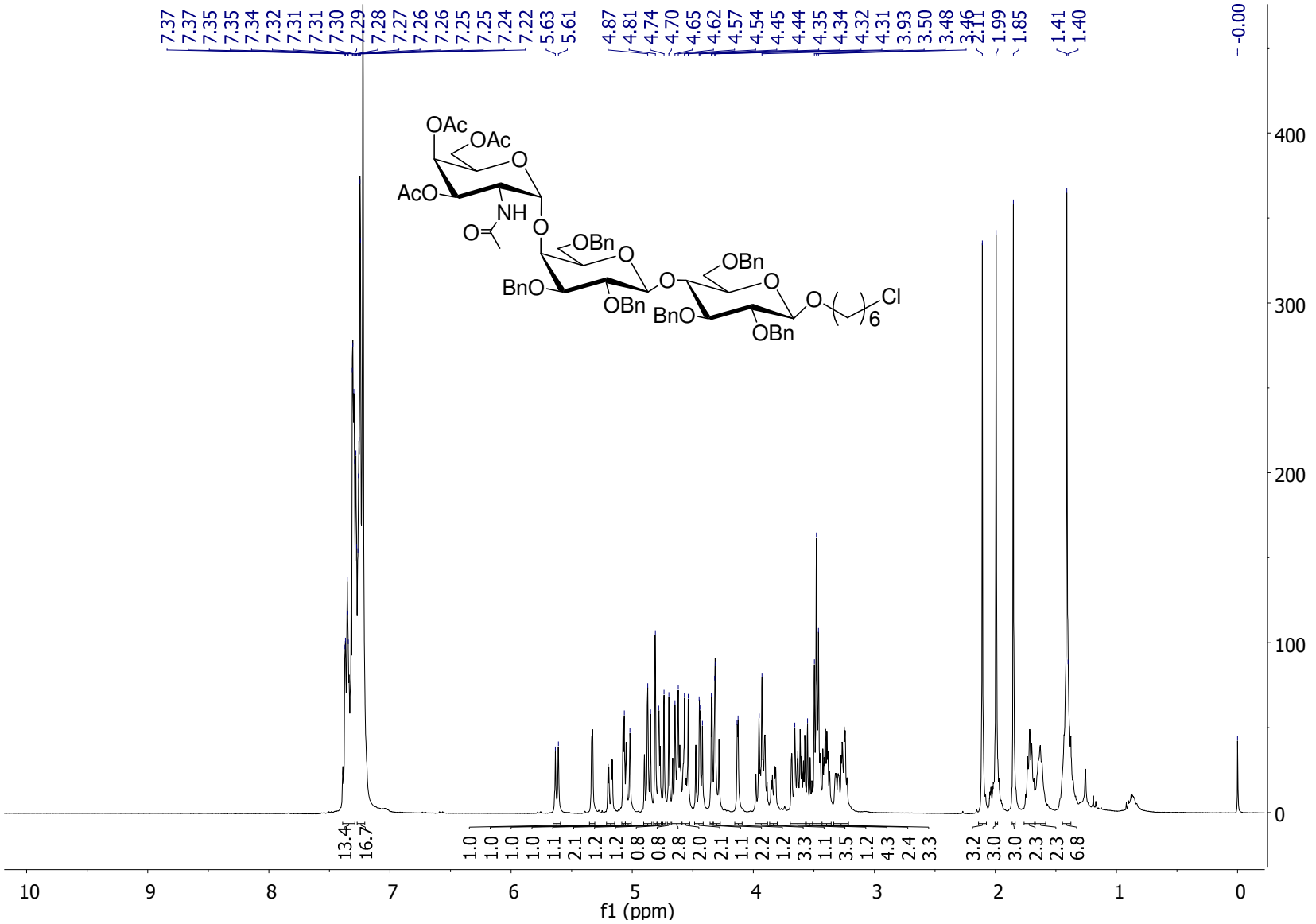
^{13}CNMR of Compound **45.**

^{13}CNMR (400 MHz, $CDCl_3$)



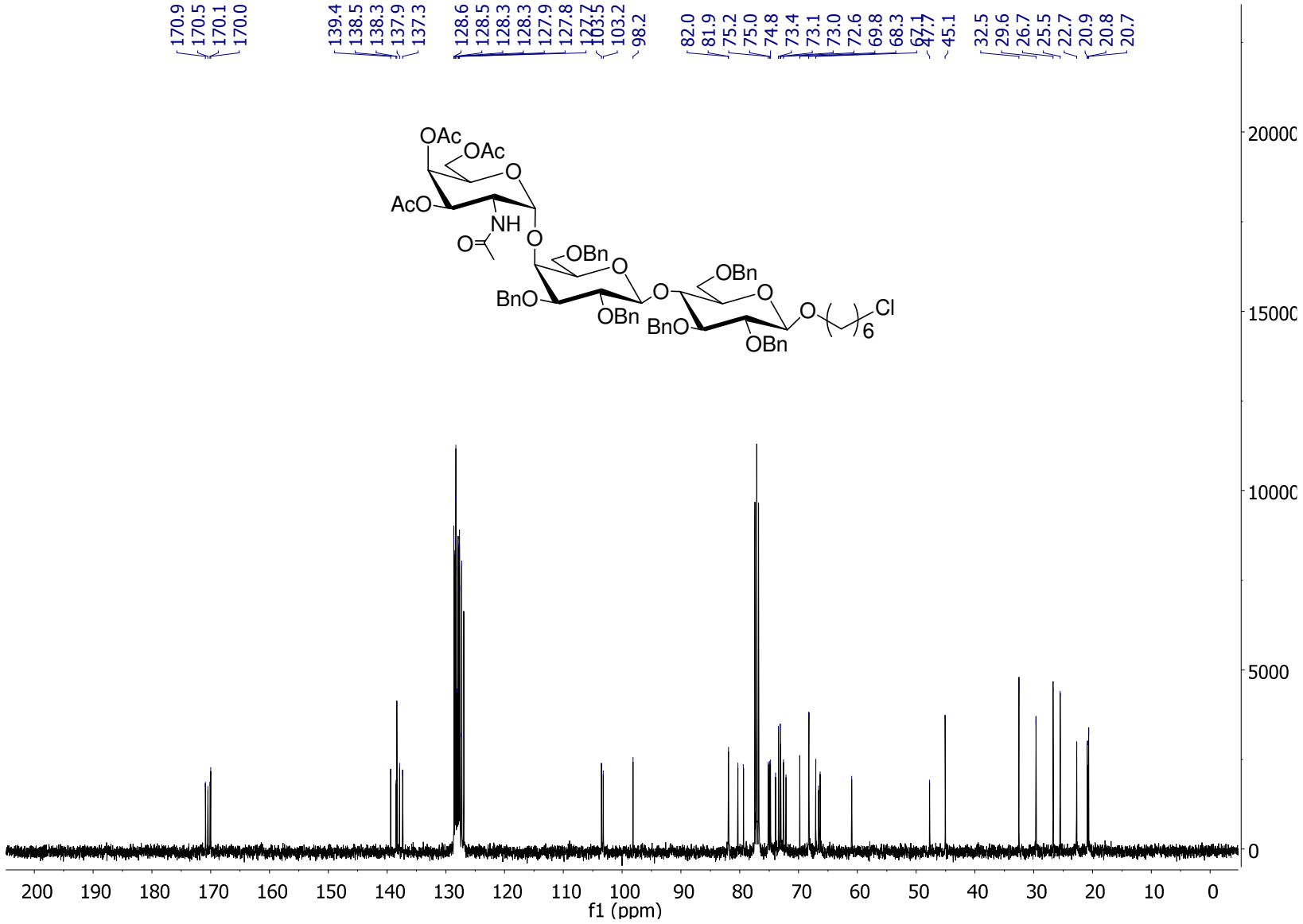
^{1}HNMR of Compound **46.**

^{1}HNMR (400 MHz, $CDCl_3$)



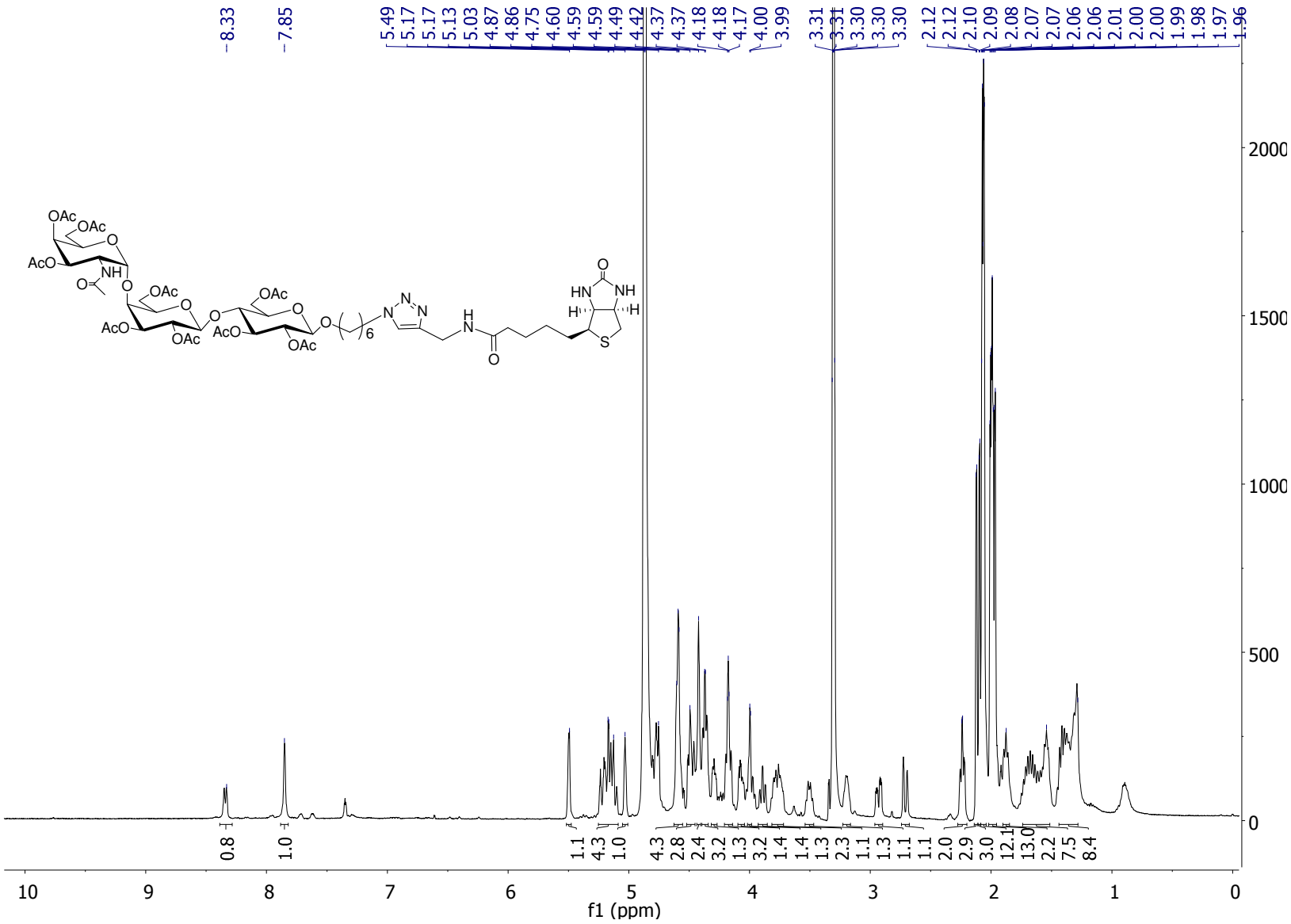
^{13}CNMR of Compound **46.**

^{13}CNMR (400 MHz, $CDCl_3$)



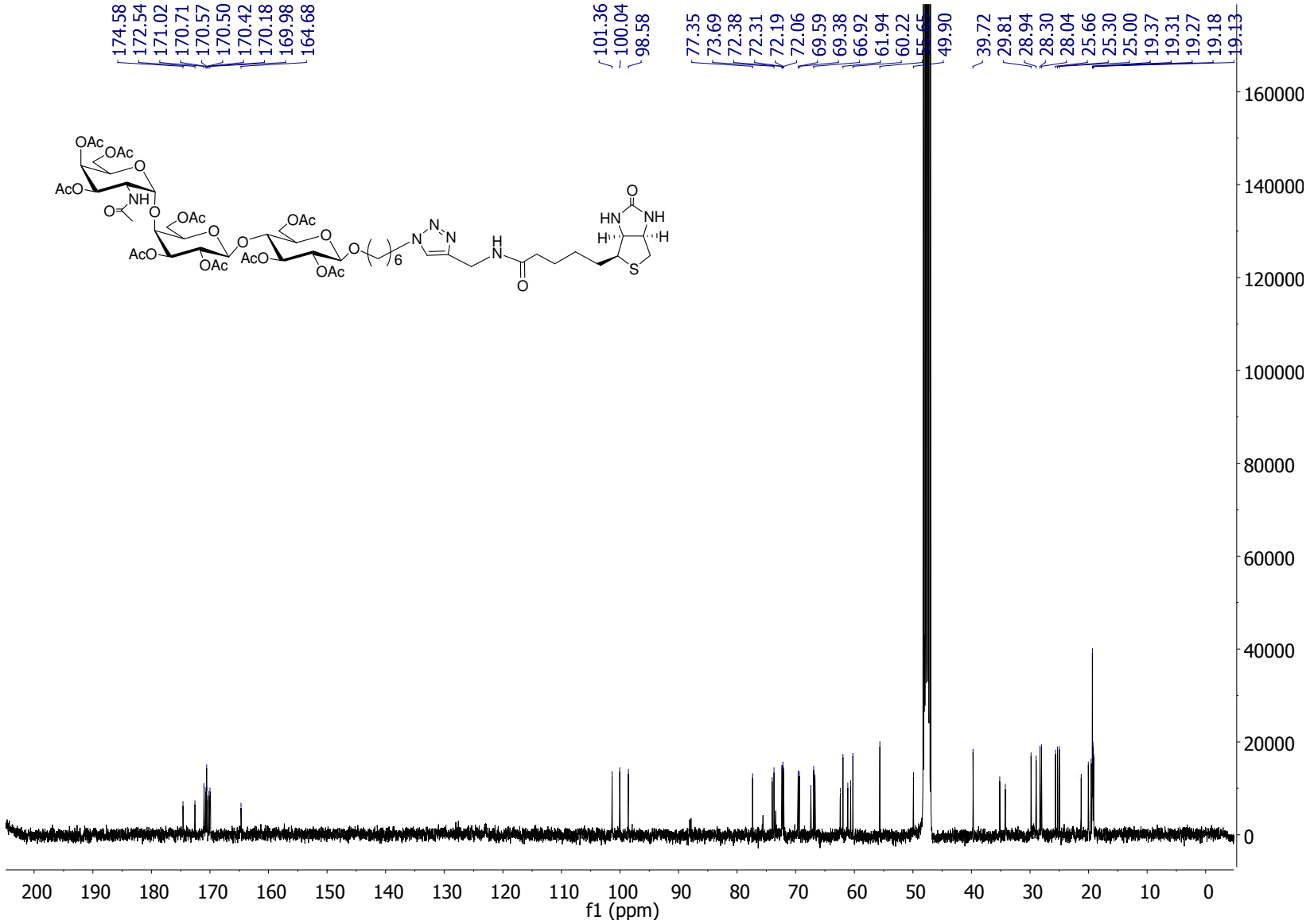
^{1}HNMR of Compound **48.**

^{1}HNMR (400 MHz, MeOH-d_4)



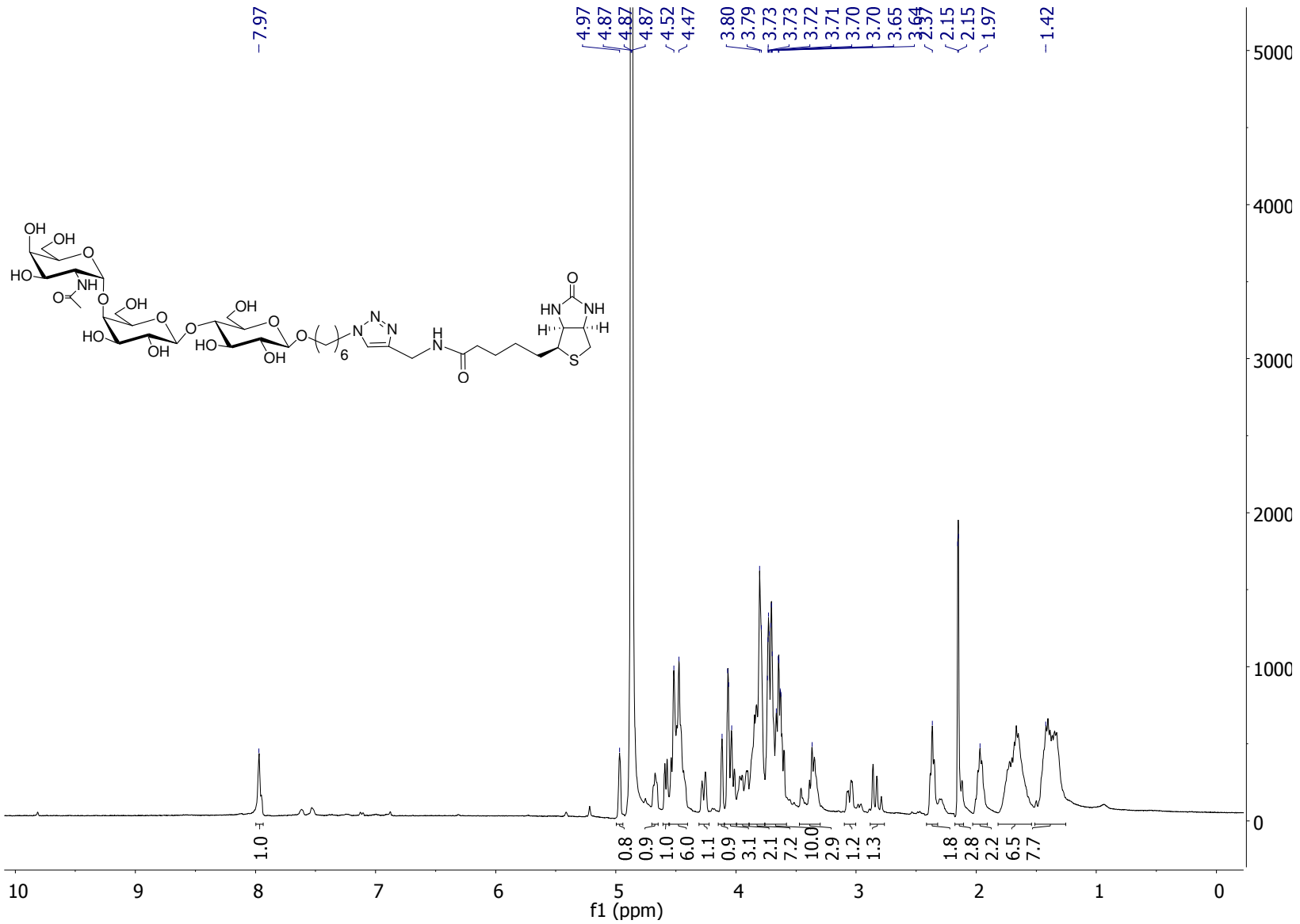
^{13}CNMR of Compound **48.**

^{13}CNMR (400 MHz, MeOH-d_4)



^{1}HNMR of Compound **5a.**

^{1}HNMR (400 MHz, D_2O)



^{13}CNMR of Compound **5a.**

^{13}CNMR (400 MHz, D_2O)