A One-Step, TEMPO-Catalyzed and Water-Mediated Stereoselective Conversion of Glycals into 2-Azido-2-Deoxysugars with a PIFA-Trimethylsilyl Azide Reagent System

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Table of Contents

1. General Experimental Section

All experiments were performed in an oven-dried apparatus and under nitrogen atmosphere in dry solvents, unless otherwise stated. Commercial grade solvents were dried by known methods, and stored over 4 Å molecular sieves. IR spectra were recorded as a thin film and expressed in cm^{-1}. High resolution mass spectra were recorded by Q-TOF using electrospray ionization (ESI) method. ^{1}H (500 MHz or 400 MHz) and ^{13}C (125 MHz or 100 MHz) NMR spectra were recorded using $CDCl_3$ as a solvent. The ratio of α- and β-anomers was calculated on the basis of the integrated intensities of anomeric protons and C-1 signals in ^{1}H and ^{13}C NMR spectra respectively. Dichloromethane was freshly distilled over calcium hydride under nitrogen atmosphere. $TMSN_3$ and TEMPO were purchased from the Sigma-Aldrich Chemical Co. and Alfa-Aesar Co. respectively. $PhI(OCOCF_3)_2$ and Bu_4NHSO_4 were purchased from Spectrochem Pvt. Ltd. (Mumbai). Optical rotations were recorded on AUTOPOL II polarimeter at 25 °C in CH_2Cl_2. TLC plates were prepared using thin layers of silica gel on microscopic slides, and visualization of spots was done by exposure to iodine or spraying with 10% H_2SO_4 and charring. Column chromatography was performed over silica gel (100−200 Mesh) using hexane and ethyl acetate as eluents.

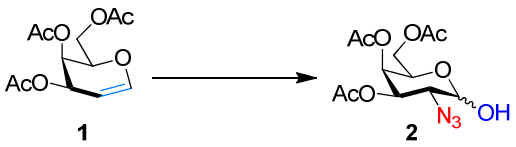
2. Experimental Details

General procedure for conversion of glycals into 2-azido-2-deoxysugars '**A'**

To a stirred solution of a glycal (200 mg, 0.730 mmol) and $TMSN_3$ (293 μL, 2.203 mmol) in CH_2Cl_2 (12 mL) at 0 °C, was added $PhI(OCOCF_3)_2$ (632 mg, 1.469 mmol), TEMPO (23 mg, 0.146 mmol), Bu_4NHSO_4 (50 mg, 0.146 mmol) and H_2O (661 μL, 37 mmol) sequentially without any intervening time.$ After the addition was completed, the reaction mixture was stirred at the same temperature for appropriate time. Upon consumption of the starting material (TLC monitoring and scarlet color of the reaction mixture turning to pale yellow color) saturated aqueous $NaHCO_3$ was added and further stirred for 15 min at 0 °C. Extraction was done with CH_2Cl_2 (3×10 mL), and the combined organic extracts were washed with water (1×10 mL) and brine (1×10 mL) then dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography to get the pure product.

[Note: $ It is important to add all the reagents including water in quick succession, or else, in cases with C3-benzyl (or silyl) protections, the amount of the corresponding enone increases.]

3. Table for optimization of reaction conditions for preparing 2-azido-2-deoxysugars from glycals



Entry	Oxidant	$TMSN_3$ (equiv)	TEMPO (equiv)	Bu_4NHSO_4 (equiv)	H_2O (equiv)	Solvent	Yield(%)
1	PIFA (1 equiv)	1	–	–	1	CH_2Cl_2	n.r.
2	PIFA (1 equiv)	1	0.1	–	1	CH_2Cl_2	18[a]
3	PIFA (2 equiv)	2	0.1	–	2	CH_2Cl_2	25[a]
4	PIFA (2 equiv)	2	0.2	0.1	5	CH_2Cl_2	40[a]
5	PIFA (2 equiv)	3	0.2	0.1	10	CH_2Cl_2	63
6	**PIFA (2 equiv)**	**3**	**0.2**	**0.2**	**50**	**CH_2Cl_2**	**80**
7	PIFA (2 equiv)	3	0.2	0.2	50	DMF	n.r.
8	PIFA (2 equiv)	3	0.2	0.2	50	THF	n.r.
9	PIFA (2 equiv)	3	0.2	0.2	50	Toluene	n.r.
10	PIDA (2 equiv)	3	0.2	0.2	50	CH_2Cl_2	n.r.
11	PIDA (2 equiv)	3	0.2	0.2	50	CH_2Cl_2	n.r.
12	PhIO (2 equiv)	3	0.2	0.2	50	CH_2Cl_2	n.r.
13	PhIO (2 equiv)	3	0.2	0.2	50	CH_3CN	n.r.
14	PhIO (2 equiv)	3	0.2	0.2	50	Toluene	n.r.

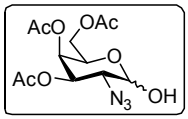
Reaction conditions: Glycals (0.730 mmol), $TMSN_3$ (2.203 mmol), $PhI(OCOCF_3)_2$ (1.469 mmol), TEMPO (0.146 mmol), Bu_4NHSO_4 (0.146 mmol), H_2O (37 mmol), CH_2Cl_2 at 0 °C, Isolated yields after purification by silica gel column chromatography; [a] Yield based on recovered starting material

Typical procedure for the synthesis of 2 in 1 mmol scale:

To a stirred solution of a glycal **1** (300 mg, 1.101 mmol) and $TMSN_3$ (439 µL, 3.305 mmol) in CH_2Cl_2 (15 mL) at 0 °C, was added $PhI(OCOCF_3)_2$ (947 mg, 2.202 mmol), TEMPO (35 mg, 0.220 mmol), Bu_4NHSO_4 (75 mg, 0.220 mmol) and H_2O (991 µL, 55.05 mmol) sequentially without any intervening time. After the addition was completed, the reaction mixture was stirred at 0 °C temperature for 35 min. Upon consumption of the starting material (TLC monitoring and scarlet color of the reaction mixture turning to pale yellow color) 5 mL of saturated aqueous $NaHCO_3$ was added and the reaction mixture further stirred for 15 min at 0 °C. Extraction was done with CH_2Cl_2 (3×10 mL), and the combined organic extracts were washed with water (1×10 mL) and brine (1×10 mL), dried over Na_2SO_4 and the solvent evaporated. The crude product was purified by column chromatography to get the pure product **2** in 80% yield (291 mg) as a colorless oil.

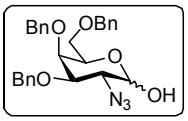
4. Characterization of products

(2R,3R,4R,5R)-2-(acetoxymethyl)-5-azido-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (2)



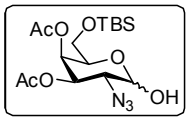
Compound **2** was prepared from **1** (200 mg, 0.735 mmol) using general procedure '**A**' in 80% yield (194 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 6:4); IR (neat) ν_{max} /cm^{-1} 3429, 2114, 1748, 1234; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.5) δ 5.47 (dd, *J* = 3.1, 1.1 Hz, 2H), 5.42 (dd, *J* = 5.2, 3.4 Hz, 3H), 5.39 (d, *J* = 3.3 Hz, 1H), 5.36 – 5.32 (m, 1H), 4.83 (dd, *J* = 10.9, 3.3 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 4.47 (dd, *J* = 7.0, 6.2 Hz, 2H), 4.15 – 4.08 (m, 6H), 3.92 (td, *J* = 6.6, 0.9 Hz, 1H), 3.75 (dd, *J* = 11.0, 3.4 Hz, 2H), 3.67 (dd, *J* = 10.9, 8.0 Hz, 1H), 3.60 (s, 1H), 2.17 (s, 3H), 2.16 (s, 5H), 2.07 (d, *J* = 1.6 Hz, 8H), 2.06 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.82, 170.31, 170.13, C_1-β-96.53, C_1-α-92.47, 71.30, 71.00, 68.46, 67.81, 66.67, 66.58, 62.06, 61.93, 61.71, 58.12, 20.85, 20.81, 20.77, 20.75; HRMS Calcd for $C_{12}H_{17}N_3NaO_8$ $[M + Na]^+$ = 354.0913, found 354.0908.

(3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-ol (4)



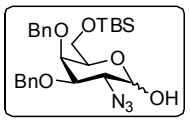
Compound **4** was prepared from **2** (200 mg, 0.480 mmol) using general procedure **'A'** in 78% yield (178 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3101, 2112, 1454, 1063; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.5) δ 7.42 – 7.21 (m, 27H), 5.29 (d, *J* = 3.3 Hz, 1H), 4.87 (dd, *J* = 11.5, 1.9 Hz, 2H), 4.71 (d, *J* = 3.3 Hz, 2H), 4.68 (t, *J* = 3.0 Hz, 1H), 4.56 – 4.47 (m, 3H), 4.41 (ddd, *J* = 18.7, 12.5, 5.9 Hz, 3H), 4.14 (t, *J* = 6.3 Hz, 1H), 3.92 (qd, *J* = 10.5, 2.9 Hz, 3H), 3.83 (d, *J* = 2.4 Hz, 1H), 3.77 (dd, *J* = 10.3, 8.0 Hz, 2H), 3.60 – 3.45 (m, 3H), 3.40 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.32 (dd, *J* = 10.3, 2.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.24, 138.15, 137.66, 137.59, 128.67, 128.56, 128.43, 128.36, 128.18, 128.15, 128.08, 128.01, 127.94, 127.91, C_1-β-96.55, C_1-α-92.44, 80.93, 77.47, 74.76, 73.81, 73.67, 73.61, 72.67, 72.48, 72.29, 69.72, 69.41, 68.78, 64.67, 60.45; HRMS Calcd for $C_{27}H_{30}N_3O_5$ $[M + H]^+$ = 476.2185, found 476.2186.

(2R,3R,4R,5R)-5-azido-2-(((tert-butyldimethylsilyl)oxy)methyl)-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (6)



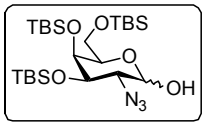
Compound **6** was prepared from **5** (200 mg, 0.581 mmol) using general procedure **'A'** in 71% yield (165 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3426, 2930, 2113, 1753, 1253; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.9) δ 5.50 (d, *J* = 2.5 Hz, 1H), 5.42 – 5.36 (m, 3H), 4.83 (dd, *J* = 10.8, 3.3 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.78 – 3.66 (m, 4H), 3.67 – 3.51 (m, 4H), 2.13 (s, 2H), 2.12 (s, 3H), 2.04 (s, 5H), 0.85 (d, *J* = 4.3 Hz, 18H), 0.01 (dd, *J* = 7.1, 4.5 Hz, 11H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.13, 170.10, C_1-β-96.52, C_1-α-92.50, 73.74, 71.65, 69.24, 68.76, 67.87, 66.51, 62.41, 61.19, 60.76, 58.43, 25.89, 25.85, 20.84, 20.78, 18.34, 18.29, -5.44, -5.47, -5.50, -5.56; HRMS Calcd for $C_{16}H_{30}N_3O_7Si$ $[M + H]^+$ = 404.1853, found 404.1851.

(3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-ol (8)



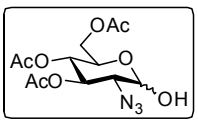
Compound **8** was prepared from **7** (200 mg, 0.454 mmol) using general procedure **'A'** in 67% yield (150 mg) as a colorless oil; R_f = 0.70 (hexane/EtOAc, 8:2); IR (neat) ν_{max} /cm^{-1} 3415, 2928, 2111, 1100; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.6) δ 7.45 – 7.22 (m, 11H), 5.29 (d, *J* = 3.2 Hz, 1H), 4.89 (d, *J* = 11.2 Hz, 1H), 4.73 (s, 1H), 4.69 (d, *J* = 2.0 Hz, 1H), 4.59 (dd, *J* = 18.6, 11.2 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.92 (ddd, *J* = 18.6, 13.8, 2.4 Hz, 1H), 3.76 (dd, *J* = 10.2, 8.0 Hz, 1H), 3.69 (dd, *J* = 8.6, 3.1 Hz, 1H), 3.67 – 3.61 (m, 1H), 3.36 (td, *J* = 10.6, 4.8 Hz, 1H), 0.88 (d, *J* = 3.7 Hz, 10H), 0.04 (t, *J* = 2.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.54, 138.39, 137.72, 137.66, 128.65, 128.41, 128.19, 128.08, 128.00, 127.79, C_1-β-96.62, C_1-α-92.53, 80.82, 75.50, 74.96, 74.93, 73.38, 72.64, 72.42, 72.16, 71.39, 64.99, 61.72, 61.20, 60.54, 26.05, 26.02, 18.39, 18.33, -5.29; HRMS Calcd for $C_{26}H_{41}N_4O_5Si$ $[M + NH_4]^+$ = 517.2846, found 517.2848.

(3R,4R,5S,6R)-3-azido-4,5-bis((tert-butyldimethylsilyl)oxy)-6-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-ol (10)



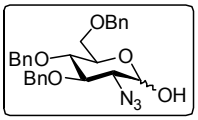
Compound **10** was prepared from **9** (200 mg, 0.409 mmol) using general procedure **'A'** in 56% yield (125 mg) as a colorless oil; R_f = 0.80 (hexane/EtOAc, 9:1); IR (neat) ν_{max} /cm^{-1} 3010, 2111, 1263; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 0.8:1) δ 5.33 (d, *J* = 3.2 Hz, 1H), 4.53 (d, *J* = 7.4 Hz, 1H), 4.05 – 3.99 (m, 2H), 3.94 (d, *J* = 2.0 Hz, 1H), 3.87 (dd, *J* = 13.4, 5.0 Hz, 2H), 3.75 – 3.64 (m, 3H), 3.64 – 3.57 (m, 1H), 3.57 – 3.49 (m, 1H), 3.41 (dd, *J* = 10.0, 2.2 Hz, 1H), 3.34 (dd, *J* = 7.9, 5.9 Hz, 1H), 0.97 (s, 9), 0.96 (s, 8H), 0.92 (d, *J* = 2.8 Hz, 19H), 0.88 (d, *J* = 1.3 Hz, 18H), 0.20 (s, 4H), 0.16 (s, 11H), 0.14 (s, 3H), 0.11 (d, *J* = 1.3 Hz, 6H), 0.06 (s, 11H), -0.00 (d, *J* = 3.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ C_1-β-96.90, C_1-α-94.10 76.15, 74.61, 71.25, 70.04, 66.48, 62.63, 61.29, 61.10, 26.37, 26.32, 26.19, 25.88, 18.66, 18.57, 18.21, 0.07, -3.68, -3.81, -4.06, -4.50, -4.63, -4.71, -5.22. ; HRMS Calcd for $C_{24}H_{57}N_4O_5Si_3$ $[M + NH_4]^+$ = 565.3637, found 565.3635.

(2R,3S,4R,5R)-2-(acetoxymethyl)-5-azido-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (12)



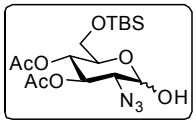
Compound **12** was prepared from **11** (200 mg, 0.735 mmol) using general procedure **'A'** in 75% yield (182 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 6:4); IR (neat) ν_{max} /cm^{-1} 3433, 2111, 1739, 1228; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.9) δ 5.55 – 5.50 (m, 1H), 5.44 (dd, *J* = 9.9, 3.8 Hz, 1H), 5.38 (s, 2H), 5.32 (t, *J* = 9.7 Hz, 1H), 5.25 (d, *J* = 3.2 Hz, 1H), 5.07 – 5.02 (m, 1H), 5.02 – 4.95 (m, 2H), 4.72 (d, *J* = 8.0 Hz, 1H), 4.60 (s, 1H), 4.30 – 4.13 (m, 8H), 4.20 – 4.08 (m, 7H), 4.08 – 4.02 (m, 3H), 3.93 (dd, *J* = 10.5, 3.1 Hz, 1H), 3.70 (ddd, *J* = 9.9, 4.6, 2.3 Hz, 1H), 3.50 – 3.44 (m, 1H), 3.40 (dd, *J* = 10.5, 3.4 Hz, 2H), 2.09 (d, *J* = 1.6 Hz, 7H), 2.07 (d, *J* = 2.2 Hz, 15H), 2.04 (dd, *J* = 4.0, 2.4 Hz, 9H), 2.01 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.31, 171.11, 171.07, 170.36, 170.32, 170.01, 169.91, C_1-β-96.26, C_1-α-92.73, 92.13, 72.76, 72.66, 72.44, 71.94, 70.85, 70.55, 68.64, 68.45, 68.43, 67.52, 66.10, 65.56, 64.87, 63.54, 62.42, 62.28, 62.10, 61.95, 61.53, 20.85, 20.82, 20.79, 20.72, 20.69, 20.57; HRMS Calcd for $C_{12}H_{21}N_4O_8$ $[M + NH_4]^+$ = 349.1359, found 349.1363.

(3R,4R,5S,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-ol (14)



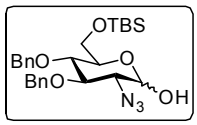
Compound **14** was prepared from **13** (200 mg, 0.480 mmol) using general procedure **'A'** in 72% yield (165 mg) as a white solid; m.p. = 205-207 °C; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3416, 2919, 2108, 1090, 697; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.8) δ 7.40 – 7.26 (m, 24H), 7.18 – 7.09 (m, 4H), 5.31 (d, *J* = 3.4 Hz 1H), 4.87 (d, *J* = 2.9 Hz, 2H), 4.83 – 4.75 (m, 3H), 4.58 – 4.45 (m, 6H), 4.12 – 4.05 (m, 1H), 4.05 – 3.97 (m, 2H), 3.70 – 3.52 (m, 6H), 3.51 – 3.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.92, 137.73, 137.66, 128.62, 128.59, 128.27, 128.22, 128.14, 128.06, 127.99, 127.94, C_1-β-96.28, C_1-α-92.17, 83.19, 80.24, 78.60, 77.80, 75.69, 75.15, 74.94, 73.65, 73.60, 70.71, 68.63, 67.51, 64.11; HRMS Calcd for $C_{27}H_{33}N_4O_5$ $[M + NH_4]^+$ = 493.2451, found 493.2450.

(2R,3S,4R,5R)-5-azido-2-(((tert-butyldimethylsilyl)oxy)methyl)-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (16)



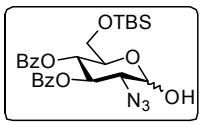
Compound **16** was prepared from **15** (200 mg, 0.581 mmol) using general procedure **'A'** in 68% yield (160 mg) as as a white solid; m.p. = 185-187 °C; R_f = 0.50 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3449, 2930, 2112, 1756, 1235; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.7) δ 5.50 (dd, *J* = 10.3, 9.4 Hz, 1H), 5.37 (d, *J* = 3.2 Hz, 1H), 5.04 – 4.96 (m, 2H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.09 (dt, *J* = 10.2, 3.5 Hz, 1H), 3.91 (s, 1H), 3.71 – 3.65 (m, 3H), 3.53 (ddd, *J* = 9.2, 4.7, 2.6 Hz, 1H), 3.43 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.37 (dd, *J* = 10.6, 3.4 Hz, 1H), 2.08 (d, *J* = 2.9 Hz, 4H), 2.02 (s, 3H), 2.00 (s, 2H), 0.90 – 0.82 (m, 18H), 0.04 (d, *J* = 5.2 Hz, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.47, 169.89, 169.79, C_1-β-96.20, C_1-α-92.05, 74.92, 73.11, 70.97, 70.25, 69.10, 68.88, 65.05, 62.47, 62.33, 61.63, 26.00, 25.81, 20.89, 20.85, 20.81, 20.77, 18.56, -5.32, -5.35; HRMS Calcd for $C_{16}H_{29}N_3NaO_7Si$ $[M + Na]^+$ = 426.1672, found 426.1679.

(3R,4R,5S,6R)-3-azido-4,5-bis(benzyloxy)-6-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-ol (18)



Compound **18** was prepared from **17** (200 mg, 0.454 mmol) using general procedure **'A'** in 68% yield (153 mg) as a colorless oil; R_f = 0.70 (hexane/EtOAc, 8:2); IR (neat) ν_{max} /cm^{-1} 3408, 2928, 2109, 1050; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.6) δ 7.41 – 7.27 (m, 16H), 4.92 – 4.81 (m, 4H), 4.70 (dd, *J* = 16.0, 11.0 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.94 – 3.88 (m, 1H), 3.87 (dd, *J* = 5.6, 3.0 Hz, 1H), 3.83 (t, *J* = 3.2 Hz, 1H), 3.79 (dd, *J* = 9.1, 7.8 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.49 – 3.43 (m, 1H), 3.39 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.33 (ddd, *J* = 9.9, 5.2, 3.0 Hz, 1H), 3.22 (s, 1H), 0.90 (d, *J* = 3.9 Hz, 17H), 0.10 – 0.01 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.29, 138.12, 137.93, 128.64, 128.40, 128.32, 128.08, 128.01, 127.96, 127.90, C_1-β-96.21, C_1-α-92.15, 83.17, 80.18, 78.29, 76.35, 75.79, 75.14, 72.15, 67.72, 64.28, 62.24, 62.11, 26.06, 18.51, -4.96, -4.98, -5.22, -5.25; HRMS Calcd for $C_{26}H_{41}N_4O_5Si$ $[M + NH_4]^+$ = 517.2846, found 517.2841.

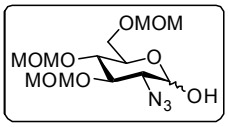
(2R,3S,4R,5R)-5-azido-2-(((tert-butyldimethylsilyl)oxy)methyl)-6-hydroxytetrahydro-2H-pyran-3,4-diyl dibenzoate (20)



Compound **20** was prepared from **19** (200 mg, 0.427 mmol) using general procedure **'A'** in 75% yield (170 mg) as a colorless oil. R_f = 0.30 (hexane/EtOAc, 6:4); IR

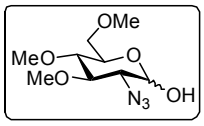
(neat) ν_{max} /cm^{-1} 2925, 2111, 1733, 1273; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.3) δ 8.00 – 7.86 (m, 6H), 7.57 – 7.44 (m, 3H), 7.43 – 7.24 (m, 7H), 6.02 – 5.94 (m, 1H), 5.57 – 5.48 (m, 1H), 5.48 – 5.37 (m, 2H), 4.91 (d, *J* = 7.9 Hz, 1H), 4.35 (dt, *J* = 10.1, 3.8 Hz, 1H), 4.09 (s, 1H), 3.85 – 3.70 (m, 4H), 3.68 (dd, *J* = 10.0, 7.9 Hz, 1H), 3.56 – 3.47 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 14H), 0.00 (d, *J* = 3.1 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.92, 165.87, 165.42, 133.50, 133.44, 133.38, 129.99, 129.87, 129.24, 129.10, 128.52, 128.48, C_1-β-96.60, C_1-α-92.59, 75.49, 73.03, 70.97, 70.85, 69.59, 69.41, 65.58, 62.83, 62.65, 62.11, 26.02, 25.98, 18.58, 18.53, -5.31; HRMS Calcd for $C_{26}H_{33}N_3NaO_7Si$ $[M + Na]^+$ = 550.1985, found 550.1984.

(3R,4R,5S,6R)-3-azido-4,5-bis(methoxymethoxy)-6-((methoxymethoxy)methyl)tetrahydro-2H-pyran-2-ol (22)



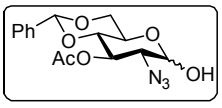
Compound **22** was prepared from **21** (200 mg, 0.719 mmol) using general procedure **'A'** in 72% yield (175 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 6:4); IR (neat) ν_{max} /cm^{-1} 3388, 2924, 2109, 1029; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.8) 4.89 (d, *J* = 6.6 Hz, 1H), 4.82 (dt, *J* = 5.8, 4.2 Hz, 4H), 4.79 – 4.74 (m, 2H), 4.70 – 4.62 (m, 7H), 4.00 (dddd, *J* = 15.1, 5.1, 4.5, 1.8 Hz, 3H), 3.91 – 3.76 (m, 2H), 3.76 – 3.58 (m, 3H), 3.46 (s, 3H), 3.44 (dd, *J* = 10.5, 5.1 Hz, 5H), 3.39 (t, *J* = 5.4 Hz, 7H), 3.35 (s, 7H), 3.26 (dd, *J* = 9.6, 8.1 Hz, 1H), 3.13 (dd, *J* = 10.4, 3.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.63, 98.58, 98.35, 97.97, 96.79, 96.74, C_1-β-96.28, C_1-α-92.31, 79.81, 77.82, 76.74, 74.32, 69.89, 66.99, 66.76, 66.69, 63.23, 63.14, 56.60, 56.57, 56.47, 56.43, 56.29, 56.08, 55.50; HRMS Calcd for $C_{12}H_{23}N_3NaO_8$ $[M + Na]^+$ = 360.1383, found 360.1385.

(3R,4R,5S,6R)-3-azido-4,5-dimethoxy-6-(methoxymethyl)tetrahydro-2H-pyran-2-ol (24)



Compound **24** was prepared from **23** (200 mg, 1.063 mmol) using general procedure **'A'** in 77% yield (203 mg) as a white solid; m.p. = 160-163°C; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 2923, 2108, 1106; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.5) δ 5.19 (d, *J* = 3.5 Hz, 1H), 4.48 (d, *J* = 8.1 Hz, 1H), 4.33 (dd, *J* = 8.2, 3.3 Hz, 1H), 3.92 (ddd, *J* = 10.0, 5.1, 2.2 Hz, 1H), 3.68 – 3.58 (m, 5H), 3.56 – 3.46 (m, 7H), 3.37 (s, 4H), 3.23 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.15 – 3.09 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ C_1-β-95.99, C_1-α-91.86, 85.11, 81.75, 80.59, 79.86, 74.46, 71.43, 71.39, 70.11, 66.85, 63.51, 60.88, 60.65, 60.61, 59.15; HRMS Calcd for $C_9H_{17}N_3NaO_5$ $[M + Na]^+$ = 270.1066, found 270.1067.

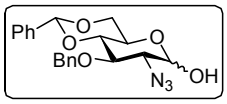
(2R,4aR,7R,8R,8aS)-7-azido-6-hydroxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-8-yl acetate (26)



Compound **26** was prepared from **25** (200 mg, 0.724 mmol) using general procedure **'A'** in 68% yield (165 mg) as a semi solid; R_f = 0.30 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3431, 2923, 2110, 1743, 1095; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.8) 7.51 – 7.40 (m, 7H), 7.40 – 7.30 (m, 10H), 5.88 (d, *J* = 7.9 Hz, 1H), 5.64 (t, *J* = 9.9 Hz, 1H), 5.59 – 5.54 (m, 1H), 5.51 – 5.48 (m, 2H), 5.37 (d, *J* = 3.4 Hz, 1H), 5.22 (dd, *J* = 10.2, 3.8 Hz, 1H), 5.17 (dd, *J* = 13.8, 5.7 Hz, 2H), 4.95 (s, 1H), 4.78 (d, *J* = 7.9 Hz, 1H), 4.72 – 4.66 (m, 1H), 4.38 (dd, *J* = 10.6, 4.8 Hz, 1H), 4.36 – 4.12 (m, 6H), 4.09 (t, *J* = 9.8 Hz, 1H), 4.01 (t, *J* = 9.8 Hz, 1H), 3.85 – 3.67 (m, 4H), 3.63 (t, *J* = 9.4 Hz, 2H), 3.53 – 3.42 (m, 3H), 3.40 (s, 1H), 3.33 (dd, *J* = 10.3, 3.5 Hz, 1H), 2.16 (s, 1H), 2.15 (d, *J* = 1.7 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.37, 170.13, 170.00, 137.14, 136.97,

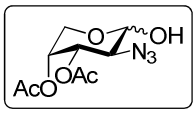
136.81, 133.38, 129.41, 129.31, 128.53, 128.41, 126.32, 126.23, 102.13, 102.04, 101.84, 101.65, 101.21, C_1-β-96.83, C_1-α-93.86, 93.28, 79.56, 78.70, 77.61, 76.25, 75.38, 72.10, 71.32, 71.18, 70.07, 69.18, 68.95, 68.82, 68.52, 68.45, 67.33, 66.70, 65.92, 65.59, 64.18, 64.03, 62.90, 62.40, 21.00, 20.83, 20.72; HRMS Calcd for $C_{15}H_{18}N_3O_6$ $[M + H]^+$ = 336.1196, found 336.1192.

(2R,4aR,7R,8R,8aS)-7-azido-8-(benzyloxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-6-ol (28)



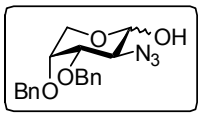
Compound **28** was prepared from **27** (200 mg, 0.617 mmol) using general procedure **'A'** in 59% yield (140 mg) as a colorless oil. R_f = 0.30 (hexane/EtOAc, 7:3); R_f = 0.50 (hexane/EtOAc, 8:2); IR (neat) ν_{max} /cm^{-1} 3430, 2922, 2113, 1095; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.9) δ 7.49 (ddd, *J* = 7.6, 6.1, 2.0 Hz, 4H), 7.44 – 7.27 (m, 15H), 5.59 (s, 1H), 5.58 (s, 1H), 5.28 (d, *J* = 3.2 Hz, 1H), 4.95 (dd, *J* = 18.5, 11.1 Hz, 2H), 4.81 (dd, *J* = 11.1, 4.5 Hz, 2H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.33 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.28 (dd, *J* = 10.3, 5.0 Hz, 1H), 4.16 – 4.08 (m, 2H), 3.79 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.73 (ddd, *J* = 11.5, 7.3, 3.8 Hz, 2H), 3.61 (t, *J* = 9.3 Hz, 1H), 3.49 (dd, *J* = 9.8, 3.6 Hz, 2H), 3.43 (ddd, *J* = 12.9, 6.4, 3.2 Hz, 2H), 2.98 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.86, 137.31, 137.16, 129.25, 129.22, 128.58, 128.56, 128.45, 128.43, 128.38, 128.09, 126.15, 126.11, 101.60, 101.48, C_1-β-96.67, C_1-α-92.87, 82.86, 81.68, 79.17, 76.34, 75.24, 75.10, 69.05, 68.62, 67.46, 66.56, 63.74, 62.92; HRMS Calcd for $C_{20}H_{21}ClN_3O_5$ $[M + Cl]^-$ = 418.1170, found 418.1177.

(3R,4S,5S,6S)-5-azido-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (30)



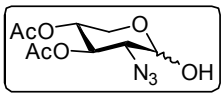
Compound **30** was prepared from **29** (200 mg, 0.999 mmol) using general procedure **'A'** in 76% yield (197 mg) as a white solid; m.p. = 137-139°C; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3417, 2927, 2113, 1747, 1241; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 0.6:1) δ 5.43 – 5.29 (m, 1H), 5.22 – 5.19 (m, 1H), 4.81 (dd, *J* = 10.8, 3.5 Hz, 1H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.22 – 4.11 (m, 1H), 4.01 (dd, *J* = 13.5, 2.1 Hz, 1H), 3.77 (dd, *J* = 10.8, 3.3 Hz, 1H), 3.73 – 3.61 (m, 2H), 2.16 (s, 3H), 2.14 (s, 1H), 2.08 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.50, 170.20, C_1-β-96.91, C_1-α-92.66, 71.10, 68.72, 68.11, 67.57, 64.59, 62.44, 60.80, 58.53, 21.07, 21.03, 20.88, 20.83; HRMS Calcd for $C_9H_{17}N_4O_6$ $[M + NH_4]^+$ = 277.1148, found 277.1143.

(2S,3S,4S,5R)-3-azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-2-ol (32)



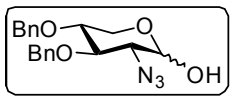
Compound **32** was prepared from **31** (200 mg, 0.674 mmol) using general procedure **'A'** in 73% yield (175 mg) as a colorless oil; R_f = 0.30 (hexane/EtOAc, 6:4); IR (neat) ν_{max} /cm^{-1} 3400, 2915, 2111; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.4) δ 7.40 – 7.28 (m, 18H), 5.30 (d, *J* = 3.0 Hz, 1H), 4.73 (d, *J* = 4.2 Hz, 1H), 4.69 (t, *J* = 3.3 Hz, 2H), 4.67 – 4.64 (m, 2H), 4.62 (q, *J* = 3.4 Hz, 3H), 4.55 (dd, *J* = 29.2, 4.9 Hz, 1H), 4.05 (dd, *J* = 12.7, 3.9 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.89 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.84 (d, *J* = 2.2 Hz, 1H), 3.80 – 3.75 (m, 3H), 3.70 (td, *J* = 3.6, 2.0 Hz, 1H), 3.46 (dd, *J* = 9.0, 3.1 Hz, 1H), 3.36 (dd, *J* = 12.7, 1.8 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 138.02, 137.81, 137.70, 137.41, 128.66, 128.62, 128.59, 128.18, 128.10, 128.04, 127.97, C_1-β-96.02, C_1-α-92.71, 78.53, 75.58, 72.57, 72.26, 71.93, 71.74, 71.69, 71.16, 63.86, 62.57, 60.54, 60.46; HRMS Calcd for $C_{19}H_{21}ClN_3O_4$ $[M + Cl]^-$ = 390.1221, found 390.1222.

(3R,4R,5R)-5-azido-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (34)



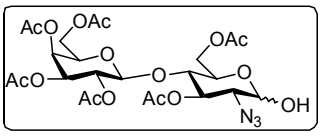
Compound **34** was prepared from **33** (200 mg, 0.999 mmol) using general procedure **'A'** in 71% yield (184 mg) as a white solid; m.p. = 155-157 °C; R_f = 0.30 (hexane/EtOAc, 6:4); IR (neat) ν_{max} /cm^{-1}3450, 2953, 2111, 1753, 1240, 1054; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.8) δ 5.52 – 5.46 (m, 1H), 5.31 (d, *J* = 3.2 Hz, 1H), 5.04 – 4.97 (m, 1H), 4.95 – 4.88 (m, 2H), 4.65 (d, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 11.6, 5.5 Hz, 1H), 4.02 (s, 1H), 3.87 (t, *J* = 10.7 Hz, 1H), 3.78 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.42 (dd, *J* = 10.0, 7.8 Hz, 1H), 3.35 – 3.28 (m, 2H), 2.10 (d, *J* = 0.8 Hz, 5H), 2.03 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.49, 170.39, 170.37, C_1-β-96.78, C_1-α-92.24, 72.16, 69.93, 69.40, 69.14, 64.84, 62.87, 61.60, 58.78, 20.86, 20.82, 20.77; HRMS Calcd for $C_9H_{13}N_3NaO_6$ $[M + Na]^+$ = 282.0702, found 282.071.

(3R,4R,5R)-3-azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-2-ol (36)



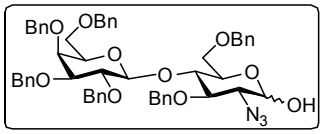
Compound **36** was prepared from **35** (200 mg, 0.674 mmol) using general procedure **'A'** in 68% yield (163 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3400, 2922, 2110, 1096; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.9) δ 7.42 – 7.24 (m, 20H), 5.15 (d, *J* = 3.3 Hz, 1H), 4.93 (d, *J* = 10.7 Hz, 1H), 4.85 (dd, *J* = 20.2, 10.5 Hz, 3H), 4.74 – 4.65 (m, 2H), 4.65 – 4.55 (m, 3H), 4.43 (d, *J* = 7.8 Hz, 1H), 3.97 – 3.89 (m, 2H), 3.79 (t, *J* = 10.8 Hz, 2H), 3.68 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.61 (ddt, *J* = 10.7, 5.2, 2.9 Hz, 2H), 3.42 – 3.32 (m, 2H), 3.28 (dd, *J* = 9.5, 8.0 Hz, 1H), 3.18 (dd, *J* = 11.3, 10.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.96, 137.94, 137.81, 128.61, 128.54, 128.34, 128.27, 128.06, 128.01, 127.93, 127.90, C_1-β-96.65, C_1-α-92.12, 81.99, 79.04, 78.37, 77.61, 75.56, 75.51, 73.40, 73.32, 66.90, 63.97, 63.63, 60.32; HRMS Calcd for $C_{19}H_{21}ClN_3O_4$ $[M + Cl]^-$ = 390.1221, found 390.1229.

(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R)-4-acetoxy-2-(acetoxymethyl)-5-azido-6-hydroxytetrahydro-2H-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (38)



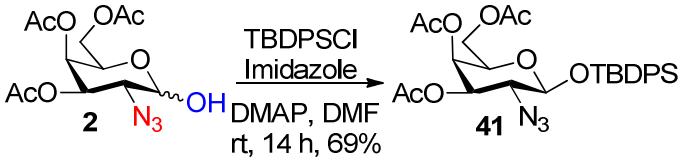
Compound **38** was prepared from **37** (200 mg, 0.357 mmol) using general procedure **'A'** in 74% yield (163 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc,1:1); IR (neat) ν_{max} /cm^{-1} 3410, 2868, 2109, 1068; ^{1}H NMR (400 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.6) δ 5.50 – 5.39 (m, 2H), 5.35 – 5.29 (m, 3H), 5.16 (s, 1H), 5.10 (dd, *J* = 7.5, 3.0 Hz, 1H), 5.06 (dd, *J* = 7.3, 3.0 Hz, 1H), 5.02 (dd, *J* = 11.2, 3.3 Hz, 1H), 4.99 – 4.87 (m, 4H), 4.68 (d, *J* = 8.0 Hz, 1H), 4.55 – 4.49 (m, 1H), 4.50 – 4.30 (m, 5H), 4.15 (tt, *J* = 5.2, 3.7 Hz, 4H), 4.12 – 4.02 (m, 5H), 4.01 – 3.81 (m, 4H), 3.75 – 3.65 (m, 2H), 3.60 (ddd, *J* = 9.8, 4.8, 1.7 Hz, 1H), 3.35 (dd, *J* = 10.4, 8.0 Hz, 1H), 3.20 (dd, *J* = 10.6, 3.4 Hz, 1H), 2.12 (dd, *J* = 5.7, 3.8 Hz, 12H), 2.09 (d, *J* = 3.4 Hz, 12H), 2.03 (d, *J* = 3.0 Hz, 7H), 2.01 (t, *J* = 4.5 Hz, 7H), 1.93 (t, *J* = 2.2 Hz, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.91, 170.71, 170.64, 170.55, 170.40, 170.29, 169.86, 169.78, 169.44, 169.22, 101.26, 100.96, C_1-β-95.99, 92.43, C_1-α-92.04, 76.35, 75.95, 74.06, 72.85, 72.11, 71.05, 70.65, 70.07, 69.19, 68.36, 66.86, 66.70, 65.16, 62.31, 62.05, 61.77, 61.16, 60.86, 20.95, 20.75, 20.69, 20.62, 20.56; HRMS Calcd for $C_{24}H_{33}N_3NaO_{16}$ $[M + Na]^+$ = 642.1759, found 642.1759.

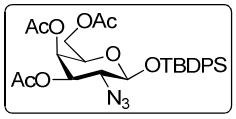
(3R,4R,5S,6R)-3-azido-4-(benzyloxy)-6-((benzyloxy)methyl)-5-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2H-pyran-2-ol (40)



Compound **40** was prepared from **39** (200 mg, 0.235 mmol) using general procedure **'A'** in 58% yield (123 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 6:4); IR (neat) ν_{max} /cm^{-1} 3416, 2921, 2109, 1453, 1095; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 1:0.5) δ 7.46 – 7.05 (m, 68H), 5.25 (s, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 5.05 (d, *J* = 10.3 Hz, 1H), 5.01 – 4.95 (m, 1H), 4.81 (td, *J* = 11.0, 2.3 Hz, 3H), 4.75 – 4.63 (m, 7H), 4.57 – 4.46 (m, 5H), 4.32 (ddd, *J* = 13.9, 9.2, 5.0 Hz, 5H), 4.22 (dd, *J* = 11.8, 8.6 Hz, 2H), 3.97 (d, *J* = 6.9 Hz, 2H), 3.93 – 3.89 (m, 2H), 3.87 – 3.81 (m, 2H), 3.80 – 3.72 (m, 3H), 3.55 (d, *J* = 10.7 Hz, 2H), 3.51 – 3.45 (m, 2H), 3.42 – 3.28 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.14, 138.90, 138.66, 138.55, 138.42, 138.30, 138.21, 138.08, 128.62, 128.51, 128.36, 128.33, 128.14, 128.02, 127.96, 127.91, 127.78, 127.69, 127.62, 127.56, 127.44, 126.10, 103.07, 102.95, C_1-β-96.17, C_1-α-92.04, 82.59, 81.41, 80.07, 78.25, 76.39, 75.44, 74.91, 73.89, 73.79, 73.55, 73.43, 73.35, 72.79, 70.97, 68.31, 68.15, 68.10, 67.27, 63.65; HRMS Calcd for $C_{54}H_{61}N_4O_{10}$ $[M + NH_4]^+$ = 925.4388, found 925.4381.

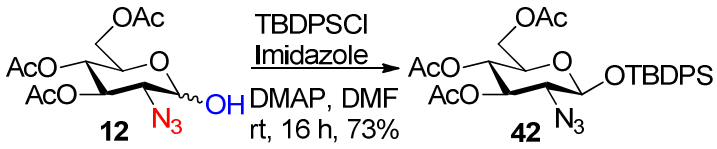
(2R,3R,4R,5R,6S)-2-(acetoxymethyl)-5-azido-6-((tert-butyldiphenylsilyl)oxy)tetrahydro-2H-pyran-3,4-diyl diacetate(41)



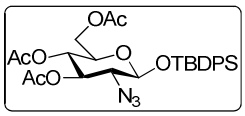


Compound **41** was prepared from **2** (100 mg, 0.301 mmol) using a literature procedure[1a] in 69% yield (119 mg) as a colorless syrup; R_f = 0.40 (hexane/EtOAc,7:3); IR (neat) ν_{max} /cm^{-1} 2941, 2113, 1763, 1257; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (ddd, *J* = 10.5, 8.0, 1.3 Hz, 4H), 7.45 – 7.34 (m, 6H), 5.23 (dd, *J* = 3.3, 0.9 Hz, 1H), 4.68 (dd, *J* = 10.8, 3.4 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 3.96 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.89 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.72 (dd, *J* = 10.8, 7.7 Hz, 1H), 3.54 (td, *J* = 6.6, 0.9 Hz, 1H), 2.16 (s, 3H), 2.02 (s, 3H), 1.90 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.32, 170.18, 169.83, 135.99, 135.92, 133.02, 132.51, 130.16, 129.99, 127.77, 127.53, 97.06, 71.36, 70.72, 66.60, 63.61, 61.32, 27.00, 26.79, 20.73, 20.62, 20.53, 19.25; HRMS Calcd for $C_{28}H_{36}N_3O_8Si$ $[M + H]^+$ = 570.2272, found 570.2270.

(2R,3S,4R,5R,6S)-2-(acetoxymethyl)-5-azido-6-((tert-butyldiphenylsilyl)oxy)tetrahydro-2H-pyran-3,4-diyl diacetate (42)

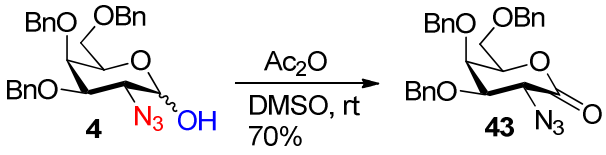


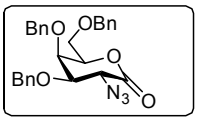
Compound **42** was prepared from **12** (100 mg, 0.301 mmol) using a literature procedure[1b] in 73% yield (126 mg) as a colorless syrup; R_f = 0.40 (hexane/EtOAc,7:3); IR (neat) ν_{max} /cm^{-1} 2935, 2111, 1753,



1260; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 4H), 7.41 (m, 6H), 5.23 (d, *J* = 2.6 Hz, 1H), 4.68 (dd, *J* = 10.8, 3.4 Hz, 1H), 4.46 (d, *J* = 7.7 Hz, 1H), 3.96 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.89 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.73 (dd, *J* = 10.8, 7.7 Hz, 1H), 3.54 (dt, *J* = 6.7, 3.3 Hz, 1H), 2.17 (s, 3H), 2.03 (s, 3H), 1.91 (s, 3H), 1.13 (s, 9H);^{13}C NMR (125 MHz, $CDCl_3$) δ 170.37, 170.22, 169.88, 136.00, 135.94, 133.01, 132.49, 130.18, 130.01, 127.79, 127.55, 97.07, 71.36, 70.71, 66.60, 63.60, 61.33, 26.90, 20.78, 20.70, 20.64, 19.27; HRMS Calcd for $C_{28}H_{36}N_3O_8Si$ $[M + H]^+$ = 570.2272, found 570.2275.

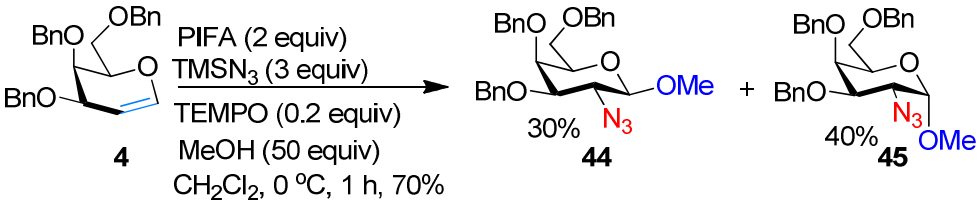
(3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-one (43)



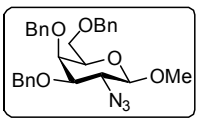


Compound **43** was prepared from **4** (100 mg, 0.211 mmol) using a literature procedure[2] in 70% yield (70 mg) as a colorless oil; R_f = 0.60 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 2923, 2113, 1746, 1207; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 16H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.69 (s, 2H), 4.60 (dd, *J* = 10.8, 6.1 Hz, 2H), 4.47 (dd, *J* = 25.7, 11.7 Hz, 2H), 4.34 – 4.27 (m, 1H), 4.16 (s, 1H), 3.72 – 3.62 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.53, 137.50, 137.34, 137.10, 128.75, 128.66, 128.56, 128.46, 128.32, 128.22, 128.19, 128.16, 128.10, 127.92, 78.95, 77.99, 74.98, 73.82, 72.67, 71.27, 67.38, 61.66; HRMS Calcd for $C_{27}H_{28}N_3O_5$ $[M + H]^+$ = 474.2029, found 474.2029.

(2S,3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-methoxytetrahydro-2H-pyran (44)



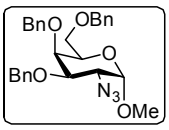
To a stirred solution of compound 3 (200 mg, 0. 480 mmol) and $TMSN_3$ (191 µL, 1.441 mmol) in dry CH_2Cl_2 (15 mL) at 0 °C was added $PhI(OCOCF_3)_2$ (413 mg, 0.961 mmol), TEMPO (15 mg, 0.096 mmol), Bu_4NHSO_4 (33 mg, 0.096 mmol) and MeOH (971 µL, 24.025 mmol). After the addition was completed, the reaction mixture was stirred at the same temperature for 1 h. Upon consumption of the starting material (TLC monitoring), it was quenched with aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (2 X 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over Na_2SO_4. Concentration in vacuo gave a crude residue which was purified by silica gel column chromatography with hexane:EtOAc eluent to afford **44** and **45** in 70% overall yield (165 mg) with α-anomer 40% (95 mg) β-anomer 30 % (70 mg) as a colorless oil. **Data for β-isomer:** R_f = 0.45 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 2922, 2109, 1454, 1052; ^{1}H



NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 16H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.72 – 4.64 (m, 2H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.44 (q, *J* = 11.8 Hz, 2H), 4.10 (d, *J* = 8.0 Hz,

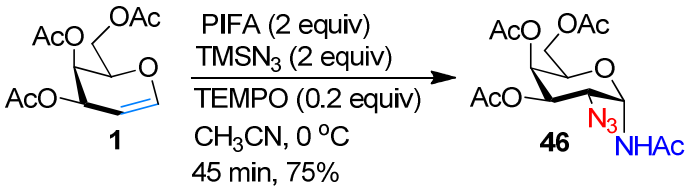
1H), 3.89 (d, *J* = 2.5 Hz, 1H), 3.80 (dd, *J* = 10.3, 8.0 Hz, 1H), 3.60 (dd, *J* = 8.3, 3.3 Hz, 2H), 3.53 (s, 3H), 3.41 (dt, *J* = 5.6, 4.3 Hz, 1H), 3.36 – 3.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.41, 137.90, 137.69, 128.64, 128.60, 128.37, 128.05, 128.02, 127.94, 127.80, 103.24, 80.97, 74.70, 73.72, 73.67, 72.61, 72.16, 68.66, 63.33, 57.12.; HRMS Calcd for $C_{28}H_{35}N_4O_5$ $[M + NH_4]^+$ = 507.2607, found 507.2606.

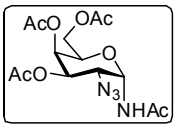
(2R,3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-methoxytetrahydro-2H-pyran(45)



Data for α-isomer: R_f = 0.50 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 2922, 2111, 1453, 1070; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 16H), 4.88 (d, *J* = 11.3 Hz, 1H), 4.80 (d, *J* = 2.4 Hz, 1H), 4.75 – 4.68 (m, 2H), 4.56 – 4.49 (m, 2H), 4.43 (dd, *J* = 11.7, 7.1 Hz, 1H), 4.01 (d, *J* = 6.4 Hz, 1H), 3.96 – 3.87 (m, 3H), 3.64 – 3.50 (m, 3H), 3.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.43, 137.98, 137.72, 128.67, 128.58, 128.44, 128.37, 128.28, 128.06, 128.01, 127.95, 127.86, 127.71, 99.14, 77.79, 74.93, 73.69, 73.58, 72.45, 69.63, 68.93, 60.18, 55.56; HRMS Calcd for $C_{28}H_{35}N_4O_5$ $[M + NH_4]^+$ = 507.2607, found 507.2606.

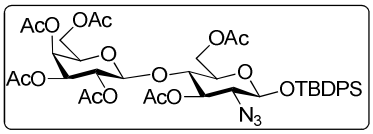
(2R,3R,4R,5R,6S)-6-acetamido-2-(acetoxymethyl)-5-azidotetrahydro-2H-pyran-3,4-diyldiacetate (46)





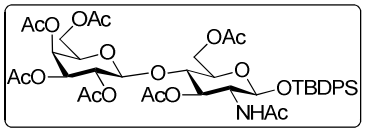
To a stirred solution of 1 (100 mg, 0. 367 mmol) and $TMSN_3$ (98 µL, 0.734 mmol) in CH_3CN (4 mL) at 0 °C was added $PhI(OCOCF_3)_2$ (316 mg, 0.734 mmol), TEMPO (12 mg, 0.073 mmol), After the addition was completed, the reaction mixture was stirred at same temperature for 45 min. Upon consumption of starting material (TLC monitoring), it was quenched with aqueous $NaHCO_3$ (3 mL) and extracted with CH_2Cl_2 (2 X 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over Na_2SO_4. Concentration in vacuo gave a crude residue which was purified by silica gel column chromatography with hexane:EtOAc eluent to afford **46** in 75 % yield (102 mg); R_f = 0.30 (hexane/EtOAc, 1:1); IR (neat) ν_{max} /cm^{-1} 2216, 2924, 2114, 1749, 1234; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 1H), 5.89 (dd, *J* = 7.5, 5.7 Hz, 1H), 5.37 (d, *J* = 2.9 Hz, 1H), 5.24 (dd, *J* = 11.1, 3.2 Hz, 1H), 4.18 (dd, *J* = 11.1, 5.4 Hz, 1H), 4.13 (t, *J* = 7.1 Hz, 2H), 4.09 – 4.04 (m, 1H), 2.18 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.56, 170.73, 170.37, 75.72, 69.74, 67.10, 66.95, 61.57, 56.85, 23.35, 20.82, 20.79, 20.72; HRMS Calcd for $C_{14}H_{20}N_4NaO_8$ $[M + Na]^+$ = 395.1179, found 395.1162.

(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R,6S)-4-acetoxy-2-(acetoxymethyl)-5-azido-6-((tert-butyldiphenylsilyl)oxy)tetrahydro-2H-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (47)



To a stirred solution of **38** (1 g, 1.615 mmol) in dry DMF (15 mL) was added imidazole (220 mg, 3.230 mmol), a catalytic amount of 4-(dimethylamino) pyridine (DMAP, 20 mg, 0.161 mmol) followed by *tert*-butylchlorodiphenylsilane (840 µL, 3.230 mmol) and stirring continued at room temperature for 10 h. Upon consumption of the starting material (TLC monitoring) DMF was removed under reduced pressure and the residue was diluted with Et_2O and extracted with cold ether (3 X 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over Na_2SO_4. Concentration in vacuo gave a crude residue which was purified by silica gel column chromatography with hexane:EtOAc eluent to afford **47** in 76 % yield (1.05 g) as a colorless syrup; R_f = 0.45 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = +21.5 (c 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 2112, 1751, 1369, 1222, 1063; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 4H), 7.47 – 7.28 (m, 6H), 5.07 – 4.97 (m, 1H), 4.96 – 4.83 (m, 2H), 4.50 – 4.35 (m, 2H), 4.25 – 4.09 (m, 2H), 4.09 – 3.96 (m, 2H), 3.93 (dd, *J* = 11.8, 5.5 Hz, 1H), 3.88 – 3.75 (m, 1H), 3.66 (t, *J* = 9.5 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.25 – 3.11 (m, 1H), 2.14 – 2.10 (s, 3H), 2.10 (s, 3H), 2.05 – 2.02 (s, 3H), 1.96 (s, 3H), 1.95 – 1.93 (s, 3H), 1.92 (s, *J* = 1.9 Hz, 3H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.32, 170.17, 170.14, 170.03, 169.43, 168.90, 135.91, 135.83, 135.66, 132.89, 132.22, 130.17, 129.92, 127.91, 127.76, 127.54, 127.45, 100.99, 96.54, 76.31, 72.56, 72.27, 71.04, 70.80, 69.21, 66.79, 66.76, 61.86, 60.99, 26.78, 26.73, 20.90, 20.64, 20.58, 20.50, 19.14, 19.08; HRMS Calcd for $C_{40}H_{55}N_4O_{16}Si$ $[M + NH_4]^+$ = 875.3382, found 875.3383.

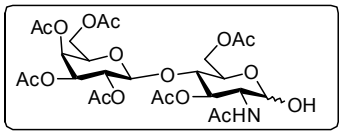
(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R,6S)-5-acetamido-4-acetoxy-2-(acetoxymethyl)-6-((tert-butyldiphenylsilyl)oxy)tetrahydro-2H-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (48)



To a solution of **47** (1 g, 1.165 mmol) in acetic anhydride (15 mL) at 0 °C was added Zn dust (2.536 g, 38.445) and acetic acid (5.991 mL, 104.850 mmol) and stirred at room temperature for 1 h. Upon consumption of the starting material (TLC monitoring), the reaction mixture was filtered through Celite and extracted with EtOAc (2 X 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over Na_2SO_4. Concentration in vacuo gave a residue which was purified by silica gel column chromatography with hexane:EtOAc eluent to afford **48** in 82 % yield (830 mg) as a colorless syrup. R_f = 0.30 (hexane/EtOAc, 1:1); $[\alpha]_D^{28}$ = +36.0 (c 0.5, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3364, 1751, 1369, 1227, 1059; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.57 (m, 7H), 7.47 – 7.30 (m, 10H), 5.80 (d, *J* = 8.5 Hz, 1H), 5.52 (d, *J* = 9.9 Hz, 1H), 5.34 (d, *J* = 3.3 Hz, 1H), 5.32 – 5.30 (m, 1H), 5.11 – 5.02 (m, 2H), 4.99 – 4.94 (m, 2H), 4.87 (dt, *J* = 10.4, 5.7 Hz, 2H), 4.77 (d, *J* = 1.4 Hz, 1H), 4.63 (ddd, *J* = 13.3, 8.1, 4.5 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.48 (dt, *J* = 13.7, 6.8 Hz, 2H), 4.33 (dd, *J* = 11.6, 2.2 Hz, 1H), 4.26 – 4.16 (m, 2H), 4.16 – 4.04 (m2H), 4.01 (dd, *J* = 11.7, 6.2 Hz, 1H), 3.88 (dt, *J* = 12.1, 6.5 Hz, 1H), 3.79 – 3.72 (m, 1H), 3.67 (t, *J* = 9.5 Hz, 1H), 3.39 – 3.23 (m, 1H), 2.11 (d, *J* = 3.5 Hz, 5H), 2.04 (dd, *J* = 7.2, 2.6 Hz, 10H), 2.03 – 1.97 (m, 11H), 1.94 (d, *J* = 1.5 Hz, 6H), 1.86 (s, 3H), 1.05 (d, *J* = 5.6 Hz, 13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.72, 170.64, 170.25, 170.20, 170.04, 170.00, 169.90, 169.87, 169.58, 169.13, 135.87, 135.67, 135.57, 135.41,

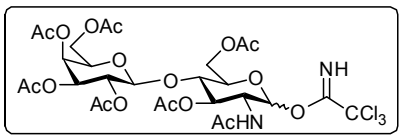
132.76, 132.69, 132.43, 132.04, 130.20, 130.05, 129.96, 129.87, 127.87, 127.66, 127.61, 127.40, 101.01, 100.69, 95.95, 93.74, 76.42, 74.33, 73.16, 72.67, 72.55, 72.39, 70.87, 70.81, 70.66, 70.47, 69.17, 66.72, 66.67, 62.68, 62.20, 60.94, 60.88, 55.29, 52.09, 26.86, 26.60, 26.57, 23.23, 23.15, 20.84, 20.75, 20.61, 20.57, 20.54, 20.49, 20.39, 19.06, 18.99; HRMS Calcd for $C_{42}H_{56}NO_{17}Si$ $[M + H]^+$ = 874.3318, found 874.3318.

(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R)-5-acetamido-4-acetoxy-2-(acetoxymethyl)-6-hydroxytetrahydro-2H-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (49)



To a stirred solution of **48** (700 mg, 0.800 mmol) in dry THF at 0 °C was added a freshly prepared buffered TBAF solution (1.7 mL) following a literature procedure[1b] and stirred for 15 min at same temperature. Upon consumption of the starting material (TLC monitoring), the reaction mixture was diluted with water and extracted with EtOAc (2 X 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over Na_2SO_4. Concentration in vacuo gave a residue which was purified by silica gel column chromatography with hexane:EtOAc eluent to afford **49** in 83 % yield (423 mg) as a colorless semi solid; R_f = 0.30 (hexane/EtOAc, 3:7); IR (neat) ν_{max} /cm^{-1} 3360, 1754, 1364, 1232, 1056; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (d, *J* = 9.7 Hz, 1H), 5.46 (t, *J* = 10.0 Hz, 1H), 5.38 – 5.27 (m, 2H), 5.14 (d, *J* = 3.0 Hz, 1H), 5.12 – 5.01 (m, 2H), 5.00 – 4.90 (m, 2H), 4.53 (t, *J* = 9.7 Hz, 1H), 4.40 (t, *J* = 9.7 Hz, 2H), 4.24 – 4.13 (m, 2H), 4.14 – 3.93 (m, 5H), 3.85 (t, *J* = 6.8 Hz, 1H), 3.73 (t, *J* = 9.4 Hz, 1H), 2.11 (d, *J* = 6.0 Hz, 4H), 2.08 (d, *J* = 6.9 Hz, 5H), 2.04 – 1.98 (m, 15H), 1.97 (s, 4H), 1.93 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.15, 171.00, 170.69, 170.57, 170.44, 170.17, 170.02, 169.91, 169.37, 100.97, 93.23, 91.51, 75.95, 74.56, 71.16, 70.95, 70.69, 70.48, 70.07, 69.70, 69.25, 68.44, 68.26, 66.68, 62.91, 62.23, 60.92, 60.73, 52.14, 50.89, 20.80, 20.69; HRMS Calcd for $C_{26}H_{38}NO_{17}$ $[M + H]^+$ = 636.2140, found 636.2133.

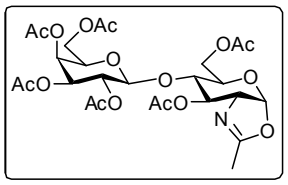
(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R)-5-acetamido-4-acetoxy-2-(acetoxymethyl)-6-(2,2,2-trichloro-1-iminoethoxy)tetrahydro-2H-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (50)



DBU (28 μL, 0.188 mmol) was added to a stirred solution of CCl_3CN (568 μL, 5.661 mmol) and **49** (400 mg, 0.629 mmol) in dry CH_2Cl_2 (10 mL) under nitrogen at 0 °C and stirred for 2 h. On consumption of the starting material (TLC monitoring), the reaction mixture was diluted with CH_2Cl_2 (5 ml) and further extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL), and then dried over Na_2SO_4. Concentration in vacuo gave a residue which was purified by silica gel column chromatography with hexane:EtOAc as eluent to afford **50** in 85% yield (418 mg) as colorless oil; R_f = 0.40 (hexane/EtOAc, 1:1); IR (neat) ν_{max} /cm^{-1} 3330, 1763, 1678; ^{1}H NMR (500 MHz, $CDCl_3$) mixture of anomers (α/β = 0.2:1) δ 8.76 (s, 1H), 6.28 (d, *J* = 3.7 Hz, 1H), 5.68 (d, *J* = 9.0 Hz, 1H), 5.37 – 5.32 (m, 1H), 5.29 (dd, *J* = 10.9, 9.1 Hz, 1H), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.95 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.54 (d, *J* = 7.9 Hz, 1H), 4.47 – 4.41 (m, 2H), 4.15 – 4.05 (m, 3H), 4.00 (ddd, *J* = 10.0, 4.1, 1.9 Hz, 1H), 3.89 (dd, *J* = 17.3, 7.8 Hz, 2H), 2.13 (s, 3H), 2.09 (d, *J* = 0.7 Hz, 6H), 2.05 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.33, 170.43, 170.36, 170.29, 170.17, 170.14, 169.28, 160.62, 101.43, C_1-β-94.81,

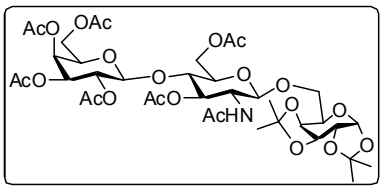
C_1-α-90.95, 75.82, 71.17, 71.04, 70.87, 69.32, 66.77, 61.73, 60.94, 52.07, 23.14, 20.99, 20.90, 20.73, 20.60; HRMS Calcd for $C_{28}H_{38}C_{l3}N_2O_{17}$ $[M + H]^+$ = 779.1236, found 779.1235.

(2S,3R,4S,5S,6R)-2-(((3aR,5R,6S,7R,7aR)-7-acetoxy-5-(acetoxymethyl)-2-methyl-5,6,7,7a-tetrahydro-3aH-pyrano[3,2-d]oxazol-6-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (51)



To a solution of **50** (400 mg, 0.512 mmol) in dry CH_2Cl_2 at –30 °C was added TMSOTf (19 µl, 0.102 mmol), and the resulting mixture was stirred at the same temperature for 1.5 h. After the reaction was complete (TLC monitoring), it was quenched with aqueous $NaHCO_3$ (3 mL) and extracted with CH_2Cl_2 (2 X 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over Na_2SO_4. Concentration in vacuo gave a crude residue which was purified by silica gel column chromatography with hexane:EtOAc eluent to afford **52** in 74 % yield (234 mg) as a colorless syrup. R_f = 0.30 (hexane/EtOAc, 3:7); IR (neat) ν_{max} /cm^{-1} 3328, 1759, 1672; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (d, *J* = 7.3 Hz, 1H), 5.62 (d, *J* = 1.5 Hz, 1H), 5.35 (dd, *J* = 3.4, 0.7 Hz, 1H), 5.15 (dd, *J* = 10.3, 8.0 Hz, 1H), 4.99 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 4.19 (dd, *J* = 12.0, 2.3 Hz, 1H), 4.16 – 4.07 (m, 3H), 4.05 (dd, *J* = 12.0, 5.8 Hz, 1H), 3.93 (t, *J* = 6.5 Hz, 1H), 3.64 (d, *J* = 9.4 Hz, 1H), 3.50 – 3.45 (m, 1H), 2.14 (s, 3H), 2.09 – 2.07 (m, 9H), 2.02 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.67, 170.40, 170.14, 169.52, 169.34, 166.95, 102.48, 99.21, 78.08, 71.13, 70.99, 70.61, 68.98, 67.65, 67.00, 65.09, 63.64, 61.19, 21.08, 20.86, 20.77, 20.73, 20.72, 20.61, 13.99; HRMS Calcd for $C_{26}H_{36}NO_{16}$ $[M + H]^+$ = 618.2034, found 618.2032.

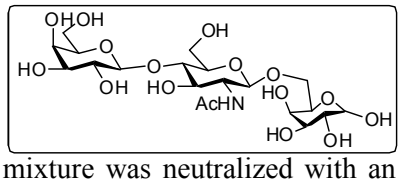
(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R,6R)-5-acetamido-4-acetoxy-2-(acetoxymethyl)-6-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)tetrahydro-2H-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (53)



To a mixture of **51** (100 mg, 0.162 mmol), compound **52** (64 mg, 0.242 mmol) and freshly activated molecular sieves (4Å, 50 mg) in dry CH_2Cl_2 (4 mL) at room temperature under nitrogen were added $Yb(OTf)_3$ (30 mg, 0.048 mmol) and the solution refluxed for 16 h. Upon consumption of the starting material (TLC monitoring), the solids were filtered off through a pad of Celite and washed with CH_2Cl_2. Concentration of solvent in vacuo gave a residue which was purified by silica gel column chromatography with hexane:EtOAc as eluent to afford **53** in 68% yield (97 mg) as a colorless oil; R_f = 0.20 (hexane/EtOAc, 2:8); IR (neat) ν_{max} /cm^{-1} 3335, 1751, 1668, 1286; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 (d, *J* = 9.2 Hz, 1H), 5.52 (d, *J* = 5.1 Hz, 1H), 5.35 (d, *J* = 3.3 Hz, 1H), 5.11 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.03 (dd, *J* = 9.9, 8.6 Hz, 1H), 4.96 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.61 – 4.55 (m, 2H), 4.52 – 4.46 (m, 2H), 4.30 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.18 – 4.03 (m, 6H), 3.96 – 3.90 (m, 2H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.81 (t, *J* = 8.8 Hz, 1H), 3.70 (dd, *J* = 12.7, 8.9 Hz, 1H), 3.64 – 3.56 (m, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 1.96 (d, *J* = 1.5 Hz, 6H), 1.50 (s, 3H), 1.44 (s, 3H), 1.31 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.80, 170.55, 170.51, 170.47, 170.27, 170.16, 169.40, 109.56, 108.80, 101.97, 101.18, 96.43, 76.07, 73.34, 72.92, 71.24, 71.10, 70.89, 70.45, 69.33, 68.89, 68.83, 68.56, 66.83, 62.47, 60.98, 53.50, 26.27, 26.11,

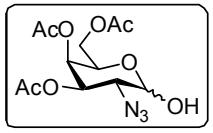
25.10, 24.46, 23.42, 21.01, 20.77, 20.64; HRMS Calcd for $C_{38}H_{56}NO_{22}$ $[M + H]^+$ = 878.3294, found 878.3293.

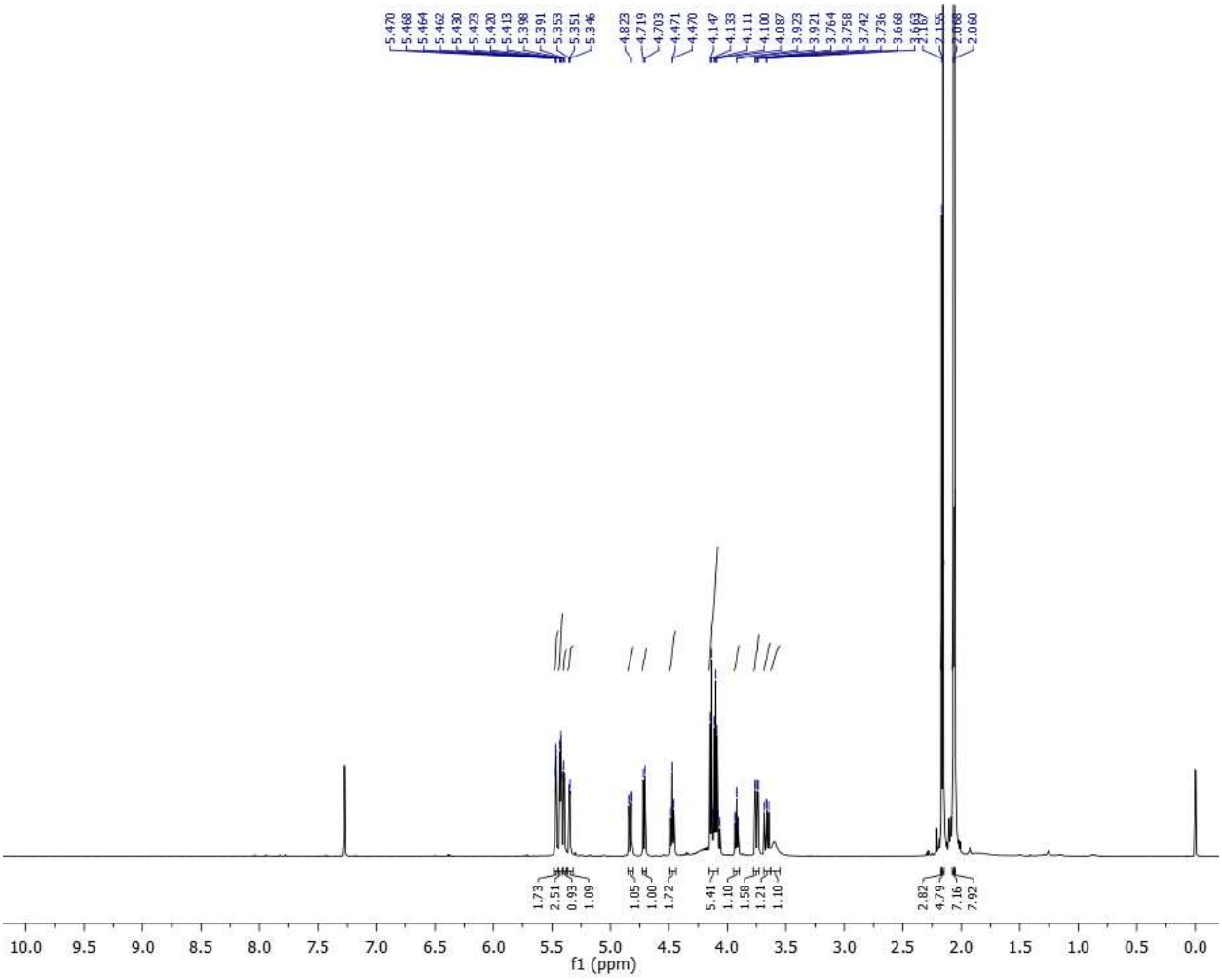
N-((2R,3R,4R,5S,6R)-4-hydroxy-6-(hydroxymethyl)-2-(((2R,3R,4S,5R)-3,4,5,6-tetrahydroxytetrahydro-2H-pyran-2-yl)methoxy)-5-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2H-pyran-3-yl)acetamide (54)



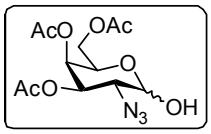
Compound **53** (75 mg, 0.085 mmol) was dissolved in dry CH_3OH (2 mL), Na metal (10 mg, 0.004 mmol) was added to it at 0 °C and stirred under nitrogen for 20 min at same temperature. Upon consumption of the starting material (TLC monitoring), reaction mixture was neutralized with an acidic ion exchange resin (Amberlite IR-120), filtered through cotton plug and the solvent removed under vacuum. The resulting crude product was dissolved in mixture of trifluoroacetic acid/water (9:1) (1 mL) and stirred for 15 min at room temperature. The product was purified by washing with excess of ethanol. The solvent was decanted, and the residue was dried under vacuum to afford pure product **54** (31 mg, 67%) as a white solid; m.p. = 156-158 °C; $[\alpha]_D^{28}$ = +0.083 (c 0.3, H_2O); IR (neat) ν_{max} /cm^{-1} 3425, 1648, 1071, 1031; ^1H NMR (500 MHz, D_2O) δ 4.61 (d, *J* = 6.1 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 6.3 Hz, 1H), 3.95 – 3.55 (m, 18H), 2.07 (s, 3H). ^{13}C NMR (125 MHz, D_2O) δ 174.79, 103.03, 101.64, 96.59, 78.63, 75.48, 74.88, 73.79, 72.80, 72.66, 72.46, 72.01, 71.10, 69.33, 69.13, 69.03, 68.80, 68.69, 61.13, 60.20, 57.56, 55.14, 22.31; HRMS Calcd for $C_{20}H_{34}NO_{16}$ [M–H] = 544.1878, found 544.1873.

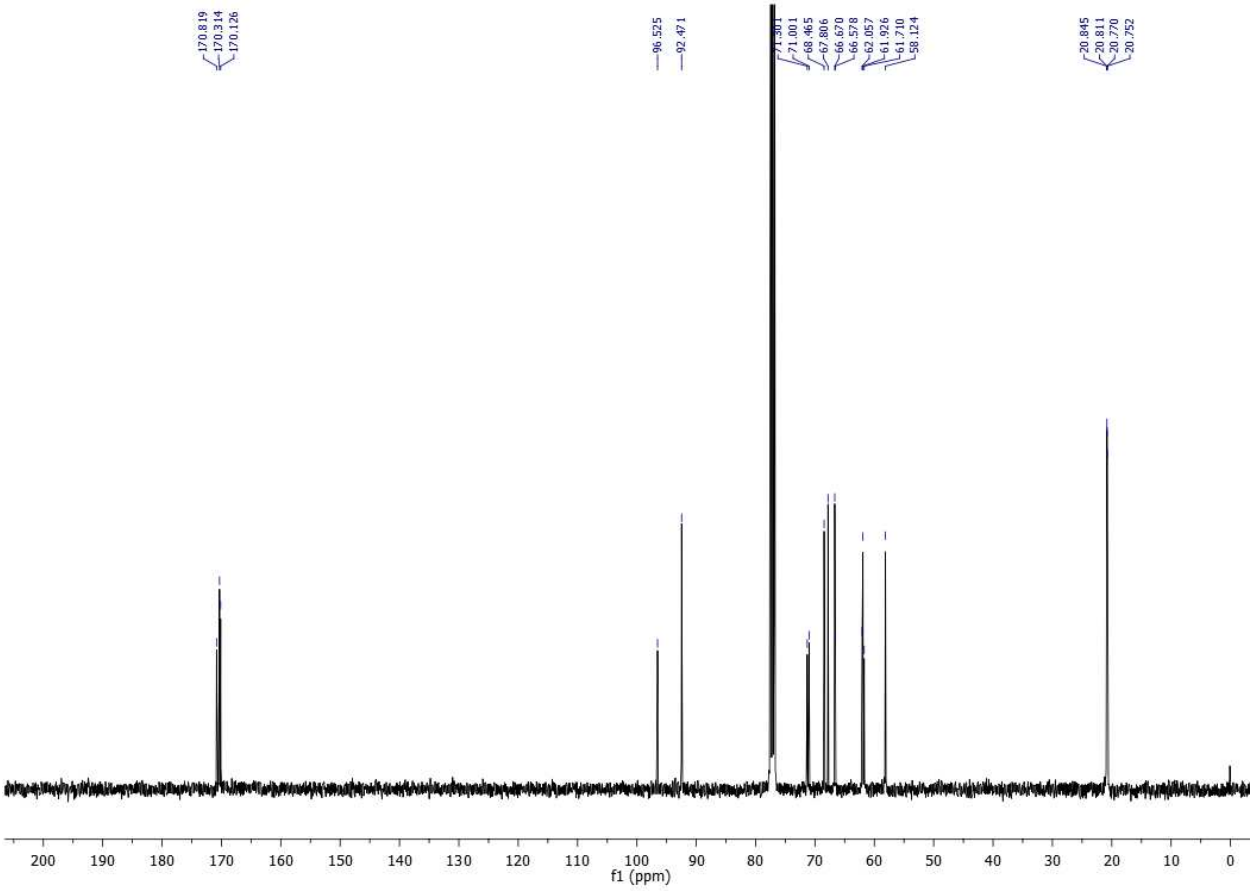
5. NMR Spectra



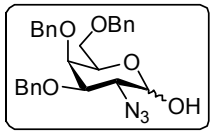


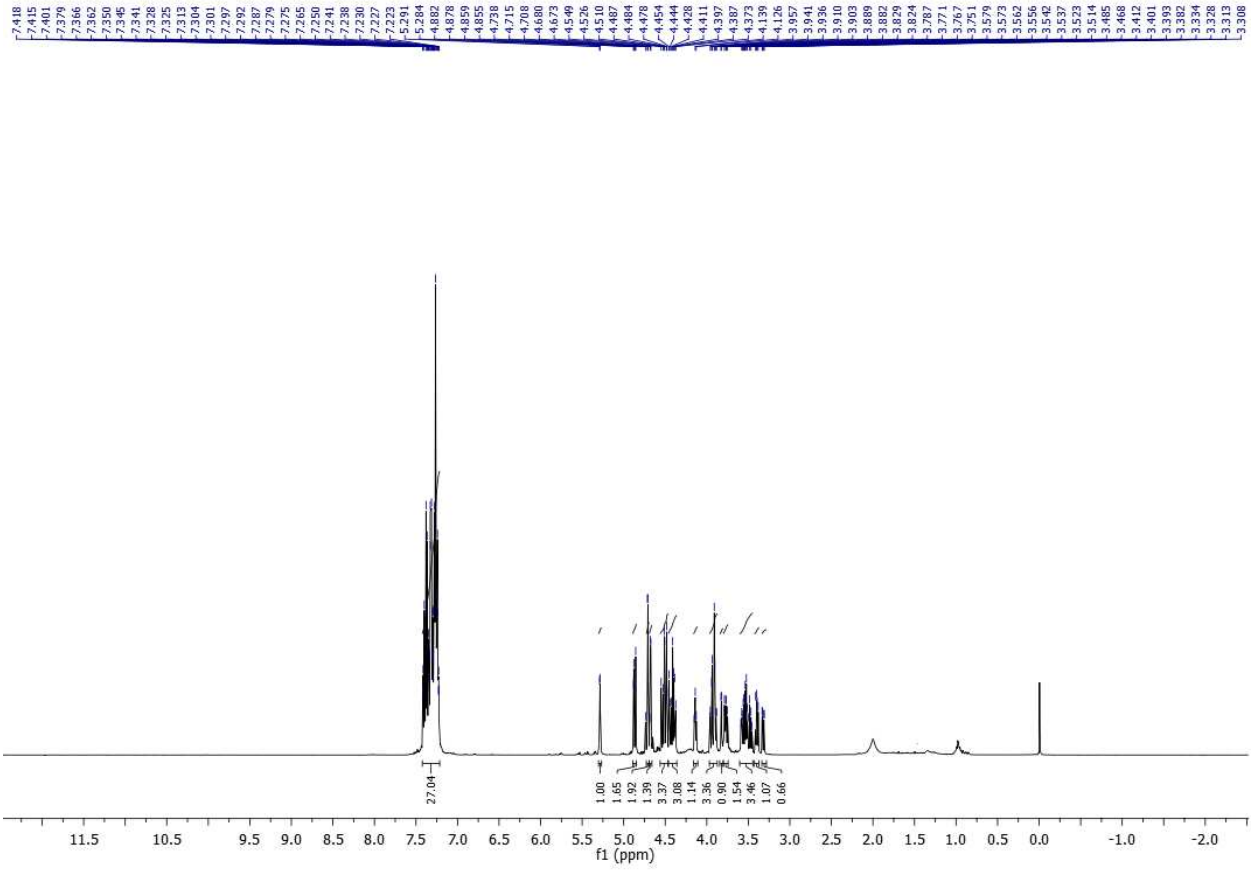
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2**



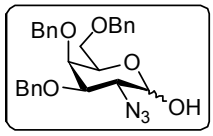


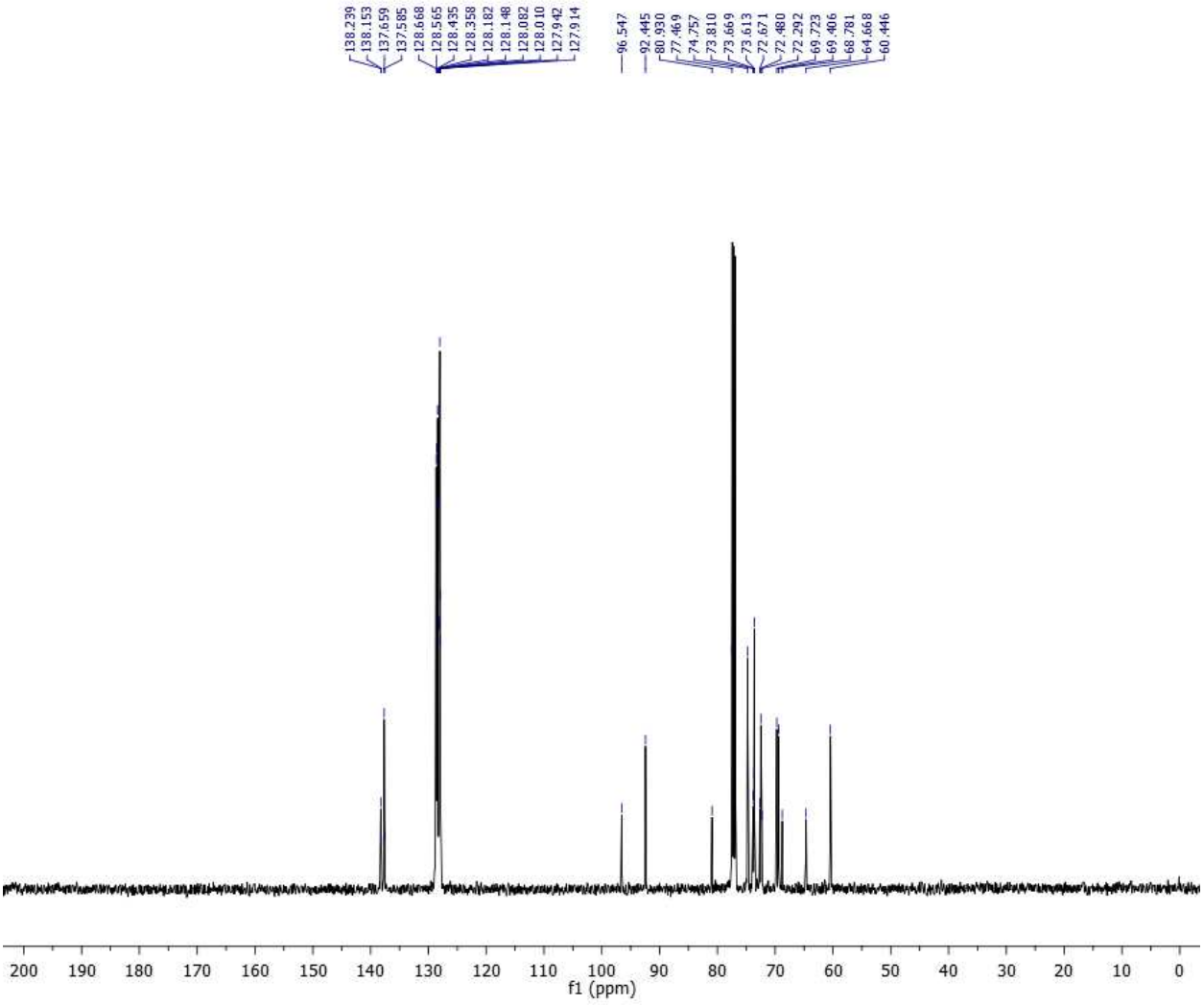
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2**



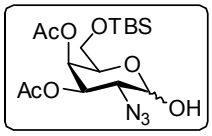


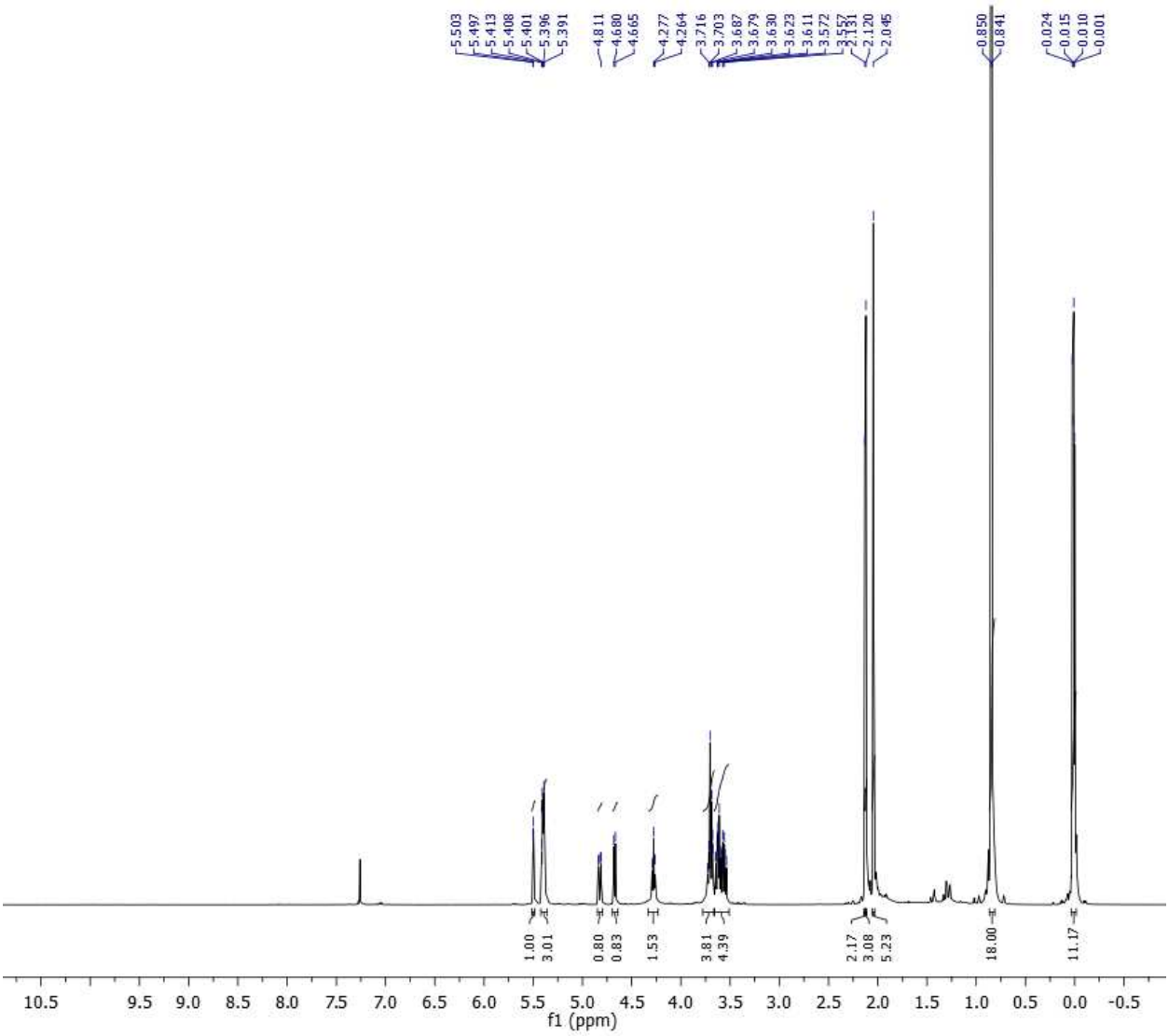
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4**



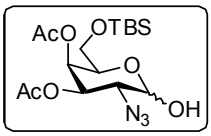


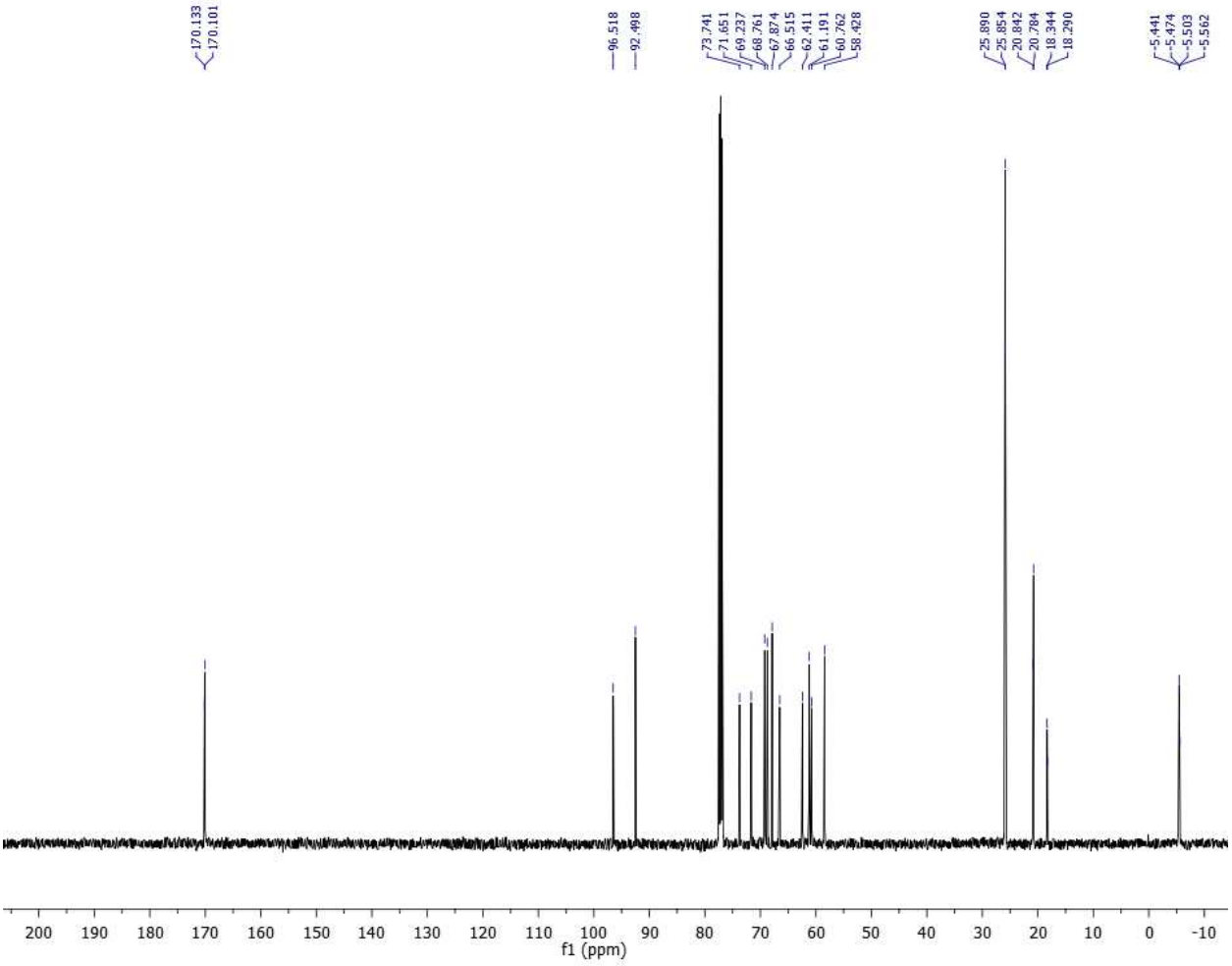
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **4**



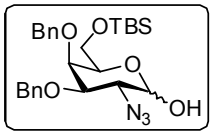


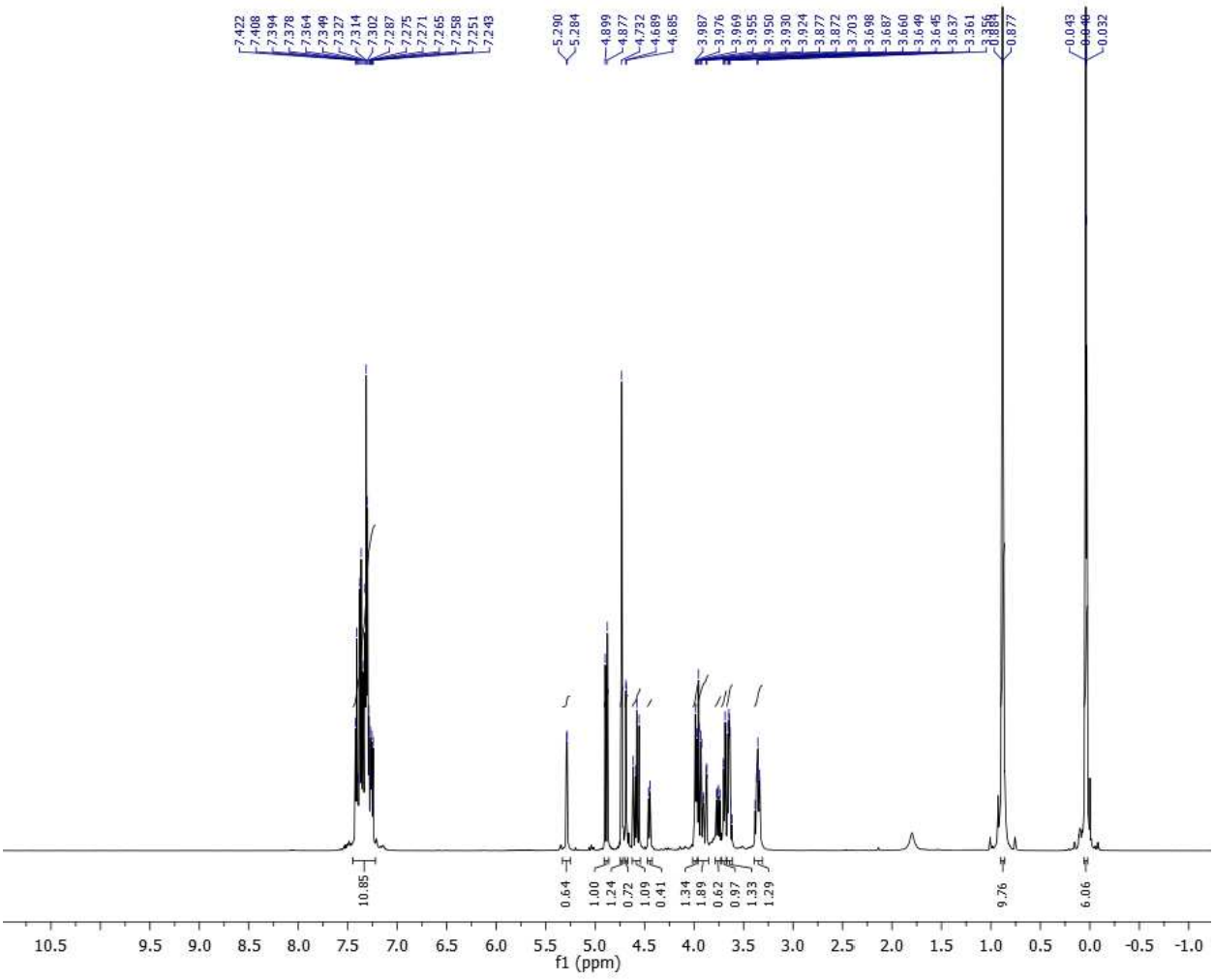
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6**



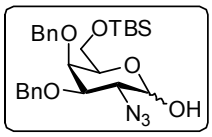


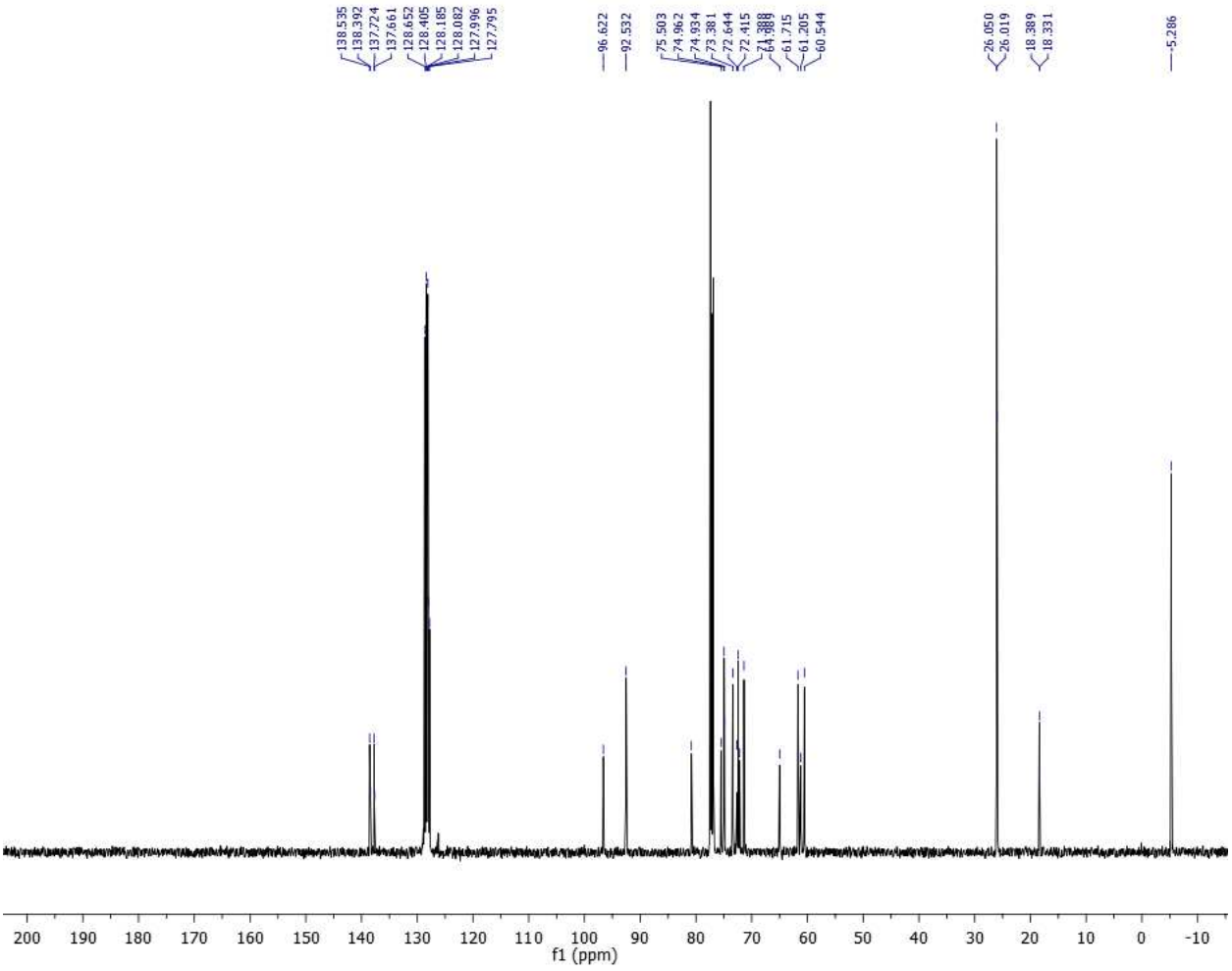
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **6**



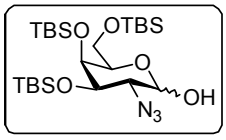


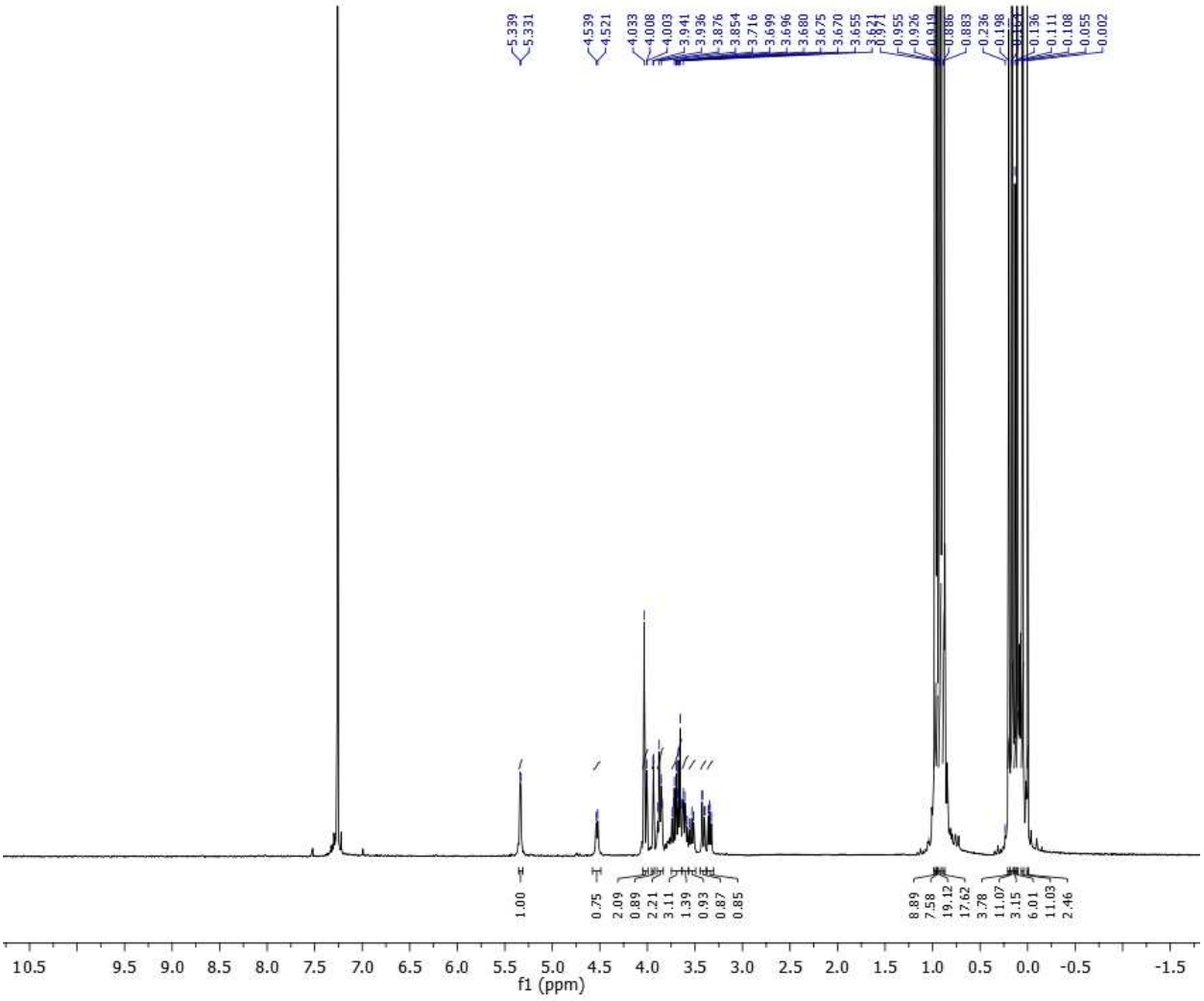
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **8**



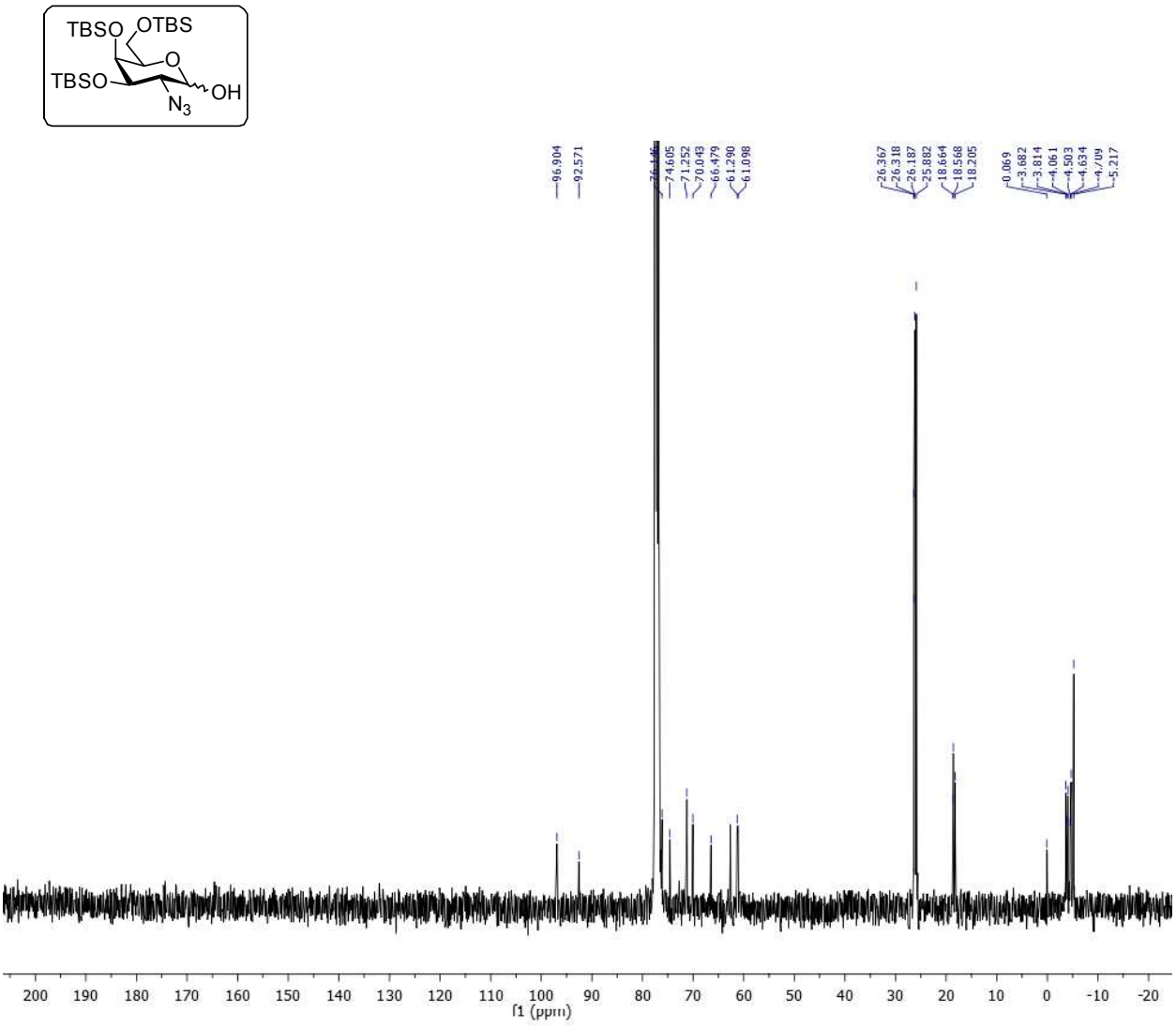


^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **8**

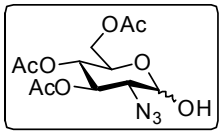


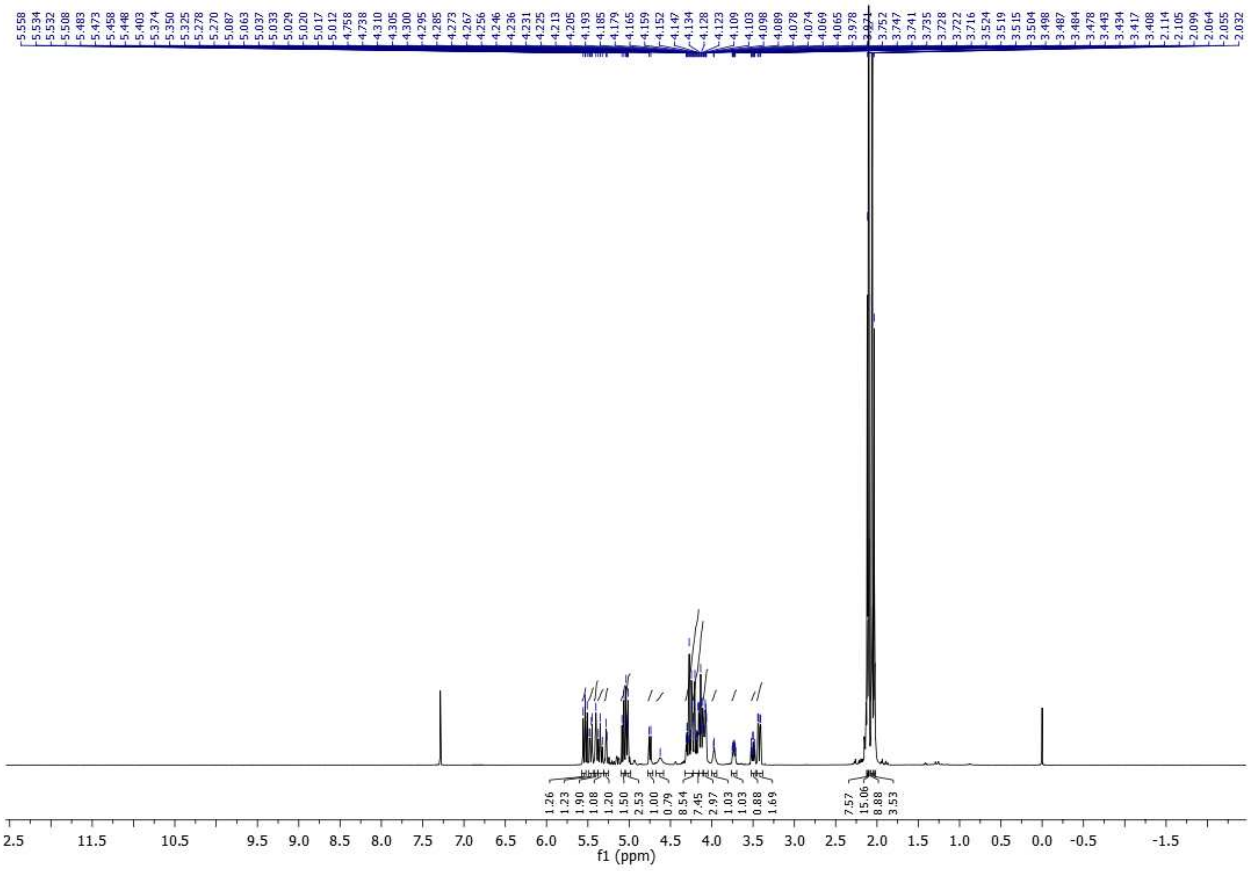


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**

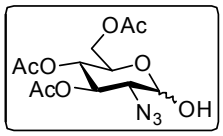


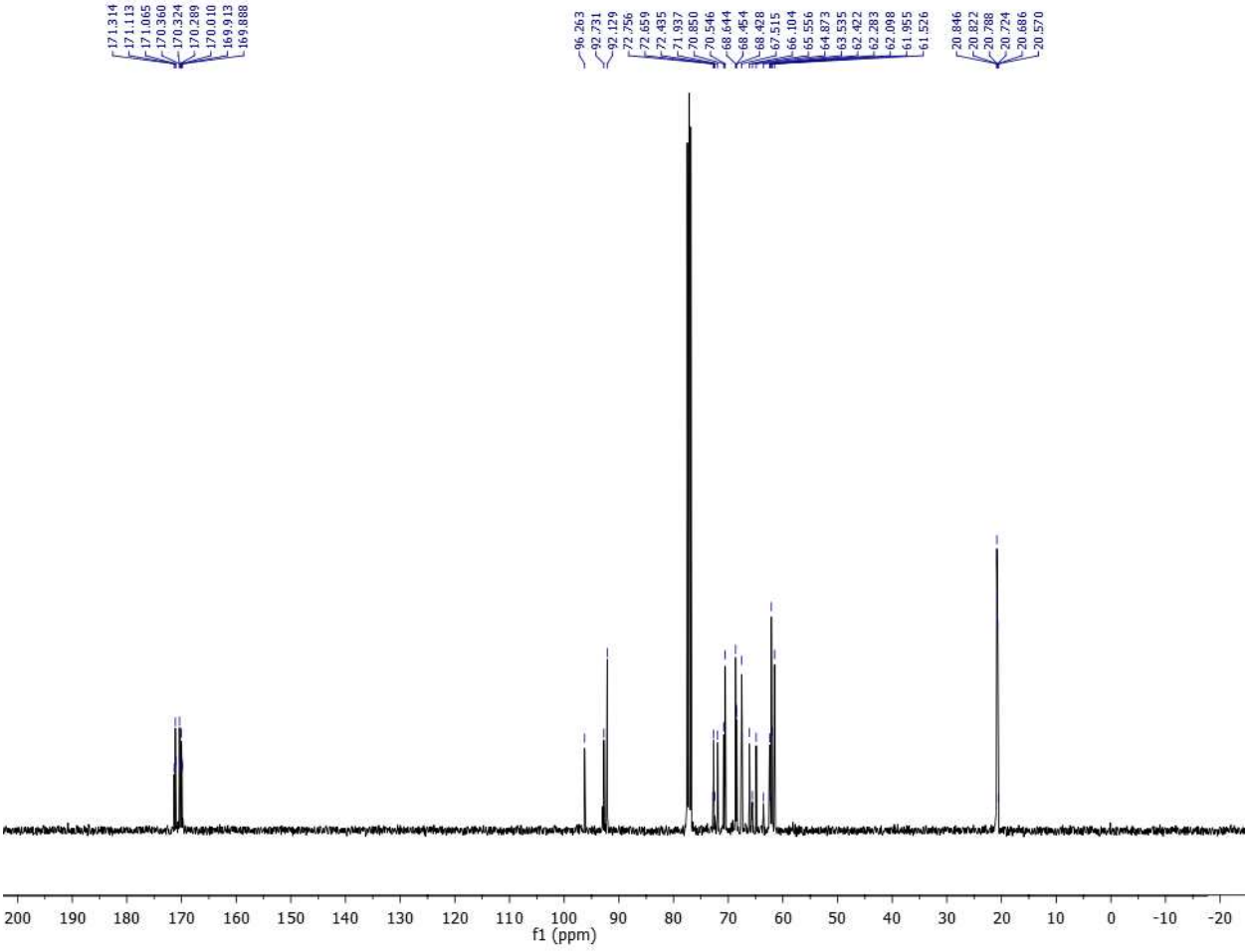
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **10**



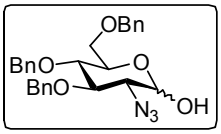


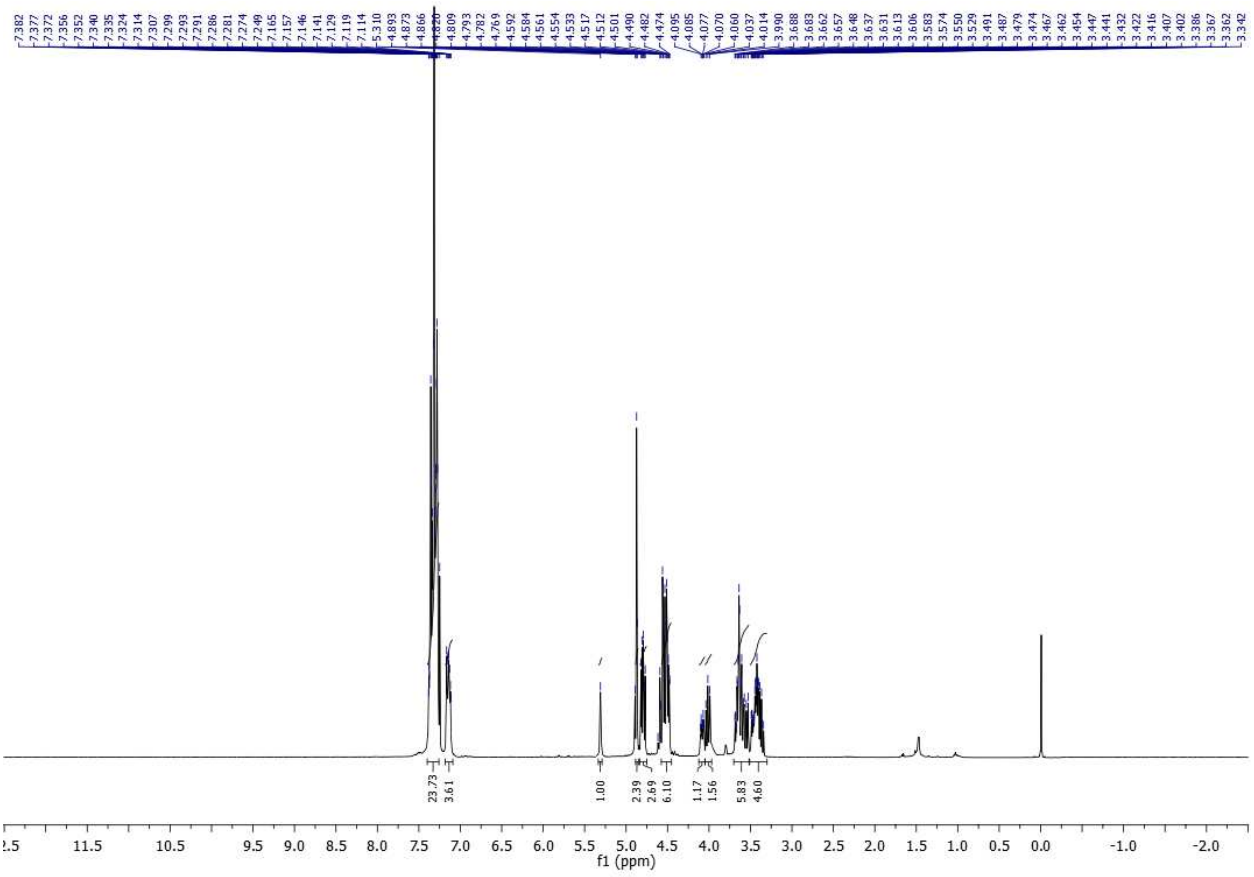
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **12**



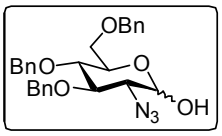


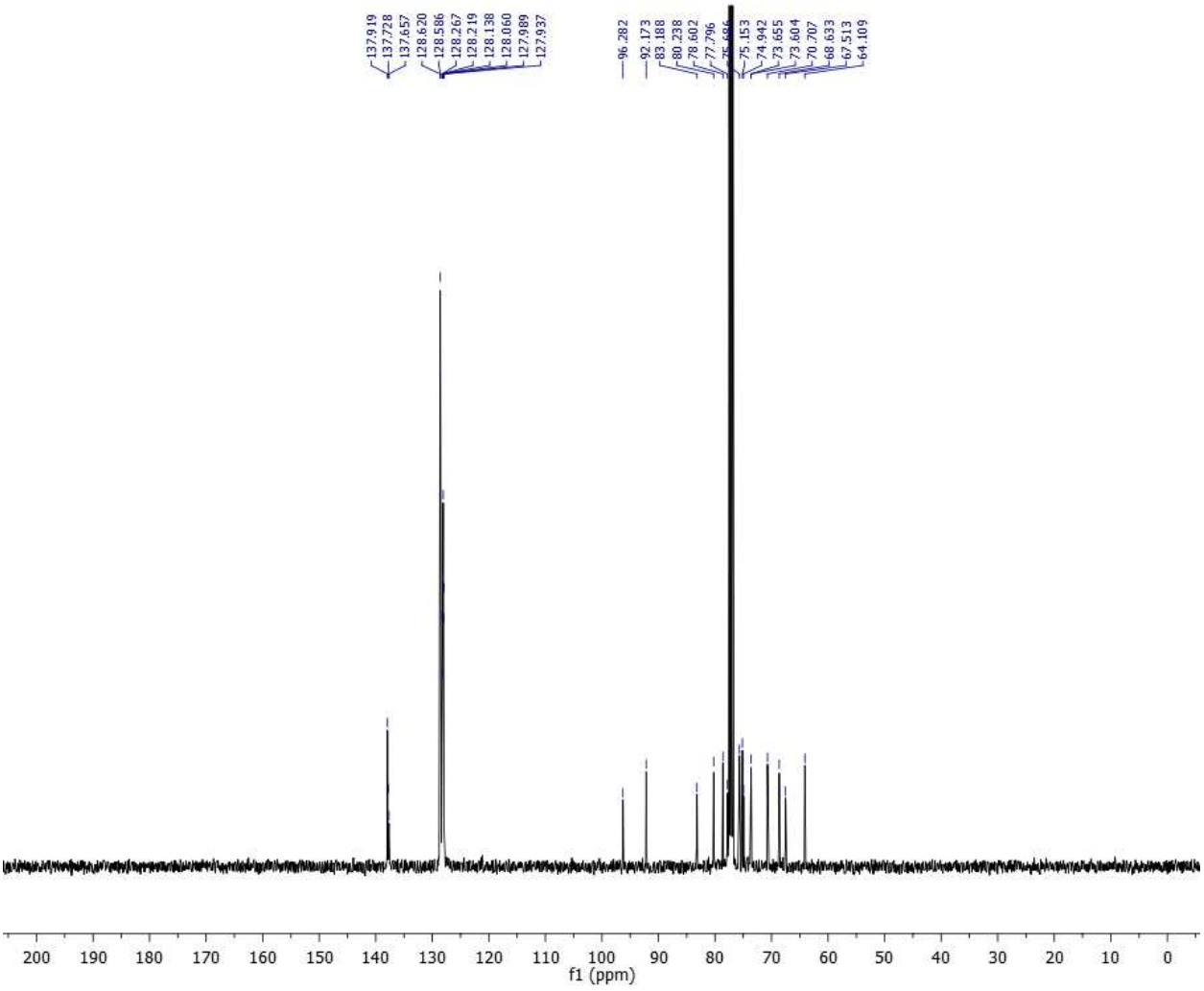
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **12**



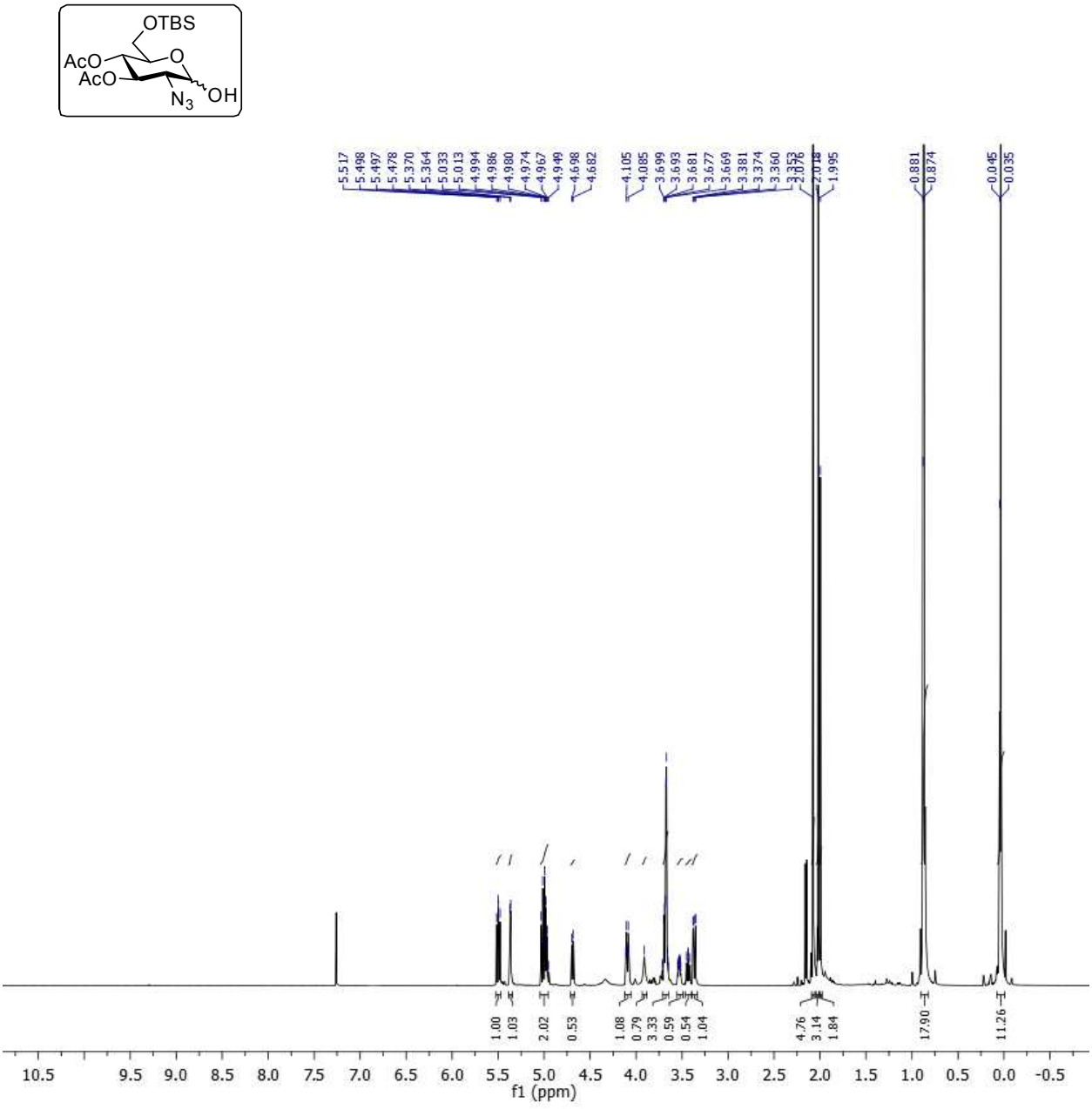


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**

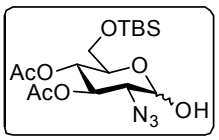


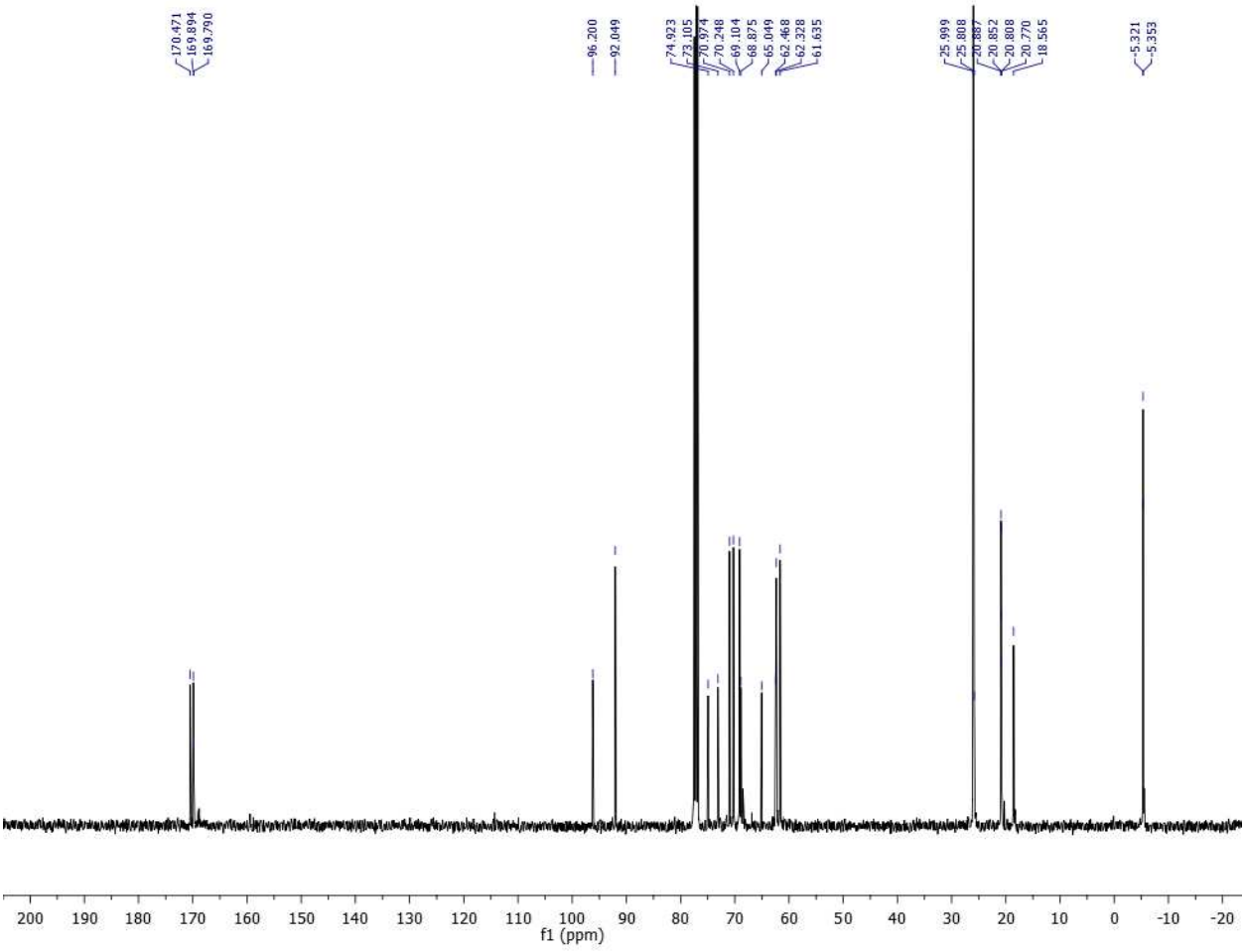


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **14**

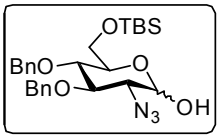


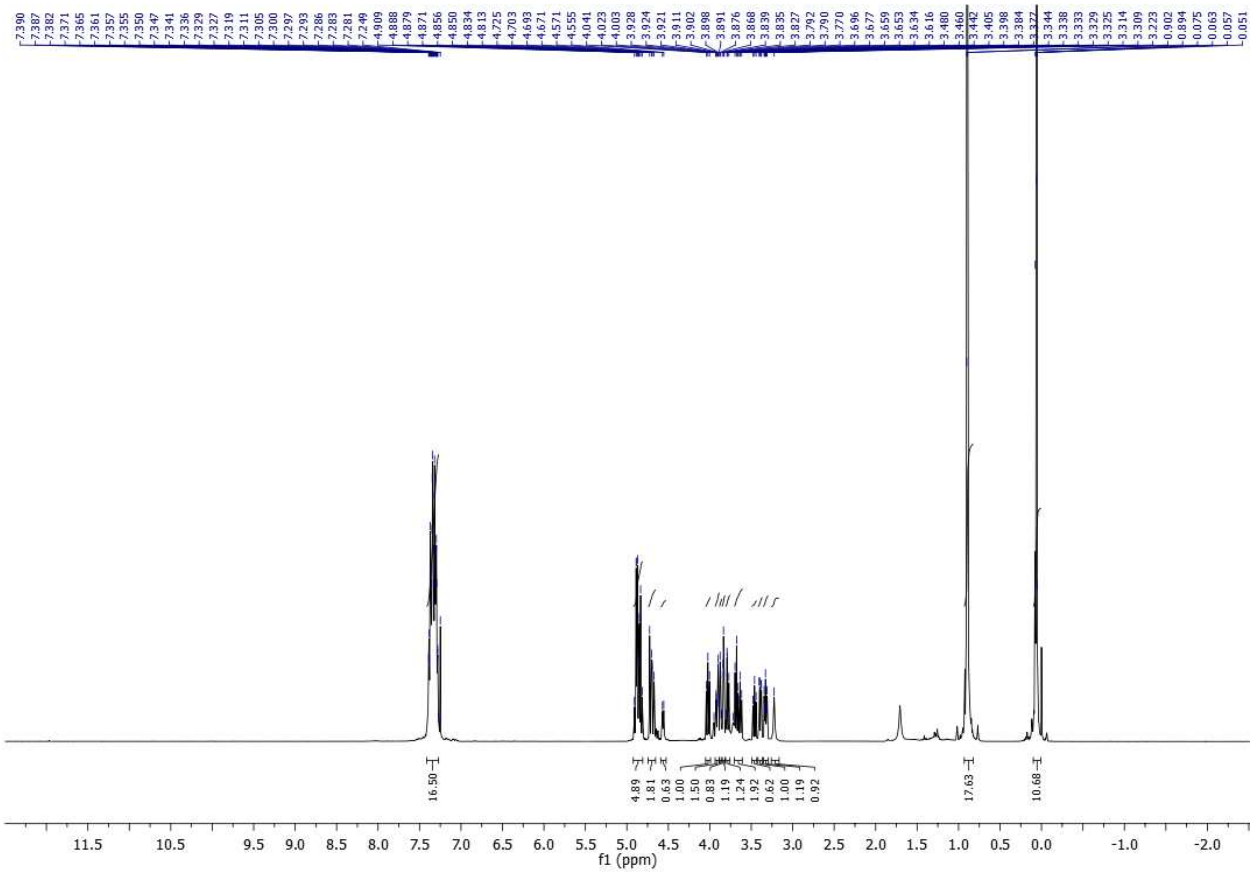
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **16**



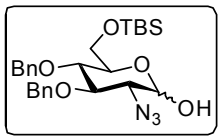


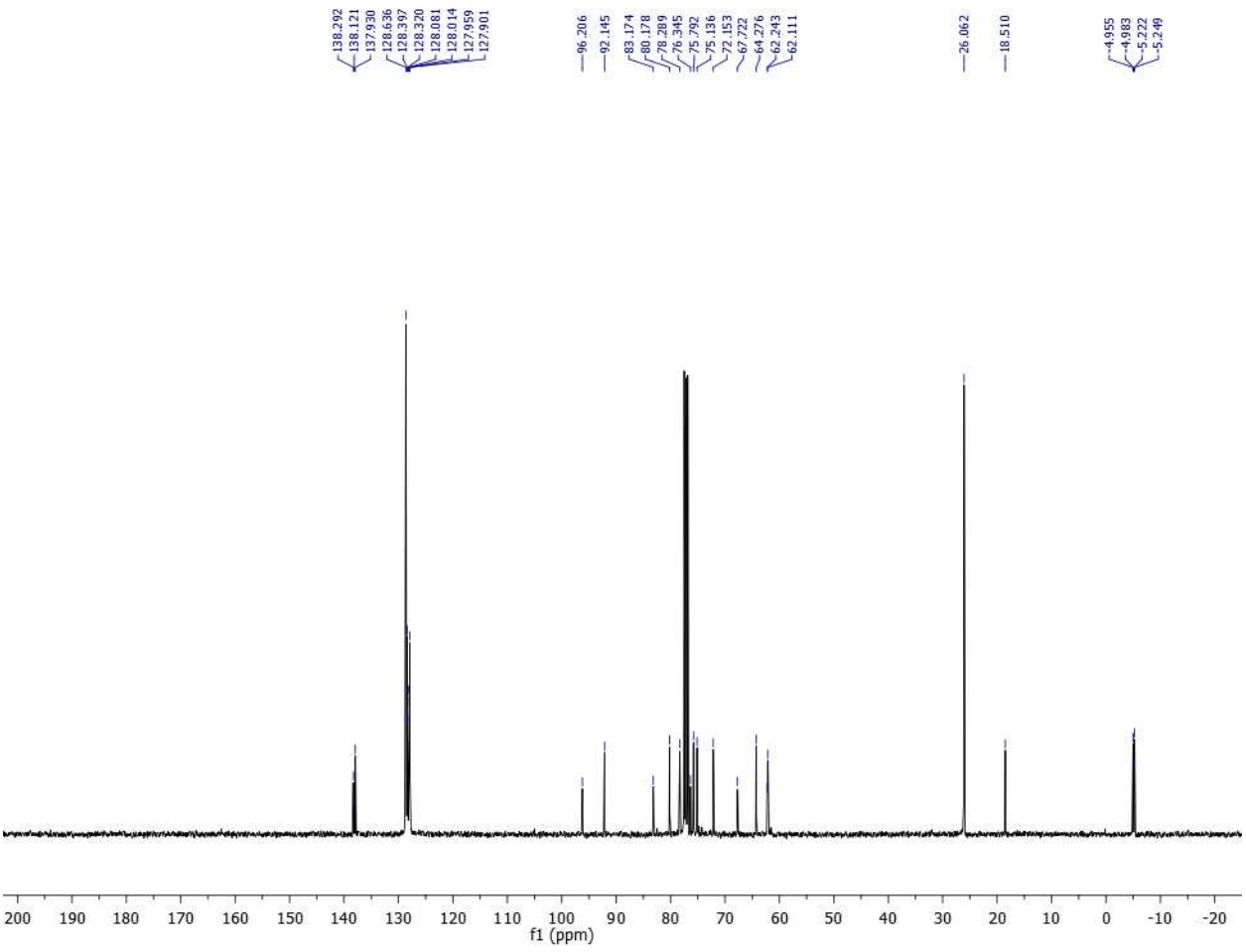
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **16**



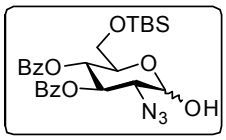


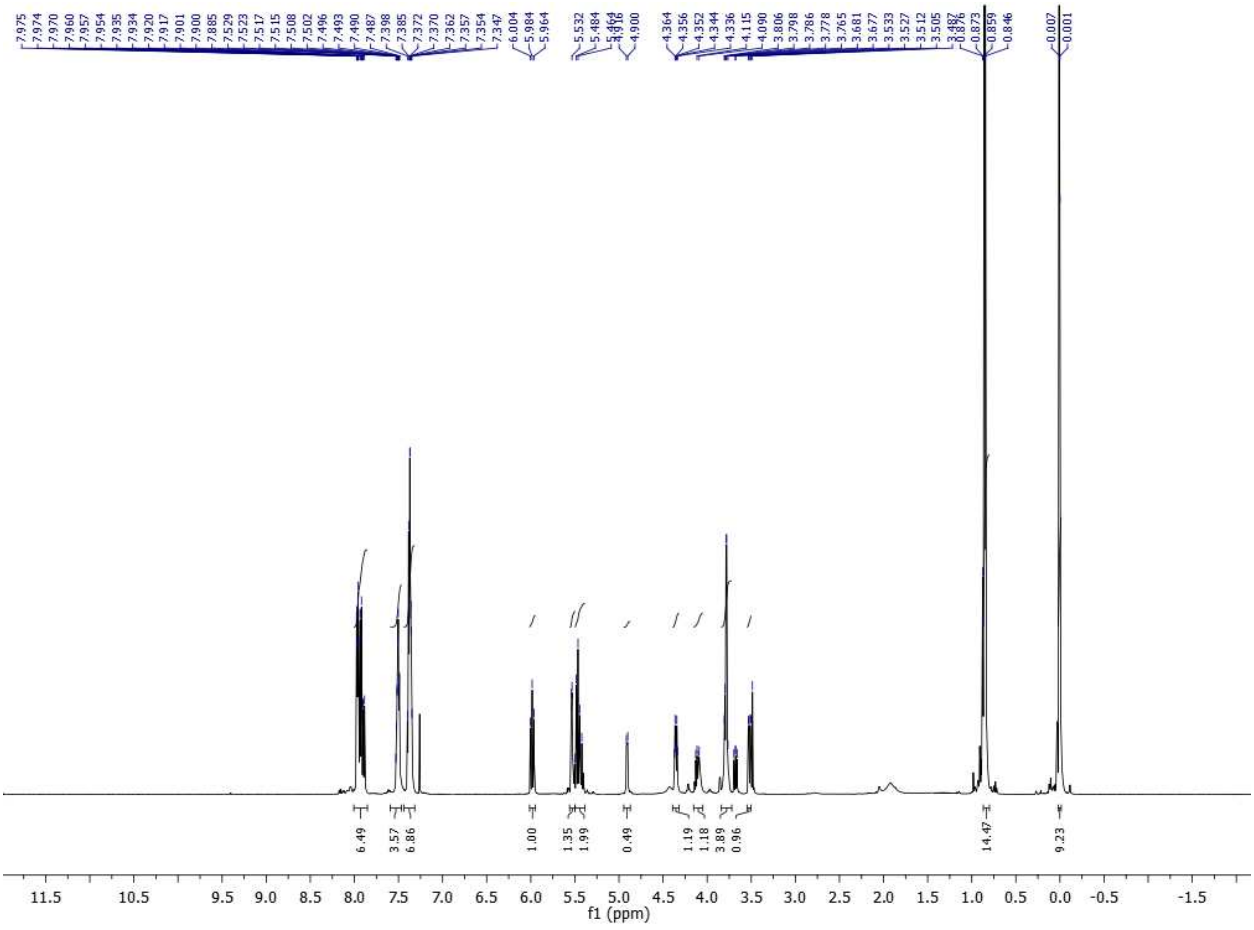
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **18**



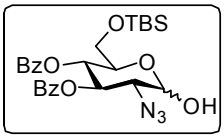


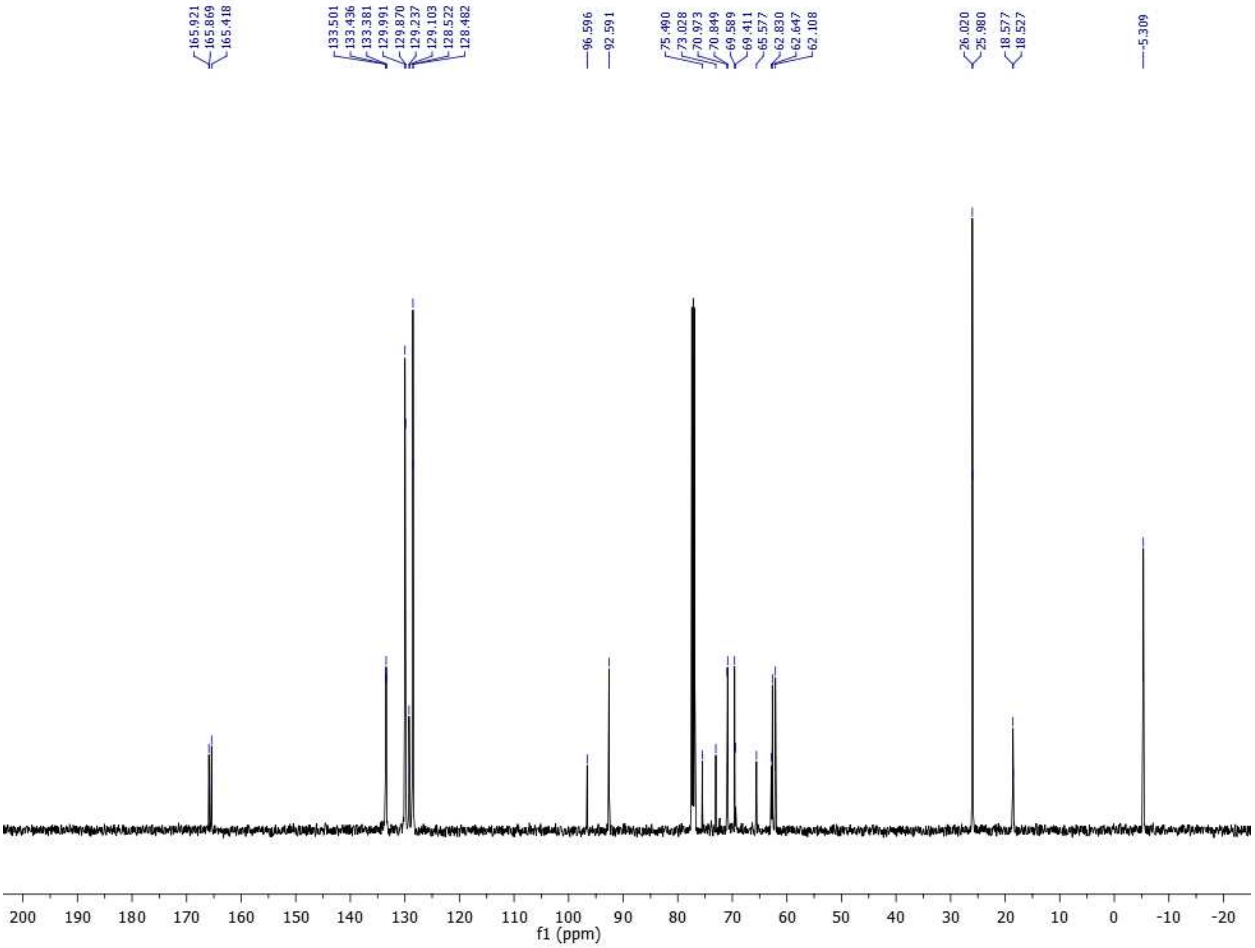
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **18**



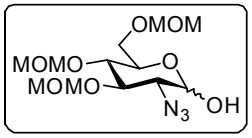


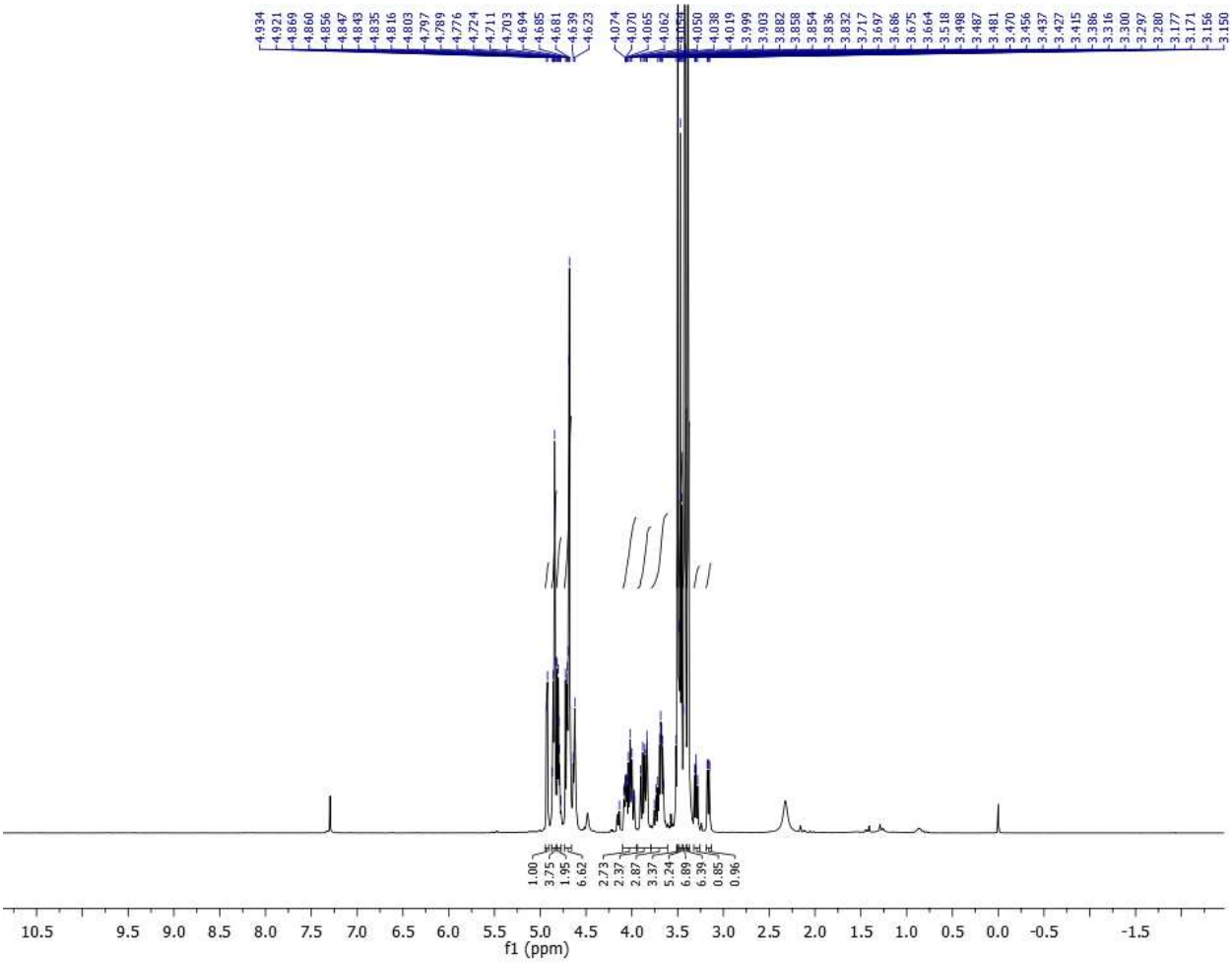
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **20**



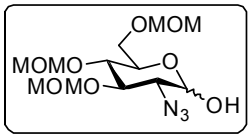


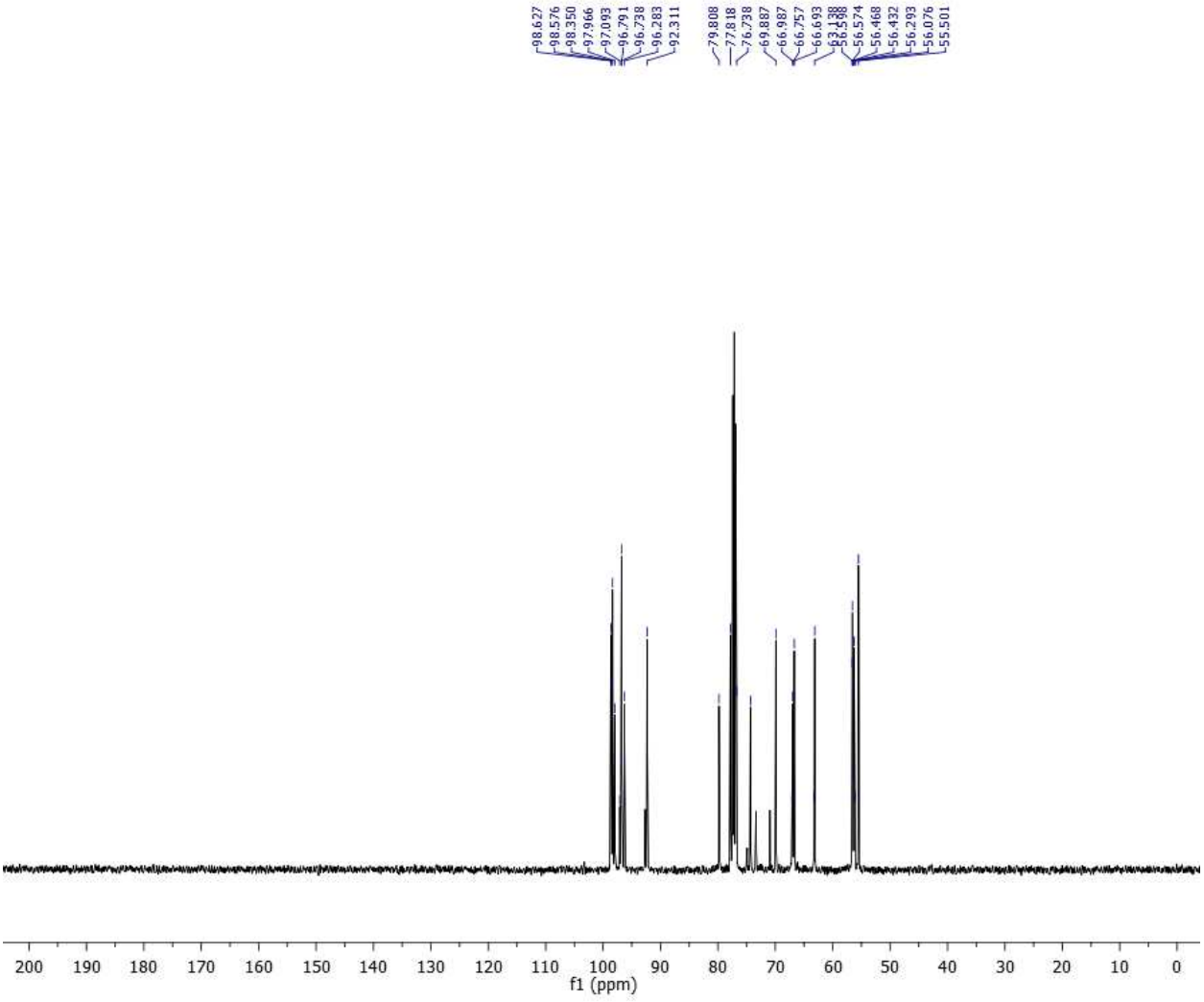
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **20**



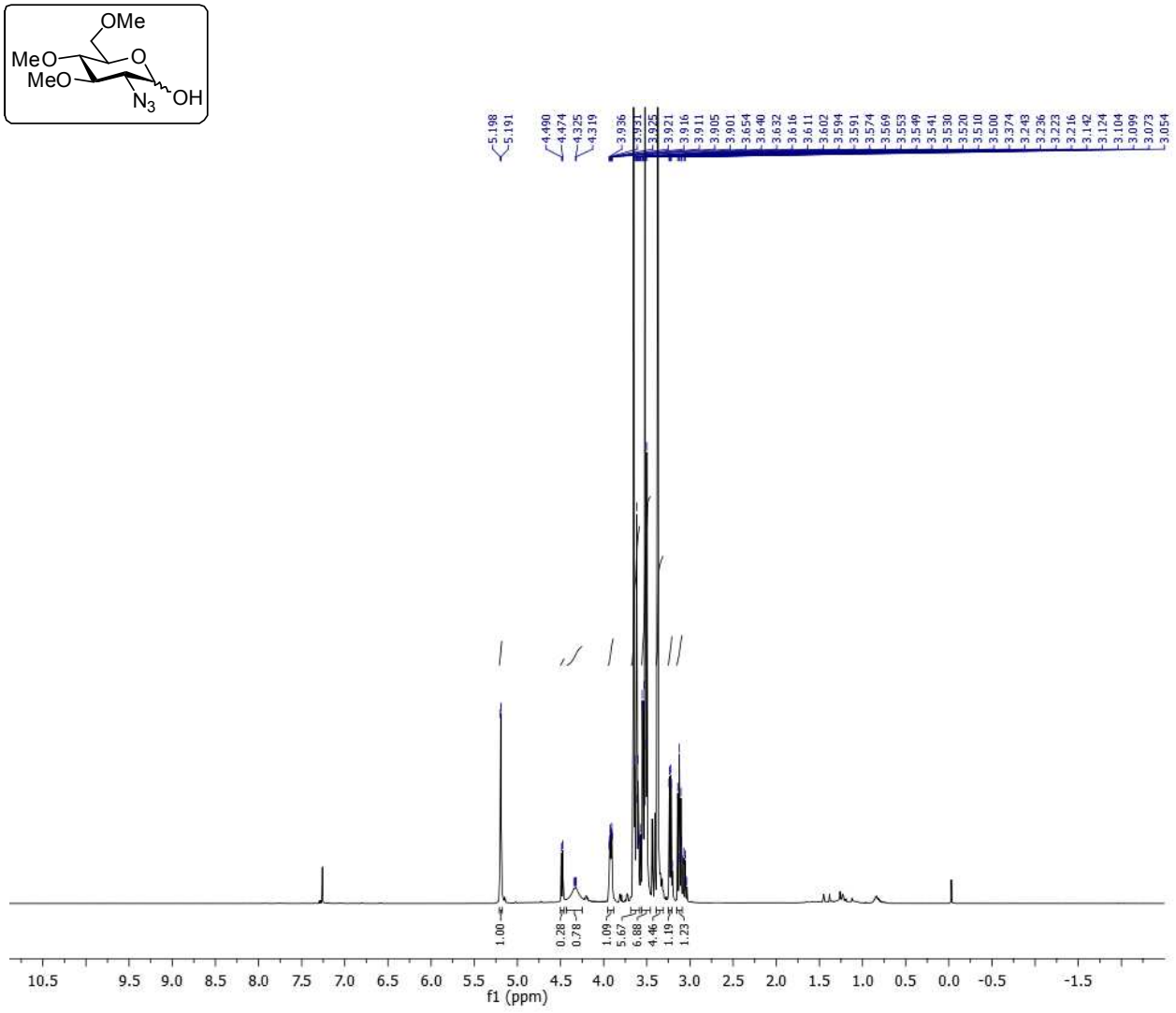


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **22**

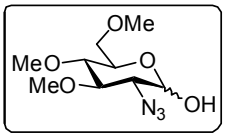


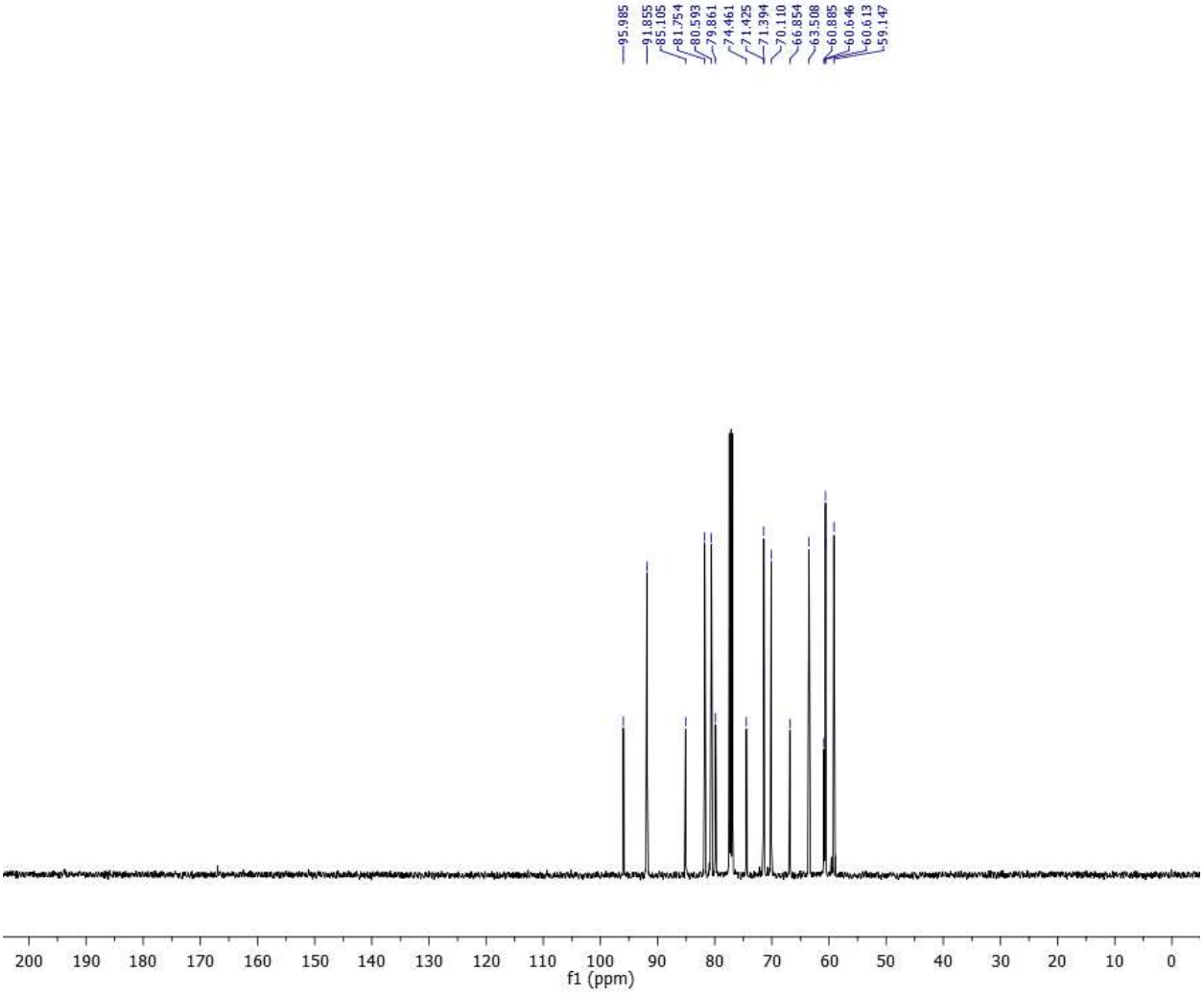


^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **22**

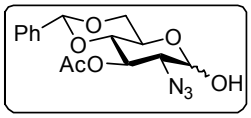


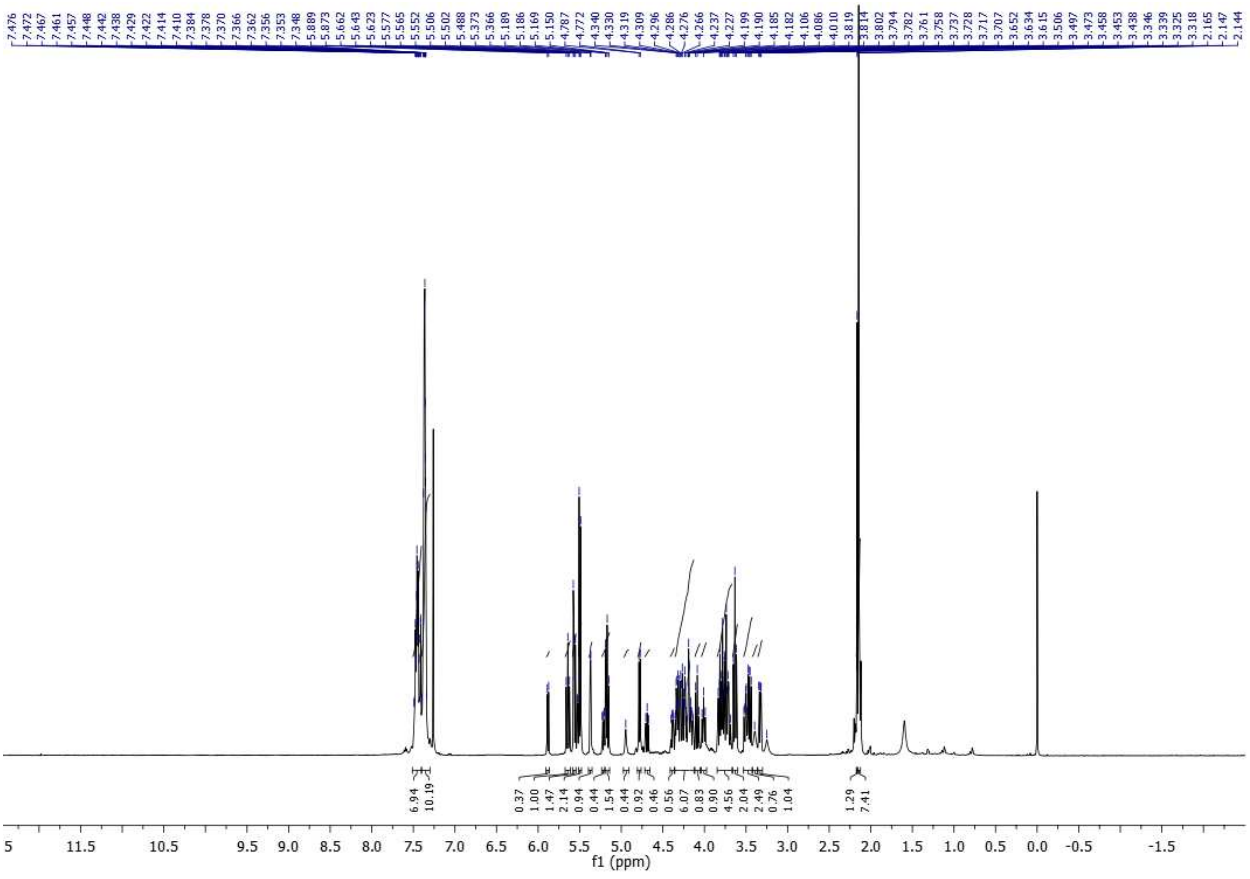
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **24**



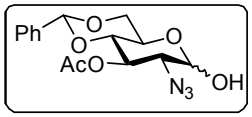


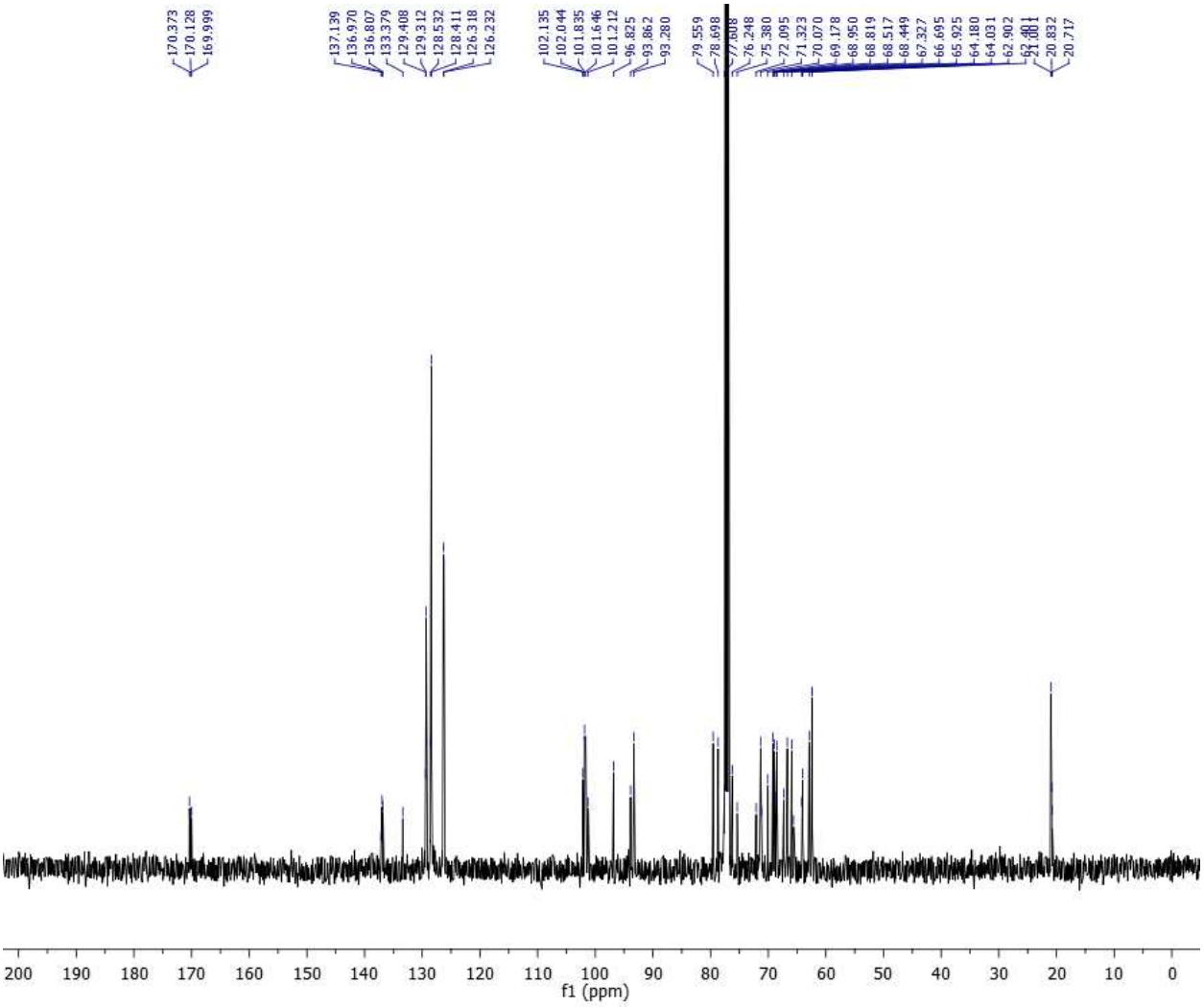
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **24**



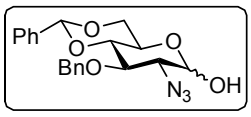


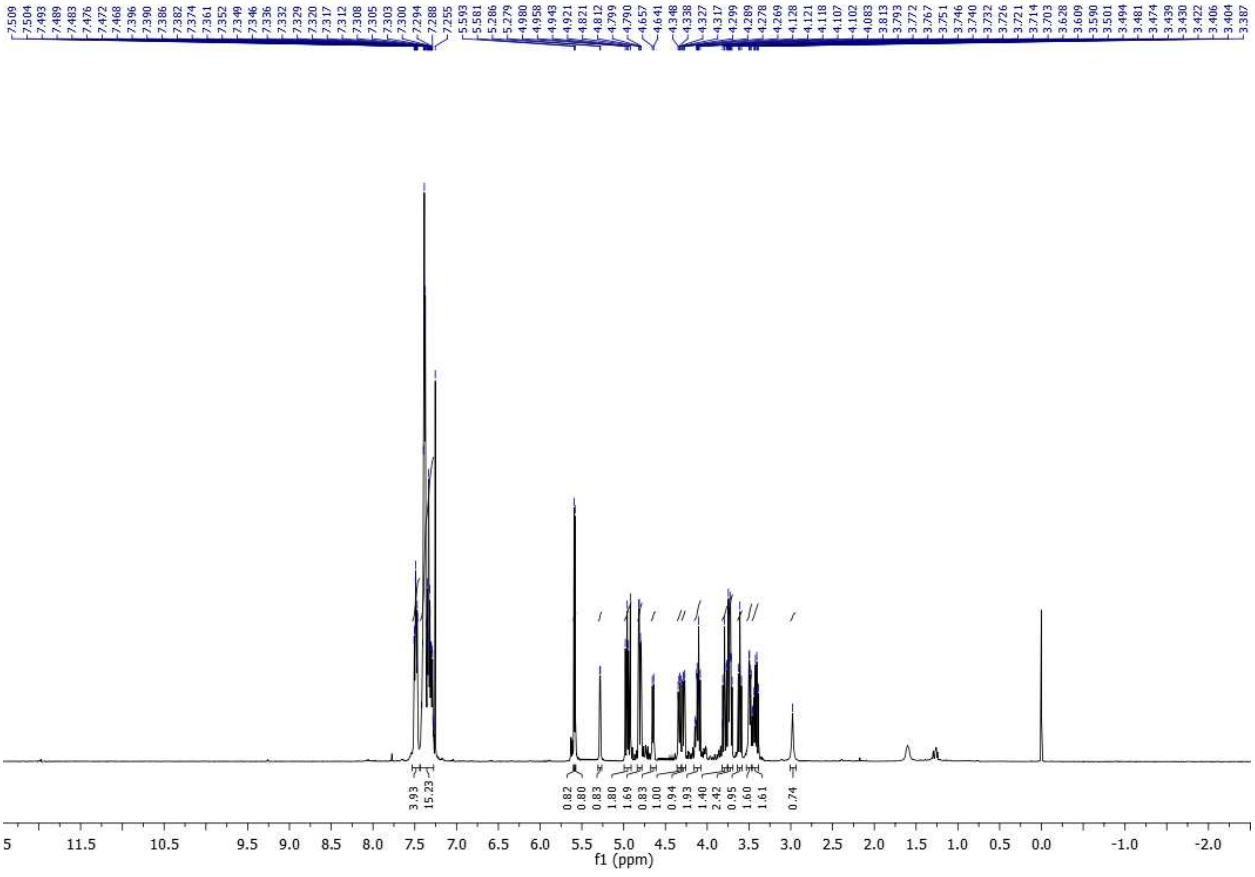
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **26**



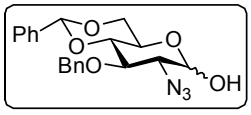


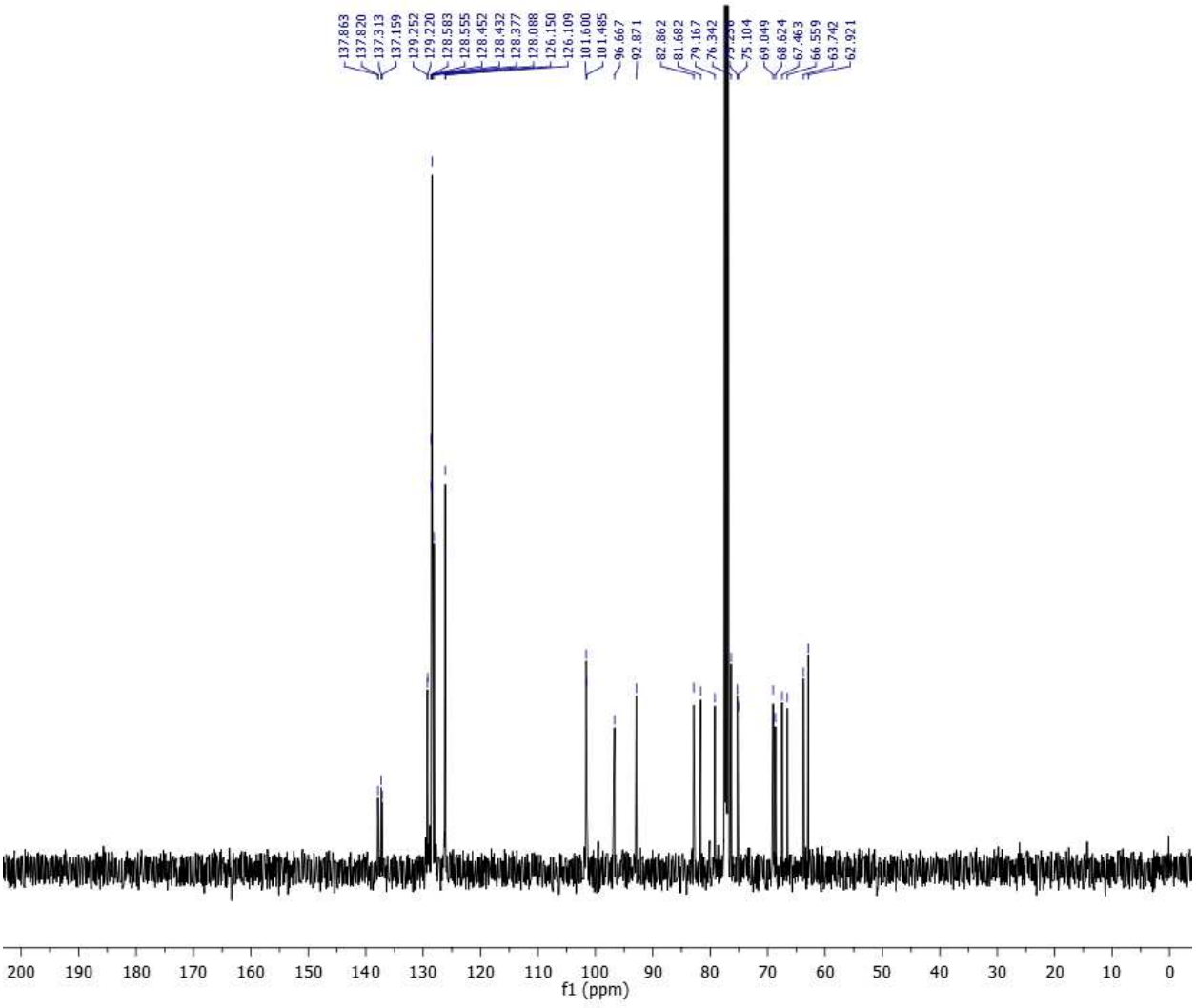
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **26**



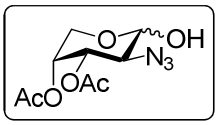


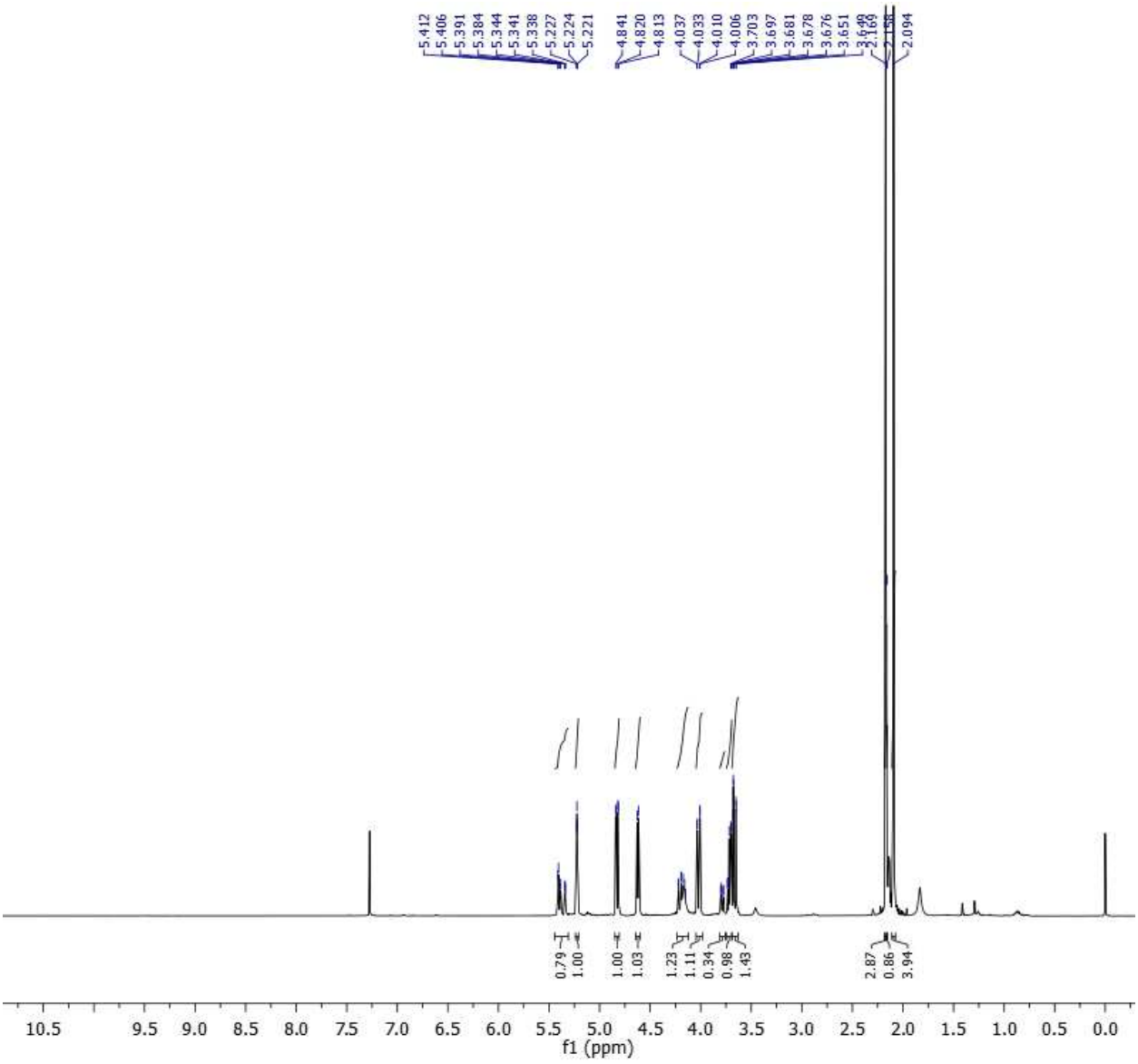
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **28**



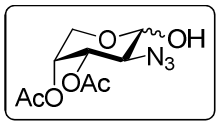


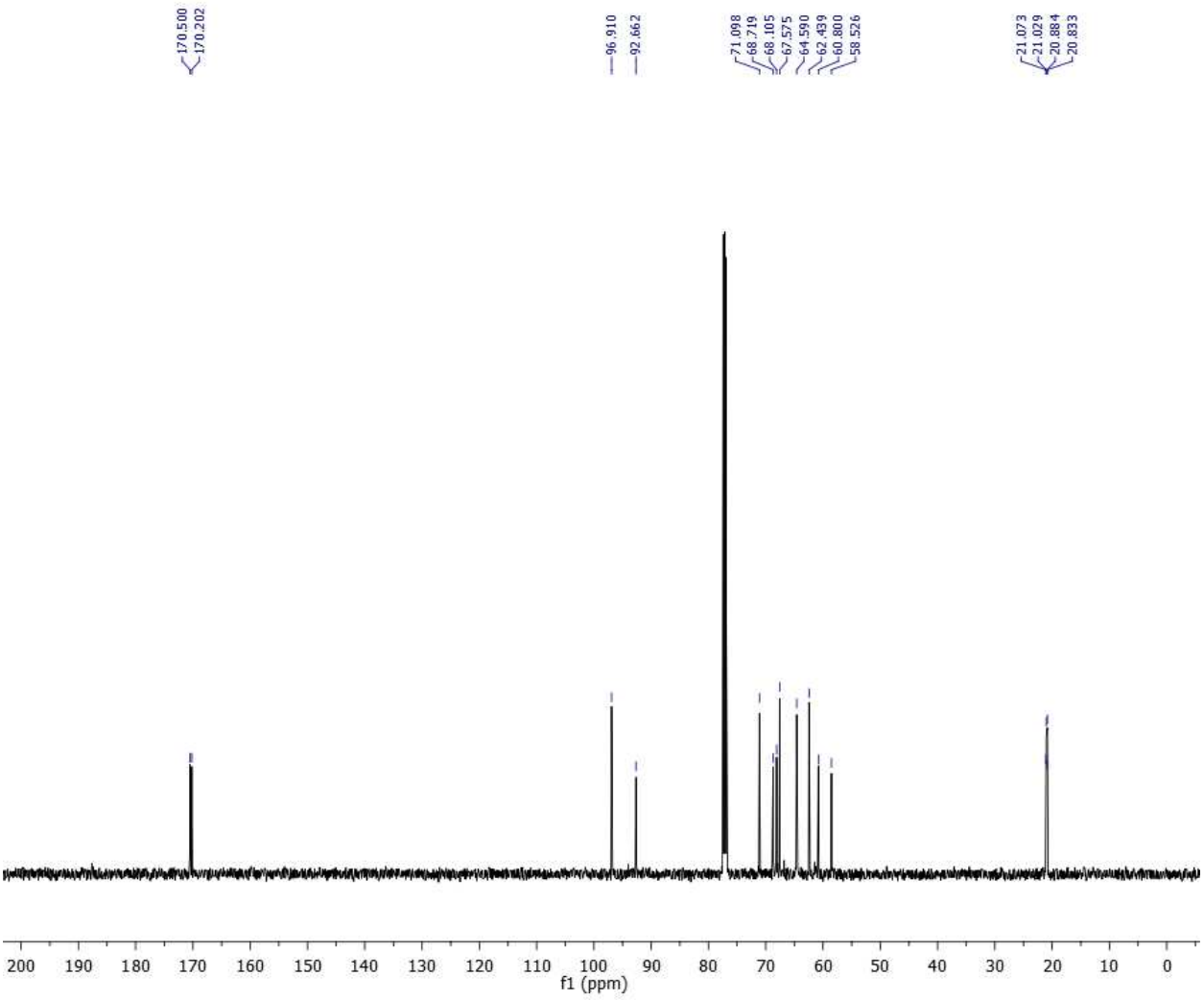
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **28**



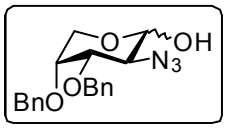


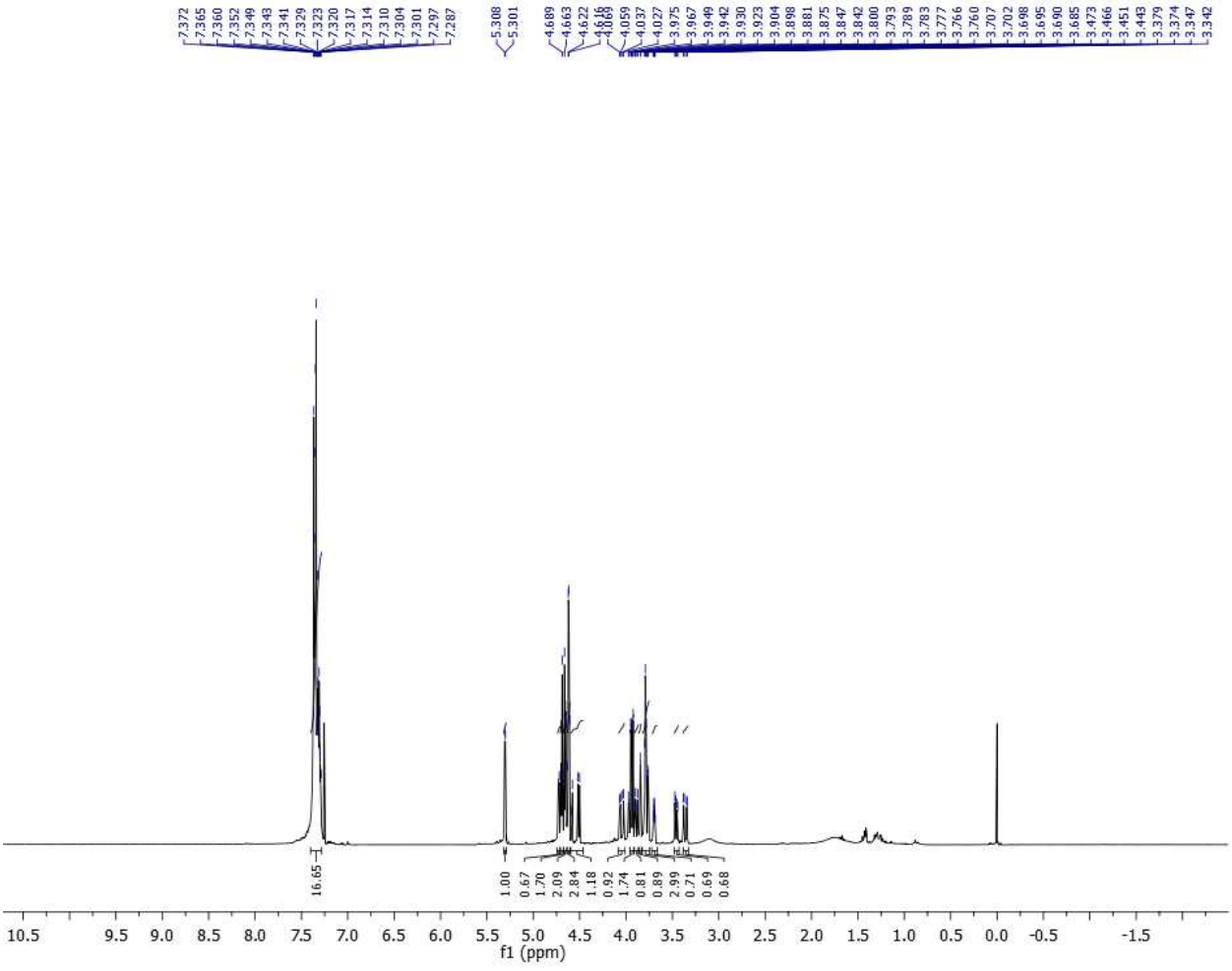
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **30**



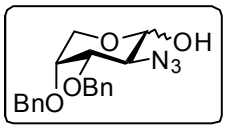


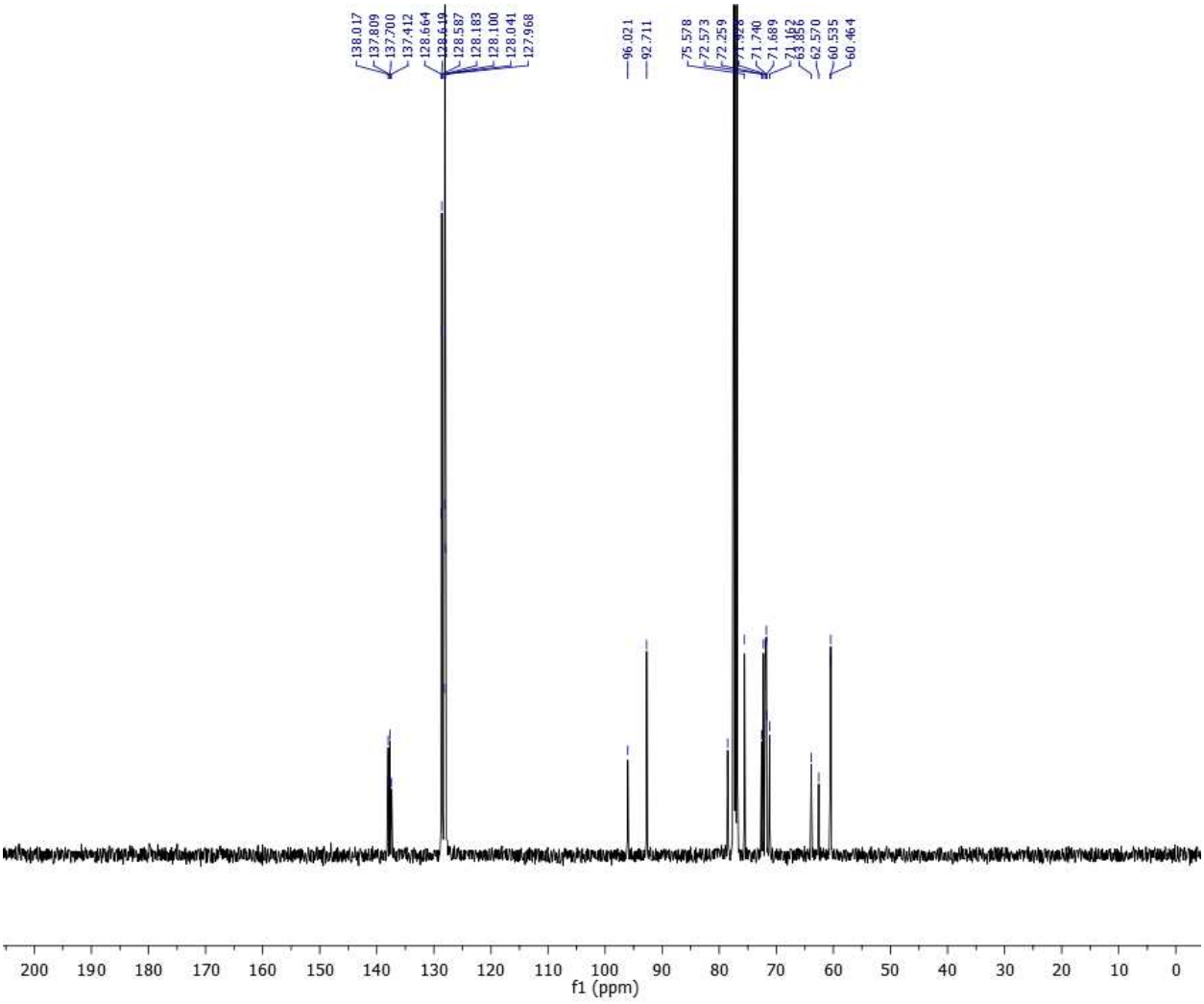
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **30**



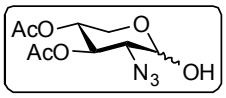


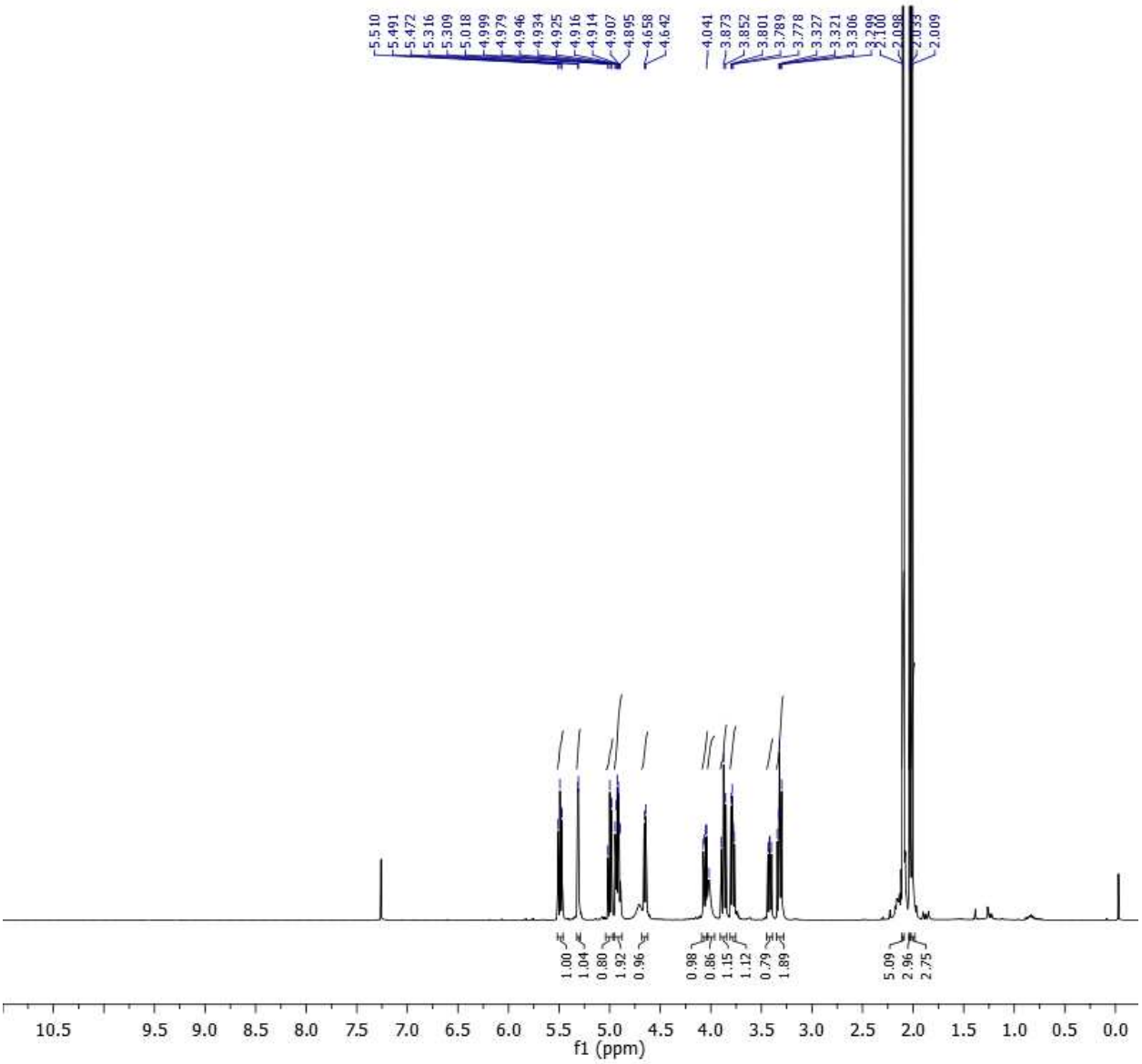
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **32**



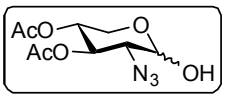


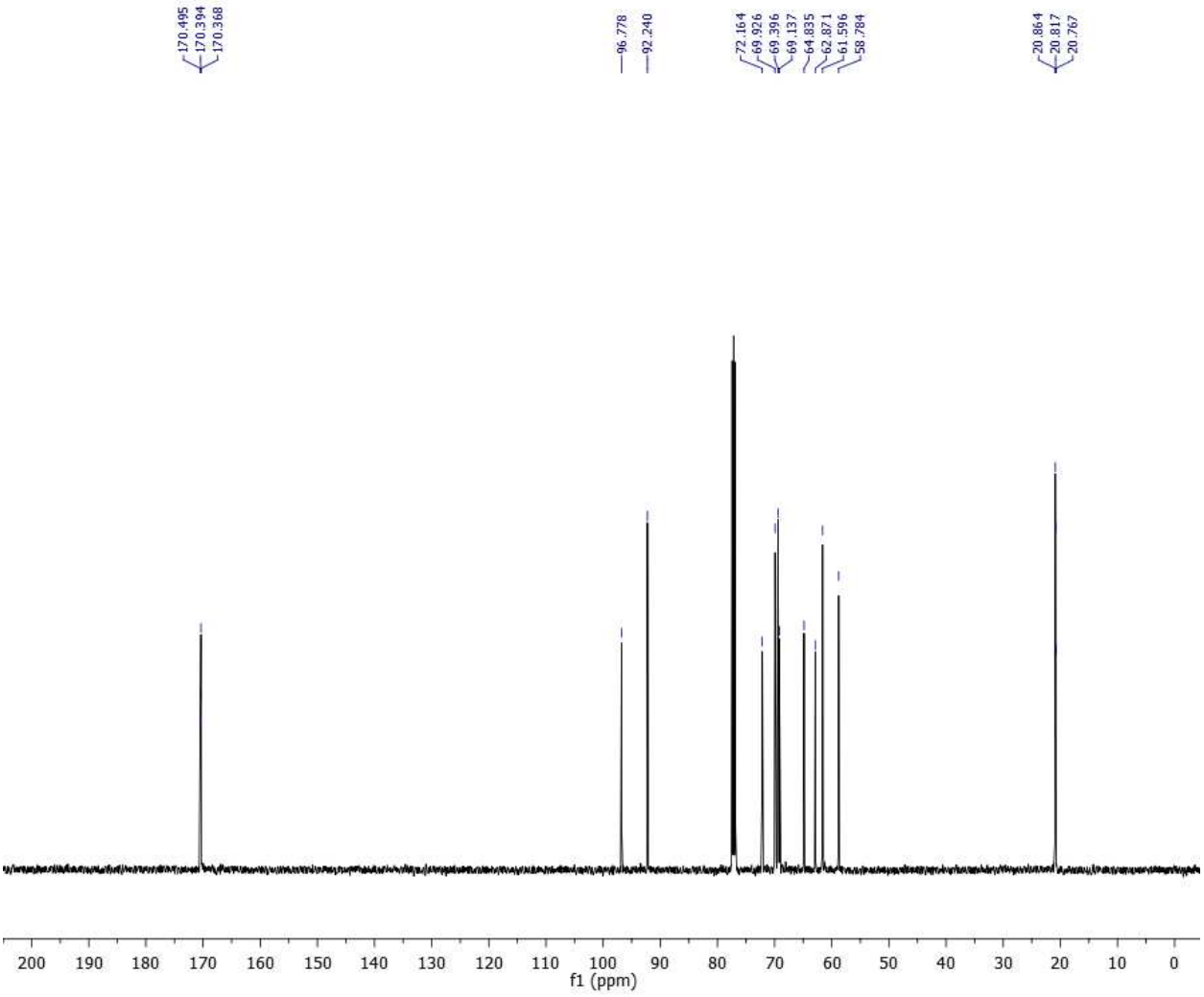
^{13}C NMR spectrum (100 MHz, $CDCl_3$)of compound **32**



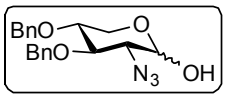


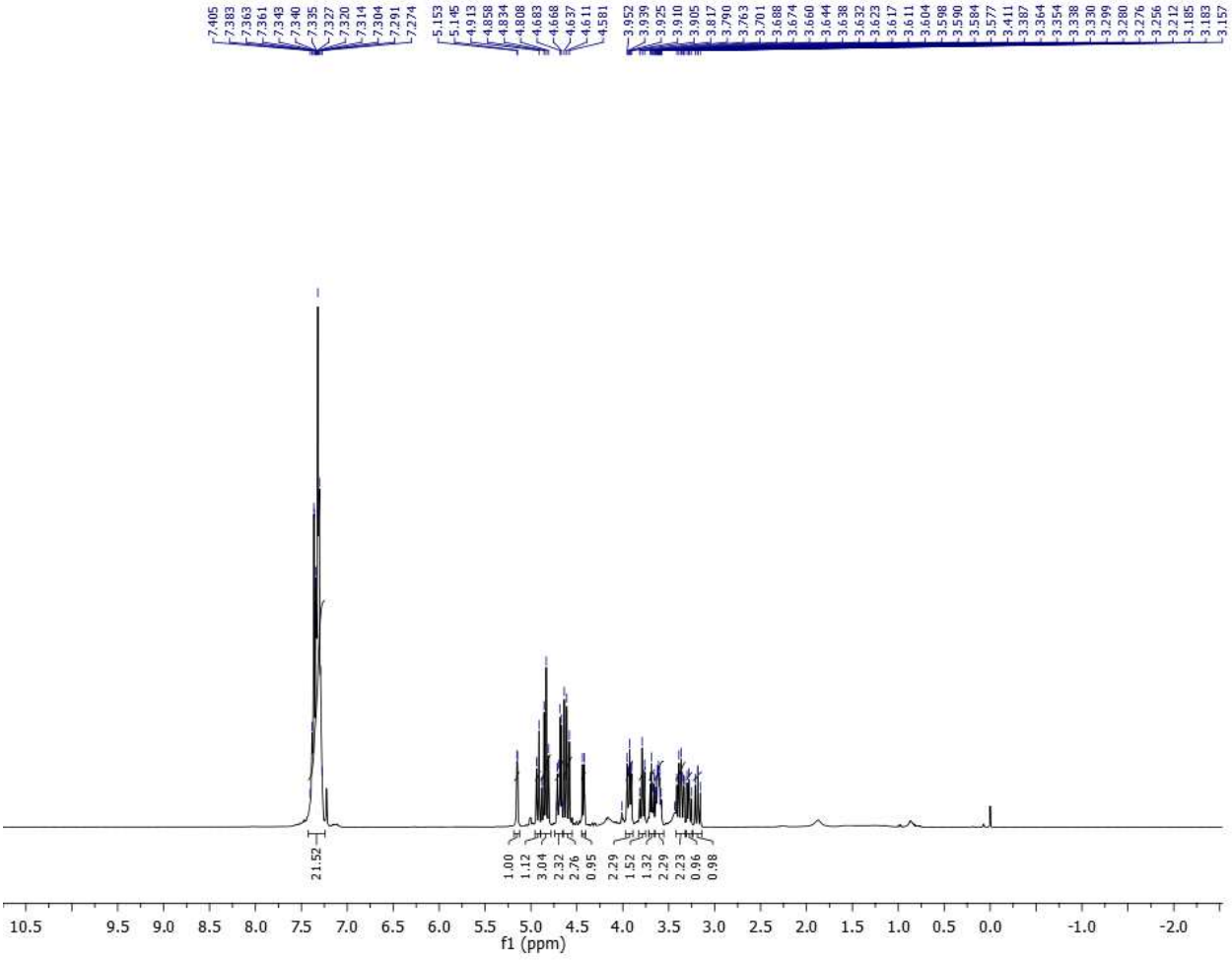
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **34**



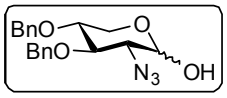


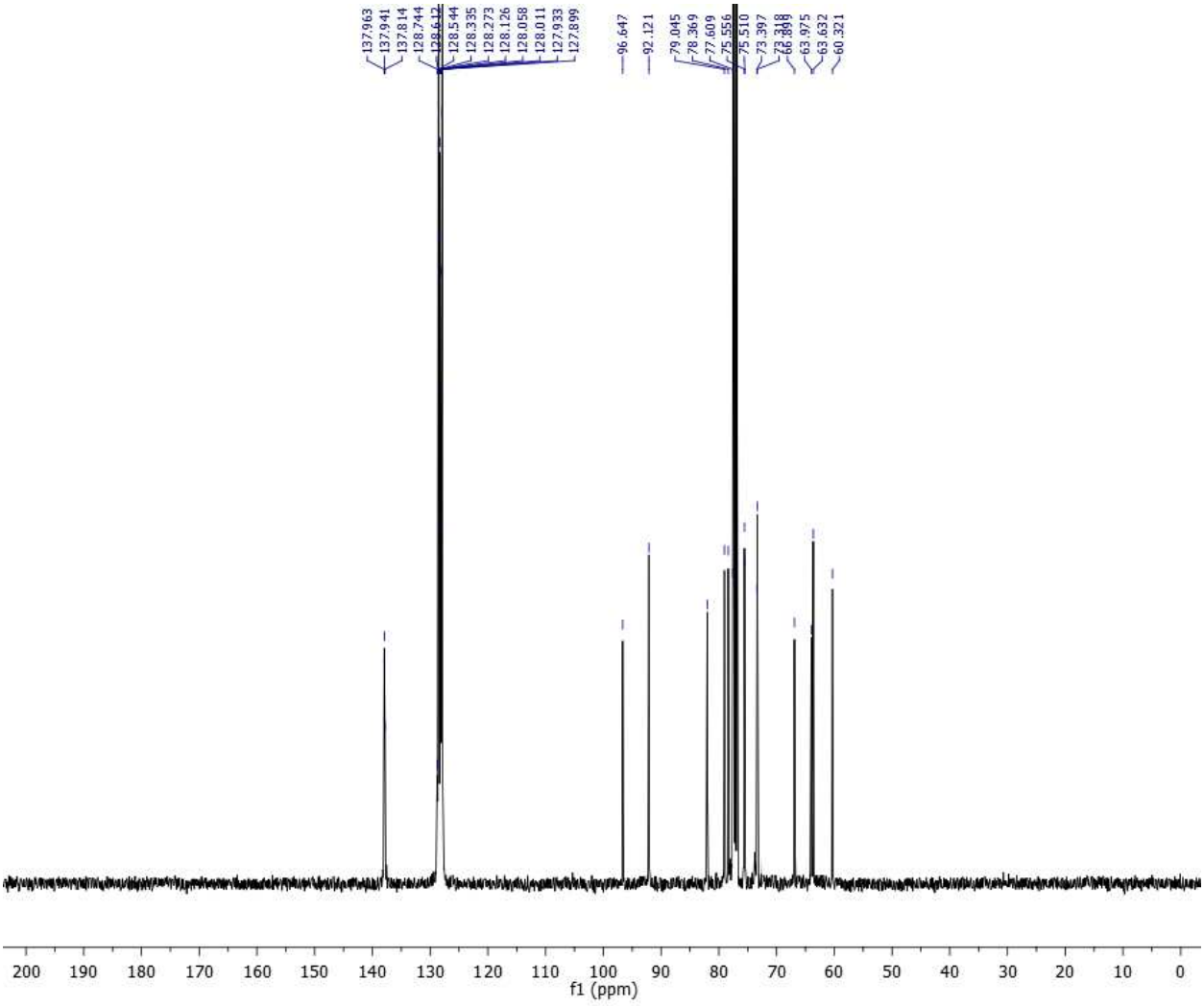
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **34**



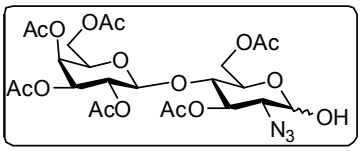


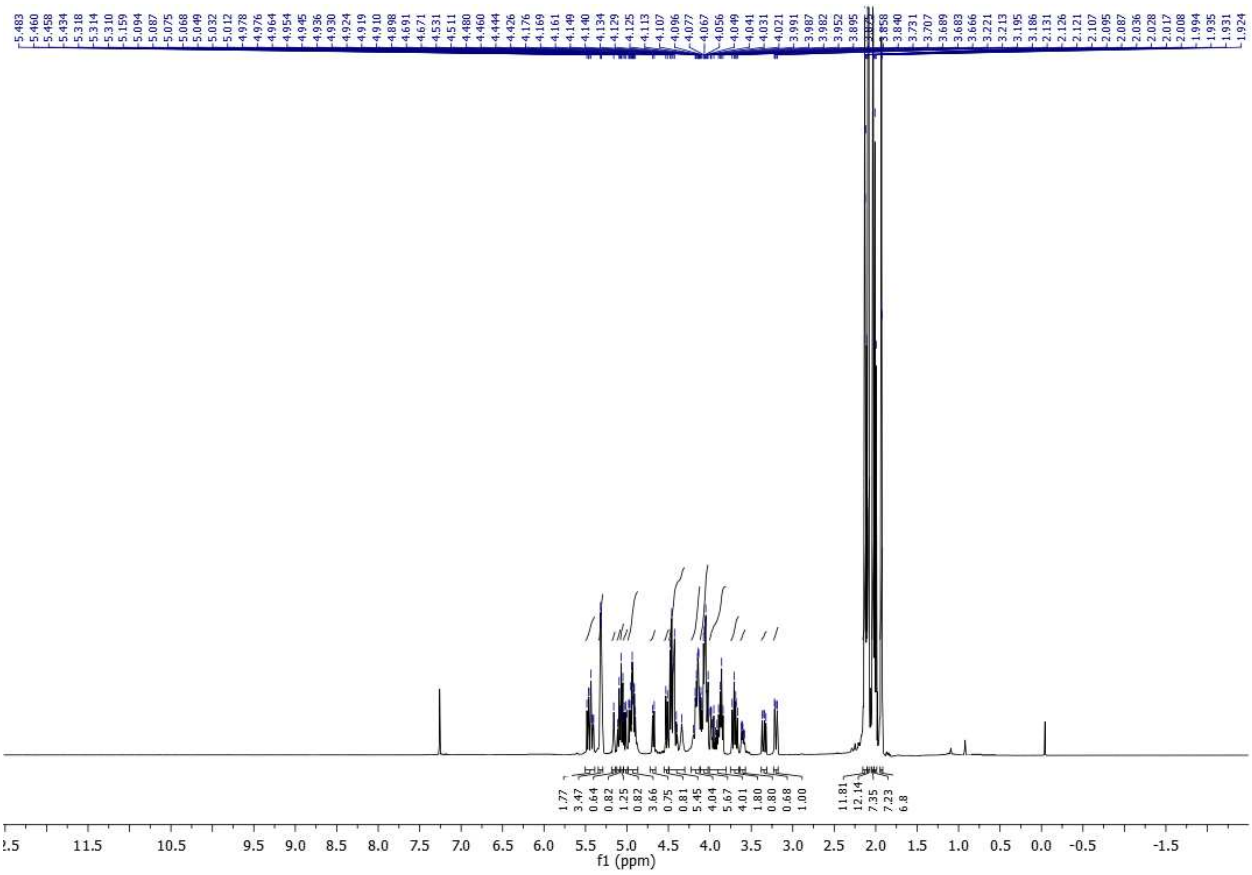
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **36**



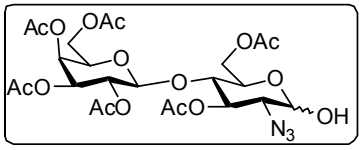


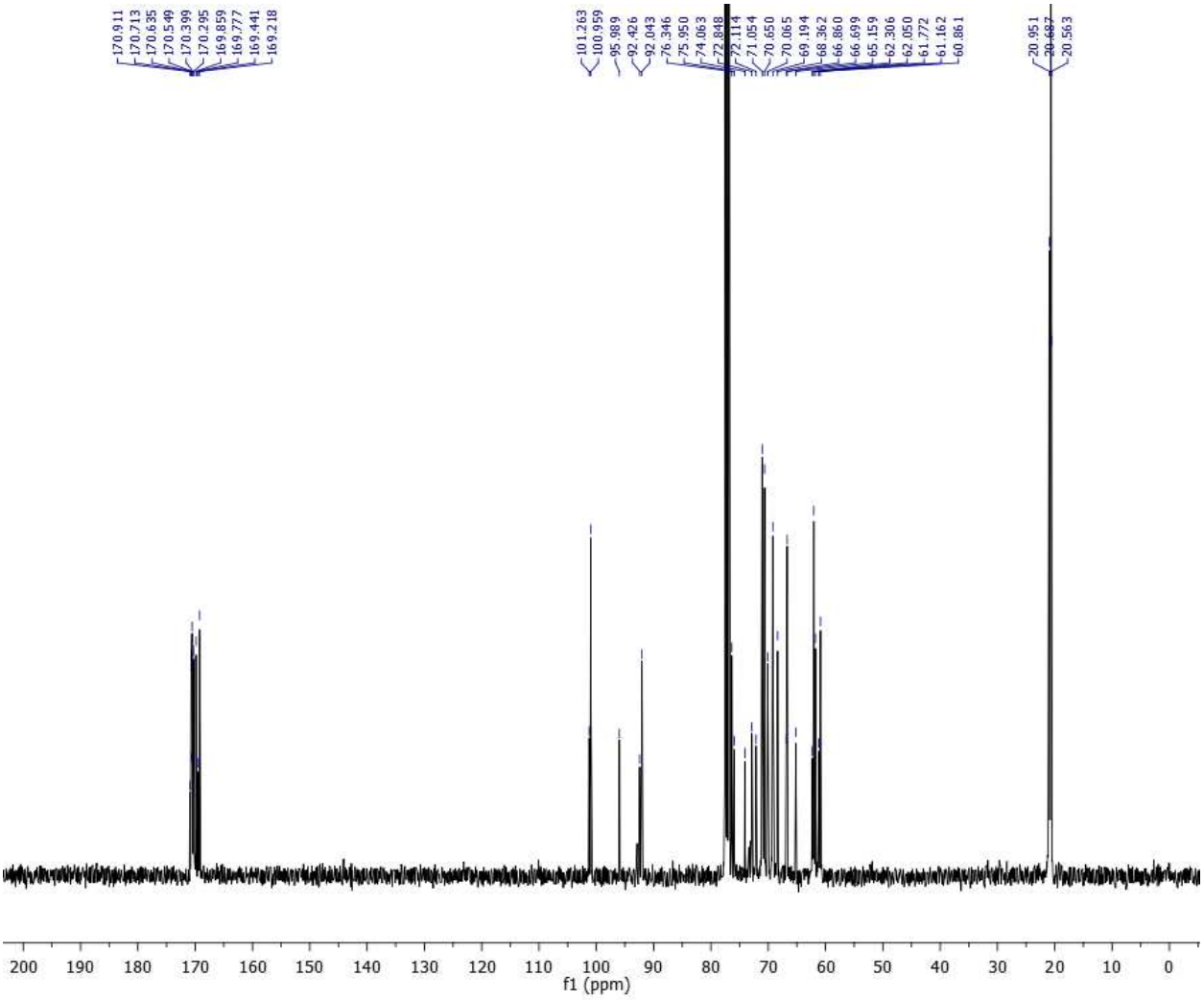
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **36**



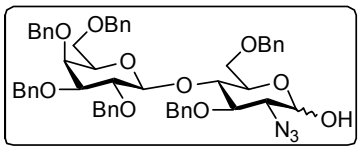


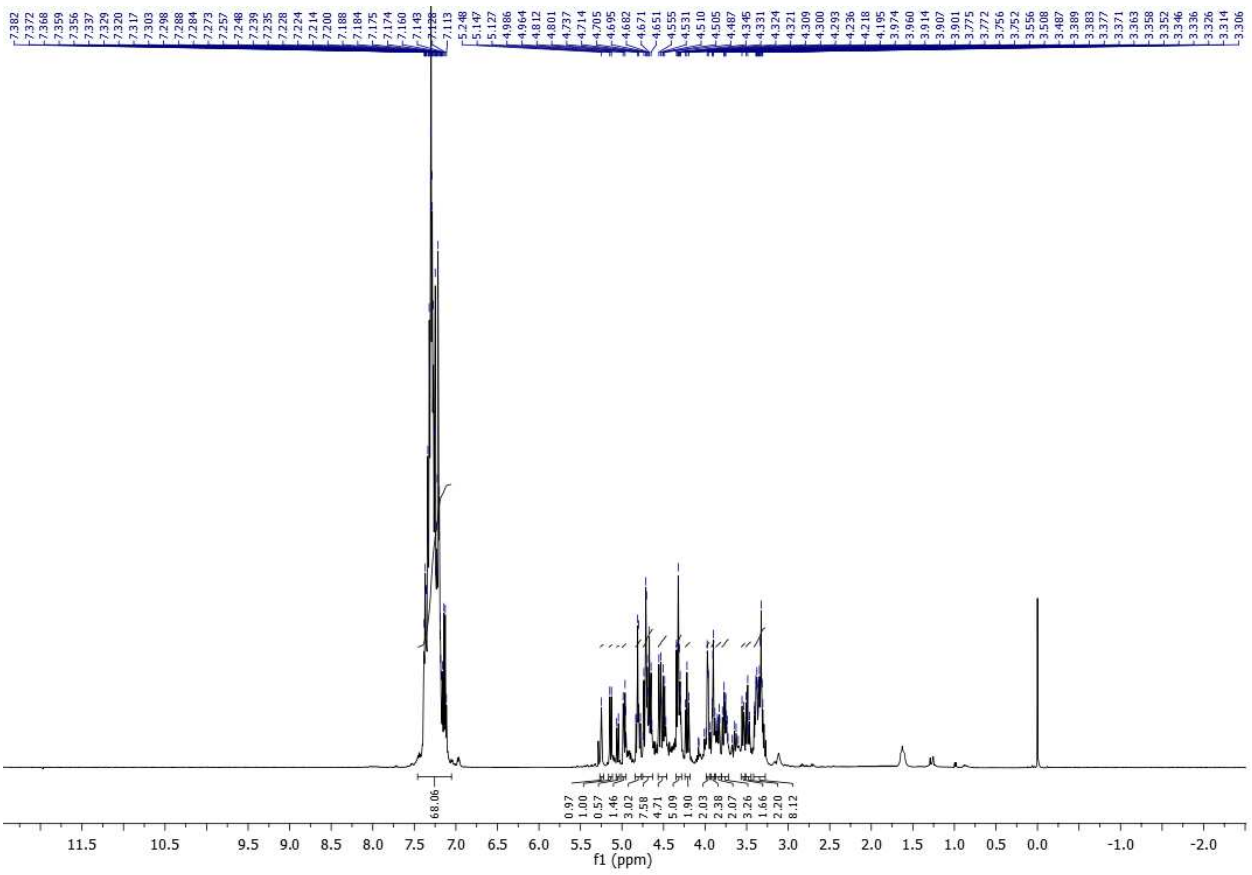
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **38**



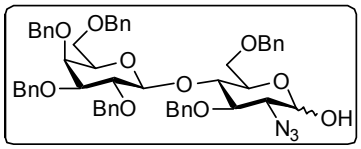


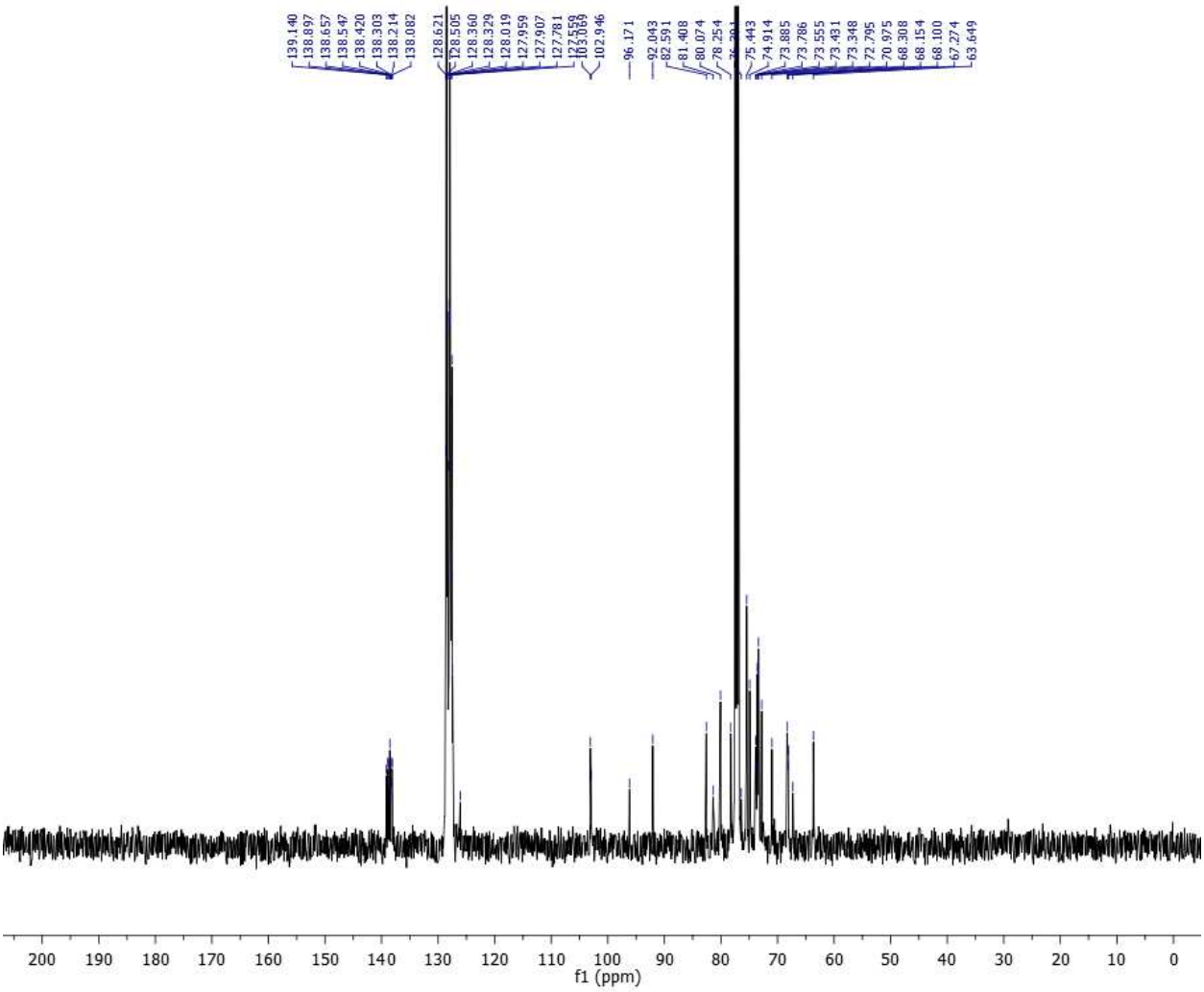
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **38**



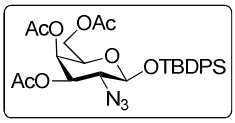


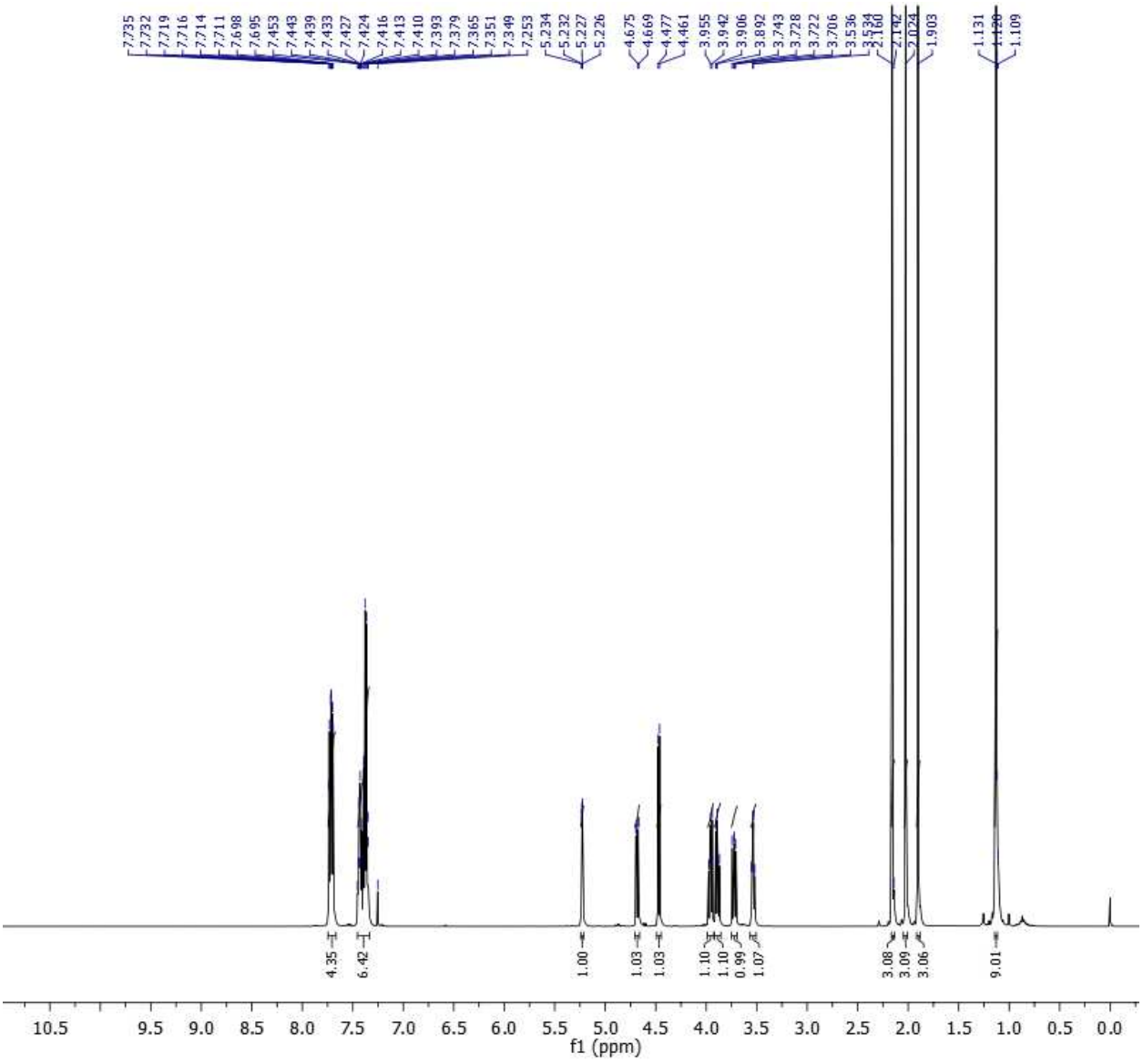
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **40**



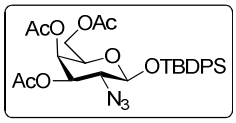


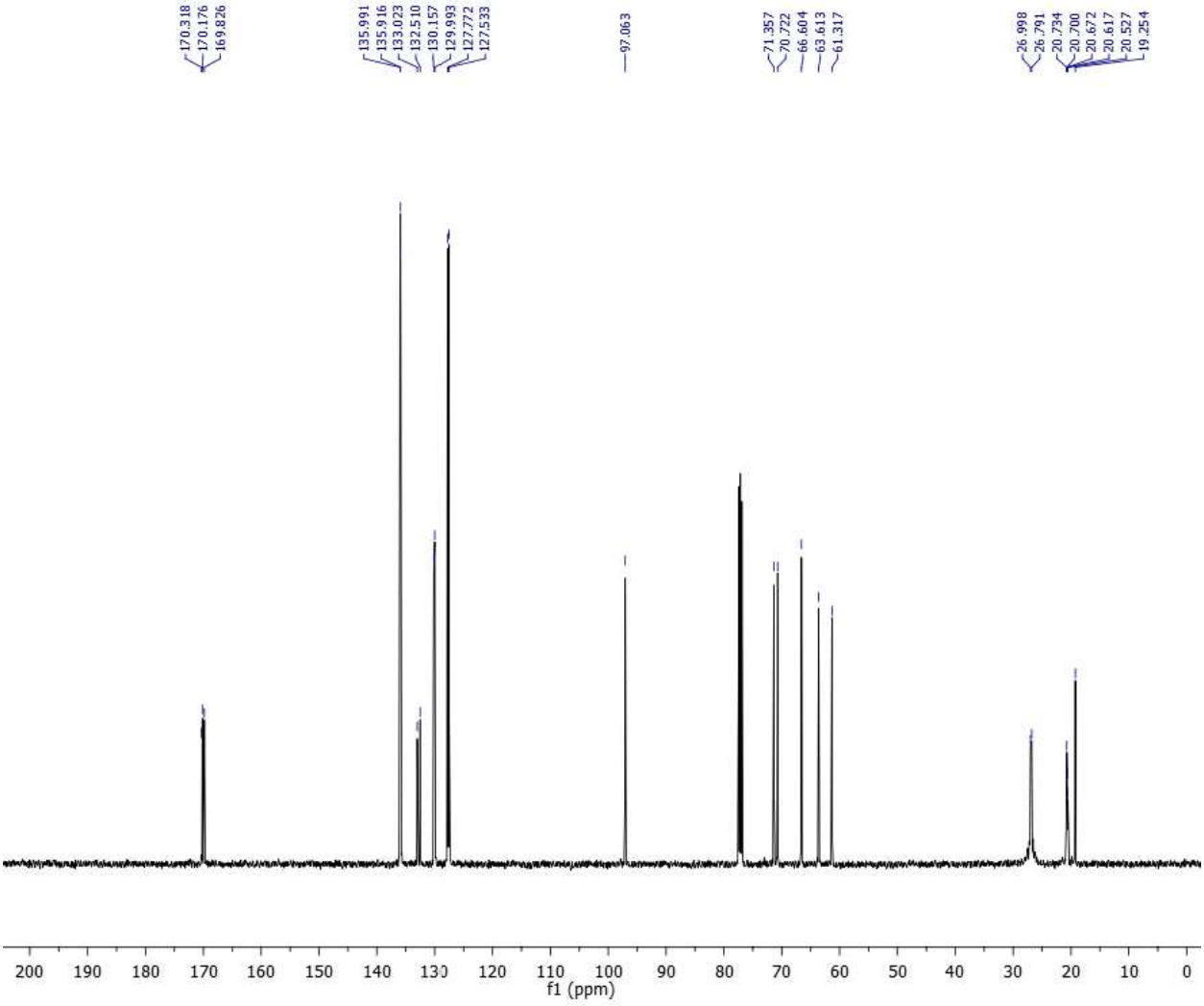
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **40**



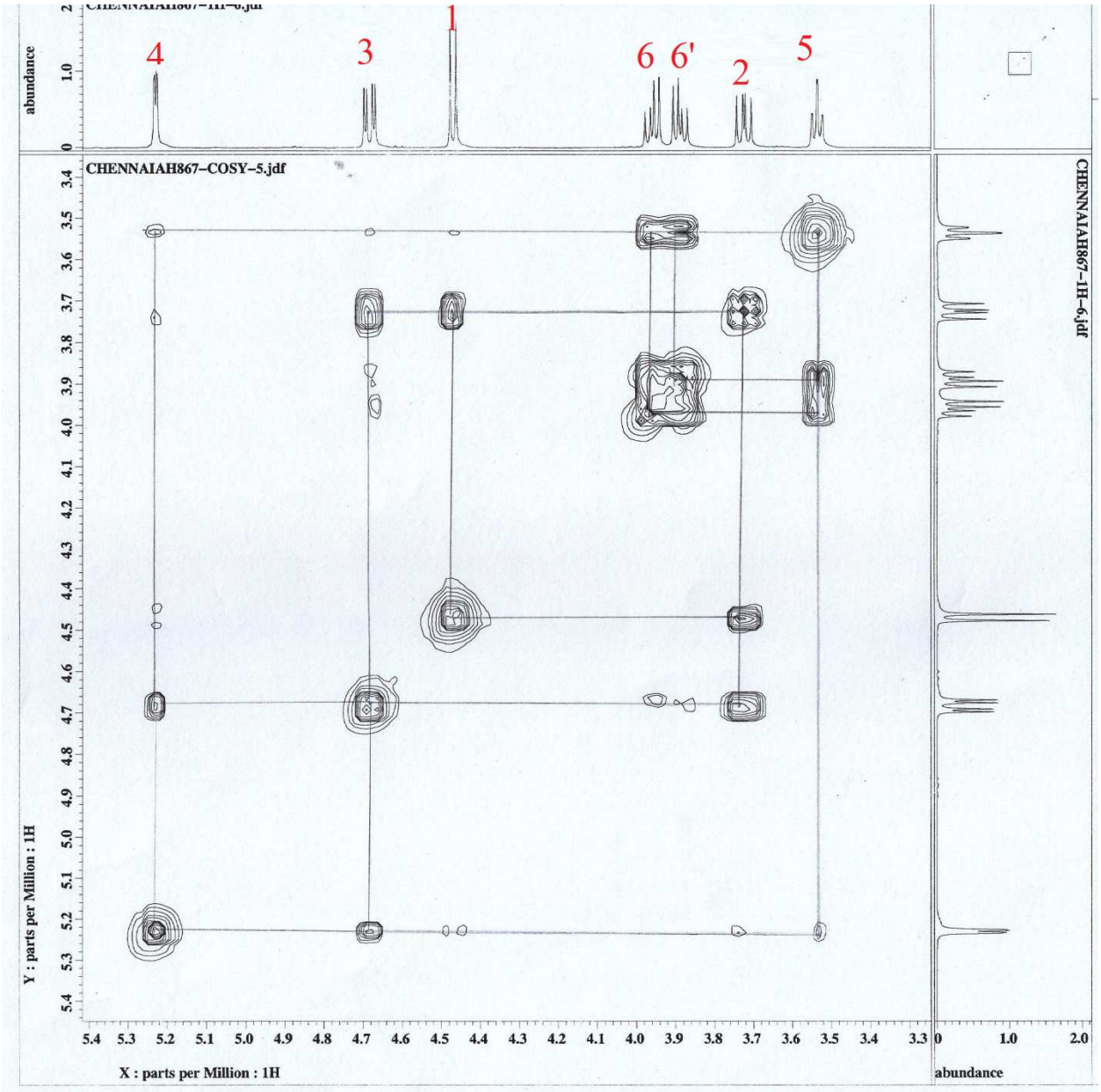


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **41**

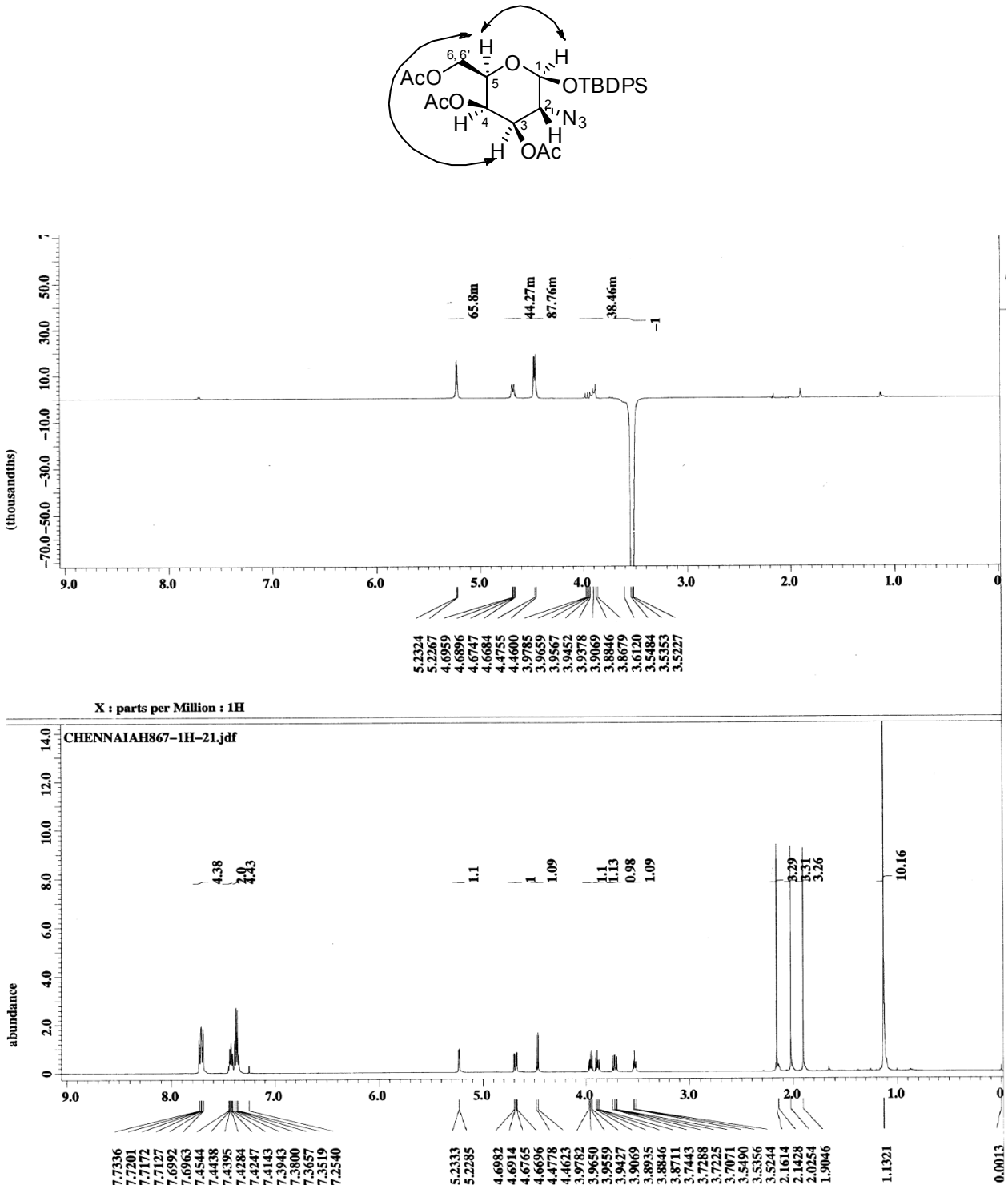




^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **41**

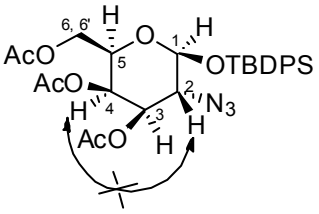


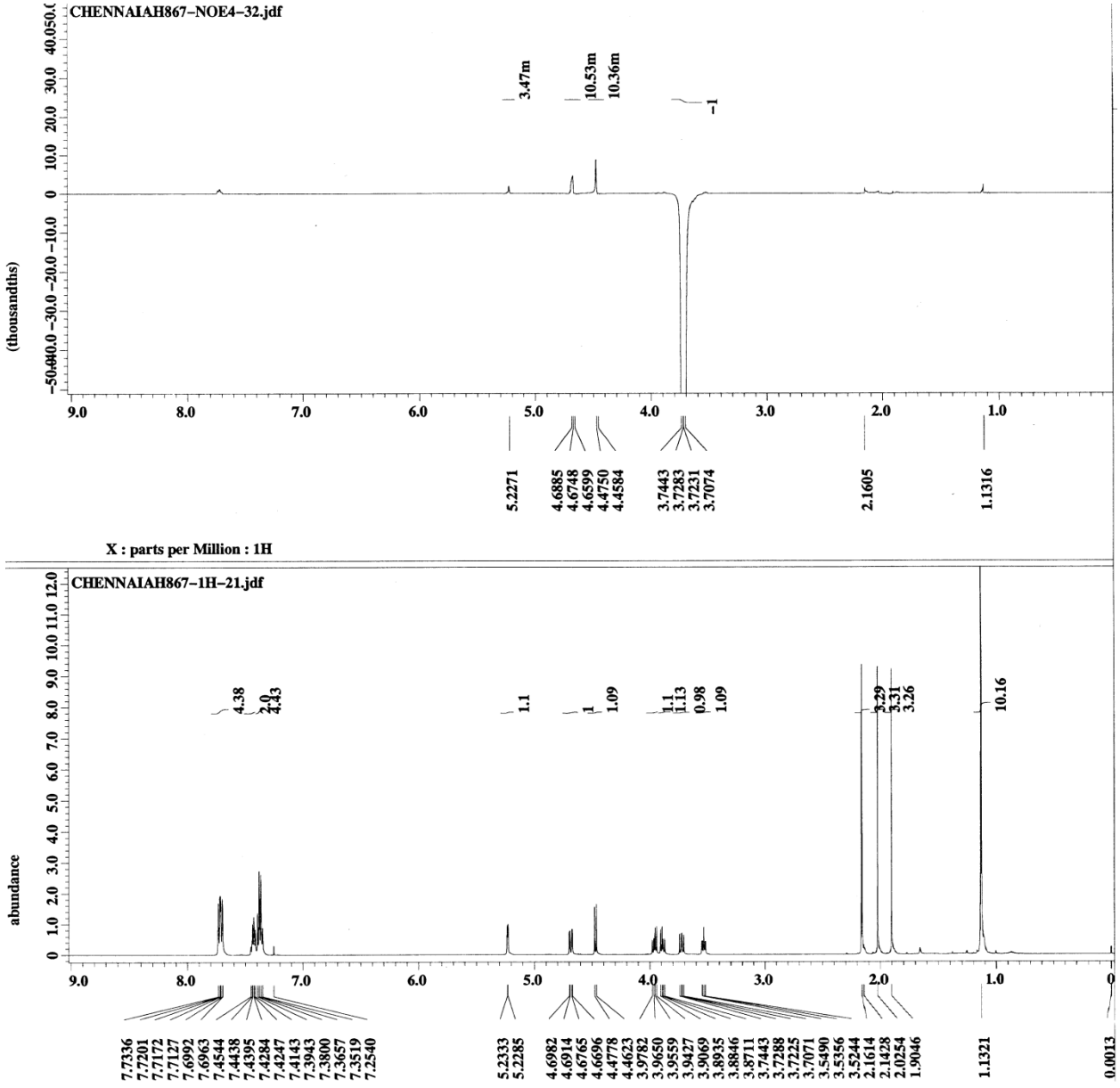
^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$) of compound **41**



nOe spectrum (500 MHz, $CDCl_3$, irradiation of H-5) of compound **41**

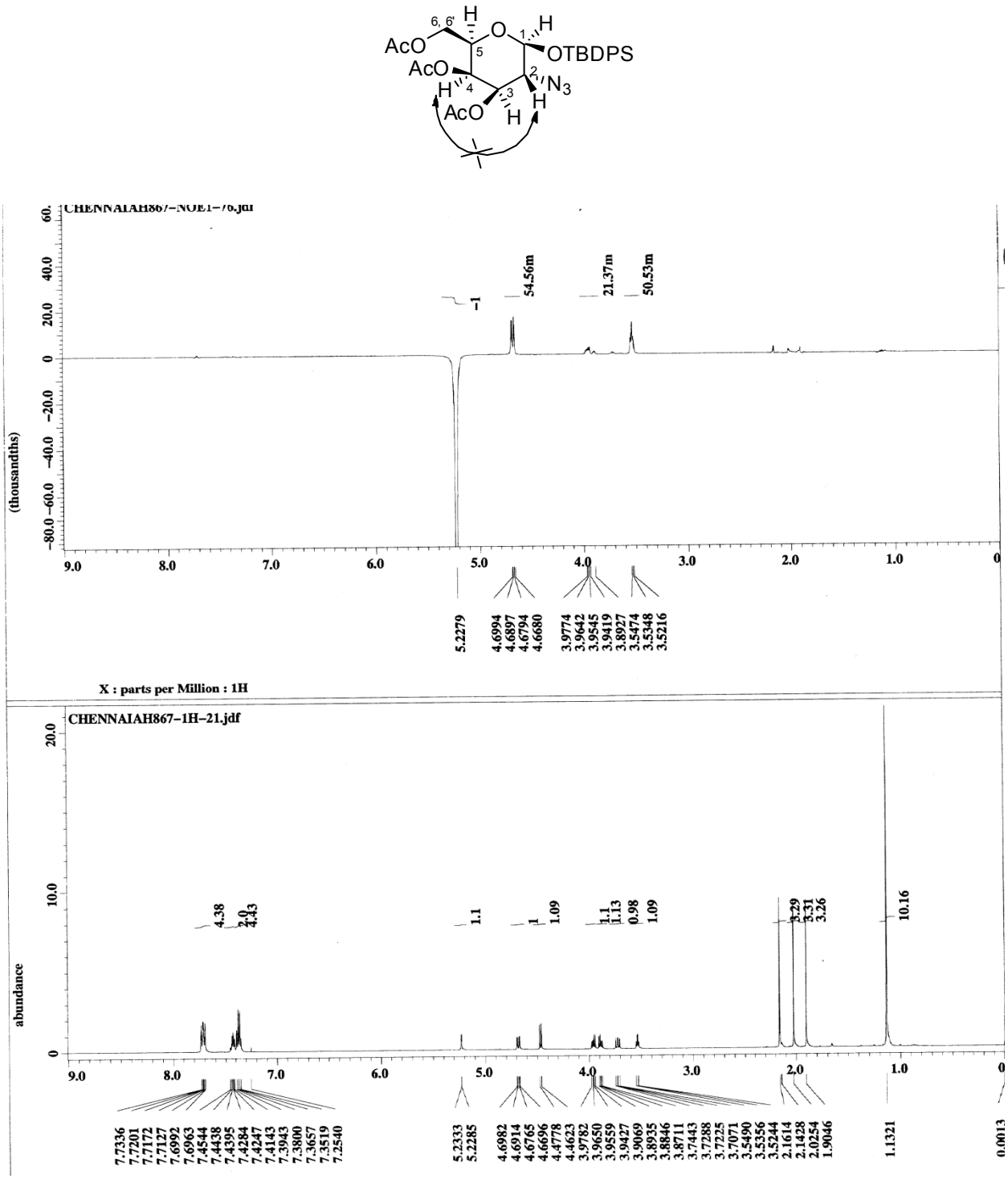
(Irradiation of proton H-5, led to the enhancement for protons H-1 and H-3, indicating that H-5, H-1 and H-3 are cis oriented)





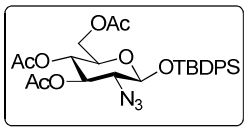
nOe spectrum (500 MHz, $CDCl_3$, irradiation of H-2) of compound **41**

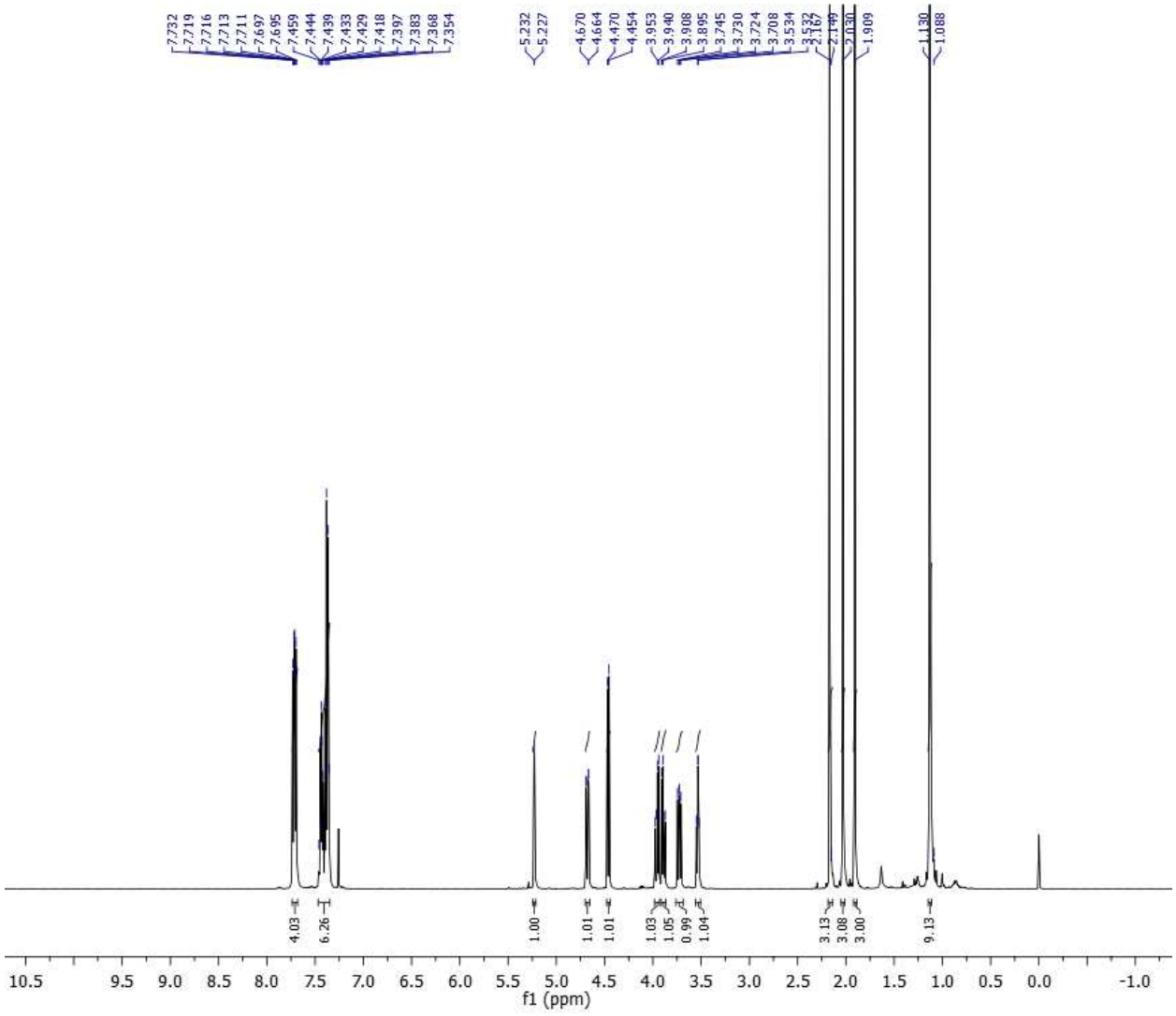
(Upon irradiation of proton H-2, no enhancement was observed for the signal of proton H-4)



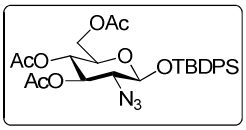
nOe spectrum (500 MHz, $CDCl_3$, irradiation of H-4) of compound **41**

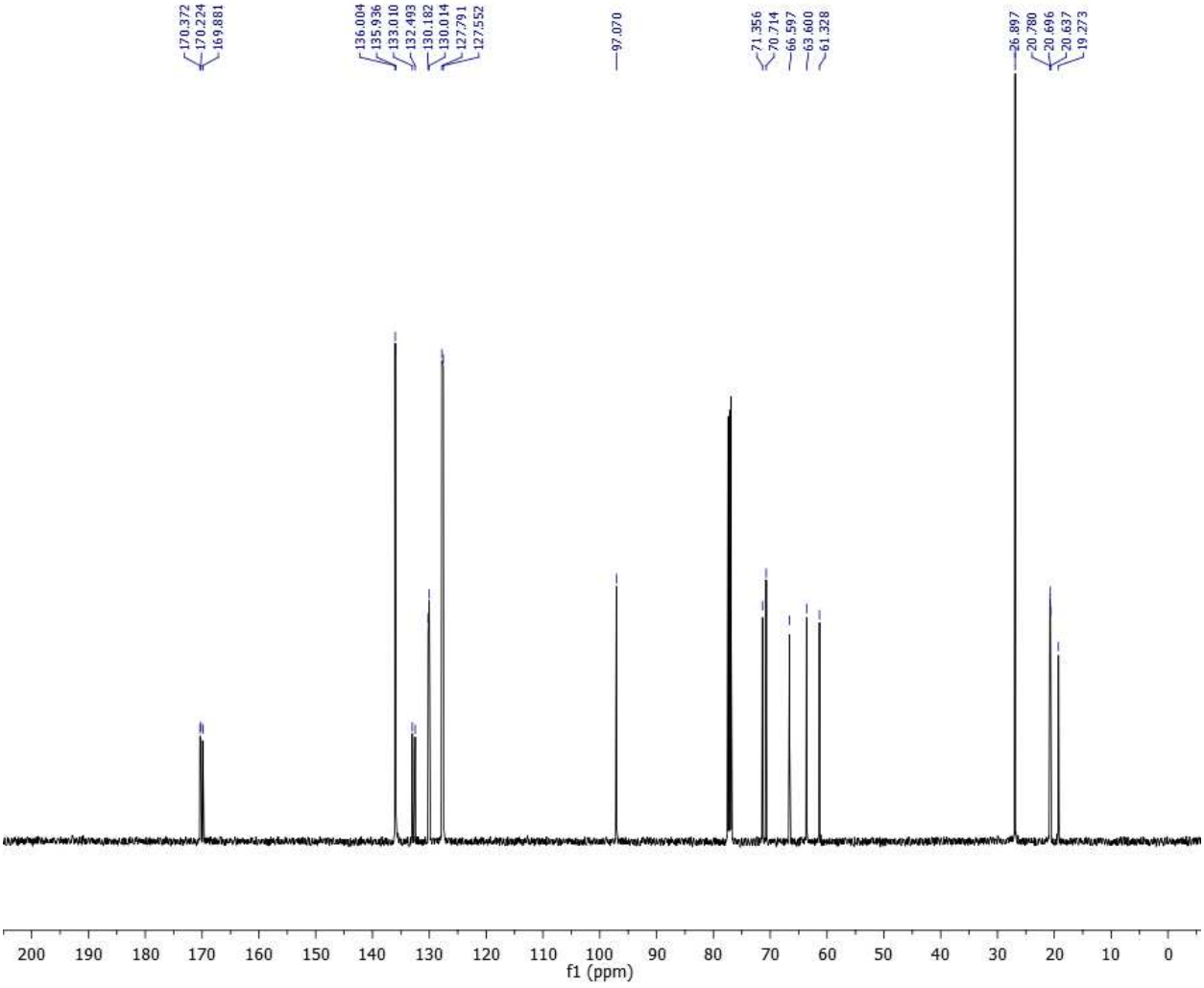
(Upon irradiation of proton H-4, no enhancement was observed for the signal of proton H-2)



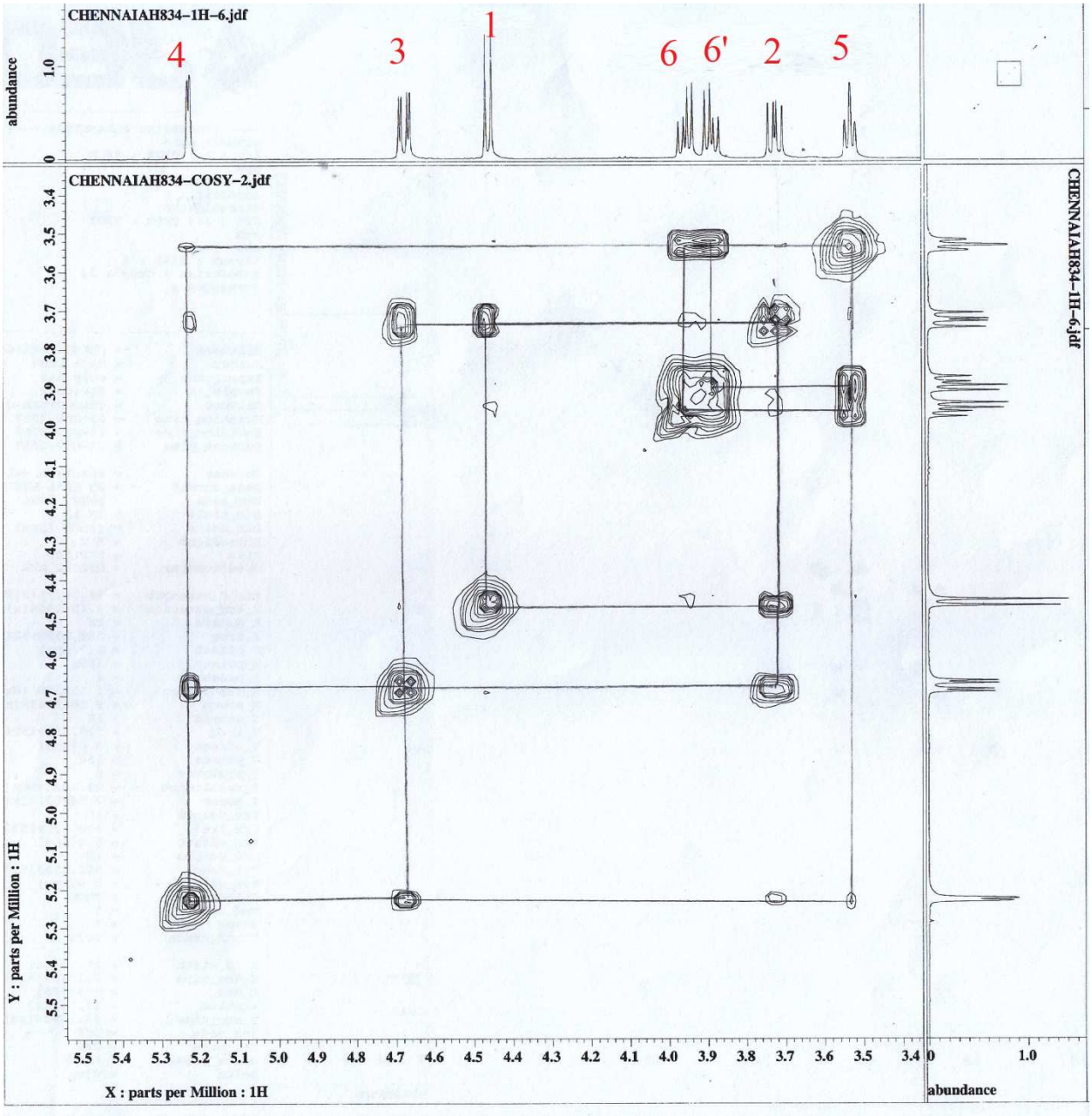


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **42**

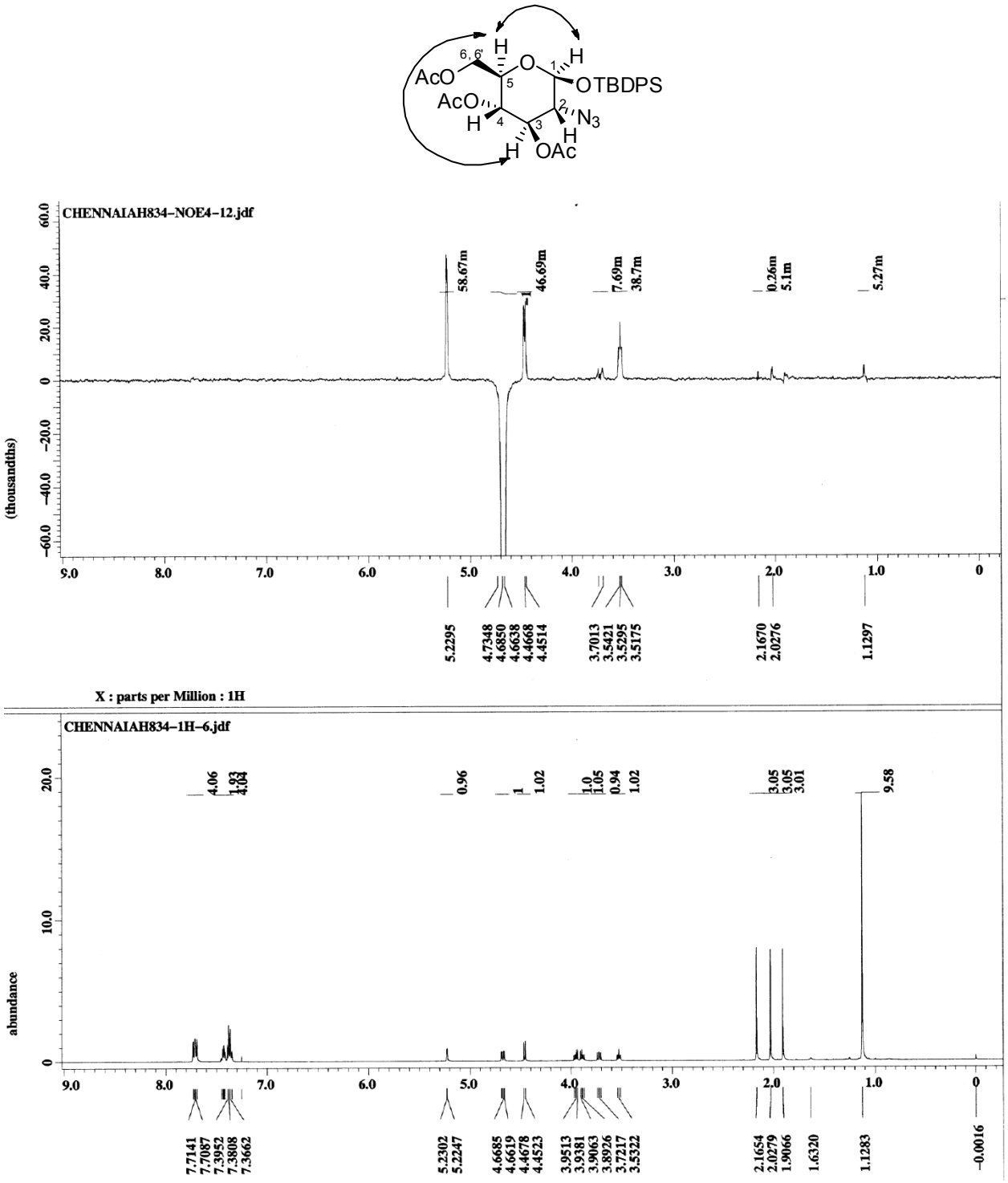




^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **42**

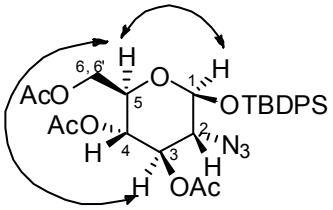


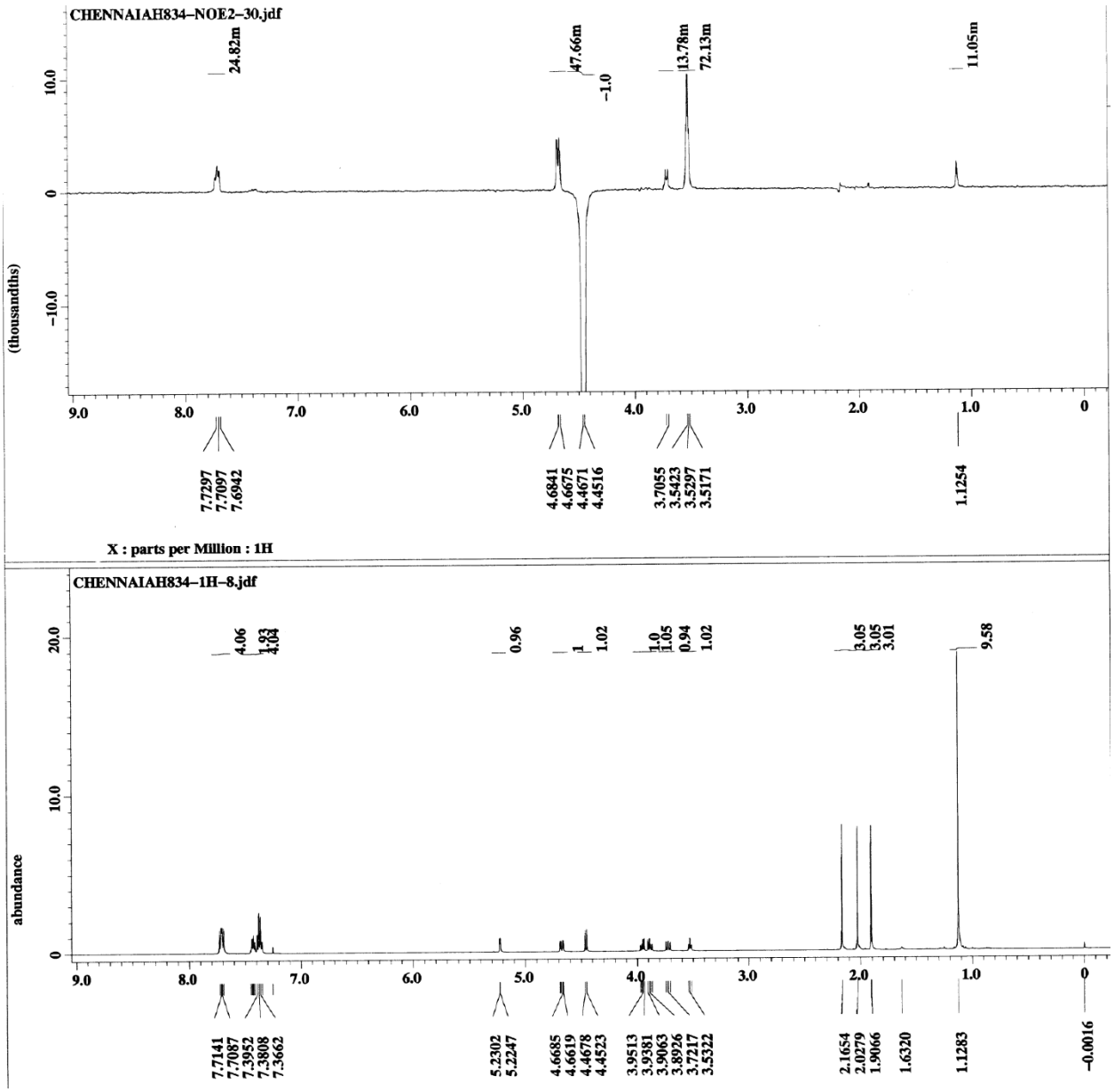
^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$) of compound **42**



nOe spectrum (500 MHz, $CDCl_3$, irradiation of H-3) of compound **42**

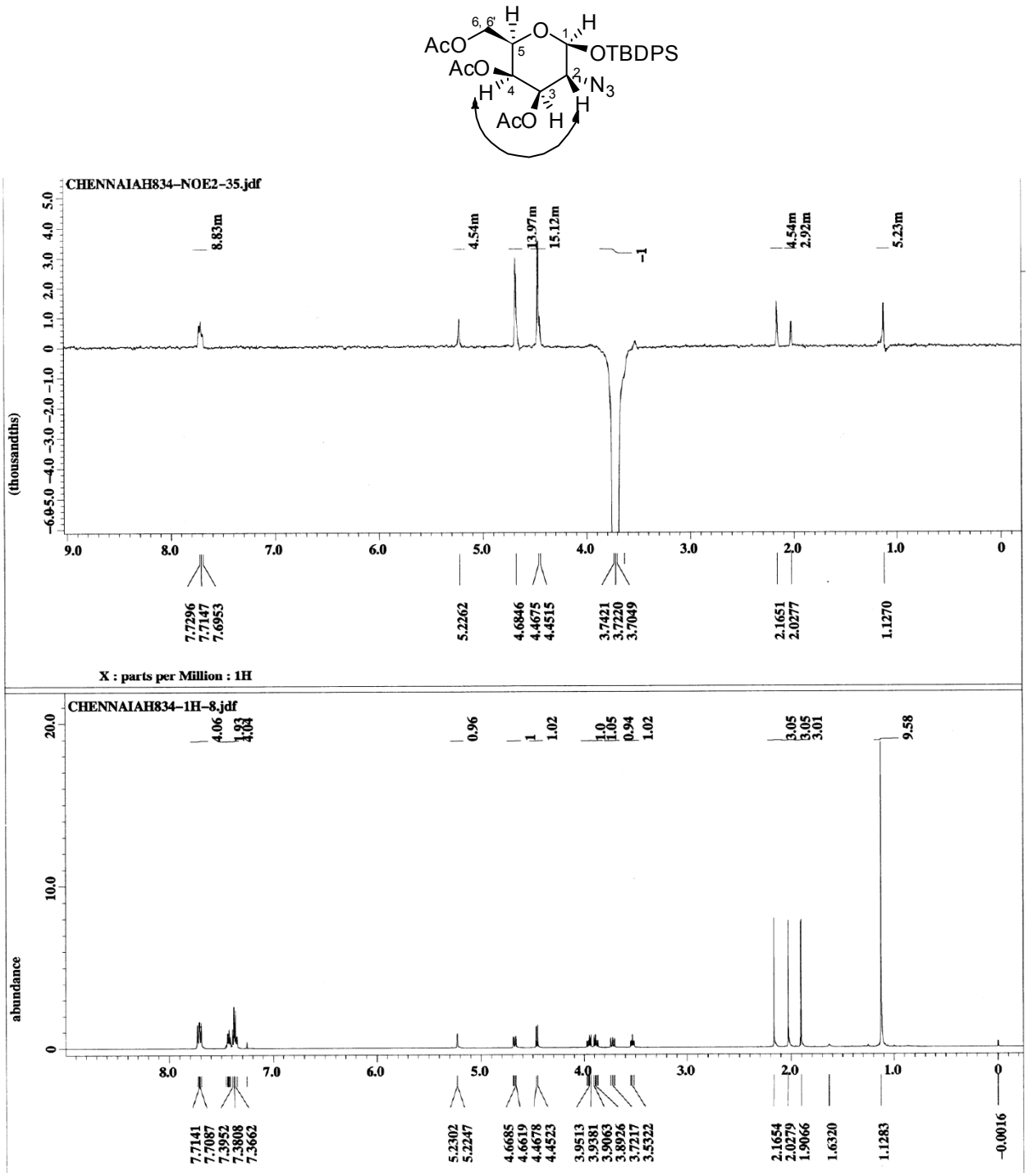
(Irradiation of proton H-3, led to the enhancement for protons H-1 and H-5, indicating that H-3, H-1 and H-5 are cis oriented)





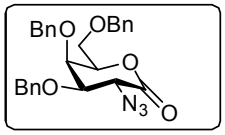
nOe spectrum (500 MHz, $CDCl_3$, irradiation of H-1) of compound **42**

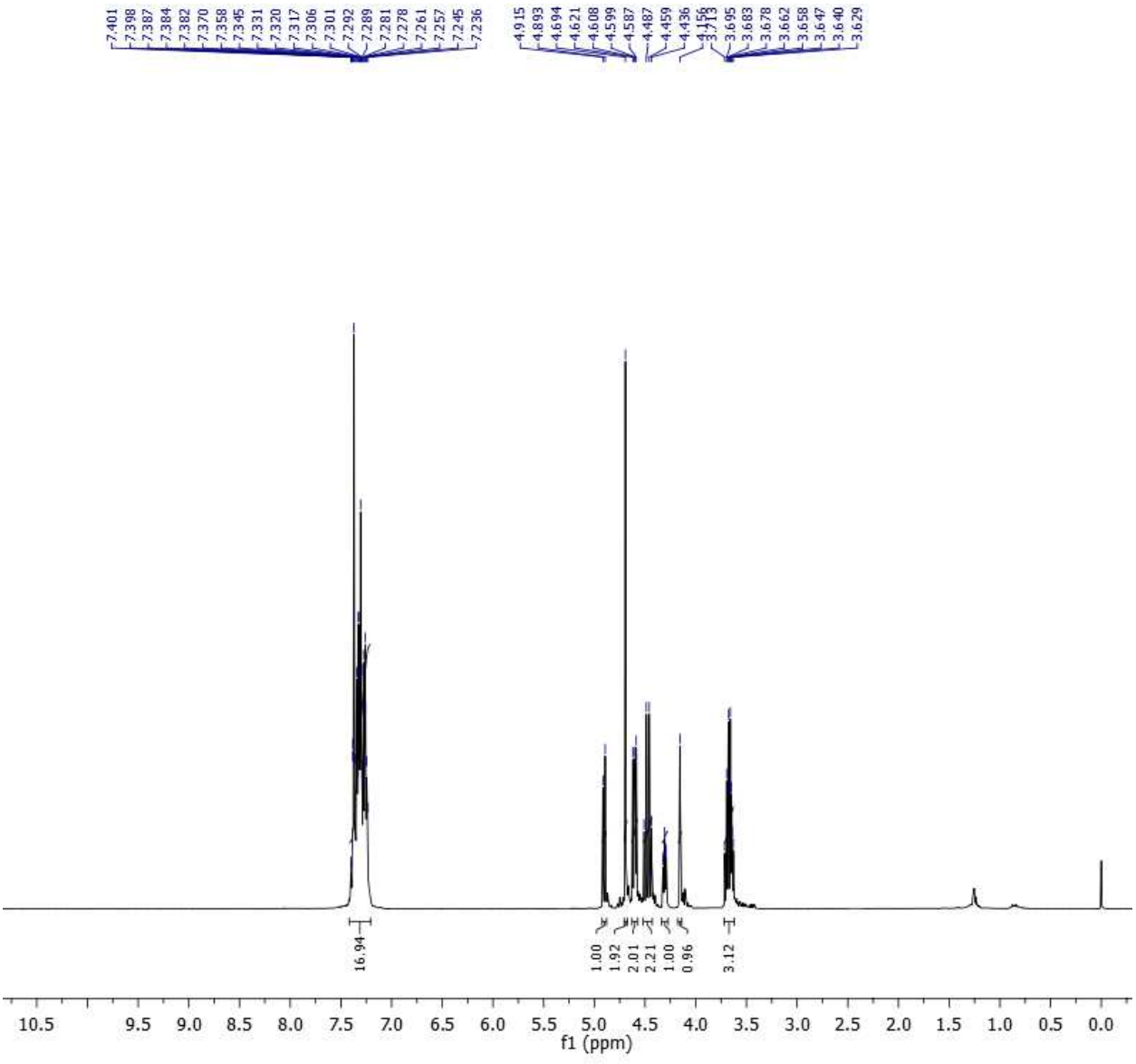
(Irradiation of proton H-1, led to the enhancement for protons H-3 and H-5, indicating that H-1, H-3 and H-5 are cis oriented)



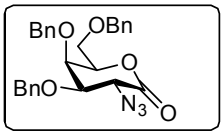
nOe spectrum (500 MHz, $CDCl_3$, irradiation of H-2) of compound **42**

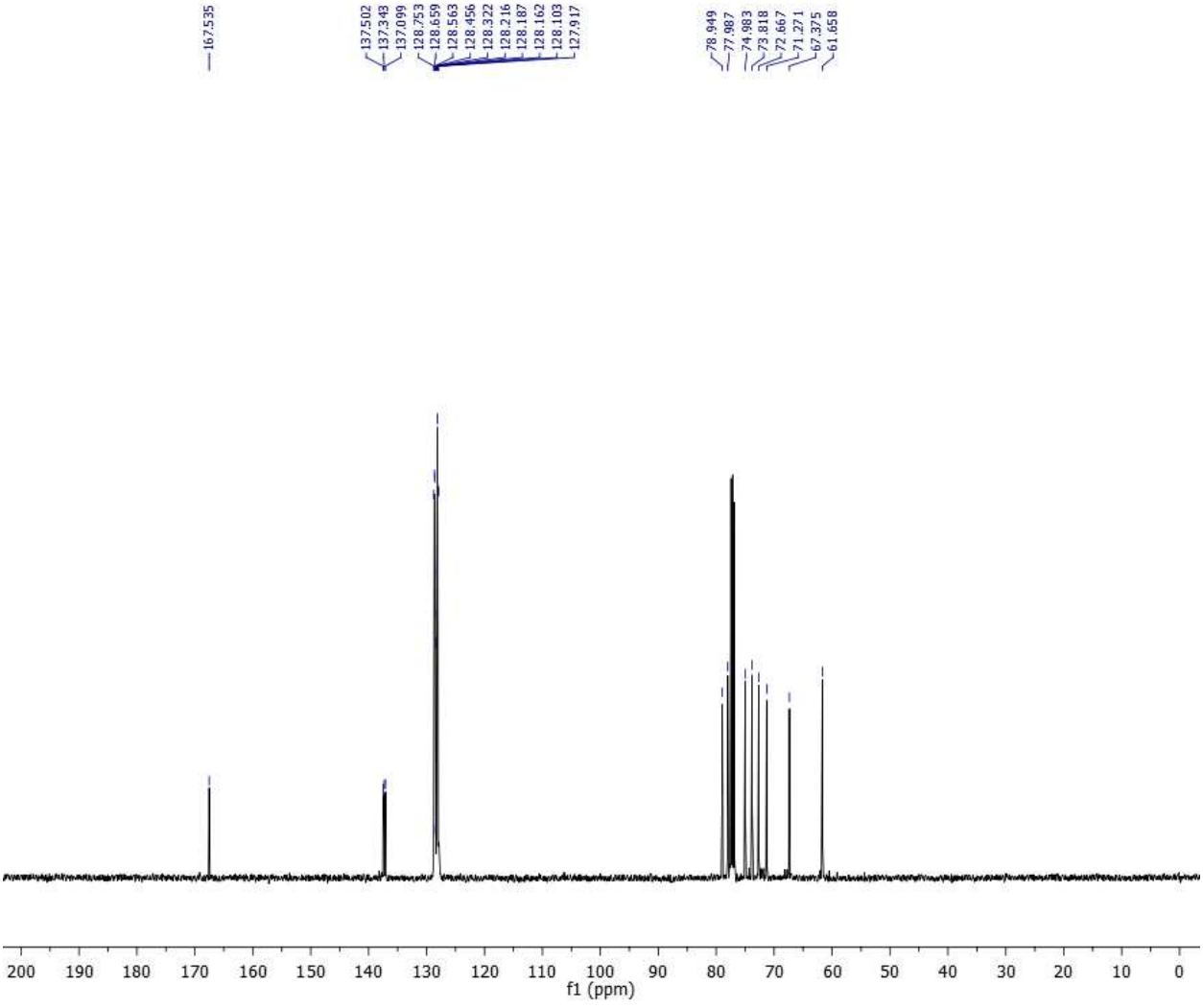
(Irradiation of proton H-2, led to the enhancement for proton H-4, indicating that H-2, H-4 are cis oriented)



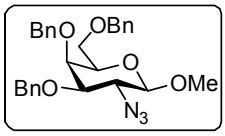


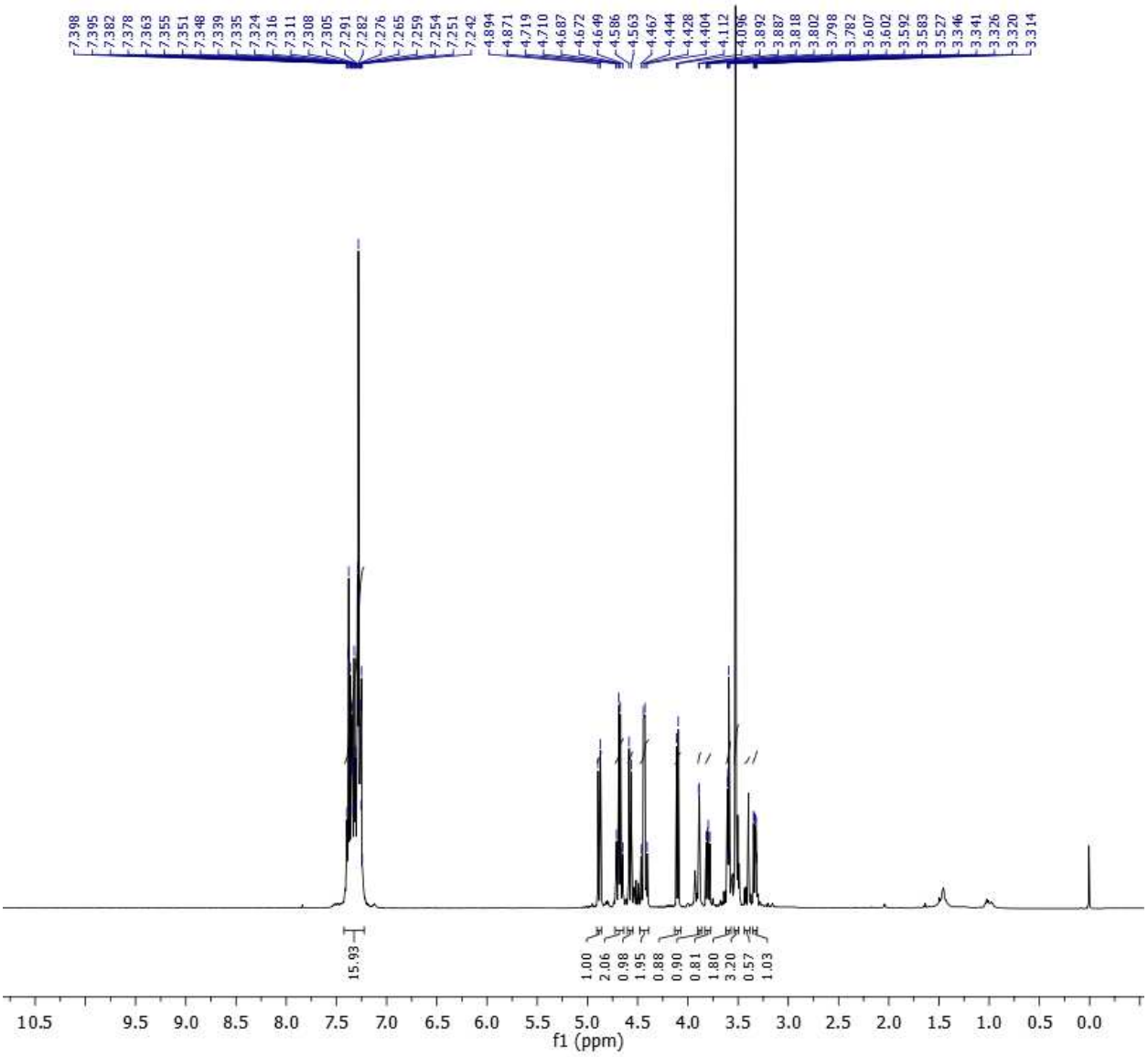
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **43**



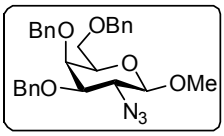


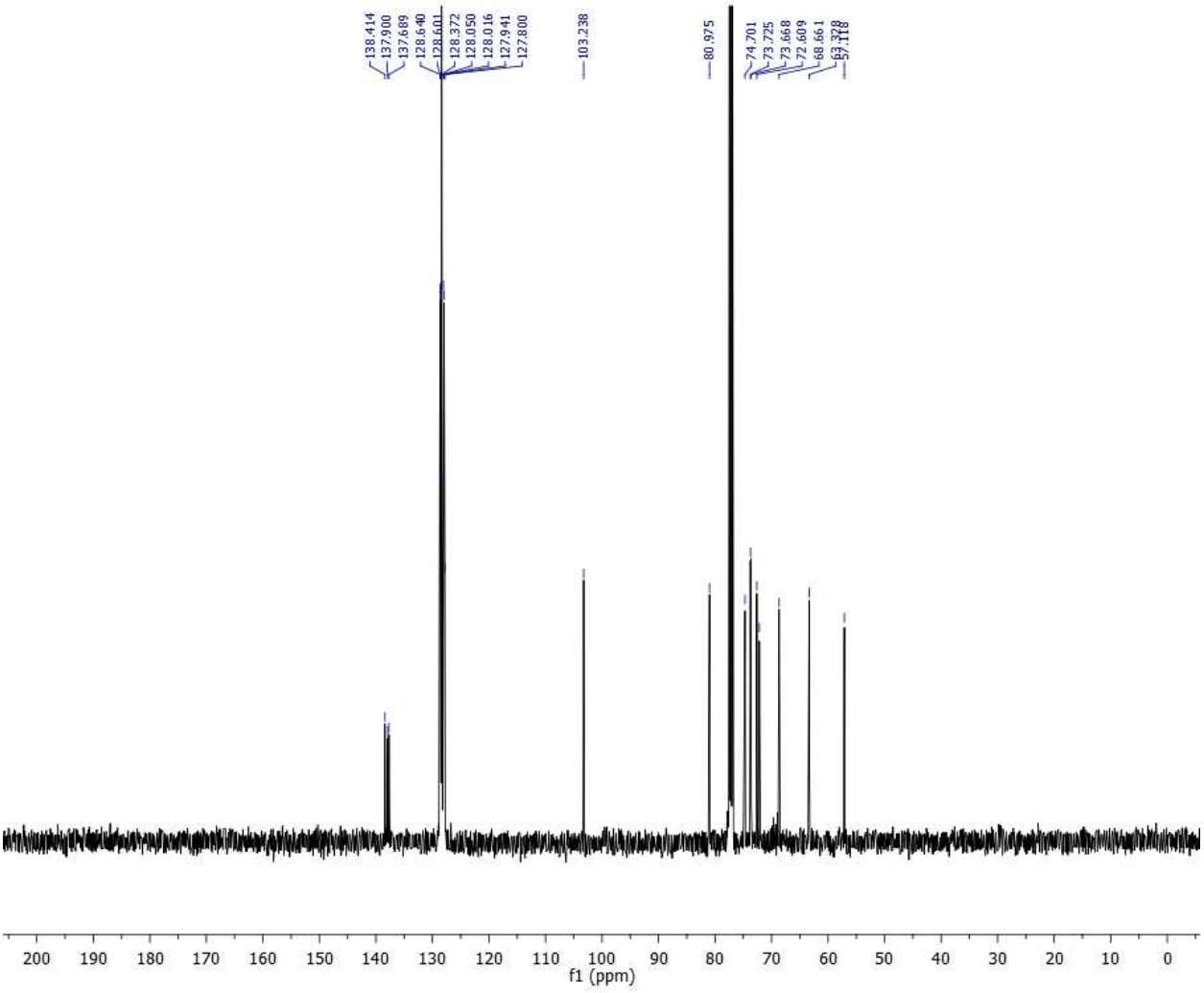
^{13}C NMR spectrum (500 MHz, $CDCl_3$) of compound **43**



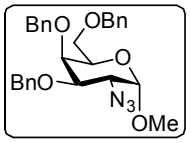


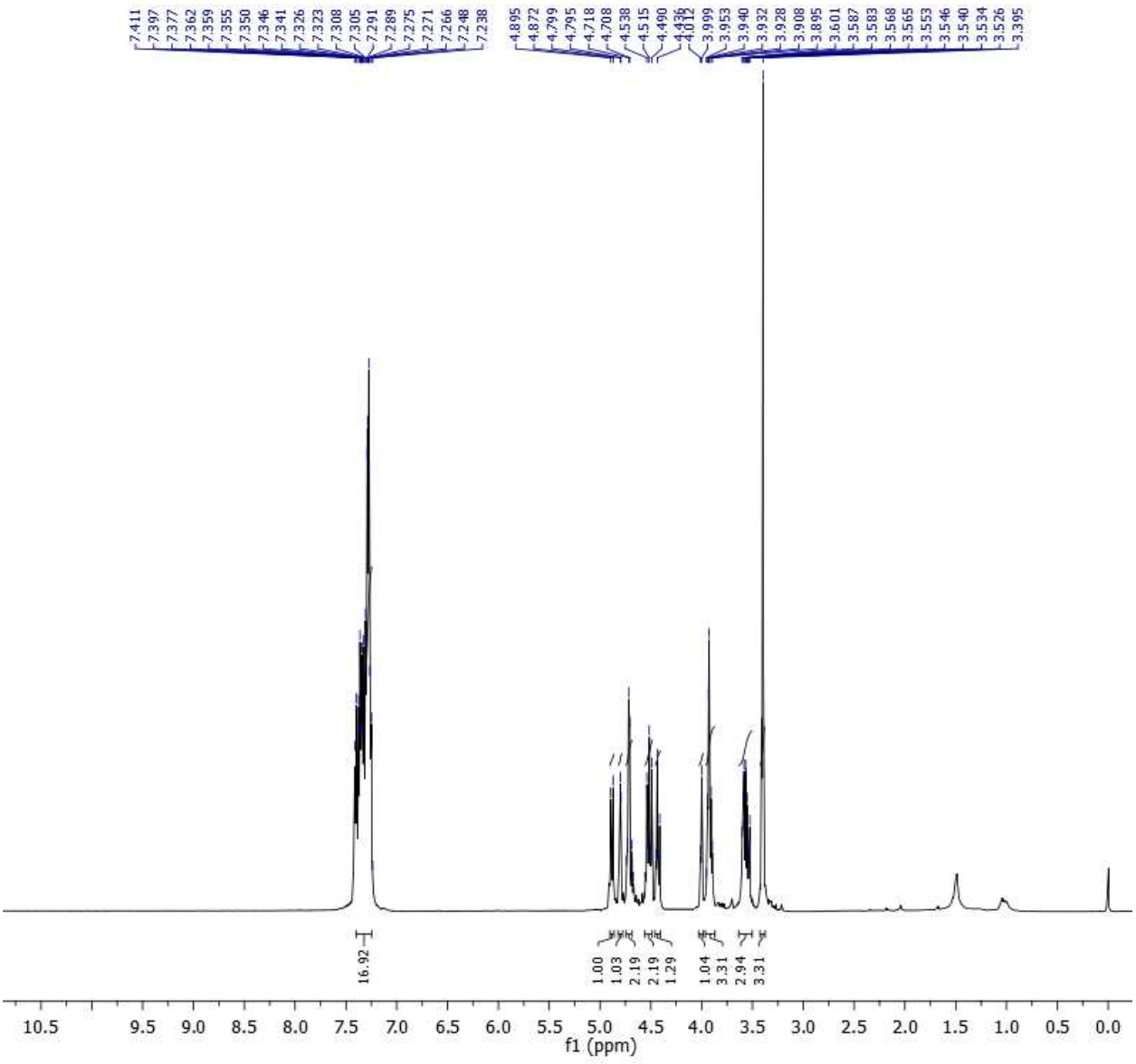
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **44**



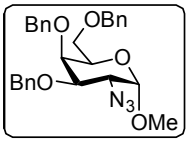


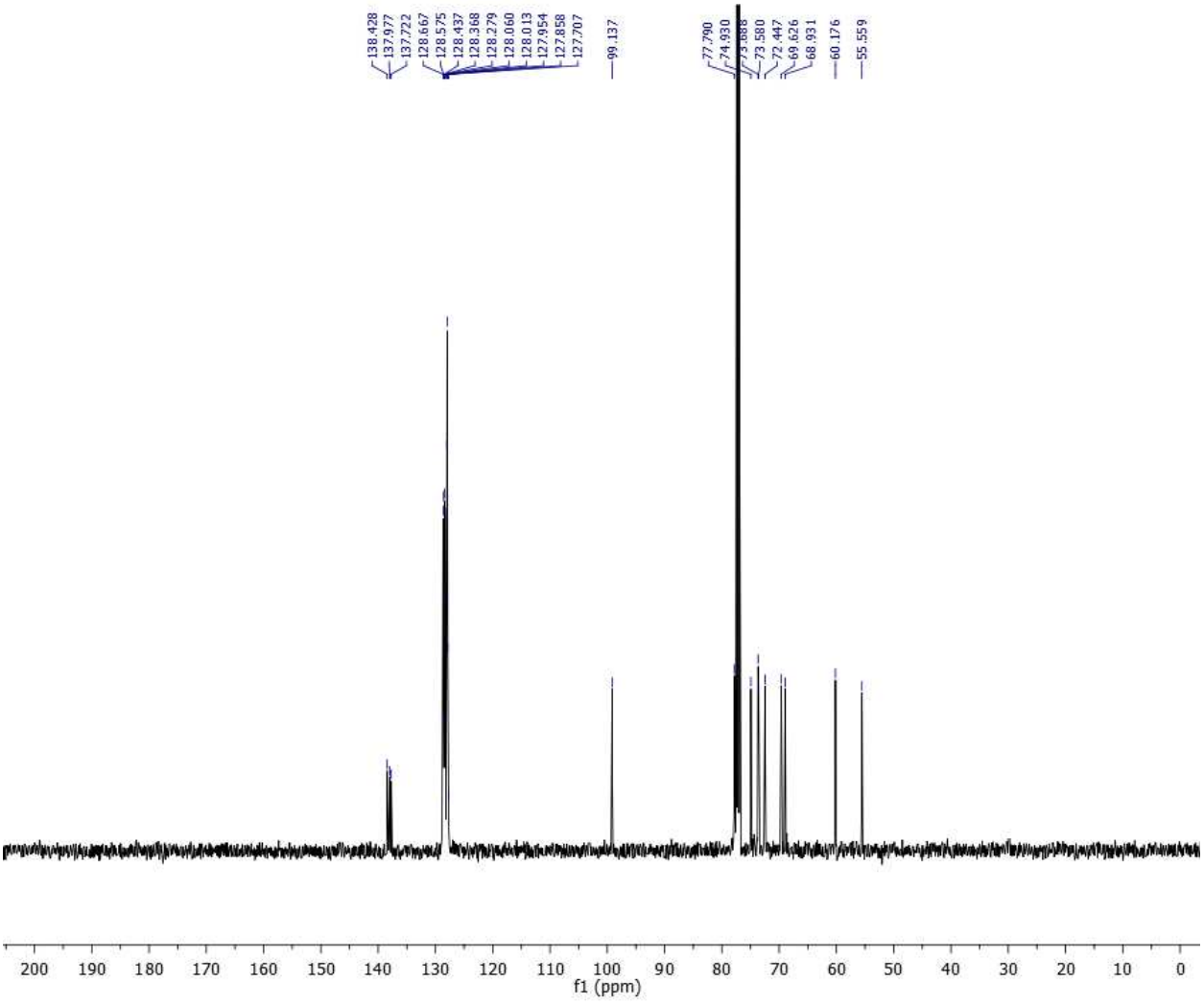
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **44**



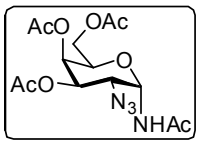


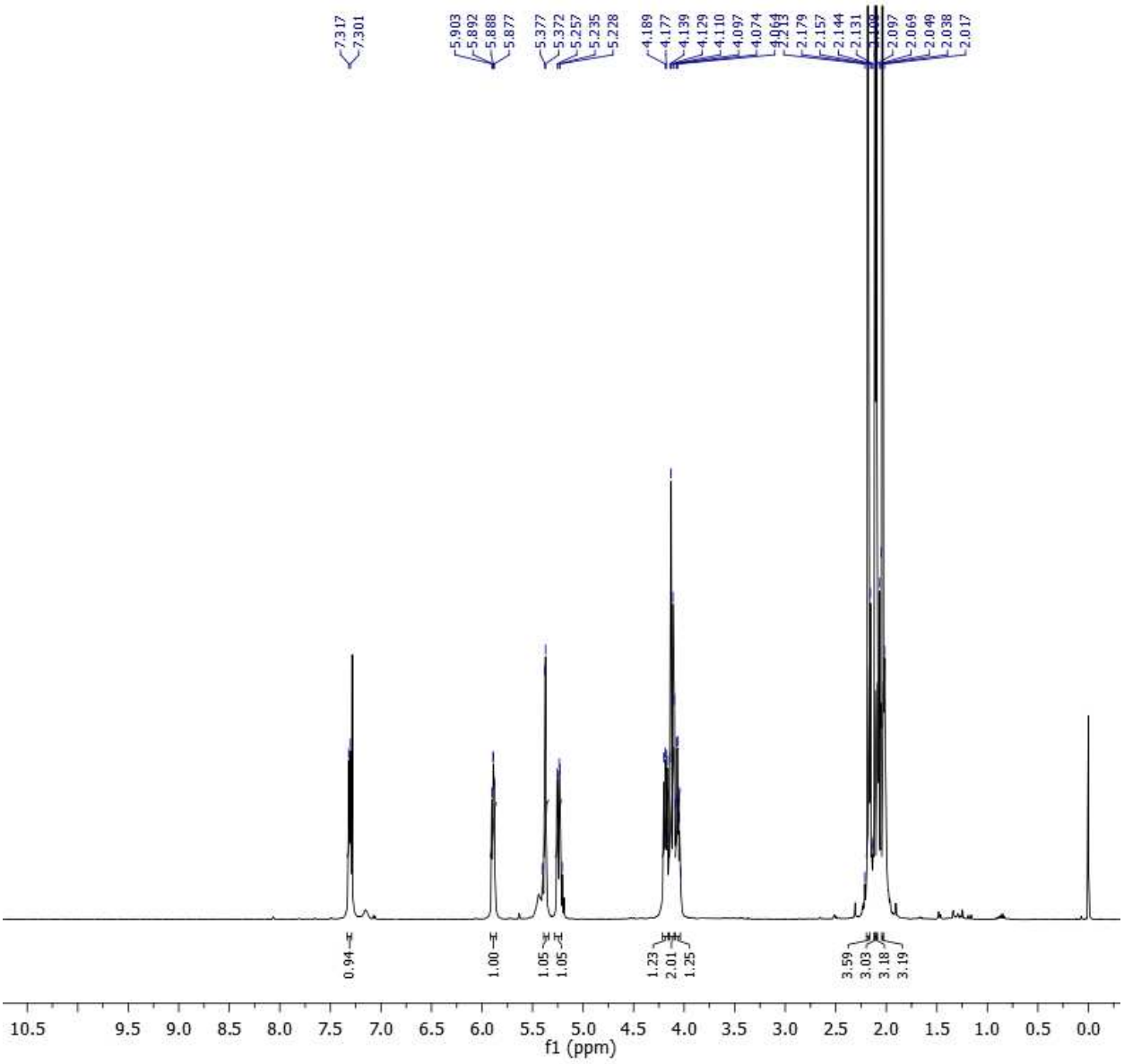
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **45**



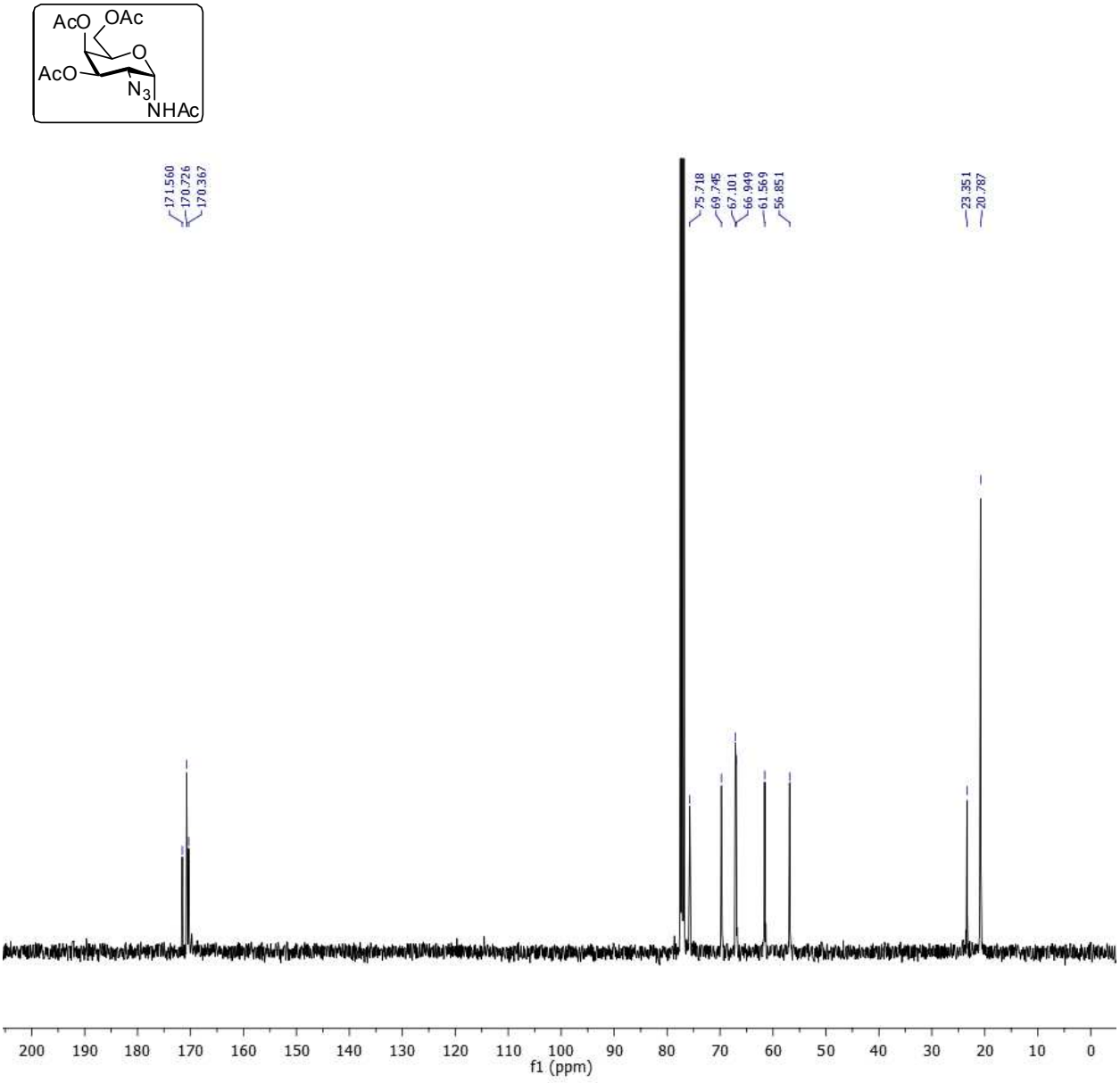


^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **45**

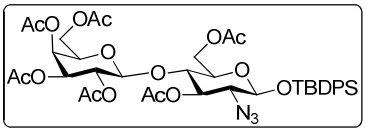


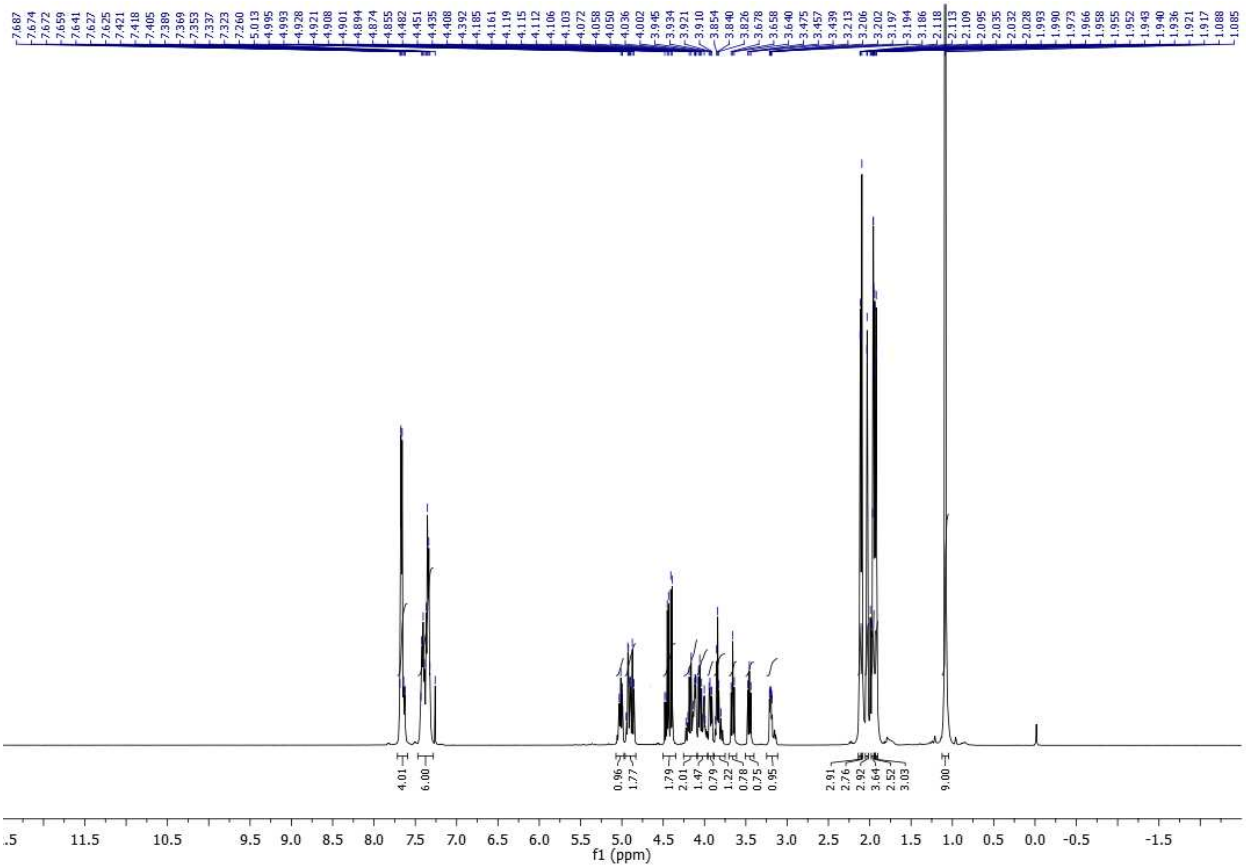


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **46**

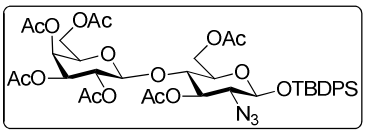


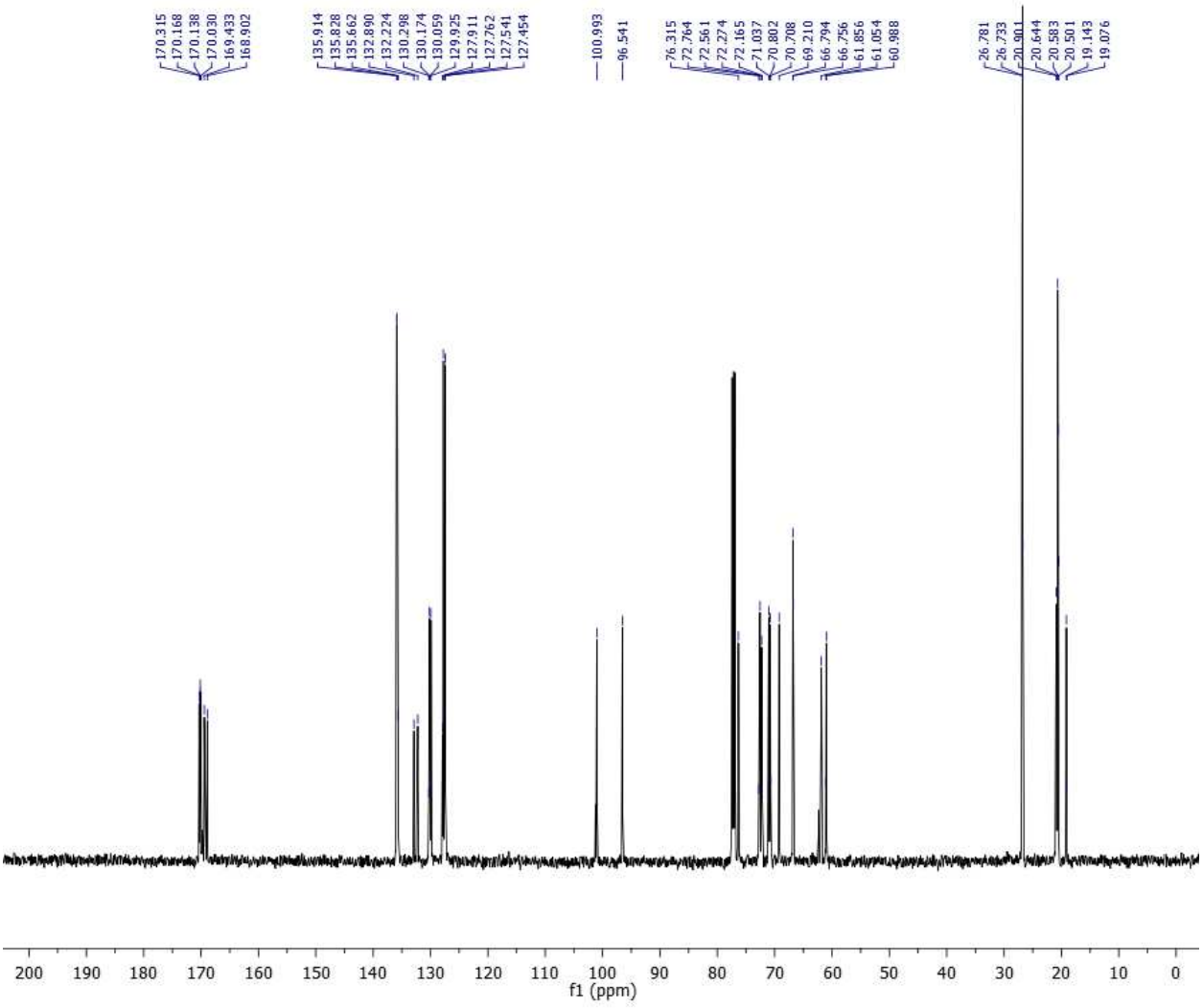
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **46**



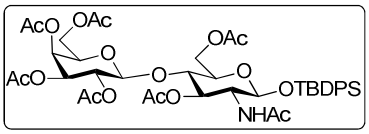


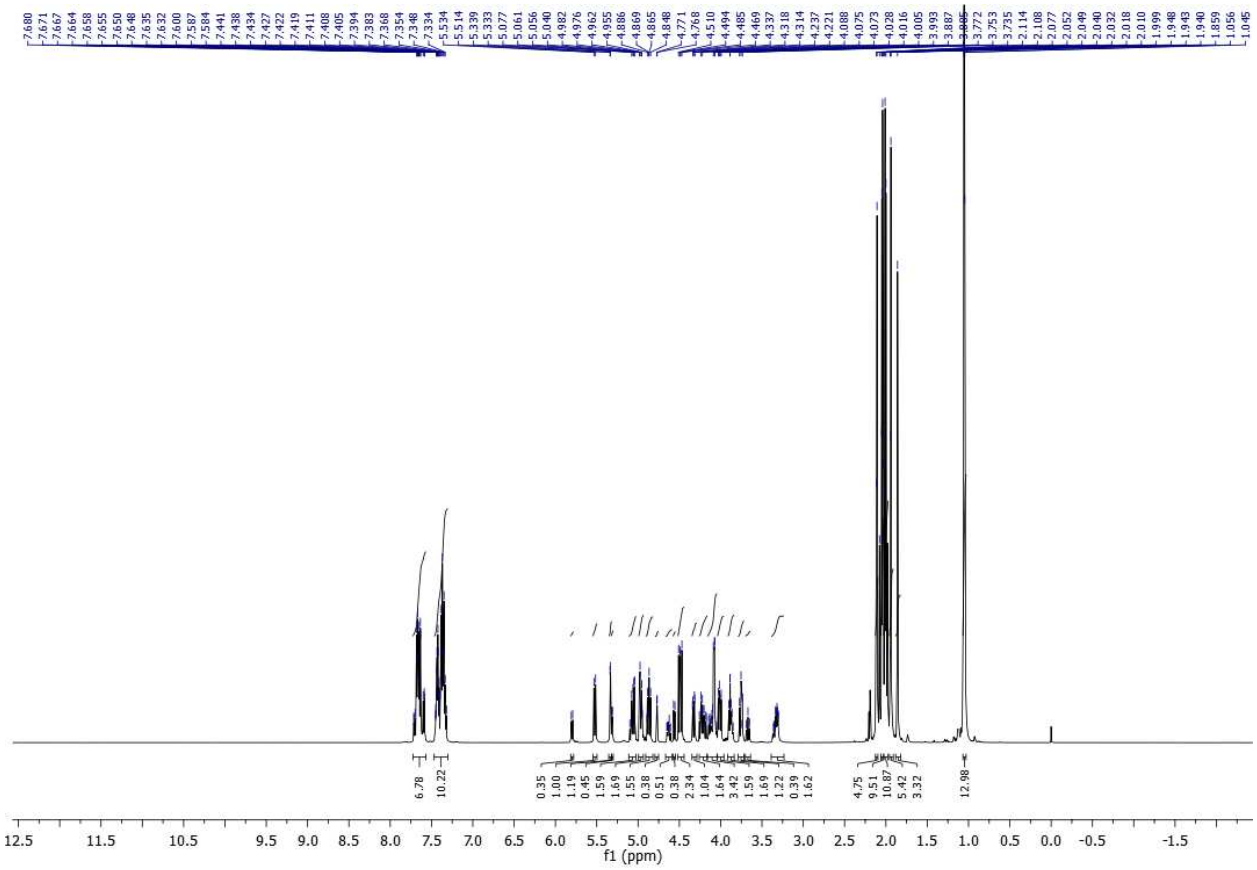
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **47**



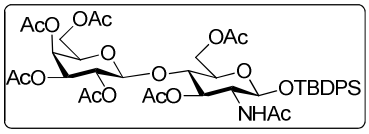


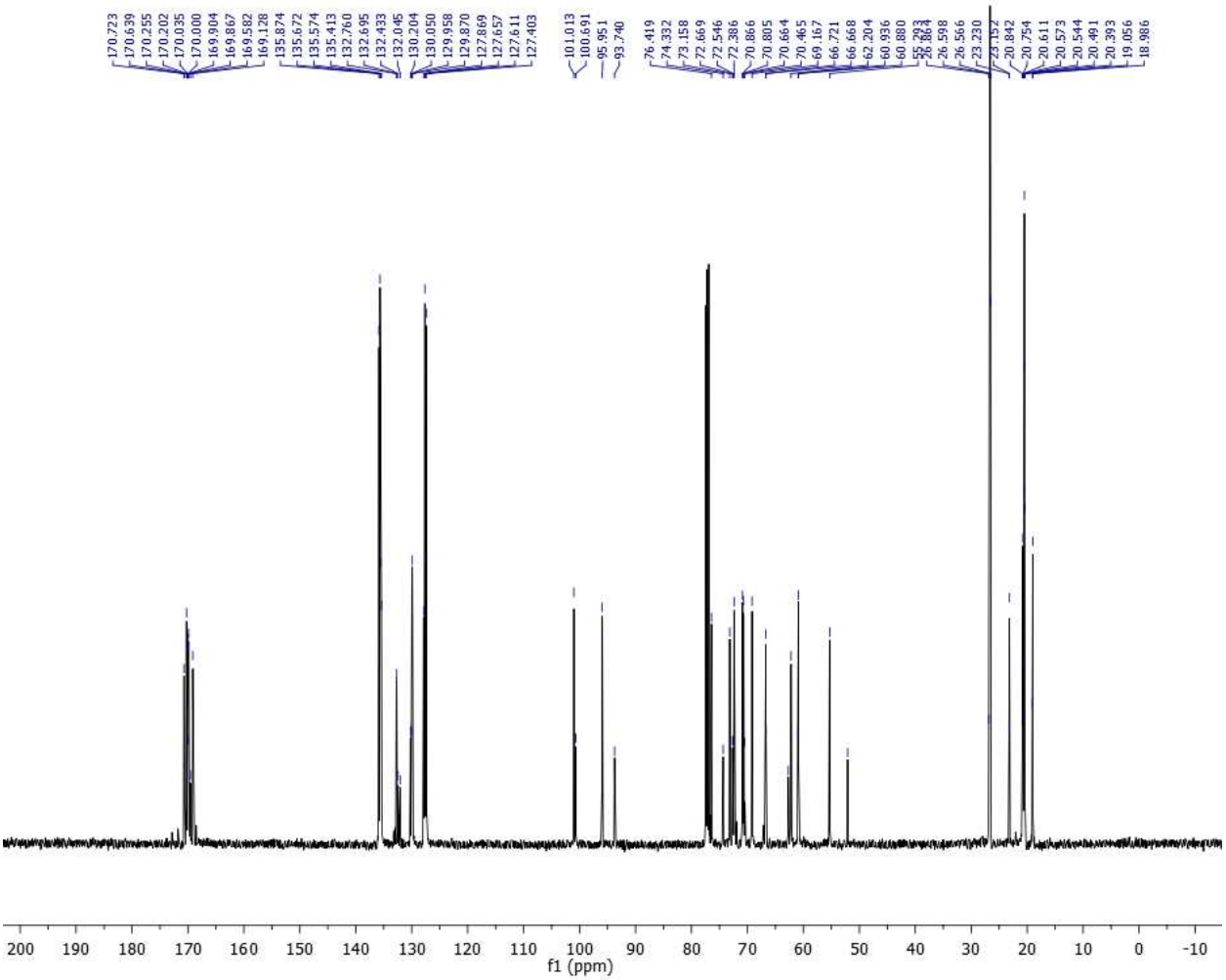
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **47**



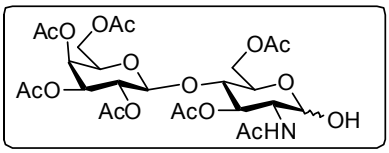


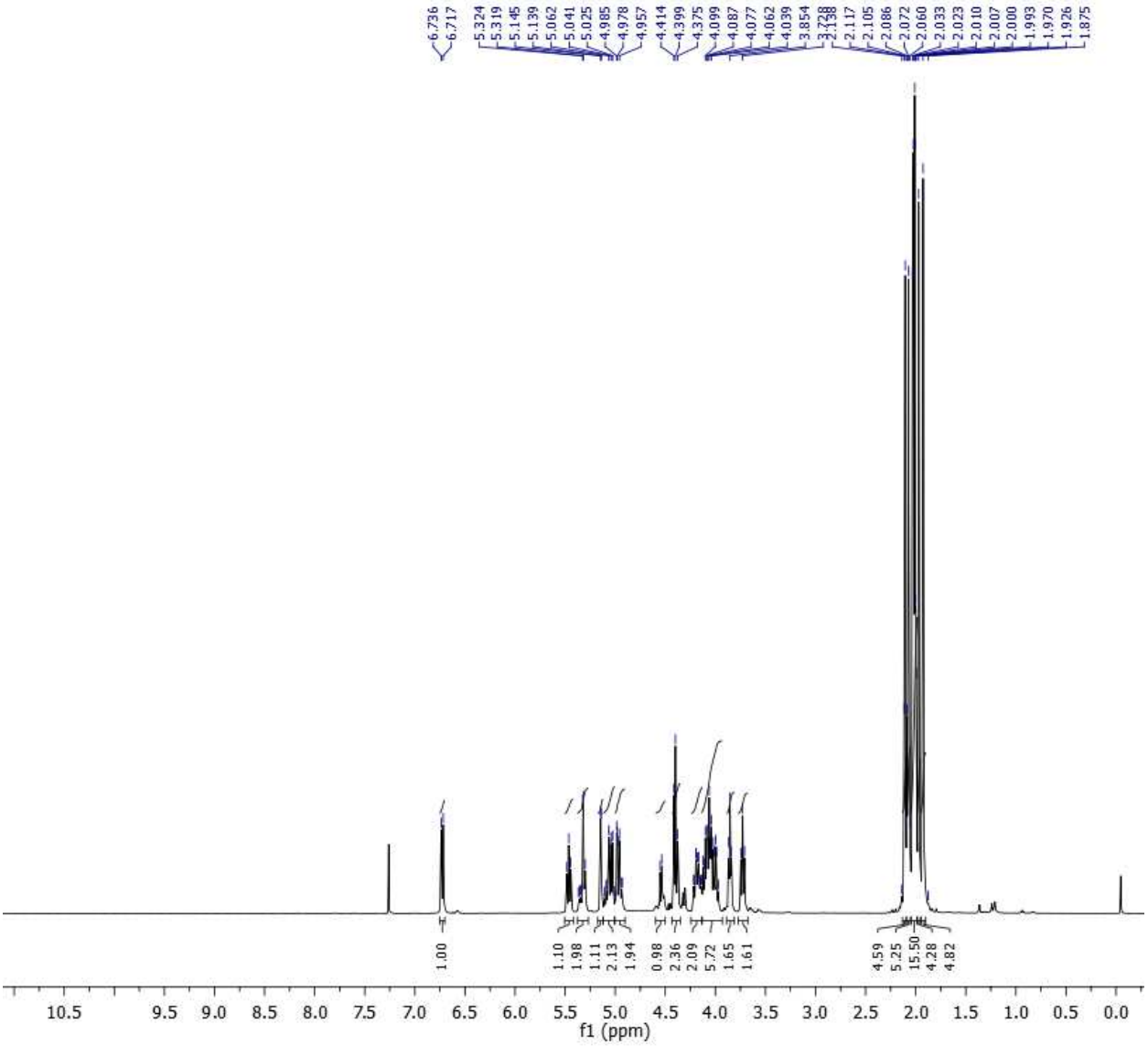
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **48**



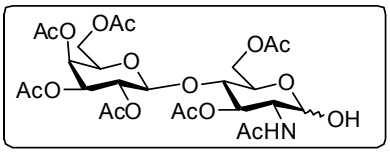


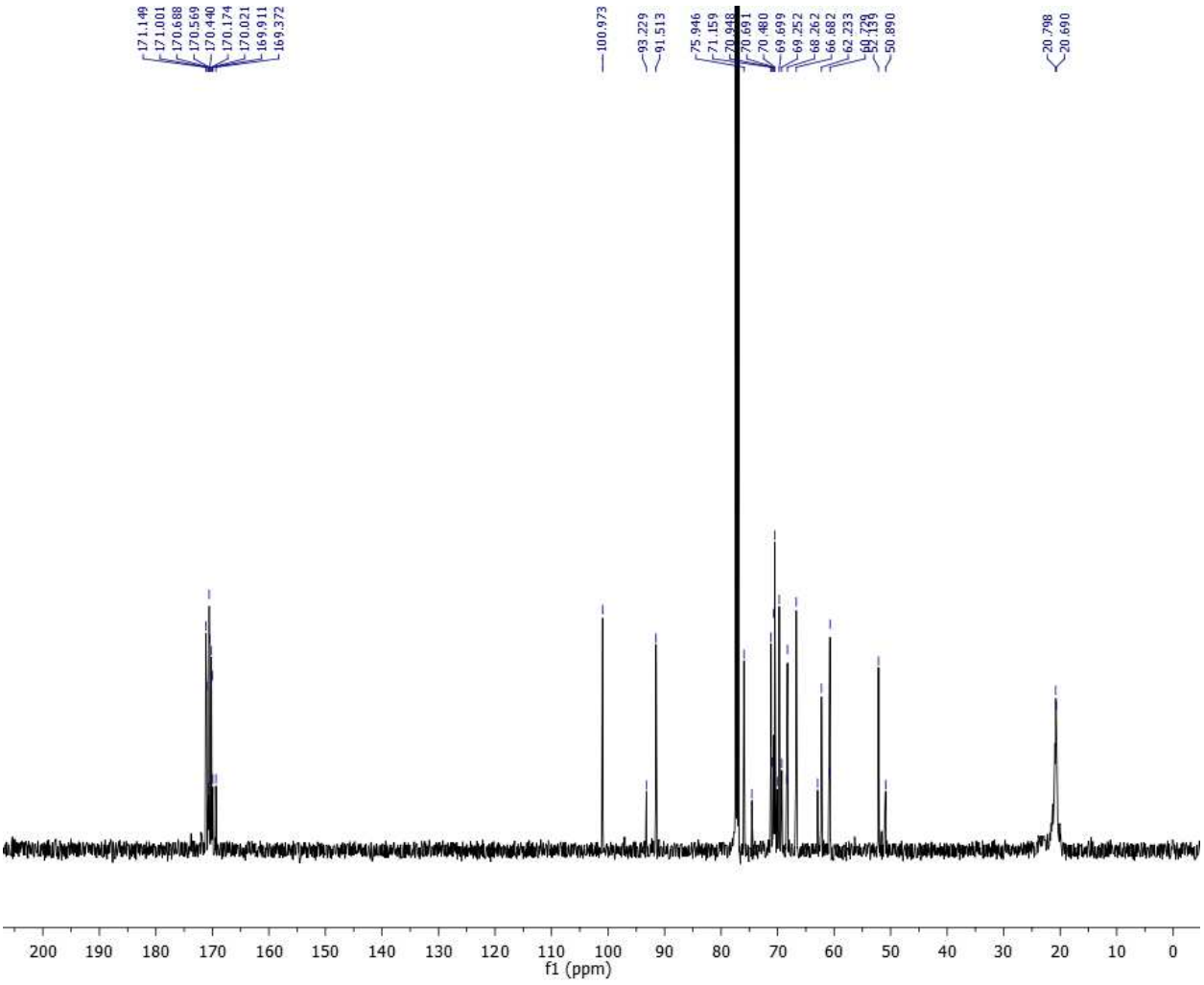
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **48**



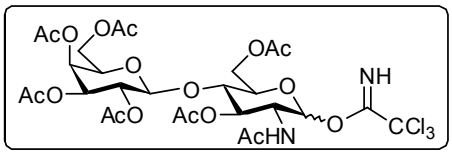


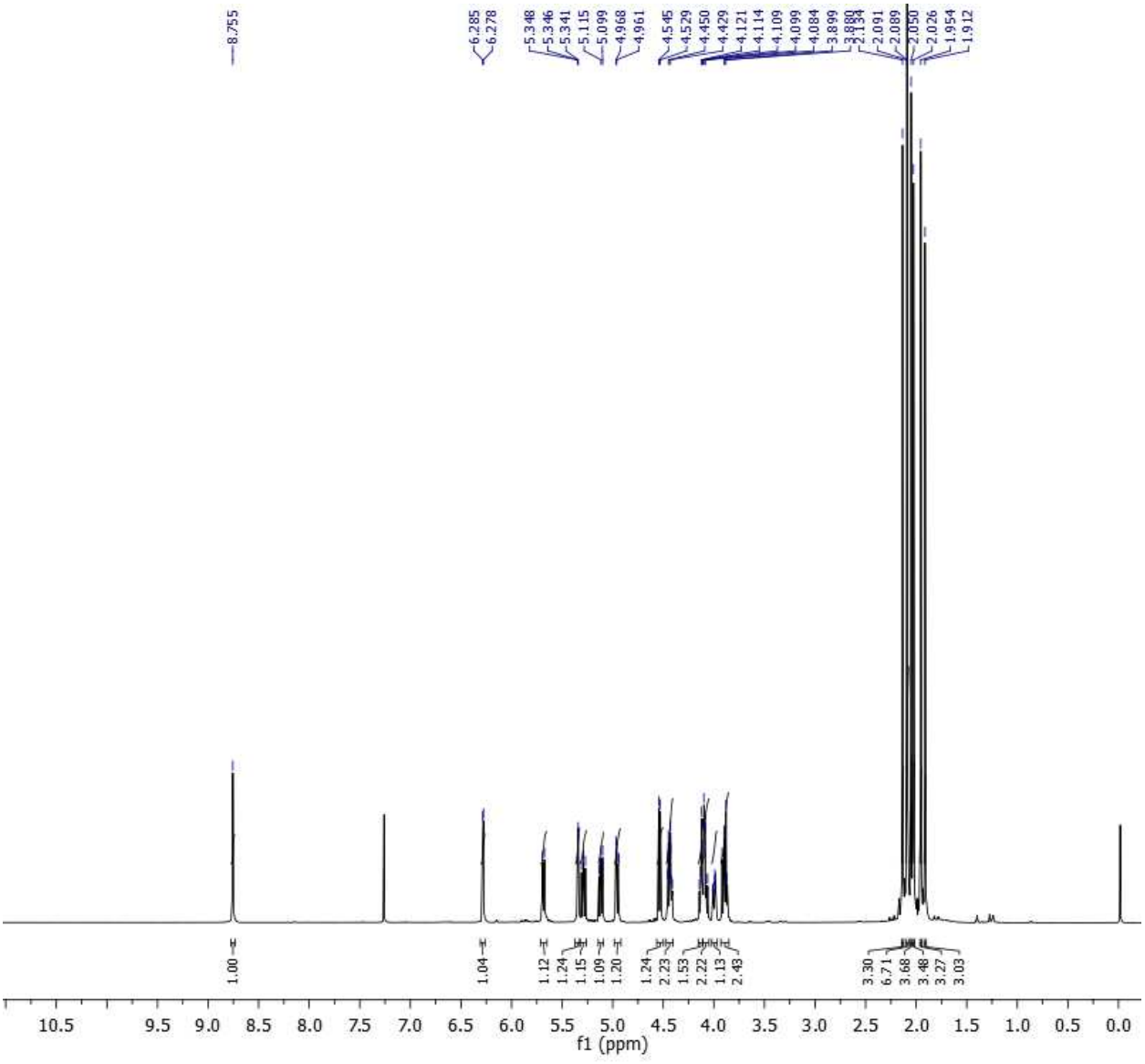
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **49**



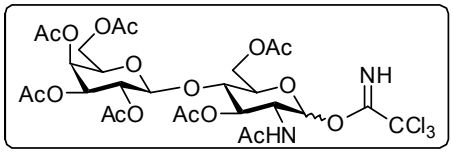


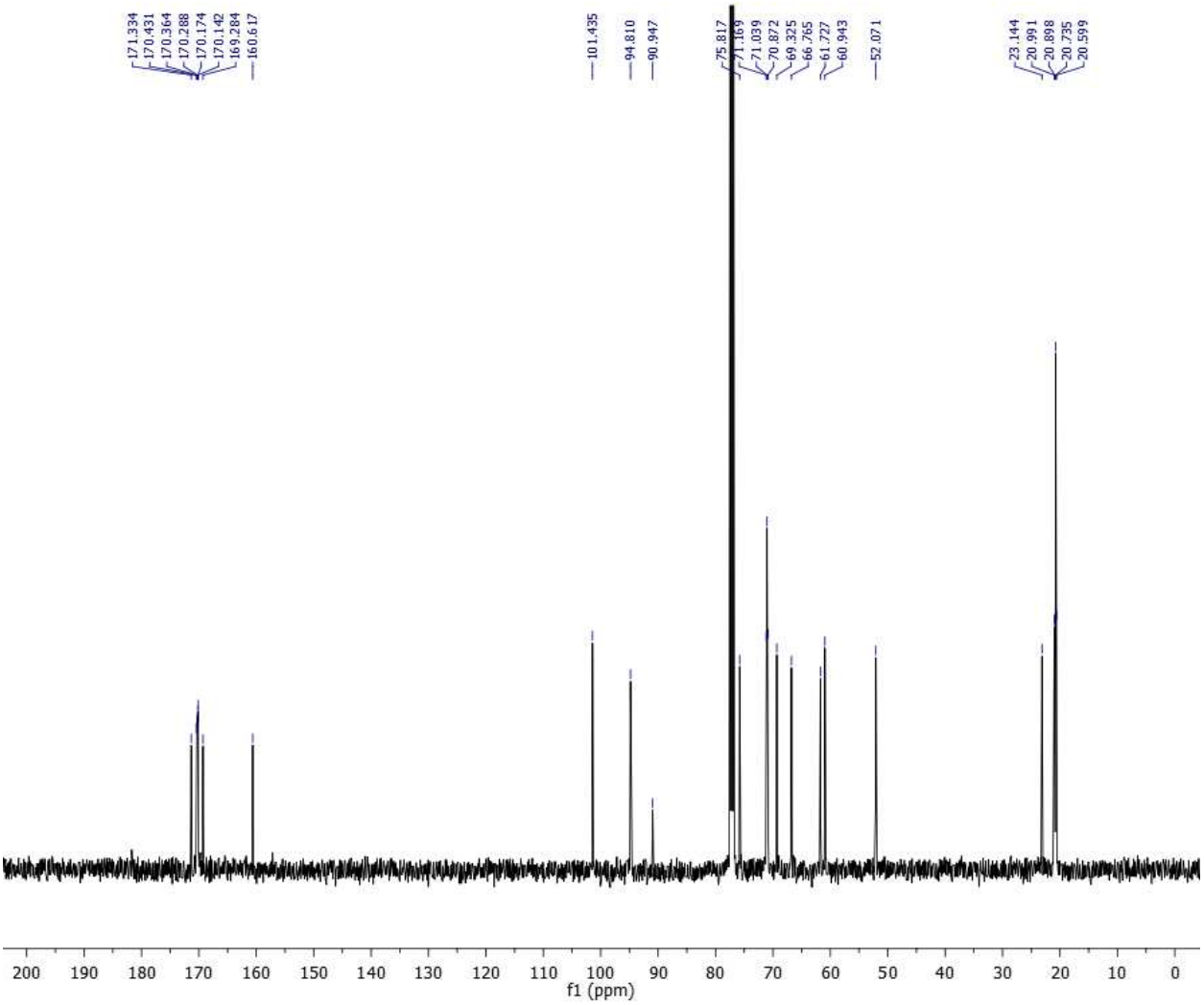
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **49**



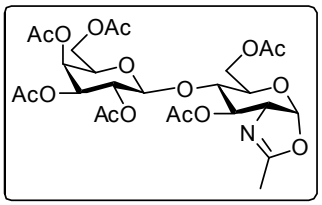


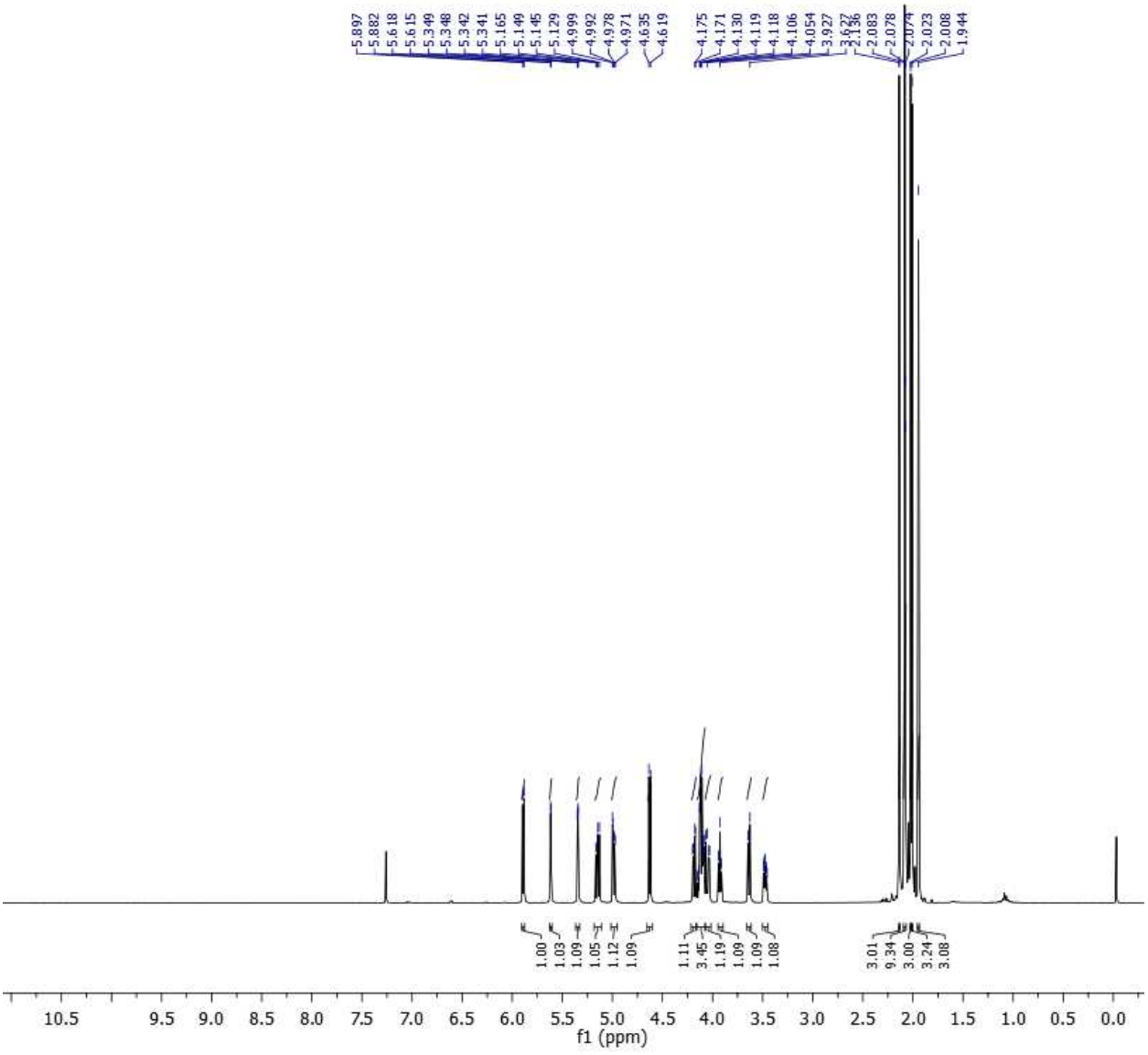
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **50**



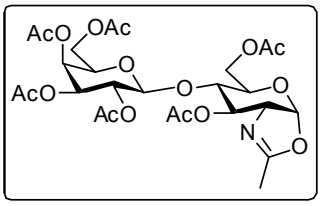


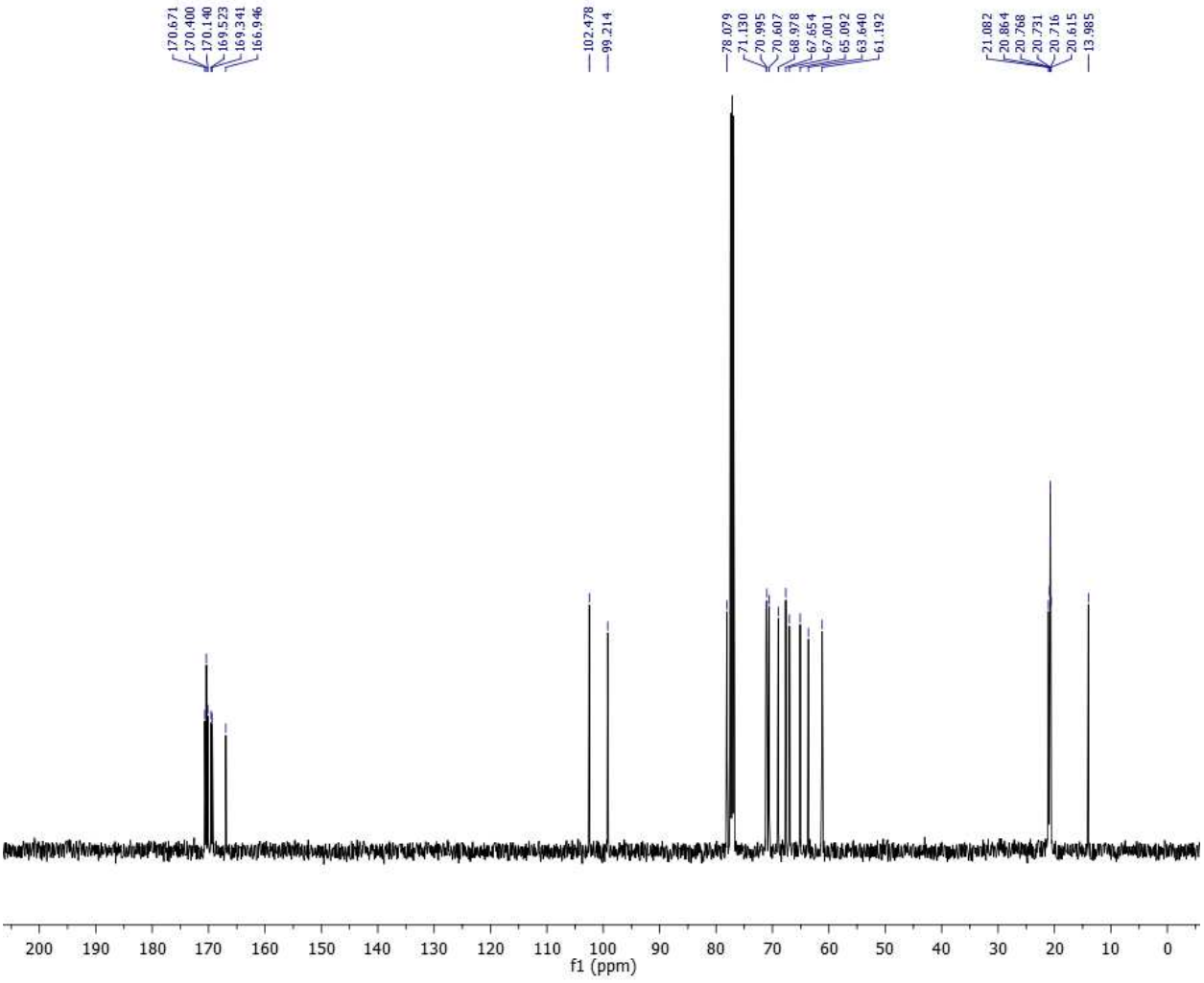
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **50**



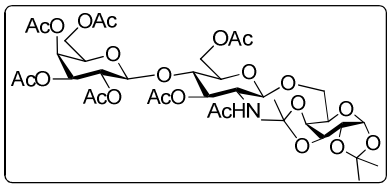


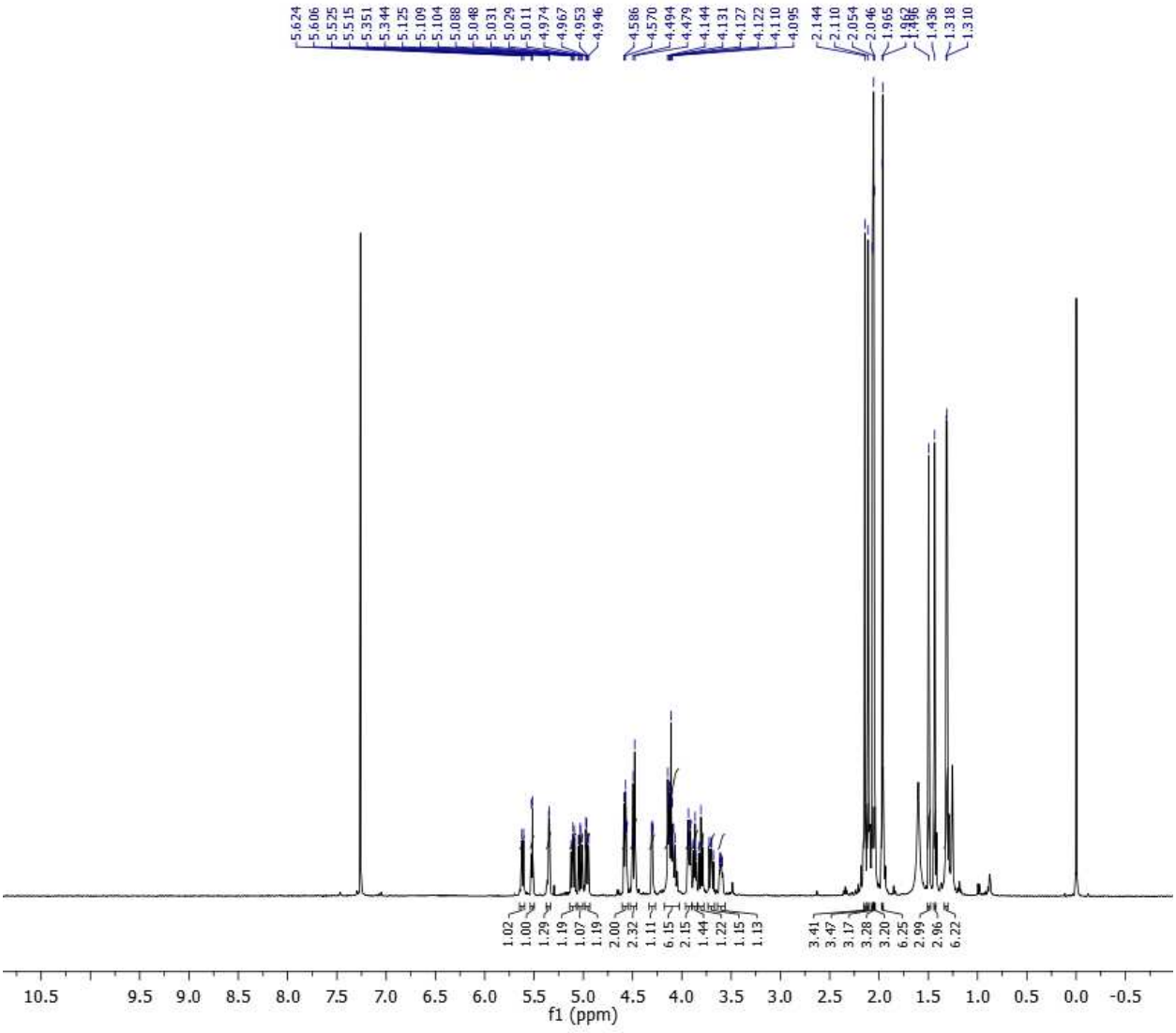
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **51**



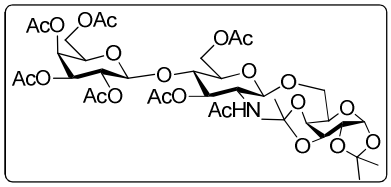


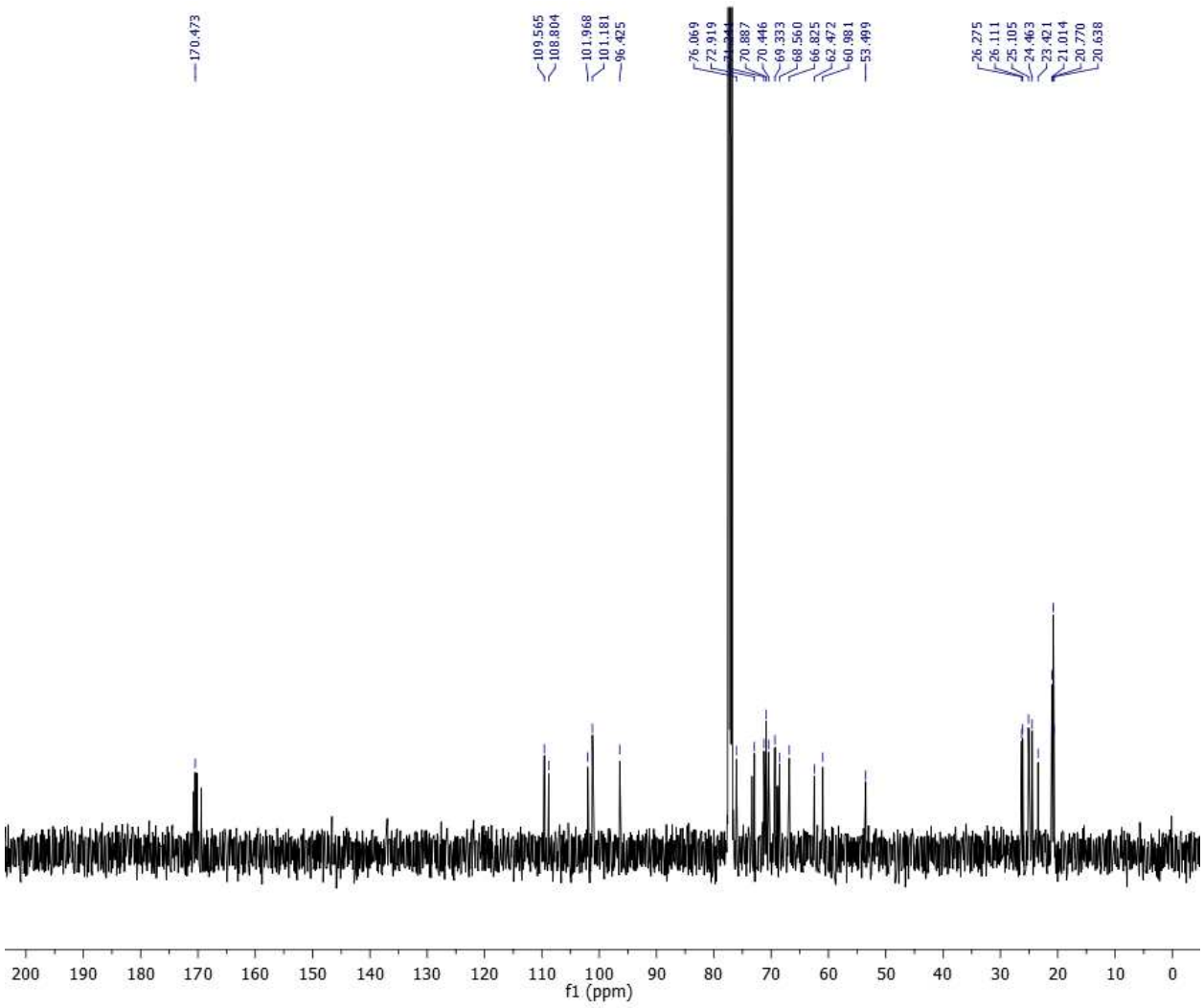
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **51**



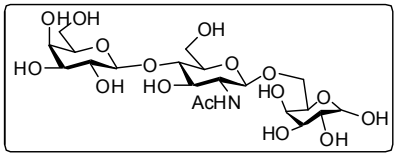


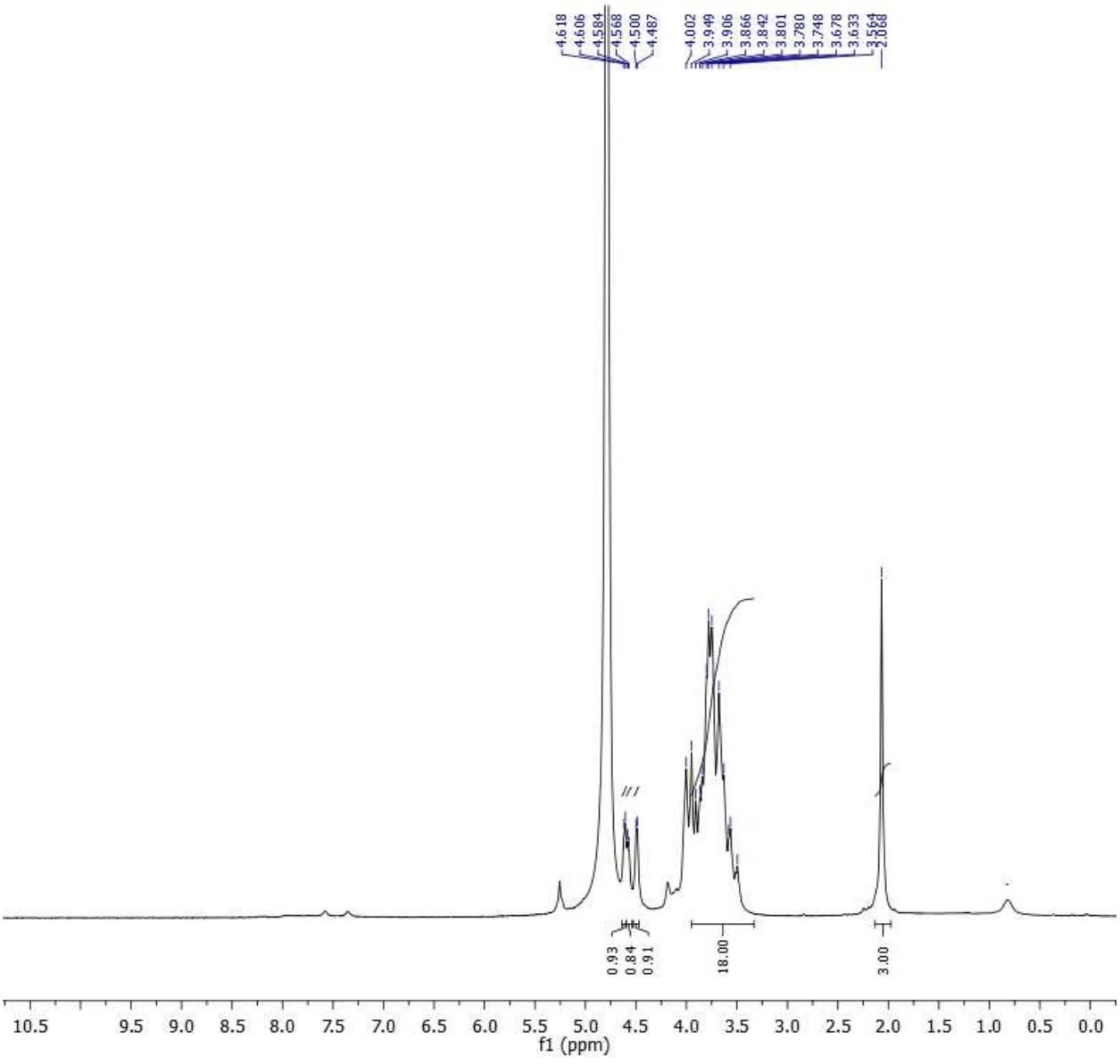
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **53**



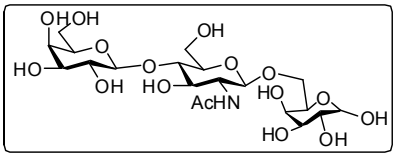


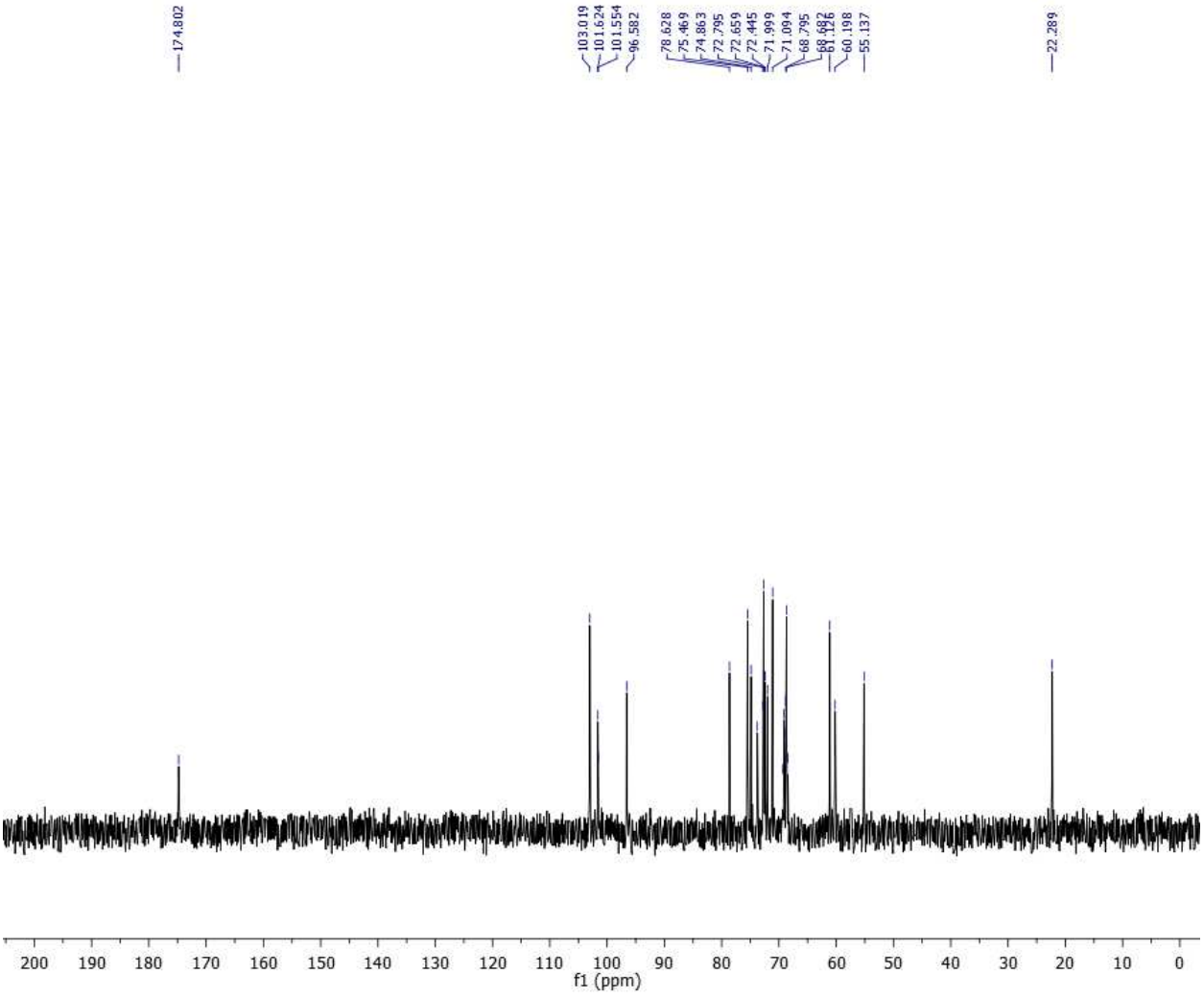
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **53**





^{1}H NMR spectrum (500 MHz, D_2O) of compound **54**

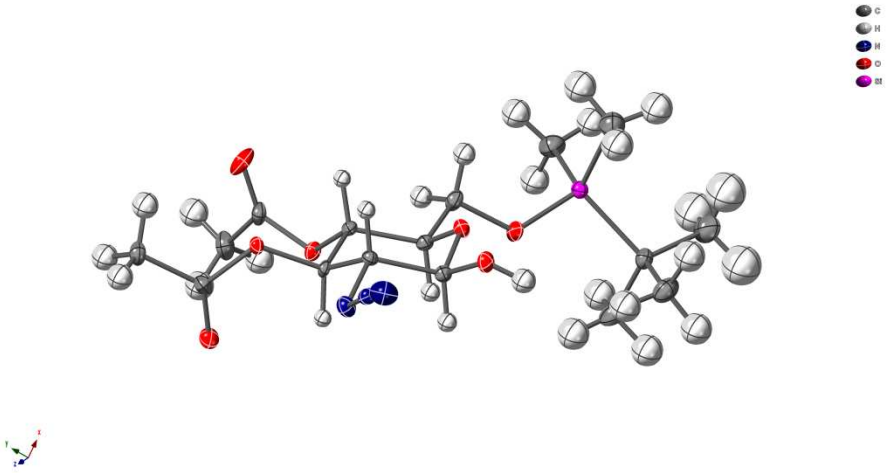




^{13}C NMR spectrum (125 MHz, D_2O) of compound **54**

Crystallography

Compounds **16**, **24, 30** and **34** were crystallized by slow evaporation of their solution in $CDCl_3$ and EtOH over a period of 95 h. The crystals of suitable quality were mounted in glass capillaries, cooled to 273 K and the intensity data were collected on a Bruker APEX-II CCD detector system with Mo-sealed Siemens ceramic diffraction tube (λ = 0.71073) and a highly oriented graphite monochromator operating at 50 kV and 30 mA. The data were collected on a hemisphere mode and processed with SAINT-Plus.[3] Empirical absorption corrections were made using SADABS.[3] The structures were solved by direct methods using Olex2 package and refined by full matrix least-squares method based on F2 using ShelXL (Sheldrick, 2015) program.[4] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their respective non-hydrogen atoms.

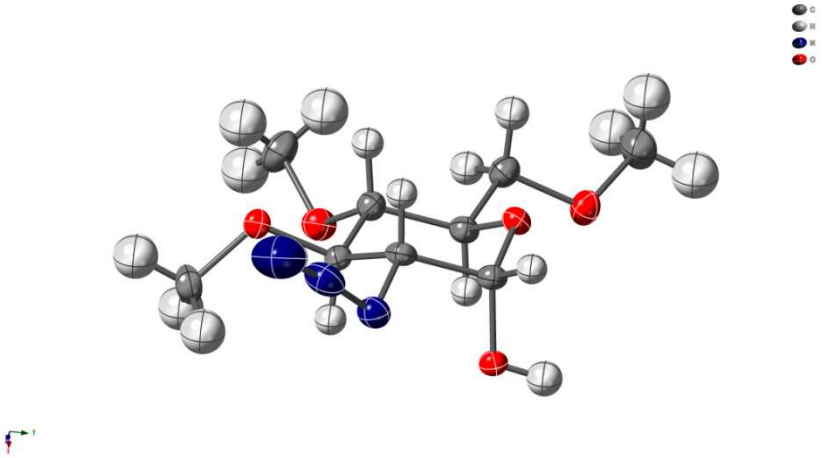


6. Figure 1: X-ray ORTEP diagram showing 30% probability thermal ellipsoids of compound **16 (CCDC 1812127)**

Table 1. Crystal data and structure refinement of compound **16**

Identification code	**16**
Empirical formula	C16 H29 N3 O7 Si
Formula weight	403.17

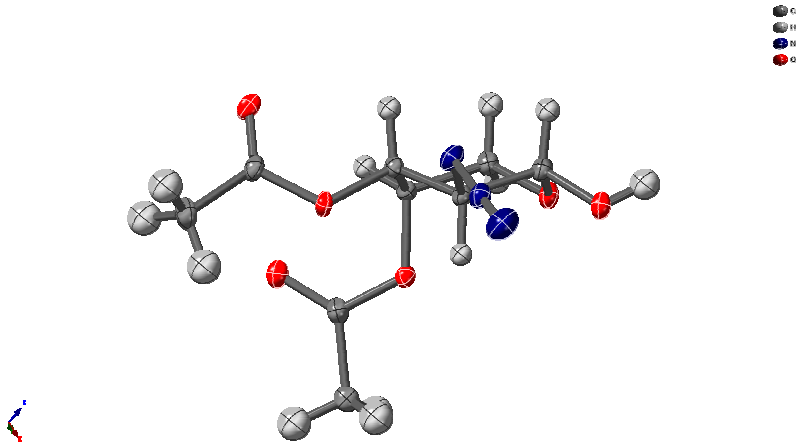
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.4477(4) Å	α= 90°.
	b = 7.9135(3) Å	β= 109.7860(10)°.
	c = 13.5683(5) Å	γ = 90°.
Volume	1055.57(7) $Å^3$	
Z	2	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	0.282 mm^{-1}	
F(000)	492	
Theta range for data collection	2.14 to 28.29°.	
Index ranges	-13<=h<=13, -10<=k<=10, -18<=l<=18	
Reflections collected	16848	
Independent reflections	5238 [R(int) = 0.0768]	
Completeness to theta = 28.29°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5238 / 1 / 252	
Goodness-of-fit on F^2	0.977	
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1426	
R indices (all data)	R1 = 0.0837, wR2 = 0.1652	
Absolute structure parameter	0.01(18)	
Largest diff. peak and hole	0.377 and -0.326 $e.Å^{-3}$	



7. Figure 2: X-ray ORTEP diagram showing 30% probability thermal ellipsoids of compound **24 (CCDC 1818675)**

Table 2. Crystal data and structure refinement for **24**

Identification code	**24**	
Empirical formula	C9 H17 N3 O5	
Formula weight	247.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P 2_1 2_1 2_1	
Unit cell dimensions	a = 4.5258(5) Å	α= 90°.
	b = 14.2965(16) Å	β= 90°.
	c = 18.8278(19) Å	γ = 90°.
Volume	1218.2(2) $Å^3$	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.110 mm^{-1}	
F(000)	528	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.16 to 25.98°.	
Index ranges	-5<=h<=5, -17<=k<=17, -23<=l<=23	
Reflections collected	15840	
Independent reflections	2401 [R(int) = 0.0819]	
Completeness to theta = 25.98°	99.9 %	
Max. and min. transmission	0.9783 and 0.9783	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2401 / 0 / 158	
Goodness-of-fit on F^2	1.158	
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1072	
R indices (all data)	R1 = 0.0771, wR2 = 0.1501	
Absolute structure parameter	-2(2)	
Largest diff. peak and hole	0.350 and -0.378 $e.Å^{-3}$	

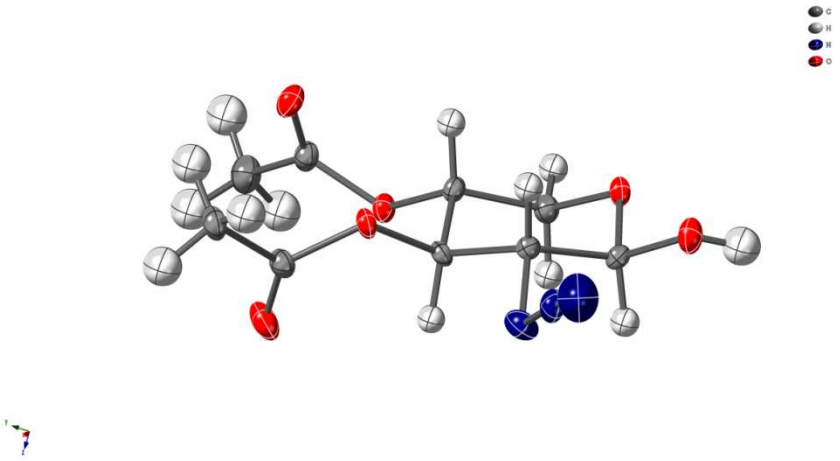


8. Figure 3: X-ray ORTEP diagram showing 30% probability thermal ellipsoids of compound **30** (CCDC **1826411**)

Table 3. Crystal data and structure refinement for **30**

Identification code	**30**	
Empirical formula	C9 H13 N3 O6	
Formula weight	259.22	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	triclinic	
Space group	P1	
Unit cell dimensions	a = 5.5601(5) pm	α= 104.486(3)°.
	b = 6.9368(5) pm	β= 105.146(3)°.
	c = 8.3942(7) pm	γ = 92.947(2)°.
Volume	0.30021(4) nm^3	
Z	1	
Density (calculated)	1.434 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	136	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.06 to 28.28°.	
Index ranges	-7<=h<=7, -9<=k<=9, -11<=l<=11	
Reflections collected	4697	
Independent reflections	2913 [R(int) = 0.0370]	
Completeness to theta = 28.28°	99.8 %	
Max. and min. transmission	0.9761 and 0.9761	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2913 / 3 / 166
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.0942
R indices (all data)	R1 = 0.0535, wR2 = 0.1007
Absolute structure parameter	-1.3(10)
Largest diff. peak and hole	0.258 and -0.233 e.Å^{-3}



9. Figure 4: X-ray ORTEP diagram showing 30% probability thermal ellipsoids of compound **34** (CCDC **1818677**)

Table 4. Crystal data and structure refinement for compound **34**

Identification code	**34**	
Empirical formula	C9 H13 N3 O6	
Formula weight	259.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	tetragonal	
Space group	P 4_1	
Unit cell dimensions	a = 8.7528(5) Å	α= 90°.
	b = 8.7528(5) Å	β= 90°.
	c = 15.7972(12) Å	γ = 90°.
Volume	1210.25(13) Å^3	
Z	4	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	0.121 mm^{-1}	

F(000)	544
Theta range for data collection	2.33 to 28.24°.
Index ranges	-11<=h<=11, -11<=k<=11, -20<=l<=21
Reflections collected	19108
Independent reflections	2983 [R(int) = 0.1085]
Completeness to theta = 28.24°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2983 / 1 / 166
Goodness-of-fit on F^2	1.160
Final R indices [I>2sigma(I)]	R1 = 0.0620, wR2 = 0.1360
R indices (all data)	R1 = 0.0927, wR2 = 0.1756
Absolute structure parameter	-0.3(19)
Largest diff. peak and hole	0.395 and -0.473 e.$Å^{-3}$

10. References

1. (a) Ichikawa, S.; Matsuda, A. *Nucleosides, Nucleotides Nucleic Acids.* **2004**, *23*, 239−253; (b) Johnson, C. L.; Guo, Z. *J. Carbohydr. Chem*., **2013**, *32*, 301–323
2. Kuzuhara, H.; Oguchi, N.; Ohrui, H.; Emoto, S. *Carbohydr. Res*., **1972**, *23*, 217–222.
3. Bruker, SMART, SAINT-Plus, SADABS. Bruker Axs Inc. 1998 Madison, Wisconcin, USA
4. G. M. Sheldrick, Acta Cryst., 2015, C 71, 3.