Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Conversion of Glycals into Vicinal-1,2-Diazides and 1,2-(or 2,1)-Azidoacetates Using Hypervalent Iodine Reagents and Me_3SiN_3. Application in the Synthesis of N-Glycopeptides, Pseudotrisaccharides and an Iminosugar

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General procedures:

All experiments were performed in oven-dried apparatus and under nitrogen atmosphere in dry solvents, unless indicated otherwise. Commercial grade solvents were dried by known methods, and dry solvents were 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. Dichloromethane was freshly distilled over calcium hydride under nitrogen atmosphere. $TMSN_3$ and TMSOTf were purchased from Sigma-Aldrich Chemical Co. $PhI(OOCCF_3)_2$ and $PhI(OAc)_2$ were purchased from Spectrochem Pvt. Ltd (Mumbai). Optical rotations were recorded on AUTOPOL II polarimeter at 25 °C in DCM solvent. 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.

Note: Standard precautions should be taken while handling $TMSN_3$ during the diazidation reactions. All diazides were synthesized on 150 mg scale since above this scale explosions were observed.

(2R,3R,4R,5R,6S)-2-(acetoxymethyl)-5,6-diazidotetrahydro-2H-pyran-3,4-diyl diacetate 7a:

To a cooled solution of **6a** (100 mg, 0.36 mmol), $TMSN_3$ (0.14 ml, 1.10 mmol) and $PhI(OOCCF_3)_2$ (158 mg, 0.36 mmol) in dry CH_2Cl_2 (3 mL) at -30 °C under N_2 atmosphere was added TMSOTf (20 μL, 0.10 mmol). The reaction mixture was stirred at this temperature for 30 min. On consumption of starting material (TLC monitoring) the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (3 mL). 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) and then dried over Na_2SO_4. Evaporation of the solvent followed by silica gel column chromatography of the crude residue with hexane:EtOAc eluent afforded **7a** in 61% yield (61 mg) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 7:3). $[\alpha]_D^{28}$ = –11.7 (*c* 0.5, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3336, 2112, 1748, 1351, 1237, 1067; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (d, *J* = 4.1 Hz, 1H), 5.47–5.43 (m, 1H), 5.21 (dd, *J* = 10.9, 3.2 Hz, 1H), 4.37 (t, *J* = 6.4 Hz, 1H), 4.13 (dd, *J* = 6.5, 2.2 Hz, 2H), 3.94 (dd, *J* = 10.9, 4.1 Hz, 1H), 2.17 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.7, 88.2, 68.9, 68.8, 67.1, 61.5, 57.2, 20.7, 20.6; HRMS Calcd for $C_{12}H_{16}N_6O_7$ $[M + H]^+$ = 357.1159; found 357.1159.

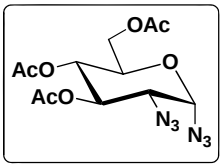
(2S,3R,4R,5R,6R)-2,3-diazido-4,5bis(benzyloxy)6((benzyloxy)methyl) tetrahydro2H-pyran 5:

Compound **5** was prepared from **1** (100 mg, 0.24 mmol) using the procedure described for **7a** in 47% yield (57 mg) as a colourless oil; R_f = 0.70 (hexane/EtOAc,8:2);$[\alpha]_D^{28}$ = + 8.0 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3036, 2118, 1459, 1252, 1079; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 15H), 5.37 (d, *J* = 4.2 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 4.67 (q, *J* = 11.3 Hz, 2H), 4.49 (dd, *J* = 11.5, 5.9 Hz, 2H), 4.41 (d, *J* = 11.8 Hz, 1H), 4.08–3.95 (m, 3H), 3.76 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.61–3.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0,

137.6, 137.2, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.3, 88.7, 77.7, 74.9, 73.6, 73.5, 72.8, 72.2, 71.6, 68.2, 59.3; HRMS Calcd for $C_{27}H_{29}N_6O_4$ $[M + H]^+$ = 501.2250; found 501.2248.

(2R,3S,4R,5R,6S)-2-(acetoxymethyl)-5,6-diazidotetrahydro-2H-pyran-3,4-diyl diacetate 9a:

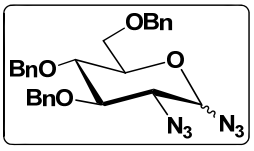
Compound **9a** was prepared from **8a** (100 mg, 0.36 mmol) using the procedure described for **7a** in 58%



yield (76 mg) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = + 28.0 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3345, 2959, 2108, 1747, 1369, 1222, 1046, 600; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (d, *J* = 4.1 Hz, 1H), 5.39–5.32 (m, 1H), 5.06–4.99 (m, 1H), 4.29 (dt, *J* = 5.9, 2.9 Hz, 1H), 4.19–4.10 (m, 2H), 3.66 (dd, *J* = 10.3, 4.2 Hz, 1H), 2.09 (d, *J* = 2.2 Hz, 6H), 2.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 169.7, 87.9, 70.8, 69.8, 68.1, 61.6, 60.8, 20.8, 20.7, 20.6; HRMS Calcd for $C_{12}H_{16}N_6NaO_7$ $[M + Na]^+$ = 379.0978; found 379.0979.

(3R,4R,5S,6R)-2,3-diazido-4,5-bis(benzyloxy)-6 ((benzyloxy) methyl) tetrahy dro-2H-pyran 9b :

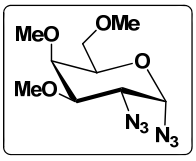
Compound **9b** was prepared from **8b** (100 mg, 0.24 mmol) using the procedure described for **7a** in 56%



yield (67 mg) as a colourless oil; R_f = 0.70 (hexane /EtOAc, 8:2); IR (neat) ν_{max} /cm^{-1} 3030, 2948, 2107, 1454, 1246, 1075; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.22 (m, 24H), 7.20–7.12 (m, 4H), 5.40 (d, *J* = 9.1 Hz, 1H), 5.32 (d, *J* = 4.1 Hz, 1H), 4.85 (d, *J* = 2.4 Hz, 1H), 4.83–4.77 (m, 2H), 4.69 (s, 2H), 4.62 (dd, *J* = 25.8, 12.1 Hz, 2H), 4.54–4.46 (m, 4H), 3.97–3.89 (m, 3H), 3.88–3.80 (m, 2H), 3.78–3.74 (m, 2H), 3.72 (dd, *J* = 7.5, 6.3 Hz, 2H), 3.68 (t, *J* = 2.0 Hz, 1H), 3.66 (t, *J* = 2.0 Hz, 1H), 3.57 (dd, *J* = 9.9, 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.8, 137.7, 137.6, 137.5, 128.7, 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 88.4, 88.3, 80.5, 79.0, 77.8, 75.7, 75.3, 75.1, 73.9, 73.9, 73.6, 73.6, 73.1, 72.9, 68.4, 68.0, 63.2, 61.0. HRMS Calcd for $C_{27}H_{29}N_6O_4$ $[M + H]^+$ = 501.2250; found 501.2250.

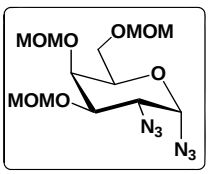
(2S,3R,4R,5R,6R)-2,3-diazido-4,5-dimethoxy-6-(methoxymethyl)tetrahydro-2H-pyran 7b:

Compound **7b** was prepared from **6b** (100 mg, 0.53 mmol) using the procedure described for **7a** in 56%



yield (81 mg) as a colourless oil; R_f = 0.40 (hexane/EtOAc, 7:3). $[\alpha]_D^{28}$ = – 7.7 (*c* 0.3, CH_2Cl_2). IR (neat) ν_{max} /cm^{-1}: 3324, 2110, 1338, 1161; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37 (d, *J* = 4.2 Hz, 1H), 4.00 (t, *J* = 6.5 Hz, 1H), 3.89 (dd, *J* = 10.4, 4.2 Hz, 1H), 3.77–3.73 (m, 1H), 3.57 (s, 3H), 3.56 (d, *J* = 0.8 Hz, 1H), 3.54 (s, 3H), 3.52 (d, *J* = 2.9 Hz, 1H), 3.51–3.49 (m, 1H), 3.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 88.8, 79.5, 74.4, 71.5, 70.6, 61.4, 59.3, 59.1, 57.5; HRMS Calcd for $C_9H_{17}N_6O_4$ $[M + H]^+$ = 273.1311; found 273.1310.

(2S,3R,4R,5R,6R)-2,3-diazido-4,5-bis(methoxymethoxy)-6-(methoxymethoxy) methyl)tetrahydro-2H-pyran 7c:

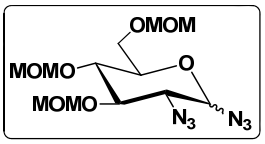


Compound **7c** was prepared from **6c** (100 mg, 0.35 mmol) using the procedure described for **7a** in 51% yield (67 mg) as a colourles oil; R_f = 0.40 (hexane/ EtOAc, 7:3); $[\alpha]_D^{28}$ = + 28.0 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3317, 2111, 1341, 1152,

981. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (d, *J* = 3.6 Hz, 1H), 4.83 (dd, *J* = 9.0, 3.3 Hz, 2H), 4.71 – 4.66 (m, 2H), 4.64 (d, *J* = 6.7 Hz, 2H), 4.06 (dd, *J* = 11.0, 4.1 Hz, 2H), 3.97–3.88 (m, 2H), 3.73–3.62 (m, 2H), 3.45 (d, *J* = 1.2 Hz, 3H), 3.40 (s, 3H), 3.36 (t, *J* = 3.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.6, 96.9, 95.2, 88.6, 73.7, 72.1, 71.8, 66.5, 59.3, 56.3, 56.2, 55. 6; HRMS Calcd for $C_{12}H_{22}N_6NaO_7$ $[M + Na]^+$ = 385.1448; found 385.1446.

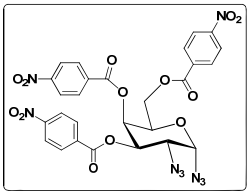
(2S,3R,4R,5S,6R)-2,3-diazido-4,5-bis(methoxymethoxy)-6-((methoxymethoxy)methyl)tetrahydro-2H-pyran 9c:

Compound **9c** was prepared from **8c** (100 mg, 0.35 mmol) using the procedure described for **7a** in 58 %



yield (76 mg) as a colourless oil; R_f = 0.60 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1}: 3328, 2110, 1338, 1158: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (d, *J* = 9.0 Hz, 1H), 5.36 (d, *J* = 4.1 Hz, 1H), 4.89–4.79 (m, 2H), 4.77–4.72 (m, 3H), 4.71 (d, *J* = 2.2 Hz, 1H), 4.68 (dt, *J* = 3.0, 1.9 Hz, 4H), 4.62 (d, *J* = 1.3 Hz, 1H), 3.96 (ddd, *J* = 8.9, 3.7, 1.5 Hz, 1H), 3.93–3.78 (m, 5H), 3.77 (t, *J* = 3.7 Hz, 1H), 3.74 (dd, *J* = 3.8, 2.5 Hz, 1H), 3.73–3.65 (m, 1H), 3.48 (d, *J* = 1.5 Hz, 4H), 3.46–3.41 (m, 3H), 3.39 (d, *J* = 2.8 Hz, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.4, 98.1, 96.9, 96.8, 88.2, 88.1, 84.0, 81.1, 73.1, 71.4, 71.3, 69.1, 66.5, 66.1, 65.8, 62.5, 61.5, 56.4, 56.3, 55.5, 55.5, 55.4; HRMS Calcd for $C_{12}H_{22}N_6NaO_7$ $[M + Na]^+$ = 385.1448 found; 385.1446.

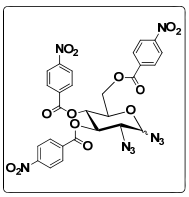
(2R,3R,4R,5R,6S)-5,6-diazido-2-(((4-nitrobenzoyl)oxy)methyl)tetrahydro-2H-pyran-3,4-diyl bis(4-nitrobenzoate) 7e:



Compound **7e** was prepared from **6e** (100 mg, 0.16 mmol) using the procedure described for **7a** in 47% yield (54 mg) as a colourless oil; R_f = 0.40 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = + 7.7 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3214, 2117, 1741, 1539, 1337, 1047; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36–7.99 (m, 12H), 6.00 (d, *J* = 2.7 Hz, 1H), 5.75 (d, *J* = 4.1 Hz, 1H), 5.64 (dd, *J* = 10.9, 3.1 Hz, 1H), 4.79 (t, *J* = 6.6 Hz, 1H), 4.62 (dd, *J* = 11.5, 7.0 Hz, 1H), 4.47 (dd, *J* = 11.5, 6.0 Hz, 1H), 4.24 (dd, *J* = 10.9, 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 163.8, 163.5, 151.3, 151.0, 150.9, 134.4, 133.9, 133.7, 131.1, 131.0, 130.9, 124.1, 123.9, 123.8, 88.3, 70.4, 68.9, 68.9, 62.6, 57.7; HRMS Calcd for $C_{27}H_{20}N_9O_{13}$ $[M + H]^+$ = 678.1181 found; 678.1180.

(2R,3S,4R,5R)-5,6-diazido-2-(((4-nitrobenzoyl)oxy)methyl)tetrahydro-2H-pyran-3,4-diyl bis(4-nitrobenzoate) 9e:

Compound **9e** was prepared from **8e** (100 mg, 0.16 mmol) using the procedure described for **7a** in 52%



yield (59 mg) as a colourless oil; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1}: 3210, 2111, 1746, 1548, 1341: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–8.09 (m, 25H), 5.97–5.82 (m, 3H), 5.71 (d, *J* = 4.1 Hz, 1H), 5.64–5.58 (m, 2H), 4.71–4.63 (m, 3H), 4.62–4.51 (m, 3H), 4.27 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.97 (dd, *J* = 10.4, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 164.1, 163.7, 163.6, 151.1, 151.0, 150.8, 134.8, 134.7, 133.7, 133.5, 133.4, 131.2, 131.1, 131.1, 131.0, 130.9, 123.9, 123.8, 123.7, 123.7, 88.0, 87.9, 71.8, 71.5, 70.5, 69.7, 69.6, 67.0, 63.1, 62.9, 61.4, 60.9; HRMS Calcd for $C_{27}H_{20}N_9O_{13}$ $[M + H]^+$ = 678.1181; found 678.1180.

(2R,3S,4R,5R)-5,6-diazido-2-((benzoyloxy)methyl)tetrahydro-2H-pyran-3,4-diyl dibenzoate 9d:

Compound **9d** was prepared from **8d** (100 mg, 0.21 mmol) using the procedure described for **7a** in 48% yield (57 mg) as a colourless oil; R_f = 0.40 (hexane/ EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3068, 2971, 2112, 1724, 1276, 1110; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–7.83 (m, 10H), 7.57–7.30 (m, 16H), 5.90 (dt, *J* = 20.0, 9.9 Hz, 2H), 5.78 (dd, *J* = 9.9, 3.6 Hz, 1H), 5.60 (dd, *J* = 18.4, 7.0 Hz, 2H), 5.52 (d, *J* = 1.7 Hz, 1H), 4.62 (dt, *J* = 4.3, 2.7 Hz, 1H), 4.59–4.53 (m, 1H), 4.53–4.49 (m, 1H), 4.49–4.42 (m, 1H), 4.20 (dd, *J* = 3.6, 1.9 Hz, 1H), 3.84 (dd, *J* = 10.4, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 165.6, 165.5, 165.3, 133.8, 133.7, 133.7, 133.6, 133.3, 133.2, 130.0, 129.9, 129.9, 129.8, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.3, 88.1, 88.0, 71.6, 70.8, 70.7, 70.2, 69.1, 66.3, 62.9, 62.6, 61.4, 61.2; HRMS Calcd for $C_{27}H_{23}N_6O_7$ $[M + H]^+$ = 543.1628; found 543.1626.

(2R,3R,4R,5R,6S)-5,6-diazido-2-((benzoyloxy)methyl)tetrahydro-2H-pyran-3,4-diyl dibenzoate 7d:

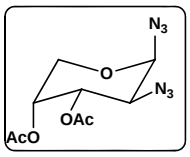
Compound **7d** was prepared from **6d** (100 mg, 0.21 mmol) using the procedure described for **7a** in 51% yield (60 mg) as a colourless oil; R_f = 0.50 (hexane/ EtOAc, 7:3); $[\alpha]_D^{28}$ = + 12.7 (*c* 0.4, CH_2Cl_2); IR (neat) ν_{max} /cm^1 3327, 2111, 1732, 1323, 1053; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.5, 0.7 Hz, 4H), 7.93–7.82 (m, 2H), 7.67–7.27 (m, 10H), 6.00 (d, *J* = 2.7 Hz, 1H), 5.70 (d, *J* = 4.1 Hz, 1H), 5.63 (dd, *J* = 10.8, 3.2 Hz, 1H), 4.72 (t, *J* = 6.5 Hz, 1H), 4.59 (dd, *J* = 11.5, 7.1 Hz, 1H), 4.38 (dd, *J* = 11.5, 5.6 Hz, 1H), 4.22 (dd, *J* = 10.8, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.2, 133.8, 133.65, 133.4, 130.0, 129.9, 129.9, 129.8, 129.3, 128.9, 128.7, 128.5, 88.4, 69.5, 69.4, 68.0, 62.3, 58.0; HRMS Calcd for $C_{27}H_{23}N_6O_7$ $[M + H]^+$ = 543.1628; found 543.1627.

(((2R,3R,4R,5R)-5,6-diazido-2-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydro-2H-pyran-3,4-diyl)bis(oxy))bis(tert-butyldimethylsilane) 9f:

Compound **9f** was prepared from **8f** (100 mg, 0.20 mmol) using the procedure described for **7a** in 45% yield (53 mg) as a colourless oil; R_f = 0.80 (hexane/ EtOAc, 9:1); IR (neat) ν_{max} /cm^{-1} 2930, 2111, 1253, 1089, 837, 779; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (d, *J* = 4.1 Hz, 1H), 5.35 (d, *J* = 9.0 Hz, 1H), 4.01–3.89 (m, 11H), 3.83 (dddd, *J* = 12.5, 12.0, 9.5, 7.0 Hz, 10H), 3.76–3.53 (m, 8H), 3.41 (dd, *J* = 10.1, 4.2 Hz, 2H), 0.91 (dd, *J* = 2.2, 0.8 Hz, 30H), 0.11 (dd, *J* = 4.1, 1.8 Hz, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.3, 73.1, 72.8, 72.3, 72.1, 70.8, 70.5, 64.7, 64.2, 62.6, 62.4, 26.0, 18.4, -5.2; HRMS Calcd for $C_{24}H_{53}N_6O_4S_{i3}$ $[M + H]^+$ = 573.3436; found 573.3431.

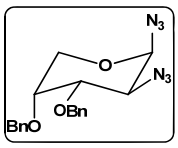
(3R,4S,5S,6R)-5,6-diazidotetrahydro-2H-pyran-3,4-diyl diacetate 11a:

Compound **11a** was prepared from **10a** (100 mg, 0.49 mmol) using the procedure described for **7a** in 49% yield (69 mg) as a colourless oil; R_f = 0.40 (hexane/EtOAc, 8:2); $[\alpha]_D^{28}$ = + 18.0 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 2938, 2109, 1747, 1372, 1231, 1097; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (d, *J* = 4.0 Hz, 1H), 5.32 (s, 1H), 5.19 (dd, *J* = 10.7, 3.2 Hz, 1H), 4.10 (d, *J* = 13.2 Hz, 1H), 3.95 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.82 (dd, *J* = 13.2, 2.1 Hz, 1H), 2.15 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.6, 88.6, 68.3, 67.9, 62.5, 57.5, 20.8, 20.6; HRMS Calcd for $C_9H_{13}N_6O_5$ $[M + H]^+$ = 285.0947;found 285.0942.



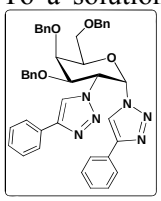
(2R,3S,4S,5R)-2,3-diazido-4,5-bis(benzyloxy)tetrahydro-2H-pyran 11b:

Compound **11b** was prepared from **10b** (100 mg, 0.33 mmol) using the procedure described for **7a** in 53% yield (68 mg) as a colourless oil; R_f = 0.60 (hexane/EtOAc, 8:2); $[\alpha]_D^{28}$ = + 35.0 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3024, 2952, 2115, 1444, 1238, 1071; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 10.1, 7.4, 4.6 Hz, 11H), 5.39 (d, *J* = 3.9 Hz, 1H), 4.66 (d, *J* = 4.9 Hz, 2H), 4.60 (s, 2H), 4.05 (dd, *J* = 9.3, 3.9 Hz, 1H), 3.90–3.86 (m, 1H), 3.78–3.73 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.4, 128.7, 128.6, 128.2, 128.1, 128.0, 88.9, 75.9, 72.0, 71.9, 71.8, 62.4, 59.4; HRMS Calcd for $C_{19}H_{21}N_6O_3$ $[M + H]^+$ = 381.1675; found, 381.1675.

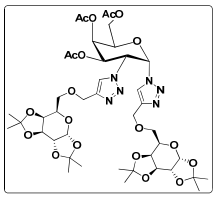


1,1'-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2,3-diyl)bis(4-phenyl-1H-1,2,3-triazole) 13:

To a solution of **7b** (100 mg, 0.199 mmol) and phenylacetylene (44 μL, 0.39 mmol) in 1:1 ratio of H_2O/EtOH (4 mL) were added sodium ascorbate (18 mg, 0.08 mmol) and copper(II) sulfate pentahydrate (7.2 mg, 0.03 mmol). The heterogeneous mixture was stirred vigorously at 60 °C for 6 h. Upon consumption of starting material (TLC monitoring) the reaction mixture was diluted with 5 mL of water and extraction was done with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (1 × 5 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 **13** in 80% yield (113 mg) as a colourless oil; R_f = 0.40 (hexane/EtOAc, 8:2); $[\alpha]_D^{28}$ = -31.0 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3137, 3031, 2923, 1454, 1104, 1074, 1027, 739, 764, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.99 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40– .32 (m, 8H), 7.32 – 7.23 (m, 9H), 7.18 – 7.13 (m, 2H), 6.49–6.44 (m, 1H), 6.37 (d, *J* = 2.7 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 4.71–4.60 (m, 3H), 4.51 (dd, *J* = 22.8, 11.4 Hz, 2H), 4.18 (t, *J* = 8.5 Hz, 1H), 3.89 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.82–3.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.3, 146.3, 137.7, 137.2, 136.9, 135.2, 130.4, 129.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 126.0, 125.8, 123.6, 120.0, 119.1, 108.3, 84.5, 78.8, 74.8, 74.4, 73.8, 72.4, 68.7, 68.1, 66.6, 58.5; HRMS Calcd for $C_{43}H_{40}N_6NaO_4$ $[M + Na]^+$ = 727.3009; found 727.3006.

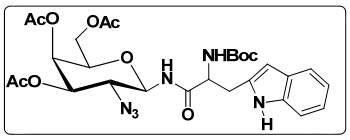


(2R,3R,4R,5R,6S)-2-(acetoxymethyl)-5,6-bis(4-((((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetra hy dro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran 5-yl)methoxy)methyl)-1H-1,2,3-triazol-1-yl)tetra h y d ro-2H-pyran-3,4-diyl diacetate 15:



To a solution of **7a** (100 mg, 0.28 mmol) and **14** (168 mg, 0.56 mmol) in 1:1 ratio of H_2O/EtOH (4 mL) were added sodium ascorbate (25 mg, 0.12 mmol) and copper(II) sulfate pentahydrate (11 mg, 0.04 mmol). The heterogeneous mixture was stirred vigorously at 60 °C for 8h. Upon consumption of starting material (TLC monitoring) the reaction mixture was diluted with **5 mL of water** and extraction was done with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (1 × 5 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 **15** in 75 % yield (200 mg) as a colourless oil; R_f= 0.40 (hexane/EtOAc 6:4); $[\alpha]_D^{28}$ = -26.0 (*c* 0.5, CH_2Cl_2)IR (neat) ν_{max} /cm^{-1} 3129, 3062, 2914, 2868, 1458, 1040, 1021, 1027, 739, 764, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 4.4 Hz, 1H), 7.13 (s, 1H), 6.68 (dd, *J* = 12.0, 3.4 Hz,1), 6.40 (d, *J* = 5.8 Hz, 1H), 5.77 (dd, *J* = 11.9, 5.8 Hz, 1H), 5.72 (d, *J* = 3.0 Hz, 1H), 5.48 (dd, *J* = 4.9, 1.9 Hz, 2H), 4.70 (t, *J* = 6.5 Hz, 1H), 4.61 (s, 2H), 4.56 (dd, *J* = 7.9, 2.3 Hz, 2H), 4.45 (d, *J* = 5.6 Hz, 2H), 4.27 (td, *J* = 5.1, 2.3 Hz, 2H), 4.21–4.13 (m, 3H), 4.10–4.01 (m, 1H), 3.95–3.90 (m, 1H), 3.90 – 3.85 (m, 1H), 3.65 (dd, *J* = 10.2, 5.3 Hz, 1H), 3.58 (dd, *J* = 10.2, 7.0 Hz, 1H), 3.51 (dd, *J* = 10.1, 5.7 Hz, 1H), 3.45 (dd, *J* = 10.1, 6.8 Hz, 1H), 2.20 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H), 1.50 (s, 3H), 1.48 (s, 3H), 1.40 (d, *J* = 2.5 Hz, 6H), 1.31 – 1.28 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 169.9, 169.4, 145.7, 145.5, 125.3, 121.2, 109.4, 109.3, 108.6, 96.4, 96.3, 84.0, 71.2, 71.1, 71.0, 70.7, 70.6, 70.5, 69.7, 69.2, 66.9, 66.7, 66.5, 64.6, 64.3, 61.1, 57.5, 26.2, 26.1, 26.0, 25.0, 24.9, 24.5, 20.7, 20.6, 20.4; HRMS Calcd for $C_{42}H_{61}N_6O_{19}$ $[M + H]^+$ = 953.3991; found 953.3990.

(2R,3R,4R,5R,6R)-2-(acetoxymethyl)-5-azido-6-(2-((tert-butoxycarbonyl)amino)-3-(1H-indol-2-yl)propanamido)tetrahydro-2H-pyran-3,4-diyl diacetate 18:

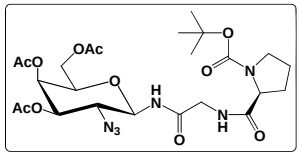


To a stirred solution of **7a** (100 mg, 0.28 mmol) in acetonitrile/ethanol (1:1, 4 mL) was added tetrathiomolybdate (118 mg, 0.28 mmol) and stirring continued at room temperature for 8 h. Upon consumption of starting material (TLC monitoring) the solvent was evaporated under reduced pressure. The black residue was extracted with CH_2Cl_2/ether (1:10, 4 X 5 mL) and filtered through a pad of Celite. The solvent was evaporated to give the crude amine **16**. 2-((tert-butoxycarbonyl)amino)-3-(1H-indol-2-yl)propanoic acid (74 mg, 0.25 mmol) was taken in a round bottomed flask under nitrogen and dissolved in dry CH_2Cl_2 (2 mL). The reaction flask was then cooled to 0 °C and to it hydroxybenzotriazole (58 mg, 0.37 mmol) followed by EDC (57 mg, 0.37 mmol) were added and the reaction mixture stirred at 0 °C for 15 min. The crude glycosyl amine **16** was dissolved in dry CH_2Cl_2 (2 mL), and N,N-diisopropylethylamine (44 μL, 0.25 mmol) was added successively to the reaction mixture at 0 °C and allowed to stir at room temp for 8 h. After completion of reaction (TLC monitoring) it was extracted with CH_2Cl_2 (2 x 10 mL). The organic layer was washed with 1N HCl (2 x 5 mL) followed by saturated aqueous $NaHCO_3$ solution (2 x 5 mL) and with brine. The organic layer was dried over Na_2SO_4. Evaporation of the solvent gave a residue which was purified by column chromatography with hexane:EtOAc as eluent to afford **18** in 78% (135 mg) over two steps as a colourless oil; R_f = 0.30 (hexane/EtOAc, 1:1); IR (neat) ν_{max} /cm^{-1}: 3342, 2117, 1741, 1702, 1630; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6

Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.09 (d, *J* = 9.1 Hz, 1H), 5.32 (d, *J* = 2.8 Hz, 1H), 5.04 (s, 1H), 4.98 (d, *J* = 7.0 Hz, 1H), 4.89 (dd, *J* = 11.3, 3.0 Hz, 1H), 4.50 (ddd, *J* = 11.4, 9.3, 4.2 Hz, 1H), 4.43 (dd, *J* = 12.2, 5.7 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 1H), 4.11 (dd, *J* = 11.3, 5.9 Hz, 1H), 4.05 (dd, *J* = 11.3, 7.0 Hz, 1H), 3.43 (dd, *J* = 14.7, 5.0 Hz, 1H), 3.11 (dd, *J* = 14.8, 5.8 Hz, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 1.91 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 170.8, 170.5, 170.2, 155.4, 136.4, 127.1, 122.9, 122.7, 119.9, 119.1, 111.4, 110.2, 88.4, 80.6, 68.7, 67.3, 67.0, 61.7, 54.8, 47.0, 28.36, 20.7, 20.5; HRMS Calcd for $C_{28}H_{37}N_6O_{10}$ $[M + H]^+$ = 617.2571 found; 617.2570.

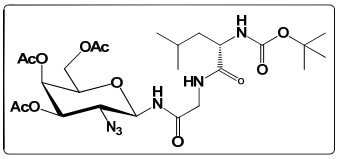
(2R,3R,4R,5R,6R)-2-(acetoxymethyl)-5-azido-6-(2-((S)-1-(tert-butoxycarbonyl)pyrrolidine-2-carboxamido)acetamido)tetrahydro-2H-pyran-3,4-diyl diacetate 19:

Compound **19** was prepared from **7a** (100 mg, 0.28 mmol) and (S)-2-(1-(tert-butoxycarbonyl)pyrrolidine-2-carboxamido) acetic acid (76 mg, 0.28 mmol) using the procedure described for **18** in 80% yield (131 mg, over two steps) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 4:6); $[\alpha]_D^{28}$ = -18.0 (*c* 0.2, CH_2Cl_2) IR (neat) ν_{max} /cm^{-1}: 3357, 2111, 1738, 1709, 1627. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–6.76 (m, 1H), 6.34 (s, 1H), 5.61 (dd, *J* = 16.5, 3.8 Hz, 1H), 5.37 (t, *J* = 7.8 Hz, 1H), 5.12–5.03 (m, 1H), 4.57 (s, 1H), 4.30 (dt, *J* = 12.6, 6.5 Hz, 2H), 4.24–4.13 (m, 2H), 4.14–4.01 (m, 2H), 3.70 (s, 1H), 3.41 (d, *J* = 48.2 Hz, 2H), 2.15 (d, *J* = 7.9 Hz, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.98 – 1.85 (m, 3H), 1.46 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 170.6, 170.5, 169.6, 155.9, 128.3, 88.5, 88.3, 80.7, 69.7, 69.3, 68.7, 68.6, 67.2, 66.9, 62.5, 61.8, 59.9, 49.9, 47.2, 41.1, 28.4, 23.1, 23.0, 20.9, 20.8, 20.7; HRMS Calcd for $C_{24}H_{37}N_6O_{11}$ $[M + H]^+$ = 585.2520 found; 585.2520.



(2R,3R,4R,5R,6R)-2-(acetoxymethyl)-5-azido-6-(2-((S)-2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)acetamido)tetrahydro-2H-pyran-3,4-diyl diacetate 20:

Compound **20** was prepared from **7a** (100 mg, 0.30 mmol) and (S)-2-(2-((tert-butoxycarbonyl) amino)-4-methylpentanamido) acetic acid (86 mg, 0.30 mmol), using the procedure described for **18,** in 76% yield (128 mg, over two steps) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 6:4); $[\alpha]_D^{28}$ = + 36.0 (*c* 0.4, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3412, 2111, 1741, 1697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.39 (m, 1H), 7.37 (t, *J* = 5.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 4.1 Hz, 1H), 5.43 (d, *J* = 15.1 Hz, 2H), 5.15–5.02 (m, 1H), 4.61–4.47 (m, 1H), 4.35 (t, *J* = 6.5 Hz, 1H), 4.23–4.07 (m, 3H), 4.07–3.97 (m, 1H), 3.98–3.87 (m, 1H), 2.15 (s, 3H), 2.06 (d, *J* = 2.5 Hz, 3H), 1.99 (s, 3H), 1.66 (ddd, *J* = 13.6, 11.9, 5.5 Hz, 2H), 1.56–1.48 (m, 1H), 1.44 (d, *J* = 5.8 Hz, 9H), 0.94 (dd, *J* = 8.2, 4.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 170.5, 170.4, 170.1, 169.7, 169.3, 155.9, 140.8, 128.3, 126.7, 126.1, 117.3, 110.9, 88.3, 80.4, 80.3, 68.6, 67.6, 67.3, 66.9, 61.7, 53.3, 47.4, 43.0, 41.1, 28.2, 28.1, 27.5, 24.6, 22.9, 21.6, 20.6, 20.4, 20.3; HRMS Calcd for $C_{25}H_{41}N_6O_{11}$ $[M + H]^+$ = 601.2833 found; 601.2833.



(2R,3R,4R,5R,6R)-2-(acetoxymethyl)-5-azido-6-((S)-2-((tert-butoxycarbonyl)amino)propanamido) tetrahydro-2H-pyran-3,4-diyl diacetate 21:

Compound **21** was prepared from **7a** (100 mg, 0.30 mmol) and (S)-2-((tert-butoxycarbonyl)amino)propanoic acid (53 mg, 0.30 mmol), using the procedure described for **18,** in 81% yield (114 mg, over two steps) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 6:4); $[\alpha]_D^{28}$ = –31.0 (*c* 0.5, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3420, 3319, 2110, 1742, 1701, 1679, 1650, 1507, 1374;^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 1H), 5.52 (d, *J* = 4.1 Hz, 1H), 5.40–5.33 (m, 1H), 5.24–5.11 (m, 1H), 5.08–4.97 (m, 1H), 4.56–4.45 (m, 1H), 4.31 (t, *J* = 6.4 Hz, 1H), 4.15–4.04 (m, 3H), 2.13 (d, *J* = 1.6 Hz, 3H), 2.03 (d, *J* = 1.7 Hz, 3H), 1.95 (d, *J* = 1.7 Hz, 3H), 1.41 (s, 9H), 1.28 (dd, *J* = 7.0, 1.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 173.6, 170.7, 170.5, 170.2, 155.6, 88.5, 80.4, 68.8, 67.6, 67.0, 61.7, 50.2, 47.3, 28.4, 28.3, 20.7, 20.6, 18.6, 18.1; HRMS Calcd for $C_{20}H_{32}N_5O_{10}$ [M + H]$^+$ = 502.2149 found; 502.2146.

(2R,3S,4R,5R,6R)-2-(acetoxymethyl)-5-azido-6-(2-((S)-2-((tert-butoxycarbonyl)amino)-4-methyl-pentanamido)acetamido)tetrahydro-2H-pyran-3,4-diyl diacetate 22:

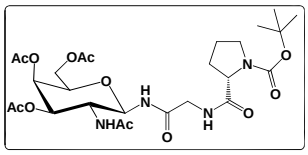
Compound **22** was prepared from **8a** (100 mg, 0.30 mmol) (S)-2-(2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)acetic acid (86 mg, 0.30 mmol), using the procedure described for **18,** in 82% yield (138 mg) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 6:4); $[\alpha]_D^{28}$ = –7.0 (*c* 0.2, CH_2Cl_2) IR (neat) ν_{max} /cm^{-1}: 3349, 2118, 1740, 1711, 1638, 1503. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 4.7 Hz, 1H), 6.65 (s, 1H), 5.50 (d, *J* = 4.2 Hz, 1H), 5.18–4.98 (m, 3H), 4.40–4.23 (m,2H), 4.14 (ddd, *J* = 7.9, 7.3, 2.2 Hz,3H), 3.91 (s, 2H), 2.11 (s, 3H), 2.04 (s, 6H), 1.89 (d, *J* = 15.0 Hz,2H), 1.81–1.63 (m, 2H), 1.52 (dt, *J* = 13.1, 4.1 Hz, 1H), 1.50–1.42 (m, 9H), 0.95 (dd, *J* = 12.9, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 171.6, 170.8, 169.4, 169.3, 156.0, 87.9, 80.5, 70.3, 69.8, 67.7, 61.7, 53.1, 51.6, 43.2, 40.9, 28.3, 24.6, 23.2, 21.7, 20.8, 20.7; HRMS Calcd for $C_{25}H_{41}N_6O_{11}$ [M + H]$^+$ = 601.2833; found 601.2833.

(2R,3S,4R,5R,6R)-2-(acetoxymethyl)-5-azido-6-((S)-2-((tert-butoxycarbonyl)amino)propanamido) tetrahydro-2H-pyran-3,4-diyl diacetate 23:

Compound **23** was prepared from **8a** (100 mg, 0.30 mmol) and (S)-2-((tert-butoxycarbonyl)amino)propanoic acid (53 mg, 0.30 mmol), using the procedure described for **18,** in 75% yield (106 mg, over two steps) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 6:4); $[\alpha]_D^{28}$ = –52.0 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3411, 3323, 2111, 1743, 1669, 1374. ^{1}H NMR (500 MHz, , $CDCl_3$) δ 5.96 (d, *J* = 8.9 Hz, 1H), 5.32 (s, 1H), 5.23 (dd, *J* = 9.4, 4.3 Hz, 1H), 5.06 (d, *J* = 6.3 Hz, 1H), 4.49–4.38 (m, 2H), 4.17 – 4.03 (m, 2H), 3.73 (dd, *J* = 16.9, 7.6 Hz, 2H), 2.13 (s, 3H), 2.10–2.02 (m, 6H), 1.43 (s, 10H), 1.36 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 173.6, 170.7, 170.5, 170.2, 155.1, 88.5, 80.4, 68.8, 67.6, 67.0, 61.78, 50.2, 47.3, 28.4, 28.3, 20.7, 20.6, 18.6, 18.1; HRMS Calcd for $C_{20}H_{32}N_5O_{10}$ [M + H]$^+$ = 502.2149; found 502.2147.

(2R,3R,4R,5R,6S)-5-acetamido-2-(acetoxymethyl)-6-(2-((S)-1-(tert-butoxycarbonyl)pyrrolidine-2-carboxamido)acetamido)tetrahydro-2H-pyran-3,4-diyl diacetate 24:

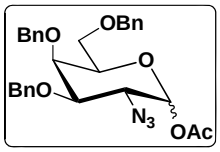
Compound **19** (55 mg, 0.09 mmol) dissolved in acetic anhydride (1 mL, 10.34 mmol) was cooled to 0 °C.



Zn dust (300 mg) and acetic acid (0.5 mL, 8.46 mmol) were added to this solution and the reaction stirred at rt for 7 h. The reaction was diluted with ethyl acetate (10 mL) and filtered through Celite. Evaporation of the solvent gave a residue which was purified by column chromatography with hexane:EtOAc eluent afforded **24** in 85% yield (48 mg) as a colourless oil; R_f = 0.30 (hexane/EtOAc, 1:1); $[\alpha]_D^{28}$ = -25.0 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3410, 1735, 1695, 1628. ^{1}H NMR (400 MHz, DMSO-D6) δ 8.46 (d, *J* = 9.2 Hz, 1H), 8.29 – 8.14 (m, 2H), 7.88 (d, *J* = 9.1 Hz, 1H), 5.23 (d, *J* = 3.3 Hz, 1H), 5.14–5.02 (m, 3H), 3.98 (qdd, *J* = 17.9, 16.4, 8.2 Hz, 11H), 3.75 (d, *J* = 6.1 Hz, 1H), 3.69 (dd, *J* = 13.0, 5.9 Hz, 3H), 3.65–3.59 (m, 1H), 3.35 (d, *J* = 4.5 Hz, 3H), 3.31 – 3.19 (m, 3H), 2.08 (s, 6H), 1.97 (s, 6H), 1.82 (d, *J* = 2.9 Hz, 5H), 1.80–1.74 (m, 14H), 1.38 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (400 MHz, DMSO-D6) δ 172.9, 172.6, 171.4, 169.9, 169.8, 168.9, 153.7, 153.3, 79.3, 79.1, 78.9, 78.7, 78.6, 78.5, 71.6, 71.2, 66.7, 61.6, 59.6, 54.9, 48.3, 46.7, 46.4, 30.9, 29.9, 28.1, 28.0, 23.7, 23.1, 22.7, 22.6, 22.5, 21.9, 20.7, 20.6, 20.5; HRMS Calcd for $C_{26}H_{41}N_4O_{12}$ $[M + H]^+$ = 601.2721found 601.2721. HRMS Calcd for $C_{26}H_{41}N_4O_{12}$ $[M + H]^+$ = 601.2721; found 601.2721.

Procedure for preparation of compounds 2 and 3: To a cooled solution of **1** (100 mg, 0.24 mmol), $TMSN_3$ (95 μL,0.72 mmol) and $PhI(OAc)_2$ (78 mg, 0.24 mmol) in dry CH_2Cl_2 (5 mL) at –30 °C under N_2 atmosphere was added TMSOTf (13 μL, 0.10 mmol). The reaction mixture was stirred at this temperature for 30 min. On consumption of starting material (TLC monitoring), the reaction mixture was quenched with satd. aqueous $NaHCO_3$ (3 mL). 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) 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 as eluent to afford an inseparable mixture of compounds **2** and **3** in 61% overall yield (75 mg) as a colourless oil. To the stirred solution of this mixture of azidoacetates **2** and **3** (75 mg, 0.14 mmol) in acetonitrile/ethanol (1:1, 3 mL) was added tetrathiomolybdate (61 mg, 0.14 mmol) and stirred at room temperature for 10 h. Upon completion of selective reduction of the anomeric azide to amine (TLC monitoring until there was no improvement in product formation) the solvent was evaporated under reduced pressure, the black residue was extracted with CH_2Cl_2/ether (1:10, 4 x 5 mL) and filtered through a pad of Celite, and the solvent evaporated. The residue was purified by column chromatography (eluents: $CHCl_3$/MeOH, 9:1) to give the unreacted azidoacetate **3** (41 mg) and glycosyl amine (15 mg). This amine was characterized as the corresponding acetate **25,** prepared by using acetic anhydride (3 μL, 0.03 mmol) and Et_3N (4 μL, 0.03 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C in 80% yield (13 mg) as a colorless oil.

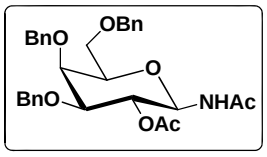
(3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl acetate 3:



R_f = 0.40 (hexane/EtOAc, 8:2); IR (neat) ν_{max} /cm^{-1} 3078, 3031, 2922, 2862, 2111, 1753, 1488, 1461, 1381, 1307, 1220, 1138, 1091, 1024,927; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 32H), 6.23 (d, *J* = 3.8 Hz, 1H), 5.40 (d, *J* = 8.6 Hz, 1H), 4.88 (d, *J* = 11.3 Hz, 2H), 4.77–4.62 (m, 4H), 4.61–4.52 (m, 2H), 4.49 – 4.37 (m, 5H), 4.08 (dd, *J* = 10.6, 3.5 Hz, 2H), 4.01–3.86 (m, 4H), 3.69–3.58 (m, 4H), 3.58–3.47 (m, 2H), 3.43 (dd,

J = 10.3, 2.8 Hz, 1H), 2.13 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.2, 138.2, 137.8, 137.5, 137.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.5, 93.1, 91.2, 80.8, 77.7, 75.3, 74.8, 74.3, 73.7, 73.6, 72.8, 72.5, 72.2, 71.8, 71.7, 68.1, 67.7, 61.9, 59.0, 21.2, 21.1; HRMS Calcd for $C_{29}H_{31}N_3NaO_6$ $[M + Na]^+$ = 540.2111; found 540.2108.

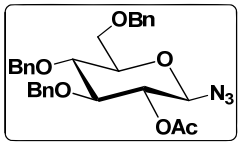
(2R,3R,4S,5S,6R)-2-acetamido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl acetate 25:



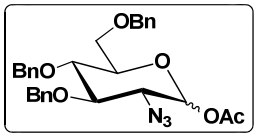
R_f=0.20 (hexane/EtOAc,6:4); $[\alpha]_D^{28}$ = + 10.0 (*c* 0.3, CH_2Cl_2); IR(neat) ν_{max}cm^{-1} 3321, 2953, 2924, 1744, 1693, 1454, 1372, 1235, 1083, 1028, 736, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.16 (m, 16H), 6.31 (d, *J* = 9.2 Hz, 1H), 5.22 (t, *J* = 9.6 Hz, 1H), 5.06 (t, *J* = 9.3 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.62–4.52 (m, 2H), 4.47–4.37 (m, 2H), 4.02 (d, *J* = 2.4 Hz, 1H), 3.75–3.66 (m, 1H), 3.67–3.49 (m, 3H), 2.02 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, , $CDCl_3$) δ 171.6, 171.5, 170.5, 138.3, 137.9, 137.8, 137.8, 137.7, 137.7, 128.5, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 80.2, 78.6, 74.9, 74.8, 73.6, 73.0, 72.4, 71.3, 67.8, 23.5, 21.0; HRMS Calcd for $C_{31}H_{36}NO_7$ $[M + H]^+$ = 534.2492; found 534.2492.

(2R,3R,4S,5R,6R)-2-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl acetate 26:

To a cooled solution of **7b** (100 mg, 0.24 mmol), $TMSN_3$ (95 μL,0.72 mmol) and $PhI(OAc)_2$ (78 mg,0.24 mmol) in dry CH_2Cl_2 (5 mL) at –30 °C under N_2 atmosphere was added TMSOTf (13 μL, 0.10 mmol). The reaction mixture was stirred at this temperature for 30 min. On consumption of starting material (TLC monitoring) the reaction mixture was quenched with satd. aq. $NaHCO_3$ (3 mL). 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), 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 afforded **26** in 19% (24 mg) and **27** in 37% 48 mg (72 mg, 56 % overall yield) as a colorless oil. R_f = 0.40 (hexane/EtOAc, 8:2); data for **26** $[\alpha]_D^{28}$ = -6.0 (*c* 0.4, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3110, 3071, 3022, 2872, 2111, 1758, 1489, 1460, 1365, 1221, 1126, 936,732, 692; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.22 (m, 13H), 7.20–7.14 (m, 2H), 4.96 (t, *J* = 9.1 Hz, 1H), 4.78 (dd, *J* = 11.1, 8.9 Hz, 2H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.61–4.49 (m, 3H), 4.43 (d, *J* = 8.8 Hz, 1H), 3.73–3.71 (m, 2H), 3.70–3.66 (m, 1H), 3.64 (d, *J* = 9.1 Hz, 1H), 3.54 (ddd, *J* = 9.6, 3.9, 2.3 Hz, 1H), 1.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 137.9, 137.8, 137.7, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.7, 127.5, 87.9, 82.7, 77.4, 75.1, 75.0, 73.4, 72.5, 68.2, 20.7; HRMS Calcd for $C_{29}H_{31}N_3NaO_6$ $[M + Na]^+$ = 540.2111; found 540.2108.

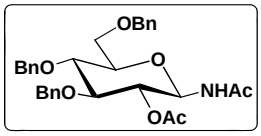


(3R,4R,5S,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-ylacetate 27:



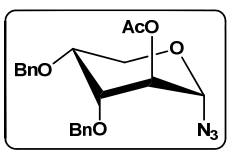
R_f = 0.40 (hexane/EtOAc, 8:2);IR (neat) ν_{max} /cm^{-1} 3088, 3063, 3031, 2917, 2867, 2112,1756, 1496, 1454, 1370,1321, 1222, 1138, 1091, 1046, 1027, 932, 737, 698. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.21 (m, 28H), 7.20–7.10 (m, 4H), 6.25 (d, *J* = 3.6 Hz, 1H), 5.46 (d, *J* = 8.3 Hz, 1H), 4.89 (d, *J* = 4.8 Hz, 2H), 4.86 (s, 1H), 4.84–4.81 (m, 2H), 4.81–4.76 (m, 2H), 4.61 (dd, *J* = 12.1, 6.3 Hz, 2H), 4.54 (dd, *J* = 13.8, 8.9 Hz, 3H), 4.47 (dd, *J* = 12.1, 8.4 Hz, 3H), 3.97–3.90 (m, 2H), 3.87–3.79 (m, 3H), 3.78 (d, *J* = 2.1 Hz, 1H), 3.73 (ddd, *J* = 11.0, 7.1, 1.7 Hz, 3H), 3.65 (d, *J* = 10.9 Hz, 1H), 3.60 (d, *J* = 3.7 Hz, 1H), 3.59–3.55 (m, 1H), 3.53 (dd, *J* = 10.1, 6.0 Hz, 2H), 2.17 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 169.0, 137.8, 137.7, 128.6, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 93.0, 90.7, 83.1, 80.5, 77.5, 75.8, 75.7, 75.8, 75.3, 75.1, 73.7, 73.6, 73.2, 67.9, 65.1, 62.7, 21.1, 21.0; HRMS Calcd for $C_{29}H_{35}N_4O_6$ [M + NH_4]$^+$ = 535.2557; found 535.2559.

(2R,3R,4S,5R,6R)-2-acetamido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl acetate 28:



To a stirred solution of **26** (24 mg, 0.04 mmol) in acetonitrile/ethanol (1:1, 2 mL) was added tetrathiomolybdate (19 mg, 0.04 mmol) and stirred at room temperature for 10 h. Upon consumption of starting material (TLC monitoring) the solvent was evaporated under reduced pressure. The black residue was extracted with CH_2Cl_2/ether (1:10, 4 X 5 mL) and filtered through a pad of Celite. The solvent was evaporated to give the glycosyl amine (16 mg) which was acetylated with acetic anhydride (3 μL, 0.03 mmol) and Et_3N (4 μL, 0.03 mmol) in dry DCM at 0 °C. The reaction mixture was stirred for 1 h and upon consumption of starting material (TLC monitoring) the reaction mixture was diluted with DCM (30 mL), washed with saturated aqueous $NaHCO_3$ (2 X 5 mL), water (5 mL), brine (5 mL), and then dried over Na_2SO_4. The crude residue was purified by silica gel column chromatography with hexane:EtOAc as eluent to afford **28** in 80 % yield (14 mg) as a colourless oil. R_f=0.20 (hexane / EtOAc, 6:4); $[\alpha]_D^{28}$ = + 26.0 (*c* 0.4, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3318, 2968, 2947, 1737, 1668, 1442, 1379, 1257, 1068, 1034, 726,679; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 12H), 7.13 (dd, *J* = 6.9, 2.6 Hz, 2H), 6.30 (d, *J* = 9.3 Hz, 1H), 5.11 (t, *J* = 9.4 Hz, 1H), 4.90–4.74 (m, 3H), 4.67 (dd, *J* = 26.1, 11.8 Hz, 2H), 4.49 (dd, *J* = 18.76, 11.4 Hz, 2H), 3.82–3.72 (m, 3H), 3.58–3.52 (m, 1H), 1.96 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 170.5, 138.2, 137.9, 137.8, 132.1, 130.8, 128.9, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 127.8, 127.6, 83.2, 78.3, 77.6, 76.5, 75.5, 75.1, 73.6, 73.2, 68.1, 23.6, 23.4, 21.0, 20.8; HRMS Calcd for $C_{31}H_{36}NO_7$ [M + H]$^+$ = 534.2492; found 534.2494.

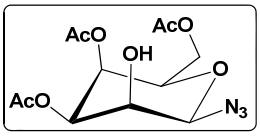
(2S,3S,4R,5R)-2-azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-yl acetate 29:



Compound **29** was prepared from **10b** (100 mg, 0.33 mmol) using the procedure described for **26** in 56% yield (75 mg) as a colourless oil; R_f = 0.60 (hexane /EtOAc, 8:2); $[\alpha]_D^{28}$ = + 15.4 (*c* 0.2, CH_2Cl_2); IR(neat) ν_{max}cm^{-1} 3018, 2941, 2885, 2117, 1764, 1474, 1452, 1374, 1312, 1129, 1086, 934; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.27 (m, 13H), 5.27–5.21 (m, 1H), 4.70–4.57 (m, 5H), 4.53 (dd, *J* = 9.6, 2.5 Hz, 2H), 4.14 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.10–4.03 (m, 1H), 3.76 (t, *J* = 4.5 Hz, 1H), 3.57 (dd, *J* = 8.3, 3.1 Hz, 1H), 3.45 (dd, *J* =

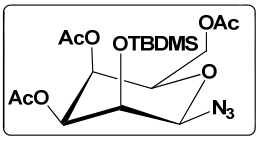
12.4, 1.8 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.9, 137.7, 128.4, 127.8, 127.8, 127.6, 88.3, 77.0, 71.7, 71.6, 71.5, 71.4, 69.9, 64.3, 20.9; HRMS Calcd for $C_{21}H_{27}N_4O_5$ $[M + NH_4]^+$ = 415.1981 found, 415.1981.

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



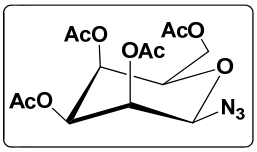
To a cooled solution of **6** (100 mg, 0.37 mmol), $TMSN_3$ (145 μL, 1.10 mmol) and $PhI(OAc)_2$ (120 mg, 0.37 mmol) in dry CH_2Cl_2 (5 mL) at –30 °C under N_2 atmosphere was added TMSOTf (67 μL, 0.37 mmol). The reaction mixture was stirred at this temperature for 30 min. On consumption of starting material (TLC monitoring) the reaction mixture was quenched with satd. aq. $NaHCO_3$ (3 mL). 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), 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 afforded **30** in 68% yield (83 mg) as a colorless oil. R_f = 0.40 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = –1.0 (*c* 0.6, CH_2Cl_2); IR (neat) ν_{max}/cm^{-1} 3562, 2925, 2117, 1746,1373, 1241, 1084. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42–5.37 (m, 1H), 4.93 (t, *J* = 3.4 Hz, 1H), 4.56 (s, 1H), 4.22 (d, *J* = 6.7 Hz, 2H), 4.02–3.96 (m, 2H), 2.74–2.67 (m, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 169.4, 87.7, 73.6, 69.9, 69.0, 66.2, 61.3, 20.7; HRMS Calcd for $C_{12}H_{21}N_4O_8$ $[M + NH_4]^+$ = 349.1359; found 349.1369.

(2R,3S,4S,5S,6R)-2-(acetoxymethyl)-6-azido-5-((tert-butyldimethylsilyl)oxy)tetrahydro-2H-pyran-3,4-diyl diacetate 31:



To a solution of **30** (100 mg, 0.30 mmol) in dry DMF (5 mL) at room temperature was added imidazole (25 mg, 0.36 mmol). The solution was stirred for 10 min. and then TBDMSCl (55 mg, 0.36 mmol) was added to it and stirred for two hours room temperature. Satd. aq. NH_4Cl was added and the reaction mixture extracted with EtOAc (2 x 10 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by column chromatography with hexane:EtOAc as eluent to afford **31** in 72 % yield (96 mg). R_f = 0.70 (hexane/EtOAc, 8:2); $[\alpha]_D^{28}$ = + 38 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 2927, 2115, 1253, 1068, 851, 768; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24–5.21 (m, 1H), 5.02–4.95 (m, 1H), 4.84 (dd, *J* = 6.8, 4.7 Hz, 1H), 4.20–4.06 (m, 2H), 3.83–3.74 (m, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.94 (m, 1H), 0.91 (s, 9H), 0.13 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.1, 95.1, 71.1, 68.6, 65.4, 62.2, 34.6, 25.8, 20.9, 20.8, 20.7, 18.1, -4.1, -5.0; HRMS Calcd for $C_{18}H_{35}N_4O_8Si$ $[M + NH_4]^+$ = 463.2224; found 463.2231.

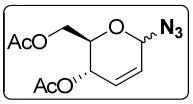
(2R,3S,4S,5S,6R)-2-(acetoxymethyl)-6-azidotetrahydro-2H-pyran-3,4,5-triyl triacetate 32:



To a stirred solution of **30** (100 mg, 0.30 mmol) in dry CH_2Cl_2 (2 mL) was added acetic anhydride (28 μL, 0.30 mmol) and Et_3N (42 μL, 0.30 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h and upon consumption of starting material (TLC monitoring) it was diluted with dichloromethane (3 mL), washed with satd. aq. $NaHCO_3$ (2 x 3 mL), water (3 mL), brine (3 mL), and dried over Na_2SO_4. The crude residue was purified by silica gel column chromatography with hexane:EtOAc as eluent to afford **32** in 85 % yield (96

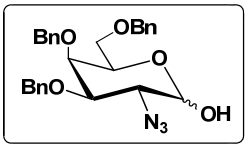
mg) as a colorless oil. R_f = 0.50 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = + 15.1 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3562, 2932, 2111, 1744, 1373, 1244; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35–5.29 (m, 2H), 5.08 (t, *J* = 3.6 Hz, 1H), 4.77 (d, *J* = 1.3 Hz, 1H), 4.25 (dd, *J* = 6.5, 1.8 Hz, 2H), 4.07–4.01 (m, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 169.2, 169.1, 87.7, 77.4, 77.1, 76.8, 73.8, 72.4, 70.5, 67.7, 61.5, 20.5, 20.4; HRMS Calcd for $C_{14}H_{23}N_4O_9$ $[M + NH_4]^+$ = 391.1465; found 391.1461.

((2R,3S)-3-acetoxy-6-azido-3,6-dihydro-2H-pyran-2-yl)methyl acetate 33:



To a cooled solution of **8a** (100 mg, 0.37 mmol), $TMSN_3$ (145 µL, 1.10 mmol) and $PhI(OAc)_2$ (120 mg, 0.37 mmol) in dry CH_2Cl_2 (5 mL) at −30 °C under N_2 atmosphere was added TMSOTf (67 µL, 0.37 mmol). The reaction mixture was stirred at this temperature for 30 min. On consumption of starting material (TLC monitoring) the reaction mixture was quenched with satd. aq. $NaHCO_3$ (3 mL). 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), 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 as eluent to afford **33** in 76 % yield (71 mg, α:β = 60:40) as a colourless oil. R_f = 0.60 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3012, 2987, 2113, 1738, 1359, 1231, 1062, 921, 758, 675; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, *J* = 5.9 Hz, 2H), 5.96 (dt, *J* = 10.4, 1.3 Hz, 1H), 5.82–5.76 (m, 1H), 5.60–5.55 (m, 1H), 5.32 (dd, *J* = 9.5, 1.8 Hz, 1H), 5.11–5.06 (m, 2H), 4.89 (d, *J* = 5.9 Hz, 2H), 4.40–4.36 (m, 2H), 4.32 (d, *J* = 2.2 Hz, 2H), 4.29–4.21 (m, 10H), 4.14–4.08 (m, 1H), 2.15 (s, 7H), 2.11 (d, *J* = 2.5 Hz, 7H), 2.08 (s, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.5, 170.1, 169.6, 169.4, 146.9, 145.7, 129.6, 126.3, 98.0, 96.4, 84.2, 74.3, 70.5, 68.7, 67.9, 67.4, 64.5, 62.5, 61.7, 61.4, 57.6, 53.3, 20.9, 20.7, 20.6, 20.5; HRMS Calcd for $C_{10}H_{13}N_3NaO_5$ $[M + Na]^+$ = 278.0753; found 278.0761.

(3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-ol 34:



Benzylamine (159 µL, 1.45 mmol) was added to the stirred solution of **3** (500 mg, 0.93 mmol) in THF (10 mL) at rt. After 24 h, the mixture was diluted with ethyl acetate (25 mL) and washed with 30% aq. citric acid solution (2 x 10 mL). Then it was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (eluents: hexane:ethyl acetate) to afford the desired **34** in 72% (330 mg) as a colorless oil; R_f = 0.50 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 3475, 2923, 2869, 2114, 1750, 1454, 1367, 1222, 1103, 1082, 736, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.20 (m, 35H), 5.26 (d, *J* = 3.1 Hz, 1H), 4.90–4.86 (m, 1H), 4.86–4.82 (m, 1H), 4.70 (dd, *J* = 7.0, 4.8 Hz, 3H), 4.67 (d, *J* = 2.0 Hz, 1H), 4.61–4.54 (m, 2H), 4.54–4.49 (m, 2H), 4.47 (d, *J* = 3.5 Hz, 2H), 4.44 (d, *J* = 4.2 Hz, 1H), 4.41 (d, *J* = 2.8 Hz, 1H), 4.40–4.34 (m, 1H), 4.14 (t, *J* = 6.5 Hz, 1H), 3.98–3.92 (m, 2H), 3.90 (dd, *J* = 4.1, 2.1 Hz, 2H), 3.88–3.81 (m, 2H), 3.77 (dd, *J* = 10.3, 8.0 Hz, 1H), 3.70–3.63 (m, 1H), 3.63–3.56 (m, 2H), 3.56–3.44 (m, 2H), 3.40 (dt, *J* = 9.0, 4.4 Hz, 2H), 3.31 (dd, *J* = 10.3, 2.8 Hz, 1H), 2.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.8, 137.7, 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 127.8, 127.5, 88.6, 80.2, 76.0, 74.7, 73.7, 72.6, 72.2, 70.3, 68.4, 60.5; HRMS Calcd for $C_{27}H_{30}N_3O_5$ $[M + H]^+$ = 476.2185; found 476.2181.

(3R,4R,5R,6R)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((2R,3R,4S,5R,6R)-3,4,5-tris (benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran 37:

DBU (9 μL, 0.06 mmol) was added to a stirred solution of CCl_3CN (60 μL, 0.6 mmol) and **34** (100 mg, 0.20 mmol) in dry CH_2Cl_2 (3 mL) under nitrogen at 0 °C and stirred for 2 h. On consumption of starting material (TLC monitoring) the reaction mixture was diluted with CH_2Cl_2 (5 ml) and 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 as eluent afforded **35** in 76% yield (99 mg) as colorless oil. To a mixture of **35** (100 mg, 0.16 mmol), compound **36** (88 mg, 0.16 mmol) and freshly activated molecular sieves (4Å, 50 mg) in dry CH_2Cl_2 (4 mL) at –30 °C under nitrogen was added TMSOTf (6 μL, 0.03 mmol) and stirred for 35 min at same temperature. Upon consumption of starting material (TLC monitoring) the solids were filtered off through a pad of Celite and washed with CH_2Cl_2 (5 mL). The combined filtrate was washed with satd. aq. $NaHCO_3$ (2 x 5 mL) and water (2 x 5 mL). The organic phase was separated, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford **37** in 76% (123 mg) as a colorless oil R_f = 0.60 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 2932, 2841, 2111, 1735, 1472, 1117, 1034, 721. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.43–7.36 (m, 6H), 7.36–7.17 (m, 38H), 5.03 (d, *J* = 2.7 Hz, 1H), 4.92–4.81 (m, 6H), 4.75–4.70 (m, 1H), 4.69–4.62 (m, 3H), 4.54 (dt, *J* = 11.4, 8.3 Hz, 3H), 4.47–4.39 (m, 2H), 3.97 (d, *J* = 11.0 Hz, 2H), 3.91 – 3.83 (m, 3H), 3.80 (dd, *J* = 9.5, 2.7 Hz, 3H), 3.71 (t, *J* = 8.5 Hz, 1H), 3.60–3.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.1, 137.7, 133.9, 131.8, 129.0, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.4, 98.5, 87.3, 86.9, 80.8, 78.7, 78.0, 77.4, 75.94, 75.5, 75.1, 74.9, 73.5, 72.2, 69.5, 68.7, 66.7, 60.0; HRMS Calcd for $C_{60}H_{62}N_3O_9S$ $[M + H]^+$ = 1000.4207; found 1000.4202.

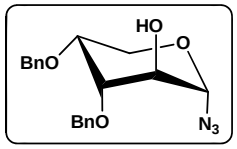
1-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((2R,3R,4S,5R,6R)-3,4,5-tris (benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3-yl)-4-((((3aR,5R,6S,7S,7aR)-6,7-dimethoxy-2,2-dimethyl-tetrahydro-3aH-[1,3]dioxolo[4,5-b]pyran-5-yl) methoxy)methyl)-1H-1,2,3-triazole 38:

To a solution of **37** (50 mg,0.05 mmol) and **14** (15 mg, 0.05 mmol) in 1:1 ratio of H_2O/EtOH (2 mL) was added sodium ascorbate (4.3 mg, 0.02 mmol) and copper(II) sulfate pentahydrate (2 mg, 0.007 mmol). The heterogeneous mixture was stirred vigorously at 60 °C for 9 h. Upon consumption of starting material (TLC monitoring) the reaction mixture was diluted with 5 mL of water and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (1 × 5 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 as eluent to afford **38** in 70% yield (45 mg) as a colorless oil; R_f = 0.40 (hexane/EtOAc, 7:3); IR (neat) ν_{max} /cm^{-1} 2941, 2117, 1731, 1464, 1122, 10363; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 2H), 7.36–7.22 (m, 28H), 7.20 (dd, *J* = 6.9, 5.7 Hz, 3H), 7.05 (d, *J* = 6.9 Hz, 2H), 5.53 (d, *J* = 5.0 Hz, 1H), 5.32 (dd, *J* = 11.2, 3.4 Hz, 1H), 5.13 (d, *J* = 3.4 Hz, 1H), 4.95–4.86 (m, 3H), 4.83–4.69 (m, 4H), 4.63 (dd, *J* = 18.0, 11.1 Hz, 2H), 4.57–4.50 (m, 4H), 4.49–4.37 (m, 3H), 4.31–4.24 (m, 3H), 4.18–4.10 (m, 2H), 4.06 (s, 1H), 3.98 (t, *J* = 6.0 Hz, 1H), 3.76 (dd, *J* = 11.4, 5.1 Hz, 1H),

3.71 (dd, J = 10.3, 5.3 Hz, 1H), 3.69 – 3.65 (m, 1H), 3.65 – 3.54 (m, 5H), 3.37 – 3.30 (m, 2H), 3.17 (t, J = 9.4 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.28 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 138.5, 138.3, 138.0, 137.2, 131.9, 129.1, 128.7, 128.6, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 123.1, 111.8, 109.3, 108.6, 98.1, 96.4, 87.6, 86.6, 81.1, 78.7, 78.3, 75.8, 75.0, 73.6, 73.2, 72.1, 71.3, 70.8, 69.9, 69.4, 68.7, 66.3, 66.6, 64.8, 60.6, 56.2, 26.2, 26.1, 25.0, 24.5; HRMS Calcd for $C_{74}H_{84}N_3O_{15}S$ $[M + H]^+$ = 1286.5623; found 1286.5623.

(2S,3S,4S,5R)-2-azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-ol 39:

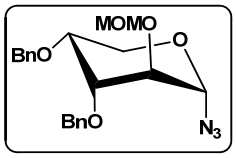
To a solution of **29** (500 mg, 1.25 mmol) in dry MeOH (20 mL) at 0 °C was added a catalytic amount of



NaOMe. The mixture was stirred for 1 h at room temperature and after completion of reaction (TLC monitoring) MeOH was evaporated, extracted with EtOAc (3 × 20 mL) and the organic layer washed with water and brine, and dried over Na_2SO_4. Evaporation of the solvent followed by purification using column chromatography gave **39** in 70% yield (312 mg) as a colorless oil; R_f = 0.45 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = + 45.4 (c 0.2, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3321, 2117, 1451, 1361, 1069, 1021, 932, 768; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.22 (m, 9H), 4.74 (d, J = 12.4 Hz, 1H), 4.62 (t, J = 11.8 Hz, 2H), 4.51 (d, J = 11.9 Hz, 1H), 4.44 (d, J = 8.3 Hz, 1H), 4.15 (dd, J = 13.0, 2.2 Hz, 1H), 3.97–3.86 (m, 1H), 3.75 (s, 1H), 3.40 (ddd, J = 9.3, 2.2, 0.9 Hz, 2H), 2.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.6, 128.6, 128.5, 128.1, 128.0, 128.0, 127.9, 90.9, 80.4, 71.7, 71.4, 70.3, 65.5; HRMS Calcd for $C_{19}H_{21}N_3NaO_4$ $[M + Na]^+$ = 378.1430; found 378.1432.

(2S,3S,4R,5R)-2-azido-4,5-bis(benzyloxy)-3-(methoxymethoxy)tetrahydro-2H-pyran 40:

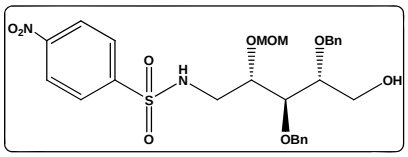
To a solution of **39** (300 mg, 0.84 mmol) dissolved in dry CH_2Cl_2 (10mL) was added N,N



diisopropylethylamine (DIPEA) (77 μL, 1.00 mmol) and MOM-Cl (175 μL, 1.00 mmol) at 0°C followed by addition of a catalytic amount of DMAP. The mixture was stirred at ambient temperature for 16 h and then diluted with CH_2Cl_2 (10 mL). The organic layer was washed with satd. aq. $NaHCO_3$ (10 mL), and brine (10 mL), and dried over Na_2SO_4. The crude product was purified by column chromatography with hexane:EtOAc as eluent to afford **40** in 80% yield (270 mg) as a colorless oil; R_f = 0.50 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = + 26.5 (c 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3314, 2111, 1438, 1061, 932, 757; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40– 7.08 (m, 9H), 4.87–4.81 (m, 1H), 4.75 (t, J = 5.2 Hz, 1H), 4.72–4.65 (m, 1H), 4.65 – 4.54 (m, 3H), 4.52 (d, J = 7.3 Hz, 1H), 4.11 (dd, J = 12.4, 3.7 Hz, 1H), 3.85 (t, J = 7.9 Hz, 1H), 3.73 (s, 1H), 3.51 (dd, J = 8.5, 3.1 Hz, 1H), 3.43–3.38 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 143.4, 133.9, 133.3, 133.2, 133.1, 103.0, 95.5, 85.0, 82.8, 82.5, 82.3, 80.1, 69.8, 61.6; HRMS Calcd for $C_{21}H_{26}N_3O_5$ $[M + H]^+$ = 400.1872; found 400.1870.

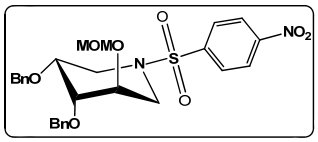
N-((2S,3S,4R)-3,4-bis(benzyloxy)-5-hydroxy-2-(methoxymethoxy)pentyl)-4-nitrobenzene-sulfonamide 41:

To a suspension of $LiAlH_4$ (71 mg, 1.87 mmol) in dry THF (3 mL), was added a solution of **40** (250 mg, 0.62 mmol) in THF (3 mL) very slowly at 0^o C. Then the reaction mixture was allowed to come at room temperature and refluxed for 5 h. It was then cooled to 0^oC and quenched with EtOAc (5 mL) followed by 1N NaOH (5 mL) solution. After stirring for 10 min the resulting white precipitate was removed by filtration through a celite pad and the filtrate extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with water followed by brine, dried over Na_2SO_4 and concentrated under reduced pressure to get the crude amine (194 mg). To a stirred solution of crude amine (140 mg, 0.37 mmol) in CH_2Cl_2 at 0^oC, was added NEt_3 (52 μL, 0.37 mmol), followed by addition of nosyl chloride (82 mg, 0.37 mmol). The reaction mixture was stirred for 2 h at room temperature. On completion of reaction (TLC monitoring), it was quenched by the addition of saturated solution of NH_4Cl (5 mL) and the mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL) and dried over Na_2SO_4. Solvent evaporation followed by purification through column chromatography with hexane:EtOAc eluent afforded **41** in 84% yield (over two steps 295 mg) as a colourless oil; R_f = 0.25 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = - 12.7 (*c* 0.5, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1}: 3314, 1545, 1438, 1345, 1150, 1054, 941; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.17 (m, 2H), 7.89–7.82 (m, 2H), 7.36–7.25 (m, 13H), 5.81 (dd, *J* = 7.7, 3.8 Hz, 1H), 4.75–4.69 (m, 1H), 4.65–4.59 (m, 2H), 4.58–4.51 (m, 2H), 4.43 (dd, *J* = 20.3, 9.1 Hz, 2H), 3.93 (dt, *J* = 8.0, 4.1 Hz, 1H), 3.77 (ddd, *J* = 10.3, 7.7, 2.7 Hz, 2H), 3.69 (dd, *J* = 6.9, 3.2 Hz, 1H), 3.67 – 3.62 (m, 1H), 3.36 – 3.30 (m, 1H), 3.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 145.6, 137.5, 137.5, 137.4, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 124.2, 97.8, 78.9, 78.5, 77.5, 74.6, 71.6, 59.3, 55.8, 55.8, 44.6; HRMS Calcd for $C_{27}H_{33}N_2O_9S$ $[M + H]^+$ = 561.1907; found 561.1904

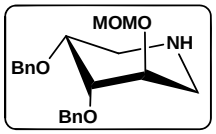


(3R,4R,5R)-3,4-bis(benzyloxy)-5-(methoxymethoxy)-1-((4-nitrophenyl)sulfonyl)piperidine 42:

Triphenylphosphine (89 mg, 0.34 mmol) and diethyl azodicarboxylate (54 μL, 0.34 mmol) were added at room temperature to a stirred solution of **41** (175 mg, 0.34 mmol) in dry toluene (4 mL). The reaction mixture was stirred for a further 8 h and after completion of reaction (TLC monitoring), solvent was evaporated and the crude product was purified by column chromatography with hexane:EtOAc eluent afforded **42** in 73% yield (123 mg) as a colorless oil; R_f = 0.50 (hexane/EtOAc, 7:3); $[\alpha]_D^{28}$ = - 26.4 (*c* 0.1, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3125, 1538, 1457,1352, 1142, 1054, 941; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.90 (dd, *J* = 9.0, 2.1 Hz, 2H), 7.38–7.19 (m, 10H), 4.66 (dd, *J* = 17.2, 9.5 Hz, 2H), 4.61–4.53 (m, 4H), 3.87–3.80 (m, 1H), 3.78 (dd, *J* = 6.9, 4.5 Hz, 1H), 3.66 (dd, *J* = 4.8, 2.4 Hz, 1H), 3.59–3.44 (m, 2H), 3.29 (s, 3H), 3.09 (t, *J* = 10.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 143.5, 138.1, 137.9, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 124.3, 96.0, 73.1, 72.9, 72.17, 71.5, 55.8, 45.6, 44.7; HRMS Calcd for $C_{27}H_{30}N_2O_8S$ $[M + H]^+$ = 542.1723; found 542.1720.

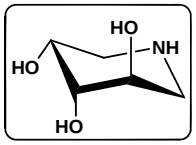


(3R,4R,5R)-3,4-bis(benzyloxy)-5-(methoxymethoxy)piperidine 43:

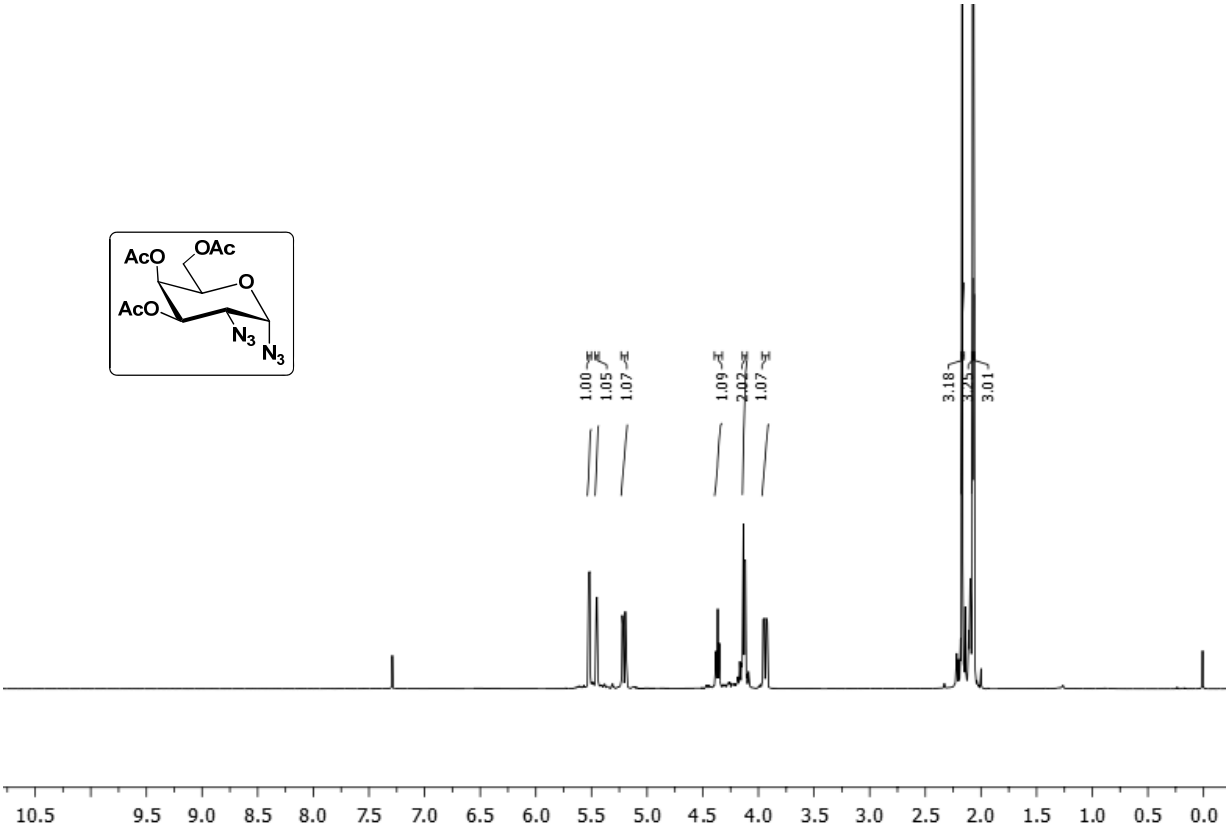


Potassium carbonate (92 mg, 0.66 mmol) and PhSH (23 μL, 0.22 mmol) were added to a stirred solution of **42** (120 mg, 0.22 mmol) in dry DMF (4 mL) and stirring continued for 24 h at room temperature. After completion of the reaction it was extracted with diethyl ether (20 mL) and washed with water and brine, and dried with Na_2SO_4. The organic layer was concentrated to provide a crude product which was purified by column chromatography with hexane:EtOAc as eluent to afford **43** in 68% yield (54 mg) as a colourless oil; R_f = 0.40 (hexane/EtOAc,7:3); $[\alpha]_D^{28}$ = + 32.7 (*c* 0.3, CH_2Cl_2); IR (neat) ν_{max} /cm^{-1} 3378, 1427, 1356, 1159; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.22 (m, 10H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.69–4.63 (m, 4H), 4.60 (dd, *J* = 13.4, 6.5 Hz, 2H), 3.90 (s, 1H), 3.87–3.78 (m, 1H), 3.59 (s, 1H), 3.29 (s, 3H), 2.62 (d, *J* = 37.1 Hz, 2H), 2.42 (d, *J* = 12.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 138.8, 138.7, 128.4, 127.8, 127.8, 127.6, 116.3, 96.3, 73.6, 72.6, 71.4, 55.5, 46.1; HRMS Calcd for $C_{21}H_{28}NO_4$ $[M + H]^+$ = 358.2018; found 358.2016.

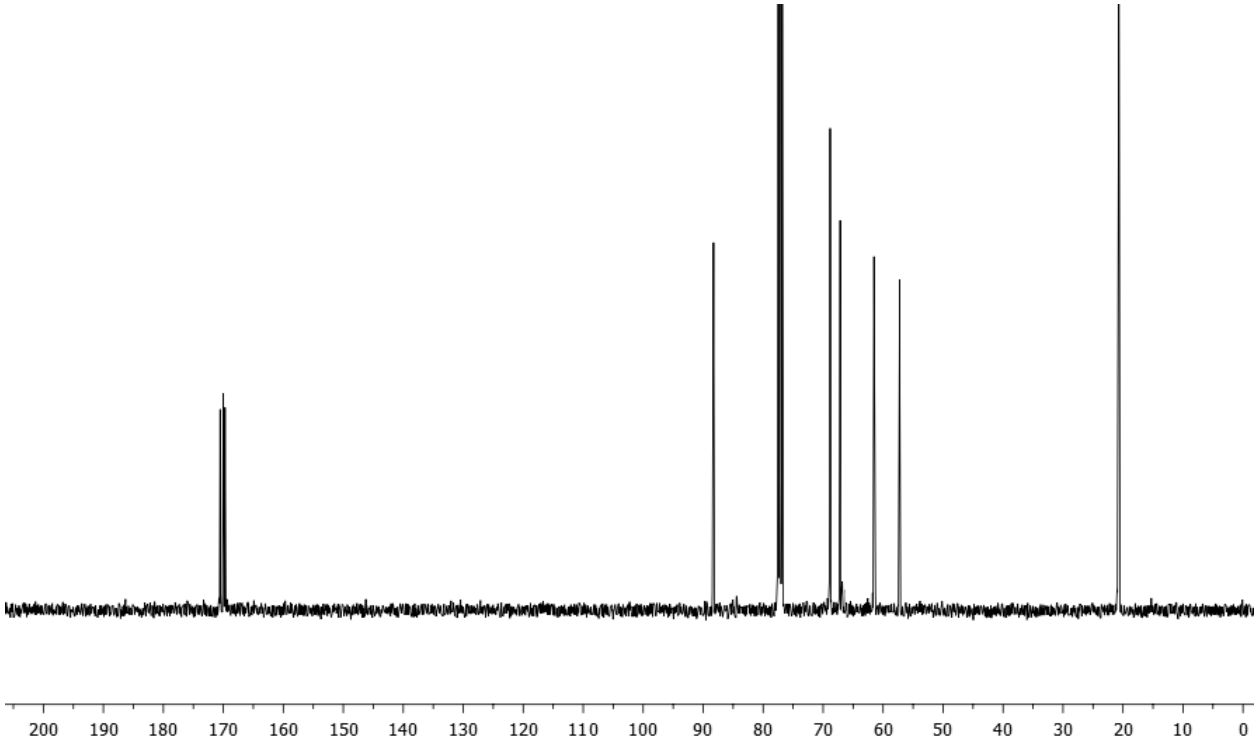
(3R,5R)-piperidine-3,4,5-triol 44:



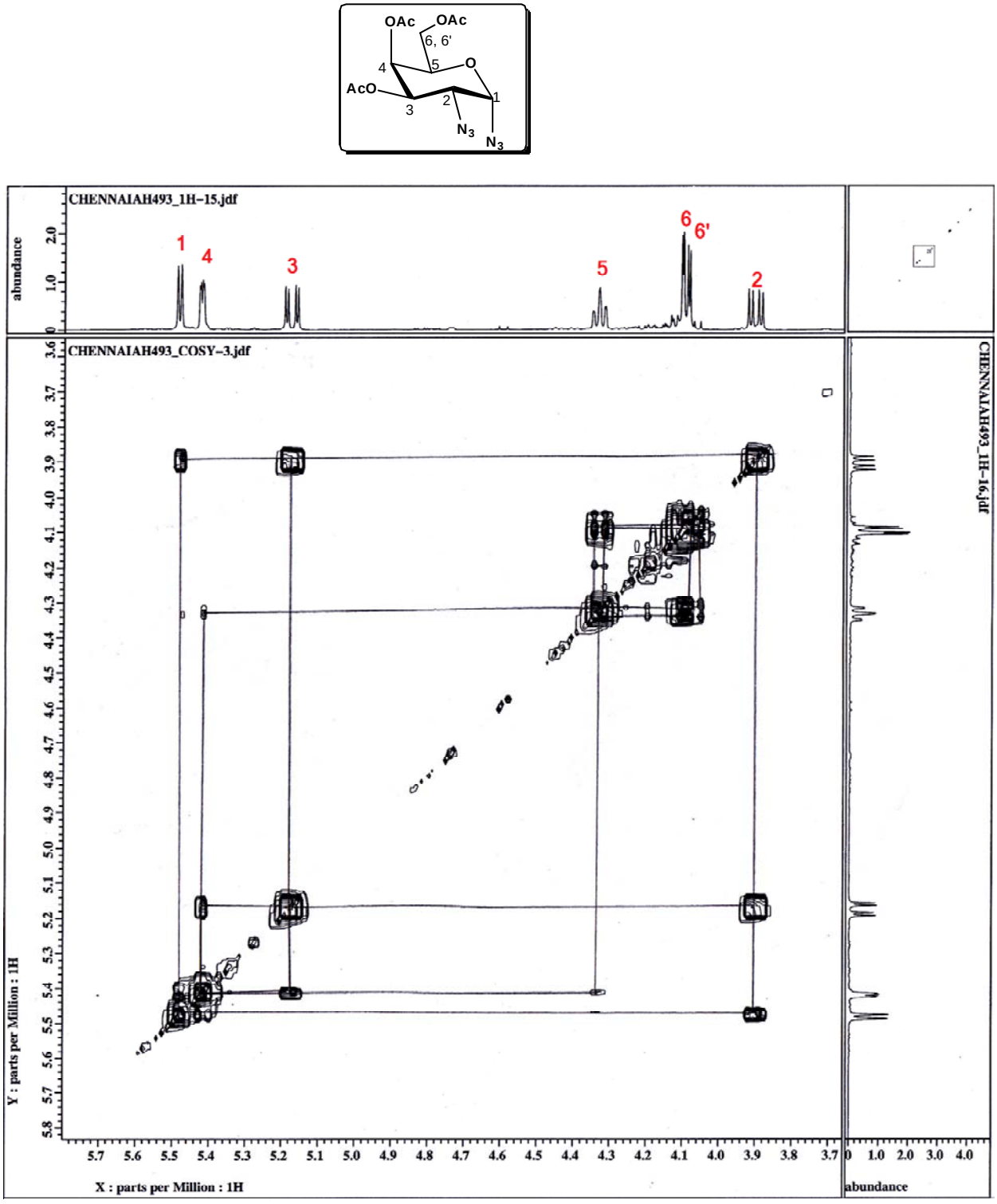
Compound **43** (50 mg, 0.14 mmol) was dissolved in dry CH_3OH (2 mL), and $Pd(OH)_2/C$ (10 mg, 20% w/w) was added to it. The mixture was stirred under 1 atm of H_2 (balloon) overnight, following which 1 N HCl (1 mL) was added, and subsequently the mixture was stirred under 1 atm of H_2 for 32 h. The catalyst was filtered through a Celite bed and washed with MeOH. The solvent was removed under vacuum, and the residue washed repeatedly with hexane. The compound was purified by washing with excess of 50% EtOAc/Hexane solution. The solvent was decanted, and the residue was dried under vacuum to afford pure **44** (11 mg, 60%) as a white semi solid. which was then analyzed spectroscopically. The data matched well with the literature data.[27]



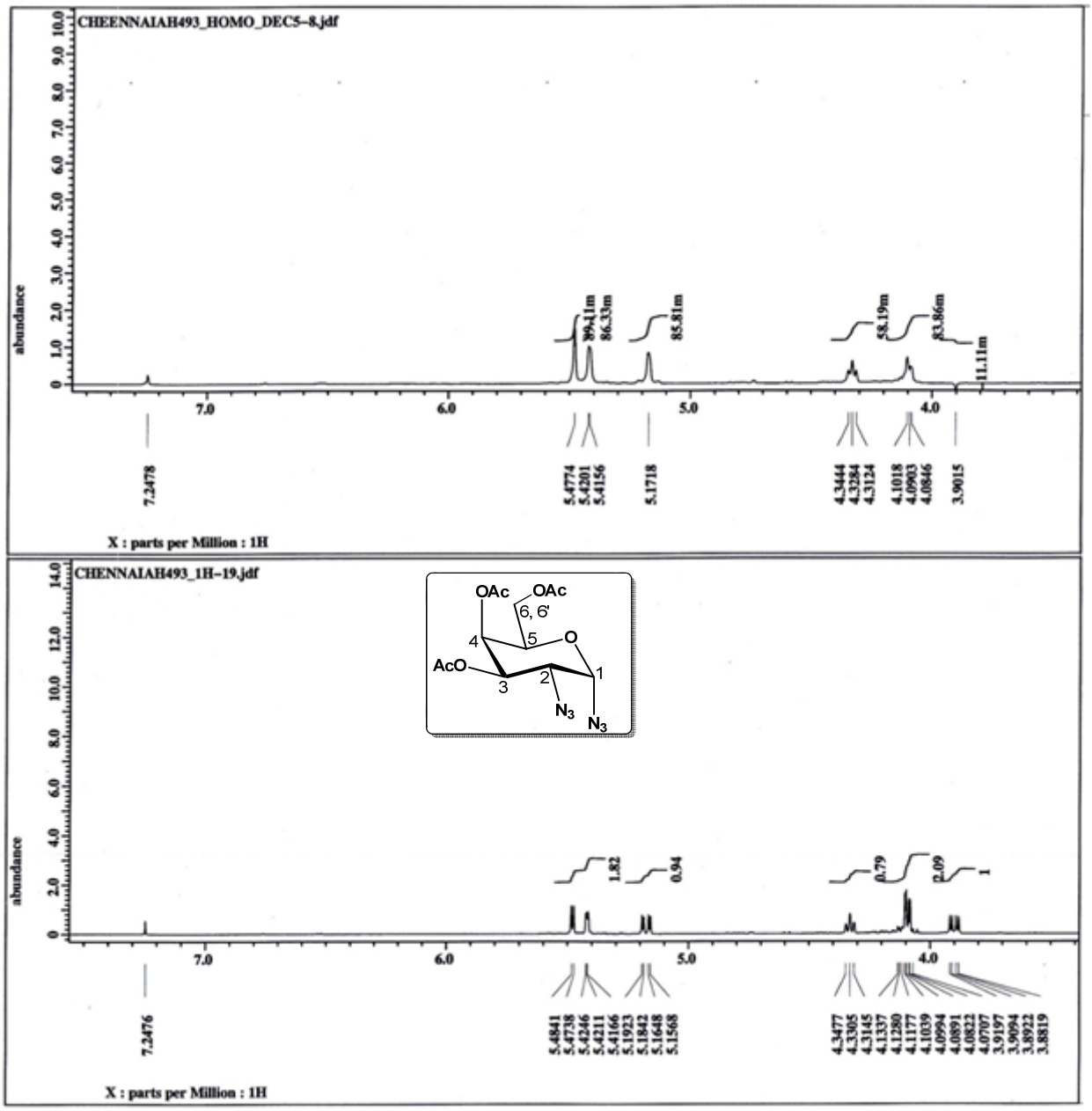
^{1}H NMR spectrum of compound **7a**



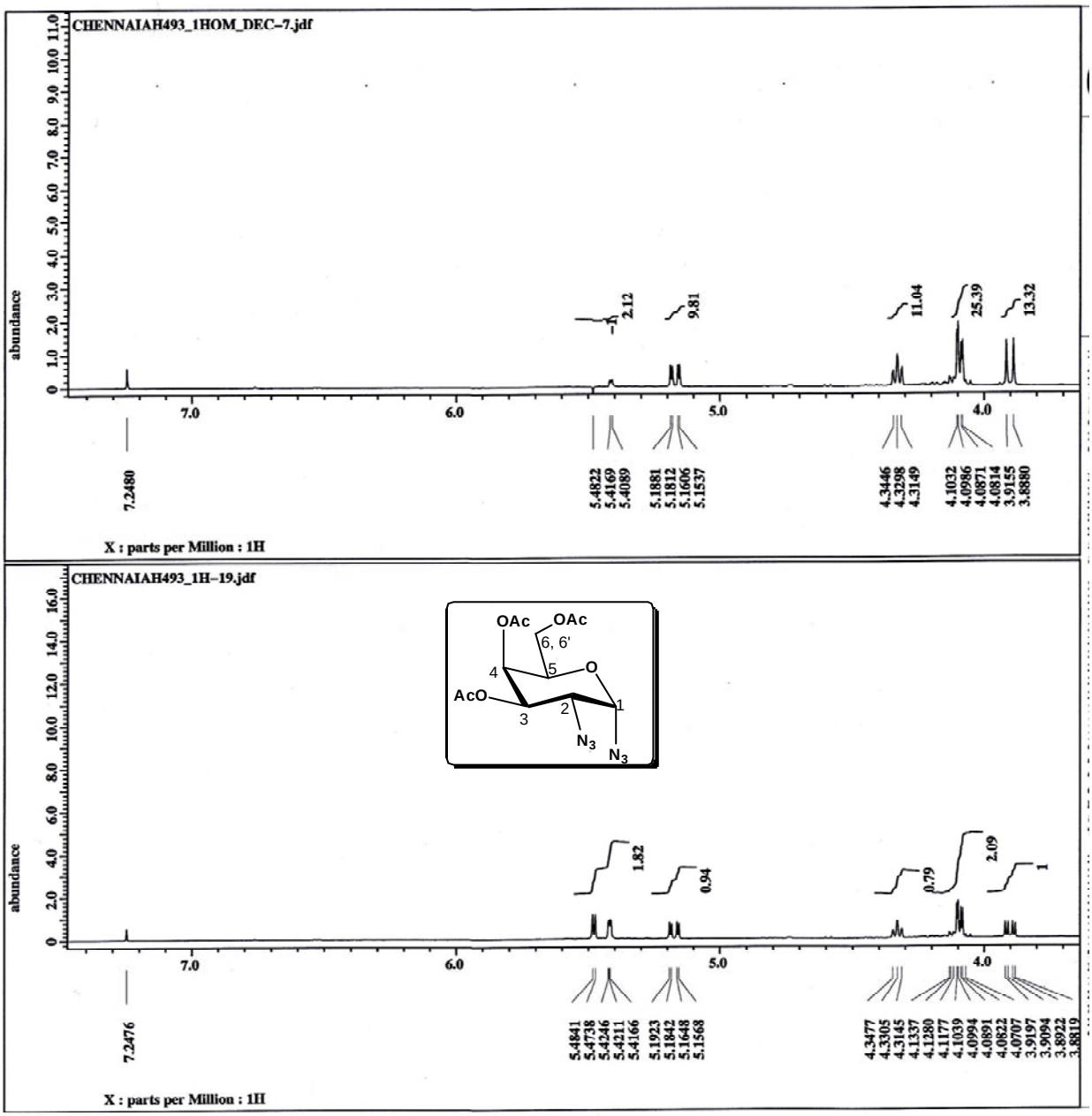
^{13}C NMR spectrum of compound **7a**



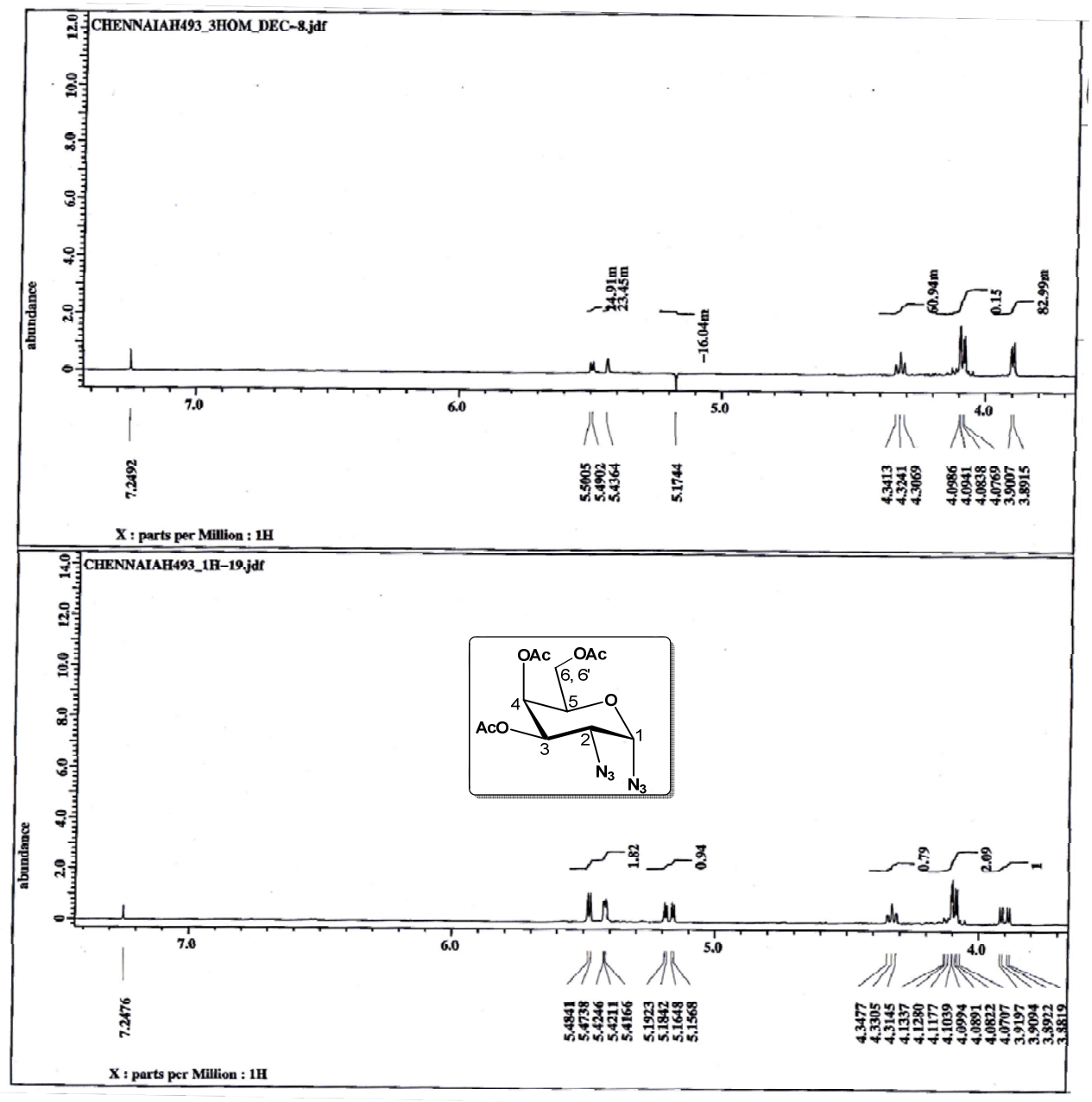
^{1}H-^{1}H COSY NMR spectrum of compound **7a**



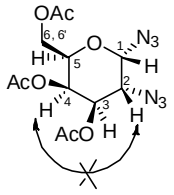
^{1}H-^{1}H homonuclear decoupling (H-2) NMR spectrum of compound **7a**



^{1}H-^{1}H homonuclear decoupling (H-1) NMR spectrum of compound **7a**

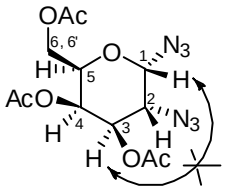


^{1}H-^{1}H homonuclear decoupling (H-3) spectra of Compound **7a**



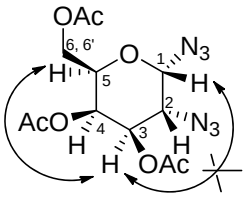
nOe spectrum (irradiation of H̃4) of compound **7a**

(Upon irradiation of proton H-4, no enhancement was observed for proton H-2 indicating that H-2 and H-4 are trans-oriented)



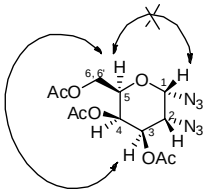
nOe spectrum (irradiation of H-1) of compound **7a**

(Upon irradiation of proton H-1, no enhancement was observed for proton H-3 indicating that H-1 and H-3 are not cis-oriented)



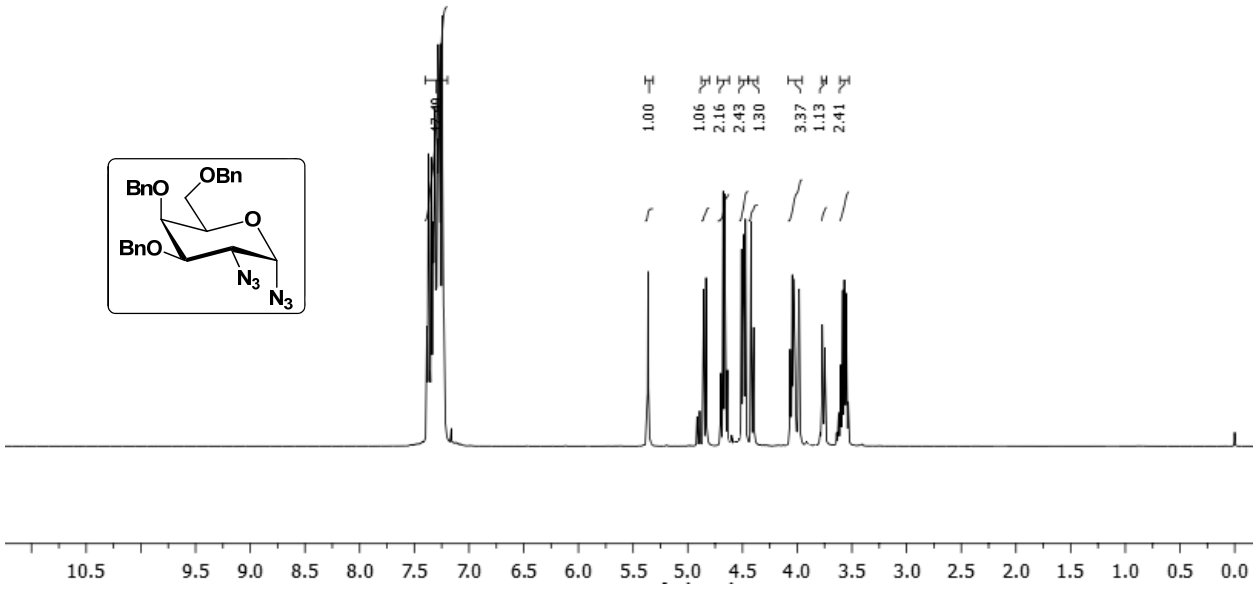
nOe spectrum (irradiation of H-3) of compound **7a**

(Irradiation of proton H-3 led to the enhancement of the signal for proton H-5 and no enhancement was observed for proton H-1, indicating that H-1 and H-3 are not cis-oriented)

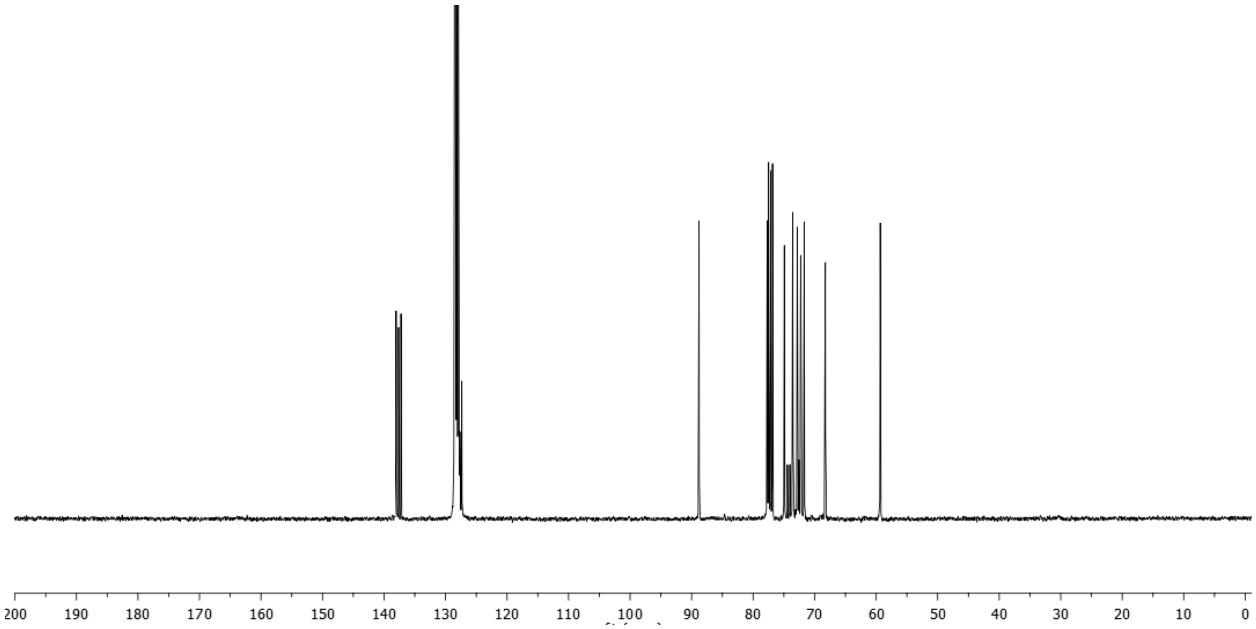


nOe spectrum (irradiation of H-5) of compound **7a**

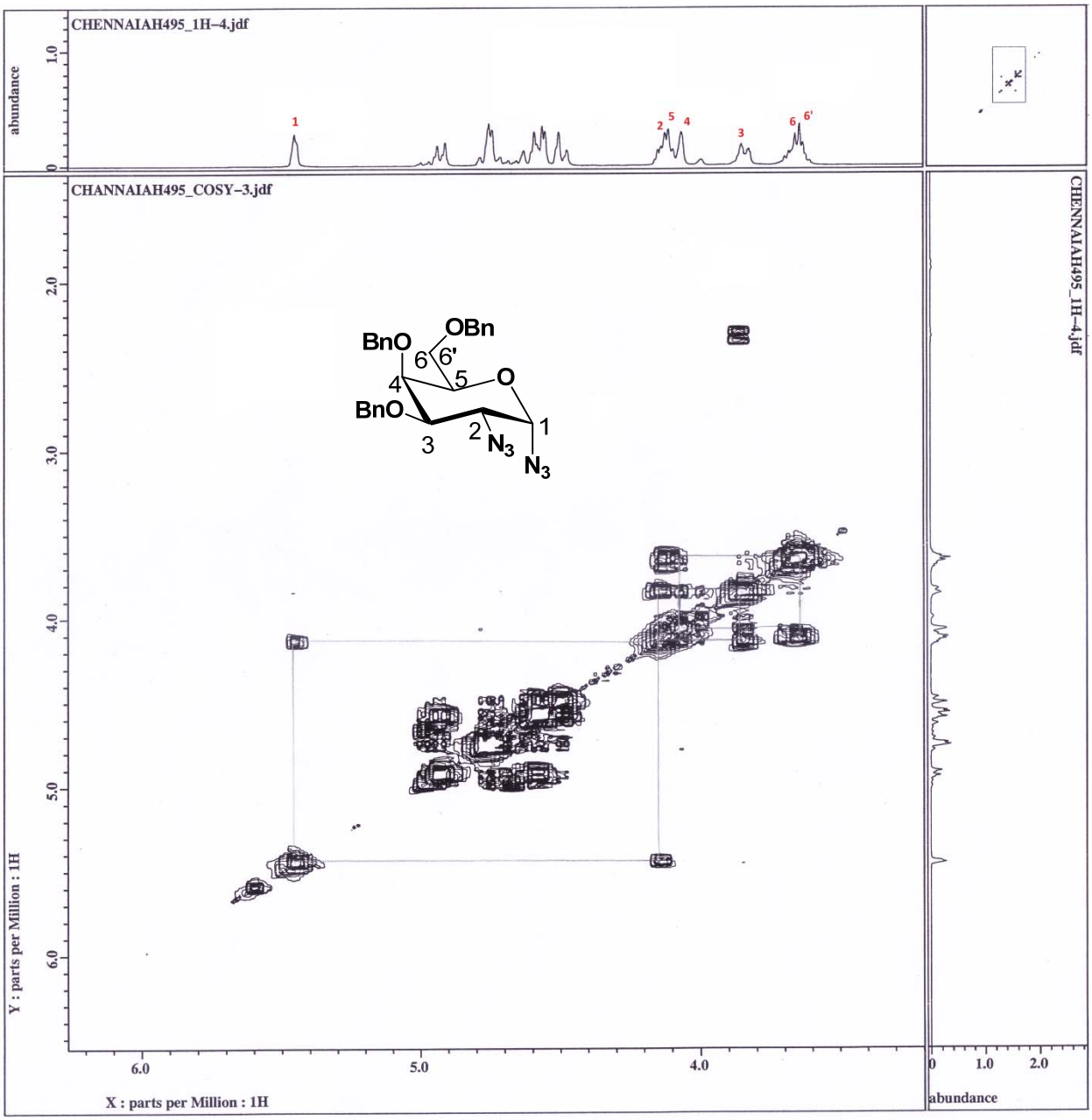
(Irradiation of proton H-5, led to the enhancement for proton H-3 and no enhancement was observed for proton H-1, indicating that H-1 and H-5 are trans oriented)



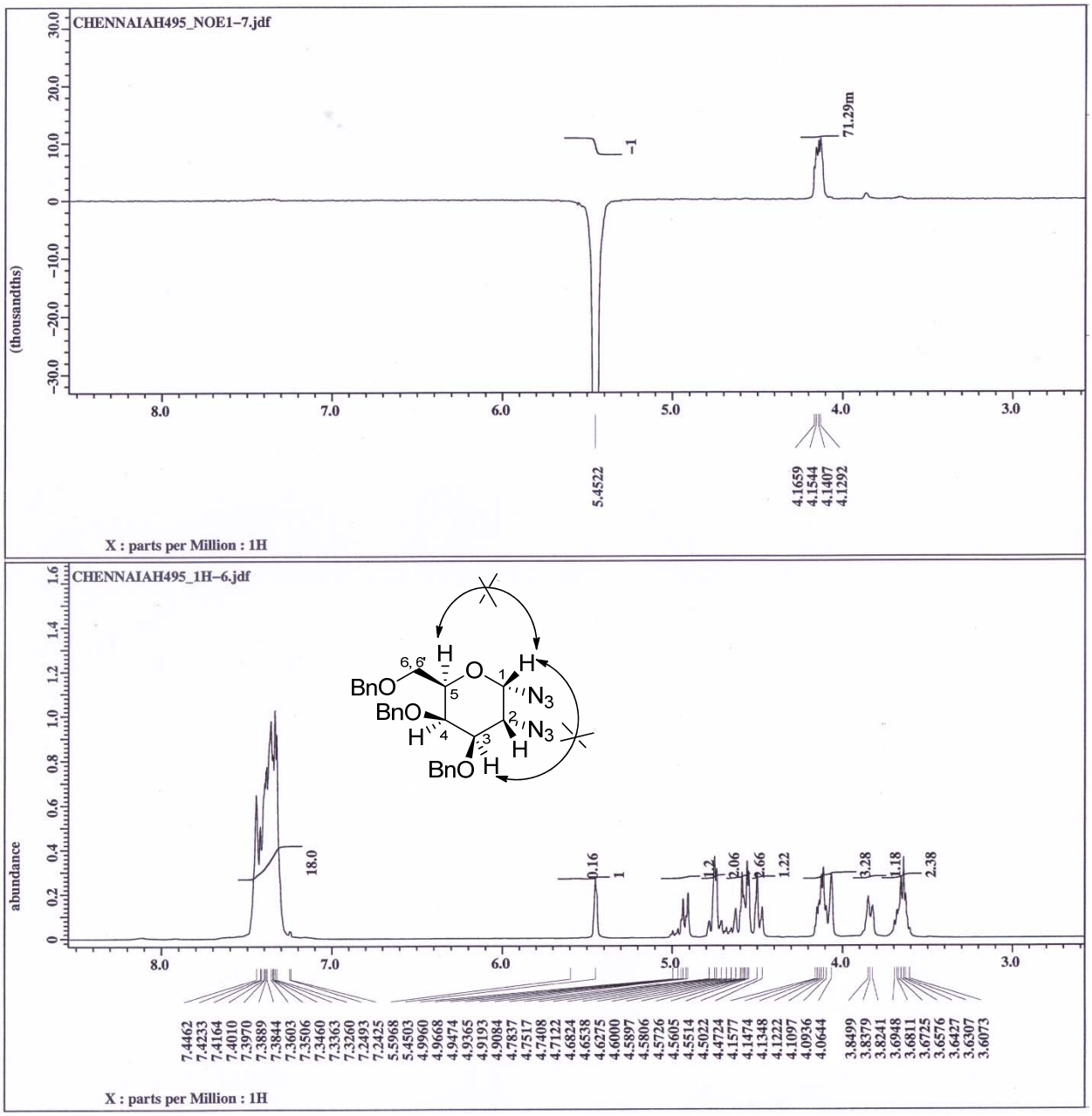
^{1}H NMR spectrum of compound **7b**



^{13}C NMR spectrum of compound **7b**

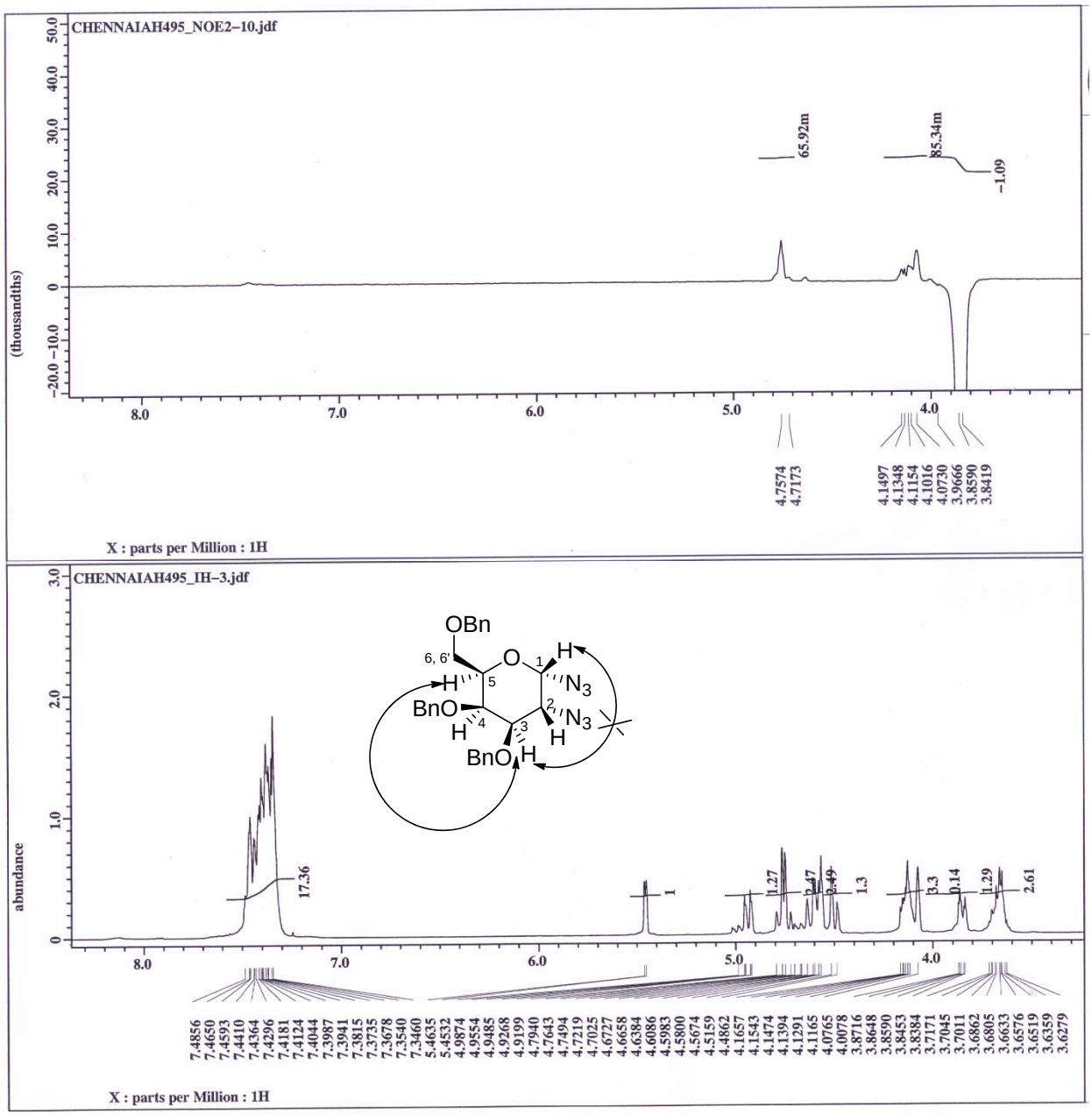


^{1}H-^{1}H COSY NMR spectrum of compound **7b**



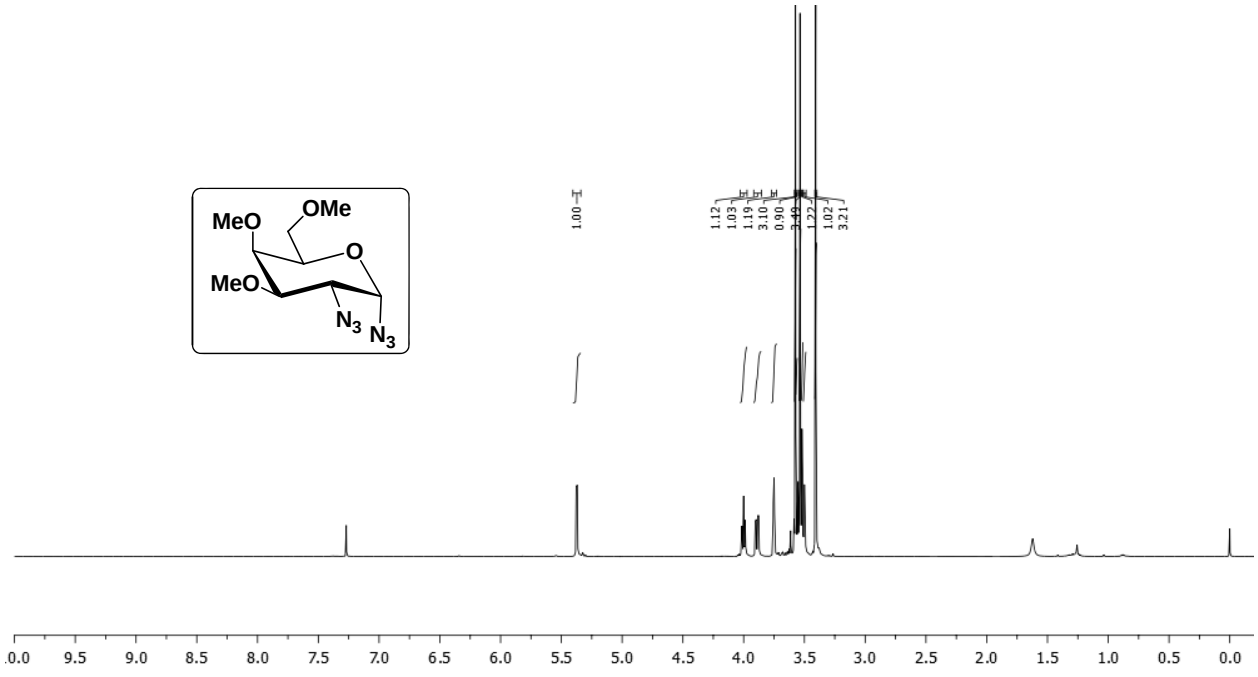
nOe spectrum (irradiation of H-1) of compound **7b**

(Upon irradiation of proton H-1, no enhancement was observed for the signals of protons H-3 and H-5)

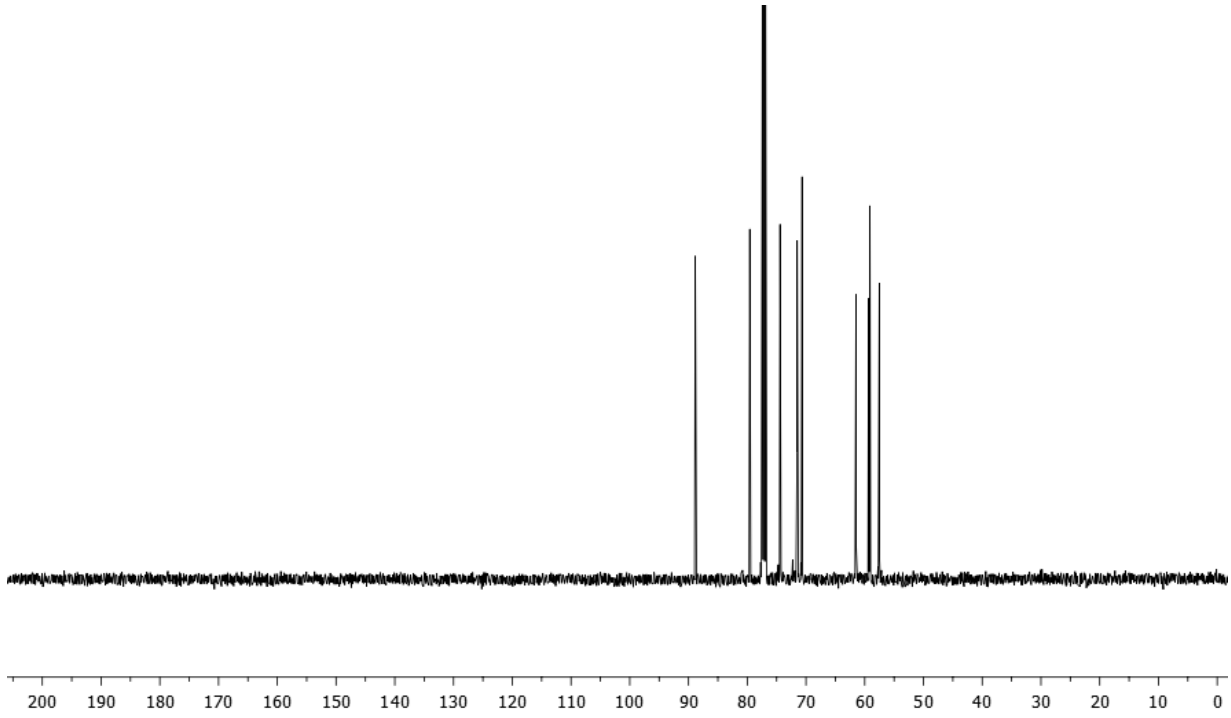


nOe spectrum (irradiation of H-3) of compound **7b**

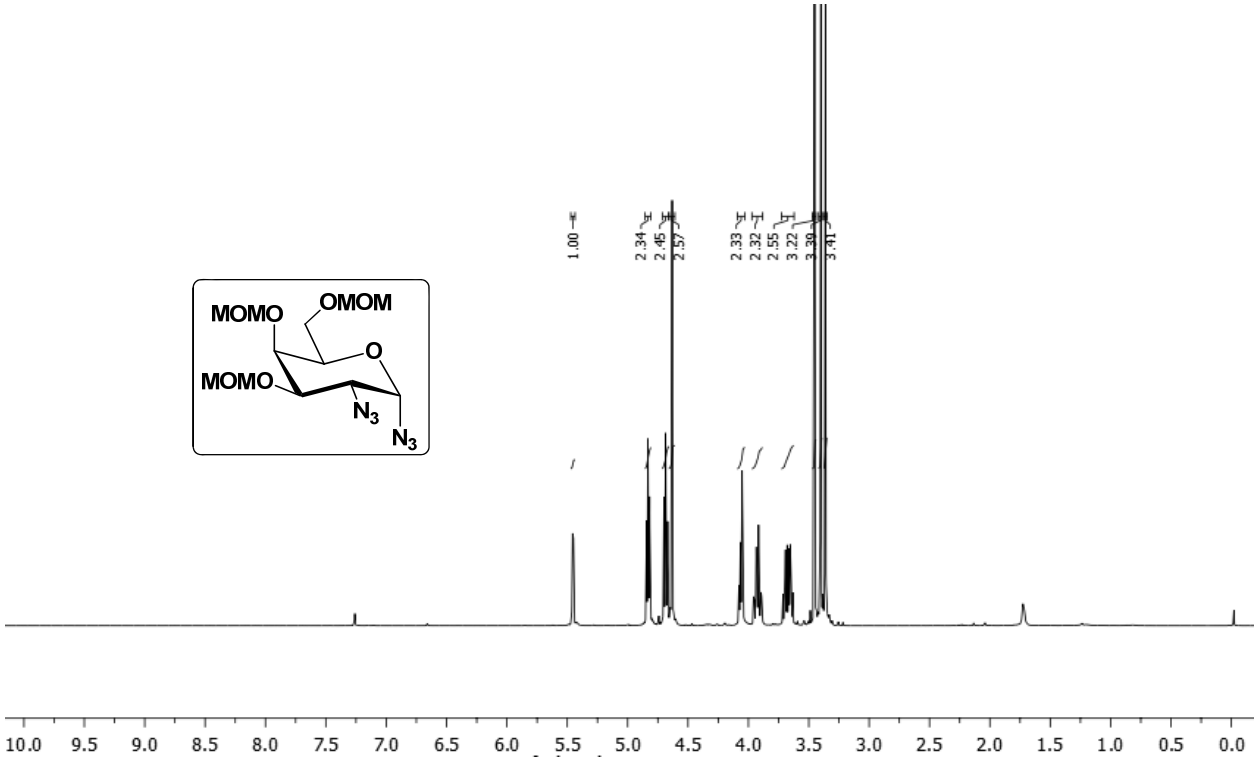
(Irradiation of proton H-3 led to the enhancement for proton H-5 but no enhancement was observed for the signal for proton H-1, indicating that H-1 and H-3 are trans oriented)



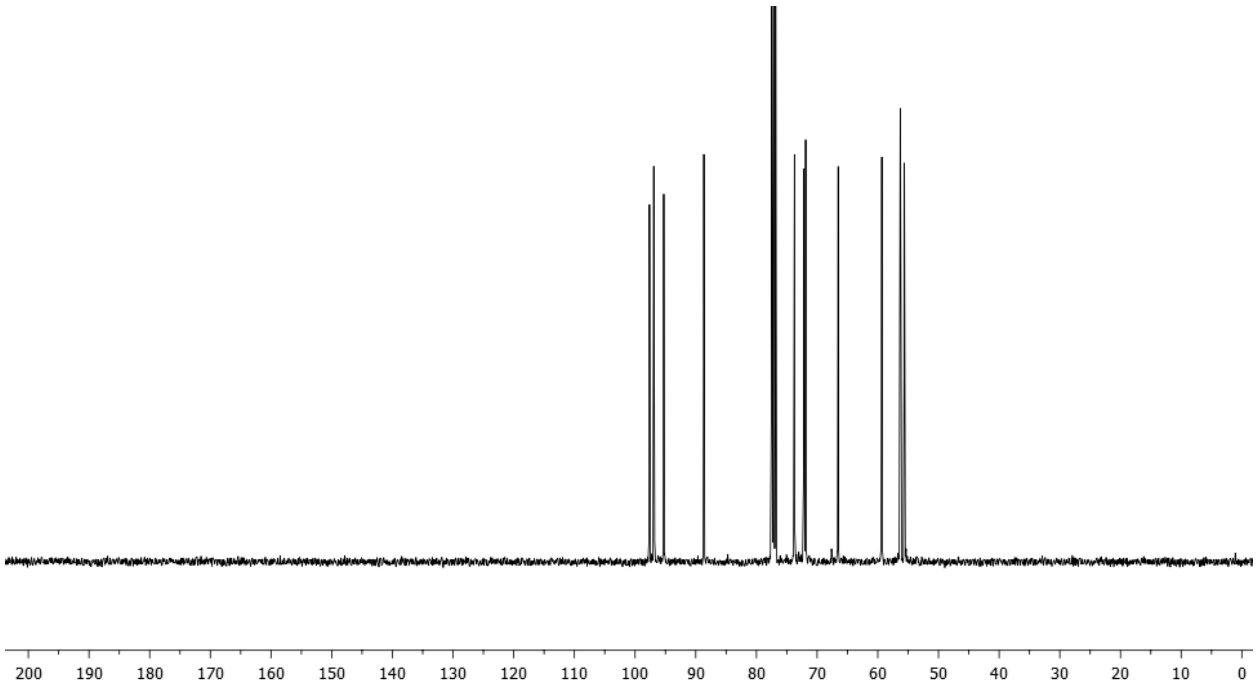
^{1}H NMR spectrum of compound **7c**



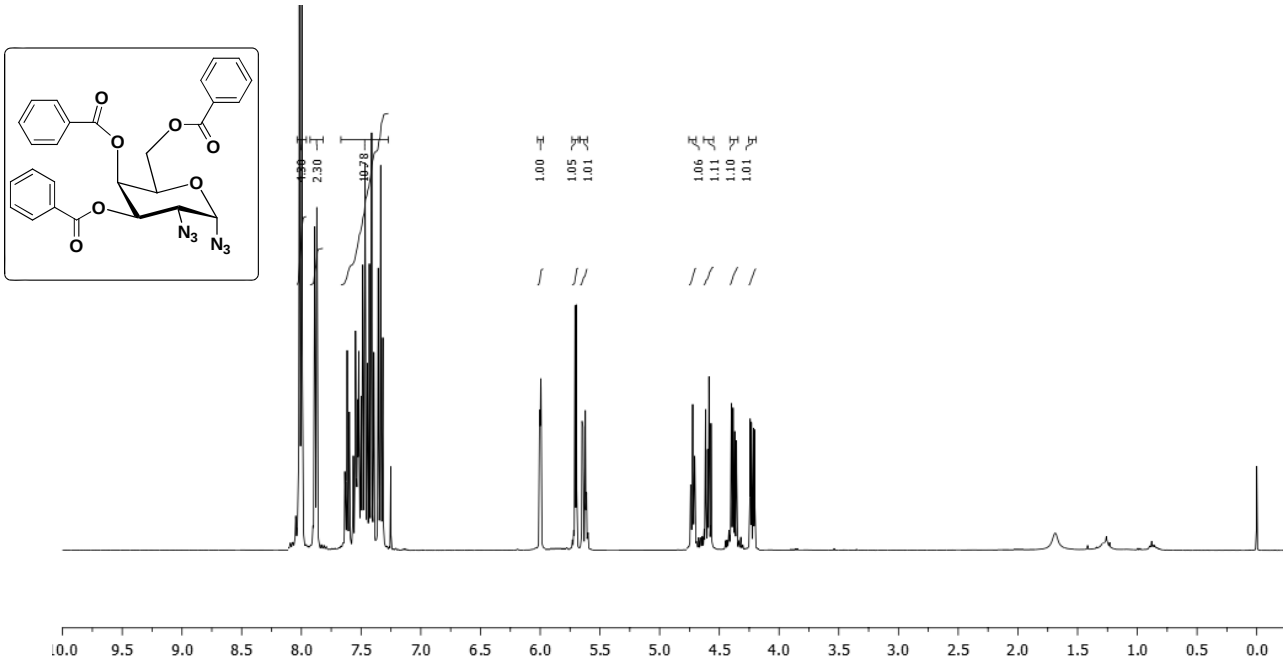
^{13}C NMR spectrum of compound **7c**



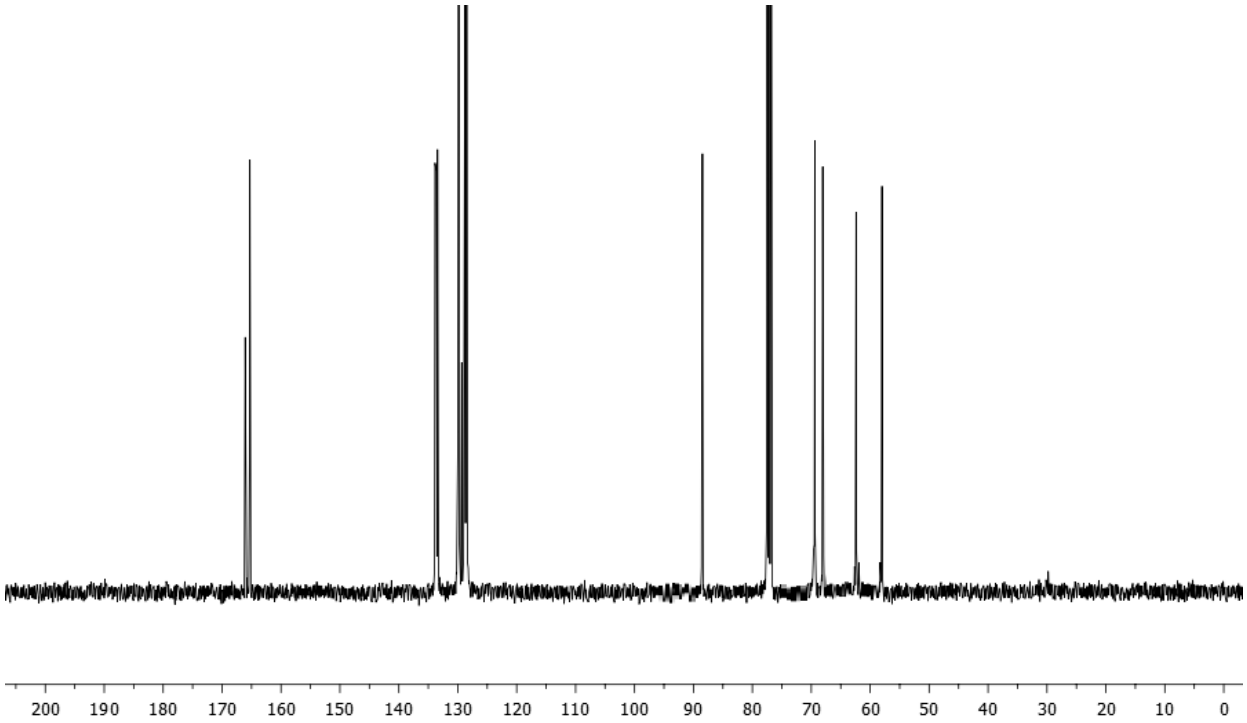
^{1}H NMR spectrum of compound **7d**



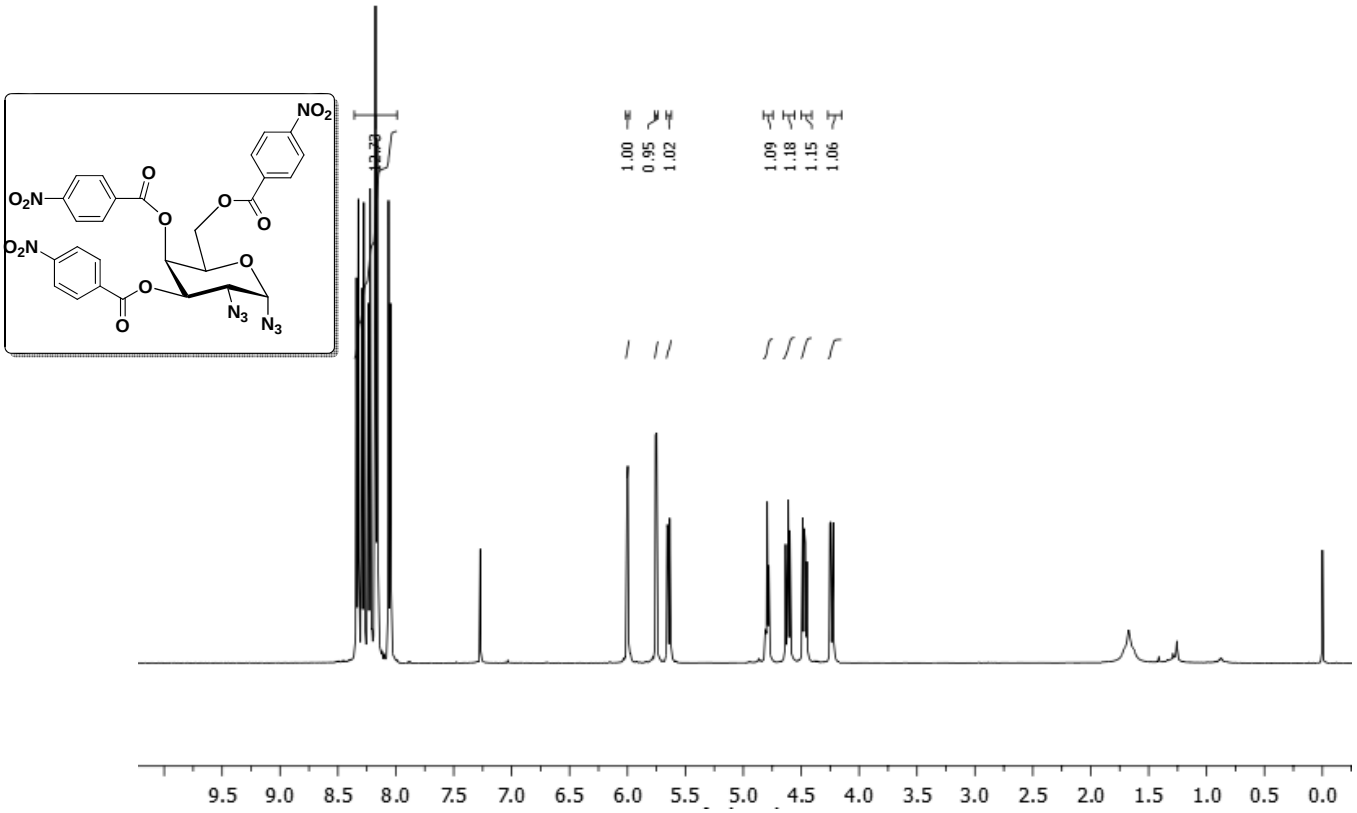
^{13}C NMR spectrum of compound **7d**



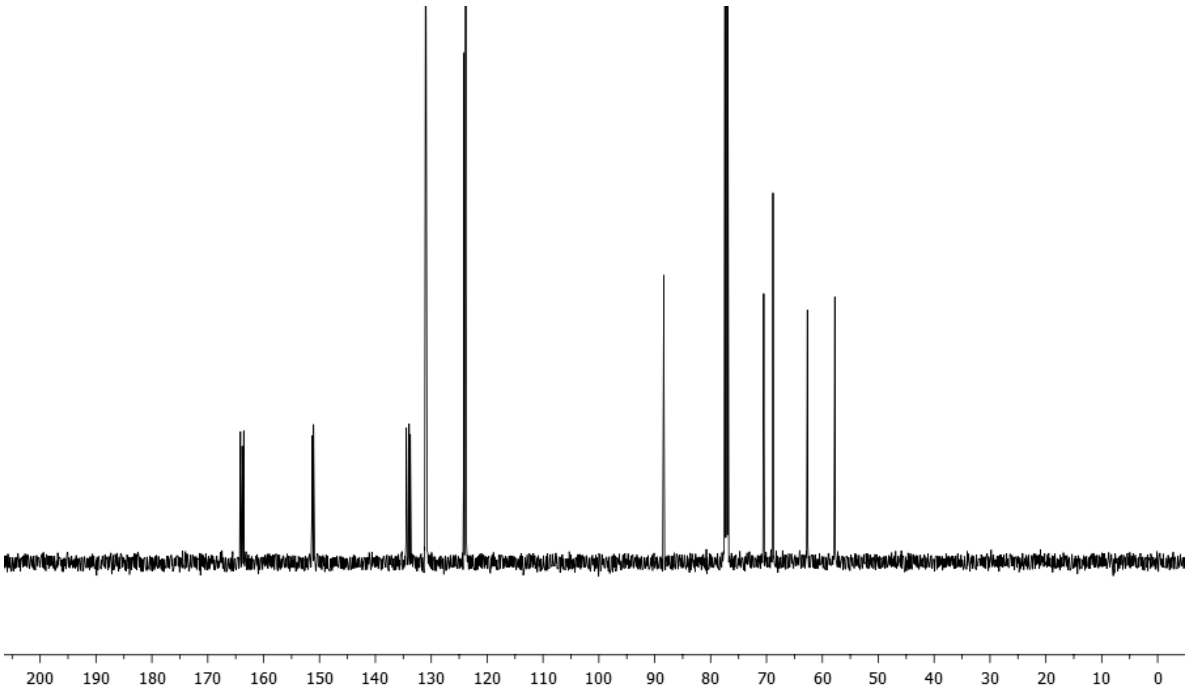
^{1}H NMR spectrum of compound **7e**



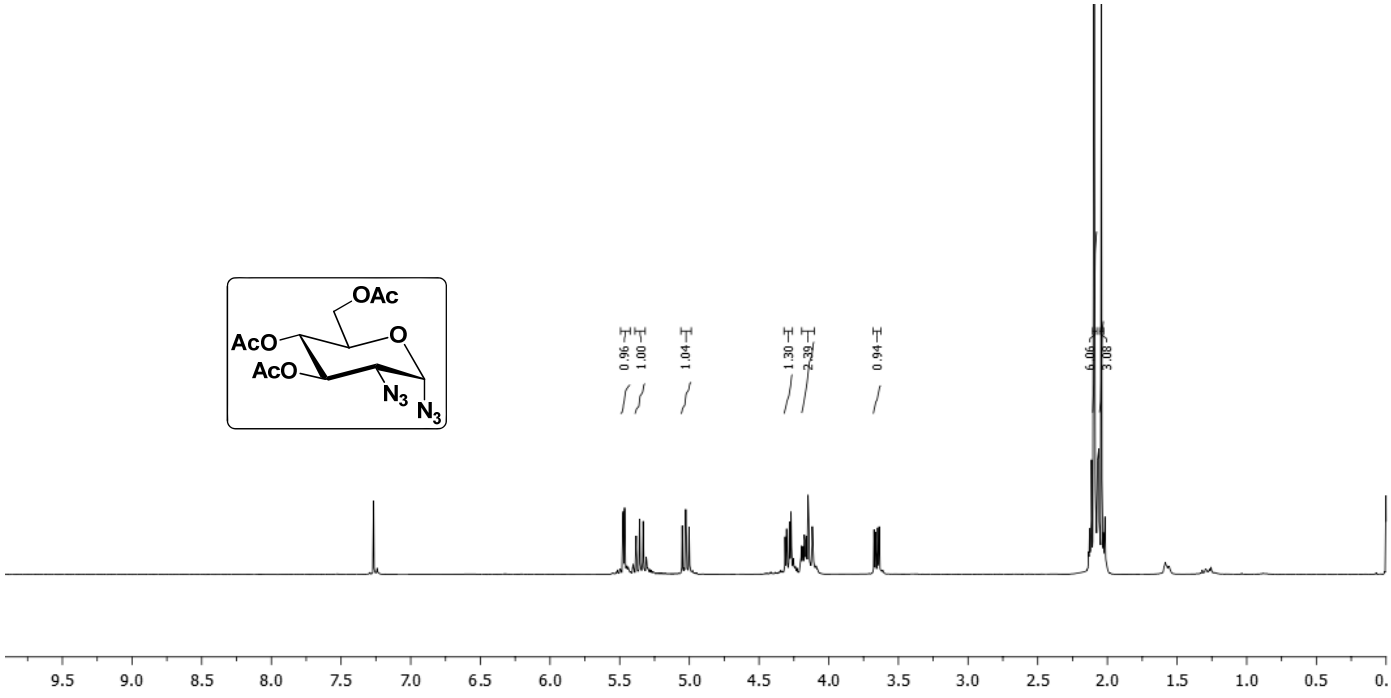
^{13}C NMR spectrum of compound **7e**



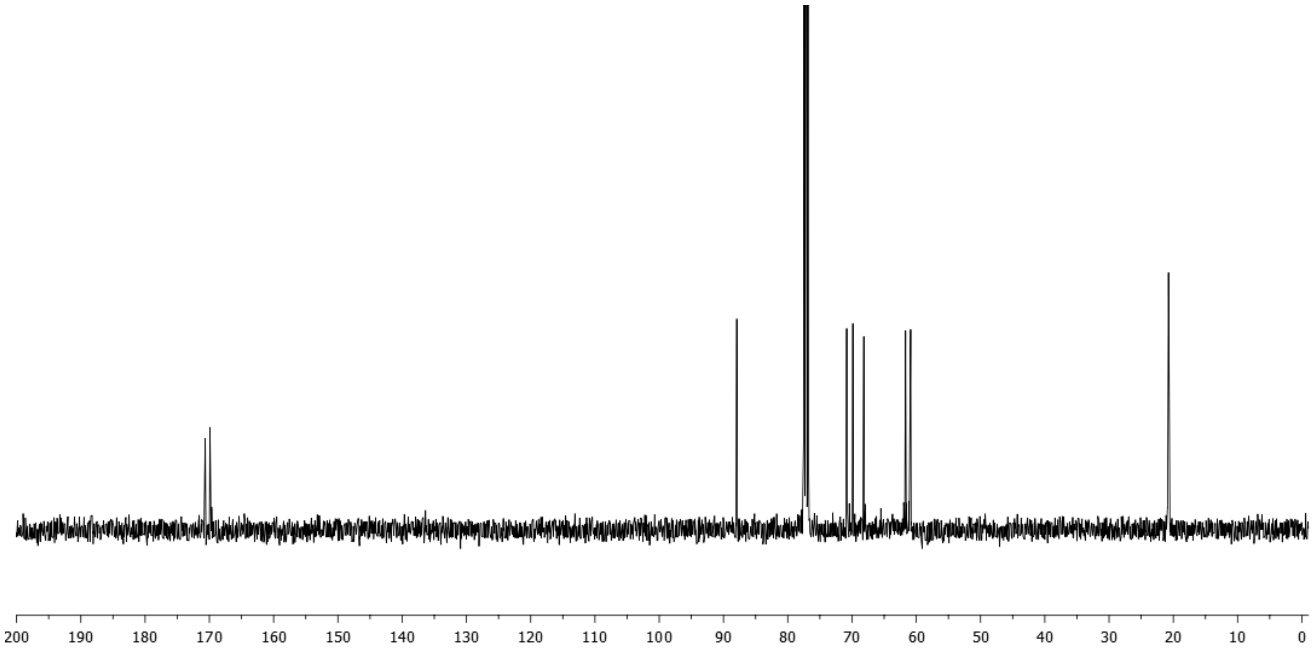
^{1}H NMR spectrum of compound **7f**



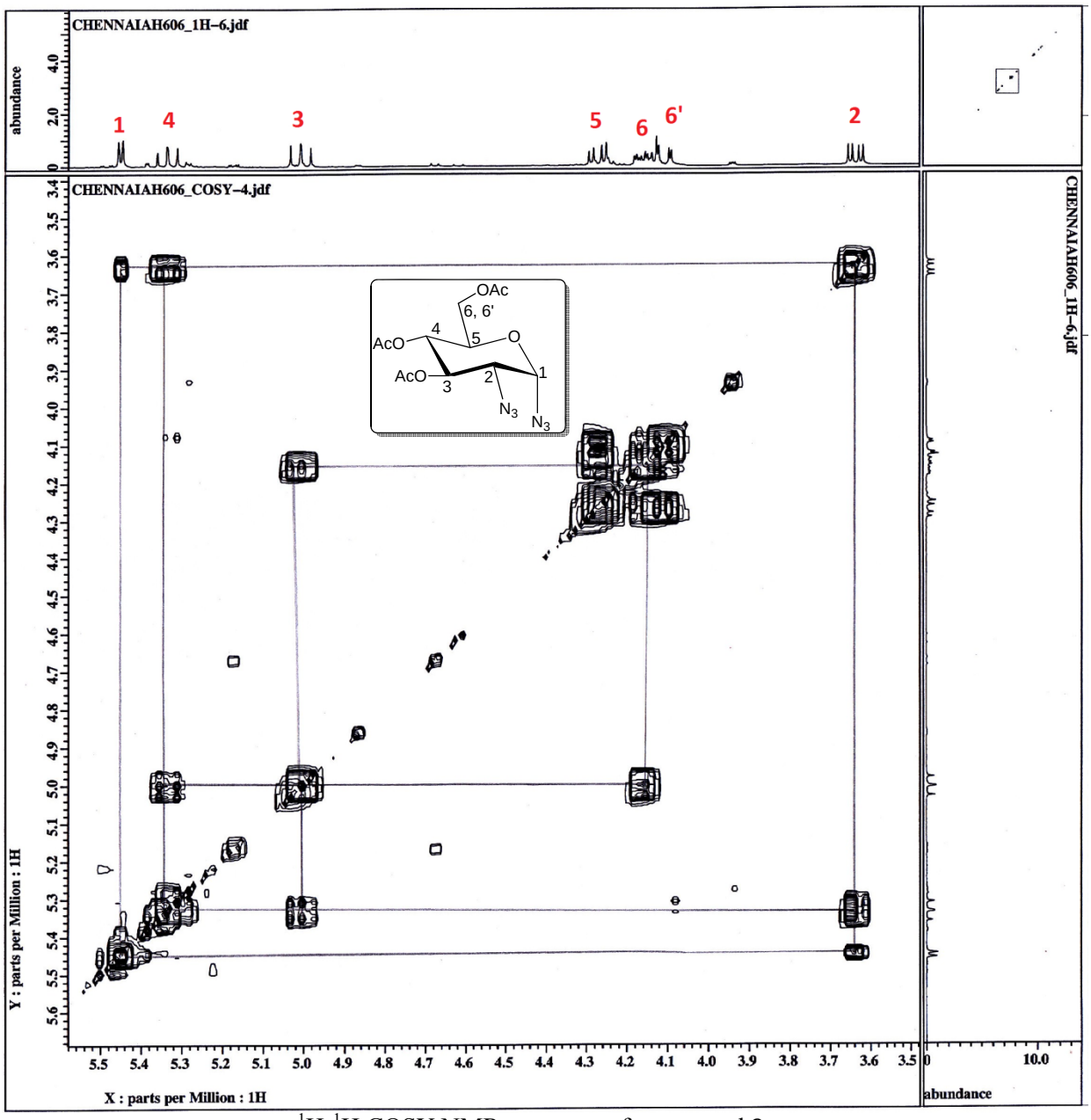
^{13}C NMR spectrum of compound **7f**



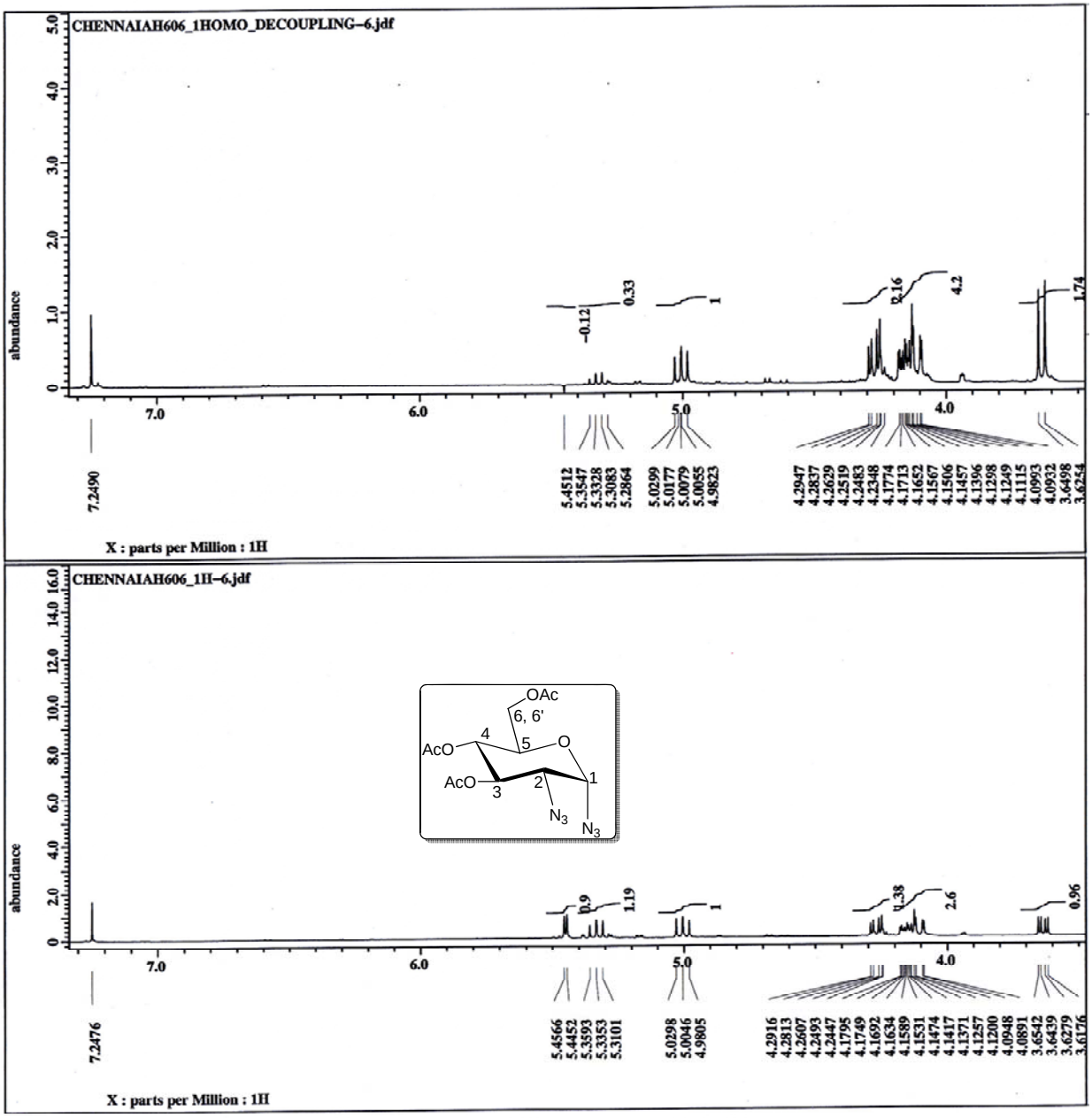
^{1}H NMR spectrum of compound **9a**



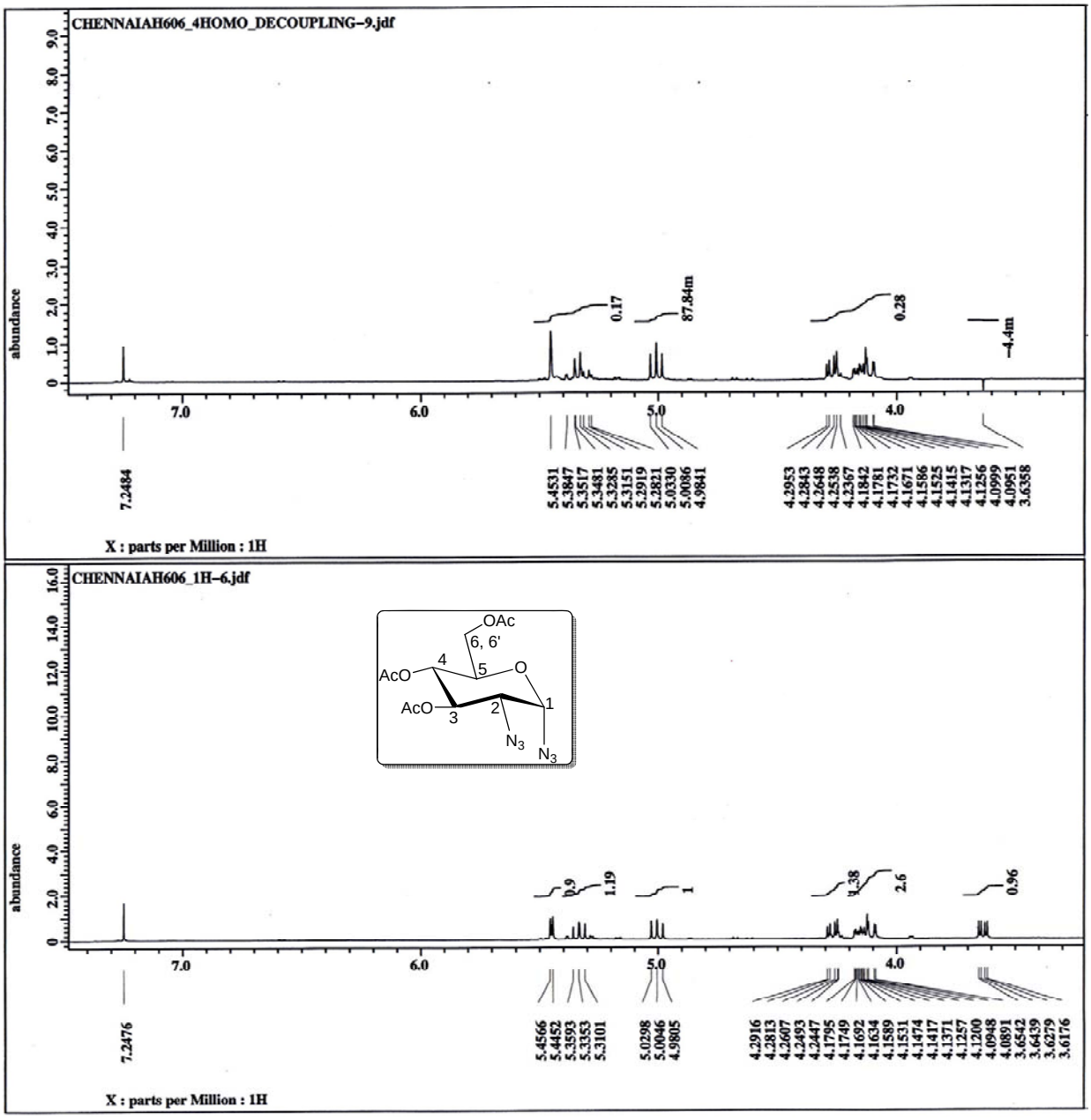
^{13}C NMR spectrum of compound **9a**



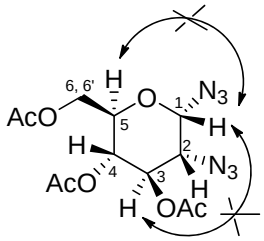
^{1}H-^{1}H COSY NMR spectrum of compound **9a**



^{1}H-^{1}H homonuclear decoupling (H-1) NMR spectrum of compound **9a**

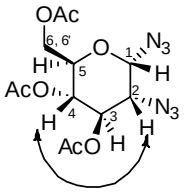


^{1}H-^{1}H homonuclear decoupling (H-2) NMR spectrum of compound **9a**



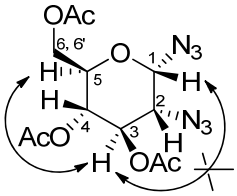
nOe spectrum (irradiation of H-1) of compound **9a**

(Upon irradiation of proton H-1, no enhancement was observed for the signals of protons H-3 and H-5)



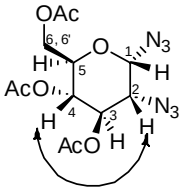
nOe spectrum (irradiation of H-4) of compound **9a**

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



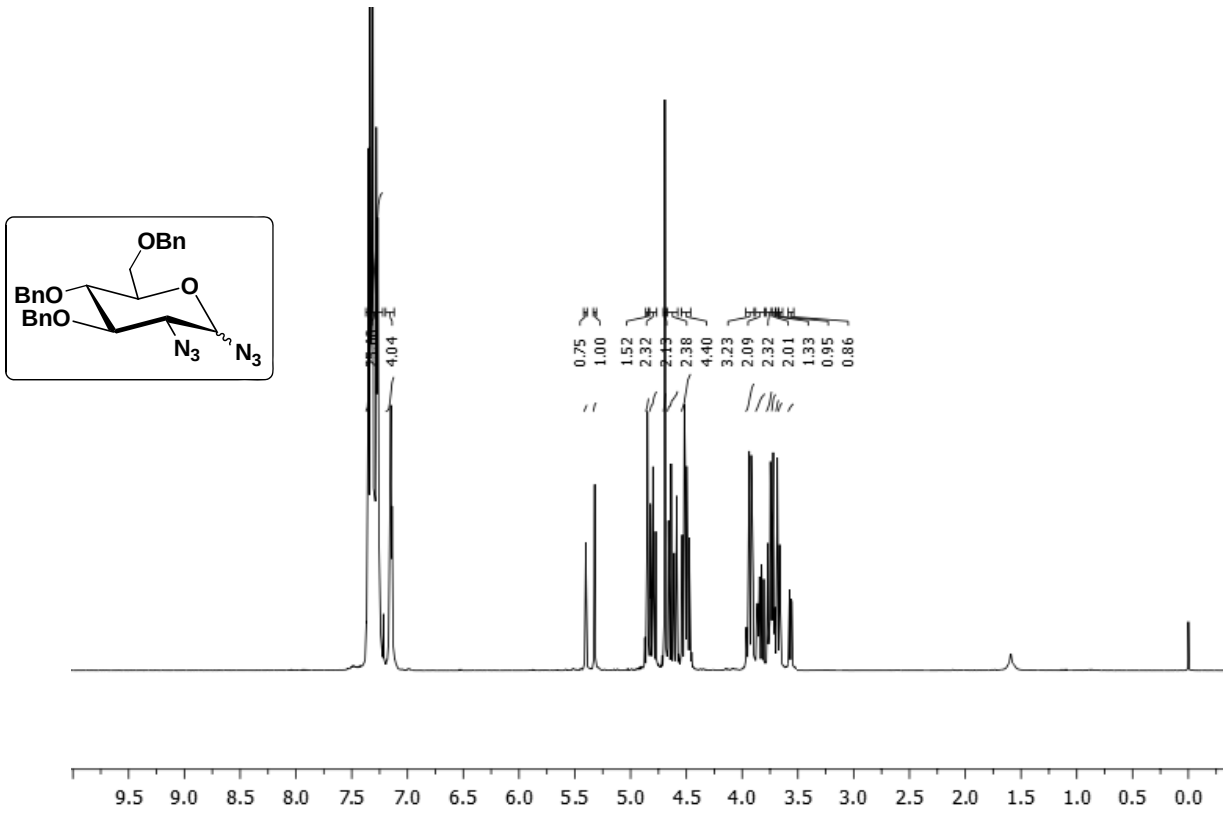
nOe spectrum (irradiation of H-3) of compound **9a**

(Irradiation of proton H-3 led to the enhancement of signals for proton H-5, and no enhancement was observed for the signal of proton H-1, indicating that H-1 and H-3 are trans oriented)

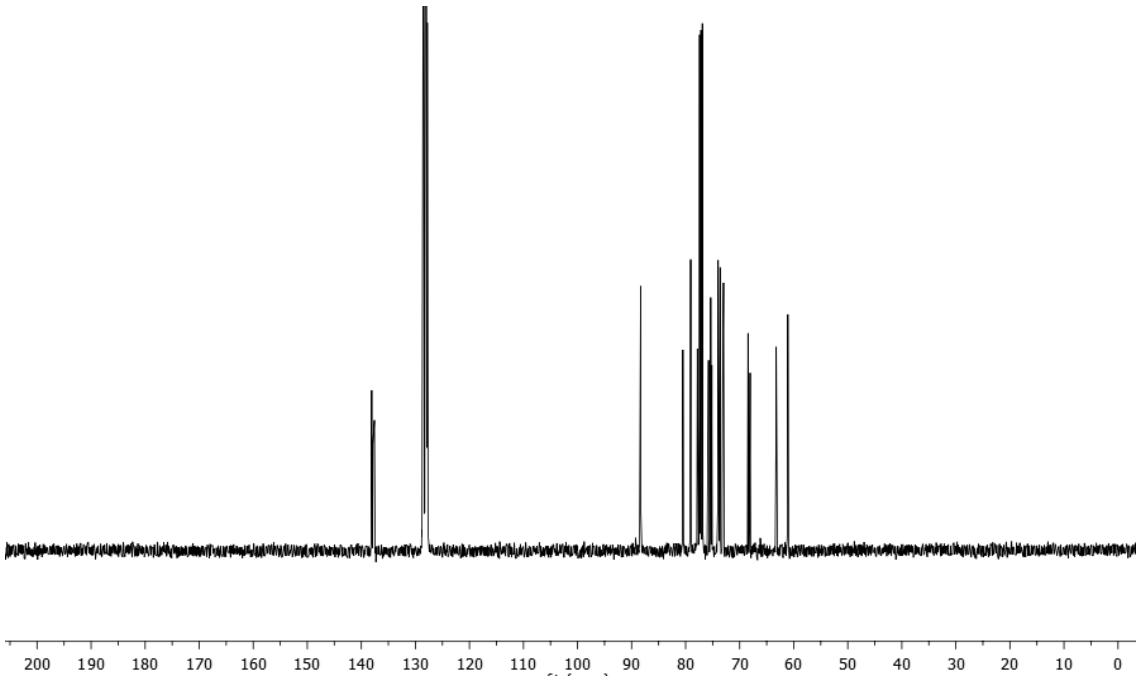


nOe spectrum (irradiation of H-2) of compound **9a**

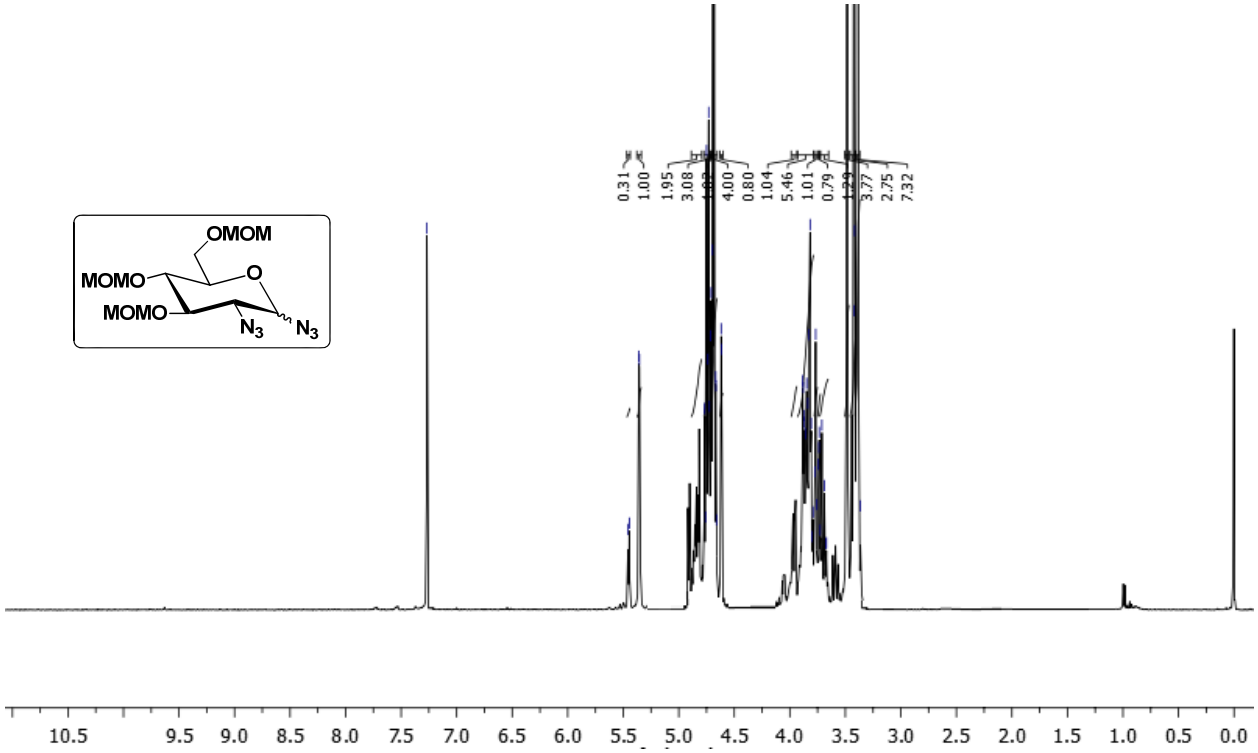
(Irradiation of proton H-2 led to the enhancement of signal for proton H-4, indicating that H-2 and H-4 are cis oriented)



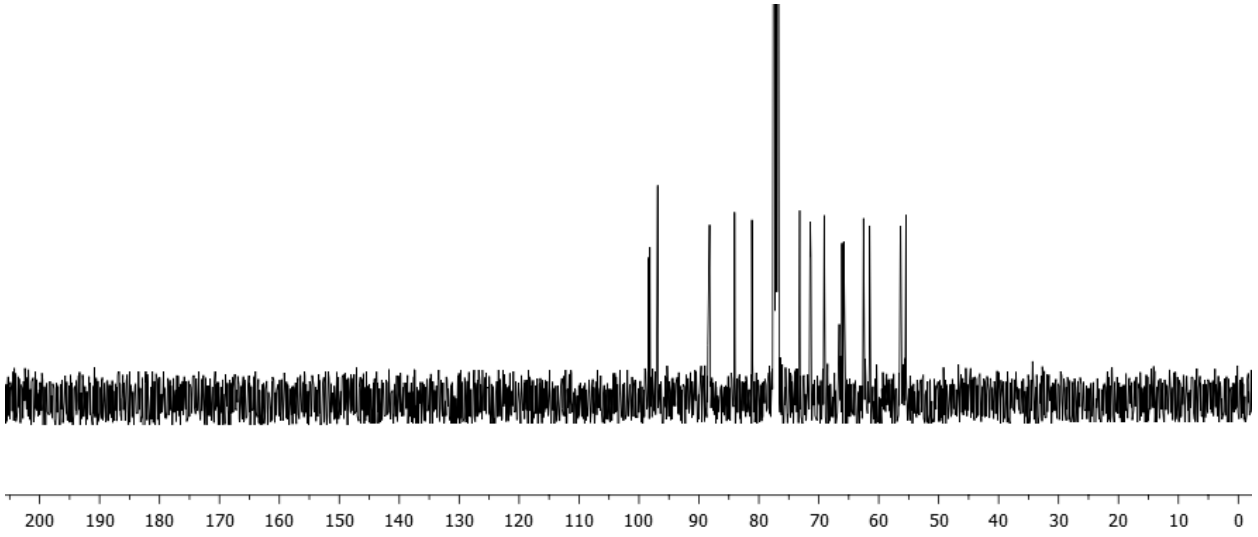
^{1}H NMR spectrum of compound **9b**



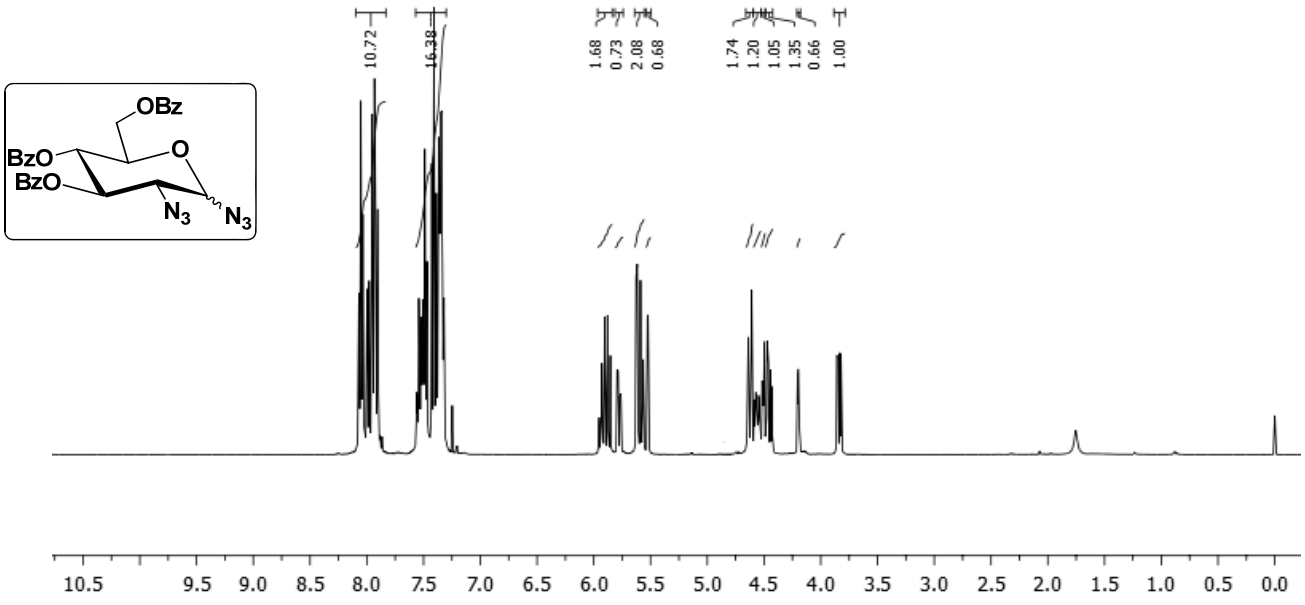
^{13}C NMR spectrum of compound **9b**



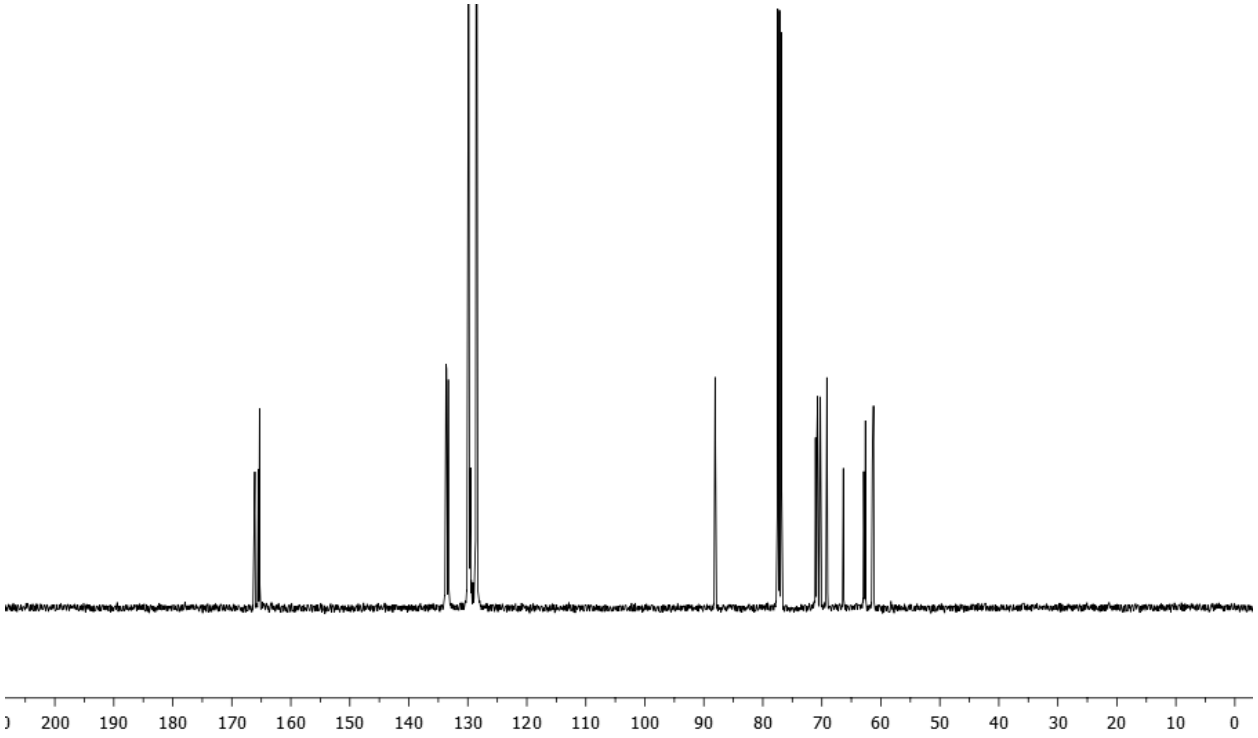
^{1}H NMR spectrum of compound **9c**



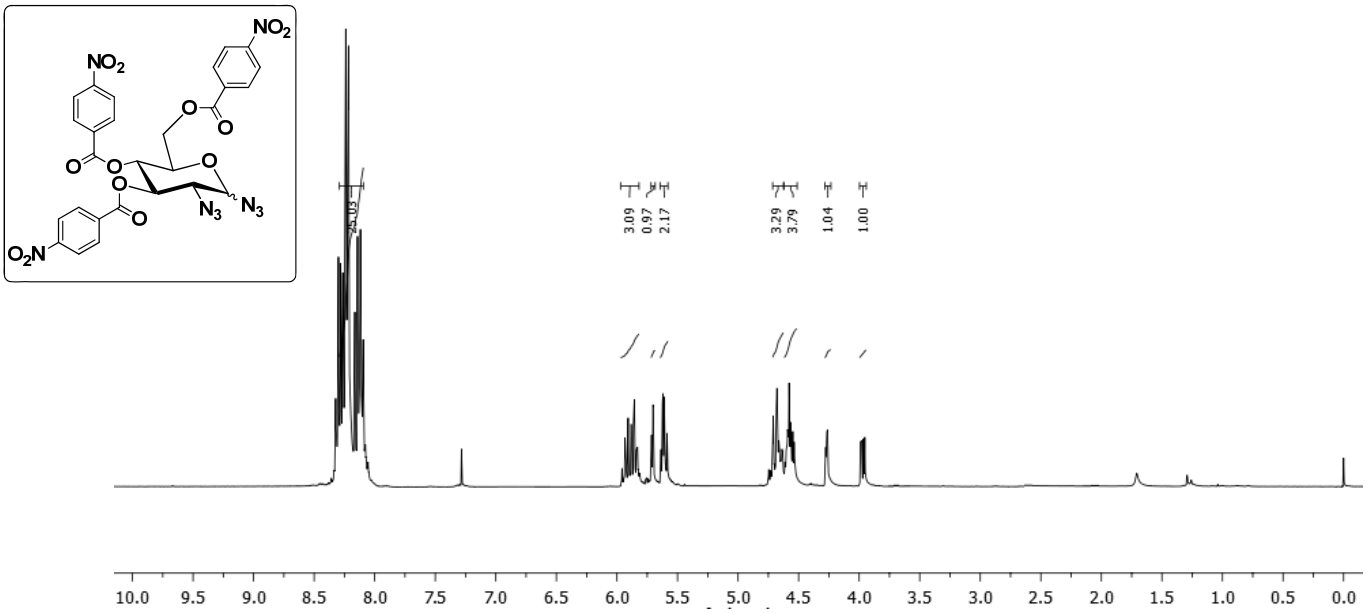
^{13}C NMR spectrum of compound **9c**



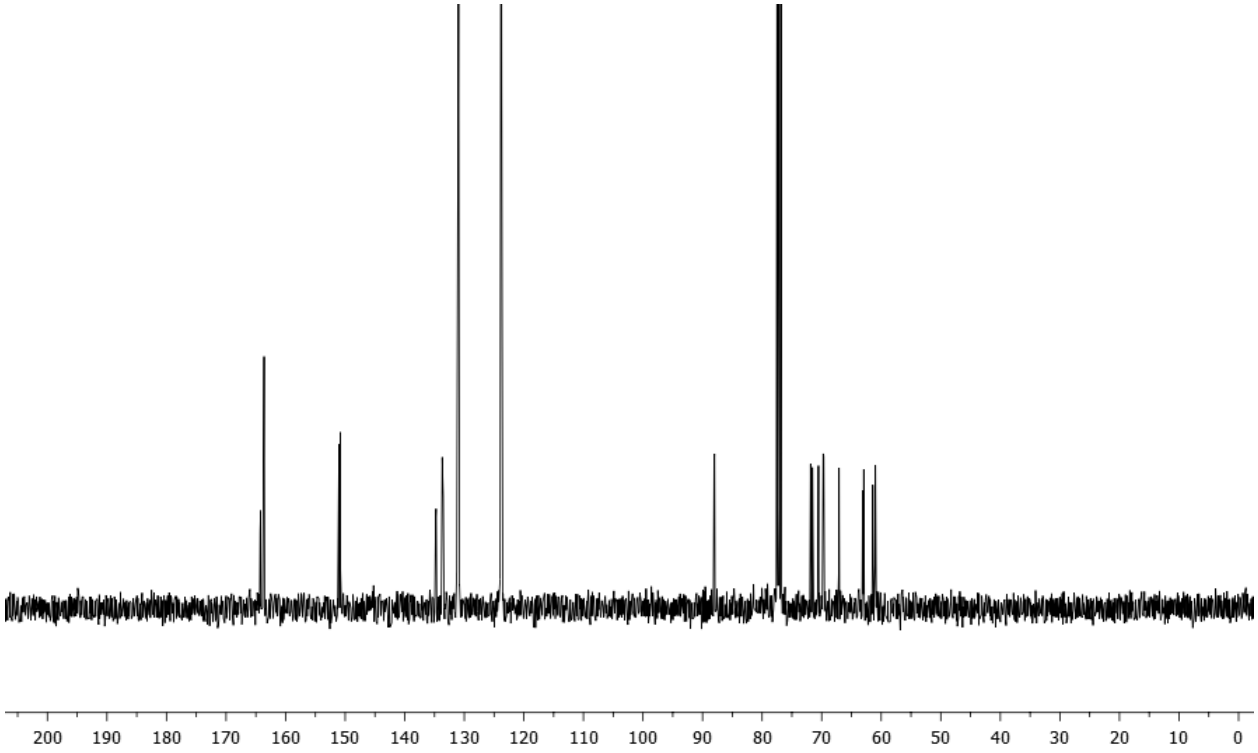
^{1}H NMR spectrum of compound **9d**



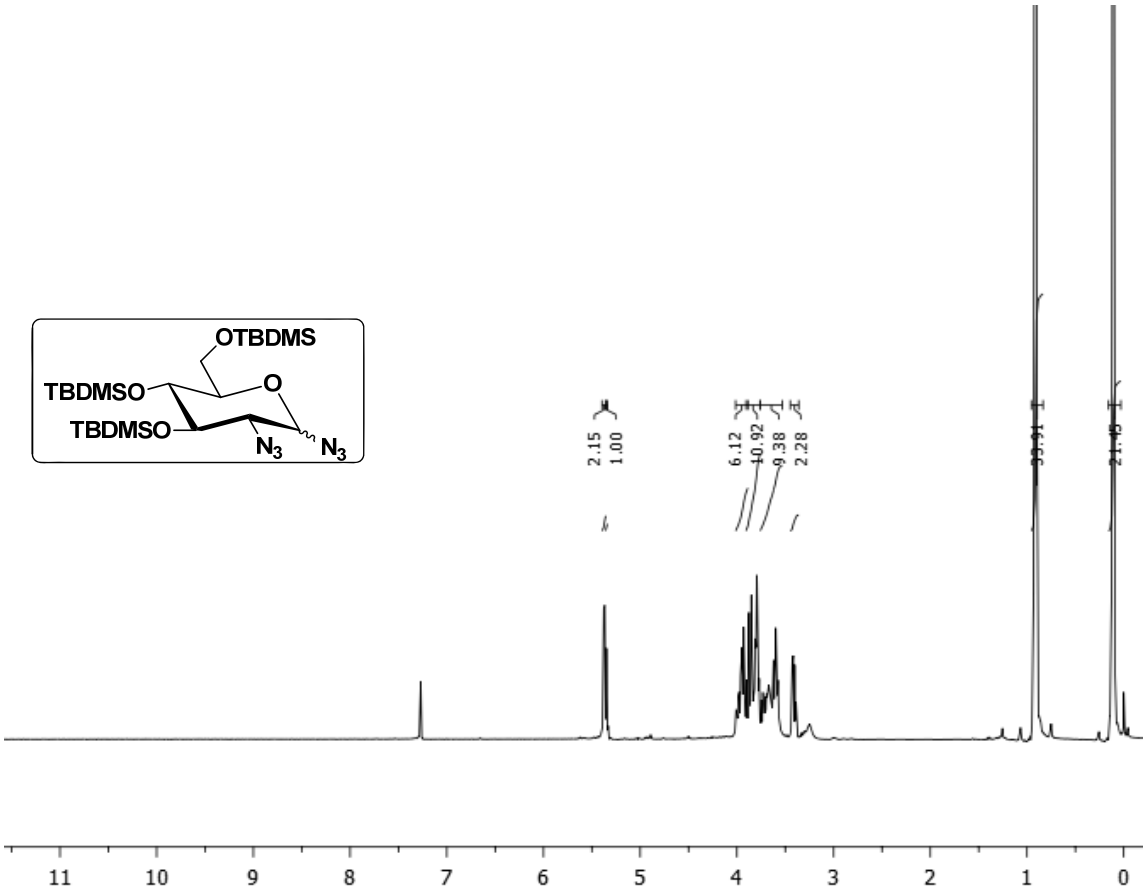
^{13}C NMR spectrum of compound **9d**



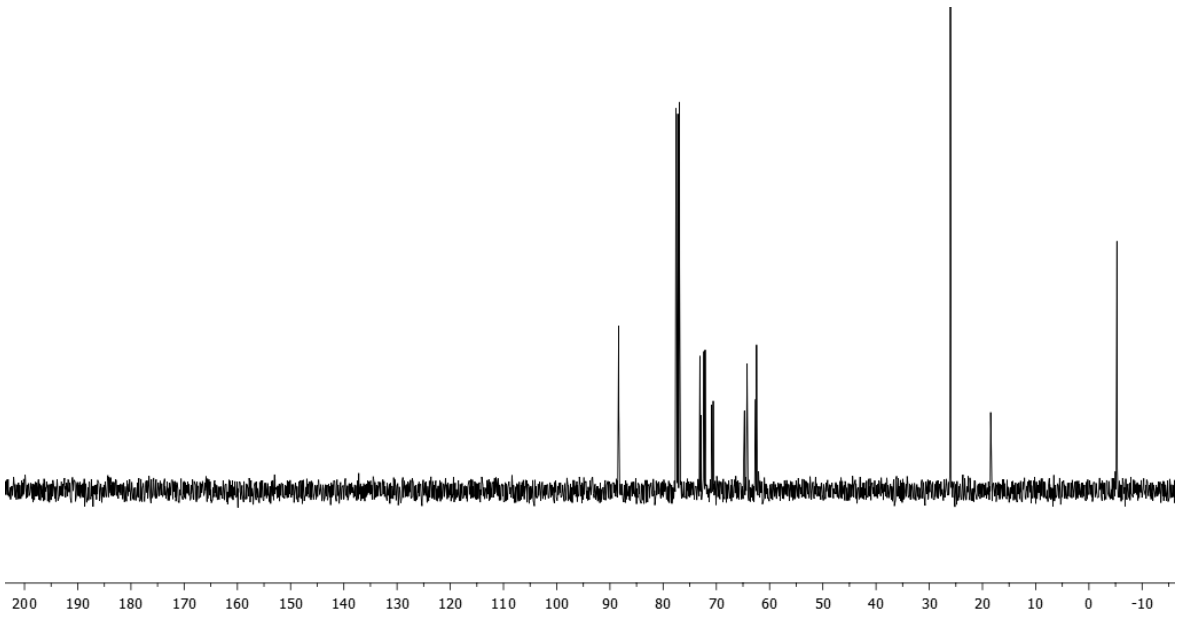
^{1}H NMR spectrum of compound **9e**



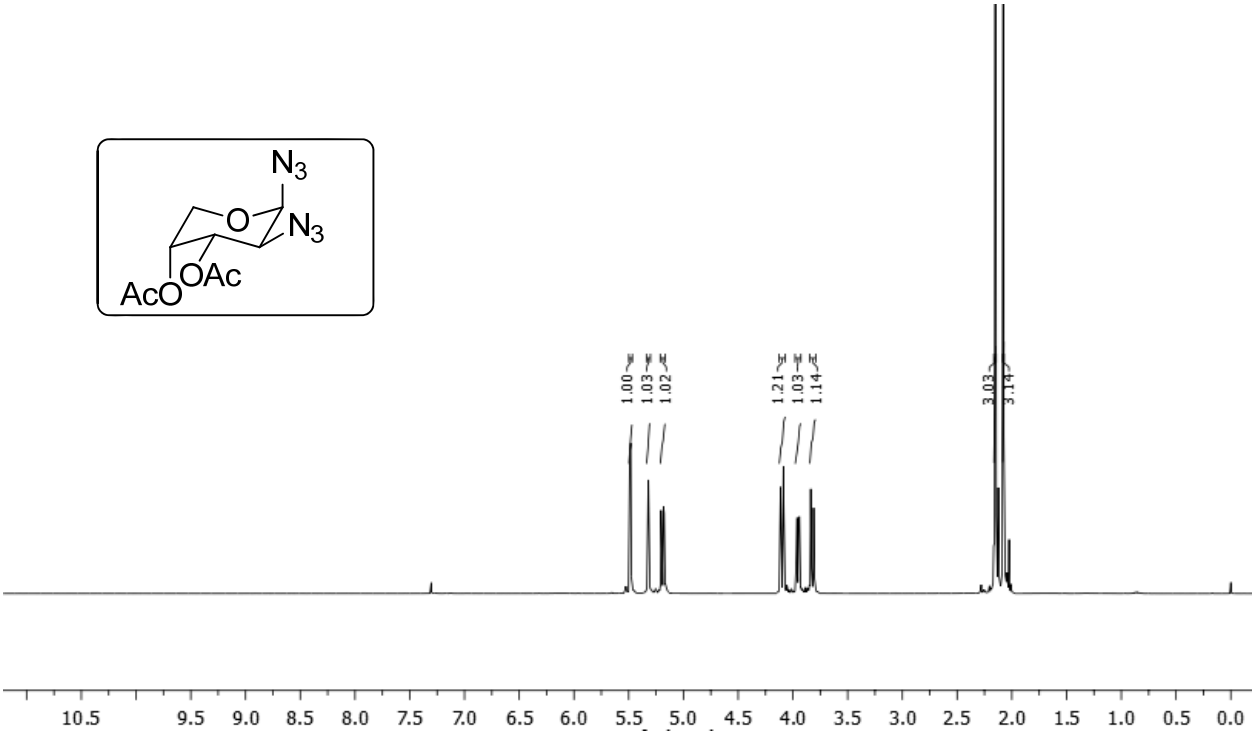
^{13}C NMR spectrum of compound **9e**



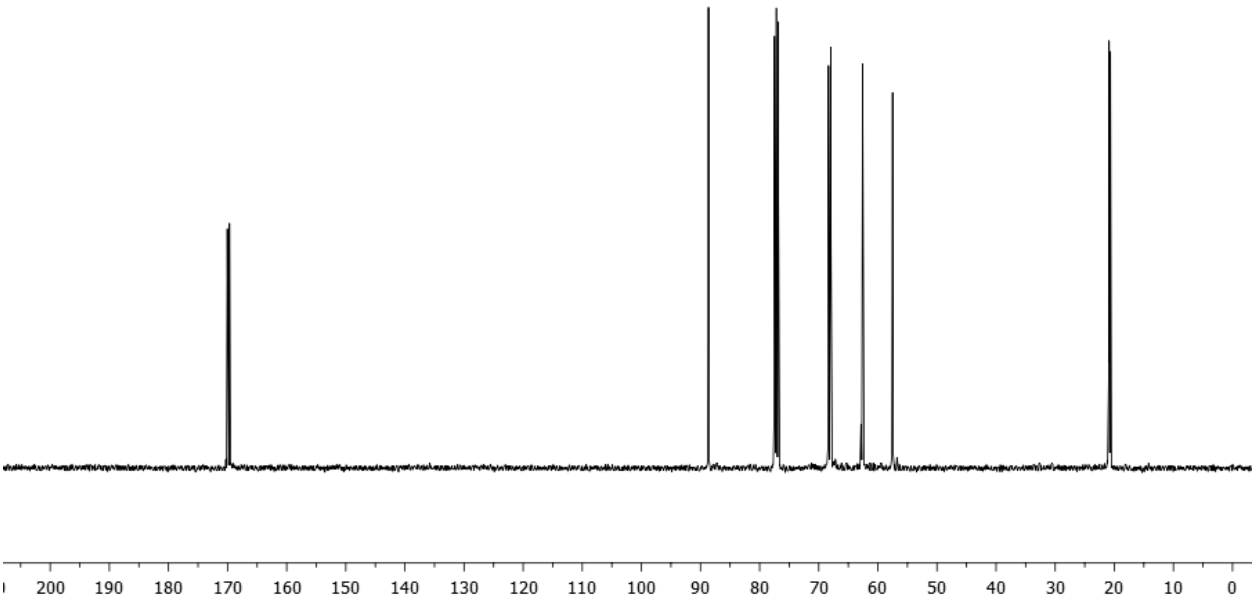
^{1}H NMR spectrum of compound **9f**



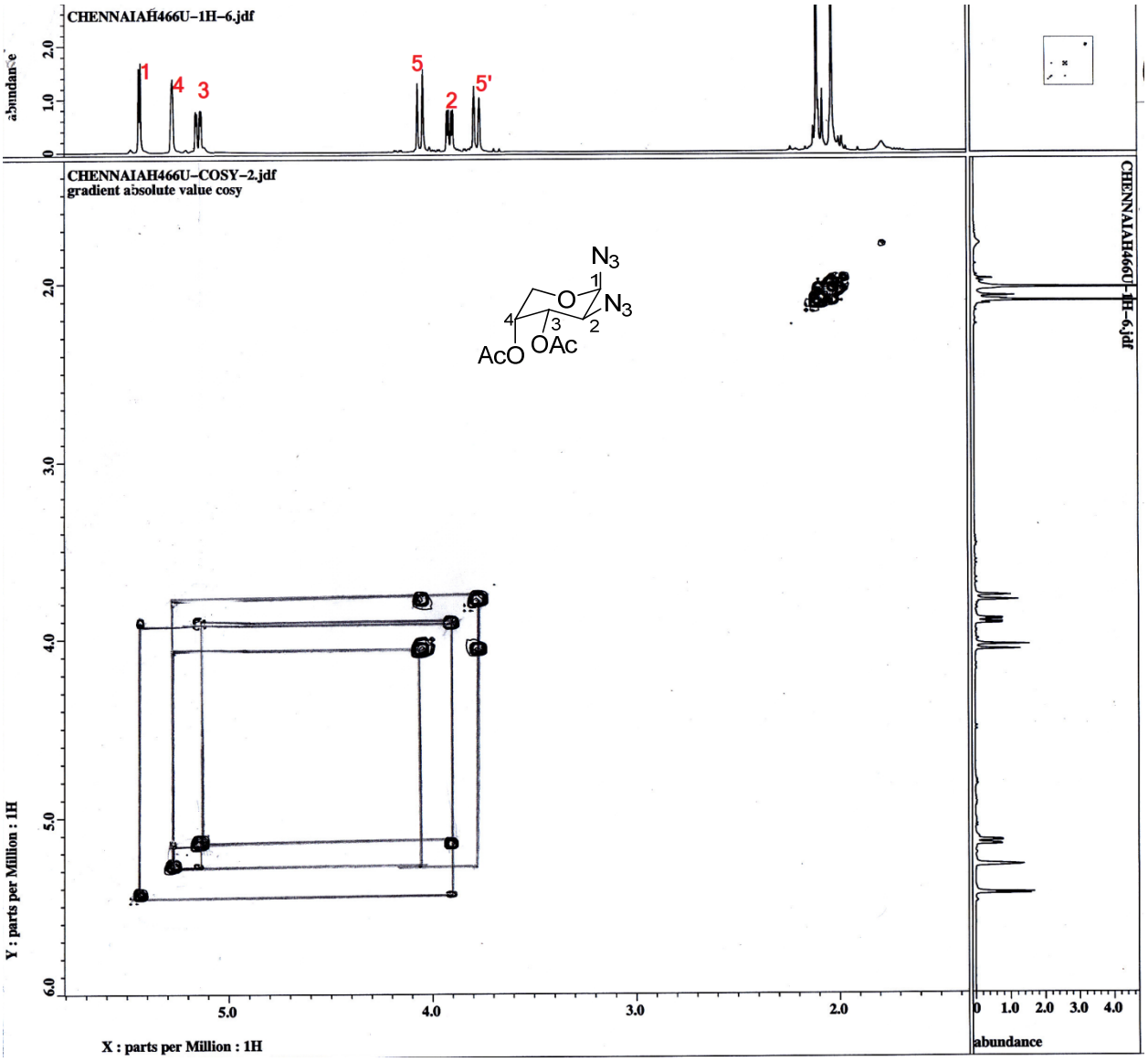
^{13}C NMR spectrum of compound **9f**



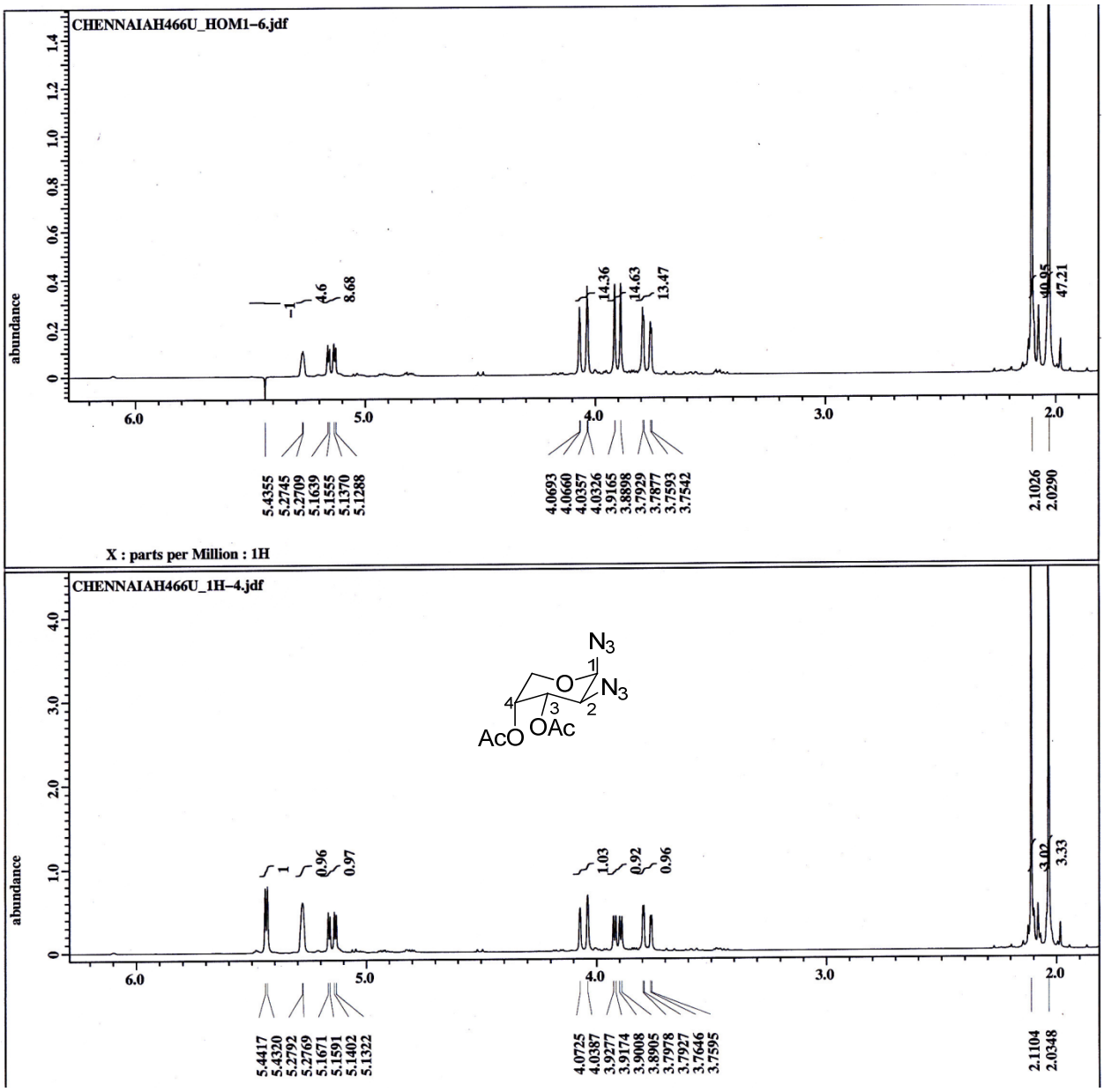
^{1}H NMR spectrum of compound **11a**



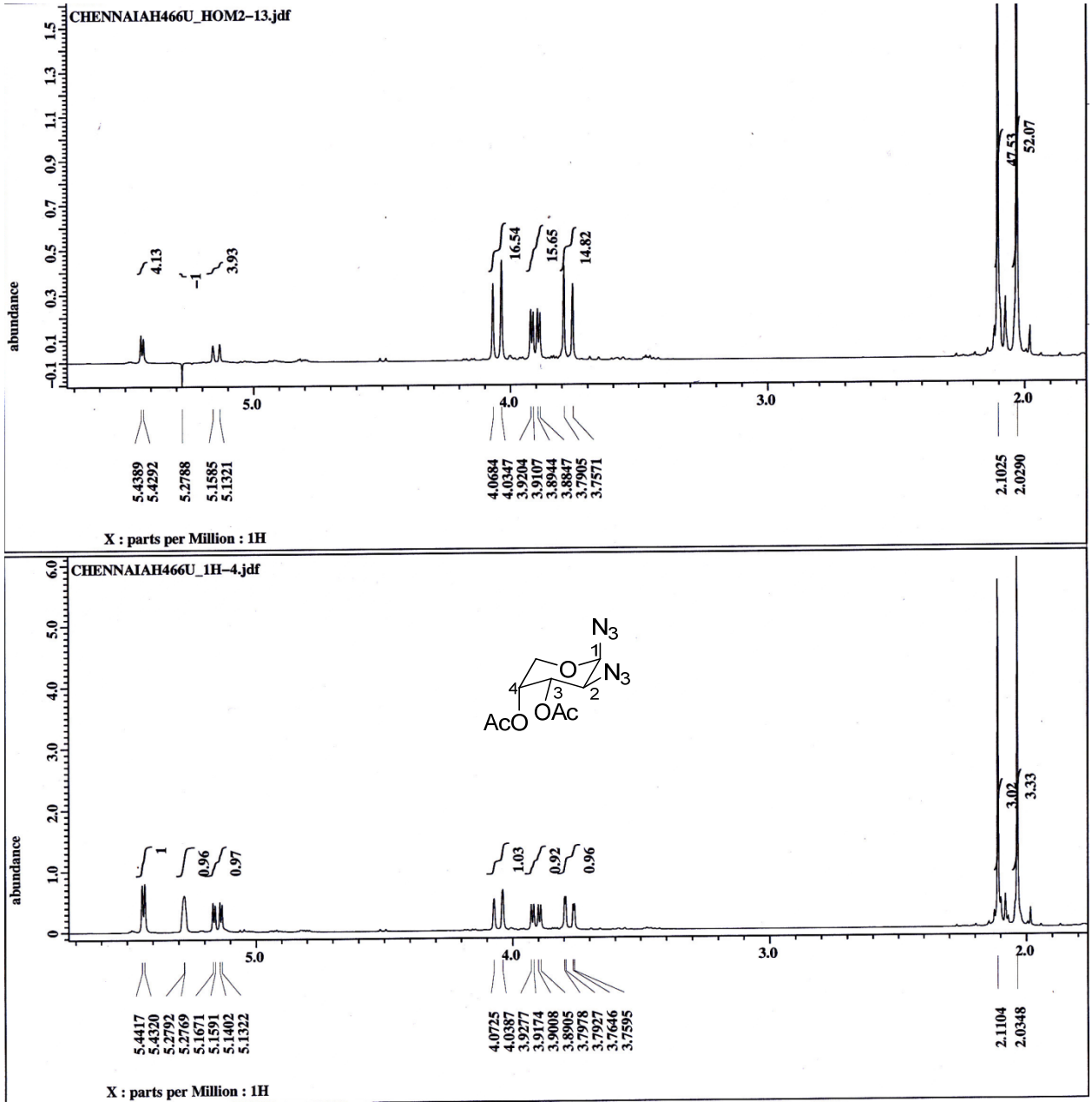
^{13}C NMR spectrum of compound **11a**



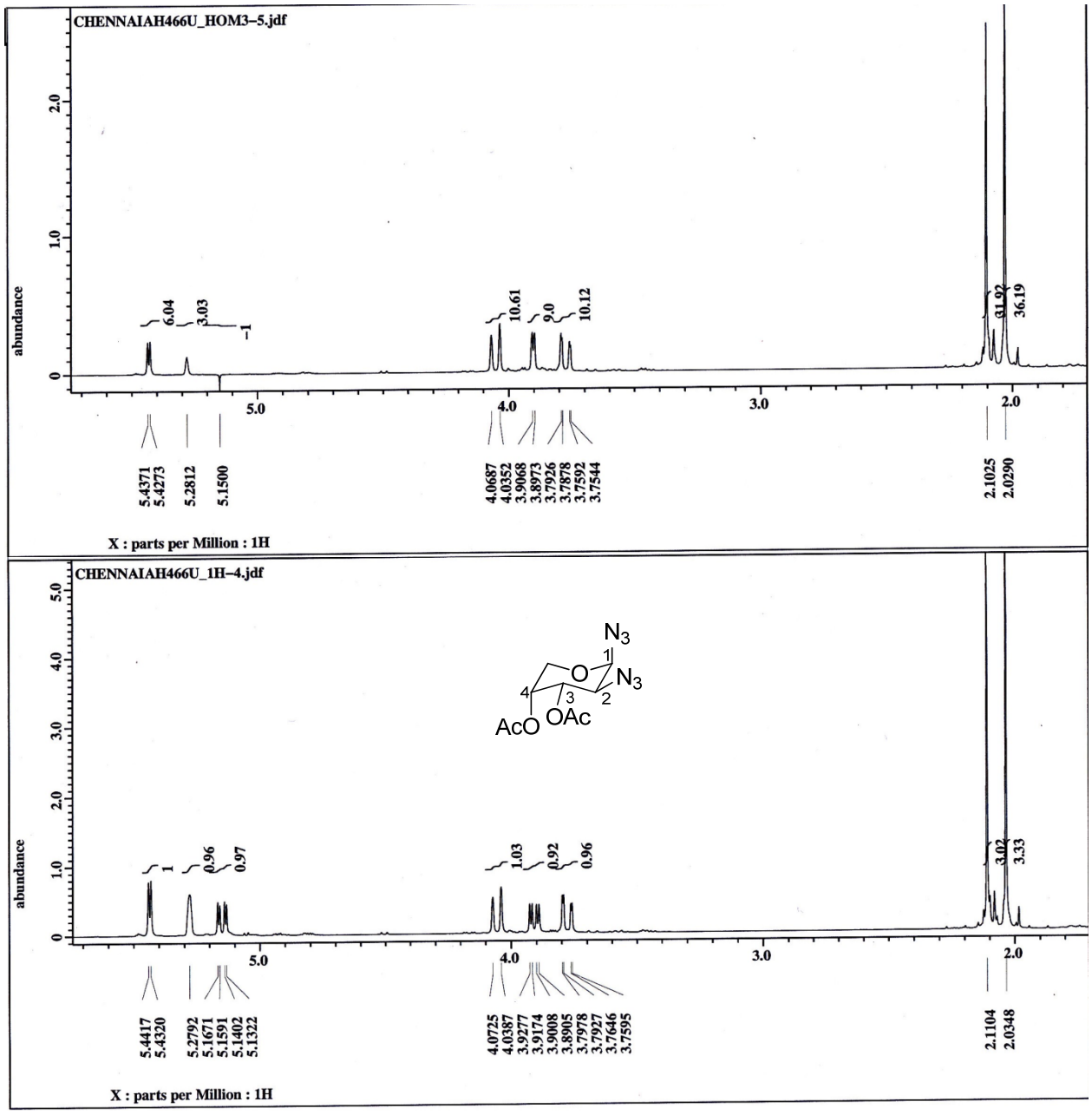
^{1}H-^{1}H COSY NMR spectrum of compound **11a**



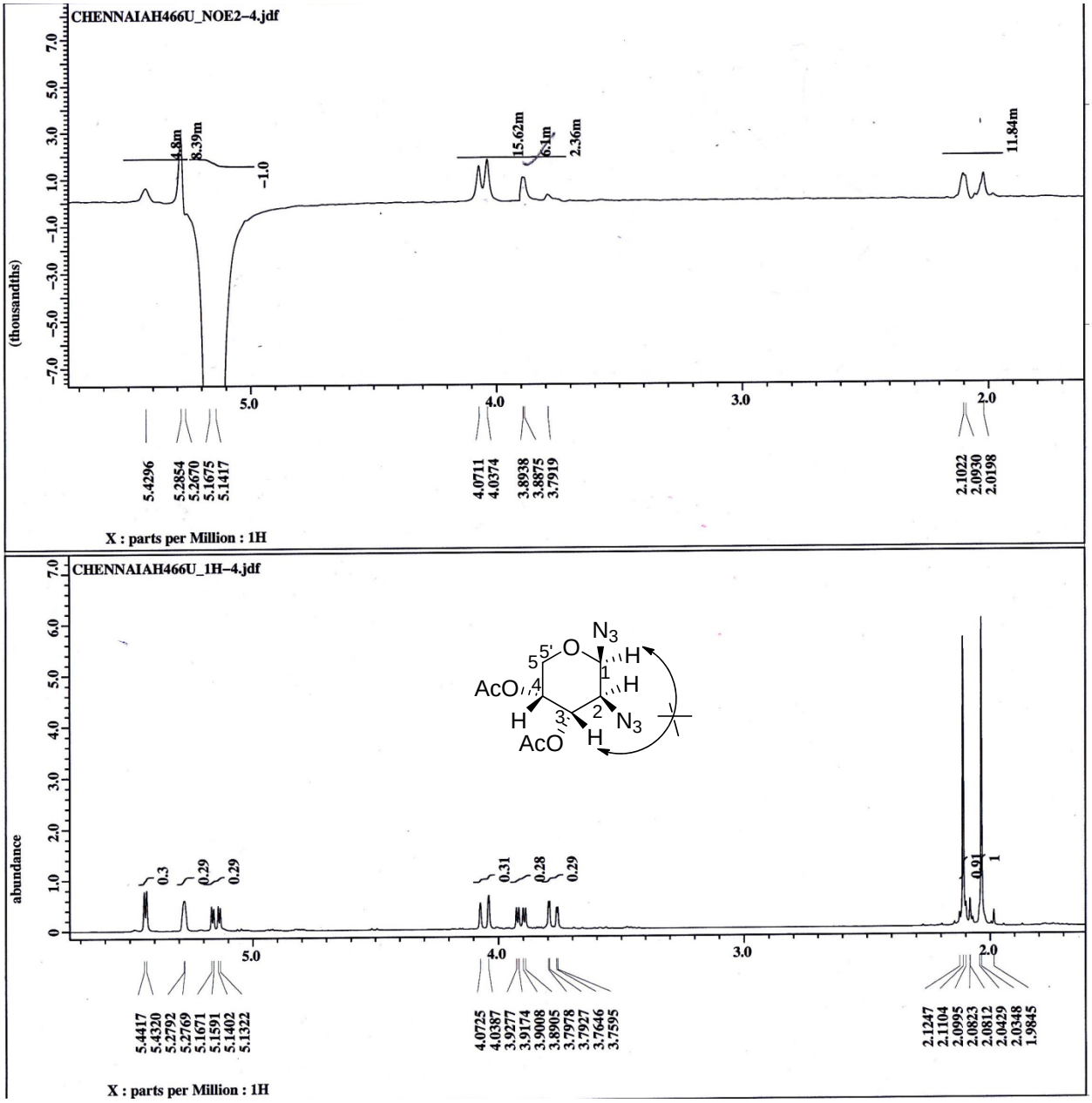
^{1}H-^{1}H homonuclear decoupling (H-1) NMR spectrum of compound **11a**



^{1}H-^{1}H homonuclear decoupling (H-4) NMR spectrum of compound **11a**

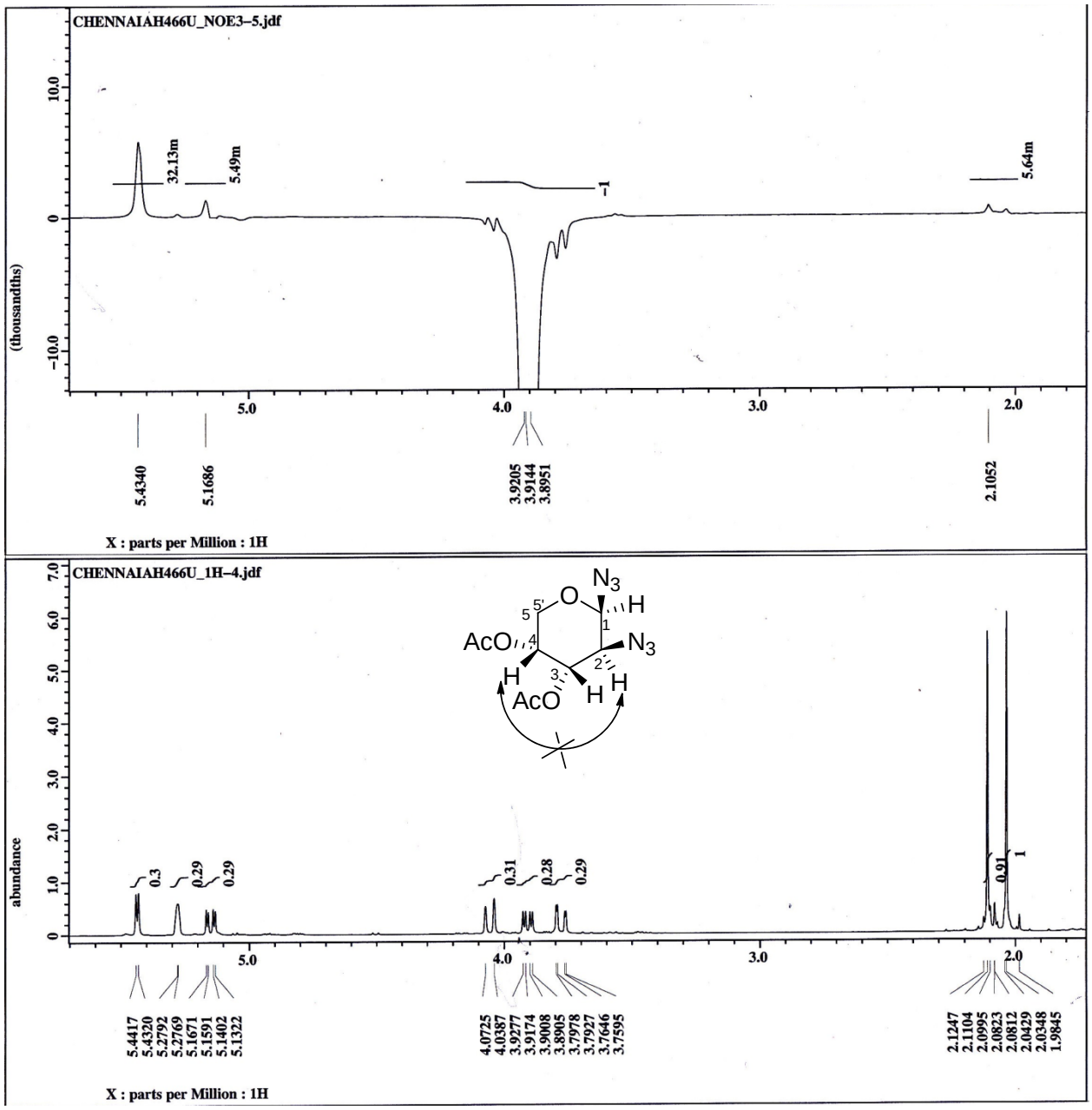


^{1}H-^{1}H homonuclear decoupling (H-3) NMR spectrum of compound **11a**



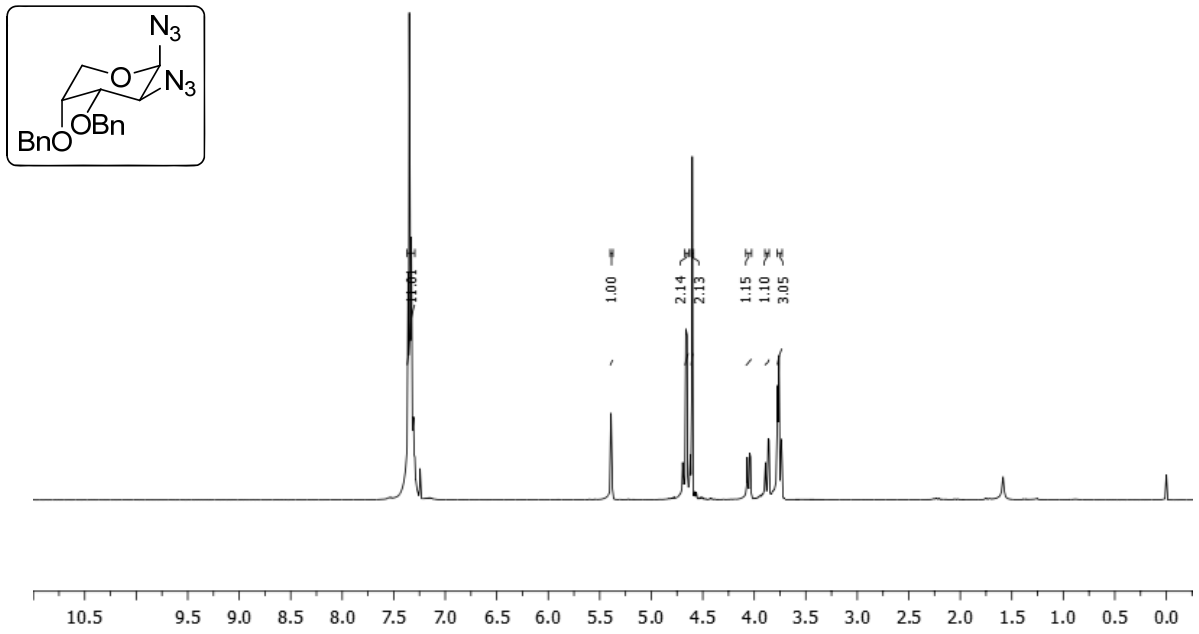
nOe spectrum (irradiation of H-3) of compound **11a**

(Upon irradiation of proton H-3, no enhancement was observed for the signal of proton H-1)

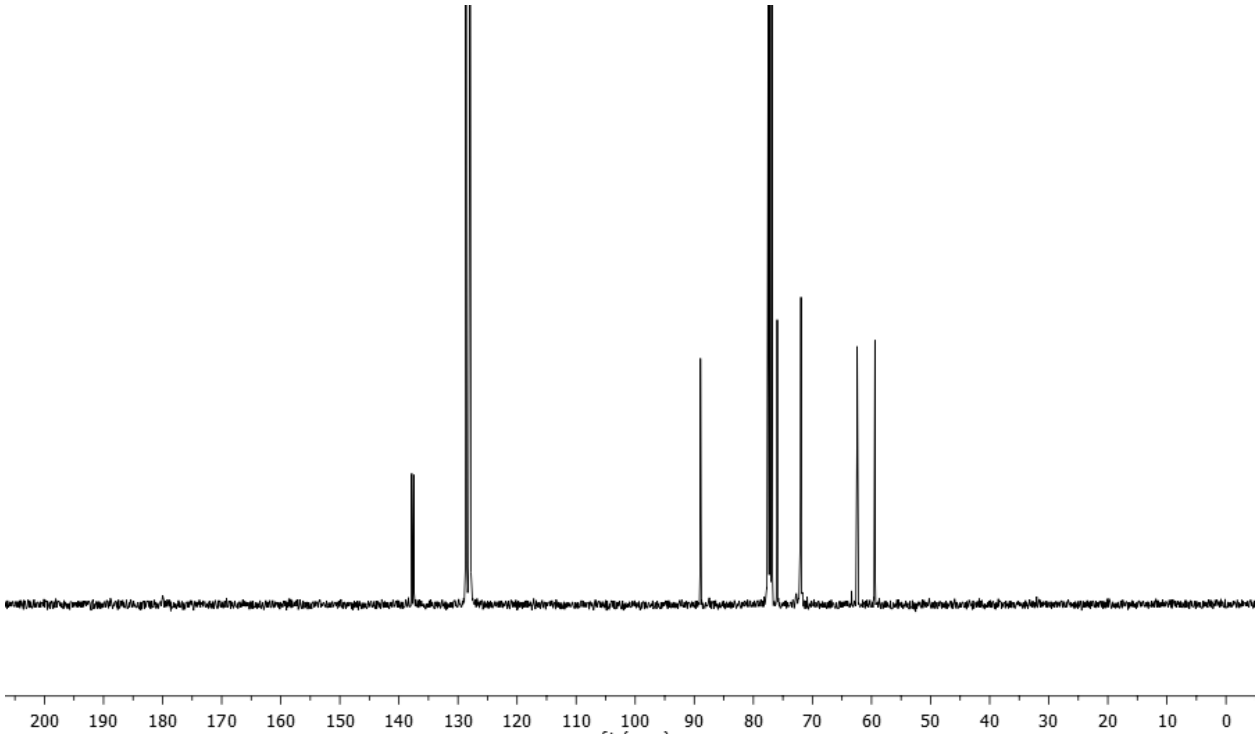


nOe spectrum (irradiation of H-2) of compound **11a**

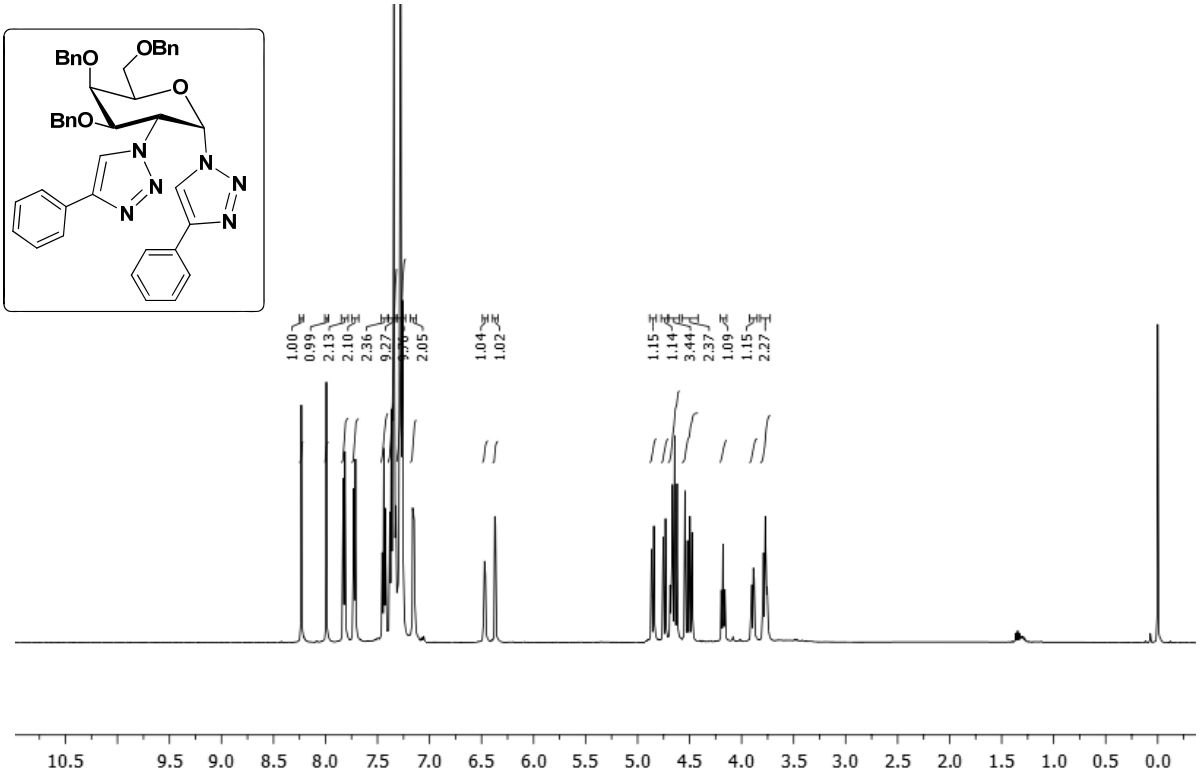
(Upon irradiation of proton H-2, no enhancement was observed for the signal of proton H-4, indicating that H-2 and H-4 are trans oriented)



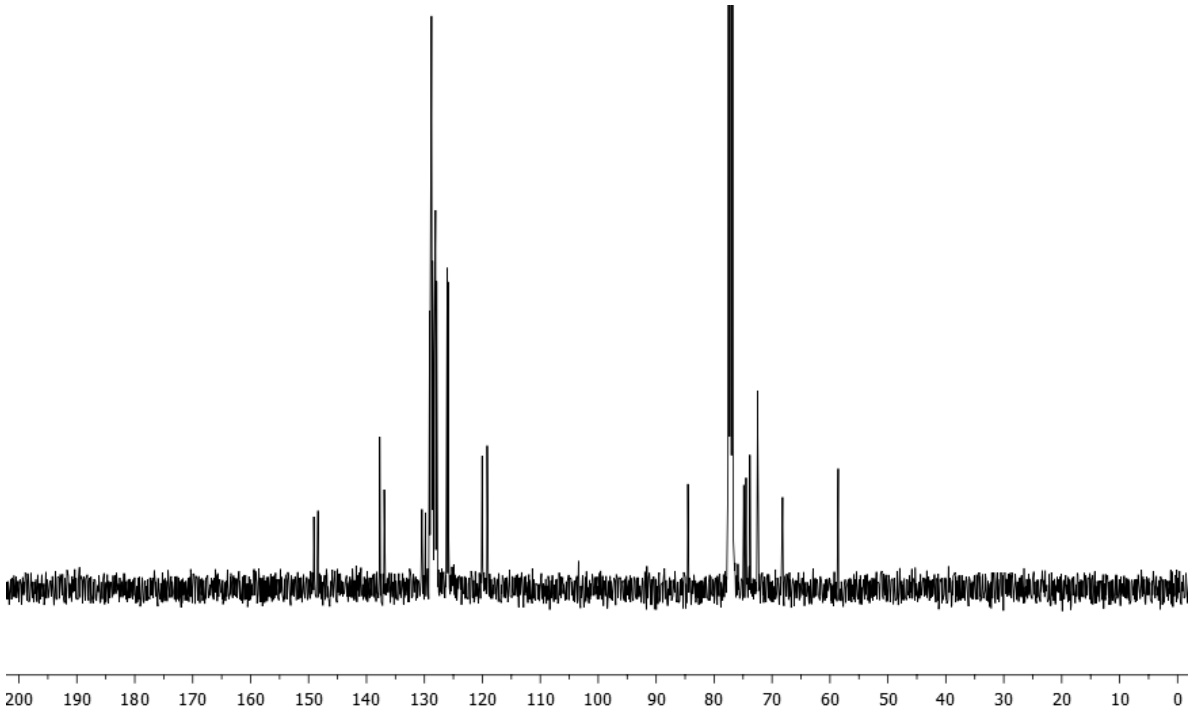
^{1}H NMR spectrum of compound **11b**



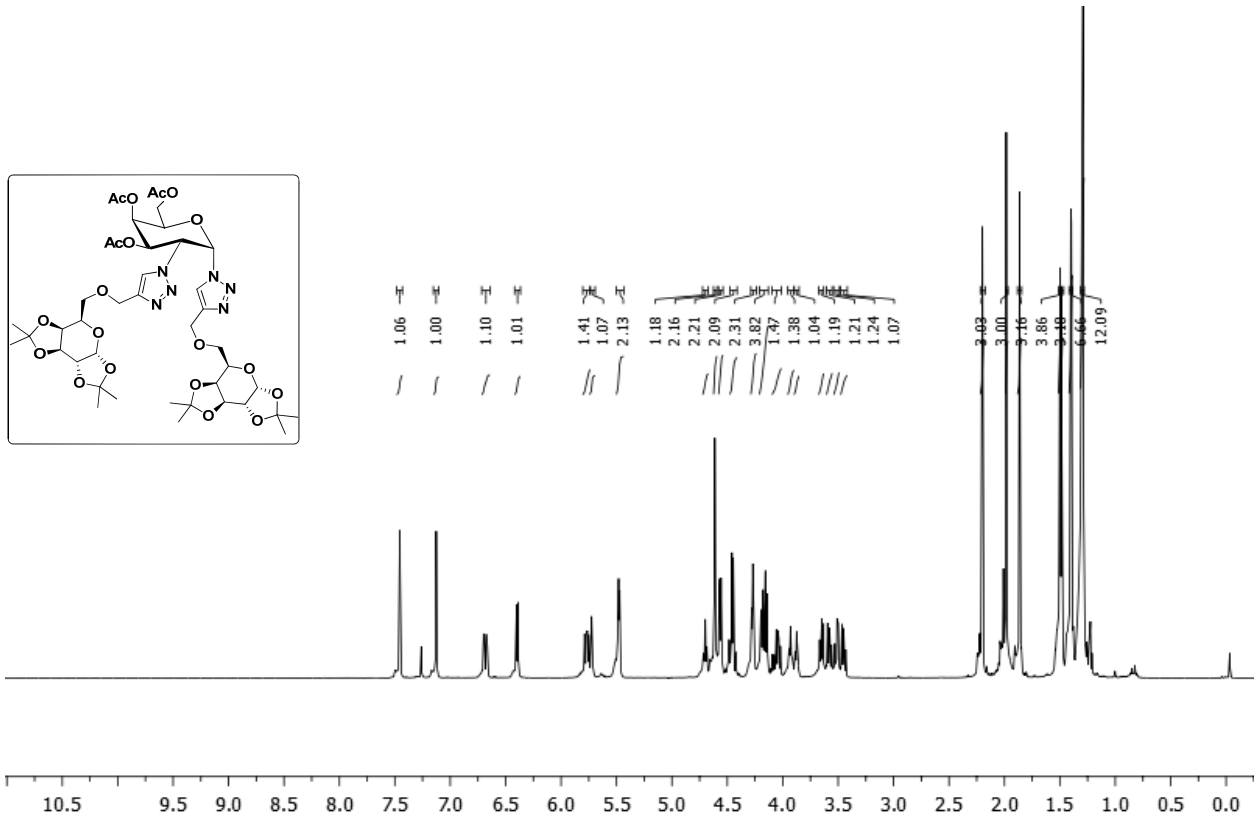
^{13}C NMR spectrum of compound **11b**



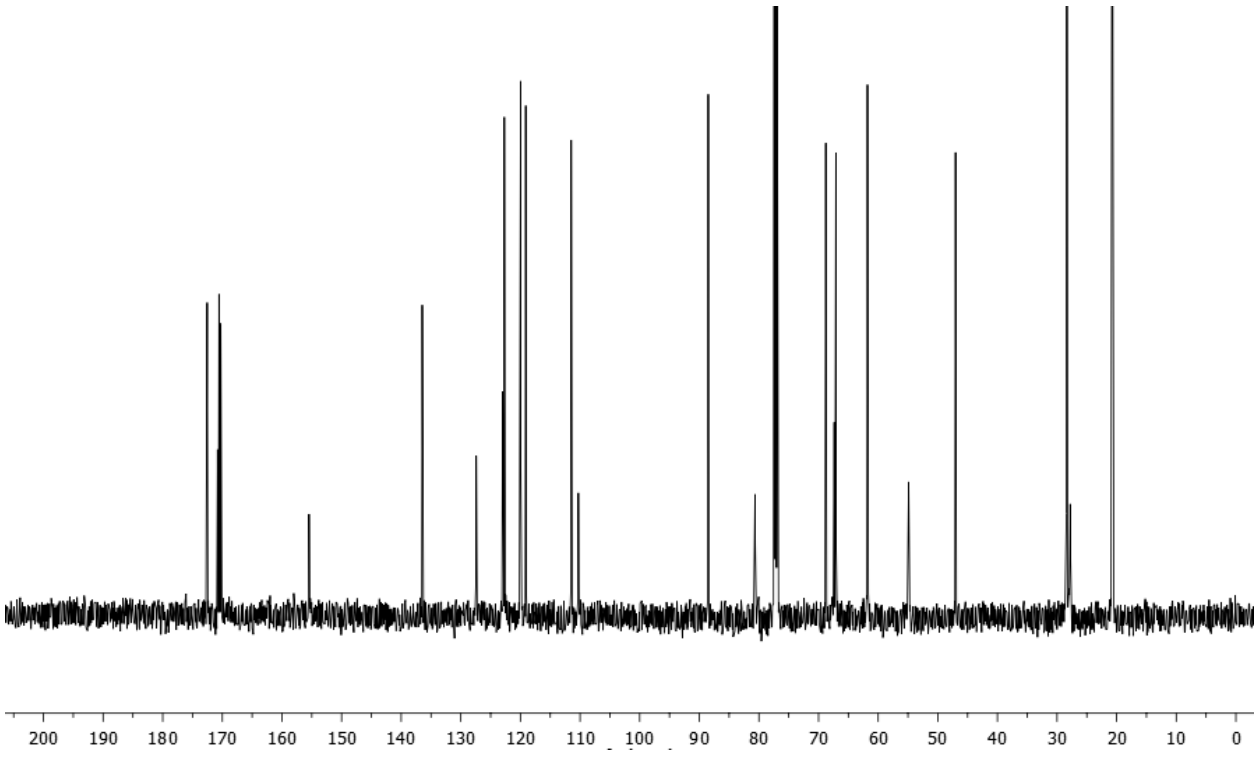
^{1}H NMR spectrum of compound **13**



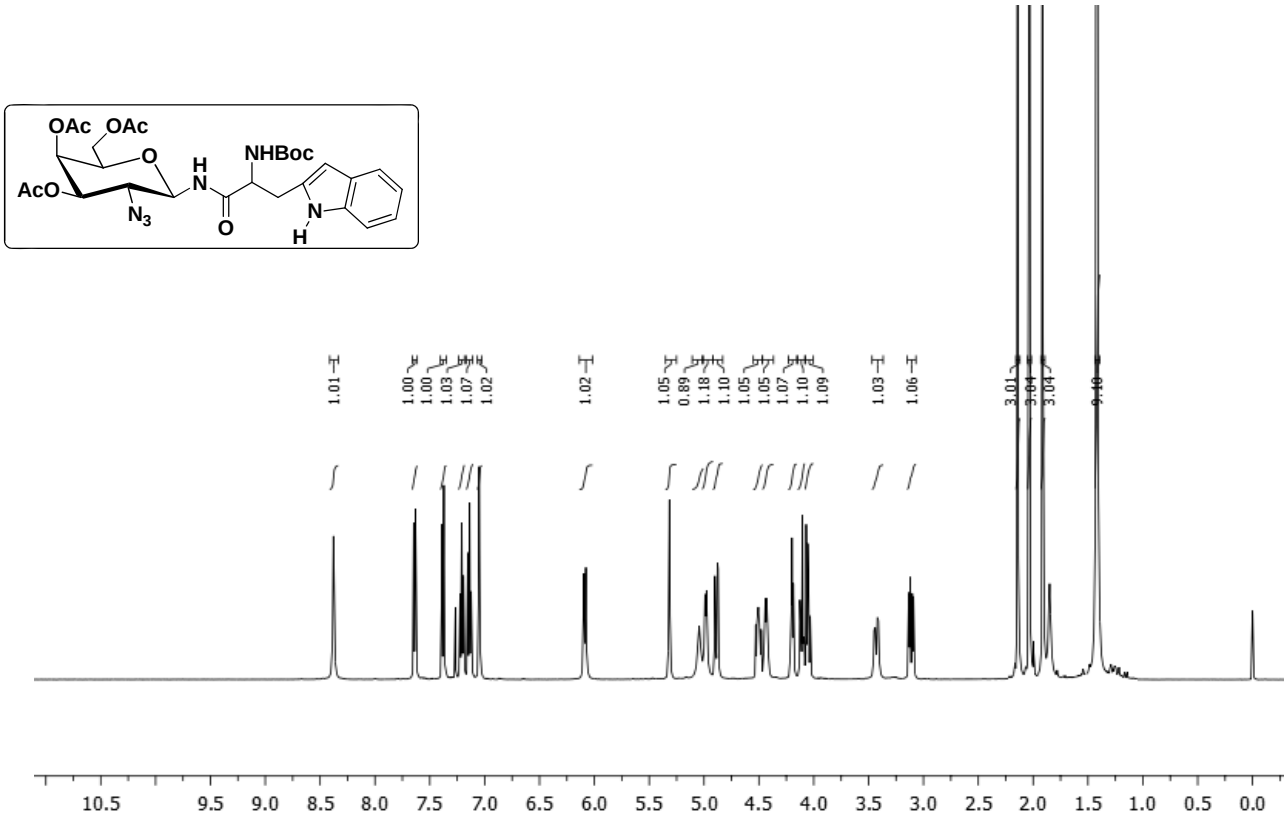
^{13}C NMR spectrum of compound **13**



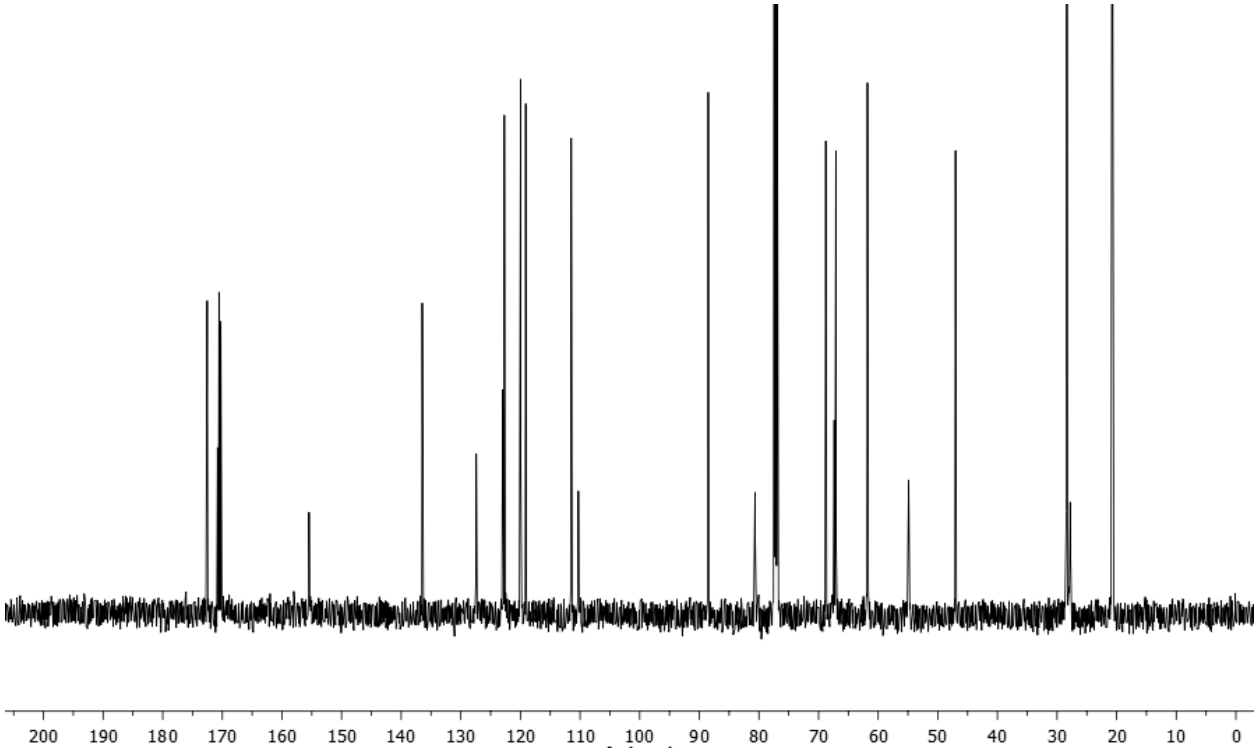
^{1}H NMR spectrum of compound **15**



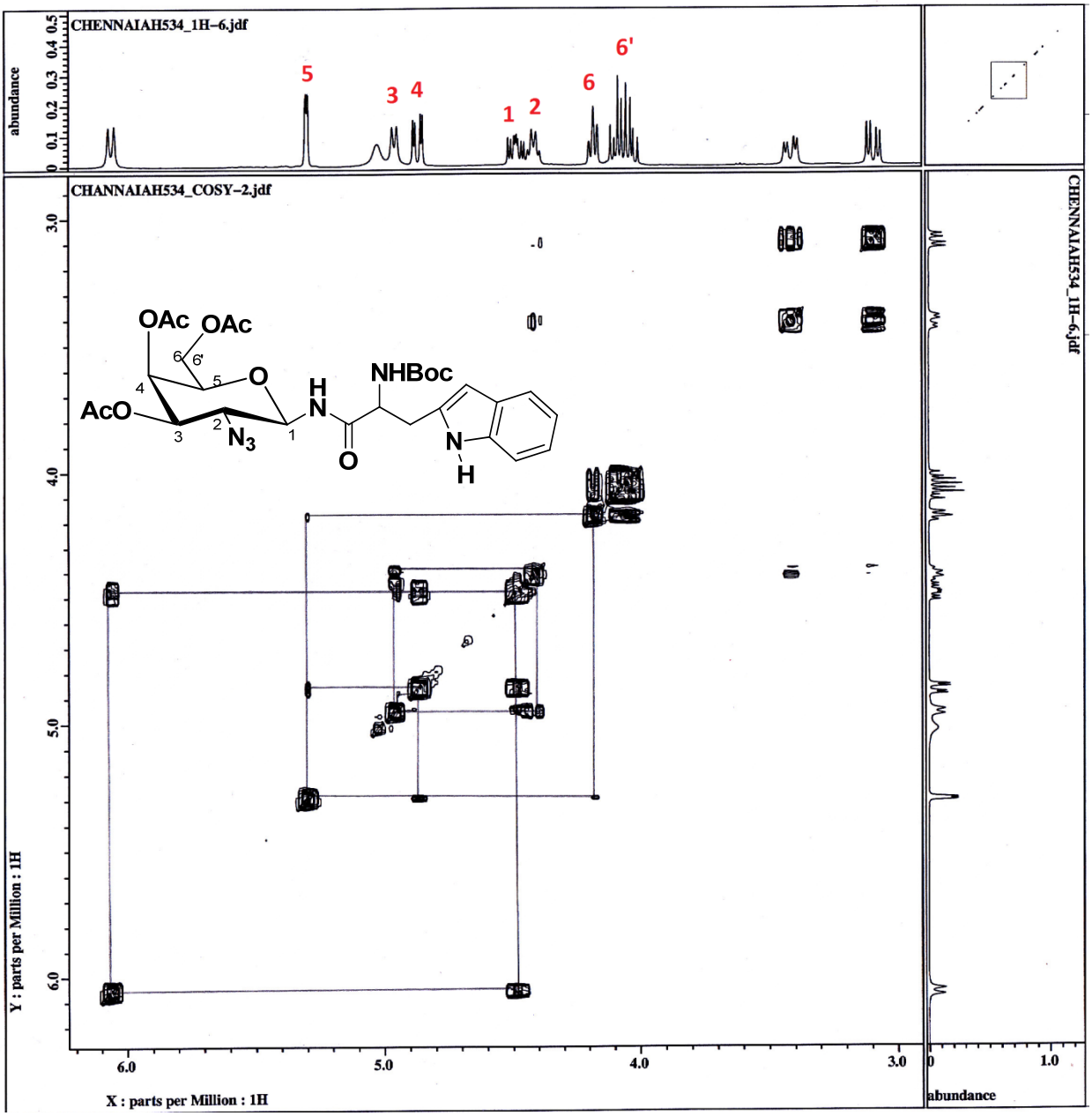
^{13}C NMR spectrum of compound **15**



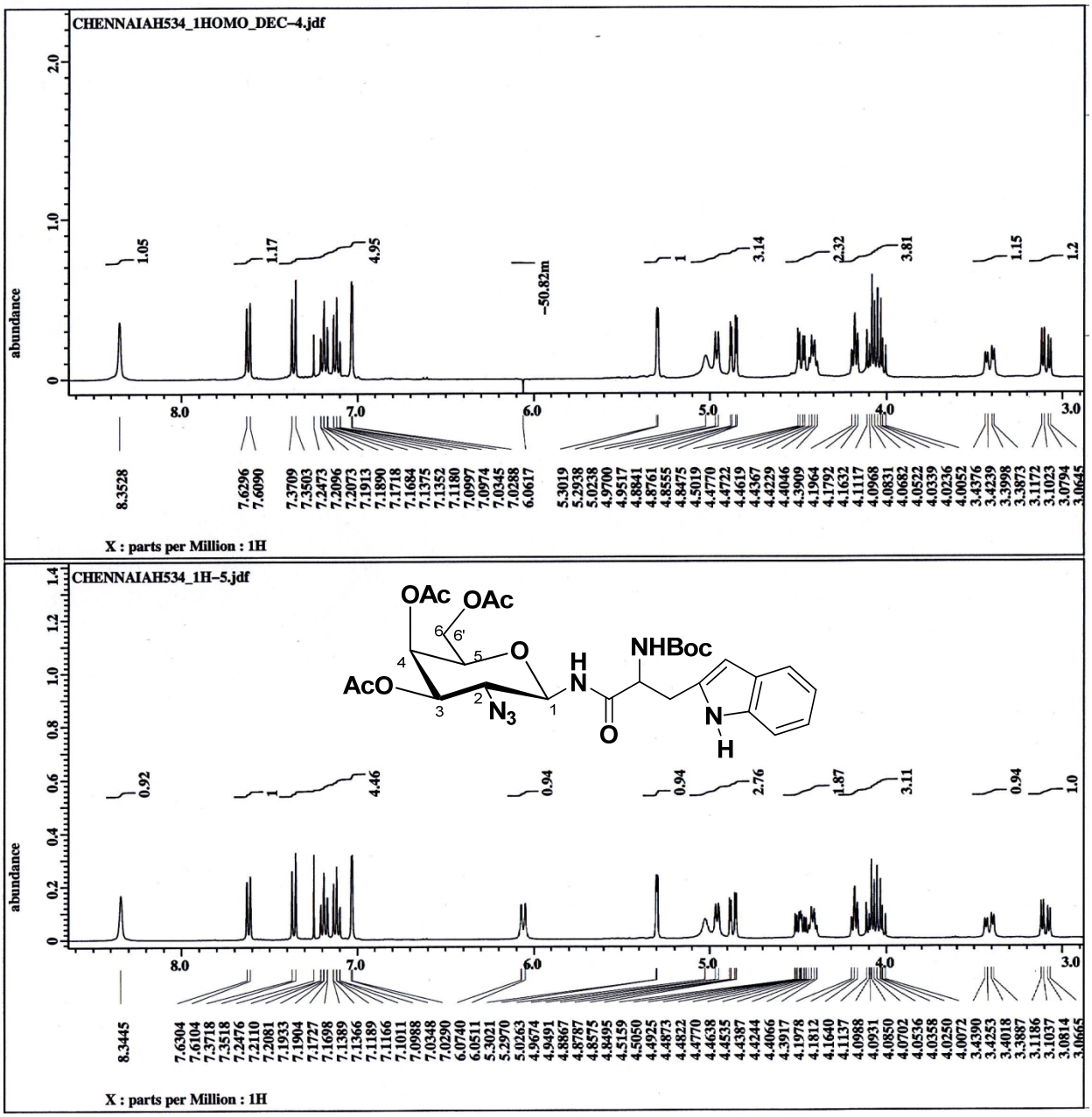
^{1}H NMR spectrum of compound **18**



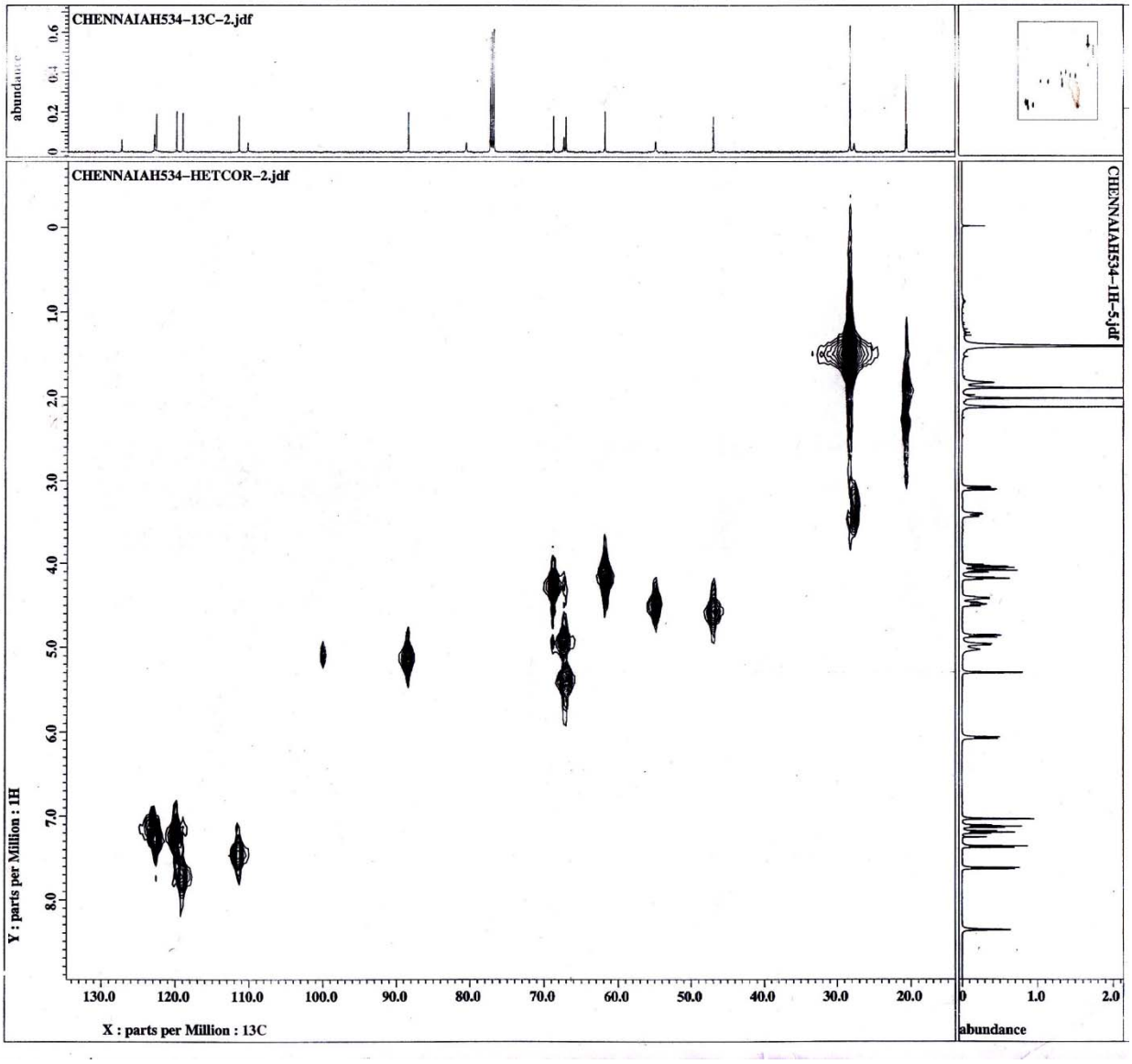
^{13}C NMR spectrum of compound **18**



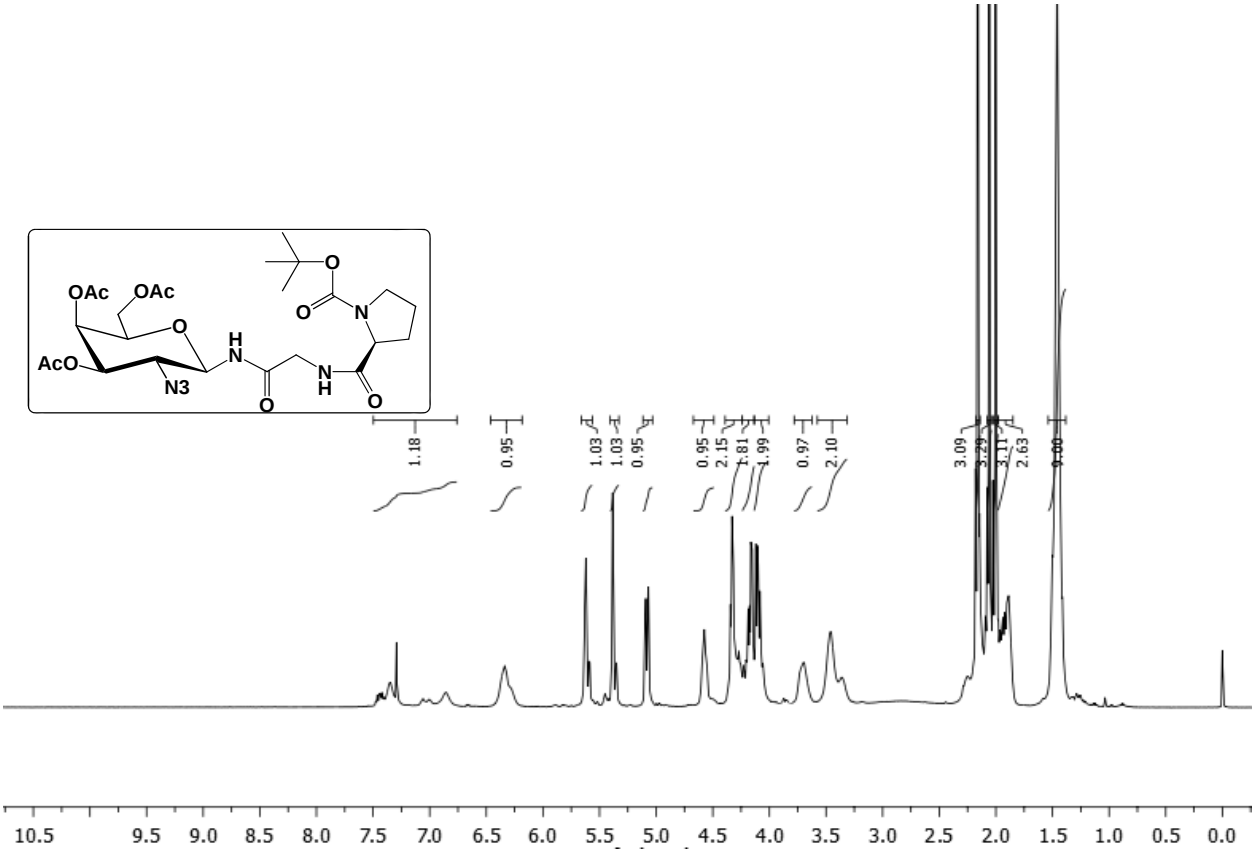
^{1}H-^{1}H COSY NMR spectrum of compound **18**



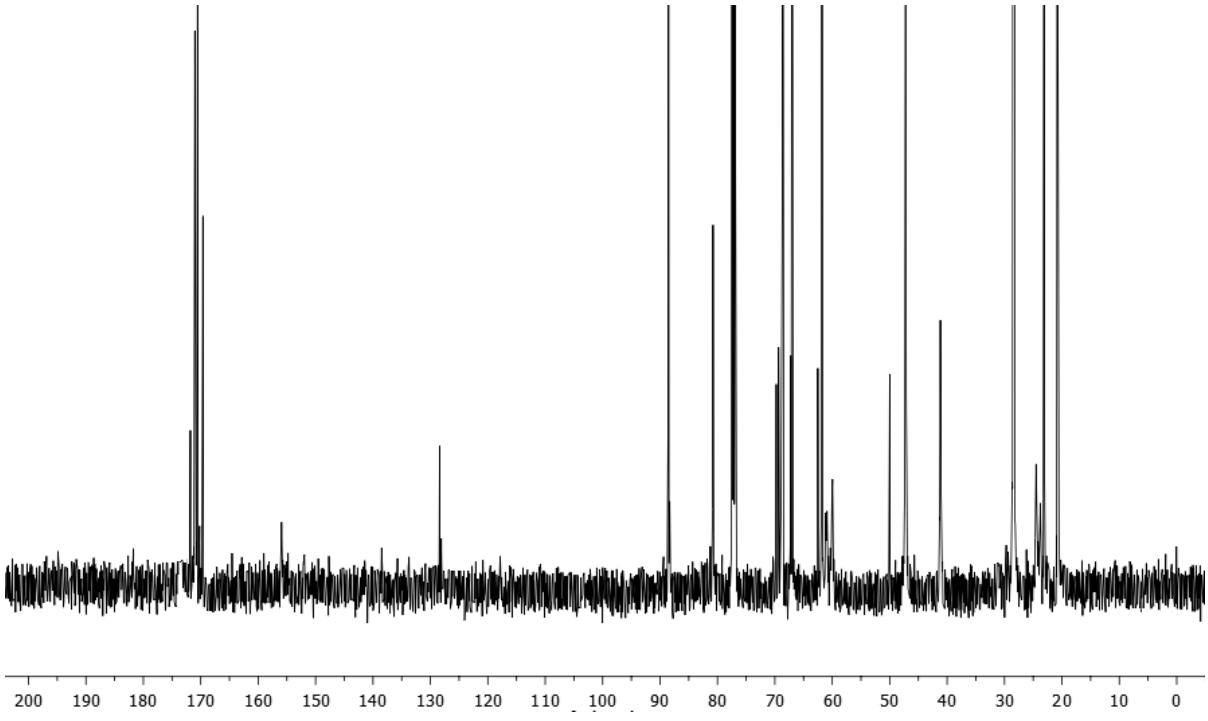
^{1}H-^{1}H homonuclear decoupling (NH) NMR spectrum of compound **18**



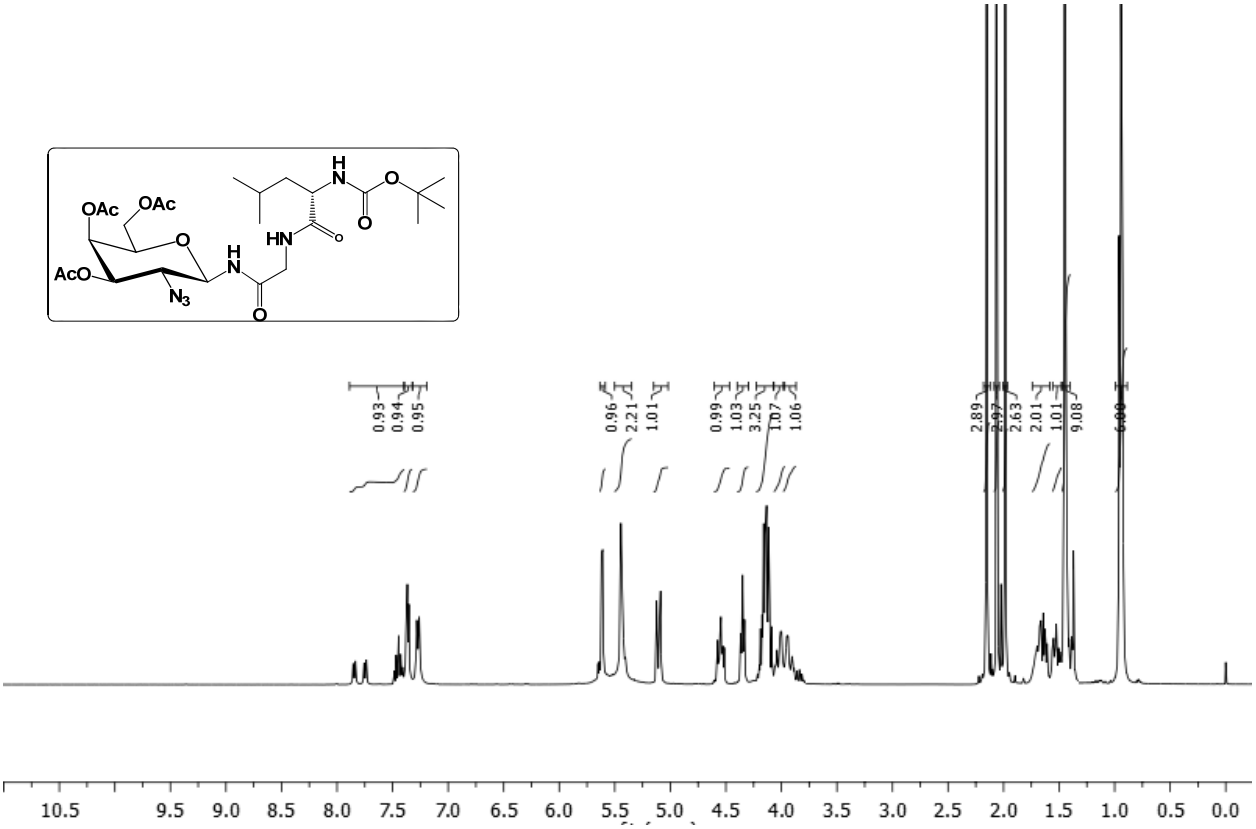
^{13}C-^{1}H HETCOR NMR spectrum of compound **18**



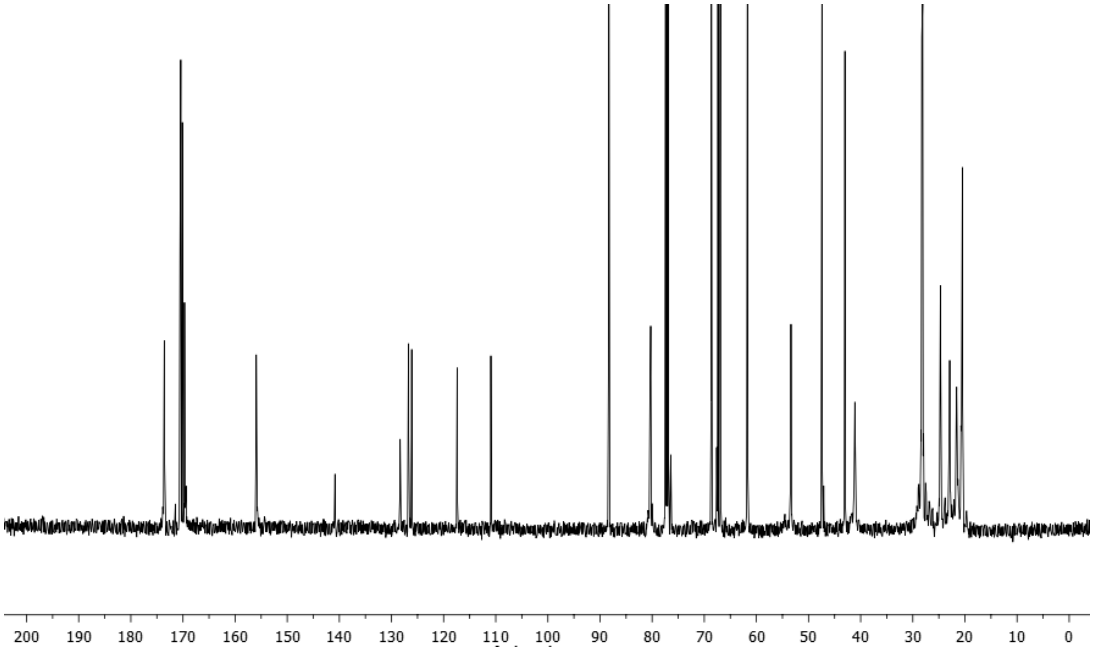
^{1}H NMR spectrum of compound **19**



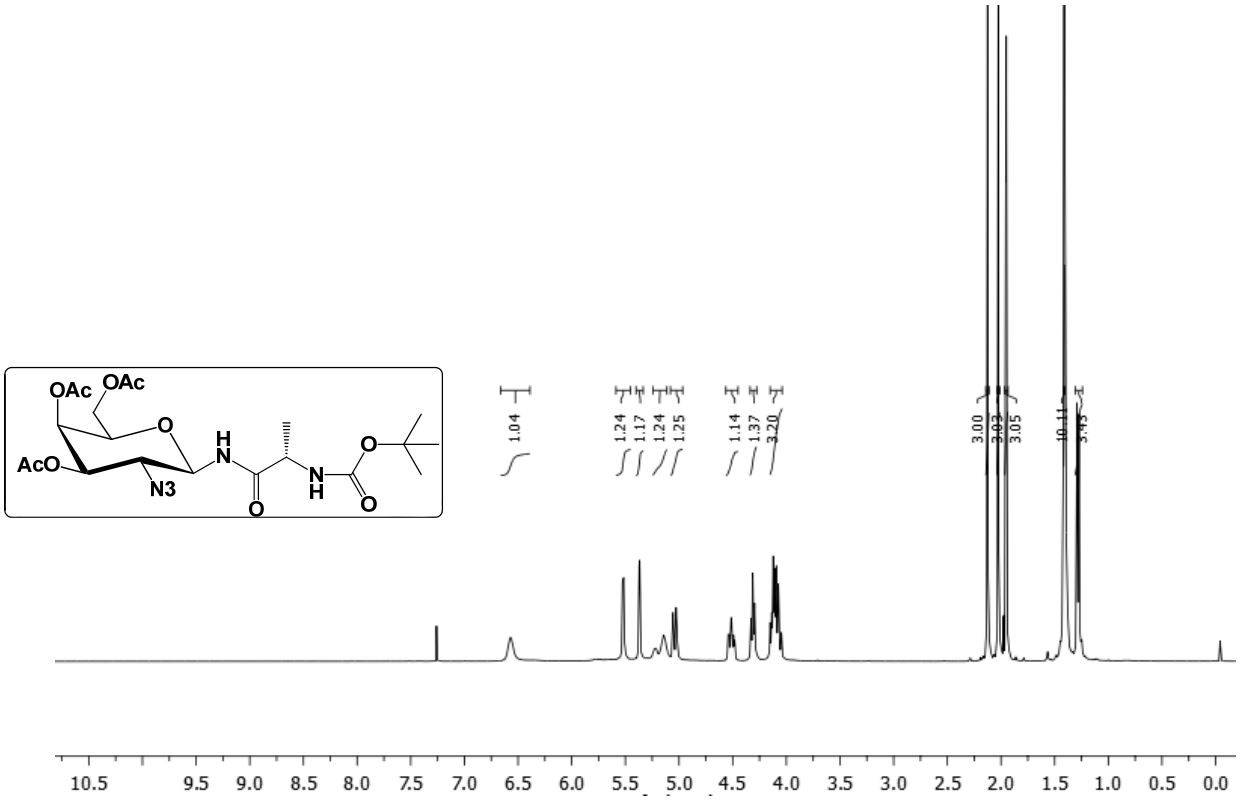
^{13}C NMR spectrum of compound **19**



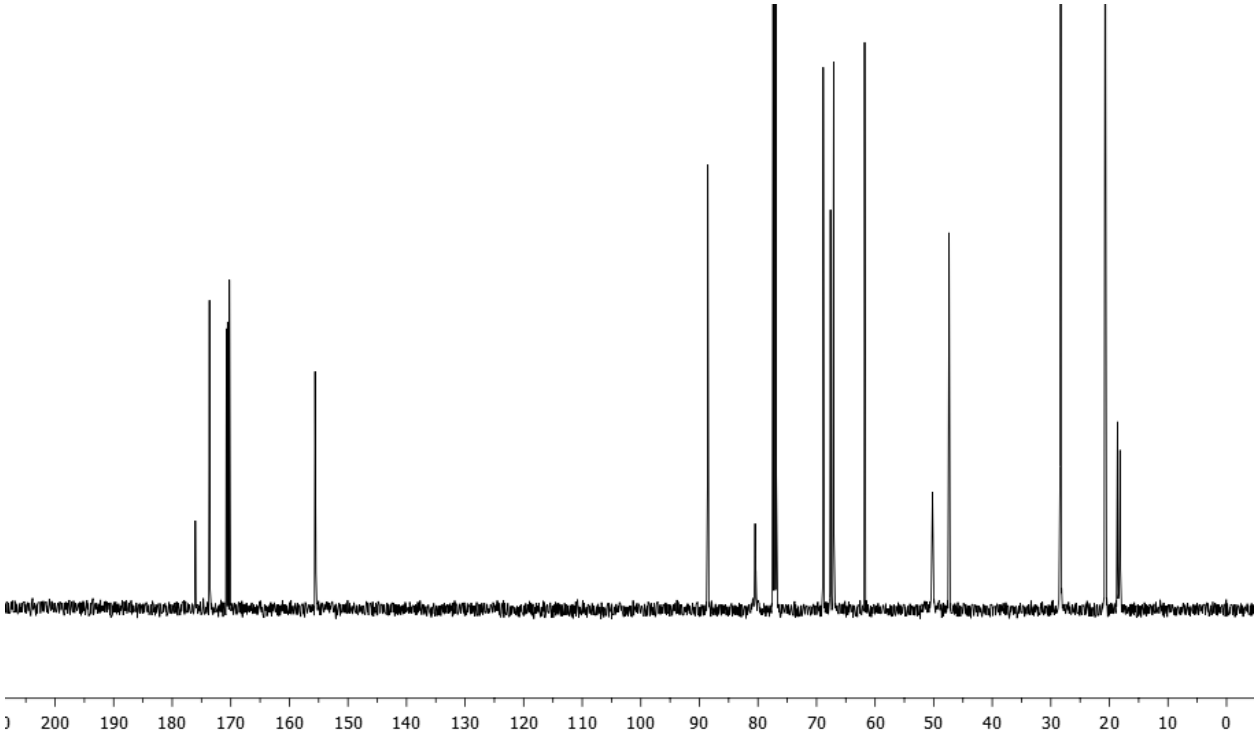
^{1}H NMR spectrum of compound **20**



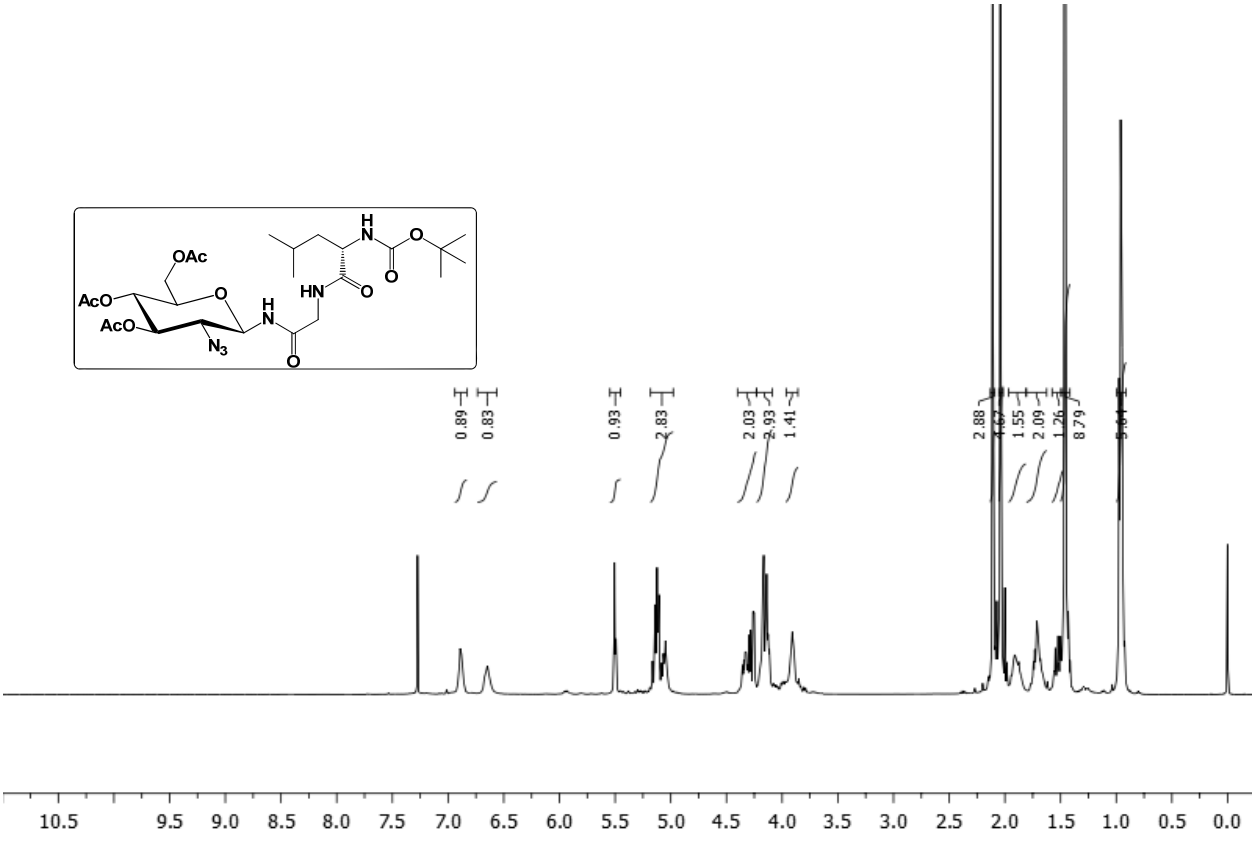
^{13}C NMR spectrum of compound **20**



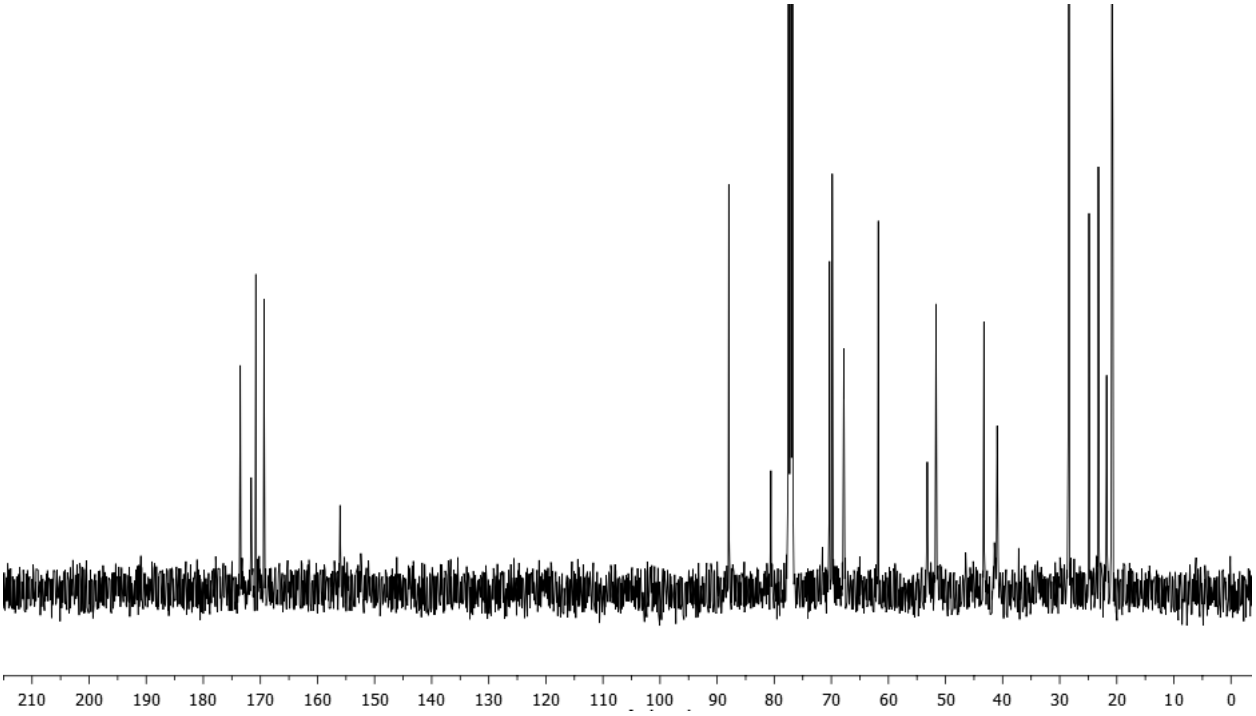
^{1}H NMR spectrum of compound **21**



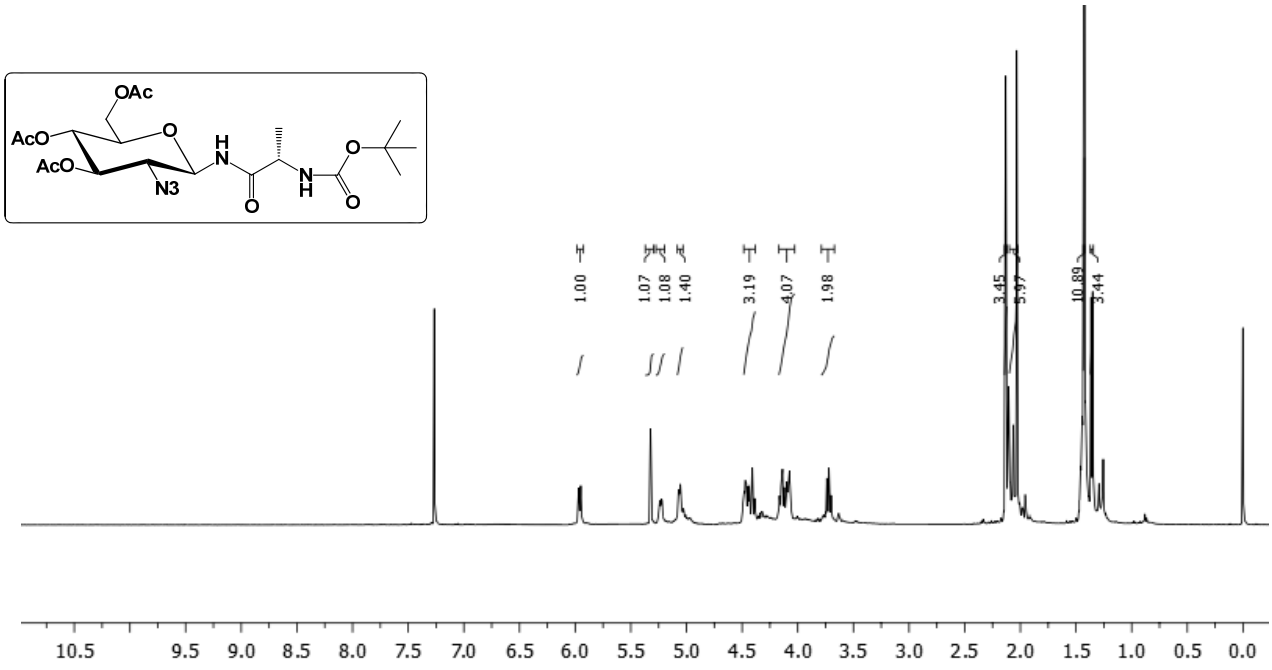
^{13}C NMR spectrum of compound **21**



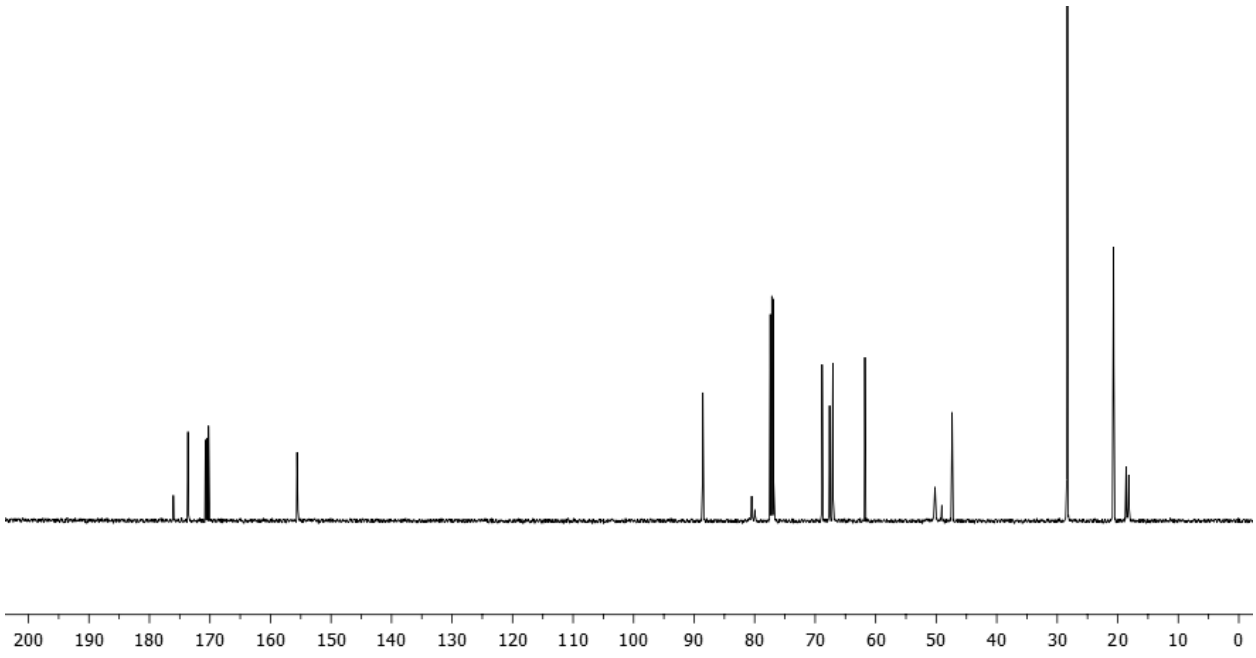
^{1}H NMR spectrum of compound **22**



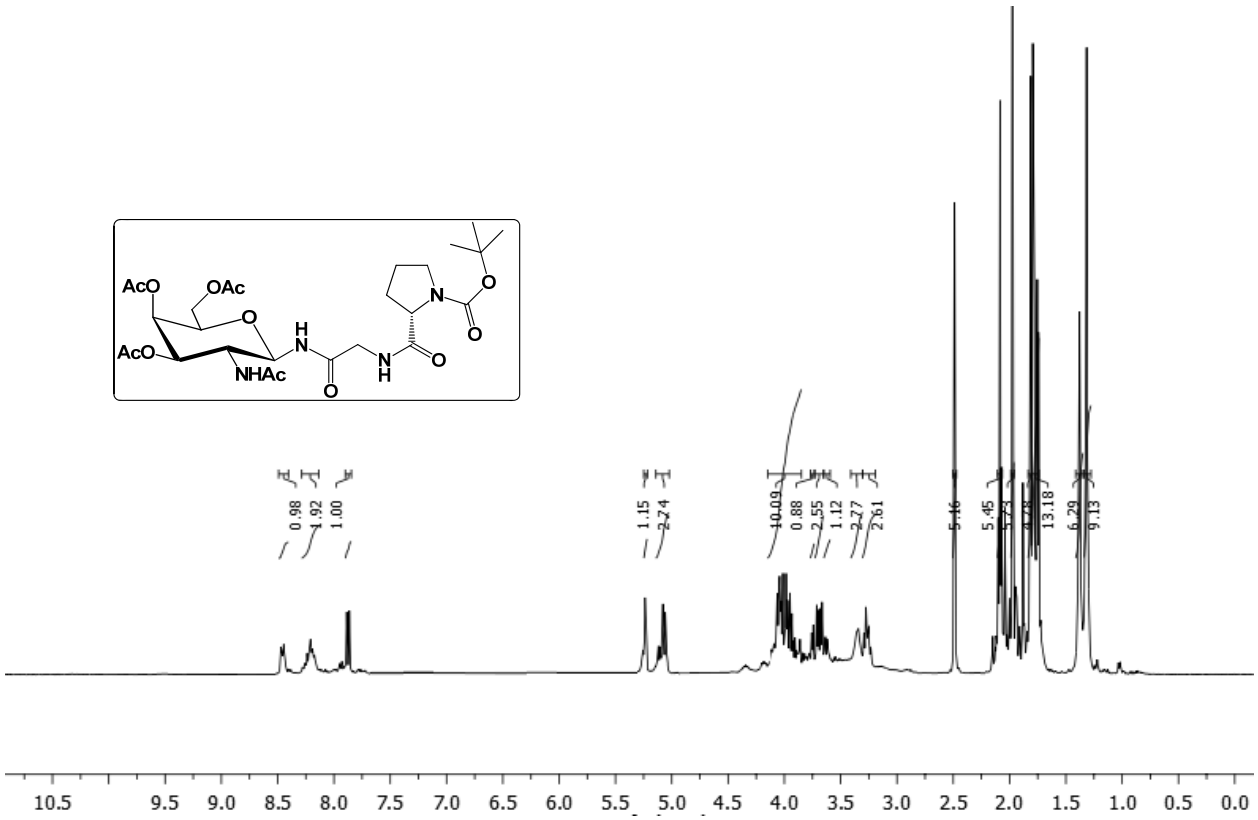
^{13}C NMR spectrum of compound **22**



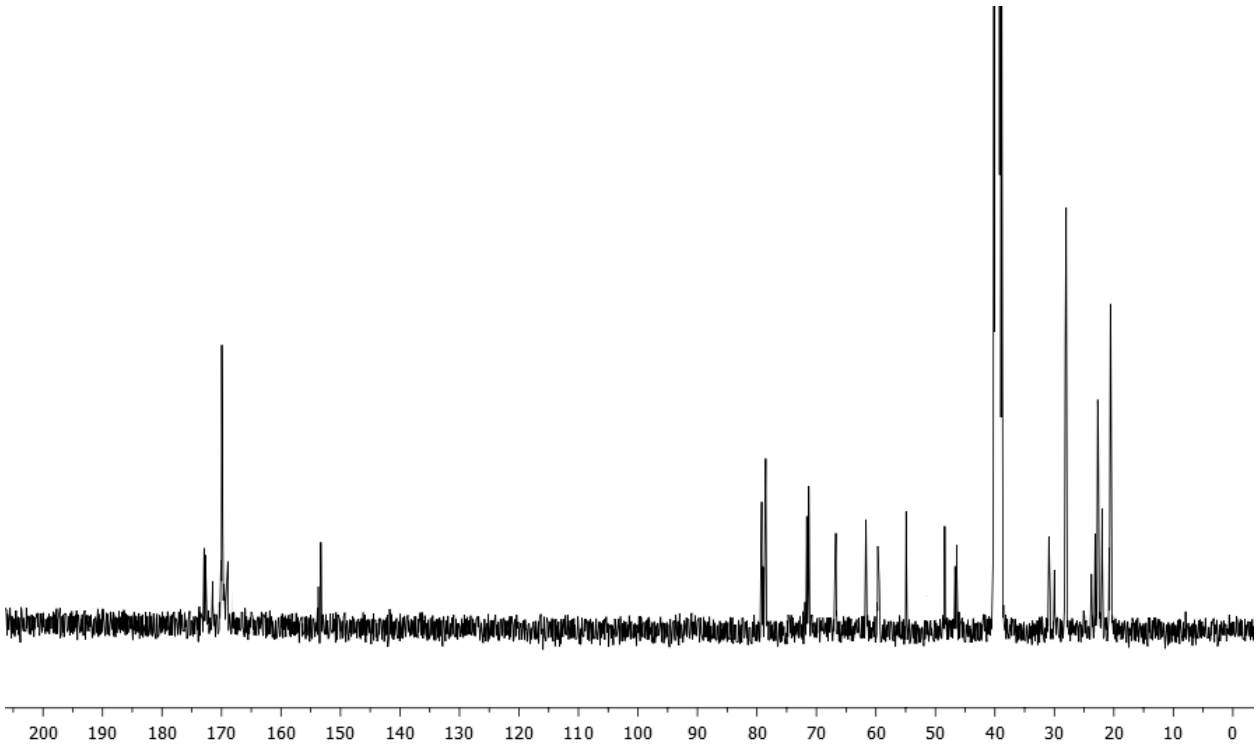
^{1}H NMR spectrum of compound **23**



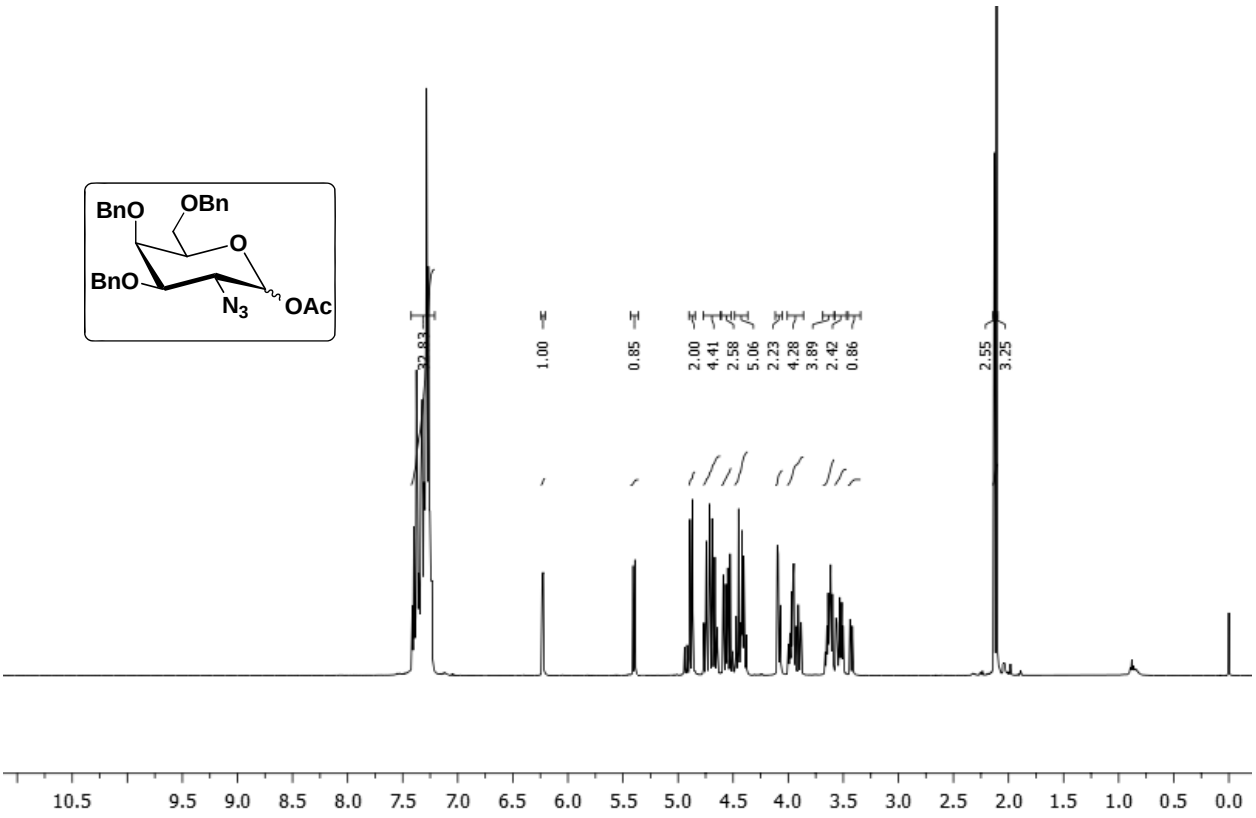
^{13}C NMR spectrum of compound **23**



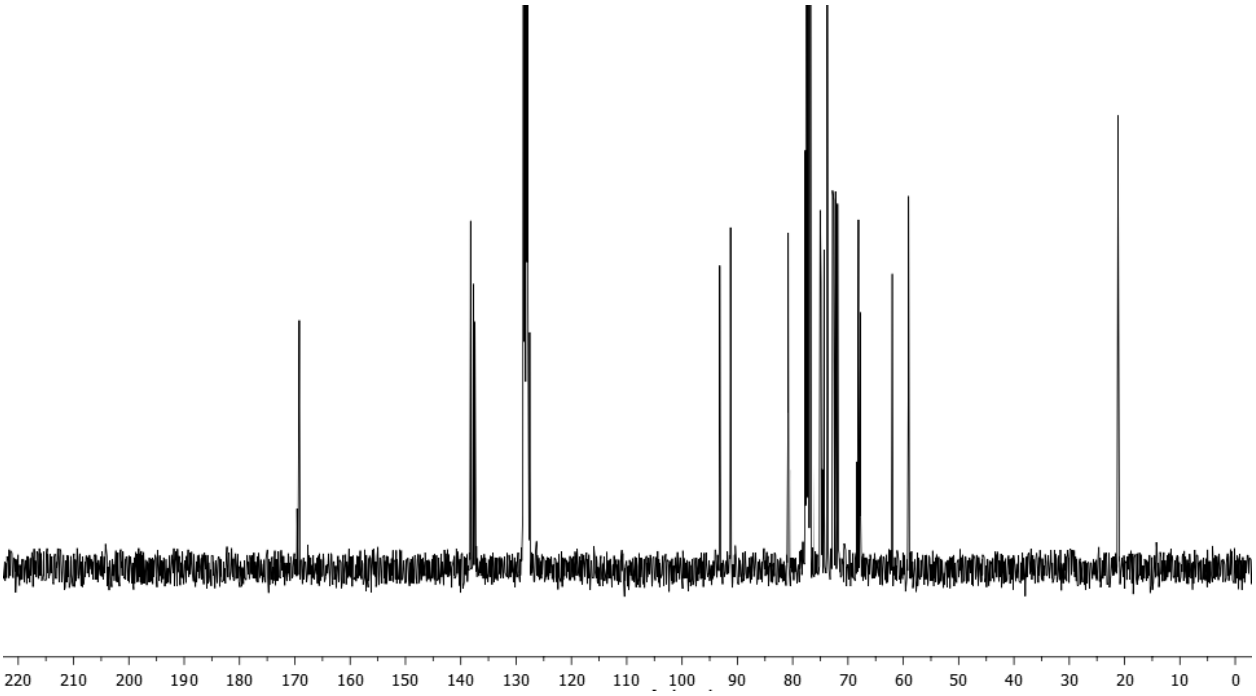
^{1}H NMR spectrum of compound **24**



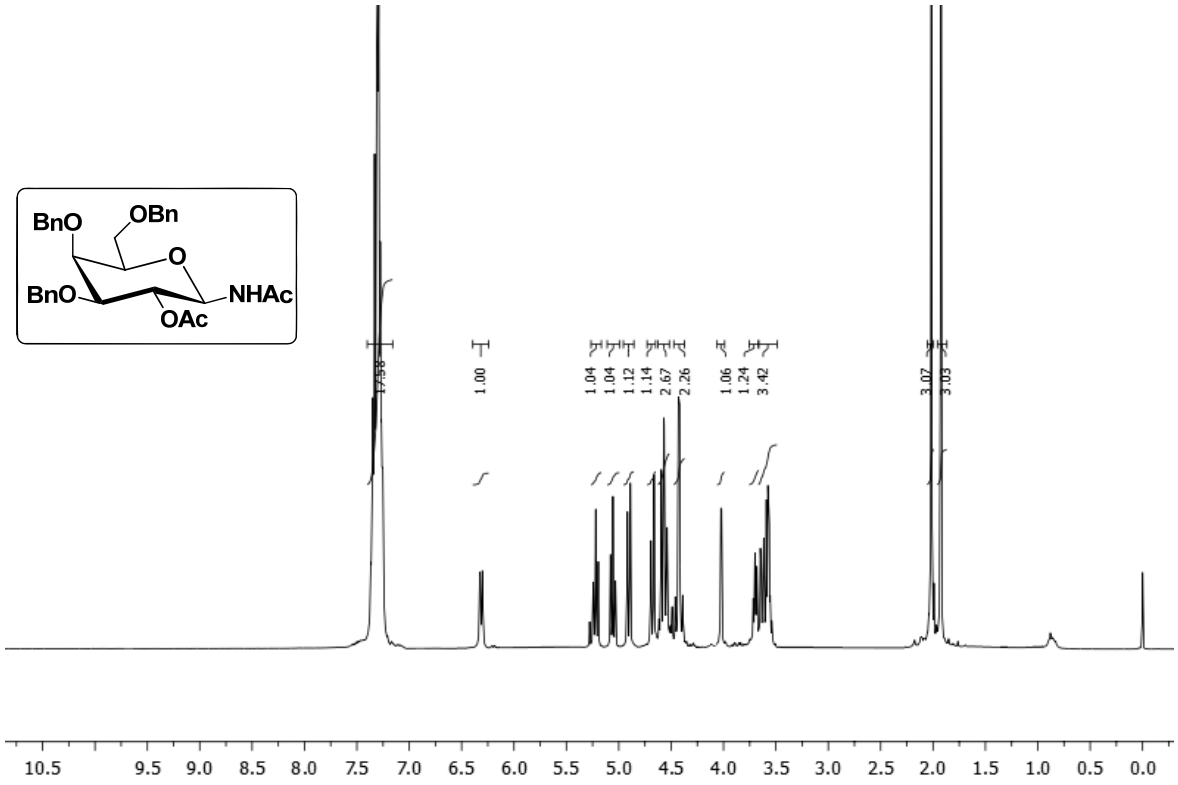
^{13}C NMR spectrum of compound **24**



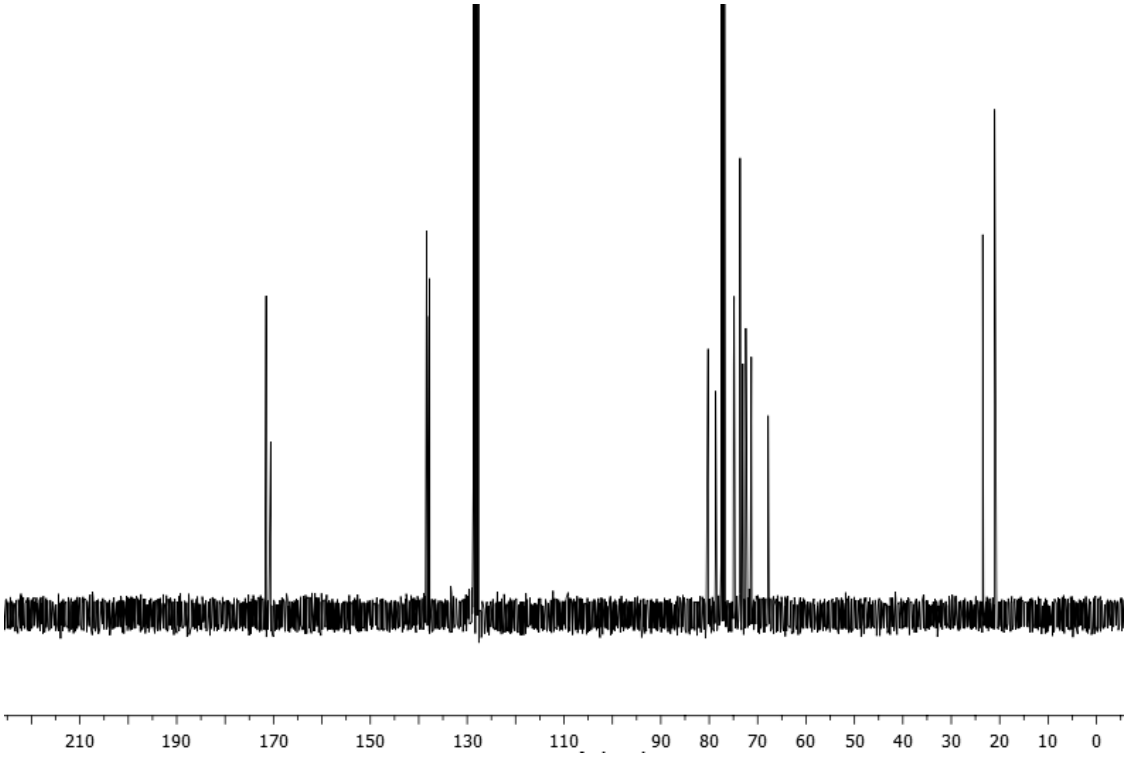
^{1}H NMR spectrum of compound **3**



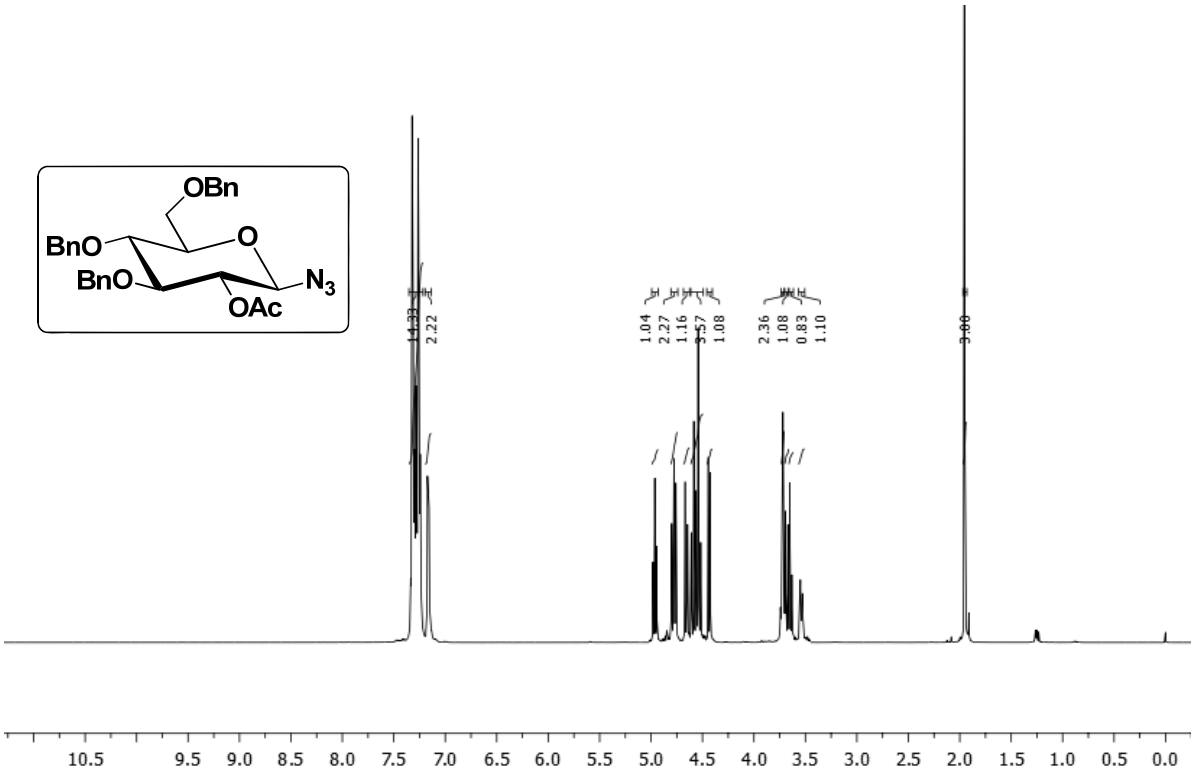
^{13}C NMR spectrum of compound **3**



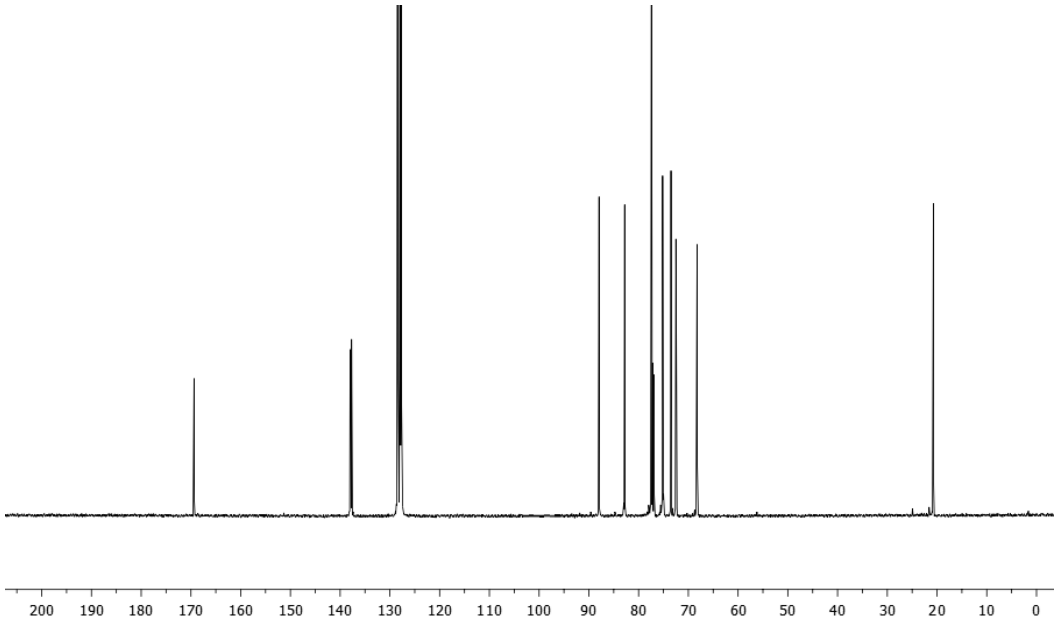
^{1}H NMR spectrum of compound **25**



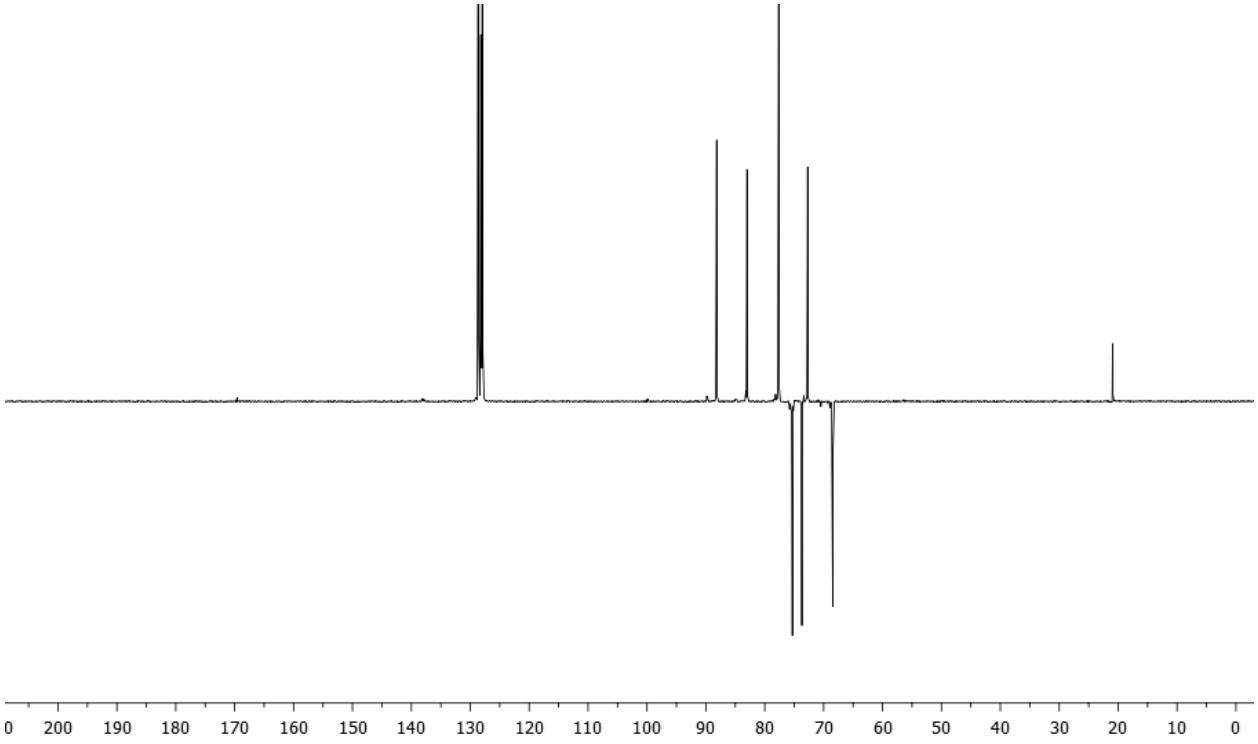
^{13}C NMR spectrum of compound **25**



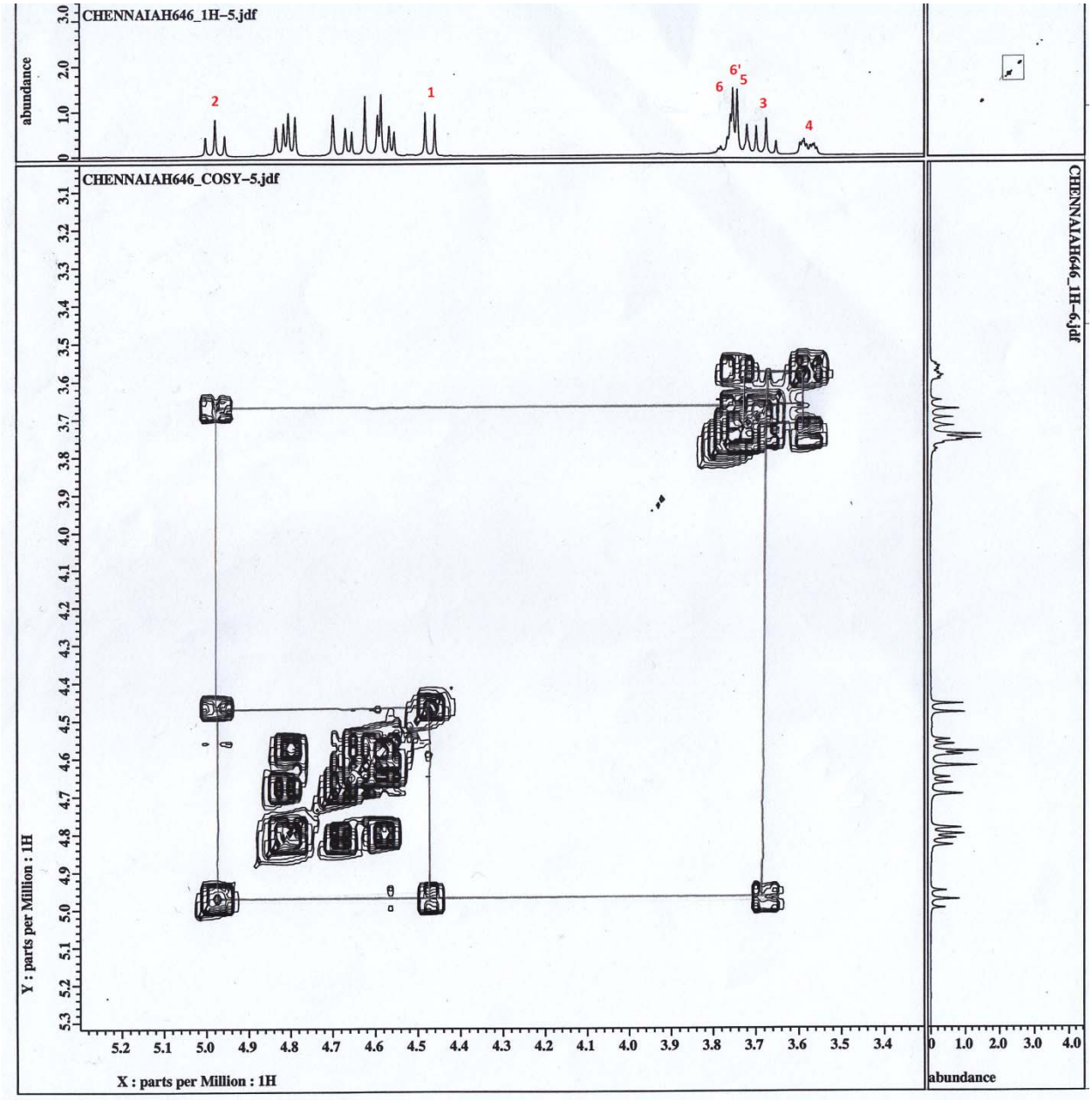
^{1}H NMR spectrum of compound **26**



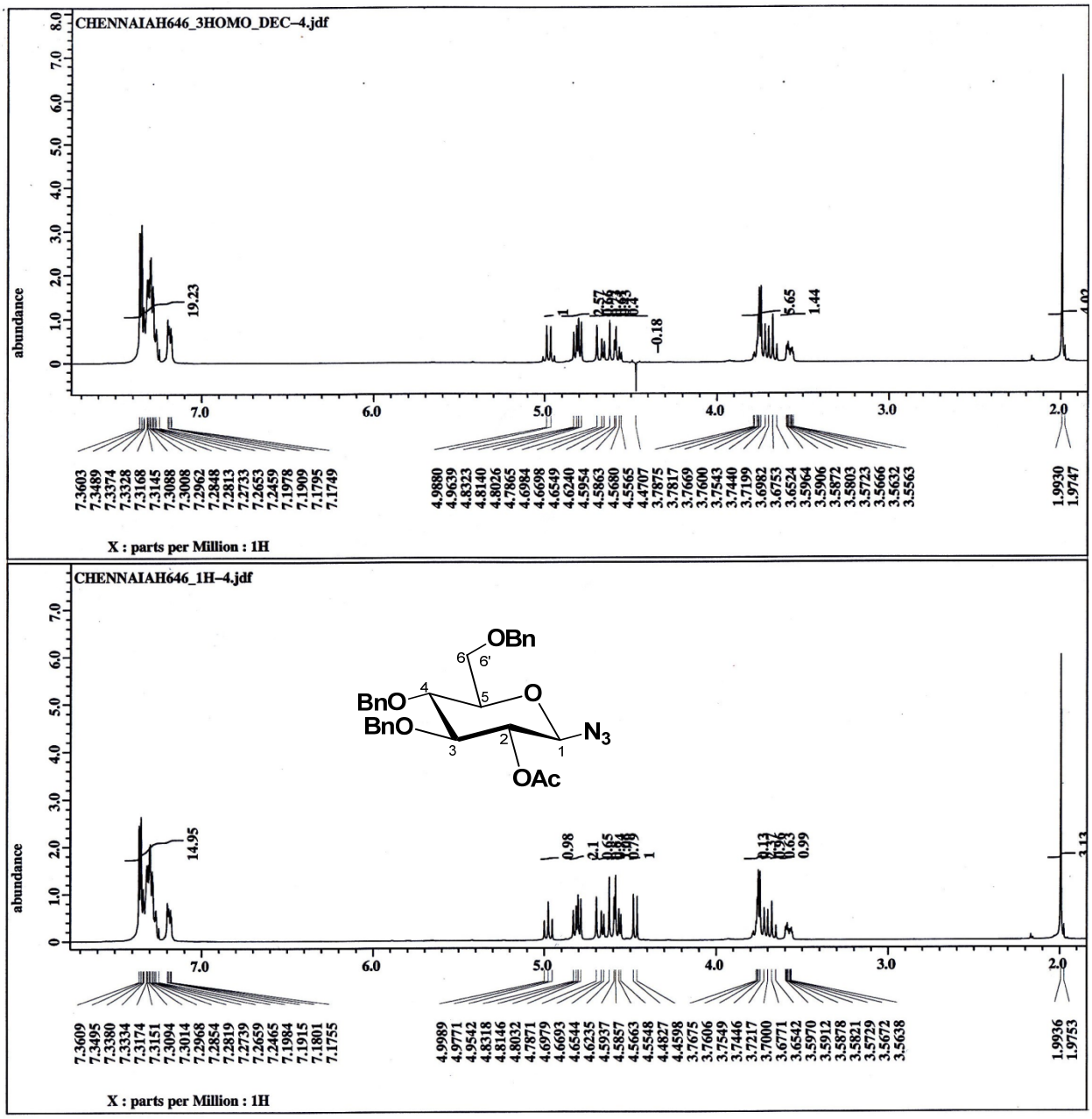
^{13}C NMR spectrum of compound **26**



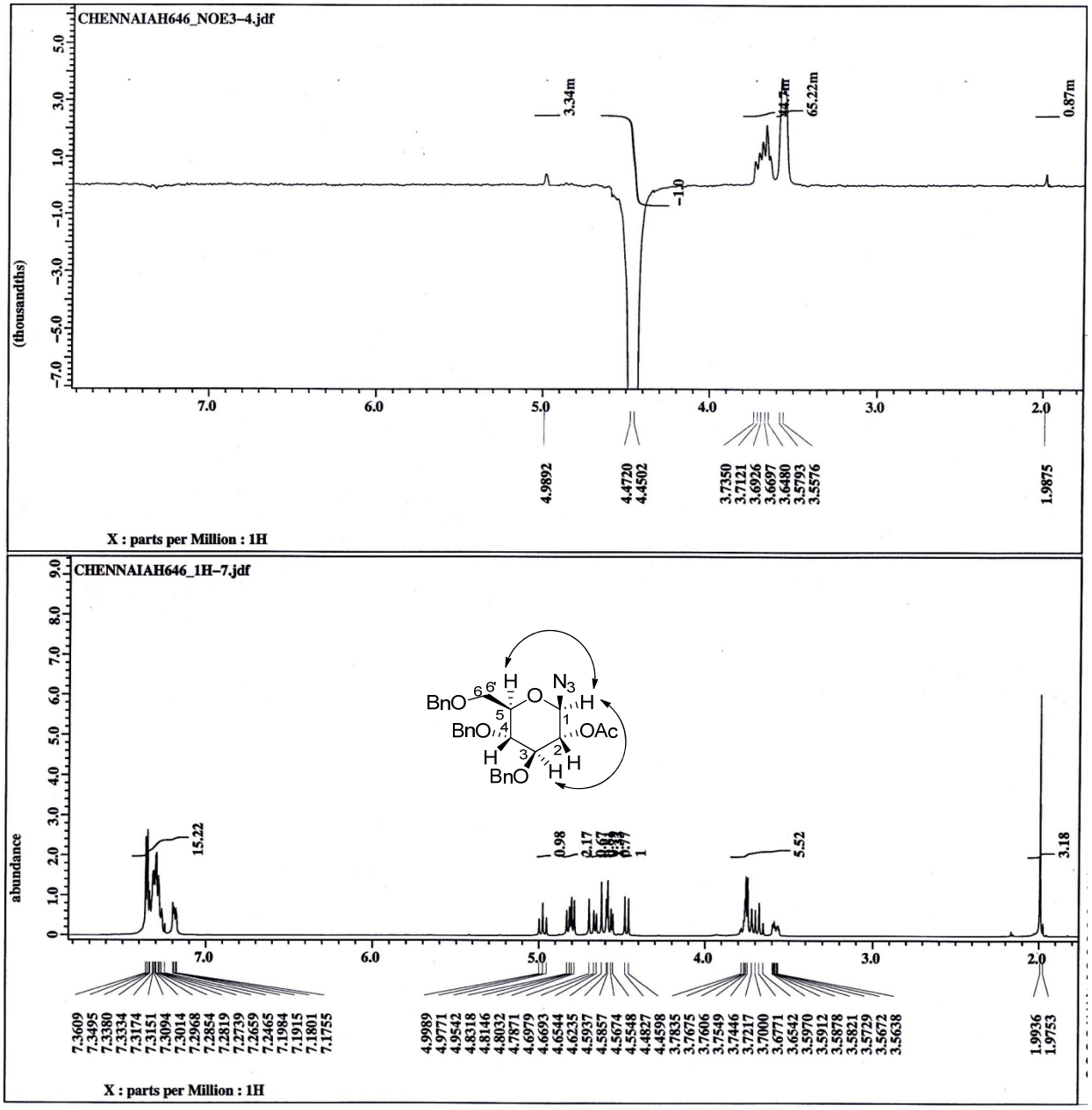
DEPT-135 spectrum of compound **26**



^{1}H-^{1}H COSY NMR spectrum of compound **26**

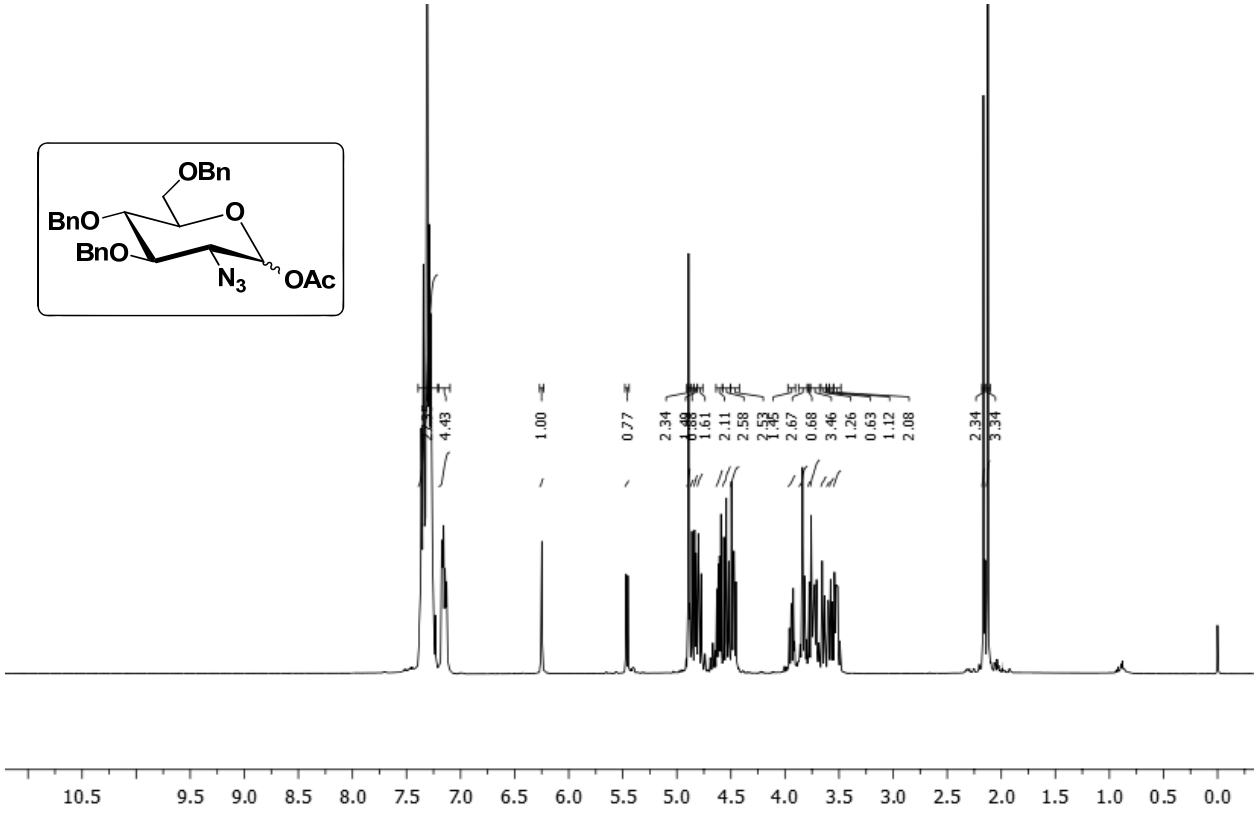


^{1}H-^{1}H homonuclear decoupling (H-1) NMR spectrum of compound **26**

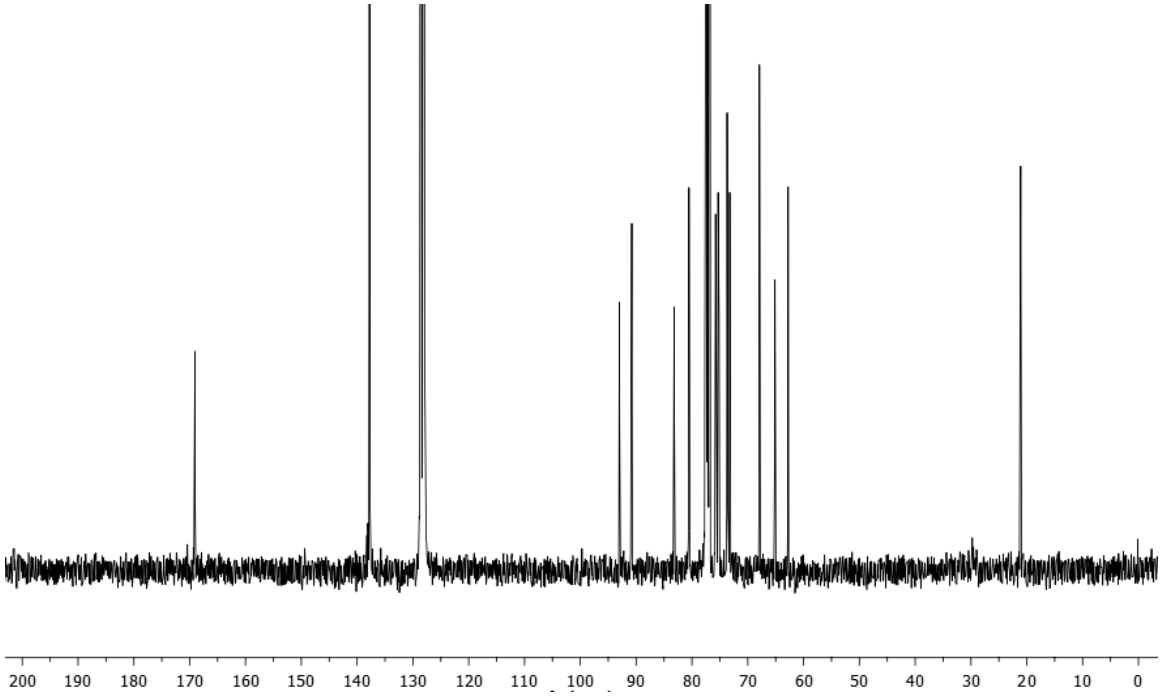


nOe spectrum (irradiation of H□1) of compound **26**

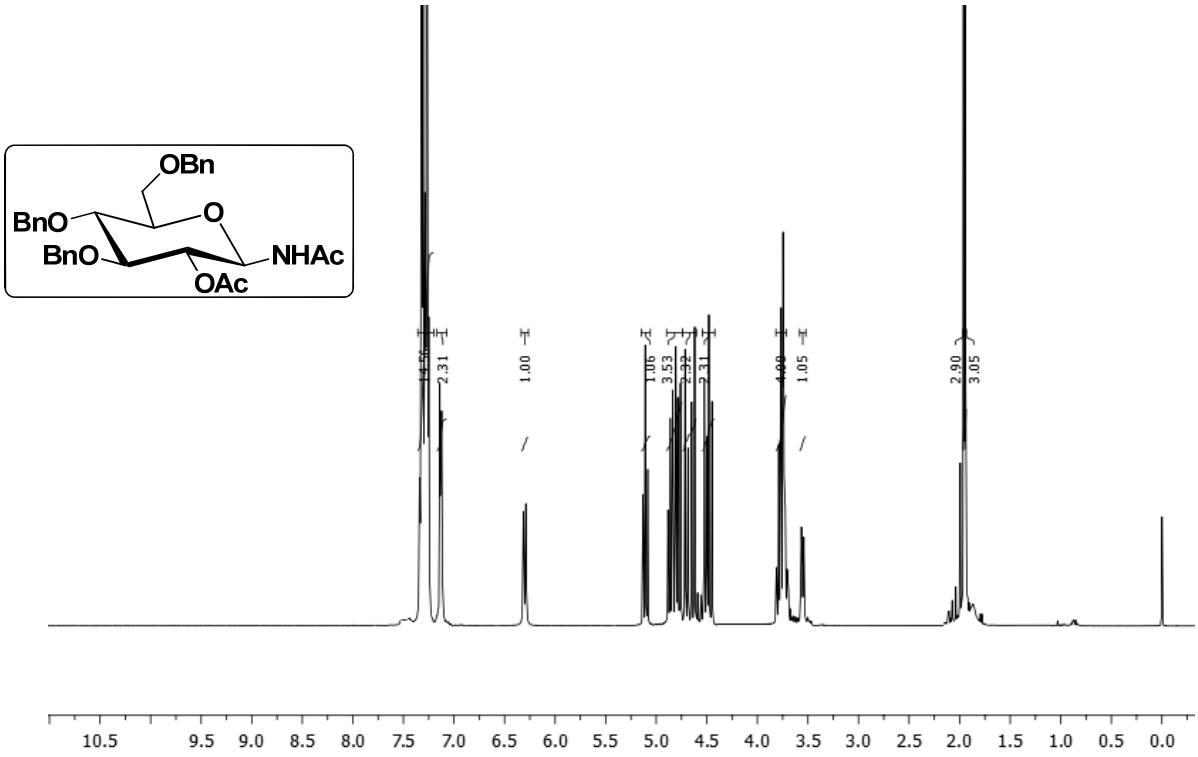
(Irradiation of proton H-1, led to the enhancement for protons H-3 and H-5, indicating that H-1, H-3 and H-5 are cis oriented)



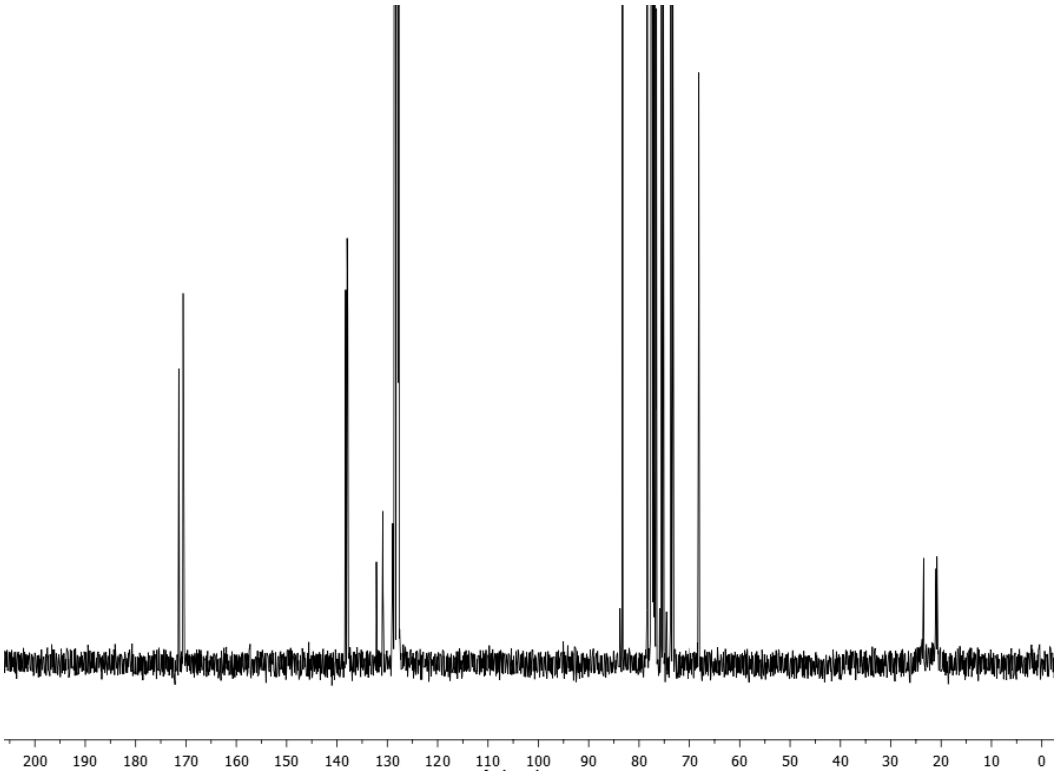
^{1}H NMR spectrum of compound **27**



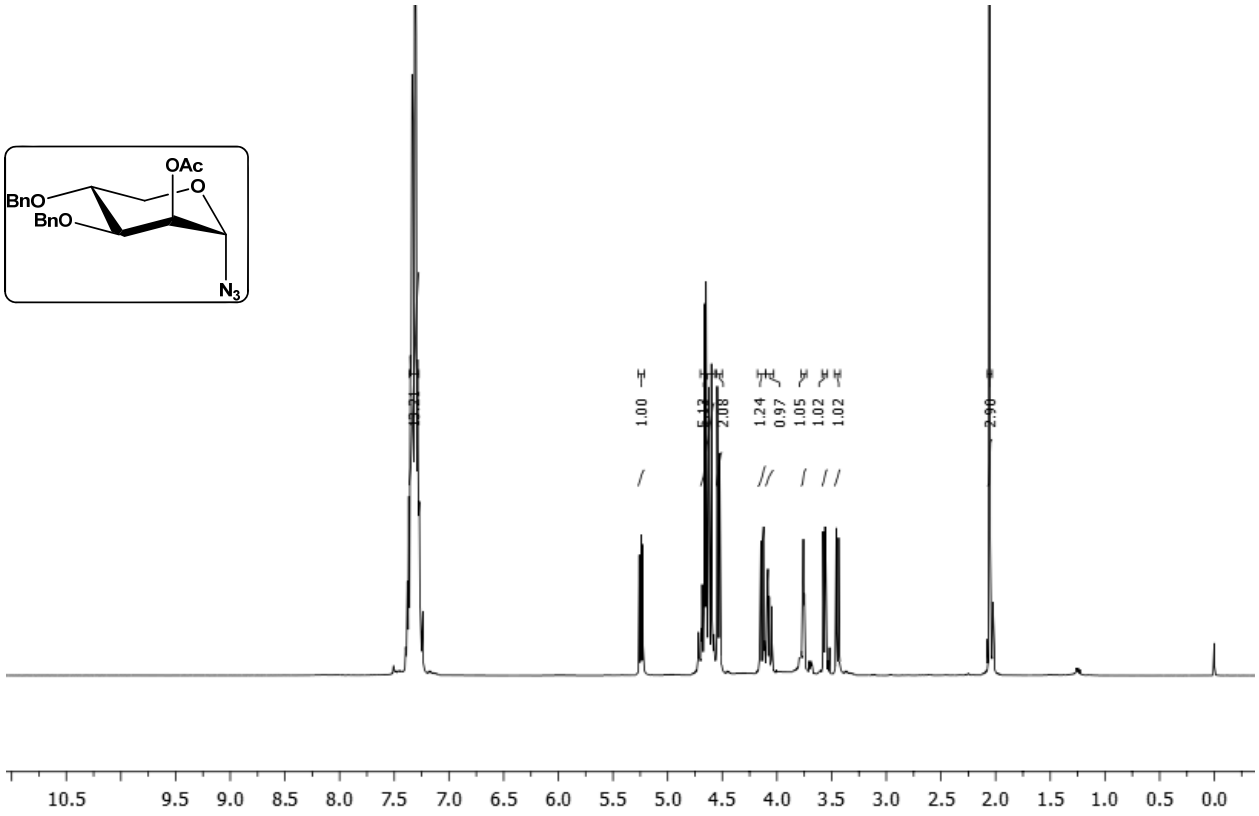
^{13}C NMR spectrum of compound **27**



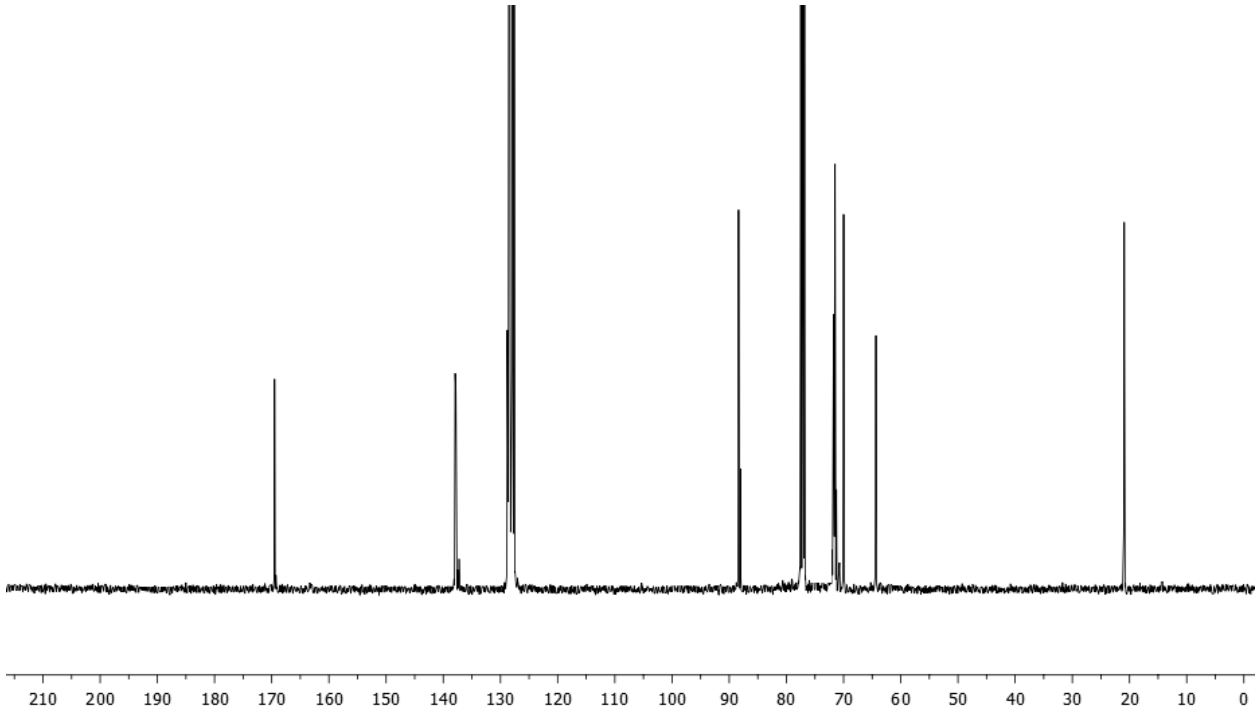
^{1}H NMR spectrum of compound **28**



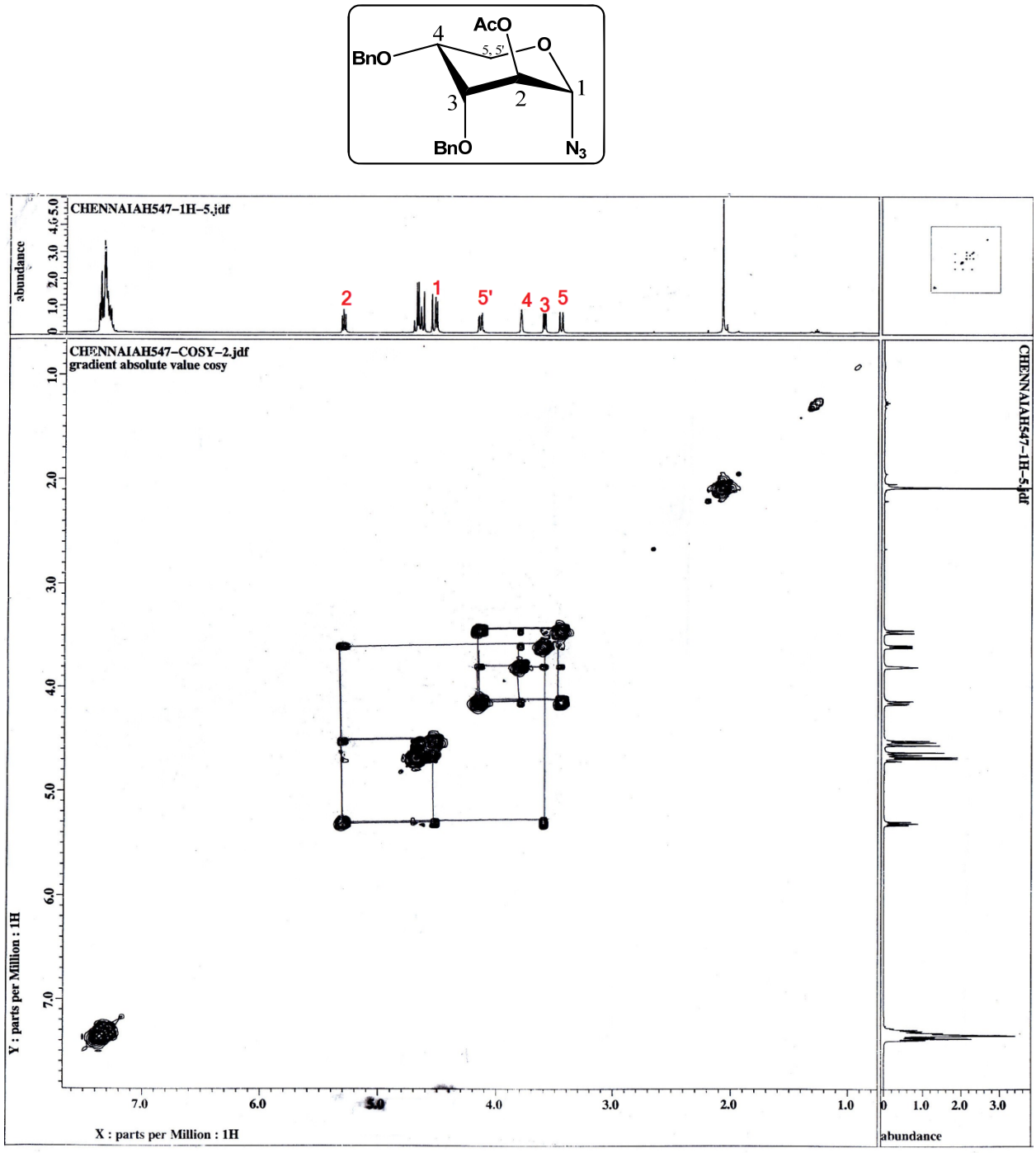
^{13}C NMR spectrum of compound **28**



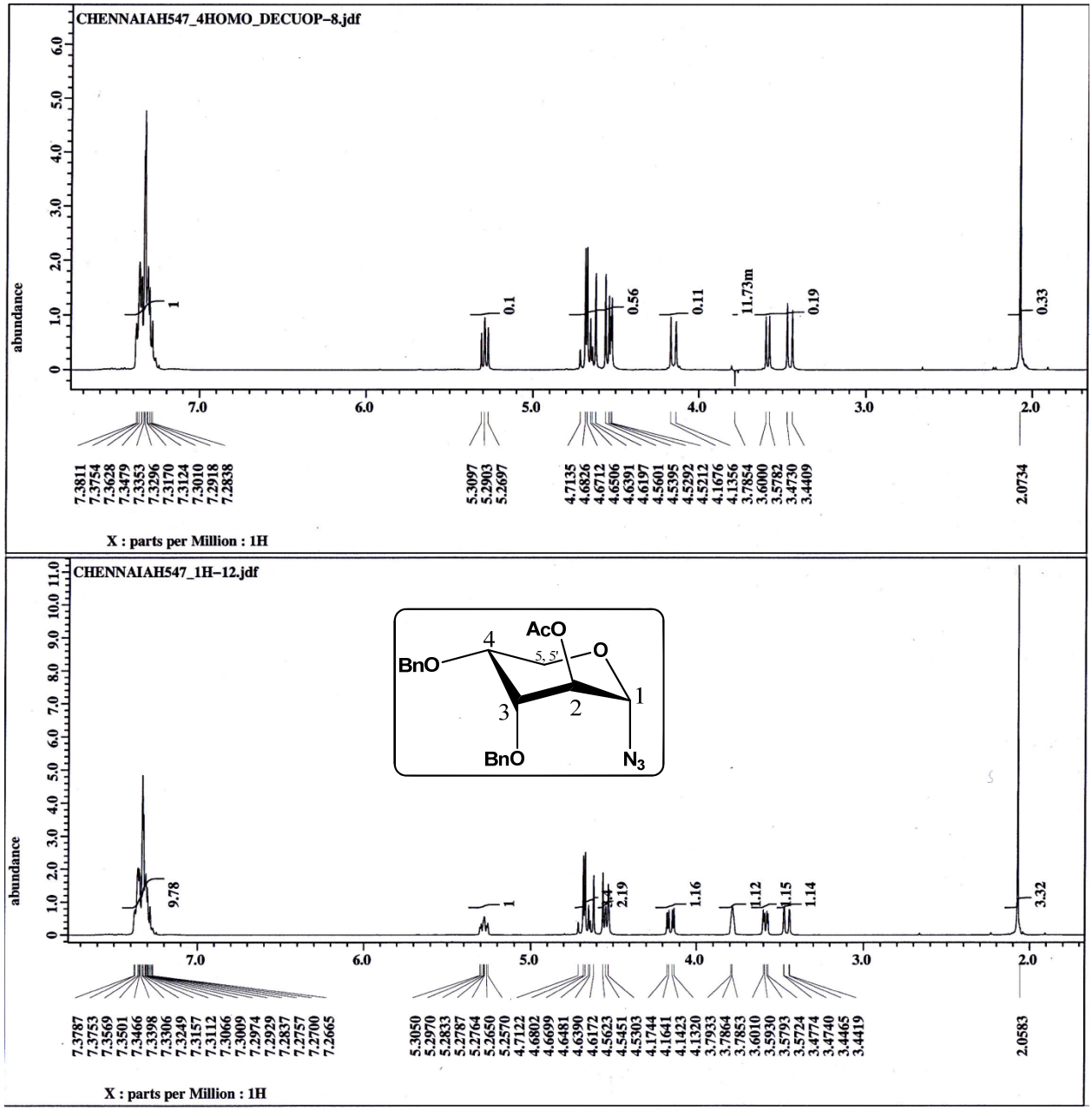
^{1}H NMR spectrum of compound **29**



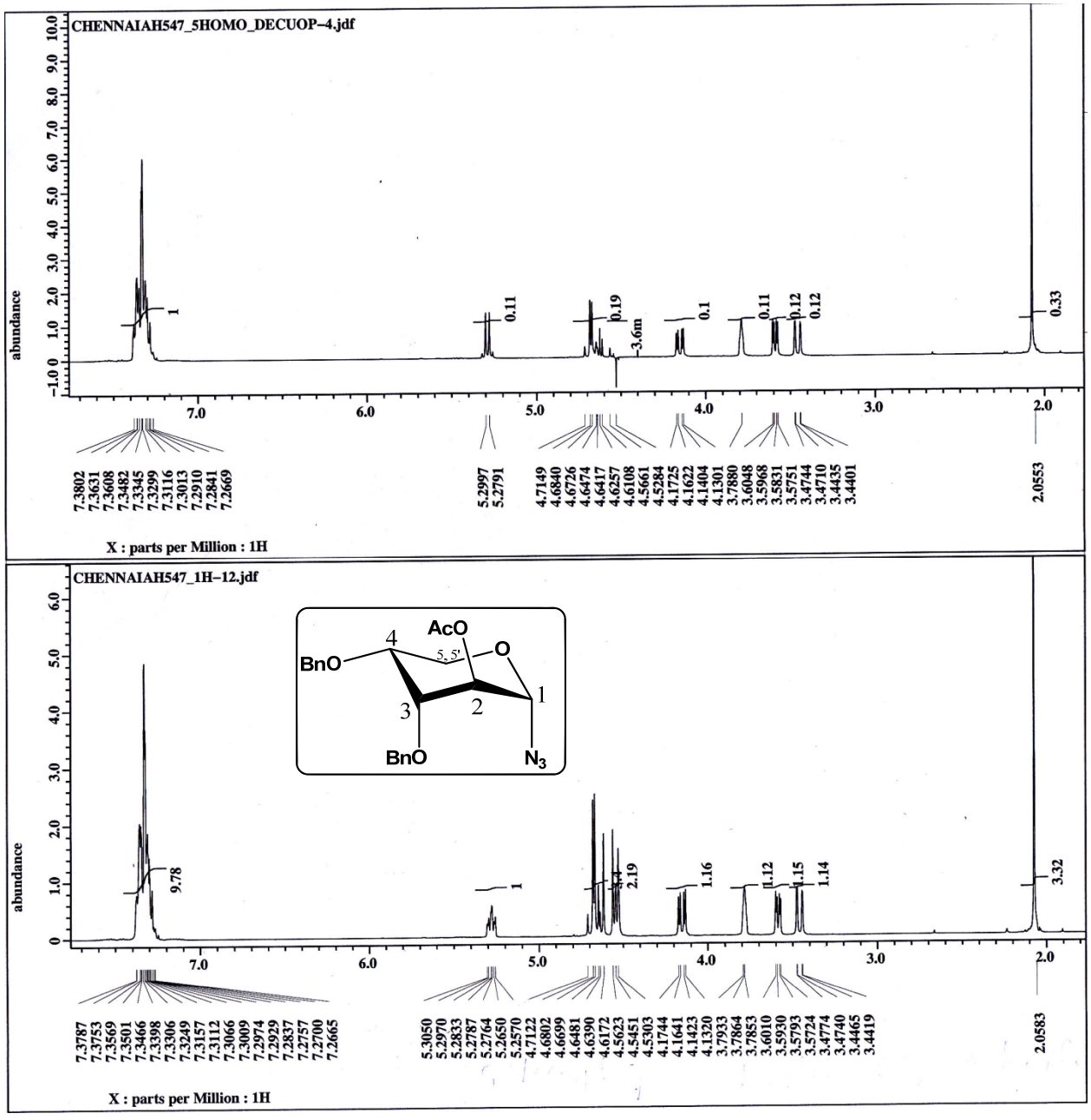
^{13}C NMR spectrum of compound **29**



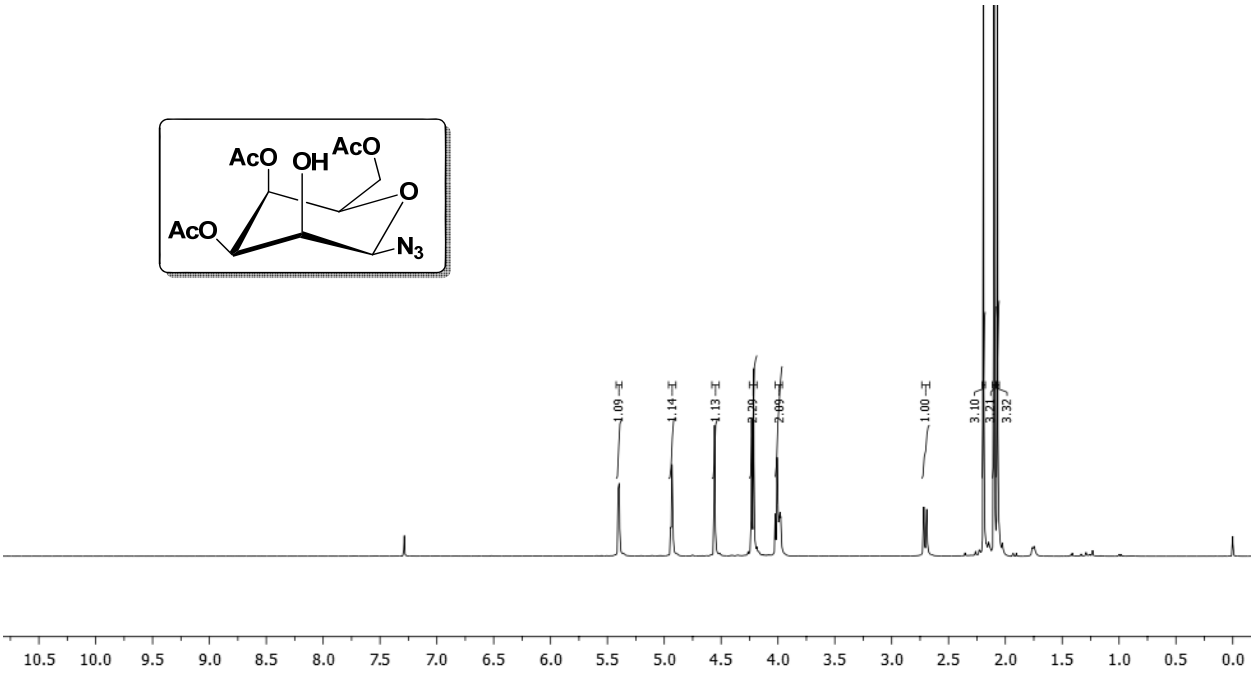
^{1}H-^{1}H COSY NMR spectrum of compound **29**



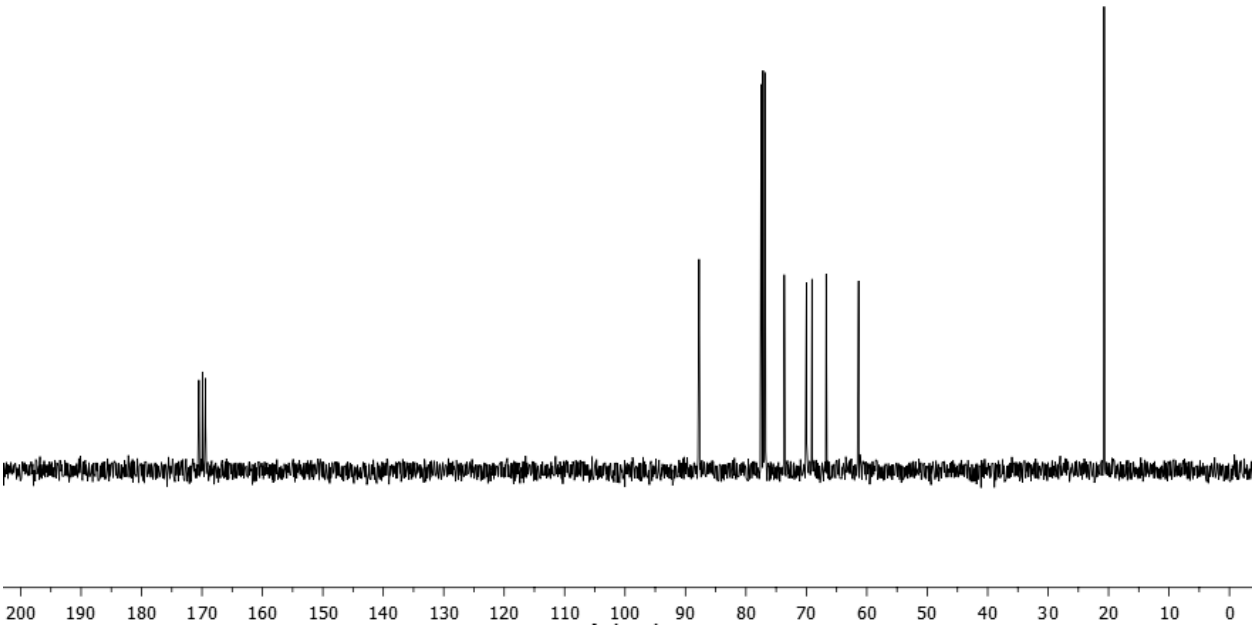
^{1}H-^{1}H homonuclear decoupling (H-4) NMR spectrum of compound **29**



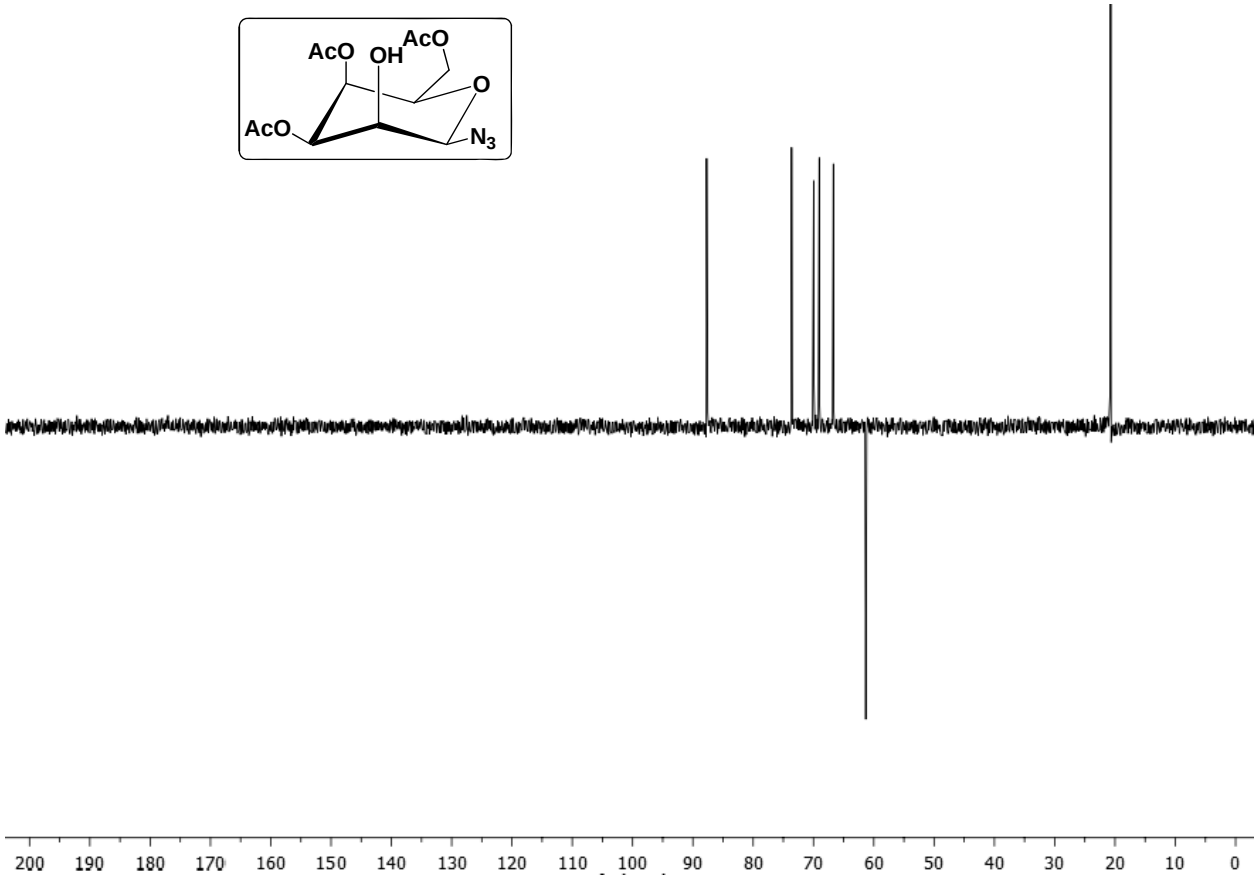
^{1}H-^{1}H homonuclear decoupling (H-1) NMR spectrum of compound **29**



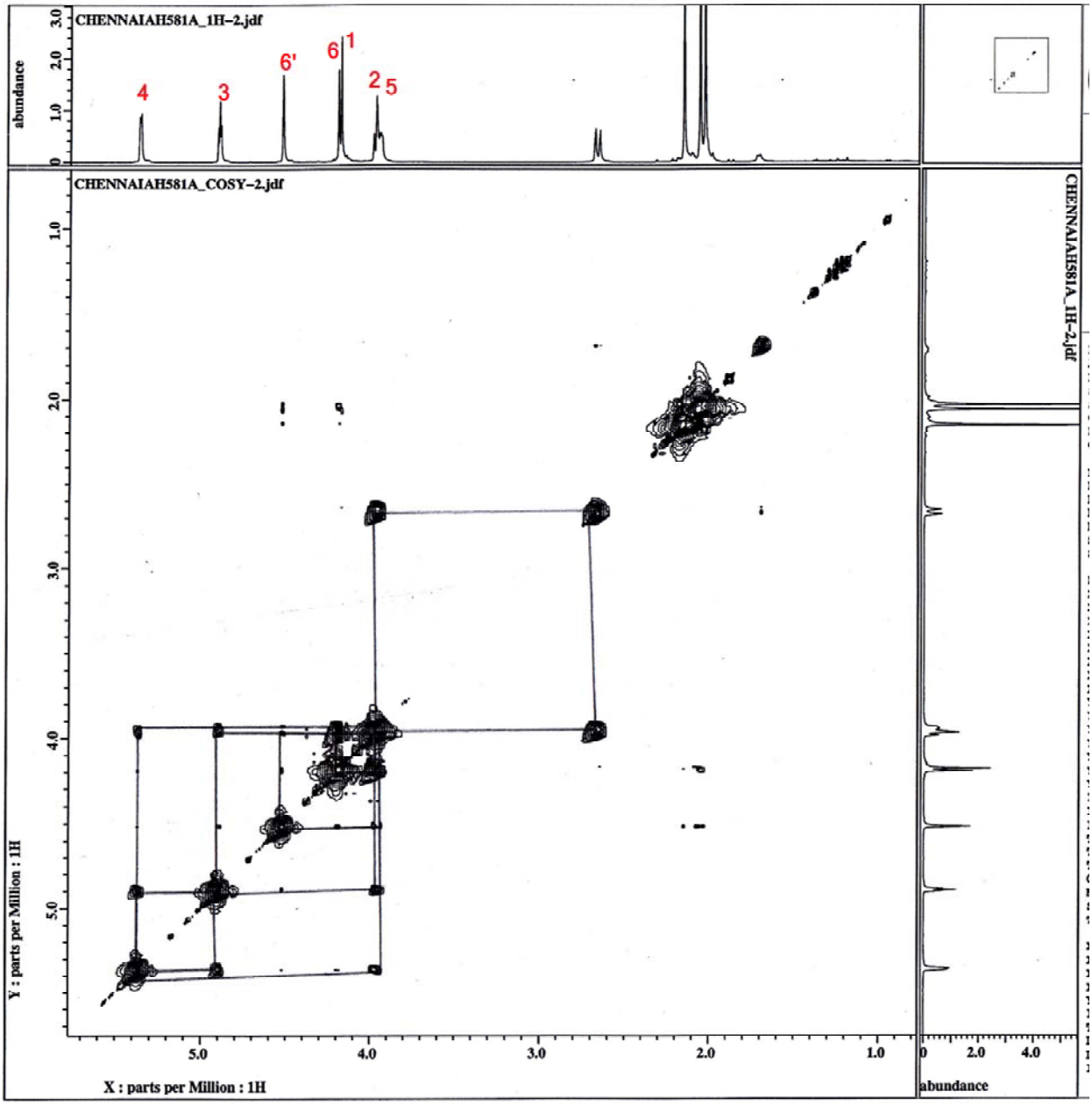
^{1}H NMR spectrum of compound **30**



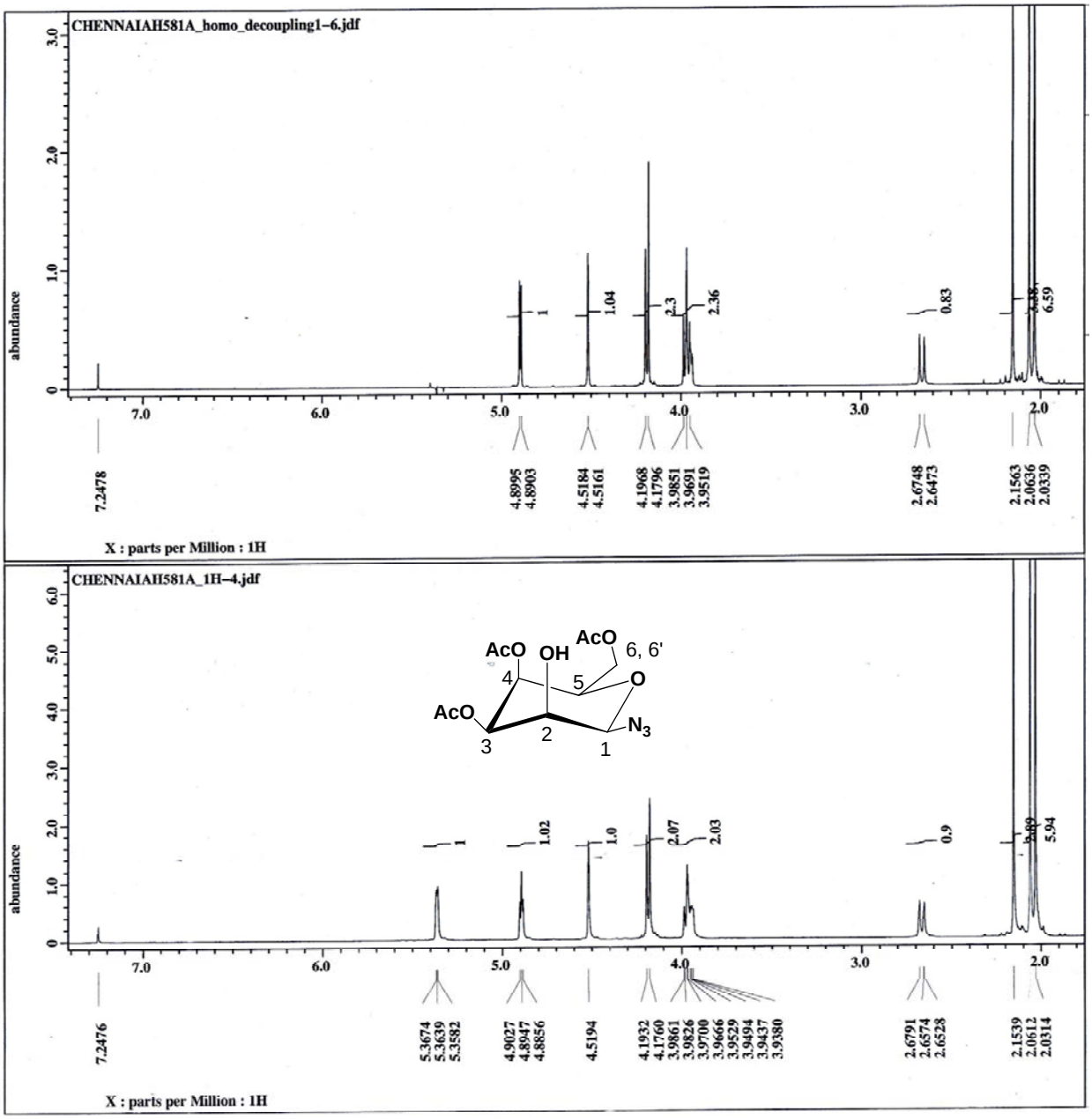
^{13}C NMR spectrum of compound **30**



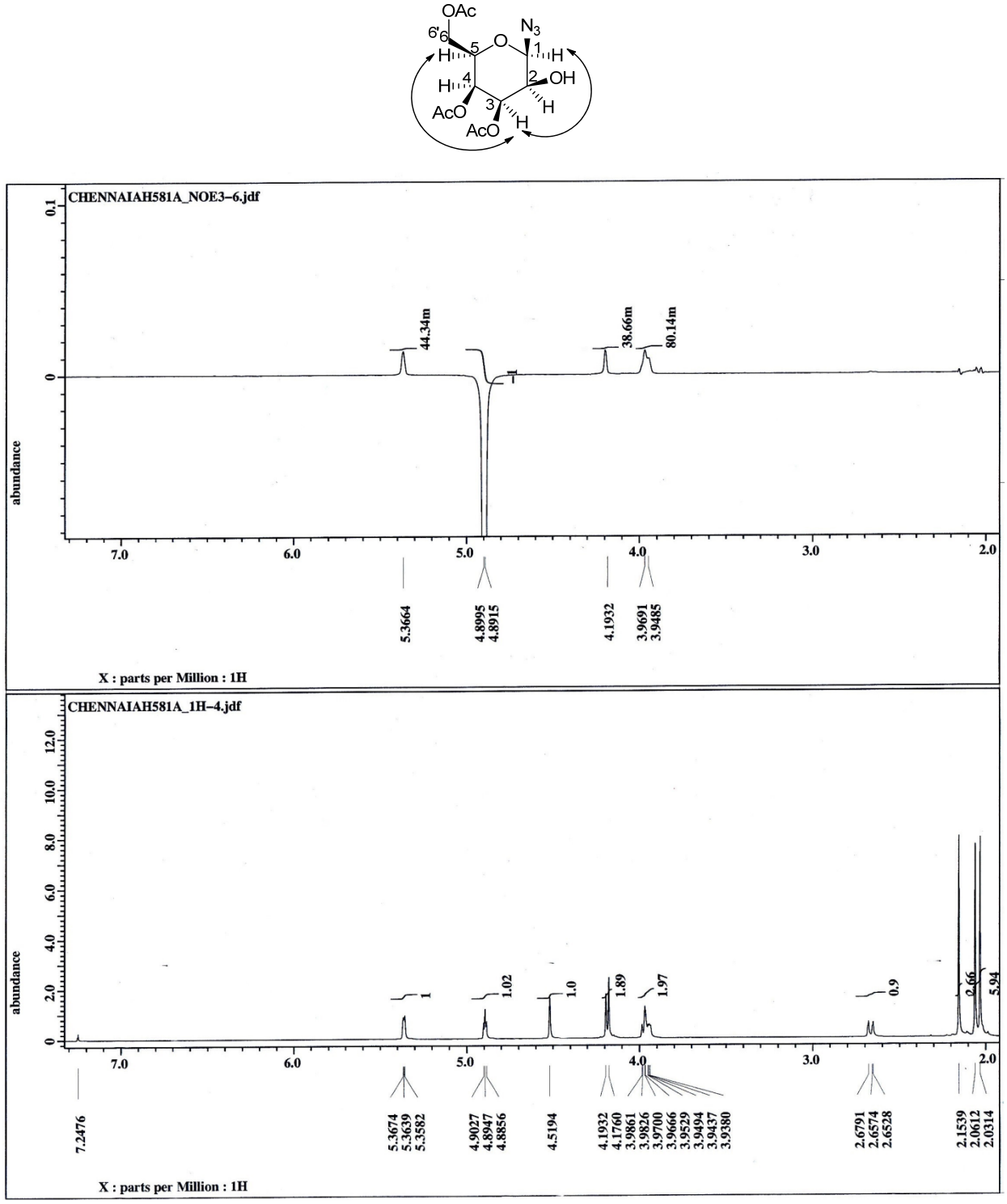
DEPT-135 spectrum of compound **30**



^{1}H-^{1}H COSY NMR spectrum of compound **30**

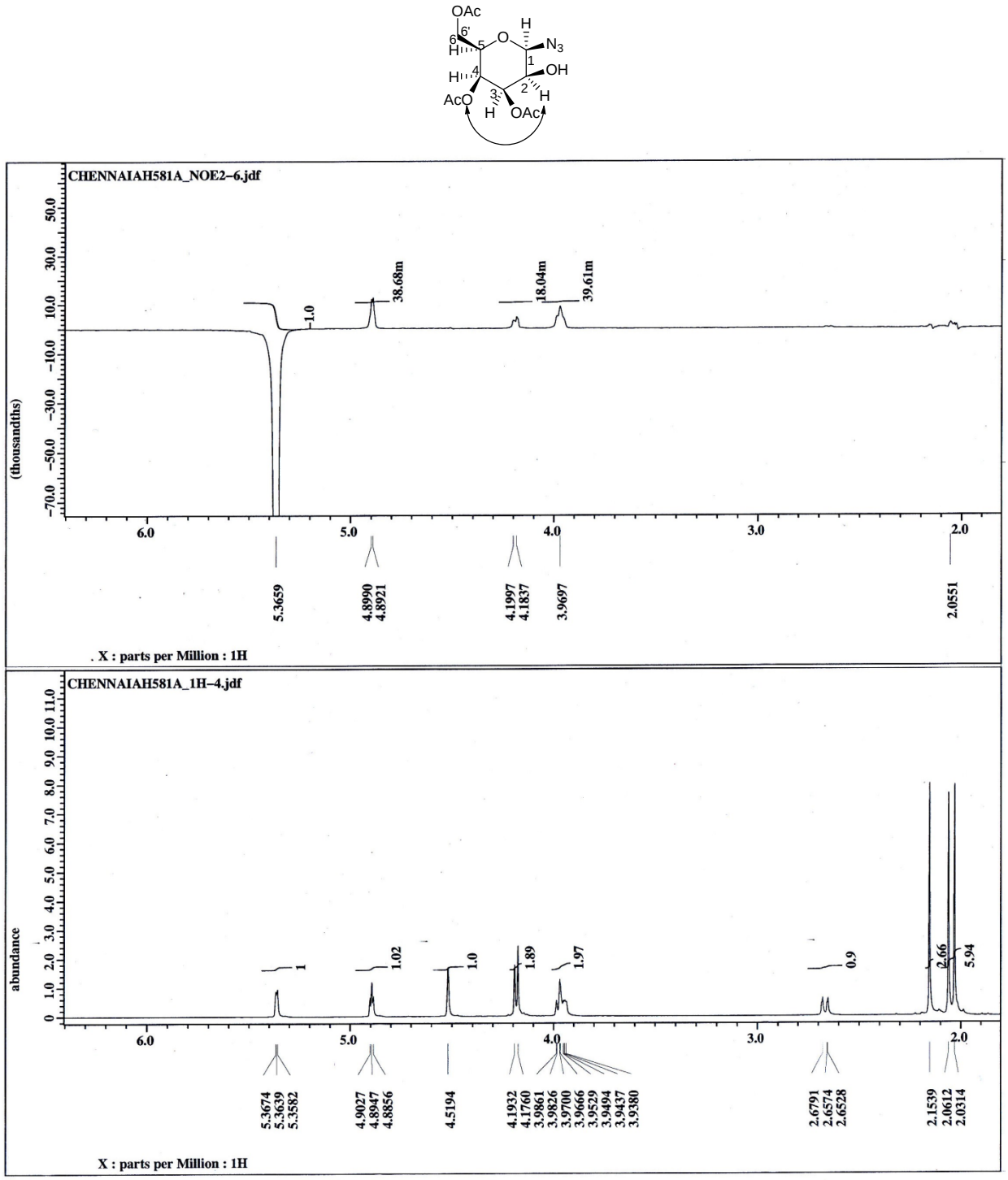


^{1}H-^{1}H homonuclear decoupling (H-4) NMR spectrum of compound **30**



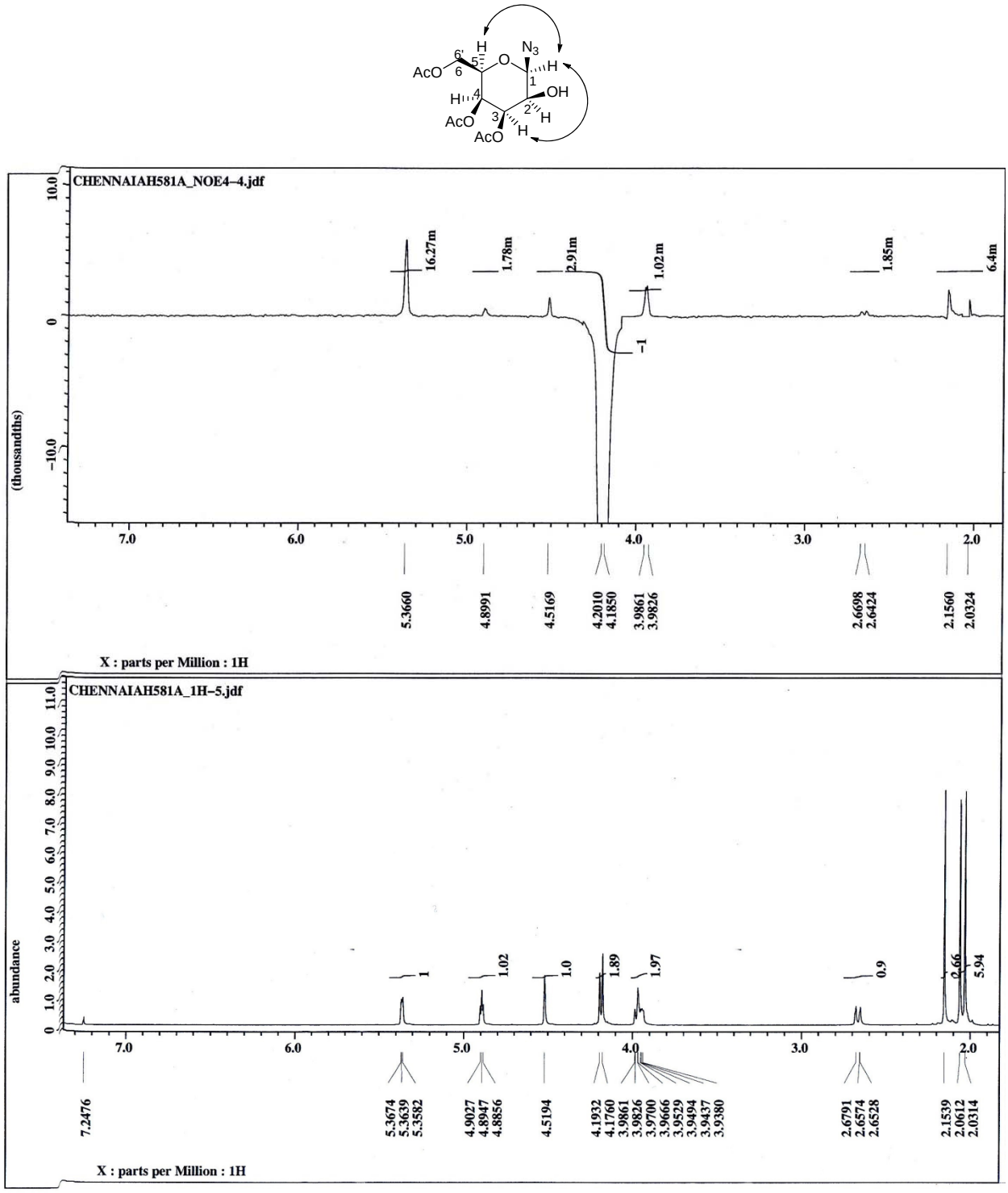
nOe spectrum (irradiation of H-3) of compound **30**

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



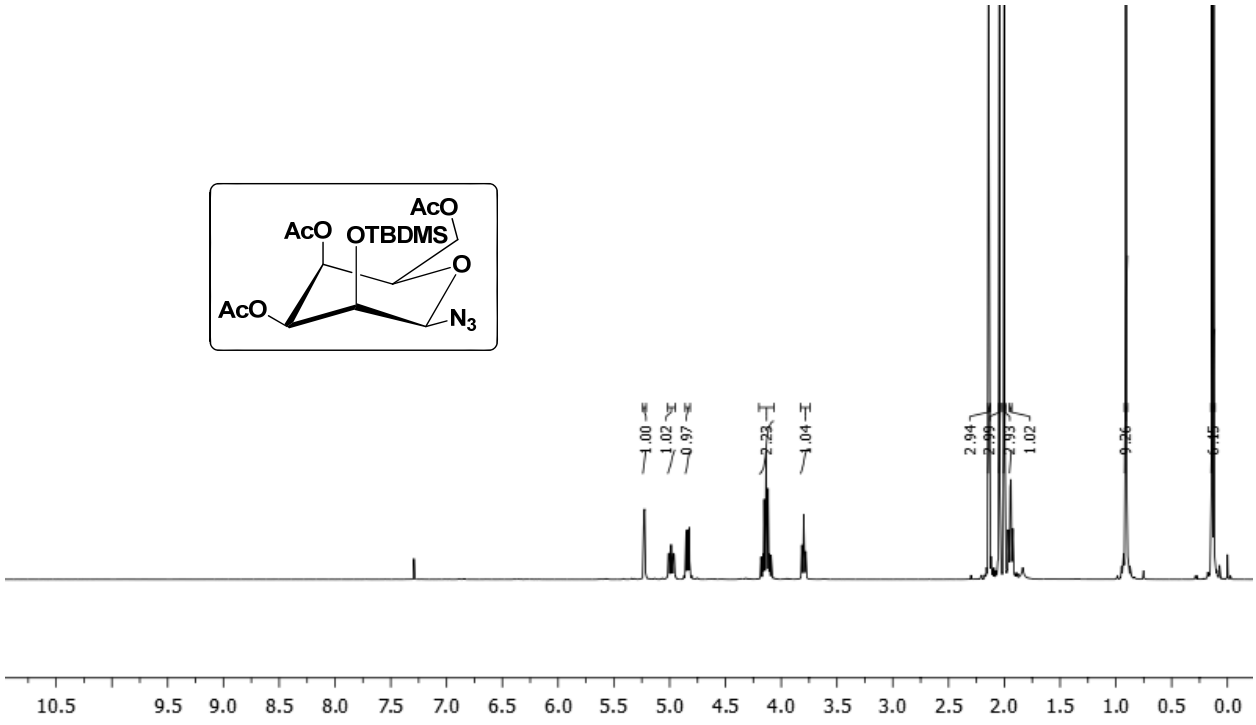
nOe spectrum (irradiation of H-4) of compound **30**

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

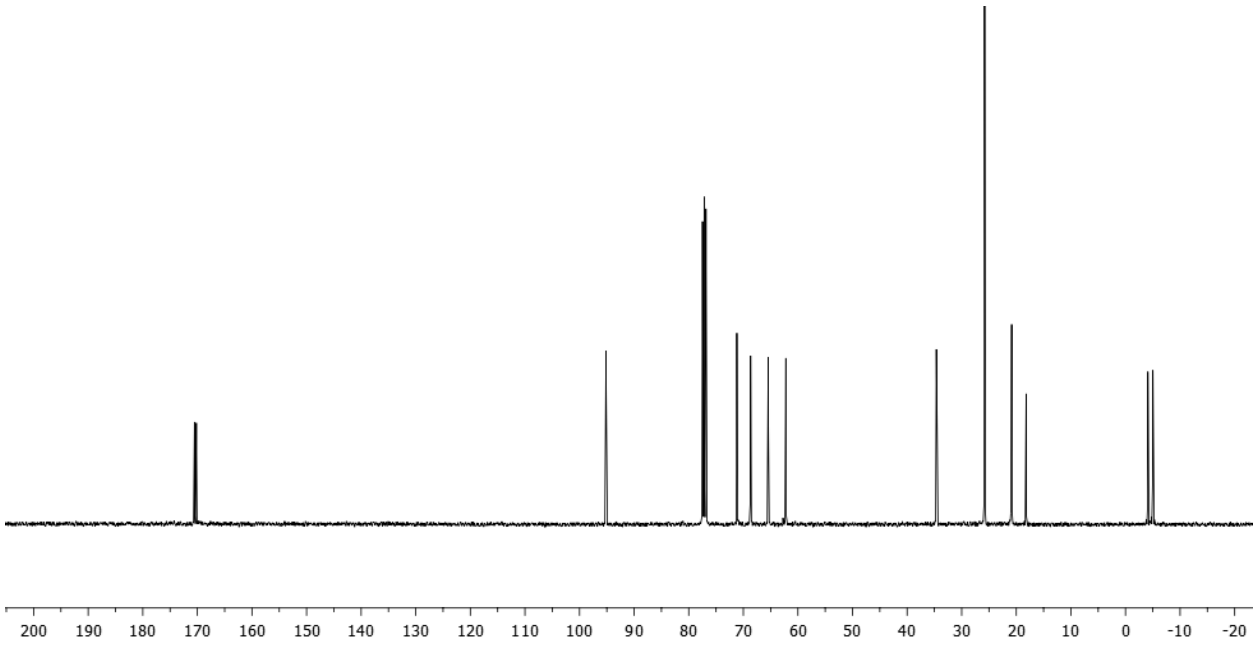


nOe spectrum (irradiation of H-1) of compound **30**

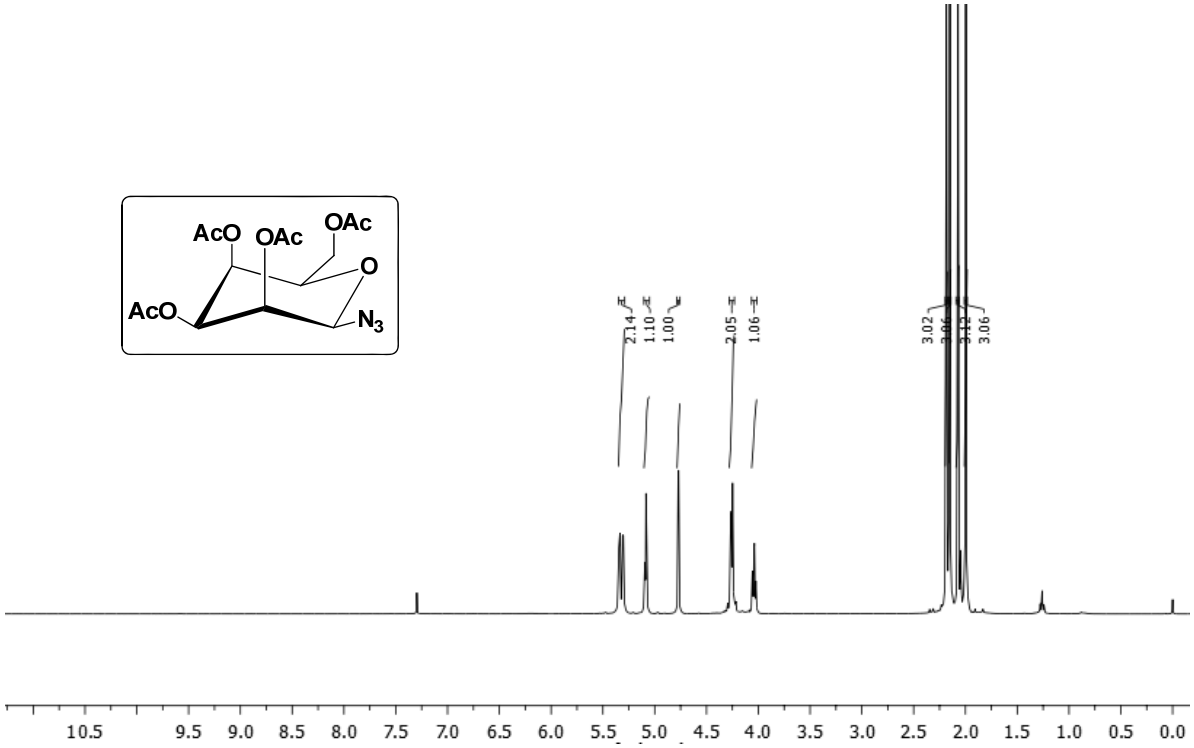
(Irradiation of proton H-1, led to the enhancement for protons H-3 and H-5, indicating that H-1, H-3 and H-5 are cis oriented)



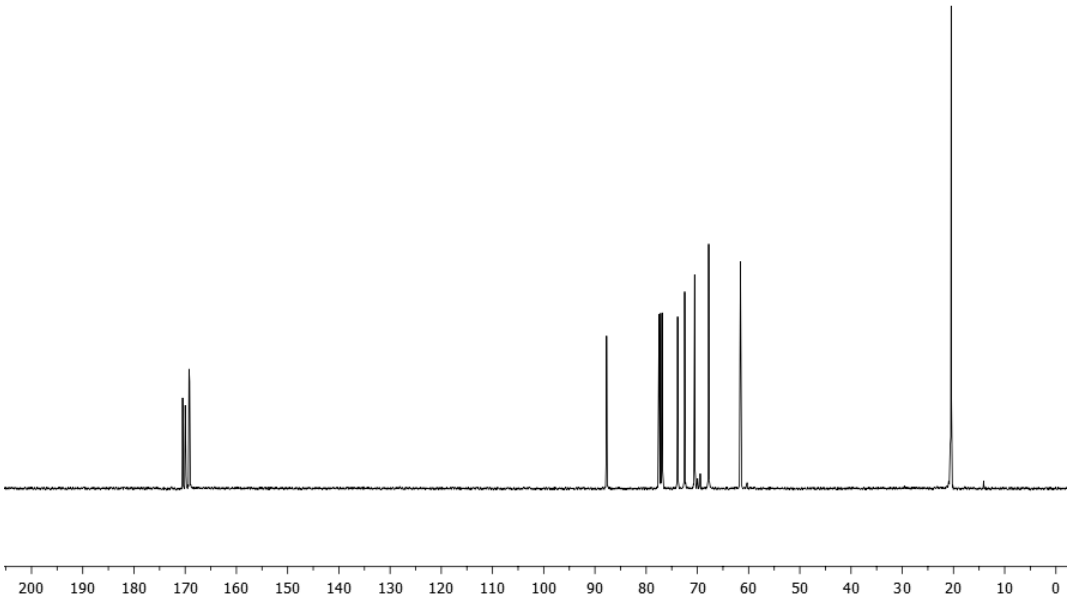
^{1}H NMR spectrum of compound **31**



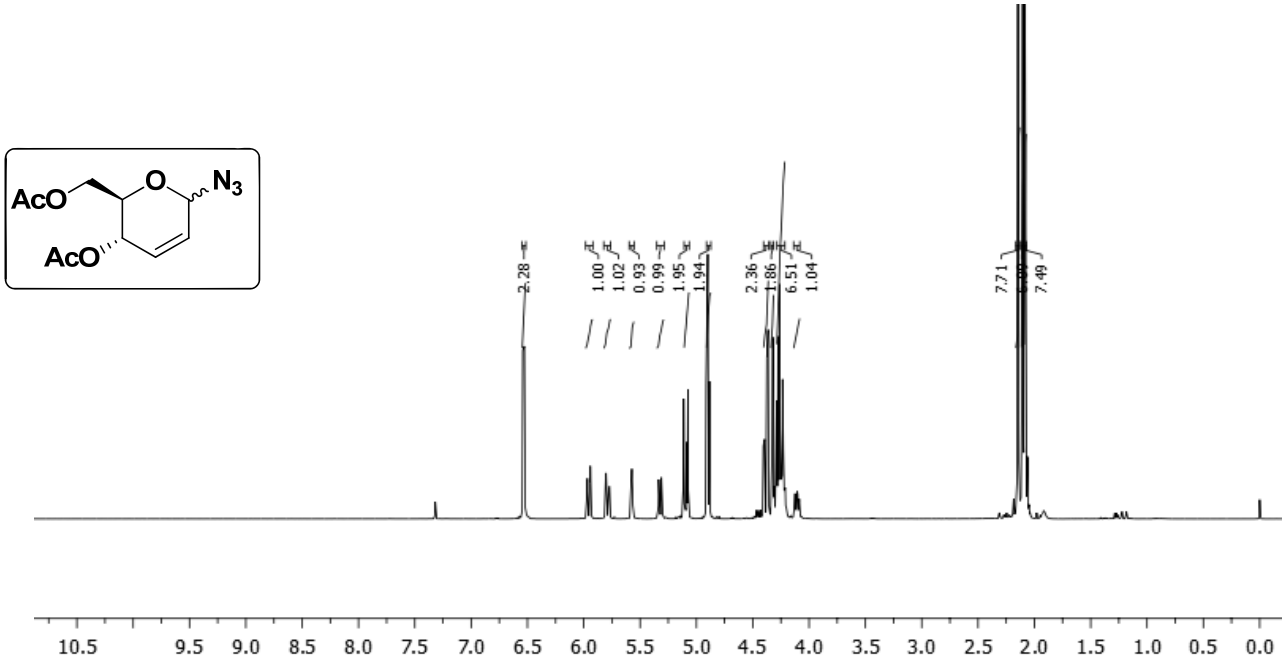
^{13}C NMR spectrum of compound **31**



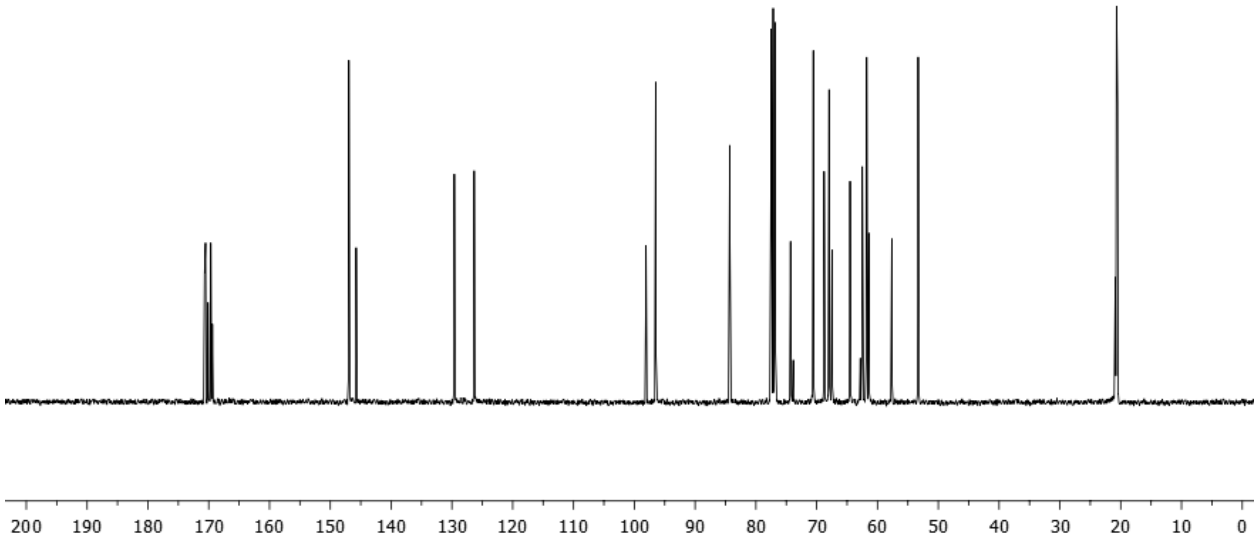
^{1}H NMR spectrum of compound **32**



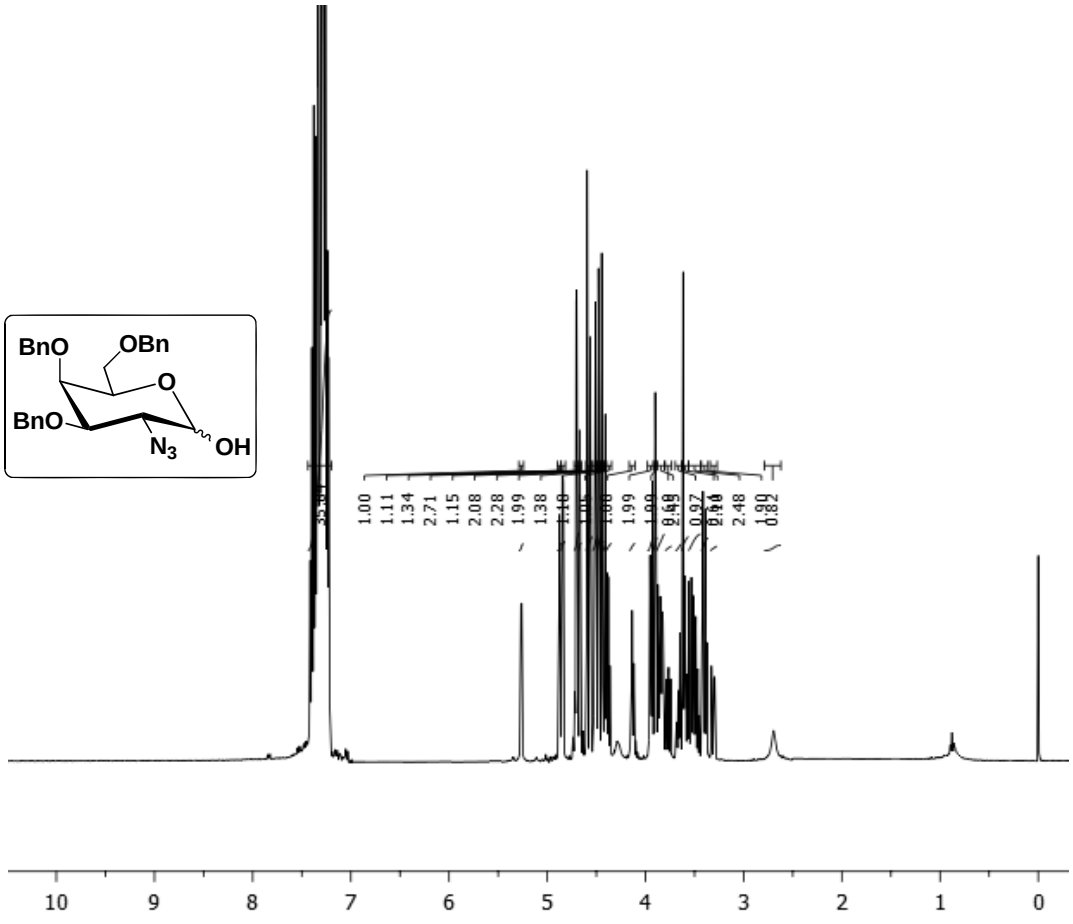
^{13}C NMR spectrum of compound **32**



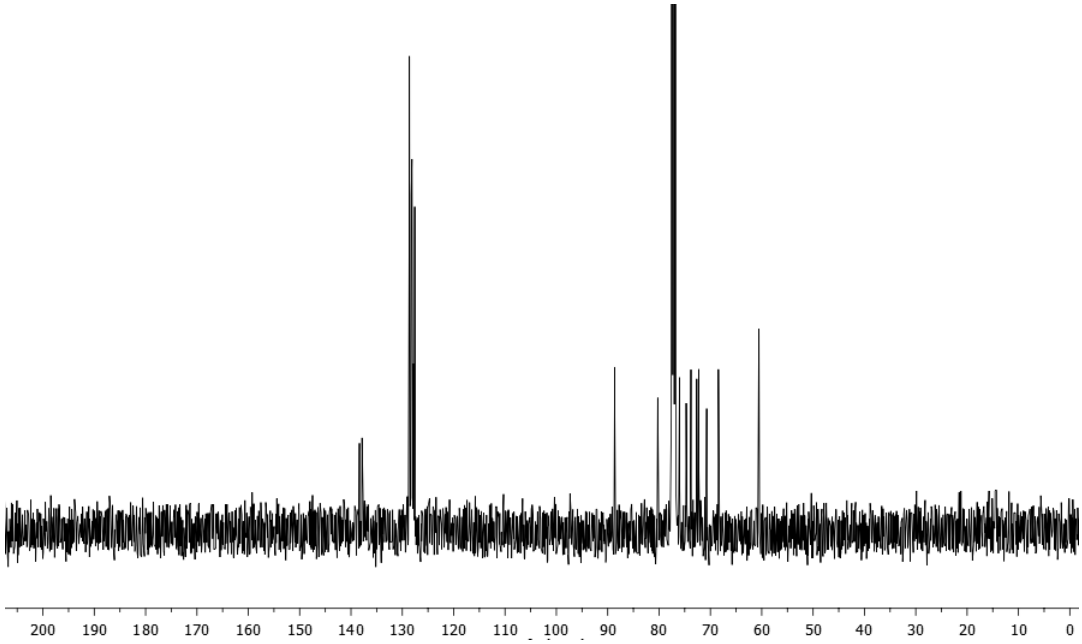
^{1}H NMR spectrum of compound **33**



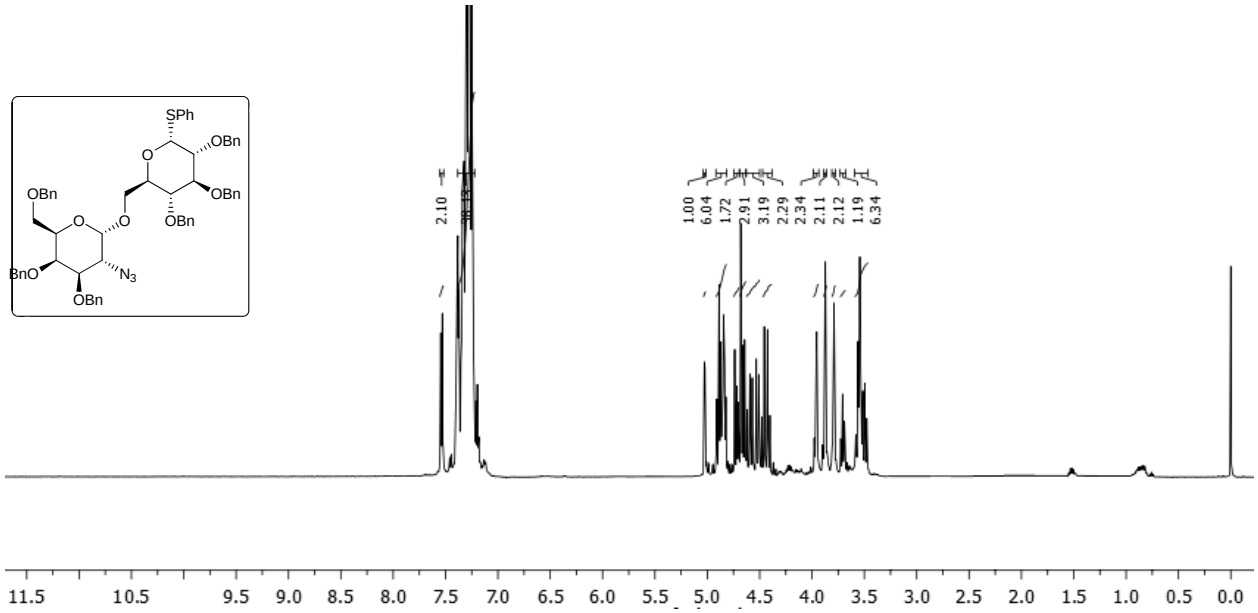
^{13}C NMR spectrum of compound **33**



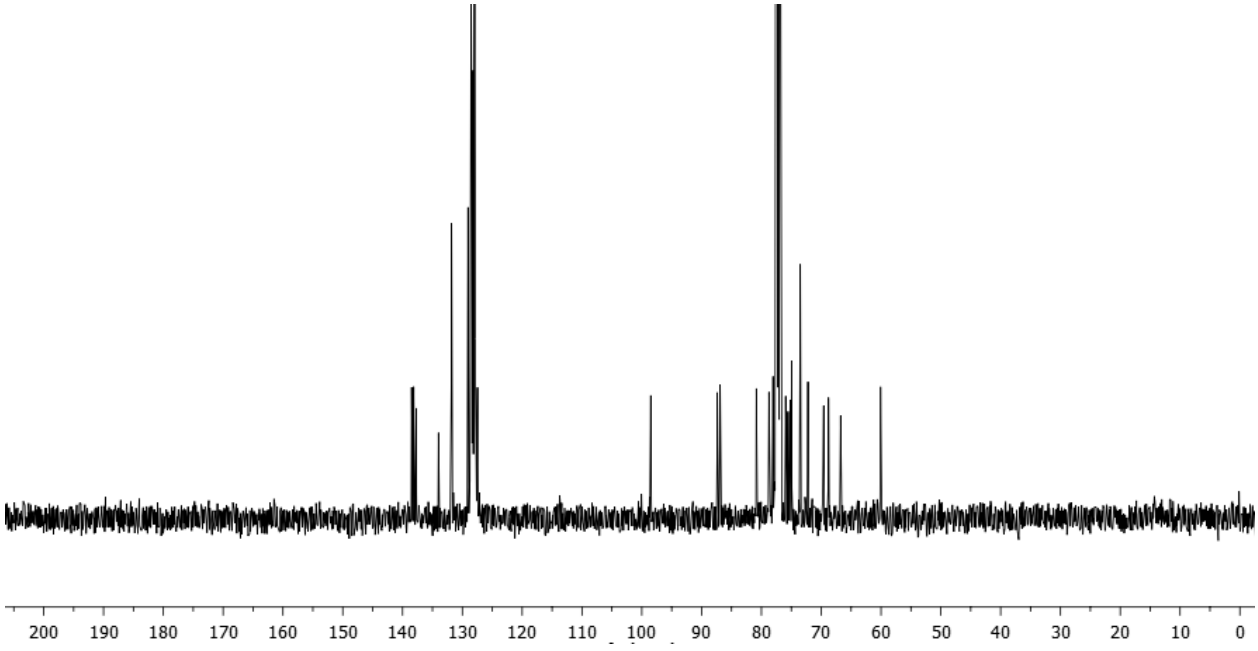
^{1}H NMR spectrum of compound **34**



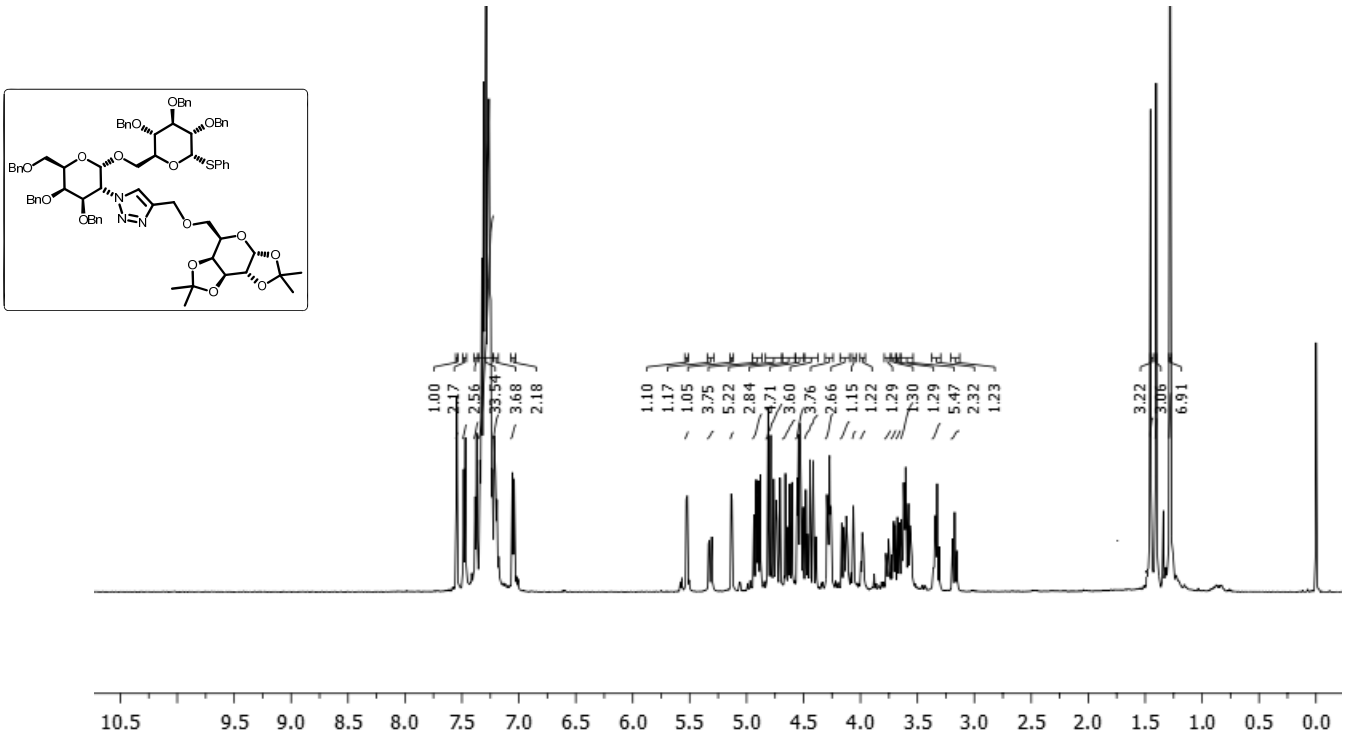
^{13}C NMR spectrum of compound **34**



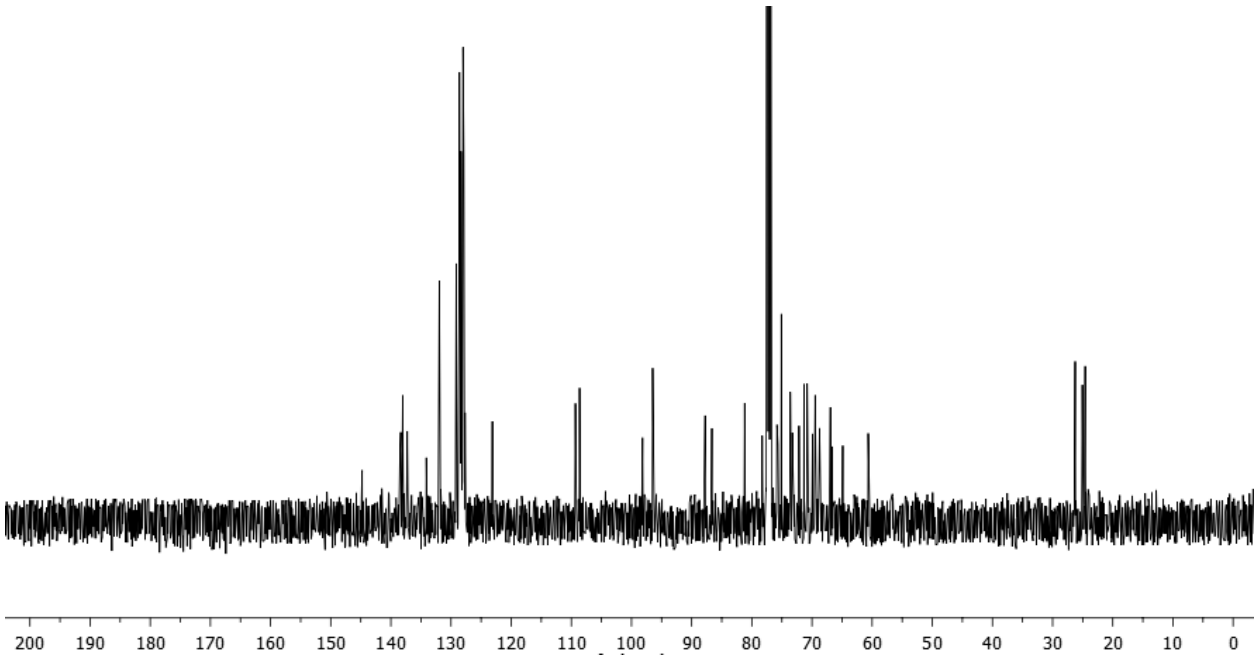
^{1}H NMR spectrum of compound **37**



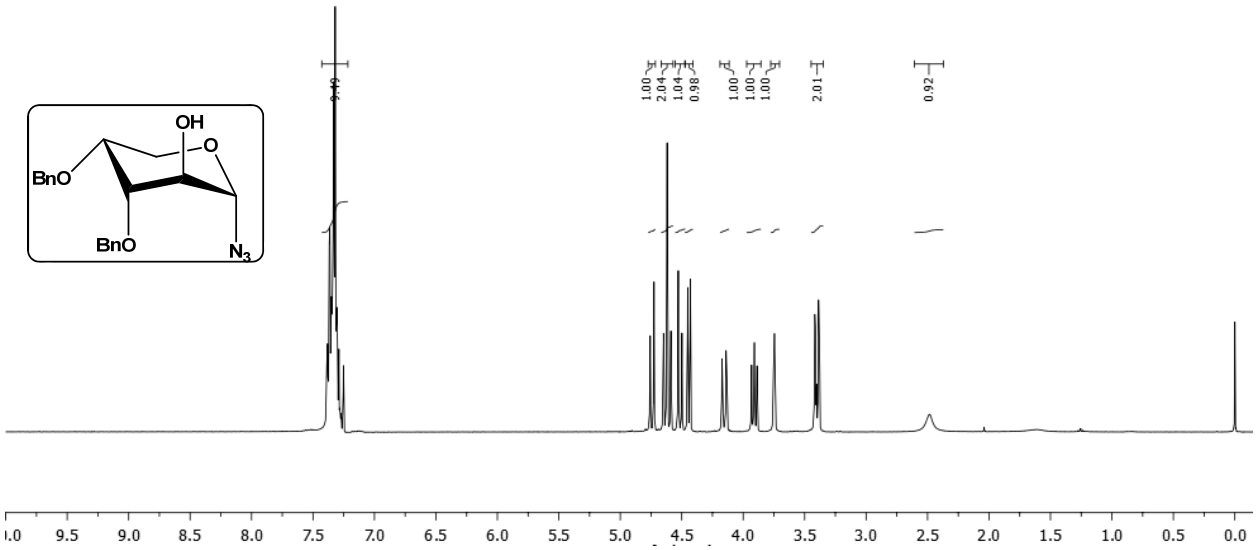
^{13}C NMR spectrum of compound **37**



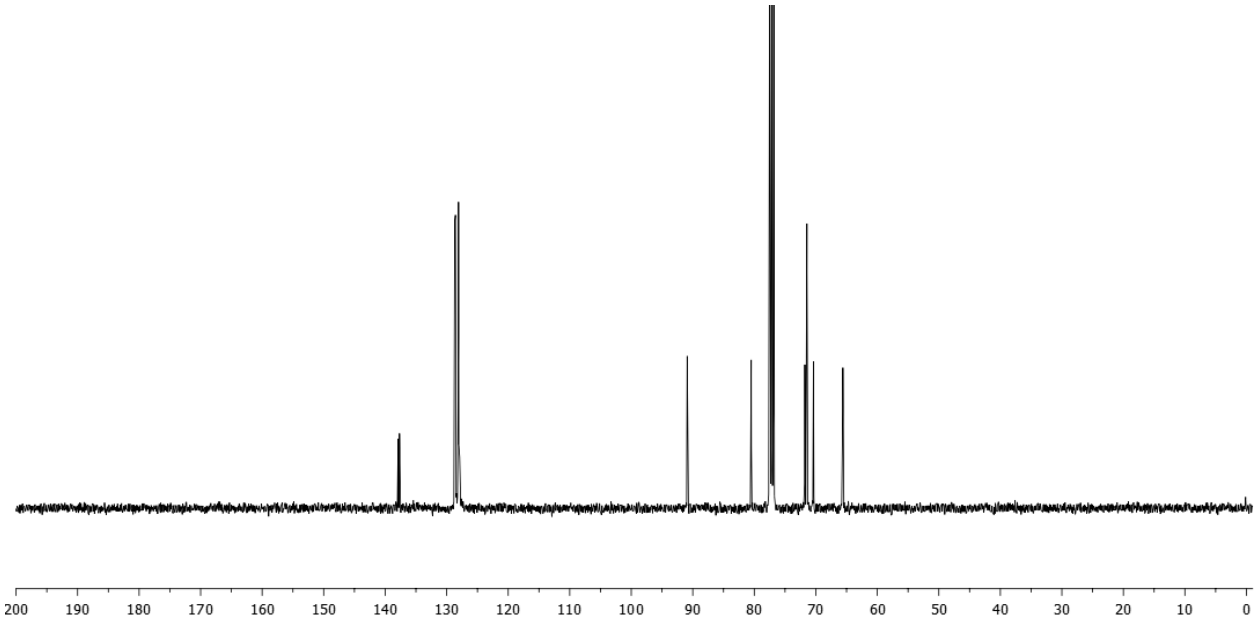
^{1}H NMR spectrum of compound **38**



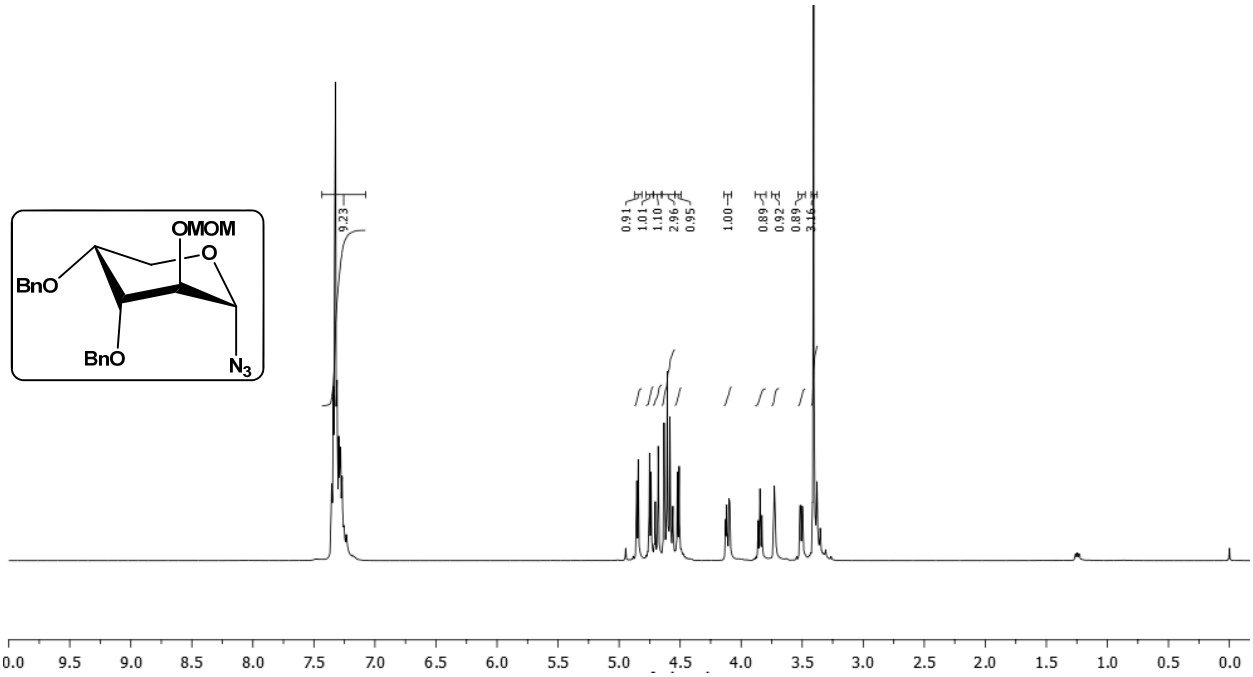
^{13}C NMR spectrum of compound **38**



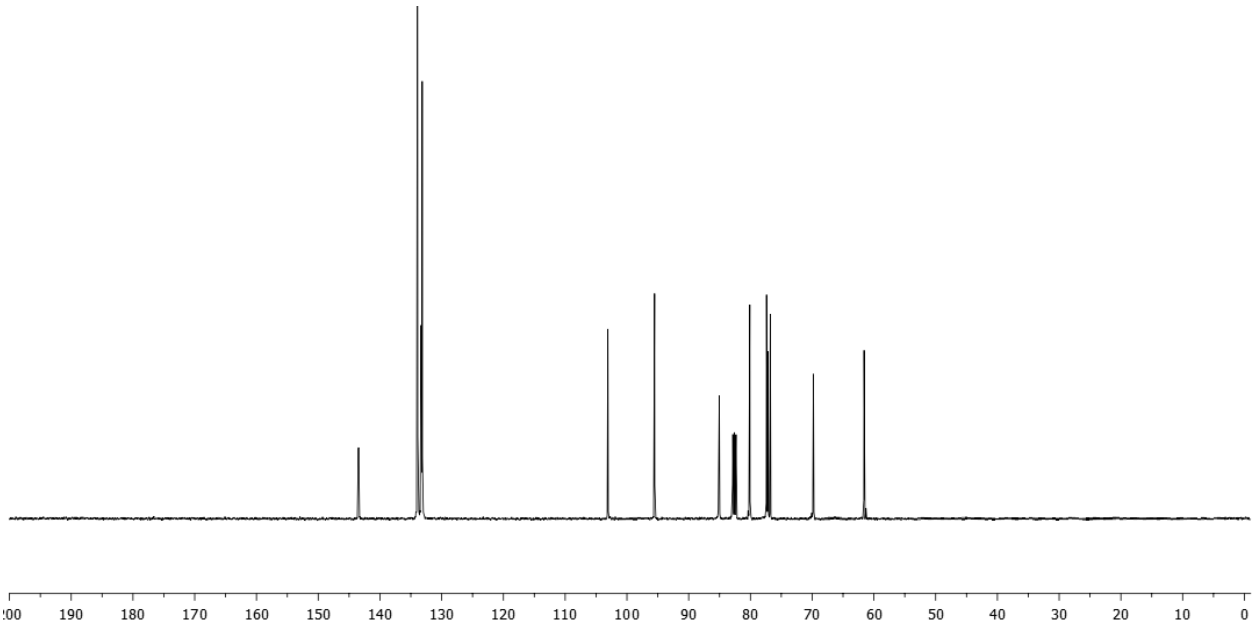
^{1}H NMR spectrum of compound **39**



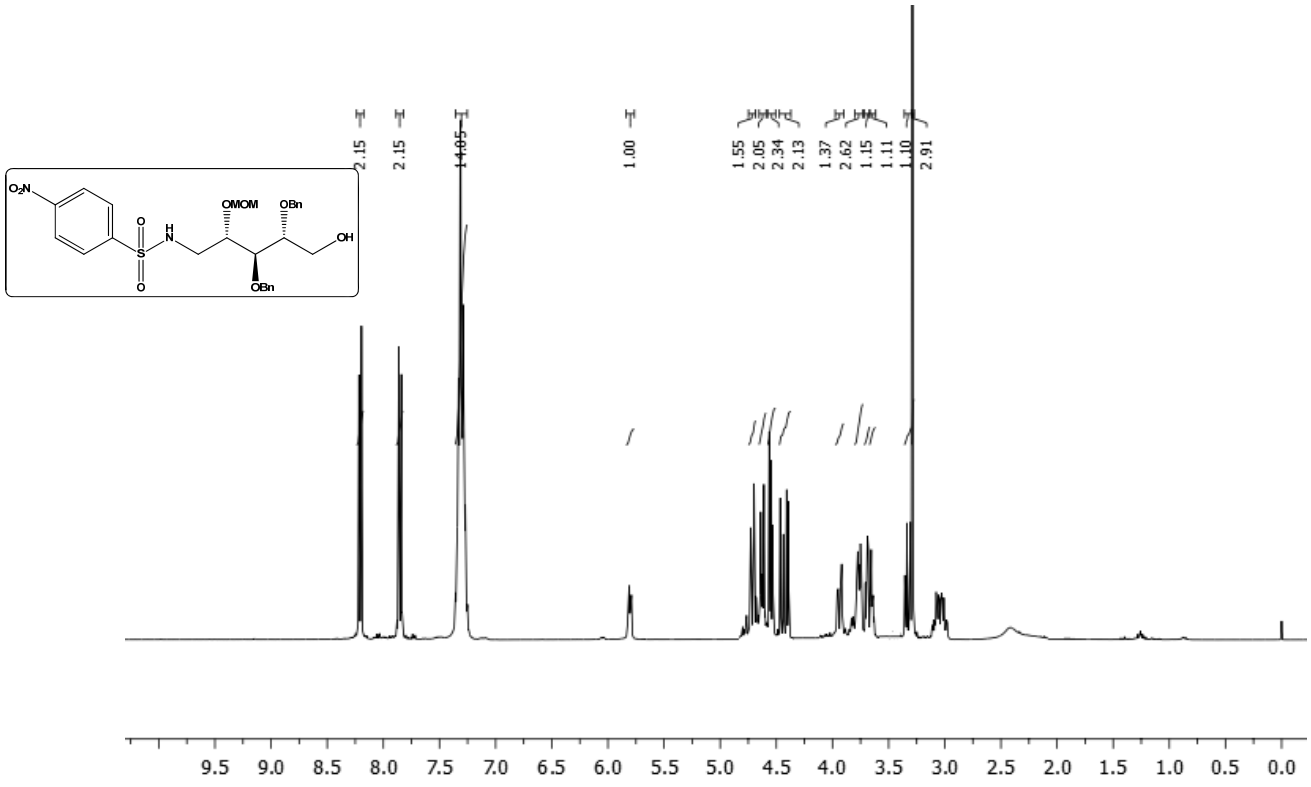
^{13}C NMR spectrum of compound **39**



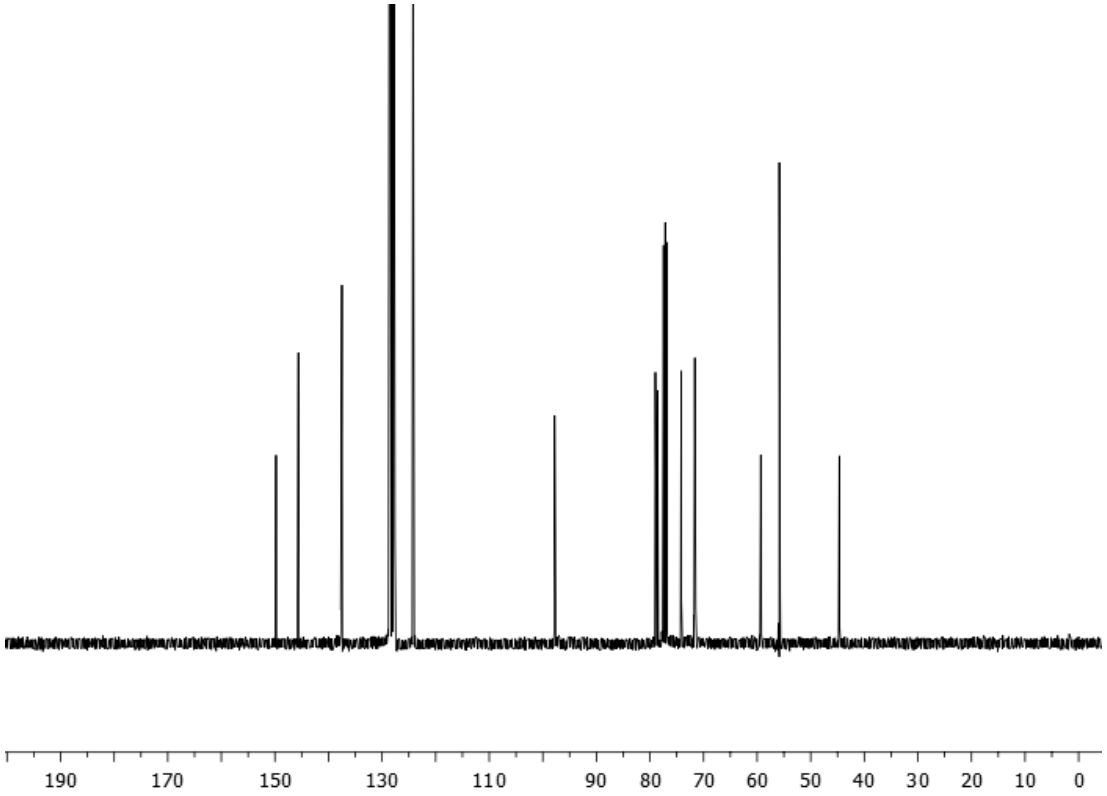
^{1}H NMR spectrum of compound **40**



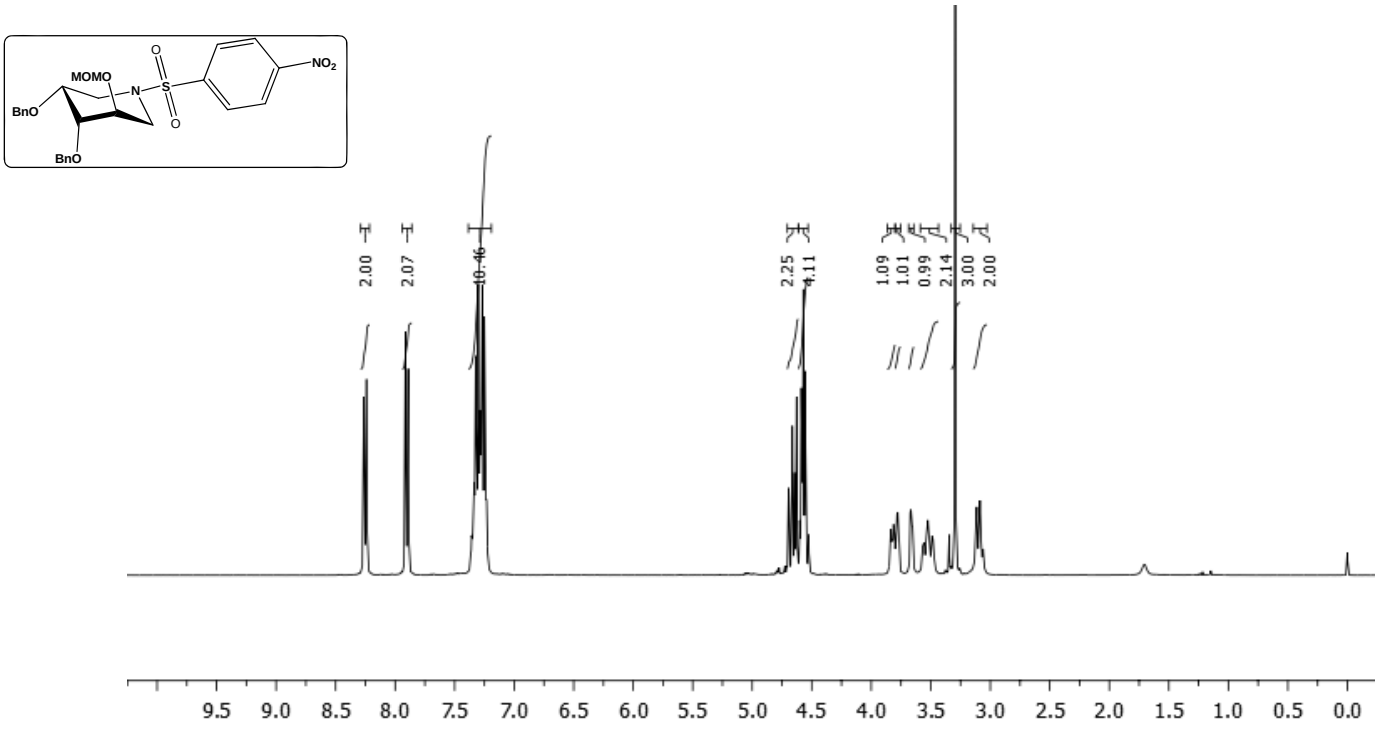
^{13}C NMR spectrum of compound **40**



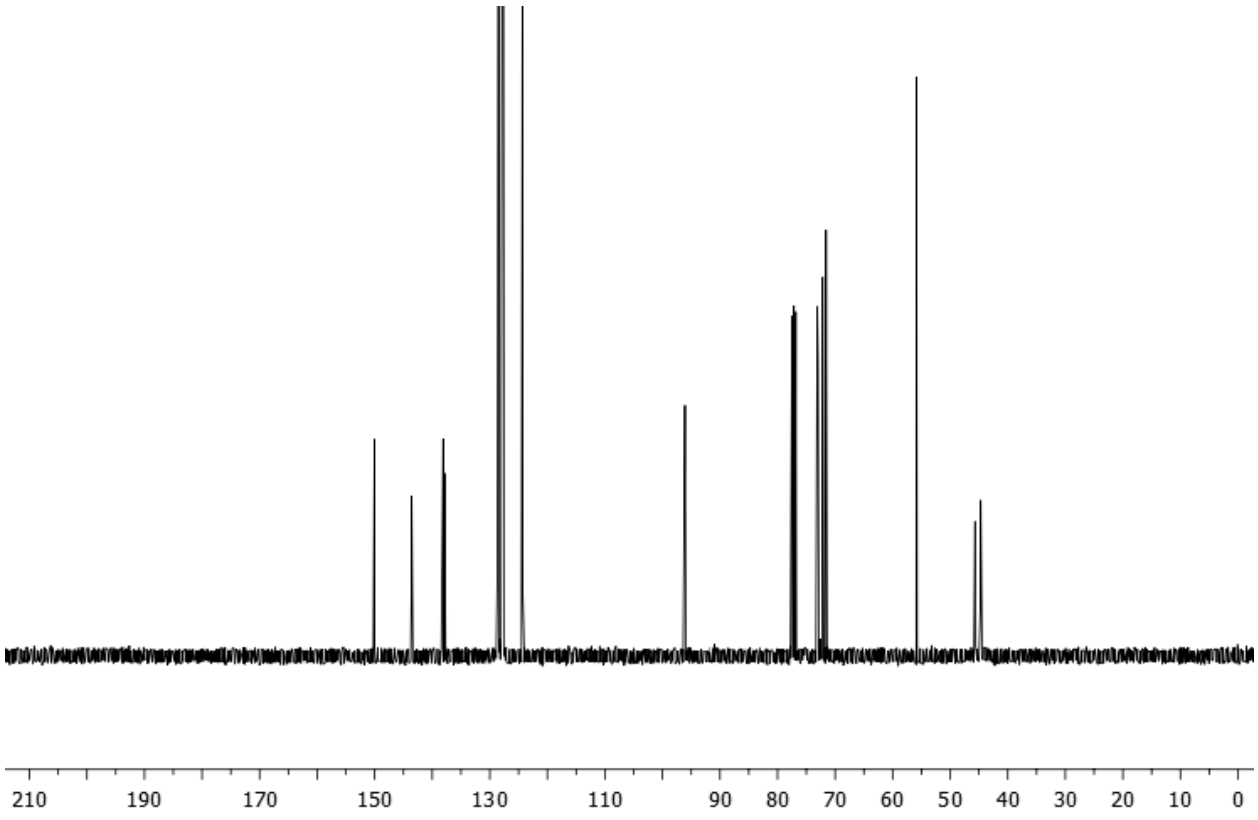
^{1}H NMR spectrum of compound **41**



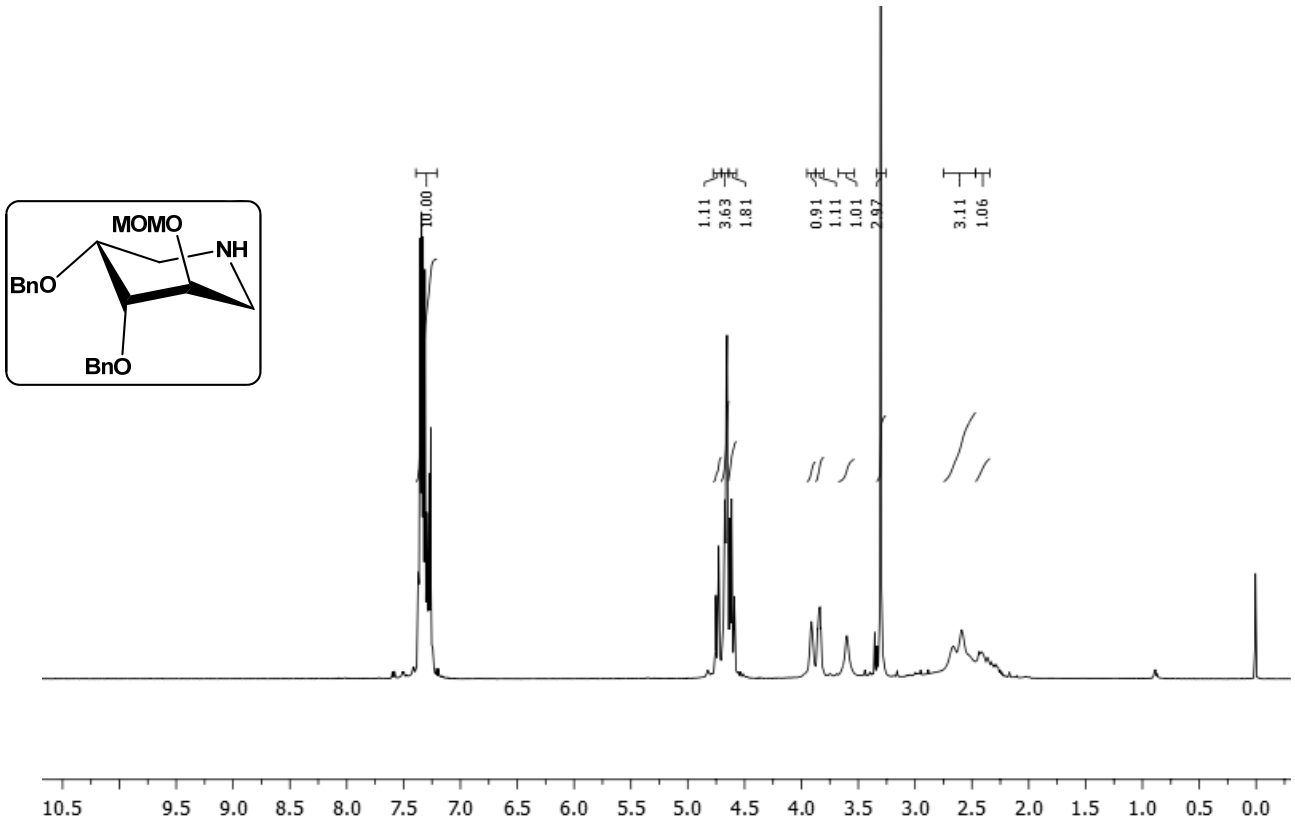
^{13}C NMR spectrum of compound **41**



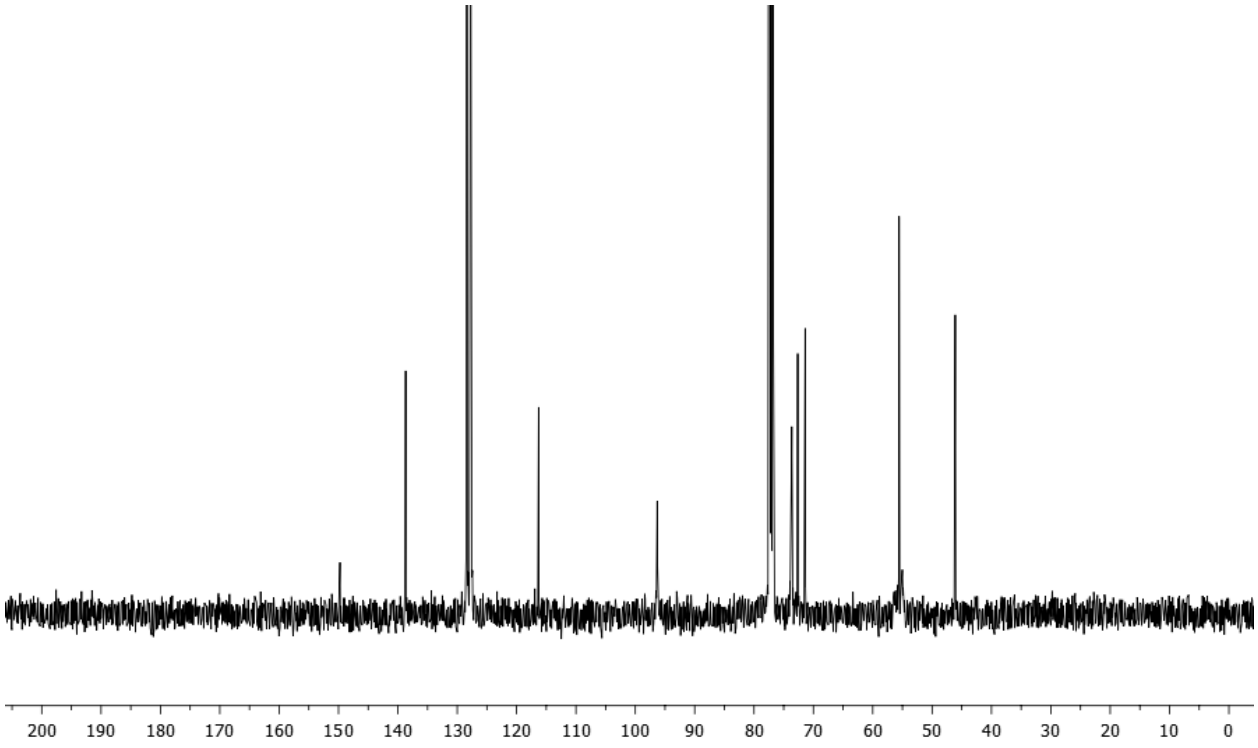
^{1}H NMR spectrum of compound **42**



^{13}C NMR spectrum of compound **42**



^{1}H NMR spectrum of compound **43**



^{13}C NMR spectrum of compound **43**

Crystallography.

Compounds **5** and **30** are readily crystallized by slow evaporation of its solution in $CDCl_3$ and $CHCl_3$ over a period of 72 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 ($\lambda = 0.71073$) 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.[1] Empirical absorption corrections were made using SADABS.[1] 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.[2] All the nonhydrogen 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.

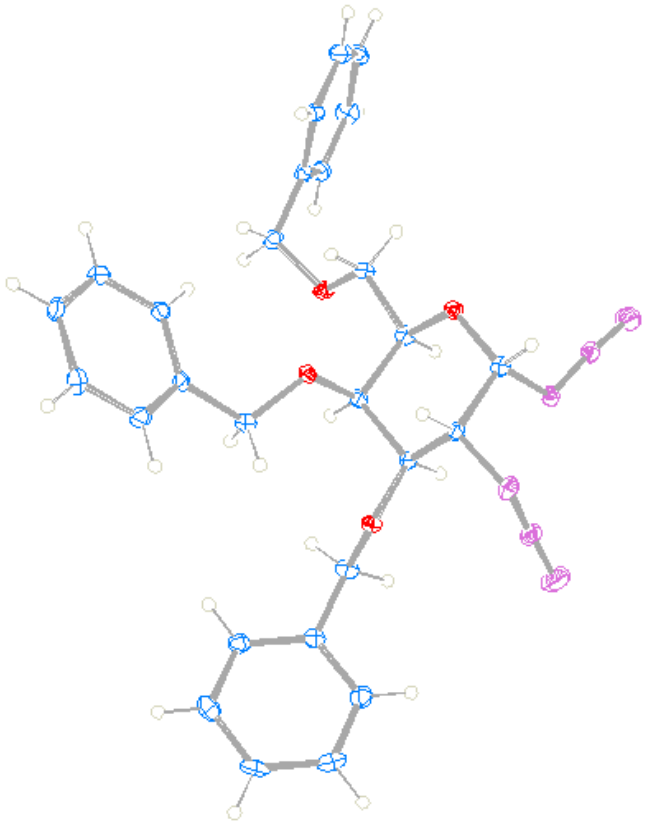


Figure 1: X-ray[3] ORTEP diagram showing 30% probability thermal ellipsoids of compound **5**

Table 1. Crystal data and structure refinement of compound **5**

Identification code	**5**	
Empirical formula	C27H28N6O4	
Formula weight	500.21	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 10.8746(7) Å	α= 90°.
	b = 9.3560(6) Å	β= 108.166(2)°.
	c = 12.7699(9) Å	γ = 90°.
Volume	1234.49(14) $Å^3$	
Z	2	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	464	
Theta range for data collection	1.97 to 27.00°.	
Index ranges	-13<=h<=13, -11<=k<=11, -15<=l<=16	
Reflections collected	11490	
Independent reflections	5368 [R(int) = 0.0399]	
Completeness to theta = 27.00°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5368 / 1 / 298	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.1058	
R indices (all data)	R1 = 0.0869, wR2 = 0.1278	
Absolute structure parameter	0.0(12)	
Largest diff. peak and hole	0.221 and -0.270 $e.Å^{-3}$	

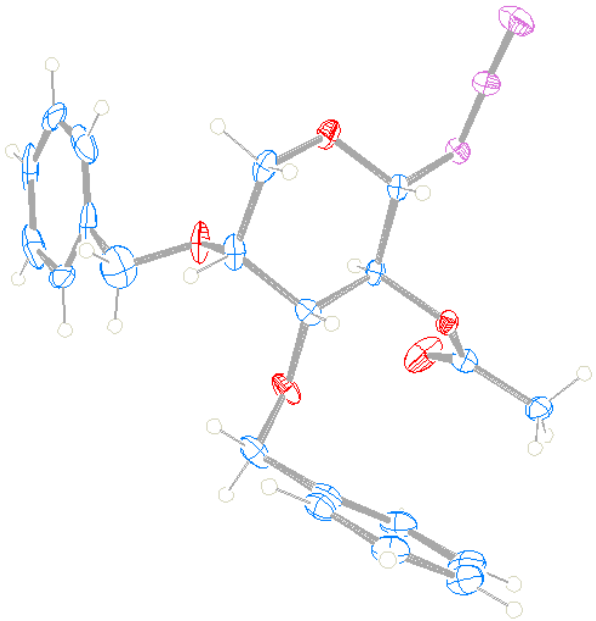


Figure 1: X-ray[4] ORTEP diagram showing 30% probability thermal ellipsoids of compound **29.** One $CHCl_3$ molecule have been omitted for clarity**.**

Table 2. Crystal data and structure refinement of compound **29**

Identification code	**29**	
Empirical formula	C21 H23 N3 O5,C1 H1 Cl3	
Formula weight	515.07	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.8335(4) Å	α= 90°.
	b = 14.0885(6) Å	β= 90°.
	c = 17.7805(9) Å	γ = 90°.
Volume	2463.30(19) $Å^3$	
Z	4	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	0.204 mm^{-1}	
F(000)	996	
Crystal size	0.2 x 0.16 x 0.14 mm^3	
Theta range for data collection	2.29 to 26.99°.	

Index ranges	-12<=h<=12, -17<=k<=17, -22<=l<=22
Reflections collected	22921
Independent reflections	5371 [R(int) = 0.0468]
Completeness to theta = 26.99°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5371 / 0 / 275
Goodness-of-fit on F^2	1.200
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1616
R indices (all data)	R1 = 0.0866, wR2 = 0.1772
Absolute structure parameter	0.07(9)
Largest diff. peak and hole	1.069 and -0.368 e.$Å^{-3}$

1) Bruker, SMART, SAINT-Plus, SADABS. Bruker Axs Inc. 1998 Madison, Wisconcin, USA

2) G. M. Sheldrick, Acta Cryst., 2015, C 71, 3.

3) CCDC 1554252 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

4) CCDC 1554251 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.