Supporting Information

Evidence of Robust Participation by equatorial 4-*O* group in glycosylation on a 2-Azido-2-deoxy-glucopyranosyl Donor

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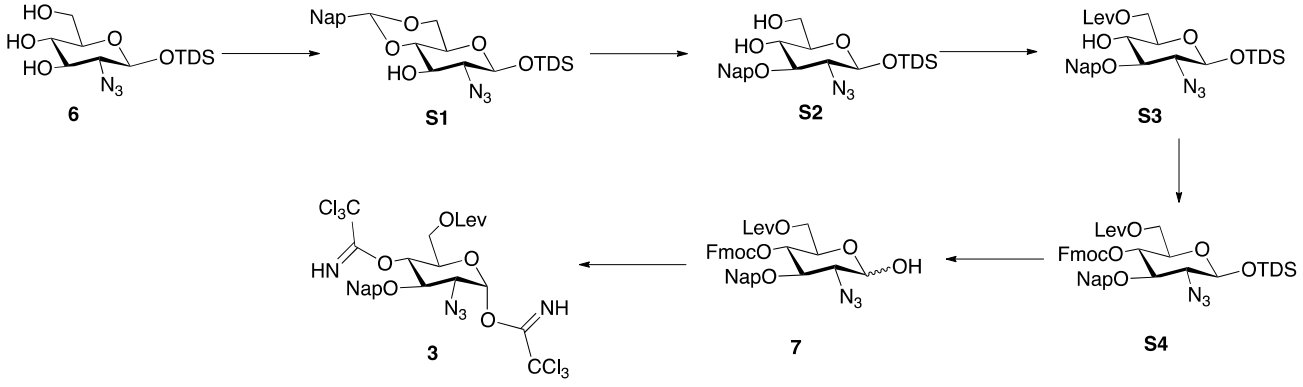
General procedures

^{1}H and ^{13}C (data from HSQC) NMR spectra were recorded on Varian Mercury 300 MHz, 400 MHz or Bruker 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) (δ = 0). NMR data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), integration. All NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, COSY, HSQC and HMBC experiments. Mass spectra were recorded on a Q-Tof Ultima Global mass spectrometer or a Shimadzu LCMS-IT-TOF mass spectrometer. TLC-analysis was performed on silica gel 60 F254 (EMD Chemicals Inc.) with detection by UV-absorption (254 nm) when applicable, and by spraying with a solution of $(NH_4)_6Mo_7O_{24}\cdot H_2O$ (25 g L^{-1}) in 5% sulfuric acid in ethanol followed by charring. All reactions were carried out under an argon atmosphere.



Scheme S1. Synthesis of compound **3**.

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Dimethylthexylsilyl 2-azido-2-deoxy-4,6-*O*-(2-methyl-naphthylidine)-β-D-glucopyranoside (S1)

To a solution of **6** (20.6 g, 59.3 mmol) in CH_3CN (250 mL), 2-(dimethoxymethyl)naphthalene (18.0 g, 89.0 mmol) and a catalytic amount of *p*-TsOH.H_2O (1.1 g, 6.0 mmol) were added. The reaction mixture was kept stirring at r.t. overnight. The reaction mixture was diluted with EtOAc (500 mL), washed with saturated aqueous $NaHCO_3$ solution (200 mL) and brine (200 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc: Hexane = 1:3) to afford **7** as a colorless oil (22.5 g, 87%). ^{1}H NMR (300 M, $CDCl_3$): δ7.99 – 7.84 (m, 7H, Ar-*H*), 5.60 (s, 1H, NapC*H*-), 4.49 (d, *J* = 7.3 Hz, 1H, H1), 4.26 (dd, *J* = 10.3, 5.0 Hz, 1H, H6a), 3.72 (t, *J* = 10.2 Hz, 1H, H6b), 3.52 – 3.38 (m, 2H, H3, H4), 3.32 – 3.20 (m, 2H, H2, H5), 1.78 – 1.64 (m, 1H), 0.96 – 0.93 (m, 12H, 4 × -CH_3), 0.22 (s, 3H, CH_3), 0.22 (s, 3H, CH_3). ^{13}C NMR (75 M, $CDCl_3$): δ 134.35, 133.80, 132.90, 128.41, 128.30, 127.77, 126.60, 126.31, 126.01, 123.79, 101.92 (Nap*C*H=), 97.36 (C1), 80.79, 71.71, 69.04, 68.53, 66.19, 33.95, 24.83, 19.99, 19.86, 18.56, 18.45, -2.11, -3.19. ESI-MS: m/z calcd for $C_{25}H_{35}N_3NaO_5Si^+$ $[M+Na]^+$ 508.2, found 508.2.

Dimethylthexylsilyl 2-azido-2-deoxy-3-*O*-(2-methyl-naphthyl)-β-D-glucopyranoside (S2)

To a solution of **7** (22.5 g, 51.7 mmol) in DMF (250 mL) at 0 °C was added 2-(bromomethyl)naphthalene (13.7 g, 62.0 mmol) and NaH (60% dispersion in oil, 2.5 g, 62.0 mol). The reaction mixture was kept stirring at r.t. for 5 h. Upon completion, the reaction mixture was quenched by adding saturated aqueous NH_4Cl solution (100 mL), and then diluted by ethyl acetate (500 mL). The organic phase was separated and then washed with brine (200 mL). The organic phase was separated, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid.

The above residue was dissolved in DCM (100 mL). To this solution, a fresh prepared DCM-TFA-H_2O solution (150 mL: 15 mL: 1.5 mL) was added at 0 °C. The reaction mixture was kept stirring at 0 °C. for 2 h. Upon completion, the reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ solution (150 mL) and then diluted by DCM (500 mL). The organic phase was separated and washed with brine (200 mL), and then was dried ($MgSO_4$) and concentrated in vacuo to form a yellow syrup. The syrup was purified by silica gel column chromatography (EtOAc: Hexane = 1:3) to afford **8** as a colorless oil (17.2 g, 68% over 2 steps). ^{1}H NMR (300 M, $CDCl_3$): δ 7.88 – 7.79 (m, 4H, Ar-*H*), 7.53 – 7.44 (m, 3H, Ar-*H*), 5.11 (d, *J* = 11.3 Hz, 1H, NapC*H*), 4.87 (d, *J* = 11.3 Hz, 1H, NapC*H*), 4.56 (d, *J* = 7.8 Hz, 1H, H1), 3.88 – 3.67 (m, 2H, H6a,b), 3.60 (t, *J* = 8.9 Hz, 1H, H4), 3.35 – 3.21 (m, 3H, H2, H3, H5), 2.63 (bs, 1H, 4-O*H*), 2.10 – 2.00 (m, 1H, 6-O*H*), 1.73 – 1.61 (m, 1H), 0.97 – 0.84 (m, 12H, 4 × -CH_3), 0.21 (s, 3H, CH_3), 0.19 (s, 3H, CH_3). ^{13}C NMR (75 M, $CDCl_3$): δ 135.42, 133.27, 133.09, 128.54, 127.94, 127.74, 126.93, 126.28, 126.11, 125.78, 97.03 (C1), 82.35,

75.04, 70.61, 68.51, 62.60, 33.90, 24.75, 19.96, 19.85, 18.48, 18.39, -2.03, -3.17. ESI-MS: m/z calcd for $C_{25}H_{37}N_3NaO_5Si^+$ $[M+Na]^+$ 510.2, found 510.2.

Dimethylthexylsilyl 2-azido-2-deoxy-3-*O*-(2-methyl-naphthyl)-6-*O*-levulinoyl-β-D-glucopyranoside (S3)

Compound **8** (12.2 g, 25.5 mmol), 2-Cl-1-methyl pyridinium iodide (16.3 g, 63.2 mmol) and levulinic acid (5.9 g, 50.8 mmol) were dissolved in DCM (250 mL). After stirred for 30 min, Dabco (10.9 g, 97.2 mmol) was added to the above solution. The reaction mixture was stirred at r.t. for 3 h. Upon completion, the reaction mixture was filtered to remove the solid. The filtration was concentrated to dryness. The residue was purified by silica gel column chromatography (EtOAc: Hexane = 1:4) to afford **9** as a colorless oil (13.9 g, 93%). ^{1}H NMR (300 M, $CDCl_3$): δ 7.89 – 7.79 (m, 4H, Ar-*H*), 7.55-7.44 (m, 3H, Ar-*H*), 5.08 (d, *J* = 11.8 Hz, 1H, NapC*H*-), 4.93 (d, *J* = 11.8 Hz, 1H, NapC*H*-), 4.52 (d, *J* = 7.6 Hz, 1H, H1), 4.38 – 4.24 (m, 2H, H6a,b), 3.51 (dd, *J* = 9.7, 8.2 Hz, 1H, H4), 3.41 – 3.35 (m, 1H, H5), 3.35 – 3.22 (m, 2H, H2, H3), 2.77 – 2.69 (m, 2H, -C*H*$_2$-), 2.62 – 2.53 (m, 2H, -C*H*$_2$-), 2.16 (s, 3H, -C*H*$_3$), 1.75 – 1.61 (m, 1H), 0.97 – 0.84 (m, 12H, 4 × -C*H*$_3$), 0.20 (s, 3H, -C*H*$_3$), 0.19 (s, 3H, -C*H*$_3$). ^{13}C NMR (75 M, $CDCl_3$): δ 206.68, 172.96, 135.45, 133.24, 133.04, 128.41, 127.92, 127.69, 126.92, 126.17, 126.01, 125.85, 97.03(C1), 82.02, 75.03, 73.60, 70.21, 68.30, 63.44, 37.87, 33.88, 29.77, 27.80, 24.79, 19.91, 19.83, 18.46, 18.36, -2.13, -3.31. ESI-MS: m/z calcd for $C_{30}H_{43}N_3NaO_7Si^+$ $[M+Na]^+$ 608.3, found 608.3.

Dimethylthexylsilyl 2-azido-2-deoxy-3-*O*-(2-methyl-naphthyl)-4-*O*-(9-fluorenylmethoxycarbonyl)-6-*O*-levulinoyl-β-D-glucopyranoside (S4)

To a solution of **9** (4.6 g, 7.8 mmol) in pyridine (50 mL) was added FmocCl (10.2 g, 39.3 mmol) and DMAP (95.3 mg, 0.78 mmol). The reaction mixture was stirred at r.t overnight. The reaction mixture was diluted with DCM (100 mL) and then washed with brine (50 mL × 3). The organic phase was separated, dried over $MgSO_4$ and concentrated in vacuo to form a yellow solid. The residue was purified by silica gel column chromatography (EtOAc: Hexane = 1:5) to afford **10** as a yellow oil (5.2 g, 82%). ^{1}H NMR (300 M, $CDCl_3$): δ 7.81 – 7.22 (m, 15H, Ar-*H*), 4.95 (d, *J* = 11.5 Hz, 1H, NapC*H*-), 4.85 (t, *J* = 8.6 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H, NapC*H*-), 4.55 (d, *J* = 7.0 Hz, 1H, H1), 4.43 (d, *J* = 10.2, 7.0 Hz, 1H, -OC*H*H-), 4.29 (d, *J* = 10.8, 7.0 Hz, 1H, -OCH*H*-), 4.22 – 4.16 (m, 2H, -OC*H*$_2$), 4.16 – 4.08 (m, 1H), 3.65 – 3.55 (m, 1H), 3.53 – 3.39 (m, 2H), 2.82 – 2.51 (m, 4H, 2 × -C*H*$_2$-), 2.17 (s, 3H, -C*H*$_3$), 1.75 – 1.63 (m, 1H), 0.98 – 0.86 (m, 12H, 4 × -C*H*$_3$), 0.23 (s, 3H, -C*H*$_3$), 0.22 (s, 3H, -C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.17, 172.13, 154.18, 143.03, 141.18, 134.93, 133.08, 132.90, 127.99, 127.83, 127.81, 127.55, 127.09, 126.54, 125.95, 125.81, 125.64, 124.97, 124.85, 119.96, 96.89, 79.81, 77.42, 77.00, 76.57, 74.97, 74.60, 71.51, 70.04, 68.23, 62.63, 46.56, 37.71,

33.87, 29.72, 27.69, 24.75, 19.89, 19.80, 18.42, 18.32, -2.21, -3.36. ESI-MS: m/z calcd for $C_{45}H_{53}N_3NaO_9Si^+$ $[M+Na]^+$ 830.3, found 830.2.

2-azido-2-deoxy-3-*O*-(2-methyl-naphthyl)-4-*O*-trichloroacetimidoyl-6-*O*-levulinoyl-D-glucopyranosyl trichloroacetimidate (3)

To a solution of **10** (4.2 g, 5.2 mmol) in pyridine (25 mL) at 0 °C was added HF.pyridine solution (70%, 10 mL). The reaction mixture was kept stirring at r.t. overnight. Upon completion, the reaction mixture was diluted with EtOAc (100 mL), washed with brine (100 mL) and saturated aqueous $NaHCO_3$ solution. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to form a syrup. The residue was purified by silica gel column chromatography (EtOAc: Hexane = 1:4) to afford **11** as a colorless oil (2.6 g, 76%).

To **11** (2.6 g, 3.9 mmol) in DCM (55 mL) at 0 °C was added trichloroacetonitrile (8.4 g, 58.4 mmol) and DBU (5.8 mg, 0.39 mmol). The reaction mixture was kept stirring at r.t. for 1 h. Upon completion, the reaction mixture was loaded to a silica gel column directly and purified by chromatography (EtOAc: Hexane = 1:4) to afford **3** as a white foam (2.6 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 14.6 Hz, 2H, 2 × N*H*-), 7.85 – 7.72 (m, 4H, Ar-*H*), 7.52 – 7.39 (m, 3H, Ar-*H*), 6.47 (d, *J* = 3.6 Hz, 1H, H1), 5.61 (t, *J* = 9.6 Hz, 1H, H4), 5.03 (d, *J* = 10.7 Hz, 1H, NapC*H*-), 4.98 (d, *J* = 10.8 Hz, 1H, NapC*H*-), 4.37 – 4.17 (m, 4H, H6a,b, H3, H5), 3.86 (dd, *J* = 10.1, 3.6 Hz, 1H, H2), 2.76 – 2.68 (m, 2H, -CH_2-), 2.65 – 2.53 (m, 2H, -CH_2-), 2.17 (s, 3H, -CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.57 (*C*=O), 171.55 (*C*=O), 160.95 (N=*C*), 159.91 (N=*C*), 133.96, 132.59, 132.46, 127.55, 127.33, 127.04, 126.23, 125.48, 125.40, 125.14, 93.57 (C1), 90.19 (-CCl_3), 90.09 (-*C*Cl_3), 77.27 (C3), 74.66 (Nap*C*H_2-), 73.61 (C4), 70.19 (C5), 62.11 (C2), 61.27 (C6), 37.12 (-*C*H_2-), 29.24 (-*C*H_3), 27.17 (-*C*H_2-)； ESI-MS: m/z calcd for $[M+H]^+$ 730.0, found 730.0; $[M+Na]^+$ 752.0, found 752.0.

Synthesis of 4 and 8: general procedure

Bistrichloroacetimidate **3** (30 mg, 0.05 mmol) was dissolved in the indicated solvent (4 mL) as described in Table 1 and cooled to 0 °C. 4 Å molecular sieves (fresh activated) and catalyst (0.l equiv.) was then added. The reaction mixture was stirred at 0 °C for 3 h and then quenched with Et_3N. The solvent was evaporated and the residue was purified by silica gel column chromatography (EtOAc: toluene = 1:10 to 1:3) to afford **4** and **8** as foamy solids.

Data for **4**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.69 (m, 4H, Ar-*H*), 7.47 – 7.36 (m, 3H, Ar-*H*), 5.27 (dd-like, 1H, *J* = 2.1, 1.2 Hz, H-4), 4.81 (d, *J* = 11.9 Hz, 1H, NapC*H*-), 4.78 (d, *J* = 11.9 Hz, 1H, NapC*H*-), 4.71 (t, 1H, *J* = 6.9 Hz, H5), 4.51 (s, 1H, H1), 4.28 (dd, 1H, H6a, *J* = 11.5, 6.7 Hz), 4.24 (dd, 1H, H6a, *J* = 11.5, 6.7 Hz),

4.04 (s-like, 2H, H2, H3), 2.64 – 2.57 (m, 2H, -CH_2-), 2.51-2.43 (m, 2H, -CH_2-), 2.06 (s, 3H, CH_3C=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3 (*C*=O), 172.1 (*C*=O), 154.7 (*C*=NH), 133.35, 133.2, 133.1, 128.7, 128.0, 127.8, 127.3, 126.5, 126.4, 125.6, 80.2 (C4), 77.4 (C3), 75.8 (C1), 74.8 (C5), 72.7 (Nap*C*H_2-), 68.0 (C2), 62.9 (C6), 37.7 (-*C*H_2-), 29.7 (*C*H_3C=O), 27.7(-*C*H_2-); ESI-HRMS: m/z calcd. for $C_{24}H_{23}Cl_3N_4NaO_6^+$ $[M+Na]^+$ 591.0575, found 591.0575.

Data for **8**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 15.1 Hz, 3H, -N*H*), 7.87 – 7.69 (m, 12H, Ar-*H*), 7.54 – 7.34 (m, 9H, Ar-*H*), 5.50 – 5.34 (m, 5H, α/β-H4, α-H1), 5.07 – 4.85 (m, 6H, α/β-NapCH_2-), 4.71 (d, *J* = 7.7 Hz, 1H, β-H1), 4.40 (ddd, *J* = 10.2, 6.7, 2.2 Hz, 2H, α-H5), 4.33 (dd, *J* = 12.0, 2.2 Hz, 2H, α-H6a), 4.30 – 4.22 (m, 4H, α-H3, β-H6a,b), 4.19 (dd, *J* = 12.0, 6.7 Hz, 2H, α-H6b), 3.98 (s-like, 1H), 3.82 – 3.76 (m, 1H), 3.71 (t, *J* = 9.5 Hz, 1H, β-H3), 3.58 (dd, *J* = 10.0, 3.5 Hz, 2H, α-H2), 3.54 (dd, *J* = 9.8, 8.0 Hz, 1H, β-H2), 2.83 – 2.69 (m, 6H, α/β-CH_2-), 2.65 – 2.52 (m, 6H, α/β-CH_2-), 2.19 (s, 9H, α/β-CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.66 (α-*C*=O), 207.08 (β-*C*=O), 172.31 (O*C*=O), 172.27(O*C*=O), 161.92 (α-*C*=NH), 161.70 (β-*C*=NH), [134.94, 133.26, 133.06, 129.03, 128.62, 128.22, 128.11, 127.97, 127.66, 126.70, 126.64, 126.08, 126.03, 125.96, 125.92, 125.77, 125.72, 125.30], 96.30 (β-C1), 91.95 (α-C1), 91.01 (-*C*Cl_3), 80.71 (β-C3), 77.97 (α-C3), 75.44 (α-C4), 75.35 (β-Nap*C*H-), 75.29 (α-Nap*C*H-), 74.68 (β-C4), 72.37 (β-C5), 67.90 (α-C5), 67.24 (β-C2), 63.77 (α-C2), 62.66 (α-C6), 62.42 (β-C6), 38.22 (α-CH_2-), 37.89 (β-CH_2), 29.89 (α-CH_3-), 29.70(β-CH_3), 28.08 (α-CH_2-), 27.95 (β-CH_2-); ESI-MS: m/z $[M+H]^+$ found 587.1, 589.1, 591.1, 593.1; $[M+Na]^+$ found 609.1, 611.1; ESI-HRMS: m/z calcd. for $C_{24}H_{25}Cl_3N_4O_7^+$ $[M+H]^+$ 587.0862, found 587.0863.

Dodecyl

2-azido-2-deoxy-3-*O*-(2-methyl-naphthyl)-4-*O*-trichloroacetimidoyl-6-*O*-levulinoyl-β-D-glucopyranoside (11)

Bistrichloroacetimidate **3** (50 mg, 0.07 mmol) and dodecyl alcohol (65 mg, 0.35 mmol) were dissolved in dry DCM (2 mL). 4 Å molecular sieves (fresh activated) were then added and the reaction mixture was stirred at r t for 30 min. The reaction mixture was cooled to 0 °C and TMSOTf (1.6 mg, 0.007 mmol) was added. The reaction mixture was stirred at 0 °C for 3 h and then quenched with saturated aqueous $NaHCO_3$ solution (1 mL). The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous $NaHCO_3$ solution (10 mL) and brine (10 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to form a syrup. The residue was purified by silica gel column chromatography (EtOAc: Toluene = 1:6) to afford **11** as a colorless oil (24 mg, 47%) and **4** (16 mg, 41%) as a foamy solid.

Data for **11**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (s, 1H, -N*H*), 7.86 – 7.70 (m, 4H, Ar-*H*), 7.51 – 7.36 (m, 3H, Ar-*H*), 5.42 (t, *J* = 9.5 Hz, 1H, H4), 4.98 (d, *J* = 10.9 Hz, 1H, NapC*H*-), 4.90 (d, *J* = 10.9 Hz, 1H, NapC*H*-), 4.36 (d, *J* = 8.1 Hz, 1H, H1), 4.30 – 4.20 (m, 2H, H6ab), 3.93 (dt, *J* = 9.4, 6.5 Hz, 1H, OC*H*H-), 3.73 (dt, *J* = 10.0, 3.9 Hz, 1H, H5), 3.65 (t, *J* = 9.5 Hz, 1H, H3), 3.60 – 3.51 (m, 2H, H2, OCH*H*-), 2.79 – 2.69 (m, 2H, Lev-CH_2-), 2.66 – 2.52 (m, 2H, Lev-CH_2-), 2.18 (s, 3H, Lev-CH_3), 1.73 – 1.62 (m, 2H, lipid-CH_2-), 1.44 – 1.36 (m, 2H, lipid-CH_2-), 1.35 – 1.19 (m, 16H, lipid-CH_2-), 0.88 (t, *J* = 7.0 Hz, 3H, lipid-CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.29 (*C*=O), 172.34 (*C*=O), 161.63 (*C*=N), 135.07, 133.23, 133.04, 128.06, 127.94, 127.66, 126.54, 126.04, 125.90, 125.71, 102.17 (C1), 90.96 (-*C*Cl_3), 80.67 (C3), 75.21 (Nap*C*H_2-), 74.57 (C4), 72.15 (C5), 70.61 (lipid-O*C*H_2-), 66.06 (C2), 62.60 (C6), 37.81 (Lev-*C*H_2-), 31.93, 29.88, 29.79, 29.67, 29.65, 29.61, 29.57, 29.53, 29.48, 29.41, 29.36, 27.89 (Lev-*C*H_2-), 25.92, 22.70, 14.12 (lipid-*C*H_3); ESI-MS: m/z $[M+H]^+$ found 755.3, 757.3, 759.3; ESI-HRMS: m/z calcd. for $C_{36}H_{50}Cl_3N_4O_7^+$ $[M+H]^+$ 755.2740, found 755.2744.

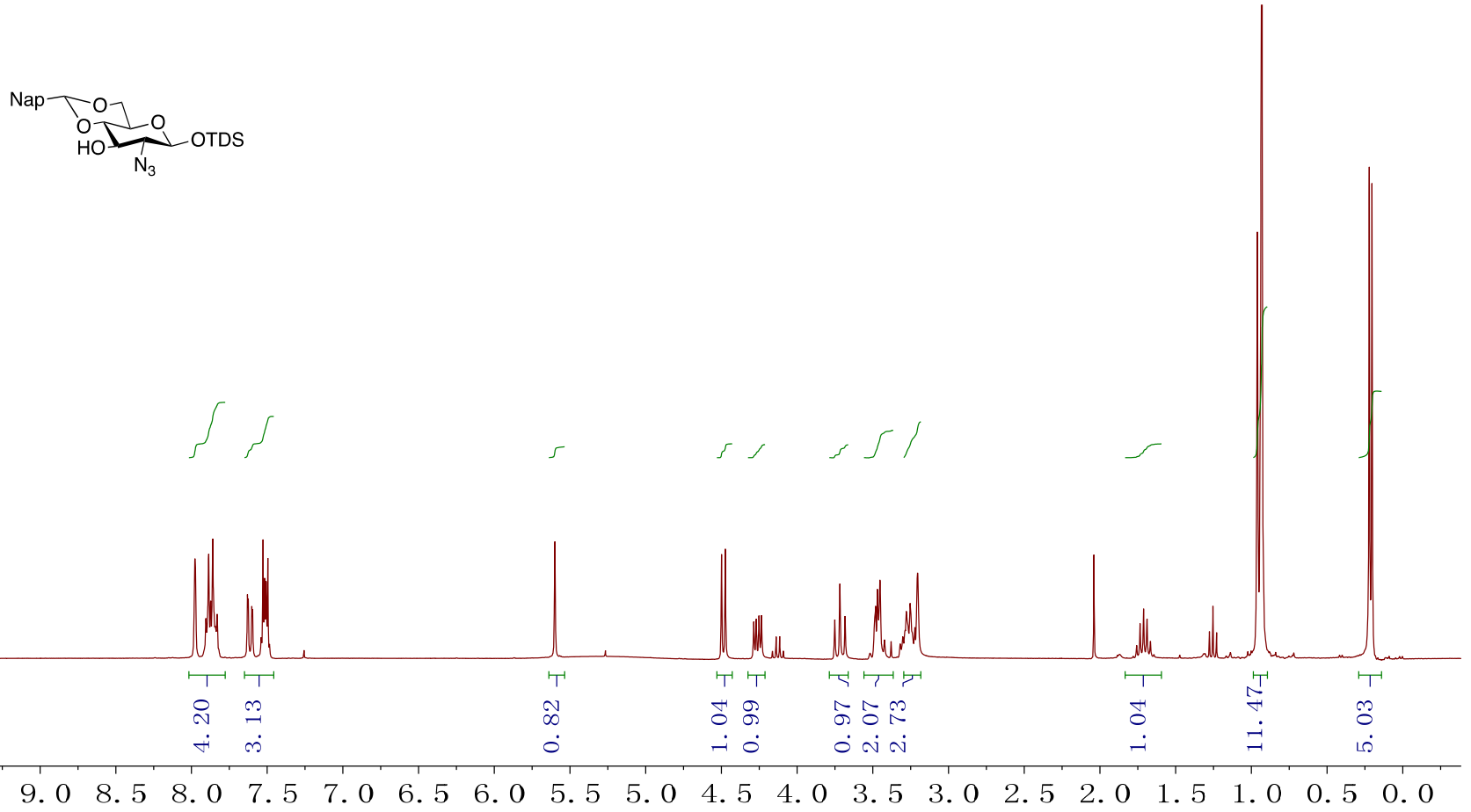
Synthesis of 13:

Compound **4** (30 mg, 0.05 mmol) was dissolved in CH_3ONa methanol solution (*p*H = 9) and the reaction mixture was stirred at r.t. for 3 h. Dowex 50 resin was added to neutralize the reaction. After removal of resin and solvent, the residue was purified by silica gel column chromatography (EtOAc: hexane = 1:3) to afford **13** as a colorless oil (25 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 4H, Ar-*H*), 7.52 (m, 2H, Ar-*H*), 7.47 (dd, *J* = 8.4,1.7 Hz, 1H, Ar-*H*), 5.39 – 5.35 (m, 1H, H4), 4.90 (d, 1H, *J* = 11.8 Hz, 1H, NapC*H*-), 4.88 (d, *J* = 11.8 Hz, 1H, NapC*H*-), 4.68 (dd, *J* = 6.0 Hz, 1H, H5), 4.58 (bs, 1H, H1), 4.16 (bs, 2H, H2, H3), 3.88 – 3.76 (m, 2H, H6a,b), 2.16 (dd, *J* = 8.6, 3.9 Hz, 1H, 6-O*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.82, 133.35, 133.19, 133.11, 128.93, 127.97, 127.82, 127.64, 126.62, 125.60, 91.73, 80.35, 77.55, 77.44, 76.67, 73.04, 68.25, 62.41; ESI-HRMS: m/z calcd. for $C_{19}H_{18}Cl_3N_4O_4^+$ $[M+H]^+$ 471.0388, found 471.0390.

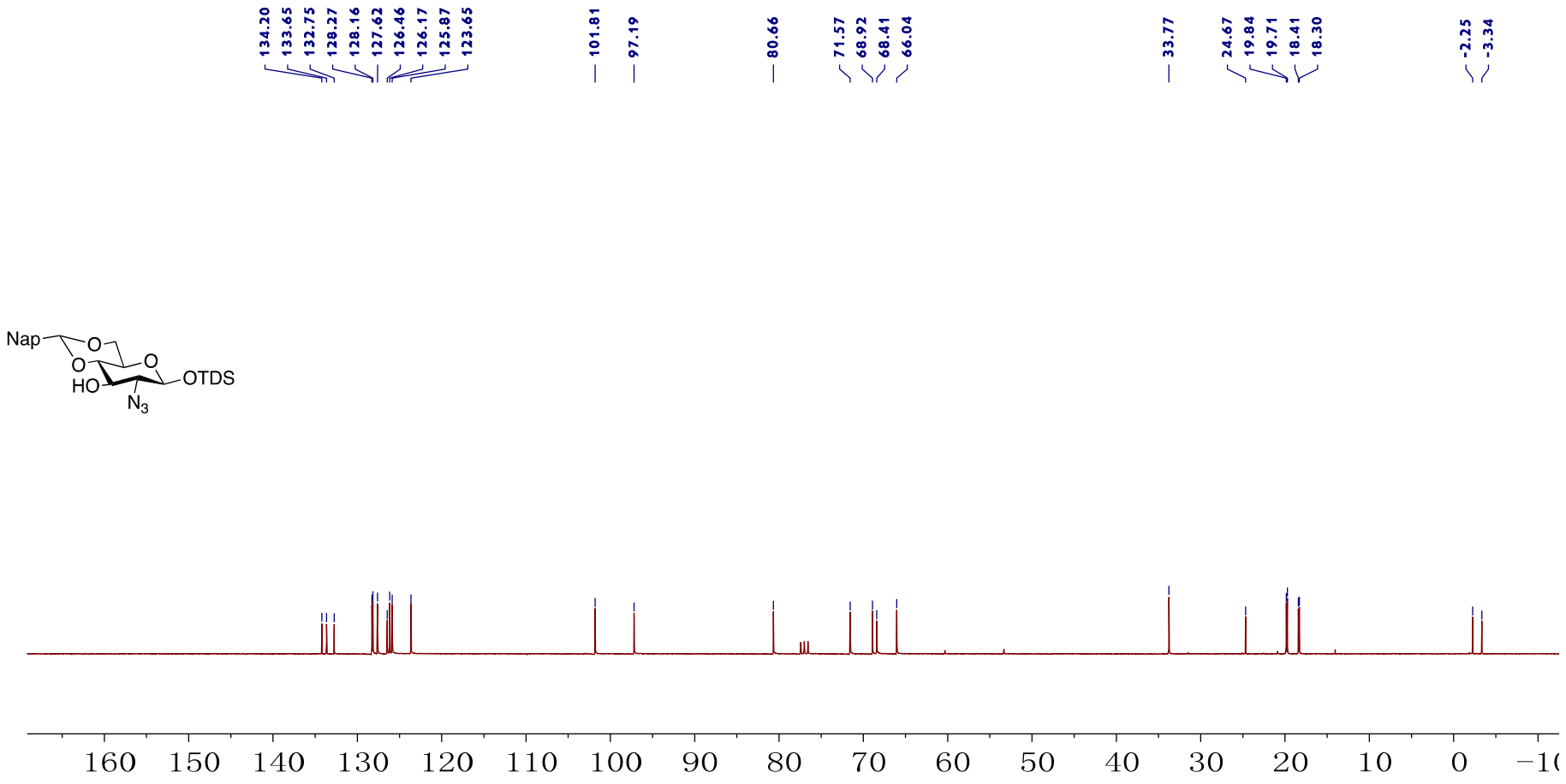
Synthesis of 14:

Compound **4** (30 mg, 0.05 mmol) was dissolved in toluene/TFA (1:10, 1.1 mL) and the reaction mixture was stirred at r.t. for 3 h. Saturated aqueous $NaHCO_3$ solution (1 mL) was added to the above reaction mixture to quench the reaction. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous $NaHCO_3$ solution (10 mL) and brine (10 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to form a syrup. The residue was purified by silica gel column chromatography (EtOAc: Toluene = 1:4) to afford **14** as a colorless oil (22 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.69 (m, 4H, Ar-*H*), 7.53 – 7.35 (m, 3H, Ar-*H*), 5.17 (t, *J* = 9.7 Hz, 1H, H4), 5.05 (d, *J* = 10.8 Hz, 1H, NapC*H*-), 4.88 (d, *J* = 10.8 Hz, 1H, NapC*H*-), 4.28 (dd, *J* = 12.3, 2.3 Hz, 1H, H6a), 4.19 (dd, *J* = 12.3, 4.7 Hz, 1H, H6b), 4.13 (d, *J* = 9.2 Hz, 1H, H1), 3.78 – 3.71 (m, 1H, H5), 3.66 (t, *J* = 9.4 Hz, 1H, H3), 3.34 (t, *J* = 9.3 Hz, 1H, H2), 2.85 – 2.69 (m, 2H,

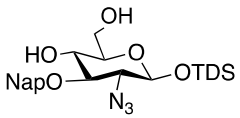
-C*H*$_2$-), 2.69 – 2.55 (m, 2H, -CH$_2$-), 2.19 (s, 3H, -CH$_3$), 2.19-2.05 (bs, 2H, -N*H*$_2$, exchangeable with D$_2$O); ^{13}C NMR (151 MHz, CDCl$_3$) δ 206.32 (*C*=O), 172.25 (O*C*=O), 160.83 (Cl$_3$C-*C*=O), 134.58, 133.25, 133.09, 128.26, 128.23, 128.01, 127.67, 126.64, 126.13, 126.03, 125.57, 89.48 (Cl$_3$*C*), 85.94 (C1), 80.94 (C3), 75.55 (Nap*C*H$_2$-), 74.81 (C4), 72.36 (C5), 67.71 (C2), 62.22 (C6), 37.85 (-*C*H$_2$-), 29.83 (-*C*H$_3$), 27.84 (-*C*H$_2$-); ESI-MS: m/z [M+H]$^+$ found 587.1, 589.1, 591.1, 593.1; [M+Na]$^+$ found 609.1, 611.1; ESI-HRMS: m/z calcd. for $C_{24}H_{25}Cl_3N_4O_7^+$ [M+H]$^+$ 587.0862, found 587.0865.

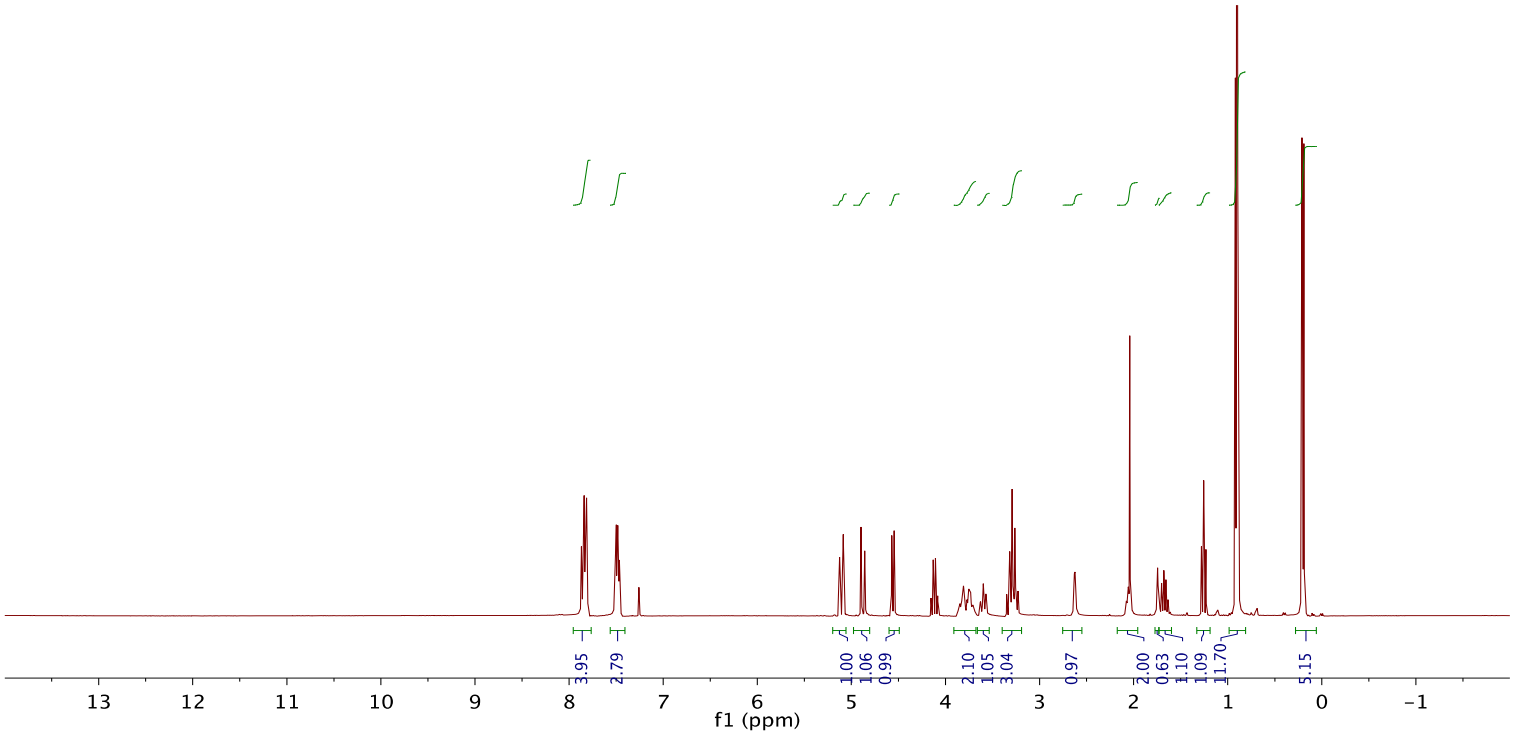


^{1}H NMR of **S1** (300 M, $CDCl_3$)

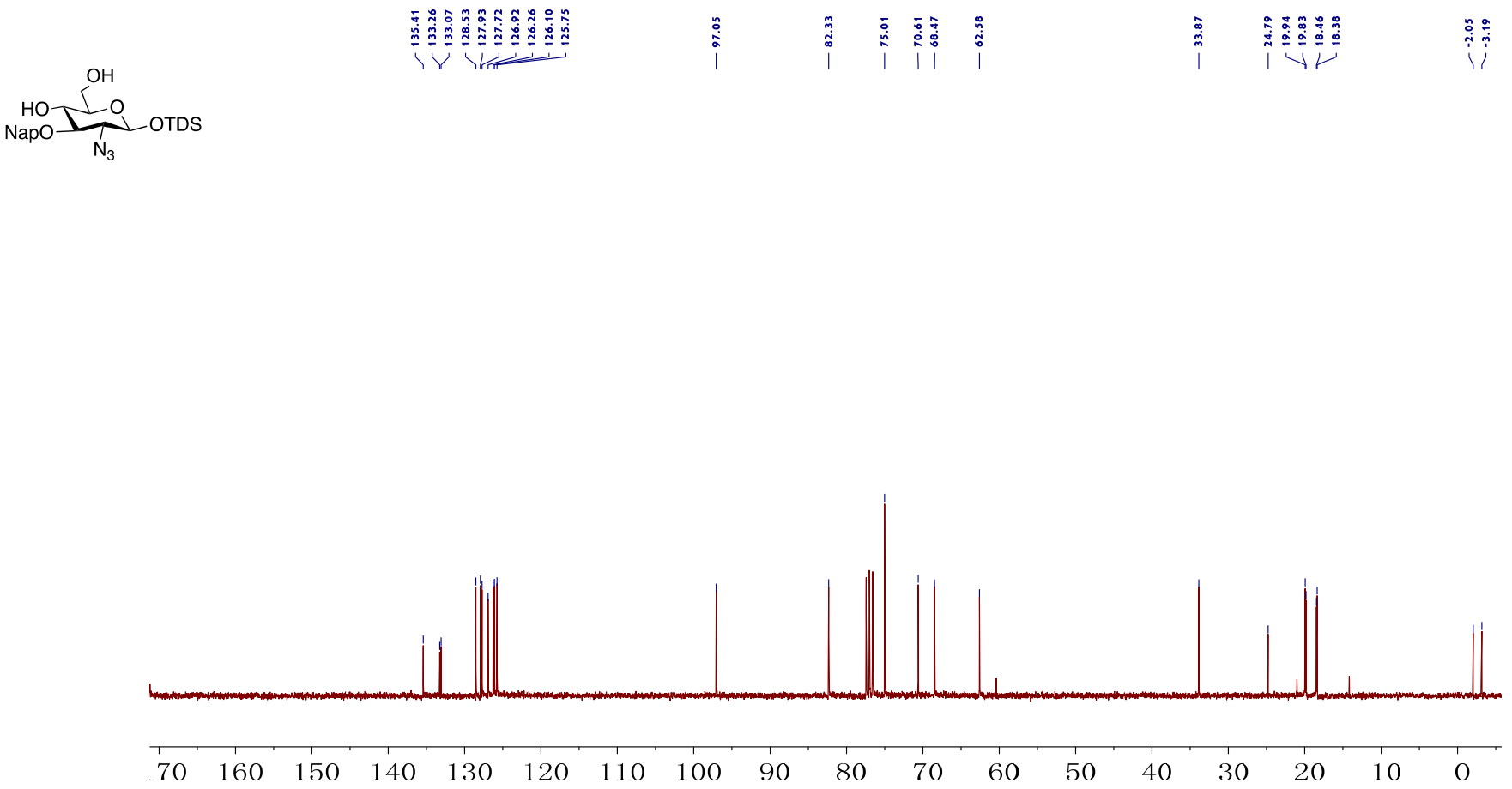


^{13}C NMR of **S1** (75 M, $CDCl_3$)

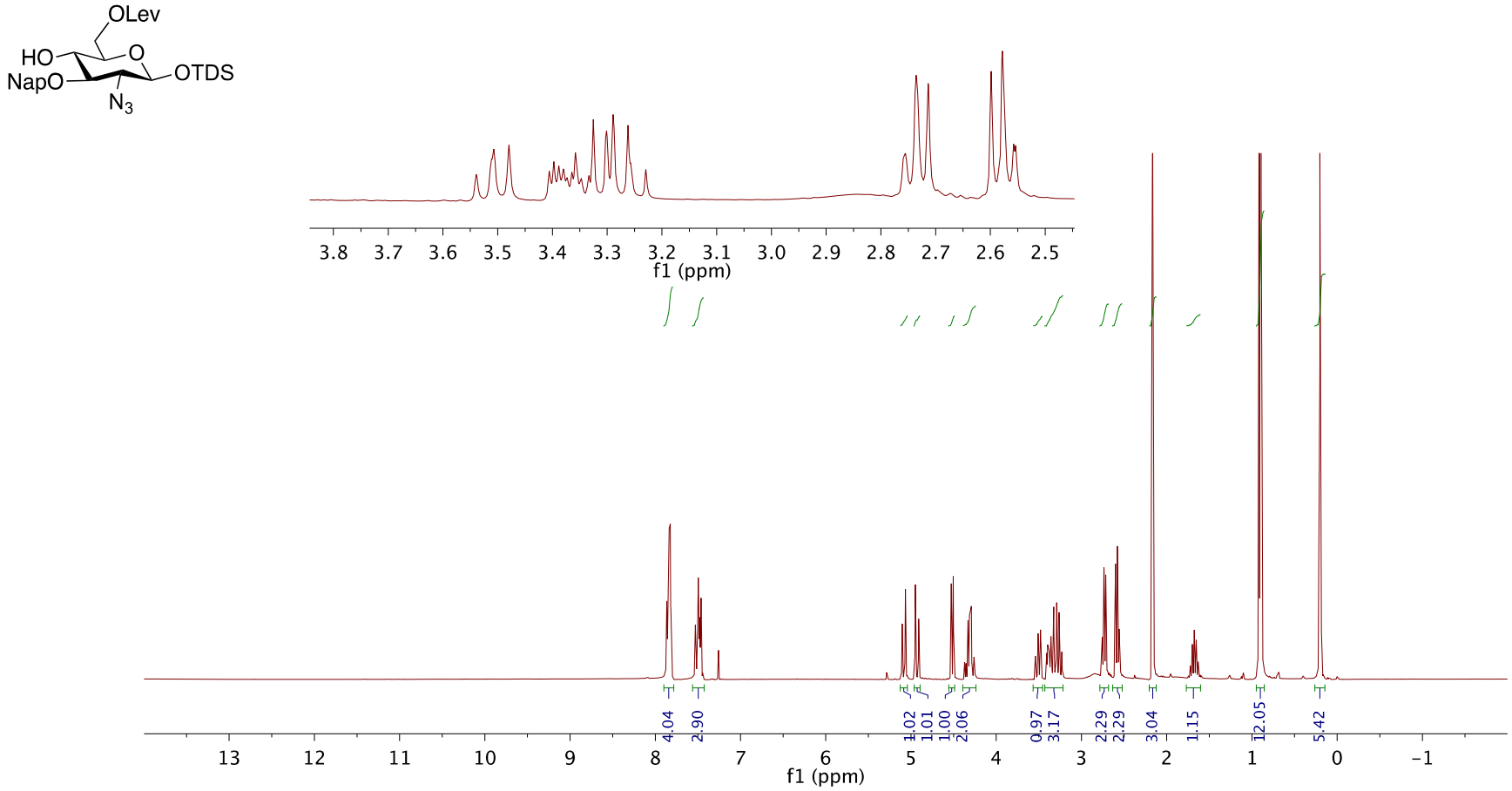




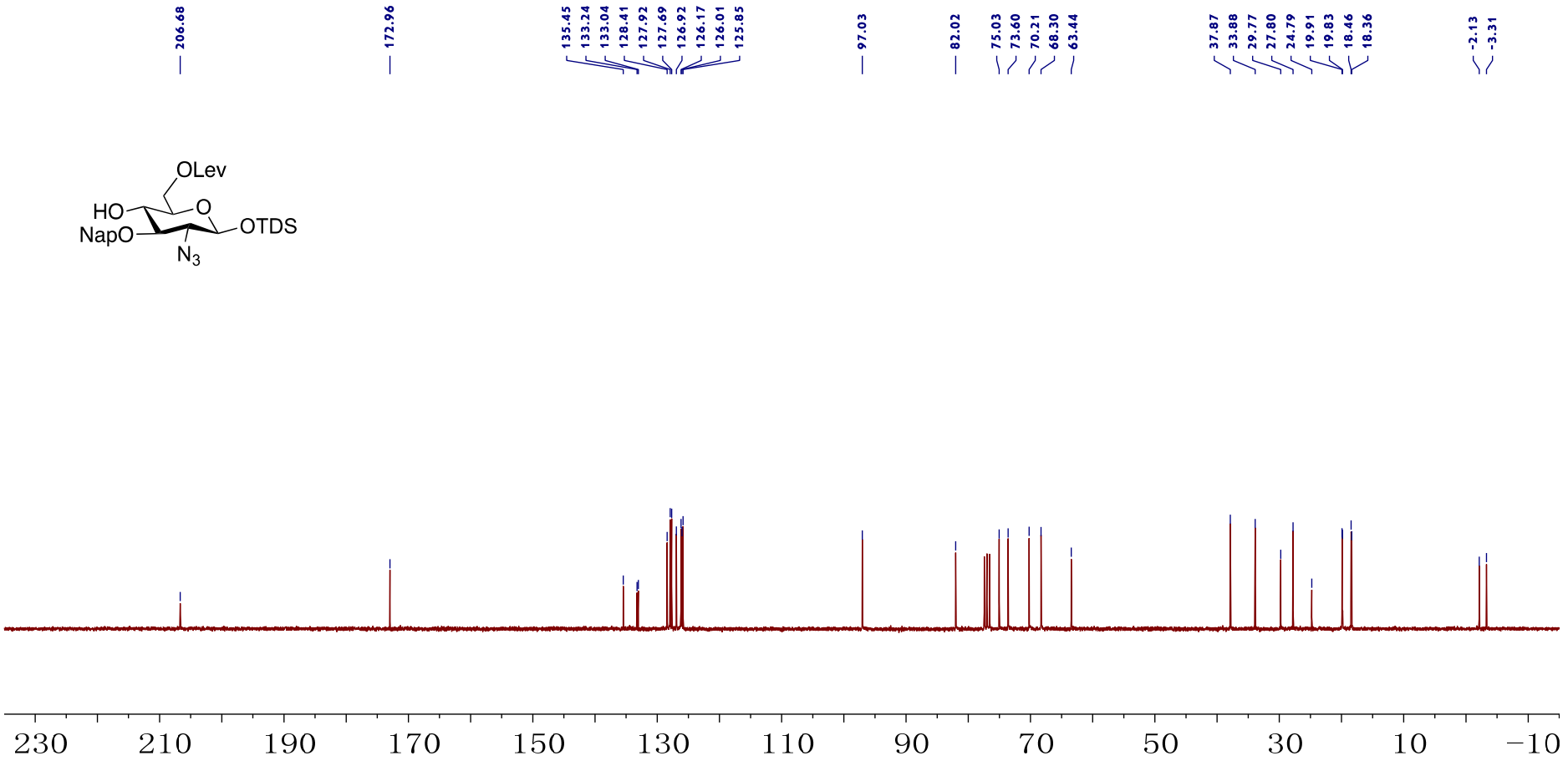
^{1}H NMR of **S2** (300 M, $CDCl_3$)



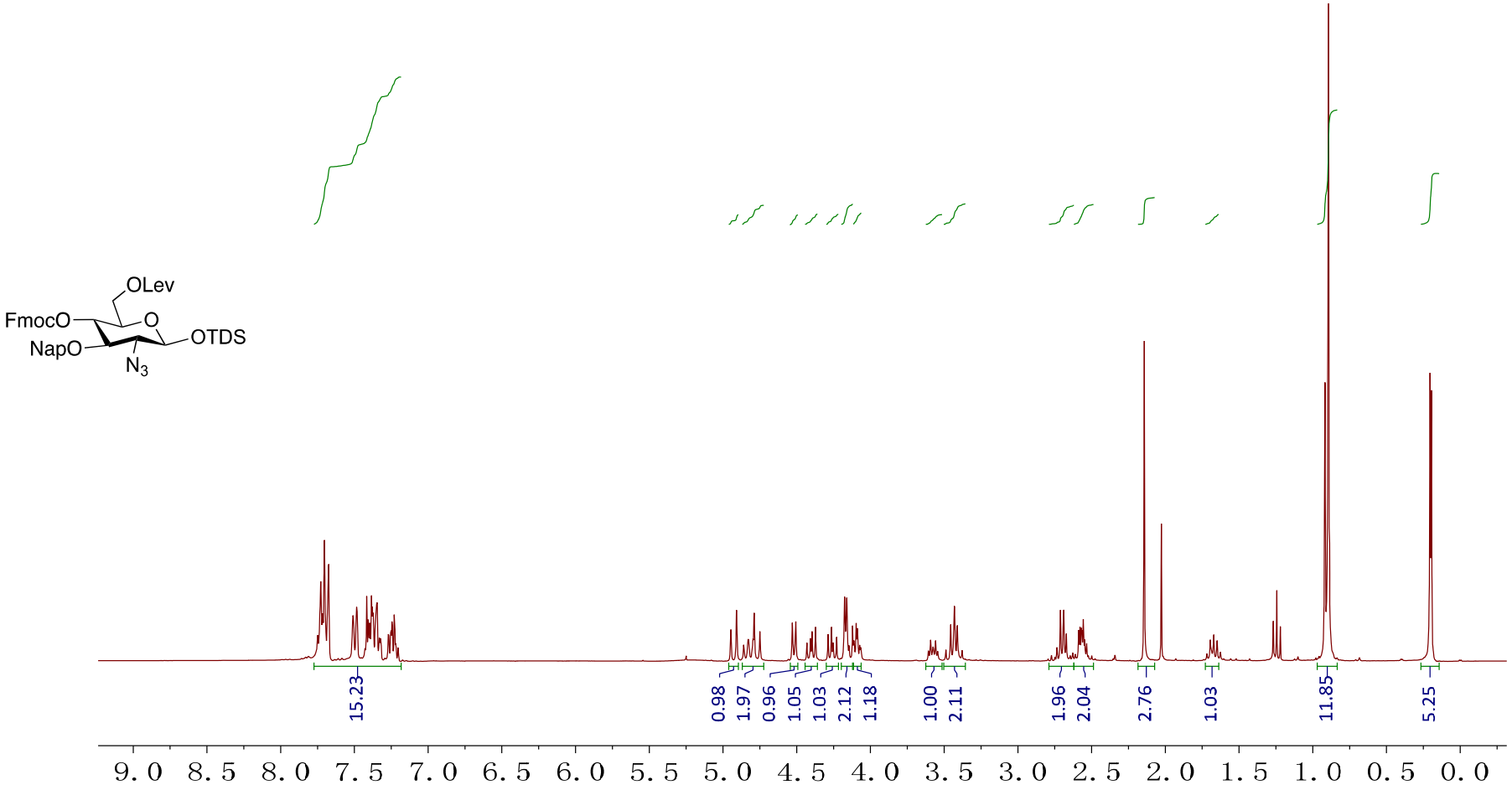
^{13}C NMR of **S2** (75 M, $CDCl_3$)


OLev
HO
O
NapO
OTDS
N3
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5
f1 (ppm)
4.04 2.90 1.02 1.01 1.00 2.06 0.97 3.17 2.29 2.29 3.04 1.15 12.05 5.42
13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

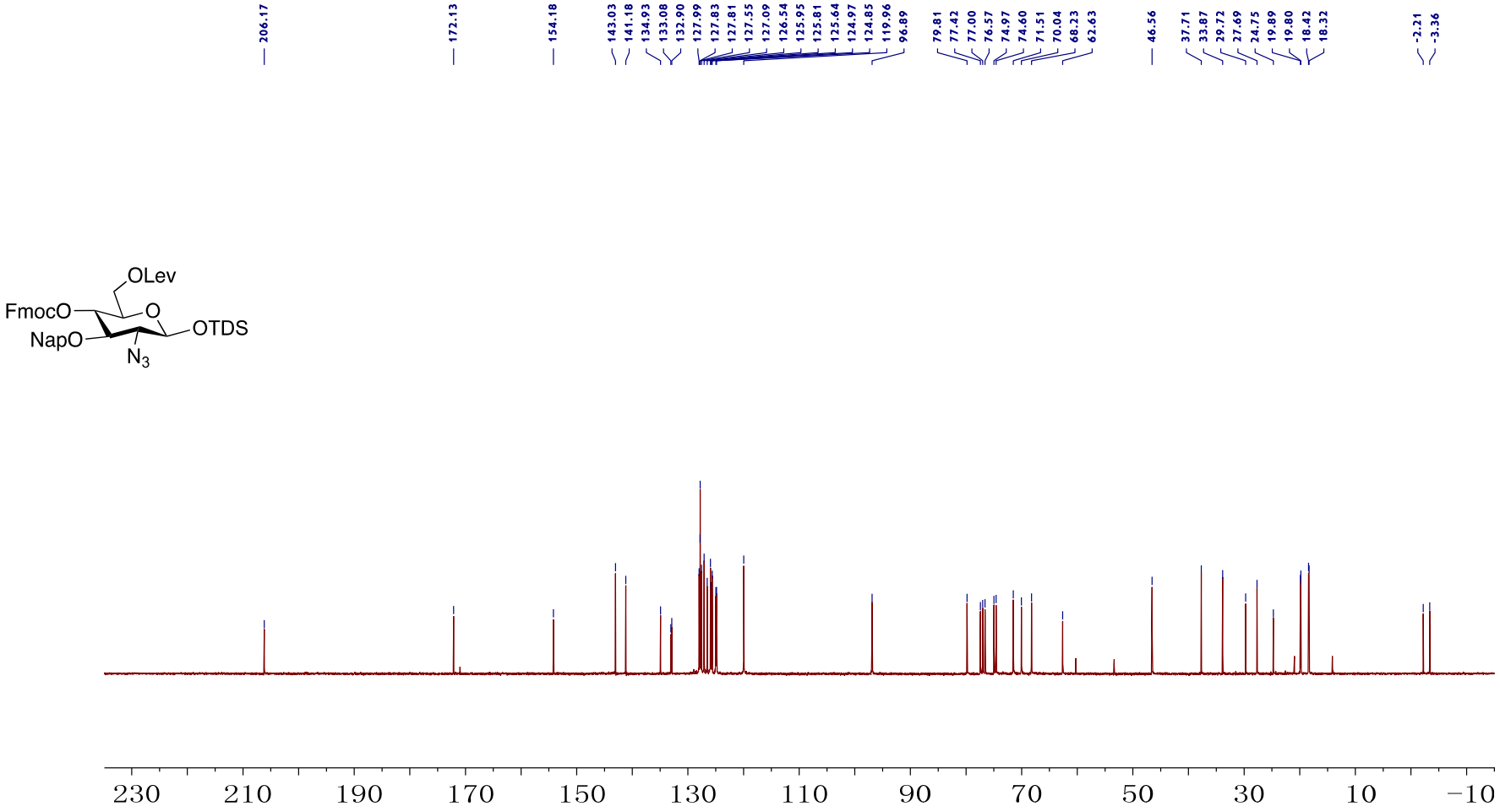
^{1}H NMR of **S3** (300 M, $CDCl_3$)



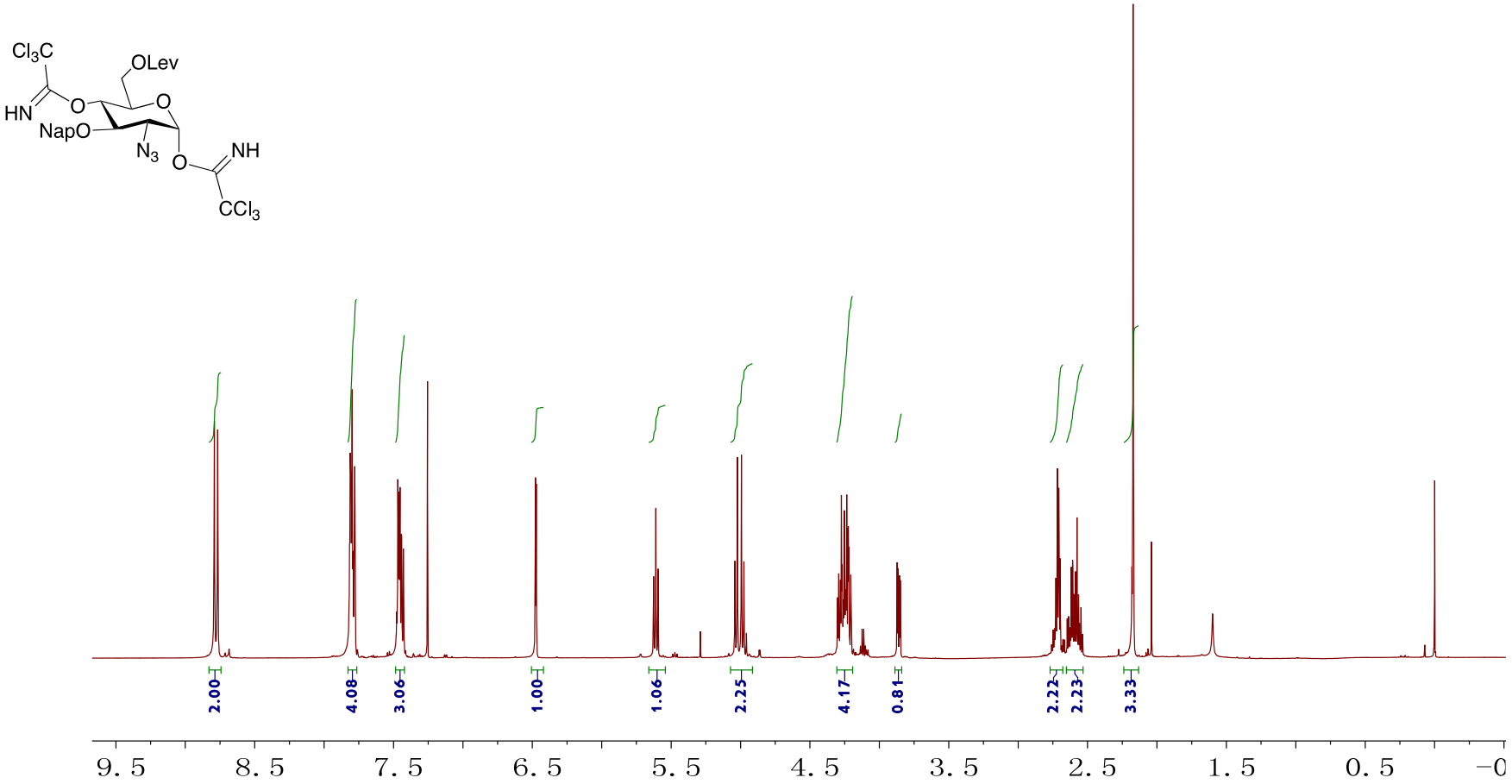
^{13}C NMR of **S3** (75 M, $CDCl_3$)



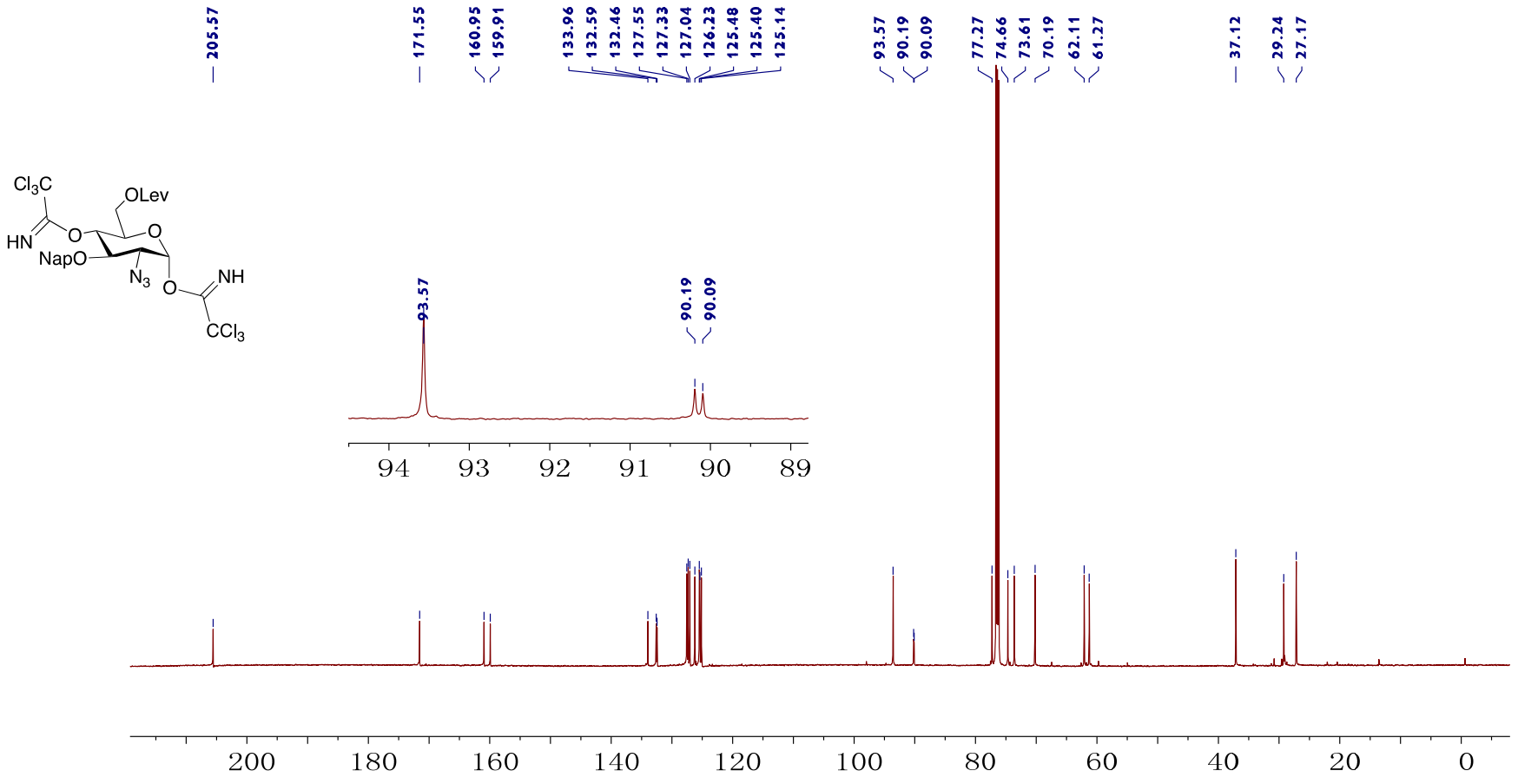
^{1}H NMR of **S4** (300 M, $CDCl_3$)



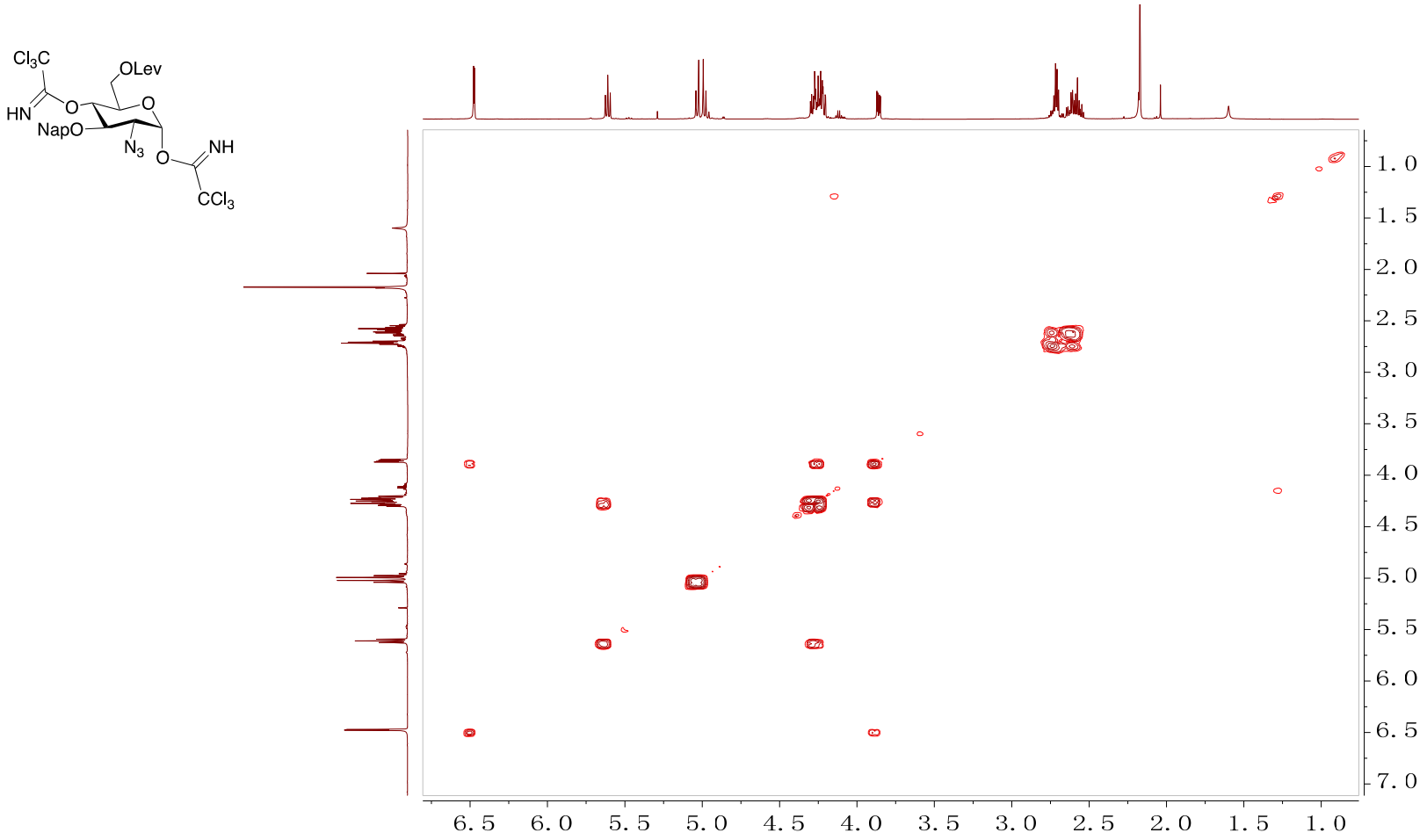
^{13}C NMR of **S4** (75 M, $CDCl_3$)



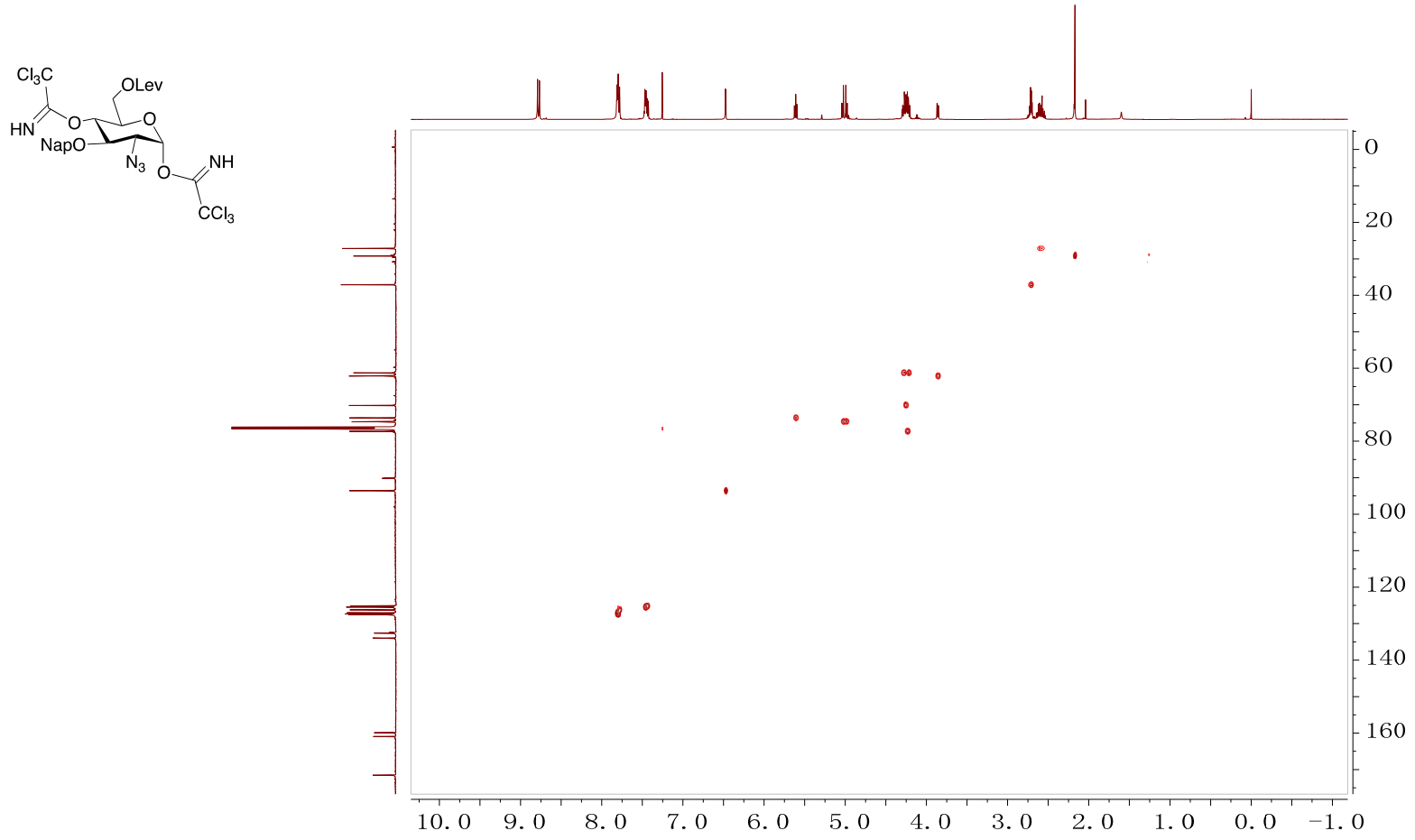
^{1}HNMR of **3** (600 MHz, $CDCl_3$)



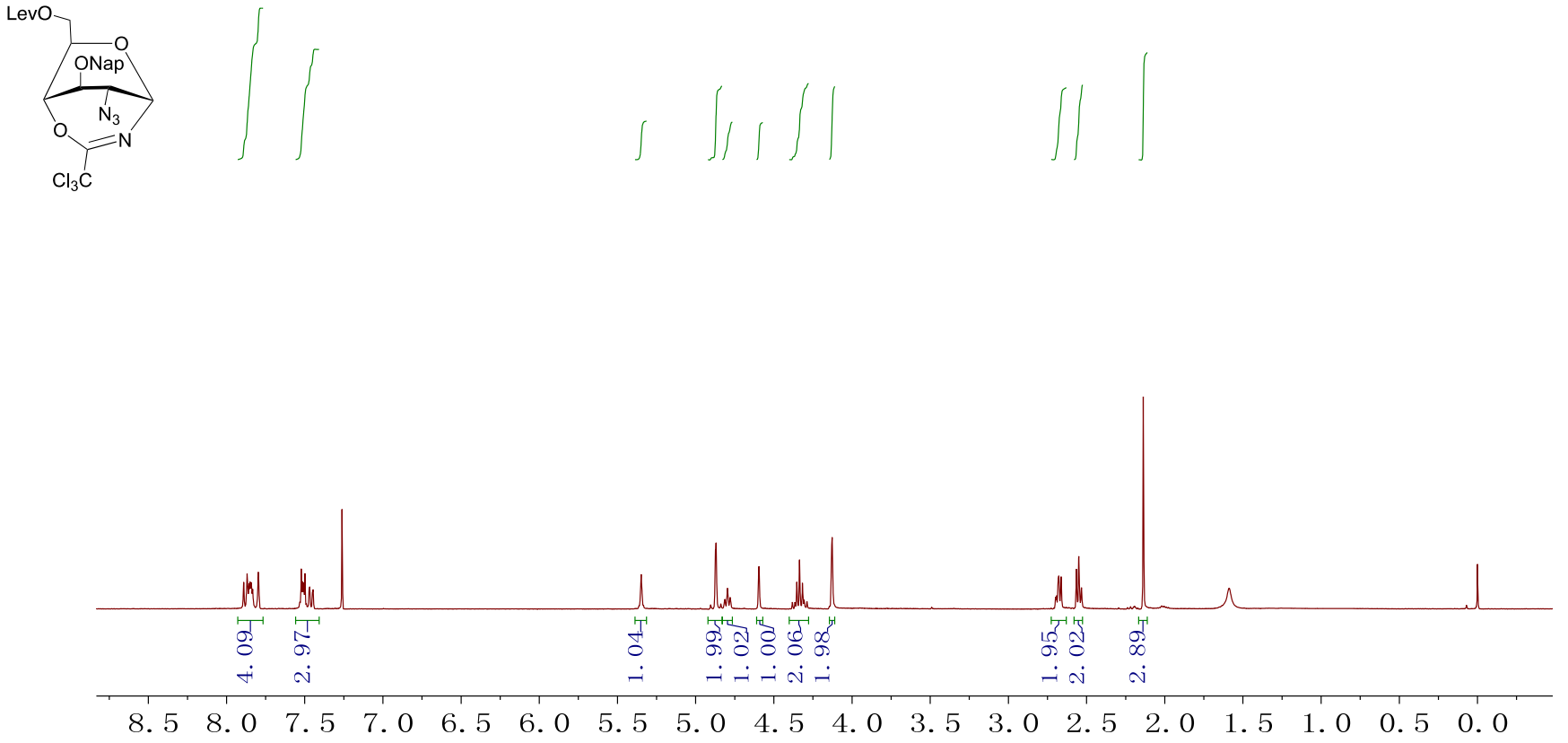
^{13}C NMR of **3** (151 MHz, $CDCl_3$)



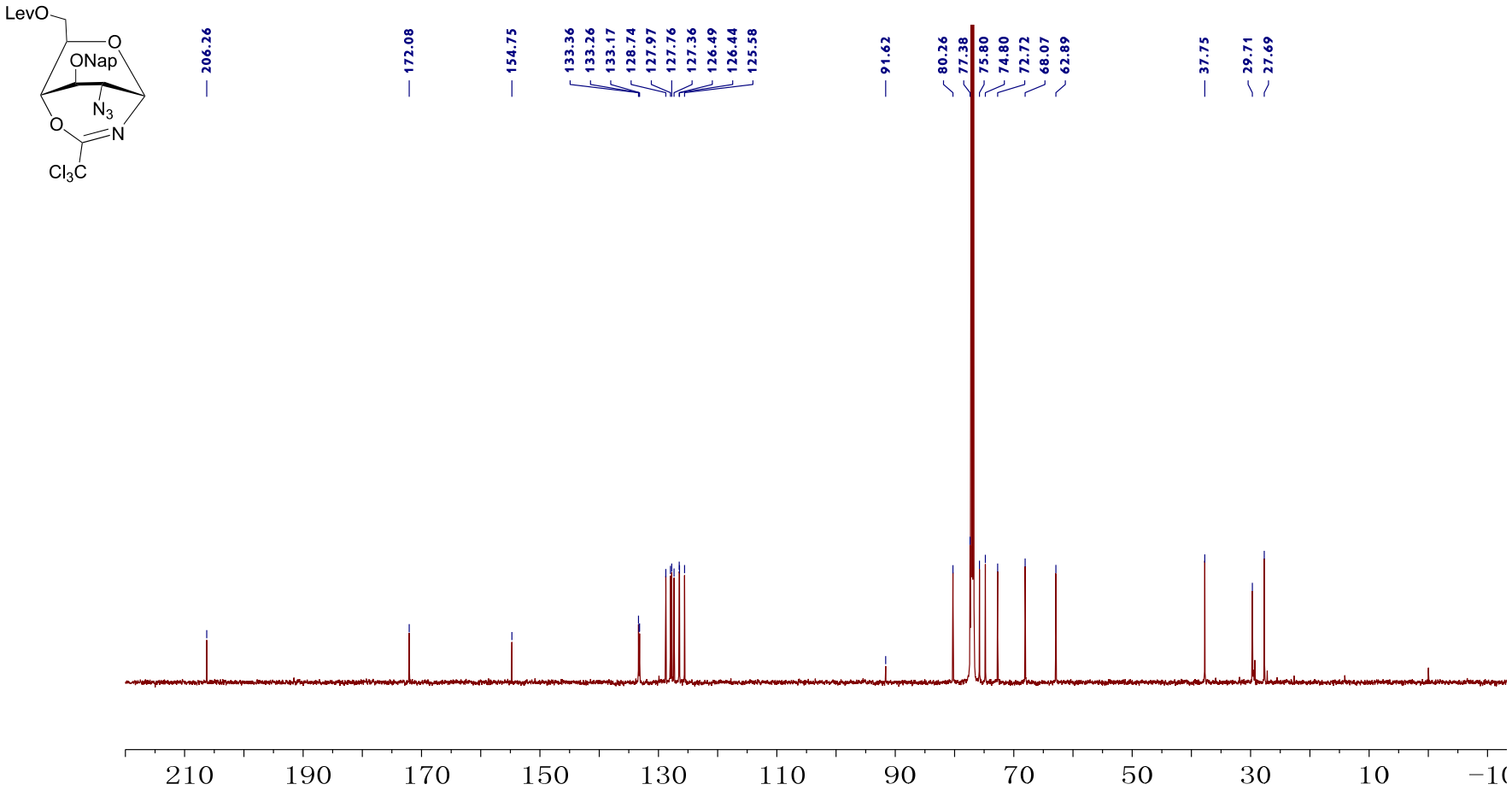
^{1}H-^{1}H COSY of **3**



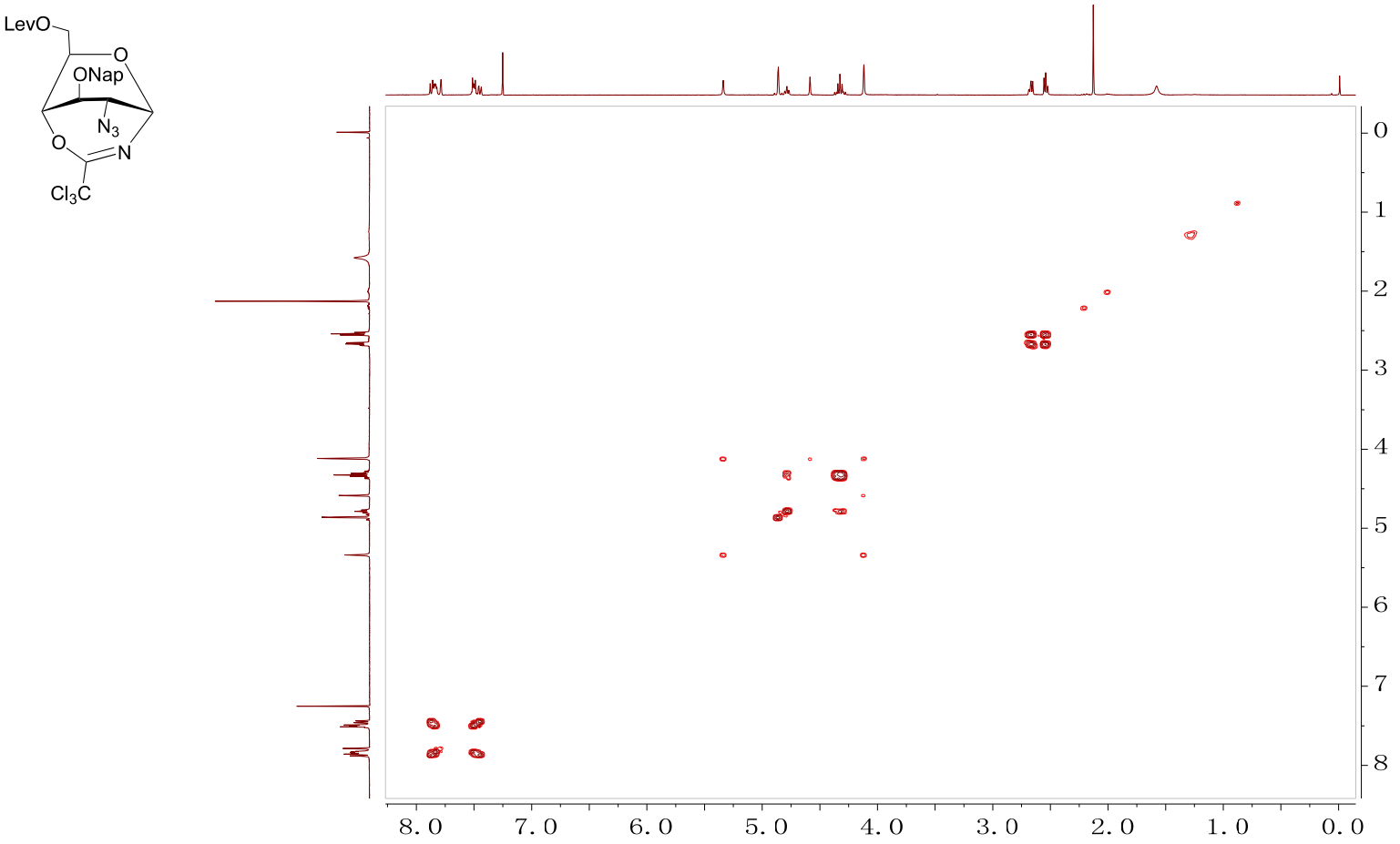
HSQC of **3**


LevO
O
ONap
N3
O
N
Cl3C
4.09
2.97
1.04
1.99
1.02
1.00
2.06
1.98
1.95
2.02
2.89
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

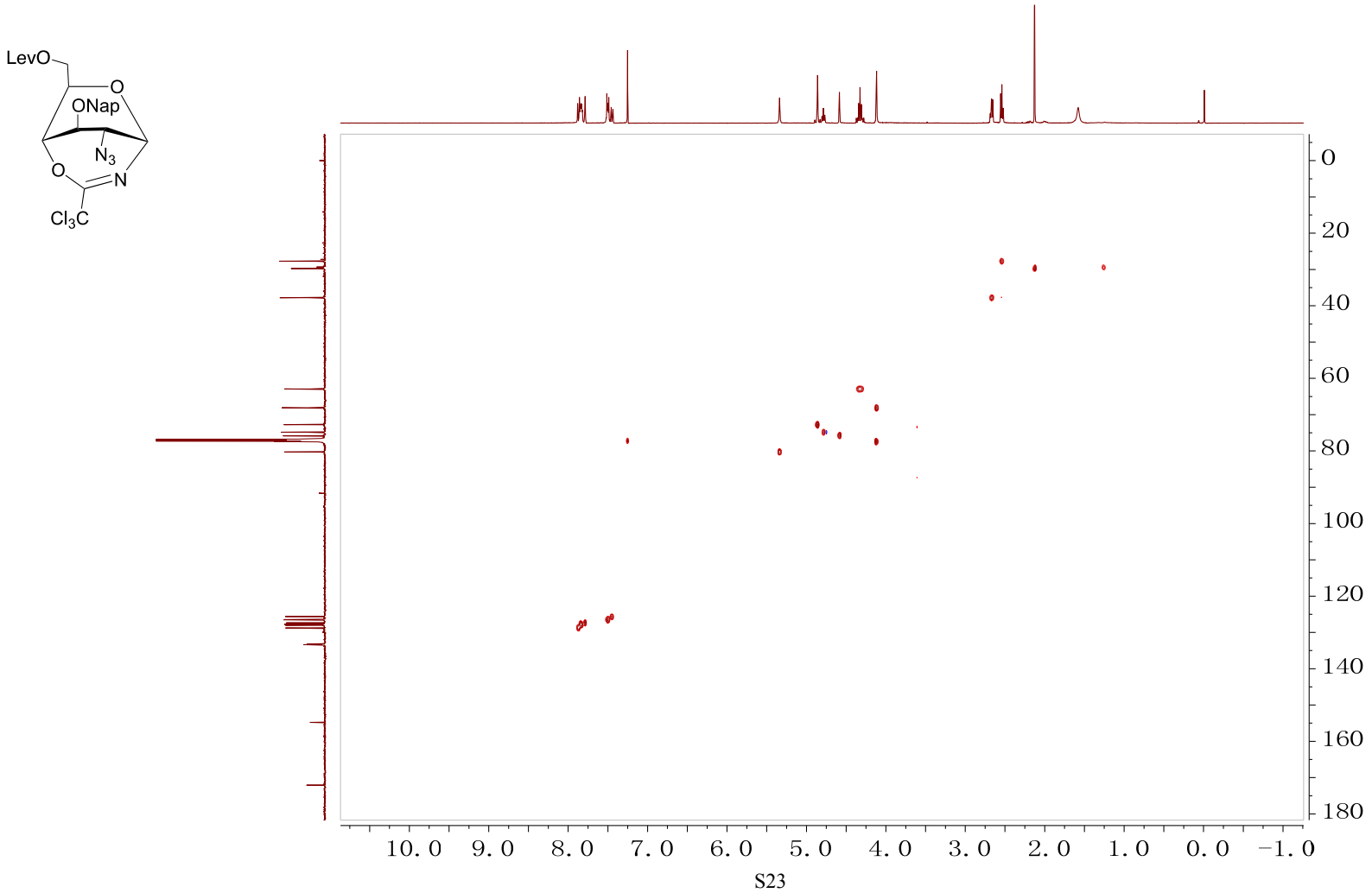
^{1}HNMR of **4** (600 MHz, $CDCl_3$)



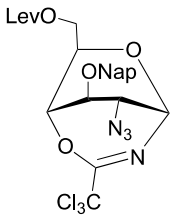
^{13}C NMR of **4** (125 MHz, $CDCl_3$)

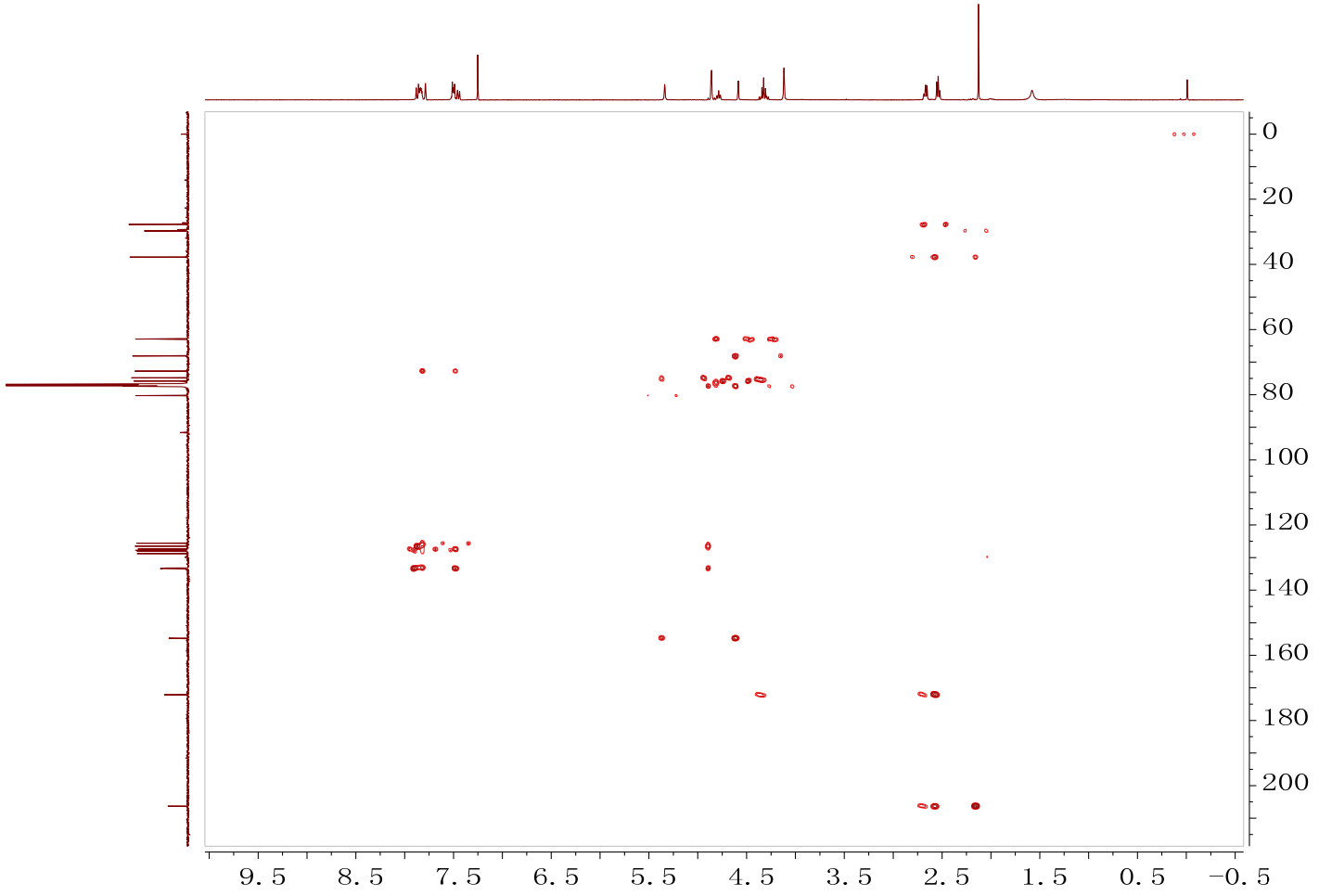


^{1}H-^{1}H COSY of **4**

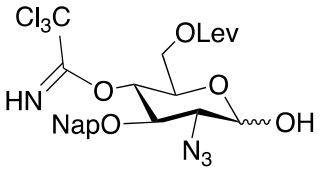


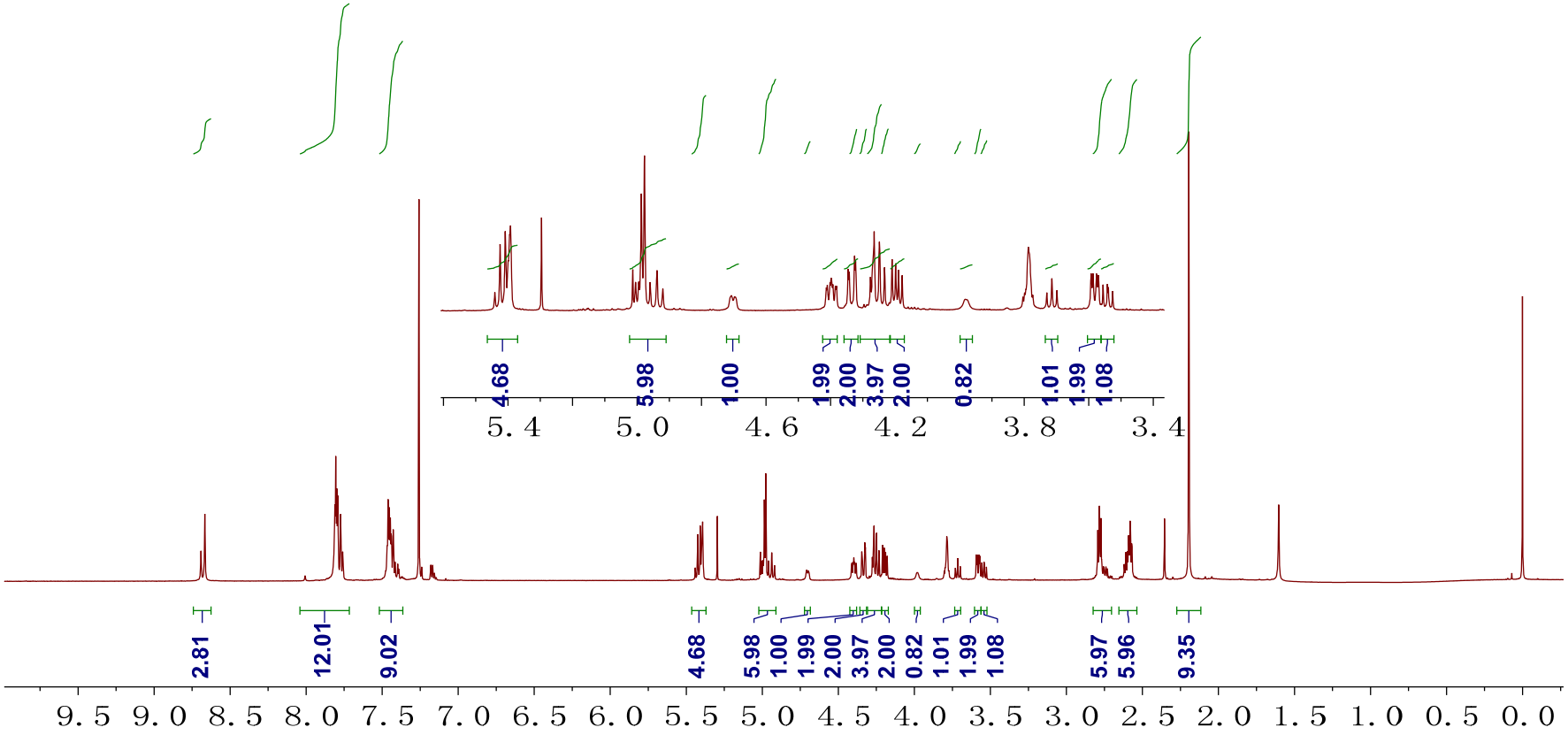
HSQC of **4**


LevO
O
ONap
N3
O
N
Cl3C

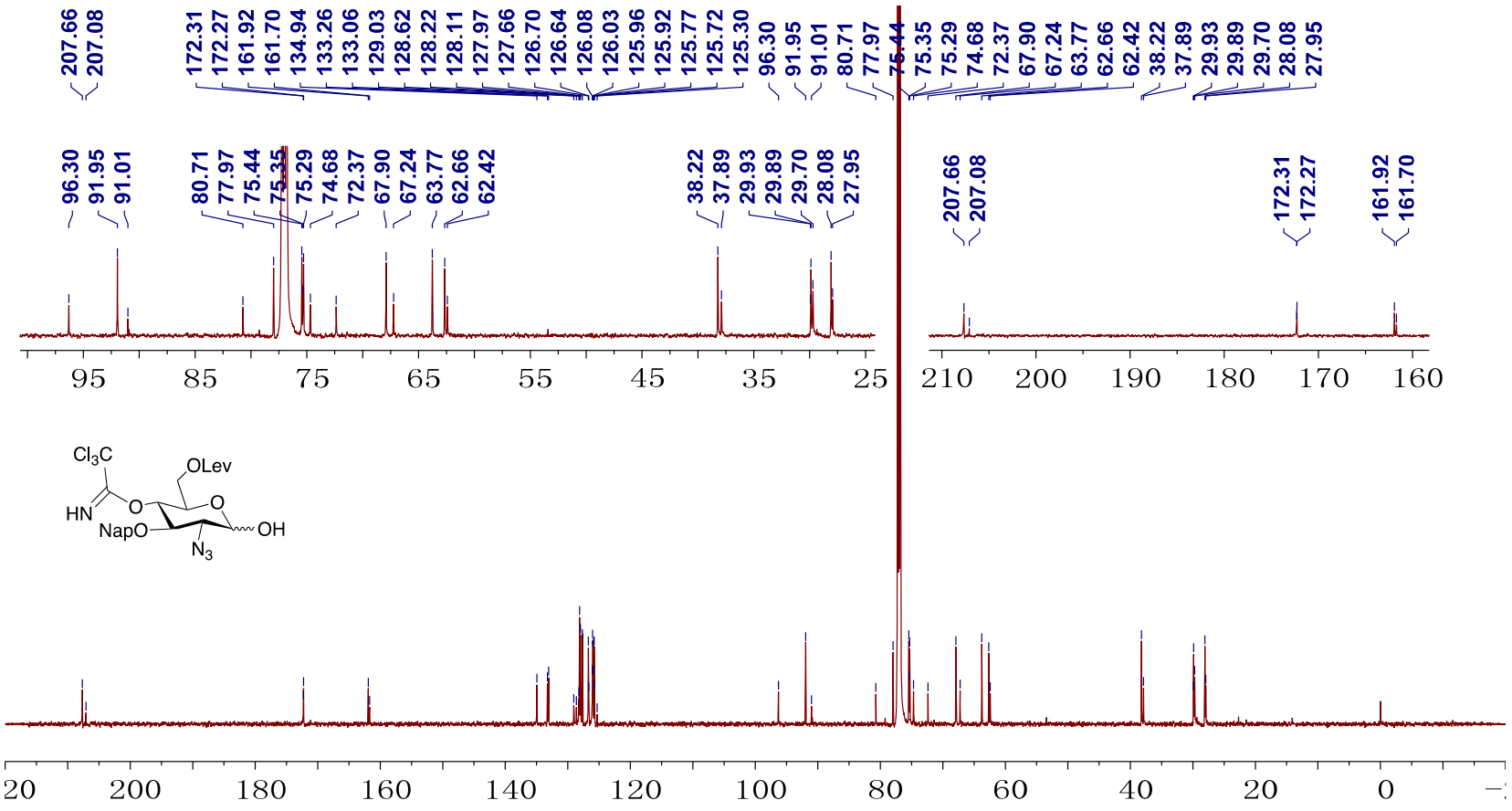

0
20
40
60
80
100
120
140
160
180
200
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5

HMBC of **4**

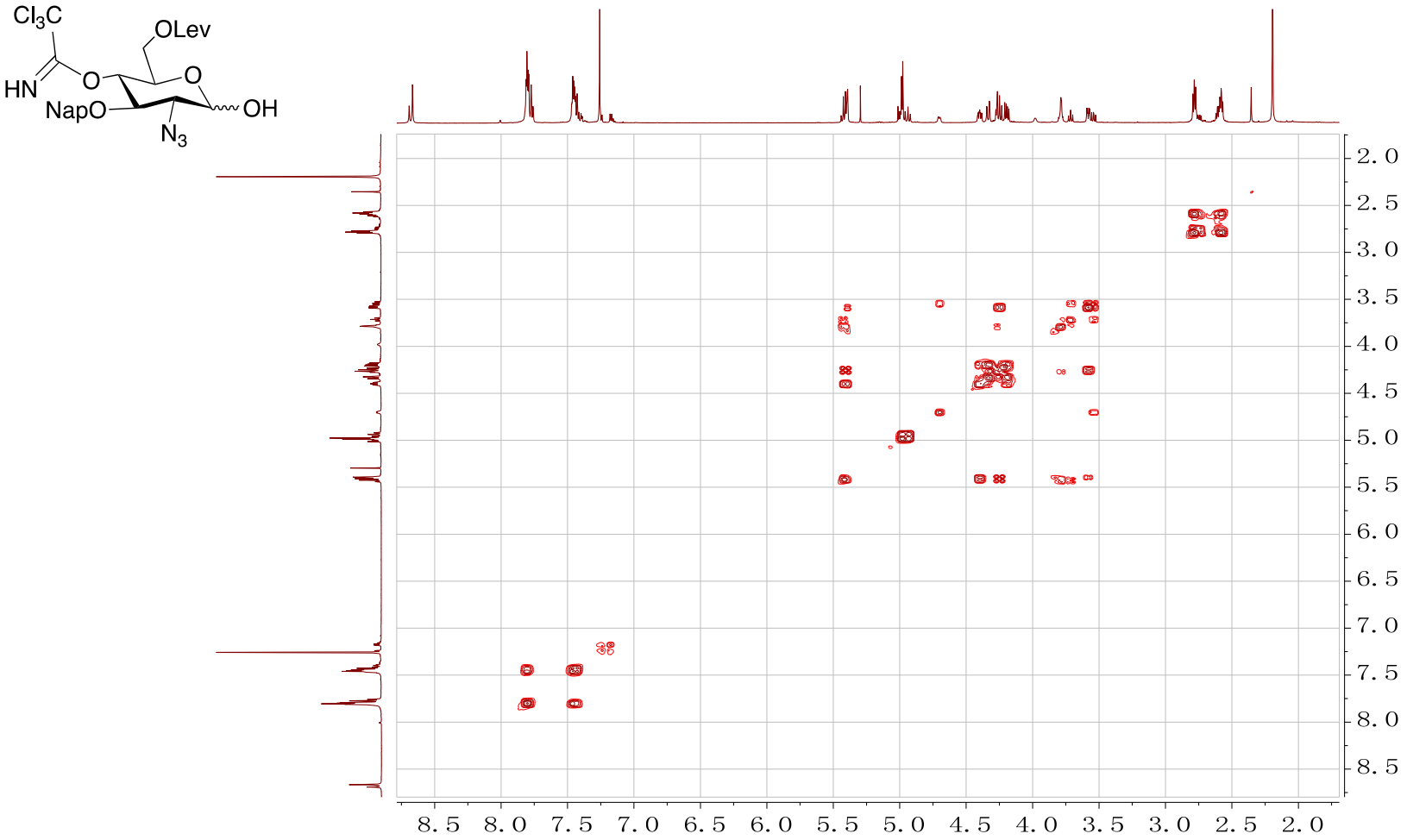




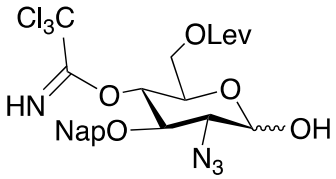
^{1}H NMR of **8** (600 MHz, $CDCl_3$)

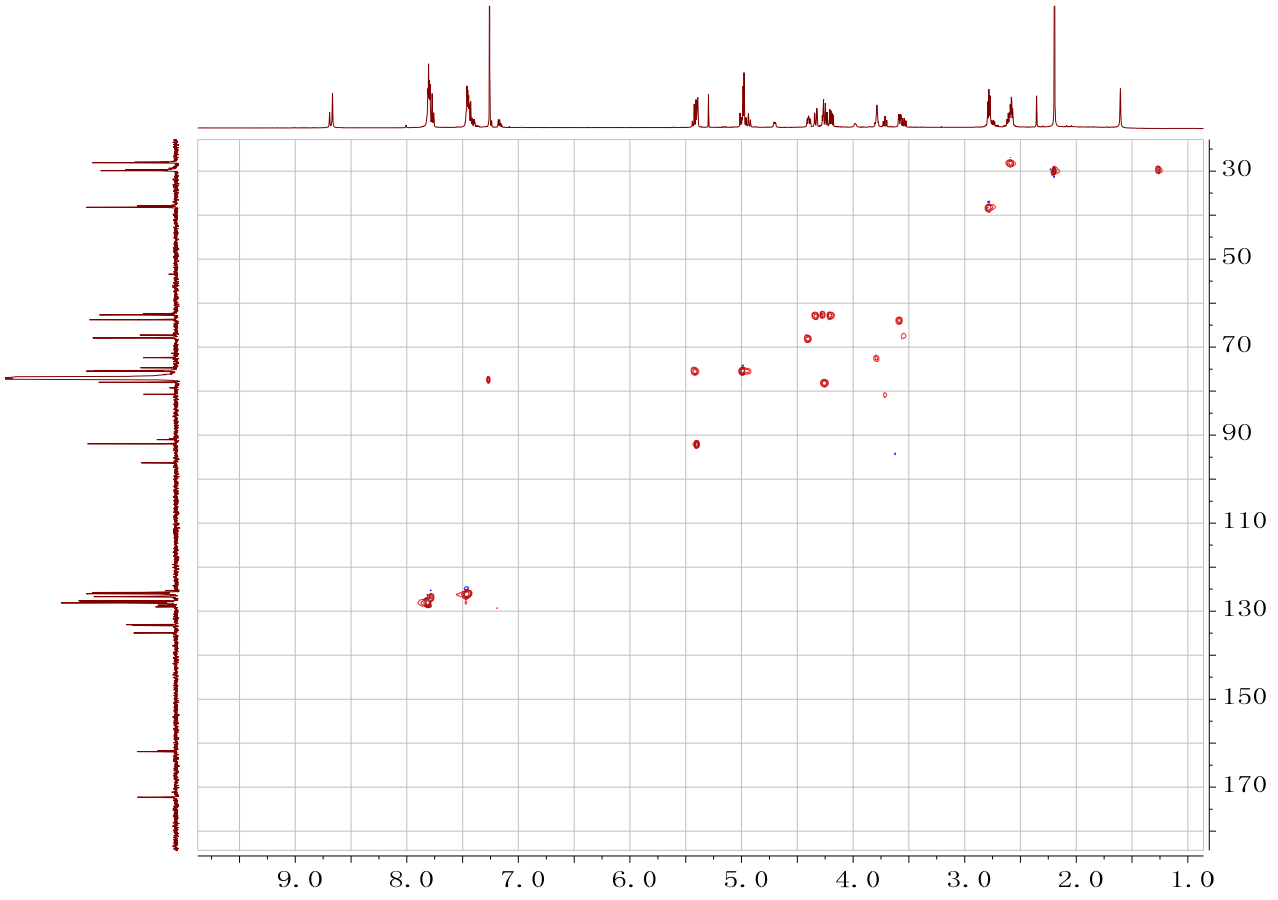


^{13}C NMR of **8** (151 MHz, $CDCl_3$)

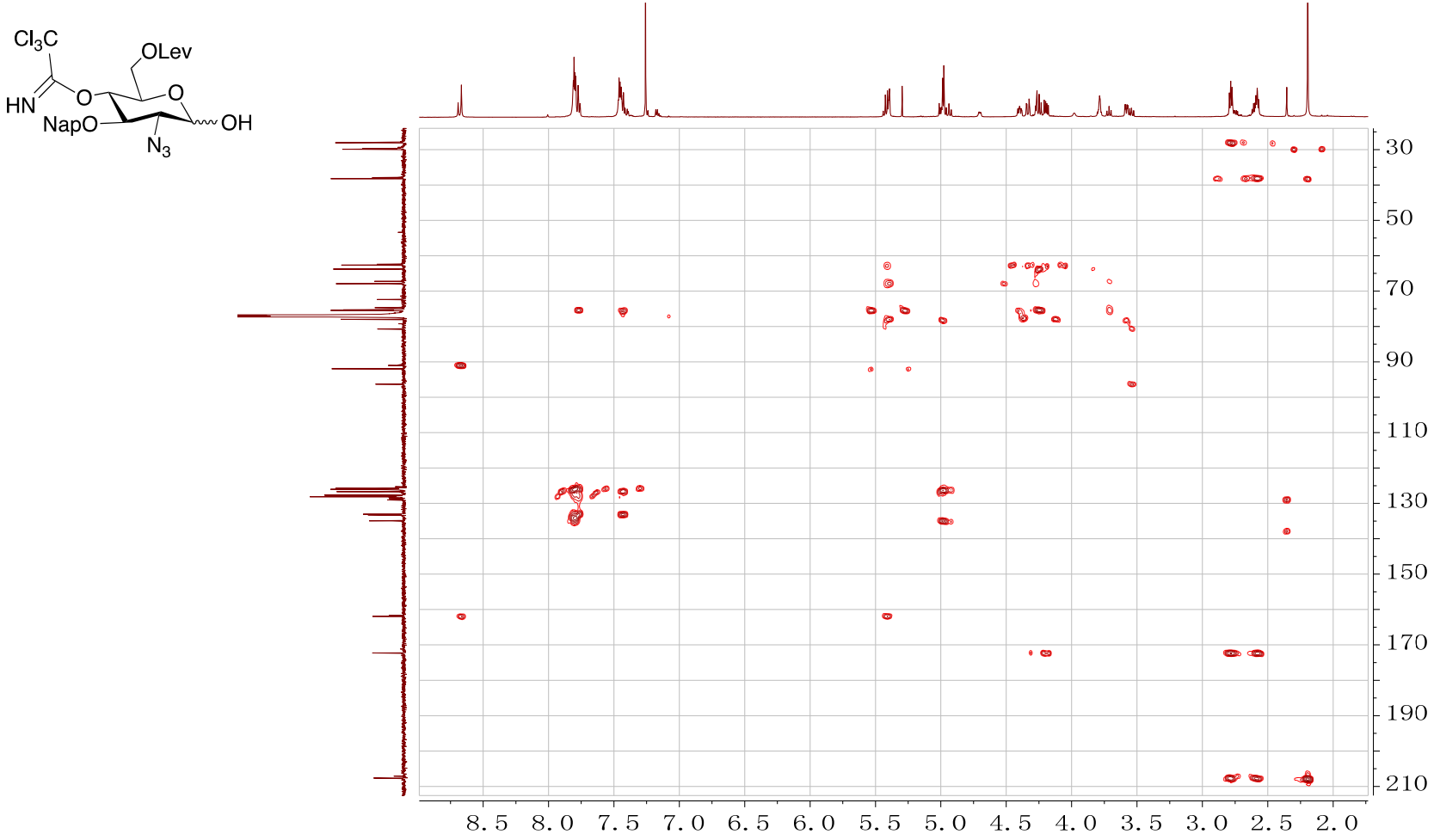


^{1}H-^{1}H COSY of **8**

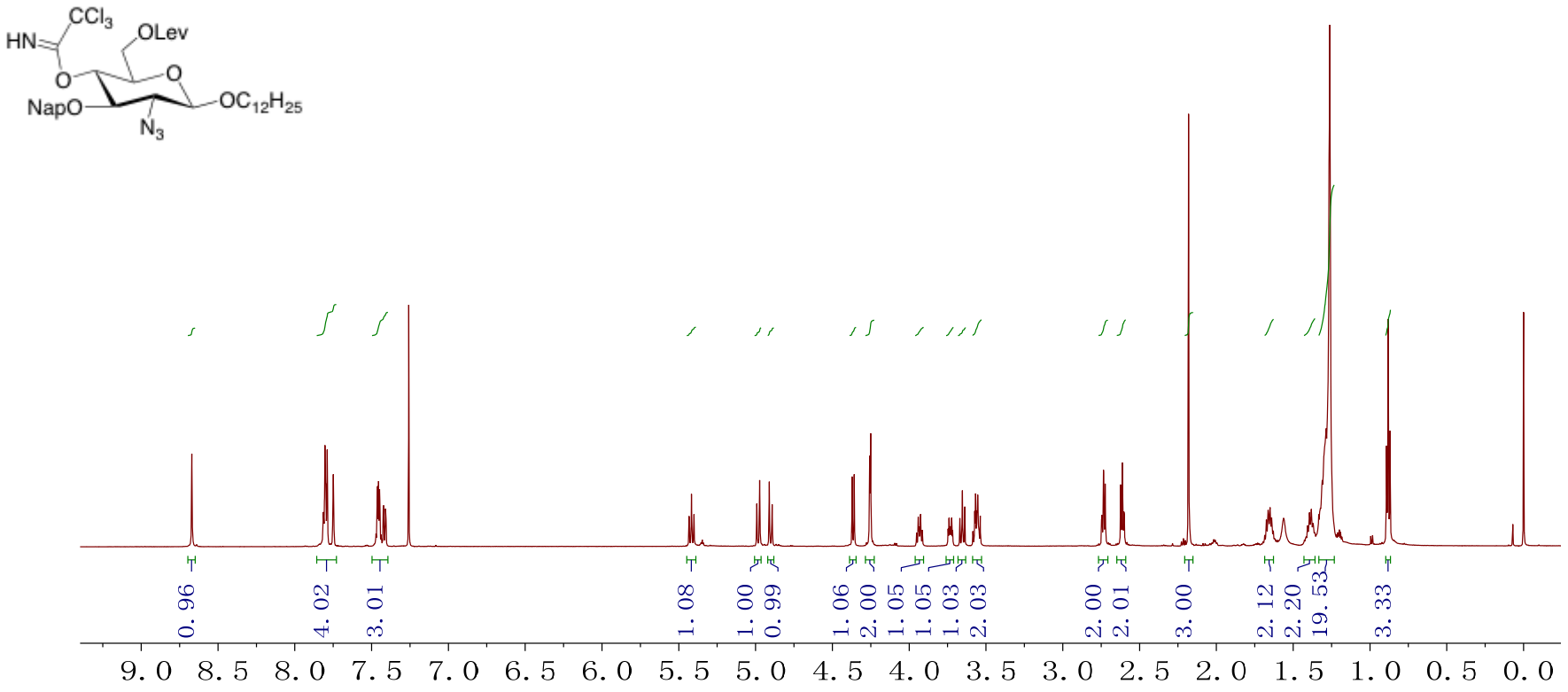

Cl3C
OLev
HN
O
O
NapO
OH
N3


30
50
70
90
110
130
150
170
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

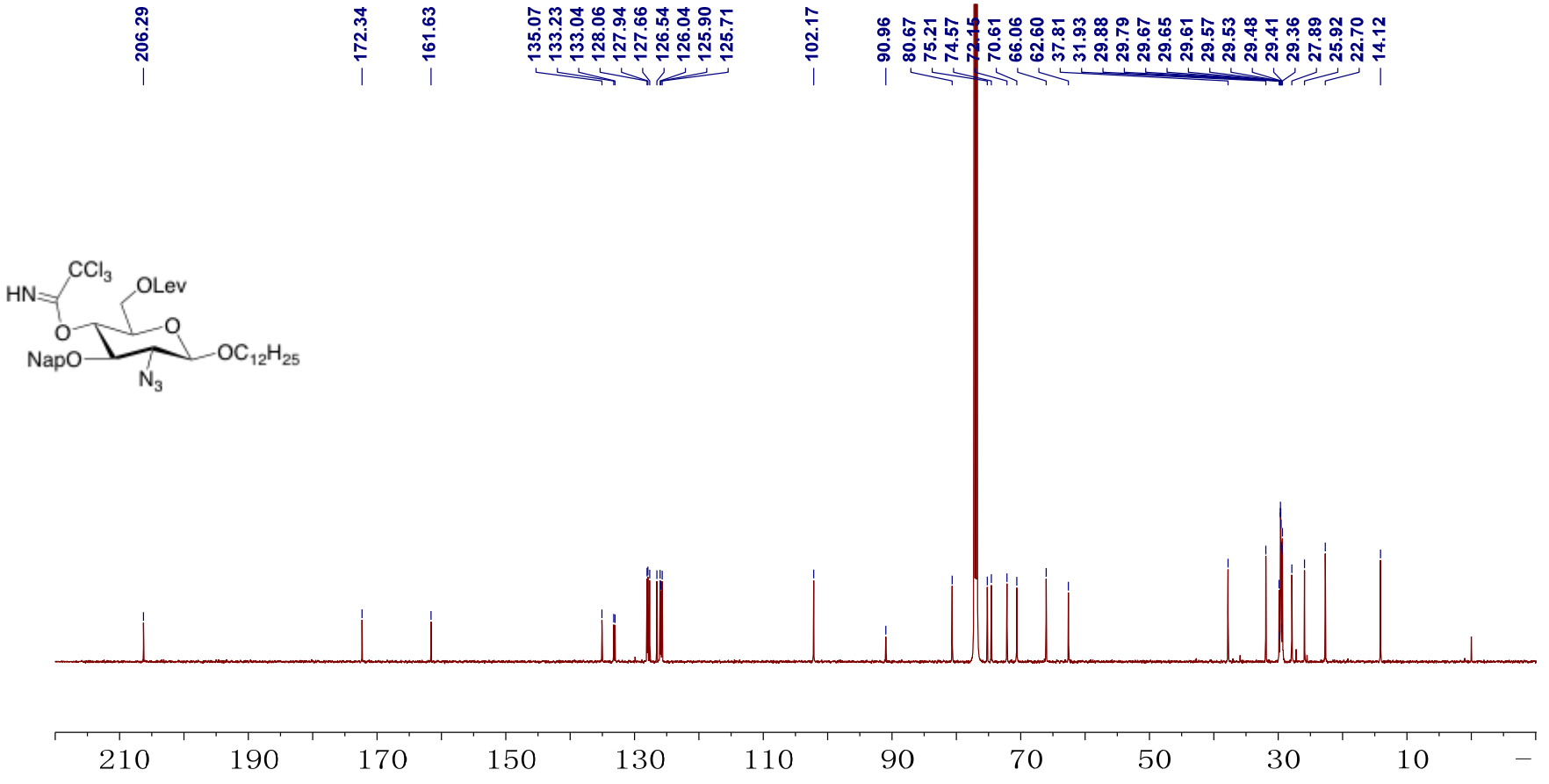
HSQC of **8**


Cl3C
OLev
HN
O
O
NapO
OH
N3
30
50
70
90
110
130
150
170
190
210
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

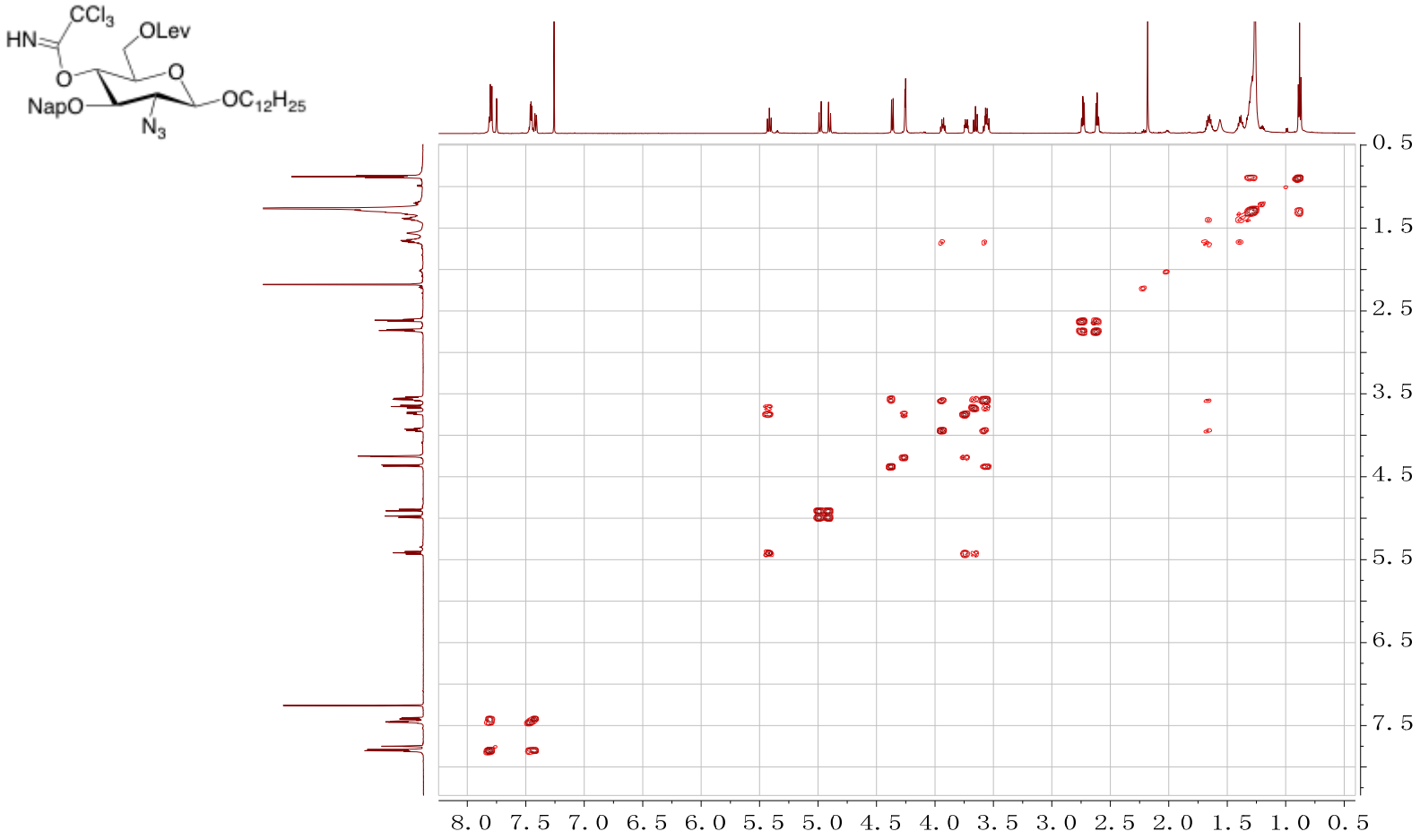
HMBC of **8**



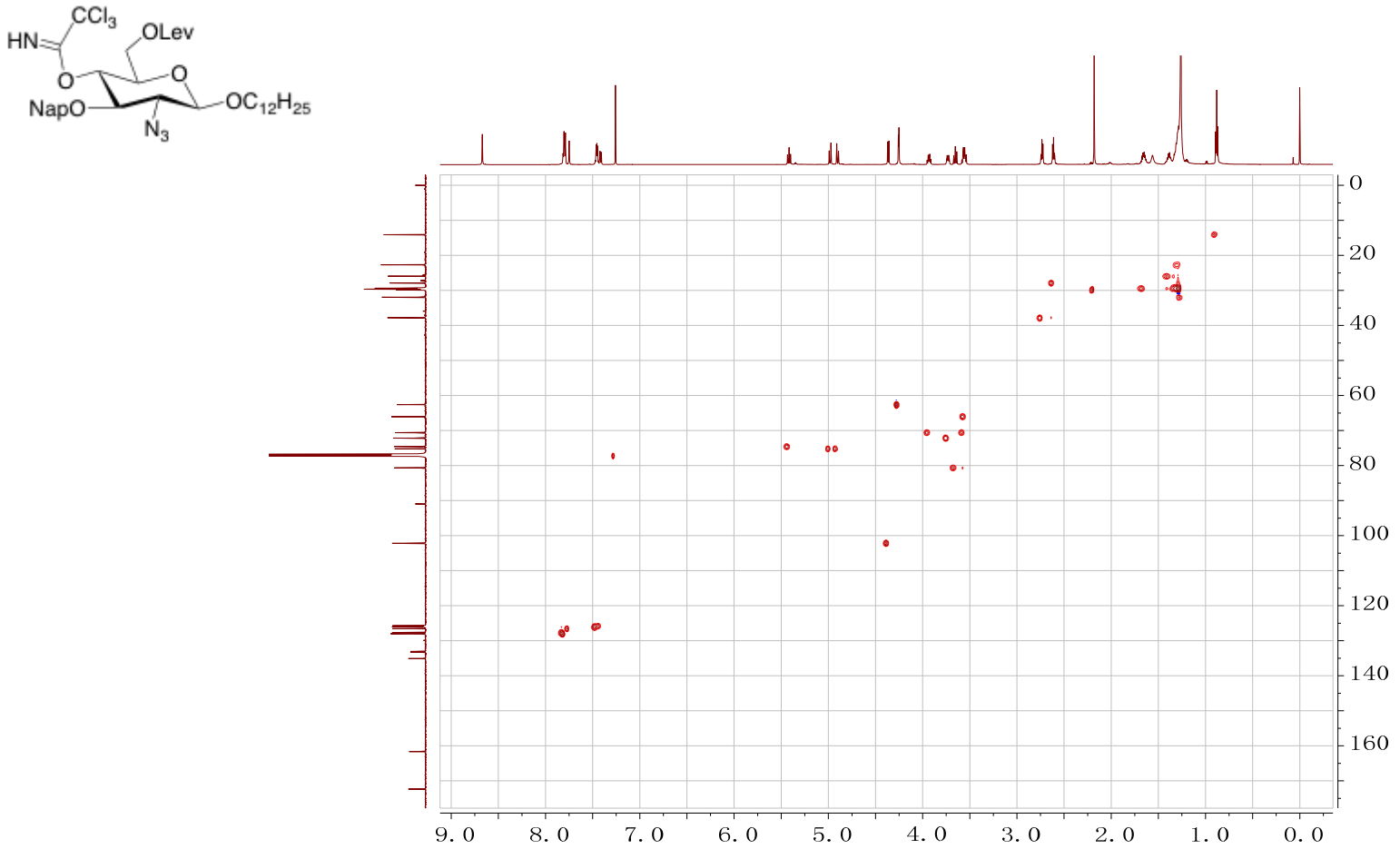
^{1}HNMR of **11** (600 MHz, $CDCl_3$)



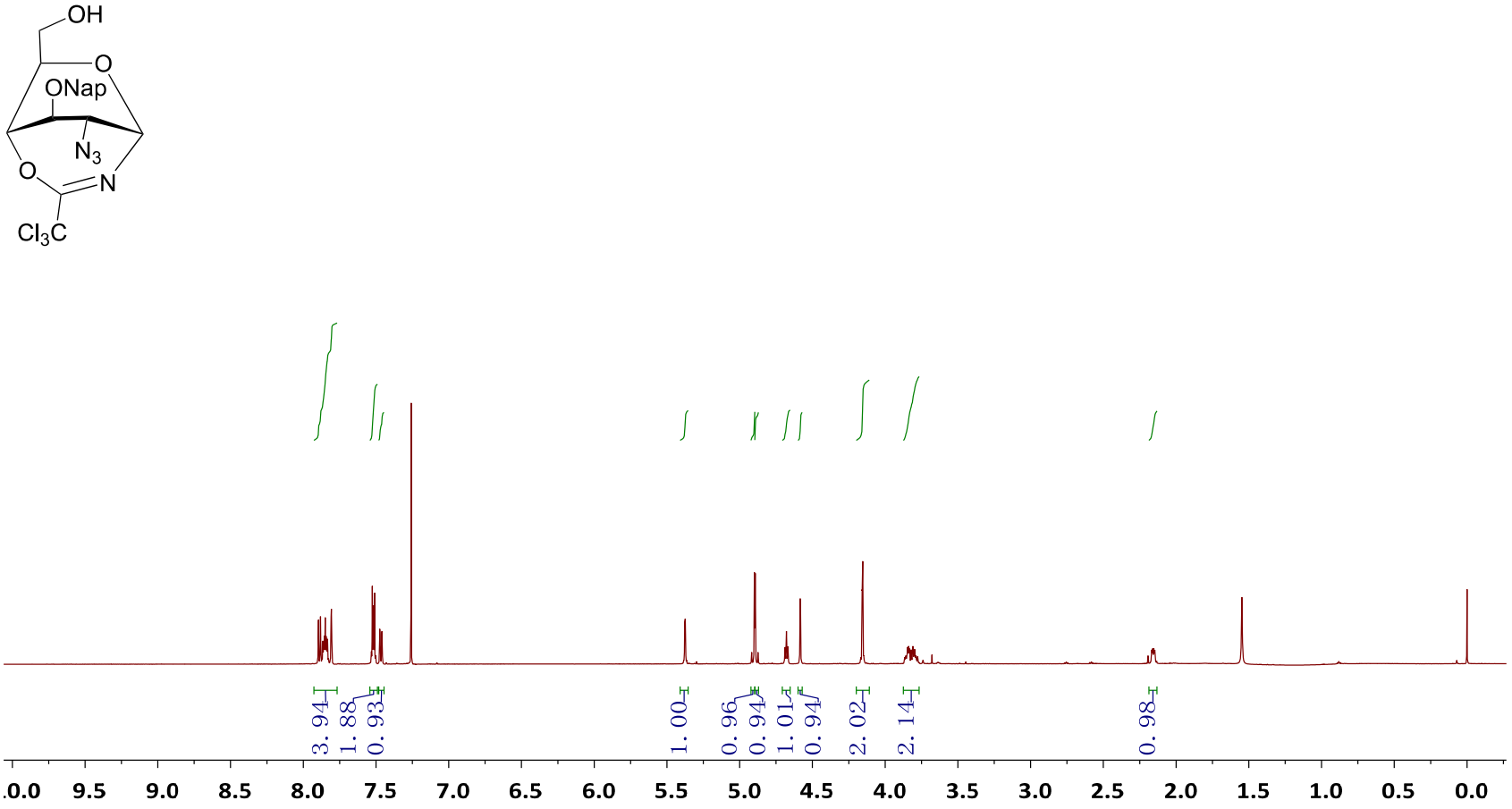
^{13}CNMR of **11** (151 MHz, $CDCl_3$)



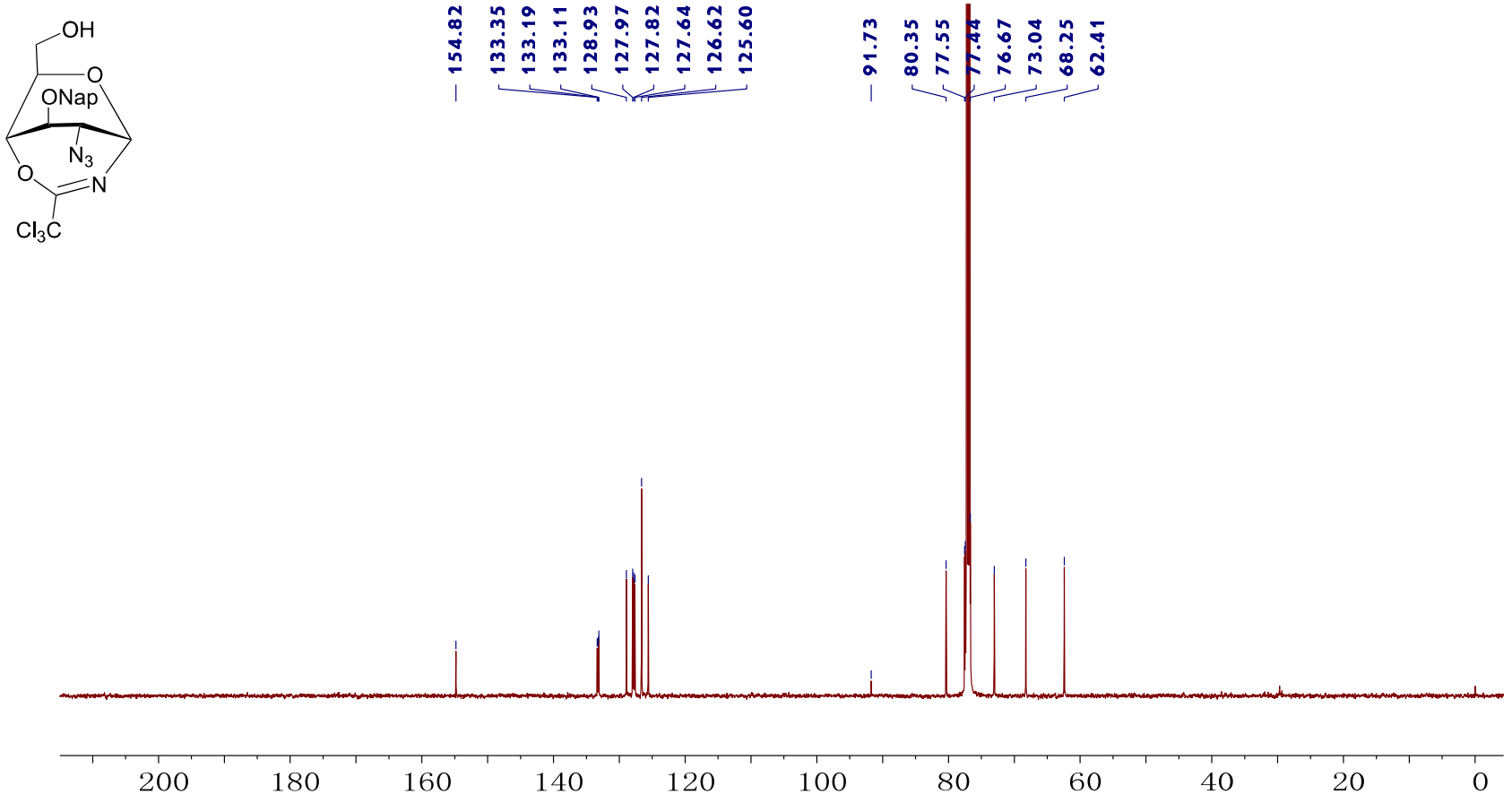
^{1}H-^{1}H COSY of **11**


HN
CCl3
OLev
O
O
NapO
N3
OC12H25
0
20
40
60
80
100
120
140
160
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

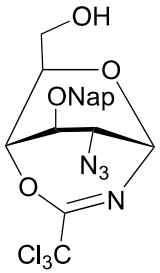
HSQC of **11**

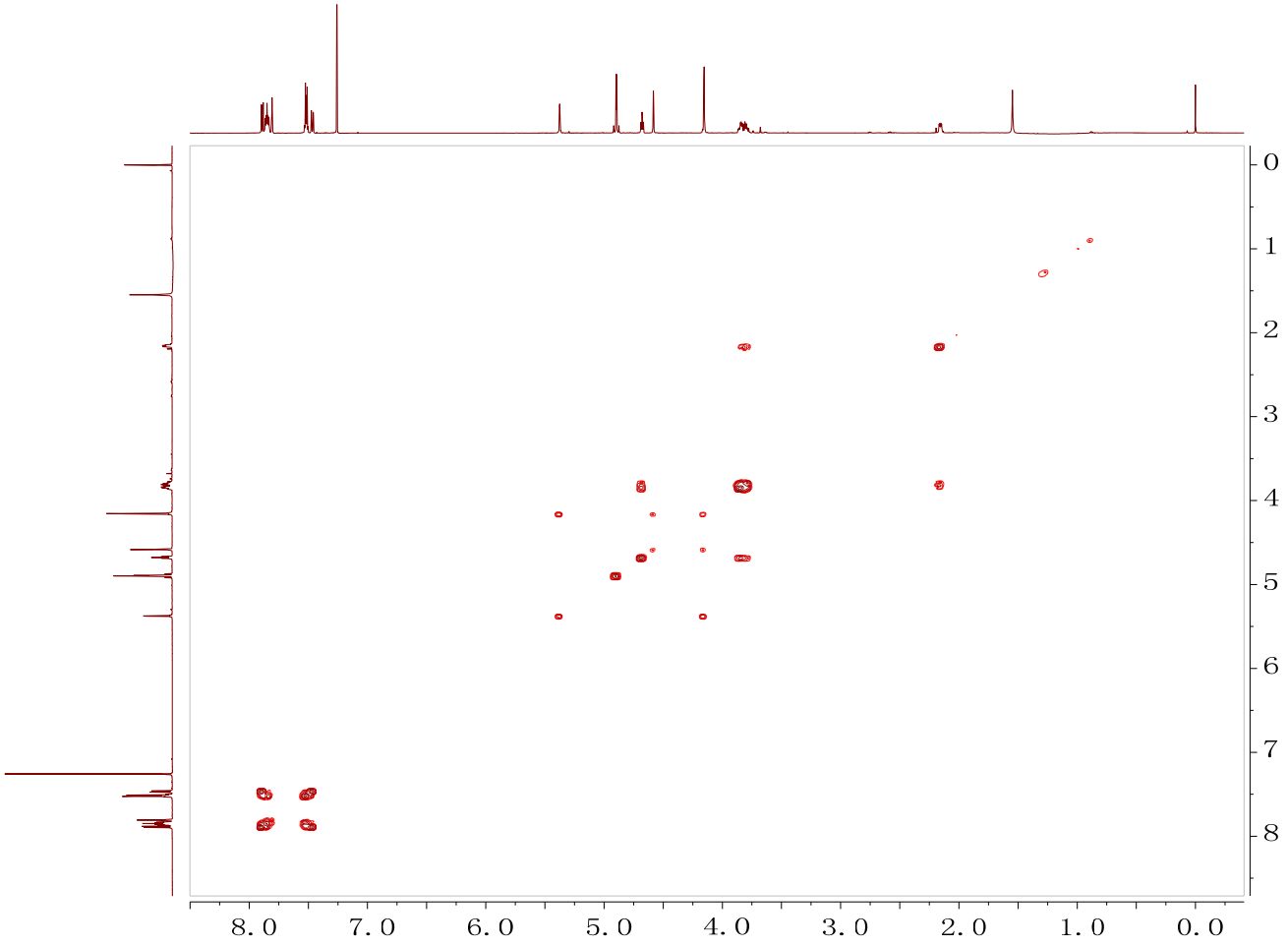


^{1}HNMR of **13** (600 MHz, $CDCl_3$)

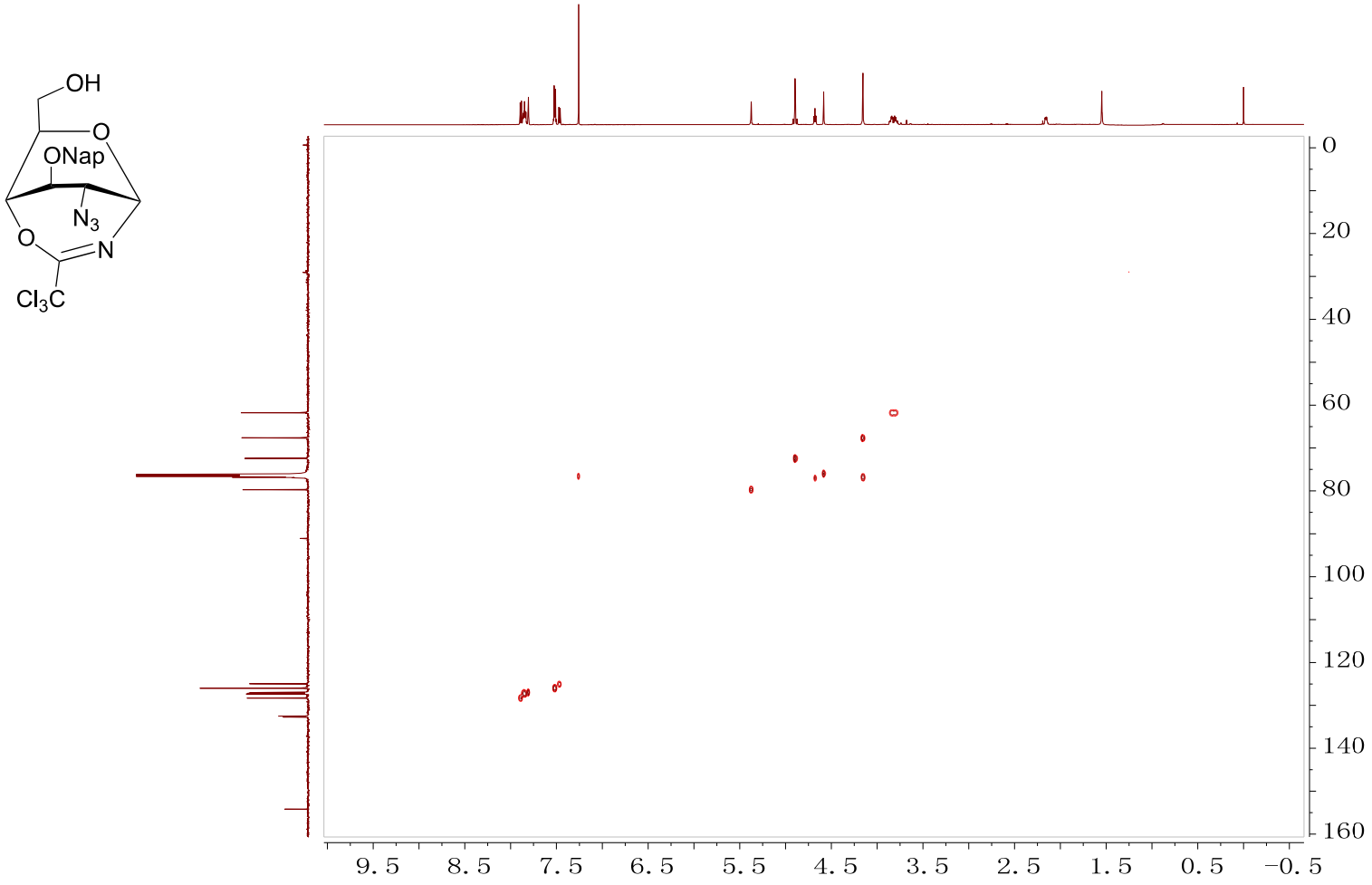


^{13}C NMR of **13** (125 MHz, $CDCl_3$)

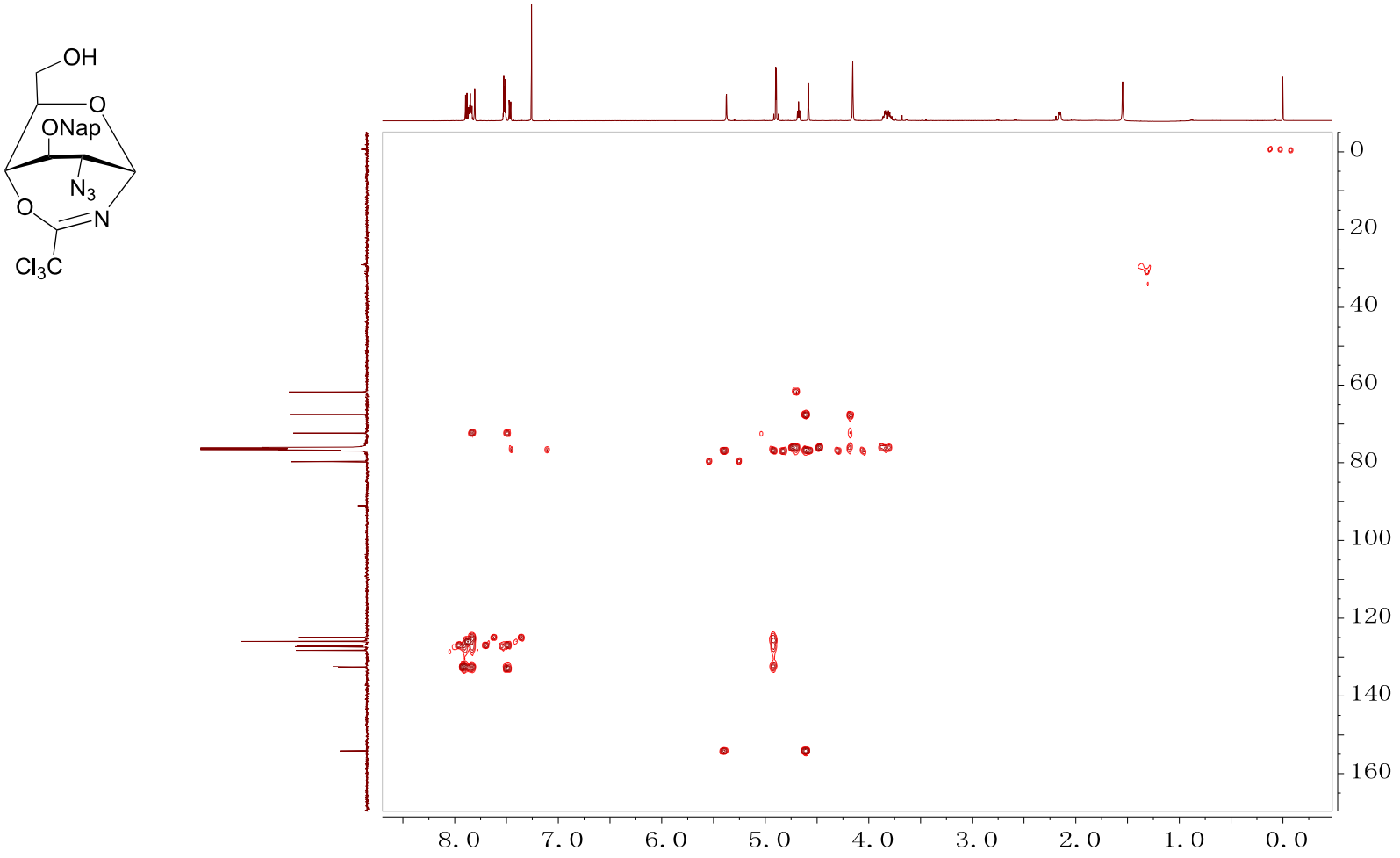




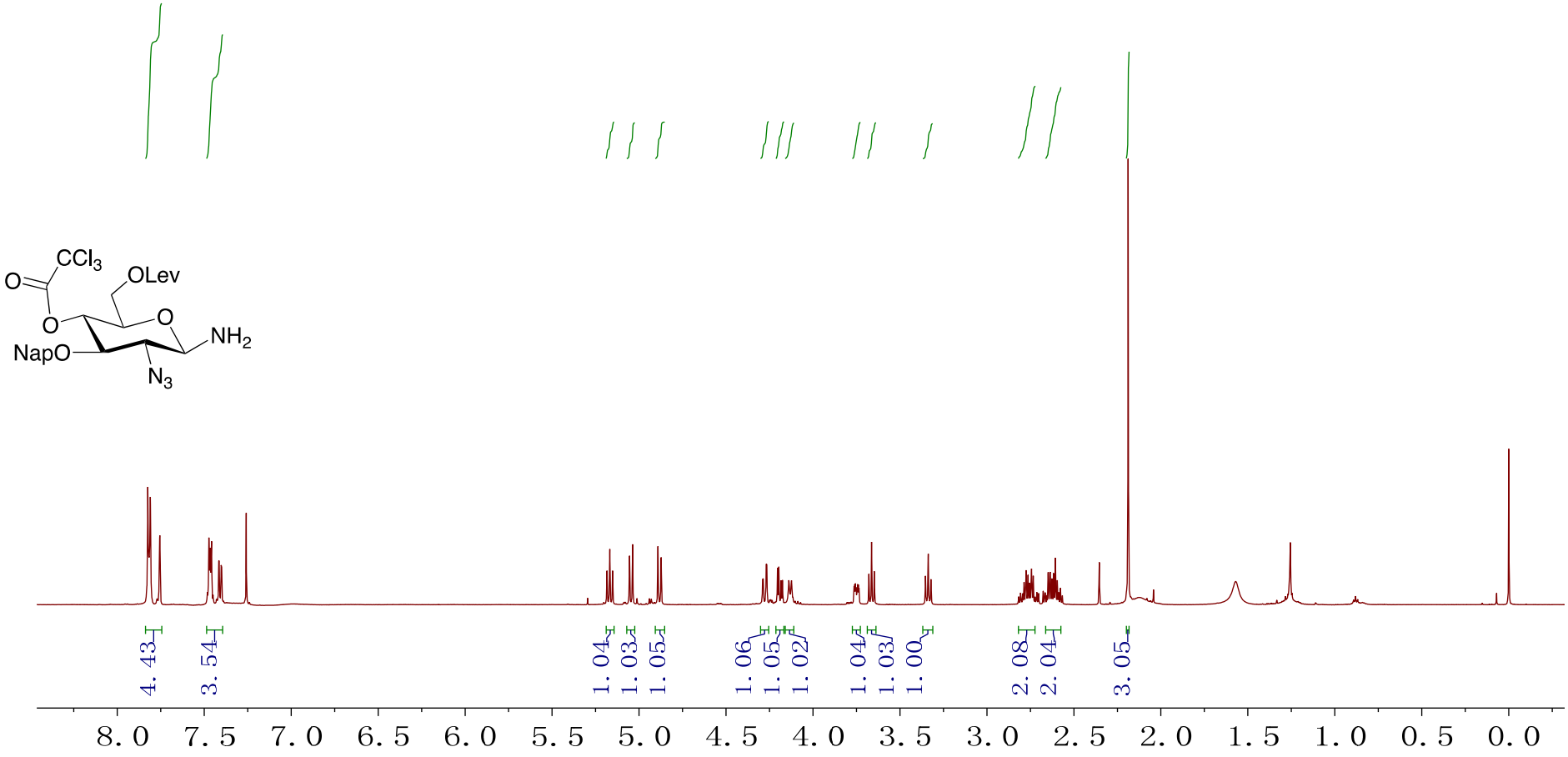
^{1}H-^{1}H COSY of **13**


OH
O
ONap
N3
O
N
Cl3C
0
20
40
60
80
100
120
140
160
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5

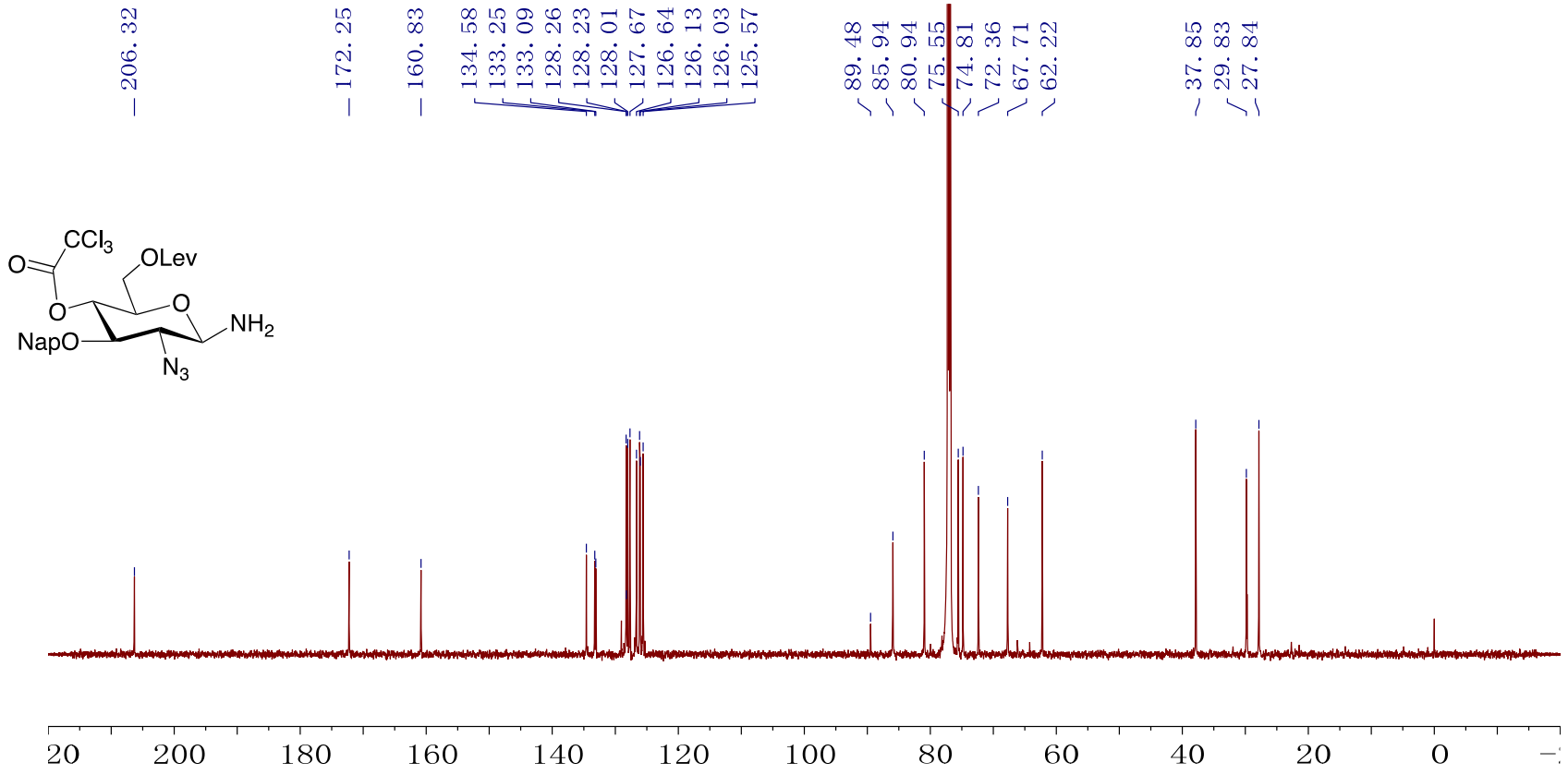
HSQC of **13**


OH
O
ONap
N3
O
N
Cl3C
0
20
40
60
80
100
120
140
160
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

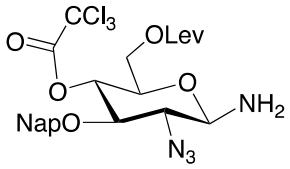
HMBC of **13**

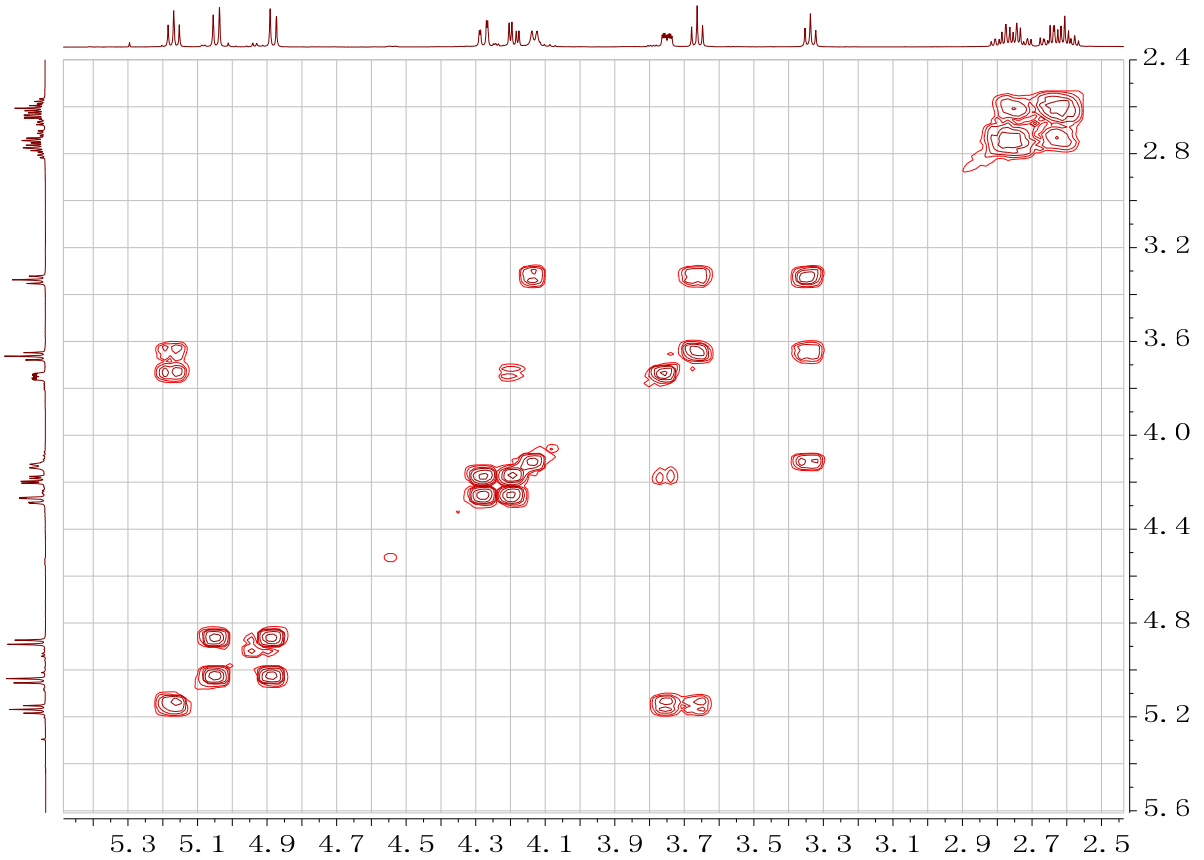


^{1}H NMR of **14** (600 MHz, $CDCl_3$)

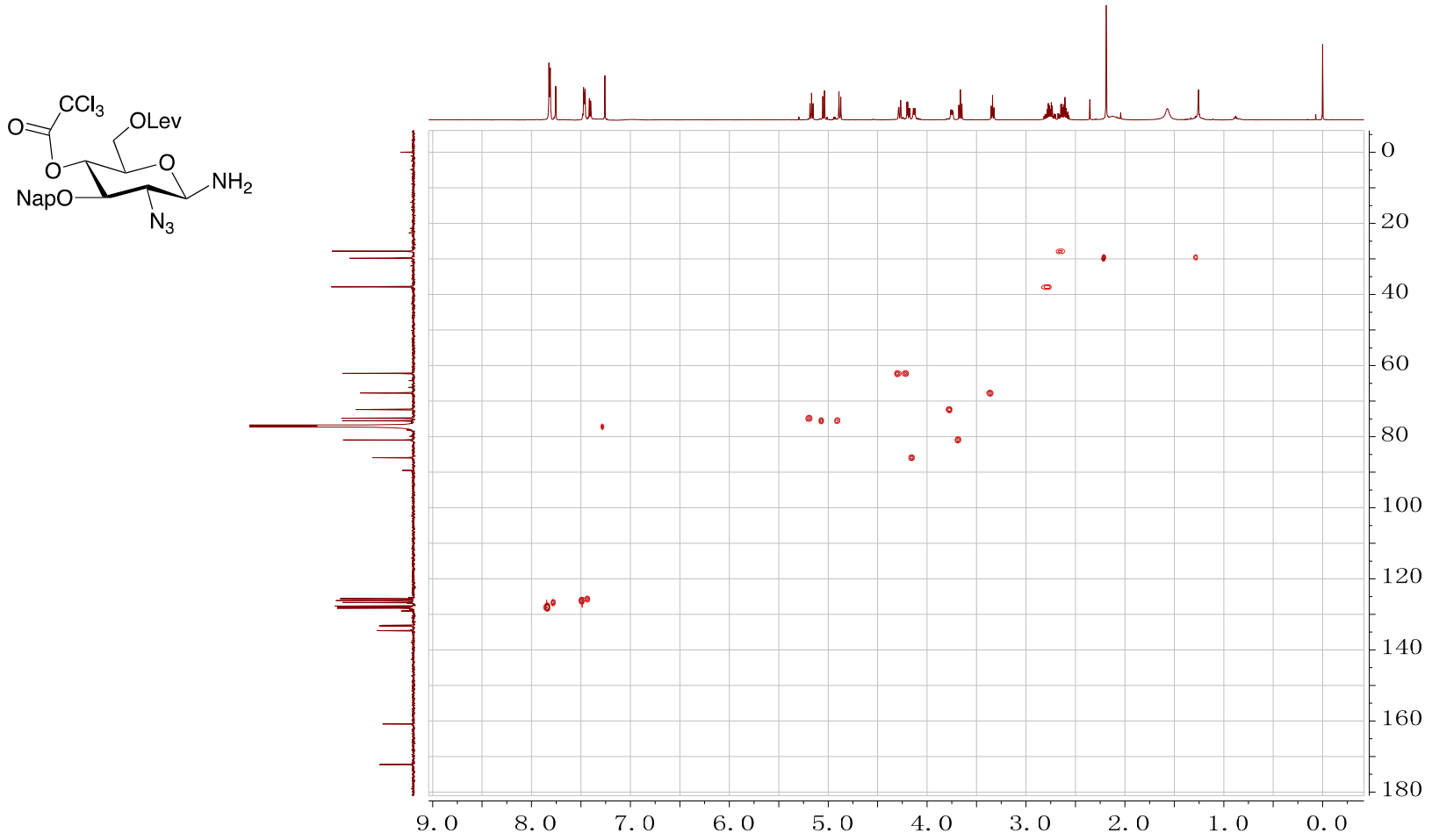


^{13}C NMR of **14** (151 MHz, $CDCl_3$)

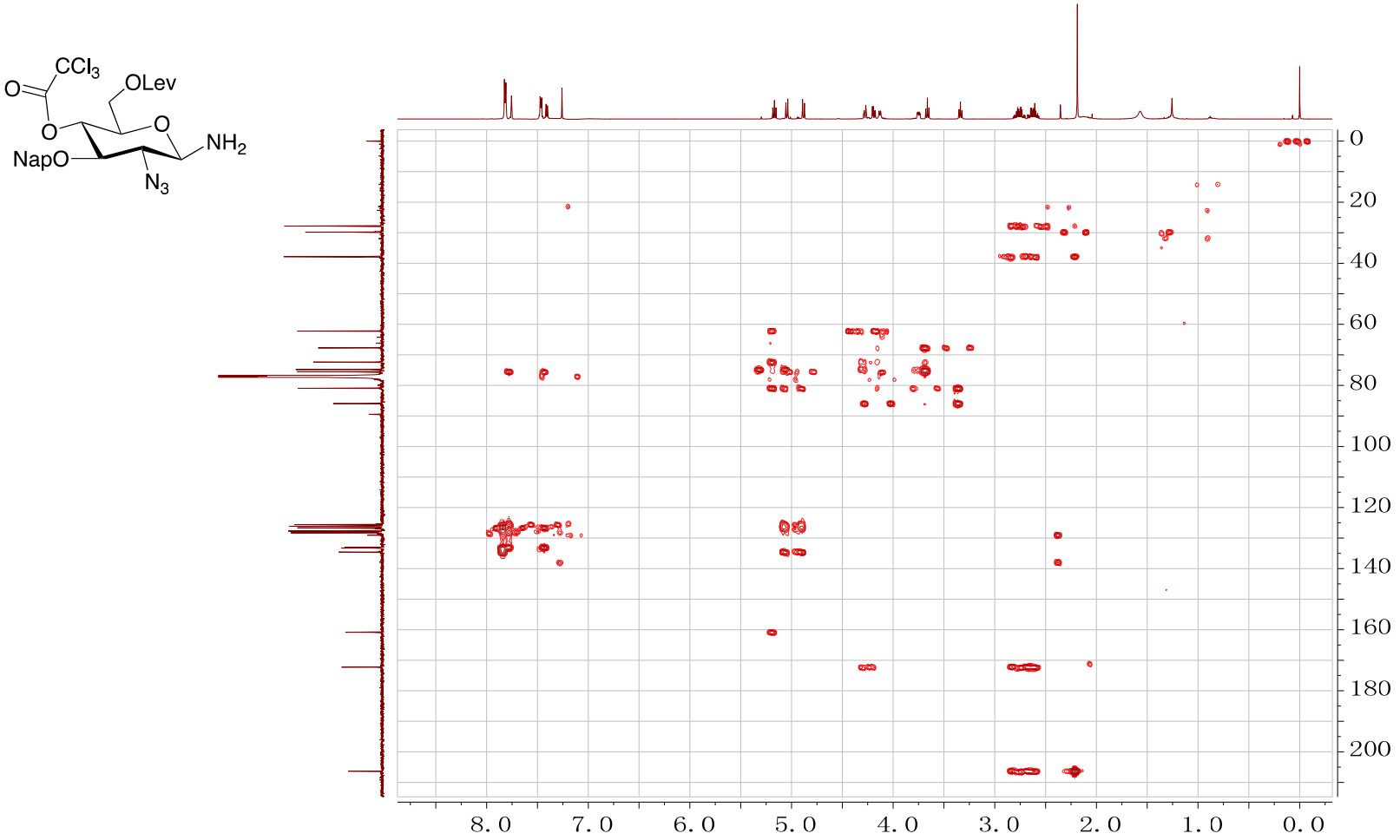




^{1}H-^{1}H COSY of **14**


CCl3
OLev
O
O
O
NH2
NapO
N3
0
20
40
60
80
100
120
140
160
180
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

HSQC of **14**


CCl3
O
OLev
O
O
NH2
NapO
N3
0
20
40
60
80
100
120
140
160
180
200
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

HMBC of **14**