Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

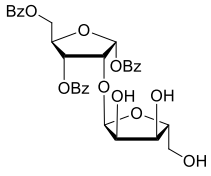
Synthesis of Ribosyl-ribosyl-adenosine-5',5'',5'''(triphosphate)—the Naturally Occurring Branched fragment of Poly ADP Ribose

*Qiang Liu, Hans. A. V. Kistemaker, Herman S. Overkleeft[a] Gijsbert A. van der Marel[a] and Dmitri V. Filippov**

Experimental Section

General procedures

All solvents used were stored over molecular sieves and all reactions were carried out in oven or flame-dried glassware. Unless stated otherwise, all solvents were removed by rotary evaporation under reduced pressure at 40°C. Reactions were monitored by TLC-analysis using Merk 25 DC plastikfolien 60 F254 with detection by spraying with 20% H_2SO_4 in MeOH or $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (25g/L) and $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$ in 10% sulfuric acid, followed by charring at approx. 150°C. LC-MS analysis was performed on a Thermo Finnigan LCQ Advantage MAX ion-trap mass spectrometer with an electrospray ion source coupled to Surveyor HPLC system (Thermo Finnegan) using an analytical Gemini C18 column (Phenomex, 50 x 4.60 mm, 3 micron) in combination with eluents A: H_2O; B: MeCN and C: 1% aq. TFA as the solvent system. High resolution mass spectra were recorded by direct injection (2 µL of a 2 µM solution in water/acetonitrile; 50/50; v/v and 0.1% formic acid) on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source in positive mode with resolution R = 60000 at m/z 400 (mass range m/z = 150-2000) and dioctylpthalate (m/z = 391.2842) as a "lock mass". The high resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan). ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were measured on Brüker DPX-300 (300 MHz), Brüker AV-400 (400 MHz) or a Brüker AV-500 (500 MHz) and all individual signal was assigned using 2D-NMR spectroscopy. Chemical shifts were given in ppm (δ) relative to TMS (0 ppm) or indirectly referenced to H_3PO_4 (0.00 ppm) in D_2O via the solvent residual signal and coupling constants were given in Hz. Infrared (IR) spectra were record on a Shimadzu FT-IR 8300. Optical rotation was measured by MCP 100 Modular Circular Polarimeter using methanol as solvent.



α-1,3,5-tri-*O*-benzoylparobiose (3)

Compound **2** (6.90 g, 7.41 mmol) was dissolved in *t*BuOH/Dioxane/H_2O (120 ml, 4/4/1; v/v/v) and Pd/C (370 mg, 10% loading) was added. H_2 was bubbled through the solution for 72 h. TLC analysis showed an incomplete conversion, therefore, 300 mg Pd/C was added and the reaction was stirred under H_2 for 4 days after which the reaction mixture was filtered over celite, concentrated under reduced pressure and co-evaporated with pyridine (1 x) and toluene (1 x). 60 mL pyridine was added and the mixture was cooled to 0°C.Next, Et_3N (15.5 mL, 111.0 mmol) and $Et_3N\cdot 3HF$ (18 mL, 111.0 mmol) were added. The mixture was stirred for 18 h at room temperature and quenched by aq. $NaHCO_3$ (sat.). The mixture was extracted with EtOAc (3 x 240 mL) and the combined organic layers were dried over $MgSO_4$. After concentration under reduced pressure, the crude product was purified by silica gel chromatography (pentane/EtOAc, 25/75 – 20/80) to obtain **3** as a white foam (3.20 g, 5.38 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 6H, arom.), 7.62 – 7.57 (m, 3H, arom), 7.49 – 7.46 (m, 2H, arom), 7.42 – 7.36 (m, 4H, arom), 6.76 (d, *J* = 4.2 Hz, 1H, H1'), 5.74 (dd, *J* = 6.3, 2.0 Hz, 1H, H3'), 5.20 (d, *J* = 4.2 Hz, 1H, H1''), 4.88 (td, *J* = 3.7, 1.9 Hz, 1H, H4'), 4.75 (dd, *J* = 6.3, 4.2 Hz, 1H, H2'), 4.63 (AB, *J* = 12.1, 3.8 Hz, 2H, H5'), 4.04 – 3.94 (m, 2H, H2'',

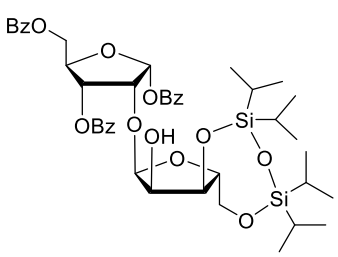
H4''), 3.89 – 3.84 (m, 1H, H3'), 3.66 (AB, *J* = 12.1, 3.8 Hz, 1H, H5''), 3.56 (AB, *J* = 12.1, 3.8 Hz, 1H, H5''), 2.70 (d, *J* = 9.6 Hz, 1H, OH), 2.52 (d, *J* = 9.1 Hz, 1H, OH), 1.85 (s, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.84 (CO Bz), 166.14 (CO Bz), 165.93(CO Bz), 133.98, 133.69, 133.60, 130.06, 130.04, 129.80 (arom.), 129.66, 129.51, 129.04 (cq. arom.), 128.74, 128.73, 128.59 (arom.), 102.27 (C1''), 95.31 (C1'), 86.39 (C4''), 82.77 (C4'), 77.48, 77.16 76.84, 75.40(C2'), 72.33(C2''), 72.21 (C3'), 70.53 (C3''), 64.22 (C5'), 62.61 (C5'').

IR (film): 3482 (br), 2930, 1717, 1267, 1117, 1093, 1068, 1022, 710 cm^{-1}.

HRMS (ESI^+) calcd for $C_{31}H_{30}O_{12}Na$ (M+Na) 617.1629. Found 617.1627.

$[\alpha]_D^{20}$ +102.8 (c = 1, in MeOH)

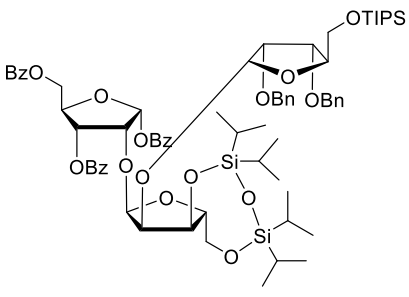


α-1,3,5-tri-*O*-benzoyl-3',5'-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-parobiose (4)

Compound **3** (6.66 g, 11.2 mmol) and imidazole (2.29 g, 33.6 mmol) were co-evaporated with toluene (2 x), dissolved in DCM (66 mL) and then TIPDCl (4.3 mL, 13.4 mmol) was added. The reaction was stirred at room temperature for 15 h and quenched upon the addition of H_2O (200 mL). The mixture was washed by DCM (3 x 100 mL) and the organic layer was dried by $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (DCM/acetone, 100/0 – 97/3) to obtain **4** as colorless foam (7.83 g, 9.35 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.03 (m, 6H, arom.), 7.63 – 7.53 (m, 3H, arom.), 7.48 (t, *J* = 7.6 Hz, 2H, arom), 7.44 – 7.34 (m, 4H, arom.), 6.79 (d, *J* = 4.2 Hz, 1H, H1'), 5.67 (dd, *J* = 6.3, 2.0 Hz, 1H, H3'), 5.19 (d, *J* = 4.0 Hz, 1H, H1''), 4.77 (m, 2H, H2', H4'), 4.65 (AB, *J* = 12.1, 3.5 Hz, 2H, H5'), 4.14 – 4.01 (m, 2H, H2'' H3''), 3.95 – 3.90 (m, 1H, H4''), 3.81 (AB, *J* = 11.8, 3.5 Hz, 1H, H5''), 3.66 (AB, *J* = 11.6, 8.3 Hz, 1H, H5''), 2.85 (d, *J* = 8.2 Hz, 1H, OH), 1.03 (m, 6H, CH_3, TIPDS), 1.00 – 0.83 (m, 18H, CH_3, TIPDS), 0.80 (d, *J* = 7.3 Hz, 2H, CH, TIPDS), 0.73 (d, *J* = 7.2 Hz, 2H, CH, TIPDS).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 165.70 (CO Bz), 133.50, 133.48, 133.45, 130.14, 129.97 (arom.), 129.92 (cq. arom.), 129.80 (arom.), 129.63 (cq. arom.), 128.67, 128.57, 128.49 (arom.), 101.93 (C1''), 95.13(C1'), 83.81(C4''), 83.32(C4'), 75.67 (C2'), 71.93 (C3'), 71.03 (C2''), 70.77 (C3''), 64.30 (C5'), 63.39 (C5''), 17.55, 17.49, 17.45, 17.41, 17.06, 16.98, 16.82, 16.68, 13.44, 13.24, 13.01, 12.33 (CH, CH_3, TIPDS).



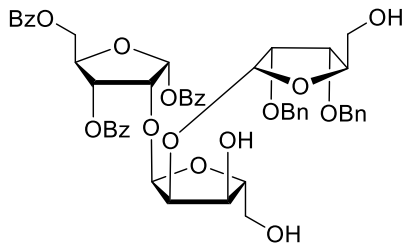
α-1,3,5-tri-*O*-benzoyl-3',5'-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-2'',3''-di-*O*-benzyl-5''-*O*-triisopropylsilylparotriose (6)

Compounds **4** (7.8 g, 9.32 mmol) and **5** (7.36 g, 11.18 mmol) were co-evaporated with toluene (2 x), 1,4-dioxane (2 x) and DCE (1 x). Dry DCM (150 mL) and freshly activated 4Å molecular sieves were added to the mixture. The mixture was stirred under argon at room temperature for 2 h and then cooled to -78°C. Next, TMSOTf (50 µL, 0.28 mmol) was added,

the reaction mixture was stirred at the same temperature for 30 minutes and then was quenched by addition of triethylamine. The reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography (pentane/EtOAc, 70/30 – 50/50) to obtain **6** as a white foam (9.7 g, 7.43 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 2H, arom.), 8.08 (t, *J* = 7.6 Hz, 4H, arom.), 7.59 – 7.54 (m, 2H, arom), 7.48 (q, *J* = 7.4 Hz, 3H), 7.37 (t, *J* = 7.7 Hz, 2H, arom.), 7.29 – 7.11 (m, 12H, arom.), 6.79 (d, *J* = 4.0 Hz, 1H, H1'), 5.59 (dd, *J* = 6.3, 1.7 Hz, 1H, H3'), 5.36 (d, *J* = 3.4 Hz, 1H, H1''), 5.28 (d, *J* = 3.9 Hz, 1H, H1'''), 4.85 (dd, *J* = 6.2, 4.1 Hz, 1H, H2'), 4.76 – 4.67 (m, 2H, CH_2 Bn, H4'), 4.62 (AB, *J* = 12.0, 3.5 Hz, 1H, H5'), 4.52 (AB, *J* = 12.0, 4.0 Hz, 1H, H5'), 4.49 – 4.36 (m, 2H, CH_2 Bn, H2''), 4.32 (d, *J* = 11.8 Hz, 1H, CH_2 Bn), 4.25 – 4.01 (m, 4H, H3'', H4''', H4'', CH_2 Bn), 3.95 (d, *J* = 11.4 Hz, 1H, CH_2 Bn), 3.83 (AB, *J* = 13.1, 2.3 Hz, 1H, H5''), 3.78 – 3.63 (m, 4H, H5'',H5''', H3'''), 3.43 (dd, *J* = 6.4, 3.9 Hz, 1H, H2'''), 1.11 – 0.94 (m, 42H, CH_3, TIPS, TIPDS,), 0.93–0.88 (m, 7H, CH, TIPS, TIPDS).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 165.99, 165.66 (CO Bz), 138.94, 138.68 (cq. arom.), 133.50, 133.47, 133.30, 130.14 (arom.), 130.04 (cq. arom.), 129.99, 129.93 (arom.), 129.77, 129.68 (cq. arom.), 128.62, 128.55, 128.13, 128.00, 127.85, 127.69, 127.35, 127.16 (arom.), 102.21 (C1''), 101.23 (C1'''), 95.07 (C1'), 83.34 (C4'), 81.18 (C4'''), 81.12 (C4''), 77.36 (C2'''), 75.56 (C3'''), 75.12 (C2'), 73.58 (C2''), 72.35 (C3'), 72.30 (CH_2 Bn), 71.78 (CH_2 Bn), 69.04 (C3''), 64.25 (C5'), 62.61 (C5''), 59.95 (C5'''), 18.07, 17.52, 17.47, 17.42, 17.22, 17.18, 17.09, 16.96, 13.61, 13.13, 12.77, 12.59, 12.03 (CH_3, CH_2, TIPDS, TIPS).



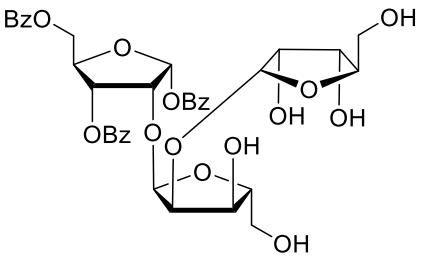
α-1,3,5-tri-*O*-benzoyl-2'',3''-di-*O*-benzylparotriose (7)

Compound **6** (7.7 g, 5.90 mmol) and 60 mL pyridine were added into a flask and the mixture was cooled to 0℃. Subsequently, $Et_3N{\cdot}3HF$ (14.5 mL, 88.53 mmol) was added under argon. The reaction was stirred at room temperature for 24 h and then additional 1.5 ml $Et_3N \cdot 3HF$ was added at 0℃. The mixture was stirred for 5 h at room temperature and quenched by addition of aq. $NaHCO_3$ (sat.). 50 mL H_2O was added and the mixture was extracted by EtOAc (3 x 80 mL). The combined organic layers were dried over $MgSO_4$. The mixture was filtered and then concentrated under reduced pressure. Purification by silica gel chromatography (pentane/actone, 70/30 – 50/50) furnished **7** as a white foam (4.3 g, 4.74 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 6H, arom.), 7.60 – 7.52 (m, 3H,), 7.47 – 7.43 (m, 2H), 7.42 – 7.29 (m, 4H), 7.29 – 7.19 (m, 8H), 7.19 – 7.10 (m, 2H), 6.80 (d, *J* = 4.1 Hz, 1H, H1'), 5.64 (dd, *J* = 6.3, 2.4 Hz, 1H, H3'), 5.37 (d, *J* = 3.6 Hz, 1H, H1''), 5.31 (d, *J* = 3.7 Hz, 1H, H1'''), 4.79 (dd, *J* = 6.3, 4.1 Hz, 1H, H2'), 4.75 (td, *J* = 3.9, 2.4 Hz, 1H, H4'), 4.62 (AB, *J* = 12.0, 3.6 Hz, 1H, H5'), 4.57 (d, *J* = 11.9 Hz, 1H, CH_2, Bn), 4.52 (AB, *J* = 12.0, 4.3 Hz, 1H, H5'), 4.43 – 4.36 (m, 2H, CH_2, Bn), 4.30 (dd, *J* = 5.4, 3.6 Hz, 1H, H2'), 4.10 (q, *J* = 3.3 Hz, 1H, H4''), 4.04 (d, *J* = 11.4 Hz, 1H, CH_2, Bn), 4.01 – 3.90 (m, 2H, H4'', H3''), 3.70 (dd, *J* = 5.9, 3.1 Hz, 1H, H3'''), 3.65 – 3.43 (m, 5H, OH, H2''', H5'', H5'''), 3.36 – 3.30 (m, 1H, H5'''), 1.76 (d, *J* = 6.1 Hz, 1H, OH), 1.53 (dd, *J* = 8.4, 4.8 Hz, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.14 (CO, Bz), 165.70 (CO, Bz), 137.85, 137.73 (cq. arom.),

133.64, 133.61, 133.50, 130.27, 130.10 (arom.), 129.94 (cq. arom), 129.89 (arom.), 129.70, 129.66 (cq. arom.), 128.65, 128.61, 128.57, 128.51, 128.48, 128.46, 128.41, 128.30, 127.98, 127.80, 127.77 (arom.), 102.66 (C1''), 99.56 (C1'''), 95.65 (C1'), 84.40 (C3''), 83.72 (C4''), 82.94 (C4'), 79.44 (C2'''), 76.07 (C3'''), 75.63 (C2'), 72.99 (cq. CH2, Bn), 72.86 (C2''), 72.32 (CH2, Bn), 71.97 (C3'), 70.30 (C4''), 64.19 (C5'), 62.60 (C5'''), 62.03 (C5'').
IR (film): 3456 (bs), 2920, 1722, 1267, 1096, 1069, 1024, 712 cm^{-1}.
HRMS (ESI^+) calcd for $C_{50}H_{50}O_{16}Na$ (M+Na) 929.2991. Found 929.2999.
$[\alpha]_D^{20}$ +98.3 (c = 1, in MeOH)

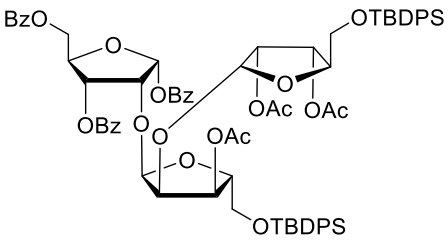


α-1,3,5-tri-*O*-benzoylparobiose (8)

Compound **7** (420 mg, 0.46 mmol) was dissolved in MeOH (10 mL), Pd/C (100 mg, 10% loading) and few drops of AcOH were added. The mixture was sonicated under argon for 5 minutes then H_2 was bubbled for 24 h. The reaction was filtered over celite and the residue was concentrated under reduced pressure and purified by silica gel chromatography (DCM/MeOH, 95/5 – 92/8) to obtain **8** as a white foam (292 mg, 0.40 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.00 (m, 6H), 7.62 – 7.52 (m, 3H, arom), 7.49 – 7.33 (m, 6H, arom.), 6.76 (d, *J* = 4.2 Hz, 1H, H1'), 5.69 (dd, *J* = 6.3, 1.7 Hz, 1H, H3'), 5.27 (d, *J* = 3.9 Hz, 1H, H1''), 4.95 (d, *J* = 3.9 Hz, 1H, H1'''), 4.87 – 4.79 (m, 1H, H4'), 4.72 (dd, *J* = 6.3, 4.2 Hz, 1H, H2'), 4.67 – 4.53 (m, 2H, H5'), 4.10 – 4.02 (m, 1H, H2''), 3.96 – 3.93 (m, 3H, H3'', H4''', H4''), 3.73 – 3.35 (m, 7H, H3''', H2''', H5'', H5''', OH), 3.29 (d, *J* = 7.6 Hz, 1H, OH), 3.14 (d, *J* = 9.6 Hz, 1H, OH), 3.04 – 2.98 (m, 2H, OH).

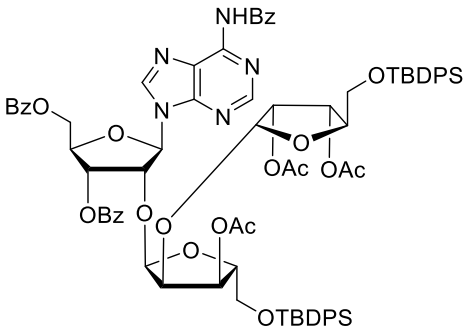
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.65 (CO, Bz), 166.17 (CO, Bz), 165.92 (CO, Bz), 133.85, 133.76, 133.52, 130.13, 129.76 (arom.), 129.50, 129.47, 129.07 (cq. arom.), 128.65, 128.56 (arom.), 101.41 (C1''), 100.98 (C1'''), 95.33 (C1'), 86.31 (C4''), 85.71 (C4'''), 83.18 (C4'), 75.30 (C2'), 75.21 (C2''), 72.45 (C2'''), 72.14 (C3'), 70.91 (C3''), 70.84 (C3'''), 64.29 (C5'), 62.76 (C5'''), 62.16 (C5'').
IR (film): 3466 (bs), 2934, 1717, 1269, 1119, 1094, 1069, 1024, 710 cm^{-1}.
HRMS (ESI^+) calcd for $C_{36}H_{38}O_{16}Na$ (M+Na) 749.2052. Found 749.2051.
$[\alpha]_D^{20}$ +115.8 (c = 1, in MeOH)



α-1,3,5-tri-*O*-benzoyl-3'-*O*-acetyl-5'-*O*-tertbutyldiphenylsilyl-2'',3''-di-*O*-acetyl-5''-*O*-tertbutyldiphenylsilylparotriose (9)

Compound **8** (2.7 g, 3.72 mmol) was co-evaporated with pyridine (2 x) and then argon was applied. Pyridine (38 mL) and TBDPSCl (4 mL, 15.15 mmol) were added and the mixture was stirred under argon at room temperature for 6 h. Ac_2O (11 mL, 113.4 mmol) was added into the reaction and the mixture was stirred for 16 h after which the reaction was quenched by addition of aq. $NaHCO_3$ (sat.). The mixture was extracted by DCM (3 x 50 mL) and dried by $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography

(pentane/actone, 100/0 – 80/20) furnished **9** as a white foam (3.1 g, 2.33 mmol, 63%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 2H, arom.), 8.18 – 8.12 (m, 2H, arom.), 8.10 – 8.05 (m, 2H, arom.), 7.69 – 7.49 (m, 11H, arom.), 7.45 – 7.30 (m, 18H, arom.), 6.80 (d, *J* = 4.3 Hz, 1H, H1'), 5.72 (dd, *J* = 6.3, 1.8 Hz, 1H, H3'), 5.46 (dd, *J* = 6.6, 1.9 Hz, 1H, H3''), 5.39 (dd, *J* = 7.0, 3.2 Hz, 1H, H3'''), 5.32 (d, *J* = 4.2 Hz, 1H, H1''), 5.29 (d, *J* = 4.5 Hz, 1H, H1'''), 4.89 (dd, *J* = 7.0, 4.4 Hz, 1H, H2'''), 4.77 (td, *J* = 3.7, 1.7 Hz, 1H, H4'), 4.72 – 4.56 (m, 3H, H2', H5'), 4.36 (dd, *J* = 6.6, 4.2 Hz, 1H, H2''), 4.09 – 4.06 (m, 2H, H4''', H4''), 3.81 (AB, *J* = 11.2, 2.7 Hz, 1H, H5''), 3.74 – 3.57 (m, 3H, H5'', H5'''), 2.01 (s, 3H, Ac), 1.79 (s, 3H, Ac), 1.64 (s, 3H, Ac), 1.05 (s, 9H, CH_3, TBDPS), 0.97 (s, 9H, CH_3, TBDPS).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.70, 170.09, 169.70 (CO, Ac), 166.17, 166.14, 165.56 (CO, Bz), 135.75, 135.72, 135.70, 135.67, 133.51, 133.49 (arom.), 133.13, 133.09, 133.02, 132.95, 130.25 (cq. arom.), 130.15, 130.12, 129.95, 129.93, 129.89, 129.85, 129.79 (arom.), 129.73 (cq. arom), 128.69, 128.50, 127.92, 127.90, 127.87 (arom.), 101.29 (C1''), 99.52 (C1'''), 95.16 (C1'), 83.73 (C4''), 83.66 (C4'), 83.14 (C4'''), 76.35 (C2'), 74.62 (C2''), 71.75 (C2'''), 71.66 (C3'), 71.26 (C3''), 69.82 (C3'''), 64.44 (C5'), 63.90 (C5''), 63.42 (C5'''), 26.90 (CH_3, TBDPS), 26.85 (CH_3, TBDPS), 20.70 (Ac), 20.39 (Ac), 20.17 (Ac), 19.38 (cq. TBDPS), 19.29 (cq. TBDPS).
IR (film): 1728, 1265, 1252, 1112, 1067, 1042, 1026, 709 cm^{-1}.
HRMS (ESI^+) calcd for $C_{74}H_{80}O_{19}Si_2Na$ (M+Na) 1351.4725. Found 1351.4734.
$[\alpha]_D^{20}$ +72.8 (c = 1, in MeOH)



6-*N*-benzoyl-9-(3',5'-di-*O*-benzoyl-3''-*O*-acetyl-5''-*O*-tertbutyldiphenylsilyl-2''',3'''-di-*O*-acetyl-5'''-*O*-tertbutyldiphenylsilyl-β-parotriosyl)adenine (10)

Compound **9** (1.1 g, 0.83 mmol) and N^6-benzoyladenine (0.41 g, 1.71 mmol) were co-evaporated with toluene (2 x), 1,4-dioxane (2 x), MeCN (1 x) and dissolved in dry MeCN (14 mL) under argon. *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (3.2 mL, 12 mmol) was added and the mixture was stirred at room temperature until everything was dissolved. $HClO_4$-SiO_2 (4.3 g, 0.4 mmol/g, 1.71 mmol) was added and the mixture was refluxed for 48 h. Then the reaction was quenched by aq. $NaHCO_3$ (sat.) then filtered. The mixture was extracted with EtOAc (3 x 100 mL), dried by $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography (pentane/acetone, 100/0 – 85/15 – 75/25 – 70/30) gave **10** as a white foam (0.99 g, 0.68 mmol, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H, NH), 8.68 (s, 1H, H2), 8.41 (s, 1H, H8), 8.08 (tt, *J* = 6.6, 1.4 Hz, 4H, arom.), 8.00 – 7.93 (m, 2H, arom.), 7.65 – 7.45 (m, 13H, arom.), 7.45 – 7.27 (m, 16H, arom.), 6.32 (d, *J* = 4.6 Hz, 1H, H1'), 5.95 (t, *J* = 5.3 Hz, 1H, H3'), 5.70 (t, *J* = 5.0 Hz, 1H, H2'), 5.44 (dd, *J* = 6.9, 2.4 Hz, 1H, H3''), 5.40 (dd, *J* = 7.4, 3.5 Hz, 1H, H3'''), 5.25 (d, *J* = 4.4 Hz, 1H, H1''), 5.17 (d, *J* = 4.3 Hz, 1H, H1'''), 4.94 (dd, *J* = 7.3, 4.4 Hz, 1H, H2'''), 4.89 (AB, *J* = 12.0, 3.8 Hz, 1H, H5'), 4.79 – 4.74 (m, 1H, H4'), 4.70 (AB, *J* = 12.0,

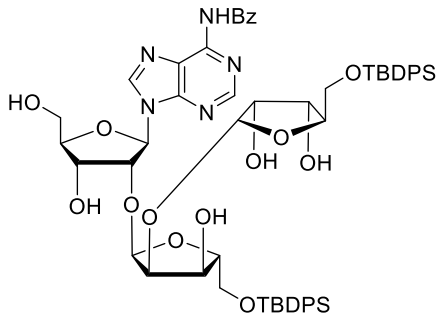
4.9 Hz, 1H, H5'), 4.32 (dd, *J* = 6.9, 4.3 Hz, 1H, H2''), 4.10 (q, *J* = 3.1 Hz, 1H, H4'''), 4.01 (q, *J* = 2.8 Hz, 1H, H4'), 3.78 (AB, *J* = 11.4, 2.7 Hz, 1H, H5'''), 3.70 (AB, *J* = 11.3, 3.2 Hz, 1H, H5'''), 3.58 (AB, *J* = 11.2, 2.8 Hz, 1H, H5''), 3.44 (AB, *J* = 11.2, 3.3 Hz, 1H, H5''), 2.11 (s, 3H, Ac), 2.08 (s, 3H, Ac), 1.68 (s, 3H, Ac), 1.01 (s, 9H, CH_3, TBDPS), 0.96 (s, 9H, CH_3, TBDPS).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.53, 169.88, 169.79 (CO, Ac), 166.25, 165.35, 164.45 (CO, Bz), 152.87 (CH, C2), 151.35, 149.74 (cq. arom.), 135.61, 135.59 (arom.), 133.71 (aq. arom.), 133.59, 133.44 (arom.), 132.96, 132.91, 132.87 (cq. arom,), 132.82 (arom.), 132.75 (aq. arom.), 129.90, 129.88, 129.85, 129.83 (arom.), 129.57, 129.53 (cq. arom.), 128.92, 128.59, 128.54, 127.88, 127.86, 127.82, 127.81, 127.79 (arom.), 123.92 (cq. arom.), 101.19 (C1''), 98.61 (C1'''), 89.09 (C1'), 83.02 (C4'''), 82.38 (C4''), 80.46 (C4'), 72.98 (C2''), 72.44 (C3'), 71.74 (C2'''), 70.96 (C3''), 69.79 (C3'''), 63.58 (C5'), 63.52 (C5''), 63.13 (C5'''), 26.83, 26.76 (CH_3, Ac), 20.75, 20.66, 20.40 (CH_3, TBDPS), 19.25 (cq. TBDPS).

IR (film): 2930, 1728, 1238, 1111, 1069, 1038, 1028, 702 cm^{-1}.

HRMS (ESI^+) calcd for $C_{79}H_{84}N_5O_{18}Si_2$ $(M+H)^+$ 1446.5344. Found 1446.5344.

$[\alpha]_D^{20}$ +31.4 (c = 1, in MeOH)



6-*N*-benzoyl-9-(5'',5'''-di-*O*-tertbutyldiphenylsilyl-β-parotriosyl)adenine (11)

Compound **10** (984 mg, 0.68 mmol) was dissolved in pyridine/EtOH (7 mL; 2/1 v/v), cooled to 0°C after which aqueous NaOH (4.1 mL, 1 M) was slowly added. The reaction mixture was stirred for 2 h at the same temperature after which Amberlite-H^+ was added until pH = 6. The mixture was filtered, concentrated under reduced pressure and purified by silica gel chromatography (DCM/methanol, 100/0 – 97/3 – 95/5) to obtain **11** as a white foam (641 mg, 0.58 mmol, 85%).

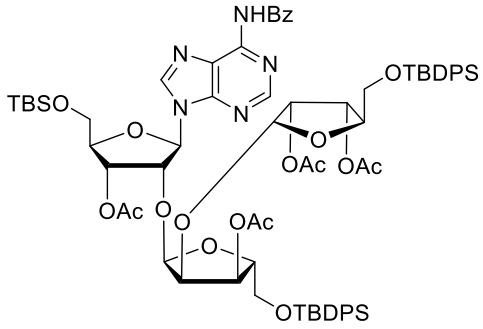
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H, NH), 8.80 (s, 1H, H2), 8.53 (s, 1H, H8), 8.03 – 7.92 (m, 2H, arom.), 7.62 – 7.59 (m, 8H), 7.56 – 7.49 (m, 1H, arom.), 7.46 – 7.23 (m, 14H, arom.), 6.23 (d, *J* = 7.3 Hz, 1H, H1'), 5.12 (d, *J* = 4.4 Hz, 1H, H1''), 4.99 (d, *J* = 4.0 Hz, 1H, H1'''), 4.94 (dd, *J* = 7.4, 4.7 Hz, 1H, H2'), 4.60 (d, *J* = 4.7 Hz, 1H, H3'), 4.44 (t, *J* = 4.8 Hz, 2H, H2''), 4.39 – 4.22 (m, 5H, H3''', H4', H2''', H3''', H4''), 4.20 (q, *J* = 2.8 Hz, 1H, H4'''), 3.97 (AB, *J* = 13.0, 1.8 Hz, 1H, H5'), 3.77 – 3.65 (m, 5H, H5', H5'', H5'''), 3.73 – 3.63 (m, 4H), 0.99 (s, 9H, TBDPS), 0.98 (s, 9H, TBDPS)

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.04 (CO, Bz), 152.21 (C2), 150.66, 150.30 (cq. arom.), 144.26 (C8), 135.61, 135.59, 135.56 (arom.), 133.58, 133.06 (cq. arom.), 132.91 (arom.), 132.83, 132.65 (cq. arom), 130.00, 129.97, 129.93, 129.86, 128.85, 128.09, 127.91, 127.87, 127.82 (arom.), 124.36 (cq. arom.), 101.94 (C1'''), 101.08 (C1''), 89.48 (C1'), 88.17 (C4'), 86.40 (C4''), 86.19 (C4'''), 80.01 (C2'), 76.99 (C2''), 73.22 (C2'''), 72.92 (C3'), 72.15 (C3''), 71.16 (C3'''), 64.32 (C5'''), 64.13 (C5''), 63.27 (C5'), 26.88 (CH_3, TBDPS), 26.86 (CH_3, TBDPS), 19.26 (cq. TBDPS), 19.23 (cq. TBDPS).

IR (film): 3329 (bs), 2930, 2857, 1701, 1612, 1458, 1105, 1072, 1037, 702 cm^{-1}.

HRMS (ESI^+) calcd for $C_{59}H_{70}N_5O_{13}Si_2$ $(M+H)^+$ 1112.4503. Found 1112.4511.

$[\alpha]_D^{20}$ +48.7 (c = 1, in MeOH)



6-*N*-benzoyl-9-(3',3''2''',3'''-tetra-*O*-acetyl-5'-*O*-tertbutyldimethylsilyl-5'',5'''-di-*O*-tertbutyldiphenylsilyl-β-parotriosyl)adenine (12)

Compound **11** (146 mg, 0.13 mmol) was dissolved in dry pyridine (1.3 mL), TBSCl (50 mg, 0.32 mmol) was added and the reaction was stirred for 6 hours at room temperature. TLC showed an incomplete conversion and additional TBSCl (100 mg, 0.66 mmol) was added. The mixture was stirred at room temperature for 5 h after which Ac_2O (0.37 ml, 3.9 mmol) was added. The mixture was stirred at 0°C for 10 h then quenched by aq. $NaHCO_3$ (sat.). 20 mL H_2O was added and the mixture was extracted with DCM (3 x 15 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by silica gel chromatography (pentane/actone, 100/0 – 90/10 – 85/15 – 80/20) to obtain **12** as a white foam (133 mg, 0.09 mmol, 69%).

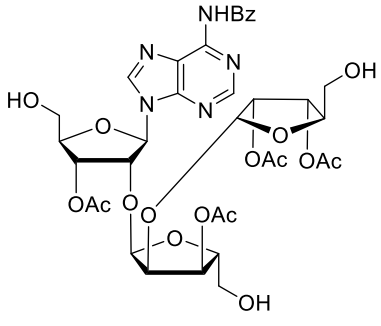
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H, NH), 8.80 (s, 1H, H2), 8.51 (s, 1H, H8), 8.05 – 7.95 (m, 2H, arom.), 7.69 – 7.54 (m, 9H, arom.), 7.50 (t, *J* = 7.6 Hz, 2H, arom.), 7.45 – 7.29 (m, 12H, arom.), 6.33 (d, *J* = 3.8 Hz, 1H, H1'), 5.53 (dd, *J* = 6.8, 2.1 Hz, 1H, H3''), 5.45 (dd, *J* = 7.3, 3.0 Hz, 1H, H3'''), 5.41 (t, *J* = 5.5 Hz, 1H, H3'), 5.34 – 5.32 (m, 2H, H1'', H1'''), 5.10 (t, *J* = 4.6 Hz, 1H, H2'), 5.05 (dd, *J* = 7.1, 4.5 Hz, 1H, H2'''), 4.39 – 4.34 (m, 2H, H2'', H4'), 4.18 (t, *J* = 2.9 Hz, 1H, H4'''), 4.10 – 4.07 (m, 2H, H4'', H5'), 3.93 – 3.68 (m, 5H, H5', H5'', H5'''), 2.14 (s, 3H, Ac), 2.11 (s, 6H, 2Ac), 2.06 (s, 3H, Ac), 1.04 (s, 9H, TBDPS), 1.01 (s, 9H, TBDPS), 0.93 (s, 9H, CH_3, TBS), 0.12 (s, 6H, CH_3, TBS).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.53, 169.94, 169.71, 169.62 (CO, Ac), 164.61 (CO, Bz), 152.86 (C2), 151.42, 149.58 (cq. arom.), 141.76 (C8), 135.65, 135.62, 135.59 (arom.), 133.83, 133.00, 132.96, 132.83 (cq. arom.), 132.74, 129.89, 129.85, 128.87, 127.93, 127.85, 127.82 (arom), 123.51 (cq. arom.), 100.71 (C1''), 99.37 (C1'''), 88.06 (C1'), 83.30 (C4''), 82.85 (C4', C4'''), 77.99 (C2'), 73.86 (C2''), 71.60 (C2'''), 71.30 (C3''), 71.04 (C3'), 69.97 (C3'''), 63.77 (C5''), 63.34 (C5'''), 62.11 (C5'), 26.82, 26.80 (CH_3, TBDPS), 26.02 (CH_3, TBS), 21.04, 20.86, 20.78, 20.46 (CH_3, Ac), 19.27 (cq. TBDPS), 18.53 (cq. TBS), -5.31, -5.40 ($SiCH_3$, TBS).

IR (film): 2951, 2930, 2859, 1746, 1236, 1113, 1043, 702 cm^{-1}.

HRMS (ESI^+) calcd for $C_{73}H_{92}N_5O_{17}Si_3$ $(M+H)^+$ 1394.5790. Found 1394.5789.

$[\alpha]_D^{20}$ +70.0 (c = 1, in MeOH)



6-*N*-benzoyl-9-(3',3''2''',3'''-tetra-*O*-acetyl-β-parotriosyl)adenine (13)

Compound **12** (133 mg, 0.09 mmol) was dissolved in pyridine (1 mL), cooled to 0°C after which HF·pyridine (0.12 mL, 4.3 mmol) was added. The reaction was stirred for 1.5 hours at 0°C after which was quenched by aq. $NaHCO_3$ (sat.) then extracted with EtOAc (4 x 10 mL),

dried over $MgSO_4$, concentrated under reduced pressure and purified by silica gel chromatography (DCM/methanol, 100/0 – 100/1 – 96/4) to obtain **13** as a white foam (62 mg, 77 μmol, 86%).

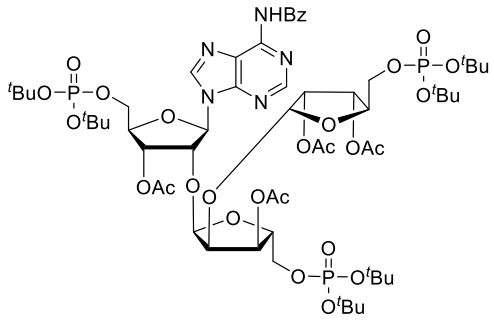
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H, NH), 8.64 (s, 1H, H2), 8.59 (s, 1H, H8), 8.02 (d, *J* = 7.4 Hz, 2H, arom.), 7.62 – 7.53 (m, 1H, arom.), 7.49 (t, *J* = 7.6 Hz, 2H, arom.), 6.24 (d, *J* = 10.9 Hz, 1H, OH), 6.10 (d, *J* = 7.8 Hz, 1H, H1'), 5.61 (d, *J* = 5.4 Hz, 1H, H3'), 5.17 (dd, *J* = 7.3, 4.2 Hz, 1H, H3''), 5.12 – 5.08 (m, 2H, H2', H3'''), 4.96 (d, *J* = 4.4 Hz, 1H, H1''), 4.91 (dd, *J* = 7.3, 4.5 Hz, 1H, H2''), 4.68 (d, *J* = 4.2 Hz, 1H, H1'''), 4.24 (s, 1H, H4'), 4.03 – 3.98 (m, 3H, H4'', H2''', H4'''), 3.91 (AB, *J* = 12.6 Hz, 1H, H5'), 3.82 – 3.48 (m, 5H, H5', H5'', H5'''), 3.41 (bs, 1H, OH), 2.99 (bs, 1H, OH), 2.14 (s, 3H, Ac), 2.13 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.06 (s, 3H, Ac).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 170.03, 169.71 (CO, Ac), 165.25 (CO, Bz), 152.04 (C2), 150.72, 150.52 (cq. arom.), 144.26 (C8), 133.28 (cq, arom), 133.06, 128.90, 128.21 (arom.), 124.72 (cq. arom.), 101.58 (C1'''), 98.42 (C1''), 89.08 (C1'), 86.54 (C4'), 82.24 (C4''), 82.09 (C4'''), 77.68 (C2'), 73.89 (C3'), 72.12 (C2''), 71.44 (C2'''), 70.41 (C3''), 69.68 (C3'''), 62.79 (C5'), 61.79 (C5''), 61.54 (C5'''), 21.15, 20.97, 20.76, 20.72 (CH_3, Ac).

IR (film): 3352 (bs), 2932, 1738, 1612, 1584, 1456, 1369, 1238, 1092, 1043 cm^{-1}.

HRMS (ESI$^+$) calcd for $C_{35}H_{42}N_5O_{17}$ $(M+H)^+$ 804.2570. Found 804.2573.

$[\alpha]_D^{20}$ +78.3 (c = 1, in MeOH)



6-*N*-benzoyl-9-(3',3''2''',3'''-tetra-*O*-acetyl-5',5'',5'''-tri-*O*-(ditertbutylphosphoryl)-β-parotriosyl)adenine (14)

1-Methyl-imidazole·HCl (200 mg, 1.68 mmol) and 1-methyl-imidazole (88 μL, 1.1 mmol) were co-evaporated with dry CH_3CN (3 x), then N_2 was applied. To this mixture, freshly activated molecular sieves and dry DMF (0.9 mL) were added and the activator solution was stirred at room temperature for 2 hours under N_2. Next, compound **13** (73 mg, 91 μmol) was co-evaporated with dry 1,4-dioxane (3 x) and then mixed with the activator solution, after which di-tert-butyl-*N*,*N*-diisopropylphosphoramidite (0.28 mL, 0.9 mmol) was added and the reaction was stirred at room temperature for 1 hour. Then *t*BuOOH in decane (0.56 mL, 5.5 M, 3.08 mmol) was added at 0°C and the reaction mixture was stirred for 1 hour at room temperature. The reaction was quenched by aq. $NaHCO_3$ (sat.), extracted with EtOAc (3 x 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography (DCM/MeOH, 100/0 – 95/5) followed by LH-20 gel filtration (DCM/methanol, 50/50) gave **14** as a white foam (70 mg, 51 μmol, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H, NH), 8.81 (s, 1H, H2), 8.45 (s, 1H, H8), 8.10 – 7.99 (m, 2H, arom.), 7.67 – 7.58 (m, 1H, arom.), 7.53 (dd, *J* = 8.3, 6.7 Hz, 2H, arom.), 6.26 (d, *J* = 4.7 Hz, 1H, H1'), 5.50 (t, *J* = 5.1 Hz, 1H, H3'), 5.37 (dd, *J* = 7.1, 2.8 Hz, 1H, H3''), 5.33 – 5.26 (m, 1H, H2'), 5.23 (dd, *J* = 7.4, 3.6 Hz, 1H, H3'''), 5.19 (d, *J* = 4.3 Hz, 1H, H1''), 5.17 (d, *J* = 4.4 Hz, 1H, H1'''), 4.86 (dd, *J* = 7.4, 4.4 Hz, 1H, H2'''), 4.44 (tt, *J* = 4.2, 2.1 Hz, 1H, H4'), 4.38 – 4.33 (m, 1H, H5'), 4.26 – 4.18 (m, 4H, H5', H4'', H4''', H2''), 4.15 – 3.97 (m,

4H, H5'', H5'''), 2.17 (s, 3H, Ac), 2.14 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.07 (s, 3H, Ac), 1.56 – 1.39 (m, 54H, *t*Bu).

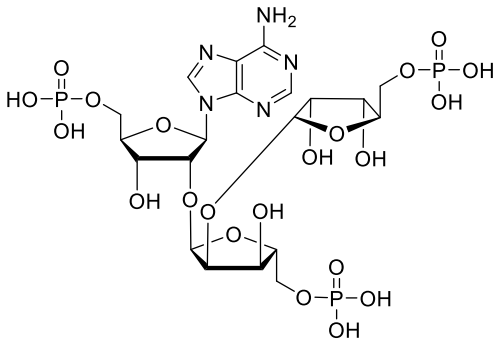
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.46, 169.70, 169.56, 169.49 (CO, Ac), 164.61 (CO, Bz), 152.88 (C2), 151.45, 149.79 (cq. arom.), 142.46 (C8), 133.82 (cq. arom.), 132.85, 128.96, 127.99 (arom.), 123.80 (cq. arom.), 100.58 (C1''), 98.85 (C1'''), 88.10 (C1'), 83.22, 83.17, 83.15, 83.10, 82.96, 82.92, 82.90, 82.85, 82.82 (cq. *t*Bu), 81.20, 81.12, 81.04, 80.86, 80.77 (C4', C4'', C4'''), 77.02, 72.94 (C2''), 71.51 (C3'), 71.23 (C2'''), 70.48 (C3''), 69.56 (C3'''), 65.85, 65.79 (C5'''), 65.55, 65.50 (C5''), 65.03, 64.97 (C5'), 29.97, 29.93, 29.88 (CH_3, *t*Bu), 21.00, 20.97, 20.76, 20.52 (CH_3, Ac).

^{31}P NMR (162 MHz, $CDCl_3$) δ -9.85, -9.99, -10.04.

IR (film): 2980, 1746, 1371, 1244, 1040, 997.2 cm^{-1}.

HRMS (ESI$^+$) calcd for $C_{59}H_{92}N_5O_{26}P_3$ $(M+H)^+$ 1379.5243. Found 1380.5339.

$[\alpha]_D^{20}$ +41.1 (c = 1, in MeOH)



_O_- α-D-ribofuranosyl-(1'''→2'')-_O_ -α-D-ribofuranosyl-(1''→2')-adenosine-5',5'',5'''-tris(phosphate) [β-Parotriosyladenine-5',5'',5'''-tri-_O_-phosphate] (1)

Compound **14** (20 mg, 14.5 μmol) was dissolved in HFIP (0.6 mL), concentrated HCl was added (7.2 μL, 87 μmol) and the reation mixture was stirred at room temperature for 1 h (^{31}P-NMR spectroscopy showed complete cleavage of the tert-butyl groups). 80 μL NH_4OH (35%) was added to quench the reaction and the mixture was concentrated under reduced pressure. Upon co-evaporation of the residue with 1,4-dioxane (3 x), NH_4OH (35%, 2 mL) was added and the mixture was stirred at room temperature for 3 days. LCMS showed complete reaction and then the mixture was concentrated under reduced pressure. The residue was purified by HW-40 gel filtration (0.15 M, NH_4OAc in MiliQ H_2O). Repeated lyophilization furnished **1** as a white solid (11.0 mg, 14.2 μmol, 98%).

^{1}H NMR (400 MHz, D_2O) δ 8.60 (s, 1H, H8), 8.26 (s, 1H, H2), 6.27 (d, *J* = 6.3 Hz, 1H, H1'), 5.36 (d, *J* = 3.8 Hz, 1H, H1''), 4.98 (d, *J* = 4.4 Hz, 1H, H1'''), 4.93 (dd, *J* = 6.3, 5.1 Hz, 1H, H2'), 4.60 (dd, *J* = 5.1, 3.0 Hz, 1H, H3'), 4.39 – 4.38 (m, 1H, H4'), 4.35 – 4.30 (m, 1H, H4''), 4.29 – 4.19 (m, 3H, H2'', H3'', H4'''), 4.05 (dd, *J* = 6.2, 3.0 Hz, 1H, H3'''), 4.02 – 4.00 (m, 2H, H5'), 3.95 (dd, *J* = 6.3, 4.3 Hz, 1H, H2'''), 3.86 – 3.74 (m, 4H, H5'', H5''').

^{13}C NMR (101 MHz, D_2O) δ 155.66 (cq. arom. C6), 153.00 (cq. arom. C2), 149.11 (cq. arom. C4), 140.29 (cq. arom. C8), 118.61 (cq. arom. C5), 101.46 (C1'''), 101.12 (C1''), 85.25 (C1'), 85.17 (C4'), 84.46 (C4''), 84.22 (C4'''), 80.25 (C2'), 75.55 (C2''), 71.29 (C2'''), 70.71 (C3'), 69.95 (C3''), 69.78 (C3'''), 63.90 (C5'', C5'''), 63.76 (C5').

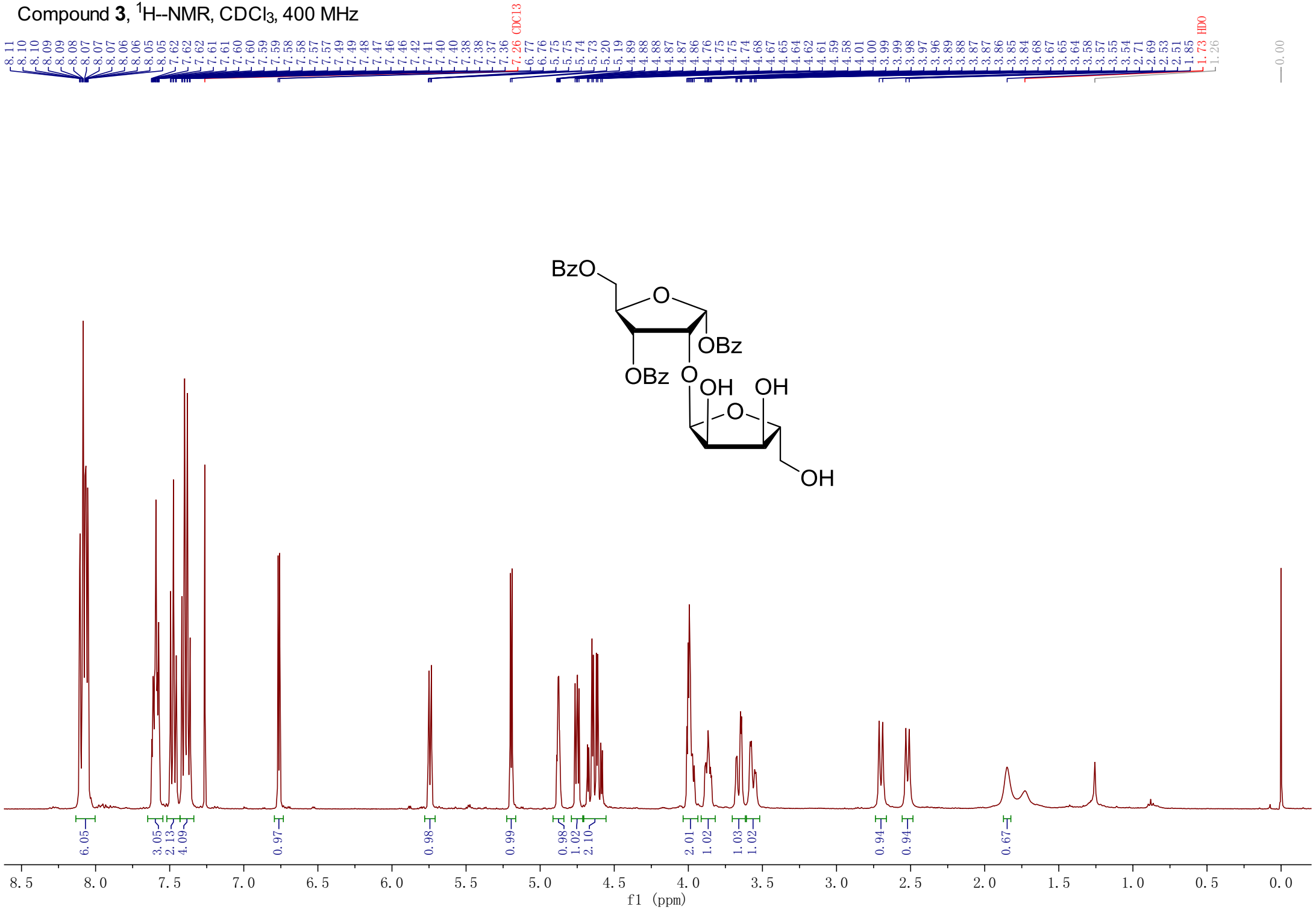
^{31}P NMR (162 MHz, D_2O) δ 3.53, 3.48, 3.46.

IR (film): 3180 (bs), 1686, 1647, 1420, 1034, 930, 795, 783, 719 cm^{-1}.

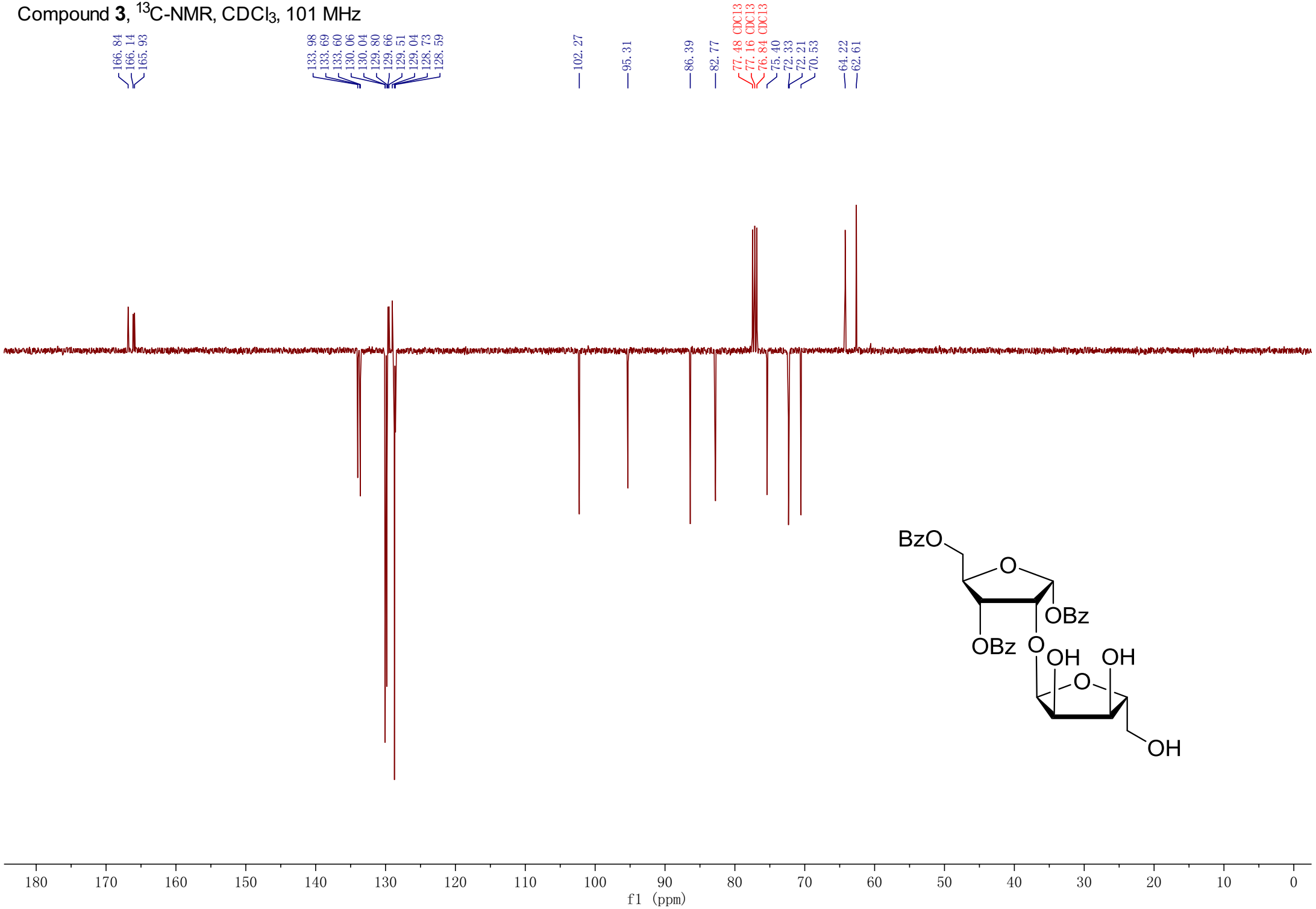
HRMS (ESI$^+$) calcd for $C_{20}H_{33}N_5O_{21}P_3$ $(M+H)^+$ 772.0875. Found 772.0874.

$[\alpha]_D^{20}$ +29.6 (c = 1, in MeOH)

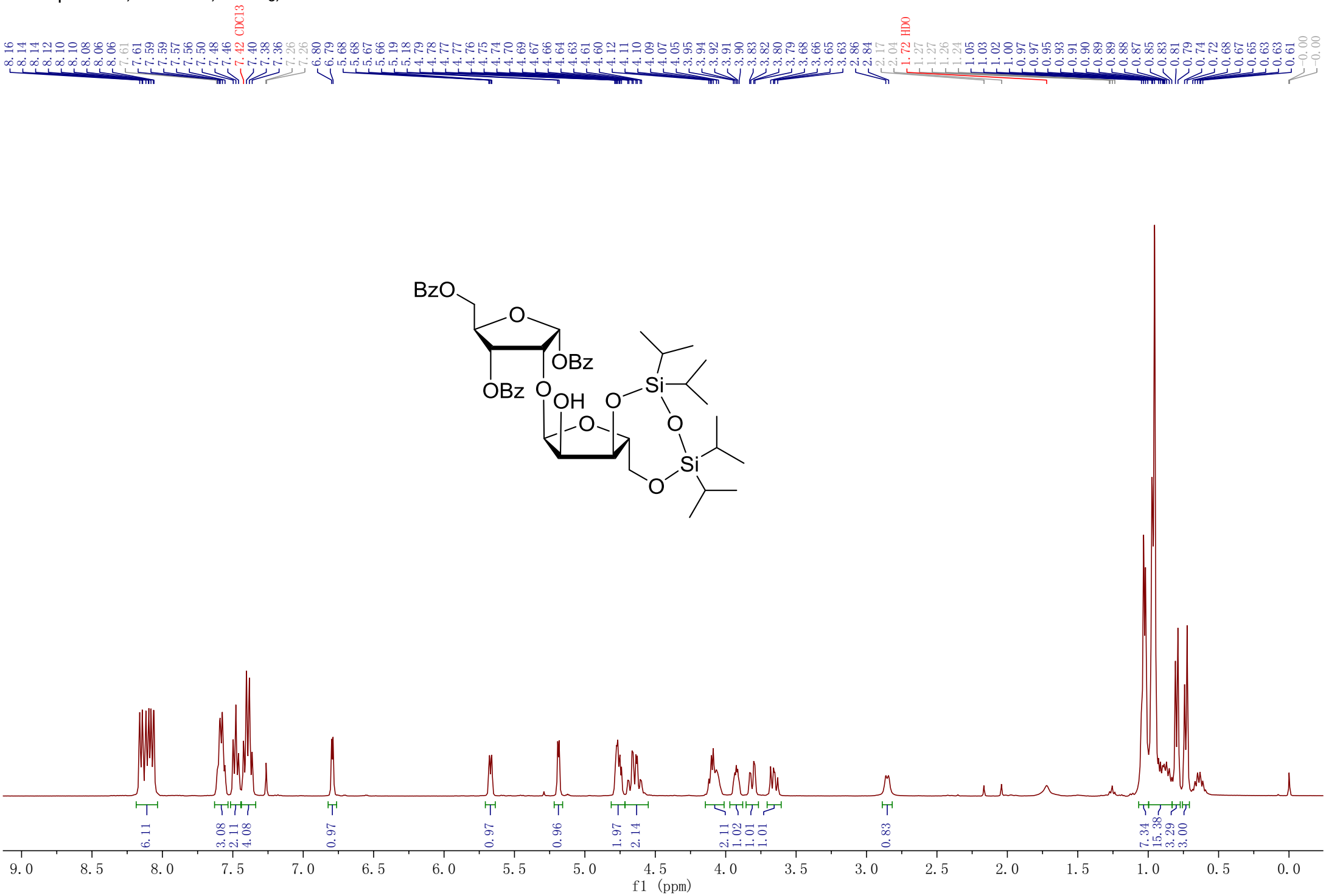
Compound **3**, ^{1}H--NMR, $CDCl_3$, 400 MHz



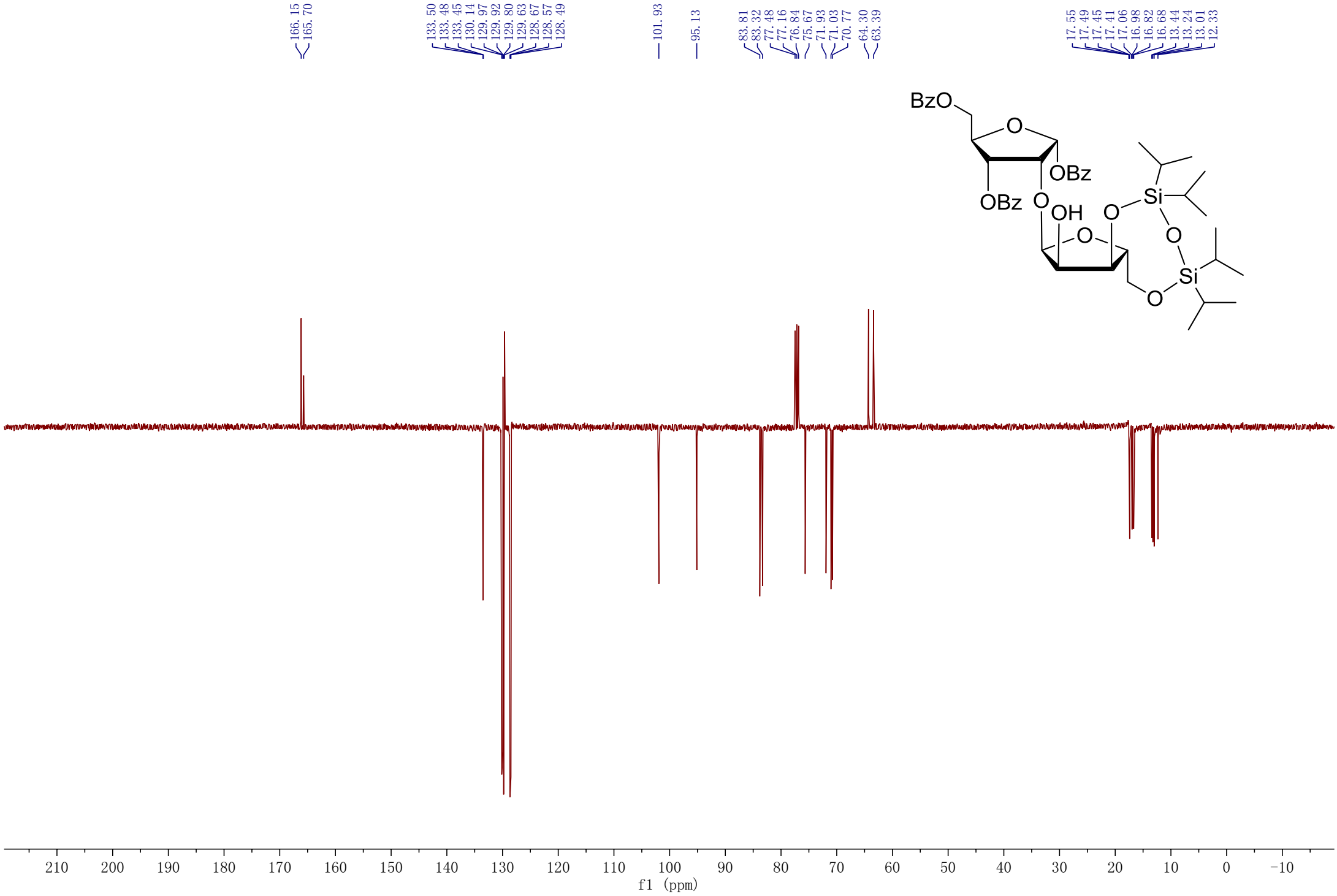
Compound **3**, ^{13}C-NMR, $CDCl_3$, 101 MHz



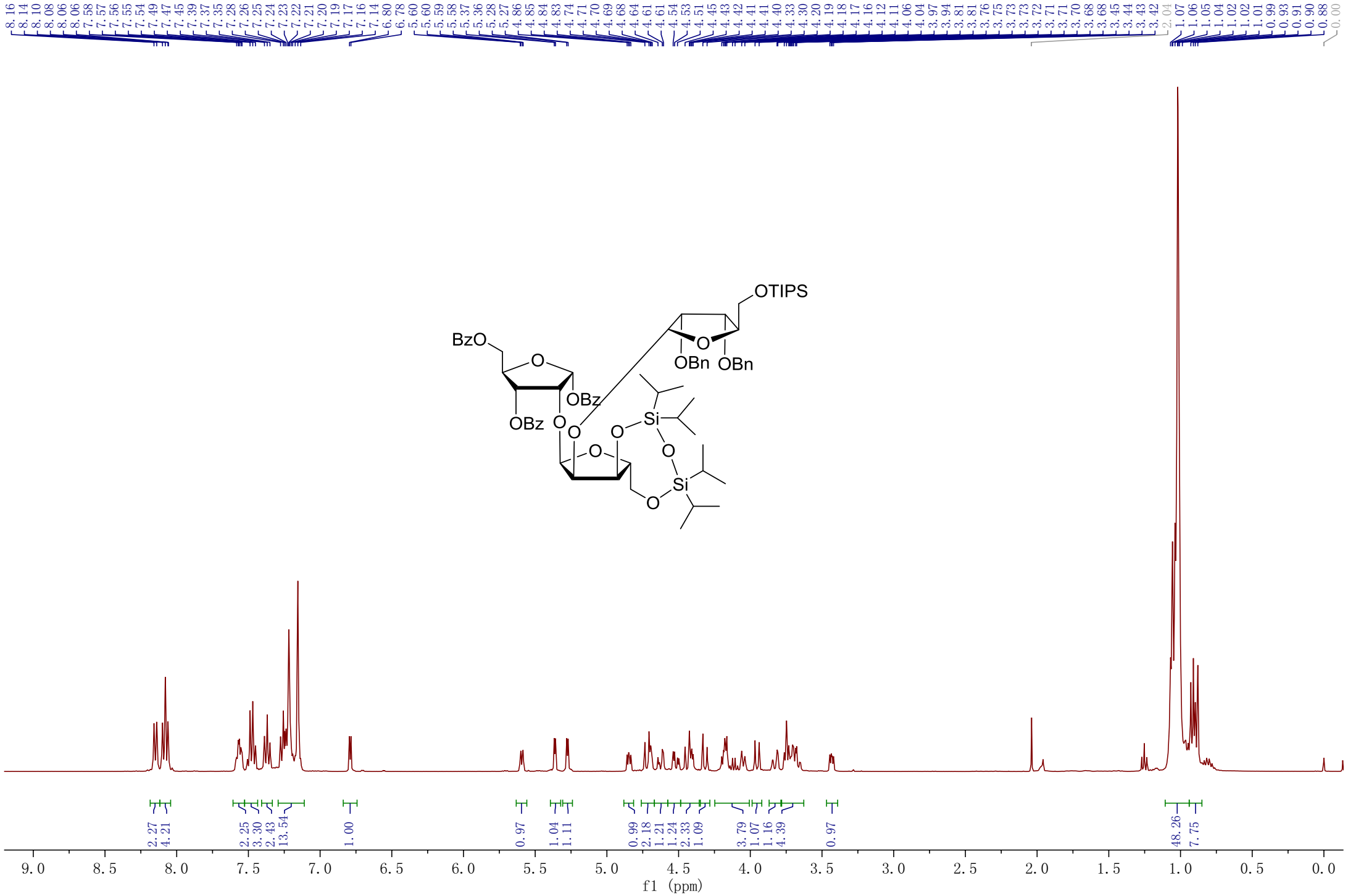
Compound **4**, ^{1}H--NMR, $CDCl_3$, 400 MHz



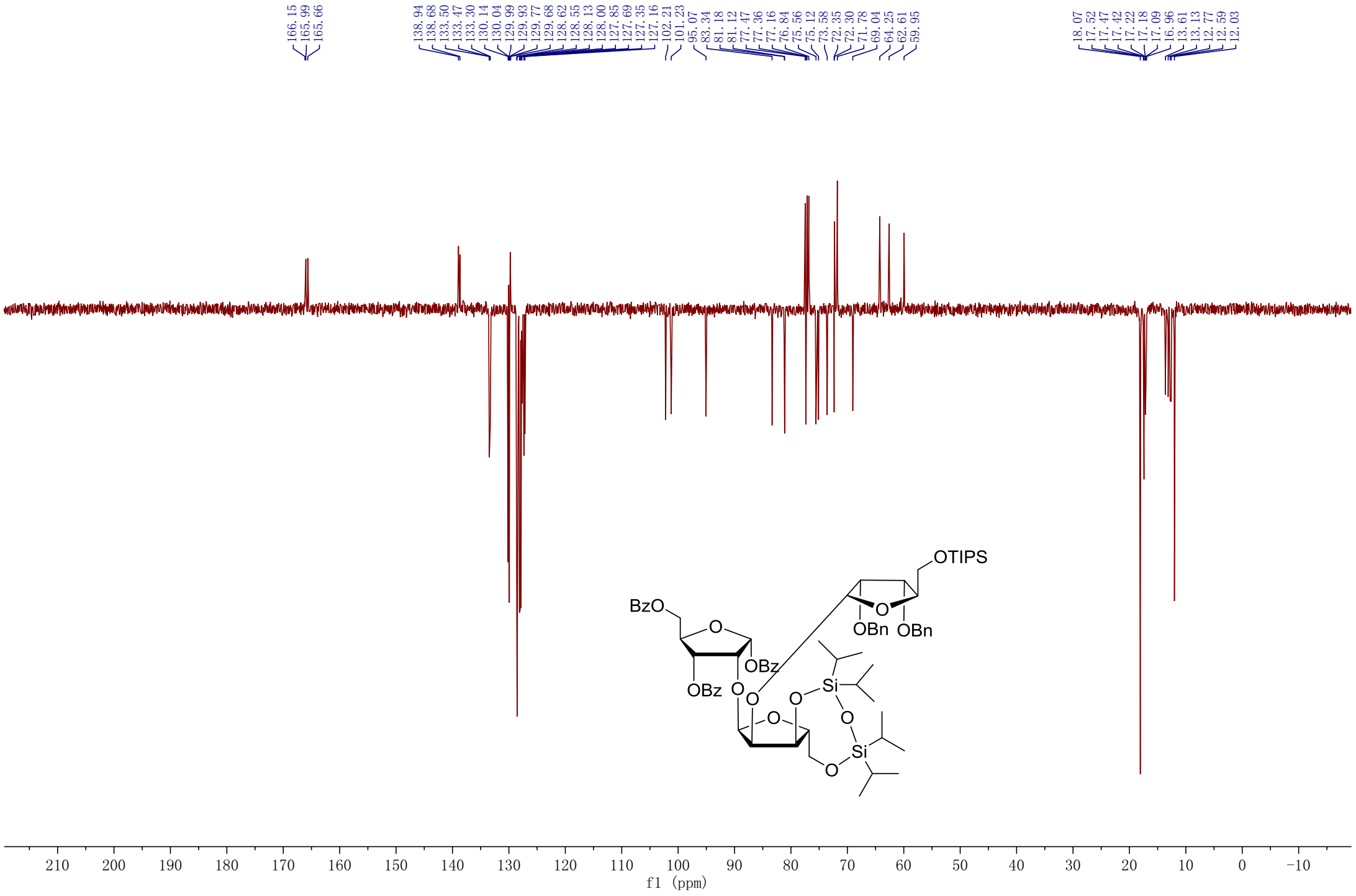
Compound **4**, ^{13}C-NMR, $CDCl_3$, 101 MHz



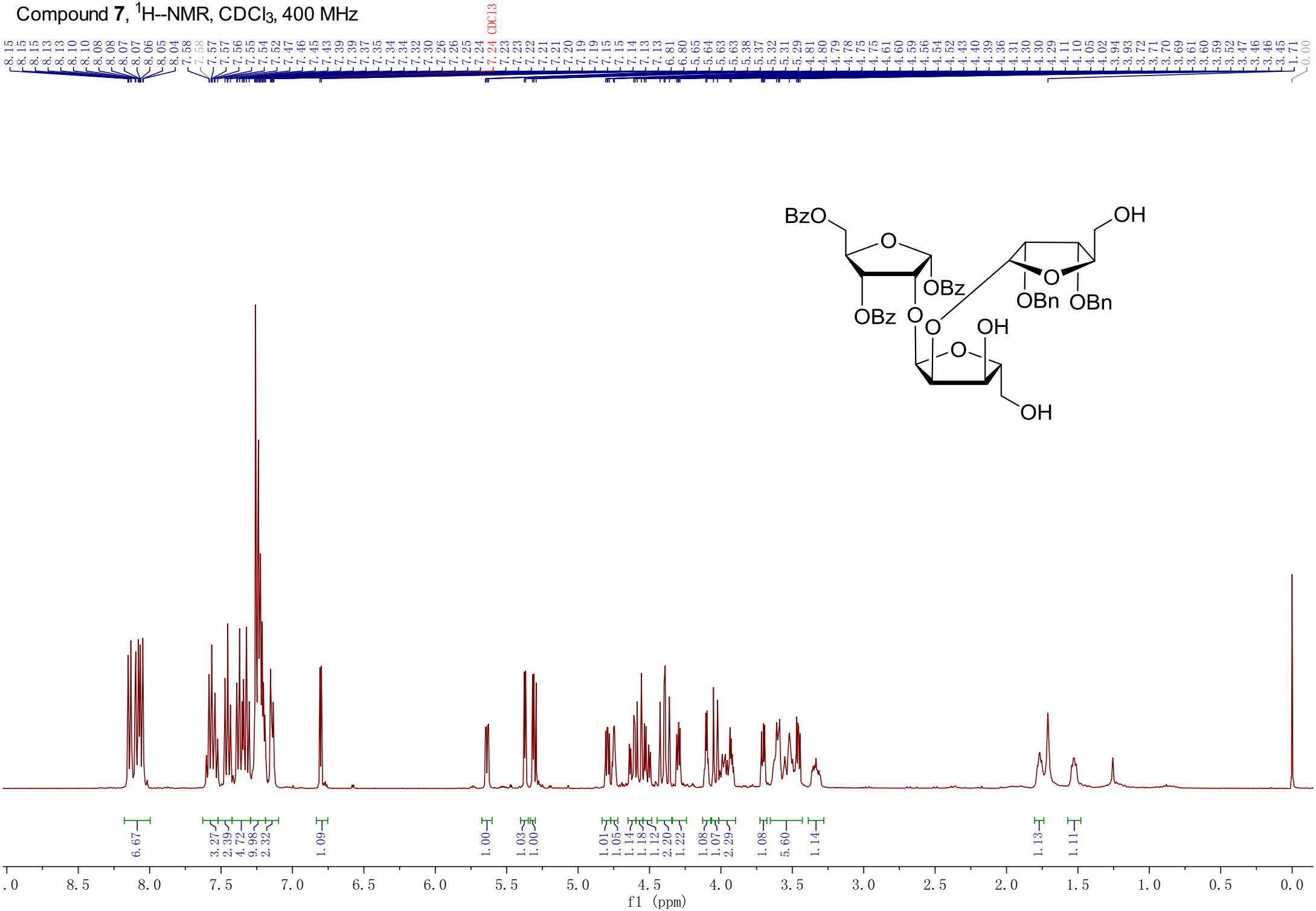
Compound **6**, ^{1}H--NMR, $CDCl_3$, 400 MHz



Compound **6**, ^{13}C-NMR, $CDCl_3$, 101 MHz



Compound **7**, ^{1}H--NMR, $CDCl_3$, 400 MHz



Compound **7**, ^{13}C-NMR, $CDCl_3$, 101 MHz

166.14
165.70
137.85
137.73
133.64
133.61
133.50
130.27
130.10
129.94
129.89
129.70
129.66
128.65
128.61
128.57
128.51
128.48
128.46
128.41
128.30
127.98
127.80
127.77
102.66
99.56
95.65
84.40
83.72
82.94
79.44
77.48
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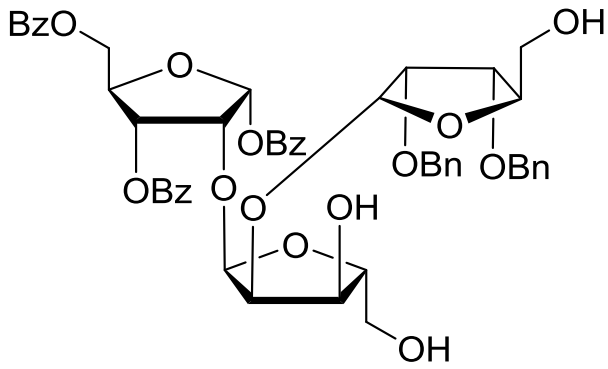
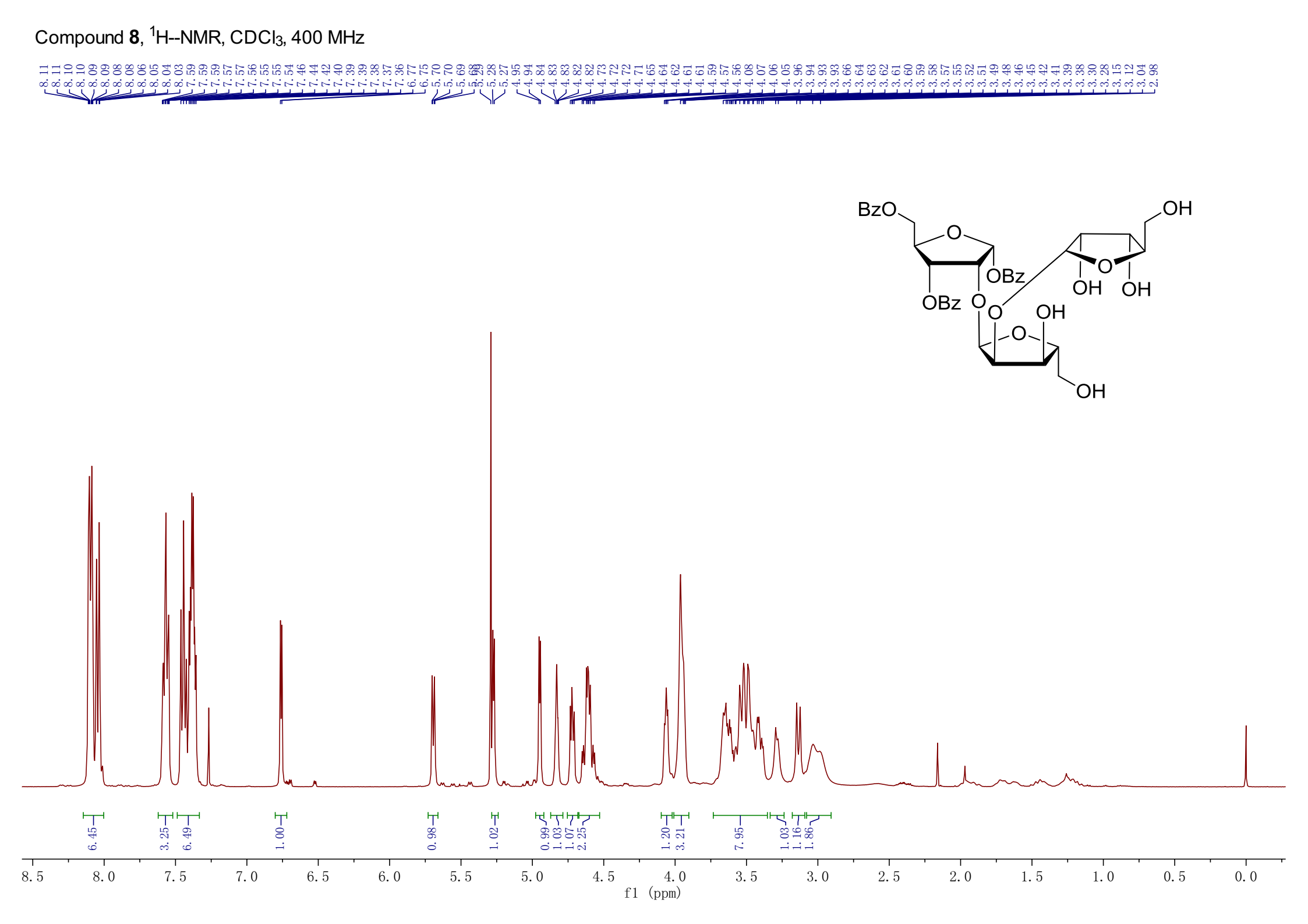
72.99
72.86
72.32
71.97
70.30
64.19
62.60
62.03



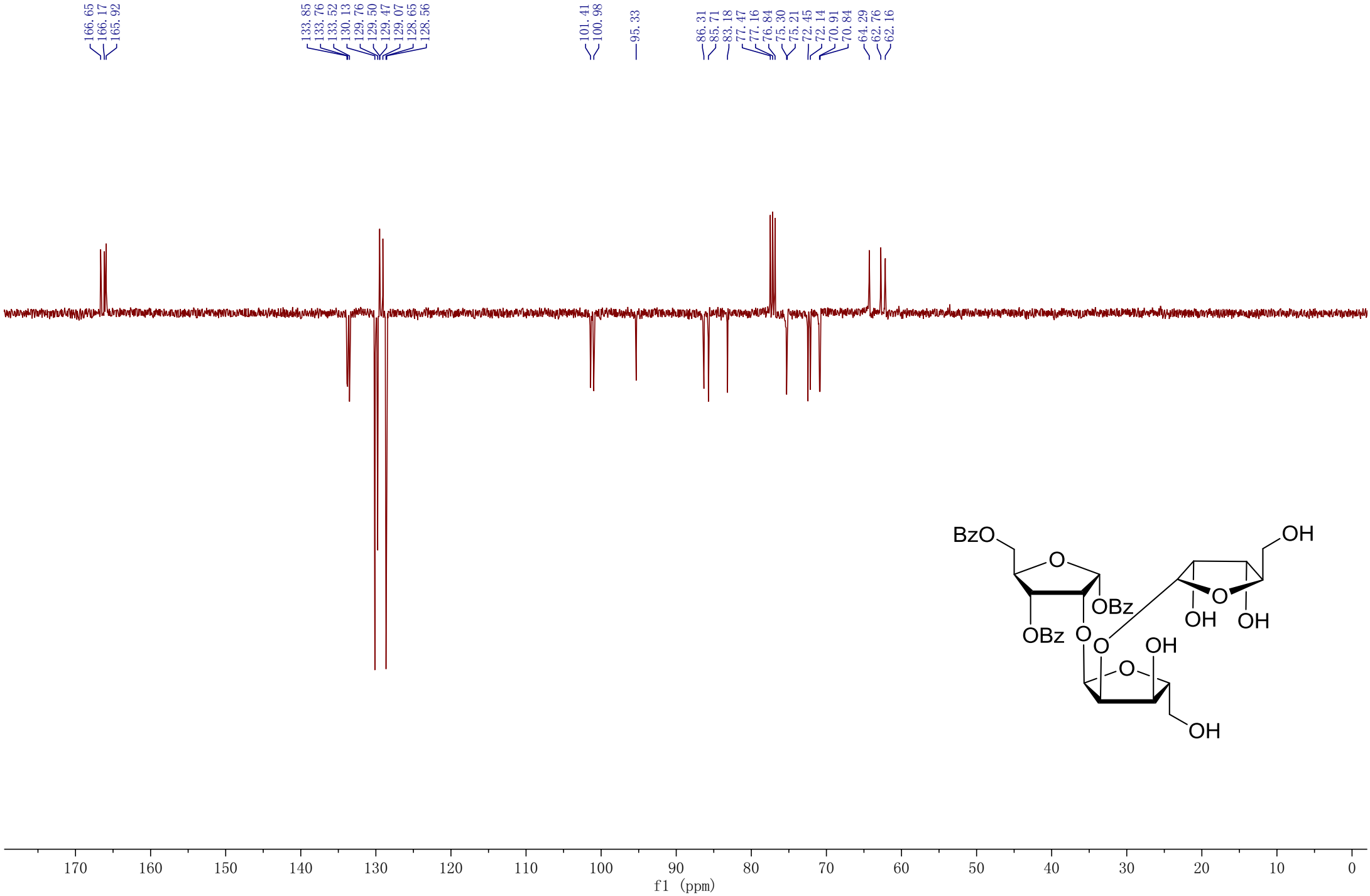
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

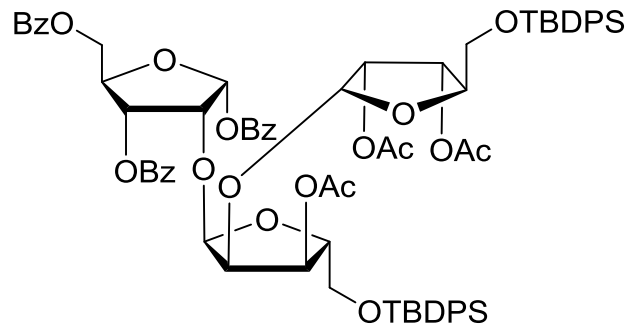
Compound **8**, ^{1}H--NMR, $CDCl_3$, 400 MHz



Compound **8**, ^{13}C-NMR, $CDCl_3$, 101 MHz

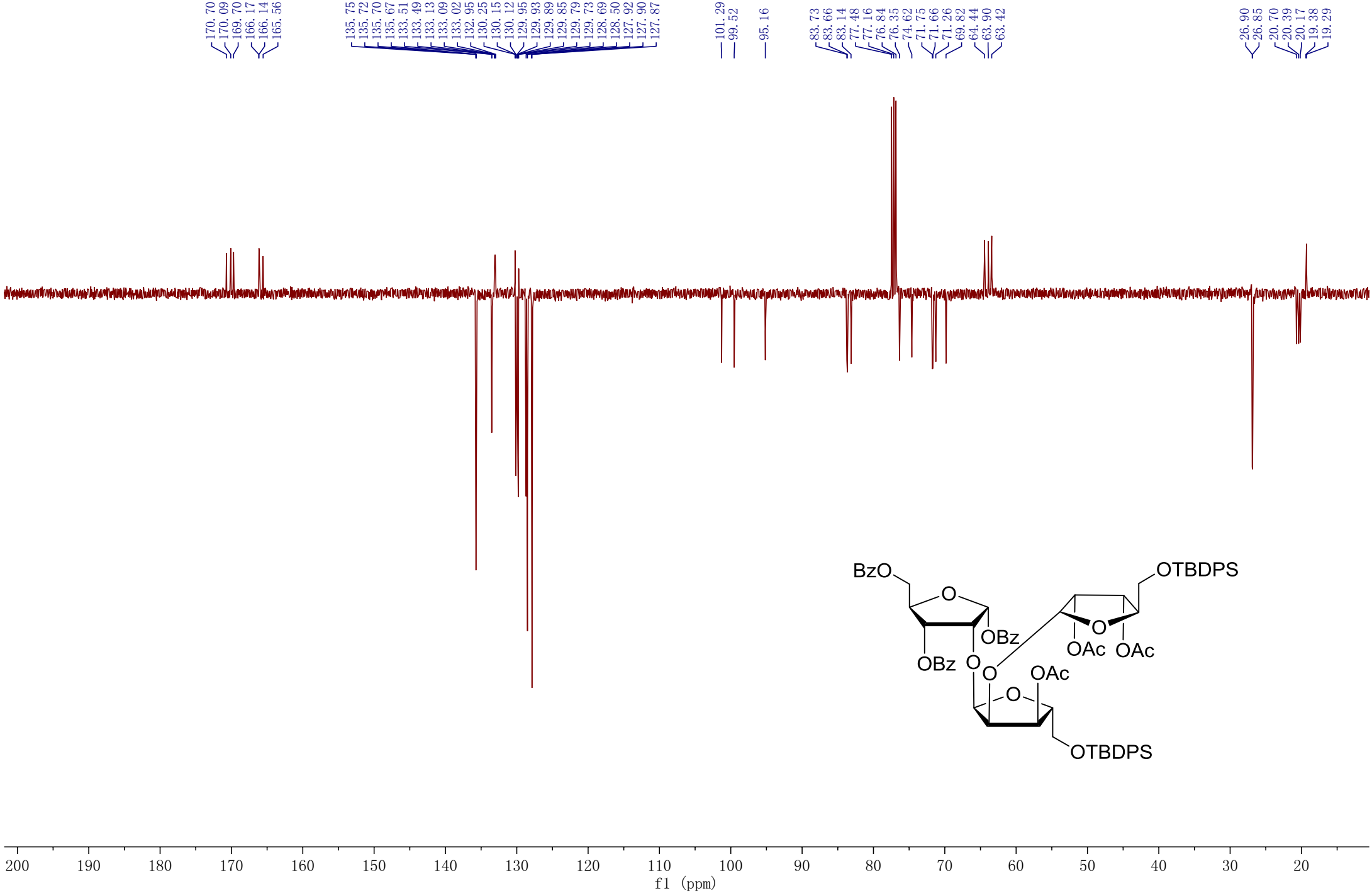


Compound **9**, ^{1}H-NMR, $CDCl_3$, 400 MHz

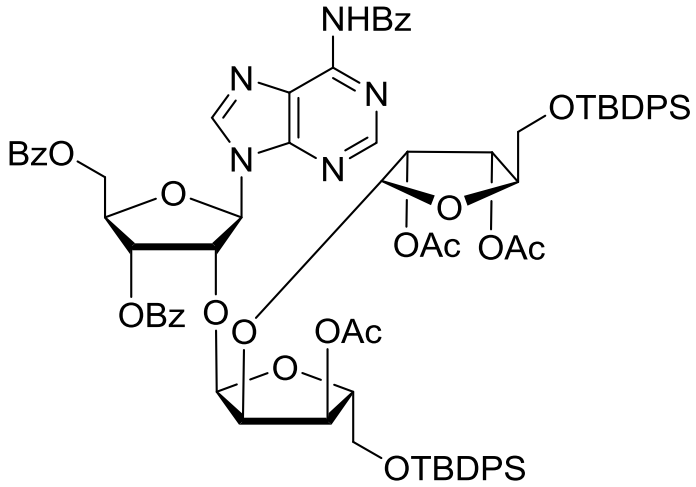


f1 (ppm)

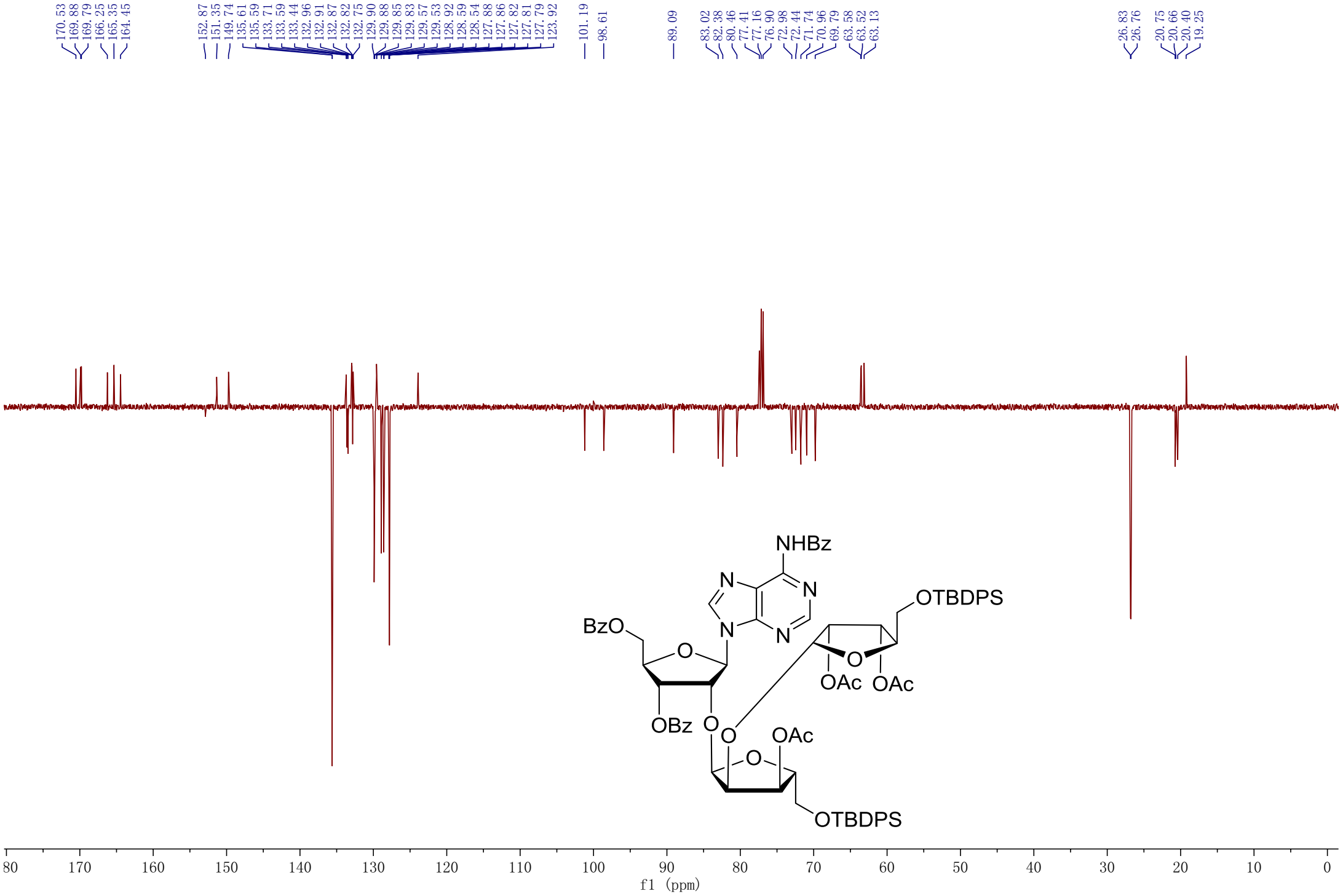
Compound **9**, ^{13}C-NMR, $CDCl_3$, 101 MHz



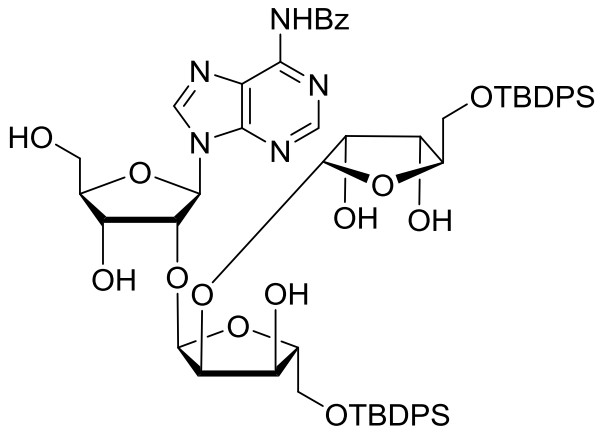
Compound **10**, ^{1}H-NMR, $CDCl_3$, 500 MHz



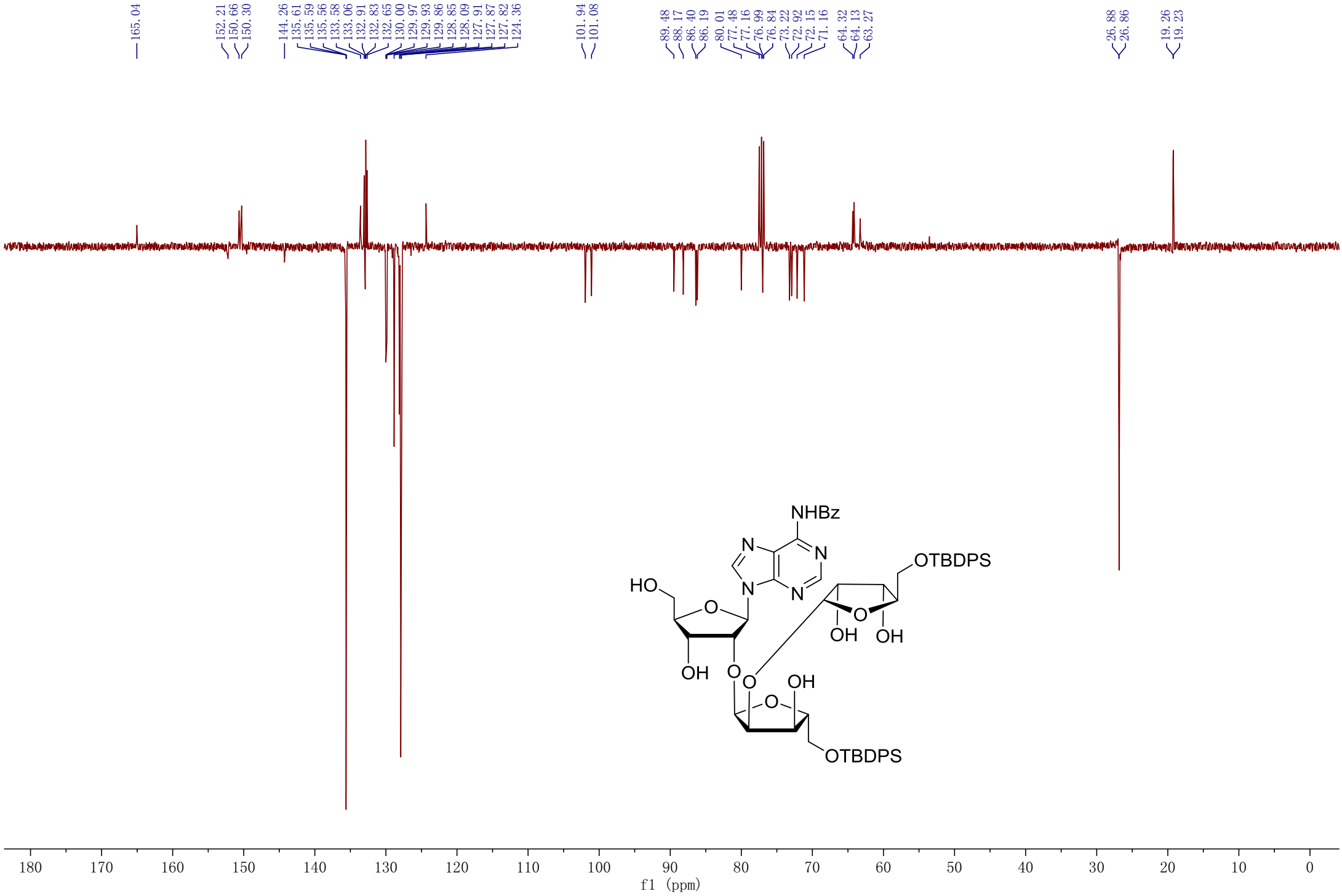
Compound **10**, ^{13}C-NMR, $CDCl_3$, 126 MHz



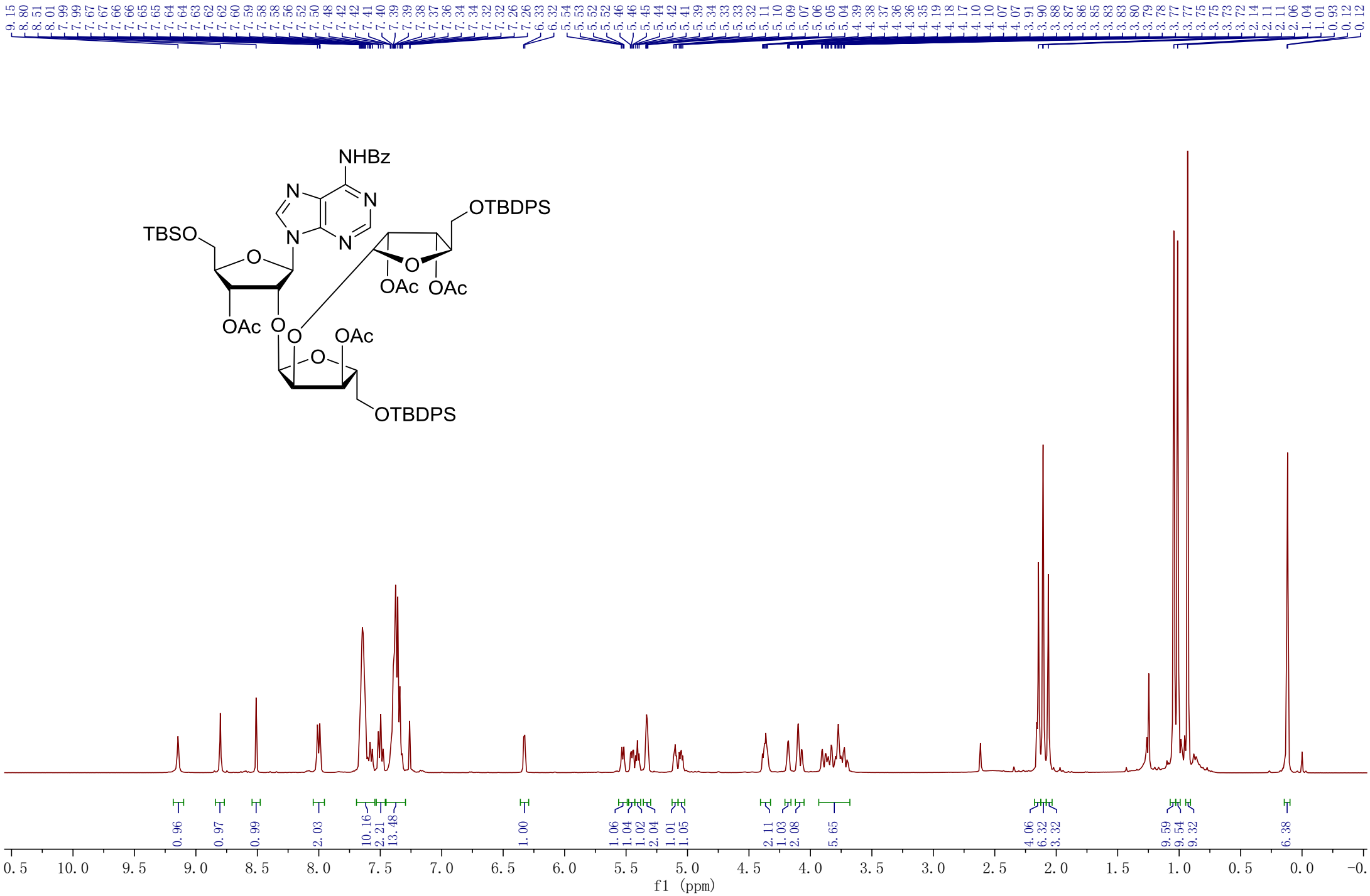
Compound **11**, ^{1}H-NMR, $CDCl_3$, 400 MHz



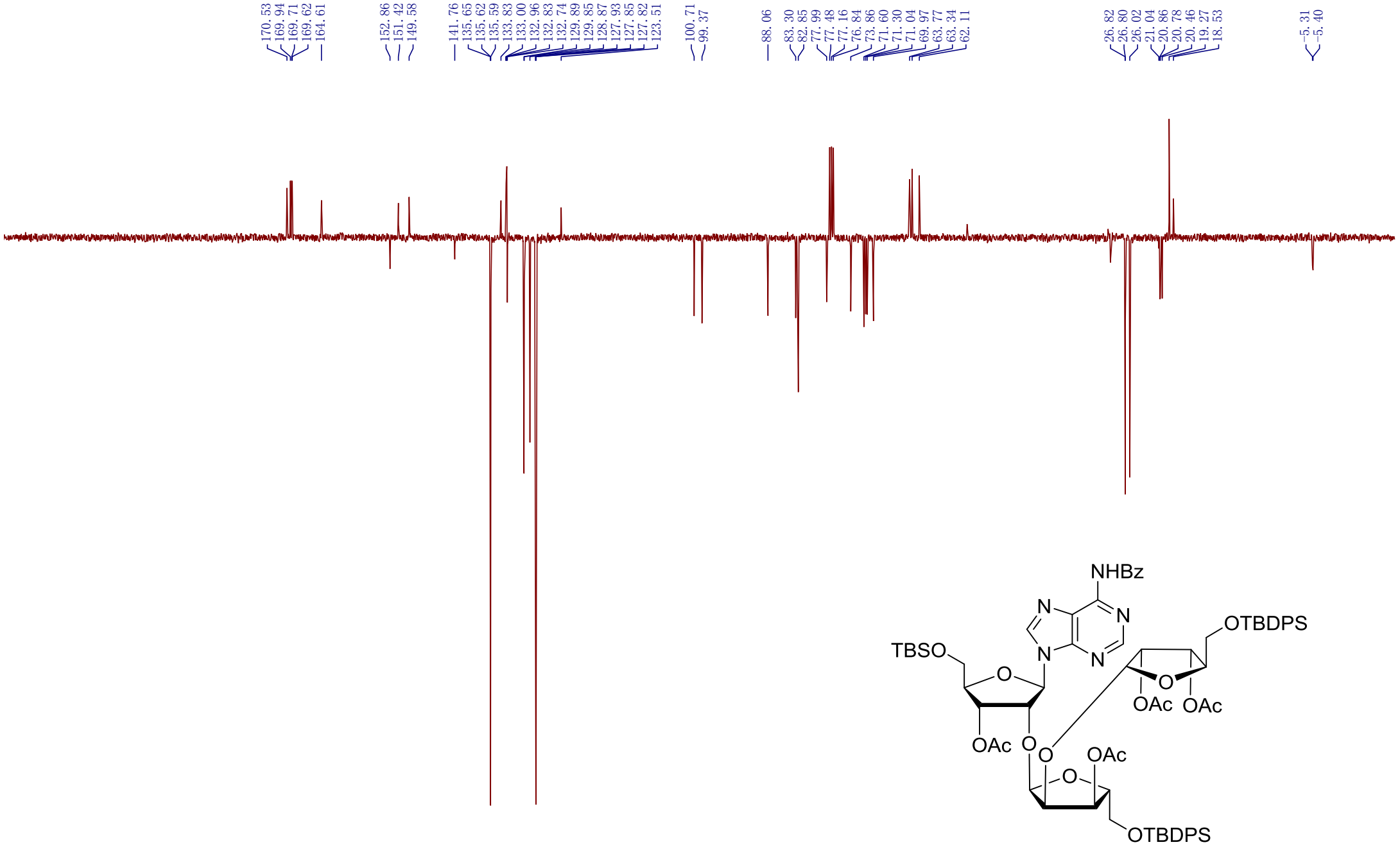
Compound **11**, ^{13}C-NMR, $CDCl_3$, 101 MHz



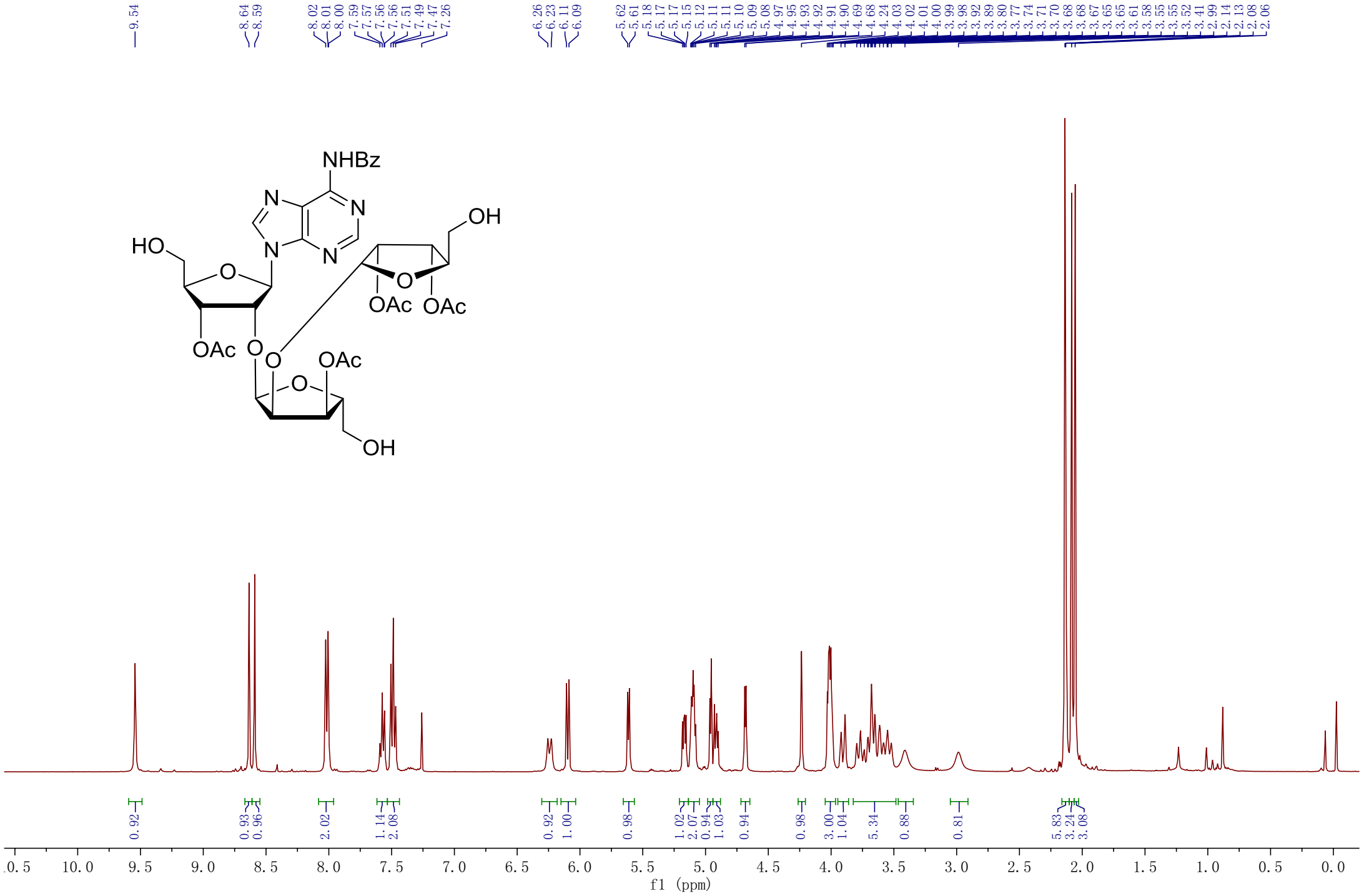
Compound **12**, ^{1}H-NMR, $CDCl_3$, 400 MHz



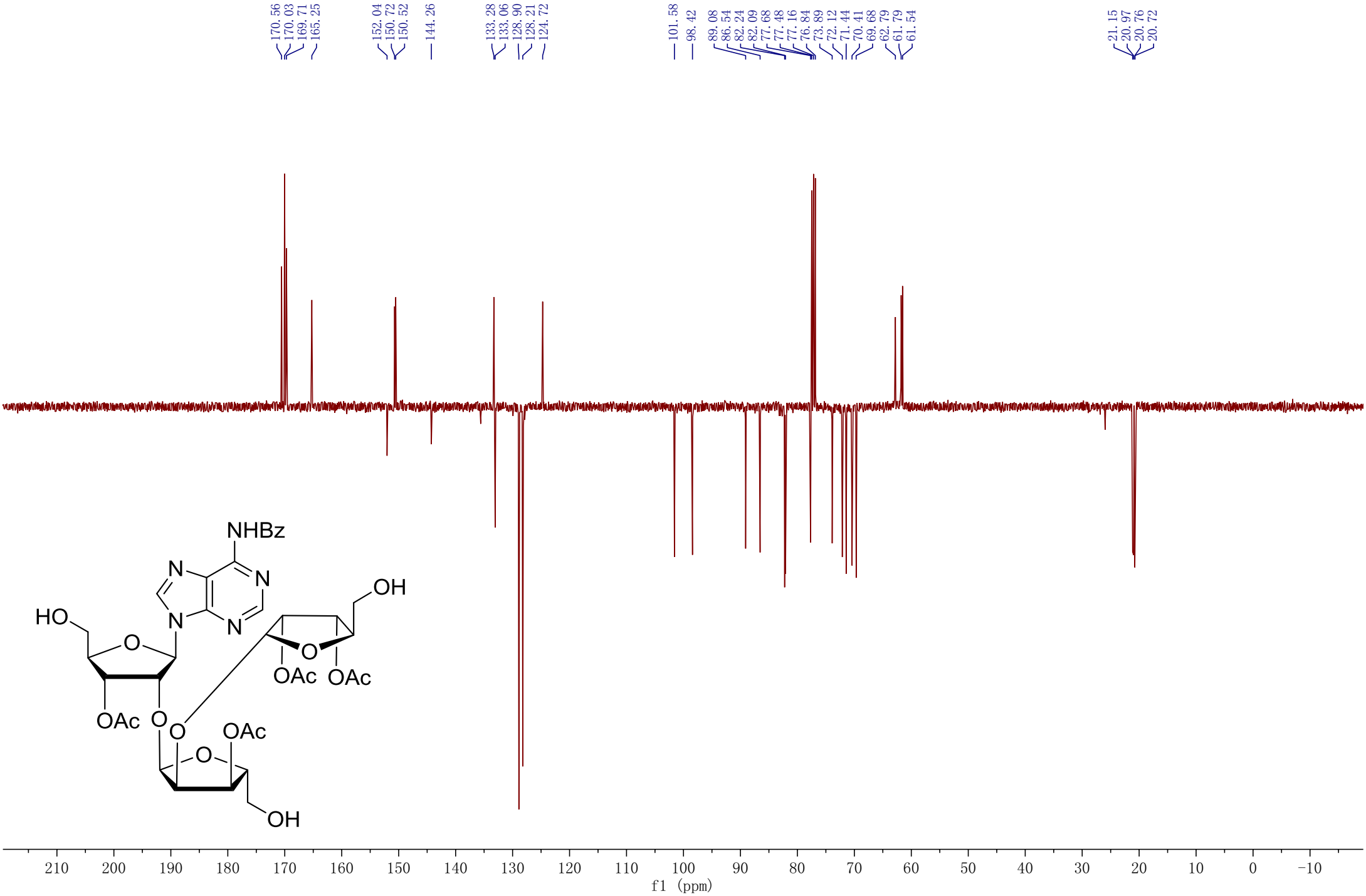
Compound **12**, ^{13}C-NMR, $CDCl_3$, 101 MHz



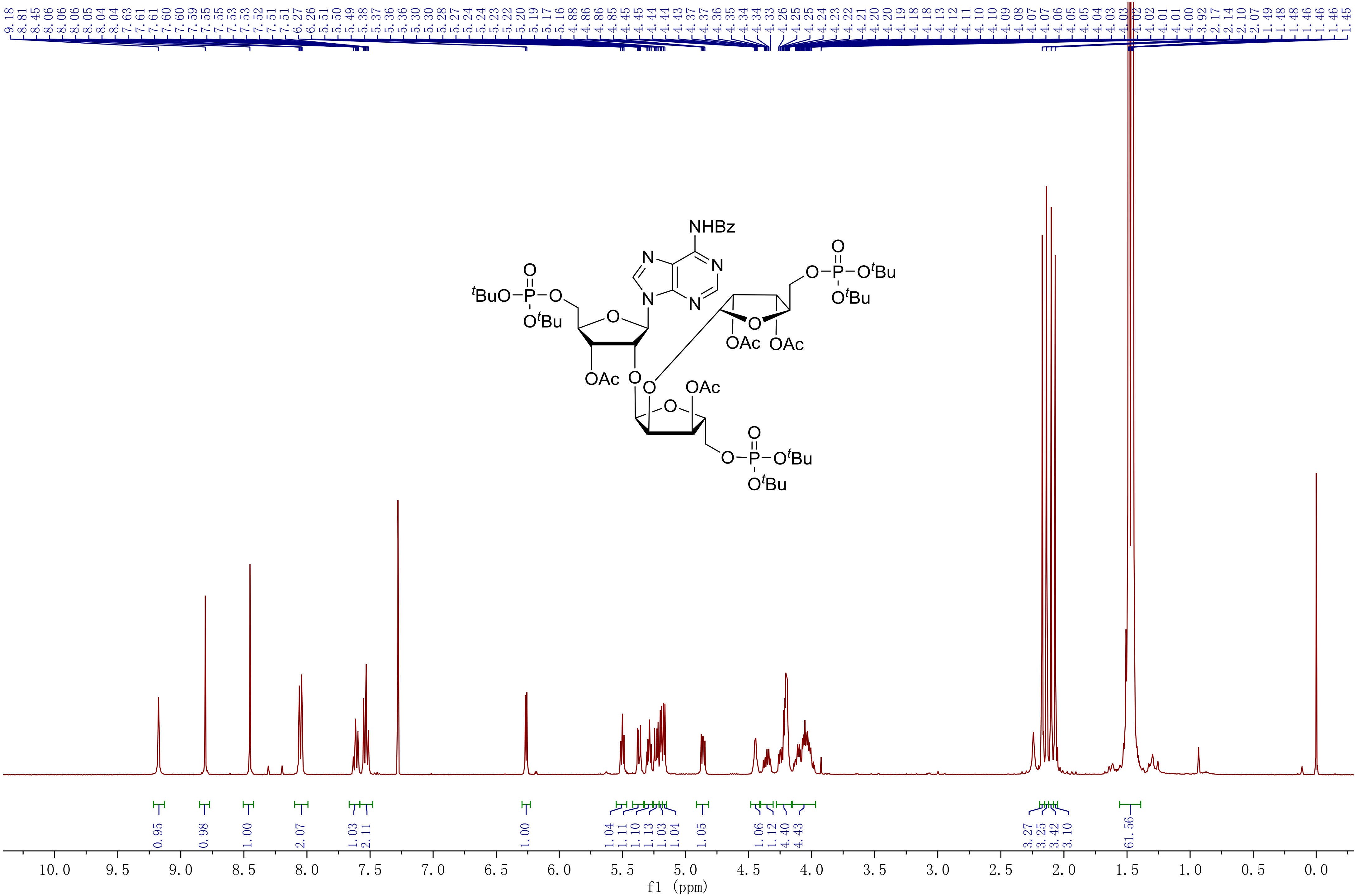
Compound **13**, ^{1}H-NMR, $CDCl_3$, 400 MHz



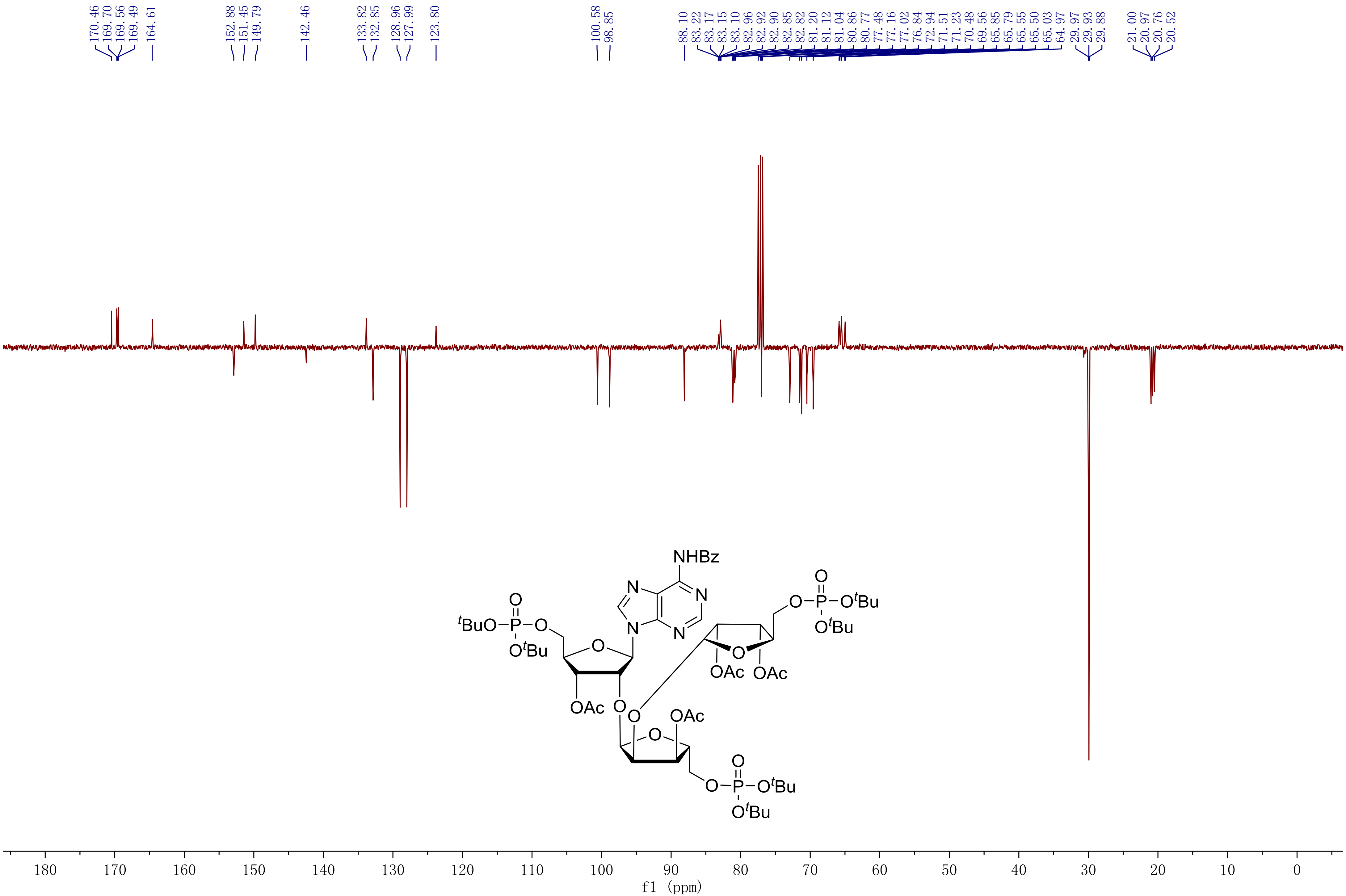
Compound **13**, ^{13}C-NMR, $CDCl_3$, 101 MHz



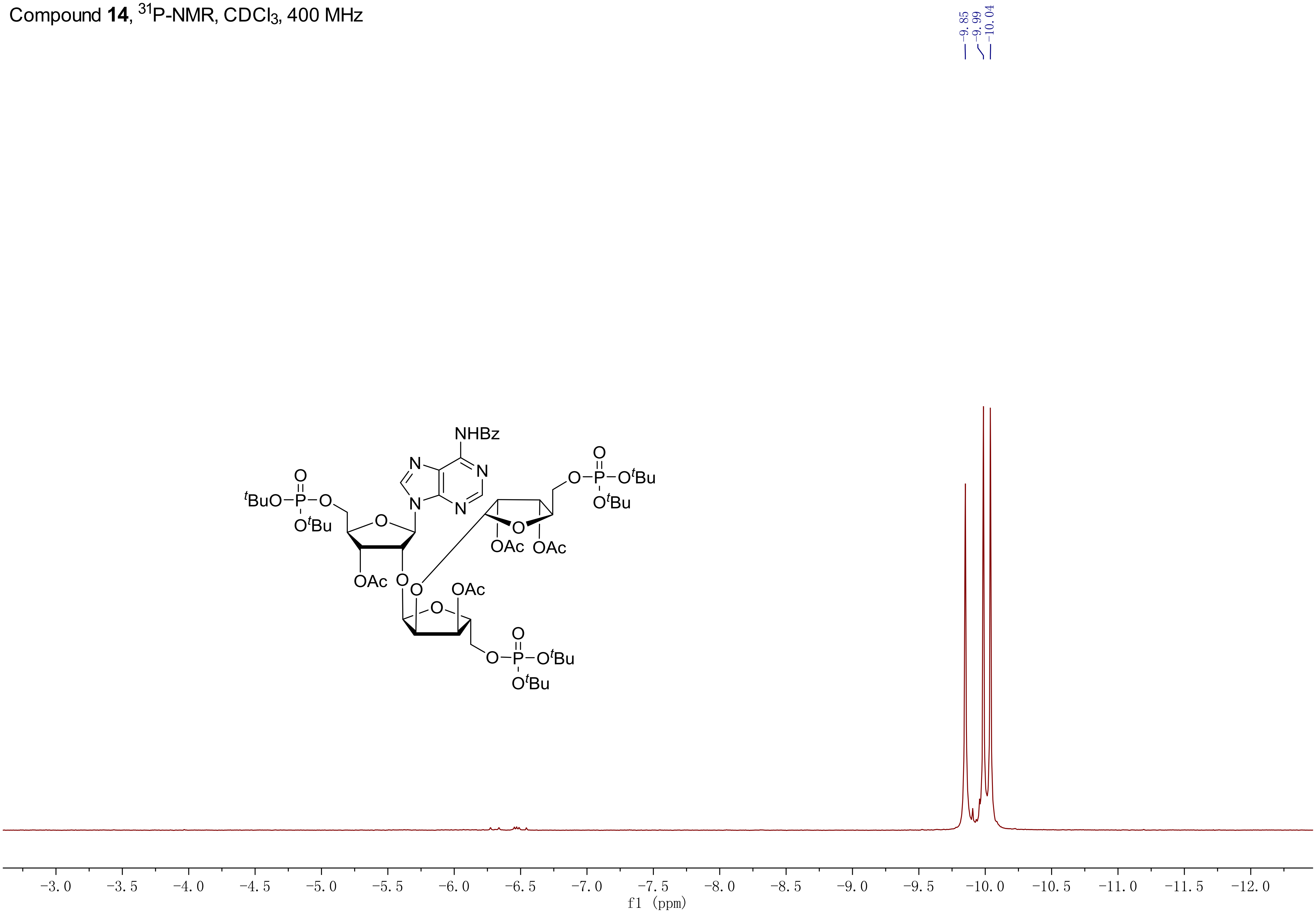
Compound **14**, ^{1}H-NMR, $CDCl_3$, 400 MHz



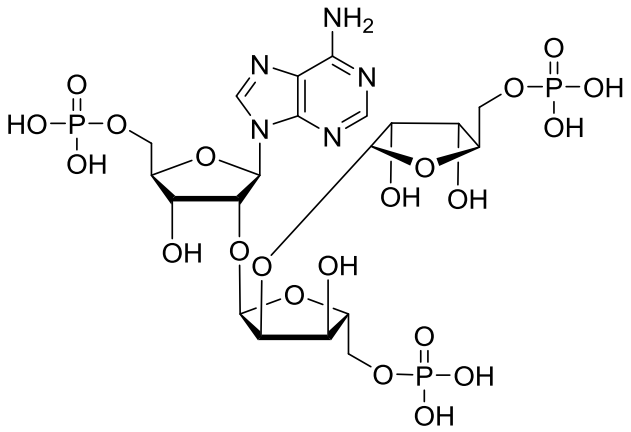
Compound **14**, ^{13}C-NMR, $CDCl_3$, 101 MHz



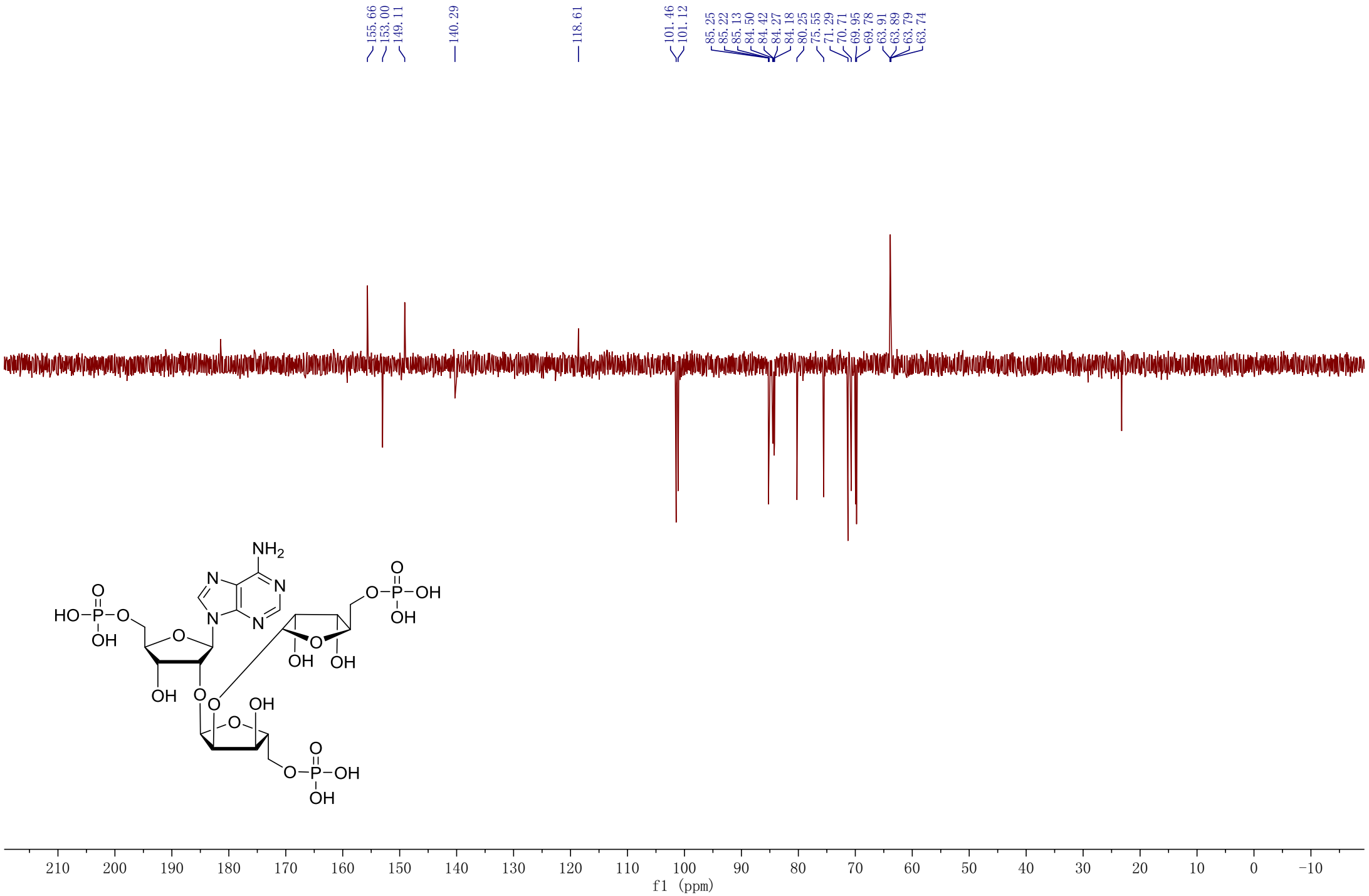
Compound **14**, ^{31}P-NMR, $CDCl_3$, 400 MHz



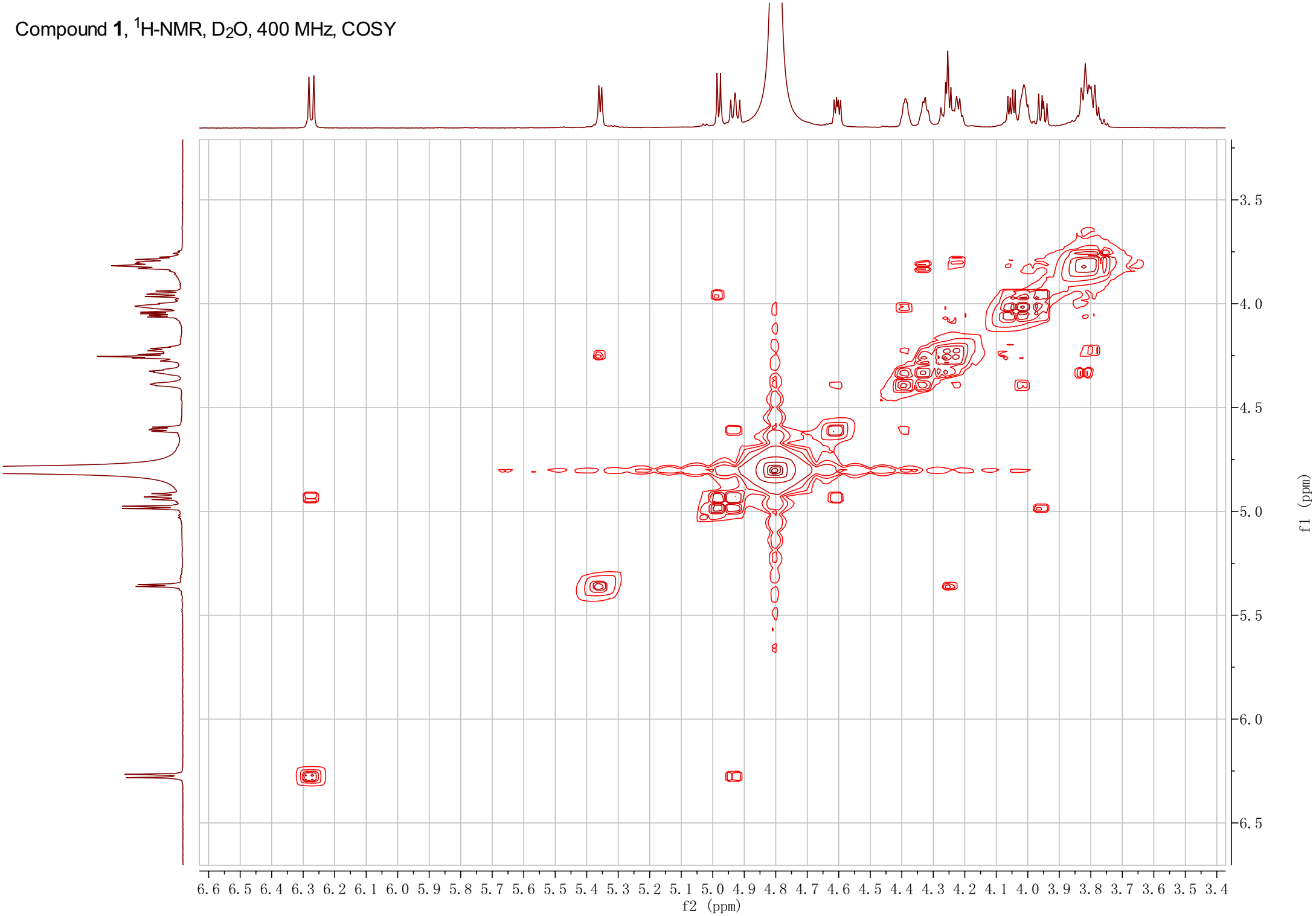
Compound **1**, ^{1}H-NMR, D_2O (pH=7), 400 MHz



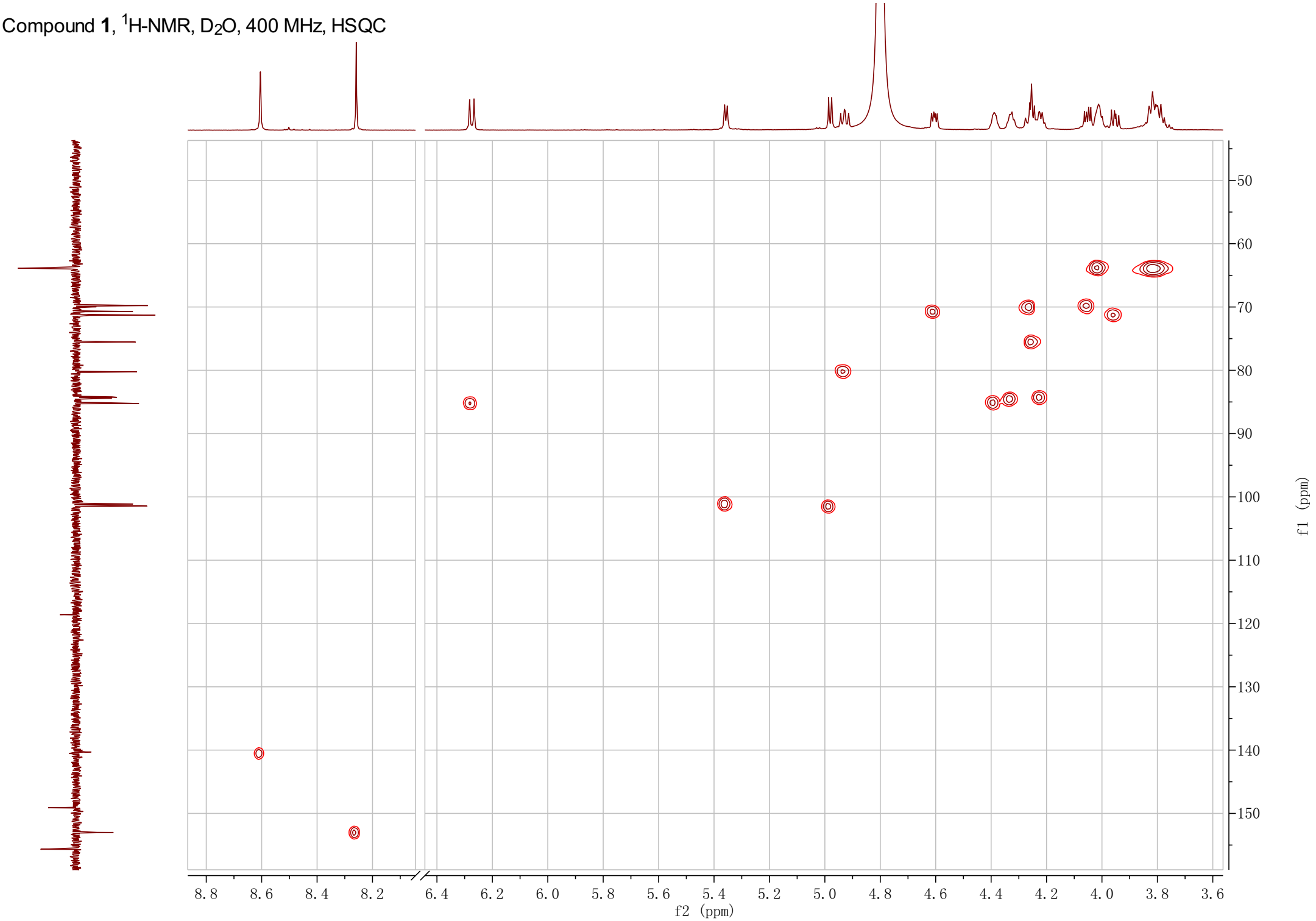
Compound **1**, ^{13}C-NMR, D_2O, 400 MHz



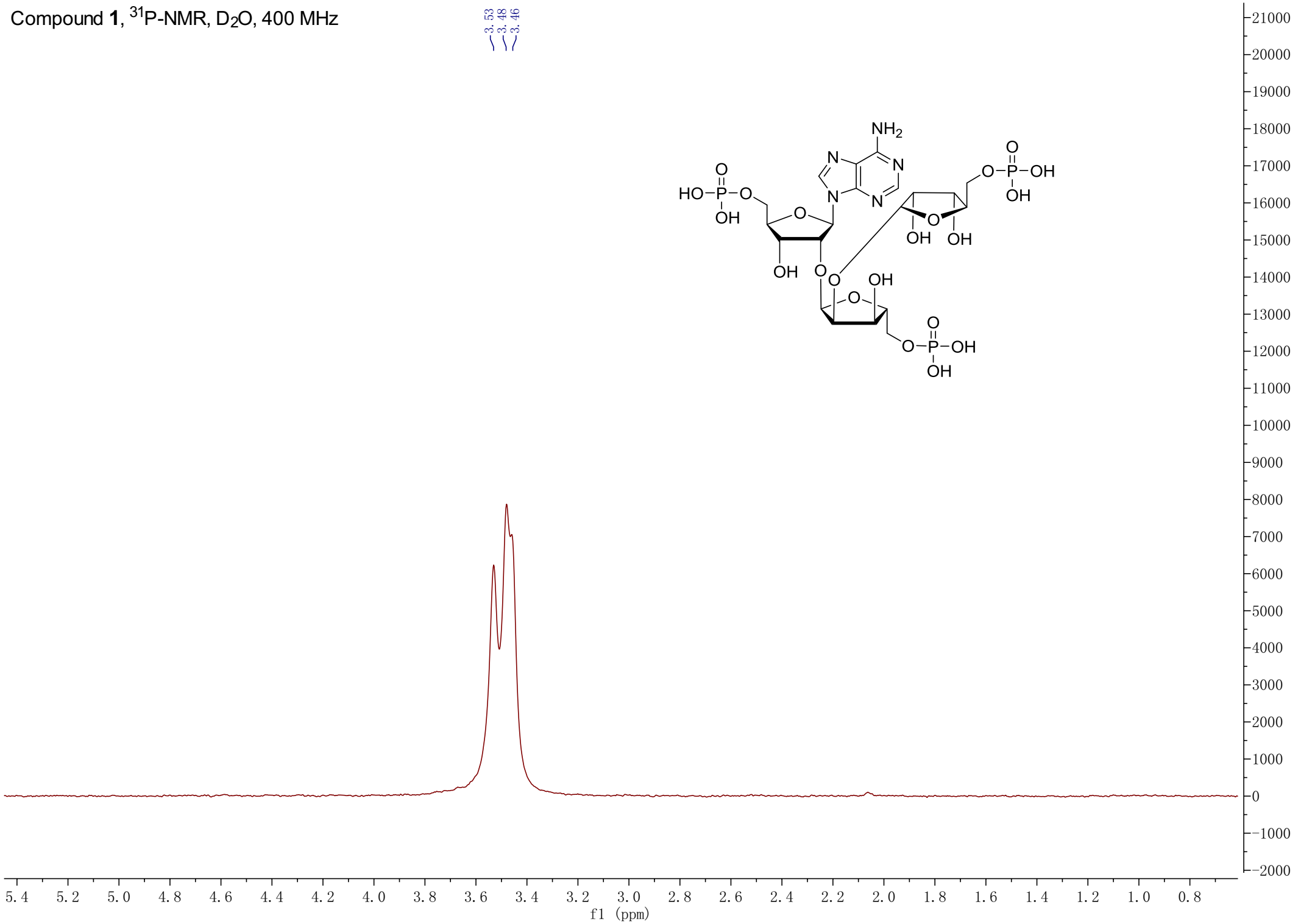
Compound **1**, ^{1}H-NMR, D_2O, 400 MHz, COSY



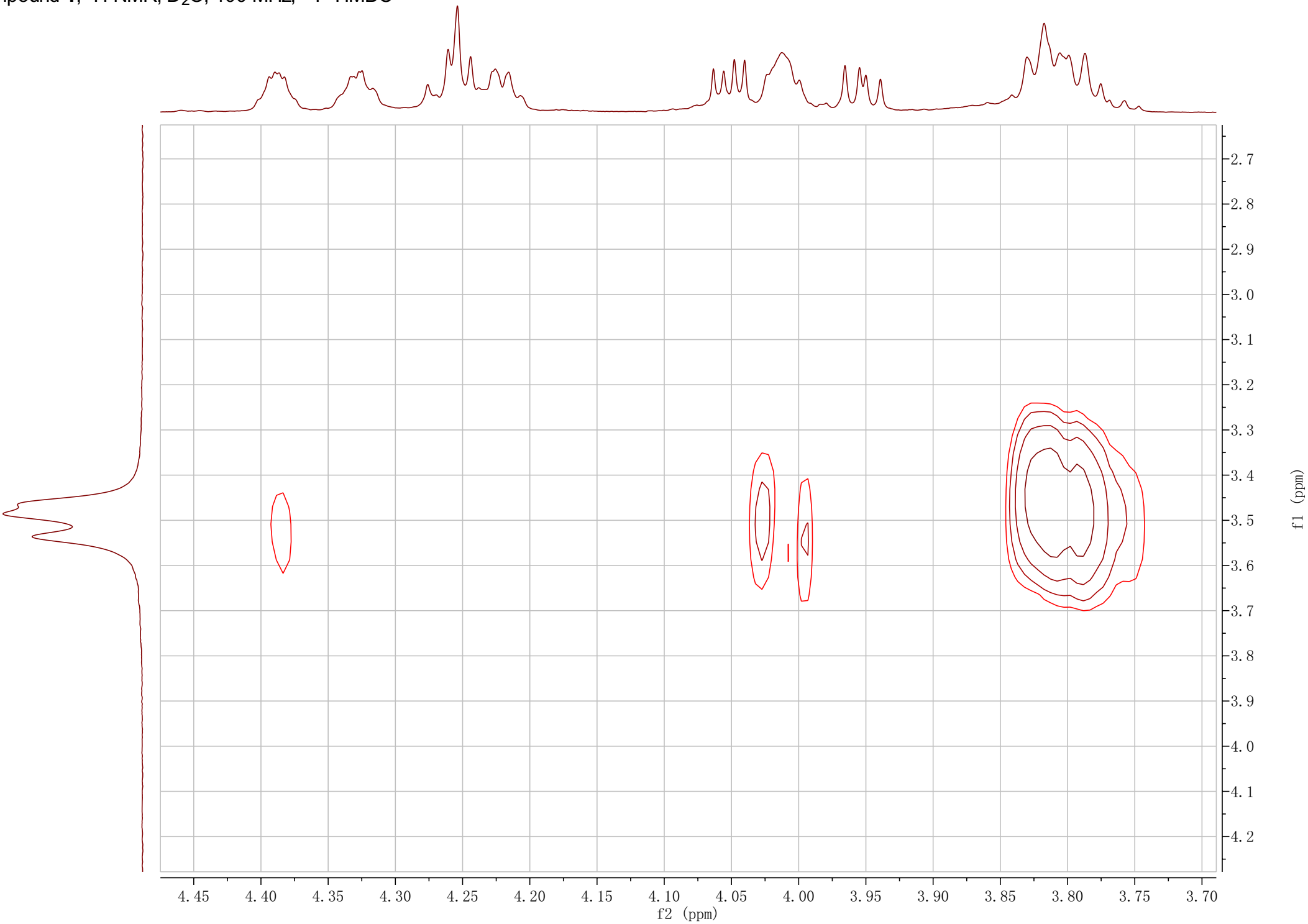
Compound **1**, ^{1}H-NMR, D_2O, 400 MHz, HSQC



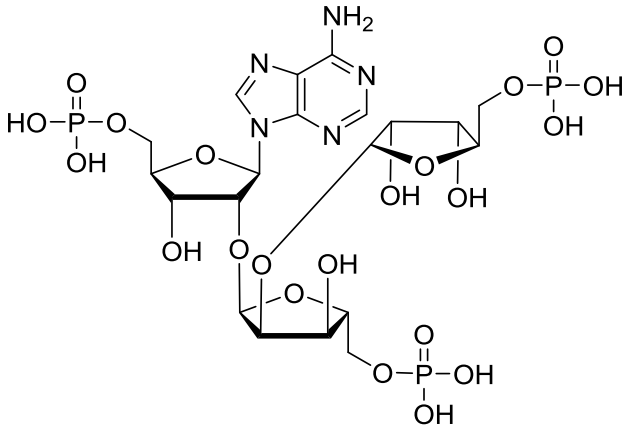
Compound **1**, ^{31}P-NMR, D_2O, 400 MHz



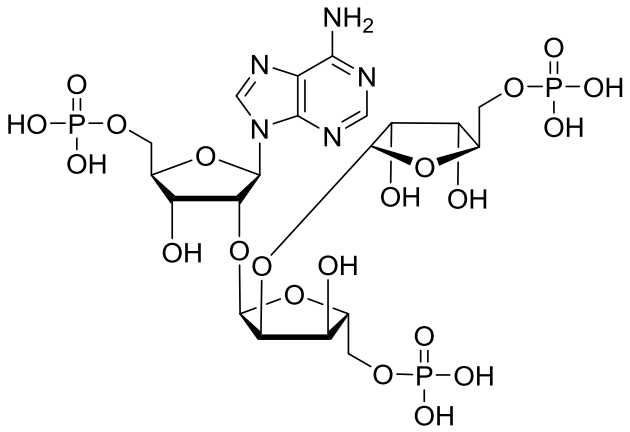
Compound **1**, ^{1}H-NMR, D_2O, 400 MHz, ^{31}P-HMBC



Compound **1**, ^{1}H-NMR, D_2O with CD_3COOD (pH=3), 400 MHz



Compound **1**, ^{1}H-NMR, D_2O with CD_3COOD (pH=3), 300 MHz



8.60 8.39 6.36 6.34 5.40 5.39 5.10 5.09 4.93 4.91 4.89 4.87 4.87 4.80 4.73 4.64 4.63 4.62 4.61 4.45 4.44 4.43 4.36 4.36 4.35 4.31 4.29 4.28 4.27 4.25 4.17 4.16 4.15 4.15 4.13 4.13 4.12 4.11 4.10 4.07 4.05 4.04 4.03 3.96 3.96 3.95 3.94 3.94 3.93 3.93 3.92 2.05 1.38

0.96 0.98 1.00 1.08 1.18 1.43 0.86 0.95 1.17 2.91 2.94 1.03 4.03

9.5 9.0 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

f1 (ppm)