Supporting information

An orthogonal and reactivity-based one-pot glycosylation strategy for both glycans and nucleosides synthesis: access to TMG-chitotriomycin, lipochitooligosaccharides and capuramycin

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Contents

1. General Information

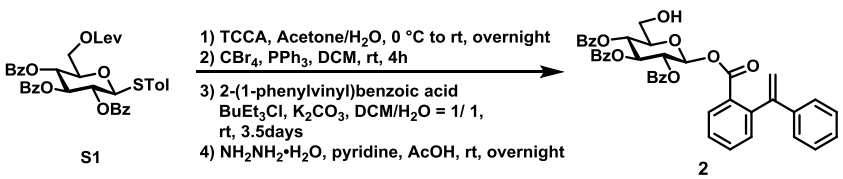
Commercial reagents, starting materials, and solvents were purchased and used as received or distilled from the appropriate drying agent. Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon with dry solvents unless otherwise stated. Crushed 3Å or 4Å molecular sieves were activated by flame-drying immediately under high vacuum prior to use. Reactions were monitored by thin layer chromatography (TLC) carried out on TLC Silica Gel 60 F254 (EMD Millipore Corporation) using UV light as visualizing tool and EtOH/H_2SO_4 (8%, v/v) as the developing agent. Column chromatography was performed on Silica Gel 60 (200-300 mesh), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden).

^{1}H, ^{13}C and COSY NMR spectra were recorded with Bruker AVANCE III 400 MHz or AVANCE III 600 MHz spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS, The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet), coupling constant in Hz, and integration. Optical rotations were measured on an Autopol VI (Serial #91058). HRMS determinations were recorded on a mass spectrometer (SHIMADZU UPLC-IT-TOF or Agilent 1290) with ESI ionization.

2. Experimental Procedures

2.1 Selective activation of other leaving groups over the PVB leaving group

Synthesis of 2,3,4-tri-O-benzoyl-β-D-glucopyranosyl-2-(1-phenylvinyl)benzoate(2)

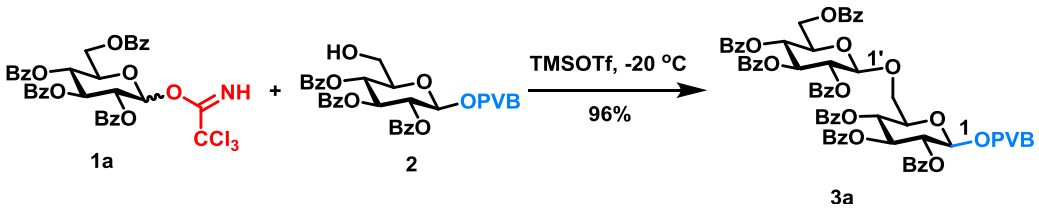


To a solution of compound **S1**[1] (2.47 g, 3.56 mmol) in acetone (72 mL) /H_2O (18 mL) was added Trichloroisocyanuric acid (TCCA) (826 mg, 3.56 mmol) at 0 ℃. The reaction mixture was

warmed gradually to room temperature and stirred for overnight. Then EtOAc was added to this mixture and washed sequentially with saturated aqueous $NaHCO_3$, H_2O, and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (petroleum ether-EtOAc, 1.5:1) afforded the hemiacetal as a syrup (1.76 g, 84%). A solution of the above hemiacetal (1.67 g, 2.84 mmol), CBr_4 (4.7 g, 14.18 mmol), and PPh_3 (3.72 g, 14.18 mmol) in CH_2Cl_2 (28 mL) was stirred at room temperature for 4 h. Then the mixture was diluted with CH_2Cl_2 and washed sequentially with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (petroleum ether-EtOAc, 3:1) afforded glycosyl bromide as a white foam (1.01 g, 55%). And then, to a solution of the above intermeidate (1.01 g, 1.544 mmol) and 2-(1-phenylvinyl) benzoic acid (0.451 g, 2.008 mmol) in CH_2Cl_2 /H_2O = 1/1 (15.4 mL) was added $BnNEt_3Cl$ (0.070 g, 0.309 mmol) and K_2CO_3 (1.067 g, 7.721 mmol). The reaction mixture was stirred at room temperature for 3.5 days before diluted with brine and extracted with CH_2Cl_2. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (petroleum ether-EtOAc, 2.5:1 to 1.8:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1), affording glycosyl *ortho*-(1-phenylvinyl)benzoate (0.938 g, 76%) as a white foam. The above intermediate (0.8 g, 1.004 mmol) was then dissolved in pyridine (6 mL) and AcOH (4 mL), and hydrazine hydrate (146 μL, 3.012 mmol) was added dropwise. After stirring at room temperature for overnight, the reaction mixture was quenched with acetone. The solution was concentrated *in vacuo* and diluted with CH_2Cl_2, washed sequentially with 1 N HCl and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (petroleum ether-EtOAc, 3.7:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **2** (0.498 g, 71%) as a white foam: $[\alpha]_D^{22}$ = +16.51 (*c* 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.86 (m, 7H, Ar), 7.60 – 7.51 (m, 3H, Ar), 7.49 – 7.29 (m, 10H, Ar), 7.26 (s, 4H, Ar), 6.05 (d, *J* = 8.2 Hz, 1H, **H-1**), 5.99 (t, *J* = 9.6 Hz, 1H, H-3), 5.77 – 5.69 (m, 2H, H-2, H-PVB), 5.57 (t, *J* = 9.7 Hz, 1H, H-4), 5.18 (s, 1H, H-PVB), 3.90 (m, 1H, H-5), 3.80 (m, 1H, H-6), 3.68 (m, 1H, H-6), 2.36 (s, 1H, H-OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.97, 165.74, 164.99, 164.70, 149.07, 143.94, 140.55, 133.80, 133.47, 133.38, 132.79, 131.70, 130.67, 130.01, 129.89,

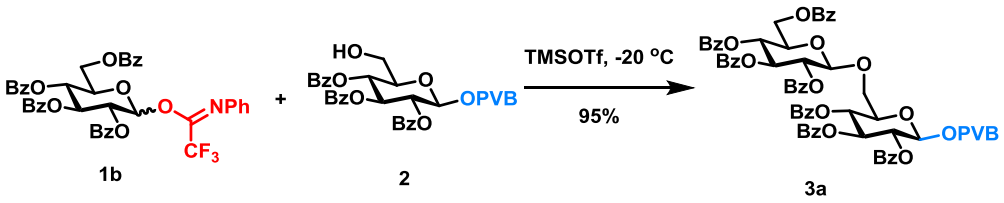
129.81, 128.88, 128.81, 128.59, 128.57, 128.55, 128.46, 128.40, 128.20, 127.88, 127.54, 126.64, 114.41, 92.42, 75.46, 72.90, 70.78, 69.05, 61.05. HRMS (ESI) calcd for $C_{42}H_{34}O_{10}Na$ $[M+Na]^+$ 721.2044, found 721.2046.

O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyrano syl- 2-(1-phenylvinyl) benzoate(3a)



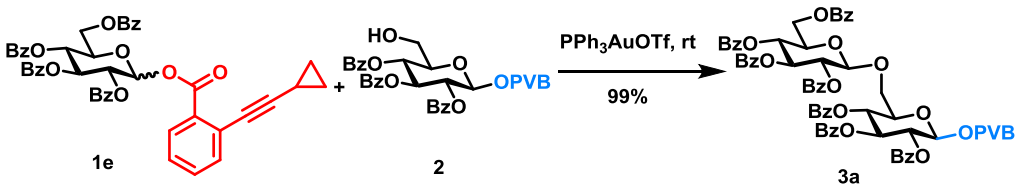
A mixture of donor **1a**[2] (51.0 mg, 0.069 mmol), acceptor **2** (40.0 mg, 0.057 mmol) and 4Å MS (100 mg) in dry CH_2Cl_2 (0.8 mL) was stirred at room temperature for 15 min, then cooled to -20 ℃. TMSOTf (110 μL, 10 μL in 1 mL CH_2Cl_2, 0.006 mmol) was added to the mixture dropwise. The resulting mixture was stirred at -20 ℃. After being stirred for another 1h, the reaction was quenched with Et_3N (0.5 mL) and filtered. The filtrates were concentrated *in vacuo* to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 4:1 to 2:1) to afford **3a** (70.0 mg, 96%) as a syrup. $[\alpha]_D^{21}$ = +13.16 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 4H, Ar), 7.97 – 7.77 (m, 11H, Ar), 7.61 – 7.24 (m, 27H, Ar), 7.23 – 7.19 (m, 2H, Ar), 5.98 (d, *J* = 8.1 Hz, 1H, **H-1**), 5.93 (t, *J* = 9.6 Hz, 1H), 5.82 (t, *J* = 9.5 Hz, 1H), 5.74 (s, 1H, H-PVB), 5.66 – 5.49 (m, 3H, H-2, H-2'), 5.42 (t, *J* = 9.7 Hz, 1H), 5.13 (s, 1H, H-PVB), 5.03 (d, *J* = 7.8 Hz, 1H, **H-1'**), 4.59 (d, *J* = 12.0 Hz, 1H), 4.47 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.14 – 3.98 (m, 3H), 3.90 (dd, *J* = 12.0, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 165.83, 165.62, 165.31, 165.30, 165.17, 164.90, 164.59, 149.02, 144.04, 140.46, 133.53, 133.49, 133.42, 133.31, 133.27, 133.21, 133.17, 132.56, 131.53, 130.83, 130.08, 129.93, 129.92, 129.88, 129.84, 129.69, 129.42, 129.02, 128.95, 128.86, 128.79, 128.70, 128.51, 128.49, 128.44, 128.41, 128.38, 128.35, 128.26, 127.80, 127.60, 126.73, 114.46, 100.52, 92.47, 75.13, 73.09, 72.91, 72.23, 71.89, 70.85, 69.92, 69.25, 66.87, 63.17. HRMS (ESI) calcd for $C_{76}H_{60}O_{19}Na$ $[M+Na]^+$ 1299.3621, found 1299.3605.

O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyrano syl- 2-(1-phenylvinyl) benzoate(3a)



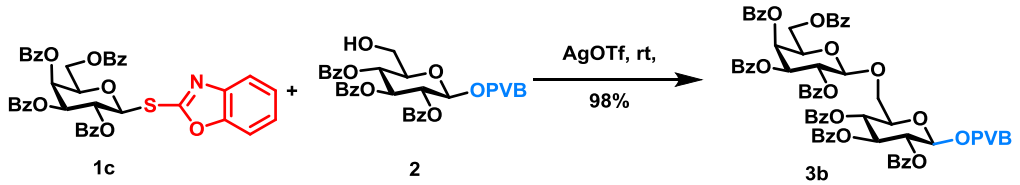
A mixture of donor **1b**[3] (53.0 mg, 0.069 mmol), acceptor **2** (40.0 mg, 0.057 mmol) and 4Å MS (100 mg) in dry CH_2Cl_2 (0.8 mL) was stirred at room temperature for 15 min, then cooled to -20 ℃. TMSOTf (110 μL, 10 μL in 1 mL CH_2Cl_2, 0.006 mmol) was added to the mixture dropwise. The resulting mixture was stirred at -20 ℃. After being stirred for another 1 h, the reaction was quenched with Et_3N (0.5 mL) and filtered. The filtrates were concentrated *in vacuo* to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 3:1 to 2:1) to afford **3a** (69 mg, 95%) as a syrup. $[\alpha]_D^{21}$ = +13.16 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 4H, Ar), 7.97 – 7.77 (m, 11H, Ar), 7.61 – 7.24 (m, 27H, Ar), 7.23 – 7.19 (m, 2H, Ar), 5.98 (d, *J* = 8.1 Hz, 1H, **H-1**), 5.93 (t, *J* = 9.6 Hz, 1H), 5.82 (t, *J* = 9.5 Hz, 1H), 5.74 (s, 1H, H-PVB), 5.66 – 5.49 (m, 3H, H-2, H-2'), 5.42 (t, *J* = 9.7 Hz, 1H), 5.13 (s, 1H, H-PVB), 5.03 (d, *J* = 7.8 Hz, 1H, **H-1'**), 4.59 (d, *J* = 12.0 Hz, 1H), 4.47 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.14 – 3.98 (m, 3H), 3.90 (dd, *J* = 12.0, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 165.83, 165.62, 165.31, 165.30, 165.17, 164.90, 164.59, 149.02, 144.04, 140.46, 133.53, 133.49, 133.42, 133.31, 133.27, 133.21, 133.17, 132.56, 131.53, 130.83, 130.08, 129.93, 129.92, 129.88, 129.84, 129.69, 129.42, 129.02, 128.95, 128.86, 128.79, 128.70, 128.51, 128.49, 128.44, 128.41, 128.38, 128.35, 128.26, 127.80, 127.60, 126.73, 114.46, 100.52, 92.47, 75.13, 73.09, 72.91, 72.23, 71.89, 70.85, 69.92, 69.25, 66.87, 63.17. HRMS (ESI) calcd for $C_{76}H_{60}O_{19}Na$ $[M+Na]^+$ 1299.3621, found 1299.3605.

O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyrano syl- 2-(1-phenylvinyl) benzoate(3a)



A mixture of donor **1e**[4] (131 mg, 0.172 mmol), acceptor **2** (100 mg, 0.143 mmol) and 3Å MS (252 mg) in dry CH_2Cl_2 (1.4 mL) was stirred at room temperature for 15 min, to which a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.36 mL, 0.079 M) was added to the mixture slowly. The resulting mixture was stirred at room temperature. After being stirred for another 2.5 h, the reaction was quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.5:1 to 2:1) to afford **3a** (181 mg, 99%) as a syrup. $[\alpha]_D^{21}$ = +13.16 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 4H, Ar), 7.97 – 7.77 (m, 11H, Ar), 7.61 – 7.24 (m, 27H, Ar), 7.23 – 7.19 (m, 2H, Ar), 5.98 (d, *J* = 8.1 Hz, 1H, **H-1**), 5.93 (t, *J* = 9.6 Hz, 1H), 5.82 (t, *J* = 9.5 Hz, 1H), 5.74 (s, 1H, H-PVB), 5.66 – 5.49 (m, 3H, H-2, H-2'), 5.42 (t, *J* = 9.7 Hz, 1H), 5.13 (s, 1H, H-PVB), 5.03 (d, *J* = 7.8 Hz, 1H, **H-1'**), 4.59 (d, *J* = 12.0 Hz, 1H), 4.47 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.14 – 3.98 (m, 3H), 3.90 (dd, *J* = 12.0, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 165.83, 165.62, 165.31, 165.30, 165.17, 164.90, 164.59, 149.02, 144.04, 140.46, 133.53, 133.49, 133.42, 133.31, 133.27, 133.21, 133.17, 132.56, 131.53, 130.83, 130.08, 129.93, 129.92, 129.88, 129.84, 129.69, 129.42, 129.02, 128.95, 128.86, 128.79, 128.70, 128.51, 128.49, 128.44, 128.41, 128.38, 128.35, 128.26, 127.80, 127.60, 126.73, 114.46, 100.52, 92.47, 75.13, 73.09, 72.91, 72.23, 71.89, 70.85, 69.92, 69.25, 66.87, 63.17. HRMS (ESI) calcd for $C_{76}H_{60}O_{19}Na$ $[M+Na]^+$ 1299.3621, found 1299.3605.

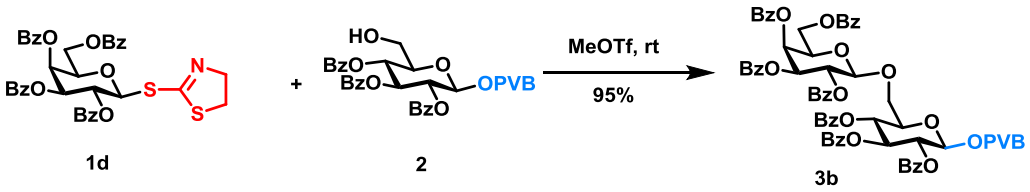
O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyranosyl- 2-(1-phenylvinyl) benzoate(3b)



SBox donor **1c**[5] (40 mg, 0.055 mmol) and acceptor **2** (32 mg, 0.046 mmol) were dissolved in dry CH_2Cl_2 (1mL). To this solution was added 4Å Molecular sieves (140mg). After stirring for 15 min

at room temperature, AgOTf (24 mg, 0.093 mmol) was added. The reaction mixture was stirred for another 2.5 h. The reaction mixture wasthen quenched with Et_3N (0.5 mL), filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 5:1 to 3:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **3b** (57.1mg, 98%) as a syrup. $[\alpha]_D^{21}$ = +55.34 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.01 (m, 6H, Ar), 7.96 – 7.77 (m, 9H, Ar), 7.65 – 7.24 (m, 27H, Ar), 7.22 (s, 2H, Ar), 6.05 – 5.92 (m, 2H, **H-1)**, 5.88 – 5.78 (m, 2H, H-2'), 5.75 (s, 1H, H-PVB), 5.65 – 5.52 (m, 2H, H-2), 5.42 (t, *J* = 9.8 Hz, 1H), 5.12 (s, 1H, H-PVB), 5.05 (d, *J* = 7.9 Hz, 1H, **H-1'**), 4.66 – 4.55 (m, 1H), 4.42 – 4.33 (m, 1H), 4.23 – 4.16 (m, 1H), 4.14 – 4.02 (m, 2H), 3.97 (dd, *J* = 12.8, 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.04, 165.66, 165.63, 165.62, 165.54, 165.28, 164.90, 164.64, 148.99, 143.98, 140.44, 133.60, 133.45, 133.37, 133.35, 133.31, 133.21, 132.61, 131.59, 130.79, 130.10, 130.02, 129.90, 129.83, 129.53, 129.50, 129.13, 128.95, 128.83, 128.69, 128.64, 128.61, 128.52, 128.46, 128.37, 128.27, 127.82, 127.65, 126.71, 114.42, 100.81, 92.52, 75.57, 72.92, 71.97, 71.36, 70.84, 69.80, 69.07, 68.22, 66.75, 62.09. HRMS (ESI) calcd for $C_{76}H_{60}O_{19}Na$ $[M+Na]^+$ 1299.3621, found 1299.3627.

O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyra nosyl- 2-(1-phenylvinyl) benzoate(3b)

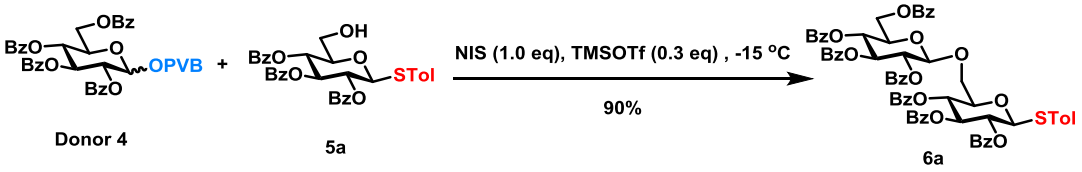


STaz donor **1d**[6] (52 mg, 0.075 mmol) and acceptor **2** (35 mg, 0.050 mmol) were dissolved in dry CH_2Cl_2 (0.9 mL). To this solution was added 3Å Molecular sieves (120mg). After stirring for 15 min at room temperature, MgOTf (19 μL, 0.165mmol) was added slowly. The reaction mixture was stirred for another 2.5 h. The reaction mixture wasthen quenched with Et_3N (0.5 mL), filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 5:1 to 3:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **3b** (60.6mg, 95%) as a syrup. $[\alpha]_D^{21}$ = +55.34 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.01 (m, 6H, Ar), 7.96 – 7.77 (m, 9H, Ar), 7.65 – 7.24

(m, 27H, Ar), 7.22 (s, 2H, Ar), 6.05 – 5.92 (m, 2H, **H-1)**, 5.88 – 5.78 (m, 2H, H-2'), 5.75 (s, 1H, H-PVB), 5.65 – 5.52 (m, 2H, H-2), 5.42 (t, *J* = 9.8 Hz, 1H), 5.12 (s, 1H, H-PVB), 5.05 (d, *J* = 7.9 Hz, 1H, **H-1'**), 4.66 – 4.55 (m, 1H), 4.42 – 4.33 (m, 1H), 4.23 – 4.16 (m, 1H), 4.14 – 4.02 (m, 2H), 3.97 (dd, *J* = 12.8, 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.04, 165.66, 165.63, 165.62, 165.54, 165.28, 164.90, 164.64, 148.99, 143.98, 140.44, 133.60, 133.45, 133.37, 133.35, 133.31, 133.21, 132.61, 131.59, 130.79, 130.10, 130.02, 129.90, 129.83, 129.53, 129.50, 129.13, 128.95, 128.83, 128.69, 128.64, 128.61, 128.52, 128.46, 128.37, 128.27, 127.82, 127.65, 126.71, 114.42, 100.81, 92.52, 75.57, 72.92, 71.97, 71.36, 70.84, 69.80, 69.07, 68.22, 66.75, 62.09. HRMS (ESI) calcd for $C_{76}H_{60}O_{19}Na$ $[M+Na]^+$ 1299.3621, found 1299.3627.

2.2 Selective activation of glycosyl PVB over other leaving groups

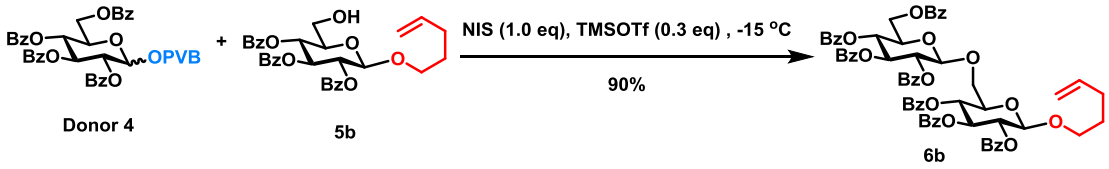
***p*-methylphenyl-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-1-thio-β -D- glucopyranoside (6a)**



To a solution of donor **4**[7] (80.5 mg, 0.100 mmol) and thioglycoside acceptor **5a**[8] (50 mg, 0.084 mmol) in dry CH_2Cl_2 (0.84 mL) was added 4Å Molecular sieves (200 mg). After stirring for 15 min at room temperature, the reaction mixture was cooled to -15 ℃, and NIS (18.8 mg, 0.084 mmol), TMSOTf (4.5 μL, 0.025 mmol) were added successively at -15 ℃. The reaction mixture was stirred for another 2h, and then quenched with Et_3N (0.5 mL), filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 4:1 to 3.5:1) to afford **6a**[9] (87.6 mg, 90%) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.8 Hz, 2H, Ar), 8.03 – 7.93 (m, 6H, Ar), 7.88 (t, *J* = 6.9 Hz, 4H, Ar), 7.79 (d, *J* = 7.8 Hz, 2H, Ar), 7.62 – 7.19 (m, 25H, Ar), 5.92 (t, *J* = 9.6 Hz, 1H, H-3'), 5.84 (t, *J* = 9.5 Hz, 1H, H-3), 5.67 (t, *J* = 9.7 Hz, 1H, H-4'), 5.57 (t, *J* = 8.8 Hz, 1H, H-2'), 5.39 (t, *J* = 9.7 Hz, 1H, H-2), 5.31 (t, *J* = 9.6 Hz, 1H, H-4), 5.08 (d, *J* = 7.9 Hz, 1H, **H-1'**), 4.87 (d, *J* = 10.0 Hz, 1H,

H-1), 4.66 (dd, *J* = 12.4, 3.1 Hz, 1H, H-6'), 4.47 (dd, *J* = 12.2, 5.2 Hz, 1H, H-6'), 4.19 – 4.10 (m, 1H, H-5'), 4.10 – 3.95 (m, 3H, H-5, 2H-6), 2.40 (s, 3H, CH_3-STol).

Pent-4-en-yl-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyranoside (6b)

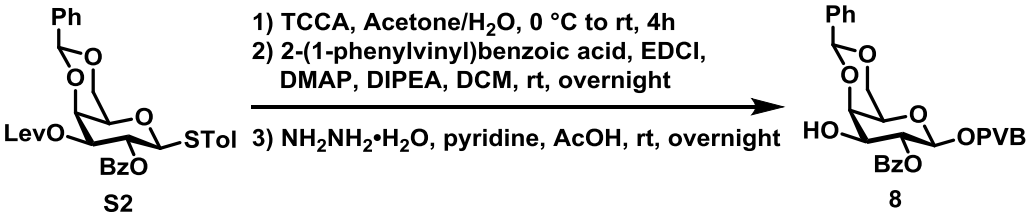


To a solution of donor **4**[7] (85.9 mg, 0.107 mmol) and acceptor **5b**[9] (50 mg, 0.089 mmol) in dry CH_2Cl_2 (0.9 mL) was added 4Å Molecular sieves (200 mg). After stirring for 15 min at room temperature, the reaction mixture was cooled to -15 ℃, and NIS (20.1 mg, 0.089 mmol), TMSOTf (4.8 μL, 0.027 mmol) were added successively at -15 ℃. The reaction mixture was stirred for another 2.5h, and then quenched with Et_3N (0.5 mL), filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 4:1 to 3.5:1) to afford **6b**[9] (90.5 mg, 90%) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.7 Hz, 2H, Ar), 7.99 (d, *J* = 7.8 Hz, 2H, Ar), 7.97 – 7.87 (m, 6H, Ar), 7.87 – 7.79 (m, 4H, Ar), 7.60 – 7.48 (m, 6H, Ar), 7.48 – 7.33 (m, 10H, Ar), 7.32 – 7.25 (m, 5H, Ar), 5.93 (t, *J* = 9.6 Hz, 1H, H-3'), 5.84 (t, *J* = 9.6 Hz, 1H, H-3), 5.71 – 5.53 (m, 3H, H-2', H-4', CH-n-Pent), 5.43 (t, *J* = 8.9 Hz, 1H, H-2), 5.34 (t, *J* = 9.7 Hz, 1H, H-4), 5.04 (d, *J* = 7.8 Hz, 1H, **H-1'**), 4.83 (d, *J* = 10.0 Hz, 1H, CH_2-n-Pent), 4.81 (d, *J* = 16.8 Hz, 1H, CH_2-n-Pent), 4.68 – 4.61 (m, 2H, **H-1**, H-6'), 4.46 (dd, *J* = 12.2, 5.1 Hz, 1H, H-6'), 4.20 – 4.14 (m,, 1H, H-5'), 4.11 (d, *J* = 11.2 Hz, 1H, H-6), 4.04 (t, *J* = 9.0 Hz, 1H, H-5), 3.91 (dd, *J* = 11.4, 7.9 Hz, 1H, H-6), 3.70 – 3.61 (m, 1H, H-n-Pent), 3.29 – 3.17 (m, 1H, H-n-Pent), 1.96 – 1.84 (m, 2H, CH_2-n-Pent), 1.53 – 1.32 (m, 2H, CH_2-n-Pent).

2.3 One-Pot synthesis of oligosaccharides based on glycosyl PVB.

2.3.1 Preparation of new glycosyl donors and acceptors

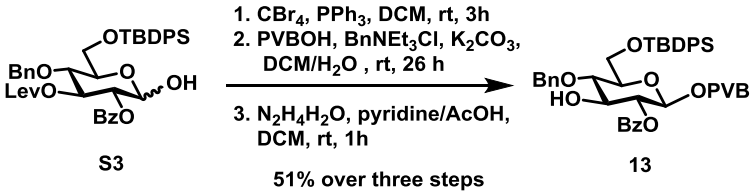
2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-2-(1-phenylvinyl) benzoate (8)



Compound **S2**[9] (328.7 mg, 0.570 mmol) was dissolved in acetone/H_2O (14.3mL, v/v 4/1), and TCCA (132.5 mg, 0.570 mmol) was added slowly at 0 ℃. Then the resulting mixture was allowed to warm to room temperature. After stirring at room temperature for 4h, the reaction mixture was diluted with ethyl acetate and washed with saturated aqueous $NaHCO_3$, H_2O, and brine. The organic layer was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (petroleum ether- EtOAc, 2:1 to 1.2:1) to give the hemiacetal intermediate (224.6 mg, 83.7%). The above intermediate (224.6 mg, 0.477 mmol) and 2-(1-phenylvinyl) benzoic acid (117.7 mg, 0.525 mmol) were dissolved in dry DCM (4.8 mL), followed with the addition of EDCI (164.7 mg, 0.859 mmol), DMAP (58.3 mg, 0.477 mmol) and DIPEA (0.24 mL, 1.432 mmol). The resulting mixture was stirred for overnight at room temperature. Upon completion, the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 2.5:1 to 2:1) to afford the glycosyl *ortho*-(1-phenylvinyl)benzoate (265 mg, 81.8%, only β). The above intermediate (260.8 mg, 0.385 mmol) was then dissolved in pyridine/AcOH (3.8 mL, v/v 3/2), then $NH_2NH_2 \cdot H_2O$ (56 μL, 1.16 mmol) was added. After stirring at room temperature for overnight, the solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 2.5:1) to give **8** (199.8 mg, 90%) as a white foam. $[\alpha]_D^{21}$ = +12.36 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.96 (m, 3H, Ar), 7.65 – 7.36 (m, 13H, Ar), 7.32 – 7.21 (m, 3H, Ar), 5.90 (d, *J* = 8.4 Hz, 1H, **H-1**), 5.66 (s, 1H,), 5.62 – 5.55 (m, 2H, H-2), 5.08 (s, 1H), 4.28 (d, *J* = 12.6 Hz, 1H, H-6), 4.23 (d, *J* = 3.7 Hz, 1H, H-4), 4.01 (d, *J* = 12.6 Hz, 1H, H-6), 3.94 (dd, *J* = 9.9, 3.6 Hz, 1H, H-3), 3.62 (s, 1H, H-5), 2.76 (s, 1H, H-OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.03, 165.01, 148.96, 143.86, 140.28, 137.34, 133.32, 132.46, 131.37, 130.79, 129.89, 129.44, 129.38, 128.76, 128.39, 128.35, 128.20, 127.67, 127.48, 126.54, 126.45,

114.07, 101.38, 92.30, 75.35, 71.82, 71.63, 68.66, 67.33. HRMS (ESI) calcd for $C_{35}H_{30}O_8Na$ $[M+Na]^+$ 601.1833, found 601.1831.

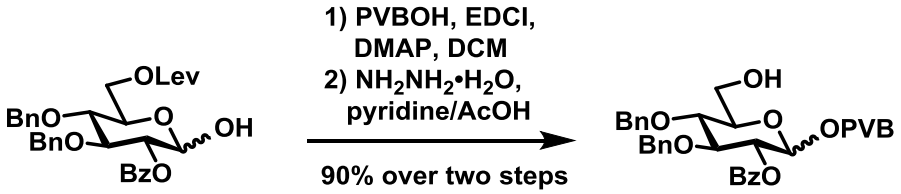
2-*O*-benzoyl-4-O-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-glucopyranosyl 2-(1-phenylvinyl) benzoate (13)



The hemiacetal **S3**[9] (600 mg, 0.844 mmol), CBr_4 (1.4 g, 4.22 mmol) and PPh_3 (1.105 g, 4.22 mmol) were dissolved in 8.5 mL CH_2Cl_2. The mixture was stirred at room temperature for 3 h, then diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/3, with 2% v/v Et_3N) to afford glycosyl bromide (490 mg, 75%) as a light yellow foam. The above foam (127 mg, 0.164 mmol), 2-(1-phenylvinyl) benzoic acid (48 mg, 0.213 mmol) were dissolved in CH_2Cl_2/H_2O = 0.85 mL/ 0.85 mL, then $BnNEt_3Cl$ (8 mg, 0.033 mmol) and K_2CO_3 (113 mg, 2.235 mmol) were added at room temperature. The solution was stirred for 24 h, then diluted with CH_2Cl_2, washed with brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/4,) to afford glycosyl PVB (114 mg, 76%) as a white foam. To a solution of this foam (114 mg, 0.124 mmol) in 2.5 mL dry CH_2Cl_2 was added 1 M hydrazine hydrate (0.25 mL, 0.248 mmol, hydrazine hydrate/pyridine/AcOH = 125 μL/1.4 mL/1 mL) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was quenched with acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/4) to afford **13** (91 mg, 90%) as a white foam; $[\alpha]_D^{22}$ = -48.34 (c 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 6.7 Hz, 3H), 7.60 (t, *J* = 7.3 Hz, 4H), 7.48 – 7.38 (m, 2H), 7.36 – 7.15 (m, 15H), 7.15 – 6.99 (m, 5H), 5.80 (d, *J* = 8.2 Hz, 1H, **H-1**), 5.45 (s, 1H, CH_2-PVB), 5.12 (t, *J* = 8.3 Hz, 1H, H-2), 4.90 (s, 1H, CH_2-PVB), 4.80 (d, *J* = 11.1 Hz, 1H, CH_2-Bn), 4.70 (d, *J* = 11.1 Hz, 1H, CH_2-Bn), 3.94 – 3.78 (m, 4H, H-3, H-4, H-5, and H-6a), 3.41 (d, *J* = 7.6 Hz, 1H, H-6b), , 2.64 (s, 1H, OH), 1.00 (s, 9H, CH_3-TBDPS).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 164.97, 148.83, 143.81, 140.20, 138.15, 135.90, 135.65, 133.55, 133.45, 132.97, 132.34, 131.39, 130.63, 130.02, 129.74, 129.66, 129.27, 129.17, 128.63, 128.44, 128.16, 128.02, 127.99, 127.76, 127.67, 127.60, 127.53, 126.48, 114.11, 92.32, 77.62, 77.43, 77.11, 76.79, 76.40, 75.99, 75.18, 73.85, 62.24, 26.93, 19.46. HRMS (ESI) calcd for $C_{51}H_{50}O_8Na$ $[M+Na]^+$ 841.3167, found 841.3152.

2-*O*-benzoyl-3,4-di-*O*-benzyl-α/β-D-glucopyranosyl 2-(1-phenylvinyl) benzoate (21)

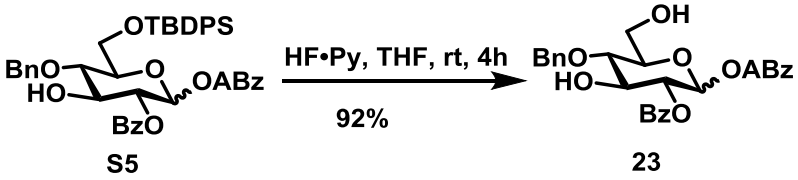


S4 **21**

The hemiacetal **S4** [10] (1.15 g, 2.05 mmol), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI) (709 mg, 3.69 mmol) and 4-dimethylaminopyridine (DMAP) (251 mg, 2.05) were dissolved in 10.3 mL CH_2Cl_2. Then acid 2-(1-phenylvinyl) benzoic acid [1] (506 ml, 2.26 mmol) and N,N-diisopropylethylamine (DIPEA) (1.02 mL, 6.16 mmol) were added successively at room temperature under Ar. The resulting mixture was stirred for 3.5 h at this temperature and concentrated *in vacuo* to produce the crude syrup. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether/=1/3) to afford a white foam (1.52 g, 96%). This above foam (1.52 g, 1.97 mmol) was dissolved in pyridine (6 mL) and AcOH (4 mL), then hydrazine hydrate (0.19 mL, 3.94 mmol) was slowly added at room temperature under Ar. The mixture was stirred for 3 h and quenched with acetone, diluted with EtOAc, washed with 2 N HCl, saturated aqueous $NaHCO_3$ and brine successively. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2.5) to afford **21** as a white foam (1.32 g, 95%, α/β = 1/3). Data for the β-anomer: $[\alpha]_D^{25}$ = +32.68 (c 0.10, CHCl3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.24 (m, 9H), 7.22 – 7.15 (m, 5H), 7.10 (s, 5H), 5.77 (d, *J* = 8.2 Hz, 1H, **H-1**), 5.63 (s, 1H, CH_2-PVB), 5.43 (t, *J* = 8.7 Hz, 1H, H-2), 5.07 (s, 1H, CH_2-PVB), 4.84 (d, *J* = 11.0 Hz, 1H, CH_2-Bn), 4.75 (d, *J* = 11.0 Hz, 1H, CH_2-Bn), 4.66 (d, *J* = 10.2 Hz, 2H), 3.85 (t, *J* = 9.1 Hz, 1H), 3.79 – 3.71 (m, 2H),

3.68 – 3.56 (m, 1H), 3.48 (d, *J* = 9.0 Hz, 1H), 1.79 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.16, 164.88, 149.08, 143.86, 140.66, 137.82, 137.67, 133.42, 132.73, 131.71, 130.66, 129.91, 129.51, 128.75, 128.66, 128.55, 128.42, 128.20, 128.16, 127.90, 127.87, 127.47, 126.64, 114.39, 92.49, 82.51, 77.18, 76.21, 75.27, 75.21, 72.49, 61.34. HRMS (ESI) calcd for $C_{42}H_{38}O8Na$ $[M+Na]^+$ 693.2459, found 693.2454.

2-*O*-benzoyl-4-*O*-benzyl-α/β-D-glucopyranosyl 2-(cyclopropylethynyl) benzoate (23)



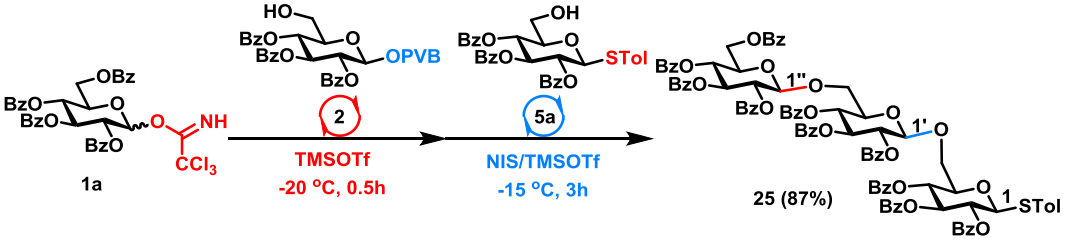
S5 **23**

To a solution of compound **S5**[9] (384 mg, 0.49 mmol) in 3 mL THF was added 70% HF-pyridine (0.44 mL, 4.9 mmol) at room temperature. The mixture was stirred at this temperature for 4 h, then quenched with Et_3N, diluted with EtOAc, washed with saturated aqueous $NaHCO_3$. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford **23** (244 mg, α/β = 1/2) as a white foam. Data for the β-anomer: $[\alpha]_D^{23}$ = +26.38 (c 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.27 (m, 8H), 7.27 – 7.17 (m, 2H), 6.07 (d, *J* = 8.1 Hz, 1H, **H-1**), 5.34 (t, *J* = 8.8 Hz, 1H, H-2), 4.88 (d, *J* = 11.3 Hz, 1H, CH_2-Bn), 4.77 (d, *J* = 11.3 Hz, 1H, CH_2-Bn), 4.07 (t, *J* = 9.0 Hz, 1H, H-3), 4.02 – 3.94 (m, 1H, H-5), 3.84 – 3.60 (m, 3H, H-4 and H-6), 2.99 (s, 1H, OH), 2.08 (s, 1H, OH), 1.57 – 1.44 (m, 1H, CH-ABz), 0.96 – 0.74 (m, 4H, $2CH_2$-ABz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.55, 163.01, 137.18, 133.72, 132.79, 131.73, 130.12, 129.19, 128.65, 128.38, 127.95, 127.76, 127.49, 127.45, 126.42, 124.94, 99.73, 91.70, 75.59, 75.02, 74.28, 73.64, 73.05, 60.80, 8.31, 8.28. HRMS (ESI) calcd for $C_{32}H_{30}O8Na$ $[M+Na]^+$ 565.1833, found 565.1833.

2.3.2 One-pot glycosylation for the synthesis of oligosaccharides

***p*-Methylphenyl**

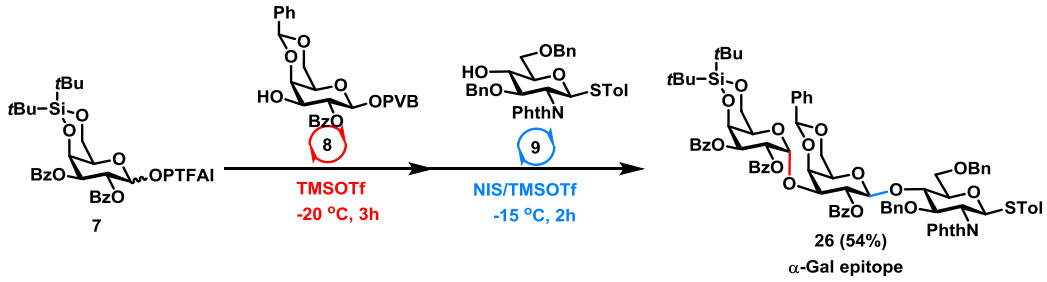
(2,3,4,6-*tetra*-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D- glucopyranoside (25)



A suspension of glucosyl trichloroacetimidate **1a**[2] (56.5 mg, 0.076 mmol), glucosyl PVB acceptor **2** (44.4 mg, 0.064 mmol), and activated 3Å MS (300 mg) in dry CH_2Cl_2 (1.2 mL) was stirred at room temperature for 15 min and was then cooled to -20 ℃. TMSOTf (120 μL, 10 μL in 1 mL CH_2Cl_2, 0.006 mmol) was added to the mixture dropwise. After being stirred at -20 ℃ for another 0.5 h, the reaction mixture was warmed up to -15 ℃, to which glucosyl acceptor **5a**[8] (34.2 mg, 0.057 mmol) and NIS (14.3 mg, 0.064 mmol) and TMSOTf (2.4 μL, 0.013 mmol) were added successively. The resulting mixture was stirred at -15 ℃ for another 3h, then was quenched with Et_3N (0.7mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.5:1 to 2:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **25** (82.2 mg, 87%) as a syrup. $[\alpha]_D^{29}$ = -3.86 (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (t, *J* = 6.6 Hz, 4H, Ar), 8.00 (d, *J* = 7.7 Hz, 2H, Ar), 7.98 – 7.87 (m, 10H, Ar), 7.81 (t, *J* = 7.2 Hz, 4H, Ar), 7.60 – 7.26 (m, 30H, Ar), 7.25 – 7.14 (m, 4H, Ar), 6.17 (t, *J* = 9.7 Hz, 1H, H-3”), 5.88 (t, *J* = 9.5 Hz, 1H, H-3), 5.72 (t, *J* = 9.5 Hz, 2H, H-3’, H-4”), 5.63 – 5.49 (m, 3H, H-2, H-4, H-2’’), 5.29 – 5.17 (m, 2H, **H-1”**, H-2’), 5.12 (t, *J* = 9.6 Hz, 1H, H-4’), 4.99 (d, *J* = 9.9 Hz, 1H, **H-1**), 4.71 – 4.60 (m, 2H, **H-1’**, H-6”), 4.49 (dd, *J* = 12.2, 5.4 Hz, 1H, H-6”), 4.45 – 4.37 (m, 1H, H-5”), 4.10 – 4.00 (m, 2H), 3.99 – 3.82 (m, 3H, H-5, H-5’), 3.66 (dd, *J* = 11.2, 5.1 Hz, 1H), 2.36 (s, 3H, CH_3-STol); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.19, 165.88, 165.86, 165.66, 165.37, 165.33, 165.05, 165.03, 138.69, 133.58, 133.56, 133.42, 133.35, 133.27, 133.24, 133.19, 133.15, 130.06, 130.01, 129.99, 129.93, 129.91, 129.84, 129.77, 129.70, 129.52, 129.46, 129.38, 129.17, 129.02, 128.96, 128.91, 128.78, 128.68, 128.57, 128.51, 128.47, 128.42, 128.39, 128.37, 128.34, 128.30, 128.26, 101.53, 100.59, 86.68, 77.51, 74.32, 74.13, 72.85, 72.75, 72.33, 72.19, 71.81, 70.71, 70.32, 69.83, 69.72, 68.51, 63.28, 21.31. HRMS (ESI) calcd for $C_{95}H_{78}O_{25}SNa$ $[M+Na]^+$ 1673.4445, found 1673.4436.

***p*-Methylphenyl**

(2,3-*di*-*O*-benzoyl-4,6-(di-*tert*-butylsilylidene)-α-D-galacopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-benzylidene-β-D-galacopyranosyl)-(1→4)-2-*N*-phthalimido-3,6-di-*O*-benzyl-2-deoxy-1-thio-β-D-glucopyranoside (26)

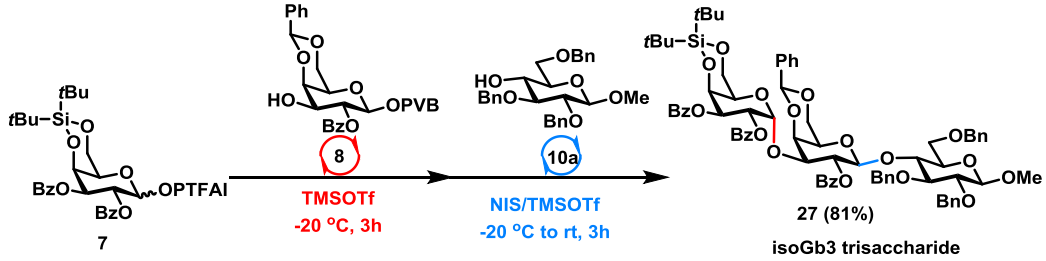


A suspension of glucosyl trifluoroacetimidate **7**[11] (50.3 mg, 0.072 mmol), glucosyl PVB acceptor **8** (32.0 mg, 0.055 mmol), and activated 3Å MS (280 mg) in dry CH_2Cl_2 (1.0 mL) was stirred at room temperature for 15 min and was then cooled to -20 ℃. TMSOTf (200 μL, 10 μL in 1 mL CH_2Cl_2, 0.011 mmol) was added to the mixture dropwise. After being stirred at -20 ℃ for another 3h, the reaction mixture was warmed up to -15 ℃, to which glucosyl acceptor **9**[12] (29.7 mg, 0.050 mmol) and NIS (12.4 mg, 0.055 mmol) and TMSOTf (100 μL, 10 μL in 1 mL CH_2Cl_2, 0.006 mmol) were added successively. The resulting mixture was stirred at -15 ℃ for another 2 h, then was quenched with Et_3N (0.6mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.6:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **26** (39.5 mg, 54%) as a syrup. $[\alpha]_D^{29}$ = +193.12 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 2H, Ar), 7.96 (d, *J* = 7.8 Hz, 2H, Ar), 7.89 – 7.78 (m, 3H, Ar), 7.73 – 7.47 (m, 8H, Ar), 7.46 – 7.33 (m, 8H, Ar), 7.24 (d, *J* = 7.8 Hz, 2H, Ar), 7.14 – 7.07 (m, 4H, Ar), 7.04 – 6.88 (m, 6H, Ar), 6.80 – 6.66 (m, 3H, Ar), 5.69 (t, *J* = 8.8 Hz, 1H, H-2'), 5.61 (d, *J* = 3.8 Hz, 1H, **H-1"**), 5.54 (dd, *J* = 10.5, 3.4 Hz, 1H, H-2''), 5.41 dd, *J* = 10.4, 2.4 Hz, 1H, H-3''), 5.35 (d, *J* = 10.2 Hz, 1H, **H-1**), 5.06 (s, 1H, H-CHPh), 4.94 (d, *J* = 12.6 Hz, 1H, H-Bn), 4.81 (d, *J* = 7.9 Hz, 1H, **H-1'**), 4.72 (d, *J* = 12.0 Hz, 1H, H-Bn), 4.59 – 4.50 (m, 2H, H-4", H-Bn), 4.42 (d, *J* = 12.0 Hz, 1H, H-Bn), 4.30 – 4.16 (m, 3H, H-2), 4.15 – 4.06 (m, 2H), 3.91 – 3.74 (m, 4H, H-3'), 3.69 – 3.57 (m, 3H), 3.41 (d, *J* = 9.8 Hz, 1H), 3.23 (s, 1H), 2.25 (s, 3H, CH_3-STol), 1.06 (s, 9H, 9H-tBu), 0.87 (s, 9H, 9H-tBu); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.89, 167.46, 166.81, 165.86, 164.76, 138.67,

138.54, 138.14, 137.56, 133.83, 133.71, 133.60, 133.54, 133.35, 133.07, 131.85, 131.74, 130.04, 129.83, 129.73, 129.71, 129.58, 129.00, 128.86, 128.58, 128.45, 128.39, 128.33, 128.06, 127.93, 127.85, 127.74, 126.82, 126.12, 123.45, 123.37, 100.71, 100.56, 95.78, 83.55, 79.08, 78.20, 77.79, 75.30, 73.62, 72.84, 70.97, 70.84, 70.75, 69.29, 68.60, 68.00, 67.35, 66.64, 66.34, 55.01, 27.49, 27.28, 23.25, 21.20, 20.77. HRMS (ESI) calcd for $C_{83}H_{85}NO_{19}SSiNa$ $[M+Na]^+$ 1482.5098, found 1482.5106.

Methyl

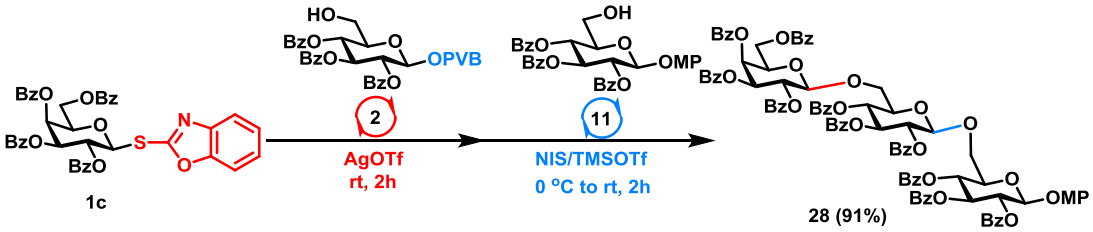
(2,3-di-*O*-benzoyl-4,6-(di-*tert*-butylsilylidene)-α-D-galacopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-benzylidene-β-D-galacopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (27)



A suspension of glucosyl trifluoroacetimidate **7**[11] (57.6 mg, 0.082 mmol), glucosyl PVB acceptor **8** (36.6 mg, 0.063 mmol), and activated 3Å MS (340 mg) in dry CH_2Cl_2 (1.2 mL) was stirred at room temperature for 15 min and was then cooled to -20 ℃. TMSOTf (2.7 μL, 0.015 mmol) was added to the mixture dropwise. After being stirred at -20 ℃ for another 3 h, to which glucosyl acceptor **10a**[13] (26.0 mg, 0.057 mmol), NIS (17.1 mg, 0.076 mmol) and TMSOTf (150 μL, 10 μL in 1 mL CH_2Cl_2, 0.008 mmol) were added successively. The resulting mixture was warmed gradually to room temperature and stirred for 3 h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 4:1 to 2:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **27**[9] (61.1 mg, 81%) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.7 Hz, 2H, Ar), 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.85 (d, *J* = 7.7 Hz, 2H, Ar), 7.64 (t, *J* = 7.3 Hz, 1H, Ar), 7.55 – 7.47 (m, 3H, Ar), 7.42 – 7.23 (m, 17H, Ar), 7.21 – 7.10 (m, 6H, Ar), 7.06 (t, *J* = 7.6 Hz, 2H, Ar), 5.64 (t, *J* = 9.2 Hz, 1H, H-2'), 5.61 – 5.52 (m, 2H, **H-1''**, H-2''), 5.43 (dd, *J* = 10.3, 2.9 Hz, 1H, H-3''), 5.10 – 5.01 (m, 2H, H-CHPh, H-Bn), 4.85 (t, *J* = 10.8 Hz, 2H, H-Bn, H-Bn), 4.80 (d, *J* = 7.9 Hz, 1H, **H-1'**), 4.70 (d, *J* = 11.1 Hz,

1H, H-Bn), 4.61 (d, *J* = 12.2 Hz, 1H, H-Bn), 4.55 (d, *J* = 3.0 Hz, 1H, H-4”), 4.29 (d, *J* = 12.2 Hz, 1H, H-Bn), 4.23 (d, *J* = 7.7 Hz, 1H, **H-1**), 4.09 (d, *J* = 12.2 Hz, 1H), 4.02 (d, *J* = 1.7 Hz, 1H, H-4’), 3.94 (t, *J* = 9.2 Hz, 1H, H-4), 3.83 – 3.69 (m, 3H, H-3’), 3.67 – 3.54 (m, 5H, H-3), 3.51 (s, 3H, 3H-OCH_3), 3.41 (t, *J* = 8.4 Hz, 1H, H-2), 3.30 – 3.23 (m, 1H), 2.99 (s, 1H), 1.06 (s, 9H, 9H-tBu), 0.87 (s, 9H, 9H-tBu).

***p*-Methoxyphenyl (2,3,4,6-tetra-*O*-benzoyl-β-D-galacopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (28)**

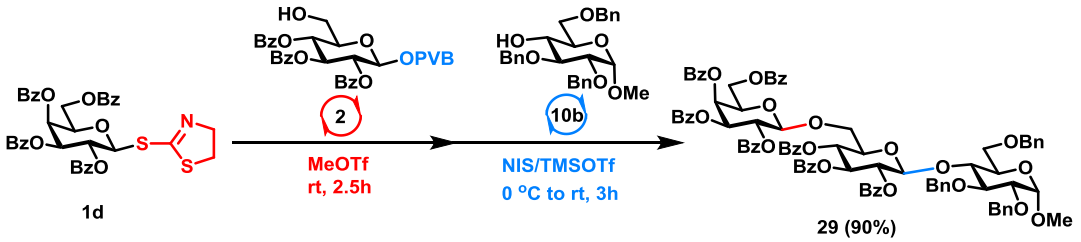


A suspension of SBox donor **1c**[5] (58.2 mg, 0.080 mmol), glucosyl PVB acceptor **2** (42.9 mg, 0.061 mmol), and activated 3Å MS (240 mg) in dry CH_2Cl_2 (1 mL) was stirred at room temperature for 15 min, to which AgOTf (31.5 mg, 0.123 mmol) was added to the mixture. After being stirred at room temperature for another 2h, the reaction mixture was cooled to 0 ℃, to which glucosyl acceptor **11**[14](30.9 mg, 0.052 mmol), NIS (17.4 mg, 0.077 mmol) and TMSOTf (2.8 μL, 0.015 mmol) were added successively at 0 ℃ . The resulting mixture was warmed gradually to room temperature and stirred for 2 h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.5:1) to afford **28** (92.2 mg, 91%) as a syrup. $[\alpha]_D^{29}$ = +25.72 (*c* 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.7 Hz, 2H, Ar), 8.06 (t, *J* = 6.8 Hz, 4H, Ar), 8.03 - 7.98 (m, 4H, Ar), 7.95 – 7.85 (m, 8H, Ar), 7.79 (d, *J* = 7.7 Hz, 2H, Ar), 7.64 – 7.25 (m, 30H, Ar), 7.01 (d, *J* = 8.5 Hz, 2H, Ar), 6.86 (d, *J* = 8.7 Hz, 2H, Ar), 6.08 (d, *J* = 3.3 Hz, 1H, H-4”), 5.99 – 5.90 (m, 2H, H-3, H-3”), 5.89 – 5.80 (m, 2H, H-2, H-2”), 5.72 (t, *J* = 9.6 Hz, 1H, H-3’), 5.64 (t, *J* = 9.5 Hz, 1H, H-4), 5.29 – 5.08 (m, 4H, **H-1**, H-2’, H-4’, **H-1”**), 4.71 (d, *J* = 7.8 Hz, 1H, **H-1’**), 4.64 (dd, *J* = 10.6, 6.0 Hz, 1H), 4.55 – 4.42 (m, 2H), 4.13 – 3.96 (m, 3H, H-5), 3.95 – 3.85 (m, 2H, H-5’), 3.77 (s, 3H, CH_3-OMP), 3.69 (dd, *J* = 11.1, 5.0 Hz, 1H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 166.07, 165.84, 165.67, 165.64, 165.60, 165.52, 165.36, 165.09, 165.06, 155.94, 151.08, 133.61, 133.58, 133.35, 133.29, 133.23, 130.12, 130.09, 129.95, 129.90, 129.88, 129.85, 129.73, 129.56, 129.41, 129.39, 129.36, 129.15, 129.11, 128.97, 128.95, 128.89, 128.72, 128.69, 128.62, 128.58, 128.50, 128.46, 128.43, 128.36, 119.08, 114.79, 101.74, 100.97, 100.27, 77.36, 74.36, 74.02, 72.77, 71.94, 71.83, 71.48, 70.47, 70.27, 69.51, 68.62, 68.12, 62.26, 55.72. HRMS (ESI) calcd for $C_{95}H_{78}O_{27}Na$ $[M+Na]^+$ 1673.4623, found 1673.4622.

Methyl

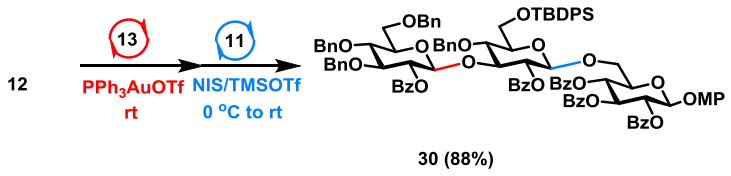
(2,3,4,6-tetra-*O*-benzoyl-β-D-galacopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→4)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (29)



A suspension of STaz galactoside donor **1d**[6] (64.4 mg, 0.092 mmol), glucosyl PVB acceptor **2** (43.5 mg, 0.062 mmol), and activated 3Å MS (280 mg) in dry CH_2Cl_2 (1 mL) was stirred at room temperature for 15 min, to which MeOTf (24 μL, 0.206 mmol) was added to the mixture slowly. After being stirred at room temperature for 2.5 h, the reaction mixture was cooled to 0 ℃, to which glucosyl acceptor **10b**[13] (24.3 mg, 0.052 mmol), NIS (17.6 mg, 0.078 mmol) and TMSOTf (2.8 μL, 0.016 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 3 h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 4:1 to 3.5:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **29** (71.4 mg, 90%) as a syrup. $[\alpha]_D^{29}$ = +34.65 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.01 (m, 6H, Ar), 7.96 (d, *J* = 7.8 Hz, 2H, Ar), 7.92 – 7.81 (m, 4H, Ar), 7.74 (d, *J* = 7.8 Hz, 2H, Ar), 7.67 (d, *J* = 7.6 Hz, 2H, Ar), 7.61 – 7.18 (m, 34H, Ar), 5.87 – 5.75 (m, 2H, H-2'', H-4''), 5.71 – 5.58 (m, 2H, H-3'', H-3'), 5.46 (t, *J* = 9.1 Hz, 1H, H-2'), 5.37 (t, *J* = 9.8 Hz, 1H, H-4'), 5.30 – 5.16 (m, 2H, **H-1''**, H-Bn), 5.07 (d, *J* = 11.9 Hz, 1H, H-Bn), 4.96 (d, *J* = 11.9 Hz, 1H, H-Bn), 4.88 – 4.76 (m,

2H, **H-1'**, H-Bn), 4.62 (s, 1H, **H-1**), 4.37 – 4.23 (m, 2H, H-Bn), 4.20 – 3.92 (m, 6H, H-Bn), 3.86 – 3.72 (m, 2H, H-2, H-5'), 3.60 (d, *J* = 9.1 Hz, 2H), 3.41 (t, *J* = 12.4 Hz, 2H), 3.33 (s, 3H, 3H-OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86, 165.84, 165.70, 165.55, 165.42, 165.37, 164.76, 139.74, 138.77, 137.84, 133.59, 133.45, 133.33, 133.24, 133.18, 133.09, 130.03, 129.98, 129.84, 129.78, 129.74, 129.67, 129.30, 129.18, 129.16, 128.96, 128.90, 128.85, 128.81, 128.71, 128.59, 128.53, 128.48, 128.42, 128.38, 128.35, 128.31, 128.25, 128.16, 127.94, 127.75, 100.68, 100.01, 98.39, 81.32, 80.16, 77.36, 77.01, 76.46, 74.79, 73.77, 73.33, 73.07, 72.23, 71.72, 70.46, 70.41, 69.97, 69.70, 68.36, 67.85, 66.73, 61.67, 55.40. HRMS (ESI) calcd for $C_{89}H_{80}O_{23}Na$ $[M+Na]^+$ 1539.4983, found 1539.4984.

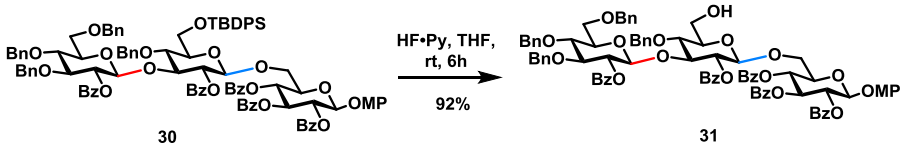
***p*-Methoxyphenyl (3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (30)**



A suspension of glucosyl donor **12**[15] (40 mg, 0.054 mmol), acceptor **13** (34 mg, 0.042 mmol), and activated 3Å MS (200 mg) in dry CH_2Cl_2 (1.2 mL) was stirred at room temperature for 30 min under Ar. Then a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.8 mL, 0.01M) was added, the mixture was stirred at room temperature for 6 h. Then acceptor **11**[14] (25 mg, 0.042 mmol), NIS (14 mg, 0.062 mmol) and TMSOTf (0.1 mL, 22 μL in 1 mL CH_2Cl_2, 0.012 mmol) were added successively at 0 ℃. The reaction mixture was warmed gradually to room temperature and stirred for 3 h, then quenched with Et_3N, filtered with Celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Petroleum ether =1/3) to give **30** (63 mg, 88 %) as a white solid: $[\alpha]_D^{22}$ = +28.07 (c 0.12, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 -7.84 (m, 6H, Ar-H), 7.78 (d, *J* = 7.8 Hz, 4H, Ar-H), 7.68 (d, *J* = 6.9 Hz, 2H, Ar-H), 7.66 – 7.56 (m, 4H, Ar-H), 7.51 – 7.22 (m, 30H, Ar-H), 7.16 (d, *J* = 3.8 Hz, 4H), 7.09 (d, *J* = 6.4 Hz, 3H, Ar-H), 7.02 (d, *J* = 5.7 Hz, 2H, Ar-H), 6.87 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.74 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.78 (t, *J*

= 9.6 Hz, 1H, H-3), 5.58 (t, *J* = 8.7 Hz, 1H, H-2), 5.26 – 5.33 (m, 2H, H-4, H-2''), 5.15 (t, *J* = 8.1 Hz, 1H, H-2'), 5.11 (d, *J* = 10.8 Hz, 1H, H-Bn), 5.00 (d, *J* = 7.8 Hz, 1H, **H-1**), 4.89 (d, *J* = 8.0 Hz, 1H, **H-1''**), 4.76 (d, *J* = 10.8 Hz, 1H, H-Bn), 4.62 – 4.53 (m, 4H, **H-1'**), 4.51 – 4.42 (m, 3H), 4.24 (t, *J* = 8.6 Hz, 1H), 3.92 – 3.73 (m, 6H), 3.74 – 3.65 (m, 5H), 3.64 – 3.53 (m, 3H), 3.38 (d, *J* = 9.2 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.73, 165.44, 165.29, 165.07, 164.54, 155.79, 151.18, 138.64, 138.43, 137.90, 137.65, 135.81, 135.61, 133.55, 133.42, 133.29, 133.23, 133.14, 133.02, 130.00, 129.93, 129.87, 129.82, 129.79, 129.70, 129.64, 129.29, 128.89, 128.73, 128.57, 128.53, 128.49, 128.44, 128.41, 128.36, 128.30, 128.26, 128.22, 128.18, 128.08, 127.95, 127.92, 127.72, 127.67, 127.52, 127.41, 119.27, 114.63, 100.98, 100.61, 100.24, 83.15, 79.56, 78.17, 76.01, 75.75, 75.57, 75.25, 75.06, 74.55, 74.14, 74.00, 73.53, 72.86, 71.85, 69.74, 69.13, 67.26, 62.90, 55.66, 26.84, 19.23. HRMS (ESI) calcd for $C_{33}H_{36}O_8SNa$ $[M+Na]^+$: 615.2023, found: 615.2020. HRMS (ESI) calcd for $C_{104}H_{100}O_{22}SiNa$ $[M+Na]^+$ 1751.6368, found 1751.6360.

***p*-Methoxyphenyl (3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (31)**

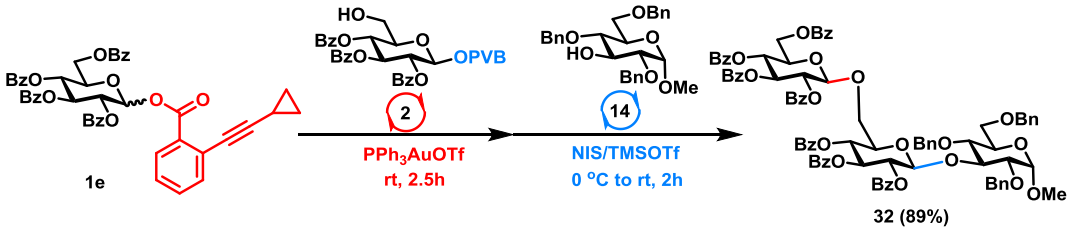


To a solution of compound **30** (121 mg, 0.07 mmol) in 1 mL THF was added 70% HF·pyridine (100 μL, 0.7 mmol) at room temperature. The mixture was stirred vigorously at room temperature for 6 h, then it was quenched with $NaHCO_3$, filtered and concentrated. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford **31** (96 mg, 92%) as a white solid; $[\alpha]_D^{23}$ = +17.91 (c 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.8 Hz, 4H), 7.87 (d, *J* = 7.8 Hz, 4H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.52 – 7.39 (m, 8H), 7.38 – 7.31 (m, 5H), 7.37 – 7.19 (m, 16H), 7.18 – 7.13 (m, 2H), 7.08 (d, *J* = 6.9 Hz, 2H), 7.01 (d, *J* = 6.1 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.77 (t, *J* = 9.6 Hz, 1H, H-3), 5.59 (t, *J* = 8.7 Hz, 1H, H-2), 5.46 (t, *J* = 9.5 Hz, 1H, H-4), 5.24 (t, *J* = 8.7 Hz, 1H, H-2''), 5.03 (d, *J* = 7.8 Hz, 1H, **H-1**), 4.99 (d, *J* = 11.0 Hz, 1H, H-Bn),

4.89 (t, *J* = 8.3 Hz, 1H), 4.79 (d, *J* = 7.9 Hz, 1H, **H-1”**), 4.75 (d, *J* = 11.0 Hz, 1H, H-Bn), 4.60 – 4.44 (m, 7H, **H-1’**), 4.17 (t, *J* = 8.6 Hz, 1H), 3.95 – 3.81 (m, 3H), 3.73 (d, *J* = 10.3 Hz, 3H), 3.69 (s, 3H), 3.62 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.57 – 3.47 (m, 3H), 3.35 – 3.28 (m, 1H), 3.23 (t, *J* = 9.0 Hz, 1H), 2.36 – 2.24 (m, 1H, H-OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.96, 165.72, 165.26, 165.07, 164.32, 155.80, 151.09, 138.35, 138.29, 137.80, 137.63, 133.64, 133.38, 133.30, 133.27, 133.13, 130.00, 129.86, 129.81, 129.72, 129.61, 129.22, 128.86, 128.63, 128.53, 128.50, 128.45, 128.43, 128.41, 128.35, 128.32, 128.30, 128.25, 128.11, 127.97, 127.89, 127.67, 127.57, 127.51, 119.19, 114.59, 100.99, 100.13, 99.79, 82.98, 78.99, 78.11, 75.53, 75.50, 75.22, 75.13, 74.81, 73.95, 73.71, 73.52, 73.43, 72.70, 71.81, 70.49, 69.05, 67.46, 62.09, 55.64. HRMS (ESI) calcd for $C_{88}H_{82}O_{22}Na$ $[M+Na]^+$ 1513.5190, found 1513.5195.

Methyl

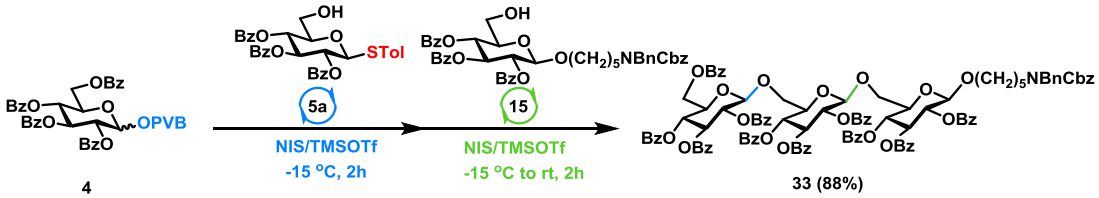
(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (32)



A mixture of ABz galactoside donor **1e**[4] (61.7 mg, 0.081 mmol), glucosyl PVB acceptor **2** (47 mg, 0.067 mmol), and activated 3Å MS (300 mg) in dry CH_2Cl_2 (1.1 mL) was stirred at room temperature for 15 min, to which a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (1.0 mL, 0.014 M) was added to the mixture slowly. The resulting mixture was stirred at room temperature. After being stirred for another 2.5 h, the reaction mixture was cooled to 0 ℃, to which glucosyl acceptor **14**[16] (26.2 mg, 0.057 mmol), NIS (19.1 mg, 0.085 mmol) and TMSOTf (3.0 μL, 0.017 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 2 h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 3.4:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **32** (76 mg, 89%) as a syrup. $[\alpha]_D^{29}$ = +16.65 (*c* 0.15,

$CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 7.6 Hz, 2H, Ar), 8.02 (d, *J* = 7.7 Hz, 2H, Ar), 7.97 (d, *J* = 7.8 Hz, 2H, Ar), 7.92 – 7.79 (m, 8H, Ar), 7.57 – 7.46 (m, 7H, Ar), 7.45 – 7.25 (m, 27H, Ar), 7.09 (dd, *J* = 6.6, 2.8 Hz, 2H, Ar), 5.87 (t, *J* = 9.7 Hz, 1H, H-3''), 5.76 (t, *J* = 9.6 Hz, 1H), 5.64 (dd, *J* = 10.0, 7.9 Hz, 1H, H-2''), 5.60 – 5.49 (m, 3H, **H-1'**, H-4'), 5.43 (t, *J* = 9.8 Hz, 1H, H-4''), 5.37 (d, *J* = 7.9 Hz, 1H, **H-1''**), 5.23 (d, *J* = 11.1 Hz, 1H, H-Bn), 4.77 (d, *J* = 11.1 Hz, 1H, H-Bn), 4.68 (d, *J* = 12.0 Hz, 1H, H-Bn), 4.63 – 4.52 (m, 4H, **H-1**, H-Bn, H-Bn), 4.31 (d, *J* = 10.0 Hz, 1H), 4.24 (d, *J* = 12.4 Hz, 1H, H-Bn), 4.10 (dd, *J* = 12.5, 8.7 Hz, 2H), 4.02 (dd, *J* = 12.4, 2.9 Hz, 1H), 3.97 – 3.84 (m, 5H, H-5''), 3.62 – 3.56 (m, 1H, H-5'), 3.46 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.11 (s, 3H, 3H-OCH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.23, 165.84, 165.81, 165.56, 165.45, 165.27, 164.93, 138.62, 138.26, 138.12, 133.66, 133.35, 133.33, 133.30, 133.13, 133.05, 130.42, 129.96, 129.93, 129.85, 129.79, 129.78, 129.76, 129.33, 129.32, 129.08, 129.04, 128.86, 128.70, 128.67, 128.64, 128.53, 128.48, 128.42, 128.40, 128.38, 128.35, 128.03, 127.94, 127.85, 127.58, 101.21, 100.15, 98.24, 81.05, 79.98, 77.04, 76.39, 76.10, 73.88, 73.80, 73.06, 72.72, 72.44, 71.48, 71.27, 69.99, 69.93, 69.74, 68.80, 66.74, 62.52, 55.25. HRMS (ESI) calcd for $C_{89}H_{80}O_{23}Na$ $[M+Na]^+$ 1539.4983, found 1539.4979.

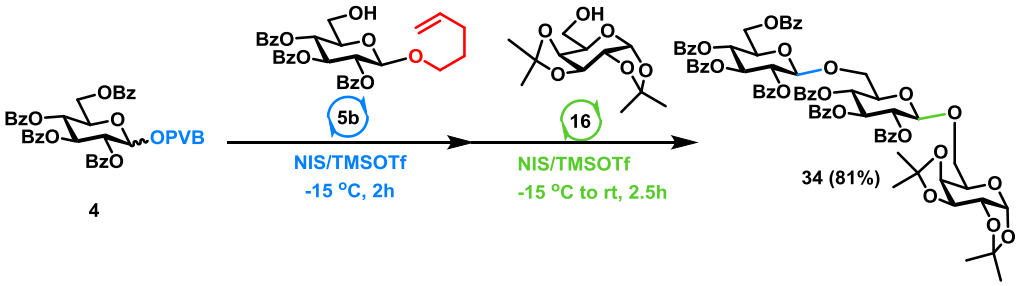
_N_-benzyl-benzyloxycarbonyl-5-aminopentyl (2,3,4,6-tetra-_O_-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-_O_-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-_O_-benzoyl-β-D-glucopyranoside (33)



A mixture of PVB galactoside donor **4**[7] (50.6 mg, 0.063 mmol), thioglycoside acceptor **5a**[8] (37.7 mg, 0.063 mmol), and activated 3Å MS (300 mg) in dry CH_2Cl_2 (1.1 mL) was stirred at room temperature for 15 min and was then cooled to -15 ℃. NIS (14.2 mg, 0.063 mmol) and TMSOTf (3.4 μL, 0.019 mmol) were added successively. After being stirred at -15 ℃ for another 2 h, to which glucosyl acceptor **15**[9] (42.4 mg, 0.053 mmol) and NIS (17.9 mg, 0.079 mmol) and TMSOTf (3.0 μL, 0.016 mmol) were added successively at -15 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 2 h, then was quenched with Et_3N (0.8mL)

and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.5:1) to afford **33** (86.3 mg, 88%) as a syrup. $[\alpha]_D^{29}$ = -12.69 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.8 Hz, 4H, Ar), 8.02 (d, *J* = 7.8 Hz, 2H), 8.00 – 7.91 (m, 8H, Ar), 7.91 – 7.83 (m, 4H, Ar), 7.80 (d, *J* = 7.8 Hz, 2H, Ar), 7.61 – 7.25 (m, 35H, Ar), 7.24 – 7.14 (m, 5H, Ar), 6.20 (t, *J* = 9.8 Hz, 1H), 5.94 (t, *J* = 9.6 Hz, 1H), 5.81 – 5.69 (m, 2H), 5.65 – 5.53 (m, 3H), 5.32 (t, *J* = 8.8 Hz, 1H), 5.27 – 5.14 (m, 4H, **H-1"**), 4.78 – 4.62 (m, 3H, **H-1'**, **H-1**), 4.54 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.49 – 4.33 (m, 3H), 4.16 (d, *J* = 10.9 Hz, 1H), 4.05 (d, *J* = 10.9 Hz, 1H), 4.02 – 3.89 (m, 3H), 3.82 – 3.69 (m, 2H, H-Linker), 3.32 – 3.16 (m, 1H, H-Linker), 3.11 – 2.90 (m, 2H, 2H-Linker), 1.48 – 1.32 (m, 4H, 4H-Linker), 1.18 – 1.02 (m, 2H, 2H-Linker); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 165.80, 165.78, 165.64, 165.58, 165.31, 165.00, 164.95, 156.66, 156.01, 138.02, 136.90, 133.51, 133.32, 133.20, 133.12, 130.03, 129.97, 129.84, 129.81, 129.78, 129.69, 129.64, 129.47, 129.38, 129.35, 129.04, 128.96, 128.90, 128.84, 128.82, 128.70, 128.65, 128.55, 128.47, 128.37, 128.33, 128.28, 128.21, 128.03, 127.86, 127.76, 127.32, 127.29, 127.26, 127.13, 101.37, 101.07, 100.93, 77.36, 74.43, 73.56, 72.92, 72.73, 72.28, 72.15, 71.93, 71.89, 70.84, 69.66, 69.63, 68.92, 68.27, 67.12, 63.27, 50.59, 50.27, 47.16, 46.19, 29.73, 28.95, 27.79, 27.40, 23.11. HRMS (ESI) calcd for $C_{108}H_{95}NO_{28}Na$ $[M+Na]^+$ 1876.5933, found 1876.5933.

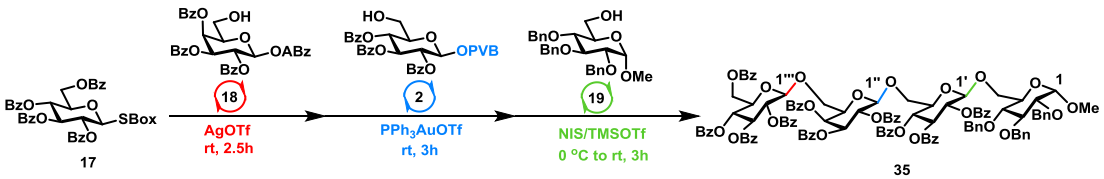
(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-1,2:3,4-*O*-diisopropylidene-α-D-galactopyranose (34)



A mixture of PVB galactoside donor **4**[7] (78.8 mg, 0.098 mmol), glucosyl acceptor **5b**[9] (50 mg, 0.089 mmol), and activated 3Å MS (300 mg) in dry CH_2Cl_2 (1.6 mL) was stirred at room temperature for 15 min and was then cooled to -15 ℃. NIS (20.1 mg, 0.089 mmol) and TMSOTf (4.8 μL, 0.027 mmol) were added successively. After being stirred at -15 ℃ for another 2h, to which acceptor **16** (19.5 mg, 0.075 mmol), NIS (25.3 mg, 0.113 mmol) and TMSOTf (4.1 μL,

0.022 mmol) were added successively at -15 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 2.5 h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.7:1 to 2.5:1) to afford **34** (79.6 mg, 81%) as a syrup. $[\alpha]_D^{29}$ = -18.29 (*c* 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.02 (m, 4H, Ar), 7.96 (d, *J* = 7.8 Hz, 2H, Ar), 7.91 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 – 7.83 (m, 4H, Ar), 7.80 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.55 – 7.47 (m, 5H, Ar), 7.47 – 7.33 (m, 12H, Ar), 7.32 – 7.26 (m, 3H, Ar), 5.90 (t, *J* = 9.6 Hz, 1H, H-3''), 5.82 (t, *J* = 9.5 Hz, 1H, H-3'), 5.63 (t, *J* = 9.6 Hz, 1H, H-4''), 5.54 (t, *J* = 8.8 Hz, 1H, H-2''), 5.48 – 5.35 (m, 3H, **H-1**, H-2', H-4'), 5.05 (d, *J* = 7.8 Hz, 1H, **H-1''**), 4.84 (d, *J* = 7.8 Hz, 1H, **H-1'**), 4.62 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.54 – 4.44 (m, 2H, H-3), 4.25 (dd, *J* = 5.0, 2.3 Hz, 1H, H-2), 4.20 – 4.13 (m, 2H, H-5''), 4.12 – 4.01 (m, 2H, H-5'), 4.00 – 3.92 (m, 2H), 3.88 (t, *J* = 6.0 Hz, 1H), 3.73 (dd, *J* = 10.9, 6.5 Hz, 1H), 1.48 (s, 3H, 3H-CH_3), 1.33 (s, 3H, 3H-CH_3), 1.23 (s, 6H, 3H-CH_3, 3H-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.18, 165.75, 165.36, 165.24, 165.21, 165.13, 133.49, 133.26, 133.23, 133.20, 133.07, 130.04, 129.92, 129.90, 129.87, 129.81, 129.65, 129.49, 129.34, 128.99, 128.92, 128.90, 128.87, 128.52, 128.49, 128.46, 128.36, 128.31, 128.26, 109.36, 108.45, 101.34, 101.22, 96.23, 74.07, 73.00, 72.97, 72.34, 71.87, 71.76, 70.93, 70.62, 70.57, 69.98, 69.74, 68.52, 68.19, 67.27, 63.14, 26.11, 25.84, 24.96, 24.33. HRMS (ESI) calcd for $C_{73}H_{68}O_{23}Na$ $[M+Na]^+$ 1335.4044, found 1335.4034.

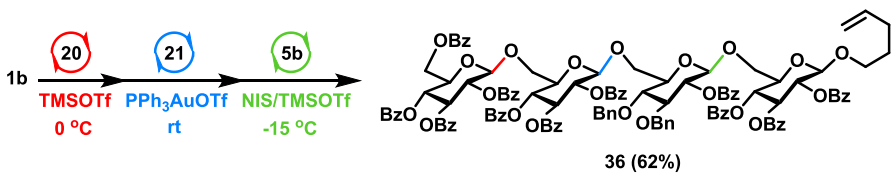
Methyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-galacopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (35)



A suspension of SBox glucoside donor **17**[5] (167.1mg, 0.23mmol), galactosyl ABz **18**[9] (125.4 mg, 0.19 mmol), and activated 3Å MS (700 mg) in dry CH_2Cl_2 (3mL) was stirred at room temperature for 15 min, to which AgOTf (97.6 mg, 0.38 mmol) was added to the mixture. After

being stirred at room temperature for 2.5h, glucosyl PVB **2** (119.5 mg, 0.171 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (1 mL, 0.038 M) were added successively. The resulting mixture was stirred at room temperature for another 3h, the reaction mixture was cooled to 0 ℃, then acceptor **19**[17] (71 mg, 0.154 mmol), NIS (42.7mg, 0.19 mmol) and TMSOTf (8.7 μL, 0.048 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 3 h, then was quenched with Et_3N (3.0mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.6:1 to 1.5:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **35**[9] (199.3 mg, 65%) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.85 (m, 16H, Ar), 7.81 – 7.71 (m, 4H, Ar), 7.58 – 7.47 (m, 5H, Ar), 7.46 – 7.15 (m, 38H, Ar), 7.02 (d, *J* = 7.1 Hz, 2H, Ar), 6.03 (t, *J* = 9.7 Hz, 1H, H-3’’’), 5.90 – 5.77 (m, 2H, H-3’, H-4”), 5.74 – 5.64 (m, 2H, H-2”, H-4’’’), 5.59 – 5.36 (m, 4H, H-2’, H-4’, H-3”, H-2’’’), 5.00 (d, *J* = 7.9 Hz, 1H, **H-1’’’**), 4.91 (d, *J* = 10.9 Hz, 1H, H-Bn), 4.80 – 4.72 (m, 2H, **H-1”**, H-Bn), 4.68 (d, *J* = 11.0 Hz, 1H, H-Bn), 4.64 – 4.55 (m, 2H, **H-1**, H-Bn), 4.54 – 4.46 (m, 2H, **H-1’**), 4.42 (d, *J* = 11.3 Hz, 1H, H-Bn), 4.30 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.22 (d, *J* = 11.4 Hz, 1H, H-Bn), 4.16 (d, *J* = 9.8 Hz, 1H), 4.10 – 3.99 (m, 3H), 3.96 – 3.77 (m, 5H), 3.47 (d, *J* = 10.1 Hz, 1H), 3.43 – 3.21 (m, 6H, H-2, 3H-OCH_3).

Pent-4-enyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzyl-2-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (36)



36 (62%)

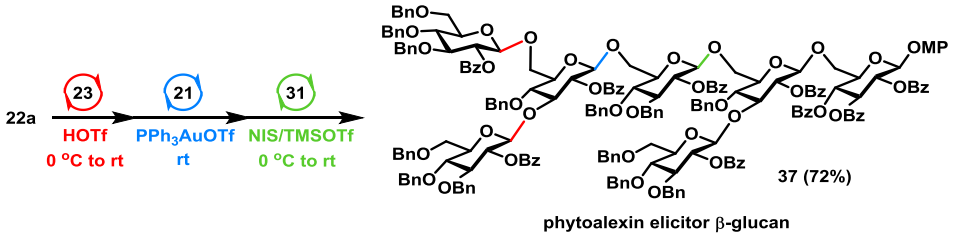
A suspension of glucosyl donor **1b**[3] (61 mg, 0.080 mmol), acceptor **20**[9] (45 mg, 0.067 mmol), and activated 3Å MS (180 mg) in dry CH_2Cl_2 (1.7 mL) was stirred at room temperature for 30 min under Ar. Then the mixture was cooled to 0 ℃ and a solution of TMSOTf in CH_2Cl_2 (0.1 mL, 24μL in 1 mL CH_2Cl_2, 0.0135 mmol) was added to the mixture dropwise. After being stirred at

0 ℃ for another 1.0 h, the reaction mixture was warmed to room temperature, to which glucosyl PVB acceptor **21** (43.0 mg, 0.061 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.7 mL, 0.02 M, 0.014 mmol) were added successively. The resulting mixture was stirred at room temperature for another 2.0 h, then acceptor **5b**[9] (42 mg, 0.073 mmol), NIS (17 mg, 0.073 mmol) and TMSOTf (0.1 mL, 22 μL in 1 mL CH_2Cl_2, 0.012 mmol) were added successively at -15 ℃. The reaction mixture was stirred at -15 ℃ for 3 h, then quenched with Et_3N, filtered with Celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Petroleum ether =1/2.5) to give **36** (77 mg, 62 %) as a white solid: $[\alpha]_D^{23}$ = -2.05 (c 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 -7.07 (m, 18H), 7.60 (t, *J* = 7.8 Hz, 4H), 7.57 – 7.48 (m, 4H), 7.46 – 7.29 (m, 17H), 7.28 – 6.99 (m, 16H), 6.97 – 6.87 (m, 4H), 6.78 (t, *J* = 7.7 Hz, 2H), 6.18 (t, *J* = 9.7 Hz, 1H, H-3'''), 5.88 (q, *J* = 10.0 Hz, 2H), 5.75 – 5.59 (m, 4H), 5.50 (q, *J* = 9.3 Hz, 2H), 5.38 (t, *J* = 9.6 Hz, 1H), 5.18 (t, *J* = 8.6 Hz, 1H, H-2'), 5.02 (d, *J* = 7.8 Hz, 1H, **H-1'''**), 4.83 (d, *J* = 10.3 Hz, 1H), 4.78 (d, *J* = 17.1 Hz, 1H), 4.74 – 4.60 (m, 4H, **H-1'**, **H-1''**, **H-1**), 4.54 (d, *J* = 11.2 Hz, 2H), 4.42 (d, *J* = 5.6 Hz, 1H), 4.33 (s, 1H), 4.28 (dd, *J* = 7.7, 4.0 Hz, 1H), 4.24 (d, *J* = 11.1 Hz, 1H), 4.10 – 3.95 (m, 5H), 3.87 (dd, *J* = 11.9, 8.8 Hz, 1H), 3.79 (dt, *J* = 10.7, 5.6 Hz, 1H), 3.73 (d, *J* = 10.8 Hz, 1H), 3.62 (t, *J* = 9.1 Hz, 1H), 3.52 (t, *J* = 9.3 Hz, 1H), 3.40 – 3.28 (m, 2H), 2.87 – 2.78 (m, 1H), 1.98 – 1.81 (m, 2H), 1.59 – 1.40 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.27, 166.00, 165.91, 165.90, 165.86, 165.47, 165.32, 165.27, 165.22, 165.16, 164.97, 138.08, 138.06, 137.92, 133.71, 133.57, 133.50, 133.37, 133.34, 133.32, 133.30, 133.19, 133.07, 130.30, 130.16, 130.14, 130.08, 130.03, 129.98, 129.95, 129.92, 129.89, 129.87, 129.73, 129.71, 129.69, 129.67, 129.65, 129.29, 129.04, 128.97, 128.93, 128.86, 128.78, 128.71, 128.68, 128.61, 128.59, 128.56, 128.53, 128.46, 128.45, 128.43, 128.40, 128.31, 128.22, 128.01, 127.99, 127.77, 127.75, 127.65, 115.13, 101.99, 101.32, 101.27, 100.77, 83.14, 75.40, 74.96, 74.66, 74.13, 74.02, 73.93, 73.03, 72.96, 72.90, 72.75, 72.34, 72.19, 72.00, 70.59, 69.90, 69.76, 69.64, 69.30, 67.89, 67.63, 63.30, 30.02, 29.90, 28.74. HRMS (ESI) calcd for $C_{120}H_{106}O_{32}Na_2$ $[M+2Na]^{2+}$ 1052.3226, found 1052.3223.

***p*-Methoxyphenyl**

[2-O-benzoyl-4-O-benzyl-(3,6-di-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-β-

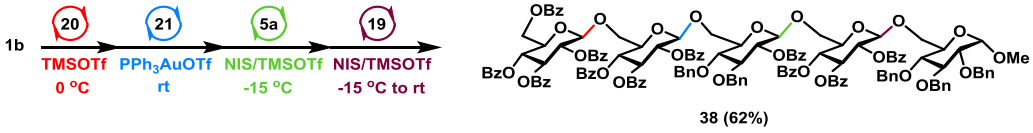
D-glucopyranosyl]-(1→6)-(2-O-benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-[2-O-benzoyl-4-O-benzyl-(3-*O*-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]- (1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (37)



A suspension of glucosyl donor **22a**[18] (60 mg, 0.083 mmol), acceptor **23** (18 mg, 0.033 mmol), and activated 3Å MS (200 mg) in dry CH_2Cl_2 (1.5 mL) was stirred at room temperature for 30 min under Ar. Then the mixture was cooled to 0 ℃ and a solution of TfOH in CH_2Cl_2 (0.1 mL, 6 μL in 1 mL CH_2Cl_2, 0.007 mmol) was added to the mixture dropwise. After being stirred at 0 ℃ for another 1h, the reaction mixture was warmed to room temperature, to which glucosyl PVB acceptor **21** (21.0 mg, 0.03 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.7 mL, 0.01 M, 0.007 mmol) were added successively. The resulting mixture was stirred at room temperature for another 2.5 h, then acceptor **31** (44 mg, 0.03 mmol), NIS (11 mg, 0.045 mmol) and TMSOTf (0.1 mL, 11 μL in 1 mL CH_2Cl_2, 0.006 mmol) were added successively at 0 ℃. The reaction mixture was warmed gradually to room temperature and stirred for 3 h, then quenched with Et_3N, filtered with Celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Petroleum ether =1/2) to give **37** (72 mg, 72 %) as a white solid: $[\alpha]_D^{23}$ = +21.13 (c 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.63 (m, 18H), 7.55 – 7.40 (m, 4H), 7.38 – 6.89 (m, 88H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 5.62 (t, *J* = 9.6 Hz, 1H), 5.47 (t, *J* = 8.8 Hz, 1H), 5.22 – 5.09 (m, 4H), 5.04 – 4.96 (m, 2H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.80 – 4.61 (m, 8H), 4.61 – 4.24 (m, 22H), 4.20 – 4.01 (m, 7H), 3.89 (t, *J* = 7.9 Hz, 1H), 3.77 – 3.51 (m, 16H), 3.51 – 3.28 (m, 12H), 3.28 – 3.05 (m, 5H), 2.96 (t, *J* = 8.3 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 164.66, 164.40, 164.21, 164.07, 163.99, 163.34, 162.90, 154.67, 149.86, 137.43, 137.30, 137.29, 137.16, 137.15, 137.11, 137.08, 136.80, 136.75, 136.57, 136.55, 132.37, 132.20, 132.16, 132.09, 132.00, 131.98, 131.95, 128.97, 128.95, 128.90, 128.88, 128.79, 128.77, 128.74, 128.71, 128.70, 128.66, 128.58, 128.53, 128.24, 127.82, 127.77, 127.63, 127.60, 127.57, 127.50, 127.46, 127.43, 127.39, 127.36, 127.31, 127.29, 127.24, 127.20, 127.16, 127.14,

127.11, 127.06, 127.03, 127.00, 126.97, 126.89, 126.86, 126.81, 126.76, 126.73, 126.67, 126.64, 126.61, 126.57, 126.54, 126.52, 126.49, 126.43, 126.40, 126.37, 126.35, 126.30, 118.09, 113.46, 100.22, 99.87, 99.62, 99.50, 99.10, 98.86, 98.50, 81.99, 81.94, 81.67, 81.51, 78.08, 77.98, 77.13, 77.04, 76.90, 76.21, 76.16, 76.00, 75.79, 74.91, 74.48, 74.43, 74.18, 74.16, 74.07, 74.02, 73.98, 73.93, 73.84, 73.65, 73.47, 73.17, 73.11, 73.01, 72.80, 72.78, 72.61, 72.56, 72.47, 72.42, 72.40, 71.62, 70.80, 68.70, 67.98, 67.94, 67.62, 67.58, 66.12, 65.96, 65.53, 54.52. HRMS (ESI) calcd for $C_{203}H_{192}O_{46}Na_2$ $[M+2Na]^{2+}$ 1705.6235, found 1705.6233.

Methyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (38)

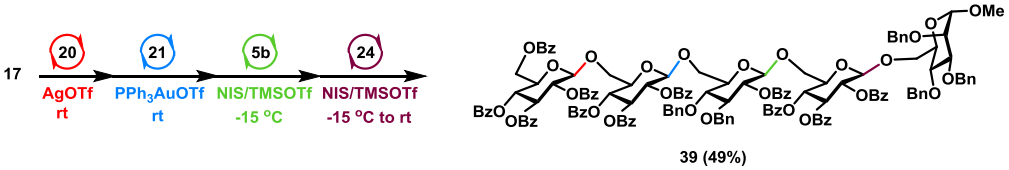


A suspension of glucosyl donor **1b**[9] (54 mg, 0.071 mmol), glucosyl ABz acceptor **20**[9] (40 mg, 0.060 mmol), and activated 3Å MS (160 mg) in dry CH_2Cl_2 (1.6 mL) was stirred at room temperature for 30 min under Ar. Then the mixture was cooled to 0 ℃ and a solution of TMSOTf in CH_2Cl_2 (0.1 mL, 21μL in 1 mL CH_2Cl_2, 0.012 mmol) was added to the mixture dropwise. After being stirred at 0 ℃ for another 1.0 h, the reaction mixture was warmed to room temperature, to which glucosyl PVB acceptor **21** (38 mg, 0.054 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (1 mL, 0.012M) were added successively. The resulting mixture was stirred at room temperature for another 2.0 h. Then it was cooled to - 15 ℃, and acceptor **5a**[8] (32 mg, 0.054 mmol), NIS (13 mg, 0.057 mmol), TMSOTf (0.1 mL, 20 μL in 1 mL CH_2Cl_2, 0.0114 mmol) were added successively. The above mixture was kept stirring for 3 h at - 15 ℃, then acceptor **19**[17] (23 mg, 0.049 mmol), NIS (17 mg, 0.077 mmol), TMSOTf (0.1 mL, 10 μL in 1 mL CH_2Cl_2, 0.005 mmol) were added successively. The resulting mixture was warmed gradually to room temperature and stirred for 2 h, then quenched with Et_3N, filtered with Celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Petroleum ether =1/2) to give **38** (73 mg, 62 %) as a white solid: $[\alpha]_D^{23}$ = -2.54 (c 0.18,

$CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.80 (m, 10H), 7.79 – 7.67 (m, 8H), 7.57 – 7.49 (m, 1H), 7.41 – 6.96 (m, 48 H), 6.93 – 6.80 (m, 7H), 6.69 (t, *J* = 7.7 Hz, 2H), 6.08 (t, *J* = 9.7 Hz, 1H), 5.78 (q, *J* = 9.4 Hz, 2H), 5.66 – 5.44 (m, 3H, **H-1**), 5.44 (dt, *J* = 12.4, 8.8 Hz, 2H), 5.30 (t, *J* = 9.7 Hz, 1H), 5.08 (t, *J* = 8.5 Hz, 1H), 4.94 (d, *J* = 7.8 Hz, 1H, **H-1””**), 4.80 (d, *J* = 11.0 Hz, 1H), 4.67 – 4.55 (m, 5H, **H-1’**, **H-1’”**), 4.54 – 4.37 (m, 7H, **H-1”**), 4.35 – 4.07 (m, 7H), 4.06 – 3.72 (m, 9H), 3.65 (d, *J* = 10.7 Hz, 1H), 3.56 – 3.34 (m, 5H), 3.34 – 3.23 (m, 3H), 3.16 (s, 3H), 2.74 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.22, 165.90, 165.89, 165.85, 165.83, 165.45, 165.33, 165.18, 165.16, 164.96, 139.05, 138.49, 138.33, 138.13, 137.96, 133.70, 133.54, 133.51, 133.35, 133.32, 133.30, 133.28, 133.17, 133.11, 133.07, 130.12, 130.02, 129.98, 129.90, 129.88, 129.84, 129.82, 129.73, 129.69, 129.67, 129.60, 128.99, 128.93, 128.89, 128.74, 128.63, 128.59, 128.56, 128.52, 128.48, 128.46, 128.41, 128.38, 128.36, 128.30, 128.24, 128.20, 128.03, 127.99, 127.90, 127.82, 127.73, 127.68, 127.66, 127.63, 127.62, 127.54, 127.44, 101.89, 101.39, 101.16, 100.73, 98.36, 83.15, 82.02, 80.02, 75.54, 75.48, 74.75, 74.64, 74.53, 74.12, 73.99, 73.96, 73.60, 72.99, 72.90, 72.86, 72.66, 72.29, 72.05, 71.94, 70.34, 69.85, 69.73, 69.60, 68.20, 67.59, 67.47, 63.24, 55.39. HRMS (ESI) calcd for $C_{143}H_{128}O_{37}Na_2$ $[M+2Na]^{2+}$ 1241.3959, found 1241.3952.

Methyl

(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)- (1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (39)



39 (49%)

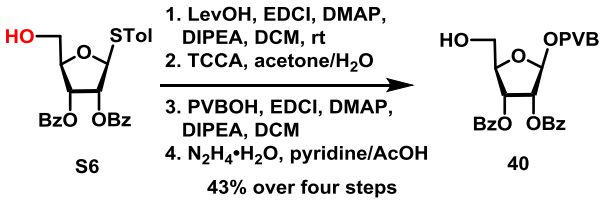
A suspension of glucosyl donor **17**[5] (60 mg, 0.082 mmol), glucosyl ABz acceptor **20**[9] (46 mg, 0.070 mmol), and activated 3Å MS (200 mg) in dry CH_2Cl_2 (2.0 mL) was stirred at room temperature for 30 min under Ar. Then AgOTf (36 mg, 0.14 mmol) was added at room temperature, after being stirred for 2.0 h, glucosyl PVB acceptor **21** (44 mg, 0.063 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.7 mL, 0.02 M) were added. The resulting

mixture was stirred at room temperature for another 3.0 h. Then it was cooled to - 15 ℃, and acceptor **5b**[8] (43 mg, 0.076 mmol), NIS (17 mg, 0.075 mmol), TMSOTf (0.1 mL, 34 μL in 1 mL CH_2Cl_2, 0.019 mmol) were added successively. The above mixture was kept stirring for 3 h at - 15 ℃, then acceptor **24**[19] (26 mg, 0.057mmol), NIS (20 mg, 0.088 mmol), TMSOTf (0.1 mL, 11 μL in 1 mL CH_2Cl_2, 0.006 mmol) were added successively. The resulting mixture was warmed gradually to room temperature and stirred for 2 h, then quenched with Et_3N, filtered with Celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Petroleum ether =1/2) and Sephadex LH-20 ($CHCl_2$/MeOH = 1/1) to give **39** (68 mg, 49 %) as a white solid: $[\alpha]_D^{23}$ = -9.10 (c 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.82 (m, 10H), 7.80 – 7.67 (m, 8H), 7.51 – 7.42 (m, 5H), 7.41 – 6.95 (m, 50H), 6.93 – 6.85 (m, 2H), 6.83 – 6.71 (m, 3H), 6.60 (t, *J* = 7.7 Hz, 2H), 6.15 (t, *J* = 9.6 Hz, 1H), 5.80 (t, *J* = 9.9 Hz, 2H), 5.74 – 5.64 (m, 2H, **H-1)**, 5.58 (t, *J* = 9.6 Hz, 1H), 5.50 – 5.39 (m, 2H), 5.32 (t, *J* = 9.7 Hz, 1H), 5.09 (t, *J* = 8.5 Hz, 1H), 4.97 (d, *J* = 7.7 Hz, 1H, **H-1''''**), 4.70 – 4.61 (m, 3H, **H-1'**, **H-1''**, **H-1''')**, 4.60 – 4.52 (m, 3H), 4.52 – 4.43 (m, 4H), 4.41 – 4.36 (m, 1H), 4.35 – 4.19 (m, 5H), 4.10 (d, *J* = 11.0 Hz, 1H), 4.02 (d, *J* = 11.6 Hz, 2H), 3.96 – 3.85 (m, 3H), 3.84 – 3.68 (m, 4H), 3.7 – 3.56 (m, 5H), 3.49 (t, *J* = 9.0 Hz, 1H), 3.41 (t, *J* = 9.2 Hz, 1H), 3.29 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.84 (s, 3H), 2.65 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.25, 165.94, 165.90, 165.85, 165.45, 165.43, 165.25, 165.17, 164.97, 164.89, 138.59, 138.53, 138.17, 138.02, 133.76, 133.67, 133.54, 133.32, 133.29, 133.26, 133.21, 132.97, 132.93, 130.22, 130.09, 130.02, 130.01, 129.92, 129.88, 129.83, 129.75, 129.74, 129.71, 129.64, 129.60, 129.56, 129.19, 129.01, 128.96, 128.92, 128.88, 128.75, 128.71, 128.63, 128.59, 128.57, 128.54, 128.52, 128.50, 128.48, 128.43, 128.42, 128.29, 128.27, 128.11, 127.91, 127.88, 127.78, 127.72, 127.70, 127.68, 127.64, 127.63, 127.60, 102.09, 101.98, 101.11, 100.61, 98.91, 83.13, 80.48, 75.69, 75.01, 74.97, 74.77, 74.76, 74.57, 74.03, 74.00, 73.95, 73.02, 72.93, 72.88, 72.84, 72.28, 72.07, 72.03, 71.94, 71.36, 70.51, 70.22, 69.85, 69.68, 69.59, 67.49, 67.24, 63.28, 54.53. HRMS (ESI) calcd for $C_{143}H_{128}O_{37}Na_2$ $[M+2Na]^{2+}$ 1241.3959, found 1241.3952.

2.4 One-Pot synthesis of nucleosides based on glycosyl PVB.

2.4.1 Preparation of new glycosyl donors and acceptors

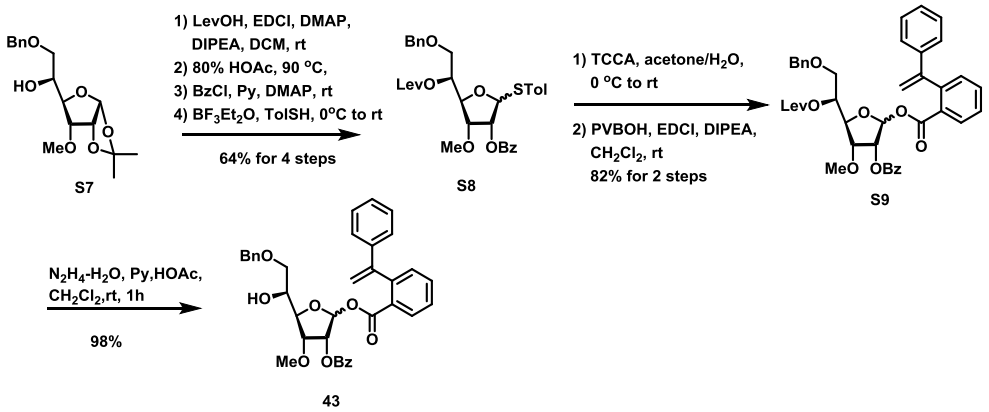
2,3-Di-*O*-benzoyl-β-D-ribofuranoyl 2-(1-phenylvinyl) benzoate (40)



The known compound **S6**[20] (1.45 g, 3.13mmol), EDCI (1.08 g, 5.63 mmol) and DMAP (382 mg, 3.13 mmol) were dissolved in 16 mL CH_2Cl_2. Then levulinic acid (0.48 ml, 4.7 mmol) and DIPEA (1.55 mL, 9.38 mmol) were added successively at room temperature under Ar. The resulting mixture was stirred for 6 h at this temperature and concentrated *in vacuo* to produce the crude oil. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/4) afforded a white solid (1.76 g, 85%). The above solid (1.49 g, 2.66 mmol) was dissolved with acetone/H_2O (53 mL/ 13 mL), and trichloroisocyanuric acid (618 mg, 2.66 mmol) was added at 0 ℃. The mixture was stirred for 4 h at 0 ℃ and quenched with saturated aqueous $NaHCO_3$, then it was diluted with EtOAc, washed with H_2O and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford the hemiacetal as a white foam (1.21 g, 81%). The hemiacetal (984 mg, 2.15 mmol), EDCI (744 mg, 3.88 mmol) and DMAP (263 mg, 2.15 mmol) were dissolved in 10 mL CH_2Cl_2. Then 2-(1-Phenylvinyl) benzoic acid (531 mg, 2.37 mmol) and DIPEA (1.1 mL, 6.47 mmol) were added successively at room temperature under Ar. The resulting mixture was stirred for 5 h at this temperature and concentrated *in vacuo* to produce the crude oil. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford glycosyl PVB as a white solid (1.43 g, 96%). To a solution of this intermediate (1.38 g, 2.08 mmol) in 6 mL pyridine and 4 mL AcOH was added hydrazine hydrate (0.21 mL, 4.16 mmol) at room temperature. The mixture was stirred at room temperature for 8 h. Then it was quenched with acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/3) to afford **40** (1.17 g, 91%) as a white foam; $[\alpha]_D^{20}$ = +15.14 (c 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.49 (dd, *J* = 15.7, 7.7

Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.26 (m, 5H), 7.26 – 7.20 (m, 2H), 6.28 (s, 1H, **H-1**), 5.87 (s, 1H, CH_2-PVB), 5.56 – 5.51 (m, 1H, H-3), 5.47 (d, *J* = 4.8 Hz, 1H, H-2), 5.28 (s, 1H, CH_2-PVB), 4.40 (dt, *J* = 7.1, 3.9 Hz, 1H, H-4), 3.77 (dd, *J* = 12.4, 3.3 Hz, 1H, H-5a), 3.60 (dd, *J* = 12.4, 4.5 Hz, 1H, H-5b), 2.01 (s, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.74, 165.51, 164.86, 148.98, 143.03, 140.03, 133.58, 133.50, 132.52, 131.53, 130.54, 129.83, 129.75, 129.58, 128.99, 128.84, 128.53, 128.45, 128.41, 127.93, 127.86, 126.61, 114.29, 99.05, 83.19, 75.19, 71.00, 62.41. HRMS (ESI) calcd for $C_{34}H_{28}O_8Na$ $[M+Na]^+$: 587.1676, found: 587.1673.

6-O-benzyl-3-O-methyl-2-O-benzoyl-L-talofuranoyl 2-(1-phenylvinyl) benzoate (43)



The known compound **S7**[21] (2.3 g, 5.8 mmol) was dissolved in 20 mL dry CH_2Cl_2, then DMAP (354 mg, 2.9 mmol), EDCI (2 g, 10.44 mmol) , DIPEA (2.8 mL, 17.4 mmol) and levulinic acid (0.89 mL, 8.7 mmol) were added successively at room temperature under Ar. The mixture was stirred at room temperature overnight. Then it was quenched with H_2O, extracted with CH_2Cl_2, and washed with brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/1.5) afforded a light yellow solid (2.25 g, 92%). The above solid (2.25 g, 5.33 mmol) was dissolved in 32 mL AcOH and 8 mL H_2O, this solution was stirred at 90 ℃ for 6 h, then the mixture was concentrated *in vacuo* to give the crude light yellow oil. To a solution of the crude in 20 mL pyridine was added 4-dimethylamino-pyridine (195 mg, 1.59 mmol) and benzoyl chloride (1.55 mL, 13.25 mmol) at 0 ℃ under Ar. The mixture was stirred at room temperature overnight and diluted with CH_2Cl_2, washed with 1 N HCl and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) afforded a light yellow oil (2.7 g, 86%). To a

solution of the above yellow oil (2.7 g, 4.57 mmol) and *p*-toluenethiol (680 mg, 5.48 mmol) was slowly added BF_3Et_2O (0.846 mL, 6.85 mmol) at 0 ℃ under Ar. The mixture was stirred at room temperature for 2 h, then it was quenched with saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, and washed with brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2.7) afforded **S8** as a light yellow oil (2.19 g, 81%, α/β = 1/2).

The β-anomer: R_f = 0.45 (EtOAc/Petroleum ether =1/2.5), the α-anomer: R_f = 0.41 (EtOAc/Petroleum ether =1/2.5). Data for the β-anomer: $[\alpha]_D^{20}$ = -89.46 (c 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.41 (m, 4H), 7.38 – 7.28 (m, 5H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.55 – 5.48 (m, 1H, H-2), 5.43 (d, *J* = 2.7 Hz, 1H, **H-1**), 5.33 (dd, *J* = 6.1, 3.0 Hz, 1H, H-5), 4.56 (dd, *J* = 12.0, 2.9 Hz, 2H, CH_2-Bn), 4.27 (dd, *J* = 7.2, 3.0 Hz, 1H, H-4), 3.99 (dd, *J* = 7.2, 4.6 Hz, 1H, H-3), 3.69 (d, *J* = 6.2 Hz, 2H, H-6a and H-6b), 3.34 (s, 3H, OMe), 2.86 – 2.78 (m, 2H, CH_2-Lev), 2.71 – 2.56 (m, 2H, CH_2-Lev), 2.33 (s, 3H, CH_3-Lev), 2.18 (s, 3H, CH_3-STol). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.41, 172.31, 165.43, 138.40, 137.95, 133.78, 133.38, 129.89, 129.81, 129.42, 128.64, 128.46, 128.39, 127.69, 127.67, 89.13, 80.57, 79.39, 73.15, 70.71, 68.57, 59.06, 38.03, 29.85, 28.20, 21.18. HRMS (ESI) calcd for $C_{33}H_{36}O_8SNa$ $[M+Na]^+$: 615.2023, found: 615.2020.

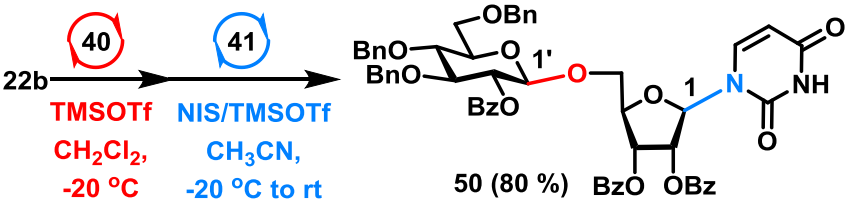
To a solution of compound **S8** (816 mg, 1.37 mmol) in acetone (30 mL) and H_2O (7.5 mL) was added trichloroisocyanuric acid (317 mg, 1.37 mmol) at 0 ℃. The mixture was kept stirring at 0 ℃ for 3 h, then it was quenched with saturated aqueous $NaHCO_3$, extracted with EtOAc, and washed with H_2O. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) afforded a colorless syrup (582 mg, 87%). The above syrup (582 mg, 1.20 mmol) was dissolved in 12 mL CH_2Cl_2, then DMAP (143 mg, 1.20 mmol), EDCI (412 mg, 2.15 mmol), DIPEA(0.59 mL, 3.60 mmol) and 2-(1-Phenylvinyl) benzoic acid (323 mg, 1.32 mmol) were successively added at room temperature under Ar. The mixture was stirred at room temperature for 1 h. Then it was quenched with H_2O, extracted with CH_2Cl_2, and washed with brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/1.8) afforded **S9** (775 mg, 94%, α/β = 1/2) as a white

solid. The β-anomer: R_f = 0.35 (EtOAc/Petroleum ether =1/2), the α-anomer: R_f = 0.31 (EtOAc/Petroleum ether =1/2). Data for the β-anomer: $[\alpha]_D^{20}$ = -6.24 (c 0.23, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.49 – 7.38 (m, 3H), 7.37 – 7.17 (m, 11H), 6.10 (s, 1H, CH_2-PVB), 5.82 (s, 1H, CH_2-PVB), 5.23 (d, *J* = 4.4 Hz, 1H, H-2), 5.23 (s, 1H, **H-1**), 5.17 (q, *J* = 5.2 Hz, 1H, H-5), 4.52 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.48 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.20 (dd, *J* = 8.3, 4.7 Hz, 1H, H-4), 3.67 (dd, *J* = 8.3, 4.4 Hz, 1H, H-3), 3.58 – 3.48 (m, 2H, H-6), 3.17 (s, 3H, OMe), 2.74 – 2.56 (m, 2H, CH_2-Lev), 2.41 – 2.37 (m, 2H, CH_2-Lev), 2.14 (s, 3H, CH_3-Lev). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.24, 172.18, 165.72, 165.07, 148.74, 142.75, 140.09, 137.89, 133.42, 131.98, 131.08, 130.48, 130.30, 129.90, 129.25, 128.47, 128.42, 128.37, 127.91, 127.71, 127.68, 127.60, 126.78, 114.45, 98.66, 80.26, 79.05, 73.21, 73.04, 71.59, 68.55, 59.09, 37.92, 29.81, 27.87. HRMS (ESI) calcd for $C_{41}H_{40}O_{10}Na$ $[M+Na]^+$: 715.2514, found: 715.2515.

To a solution of compound **S9** (750 mg, 1.08 mmol) in 17 mL dry CH_2Cl_2 was added 1 M hydrazine hydrate (2.16 mL, 2.16 mmol, hydrazine hydrate/pyridine/AcOH = 125 μL/1.4 mL/1 mL) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was quenched with acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) afforded **43** (636 mg, 98%,α/β = 1/2) as a syrup. The β-anomer: R_f = 0.36 (EtOAc/Petroleum ether =1/2), the α-anomer: R_f = 0.31 (EtOAc/Petroleum ether =1/2). Data for the β-anomer: $[\alpha]_D^{20}$ = -9.77 (c 0.18, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.49 – 7.39 (m, 3H), 7.39 – 7.20 (m, 11H), 6.18 (s, 1H, CH_2-PVB), 5.82 (s, 1H, CH_2-PVB), 5.25 (d, *J* = 4.3 Hz, 1H, H-2), 5.22 (s, 1H, **H-1**), 4.57 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.52 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.08 (dd, *J* = 8.3, 3.7 Hz, 1H, H-4), 3.82 – 3.73 (m, 2H, H-3, H-5), 3.45 (d, 2H, H-6a and H-6b), 3.17 (s, 3H, OMe), 2.13 (d, *J* = 7.1 Hz, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85, 165.10, 148.84, 142.77, 139.99, 137.91, 133.43, 132.19, 131.15, 130.33, 130.16, 129.90, 129.25, 128.48, 128.44, 128.00, 127.83, 127.79, 127.77, 126.85, 114.35, 99.18, 82.16, 78.67, 73.45, 73.21, 71.19, 70.05, 59.00. HRMS (ESI) calcd for $C_{36}H_{34}O_8Na$ $[M+Na]^+$: 617.2146, found: 617.2147.

2.4.2 One-pot glycosylation for the synthesis of nucleosides

(2-O-benzoyl-3,4,6-tri-benzyl-β-glucopyranosyl)-(1→5)-(2,3-di-*O*-benzoyl-β-D-ribofuranoyl) uracil (50)

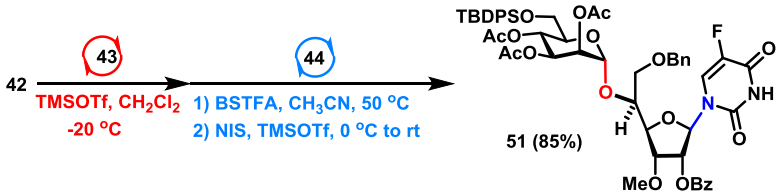


Bis(trimethylsilyl) trifluoroacetamide (BSTFA) (48 μL, 0.182 mmol) was added to a stirred suspension of acceptor **41** (11 mg, 0.091 mmol) in dry CH_3CN (1.0 mL) under Ar. The mixture was stirred at 50 ℃ for 30 min.

Glucosyl trichloroacetimidate **22b**[22] (38 mg, 0.055 mmol) and acceptor **40** (26 mg, 0.045 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1.0 mL) in the presence of 3 Å powdered molecular sieves (200 mg) under Ar. After stirring at room temperature for 0.5 h, then cooled to - 20 ℃ and TMSOTf (0.1 mL, 16 μL in 1 mL CH_2Cl_2, 0.009 mmol) was added. The resulting solution was kept stirring at – 20 ℃ for 30 min, then the reaction mixture was warmed to 0 ℃, to which was added the above fresh prepared uracil solution and stirred at 0 ℃ for another 10 min. Then NIS (16 mg, 0.068 mmol) and TMSOTf (0.1 mL, 32 μL in 1 mL CH_2Cl_2, 0.018 mmol) were added, the reaction mixture was stirred for 4 h after the temperature gradually rise to room temperature. Et_3N was added to quench the reaction. The whole mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/1) afforded **50** (36 mg, 80%) as a white solid; $[\alpha]_D^{23}$ = -49.24 (c 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H, H-NH), 7.92 (d, *J* = 7.6 Hz, 2H), 7.86 – 7.76 (m, 5H), 7.46 (d, *J* = 6.4 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.20 (m, 13H), 7.18 (s, 1H), 7.14 – 7.10 (m, 2H), 7.06 (s, 4H), 6.42 (d, *J* = 7.0 Hz, 1H, **H-1**), 5.78 (d, *J* = 7.2 Hz, 1H, H-pyrimidine), 5.54 – 5.48 (m, 1H, H-3), 5.32 – 5.24 (m, 2H, H-2 and H-2'), 4.77 (d, *J* = 10.8 Hz, 1H, H-Bn), 4.70 (d, *J* = 10.8 Hz, 1H, H-Bn), 4.67 – 4.61 (m, 2H, **H-1'**, H-Bn), 4.60 – 4.45 (m, 4H), 4.33 (s, 1H, H-4), 4.26 (d, *J* = 10.1 Hz, 1H, H-5a), 3.84 (t, *J* = 9.0 Hz, 1H, H-3'), 3.80 – 3.65 (m, 5H),, 3.55 (d, *J* = 7.9

Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.50, 165.41, 164.57, 162.75, 150.50, 140.13, 137.83, 137.81, 137.63, 133.61, 133.45, 133.26, 129.97, 129.89, 129.73, 129.34, 128.87, 128.62, 128.50, 128.48, 128.46, 128.38, 128.31, 128.03, 127.96, 127.94, 127.83, 127.77, 127.74, 103.57, 100.77, 86.01, 82.58, 82.47, 77.82, 75.40, 75.28, 75.17, 74.08, 73.75, 73.52, 72.37, 68.44, 67.86. HRMS (ESI) calcd for $C_{57}H_{52}N_2O_{14}$ $[M-H]^-$ 987.3346, found 987.3340.

[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) 5-fluorouracil (51)

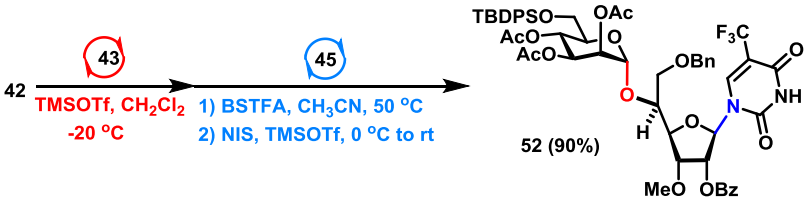


Bis(trimethylsilyl) trifluoroacetamide (BSTFA) (98 μL, 0.372 mmol) was added to a stirred suspension of acceptor **44** (16 mg, 0.124 mmol) in dry CH_3CN (1.2 mL) under Ar. The mixture was stirred at 50 ℃ for 30 min.

Mannosyl trichloroacetimidate **42**[23] (51 mg, 0.075 mmol) and glycosyl PVB acceptor **43** (37 mg, 0.062 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1.2 mL) in the presence of 3 Å powdered molecular sieves (240 mg) under Ar. After stirring at room temperature for 0.5 h, then cooled to - 20 ℃ and TMSOTf (2.2 μL, 0.012 mmol) was added. The resulting solution was kept stirring at – 20 ℃ for 30 min, then the reaction mixture was warmed to 0 ℃, to which was added the above fresh prepared uracil solution and stirred at 0 ℃ for another 10 min. Then NIS (21 mg, 0.093 mmol) and TMSOTf (4 μL, 0.022 mmol) were added, the reaction mixture was stirred for 3 h after the temperature gradually rise to room temperature. Et_3N was added to quench the reaction. The whole mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/1) afforded **51** (55 mg, 85%) as a white foam. R_f = 0.24 (EtOAc/Petroleum ether =1/1); $[\alpha]_D^{20}$ = +19.69 (c 0.15, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 4.6 Hz, 1H, NH), 8.03 (d, *J* = 7.8 Hz, 2H), 7.79 – 7.63 (m, 5H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.50 – 7.28 (m, 13H), 6.10 (d, *J* = 4.2 Hz, 1H, H-1), 5.59 – 5.47 (m, 2H, H-2, H-4'), 5.40 (dd, *J* = 9.8, 2.9 Hz, 1H,

H-3'), 5.33 (d, *J* = 3.5 Hz, 2H, H-1' and H-2'), 4.60 (q, *J* = 11.9 Hz, 2H, CH_2-Bn), 4.30 (dd, *J* = 5.6, 2.3 Hz, 1H, H-4), 4.20 (d, *J* = 6.3 Hz, 1H, H-5), 4.13 (t, *J* = 5.3 Hz, 1H, H-3), 4.00 (d, *J* = 9.3 Hz, 1H, H-5'), 3.86 – 3.72 (m, 4H, H-6 and H-6'), 3.22 (s, 3H, OMe), 2.14 (s, 3H, CH_3-OAc), 2.00 (s, 3H, CH_3-OAc), 1.96 (s, 3H, CH_3-OAc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 169.99, 169.54, 165.21, 156.72, 156.45, 148.60, 141.87, 139.50, 137.47, 135.73, 135.63, 133.60, 133.21, 133.11, 129.96, 129.73, 129.68, 128.90, 128.56, 128.52, 127.92, 127.83, 127.69, 127.61, 123.86, 123.52, 96.58, 87.89, 82.35, 78.18, 74.25, 73.78, 73.64, 72.65, 69.86, 69.61, 69.16, 65.75, 62.36, 58.83, 26.73, 20.86, 20.70, 20.65, 19.34. HRMS (ESI) calcd for $C_{53}H_{59}N_2O_{16}FSiNa$ $[M+Na]^+$: 1049.3510, found: 1049.3512.

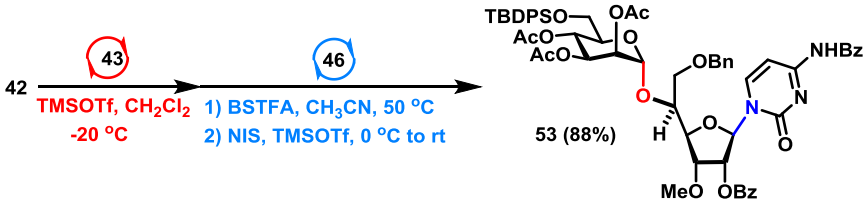
[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) trifluorothymine (52)



For donor **42**[23] (51 mg, 0.075 mmol), glycosyl PVB acceptor **43** (37 mg, 0.062mmol) and trifluorothymine **45** (22 mg, 0.123 mmol) as described for the preparation of **51** to give **52** (60 mg, 90%) as a white solid. R_f = 0.21 (EtOAc/Petroleum ether =1/1.5). $[\alpha]_D^{20}$ = +2.28 (c 0.12, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H, NH), 8.03 (d, *J* = 7.0 Hz, 3H), 7.69 (d, *J* = 8.0 Hz, 4H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.40 – 7.32 (m, 10H), 6.12 (d, *J* = 5.0 Hz, 1H, **H-1**), 5.56 – 5.49 (m, 2H, H-2 and H-4'), 5.45 (dd, *J* = 10.1, 2.9 Hz, 1H, H-3'), 5.34 (s, 1H, **H-1'**), 5.24 (s, 1H, H-2'), 4.61 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.57 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.37 (s, 1H, H-4), 4.30 – 4.18 (m, 2H, H-3, H-5), 4.03 (d, *J* = 8.5 Hz, 1H, H-5'), 3.84 – 3.73 (m, 4H, H-6' and H-6), 3.23 (s, 3H, OMe), 2.14 (s, 3H, CH_3-OAc), 1.97 (s, 3H, CH_3-OAc), 1.96 (s, 3H, CH_3-OAc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.21, 169.94, 169.61, 165.31, 158.05, 149.00, 140.85, 137.45, 135.71, 135.63, 133.65, 133.21, 129.94, 129.73, 129.67, 128.83, 128.59, 128.52, 127.91, 127.80, 127.70, 127.60, 106.08, 105.75, 96.00, 88.52, 82.88, 78.53, 74.87, 73.66, 73.09, 72.82, 69.96,

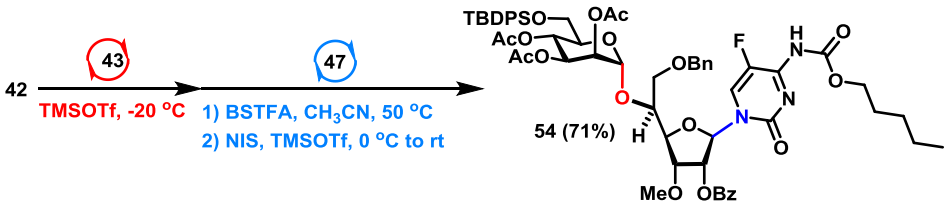
69.16, 68.91, 65.74, 62.48, 58.70, 26.74, 20.85, 20.65, 20.56, 19.34. HRMS (ESI) calcd for $C_{54}H_{59}N_2O_{16}F_3SiNa$ $[M+Na]^+$: 1099.3478, found: 1099.3477.

[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) 4-*N*-benzoylcytosine (53)



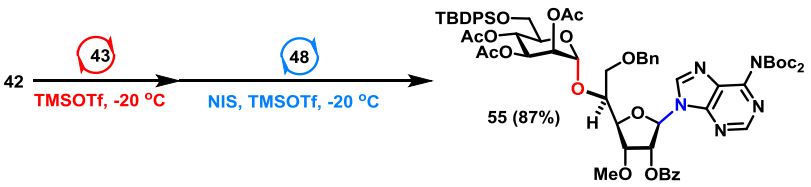
For donor **42**[23] (51 mg, 0.075 mmol), glycosyl PVB acceptor **43** (37 mg, 0.062mmol) and N^4-benzoylcytosine **46** (27 mg, 0.123 mmol) as described for the preparation of **51** to give **53** (61 mg, 88%) as a white solid. R_f = 0.18 (EtOAc/Petroleum ether =1/1). $[\alpha]_D^{20}$ = +37.57 (c 0.14, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, NH), 8.20 (d, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.73 – 7.55 (m, 7H), 7.55 – 7.28 (m, 15H), 6.24 (d, *J* = 2.6 Hz, 1H, **H-1**), 5.73 – 5.59 (m, 2H, H-4' and H-2), 5.47 - 5.43 (m, 1H, H-2'), 5.40 – 5.30 (m, 2H, **H-1'** and H-3'), 4.65 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.56 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.29 (dd, *J* = 7.3, 2.3 Hz, 1H, H-4), 4.22 – 4.16 (m, 1H, H-5), 3.99 – 3.90 (m, 2H, H-3 and H-5'), 3.88 – 3.68 (m, 4H, H-6 and H-6'), 3.18 (s, 3H, OMe), 2.14 (s, 3H, CH_3-OAc), 2.06 (s, 3H, CH_3-OAc), 1.97 (s, 3H, CH_3-OAc), 1.06 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.27, 169.98, 169.47, 164.95, 137.57, 135.76, 135.61, 133.42, 133.26, 133.12, 133.01, 129.98, 129.69, 129.66, 129.16, 129.00, 128.50, 128.45, 127.86, 127.64, 127.57, 97.81, 89.01, 81.81, 77.90, 75.17, 74.23, 73.65, 72.42, 70.65, 69.73, 69.61, 65.43, 62.08, 59.07, 26.70, 20.87, 20.81, 20.66, 19.34. HRMS (ESI) calcd for $C_{60}H_{65}N_3O_{16}SiNa$ $[M+Na]^+$: 1134.4026, found: 1134.4029.

[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) 5-fluoro-4-*N*-pentyl-carbamate cytosine (54)



For donor **42**[23] (51 mg, 0.075 mmol), glycosyl PVB acceptor **43** (37 mg, 0.062mmol) and 5 -fluorocytosine **47** (31 mg, 0.123 mmol) as described for the preparation of **51** to give **54** (50 mg, 71%) as a white solid. R_f = 0.18 (EtOAc/Petroleum ether =1/1). $[\alpha]_D^{20}$ = +51.86 (c 0.13, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H, NH), 8.04 (d, *J* = 7.7 Hz, 2H), 7.79 (s, 1H), 7.71 – 7.63 (m, 4H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.30 (m, 11H), 6.16 (d, *J* = 4.1 Hz, 1H, **H-1**), 5.54 (t, *J* = 9.7 Hz, 1H, H-4'), 5.45 (s, 1H, H-2), 5.42 – 5.28 (m, 3H, **H-1'**, H-2' and H-3'), 4.63 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.57 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.32 (dd, *J* = 5.7, 2.3 Hz, 1H, H-4), 4.25 – 4.13 (m, 3H, H-5, CH_2-pentyl), 4.09 (s, 1H, H-3), 3.99 (s, 1H, H-5'), 3.86 - 3.71 (m, 4H, H-6 and H-6'), 3.23 (s, 3H, OMe), 2.13 (s, 3H, CH_3-OAc), 1.98 (s, 3H, CH_3-OAc), 1.96 (s, 3H, CH_3-OAc), 1.78 – 1.67 (m, 2H, CH_2-pentyl), 1.42 – 1.29 (m, 4H, CH_2-pentyl), 1.07 (s, 9H, CH_3-TBDPS), 0.90 (t, *J* = 6.8 Hz, 3H, CH_3-pentyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.89, 169.47, 146.21, 137.44, 135.71, 135.62, 133.58, 133.21, 133.10, 129.97, 129.72, 129.68, 128.52, 127.92, 127.82, 127.68, 127.59, 96.67, 87.58, 82.45, 78.18, 74.26, 73.65, 72.73, 69.75, 69.48, 69.12, 66.56, 65.70, 62.39, 58.85, 28.28, 27.95, 26.72, 22.33, 20.83, 20.69, 20.63, 19.34, 13.95. HRMS (ESI) calcd for $C_{59}H_{70}N_3O_{17}FSiNa$ $[M+Na]^+$: 1162.4351, found: 1162.4350.

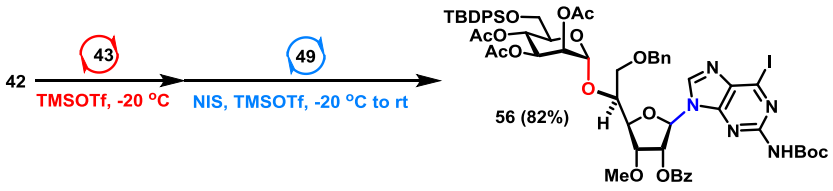
[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) 6-*N*-di-tert-butyl-carbamate-purine (55)



Mannosyl trichloroacetimidate **42**[23] (51 mg, 0.075 mmol) and glycosyl PVB acceptor **43** (37 mg, 0.062 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1.2 mL) in the presence of 3 Å powdered molecular sieves

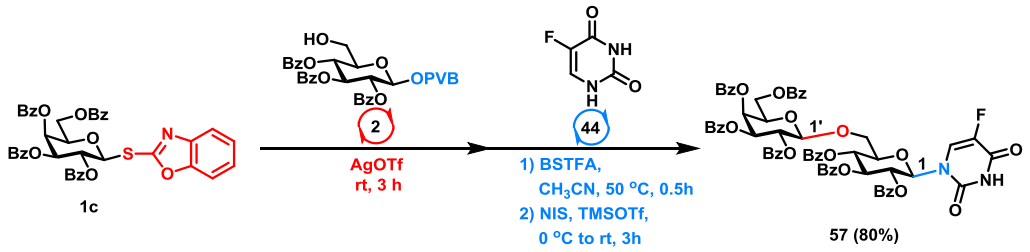
(220 mg) under Ar. After stirring at room temperature for 0.5 h, then cooled to - 20 ℃ and TMSOTf (2.2 μL, 0.012 mmol) was added. The resulting solution was kept stirring at - 20 ℃ for 30 min, to which was added the fresh prepared purine solution **48** (21 mg in 1 mL dry CH_2Cl_2) and stirred at - 20 ℃ for another 10 min. And then NIS (21 mg, 0.093 mmol) and TMSOTf (2.2 μL, 0.012 mmol) were added, the reaction mixture was stirred for 3 h at - 20 ℃. Et_3N was added to quench the reaction. The whole mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/2) afforded **55** (66 mg, 87%) as a colorless syrup. R_f = 0.25 (EtOAc/Petroleum ether =1/2). $[\alpha]_D^{20}$ = +4.48 (c 0.12, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.36 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 6.7 Hz, 2H), 7.67 (d, *J* = 6.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.30 (m, 13H), 6.44 (d, *J* = 5.7 Hz, 1H, **H-1**), 5.85 (t, *J* = 5.2 Hz, 1H, H-2), 5.55 (t, *J* = 9.7 Hz, 1H, H-4'), 5.42 – 5.35 (m, 2H, H-3' and H-2'), 5.29 (s, 1H, **H-1'**), 4.61 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.54 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.44 – 4.36 (m, 2H, H-3 and H-4), 4.21 (t, *J* = 4.0 Hz, 1H, H-5), 4.12 (d, *J* = 9.6 Hz, 1H, H-5'), 3.87 – 3.72 (m, 4H, H-6 and H-6'), 3.29 (s, 3H, OMe), 2.12 (s, 3H, CH_3-OAc), 2.00 (s, 3H, CH_3-OAc), 1.96 (s, 3H, CH_3-OAc), 1.45 (s, 18H, CH_3-Boc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.96, 169.95, 169.50, 165.23, 153.16, 152.37, 150.51, 142.87, 137.58, 135.76, 135.65, 133.59, 133.34, 133.23, 129.88, 129.67, 129.63, 129.10, 128.81, 128.49, 127.85, 127.66, 127.58, 96.78, 85.54, 83.79, 82.60, 78.52, 74.74, 73.65, 72.40, 69.79, 69.57, 69.27, 65.66, 62.46, 58.74, 27.80, 26.75, 20.86, 20.74, 20.71, 19.36. HRMS (ESI) calcd for $C_{64}H_{77}N_5O_{18}SiNa$ $[M+Na]^+$: 1254.4925, found: 1254.4921.

[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) 6-iodine-2-*N*-tert-butyl-carbamate-purine (56)



Mannosyl trichloroacetimidate **42**[23] (51 mg, 0.075 mmol) and glycosyl PVB acceptor **43** (37 mg, 0.062 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1.2 mL) in the presence of 3 Å powdered molecular sieves (220 mg) under Ar. After stirring at room temperature for 0.5 h, then cooled to - 20 ℃ and TMSOTf (2.2 μL, 0.012 mmol) was added. The resulting solution was kept stirring at - 20 ℃ for 30 min, to which was added the fresh prepared purine solution **49** (22 mg in 1 mL dry CH_2Cl_2) and stirred at - 20 ℃ for another 10 min. And then NIS (21 mg, 0.093 mmol) and TMSOTf (2.2 μL, 0.012 mmol) were added, the reaction mixture was stirred for 3h after the temperature gradually rise to room temperature. Et_3N was added to quench the reaction. The whole mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/2) afforded **56** (64 mg, 82%) as a white solid. R_f = 0.28 (EtOAc/Petroleum ether =1/2). $[\alpha]_D^{20}$ = +13.61 (c 0.15, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 3H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.62 (d, *J* = 6.9 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.28 (m, 14H), 6.11 (d, *J* = 3.1 Hz, 1H, **H-1**), 5.87 (dd, *J* = 5.5, 3.1 Hz, 1H, H-2), 5.55 (t, *J* = 9.8 Hz, 1H, H-4'), 5.35 (dd, *J* = 9.8, 3.3 Hz, 1H, H-3'), 5.31 (t, *J* = 2.6 Hz, 1H, H-2'), 5.24 (d, *J* = 1.8 Hz, 1H, H-1'), 5.10 (t, *J* = 6.1 Hz, 1H, H-3), 4.56 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.31 (t, *J* = 6.3 Hz, 1H, H-4), 4.26 (dd, *J* = 6.5, 3.1 Hz, 1H, H-5), 3.88 (d, *J* = 9.6 Hz, 1H, H-5'), 3.77 (dd, *J* = 10.6, 3.3 Hz, 1H, H-6a), 3.73 – 3.67 (m, 1H, H-6b), 3.37 (s, 4H, OMe and H-6'a), 3.30 (d, *J* = 10.6 Hz, 1H, H-6'b), 2.09 (s, 3H, CH_3-OAc), 1.99 (s, 3H, CH_3-OAc), 1.92 (s, 3H, CH_3-OAc), 1.49 (s, 9H, CH_3-TBDPS), 1.02 (s, 9H, CH_3-Boc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.19, 169.98, 169.36, 165.48, 151.79, 149.55, 147.91, 142.34, 137.91, 135.78, 135.65, 135.23, 133.60, 133.42, 133.16, 129.96, 129.60, 129.51, 128.98, 128.53, 128.36, 127.70, 127.66, 127.63, 127.52, 122.33, 96.38, 87.64, 82.26, 81.38, 78.35, 75.32, 75.23, 73.55, 71.38, 69.93, 69.67, 69.60, 65.64, 61.59, 58.56, 28.16, 26.68, 20.85, 20.83, 20.76, 19.34. HRMS (ESI) calcd for $C_{59}H_{68}N_5O_{16}ISiNa$ $[M+Na]^+$: 1280.3367, found: 1280.3384.

(2,3,4,6-Tetra-*O*-benzoyl-β-D-galacopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl) 5-fluorouracil (57)

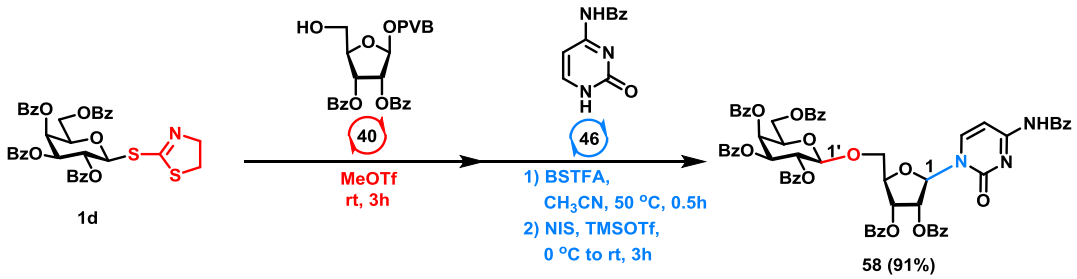


BSTFA (65.0 μL, 0.245 mmol) was added to a stirred suspension of 5-fluorouracil **44** (16.0 mg, 0.123 mmol) in dry CH_3CN (1.2 mL) under Ar atmosphere. The mixture was stirred at 50 ℃ for 30 min to prepare the silylated 5-fluorouracil.

A suspension of SBox donor **1c**[5] (60.9 mg, 0.084 mmol), glucosyl PVB acceptor **2** (43.0 mg, 0.062 mmol), and activated 3Å MS (300 mg) in dry CH_2Cl_2 (1.2 mL) was stirred at room temperature for 15 min, to which AgOTf (32.0 mg, 0.125 mmol) was added to the mixture. After being stirred at room temperature for another 3 h, the above freshly prepared silylated 5-fluorouracil solution was added to the reaction mixture, the reaction mixture was cooled to 0 ℃, then NIS (20.7mg, 0.092 mmol) and TMSOTf (5.6 μL, 0.033 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 3h, then was quenched with Et_3N (1.2mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 1.7:1 to 1:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **57** (58.0 mg, 80%) as a syrup. $[\alpha]_D^{22}$ = +52.30 (*c* 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 (s, 1H, H-NH), 8.18 (d, *J* = 7.8 Hz, 2H, Ar), 8.11 (d, *J* = 7.7 Hz, 2H, Ar), 8.01 (d, *J* = 7.6 Hz, 2H, Ar), 7.92 (d, *J* = 7.8 Hz, 2H,Ar), 7.83 (d, *J* = 7.8 Hz, 4H, Ar), 7.71 – 7.61 (m, 4H, H-=CH-, Ar), 7.59 – 7.36 (m, 13H, Ar), 7.34 – 7.24 (m, 7H, Ar), 6.15 (d, *J* = 9.2 Hz, 1H, **H-1**), 6.07 – 5.97 (m, 2H, H-3, H-4'), 5.92 (t, *J* = 9.1 Hz, 1H, H-2'), 5.78 (dd, *J* = 10.6, 3.5 Hz, 1H, H-3'), 5.48 (t, *J* = 9.9 Hz, 1H, H-4), 5.16 (t, *J* = 9.5 Hz, 1H, H-2), 4.95 (d, *J* = 7.7 Hz, 1H, **H-1'**), 4.66 (dd, *J* = 11.1, 6.1 Hz, 1H), 4.44 – 4.28 (m, 3H, H-6), 4.22 (d, *J* = 9.5 Hz, 1H, H-5), 3.76 (dd, *J* = 11.7, 3.9 Hz, 1H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.05, 165.69, 165.64, 165.61, 165.44, 165.27, 165.02, 156.64, 156.38, 148.88, 142.20, 139.82, 133.83, 133.77, 133.58, 133.47, 133.43, 133.39, 130.07, 130.00, 129.95, 129.89, 129.82, 129.73, 129.37, 129.14, 129.00, 128.79, 128.74, 128.64, 128.56, 128.48, 128.41, 128.38, 128.32, 127.94, 124.15, 123.81, 102.08, 80.79, 77.36,

75.77, 72.40, 71.49, 71.23, 70.39, 69.97, 68.22, 68.09, 66.79, 61.86. HRMS (ESI) calcd for $C_{65}H_{51}FN_2O_{19}Na$ $[M+Na]^+$ 1205.2962, found 1205.2961.

(2,3,4,6-Tetra-*O*-benzoyl-β-D-galacopyranosyl)-(1→5)-(2,3-di-*O*-benzoyl-β-D-ribofuranoyl) 4-*N*-benzoylcytosine (58)

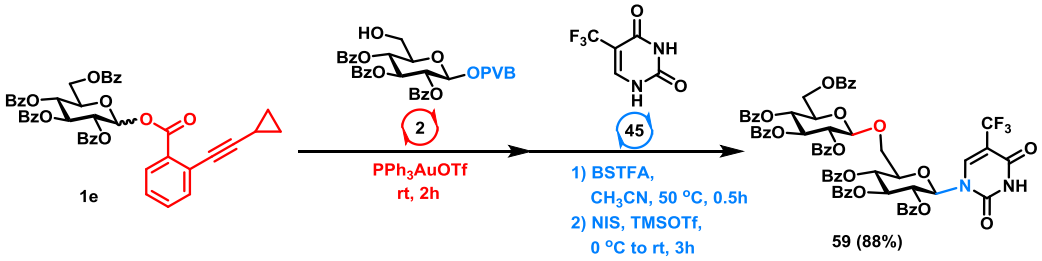


BSTFA (100.3 μL, 0.378 mmol) was added to a stirred suspension of 4-*N*-benzoylcytosine **46** (40.7 mg, 0.189 mmol) in dry CH_3CN (1.9mL) under Ar atmosphere. The mixture was stirred at 50 ℃ for 30 min to prepare the silylated 4-*N*-benzoylcytosine.

A suspension of STaz galactoside donor **1d**[6] (86.0 mg, 0.123 mmol), glucosyl PVB acceptor **40** (53.4 mg, 0.095 mmol), and activated 3Å MS (300 mg) in dry CH_2Cl_2 (1 mL) was stirred at room temperature for 15 min, to which MeOTf (22 μL, 0.194 mmol) was added to the mixture slowly. After being stirred at room temperature for 3 h, the above freshly prepared silylated 4-*N*-benzoylcytosine solution was added to the reaction mixture, the reaction mixture was cooled to 0 ℃, then NIS (32.0mg, 0.142 mmol) and TMSOTf (8.6 μL, 0.047 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 3h, then was quenched with Et_3N (1.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 1:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **58** (97.6 mg, 91%) as a syrup. $[\alpha]_D^{21}$ = -5.69 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H, H-NH), 8.37 (d, *J* = 7.6 Hz, 1H, H-=CH-), 8.15 (d, *J* = 7.3 Hz, 2H, Ar), 8.05 (d, *J* = 7.8 Hz, 2H, Ar), 8.01 – 7.88 (m, 9H, Ar), 7.82 (d, *J* = 7.7 Hz, 2H, Ar), 7.65 – 7.50 (m, 9H, Ar), 7.47 – 7.33 (m, 9H, Ar), 7.30 – 7.22 (m, 3H, Ar), 6.62 (d, *J* = 5.6 Hz, 1H, **H-1**), 6.12 (d, *J* = 3.4 Hz, 1H, H-4'), 5.99 – 5.92 (m, 1H, H-2'), 5.79 (dd, *J* = 10.4, 3.6 Hz, 1H, H-3'), 5.70 (t, *J* = 4.7 Hz, 1H, H-3), 5.58 (t, *J* = 5.7 Hz, 1H, H-2), 5.11 (d, *J* = 7.9 Hz, 1H, **H-1'**), 4.78 (dd, *J* = 10.6, 5.8 Hz, 1H), 4.58 – 4.46 (m, 4H, H-4), 4.04 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 166.10, 165.71, 165.66, 165.62, 165.38, 164.79, 133.74, 133.69, 133.53, 133.41, 133.17, 130.03, 130.00, 129.89, 129.86, 129.83, 129.41, 129.02, 128.92, 128.89, 128.81, 128.78, 128.69, 128.56, 128.54, 128.44, 128.39, 127.82, 101.65, 87.99, 82.24, 77.36, 75.09, 71.81, 71.65, 71.43, 69.84, 68.38, 68.19, 61.98. HRMS (ESI) calcd for $C_{64}H_{52}N_3O_{17}$ $[M+H]^+$ 1134.3291, found 1134.3284.

(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl) trifluorothymine (59)

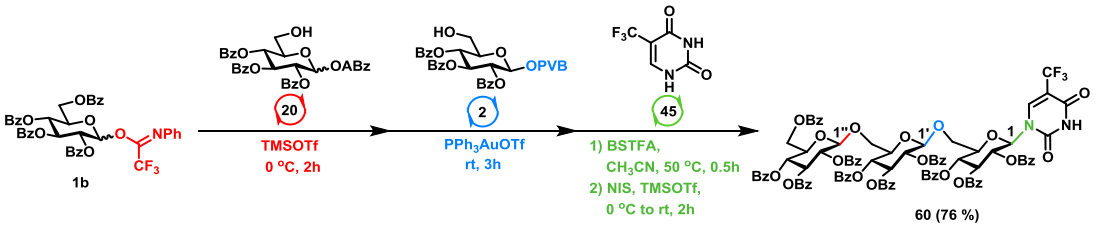


BSTFA (227.5 μL, 0.859 mmol) was added to a stirred suspension of trifluorothymine **45** (51.5 mg, 0.286 mmol) in dry CH_3CN (2.8 mL) under Ar atmosphere. The mixture was stirred at 50 ℃ for 30 min to prepare the silylated trifluorothymine.

A suspension of glucosyl ABz donor **1e**[4] (131.3 mg, 0.172 mmol), glucosyl PVB **2** (100.0 mg, 0.143 mmol), and activated 3Å MS (500 mg) in dry CH_2Cl_2 (1.7 mL) was stirred at room temperature for 15 min, to which a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.36 mL, 0.079 M) was added to the mixture slowly. After being stirred at room temperature for 2 h, the above freshly prepared silylated trifluorothymine solution was added to the reaction mixture, the reaction mixture was cooled to 0 ℃, then NIS (48.3 mg, 0.215 mmol) and TMSOTf (13.0 μL, 0.072 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred for 3h, then was quenched with Et_3N (0.8mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2.3:1 to 1.5:1), followed by purification over a Sephadex™ LH-20 column (DCM/MeOH 1:1) to afford **59** (155.0 mg, 88%) as a syrup. $[\alpha]_D^{21}$ = +22.52 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H, H-NH), 8.14 (s, 1H, H-=CH-), 8.08 (d, *J* = 7.8 Hz, 2H, Ar), 8.04 (d, *J* = 7.7 Hz, 2H, Ar), 7.97 – 7.85 (m, 6H, Ar), 7.80 (d, *J* = 7.8 Hz, 2H, Ar), 7.67 (d, *J* = 7.7 Hz, 2H, Ar), 7.59 – 7.19 (m, 21H, Ar), 6.20 (d, *J* = 9.3 Hz, 1H, **H-1**), 6.10 (t, *J* = 9.6 Hz, 1H, H-3), 6.02 (t, *J* = 9.7 Hz, 1H, H-3'), 5.73 (t, *J* = 9.7 Hz, 1H,

H-4'), 5.61 (t, *J* = 8.8 Hz, 1H, H-2'), 5.51 (t, *J* = 9.8 Hz, 1H, H-4), 5.39 (t, *J* = 9.5 Hz, 1H, H-2), 4.97 (d, *J* = 7.6 Hz, 1H, **H-1'**), 4.64 (dd, *J* = 12.6, 3.2 Hz, 1H, H-6'), 4.50 (dd, *J* = 12.3, 4.9 Hz, 1H, H-6'), 4.35 – 4.14 (m, 3H, H-5, H-5', H-6), 3.79 (dd, *J* = 11.5, 4.9 Hz, 1H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 165.88, 165.50, 165.23, 165.19, 157.69, 149.06, 141.00, 133.94, 133.79, 133.53, 133.52, 133.40, 133.37, 133.27, 129.95, 129.93, 129.89, 129.84, 129.80, 129.76, 129.55, 129.15, 128.81, 128.80, 128.61, 128.55, 128.54, 128.50, 128.43, 128.38, 128.34, 127.69, 122.98, 120.29, 106.91, 106.58, 101.72, 80.81, 77.36, 76.36, 72.55, 72.41, 71.93, 70.65, 69.65, 68.50, 67.42, 63.00. HRMS (ESI) calcd for $C_{66}H_{51}F_3N_2O_{19}Na$ $[M+Na]^+$ 1255.2930, found 1255.2924.

(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl) (1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl) trifluorothymine (60)



BSTFA (165.0 μL, 0.621 mmol) was added to a stirred suspension of trifluorothymine **45** (37.3 mg, 0.207 mmol) in dry CH_3CN (2.0 mL) under Ar atmosphere. The mixture was stirred at 50 ℃ for 30 min to prepare silylated trifluorothymine.

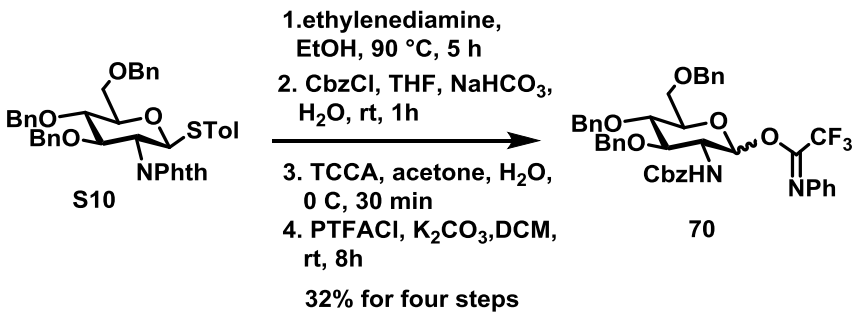
A suspension of glucosyl trifluoroacetimidate **1b**[3] (103.2 mg, 0.135 mmol), glucosyl ABz **20**[9] (75.1 mg, 0.114 mmol), and activated 3Å MS (600 mg) in dry CH_2Cl_2 (2.2 mL) was stirred at room temperature for 15 min and was then cooled to 0 ℃. TMSOTf (4.0 μL, 0.023 mmol) was added to the mixture dropwise. After being stirred at 0 ℃ for another 2 h, the reaction mixture was warmed up to room temperature, to which glucosyl PVB **2** (72.0 mg, 0.104 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (0.4mL, 0.052M) were added successively. After being stirred at room temperature for another 3h. the above freshly prepared silylated trifluorothymine solution was added to the reaction mixture, the reaction mixture was cooled to 0 ℃, then NIS (34.9mg, 0.155 mmol) and TMSOTf (5.6 μL, 0.031 mmol) were added successively at 0 ℃. The resulting mixture was warmed gradually to room temperature and stirred

for 2h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 2:1), followed by purification over a Sephadex^{TM} LH-20 column (DCM/MeOH 1:1) to afford **60** (133.4 mg, 76%) as a syrup. $[\alpha]_D^{22}$ = -12.73 (*c* 0.30, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.03 (s, 1H, H-NH), 8.27 (s, 1H, H-=CH-), 8.02 (t, *J* = 6.5 Hz, 4H, Ar), 7.94 (d, *J* = 8.1 Hz, 4H, Ar), 7.87 (t, *J* = 6.8 Hz, 4H, Ar), 7.83 (t, *J* = 6.3 Hz, 4H, Ar), 7.76 (d, *J* = 7.3 Hz, 2H, Ar), 7.64 (d, *J* = 7.4 Hz, 2H, Ar), 7.56 – 7.51 (m, 2H, Ar), 7.49 – 7.43 (m, 3H, Ar), 7.43 – 7.19 (m, 23H, Ar), 7.13 (t, *J* = 7.9 Hz, 2H, Ar), 6.17 (d, *J* = 9.2 Hz, 1H, **H-1**), 6.10 (t, *J* = 9.7 Hz, 1H, H-3''), 6.06 (t, *J* = 9.7 Hz, 1H, H-3), 5.77 (t, *J* = 9.7 Hz, 1H, H-3'), 5.68 (t, *J* = 9.6 Hz, 1H, H-4''), 5.65 – 5.60 (m, 2H, H-2, H-4), 5.55 (dd, *J* = 9.9, 7.8 Hz, 1H, H-2''), 5.18 (dd, *J* = 9.9, 7.8 Hz, 1H, H-2'), 5.14 (d, *J* = 7.8 Hz, 1H, **H-1''**), 5.08 (t, *J* = 9.7 Hz, 1H, H-4'), 4.64 (dd, *J* = 11.8, 2.3 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H, **H-1'**), 4.50 – 4.42 (m, 2H, H-5''), 4.01 (d, *J* = 10.7 Hz, 2H), 3.97 – 3.89 (m, 2H, H-5, H-5'), 3.83 (dd, *J* = 11.9, 8.3 Hz, 1H), 3.42 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.37, 166.21, 165.65, 165.62, 165.40, 165.37, 165.34, 165.24, 165.18, 165.08, 157.85, 149.19, 141.50, 133.87, 133.73, 133.61, 133.44, 133.41, 133.38, 133.30, 133.25, 133.23, 130.11, 130.00, 129.97, 129.87, 129.85, 129.83, 129.74, 129.65, 129.27, 128.83, 128.77, 128.72, 128.71, 128.61, 128.56, 128.53, 128.51, 128.49, 128.47, 128.46, 128.43, 128.36, 128.34, 128.30, 127.88, 124.14, 122.34, 120.55, 118.76, 107.07, 106.85, 106.63, 106.40, 101.61, 100.86, 81.06, 75.56, 74.08, 72.83, 72.37, 72.35, 72.31, 71.99, 71.78, 70.54, 69.83, 69.78, 69.52, 68.79, 67.43, 63.34. HRMS (ESI) calcd for $C_{93}H_{73}F_3N_2O_{27}Na$ $[M+Na]^+$ 1729.4245, found 1729.4246.

2.5 Divergent and formal synthesis of TMG-chitotriomycin and lipochitooligosaccharides

2.5.1 Preparation of new glycosyl donors and acceptors

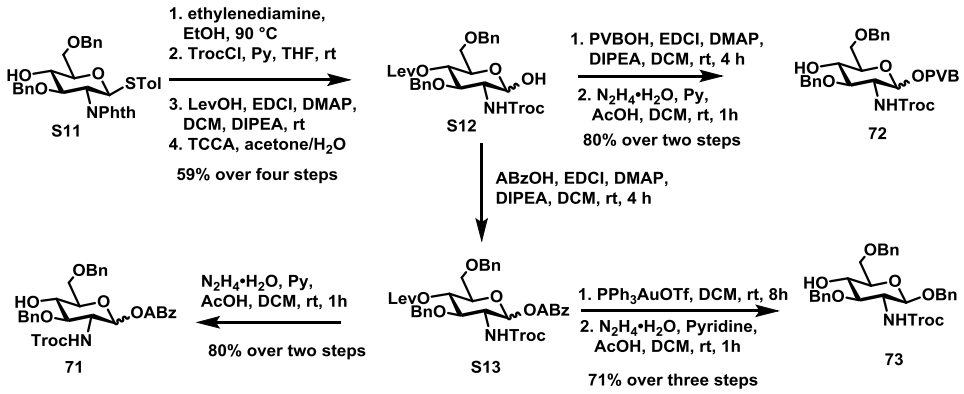
3,4,6-Tri-*O*-benzyl-2-deoxy-2-*N*-benzyloxycarbonyl-α/β-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (70)



The known compound **S10**[24] (1.65 g, 2.41 mmol) was dissolved in 32 mL dry EtOH and 8 mL ethylenediamine, then the solution was reflux at 90 ℃ for 6 h. After concentration *in vacuo*, the crude product was directly used in the next step without purification. To a solution of the above crude amine, $NaHCO_3$ (808 mg, 9.64 mmol) in THF (18 mL) and H_2O (18 mL) was slowly added benzyl chloroformate (0.52 mL, 3.62 mmol) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was diluted with EtOAc, washed with H_2O and brine successively. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether/ CH_2Cl_2 =1/3/1) afforded a white solid (1.28 g, 77 % over two steps). The above solid (710 mg, 0.96 mmol) was dissolved with acetone/H_2O (20 mL/ 5 mL), and trichloroisocyanuric acid (232 mg, 0.96 mmol) was added at 0 ℃. The mixture was stirred for 1 h at 0 ℃ and quenched with saturated aqueous $NaHCO_3$, then it was diluted with EtOAc, washed with H_2O and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether/ CH_2Cl_2 =1/2/1) to afford the hemiacetal as a white solid (480 mg, 79%). To a solution of hemiacetal (450 mg, 0.75 mmol) in CH_2Cl_2 (15 mL) was sequentially added 2,2,2-Trifluoro-*N*-phenylacetimidoyl chloride (174 mg, 0.84 mmol), K_2CO_3 (207 mg, 1.5 mmol) at room temperature under Ar. The mixture was stirred for 24 h at this temperature and concentrated *in vacuo* to give the crude. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether/Et_3N =1/10/0.33) to afford **70** as a light yellow solid (294 mg, 52%) and recovery the starting material (200 mg, 44%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.19 (m, 21H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 2H), 6.28 (s, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.85 (dd, *J* = 17.1, 11.0 Hz, 2H), 4.72 – 4.54 (m, 3H), 4.54 – 4.48 (m, 2H), 4.15 (s, 1H), 3.90 – 3.65 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.87, 143.27, 137.83, 137.73, 136.11, 128.75, 128.61, 128.56, 128.54, 128.46, 128.36, 128.32,

128.12, 128.02, 127.99, 127.88, 127.77, 124.41, 119.30, 79.46, 79.45, 77.73, 75.29, 75.22, 73.53, 68.05, 67.23, 54.11.

Synthesis of compounds 71, 72 and 73



3,5-Di-*O*-benzyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-α/β-D-glucopyranosyl 2-(cyclopropylethynyl) benzoate (71)

The known compound **S11**[25] (2.96 g, 4.97 mmol) was dissolved in 77 mL dry EtOH and 18 mL ethylenediamine, then the solution was refluxed at 90 ℃ for 6 h. After concentration *in vacuo*, the crude product was directly used in the next step without purification. To a solution of the above crude amine in THF (38 mL) and pyridine (1.2 mL) was slowly added TrocCl (1.03 mL, 7.45 mmol) at 0 ℃ under Ar. The mixture was stirred at room temperature for 1 h, then quenched with MeOH and concentrated *in vacuo*. The residue was diluted with CH_2Cl_2, washed with H_2O and brine successively. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford the product as a white solid (2.62 g, 82 % over two steps). The above solid (2.28 g, 3.57 mmol), EDCI (1.23 g, 6.43 mmol) and DMAP (216 mg, 1.78 mmol) were dissolved in 27 mL CH_2Cl_2. Then levulinic acid (0.55 ml, 5.36 mmol) and DIPEA (1.78 mL, 10.71 mmol) were added successively at room temperature under Ar. The resulting mixture was stirred for 4 h at this temperature and concentrated *in vacuo* to produce the crude oil. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether/ CH_2Cl_2 =1/2/1) to afford a white solid (2.41 g, 91%). The above solid (2.4 g, 3.24 mmol) was dissolved with acetone/H_2O (64 mL/ 16 mL), and trichloroisocyanuric acid (756 mg, 3.24 mmol) was added at 0 ℃. The mixture was stirred for 1 h at 0 ℃ and quenched with saturated aqueous $NaHCO_3$, then it was diluted with EtOAc, washed

with H_2O and brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether/ CH_2Cl_2 =1/1/1) to afford the hemiacetal **S12** as a white solid (1.63 g, 80%).

The white solid **S12** (1.0 g, 1.58 mmol), EDCI (548 mg, 2.85 mmol) and DMAP (193 mg, 1.58 mmol) were dissolved in 15 mL CH_2Cl_2. Then 2-(cyclopropylethynyl) benzoic acid (353 mg, 1.90 mmol) and DIPEA (0.78 mL, 4.75 mmol) were added successively at room temperature under Ar. The resulting mixture was stirred for 6 h at this temperature and concentrated *in vacuo* to produce the crude oil. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford a white foam **S13** (1.1 g, 87%). To a solution of **S13** (600 mg, 0.75 mmol) in 15 mL dry CH_2Cl_2 was added 1 M hydrazine hydrate (1.50 mL, 1.50 mmol, hydrazine hydrate/pyridine/AcOH = 125 μL/1.4 mL/1 mL) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was quenched with acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/3) to afford **71** (485 mg, 92%, α/β = 1.3/1) as a white foam. Data for the α-anomer: $[\alpha]_D^{24}$ = +77.43 (c 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.38 (m, 2H), 7.38 – 7.20 (m, 11H), 6.46 (d, *J* = 3.6 Hz, 1H, **H-1**), 5.35 (d, *J* = 9.4 Hz, 1H, H-NH), 5.01 – 4.70 (m, 3H, H-Troc and H-Bn), 4.63 – 4.45 (m, 3H, H-Troc and H-Bn), 4.23 (td, *J* = 9.7, 3.6 Hz, 1H, H-2), 4.00 – 3.86 (m, 3H, H-3, H-4, H-5), 3.78 (dd, *J* = 10.5, 3.0 Hz, 1H, H-6), 3.66 (dd, *J* = 10.5, 3.0 Hz, 1H, H-6), 3.32 (s, 1H, H-OH), 1.68 – 1.48 (m, 1H, H-ABz), 0.95 – 0.80 (m, 4H, H-ABz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.07, 153.54, 137.51, 136.83, 134.33, 131.64, 130.43, 129.52, 127.75, 127.73, 127.12, 127.05, 126.81, 126.69, 123.68, 99.18, 94.60, 91.76, 78.65, 74.94, 73.93, 73.27, 73.04, 71.83, 71.27, 69.05, 52.77, 8.64, 8.56. HRMS (ESI) calcd for $C_{35}H_{34}NO_8Cl_3Na$ $[M+Na]^+$ 724.1242, found 724.1242.

3,5-Di-*O*-benzyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-α/β-D-glucopyranosyl 2-(1-phenylvinyl) benzoate (72)

The white solid **S12** (483 mg, 0.765 mmol), EDCI (264 mg, 1.377 mmol) and DMAP (93 mg, 0.765 mmol) were dissolved in 7 mL CH_2Cl_2. Then 2-(1-Phenylvinyl) benzoic acid (206 mg, 0.92 mmol) and DIPEA (0.38 mL, 2.30 mmol) were added successively at room temperature under Ar.

The resulting mixture was stirred for 6 h at this temperature and concentrated *in vacuo* to produce the crude sryup. Then it was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/2) to afford a white solid (580 mg, 90%). To a solution of this solid (580 mg, 0.69 mmol) in 12 mL dry CH_2Cl_2 was added 1 M hydrazine hydrate (1.38 mL, 1.38 mmol, hydrazine hydrate/pyridine/AcOH = 125 μL/1.4 mL/1 mL) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was quenched with acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/3) to afford **72** (465 mg, 91%, α/β = 1.6/1) as a white foam. Data for the α-anomer: $[\alpha]_D^{24}$ = +54.05 (c 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 3H), 7.30 – 7.05 (m, 14H), 6.14 (d, *J* = 3.8 Hz, 1H, **H-1**), 5.93 (s, 1H, H-double bond), 5.09 (s, 1H, H-double bond), 4.66 (d, *J* = 12.0 Hz, 1H, H-Bn), 4.56 (d, *J* = 9.9 Hz, 1H, H-NH), 4.51- 4.36 (m, 3H, H-Troc and H-Bn), 4.27 (d, *J* = 11.5 Hz, 1H, H-Bn), 4.05 (d, *J* = 11.5 Hz, 1H, H-Bn), 3.89 (td, *J* = 9.9, 3.8 Hz, 1H, H-2), 3.64 – 3.53 (m, 2H, H-4, H-6), 3.53 - 3.46 (m, 2H, H-5, H-6), 2.84 (t, *J* = 9.6 Hz, 1H, H-3), 2.70 (s, 1H, H-OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 153.98, 148.85, 141.94, 138.85, 138.39, 137.67, 132.23, 131.07, 130.70, 130.62, 129.15, 128.84, 128.51, 128.42, 127.96, 127.89, 127.81, 127.67, 127.30, 127.09, 114.02, 95.44, 92.59, 80.22, 77.51, 77.39, 77.19, 76.88, 74.77, 74.70, 73.78, 72.52, 71.75, 69.72, 53.59. HRMS (ESI) calcd for $C_{38}H_{36}NO_8Cl_3Na$ $[M+Na]^+$ 762.1399, found 762.1399.

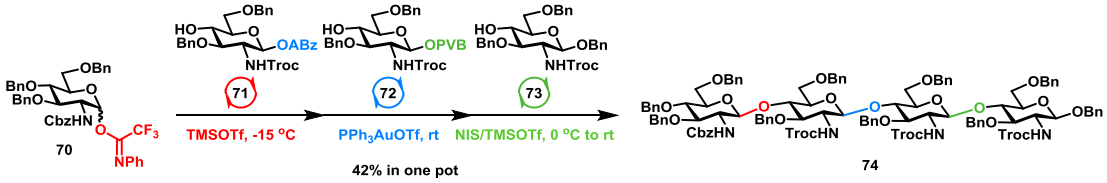
3,4,6-tri-*O*-benzyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-β-D-glucopyranoside (73)

A suspension of **S13** (500 mg, 0.625 mmol), benzyl alcohol (97 mg, 0.938 mmol), and activated 3Å MS (600 mg) in dry CH_2Cl_2 (9 mL) was stirred at room temperature for 30 min under Ar. Then a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (1 mL, 0.125 M) was added. The resulting mixture was stirred at room temperature for 6 h, then it was filtered. Then the mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =2/1) afforded a white solid (405 mg, 90%). To a solution of this solid (405 mg, 0.56 mmol) in 10 mL dry CH_2Cl_2 was added 1 M hydrazine hydrate (1.2 mL, 1.2 mmol, hydrazine hydrate/pyridine/AcOH = 125 μL/1.4 mL/1 mL) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was quenched with

acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/3) afforded **73** (318 mg, 91%) as a white solid; $[\alpha]_D^{24}$ = -23.65 (c 0.17, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.18 (m, 15H), 5.16 (d, *J* = 8.4 Hz, 1H, H-NH), 4.85 (d, *J* = 12.0 Hz, 1H, H-Bn), 4.79 – 4.50 (m, 8H, H-Bn, H-Troc and **H-1**), 3.79 – 3.71 (m, 2H, H-3 and H-4), 3.70 – 3.63 (m, 2H, H-5 and H-6), 3.45 (d, *J* = 8.9 Hz, 2H, H-2 and H-6), 2.93 (s, 1H, H-OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.09, 138.26, 137.78, 137.24, 128.58, 128.55, 128.45, 128.12, 127.96, 127.91, 127.81, 99.35, 95.57, 80.59, 77.46, 77.34, 77.14, 76.82, 74.47, 74.20, 73.98, 73.76, 72.80, 70.70, 70.40, 57.25. HRMS (ESI) calcd for $C_{30}H_{32}NO_7Cl_3Na$ $[M+Na]^+$ 646.1137, found 646.1139.

2.5.2 One-pot glycosylation for the formal synthesis of TMG-chitotriomycin and lipochitooligosaccharides

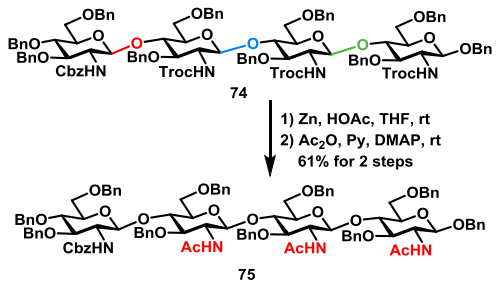
Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-*N*-benzyloxycarbonyl-β-D-glucopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-β-D-glucopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-β-D-glucopyranosyl)-(1→4)-3,5-di-*O*-benzyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-β-D-glucopyranoside (74)



A suspension of PTFAI donor **70**[26] (165 mg, 0.219 mmol), ABz **71** (110 mg, 0.157 mmol), and activated 3Å MS (500 mg) in dry CH_2Cl_2 (3 mL) was stirred at room temperature for 30 min under Ar. Then the mixture was cooled to – 15 ℃ and a solution of TMSOTf in CH_2Cl_2 (0.1 mL, 42 μL in 1 mL CH_2Cl_2, 0.024 mmol) was added to the mixture dropwise. After being stirred at -15 ℃ for 2.0 h, the reaction mixture was warmed to room temperature, to which PVB **72** (92.0 mg, 0.124 mmol) and a freshly prepared solution of PPh_3AuOTf in CH_2Cl_2 (1.0 mL, 0.03 M, 0.03 mmol) were added successively. The resulting mixture was stirred at room temperature overnight, then acceptor **73** (70 mg, 0.112 mmol), NIS (33 mg, 0.149 mmol) and TMSOTf (0.1 mL, 30 μL in 1 mL CH_2Cl_2, 0.020 mmol) were added successively at 0 ℃. The resulting mixture was warmed

gradually to room temperature and stirred for 3 h, then quenched with Et_3N, filtered with Celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Petroleum ether =1/2) and Sephadex LH-20 (CH_2Cl_2/MeOH = 1/1) to give **74** (103 mg, 42 %) as a white solid: $[\alpha]_D^{23}$ = -9.23 (c 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.09 (m, 55H, H-Ar, ArH-Bn and Cbz), 5.08 (s, 2H, H-Cbz), 5.00 – 4.90 (m, 3H), 4.87 (d, *J* = 12.1 Hz, 1H), 4.79 – 4.66 (m, 5H), 4.65 – 4.45 (m, 13H), 4.41 – 4.28 (m, 5H), 4.24 – 4.06 (m, 6H), 3.95 (t, *J* = 8.1 Hz, 1H), 3.92 – 3.85 (m, 2H), 3.79 – 3.73 (m, 2H), 3.73 – 3.65 (m, 1H), 3.64 – 3.43 (m, 10H), 3.40 – 3.33 (m, 3H), 3.30 – 3.21 (m, 1H), 3.16 – 3.01 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.12, 154.37, 154.31, 154.14, 139.29, 139.04, 138.40, 138.26, 137.96, 137.87, 137.50, 136.75, 129.23, 129.11, 128.88, 128.77, 128.75, 128.67, 128.63, 128.61, 128.58, 128.52, 128.46, 128.44, 128.40, 128.32, 128.21, 128.17, 128.12, 128.01, 127.98, 127.93, 127.84, 127.79, 127.77, 127.66, 127.58, 127.51, 101.01, 100.90, 100.55, 99.78, 95.89, 95.82, 82.32, 80.38, 80.06, 78.81, 78.57, 75.12, 75.02, 74.92, 74.70, 74.65, 74.61, 74.42, 74.28, 74.20, 73.85, 73.59, 73.49, 70.82, 69.03, 68.52, 68.18, 67.99, 66.94, 58.63, 58.06, 57.34, 56.69, 53.69. HRMS (ESI) calcd for $C_{111}H_{115}N_4O_{25}Cl_9Na_2$ $[M+2Na]^{2+}$ 1132.2416, found 1132.2410.

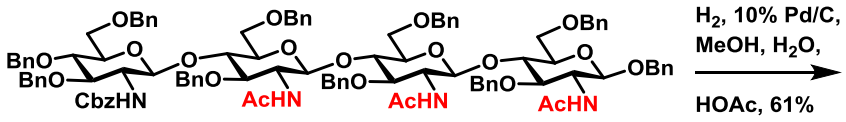
Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-*N*-benzyloxycarbonyl-β-D-glucopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (75)



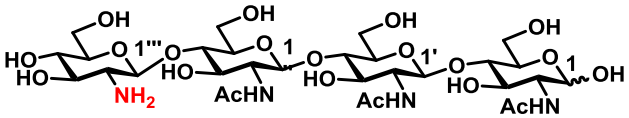
To a solution of compound **74** (102 mg, 0.046 mmol) in 13 mL AcOH was added 1.3 g Zinc powder at room temperature. The mixture was vigorously stirred for 16 h. Then it was filtered with Celite and concentrated *in vacuo* to give the crude. The above crude and DMAP (20 mg, 0.16 mmol) were dissolved in 6 mL pyridine and 2 mL Ac_2O at room temperature. The mixture was stirred overnight, then concentrated *in vacuo* to give a light yellow oil. The residue was purified

by flash column chromatography (CH_2Cl_2/MeOH = 60/1) and Sephadex LH-20 (CH_2Cl_2/MeOH = 1/1) to give **75** (51 mg, 61 %) as a white amorphous solid: $[\alpha]_D^{24}$ = -14.98 (c 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.11 (m, 55H, ArH-Bn and Cbz), 6.32 (d, *J* = 9.2 Hz, 1H, H-NHAc), 5.90 – 5.80 (m, 1H, H-NHAc), 5.14 (d, *J* = 12.2 Hz, 1H, H-Cbz), 5.04 (d, *J* = 12.2 Hz, 1H, H-Cbz), 4.87 – 4.77 (m, 3H), 4.77 – 4.65 (m, 4H), 4.65 – 4.39 (m, 13H), 4.33 – 4.20 (m, 4H), 4.14 – 4.02 (m, 3H), 4.02 - 3.90 (m, 3H), 3.85 – 3.68 (m, 5H), 3.67 – 3.49 (m, 8H), 3.47 – 3.35 (m, 4H), 3.31 – 3.22 (m, 2H), 3.19 (s, 1H), 3.12 (s, 1H), 1.94 (s, 3H, CH_3- NHAc), 1.78 (s, 3H, CH_3- NHAc), 1.62 (s, 3H, CH_3- NHAc). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.52 (N(C=O)CH_3), 170.45 (N(C=O)CH_3), 170.05 (N(C=O)CH_3), 155.97 (C=O of Cbz), 139.08, 138.69, 138.53, 138.16, 138.02, 137.98, 137.94, 137.65, 137.58, 136.34, 128.62, 128.49, 128.46, 128.44, 128.41, 128.35, 128.33, 128.26, 128.25, 128.23, 128.21, 128.19, 128.12, 128.07, 128.05, 128.02, 127.97, 127.93, 127.90, 127.81, 127.78, 127.74, 127.70, 127.64, 127.59, 127.55, 127.53, 127.50, 127.44, 127.41, 127.36, 127.32, 127.29, 100.41, 99.51, 81.83, 79.68, 79.48, 78.23, 77.18, 77.12, 76.97, 76.90, 76.75, 75.11, 74.64, 74.59, 74.26, 73.88, 73.51, 73.38, 73.35, 73.27, 71.90, 70.07, 69.87, 68.91, 68.55, 66.76, 57.57, 54.11, 53.11, 52.74, 50.74, 45.71, 23.32 (N(C=O)CH_3), 23.15 (N(C=O)CH_3), 23.11 (N(C=O)CH_3). HRMS (ESI) calcd for $C_{108}H_{118}N_4O_{22}Na_2$ $[M+2Na]^{2+}$ 934.4011, found 934.4015.

(2-Amino-2-deoxy-β-D-glucopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-2-deoxy-α,β-D-glucopyranose (76)



75

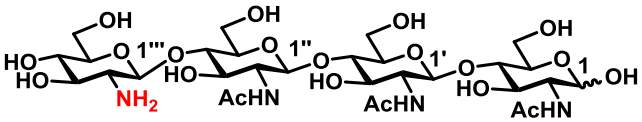


76

Compound **75** (48 mg) was dissolved in methanol/water/AcOH (10/1/0.1, 13 mL/1.3 mL/0.13 mL) and 10% palladium on activated charcoal (480 mg) was added. The flask was degassed using low

vacuum and flushed with hydrogen (3 times). The mixture was stirred under a hydrogen balloon for 30 h at room temperature, then it was filtered through a celite pad. The solution was neutralized with saturated $NaHCO_3$ and concentrated *in vacuo*. The crude residue was purified by Sephadex LH-20 (H_2O) to give **76**[27] as a white amorphous solid (13 mg, 61%,α/β = 1.4/1); ^{1}H NMR (400 MHz, D_2O) δ 5.16 (d, *J* = 2.4 Hz, 0.60H, **H-1α**), 4.67 (d, *J* = 7.5 Hz, 0.40H, **H-1β**), 4.59 – 4.55 (m, 2H, **H-1'** and **H-1"**), 4.45 (d, *J* = 8.1 Hz, 1H, **H-1"'**), 3.96 – 3.31 (m, 23H, 3H-2, 4H-3, 4H-4, 4H-5, 8H-6), 2.64 (t, *J* = 8.6 Hz, 1H, H-2"'), 2.03 (s, 6H, 2N(C=O)$\underline{CH_3}$), 2.01 (s, 3H, N(C=O)$\underline{CH_3}$). ^{13}C NMR (150 MHz, D_2O) δ 174.73, 174.60, 174.46, 102.77, 101.28, 94.84, 90.46, 79.60, 79.13, 79.02, 78.99, 78.01, 76.19, 75.60, 74.67, 74.59, 74.50, 72.47, 72.10, 71.98, 70.00, 69.55, 69.24, 60.63, 60.12, 60.05, 59.99, 59.93, 56.68, 56.12, 55.26, 55.06, 53.66, 22.17, 22.12, 21.88. HRMS (ESI) calcd for $C_{30}H_{52}N_4O_{20}Na$ $[M+Na]^+$ 811.3067 found 811.3069.

2.5.3 Comparison of the analytical data of synthetic 76 with those reported for tetrasaccharide 76



76

Position	76[27]	Synthetic 76
H-1α	5.16 (d, *J* = 1.2 Hz, 0.60H)	5.16 (d, *J* = 2.4 Hz, 0.60H)
H-1β	4.67 (d, *J* = 7.6 Hz, 0.40H)	4.67 (d, *J* = 7.5 Hz, 0.40H)
H-1'	4.59 – 4.55 (m, 2H)	4.59 – 4.55 (m, 2H)
H-1"		
H-1"'	4.45 (d, *J* = 8.2 Hz, 1H)	4.45 (d, *J* = 8.1 Hz, 1H)
3H-2		
4H-3		
4H-4	3.95 – 3.30 (m, 23H)	3.96 – 3.31 (m, 23H)
4H-5		
8H-6		
H-2"'	2.68 – 2.61 (m, 1H)	2.64 (t, *J* = 8.6 Hz, 1H)

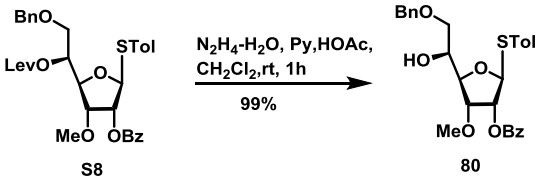
2AcNH(C<u>H</u>$_3$)	2.03 (s, 6H)	2.03 (s, 6H)
AcNH(C<u>H</u>$_3$)	2.01 (s, 3H)	2.01 (s, 3H)

Position	76[27]	Synthetic 76	Position	76[27]	Synthetic 76
AcNH (<u>C</u>=O)	174.7	174.73	pyranose	72.1	72.10
	174.6	174.60		72.0	71.98
	174.5	174.46		70.0	70.00
C-1’’’	102.7	102.77		69.6	69.55
C-1’	101.3	101.28		69.2	69.24
C-1’’	101.3	101.28	C-6	60.6	60.63
C-1β	94.8	94.84	C-6	60.1	60.12
C-1α	90.4	90.46		60.1	60.05
pyranose	79.6	79.60	C-6	60.0	59.99
	79.2	79.13	C-6	59.9	59.93
	79.0	79.02	C-2’’’	56.7	56.68
	79.0	78.99	C-2’	56.1	56.12
	78.0	78.01	C-2β	55.3	55.26
	76.2	76.19	C-2’’	55.1	55.06
	75.5	75.60	C-2α	53.6	53.66
	74.7	74.67	AcNH (<u>C</u>H$_3$)	22.2	22.17
	74.6	74.59		22.1	22.12
	74.5	74.50		21.9	21.88
	72.5	72.47			

2.6 Total synthesis of Capuramycin

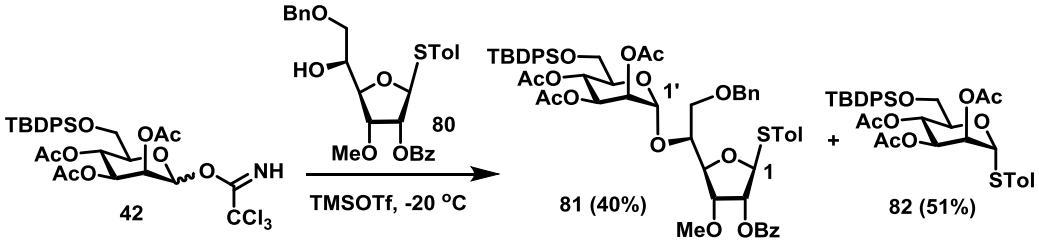
2.6.1 Aglycon transfer issues of thioglycosides

_p_-Methylphenyl 6-O-benzyl-3-O-methyl-2-O-benzoyl-1-thio-β-L-talofuranoside (80)



To a solution of compound **S8** (64 mg, 0.11 mmol) in 2 mL dry CH_2Cl_2 was added 1 M hydrazine hydrate (220 μL, 0.22 mmol, hydrazine hydrate/pyridine/AcOH = 125 μL/1.4 mL/1 mL) at room temperature. The mixture was stirred at room temperature for 1 h. Then it was quenched with acetone and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (EtOAc/Petroleum ether =1/3) to afford **80** (53 mg, 99%) as a colorless oil. R_f = 0.25 (EtOAc/Petroleum ether =1/3). $[\alpha]_D^{20}$ = -73.15 (c 0.16, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 16.7, 8.0 Hz, 4H), 7.30 – 7.21 (m, 5H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.51 (t, *J* = 3.0 Hz, 1H, H-2), 5.43 (d, *J* = 2.5 Hz, 1H, **H-1**), 4.50 (dd, *J* = 12.0, 2.9 Hz, 2H, CH_2-Bn), 4.15 – 4.09 (m, 2H, H-3 and H-6a), 3.82 (d, *J* = 6.5 Hz, 1H, H-4), 3.56 – 3.43 (m, 2H, H-5 and H-6b), 3.28 (s, 3H, OMe), 2.30 (d, 1H, *J* = 7.2 Hz, 1H, OH), 2.25 (s, 3H, CH_3-STol). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.47, 138.42, 138.00, 133.42, 132.97, 130.01, 129.92, 129.42, 128.77, 128.48, 128.43, 127.78, 127.72, 89.76, 82.46, 79.61, 73.41, 71.46, 69.48, 58.98, 21.18. HRMS (ESI) calcd for $C_{28}H_{30}O_6SNa$ $[M+Na]^+$: 517.1655, found: 517.1654.

***p*-Methylphenyl [6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-1-thio-β-L-talofuranoside (81)**



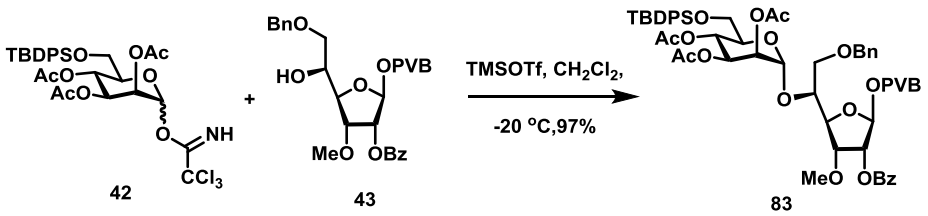
Donor **42**[23] (47 mg, 0.068 mmol) and thioglycoside acceptor **80** (28 mg, 0.057 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1 mL) in the presence of 4 Å powdered molecular sieves(100 mg) under Ar. After stirring at room temperature for 0.5 h, the solution was cooled to - 20 ℃ and TMSOTf (2.06 μL, 0.011 mmol) was added. The resulting solution was kept stirring at - 20 ℃ for 40 min, and Et_3N was added to quench the reaction. The whole mixture was filtered through a

Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/6) afforded **82** (19 mg, 51%) as a white solid and **81** (24 mg, 40%) as a white foam. The compound **82**: R_f = 0.45 (EtOAc/Petroleum ether =1/5), the compound **81**: R_f = 0.35 (EtOAc/Petroleum ether =1/5).

Data for **81** : $[\alpha]_D^{20}$ = +3.26 (c 0.16, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 7.1 Hz, 2H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.29 (m, 15H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.64 (t, *J* = 10.0 Hz, 1H, H-4'), 5.52 – 5.44 (m, 2H, H-3' and H-2), 5.38 (s, 1H, H-2'), 5.37 (s, 1H, **H-1**), 5.24 (s, 1H, **H-1'**), 4.57 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.48 (d, *J* = 12.0 Hz, 1H, 1H, CH_2-Bn), 4.20 (d, *J* = 9.8 Hz, 1H, H-5'), 4.11 – 4.01 (m, 2H, H-4, H-5), 3.98 – 3.93 (m, 1H, H-3), 3.80 (dd, *J* = 11.6, 1.9 Hz, 1H, H-6'a), 3.72 – 3.55 (m, 3H, H-6'b, H-6a and H-6b), 3.20 (s, 3H, OMe), 2.28 (s, 3H, CH_3-STol), 2.13 (s, 3H, CH_3-OAc), 2.00 (s, 3H, CH_3-OAc), 1.92 (s, 3H, CH_3-OAc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.10, 169.42, 165.38, 137.91, 137.88, 135.87, 135.66, 133.57, 133.34, 133.24, 132.82, 129.89, 129.81, 129.56, 129.53, 129.41, 129.07, 128.44, 128.41, 127.74, 127.66, 127.59, 127.52, 97.11, 88.74, 81.65, 79.55, 76.19, 75.31, 73.43, 71.36, 70.11, 69.98, 69.83, 65.97, 61.99, 58.74, 26.73, 21.11, 20.92, 20.84, 20.74, 19.35. HRMS (ESI) calcd for $C_{56}H_{64}O_{14}SiSNa$ $[M+Na]^+$: 1043.3678, found: 1043.3671.

Data for **82**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 7.7 Hz, 4H), 7.45 – 7.32 (m, 8H), 7.10 – 7.04 (m, 2H), 5.52 – 5.46 (m, 2H, H-4 and H-2), 5.45 – 5.42 (m, 1H, **H-1**), 5.30 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3), 4.43 – 4.35 (m, 1H, H-5), 3.81 (dd, *J* = 11.5, 4.7 Hz, 1H, H-6a), 3.75 – 3.68 (m, 1H, H-6b), 2.32 (s, 3H, CH_3-STol), 2.12 (s, 3H, CH_3-OAc), 2.01 (s, 3H, CH_3-OAc), 1.93 (s, 3H, CH_3-OAc), 1.06 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.08, 170.04, 169.52, 137.99, 135.81, 135.60, 133.33, 132.97, 132.25, 129.90, 129.75, 129.68, 129.65, 127.69, 127.61, 86.14, 72.44, 71.32, 69.79, 66.33, 62.61, 26.67, 21.17, 20.92, 20.77, 20.69, 19.28. HRMS (ESI) calcd for $C_{35}H_{42}O_8SiSNa$ $[M+Na]^+$: 673.2262, found: 673.2264.

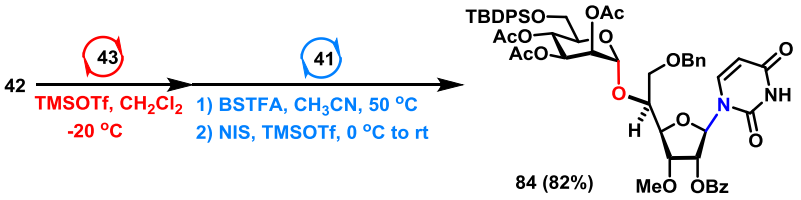
[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) 2-(1-phenylvinyl) benzoate (83)



Donor **42**[23] (109 mg, 0.16 mmol) and glycosyl PVB acceptor **43** (79 mg, 0.133 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1.8 mL) in the presence of 4 Å powdered molecular sieves (180 mg) under Ar. After stirring at room temperature for 0.5 h, the solution was cooled to - 20 ℃ and TMSOTf (4.8 μL, 0.027 mmol) was added. The resulting solution was kept stirring at - 20 ℃ for 30 min, and Et_3N was added to quench the reaction. The whole mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/3) afforded **83** (145 mg, 97%) as a white foam. R_f = 0.20 (EtOAc/Petroleum ether =1/3). $[\alpha]_D^{20}$ = +21.44 (c 0.16, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.44 (m, 6H), 7.37 – 7.23 (m, 12H), 7.22 – 7.08 (m, 7H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.00 (s, 1H, CH_2-PVB), 5.73 – 5.62 (m, 2H, CH_2-PVB and H-4'), 5.33 (dd, *J* = 10.2, 3.3 Hz, 1H, H-3'), 5.22 (t, *J* = 2.6 Hz, 1H, H-2'), 5.15 (d, *J* = 1.9 Hz, 1H, **H-1**), 4.97 (d, *J* = 4.1 Hz, 1H, H-2), 4.84 (s, 1H, **H-1'**), 4.44 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 4.38 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 4.04 (d, *J* = 10.0 Hz, 1H, H-5'), 3.89 (t, *J* = 8.2 Hz, 1H, H-4), 3.78 – 3.69 (m, 1H, H-5), 3.59 (dd, *J* = 11.8, 2.4 Hz, 1H, H-6'a), 3.48 – 3.38 (m, 1H, H-6'b), 3.30 (d, *J* = 5.4 Hz, 2H, H-6a and H-6b), 3.22 (dd, *J* = 8.6, 4.2 Hz, 1H, H-3), 2.89 (s, 3H, OMe), 2.05 (s, 3H, CH_3-OAc), 1.93 (s, 3H, CH_3-OAc), 1.90 (s, 3H, CH_3-OAc), 0.96 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.33, 170.21, 169.45, 165.73, 165.07, 148.30, 142.33, 139.54, 137.89, 135.75, 135.64, 133.64, 133.42, 133.20, 131.97, 130.73, 130.31, 129.92, 129.67, 129.55, 129.35, 129.12, 128.47, 127.95, 127.90, 127.81, 127.59, 127.56, 127.33, 126.71, 113.99, 98.50, 96.38, 81.16, 79.13, 73.65, 72.78, 70.86, 70.05, 69.95, 65.60, 61.68, 58.52, 26.66, 20.93, 20.91, 20.85, 19.29. HRMS (ESI) calcd for $C_{64}H_{68}O_{16}SiNa$ $[M+Na]^+$: 1143.4169, found: 1143.4166.

2.6.2 One-pot glycosylation and the total synthesis of Compound 88

[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl] -(1→5)-(6-*O*-benzyl-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) uracil (84)

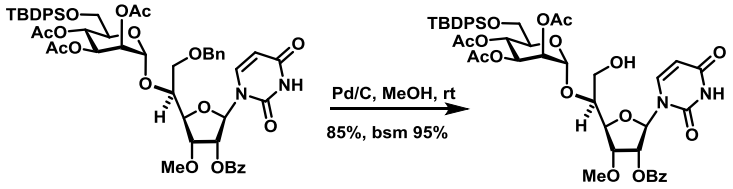


Bis(trimethylsilyl) trifluoroacetamide (BSTFA) (98 μL, 0.372 mmol) was added to a stirred suspension of acceptor **41** (14 mg, 0.124 mmol) in dry CH_3CN (1.2 mL) under Ar. The mixture was stirred at 50 ℃ for 30 min to prepare silylated uracil

Mannosyl trichloroacetimidate **42**[23] (51 mg, 0.075 mmol) and glycosyl PVB acceptor **43** (37 mg, 0.062 mmol) were co-evaporated with dry toluene, dried *in vacuo* for 10 min, and dissolved in dry CH_2Cl_2 (1.2 mL) in the presence of 3 Å powdered molecular sieves (240 mg) under Ar. After stirring at room temperature for 0.5 h, then cooled to - 20 ℃ and TMSOTf (2.2 μL, 0.012 mmol) was added. The resulting solution was kept stirring at – 20 ℃ for 30 min, then the reaction mixture was warmed to 0 ℃, to which was added the above fresh prepared silylated uracil solution and stirred at 0 ℃ for another 10 min. Then NIS (21 mg, 0.093 mmol) and TMSOTf (4 μL, 0.022 mmol) were added, the reaction mixture was stirred for 3 h after the temperature gradually rise to room temperature. Et_3N was added to quench the reaction. The whole mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (EtOAc/Petroleum ether =1/1) afforded **84** (51 mg, 82%) as a white foam. R_f = 0.20 (EtOAc/Petroleum ether =1/1). $[\alpha]_D^{20}$ = +22.58 (c 0.10, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H, NH), 8.02 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.67 (d, *J* = 6.8 Hz, 2H), 7.59 (dd, *J* = 17.4, 7.9 Hz, 2H), 7.47 – 7.30 (m, 13H), 6.25 (d, *J* = 5.1 Hz, 1H, **H-1**), 6.00 (d, *J* = 8.1 Hz, 1H, H-pyrimidine), 5.59 (t, *J* = 10.0 Hz, 1H, H-4'), 5.41 – 5.35 (m, 2H, H-2 and H-2'), 5.33 (d, *J* = 1.9 Hz, 1H, H-1'), 5.29 – 5.25 (m, 1H, H-3'), 4.60 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.55 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.28 (dd, *J* = 4.7, 2.2 Hz, 1H, H-4), 4.17 – 4.13 (m, 1H, H-5), 4.10 – 4.04 (m, 2H, H-3 and H-5'), 3.85 – 3.71 (m, 4H, H-4, H-6 and H-6'), 3.17 (s, 3H, OMe), 2.13 (s, 3H, CH_3-OAc), 2.01 (s, 3H, CH_3-OAc), 1.99 (s, 3H, CH_3-OAc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 170.24, 170.03, 169.45, 165.25, 162.95, 150.15, 139.17, 137.50, 135.78, 135.64, 133.58, 133.30, 133.16, 129.96, 129.71, 129.66, 128.89, 128.54, 128.50, 127.91, 127.86, 127.68, 127.58, 103.89, 97.28, 86.74, 82.16, 75.26, 74.44, 73.69, 72.47, 70.15, 69.67, 69.54, 65.39, 62.32, 58.73, 26.73, 20.85, 20.77, 19.37. HRMS (ESI) calcd for $C_{53}H_{60}N_2O_{16}SiNa$ $[M+Na]^+$: 1031.3604, found: 1031.3604.

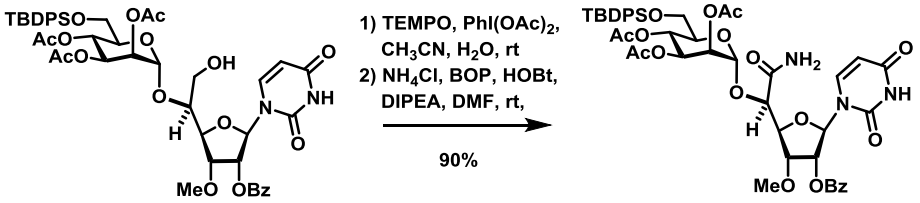
[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl]-(1→5)-(3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) uracil (84-1)



84 **84-1**

To a solution of compound **84** (200 mg, 0.198 mmol) in 20 mL MeOH was added 210 mg 10% palladiun / carbon at room temperature under hydrogen balloon. The mixture was stirred vigorously at room temperature for 48 h. The mixture was filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (CH_2Cl_2/MeOH =30/1) afforded **84-1** (154 mg, 85%) as a white solid and recovered starting material **84** (20 mg, 10%). R_f = 0.25 (CH_2Cl_2/MeOH =30/1). $[\alpha]_D^{20}$ = +9.22 (c 0.11, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 6.9 Hz, 2H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.34 (m, 8H), 6.15 (d, *J* = 4.4 Hz, 1H, **H-1**), 5.93 (d, *J* = 7.1 Hz, 1H, H-pyrimidine), 5.58 (t, *J* = 9.9 Hz, 1H, H-4'), 5.48 (t, *J* = 4.8 Hz, 1H, H-2), 5.37 (s, 1H, **H-1'**), 5.31 (dd, *J* = 10.1, 3.2 Hz, 1H, H-3'), 5.28 – 5.23 (m, 1H, H-2'), 4.31 (dd, *J* = 5.7, 2.7 Hz, 1H, H-4), 4.13 (t, *J* = 5.3 Hz, 1H, H-3), 4.08 – 3.99 (m, 2H, H-5 and H-5'), 3.97 – 3.91 (m, 2H, H-6), 3.83 – 3.71 (m, 2H, H-6'), 3.25 (s, 3H, OMe), 2.54 (s, 1H, OH), 2.15 (s, 3H, CH_3-OAc), 2.02 (s, 3H, CH_3-OAc), 1.98 (s, 3H, CH_3-OAc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.39, 170.33, 169.42, 165.31, 162.84, 150.03, 139.51, 135.77, 135.62, 133.65, 133.23, 133.08, 129.96, 129.74, 129.70, 128.86, 128.56, 127.69, 127.60, 103.74, 96.50, 88.03, 82.44, 78.43, 76.24, 74.10, 72.45, 26.70, 20.88, 20.76, 20.74, 19.34. HRMS (ESI) calcd for $C_{46}H_{54}N_2O_{16}SiNa$ $[M+Na]^+$: 941.3135, found: 941.3130.

[6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-acetyl-α-D-mannopyranosyl]-(1→5)-(5-acetamide-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) uracil (85)

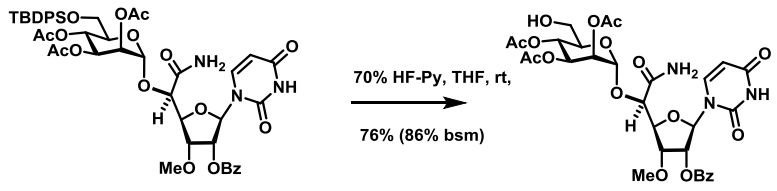


84-1 **85**

Compound **84-1** (110 mg, 0.119 mmol) was dissolved in 2 mL CH_3CN and 2 mL H_2O, then (diacetoxyiodo)benzene (115 mg, 0.357 mmol) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (3.8 mg, 0.024 mmol) were added at room temperature. The mixture was stirred vigorously at room temperature for 6 h, then concentrated *in vacuo* to give the light yellow solid. Then to a solution of the above crude in 3 mL anhydrous DMF was added 1-H-benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP) (93.5 mg, 0.178 mmol), 1-hydroxybenzotriazole (HOBt) (24 mg, 0.178 mmol), NH_4Cl (16 mg, 0.297 mmol) and N,N-diisopropylethylamine (15 μL, 0.476 mmol) at room temperature under Ar. The mixture was stirred at room temperature for another 2 h. Then it was concentrated *in vacuo* to give the light yellow solid. Purification by silica gel column chromatography (CH_2Cl_2/MeOH =30/1) afforded **85** (100 mg, 90%) as a white solid. R_f = 0.23 (CH_2Cl_2/MeOH =30/1). $[\alpha]_D^{20}$ = +4.29 (c 0.09, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 6.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.34 (m, 8H), 6.65 (s, 1H, NH- amide), 6.17 – 6.05 (m, 2H, **H-1** and NH- amide), 5.92 (d, *J* = 8.2 Hz, 1H, H-pyrimidine), 5.64 (t, *J* = 9.9 Hz, 1H, H-4'), 5.51 – 5.45 (t, *J* = 2.6 Hz, 2H, H-2 and H-2'), 5.33 (dd, *J* = 9.9, 3.3 Hz, 1H, H-3'), 5.03 (d, *J* = 1.6 Hz, 1H, **H-1'**), 4.51 – 4.41 (m, 2H, H-4 and H-5), 4.18 (t, *J* = 5.6 Hz, 1H, H-3), 3.99 (dd, *J* = 9.9, 3.0 Hz, 1H, H-5'), 3.78 (s, 2H, H-6'), 3.19 (s, 3H, OMe), 2.16 (s, 3H, CH_3-OAc), 2.04 (s, 3H, CH_3-OAc), 2.02 (s, 3H, CH_3-OAc), 1.07 (s, 9H, CH_3-TBDPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.72, 170.65, 170.40, 169.25, 165.33, 162.92, 149.98, 139.67, 135.71, 135.62, 133.71, 133.15, 132.89, 129.96, 129.82, 129.78, 128.76, 128.58, 127.72, 127.70, 103.78, 96.95, 88.17, 81.87, 77.77, 75.89, 73.80, 72.77, 69.55, 69.20,

65.10, 61.87, 58.66, 26.72, 20.81, 20.76, 19.35. HRMS (ESI) calcd for $C_{46}H_{52}N_3O_{16}SiNa$ $[M-H]^-$: 930.3122, found: 930.3125.

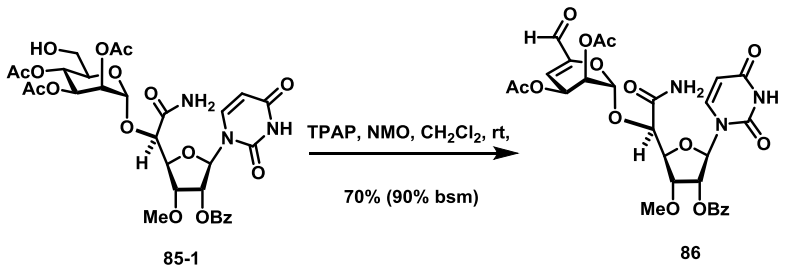
(2,3,4-Tri-acetyl-*α*-D-mannopyranosyl)-(1→5)-(5-acetamide-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) uracil (85-1)



85 **85-1**

To a solution of compound **85** (120 mg, 0.129 mmol) in 2 mL THF was added 70% HF·pyridine (166 μL, 1.29 mmol) at room temperature. The mixture was stirred vigorously at room temperature for 10 h, then it was quenched with $NaHCO_3$, filtered and concentrated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH =30/1) to afford **85-1** (50 mg, 56%) as a white solid and recover starting material **85** (35 mg, 29%). Resubjection of **85** (35 mg, 0.037 mmol) to the reaction conditions produced another 19 mg (21%) of **85-1** (total 76%) and recovered starting material **85** (12 mg, 10%). R_f = 0.28 (CH_2Cl_2/MeOH =15/1). $[\alpha]_D^{20}$ = +13.14 (c 0.12, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.81 (s, 1H, NH-amide), 6.24 (s, 1H, NH-amide), 6.02 (d, *J* = 3.2 Hz, 1H, **H-1**), 5.95 (d, *J* = 7.8 Hz, 1H, H-pyrimidine), 5.55 (t, *J* = 4.6 Hz, 1H, H-3'), 5.50 (s, 1H, H-2), 5.37 (dd, *J* = 9.8, 3.3 Hz, 1H, H-2'), 5.27 (t, *J* = 9.8 Hz, 1H, H-4'), 5.04 (s, 1H, **H-1'**), 4.50 (s, 1H, H-4), 4.47 (d, *J* = 5.8 Hz, 1H, H-5), 4.34 (t, *J* = 5.0 Hz, 1H, H-3), 4.00 (dd, *J* = 9.2, 4.6 Hz, 1H, H-5'), 3.70 (s, 2H, H-6'), 3.37 (s, 3H, OMe), 2.16 (s, 3H, CH_3-OAc), 2.11 (s, 3H, CH_3-OAc), 2.03 (s, 3H, CH_3-OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.09, 170.48, 170.40, 170.36, 165.49, 163.57, 150.29, 140.35, 133.73, 129.98, 128.76, 128.60, 103.57, 96.78, 88.74, 82.12, 77.87, 76.13, 73.97, 72.62, 69.10, 65.87, 61.43, 58.83, 20.83, 20.79, 20.69. HRMS (ESI) calcd for $C_{30}H_{35}N_3O_{16}Na$ $[M+Na]^+$: 716.1910, found: 716.1913.

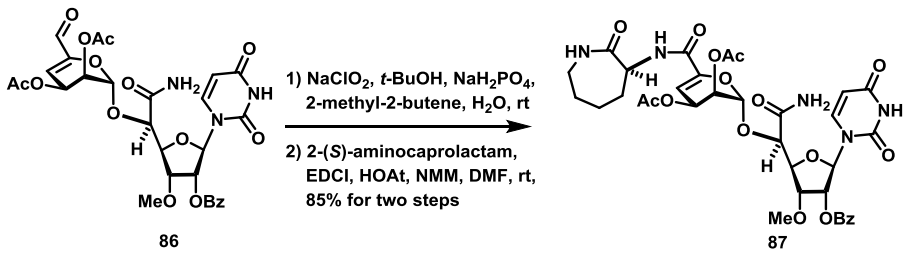
(2,3-Di-acetyl-5-formyl-4,5-dihydro-α-D-mannopyranosyl)-(1→5)-(5-acetamine-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) uracil (86)



85-1 86

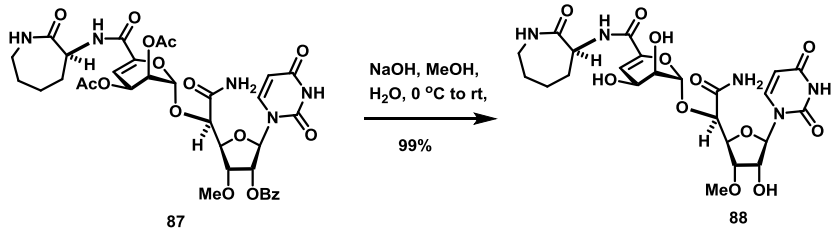
To a solution of compound **85-1** (55 mg, 0.079 mmol) in 1.4 mL CH_2Cl_2 was added 4 Å powdered molecular sieves (140 mg), 4-methylmorpholine N-oxide (NMO) (90 μL, 0.437 mmol) at room temperature under Ar. The mixture was stirred at room temperature for 20 min, then tetrapropylammonium perruthenate (TPAP) (10 mg, 0.028 mmol) was added. This solution was kept stirring at room temperature for 6 h, filtered through a Celite pad and concentrated *in vacuo*. Purification by silica gel column chromatography (CH_2Cl_2/MeOH =35/1) afforded **86** (27 mg, 55%) as a white solid and recovered starting material **85-1** (20 mg, 36%). Resubjection of **85-1** (20 mg, 0.028 mmol) to the reaction conditions produced another 8 mg (15%) of **86** (total 70%) and recovered starting material **85-1** (11 mg, 20%). R_f = 0.26 (CH_2Cl_2/MeOH =20/1). $[\alpha]_D^{20}$ = +26.86 (c 0.11, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H, NH), 9.33 (s, 1H, H-CHO), 8.02 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.10 (s, 1H, NH-amide), 6.48 (s, 1H, NH-amide), 6.03 (s, 2H, **H-1** and H-4'), 5.94 (s, 1H, H-3'), 5.88 (d, *J* = 8.0 Hz, 1H, H-pyrimidine), 5.68 (s, 1H, H-2'), 5.38 (d, *J* = 2.8 Hz, 1H, **H-1'**), 5.31 (t, *J* = 4.8 Hz, 1H, H-2), 4.64 (s, 1H, H-5), 4.60 – 4.53 (m, 1H, H-4), 4.05 – 3.99 (m, 1H, H-3), 3.29 (s, 3H, OMe), 2.11 (s, 3H, CH_3-OAc), 2.10 (s, 3H, CH_3-OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.25, 170.44, 170.21, 169.95, 165.48, 163.23, 150.14, 149.09, 140.25, 133.73, 129.98, 128.70, 128.58, 118.08, 103.58, 96.97, 82.30, 77.93, 74.07, 64.92, 64.22, 62.95, 59.01, 54.21, 44.83, 20.66, 20.65. HRMS (ESI) calcd for $C_{28}H_{29}N_3O_{14}Na$ $[M+Na]^+$: 654.1542, found: 654.1546.

(2,3-Di-acetyl-4,5-dihydro-5-(2-(S)-aminocaprolactamide)-α-D-mannopyranosyl)-(1→5)-(5-acetamide-3-*O*-methyl-2-*O*-benzoyl-β-L-talofuranoyl) uracil (87)



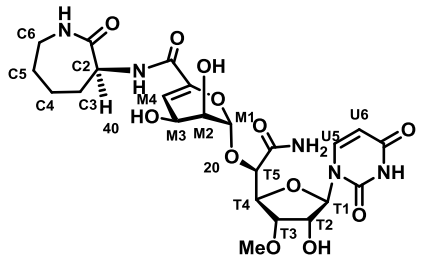
To a solution of the aldehyde **86** (21 mg, 0.033 mmol) in *t*-BuOH (1.68 mL) and 2-methyl-2-butene (1.34 mL) was added a solution of NaH_2PO_4 (24 mg, 0.20 mmol) and $NaClO_2$ (18 mg, 0.20 mmol) in H_2O (1.7 mL) at room temperature. The mixture was vigorously stirred at room temperature for 4 h, then concentrated *in vacuo* to produce a yellow solid. Washed the solid with MeOH and concentrated to give the light yellow crude. The above crude was dissolved in 1.7 mL anhydrous DMF, then 2-(S)-aminocaprolactam (17 mg, 0.1 mmol), 1-hydroxy-7-azabenzotriazole (HOAt) (12.6 mg, 0.099 mmol), EDCI (18.9 mg, 0.099 mmol), 4-methylmorpholine (NMM) (23 μL, 0.198 mmol) were added at room temperature under Ar. The mixture was stirred at room temperature for 6 h and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH =30/1) to afford **87** (21 mg, 85% over two steps) as a white solid. R_f = 0.30 (CH_2Cl_2/MeOH =20/1). $[\alpha]_D^{20}$ = +60.47 (c 0.09, $CHCl_3$), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 8.12 – 8.01 (m, 3H), 7.80 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.32 (s, 1H), 6.45 (s, 1H), 6.06 (d, *J* = 3.6 Hz, 1H, H-4'), 5.89 (d, *J* = 8.2 Hz, 1H, H-pyrimidine), 5.85 (s, 1H, **H-1**), 5.70 (t, *J* = 4.1 Hz, 1H, H-3'), 5.58 (s, 2H, H-2 and **H-1'**), 5.35 (d, *J* = 4.7 Hz, 1H, H-2'), 4.65 – 4.57 (m, 2H, CH-aminocaprolactam and H-5), 4.56 – 4.51 (m, 1H, H-4), 4.22 (s, 1H, H-3), 3.26 (s, 5H, OMe and CH_2-aminocaprolactam), 2.12 (s, 3H, CH_3-OAc), 2.05 (s, 3H, CH_3-OAc), 2.00 (m, 2H, CH_2-aminocaprolactam), 1.86 – 1.74 (m, 2H, CH_2-aminocaprolactam), 1.60 – 1.48 (m, 1H, CH_2-aminocaprolactam), 1.44 – 1.35 (m, 1H, CH-aminocaprolactam). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.03, 170.51, 170.02, 165.37, 163.30, 158.75, 150.60, 144.44, 133.62, 130.03, 128.86, 128.54, 103.47, 97.99, 81.74, 73.61, 62.92, 58.95, 51.76, 42.14, 31.41, 29.70, 28.45, 27.92, 20.76, 20.70. HRMS (ESI) calcd for $C_{34}H_{38}N_5O_{15}Na$ $[M - H]^-$: 756.2370, found: 756.2370.

Capuramycin 88

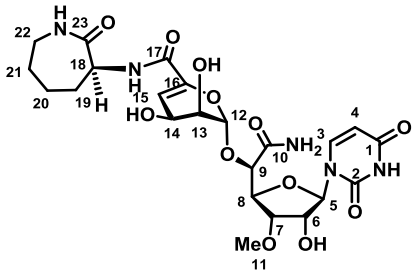


To a solution of **87** (7 mg, 0.009 mmol) in MeOH (0.8 mL) was added a solution of NaOH (1.1 mg, 0.027 mmol) in H_2O (0.4 ml) at 0 ℃. The mixture was stirred at 0 ℃ for 30 min, then it was warmed to room temperature and stirred for another 2.5 h. The solution was quenched with AcOH (3μL) and concentrated *in vacuo*. The resulting residue was purified by a Sephadex LH-20 ($CHCl_2$/MeOH = 1/1) to afford **88**[28] (5 mg, 99%) as a white solid. R_f = 0.10 (CH_2Cl_2/MeOH =8/1). $[\alpha]_D^{20}$ = +85.33 (c 0.09, H_2O), ^{1}H NMR (400 MHz, D_2O) δ 7.76 (d, *J* = 8.1 Hz, 1H), 6.07 – 6.00 (m, 1H), 5.87 (d, *J* = 8.1 Hz, 1H), 5.77 (d, *J* = 3.4 Hz, 1H), 5.40 (d, *J* = 3.4 Hz, 1H), 4.77 (d, *J* = 2.6 Hz, 1H), 4.64 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.52 (dd, *J* = 4.5, 2.7 Hz, 1H), 4.49 (dd, *J* = 6.3, 2.4 Hz, 1H), 4.40 (t, *J* = 4.2 Hz, 1H), 4.21 (t, *J* = 3.2 Hz, 1H), 3.76 (t, *J* = 5.7 Hz, 1H), 3.31(s, 3H), 3.34 – 3.24 (m, 2H), 2.06 – 1.90 (m, 2H), 1.87 – 1.73 (m, 2H), 1.69 – 1.58 (m, 1H), 1.33 – 1.43 (m, 1H). ^{13}C NMR (150 MHz, D_2O) δ 176.41, 173.15, 166.26, 161.60, 151.41, 141.68, 141.20, 109.55, 101.95, 99.48, 90.28, 81.77, 78.25, 75.67, 72.06, 64.91, 62.01, 57.97, 52.39, 41.54, 30.46, 27.74, 27.53. ^{13}C NMR (150 MHz, D_2O) δ 176.41, 173.15, 166.26, 161.60, 151.41, 141.68, 141.20, 109.55, 101.95, 99.48, 90.28, 81.77, 78.25, 75.67, 72.06, 64.91, 62.01, 57.97, 52.39, 41.54, 30.46, 27.74, 27.53. HRMS (ESI) calcd for $C_{23}H_{31}N_5O_{12}Na$ $[M+Na]^+$: 592.1861, found: 592.1863.

2.6.3 Comparison of the analytical data of Capuramycin and Synthetic 88



Position	Capuramycin[28]	Synthetic 88
U5	7.76 (d, 8.0)	7.76 (d, 8.1)
M4	6.01 (dd, 1.6, 2.4)	6.07 – 6.00 (m)
U6	5.87 (d, 8.0)	5.87 (d, 8.1)
T1	5.77 (d, 3.2)	5.77 (d, 3.4)
M1	5.40 (d, 3.2)	5.40 (d, 3.4)
T5	4.76 (d, 2.0)	4.77 (d, 2.6)
C2	4.64 (d, 11.2)	4.64 (dd, 11.2, 1.8)
M3	4.52 (dd, 2.4, 8.0)	4.52 (dd, 4.5, 2.7)
T4	Missing	4.49 (dd, 6.3, 2.4)
T2	4.39 (dd, 3.2, 4.8)	4.40 (t, 4.2)
M2	4.20 (dd, 3.2, 6.4)	4.21 (t, 3.2)
T3	3.75 (t, 4.8)	3.76 (t, 5.7)
OMe	3.31 (s)	3.31(s)
C6	3.29 (s)	3.34 - 3.24 (m)
C3	2.02-1.90 (m)	2.06 -1.90 (m)
C4	1.87- 1.73 (m)	1.87 - 1.73 (m)
C5	1.65 (m), 1.39 (m, 1H)	1.69 - 1.58 (m), 1.43- 1.33 (m)



Position	Capuramycin[28]	Synthetic 88	Position	Capuramycin[28]	Synthetic 88
C-23	176.4	176.41	C-7	78.2	78.25
C-10	173.2	173.15	C-9	75.7	75.67
C-1	166.3	166.26	C-6	72.0	72.06
C-17	161.6	161.60	C-13	64.9	64.91
C-2	151.4	151.41	C-14	62.0	62.01
C-16	141.7	141.68	C-11	58.0	57.97
C-3	141.2	141.20	C-18	52.4	52.39
C-15	109.6	109.55	C-22	41.5	41.54
C-4	102.0	101.95	C-21	30.4	30.46
C-12	99.5	99.48	C-20	27.7	27.74
C-5	90.3	90.28	C-19	27.5	27.53
C-8	81.8	81.77			

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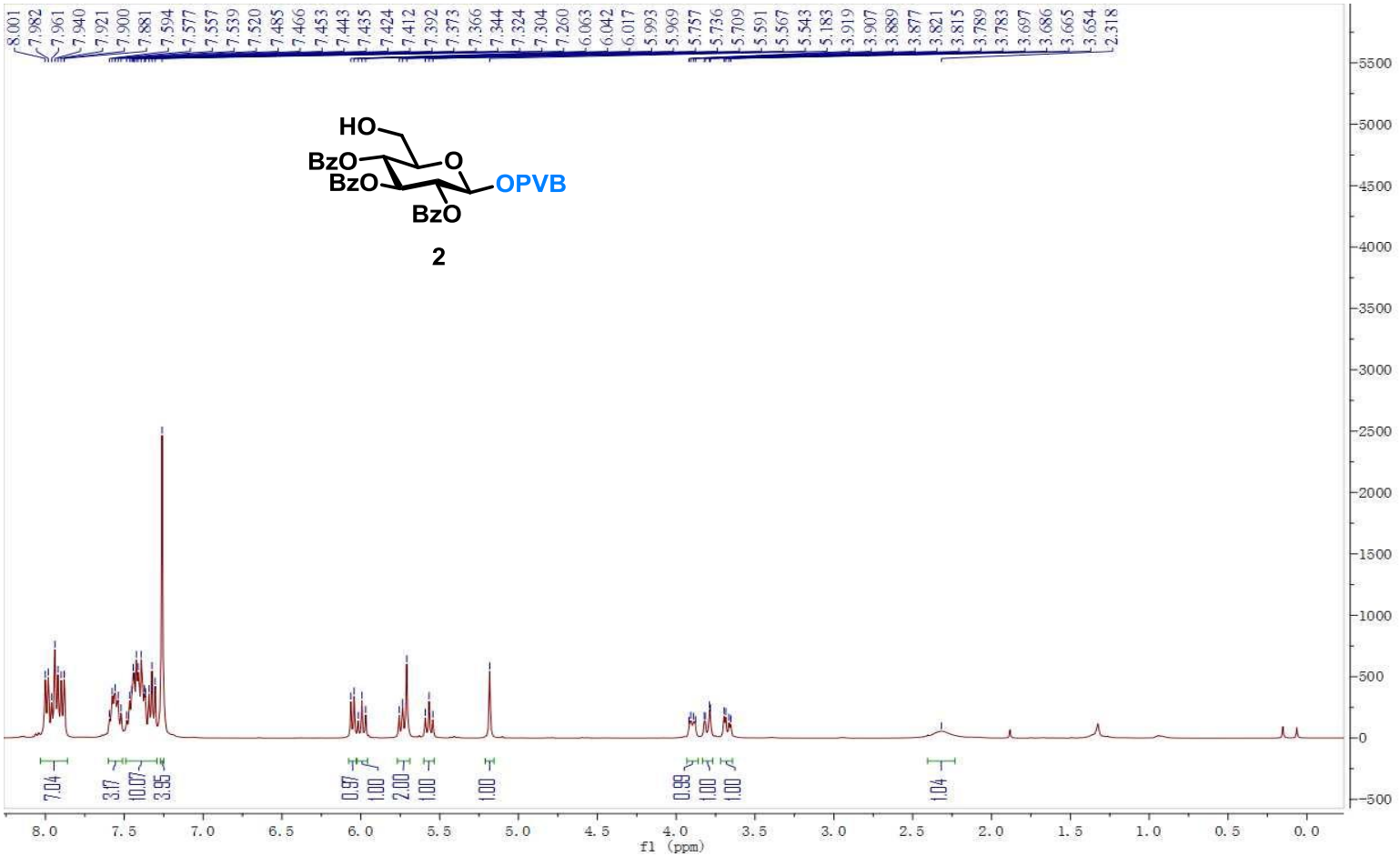
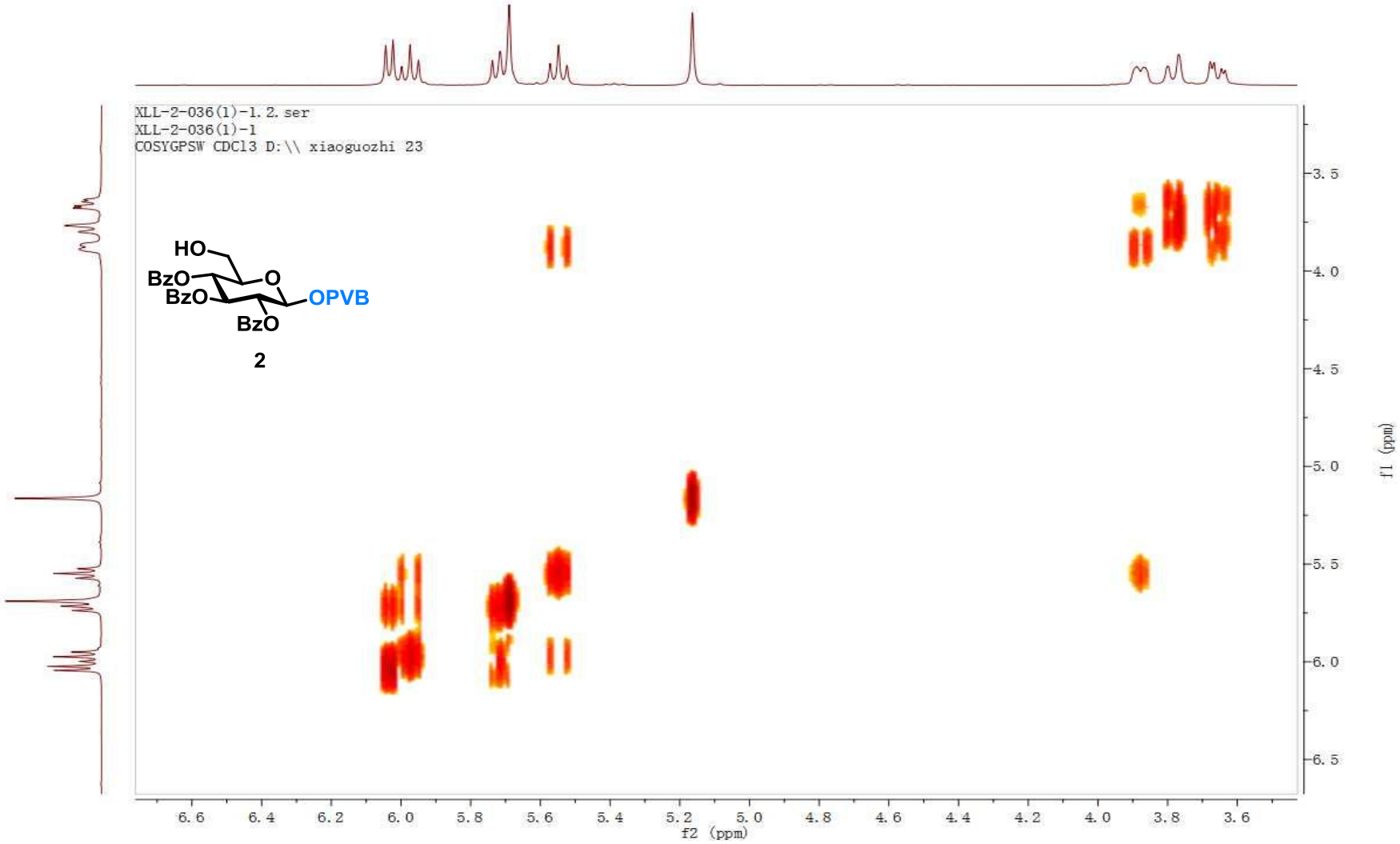
4 NMR Spectra for the New Compounds

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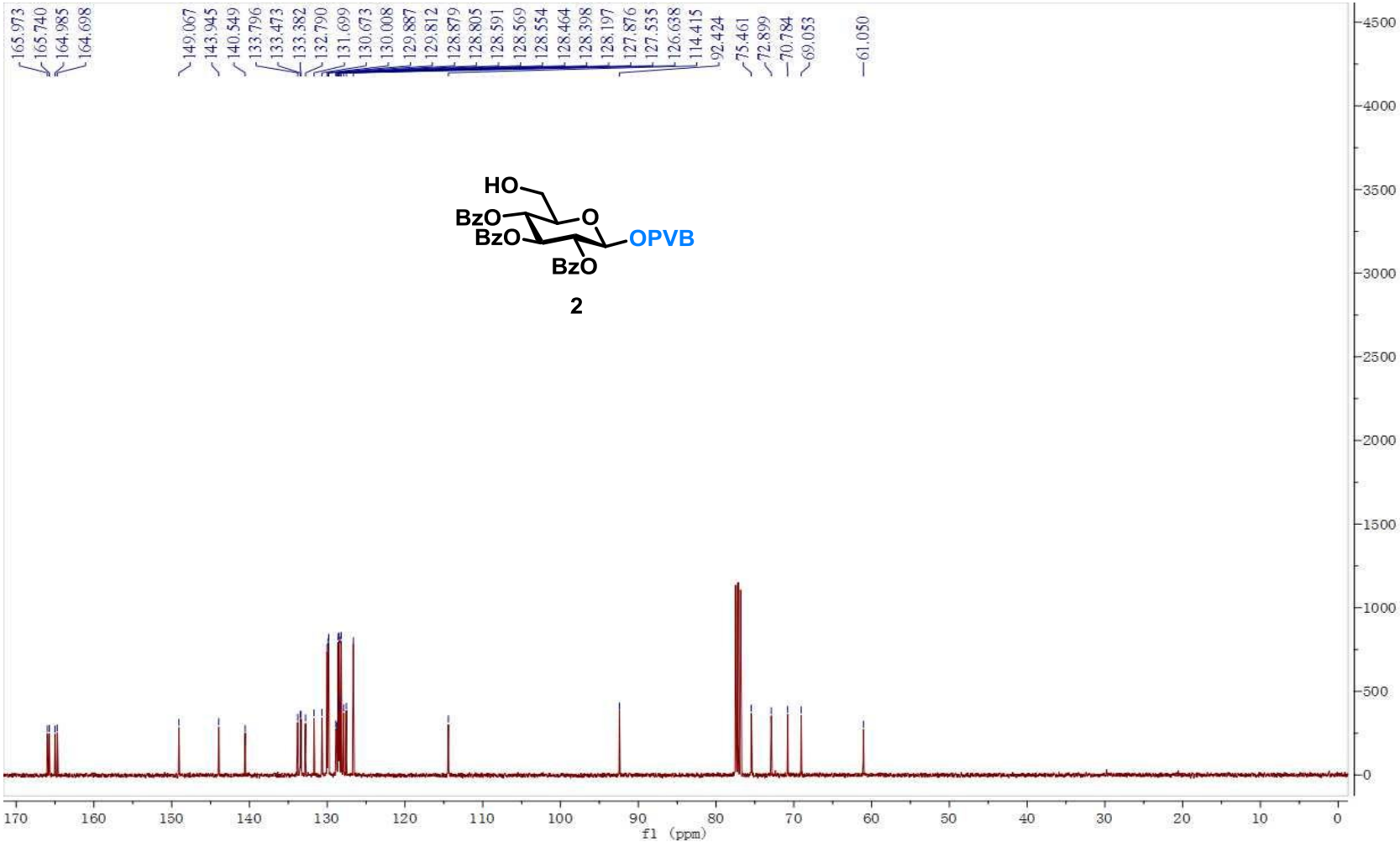
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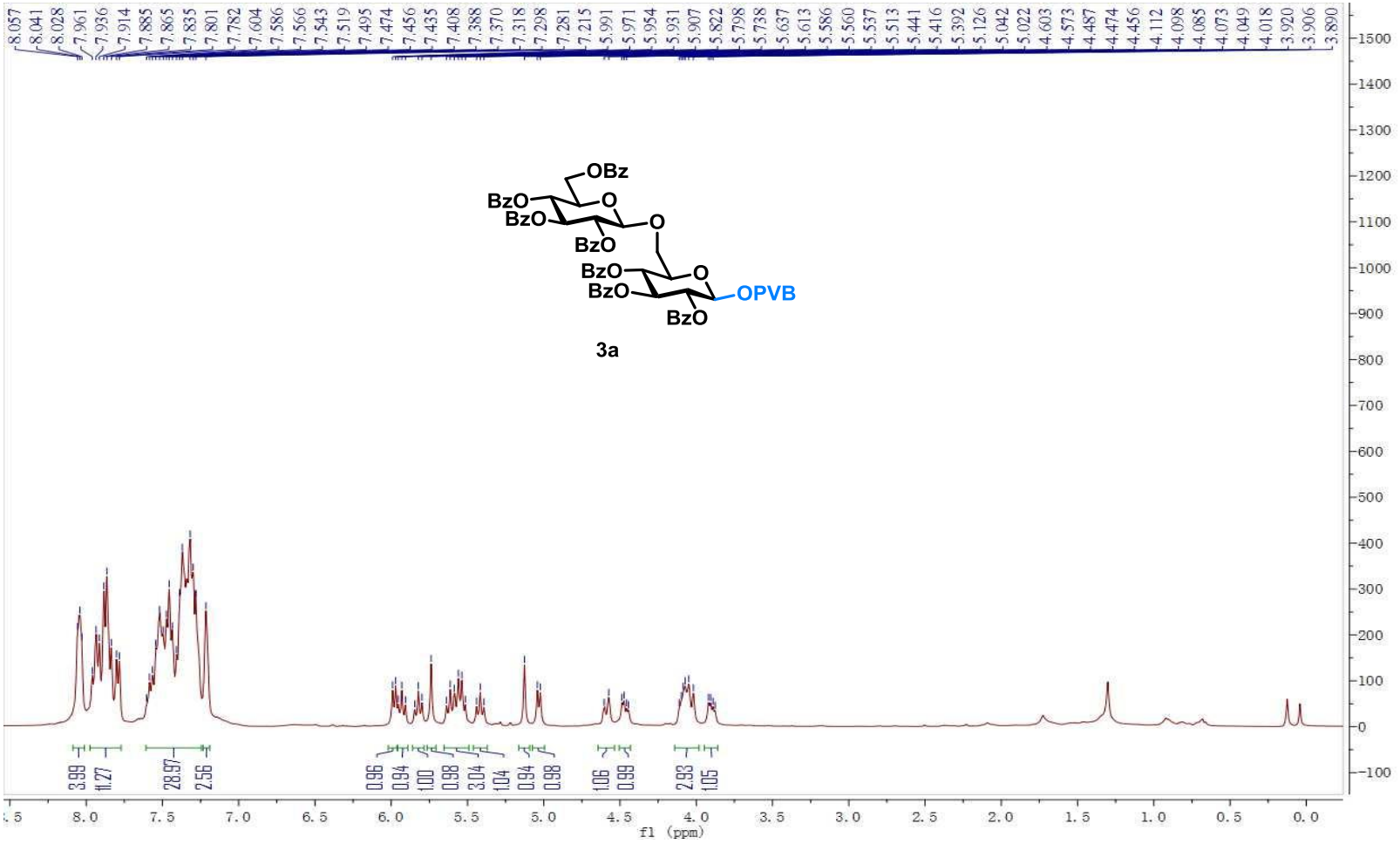
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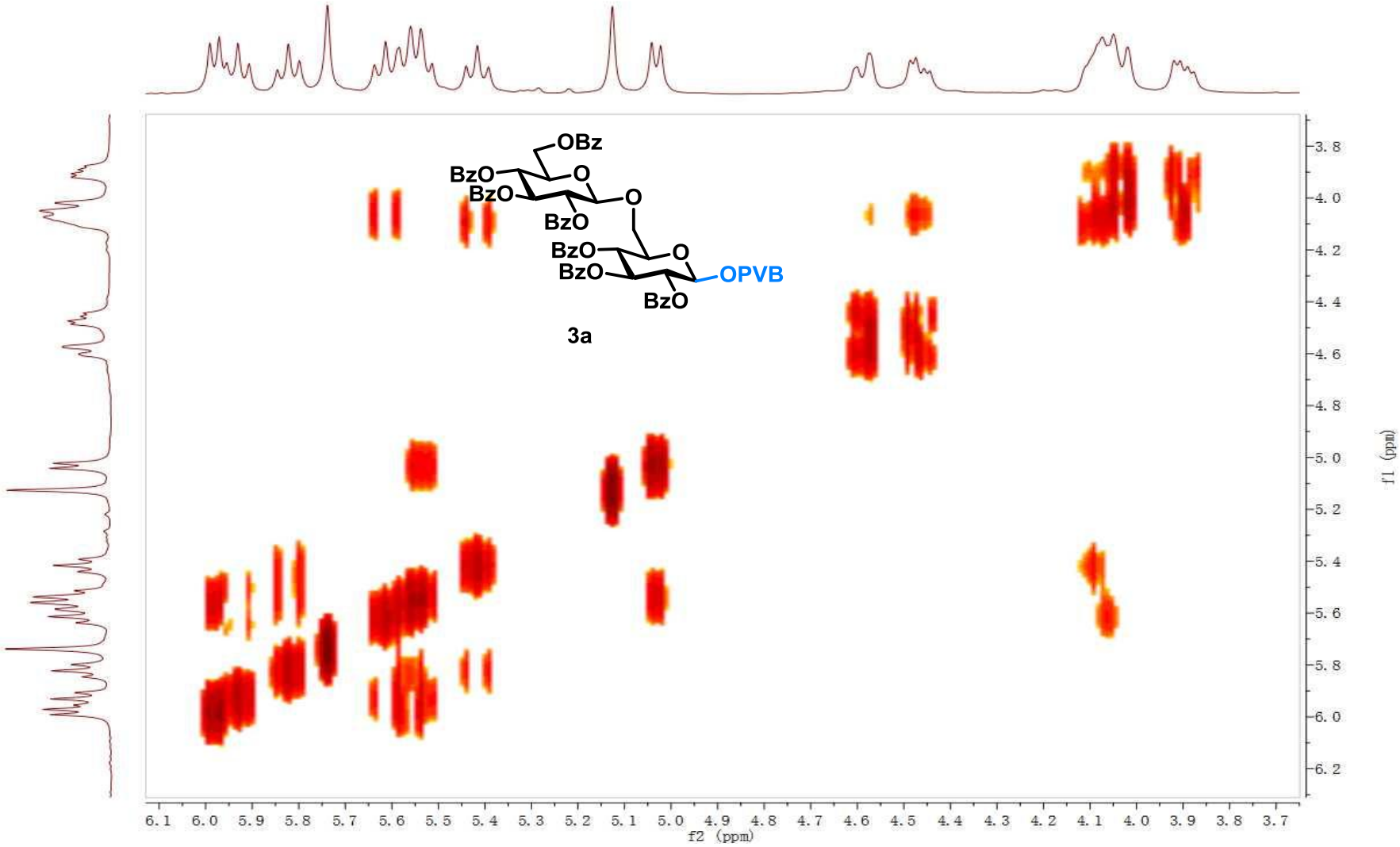
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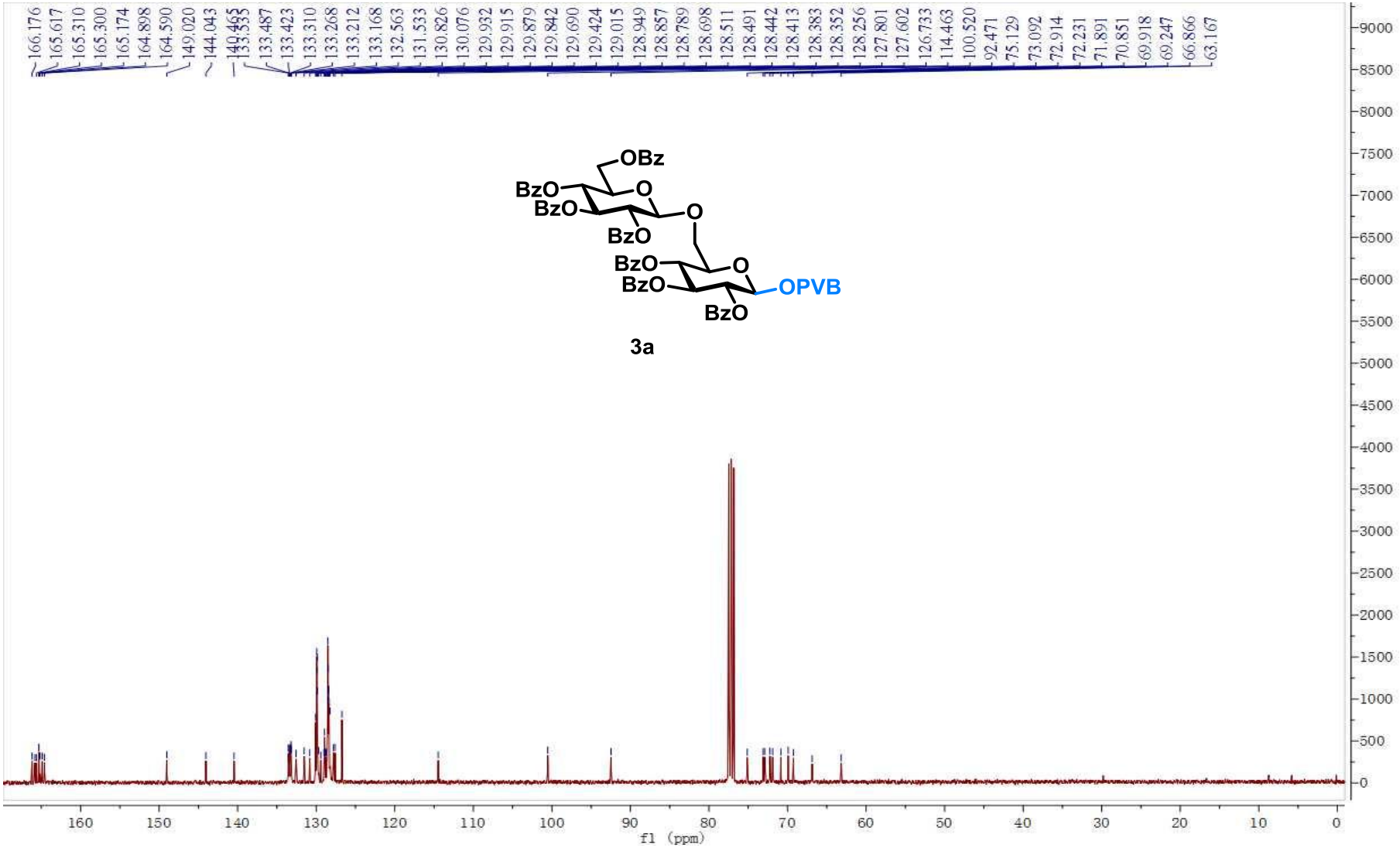
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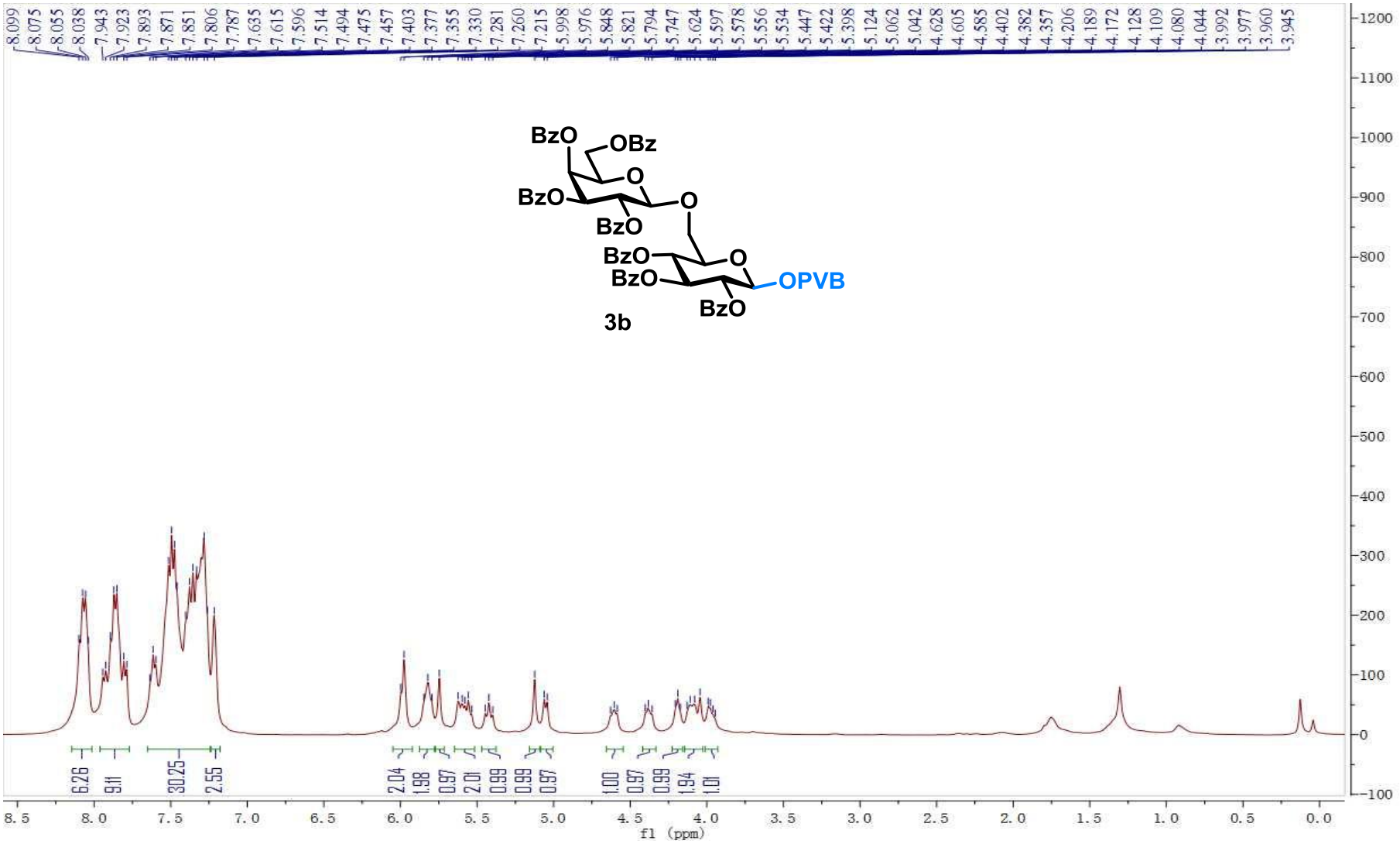
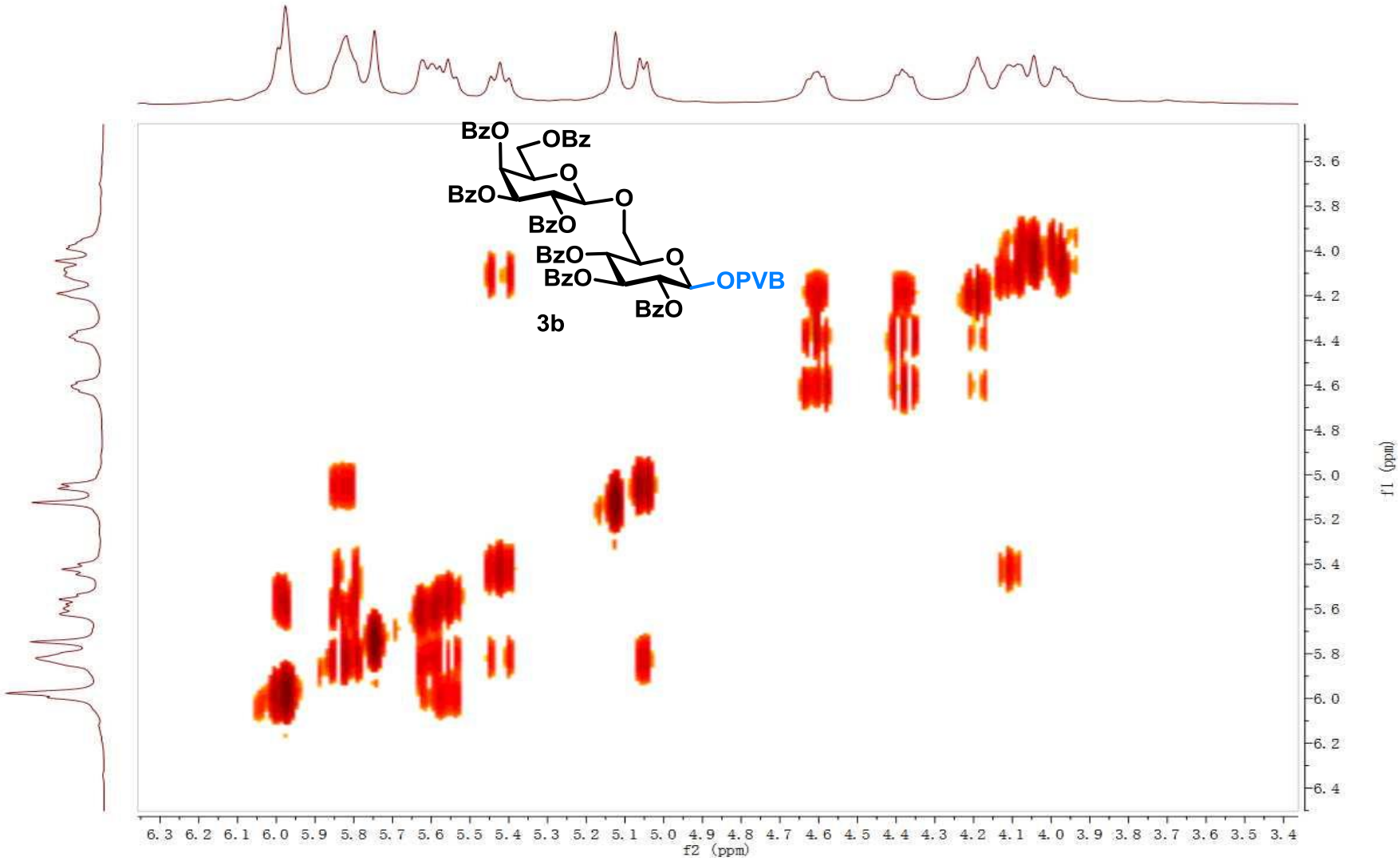
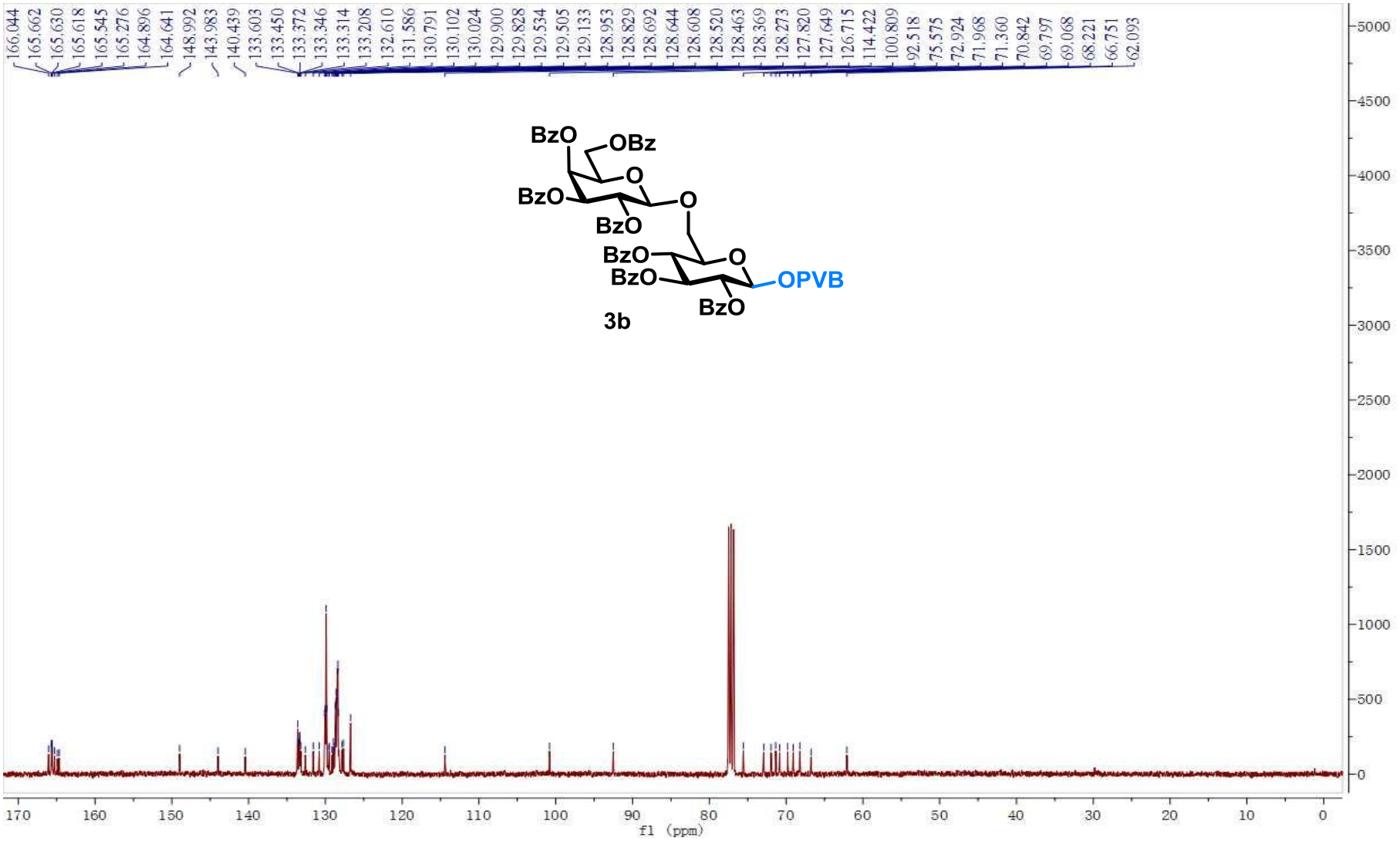
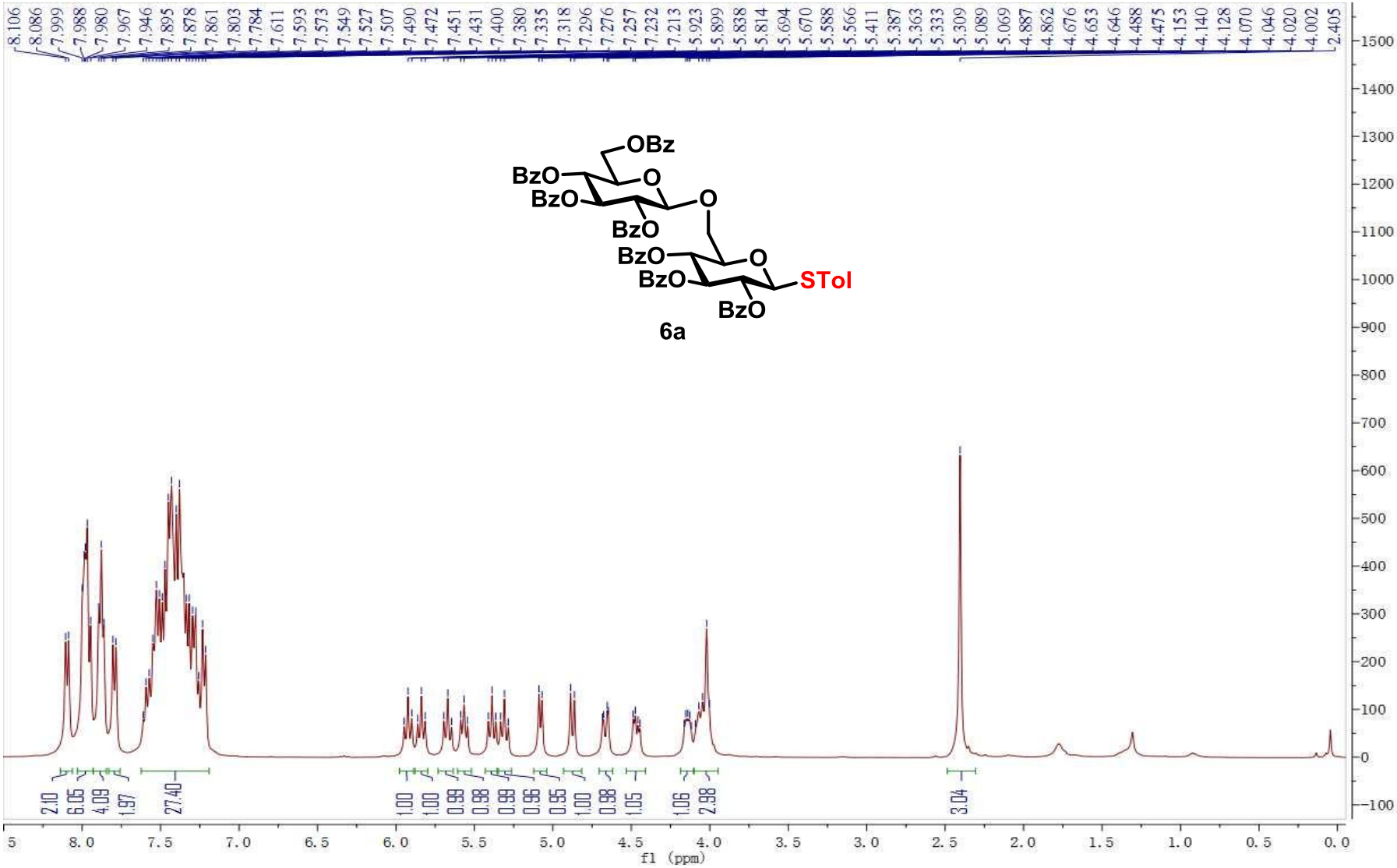
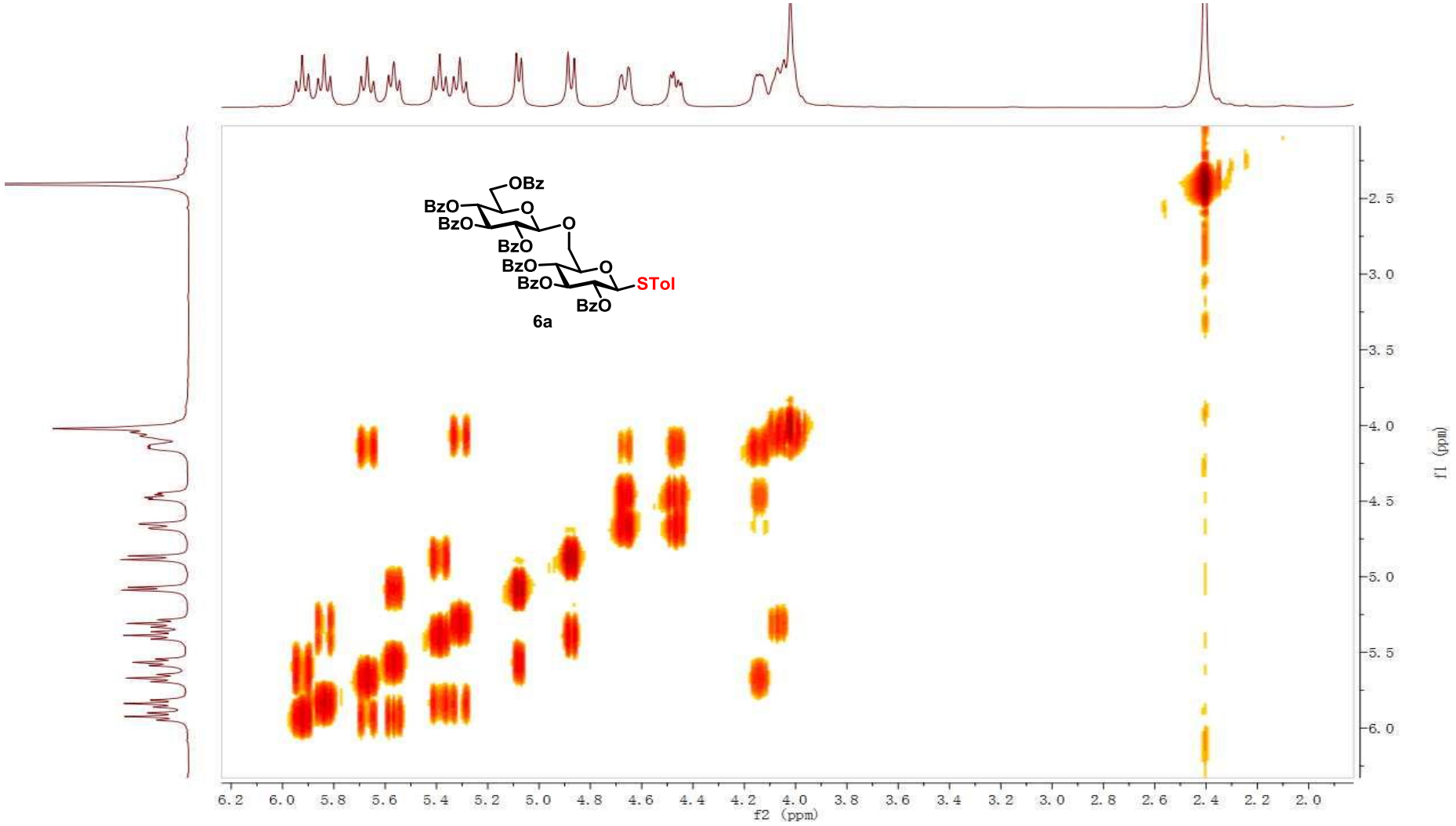
O
O
BzO
BzO
BzO
OPVB
3a
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

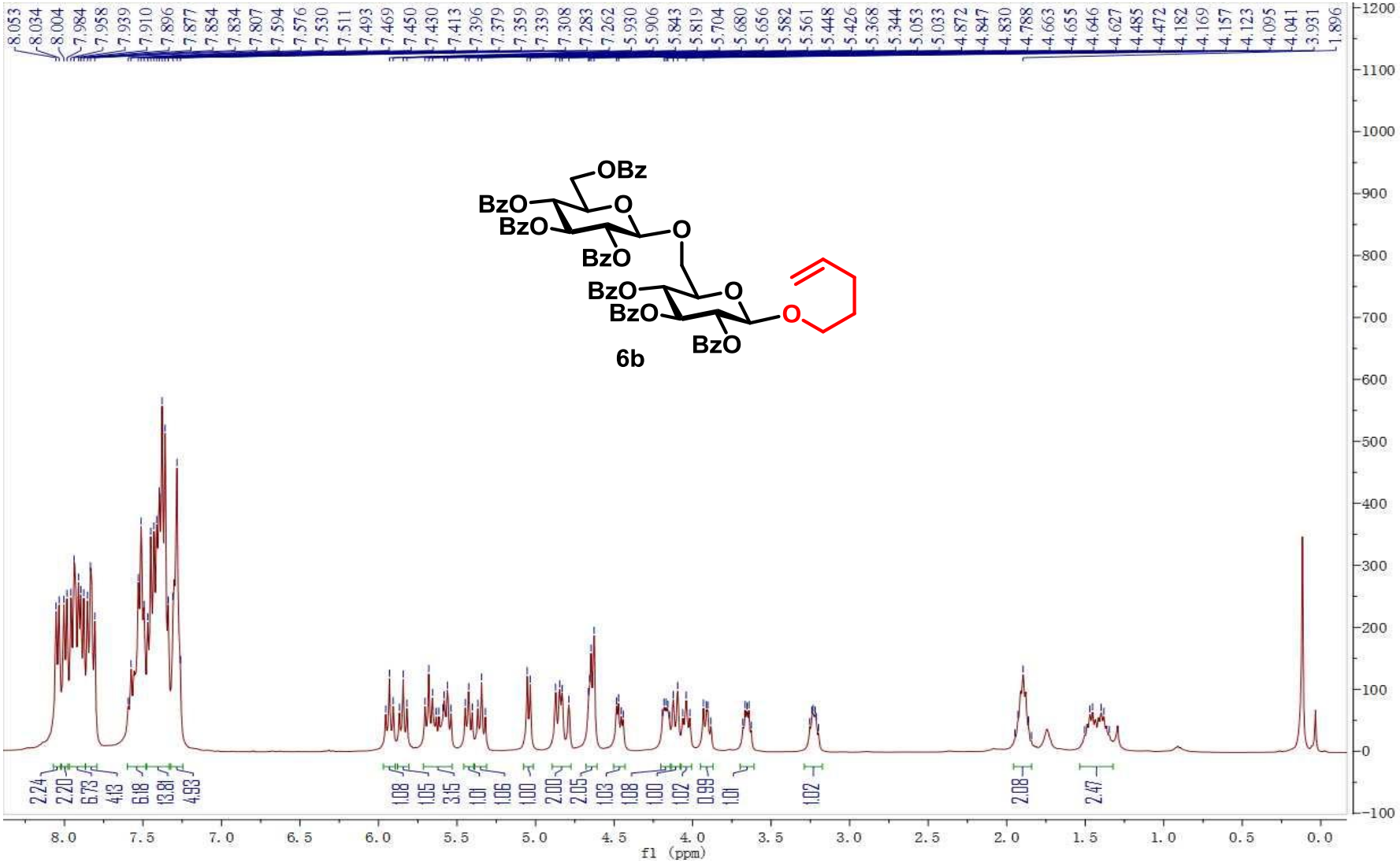

BzO
OBz
O
BzO
O
BzO
BzO
O
BzO
OPVB
BzO
3b
f1 (ppm)

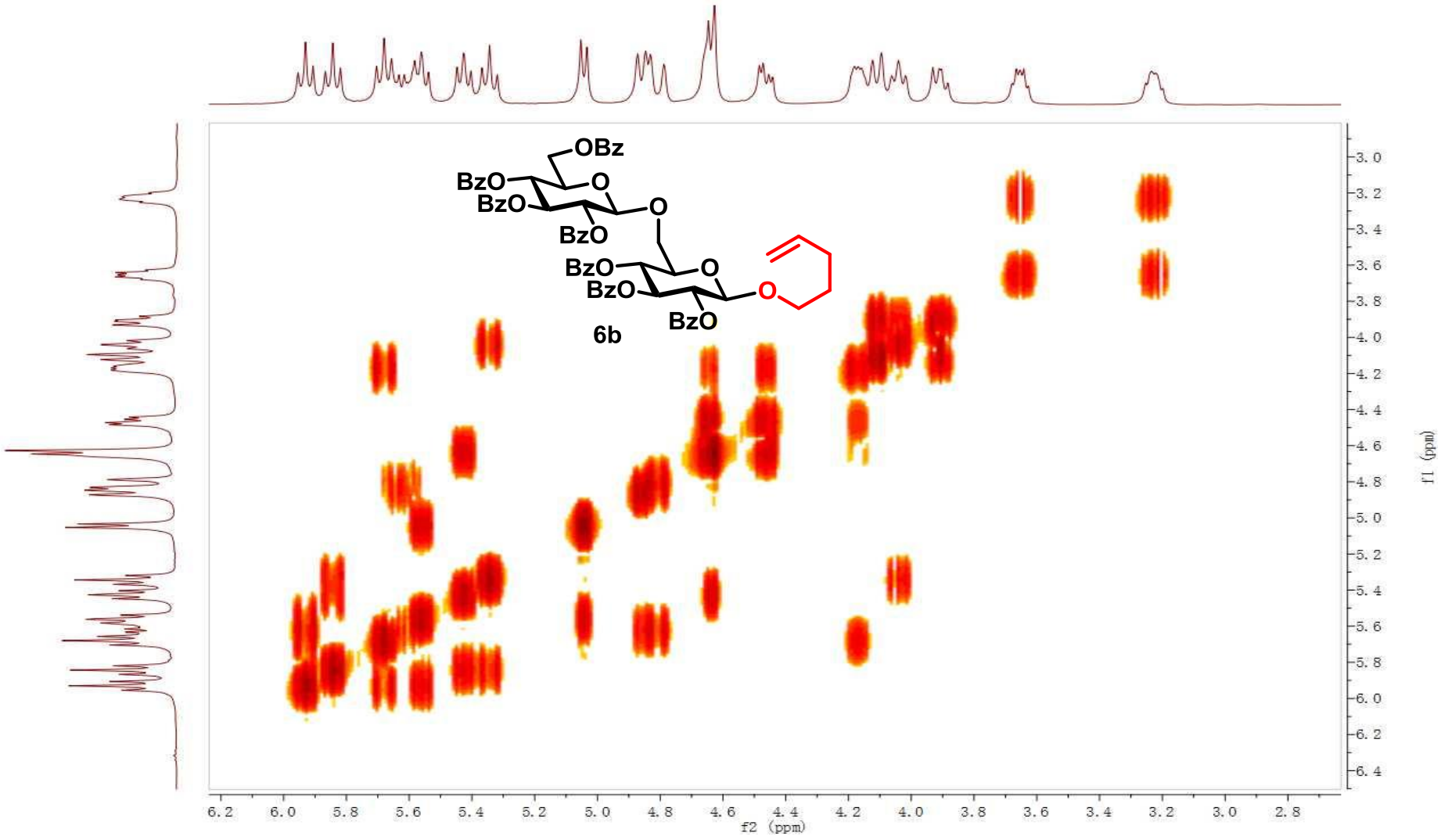

BzO
OBz
O
BzO
O
BzO
BzO
BzO
O
BzO
OPVB
3b
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4
f2 (ppm)
3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4
f1 (ppm)

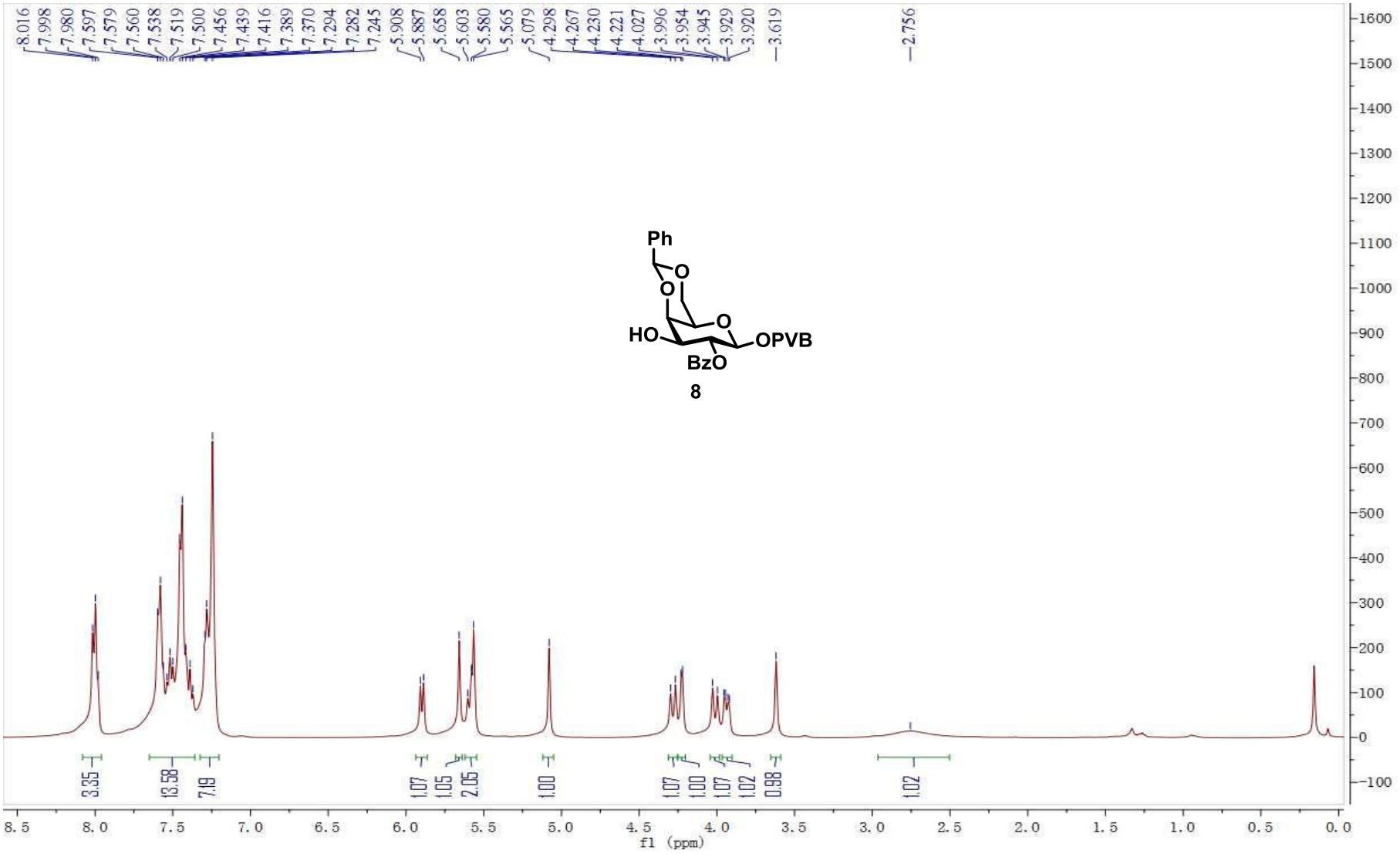

166.044
165.662
165.630
165.618
165.545
165.276
164.896
164.641
148.992
143.983
140.439
133.603
133.450
133.372
133.346
133.314
133.208
132.610
131.586
130.791
130.102
130.024
129.900
129.828
129.534
129.505
129.133
128.953
128.829
128.692
128.644
128.608
128.520
128.463
128.369
128.273
127.820
127.649
126.715
114.422
100.809
92.518
75.575
72.924
71.968
71.360
70.842
69.797
69.068
68.221
66.751
62.093
BzO
OBz
O
BzO
O
BzO
BzO
O
BzO
OPVB
BzO
3b
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

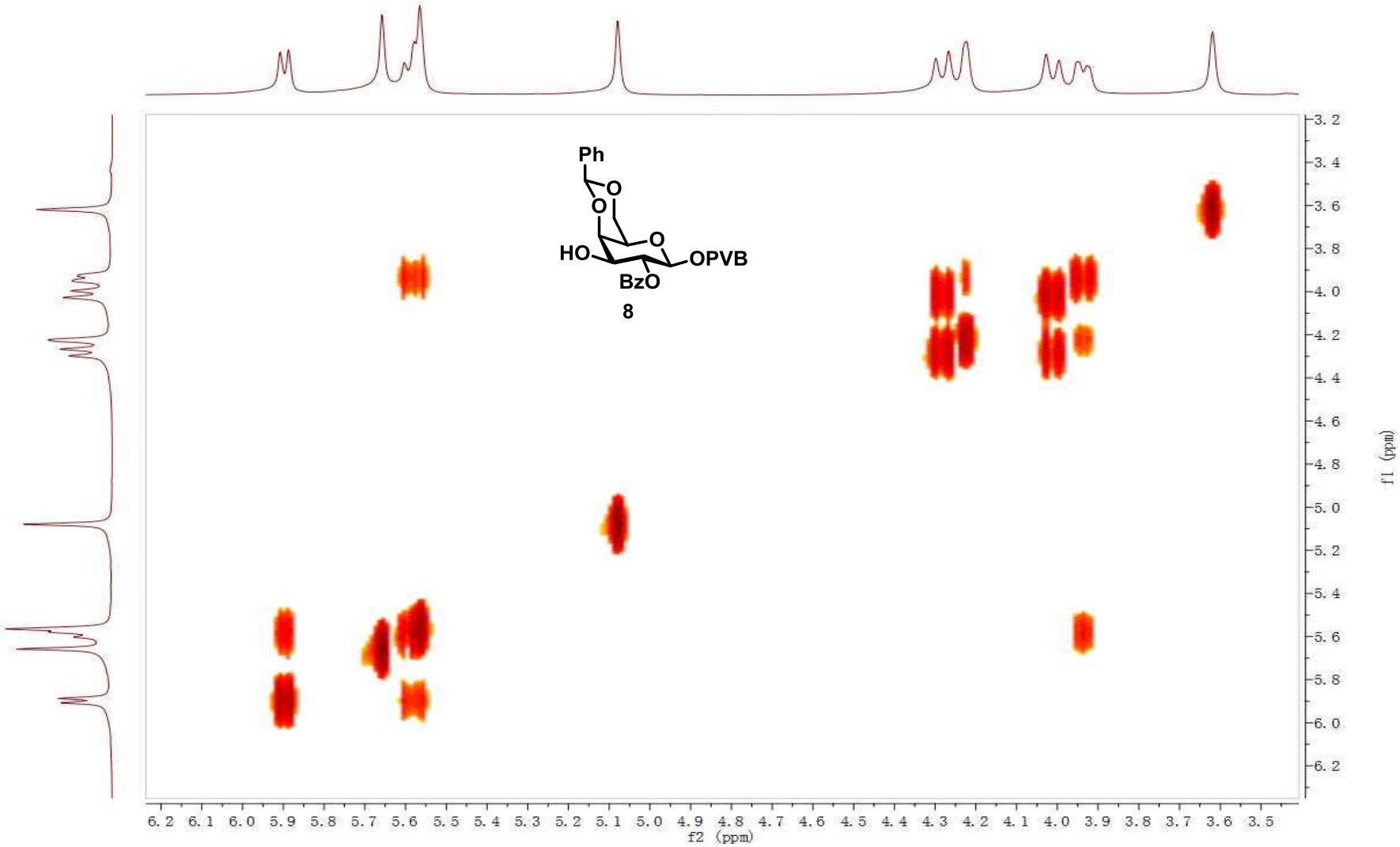

OBz
BzO
BzO
BzO
BzO
BzO
BzO
STol
6a
f1 (ppm)

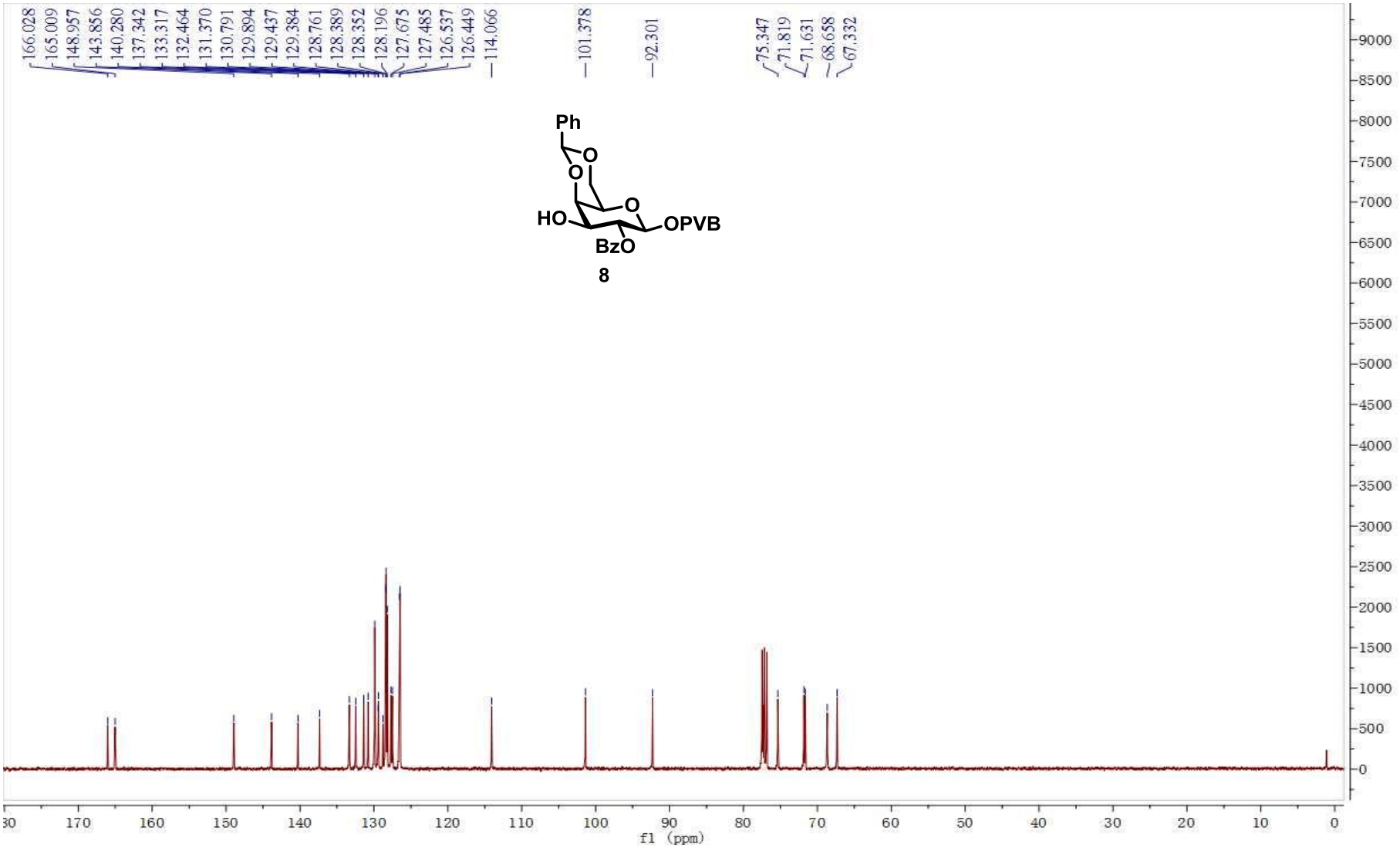

OBz
BzO
BzO
BzO
BzO
BzO
BzO
STol
6a
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f2 (ppm)
2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
f1 (ppm)

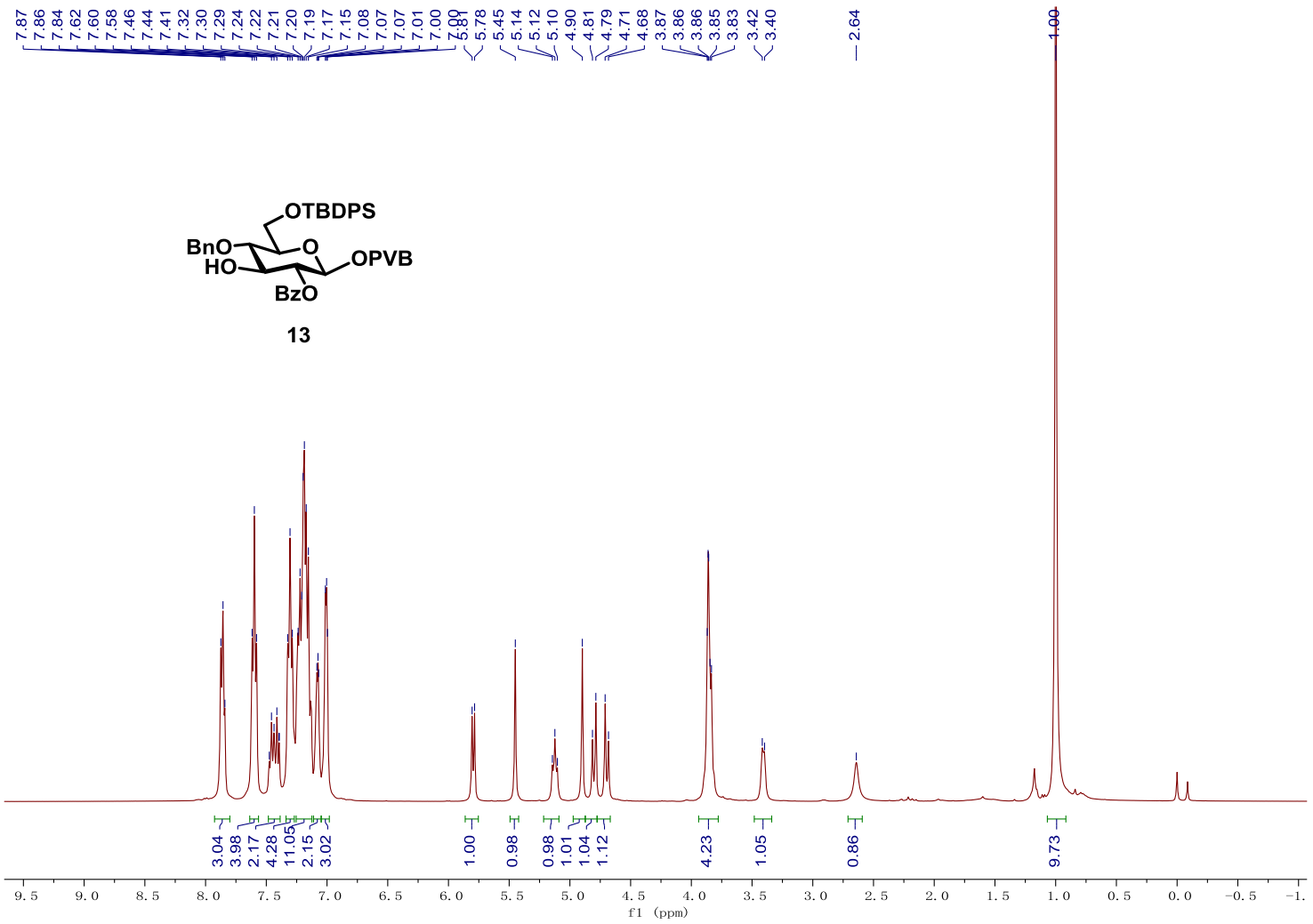

OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
6b
f1 (ppm)

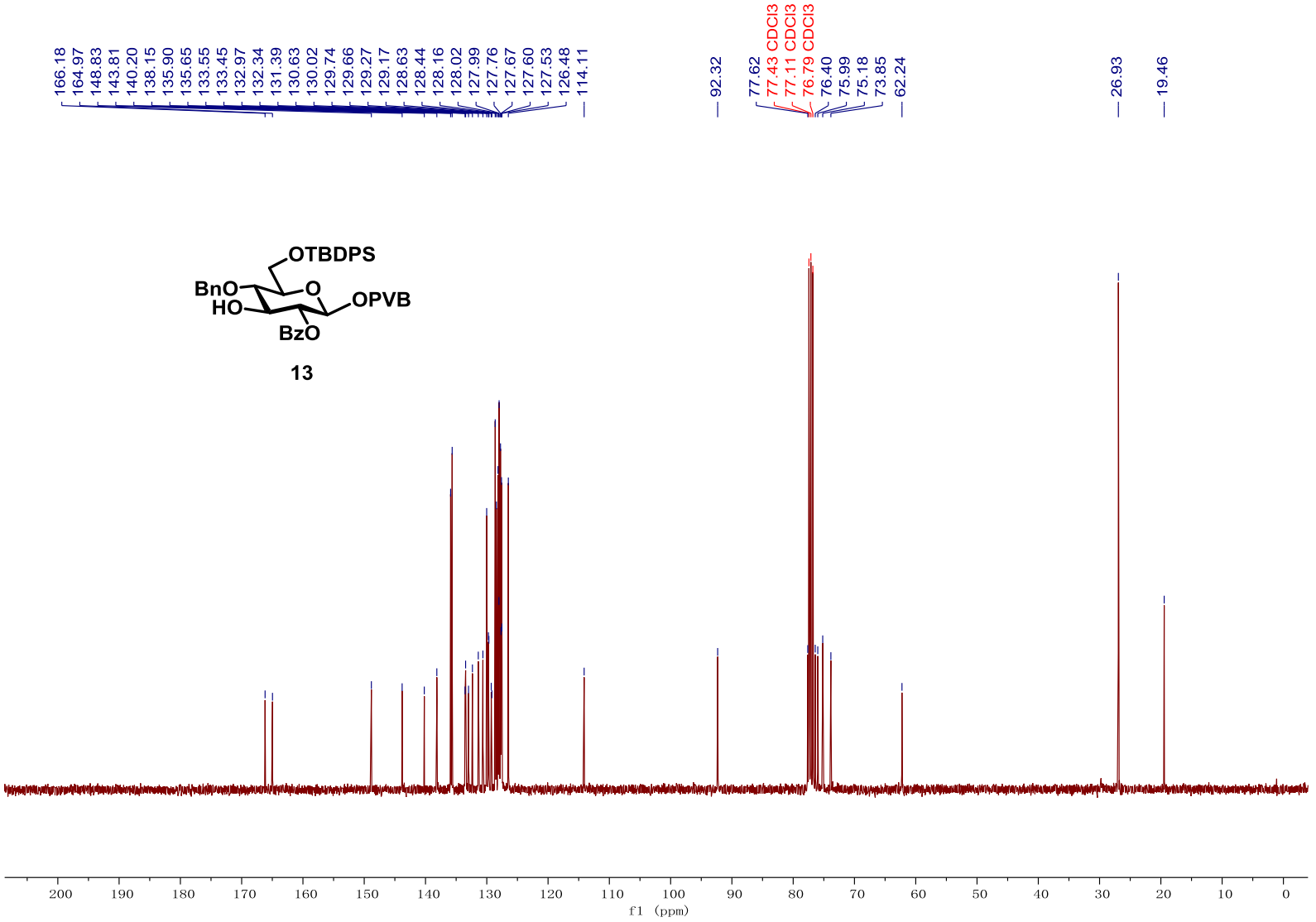

OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
BzO
6b
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
f1 (ppm)

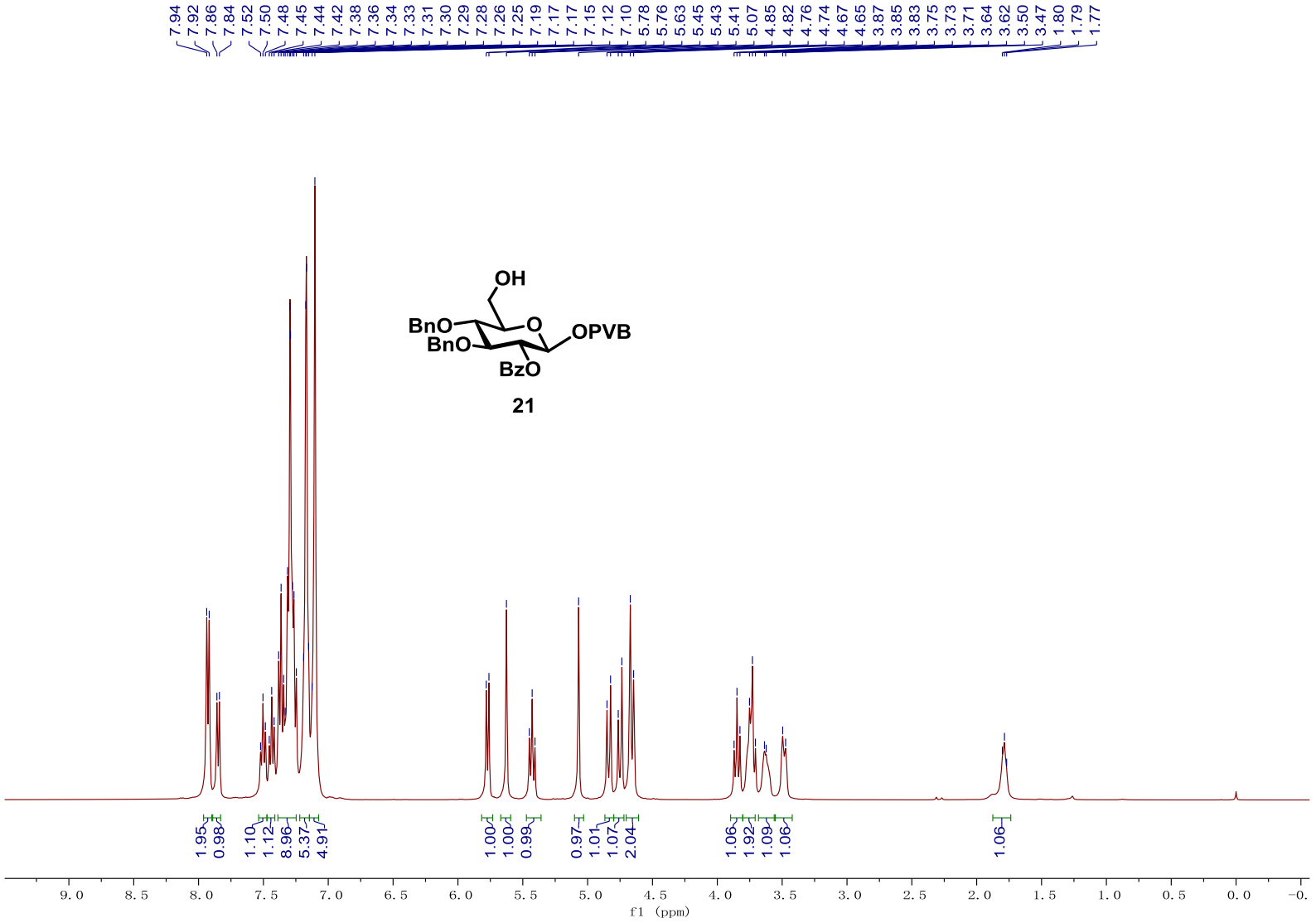

8.016
7.998
7.980
7.597
7.579
7.560
7.538
7.519
7.500
7.456
7.439
7.416
7.389
7.370
7.294
7.282
7.245
5.908
5.887
5.658
5.603
5.580
5.565
5.079
4.298
4.267
4.230
4.221
4.027
3.996
3.954
3.945
3.929
3.920
3.619
2.756
Ph
O
O
O
HO
OPVB
BzO
8
3.35
13.58
7.19
1.07
1.05
2.05
1.00
1.07
1.00
1.07
1.02
0.98
1.02
f1 (ppm)

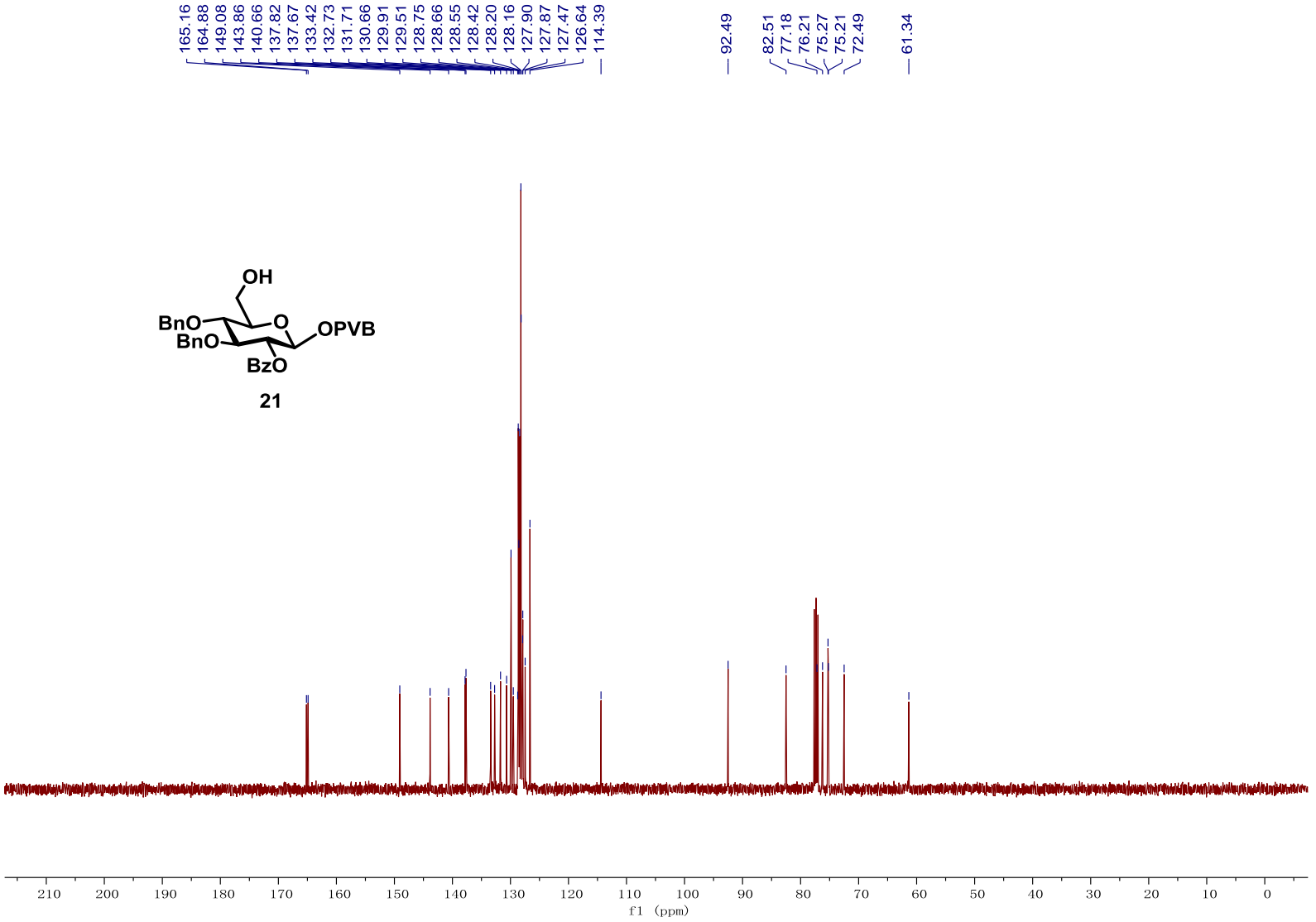

Ph
O
O
O
HO
OPVB
BzO
8
f2 (ppm)
f1 (ppm)

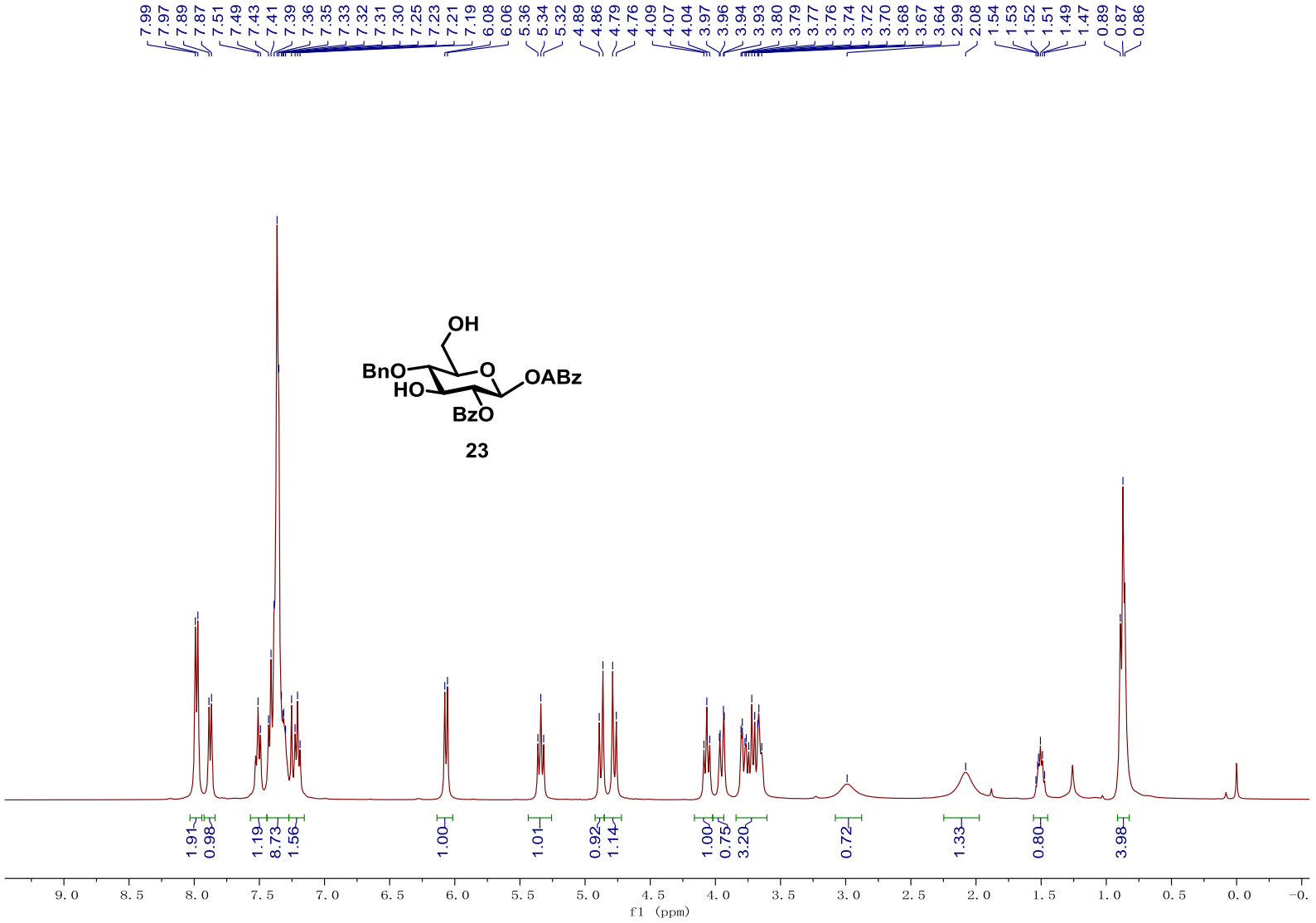

166.028
165.009
148.957
143.856
140.280
137.342
133.317
132.464
131.370
130.791
129.894
129.437
129.384
128.761
128.389
128.352
128.196
127.675
127.485
126.537
126.449
114.066
101.378
92.301
75.347
71.819
71.631
68.658
67.332
Ph
O
O
O
HO
OPVB
BzO
8
fl (ppm)

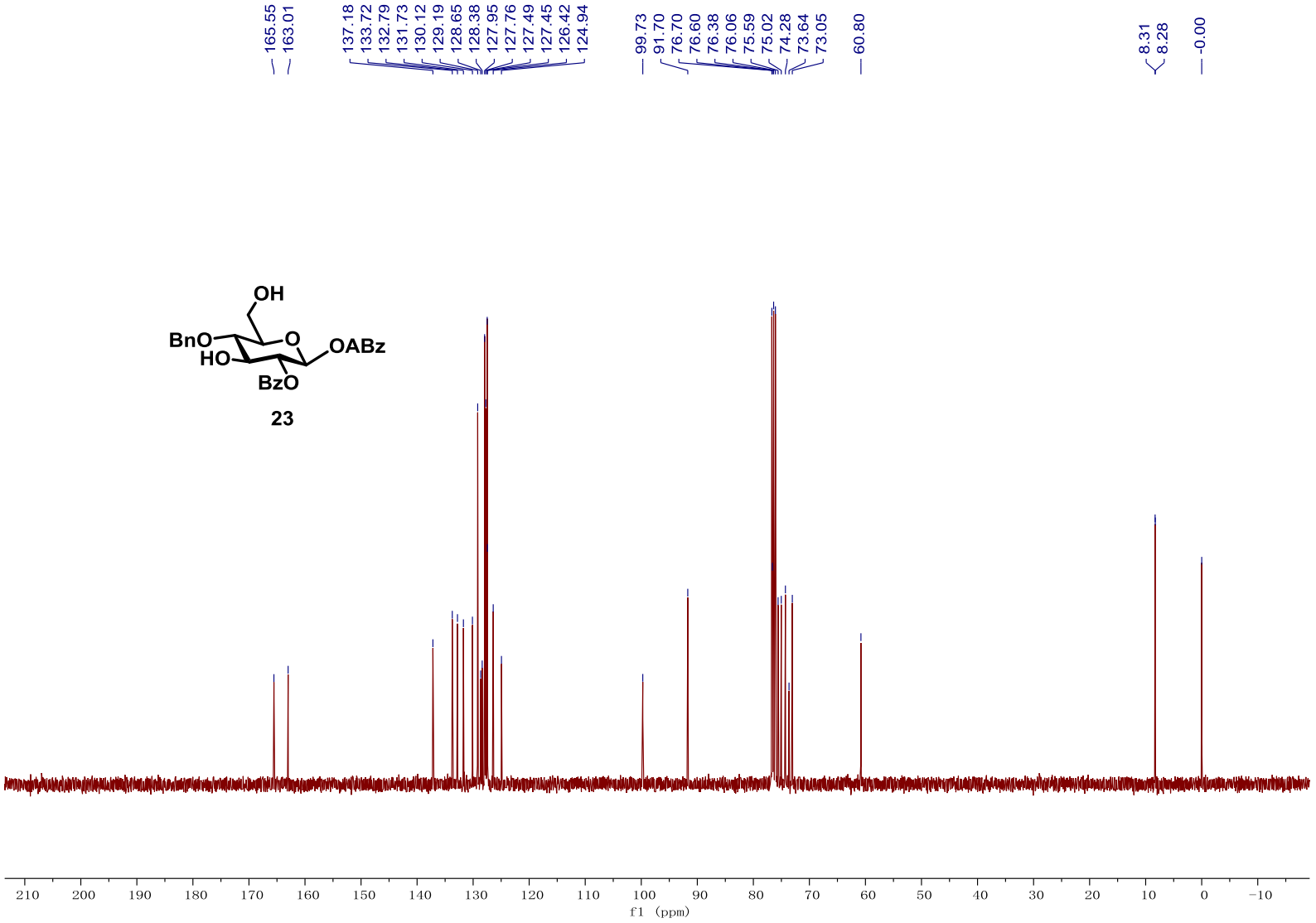

7.87
7.86
7.84
7.62
7.60
7.58
7.46
7.44
7.41
7.32
7.30
7.29
7.24
7.22
7.21
7.20
7.19
7.17
7.15
7.08
7.07
7.07
7.01
7.00
7.00
5.81
5.78
5.45
5.14
5.12
5.10
4.90
4.81
4.79
4.71
4.68
3.87
3.86
3.86
3.85
3.83
3.42
3.40
2.64
1.00
OTBDPS
BnO
O
OPVB
HO
BzO
13
3.04
3.98
2.17
4.28
11.05
2.15
3.02
1.00
0.98
0.98
1.01
1.04
1.12
4.23
1.05
0.86
9.73
f1 (ppm)

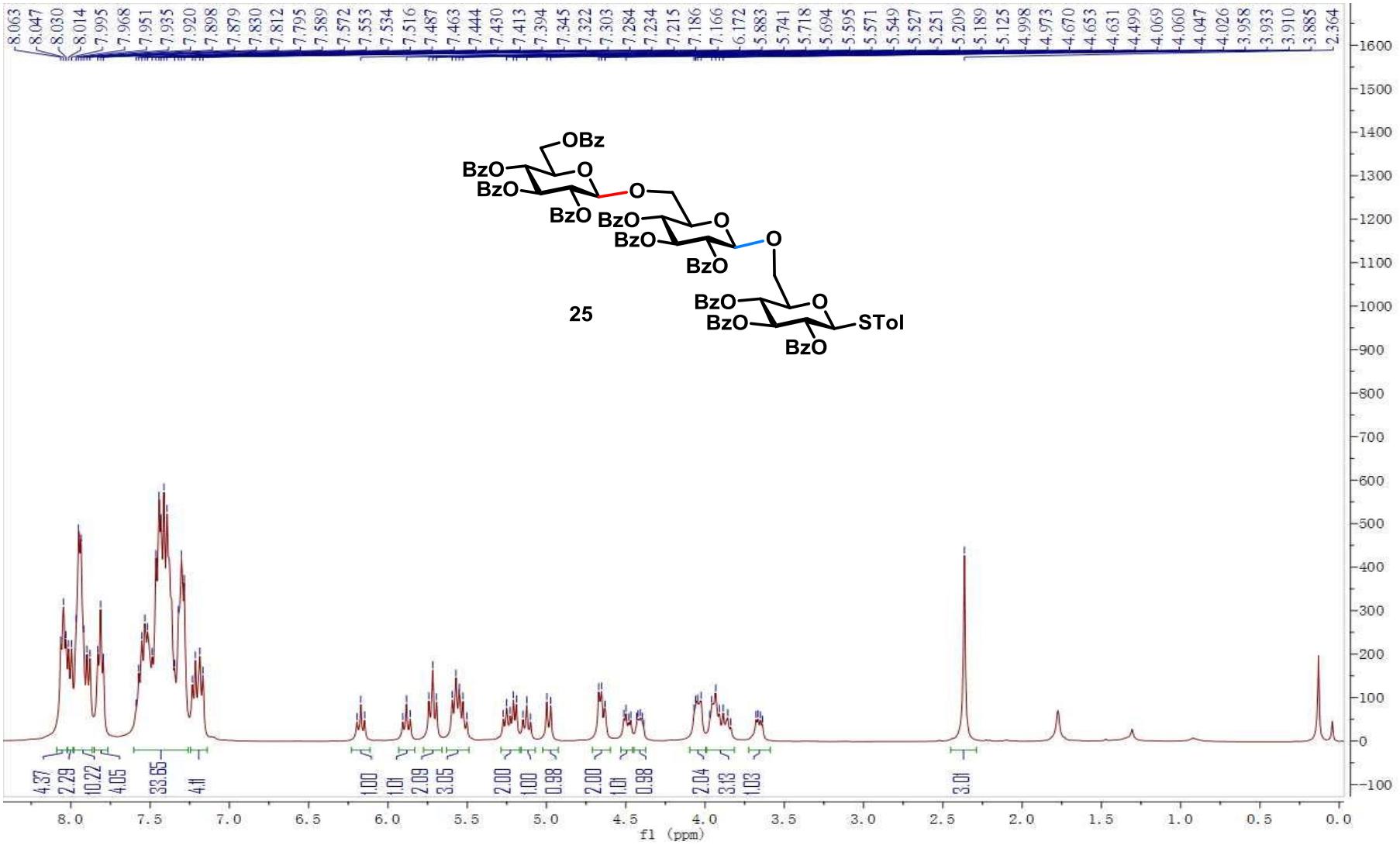

166.18
164.97
148.83
143.81
140.20
138.15
135.90
135.65
133.55
133.45
132.97
132.34
131.39
130.63
130.02
129.74
129.66
129.27
129.17
128.63
128.44
128.16
128.02
127.99
127.76
127.67
127.60
127.53
126.48
114.11
92.32
77.62
77.43 CDCl3
77.11 CDCl3
76.79 CDCl3
76.40
75.99
75.18
73.85
62.24
26.93
19.46
OTBDPS
BnO
O
OPVB
HO
BzO
13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

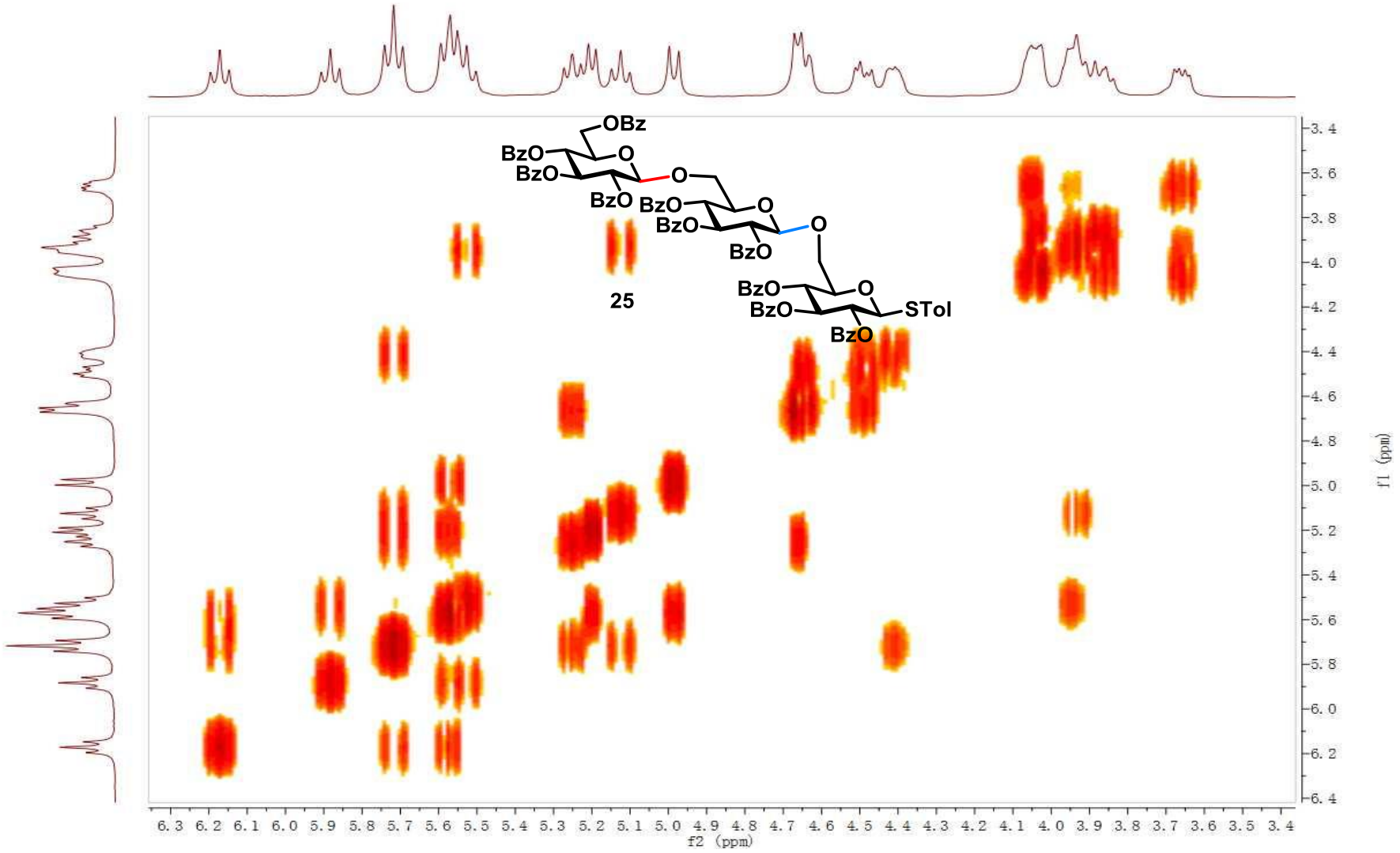

7.94
7.92
7.86
7.84
7.52
7.50
7.48
7.45
7.44
7.42
7.38
7.36
7.34
7.33
7.31
7.30
7.29
7.28
7.26
7.25
7.19
7.17
7.17
7.15
7.12
7.10
5.78
5.76
5.63
5.45
5.43
5.41
5.07
4.85
4.82
4.76
4.74
4.67
4.65
3.87
3.85
3.83
3.75
3.73
3.71
3.64
3.62
3.50
3.47
1.80
1.79
1.77
OH
BnO
BnO
O
OPVB
BzO
21
1.95
0.98
1.10
1.12
8.96
5.37
4.91
1.00
1.00
0.99
0.97
1.01
1.07
2.04
1.06
1.92
1.09
1.06
1.06
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
−0.
f1 (ppm)

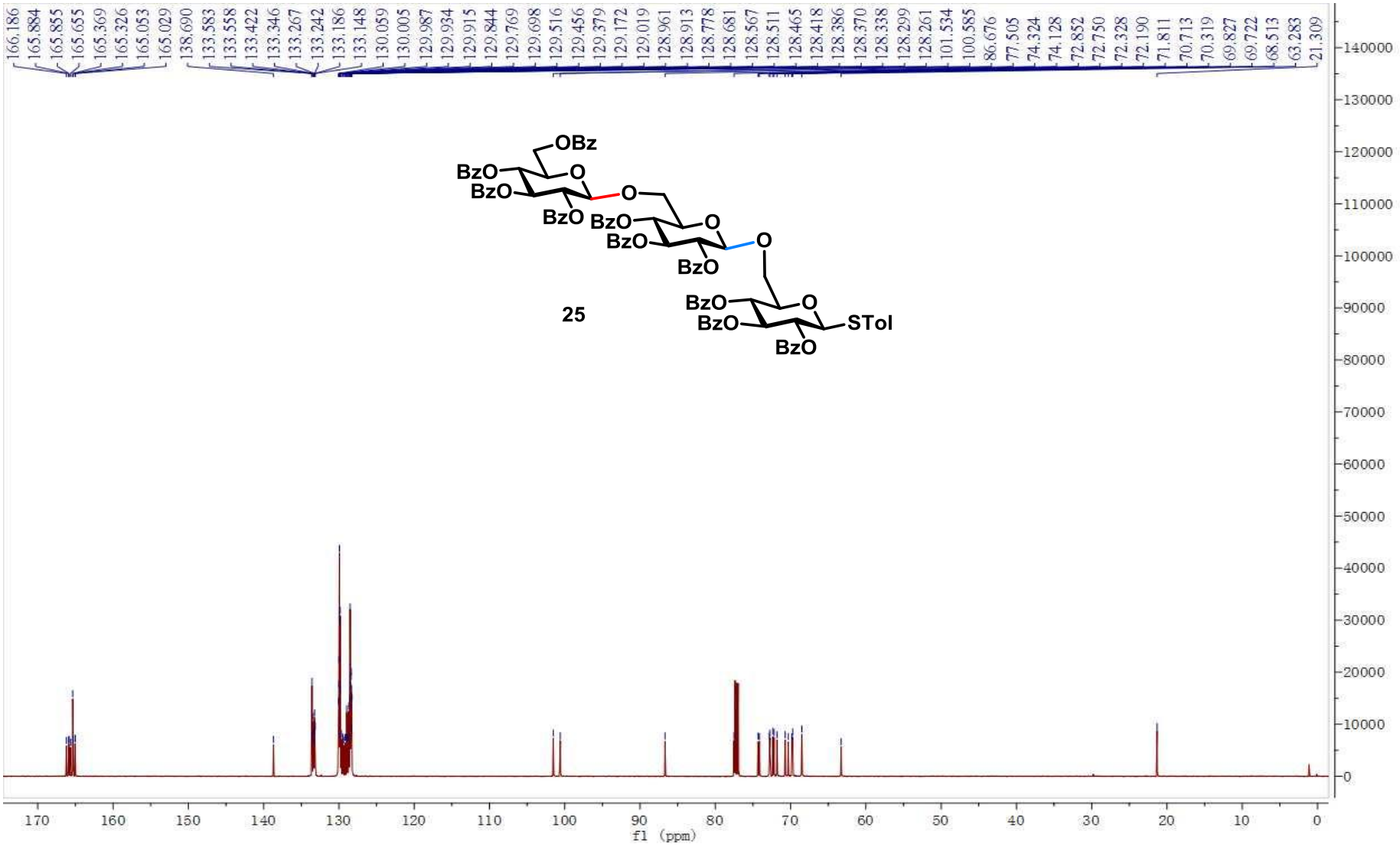

165.16
164.88
149.08
143.86
140.66
137.82
137.67
133.42
132.73
131.71
130.66
129.91
129.51
128.75
128.66
128.55
128.42
128.20
128.16
127.90
127.87
127.47
126.64
114.39
92.49
82.51
77.18
76.21
75.27
75.21
72.49
61.34
OH
BnO
BnO
O
OPVB
BzO
21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

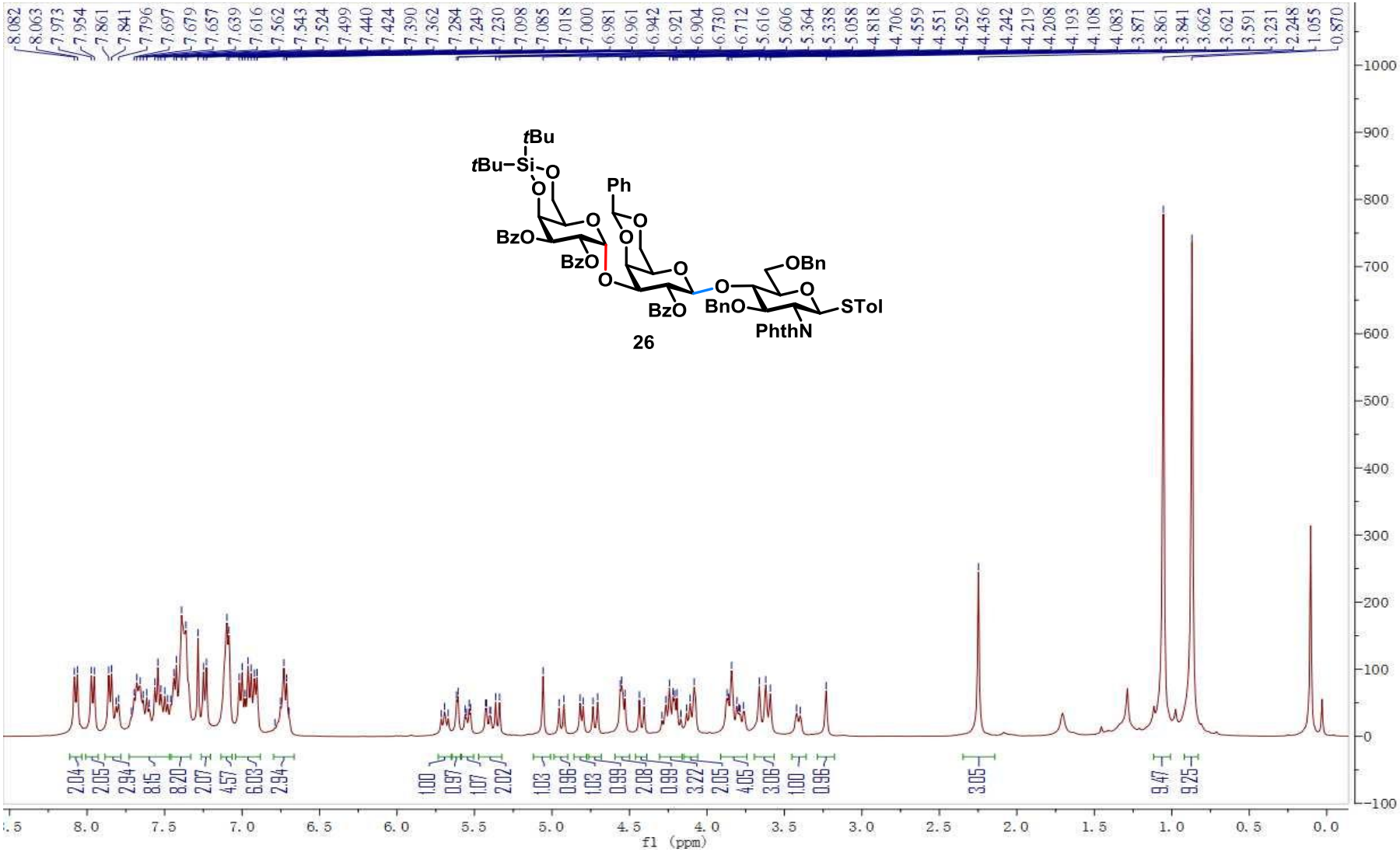

7.99
7.97
7.89
7.87
7.51
7.49
7.43
7.41
7.39
7.36
7.35
7.33
7.32
7.31
7.30
7.25
7.23
7.21
7.19
6.08
6.06
5.36
5.34
5.32
4.89
4.86
4.79
4.76
4.09
4.07
4.04
3.97
3.96
3.94
3.93
3.80
3.79
3.77
3.76
3.74
3.72
3.70
3.68
3.67
3.64
2.99
2.08
1.54
1.53
1.52
1.51
1.49
1.47
0.89
0.87
0.86
OH
BnO
O
OABz
HO
BzO
23
1.91
0.98
1.19
8.73
1.56
1.00
1.01
0.92
1.14
1.00
0.75
3.20
0.72
1.33
0.80
3.98
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
−0.
f1 (ppm)

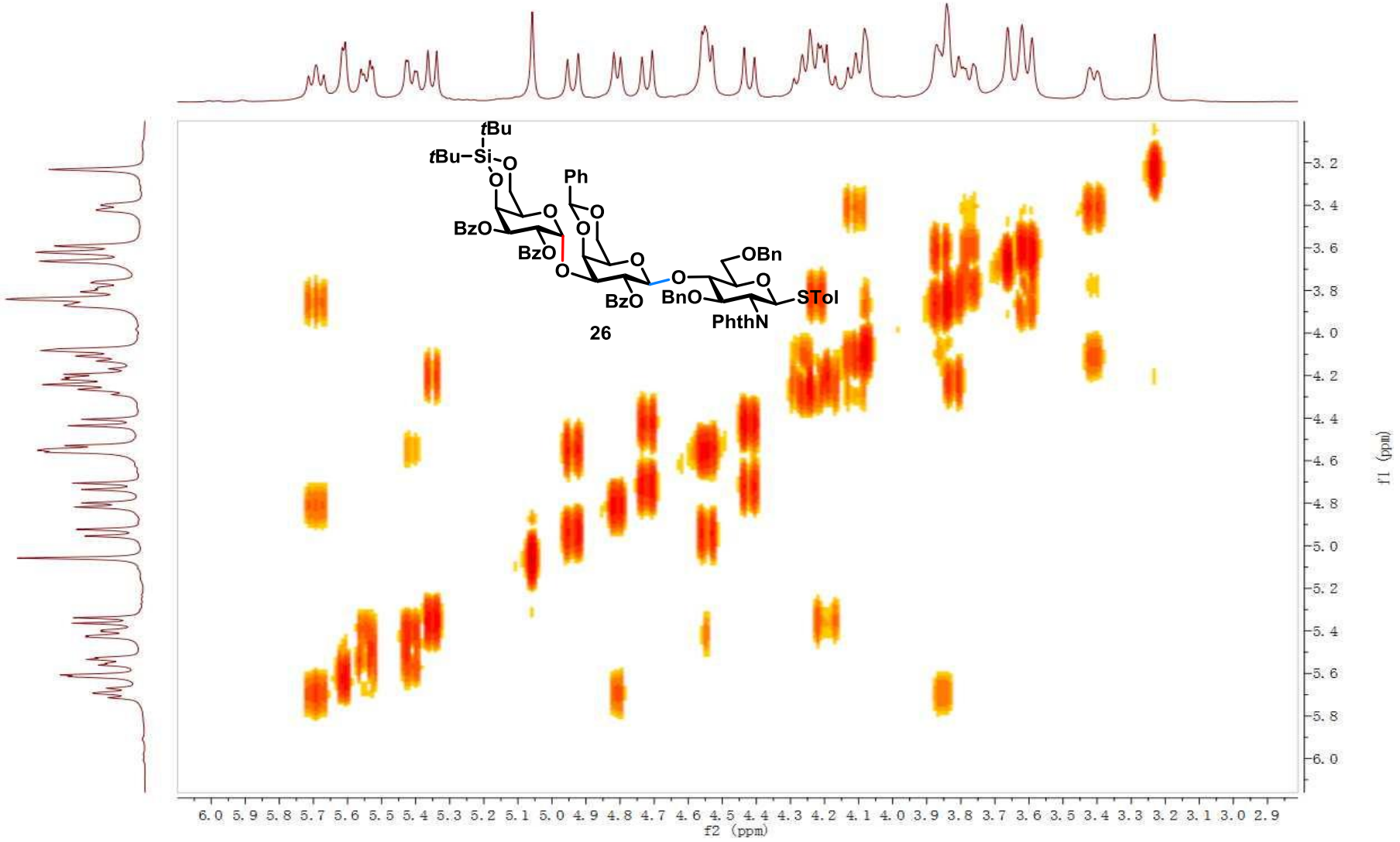

165.55
163.01
137.18
133.72
132.79
131.73
130.12
129.19
128.65
128.38
127.95
127.76
127.49
127.45
126.42
124.94
99.73
91.70
76.70
76.60
76.38
76.06
75.59
75.02
74.28
73.64
73.05
60.80
8.31
8.28
-0.00
OH
BnO
HO
O
OABz
BzO
23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

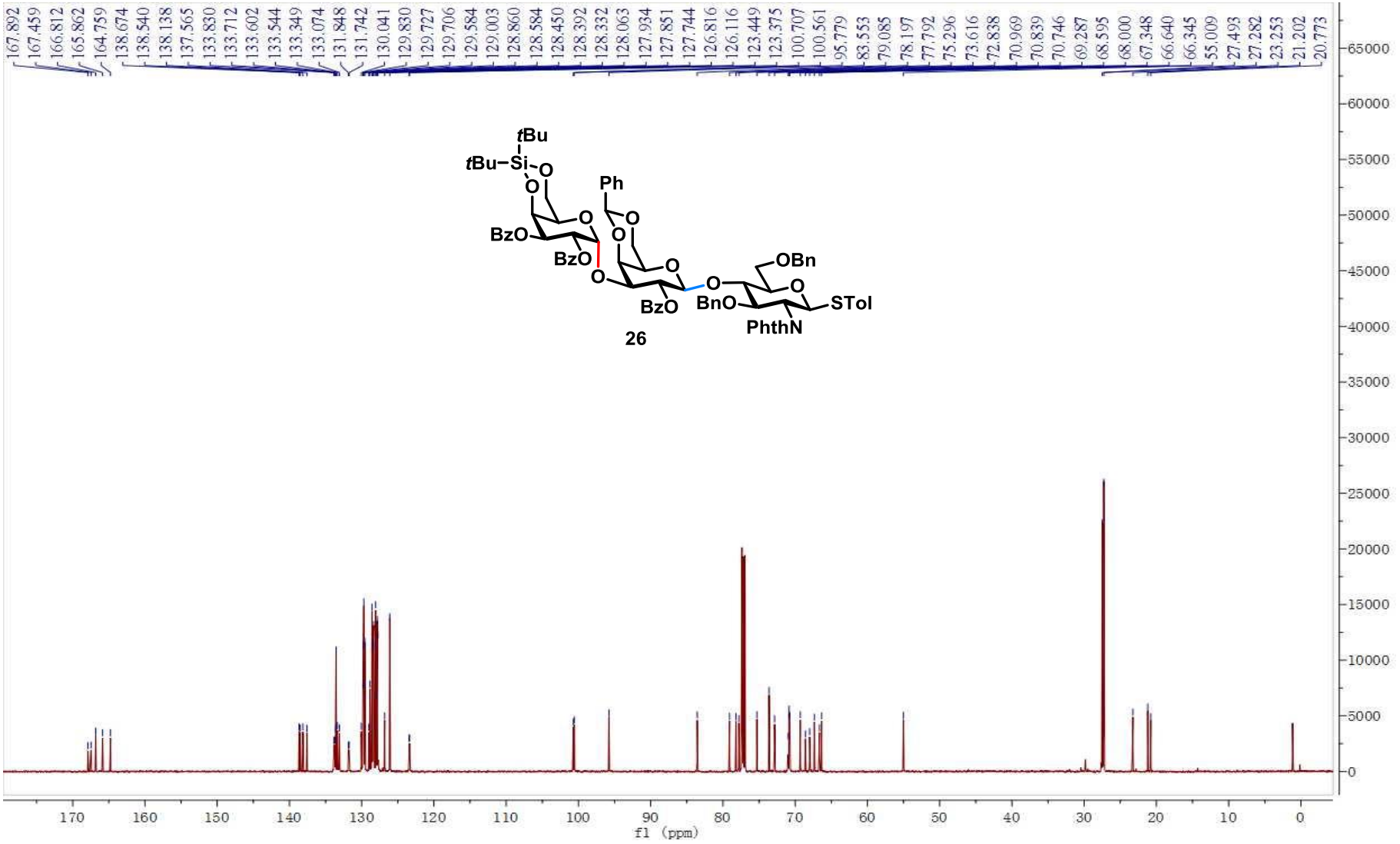

OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
STol
25
f1 (ppm)

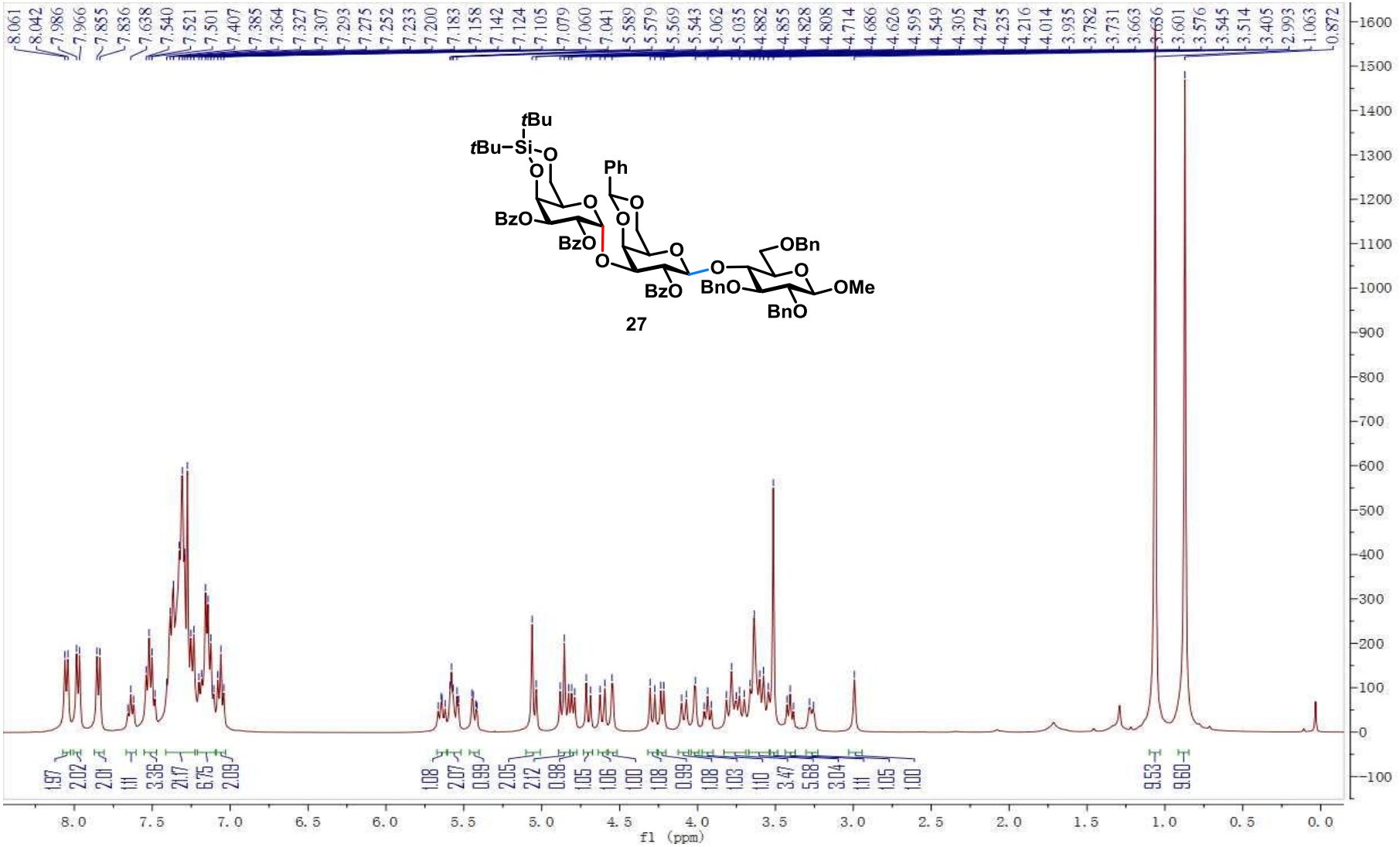

OBz
BzO
BzO
BzO
O
O
BzO
BzO
O
BzO
O
BzO
BzO
O
STol
BzO
25
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4
f2 (ppm)
3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4
f1 (ppm)

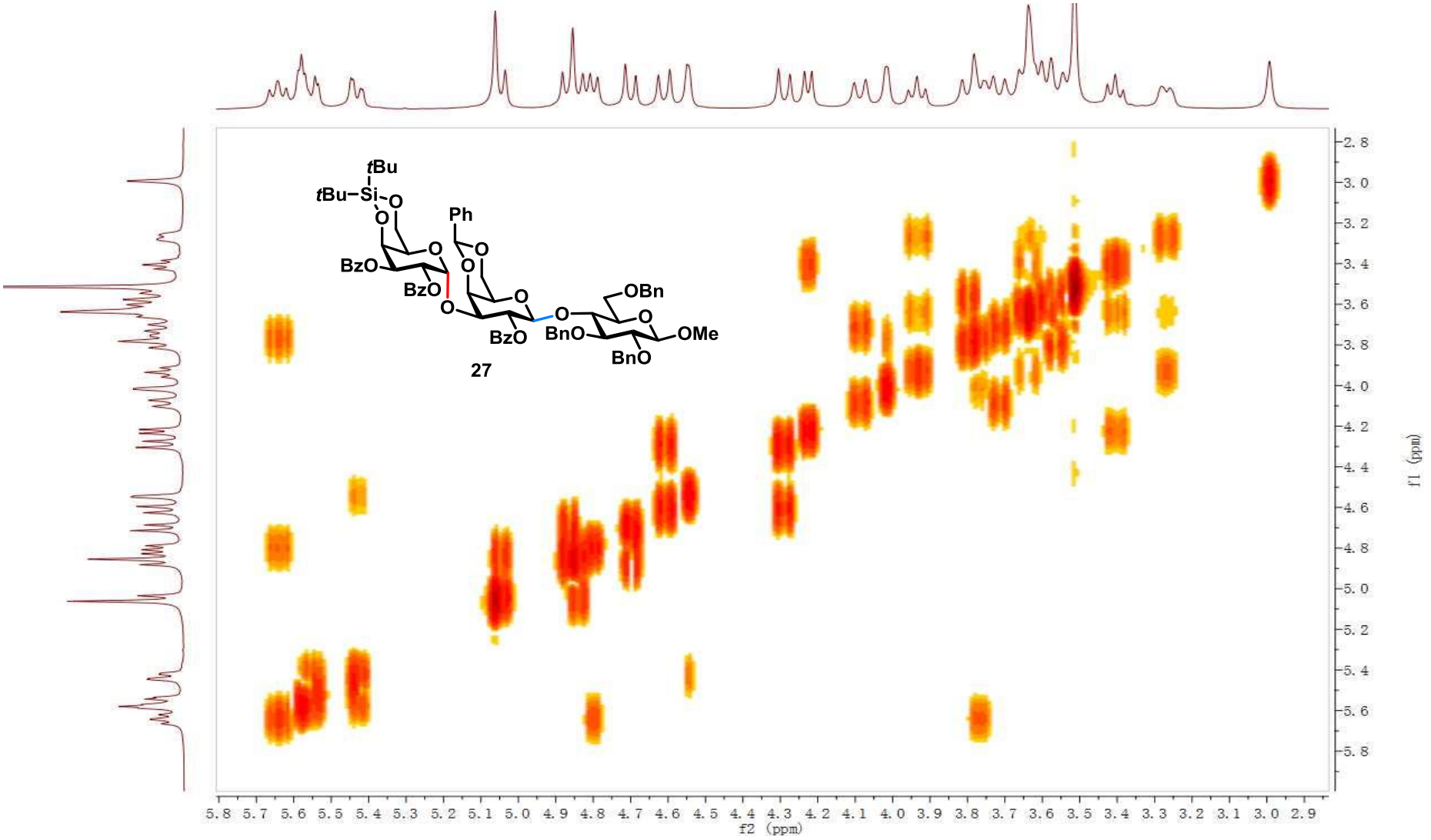

166.186
165.884
165.855
165.655
165.369
165.326
165.053
165.029
138.690
133.583
133.558
133.422
133.346
133.267
133.242
133.186
133.148
130.059
130.005
129.987
129.934
129.915
129.844
129.769
129.698
129.516
129.456
129.379
129.172
129.019
128.961
128.913
128.778
128.681
128.567
128.511
128.465
128.418
128.386
128.370
128.338
128.299
128.261
101.534
100.585
86.676
77.505
74.324
74.128
72.852
72.750
72.328
72.190
71.811
70.713
70.319
69.827
69.722
68.513
63.283
21.309
OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
STol
25
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

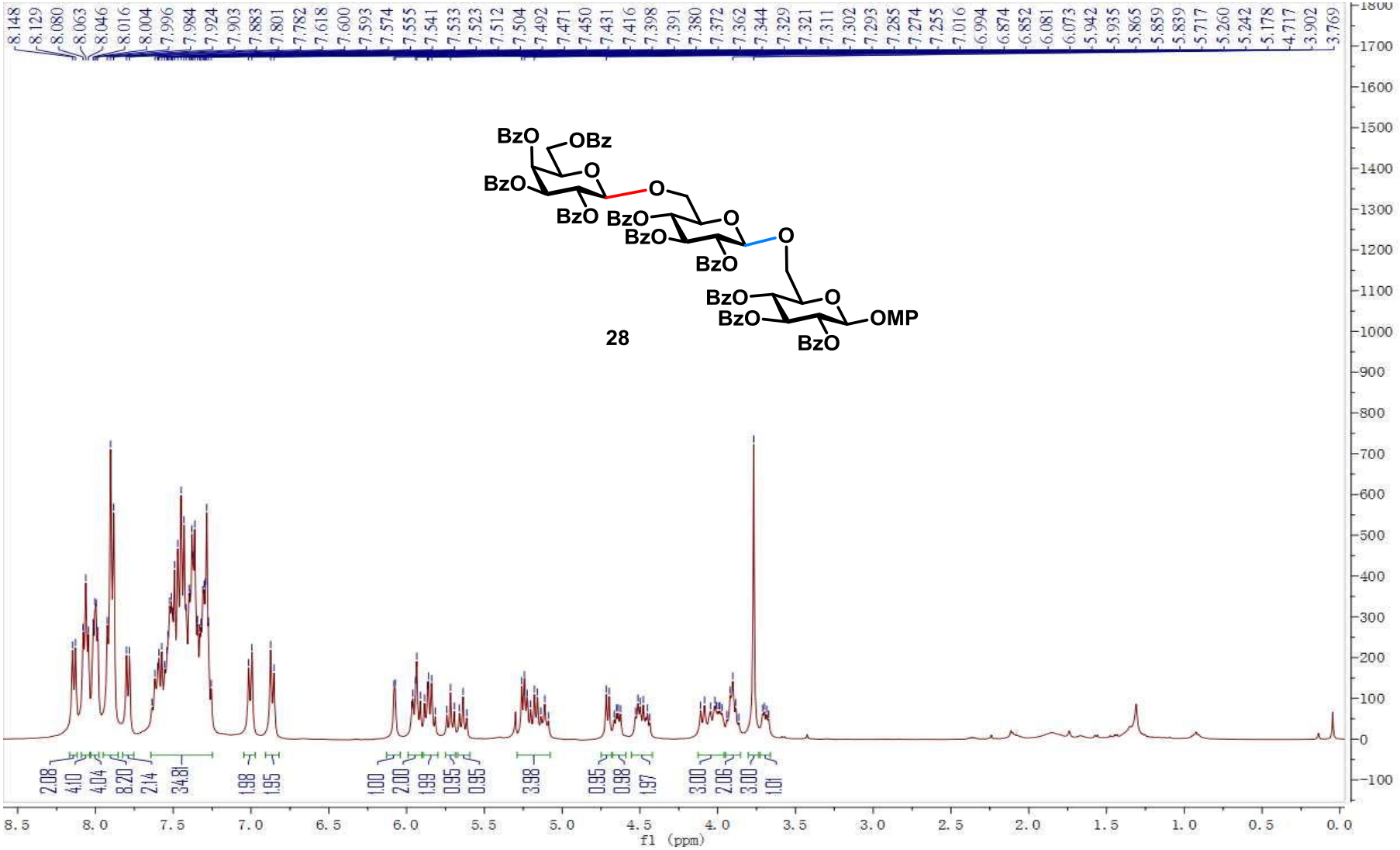

tBu
tBu–Si
O
Ph
BzO
BzO
BzO
OBn
BnO
STol
PhthN
26
f1 (ppm)

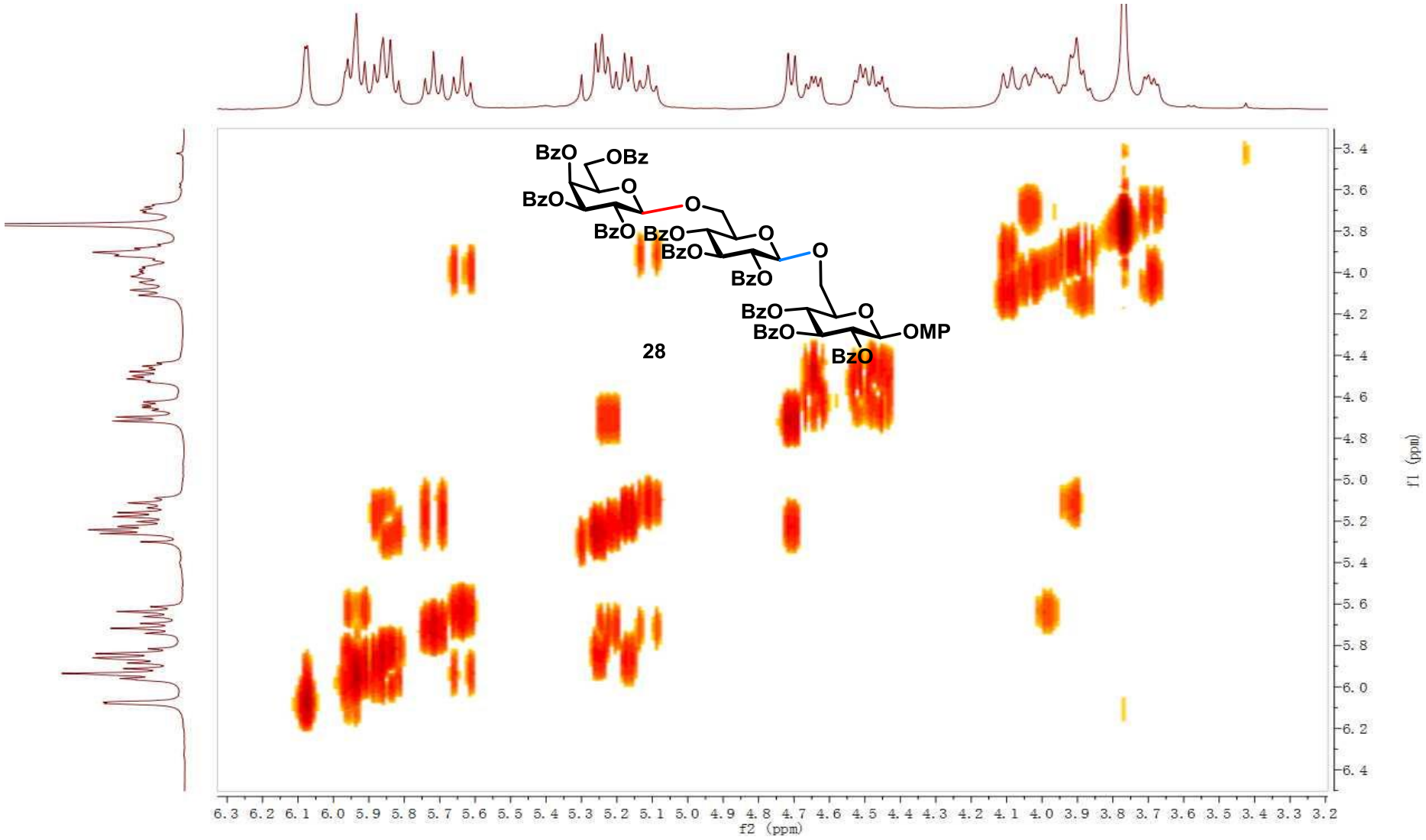

tBu
tBu–Si
O
Ph
BzO
BzO
BzO
OBn
BnO
STol
PhthN
26
f2 (ppm)
f1 (ppm)

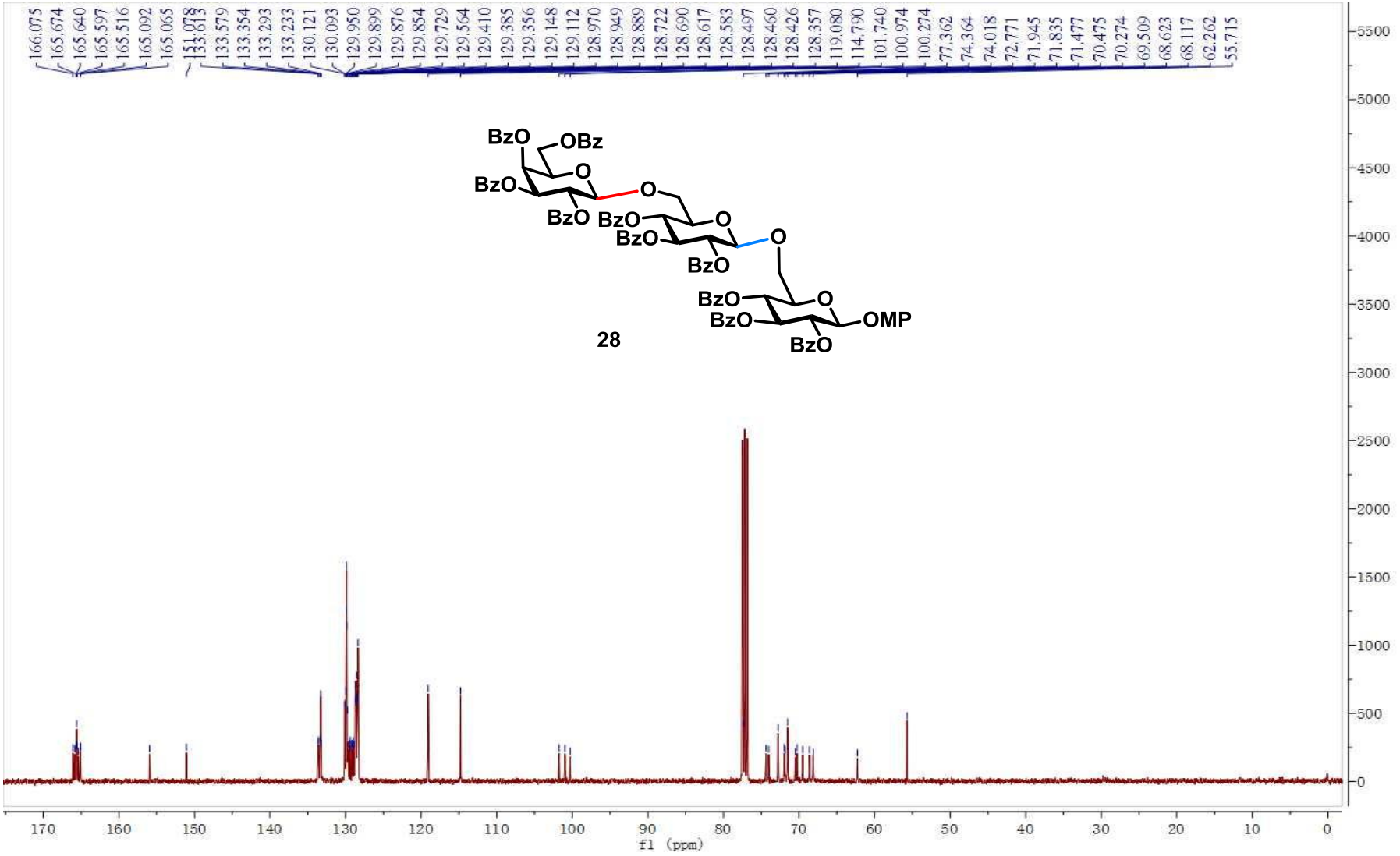

167.892
167.459
166.812
165.862
164.759
138.674
138.540
138.138
137.565
133.830
133.712
133.602
133.544
133.349
133.074
131.848
131.742
130.041
129.830
129.727
129.706
129.584
129.003
128.860
128.584
128.450
128.392
128.332
128.063
127.934
127.851
127.744
126.816
126.116
123.449
123.375
100.707
100.561
95.779
83.553
79.085
78.197
77.792
75.296
73.616
72.838
70.969
70.839
70.746
69.287
68.595
68.000
67.348
66.640
66.345
55.009
27.493
27.282
23.253
21.202
20.773
tBu
tBu–Si
O
Ph
BzO
BzO
BzO
OBn
BnO
STol
PhthN
26
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

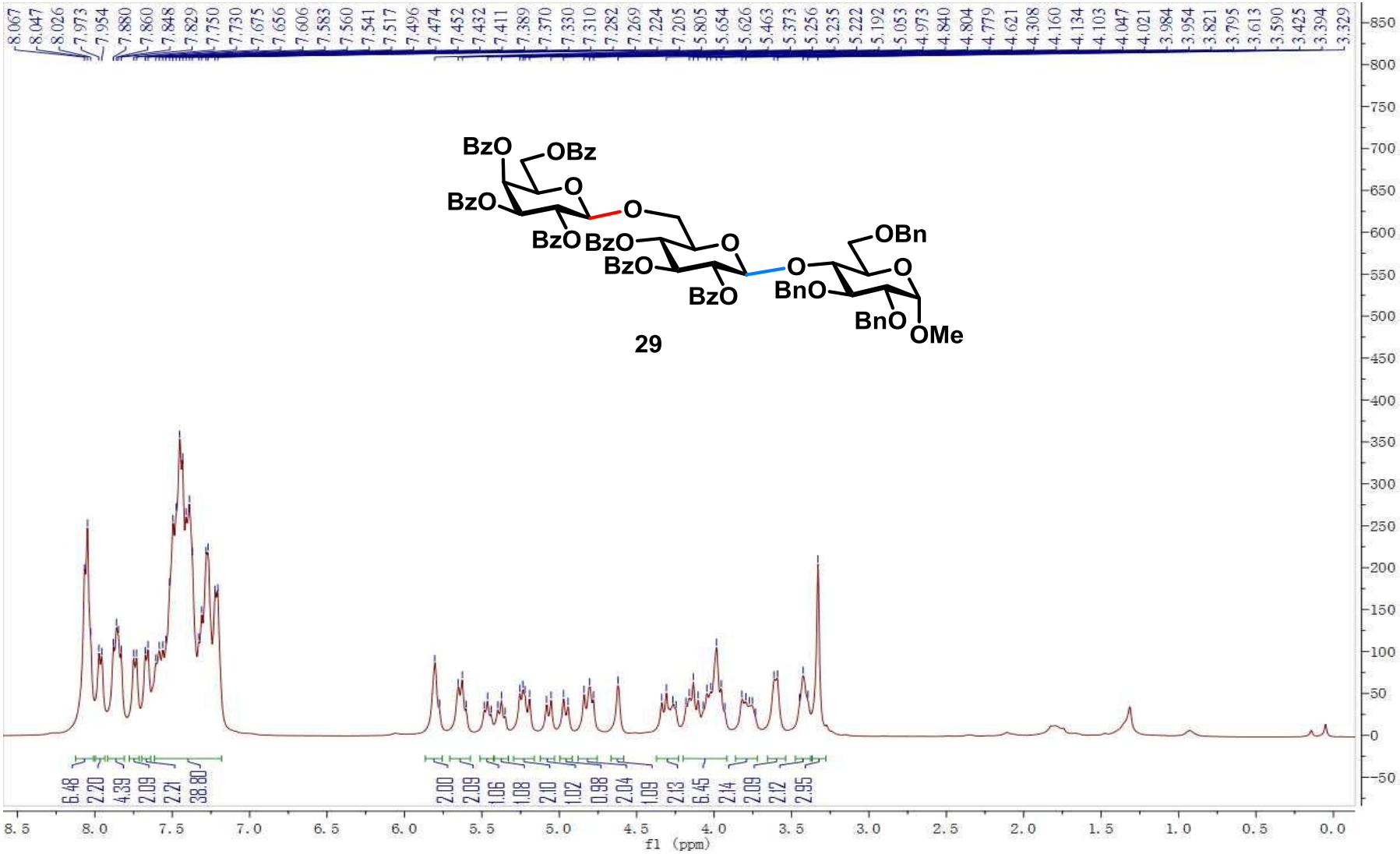

tBu
tBu–Si
O
Ph
BzO
BzO
BzO
BnO
OBn
OMe
BnO
27
f1 (ppm)

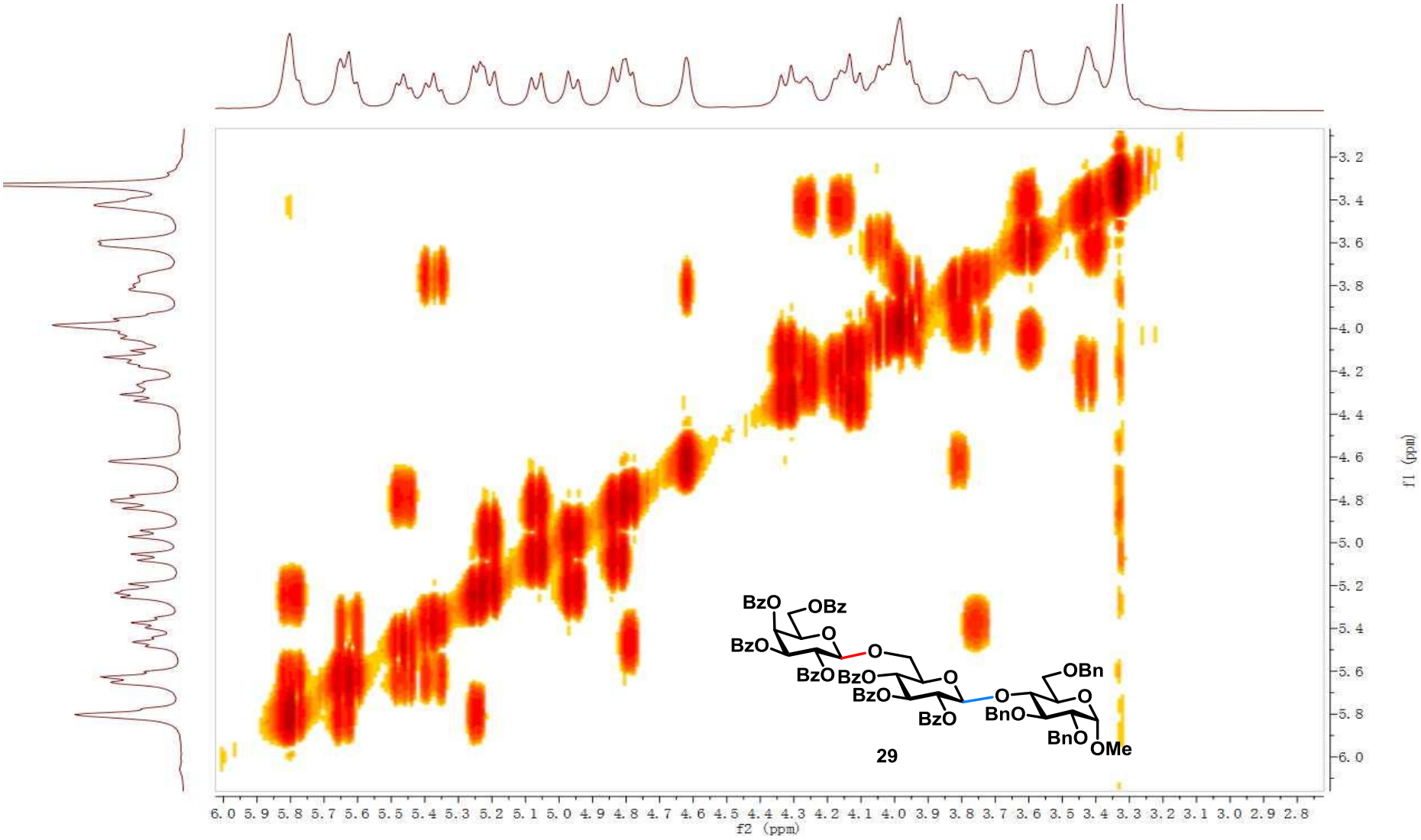

tBu
tBu–Si
O
Ph
BzO
BzO
BzO
OBn
BnO
OMe
BnO
27
f2 (ppm)
f1 (ppm)

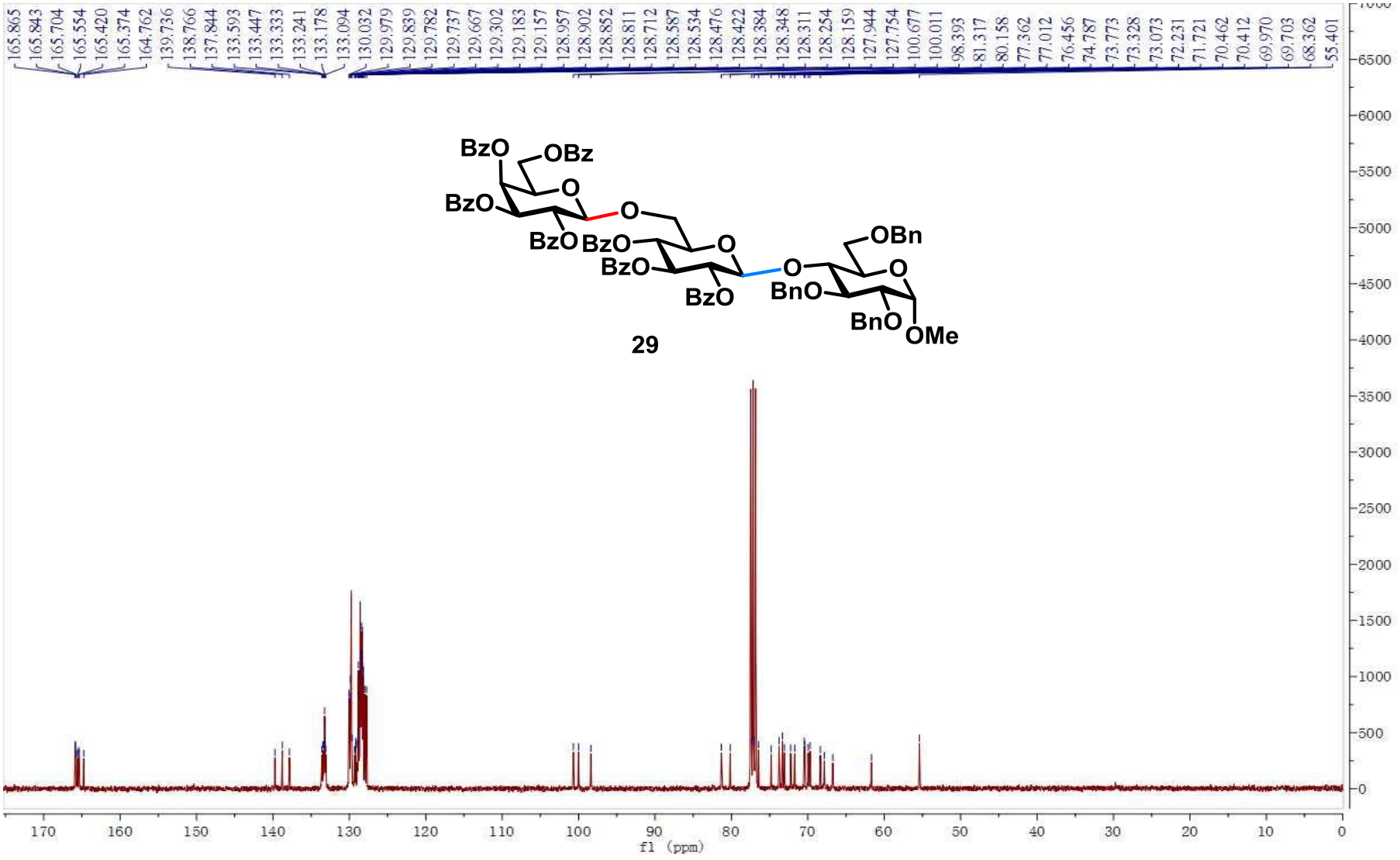

BzO
OBz
O
BzO
BzO
O
BzO
BzO
O
BzO
BzO
O
BzO
BzO
O
OMP
BzO
28
f1 (ppm)

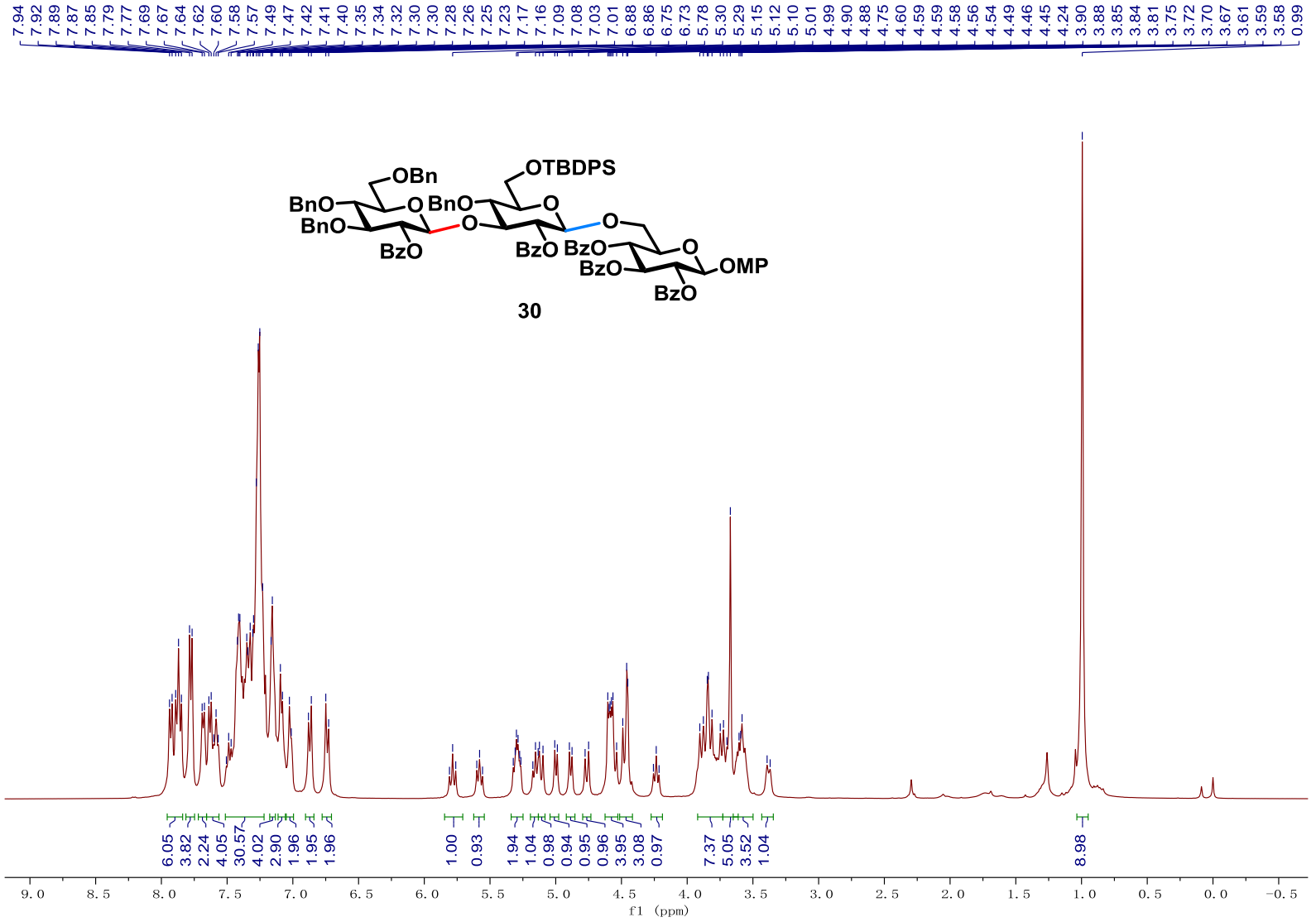

BzO
OBz
O
BzO
O
BzO
BzO
BzO
O
BzO
O
BzO
BzO
OMP
BzO
28
f2 (ppm)
f1 (ppm)


166.075
165.674
165.640
165.597
165.516
165.092
165.065
151.078
133.613
133.579
133.354
133.293
133.233
130.121
130.093
129.950
129.899
129.876
129.854
129.729
129.564
129.410
129.385
129.356
129.148
129.112
128.970
128.949
128.889
128.722
128.690
128.617
128.583
128.497
128.460
128.426
128.357
119.080
114.790
101.740
100.974
100.274
77.362
74.364
74.018
72.771
71.945
71.835
71.477
70.475
70.274
69.509
68.623
68.117
62.262
55.715
BzO
OBz
O
BzO
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
OMP
BzO
28
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

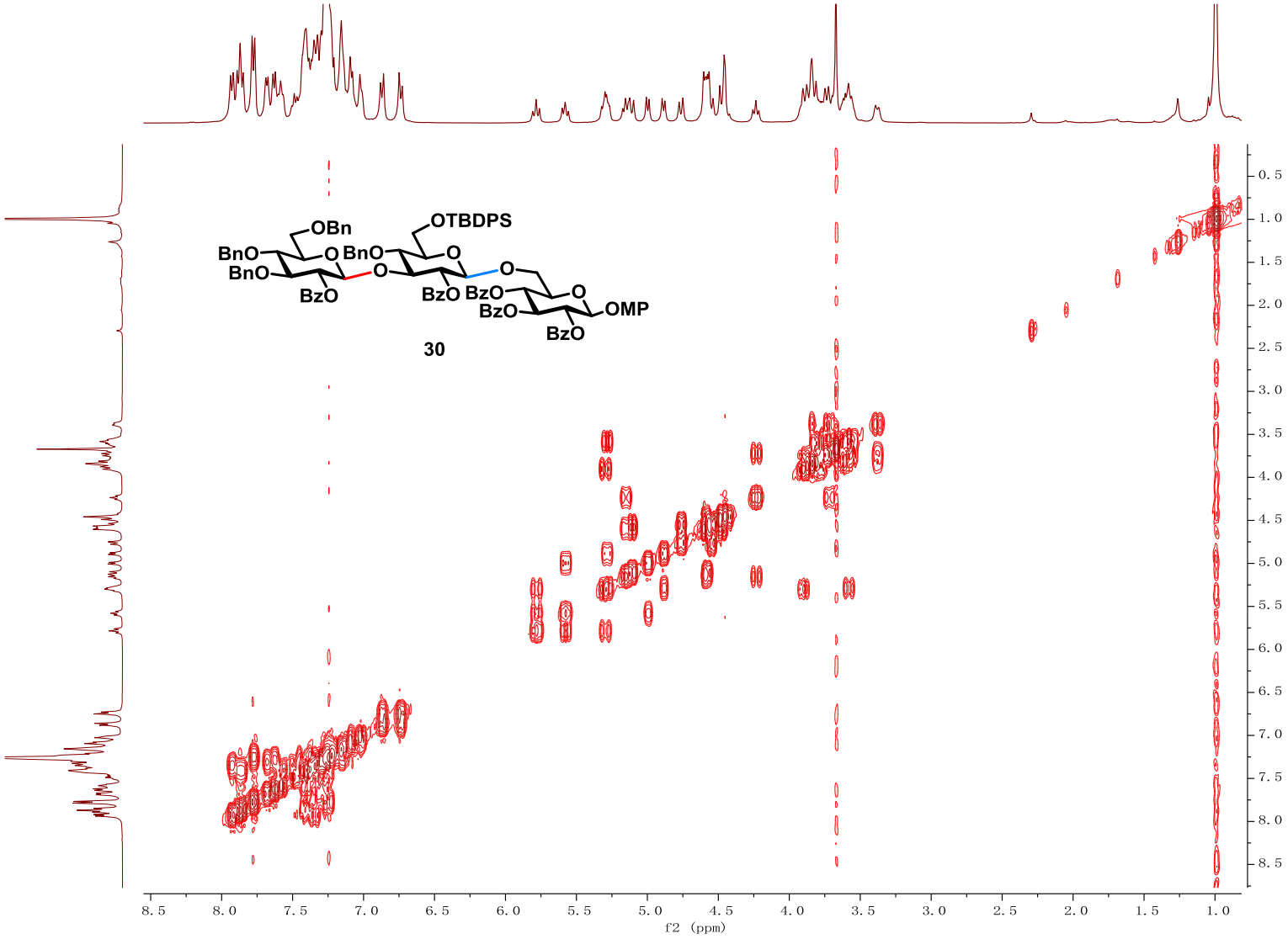

BzO
OBz
O
BzO
O
BzO
BzO
O
BzO
O
OBn
O
BnO
BnO
OMe
29
f1 (ppm)

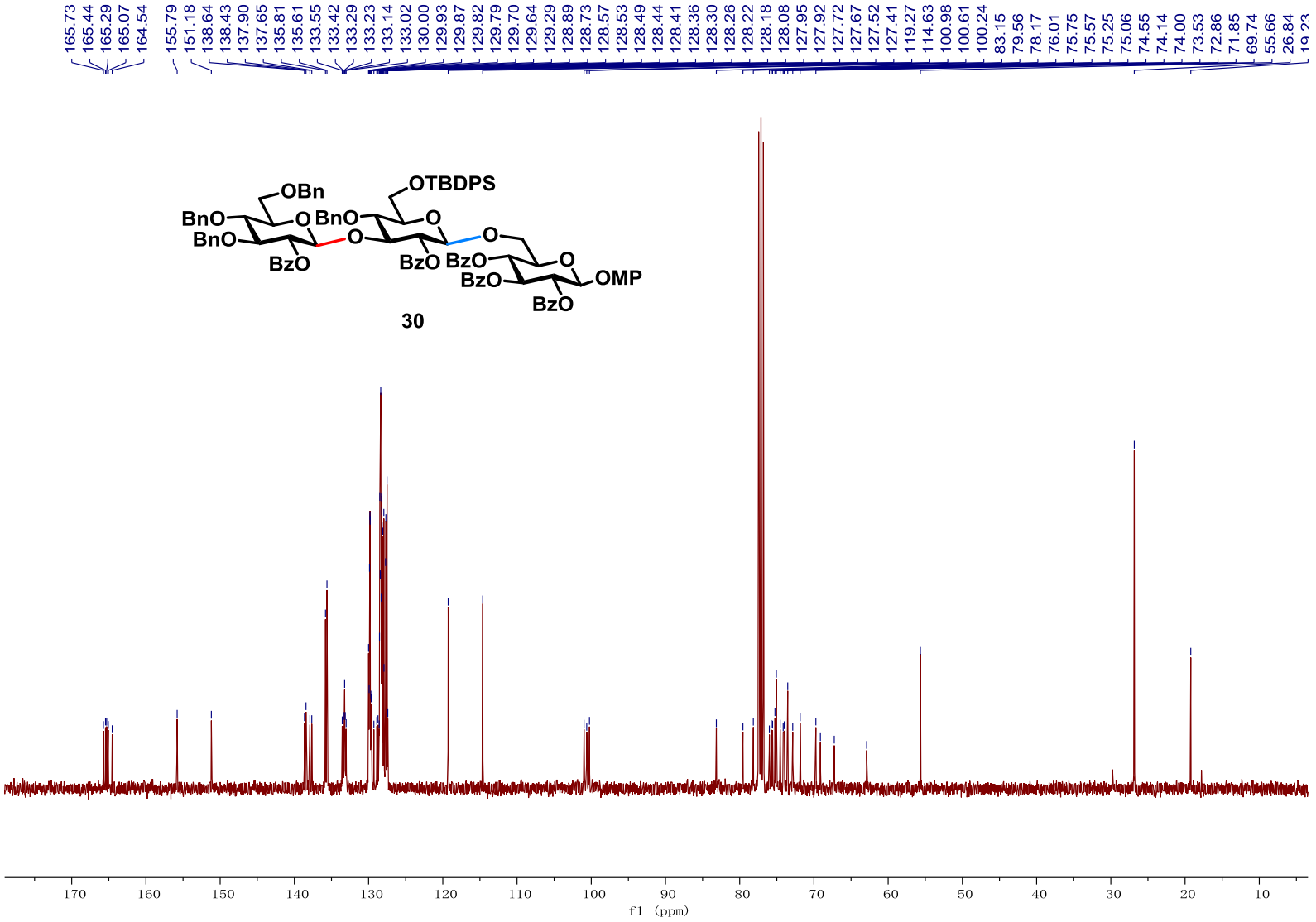

BzO
OBz
BzO
BzO
BzO
BzO
BzO
OBn
BnO
BnO
OMe
29
f2 (ppm)
f1 (ppm)

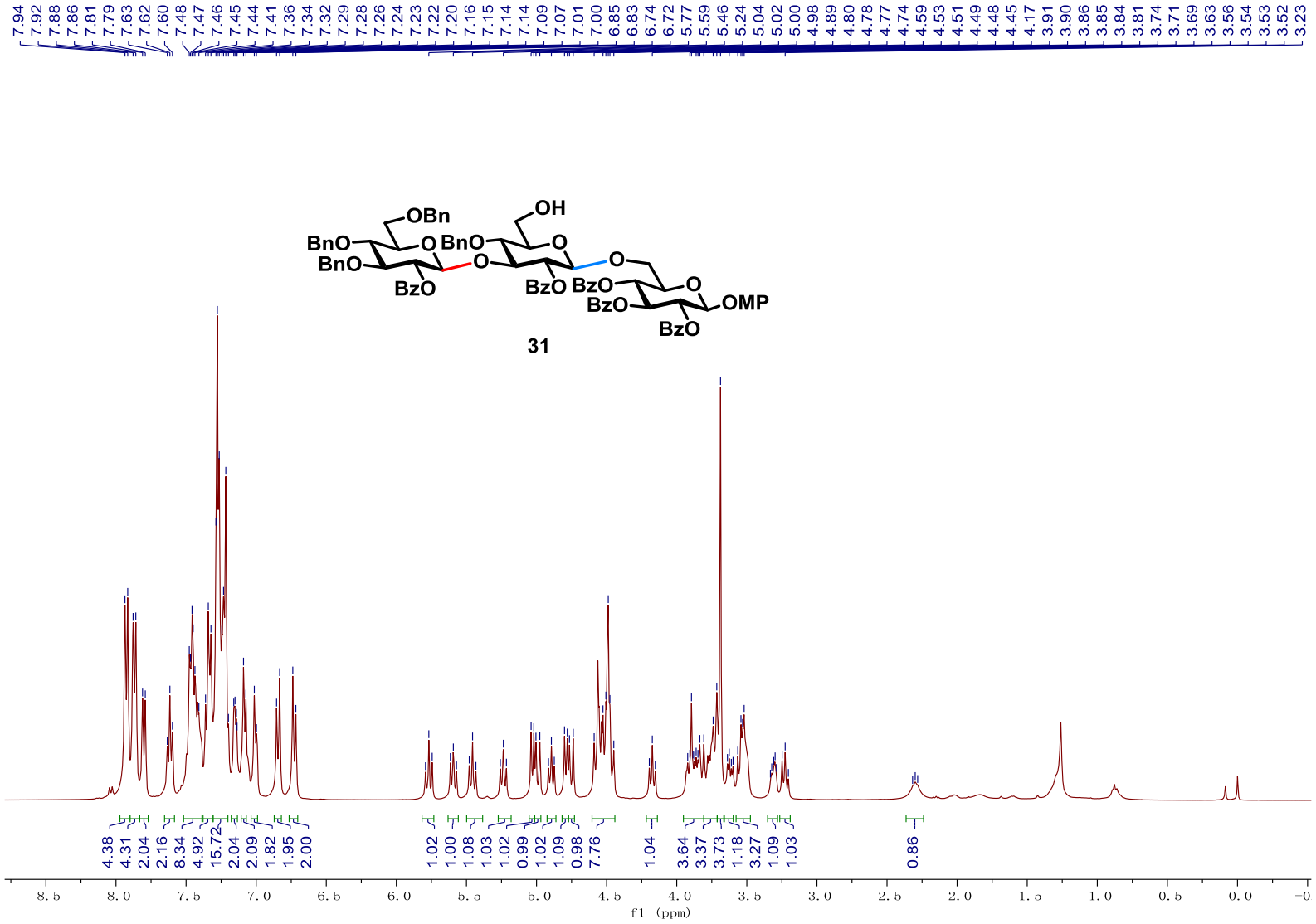

165.865
165.843
165.704
165.554
165.420
165.374
164.762
139.736
138.766
137.844
133.593
133.447
133.333
133.241
133.178
133.094
130.032
129.979
129.839
129.782
129.737
129.667
129.302
129.183
129.157
128.957
128.902
128.852
128.811
128.712
128.587
128.534
128.476
128.422
128.384
128.348
128.311
128.254
128.159
127.944
127.754
100.677
100.011
98.393
81.317
80.158
77.362
77.012
76.456
74.787
73.773
73.328
73.073
72.231
71.721
70.462
70.412
69.970
69.703
68.362
55.401
BzO
OBz
O
BzO
O
BzO
BzO
O
BzO
O
OBn
O
BnO
BnO
OMe
29
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

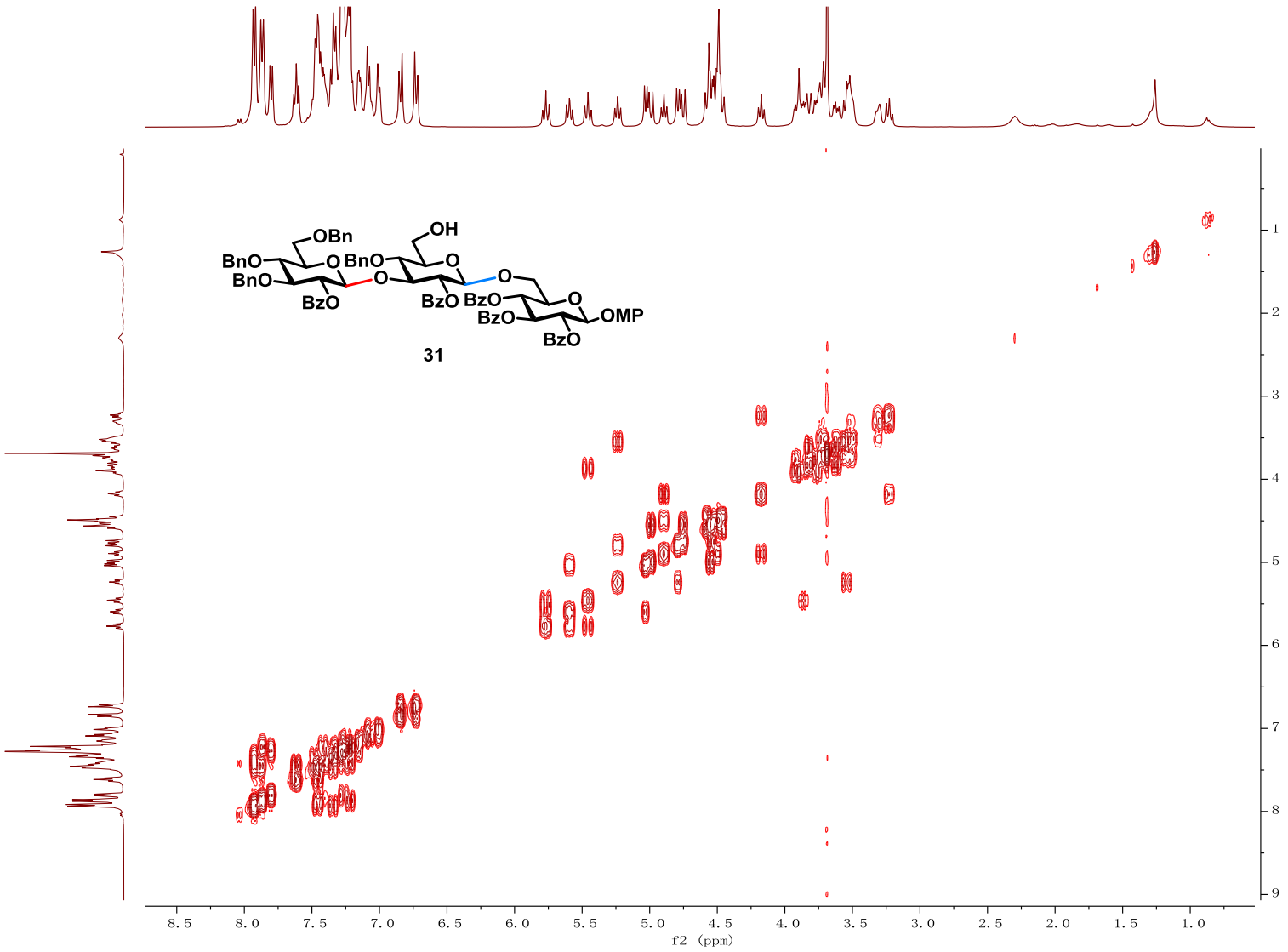

7.94 7.92 7.89 7.87 7.85 7.79 7.77 7.69 7.67 7.64 7.62 7.60 7.58 7.57 7.49 7.47 7.42 7.41 7.40 7.35 7.34 7.32 7.30 7.30 7.28 7.26 7.25 7.23 7.17 7.16 7.09 7.08 7.03 7.01 6.88 6.86 6.75 6.73 5.78 5.30 5.29 5.15 5.12 5.10 5.01 4.99 4.90 4.88 4.75 4.60 4.59 4.59 4.58 4.56 4.54 4.49 4.46 4.45 4.24 3.90 3.88 3.85 3.84 3.81 3.75 3.72 3.70 3.67 3.61 3.59 3.58 0.99
OBn
OTBDPS
BnO
BnO
BnO
BnO
BzO
BzO
BzO
BzO
BzO
OMP
6.05 3.82 2.24 4.05 30.57 4.02 2.90 1.96 1.95 1.96 1.00 0.93 1.94 1.04 0.98 0.94 0.95 0.96 3.95 3.08 0.97 7.37 5.05 3.52 1.04 8.98
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 −0.5
f1 (ppm)

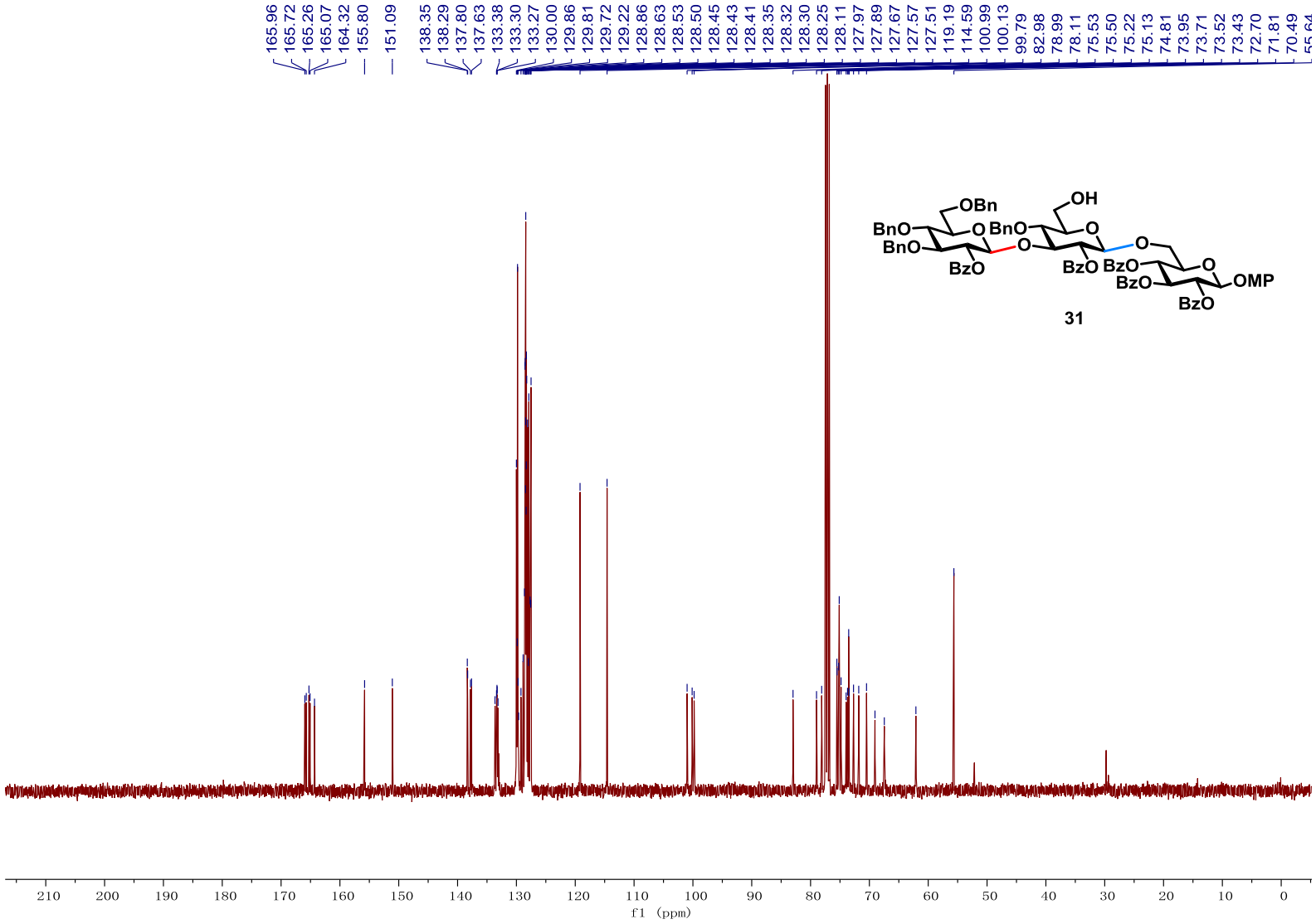
30

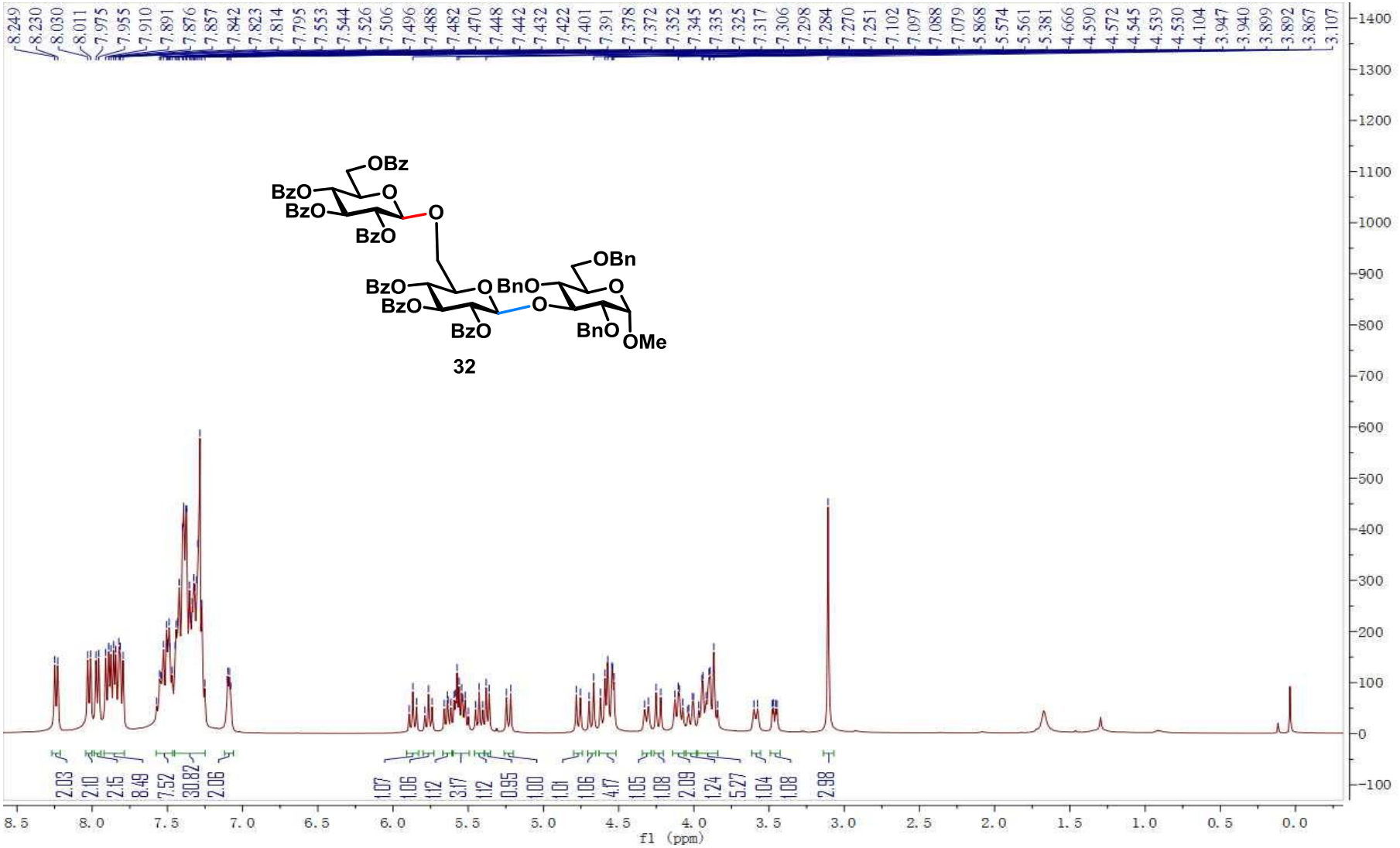

OBn
OTBDPS
BnO
BnO
BnO
BnO
O
O
O
O
O
BzO
BzO
BzO
BzO
BzO
OMP
30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5

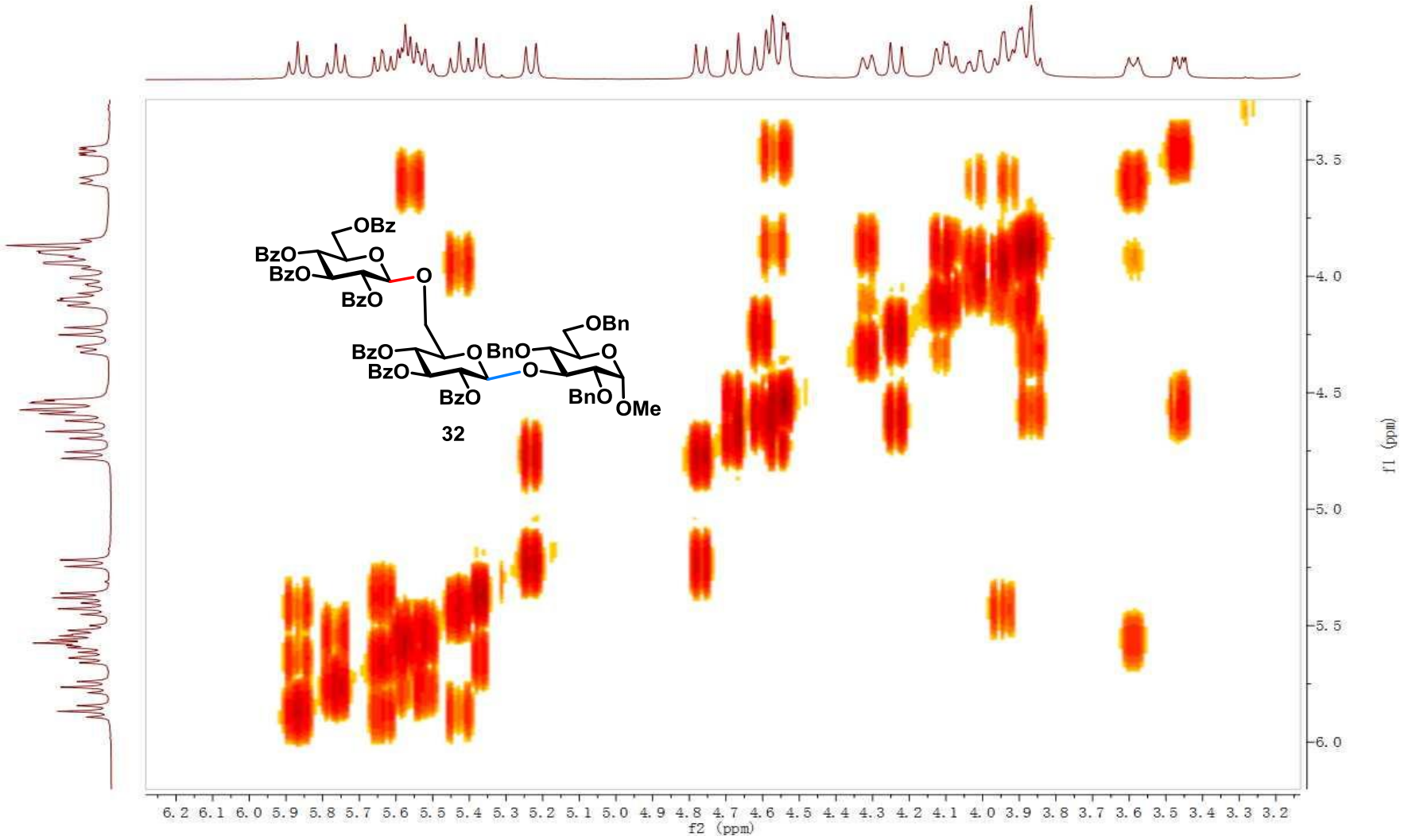

165.73
165.44
165.29
165.07
164.54
155.79
151.18
138.64
138.43
137.90
137.65
135.81
135.61
133.55
133.42
133.29
133.23
133.14
133.02
130.00
129.93
129.87
129.82
129.79
129.70
129.64
129.29
128.89
128.73
128.57
128.53
128.49
128.44
128.41
128.36
128.30
128.26
128.22
128.18
128.08
127.95
127.92
127.72
127.67
127.52
127.41
119.27
114.63
100.98
100.61
100.24
83.15
79.56
78.17
76.01
75.75
75.57
75.25
75.06
74.55
74.14
74.00
73.53
72.86
71.85
69.74
55.66
26.84
OBn
OTBDPS
BnO
BnO
BnO
BnO
BzO
BzO
BzO
BzO
OMP
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

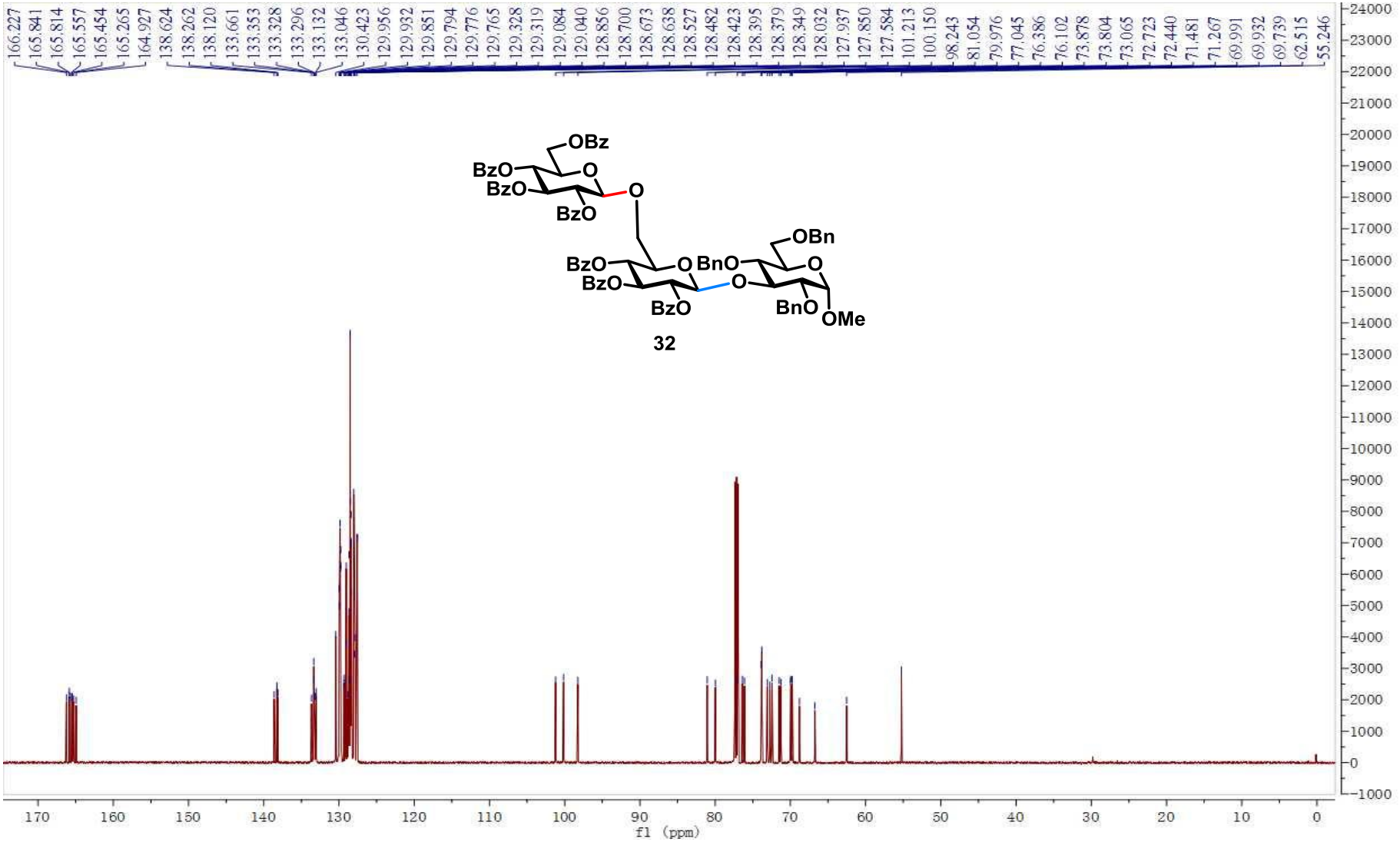

7.94 7.92 7.88 7.86 7.81 7.79 7.63 7.62 7.60 7.48 7.47 7.46 7.45 7.44 7.41 7.36 7.34 7.32 7.29 7.28 7.26 7.24 7.23 7.22 7.20 7.16 7.15 7.14 7.14 7.09 7.07 7.01 7.00 6.85 6.83 6.74 6.72 5.77 5.59 5.46 5.24 5.04 5.02 5.00 4.98 4.89 4.80 4.78 4.77 4.74 4.59 4.53 4.51 4.49 4.48 4.45 4.17 3.91 3.90 3.86 3.85 3.84 3.81 3.74 3.71 3.69 3.63 3.56 3.54 3.53 3.52 3.23
OBn
OH
BnO
BnO
BzO
BzO
BzO
BzO
OMP
BzO
31
4.38 4.31 2.04 2.16 8.34 4.92 15.72 2.04 2.09 1.82 1.95 2.00
1.02 1.00 1.08 1.03 1.02 0.99 1.02 1.09 0.98 7.76
1.04
3.64 3.37 3.73 1.18 3.27 1.09 1.03
0.86
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)

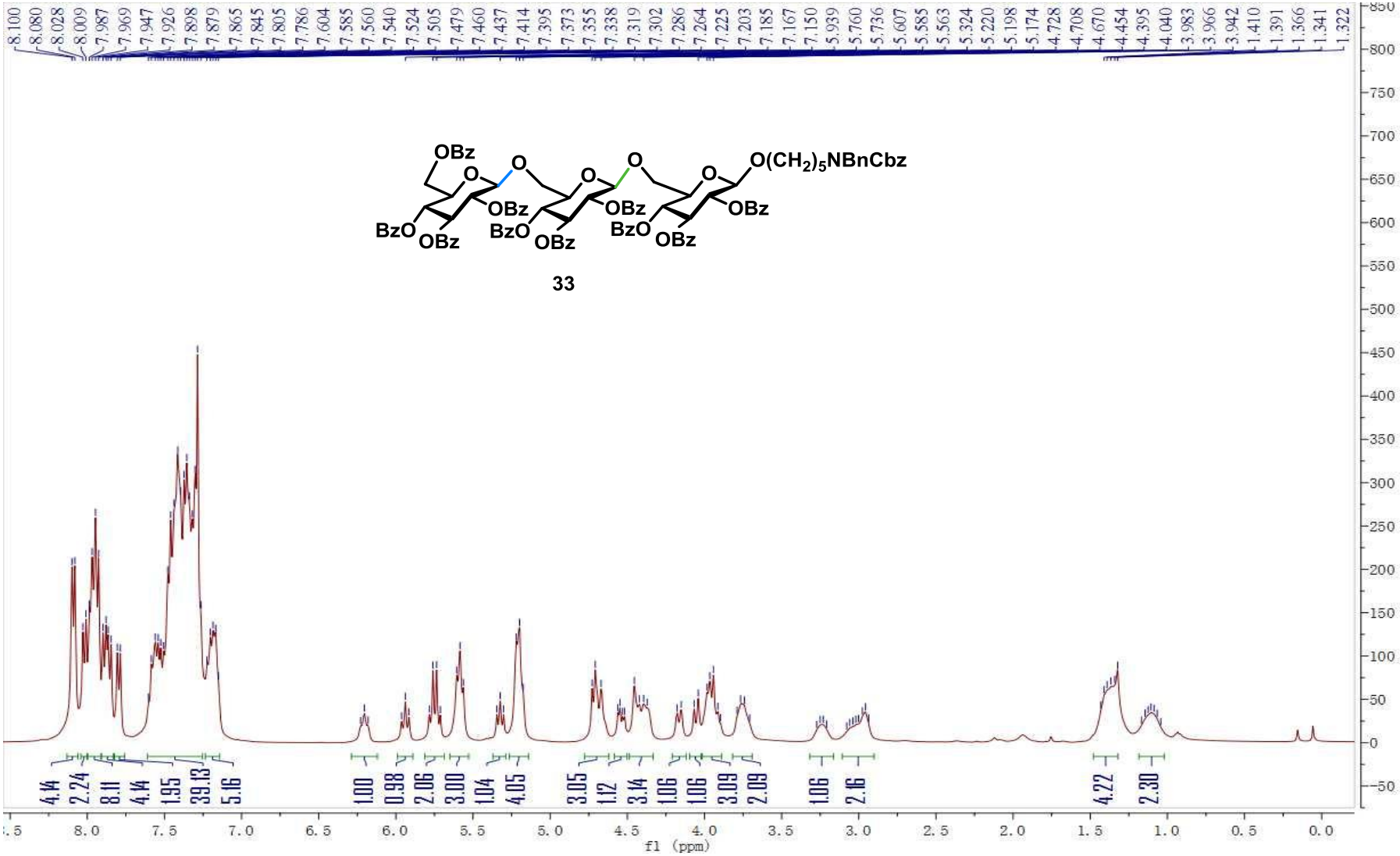

OBn
OH
BnO
BnO
BnO
O
O
O
O
O
BzO
BzO
BzO
BzO
BzO
OMP
31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9


165.96
165.72
165.26
165.07
164.32
155.80
151.09
138.35
138.29
137.80
137.63
133.38
133.30
133.27
130.00
129.86
129.81
129.72
129.22
128.86
128.63
128.53
128.50
128.45
128.43
128.41
128.35
128.32
128.30
128.25
128.11
127.97
127.89
127.67
127.57
127.51
119.19
114.59
100.99
100.13
99.79
82.98
78.99
78.11
75.53
75.50
75.22
75.13
74.81
73.95
73.71
73.52
73.43
72.70
71.81
70.49
55.64
OBn
OH
BnO
BnO
BzO
BzO
BzO
BzO
BzO
OMP
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

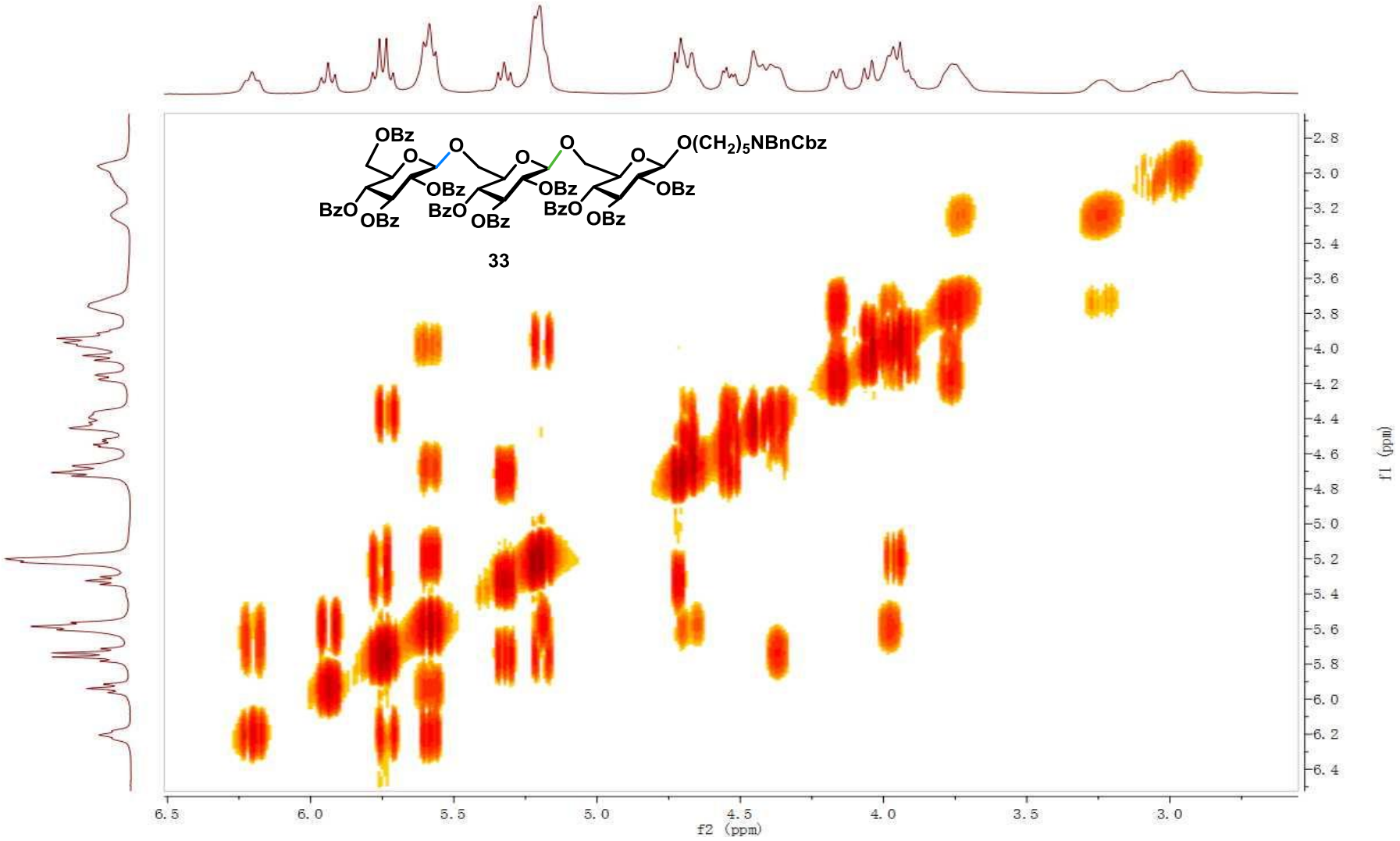

OBz
BzO
BzO
BzO
O
BzO
BzO
BzO
O
BnO
OBn
O
O
BnO
OMe
32
fl (ppm)

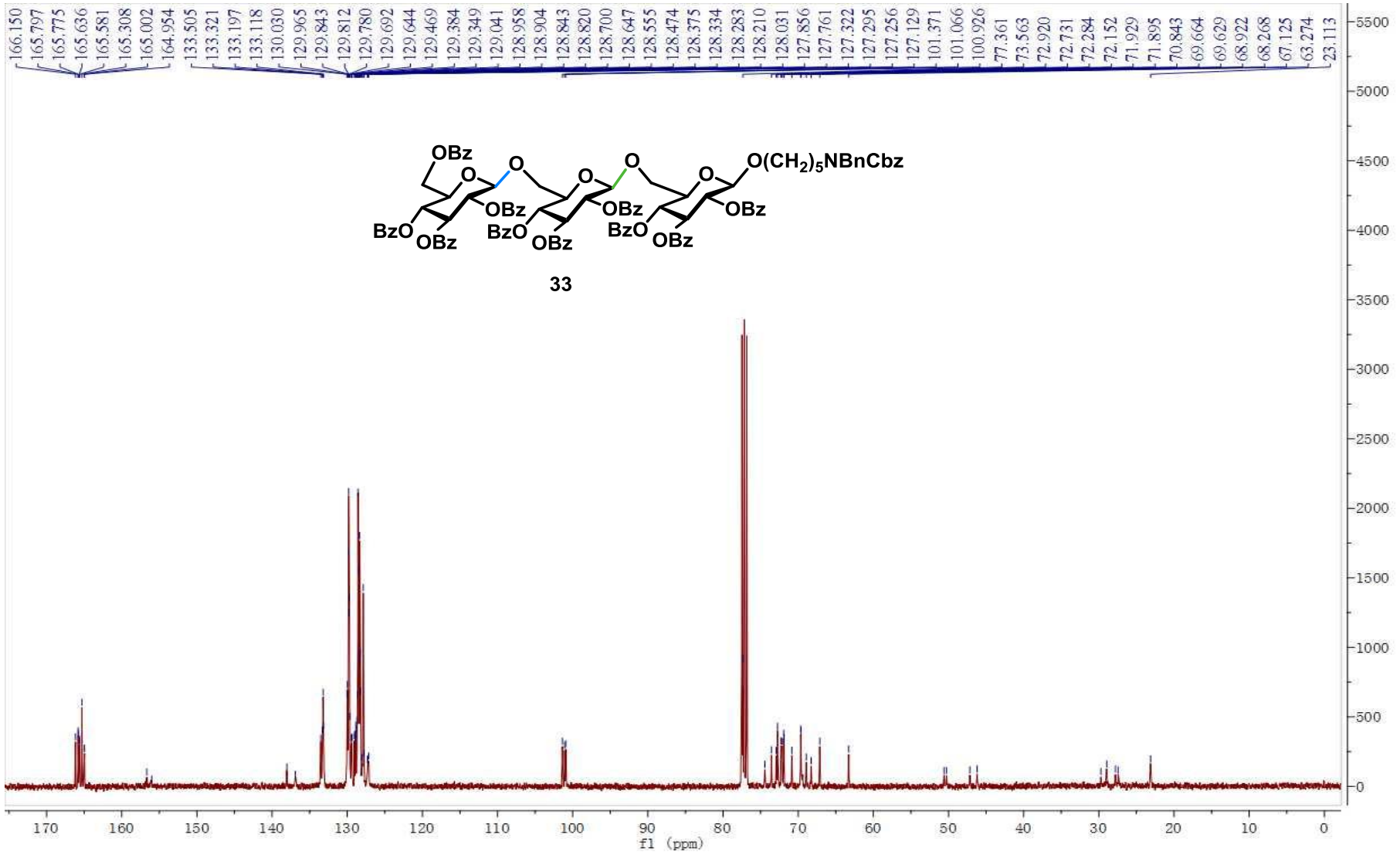

OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
BnO
O
OBn
O
BnO
OMe
32
6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
f2 (ppm)
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)


166.227
165.841
165.814
165.557
165.454
165.265
164.927
138.624
138.262
138.120
133.661
133.353
133.328
133.296
133.132
133.046
130.423
129.956
129.932
129.851
129.794
129.776
129.765
129.328
129.319
129.084
129.040
128.856
128.700
128.673
128.638
128.527
128.482
128.423
128.395
128.379
128.349
128.032
127.937
127.850
127.584
101.213
100.150
98.243
81.054
79.976
77.045
76.386
76.102
73.878
73.804
73.065
72.723
72.440
71.481
71.267
69.991
69.932
69.739
62.515
55.246
OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
BnO
O
OBn
O
BnO
OMe
32
f1 (ppm)

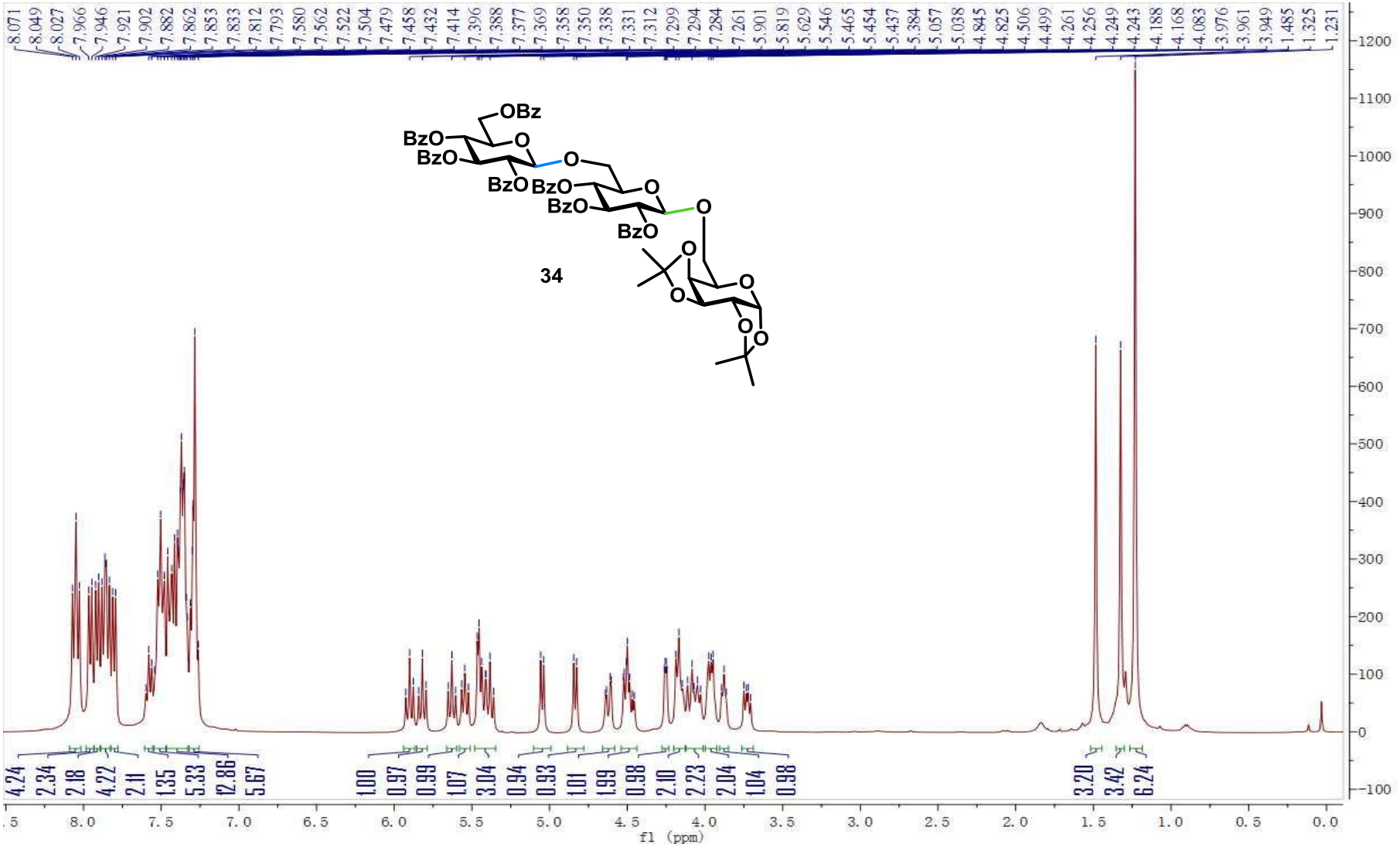

OBz
O
O
O
O
O
O(CH2)5NBnCbz
OBz
OBz
OBz
BzO
OBz
BzO
OBz
BzO
OBz
8.100
8.080
8.028
8.009
7.987
7.969
7.947
7.926
7.898
7.879
7.865
7.845
7.805
7.786
7.604
7.585
7.560
7.540
7.524
7.505
7.479
7.460
7.437
7.414
7.395
7.373
7.355
7.338
7.319
7.302
7.286
7.264
7.225
7.203
7.185
7.167
7.150
5.939
5.760
5.736
5.607
5.585
5.563
5.324
5.220
5.198
5.174
4.728
4.708
4.670
4.454
4.395
4.040
3.983
3.966
3.942
1.410
1.391
1.366
1.341
1.322
4.14
2.24
8.11
4.14
1.95
39.13
5.16
1.00
0.98
2.06
3.00
1.04
4.05
3.05
1.12
3.14
1.06
1.06
3.09
2.09
1.06
2.16
4.22
2.30
f1 (ppm)

33


OBz
O
O
O
O
O
O(CH2)5NBnCbz
BzO
OBz
BzO
OBz
BzO
OBz
OBz
OBz
OBz
33
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
f1 (ppm)


166.150
165.797
165.775
165.636
165.581
165.308
165.002
164.954
133.505
133.321
133.197
133.118
130.030
129.965
129.843
129.812
129.780
129.692
129.644
129.469
129.384
129.349
129.041
128.958
128.904
128.843
128.820
128.700
128.647
128.555
128.474
128.375
128.334
128.283
128.210
128.031
127.856
127.761
127.322
127.295
127.256
127.129
101.371
101.066
100.926
77.361
73.563
72.920
72.731
72.284
72.152
71.929
71.895
70.843
69.664
69.629
68.922
68.268
67.125
63.274
23.113
OBz
O
O
O
O
O
O(CH2)5NBnCbz
OBz
OBz
OBz
BzO
OBz
BzO
OBz
BzO
OBz
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

33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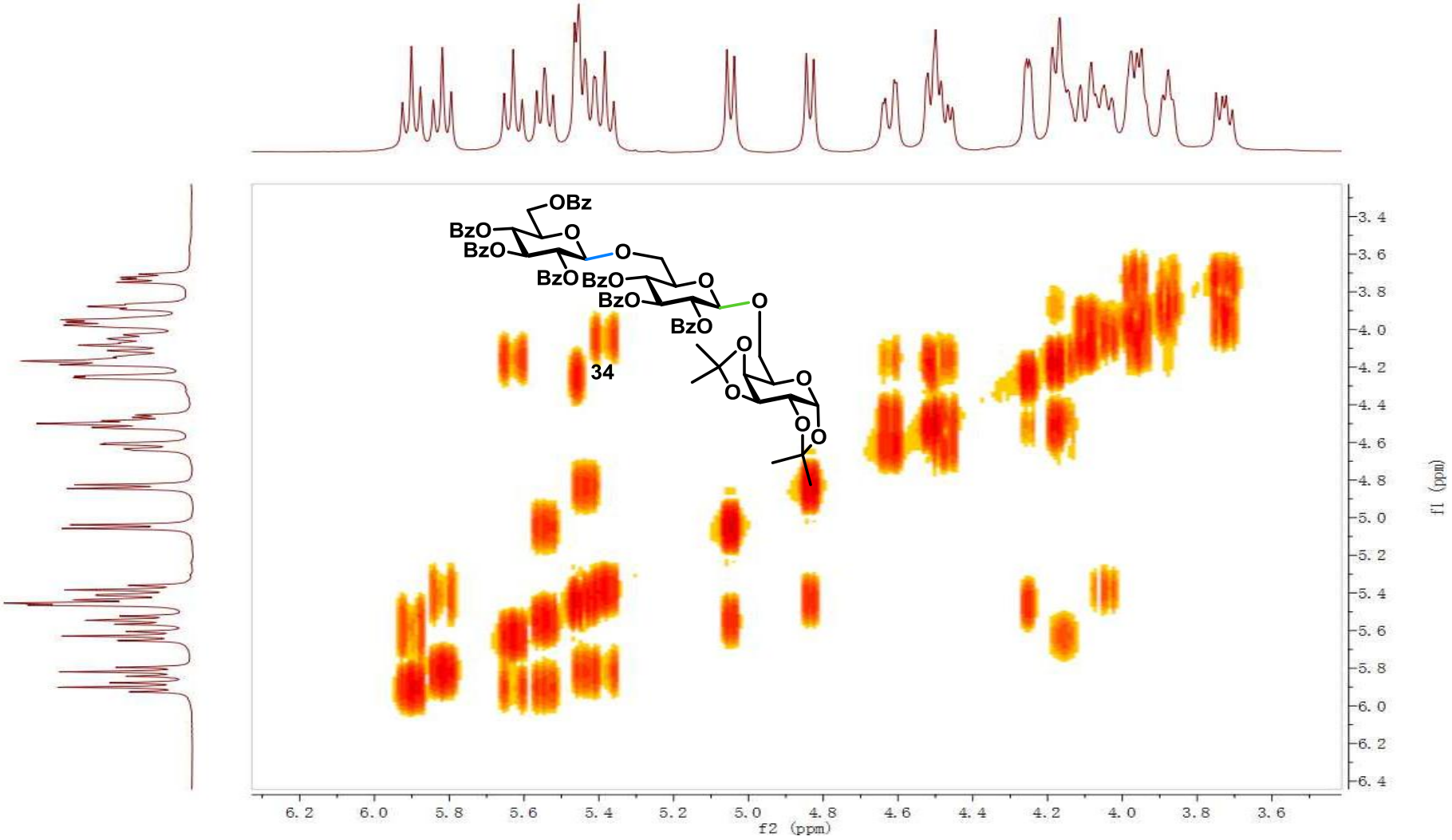
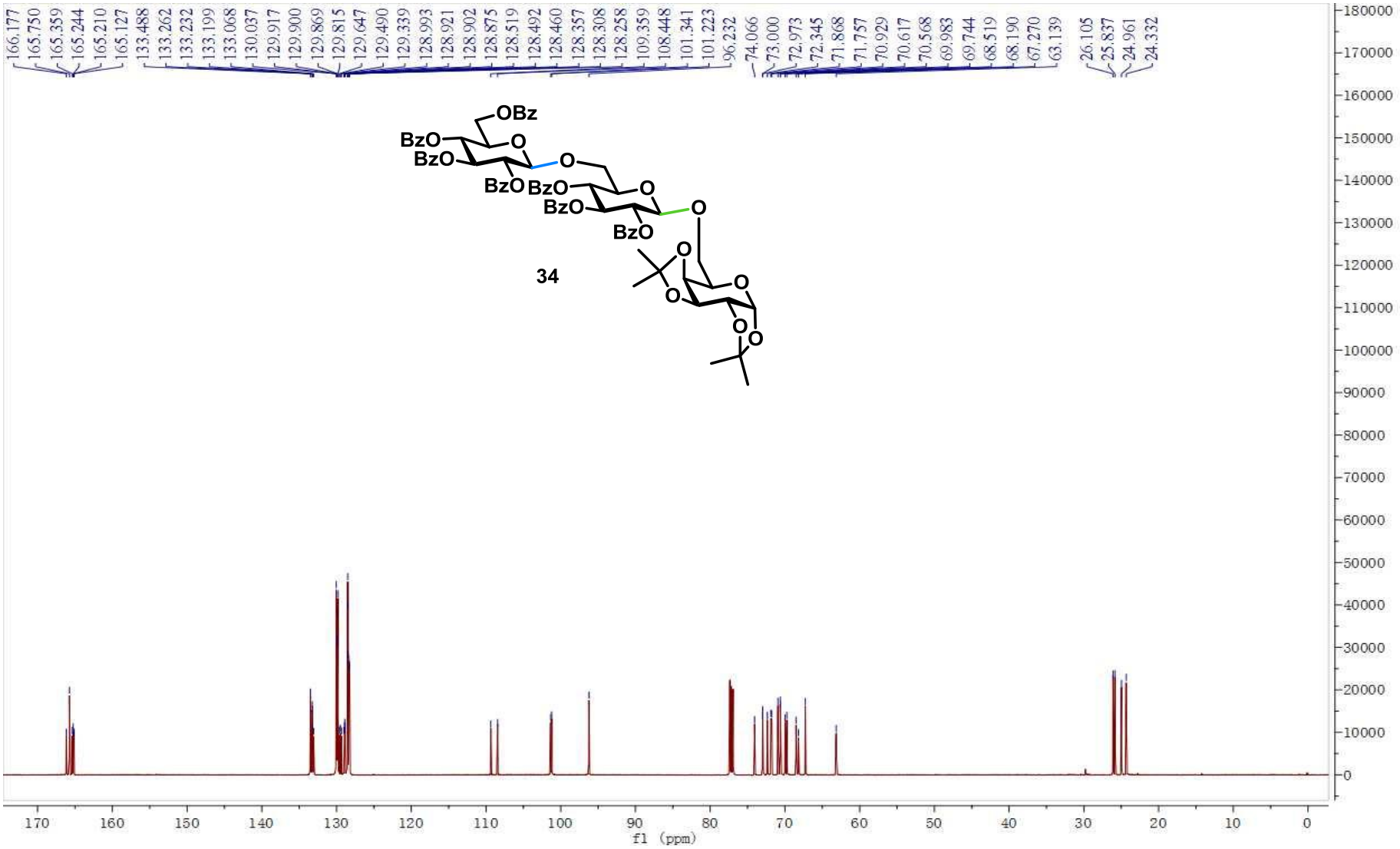
BzO
BzO
BzO
BzO
BzO
O
34
f1 (ppm)


OBz
BzO
BzO
BzO
BzO
BzO
BzO
O
O
O
O
O
O
O
O
O
O
34
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
f2 (ppm)
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
f1 (ppm)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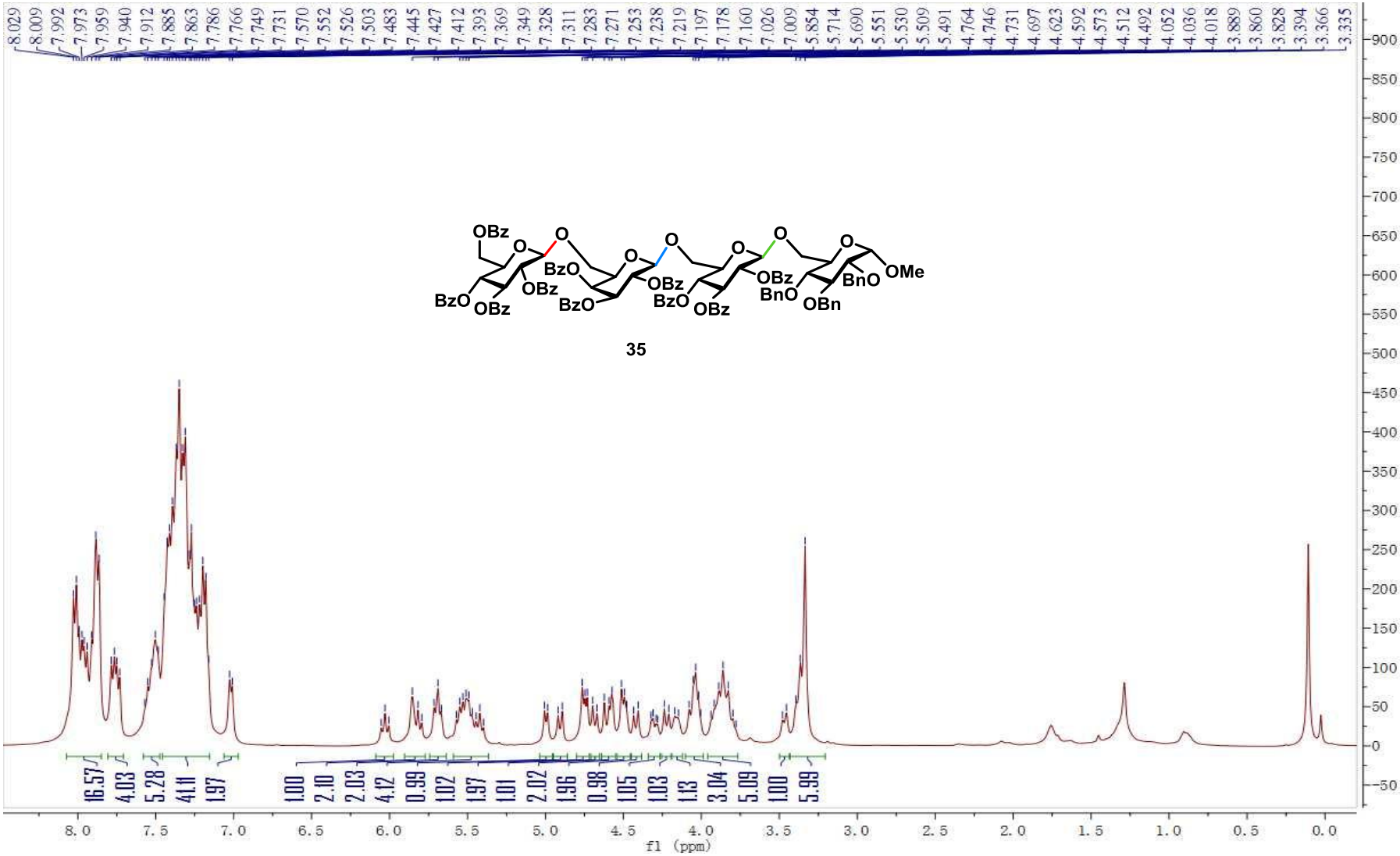
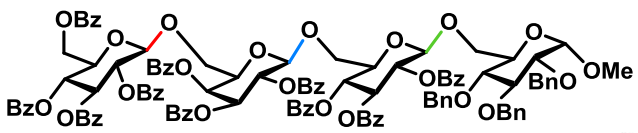
165.750
165.359
165.244
165.210
165.127
133.488
133.262
133.232
133.199
133.068
130.037
129.917
129.900
129.869
129.815
129.647
129.490
129.339
128.993
128.921
128.902
128.875
128.519
128.492
128.460
128.357
128.308
128.258
109.359
108.448
101.341
101.223
96.232
74.066
73.000
72.973
72.345
71.868
71.757
70.929
70.617
70.568
69.983
69.744
68.519
68.190
67.270
63.139
26.105
25.837
24.961
24.332
OBz
BzO
BzO
BzO
BzO
BzO
BzO
O
O
O
O
O
O
O
O
O
O
34
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

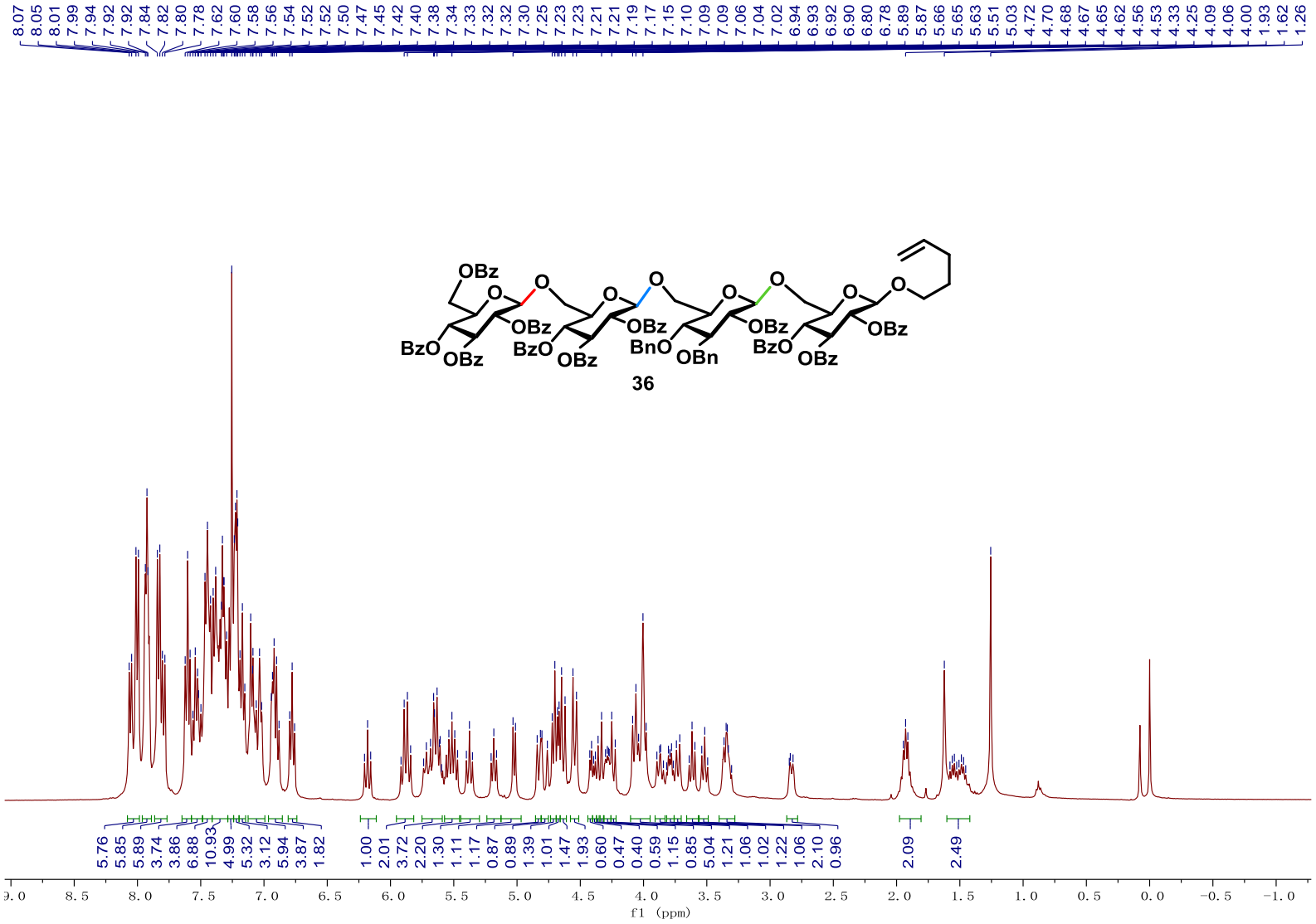

8.029
8.009
7.992
7.973
7.959
7.940
7.912
7.885
7.863
7.786
7.766
7.749
7.731
7.570
7.552
7.526
7.503
7.483
7.445
7.427
7.412
7.393
7.369
7.349
7.328
7.311
7.283
7.271
7.253
7.238
7.219
7.197
7.178
7.160
7.026
7.009
5.854
5.714
5.690
5.551
5.530
5.509
5.491
4.764
4.746
4.731
4.697
4.623
4.592
4.573
4.512
4.492
4.052
4.036
4.018
3.889
3.860
3.828
3.394
3.366
3.335
OBz
BzO
OBz
BzO
OBz
BzO
OBz
BzO
OBz
BnO
OBn
BnO
OMe
16.57
4.03
5.28
41.11
1.97
1.00
2.10
2.03
4.12
0.99
1.02
1.97
1.01
2.02
1.96
0.98
1.05
1.03
1.13
3.04
5.09
1.00
5.99
f1 (ppm)

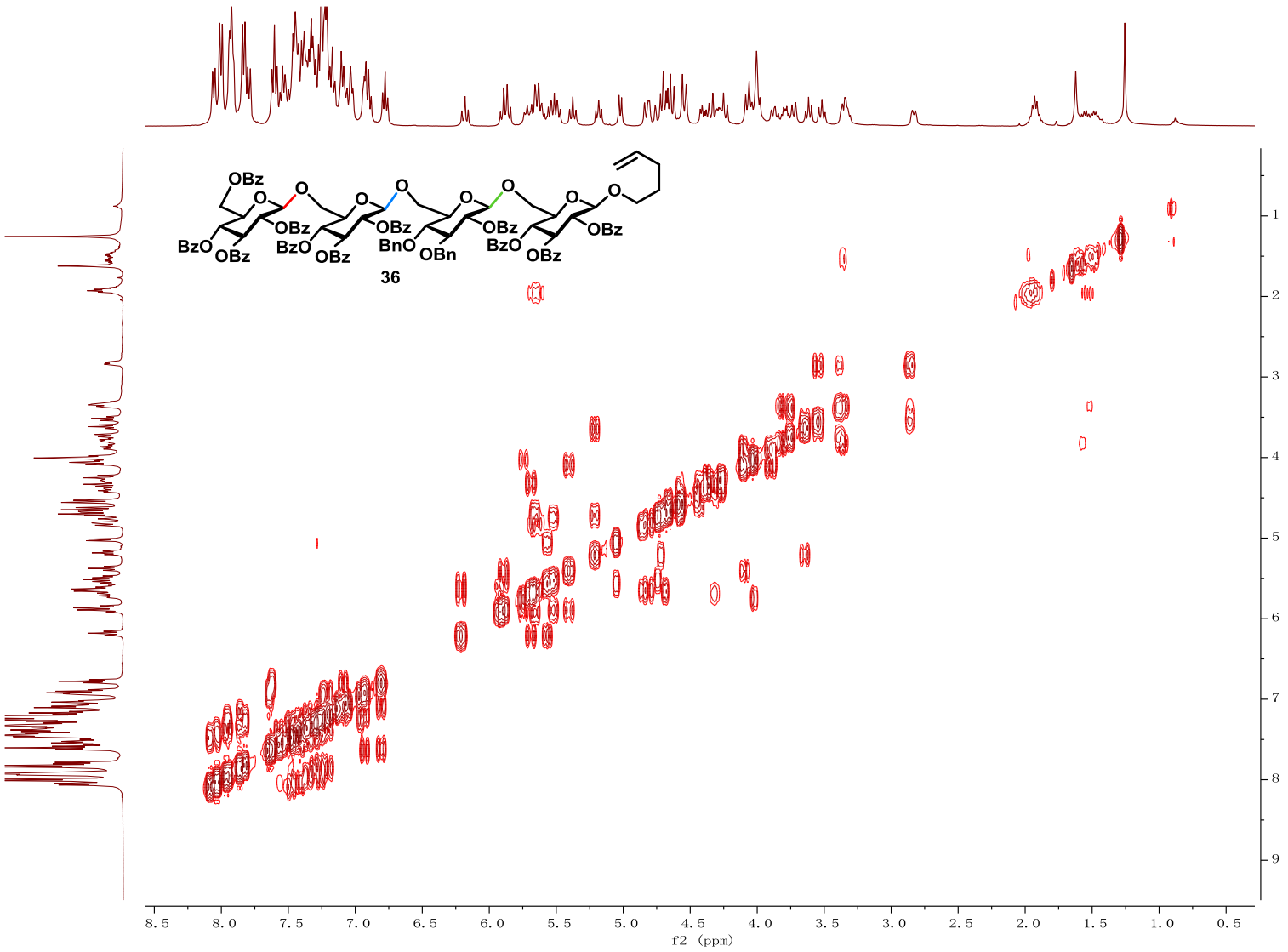
35

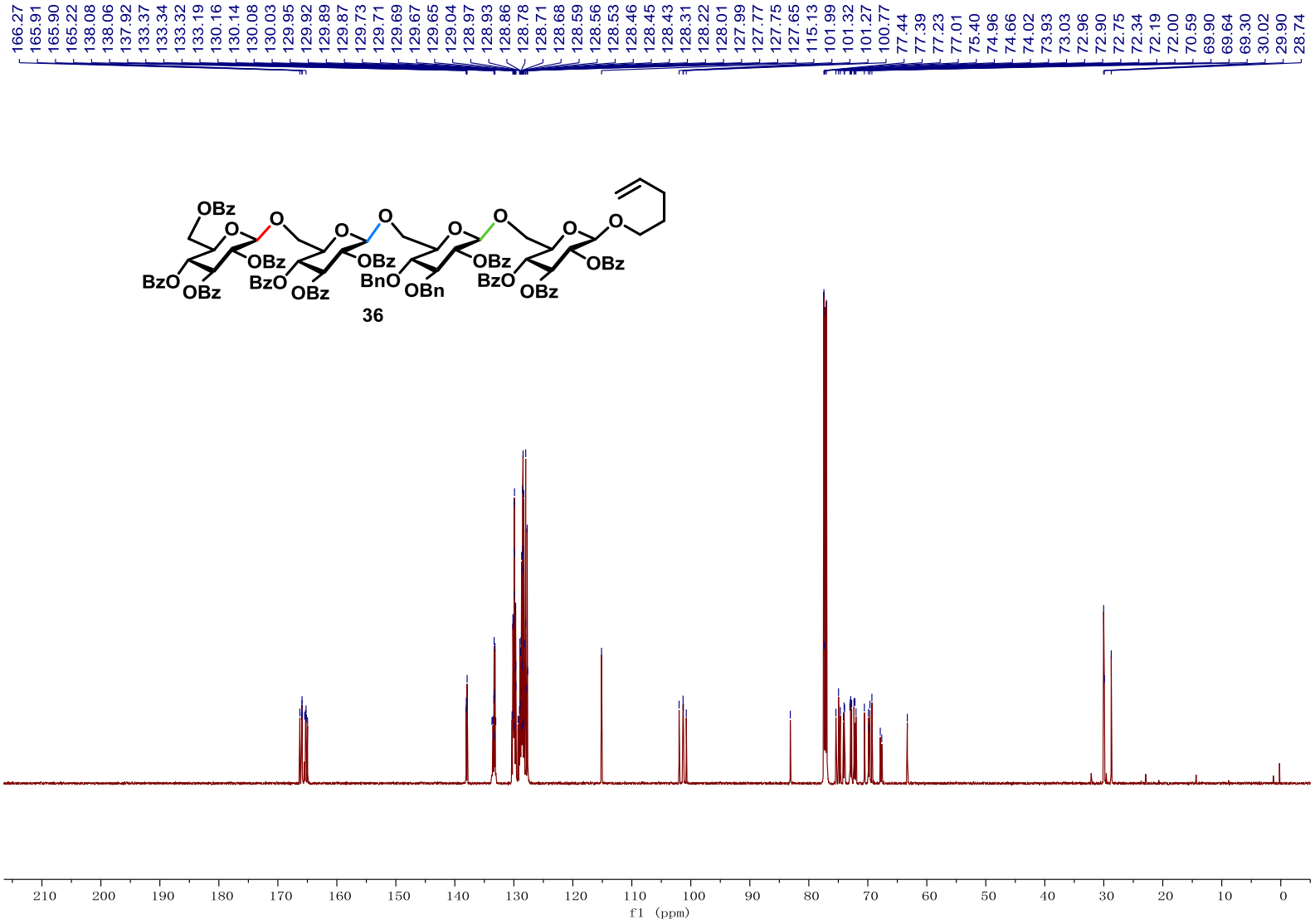

OBz
O
BzO
OBz
BzO
OBz
BzO
OBz
BzO
OBz
BnO
OBn
BnO
OMe

35

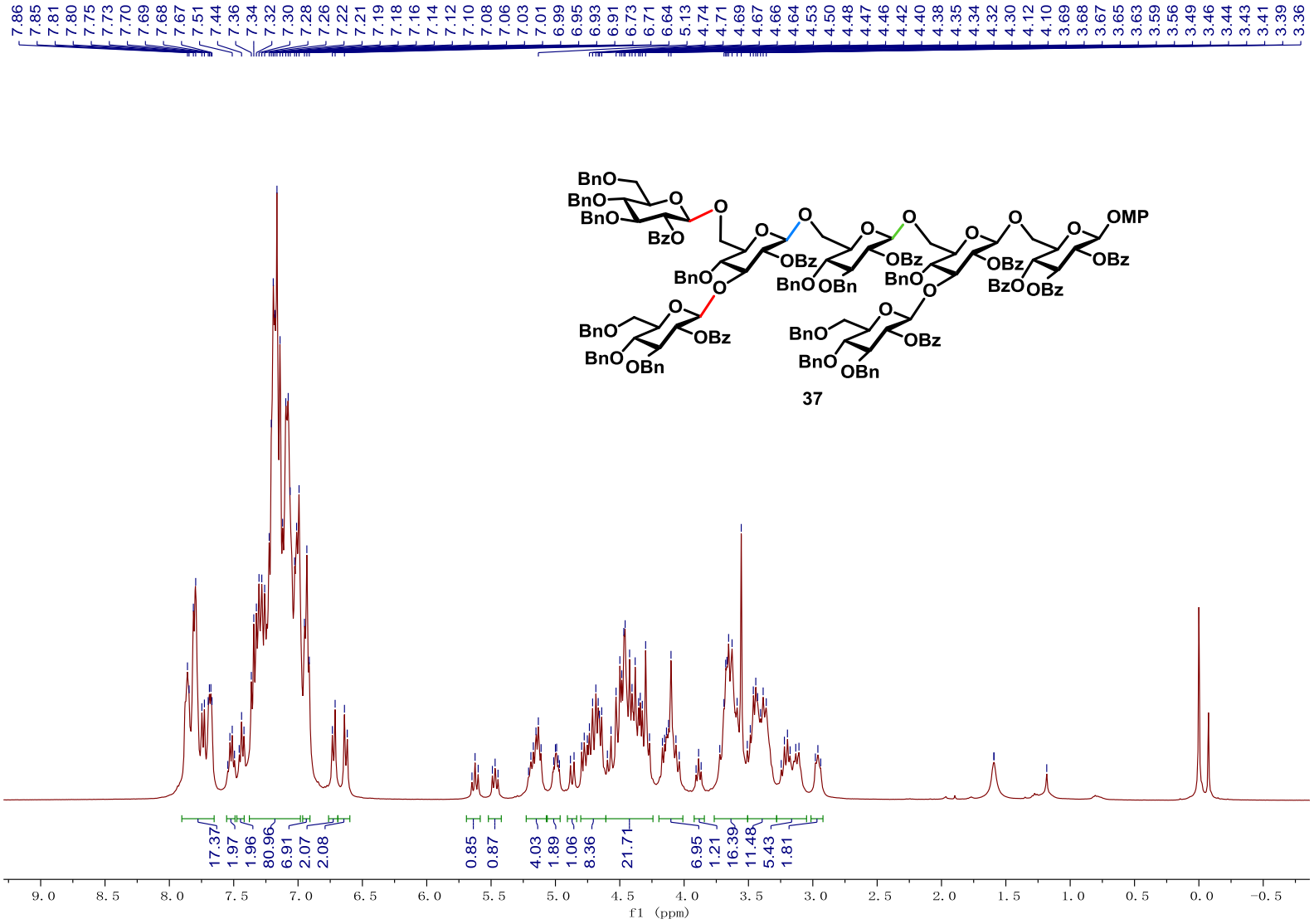
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)


8.07 8.05 8.01 7.99 7.94 7.92 7.92 7.84 7.82 7.80 7.78 7.62 7.60 7.58 7.56 7.54 7.52 7.52 7.50 7.47 7.45 7.42 7.40 7.38 7.34 7.33 7.32 7.32 7.30 7.25 7.23 7.23 7.21 7.21 7.19 7.17 7.15 7.10 7.09 7.09 7.06 7.04 7.02 6.94 6.93 6.92 6.90 6.80 6.78 5.89 5.87 5.66 5.65 5.63 5.51 5.03 4.72 4.70 4.68 4.67 4.65 4.62 4.56 4.53 4.33 4.25 4.09 4.06 4.00 1.93 1.62 1.26
OBz
BzO
BnO
OBn
36
5.76 5.85 5.89 3.74 3.86 6.88 10.93 4.99 5.32 3.12 5.94 3.87 1.82
1.00 2.01 3.72 2.20 1.30 1.11 1.17 0.87 0.89 1.39 1.01 1.47 1.93 0.60 0.47 0.40 0.59 1.15 0.85 5.04 1.21 1.06 1.02 1.22 1.06 2.10 0.96
2.09 2.49
f1 (ppm)

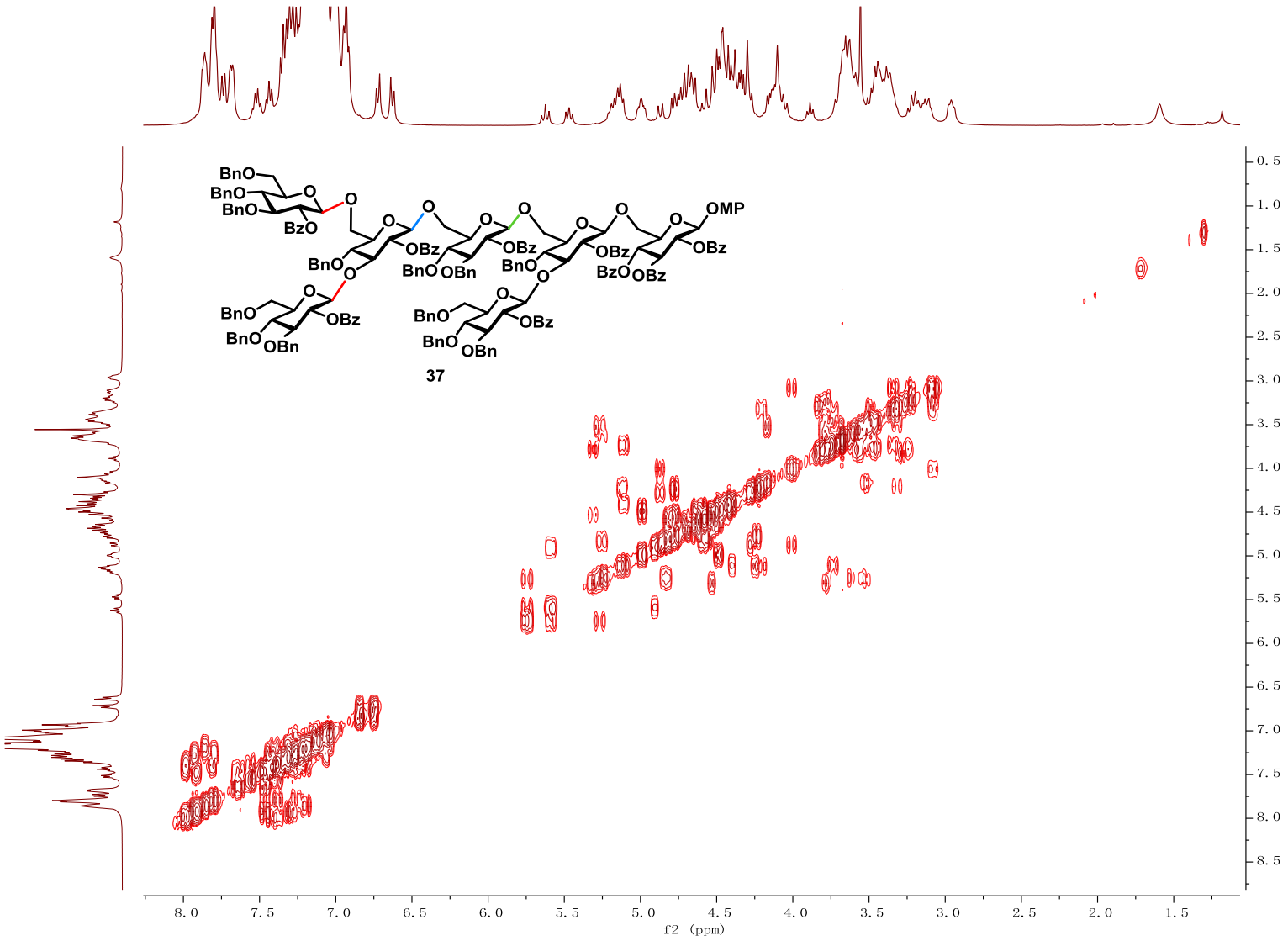

OBz
BzO
OBz
BnO
OBn
36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
9

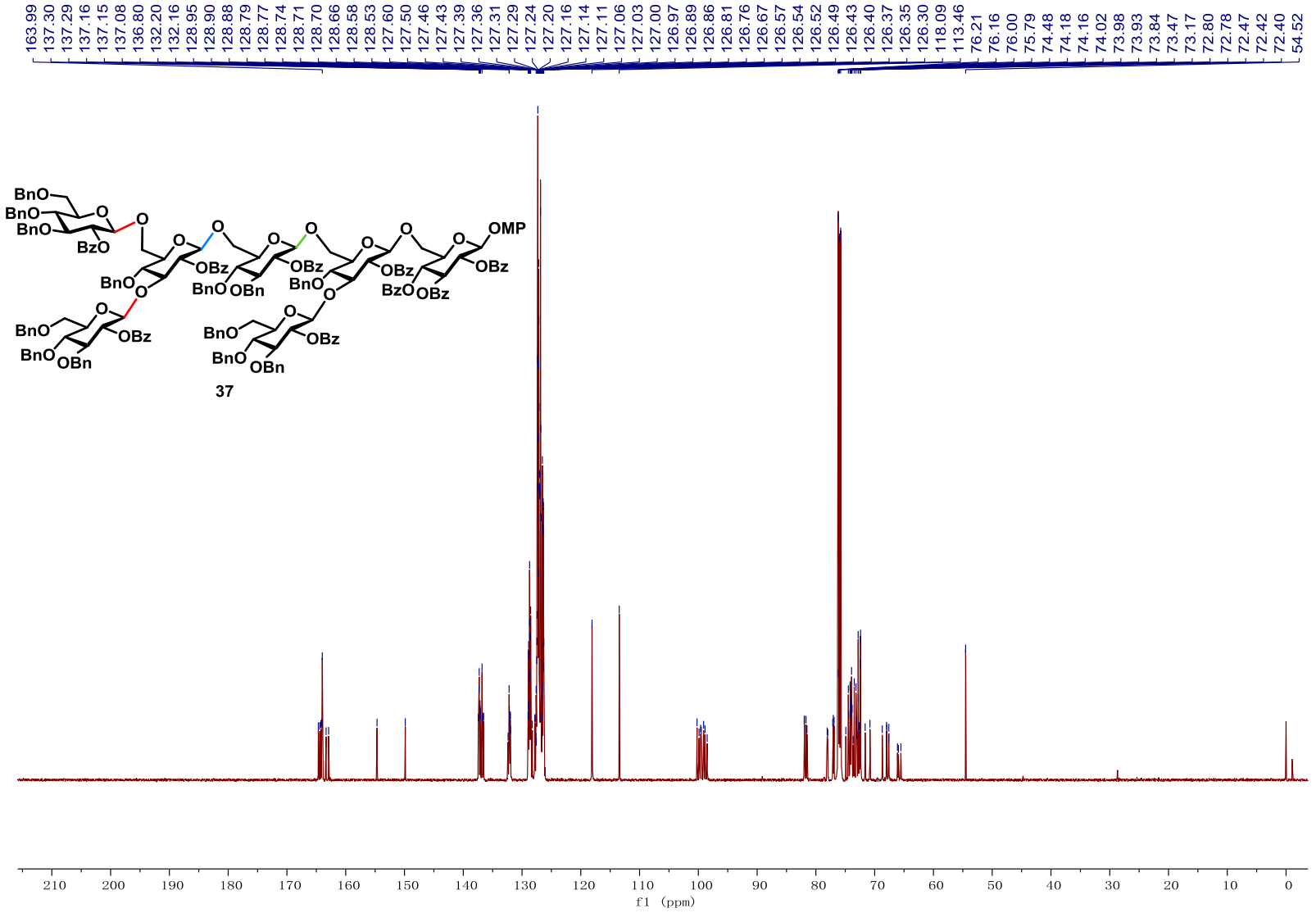

166.27
165.91
165.90
165.22
138.08
138.06
137.92
133.37
133.34
133.32
133.19
130.16
130.14
130.08
130.03
129.95
129.92
129.89
129.87
129.73
129.71
129.69
129.67
129.65
129.04
128.97
128.93
128.86
128.78
128.71
128.68
128.59
128.56
128.53
128.46
128.45
128.43
128.31
128.22
128.01
127.99
127.77
127.75
127.65
115.13
101.99
101.32
101.27
100.77
77.44
77.39
77.23
77.01
75.40
74.96
74.66
74.02
73.93
73.03
72.96
72.90
72.75
72.34
72.19
72.00
70.59
69.90
69.64
69.30
30.02
29.90
28.74
OBz
BzO
OBz
BnO
OBn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

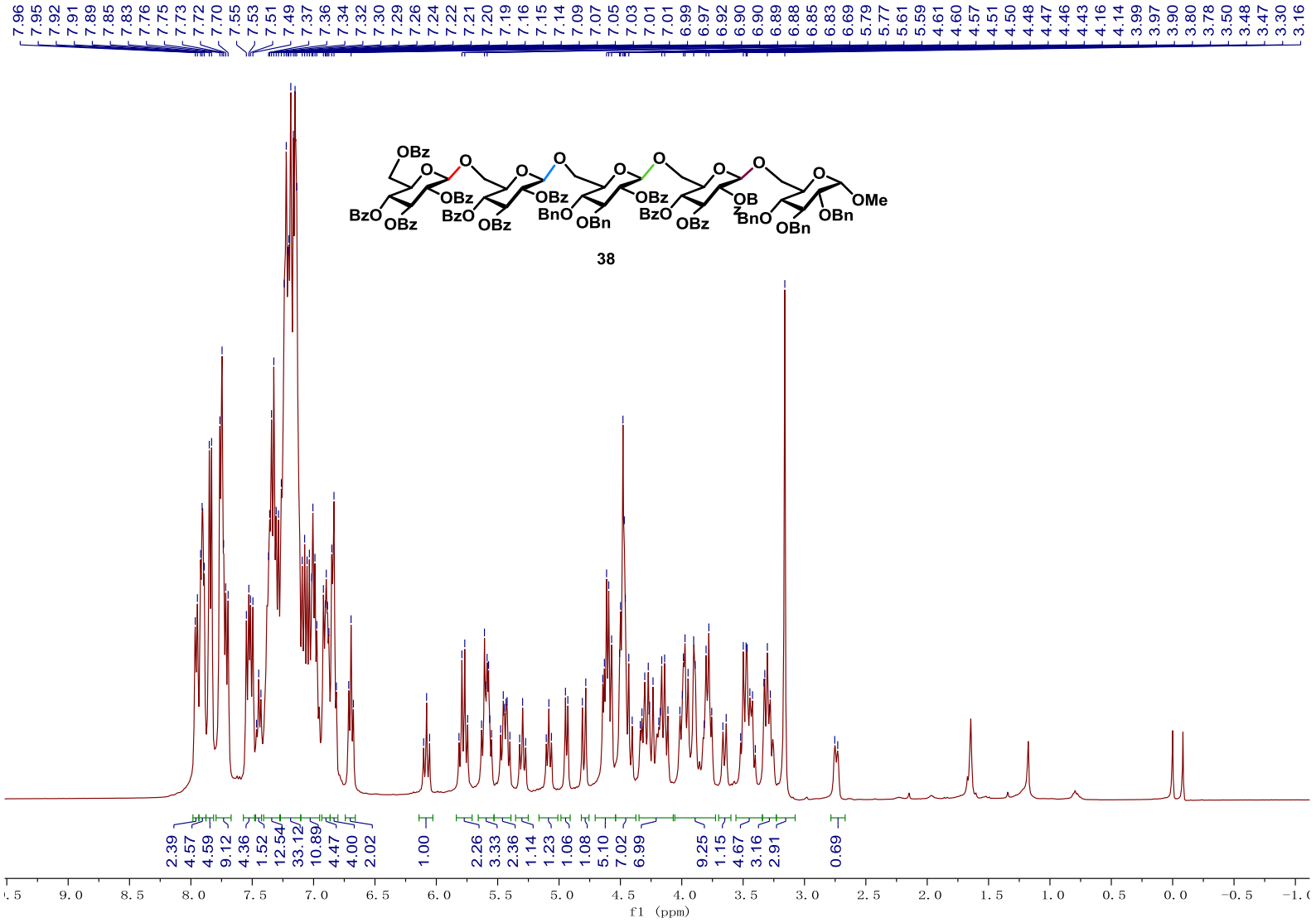
36

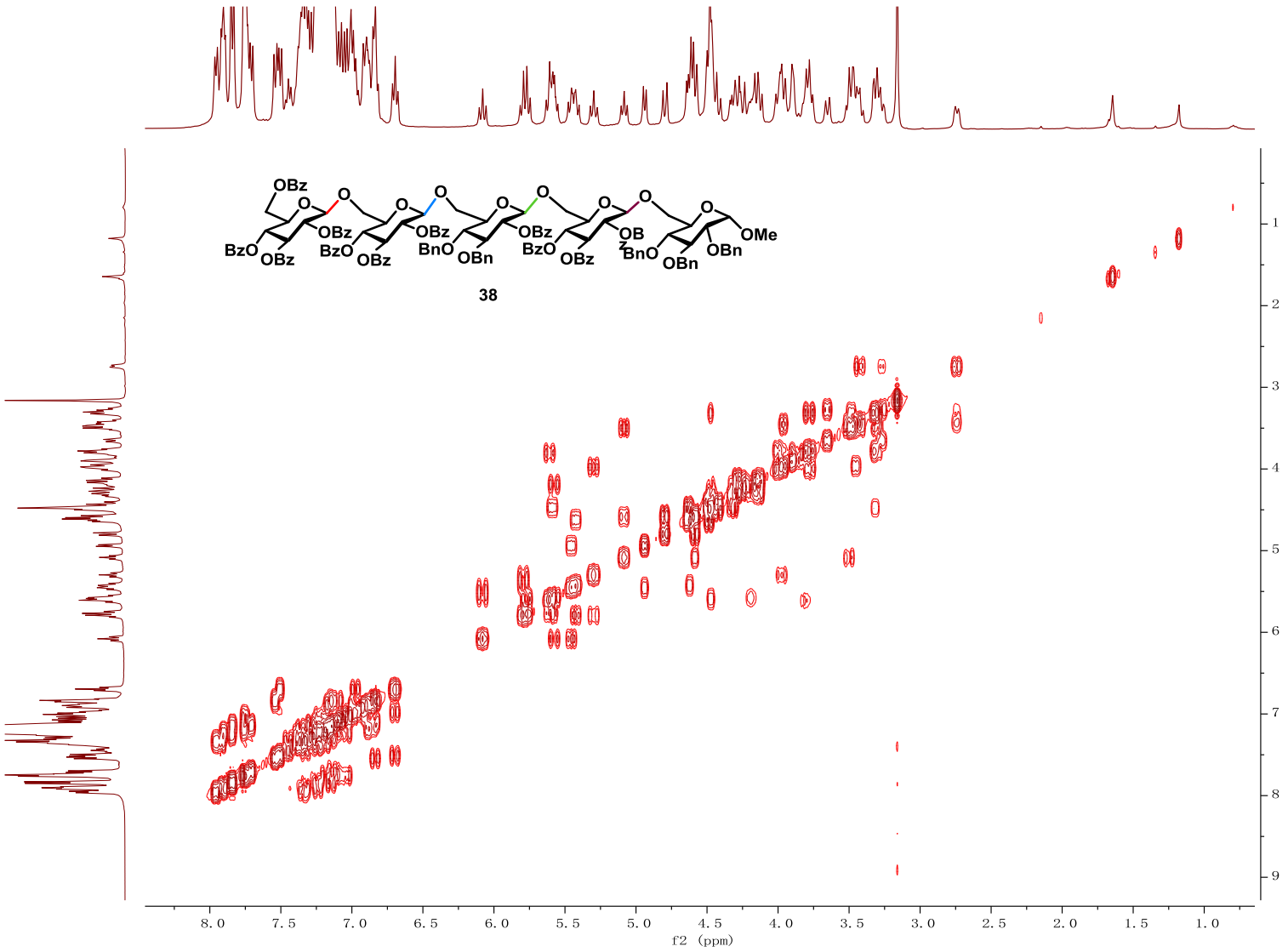

7.86 7.85 7.81 7.80 7.75 7.73 7.70 7.69 7.68 7.67 7.51 7.44 7.36 7.34 7.32 7.30 7.28 7.26 7.22 7.21 7.19 7.18 7.16 7.14 7.12 7.10 7.08 7.06 7.03 7.01 6.99 6.95 6.93 6.91 6.73 6.71 6.64 5.13 4.74 4.71 4.69 4.67 4.66 4.64 4.53 4.50 4.48 4.47 4.46 4.42 4.40 4.38 4.35 4.34 4.32 4.30 4.12 4.10 3.69 3.68 3.67 3.65 3.63 3.59 3.56 3.49 3.46 3.44 3.43 3.41 3.39 3.36
BnO
BnO
BnO
BzO
O
OBz
OBn
OMP
17.37 1.97 1.96 80.96 6.91 2.07 2.08 0.85 0.87 4.03 1.89 1.06 8.36 21.71 6.95 1.21 16.39 11.48 5.43 1.81
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 −0.5
f1 (ppm)

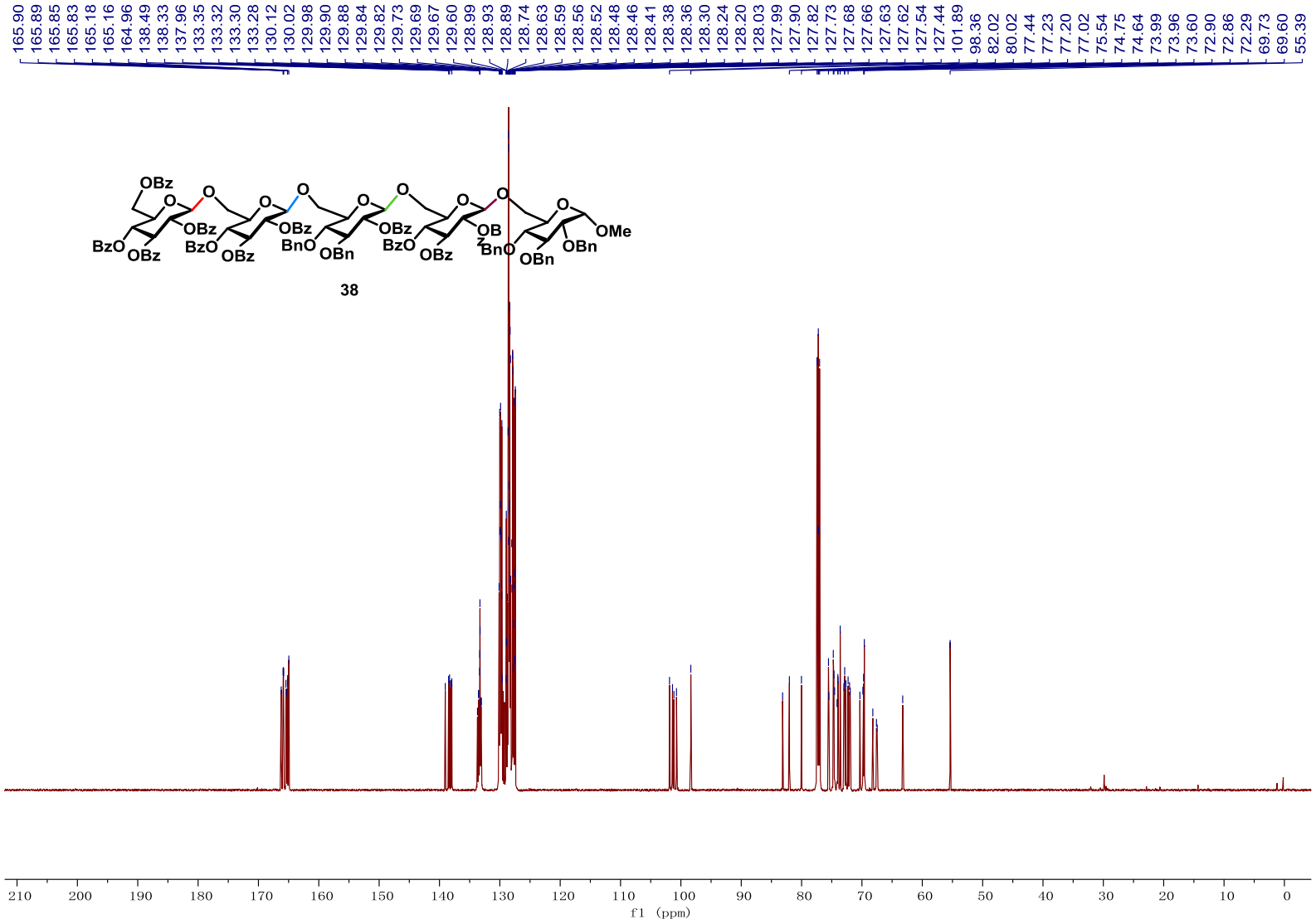
37


BnO
BnO
BnO
BzO
O
OBz
BnO
OBn
OMP
37
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
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5


163.99
137.30
137.29
137.16
137.15
137.08
136.80
132.20
132.16
128.95
128.90
128.88
128.79
128.77
128.74
128.71
128.70
128.66
128.58
128.53
127.60
127.50
127.46
127.43
127.39
127.36
127.31
127.29
127.24
127.20
127.16
127.14
127.11
127.06
127.03
127.00
126.97
126.89
126.86
126.81
126.76
126.67
126.57
126.54
126.52
126.49
126.43
126.40
126.37
126.35
126.30
118.09
113.46
76.21
76.16
76.00
75.79
74.48
74.18
74.16
74.02
73.98
73.93
73.84
73.47
73.17
72.80
72.78
72.47
72.42
72.40
54.52
BnO
BnO
BnO
BzO
O
OBz
BnO
BnO
OBn
OMP
BnO
OBn
BnO
OBn
BnO
OBn
BzO
OBz
37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.96 7.95 7.92 7.91 7.89 7.85 7.83 7.76 7.75 7.73 7.72 7.70 7.55 7.53 7.51 7.49 7.37 7.36 7.34 7.32 7.30 7.29 7.26 7.24 7.22 7.21 7.20 7.19 7.16 7.15 7.14 7.09 7.07 7.05 7.03 7.01 7.01 6.99 6.97 6.92 6.90 6.90 6.89 6.88 6.85 6.83 6.69 5.79 5.77 5.61 5.59 4.61 4.60 4.57 4.51 4.50 4.48 4.47 4.46 4.43 4.16 4.14 3.99 3.97 3.90 3.80 3.78 3.50 3.48 3.47 3.30 3.16
OBz
BzO
OBz
OBz
BzO
OBz
OBz
BnO
OBn
OBz
BzO
OBz
OB
z
BnO
OBn
OBn
OMe
38
2.39 4.57 4.59 9.12 4.36 1.52 12.54 33.12 10.89 4.47 4.00 2.02 1.00 2.26 3.33 2.36 1.14 1.23 1.06 1.08 5.10 7.02 6.99 9.25 1.15 4.67 3.16 2.91 0.69
f1 (ppm)


OBz
BzO
OBz
OBz
BzO
OBz
OBz
BnO
OBn
OBz
BzO
OBz
OB
z
BnO
OBn
OMe
OBn
38
1
2
3
4
5
6
7
8
9
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
f2 (ppm)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165.83
165.18
165.16
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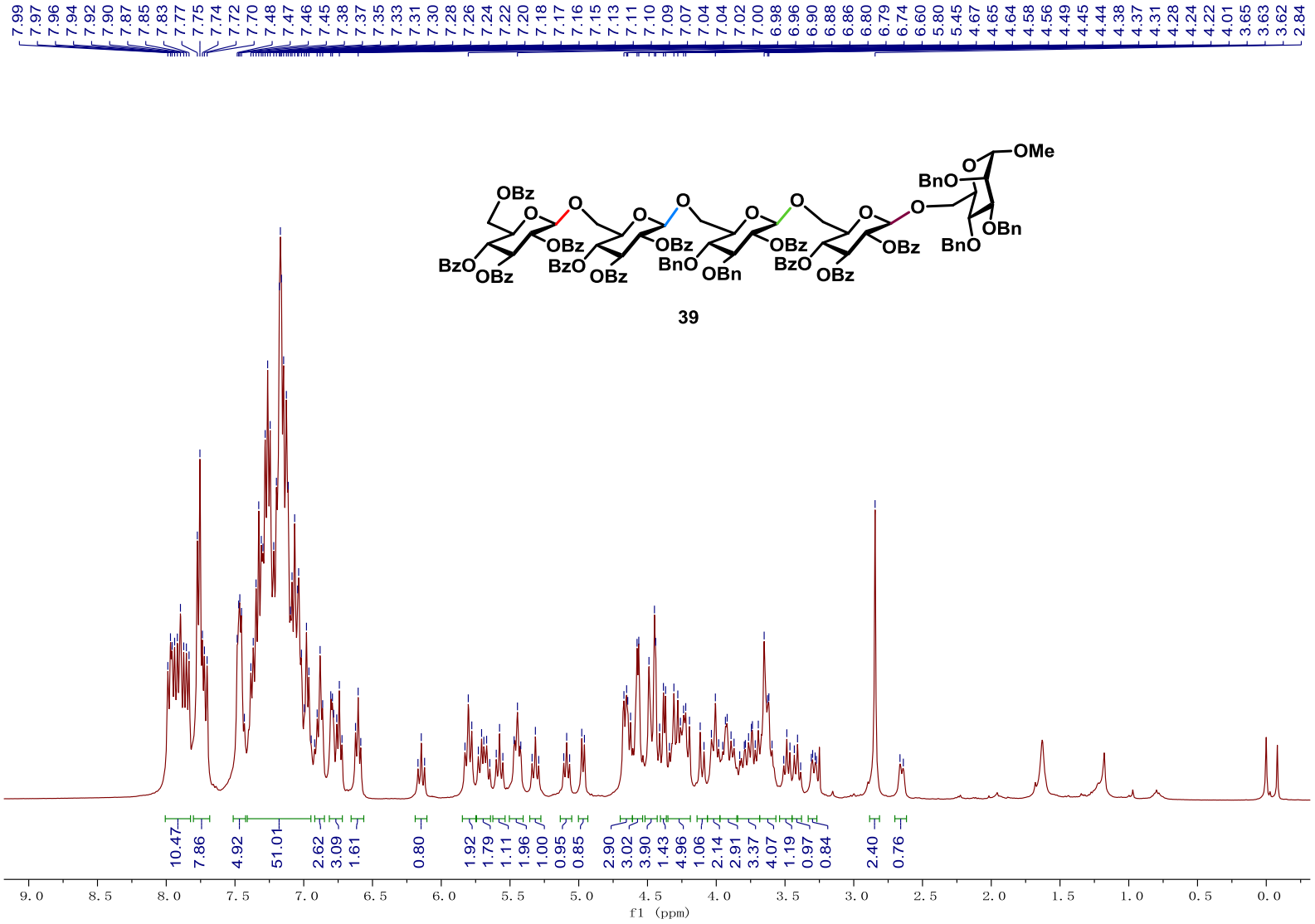
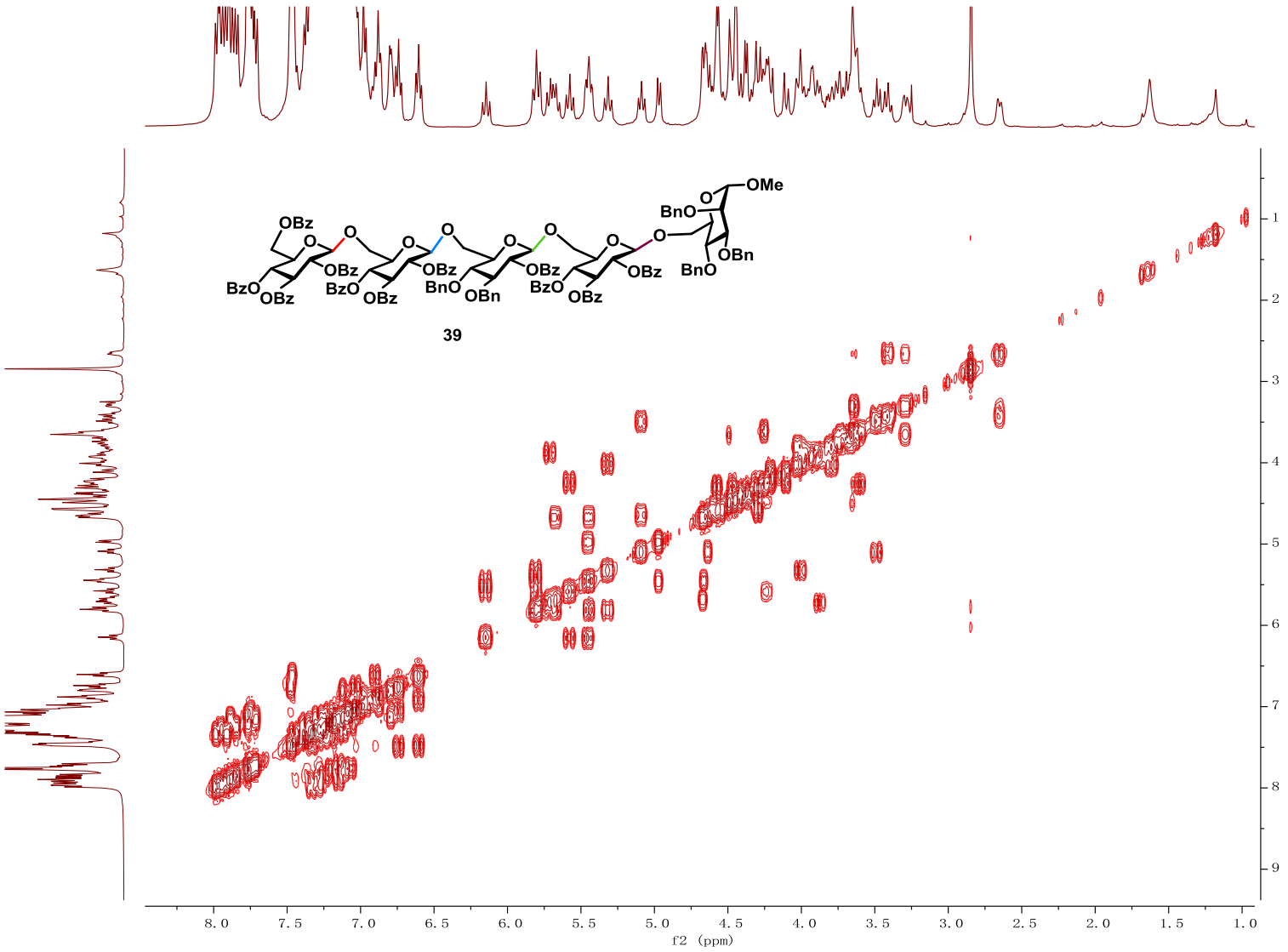
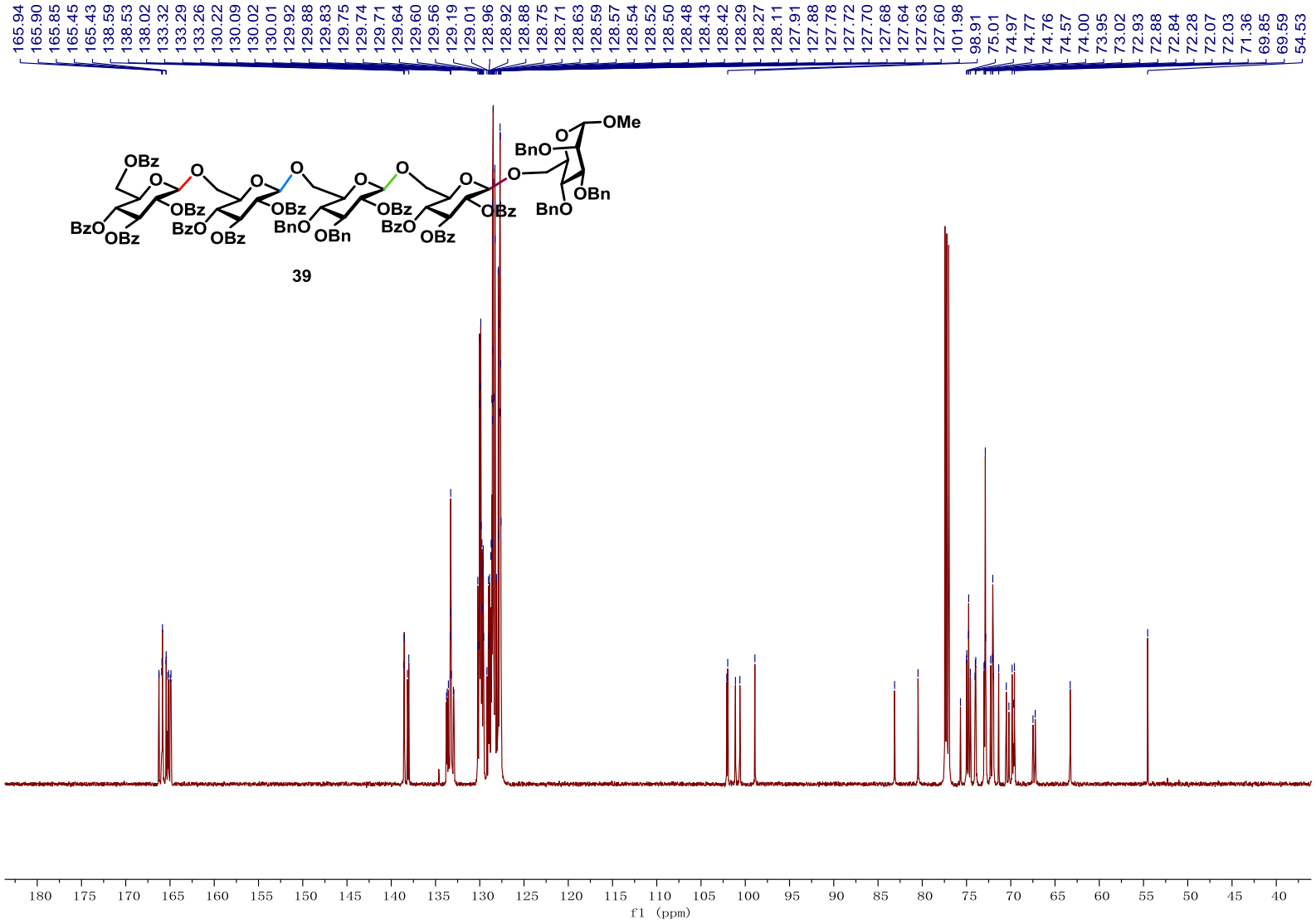
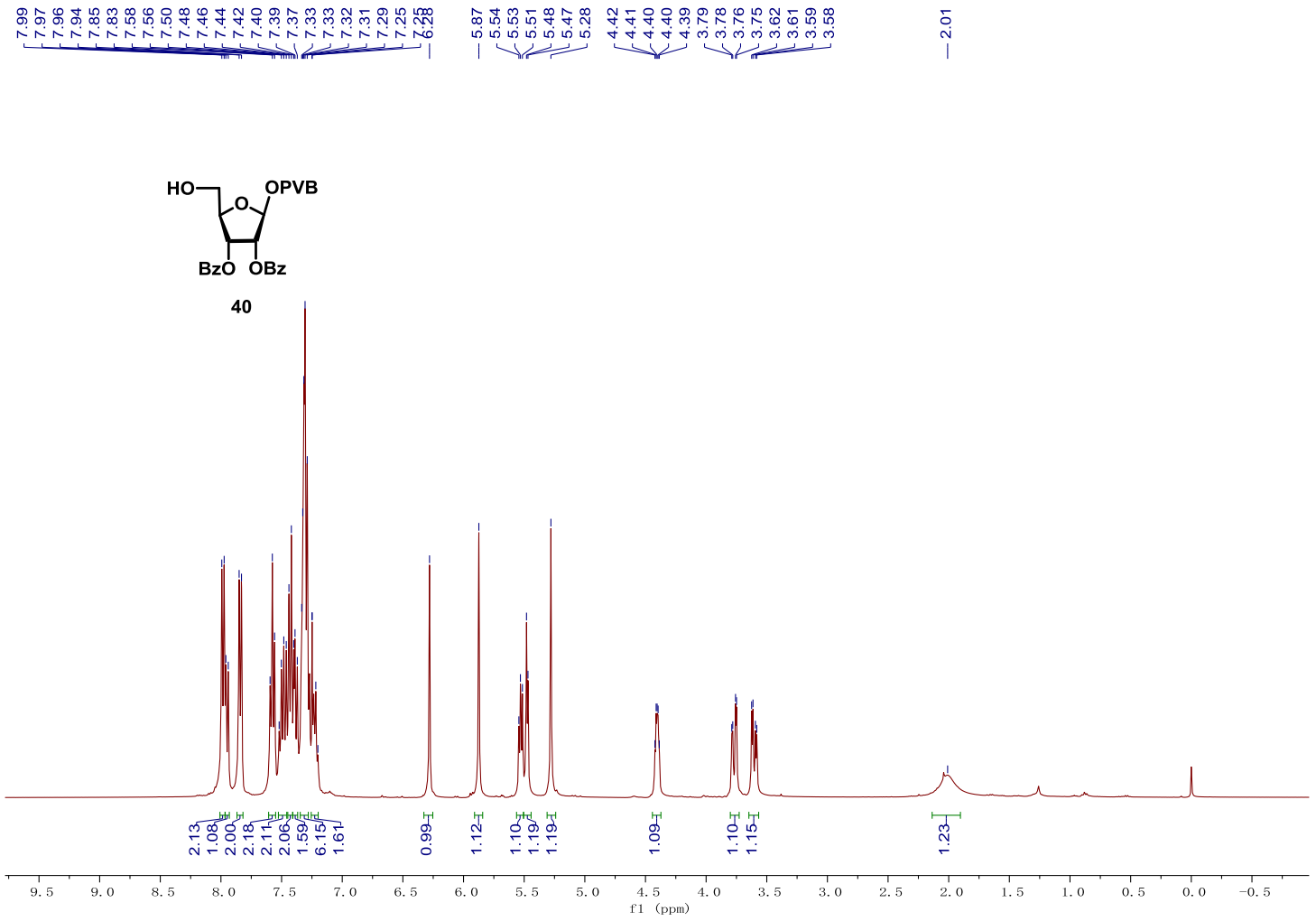
138.49
138.33
137.96
133.35
133.32
133.30
133.28
130.12
130.02
129.98
129.90
129.88
129.84
129.82
129.73
129.69
129.67
129.60
128.99
128.93
128.89
128.74
128.63
128.59
128.56
128.52
128.48
128.46
128.41
128.38
128.36
128.30
128.24
128.20
128.03
127.99
127.90
127.82
127.73
127.68
127.66
127.63
127.62
127.54
127.44
101.89
98.36
82.02
80.02
77.44
77.23
77.20
77.02
75.54
74.75
74.64
73.99
73.96
73.60
72.90
72.86
72.29
69.73
69.60
55.39
OBz
BzO
OBz
OBz
BzO
OBz
OBz
BnO
OBn
OBz
BzO
OBz
OB
z
BnO
OBn
OBn
OMe
38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

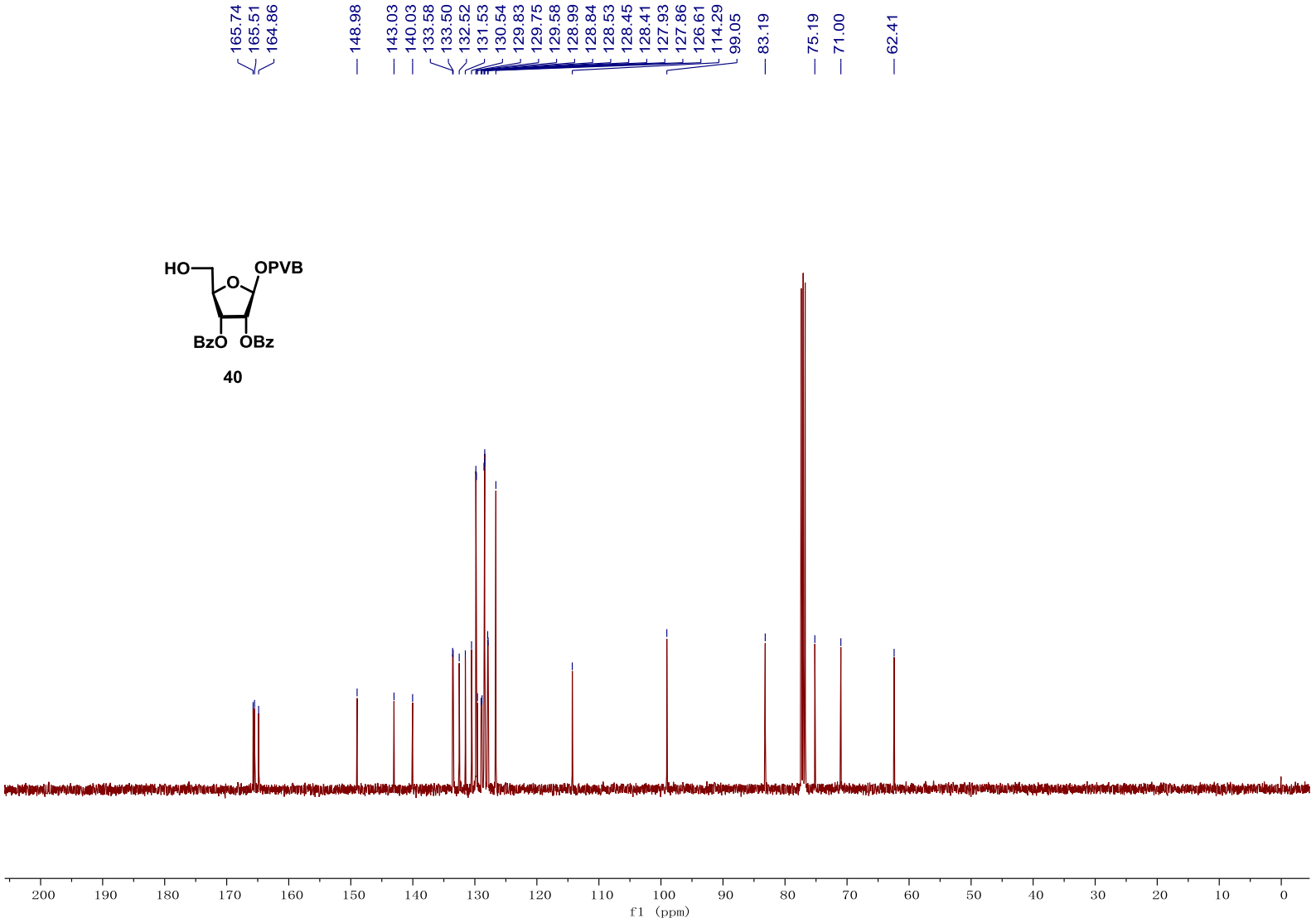

7.99 7.97 7.96 7.94 7.92 7.90 7.87 7.85 7.83 7.77 7.75 7.74 7.72 7.70 7.48 7.47 7.46 7.45 7.38 7.37 7.35 7.33 7.31 7.30 7.28 7.26 7.24 7.22 7.20 7.18 7.17 7.16 7.15 7.13 7.11 7.10 7.09 7.07 7.04 7.04 7.02 7.00 6.98 6.96 6.90 6.88 6.86 6.80 6.79 6.74 6.60 5.80 5.45 4.67 4.65 4.64 4.58 4.56 4.49 4.45 4.44 4.38 4.37 4.31 4.28 4.24 4.22 4.01 3.65 3.63 3.62 2.84
OMe
BnO
OBn
OBz
BzO
10.47 7.86 4.92 51.01 2.62 3.09 1.61 0.80 1.92 1.79 1.11 1.96 1.00 0.95 0.85 2.90 3.02 3.90 1.43 4.96 1.06 2.14 2.91 3.37 4.07 1.19 0.97 0.84 2.40 0.76
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)

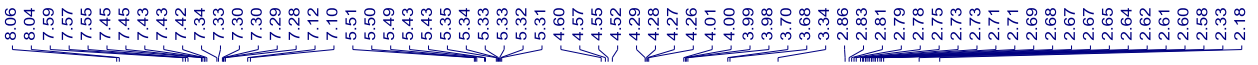
39


OBz
BzO
OBz
OBz
BzO
OBz
OBz
BnO
OBn
OBz
BzO
OBz
OBz
BnO
OBn
OMe
39
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


165.94
165.90
165.85
165.45
165.43
138.59
138.53
138.02
133.32
133.29
133.26
130.22
130.09
130.02
130.01
129.92
129.88
129.83
129.75
129.74
129.71
129.64
129.60
129.56
129.19
129.01
128.96
128.92
128.88
128.75
128.71
128.63
128.59
128.57
128.54
128.52
128.50
128.48
128.43
128.42
128.29
128.27
128.11
127.91
127.88
127.78
127.72
127.70
127.68
127.64
127.63
127.60
101.98
98.91
75.01
74.97
74.77
74.76
74.57
74.00
73.95
73.02
72.93
72.88
72.84
72.28
72.07
72.03
71.36
69.85
69.59
54.53
OBz
BzO
OBz
OBz
BzO
OBz
OBz
BnO
OBn
OBz
BzO
OBz
OBz
BnO
OBn
OMe
39
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
f1 (ppm)


7.99
7.97
7.96
7.94
7.85
7.83
7.58
7.56
7.50
7.48
7.46
7.44
7.42
7.40
7.39
7.37
7.33
7.32
7.31
7.29
7.25
7.25
6.28
5.87
5.54
5.53
5.51
5.48
5.47
5.28
4.42
4.41
4.40
4.40
4.39
3.79
3.78
3.76
3.75
3.62
3.61
3.59
3.58
2.01
HO
OPVB
O
BzO
OBz
40
2.13
1.08
2.00
2.18
2.11
2.06
1.59
6.15
1.61
0.99
1.12
1.10
1.19
1.19
1.09
1.10
1.15
1.23
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
-0.5
f1 (ppm)


165.74
165.51
164.86
148.98
143.03
140.03
133.58
133.50
132.52
131.53
130.54
129.83
129.75
129.58
128.99
128.84
128.53
128.45
128.41
127.93
127.86
126.61
114.29
99.05
83.19
75.19
71.00
62.41
HO
OPVB
O
BzO
OBz
40
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.04
7.59
7.57
7.55
7.45
7.45
7.43
7.43
7.42
7.34
7.33
7.30
7.30
7.29
7.28
7.12
7.10
5.51
5.50
5.49
5.43
5.43
5.35
5.34
5.33
5.33
5.32
5.31
4.60
4.57
4.55
4.52
4.29
4.28
4.27
4.26
4.01
4.00
3.99
3.98
3.70
3.68
3.34
2.86
2.83
2.81
2.79
2.78
2.75
2.73
2.73
2.71
2.71
2.69
2.68
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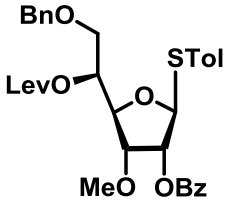
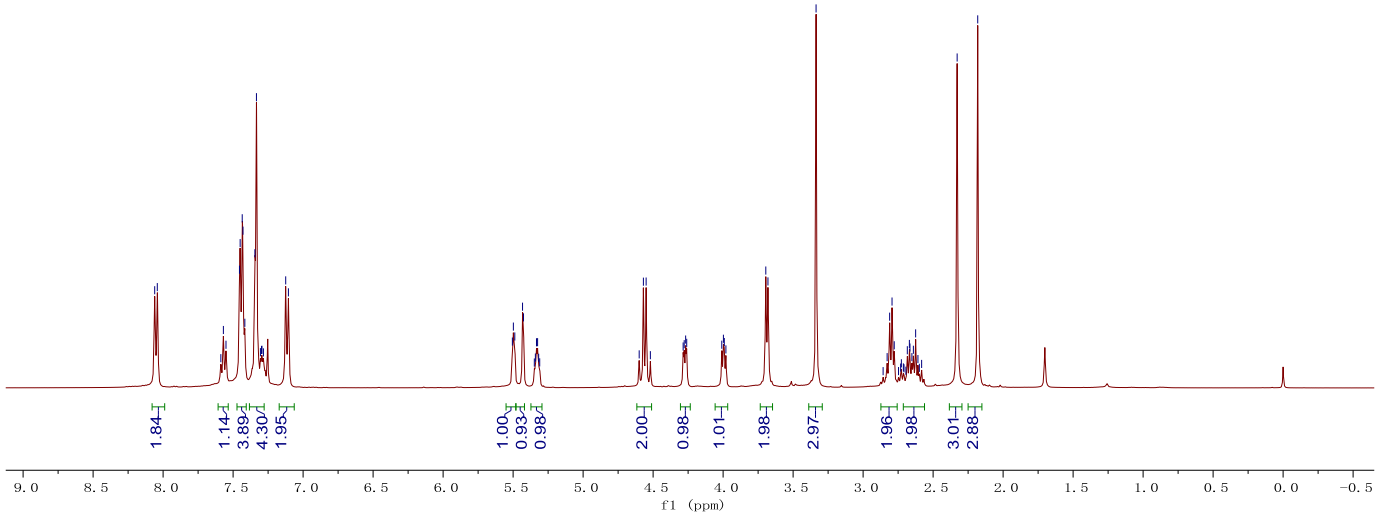
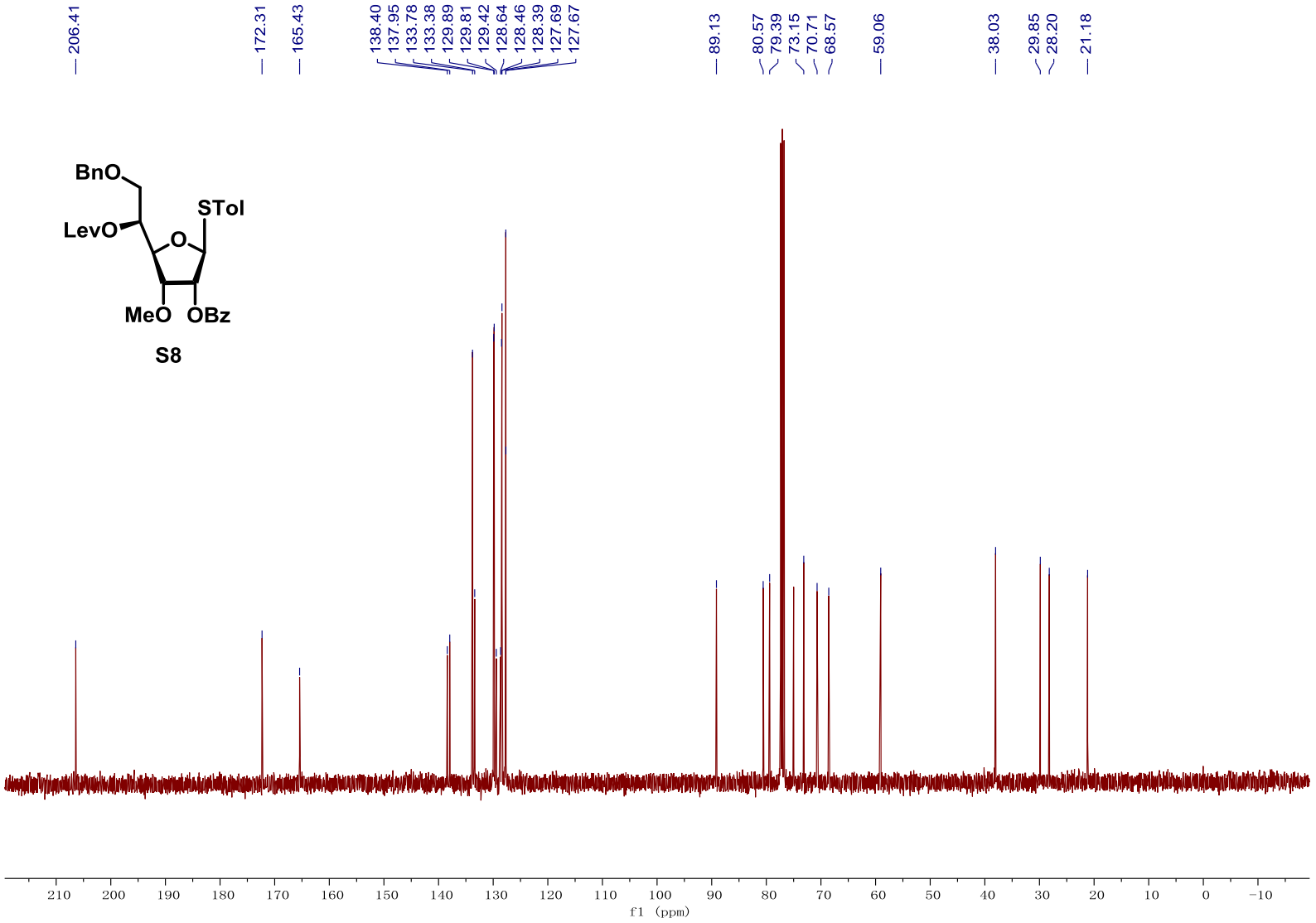
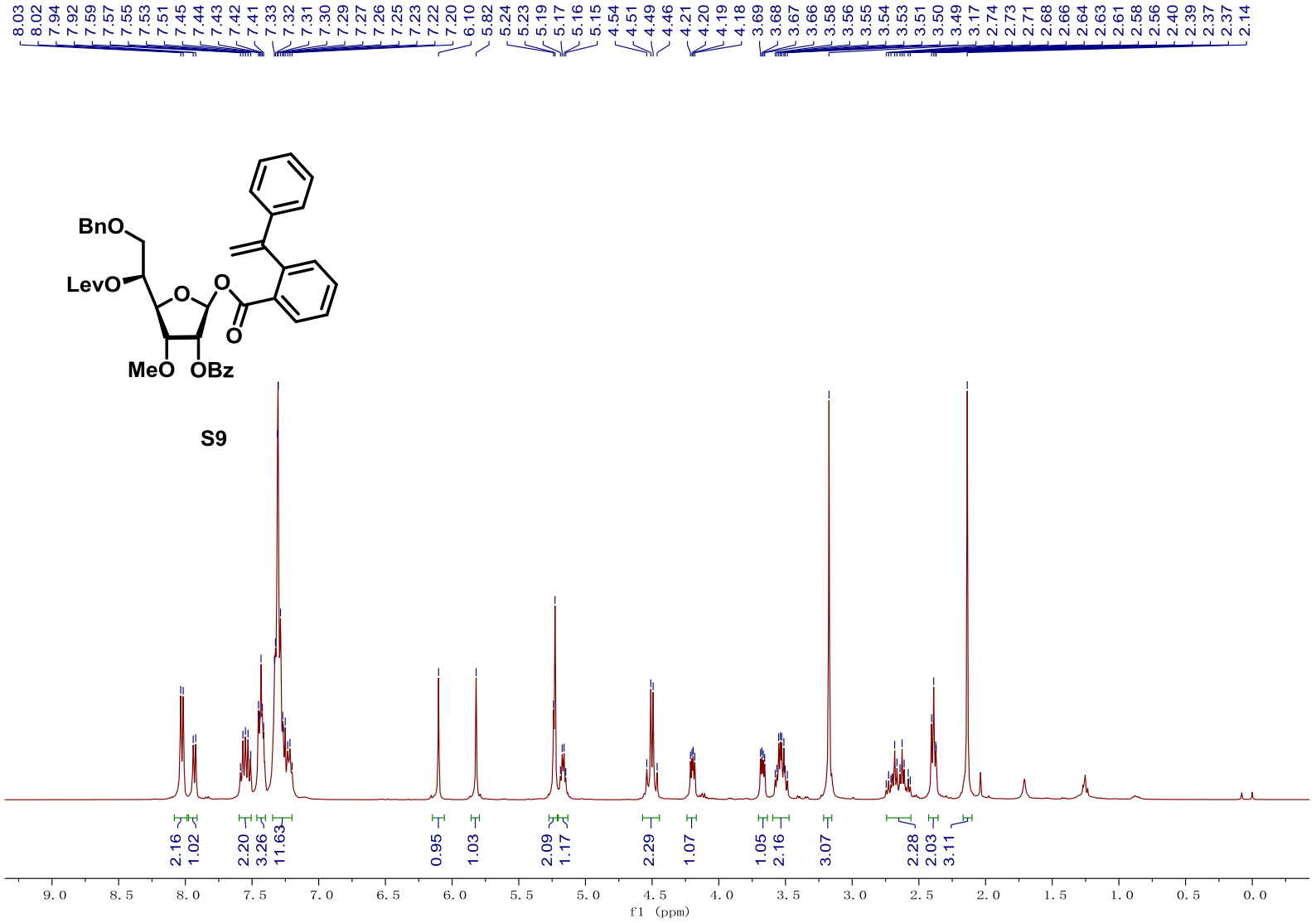
2.62
2.61
2.60
2.58
2.33
2.18

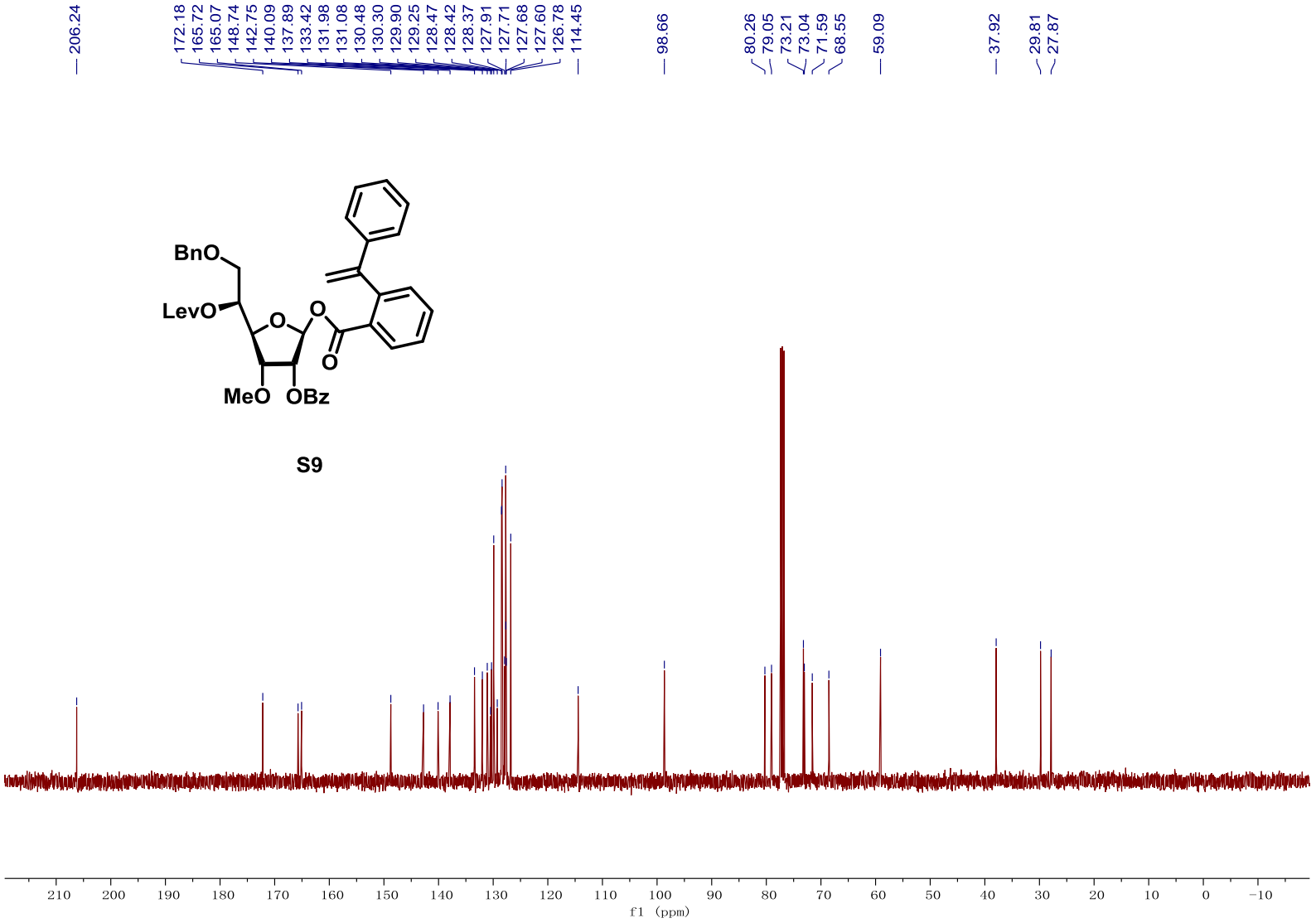

BnO
STol
LevO
O
MeO
OBz

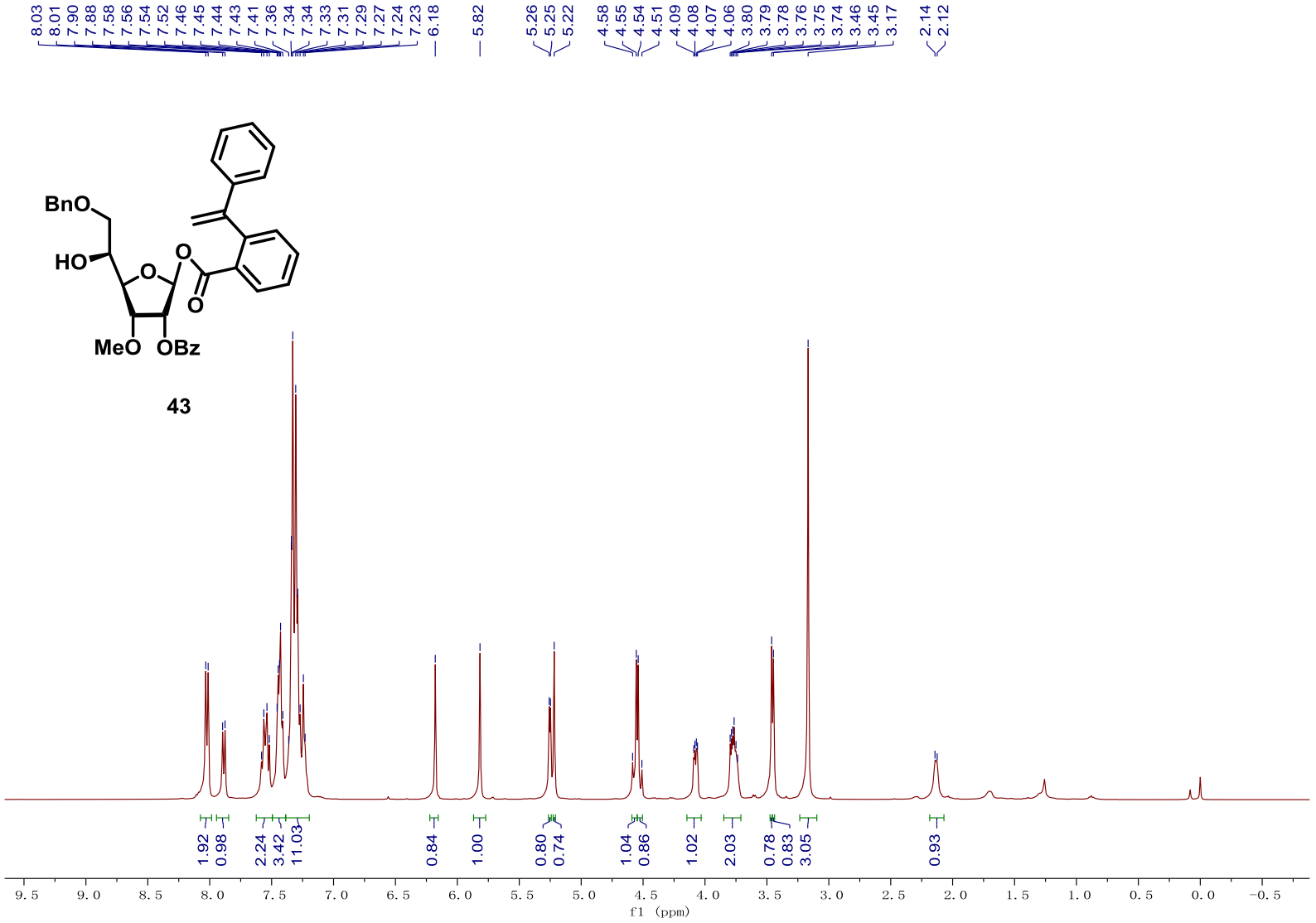
S8

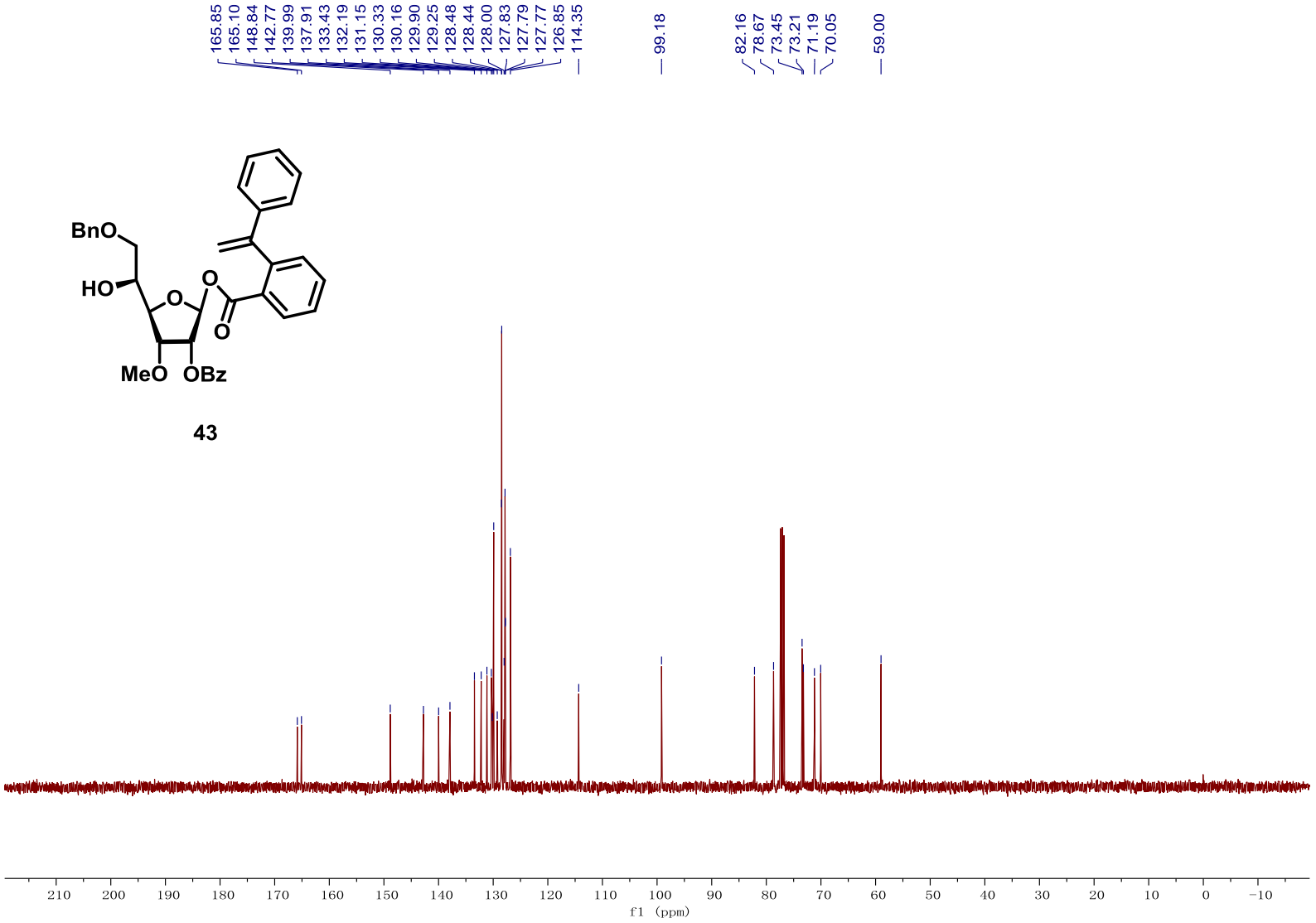

1.84
1.14
3.89
4.30
1.95
1.00
0.93
0.98
2.00
0.98
1.01
1.98
2.97
1.96
1.98
3.01
2.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


206.41
172.31
165.43
138.40
137.95
133.78
133.38
129.89
129.81
129.42
128.64
128.46
128.39
127.69
127.67
89.13
80.57
79.39
73.15
70.71
68.57
59.06
38.03
29.85
28.20
21.18
BnO
LevO
STol
O
MeO
OBz
S8
f1 (ppm)

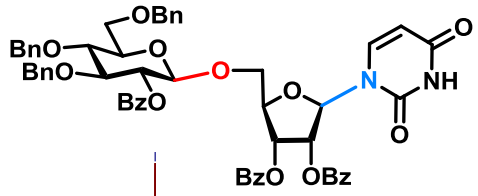

8.03 8.02 7.94 7.92 7.59 7.57 7.55 7.53 7.51 7.45 7.44 7.43 7.42 7.41 7.33 7.32 7.31 7.30 7.29 7.27 7.26 7.25 7.23 7.22 7.20 6.10 5.82 5.24 5.23 5.19 5.17 5.16 5.15 4.54 4.51 4.49 4.46 4.21 4.20 4.19 4.18 3.69 3.68 3.67 3.66 3.58 3.56 3.55 3.54 3.53 3.51 3.50 3.49 3.17 2.74 2.73 2.71 2.68 2.66 2.64 2.63 2.61 2.58 2.56 2.40 2.39 2.37 2.37 2.14
BnO
LevO
O
O
O
MeO
OBz
S9
2.16 1.02 2.20 3.26 11.63 0.95 1.03 2.09 1.17 2.29 1.07 1.05 2.16 3.07 2.28 2.03 3.11
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)


206.24
172.18
165.72
165.07
148.74
142.75
140.09
137.89
133.42
131.98
131.08
130.48
130.30
129.90
129.25
128.47
128.42
128.37
127.91
127.71
127.68
127.60
126.78
114.45
98.66
80.26
79.05
73.21
73.04
71.59
68.55
59.09
37.92
29.81
27.87
BnO
LevO
O
O
O
MeO
OBz
S9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

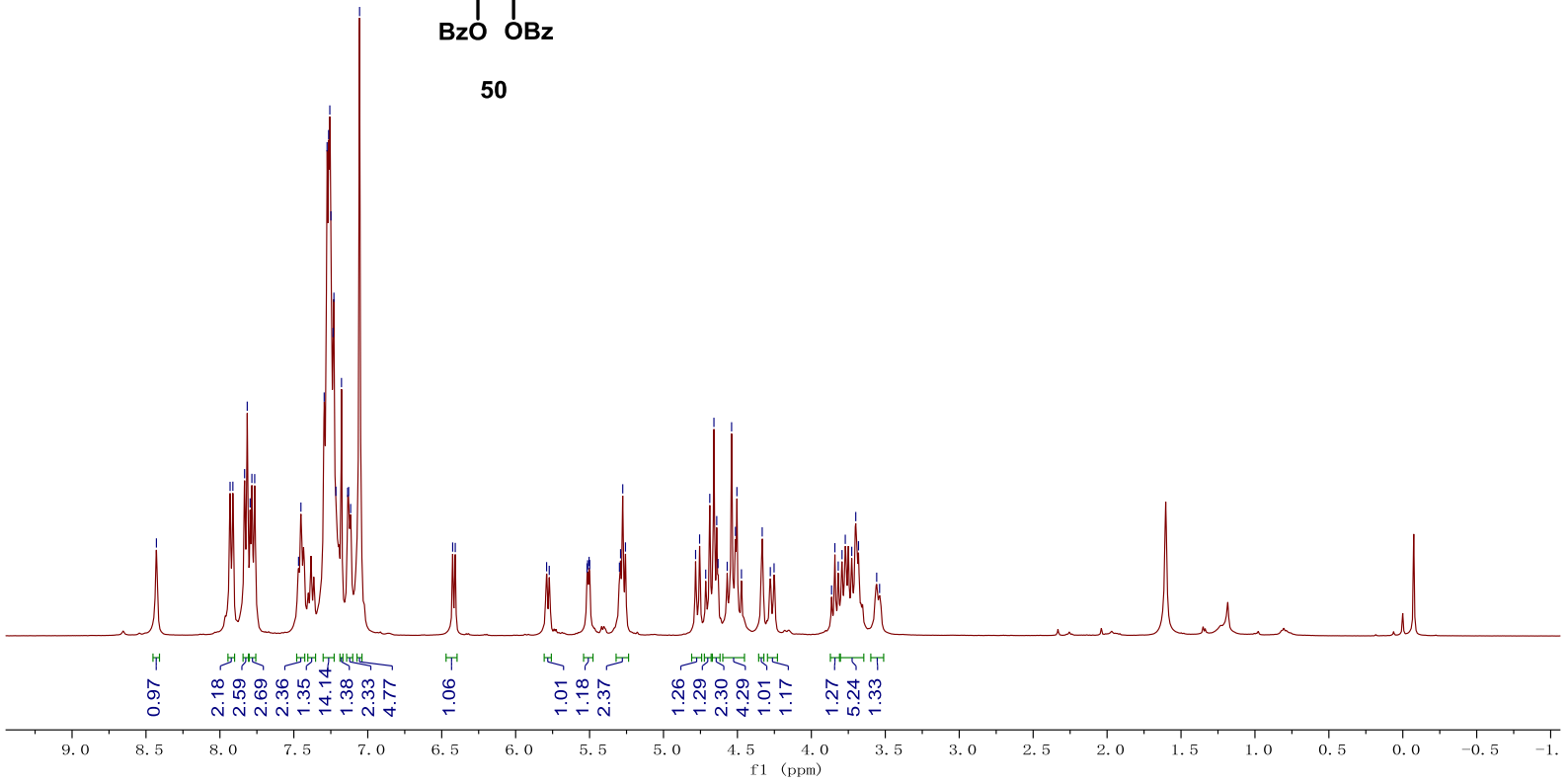

8.03
8.01
7.90
7.88
7.58
7.56
7.54
7.52
7.46
7.45
7.44
7.43
7.41
7.36
7.34
7.34
7.33
7.31
7.29
7.27
7.24
7.23
6.18
5.82
5.26
5.25
5.22
4.58
4.55
4.54
4.51
4.09
4.08
4.07
4.06
3.80
3.79
3.78
3.76
3.75
3.74
3.46
3.45
3.17
2.14
2.12
BnO
HO
O
O
O
MeO
OBz
43
1.92
0.98
2.24
3.42
11.03
0.84
1.00
0.80
0.74
1.04
0.86
1.02
2.03
0.78
0.83
3.05
0.93
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
−0.5
f1 (ppm)

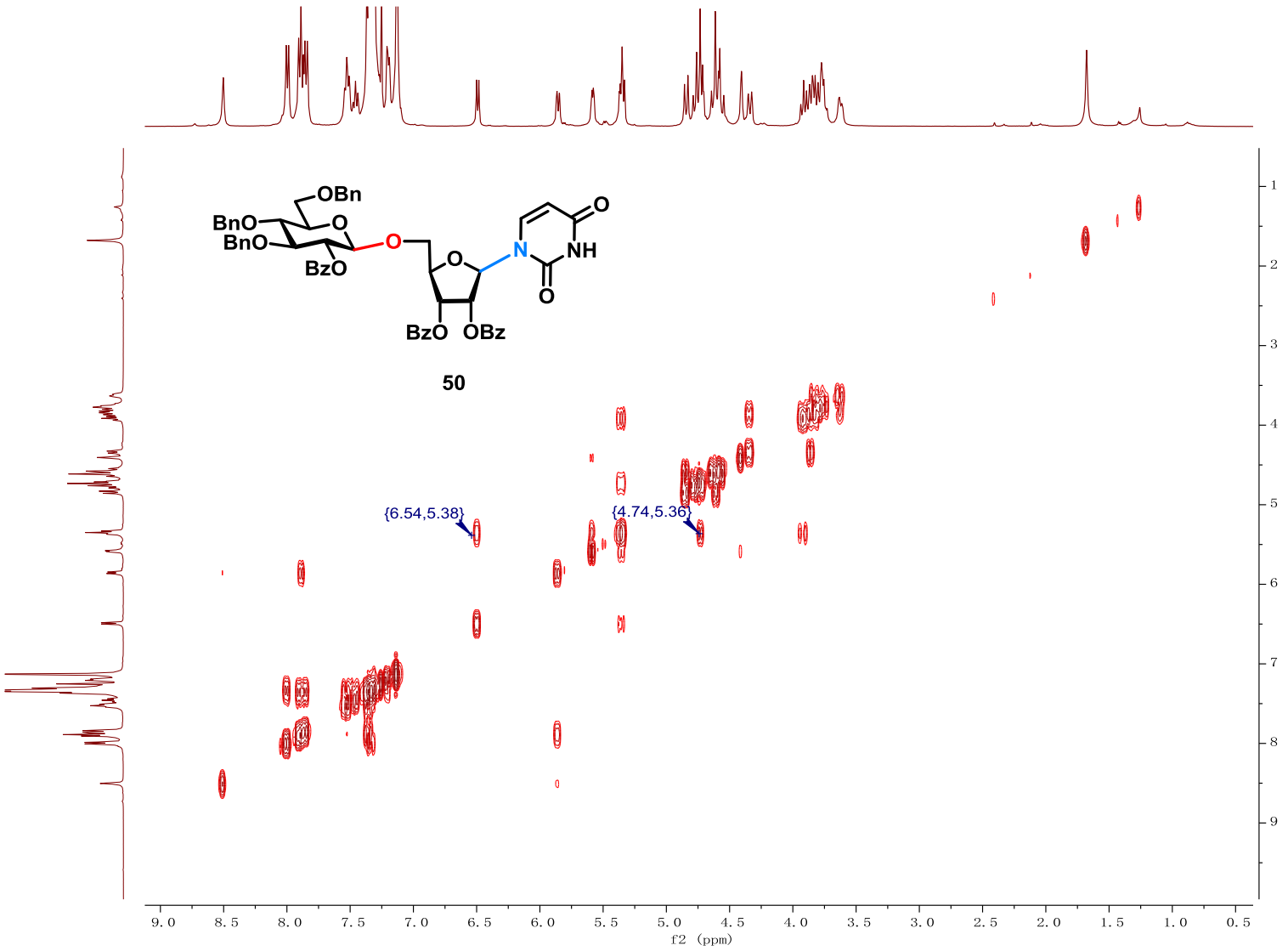

165.85
165.10
148.84
142.77
139.99
137.91
133.43
132.19
131.15
130.33
130.16
129.90
129.25
128.48
128.44
128.00
127.83
127.79
127.77
126.85
114.35
99.18
82.16
78.67
73.45
73.21
71.19
70.05
59.00
BnO
HO
O
O
O
MeO
OBz
43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

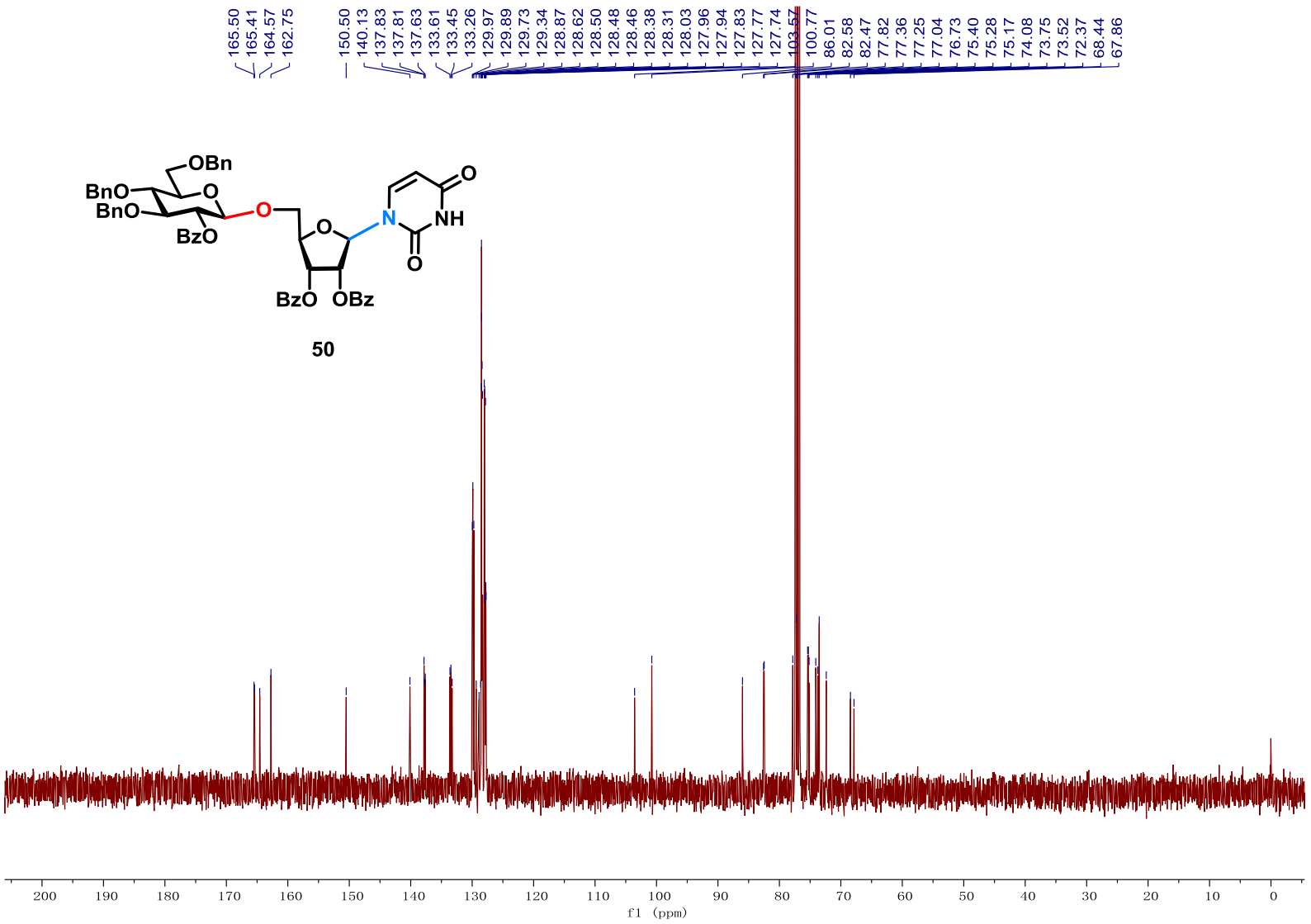

8.429
7.931
7.912
7.833
7.815
7.796
7.784
7.765
7.468
7.452
7.295
7.275
7.265
7.257
7.249
7.235
7.229
7.216
7.178
7.136
7.130
7.116
7.055
6.426
6.408
5.791
5.773
5.517
5.513
5.503
5.499
5.298
5.290
5.276
5.257
4.783
4.756
4.715
4.687
4.659
4.640
4.631
4.569
4.539
4.513
4.503
4.473
4.332
4.277
4.252
3.863
3.841
3.818
3.792
3.771
3.727
3.700
3.681
3.558
3.539

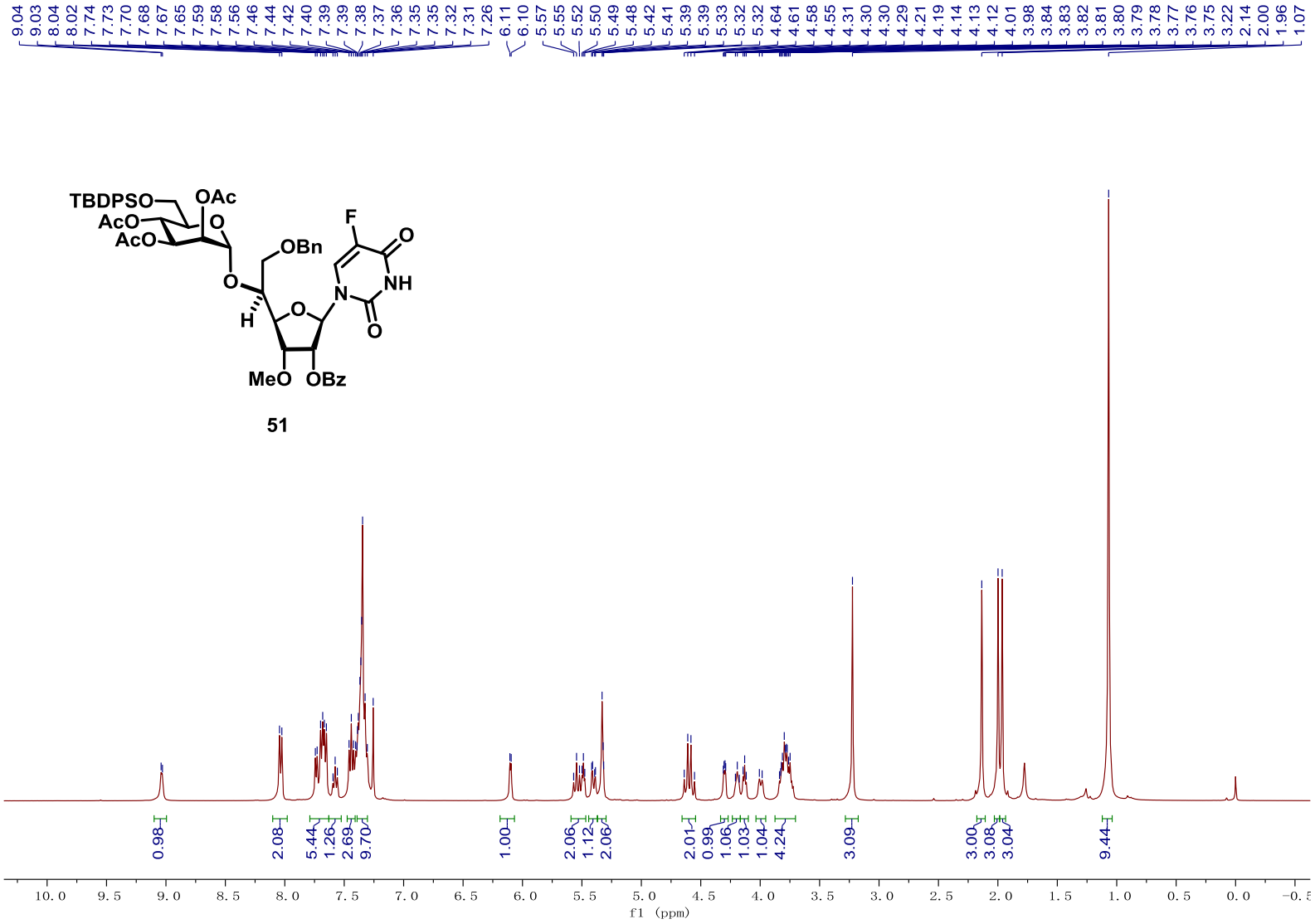

OBn
BnO
BnO
O
BzO
O
O
N
NH
O
O
BzO
OBz

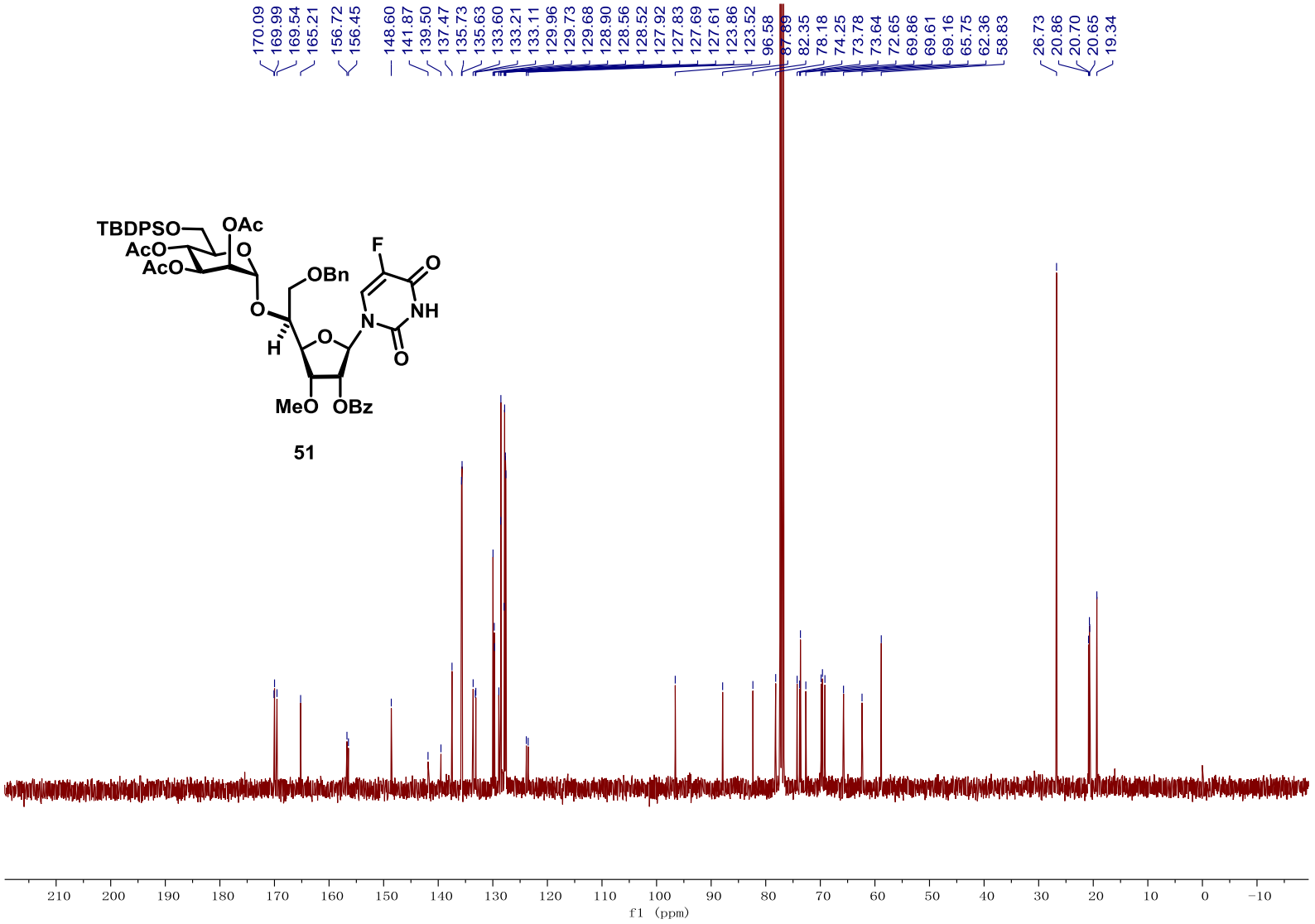
50

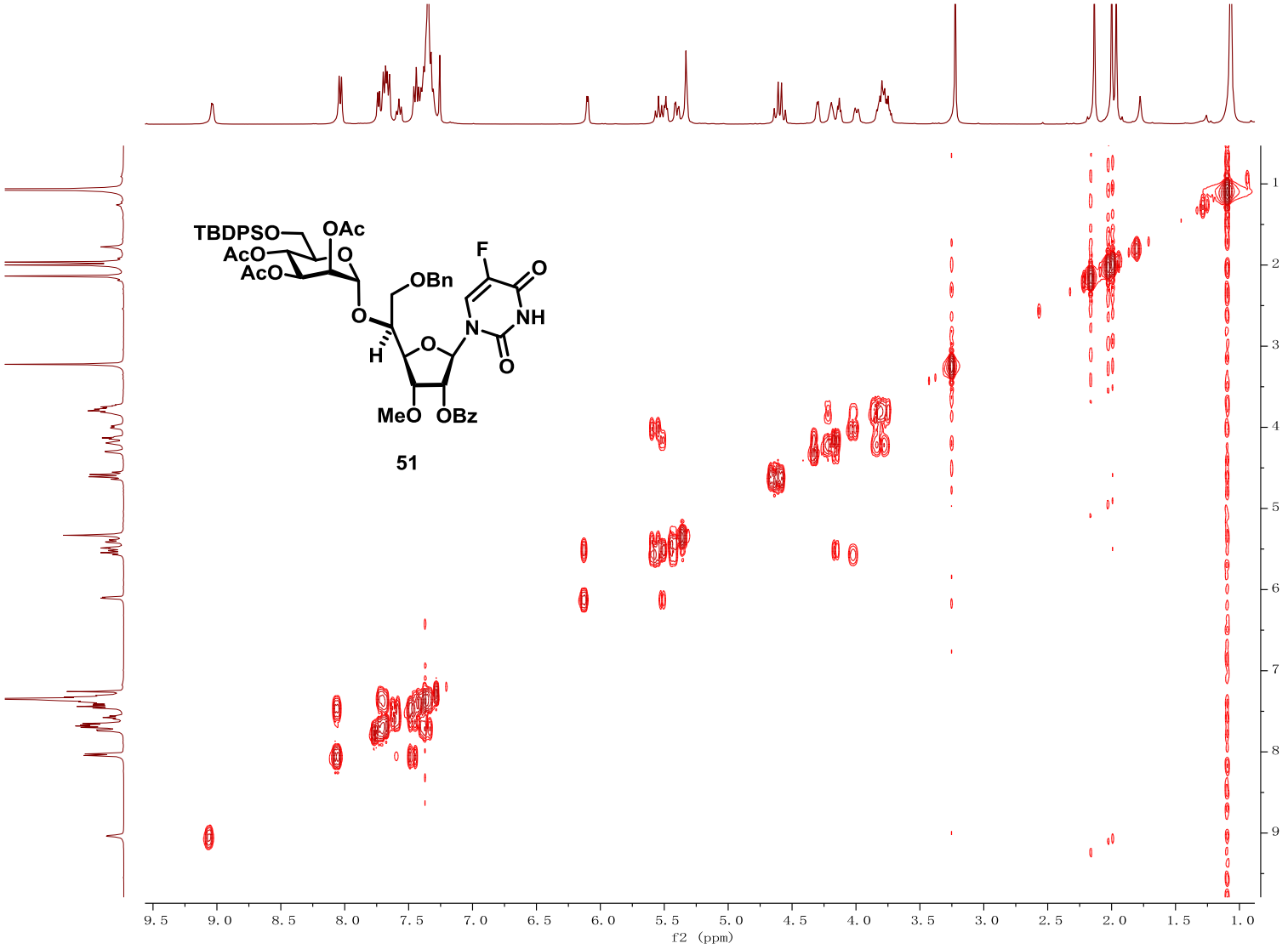

0.97
2.18
2.59
2.69
2.36
1.35
14.14
1.38
2.33
4.77
1.06
1.01
1.18
2.37
1.26
1.29
2.30
4.29
1.01
1.17
1.27
5.24
1.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.
f1 (ppm)

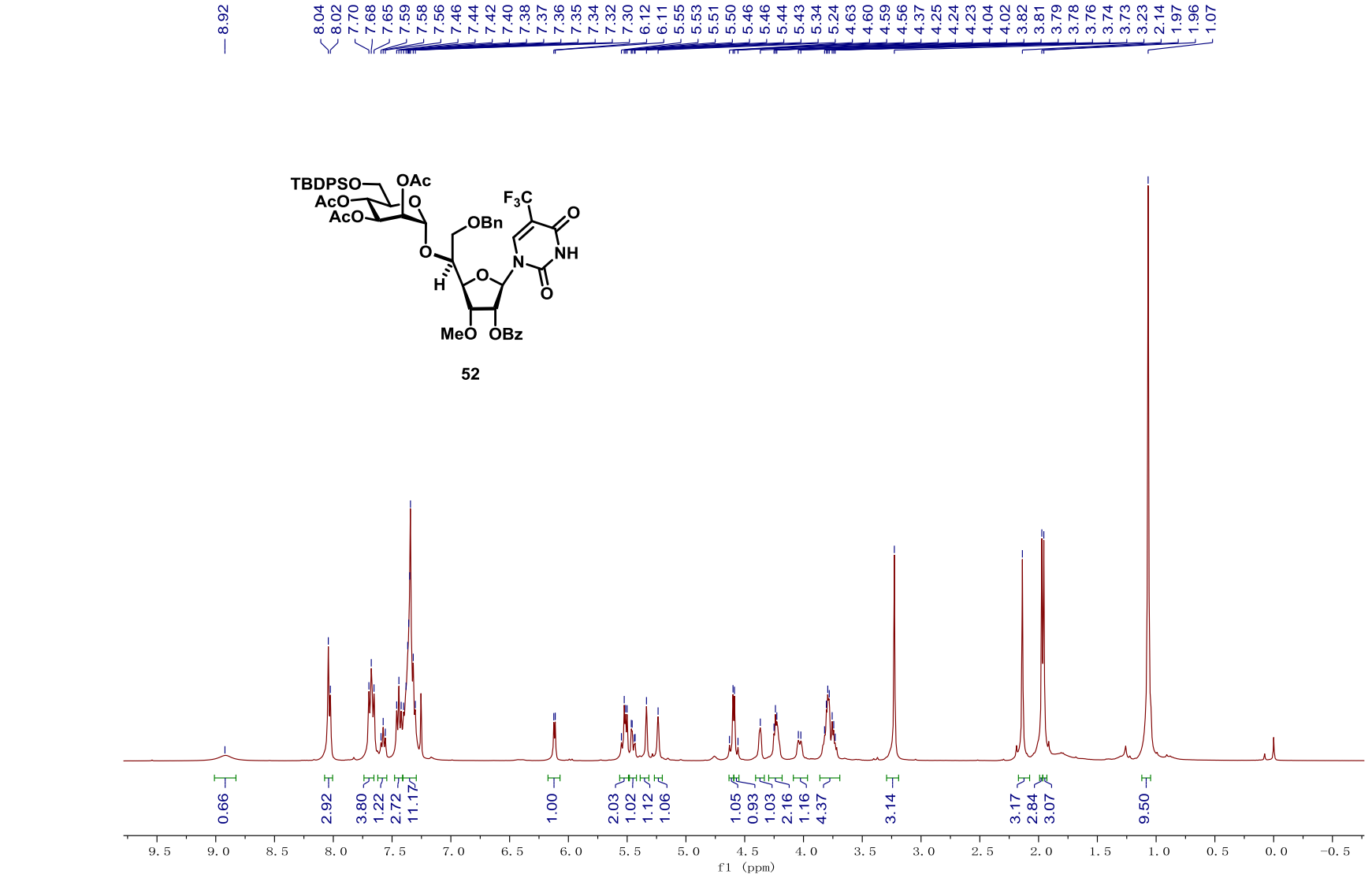

OBn
BnO
BnO
O
O
BzO
O
N
NH
O
O
BzO
OBz
50
{6.54,5.38}
{4.74,5.36}
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
9


165.50
165.41
164.57
162.75
150.50
140.13
137.83
137.81
137.63
133.61
133.45
133.26
129.97
129.89
129.73
129.34
128.87
128.62
128.50
128.48
128.46
128.38
128.31
128.03
127.96
127.94
127.83
127.77
127.74
103.57
100.77
86.01
82.58
82.47
77.82
77.36
77.25
77.04
76.73
75.40
75.28
75.17
74.08
73.75
73.52
72.37
68.44
67.86
OBn
BnO
BnO
BzO
O
O
N
NH
O
O
BzO
OBz
50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

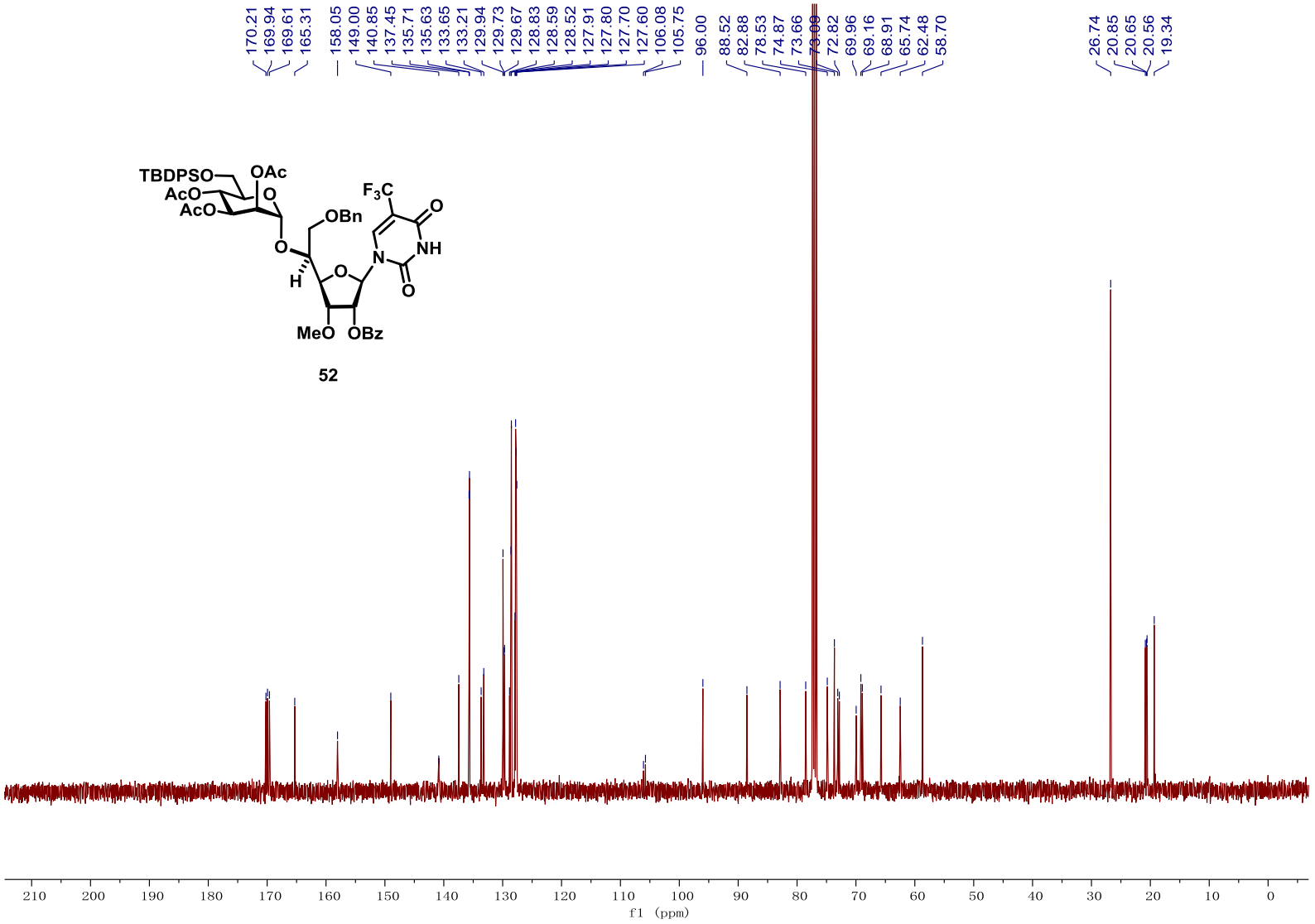

9.04 9.03 8.04 8.02 7.74 7.73 7.70 7.68 7.67 7.65 7.59 7.58 7.56 7.46 7.44 7.42 7.40 7.39 7.39 7.38 7.37 7.36 7.35 7.35 7.32 7.31 7.26 6.11 6.10 5.57 5.55 5.52 5.50 5.49 5.48 5.42 5.41 5.39 5.39 5.33 5.32 5.32 4.64 4.61 4.58 4.55 4.31 4.30 4.30 4.29 4.21 4.19 4.14 4.13 4.12 4.01 3.98 3.84 3.83 3.82 3.81 3.80 3.79 3.78 3.77 3.76 3.75 3.22 2.14 2.00 1.96 1.07
TBDPSO
OAc
AcO
AcO
O
O
OBn
F
O
NH
N
O
H
O
MeO
OBz
51
0.98 2.08 5.44 1.26 2.69 9.70 1.00 2.06 1.12 2.06 2.01 0.99 1.06 1.03 1.04 4.24 3.09 3.00 3.08 3.04 9.44
10.0 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)

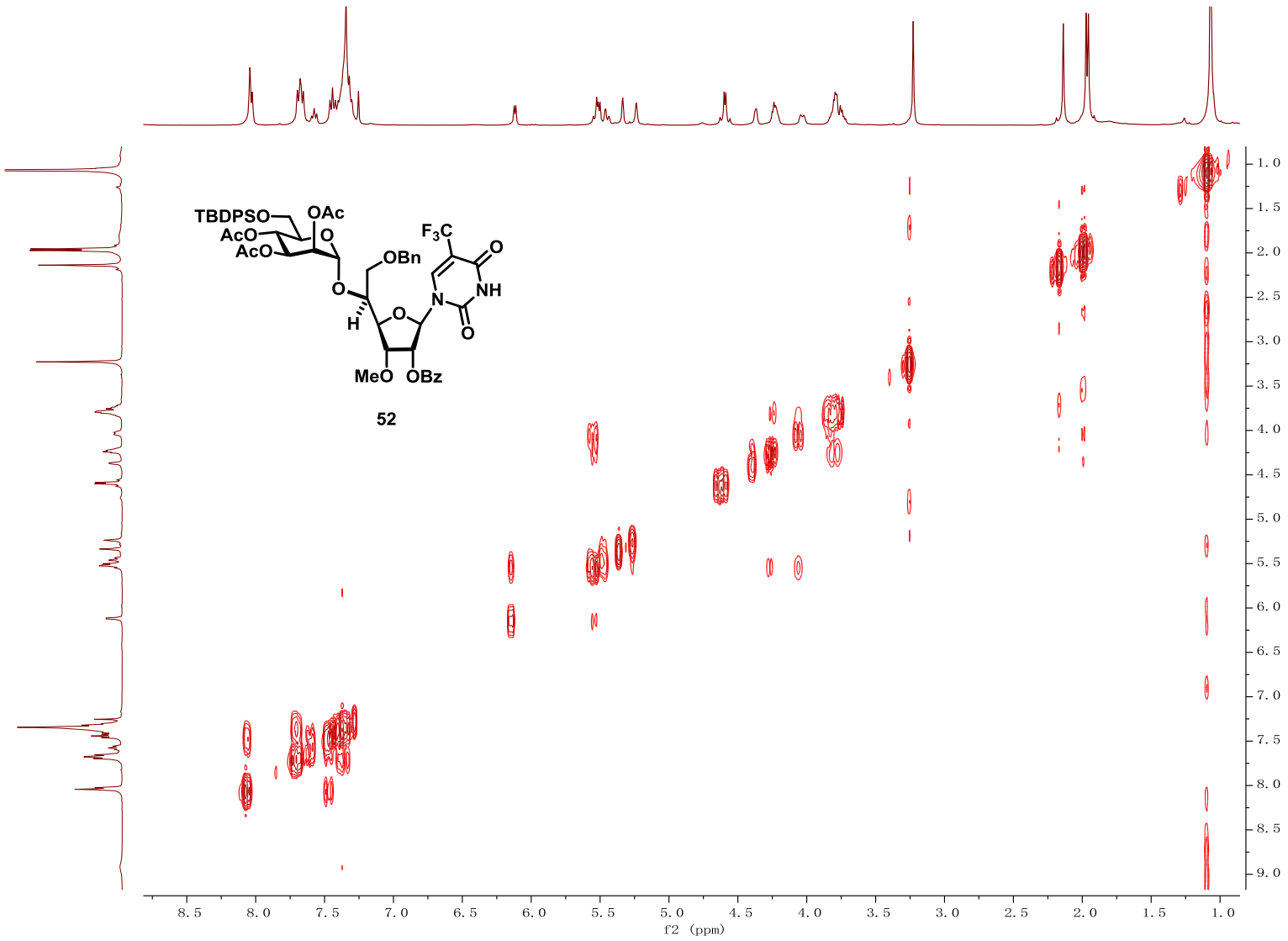

170.09
169.99
169.54
165.21
156.72
156.45
148.60
141.87
139.50
137.47
135.73
135.63
133.60
133.21
133.11
129.96
129.73
129.68
128.90
128.56
128.52
127.92
127.83
127.69
127.61
123.86
123.52
96.58
87.89
82.35
78.18
74.25
73.78
73.64
72.65
69.86
69.61
69.16
65.75
62.36
58.83
26.73
20.86
20.70
20.65
19.34
TBDPSO
OAc
AcO
AcO
O
OBn
O
F
O
NH
N
H
O
O
MeO
OBz
51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

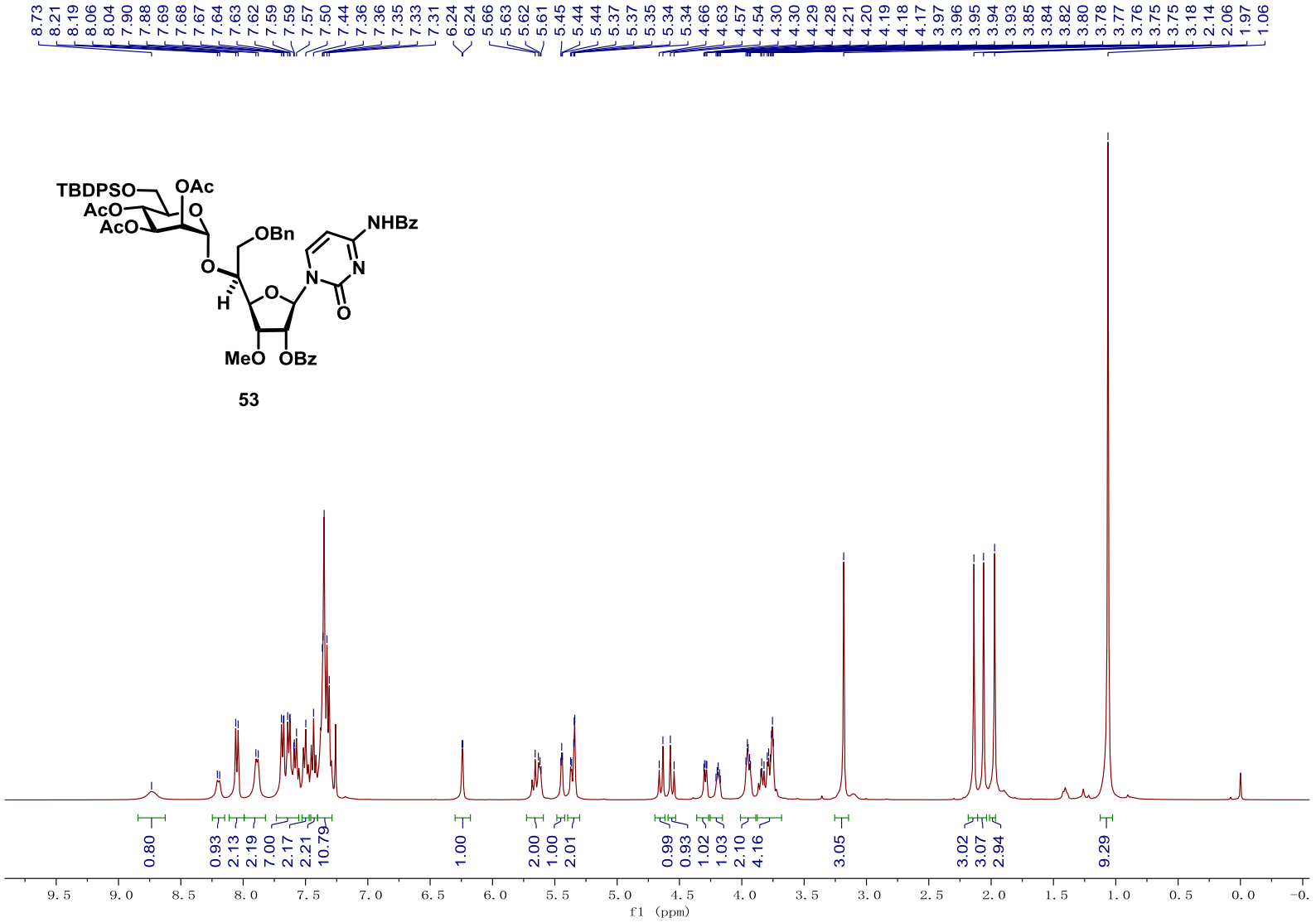

TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
F
O
NH
O
MeO
OBz
51
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9

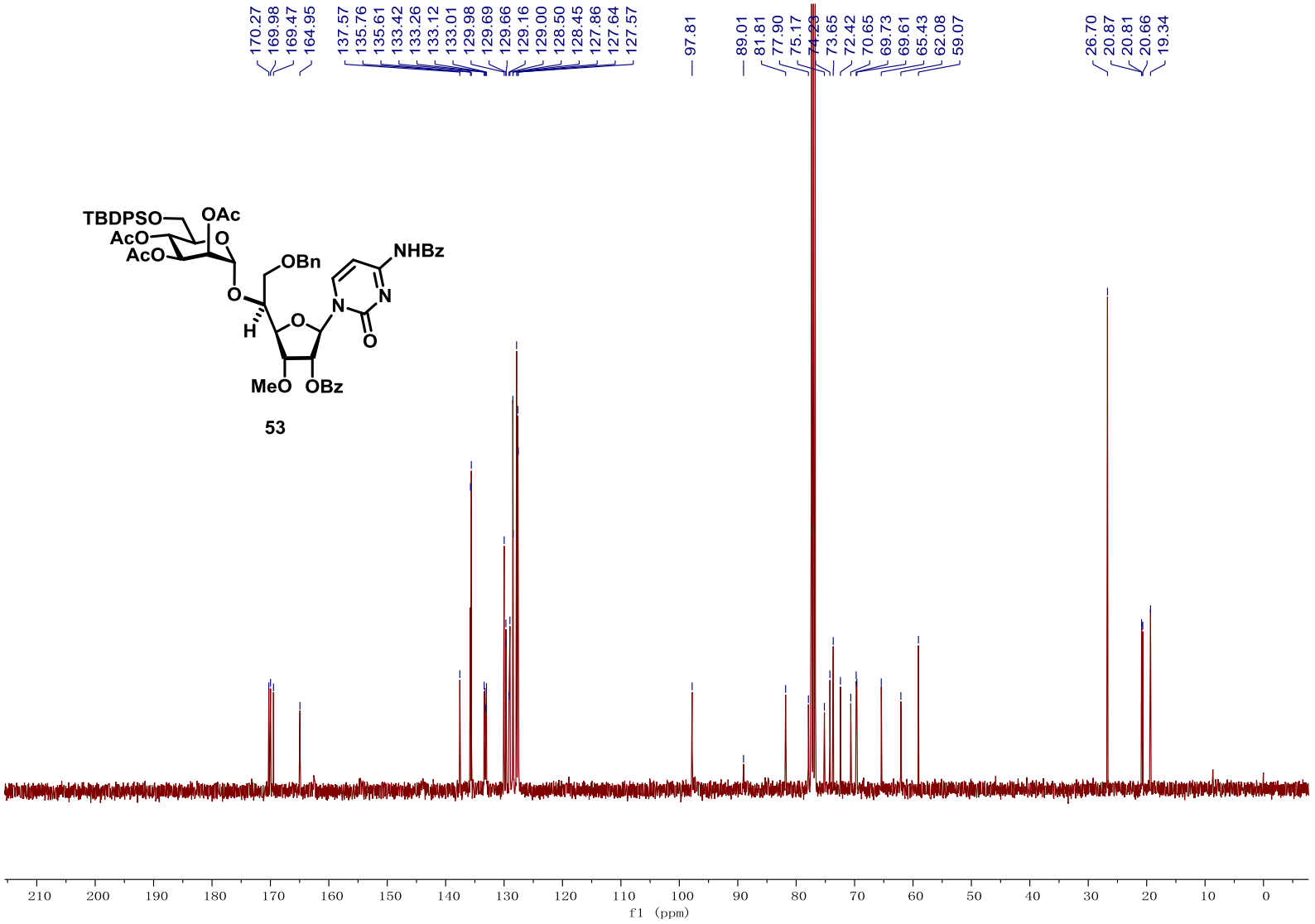

8.92
8.04
8.02
7.70
7.68
7.65
7.59
7.58
7.56
7.46
7.44
7.42
7.40
7.38
7.37
7.36
7.35
7.34
7.32
7.30
6.12
6.11
5.55
5.53
5.51
5.50
5.46
5.44
5.43
5.34
5.24
4.63
4.60
4.59
4.56
4.37
4.25
4.24
4.23
4.04
4.02
3.82
3.81
3.79
3.78
3.76
3.74
3.73
3.23
2.14
1.97
1.96
1.07
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
F3C
O
N
NH
N
O
MeO
OBz
0.66
2.92
3.80
1.22
2.72
11.17
1.00
2.03
1.02
1.12
1.06
1.05
0.93
1.03
2.16
1.16
4.37
3.14
3.17
2.84
3.07
9.50
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
−0.5
f1 (ppm)

52

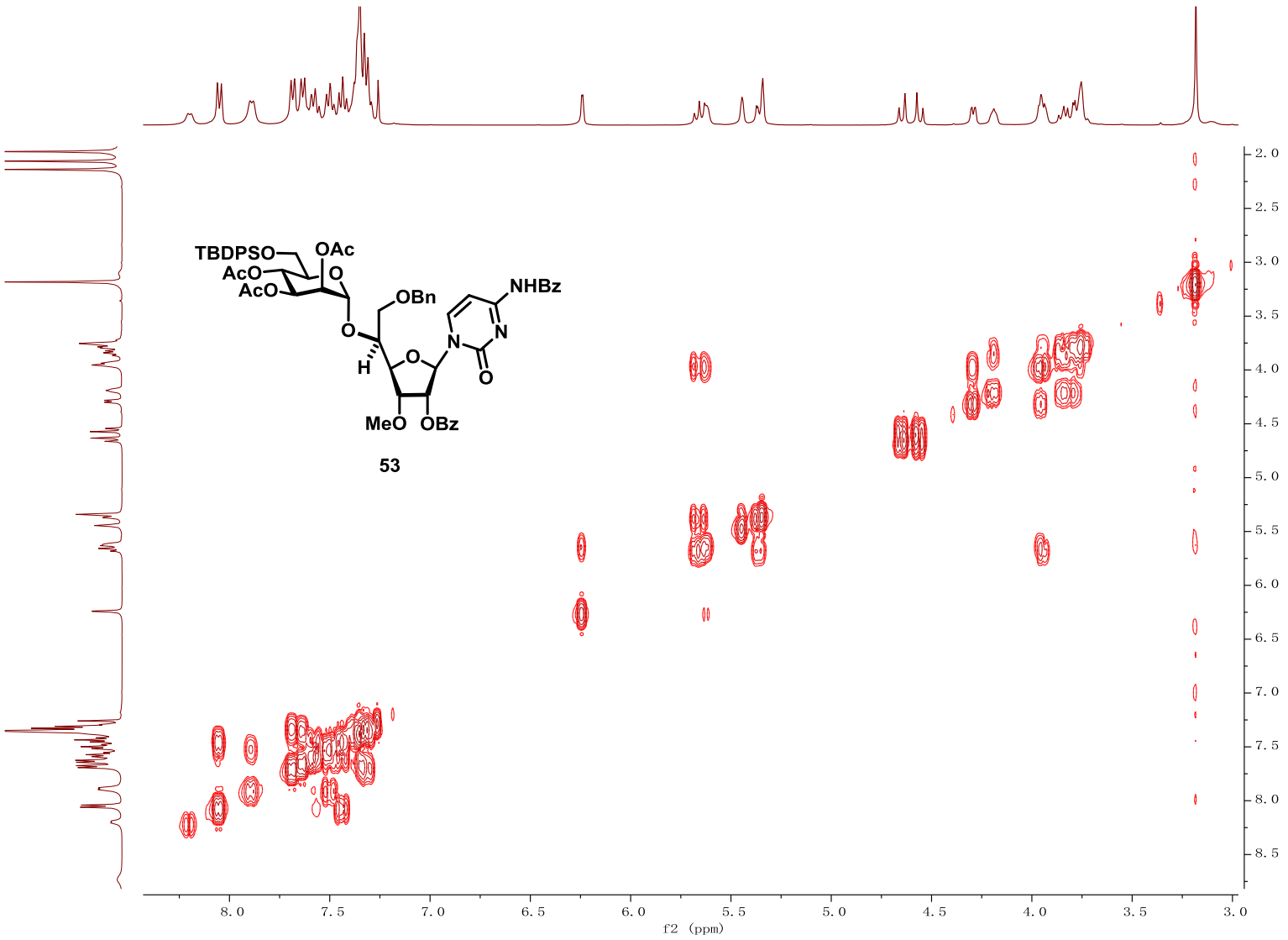

170.21
169.94
169.61
165.31
158.05
149.00
140.85
137.45
135.71
135.63
133.65
133.21
129.94
129.73
129.67
128.83
128.59
128.52
127.91
127.80
127.70
127.60
106.08
105.75
96.00
88.52
82.88
78.53
74.87
73.66
73.09
72.82
69.96
69.16
68.91
65.74
62.48
58.70
26.74
20.85
20.65
20.56
19.34
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
F3C
O
NH
N
O
MeO
OBz
52
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

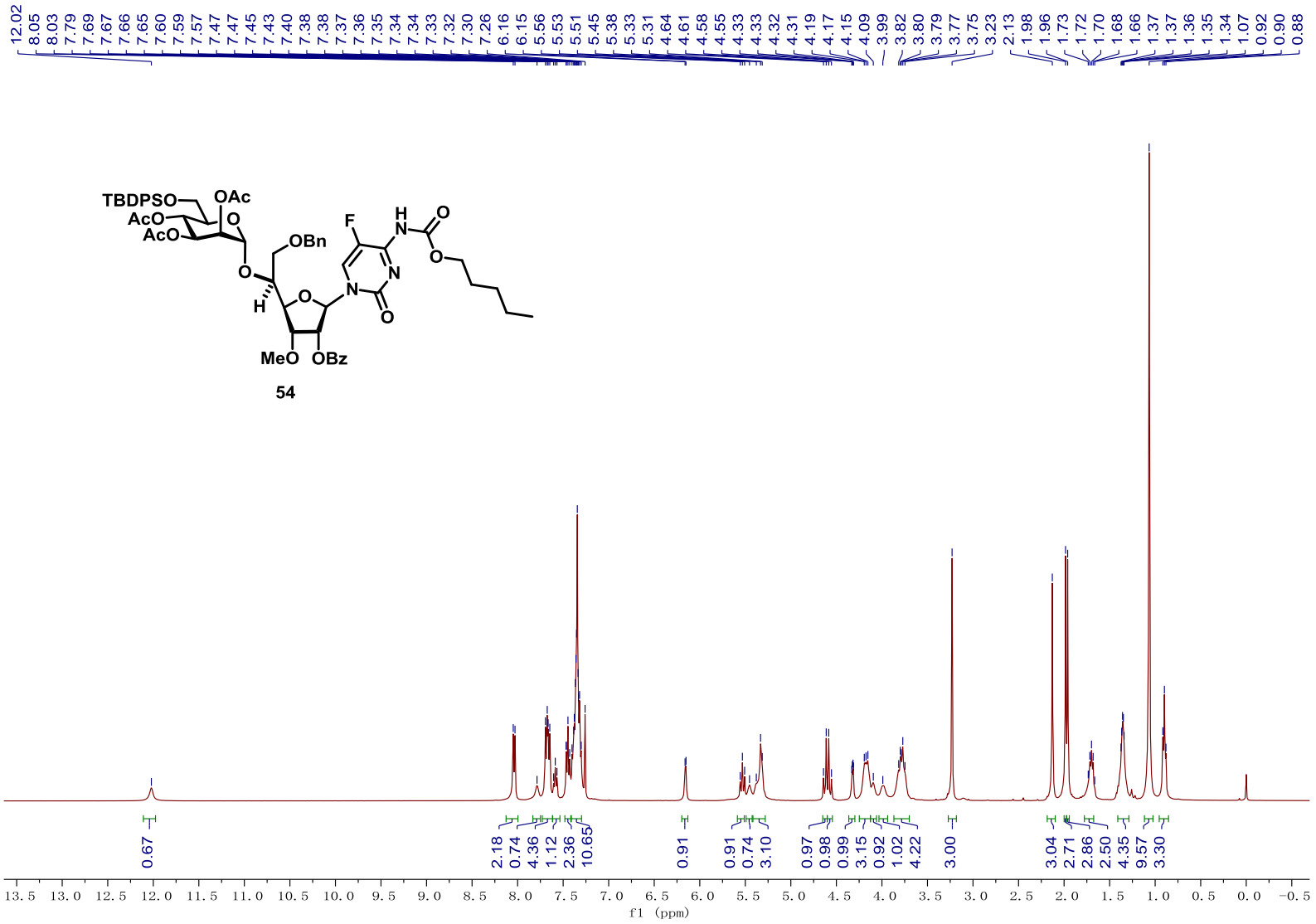

TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
F3C
O
NH
N
O
MeO
OBz
52
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0

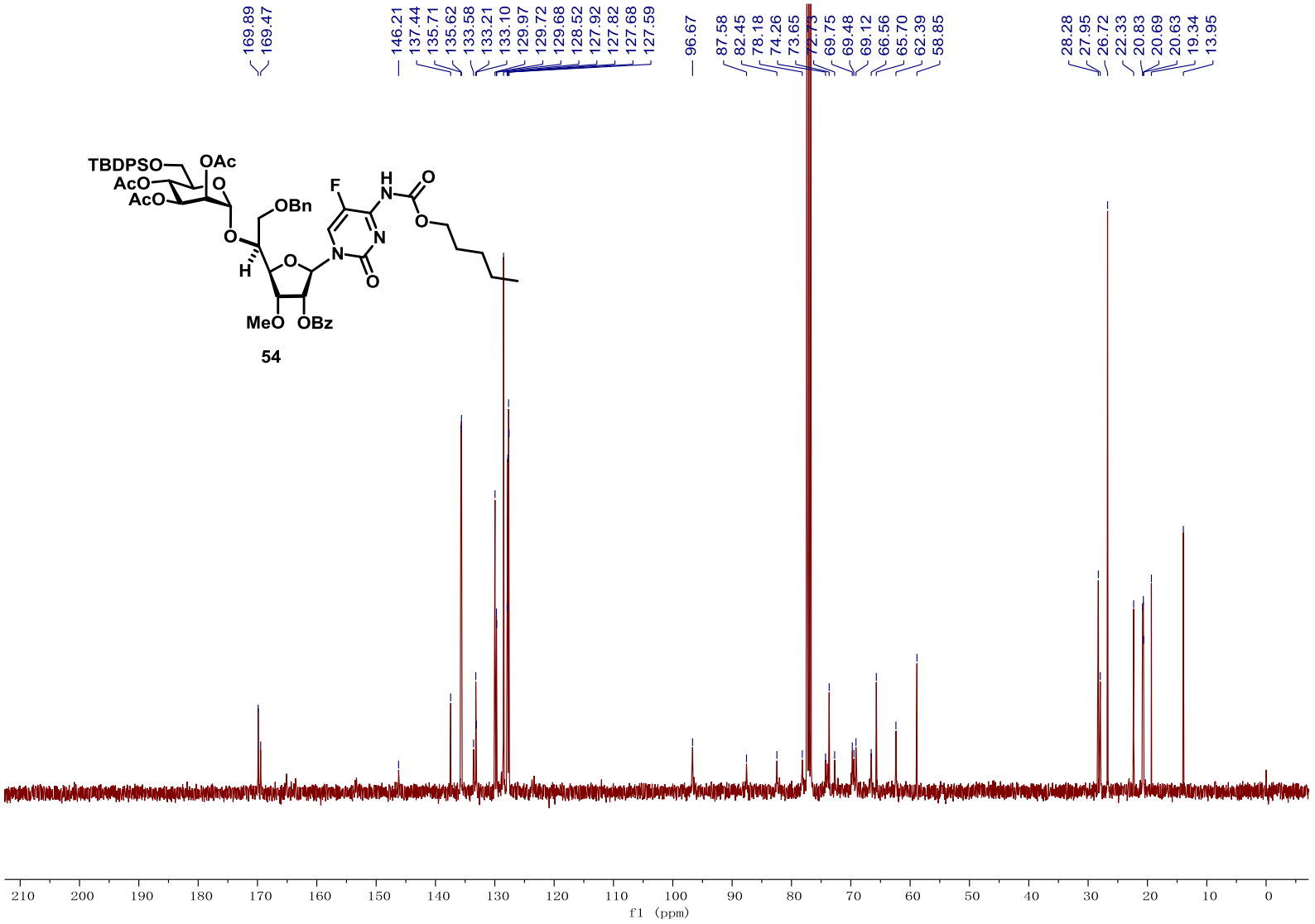

8.73 8.21 8.19 8.06 8.04 7.90 7.88 7.69 7.68 7.67 7.64 7.63 7.62 7.59 7.59 7.57 7.50 7.44 7.36 7.36 7.35 7.33 7.31 6.24 6.24 5.66 5.63 5.62 5.61 5.45 5.44 5.44 5.37 5.37 5.35 5.34 5.34 4.66 4.63 4.57 4.54 4.30 4.30 4.29 4.28 4.21 4.20 4.19 4.18 4.17 3.97 3.96 3.95 3.94 3.93 3.85 3.84 3.82 3.80 3.78 3.77 3.76 3.75 3.75 3.18 2.14 2.06 1.97 1.06
TBDPSO
OAc
AcO
AcO
O
OBn
NHBz
O
N
N
O
H
O
MeO
OBz
53
0.80 0.93 2.13 2.19 7.00 2.17 2.21 10.79 1.00 2.00 1.00 2.01 0.99 0.93 1.02 1.03 2.10 4.16 3.05 3.02 3.07 2.94 9.29
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 −0.
f1 (ppm)

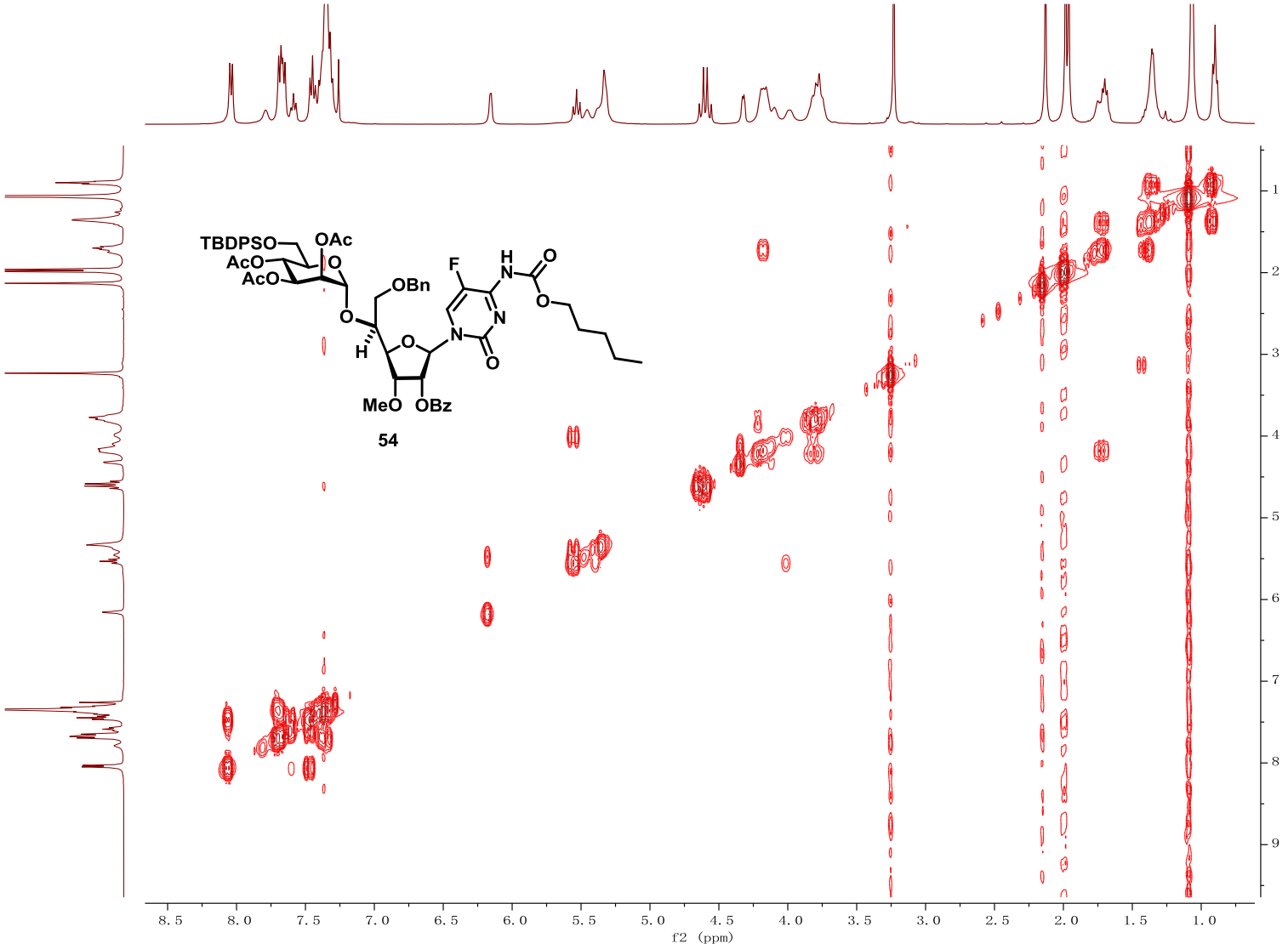

170.27
169.98
169.47
164.95
137.57
135.76
135.61
133.42
133.26
133.12
133.01
129.98
129.69
129.66
129.16
129.00
128.50
128.45
127.86
127.64
127.57
97.81
89.01
81.81
77.90
75.17
74.23
73.65
72.42
70.65
69.73
69.61
65.43
62.08
59.07
26.70
20.87
20.81
20.66
19.34
TBDPSO
OAc
AcO
AcO
O
OBn
NHBz
O
N
N
O
H
O
MeO
OBz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

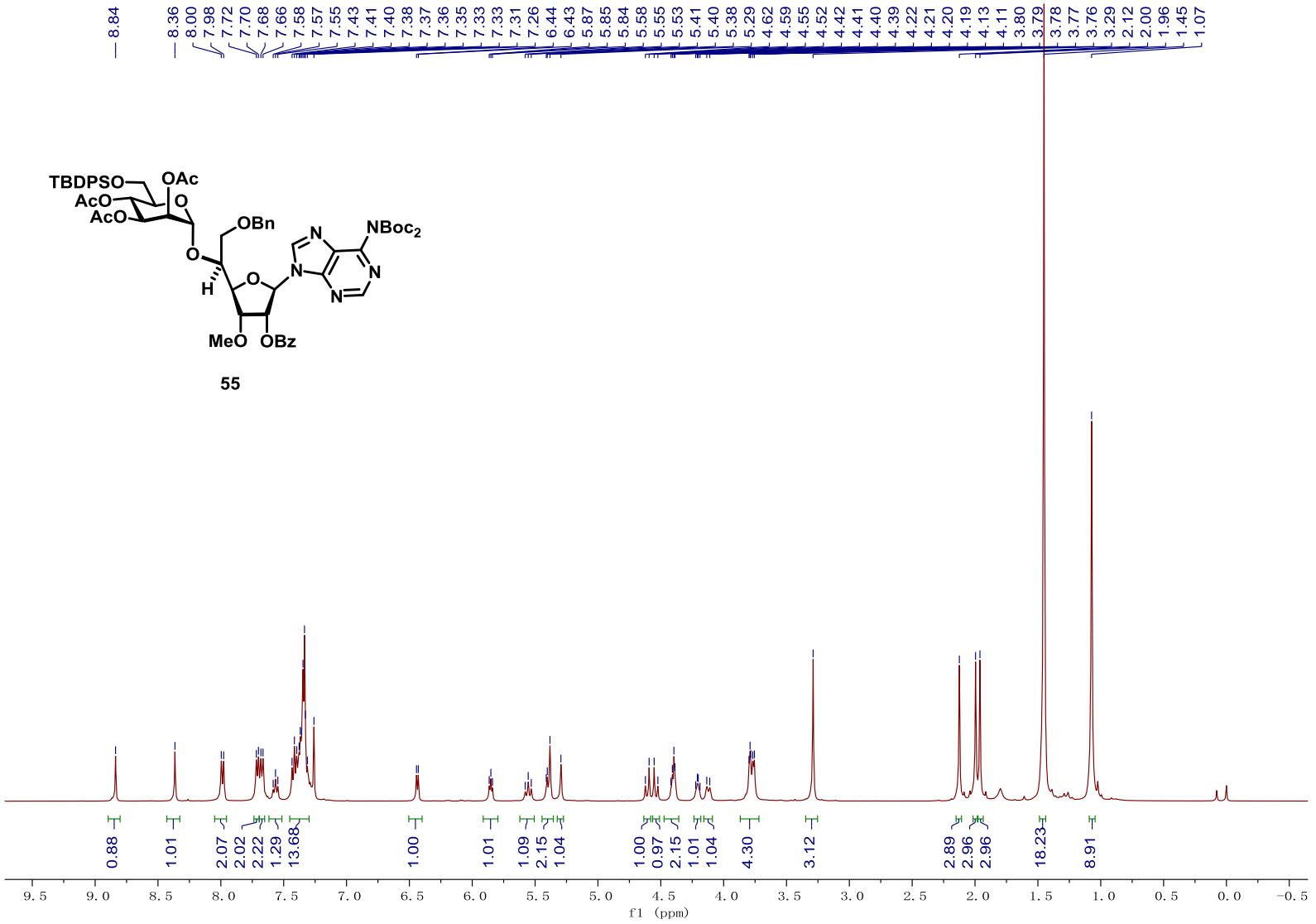
53

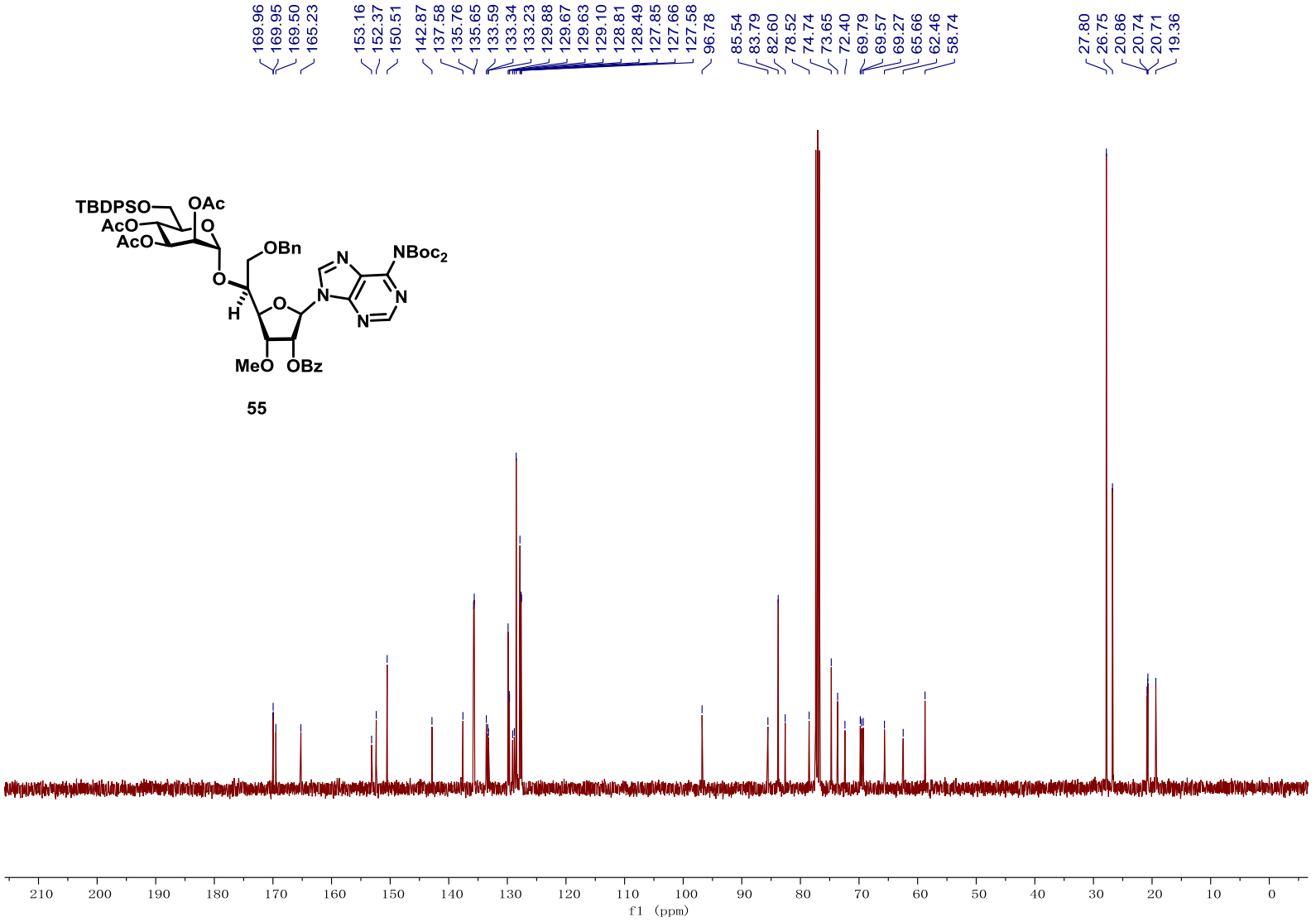

TBDPSO
OAc
AcO
AcO
OBn
NHBz
MeO
OBz
53
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5

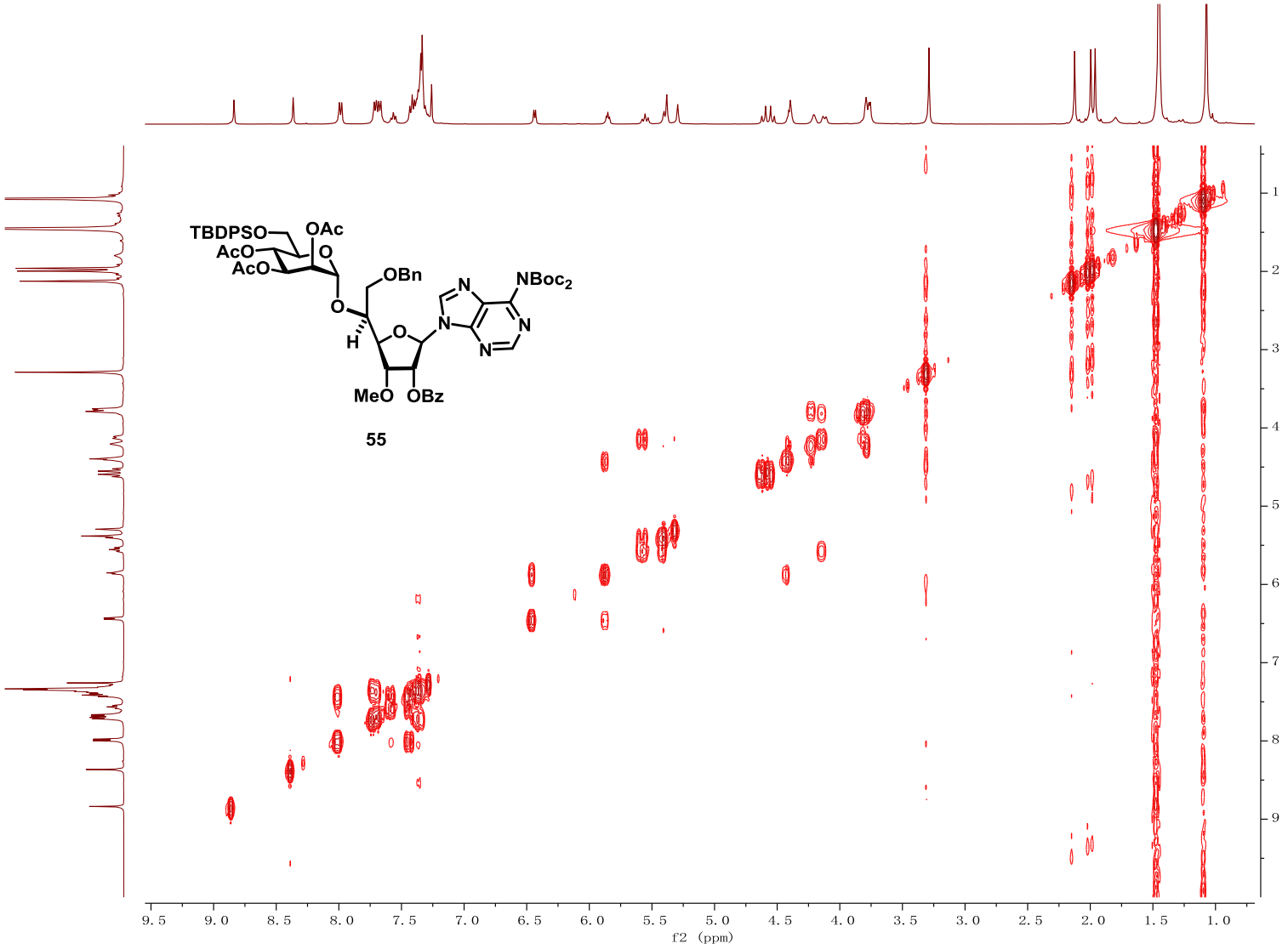

12.02 8.05 8.03 7.79 7.69 7.67 7.66 7.65 7.60 7.59 7.57 7.47 7.47 7.45 7.43 7.40 7.38 7.38 7.37 7.36 7.35 7.34 7.34 7.33 7.32 7.30 7.26 6.16 6.15 5.56 5.53 5.51 5.45 5.38 5.33 5.31 4.64 4.61 4.58 4.55 4.33 4.33 4.32 4.31 4.19 4.17 4.15 4.09 3.99 3.82 3.80 3.79 3.77 3.75 3.23 2.13 1.98 1.96 1.73 1.72 1.70 1.68 1.66 1.37 1.37 1.36 1.35 1.34 1.07 0.92 0.90 0.88
TBDPSO
OAc
AcO
AcO
OBn
F
H
N
O
O
N
O
O
N
O
H
MeO
OBz
54
0.67
2.18
0.74
4.36
1.12
2.36
10.65
0.91
0.91
0.74
3.10
0.97
0.98
0.99
3.15
0.92
1.02
4.22
3.00
3.04
2.71
2.86
2.50
4.35
9.57
3.30
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 −0.5
f1 (ppm)

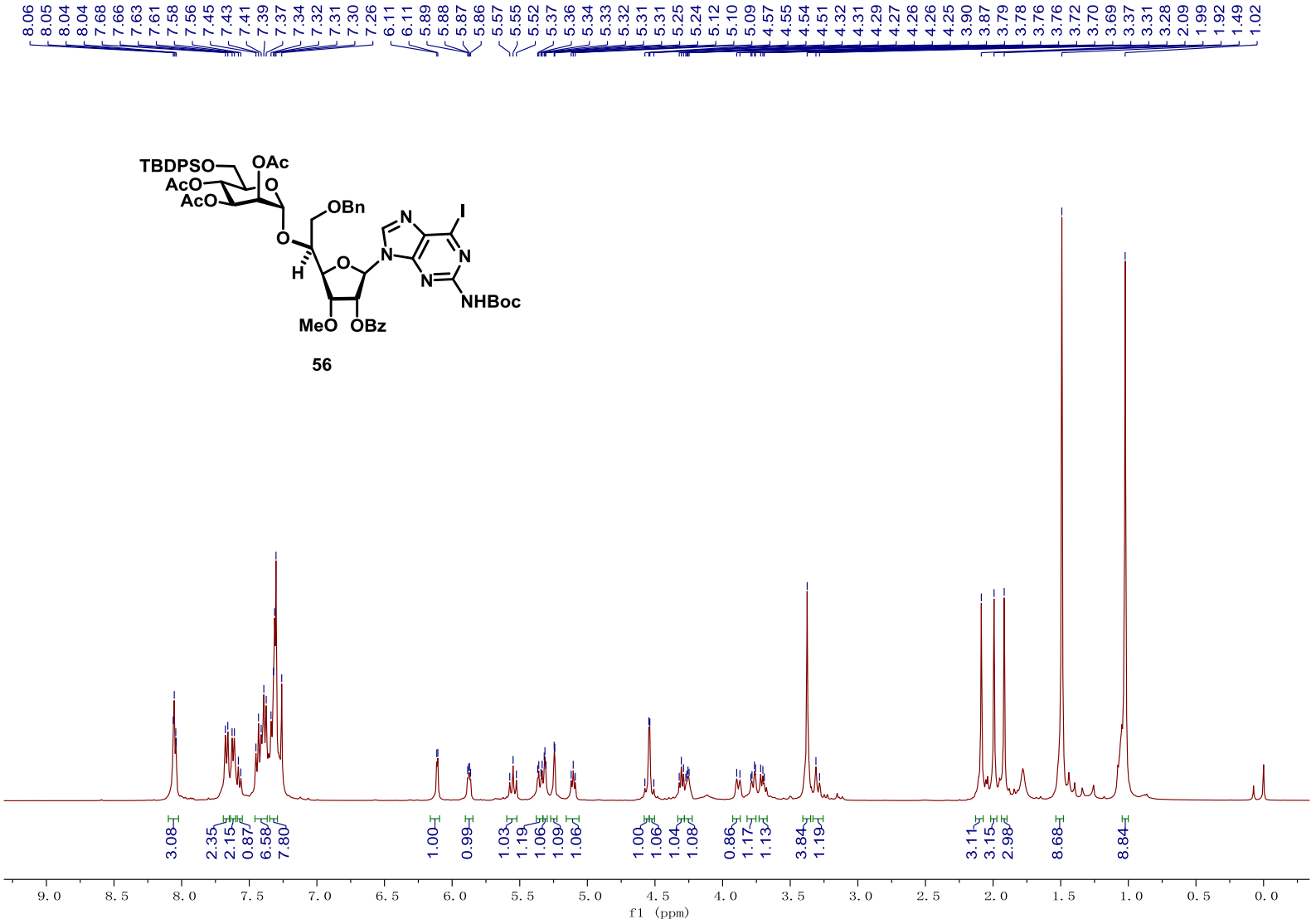

169.89
169.47
146.21
137.44
135.71
135.62
133.58
133.21
133.10
129.97
129.72
129.68
128.52
127.92
127.82
127.68
127.59
96.67
87.58
82.45
78.18
74.26
73.65
72.73
69.75
69.48
69.12
66.56
65.70
62.39
58.85
28.28
27.95
26.72
22.33
20.83
20.69
20.63
19.34
13.95
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
F
H
N
O
N
N
O
O
MeO
OBz
54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

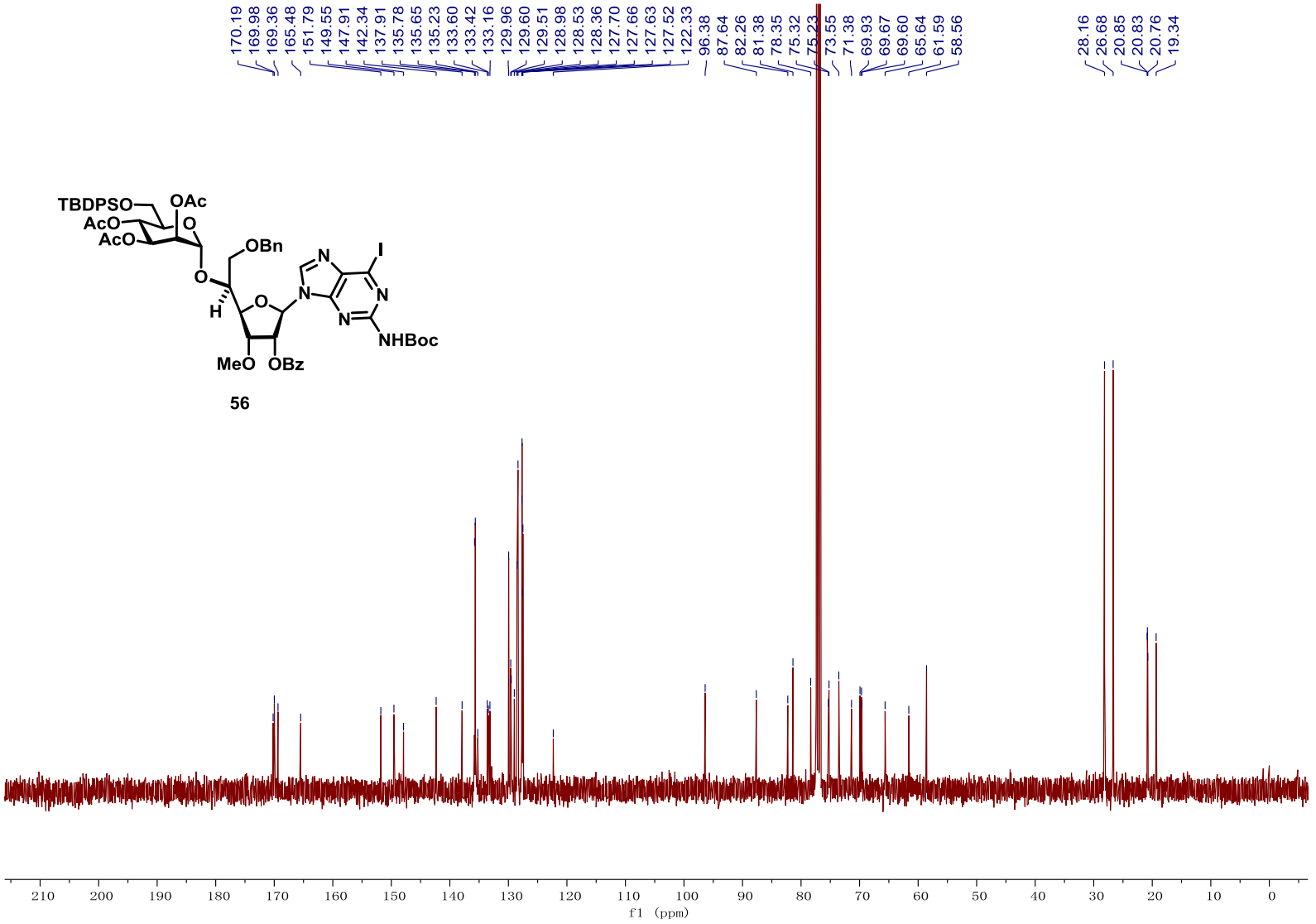

TBDPSO
OAc
AcO
AcO
OBn
F
H
N
O
N
O
O
O
H
O
N
O
MeO
OBz
54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9

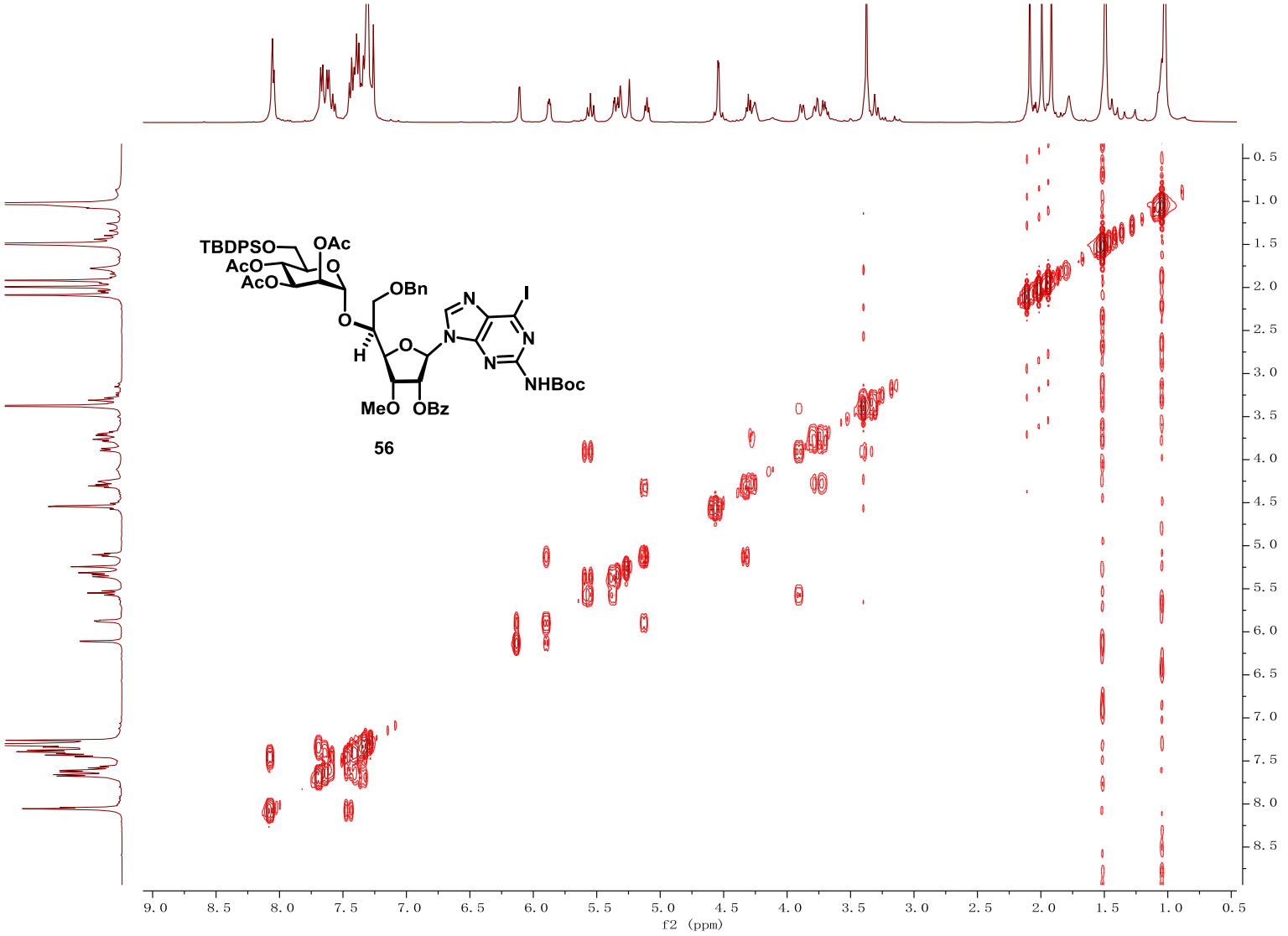

8.84
8.36
8.00
7.98
7.72
7.70
7.68
7.66
7.58
7.57
7.55
7.43
7.41
7.40
7.38
7.37
7.36
7.35
7.33
7.33
7.31
7.26
6.44
6.43
5.87
5.85
5.84
5.58
5.55
5.53
5.41
5.40
5.38
5.29
4.62
4.59
4.55
4.52
4.42
4.41
4.40
4.39
4.22
4.21
4.20
4.19
4.13
4.11
3.80
3.79
3.78
3.77
3.76
3.29
2.12
2.00
1.96
1.45
1.07
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
N
N
N
NBoc2
MeO
OBz
55
0.88
1.01
2.07
2.02
2.22
1.29
13.68
1.00
1.01
1.09
2.15
1.04
1.00
0.97
2.15
1.01
1.04
4.30
3.12
2.89
2.96
2.96
18.23
8.91
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
−0.5
f1 (ppm)

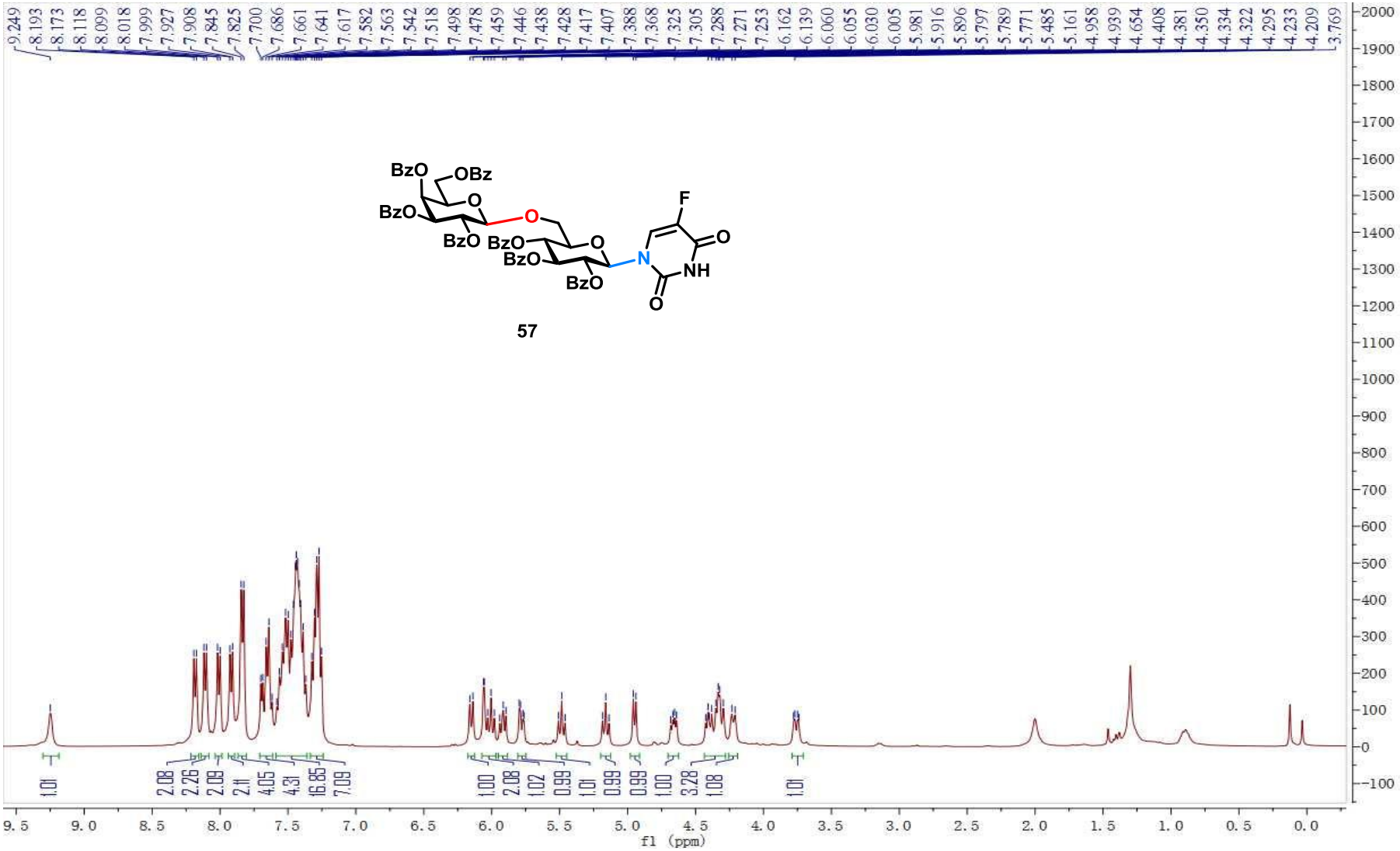

169.96
169.95
169.50
165.23
153.16
152.37
150.51
142.87
137.58
135.76
135.65
133.59
133.34
133.23
129.88
129.67
129.63
129.10
128.81
128.49
127.85
127.66
127.58
96.78
85.54
83.79
82.60
78.52
74.74
73.65
72.40
69.79
69.57
69.27
65.66
62.46
58.74
27.80
26.75
20.86
20.74
20.71
19.36
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
N
N
N
NBoc2
MeO
OBz
55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

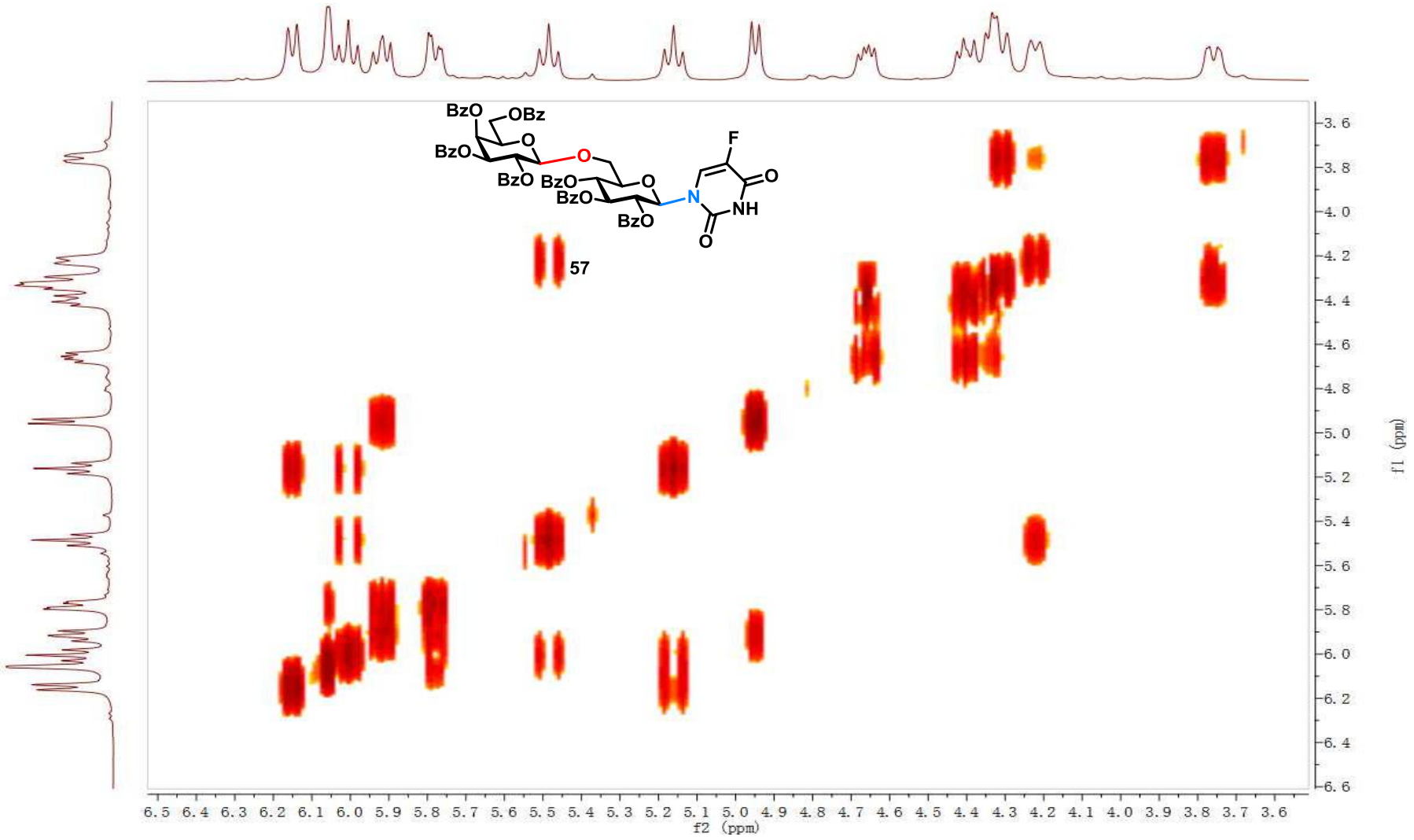

TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
N
N
N
NBoc2
MeO
OBz
55
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9

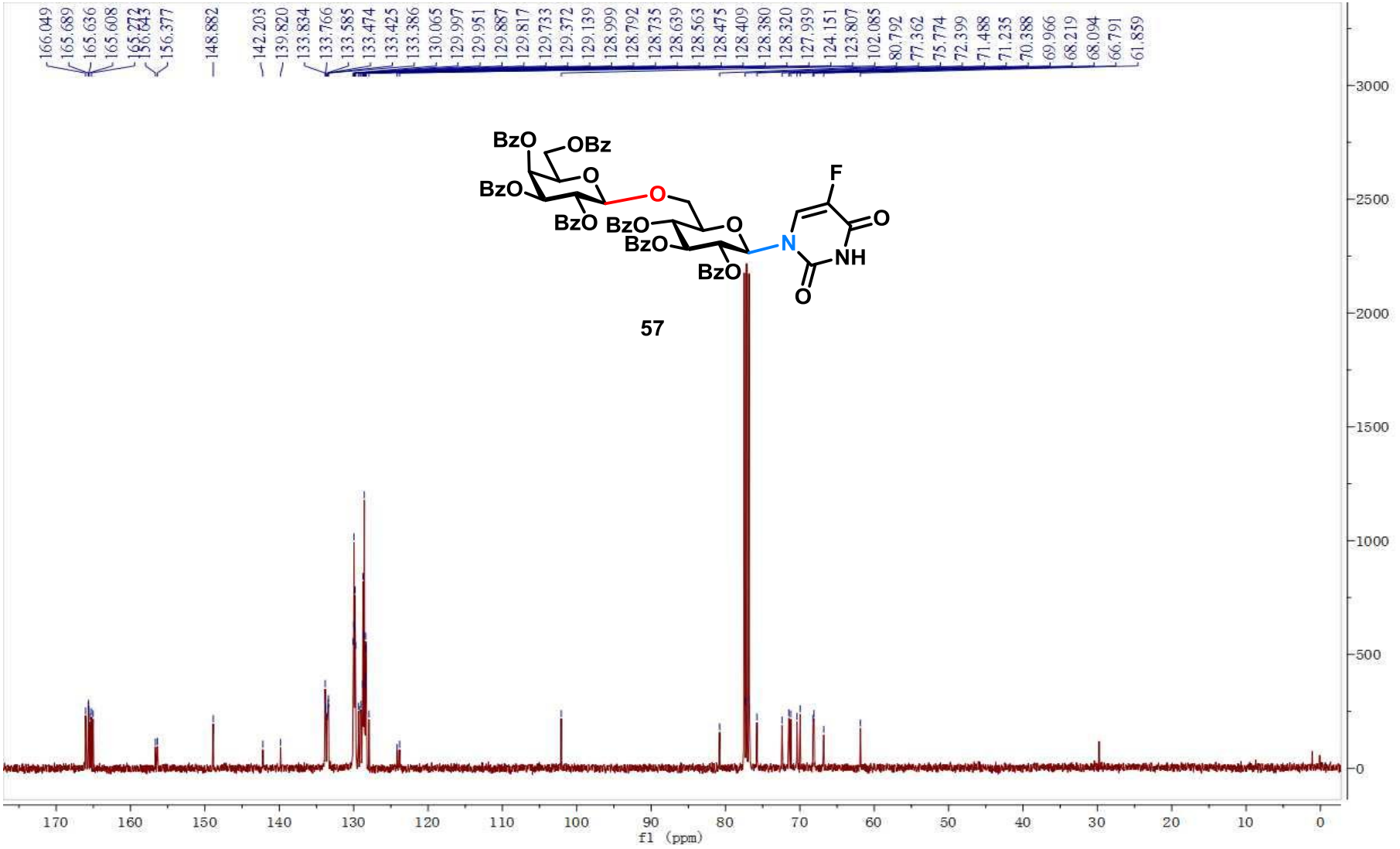

8.06 8.05 8.04 8.04 7.68 7.66 7.63 7.61 7.58 7.56 7.45 7.43 7.41 7.39 7.37 7.34 7.32 7.31 7.30 7.26 6.11 6.11 5.89 5.88 5.87 5.86 5.57 5.55 5.52 5.37 5.36 5.34 5.33 5.32 5.31 5.31 5.25 5.24 5.12 5.10 5.09 4.57 4.55 4.54 4.51 4.32 4.31 4.29 4.27 4.26 4.26 4.25 3.90 3.87 3.79 3.78 3.76 3.76 3.72 3.70 3.69 3.37 3.31 3.28 2.09 1.99 1.92 1.49 1.02
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
N
I
N
N
N
NHBoc
MeO
OBz
56
3.08 2.35 2.15 0.87 6.58 7.80 1.00 0.99 1.03 1.19 1.06 1.09 1.06 1.00 1.06 1.04 1.08 0.86 1.17 1.13 3.84 1.19 3.11 3.15 2.98 8.68 8.84
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)

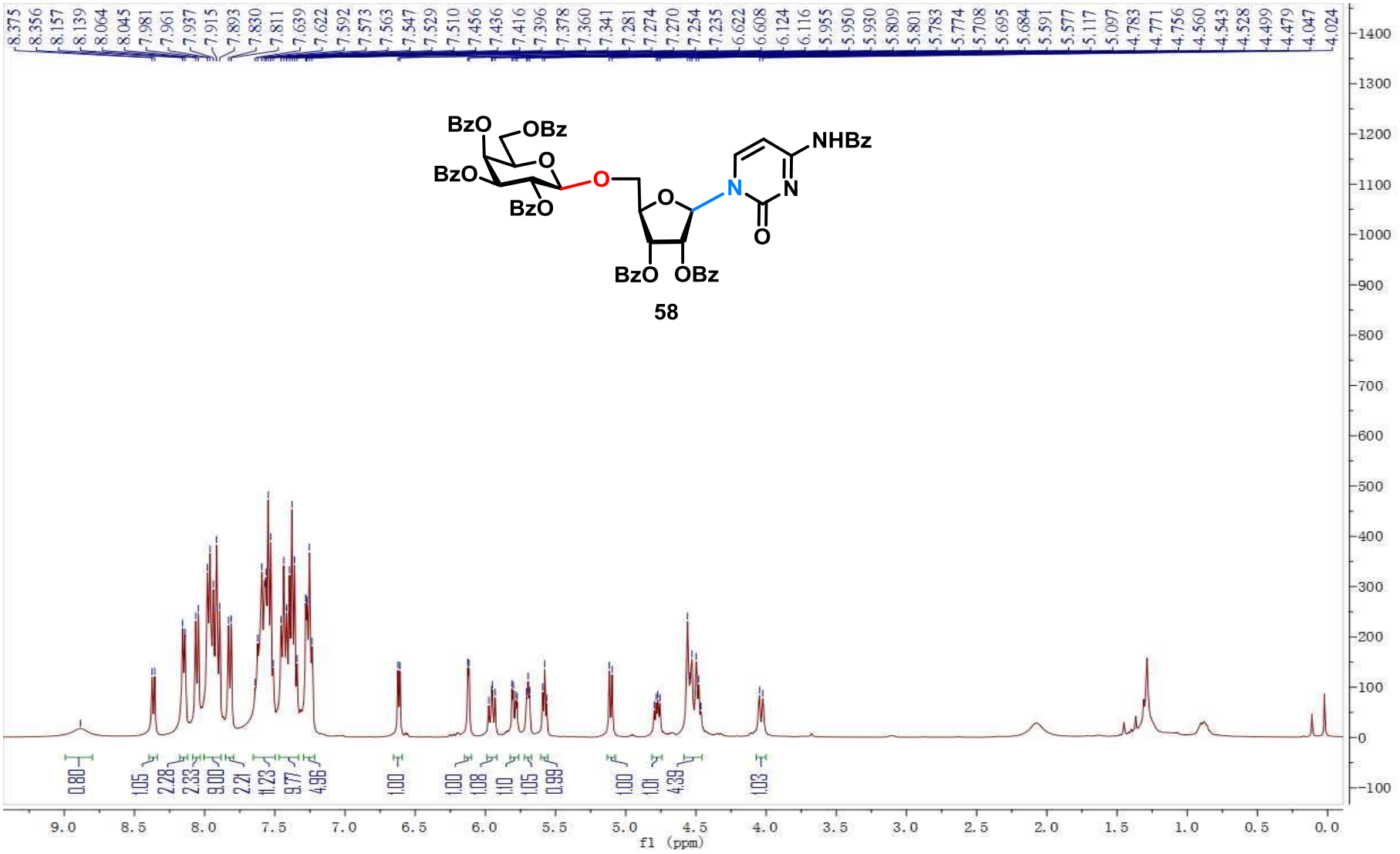

170.19
169.98
169.36
165.48
151.79
149.55
147.91
142.34
137.91
135.78
135.65
135.23
133.60
133.42
133.16
129.96
129.60
129.51
128.98
128.53
128.36
127.70
127.66
127.63
127.52
122.33
96.38
87.64
82.26
81.38
78.35
75.32
75.23
73.55
71.38
69.93
69.67
69.60
65.64
61.59
58.56
28.16
26.68
20.85
20.83
20.76
19.34
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
N
I
N
N
NHBoc
MeO
OBz
56
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

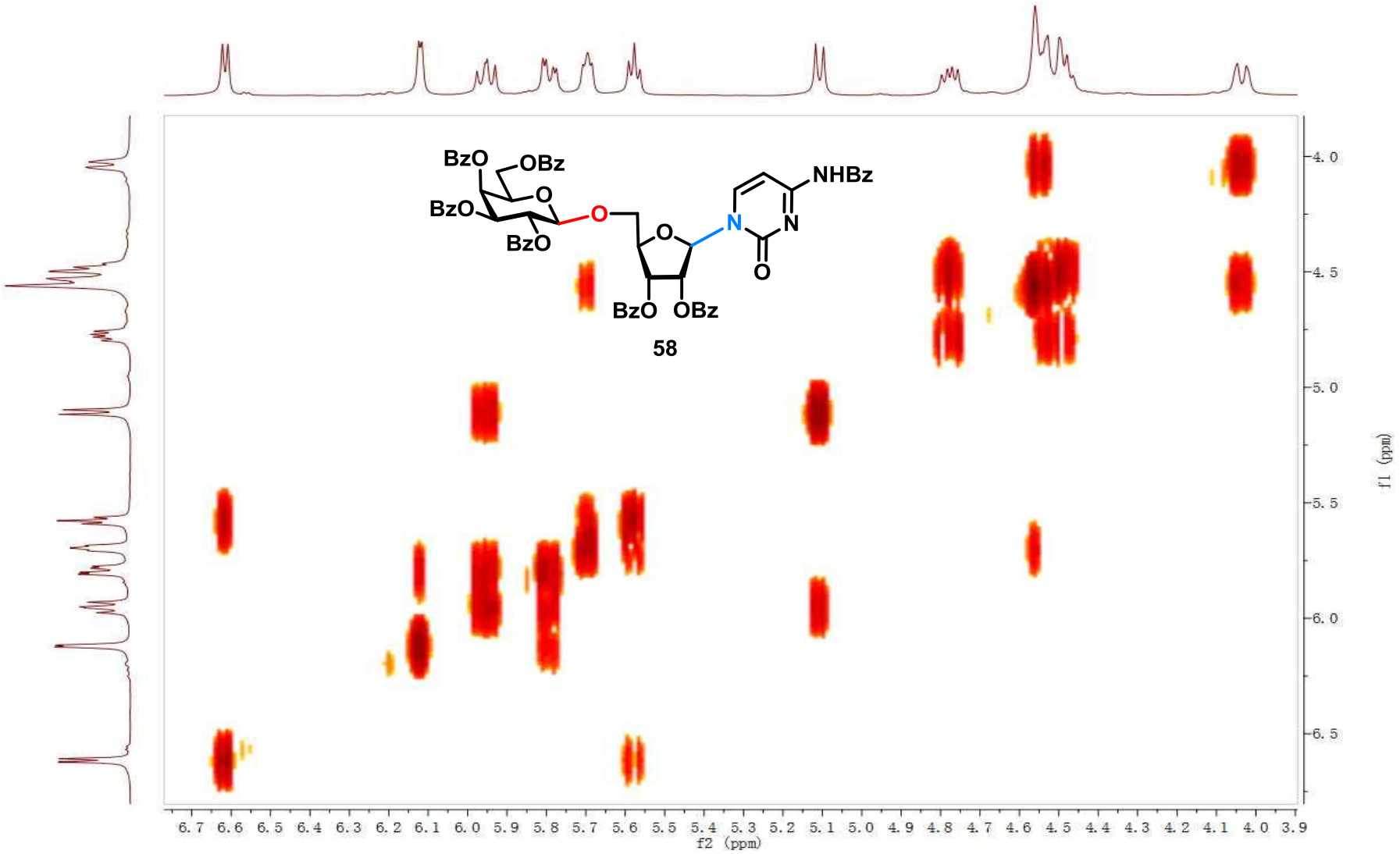

TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
N
N
N
I
N
NHBoc
MeO
OBz
56
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5

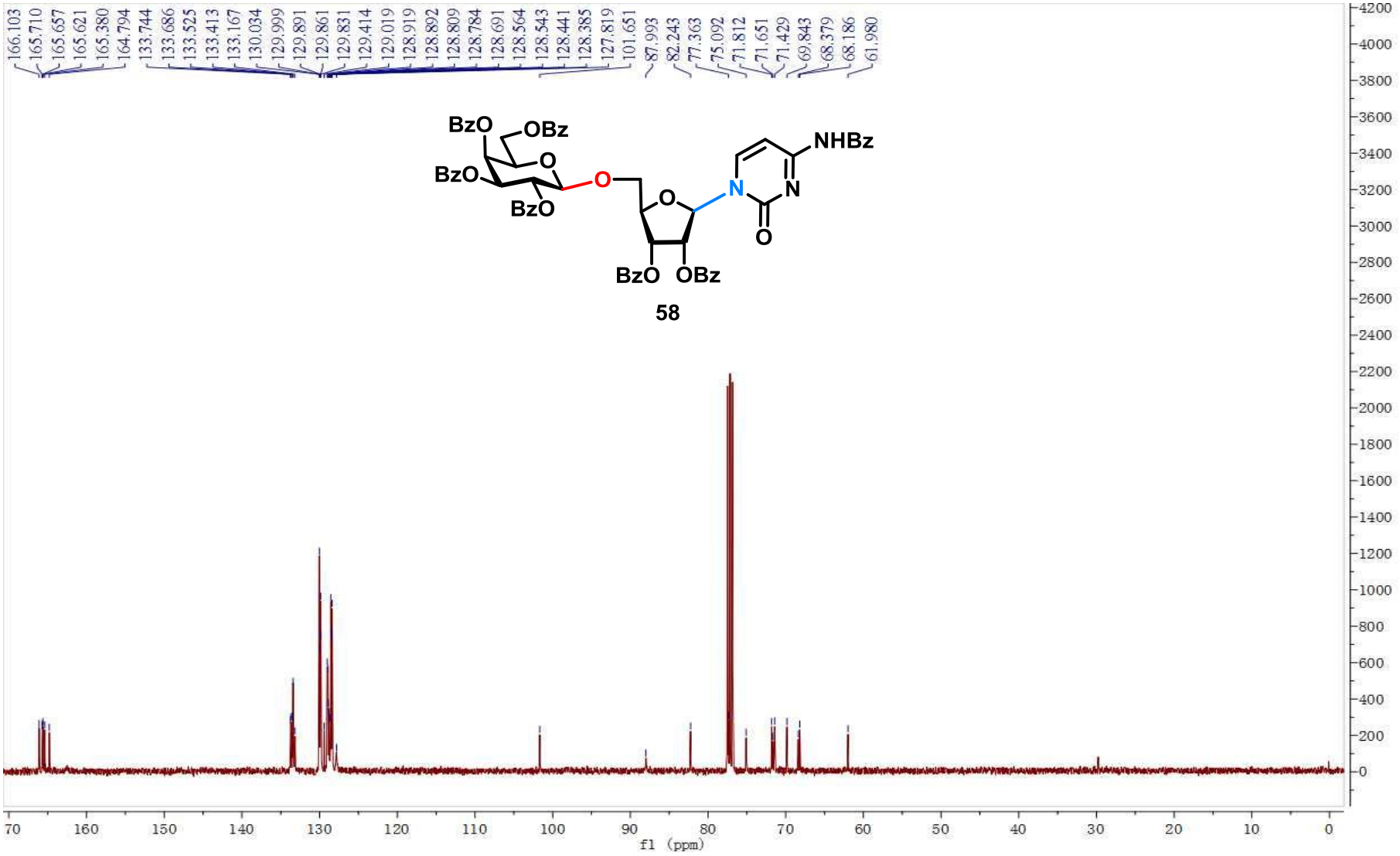

BzO
OBz
BzO
BzO
BzO
BzO
BzO
O
O
O
N
F
O
NH
O
57
fl (ppm)

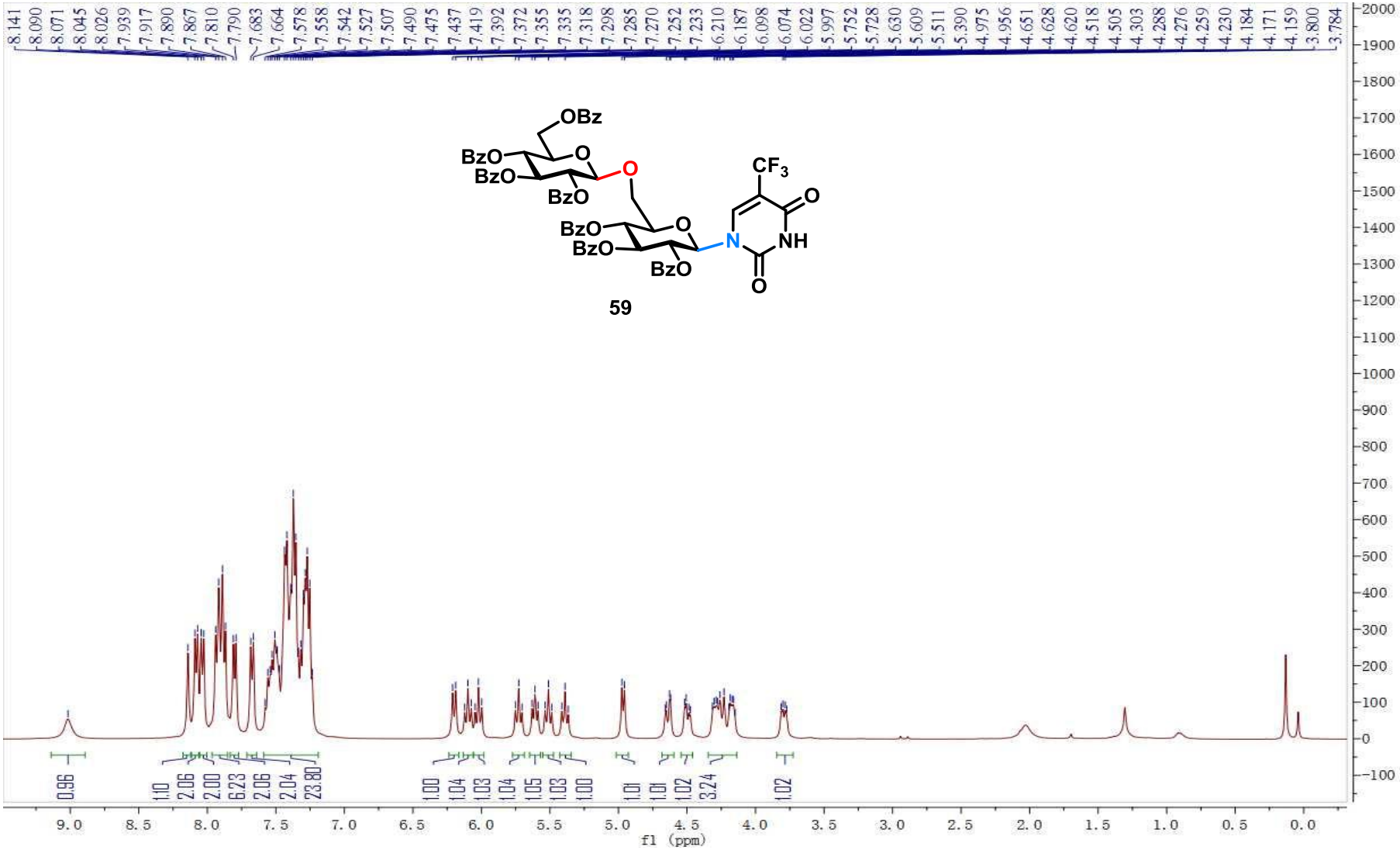

BzO
OBz
O
BzO
O
BzO
BzO
BzO
O
BzO
N
F
O
NH
O
57
f2 (ppm)
f1 (ppm)

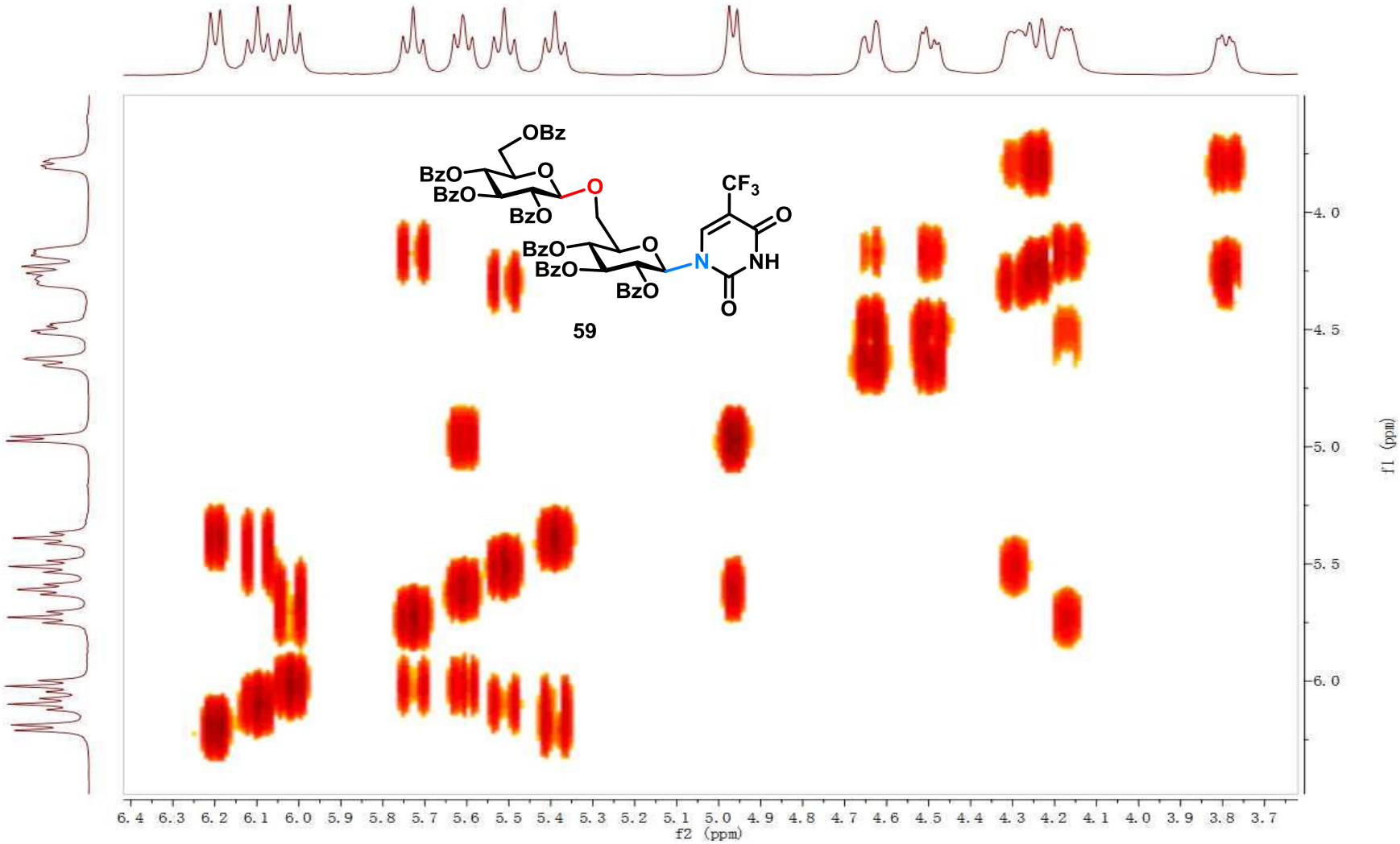

166.049
165.689
165.636
165.608
165.272
165.243
156.377
148.882
142.203
139.820
133.834
133.766
133.585
133.474
133.425
133.386
130.065
129.997
129.951
129.887
129.817
129.733
129.372
129.139
128.999
128.792
128.735
128.639
128.563
128.475
128.409
128.380
128.320
127.939
124.151
123.807
102.085
80.792
77.362
75.774
72.399
71.488
71.235
70.388
69.966
68.219
68.094
66.791
61.859
BzO
OBz
O
BzO
BzO
BzO
BzO
O
O
N
F
O
NH
O
57
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

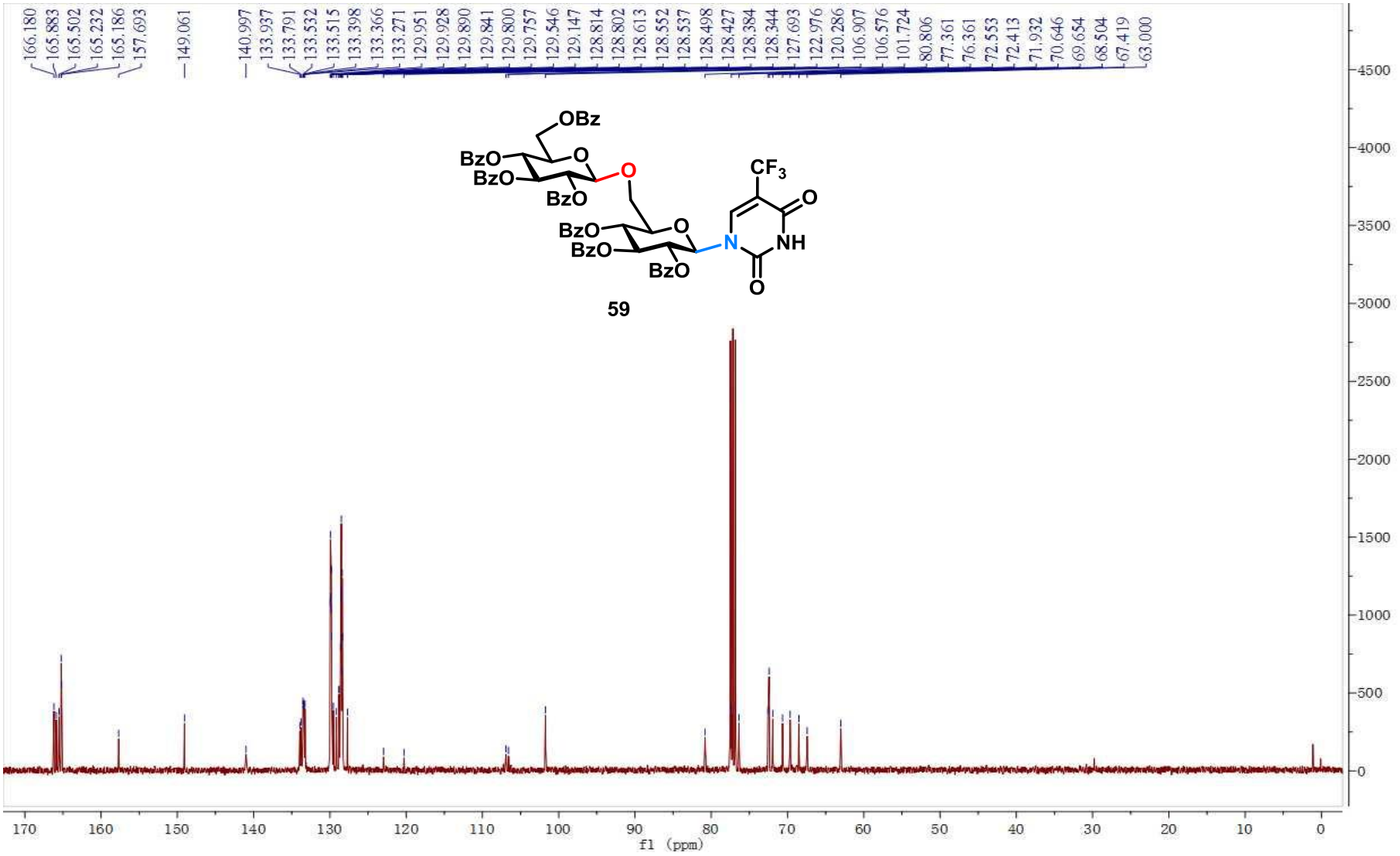

BzO
OBz
BzO
BzO
O
O
N
N
NHBz
O
BzO
OBz
58
fl (ppm)


BzO
OBz
BzO
BzO
O
O
O
N
N
NHBz
O
BzO
OBz
58
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)
6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9
f2 (ppm)


166.103
165.710
165.657
165.621
165.380
164.794
133.744
133.686
133.525
133.413
133.167
130.034
129.999
129.891
129.861
129.831
129.414
129.019
128.919
128.892
128.809
128.784
128.691
128.564
128.543
128.441
128.385
127.819
101.651
87.993
82.243
77.363
75.092
71.812
71.651
71.429
69.843
68.379
68.186
61.980
BzO
OBz
BzO
BzO
O
O
N
NHBz
N
O
BzO
OBz
58
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
CF3
O
N
NH
O
59
fl (ppm)


OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
N
CF3
O
NH
O
59
4.0
4.5
5.0
5.5
6.0
f1 (ppm)
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7
f2 (ppm)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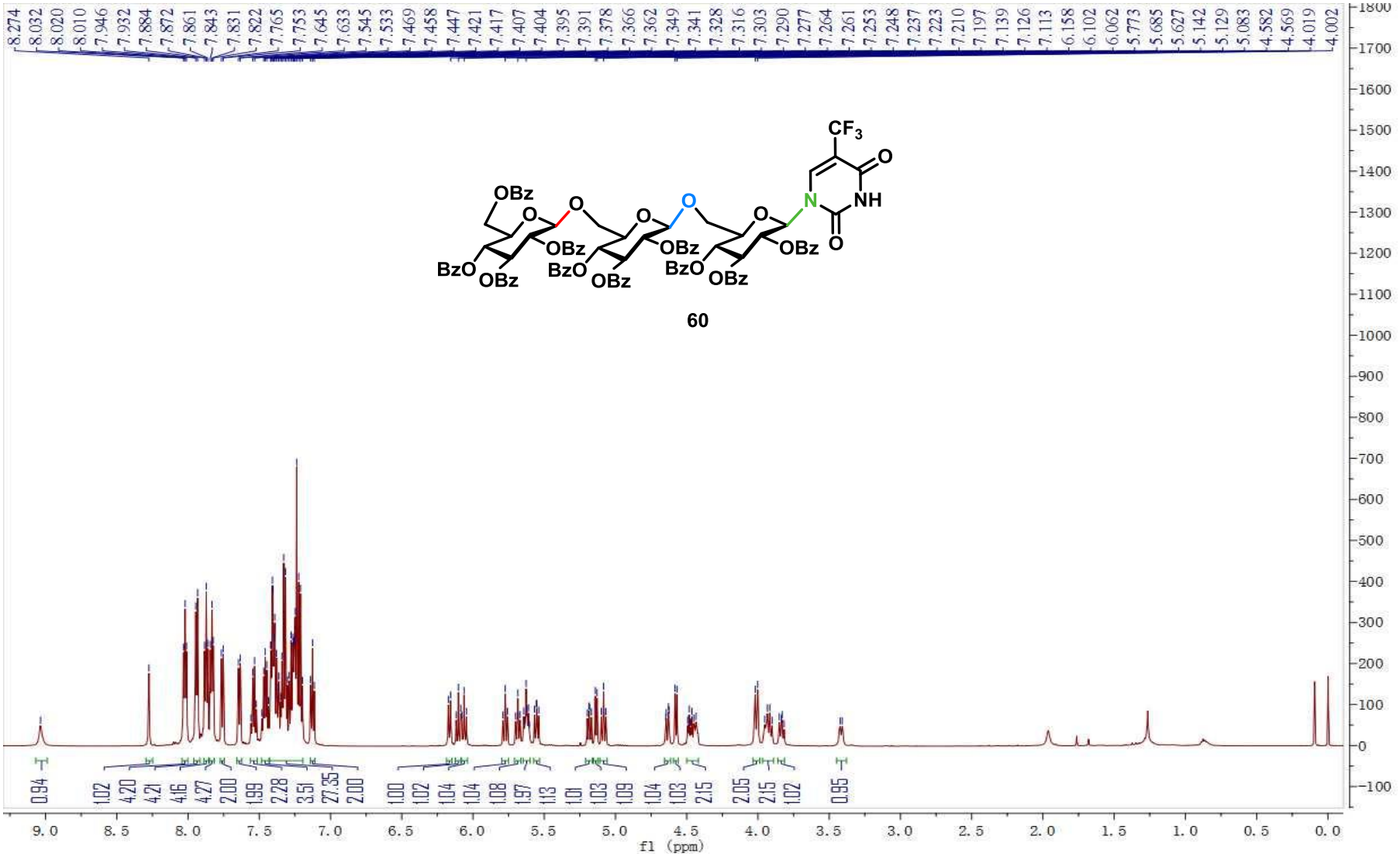
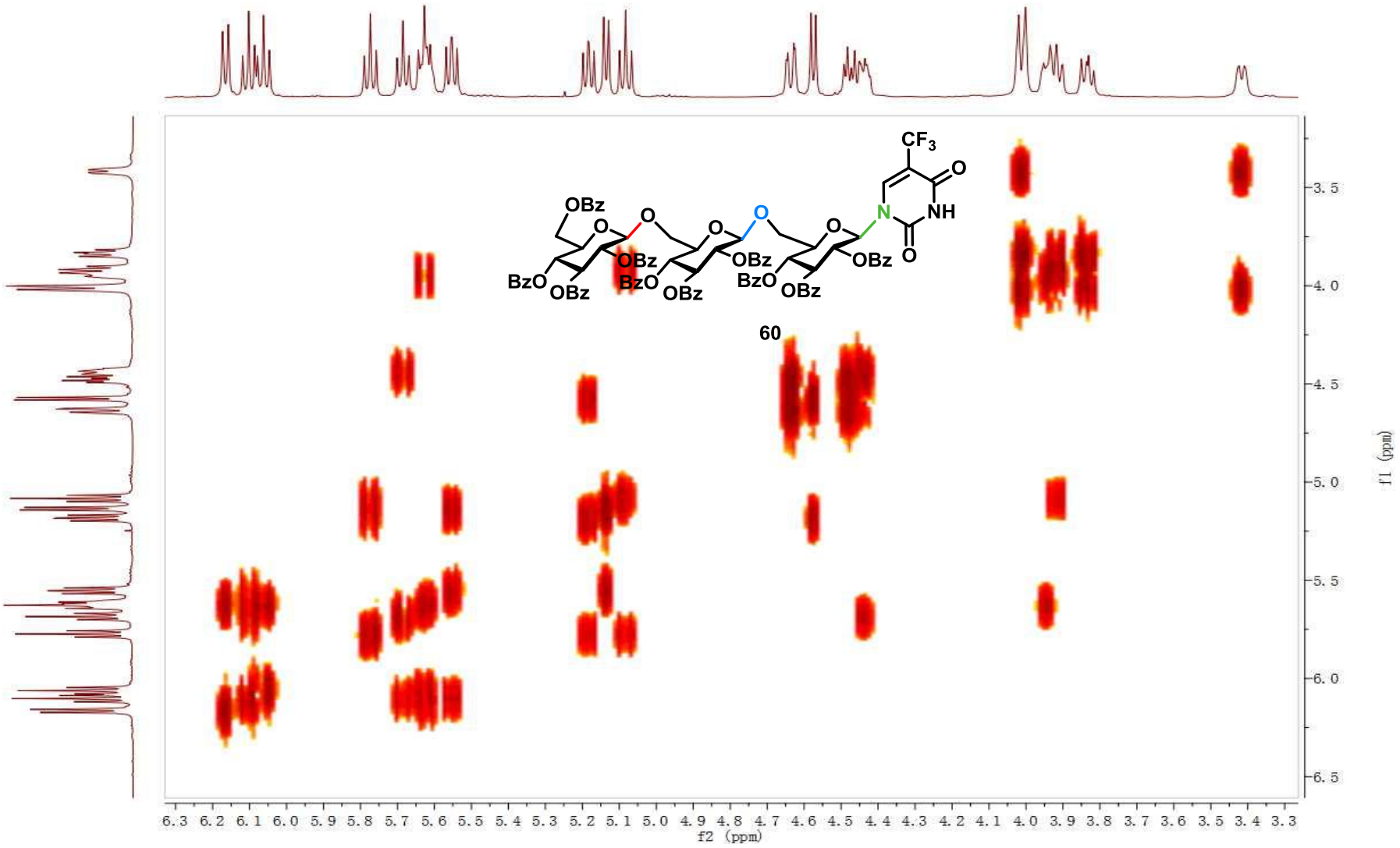
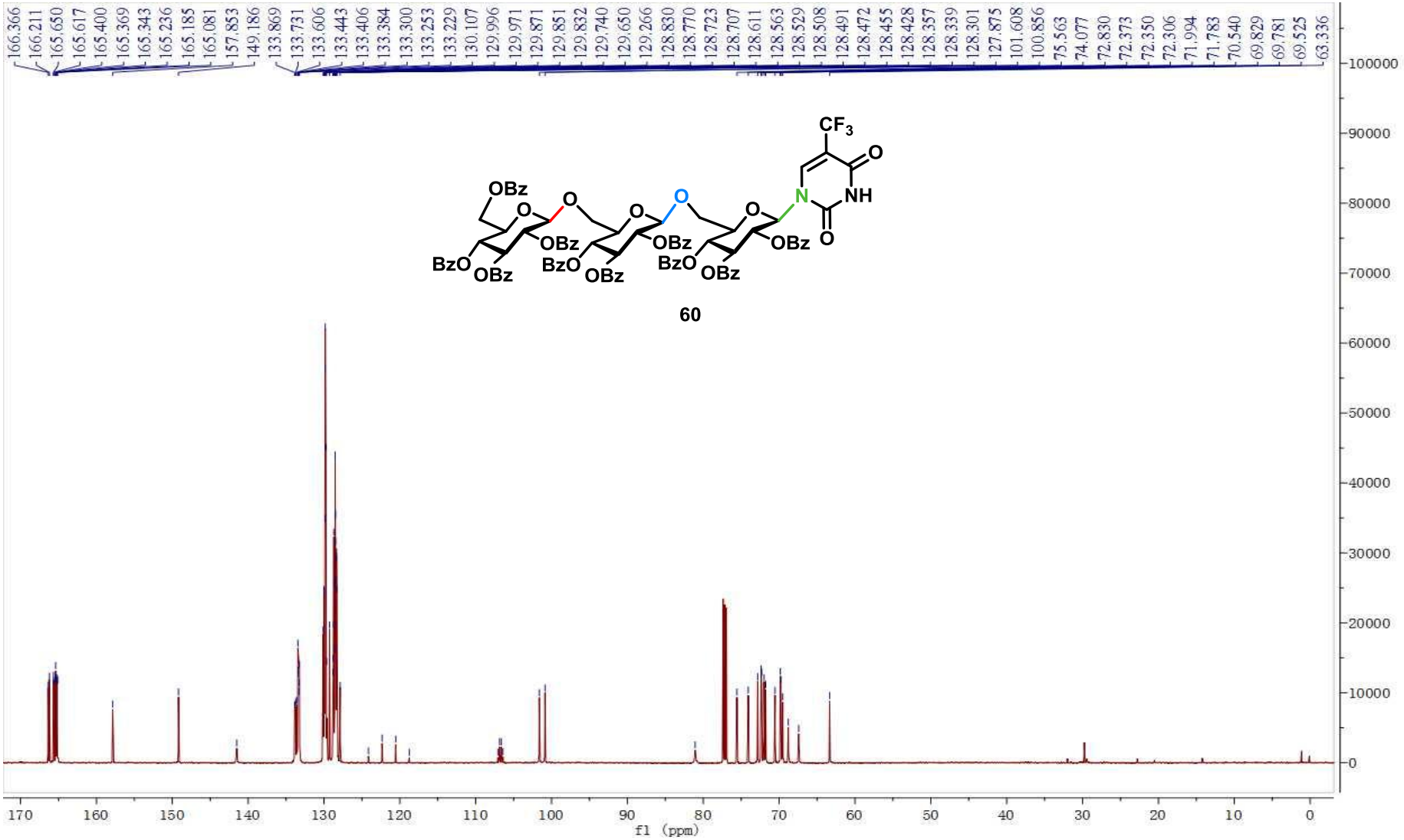
165.883
165.502
165.232
165.186
157.693
149.061
140.997
133.937
133.791
133.532
133.515
133.398
133.366
133.271
129.951
129.928
129.890
129.841
129.800
129.757
129.546
129.147
128.814
128.802
128.613
128.552
128.537
128.498
128.427
128.384
128.344
127.693
122.976
120.286
106.907
106.576
101.724
80.806
77.361
76.361
72.553
72.413
71.932
70.646
69.654
68.504
67.419
63.000
OBz
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
N
CF3
O
NH
O
59
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

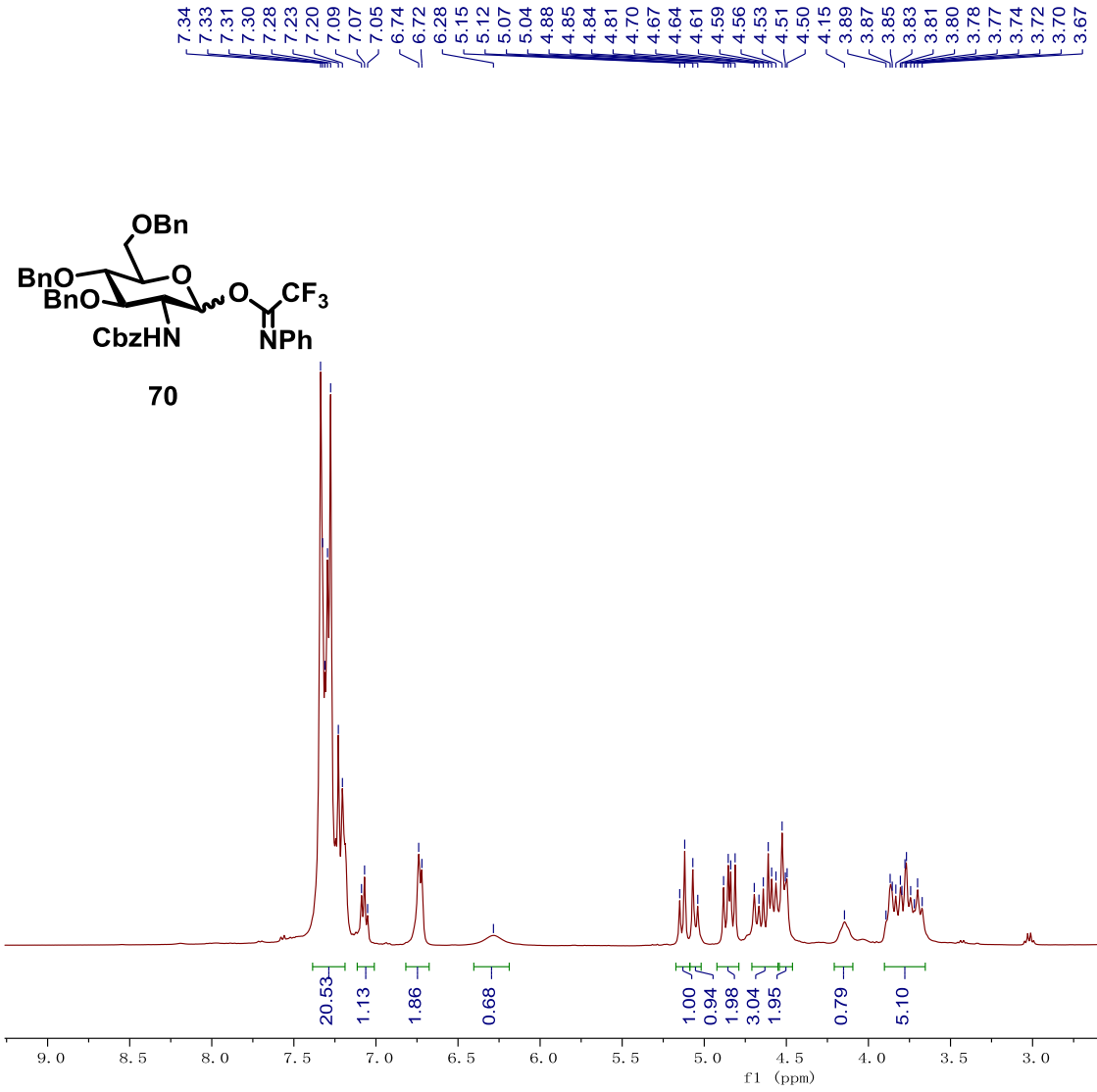

8.274 8.032 8.020 8.010 7.946 7.932 7.884 7.872 7.861 7.843 7.831 7.822 7.765 7.753 7.645 7.633 7.545 7.533 7.469 7.458 7.447 7.421 7.417 7.407 7.404 7.395 7.391 7.378 7.366 7.362 7.349 7.341 7.328 7.316 7.303 7.290 7.277 7.264 7.261 7.253 7.248 7.237 7.223 7.210 7.197 7.139 7.126 7.113 6.158 6.102 6.062 5.773 5.685 5.627 5.142 5.129 5.083 4.582 4.569 4.019 4.002
CF3
O
NH
O
N
OBz
BzO
O
0.94 1.02 4.20 4.21 4.16 4.27 2.00 1.99 2.28 3.51 27.35 2.00 1.00 1.02 1.04 1.04 1.08 1.97 1.13 1.01 1.03 1.09 1.04 1.03 2.15 2.05 2.15 1.02 0.95
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)

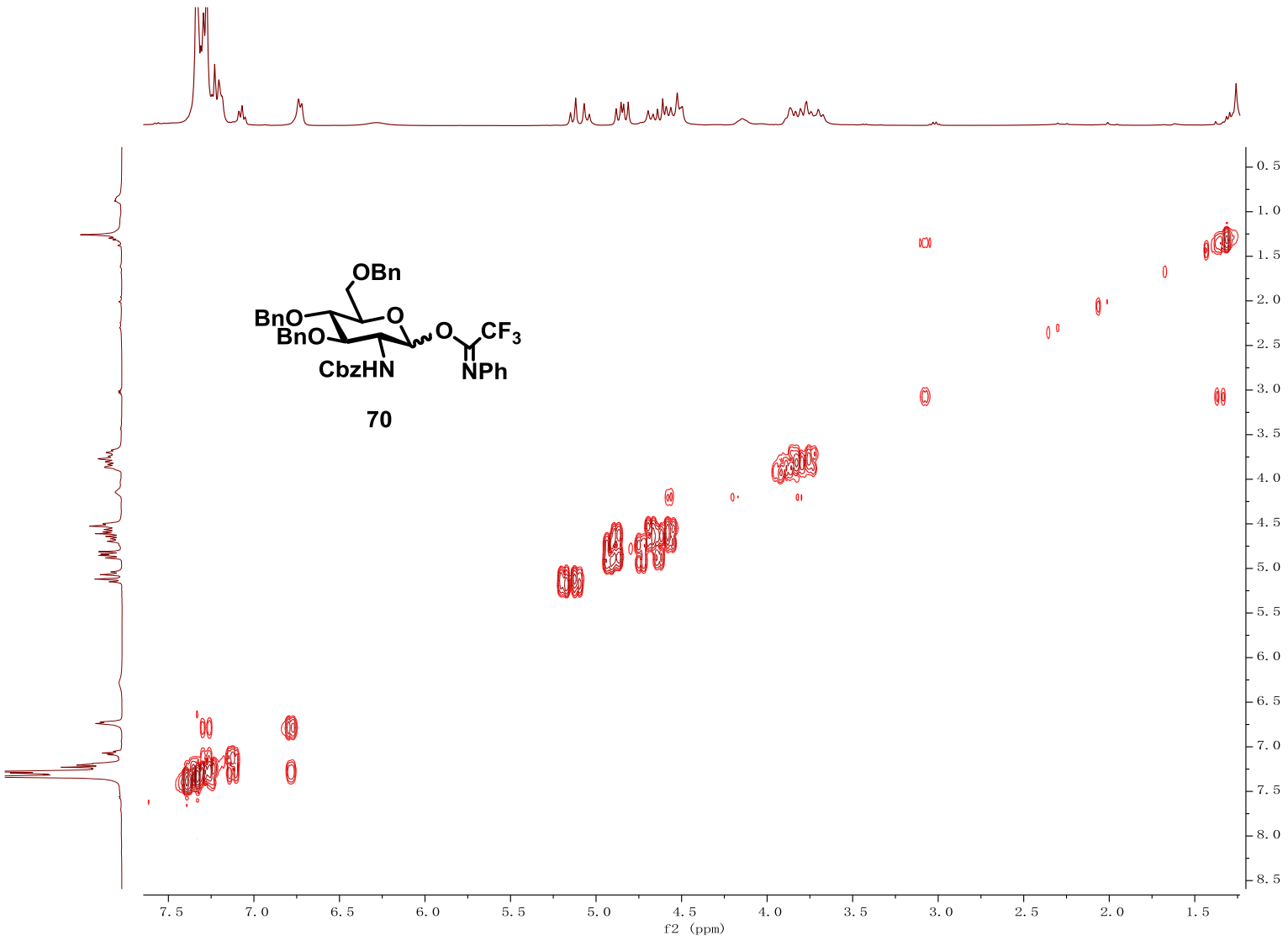
60

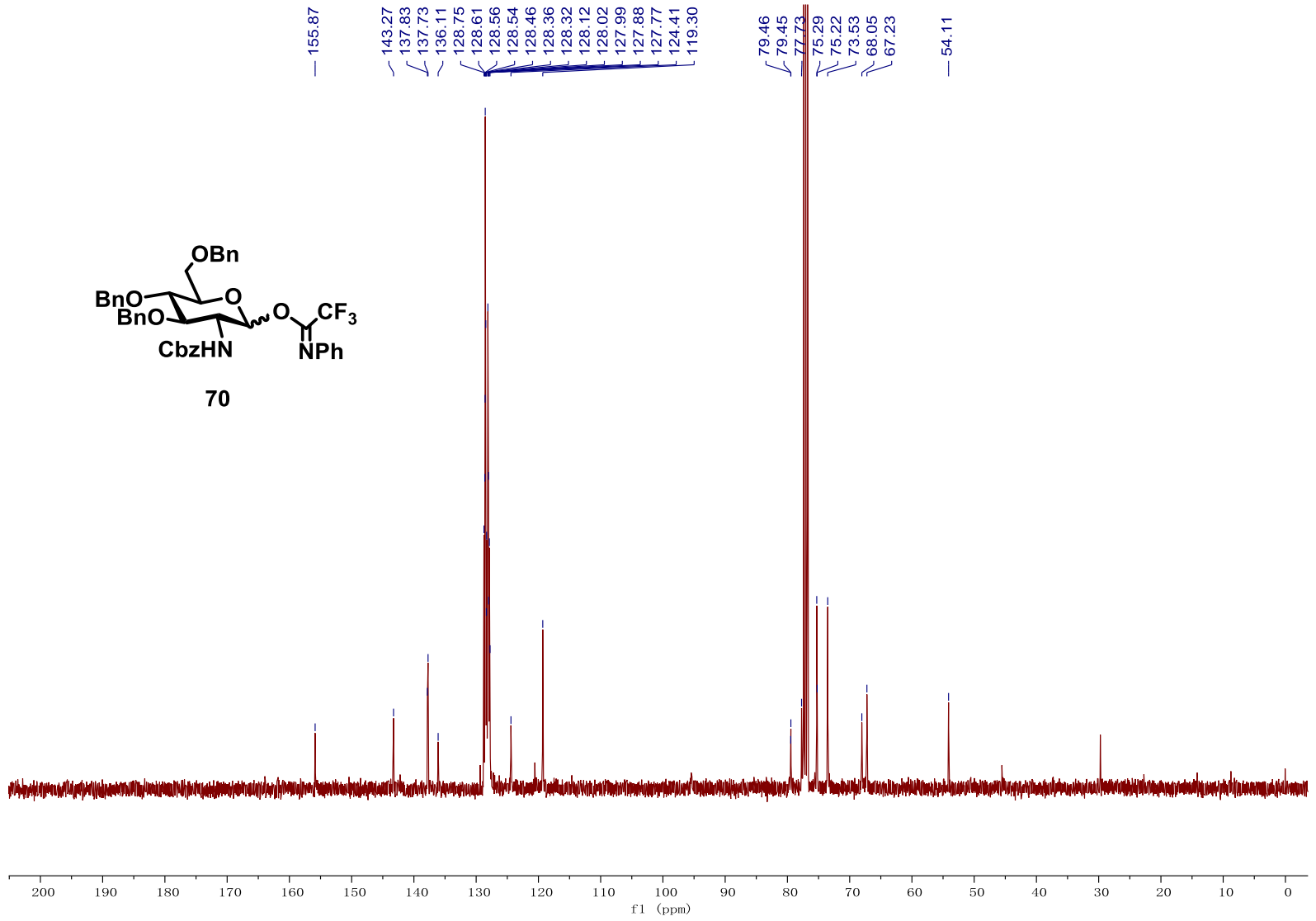

CF3
O
NH
O
N
OBz
O
O
O
O
O
OBz
OBz
OBz
BzO
OBz
BzO
OBz
BzO
OBz
60
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3
f2 (ppm)


166.366
166.211
165.650
165.617
165.400
165.369
165.343
165.236
165.185
165.081
157.853
149.186
133.869
133.731
133.606
133.443
133.406
133.384
133.300
133.253
133.229
130.107
129.996
129.971
129.871
129.851
129.832
129.740
129.650
129.266
128.830
128.770
128.723
128.707
128.611
128.563
128.529
128.508
128.491
128.472
128.455
128.428
128.357
128.339
128.301
127.875
101.608
100.856
75.563
74.077
72.830
72.373
72.350
72.306
71.994
71.783
70.540
69.829
69.781
69.525
63.336
CF3
O
NH
O
N
O
O
O
O
OBz
BzO
OBz
OBz
BzO
OBz
OBz
BzO
OBz
OBz
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

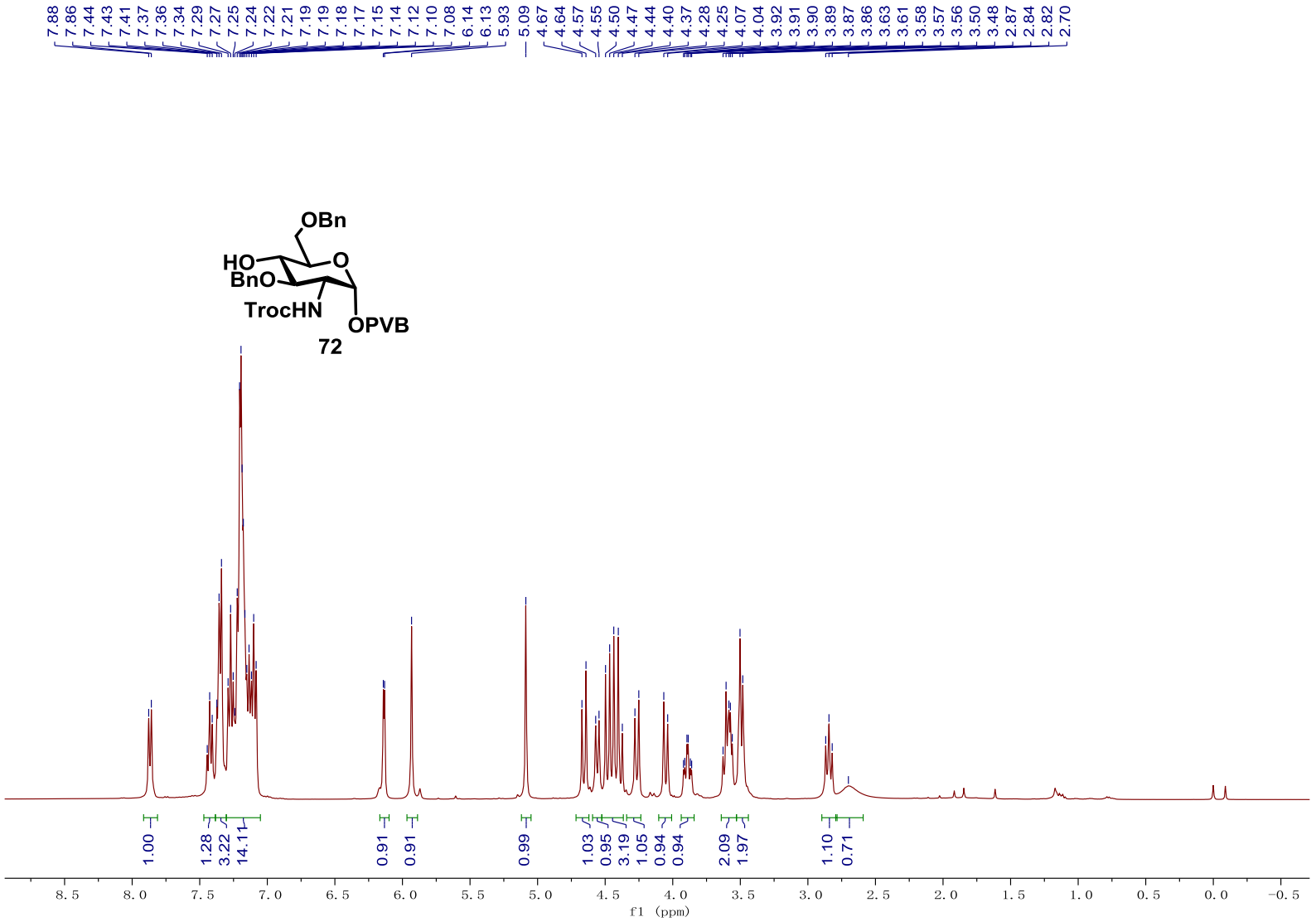
60

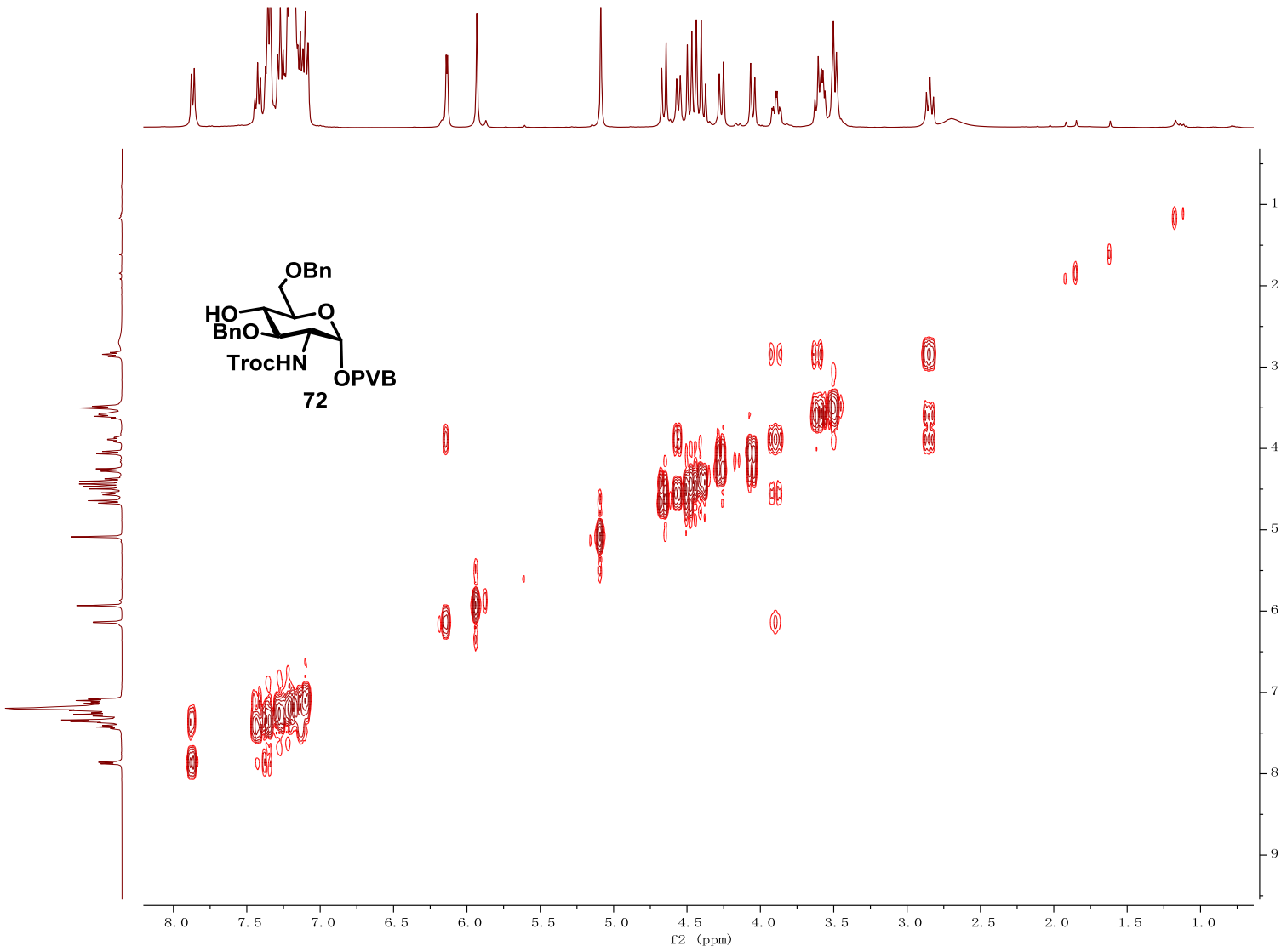

7.34
7.33
7.31
7.30
7.28
7.23
7.20
7.09
7.07
7.05
6.74
6.72
6.28
5.15
5.12
5.07
5.04
4.88
4.85
4.84
4.81
4.70
4.67
4.64
4.61
4.59
4.56
4.53
4.51
4.50
4.15
3.89
3.87
3.85
3.83
3.81
3.80
3.78
3.77
3.74
3.72
3.70
3.67
OBn
BnO
BnO
O
O
CF3
CbzHN
NPh
70
20.53
1.13
1.86
0.68
1.00
0.94
1.98
3.04
1.95
0.79
5.10
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)

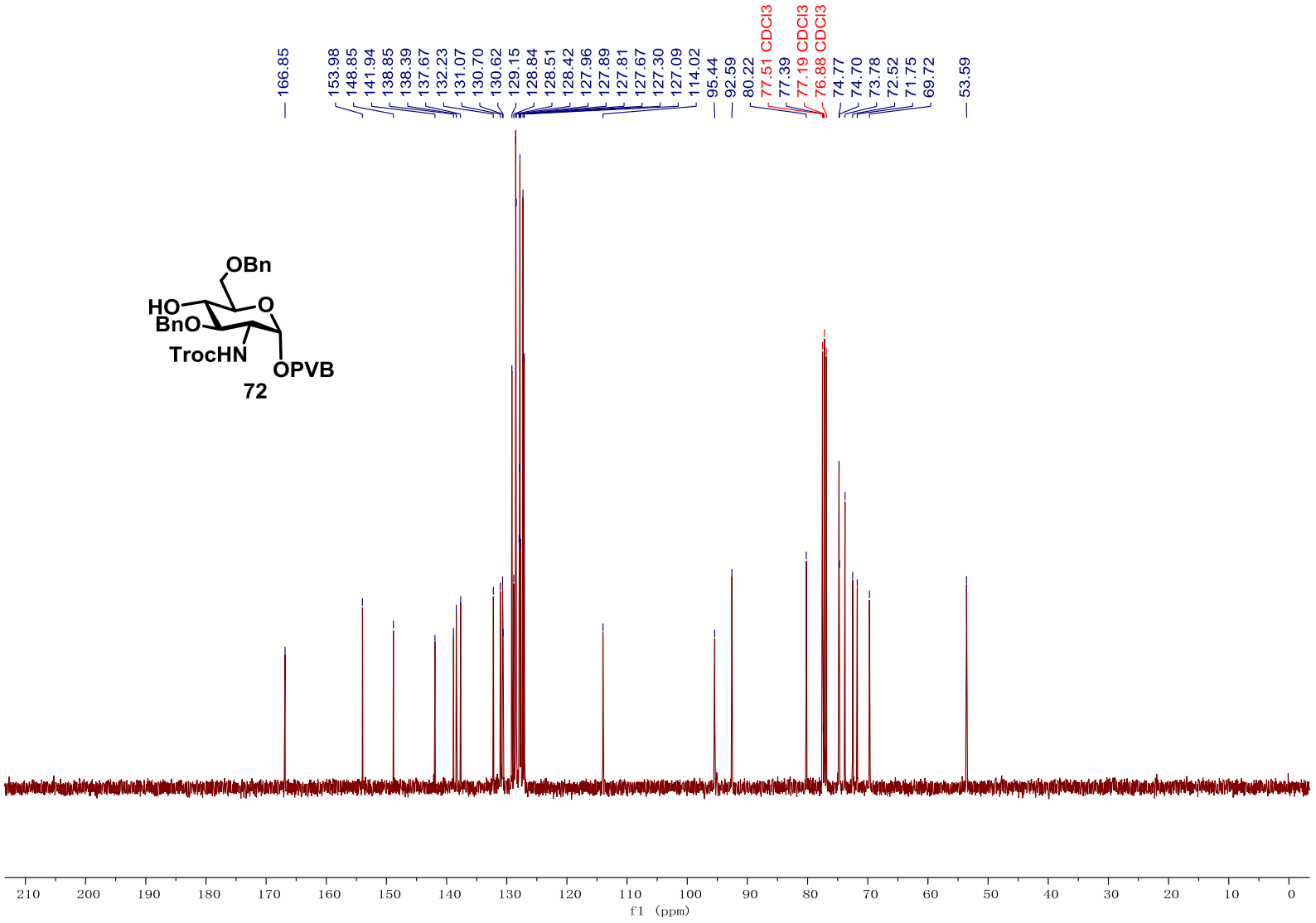

OBn
BnO
BnO
O
O
CF3
CbzHN
NPh
70
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)


155.87
143.27
137.83
137.73
136.11
128.75
128.61
128.56
128.54
128.46
128.36
128.32
128.12
128.02
127.99
127.88
127.77
124.41
119.30
79.46
79.45
77.73
75.29
75.22
73.53
68.05
67.23
54.11
OBn
BnO
BnO
O
O
CF3
CbzHN
NPh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

70


7.88
7.86
7.44
7.43
7.41
7.37
7.36
7.34
7.29
7.27
7.25
7.24
7.22
7.21
7.19
7.19
7.18
7.17
7.15
7.14
7.12
7.10
7.08
6.14
6.13
5.93
5.09
4.67
4.64
4.57
4.55
4.50
4.47
4.44
4.40
4.37
4.28
4.25
4.07
4.04
3.92
3.91
3.90
3.89
3.87
3.86
3.63
3.61
3.58
3.57
3.56
3.50
3.48
2.87
2.84
2.82
2.70
OBn
HO
O
BnO
TrocHN
OPVB
72
1.00
1.28
3.22
14.11
0.91
0.91
0.99
1.03
0.95
3.19
1.05
0.94
0.94
2.09
1.97
1.10
0.71
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
−0.5
f1 (ppm)


OBn
HO
O
BnO
TrocHN
OPVB
72
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
f2 (ppm)
1
2
3
4
5
6
7
8
9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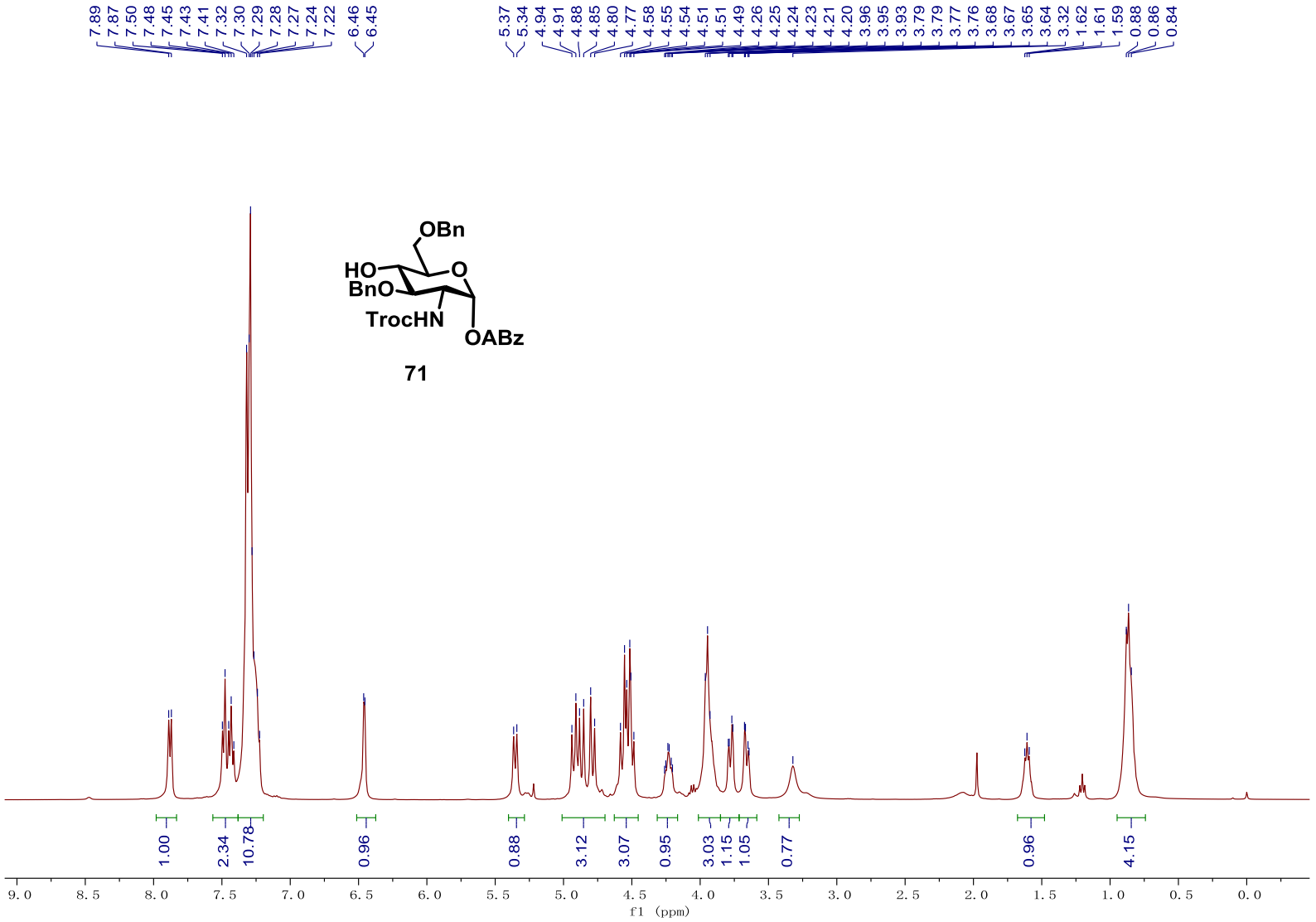
153.98
148.85
141.94
138.85
138.39
137.67
132.23
131.07
130.70
130.62
129.15
128.84
128.51
128.42
127.96
127.89
127.81
127.67
127.30
127.09
114.02
95.44
92.59
80.22
77.51 CDCl3
77.39
77.19 CDCl3
76.88 CDCl3
74.77
74.70
73.78
72.52
71.75
69.72
53.59
OBn
HO
BnO
O
TrocHN
OPVB
72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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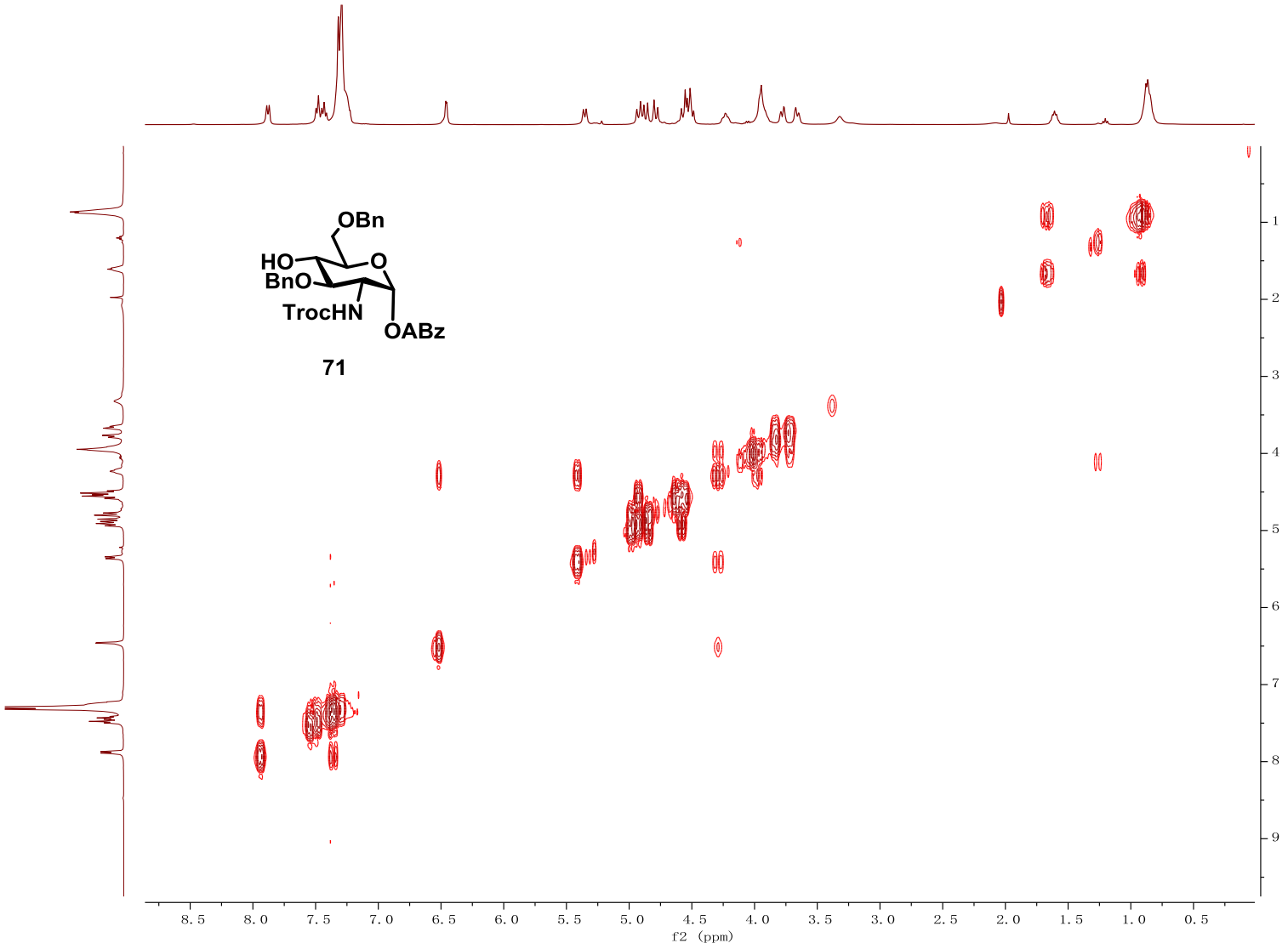
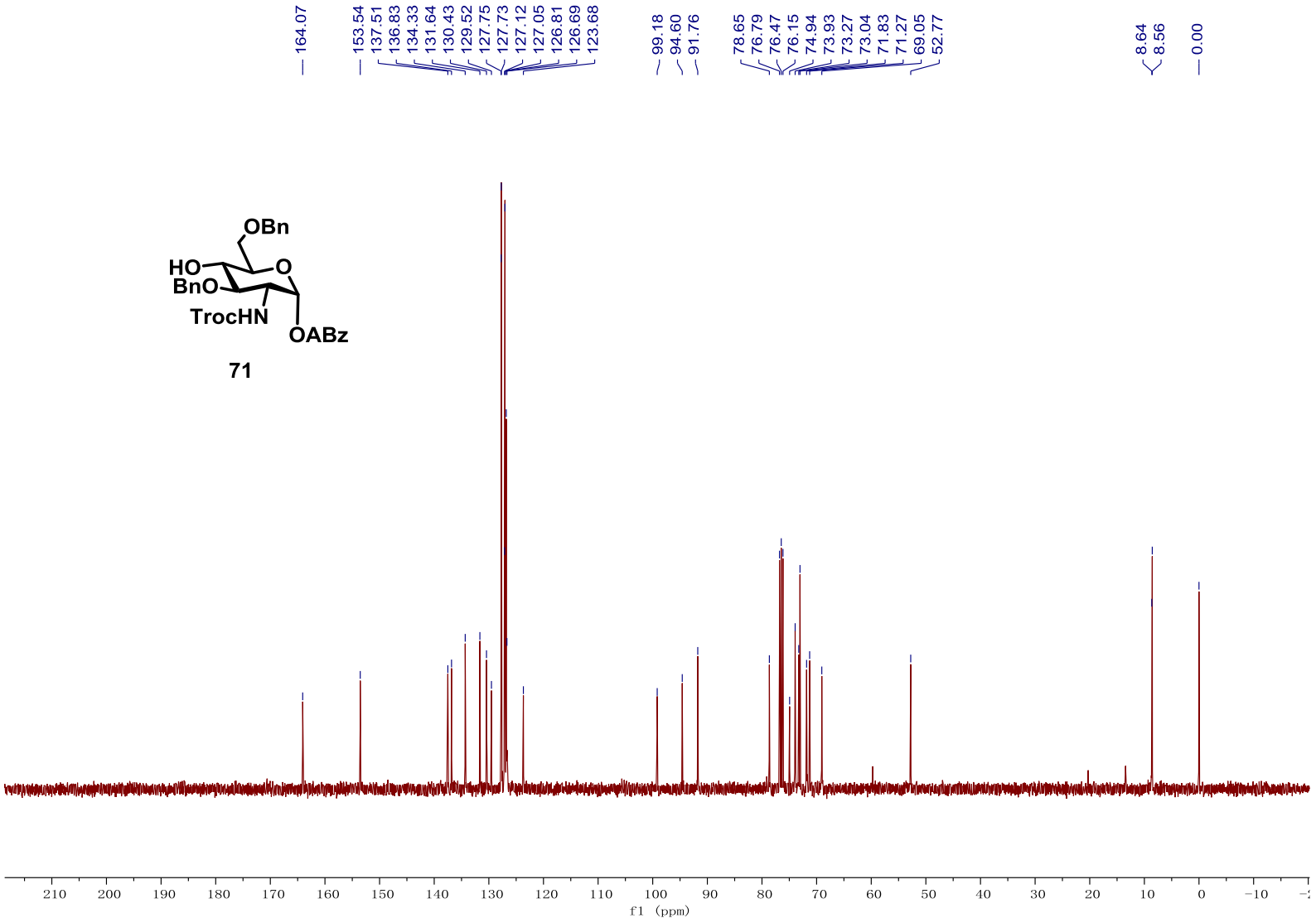
7.50
7.48
7.45
7.43
7.41
7.32
7.30
7.29
7.28
7.27
7.24
7.22
6.46
6.45
5.37
5.34
4.94
4.91
4.88
4.85
4.80
4.77
4.58
4.55
4.54
4.51
4.51
4.49
4.26
4.25
4.24
4.23
4.21
4.20
3.96
3.95
3.93
3.79
3.79
3.77
3.76
3.68
3.67
3.65
3.64
3.32
1.62
1.61
1.59
0.88
0.86
0.84
OBn
HO
O
BnO
TrocHN
OABz
71
1.00
2.34
10.78
0.96
0.88
3.12
3.07
0.95
3.03
1.15
1.05
0.77
0.96
4.15
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)


OBn
HO
O
BnO
TrocHN
OABz
71
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


164.07
153.54
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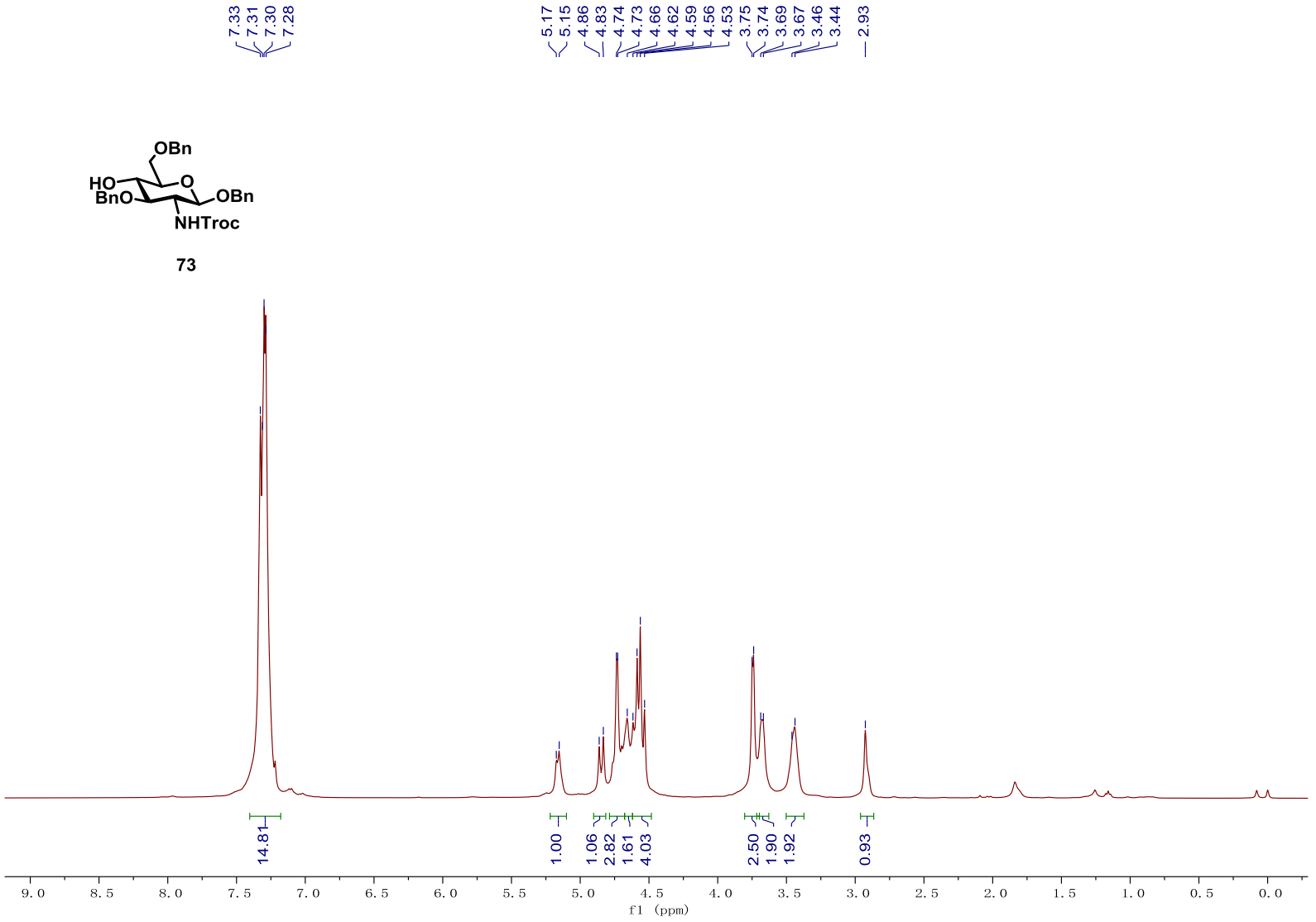
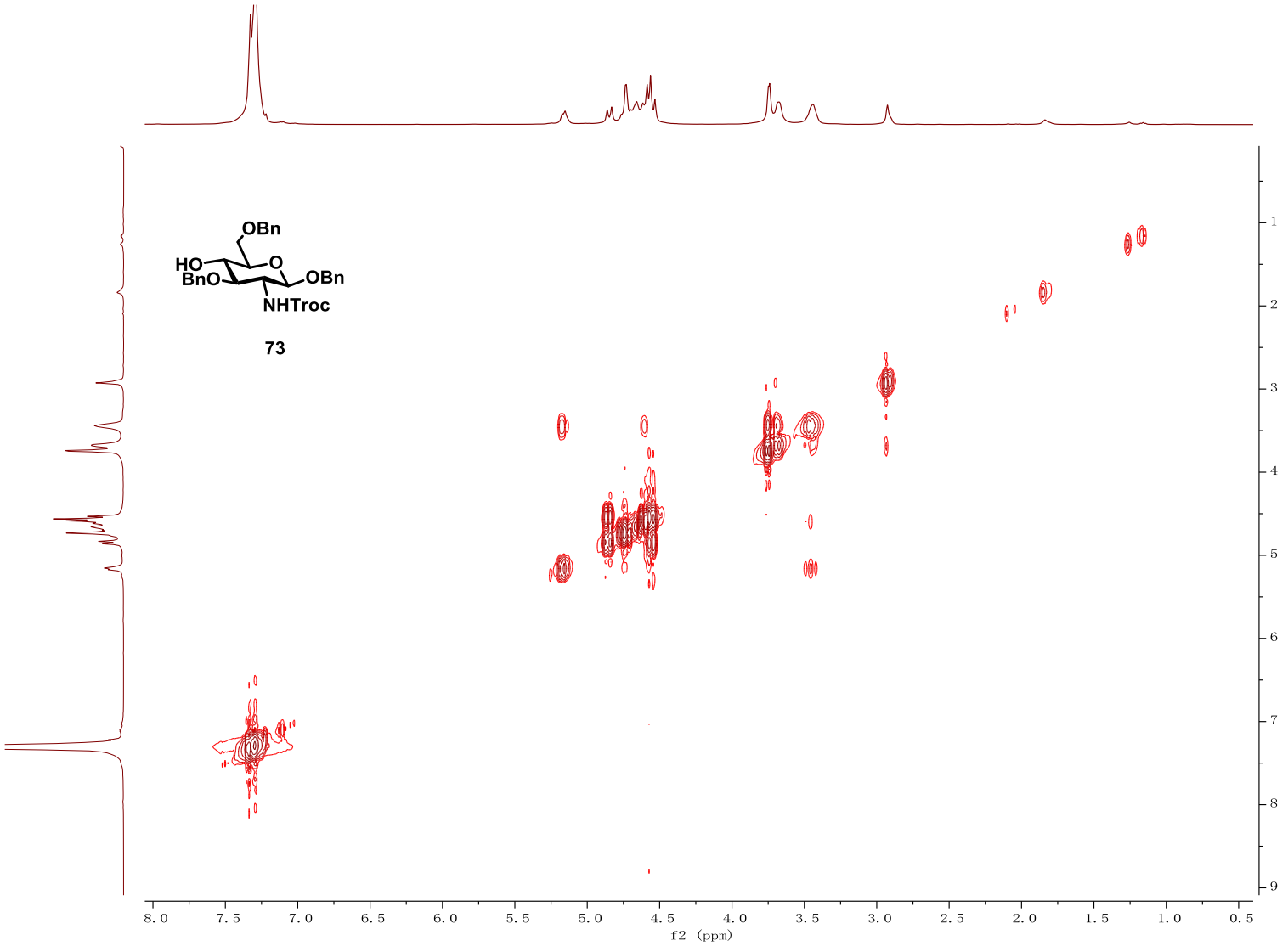
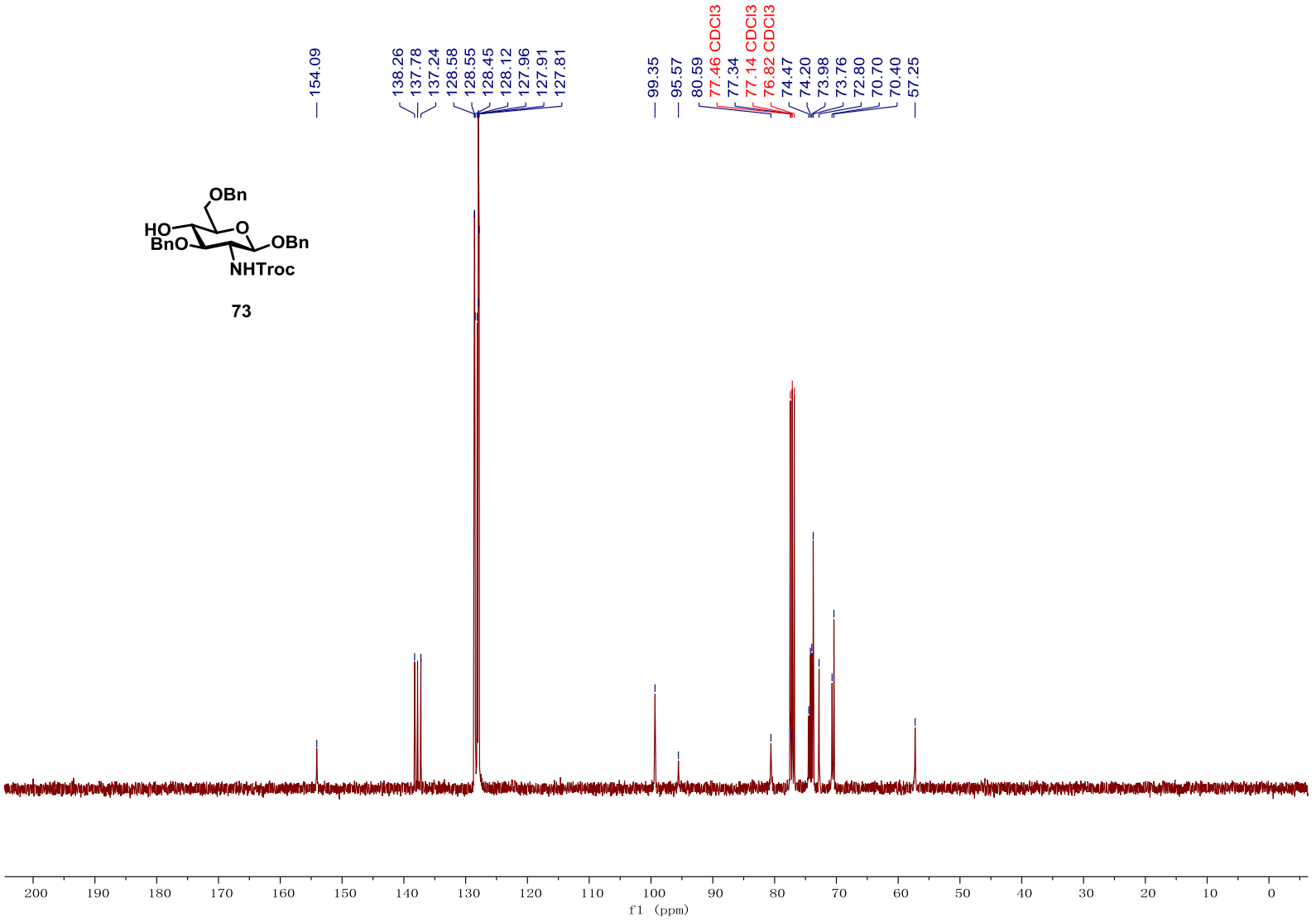
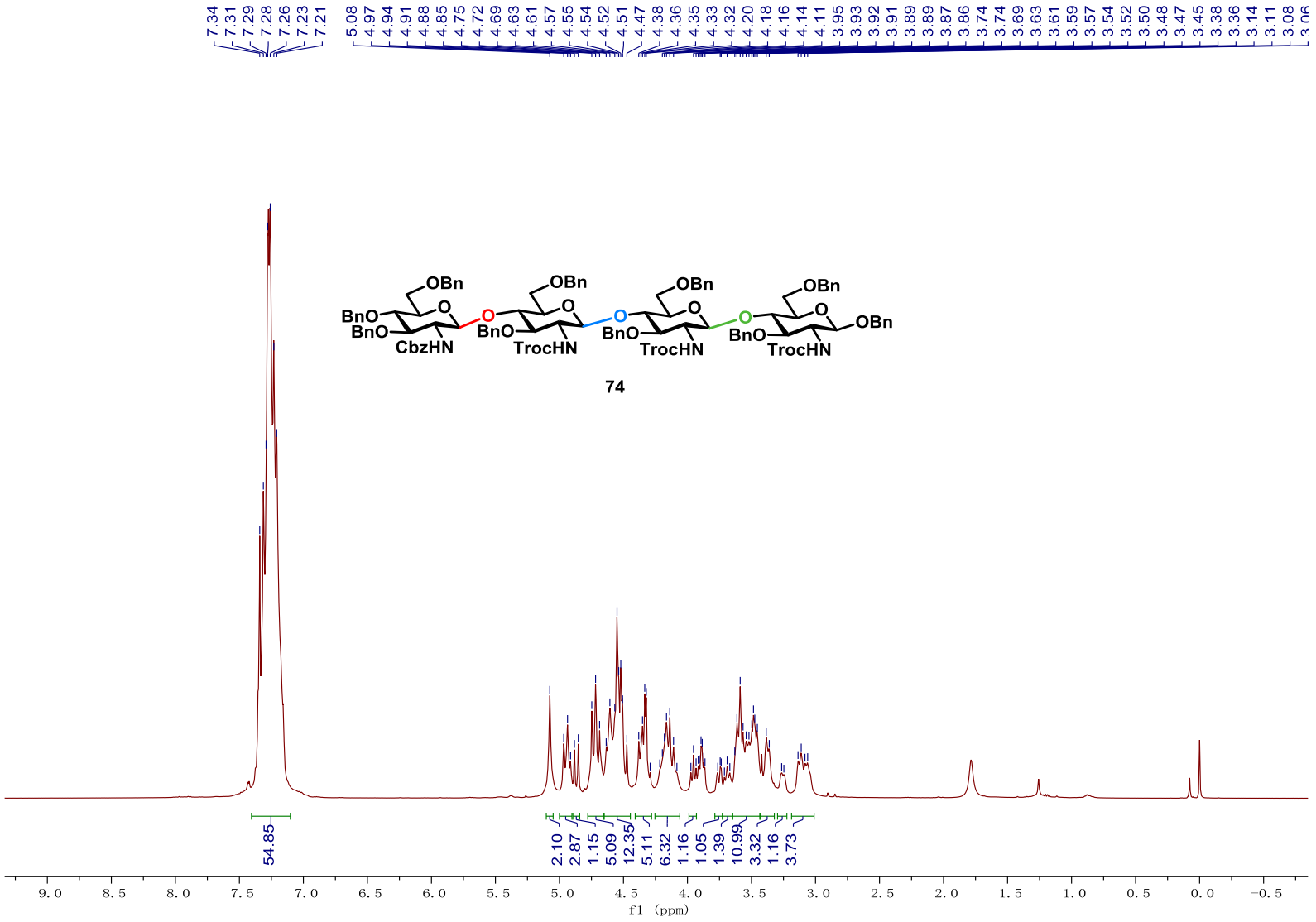
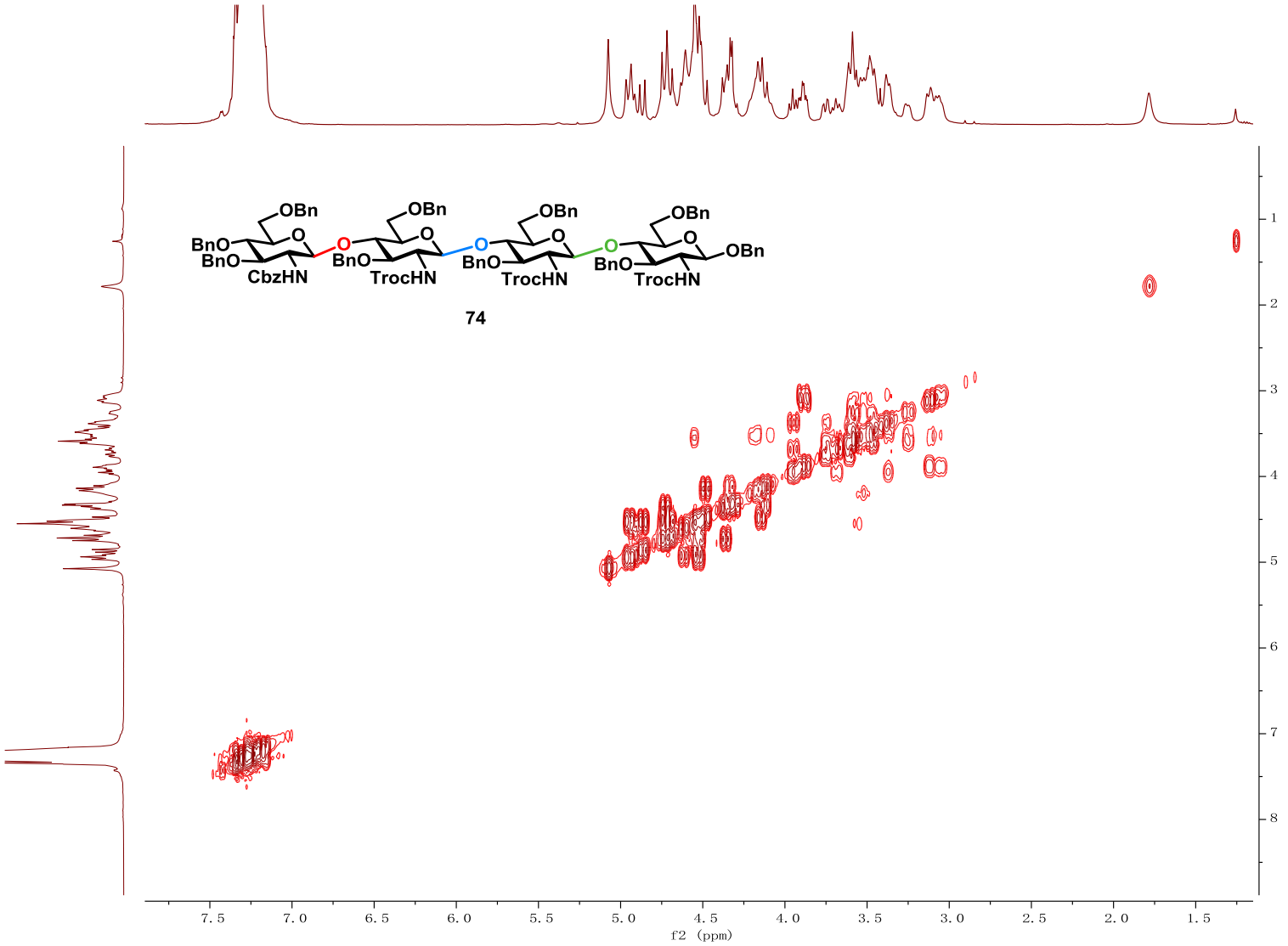
136.83
134.33
131.64
130.43
129.52
127.75
127.73
127.12
127.05
126.81
126.69
123.68
99.18
94.60
91.76
78.65
76.79
76.47
76.15
74.94
73.93
73.27
73.04
71.83
71.27
69.05
52.77
8.64
8.56
0.00
OBn
HO
O
BnO
TrocHN
OABz
71
f1 (ppm)

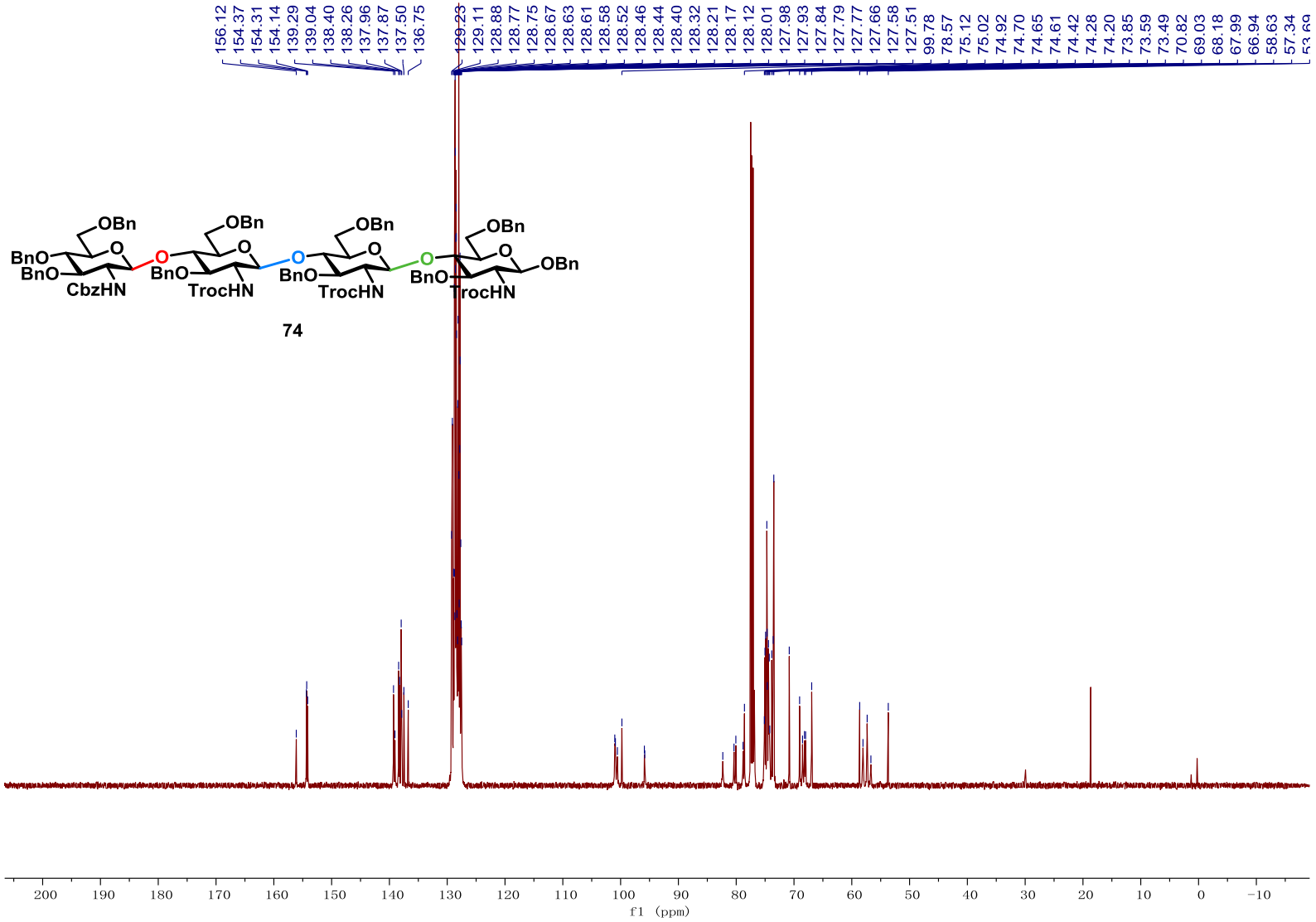

7.33
7.31
7.30
7.28
5.17
5.15
4.86
4.83
4.74
4.73
4.66
4.62
4.59
4.56
4.53
3.75
3.74
3.69
3.67
3.46
3.44
2.93
OBn
HO
O
OBn
BnO
NHTroc
73
14.81
1.00
1.06
2.82
1.61
4.03
2.50
1.90
1.92
0.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OBn
HO
O
BnO
OBn
NHTroc
73
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


154.09
138.26
137.78
137.24
128.58
128.55
128.45
128.12
127.96
127.91
127.81
99.35
95.57
80.59
77.46 CDCl3
77.34
77.14 CDCl3
76.82 CDCl3
74.47
74.20
73.98
73.76
72.80
70.70
70.40
57.25
OBn
HO
O
BnO
OBn
NHTroc
73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.34 7.31 7.29 7.28 7.26 7.23 7.21
5.08 4.97 4.94 4.91 4.88 4.85 4.75 4.72 4.69 4.63 4.61 4.57 4.55 4.54 4.52 4.51 4.47 4.38 4.36 4.35 4.33 4.32 4.20 4.18 4.16 4.14 4.11 3.95 3.93 3.92 3.91 3.89 3.89 3.87 3.86 3.74 3.74 3.69 3.63 3.61 3.59 3.57 3.54 3.52 3.50 3.48 3.47 3.45 3.38 3.36 3.14 3.11 3.08
OBn
BnO
BnO
CbzHN
TrocHN
74
54.85
2.10 2.87 1.15 5.09 12.35 5.11 6.32 1.16 1.05 1.39 10.99 3.32 1.16 3.73
f1 (ppm)


OBn
BnO
BnO
CbzHN
TrocHN
TrocHN
TrocHN
74
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
f2 (ppm)
1
2
3
4
5
6
7
8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154.14
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139.04
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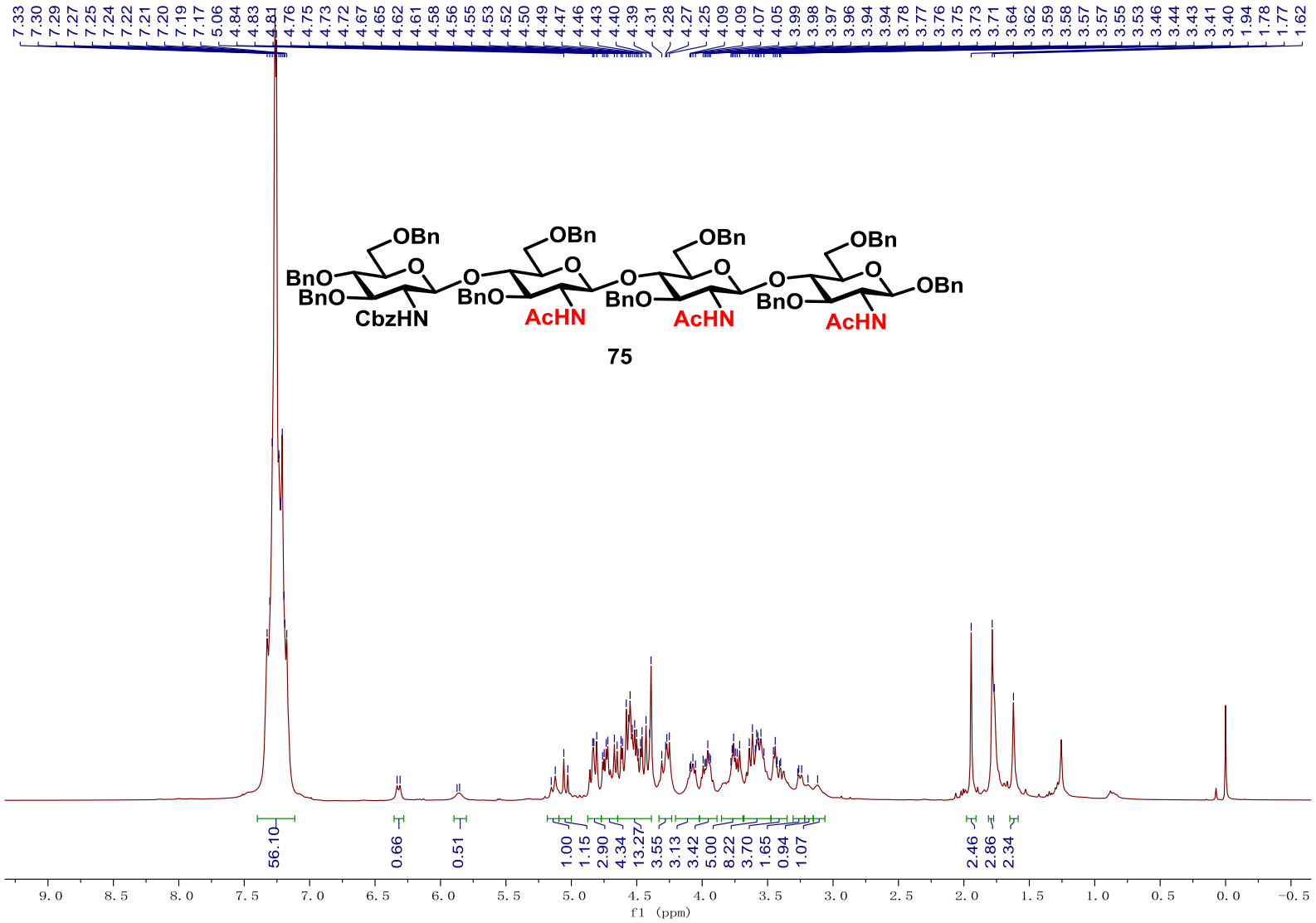
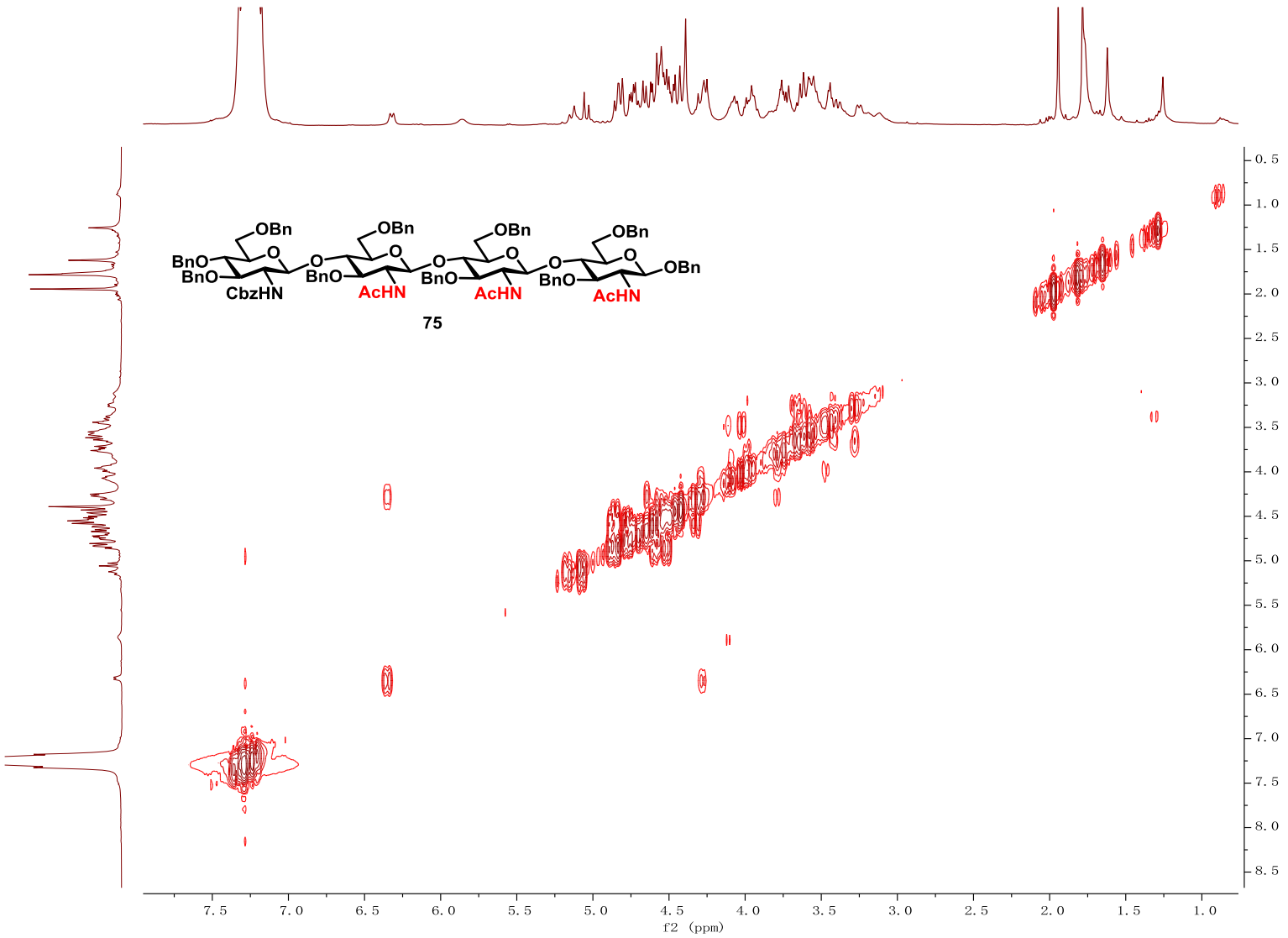
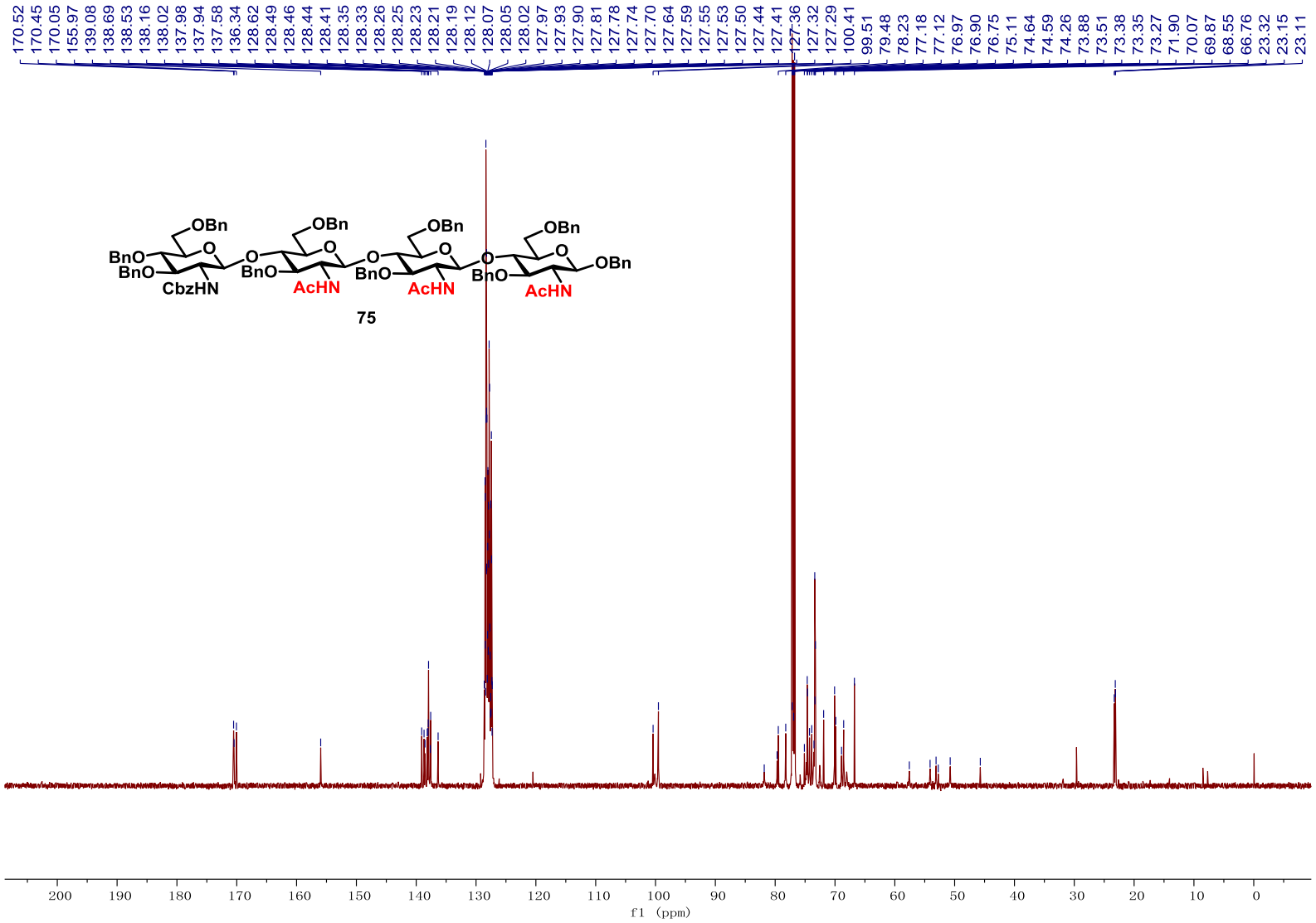
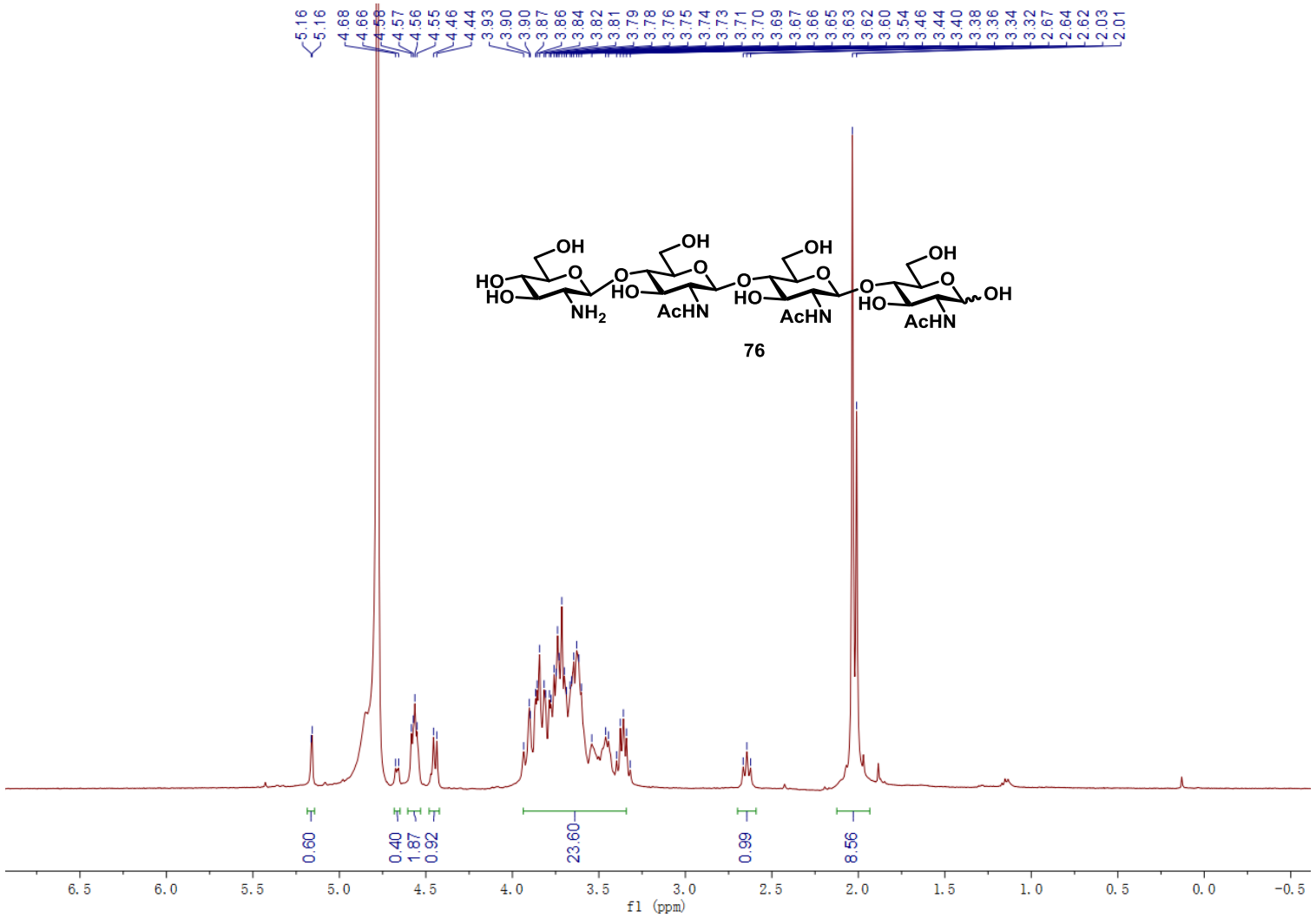
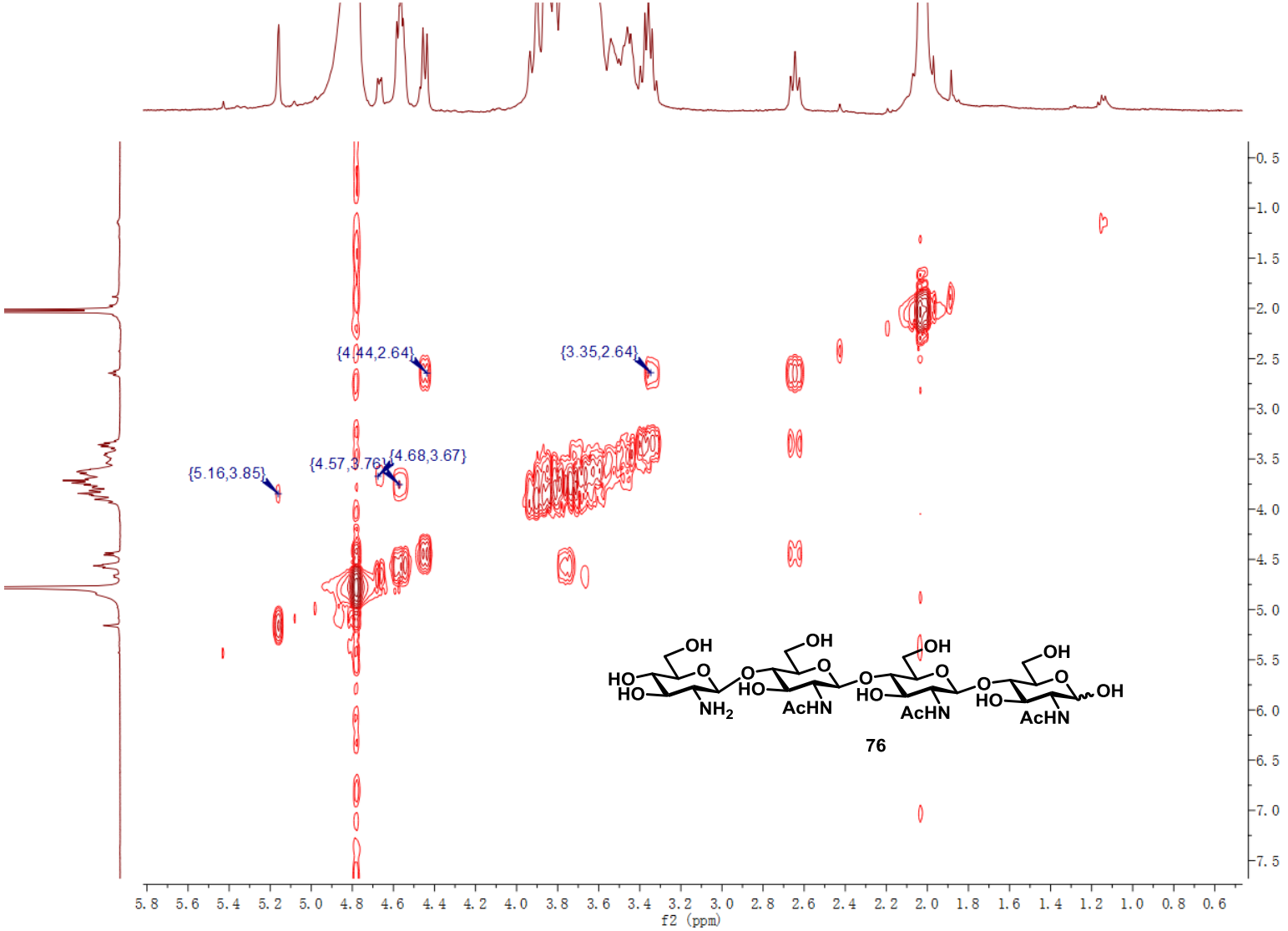
138.26
137.96
137.87
137.50
136.75
129.23
129.11
128.88
128.77
128.75
128.67
128.63
128.61
128.58
128.52
128.46
128.44
128.40
128.32
128.21
128.17
128.12
128.01
127.98
127.93
127.84
127.79
127.77
127.66
127.58
127.51
99.78
78.57
75.12
75.02
74.92
74.70
74.65
74.61
74.42
74.28
74.20
73.85
73.59
73.49
70.82
69.03
68.18
67.99
66.94
58.63
57.34
OBn
BnO
CbzHN
TrocHN
74
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.33 7.30 7.29 7.27 7.25 7.24 7.22 7.21 7.20 7.19 7.17 5.06 4.84 4.83 4.81 4.76 4.75 4.73 4.72 4.67 4.65 4.62 4.61 4.58 4.56 4.55 4.53 4.52 4.50 4.49 4.47 4.46 4.43 4.40 4.39 4.31 4.28 4.27 4.25 4.09 4.09 4.07 4.05 3.99 3.98 3.97 3.96 3.94 3.94 3.78 3.77 3.76 3.75 3.73 3.71 3.64 3.62 3.59 3.58 3.57 3.57 3.55 3.53 3.46 3.44 3.43 3.41 3.40 1.94 1.78 1.77 1.62
OBn
BnO
BnO
CbzHN
AcHN
AcHN
AcHN
75
56.10
0.66
0.51
1.00
1.15
2.90
4.34
13.27
3.55
3.13
3.42
5.00
8.22
3.70
1.65
0.94
1.07
2.46
2.86
2.34
f1 (ppm)

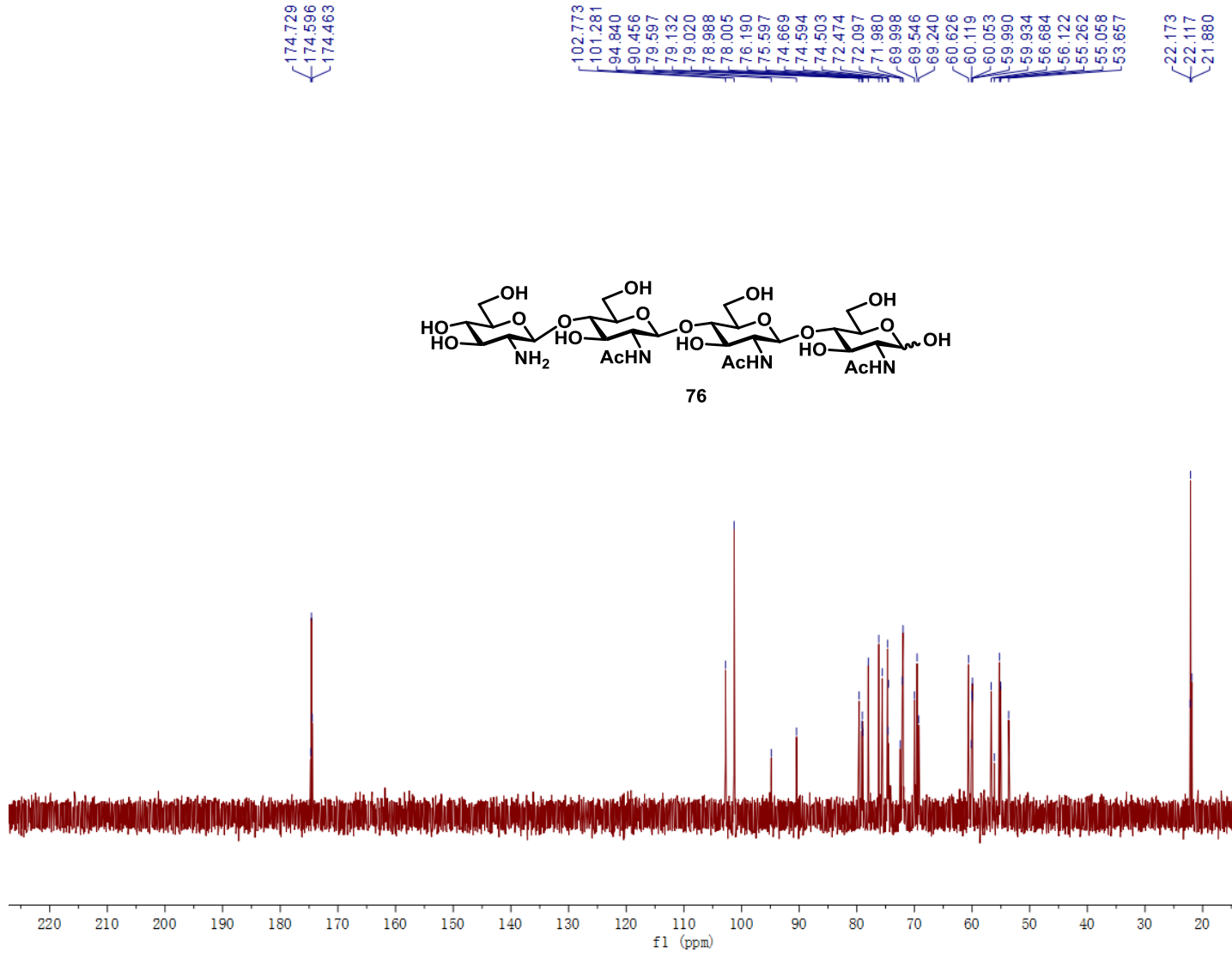

OBn
BnO
BnO
CbzHN
AcHN
AcHN
AcHN
75
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)


170.52
170.45
170.05
155.97
139.08
138.69
138.53
138.16
138.02
137.98
137.94
137.58
136.34
128.62
128.49
128.46
128.44
128.41
128.35
128.33
128.26
128.25
128.23
128.21
128.19
128.12
128.07
128.05
128.02
127.97
127.93
127.90
127.81
127.78
127.74
127.70
127.64
127.59
127.55
127.53
127.50
127.44
127.41
127.36
127.32
127.29
100.41
99.51
79.48
78.23
77.18
77.12
76.97
76.90
76.75
75.11
74.64
74.59
74.26
73.88
73.51
73.38
73.35
73.27
71.90
70.07
69.87
68.55
66.76
23.32
23.15
23.11
OBn
BnO
BnO
CbzHN
AcHN
AcHN
AcHN
75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

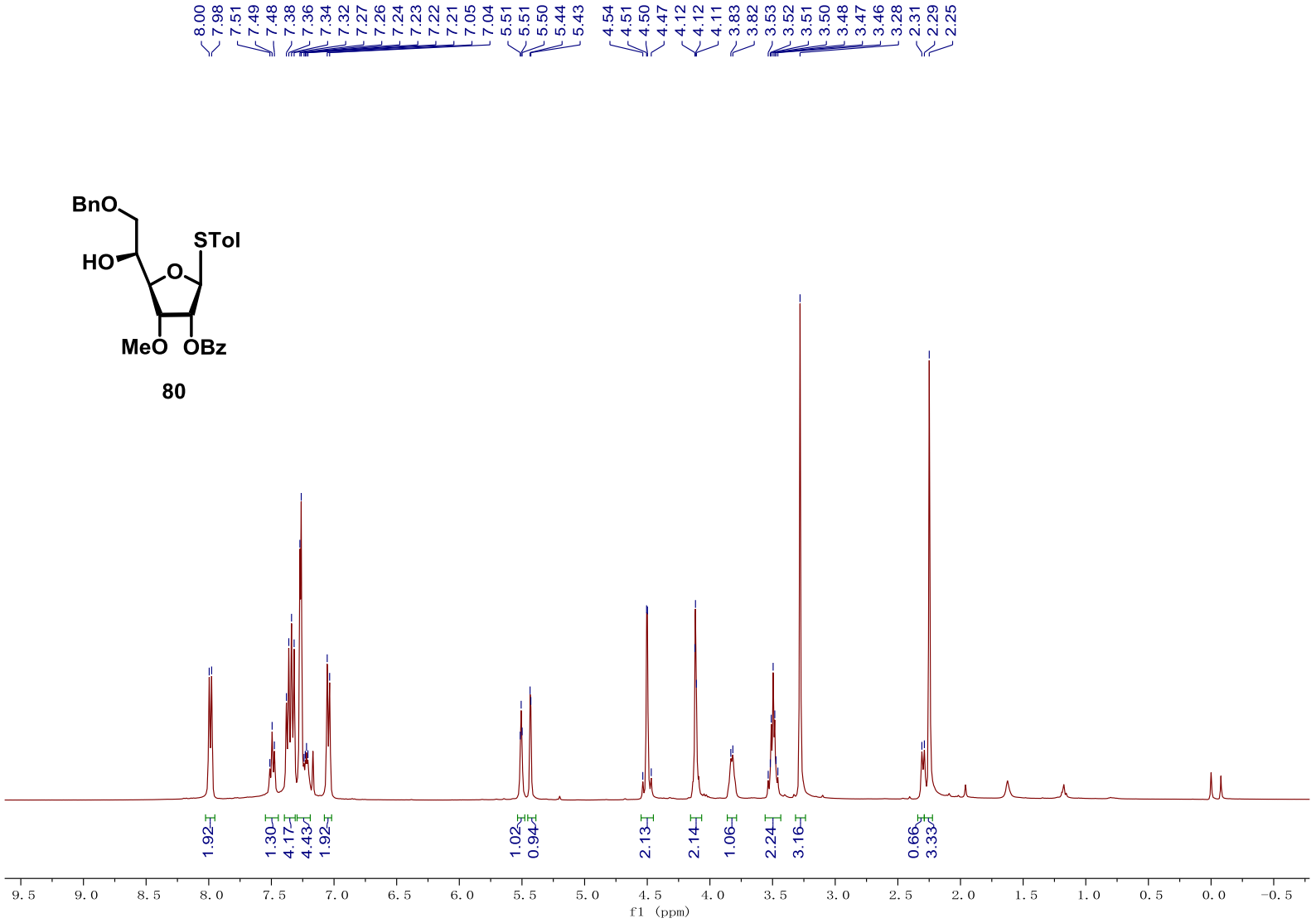

5.16
5.16
4.68
4.66
4.58
4.57
4.56
4.55
4.46
4.44
3.93
3.90
3.90
3.87
3.86
3.84
3.82
3.81
3.79
3.78
3.76
3.75
3.74
3.73
3.71
3.70
3.69
3.67
3.66
3.65
3.63
3.62
3.60
3.54
3.46
3.44
3.40
3.38
3.36
3.34
3.32
2.67
2.64
2.62
2.03
2.01
OH
HO
HO
O
NH2
AcHN
76
0.60
0.40
1.87
0.92
23.60
0.99
8.56
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

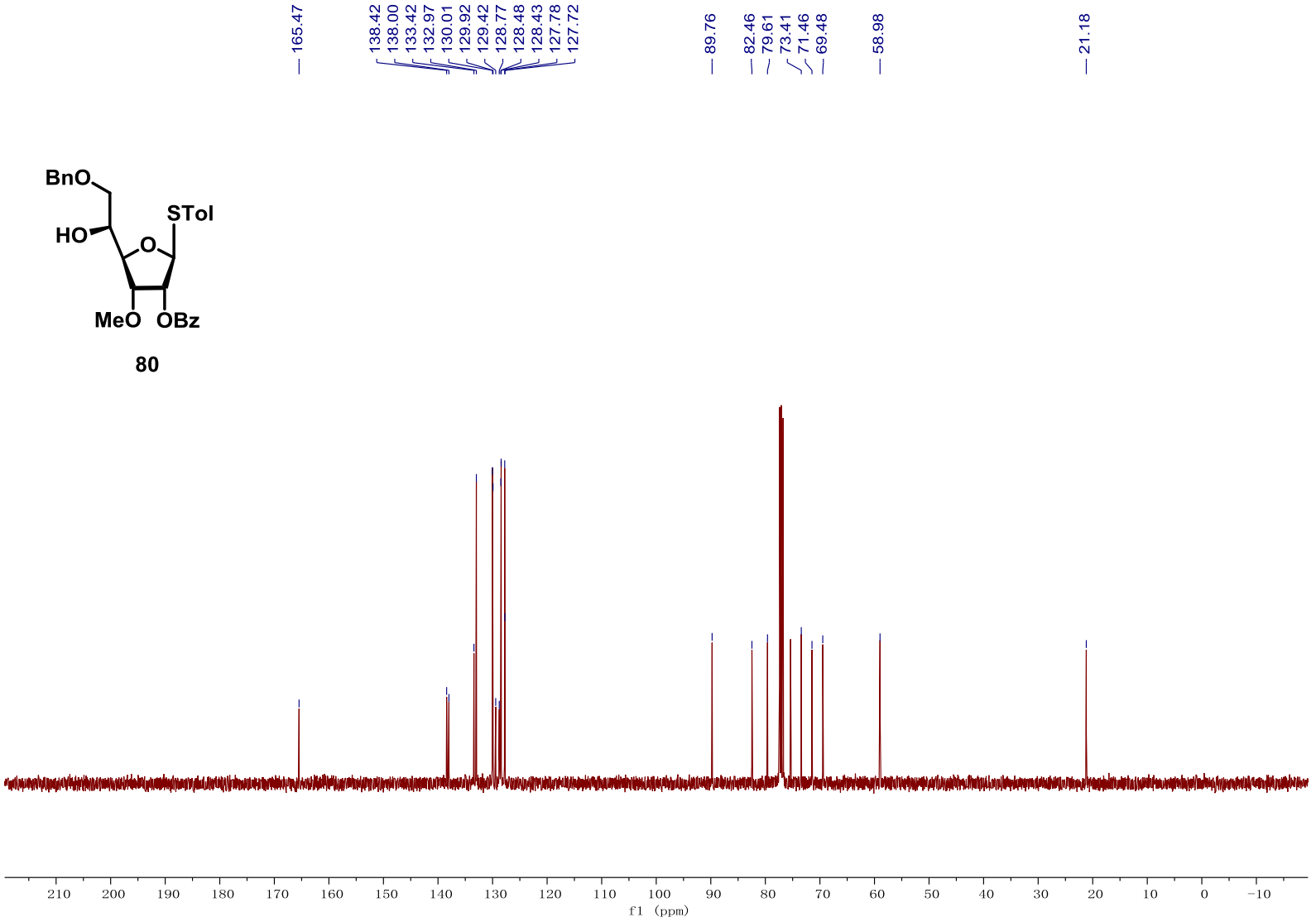


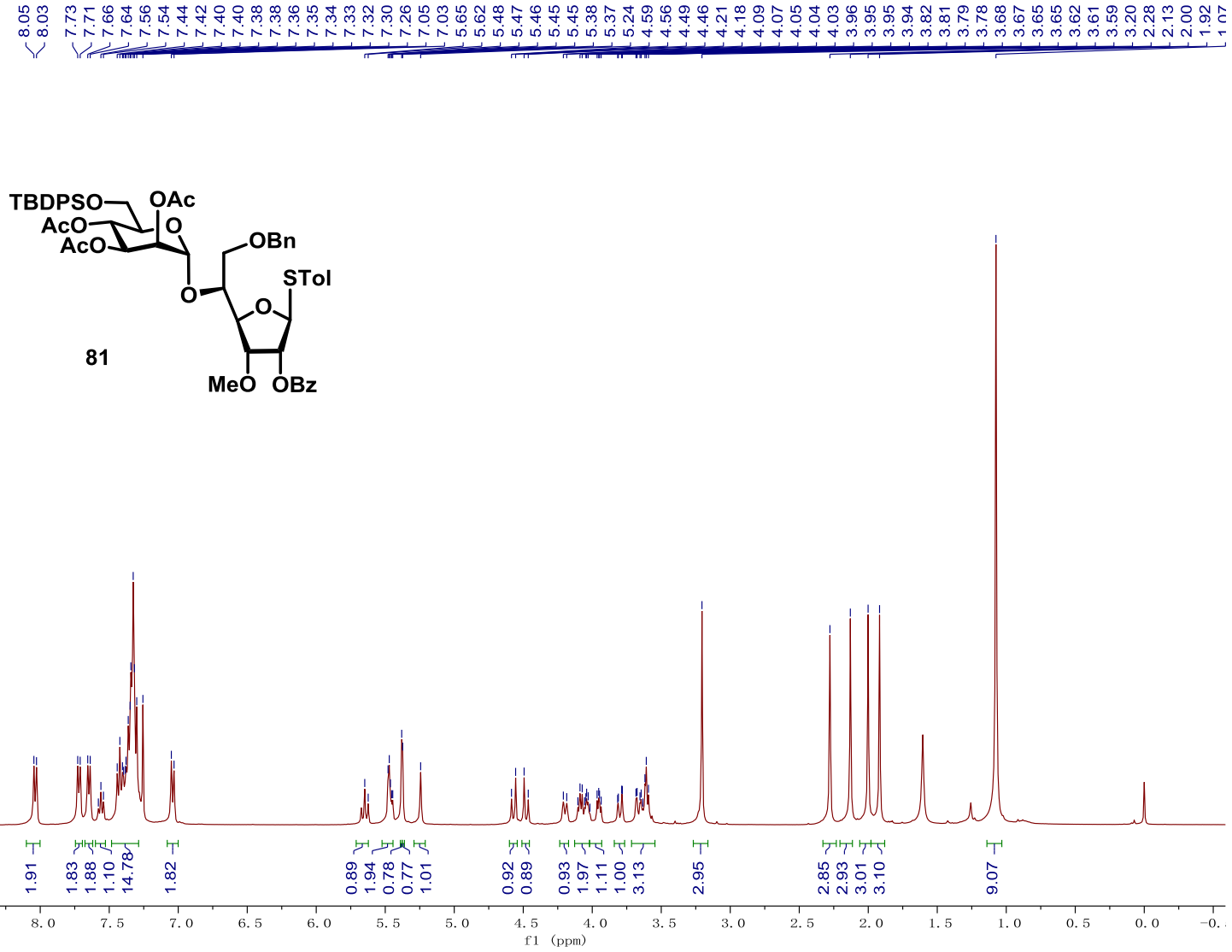
76

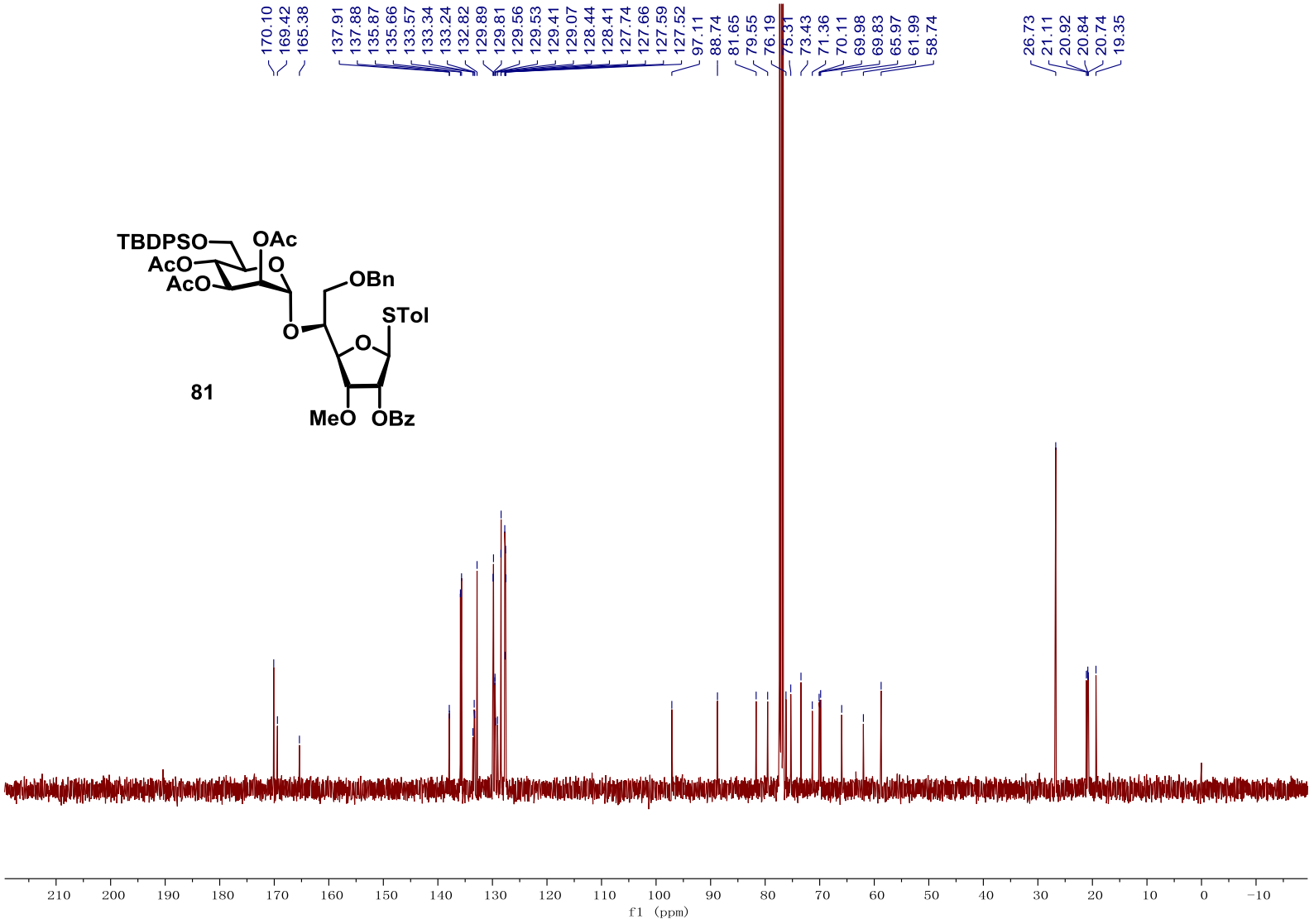

174.729
174.596
174.463
102.773
101.281
94.840
90.456
79.597
79.132
79.020
78.988
78.005
76.190
75.597
74.669
74.594
74.503
72.474
72.097
71.980
69.998
69.546
69.240
60.626
60.119
60.053
59.990
59.934
56.684
56.122
55.262
55.058
53.657
22.173
22.117
21.880
OH
HO
HO
NH2
AcHN
AcHN
AcHN
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

76


8.00
7.98
7.51
7.49
7.48
7.38
7.36
7.34
7.32
7.27
7.26
7.24
7.23
7.22
7.21
7.05
7.04
5.51
5.51
5.50
5.44
5.43
4.54
4.51
4.50
4.47
4.12
4.12
4.11
3.83
3.82
3.53
3.52
3.51
3.50
3.48
3.47
3.46
3.28
2.31
2.29
2.25
BnO
HO
STol
O
MeO
OBz
80
1.92
1.30
4.17
4.43
1.92
1.02
0.94
2.13
2.14
1.06
2.24
3.16
0.66
3.33
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
−0.5
f1 (ppm)


165.47
138.42
138.00
133.42
132.97
130.01
129.92
129.42
128.77
128.48
128.43
127.78
127.72
89.76
82.46
79.61
73.41
71.46
69.48
58.98
21.18
BnO
HO
STol
O
MeO
OBz
80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.05 8.03 7.73 7.71 7.66 7.64 7.56 7.54 7.44 7.42 7.40 7.40 7.38 7.38 7.36 7.35 7.34 7.33 7.32 7.30 7.26 7.05 7.03 5.65 5.62 5.48 5.47 5.46 5.45 5.45 5.38 5.37 5.24 4.59 4.56 4.49 4.46 4.21 4.18 4.09 4.07 4.05 4.04 4.03 3.96 3.95 3.95 3.94 3.82 3.81 3.79 3.78 3.68 3.67 3.65 3.65 3.62 3.61 3.59 3.20 2.28 2.13 2.00 1.92
TBDPSO
OAc
AcO
AcO
O
OBn
STol
O
O
MeO
OBz
81
1.91 1.83 1.88 1.10 14.78 1.82 0.89 1.94 0.78 0.77 1.01 0.92 0.89 0.93 1.97 1.11 1.00 3.13 2.95 2.85 2.93 3.01 3.10 9.07
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)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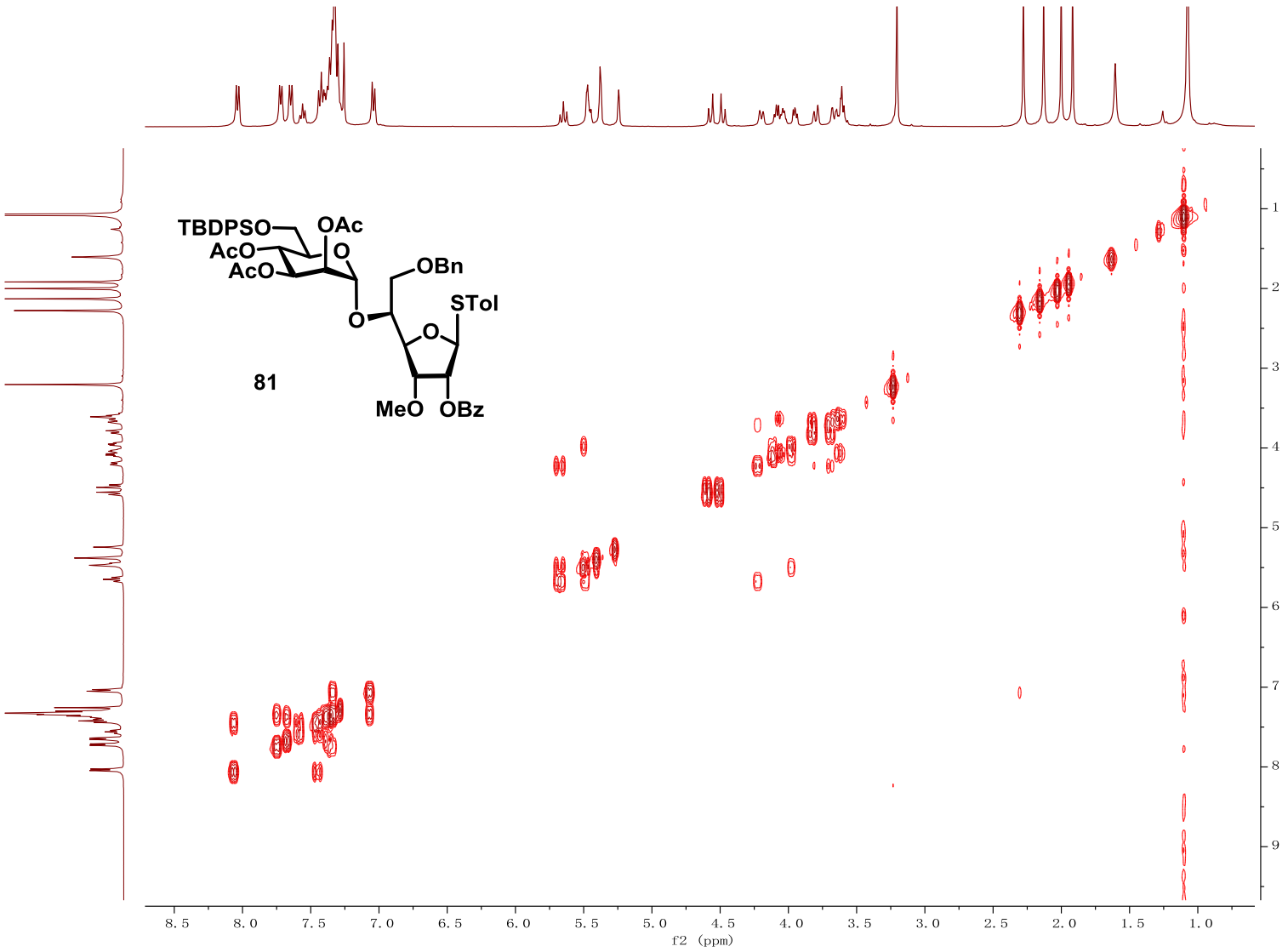
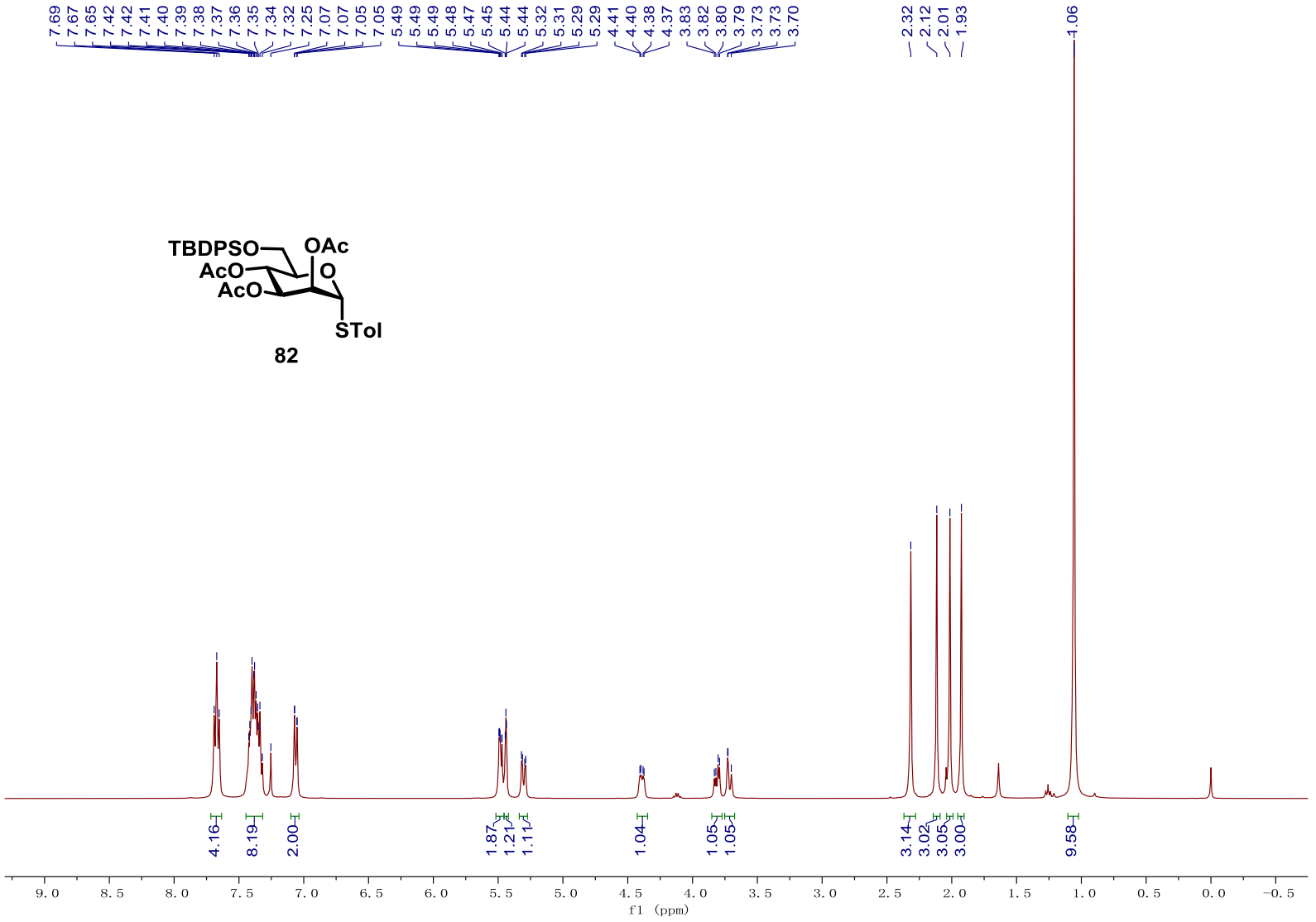
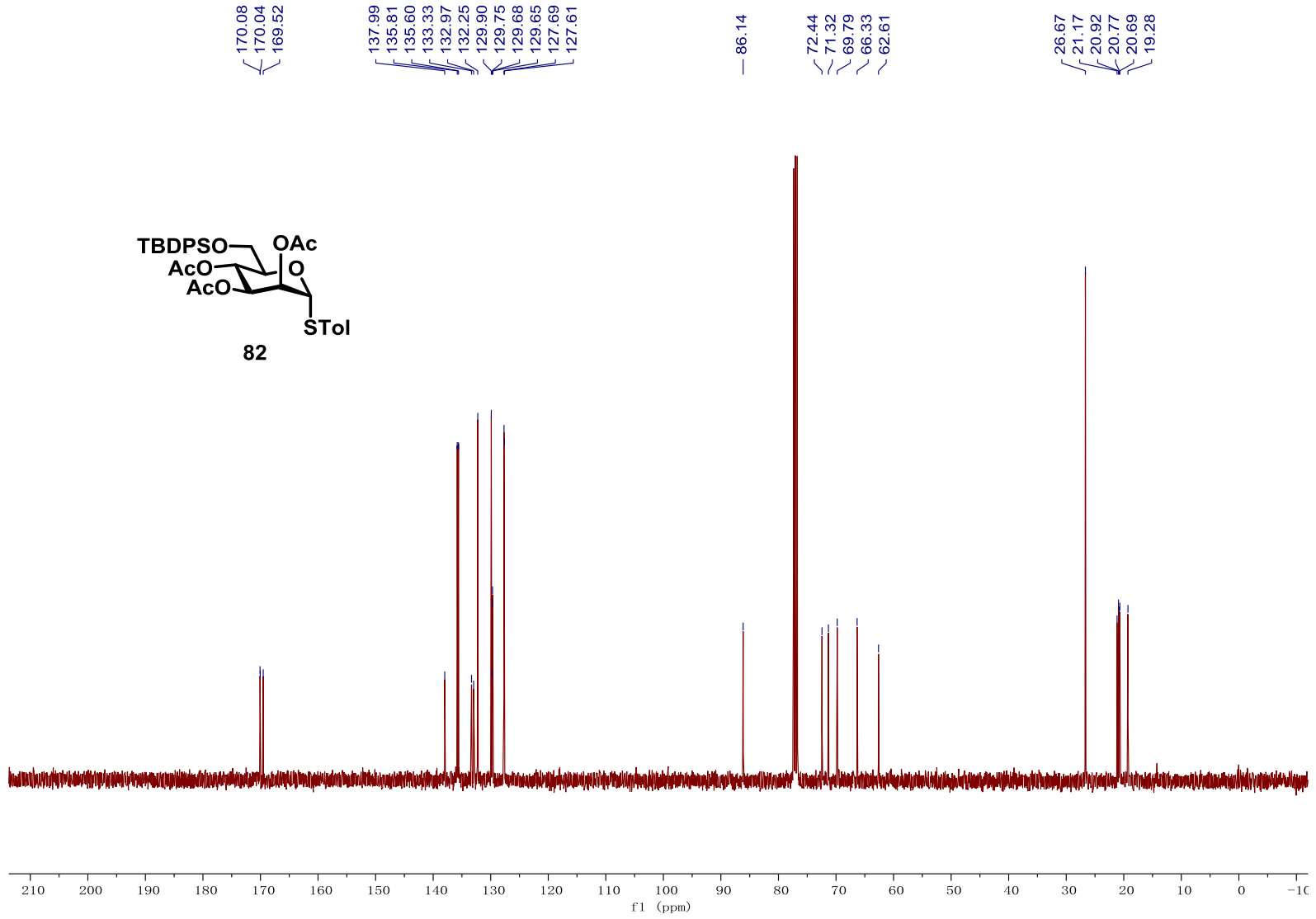
169.42
165.38
137.91
137.88
135.87
135.66
133.57
133.34
133.24
132.82
129.89
129.81
129.56
129.53
129.41
129.07
128.44
128.41
127.74
127.66
127.59
127.52
97.11
88.74
81.65
79.55
76.19
75.31
73.43
71.36
70.11
69.98
69.83
65.97
61.99
58.74
26.73
21.11
20.92
20.84
20.74
19.35
TBDPSO
OAc
AcO
AcO
O
OBn
O
STol
O
MeO
OBz
81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TBDPSO
OAc
AcO
AcO
O
OBn
STol
O
O
MeO
OBz
81
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


7.69 7.67 7.65 7.42 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.32 7.25 7.07 7.07 7.05 7.05 5.49 5.49 5.49 5.48 5.47 5.45 5.44 5.44 5.32 5.31 5.29 5.29 4.41 4.40 4.38 4.37 3.83 3.82 3.80 3.79 3.73 3.73 3.70 2.32 2.12 2.01 1.93 1.06
TBDPSO
OAc
AcO
O
AcO
STol
82
4.16 8.19 2.00 1.87 1.21 1.11 1.04 1.05 1.05 3.14 3.02 3.05 3.00 9.58
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 −0.5
f1 (ppm)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170.04
169.52
137.99
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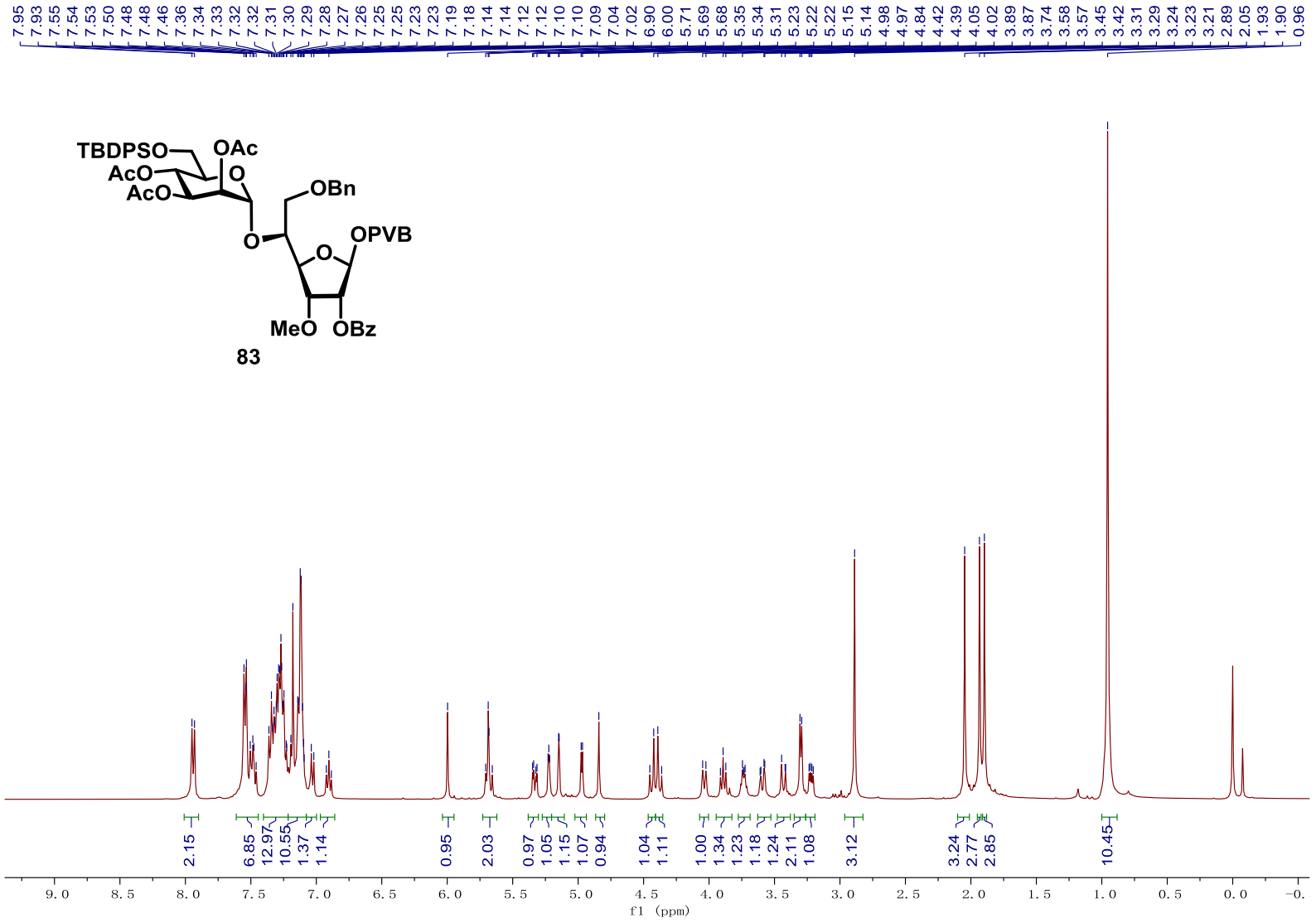
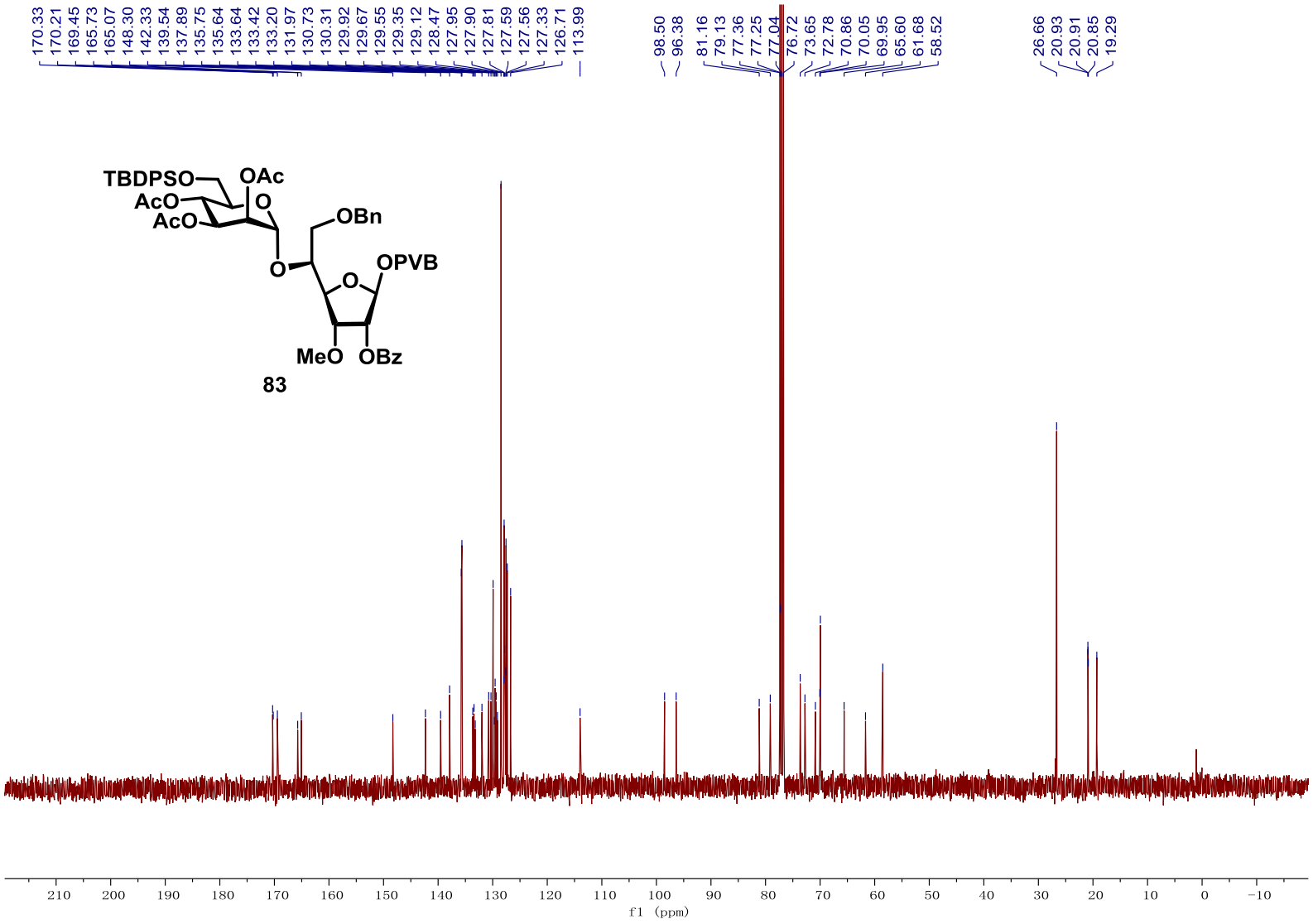
135.60
133.33
132.97
132.25
129.90
129.75
129.68
129.65
127.69
127.61
86.14
72.44
71.32
69.79
66.33
62.61
26.67
21.17
20.92
20.77
20.69
19.28
TBDPSO
OAc
AcO
O
AcO
STol
82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.95 7.93 7.55 7.54 7.53 7.50 7.48 7.48 7.46 7.36 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.25 7.23 7.23 7.19 7.18 7.14 7.14 7.12 7.12 7.10 7.10 7.09 7.04 7.02 6.90 6.00 5.71 5.69 5.68 5.35 5.34 5.31 5.23 5.22 5.22 5.15 5.14 4.98 4.97 4.84 4.42 4.39 4.05 4.02 3.89 3.87 3.74 3.58 3.57 3.45 3.42 3.31 3.29 3.24 3.23 3.21 2.89 2.05 1.93 1.90 0.96
TBDPSO
OAc
AcO
O
AcO
OBn
O
OPVB
O
MeO
OBz
83
2.15 6.85 12.97 10.55 1.37 1.14 0.95 2.03 0.97 1.05 1.15 1.07 0.94 1.04 1.11 1.00 1.34 1.23 1.18 1.24 2.11 1.08 3.12 3.24 2.77 2.85 10.45
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 −0.
f1 (ppm)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170.21
169.45
165.73
165.07
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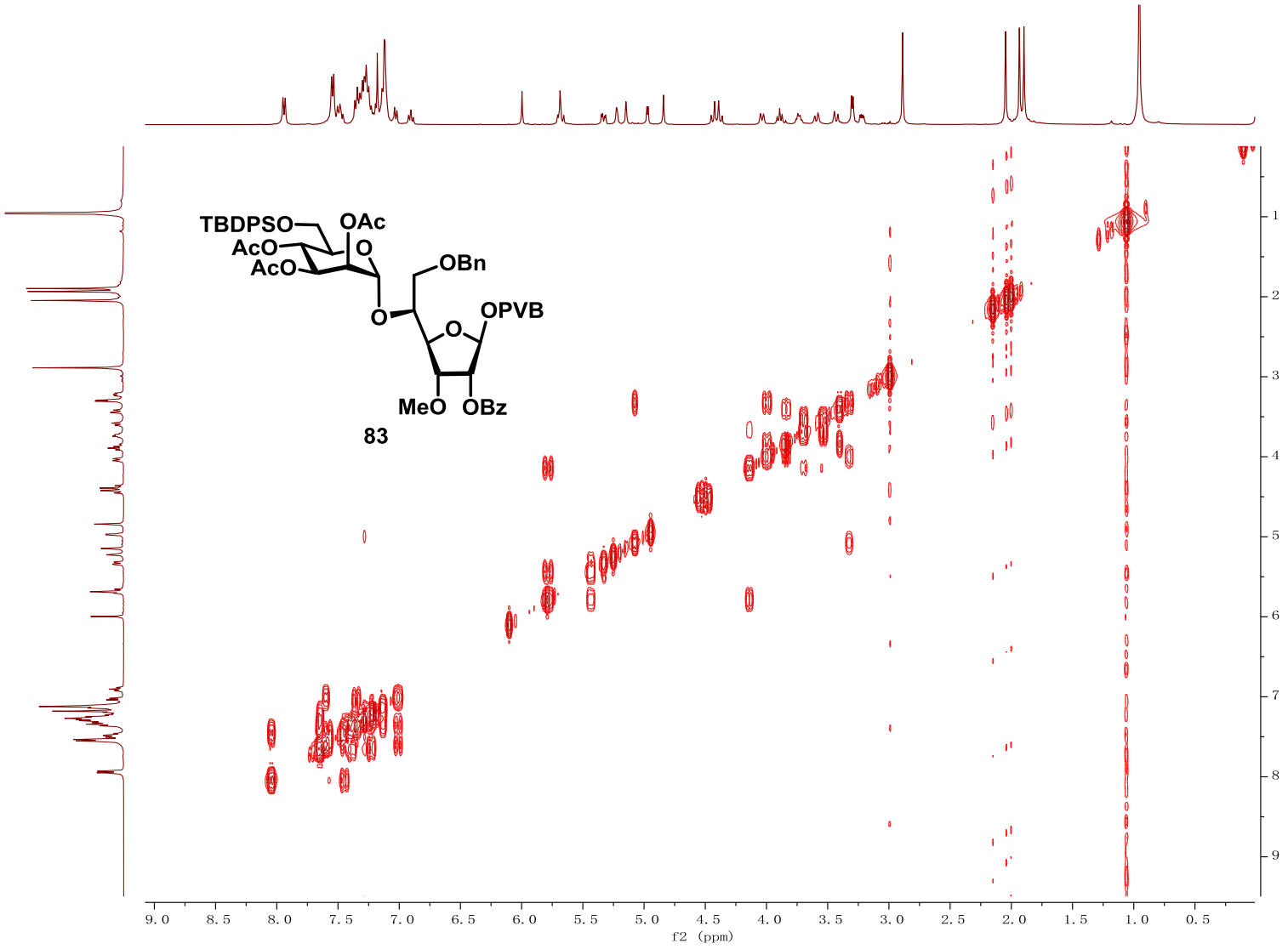
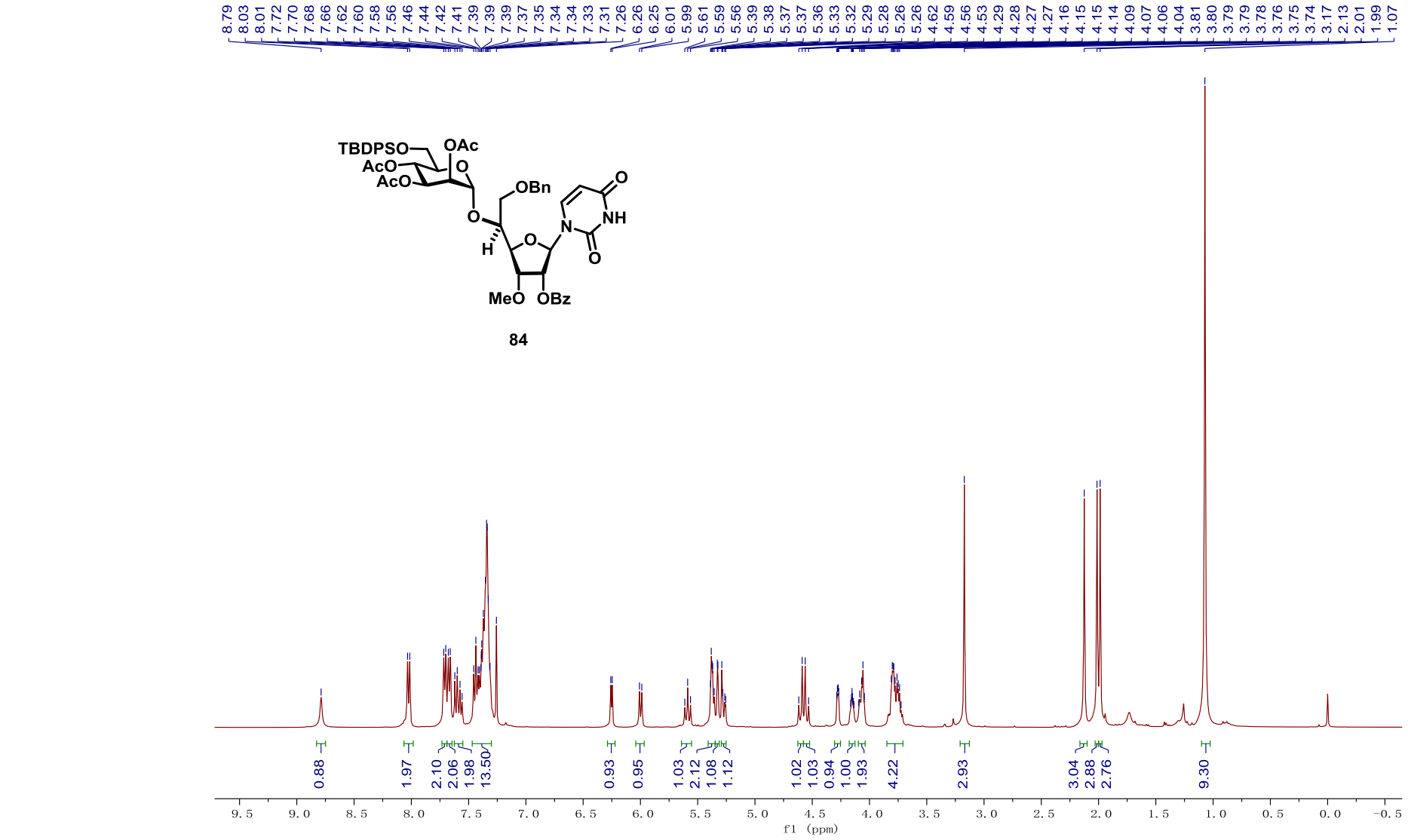
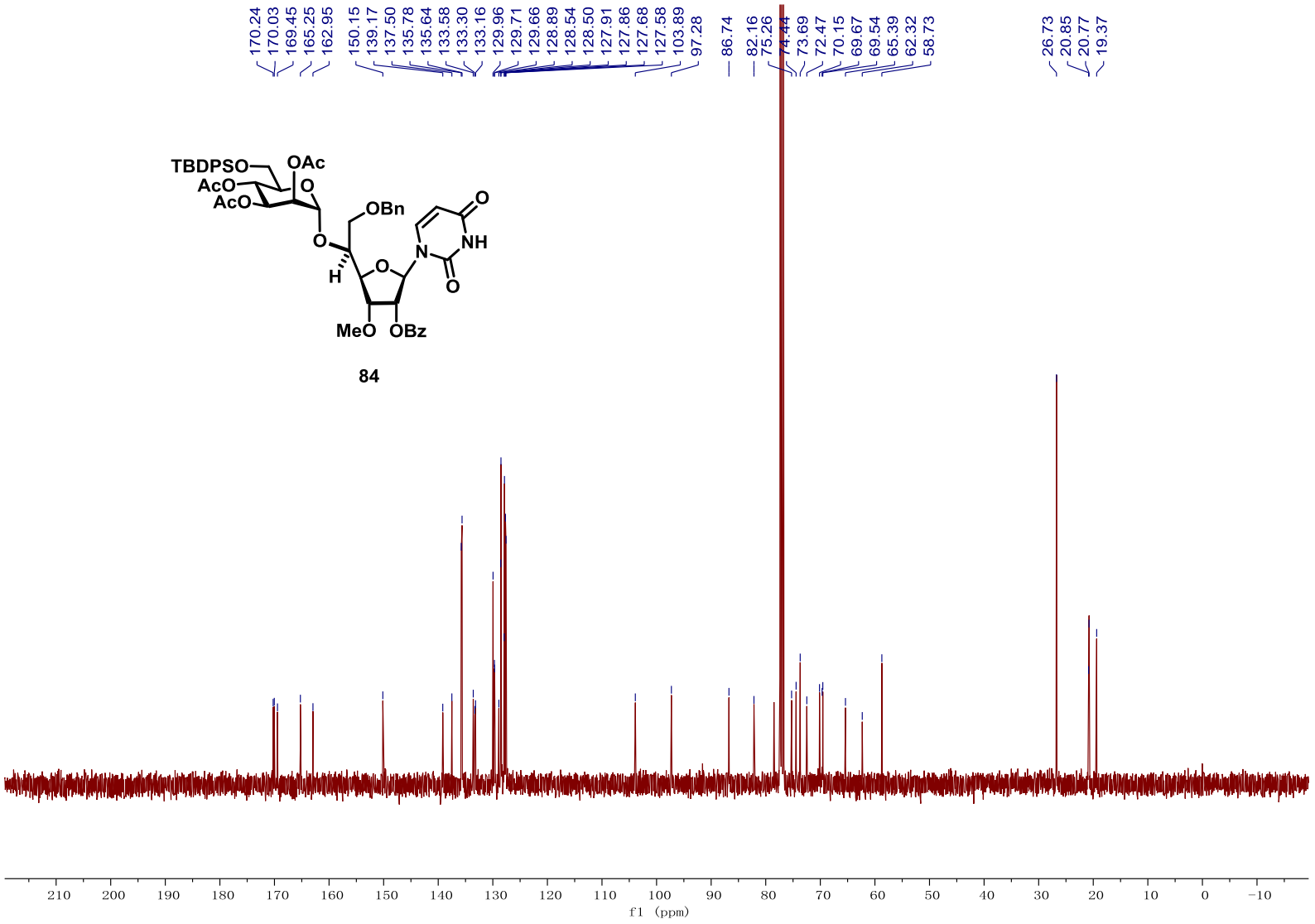
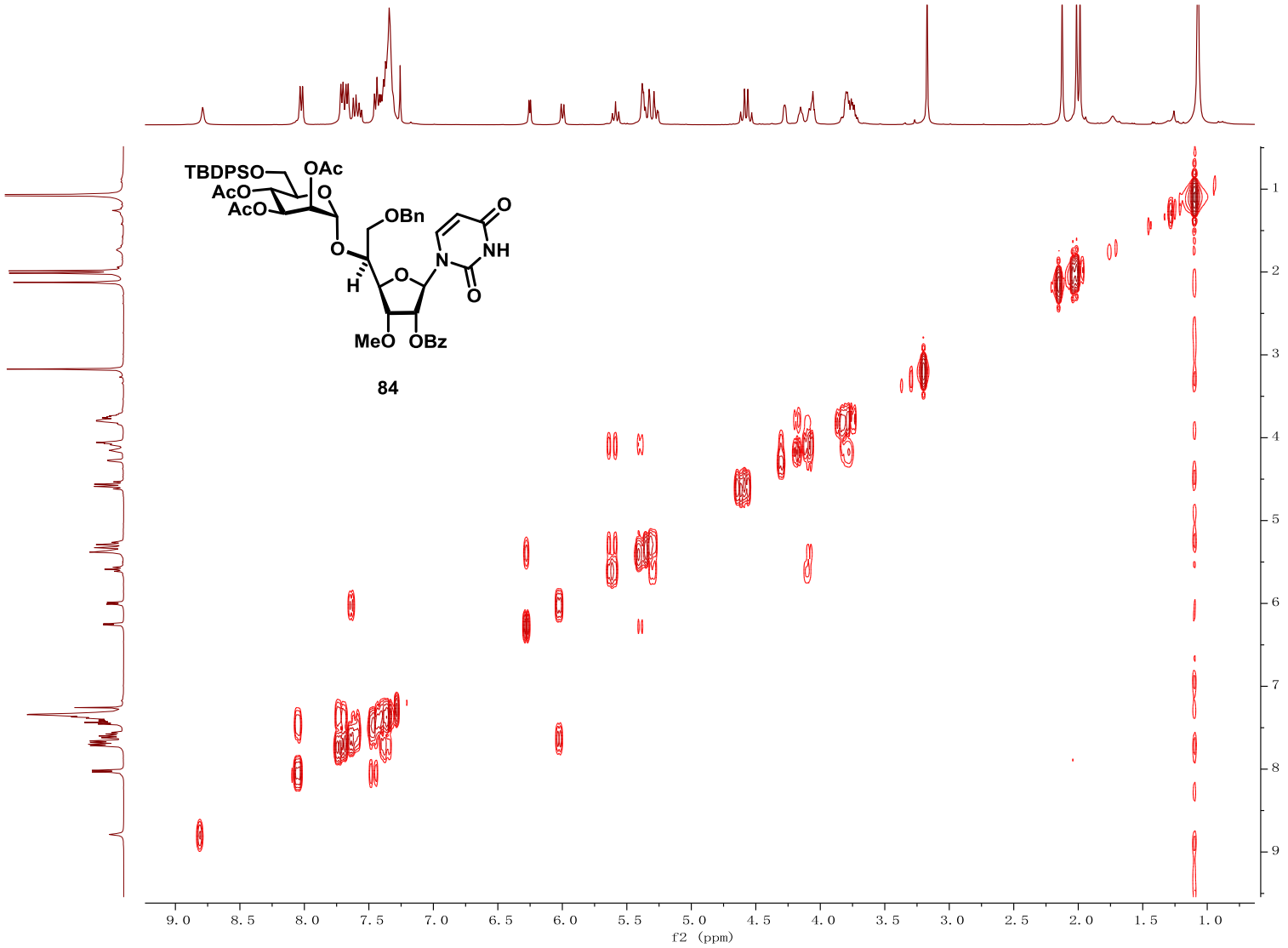
142.33
139.54
137.89
135.75
135.64
133.64
133.42
133.20
131.97
130.73
130.31
129.92
129.67
129.55
129.35
129.12
128.47
127.95
127.90
127.81
127.59
127.56
127.33
126.71
113.99
98.50
96.38
81.16
79.13
77.36
77.25
77.04
76.72
73.65
72.78
70.86
70.05
69.95
65.60
61.68
58.52
26.66
20.93
20.91
20.85
19.29
TBDPSO
OAc
AcO
AcO
O
OBn
O
O
OPVB
MeO
OBz
83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TBDPSO
OAc
AcO
AcO
O
OBn
O
OPVB
O
MeO
OBz
83
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


8.79 8.03 8.01 7.72 7.70 7.68 7.66 7.62 7.60 7.58 7.56 7.46 7.44 7.42 7.41 7.39 7.39 7.39 7.37 7.35 7.34 7.34 7.33 7.31 7.26 6.26 6.25 6.01 5.99 5.61 5.59 5.56 5.39 5.38 5.37 5.37 5.36 5.33 5.32 5.29 5.28 5.26 5.26 4.62 4.59 4.56 4.53 4.29 4.28 4.27 4.27 4.16 4.15 4.15 4.14 4.09 4.07 4.06 4.04 3.81 3.80 3.79 3.79 3.78 3.76 3.75 3.74 3.17 2.13 2.01 1.99 1.07
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
NH
O
O
MeO
OBz
84
0.88 1.97 2.10 2.06 1.98 13.50 0.93 0.95 1.03 2.12 1.08 1.12 1.02 1.03 0.94 1.00 1.93 4.22 2.93 3.04 2.88 2.76 9.30
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 -0.5
f1 (ppm)


170.24
170.03
169.45
165.25
162.95
150.15
139.17
137.50
135.78
135.64
133.58
133.30
133.16
129.96
129.71
129.66
128.89
128.54
128.50
127.91
127.86
127.68
127.58
103.89
97.28
86.74
82.16
75.26
74.44
73.69
72.47
70.15
69.67
69.54
65.39
62.32
58.73
26.73
20.85
20.77
19.37
TBDPSO
OAc
AcO
AcO
O
OBn
O
H
O
N
NH
O
O
MeO
OBz
84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TBDPSO
OAc
AcO
AcO
O
OBn
O
NH
N
O
H
O
O
MeO
OBz
84
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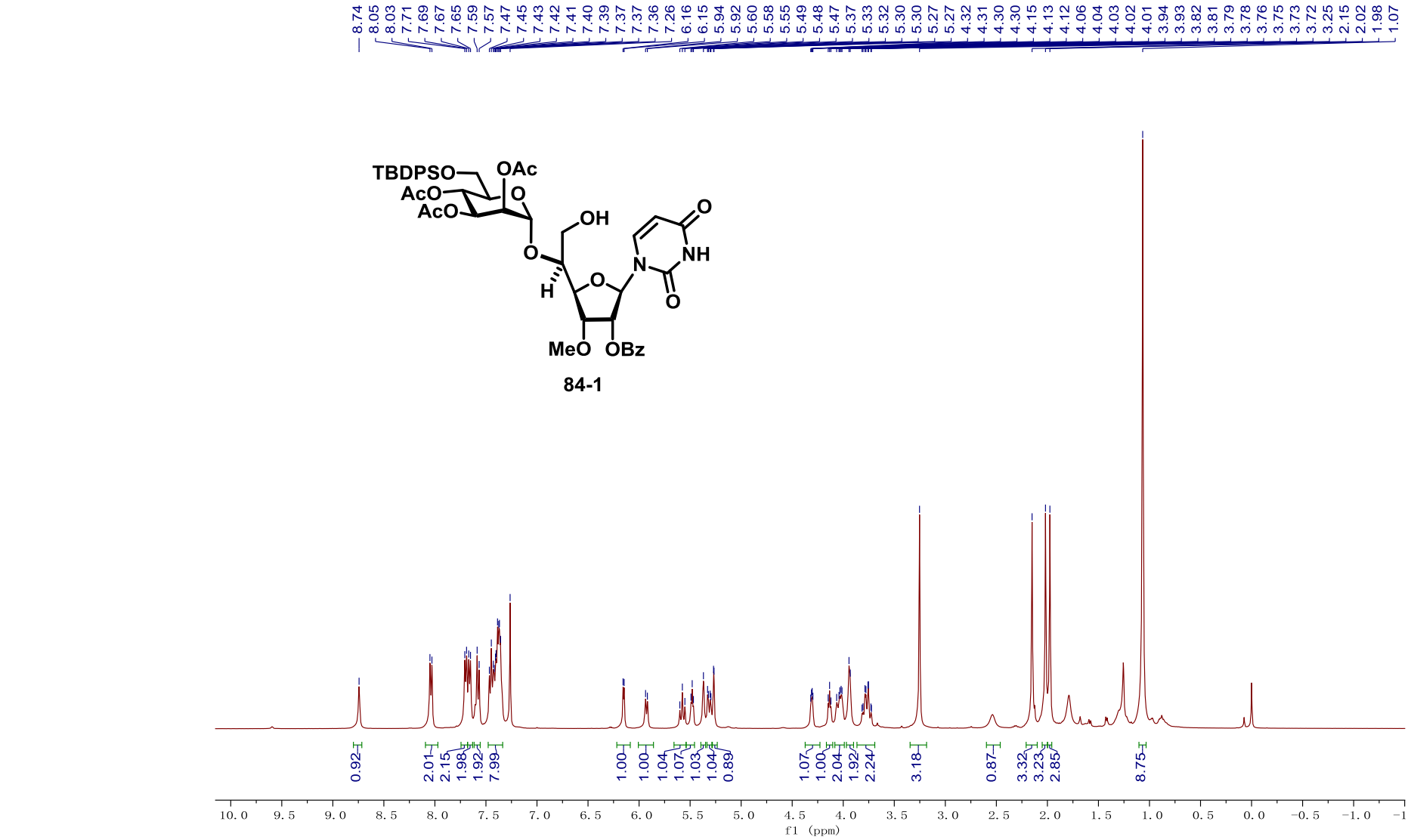
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9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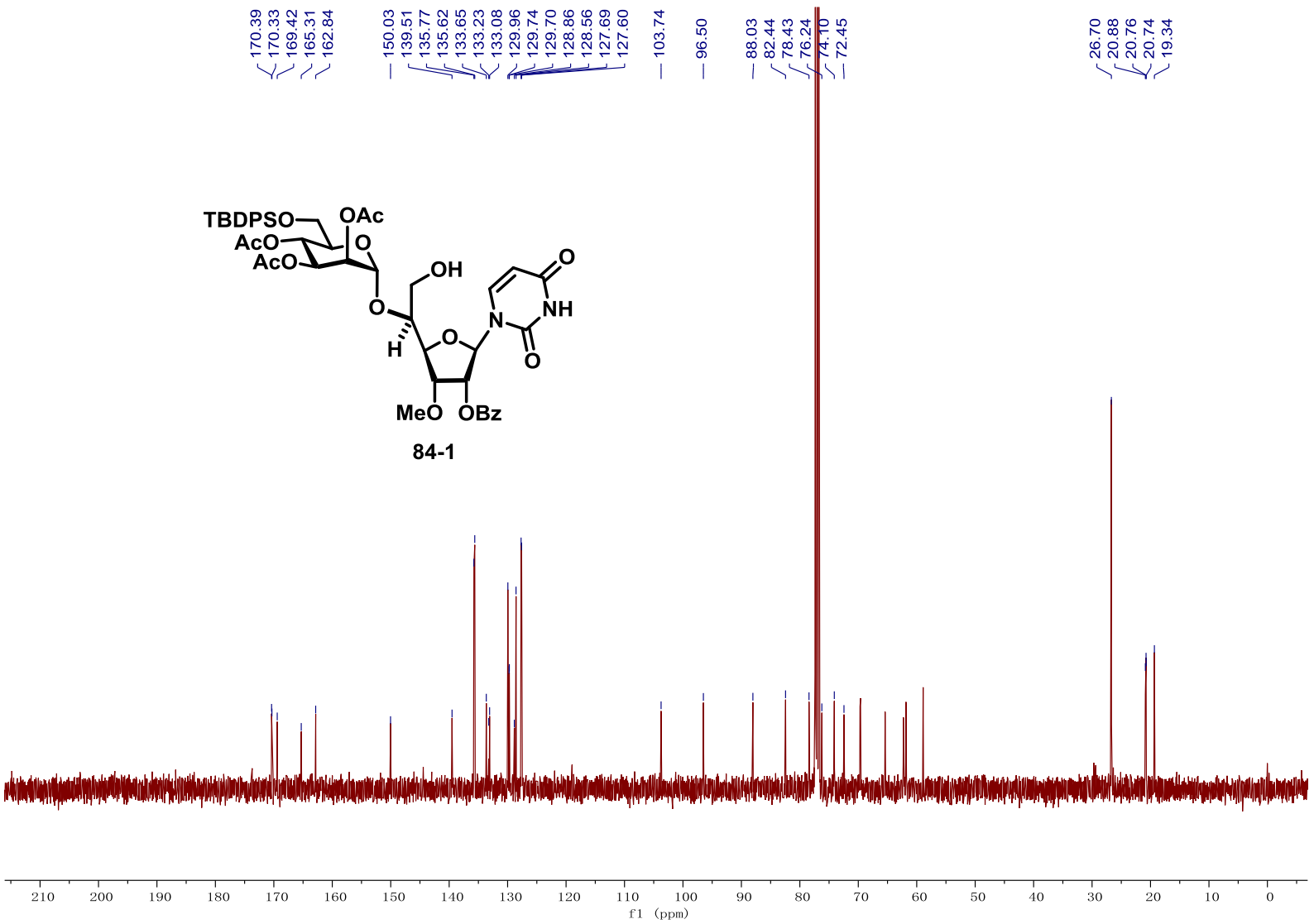
TBDPSO
OAc
AcO
AcO
O
OH
O
H
O
N
NH
O
O
MeO
OBz
84-1
0.92 2.01 2.15 1.98 1.92 7.99 1.00 1.00 1.04 1.07 1.03 1.04 0.89 1.07 1.00 2.04 1.92 2.24 3.18 0.87 3.32 3.23 2.85 8.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1
f1 (ppm)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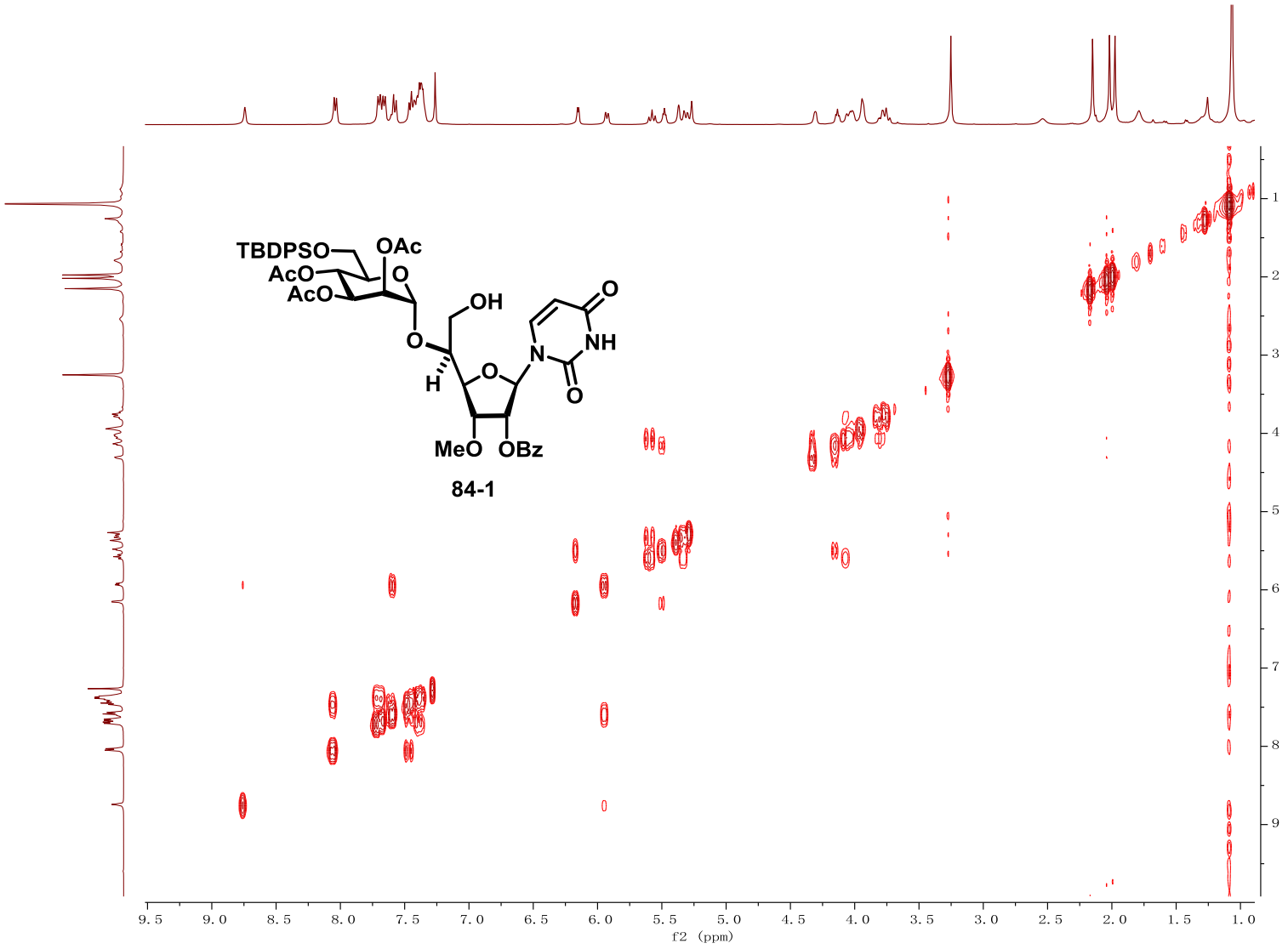
135.77
135.62
133.65
133.23
133.08
129.96
129.74
129.70
128.86
128.56
127.69
127.60
103.74
96.50
88.03
82.44
78.43
76.24
74.10
72.45
26.70
20.88
20.76
20.74
19.34
TBDPSO
OAc
AcO
AcO
O
OH
O
H
O
N
NH
O
O
MeO
OBz
84-1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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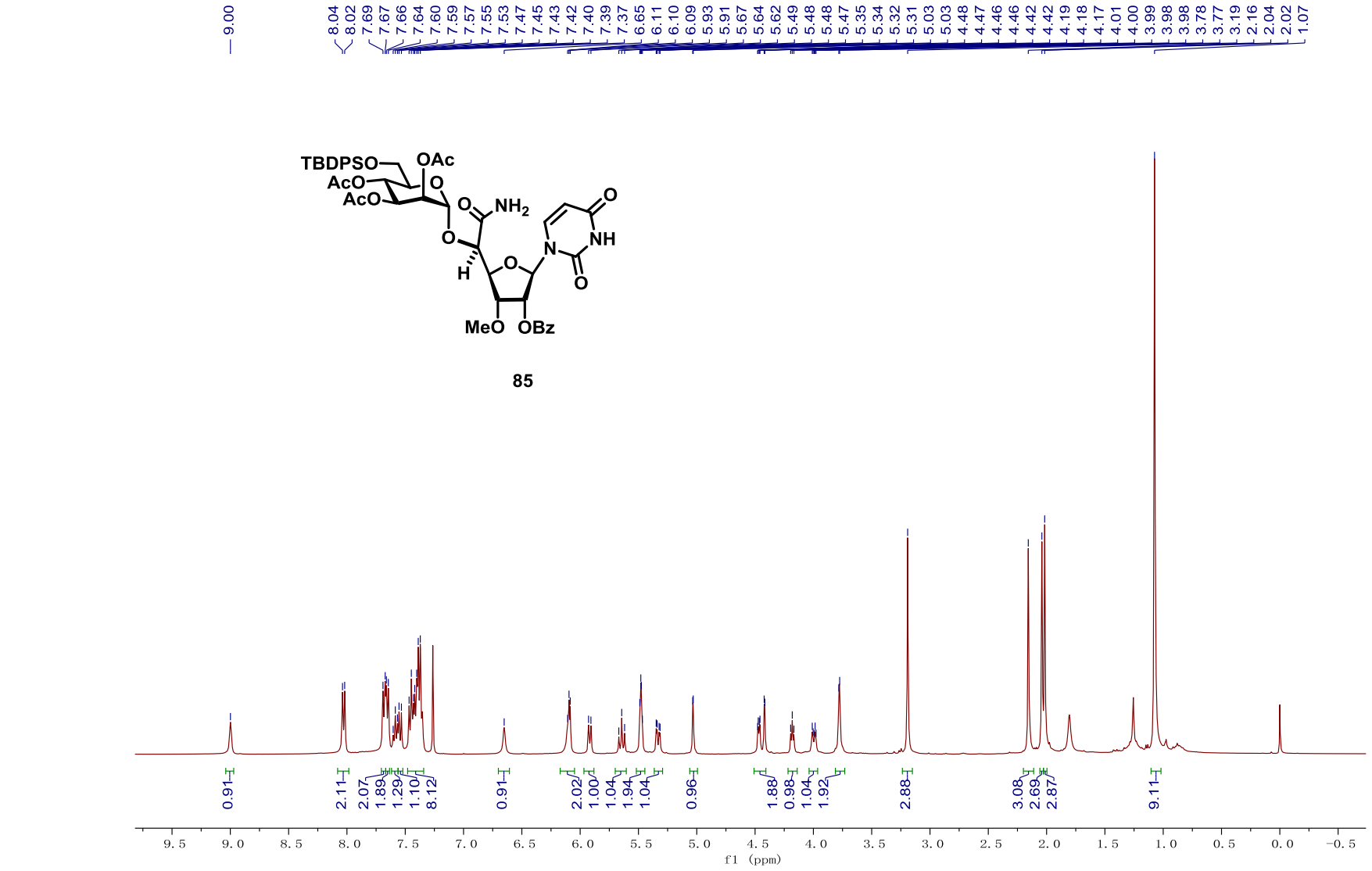
AcO
AcO
OAc
O
OH
O
H
O
N
NH
O
O
MeO
OBz
84-1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9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8.02
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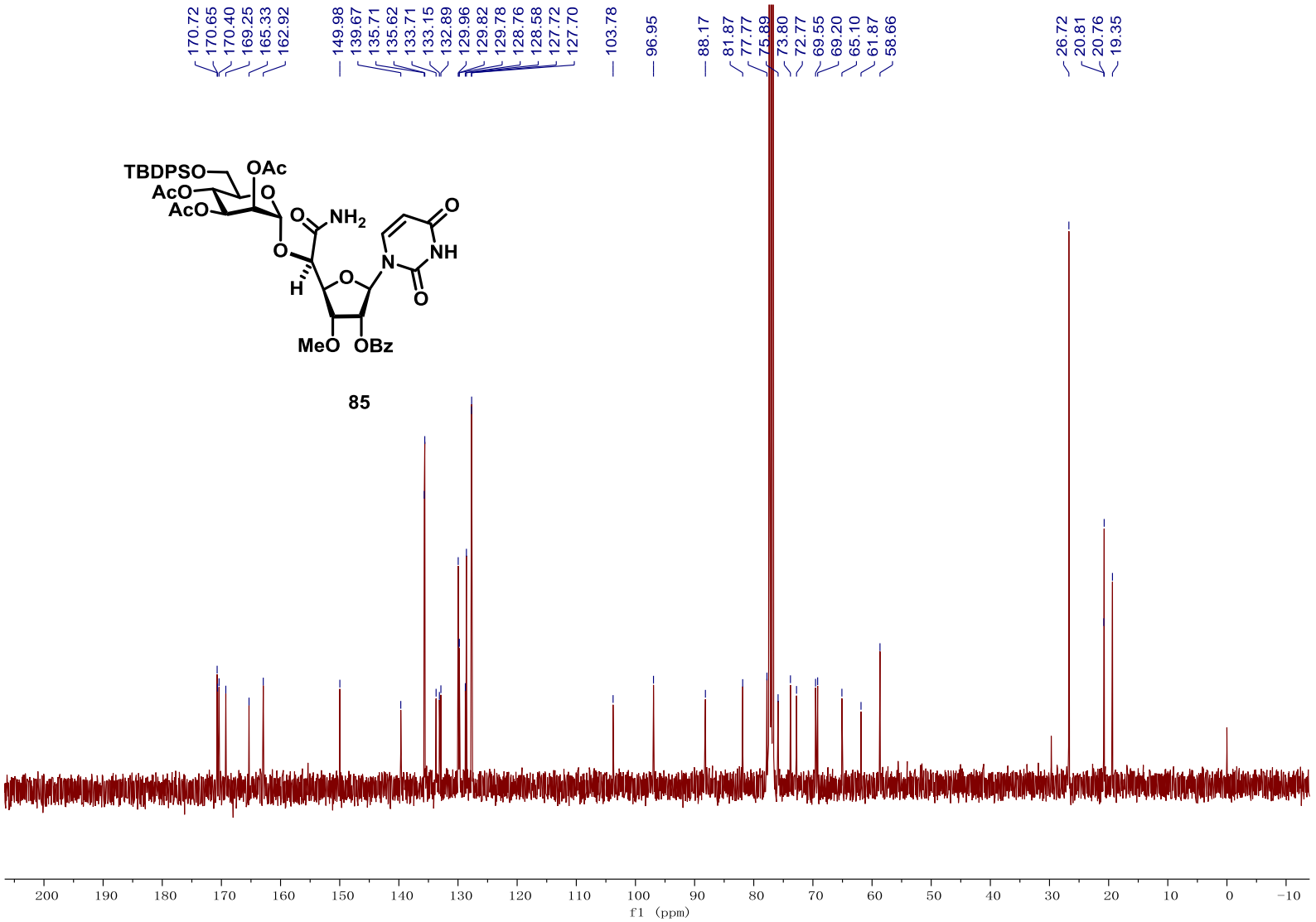
7.60
7.59
7.57
7.55
7.53
7.47
7.45
7.43
7.42
7.40
7.39
7.37
6.65
6.11
6.10
6.09
5.93
5.91
5.67
5.64
5.62
5.49
5.48
5.48
5.47
5.35
5.34
5.32
5.31
5.03
5.03
4.48
4.47
4.46
4.46
4.42
4.42
4.19
4.18
4.17
4.01
4.00
3.99
3.98
3.98
3.78
3.77
3.19
2.16
2.04
2.02
1.07
TBDPSO
OAc
AcO
AcO
O
O
NH2
O
NH
N
O
O
H
O
MeO
OBz
0.91
2.11
2.07
1.89
1.29
1.10
8.12
0.91
2.02
1.00
1.04
1.94
1.04
0.96
1.88
0.98
1.04
1.92
2.88
3.08
2.69
2.87
9.11
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
−0.5
f1 (ppm)

85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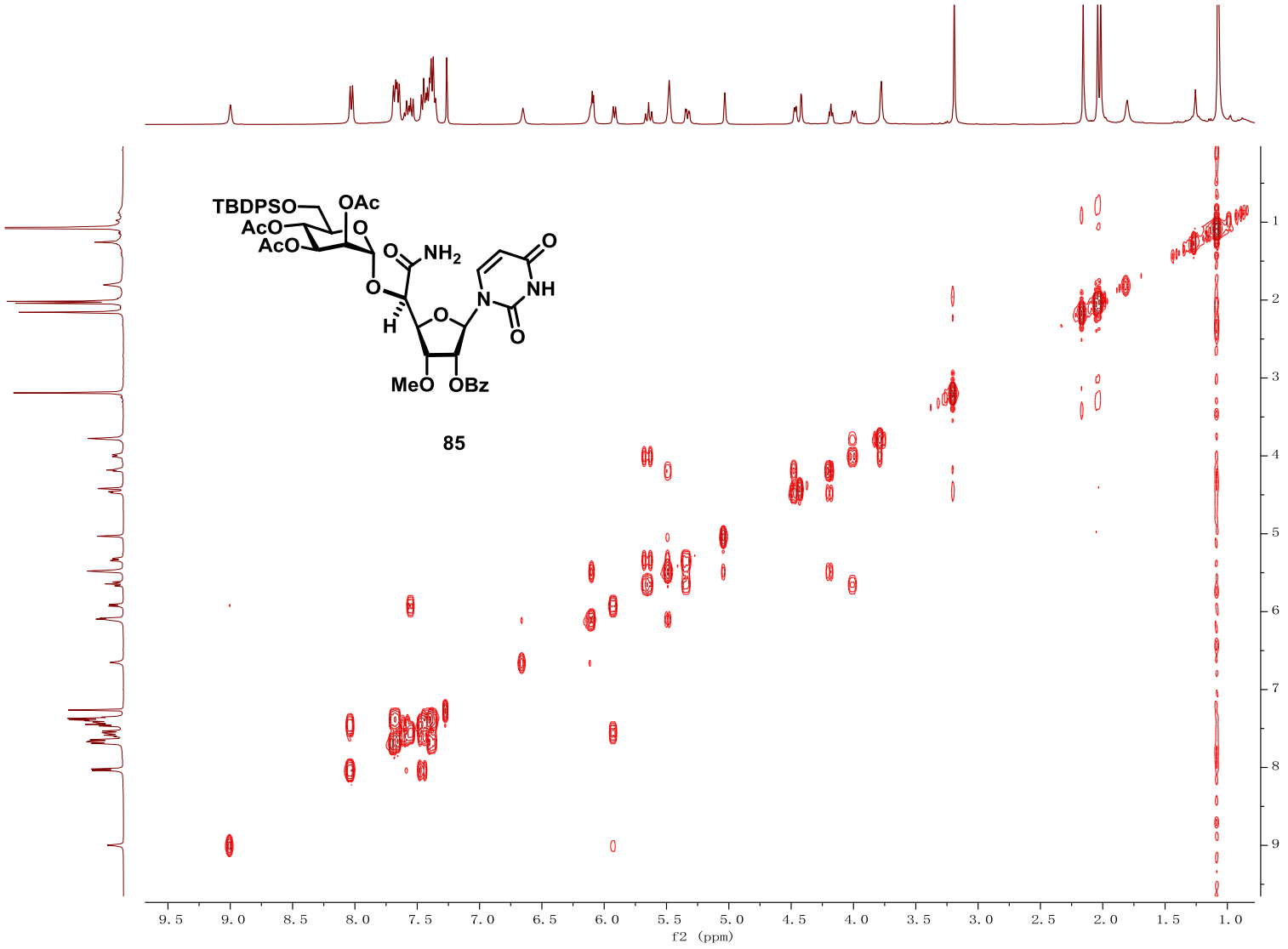
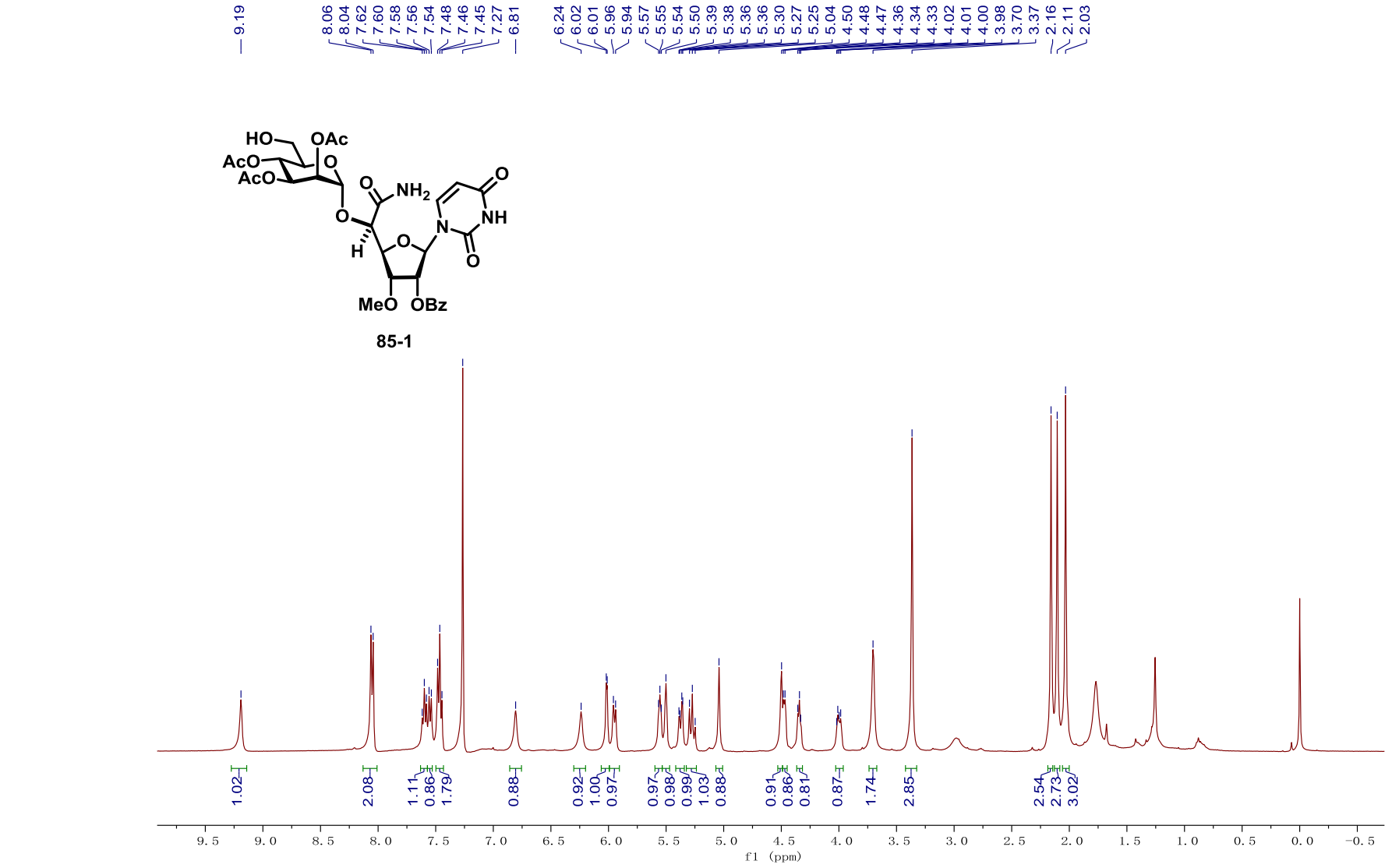
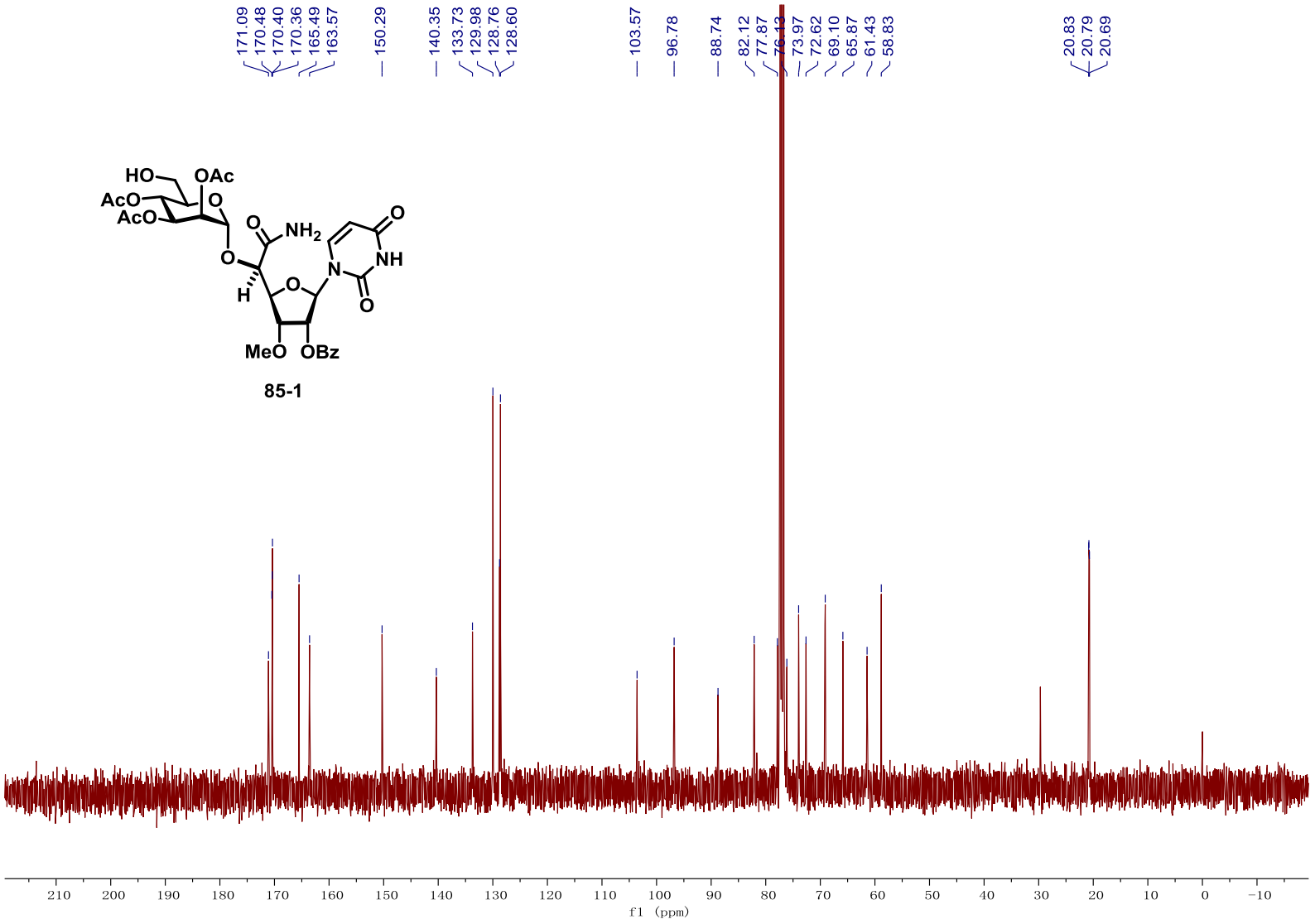
170.65
170.40
169.25
165.33
162.92
149.98
139.67
135.71
135.62
133.71
133.15
132.89
129.96
129.82
129.78
128.76
128.58
127.72
127.70
103.78
96.95
88.17
81.87
77.77
75.89
73.80
72.77
69.55
69.20
65.10
61.87
58.66
26.72
20.81
20.76
19.35
TBDPSO
OAc
AcO
AcO
O
O
NH2
O
H
O
N
NH
O
O
MeO
OBz
85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TBDPSO
OAc
AcO
AcO
O
O
NH2
O
NH
N
O
O
H
O
MeO
OBz
85
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


9.19
8.06
8.04
7.62
7.60
7.58
7.56
7.54
7.48
7.46
7.45
7.27
6.81
6.24
6.02
6.01
5.96
5.94
5.57
5.55
5.54
5.50
5.39
5.38
5.36
5.36
5.30
5.27
5.25
5.04
4.50
4.48
4.47
4.36
4.34
4.33
4.02
4.01
4.00
3.98
3.70
3.37
2.16
2.11
2.03
HO
OAc
AcO
AcO
O
O
NH2
O
O
NH
N
H
O
O
MeO
OBz
85-1
1.02
2.08
1.11
0.86
1.79
0.88
0.92
1.00
0.97
0.97
0.98
0.99
1.03
0.88
0.91
0.86
0.81
0.87
1.74
2.85
2.54
2.73
3.02
f1 (ppm)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170.48
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170.36
165.49
163.57
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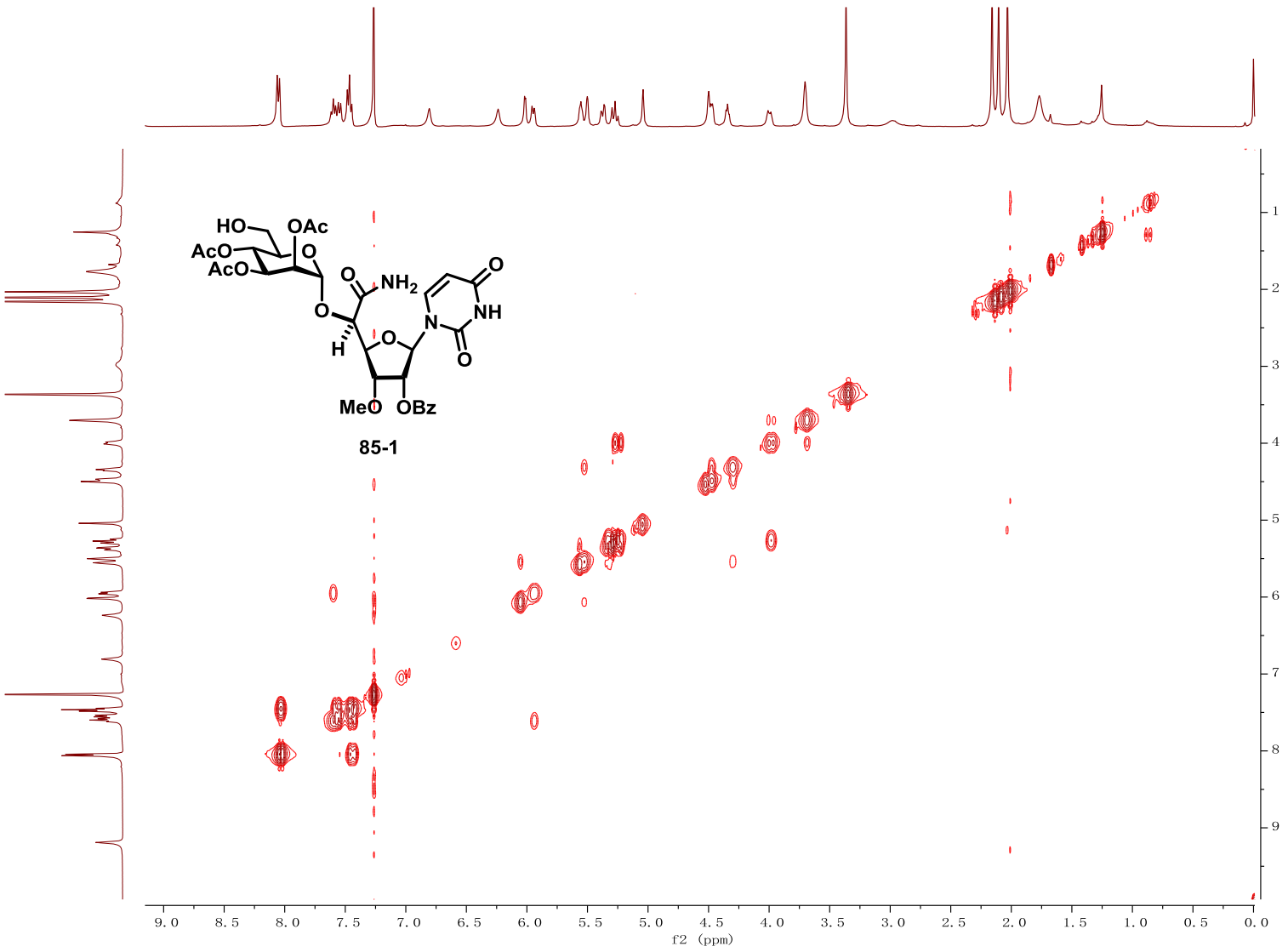
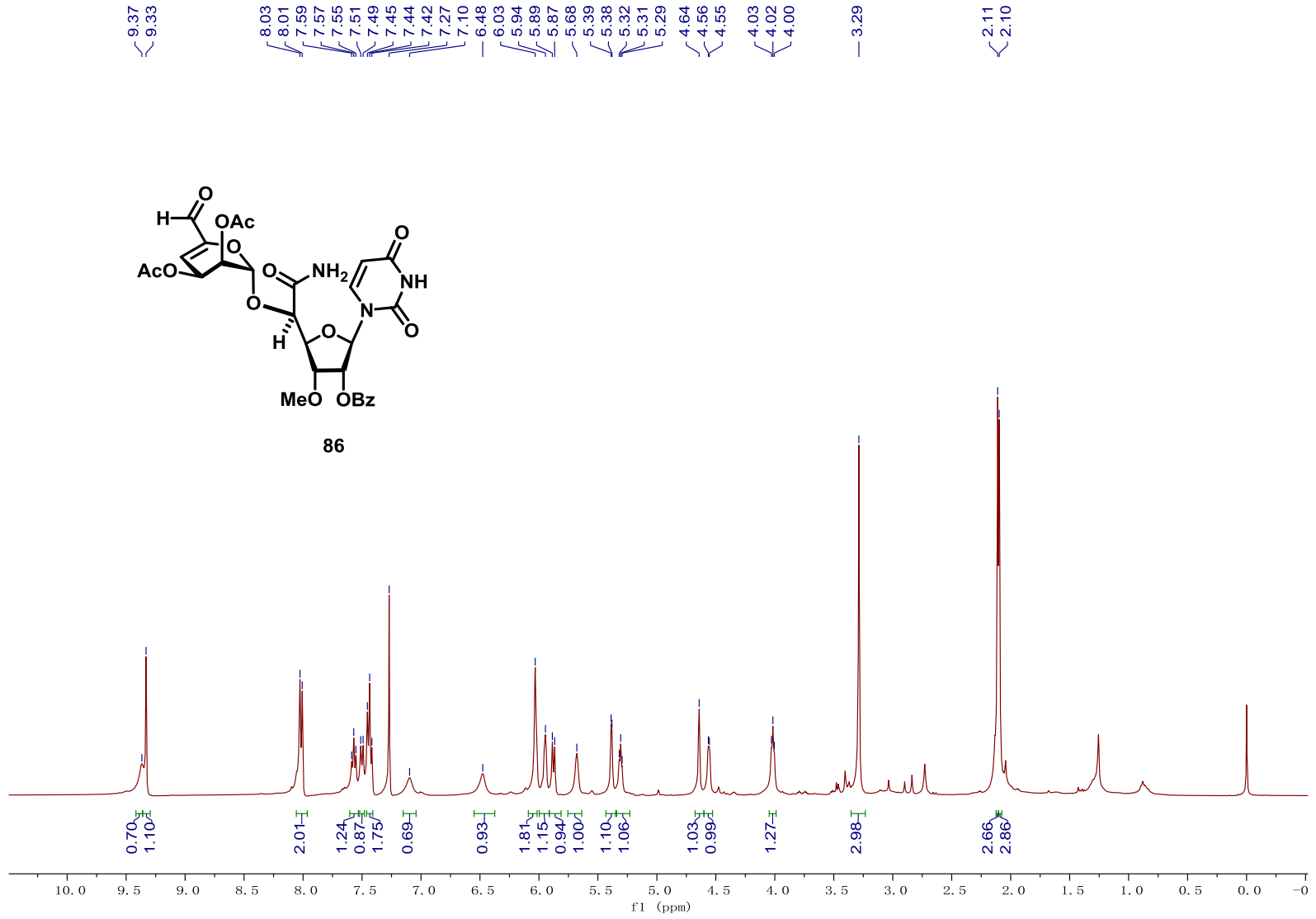
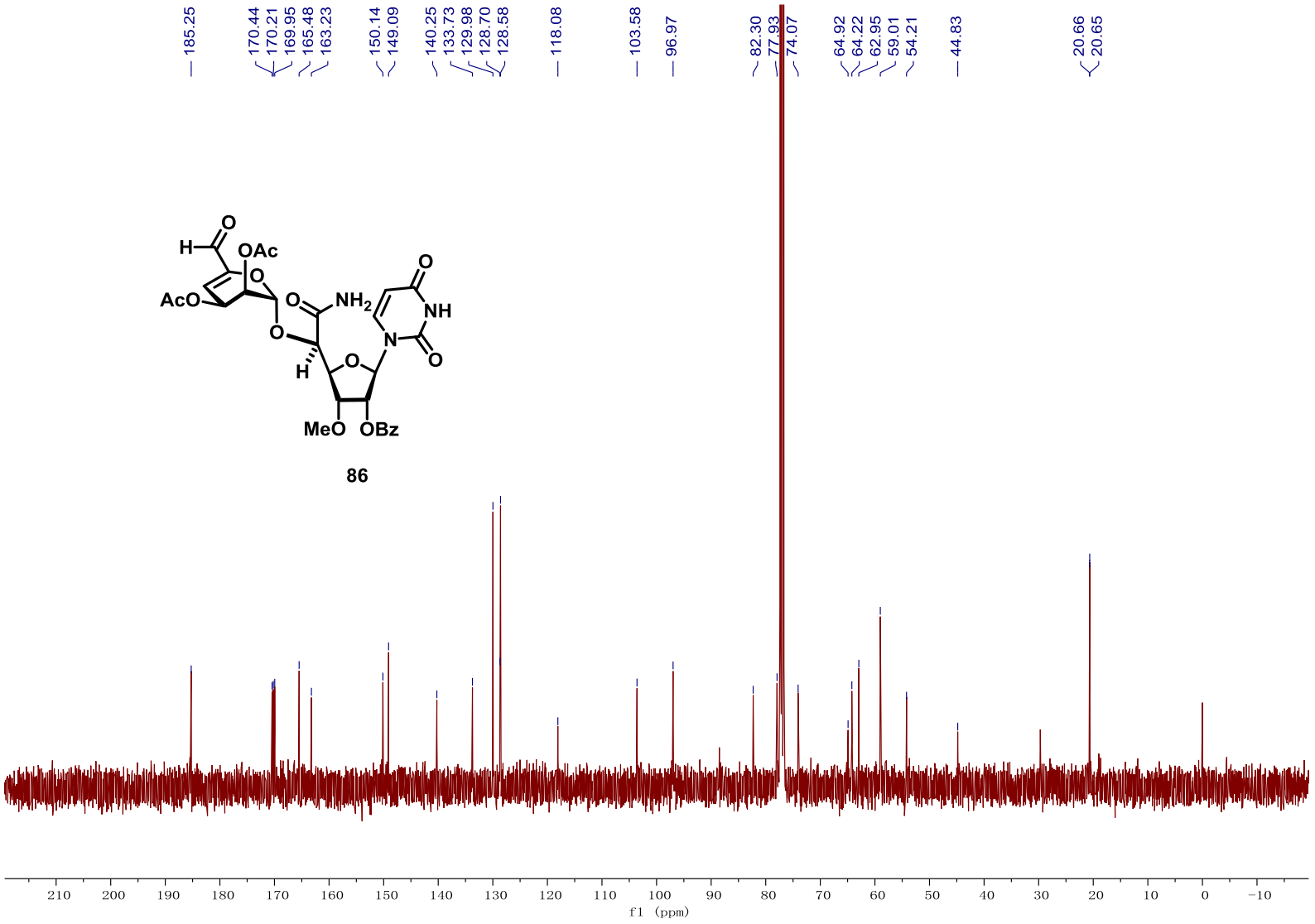
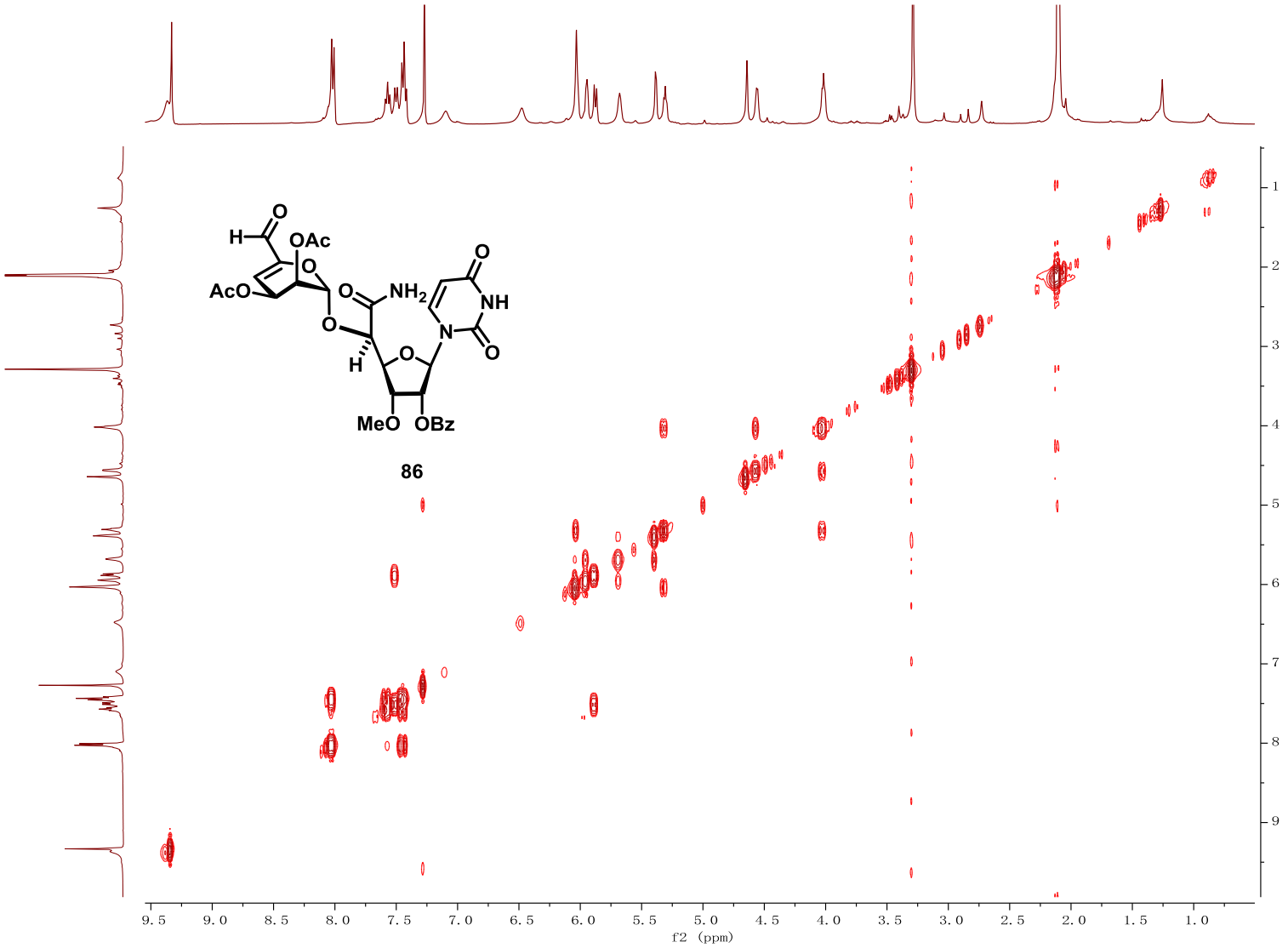
140.35
133.73
129.98
128.76
128.60
103.57
96.78
88.74
82.12
77.87
76.13
73.97
72.62
69.10
65.87
61.43
58.83
20.83
20.79
20.69
HO
OAc
AcO
AcO
O
NH2
O
O
NH
N
O
O
H
MeO
OBz
85-1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

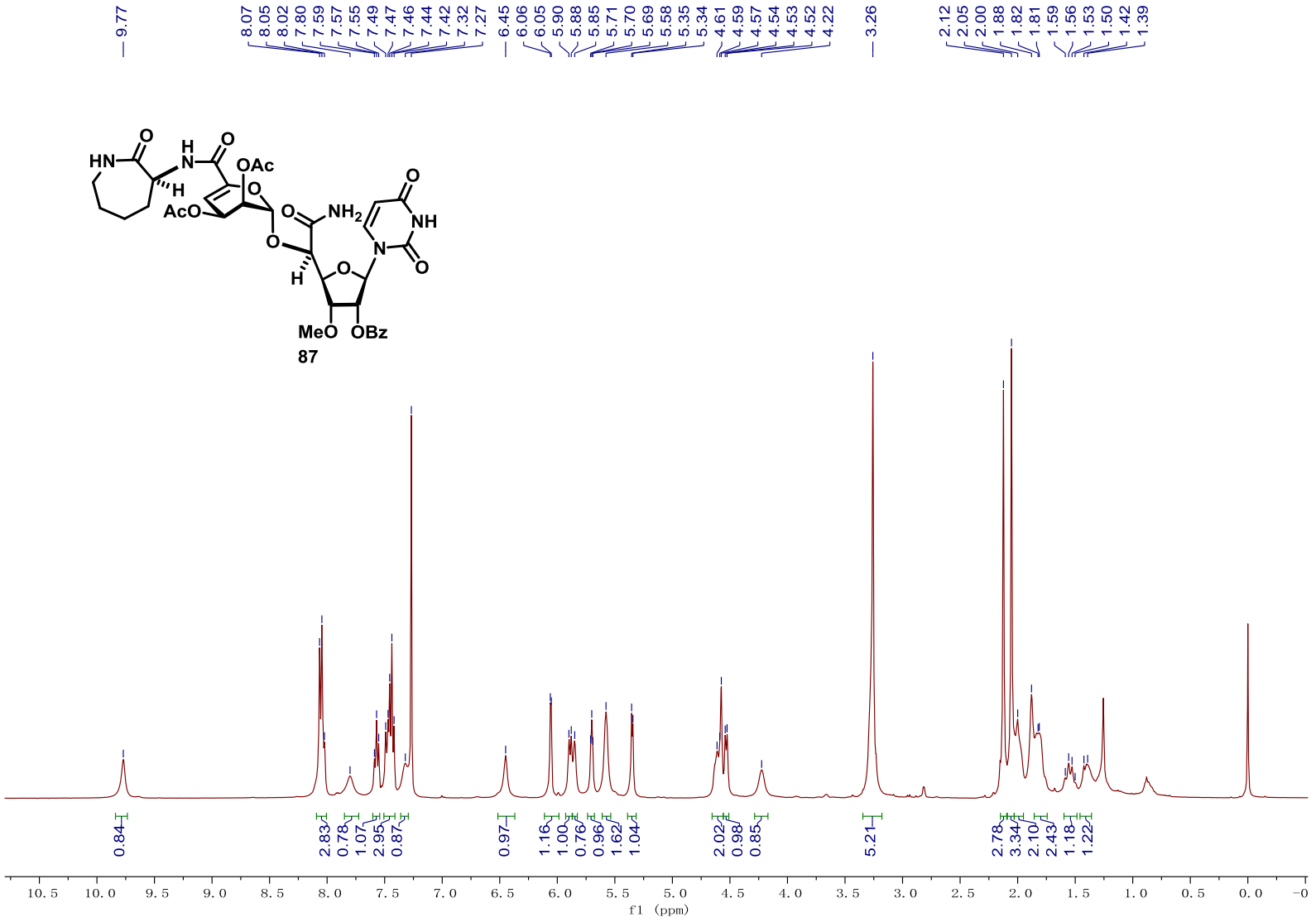

HO
OAc
AcO
AcO
O
O
NH2
O
NH
N
O
O
H
MeO
OBz
85-1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
1
2
3
4
5
6
7
8
9


9.37
9.33
8.03
8.01
7.59
7.57
7.55
7.51
7.49
7.45
7.44
7.42
7.27
7.10
6.48
6.03
5.94
5.89
5.87
5.68
5.39
5.38
5.32
5.31
5.29
4.64
4.56
4.55
4.03
4.02
4.00
3.29
2.11
2.10
H
O
OAc
O
AcO
O
O
NH2
NH
N
O
O
H
O
MeO
OBz
0.70
1.10
2.01
1.24
0.87
1.75
0.69
0.93
1.81
1.15
0.94
1.00
1.10
1.06
1.03
0.99
1.27
2.98
2.66
2.86
10.0
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
−0
f1 (ppm)

86


185.25
170.44
170.21
169.95
165.48
163.23
150.14
149.09
140.25
133.73
129.98
128.70
128.58
118.08
103.58
96.97
82.30
77.93
74.07
64.92
64.22
62.95
59.01
54.21
44.83
20.66
20.65
H
OAc
O
AcO
O
O
NH2
O
NH
N
O
O
H
O
MeO
OBz
86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


H
OAc
AcO
O
O
O
NH2
O
NH
N
O
O
H
MeO
OBz
86
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
f2 (ppm)
1
2
3
4
5
6
7
8
9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8.05
8.02
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7.59
7.57
7.55
7.49
7.47
7.46
7.44
7.42
7.32
7.27
6.45
6.06
6.05
5.90
5.88
5.85
5.71
5.70
5.69
5.58
5.35
5.34
4.61
4.59
4.57
4.54
4.53
4.52
4.22
3.26
2.12
2.05
2.00
1.88
1.82
1.81
1.59
1.56
1.53
1.50
1.42
1.39
HN
H
N
O
OAc
AcO
O
NH2
NH
N
MeO
OBz
87
0.84
2.83
0.78
1.07
2.95
0.87
0.97
1.16
1.00
0.76
0.96
1.62
1.04
2.02
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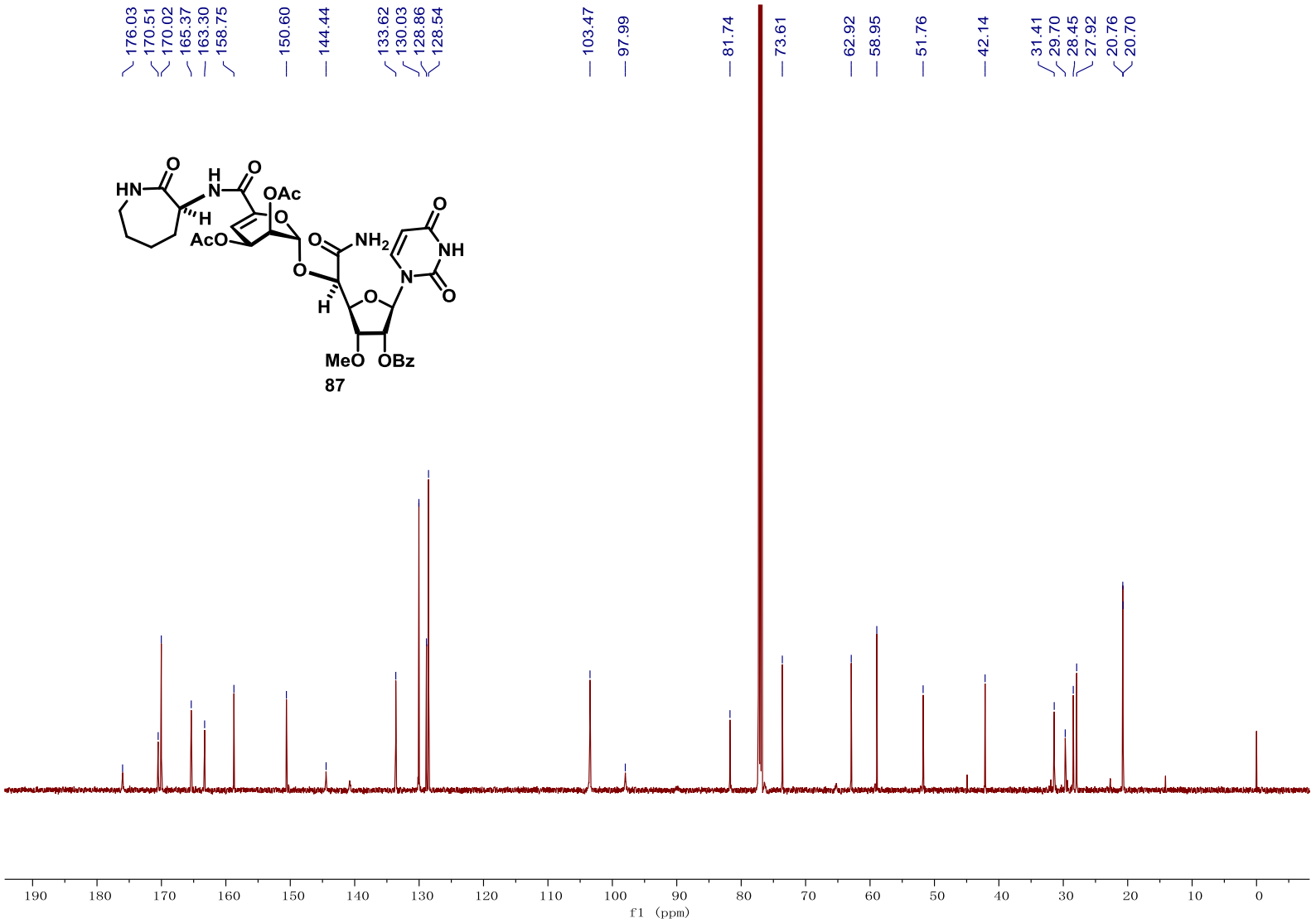
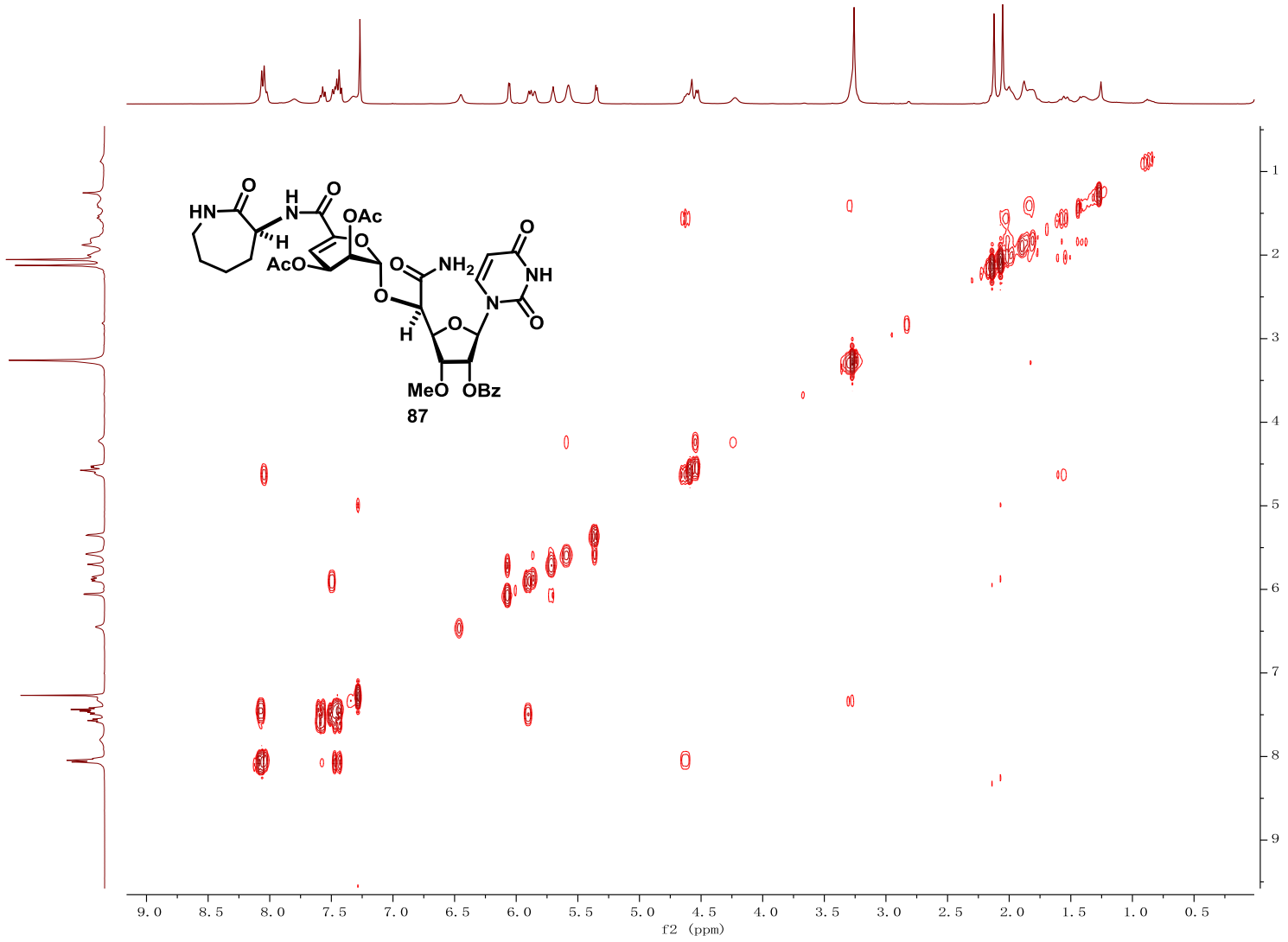
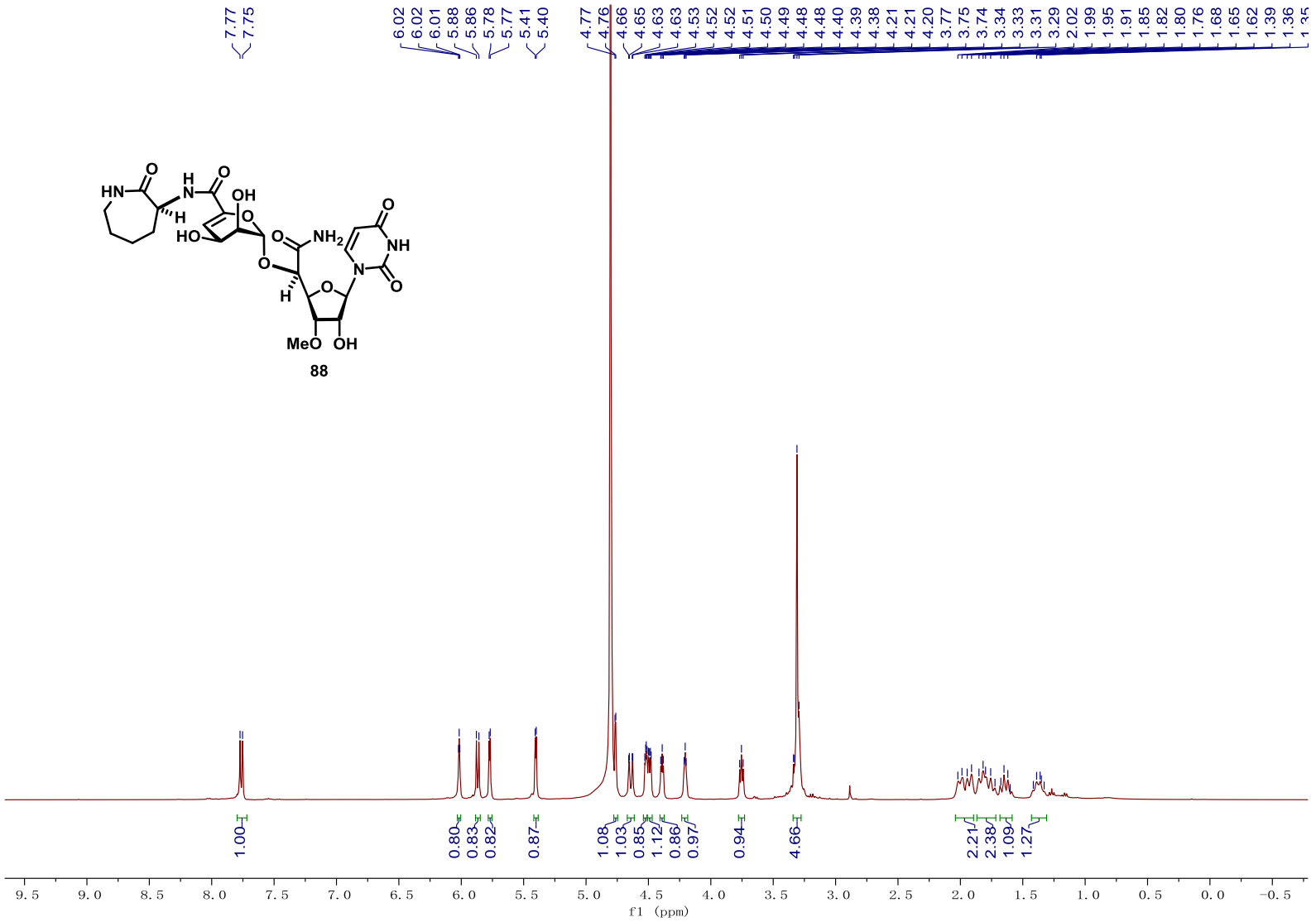
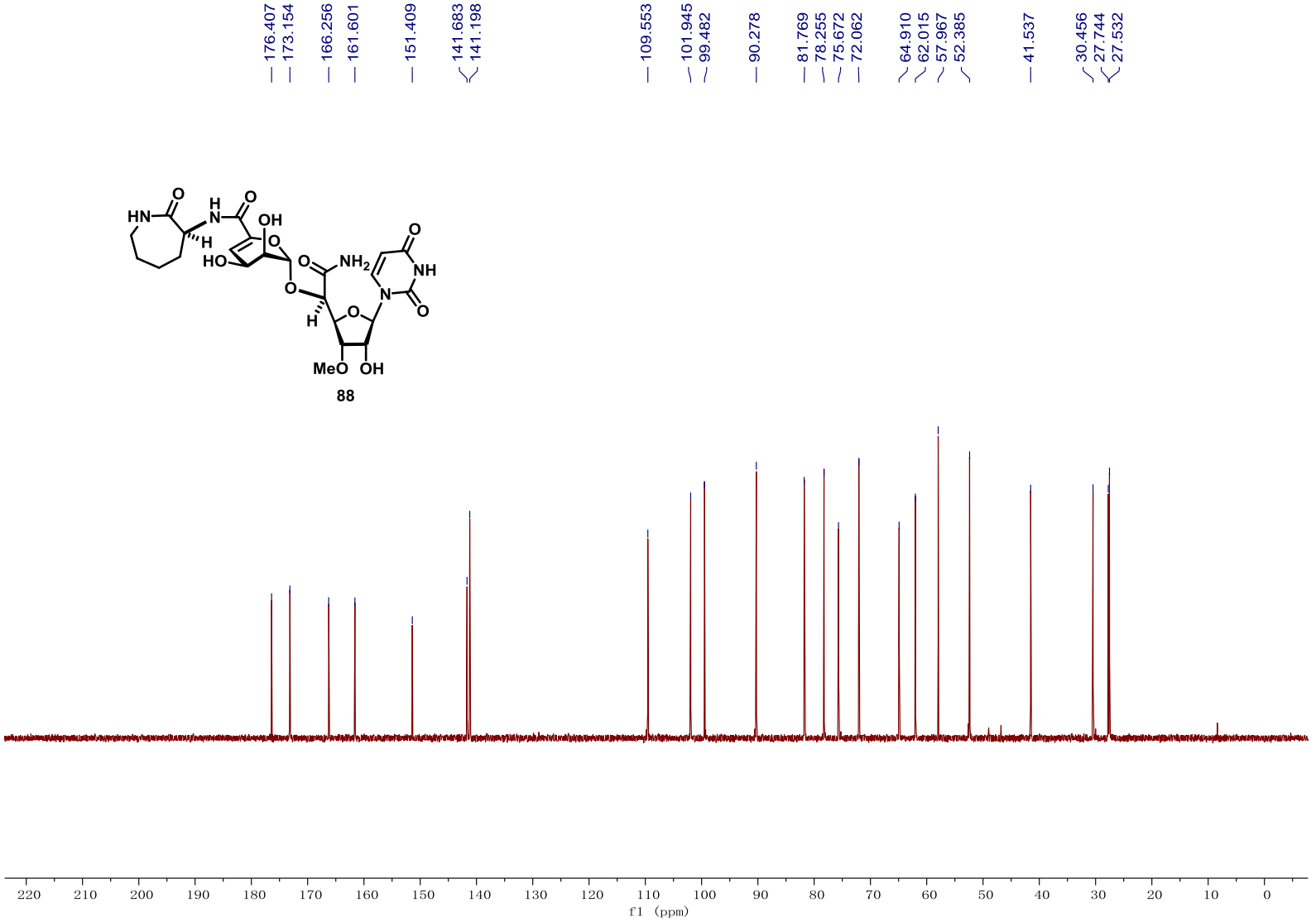
0.85
5.21
2.78
3.34
2.10
2.43
1.18
1.22
f1 (ppm)


176.03
170.51
170.02
165.37
163.30
158.75
150.60
144.44
133.62
130.03
128.86
128.54
103.47
97.99
81.74
73.61
62.92
58.95
51.76
42.14
31.41
29.70
28.45
27.92
20.76
20.70
HN
O
H
N
O
OAc
AcO
O
O
O
NH2
NH
N
O
O
H
MeO
OBz
87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HN
O
H
N
O
OAc
H
AcO
O
O
O
NH2
O
NH
N
O
O
H
MeO
OBz
87
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
f2 (ppm)
1
2
3
4
5
6
7
8
9


7.77
7.75
6.02
6.02
6.01
5.88
5.86
5.78
5.77
5.41
5.40
4.77
4.76
4.66
4.65
4.63
4.63
4.53
4.52
4.52
4.51
4.50
4.49
4.48
4.48
4.40
4.39
4.38
4.21
4.21
4.20
3.77
3.75
3.74
3.34
3.33
3.31
3.29
2.02
1.99
1.95
1.91
1.85
1.82
1.80
1.76
1.68
1.65
1.62
1.39
1.36
HN
O
H
N
O
OH
O
HO
O
O
NH2
O
NH
N
O
H
O
MeO
OH
88
1.00
0.80
0.83
0.82
0.87
1.08
1.03
0.85
1.12
0.86
0.97
0.94
4.66
2.21
2.38
1.09
1.27
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
−0.5
f1 (ppm)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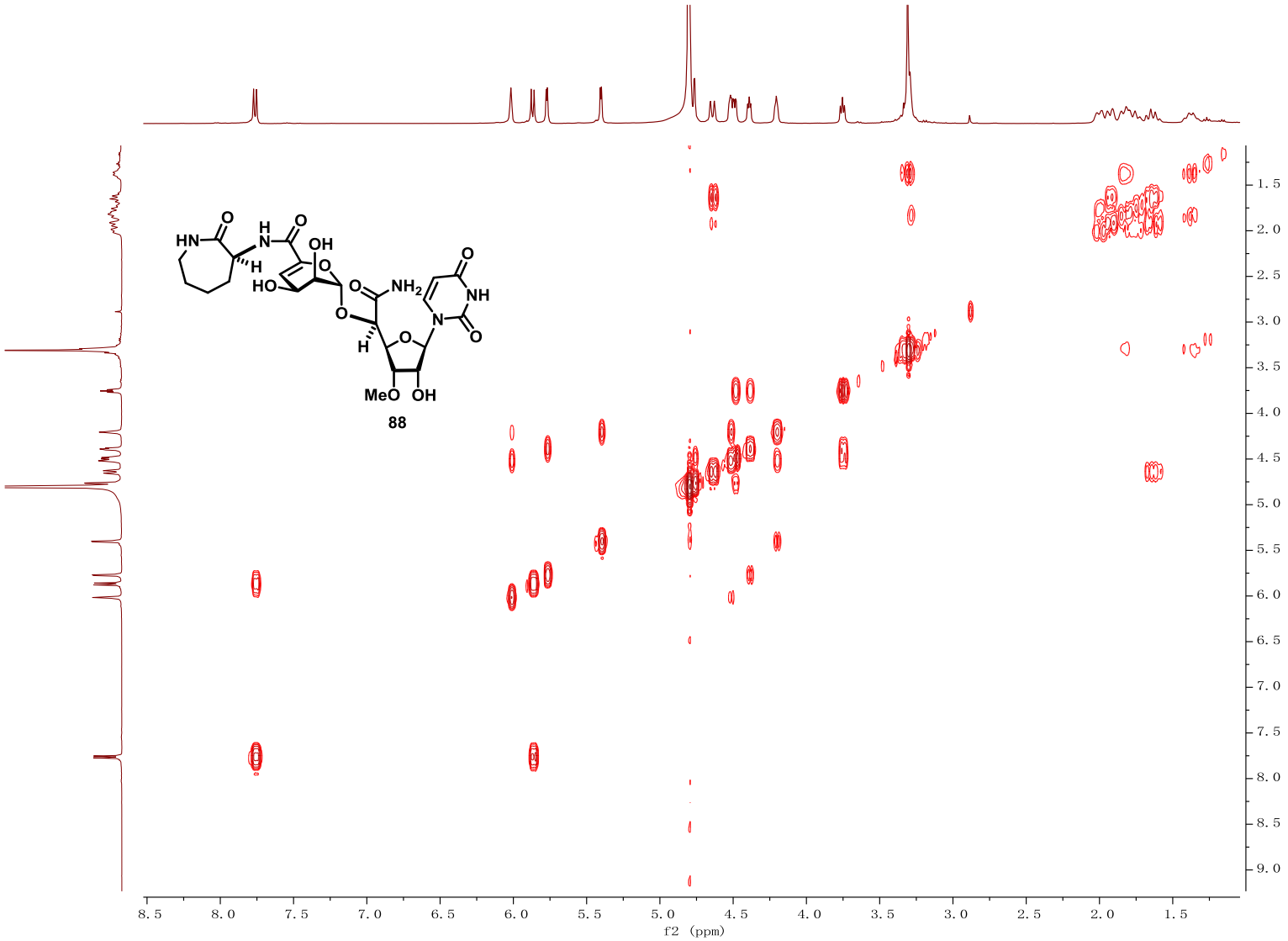
173.154
166.256
161.601
151.409
141.683
141.198
109.553
101.945
99.482
90.278
81.769
78.255
75.672
72.062
64.910
62.015
57.967
52.385
41.537
30.456
27.744
27.532
HN
O
H
N
O
OH
HO
O
O
O
NH2
NH
N
O
H
O
MeO
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

88


HN
O
H
N
O
OH
HO
O
O
NH2
NH
N
O
H
O
MeO
OH
88
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
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
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