Supporting Information for

Synthetic Investigation toward Apigenin 5-*O*-glycoside Camellianin B as well as the Chemical Structure Revision

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Contents

7,4'-Di-*O*-hexanoyl apigenin (4a)

To a suspension of apigenin (3.0 g, 11.1 mmol) in acetone (80 mL) was added Et_3N (3.8 mL 27.8 mmol) and hexanoyl chloride (3.9 mL, 27.8 mmol) successively at 0 ^oC. The resulting mixture was then stirred at room temperature for another 7 h, at which time TLC shown that all starting material disappeared. Ethyl acetate (120 mL) was added to diluted the reaction, and the resulting solution was washed successively with water, 1 N HCl, saturated $NaHCO_3$, and brine, and then dried over Na_2SO_4. Filtration and concentration to yield the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 9 : 1) to afford **4a** (3.9 g, 76%) as a yellow powder: ^1H NMR (400 MHz, $CDCl_3$) δ 12.68 (s, 1 H), 7.88 (dd, *J* = 2.4, 6.8 Hz, 2 H), 7.26 (dd, *J* = 2.4, 6.8 Hz, 2 H), 6.82 (d, *J* = 2.0 Hz, 1 H), 6.66 (s, 1 H), 6.54 (d, *J* = 2. 0 Hz, 1 H), 2.60 (td, *J* = 7.2, 2.8 Hz, 4 H), 1.81-1.73 (m, 2 H), 1.43-1.36 (m, 8 H), 0.96 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 171.7, 171.2, 163.8, 161.8, 156.6, 156.1, 153.8, 128.3, 127.7, 122.5, 108.7, 105.9, 105.5, 101.0, 34.4, 34.3, 31.2 (2 C), 24.5 (2 C), 22.3, 13.9; HRMS (MALDI) Calcd for $C_{27}H_{31}O_7$ $[M+H]^+$ 467.2064, found 467.2064.

7,4'-Di-*O*-benzyl apigenin (4b)

To a suspension of apigenin (2.0 g, 7.4 mmol) and K_2CO_3 (2.5 g, 18.1 mmol) in dry DMF (30 mL) was added BnBr (2.2 mL, 18.5 mmol) at room temperature. The resulting mixture was then stirred at the same temperature for another 10 h, and TLC shown all starting material disappeared. Ethyl acetate (120 mL) was added to dilute the reaction mixture, the resulting solution was washed successively with water, 1 N HCl, saturated $NaHCO_3$, brine, and then dried over Na_2SO_4. Filtration and concentration to generate the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 5 : 1) to afford **4b** (2.3 g, 68%) as a yellow powder: ^1H NMR (400 MHz, $CDCl_3$) δ 12.80 (s, 1 H), 7.82 (dd, *J* = 2.0, 6.8 Hz, 2 H), 7.45-7.33 (m, 10 H), 7.08 (dd, *J* = 2.0, 6.8 Hz, 2 H), 6.55 (s, 1 H), 6.54 (d, *J* = 2.0 Hz, 1 H), 6.43 (d, *J* = 2.0 Hz, 1 H), 5.14 (d, s, 2 H), 5.12 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 164.5, 164.0, 162.2, 161.7, 157.7, 136.1, 135.8, 128.8, 128.4, 128.3, 128.1, 127.5, 123.8, 115.4, 105.8, 104.4, 98.8, 93.5, 70.4, 70.2; HRMS (MAILDI)

Calcd for $C_{29}H_{23}O_5$ $[M+H]^+$ 451.1540, found 451.1540.

Dimethylthexylsilyl 3-*O*-benzyl-4,6-di-*O*-benzylidene-β-D-glucopyranoside (6)

To a solution of 3-*O*-benzyl-4,6-di-*O*-benzylidene-D-glucoside **5**[S1] (4.5 g, 12.6 mmol) and imidazole (1.8 g, 26.4 mmol) in dry CH_2Cl_2 (35 mL) was added TDSCl (5.1 mL, 22.7 mmol) dropwise at room temperature. The resultant mixture was stirred at the same temperature for 10 h, then ethyl acetate was added to dilute the reaction. The solution was washed successively with water, saturated $NaHCO_3$, brine, and then dried over Na_2SO_4. Filtration was followed by evaporation to give a syrup which was further purified by silica gel chromatography (eluent system: PE/EA = 30 : 1) to generate **6** (5.2 g, 82%) as a syrup: $[\alpha]^{28}_D$ = -18.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.67 (m, 2 H), 7.40-7.35 (m, 5 H), 7.34-7.24 (m, 3 H), 5.55 (s, 1 H), 4.97 (AB, 2 H), 4.64 （d, *J* = 7.6 Hz, 1 H), 4.31 (dd, *J* = 5.2, 10.4 Hz, 1 H), 3.82 (t, *J* = 10.4 Hz, 1 H), 3.74 (t, *J* = 9.2 Hz, 1 H), 3.67 (t, *J* = 8.8 Hz, 1 H), 3.52 (dd, *J* = 7.6, 8.8 Hz, 1 H), 3.47-3.41 (m, 1 H), 2.35 (brs, 1 H), 1.68-1.60 (m, 1 H), 0.90-0.87 (m, 12 H), 0.18 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 139.3, 130.9, 130.3, 130.1, 129.9, 129.6, 128.0, 103.2, 100.1, 83.4, 82.2, 78.2, 76.5, 70.7, 68.5, 36.0, 26.8, 22.1, 21.9, 20.5, 20.4, 0.0, -1.3; HRMS (MALDI) Calcd for $C_{28}H_{40}O_6SiNa$ $[M+Na]^+$ 523.2486, found 523.2485.

Dimethylthexylsilyl

2-*O*-benzoyl-3-*O*-benzyl-4,6-di-*O*-benzylidene-β-D-glucopyranoside (7)

To a solution of **6** (2.0 g, 4.0 mmol) in dry pyridine (25 mL) was added BzCl (1.4 mL, 12.0 mmol) at 0 ^{o}C. The reaction mixture was then warmed to room temperature and the stirring was continued for another 7 h. Ethyl acetate was added to dilute the reaction, and the solution was washed successively with water, 1 N HCl, saturated $NaHCO_3$, brine and then dried over Na_2SO_4. Filtration and concentration yielded the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 25 : 1) to generate **7** (2.2 g, 91%) as a white solid: $[\alpha]^{28}_D$ = 16.3 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2 H), 7.46-7.38 (m, 3 H), 7.33-7.24 (m, 5 H), 7.03-6.93 (m, 5 H), 5.47 (s, 1 H), 5.16 (td, *J* = 7.6, 1.2 Hz, 1 H), 4.74 (d, *J* = 7.6 Hz, 1 H), 4.71 (AB, 2 H), 4.23 (dd, *J* = 4.8, 10.4 Hz, 1 H), 3.78-3.69

(m, 3 H), 3.40-3.35 (m, 1 H), 1.40-1.33 (m, 1 H), 0.61-0.58 (m, 12 H), 0.00 (s, 3 H), -0.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 140.0, 139.3, 134.9, 132.1, 131.7, 130.9, 130.2, 130.0, 129.9, 129.4, 128.0, 103.2, 98.5, 83.8, 79.8, 77.2, 75.7, 70.8, 68.4, 35.7, 26.6, 21.7 (2 C), 20.3 (2 C), 0.0, -1.5; HRMS (MALDI) Calcd for $C_{35}H_{44}O_7SiNa$ $[M+Na]^+$ 627.2749, found 627.2746.

2-*O*-Benzoyl-3-*O*-benzyl-4,6-di-*O*-benzylidene-β-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (8)

To a solution of **7** (1.0 g, 1.6 mmol) in dry THF (10 mL) wad added HF·pyridine (2.9 mL) dropwise at 0 ^{o}C. After stirring at 0 ^{o}C for another 30 minutes, the reaction temperature was then warmed to room temperature and the stirring was continued for another 11 h. Ethyl acetate was added to dilute the reaction and the resultant solution was washed with water, saturated $NaHCO_3$, brine and then dried over Na_2SO_4. Filtration was followed by concentration under reduced pressure to give a residue which was further purified by silica gel chromatography (eluent system: PE/EA = 6 : 1) to generate the lactol intermediate.

The above obtained lactol (535 mg, 1.2 mmol) was dissolved in dry CH_2Cl_2 (5 mL), to which *ortho*-cyclopropylethynylbenzoic acid (279 mg, 1.5 mmol), DMAP (199 mg, 1.6 mmol), DIPEA (0.5 mL, 2.9 mmol), and EDCI (308 mg, 1.6 mmol) were added successively. The resultant solution was stirred at room temperature for 6 h, then ethyl acetate was added. The resultant solution was washed with water, brine successively, and then dried over Na_2SO_4. Filtration and concentration under reduced pressure to generate the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 5 : 1) to afford **8** (743.7 mg, 94%) as a white solid. For β-isomer: $[\alpha]^{28}_D$ = 36.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.91 (m, 3 H), 7.56-7.51 (m, 3 H), 7.46-7.35 (m, 7 H), 7.26 (td, *J* = 7.2, 2.0 Hz, 1 H), 7.17-7.08 (m, 5 H), 6.10 (d, *J* = 8.0 Hz, 1 H), 5.64 (s, 1 H), 5.62 (t, *J* = 8.4 Hz, 1 H), 4.88 (AB, 2 H), 4.47 (dd, *J* = 4.8, 10.0 Hz, 1 H), 4.03 (t, *J* = 8.8 Hz, 1 H), 3.98 (t, *J* = 8.8 Hz, 1 H), 3.87 (t, *J* = 10.0 Hz, 1 H), 3.78 (td, *J* = 9.2, 4.8 Hz, 1 H), 1.54-1.47 (m, 1 H), 0.90-0.85 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 162.8, 136.9, 136.4, 133.7, 132.6, 131.7, 130.2, 129.2, 128.6, 128.4, 127.7, 127.6, 127.5, 127.4, 127.0, 126.4,

125.3, 125.0, 100.7, 99.7, 92.2, 80.8, 77.3, 73.6, 73.5, 71.6, 67.8, 66.3, 8.3, 8.2; HRMS (ESI) Calcd for $C_{39}H_{35}O_8$ $[M+H]^+$ 631.2326, found 631.2329.

7,4'-Di-*O*-hexanoyl-5-*O*-(2"-*O*-benzoyl-3"-*O*-benzyl-4",6"-di-*O*-benzylidene-β-D-glucopyranosyl) apigenin (9)

To a solution of **8** (200 mg, 0.3 mmol) and **4a** (123 mg, 0.26 mmol) in dry CH_2Cl_2 (5 mL) was added activated 4Å MS under N_2 atmosphere. The resulting mixture was stirred at room temperature for 30 minutes before $Ph_3PAuNTf_2$ (39 mg, 0.05 mmol) was added. The reaction mixture was then stirred at the same temperature for another 6 h. Filtration to remove MS and evaporation under reduced pressure to give a residue, which was further purified by silica gel chromatography (eluent system: PE/EA = 4 : 1) to afford **9** (147 mg, 61%) as a white solid: $[\alpha]^{28}_D$ = -14.8 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2 H), 7.80-7.77 (m, 2 H), 7.55-7.50 (m, 3 H), 7.42-7.37 (m, 5 H), 7.21-7.09 (m, 7 H), 7.08 (d, *J* = 2.4 Hz, 1 H), 6.84 (d, *J* = 2.0 Hz, 1 H), 6.49 (s, 1 H), 5.77 (t, *J* = 7.6 Hz, 1 H), 5.66 (s, 1 H), 5.47 (d, *J* = 7.2 Hz, 1 H), 4.88 (AB, 2 H), 4.43 (dd, *J* = 4.8, 10.4 Hz, 1 H), 4.17 (t, *J* = 9.2 Hz, 1 H), 4.00 (dd, *J* = 7.6, 8.8 Hz, 1 H), 3.91 (t, *J* = 10.0 Hz, 1 H), 3.75 (td, *J* = 9.6, 4.8 Hz, 1 H), 2.60 (q, *J* = 7.2 Hz, 4 H), 1.80-1.73 (m, 4 H), 1.43-1.35 (m, 8 H), 0.96-0.91 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 171.8, 171.2, 165.1, 160.3, 158.0, 156.7, 154.0, 153.2, 137.9, 137.2, 132.9, 130.2, 130.0, 129.1, 128.7, 128.3, 128.2 (2 C), 128.1, 127.5, 127.3, 126.1, 122.3, 114.0, 108.8, 108.6, 106.2, 101.4, 100.4, 81.0, 78.0, 73.7, 73.0, 68.8, 66.6, 34.4 (2 C), 31.2 (2 C), 24.5, 24.4, 22.3, 13.9; HRMS (MALDI) Calcd for $C_{54}H_{54}O_{13}Na$ $[M+Na]^+$ 933.3457, found 933.3453.

7,4'-Di-*O*-hexanoyl-5-*O*-(2"-*O*-benzoyl-3"-*O*-benzyl-β-D-glucopyranosyl) apigenin (10)

To a solution of **9** (117 mg, 0.13 mmol) and EtSH (74 μL, 1.0 mmol) in dry CH_2Cl_2 (4 mL) was added TFA (48 μL, 0.64 mmol) and BzCl (3 μL, 0.03 mmol) at 0 ^{o}C. The resulting mixture was stirred at the same temperature for another 45 minutes, at which time TLC shown that all starting material disappeared. Saturated $NaHCO_3$ solution was added to quench the reaction, which was followed by addition of ethyl acetate to dilute the reaction mixture. The resultant solution was washed with saturated $NaHCO_3$,

brine, and then dried over Na_2SO_4. Filtration and concentration to yield the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 4 : 3) to give **10** (87 mg, 83%) as a yellow solid: $[\alpha]^{28}_D$ = -6.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 1.2, 8.0 Hz, 2 H), 7.74 (dd, *J* = 1.5, 6.8 Hz, 6.8 Hz, 2 H), 7.52-7.48 (m, 1 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.21-7.10 (m, 7 H), 6.97 (d, *J* = 2.0 Hz, 1 H), 6.83 (d, *J* = 2.0 Hz, 1 H), 6.44 (s, 1 H), 7.65 (dd, *J* = 7.2, 8.8 Hz, 1 H), 5.34 (d, *J* = 7.6 Hz, 1 H), 4.79 (AB, 2 H), 4.15 (t, *J* = 9.2 Hz, 1 H), 3.95 (m, 2 H), 3.83 (t, *J* = 9.2 Hz, 1 H), 3.64-3.60 (m, 1 H), 3.43 (brs, 2 H), 2.60 (q, *J* = 3.6 Hz, 4 H), 1.79-1.72 (m, 4 H), 1.41-1.37 (m, 8 H), 0.96-0.92 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 132.9, 130.2, 130.0, 128.5, 128.3, 128.2 (2 C), 127.7, 127.3, 122.2, 113.4, 108.7, 107.5, 105.7, 100.0, 82.0, 74.2, 73.2, 69.7, 62.0, 34.4 (2 C), 31.2 (2 C), 24.5, 24.4, 22.3, 13.9; HRMS (MALDI) Calcd for $C_{47}H_{50}O_{13}Na$ $[M+Na]^+$ 845.3144, found 845.3140.

7,4'-Di-*O*-hexanoyl-5-*O*-(2'',6''-di-*O*-benzoyl-3''-*O*-benzyl-β-D-glucopyranosyl) apigenin (11)

To a solution of **10** (58 mg, 0.07 mmol) and pyridine (56 μL, 0.7 mmol) in dry CH_2Cl_2 (2 mL) was added BzCl (12 μL, 0.1 mmol) dropwise at 0 ^oC. After the addition was completed, the resultant mixture was stirred at the same temperature for another 1 h. Ethyl acetate was added to dilute the reaction, the resulting solution was washed with water, 1 N HCl, and brine, and then dried over Na_2SO_4. Filtration was followed by evaporation under reduced pressure to afford the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 2 : 1) to produce **11** (56 mg, 86%) as a yellow solid: $[\alpha]^{28}_D$ = -34.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 2 H), 7.98 (dt, *J* = 2.0, 6.4 Hz, 2 H), 7.80-7.76 (m, 2 H), 7.61-7.36 (m, 7 H), 7.26-7.16 (m, 6 H), 7.04 (d, *J* = 2.4 Hz, 1 H), 6.85 (d, *J* = 2.0 Hz, 1 H), 6.48 (s, 1 H), 5.75 (dd, *J* = 6.8, 8.4 Hz, 1 H), 5.43 (d, *J* = 6.8 Hz, 1 H), 4.85 (AB, 2 H), 4.67-4.65 (m, 2 H), 4.09 (t, *J* = 9.2 Hz, 1 H), 3.91-3.84 (m, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.48 (td, *J* = 7.6, 2.0 Hz, 2 H), 1.79-1.67 (m, 4 H), 1.41-1.33 (m, 8 H), 0.95-0.91 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 171.9, 171.2, 166.8, 165.3, 160.3, 157.9, 156.8, 154.1, 153.2, 137.8, 133.4, 133.1, 133.0, 130.1 (2 C),

130.0, 129.8, 129.6, 128.6, 128.5, 128.4, 128.3 (2 C), 128.2, 127.9, 127.4, 122.3, 113.6, 108.7, 107.8, 105.8, 99.6, 81.8, 74.6, 74.3, 73.3, 69.3, 63.4, 34.4, 34.3, 31.2 (2 C), 24.6, 24.4, 22.3 (2 C), 13.9; HRMS (MALDI) Calcd for $C_{54}H_{55}O_{14}$ $[M+H]^+$ 927.3586, found 927.3589.

Allyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-α-L-rhamnosylpyranose (S2)

To a solution of allyl 3,4-di-*O*-benzyl-α-L-rhamnosylpyranose **S1**[S2] (1.58 g, 4.1 mmol) and pyridine (5 mL, 61.5 mmol) in CH_2Cl_2 (7 mL) was added BzCl (1.0 mL, 8.2 mmol) dropwise by syringe at 0 ^oC. The reaction mixture was then warmed to room temperature and the stirring was continued for another 3 h. Ethyl acetate was added and the resultant solution was washed with water, 1 N HCl, saturated $NaHCO_3$, brine successively, and then dried over Na_2SO_4. Filtration and evaporation under reduced pressure yielded the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 6 : 1) to afford **S2** (1.72 g, 86%) as a syrup: $[\alpha]^{28}_D$ = 14.0 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 2.0, 6.8 Hz, 2 H), 7.49-7.45 (m, 1 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.30-7.16 (m, 10 H), 5.90-5.81 (m, 1 H), 5.67-5.66 (m, 1 H), 5.28-5.23 (m, 1 H), 5.18-5.14 (m, 1 H), 4.93 (AB, 2 H), 4.90 (s, 1 H), 4.78 (AB, 2 H), 4.16-4.08 (m, 1 H), 3.97-3.92 (m, 1 H), 3.89-3.82 (m, 1 H), 3.61 (td, *J* = 9.2, 1.6 Hz, 1 H), 1.39 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.7, 138.3, 133.8, 133.3, 130.2, 130.1, 128.6, 128.5 (2 C), 128.3, 128.2, 127.9, 127.8, 117.8, 97.0, 80.3, 78.5, 75.5, 71.7, 69.7, 68.2, 68.0, 18.4; HRMS (ESI) Calcd for $C_{30}H_{33}O_6$ $[M+H]^+$ 489.2272, found 489.2272.

2-*O*-Benzoyl-3,4-di-*O*-benzyl-L-rhamnosyl *ortho*-cyclopropylethynylbenzoate (13)

To a solution of **S2** (1.0 g, 2.0 mmol) in a mixed solvent of CH_2Cl_2 and MeOH (V/V = 1 : 1, 7 mL) was added $PdCl_2$ (84.0 mg, 0.47 mmol) at room temperature. The resulting solution was stirred at the same temperature for another 10 h. The catalyst was removed by filtration through a pad of silica gel, and the filtrate was evaporated under reduced pressure. Thus obtained residue was then purified by silica gel chromatography (eluent system: PE/EA = 5 : 1) to yield the Allyl group removed lactol intermediate.

The above obtained lactol was then dissolved in dry CH_2Cl_2 (8 mL), to which *ortho*-cyclopropylethynylbenzoic acid (325 mg, 1.7 mmol), DMAP (250 mg, 2.0 mmol), DIPEA (0.68 mL, 3.6 mmol), and EDCI (387 mg, 2.0 mmol) were added sequentially at room temperature, and the resulting mixture was then stirred at the same temperature for another 5 h, ethyl acetate was added to dilute the reaction, the resultant solution was washed with water, brine, and then dried over Na_2SO_4. Filtration was followed by concentration to yield the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 30 : 1) to afford **13** (820 mg, 65%) as a white solid. For α isomer: $[\alpha]^{28}_D$ = -4.1 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 2 H), 7.86 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.63-7.59 (m, 1 H), 7.51 (td, *J* = 6.4, 1.6 Hz, 3 H), 7.46 (td, *J* = 7.2, 1.6 Hz, 1 H), 7.34-7.23 (m, 11 H), 6.23 (d, *J* = 2.0 Hz, 1 H), 5.77 (dd, *J* = 2.4, 3.6 Hz, 1 H), 4.94 (AB, 2 H), 4.87 (AB, 2 H), 4.27 (dd, *J* = 3.6, 9.6 Hz, 1 H), 4.13-4.06 (m, 1 H), 3.67 (t, *J* = 9.6 Hz, 1 H), 1.60-1.54 (m, 1 H), 1.43 (d, *J* = 6.0 Hz, 3 H), 0.86-0.75 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.3, 137.5, 137.0, 133.8, 132.6, 131.4, 130.0, 129.9, 129.3, 129.0, 127.8, 127.6 (2 C), 127.4 (2 C), 127.0 (2 C), 126.4, 124.2, 99.4, 91.4, 78.9, 77.2, 74.9, 74.0, 71.1, 69.8, 67.7, 17.5, 8.3, 0.0; HRMS (MALDI) Calcd for $C_{39}H_{36}O_7Na$ $[M+Na]^+$ 639.2353, found 639.2354; For β-isomer: $[\alpha]^{28}_D$ = 21.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 2 H), 7.72 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.63-7.58 (m, 1 H), 7.51-7.47 (m, 2 H), 7.43 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.37-7.24 (m, 11 H), 7.11 (td, *J* = 8.0, 1.6 Hz, 1 H), 6.07 (d, *J* = 1.2 Hz, 1 H), 5.96 (dd, *J* = 1.2, 3.2 Hz, 1 H), 4.96 (AB, 2 H), 4.85 (AB, 2 H), 3.89 (dd, *J* = 3.2, 8.8 Hz, 1 H), 3.71-3.64 (m, 1 H), 3.63 (t, *J* = 8.8 Hz, 1 H), 1.52-1.47 (m, 1 H), 1.46 (d, *J* = 6.0 Hz, 3 H), 0.88-0.85 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 162.6, 137.4, 136.8, 133.6, 132.5, 131.4, 130.0, 129.4, 129.3, 129.2, 127.8, 127.7, 127.5, 127.4, 127.2, 126.2, 124.9, 99.4, 91.0, 79.2, 78.8, 74.8, 73.6, 72.1, 70.8, 67.8, 17.4, 8.2, 0.0; HRMS (MALDI) Calcd for $C_{39}H_{36}O_7Na$ $[M+Na]^+$ 639.2353, found 639.2353.

7,4'-Di-*O*-hexanoyl-5-*O*-(4''-*O*-(2'''-*O*-benzoyl-3''',4'''-di-*O*-benzyl-α-L-rhamnopyranosyl)-2'',6''-di-*O*-benzoyl-3''-*O*-benzyl-β-D-glucopyranosyl) apigenin (14)

To a solution of **13** (168 mg, 0.27 mmol) and **11** (42 mg, 0.045 mmol) in dry CH_2Cl_2

(6 mL) was added 4Å MS under N_2 atmosphere. The resulting mixture was stirred at room temperature for 30 minutes and then $Ph_3PAuOTf$ prepared by combination of Ph_3PAuCl and AgOTf in dry CH_2Cl_2 in the presence of 5Å MS (0.025 mol/L, 1.08 mL, 0.027 mmol) was added. The stirring was continued at room temperature for 7 h. The mixture was filtered, the filtrate was concentrated under reduced pressure to yield a residue which was further purified by silica gel chromatography (eluent system: PE/EA = 3 : 1) to provide **14** (61 mg, 91%) as a white solid: $[\alpha]^{28}_D$ = -27.8 (*c* 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 2 H), 8.01-7.95 (m, 4 H), 7.81 (d, *J* = 8.8 Hz, 2 H), 7.58-7.09 (m, 23 H), 7.02 (d, *J* = 2. 0 Hz, 1 H), 6.86 (d, *J* = 2.0 Hz, 1 H), 6.50 (s, 1 H), 5.81 (t, *J* = 6.4 Hz, 1 H), 5.55 (t, *J* = 2.4 Hz, 1 H), 5.51 (d, *J* = 6.0 Hz, 1 H), 5.21 (d, *J* = 2.0 Hz, 1 H), 4.92-4.88 (m, 2 H), 4.85 (d, *J* = 10.8 Hz, 1 H), 4.76 (d, *J* = 10.4 Hz, 1 H), 4.72 (d, *J* = 11.6 Hz, 1 H), 4.62 (d, *J* = 10.8 Hz, 1 H), 4.54 (d, *J* = 11.6 Hz, 1 H), 4.47 (dd, *J* = 4.8, 12.4 Hz, 1 H), 4.36 (t, *J* = 8.0 Hz, 1 H), 4.05-3.96 (m, 4 H), 3.54 (t, *J* = 9.6 Hz, 1 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.47 (t, *J* = 7.6 Hz, 2 H), 1.79-1.68 (m, 4 H), 1.42-1.34 (m, 8 H), 1.16 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 171.9, 171.2, 165.9, 165.8, 165.2, 160.3, 157.8, 156.6, 154.0, 153.2, 138.6, 138.0, 137.4, 133.2, 133.1, 132.9, 130.0, 129.9 (2 C), 129.8, 129.7, 128.7, 128.5, 128.4, 128.3 (2 C), 128.2, 128.0 (2 C), 127.6 (2 C), 127.4, 122.3, 113.8, 108.8, 108.7, 106.0, 99.3, 97.7, 80.4, 80.0, 77.6, 75.3, 74.3, 74.2, 73.8, 72.8, 71.5, 69.6, 68.7, 63.1, 34.4, 34.3, 31.3, 31.2, 24.6, 24.4, 22.3, 18.0, 14.0; HRMS (MALDI) Calcd for $C_{81}H_{81}O_{19}$ $[M+H]^+$ 1357.5367, found 1357.5364.

Apigenin 5-*O*-(4”-O-α-L-rhamnosyl)-β-D-glucopyranoside (1)

To a solution of **14** (41 mg, 0.03 mmol) in a mixed solvent of EtOH, CH_2Cl_2, and ethyl acetate (V/V/V = 2 : 1 : 1, 4 mL) was added Pd/C (41 mg) at room temperature. The reaction vessel was evacuated and then refilled with H_2, and this process was repeated for three times, and the resultant dark suspension was stirred at room temperature for another 20 h. Filtration through a pad of silica gel and then the dark solid was then washed with CH_2Cl_2 thoroughly. The filtrates were combined and concentrated under reduced pressure to give a residue which was further purified by silica gel chromatography (eluent system: PE/EA = 2 : 1) to afford the debenzylated

intermediate.

The above obtained debenzylated intermediate (34 mg, 0.027 mmol) was dissolved in absolute MeOH (3 mL), to which a freshly prepared NaOMe solution in absolute MeOH was added dropwise at 0 ^{o}C. The resultant solution was stirred at 0 ^{o}C for another 30 minutes, and then the temperature was warmed to room temperature, and the stirring was continued for 1.5 h. Weak acid resin (Amberlite IRC-76) was added to quench the reaction, and the mixture was stirred at room temperature for another 1.5 h. Filtration, washing the resin with MeOH thoroughly, and concentration of the filtrate to afford the crude product which was further purified by C18 RP chromatography (eluent system: MeOH/H_2O = 1 : 2) to provide **1** (13 mg, 76%) as a light yellow solid: $[\alpha]^{28}_{D}$ = -35.3 (*c* 0.4, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.84 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 2.4 Hz, 1 H), 6.71 (d, *J* = 2.4 Hz, 1 H), 6.58 (s, 1 H), 5.79 (s, 1 H), 4.90 (d, *J* = 1.6 Hz, 1 H), 4.89 (d, *J* = 7.2 Hz, 1 H), 4.04-4.00 (m, 1 H), 3.93 (dd, *J* = 2.0, 12.4 Hz, 1 H), 3.76-3.61 (m, 5 H), 3.58-3.53 (m, 1 H), 3.44 (t, *J* = 9.6 Hz, 1 H), 1.12 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, CD_3OD) δ 179.0, 163.6, 162.9, 161.2, 159.3, 158.6, 127.9, 121.7, 115.6, 107.9, 105.1, 103.3 (2 C), 101.5, 97.9, 77.7, 76.0, 74.6, 73.4, 72.4, 71.1, 70.8, 69.3, 60.4, 16.4; HRMS (MALDI) Calcd for $C_{27}H_{31}O_{14}$ $[M+H]^{+}$ 579.1708, found 579.1709.

Dimethylthexylsilyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranoside (15)

To a solution of **7** (1.1 g, 1.9 mmol) and Et_3SiH (1.58 mL, 10.0 mmol) in dry CH_2Cl_2 (15 mL) was added TFA (1 N in DCM, 10 mL, 10 mmol) dropwise at 0 ^{o}C. After stirring at the same temperature for another 7 h, saturated $NaHCO_3$ was added to quench the reaction, and then diluted with ethyl acetate. The solution was washed with saturated $NaHCO_3$, brine, and then dried over Na_2SO_4. Filtration was followed by concentration under reduced pressure to yield the crude product which was further purified by silica gel chromatography (eluent system: PE/EA = 6 : 1) to provide **15** (1.0 mg, 91%) as a yellow syrup: $[\alpha]^{28}_{D}$ = -2.0 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2 H), 7.58-7.54 (m, 1 H), 7.45 (td, *J* = 6.4, 2.0 Hz, 2 H), 7.38-7.28 (m, 5 H), 7.21-7.16 (m, 5 H), 5.24 (dd, *J* = 8.0, 10.0 Hz, 1 H), 4.79 (d, *J* = 8.0 Hz, 1 H), 4.74 (AB, 2 H), 4.64 (AB, 2 H), 3.83 (t, *J* = 9.2 Hz, 1 H), 3.78 (d, *J* =

4.8 Hz, 2 H), 3.67 (t, *J* = 9.2 Hz, 1 H), 3.56-3.51 (m, 1 H), 2.76 (brs, 1 H), 1.52-1.45 (m, 1 H), 0.72 (q, *J* = 3.6 Hz, 12 H), 0.14 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 140.0, 139.7, 134.8, 132.1, 131.6, 130.3, 130.2 (2 C), 129.9, 129.6 (3 C), 97.9, 84.0, 77.0, 76.0, 75.6, 74.2, 72.5, 35.7, 26.5, 21.7, 21.6, 20.2 (2 C), 0.0, -1.6; HRMS (MALDI) Calcd for $C_{35}H_{46}O_7SiNa$ $[M+Na]^+$ 629.2905, found 629.2904.

Dimethylthexylsilyl

4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranoside (16)

Similar procedure as that used for the synthesis of **9** was adopted to get **16** (0.9 mg, 92%) as a white solid: $[\alpha]^{28}_D$ = 60.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2 H), 7.88-7.85 (m, 2 H), 7.75-7.72 (m, 2 H), 7.70-7.67 (m, 2 H), 7.44-7.15 (m, 12 H), 7.11-6.98 (m, 7 H), 6.85-6.81 (m, 3 H), 5.67 (dd, *J* = 3.6, 10.4 Hz, 1 H), 5.46-5.42 (m, 2 H), 5.25 (dd, *J* = 7.6, 9.2 Hz, 1 H), 5.16 (d, *J* = 3.6 Hz, 1 H), 4.70 (d, *J* = 7.2 Hz, 1 H), 4.66 (AB, 2 H), 4.51 (AB, 2 H), 4.22-4.15 (m, 1 H), 4.08 (t, *J* = 10.0 Hz, 1 H), 3.77-3.72 (m, 2 H), 3.65 (dd, *J* = 2.0, 11.6 Hz, 1 H), 3.46 (dt, *J* = 9.6, 2.4 Hz, 1 H), 1.37-1.30 (m, 1 H), 0.69 (d, *J* = 6.0 Hz, 3 H), 0.57-0.54 (m, 12 H), 0.00 (s, 3 H), -0.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (2 C), 166.9, 140.0, 139.5, 135.4, 135.1, 135.0, 134.8, 131.9, 131.8, 131.5 (3 C), 131.2, 131.0, 130.4, 130.2 (2 C), 130.1, 129.9, 129.6, 129.4, 129.3, 129.2, 99.0, 98.0, 83.0, 77.7, 77.1, 76.4, 76.2, 75.0, 73.6, 73.0, 71.8, 70.0, 69.0, 35.7, 26.5, 21.7, 21.6, 20.3, 20.2, 18.9, 0.0, -1.5; HRMS (MALDI) Calcd for $C_{62}H_{68}O_{14}SiNa$ $[M+Na]^+$ 1087.4274, found 1087.4265.

4-*O*-(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranosyl *ortho*-cyclopropylethynylbenzote (17)

Similar procedure as that used for the synthesis of **8** was applied to get disaccharide donor **17** (368 mg, 80%) as a white solid. For α-isomer: $[\alpha]^{28}_D$ = -62.8 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2 H), 8.00 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.92-7.85 (m, 6 H), 7.63-7.13 (m, 21 H), 7.03-6.97 (m, 3 H), 6.78 (d, *J* = 3.6 Hz, 1 H), 5.76 (dd, *J* = 3.6, 10.4 Hz, 1 H), 5.64-5.56 (m, 3 H), 5.34 (d, *J* = 1.6 Hz, 1 H), 4.97 (AB, 2 H), 4.65 (AB, 2 H), 4.46-4.35 (m, 4 H), 4.00 (dd, *J* = 2.0, 12.4 Hz, 1 H), 3.85

(d, *J* = 11.6 Hz, 1 H), 1.61 (m, 1 H), 1.04-0.99 (m, 2 H), 0.98-0.86 (m, 2 H), 0.86 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.8 (2 C), 164.4, 163.5, 136.8, 136.7, 134.1, 132.7, 132.4 (2 C), 132.3, 131.3, 130.1, 129.6, 129.0, 128.8, 128.7, 128.5, 128.4 (2 C), 128.2, 127.7, 127.5 (2 C), 127.4, 127.3, 126.9, 126.7 (2 C), 126.4, 124.1, 99.3, 96.2, 90.0, 77.3, 74.5, 74.1, 72.9 (2 C), 72.4, 72.1, 70.8, 70.2, 69.1, 66.8, 66.3, 16.1, 8.4 (2 C), 0.0; HRMS (MALDI) Calcd for $C_{66}H_{58}O_{15}Na$ $[M+Na]^+$ 1113.3668, found 1113.3665.

7,4'-Di-*O*-hexanoyl-5-*O*-(4''-*O*-(2''',3''',4'''-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2''-*O*-benzoyl-3'',6''-di-*O*-benzyl-β-D-glucopyranosyl) apigenin (18)

Similar procedure as that used for the synthesis of **9** was adopted to get **18** (42 mg, 48%) as a white solid: $[\alpha]^{28}_D$ = 8.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2 Hz, 2 H), 8.09-8.06 (m, 2 H), 7.94 (dd, *J* = 1.2, 8.0 Hz, 2 H), 7.87 (dd, *J* = 1.2, 8.0 Hz, 2 H), 7.83-7.80 (m, 2 H), 7.63-7.59 (m, 1 H), 7.55-7.37 (m, 9 H), 7.33-7.05 (m, 15 H), 7.02 (d, *J* = 2.4 Hz, 1 H), 6.51 (s, 1 H), 5.94 (t, *J* = 6.8 Hz, 1 H), 5.82 (dd, *J* = 3.2, 10.0 Hz, 1 H), 5.64-5.58 (m, 2 H), 5.46 (d, *J* = 6.4 Hz, 1 H), 5.32 (d, *J* = 1.6 Hz, 1 H), 4.98 (AB, 2 H), 4.65 (AB, 2 H), 4.48 (t, *J* = 8.8 Hz, 1 H), 4.38-4.29 (m, 1 H), 4.07 (t, *J* = 8.0 Hz, 1 H), 3.95 (dd, *J* = 2.0, 12.0 Hz, 1 H), 3.90-3.86 (m, 2 H), 2.60 (t, *J* = 7.2 Hz, 2 H), 2.51 (dd, *J* = 6.8, 8.0 Hz, 2 H), 1.79-1.69 (m, 4 H), 1.41-1.35 (m, 8 H), 0.96-0.91 (m, 6 H), 0.90 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 171.9, 171.2, 165.7 (2 C), 165.2, 160.3, 157.9, 156.9, 154.0, 163.1, 138.0, 137.5, 133.5, 133.3, 133.2, 133.0, 130.1, 130.0, 129.9, 129.7 (2 C), 129.4, 129.2, 128.8, 128.6, 128.5, 128.4 (2 C), 128.3 (2 C), 128.2 (2 C), 128.0, 127.5, 127.4 (2 C), 127.3, 122.3, 114.2, 109.8, 108.9, 106.3, 100.1, 97.3, 81.1, 75.6, 74.3, 74.2, 73.2, 73.1, 71.7, 71.1, 70.0, 68.3, 67.3, 34.4, 34.3, 31.3, 31.2, 24.6, 24.4, 22.3 (2 C), 17.1, 14.0; HRMS (MALDI) Calcd for $C_{81}H_{78}O_{20}Na$ $[M+Na]^+$ 1393.4984, found 1393.4965.

Dimethylthexylsilyl 4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2-*O*-benzoyl -β-D-glucopyranoside (19)

To a solution of **16** (300 mg, 0.3 mmol) in a mixed solvent of CH_2Cl_2 and MeOH (V/V = 1 : 1, 8 mL) was added was added Pd/C (150 mg) at room temperature. The reaction vessel was evacuated and then refiled with H_2, and this process was repeated

for three times, then the black suspension was stirred at room temperature for 16 h. Filtration and the filtrate was concentrated under reduced pressure to yield the crude product which was further purified by silica gel chromatography (PE/EA = 4 : 1) to provide **19** (224 mg, 90%) as a white solid: $[\alpha]^{28}_{D}$ = 58.4 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (m, 4 H), 7.80-7.77 (m, 2 H), 7.68-7.66 (m, 2 H), 7.44-7.22 (m, 6 H), 7.20-7.16 (m, 2 H), 7.11-7.07 (m, 2 H), 5.64 (dd, *J* = 3.6, 10.4 Hz, 1 H), 5.55 (t, *J* = 10.0 Hz, 1 H), 5.47 (dd, *J* = 2.0, 3.6 Hz, 1 H), 5.09 (d, *J* = 2.0 Hz, 1 H), 4.95 (dd, *J* = 7.6, 8.8 Hz, 1 H), 4.78 (d, *J* = 7.6 Hz, 1 H), 4.42-4.35 (m, 1 H), 3.87 (dd, *J* = 2.4, 12.4 Hz, 1 H), 3.82-3.73 (m, 3 H), 3.46-3.42 (m, 1 H), 1.37-1.30 (m, 1 H), 1.17 (d, *J* = 6.4 Hz, 3 H), 0.57-0.54 (m, 12 H), 0.00 (s, 3 H), -0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.5 (3 C), 135.4, 135.1, 135.0 (2 C), 131.8, 131.7, 131.6, 131.5 (2 C), 131.0 (2 C), 130.9, 130.4, 130.2, 130.1, 100.5, 97.5, 81.2, 78.2, 76.8, 76.1, 73.2, 72.7, 71.6, 69.6, 63.3, 35.6, 26.5, 21.7, 21.6, 20.2 (2 C), 19.3, 0.0, -1.5; HRMS (MALDI) Calcd for $C_{48}H_{56}O_{14}SiNa$ $[M+Na]^+$ 907.3332, found 907.3329.

Dimethylthexylsilyl

4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl

-β-D-glucopyranoside (20)

To a solution of **19** (200 mg, 0.2 mmol) and DMAP (24 mg, 0.2 mmol) in dry pyridine (3 mL) was added BzCl (0.1 mL, 0.9 mmol) dropwise at 0 ^{o}C. After the addition was completed, the ice-bath was removed and the reaction mixture was stirred at 60 ^{o}C for another 6 h. Ethyl acetate was added to dilute the reaction and the solution was washed with water, 1 N HCl, saturated $NaHCO_3$, brine successively, and then dried over Na_2SO_4. Filtration and concentration yield a residue which was further purified by silica gel chromatography (eluent system: PE/EA = 5 : 1) to give **20** (227 mg, 92%) as a white solid: $[\alpha]^{28}_{D}$ = 49.3 (*c* 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.10 (m, 2 H), 8.00-7.82 (m, 10 H), 7.58-7.34 (m, 14 H), 7.30 (q, *J* = 8.4 Hz, 4 H), 5.87 (t, *J* = 9.6 Hz, 1 H), 5.72 (dd, *J* = 3.2, 10.4 Hz, 1 H), 5.58 (q, *J* = 2.0 Hz, 1 H), 5.55 (t, *J* = 10.0 Hz, 1 H), 5.41 (dd, *J* = 7.6, 10.0 Hz, 1 H), 5.24 (d, *J* = 1.6 Hz, 1 H), 5.06-5.02 (m, 2 H), 4.70 (dd, *J* = 4.8, 12.4 Hz, 1 H), 4.31 (t, 9.2 Hz, 1 H), 4.09-3.98 (m, 2 H), 1.50-1.43 (m, 1 H), 0.77 (d, *J* = 5.4 Hz, 3 H), 0.70-0.68 (m, 12 H), 0.12 (s, 3

H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.6 (2 C), 167.5, 167.2, 135.4, 135.3, 135.2 (2 C), 135.0, 132.0, 131.9, 131.7 (2 C), 131.6, 131.4, 131.2 (3 C), 130.5, 130.4 (2 C), 130.3 (2 C), 100.8, 97.9, 76.2, 75.9, 75.6, 73.3, 73.1, 71.5, 69.8, 64.7, 35.9, 26.7, 21.8 (2 C), 20.4, 20.3, 19.1, 0.0, -1.5; HRMS (MALDI) Calcd for $C_{62}H_{64}O_{16}SiNa$ $[M+Na]^+$ 1115.3865, found 1115.3857.

4-*O*-(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl *ortho*-cyclopropylethynylbenzote (21)

Similar procedure as that used for the synthesis of **8** was applied to get disaccharide donor **21** (102 mg, 80%) as a white solid. For α-isomer: $[\alpha]^{28}_D$ = 84 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2 H), 8.03-8.00 (m, 2 H), 7.92-7.82 (m, 9 H), 7.57-7.20 (m, 21 H), 6.32 (d, *J* = 8.0 Hz, 1 H), 6.01 (t, *J* = 9.2 Hz, 1 H), 5.75-5.70 (m, 2 H), 5.59-5.56 (m, 1 H), 5.55 (t, 10.0 Hz, 1 H), 5.28 (d, *J* = 1.6 Hz, 1 H), 5.08 (dd, *J* = 2.0, 12.8 Hz, 1 H), 4.74 (dd, *J* = 3.6, 12.8 Hz, 1 H), 4.52 (t, *J* = 9.6 Hz, 1 H), 4.32-4.28 (m, 1 H), 4.06-4.02 (m, 1 H), 1.53-1.47 (m, 1 H), 0.88-0.86 (m, 4 H), 0.81 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.1, 164.9, 164.7, 164.6, 162.6, 133.6, 132.7, 132.6, 132.4, 132.3, 131.7, 130.1, 129.2, 129.1, 129.0 (2 C), 128.7, 128.5 (2 C), 128.4, 128.1, 127.7 (2 C), 127.6 (2 C), 126.3, 125.1, 99.9, 98.3, 91.6, 75.7, 73.6, 73.5, 73.2, 70.7, 70.6, 70.4, 68.7, 67.2, 61.7, 16.4, 8.3 (2 C), 0.0; HRMS (MALDI) Calcd for $C_{66}H_{54}O_{17}Na$ $[M+Na]^+$ 1141.3253, found 1141.3256.

7,4'-Di-*O*-hexanoyl-5-*O*-(4"-*O*-(2"',3"',4"'-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2",3",6"-tri-*O*-benzoyl-β-D-glucopyranosyl) apigenin (22)

Similar procedure as that used for the synthesis of **9** was adopted to provide **22** (43 mg, 46%) as a white solid: $[\alpha]^{28}_D$ = 32.5 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.2 Hz, 2 H), 8.07 (d, *J* = 7.2 Hz, 2 H), 7.95 (d, *J* = 7.6 Hz, 4 H), 7.88-7.80 (m, 6 H), 7.56-7.45 (m, 5 H), 7.44-7.35 (m, 10 H), 7.32 (t, *J* = 7.6 Hz, 3 H), 7.24 (d, *J* = 7.2 Hz, 2 H), 6.96 (d, *J* = 2.0 Hz, 1 H), 6.82 (d, *J* = 2.0 Hz, 1 H), 6.48 (s, 1 H), 5.93 (dd, *J* = 6.4, 8.8 Hz, 1 H), 5.82 (t, *J* = 5.6 Hz, 1 H), 5.75 (dd, *J* = 3.2, 10.0 Hz, 1 H), 5.70 (d, *J* = 5.6 Hz, 1 H), 5.62 (q, *J* = 1.6 Hz, 1 H), 5.59 (t, *J* = 10.0 Hz, 1 H), 5.34 (d, *J* = 1.2 Hz, 1 H), 5.20 (dd, *J* = 2.0, 12.8 Hz, 1 H), 4.91 (t, *J* = 9.2 Hz, 1 H), 4.62 (dd, *J* = 3.6, 12.8 Hz, 1 H), 4.36-4.33 (m, 1 H), 4.15-4.08 (m, 1 H), 2.61 (t, *J* =

7.6 Hz, 2 H), 2.56 (t, *J* = 7.2 Hz, 2 H), 1.79-1.74 (m, 4 H), 1.41-1.38 (m, 8 H), 0.97-0.92 (m, 6 H), 0.88 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 171.9, 171.2, 166.1, 165.7, 165.6, 165.5, 165.1, 160.0, 157.8, 156.2, 154.0, 153.1, 133.4, 133.3, 133.2, 132.7, 130.3, 130.0, 129.9, 129.8, 129.7, 129.5 (2 C), 129.4, 129.2 (2 C), 128.8, 128.5, 128.4 (2 C), 128.3 (2 C), 128.1, 127.3, 122.3, 113.4, 108.9, 106.6, 105.7, 98.9, 97.6, 75.7, 74.3, 73.8, 72.7, 71.4, 71.0, 69.6, 67.8, 62.1, 34.4, 31.3, 31.2, 24.6, 24.4, 22.3, 17.2, 14.0 (2 C); HRMS (MALDI) Calcd for $C_{81}H_{75}O_{22}$ $[M+H]^+$ 1399.4750, found 1399.4737.

Synthesis of authentic camellianin B via decetylation of camellianin A

To a solution of commercially available camellianin A (10 mg, 0.016 mmol) in methol (2 mL) was added freshly prepared NaOMe solution in MeOH (50 μL) at 0 ^{o}C. Then the reaction temperature was gradually raised to rt, and the stirring was continued for another 1 h at room temperature. Acid resin (Amberlite IRC-76) was added to quench the reaction and adjust the pH value to 4. Filtration and concentration under reduced pressure to yield a residue which was further purified by C_{18} RP chromatography (eluent system: MeOH/H_2O = 1 : 2) to afford the proposed camellianin A (8.5 mg, 91%) as a white solid: $[\alpha]^{28}_D$ = -24.2 (*c* 0.36, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.82 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.62 (d, *J* = 2.4 Hz, 1 H), 6.60 (d, *J* = 2. 4 Hz, 1 H), 6.51 (s, 1 H), 5.38 (d, *J* = 1.6 Hz, 1 H), 5.30 (d, *J* = 7.2 Hz, 1 H), 3.96-3.83 (m, 4 H), 3.70-3.65 (m, 2 H), 3.63 (dd, *J* = 7.2, 8.0 Hz, 1 H), 3.58-3.54 (m, 2 H), 1.13 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, CD_3OD) δ 178.1, 163.2, 162.1, 160.9, 159.5, 158.1, 127.7, 121.9, 115.5, 107.4, 105.2, 100.1, 99.3, 99.0, 96.3, 77.6, 77.2, 76.6, 72.9, 70.9, 70.7, 70.0, 68.7, 61.2, 16.6.

Acetylation of authentic camellianin B which was obtained by deacetylation of camellianin A

To a solution of camellianin B derived from authentic camellianin A (8.5 mg, 0.015 mmol) in dry pyridine (1 mL) was added DMAP (2 mg) and Ac_2O (1 mL) dropwise at 0 ^{o}C. After the addition was completed, the ice-bath was removed and the reaction mixture was stirred at 35 ^{o}C for another 37 h. General procedure was adopted to get the crude product which was further purified by silica gel chromatography (eluent

system: PE/EA = 2 : 3) to afford the proposed peracetylated camellianin B (13 mg, 98%) as a white powder: $[\alpha]^{28}_{D}$ = -60.0 (*c* 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 2.0 Hz, 1 H), 6.75 (d, *J* = 2.0 Hz, 1 H), 6.62 (s, 1 H), 5.44 (d, *J* = 2.0 Hz, 1 H), 5.36 (t, *J* = 8.8 Hz, 1 H), 5.28 (d, *J* = 6.4 Hz, 1 H), 5.22-5.15 (m, 3 H), 5.02 (t, *J* = 9.6 Hz, 1 H), 4.32-4.20 (m, 2 H), 4.16-4.13 (m, 1 H), 3.98-3.88 (m, 2 H), 2.37 (s, 3 H), 2.35 (s, 3 H), 2.17 (s, 6 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.97 (s, 6 H), 0.96 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 170.6, 170.5, 170.2, 170.0, 169.8, 169.6, 169.0, 168.2, 160.4, 158.1, 156.6, 153.9, 153.1, 128.7, 127.4, 122.4, 113.7, 109.0, 106.5, 105.8, 99.7, 97.5, 73.2, 72.0, 70.9, 69.6, 68.9, 68.2, 67.1, 62.1, 21.2 (2 C), 21.0, 20.8, 20.7 (2 C), 20.6, 17.1.

Comparison of reported data of camellianin B

Table S1. ^{1}H NMR comparison of reported data of camellianin B

Number	Data reported by Cheng et al.[S3] (DMSO-d_6)	Data reported by Deng et al.[S4] (DMSO-d_6 400 MHz)
H-3	6.75 (s, 1 H)	6.52 (s, 1 H)
H-6 and 8	6.83 (d, *J* = 2.5 Hz, 2 H)	For **H-6**: 6.50 (s, 1 H); For **H-8**: 6.60 (s, 1 H)
H-3’ and 5’	7.20 (d, *J* = 8.0 Hz, 2 H)	6.91 (d, *J* = 8.7 Hz, 2 H)
H-2’ and 6’	8.16 (d, *J* = 8.0 Hz, 2 H)	7.86 (d, *J* = 8.7 Hz, 2 H)
H-4’	11.72 (s, 1 H)	10.21 (s, 1 H)
H-7	12.32 (s, 1 H)	10.76 (s, 1 H)
H-6’’’	1.17 (d, *J* = 6.0 Hz, 3 H)	1.17 (d, *J* = 6.0 Hz, 3 H)
H-2’’, 3’’, 4’’, 5’’, 6’’, 2’’’, 3’’’, 4’’’, and 5’’’	4.96-3.10 (m, 10 H)	4.96-3.10 (m, 10 H)
H-1’’	5.50 (d, *J* = 6.0 Hz, 1 H)	5.24 (d, *J* = 5.9 Hz, 1 H)
H-1’’’	5.42 (s, 1 H)	5.19 (s, 1 H)

^{1}H NMR and ^{13}C NMR comparison of camellianin B between synthetic sample and authentic sample derived from camellianin A

Table S2. ^{1}H NMR comparison of reported data for camellianin B

Number[a]	Sample derived from camellianin A (CD_3OD, 400 MHz)	Synthetic sample (CD_3OD, 400 MHz)
1	7.82 (d, *J* = 8.8 Hz, 2 H)	7.84 (d, *J* = 8.8 Hz, 2 H)
2	6.93 (d, *J* = 8.8 Hz, 2 H)	6.93 (d, *J* = 8.8 Hz, 2 H)
3	6.62 (d, *J* = 2.4 Hz, 1 H)	6.78 (d, *J* = 2.4 Hz, 1 H)
4	6.60 (d, *J* = 2.4 Hz, 1 H)	6.71 (d, *J* = 2.4 Hz, 1 H)
5	6.51 (s, 1 H)	6.58 (s, 1 H)
6	5.38 (d, *J* = 1.6 Hz, 1 H)	4.90 (d, *J* = 1.6 Hz, 1 H)
7	5.30 (d, *J* = 7.2 Hz, 1 H)	4.89 (d, *J* = 7.2 Hz, 1 H)
8	3.96-3.83 (m, 4 H)	4.04-4.00 (m, 1 H), 3.93 (dd, *J* = 2.0, 12.4 Hz, 1 H), 3.87 (dd, *J* = 1.6, 3.2 Hz, 1 H)
9	3.70-3.65 (m, 2 H)	3.76-3.61 (m, 5 H)
10	3.63 (dd, *J* = 7.2, 8.0 Hz, 1 H)	3.58-3.53 (m, 1 H)
11	3.58-3.54 (m, 2 H)	3.44 (t, *J* = 9.6 Hz, 1 H)
12	1.13 (d, *J* = 6.4 Hz, 3 H)	1.29 (d, *J* = 6.0 Hz, 3 H)

[a] Sequence number

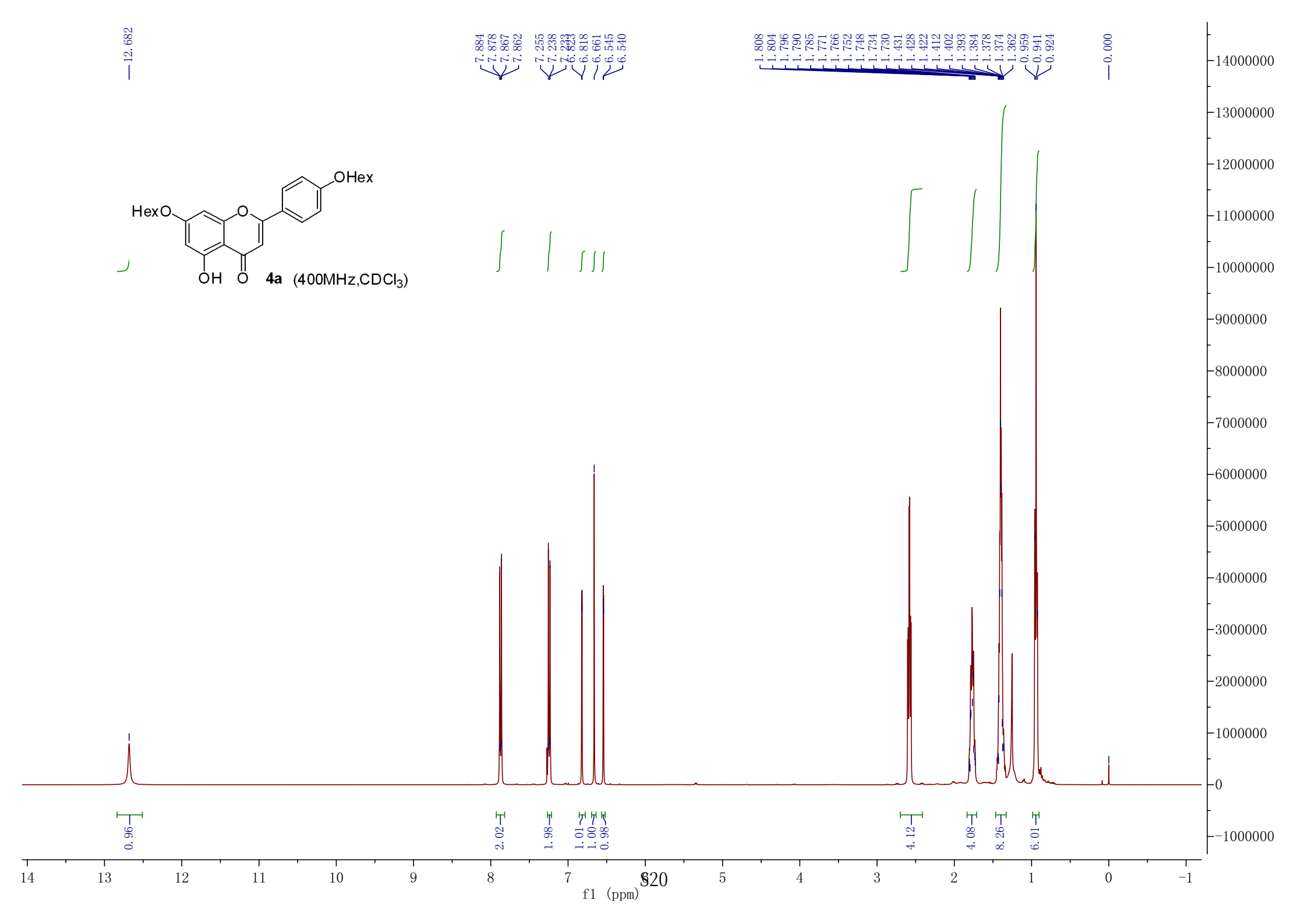
References:

[S1] Nitz, M.; Bundle, D. R. *J. Org. Chem*. **2001**, *66*, 8411-8423.

[S1] (a) Boutet, J.; Mulard, L. A. *Eur. J. Org. Chem*. **2008**, 5526-5542. (b) Barroso, S.; Geerdink, D.; Horst, B. t.; Casas-Arce, E.; Minnaard, A. J. *Eur. J. Org. Chem*. **2013**, 4642-4654.

[S3] Cheng, G.; Jin, J.; Wen, Y. *Acta Pharmaceutica. Sinica* **1987**, *22*, 203-207.

[S4] Li, W.; Dai, R.-J.; Yu, Y.-H.; Li, L.; Wu, C.-M.; Luan, W.-W.; Meng W.-W.; Zhuang, X.-S.; Deng, Y.-L. *Biol. Pharm. Bull*. **2007**, *30*, 1123-1129.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1.804
1.796
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1.771
1.766
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1.431
1.428
1.422
1.412
1.402
1.393
1.384
1.378
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1.362
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0.941
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0.000
HexO
OHex
OH
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O
4a (400MHz,CDCl3)
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1.98
1.01
1.00
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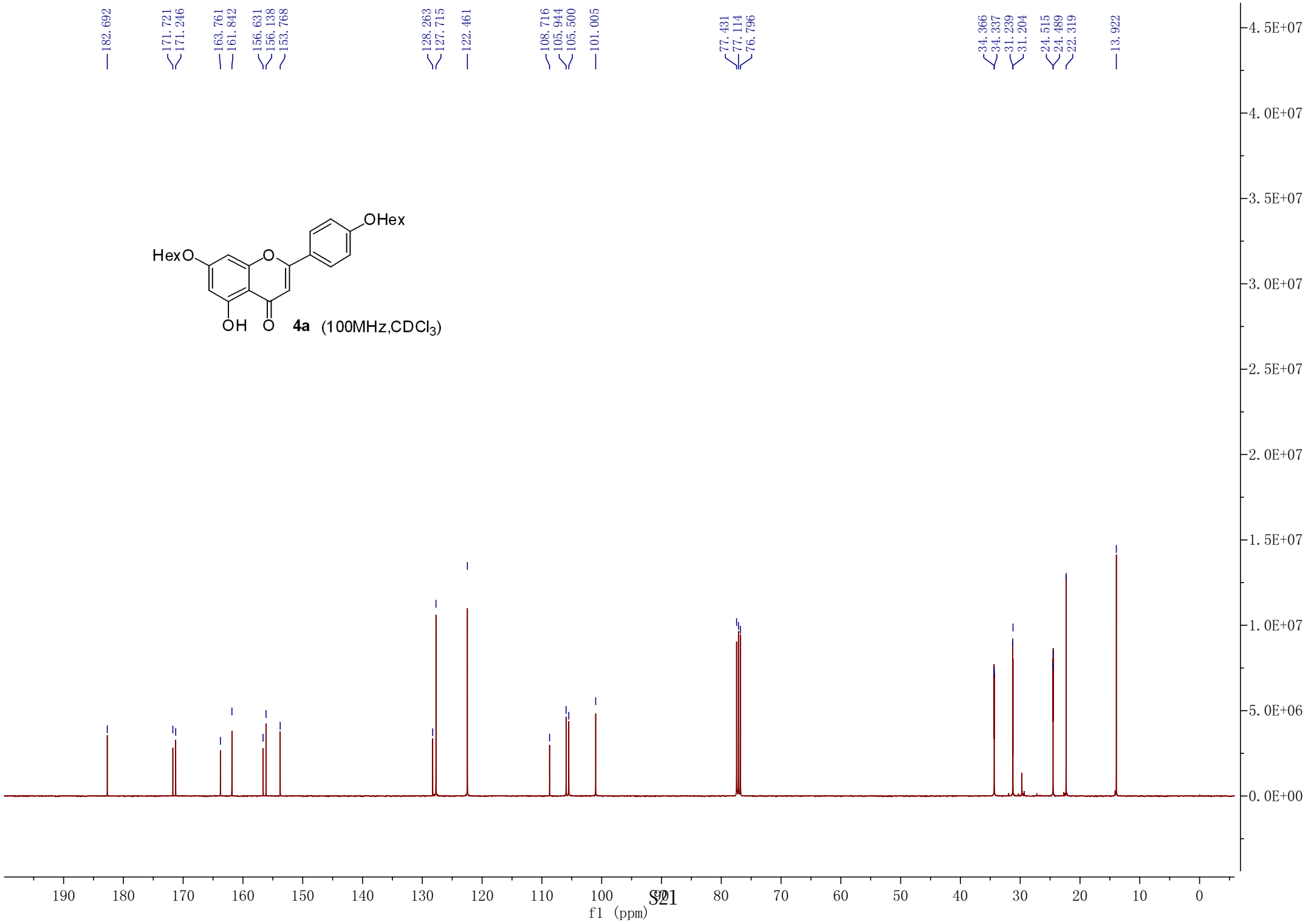
8.26
6.01
f1 (ppm)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127.715
122.461
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105.944
105.500
101.005
77.431
77.114
76.796
34.366
34.337
31.239
31.204
24.515
24.489
22.319
13.922
OHex
HexO
O
OH
O
4a (100MHz,CDCl3)
4.5E+07
4.0E+07
3.5E+07
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2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
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180
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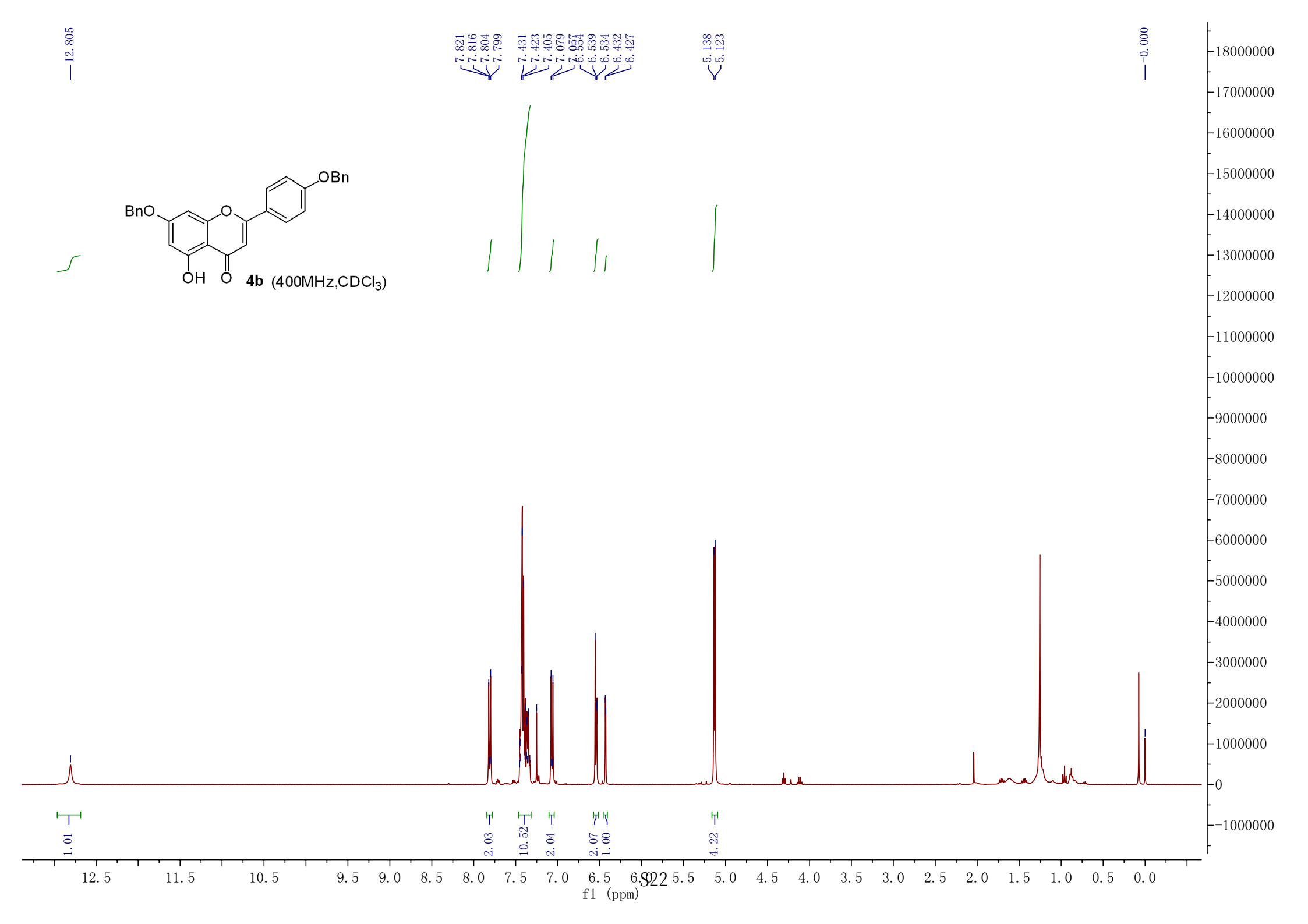
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6.432
6.427
5.138
5.123
0.000
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OBn
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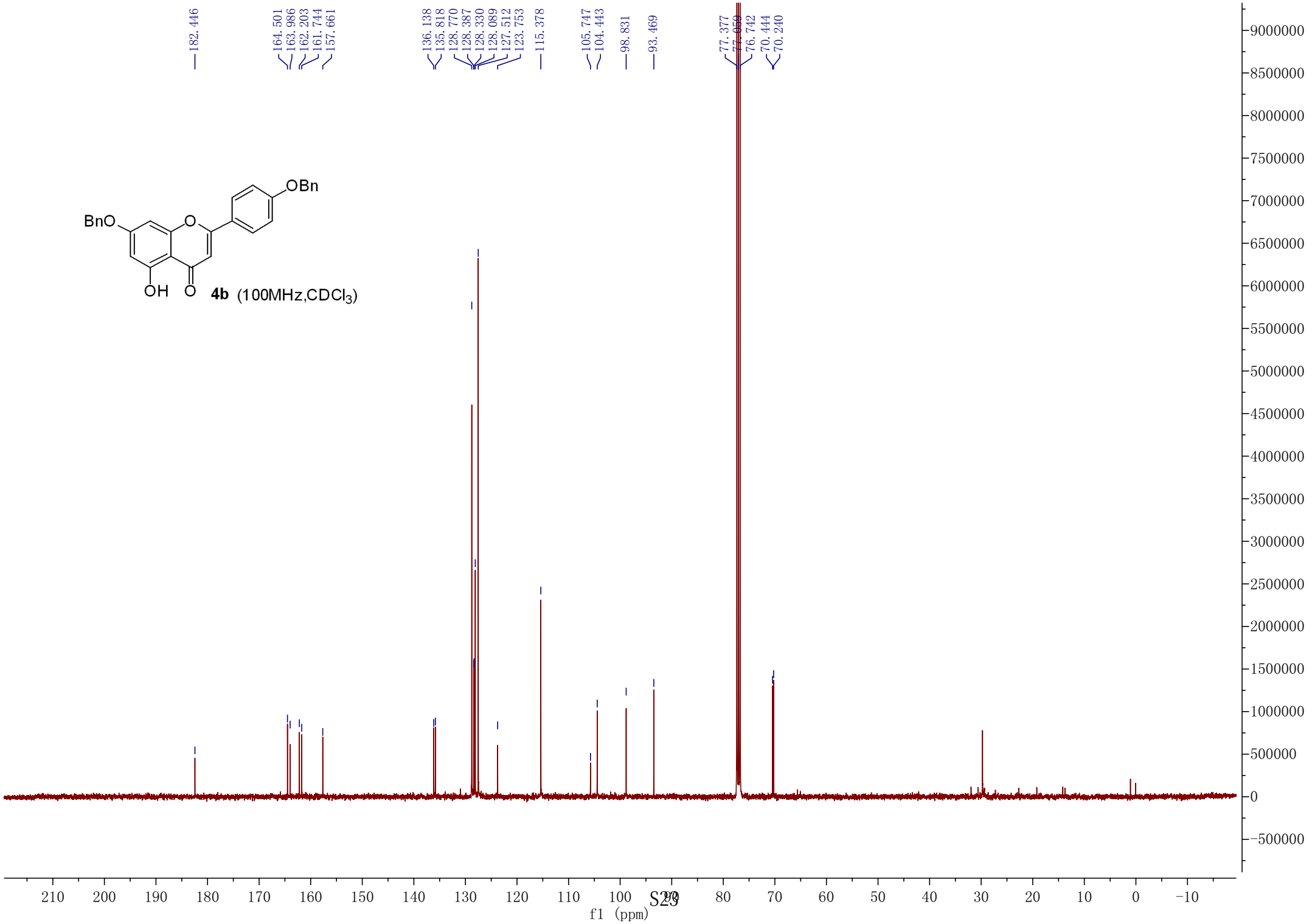
2.07
1.00
4.22
f1 (ppm)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123.753
115.378
105.747
104.443
98.831
93.469
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OBn
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OH
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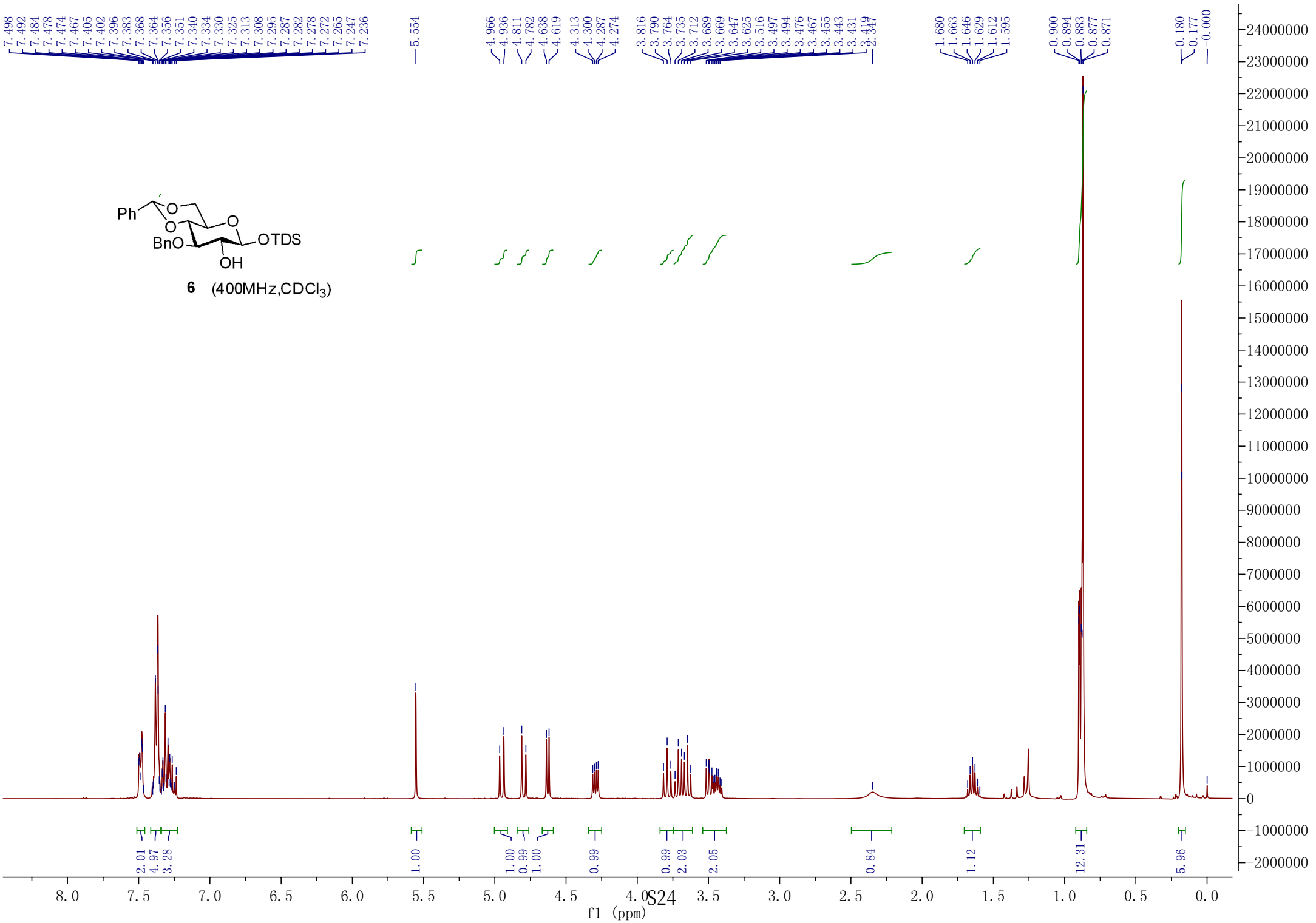
f1 (ppm)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OH
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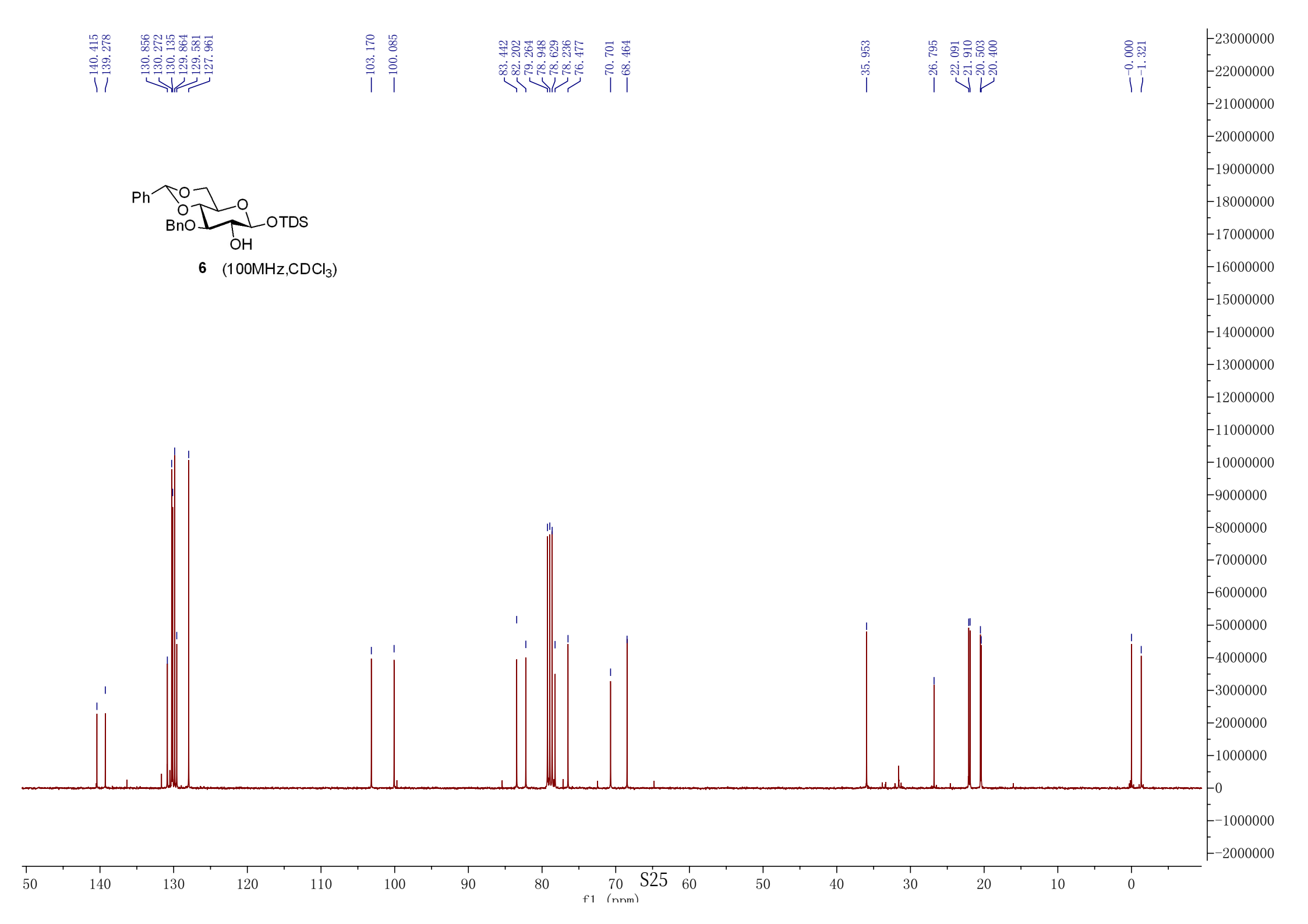
f1 (ppm)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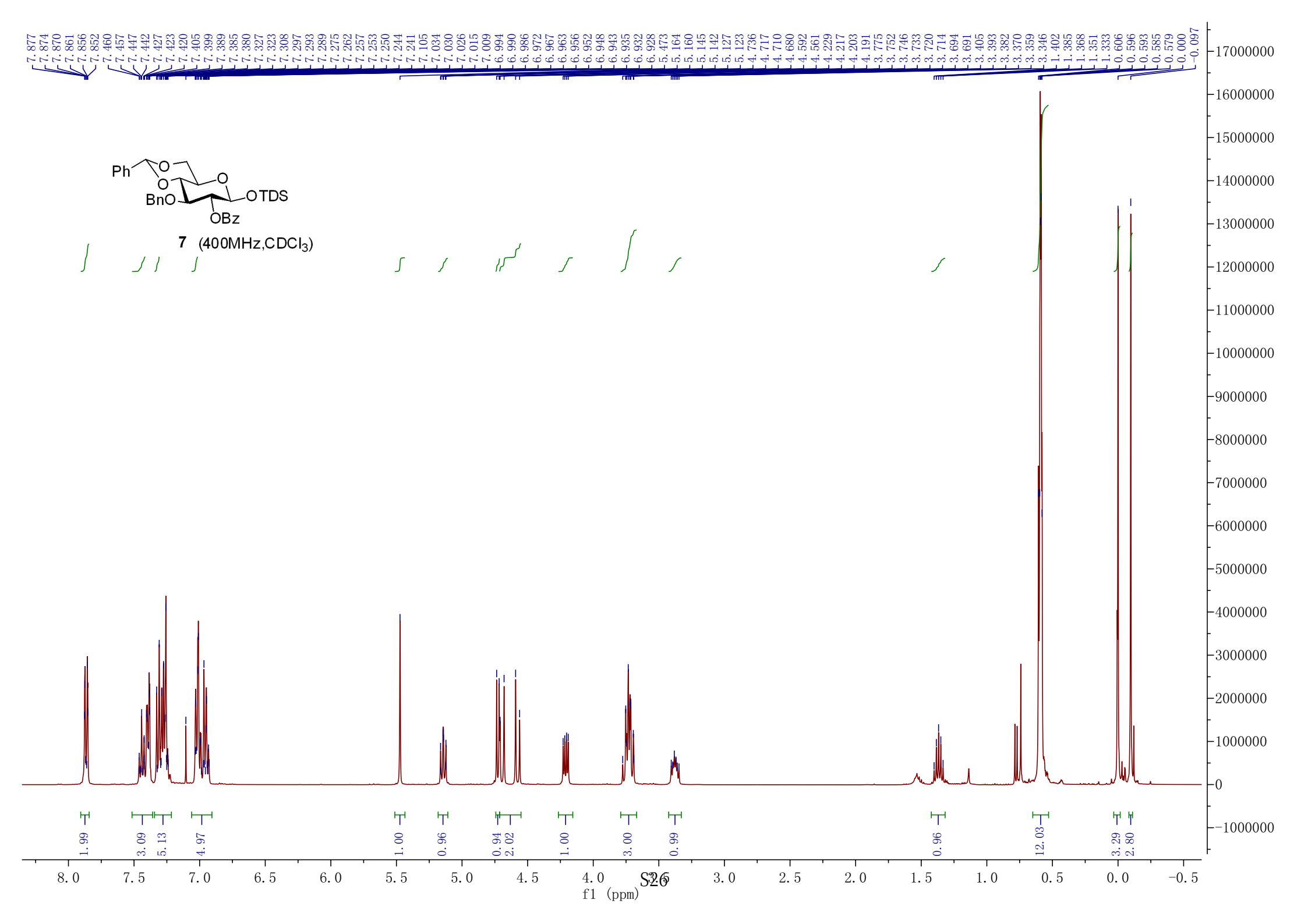
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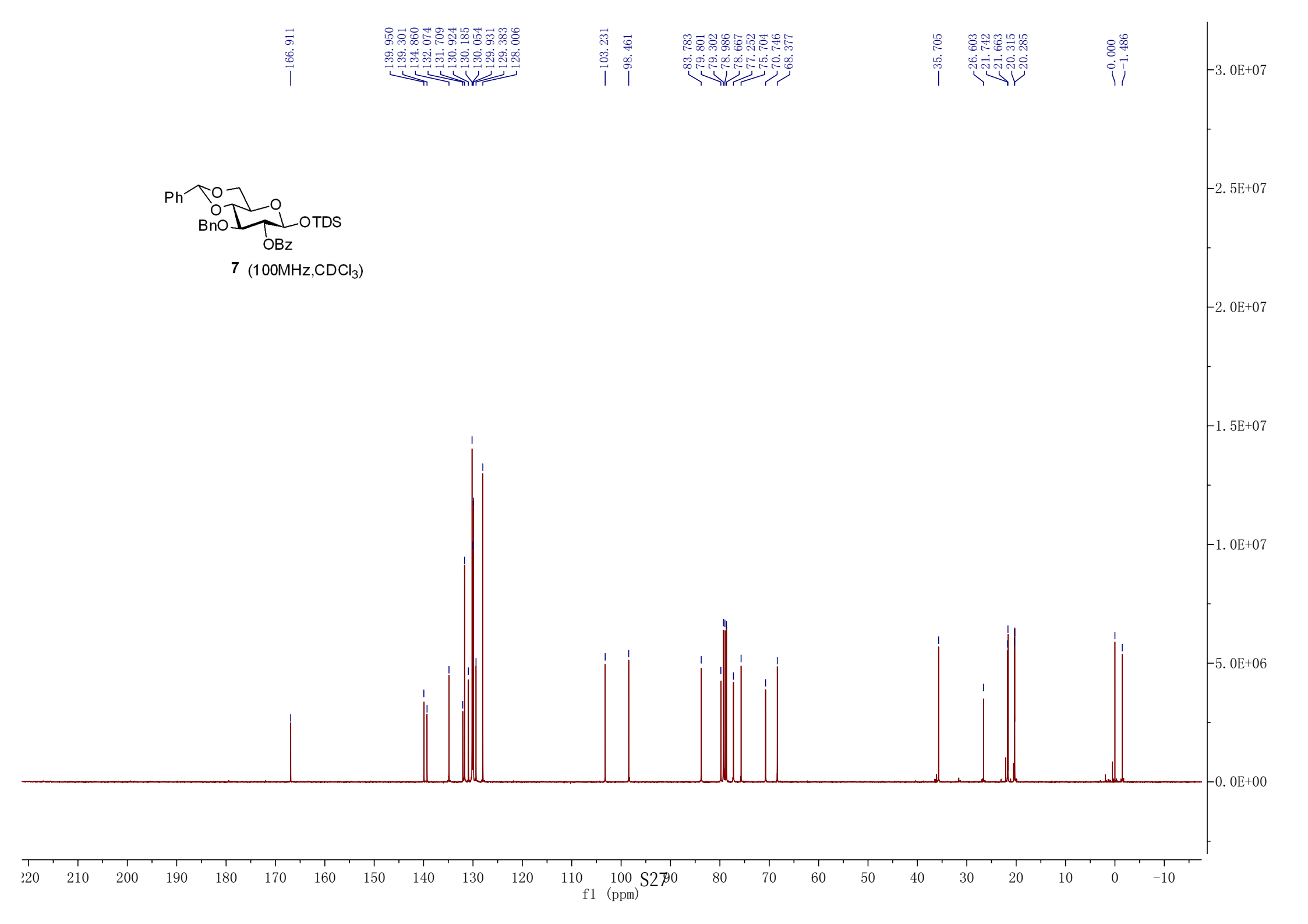
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79.302
78.986
78.667
77.252
75.704
70.746
68.377
35.705
26.603
21.742
21.663
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O
O
BnO
OTDS
OBz
7 (100MHz,CDCl3)
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2.0E+07
1.5E+07
1.0E+07
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200
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180
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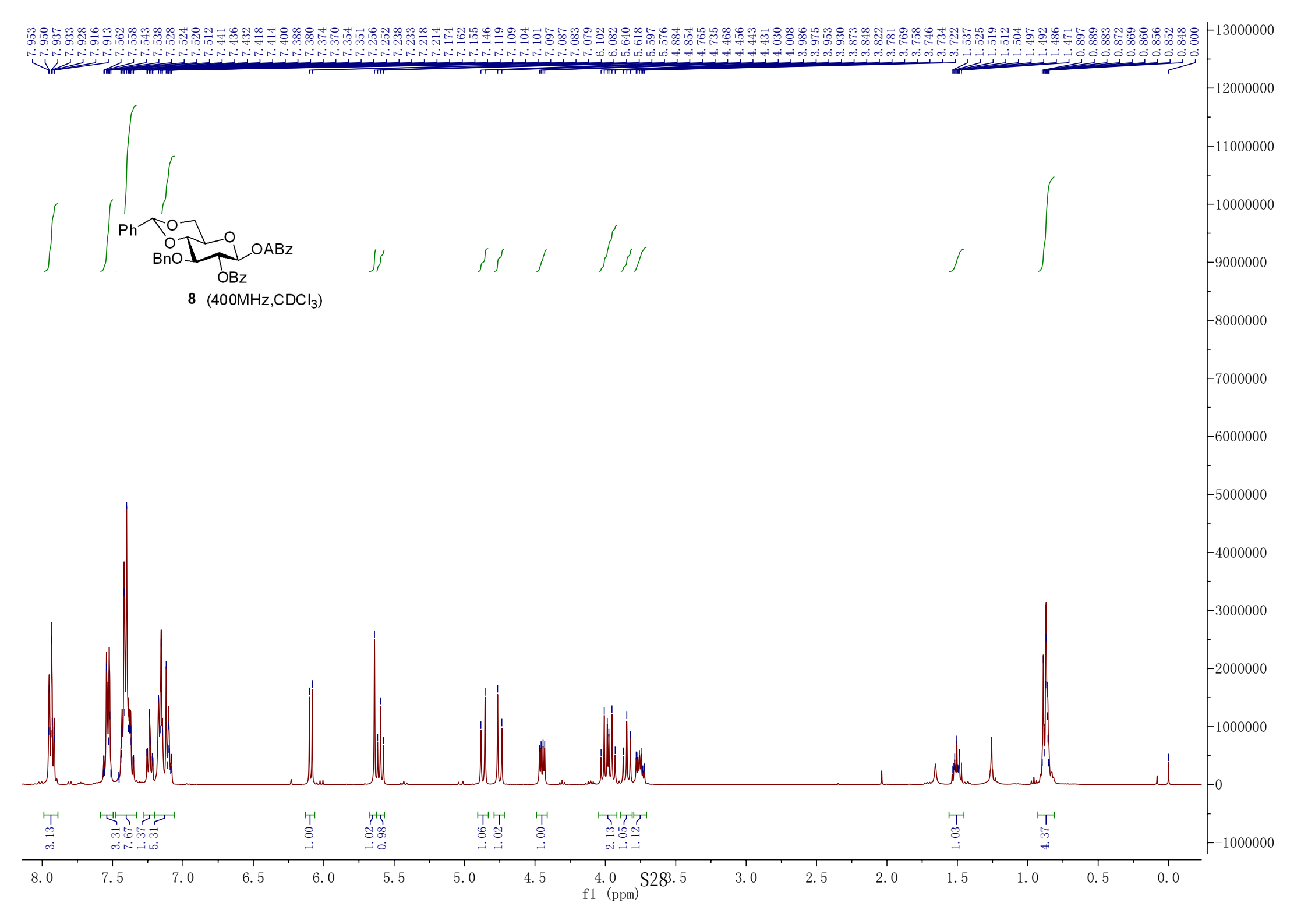
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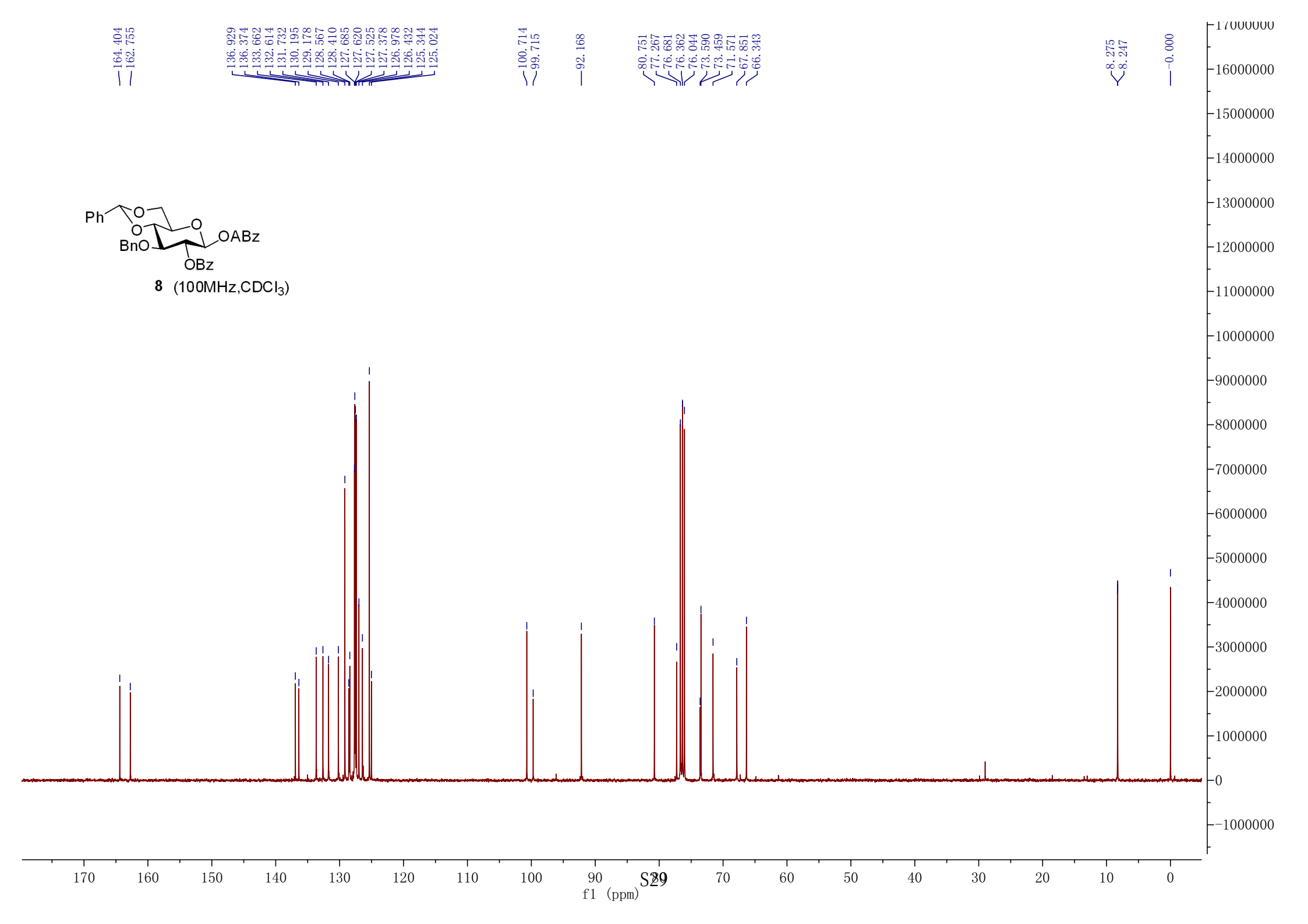
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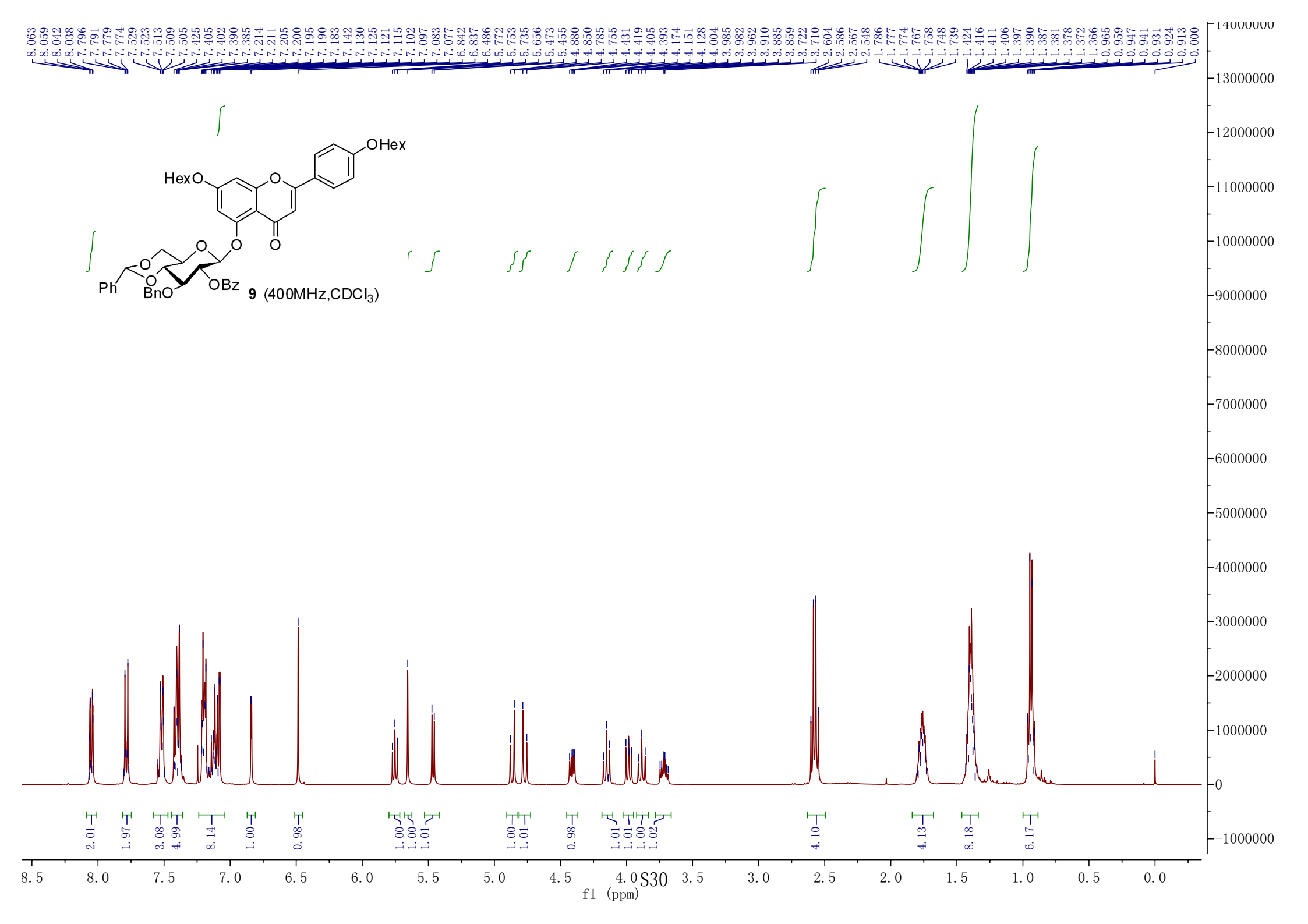
f1 (ppm)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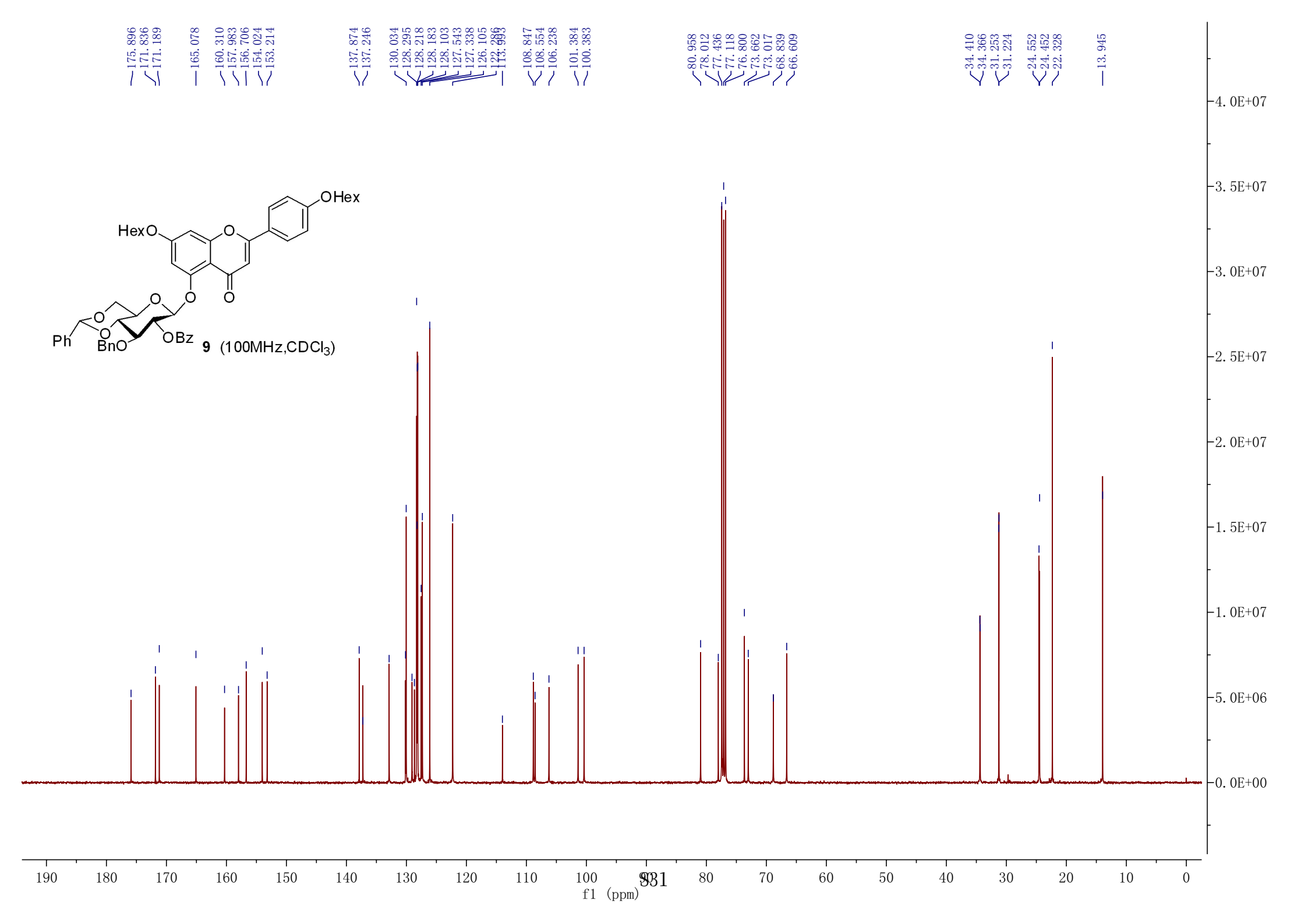
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BnO
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180
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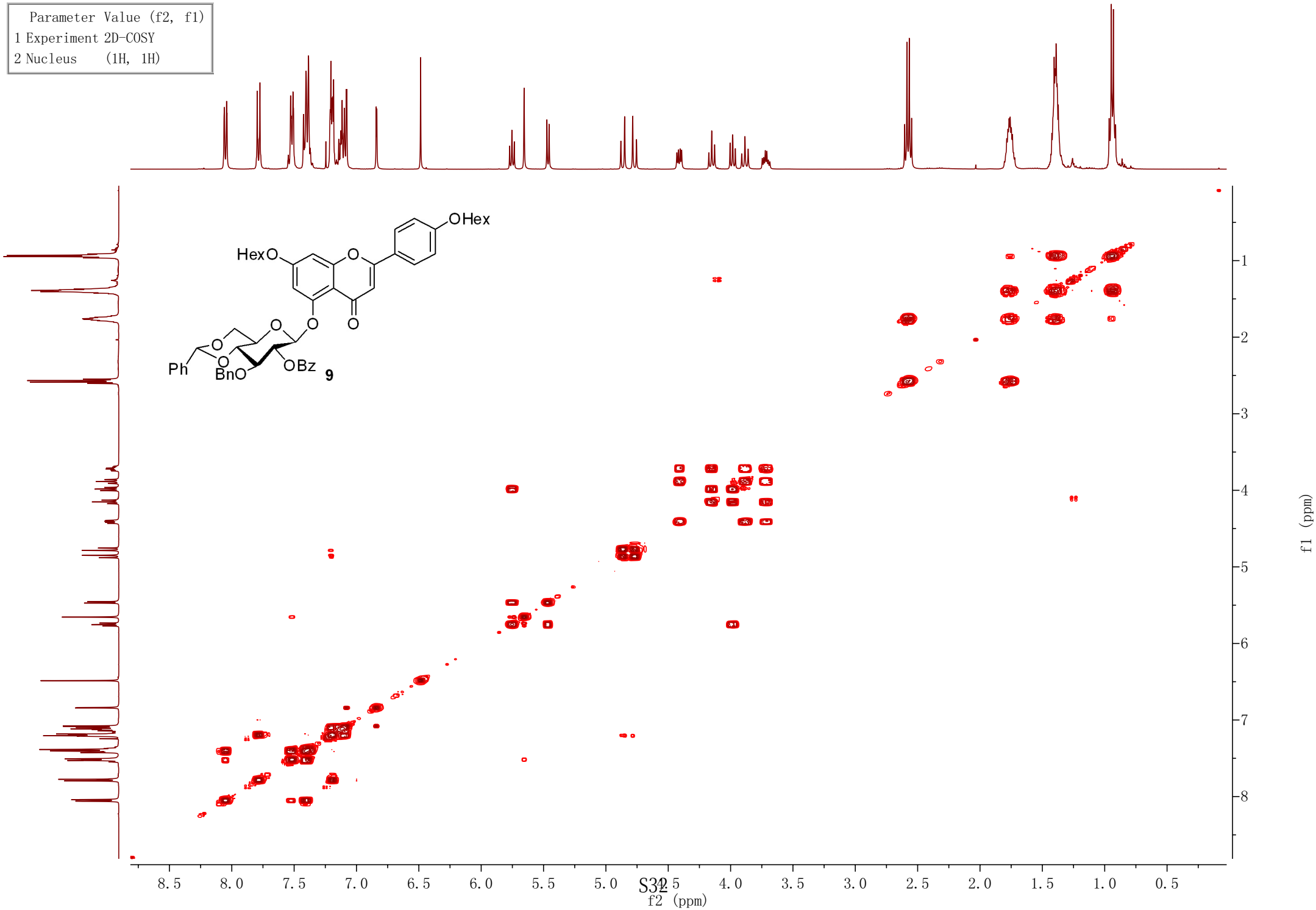
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BnO
OBz
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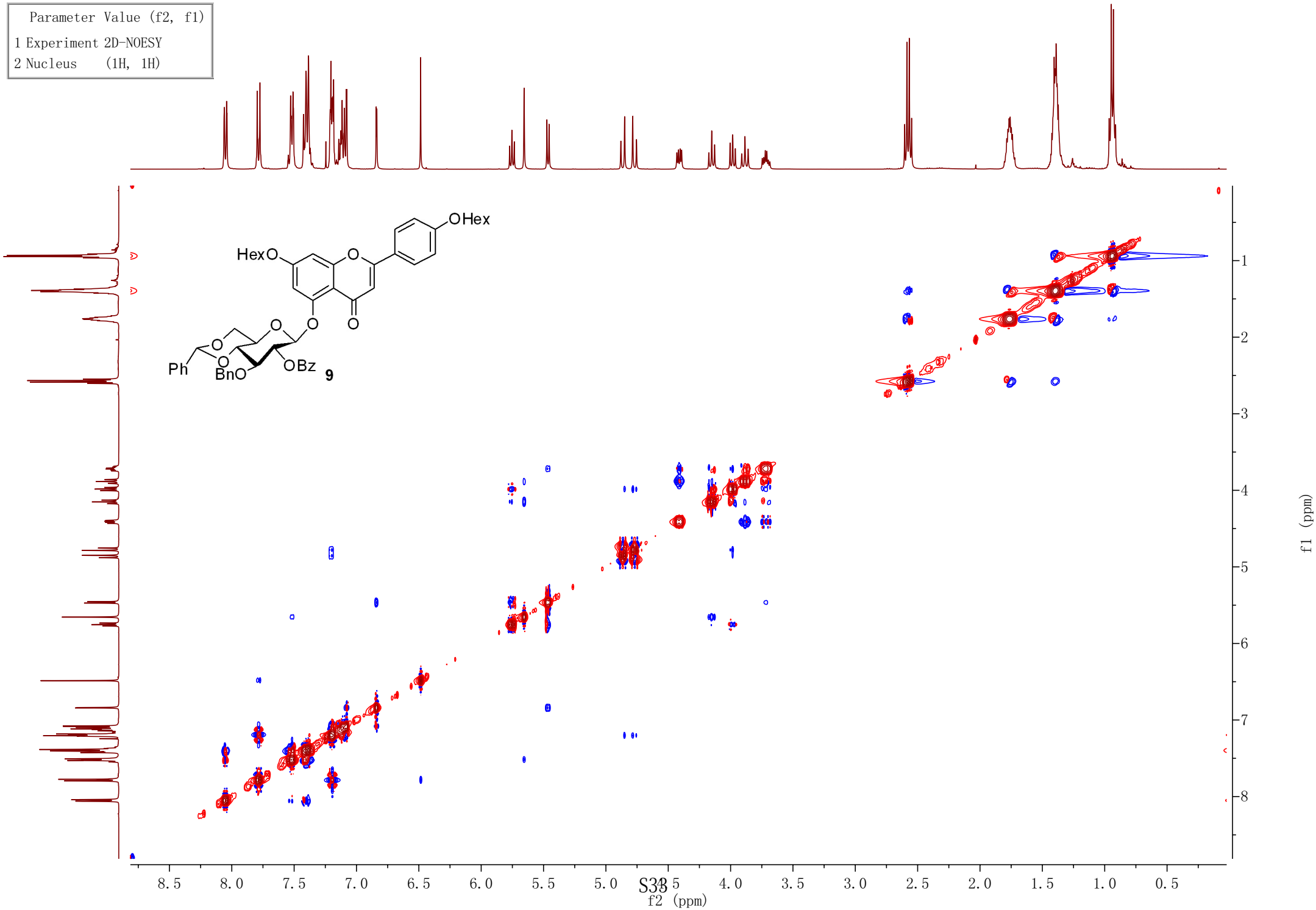
f1 (ppm)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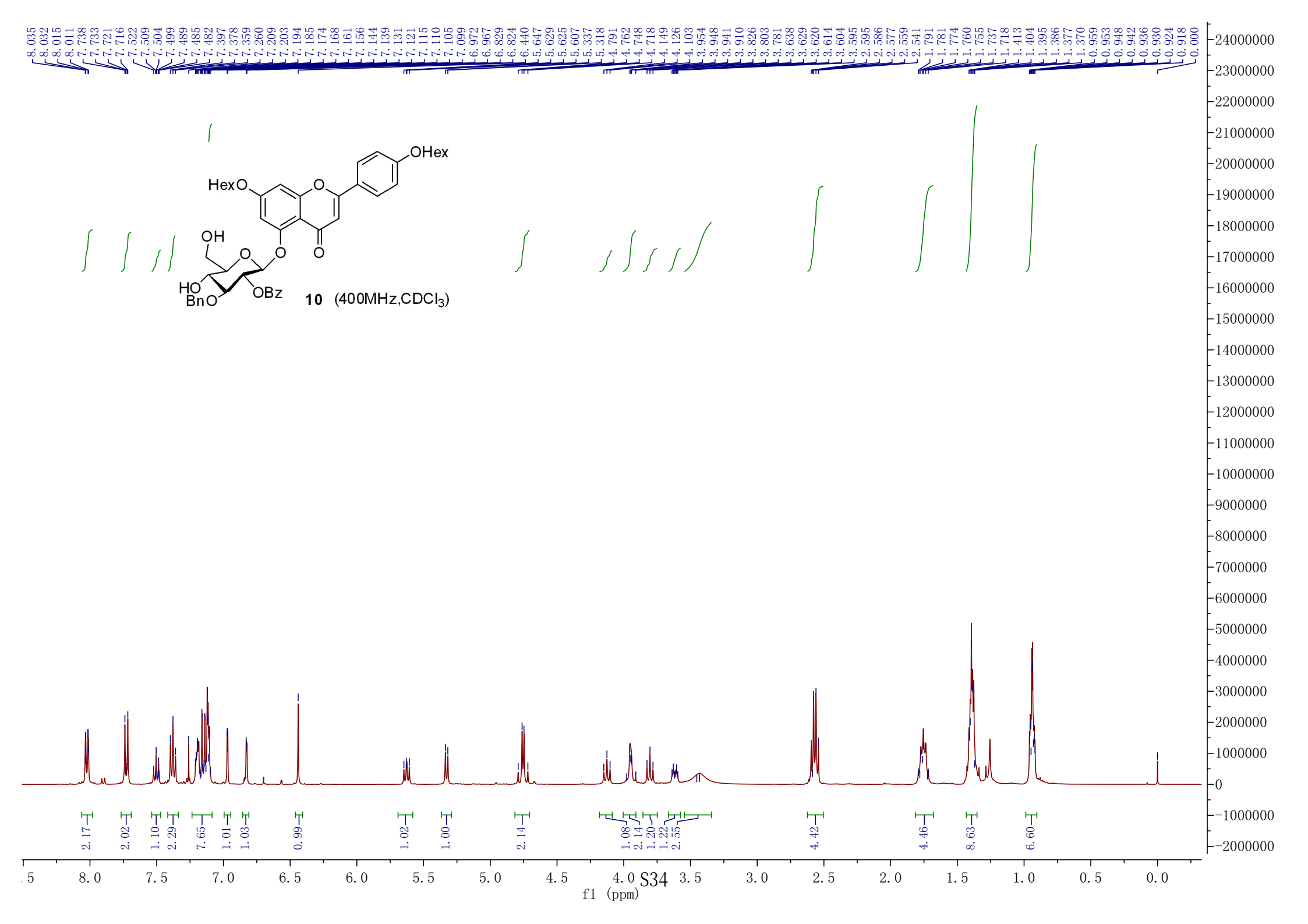
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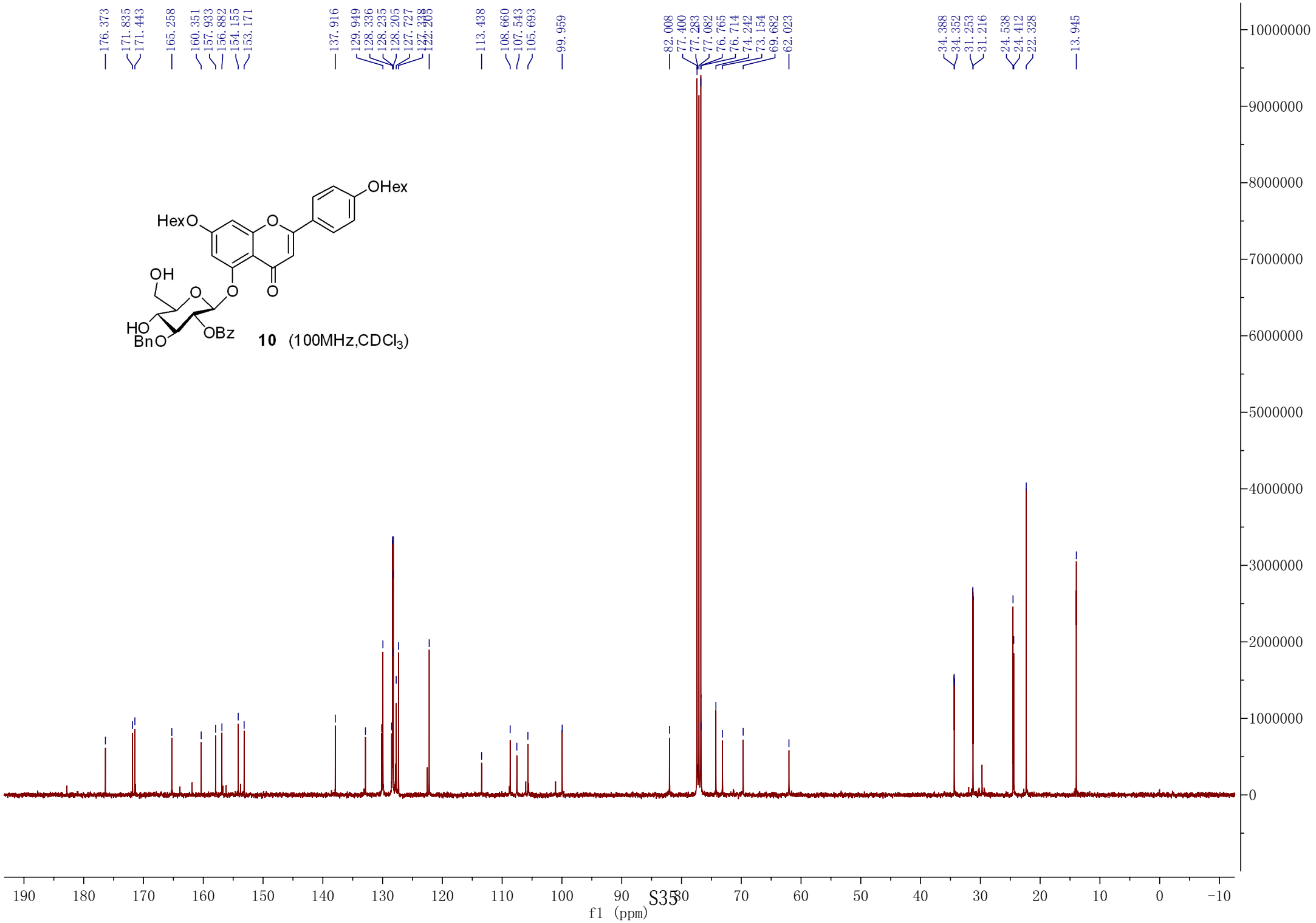
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31.216
24.538
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22.328
13.945
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HexO
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OH
O
O
O
HO
BnO
OBz
10 (100MHz,CDCl3)
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8000000
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6000000
5000000
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3000000
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0
190
180
170
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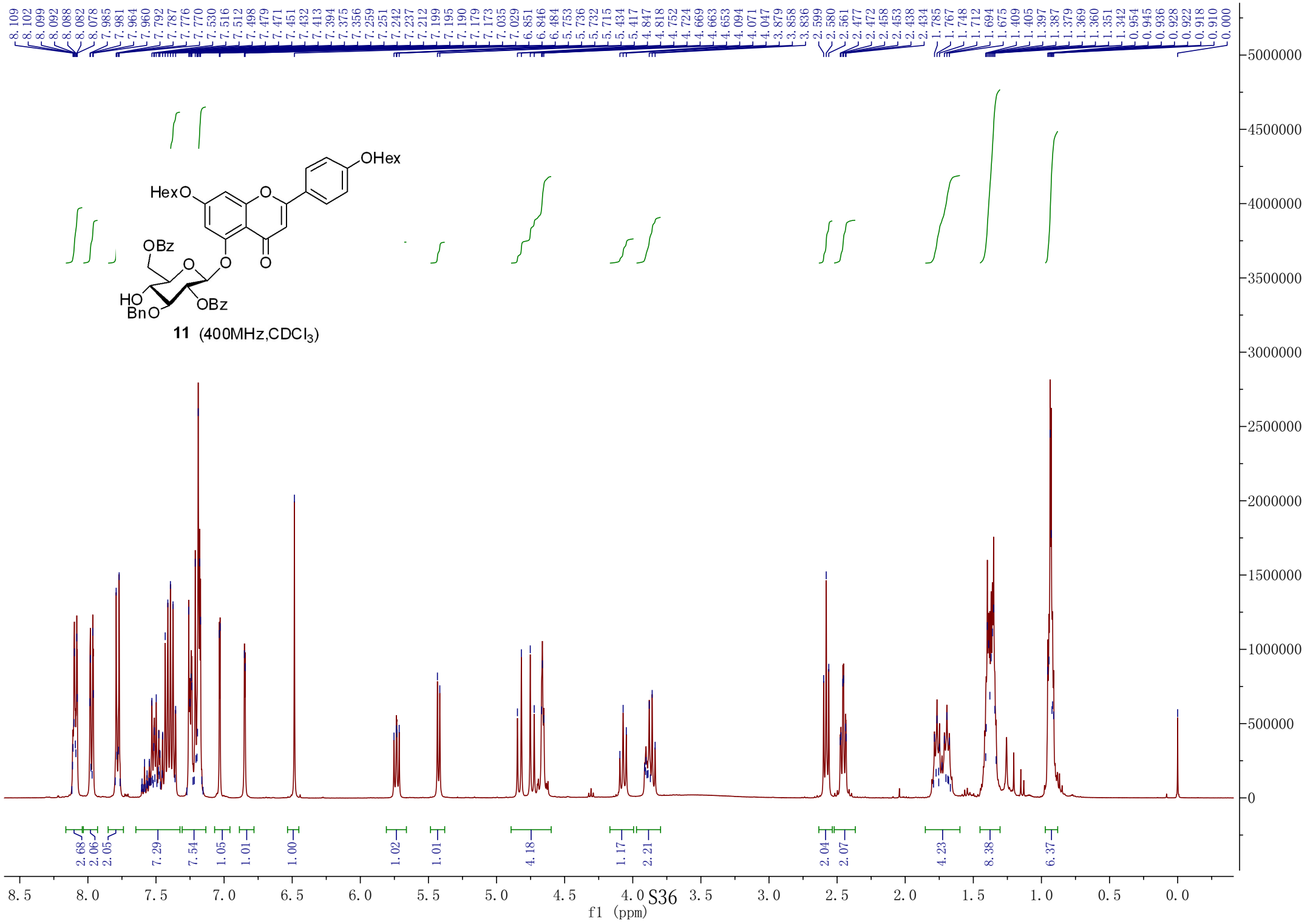
f1 (ppm)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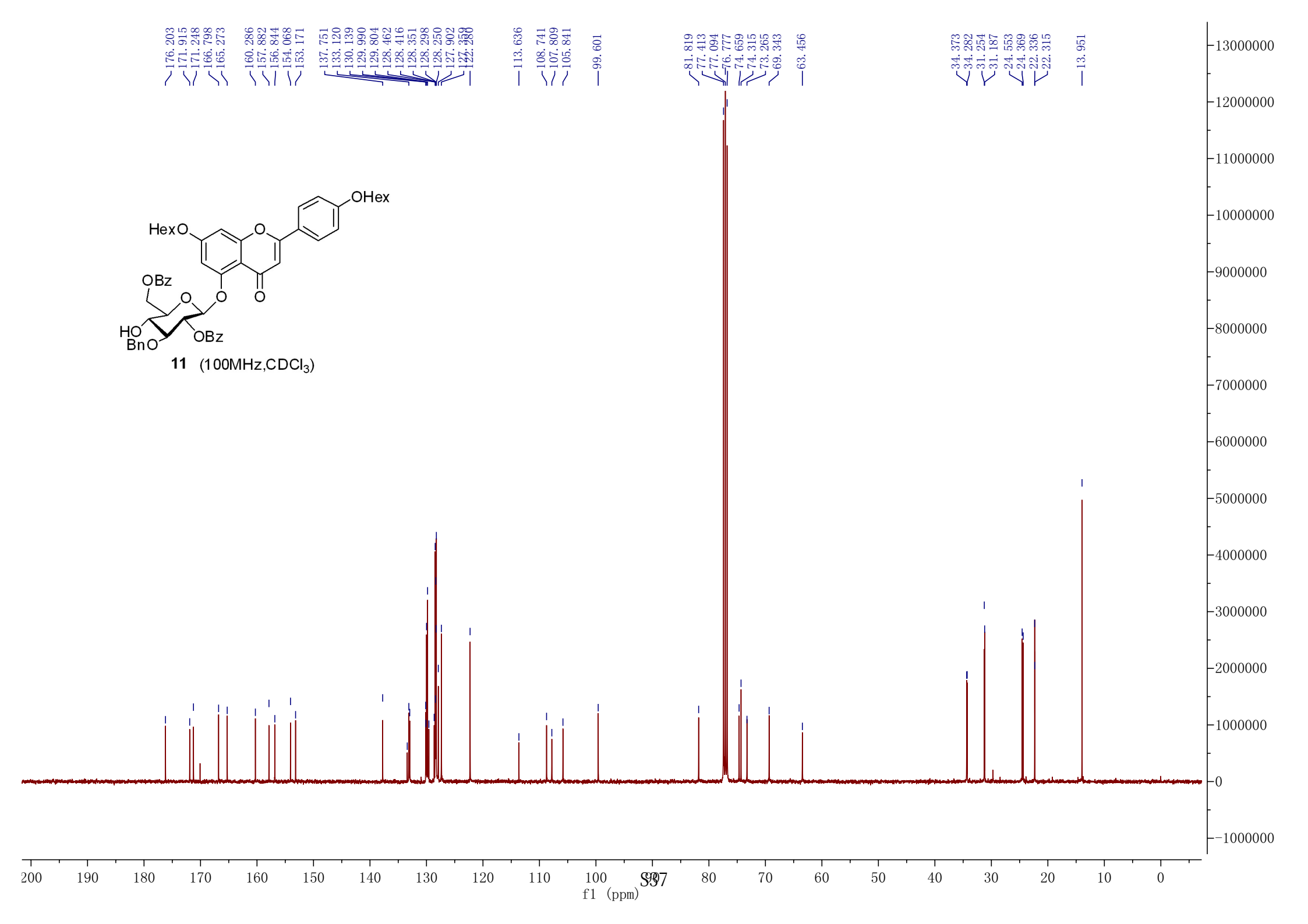
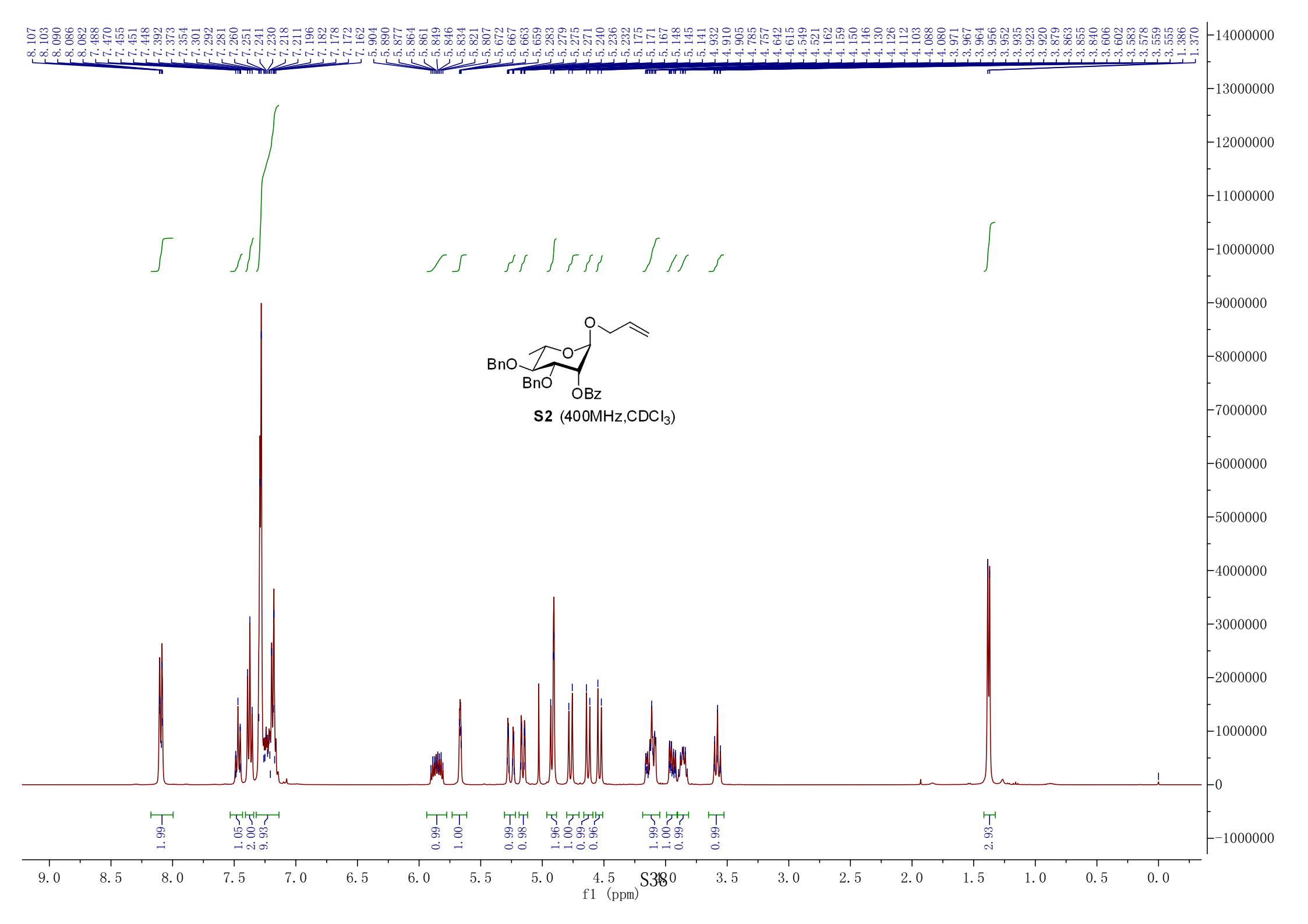
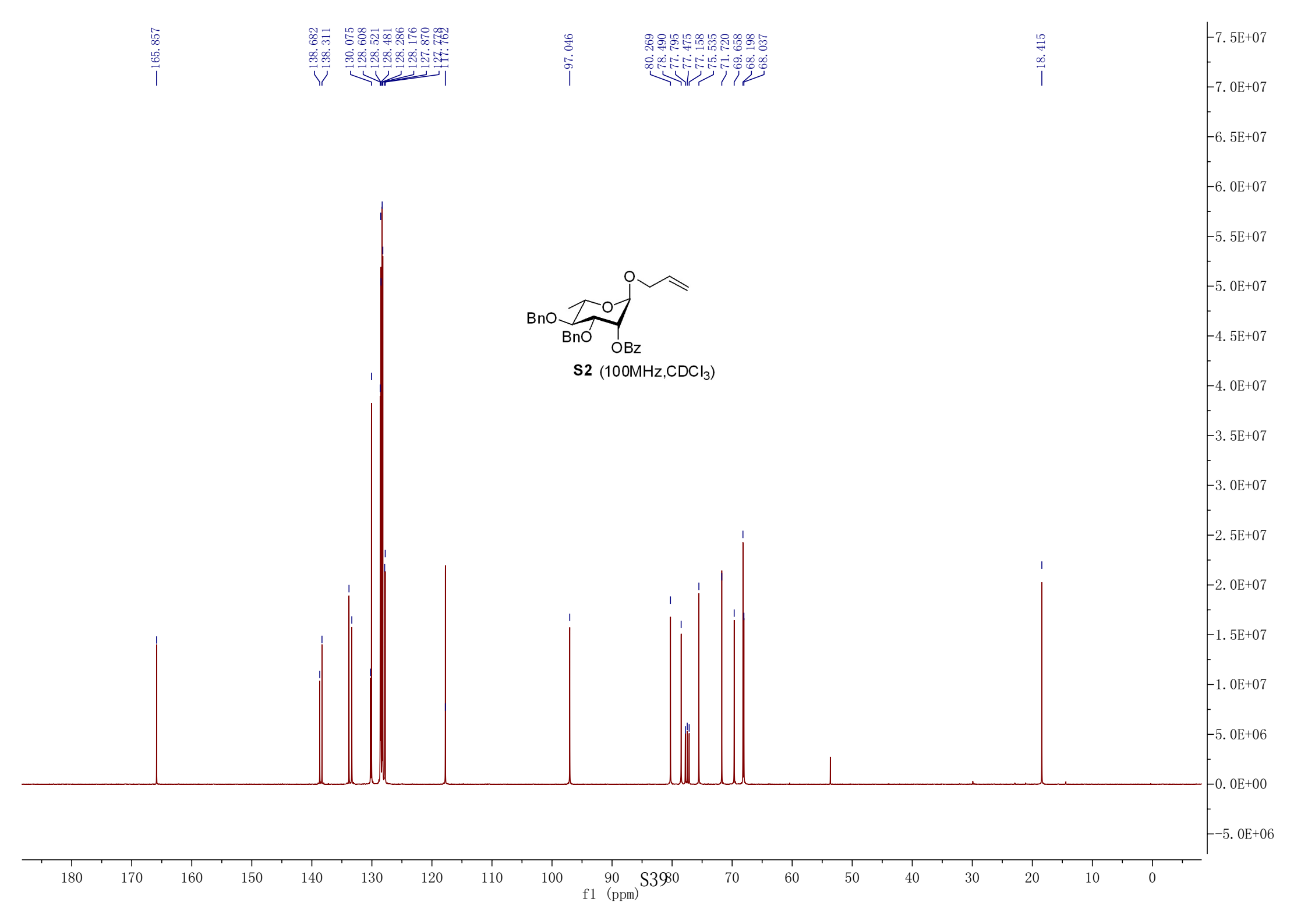
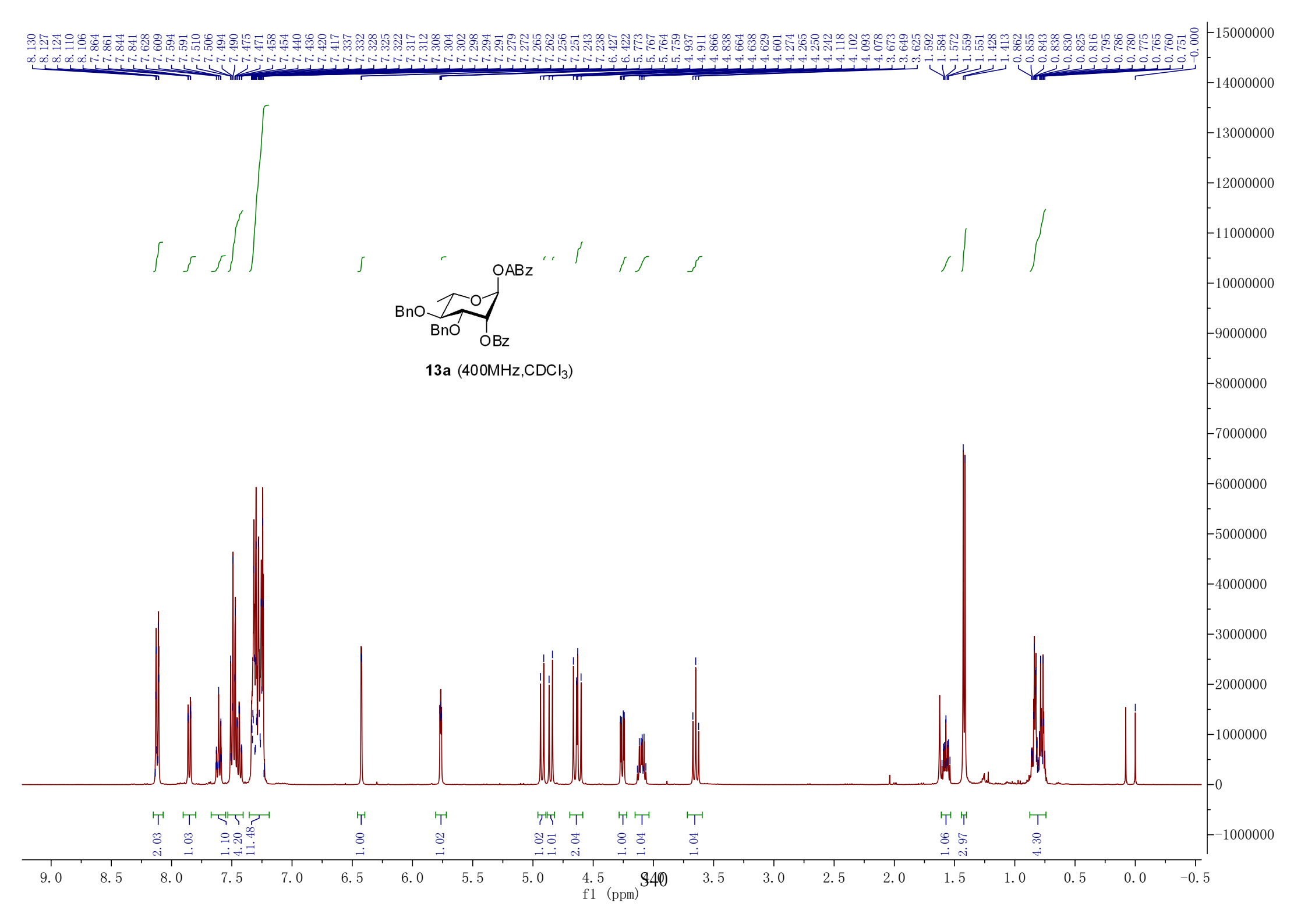
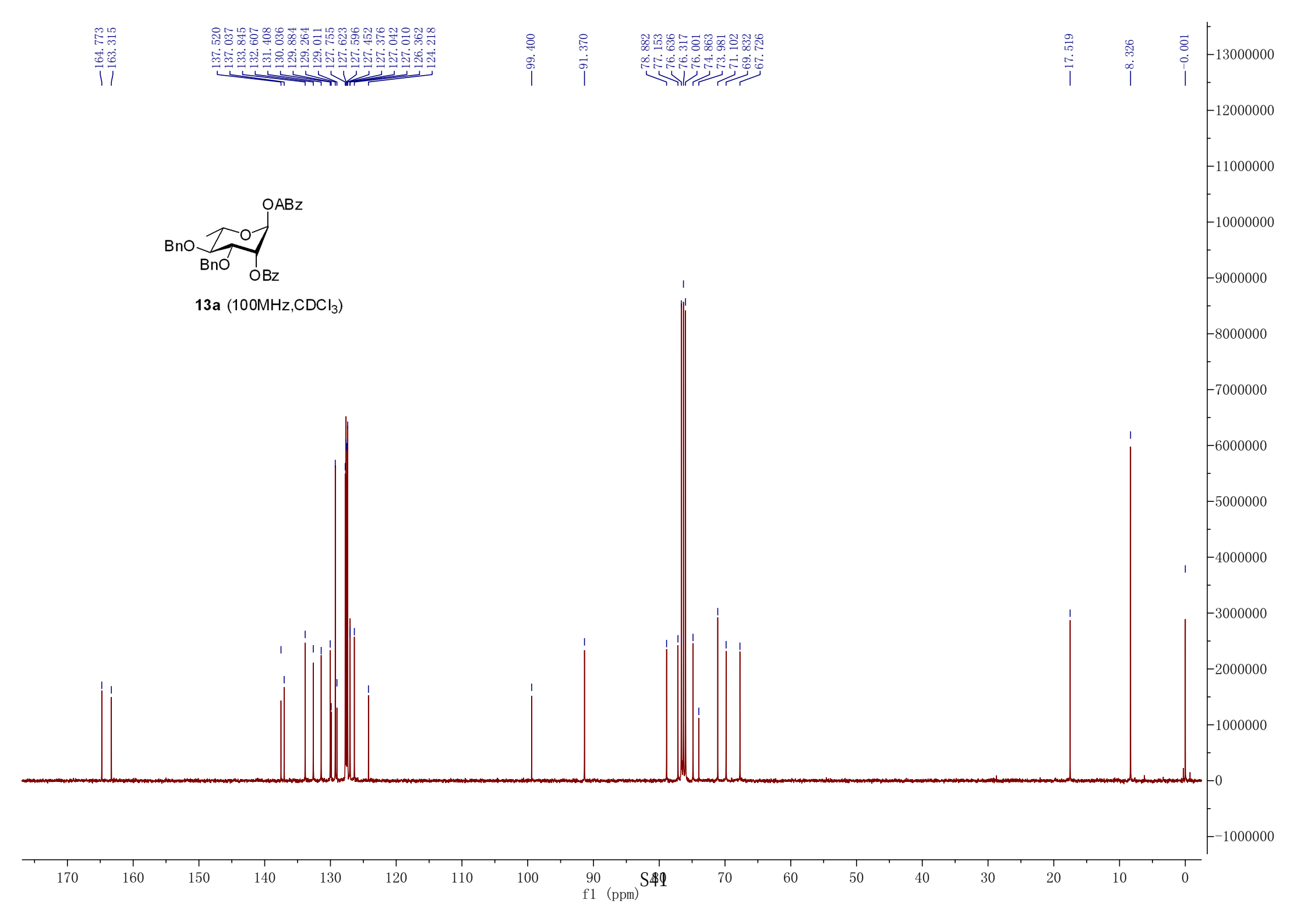
11 (400MHz,CDCl3)
f1 (ppm)

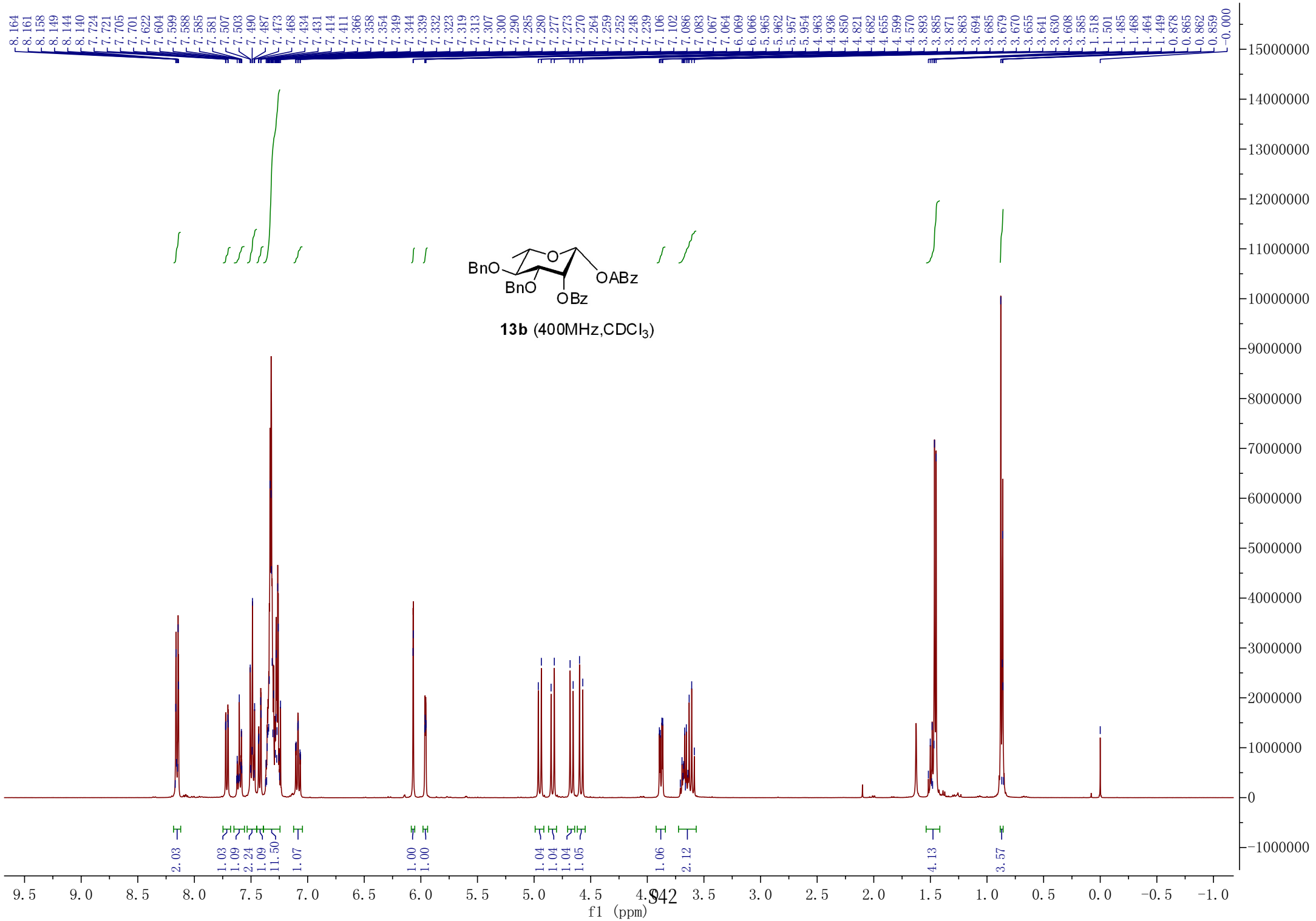

176.203
171.915
171.248
166.798
165.273
160.286
157.882
156.844
154.068
153.171
137.751
133.120
130.139
129.990
129.804
128.462
128.416
128.351
128.298
128.250
127.902
113.636
108.741
107.809
105.841
99.601
81.819
77.413
77.094
76.777
74.659
74.315
73.265
69.343
63.456
34.373
34.282
31.254
31.187
24.553
24.369
22.336
22.315
13.951
OHex
HexO
OBz
HO
BnO
OBz
11 (100MHz,CDCl3)
f1 (ppm)

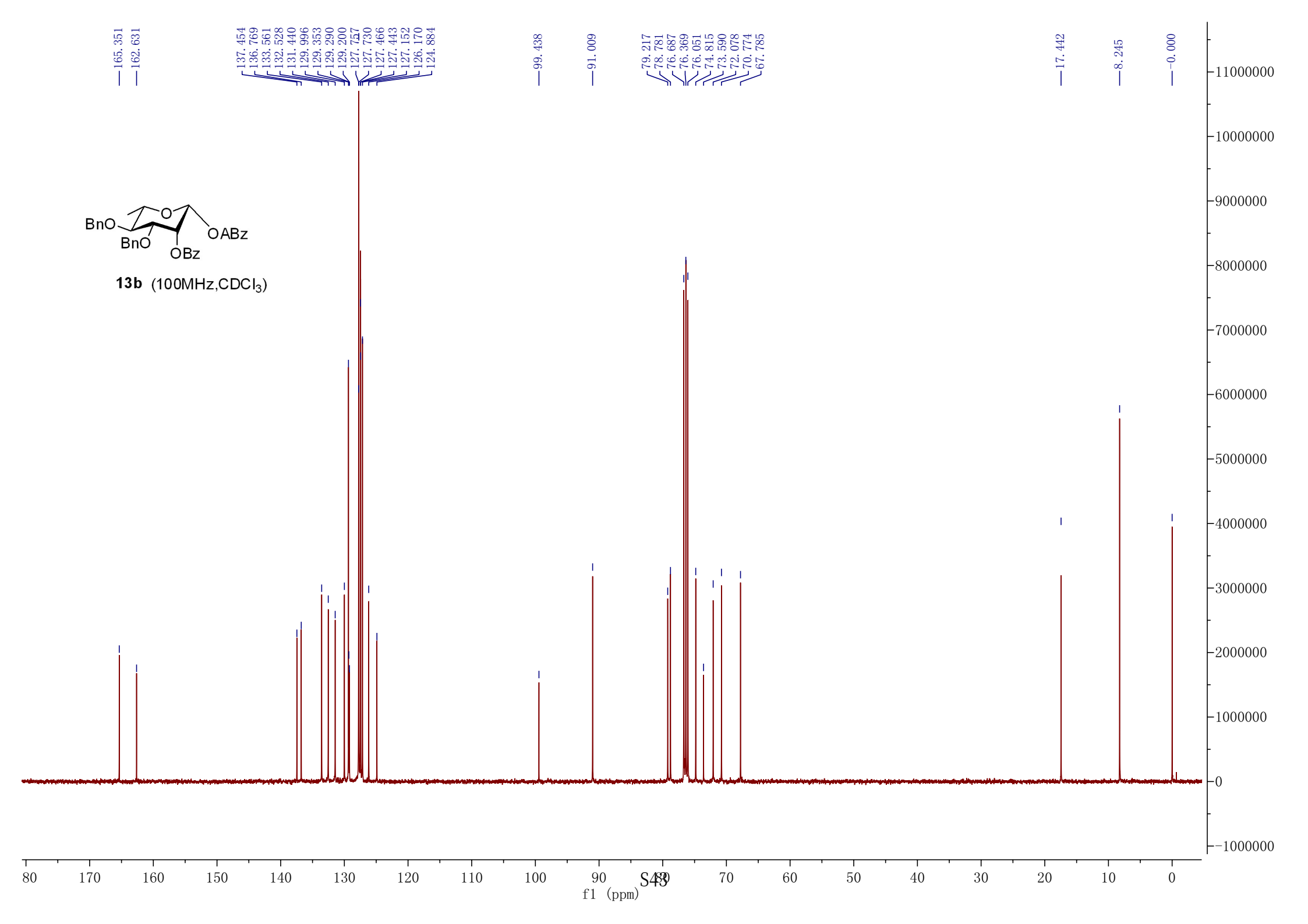

8.107 8.103 8.090 8.086 8.082 7.488 7.470 7.455 7.451 7.448 7.392 7.373 7.354 7.301 7.292 7.281 7.260 7.251 7.241 7.230 7.218 7.211 7.196 7.182 7.178 7.172 7.162 5.904 5.890 5.877 5.864 5.861 5.849 5.846 5.834 5.821 5.807 5.672 5.667 5.663 5.659 5.283 5.279 5.275 5.271 5.240 5.236 5.232 5.175 5.171 5.167 5.148 5.145 5.141 4.932 4.910 4.905 4.785 4.757 4.642 4.615 4.549 4.521 4.162 4.159 4.150 4.146 4.130 4.126 4.112 4.103 4.088 4.080 3.971 3.967 3.964 3.956 3.952 3.935 3.923 3.920 3.879 3.863 3.855 3.840 3.606 3.602 3.583 3.578 3.559 3.555 1.386 1.370
BnO
BnO
OBz
S2 (400MHz,CDCl3)
1.99 1.05 2.00 9.93 0.99 1.00 0.99 0.98 1.96 1.00 0.99 0.96 1.99 1.00 0.99 0.99 2.93
f1 (ppm)

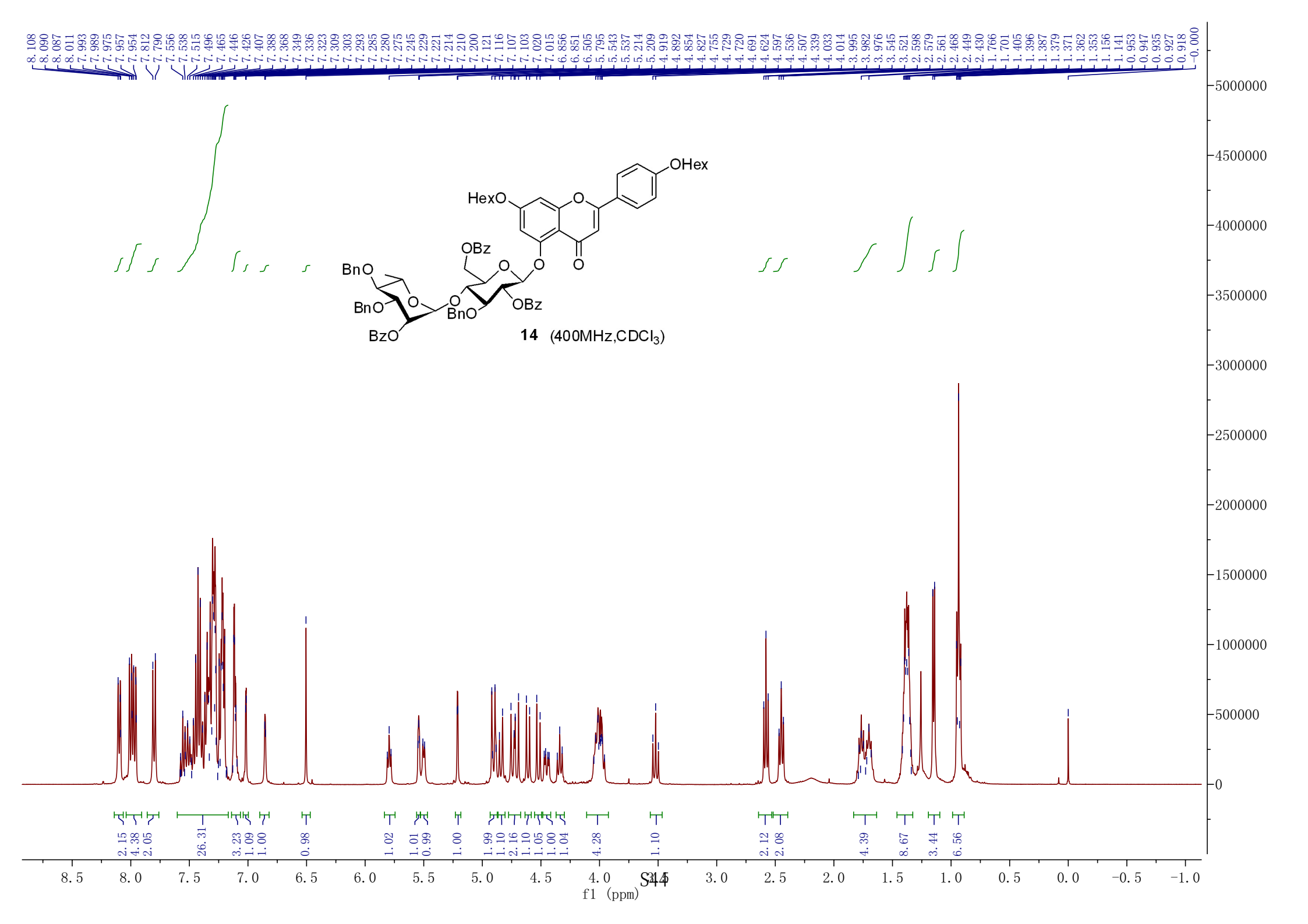

165.857
138.682
138.311
130.075
128.608
128.521
128.481
128.286
128.176
127.870
97.046
80.269
78.490
77.795
77.475
77.158
75.535
71.720
69.658
68.198
68.037
18.415
BnO
BnO
OBz
O
O
S2 (100MHz,CDCl3)
f1 (ppm)

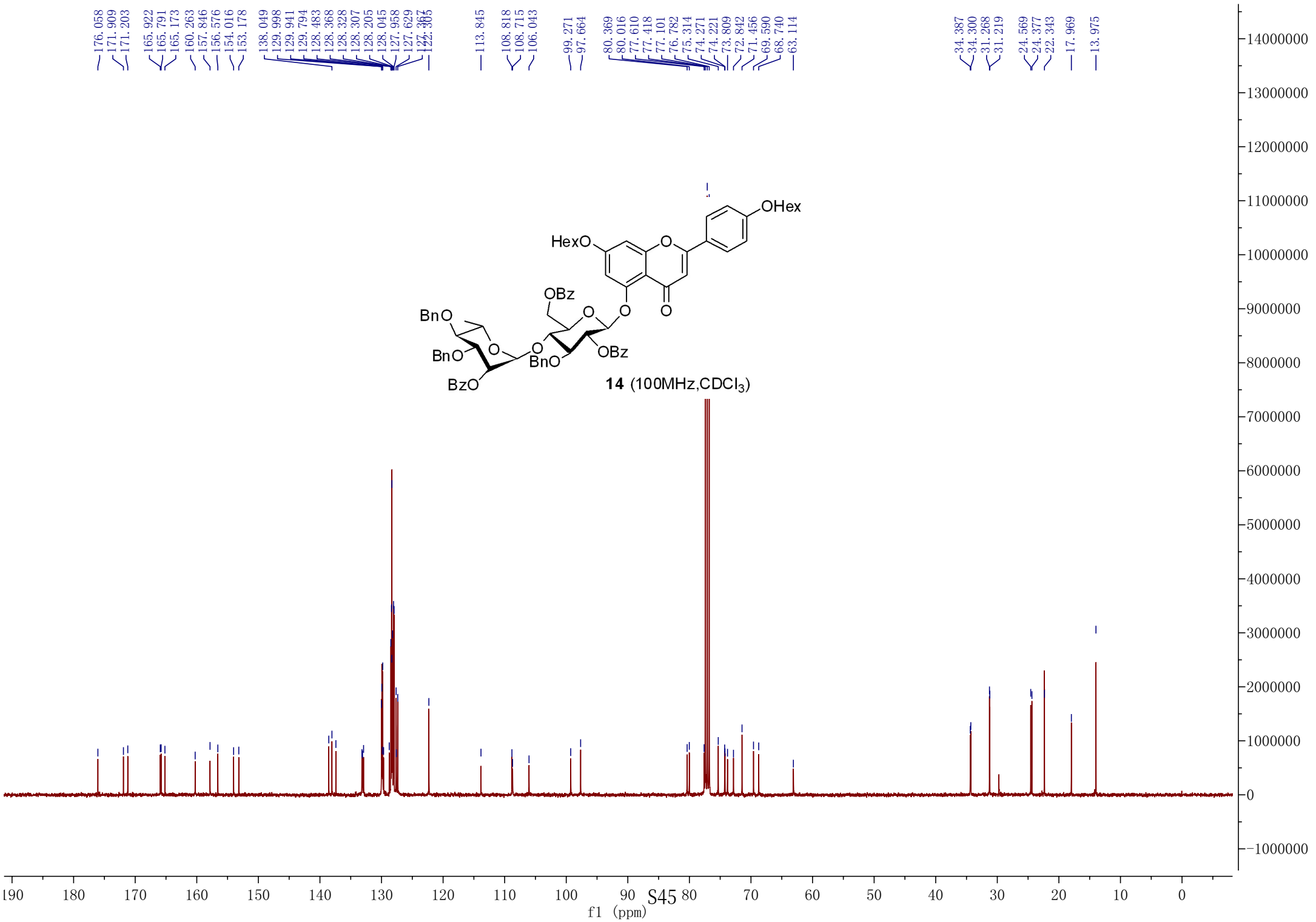

OABz
BnO
O
BnO
OBz
13a (400MHz,CDCl3)
f1 (ppm)

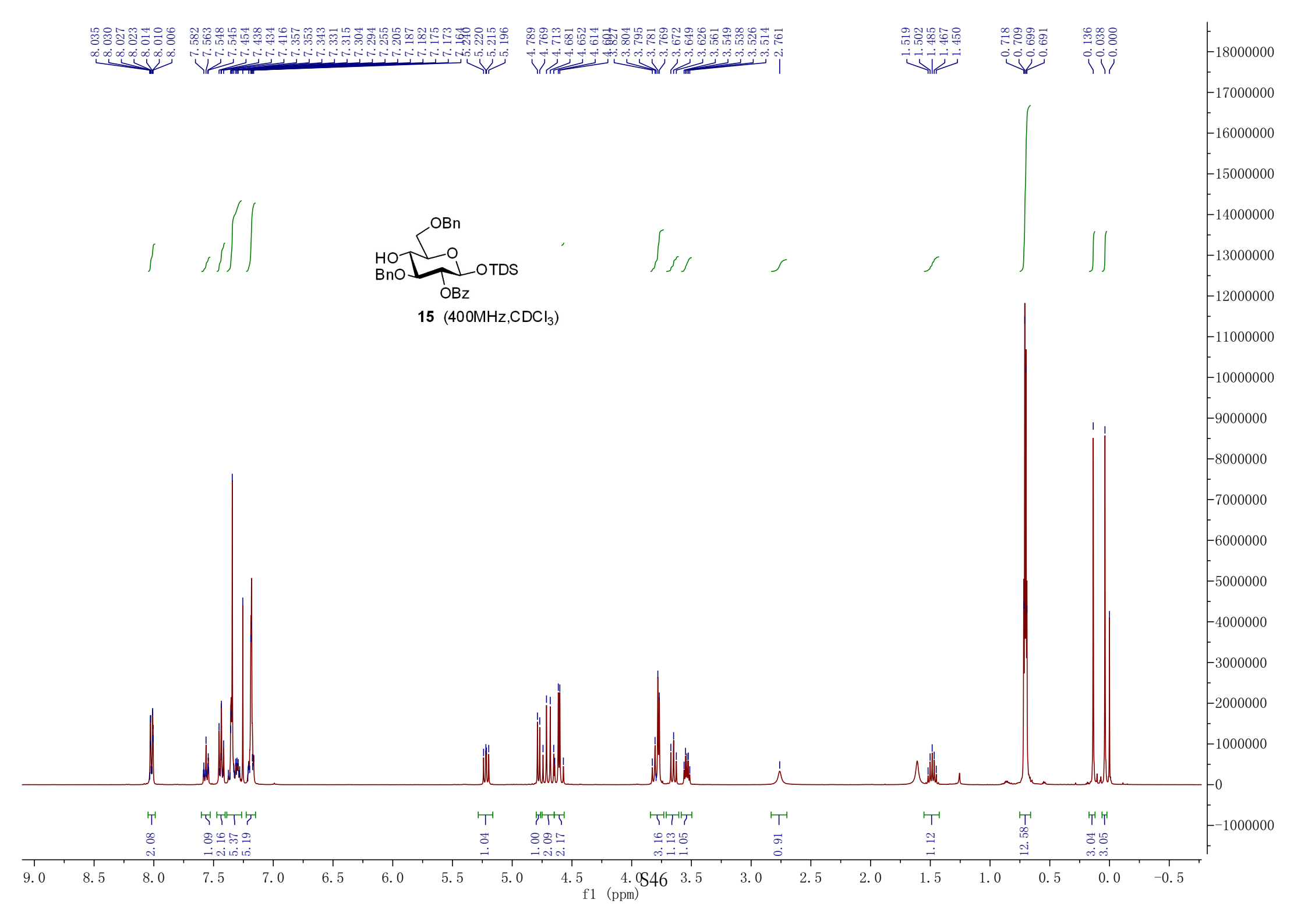

164.773
163.315
137.520
137.037
133.845
132.607
131.408
130.036
129.884
129.264
129.011
127.755
127.623
127.596
127.452
127.376
127.042
127.010
126.362
124.218
99.400
91.370
78.882
77.153
76.636
76.317
76.001
74.863
73.981
71.102
69.832
67.726
17.519
8.326
-0.001
OABz
BnO
BnO
O
OBz
13a (100MHz,CDCl3)
f1 (ppm)

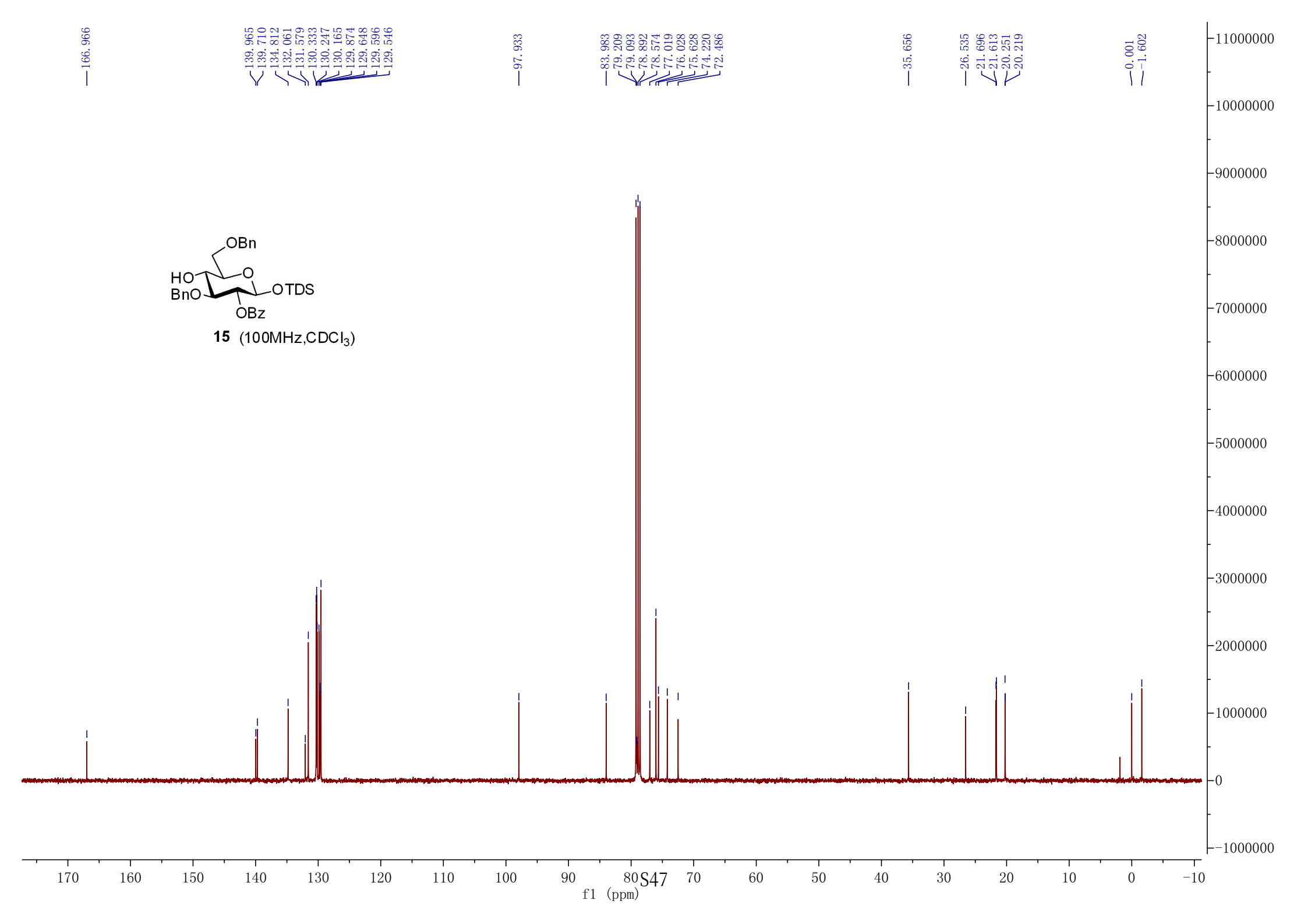

BnO
BnO
OBz
OABz
13b (400MHz,CDCl3)
f1 (ppm)

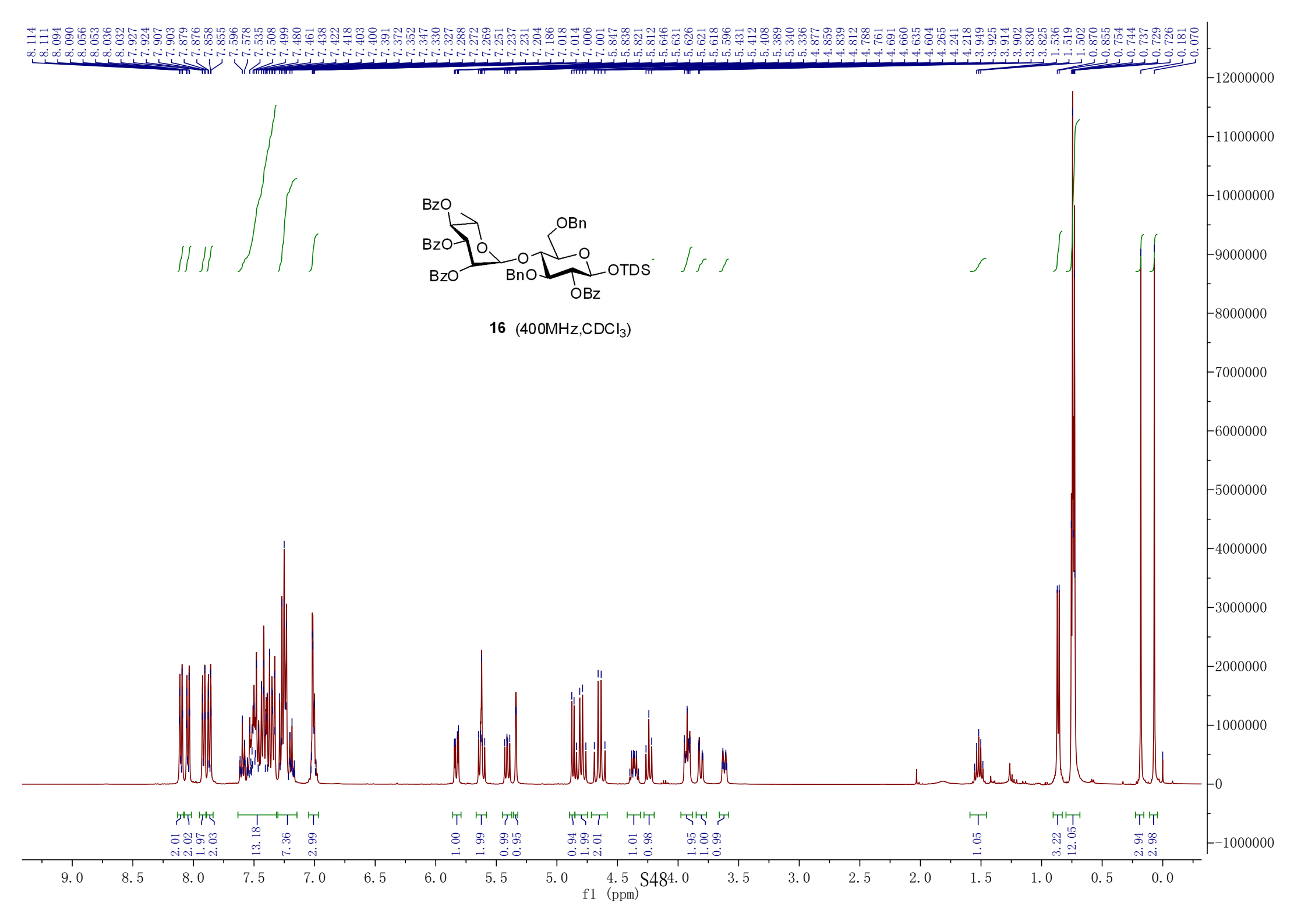

165.351
162.631
137.454
136.769
133.561
132.528
131.440
129.996
129.353
129.290
129.200
127.757
127.730
127.466
127.443
127.152
126.170
124.884
99.438
91.009
79.217
78.781
76.687
76.369
76.051
74.815
73.590
72.078
70.774
67.785
17.442
8.245
0.000
BnO
BnO
OBz
OABz
13b (100MHz,CDCl3)
f1 (ppm)

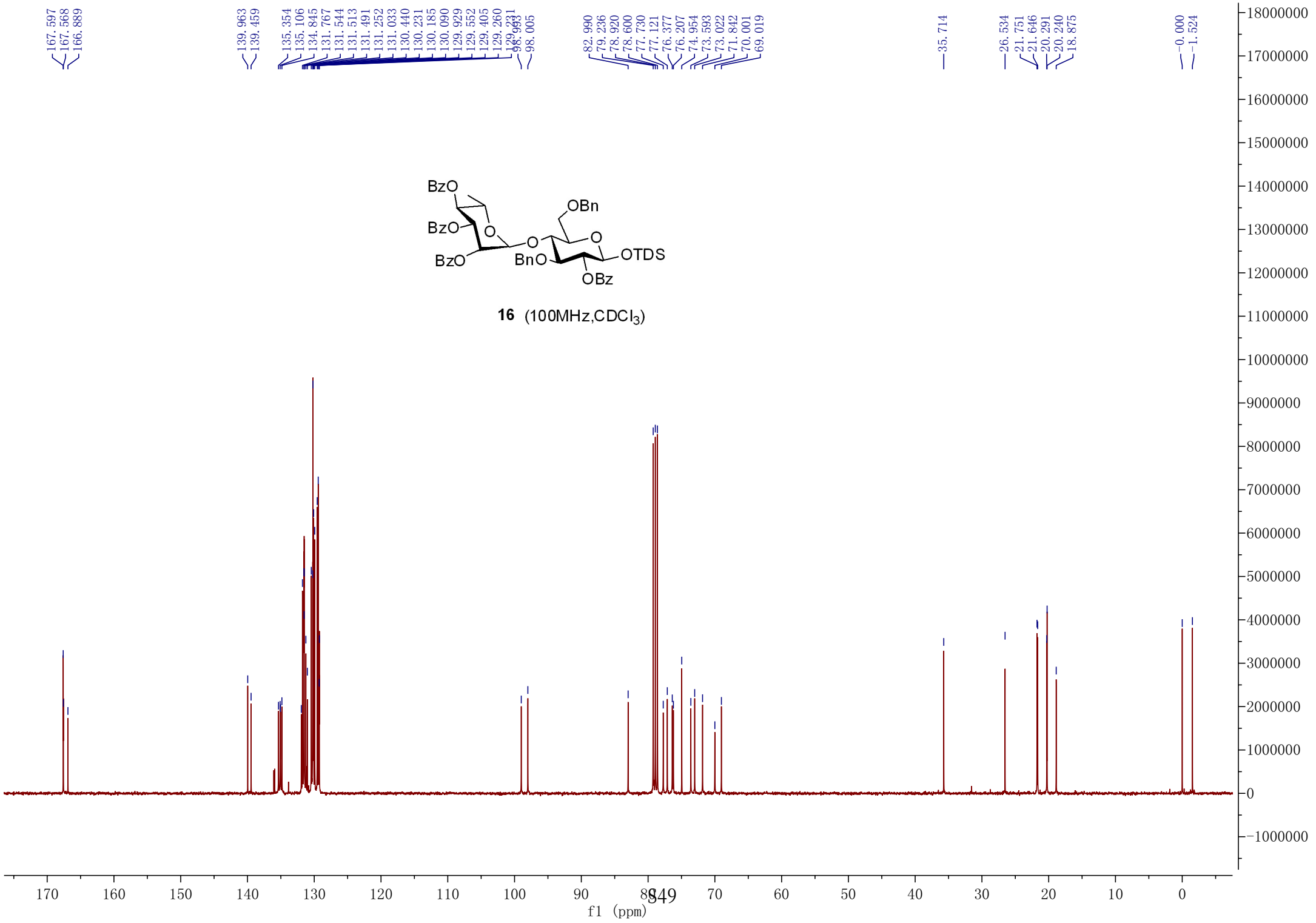

OHex
HexO
O
OBz
O
O
BnO
BnO
O
O
BnO
OBz
BzO
14 (400MHz,CDCl3)
f1 (ppm)

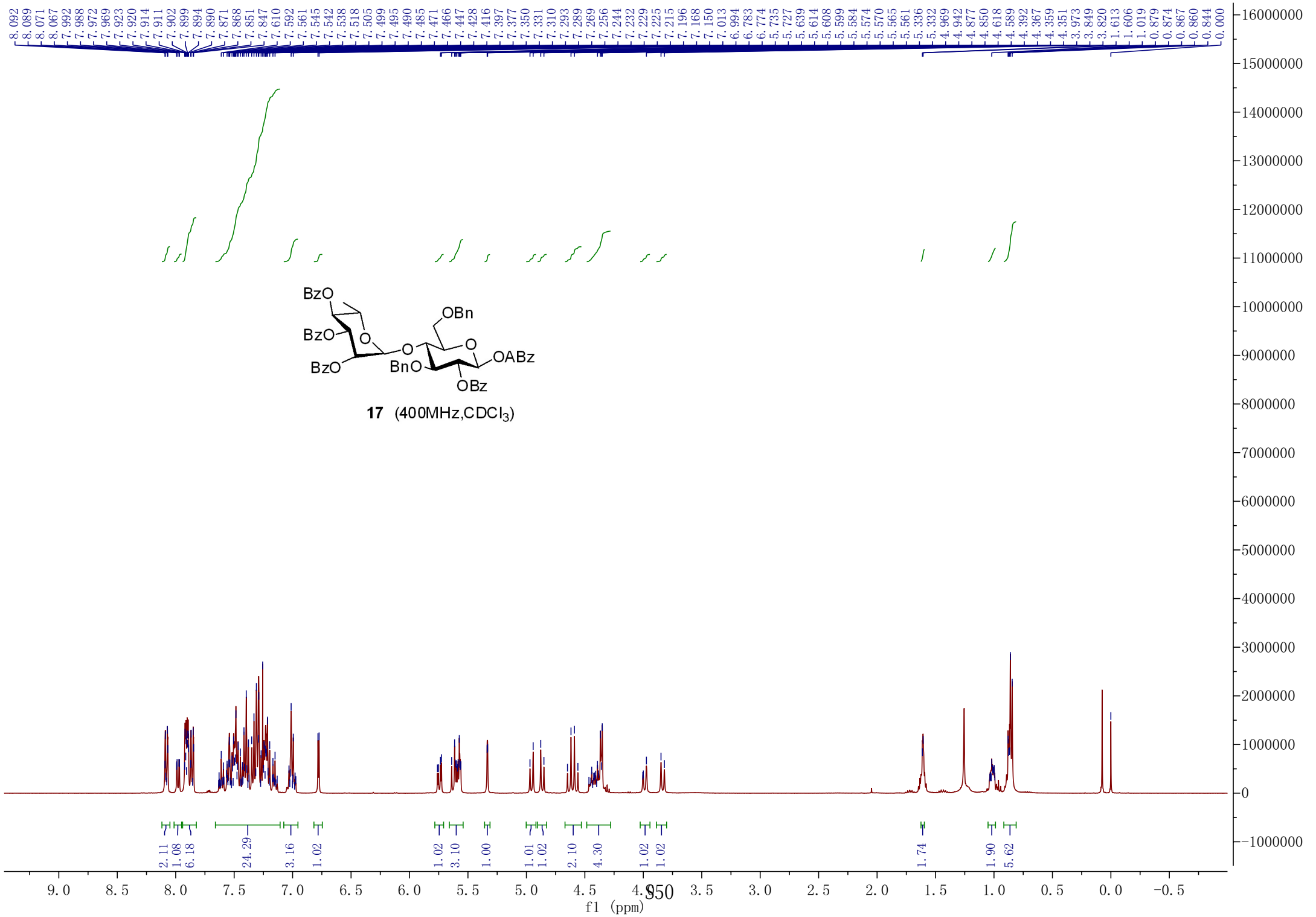

176.058
171.909
171.203
165.922
165.791
165.173
160.263
157.846
156.576
154.016
153.178
138.049
129.998
129.941
129.794
128.483
128.368
128.328
128.307
128.205
128.045
127.958
127.629
113.845
108.818
108.715
106.043
99.271
97.664
80.369
80.016
77.610
77.418
77.101
76.782
75.314
74.271
74.221
73.809
72.842
71.456
69.590
68.740
63.114
34.387
34.300
31.268
31.219
24.569
24.377
22.343
17.969
13.975
OHex
HexO
OBz
BnO
BnO
BnO
OBz
BzO
14 (100MHz,CDCl3)
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
−1000000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

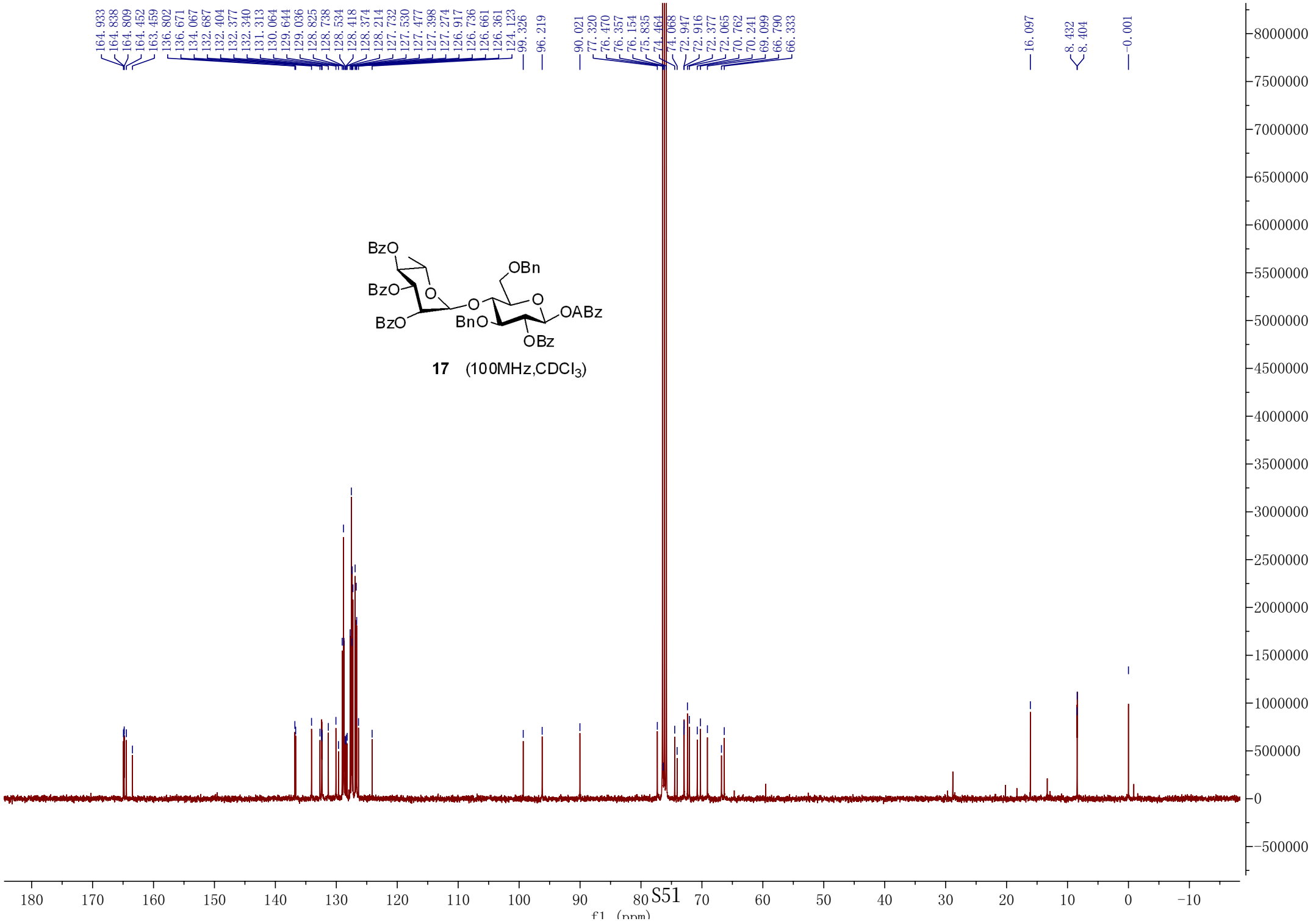

OBn
HO
O
BnO
OTDS
OBz
15 (400MHz,CDCl3)
f1 (ppm)


166.966
139.965
139.710
134.812
132.061
131.579
130.333
130.247
130.165
129.874
129.648
129.596
129.546
97.933
83.983
79.209
79.093
78.892
78.574
77.019
76.028
75.628
74.220
72.486
35.656
26.535
21.696
21.613
20.251
20.219
0.001
-1.602
OBn
HO
O
BnO
OTDS
OBz
15 (100MHz,CDCl3)
f1 (ppm)

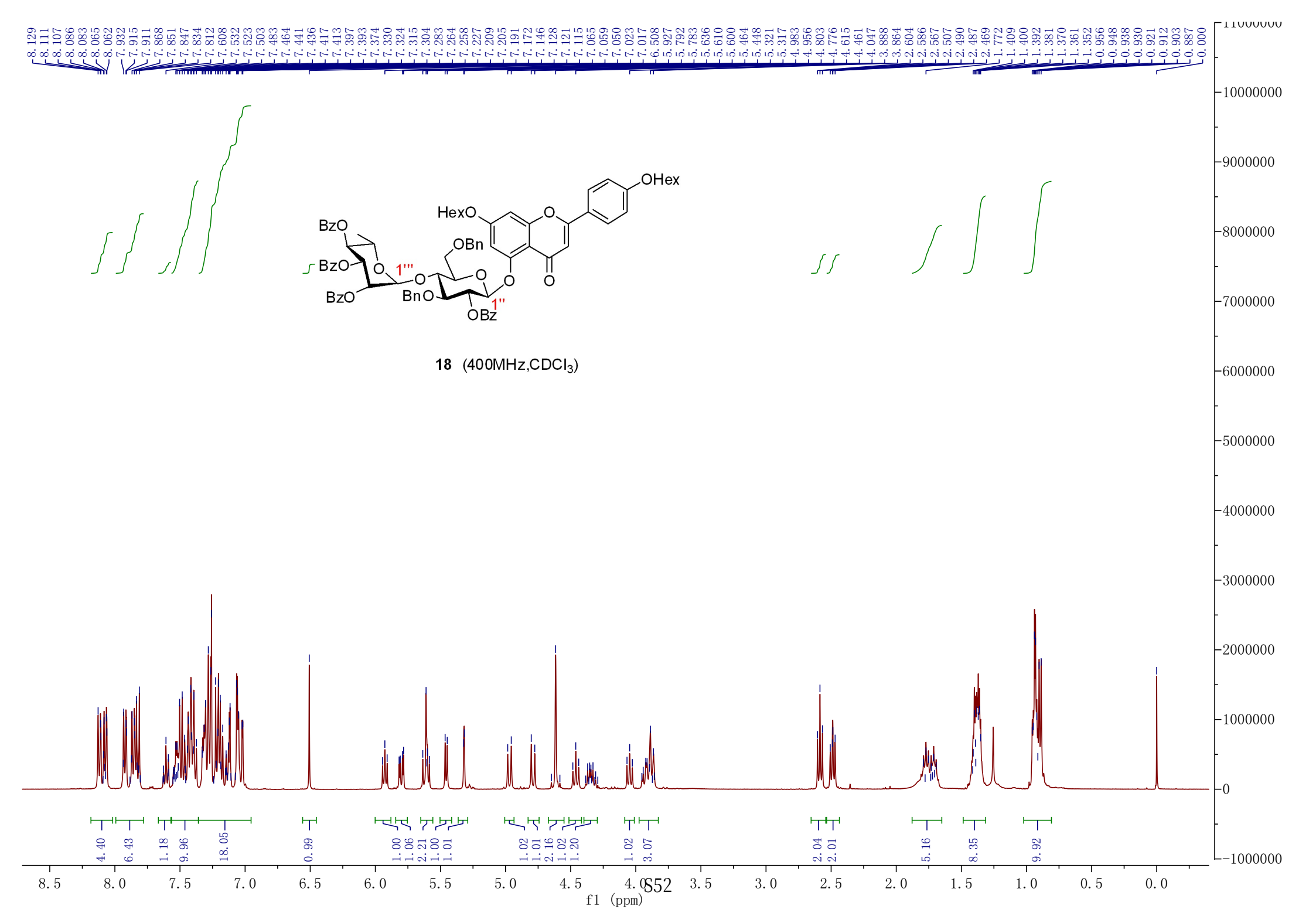

BzO
BzO
BzO
O
O
OBn
O
BnO
OTDS
OBz
16 (400MHz,CDCl3)
f1 (ppm)

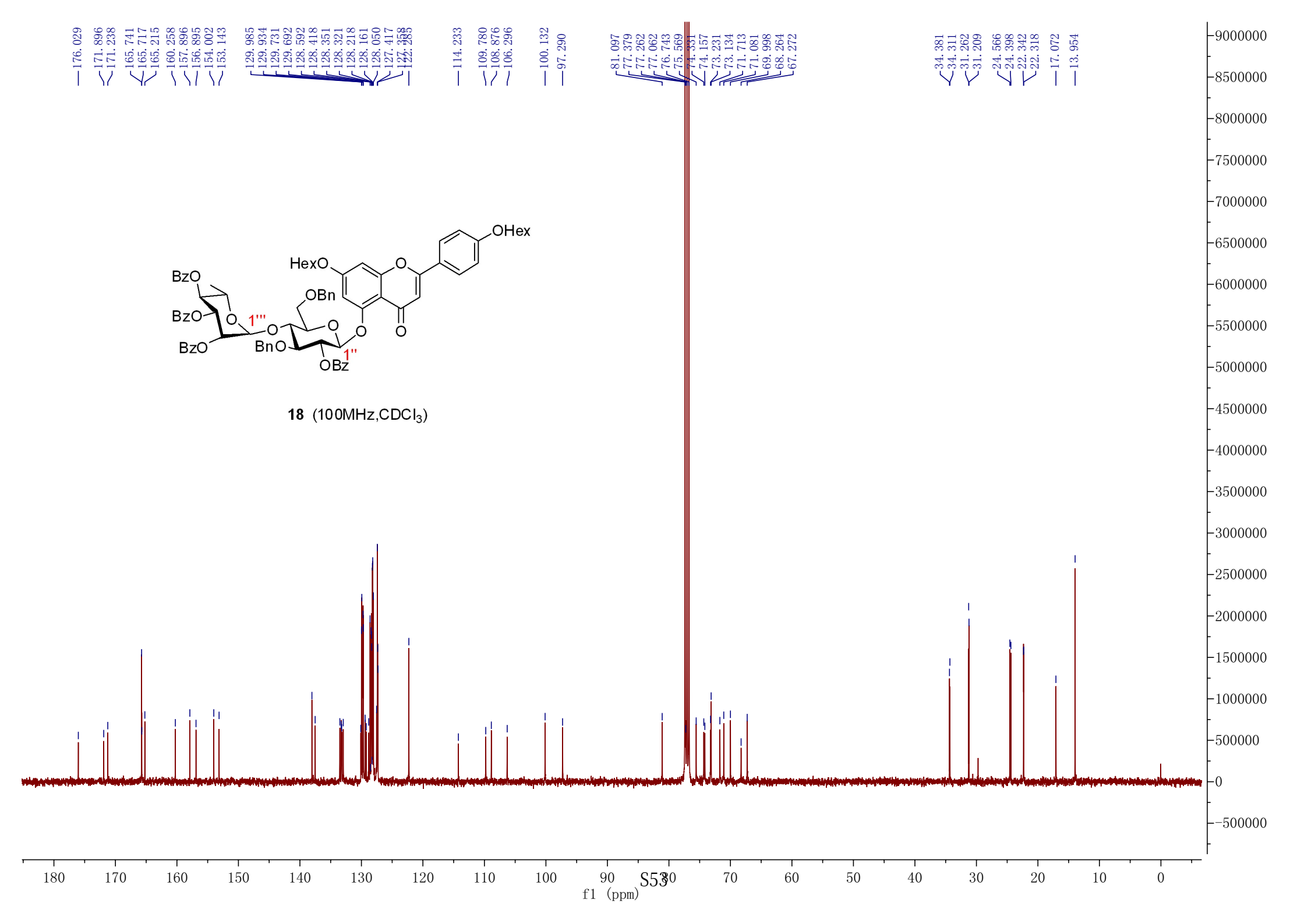

167.597
167.568
166.889
139.963
139.459
135.354
135.106
134.845
131.767
131.544
131.513
131.491
131.252
131.033
130.440
130.231
130.185
130.090
129.929
129.552
129.405
129.260
98.993
98.005
82.990
79.236
78.920
78.600
77.730
77.121
76.377
76.207
74.954
73.593
73.022
71.842
70.001
69.019
35.714
26.534
21.751
21.646
20.291
20.240
18.875
0.000
-1.524
BzO
BzO
BzO
O
O
OBn
O
BnO
OTDS
OBz
16 (100MHz,CDCl3)
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BzO
BzO
BzO
O
O
OBn
O
OABz
BnO
OBz
17 (400MHz,CDCl3)
f1 (ppm)

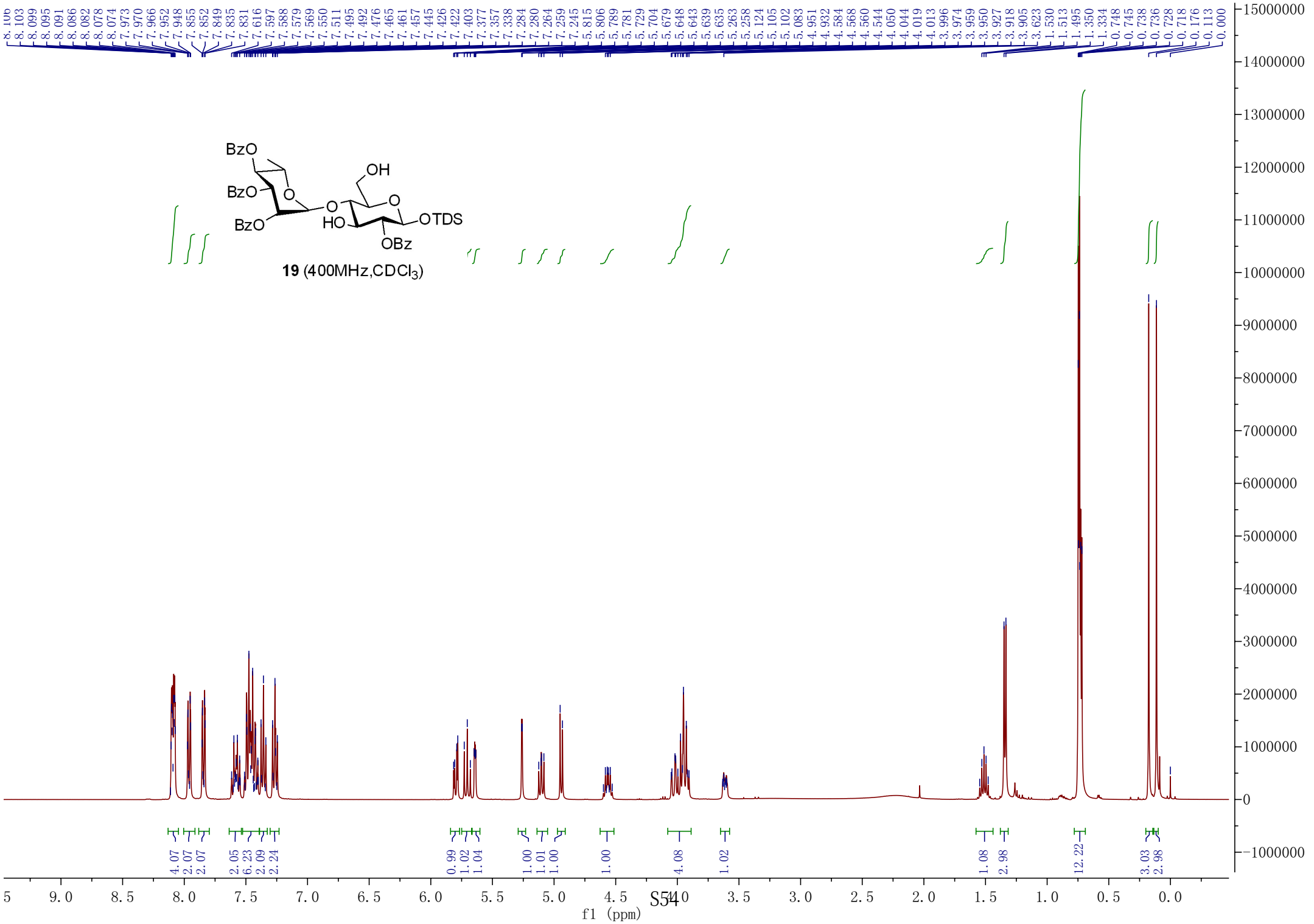


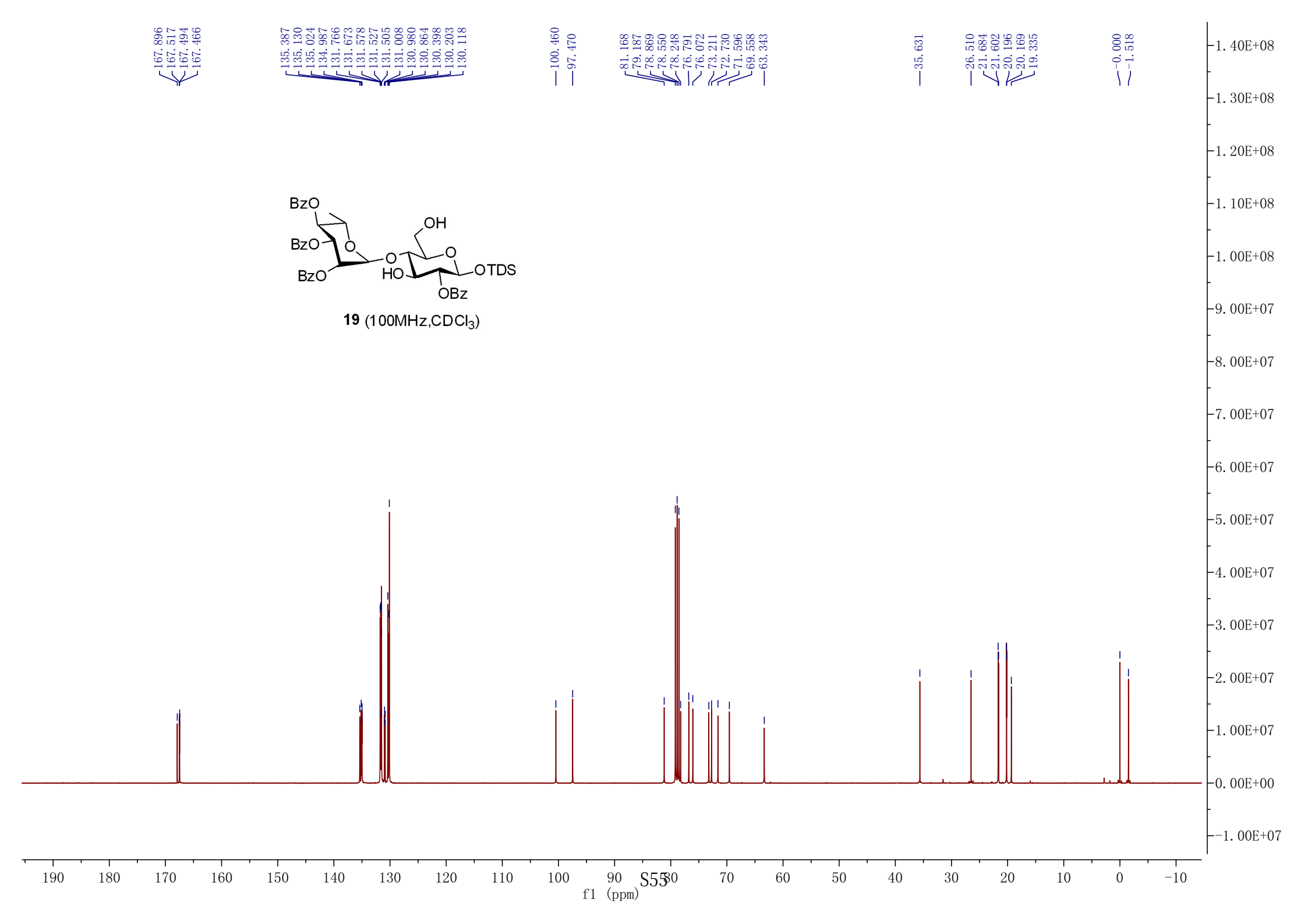
17 (100MHz,$CDCl_3$)


OHex
HexO
OBn
BzO
BzO
BzO
1'''
BnO
1''
OBz
18 (400MHz,CDCl3)
f1 (ppm)

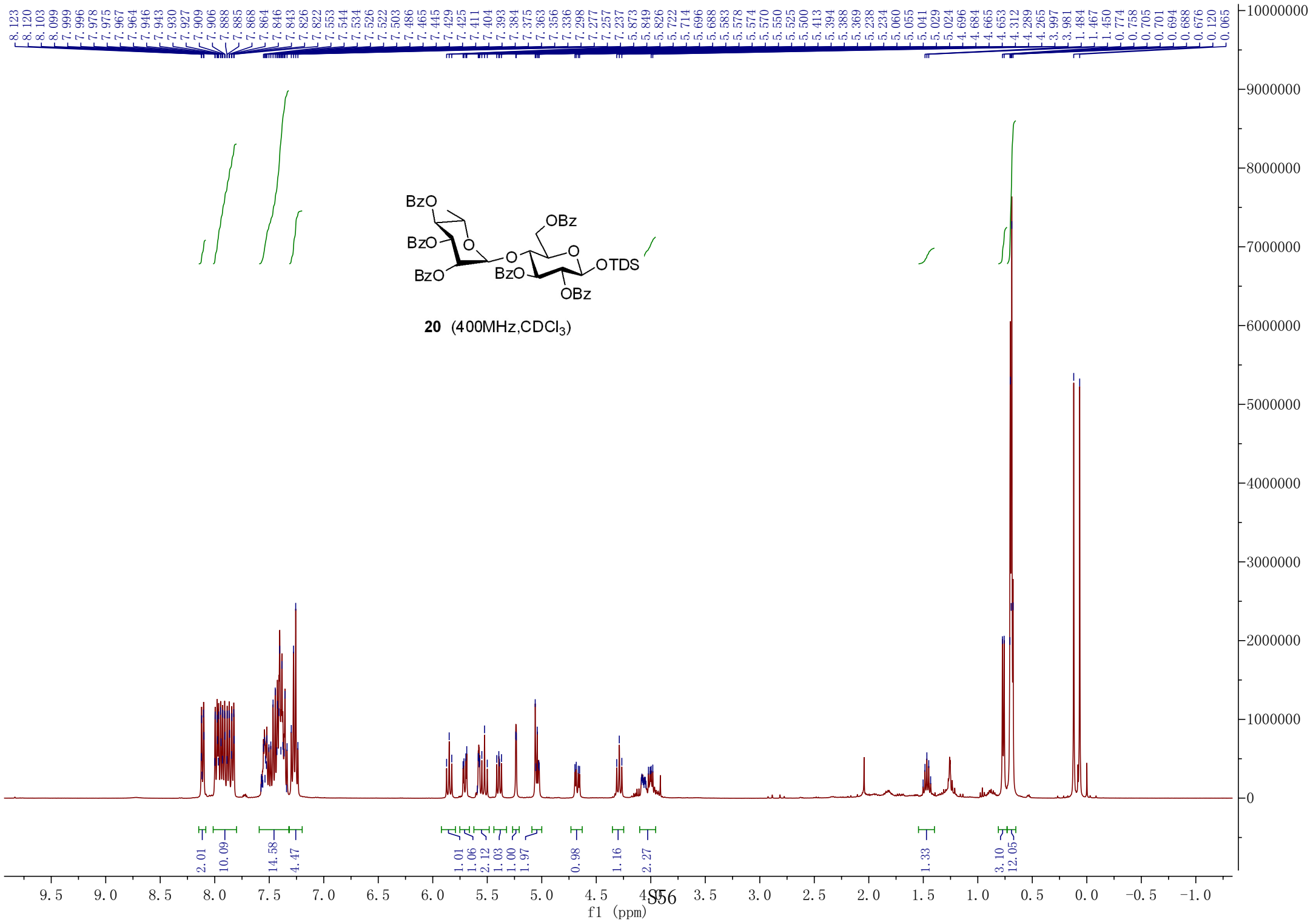


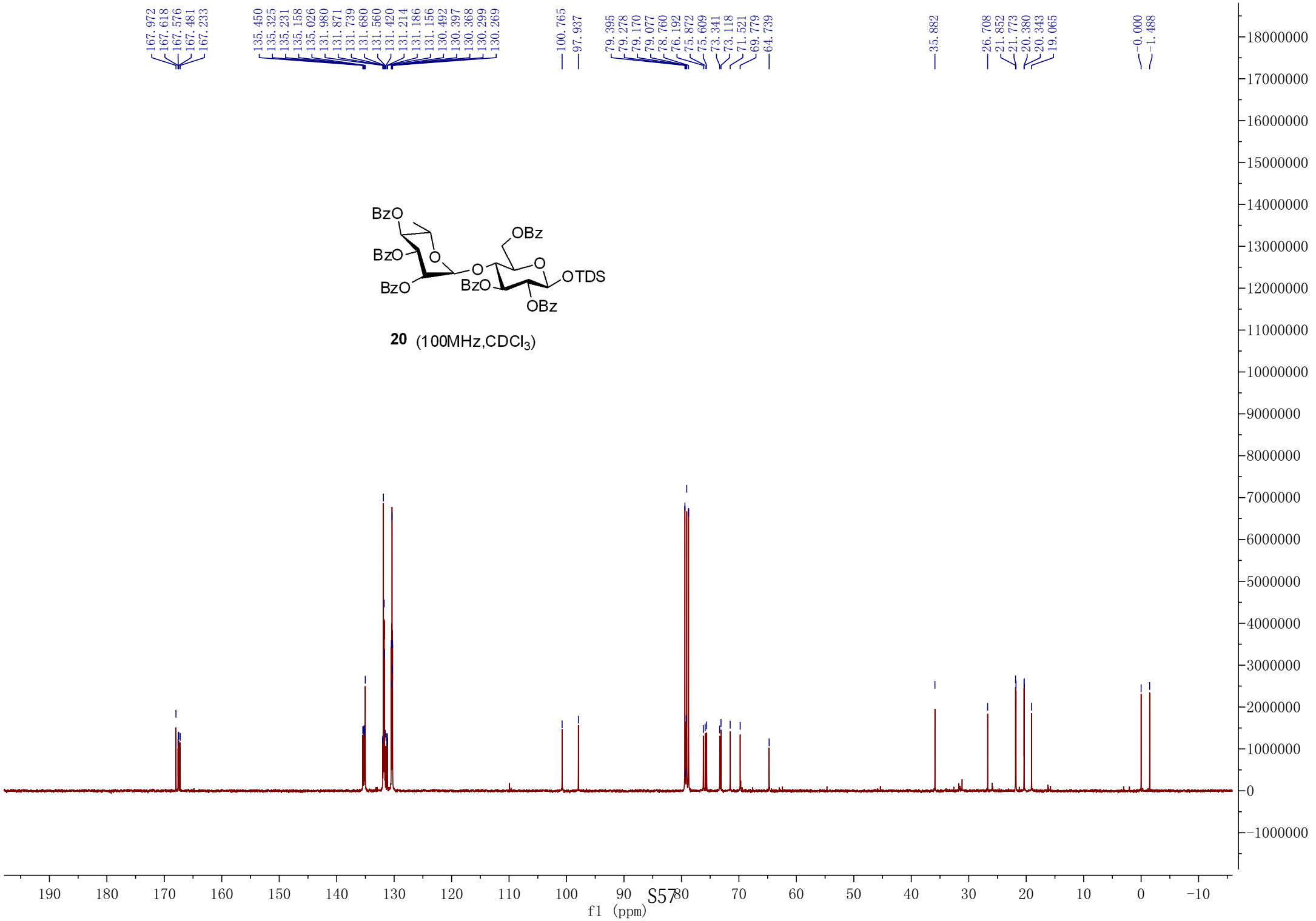
18 (100MHz,$CDCl_3$)

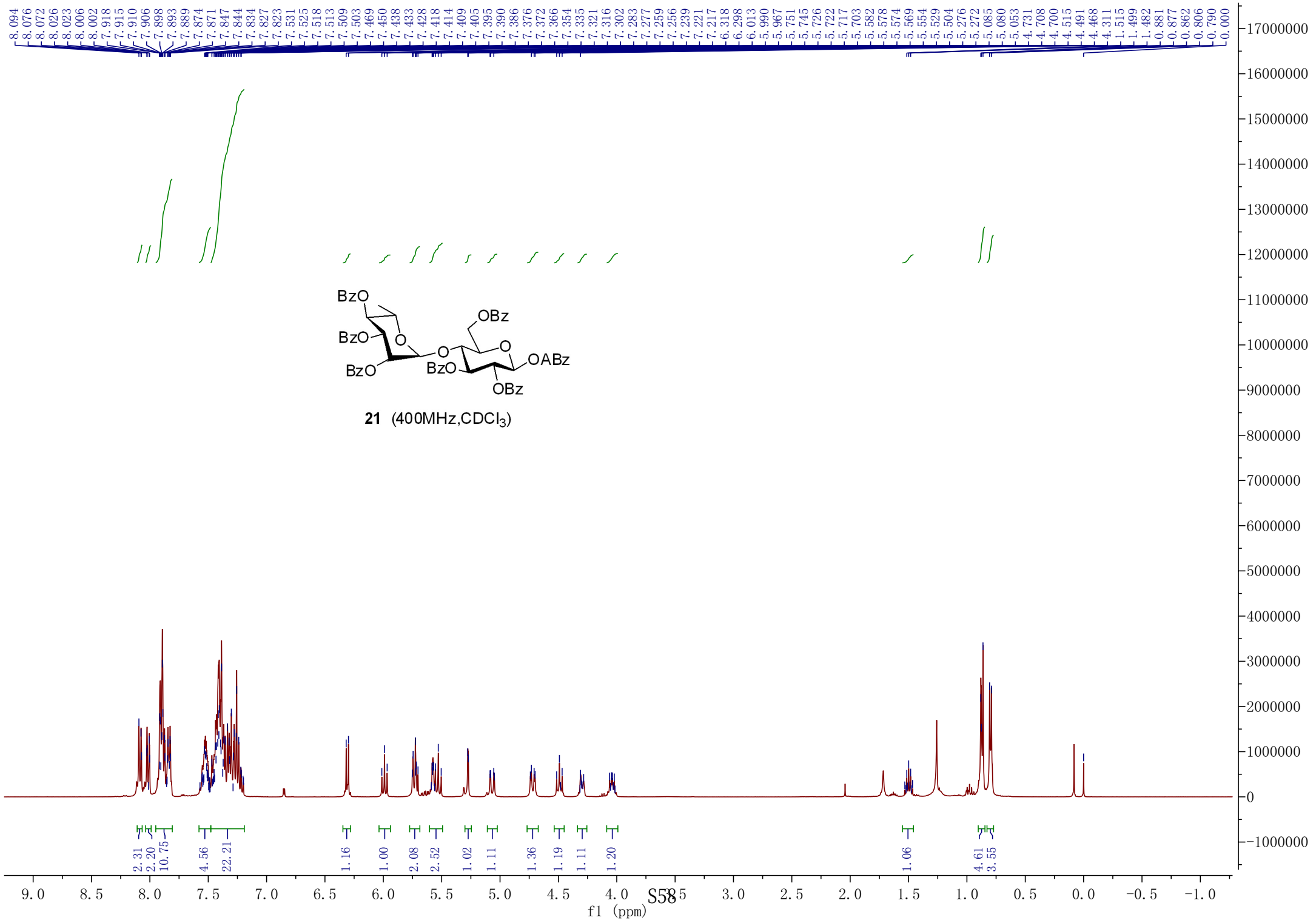

BzO
BzO
BzO
O
O
HO
OH
O
OTDS
OBz
19 (400MHz,CDCl3)
f1 (ppm)

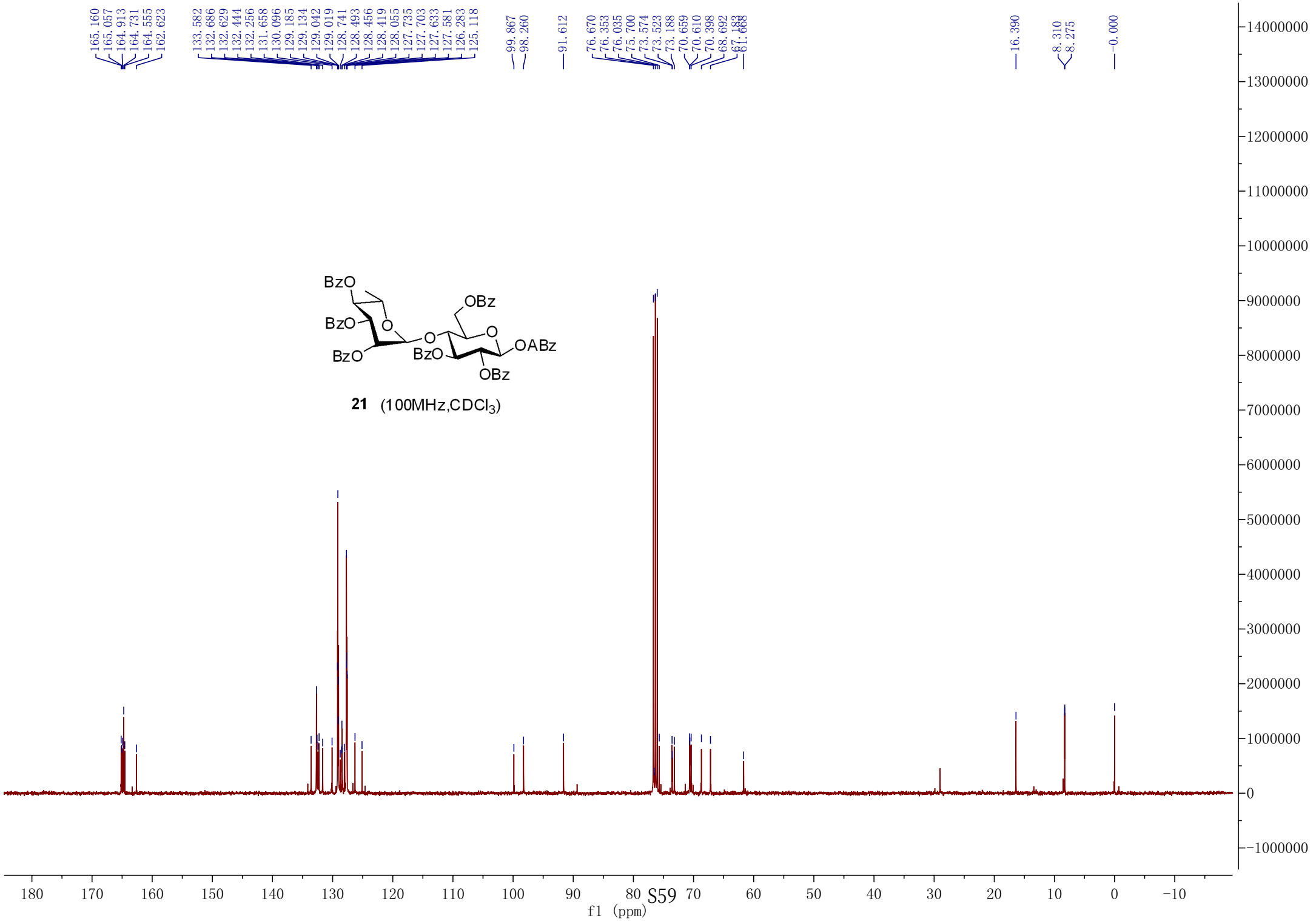


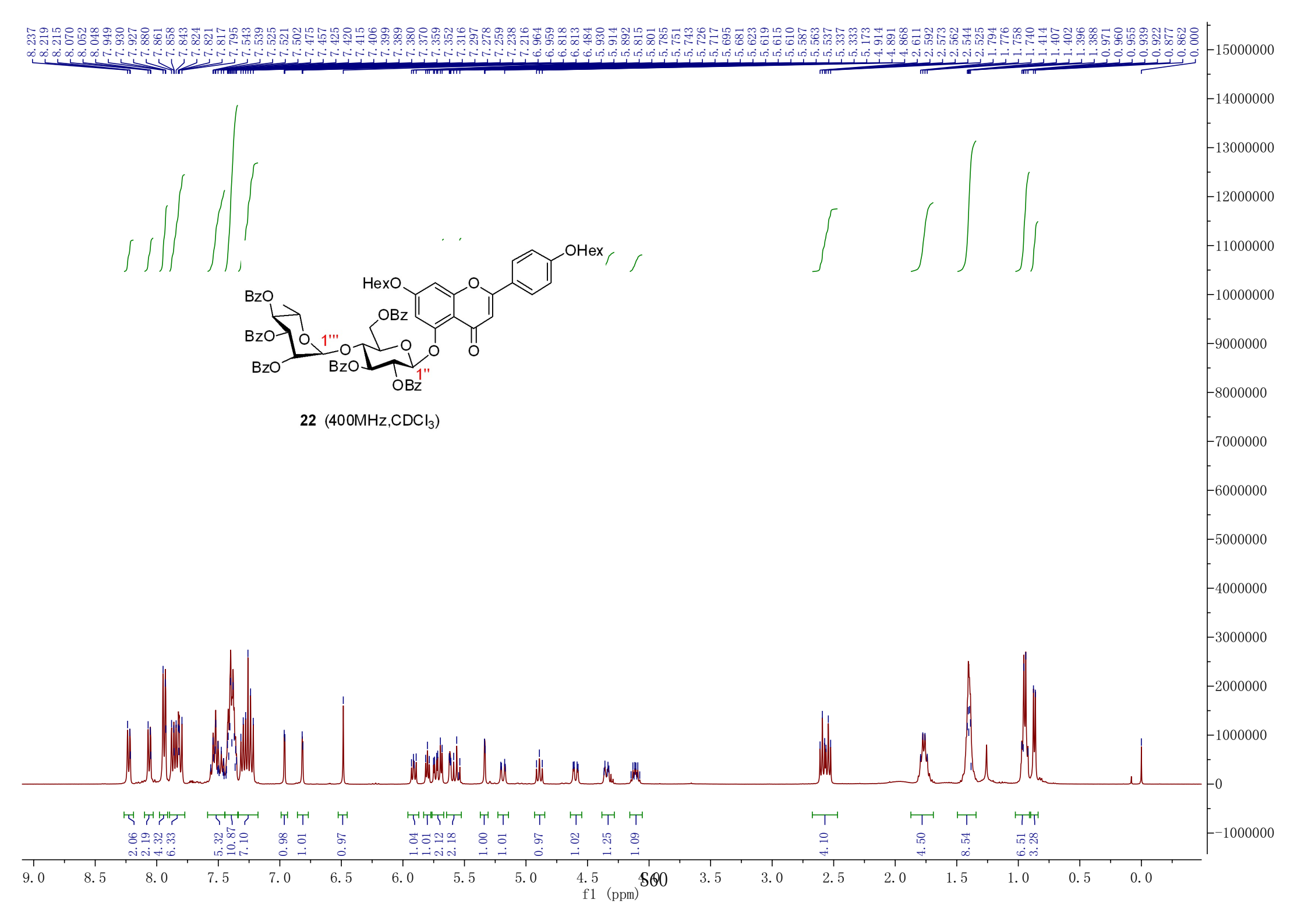
19 (100MHz,$CDCl_3$)


BzO
BzO
BzO
O
O
OBz
O
OTDS
BzO
OBz
20 (400MHz,CDCl3)
f1 (ppm)

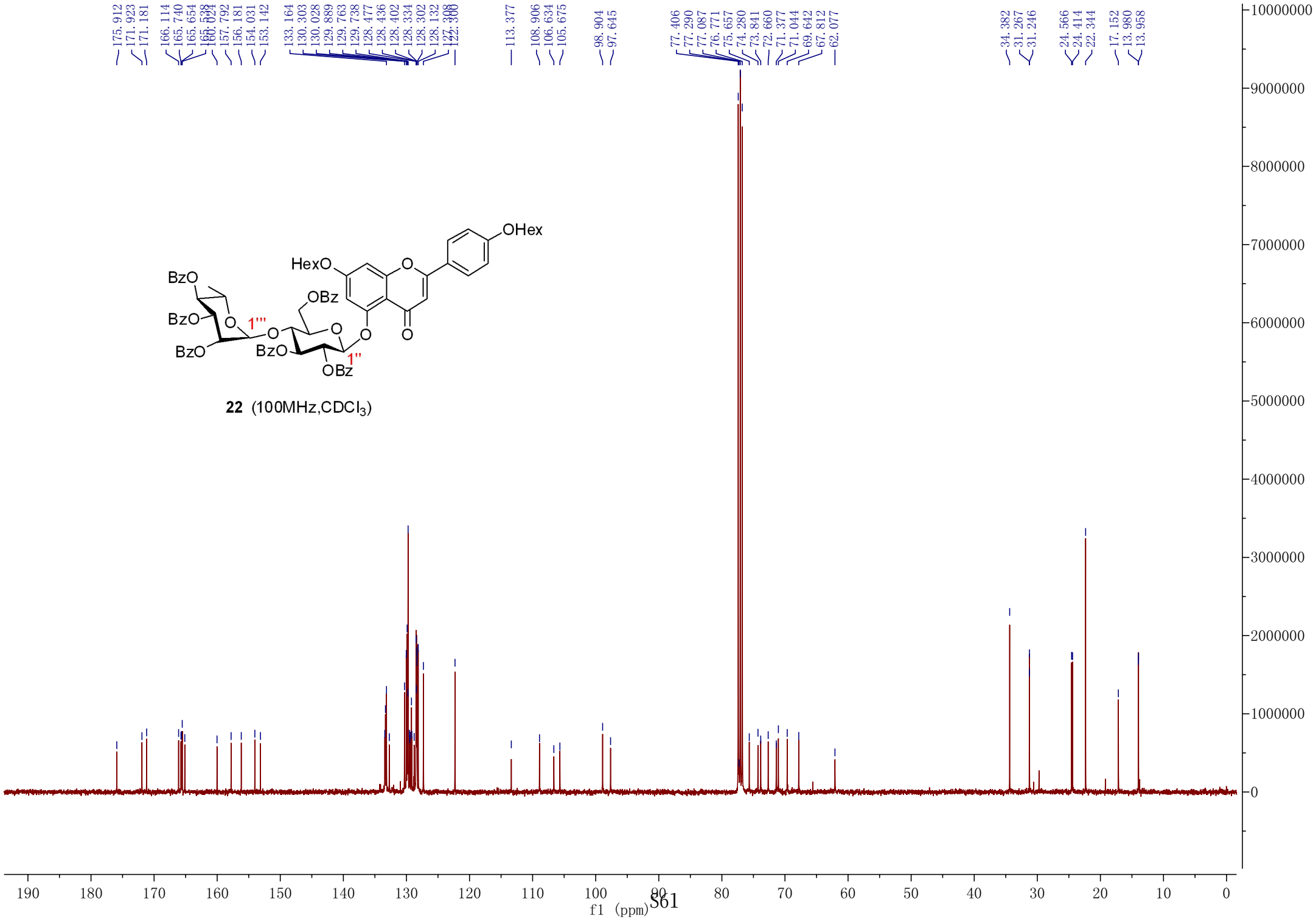

167.972
167.618
167.576
167.481
167.233
135.450
135.325
135.231
135.158
135.026
131.980
131.871
131.739
131.680
131.560
131.420
131.214
131.186
131.156
130.492
130.397
130.368
130.299
130.269
100.765
97.937
79.395
79.278
79.170
79.077
78.760
76.192
75.872
75.609
73.341
73.118
71.521
69.779
64.739
35.882
26.708
21.852
21.773
20.380
20.343
19.065
0.000
-1.488
BzO
BzO
BzO
O
O
OBz
O
BzO
OTDS
OBz
20 (100MHz,CDCl3)
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

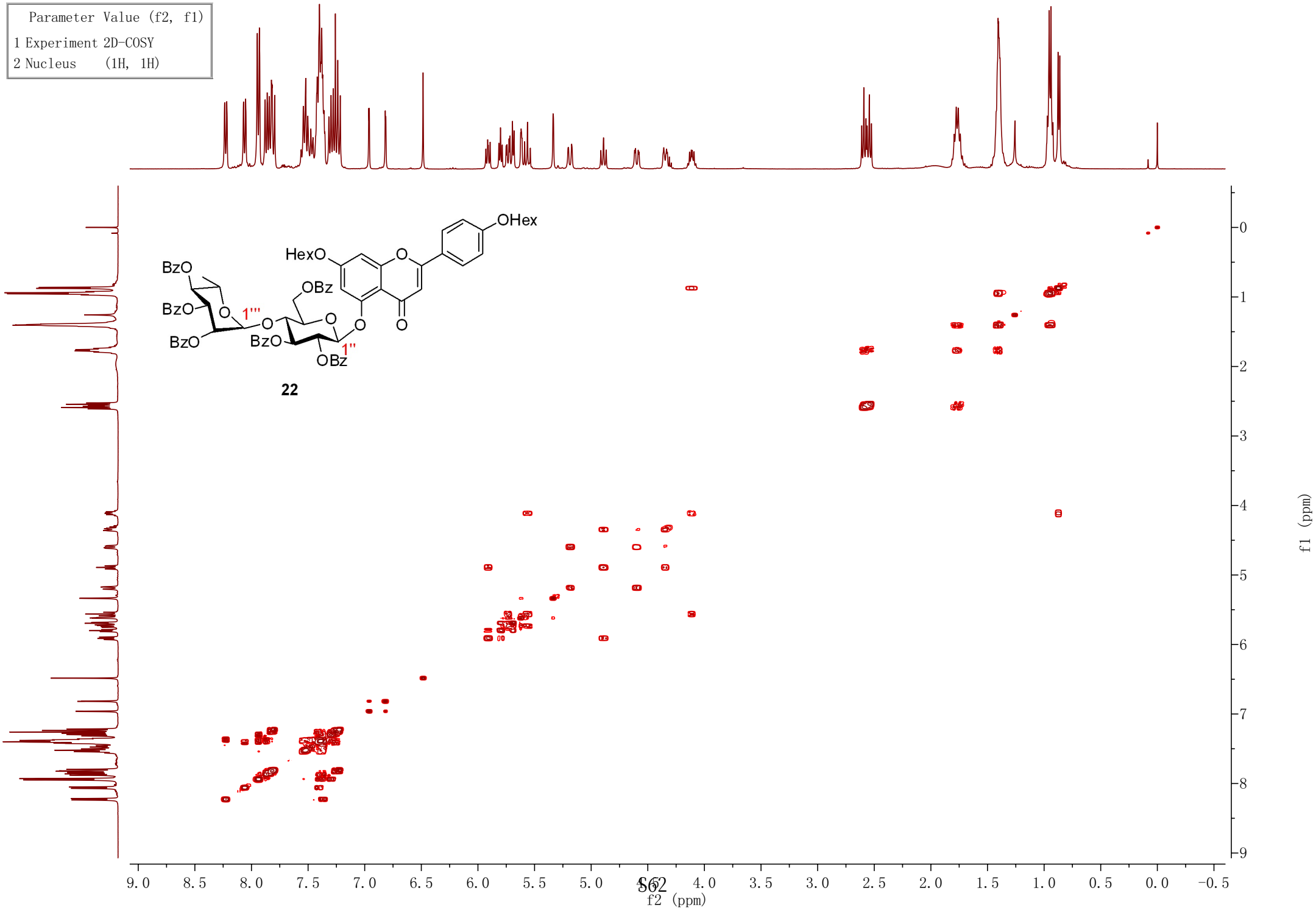

BzO
BzO
BzO
O
O
BzO
O
OBz
OABz
OBz
21 (400MHz,CDCl3)
f1 (ppm)

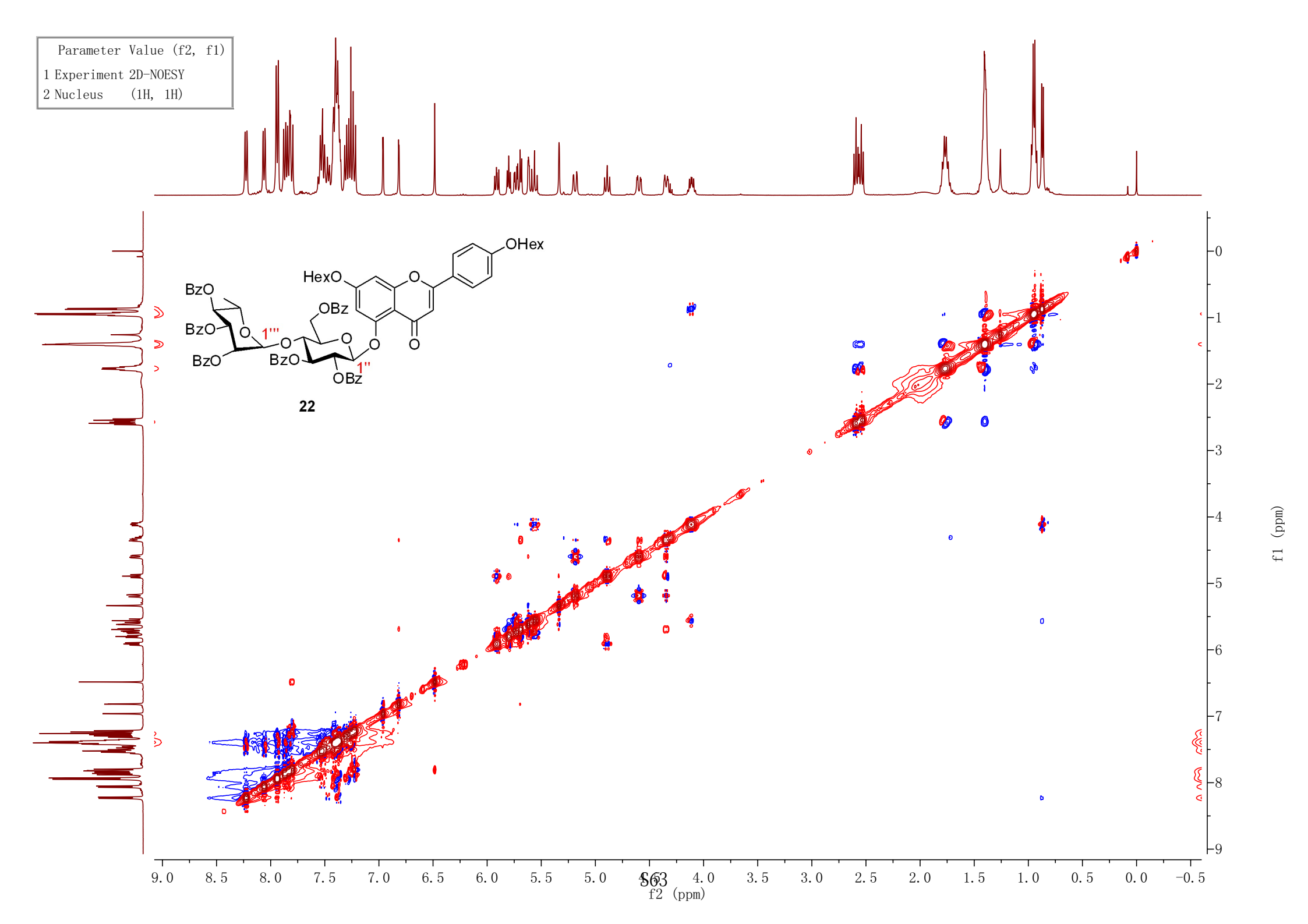

165.160
165.057
164.913
164.731
164.555
162.623
133.582
132.686
132.629
132.444
132.256
131.658
130.096
129.185
129.134
129.042
129.019
128.741
128.493
128.456
128.419
128.055
127.735
127.703
127.633
127.581
126.283
125.118
99.867
98.260
91.612
76.670
76.353
76.035
75.700
73.574
73.523
73.188
70.659
70.610
70.398
68.692
67.183
61.668
16.390
8.310
8.275
-0.000
BzO
BzO
BzO
O
O
OBz
O
BzO
OABz
OBz
21 (100MHz,CDCl3)
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

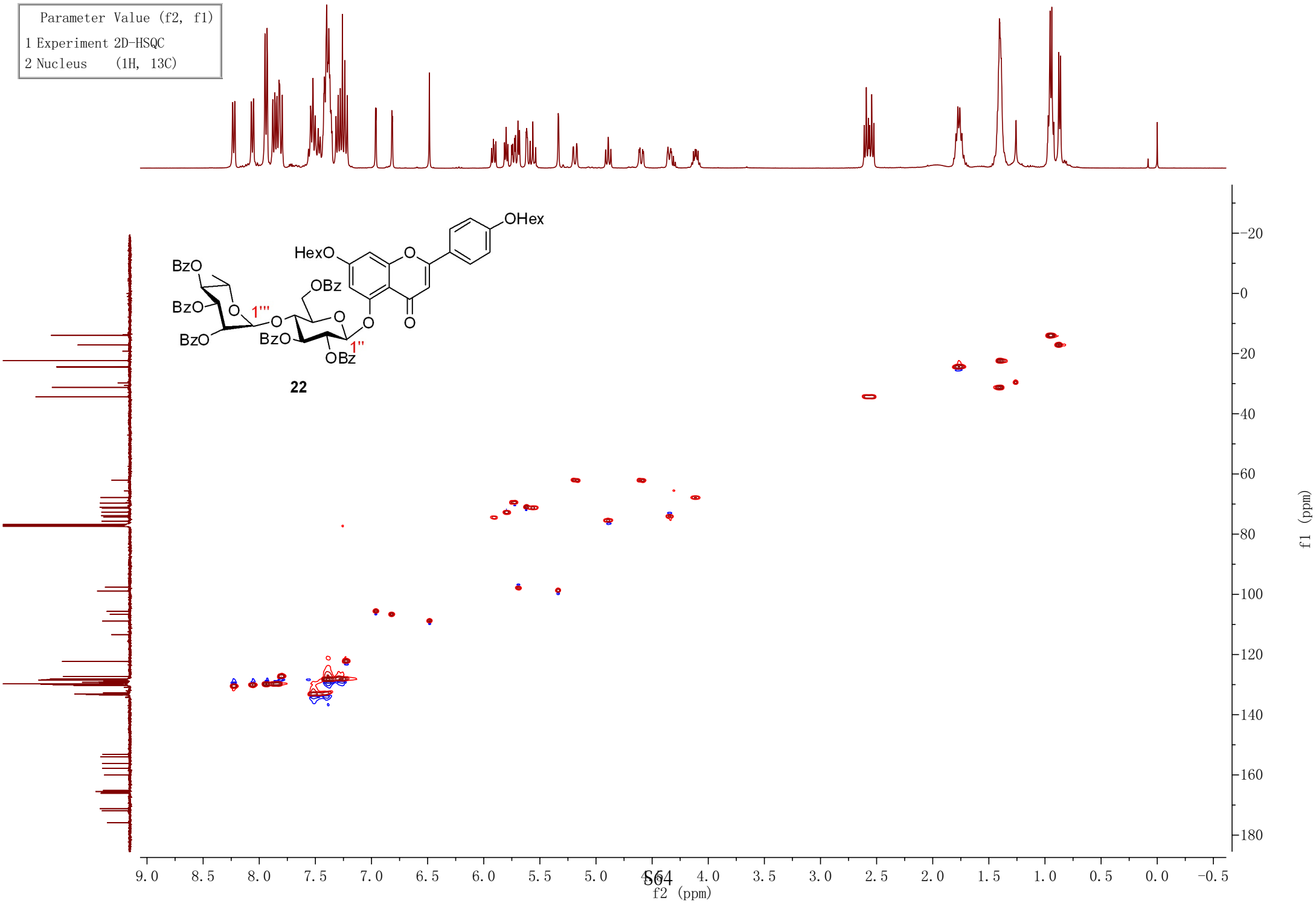


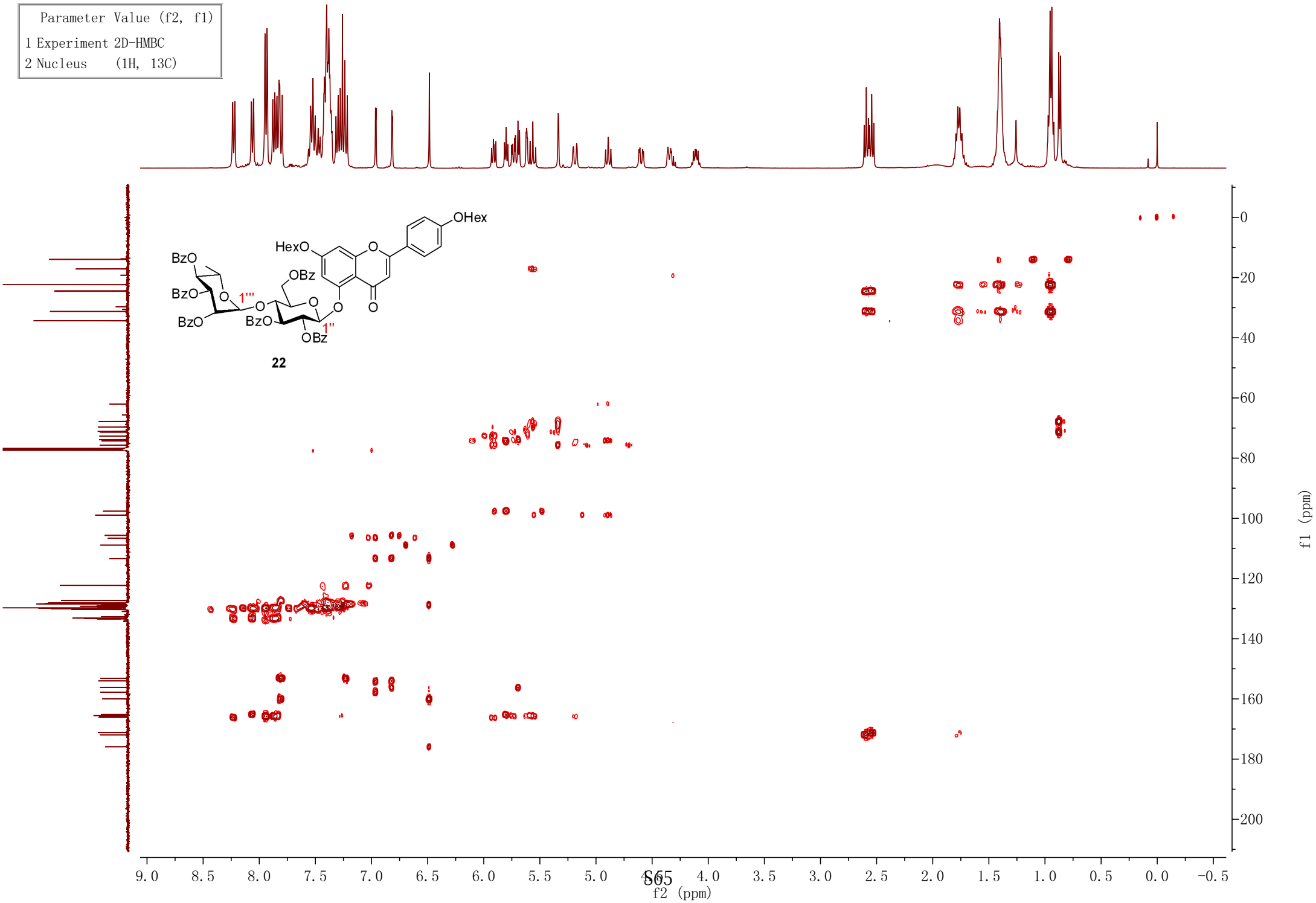
22 (400MHz,$CDCl_3$)

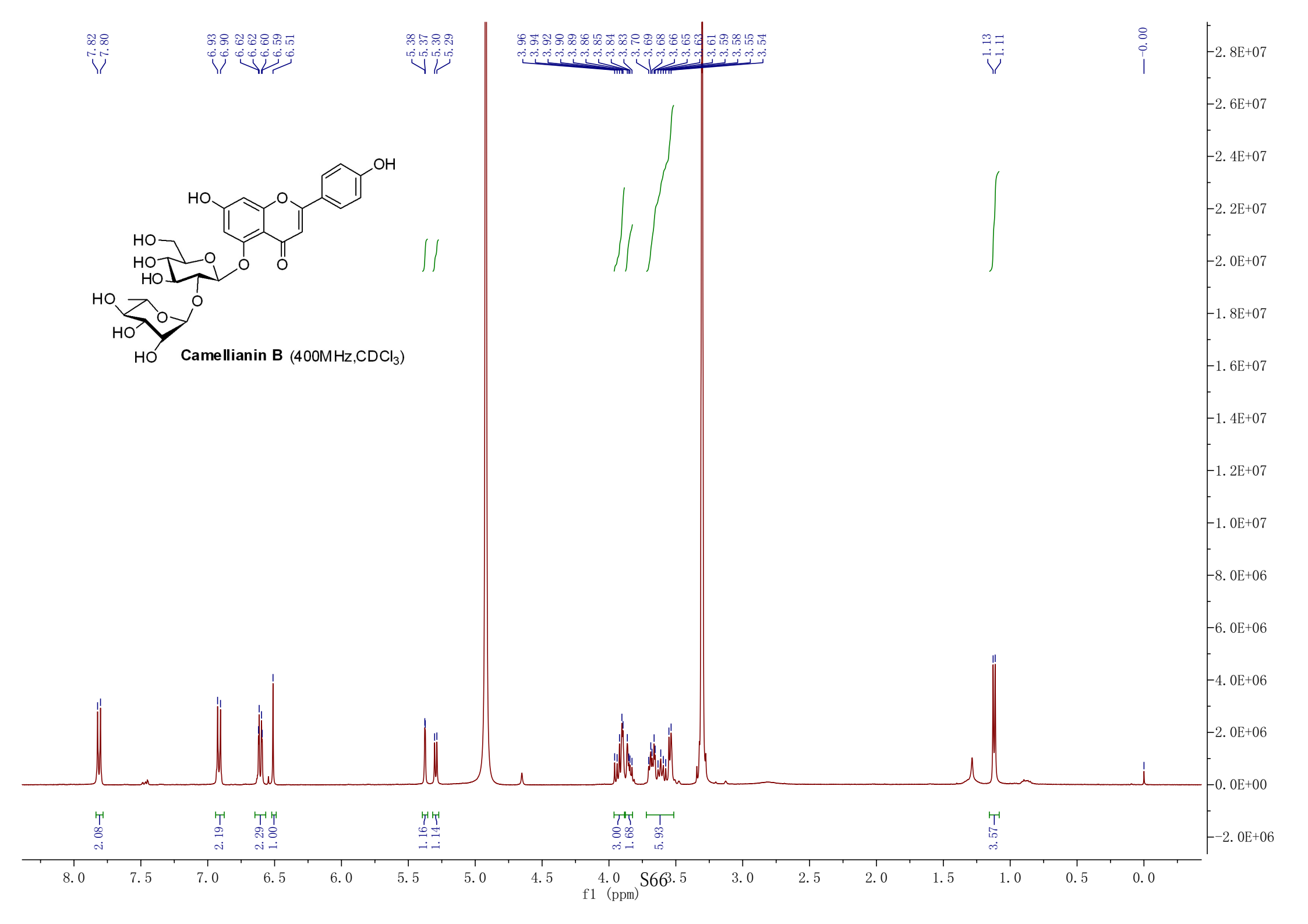

175.912
171.923
171.181
166.114
165.740
165.654
157.792
156.181
154.031
153.142
133.164
130.303
130.028
129.889
129.763
129.738
128.477
128.436
128.402
128.334
128.302
128.132
113.377
108.906
106.634
105.675
98.904
97.645
77.406
77.290
77.087
76.771
75.657
74.280
73.841
72.660
71.377
71.044
69.642
67.812
62.077
34.382
31.267
31.246
24.566
24.414
22.344
17.152
13.980
13.958
OHex
HexO
O
BzO
BzO
BzO
OBz
1'''
O
O
O
BzO
1''
OBz
O
22 (100MHz,CDCl3)
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

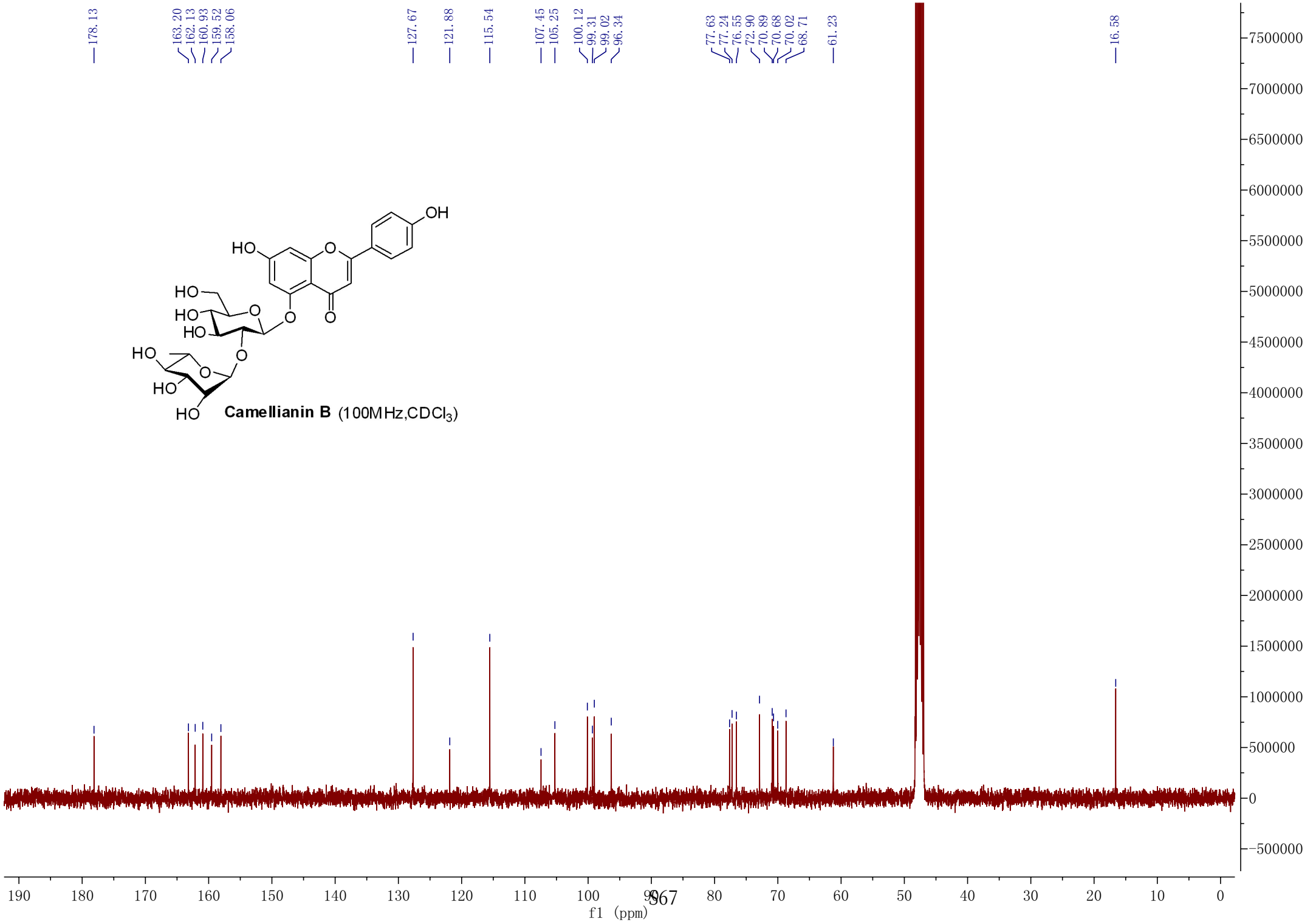

Parameter Value (f2, f1)
1 Experiment 2D-COSY
2 Nucleus (1H, 1H)
OHex
HexO
OBz
BzO
BzO
BzO
BzO
OBz
1'''
1''
22
f2 (ppm)
f1 (ppm)

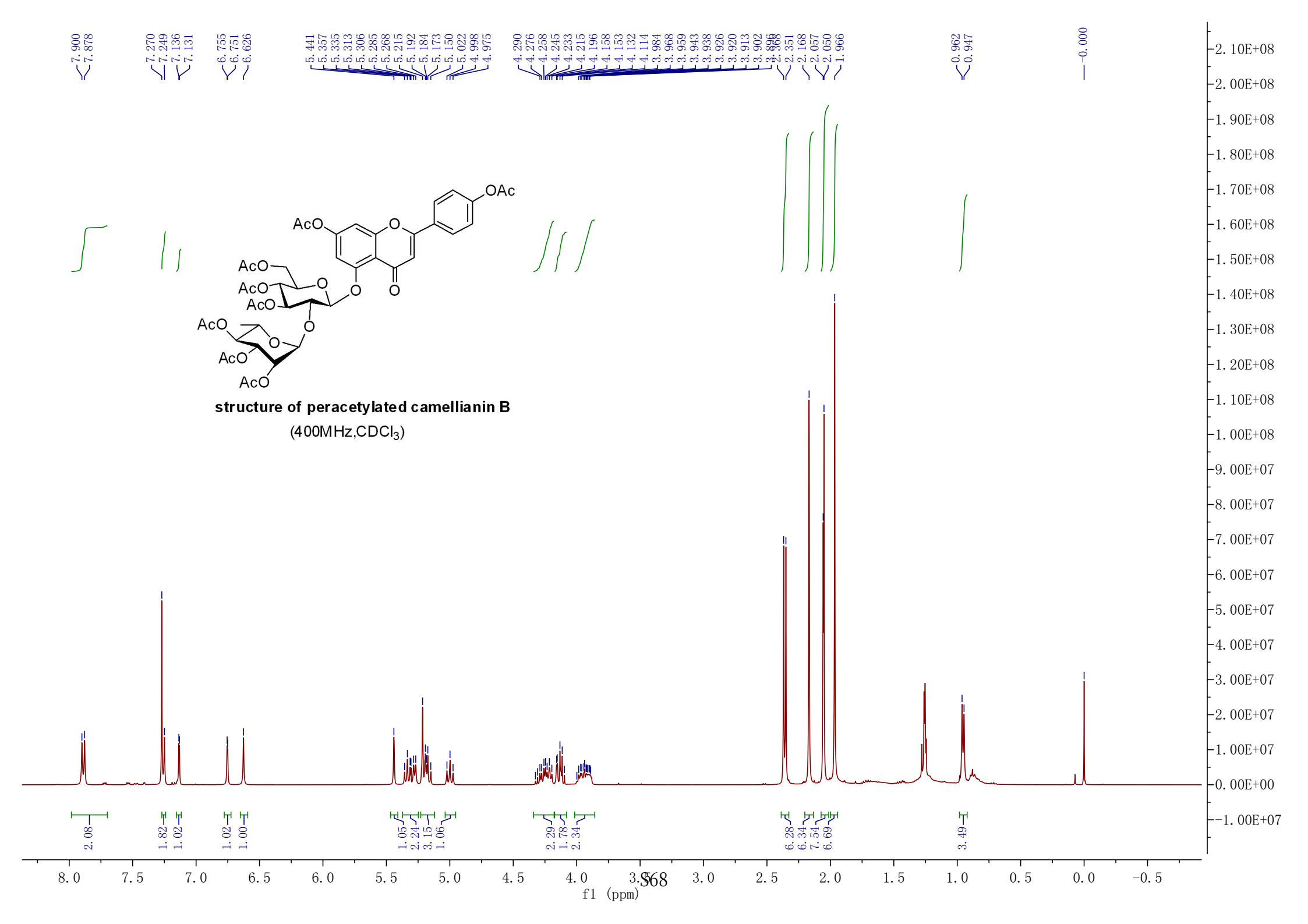

Parameter Value (f2, f1)
1 Experiment 2D-NOESY
2 Nucleus (1H, 1H)
OHex
HexO
OBz
BzO
BzO
BzO
BzO
1'''
1''
OBz
22
f2 (ppm)
f1 (ppm)

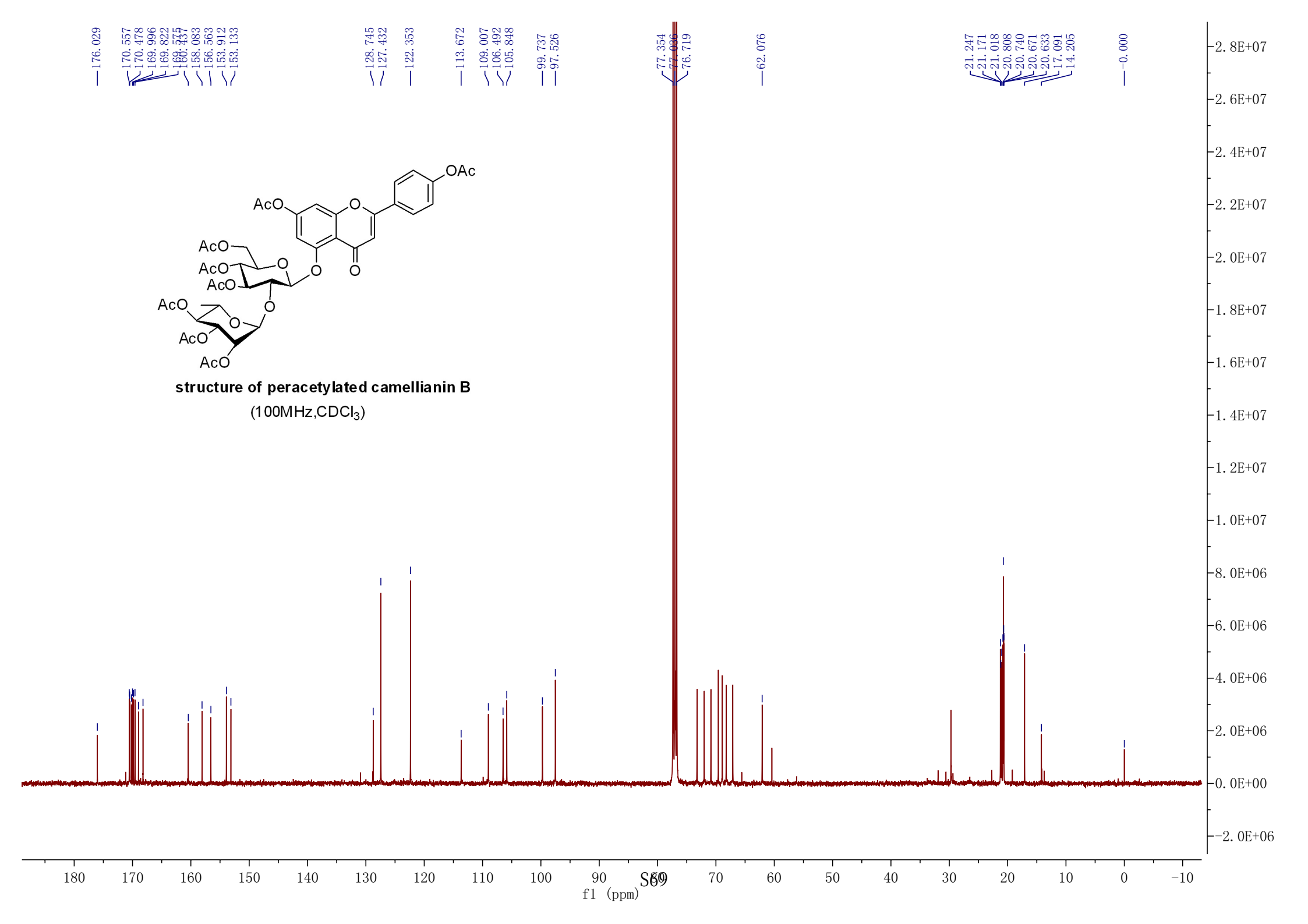

Parameter Value (f2, f1)
1 Experiment 2D-HSQC
2 Nucleus (1H, 13C)
OHex
HexO
OBz
BzO
BzO
BzO
1'''
1''
OBz
22
f2 (ppm)
f1 (ppm)

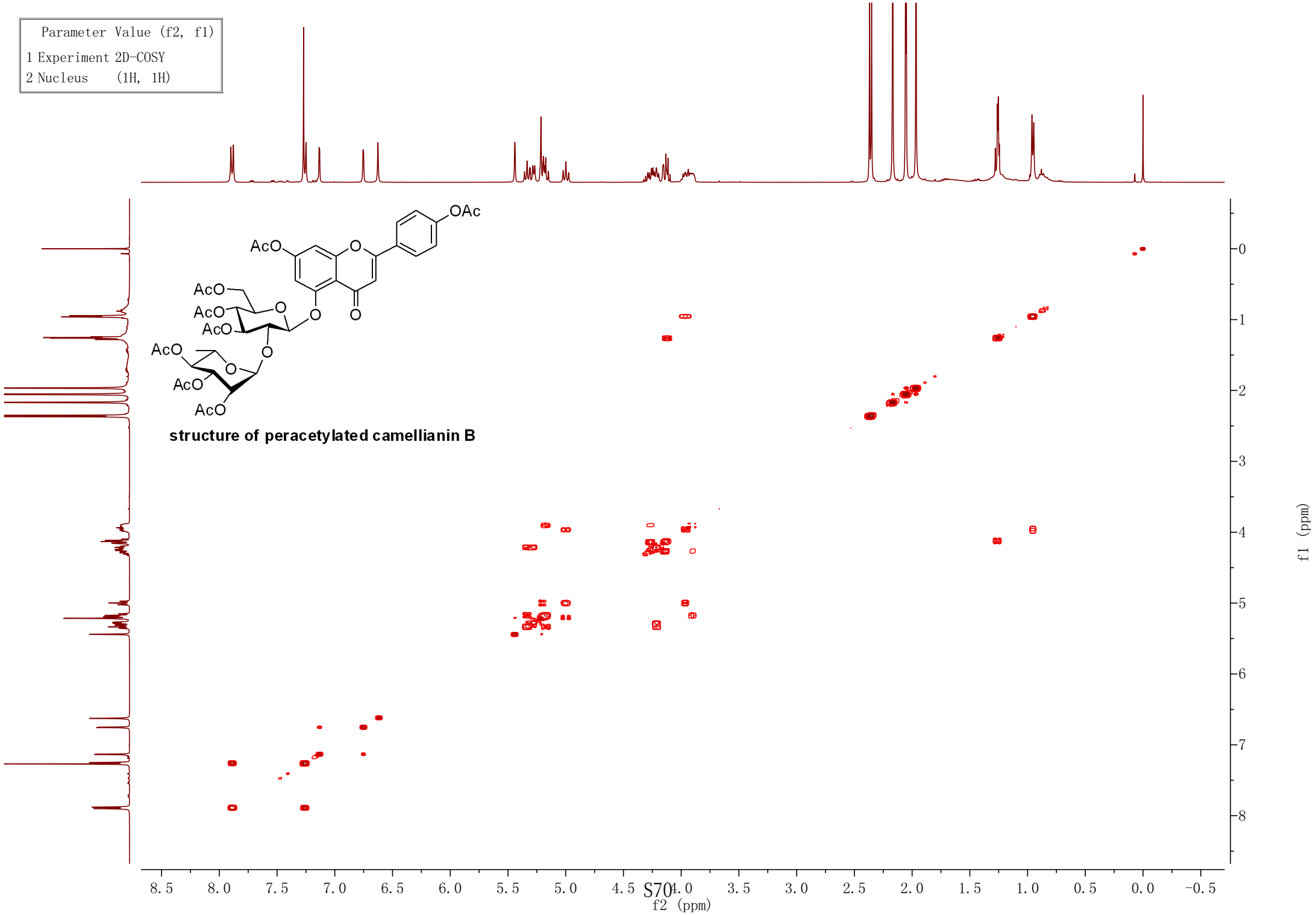

Parameter Value (f2, f1)
1 Experiment 2D-HMBC
2 Nucleus (1H, 13C)
OHex
HexO
OBz
BzO
BzO
BzO
BzO
1'''
1''
OBz
22
f2 (ppm)
f1 (ppm)

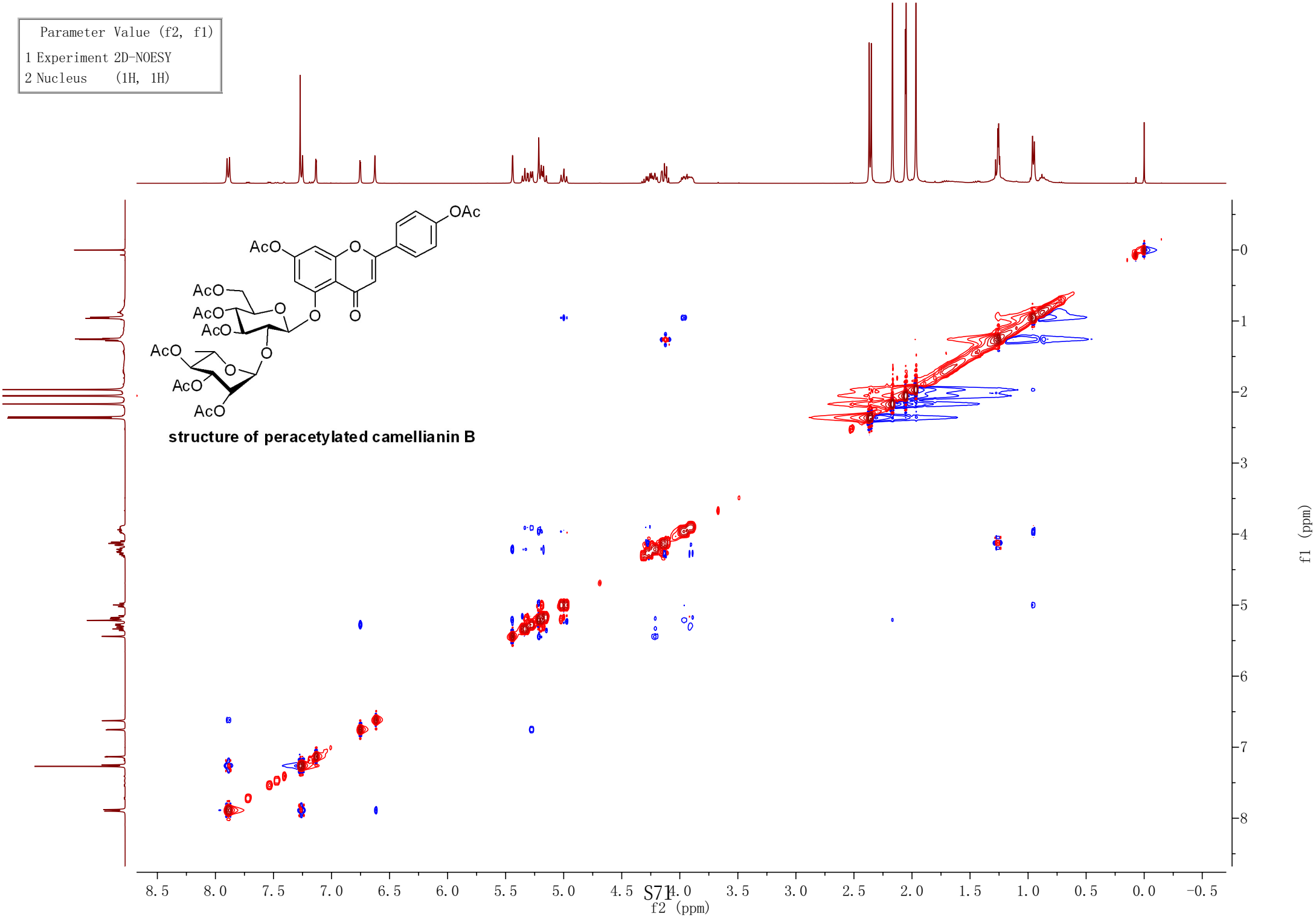

7.82
7.80
6.93
6.90
6.62
6.62
6.60
6.59
6.51
5.38
5.37
5.30
5.29
3.96
3.94
3.92
3.90
3.89
3.86
3.85
3.84
3.83
3.70
3.69
3.68
3.66
3.65
3.63
3.61
3.59
3.58
3.55
3.54
1.13
1.11
0.00
OH
HO
O
HO
HO
HO
HO
HO
HO
O
O
O
O
O
Camellianin B (400MHz,CDCl3)
2.08
2.19
2.29
1.00
1.16
1.14
3.00
1.68
5.93
3.57
2.8E+07
2.6E+07
2.4E+07
2.2E+07
2.0E+07
1.8E+07
1.6E+07
1.4E+07
1.2E+07
1.0E+07
8.0E+06
6.0E+06
4.0E+06
2.0E+06
0.0E+00
-2.0E+06
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)

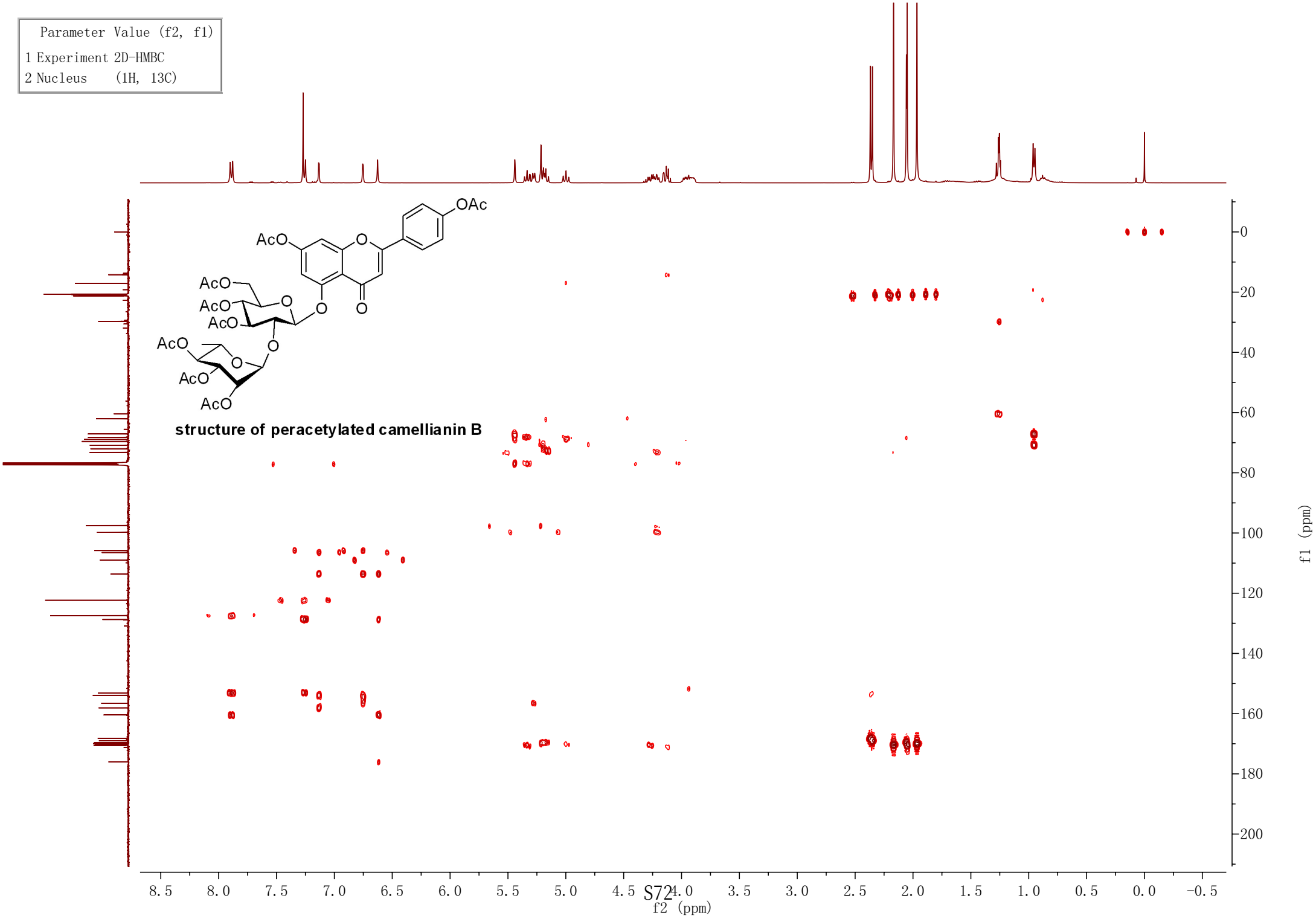

178.13
163.20
162.13
160.93
159.52
158.06
127.67
121.88
115.54
107.45
105.25
100.12
99.31
99.02
96.34
77.63
77.24
76.55
72.90
70.89
70.68
70.02
68.71
61.23
16.58
OH
HO
O
HO
HO
HO
HO
HO
O
O
O
O
O
HO
HO
Camellianin B (100MHz,CDCl3)
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

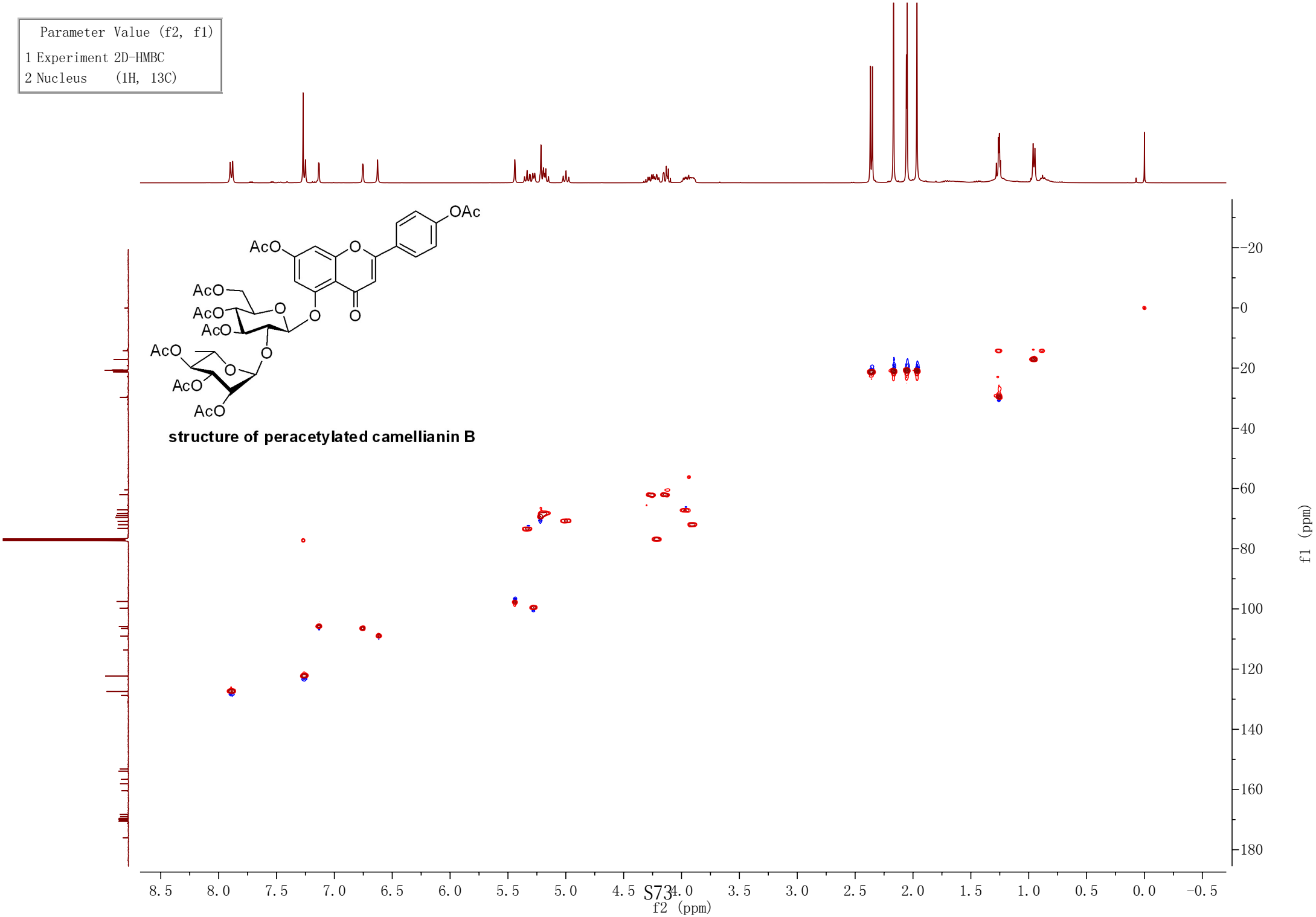

structure of peracetylated camellianin B
(400MHz,CDCl3)
f1 (ppm)

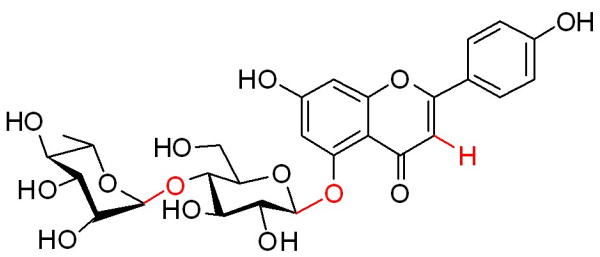

176.029
170.557
170.478
169.996
169.822
158.083
156.563
153.912
153.133
128.745
127.432
122.353
113.672
109.007
106.492
105.848
99.737
97.526
77.354
77.036
76.719
62.076
21.247
21.171
21.018
20.808
20.740
20.671
20.633
17.091
14.205
-0.000
OAc
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
O
structure of peracetylated camellianin B
(100MHz,CDCl3)
f1 (ppm)


Parameter Value (f2, f1)
1 Experiment 2D-COSY
2 Nucleus (1H, 1H)
OAc
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
O
O
O
structure of peracetylated camellianin B
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
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

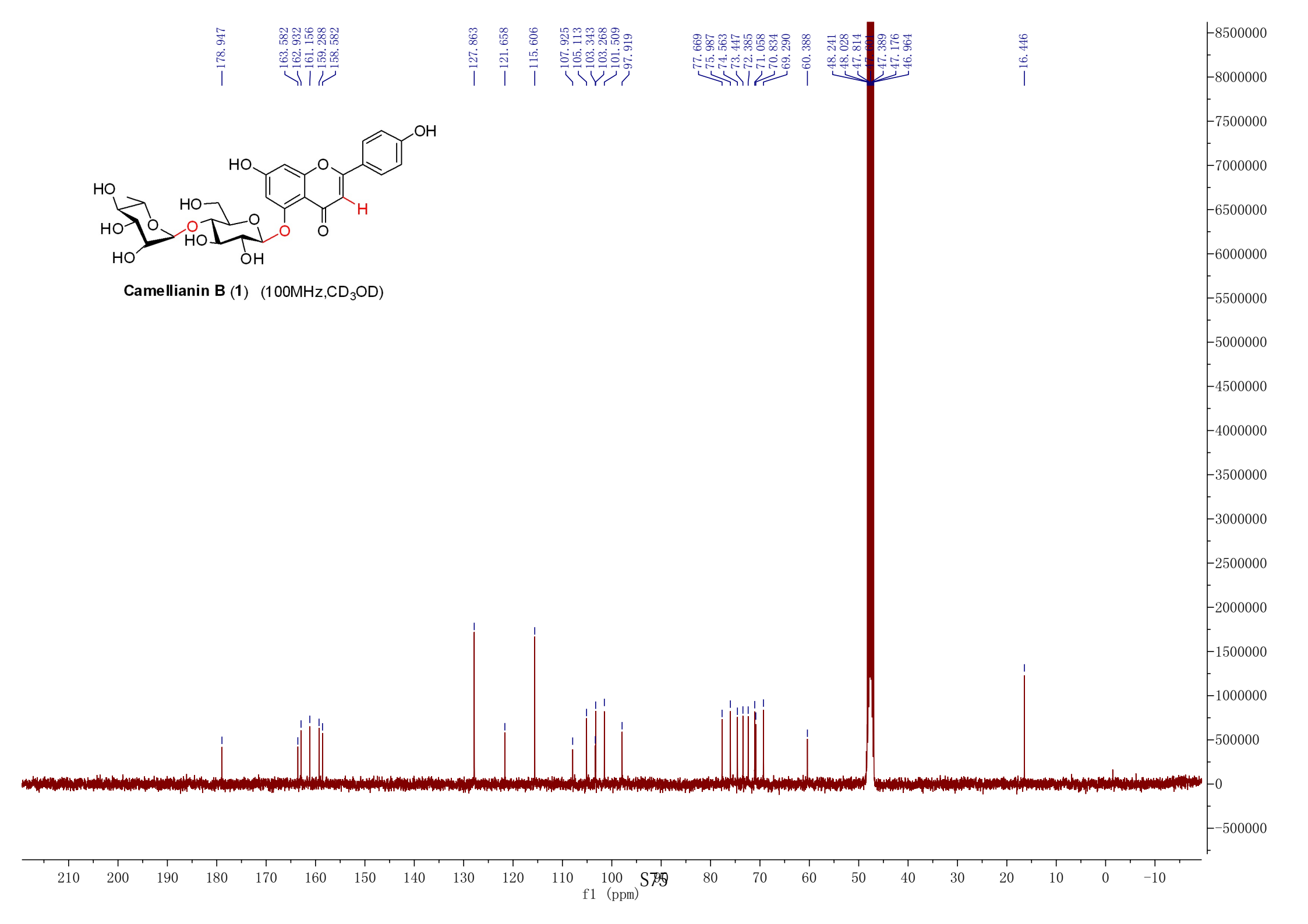

Parameter Value (f2, f1)
1 Experiment 2D-NOESY
2 Nucleus (1H, 1H)
structure of peracetylated camellianin B
f2 (ppm)
f1 (ppm)

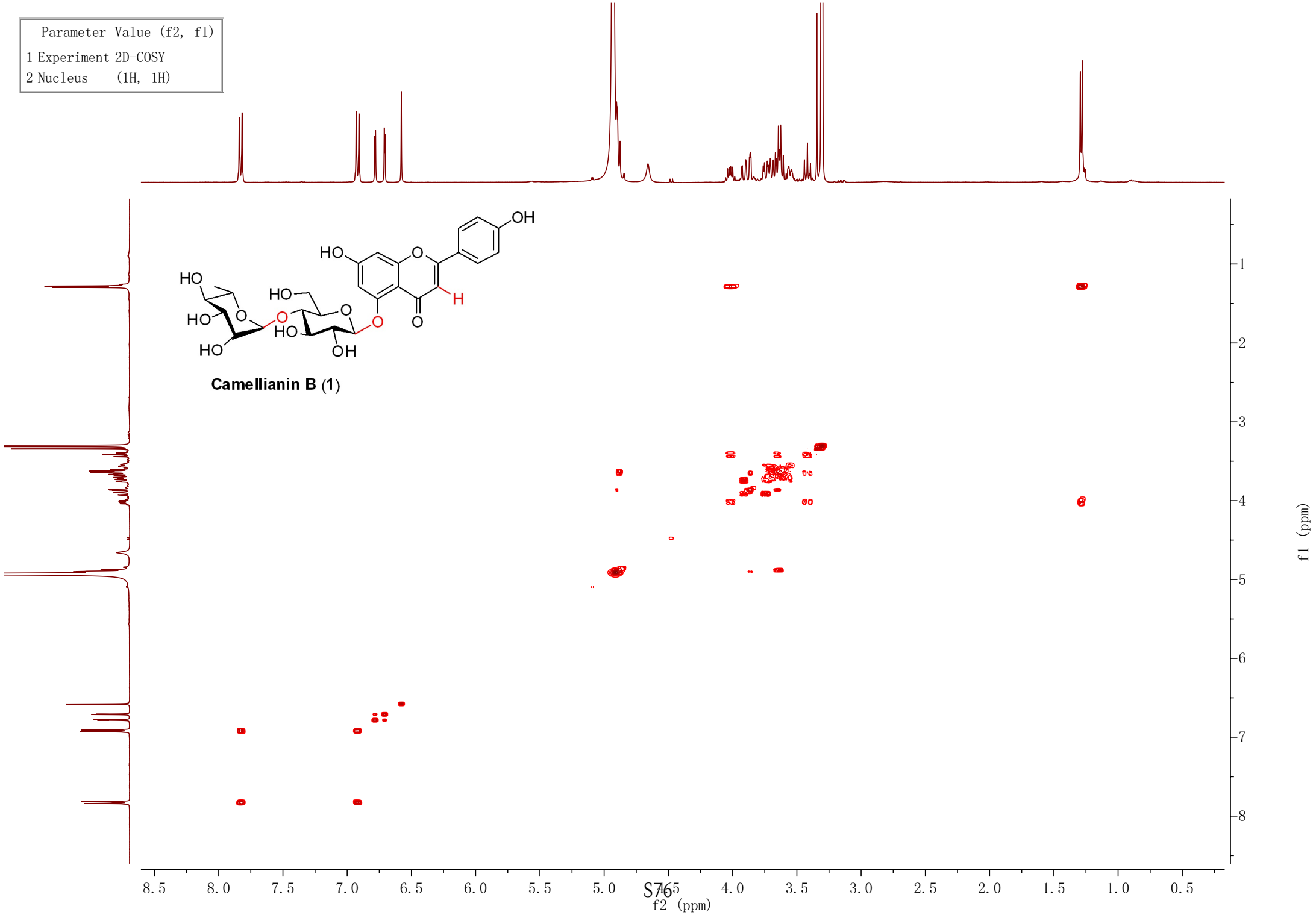

Parameter Value (f2, f1)
1 Experiment 2D-HMBC
2 Nucleus (1H, 13C)
structure of peracetylated camellianin B
f2 (ppm)
f1 (ppm)

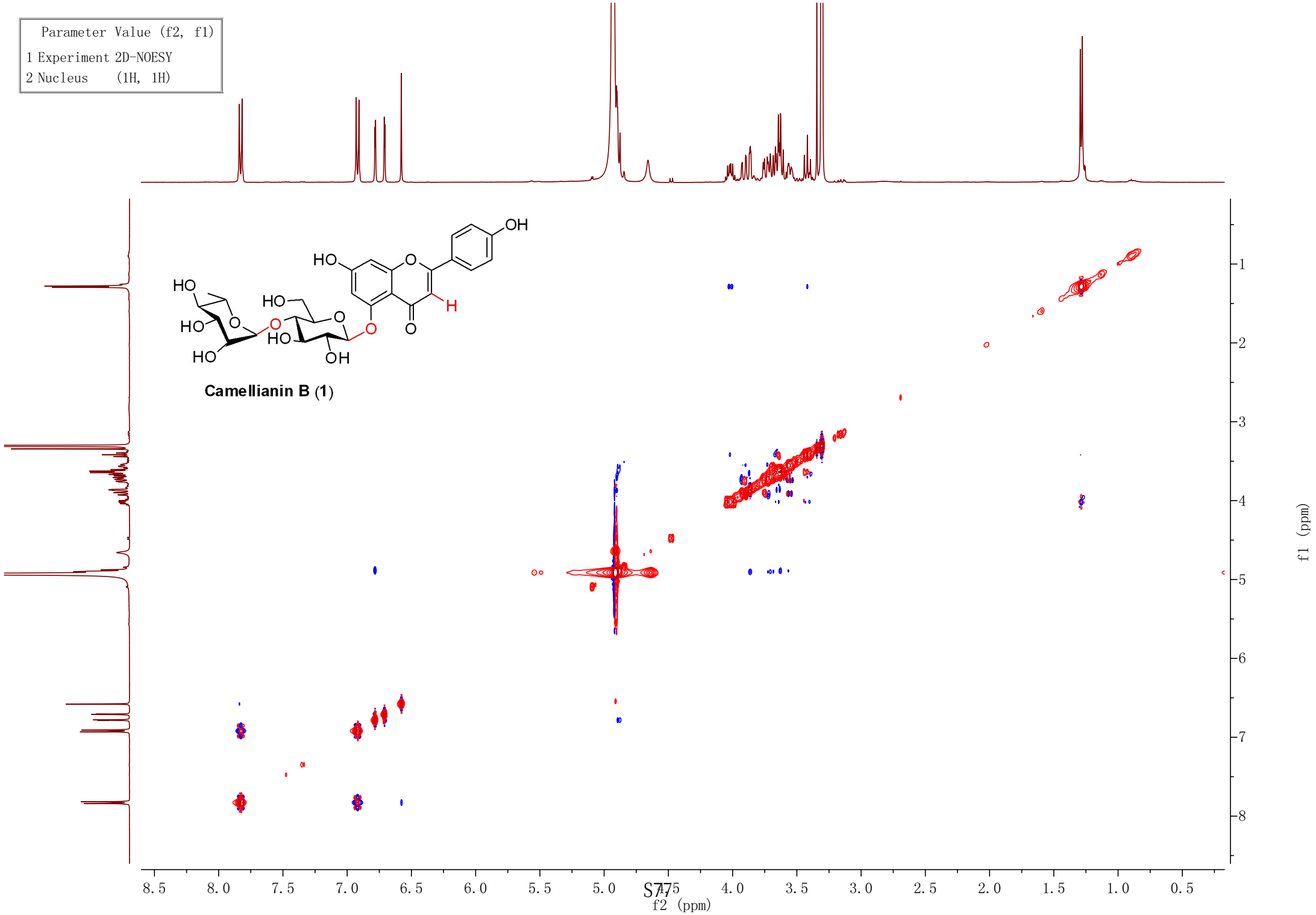

Parameter Value (f2, f1)
1 Experiment 2D-HMBC
2 Nucleus (1H, 13C)
OAc
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
O
O
structure of peracetylated camellianin B
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)

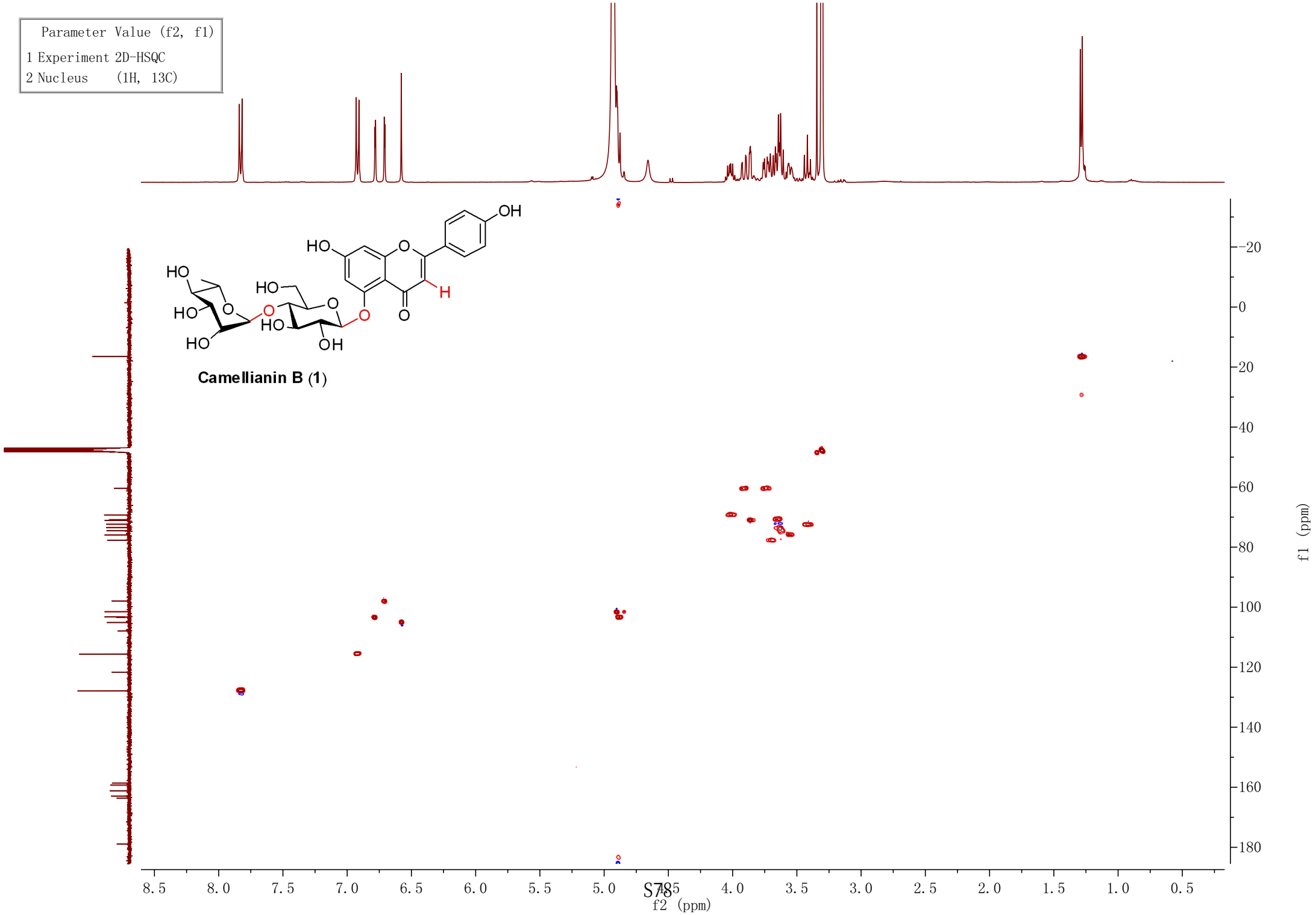


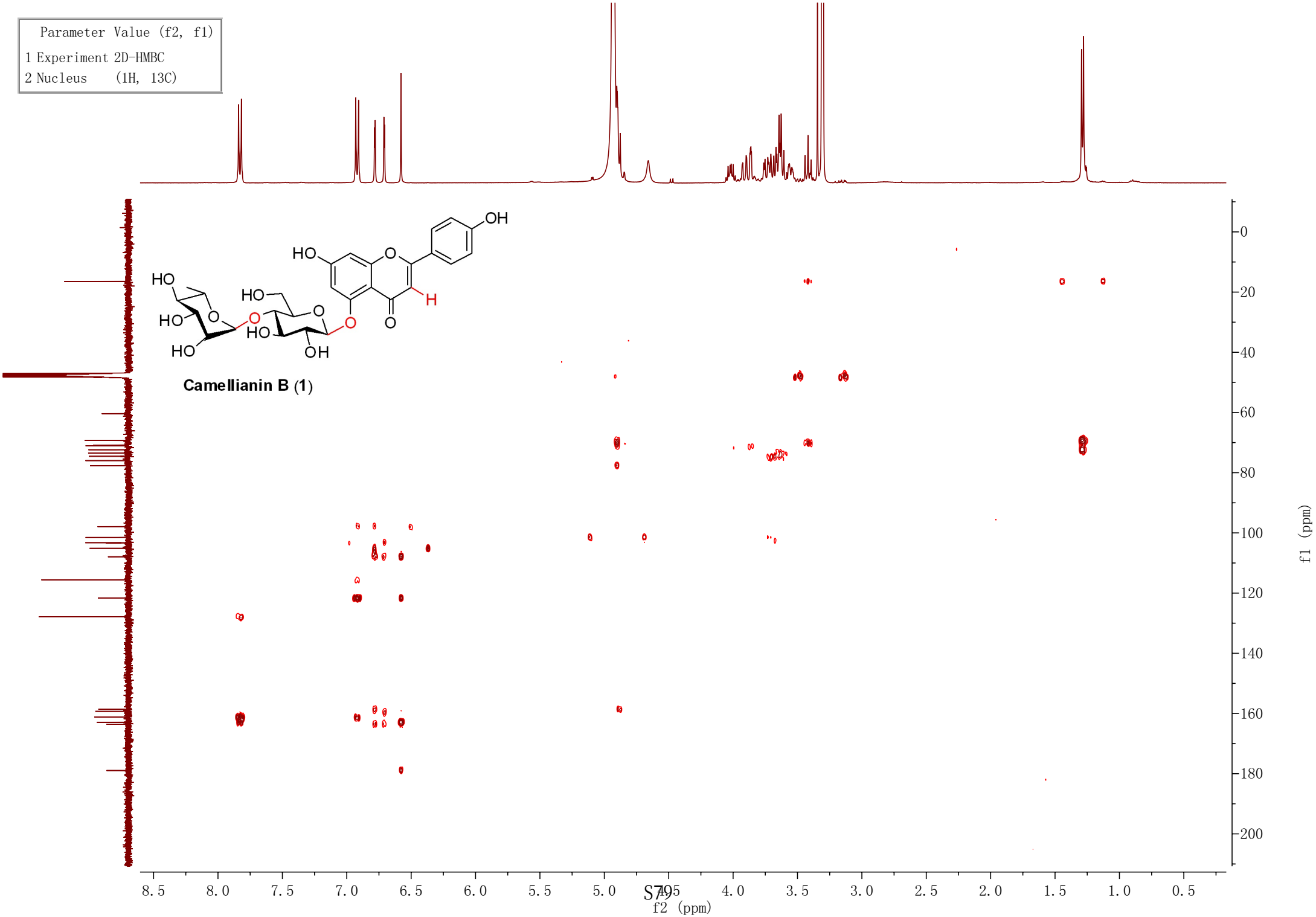
Camellianin B (**1**) (400MHz,CD_3OD)


178.947
163.582
162.932
161.156
159.288
158.582
127.863
121.658
115.606
107.925
105.113
103.343
103.268
101.509
97.919
77.669
75.987
74.563
73.447
72.385
71.058
70.834
69.290
60.388
48.241
48.028
47.814
47.389
47.176
46.964
16.446
HO
HO
HO
HO
HO
HO
O
O
O
O
O
O
H
OH
Camellianin B (1) (100MHz,CD3OD)
f1 (ppm)


Parameter Value (f2, f1)
1 Experiment 2D-COSY
2 Nucleus (1H, 1H)
Camellianin B (1)
f2 (ppm)
f1 (ppm)


Parameter Value (f2, f1)
1 Experiment 2D-NOESY
2 Nucleus (1H, 1H)
Camellianin B (1)
f2 (ppm)
f1 (ppm)


Parameter Value (f2, f1)
1 Experiment 2D-HSQC
2 Nucleus (1H, 13C)
Camellianin B (1)
f2 (ppm)
f1 (ppm)


Parameter Value (f2, f1)
1 Experiment 2D-HMBC
2 Nucleus (1H, 13C)
Camellianin B (1)
f2 (ppm)
f1 (ppm)