Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Highly stereoselective α-glycosylation with $GalN_3$ donors enabled collective synthesis of mucin-related tumor associated carbohydrates antigens

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General Methods

All reactions were carried out under an argon atmosphere with anhydrous solvents under anhydrous conditions, unless otherwise noted. All glycosylation reactions were performed in the presence of 3Å or 4Å molecular sieves, which were flame-dried immediately before use in the reaction under high vacuum. Tetrahydrofuran (THF) was distilled immediately before use from sodium-benzophenoneketyl. Methylene chloride (DCM) was distilled from calcium hydride and stored under an argon atmosphere. Toluene was distilled immediately from calcium chloride before use. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on TLC Silica gel 60 F_{254} or TLC Silica gel 60 RP-18 $F_{254}S$ (EMD Millipore Corporation) using UV light (254 nm) as visualizing agent and 10% PMA/EtOH solution or 10% H_2SO_4/EtOH solution as developing agent. Flash column chromatography was performed on silica gel, LiChroprep® RP-18 (EMD Millipore Corporation) or Sephadex™ LH-20 (GE Healthcare).

The ^{1}H-NMR, ^{13}C-NMR, H-H COSY and HSQC spectra were measured by a Brucker AVANCE III 400MHz spectrometer, Brucker Avance III 600MHz spectrometer or Brucker AV 800MHz spectrometer by using $CDCl_3$ or D_2O as internal references: $CDCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm) or D_2O (^{1}H NMR δ = 4.79 ppm). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Electron spray ionization (ESI) and high-resolution electron spray ionization (HRESI) were obtained on an Agilent 1290 spectrometer. MALDI-TOF spectra were recorded on a new ultrafleXtreme. The specific rotation was obtained on a Jasco P-1020, using $CHCl_3$ or H_2O as solvent.

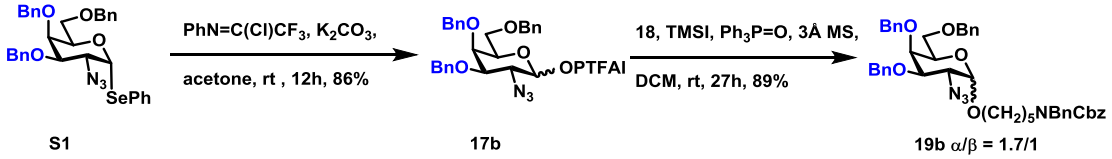
General Experimental Procedures

A mixture of glycosyl PTFAI donor (1.5 equiv) and the acceptor (1.0 equiv) was co-evaporated with anhydrous toluene for three times. Then the mixture together with $Ph_3P=O$ (6.0 equiv to the donor) were dissolved in dry DCM (0.1 M) and stirred over fresh-dried 3Å molecular sieves under argon at room temperature for 15 min. Subsequently, TMSI (1.0 equiv to the donor) was added dropwise. The reaction was stirred at room temperature. Upon completion, the solution was diluted with DCM and the reaction was quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The products were purified by flash column chromatography.

Experimental procedures

Optimization of the reaction

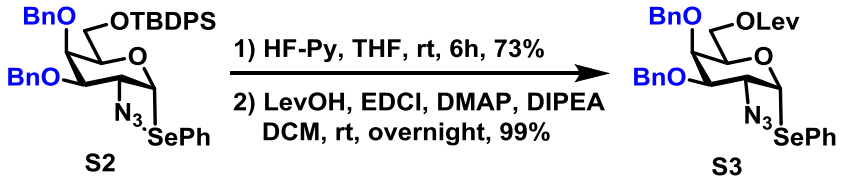
N-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy -D-galactopyranoside (19b)



S1 17b 19b α/β = 1.7/1

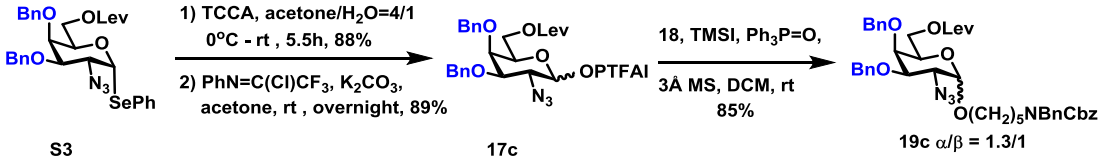
Compound **S1**[1] (104.1 mg, 0.22 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride[2] (54.5 mg, 0.26 mmol) was dissolved in acetone (1 mL), and K_2CO_3 (45.5 mg, 0.33 mmol) was added. The reaction was stirred at room temperature for 12 h, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17b** (131 mg, 93%) (Compound **17b** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedures** at 30 ℃ for 27 h, using donor **17b** (129 mg, 0.20 mmol), acceptor **18** (98 mg, 0.30 mmol), DCM (2 mL), Ph_3P=O (333.1 mg, 1.20 mmol) and TMSI (29 μL, 0.20 mmol). The product was purified by silica gel column chromatography (PE-EA, 6:1) to afford **19b** (138.4 mg, 89%, α/β = 1.7:1) as a yellowish syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.11 (m, 25H, Ar), 5.21 – 5.11 (m, 2H, CH_2-Cbz), 4.91 – 4.83 (m, 2H, H-1α, CH_2-Bn), 4.74 – 4.63 (m, 2H, CH_2-Bn), 4.59 – 4.37 (m, 5H, CH_2-Bn), 4.15 (s, H-1β), 4.02 (s, 1H), 3.93 (s, 1H), 3.87 – 3.77 (m, 2H), 3.65 – 3.51 (m, 2H), 3.50 – 3.31 (m, 2H), 3.30 – 3.15 (m, 2H, CH_2), 1.62 – 1.46 (m, 4H, CH_2), 1.36 – 1.29 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 156.1, 138.3, 137.95, 137.89, 137.8, 137.7, 137.6, 136.9, 128.52, 128.49, 128.46, 128.43, 128.41, 128.3, 128.2, 128.1, 127.9, 127.87, 127.82, 127.78, 127.7, 127.6, 127.2, 102.4 (C-1β), 98.2（C-1α）, 80.6, 77.3, 74.8, 74.6, 73.5, 72.5, 72.3, 72.2, 69.6, 68.8, 68.5, 68.1, 67.1, 63.4, 59.8, 50.5, 50.2, 47.1, 46.2, 31.9, 29.7, 29.4, 29.2, 29.1, 27.9, 27.5, 23.4, 23.2, 22.7. HRMS (ESI) calcd for $C_{47}H_{56}N_5O_7$ $[M+NH_4]^+$ 802.4174, found 802.4183.

Phenyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-1-seleno-α-D-galacto-pyranoside (S3)



The **S2**[2] (244 mg, 0.32 mmol) was dissolved in anhydrous THF (1 mL), and HF/pyridine (70%, 0.29 mL, 3.20 mmol) was added dropwise. The resulting mixture was stirred for 6 h at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 4:1) to give the intermediate (121.6 mg, 73%). To a solution of the above intermediate (121.6 mg, 0.23 mmol) and levulinic acid (LevOH) (53.8 mg, 0.46 mmol) in anhydrous DCM (1 mL) was added 4-dimethylaminopyridine (DMAP) (5.7 mg, 0.046 mmol), *N*-(3-dimethylamino- propyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI) (133.3 mg, 0.70 mmol) and *N*,*N*-diisopropylethylamine (DIPEA) (0.11 mL, 0.70 mmol). The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 3.5:1) to afford **S3** (143 mg, 99%) as a white solid. $[\alpha]_D^{25}$ = +321.5 (c 0.15, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H, Ar), 7.47 – 7.24 (m, 13H, Ar), 5.96 (d, *J* = 5.4 Hz, 1H, H-1), 4.92 (d, *J* = 11.3 Hz, 1H, CH_2-Bn), 4.78 (s, 2H, CH_2-Bn), 4.57 (d, *J* = 11.3 Hz, 1H, CH_2-Bn), 4.41 – 4.33 (m, 2H, H-2), 4.16 – 4.08 (m, 2H), 3.96 (s, 1H, H-4), 3.73 (dd, *J* = 10.4, 2.6 Hz, 1H, H-3), 2.66 (t, *J* = 6.5 Hz, 2H, CH_2-Lev), 2.46 – 2.40 (m, 2H, CH_2-Lev), 2.14 (s, 3H, CH_3-Lev). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 172.4, 137.9, 137.3, 134.53, 134.48, 129.1, 128.7, 128.5, 128.3, 128.21, 128.18, 128.0, 127.9, 85.2 (C-1), 80.2, 74.8, 72.8, 72.7, 71.0, 63.2, 60.9, 37.9, 29.9, 27.7. HRMS (ESI) calcd for $C_{31}H_{33}N_3O_6SeNa$ $[M+Na]^+$ 640.1486, found 640.1475.

***N*-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-D-galactopyranoside (19c)**

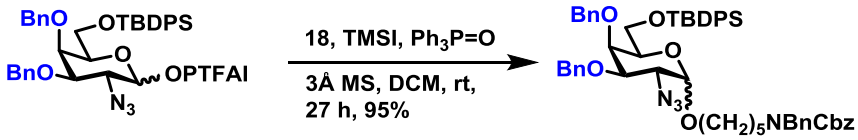


S3 17c 19c α/β = 1.3/1

To a solution of compound **S3** (143 mg, 0.23 mmol) in acetone/H_2O (4.5 mL/1.1 mL) was added Trichloroisocyanuric acid (TCCA) (53.3 mg, 0.23 mmol) at 0 ℃. The reaction mixture was warmed gradually to room temperature and stirred for 5.5 h. 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, 2:1 to 1.5:1) afforded hemiacetal intermediate (97.8 mg, 88%). The above intermediate (97.8 mg, 0.20 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (50.4 mg, 0.24 mmol) was dissolved in acetone (0.5 mL), and K_2CO_3 (42 mg, 0.30 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 6:1 to 3:1, containing 2% Et_3N) to give **17c** (118 mg, 89%) (Compound **17c** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedures** at rt for 3d, using donor **17c** (118 mg, 0.18 mmol), acceptor **18** (89.6 mg, 0.27 mmol), DCM (1.8 mL), Ph_3P=O (304.7 mg, 1.10 mmol) and TMSI (26 μL, 0.18 mmol). The product was purified by silica gel column chromatography (PE-EA, 2.5:1) to afford **19c** (122.4 mg, 85%, α/β = 1.3:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 19H, Ar), 7.19 -7.15 (m, 1H, Ar), 5.24 – 5.11 (m, 2H, CH_2-Cbz), 4.96 – 4.90 (m, 1H, CH_2-Bn), 4.89 – 4.85 (m, 1H, H-1α), 4.80 – 4.70 (m, 2H, CH_2-Bn), 4.62 (d, *J* = 11.5 Hz, CH_2-Bn β), 4.57 (d, *J* = 11.3 Hz, 1H, CH_2-Bn α) 4.52 – 4.47 (m, 1H), 4.23 (dd, *J* = 11.1, 6.3 Hz), 4.19 – 4.14 (m, 1H), 4.13 – 4.09 (m, 1H), 3.98 – 3.78 (m, 3H), 3.68 – 3.55 (m, 1H),

3.52 – 3.18 (m, 4H, CH_2), 2.74 – 2.64 (m, 2H, CH_2-Lev), 2.54 – 2.42 (m, 2H, CH_2-Lev), 2.17 (s, 1H, CH_3-Lev β), 2.16 (s, 2H, CH_3-Lev α), 1.64 – 1.47 (m, 4H, CH_2), 1.39 – 1.28 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 206.3, 172.4, 172.3, 156.7, 156.2, 138.1, 138.03, 137.99, 137.6, 137.5, 136.9, 128.59, 128.56, 128.54, 128.47, 128.4, 128.33, 128.29, 128.0, 127.95, 127.92, 127.89, 127.84, 127.83, 127.80, 127.3, 102.4 (C-1β), 98.2 (C-1α), 80.6, 77.3, 74.7, 74.5, 73.1, 72.7, 72.4, 72.0, 71.8, 69.8, 68.6, 68.2, 67.2, 63.4, 63.3, 62.9, 59.7, 53.5, 50.5, 50.3, 47.2, 46.2, 37.9, 37.8, 29.8, 29.7, 29.4, 29.2, 29.1, 27.82, 27.78, 27.5, 23.4, 23.2, 22.7. HRMS (ESI) calcd for $C_{45}H_{56}N_5O_9$ $[M+NH_4]^+$ 810.4073, found 810.4074.

_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4-di-_O_-benzyl-6-_O_-tert-butyldiphenylsilyl-2-deoxy-D-galactopyranoside (19d)

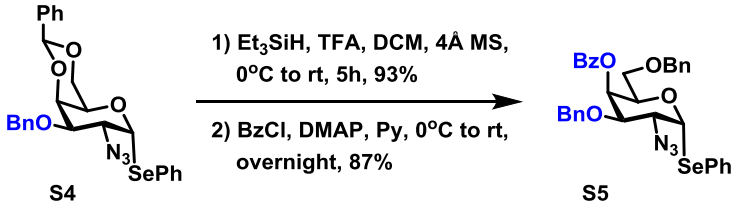


17d **19d** α/β = 1.5/1

The glycosylation reaction was carried out according to **General Experimental Procedures** at 30 ℃ for 27 h, using donor **17d**[3] (103 mg, 0.13 mmol) (Compound **17d** was used directly without further structural characterization), acceptor **18** (63.6 mg, 0.19 mmol), DCM 1.3 mL, Ph_3P=O (216.4 mg, 0.78 mmol) and TMSI (19 μL, 0.13 mmol). The product was purified by silica gel column chromatography (PE-EA, 10:1 to 7:1) to afford **19d** (114.5 mg, 95%, α/β = 1.5:1) as a yellowish syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 4H, Ar), 7.44 – 7.11 (m, 26H, Ar), 5.21 – 5.12 (m, 2H, CH_2-Cbz), 4.90 (t, J = 10.8 Hz, 1H, CH_2-Bn), 4.82 (s, 1H, H-1α), 4.76 – 4.67 (m, 2H, CH_2-Bn), 4.58 (t, J = 10.4 Hz, 1H, CH_2-Bn), 4.53 – 4.43 (m, 2H, CH_2-Bn), 4.09 (s, H-1β), 4.03 (s), 3.97 – 3.87 (m, 1H), 3.83 – 3.68 (m, 4H, H-2α, H-2β), 3.56 – 3.44 (m, 1H), 3.38 – 3.12 (m, 4H, CH_2), 1.61 – 1.44 (m, 4H, CH_2), 1.34 – 1.26 (m, 2H, CH_2), 1.05 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.54, 138.46, 138.0, 137.9, 137.8, 136.9, 135.62, 135.59, 133.35, 133.25, 129.9, 128.63, 128.61, 128.58, 128.52, 128.3, 128.2, 128.1, 128.03, 128.96, 127.92, 127.91, 127.85, 127.81, 127.7, 127.6,

127.3, 102.5 (C-1β), 98.1 (C-1α), 80.6, 77.4, 75.0, 74.9, 74.8, 73.6, 72.7, 72.6, 72.4, 71.2, 69.7, 67.9, 67.3, 67.2, 63.5, 62.7, 62.3, 60.0, 50.6, 50.3, 47.2, 46.3, 29.8, 29.3, 29.2, 27.0, 23.5, 23.3, 19.3. HRMS (ESI) calcd for $C_{56}H_{68}N_5O_7Si$ $[M+NH_4]^+$ 950.4883, found 950.4888.

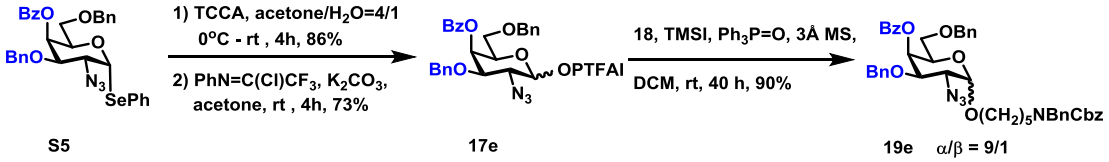
Phenyl 2-azido-4-*O*-benzoyl-3,6-di-*O*-benzyl-2-deoxy-1-seleno-α-D-galacto-pyranoside (S5)



To a solution of the **S4**[1] (110.7 mg, 0.21 mmol) in new-distilled DCM (1 mL) was stirred over fresh-dried 4Å molecular sieves under argon at room temperature for 15 min. Then the solution was cooled to 0 ℃, Et_3SiH (0.34 mL, 2.12 mmol) and trifluoroacetic acid (TFA) (0.16 mL, 2.12 mmol) was added respectively. The resulting mixture was allowed to warm to room temperature and stirred for 5 h. Upon completion, the reaction mixture was quenched with Et_3N, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 6:1) to afford the intermediate (103.4 mg, 93%). The above intermediate (103 mg, 0.20 mmol) was dissolved in anhydrous pyridine (1 mL). The solution was cooled to 0 ℃, DMAP (24 mg, 0.20 mmol) was added, then BzCl (0.03 mL, 0.29 mmol) was added slowly. The resulting mixture was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction mixture was diluted in EA, washed with 3M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford **S5** (110.4 mg, 87%) as colorless syrup. $[\alpha]_D^{23}$ = + 226.6 (c 0.23, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H, Ar), 7.62 (d, *J* = 7.5 Hz, 2H, Ar), 7.56 (t, *J* = 7.4 Hz, 1H, Ar), 7.43 (t, *J* = 7.6 Hz, 2H, Ar), 7.36 (d, *J* = 7.2 Hz, 2H, Ar), 7.32 – 7.16 (m, 11H, Ar), 6.00 (d,

J = 5.4 Hz, 1H, H-1), 5.94 (d, *J* = 3.2 Hz, 1H, H-4), 4.90 (d, *J* = 10.7 Hz, 1H, CH_2-Bn), 4.71 (t, *J* = 6.4 Hz, 1H, H-5), 4.56 (d, *J* = 10.8 Hz, 1H, CH_2-Bn), 4.47 – 4.33 (m, 2H, CH_2-Bn), 4.23 (dd, *J* = 10.3, 5.4 Hz, 1H, H-2), 3.86 (dd, *J* = 10.2, 3.2 Hz, 1H, H-3), 3.62 – 3.42 (m, 2H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 137.6, 137.0, 135.14, 135.08, 133.4, 129.9, 129.7, 129.2, 128.6, 128.5, 128.4, 128.3, 128.13, 128.09, 128.05, 127.9, 127.8, 85.3 (C-1), 77.4, 73.7, 71.8, 70.9, 68.3, 66.9, 60.8. HRMS (ESI) calcd for $C_{33}H_{35}N_4O_5Se$ $[M+NH_4]^+$ 641.1827, found 641.1821.

_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-4-_O_-benzoyl-3,6-di-_O_-benzyl-2-deoxy-D-galactopyranoside (19e)

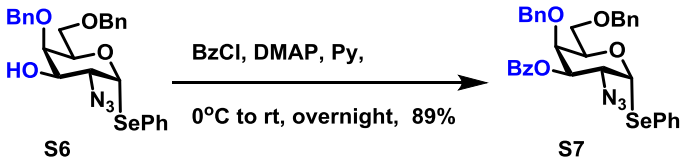


S5 17e 19e α/β = 9/1

To a solution of compound **S5** (153 mg, 0.24 mmol) in acetone/H_2O (4.9 mL/1.2 mL) was added TCCA (56.6 mg, 0.24 mmol) at 0 ℃. The reaction mixture was warmed gradually to room temperature and stirred for 4 h. 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, 10:1 to 5:1) afforded hemiacetal intermediate (102.9 mg, 86%). The above intermediate (102.9 mg, 0.21 mmol) and 2, 2, 2-trifluoro-*N*-phenylacetimidoyl chloride (52.4 mg, 0.25 mmol) was dissolved in acetone (0.5 mL), and K_2CO_3 (43.8 mg, 0.32 mmol) was added. The reaction was stirred at room temperature for 4 h, then filtered and concentered *in vacuo*. The residue was purified by flash column chromatography (petroleum ether containing 2% Et_3N) to give **17e** (101.6 mg, 73%) (Compound **17e** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedures** at room temperature for 40 h, using donor **17e** (101.6 mg, 0.15 mmol), acceptor **18** (75.1 mg, 0.23 mmol), DCM (1.5 mL), Ph_3P=O (255.3 mg, 0.92 mmol) and TMSI (22 μL, 0.15 mmol). The product was purified by

silica gel column chromatography (PE-EA, 10:1 to 5:1) to afford **19e** (111.2 mg, 90%, α/β = 9:1) as a colorless syrup. $[\alpha]_D^{25}$ = +105.1 (c 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H, Ar), 7.58 – 7.15 (m, 23H, Ar), 5.92 (s, 1H, H-4α), 5.80 (s, H-4β), 5.23 – 5.07 (m, 2H, CH_2-Cbz), 4.96 (s, 1H, H-1α), 4.92 – 4.76 (m, 1H, CH_2-Bn), 4.59 – 4.35 (m, 5H, CH_2-Bn), 4.19 (s, 1H), 4.12 – 4.00 (m, 1H, H-3α), 3.79 – 3.35 (m, 5H, H-2α), 3.27 – 3.20 (m, 2H, CH_2), 1.68 – 1.47 (m, 4H, CH_2), 1.42 – 1.27 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 156.8, 156.3, 138.0, 137.7, 137.2, 136.9, 133.3, 130.1, 129.9, 129.8, 129.6, 128.62, 128.60, 128.5, 128.4, 128.3, 128.00, 127.95, 127.91, 127.89, 127.8, 127.4, 102.5 (C-1β), 98.2 (C-1α), 77.4, 74.4, 73.8, 73.7, 72.7, 71.8, 71.7, 68.6, 68.4, 68.2, 67.4, 67.2, 66.2, 63.1, 59.6, 50.6, 50.3, 47.2, 46.2, 29.8, 29.1, 27.9, 27.5, 23.4, 23.2. HRMS (ESI) calcd for $C_{47}H_{54}N_5O_8$ $[M+NH_4]^+$ 816.3967, found 816.3968.

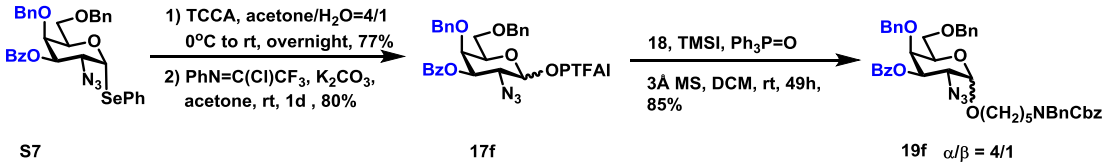
Phenyl 2-azido-3-*O*-benzoyl-4,6-di-*O*-benzyl-2-deoxy-1-seleno-α-D-galacto-pyranoside (S7)



To a solution of compound **S6**[3] (93.4 mg, 0.18 mmol) in anhydrous pyridine (1.3 mL) was cooled to 0 ℃, DMAP (21.8 mg, 0.18 mmol) was added, then BzCl (0.04 mL, 0.36 mmol) was added slowly. The resulting mixture was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction mixture was diluted in EA, washed with 4M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 20:1) to afford **S7** (98.8 mg, 89%) as colorless syrup. $[\alpha]_D^{23}$ = +318.5 (c 0.20, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H, Ar), 7.61 (d, *J* = 7.5 Hz, 3H, Ar), 7.46 (t, *J* = 7.6 Hz, 2H, Ar), 7.35 – 7.13 (m, 13H, Ar), 6.01 (d, *J* = 5.4 Hz, 1H, H-1), 5.29 (dd, *J* = 10.8, 2.9 Hz, 1H, H-3), 4.65 – 4.55 (m, 3H, H-2, H-5, CH_2-Bn), 4.51 – 4.37 (m, 3H, CH_2-Bn,), 4.28 (d,

J = 2.9 Hz, 1H, H-4), 3.61 (dd, *J* = 9.6, 7.0 Hz, 1H, H-6), 3.48 (dd, *J* = 9.5, 6.1 Hz, 1H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.9, 137.7, 135.0, 133.7, 130.0, 129.20, 129.16, 128.7, 128.5, 128.4, 128.2, 128.05, 128.03, 127.96, 127.91, 127.87, 127.85, 85.1 (C-1), 75.4, 74.7, 74.3, 73.5, 71.7, 68.1, 60.0. HRMS (ESI) calcd for $C_{33}H_{31}N_3O_5SeNa$ $[M+Na]^+$ 646.1381, found 646.1385.

_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3-_O_-benzoyl-4,6-di-_O_-benzyl-2-deoxy-D-galactopyranoside (19f)

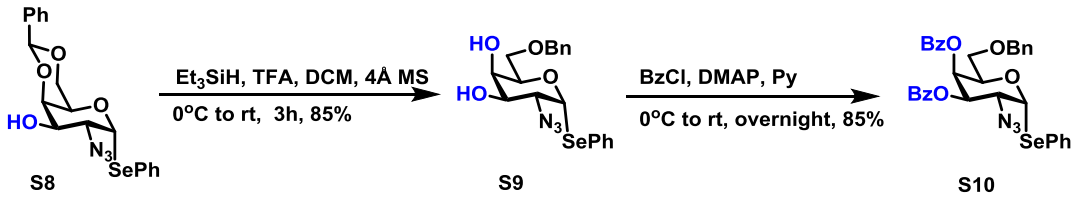


S7 17f 19f α/β = 4/1

To a solution of **S7**[3] (300 mg, 0.48 mmol) in acetone/H_2O (9.6 mL/2.4 mL) was cooled to 0 ℃, and TCCA (166 mg, 0.72 mmol) was added. The resulting mixture was stirred overnight at room temperature. The solution was diluted with EtOAc, washed with saturated $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to give the intermediate (180 mg, 77%). The above intermediate (180 mg, 0.37 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (114 mg, 0.55 mmol) was dissolved in acetone (3 mL), and K_2CO_3 (76 mg, 0.55 mmol) was added. The reaction was stirred 1d at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether containing 2% Et_3N) to give **17f** (190 mg, 80%) (Compound **17f** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedures** at rt for 49 h, using donor **17f** (170 mg, 0.26 mmol), acceptor **18** (126 mg, 0.39 mmol) with DCM (2.6 mL), Ph_3P=O (429 mg, 1.54 mmol) and TMSI (36 μL, 0.26 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1) to afford **19f** (172 mg, 85%, α/β =4:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H, Ar), 7.59 (t, *J* = 7.4 Hz,

1H, Ar), 7.45 (t, *J* = 7.7 Hz, 2H, Ar), 7.40 – 7.14 (m, 20H, Ar), 5.55 (dd, *J* = 11.1, 2.9 Hz, 1H, H-3), 5.17 (d, *J* = 11.9 Hz, 2H, CH_2-Cbz), 4.98 (m, 1H), 4.65 (d, *J* = 11.3 Hz, 1H, CH_2-Bn), 4.53 – 4.41 (m, 5H, CH_2-Bn),4.37 – 4.29 (m, H-1β), 4.21 (s, 1H, H-4), 4.16 – 4.08 (m, 1H, H-5), 3.93 (dd, *J* = 11.1, 3.5 Hz, 1H, H-2), 3.74 – 3.63 (m, 1H, CH_2), 3.62 – 3.53 (m, 2H, H-6), 3.48 – 3.34 (m, 1H, CH_2), 3.31 – 3.16 (m, 2H, CH_2), 1.64 – 1.48 (m, 4H, CH_2), 1.40 – 1.27 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 156.8, 156.2, 138.0, 137.85, 137.81, 136.9, 133.5, 130.0, 129.4, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.04, 128.96, 127.91, 127.87, 127.83, 127.78, 127.3, 102.4 (C-1β), 98.3 (C-1α), 77.4, 75.3, 75.2, 74.9, 74.4, 73.6, 73.5, 73.4, 71.8, 70.0, 69.3, 68.5, 68.2, 67.2, 61.8, 60.4, 58.4, 50.6, 50.3, 47.2, 46.3, 41.4, 31.6, 29.2, 28.0, 27.7, 27.6, 23.4, 23.2, 22.72, 22.70. HRMS (ESI) calcd for $C_{47}H_{50}N_4O_8Na$ $[M+Na]^+$ 821.3521, found 821.3522.

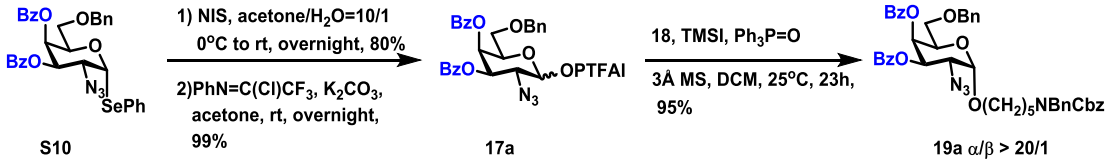
Phenyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-1-seleno-α-D-galacto-pyranoside (S10)



To a solution of the **S8**[3] (5.88 g, 13.60 mmol) in new-distilled DCM (67 mL) was stirred over fresh-dried 4Å molecular sieves under argon at room temperature for 15 min. Then the solution was cooled to 0 ℃, Et_3SiH (21.7 mL, 135.96 mmol) and TFA (10.5 mL, 135.96 mmol) was added respectively. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. Upon completion, the reaction mixture was quenched with Et_3N, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 2.5:1) to afford the intermediate **S9** (4.99 g, 85%). The above intermediate (5.56 g, 12.80 mmol) was dissolved in anhydrous pyridine (42 mL). The solution was cooled to 0 ℃, DMAP (1.56 g, 12.80 mmol) was added, then BzCl (4.5 mL, 38.40 mmol) was added slowly. The resulting mixture was allowed to warm to room temperature and stirred

overnight. Upon completion, the reaction mixture was diluted in EA, washed with 3M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford **S10** (7.50 g, 85%) as white solid. $[\alpha]_D^{23}$ = +182.4 (c 0.20, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H, Ar), 7.92 – 7.86 (m, 2H, Ar), 7.69 – 7.63 (m, 2H, Ar), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H, Ar), 7.44 (t, *J* = 7.7 Hz, 2H, Ar), 7.35 (t, *J* = 7.7 Hz, 2H, Ar), 7.31 – 7.26 (m, 1H, Ar), 7.25 – 7.17 (m, 7H, Ar), 6.12 (d, *J* = 5.4 Hz, 1H, H-1), 5.96 (d, *J* = 3.2 Hz, 1H, H-4), 5.48 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.90 (t, *J* = 6.3 Hz, 1H, H-5), 4.51 (dd, *J* = 10.8, 5.5 Hz, 1H, H-2), 4.46 – 4.32 (m, 2H, CH_2-Bn), 3.63 – 3.50 (m, 2H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 165.3, 137.6, 135.3, 133.6, 133.5, 129.9, 129.3, 128.7, 128.5, 128.4, 128.3, 127.84, 127.79, 84.9 (C-1), 73.6, 72.2, 70.7, 68.5, 68.1, 59.9. HRMS (ESI) calcd for $C_{33}H_{29}N_3O_6SeK$ $[M+K]^+$ 676.0913, found 676.0904.

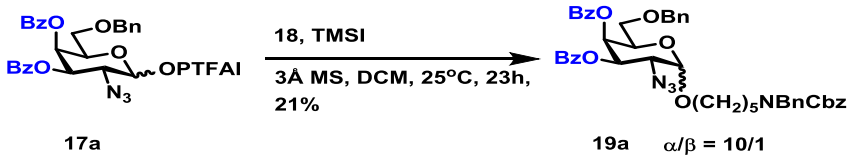
_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4-di-_O_-benzoyl-6-_O_-benzyl-2-deoxy-D-galactopyranoside (19a)



Compound **S10** (1.02 g, 1.59 mmol) was dissolved in acetone/H_2O (14 mL/1.4 mL), then *N*-iodosuccinimide (NIS) (537.4 mg, 2.39 mmol) was added. The resulting mixture was allowed to warm to room temperature and stirred overnight. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to give the intermediate (637.8 mg, 80%). The above intermediate (637.8 mg, 1.27 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (289.2 mg, 1.39 mmol) was dissolved in acetone (2 mL), and K_2CO_3 (262.5 mg, 1.90 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The

residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17a** (843 mg, 99%) (Compound **17a** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at 25℃ for 23 h, using acceptor **18** (120.2 mg, 0.37 mmol) with **17a** (165.1 mg, 0.24 mmol), DCM (2.4 mL), Ph_3P=O (408.6 mg, 1.47 mmol) and TMSI (35 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **19a** (188.5 mg, 95%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{23}$ = +137.0 (c 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 – 7.40 (m, 3H, Ar), 7.39 – 7.12 (m, 17H, Ar), 5.93 (s, 1H, H-4), 5.78 – 5.73 (m, 1H, H-3), 5.23 – 5.07 (m, 3H, CH_2-Cbz, H-1), 4.50 (d, *J* = 10.9 Hz, 3H, CH_2-Bn), 4.42 – 4.33 (m, 2H, CH_2-Bn, H-5), 3.87 – 3.70 (m, 2H, H-2, CH_2), 3.64 – 3.40 (m, 3H, H-6, CH_2), 3.35 – 3.16 (m, 2H, CH_2), 1.73 – 1.48 (m, 4H, CH_2), 1.45 – 1.29 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 156.8, 156.3, 138.0, 137.6, 136.9, 133.4, 133.3, 129.9, 129.83, 129.80, 129.5, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.71, 127.67, 127.3, 102.6 (C-1β), 98.4 (C-1α), 77.4, 73.6, 69.1, 69.0, 68.6, 68.31, 68.27, 67.2, 58.3, 50.6, 50.4, 47.2, 46.2, 29.7, 29.1, 27.9, 27.6, 23.4. HRMS (ESI) calcd for $C_{47}H_{52}N_5O_9$ $[M+NH_4]^+$ 830.3760, found 830.3763.

Glycosylation between 17a and 18 using TMSI only

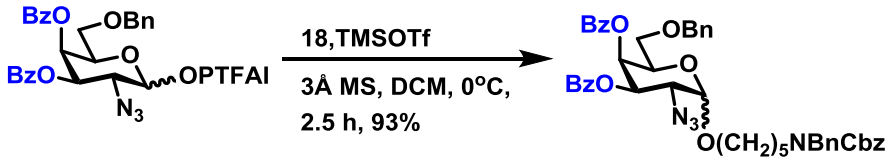


17a 19a α/β = 10/1

A mixture of donor **17a** (165 mg, 0.24 mmol) and acceptor *N*-(benzyl) benzyloxycarbonyl-5-aminopentanol **18** (120.1 mg, 0.37 mmol) was co-evaporated with dry toluene for three times. Then the mixture was dissolved in new distilled DCM (2.4 mL) and stirred over fresh-dried 3Å molecular sieves under argon at room temperature for 15 min, then TMSI (35 μL, 0.24 mmol) was added dropwise to the mixture. After being stirred for another 23 h at room temperature, the reaction was

quenched with NaS_2O_3 aq. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The products were purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to afford **19a** (42.3 mg, 21%, α/β = 10:1) as a syrup.

Glycosylation between 17a and 18 using TMSOTf instead of TMSI and Ph_3PO

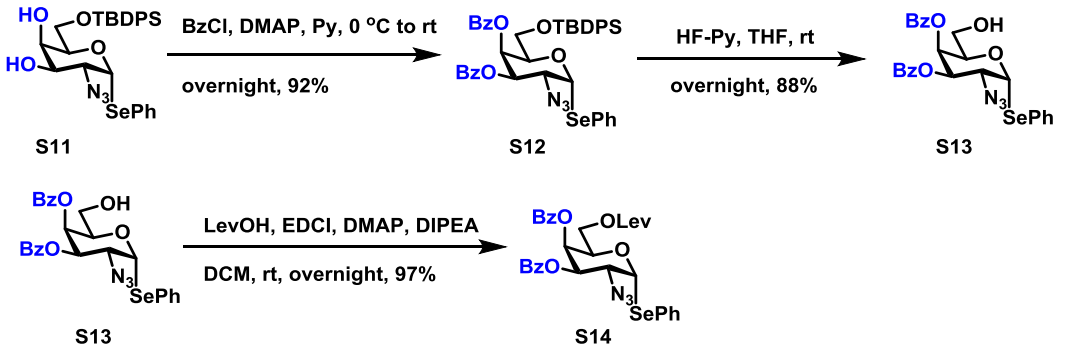


17a **19a** α/β = 2.8/1

A mixture of donor **17a** (132.5 mg, 0.20 mmol) and acceptor **18** *N*-(benzyl) benzyloxycarbonyl-5-aminopentanol (96.5 mg, 0.29 mmol) was co-evaporated with anhydrous toluene for three times. Then the mixture was dissolved in new distilled DCM (2.0 mL) and stirred over fresh-dried 3Å molecular sieves under argon at room temperature for 15 min, then cooled to 0 ℃, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (7 μL, 0.039 mmol) was added dropwise to the mixture. After being stirred for another 2.5 h, the reaction was quenched with Et_3N and filtered. The filtrates were concentrated *in vacuo* to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 3.5:1) to afford **19a** (148.4 mg, 93%, α/β = 2.8:1) as a syrup.

Reaction scope of $GalN_3$ PTFAI donors

Phenyl 2-azido-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-levulinoyl-1-seleno-α-D-galacto-pyranoside (S14)

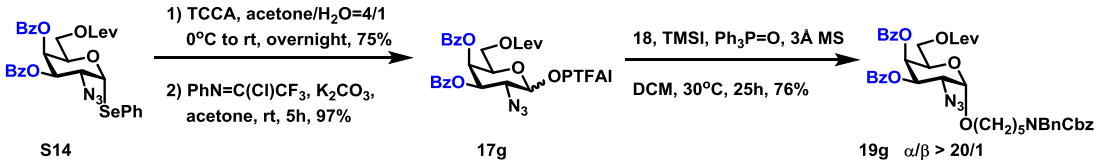


Compound **S11**[3] (2.17 g, 3.73 mmol) was dissolved in anhydrous pyridine (12 mL). The solution was cooled to 0 ℃, DMAP (456.0 mg, 3.73 mmol) was added, then BzCl (1.3 mL, 11.20 mmol) was added slowly. The resulting mixture was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction mixture was diluted in EA, washed with 3M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford **S12** (2.71 g, 92%). $[\alpha]_D^{24}$ = +271.6 (c 0.22, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H, Ar), 7.92 (d, *J* = 7.8 Hz, 2H, Ar), 7.62 (t, *J* = 7.4 Hz, 3H, Ar), 7.56 (d, *J* = 7.5 Hz, 2H, Ar), 7.49 (d, *J* = 7.4 Hz, 1H, Ar), 7.47 – 7.32 (m, 9H, Ar), 7.24 (q, *J* = 6.8 Hz, 2H, Ar), 7.17 (t, *J* = 7.4 Hz, 2H, Ar), 7.08 (t, *J* = 7.5 Hz, 2H, Ar), 6.12 (d, *J* = 3.2 Hz, 1H, H-4), 6.05 (d, *J* = 5.4 Hz, 1H, H-1), 5.57 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.74 (t, *J* = 7.2 Hz, 1H, H-5), 4.48 (dd, *J* = 10.8, 5.4 Hz, 1H, H-2), 3.71 (t, *J* = 9.2 Hz, 1H, H-6), 3.55 (dd, *J* = 10.0, 5.9 Hz, 1H, H-6), 0.98 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 165.2, 135.6, 135.54, 135.50, 135.2, 133.44, 133.40, 132.9, 132.5, 129.92, 129.87, 129.8, 129.74, 129.67, 129.29, 129.26, 128.7, 128.5, 128.2, 127.91, 127.88, 127.8, 127.7, 84.7 (C-1), 72.2, 71.7, 67.7, 61.0, 60.0, 26.8, 19.1. HRMS (ESI) calcd for $C_{42}H_{45}N_4O_6SeSi$ $[M+NH_4]^+$ 803.2328, found 803.2325.

The **S12** (1.48 g, 1.89 mmol) was then dissolved in anhydrous THF (6.0 mL), and HF/pyridine (70%, 1.7 mL, 18.68 mmol) was added dropwise. The resulting mixture was stirred overnight at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue

was purified by column chromatography on silica gel (PE:EA = 4:1) to give **S13** (913.4 mg, 88%,). To a solution of **S13** (460 mg, 0.83 mmol) and levulinic acid (145 mg, 1.25 mmol) in anhydrous DCM (8.3 mL) was added 4-dimethylaminopyridine (DMAP) (101.7 mg, 0.83 mmol), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI) (287.3 mg, 1.50 mmol) and *N*, *N*-diisopropylethylamine (DIPEA) (0.41 mL, 2.50 mmol). The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 5:1) to afford **S14** (522.8 mg, 97%). $[\alpha]_D^{21}$ = +376.2 (c 0.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H, Ar), 7.90 – 7.86 (m, 2H, Ar), 7.70 – 7.65 (m, 2H, Ar), 7.61 (t, *J* = 7.4 Hz, 1H, Ar), 7.53 (t, *J* = 7.5 Hz, 1H, Ar), 7.45 (t, *J* = 7.7 Hz, 2H, Ar), 7.38 – 7.30 (m, 5H, Ar), 6.16 (d, *J* = 5.4 Hz, 1H, H-1), 5.90 (d, *J* = 3.2 Hz, 1H, H-4), 5.47 (dd, *J* = 10.8, 3.3 Hz, 1H, H-3), 4.89 (t, *J* = 6.5 Hz, 1H, H-5), 4.53 (dd, *J* = 10.8, 5.4 Hz, 1H, H-2), 4.25 – 4.11 (m, 2H, H-6), 2.66 (t, *J* = 6.6 Hz, 2H, CH_2-Lev), 2.47 (t, *J* = 6.7 Hz, 2H, CH_2-Lev), 2.14 (s, 3H, CH_3-Lev). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 172.2, 165.34, 165.32, 134.9, 133.8, 133.6, 129.92, 129.90, 129.4, 129.2, 129.1, 128.8, 128.5, 128.4, 127.8, 84.5 (C-1), 71.9, 69.6, 68.0, 62.1, 59.7, 37.9, 29.9, 29.8, 27.8. HRMS (ESI) calcd for $C_{31}H_{29}N_3O_8SeNa$ $[M+Na]^+$ 668.1072, found 668.1067.

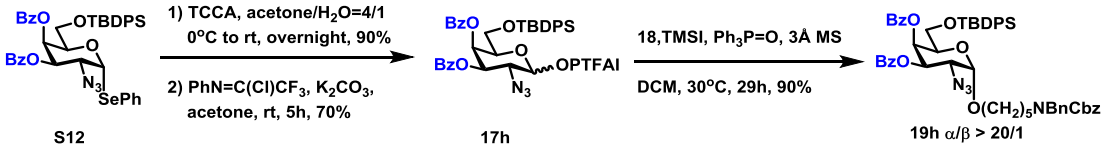
_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4-di-_O_-benzoyl-2-deoxy -6-_O_-levulinoyl-D-galactopyranoside (19g)



To a solution of **S14** (522.8 mg, 0.80 mmol) in acetone/H_2O (16 mL/4 mL) was cooled to 0 ℃, and TCCA (186.8 mg, 0.80 mmol) was added. The resulting mixture was stirred overnight at room temperature. The solution was diluted with EtOAc, washed with saturated $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column

chromatography (petroleum ether-EtOAc, 2.5:1 to 1:1) to give the intermediate (306.2 mg, 75%). The above intermediate (306.0 mg, 0.60 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (149.0 mg, 0.72 mmol) was dissolved in acetone (1.0 mL), and K_2CO_3 (124.0 mg, 0.90 mmol) was added. The reaction was stirred for 5h at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 10:1 to 3.2:1, containing 2% Et_3N) to give **17g** (395.3 mg, 97%) (Compound **17g** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at 30°C for 25 h, using donor **17g** (195.5 mg, 0.29 mmol), acceptor **18** (140.7 mg, 0.43 mmol) with DCM (2.8 mL), Ph_3P=O (478.2 mg, 1.72 mmol) and TMSI (41 μL, 0.29 mmol). The product was purified by silica gel column chromatography (PE-EA, 2:1) to afford **19g** (179.0 mg, 76%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{25}$ = +174.6 (c 0.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H, Ar), 7.87 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 (t, *J* = 7.4 Hz, 1H, Ar), 7.53 – 7.42 (m, 3H, Ar), 7.42 – 7.15 (m, 12H, Ar), 5.86 (s, 1H, H-4), 5.74 (d, *J* = 10.8 Hz, 1H, H-3), 5.26 – 5.05 (m, 3H, CH_2-Cbz, H-1), 4.57 – 4.48 (m, 2H, CH_2-Bn), 4.45 – 4.33 (m, 1H), 4.30 – 4.21 (m, 1H), 4.20 – 4.08 (m, 1H), 3.89 – 3.70 (m, 2H, H-2, CH_2), 3.60 – 3.41 (m, 1H, CH_2), 3.35 – 3.16 (m, 2H, CH_2), 2.68 (t, *J* = 6.5 Hz, 2H, CH_2-Lev), 2.52 (t, *J* = 6.6 Hz, 2H, CH_2-Lev), 2.13 (s, 3H, CH_3-Lev), 1.75 – 1.50 (m, 4H, CH_2), 1.47 – 1.31 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 206.2, 172.1, 165.32, 165.27, 156.6, 156.1, 149.7, 137.9, 136.8, 135.9, 133.5, 133.3, 129.7, 129.1, 129.0, 128.6, 128.5, 128.41, 128.38, 128.3, 127.85, 127.77, 127.2, 123.7, 98.3 (C-1), 68.7, 68.4, 67.1, 66.9, 62.1, 58.0, 53.5, 50.5, 50.3, 47.1, 46.2, 37.7, 30.8, 29.6, 29.0, 27.9, 27.8, 27.7, 27.5, 23.3. HRMS (ESI) calcd for $C_{45}H_{52}N_5O_{11}$ $[M+NH_4]^+$ 838.3658, found 838.3668.

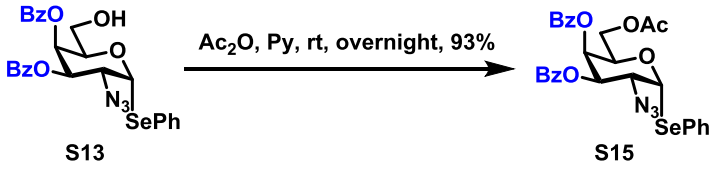
_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-D-galactopyranoside (19h)



To a solution of **S12** (628.8 mg, 0.80 mmol) in acetone/H_2O (16 mL/4 mL) was cooled to 0 ℃, and TCCA (184.8 mg, 0.80 mmol) was added. The resulting mixture was stirred overnight at room temperature. The solution was diluted with EtOAc, washed with saturated $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to give the intermediate (466.0 mg, 90%). The above intermediate (466 mg, 0.72 mmol) and 2,2,2-trifluoro-*N*-phenyl-acetimidoyl chloride (178.1 mg, 0.86 mmol) was dissolved in acetone (1 mL), and K_2CO_3 (148.2 mg, 1.07 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 50:1, containing 2% Et_3N) to give **17h** (414 mg, 70%) (Compound **17h** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at 30℃ for 29 h, using acceptor **18** (121.8 mg, 0.37 mmol) with **17h** (204 mg, 0.25 mmol), DCM (2.5 mL), Ph_3P=O (413.9 mg, 1.49 mmol) and TMSI (35 μL, 0.25 mmol). The product was purified by silica gel column chromatography (PE-EA, 6:1) to afford **19h** (215.5 mg, 90%, α/β > 20:1) as a colorless syrup. $[\alpha]_D^{25}$ = + 115.1 (c 0.19, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.7 Hz, 2H, Ar), 7.65 (d, *J* = 6.8 Hz, 2H, Ar), 7.59 – 7.18 (m, 22H, Ar), 7.14 (t, *J* = 7.4 Hz, 2H, Ar), 6.04 (d, *J* = 3.4 Hz, 1H, H-4), 5.82 (d, *J* = 11.0 Hz, 1H, H-3), 5.20-5.07 (m, 3H), 4.52 (d, *J* = 10.7 Hz, 2H), 4.34 – 4.20 (m, 1H), 3.80 (dd, *J* = 11.1, 3.4 Hz, 1H, H-2), 3.77 – 3.62 (m, 3H), 3.52 – 3.36 (m, 1H), 3.35 – 3.18 (m, 2H), 1.70 – 1.51 (m, 4H, CH_2), 1.46 – 1.30 (m, 2H, CH_2), 1.01 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 165.2, 156.7, 156.2, 137.9, 136.8, 135.5, 135.4, 133.3, 133.2, 132.9, 132.7, 129.81, 129.78, 129.73, 129.68, 129.6, 129.3, 128.5, 128.4, 128.2, 127.9, 127.81, 127.77, 127.74, 127.6, 127.3, 127.2, 98.3 (C-1), 77.2, 69.5, 69.1, 68.4, 67.2, 61.7, 58.3, 50.6, 50.3, 47.1, 46.2, 29.1, 27.9, 27.5,

26.7, 23.4, 19.0. HRMS (ESI) calcd for $C_{56}H_{64}N_5O_9Si$ $[M+NH_4]^+$ 978.4468, found 978.4469.

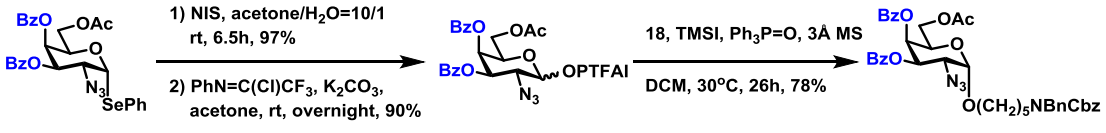
Phenyl 6-*O*-acetyl-2-azido-3,4-di-*O*-benzoyl-2-deoxy-1-seleno-α-D-galacto-pyranoside (S15)



S13 S15

Compound **S13** (757 mg, 1.37 mmol) was dissolved in anhydrous pyridine (2.6 mL), then Ac_2O (0.26 mL, 2.74 mmol) was added slowly. The resulting mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was diluted in EA, washed with 4M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 5:1) to afford **S15** (760.9 mg, 93%) as white solid. $[\alpha]_D^{23}$ = +443.6 (c 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H, Ar), 7.89 (d, *J* = 7.7 Hz, 2H, Ar), 7.67 (dd, *J* = 7.2, 2.2 Hz, 2H, Ar), 7.61 (t, *J* = 7.4 Hz, 1H, Ar), 7.53 (t, *J* = 7.5 Hz, 1H, Ar), 7.45 (t, *J* = 7.6 Hz, 2H, Ar), 7.38 – 7.30 (m, 5H, Ar), 6.18 (d, *J* = 5.4 Hz, 1H, H-1), 5.93 (d, *J* = 3.2 Hz, 1H, H-4), 5.49 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.90 (t, *J* = 6.4 Hz, 1H, H-5), 4.55 (dd, *J* = 10.8, 5.4 Hz, 1H, H-2), 4.23 – 4.10 (m, 2H, H-6), 1.95 (s, 3H, CH_3-Ac). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 165.4, 165.3, 135.0, 133.8, 133.6, 129.90, 129.86, 129.4, 129.0, 128.9, 128.8, 128.5, 128.4, 127.7, 84.3 (C-1), 72.0, 69.5, 68.0, 62.0, 59.6, 20.7. HRMS (ESI) calcd for $C_{28}H_{25}N_3O_7SeNa$ $[M+Na]^+$ 612.0809, found 612.0817.

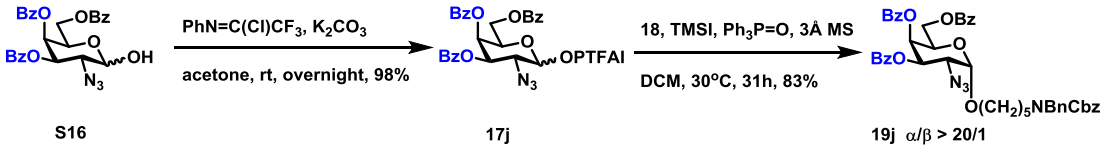
***N*-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 6-*O*-acetyl-2-azido-3,4-di-*O*-benzoyl-2-deoxy-D-galactopyranoside (19i)**



S15 17i 19i α/β > 20/1

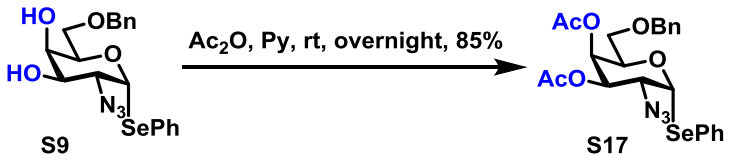
Compound **S15** (701 mg, 1.18 mmol) was dissolved in acetone/H_2O (10 mL/1 mL) and NIS (397.9 mg, 1.77 mmol) was added. The resulting mixture was stirred for 6.5 h. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 2:1) to give the intermediate (524 mg, 97%). The above intermediate (391 mg, 0.86 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (160.4 mg, 0.77 mmol) was dissolved in acetone (1 mL), and K_2CO_3 (177.9 mg, 1.29 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17i** (435.7 mg, 90%) (Compound **17i** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at 30℃ for 26 h, using acceptor **18** (158.9 mg, 0.49 mmol) with **17i** (202.0 mg, 0.32 mmol), DCM (3.2 mL), Ph_3P=O (540.2 mg, 1.94 mmol) and TMSI (46 μL, 0.32 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **19i** (193.4 mg, 78%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{25}$ = + 176.1 (c 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 2H, Ar), 7.87 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 – 7.41 (m, 3H, Ar), 7.40 – 7.17 (m, 12H, Ar), 5.89 (s, 1H, H-4), 5.75 (d, *J* = 10.9 Hz, 1H, H-3), 5.24 – 5.07 (m, 3H, H-1, CH_2-Cbz), 4.52 (d, *J* = 6.7 Hz, 2H, CH_2-Bn), 4.43 – 4.34 (m, 1H), 4.26 – 4.12 (m, 2H), 3.87 (dd, *J* = 11.1, 3.4 Hz, 1H, H-2), 3.81 – 3.68 (m, 1H, CH_2), 3.59 – 3.43 (m, 1H, CH_2), 3.35 – 3.19 (m, 2H, CH_2), 1.99 (s, 3H, CH_3-Ac), 1.75 – 1.50 (m, 4H, CH_2), 1.46 – 1.31 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 165.4, 156.7, 156.2, 137.9, 136.8, 133.6, 133.3, 129.9, 129.8, 129.2, 129.1, 128.6, 128.53, 128.45, 128.4, 128.3, 127.9, 127.8, 127.3, 98.4 (C-1), 68.8, 68.7, 68.5, 67.2, 67.0, 62.1, 58.1, 50.6, 50.3, 47.1, 46.2, 29.1, 27.9, 27.5, 23.4, 20.6. HRMS (ESI) calcd for $C_{42}H_{45}N_4O_{10}$ $[M+H]^+$ 765.3130, found 765.3135.

_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-3,4,6-tri-_O_-benzoyl-2-deoxy-D-galactopyranoside (19j)



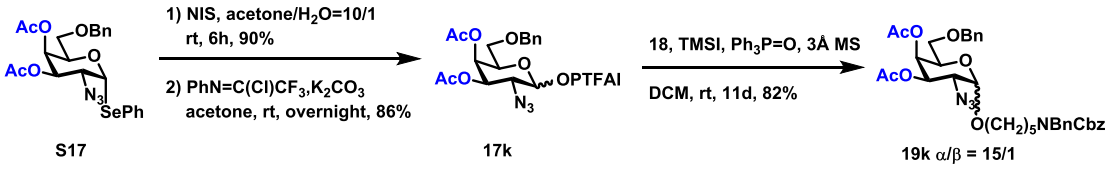
Compound **S16**[4] (592.8 mg, 1.15 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (261.6 mg, 1.26 mmol) was dissolved in acetone (2 mL), and K_2CO_3 (238.3 mg, 1.72 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17j** (774.5 mg, 98%) (Compound **17j** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at 30℃ for 31 h, using acceptor **18** (158.7 mg, 0.48 mmol) with **17j** (222.5 mg, 0.32 mmol), DCM 3.2 mL, Ph_3P=O (539.5 mg, 1.94 mmol) and TMSI (47 μL, 0.32 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **19j** (223.1 mg, 83%, α/β > 20:1) as a colorless syrup. $[\alpha]_D^{25}$ = + 136.3 (c 0.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 4H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 – 7.53 (m, 1H, Ar), 7.51 – 7.40 (m, 4H, Ar), 7.40 – 7.15 (m, 14H, Ar), 6.01 (s, 1H, H-4), 5.82 (d, *J* = 10.4 Hz, 1H, H-3), 5.25 – 5.11 (m, 3H, CH_2-Cbz, H-1), 4.62 – 4.45 (m, 4H, CH_2-Bn), 4.36 (d, *J* = 10.6 Hz, 1H), 3.92 (d, *J* = 10.8 Hz, 1H, H-2), 3.82 – 3.68 (m, 1H, CH_2), 3.58 – 3.42 (m, 1H, CH_2), 3.33 – 3.17 (m, 2H, CH_2), 1.74 – 1.45 (m, 4H, CH_2), 1.41 – 1.27 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.33, 165.27, 156.6, 156.1, 137.9, 136.8, 133.5, 133.3, 133.2, 129.9, 129.8, 129.73, 129.65, 129.6, 129.4, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 127.8, 127.2, 98.3 (C-1), 68.8, 68.7, 68.6, 67.1, 67.1, 62.5, 58.1, 50.5, 50.2, 47.0, 46.1, 29.6, 29.0, 27.8, 27.4, 23.3. HRMS (ESI) calcd for $C_{47}H_{50}N_5O_{10}$ $[M+NH_4]^+$ 844.3552, found 844.3560.

Phenyl 3,4-di-*O*-acetyl-2-azido-6-*O*-benzyl-2-deoxy-1-seleno-α-D-galacto-pyranoside (S17)



Compound **S9** (839 mg, 1.93 mmol) was dissolved in anhydrous pyridine (3.8 mL), then Ac_2O (0.73 mL, 7.73 mmol) was added slowly. The resulting mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was diluted in EA, washed with 4M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 6:1) to afford **S17** (820 mg, 85%) as white solid. $[\alpha]_D^{23}$ = +27.7 (c 0.19, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H, Ar), 7.36 – 7.22 (m, 6H, Ar), 7.18 (t, *J* = 7.5 Hz, 2H, Ar), 5.96 (d, *J* = 5.4 Hz, 1H, H-1), 5.54 (d, *J* = 3.2 Hz, 1H, H-4), 5.11 (dd, *J* = 10.9, 3.3 Hz, 1H, H-3), 4.66 (t, *J* = 6.3 Hz, 1H, H-5), 4.47 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.38 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.24 (dd, *J* = 10.9, 5.4 Hz, 1H, H-2), 3.49 – 3.38 (m, 2H, H-6), 2.22 – 1.93 (m, 6H, CH_3-Ac). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.6, 137.6, 135.1, 129.2, 128.5, 128.2, 127.91, 127.88, 127.8, 84.6 (C-1), 73.5, 71.4, 70.2, 67.8, 67.7, 59.1, 20.74, 20.69. HRMS (ESI) calcd for $C_{23}H_{25}N_3O_6SeNa$ $[M+Na]^+$ 536.0860, found 536.0863.

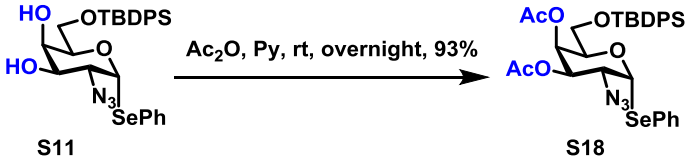
_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 3,4-di-_O_-acetyl-2-azido-6-_O_-benzyl-2-deoxy-D-galactopyranoside (19k)



Compound **S17** (820 mg, 1.58 mmol) was dissolved in acetone/H_2O (14 mL/1.4 mL), then NIS (533.8 mg, 2.37 mmol) was added. The resulting mixture was stirred for 6 h. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 2:1)

to give the intermediate (539 mg, 90%). The above intermediate (539 mg, 1.42 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (294.9 mg, 1.42 mmol) was dissolved in acetone (1.4 mL), and K_2CO_3 (294.5 mg, 2.13 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17k** (671.6 mg, 86%) (Compound **17k** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at rt for 11 d, using acceptor **18** (128.3 mg, 0.39 mmol) with **17k** (143.8 mg, 0.26 mmol), DCM 2.6 mL, Ph_3P=O (436.1 mg, 1.57 mmol) and TMSI (37 μL, 0.26 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **19k** (143.9 mg, 82%, α/β =15:1) as a colorless syrup. $[\alpha]_D^{25}$ = +98.9 (c 0.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 6.99 (m, 15H, Ar), 5.42 (d, *J* = 3.3 Hz, 1H, H-4α), 5.28 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3α), 5.09 (d, *J* = 10.5 Hz, 2H, CH_2-Cbz), 4.86 (s, 1H, H-1α), 4.68 (dd, *J* = 10.9, 3.3 Hz, H-3β), 4.48 – 4.28 (m, 4H, CH_2-Bn), 4.11 – 4.01 (m, 1H, H-5α), 3.66 – 3.54 (m, 1H, CH_2), 3.49 (dd, *J* = 11.1, 3.5 Hz, 1H, H-2α), 3.43 – 3.25 (m, 3H, H-6α, CH_2), 3.22 – 3.08 (m, 2H, CH_2), 1.95 (s, 6H, CH_3-Ac), 1.58 – 1.36 (m, 4H, CH_2), 1.32 – 1.20 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.8, 156.7, 156.2, 138.0, 137.6, 136.9, 128.6, 128.5, 128.4, 127.92, 127.88, 127.82, 127.80, 127.3, 102.4 (C-1β), 98.1 (C-1α), 73.6, 73.5, 72.1, 71.2, 70.3, 68.5, 68.4, 68.2, 67.9, 67.8, 67.5, 67.2, 67.0, 61.2, 57.6, 50.6, 50.3, 47.1, 46.2, 29.4, 29.2, 29.0, 27.9, 27.5, 23.4, 23.2, 22.7, 20.70, 20.66, 20.6. HRMS (ESI) calcd for $C_{37}H_{48}N_5O_9$ $[M+NH_4]^+$ 706.3447, found 706.3449.

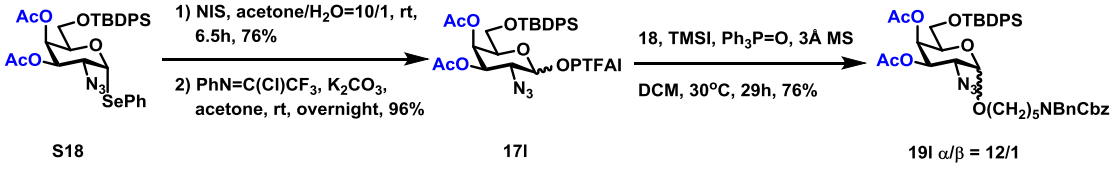
Phenyl 3,4-di-*O*-acetyl-2-azido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-seleno-α-D-galactopyranoside (S18)



S11 S18

Compound **S11** (1.58 g, 2.71 mmol) was dissolved in anhydrous pyridine (5.4 mL), then Ac_2O (1.0 mL, 10.84 mmol) was added slowly. The resulting mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was diluted in EA, washed with 4M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford **S18** (1.68 g, 93%) as yellow solid. $[\alpha]_D^{23}$ = + 184.2 (c 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H, Ar), 7.52 – 7.47 (m, 2H, Ar), 7.44 – 7.33 (m, 6H, Ar), 7.26 – 7.21 (m, 1H, Ar), 7.15 (t, *J* = 7.5 Hz, 2H, Ar), 5.89 (d, *J* = 5.4 Hz, 1H, H-1), 5.68 – 5.64 (m, 1H, H-4), 5.16 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.51 (t, *J* = 7.0 Hz, 1H, H-5), 4.21 (dd, *J* = 10.9, 5.4 Hz, 1H, H-2), 3.57 (dd, *J* = 10.0, 8.1 Hz, 1H, H-6), 3.49 (dd, *J* = 10.0, 5.9 Hz, 1H, H-6), 2.07 (s, 3H, CH_3-Ac), 2.03 (s, 3H, CH_3-Ac), 1.02 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.6, 135.6, 135.5, 135.0, 132.9, 132.7, 129.9, 129.1, 128.1, 127.80, 127.78, 127.7, 84.5 (C-1), 71.4, 71.2, 67.0, 60.9, 59.1, 26.7, 20.7, 20.5, 19.1. HRMS (ESI) calcd for $C_{32}H_{37}N_3O_6SeSiK$ $[M+K]^+$ 700.1308, found 700.1308.

***N*-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 3,4-di-*O*-acetyl-2-azido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-D-galactopyranoside (19l)**

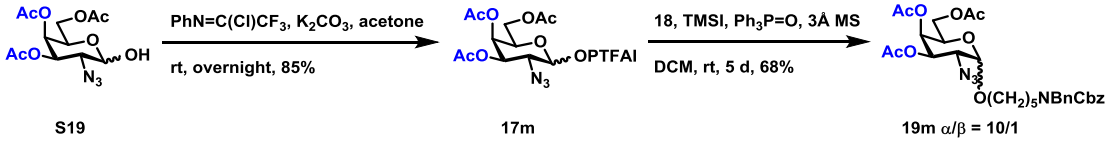


S18 17l 19l α/β = 12/1

Compound **S18** (470 mg, 0.70 mmol) was dissolved in acetone/H_2O (6.4 mL/0.6 mL), then NIS (212.8 mg, 0.95 mmol) was added. The resulting mixture was stirred for 6.5 h. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 6:1) to give the intermediate (282.3 mg, 76%). The above intermediate (220.3 mg, 0.42 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (103.9 mg, 0.50 mmol) was

dissolved in acetone (1.0 mL), and K_2CO_3 (86.4 mg, 0.63 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17l** (280 mg, 96%) (Compound **17l** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at 30℃ for 29 h, using acceptor **18** (93.3 mg, 0.28 mmol) with **17l** (132.7 mg, 0.19 mmol), DCM (1.9 mL), Ph_3P=O (317.1 mg, 1.14 mmol) and TMSI (27 μL, 0.19 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **19l** (120.8 mg, 76%, α/β =12:1) as a colorless syrup. $[\alpha]_D^{25}$ = + 62.5 (c 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.1 Hz, 4H, Ar), 7.43 – 7.15 (m, 16H, Ar), 5.59 (d, *J* = 3.3 Hz, 1H, H-4α), 5.52 (d, *J* = 3.3 Hz, H-4β) 5.40 (dd, *J* = 11.2, 3.2 Hz, 1H, H-3α), 5.18 (d, *J* = 12.0 Hz, 2H, CH_2-Cbz), 4.90 (s, 1H, H-1α), 4.50 (d, *J* = 8.5 Hz, 2H, CH_2-Bn), 4.10 – 4.02 (m, 1H, H-5α), 3.73 – 3.59 (m, 3H, H-6α, CH_2), 3.55 (dd, *J* = 11.2, 3.5 Hz, 1H, H-2), 3.42 – 3.16 (m, 3H, CH_2), 2.04 (s, 3H, CH_3-Ac), 2.00 (s, 3H, CH_3-Ac), 1.65 – 1.47 (m, 4H, CH_2), 1.39 – 1.28 (m, 2H, CH_2), 1.03 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.84, 169.80, 156.7, 156.2, 137.9, 136.8, 135.6, 135.5, 133.0, 132.9, 129.9, 129.8, 128.52, 128.50, 128.4, 127.84, 127.81, 127.77, 127.74, 127.3, 102.3 (C-1β), 98.0 (C-1α), 73.2, 69.1, 68.4, 68.3, 67.7, 67.1, 66.4, 61.6, 61.2, 57.6, 53.4, 50.6, 50.3, 47.1, 46.2, 29.0, 27.9, 27.5, 26.7, 23.3, 20.7, 20.6, 19.0. HRMS (ESI) calcd for $C_{46}H_{60}N_5O_9Si$ $[M+NH_4]^+$ 854.4155, found 854.4156.

N-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranoside (19m)

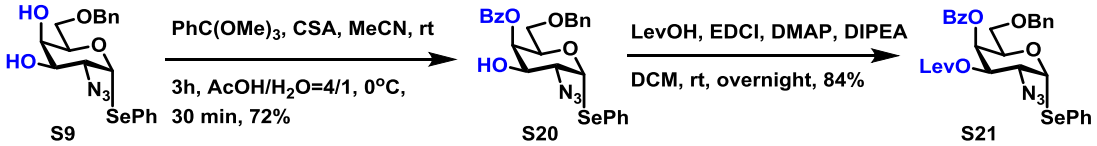


S19 17m 19m α/β = 10/1

The compound **S19**[1] (285.7 mg, 0.86 mmol) and 2,2,2-trifluoro-*N*-phenyl-acetimidoyl chloride (214.8 mg, 1.03 mmol) was dissolved in acetone (1.5 mL), and K_2CO_3 (178.7 mg, 1.29 mmol) was added. The reaction was stirred overnight at room

temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 12:1 to 4:1, containing 1% Et_3N) to give **17m** (368 mg, 85%) (Compound **17m** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at rt for 5 d, using acceptor **18** (196.5 mg, 0.60 mmol) with **17m** (201 mg, 0.40 mmol), DCM (4.4 mL), Ph_3P=O (668.1 mg, 2.40 mmol) and TMSI (57 μL, 0.40 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **19m** (167 mg, 68%, α/β =10:1) as a colorless syrup. $[\alpha]_D^{25}$ = +95.1 (c 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.04 (m, 10H, Ar), 5.36 (s, 1H, H-4α), 5.27 (d, *J* = 11.5 Hz, 1H, H-3α), 5.08 (d, *J* = 12.9 Hz, 2H, CH_2-Cbz), 4.86 (s, 1H, H-1α), 4.69 (d, *J* = 11.0 Hz, H-3β), 4.47 – 4.35 (m, 2H, CH_2-Bn), 4.15 – 3.93 (m, 3H), 3.64 – 3.46 (m, 2H, H-2α), 3.43 – 3.26 (m, 1H), 3.25 – 3.10 (m, 2H, CH_2), 2.04 (s, 3H, CH_3-Ac), 1.95 (s, 3H, CH_3-Ac), 1.92 (s, 3H, CH_3-Ac), 1.59 – 1.38 (m, 4H, CH_2), 1.32 – 1.18 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.92, 169.89, 169.6, 156.6, 156.1, 137.9, 136.8, 128.4, 128.3, 127.84, 127.81, 127.7, 127.2, 102.2 (C-1β), 98.0 (C-1α), 70.9, 70.5, 70.2, 68.5, 68.1, 67.6, 67.0, 66.5, 66.3, 61.6, 61.2, 60.9, 57.3, 50.5, 50.3, 47.0, 46.1, 29.6, 29.0, 28.9, 27.8, 27.4, 23.2, 23.0, 20.51, 20.46. HRMS (ESI) calcd for $C_{32}H_{41}N_4O_{10}$ $[M+H]^+$ 641.2817, found 641.2810.

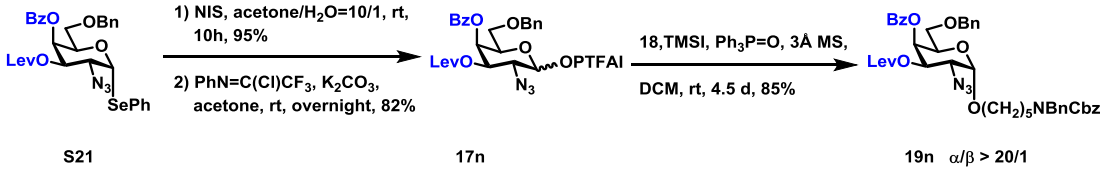
Phenyl 2-azido-4-*O*-benzoyl-6-*O*-benzyl-3-*O*-levulinoyl-2-deoxy-1-seleno-α-D-galactopyranoside (S21)



Compound **S9** (152 mg, 0.35 mmol) was stirred with trimethyl orthobenzoate (0.52 mL, 2.80 mmol) in acetonitrile (1.7 mL) at room temperature for some time. Then 10-camphorsulfonic acid (CSA) (24.4 mg, 0.11 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure, and the temperature was brought down to 0 °C, 80%

aq acetic acid (1.7 mL) was then added, and the reaction was stirred at 0 ℃ for 30 min. The reaction mixture was quenched carefully with saturated $NaHCO_3$. The product was extracted with dichloromethane (25 mL × 3), and the combined organic layer was washed with distilled water (100 mL × 1). The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 8:1) to afford the intermediate **S20** (135.5 mg, 72%). To a solution of the above intermediate (56.1 mg, 0.10 mmol) and levulinic acid (18.1 mg, 0.16 mmol) in anhydrous DCM (1 mL) was added DMAP (12.7 mg, 0.10 mmol), EDCI (36.0 mg, 0.19 mmol) and DIPEA (0.051 mL, 0.31 mmol). The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 4.3:1) to afford **S21** (55.8 mg, 84%). $[\alpha]_D^{24}$ = +210.3 (c 0.32, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H, Ar), 7.66 – 7.58 (m, 3H, Ar), 7.46 (t, *J* = 7.7 Hz, 2H, Ar), 7.30 – 7.15 (m, 8H, Ar), 6.05 (d, *J* = 5.4 Hz, 1H, H-1), 5.78 (d, *J* = 3.7 Hz, 1H, H-4), 5.22 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.79 (t, *J* = 6.4 Hz, 1H, H-5), 4.42 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.37 – 4.30 (m, 2H, H-2, CH_2-Bn), 3.57 – 3.45 (m, 2H, H-6), 2.87 – 2.77 (m, 1H, CH_2-Lev), 2.75 – 2.66 (m, 1H, CH_2-Lev), 2.65 – 2.55 (m, 1H, CH_2-Lev), 2.53 – 2.44 (m, 1H, CH_2-Lev), 2.15 (s, 3H, CH_3-Lev). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 171.7, 165.6, 137.6, 135.2, 133.7, 129.9, 129.4, 129.3, 128.8, 128.4, 128.3, 127.82, 127.80, 84.7 (C-1), 73.5, 71.9, 70.5, 68.3, 67.9, 59.4, 37.9, 29.8, 28.0. HRMS (ESI) calcd for $C_{31}H_{31}N_3O_7SeNa$ $[M+Na]^+$ 654.1279, found 654.1281.

N-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-azido-4-*O*-benzoyl-6-*O*-benzyl-3-*O*-levulinoyl-2-deoxy-D-galactopyranoside (19n)

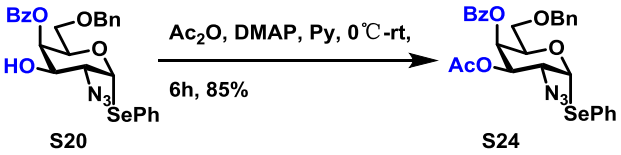


S21 **17n** **19n** α/β > 20/1

Compound **S21** (524 mg, 0.82 mmol) was dissolved in acetone/H_2O (7.4 mL/0.7

mL), then NIS (278 mg, 1.24 mmol) was added. The resulting mixture was stirred for 10 h. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 2:1) to give the intermediate (387 mg, 95%). The above intermediate (280 mg, 0.56 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (116 mg, 0.56 mmol) was dissolved in acetone (5.6 mL), and K_2CO_3 (116 mg, 0.85 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 20:1 to 10:1, containing 1% Et_3N) to give **17n** (309 mg, 82%) (Compound **17n** was used directly without further structural characterization). The glycosylation reaction was carried out according to General **Experimental Procedure** at rt for 4.5 d, using acceptor **18** (250 mg, 0.67 mmol) with **17n** (300 mg, 0.45 mmol), DCM 4.5 mL, Ph_3P=O (748 mg, 2.69 mmol) and TMSI (64 μL, 0.45 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **19n** (225 mg, 85%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{24}$ = +107.3 (c 0.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H, Ar), 7.54 (t, *J* = 7.4 Hz, 1H, Ar), 7.39 (t, *J* = 7.6 Hz, 2H, Ar), 7.33 – 7.06 (m, 15H, Ar), 5.67 (d, *J* = 3.2 Hz, 1H, H-4), 5.39 (dd, *J* = 11.2, 3.2 Hz, 1H, H-3), 5.11 (d, *J* = 12.0 Hz, 2H, CH_2-Cbz), 4.95 (s, 1H, H-1), 4.46 – 4.38 (m, 3H, CH_2-Bn), 4.29 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.24 – 4.15 (m, 1H, H-5), 3.69 – 3.57 (m, 2H, H-2, CH_2), 3.49 – 3.30 (m, 3H, H-6, CH_2), 3.25 – 3.06 (m, 2H, CH_2), 2.77 – 2.66 (m, 1H, CH_2-Lev), 2.65 – 2.57 (m, 1H, CH_2-Lev), 2.56 – 2.45 (m, 1H, CH_2-Lev), 2.44 – 2.34 (m, 1H, CH_2-Lev), 2.05 (s, 3H, CH_3-Lev), 1.61 – 1.41 (m, 4H, CH_2), 1.32 – 1.21 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 171.7, 165.6, 156.7, 156.2, 138.0, 137.5, 136.9, 133.5, 129.9, 129.8, 129.4, 128.7, 128.62, 128.56, 128.5, 128.3, 127.94, 127.88, 127.8, 127.7, 127.6, 127.3, 98.3 (C-1), 77.4, 73.5, 68.84, 68.76, 68.6, 68.1, 67.2, 57.9, 53.5, 50.6, 50.4, 47.1, 46.2, 37.9, 29.7, 29.1, 28.0, 23.4. HRMS (ESI) calcd for $C_{45}H_{54}N_5O_{10}$ $[M+NH_4]^+$ 824.3865, found 824.3872.

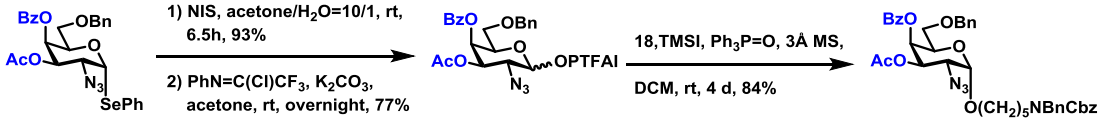
Phenyl 3-*O*-acetyl-2-azido-4-*O*-benzoyl-6-*O*-benzyl-2-deoxy-1-seleno-α-D-galacto-pyranoside (S24)



S20 S24

Compound **S20** (404mg, 0.82 mmol) was dissolved in anhydrous pyridine (3 mL). The solution was cooled to 0 ℃, DMAP (100 mg, 0.82 mmol) was added, then Ac_2O (0.11 mL, 1.22 mmol) was added slowly. The resulting mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was diluted in EA, washed with 3M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE-EA = 8:1) to afford **S24** (403 mg, 85%) as a white solid. $[\alpha]_D^{24}$ = + 199.8 (c 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H, Ar), 7.66 – 7.58 (m, 3H, Ar), 7.46 (t, *J* = 7.6 Hz, 2H, Ar), 7.30 – 7.15 (m, 8H, Ar), 6.05 (d, *J* = 5.4 Hz, 1H, H-1), 5.80 (d, *J* = 3.2 Hz, 1H, H-4), 5.22 (dd, *J* = 10.9, 3.2 Hz, 1H, H-3), 4.80 (t, *J* = 6.3 Hz, 1H, H-5), 4.42 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.38 – 4.30 (m, 2H, H-2, CH_2-Bn), 3.59 – 3.45 (m, 2H, H-6), 2.03 (s, 3H, CH_3-Ac). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 165.5, 137.6, 135.2, 133.6, 129.9, 129.4, 129.2, 128.7, 128.4, 128.3, 127.80, 127.78, 84.7 (C-1), 73.5, 71.7, 70.5, 68.3, 67.9, 59.3, 20.8. HRMS (ESI) calcd for $C_{28}H_{27}N_3O_6SeNa$ $[M+Na]^+$ 598.1017, found 598.1015.

***N*-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 3-*O*-acetyl-2-azido-4-*O*-benzoyl-6-*O*-benzyl-2-deoxy-D-galactopyranoside (19o)**

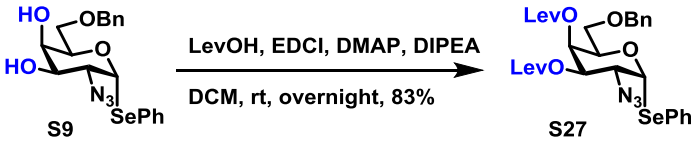


S21 17o 19o α/β > 20/1

Compound **S24** (409 mg, 0.71 mmol) was dissolved in acetone/H_2O (6.4 mL/0.6 mL), then NIS (238 mg, 1.06 mmol) was added. The resulting mixture was stirred for 6.5 h. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water

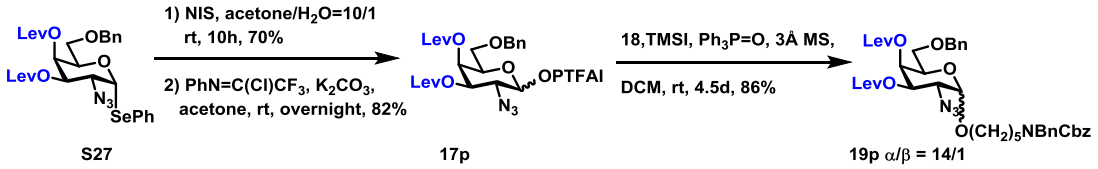
and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to give the intermediate (287 mg, 93%). The above intermediate (287 mg, 0.65 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (134 mg, 0.65 mmol) was dissolved in acetone (6.5 mL), and K_2CO_3 (134 mg, 0.98 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether, containing 2% Et_3N) to give **17o** (306 mg, 77%) (Compound **17o** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at rt for 4 d, using acceptor **18** *N*-(benzyl)benzyloxycarbonyl-5-aminopentanol (279 mg, 0.75 mmol) with **17o** (306 mg, 0.5 mmol), DCM (5 mL), Ph_3P=O (834 mg, 3.0 mmol) and TMSI (70 μL, 0.5 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) and LH-20 (MeOH/DCM =1:1) to afford **19o** (309 mg, 84%, α/β > 20:1) as a colorless syrup. $[\alpha]_D^{24}$ = + 92.9 (c 0.61, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H, Ar), 7.59 (t, *J* = 7.5 Hz, 1H, Ar), 7.45 (t, *J* = 7.6 Hz, 2H, Ar), 7.40 – 7.13 (m, 15H, Ar), 5.80 – 5.73 (m, 1H, H-4), 5.52 – 5.43 (m, 1H, H-3), 5.18 (d, *J* = 11.8 Hz, 2H, CH_2-Cbz), 5.03 (s, 1H, H-1), 4.54 – 4.44 (m, 3H, CH_2-Bn), 4.36 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.32 – 4.23 (m, 1H, H-5), 3.77 – 3.65 (m, 2H, H-2, CH_2), 3.59 – 3.39 (m, 3H, H-6, CH_2), 3.33 – 3.17 (m, 2H, CH_2), 2.00 (s, 3H, CH_3-Ac), 1.71 – 1.45 (m, 4H, CH_2), 1.41 – 1.27 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 165.6, 156.8, 156.3, 138.0, 137.6, 133.5, 129.9, 129.6, 128.64, 128.62, 128.54, 128.51, 128.43, 128.40, 128.0, 127.95, 127.93, 127.87, 127.82, 127.75, 127.69, 127.4, 98.3 (C-1), 73.6, 68.8, 68.7, 68.20, 68.15, 67.3, 57.9, 50.7, 50.4, 47.2, 46.3, 29.1, 28.0, 27.6, 23.4, 20.8. HRMS (ESI) calcd for $C_{42}H_{47}N_4O_9$ $[M+H]^+$ 751.3338, found 751.3334.

Phenyl 2-azido-6-*O*-benzyl-2-deoxy-3,4-di-*O*-levulinoyl-1-seleno-α-D-galacto-pyranoside (S27)



Compound **S9** (400 mg, 0.92 mmol) and levulinic acid (320 mg, 2.76 mmol) in anhydrous DCM (3 mL) was added DMAP (224 mg, 1.88 mmol), EDCI (634 mg, 3.31 mmol) and DIPEA (0.91 mL, 5.51 mmol). The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 4:1) to afford **S27** (480 mg, 83%) as a syrup. $[\alpha]_D^{24}$ = + 186.3 (c 0.22, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H, Ar), 7.36 – 7.22 (m, 6H, Ar), 7.18 (t, *J* = 7.5 Hz, 2H, Ar), 5.97 (d, *J* = 5.4 Hz, 1H, H-1), 5.54 (d, *J* = 3.3 Hz, 1H, H-4), 5.08 (dd, *J* = 10.9, 3.2 Hz, 1H, H-3), 4.65 (t, *J* = 6.3 Hz, 1H, H-5), 4.48 – 4.37 (m, 2H, CH_2-Bn), 4.25 (dd, *J* = 10.8, 5.4 Hz, 1H, H-2), 3.51 – 3.39 (m, 2H, H-6), 2.87 – 2.68 (m, 4H, CH_2-Lev), 2.67 – 2.57 (m, 2H, CH_2-Lev), 2.56 – 2.46 (m, 2H, CH_2-Lev), 2.19 (s, 3H, CH_3-Lev), 2.17 (s, 3H, CH_3-Lev). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 206.0, 171.9, 171.7, 137.8, 135.1, 129.2, 128.5, 128.2, 128.0, 127.9, 127.8, 84.7 (C-1), 73.5, 71.7, 70.3, 67.9, 59.2, 37.9, 37.8, 29.9, 29.8, 27.9, 27.8. HRMS (ESI) calcd for $C_{29}H_{33}N_3O_8SeNa$ $[M+Na]^+$ 648.1385, found 648.1386.

N-(Benzyl)benzyloxycarbonyl-5-aminopentyl 2-azido-6-*O*-benzyl-2-deoxy-3,4-di-*O*-levulinoyl-D-galactopyranoside (19p)



Compound **S27** (400 mg, 0.63 mmol) was dissolved in acetone/H_2O (5.7 mL/0.6 mL), then NIS (214 mg, 0.95 mmol) was added. The resulting mixture was stirred for 10 h. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 1:1)

to give the intermediate (217 mg, 70%). The above intermediate (217 mg, 0.44 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (137 mg, 0.66 mmol) was dissolved in acetone (4.4 mL), and K_2CO_3 (91 mg, 0.66 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 10:1 to 3:1, containing 1% Et_3N) to give **17p** (240 mg, 82%) (Compound **17p** was used directly without further structural characterization). The glycosylation reaction was carried out according to **General Experimental Procedure** at rt for 4.5 d, using acceptor **18** (202 mg, 0.54 mmol) with **17p** (240 mg, 0.36 mmol), DCM 3.6 mL, Ph_3P=O (606 mg, 2.18 mmol) and TMSI (51 μL, 0.36 mmol). The product was purified by silica gel column chromatography (PE-EA, 2:1) to afford **19p** (250 mg, 86%, α/β =14:1) as a colorless syrup. $[\alpha]_D^{24}$ = + 74.8 (c 0.17, $CHCl_3$). α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 6.96 (m, 15H, Ar), 5.50 (d, *J* = 3.3 Hz, 1H, H-4), 5.33 (dd, *J* = 11.0, 3.2 Hz, 1H, H-3), 5.17 (d, *J* = 10.5 Hz, 2H, CH_2-Cbz), 4.94 (s, 1H, H-1), 4.54 – 4.40 (m, 4H, CH_2-Bn), 4.19 – 4.07 (m, 1H, H-5), 3.73 – 3.55 (m, 2H, H-2, CH_2), 3.53 – 3.33 (m, 3H, H-6, CH_2), 3.30 – 3.15 (m, 2H, CH_2), 2.84 – 2.67 (m, 4H, CH_2-Lev), 2.66 – 2.56 (m, 2H, CH_2-Lev), 2.56 – 2.45 (m, 2H, CH_2-Lev), 2.17 (s, 3H, CH_3-Lev), 2.16 (s, 3H, CH_3-Lev), 1.66 – 1.46 (m, 4H, CH_2), 1.39 – 1.21 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 206.1, 171.9, 171.8, 156.7, 156.2, 138.0, 137.8, 136.9, 128.6, 128.5, 128.44, 128.40, 128.0, 127.9, 127.84, 127.77, 127.3, 98.1 (C-1), 73.5, 68.7, 68.5, 68.3, 68.0, 67.8, 67.2, 57.7, 50.6, 50.3, 47.1, 46.2, 37.88, 37.85, 37.8, 29.85, 29.77, 29.1, 27.9, 27.7, 23.4. HRMS (ESI) calcd for $C_{43}H_{56}N_5O_{11}$ $[M+NH_4]^+$ 818.3971, found 818.3979.

Reaction Scope of acceptors

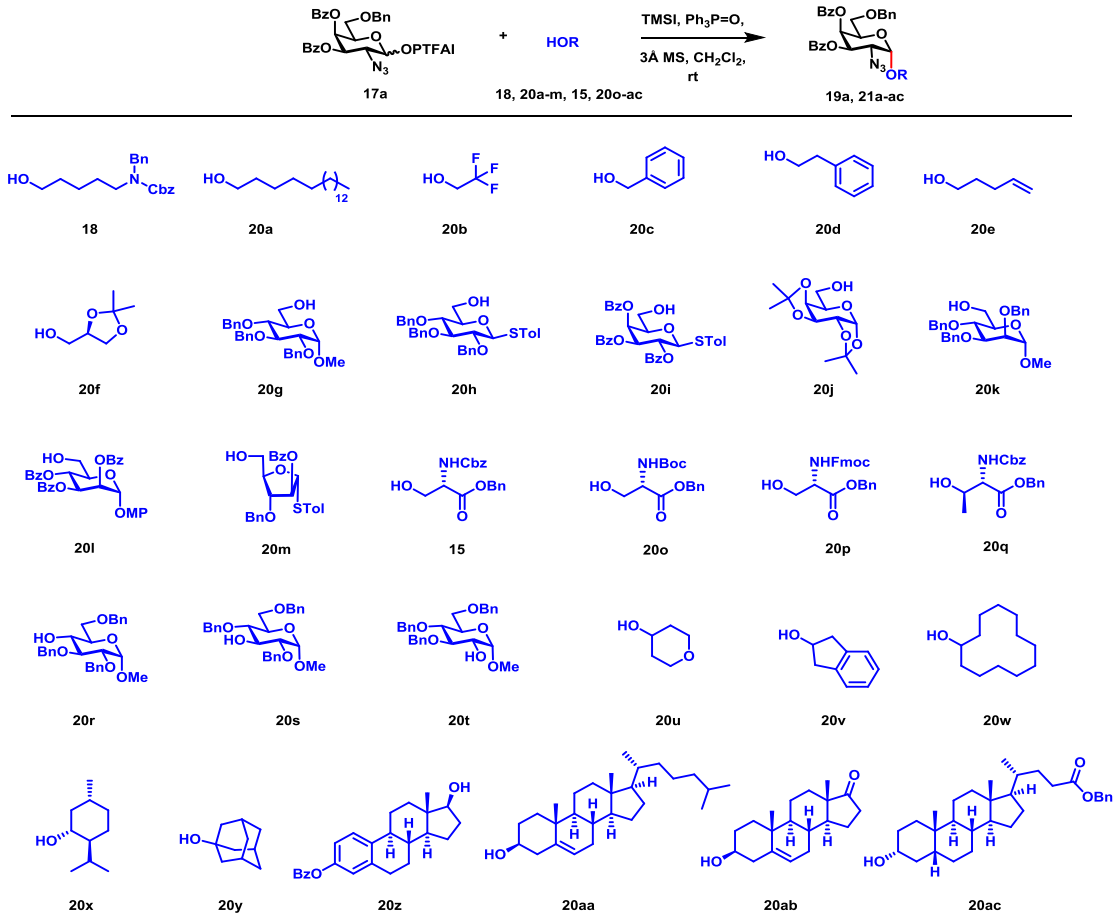
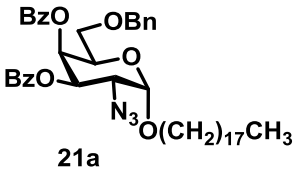


Figure S1. The acceptors **18, 20a-m, 15, 20o-ac** using in the stereoselective glycosylation

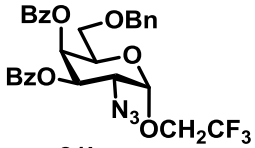
Octadecyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21a)



The glycosylation reaction was carried out according to **General Experimental Procedure** at 25℃ for 24 h, using acceptor 1-octadecanol **20a** (92.5 mg, 0.34 mmol) with **17a** (153.8 mg, 0.23 mmol), DCM 2.3 mL, Ph_3P=O (380.7 mg, 1.37 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 25:1 to 20:1 to 10:1) to afford **21a** (152.6 mg, 92%,

α/β >20:1) as a colorless syrup. $[\alpha]_D^{23}$ = + 149.3 (c 0.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H, Ar), 7.88 (d, *J* = 7.6 Hz, 2H, Ar), 7.57 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 – 7.39 (m, 3H, Ar), 7.30 (t, *J* = 7.7 Hz, 2H, Ar), 7.25 – 7.13 (m, 5H, Ar), 5.94 (d, *J* = 3.3 Hz, 1H, H-4), 5.77 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.14 (d, *J* = 3.4 Hz, 1H, H-1), 4.52 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.44 – 4.37 (m, 2H, CH_2-Bn, H-5), 3.87 – 3.77 (m, 2H, H-2, CH_2-Octadecyl), 3.64 – 3.51 (m, 3H, CH_2-Octadecyl, H-6), 1.74 – 1.65 (m, 2H, CH_2-Octadecyl), 1.41 (q, *J* = 7.3 Hz, 2H, CH_2-Octadecyl), 1.30 – 1.25 (m, 28H), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3-Octadecyl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 137.7, 133.4, 133.2, 129.9, 129.8, 129.6, 129.4, 128.6, 128.42, 128.37, 128.3, 127.71, 127.67, 98.5 (C-1), 73.6, 69.2, 69.1, 69.0, 68.32, 68.28, 58.4, 32.0, 29.80, 29.78, 29.75, 29.73, 29.67, 29.53, 29.50, 29.4, 26.3, 22.8, 14.2. HRMS (ESI) calcd for $C_{45}H_{65}N_4O_7$ $[M+NH_4]^+$ 773.4848, found 773.4857.

2,2,2-Trifluoroethyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranoside (21b)

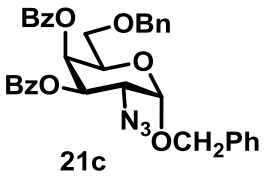


21b

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 2.5 d, using acceptor 2,2,2-trifluoroethanol **20b** (35.0 mg, 0.35 mmol) with **17a** (157.7 mg, 0.23 mmol), DCM 2.3 mL, Ph_3P=O (390.3 mg, 1.40 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 10:1) to afford **21b** (117 mg, 86%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{21}$ = + 204.5 (c 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 2H, Ar), 7.79 (d, *J* = 7.7 Hz, 2H, Ar), 7.51 (t, *J* = 7.4 Hz, 1H, Ar), 7.44 – 7.32 (m, 3H, Ar), 7.23 (t, *J* = 7.7 Hz, 2H, Ar), 7.17 – 7.07 (m, 5H, Ar), 5.87 (d, *J* = 3.2 Hz, 1H, H-4), 5.66 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.16 (d, *J* = 3.5 Hz, 1H, H-1), 4.42 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.35 – 4.28 (m, 2H, CH_2-Bn, H-5), 4.06 – 3.91 (m, 2H, CH_2-Trifluoroethyl), 3.87 (dd, *J* = 11.1, 3.6 Hz, 1H, H-2), 3.56 – 3.46 (m, 2H, H-6).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 165.3, 137.5, 133.6, 133.4, 130.0, 129.90, 129.85, 129.4, 129.2, 128.7, 128.5, 128.4, 127.8, 127.7, 124.9, 122.2, 99.1 (C-1), 73.6, 69.2, 68.8, 68.6, 68.0, 65.7, 65.3, 65.0, 64.6, 58.0. HRMS (ESI) calcd for $C_{29}H_{30}N_4O_7F_3$ $[M+NH_4]^+$ 603.2061, found 603.2071.

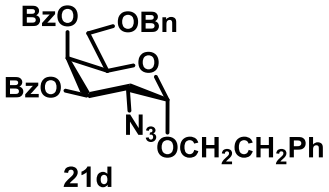
Benzyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside(21c)



21c

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 23 h, using acceptor benzyl alcohol **20c** (39.2 mg, 0.36 mmol) with **17a** (163.2 mg, 0.24 mmol), DCM 2.4 mL, Ph_3P=O (403.9 mg, 1.45 mmol) and TMSI (35 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1 to 5:1) to afford **21c** (135.6 mg, 94%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{23}$ = + 211.3 (c 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.50 – 7.40 (m, 5H, Ar), 7.40 – 7.28 (m, 6H, Ar), 7.26 – 7.16 (m, 4H, Ar), 5.94 (d, *J* = 3.3 Hz, 1H, H-4), 5.81 (dd, *J* = 11.0, 3.3 Hz, 1H, H-3), 5.24 (d, *J* = 3.5 Hz, 1H, H-1), 4.84 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.69 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.52 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.47 – 4.35 (m, 2H, CH_2-Bn, H-5), 3.92 (dd, *J* = 11.0, 3.5 Hz, 1H, H-2), 3.59 (d, *J* = 6.4 Hz, 2H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 137.7, 136.5, 133.4, 133.3, 129.85, 129.82, 129.5, 129.3, 128.64, 128.60, 128.5, 128.4, 128.35, 128.26, 128.20, 127.72, 127.68, 97.2 (C-1), 73.6, 70.0, 69.3, 69.0, 68.5, 68.3, 58.4. HRMS (ESI) calcd for $C_{34}H_{35}N_4O_7$ $[M+NH_4]^+$ 611.2500, found 611.2501.

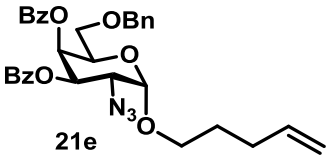
Phenethyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21d)



21d

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 23 h, using acceptor phenethyl alcohol **20d** (42.2 mg, 0.35 mmol) with **17a** (155.4 mg, 0.23 mmol), DCM 2.3 mL, Ph_3P=O (384.5 mg, 1.38 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1 to 5:1) to afford **21d** (129.1 mg, 92%, α/β >20:1) as a colorless syrup. $[\alpha]_D^{23}$ = + 222.4 (c 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.90 (d, *J* = 7.7 Hz, 2H, Ar), 7.59 (t, *J* = 7.4 Hz, 1H, Ar), 7.50 (t, *J* = 7.4 Hz, 1H, Ar), 7.44 (t, *J* = 7.7 Hz, 2H, Ar), 7.37 – 7.15 (m, 12H, Ar), 5.83 (d, *J* = 3.2 Hz, 1H, H-4), 5.74 (dd, *J* = 11.0, 3.3 Hz, 1H, H-3), 5.18 (d, *J* = 3.4 Hz, 1H, H-1), 4.47 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.35 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.07 – 3.95 (m, 2H), 3.90 – 3.78 (m, 2H, H-2), 3.55 – 3.45 (m, 2H), 3.08 – 2.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.40, 165.38, 138.4, 137.7, 133.4, 133.3, 129.84, 129.81, 129.5, 129.3, 129.1, 128.59, 128.57, 128.4, 127.7, 127.62, 126.60, 98.1 (C-1), 73.4, 69.2, 69.1, 69.0, 68.3, 68.2, 58.4, 36.1. HRMS (ESI) calcd for $C_{35}H_{37}N_4O_7$ $[M+NH_4]^+$ 625.2657, found 625.2660.

Pent-4-en-yl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21e)

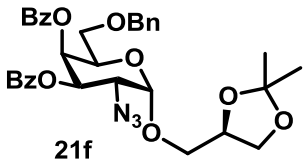


21e

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 23 h, using acceptor 4-penten-1-ol **20e** (30.0 mg, 0.35 mmol) with **17a** (156.5 mg, 0.23 mmol), DCM 2.3 mL, Ph_3P=O (387.4 mg, 1.39 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1 to 10:1) to afford **21e** (121.4 mg, 91%, α/β >20:1) as a

colorless syrup. $[\alpha]_D^{21}$ = + 227.4 (c 0.13, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 (t, *J* = 7.4 Hz, 1H, Ar), 7.47 (m, 7.5 Hz, 3H, Ar), 7.32 (t, *J* = 7.7 Hz, 2H, Ar), 7.22 (t, *J* = 7.4 Hz, 5H, Ar), 5.93 (d, *J* = 3.3 Hz, 1H, H-4), 5.89 – 5.80 (m, 1H, CH=-Pent), 5.77 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.15 (d, *J* = 3.4 Hz, 1H, H-1), 5.08 (d, *J* = 17.2 Hz, 1H, CH_2=-Pent), 5.01 (d, *J* = 10.2 Hz, 1H, CH_2=-Pent), 4.53 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.44 – 4.37 (m, 2H, CH_2-Bn, H-5), 3.90 – 3.77 (m, 2H, H-2, CH_2-Pent), 3.65 – 3.53 (m, 3H, H-6, CH_2-Pent), 2.21 (q, *J* = 7.2 Hz, 2H, CH_2-Pent), 1.84 – 1.75 (m, 2H, CH_2-Pent). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.4, 137.9, 137.7, 133.5, 133.3, 129.90, 129.87, 129.6, 129.4, 128.6, 128.42, 128.39, 127.8, 127.7, 115.3, 98.5 (C-1), 73.6, 69.13, 69.05, 68.4, 68.3, 68.2, 58.4, 30.4, 28.7. HRMS (ESI) calcd for $C_{32}H_{37}N_4O_7$ $[M+NH_4]^+$ 589.2657, found 589.2663.

(S)-(+)-2,2-dimethyl-1,3-dioxolane-4-methyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21f)

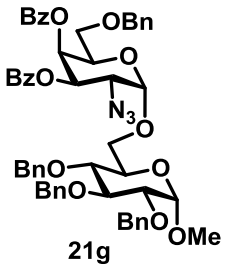


21f

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25℃ for 25 h, using acceptor (S)-(+)-2,2-dimethyl-1,3-dioxolane-4-methanol **20f** (44.7 mg, 0.34 mmol) with **17a** (152 mg, 0.23 mmol), DCM 2.3 mL, Ph_3P=O (376.2 mg, 1.35 mmol) and TMSI (32 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 10:1 to 5:1) to afford **21f** (129.8 mg, 93%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = + 195.6 (c 0.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H, Ar), 7.91 – 7.84 (m, 2H, Ar), 7.59 (t, *J* = 7.4 Hz, 1H, Ar), 7.53 – 7.41 (m, 3H, Ar), 7.32 (t, *J* = 7.7 Hz, 2H, Ar), 7.26 – 7.14 (m, 5H, Ar), 5.94 (d, *J* = 3.2 Hz, 1H, H-4), 5.75 (dd, *J* = 11.0, 3.4 Hz, 1H, H-3), 5.24 (d, *J* = 3.5 Hz, 1H, H-1), 4.52 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.48 – 4.34 (m, 3H, H-5, CH_2-Bn, CH), 4.12 (dd, *J* = 8.4, 6.3 Hz, 1H, CH_2), 3.90 (dd, *J* = 11.0, 3.5 Hz, 1H,

H-2), 3.86 – 3.79 (m, 2H, CH_2), 3.72 (dd, *J* = 10.6, 5.3 Hz, 1H, CH_2), 3.65 – 3.54 (m, 2H, H-6), 1.47 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.40, 165.38, 137.6, 133.5, 133.3, 129.9, 129.8, 129.5, 129.3, 128.6, 128.39, 128.37, 127.73, 127.71, 109.7, 98.7 (C-1), 74.4, 73.6, 69.14, 69.05, 68.9, 68.5, 68.2, 66.8, 58.4, 26.9, 25.5. HRMS (ESI) calcd for $C_{33}H_{39}N_4O_9$ $[M+NH_4]^+$ 635.2712, found 635.2716.

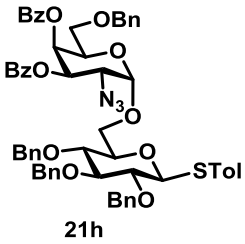
Methyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21g)



21g

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 36 h, using acceptor **20g**[5] (88.8 mg, 0.19 mmol) with **17a** (193.4 mg, 0.29 mmol), DCM 1.9 mL, Ph_3P=O (478.6 mg, 1.72 mmol) and TMSI (41 μL, 0.29 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **21g** (184 mg, 99%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = +149.1 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H, Ar), 7.86 (d, *J* = 7.7 Hz, 2H, Ar), 7.53 (t, *J* = 7.5 Hz, 1H, Ar), 7.46 – 7.22 (m, 20H, Ar), 7.22 – 7.13 (m, 5H, Ar), 5.87 (s, 1H, H-4_{GalN}), 5.68 (d, *J* = 11.0 Hz, 1H, H-3_{GalN}), 5.22 (s, 1H, H-1_{GalN}), 4.97 (dd, *J* = 15.9, 11.2 Hz, 2H, CH_2-Bn), 4.85 – 4.72 (m, 2H, CH_2-Bn), 4.69 – 4.57 (m, 3H, CH_2-Bn, H-1_{Glc}), 4.43 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.32 (d, *J* = 11.7 Hz, 2H, CH_2-Bn, H-5_{GalN}), 4.02 (t, *J* = 9.4 Hz, 1H), 3.91 – 3.73 (m, 4H, H-2_{GalN}), 3.62 – 3.46 (m, 4H, H-2_{Glc}, H-6_{GalN}), 3.39 (s, 3H, CH_3-OMe). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 138.8, 138.3, 138.2, 137.6, 133.4, 133.2, 129.8, 129.7, 129.5, 129.3, 128.53, 128.46, 128.4, 128.35, 128.29, 128.1, 127.91, 127.87, 127.8, 127.6, 127.5, 98.5 (C-1_{GalN}), 98.1 (C-1_{Glc}), 82.1, 80.1, 77.8, 75.7, 75.1, 73.42, 73.37, 70.1, 68.9, 68.1, 66.7, 58.5, 55.2. HRMS (ESI) calcd for $C_{55}H_{59}N_4O_{12}$ $[M+NH_4]^+$ 967.4124, found 967.4134.

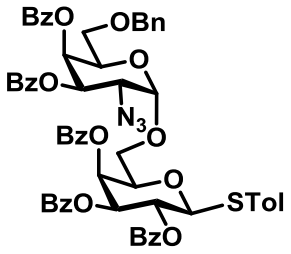
***p*-Methylphenyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21h)**



21h

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 4 d, using acceptor **20h**[6] (89.5 mg, 0.16 mmol) with **17a** (162.7 mg, 0.24 mmol), DCM 1.6 mL, $Ph_3P=O$ (402.6 mg, 1.45 mmol) and TMSI (35 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1) to afford **21h** (151.1 mg, 90%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = +122.8 (c 0.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H, Ar), 7.92 – 7.87 (m, 2H, Ar), 7.59 (t, *J* = 7.5 Hz, 1H, Ar), 7.53 – 7.38 (m, 8H, Ar), 7.37 – 7.25 (m, 15H, Ar), 7.24 – 7.14 (m, 6H, Ar), 5.78 (d, *J* = 3.3 Hz, 1H, H-4_{GalN}), 5.65 (dd, *J* = 11.0, 3.3 Hz, 1H, H-3_{GalN}), 5.27 (d, *J* = 3.5 Hz, 1H, H-1_{GalN}), 4.96 – 4.84 (m, 4H, CH_2-Bn), 4.76 – 4.66 (m, 3H, CH_2-Bn, H-1_{Glc}), 4.49 – 4.37 (m, 2H, CH_2-Bn), 4.28 (t, *J* = 6.3 Hz, 1H, H-5_{GalN}), 3.88 (dd, *J* = 11.1, 3.4 Hz, 3H, H-2_{GalN}), 3.74 (t, *J* = 8.8 Hz, 1H), 3.64 (t, *J* = 9.3 Hz, 1H), 3.60 – 3.45 (m, 4H, H-6_{GalN}, H-2_{Glc}), 2.29 (s, 3H, CH_3-STol). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.3, 138.5, 138.23, 138.19, 137.85, 137.83, 133.5, 133.3, 132.1, 130.0, 129.91, 129.88, 129.84, 129.7, 129.4, 128.65, 128.63, 128.53, 128.50, 128.43, 128.38, 128.3, 128.02, 127.98, 127.92, 127.89, 127.78, 127.69, 127.66, 98.6(C-1_{GalN}), 87.5 (C-1_{Glc}), 87.0, 81.0, 78.8, 77.7, 75.9, 75.5, 75.2, 73.4, 69.2, 69.0, 68.3, 68.1, 66.8, 58.7, 21.2. HRMS (ESI) calcd for $C_{61}H_{63}N_4O_{11}S$ $[M+NH_4]^+$ 1059.4209, found 1059.4205.

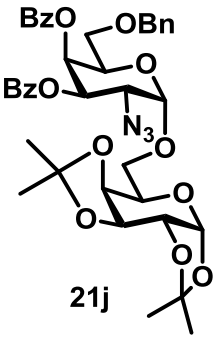
***p*-Methylphenyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (21i)**



21i

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 5 d, using acceptor **20i**[7] (87.2 mg, 0.15 mmol) with **17a** (147.4 mg, 0.22 mmol), DCM 1.5 mL, Ph_3P=O (364.9 mg, 1.31 mmol) and TMSI (31 μL, 0.22 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1) to afford **21i** (135.6 mg, 86%, α/β >20:1) as a white solid. $[\alpha]_D^{25}$ =+ 182.7 (c 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 11.0, 7.8 Hz, 4H, Ar), 7.90 (dd, *J* = 10.9, 7.9 Hz, 4H, Ar), 7.76 (d, *J* = 7.8 Hz, 2H, Ar), 7.58 (t, *J* = 7.5 Hz, 2H, Ar), 7.50 (t, *J* = 8.0 Hz, 4H, Ar), 7.46 – 7.36 (m, 7H, Ar), 7.32 (t, *J* = 7.7 Hz, 2H, Ar), 7.26 – 7.15 (m, 9H, Ar), 5.98 (d, *J* = 3.2 Hz, 1H, H-4_{Gal}), 5.85 (d, *J* = 3.2 Hz, 1H, H-4_{GalN}), 5.79 (t, *J* = 9.9 Hz, 1H, H-2_{Gal}), 5.71 (dd, *J* = 11.0, 3.2 Hz, 1H, H-3_{GalN}), 5.62 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3_{Gal}), 5.12 – 5.06 (m, 2H, H-1_{GalN}, H-1_{Gal}), 4.49 (dd, *J* = 12.2, 5.7 Hz, 2H, H-5_{GalN}, CH_2-Bn), 4.41 (d, *J* = 12.1 Hz, 1H, CH_2-Bn), 4.36 – 4.31 (m, 1H), 4.07 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.89 (dd, *J* = 11.0, 3.6 Hz, 1H, H-2_{GalN}), 3.79 (dd, *J* = 10.5, 4.4 Hz, 1H, H-6_{Gal}), 3.64 – 3.51 (m, 2H, H-6_{GalN}), 2.37 (s, 3H, CH_3-STol). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 165.5, 165.42, 165.35, 165.26, 138.6, 137.8, 133.6, 133.48, 133.46, 133.39, 133.31, 133.26, 130.1, 130.0, 129.94, 129.90, 129.86, 129.6, 129.5, 129.4, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 127.9, 127.72, 127.68, 98.7 (C-1_{GalN}), 85.9 (C-1_{Gal}), 76.6, 73.5, 73.2, 69.2, 69.0, 68.5, 68.3, 68.2, 68.0, 58.5, 21.3. HRMS (ESI) calcd for $C_{61}H_{57}N_4O_{14}S$ $[M+NH_4]^+$ 1101.3586, found 1101.3589.

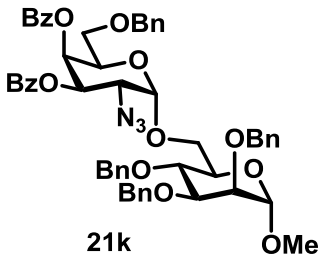
_O_-(2-azido-3,4-di-_O_-benzoyl-6-_O_-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→6)-1,2,3,4-di-_O_-isopropylidene-α-D-galactopyranoside (21j)



21j

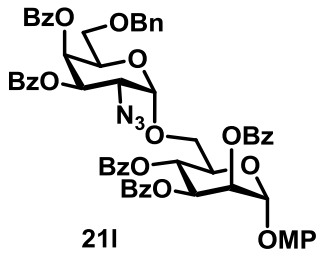
The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 25 h, using acceptor **20j** (57.2 mg, 0.22 mmol) with **17a** (227.8 mg, 0.33 mmol), DCM 2.2 mL, Ph_3P=O (551.3 mg, 1.98 mmol) and TMSI (47 μL, 0.33 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **21j** (162 mg, 99%, α/β >20:1) as a yellow solid. $[\alpha]_D^{22}$ = + 115.1 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.52 – 7.39 (m, 3H, Ar), 7.31 (t, *J* = 7.7 Hz, 2H, Ar), 7.25 – 7.13 (m, 5H, Ar), 5.95 (d, *J* = 3.3 Hz, 1H, H-4_{GalN}), 5.78 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3_{GalN}), 5.54 (d, *J* = 5.0 Hz, 1H, H-1_{Gal}), 5.22 (d, *J* = 3.4 Hz, 1H, H-1_{GalN}), 4.64 (dd, *J* = 7.8, 2.4 Hz, 1H, H-3_{Gal}), 4.55 – 4.48 (m, 2H, H-$5_{GalN,}$ CH_2-Bn), 4.43 – 4.31 (m, 3H, H-2_{Gal}, H-4_{Gal}, CH_2-Bn), 4.10 (t, *J* = 6.5 Hz, 1H, H-5_{Gal}), 3.95 (dd, *J* = 10.1, 6.3 Hz, 1H, H-6_{Gal}), 3.89 – 3.80 (m, 2H, H-2_{GalN}, H-6_{Gal}), 3.60 (m, *J* = 9.7, 6.3 Hz, 2H, H-6_{GalN}), 1.59 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.34 (s, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 137.7, 133.4, 133.2, 129.9, 129.8, 129.6, 129.4, 128.6, 128.4, 128.3, 127.7, 127.6, 109.4, 108.8, 98.7 (C-1_{GalN}), 96.4 (C-1_{Gal}), 73.4, 71.0, 70.8, 69.0, 68.9, 68.1, 68.0, 67.4, 66.5, 58.5, 26.2, 26.1, 25.1, 24.5. HRMS (ESI) calcd for $C_{39}H_{47}N_4O_{12}$ $[M+NH_4]^+$ 763.3185, found 763.3192.

Methyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (21k)



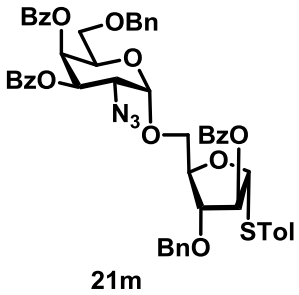
The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 25h, using acceptor **20k**[8] (70.3 mg, 0.15 mmol) with **17a** (153.3 mg, 0.23 mmol), DCM 1.5 mL, Ph_3P=O (374.4 mg, 1.36 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1 to 3:1) to afford **21k** (132.3 mg, 92%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = + 166.9 (c 0.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H, Ar), 7.87 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 – 7.41 (m, 3H, Ar), 7.39 – 7.25 (m, 18H, Ar), 7.23 – 7.18 (m, 3H, Ar), 7.17 – 7.12 (m, 1H, Ar), 5.93 (d, *J* = 3.2 Hz, 1H, H-4_{GalN}), 5.76 (dd, *J* = 11.0, 3.3 Hz, 1H, H-3_{GalN}), 5.29 (d, *J* = 3.4 Hz, 1H, H-1_{GalN}), 4.99 (d, *J* = 11.2 Hz, 1H, CH_2-Bn), 4.77 – 4.67 (m, 3H, CH_2-Bn, H-1_{Man}), 4.64 (m, 3H, CH_2-Bn), 4.52 – 4.46 (m, 2H, CH_2-Bn, H-5_{GalN}), 4.38 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 3.96 – 3.89 (m, 4H), 3.88 – 3.83 (m, 2H, H-2_{GalN}), 3.81 (d, *J* = 2.0 Hz, 1H, H-2_{Man}), 3.64 – 3.51 (m, 2H, H-6_{GalN}), 3.37 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.7, 138.6, 138.5, 137.7, 133.4, 133.3, 129.90, 129.88, 129.7, 129.5, 128.6, 128.49, 128.46, 128.44, 128.40, 128.38, 128.0, 127.90, 127.85, 127.80, 127.73, 127.70, 127.65, 99.1 (C-1_{Man}), 98.2 (C-1_{GalN}), 80.5, 75.2, 74.9, 73.5, 72.9, 72.2, 71.5, 69.1, 69.0, 68.1, 68.0, 67.2, 58.5, 54.9. HRMS (ESI) calcd for $C_{55}H_{59}N_4O_{12}$ $[M+NH_4]^+$ 967.4124, found 967.4130.

***p*-Methoxyphenyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (21l)**



The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 36 h, using acceptor **20l**[9] (94.2 mg, 0.16 mmol) with **17a** (159.9 mg, 0.24 mmol), DCM 1.6 mL, $Ph_3P=O$ (394.2 mg, 1.42 mmol) and TMSI (34 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1 to 3.5:1) to afford **21l** (158.9 mg, 93%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = + 42.8 (c 0.13, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H, Ar), 8.05 – 8.00 (m, 2H, Ar), 7.94 (m, 2H, Ar), 7.92 – 7.84 (m, 4H, Ar), 7.60 – 7.40 (m, 10H, Ar), 7.35 (q, *J* = 7.7 Hz, 4H, Ar), 7.31 – 7.24 (m, 2H, Ar), 7.21 – 7.15 (m, 2H, Ar), 7.14 – 7.06 (m, 4H, Ar), 6.98 – 6.93 (m, 2H, Ar), 6.13 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3_{Man}), 6.07 (t, *J* = 10.0 Hz, 1H, H-4_{Man}), 5.91 – 5.88 (m, 2H, H-4_{GalN}, H-2_{Man}), 5.76 (dd, *J* = 11.0, 3.3 Hz, 1H, H-3_{GalN}), 5.69 (d, *J* = 1.8 Hz, 1H, H-1_{Man}), 5.16 (d, *J* = 3.5 Hz, 1H, H-1_{GalN}), 4.62 – 4.55 (m, 1H, H-5_{Man}), 4.37 (t, *J* = 6.5 Hz, 1H, H-5_{GalN}), 4.33 (d, *J* = 12.1 Hz, 1H, CH_2-Bn), 4.20 (d, *J* = 12.1 Hz, 1H, CH_2-Bn), 4.09 (dd, *J* = 11.0, 6.0 Hz, 1H, H-6_{Man}), 3.91 (dd, *J* = 11.0, 3.4 Hz, 1H, H-2_{GalN}), 3.80 – 3.79 (m, 1H, H-6_{Man}), 3.78 (s, 3H, CH_3-MP), 3.49 – 3.37 (m, 2H, H-6_{GalN}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.71, 165.67, 165.4, 165.2, 155.9, 150.1, 137.6, 133.62, 133.60, 133.4, 133.3, 130.1, 130.0, 129.92, 129.89, 129.87, 129.6, 129.5, 129.3, 129.2, 129.1, 128.7, 128.63, 128.61, 128.4, 128.3, 127.63, 127.60, 118.5, 115.0, 98.3 (C-1_{GalN}), 97.4 (C-1_{Man}), 73.4, 70.7, 70.23, 70.18, 69.5, 69.0, 68.2, 68.1, 67.2, 58.6, 55.8. HRMS (ESI) calcd for $C_{61}H_{57}N_4O_{16}$ $[M+NH_4]^+$ 1101.3764, found 1101.3766.

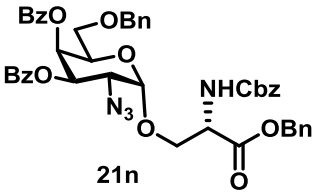
***p*-methylphenyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranosyl)-(1→5)-2-*O*-benzoyl-3-benzyl-1-thio-α-D-arabinoglycoside (21m)**



21m

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 34 h, using acceptor **20m**[10] (73.1 mg, 0.16 mmol) with **17a** (164.1 mg, 0.24 mmol), DCM 1.6 mL, Ph_3P=O (406.2 mg, 1.46 mmol) and TMSI (35 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1) to afford **21m** (149.2 mg, 98%, α/β >20:1) as a white solid. $[\alpha]_D^{22}$ = + 199.5 (c 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H, Ar), 7.96 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.8 Hz, 2H, Ar), 7.59 (t, *J* = 7.4 Hz, 1H, Ar), 7.54 – 7.36 (m, 11H, Ar), 7.33 (m, 4H, Ar), 7.29 – 7.22 (m, 1H, Ar), 7.20 – 7.09 (m, 6H, Ar), 5.81 (d, *J* = 3.3 Hz, 1H, H-4_{GalN}), 5.63 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3_{GalN}), 5.59 (d, *J* = 3.0 Hz, 2H, H-1_{Ara}, H-2_{Ara}), 5.21 (d, *J* = 3.5 Hz, 1H, H-1_{GalN}), 4.83 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 4.65 – 4.57 (m, 2H, H-4_{Ara}, CH_2-Bn), 4.44 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.34 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.27 (dd, *J* = 6.6, 2.3 Hz, 1H, H-3_{Ara}), 4.20 (t, *J* = 6.3 Hz, 1H, H-5_{GalN}), 3.94 – 3.83 (m, 3H, H-2_{GalN}, H-5_{Ara}, H-6_{Ara}), 3.56 – 3.44 (m, 2H, H-6_{GalN}), 2.32 (s, 3H, CH_3-STol). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 165.4, 165.2, 138.1, 137.7, 137.3, 133.53, 133.49, 133.3, 133.2, 130.1, 130.0, 129.90, 129.86, 129.6, 129.4, 128.7, 128.65, 128.60, 128.5, 128.43, 128.41, 128.2, 127.73, 127.71, 98.5 (C-1_{GalN}), 91.4 (C-1_{Ara}), 82.64, 82.58, 80.8, 73.5, 72.8, 69.2, 69.0, 68.33, 68.27, 66.5, 58.6, 21.2. HRMS (ESI) calcd for $C_{53}H_{53}N_4O_{11}S$ $[M+NH_4]^+$ 953.3426, found 953.3418.

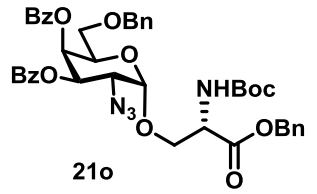
L-Serine *N*-(benzyloxycarbonyl)-*O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (21n)



21n

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25℃ for 8 d, using acceptor **15** (93.2 mg, 0.28 mmol) with **17a** (127.3 mg, 0.19 mmol), DCM 1.9 mL, Ph_3P=O (315.1 mg, 1.13 mmol) and TMSI (27 μL, 0.19 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **21n** (112.3 mg, 73%, α/β >20:1) as a yellow solid. $[\alpha]_D^{25}$ = + 168.8 (c 0.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H, Ar), 7.87 (d, *J* = 7.7 Hz, 2H, Ar), 7.59 (t, *J* = 7.4 Hz, 1H, Ar), 7.50 (t, *J* = 7.5 Hz, 1H, Ar), 7.44 (t, *J* = 7.7 Hz, 2H, Ar), 7.40 – 7.28 (m, 12H, Ar), 7.22 – 7.14 (m, 5H, Ar), 6.10 (d, *J* = 8.5 Hz, 1H, NH-Ser), 5.81 (d, *J* = 3.3 Hz, 1H, H-4), 5.60 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.24 (s, 2H), 5.16 – 5.07 (m, 2H), 5.05 (d, *J* = 3.6 Hz, 1H, H-1), 4.67 (d, *J* = 8.2 Hz, 1H, CH-Ser), 4.47 (d, *J* = 12.2 Hz, 1H, CH_2-Bn), 4.36 – 4.23 (m, 3H, H-5, CH_2-Bn, CH_2-Ser), 4.06 (dd, *J* = 10.9, 3.0 Hz, 1H, CH_2-Ser), 3.80 (dd, *J* = 11.1, 3.6 Hz, 1H, H-2), 3.57 – 3.44 (m, 2H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 165.4, 165.3, 156.2, 137.5, 136.3, 135.2, 133.5, 133.4, 129.9, 129.8, 129.4, 129.2, 128.8, 128.69, 128.65, 128.60, 128.43, 128.40, 128.36, 128.3, 127.7, 99.9 (C-1), 73.5, 70.5, 68.8, 68.75, 68.71, 68.0, 67.9, 67.3, 58.3, 54.8. HRMS (ESI) calcd for $C_{45}H_{46}N_5O_{11}$ $[M+NH_4]^+$ 832.3188, found 832.3192.

L-Serine *N*-(*t*-Butyloxycarbonyl)-*O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester(21o)

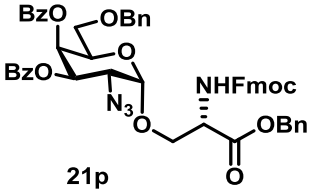


21o

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25℃ for 7 d, using acceptor *N*-Boc-L-serine benzyl ester **20o** (42.3 mg, 0.14 mmol) with **17a** (145 mg, 0.21 mmol), DCM 1.4 mL, Ph_3P=O (358.9 mg, 1.29

mmol) and TMSI (31 μL, 0.21 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **21o** (62.1 mg, 55%, α/β >20:1) as a yellow solid. $[\alpha]_D^{20}$ = + 180.4 (c 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H, Ar), 7.87 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 (t, *J* = 7.4 Hz, 1H, Ar), 7.45 (t, *J* = 7.7 Hz, 2H, Ar), 7.40 – 7.29 (m, 7H, Ar), 7.24 – 7.13 (m, 5H, Ar), 5.87 (d, *J* = 3.3 Hz, 1H, H-4), 5.69 – 5.55 (m, 2H, H-3, NH-Ser), 5.28 – 5.18 (m, 2H, CH_2-Bn), 5.05 (d, *J* = 3.6 Hz, 1H, H-1), 4.65 – 4.56 (m, 1H, CH-Ser), 4.52 (d, *J* = 12.1 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 1H, H-5), 4.18 (dd, *J* = 10.6, 3.3 Hz, 1H, CH_2-Ser), 4.04 (dd, *J* = 10.6, 3.1 Hz, 1H, CH_2-Ser), 3.81 (dd, *J* = 11.1, 3.5 Hz, 1H, H-2), 3.61-3.44 (m, 2H, H-6), 1.46 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 165.42, 165.37, 155.7, 137.5, 135.3, 133.5, 133.4, 129.92, 129.87, 129.5, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 127.80, 127.77, 99.6 (C-1), 80.4, 73.6, 70.1, 68.9, 68.7, 68.6, 67.9, 67.8, 58.3, 54.3, 28.4. HRMS (ESI) calcd for $C_{42}H_{44}N_4O_{11}Na$ $[M+Na]^+$ 803.2899, found 803.2911.

L-Serine *N*-(9H-fluoren-9-ylmethoxy)carbonyl)-*O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2- deoxy-α-D-galactopyranosyl)-benzyl ester(21p)

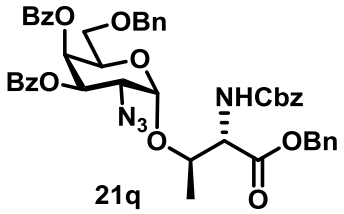


21p

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25°C for 7 d, using acceptor Fmoc-O-benzyl-L-serine **20p** (52.8 mg, 0.13 mmol) with **17a** (128 mg, 0.19 mmol), DCM 1.3 mL, Ph_3P=O (316.8 mg, 1.14 mmol) and TMSI (27 μL, 0.19 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **21p** (84 mg, 74%, α/β >20:1) as a yellow solid. $[\alpha]_D^{20}$ = +122.8 (c 0.32, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.8 Hz, 2H, Ar), 7.75 (d, *J* = 7.5 Hz, 2H, Ar), 7.62 (d, *J* = 7.8 Hz, 3H, Ar), 7.51 (t, *J* = 7.5 Hz, 1H, Ar), 7.46 (t, *J* = 7.7 Hz, 2H, Ar), 7.41 – 7.27 (m, 11H, Ar), 7.20 – 7.12 (m, 5H, Ar), 6.22 (d, *J* = 8.4 Hz, 1H, NH-Ser), 5.84 (d, *J* = 3.2

Hz, 1H, H-4), 5.65 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.27 (s, 2H, CH_2-Bn), 5.04 (d, *J* = 3.6 Hz, 1H, H-1), 4.67 (d, *J* = 8.3 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.40 – 4.26 (m, 5H), 4.21 (t, *J* = 7.3 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.82 (dd, *J* = 11.2, 3.6 Hz, 1H, H-2), 3.59 – 3.44 (m, 2H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 165.4, 156.1, 144.0, 143.9, 141.40, 141.37, 137.5, 135.2, 133.6, 133.4, 129.92, 129.86, 129.4, 129.2, 128.8, 128.73, 128.68, 128.5, 128.4, 127.8, 127.7, 127.22, 127.21, 125.4, 125.3, 120.0, 100.0 (C-1), 77.4, 73.5, 70.6, 68.9, 68.83, 68.78, 68.2, 67.9, 67.4, 58.4, 54.8, 47.2, 29.8. HRMS (ESI) calcd for $C_{52}H_{46}N_4O_{11}Na$ $[M+Na]^+$ 925.3055, found 925.3060.

L-Threonine *N*-(benzyloxycarbonyl)-*O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (21q)

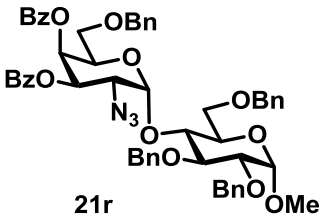


21q

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25℃ for 7 d, using acceptor Benzyloxycarbonyl-L-threonine benzyl ester **20q** (108 mg, 0.31 mmol) with **17a** (141.4 mg, 0.21 mmol), DCM 2.1 mL, Ph_3P=O (350 mg, 1.26 mmol) and TMSI (30 μL, 0.19 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1) to afford **21q** (94.1 mg, 54%, α/β >20:1) as a yellow solid. $[\alpha]_D^{24}$ = +192.3 (c 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H, Ar), 7.87 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 (t, *J* = 7.4 Hz, 1H, Ar), 7.45 (t, *J* = 7.7 Hz, 2H, Ar), 7.40 – 7.28 (m, 12H, Ar), 7.23 – 7.13 (m, 5H, Ar), 5.87 (d, *J* = 3.2 Hz, 1H, H-4), 5.68 (d, *J* = 9.6 Hz, 1H), 5.58 (dd, *J* = 11.1, 3.2 Hz, 1H, H-3), 5.27 – 5.16 (m, 2H), 5.16 (s, 2H), 5.01 (d, *J* = 3.7 Hz, 1H, H-1), 4.54 – 4.47 (m, 3H), 4.41 – 4.34 (m, 2H, H-5), 3.79 (dd, *J* = 11.1, 3.7 Hz, 1H, H-2), 3.58 – 3.49 (m, 2H, H-6), 1.38 (d, *J* = 6.4 Hz, 3H, CH_3-Thr). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 165.4, 165.3, 157.0, 137.5, 136.3, 135.2, 133.6, 133.4, 129.89, 129.85, 129.4, 129.2, 128.8, 128.7, 128.64, 128.62, 128.4, 128.4, 128.2,

128.1, 127.82, 127.78, 127.7, 99.4 (C-1), 76.8, 73.6, 69.3, 68.72, 68.69, 68.2, 67.7, 67.3, 59.0, 58.7, 18.7. HRMS (ESI) calcd for $C_{46}H_{44}N_4O_{11}Na$ $[M+Na]^+$ 851.2904, found 851.2904.

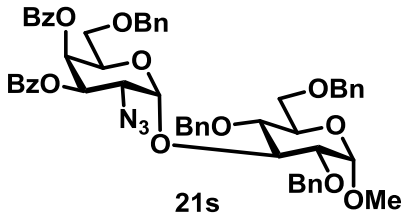
Methyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (21r)



21r

The glycosylation reaction was carried out according to **General Experimental Procedure** at 25 ℃ for 59 h, using acceptor **20r**[11] (68.2 mg, 0.15 mmol) with **17a** (148.6 mg, 0.22 mmol), DCM 1.5 mL, $Ph_3P=O$ (367.7 mg, 1.32 mmol) and TMSI (32 μL, 0.22 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1 to 3:1) to afford **21r** (126.3 mg, 91%, α/β >20:1) as a yellow solid. $[\alpha]_D^{23}$ = + 156.6 (c 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.56 (t, *J* = 7.5 Hz, 1H, Ar), 7.49 (t, *J* = 7.4 Hz, 1H, Ar), 7.44 – 7.25 (m, 20H, Ar), 7.14 – 7.06 (m, 4H, Ar), 5.94 (d, *J* = 3.8 Hz, 1H, H-1_{GalN}), 5.87 (d, *J* = 3.2 Hz, 1H, H-4_{GalN}), 5.66 (dd, *J* = 11.2, 3.2 Hz, 1H, H-3_{GalN}), 5.15 (d, *J* = 11.0 Hz, 1H, CH_2-Bn), 4.89 (d, *J* = 11.0 Hz, 1H, CH_2-Bn), 4.73 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.67 – 4.60 (m, 3H, CH_2-Bn, H-1_{Glc}), 4.54 (d, *J* = 12.3 Hz, 1H, CH_2-Bn), 4.31 – 4.21 (m, 2H, H-5_{GalN}, CH_2-Bn), 4.18 – 4.06 (m, 2H, H-3_{Glc}, CH_2-Bn), 4.01 (t, *J* = 9.1 Hz, 1H, H-4_{Glc}), 3.89 – 3.69 (m, 4H, H-2_{GalN}, H-5_{Glc}, H-6_{Glc}), 3.62 (dd, *J* = 9.5, 3.5 Hz, 1H, H-2_{Glc}), 3.40 (s, 3H, CH_3-OMe), 3.36 (d, *J* = 6.5 Hz, 2H, H-6_{GalN}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 139.0, 138.4, 138.0, 137.6, 133.4, 133.3, 129.9, 129.8, 129.6, 129.4, 128.6, 128.5, 128.43, 128.41, 128.37, 128.26, 128.22, 128.1, 127.7, 127.6, 127.5, 127.4, 98.2 (C-1_{GalN}), 97.7 (C-1_{Glc}), 82.0, 80.7, 74.9, 73.8, 73.5, 73.3, 73.2, 69.5, 69.4, 69.0, 68.7, 68.6, 67.8, 58.4, 55.4. HRMS (ESI) calcd for $C_{55}H_{59}N_4O_{12}$ $[M+NH_4]^+$ 967.4124, found 967.4133.

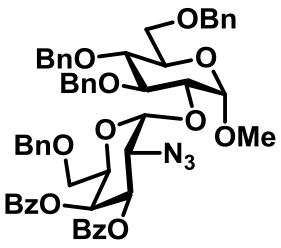
Methyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→3)-2,4,6- tri-*O*-benzyl-α-D-glucopyranoside (21s)



21s

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 50h, using acceptor **20s**[12] (66.4 mg, 0.14 mmol) with **17a** (144.6 mg, 0.21 mmol), DCM 1.4 mL, Ph_3P=O (357.9 mg, 1.29 mmol) and TMSI (31 μL, 0.21 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **21s** (134.4 mg, 99%, α/β >20:1) as a white solid. $[\alpha]_D^{21}$ = + 165.2 (c 0.31, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.5 Hz, 4H, Ar), 7.54 (t, *J* = 7.5 Hz, 1H, Ar), 7.49 (t, *J* = 7.5 Hz, 1H, Ar), 7.46 – 7.37 (m, 6H, Ar), 7.37 – 7.24 (m, 12H, Ar), 7.22 – 7.18 (m, 2H, Ar), 7.16 – 7.08 (m, 4H, Ar), 5.88 – 5.81 (m, 2H, H-4_{GalN}, H-3_{GalN}), 5.72 (d, *J* = 3.5 Hz, 1H, H-1_{GalN}), 4.93 – 4.84 (m, 2H, H-5_{GalN}, CH_2-Bn), 4.78 – 4.71 (m, 2H, H-1_{Glc}, CH_2-Bn), 4.65 (d, *J* = 11.5 Hz, 2H, CH_2-Bn), 4.56 (d, *J* = 10.9 Hz, 1H, CH_2-Bn), 4.51 (d, *J* = 12.1 Hz, 1H, CH_2-Bn), 4.28 (t, *J* = 9.4 Hz, 1H, H-3_{Glc}), 4.22 (s, 2H, CH_2-Bn), 3.91 – 3.79 (m, 2H, H-2_{GalN}, H-4_{Glc}), 3.76 (d, *J* = 9.5 Hz, 2H), 3.70 – 3.59 (m, 2H, H-2_{Glc}), 3.49 (dd, *J* = 9.9, 5.9 Hz, 1H, H-6_{GalN}), 3.37 – 3.28 (m, 4H, CH_3-OMe, H-6_{GalN}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.4, 138.2, 138.1, 137.78, 137.76, 133.2, 129.9, 129.81, 129.76, 129.5, 128.74, 128.66, 128.58, 128.50, 128.47, 128.42, 128.37, 128.31, 128.2, 128.1, 128.0, 127.9, 127.83, 127.77, 127.6, 127.4, 127.3, 98.1 (C-1_{GalN}), 97.6 (C-1_{Glc}), 79.4, 78.6, 75.8, 74.0, 73.7, 73.3, 73.0, 70.1, 69.3, 69.2, 68.4, 67.9, 67.4, 58.7, 55.1. HRMS (ESI) calcd for $C_{55}H_{59}N_4O_{12}$ $[M+NH_4]^+$ 967.4124, found 967.4129.

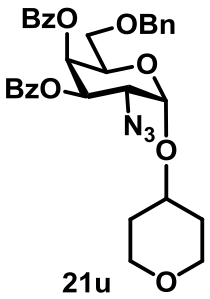
Methyl *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (21t)



21t

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 60h, using acceptor **20t**[13] (73.9 mg, 0.16 mmol) with **17a** (160.7 mg, 0.24 mmol), DCM 1.6 mL, Ph_3P=O (397.9 mg, 1.43 mmol) and TMSI (34 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1-3:1) to afford **21t** (135.6 mg, 90%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = +192.7 (c 0.33, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H, Ar), 7.90 (d, *J* = 7.9 Hz, 2H, Ar), 7.58 – 7.45 (m, 4H, Ar), 7.44 – 7.22 (m, 15H, Ar), 7.22 – 7.10 (m, 7H, Ar), 5.83 (d, *J* = 11.2 Hz, 1H, H-3_{GalN}), 5.67 (s, 1H, H-4_{GalN}), 5.28 (s, 1H, H-1_{GalN}), 5.01 (m, 2H, H-1_{Glc}, CH_2-Bn), 4.88 (d, *J* = 10.8 Hz, 2H, CH_2-Bn), 4.69 – 4.46 (m, 4H, H-5_{GalN}, CH_2-Bn), 4.18 (s, 2H, CH_2-Bn), 4.11 (t, *J* = 9.5 Hz, 1H, H-3_{Glc}), 3.96 (d, *J* = 10.5 Hz, 2H, H-2_{GalN}, H-2_{Glc}), 3.81 (dd, *J* = 22.4, 10.5 Hz, 2H), 3.69 (d, *J* = 10.3 Hz, 2H, H-4_{Glc}), 3.52 – 3.41 (m, 4H, H-6_{GalN}, CH_3-OMe), 3.27 (t, *J* = 7.9 Hz, 1H, H-6_{GalN}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 165.2, 138.3, 138.2, 138.0, 137.9, 133.3, 133.2, 129.8, 129.7, 129.6, 129.4, 128.6, 128.5, 128.4, 128.3, 128.25, 128.17, 127.94, 127.90, 127.8, 127.7, 127.6, 127.5, 127.4, 96.5 (C-1_{Glc}), 95.1 (C-1_{GalN}), 80.8, 78.4, 76.4, 75.03, 74.96, 73.6, 72.8, 70.4, 69.1, 69.0, 68.6, 68.1, 67.7, 60.3, 58.2, 55.4. HRMS (ESI) calcd for $C_{55}H_{59}N_4O_{12}$ $[M+NH_4]^+$ 967.4124, found 967.4120.

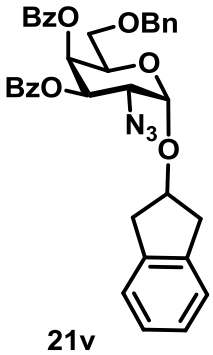
Tetrahydropyran-4-yl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranoside (21u)



21u

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 43h, using acceptor **20u** (19.5 mg, 0.19 mmol) with **17a** (193.2 mg, 0.29 mmol), DCM 1.9 mL, Ph_3P=O (478.1 mg, 1.72 mmol) and TMSI (41 μL, 0.29 mmol). The product was purified by silica gel column chromatography (PE-EA, 5:1) to afford **21u** (98.2 mg, 88%, α/β >20:1) as a white solid. $[\alpha]_D^{25}$ = +193.1 (c 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.61 (t, *J* = 7.5 Hz, 1H, Ar), 7.54 – 7.42 (m, 3H, Ar), 7.33 (t, *J* = 7.6 Hz, 2H, Ar), 7.22 (s, 5H, Ar), 5.93 (s, 1H, H-4), 5.79 (d, *J* = 11.2 Hz, 1H, H-3), 5.32 (s, 1H, H-1), 4.54 – 4.46 (m, 2H, CH_2-Bn), 4.41 (d, *J* = 12.1 Hz, 1H, CH_2-Bn), 4.02 – 3.90 (m, 3H), 3.83 (d, *J* = 11.2 Hz, 1H, H-2), 3.59 (d, *J* = 6.4 Hz, 2H), 3.54 – 3.42 (m, 2H), 2.05 – 1.93 (m, 2H), 1.85 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.50, 165.46, 137.6, 133.5, 133.4, 129.92, 129.88, 129.5, 129.3, 128.7, 128.4, 127.8, 127.6, 97.1 (C-1), 74.0, 73.6, 69.0, 68.9, 68.7, 68.4, 65.6, 65.5, 58.1, 33.5, 31.8. HRMS (ESI) calcd for $C_{32}H_{33}N_3O_8Na$ $[M+Na]^+$ 610.2165, found 610.2164.

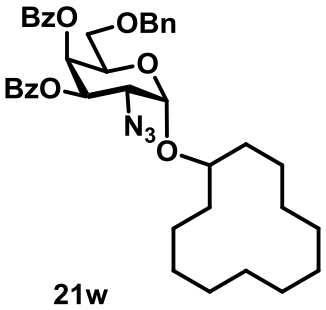
2,3-Dihydro-1*H*-inden-2-yl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21v)



21v

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 48 h, using acceptor **20v** (20.6 mg, 0.15 mmol) with **17a** (155.4 mg, 0.23 mmol), DCM 1.5 mL, Ph_3P=O (384.5 mg, 1.38 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1-10:1) to afford **21v** (87.6 mg, 92%, α/β >20:1) as a white solid. $[\alpha]_D^{25}$ = +230.0 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H, Ar), 7.86 (d, *J* = 7.6 Hz, 2H, Ar), 7.59 (t, *J* = 7.5 Hz, 1H, Ar), 7.51 – 7.40 (m, 3H, Ar), 7.34 – 7.13 (m, 11H, Ar), 5.90 (s, 1H, H-4), 5.73 (d, *J* = 11.1 Hz, 1H, H-3), 5.33 (s, 1H, H-1), 4.71 (t, *J* = 6.1 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.48 – 4.37 (m, 2H, CH_2-Bn), 3.82 (d, *J* = 11.0 Hz, 1H, H-2), 3.68 – 3.54 (m, 2H), 3.31 – 3.19 (m, 3H), 3.13 (dd, *J* = 16.2, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 140.5, 140.2, 137.6, 133.5, 133.3, 129.88, 129.85, 129.5, 129.3, 128.6, 128.5, 128.42, 128.37, 127.8, 127.7, 126.8, 124.74, 124.71, 98.3 (C-1), 80.6, 73.6, 69.0, 68.9, 68.7, 68.4, 58.1, 39.9, 39.3. HRMS (ESI) calcd for $C_{36}H_{33}N_3O_7Na$ $[M+Na]^+$ 642.2216, found 642.2216.

Cyclododecyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21w)

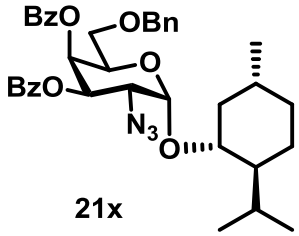


21w

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25℃ for 38 h, using acceptor **20w** (27.9 mg, 0.15 mmol) with **17a** (153.3 mg, 0.23 mmol), DCM 1.5 mL, Ph_3P=O (379.4 mg, 1.36 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 25:1) to afford **21w** (93.6 mg, 92%, α/β >20:1) as a white solid. $[\alpha]_D^{25}$ = +261.6 (c 0.11, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H, Ar), 7.88 (d, *J* = 7.6 Hz, 2H, Ar), 7.57 (d, *J* = 8.8 Hz, 1H, Ar), 7.53 – 7.40 (m, 3H, Ar),

7.36 – 7.28 (m, 2H, Ar), 7.27 – 7.13 (m, 5H, Ar), 5.94 (s, 1H, H-4), 5.76 (d, *J* = 11.1 Hz, 1H, H-3), 5.27 (s, 1H, H-1), 4.58 – 4.34 (m, 3H, H-5, CH_2-Bn), 3.96 – 3.77 (m, 2H, H-2), 3.59 (s, 2H, H-6), 1.83 – 1.70 (m, 2H), 1.63 (s, 2H), 1.52 – 1.24 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.45, 165.41, 137.6, 133.4, 133.3, 129.9, 129.8, 129.5, 129.3, 128.6, 128.3, 127.68, 127.66, 97.0 (C-1), 76.9, 76.8, 73.5, 69.1, 69.0, 68.3, 58.3, 30.0, 28.6, 24.64, 24.55, 24.1, 23.6, 23.5, 23.1, 22.9, 21.3, 20.6. HRMS (ESI) calcd for $C_{39}H_{47}N_3O_7Na$ $[M+Na]^+$ 692.3312, found 692.3311.

(+)-Menthyl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21x)

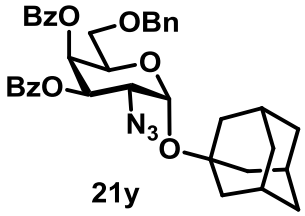


21x

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 44 h, using acceptor **20x** (28.0 mg, 0.18 mmol) with **17a** (181 mg, 0.27 mmol), DCM 1.8 mL, Ph_3P=O (448.0 mg, 1.61 mmol) and TMSI (38 μL, 0.27 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1-10:1) to afford **21x** (105.4 mg, 92%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = +192.2 (c 0.11, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.8 Hz, 2H, Ar), 7.59 (t, *J* = 7.5 Hz, 1H, Ar), 7.52 – 7.40 (m, 3H, Ar), 7.32 (t, *J* = 7.7 Hz, 2H, Ar), 7.26 – 7.14 (m, 5H, Ar), 5.92 (d, *J* = 3.3 Hz, 1H, H-4), 5.71 (dd, *J* = 11.2, 3.3 Hz, 1H, H-3), 5.21 (d, *J* = 3.6 Hz, 1H, H-1), 4.57 (t, *J* = 6.3 Hz, 1H, H-5), 4.52 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 4.40 (d, *J* = 12.0 Hz, 1H, CH_2-Bn), 3.97 (dd, *J* = 11.1, 3.6 Hz, 1H, H-2), 3.65 – 3.53 (m, 2H, H-6), 3.51 – 3.43 (m, 1H), 2.42 – 2.32 (m, 1H), 2.23 (d, *J* = 12.3 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.37 (t, *J* = 11.3 Hz, 2H), 1.14 (q, *J* = 11.8 Hz, 1H), 1.05 – 0.91 (m, 4H, CH_3), 0.87 (d, *J* = 6.5 Hz, 3H, CH_3), 0.81 (d, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.51, 165.45, 137.7, 133.4, 133.3, 129.89, 129.87, 129.7, 129.5, 128.6, 128.4, 127.7, 127.6, 99.7 (C-1),

81.8, 73.6, 69.6, 69.2, 68.6, 68.4, 59.3, 48.8, 42.8, 34.3, 31.9, 25.0, 22.9, 22.3, 21.4, 16.0. HRMS (ESI) calcd for $C_{37}H_{47}N_4O_7$ $[M+NH_4]^+$ 659.3439, found 659.3446.

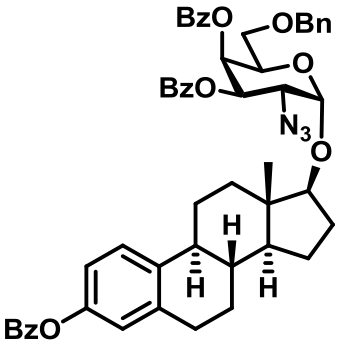
Tricyclo[3.3.1.1^{3,7}]dec-1-yl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21y)



21y

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 5.5 d, using acceptor **20y** (35.3 mg, 0.23 mmol) with **17a** (234.7 mg, 0.35 mmol), DCM 2.3 mL, $Ph_3P=O$ (580.8 mg, 2.09 mmol) and TMSI (50 μL, 0.35 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1) to afford **21y** (136.9 mg, 93%, α/β >20:1) as a white solid. $[\alpha]_D^{23}$ = +183.9 (c 0.33, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 – 7.39 (m, 3H, Ar), 7.31 (t, *J* = 7.7 Hz, 2H, Ar), 7.25 – 7.13 (m, 5H, Ar), 5.94 (d, *J* = 3.2 Hz, 1H, H-4), 5.83 (dd, *J* = 11.2, 3.2 Hz, 1H, H-3), 5.57 (d, *J* = 3.5 Hz, 1H, H-1), 4.63 (t, *J* = 6.5 Hz, 1H, H-5), 4.51 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 4.40 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 3.72 (dd, *J* = 11.2, 3.5 Hz, 1H, H-2), 3.59 (d, *J* = 6.5 Hz, 2H, H-6), 2.17 (t, *J* = 3.5 Hz, 3H), 1.93 (q, *J* = 11.6 Hz, 6H), 1.65 (d, *J* = 3.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.49, 165.45, 137.7, 133.4, 133.2, 129.9, 129.8, 129.6, 129.4, 128.6, 128.3, 127.61, 127.56, 91.9 (C-1), 76.1, 73.5, 69.2, 68.9, 68.4, 67.8, 58.1, 42.4, 36.2, 30.7. HRMS (ESI) calcd for $C_{37}H_{43}N_4O_7$ $[M+NH_4]^+$ 655.3126, found 655.3128.

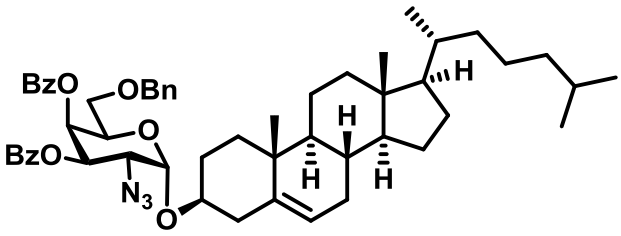
17-*O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl) estradiol benzoate (21z)



21z

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 8 d, using acceptor **20z** (53.1 mg, 0.14 mmol) with **17a** (142.7 mg, 0.21 mmol), DCM 1.4 mL, Ph_3P=O (352.2 mg, 1.27 mmol) and TMSI (30 μL, 0.21 mmol). The product was purified by silica gel column chromatography (PE-EA, 7:1) to afford **21z** (121.1 mg, 99%, α/β >20:1) as a white solid. $[\alpha]_D^{25}$ = +161.8 (c 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.7 Hz, 2H, Ar), 8.00 (d, *J* = 7.8 Hz, 2H, Ar), 7.89 (d, *J* = 7.8 Hz, 2H, Ar), 7.60 (q, *J* = 6.9 Hz, 2H, Ar), 7.53 – 7.41 (m, 5H, Ar), 7.33 (q, *J* = 7.8 Hz, 3H, Ar), 7.28 – 7.14 (m, 5H, Ar), 7.00 (dd, *J* = 8.5, 2.4 Hz, 1H, Ar), 6.94 (d, *J* = 2.5 Hz, 1H, Ar), 5.97 (d, *J* = 3.2 Hz, 1H, H-4), 5.79 (dd, *J* = 11.1, 3.1 Hz, 1H, H-3), 5.21 (d, *J* = 3.4 Hz, 1H, H-1), 4.59 – 4.50 (m, 2H, CH_2-Bn, H-5), 4.44 (d, *J* = 11.8 Hz, 1H, CH_2-Bn),), 3.89 – 3.75 (m, 2H, H-2), 3.63 (q, *J* = 9.8, 8.3 Hz, 2H, H-6), 2.94 – 2.83 (m, 2H), 2.35 – 2.07 (m, 4H), 1.95 – 1.85 (m, 1H), 1.80 – 1.66 (m, 2H), 1.63 – 1.43 (m, 3H), 1.43 – 1.32 (m, 2H), 1.25 – 1.17 (m, 1H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.49, 165.45, 148.8, 138.3, 138.0, 137.7, 133.53, 133.47, 133.3, 130.2, 129.9, 129.84, 129.77, 129.5, 129.3, 128.61, 128.58, 128.5, 128.4, 127.9, 127.8, 127.7, 127.6, 126.6, 121.7, 118.8, 97.3 (C-1), 86.6, 73.5, 69.2, 68.7, 68.5, 68.4, 58.3, 50.1, 44.2, 43.0, 38.2, 37.3, 29.6, 27.1, 26.9, 26.1, 23.2, 12.2. HRMS (ESI) calcd for $C_{52}H_{55}N_4O_9$ $[M+NH_4]^+$ 879.3964, found 879.3972.

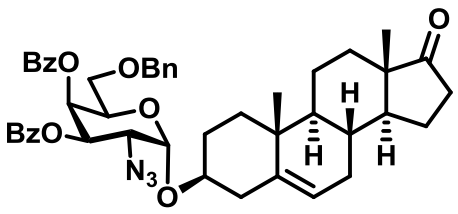
(3β)-Cholest-5-en-3-yl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galacto-pyranoside (21aa)



21aa

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 47 h, using acceptor **20aa** (64.6 mg, 0.17 mmol) with **17a** (169.1mg, 0.25 mmol), DCM 1.7 mL, Ph_3P=O (418.5 mg, 1.50 mmol) and TMSI (36 μL, 0.25 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1) to afford **21aa** (136.7 mg, 94%, α/β >20:1) as a yellow solid. $[\alpha]_D^{21}$ = +143.3 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.8 Hz, 2H, Ar), 7.60 (t, *J* = 7.5 Hz, 1H, Ar), 7.53 – 7.41 (m, 3H, Ar), 7.32 (t, *J* = 7.7 Hz, 2H, Ar), 7.26 – 7.15 (m, 5H, Ar), 5.92 (d, *J* = 3.2 Hz, 1H, H-4), 5.78 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.34 – 5.28 (m, 2H, H-1), 4.56 – 4.48 (m, 2H, H-5, CH_2-Bn), 4.41 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 3.79 (dd, *J* = 11.1, 3.5 Hz, 1H, H-2), 3.66 – 3.54 (m, 3H, H-6), 2.46 (d, *J* = 8.1 Hz, 2H), 2.06 – 1.93 (m, 3H), 1.92 – 1.79 (m, 2H), 1.70 – 1.44 (m, 8H), 1.42 – 1.28 (m, 4H), 1.21 – 1.08 (m, 5H), 1.08 – 0.98 (m, 6H), 0.92 (d, *J* = 6.4 Hz, 4H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 140.5, 137.7, 133.5, 133.3, 130.0, 129.9, 129.7, 129.5, 128.7, 128.43, 128.40, 127.8, 127.7, 122.4, 97.4 (C-1), 79.5, 73.6, 69.3, 69.1, 68.52, 68.47, 58.3, 57.0, 56.4, 50.4, 42.5, 40.2, 40.0, 39.7, 37.2, 36.9, 36.4, 35.9, 32.13, 32.07, 28.4, 28.2, 24.5, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. HRMS (ESI) calcd for $C_{54}H_{73}N_4O_7$ $[M+NH_4]^+$ 889.5474, found 889.5470.

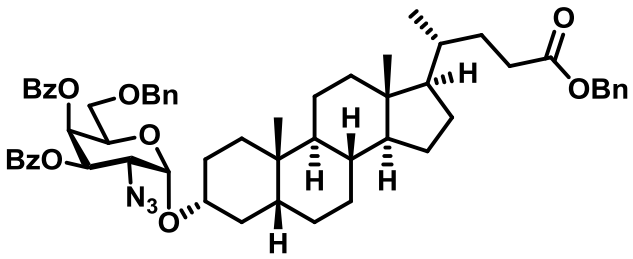
3β-*O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl) dehydroepiandrosterone (21ab)



21ab

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 3 d, using acceptor **20ab** (44.3 mg, 0.15 mmol) with **17a** (155.4mg, 0.23 mmol), DCM 1.5 mL, $Ph_3P=O$ (384.7 mg, 1.38 mmol) and TMSI (33 μL, 0.23 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **21ab** (111.7 mg, 94%, α/β >20:1) as a white solid. $[\alpha]_D^{22}$ = +186.7 (c 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 (t, *J* = 7.4 Hz, 1H, Ar), 7.53 – 7.42 (m, 3H, Ar), 7.32 (t, *J* = 7.7 Hz, 2H, Ar), 7.28 – 7.15 (m, 5H, Ar), 5.92 (d, *J* = 3.3 Hz, 1H, H-4), 5.78 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3), 5.32 (m, 2H, H-1), 4.57 – 4.48 (m, 2H, H-5, CH_2-Bn), 4.42 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 3.80 (dd, *J* = 11.1, 3.5 Hz, 1H, H-2), 3.67 – 3.55 (m, 3H, H-6), 2.54 – 2.41 (m, 3H), 2.16 – 1.99 (m, 3H), 1.98 – 1.82 (m, 3H), 1.73 – 1.61 (m, 4H), 1.58 – 1.44 (m, 2H), 1.35 – 1.28 (m, 2H), 1.14 – 0.97 (m, 5H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 165.51, 165.48, 140.7, 137.7, 133.5, 133.3, 129.93, 129.89, 129.6, 129.4, 128.7, 128.5, 128.4, 127.75, 127.72, 121.6, 97.3 (C-1), 79.1, 73.6, 69.2, 69.1, 68.55, 68.52, 58.2, 51.9, 50.4, 47.7, 40.1, 37.1, 37.0, 36.0, 31.64, 31.60, 31.0, 28.1, 22.0, 20.5, 19.5, 13.7. HRMS (ESI) calcd for $C_{46}H_{55}N_4O_8$ $[M+NH_4]^+$ 791.4014, found 791.4013.

5-β-cholan-24-oic acid benzyl ester-3-α-yl 2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21ac)

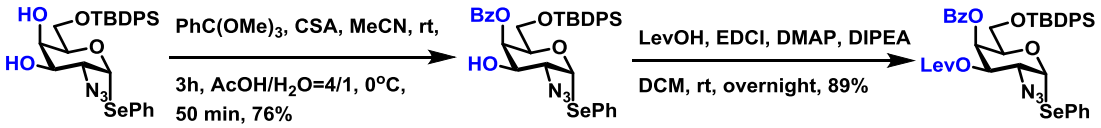


21ac

The glycosylation reaction was carried out according to **General Experimental Procedures** at 25 ℃ for 4 d, using acceptor **20ac** (69 mg, 0.15 mmol) with **17a** (149.6mg, 0.22 mmol), DCM 1.5 mL, Ph_3P=O (370.2 mg, 1.33 mmol) and TMSI (32 μL, 0.22 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1) to afford **21ac** (121.4 mg, 86%, α/β >20:1) as a white solid. $[\alpha]_D^{21}$ = +141.4 (c 0.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.88 (d, *J* = 7.7 Hz, 2H, Ar), 7.58 (t, *J* = 7.5 Hz, 1H, Ar), 7.51 – 7.40 (m, 3H, Ar), 7.37 – 7.28 (m, 7H, Ar), 7.23 – 7.13 (m, 5H, Ar), 5.93 (d, *J* = 3.3 Hz, 1H, H-4), 5.79 (dd, *J* = 11.0, 3.3 Hz, 1H, H-3), 5.30 (d, *J* = 3.5 Hz, 1H, H-1), 5.11 (d, *J* = 2.9 Hz, 2H, CH_2-Bn), 4.57 – 4.46 (m, 2H, CH_2-Bn, H-5), 4.40 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 3.84 (dd, *J* = 11.1, 3.5 Hz, 1H, H-2), 3.74 – 3.65 (m, 1H), 3.59 (q, *J* = 9.6, 7.9 Hz, 2H, H-6), 2.45 – 2.35 (m, 1H), 2.33 – 2.21 (m, 1H), 1.98 – 1.90 (m, 2H), 1.89 – 1.76 (m, 4H), 1.66 (d, *J* = 12.5 Hz, 1H), 1.61 – 1.49 (m, 2H), 1.48 – 1.32 (m, 8H), 1.30 – 1.18 (m, 4H), 1.11 (q, *J* = 10.4, 9.6 Hz, 3H), 1.04 – 0.96 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 6H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 165.41, 165.39, 137.6, 136.2, 133.4, 133.2, 129.84, 129.81, 129.5, 129.3, 128.6, 128.3, 128.25, 128.18, 127.6, 127.5, 97.2 (C-1), 79.5, 73.5, 69.2, 69.1, 68.4, 68.3, 66.1, 58.3, 56.3, 55.9, 42.8, 42.2, 40.4, 40.1, 35.9, 35.4, 35.3, 34.7, 32.7, 31.3, 31.0, 28.5, 28.2, 27.3, 26.4, 24.2, 23.5, 20.9, 18.3, 12.1. HRMS (ESI) calcd for $C_{58}H_{73}N_4O_9$ $[M+NH_4]^+$ 969.5372, found 969.5373.

Preparation of the common intermediate 16

Phenyl 2-azido-4-*O*-benzoyl-6-*O*-tert-butyldiphenylsilyl-2-deoxy-3-*O*-levulinoyl-1-seleno-α-D-galactopyranoside (S31)

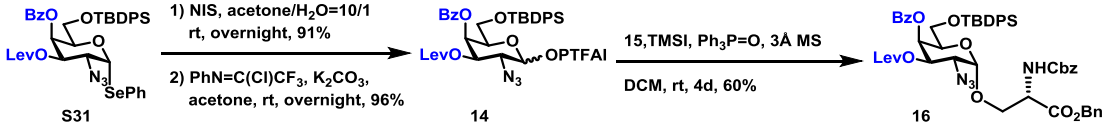


S11 S30 S31

Compound **S11** (6.80 g, 11.67 mmol) was stirred with trimethyl orthobenzoate (17.3 mL, 93.38 mmol) in acetonitrile (58 mL) at room temperature for some time. Then 10-camphorsulfonic acid (CSA) (813.5 mg, 3.50 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure, and the temperature was brought down to 0 ℃, 80% aq acetic acid (58 mL) was then added, and the reaction was stirred at 0 ˚C for 50 min. The reaction mixture was quenched carefully with saturated $NaHCO_3$. The product was extracted with dichloromethane (250 mL × 3), and the combined organic layer was washed with distilled water (300 mL). The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 8:1) to afford the intermediate **S30** (6.07 g, 76%). To a solution of the above intermediate (6.07 g, 8.84 mmol) and levulinic acid (1.54 g, 13.26 mmol) in anhydrous DCM (88 mL) was added DMAP (1.08 g, 8.84 mmol), EDCI (3.05 g, 15.91 mmol) and DIPEA (4.4 mL, 26.52 mmol). The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 5:1) to afford **S31** (6.18 g, 89%) as a white solid. $[\alpha]_D^{23}$ = + 273.2 (c 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H, Ar), 7.65 – 7.57 (m, 3H, Ar), 7.54 – 7.50 (m, 2H, Ar), 7.50 – 7.34 (m, 7H, Ar), 7.24 (dd, *J* = 8.5, 6.5 Hz, 2H, Ar), 7.16 (dd, *J* = 8.2, 6.7 Hz, 2H, Ar), 7.06 (t, *J* = 7.5 Hz, 2H, Ar), 5.98 (d, *J* = 5.4 Hz, 1H, H-1), 5.95 – 5.92 (m, 1H, H-4), 5.29 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.66 – 4.58 (m, 1H, H-5), 4.31 (dd, *J* = 10.7, 5.4 Hz, 1H, H-2), 3.65 (dd, *J* = 9.9, 8.5 Hz, 1H, H-6), 3.48 (dd, *J* = 9.9, 5.8 Hz, 1H, H-6), 2.92 – 2.82 (m, 1H, CH_2-Lev), 2.77 – 2.59 (m, 2H, CH_2-Lev), 2.56 – 2.47 (m, 1H, CH_2-Lev), 2.16 (s, 3H, CH_3-Lev), 0.97 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 171.7, 165.5, 135.6, 135.4,

135.2, 133.6, 132.8, 132.4, 129.93, 129.90, 129.7, 129.5, 129.2, 128.7, 128.2, 127.9, 127.7, 84.4 (C-1), 72.0, 71.3, 67.5, 60.8, 59.4, 38.0, 29.9, 28.0, 26.7, 19.1. HRMS (ESI) calcd for $C_{40}H_{43}N_3O_7SiSeNa$ $[M+Na]^+$ 802.1987, found 802.1986.

L-Serine *N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-6-*O*-tert-butyl-diphenylsilyl-2-deoxy-3-*O*-levulinoyl-α-D-galactopyranosyl)-benzyl ester (16)

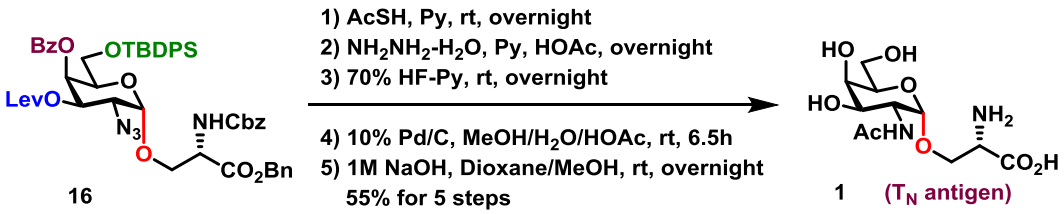


Compound **S31** (5.28 g, 6.72 mmol) was dissolved in acetone/H_2O (60 mL/6 mL), and NIS (2.27g, 10.08 mmol) was added. The resulting mixture was stirred overnight. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to give the intermediate (3.93 g, 91%). The above intermediate (2.25 mg, 3.48 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (794.8 mg, 3.83 mmol) was dissolved in acetone (34 mL), and K_2CO_3 (721.4 mg, 5.22 mmol) was added. The reaction was stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 10:1 to 4:1, containing 1% Et_3N) to give **14** (2.73 g, 96%) (Compound **14** was used directly without further structural characterization). PTFAI donor **14** (2.51 g, 3.07 mmol) was co-evaporated with anhydrous toluene for three times. Then PTFAI donor with Ph_3P=O (5.13 g, 18.44 mmol) were dissolved in new distilled DCM (30 mL) and stirred over fresh-dried 3Å molecular sieves under argon at room temperature for 15 min. TMSI (0.44 mL, 0.35 mmol)) was added dropwise subsequently. After the mixture was stirred for 1 h, acceptor *N*-Benzyloxycarbonyl -L-serine Benzyl Ester **15** (3.52 g, 4.61 mmol) was added. The reaction was stirred at room temperature for 5 d. Upon completion, the solution was diluted with EtOAc and the reaction was quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in*

vacuo. The products were purified by flash column chromatography (PE-EA=4:1) to afford **16** (1.77 g, 60%, α/β >20:1) as a yellow solid. $[\alpha]_D^{25}$ = +102.7 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H, Ar), 7.62 (d, *J* = 6.9 Hz, 3H, Ar), 7.50 – 7.41 (m, 4H, Ar), 7.39 – 7.21 (m, 14H, Ar), 7.07 (t, *J* = 7.4 Hz, 2H, Ar), 5.81 (d, *J* = 3.1 Hz, 1H, H-4), 5.78 (d, *J* = 8.9 Hz, 1H, NH-Ser), 5.38 (dd, *J* = 11.2, 3.2 Hz, 1H, H-3), 5.24 (q, *J* = 12.2 Hz, 2H), 5.07 (s, 2H), 4.87 (d, *J* = 3.6 Hz, 1H, H-1), 4.62 – 4.56 (m, 1H, CH-Ser), 4.15 – 4.06 (m, 2H, H-5, CH_2-Ser), 3.94 (dd, *J* = 11.0, 3.1 Hz, 1H, CH_2-Ser), 3.73 – 3.55 (m, 3H, H-2, H-6), 2.88 – 2.78 (m, 1H, CH_2-Lev), 2.75 – 2.55 (m, 2H, CH_2-Lev), 2.53 – 2.43 (m, 1H, CH_2-Lev), 2.14 (s, 3H, CH_3-Lev), 0.96 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 171.8, 169.7, 165.5, 156.2, 136.2, 135.6, 135.5, 135.2, 133.5, 132.8, 132.6, 129.9, 129.8, 129.6, 128.8, 128.71, 128.69, 128.6, 128.3, 127.9, 127.7, 99.5 (C-1), 69.8, 68.7, 67.89, 67.86, 67.3, 61.3, 58.0, 54.6, 38.0, 29.8, 28.0, 26.7, 19.1. HRMS (ESI) calcd for $C_{52}H_{56}N_4O_{12}SiNa$ $[M+Na]^+$ 979.3562, found 979.3563.

Synthesis of T_N antigen 1 from 16

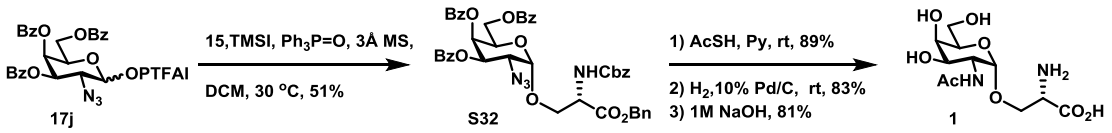
***O*-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl]-L-serine (1)**



To a solution of compound **16** (228.8 mg, 0.24 mmol) in pyridine (4.8 mL) was added Thioacetic acid (AcSH) (3.6 mL, 48 mmol). The reaction mixture was stirred overnight. Then the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography (petroleum ether-EtOAc, 2:1) afforded intermediate (213.4 mg, 92%). The above intermediate (213.4 mg, 0.22 mmol) was dissolved in Py/HOAc (1.2 mL/0.8 mL), subsequently 80% $NH_2NH_2{\cdot}H_2O$ (0.031 mL, 0.65 mmol) was added. After stirring overnight at room temperature, the reaction mixture was diluted with ethyl acetate, washed with 3M HCl, saturated $NaHCO_3$ solution and brine. The

organic layer was filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether-ethyl acetate, 1:1.3) to give the intermediate (171.3 mg, 89%). To a solution of above intermediate (171 mg, 0.20 mmol) in anhydrous THF (2 mL) was added HF/pyridine (70%, 18 mL, 1.95 mmol) dropwise. After stirring overnight at room temperature, the reaction mixture was quenched with Et_3N (1mL), diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 30:1) to afford the intermediate (114.5 mg, 92%). A mixture of the above intermediate (78 mg, 0.12 mmol) and Pd/C (260.8 mg, 10%) in MeOH/H_2O/HOAc (6 mL/0.6 mL/0.06 mL) was stirred under an atmosphere of H_2 at room temperature for 6.5 h, after which the reaction mixture was filtered and concentrated *in vacuo* to afford the crude product (50.5 mg, 100%). The mixture solution of above crude product (50.5 mg, 12 mmol) in 1M NaOH/Dioxane/MeOH (1.2 mL/0.9 mL/0.9 mL) was stirred overnight at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **1** (27.6 mg, 73%) as a white solid. $[\alpha]_D^{22}$ = +178.5 (c 0.16, H_2O). 1H NMR (600 MHz, D_2O) δ 4.92 (d, *J* = 3.8 Hz, 1H, H-1), 4.20 (dd, *J* = 11.1, 3.8 Hz, 1H, H-2), 4.11 (dd, *J* = 11.0, 2.9 Hz, 1H), 4.01 – 3.87 (m, 5H, H-3), 3.82 – 3.72 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, D_2O) δ 174.3, 171.3, 97.6 (C-1), 71.0, 68.1, 67.1, 66.3, 60.9, 54.2, 49.3, 21.7. HRMS (ESI) calcd for $C_{11}H_{19}N_2O_8$ $[M-H]^-$ 307.1147, found 307.1149.

Synthesis of T_N antigen 1 from S32

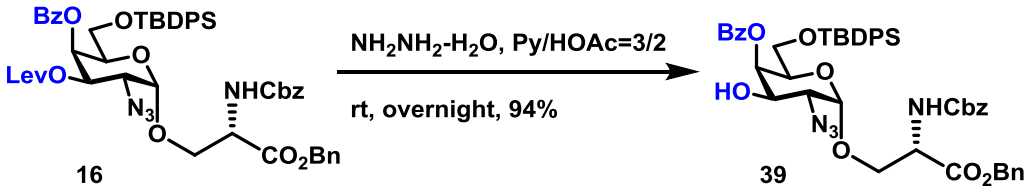


The glycosylation reaction was carried out according to **General Experimental Procedures** at 30℃ for 5.5 d, using acceptor **15** (412.3 mg, 1.25 mmol) with **17j** (574.9 mg, 0.83 mmol), DCM 8.3 mL, Ph_3P=O (1.39 g, 5.01 mmol) and TMSI (0.12

mL, 0.83 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **S32** (353.5 mg, 51%, α/β >20:1) as a yellow solid. To a solution of compound **S32** (322.6 mg, 0.39 mmol) in pyridine (7.6 mL) was added AcSH (5.8 mL, 77.84 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated in vacuo. The residue was purified by flash chromatography (PE/EA, 1.2:1-1:1) to afford intermediate (293.1 mg, 89%). A mixture of the above intermediate (140 mg, 0.17 mmol) and Pd/C (352.7 mg, 10%) in MeOH/H_2O/HOAc (6 mL/0.6 mL/0.06 mL) was stirred under an atmosphere of H_2 at room temperature for 6 h, after which the reaction mixture was filtered and concentrated *in vacuo* to afford the residue (84.4 mg, 83%).. To a solution of above residue (55 mg, 0.07 mmol) in dioxane/MeOH (1.5 mL/1.5 mL) was added 1.5 mL 1M NaOH aq. The reaction was stirred overnight at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **1** (34.1 mg, 81%) as a white solid.

Preparation of donors 32-34 and acceptors 39 and S33

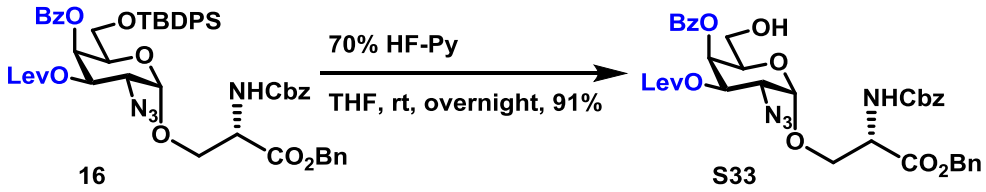
L-Serine *N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-6-*O*-tert-butyl-diphenylsilyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (39)



Compound **16** (200 mg, 0.21 mmol) was dissolved in anhydrous pyridine/AcOH (1.2 mL/0.8 mL), then NH_2NH_2**.**H_2O (0.03 mL, 0.63 mmol) was added at room temperature. The reaction was stirred until TLC-analysis indicated full consumption of the starting material. Then the reaction was quenched with acetone and the mixture was concentrated under vacuum. The products were purified by flash column chromatography (PE:EA=5:1) to afford **39** (168.8 mg, 94%) as a white solid. $[\alpha]_D^{24}$ = +63.0 (c 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) 7.90 (d, *J* = 7.7 Hz, 2H, Ar), 7.55

(d, *J* = 7.0 Hz, 2H, Ar), 7.50 (t, *J* = 7.5 Hz, 1H, Ar), 7.36 (t, *J* = 8.0 Hz, 4H, Ar), 7.27 (m, 9H, Ar), 7.17 (m, 5H, Ar), 6.99 (t, *J* = 7.4 Hz, 2H, Ar), 5.73 (d, *J* = 8.6 Hz, 1H, NH-Ser), 5.61 – 5.56 (m, 1H, H-4), 5.19 (d, *J* = 12.1 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.95 (t, *J* = 10.0 Hz, 2H), 4.73 (d, *J* = 3.6 Hz, 1H, H-1), 4.55 – 4.47 (m, 1H, CH-Ser), 4.09 – 3.92 (m, 3H, H-3, H-5, CH_2-Ser), 3.87 – 3.77 (m, 1H, CH_2-Ser), 3.68 – 3.51 (m, 2H, H-6), 3.36 (dd, *J* = 10.7, 3.4 Hz, 1H, H-2), 2.70 (s, 1H), 0.89 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 167.0, 156.1, 136.1, 135.6, 135.4, 135.2, 133.5, 132.8, 132.6, 130.0, 129.9, 129.8, 129.5, 128.78, 128.76, 128.64, 128.59, 128.3, 127.9, 127.7, 99.6 (C-1), 70.7, 69.9, 67.8, 67.5, 67.3, 61.3, 60.4, 54.6, 26.7, 19.1. HRMS (ESI) calcd for $C_{47}H_{50}N_4O_{10}SiNa$ $[M+Na]^+$ 881.3194, found 881.3194.

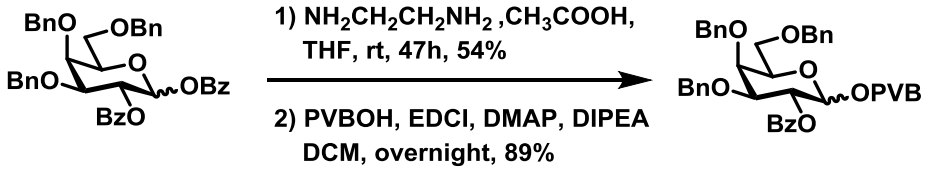
L-Serine *N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-3-*O*-levulinoyl-α-D-galactopyranosyl)-benzyl ester (S33)



Compound **16** (430 mg, 0.45 mmol) was then dissolved in anhydrous THF (1.5 mL), and HF/pyridine (70%, 0.4 mL, 4.49 mmol) was added dropwise. The resulting mixture was stirred overnight at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 2:1) to afford **S33** (293.9 mg, 91%,) as a white solid. $[\alpha]_D^{24}$ = + 191.0 (c 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H, Ar), 7.62 (t, *J* = 7.5 Hz, 1H, Ar), 7.47 (t, *J* = 7.6 Hz, 2H, Ar), 7.42 – 7.29 (m, 10H, Ar), 6.10 (d, *J* = 8.2 Hz, 1H, NH-Ser), 5.55 (s, 1H, H-4), 5.32 (d, *J* = 11.2 Hz, 1H, H-3), 5.22 (t, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 4.98 (s, 1H, H-1), 4.63 (d, *J* = 8.1 Hz, 1H, CH-Ser), 4.22 (d, *J* = 11.0 Hz, 1H, CH_2-Ser), 4.10 – 3.92 (m, 2H, H-5, CH_2-Ser), 3.73 – 3.56 (m, 2H, H-2, H-6), 3.45 (d, *J* = 10.4 Hz, 1H, H-6), 2.80 – 2.63 (m, 2H, CH_2-Lev), 2.60 – 2.51 (m, 1H, CH_2-Lev), 2.50 – 2.39 (m,

1H, CH_2-Lev), 2.10 (s, 3H, CH_3-Lev). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 171.7, 169.8, 166.1, 156.1, 136.3, 135.1, 133.9, 129.9, 129.0, 128.80, 128.76, 128.7, 128.3, 128.2, 99.7 (C-1), 70.3, 70.2, 68.7, 68.5, 68.0, 67.3, 61.1, 58.0, 54.8, 37.9, 29.7, 27.9. HRMS (ESI) calcd for $C_{36}H_{38}N_4O_{12}Na$ $[M+Na]^+$ 741.2384, found 741.2383.

3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-D-galatopyranosyl-2-(1-phenylvinyl)benzoate (32)

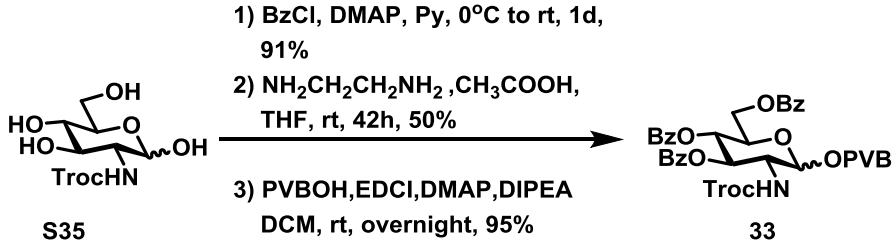


S34 32

Anhydrous ethylenediamine (0.96 mL, 14.34 mmol) and acetic acid (0.41 mL, 7.17 mmol)are dissolved in anhydrous tetrahydrofuran (35 mL), then **S34**[14] (4.72 g, 7.17 mmol)dissolved in tetrahydrofuran (35 mL) is added, and stirred at room temperature for 47 h. After the reaction is completed, the reaction mixture was diluted with ethyl acetate and washed with 1M HCl , saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 5:1 to 3:1) to give the intermediate (2.12 g, 54%,) as a white solid. The above intermediate (2.12 g, 3.83 mmol) and PVBOH [2-(1-phenylvinyl) benzoic acid][15] (1.03 mg, 4.59 mmol) was dissolved in anhydrous DCM (38 mL), and DMAP (467.7 mg, 3.83 mmol), EDCI (1.32 g, 6.89 mmol), DIPEA (1.9 mL, 11.48 mmol) was added, respectively. The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated in vacuum. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 8:1) to afford **32** (2.60 g, 89%). β-isomer: $[\alpha]_D^{25}$ = +29.9 (c 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 3H, Ar), 7.55 (t, *J* = 7.5 Hz, 1H, Ar), 7.48 – 7.25 (m, 15H, Ar), 7.24 – 7.16 (m, 2H, Ar), 7.15 – 7.04 (m, 8H, Ar), 5.82 (t, *J* = 9.1 Hz, 1H, H-2), 5.70 (d, *J* = 8.3 Hz, 1H, H-1), 5.53 (s, 1H, CH_2=C-PVB), 4.98 (m, 2H, CH_2=C-PVB, CH_2-Bn), 4.63 (dd, *J* = 11.9, 5.2 Hz, 2H,

CH_2-Bn), 4.46 (d, *J* = 12.5 Hz, 1H, CH_2-Bn), 4.41 (s, 2H, CH_2-Bn), 4.07 – 4.01 (m, 1H, H-4), 3.73 – 3.59 (m, 3H, H-3), 3.51 (dd, *J* = 8.9, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 164.7, 149.2, 143.9, 140.4, 138.4, 137.8, 137.5, 133.2, 132.4, 131.4, 130.9, 130.0, 129.8, 128.9, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.82, 127.80, 127.75, 127.4, 126.5, 114.0, 93.0 (C-1), 79.9, 74.8, 74.5, 73.7, 72.4, 71.9, 70.7, 67.8. HRMS (ESI) calcd for $C_{49}H_{44}O_8Na$ $[M+Na]^+$ 783.2934, found 783.2932.

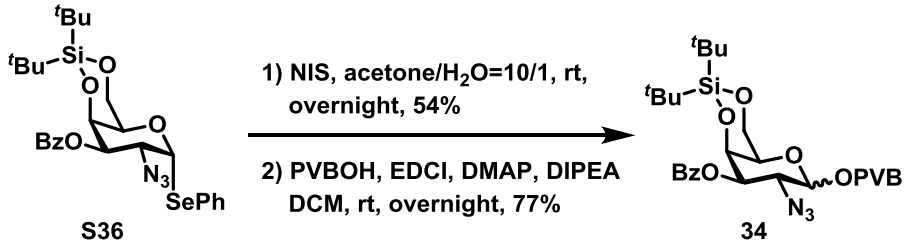
3,4,6-tri-*O*-benzoyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-D-glucopyrano-syl-2-(1-phenylvinyl)benzoate (33)



Compound **S35**[16] (2.57 g, 7.24 mmol) was dissolved in anhydrous pyridine (14 mL). The solution was cooled to 0 ℃, DMAP (883.9 mg, 7.24 mmol) was added, and then BzCl (5 mL, 43.41 mmol) was added slowly. The resulting mixture was allowed to warm to room temperature and stirred 1d. Upon completion, the reaction mixture was diluted in EA, washed with 3M HCl, saturated $NaHCO_3$ solution and brine. The combined organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 10:1 to 6:1) to give the intermediate (5.08 g, 91%). Anhydrous ethylenediamine (0.88 mL, 13.18 mmol) and acetic acid (0.38 mL, 6.59 mmol)are dissolved in anhydrous tetrahydrofuran (32 mL), then above intermediate (5.08 g, 6.59 mmol) dissolved in tetrahydrofuran (32 mL) was added, and stirred at room temperature for 42 h. After the reaction is completed, the reaction mixture was diluted with ethyl acetate and washed with 1M HCl, saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 5:1 to 3:1) to give the intermediate (2.21 g, 50%,) as a white solid. The above intermediate (2.21 g, 3.32 mmol) and PVBOH (893.4 mg, 3.98 mmol) was dissolved in anhydrous DCM (33

mL), and DMAP (405.6 mg, 3.32 mmol), EDCI (1.15 g, 5.98 mmol), DIPEA (1.6 mL, 9.96 mmol) was added, respectively. The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated in vacuum. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 6:1) to afford **33** (2.76 g, 95%). α-isomer: $[\alpha]_D^{25}$ = + 72.2 (c 0.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H, Ar), 7.98 (d, *J* = 7.8 Hz, 2H, Ar), 7.90 (d, *J* = 7.7 Hz, 2H, Ar), 7.85 (d, *J* = 7.8 Hz, 2H, Ar), 7.60 (t, *J* = 7.6 Hz, 1H, Ar), 7.55 – 7.45 (m, 6H, Ar), 7.43 – 7.31 (m, 9H, Ar), 7.30 – 7.23 (m, 1H, Ar), 6.47 (d, *J* = 3.8 Hz, 1H, H-1), 6.20 (s, 1H, CH_2=C-PVB), 5.60 (t, *J* = 9.9 Hz, 1H, H-4), 5.40 (t, *J* = 10.4 Hz, 1H, H-3), 5.36 (s, 1H, CH_2=C-PVB), 4.92 (d, *J* = 9.7 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.49 – 4.41 (m, 2H, H-2), 4.35 (dd, *J* = 12.5, 2.8 Hz, 1H, H-6), 4.20 (dd, *J* = 12.4, 4.3 Hz, 1H, H-6), 3.83 – 3.75 (m, 1H, H-5). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 166.3, 166.1, 165.1, 154.2, 149.4, 142.6, 138.9, 133.63, 133.60, 133.2, 133.0, 131.4, 131.3, 130.0, 129.94, 129.86, 129.7, 129.6, 129.0, 128.9, 128.8, 128.66, 128.53, 128.49, 128.1, 126.8, 113.6, 95.2, 91.7 (C-1), 74.6, 71.5, 70.4, 68.6, 62.3, 53.7. HRMS (ESI) calcd for $C_{45}H_{36}NO_{11}Cl_3Na$ $[M+Na]^+$ 894.1252, found 894.1248.

2-azido-3-O-benzoyl-2-deoxy-4,6-O-(di-tert-butylsilylene)-D-galactopyranosyl-2-(1-phenylvinyl)benzoate (34)

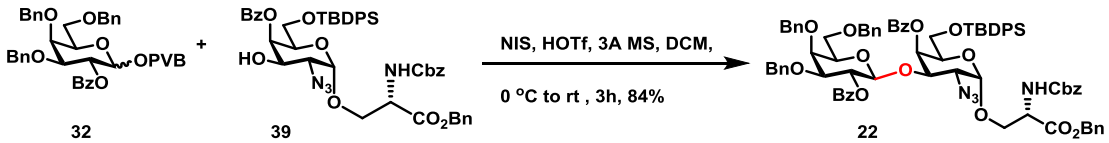


Compound **S36**[17] (505.5 mg, 0.86 mmol) was dissolved in acetone/H_2O (7.5 mL/0.8 mL), then NIS (N-Iodosuccinimide) (289.8 mg, 1.29 mmol) was added. The resulting mixture was stirred for overnight. The solution was diluted with EtOAc, washed with saturated $Na_2S_2O_3$, water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to give the intermediate (209.7 mg,

54%). The above intermediate (205 mg, 0.46 mmol) and PVBOH (122.7 mg, 0.55 mmol) was dissolved in anhydrous DCM (4.6 mL), and DMAP (55.7 mg, 0.46 mmol), EDCI (157.3 mg, 0.82 mmol), DIPEA (0.23 mL, 1.37 mmol) was added, respectively. The resulting mixture was stirred overnight at room temperature. Upon completion, the solvent was evaporated in vacuum. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 4:1) to afford **34** (230.7 mg, 77%) as a white solid. α-isomer: $[\alpha]_D^{23}$ = + 227.7 (c 0.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H, Ar), 7.94 – 7.90 (m, 1H, Ar), 7.52 – 7.42 (m, 2H, Ar), 7.40 – 7.33 (m, 3H, Ar), 7.29 – 7.24 (m, 2H, Ar), 7.24 – 7.16 (m, 3H, Ar), 7.17 – 7.11 (m, 1H, Ar), 6.33 (d, *J* = 3.6 Hz, 1H, H-1), 5.84 (s, 1H, CH_2=C-PVB), 5.17 (s, 1H, CH_2=C-PVB), 5.09 (dd, *J* = 10.8, 3.0 Hz, 1H, H-3), 4.47 (d, *J* = 3.3 Hz, 1H, H-4), 4.14 (dd, *J* = 10.7, 3.6 Hz, 1H, H-2), 3.73 (d, *J* = 2.1 Hz, 2H, H-6), 2.89 (s, 1H, H-5), 0.93 (s, 9H, CH_3-*t*-Bu), 0.81 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 165.8, 148.3, 142.8, 139.7, 133.5, 132.5, 131.5, 130.9, 130.1, 129.8, 129.7, 128.6, 128.5, 127.95, 127.87, 126.6, 114.4, 91.9 (C-1), 72.5, 69.9, 69.2, 66.6, 57.2, 27.5, 27.3, 23.3, 20.8. HRMS (ESI) calcd for $C_{36}H_{41}N_3O_7SiNa$ $[M+Na]^+$ 678.2606, found 678.2606.

Synthesis of core 1 mucin-type *O*-glycan (2)

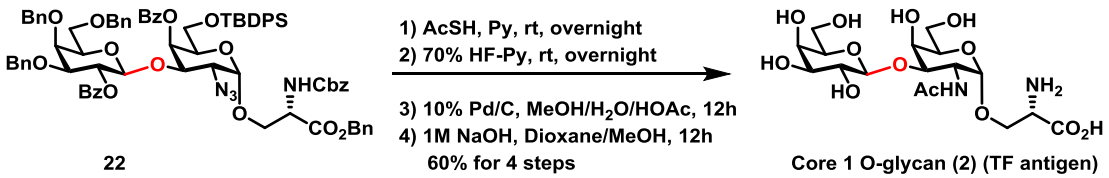
L-Serine *O*-(3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-galatopyranosyl)-(1→3)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-6-*O*-tert-butyl-diphenylsilyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (22)



A suspension of donor **32** (94.7 mg, 0.12 mmol), acceptor **39** (71.3 mg, 0.083mmol), and activated 3Å MS (170 mg) in anhydrous DCM (2.5 mL) was stirred at room temperature for 15 min and was then cooled to 0 °C. NIS (56.0 mg, 0.25 mmol) and HOTf (Trifluoromethanesulfonic acid) (6 μL, 0.062 mmol) were added successively. The resulting mixture was stirred at room temperature for 3 h, then

quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 6:1 to 5:1) to afford **22** (101.9 mg, 84%) as a white solid. $[\alpha]_D^{24}$ = +76.0 (c 0.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H, Ar), 7.86 (d, *J* = 7.6 Hz, 2H, Ar), 7.60 (d, *J* = 7.0 Hz, 2H, Ar), 7.56 (d, *J* = 7.2 Hz, 2H, Ar), 7.53 – 7.47 (m, 2H, Ar), 7.40 – 7.26 (m, 23H, Ar), 7.25 – 7.20 (m, 8H, Ar), 7.18 – 7.14 (m, 1H, Ar), 7.13 – 7.08 (m, 3H, Ar), 5.70 (d, *J* = 3.4 Hz, 1H, H-4$_{GalN}$), 5.66 (d, *J* = 9.7 Hz, 1H), 5.50 (dd, *J* = 10.1, 7.7 Hz, 1H, H-2$_{Gal}$), 5.16 – 5.03 (m, 4H, CH_2-Bn, CH_2-Cbz), 4.89 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.77 (d, *J* = 3.7 Hz, 1H, H-1$_{GalN}$), 4.73 (d, *J* = 7.8 Hz, 1H, H-1$_{Gal}$), 4.62 – 4.51 (m, 3H, CH_2-Bn), 4.48 – 4.36 (m, 3H, CH_2-Bn), 4.05 (dd, *J* = 10.7, 3.3 Hz, 1H, H-3$_{GalN}$), 3.99 – 3.91 (m, 4H), 3.70 (dd, *J* = 11.0, 5.2 Hz, 1H), 3.65 (s, 3H), 3.62 – 3.55 (m, 2H, H-3$_{Gal}$), 3.51 (dd, *J* = 10.6, 3.6 Hz, 1H, H-2$_{GalN}$), 0.99 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 165.3, 165.2, 156.1, 138.8, 138.1, 137.7, 136.2, 135.64, 135.62, 135.2, 133.25, 133.18, 132.79, 132.75, 130.4, 130.2, 129.90, 129.86, 129.73, 129.71, 128.73, 128.68, 128.61, 128.55, 128.39, 128.37, 128.35, 128.27, 128.21, 128.18, 128.0, 127.9, 127.72, 127.70, 127.68, 127.59, 127.2, 102.3 (C-1$_{Gal}$), 99.2 (C-1$_{GalN}$), 79.6, 77.4, 74.7, 74.3, 73.7, 73.6, 72.4, 71.8, 71.5, 71.2, 70.3, 68.9, 68.2, 67.7, 67.4, 62.8, 59.6, 54.4, 26.8, 19.2. HRMS (ESI) calcd for $C_{81}H_{82}N_4O_{16}SiNa$ $[M+Na]^+$ 1417.5393, found 1417.5392.

β-D-galatopyranosyl-(1→3)*O*-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl]-L-serine (2)

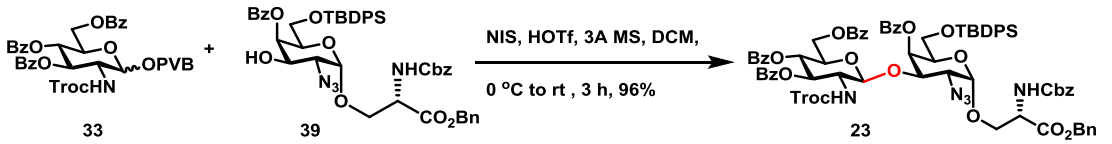


To a solution of compound **22** (245 mg, 0.17 mmol) in pyridine (3.4 mL) was added AcSH (3.09 mL, 34 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue was

purified by flash chromatography (MeOH/DCM, 1:25) to afford intermediate (213.9 mg, 86%). To a solution of above intermediate (213 mg, 0.15 mmol) in anhydrous THF (3 mL) was added HF/pyridine (70%, 0.19 mL, 1.47 mmol) dropwise. After stirring overnight at room temperature, the reaction mixture was quenched with Et_3N (1mL), diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 30:1) to afford the intermediate (174 mg, 98%). A mixture of the above intermediate (170 mg, 0.14 mmol) and Pd/C (331.4 mg, 10%) in MeOH/H_2O/HOAc (8 mL/0.8 mL/0.08 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography on RP-18 (MeOH-H_2O = 2:1) to afford the intermediate (104.7 mg, 76%). To a solution of above intermediate (104 mg, 0.10 mmol) in Dioxane/MeOH (1.5mL/1.5mL) was added 1.5 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **2** (46.3 mg, 94%) as a white solid.$[\alpha]_D^{20}$ = +82.0 (c 0.10, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.92 (d, *J* = 3.4 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 4.36 (dd, *J* = 11.0, 3.4 Hz, 1H), 4.24 (s, 1H), 4.16 – 4.03 (m, 2H), 4.02 – 3.96 (m, 2H), 3.95 – 3.87 (m, 2H), 3.83 – 3.71 (m, 4H), 3.68 – 3.59 (m, 2H), 3.55 – 3.48 (m, 1H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, D_2O) δ 174.7, 171.8, 104.7, 98.3, 76.8, 75.1, 72.6, 71.2, 70.7, 68.8, 68.7, 61.3, 61.1, 48.5, 22.2. HRMS (ESI) calcd for $C_{17}H_{29}N_2O_{13}$ $[M-H]^-$ 469.1675, found 469.1680.

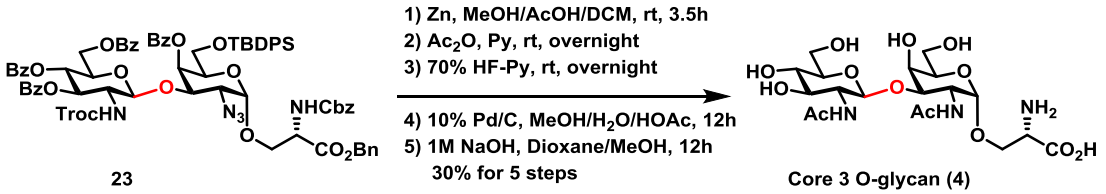
Synthesis of core 3 mucin-type *O*-glycan (4)

L-Serine *O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-*N*-2,2,2-tri-chloroethoxycarbonyl-β-D-glucopyranosyl)-(1→3)-*N*-(benzyloxycarbonyl)-*O*- (2- azido-4-*O*-benzoyl-6-*O*-tert-butyldiphenylsilyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (23)



A suspension of donor **33** (117.1 mg, 0.13 mmol), acceptor **39** (76.8 mg, 0.089 mmol), and activated 3Å MS (200 mg) in anhydrous DCM (4 mL) was stirred at room temperature for 15 min and was then cooled to 0 ℃. NIS (60.3 mg, 0.27 mmol) and HOTf (Trifluoromethanesulfonic acid) (6 μL, 0.067 mmol) were added successively. The resulting mixture was stirred at room temperature for 3 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 4:1) to afford **23** (133.3 mg, 96%) as a white solid. $[\alpha]_D^{25}$ = + 62.3 (c 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H, Ar), 7.85 (t, *J* = 7.1 Hz, 6H, Ar), 7.60 (d, *J* = 7.0 Hz, 2H, Ar), 7.53 (d, A*J* = 7.2 Hz, 2H, Ar), 7.44 (d, *J* = 7.4 Hz, 5H, Ar), 7.40 – 7.25 (m, 20H, Ar), 7.25 – 7.17 (m, 3H, Ar), 5.85 – 5.73 (m, 2H, H-4_{GalN}, H-3_{GlcN}), 5.59 (t, *J* = 9.6 Hz, 1H, H-4_{GlcN}), 5.36 – 5.17 (m, 3H), 5.15 – 5.01 (m, 3H, H-1_{GlcN}), 4.90 – 4.85 (m, 1H, H-1_{GalN}), 4.64 (d, *J* = 8.7 Hz, 1H), 4.60 – 4.47 (m, 3H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.27 – 4.20 (m, 1H, H-3_{GalN}), 4.11 – 3.95 (m, 4H, H-5_{GlcN}), 3.82 (q, *J* = 9.2 Hz, 1H, H-2_{GlcN}), 3.74 – 3.57 (m, 3H, H-2_{GalN}), 0.97 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 166.2, 166.1, 165.1, 164.8, 156.2, 154.1, 136.1, 135.63, 135.57, 135.2, 133.5, 133.4, 133.1, 133.05, 132.96, 130.0, 129.83, 129.77, 129.74, 128.9, 128.8, 128.7, 128.5, 128.44, 128.42, 128.38, 128.32, 127.7, 101.3 (C-1_{GlcN}), 98.9 (C-1_{GalN}), 95.3, 77.4, 75.3, 74.4, 72.2, 71.1, 69.9, 69.3, 69.0, 67.8, 67.4, 62.7, 62.5, 59.8, 56.9, 54.5, 26.8, 19.1. HRMS (ESI) calcd for $C_{77}H_{74}Cl_3N_5O_{19}SiNa$ $[M+Na]^+$ 1528.3711, found 1528.3712.

_O_-[2-(Acetylamino)-2-deoxy-β-D-glucopyranosyl)-(1→3)-_O_-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl]- L-serine (4)

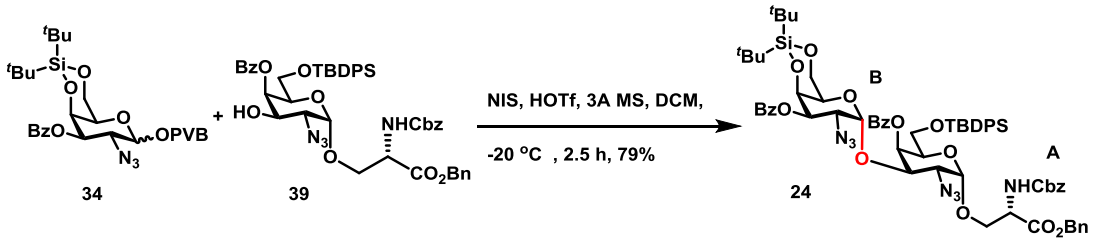


To a solution of compound **23** (260 mg, 0.17 mmol) in MeOH/AcOH/DCM (24mL/12mL/12mL)was added Zn powder (1.6 g, 25.86 mmol). The reaction mixture was stirred at room temperature for 3.5 h. Then the reaction mixture was filtered, the solvent was removed under vacuum to give the intermediate. The above intermediate was then dissolved in anhydrous pyridine (1.7 mL), and Ac_2O (0.81 mL, 8.62 mmol) was added slowly. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:50 to 1:20) to afford intermediate (183.6 mg, 77%). To a solution of above intermediate (180 mg, 0.13 mmol) in anhydrous THF (1.3 mL) was added HF/pyridine (70%, 0.17 mL, 1.29 mmol) dropwise. After stirring overnight at room temperature, the reaction mixture was quenched with Et_3N (1mL), diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 30:1) to afford the intermediate (89.2 mg, 60%). A mixture of the above intermediate (88 mg, 0.08 mmol) and Pd/C (181 mg, 10%) in MeOH/H_2O/HOAc (5 mL/0.5 mL/0.05 mL) was stirred under an atmosphere of H_2 at room temperature for 14 h, after which the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography on RP-18 (MeOH-H_2O = 4:1) to afford the intermediate (55.7 mg, 79%). To a solution of above intermediate (55 mg, 0.06 mmol) in Dioxane/MeOH (1mL/1mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **4** (24.9 mg, 82%) as a white solid. $[\alpha]_D^{20}$ = +91.5 (c 0.22, H_2O). ^{1}H NMR (600 MHz, D_2O) δ 4.85 (d, *J* = 3.8 Hz, 1H), 4.56 (d, *J* = 8.4 Hz, 1H), 4.26 (dd, *J* = 11.1, 3.8 Hz, 1H), 4.20 (d, *J* = 2.7 Hz, 1H), 4.09 (dd, *J* = 11.2,

2.9 Hz, 1H), 4.02 – 3.97 (m, 2H), 3.95 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.92 – 3.86 (m, 2H), 3.80 – 3.70 (m, 3H), 3.66 (dd, *J* = 10.3, 8.4 Hz, 1H), 3.56 – 3.51 (m, 1H), 3.44 (t, *J* = 9.2 Hz, 1H), 3.42 – 3.38 (m, 1H), 2.03 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, D_2O) δ 174.4, 173.7, 171.7, 102.3, 98.1, 76.1, 75.5, 73.3, 70.9, 69.6, 68.6, 66.6, 61.2, 60.4, 55.5, 54.4, 48.1, 22.2, 22.1. HRMS (ESI) calcd for $C_{19}H_{32}N_3O_{13}$ $[M-H]^-$ 510.1941, found 510.1945.

Synthesis of core 5 mucin-type *O*-glycan (6)

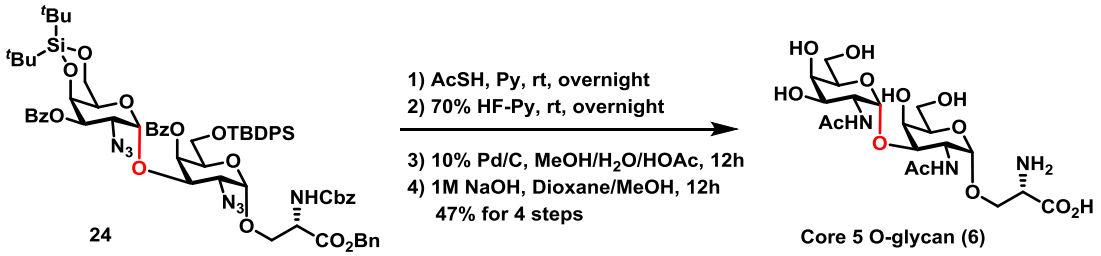
L-Serine *O*-(2-azido-3-O-benzoyl-2-deoxy-4,6-O-(di-tert-butylsilylene)-α-D-galactopyranosyl)-(1→3)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-6-*O*-tert- butyldiphenylsilyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (24)



A suspension of donor **34** (101.2 mg, 0.15 mmol), acceptor **39** (88.4 mg, 0.10 mmol), and activated 3Å MS (200 mg) in anhydrous DCM (3 mL) was stirred at room temperature for 15 min and was then cooled to -20 ℃. NIS (52.1 mg, 0.23 mmol) and HOTf (Trifluoromethanesulfonic acid) (7 μL, 0.077 mmol) were added successively. The resulting mixture was stirred at -20 ℃ for 2.5 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 5:1 to 4:1) to afford **24** (103.2 mg, 79%) as a white solid. $[\alpha]_D^{26}$ = + 178.2 (c 0.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.8, 3.9 Hz, 4H, Ar), 7.68 – 7.63 (m, 2H, Ar), 7.57 – 7.51 (m, 2H, Ar), 7.49 (d, *J* = 7.4 Hz, 2H, Ar), 7.44 – 7.32 (m, 16H, Ar), 7.30 – 7.23 (m, 2H, Ar), 7.10 (t, *J* = 7.5 Hz, 2H, Ar), 5.93 (d, *J* = 3.3 Hz, 1H, H-4_A), 5.75 (d, *J* = 8.6 Hz, 1H), 5.58 (d, *J* = 3.8 Hz, 1H, H-1_B), 5.32 (dd, *J* = 10.9, 3.0 Hz, 1H, H-3_B), 5.23 (q, *J* = 12.2 Hz, 2H), 5.06 (d, *J* = 2.5 Hz, 2H), 4.87 (d, *J* = 3.3 Hz, 2H, H-4_B, H-1_A), 4.60 (dd, *J* = 7.8, 4.0 Hz, 1H), 4.32 – 4.26 (m, 3H, H-3_A), 4.13 – 4.07 (m,

1H), 4.05 – 3.99 (m, 2H, H-2_B, H-4_B), 3.97 – 3.90 (m, 2H), 3.73 – 3.66 (m, 2H, H-2_A), 3.62 (dd, *J* = 10.1, 7.6 Hz, 1H), 1.10 (s, 9H, CH_3-*t*-Bu), 1.00 (s, 9H, CH_3-*t*-Bu), 0.95 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 165.9, 165.7, 156.1, 136.1, 135.6, 135.5, 135.2, 133.3, 132.8, 132.6, 129.9, 129.85, 129.82, 129.79, 129.71, 129.6, 128.81, 128.75, 128.65, 128.52, 128.50, 128.33, 128.30, 127.9, 127.7, 99.1 (C-1_A), 94.0 (C-1_B), 71.5, 70.4, 70.1, 69.8, 69.4, 67.8, 67.7, 67.3, 67.0, 64.9, 61.6, 59.7, 57.0, 54.5, 27.7, 27.4, 26.8, 23.3, 20.8, 19.1. HRMS (ESI) calcd for $C_{68}H_{79}N_7O_{15}Si_2Na$ $[M+Na]^+$ 1312.5070, found 1312.5072.

_O_-[2-(Acetylamino)-2-deoxy-α-D-galatopyranosyl)-(1→3)-_O_-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl]- L-serine (6)

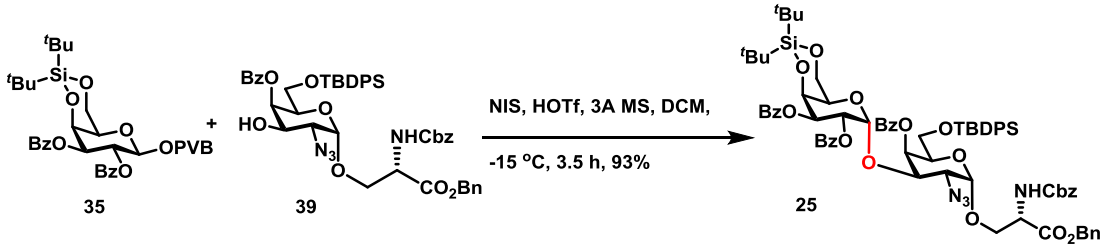


To a solution of compound **24** (109 mg, 0.08 mmol) in pyridine (1.7 mL) was added AcSH (3.06 mL, 33.78 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:25) to afford intermediate (104.4 mg, 93%). To a solution of above intermediate (104 mg, 0.08 mmol) in anhydrous THF (2 mL) was added HF/pyridine (70%, 0.2 mL, 1.57 mmol) dropwise. After stirring overnight at room temperature, the reaction mixture was quenched with Et_3N (1mL), diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 25:1) to afford the intermediate (63.2 mg, 85%). A mixture of the above intermediate (63 mg, 0.07 mmol) and Pd/C (158 mg, 10%) in MeOH/H_2O/HOAc (5 mL/0.5 mL/0.05 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column

chromatography on RP-18 (MeOH-H_2O = 1.5:1) to afford the intermediate (36.4 mg, 76%). To a solution of above intermediate (36 mg, 0.05 mmol) in dioxane/MeOH (1mL/1mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **6** (19.9 mg, 78%) as a white solid. $[\alpha]_D^{20}$ = +195.0 (c 0.08, H_2O). ^1H NMR (400 MHz, D_2O) δ 5.09 (d, *J* = 3.7 Hz, 1H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.42 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.29 – 4.15 (m, 2H), 4.15 – 4.07 (m, 1H), 4.07 – 3.97 (m, 2H), 3.99 – 3.70 (m, 9H), 2.08 (s, 3H), 2.05 (s, 3H). ^3C NMR (151 MHz, D_2O) δ 174.6, 174.4, 172.9, 97.9, 93.1, 71.7, 71.23, 71.20, 68.3, 67.7, 66.9, 64.2, 61.3, 61.0, 54.6, 49.3, 47.7, 22.0, 21.9. HRMS (ESI) calcd for $C_{19}H_{32}N_3O_{13}$ $[M-H]^-$ 510.1941, found 510.1945.

Synthesis of core 8 mucin-type *O*-glycan (9)

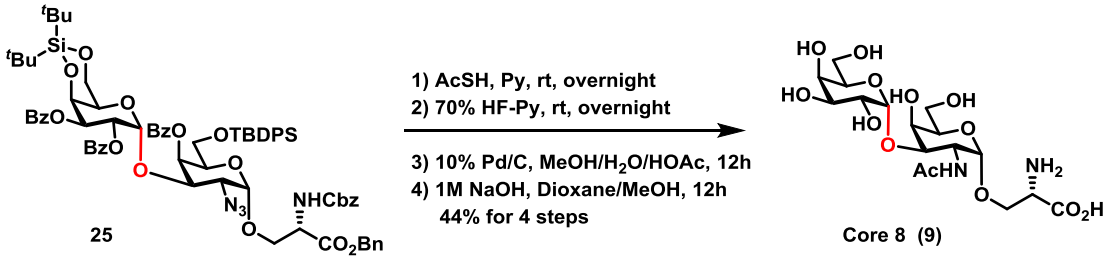
L-Serine *O*-(2,3-di-*O*-benzoyl-4,6-*O*-(di-tert-butylsilylene)-α-D-galacto-pyranosyl))-(1→3)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-6-*O*-tert-butyldiphenylsilyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (25)



A suspension of donor **35** (273.9 mg, 0.37 mmol), acceptor **39** (246.3 mg, 0.29 mmol), and activated 3Å MS (550 mg) in anhydrous DCM (11 mL) was stirred at room temperature for 15 min and was then cooled to -15 ℃. NIS (125.8 mg, 0.56 mmol) and HOTf (Trifluoromethanesulfonic acid) (13 μL, 0.15 mmol) were added successively. The resulting mixture was stirred at -15 ℃ for 3.5 h, then quenched with Et_3N (4 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 6:1 to 4:1) to afford **25** (364.5mg, 93%) as a white solid. $[\alpha]_D^{25}$ = + 164.3 (c

0.36, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H, Ar), 7.70 – 7.65 (m, 2H, Ar), 7.60 – 7.56 (m, 2H, Ar), 7.46 – 7.38 (m, 7H, Ar), 7.36 – 7.21 (m, 16H, Ar), 7.09 – 6.96 (m, 6H, Ar), 5.97 (dd, *J* = 10.8, 3.7 Hz, 1H, H-2_{Gal}), 5.77 – 5.69 (m, 3H, H-1_{Gal}, H-4_{GalN}), 5.58 (dd, *J* = 10.8, 3.0 Hz, 1H, H-3_{Gal}), 5.24 (d, *J* = 2.9 Hz, 2H), 5.07 (s, 2H), 4.91 (d, *J* = 3.3 Hz, 2H, H-1_{GalN}, H-4_{Gal}), 4.60 (dd, *J* = 7.8, 3.9 Hz, 1H), 4.31 (dd, *J* = 10.9, 2.8 Hz, 3H, H-3_{GalN}), 4.08 (d, *J* = 12.2 Hz, 2H), 3.99 – 3.90 (m, 2H), 3.79 (dd, *J* = 10.9, 3.6 Hz, 1H, H-2_{GalN}), 3.57 (dd, *J* = 10.3, 6.4 Hz, 1H), 3.49 (dd, *J* = 10.3, 6.9 Hz, 1H), 1.18 (s, 9H, CH_3-*t*-Bu), 0.98 (s, 9H, CH_3-*t*-Bu), 0.93 (s, 9H, CH_3-*t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 166.1, 166.0, 164.8, 156.1, 136.1, 135.6, 135.4, 135.2, 133.1, 132.8, 132.6, 129.8, 129.69, 129.65, 129.5, 129.4, 128.82, 128.79, 128.72, 128.63, 128.59, 128.32, 128.30, 128.27, 128.1, 128.0, 127.8, 127.7, 127.6, 98.9 (C-1_{GalN}), 93.1 (C-1_{Gal}), 71.4, 70.9, 70.6, 69.6, 69.2, 67.8, 67.6, 67.29, 67.25, 66.9, 65.5, 61.9, 60.5, 59.7, 54.5, 27.7, 27.4, 26.7, 23.4, 20.8, 19.0, 14.3. MS (Maldi-TOF) calcd for $C_{75}H_{84}N_4O_{17}Si_2Na$ $[M+Na]^+$1391.5268, found 1391.5269.

α-D-galatopyranosyl-(1→3)-*O*-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl] -L-serine (9)

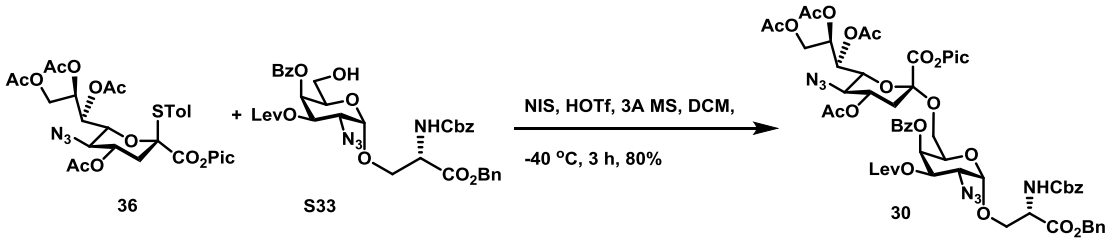


To a solution of compound **25** (362 mg, 0.26 mmol) in pyridine (5mL) was added AcSH (3.9 mL, 52.86 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (PE/EA/DCM, 6:3:1) to afford intermediate (366.2 mg, 82%). To a solution of above intermediate (323.9 mg, 0.24 mmol) in anhydrous THF (8 mL) was added HF/pyridine (70%, 0.21 mL, 2.33 mmol) dropwise. After stirring overnight at room temperature, the reaction mixture was quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The

organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 40:1) to afford the intermediate (203.8 mg, 87%). A mixture of the above intermediate (93 mg, 0.09 mmol) and Pd/C (196.6 mg, 10%) in MeOH/H_2O/HOAc (6 mL/0.6 mL/0.06 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography on RP-18 (MeOH-H_2O = 1.5:1 to 2:1) to afford the intermediate (55.5 mg, 77%). To a solution of above intermediate (55 mg, 0.07 mmol) in dioxane/MeOH (0.75 mL/0.75 mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **9** (24.8 mg, 75%) as a white solid. $[\alpha]_D^{20}$ = +256.9 (c 0.16, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 5.15 (d, *J* = 3.7 Hz, 1H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.43 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.27 (d, *J* = 2.1 Hz, 1H), 4.15 (dd, *J* = 11.0, 2.7 Hz, 1H), 4.07 – 3.92 (m, 5H), 3.89 – 3.74 (m, 7H), 2.08 (s, 3H).^{13}C NMR (126 MHz, D_2O) δ 174.0, 171.3, 97.6, 94.4, 71.9, 70.8, 70.7, 68.9, 68.6, 67.6, 66.0, 64.0, 60.8, 60.5, 54.0, 47.3, 21.6. HRMS (ESI) calcd for $C_{17}H_{29}N_2O_{13}$ $[M-H]^-$ 469.1675, found 469.1677.

Synthesis of core ST_N antigen (10)

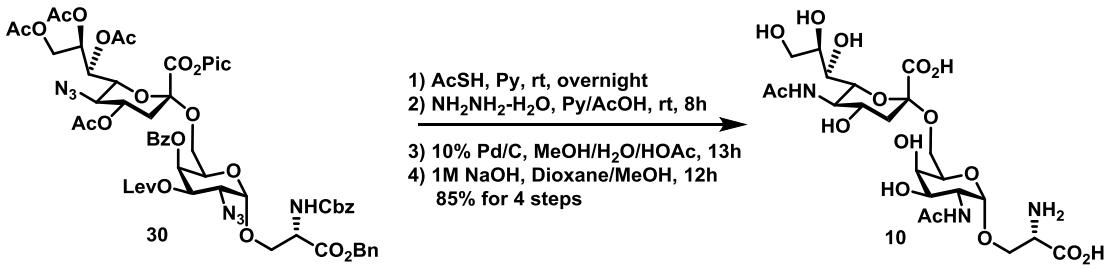
L-Serine 5-azido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deo xy- 3-*O*-levulinoyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (30)



A suspension of donor **36**[18] (122.2 mg, 0.19 mmol), acceptor **S33** (76.4 mg, 0.11 mmol), and activated 3Å MS (200 mg) in anhydrous DCM (4 mL) was stirred at room

temperature for 15 min and was then cooled to -40 ℃. NIS (100.2 mg, 0.45 mmol) and HOTf (Trifluoromethanesulfonic acid) (16.4 μL, 0.19 mmol) were added successively. The resulting mixture was stirred at -40 ℃ for 3 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 6:1 to 4:1) to afford **30** (185.2 mg, 80%) as a white solid. $[\alpha]_D^{20}$ = +36.8 (c 0.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 6.9 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.31 (m, 10H), 7.20 (s, 2H), 6.03 (d, *J* = 8.3 Hz, 1H), 5.62 (s, 1H), 5.47 (d, *J* = 9.2 Hz, 1H), 5.37 – 5.04 (m, 8H), 5.04 – 4.96 (m, 1H), 4.92 (d, *J* = 2.4 Hz, 1H), 4.73 (d, *J* = 13.3 Hz, 1H), 4.64 (d, *J* = 7.8 Hz, 1H), 4.25 – 4.06 (m, 5H), 3.89 – 3.78 (m, 2H), 3.64 (dd, *J* = 10.8, 2.3 Hz, 1H), 3.50 – 3.41 (m, 1H), 3.19 (t, *J* = 10.0 Hz, 1H), 2.82 – 2.62 (m, 3H), 2.60 – 2.41 (m, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H), 1.71 (t, *J* = 12.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 171.6, 170.7, 169.9, 169.74, 169.65, 169.5, 166.5, 165.4, 156.2, 154.2, 149.2, 137.1, 136.3, 135.2, 133., 129.8, 129.5, 128.7, 128.6, 128.6, 128.2, 128.2, 123.2, 121.2, 99.2(C-1_{GalN}), 98.5, 77.4, 71.7, 70.9, 69.4, 68.7, 68.1, 67.9, 67.8, 67.7, 67.2, 67.1, 62.6, 62.0, 60.0, 57.9, 54.6, 37.9, 37.4, 29.7, 27.9, 20.9, 20.8, 20.7. HRMS (ESI) calcd for $C_{59}H_{65}N_8O_{23}$ $[M+H]^+$ 1253.4157, found 1253.4159.

5-acetamido-3,5-dideoxy-D-glycero-D-galacto-non-2-ulopyranosylonic acid-(2→6) -*O*-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl] -L-serine (10)

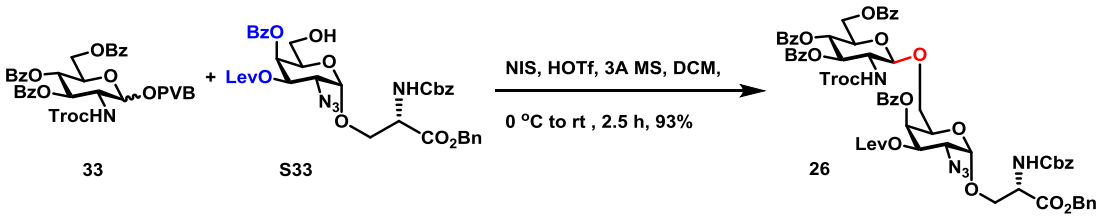


To a solution of compound **30** (180 mg, 0.14 mmol) in pyridine (3 mL) was added AcSH (5.2 mL, 57.45 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue

was purified by flash chromatography (MeOH/DCM, 1:20) to afford intermediate (184.6 mg, 100%). The above intermediate (184 mg, 0.14 mmol) was dissolved in anhydrous DCM/pyridine/AcOH (1 mL/0.3 mL/0.2 mL), then $NH_2NH_2.H_2O$ (0.026 mL, 0.43 mmol) was added at room temperature. The reaction was stirred until TLC-analysis indicated full consumption of the starting material. Then the reaction was quenched with acetone and the mixture was concentrated under vacuum. The products were purified by flash column chromatography (DCM/MeOH, 20:1) to afford the intermediate (151 mg, 89%). A mixture of the above intermediate (144 mg, 0.13 mmol) and Pd/C (288 mg, 10%) in MeOH/H_2O/HOAc (6 mL/0.6 mL/0.06 mL) was stirred under an atmosphere of H_2 at room temperature for 13 h, after which the reaction mixture was filtered and concentrated *in vacuo* to afford the intermediate. To a solution of above intermediate in dioxane/MeOH (1 mL/1 mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **10** (72.1 mg, 95%) as a white solid. $[\alpha]_D^{20}$ = +73.1 (c 0.21, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.90 (d, *J* = 3.7 Hz, 1H), 4.17 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.12 (dd, *J* = 11.0, 2.6 Hz, 1H), 4.03 (dd, *J* = 8.2, 3.6 Hz, 1H), 4.01 – 3.97 (m, 2H), 3.95 – 3.86 (m, 5H), 3.83 (d, *J* = 10.1 Hz, 1H), 3.75 – 3.62 (m, 4H), 3.58 (dd, *J* = 8.9, 1.2 Hz, 1H), 2.74 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.04 (s, 3H), 2.04 (s, 3H), 1.69 (t, *J* = 12.1 Hz, 1H).^{13}C NMR (151 MHz, D_2O) δ 175.0, 174.7, 173.4, 171.8, 100.3, 98.0, 72.6, 71.8, 69.7, 68.4, 68.2, 67.2, 66.9, 63.9, 62.6, 54.4, 51.8, 49.6, 40.2, 22.00, 21.99. HRMS (ESI) calcd for $C_{22}H_{36}N_3O_{16}$ $[M-H]^-$ 598.2101, found 598.2105.

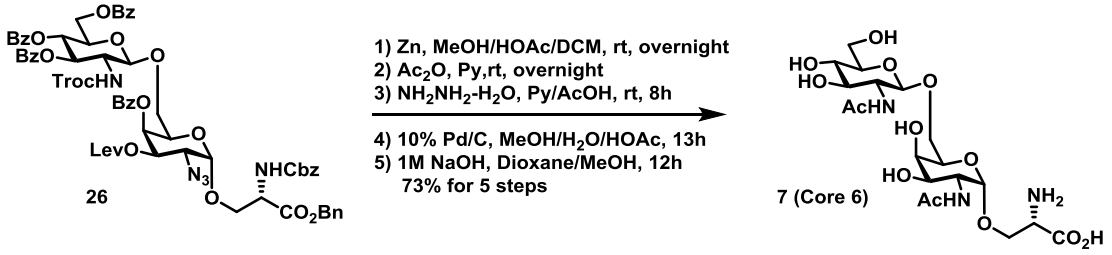
Synthesis of core 6 mucin-type *O*-glycan (7)

L-Serine *O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-*N*-2,2,2-tri-chloroethoxycarbonyl-β-D-glucopyranosyl)-(1→6)-*N*-(benzyloxycarbonyl)-*O*-(2- azido-4-*O*-benzoyl-2-deoxy-3-*O*-levulinoyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (26)



A suspension of donor **33** (111.4 mg, 0.13 mmol), acceptor **S33** (76.4 mg, 0.11 mmol), and activated 3Å MS (200 mg) in anhydrous DCM (3.3 mL) was stirred at room temperature for 15 min and was then cooled to 0 ℃. NIS (43.0 mg, 0.19 mmol) and HOTf (Trifluoromethanesulfonic acid) (3 μL, 0.038 mmol) were added successively. The resulting mixture was stirred at room temperature for 2.5 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 3:1 to 2:1) to afford **26** (134.7 mg, 93%) as a white solid. $[\alpha]_D^{24}$ = + 62.2 (c 0.30, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 2H), 7.94 – 7.89 (m, 4H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.44 (m, 6H), 7.40 – 7.27 (m, 15H), 6.03 (t, *J* = 9.0 Hz, 2H), 5.99 (t, *J* = 10.2 Hz, 1H, H-3_{GlcN}), 5.60 (d, *J* = 3.3 Hz, 1H, H-4_{GalN}), 5.52 (t, *J* = 9.7 Hz, 1H, H-4_{GlcN}), 5.35 (dd, *J* = 11.1, 3.3 Hz, 1H, H-3_{GalN}), 5.25 (s, 2H), 5.17 (s, 2H), 4.99 (d, *J* = 3.6 Hz, 1H, H-1_{GalN}), 4.95 (d, *J* = 8.3 Hz, 1H, H-1_{GlcN}), 4.81 (d, *J* = 12.1 Hz, 1H), 4.63 – 4.59 (m, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.45 (dd, *J* = 12.1, 3.2 Hz, 1H), 4.30 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.22 (dd, *J* = 7.6, 4.3 Hz, 1H), 4.14 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.10 (dd, *J* = 10.7, 3.4 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.92 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.69 – 3.60 (m, 3H, H-2_{GalN}, H-2_{GlcN}), 2.81 – 2.75 (m, 1H, CH_2-Lev), 2.71 – 2.64 (m, 1H, CH_2-Lev), 2.60 – 2.54 (m, 1H, CH_2-Lev), 2.49 – 2.41 (m, 1H, CH_2-Lev), 2.13 (s, 3H, CH_3-Lev). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.2, 171.6, 169.5, 166.1, 166.0, 165.4, 165.3, 156.1, 154.1, 136.1, 135.1, 133.8, 133.44, 133.41, 133.1, 129.9, 129.85, 129.76, 129.67, 129.57, 129.1, 129.0, 128.9, 128.8, 128.74, 128.72, 128.69, 128.64, 128.57, 128.49, 128.42, 128.35, 128.2, 100.0 (C-1_{GlcN}), 98.7 (C-1_{GalN}), 95.6, 74.3, 71.9, 71.6, 70.0, 69.0, 68.8, 68.51, 68.50, 68.1, 68.0, 67.4, 63.0, 57.7, 57.0, 54.5, 37.9, 29.8, 27.9. HRMS (ESI) calcd for $C_{66}H_{62}Cl_3N_5O_{21}Na$ $[M+Na]^+$ 1388.2901, found 1388.2899.

***O*-[2-(Acetylamino)-2-deoxy-β-D-glucopyranosyl)-(1→6)-*O*-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl]- L-serine (7)**

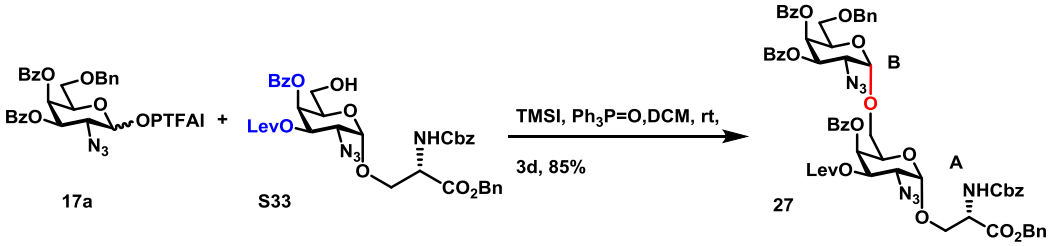


To a solution of compound **26** (125 mg, 0.09 mmol) in MeOH/AcOH/DCM (13 mL/6.5 mL/6.5mL)was added Zn powder (1.2 g, 18.28 mmol). The reaction mixture was stirred overnight at room temperature . Then the reaction mixture was filtered, the solvent was removed under vacuum to give the intermediate. The above intermediate was then dissolved in anhydrous pyridine (4.6 mL), and Ac_2O (0.43 mL, 4.57 mmol) was added slowly. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated in vacuo. The residue was purified by flash chromatography (MeOH/DCM, 1:30) to afford intermediate (110.3 mg, 97%). The above intermediate (100 mg, 0.09 mmol) was dissolved in anhydrous DCM/pyridine/AcOH (1 mL/0.3 mL/0.2 mL), then $NH_2NH_2•H_2O$ (0.016 mL, 0.26 mmol) was added at room temperature. The reaction was stirred until TLC-analysis indicated full consumption of the starting material. Then the reaction was quenched with acetone and the mixture was concentrated under vacuum. The products were purified by flash column chromatography (DCM/MeOH, 15:1) to afford the intermediate (100 mg, 99%). A mixture of the above intermediate (100 mg, 0.09 mmol) and Pd/C (206 mg, 10%) in MeOH/H_2O/HOAc (5 mL/0.5 mL/0.05 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated in vacuo. The residue was purified by column chromatography on RP-18 (MeOH-H_2O = 3:1) to afford the intermediate (68.8 mg, 83%). To a solution of above intermediate (68 mg, 0.07 mmol) in Dioxane/MeOH (1.5 mL/1.5 mL) was added 1.5 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to

pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **7** (33.8 mg, 90%) as a white solid. $[\alpha]_D^{20}$ = +110.8 (c 0.10, H_2O). ^1H NMR (600 MHz, D_2O) δ 4.87 (d, *J* = 3.5 Hz, 1H), 4.54 (d, *J* = 8.5 Hz, 1H), 4.16 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.07 (dd, *J* = 10.7, 3.0 Hz, 1H), 4.04 – 4.00 (m, 2H), 3.98 – 3.95 (m, 2H), 3.94 – 3.87 (m, 3H), 3.77 – 3.72 (m, 2H), 3.72 – 3.67 (m, 1H), 3.54 (t, *J* = 9.4 Hz, 1H), 3.48 – 3.41 (m, 2H), 2.04 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, D_2O) δ 174.7, 174.5, 171.6, 101.5, 98.0, 75.8, 73.6, 69.92, 69.86, 69.8, 68.4, 67.2, 66.5, 60.6, 55.5, 54.4, 49.5, 22.2, 22.0. HRMS (ESI) calcd for $C_{19}H_{32}N_3O_{13}$ $[M-H]^-$ 510.1941, found 510.1945.

Synthesis of core 7 mucin-type *O*-glycan (8)

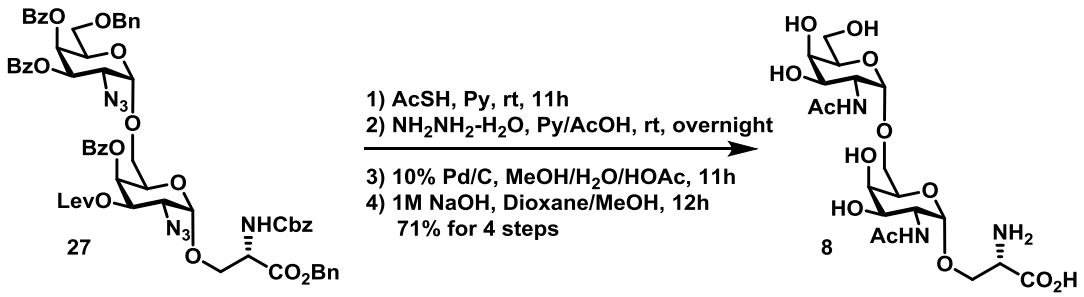
L-Serine *O*-(2-azido-3,4-di-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→6)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-3-*O*-levulinoyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (27)



PTFAI donor **17a** (180.2 mg, 0.27 mmol) was co-evaporated with anhydrous toluene for three times. Then PTFAI donor with $Ph_3P=O$ (446.1 mg, 1.60 mmol) were dissolved in new distilled DCM (1.8 mL) and stirred over fresh-dried 3Å molecular sieves (300 mg) under argon at room temperature for 15 min. TMSI (38 μL, 0.27 mmol) was added dropwise subsequently. After the mixture was stirred for 1h, acceptor **S33** (128 mg, 0.18 mmol) was added. The reaction was stirred at room temperature for 3d. Upon completion, the solution was diluted with EtOAc and the reaction was quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The products were purified by flash column chromatography (PE-EA=3:1) to afford

27 (182.7 mg, 85%) as a white solid. $[\alpha]_D^{25}$ = + 205.5 (c 0.11, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H, Ar), 7.96 – 7.90 (m, 2H, Ar), 7.88 – 7.82 (m, 2H, Ar), 7.59 (q, *J* = 7.8 Hz, 2H, Ar), 7.52 – 7.24 (m, 20H, Ar), 7.17 – 7.12 (m, 2H, Ar), 5.99 (d, *J* = 8.6 Hz, 1H), 5.89 (d, *J* = 3.2 Hz, 1H, H-4_B), 5.70 (dd, *J* = 11.0, 3.2 Hz, 1H, H-3_B), 5.61 (d, *J* = 3.3 Hz, 1H, H-4_A), 5.36 (dd, *J* = 11.1, 3.2 Hz, 1H, H-3_A), 5.24 (q, *J* = 10.2, 8.5 Hz, 2H), 5.16 (q, *J* = 12.0, 10.4 Hz, 2H), 5.02 (t, *J* = 2.7 Hz, 2H, H-1_A, H-1_B), 4.76 – 4.69 (m, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 6.7 Hz, 1H), 4.33 (d, *J* = 12.1 Hz, 1H), 4.22 (dd, *J* = 7.8, 4.4 Hz, 1H), 4.15 (dd, *J* = 10.4, 4.6 Hz, 1H), 4.09 (dd, *J* = 10.3, 3.7 Hz, 1H), 3.92 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.86 (dd, *J* = 10.5, 7.7 Hz, 1H), 3.69 (dd, *J* = 11.1, 3.6 Hz, 1H), 3.58 (dd, *J* = 10.3, 4.1 Hz, 1H), 3.51 (q, *J* = 9.7, 8.1 Hz, 2H), 2.82 – 2.73 (m, 1H, CH_2-Lev), 2.72 – 2.63 (m, 1H, CH_2-Lev), 2.61 – 2.52 (m, 1H, CH_2-Lev), 2.50 – 2.41 (m, 1H, CH_2-Lev), 2.12 (s, 3H, CH_3-Lev). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 171.6, 169.9, 165.6, 165.45, 165.37, 156.2, 137.6, 136.3, 135.3, 133.8, 133.5, 133.4, 129.9, 129.8, 129.5, 129.2, 129.1, 128.79, 128.77, 128.72, 128.63, 128.61, 128.4, 128.3, 128.2, 127.75, 127.69, 99.0, 97.8, 73.4, 69.3, 69.1, 68.9, 68.7, 68.55, 68.50, 68.02, 67.97, 67.8, 67.3, 66.5, 58.4, 57.9, 54.3, 37.9, 29.8, 27.9. HRMS (ESI) calcd for $C_{63}H_{61}N_7O_{18}Na$ $[M+Na]^+$ 1226.3971, found 1226.3970.

_O_-[2-(Acetylamino)-2-deoxy-α-D-galactoopyranosyl)-(1→6)-_O_-[2-(Acetylamino)-2- deoxy-α-D-galactopyranosyl]- L-serine (8)

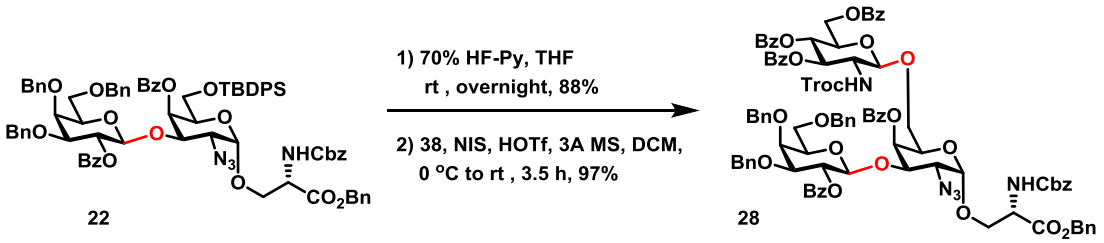


To a solution of compound **27** (180 mg, 0.15 mmol) in pyridine (3 mL) was added AcSH (5.42 mL, 59.79 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue

was purified by flash chromatography (MeOH/DCM, 1:30) to afford intermediate (184.8 mg, 100%). The above intermediate (183 mg, 0.15 mmol) was dissolved in anhydrous DCM/pyridine/AcOH (1 mL/0.3 mL/0.2 mL), then $NH_2NH_2.H_2O$ (80%, 0.027 mL, 0.44 mmol) was added at room temperature. The reaction was stirred until TLC-analysis indicated full consumption of the starting material. Then the reaction was quenched with acetone and the mixture was concentrated under vacuum. The products were purified by flash column chromatography (DCM/MeOH, 30:1) to afford the intermediate (168.5 mg, 100%). A mixture of the above intermediate (168 mg, 0.15 mmol) and Pd/C (524 mg, 10%) in MeOH/H_2O/HOAc (8 mL/0.8 mL/0.08 mL) was stirred under an atmosphere of H_2 at room temperature for 11 h, after which the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography on RP-18 (MeOH-H_2O = 1.5:1) to afford the intermediate (107.8 mg, 89%).To a solution of above intermediate (106 mg, 0.013 mmol) in dioxane/MeOH (1 mL/1 mL) was added 2 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **8** (53.3 mg, 81%) as a white solid. $[\alpha]_D^{20}$ = +149.3 (c 0.21, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.96 (d, *J* = 3.6 Hz, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.24 – 4.07 (m, 4H), 4.07 – 3.96 (m, 4H), 3.96 – 3.81 (m, 4H), 3.80 – 3.68 (m, 3H), 2.05 (s, 6H). ^{13}C NMR (151 MHz, D_2O) δ 174.64, 174.57, 171.4, 97.9, 97.1, 71.1, 69.0, 68.5, 68.5, 67.6, 67.5, 66.5, 66.3, 61.2, 54.5, 49.8, 49.5, 22.0, 21.9. HRMS (ESI) calcd for $C_{19}H_{32}N_3O_{13}$ $[M-H]^-$ 510.1941, found 510.1939.

Synthesis of core 2 mucin-type *O*-glycan (3)

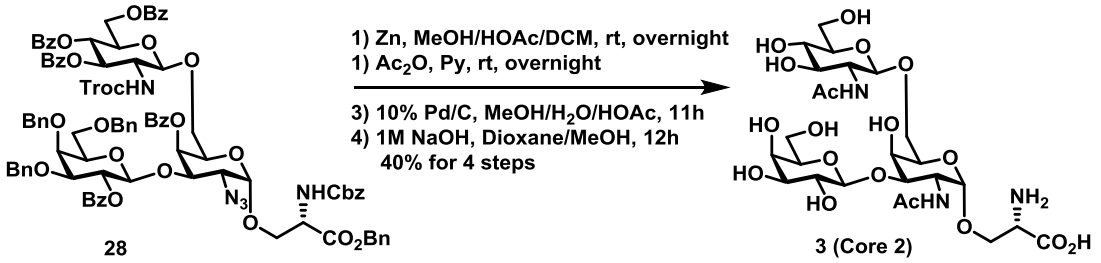
L-Serine *O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-*N*-2,2,2-tri-chloroethoxycarbonyl-β-D-glucopyranosyl)-(1→6)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-α-D-galactopyranosyl)-(3→1)-*O*-(3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-galato-pyranosyl)-benzyl ester (28)



Compound **22** (358 mg, 0.26 mmol) was then dissolved in anhydrous THF (1.0 mL), and HF/pyridine (70%, 0.23 mL, 2.56 mmol) was added dropwise. The resulting mixture was stirred overnight at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 2:1) to afford the acceptor (262.4 mg, 88%,) as a white solid. A suspension of donor **33** (115.8 mg, 0.13 mmol), acceptor (127.9 mg, 0.11 mmol), and activated 3Å MS (250 mg) in anhydrous DCM (3.3 mL) was stirred at room temperature for 15 min and was then cooled to 0 ℃. NIS (44.7 mg, 0.20 mmol) and HOTf (Trifluoromethanesulfonic acid) (5 μL, 0.053 mmol) were added successively. The resulting mixture was stirred at room temperature for 3.5 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 3:1) to afford **28** (193.8 mg, 97%) as a white solid. $[\alpha]_D^{25}$ = + 78.3 (c 0.14, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.2 Hz, 4H, Ar), 7.94 (d, *J* = 7.7 Hz, 2H, Ar), 7.89 (d, *J* = 7.9 Hz, 2H, Ar), 7.86 (d, *J* = 7.9 Hz, 2H, Ar), 7.52 (q, *J* = 7.0 Hz, 2H, Ar), 7.46 – 7.37 (m, 8H, Ar), 7.36 – 7.31 (m, 7H, Ar), 7.28 (h, *J* = 7.9, 6.9 Hz, 15H, Ar), 7.21 – 7.19 (m, 3H, Ar), 7.17 – 7.14 (m, 2H, Ar), 7.11 (d, *J* = 5.5 Hz, 3H, Ar), 6.06 – 6.00 (m, 2H, H-3_{GlcN}, H-4_{GalN}), 5.98 (d, *J* = 7.7 Hz, 1H), 5.57 – 5.51 (m, 3H, H-2_{Gal}, H-4_{GlcN}, H-3_{GalN}), 5.16 – 5.08 (m, 5H, CH_2-Cbz, CH_2-Bn), 4.96 (d, *J* = 8.2 Hz, 1H, H-1_{GlcN}), 4.87 (d, *J* = 11.9 Hz, 1H, CH_2-Bn), 4.81 (d, *J* = 3.8 Hz, 1H, H-1_{GalN}), 4.70 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 7.9 Hz, 1H, H-1_{Gal}), 4.58 (d, *J* = 12.5 Hz, 1H, CH_2-Bn), 4.56 – 4.51 (m, 2H), 4.49 (d, *J* = 11.8 Hz, 1H, CH_2-Bn), 4.43 (dd, *J* = 12.0, 5.0 Hz, 2H, CH_2-Bn), 4.38 (dd, *J* = 12.1, 5.4 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.16 (d, *J* = 10.8 Hz, 1H), 4.09 – 4.03 (m, 3H),

4.00 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.94 (d, *J* = 2.7 Hz, 1H), 3.91 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.65 – 3.58 (m, 4H, H-2_{GlcN}), 3.57 – 3.50 (m, 2H, H-2_{GalN}), 3.46 (t, *J* = 9.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 166.1, 165.93, 165.89, 165.3, 165.2, 155.9, 154.0, 138.6, 137.8, 137.6, 136.0, 135.0, 133.4, 133.3, 133.0, 132.8, 130.2, 129.9, 129.8, 129.81, 129.79, 129.73, 129.6, 129.0, 128.8, 128.7, 128.64, 128.57, 128.49, 128.47, 128.43, 128.40, 128.36, 128.35, 128.29, 128.24, 128.16, 128.09, 127.98, 127.8, 127.6, 127.5, 127.2, 102.2 (C-1_{Gal}), 100.2 (C-1_{GlcN}), 98.4 (C-1_{GalN}), 95.4, 79.4, 74.8, 74.2, 73.6, 73.5, 72.4, 71.8, 71.6, 71.5, 71.4, 70.8, 70.0, 69.9, 69.7, 68.2, 68.1, 67.7, 67.3, 63.2, 59.1, 57.1, 54.2. HRMS (ESI) calcd for $C_{95}H_{88}Cl_3N_5O_{25}Na$ $[M+Na]^+$ 1826.4726, found 1826.4731.

_O_-[2-(Acetylamino)-2-deoxy-β-D-galactoopyranosyl)-(1→6)-_O_-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl])-(3→1)-_O_-β-D-galactopyranosyl)- L-serine (3)

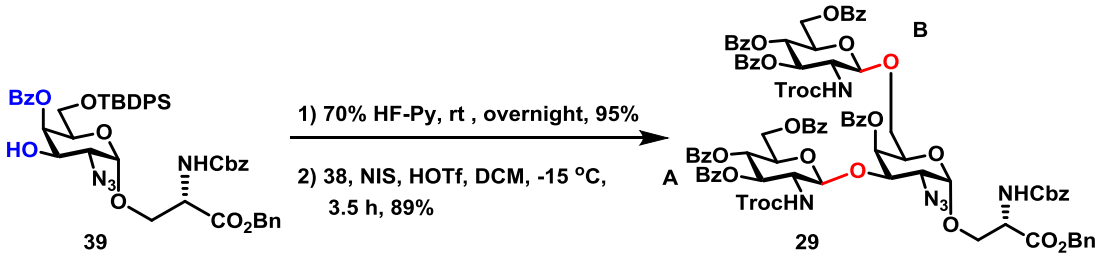


To a solution of compound **28** (180 mg, 0.10 mmol) in MeOH/AcOH/DCM (14 mL/7 mL/7 mL)was added Zn powder (652 mg, 9.97 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was filtered, the solvent was removed under vacuum to give the intermediate. The above intermediate was then dissolved in anhydrous MeOH (28 mL), and Ac_2O (0.47 mL, 4.98 mmol) was added slowly. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated in vacuo. The residue was purified by flash chromatography (MeOH/DCM, 1:30) to afford intermediate (117.3 mg, 70%). A mixture of the above intermediate (115 mg, 0.07 mmol) and Pd/C (403 mg, 10%) in MeOH/H_2O/HOAc (5 mL/0.5 mL/0.05 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography on RP-18

(MeOH-H_2O = 2:1 to 3:1) to afford the intermediate (56.7 mg, 70%). To a solution of above intermediate (55 mg, 0.05 mmol) in Dioxane/MeOH (1 mL/1 mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **3** (25.3 mg, 82%) as a white solid. $[\alpha]_D^{20}$ = +32.0 (c 0.10, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.85 (d, *J* = 3.7 Hz, 1H), 4.51 (d, *J* = 8.4 Hz, 1H), 4.43 (d, *J* = 7.7 Hz, 1H), 4.31 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.19 (d, *J* = 2.6 Hz, 1H), 4.08 – 4.01 (m, 3H), 3.98 (dd, *J* = 10.3, 2.0 Hz, 1H), 3.92 – 3.83 (m, 4H), 3.77 – 3.66 (m, 5H), 3.63 – 3.56 (m, 2H), 3.55 – 3.40 (m, 4H), 2.01 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (126 MHz, D_2O) δ 174.21, 174.09, 104.14, 101.12, 97.66, 75.89, 75.39, 74.49, 73.23, 72.00, 70.11, 69.59, 69.43, 69.32, 68.37, 68.09, 66.53, 60.52, 60.17, 55.05, 54.09, 47.86, 21.78, 21.61. HRMS (ESI) calcd for $C_{25}H_{42}N_3O_{18}$ $[M-H]^-$ 672.2469, found 672.2475.

Synthesis of core 4 mucin-type *O*-glycan (5)

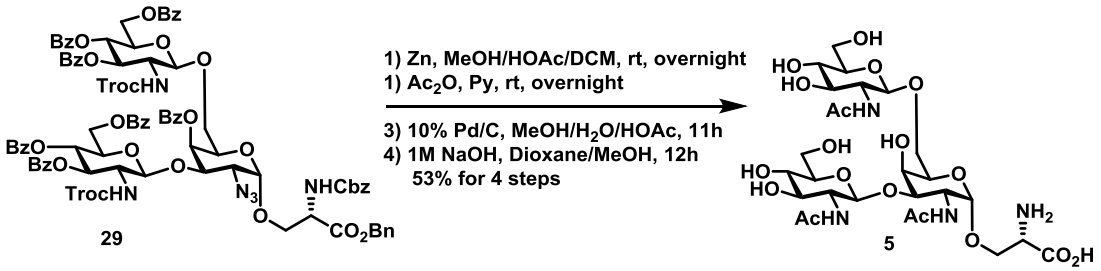
L-Serine *O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-*N*-2,2,2-tri-chloroethoxycarbonyl-β-D-glucopyranosyl)-(1→6)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-α-D-galactopyranosyl)-(3→1)-*O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonyl-β-D-glucopyranosyl)-benzyl ester (29)



Compound **39** (428 mg, 0.50 mmol) was dissolved in anhydrous THF (1.6 mL), and HF/pyridine (70%, 0.45 mL, 4.98 mmol) was added dropwise. The resulting mixture was stirred overnight at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue

was purified by column chromatography on silica gel (PE:EA = 2:1) to afford the acceptor (292.6 mg, 95%,) as a white solid. A suspension of donor **33** (211.0 mg, 0.24 mmol), acceptor (60.0 mg, 0.097 mmol), and activated 3Å MS (300 mg) in anhydrous DCM (2.9 mL) was stirred at room temperature for 15 min and was then cooled to -15 ℃. NIS (217.5 mg, 0.97 mmol) and HOTf (Trifluoromethanesulfonic acid) (21 μL, 0.24 mmol) were added successively. The resulting mixture was stirred at -15 ℃ for 3.5 h, then quenched with Et_3N (3 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 6:1 to 5:1) to afford **29** (165.3 mg, 89%) as a white solid. $[\alpha]_D^{24}$ = + 47.1 (c 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.85 (m, 16H, Ar), 7.56 – 7.45 (m, 7H, Ar), 7.43 – 7.29 (m, 22H, Ar), 6.10 (d, *J* = 9.1 Hz, 3H), 5.83 (t, *J* = 10.3 Hz, 1H), 5.71 (s, 1H, H-4_{GalN}), 5.60 (t, *J* = 9.6 Hz, 2H), 5.44 (d, *J* = 8.9 Hz, 1H), 5.28 (s, 2H), 5.20 (s, 2H), 5.04 (t, *J* = 9.5 Hz, 2H), 4.96 (s, 1H, H-1_{GalN}), 4.79 (d, *J* = 12.1 Hz, 1H), 4.71 – 4.64 (m, 2H), 4.60 (d, *J* = 11.1 Hz, 3H), 4.50 (d, *J* = 10.5 Hz, 2H), 4.40 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.22 – 4.03 (m, 7H, H-3_{GalN}), 3.92 – 3.65 (m, 3H, H-2_{GalN}, H-2_A, H-2_B), 3.51 (t, *J* = 10.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 166.2, 166.12, 166.06, 165.96, 165.33, 165.28, 165.0, 156.0, 154.1, 154.0, 136.0, 135.1, 133.5, 133.4, 133.3, 133.1, 132.9, 129.88, 129.85, 129.78, 129.71, 129.69, 129.60, 129.5, 129.4, 128.9, 128.81, 128.78, 128.73, 128.70, 128.66, 128.62, 128.59, 128.46, 128.42, 128.37, 128.31, 128.2, 101.5, 100.2, 98.2, 95.5, 95.2, 76.0, 74.4, 74.2, 72.1, 72.0, 71.93, 71.85, 71.5, 70.1, 69.7, 69.4, 69.0, 68.2, 67.8, 67.3, 63.2, 62.4, 59.2, 57.1, 56.7, 54.3. MS (Maldi-TOF) calcd for $C_{91}H_{80}N_6O_{28}Cl_6Na$ $[M+Na]^+$1937.3049, found 1937.3041.

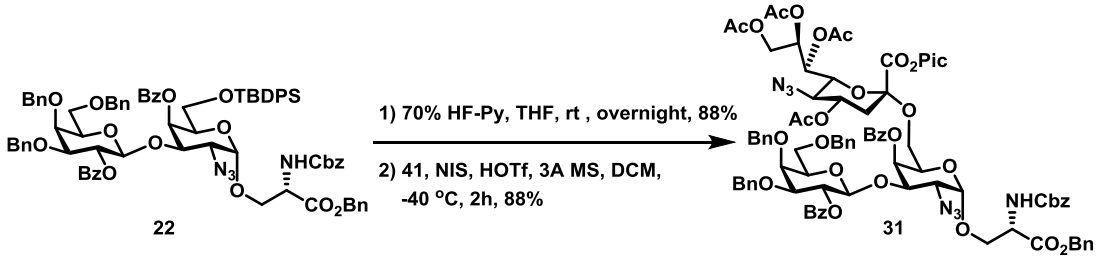
_O_-[2-(Acetylamino)-2-deoxy-β-D-glucopyranosyl)-(1→6)-_O_-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl])-(3→1)-_O_-[2-(Acetylamino)-2-deoxy-β-D-glucopyranosyl])- L-serine (5)



To a solution of compound **29** (160 mg, 0.08 mmol) in MeOH/AcOH/DCM (12 mL/6 mL/6 mL)was added Zn powder (1.64g, 25.02 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was filtered, the solvent was removed under vacuum to give the intermediate. The above intermediate was then dissolved in anhydrous Py (2 mL), and Ac_2O (0.59 mL, 6.26 mmol) was added slowly. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:30) to afford intermediate (120.7 mg, 87%). A mixture of the above intermediate (120 mg, 0.07 mmol) and Pd/C (170 mg, 10%) in MeOH/H_2O/HOAc (8 mL/0.8 mL/0.08 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo* afford the intermediate. To a solution of above intermediate in Dioxane/MeOH (2 mL/2 mL) was added 2 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O =1:1) to afford **5** (31.6 mg, 60% for two steps) as a white solid. $[\alpha]_D^{20}$ = +9.6 (c 0.15, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.85 (d, *J* = 3.6 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.26 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.21 (s, 1H), 4.14 – 4.05 (m, 2H), 4.04 – 3.99 (m, 1H), 3.97 – 3.83 (m, 4H), 3.80 – 3.66 (m, 6H), 3.59 – 3.51 (m, 2H), 3.51 – 3.40 (m, 4H), 2.05 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (151 MHz, D_2O) δ 174.4, 174.4, 173.7, 102.4, 101.5, 97.9, 76.0, 75.8, 75.6, 73.8, 73.4, 70.9, 70.1, 70.0, 69.9, 69.7, 69.5, 68.9, 60.6, 60.4, 55.51, 55.47, 48.2, 22.23, 22.16, 22.1. HRMS (ESI) calcd for $C_{27}H_{45}N_4O_{18}$ [M-H]$^-$ 713.2734, found 713.2734.

Synthesis of 2,6 STF antigen (11)

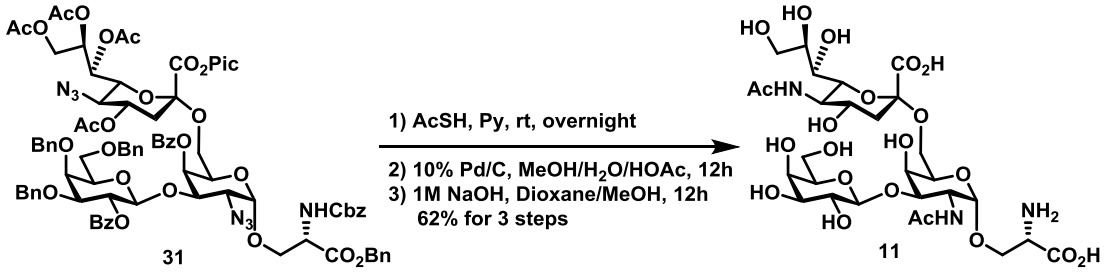
L-Serine 5-azido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-3-*O*-levulinoyl-2-deoxy-α-D-galactopyranosyl)-(3→1)-*O*-(3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-galatopyranosyl)-benzyl ester (31)



Compound **22** (358 mg, 0.26 mmol) was dissolved in anhydrous THF (1.0 mL), and HF/pyridine (70%, 0.23 mL, 2.56 mmol) was added dropwise. The resulting mixture was stirred overnight at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 2:1) to afford the acceptor (262.4 mg, 88%,) as a white foam. A suspension of donor **36** (112 mg, 0.17 mmol), acceptor (79 mg, 0.07 mmol), and activated 3Å MS (200 mg) in anhydrous DCM (3.4 mL) was stirred at room temperature for 15 min and was then cooled to -40 ℃. NIS (91.8 mg, 0.41 mmol) and HOTf (Trifluoromethanesulfonic acid) (15 μL, 0.17 mmol) were added successively. The resulting mixture was stirred at -40 ℃ for 2 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 1.5:1, containing 2% Et_3N) to afford **31** (101.3 mg, 88%) as a white solid. $[\alpha]_D^{20}$ = +18.4 (c 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H), 7.91 (d, *J* = 5.5 Hz, 4H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.39 – 7.10 (m, 31H), 6.04 (d, *J* = 8.3 Hz, 1H), 5.55 (s, 1H), 5.52 – 5.42 (m, 2H), 5.32 – 5.23 (m, 2H), 5.19 – 4.96 (m, 6H), 4.88 (d, *J* = 11.7 Hz, 1H), 4.81 (d, *J* = 2.8 Hz, 1H), 4.72 (d, *J* = 7.7 Hz, 1H), 4.62 – 4.55 (m, 2H), 4.54 – 4.36 (m, 4H), 4.25 (d, *J* = 12.1 Hz, 1H), 4.10 (dd, *J* = 12.5, 4.6 Hz, 1H), 4.06 – 4.01 (m, 1H), 4.01 – 3.91

(m, 4H), 3.87 (d, *J* = 10.5 Hz, 1H), 3.73 – 3.66 (m, 1H), 3.66 – 3.53 (m, 5H), 3.53 – 3.44 (m, 1H), 3.18 (t, *J* = 10.1 Hz, 1H), 2.67 (dd, *J* = 12.8, 4.5 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H), 1.89 (s, 3H), 1.66 (t, *J* = 12.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 169.9, 169.7, 169.5, 166.8, 165.4, 165.1, 156.2, 154.6, 149.5, 138.7, 138.1, 137.7, 136.9, 135.2, 132.73, 132.70, 130.3, 129.9, 129.8, 128.7, 128.60, 128.56, 128.5, 128.32, 128.26, 128.21, 128.17, 128.0, 127.9, 127.71, 127.66, 127.3, 123.0, 121.5, 101.8, 99.1, 98.5, 79.7, 77.4, 74.4, 73.7, 73.6, 72.6, 71.9, 71.8, 71.7, 71.0, 70.2, 69.2, 68.9, 68.4, 68.2, 68.2, 67.6, 67.5, 67.2, 63.9, 62.0, 60.1, 59.6, 54.6, 36.9, 20.9, 20.8, 20.73, 20.67. HRMS (ESI) calcd for $C_{88}H_{90}N_8O_{27}Na$ $[M+Na]^+$ 1713.5808, found 1713.5817.

5-acetamido-3,5-dideoxy-D-glycero-D-galacto-non-2-ulopyranosylonic acid-(2→6)-*O*-[2-(Acetylamino)-2-deoxy-α-D-galactopyranosyl]-(3→1)-*O*-β-D-galatopyranosyl)-L-serine (11)

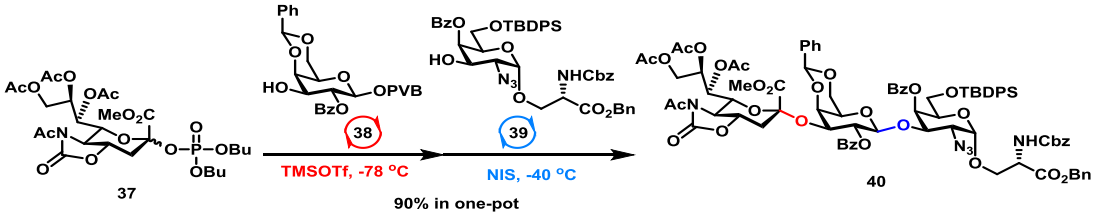


To a solution of compound **31** (80 mg, 0.05 mmol) in pyridine (1 mL) was added AcSH (1.7 mL, 18.92 mmol). The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:40 to 1:9) to afford intermediate (81.5 mg, 100%). A mixture of the above intermediate (81.5 mg, 0.05 mmol) and Pd/C (524 mg, 10%) in MeOH/H_2O/HOAc (5 mL/0.5 mL/0.05 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo* to afford the intermediate.To a solution of above intermediatein dioxane/MeOH (1 mL/1 mL) was added 2 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and

concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (H_2O) to afford **11** (22.4 mg, 62%) as a white solid. $[\alpha]_D^{20}$ = +89.7 (c 0.19, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.90 (d, *J* = 3.7 Hz, 1H), 4.46 (d, *J* = 7.7 Hz, 1H), 4.34 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.25 (d, *J* = 2.3 Hz, 1H), 4.18 – 4.02 (m, 3H), 4.00 – 3.96 (m, 1H), 3.95 – 3.80 (m, 6H), 3.79 – 3.56 (m, 9H), 3.54 – 3.48 (m, 1H), 2.74 (dd, *J* = 12.4, 4.5 Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 1.68 (t, *J* = 12.1 Hz, 1H). ^{13}C NMR (151 MHz, D_2O) δ 175.0, 174.6, 173.5, 104.6, 100.2, 98.2, 76.5, 74.9, 72.55, 72.48, 71.7, 70.5, 69.4, 68.6, 68.5, 68.2, 67.0, 63.8, 62.6, 60.9, 54.4, 51.8, 48.3, 40.2, 22.03, 21.98. HRMS (ESI) calcd for $C_{28}H_{46}N_3O_{21}$ $[M-H]^-$ 760.2629, found 760.2624.

Synthesis of 2,3 STF antigen (12)

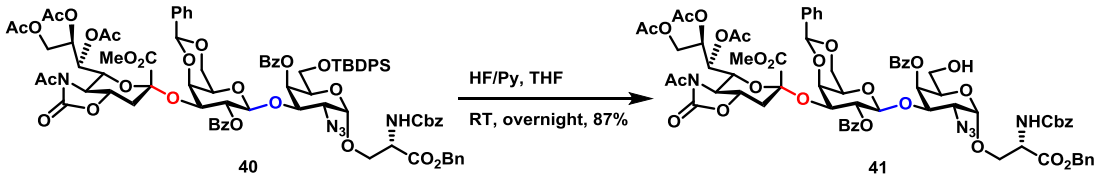
L-Serine 5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(*p*-methoxy)benzyl-α-D-galactopyranosyl-1→6)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-6-*O*-tert-butyl-diphenylsilyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (40)



A suspension of donor **37**[19] (240 mg, 0.38 mmol), PVB acceptor **38**[20] (87.4 mg, 0.15 mmol), and activated 4Å MS (430 mg) in anhydrous DCM (3.8 ml) was stirred at room temperature for 15 min and was then cooled to -78 ℃. TMSOTf (0.068 mL, 0.38 mmol) was added to the mixture dropwise. After being stirred at -78 ℃ for another 15 min, acceptor **39** (103.8 mg, 0.12 mmol), NIS (51 mg, 0.23 mmol) were added successively. The reaction was allowed to warm to -40 ℃. After being stirred at -40 ℃ for another 2 h, the reaction was quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether/ethyl acetate, 1.5:1) and Sephadex TM LH-20 (MeOH-DCM =1:1) to afford **40** (182.3 mg, 90%) as a white foam. $[\alpha]_D^{20}$ =

+82.9 (c 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 6.6 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 6.8 Hz, 2H), 7.37 – 7.22 (m, 25H), 5.90 (s, 1H), 5.78 (s, 1H), 5.67 (d, *J* = 8.7 Hz, 1H), 5.63 – 5.51 (m, 2H), 5.30 (t, *J* = 8.9 Hz, 1H), 5.22 – 5.04 (m, 5H), 4.90 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 2.8 Hz, 1H), 4.62 (d, *J* = 8.3 Hz, 1H), 4.55 – 4.46 (m, 2H), 4.42 – 4.33 (m, 2H), 4.24 (dd, *J* = 9.7, 3.5 Hz, 1H), 4.17 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.07 (d, *J* = 12.0 Hz, 1H), 4.04 – 3.96 (m, 3H), 3.91 (dd, *J* = 11.6, 9.8 Hz, 1H), 3.77 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.70 – 3.59 (m, 2H), 3.56 (dd, *J* = 10.6, 2.6 Hz, 1H), 3.49 (t, *J* = 10.4 Hz, 1H), 3.23 (s, 3H), 2.54 (dd, *J* = 11.8, 2.9 Hz, 1H), 2.34 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.81 (t, *J* = 12.4 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 171.11, 171.05, 169.8, 169.4, 165.9, 165.2, 164.9, 156.0, 153.5, 137.9, 136.1, 135.60, 135.58, 135.1, 133.3, 133.1, 132.9, 132.7, 130.2, 130.1, 129.9, 129.7, 129.7, 129.1, 128.7, 128.68, 128.65, 128.54, 128.49, 128.4, 128.24, 128.22, 128.1, 127.72, 127.70, 126.65, 101.2, 100.9, 99.5, 99.0, 76.1, 74.8, 74.4, 74.2, 74.0, 72.1, 71.2, 70.6, 69.8, 68.8, 68.5, 67.7, 67.4, 66.4, 63.3, 62.8, 59.6, 59.1, 54.4, 52.8, 36.7, 26.8, 24.5, 21.2, 21.0, 20.8, 19.2. HRMS (ESI) calcd for $C_{86}H_{91}N_5O_{28}SiNa$ $[M+Na]^+$ 1692.5512, found 1692.5513.

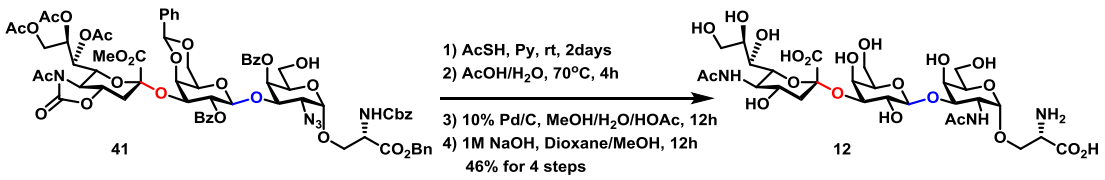
L-Serine 5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(*p*-methoxy)benzyl-α-D-galactopyranosyl-1→6)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-α-D-galactopyranosyl)-benzyl ester (41)



Compound **40** (197 mg, 0.12 mmol) was dissolved in anhydrous THF (1.2 mL), and HF/pyridine (70%, 0.15 mL, 1.18 mmol) was added dropwise. The resulting mixture was stirred overnight at room temperature, the reaction mixture was then quenched with Et_3N, diluted with ethyl acetate and washed with saturated $NaHCO_3$

solution and brine. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 1:1) to afford **41** (146.3 mg, 87%,) as a white foam. $[\alpha]_D^{20}$ = +61.0 (c 0.12, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.1 Hz, 4H), 7.63 – 7.49 (m, 2H), 7.45 – 7.24 (m, 15H), 7.11 (t, *J* = 7.1 Hz, 2H), 6.96 (d, *J* = 6.7 Hz, 2H), 5.89 (s, 1H), 5.82 (d, *J* = 6.8 Hz, 1H), 5.71 (s, 1H), 5.54 (d, *J* = 8.3 Hz, 1H), 5.48 (s, 1H), 5.33 (t, *J* = 8.2 Hz, 1H), 5.22 – 5.06 (m, 5H), 4.87 (d, *J* = 6.9 Hz, 1H), 4.81 (s, 1H), 4.59 (s, 1H), 4.54 – 4.42 (m, 2H), 4.37 (s, 1H), 4.34 – 4.22 (m, 2H), 4.11 (d, *J* = 8.9 Hz, 1H), 4.08 – 3.93 (m, 4H), 3.93 – 3.84 (m, 1H), 3.69 – 3.41 (m, 6H), 3.28 (s, 3H), 2.53 (d, *J* = 10.2 Hz, 1H), 2.34 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.81 (t, *J* = 12.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.99, 170.97, 169.6, 169.3, 168.2, 165.8, 165.0, 155.8, 153.4, 137.7, 136.1, 135.1, 133.3, 132.9, 130.2, 129.7, 129.5, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 126.4, 101.6, 101.1, 99.5, 99.1, 76.1, 75.2, 74.7, 74.3, 74.2, 74.1, 72.0, 70.6, 70.3, 69.6, 69.2, 68.3, 67.7, 67.4, 66.3, 63.2, 60.0, 59.2, 59.1, 54.5, 52.7, 36.7, 29.7, 24.4, 21.0, 20.9, 20.6. HRMS (ESI) calcd for $C_{70}H_{73}N_5O_{28}Na$ $[M+Na]^+$ 1454.4334, found 1454.4341.

5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonic acid-(2→3)-*O*-β-D-galactopyranosyl-*O*-[2-(Acetylamino)-2-deoxy-α-D-glucopyranosyl])-L-serine (12)

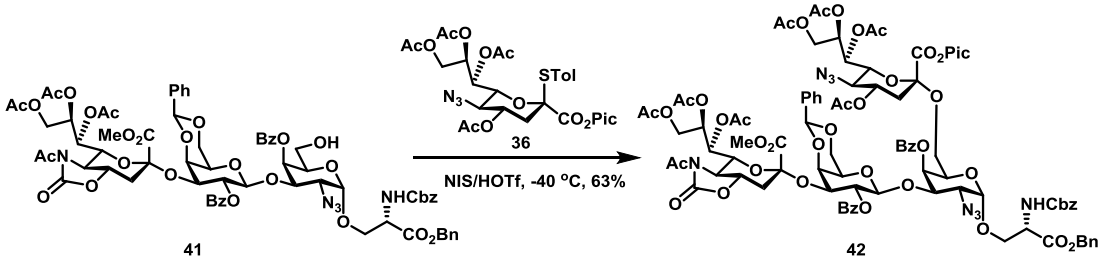


To a solution of compound **41** (56 mg, 0.04 mmol) in pyridine (2 mL) was added AcSH (0.71 mL, 7.82 mmol). The reaction mixture was stirred at room temperature for two days. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:50) to afford intermediate (47.6 mg, 84%). The above intermediate (47 mg, 0.03 mmol) was dissolved in AcOH/H_2O (2.5 mL, v/v 4:1), 70 ℃ stirred for 4 h, then the reaction mixture was concentrated *in*

vacuo. The residue was purified by flash chromatography (MeOH/DCM, 1:50 to 1:30) to afford intermediate (31.6 mg, 72%). A mixture of the above intermediate (31 mg, 0.02 mmol) and Pd/C (54 mg, 10%) in MeOH/H_2O/HOAc (4 mL/0.4 mL/0.04 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo* to afford the intermediate (21.4 mg, 83%). To a solution of above intermediatein dioxane/MeOH (1 mL/1 mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O, 1:1) to afford **12** (13.1 mg, 91%) as a white solid. $[\alpha]_D^{20}$ = +40.2 (c 0.10, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.88 (d, *J* = 3.4 Hz, 1H), 4.47 (d, *J* = 7.6 Hz, 1H), 4.30 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.22 – 4.09 (m, 3H), 4.07 – 3.98 (m, 2H), 3.97 – 3.86 (m, 3H), 3.85 – 3.74 (m, 4H), 3.73 – 3.51 (m, 8H), 3.46 (d, *J* = 9.3 Hz, 1H), 2.43 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.63 (t, *J* = 12.3 Hz, 1H). ^{13}C NMR (126 MHz, D_2O) δ 174.9, 174.3, 104.3, 102.5, 97.6, 77.1, 76.6, 74.3, 71.1, 70.6, 69.5, 68.6, 68.2, 68.0, 67.5, 65.8, 62.9, 60.8, 60.3, 54.2, 51.6, 47.9, 21.7. HRMS (ESI) calcd for $C_{28}H_{46}N_3O_{21}$ $[M-H]^-$ 760.2629, found 760.2624.

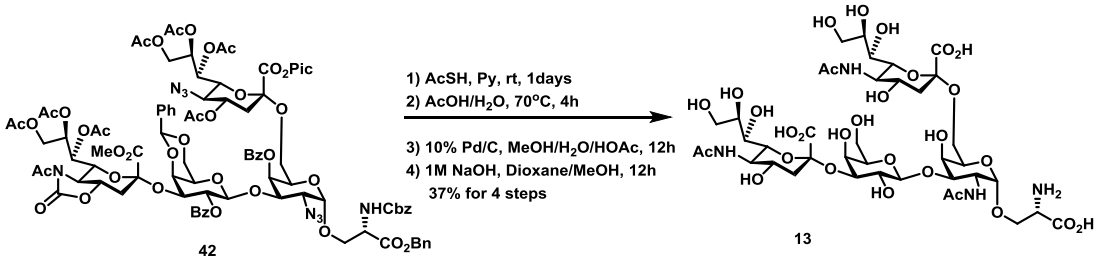
Synthesis of glycophorin (13)

L-Serine 5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(*p*-methoxy)benzyl-α-D-galactopyranosyl-1→6)-*N*-(benzyloxycarbonyl)-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-α-D-galactopyranosyl)-(3→1)-*O*-(3,4,6-tri-*O*-benzyl-2- *O*-benzoyl-β-D-galatopyranosyl)-benzyl ester (42)



A suspension of donor **36** (164.4 mg, 0.25 mmol), acceptor **41** (143 mg, 0.10 mmol), and activated 3Å MS (310 mg) in anhydrous DCM (5 mL) was stirred at room temperature for 15 min and was then cooled to -40 ℃. NIS (134.8 mg, 0.60 mmol) and HOTf (22 μL, 0.25 mmol) were added successively. The resulting mixture was stirred at -40 ℃ for 2 h, then quenched with Et_3N (1 mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether-ethyl acetate, 1:1) and Sephadex TM LH-20 (MeOH-DCM =1:1) to afford **42** (122.9 mg, 63%) as a white foam. $[\alpha]_D^{20}$ = +60.9 (c 0.18, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.89 (t, *J* = 8.2 Hz, 4H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.39 – 7.27 (m, 17H), 7.24 (d, *J* = 6.5 Hz, 3H), 7.21 – 7.18 (m, 1H), 6.06 (d, *J* = 8.4 Hz, 1H), 5.87 (s, 1H), 5.63 (d, *J* = 2.2 Hz, 1H), 5.60 – 5.52 (m, 2H), 5.44 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.32 – 5.25 (m, 3H), 5.20 – 5.16 (m, 2H), 5.15 – 5.06 (m, 4H), 5.06 – 4.99 (m, 1H), 4.89 (d, *J* = 7.9 Hz, 1H), 4.86 (d, *J* = 3.4 Hz, 1H), 4.65 – 4.57 (m, 1H), 4.54 – 4.46 (m, 2H), 4.40 (d, *J* = 3.3 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.26 (dd, *J* = 17.4, 7.7 Hz, 2H), 4.15 (dd, *J* = 10.6, 3.1 Hz, 1H), 4.12 – 4.05 (m, 2H), 4.04 – 3.97 (m, 3H), 3.92 – 3.87 (m, 2H), 3.73 – 3.67 (m, 1H), 3.67 – 3.61 (m, 2H), 3.56 – 3.46 (m, 2H), 3.22 (s, 3H), 3.18 (t, *J* = 10.1 Hz, 1H), 2.69 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.55 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.34 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.88 (s, 3H), 1.81 (t, *J* = 12.3 Hz, 1H), 1.69 (t, *J* = 12.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 171.2, 171.1, 170.9, 170.0, 169.79, 169.77, 169.6, 169.5, 166.9, 165.9, 165.3, 164.9, 156.2, 154.5, 153.5, 149.6, 137.9, 137.0, 136.3, 135.3, 132.9, 132.7, 130.22, 130.18, 129.9, 129.7, 129.1, 128.8, 128.7, 128.6, 128.4, 128.3, 128.22, 128.19, 126.6, 123.2, 121.6, 101.2, 100.6, 99.5, 99.1, 98.6, 76.2, 74.9, 74.34, 74.25, 73.2, 72.1, 71.8, 71.0, 70.6, 69.9, 69.3, 68.9, 68.5, 68.4, 68.2, 67.7, 67.6, 67.3, 66.5, 63.9, 63.3, 62.0, 60.1, 59.6, 59.1, 54.5, 52.8, 36.8, 29.8, 24.5, 21.2, 21.1, 21.0, 20.79, 20.77. HRMS (ESI) calcd for $C_{93}H_{99}N_9O_{39}Cl$ $[M+Cl]^-$ 2000.5734, found 2000.5737.

5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonic acid-(2→3)-*O*-β-D-galactopyranosyl-*O*-[2-(Acetylamino)-2-deoxy-α-D-glucopyranosyl])-(3→1)-*O*-β-D-galatopyranosyl)-L-serine (13)



To a solution of compound **42** (68 mg, 0.03 mmol) in pyridine (2 mL) was added AcSH (1.25 mL, 13.83 mmol). The reaction mixture was stirred at room temperature for one day. Then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:50 to 1:30) to afford intermediate (67 mg, 97%). The above intermediate (67 mg, 0.03 mmol) was dissolved in AcOH/H_2O (2.5 mL, v/v 4:1), 70 ℃ stirred for 4 h, then the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (MeOH/DCM, 1:30) to afford intermediate (50.6 mg, 79%). A mixture of the above intermediate (50 mg, 0.03 mmol) and Pd/C (93 mg, 10%) in MeOH/H_2O/HOAc (5 mL/0.5 mL/0.05 mL) was stirred under an atmosphere of H_2 at room temperature for 12 h, after which the reaction mixture was filtered and concentrated *in vacuo* to afford the intermediate (31.6 mg, 76%). To a solution of above intermediate (31 mg, 0.02 mmol) in dioxane/MeOH (1 mL/1 mL) was added 1 mL 1M NaOH aq. The reaction was stirred for 12 h at room temperature. After the reaction was completed, the reaction was neutralized to pH = 7 by acetic acid, then filtered and concentrated. The residue was purified by column chromatography on Sephadex TM LH-20 (MeOH-H_2O, 1:1) to afford **13** (12.8 mg, 63%) as a white solid. $[\alpha]_D^{20}$ = +35.0 (c 0.16 , H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.88 (d, *J* = 3.4 Hz, 1H), 4.49 (d, *J* = 7.6 Hz, 1H), 4.30 (dd, *J* = 11.2, 3.5 Hz, 1H), 4.23 (s, 1H), 4.22 – 4.12 (m, 2H), 4.10 – 3.99 (m, 3H), 3.98 – 3.74 (m, 10H), 3.73 – 3.53 (m, 11H), 3.49 (d, *J* = 9.7 Hz, 1H), 2.71 (dd, *J* = 12.3, 4.5 Hz, 1H), 2.46 (dd, *J* = 12.9, 4.4 Hz, 1H), 2.03 (s, 1H), 2.01 (s, 3H), 1.66 (t, *J* = 12.1 Hz, 2H). ^{13}C NMR (201 MHz, D_2O) δ 175.4, 175.0, 174.7, 174.7, 173.5,

104.8, 102.9, 100.3, 98.1, 77.6, 77.0, 74.7, 72.6, 71.7, 71.6, 69.9, 69.4, 69.1 68.6, 68.4, 68.24, 68.23, 67.9, 66.2, 63.8, 63.3, 62.6, 60.7, 54.6, 52.0, 51.8, 48.3, 40.6, 40.2, 22.11, 22.10, 22.0. HRMS (ESI) calcd for $C_{39}H_{64}N_4O_{29}$ $[M-2H]^{2-}$ 525.1755, found 525.1752.

Mechanistic studies

To shed light on the reactive intermediates formed with the TMSI and Ph_3PO reagent combination, we studied the activation of donor **17a** by NMR spectroscopy. When donor **17a** was activated with TMSI in $CDCl_3$ in the absence of Ph_3PO additive (Within 5 min), a mixture of two products was formed. The products were tentatively assigned as **α-iodide** (**Figure S1**, H-1: δ = 6.93 ppm, *J* = 3.9 Hz) and its **β-iodide** (H-1: δ = 5.65 ppm, *J* = 9.7 Hz), **α**/**β** = 4:1. In time (4 h), the **β-iodide** isomerized into its more stable **α-iodide (α**/**β** > 20:1**)**. Alternatively, treatment of a mixture of donor **17a** and Ph_3PO in $CDCl_3$ with TMSI (Within 5 min), showed a clean conversion of the imidate into the anomeric **α-iodide**. The **β-iodide** was not observed, nor could we detect the presence of any anomeric phosphonium species by NMR spectroscopy. However, through ESI-MS experiment monitoring, we detected the MS of **phosphonium iodide intermediate** (**Figure S2**).

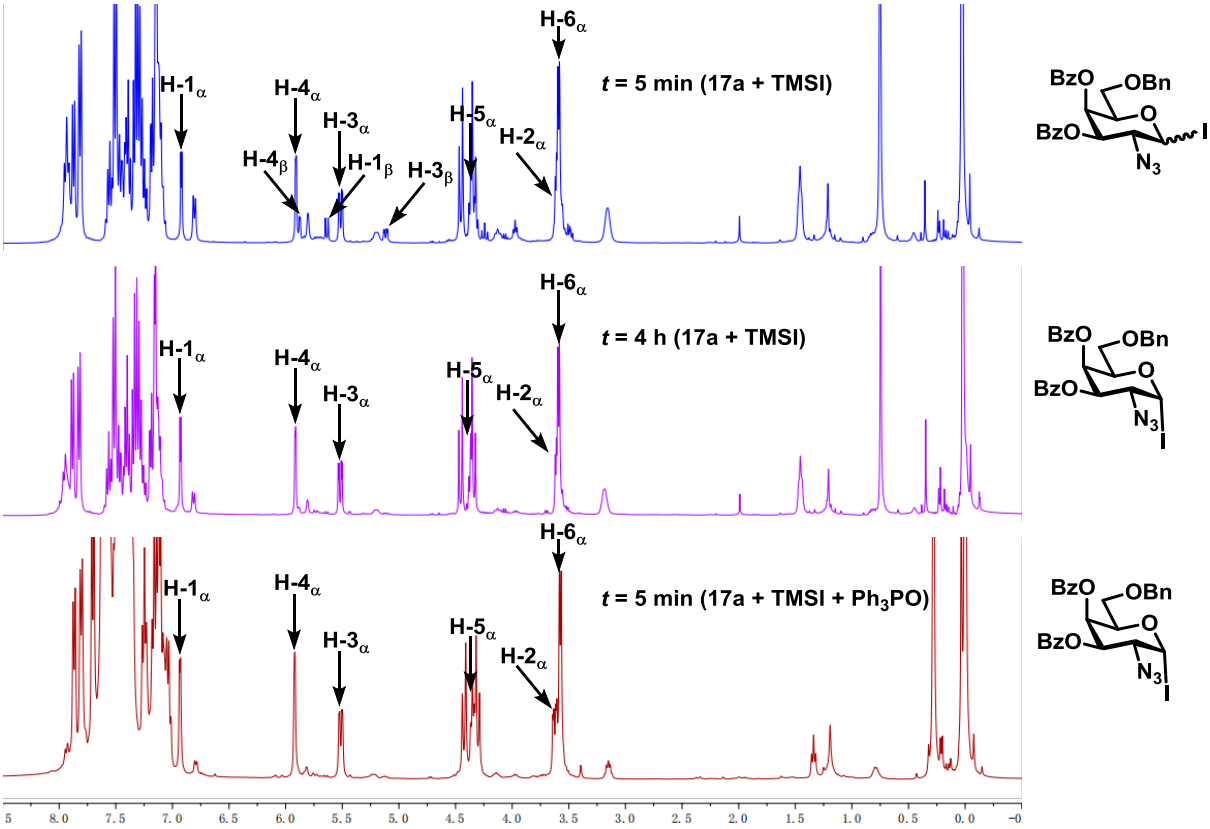


Figure S1. Detection of the anomeric iodides intermediates by ^{1}H-NMR

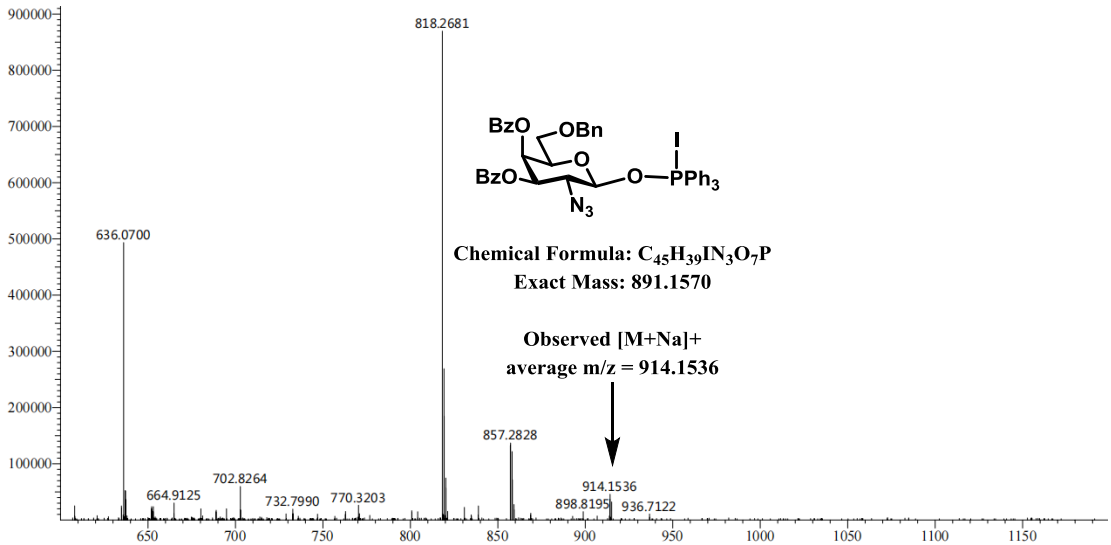
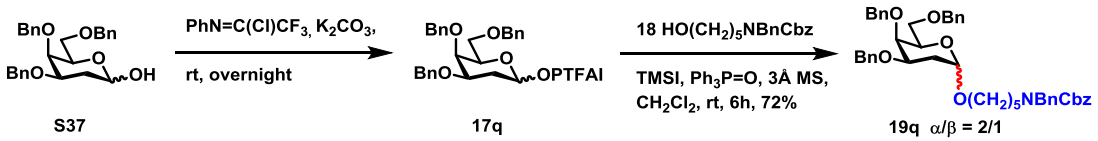


Figure S2. Detection of the phosphonium iodide intermediate by MS

Glycosylation with 2-deoxy Galactosyl PTFAI donors 17q-s

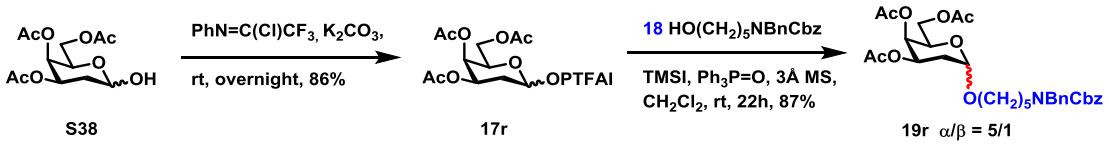
***N*-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranoside (19q)**



S37 17q 19q α/β = 2/1

To a solution of **S37**[21] (94.5 mg, 0.22 mmol) in acetone (1.0 mL) were added 2,2,2-trifluoro-N-phenylacetimidoyl chloride (58.7 mg, 0.35 mmol) and K_2CO_3 (90.2 mg, 0.65 mmol). The mixture was stirred at rt overnight, and then filtered and concentrated in vacuo to afford **17q** (This compound is unstable, so it was used directly without further structural characterization). The glycosylation reaction was carried out according to General Experimental Procedures at rt for 6 h, using donor **17q** (131.9 mg, 0.22 mmol), acceptor **18** (106.8 mg, 0.33 mmol), DCM 2.2 mL, Ph_3P=O (363.2 mg, 1.31 mmol) and TMSI (31 μL, 0.22 mmol). The product was purified by silica gel column chromatography (PE-EA, 20:1-4:1) to afford **19q** (116.2 mg, 72%, α/β = 2:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.12 (m, 25H, Ar), 5.16 (d, *J* = 10.1 Hz, 2H, CH_2-Cbz), 4.96 – 4.87 (m, 2H, H-1α, CH_2-Bn), 4.65 – 4.54 (m, 3H, CH_2-Bn), 4.51 – 4.38 (m, 4H, CH_2-Bn), 4.36 – 4.32 (m, H-1β), 3.94 – 3.80 (m, 3H, H-3α), 3.66 – 3.49 (m, 3H, H-4α), 3.35 – 3.14 (m, 3H), 2.26 – 2.16 (m, 1H, H-2), 2.13 – 1.93 (m, 1H, H-2), 1.58 – 1.43 (m, 4H, CH_2), 1.32 – 1.18 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 156.2, 139.0, 138.96, 138.7, 138.4, 138.2, 138.0, 136.9, 128.57, 128.55, 128.48, 128.43, 128.40, 127.39, 128.3, 128.23, 128.15, 128.0, 127.93, 127.86, 127.8, 127.74, 127.68, 127.63, 127.51, 127.45, 127.40, 127.3, 100.5 (C-1β), 97.8 (C-1α), 75.0, 74.3, 74.2, 74.1, 73.6, 73.5, 73.2, 71.9, 70.5, 70.2, 70.0, 69.7, 69.4, 69.0, 67.23, 67.19, 50.5, 50.3, 47.2, 46.2, 32.9, 31.6, 31.5, 31.3, 30.2, 29.7, 29.34, 29.28, 28.0, 27.6, 23.6, 23.4. HRMS (ESI) calcd for $C_{47}H_{53}NO_7Na$ [M+Na]+ 766.3714, found 766.3718.

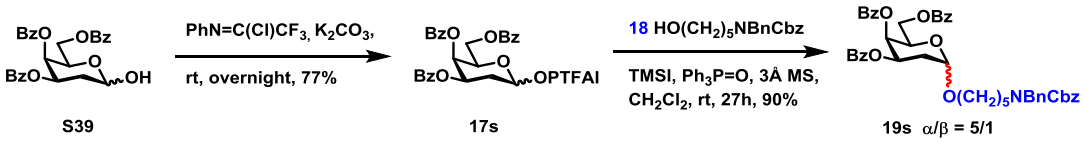
_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-deoxy-3,4,6-tri-_O_-acetyl-D-galactopyranoside (19r)



S38 17r 19r α/β = 5/1

To a solution of **S38**[21] (318.1 mg, 1.10 mmol) in acetone (2.0 mL) were added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (250.2 mg, 1.21 mmol) and K_2CO_3 (227.1 mg, 1.64 mmol). The mixture was stirred at rt overnight, and then filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (PE-EA, 30:1-4:1, containing 1% Et_3N) to afford **17r** (435.8 mg, 86%) as a yellow syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.08 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 5.46 – 5.40 (m, 1H), 5.37 – 5.26 (m, 1H), 4.30 (s, 1H), 4.22 – 4.04 (m, 3H), 2.20 – 2.12 (m, 4H), 2.08 – 2.00 (m, 7H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.48, 170.46, 170.3, 170.2, 170.02, 169.96, 145.5, 143.6, 143.4, 128.93, 128.89, 124.6, 119.5, 119.3, 94.5, 72.1, 69.5, 67.9, 66.1, 65.5, 65.2, 62.1, 61.7, 60.5, 30.5, 28.7, 20.9, 20.8, 20.75, 20.72, 14.3. HRMS (ESI) calcd for $C_{20}H_{22}NO_8F_3Na$ $[M+Na]^+$ 484.1190, found 484.1187. The glycosylation reaction was carried out according to **General Experimental Procedures** at rt for 22h, using donor **17r** (177.2 mg, 0.38 mmol), acceptor **18** (188.6 mg, 0.58 mmol), DCM 3.8 mL, Ph_3P=O (641.3 mg, 2.30 mmol) and TMSI (55 μL, 0.38 mmol). The product was purified by silica gel column chromatography (PE-EA, 3:1) to afford **19r** (199 mg, 87%, α/β = 5:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.14 (m, 10H, Ar), 5.34 – 5.31 (m, 1H, H-4α), 5.30 – 5.24 (m, 1H, H-3), 5.17 (d, *J* = 12.6 Hz, 2H, CH_2-Cbz), 5.01 – 4.92 (m, 1H, H-1α), 4.55 – 4.44 (m, 2H), 4.13 – 4.03 (m, 3H), 3.78 (t, *J* = 6.8 Hz, H-5β), 3.65 – 3.51 (m, 1H), 3.40 – 3.17 (m, 3H), 2.13 – 1.93 (m, 10H, H-2, CH_3-Ac), 1.88 – 1.80 (m, 1H, H-2), 1.62 – 1.46 (m, 4H, CH_2), 1.36 – 1.27 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 170.2, 169.9, 156.6, 156.1, 137.9, 136.8, 128.5, 128.4, 127.9, 127.8, 127.2, 100.0 (C-1β), 97.4 (C-1α), 70.9, 69.4, 68.5, 67.5, 67.1, 66.7, 66.6, 66.2, 65.4, 62.4, 61.8, 50.5, 50.3, 47.1, 46.1, 32.0, 31.5, 31.4, 30.2, 29.6, 29.15, 29.10, 27.9, 27.5, 23.5, 23.2, 20.8, 20.7, 20.6. HRMS (ESI) calcd for $C_{32}H_{42}NO_{10}$ $[M+H]^+$ 600.2803, found 600.2802.

_N_-(Benzyl)benzyloxycarbonyl-5-amino-pentyl 2-deoxy-3,4,6-tri-_O_-benzoyl-D-galactopyranoside (19s)



S39 17s 19s α/β = 5/1

To a solution of **S39**[21] (537.8 mg, 1.13 mmol) in acetone (2.0 mL) were added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (257.7 mg, 1.24 mmol) and K_2CO_3 (233.9 mg, 1.69 mmol). The mixture was stirred at rt overnight, and then filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (PE, containing 2% Et_3N) to afford **17s** (559 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.06 (m, 2H), 8.05 – 7.98 (m, 2H), 7.86 (t, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.53 – 7.46 (m, 4H), 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 2H), 7.30 – 7.21 (m, 2H), 7.14 – 7.06 (m, 1H), 6.83 – 6.70 (m, 2H), 5.95 (s, 1H), 5.82 – 5.72 (m, 1H), 4.70 – 4.56 (m, 2H), 4.49 – 4.35 (m, 1H), 2.57 – 2.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 165.6, 165.5, 165.4, 165.3, 143.5, 143.4, 133.60, 133.57, 133.34, 133.26, 133.20, 130.0, 129.9, 129.8, 129.73, 129.71, 129.51, 129.47, 129.42, 129.34, 129.30, 129.2, 128.8, 128.6, 128.5, 128.42, 128.38, 128.36, 124.4, 119.4, 119.3, 72.6, 70.0, 68.8, 67.0, 66.5, 66.1, 63.0, 62.6, 31.1, 29.3. HRMS (ESI) calcd for $C_{35}H_{28}NO_8F_3Na$ $[M+Na]^+$ 670.1659, found 670.1661. The glycosylation reaction was carried out according to **General Experimental Procedures** at rt for 22h, using donor **17s** (158.0 mg, 0.24 mmol), acceptor **18** (119.8 mg, 0.37 mmol), DCM 2.4 mL, Ph_3P=O (407.4 mg, 1.46 mmol) and TMSI (35 μL, 0.24 mmol). The product was purified by silica gel column chromatography (PE-EA, 4:1) to afford **19s** (172.9 mg, 90%, α/β = 5:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J* = 9.2 Hz, 2H, Ar), 8.02 (t, *J* = 8.1 Hz, 2H, Ar), 7.85 (d, *J* = 7.5 Hz, 2H, Ar), 7.57 (t, *J* = 7.4 Hz, 1H, Ar), 7.52 – 7.41 (m, 4H, Ar), 7.39 – 7.14 (m, 14H, Ar), 5.86 (s, 1H, H-4α), 5.80 (d, *J* = 3.0 Hz, H-4β), 5.70 (d, *J* = 11.8 Hz, 1H, H-3α), 5.43 – 5.34 (m, H-3β), 5.16 (t, *J* = 16.7 Hz, 3H, H-1α, CH_2-Cbz), 4.70 – 4.32 (m, 5H), 3.76 – 3.60 (m, 1H), 3.47 – 3.12 (m, 3H), 2.41 – 2.30 (m, 1H, H-2), 2.26 – 2.09 (m, 1H, H-2), 1.67 – 1.46 (m, 4H, CH_2), 1.38 – 1.28 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 165.7, 165.7, 165.4, 138.0, 136.9, 133.3, 133.1, 133.0, 129.9, 129.82, 129.79, 129.72, 129.65, 129.62, 129.5, 128.5, 128.42,

128.38, 128.3, 128.2, 127.9, 127.8, 127.3, 100.2 (C-1β), 97.5 (C-1α), 71.4, 69.6, 67.70, 67.65, 67.3, 67.2, 67.1, 66.4, 63.3, 62.5, 50.5, 50.3, 47.1, 46.2, 32.7, 30.8, 29.7, 29.2, 27.9, 27.5, 23.5, 23.3. HRMS (ESI) calcd for $C_{47}H_{47}NO_{10}Na$ $[M+Na]^+$ 808.3092, found 808.3095.

Computational studies

Computational details. All calculations were performed with Gaussian 09.[22] Geometry optimizations were performed in solvent with the M06-2X functional[23] and a mixed basis set of LANL2DZ for I and 6-31G(d) for other atoms. Single point energies in solvent were calculated with the M06-2X functional and a mixed basis set of SDD for I and 6-311+G(d,p) for other atoms. The SMD model[24] was used for the solvation corrections with CH_2Cl_2 as the solvent. All minima have zero imaginary frequency and all transition states have only one imaginary frequency and were confirmed by intrinsic reaction coordinate calculations. The conformational searches were performed by using CREST/xTB[25]. The 3D structures and NCI plots[26] were generated using CYLView[27] and VMD,[28] respectively.

Comparison of α-iodide with β-iodide. The control experiments shown in Figure S1 indicate that the mixture of α-iodide and β-iodide (**α**/**β** = 4:1) can be observed at the initial stage of the reaction (5 min). Then, the **α**/**β** ratio is significantly increased in 4 h (**α**/**β** > 20:1). Consistently, the computed energetics show that α-iodide is 1.8 kcal/mol more stable than β-iodide (Figure S3).

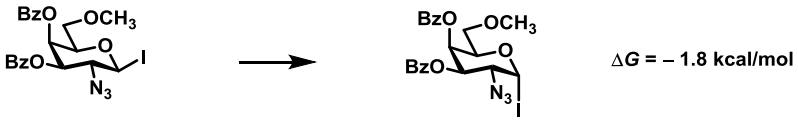


Figure S3. Energy difference between α-iodide and β-iodide.

Interactions between I and $Ph_3P=O$. For the β-anomeric phosphonium iodide species (**Int1**, Figure S4), the iodine and phosphine atoms are negatively and positively charged, respectively (charge on I: –0.977*e*; charge on P: 1.977*e*). Thus,

Int1 can be stabilized by the attractive electrostatic interactions. In addition, the NCI plots indicate that there are non-covalent interactions between I and Ph_3P=O moieties in both **Int1** and **TS4** (Figure S4), which also contribute to the stability of these structures. As such, the dissociations of I from **Int1** and **TS4** lead to less favorable **Int1a** and **TS4a**, respectively.

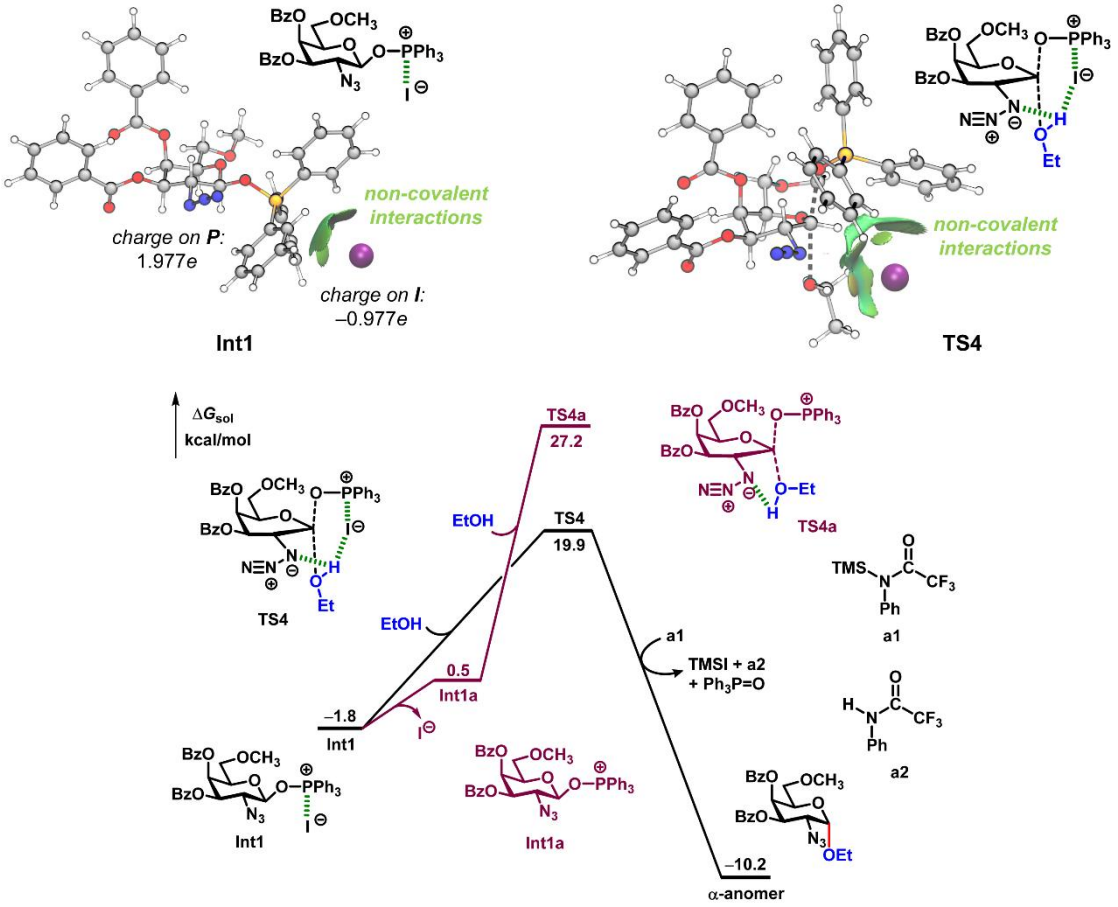


Figure S4. Interactions between I and Ph_3P=O in **Int1** and **TS4**.

Reaction of β-iodide with Ph_3P=O. As indicated in Scheme 6b in the main text, Ph_3P=O can significantly promote the S_N2 displacement of α-iodide. We further studied the reaction of β-iodide with Ph_3P=O, and the energy profiles are shown in Figure S5. The results show that Ph_3P=O can also replace the iodine atom of β-iodide. The computed S_N2 transition state (**TS5**) has a barrier of 14.7 kcal/mol, generating the α-anomeric phosphonium iodide intermediate (**Int2**). The ensuing nucleophilic attack by alcohol requires a barrier of 27.1 kcal/mol (**TS6**) to form the undesired β-anomer.

The relatively high barrier of **TS6** renders the generation of **Int2** reversible. Thus, although Ph_3P=O is more reactive than alcohol towards β-iodide (**TS5** vs. **TS1**), the overall pathway of Ph_3P=O mediated S_N2 displacement of β-iodide is less favorable than the direct S_N2 displacement of β-iodide with alcohol (**TS6** vs. **TS1**). Therefore, Ph_3P=O is less effective for the transformation of β-iodide→β-anomer. Instead, the process of β-iodide→α-anomer via **TS1** is more kinetically favorable.

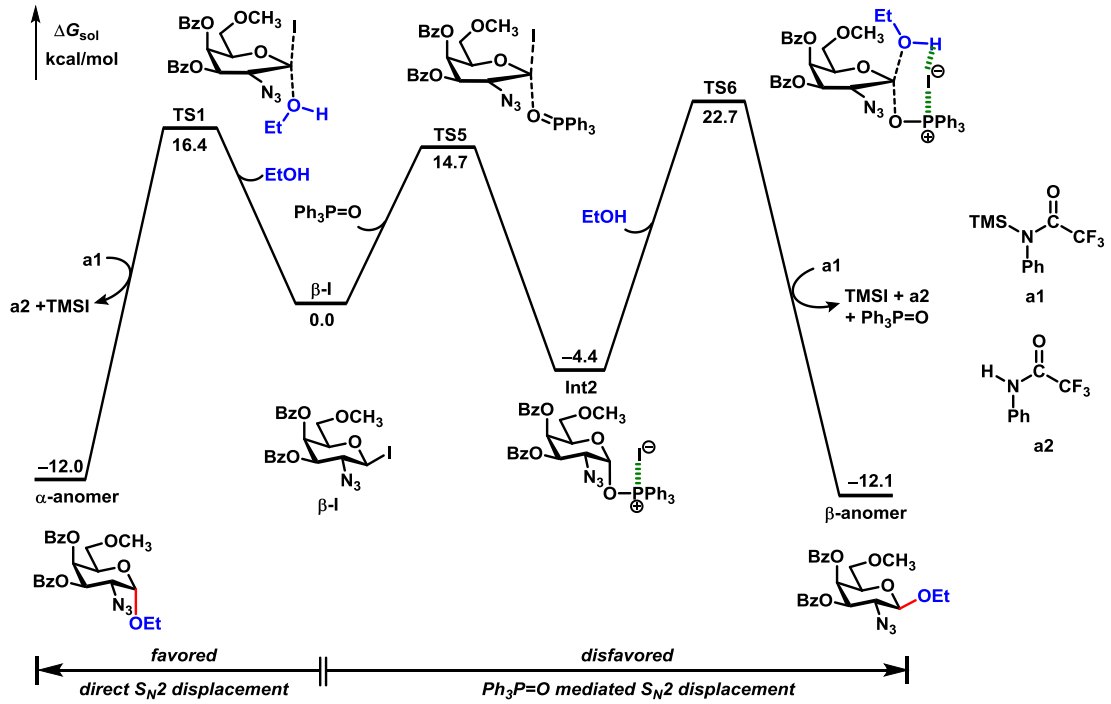


Figure S5. Energy profiles for S_N2 nucleophilic reaction of β -iodide with alcoholic acceptor.

Conformational search for key transition states. To obtain the lowest energy structures for the S_N2 displacement transition states with the β/α-anomeric phosphonium iodide species (**TS4** and **TS6**), we carried out conformational search by using CREST with the default setting. The suggested 69 conformers for **TS4** and 66 conformers for **TS6** were further calculated at the M06-2X/SDD-6-311+G(d,p)-SMD(DCM)//M06-2X/LANL2DZ-6-31(d)-SMD(DCM) level. The three lowest energy conformers of these transition states are shown in Figure S6.

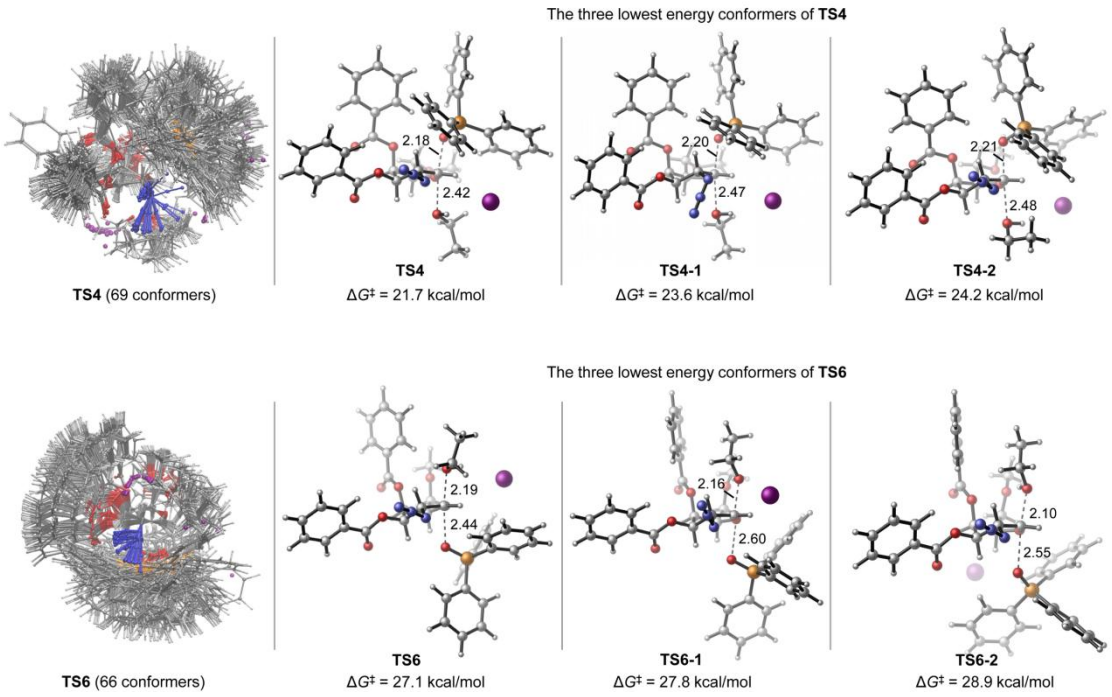


Figure S6. Results of conformational search for **TS4** and **TS6**.

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Cartesian coordinates (Å) and energies of optimized structures

α-I

M06-2X SCF energy: -1438.60457362 a.u.

M06-2X enthalpy: -1438.177163 a.u.

M06-2X free energy: -1438.269530 a.u.

M06-2X SCF energy in solution: -1439.05482081 a.u.

M06-2X enthalpy in solution: -1438.627410 a.u.

M06-2X free energy in solution: -1438.719777 a.u.

Three lowest frequencies (cm-1): 13.9839 29.6537 31.9575

Cartesian coordinates

ATOM	X	Y	Z
C	-1.619004	3.026321	-1.770657
C	-0.433210	2.322528	-2.418735
C	0.845537	3.138216	-2.249268
C	0.007189	4.195360	-0.288865
C	-1.289185	3.393425	-0.327394
H	-0.247877	1.383596	-1.876696
H	-1.872646	3.935096	-2.325804
H	-0.159998	5.149716	-0.807794
H	-2.100982	3.974052	0.115806
O	1.063839	3.494001	-0.951066
N	-0.661447	2.052739	-3.840054
N	-1.418782	1.102802	-4.061868
N	-2.087718	0.254063	-4.386035
O	-2.697526	2.099508	-1.836335
C	-3.947593	2.604415	-1.741941
O	-4.165862	3.780920	-1.570876
C	-4.986678	1.552111	-1.881525
C	-4.653205	0.201268	-2.016212
C	-6.324964	1.953244	-1.879098
C	-5.664096	-0.745006	-2.151153
H	-3.612962	-0.106054	-2.009774
C	-7.330703	1.003430	-2.017352
H	-6.560956	3.007250	-1.771586
C	-6.999690	-0.344861	-2.153543
H	-5.409851	-1.795130	-2.254438
H	-8.371187	1.312242	-2.018986
H	-7.785249	-1.086696	-2.261452
O	-1.126018	2.163655	0.386888
C	-1.686065	2.074221	1.611403
O	-2.248844	2.997970	2.152699
C	-1.521988	0.723920	2.212130
C	-0.880620	-0.318522	1.537135

C	-2.040390	0.520385	3.493775
C	-0.759482	-1.561792	2.150129
H	-0.480179	-0.157041	0.542158
C	-1.917385	-0.723796	4.101245
H	-2.536847	1.342188	3.999569
C	-1.276215	-1.764666	3.429294
H	-0.261003	-2.373516	1.630029
H	-2.320724	-0.882311	5.096328
H	-1.178494	-2.736586	3.903509
C	0.479181	4.473443	1.121936
H	-0.363859	4.865947	1.711127
H	0.815280	3.533460	1.588756
O	1.529219	5.401253	1.054735
C	2.090598	5.646196	2.323521
H	2.508742	4.727659	2.759565
H	2.892236	6.375706	2.191035
H	1.345405	6.055497	3.020810
H	1.717223	2.599357	-2.615565
I	0.848275	4.949583	-3.605837

β-I

M06-2X SCF energy: -1438.59906321 a.u.

M06-2X enthalpy: -1438.172069 a.u.

M06-2X free energy: -1438.265980 a.u.

M06-2X SCF energy in solution: -1439.05002409 a.u.

M06-2X enthalpy in solution: -1438.623030 a.u.

M06-2X free energy in solution: -1438.716941 a.u.

Three lowest frequencies (cm-1): 13.1482 21.9943 30.6398

Cartesian coordinates

ATOM	X	Y	Z
C	-1.606802	2.989976	-1.754762
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C	0.023462	4.160897	-0.290490
C	-1.283273	3.370779	-0.315069
H	-0.251203	1.316916	-1.917669
H	-1.852206	3.898078	-2.315648
H	-0.128191	5.102621	-0.838961
H	-2.096490	3.957789	0.117589
H	0.697246	4.090249	-2.838558
O	1.057692	3.398329	-0.917752

N	-0.701368	2.089916	-3.852497
N	-1.438512	1.134365	-4.108982
N	-2.095163	0.283714	-4.453899
O	-2.695036	2.074319	-1.821940
C	-3.940878	2.592770	-1.756089
O	-4.150906	3.772689	-1.597064
C	-4.987707	1.550093	-1.910368
C	-4.663049	0.199132	-2.064082
C	-6.323210	1.960377	-1.904157
C	-5.680105	-0.738314	-2.213291
H	-3.624721	-0.114575	-2.062309
C	-7.335216	1.019224	-2.055508
H	-6.552005	3.014382	-1.782043
C	-7.013011	-0.329250	-2.210205
H	-5.432783	-1.788406	-2.332365
H	-8.373670	1.334801	-2.053004
H	-7.803316	-1.064428	-2.328380
O	-1.126545	2.147724	0.410184
C	-1.670983	2.074838	1.641043
O	-2.222689	3.006645	2.180736
C	-1.506400	0.728427	2.251290
C	-0.864878	-0.317217	1.581231
C	-2.022545	0.531715	3.534809
C	-0.741769	-1.556961	2.200856
H	-0.464567	-0.159993	0.585524
C	-1.897956	-0.709219	4.148772
H	-2.518619	1.356008	4.036979
C	-1.257000	-1.753363	3.481639
H	-0.242702	-2.370738	1.684534
H	-2.299879	-0.862827	5.145211
H	-1.158019	-2.722686	3.960944
C	0.487395	4.474714	1.115644
H	-0.352681	4.899336	1.686671
H	0.802654	3.542269	1.610962
O	1.554710	5.381667	1.032322
C	2.112464	5.647636	2.298342
H	2.514198	4.733369	2.758156
H	2.925890	6.361794	2.153950
H	1.369671	6.083916	2.981883
I	2.574568	2.192008	-3.089725

EtOH

M06-2X SCF energy: -154.95933303 a.u.
M06-2X enthalpy: -154.873046 a.u.
M06-2X free energy: -154.903432 a.u.
M06-2X SCF energy in solution: -155.02019768 a.u.
M06-2X enthalpy in solution: -154.933911 a.u.
M06-2X free energy in solution: -154.964297 a.u.
Three lowest frequencies (cm-1): 266.0407 350.8119 425.1683

Cartesian coordinates

ATOM	X	Y	Z
C	2.220606	-2.881861	-7.844016
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H	2.572385	-2.383121	-8.752198
H	1.126330	-2.892366	-7.854148
C	2.728399	-2.164524	-6.610845
H	3.828031	-2.144583	-6.611972
H	2.380475	-1.121315	-6.611326
O	2.238342	-2.858397	-5.472867
H	2.563167	-2.396832	-4.684741

$Ph_3P=O$

M06-2X SCF energy: -1111.21361153 a.u.
M06-2X enthalpy: -1110.914308 a.u.
M06-2X free energy: -1110.978631 a.u.
M06-2X SCF energy in solution: -1111.44366327 a.u.
M06-2X enthalpy in solution: -1111.144360 a.u.
M06-2X free energy in solution: -1111.208683 a.u.
Three lowest frequencies (cm-1): 25.8459 28.3885 39.5182

Cartesian coordinates

ATOM	X	Y	Z
P	-0.771397	0.965232	1.007852
O	0.691558	1.115202	0.703258
C	-1.776808	2.319473	0.330645
C	-3.084661	2.143131	-0.130467
C	-1.196095	3.592083	0.305018
C	-3.809528	3.235520	-0.602161
H	-3.538760	1.155537	-0.128528
C	-1.922524	4.680590	-0.168809
H	-0.173091	3.723019	0.648211
C	-3.229964	4.502561	-0.619359
H	-4.824531	3.095339	-0.961523

H	-1.468724	5.666870	-0.188933
H	-3.796451	5.352541	-0.988504
C	-1.121707	0.932510	2.792123
C	-2.302548	1.437131	3.345326
C	-0.159850	0.346538	3.622042
C	-2.524846	1.341211	4.717352
H	-3.048349	1.907619	2.709332
C	-0.384029	0.255259	4.992822
H	0.765222	-0.027710	3.191318
C	-1.567725	0.749446	5.539486
H	-3.443007	1.733734	5.143775
H	0.364830	-0.198172	5.635232
H	-1.742669	0.677356	6.608917
C	-1.470014	-0.575375	0.343386
C	-2.589707	-1.194564	0.907321
C	-0.856263	-1.136257	-0.780621
C	-3.100486	-2.359314	0.340766
H	-3.060568	-0.773066	1.792001
C	-1.367282	-2.304018	-1.342207
H	0.025259	-0.660984	-1.202648
C	-2.490139	-2.912605	-0.783788
H	-3.969459	-2.838102	0.781775
H	-0.887801	-2.740838	-2.213055
H	-2.886884	-3.823997	-1.221254

TS1

M06-2X SCF energy: -1593.55703236 a.u.

M06-2X enthalpy: -1593.042701 a.u.

M06-2X free energy: -1593.148955 a.u.

M06-2X SCF energy in solution: -1594.06312828 a.u.

M06-2X enthalpy in solution: -1593.548797 a.u.

M06-2X free energy in solution: -1593.655051 a.u.

Three lowest frequencies (cm-1): -108.7899 16.9269 23.7794

Imaginary frequency: -108.7899 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.145963	-1.430545	0.570928
C	-0.760530	-1.202611	-0.633248
C	-2.199858	-1.162054	-0.202006
C	-1.638576	-0.485144	2.055177
C	-0.191041	-0.370997	1.616661

H	-0.518364	-0.215114	-1.044632
H	0.022405	-2.434169	0.983228
H	-1.736199	-1.316291	2.758043
H	0.442448	-0.488929	2.499103
H	-2.980257	-1.544898	-0.849428
O	-2.562904	-0.859267	0.973049
N	-0.630194	-2.245189	-1.650527
N	0.307532	-2.040974	-2.434476
N	1.131937	-1.957031	-3.196668
O	1.459929	-1.238532	0.070559
C	2.475953	-1.696643	0.846378
O	2.283172	-2.324867	1.858879
C	3.803434	-1.340574	0.288255
C	3.934003	-0.470485	-0.798181
C	4.934926	-1.890230	0.895569
C	5.202572	-0.152410	-1.272178
H	3.051807	-0.043001	-1.263197
C	6.199433	-1.574591	0.412395
H	4.809931	-2.561172	1.739617
C	6.332602	-0.704672	-0.669815
H	5.309172	0.527965	-2.111015
H	7.080588	-2.003629	0.878696
H	7.320850	-0.454799	-1.044221
O	0.023789	0.914486	1.033843
C	1.251405	1.466495	1.220768
O	2.090579	0.966860	1.932658
C	1.426085	2.728758	0.461696
C	0.414849	3.257777	-0.345013
C	2.662467	3.373367	0.565009
C	0.645335	4.439432	-1.042956
H	-0.541388	2.750932	-0.431795
C	2.885003	4.553781	-0.133412
H	3.435276	2.937947	1.190478
C	1.875904	5.086394	-0.936729
H	-0.136794	4.852082	-1.672442
H	3.843247	5.057302	-0.054402
H	2.051263	6.008333	-1.483259
C	-2.190108	0.784605	2.667497
H	-1.460128	1.159296	3.403015
H	-2.311450	1.549148	1.886630
O	-3.412630	0.463962	3.269292
C	-4.062113	1.610171	3.777615
H	-4.288006	2.326483	2.976174
H	-4.995354	1.276060	4.234788

H	-3.447105	2.111055	4.538378
I	-3.066241	1.285515	-1.708572
C	-2.628962	-5.069769	-1.148460
H	-2.592518	-4.277499	-1.902218
H	-2.344656	-6.014954	-1.621467
H	-3.660518	-5.167159	-0.791327
C	-1.692206	-4.747840	-0.000854
H	-1.696104	-5.551111	0.746869
H	-0.667571	-4.623063	-0.359577
O	-2.030161	-3.510044	0.628546
H	-2.918187	-3.604817	1.014783

TS2

M06-2X SCF energy: -1593.55202062 a.u.

M06-2X enthalpy: -1593.036514 a.u.

M06-2X free energy: -1593.141889 a.u.

M06-2X SCF energy in solution: -1594.05499449 a.u.

M06-2X enthalpy in solution: -1593.539488 a.u.

M06-2X free energy in solution: -1593.644863 a.u.

Three lowest frequencies (cm-1): -233.7037 11.6846 22.2783

Imaginary frequency: -233.7037 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.365887	-0.774385	-0.267932
C	0.774157	-0.164017	1.067969
C	1.984273	0.730631	0.913906
C	1.682927	0.949651	-1.481902
C	0.305891	0.350263	-1.295431
H	-0.049038	0.485974	1.389036
H	1.073691	-1.545676	-0.586244
H	2.332192	0.226231	-1.985004
H	-0.052368	-0.018697	-2.258887
O	2.369812	1.198388	-0.207943
N	1.072056	-1.169287	2.088787
N	0.056285	-1.592480	2.656968
N	-0.794678	-2.047059	3.238663
O	-0.918358	-1.331202	-0.023334
C	-1.386994	-2.179237	-0.974551
O	-0.748692	-2.455768	-1.961112
C	-2.731531	-2.713973	-0.646509
C	-3.425885	-2.334939	0.505997

C	-3.291236	-3.630404	-1.540606
C	-4.681184	-2.879289	0.759065
H	-2.988033	-1.623248	1.198168
C	-4.544590	-4.171276	-1.282017
H	-2.732729	-3.909222	-2.428074
C	-5.239072	-3.795986	-0.131950
H	-5.224949	-2.590538	1.652848
H	-4.979387	-4.884854	-1.974473
H	-6.218092	-4.219946	0.070508
O	-0.563206	1.371252	-0.798649
C	-1.872743	1.290030	-1.149229
O	-2.288718	0.484879	-1.947162
C	-2.701676	2.298609	-0.442643
C	-2.166848	3.136885	0.540576
C	-4.055623	2.375197	-0.779869
C	-2.993488	4.054828	1.180795
H	-1.116370	3.062026	0.805046
C	-4.874856	3.296357	-0.138207
H	-4.450568	1.709007	-1.540164
C	-4.343592	4.136284	0.840830
H	-2.585053	4.708435	1.945216
H	-5.926550	3.359233	-0.398692
H	-4.984777	4.855165	1.342098
C	1.672881	2.260768	-2.236299
H	1.076661	2.117873	-3.151988
H	1.183921	3.040922	-1.632706
O	2.998285	2.597733	-2.530440
C	3.081991	3.784933	-3.288980
H	2.647665	4.637043	-2.747328
H	4.140366	3.978261	-3.472094
H	2.562879	3.678985	-4.251680
H	2.726732	0.767254	1.708477
I	4.129900	-1.817039	0.089021
C	0.562196	1.759187	3.875936
H	0.606781	2.055477	4.927473
H	-0.490419	1.704878	3.578734
H	1.015563	0.766729	3.788697
C	1.302270	2.779266	3.042169
H	0.894089	3.782780	3.193846
H	2.370826	2.792638	3.280953
O	1.130874	2.450872	1.643804
H	1.567710	3.142584	1.109169

α-anomer

M06-2X SCF energy: -1581.66750963 a.u.

M06-2X enthalpy: -1581.165947 a.u.

M06-2X free energy: -1581.261751 a.u.

M06-2X SCF energy in solution: -1582.11547095 a.u.

M06-2X enthalpy in solution: -1581.613908 a.u.

M06-2X free energy in solution: -1581.709712 a.u.

Three lowest frequencies (cm-1): 20.0228 23.2778 29.6629

Cartesian coordinates

ATOM	X	Y	Z
C	-1.953316	2.852598	-2.168978
C	-0.829879	2.130632	-2.901918
C	0.296848	3.122078	-3.197901
C	-0.212454	4.388593	-1.245768
C	-1.407858	3.507435	-0.900441
H	-0.424954	1.346842	-2.250730
H	-2.407138	3.610684	-2.812795
H	-0.580851	5.231610	-1.845298
H	-2.188099	4.088487	-0.403041
O	0.766641	3.660882	-1.981946
N	-1.304043	1.554333	-4.171701
N	-1.934838	0.503033	-4.035507
N	-2.519323	-0.463441	-4.026274
O	-2.913934	1.850220	-1.839915
C	-4.162583	2.278132	-1.545489
O	-4.501677	3.432691	-1.650757
C	-5.046229	1.166624	-1.105371
C	-4.559905	-0.128011	-0.904527
C	-6.392066	1.459510	-0.875330
C	-5.427028	-1.127239	-0.473025
H	-3.511930	-0.347526	-1.081784
C	-7.254812	0.456815	-0.447895
H	-6.746052	2.473461	-1.032920
C	-6.771900	-0.835855	-0.246120
H	-5.052904	-2.133840	-0.313866
H	-8.301515	0.682086	-0.268824
H	-7.445207	-1.618610	0.090864
O	-0.947829	2.469570	-0.022683
C	-1.830581	1.966873	0.862396
O	-2.949356	2.402782	1.013731
C	-1.266661	0.820681	1.626147
C	0.068930	0.429401	1.496656

C	-2.125352	0.128859	2.484010
C	0.541850	-0.651645	2.233824
H	0.729588	0.969819	0.826593
C	-1.648952	-0.954377	3.213287
H	-3.160266	0.446984	2.563499
C	-0.315195	-1.342995	3.089240
H	1.579619	-0.956161	2.140193
H	-2.315266	-1.496548	3.877064
H	0.056891	-2.188394	3.660671
C	0.468061	4.930063	-0.006059
H	-0.293717	5.321963	0.687318
H	1.006516	4.117086	0.502804
O	1.354796	5.948702	-0.396740
C	2.061304	6.475691	0.702759
H	2.662375	5.701298	1.200537
H	2.726116	7.254098	0.322465
H	1.377543	6.915886	1.442904
H	1.158906	2.602763	-3.634472
O	-0.200206	4.082112	-4.068375
C	0.785315	4.908617	-4.692035
H	0.378513	5.154935	-5.677189
H	1.703171	4.324822	-4.842827
C	1.071169	6.174780	-3.904815
H	1.504959	5.949858	-2.926611
H	1.771382	6.803557	-4.465104
H	0.148236	6.745207	-3.757106

β-anomer

M06-2X SCF energy: -1581.66105663 a.u.

M06-2X enthalpy: -1581.159556 a.u.

M06-2X free energy: -1581.258953 a.u.

M06-2X SCF energy in solution: -1582.11188236 a.u.

M06-2X enthalpy in solution: -1581.610382 a.u.

M06-2X free energy in solution: -1581.709779 a.u.

Three lowest frequencies (cm-1): 11.8930 20.2896 24.0610

Cartesian coordinates

ATOM	X	Y	Z
C	-1.713840	2.941248	-1.798740
C	-0.548495	2.209140	-2.459383
C	0.718190	3.051102	-2.321719
C	-0.065186	4.106543	-0.355804

C	-1.388019	3.337641	-0.363507
H	-0.375865	1.248507	-1.958933
H	-1.947907	3.848345	-2.366483
H	-0.209412	5.036611	-0.928928
H	-2.194449	3.940924	0.059163
O	0.947674	3.316160	-0.953132
N	-0.819986	2.020099	-3.894800
N	-1.582745	1.086068	-4.148433
N	-2.261378	0.250938	-4.492646
O	-2.821644	2.044876	-1.859860
C	-4.055682	2.586894	-1.789447
O	-4.244553	3.770654	-1.629604
C	-5.124813	1.565211	-1.939780
C	-4.828465	0.209555	-2.107336
C	-6.451882	2.001233	-1.915878
C	-5.865182	-0.706556	-2.252586
H	-3.796223	-0.123655	-2.119507
C	-7.483725	1.081377	-2.062554
H	-6.658330	3.058686	-1.783177
C	-7.189686	-0.271801	-2.231192
H	-5.639655	-1.760315	-2.383003
H	-8.515806	1.417236	-2.045758
H	-7.995445	-0.990816	-2.345922
O	-1.250969	2.121340	0.379485
C	-1.743207	2.094088	1.632367
O	-2.251300	3.051623	2.170392
C	-1.582192	0.759485	2.271286
C	-0.971247	-0.309812	1.610338
C	-2.064519	0.600257	3.572907
C	-0.844646	-1.535329	2.256454
H	-0.596457	-0.180857	0.600687
C	-1.937299	-0.626930	4.213250
H	-2.537014	1.442539	4.068342
C	-1.326630	-1.694453	3.555122
H	-0.368301	-2.366980	1.746812
H	-2.313539	-0.751940	5.223766
H	-1.225517	-2.653135	4.055301
C	0.393992	4.466349	1.041793
H	-0.428597	4.960925	1.580271
H	0.659698	3.547773	1.589605
O	1.507396	5.315659	0.927646
C	2.017167	5.676838	2.190561
H	2.347064	4.793874	2.756643
H	2.873986	6.332760	2.021476

H	1.266407	6.213844	2.788369
H	0.595821	4.008201	-2.864143
O	1.779413	2.328796	-2.816974
C	2.988507	3.083682	-2.902581
H	3.288647	3.410793	-1.900885
H	2.810017	3.979713	-3.514249
C	4.043086	2.198012	-3.528167
H	3.734785	1.879189	-4.528014
H	4.988132	2.742287	-3.611496
H	4.209102	1.307968	-2.914226

TS3

M06-2X SCF energy: -2549.80888805 a.u.

M06-2X enthalpy: -2549.081576 a.u.

M06-2X free energy: -2549.216405 a.u.

M06-2X SCF energy in solution: -2550.49481485 a.u.

M06-2X enthalpy in solution: -2549.767503 a.u.

M06-2X free energy in solution: -2549.902332 a.u.

Three lowest frequencies (cm-1): -207.2552 15.3226 16.2647

Imaginary frequency: -207.2552 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.833114	-1.332956	-0.440095
C	-0.579336	-1.033471	0.377063
C	0.635999	-1.616060	-0.294214
C	-0.408384	-1.674346	-2.472288
C	-1.562509	-0.891890	-1.877564
H	-0.432994	0.054529	0.367129
H	-2.102040	-2.392703	-0.393637
H	-0.743954	-2.681200	-2.736509
H	-2.444781	-1.039051	-2.505524
O	0.679848	-1.919800	-1.520283
N	-0.610744	-1.534248	1.750527
N	-1.465194	-0.999589	2.464930
N	-2.208775	-0.598954	3.212280
O	-2.836462	-0.518895	0.150051
C	-4.124074	-0.792274	-0.182002
O	-4.424740	-1.707567	-0.907921
C	-5.071379	0.153782	0.458481
C	-4.628643	1.213326	1.255960
C	-6.436298	-0.042149	0.235411

C	-5.559156	2.073237	1.830773
H	-3.567328	1.364124	1.424197
C	-7.361084	0.819740	0.813563
H	-6.755715	-0.870797	-0.388380
C	-6.922110	1.876740	1.610792
H	-5.221613	2.897910	2.450435
H	-8.422254	0.668822	0.643018
H	-7.644686	2.550892	2.060840
O	-1.205075	0.490240	-1.840569
C	-2.213490	1.393639	-1.925107
O	-3.333237	1.100732	-2.270713
C	-1.767052	2.753468	-1.531228
C	-0.463184	2.995813	-1.085313
C	-2.705821	3.786986	-1.580748
C	-0.106798	4.280691	-0.684232
H	0.258197	2.181881	-1.054126
C	-2.340665	5.068464	-1.184036
H	-3.713302	3.571670	-1.922634
C	-1.042902	5.313896	-0.735033
H	0.903174	4.476615	-0.333797
H	-3.066762	5.874428	-1.221799
H	-0.759563	6.314532	-0.422538
C	0.223604	-0.993631	-3.667608
H	-0.581199	-0.674087	-4.348964
H	0.766900	-0.098598	-3.331278
O	1.080458	-1.915667	-4.280303
C	1.766117	-1.345730	-5.373751
H	2.402732	-0.509014	-5.053251
H	2.392667	-2.127697	-5.806811
H	1.064849	-0.980590	-6.137221
H	1.468042	-1.977485	0.303938
I	-0.157490	-4.824253	0.298354
P	2.657198	0.837443	0.458798
O	1.669015	0.291216	-0.570231
C	1.995324	0.724731	2.134434
C	2.410782	-0.283487	3.007506
C	0.922312	1.558548	2.485330
C	1.760381	-0.455549	4.228580
H	3.230951	-0.942195	2.737562
C	0.282435	1.386362	3.707314
H	0.590061	2.339514	1.803180
C	0.700354	0.376221	4.577017
H	2.081312	-1.243701	4.902051
H	-0.550408	2.027531	3.978916

H	0.190700	0.235661	5.525439
C	3.033180	2.568861	0.099465
C	3.303558	3.507526	1.099788
C	3.106593	2.936574	-1.249656
C	3.639553	4.813622	0.746924
H	3.246222	3.227364	2.148221
C	3.447247	4.240489	-1.595012
H	2.888637	2.203404	-2.022203
C	3.712123	5.178261	-0.596525
H	3.841666	5.545639	1.522455
H	3.500377	4.526329	-2.640788
H	3.974049	6.196745	-0.866641
C	4.213104	-0.078305	0.406737
C	5.277959	0.255170	1.252102
C	4.342661	-1.116955	-0.517641
C	6.467633	-0.459904	1.174627
H	5.174287	1.065753	1.970744
C	5.538463	-1.829849	-0.590291
H	3.515212	-1.359034	-1.179477
C	6.596050	-1.501814	0.253835
H	7.295496	-0.206321	1.829055
H	5.641331	-2.638249	-1.306958
H	7.526662	-2.058050	0.196085

Int1

M06-2X SCF energy: -2549.84253505 a.u.

M06-2X enthalpy: -2549.112688 a.u.

M06-2X free energy: -2549.247762 a.u.

M06-2X SCF energy in solution: -2550.52616110 a.u.

M06-2X enthalpy in solution: -2549.796314 a.u.

M06-2X free energy in solution: -2549.931388 a.u.

Three lowest frequencies (cm-1): 15.4197 17.1265 18.7516

Cartesian coordinates

ATOM	X	Y	Z
C	-1.912333	3.490247	-1.244631
C	-0.690758	2.888499	-1.930116
C	0.502156	3.801071	-1.645604
C	-0.335006	4.579216	0.383912
C	-1.627578	3.785293	0.234538
H	-0.476221	1.895606	-1.515806
H	-2.201343	4.417537	-1.750224

H	-0.476242	5.569287	-0.076247
H	-2.469361	4.325244	0.674749
H	0.330294	4.794580	-2.086888
O	0.724145	3.892278	-0.276432
N	-0.957602	2.834539	-3.373334
N	-0.253909	2.027772	-3.991037
N	0.333278	1.328550	-4.653184
O	-2.959733	2.533415	-1.345920
C	-4.220453	3.006163	-1.210850
O	-4.476149	4.186578	-1.171517
C	-5.224180	1.914337	-1.123191
C	-4.846092	0.575453	-0.990904
C	-6.574713	2.269425	-1.131012
C	-5.825059	-0.405729	-0.868000
H	-3.794827	0.307133	-0.975520
C	-7.549198	1.284507	-1.014195
H	-6.845236	3.316406	-1.224579
C	-7.174137	-0.052206	-0.881389
H	-5.535149	-1.446098	-0.758433
H	-8.599642	1.557713	-1.022108
H	-7.935371	-0.820510	-0.784417
O	-1.444926	2.535839	0.906258
C	-2.530278	1.975758	1.481276
O	-3.604960	2.526632	1.553178
C	-2.245400	0.617302	2.012727
C	-0.970504	0.047991	1.946566
C	-3.308881	-0.092226	2.577204
C	-0.763567	-1.231421	2.452702
H	-0.151113	0.603502	1.502695
C	-3.096341	-1.370890	3.079240
H	-4.291485	0.367721	2.611528
C	-1.823714	-1.939016	3.018675
H	0.224833	-1.677322	2.404662
H	-3.920289	-1.923906	3.518973
H	-1.658645	-2.937337	3.412716
C	0.090356	4.759483	1.824600
H	-0.751987	5.165962	2.406202
H	0.365218	3.783522	2.250459
O	1.186297	5.639833	1.838657
C	1.714818	5.797535	3.136858
H	2.087772	4.843375	3.534174
H	2.543587	6.505502	3.068753
H	0.960528	6.195604	3.830181
O	1.660759	3.201150	-2.194521

P	2.796317	4.018438	-3.021021
C	4.270682	3.077948	-2.679485
C	5.465849	3.732776	-2.371324
C	4.204450	1.678765	-2.740191
C	6.606587	2.975188	-2.120098
H	5.508327	4.816973	-2.334090
C	5.350019	0.936043	-2.484558
H	3.269516	1.180116	-2.983196
C	6.546959	1.585051	-2.175963
H	7.540180	3.475205	-1.885107
H	5.310534	-0.147423	-2.526884
H	7.439970	1.000292	-1.977570
C	2.873690	5.698596	-2.422794
C	2.993991	6.753443	-3.335813
C	2.848050	5.941720	-1.039656
C	3.088963	8.057695	-2.860217
H	3.026599	6.559048	-4.402994
C	2.923013	7.251787	-0.582646
H	2.735216	5.130292	-0.327325
C	3.049213	8.304859	-1.489929
H	3.192579	8.876360	-3.564381
H	2.878608	7.446515	0.483806
H	3.114840	9.325168	-1.124563
C	2.322879	3.956835	-4.741706
C	3.058933	3.199623	-5.657778
C	1.145404	4.612854	-5.131920
C	2.601360	3.083174	-6.967111
H	3.982451	2.714955	-5.356060
C	0.695145	4.481679	-6.439248
H	0.584325	5.217852	-4.422966
C	1.421298	3.714429	-7.351864
H	3.170775	2.502127	-7.684695
H	-0.217015	4.981881	-6.747469
H	1.066218	3.617370	-8.373148
I	6.002977	5.811929	-5.667958

TS4

M06-2X SCF energy: -2704.78790478 a.u.

M06-2X enthalpy: -2703.971293 a.u.

M06-2X free energy: -2704.117478 a.u.

M06-2X SCF energy in solution: -2705.53143144 a.u.

M06-2X enthalpy in solution: -2704.714820 a.u.

M06-2X free energy in solution: -2704.861005 a.u.
Three lowest frequencies (cm-1): -226.9560 7.2070 19.8614
Imaginary frequency: -226.9560 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.522199	-1.935835	0.807834
C	0.381017	-1.276873	0.042096
C	-0.824336	-1.111061	0.928751
C	0.470875	-1.228449	2.969440
C	1.720368	-1.165951	2.111104
H	0.701355	-0.265034	-0.234255
H	1.313525	-2.991460	0.999380
H	0.405351	-2.210972	3.444609
H	2.557193	-1.574466	2.682942
O	-0.771323	-1.131483	2.195721
N	-0.027391	-2.034985	-1.140817
N	0.738389	-1.894688	-2.102014
N	1.364815	-1.854046	-3.037721
O	2.647849	-1.779483	-0.044381
C	3.757441	-2.496841	0.262913
O	3.779419	-3.302400	1.161315
C	4.894442	-2.163692	-0.631006
C	4.787368	-1.179937	-1.618893
C	6.095433	-2.851647	-0.443819
C	5.888281	-0.888601	-2.417860
H	3.852912	-0.646138	-1.758316
C	7.192115	-2.555864	-1.245635
H	6.157296	-3.609268	0.331088
C	7.087902	-1.574568	-2.231554
H	5.809843	-0.125117	-3.185304
H	8.127671	-3.086957	-1.102026
H	7.945627	-1.341782	-2.855434
O	1.972860	0.199097	1.776438
C	3.265053	0.563838	1.591079
O	4.198684	-0.155016	1.858979
C	3.374989	1.932881	1.027161
C	2.239480	2.686402	0.713118
C	4.654667	2.444388	0.797126
C	2.392281	3.959937	0.170749
H	1.251550	2.269991	0.893813
C	4.799636	3.716703	0.255527
H	5.520224	1.837932	1.044429
C	3.669313	4.472697	-0.057737

H	1.513887	4.551661	-0.075395
H	5.791406	4.119784	0.077028
H	3.784843	5.465462	-0.482171
C	0.416881	-0.127905	4.022725
H	1.400039	-0.088954	4.504593
H	0.233843	0.832237	3.521229
O	-0.525181	-0.373551	5.028076
C	-1.857718	-0.014232	4.707989
H	-2.361099	-0.787403	4.116051
H	-2.389456	0.105309	5.655032
H	-1.888502	0.936491	4.158559
H	-1.823186	-1.125354	0.494204
O	-0.851777	1.064068	0.845895
P	-1.554860	1.871590	-0.244695
C	-0.979992	1.474291	-1.911926
C	-1.623950	0.465938	-2.640032
C	0.175259	2.078063	-2.427118
C	-1.133172	0.087468	-3.886682
H	-2.506304	-0.027752	-2.239769
C	0.661415	1.693986	-3.673885
H	0.689570	2.851976	-1.862025
C	0.003095	0.705614	-4.405661
H	-1.637715	-0.696164	-4.443426
H	1.552296	2.166859	-4.075161
H	0.384608	0.406507	-5.377368
C	-1.269370	3.635741	0.040162
C	-0.935070	4.037292	1.337450
C	-1.428477	4.589900	-0.970965
C	-0.747521	5.387921	1.619911
H	-0.811260	3.289812	2.116265
C	-1.237203	5.938863	-0.683218
H	-1.691869	4.284680	-1.980391
C	-0.895946	6.336850	0.609668
H	-0.481163	5.697288	2.625671
H	-1.354037	6.679451	-1.468068
H	-0.745817	7.389599	0.829158
C	-3.336497	1.575046	-0.194907
C	-3.862998	0.940548	0.933030
C	-4.182723	1.989307	-1.229303
C	-5.234225	0.712284	1.022068
H	-3.198166	0.618383	1.730895
C	-5.550110	1.755601	-1.136231
H	-3.773610	2.476308	-2.111312
C	-6.074427	1.117286	-0.011826

H	-5.643429	0.209126	1.892417
H	-6.206580	2.065683	-1.943002
H	-7.141858	0.930222	0.053668
C	-2.623473	-5.196465	1.800431
H	-3.303420	-5.411607	2.630808
H	-3.183626	-5.295783	0.864499
H	-1.817371	-5.936512	1.805909
C	-2.058549	-3.793965	1.924998
H	-2.870164	-3.051957	1.923185
H	-1.501551	-3.681697	2.861306
O	-1.131244	-3.511137	0.880045
H	-1.619443	-3.550679	0.032709
I	-3.931473	-2.599435	-1.232846

Int1a

M06-2X SCF energy: -2538.34541018 a.u.

M06-2X enthalpy: -2537.617479 a.u.

M06-2X free energy: -2537.745499 a.u.

M06-2X SCF energy in solution: -2538.96577038 a.u.

M06-2X enthalpy in solution: -2538.237839 a.u.

M06-2X free energy in solution: -2538.365859 a.u.

Three lowest frequencies (cm-1): 12.3594 16.6326 21.9195

Cartesian coordinates

ATOM	X	Y	Z
C	-1.937373	2.811947	-1.994810
C	-0.786515	2.157111	-2.761284
C	0.307653	3.204901	-2.899605
C	-0.295600	4.341557	-0.919325
C	-1.457197	3.381481	-0.661921
H	-0.391163	1.302002	-2.199448
H	-2.358767	3.626061	-2.594322
H	-0.664350	5.193495	-1.510775
H	-2.274223	3.893262	-0.148779
O	0.723002	3.655517	-1.648863
N	-1.204467	1.771916	-4.115058
N	-1.874902	0.734569	-4.161212
N	-2.483783	-0.200770	-4.322244
O	-2.920244	1.800779	-1.808826
C	-4.192373	2.229797	-1.624513
O	-4.479118	3.402737	-1.569726
C	-5.159260	1.109891	-1.506927

C	-4.754621	-0.227539	-1.542000
C	-6.509727	1.437363	-1.359446
C	-5.707724	-1.234630	-1.427031
H	-3.704204	-0.475803	-1.652820
C	-7.457087	0.427011	-1.247624
H	-6.801466	2.482518	-1.335371
C	-7.055473	-0.908304	-1.281077
H	-5.399007	-2.274919	-1.451186
H	-8.506945	0.678332	-1.133986
H	-7.796248	-1.697401	-1.191808
O	-1.008950	2.268415	0.115754
C	-1.278598	2.282278	1.438524
O	-1.819598	3.211286	1.992392
C	-0.830782	1.037651	2.117787
C	-0.197411	0.000965	1.426082
C	-1.070208	0.927188	3.489829
C	0.192233	-1.144845	2.111949
H	-0.013003	0.091666	0.360903
C	-0.680478	-0.220605	4.169880
H	-1.564439	1.743520	4.006692
C	-0.049813	-1.256385	3.480693
H	0.683741	-1.952833	1.579226
H	-0.868996	-0.309518	5.235109
H	0.252407	-2.153759	4.012410
C	0.361182	4.855983	0.344436
H	-0.399028	5.298462	1.003953
H	0.838138	4.017594	0.875724
O	1.323069	5.809421	-0.036349
C	2.130630	6.213859	1.049244
H	2.680861	5.361746	1.471746
H	2.844309	6.946156	0.666288
H	1.528588	6.675485	1.843749
H	-0.041005	4.038054	-3.528741
O	1.436736	2.597228	-3.504111
P	2.772998	3.468547	-3.764385
C	2.342346	5.147367	-4.210634
C	2.015975	6.060132	-3.195557
C	2.271636	5.514622	-5.560265
C	1.613151	7.343679	-3.545737
H	2.058450	5.770886	-2.147274
C	1.872278	6.805143	-5.892765
H	2.529433	4.805287	-6.341702
C	1.543330	7.714473	-4.888960
H	1.355732	8.053543	-2.765796

H	1.820976	7.099809	-6.935763
H	1.233535	8.720477	-5.155198
C	3.527004	2.598036	-5.133044
C	4.902986	2.716880	-5.358199
C	2.713758	1.863953	-6.004732
C	5.465091	2.094589	-6.467353
H	5.532282	3.285491	-4.678099
C	3.291177	1.244053	-7.108418
H	1.647703	1.773044	-5.818198
C	4.660806	1.361006	-7.338713
H	6.531496	2.179551	-6.648881
H	2.669839	0.667910	-7.786306
H	5.106247	0.875684	-8.201675
C	3.781389	3.446861	-2.284961
C	3.612334	2.411694	-1.358710
C	4.746930	4.440534	-2.086611
C	4.421246	2.375456	-0.228282
H	2.846449	1.657292	-1.512134
C	5.553727	4.388882	-0.953961
H	4.865274	5.249384	-2.802533
C	5.390012	3.359600	-0.028877
H	4.292658	1.581755	0.500360
H	6.304182	5.155852	-0.793821
H	6.017471	3.326360	0.856381

TS4a

M06-2X SCF energy: -2693.28461355 a.u.

M06-2X enthalpy: -2692.470284 a.u.

M06-2X free energy: -2692.608534 a.u.

M06-2X SCF energy in solution: -2693.96364658 a.u.

M06-2X enthalpy in solution: -2693.149317 a.u.

M06-2X free energy in solution: -2693.287567 a.u.

Three lowest frequencies (cm-1): -182.5182 12.0261 16.8953

Imaginary frequency: -182.5182 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.181235	-1.498114	-0.414868
C	-1.111739	-1.529998	0.669607
C	0.247935	-1.772643	0.078883
C	-0.446760	-1.155708	-2.151791
C	-1.716158	-0.584911	-1.542798

H	-1.052158	-0.538185	1.134532
H	-2.365720	-2.501667	-0.806617
H	-0.679011	-2.103575	-2.647469
H	-2.474778	-0.515465	-2.326732
O	0.541260	-1.525230	-1.129215
N	-1.362304	-2.571388	1.671575
N	-2.186763	-2.226399	2.531032
N	-2.922755	-2.022992	3.358169
O	-3.339832	-0.994308	0.233070
C	-4.529589	-1.253651	-0.366033
O	-4.605984	-1.825754	-1.427167
C	-5.678714	-0.761372	0.432907
C	-5.501477	-0.100359	1.652034
C	-6.962848	-0.985266	-0.070939
C	-6.614266	0.332121	2.365497
H	-4.502658	0.074959	2.037440
C	-8.070574	-0.551121	0.647176
H	-7.078317	-1.498527	-1.020419
C	-7.895865	0.106649	1.864741
H	-6.481556	0.843930	3.313365
H	-9.069360	-0.723097	0.258666
H	-8.762407	0.443903	2.425746
O	-1.490527	0.697996	-0.958495
C	-1.825712	1.783396	-1.700159
O	-2.133862	1.703182	-2.865526
C	-1.767491	3.045184	-0.919522
C	-1.488269	3.059209	0.450857
C	-2.009801	4.239424	-1.604798
C	-1.446289	4.272364	1.129687
H	-1.296257	2.127880	0.975253
C	-1.967698	5.448346	-0.920197
H	-2.230317	4.205757	-2.667143
C	-1.685619	5.463973	0.445861
H	-1.226453	4.288717	2.192420
H	-2.154729	6.377465	-1.449148
H	-1.651511	6.408852	0.979941
C	0.276924	-0.226812	-3.100646
H	-0.403322	0.026899	-3.926293
H	0.548833	0.702211	-2.578221
O	1.424744	-0.894526	-3.556799
C	2.268074	-0.029422	-4.292882
H	2.583114	0.829079	-3.682058
H	3.147481	-0.606392	-4.585973
H	1.762886	0.343452	-5.194084

H	1.018659	-2.257450	0.666029
O	1.141311	0.006135	1.024607
P	2.626441	0.281818	0.798356
C	3.579196	-1.187883	0.327679
C	3.561594	-1.625791	-1.004893
C	4.270772	-1.926948	1.295013
C	4.243837	-2.785780	-1.361249
H	3.010130	-1.074158	-1.763162
C	4.954679	-3.084262	0.929811
H	4.285587	-1.595111	2.329577
C	4.945083	-3.510103	-0.396995
H	4.231036	-3.119962	-2.394562
H	5.497231	-3.648804	1.681645
H	5.483855	-4.409534	-0.680215
C	3.364124	0.939136	2.313887
C	4.715482	1.298360	2.376251
C	2.542276	1.094008	3.431710
C	5.239159	1.808384	3.559061
H	5.357848	1.177433	1.506829
C	3.072802	1.607087	4.614054
H	1.495103	0.812844	3.369259
C	4.417491	1.962555	4.676785
H	6.287352	2.085934	3.610257
H	2.435221	1.727049	5.484619
H	4.829534	2.361341	5.598814
C	2.861120	1.496890	-0.521767
C	1.760127	2.288821	-0.856655
C	4.090819	1.698104	-1.159100
C	1.884724	3.285855	-1.821785
H	0.808385	2.108095	-0.365196
C	4.212719	2.698858	-2.119377
H	4.947472	1.075590	-0.911893
C	3.112190	3.492243	-2.449008
H	1.024326	3.897317	-2.080003
H	5.165769	2.856824	-2.614652
H	3.214050	4.269842	-3.200050
C	1.707425	-5.087342	-0.132968
H	2.126182	-4.238141	0.418357
H	1.257954	-5.781956	0.585496
H	2.531078	-5.606015	-0.633040
C	0.680998	-4.631815	-1.151423
H	1.119491	-3.916353	-1.855667
H	0.298778	-5.481462	-1.729422
O	-0.416039	-3.945215	-0.540954

H -0.757920 -4.479593 0.196946

α-17a

M06-2X SCF energy: -2164.38664943 a.u.

M06-2X enthalpy: -2163.825959 a.u.

M06-2X free energy: -2163.940625 a.u.

M06-2X SCF energy in solution: -2165.00886184 a.u.

M06-2X enthalpy in solution: -2164.448171 a.u.

M06-2X free energy in solution: -2164.562837 a.u.

Three lowest frequencies (cm-1): 10.6895 17.3015 22.3110

Cartesian coordinates

ATOM	X	Y	Z
C	-2.086924	0.524470	0.283243
C	-0.737688	0.311359	-0.382338
C	0.053933	1.630407	-0.397065
C	-1.074482	2.452735	1.522845
C	-1.905591	1.185555	1.648904
H	-0.155837	-0.414802	0.198529
H	-2.724729	1.151798	-0.346568
H	-1.645469	3.186724	0.940243
H	-2.879875	1.409876	2.089307
O	0.167975	2.178365	0.865405
N	-0.995087	-0.182642	-1.743503
N	-0.017477	-0.701374	-2.288521
N	0.811215	-1.190221	-2.877716
O	-2.676404	-0.762384	0.447385
C	-4.013713	-0.786255	0.641349
O	-4.706843	0.200452	0.557609
C	-4.515785	-2.150691	0.953116
C	-5.898007	-2.331794	1.036267
C	-3.648187	-3.221026	1.185824
C	-6.414156	-3.585182	1.344569
H	-6.553888	-1.485384	0.858018
C	-4.169584	-4.472225	1.499084
H	-2.575142	-3.071940	1.126175
C	-5.549890	-4.654877	1.576537
H	-7.488370	-3.728689	1.406872
H	-3.498485	-5.305054	1.684890
H	-5.953156	-5.633359	1.820667
O	-1.187609	0.278345	2.493690
C	-1.909402	-0.549342	3.277152

O	-3.115689	-0.507992	3.359071
C	-1.047494	-1.505995	4.022061
C	-1.679980	-2.473675	4.806835
C	0.347437	-1.461794	3.942187
C	-0.917512	-3.397174	5.512520
H	-2.764554	-2.492984	4.850375
C	1.105335	-2.386480	4.653520
H	0.831635	-0.708073	3.329922
C	0.474537	-3.352672	5.436385
H	-1.406579	-4.152073	6.120258
H	2.188883	-2.354174	4.596349
H	1.069499	-4.074300	5.988463
C	-0.738716	3.049593	2.872859
H	-1.650870	3.076501	3.491260
H	0.000174	2.412649	3.381727
O	-0.233504	4.343669	2.669176
C	0.128989	4.956990	3.885016
H	0.927886	4.398636	4.393708
H	0.489168	5.960881	3.650309
H	-0.730906	5.034088	4.566169
O	-0.631794	2.578453	-1.233301
C	-0.206603	2.756438	-2.489242
N	0.670612	2.043523	-3.042703
C	1.170393	2.294984	-4.342221
C	1.914083	3.443681	-4.625371
C	0.979909	1.323600	-5.329026
C	2.447390	3.622790	-5.899594
H	2.078246	4.181340	-3.845922
C	1.505975	1.519021	-6.601421
H	0.410419	0.430244	-5.090747
C	2.243084	2.666831	-6.891902
H	3.025626	4.516497	-6.114735
H	1.345192	0.766200	-7.367294
H	2.660654	2.811044	-7.883441
C	-0.939531	3.956477	-3.105056
F	-2.083510	4.202895	-2.469876
F	-0.179760	5.055563	-3.023954
F	-1.218928	3.740484	-4.389944
H	1.064262	1.479370	-0.782590

β-17a

M06-2X SCF energy: -2164.38495255 a.u.

M06-2X enthalpy: -2163.824066 a.u.
M06-2X free energy: -2163.937625 a.u.
M06-2X SCF energy in solution: -2165.00726381 a.u.
M06-2X enthalpy in solution: -2164.446377 a.u.
M06-2X free energy in solution: -2164.559936 a.u.
Three lowest frequencies (cm-1): 17.6563 18.0239 24.0054

Cartesian coordinates

ATOM	X	Y	Z
C	-1.099820	-0.008751	-0.379602
C	0.390366	-0.267997	-0.536721
C	1.112791	1.077154	-0.626788
C	-0.479184	2.218820	0.630611
C	-1.366131	0.983896	0.758493
H	0.771162	-0.804355	0.341713
H	-1.510529	0.389016	-1.313029
H	-0.780949	2.771184	-0.272083
H	-2.421019	1.267839	0.762674
H	0.818865	1.627591	-1.531785
O	0.887443	1.832009	0.521755
N	0.588185	-1.046521	-1.770284
N	1.712742	-1.547975	-1.873049
N	2.707425	-2.045247	-2.062741
O	-1.705566	-1.259482	-0.071380
C	-3.018399	-1.397924	-0.364283
O	-3.640687	-0.586122	-1.006784
C	-3.577821	-2.659599	0.189362
C	-4.846430	-3.060995	-0.233859
C	-2.880448	-3.410443	1.139521
C	-5.413173	-4.219850	0.285741
H	-5.375446	-2.459795	-0.966921
C	-3.456785	-4.561745	1.665808
H	-1.897484	-3.089852	1.468583
C	-4.720029	-4.968106	1.236973
H	-6.396256	-4.538238	-0.046775
H	-2.920862	-5.138572	2.413431
H	-5.166322	-5.869152	1.647386
O	-1.034575	0.340423	1.994319
C	-2.028528	-0.305369	2.638597
O	-3.184992	-0.273127	2.283708
C	-1.536495	-1.057852	3.823289
C	-2.456612	-1.857964	4.506433
C	-0.203666	-0.998584	4.240023
C	-2.043993	-2.598662	5.607868

H	-3.484993	-1.893277	4.160308
C	0.201897	-1.737786	5.347071
H	0.506273	-0.379343	3.701539
C	-0.715517	-2.536410	6.028866
H	-2.755895	-3.223293	6.138421
H	1.235199	-1.693062	5.676544
H	-0.394865	-3.114355	6.890545
C	-0.596811	3.131278	1.833290
H	-1.662000	3.290265	2.067333
H	-0.124767	2.648650	2.701763
O	0.037319	4.346187	1.527410
C	0.034600	5.224487	2.629615
H	0.564099	4.789947	3.489499
H	0.546196	6.138318	2.319787
H	-0.990201	5.474938	2.939946
O	2.486317	0.763783	-0.685191
C	3.322438	1.702580	-1.167151
N	2.961328	2.872412	-1.444497
C	3.819095	3.835861	-2.024964
C	4.397324	3.640759	-3.282289
C	4.009290	5.041327	-1.345083
C	5.188272	4.642296	-3.838971
H	4.215574	2.714715	-3.819004
C	4.814682	6.028167	-1.903174
H	3.528510	5.184461	-0.382009
C	5.407326	5.833263	-3.150847
H	5.635809	4.486898	-4.816176
H	4.973434	6.957668	-1.364487
H	6.028523	6.609185	-3.587361
C	4.713901	1.076526	-1.331936
F	4.871572	0.032143	-0.521145
F	4.878969	0.645000	-2.589180
F	5.674827	1.958332	-1.064330

TMSI

M06-2X SCF energy: -420.53229462 a.u.

M06-2X enthalpy: -420.409327 a.u.

M06-2X free energy: -420.453528 a.u.

M06-2X SCF energy in solution: -420.63615597 a.u.

M06-2X enthalpy in solution: -420.513188 a.u.

M06-2X free energy in solution: -420.557389 a.u.

Three lowest frequencies (cm-1): 145.5882 149.9084 165.7522

Cartesian coordinates

ATOM	X	Y	Z
Si	-0.932808	-0.039735	0.102939
C	-2.795209	0.019453	-0.002946
H	-3.159764	1.050696	-0.033343
H	-3.156036	-0.502579	-0.894522
H	-3.227659	-0.470698	0.878189
C	-0.253961	0.915742	1.554602
H	-0.596567	0.451931	2.488063
H	0.840487	0.914024	1.555846
H	-0.599146	1.954059	1.544733
C	-0.254203	-1.775517	-0.005172
H	-0.614071	-2.289546	-0.901845
H	0.839963	-1.773199	-0.021109
H	-0.580844	-2.348790	0.871484
I	-0.092942	1.164739	-1.968495

TMSI-OPTFAI

M06-2X SCF energy: -1146.30405616 a.u.

M06-2X enthalpy: -1146.049018 a.u.

M06-2X free energy: -1146.118024 a.u.

M06-2X SCF energy in solution: -1146.59343671 a.u.

M06-2X enthalpy in solution: -1146.338399 a.u.

M06-2X free energy in solution: -1146.407405 a.u.

Three lowest frequencies (cm-1): 22.7427 27.0617 41.6264

Cartesian coordinates

ATOM	X	Y	Z
Si	-0.846030	-0.054571	0.189638
C	-2.655414	0.081996	-0.234266
H	-2.964651	1.128631	-0.327891
H	-2.880162	-0.423538	-1.179531
H	-3.269655	-0.380101	0.546842
C	-0.416793	0.947586	1.705775
H	-1.052529	0.645765	2.546492
H	0.627151	0.811770	2.001676
H	-0.588984	2.014906	1.527481
C	-0.290633	-1.833191	0.283804
H	-0.381232	-2.322473	-0.692517
H	0.746794	-1.920781	0.617846
H	-0.924401	-2.384029	0.988766

O	-0.110453	0.685423	-1.195926
C	1.201727	0.788500	-1.343012
N	2.031858	0.394350	-0.474904
C	3.432058	0.423798	-0.656935
C	4.206115	1.163957	0.241326
C	4.056005	-0.342350	-1.646284
C	5.591758	1.168957	0.122266
H	3.708122	1.734431	1.019842
C	5.444705	-0.340745	-1.749168
H	3.450380	-0.940104	-2.320913
C	6.217367	0.417219	-0.872036
H	6.185971	1.757973	0.814786
H	5.922793	-0.936773	-2.521076
H	7.299557	0.416878	-0.957397
C	1.543932	1.425026	-2.698950
F	0.544511	2.187238	-3.140773
F	2.634715	2.189249	-2.623693
F	1.767216	0.474504	-3.617769

TS5

M06-2X SCF energy: -2549.80693715 a.u.

M06-2X enthalpy: -2549.078981 a.u.

M06-2X free energy: -2549.215062 a.u.

M06-2X SCF energy in solution: -2550.49414658 a.u.

M06-2X enthalpy in solution: -2549.766190 a.u.

M06-2X free energy in solution: -2549.902271 a.u.

Three lowest frequencies (cm-1): -125.6201 7.3216 15.6513

Imaginary frequency: -125.6201 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.932672	1.012293	-0.418117
C	0.541805	0.084700	0.721936
C	-0.340726	-1.048068	0.224743
C	0.295477	-0.748249	-2.075894
C	1.402861	0.160262	-1.595094
H	1.463085	-0.356471	1.114901
H	0.093636	1.644333	-0.712587
H	-0.498733	-0.136266	-2.515500
H	1.714194	0.799911	-2.424907
H	-1.142811	-1.415211	0.856453
O	-0.383481	-1.444672	-0.983059

N	-0.170054	0.837702	1.754750
N	-0.035071	0.386641	2.901165
N	0.009857	0.080951	3.984589
O	2.015462	1.792158	0.074184
C	2.317913	2.899769	-0.640701
O	1.644868	3.279755	-1.570232
C	3.540904	3.579197	-0.141559
C	4.395523	2.976017	0.785436
C	3.832403	4.845717	-0.652562
C	5.540707	3.648776	1.200312
H	4.168372	1.987669	1.171150
C	4.973411	5.516916	-0.228280
H	3.157575	5.289927	-1.377221
C	5.827496	4.917532	0.697403
H	6.210843	3.183192	1.916080
H	5.198941	6.503983	-0.619399
H	6.720915	5.440182	1.025890
O	2.496382	-0.651444	-1.163093
C	3.743073	-0.150350	-1.351259
O	3.952217	0.888900	-1.931937
C	4.791971	-1.020623	-0.764615
C	4.489500	-2.261329	-0.197493
C	6.108203	-0.549925	-0.782929
C	5.510950	-3.031620	0.348855
H	3.464575	-2.616970	-0.178142
C	7.123641	-1.323580	-0.233856
H	6.316651	0.420241	-1.223192
C	6.824541	-2.564015	0.331123
H	5.278916	-3.994410	0.793373
H	8.146675	-0.961479	-0.243310
H	7.618545	-3.166960	0.761670
C	0.739721	-1.815389	-3.049070
H	1.366371	-1.345645	-3.823972
H	1.346771	-2.569228	-2.527052
O	-0.419925	-2.382360	-3.598131
C	-0.127381	-3.491230	-4.421163
H	0.373435	-4.286759	-3.852960
H	-1.076666	-3.868491	-4.805947
H	0.513754	-3.203304	-5.265996
I	0.919078	-3.245087	1.648923
P	-3.406963	0.644099	-0.139257
O	-1.995382	0.735061	-0.677725
C	-3.487641	0.180583	1.611114
C	-3.281786	1.157293	2.594460

C	-3.590309	-1.164859	1.979870
C	-3.191743	0.789129	3.933062
H	-3.187640	2.203112	2.312909
C	-3.486962	-1.530828	3.321262
H	-3.743470	-1.929922	1.222689
C	-3.293642	-0.554825	4.295580
H	-3.035929	1.548324	4.693240
H	-3.559434	-2.576775	3.601945
H	-3.213898	-0.840642	5.340091
C	-4.277917	2.224229	-0.308328
C	-3.766720	3.139997	-1.232676
C	-5.437234	2.531969	0.412840
C	-4.416986	4.353765	-1.441994
H	-2.857640	2.899818	-1.776701
C	-6.084208	3.745862	0.199334
H	-5.828947	1.832971	1.147551
C	-5.575574	4.654664	-0.728774
H	-4.016825	5.064668	-2.158101
H	-6.981078	3.985730	0.761782
H	-6.080966	5.601943	-0.891017
C	-4.355505	-0.609624	-1.045440
C	-5.713499	-0.836291	-0.793394
C	-3.689799	-1.360635	-2.016532
C	-6.399750	-1.806977	-1.515361
H	-6.234378	-0.258902	-0.033340
C	-4.381456	-2.333476	-2.736721
H	-2.634033	-1.188336	-2.205092
C	-5.733292	-2.554598	-2.487737
H	-7.452897	-1.982838	-1.319600
H	-3.861397	-2.915907	-3.491067
H	-6.271300	-3.312644	-3.048966

Int2

M06-2X SCF energy: -2549.84288322 a.u.

M06-2X enthalpy: -2549.111928 a.u.

M06-2X free energy: -2549.248412 a.u.

M06-2X SCF energy in solution: -2550.52717205 a.u.

M06-2X enthalpy in solution: -2549.796217 a.u.

M06-2X free energy in solution: -2549.932701 a.u.

Three lowest frequencies (cm-1): 8.7588 12.5035 19.2369

Cartesian coordinates

ATOM	X	Y	Z
C	-1.622621	2.843338	-2.066320
C	-0.186033	2.406020	-2.314071
C	0.719228	3.643496	-2.373411
C	-0.715423	4.923037	-1.002533
C	-1.699229	3.773913	-0.851103
H	0.155492	1.783963	-1.478382
H	-2.018079	3.359709	-2.946071
H	-1.033239	5.536584	-1.855522
H	-2.716825	4.155107	-0.737030
O	0.604561	4.420959	-1.240472
N	-0.127494	1.679121	-3.590552
N	0.722372	0.784589	-3.631401
N	1.464786	-0.053296	-3.772607
O	-2.380776	1.665801	-1.811694
C	-3.716959	1.767719	-1.999324
O	-4.235070	2.734734	-2.506247
C	-4.448721	0.565194	-1.524949
C	-3.844536	-0.385871	-0.698328
C	-5.788299	0.430140	-1.895442
C	-4.586138	-1.472872	-0.246547
H	-2.806757	-0.267935	-0.403773
C	-6.522024	-0.663609	-1.450397
H	-6.240129	1.185999	-2.530079
C	-5.921159	-1.613779	-0.624876
H	-4.123614	-2.209265	0.403274
H	-7.561660	-0.773641	-1.742268
H	-6.495999	-2.465579	-0.273740
O	-1.326846	3.026173	0.311333
C	-2.319171	2.441146	1.015780
O	-3.493105	2.605478	0.774920
C	-1.798525	1.583108	2.112679
C	-0.430796	1.468324	2.377709
C	-2.728910	0.871941	2.875779
C	0.001095	0.644034	3.412004
H	0.285288	2.022745	1.780320
C	-2.291019	0.047209	3.905633
H	-3.785964	0.973067	2.650307
C	-0.926770	-0.065341	4.174050
H	1.061831	0.554178	3.623984
H	-3.011170	-0.507224	4.498974
H	-0.585751	-0.708689	4.979597
C	-0.623498	5.812323	0.216943
H	-1.637988	6.085473	0.547477

H	-0.125531	5.273491	1.035748
O	0.108552	6.953930	-0.156211
C	0.291246	7.842270	0.923585
H	0.868186	7.373602	1.733062
H	0.839005	8.708250	0.546304
H	-0.672815	8.179625	1.329606
O	0.299129	4.407494	-3.519500
P	1.275485	4.979160	-4.667065
C	0.181299	6.092725	-5.532167
C	-1.119175	5.663472	-5.833359
C	0.624536	7.364084	-5.904559
C	-1.974424	6.519987	-6.515159
H	-1.455137	4.672300	-5.539867
C	-0.242974	8.211667	-6.588247
H	1.633757	7.687909	-5.669604
C	-1.534792	7.790267	-6.891898
H	-2.982827	6.198025	-6.753499
H	0.095498	9.198437	-6.885763
H	-2.206555	8.454739	-7.426743
C	1.841015	3.639337	-5.708973
C	2.778828	2.722366	-5.210584
C	1.317530	3.487903	-6.997573
C	3.173103	1.647680	-5.998458
H	3.207918	2.850451	-4.219920
C	1.722825	2.410127	-7.778683
H	0.615363	4.211826	-7.398193
C	2.642799	1.491591	-7.279513
H	3.894851	0.935212	-5.613043
H	1.323844	2.296399	-8.780976
H	2.955703	0.652784	-7.893406
C	2.631958	5.819993	-3.864011
C	2.348422	6.556888	-2.703725
C	3.926892	5.780548	-4.394375
C	3.376973	7.242370	-2.068691
H	1.345839	6.588103	-2.285509
C	4.943337	6.482037	-3.752134
H	4.138345	5.223766	-5.302405
C	4.669548	7.204955	-2.592538
H	3.165779	7.803737	-1.164117
H	5.948214	6.461134	-4.160485
H	5.469111	7.743799	-2.093486
H	1.771795	3.357243	-2.456330
I	3.541615	6.431745	-8.297469

TS6

M06-2X SCF energy: -2704.78552799 a.u.

M06-2X enthalpy: -2703.967556 a.u.

M06-2X free energy: -2704.111036 a.u.

M06-2X SCF energy in solution: -2705.52827226 a.u.

M06-2X enthalpy in solution: -2704.710300 a.u.

M06-2X free energy in solution: -2704.853780 a.u.

Three lowest frequencies (cm-1): -180.9363 15.6515 21.3606

Imaginary frequency: -180.9363 cm-1

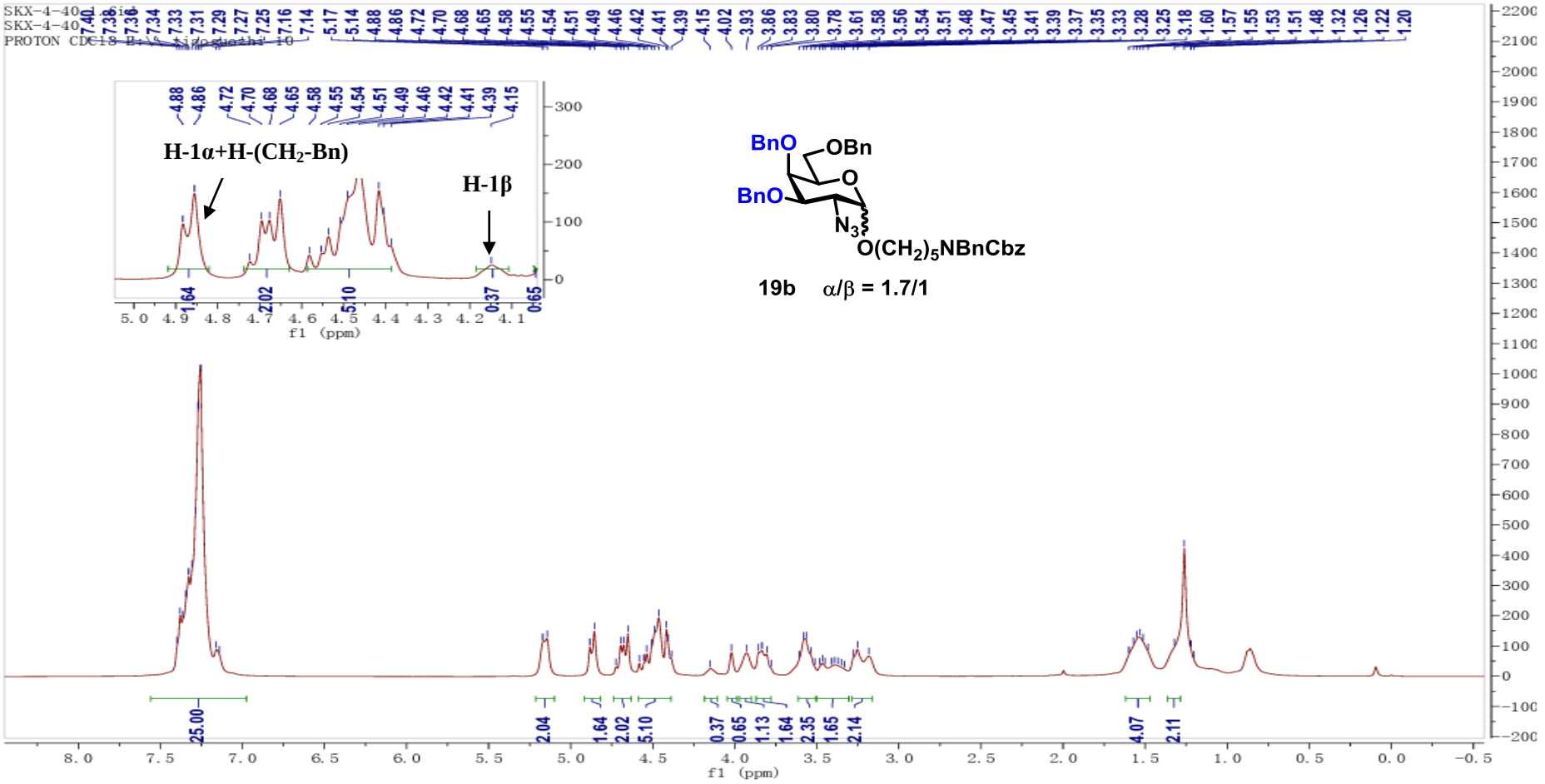
Cartesian coordinates

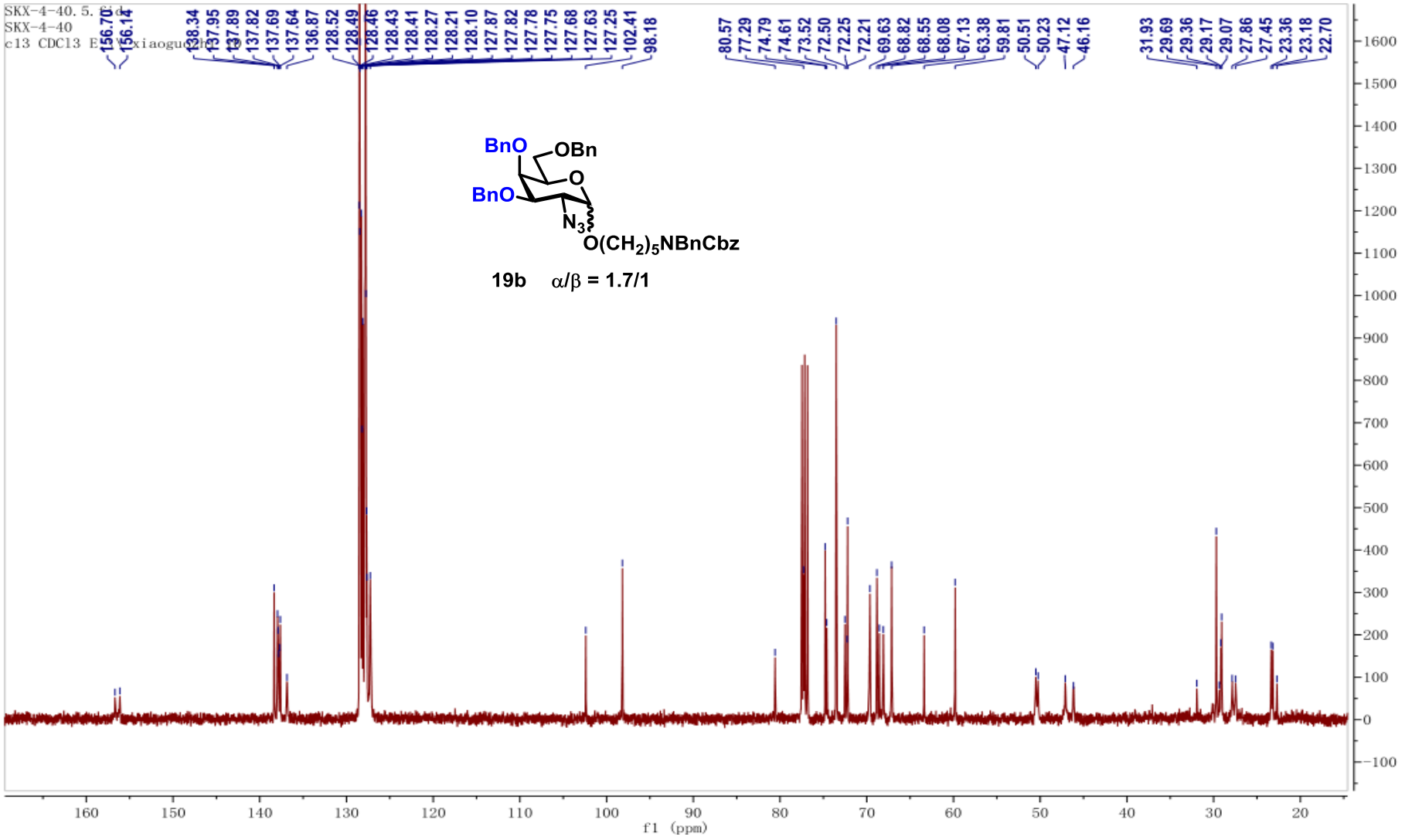
ATOM	X	Y	Z
C	-1.472728	1.339200	0.042927
C	-0.945842	0.472191	-1.092241
C	0.152252	-0.441802	-0.620516
C	-0.486200	-0.248410	1.690242
C	-1.770407	0.427860	1.227970
H	-1.770269	-0.187187	-1.391797
H	-0.747358	2.104583	0.322309
H	0.187704	0.521237	2.082591
H	-2.173573	1.001702	2.066102
O	0.262669	-0.840842	0.577717
N	-0.450472	1.239444	-2.236241
N	-1.348911	1.562575	-3.023776
N	-2.080110	1.913271	-3.806575
O	-2.658593	1.930390	-0.474700
C	-3.120589	3.023351	0.174131
O	-2.595899	3.456870	1.173148
C	-4.321447	3.601554	-0.480325
C	-4.864516	3.054895	-1.646715
C	-4.902821	4.726694	0.109921
C	-5.990630	3.638392	-2.218118
H	-4.410990	2.181182	-2.102386
C	-6.027712	5.305533	-0.465706
H	-4.465556	5.134748	1.015557
C	-6.571250	4.761028	-1.629301
H	-6.414910	3.217249	-3.123895
H	-6.481494	6.179142	-0.008771
H	-7.450317	5.213151	-2.078645
O	-2.724193	-0.528816	0.776951
C	-3.547160	-1.046666	1.717160
O	-3.641959	-0.587664	2.832270

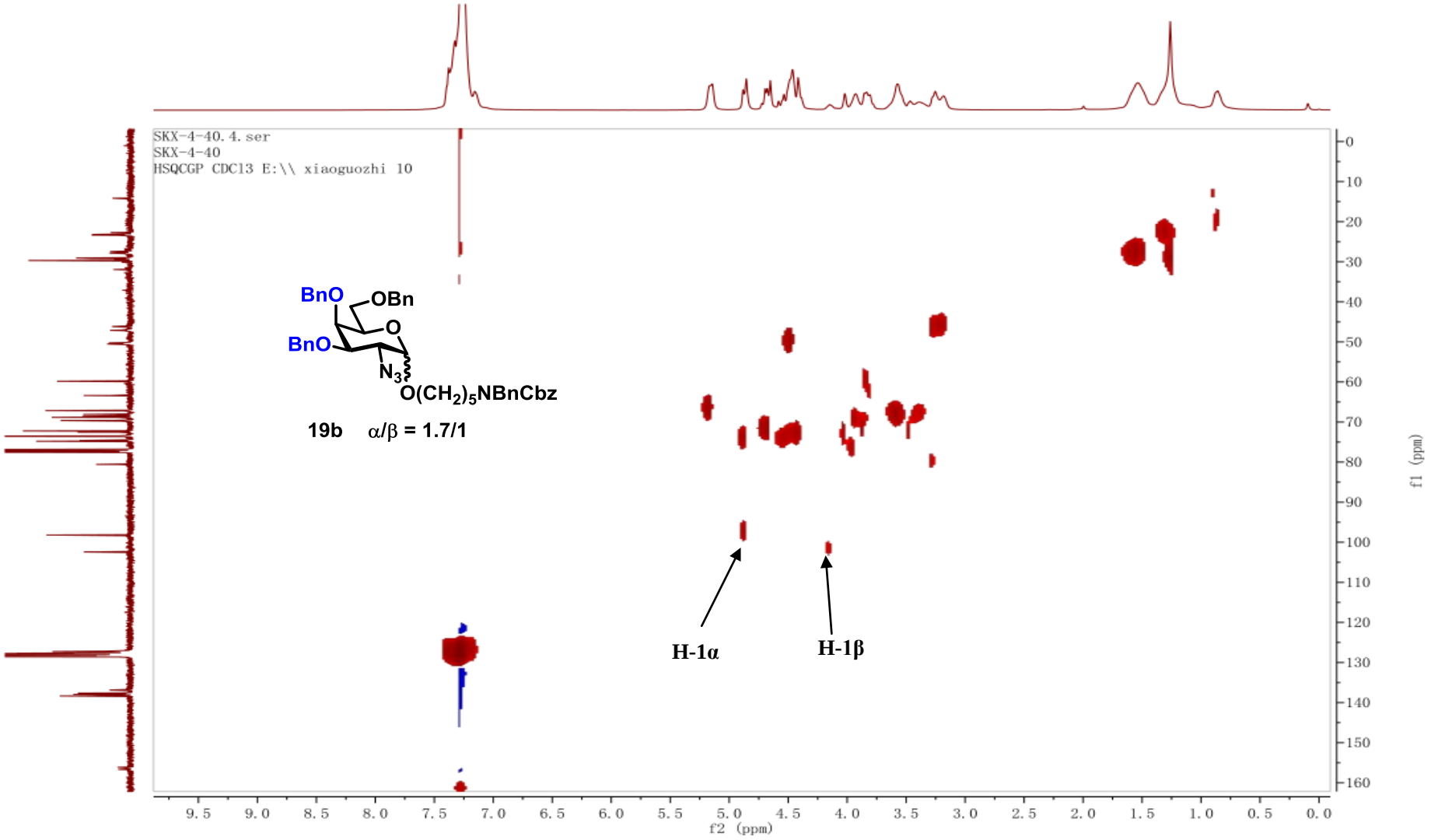
C	-4.329838	-2.201594	1.213183
C	-3.917891	-2.940323	0.100197
C	-5.473769	-2.565167	1.926803
C	-4.670656	-4.041467	-0.299716
H	-3.003806	-2.669368	-0.421823
C	-6.226709	-3.658281	1.514213
H	-5.760986	-1.983910	2.797216
C	-5.824483	-4.395500	0.400522
H	-4.355222	-4.628983	-1.156439
H	-7.121100	-3.938221	2.061632
H	-6.408245	-5.253919	0.081862
C	-0.638471	-1.347574	2.721084
H	0.361418	-1.665072	3.051086
H	-1.170074	-0.923532	3.585979
O	-1.339761	-2.424861	2.157158
C	-1.693886	-3.385279	3.130058
H	-2.391327	-2.958730	3.864947
H	-2.179715	-4.211509	2.607571
H	-0.805893	-3.762144	3.655656
H	0.974077	-0.714906	-1.279049
C	-0.967391	-3.574417	-3.510863
H	-0.248781	-4.322913	-3.161245
H	-1.974369	-3.889704	-3.220807
H	-0.914870	-3.530928	-4.603056
C	-0.646035	-2.215907	-2.921136
H	0.363317	-1.891402	-3.210306
H	-1.362873	-1.464811	-3.268727
O	-0.755938	-2.233934	-1.491401
H	-0.092992	-2.881688	-1.162247
O	1.412938	1.575930	-0.067312
P	2.872811	1.424194	0.319919
C	3.114430	0.537866	1.881034
C	3.145689	-0.861954	1.888323
C	3.122664	1.240632	3.092462
C	3.204879	-1.549977	3.097813
H	3.122195	-1.420956	0.955181
C	3.172705	0.547340	4.299150
H	3.092758	2.327129	3.094932
C	3.218400	-0.846540	4.301758
H	3.236417	-2.635533	3.094086
H	3.182167	1.095471	5.236070
H	3.264847	-1.384718	5.243866
C	3.647584	3.049194	0.525265
C	4.973204	3.176362	0.955666

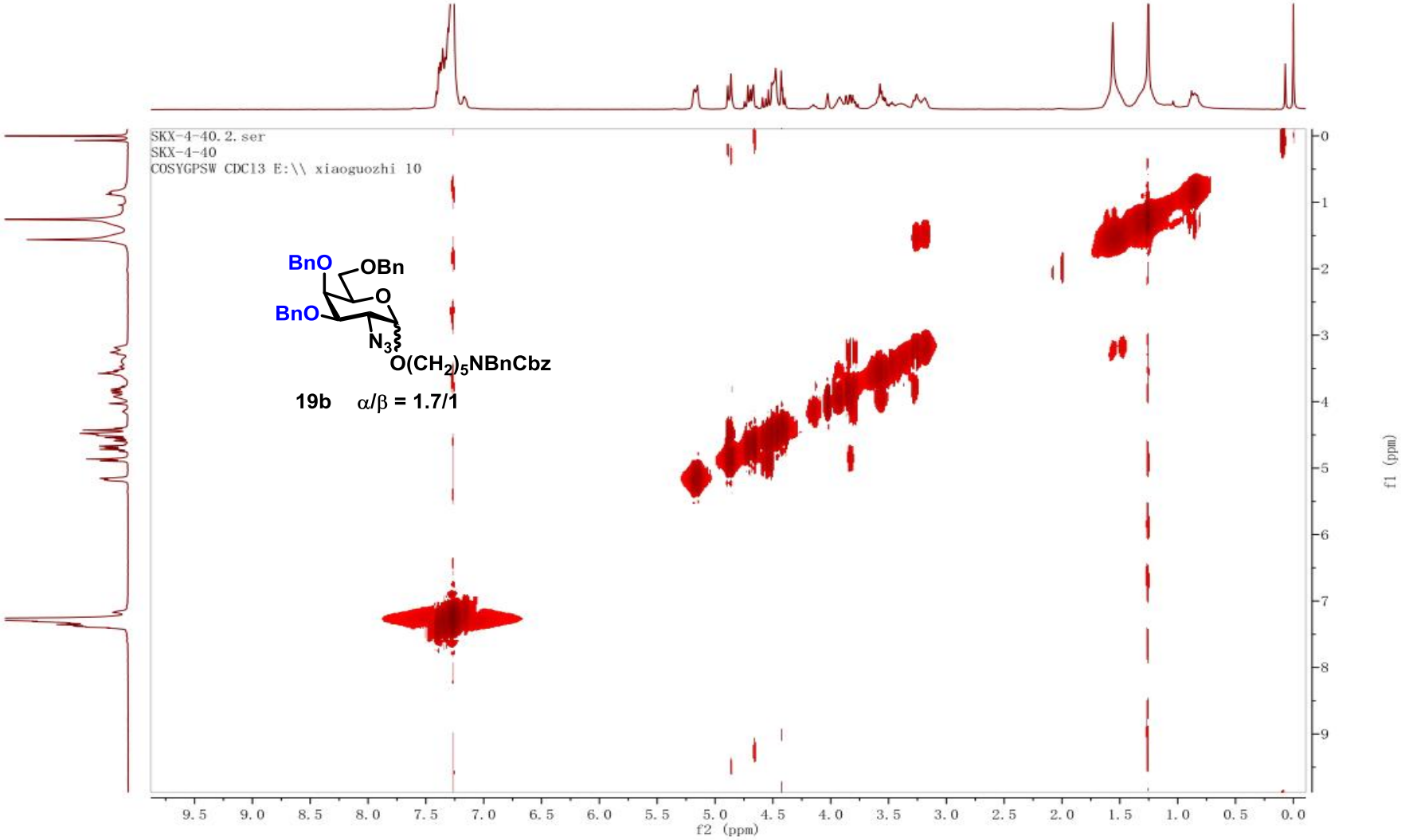
C	2.895134	4.185234	0.222354
C	5.540448	4.439993	1.081188
H	5.557781	2.291731	1.198500
C	3.468192	5.449720	0.350278
H	1.867301	4.072322	-0.110436
C	4.787667	5.575871	0.777767
H	6.567909	4.540461	1.416785
H	2.883962	6.333998	0.115467
H	5.233177	6.561008	0.877843
C	3.785919	0.528878	-0.961128
C	3.223463	0.500433	-2.241635
C	5.014439	-0.094735	-0.720541
C	3.884381	-0.158727	-3.275093
H	2.265506	0.984862	-2.419033
C	5.670974	-0.750231	-1.758154
H	5.449851	-0.087254	0.275498
C	5.105843	-0.783326	-3.032320
H	3.442610	-0.190574	-4.266327
H	6.618221	-1.245506	-1.569615
H	5.616366	-1.304584	-3.836226
I	2.500005	-3.520840	-1.149452

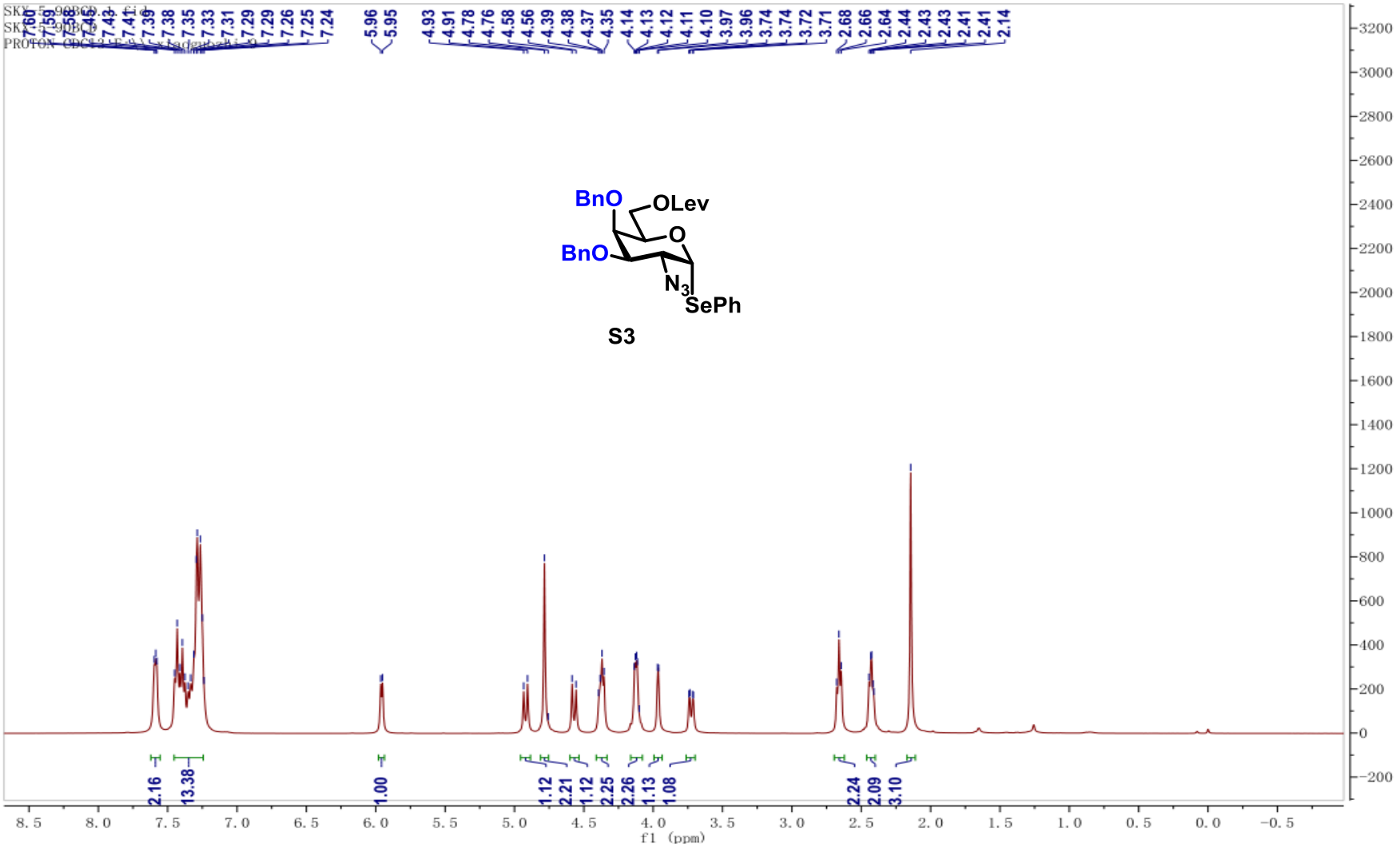
Spectroscopic Data

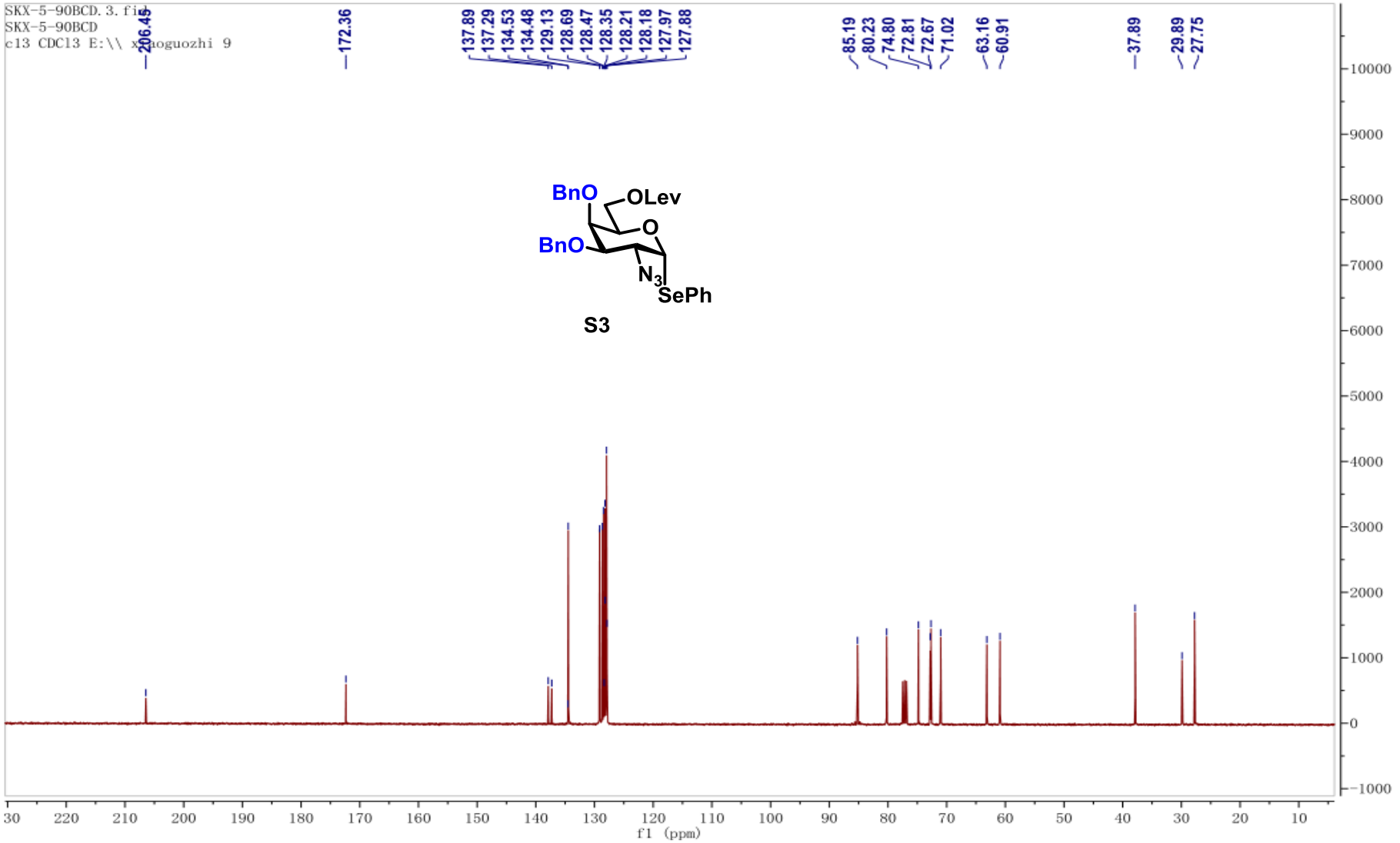


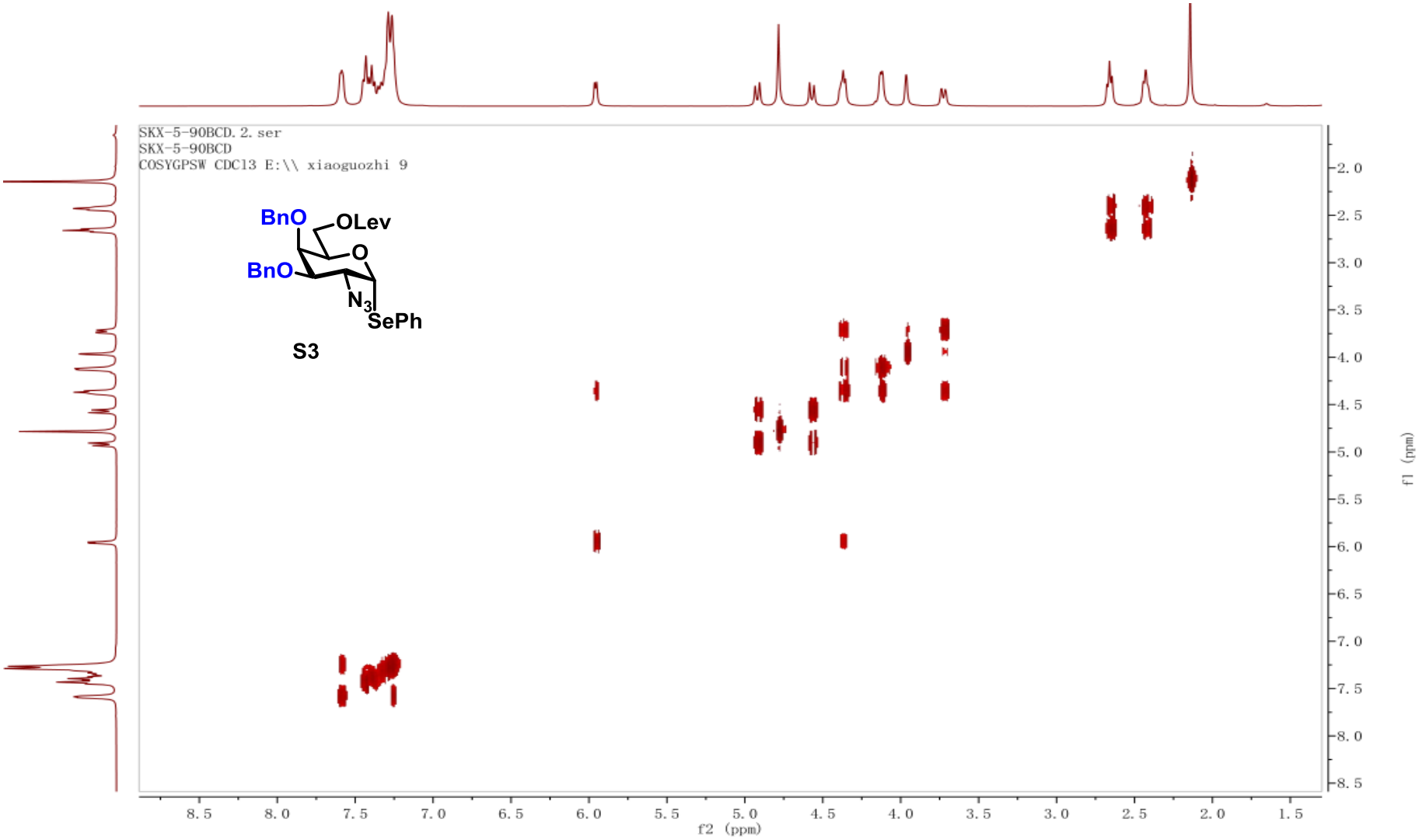

SKX-4-40.5.fid
SKX-4-40
c13 CDCl3 E:\xiaogu\2013
156.70
156.14
138.34
137.95
137.89
137.82
137.69
137.64
136.87
128.52
128.49
128.46
128.43
128.41
128.27
128.21
128.10
127.87
127.82
127.78
127.75
127.68
127.63
127.25
102.41
98.18
80.57
77.29
74.79
74.61
73.52
72.50
72.25
72.21
69.63
68.82
68.55
68.08
67.13
63.38
59.81
50.51
50.23
47.12
46.16
31.93
29.69
29.36
29.17
29.07
27.86
27.45
23.36
23.18
22.70
BnO
OBn
O
BnO
N3
O(CH2)5NBnCbz
19b α/β = 1.7/1
f1 (ppm)


SKX-4-40.4.ser
SKX-4-40
HSQCGP CDCl3 E:\\ xiaoguozhi 10
BnO
OBn
O
BnO
N3
O(CH2)5NBnCbz
19b α/β = 1.7/1
H-1α
H-1β
f2 (ppm)
f1 (ppm)


SKX-4-40.2.ser
SKX-4-40
COSYGPSW CDCl3 E:\\ xiaoguozhi 10
BnO
OBn
O
BnO
N3
O(CH2)5NBnCbz
19b α/β = 1.7/1
f2 (ppm)
f1 (ppm)


BnO
OLev
O
BnO
N3
SePh
S3
f1 (ppm)


SKX-5-90BCD.3.fid
SKX-5-90BCD
c13 CDCl3 E:\\ xiaoguozhi 9
206.45
172.36
137.89
137.29
134.53
134.48
129.13
128.69
128.47
128.35
128.21
128.18
127.97
127.88
85.19
80.23
74.80
72.81
72.67
71.02
63.16
60.91
37.89
29.89
27.75
BnO
OLev
O
BnO
N3
SePh
S3
f1 (ppm)


SKX-5-90BCD.2.ser
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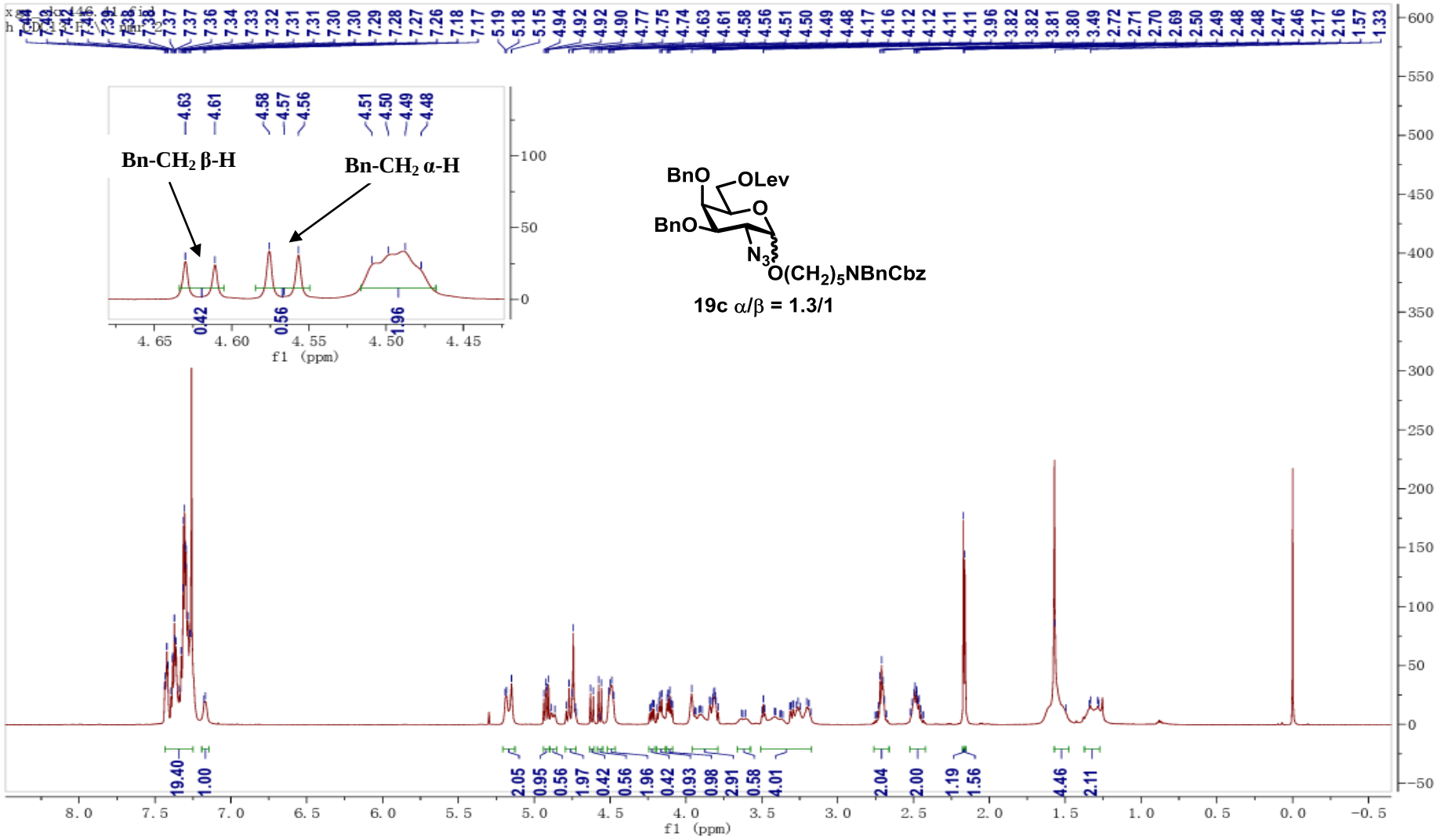
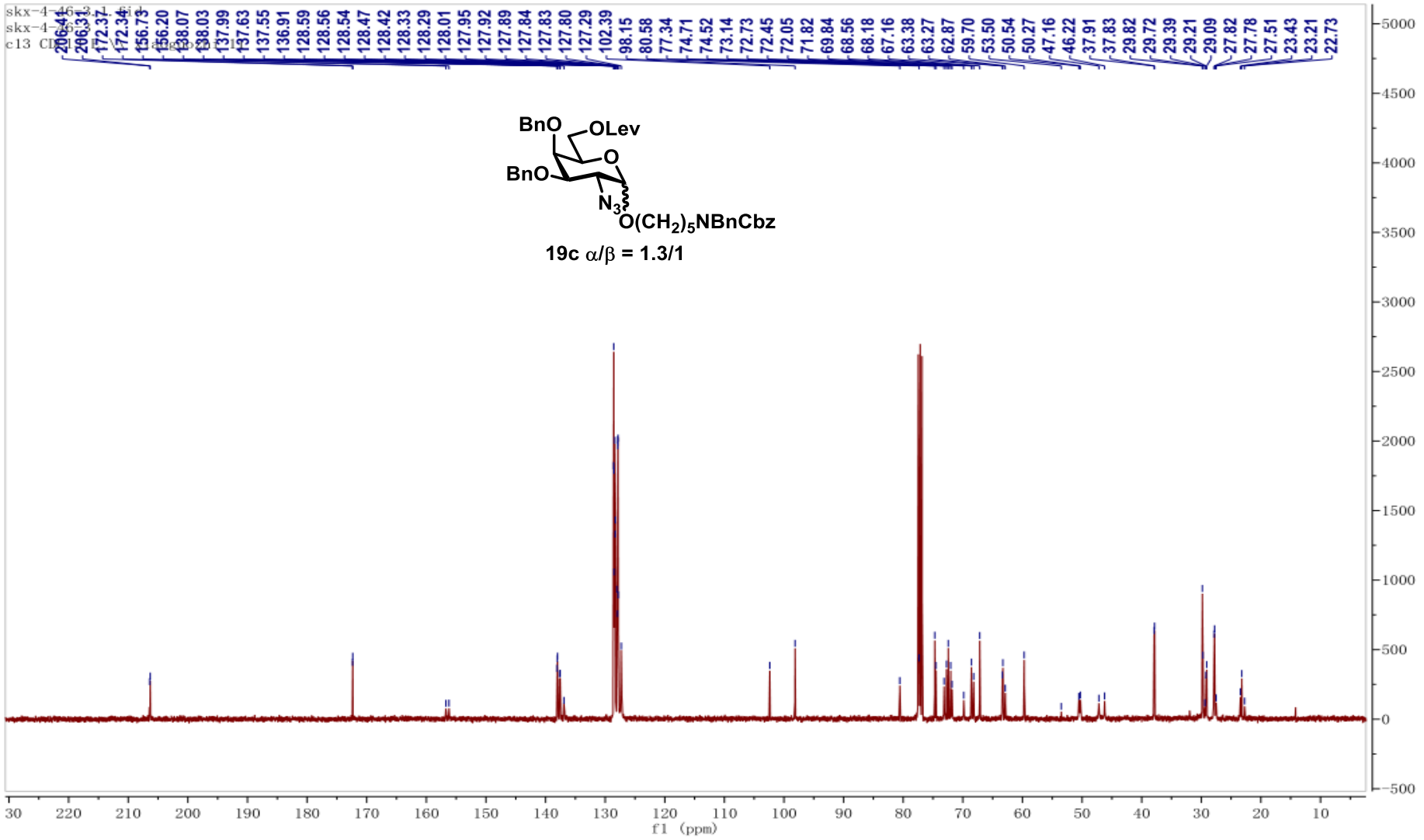
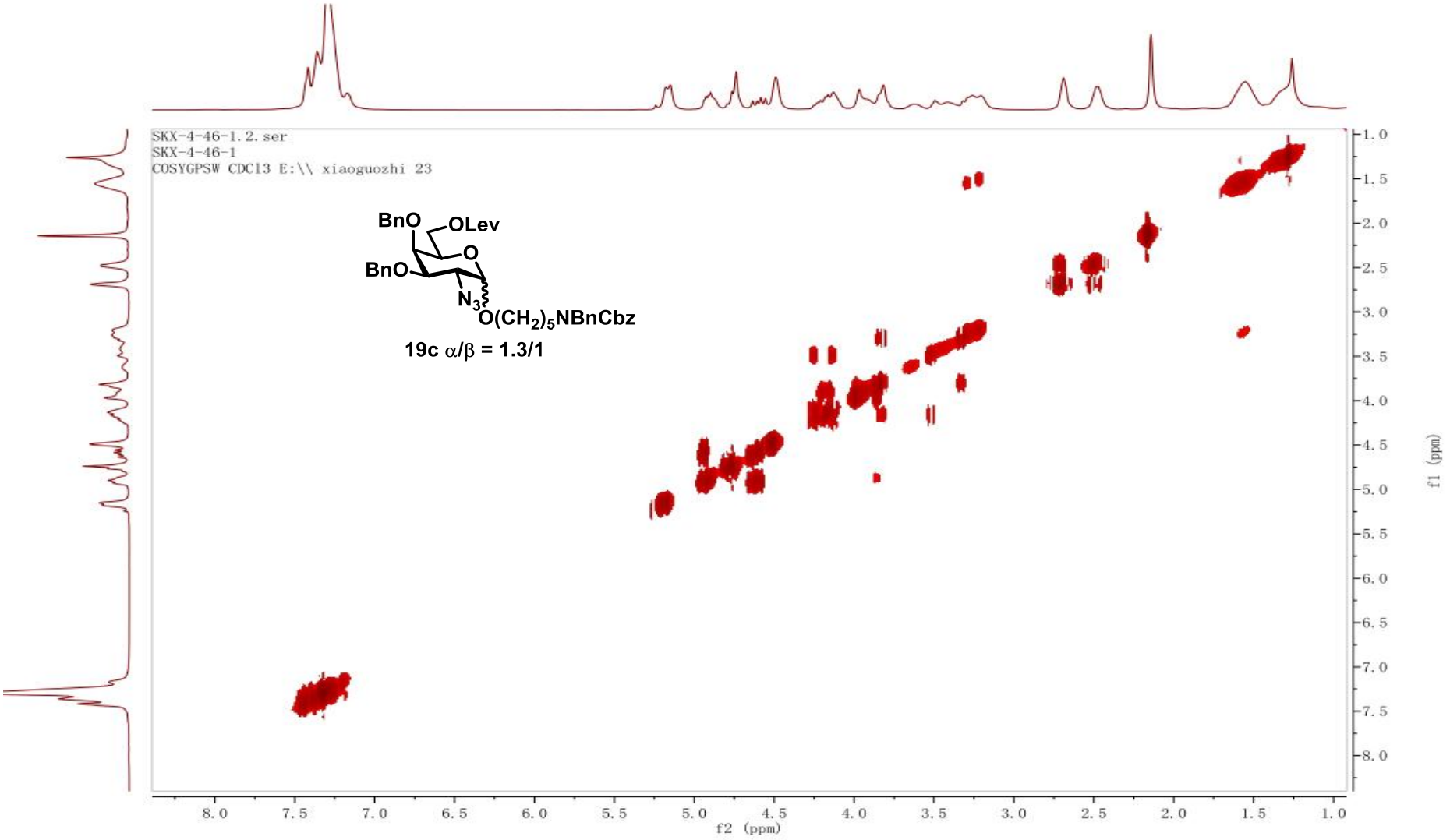
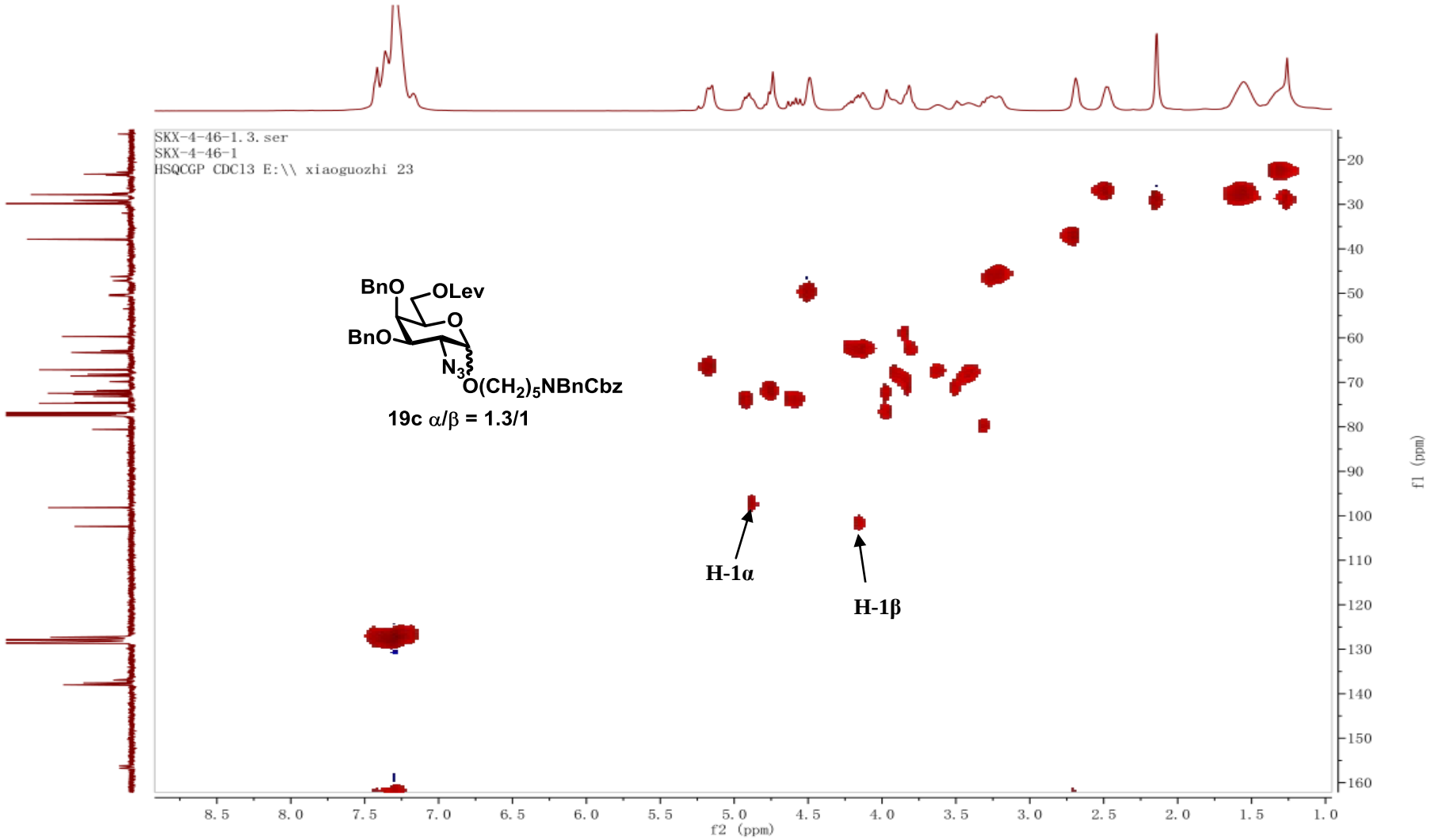
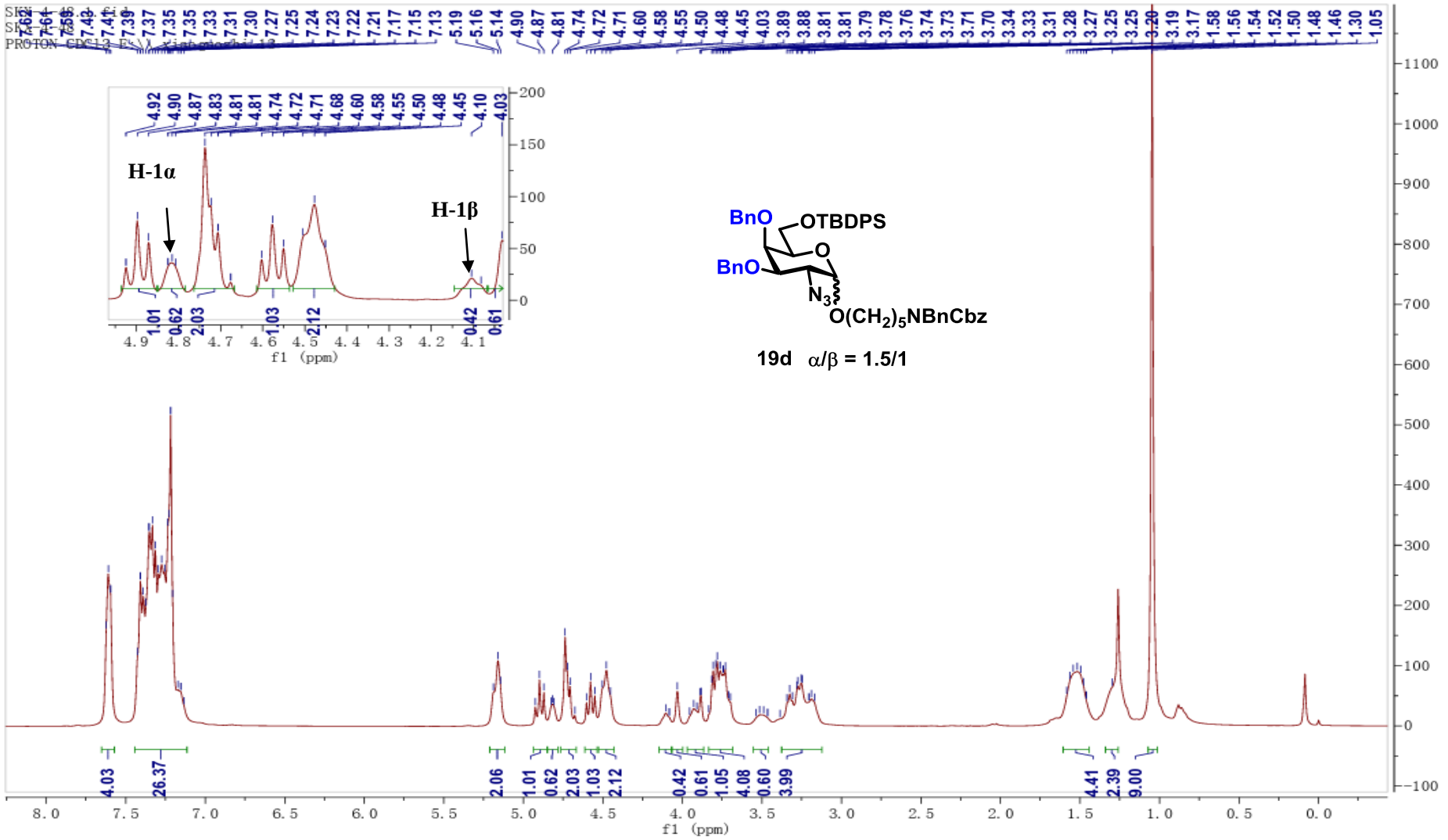
COSYGPSW CDCl3 E:\\ xiaoguozhi 9
BnO
OLev
O
BnO
N3
SePh
S3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)

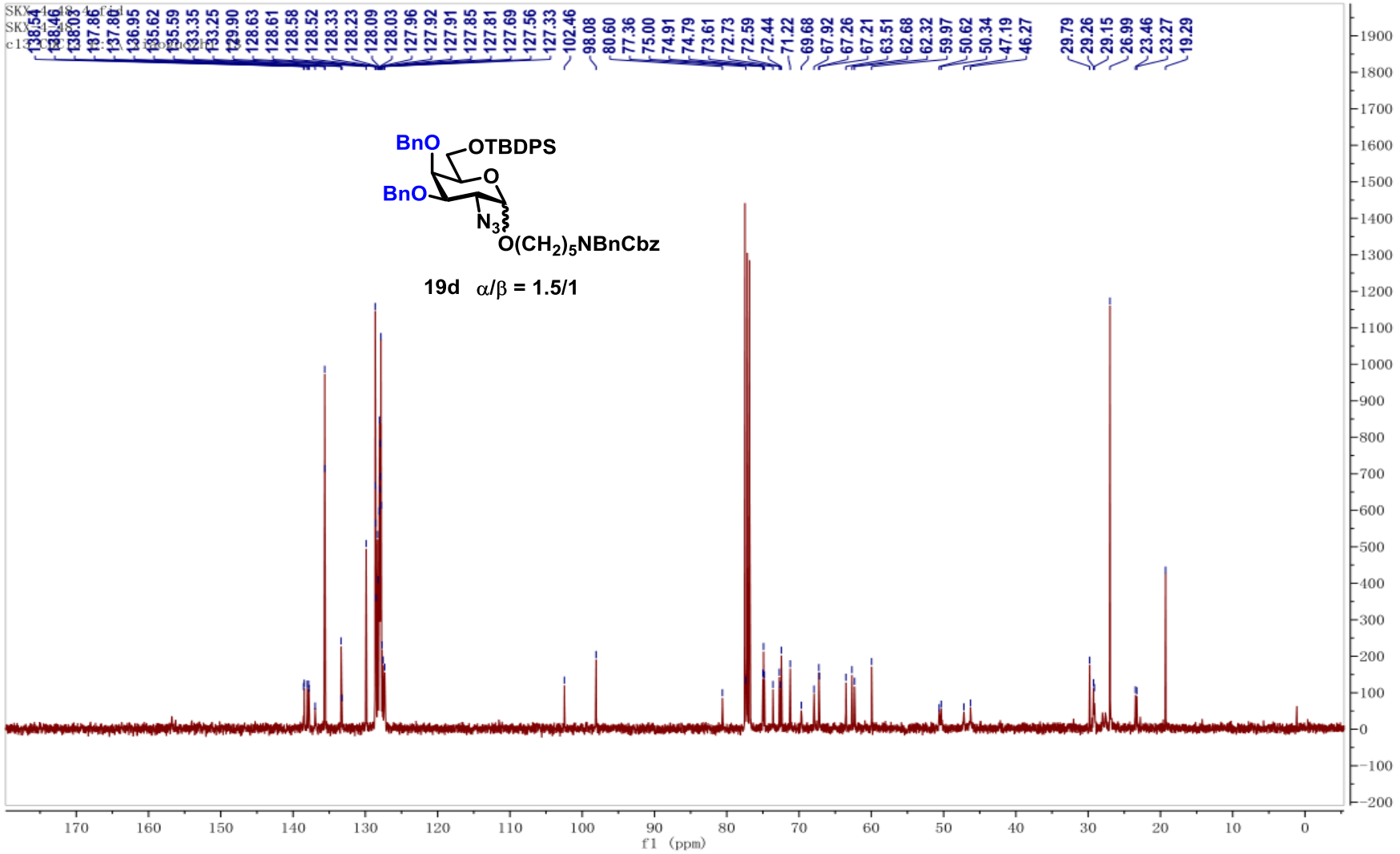

Bn-CH2 β-H
Bn-CH2 α-H
BnO
OLev
O
BnO
N3
O(CH2)5NBnCbz
19c α/β = 1.3/1
f1 (ppm)

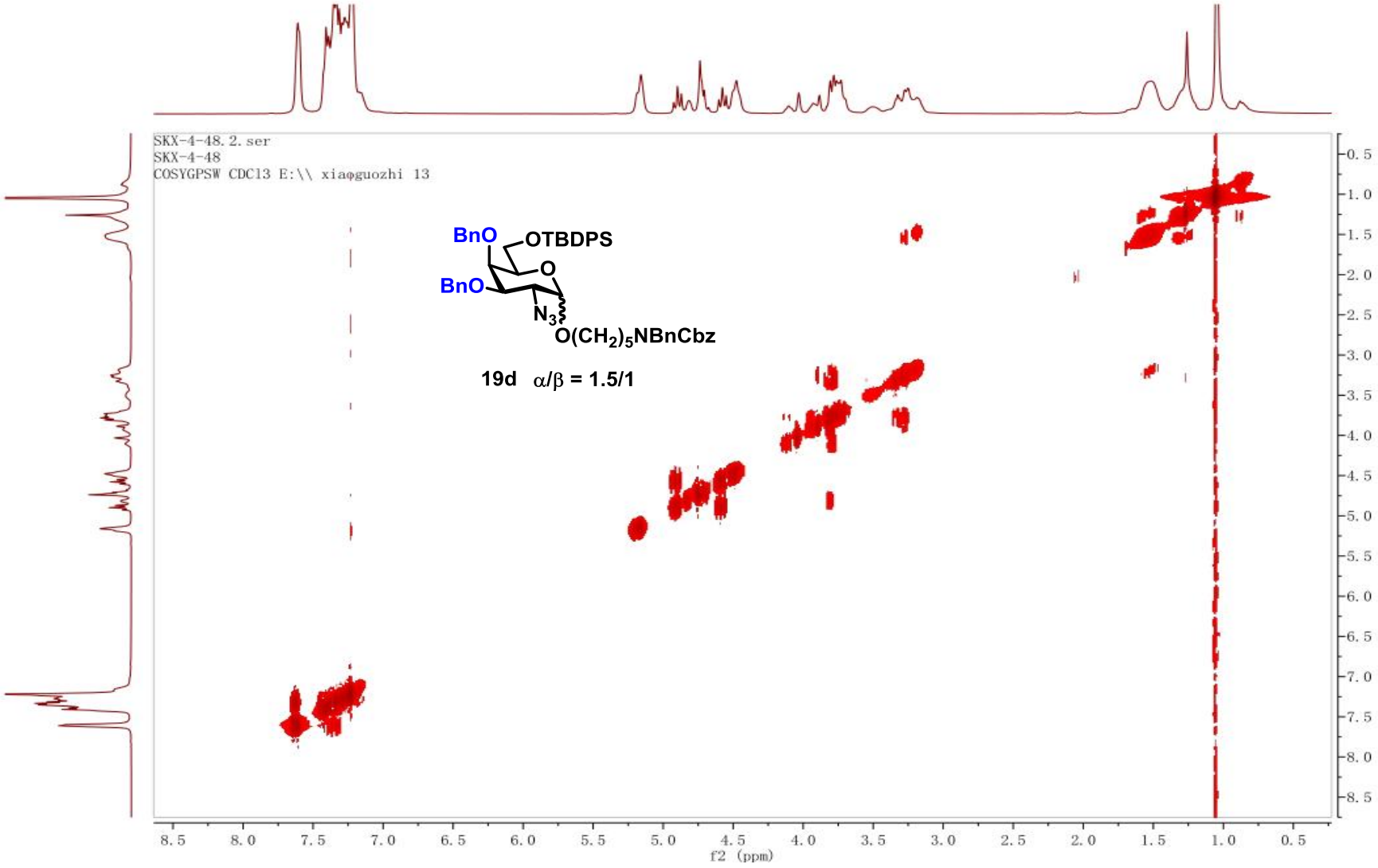

BnO
OLev
O
BnO
N3
O(CH2)5NBnCbz
19c α/β = 1.3/1
f1 (ppm)


SKX-4-46-1.2.ser
SKX-4-46-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 23
BnO
OLev
O
BnO
N3
O(CH2)5NBnCbz
19c α/β = 1.3/1
f2 (ppm)
f1 (ppm)


SKX-4-46-1.3.ser
SKX-4-46-1
HSQCGP CDC13 E:\\ xiaoguozhi 23
BnO
OLev
O
BnO
N3
O(CH2)5NBnCbz
19c α/β = 1.3/1
H-1α
H-1β
f2 (ppm)
f1 (ppm)


H-1α
H-1β
BnO
OTBDPS
O
BnO
N3
O(CH2)5NBnCbz
19d α/β = 1.5/1
f1 (ppm)


138.54
138.46
138.03
137.86
137.80
136.95
135.62
135.59
133.35
133.25
129.90
128.63
128.61
128.58
128.52
128.33
128.23
128.09
128.03
127.96
127.92
127.91
127.85
127.81
127.69
127.56
127.33
102.46
98.08
80.60
77.36
75.00
74.91
74.79
73.61
72.73
72.59
72.44
71.22
69.68
67.92
67.26
67.21
63.51
62.68
62.32
59.97
50.62
50.34
47.19
46.27
29.79
29.26
29.15
26.99
23.46
23.27
19.29
BnO
OTBDPS
O
BnO
N3
O(CH2)5NBnCbz
19d α/β = 1.5/1
f1 (ppm)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SKX-4-48
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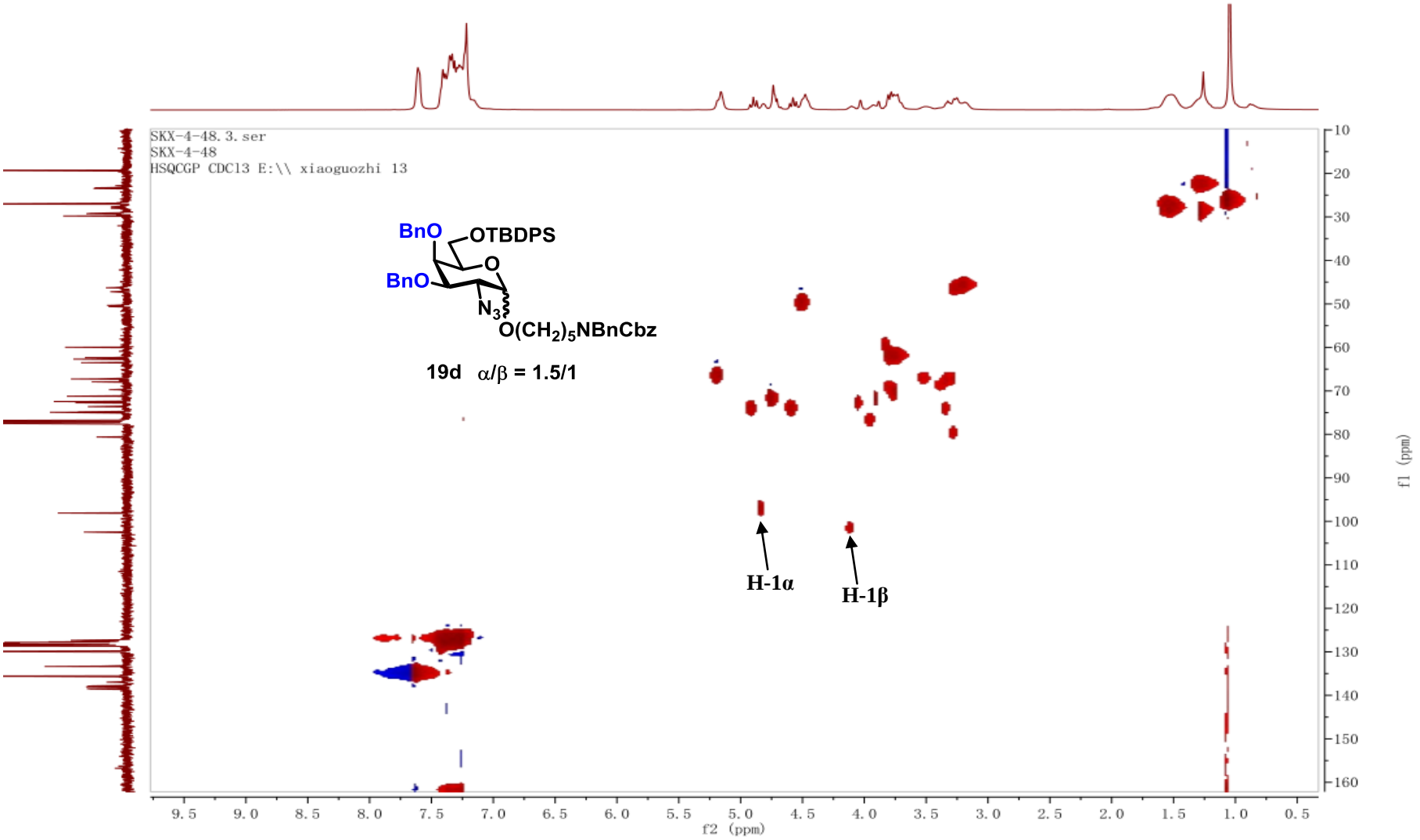
BnO
OTBDPS
O
BnO
N3
O(CH2)5NBnCbz
19d α/β = 1.5/1
f2 (ppm)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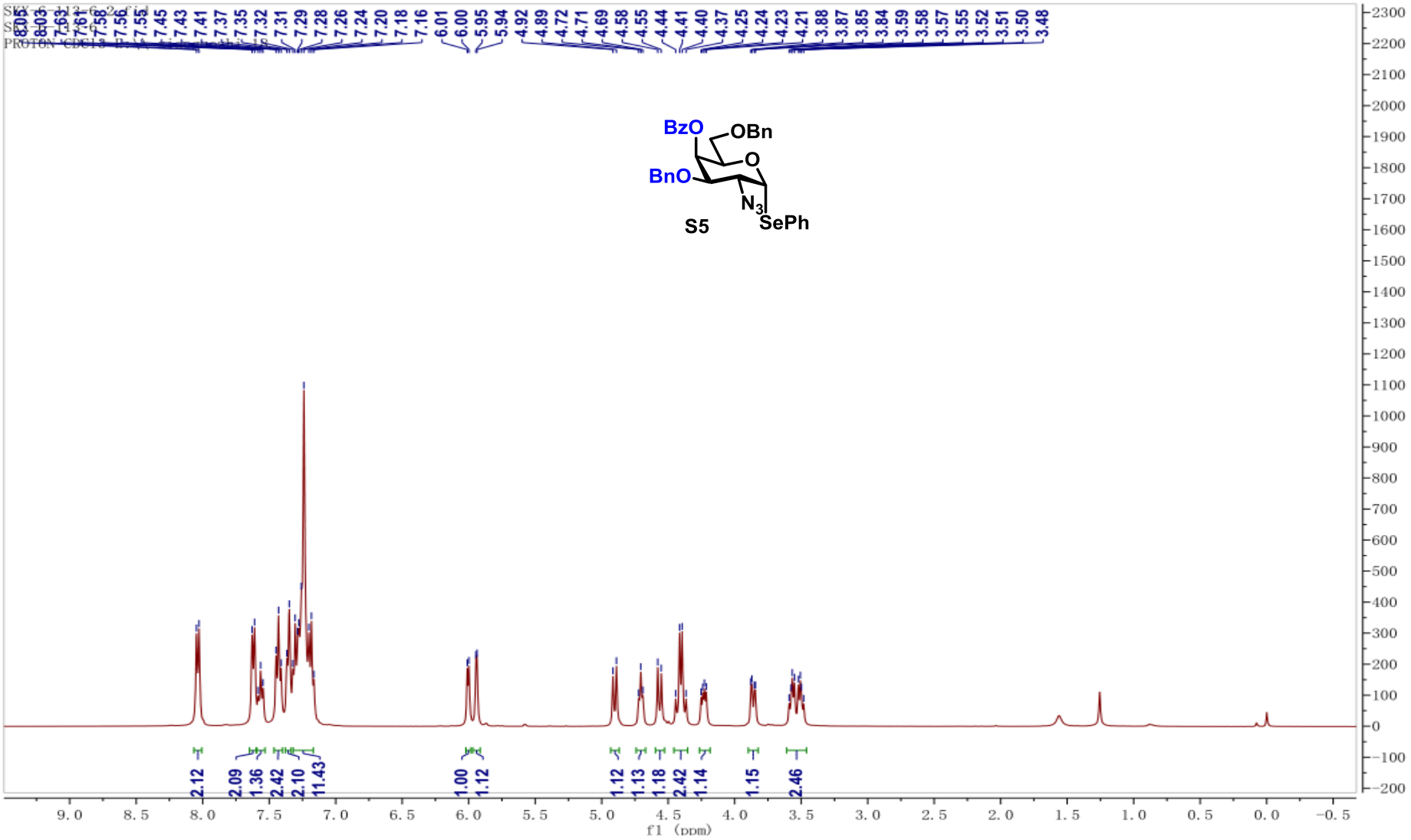
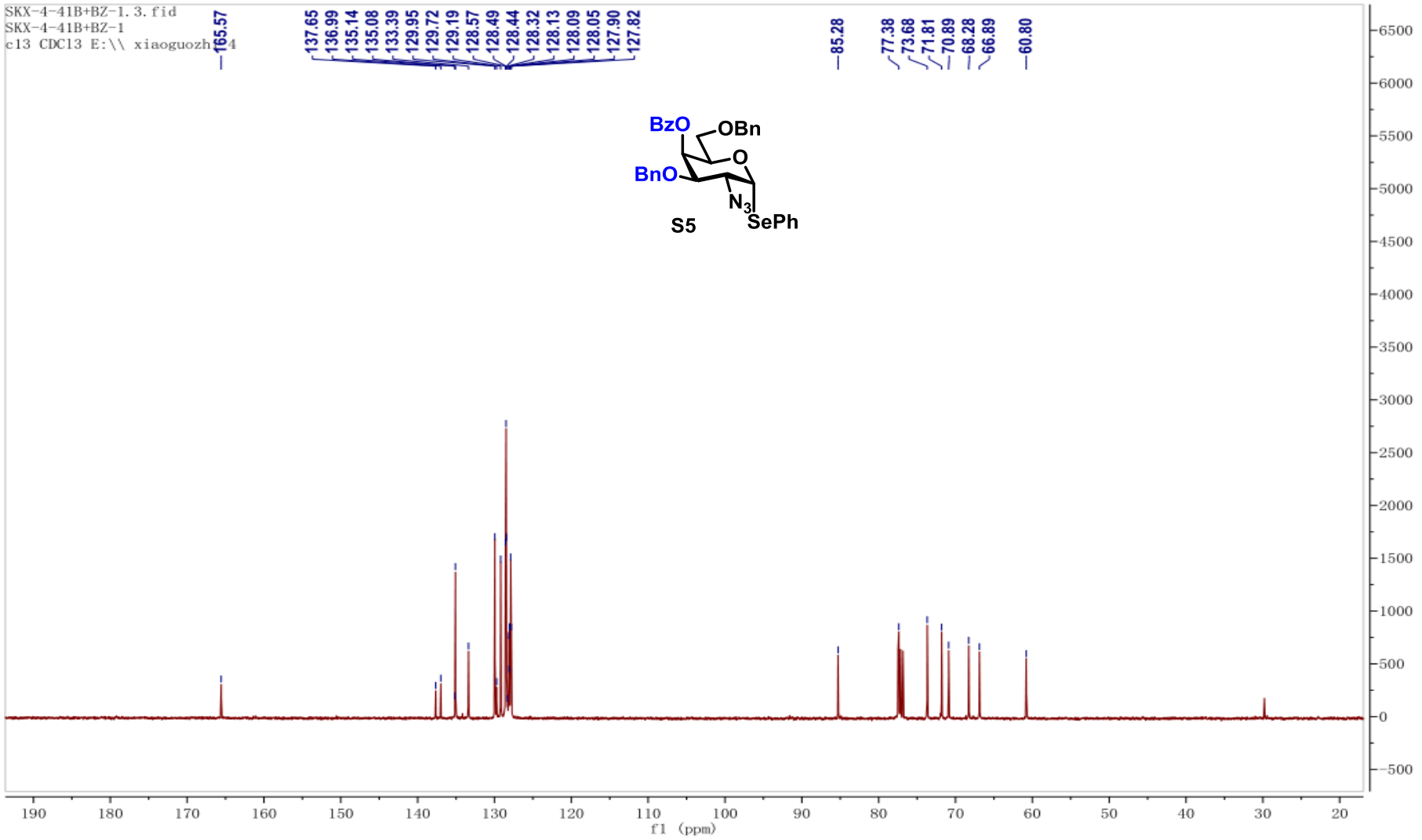
BnO
OTBDPS
O
BnO
N3
O(CH2)5NBnCbz
19d α/β = 1.5/1
H-1α
H-1β
f2 (ppm)
f1 (ppm)


BzO
OBn
O
BnO
N3
SePh
S5
f1 (ppm)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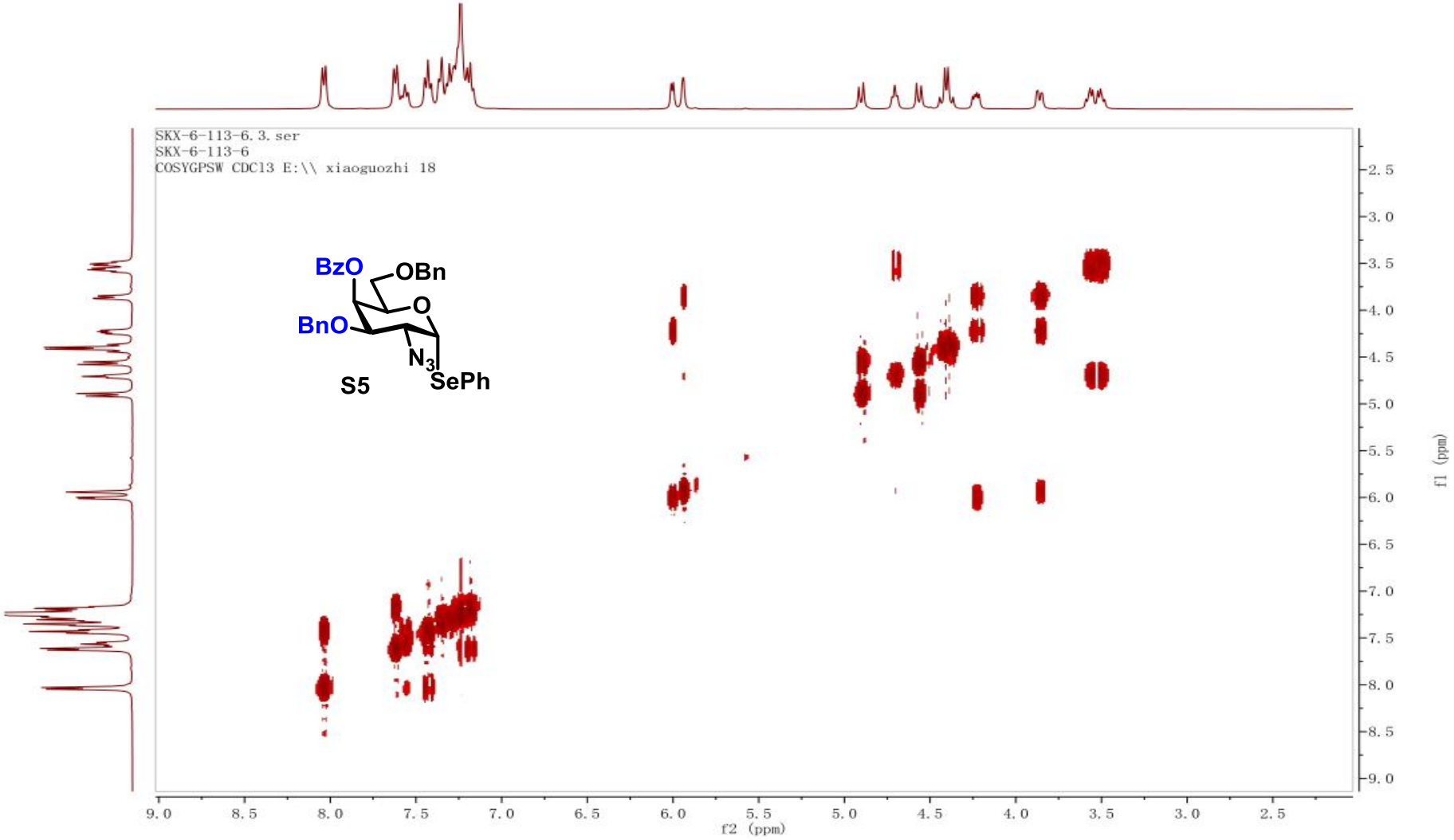
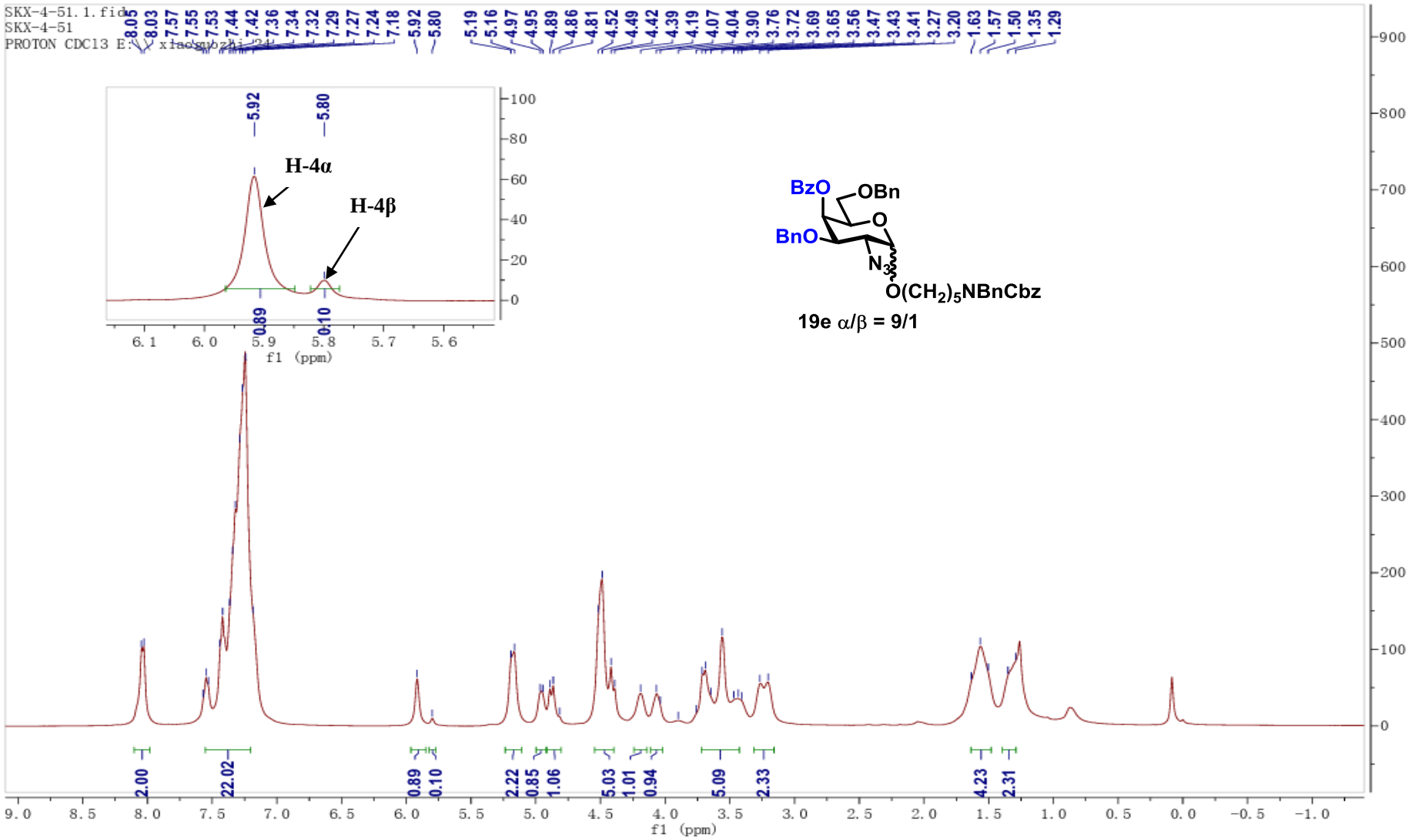
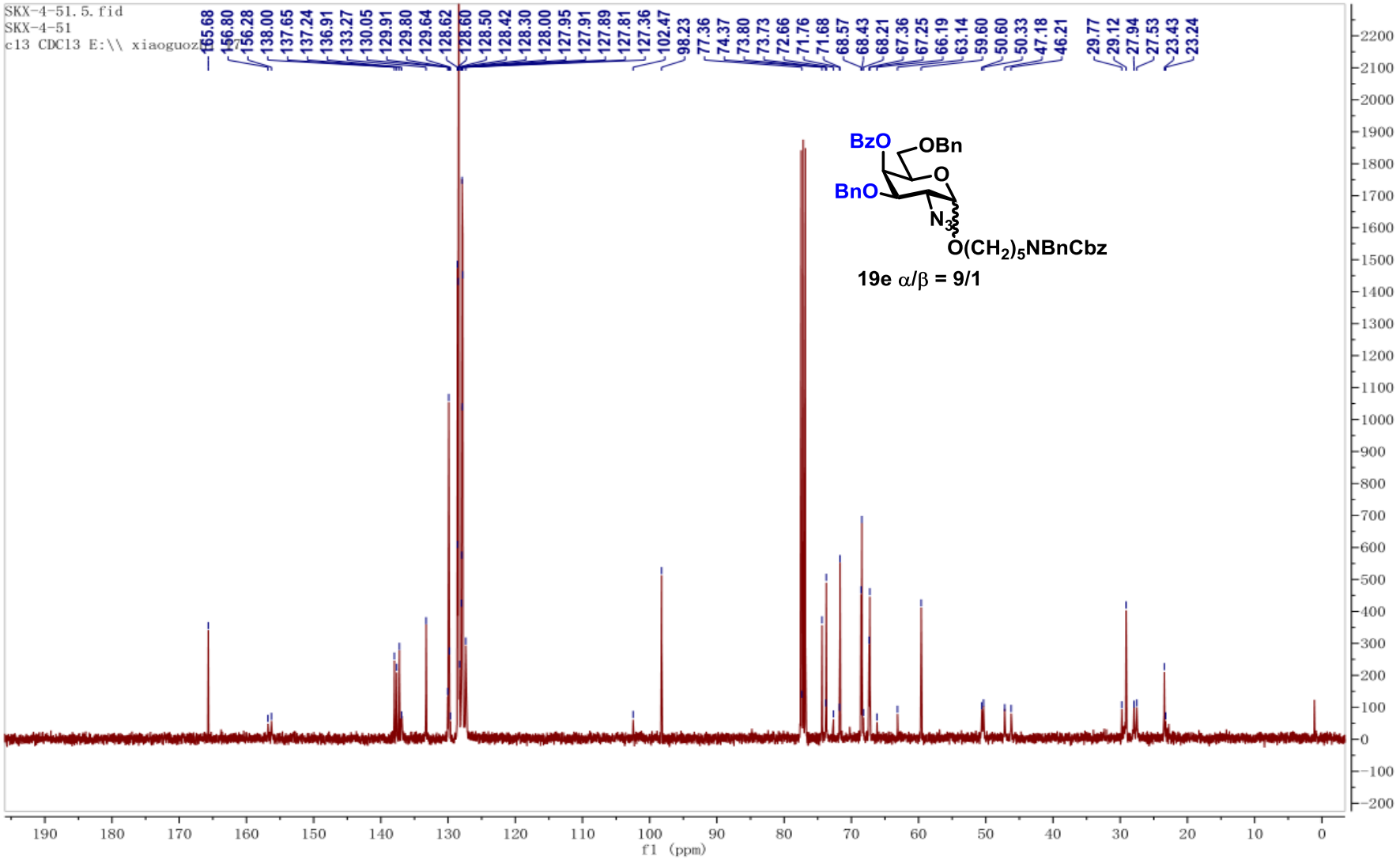
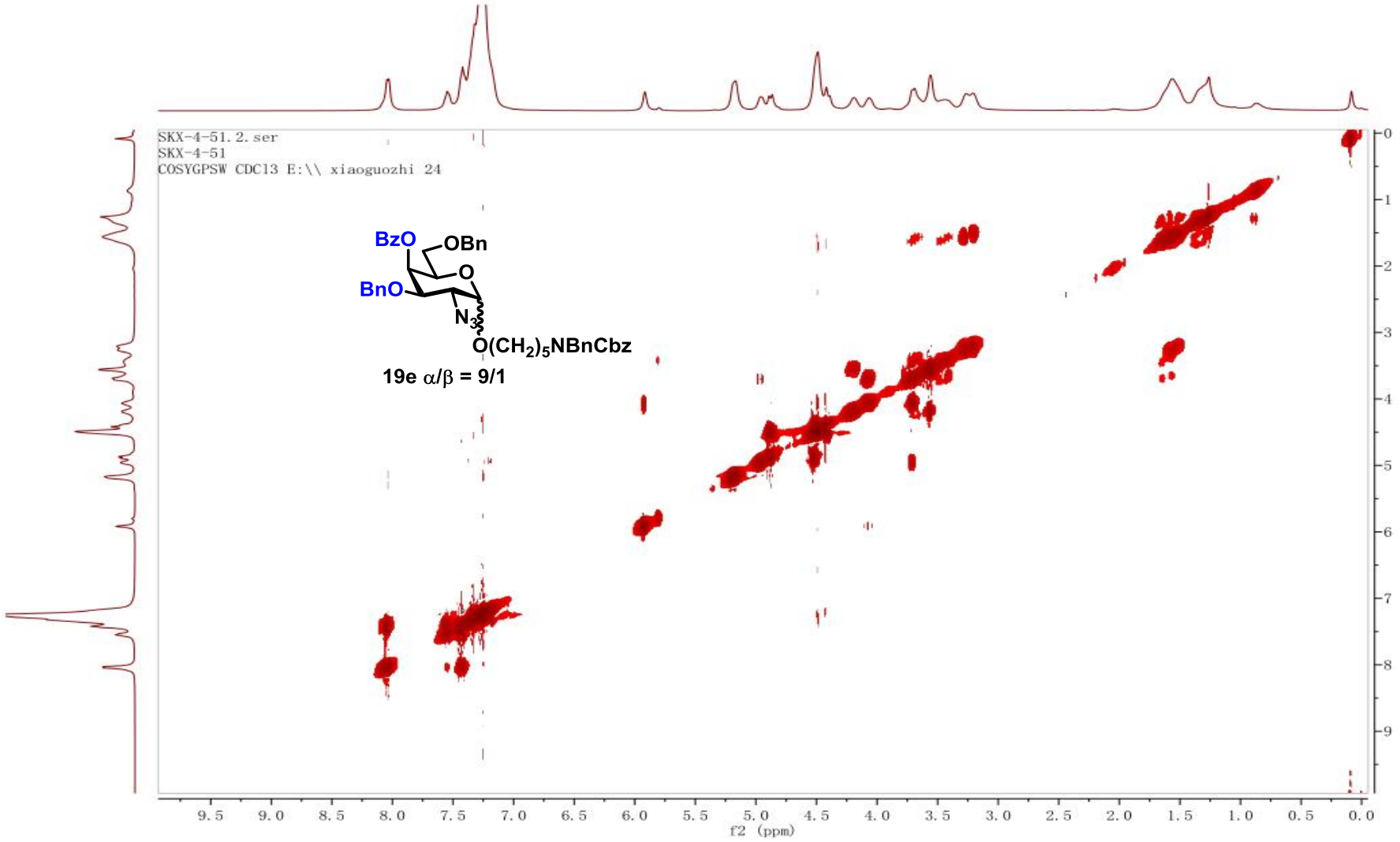
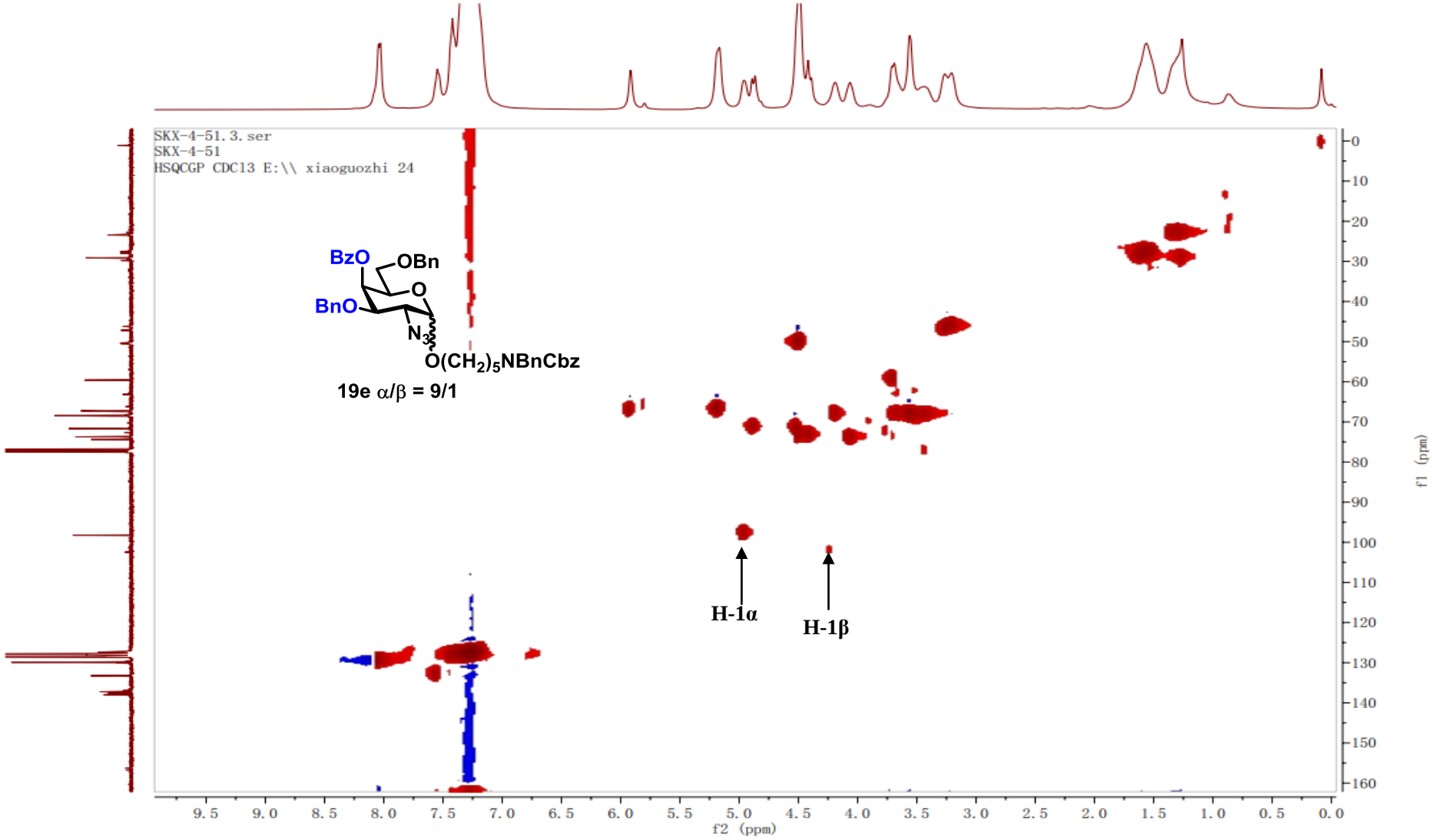
SKX-4-41B+BZ-1
c13 CDCl3 E:\\ xiaoguozh
165.57
137.65
136.99
135.14
135.08
133.39
129.95
129.72
129.19
128.57
128.49
128.44
128.32
128.13
128.09
128.05
127.90
127.82
85.28
77.38
73.68
71.81
70.89
68.28
66.89
60.80
BzO
OBn
O
BnO
N3
SePh
S5
f1 (ppm)

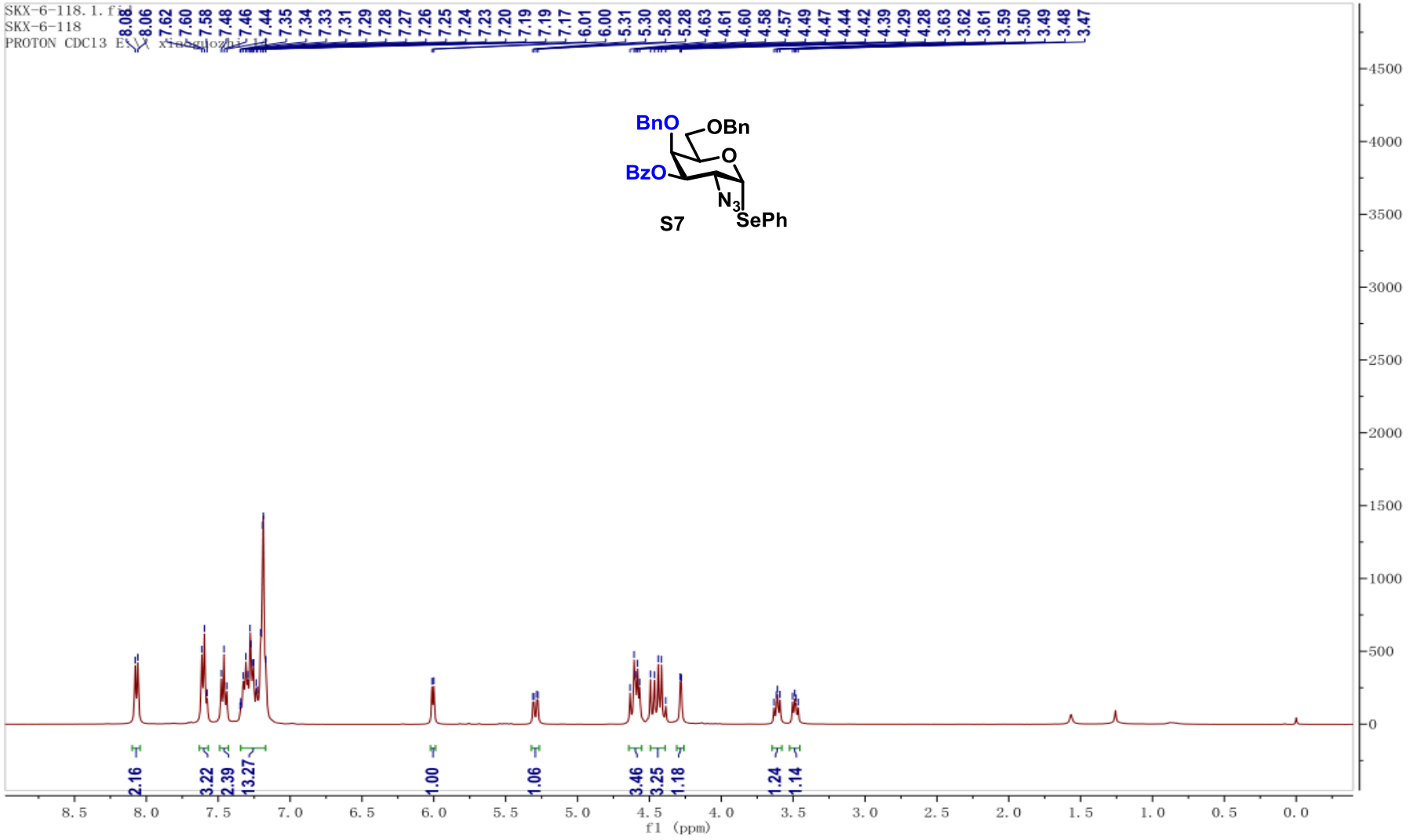

SKX-6-113-6.3.ser
SKX-6-113-6
COSYGPSW CDCl3 E:\\ xiaoguozhi 18
BzO
OBn
O
BnO
N3
SePh
S5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
f1 (ppm)

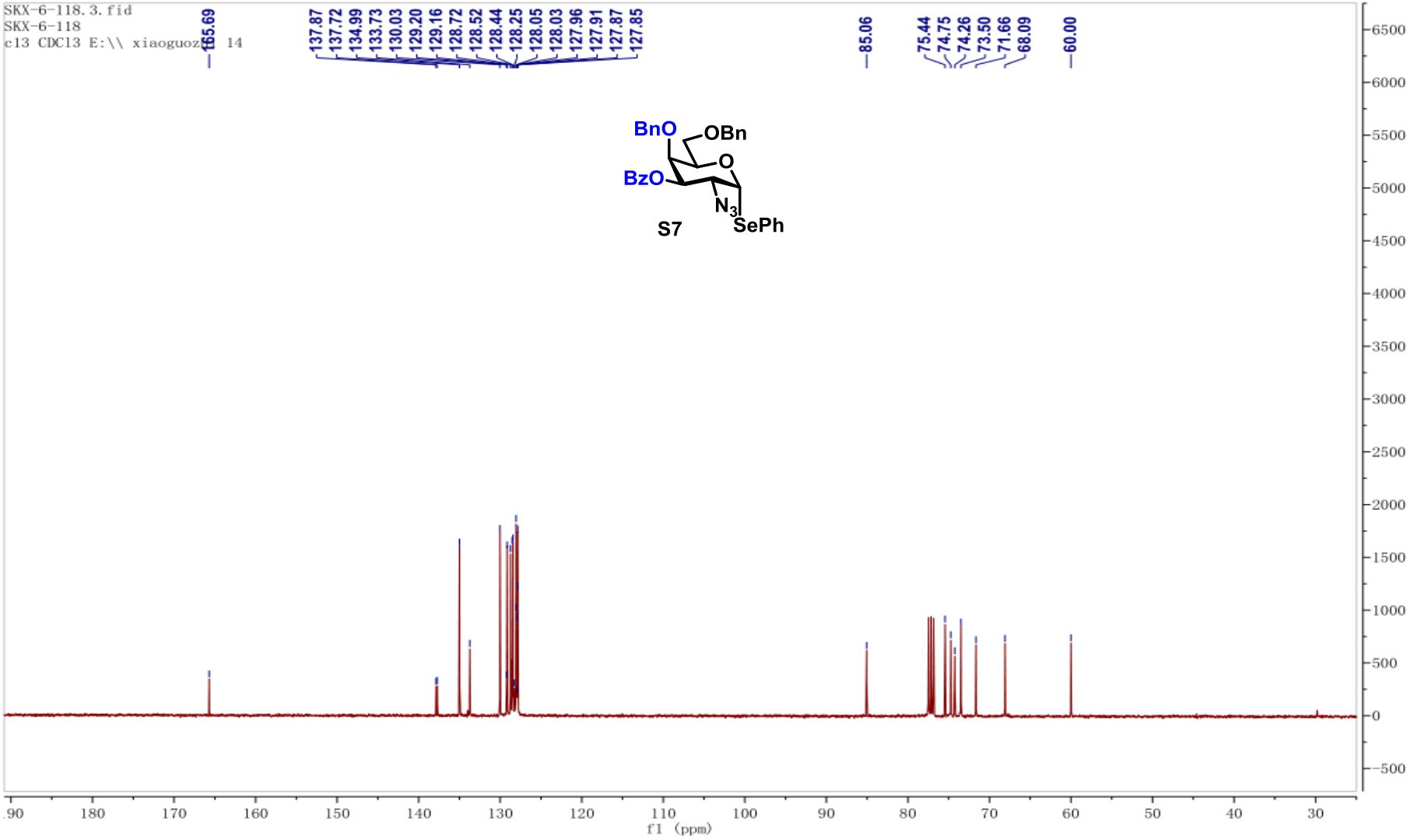

SKX-4-51.1.fid
SKX-4-51
PROTON CDC13 E:\\ xiaogubzhi 24
H-4α
H-4β
f1 (ppm)
BzO
OBn
BnO
O
N3
O(CH2)5NBnCbz
19e α/β = 9/1

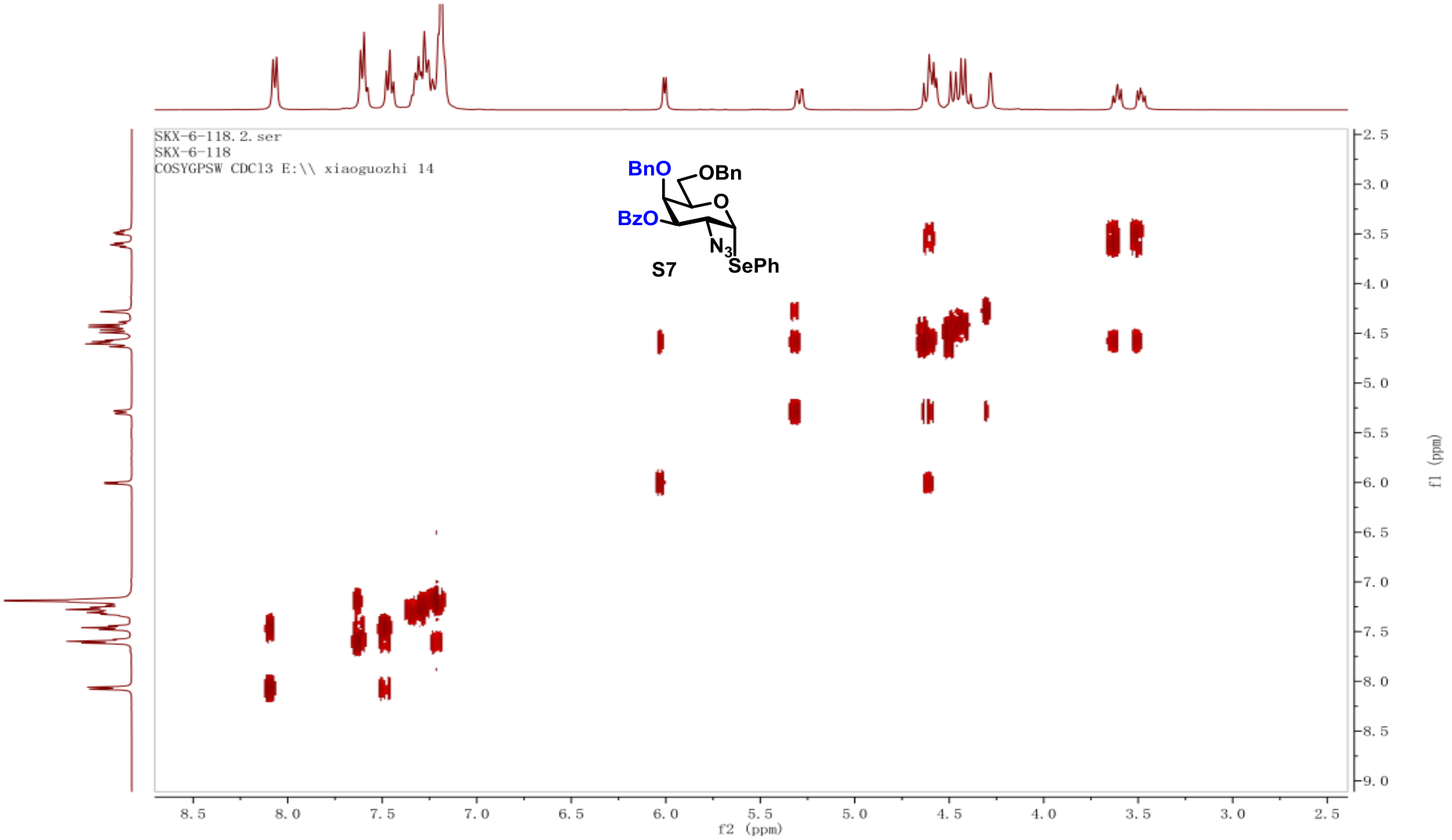

SKX-4-51.5.fid
SKX-4-51
c13 CDCl3 E:\\ xiaoguoz
165.68
156.80
156.28
138.00
137.65
137.24
136.91
133.27
130.05
129.91
129.80
129.64
128.62
128.60
128.50
128.42
128.30
128.00
127.95
127.91
127.89
127.81
127.36
102.47
98.23
77.36
74.37
73.80
73.73
72.66
71.76
71.68
68.57
68.43
68.21
67.36
67.25
66.19
63.14
59.60
50.60
50.33
47.18
46.21
29.77
29.12
27.94
27.53
23.43
23.24
BzO
OBn
O
BnO
N3
O(CH2)5NBnCbz
19e α/β = 9/1
f1 (ppm)

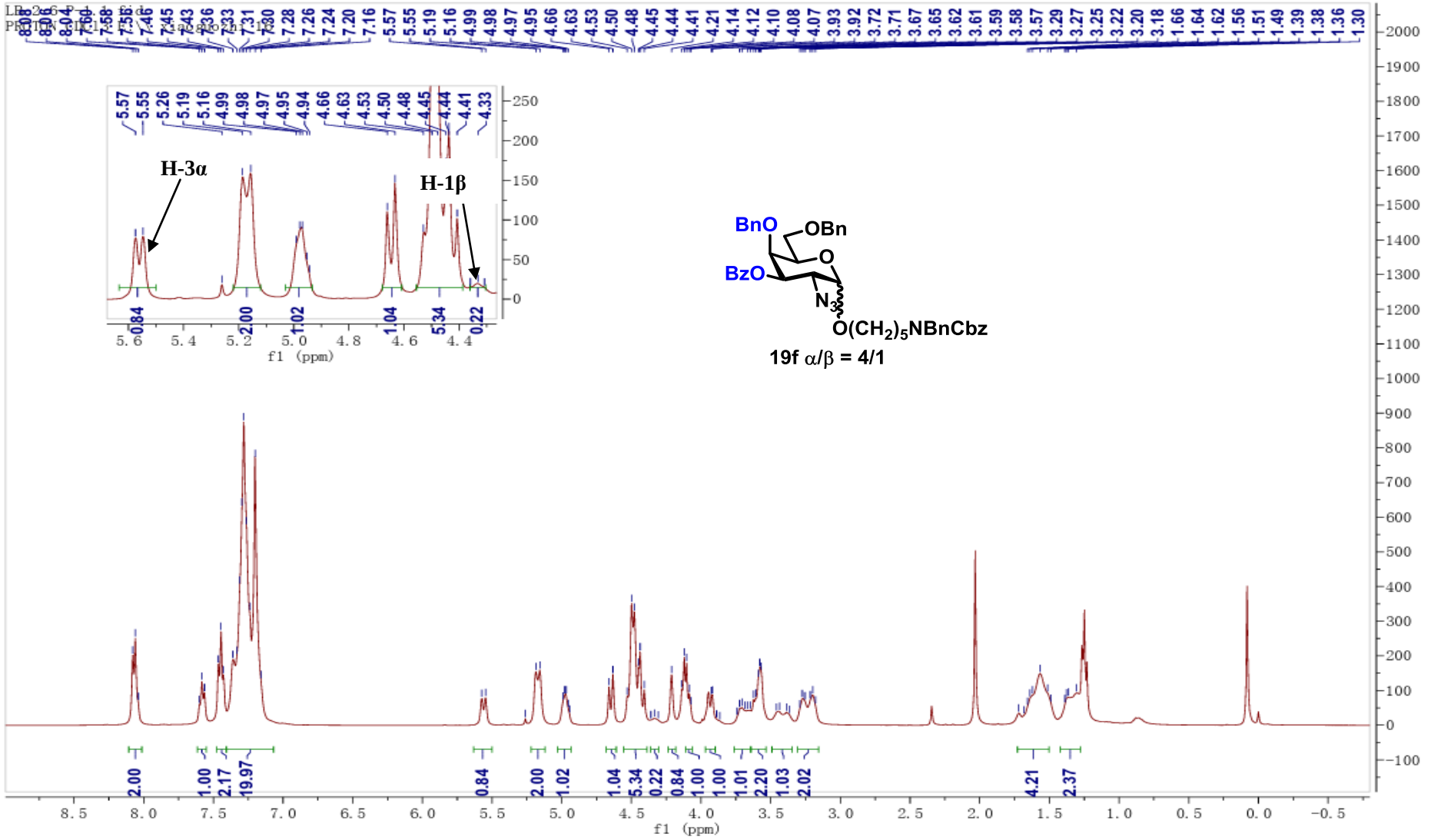

SKX-4-51.2.ser
SKX-4-51
COSYGPSW CDCl3 E:\\ xiaoguozhi 24
BzO
OBn
O
BnO
N3
O(CH2)5NBnCbz
19e α/β = 9/1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9

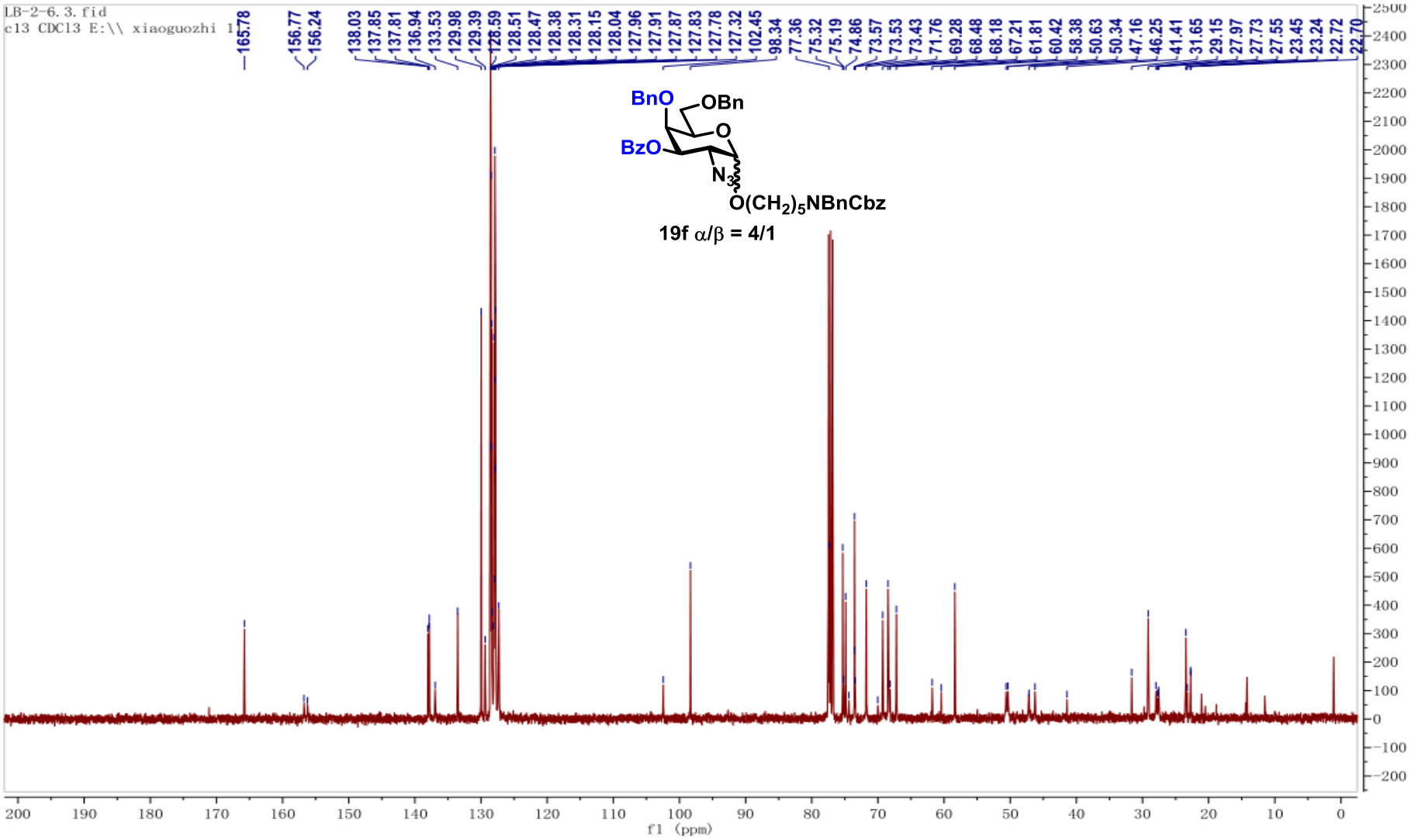

SKX-4-51.3.ser
SKX-4-51
HSQCGP CDCl3 E:\\ xiaoguozhi 24
BzO
OBn
O
BnO
N3
O(CH2)5NBnCbz
19e α/β = 9/1
H-1α
H-1β
f2 (ppm)
f1 (ppm)

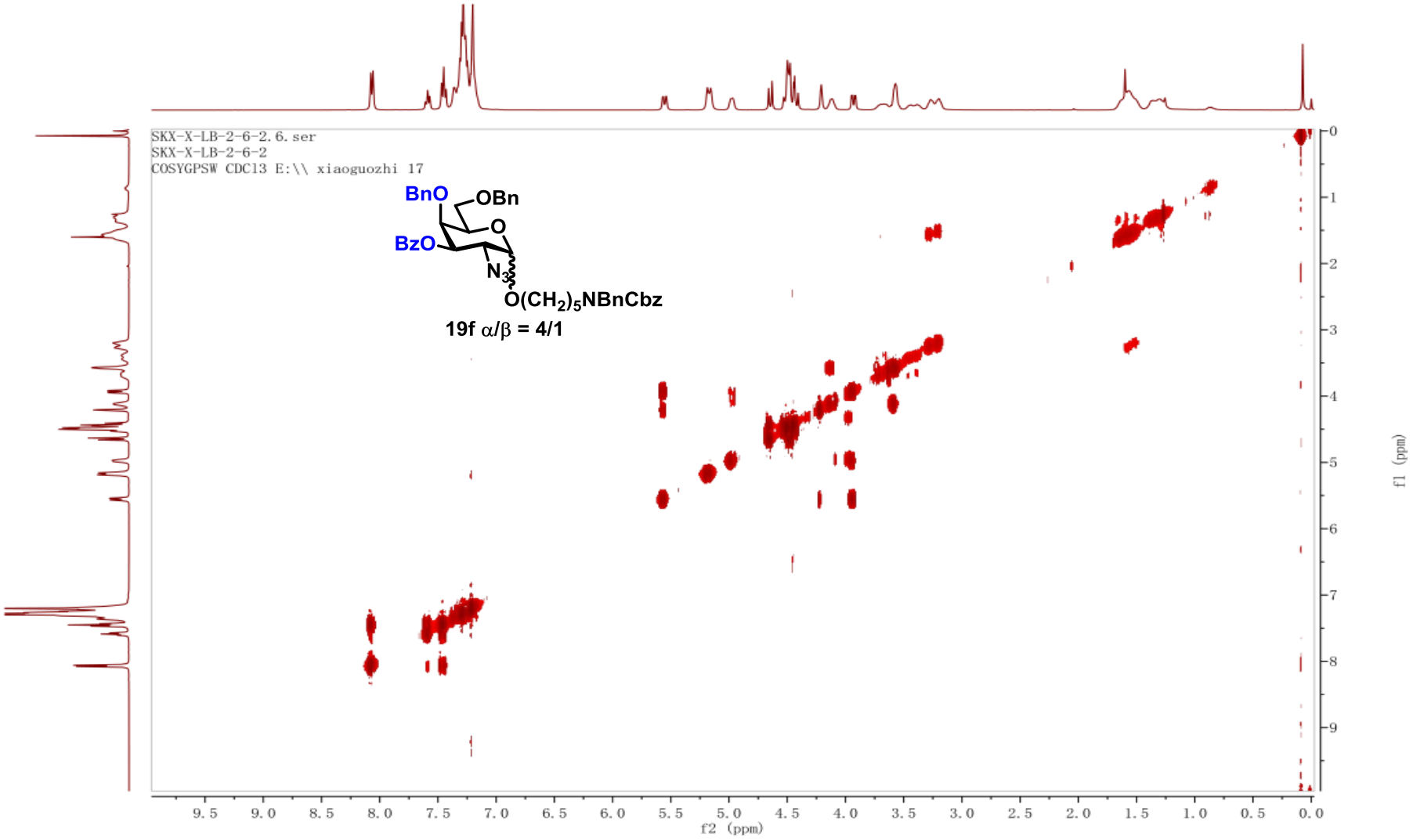

SKX-6-118.1.fid
SKX-6-118
PROTON CDC13
8.08 8.06 7.62 7.60 7.58 7.48 7.46 7.44 7.35 7.34 7.33 7.31 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.20 7.19 7.19 7.17 6.01 6.00 5.31 5.30 5.28 5.28 4.63 4.61 4.60 4.58 4.57 4.49 4.47 4.44 4.42 4.39 4.29 4.28 3.63 3.62 3.61 3.59 3.50 3.49 3.48 3.47
BnO
OBn
O
BzO
N3
SePh
S7
2.16 3.22 2.39 13.27 1.00 1.06 3.46 3.25 1.18 1.24 1.14
f1 (ppm)

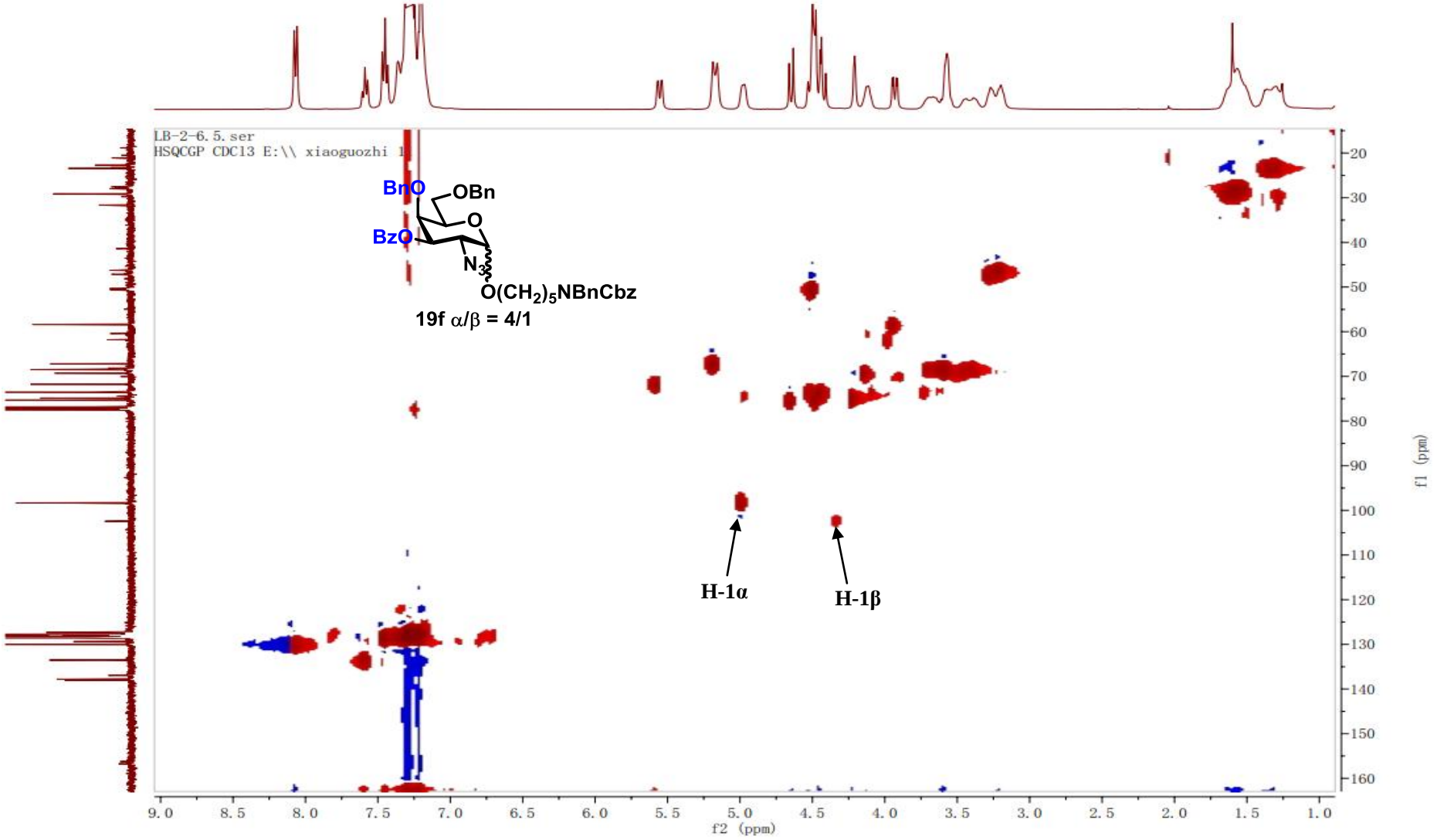

SKX-6-118.3.fid
SKX-6-118
c13 CDCl3 E:\\ xiaoguoz 14
169.69
137.87
137.72
134.99
133.73
130.03
129.20
129.16
128.72
128.52
128.44
128.25
128.05
128.03
127.96
127.91
127.87
127.85
85.06
75.44
74.75
74.26
73.50
71.66
68.09
60.00
BnO
OBn
O
BzO
N3
SePh
S7
f1 (ppm)

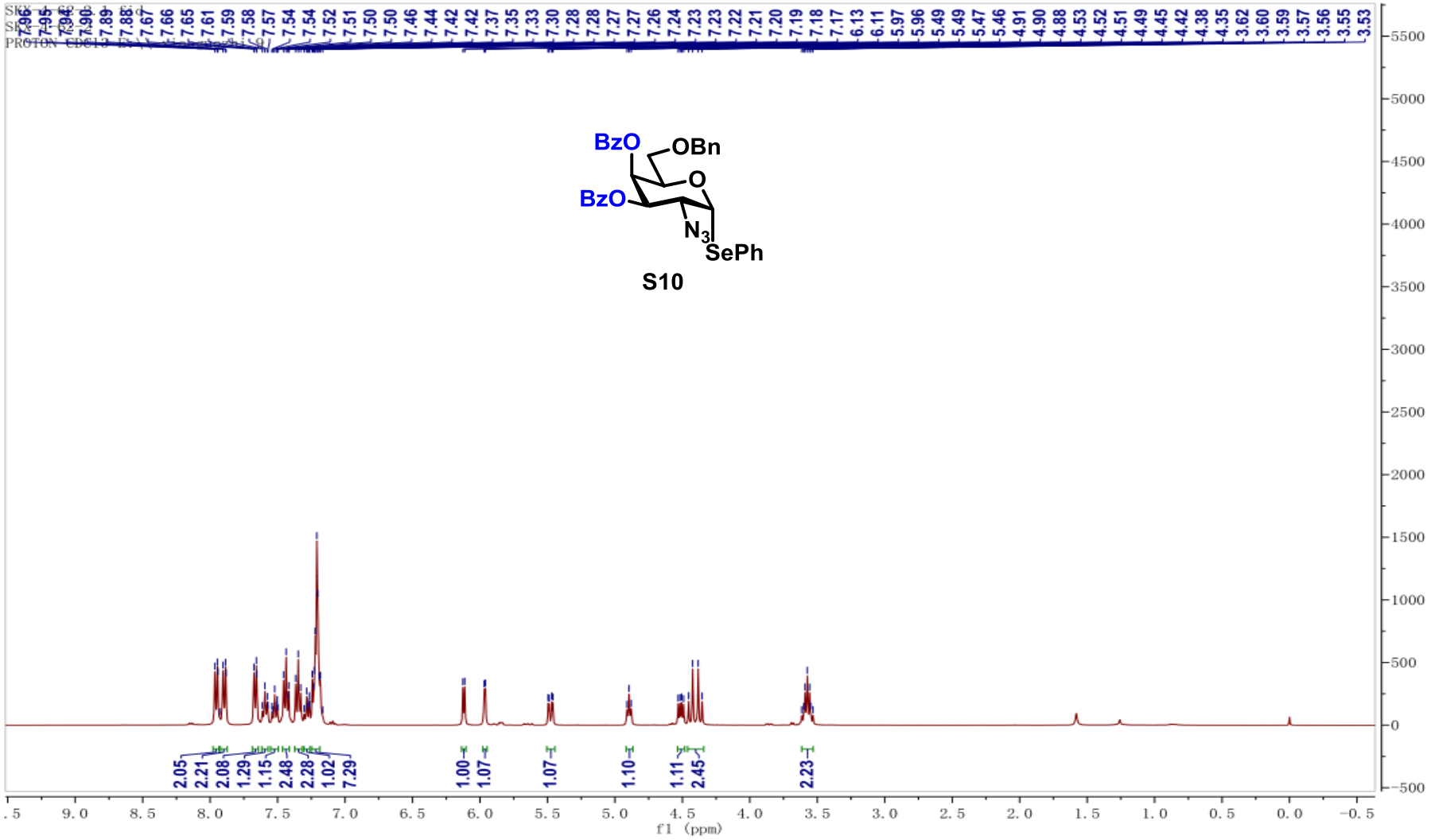

SKX-6-118.2.ser
SKX-6-118
COSYGPSW CDCl3 E:\\ xiaoguozhi 14
BnO
OBn
O
BzO
N3
SePh
S7
f2 (ppm)
f1 (ppm)

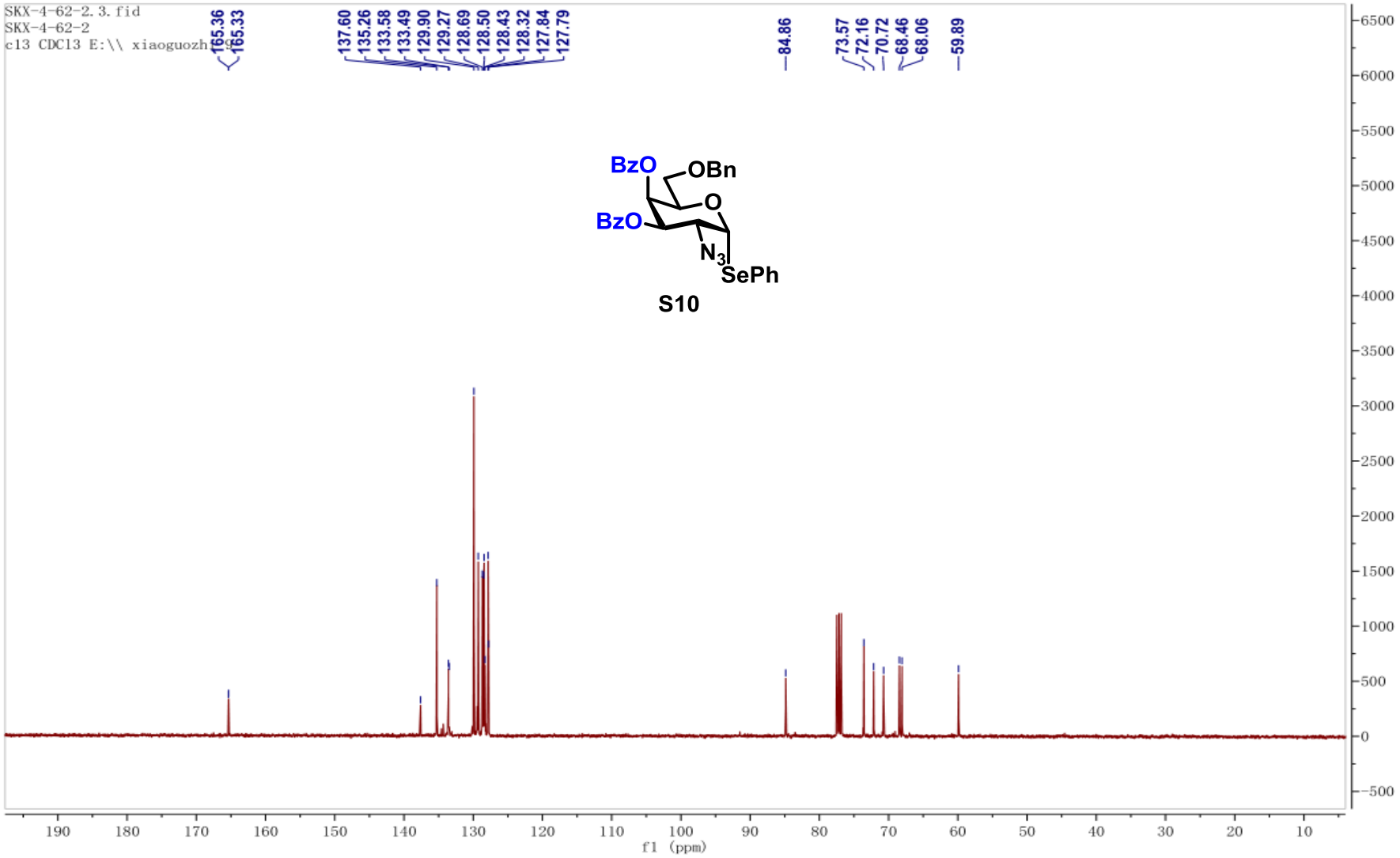

H-3α
H-1β
BnO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19f α/β = 4/1
f1 (ppm)

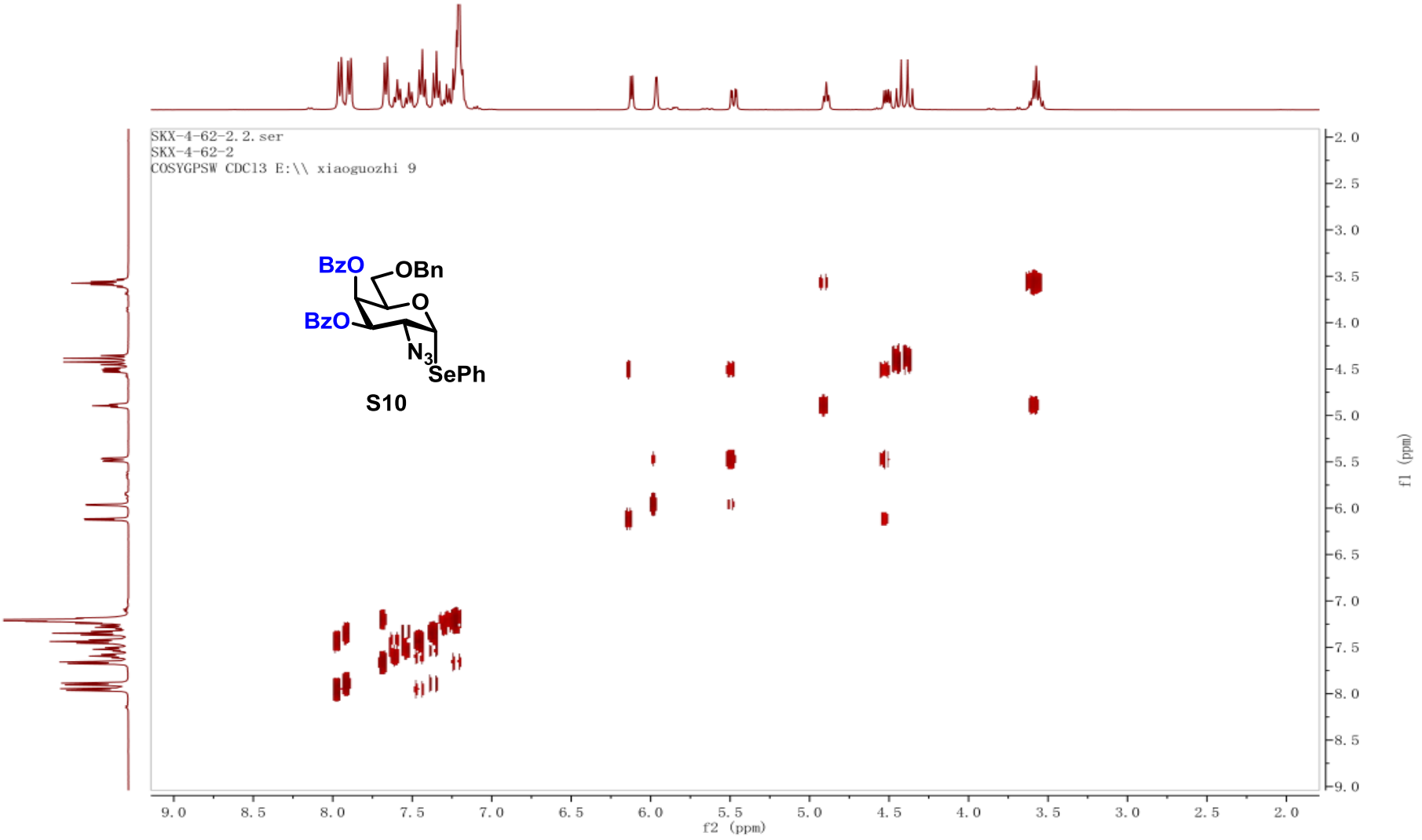

LB-2-6.3.fid
c13 CDCl3 E:\\ xiaoguozhi 1
165.78
156.77
156.24
138.03
137.85
137.81
136.94
133.53
129.98
129.39
128.59
128.51
128.47
128.38
128.31
128.15
128.04
127.96
127.91
127.87
127.83
127.78
127.32
102.45
98.34
77.36
75.32
75.19
74.86
73.57
73.53
73.43
71.76
69.28
68.48
68.18
67.21
61.81
60.42
58.38
50.63
50.34
47.16
46.25
41.41
31.65
29.15
27.97
27.73
27.55
23.45
23.24
22.72
22.70
BnO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19f α/β = 4/1
f1 (ppm)

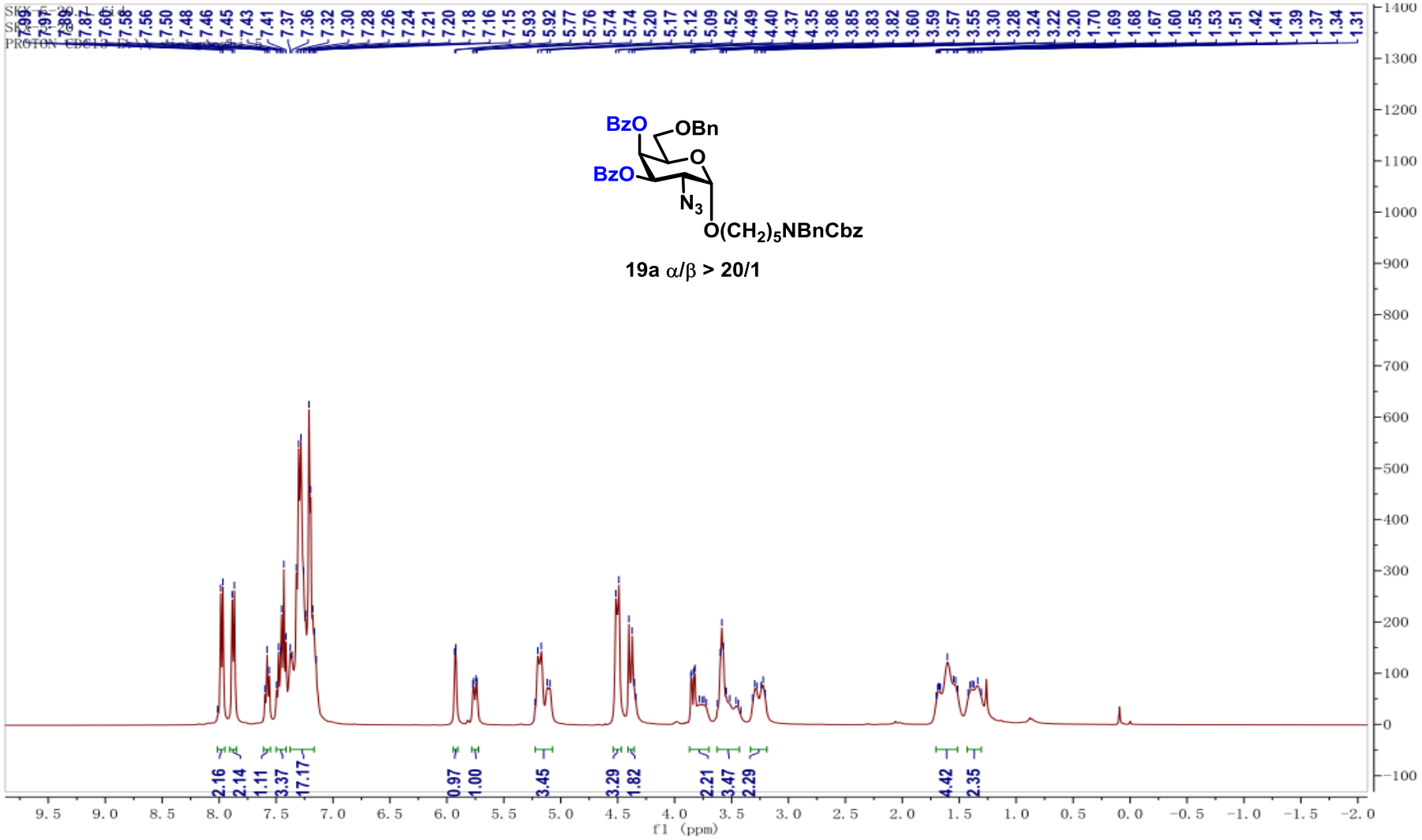

SKX-X-LB-2-6-2.6.ser
SKX-X-LB-2-6-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 17
BnO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19f α/β = 4/1
f2 (ppm)
f1 (ppm)

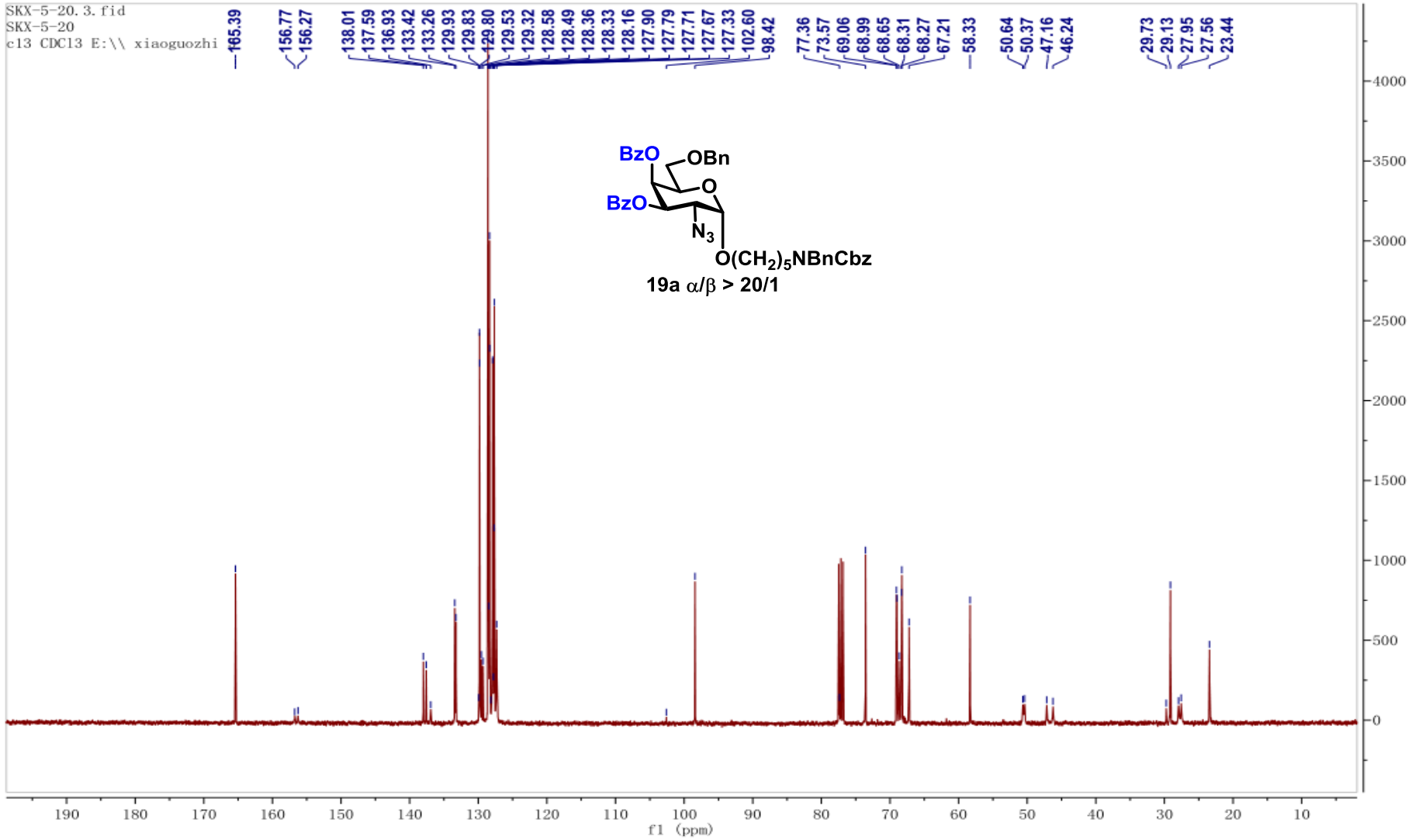

LB-2-6.5.ser
HSQCGP CDC13 E:\\ xiaoguozhi 1
BnO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19f α/β = 4/1
H-1α
H-1β
f2 (ppm)
f1 (ppm)

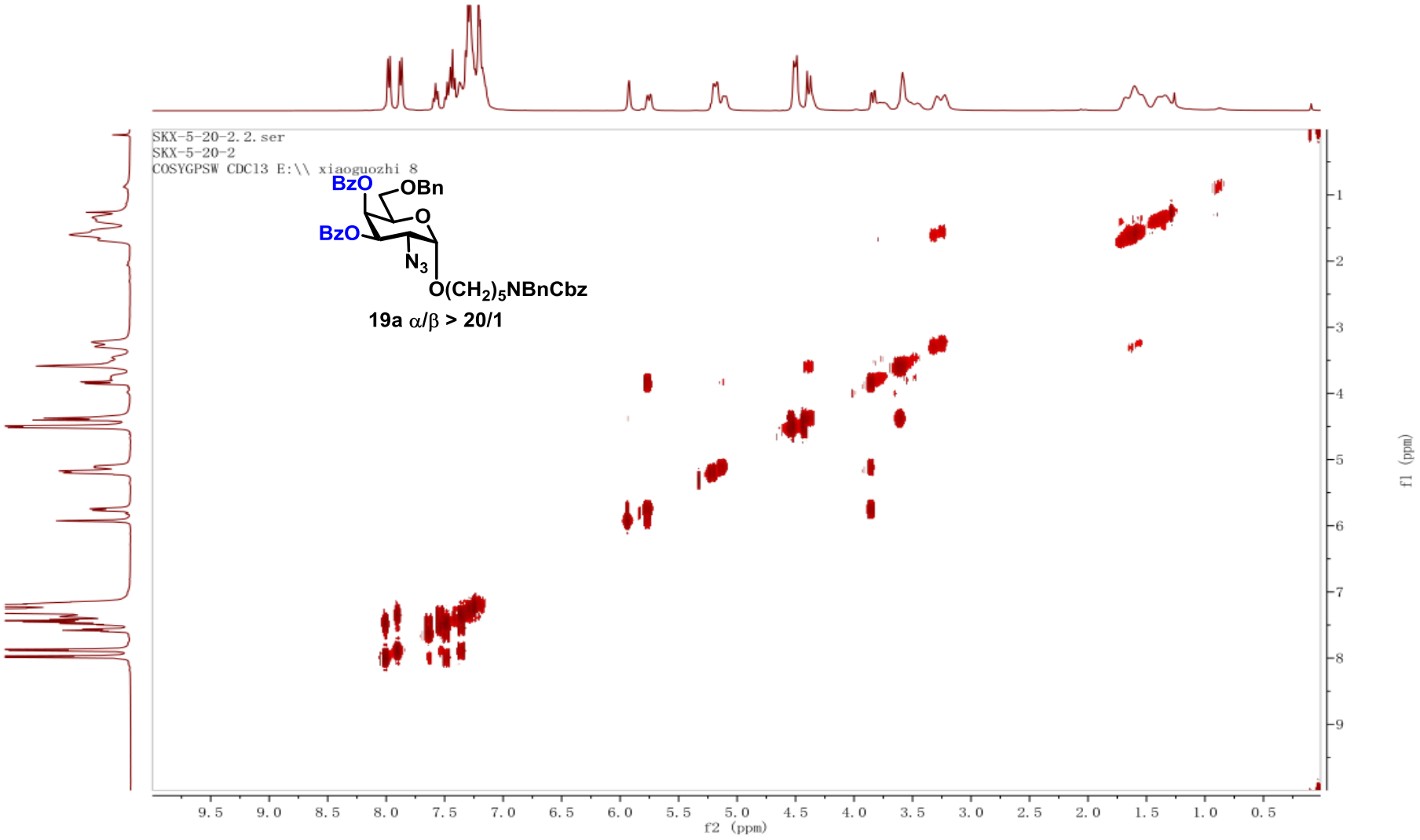

BzO
OBn
O
BzO
N3
SePh
S10
f1 (ppm)

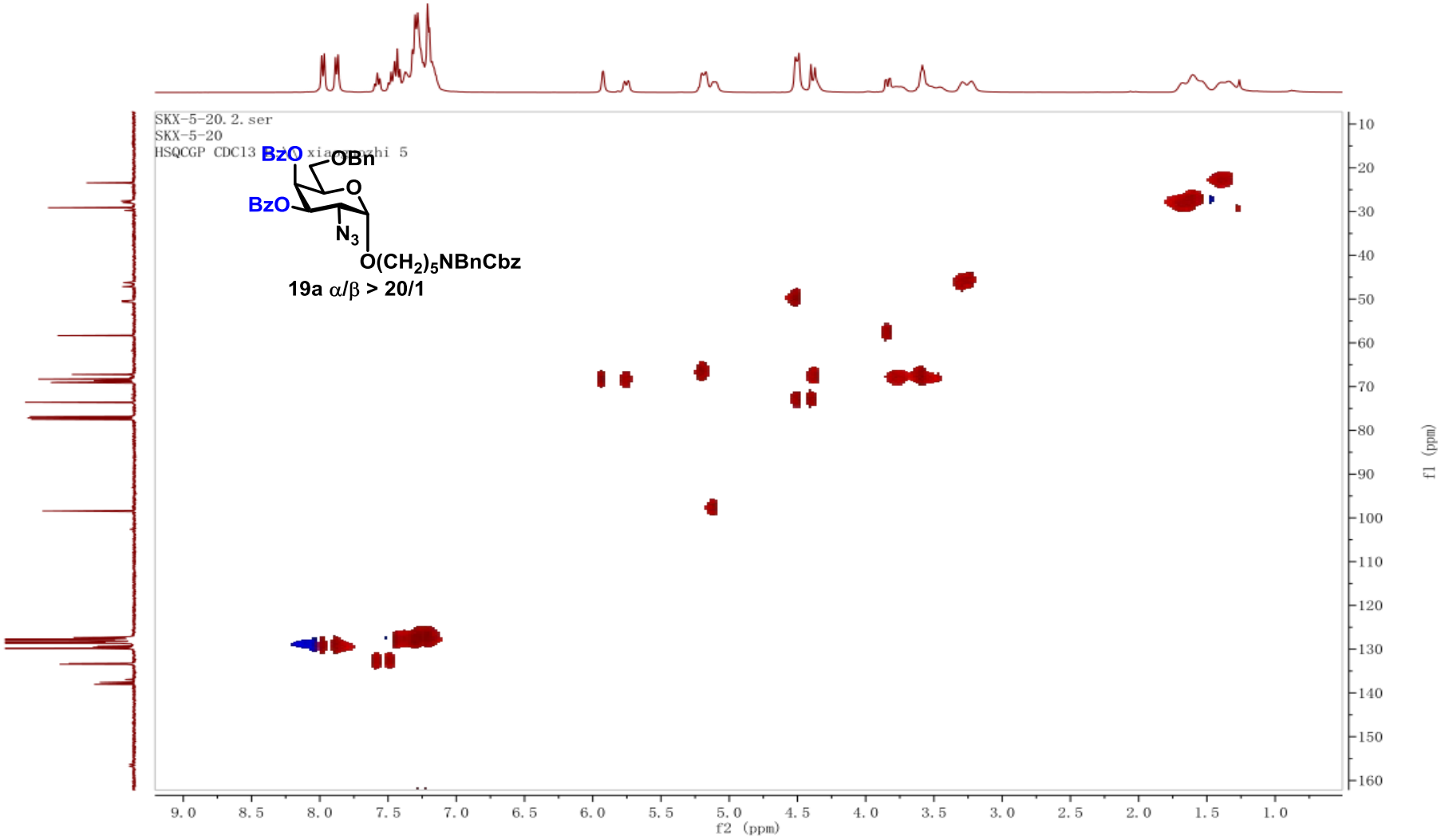

SKX-4-62-2.3.fid
SKX-4-62-2
c13 CDCl3 E:\\ xiaoguozh
165.36
165.33
137.60
135.26
133.58
133.49
129.90
129.27
128.69
128.50
128.43
128.32
127.84
127.79
84.86
73.57
72.16
70.72
68.46
68.06
59.89
BzO
OBn
O
BzO
N3
SePh
S10
f1 (ppm)

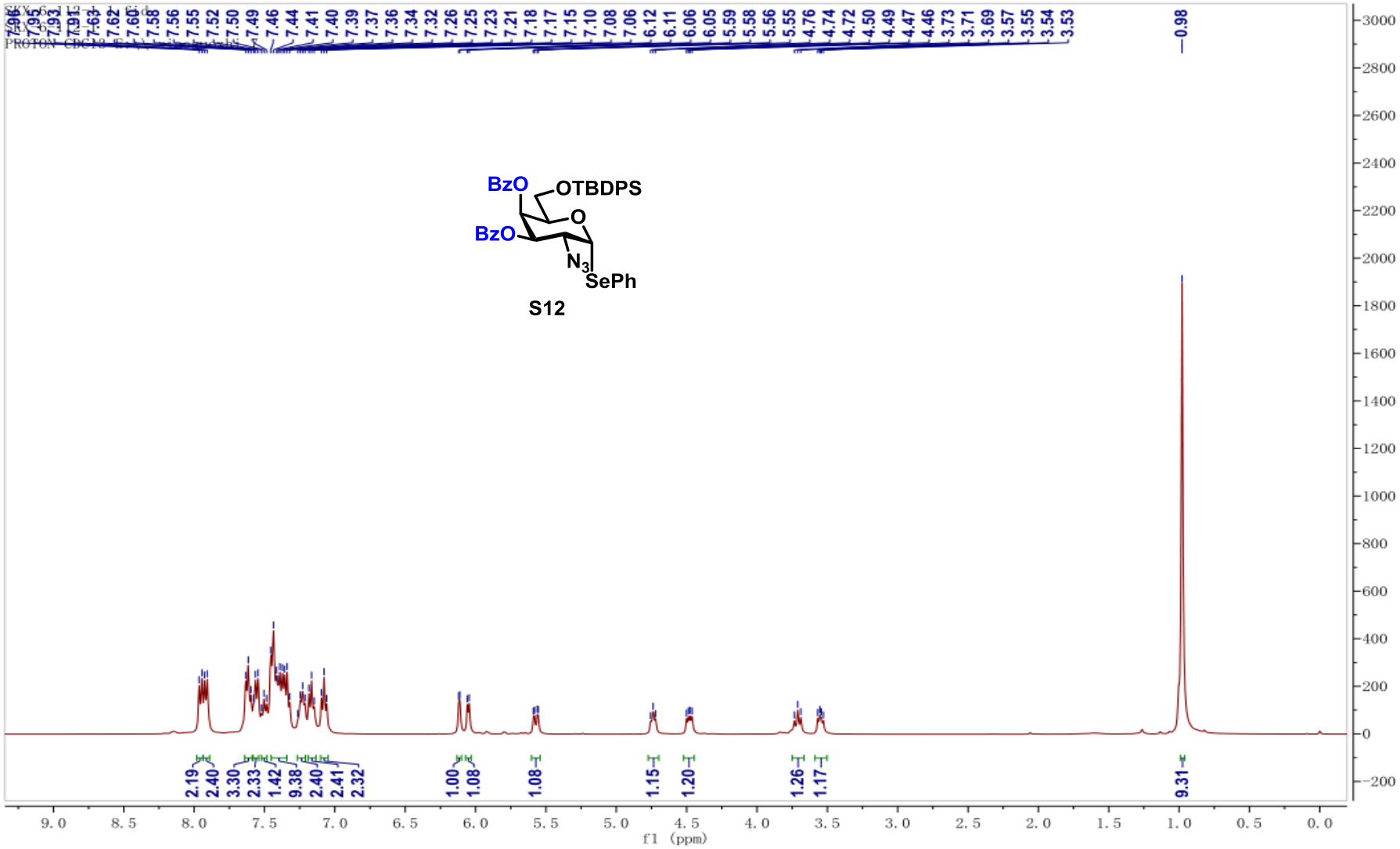

SKX-4-62-2.2.ser
SKX-4-62-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 9
BzO
OBn
O
BzO
N3
SePh
S10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
f1 (ppm)

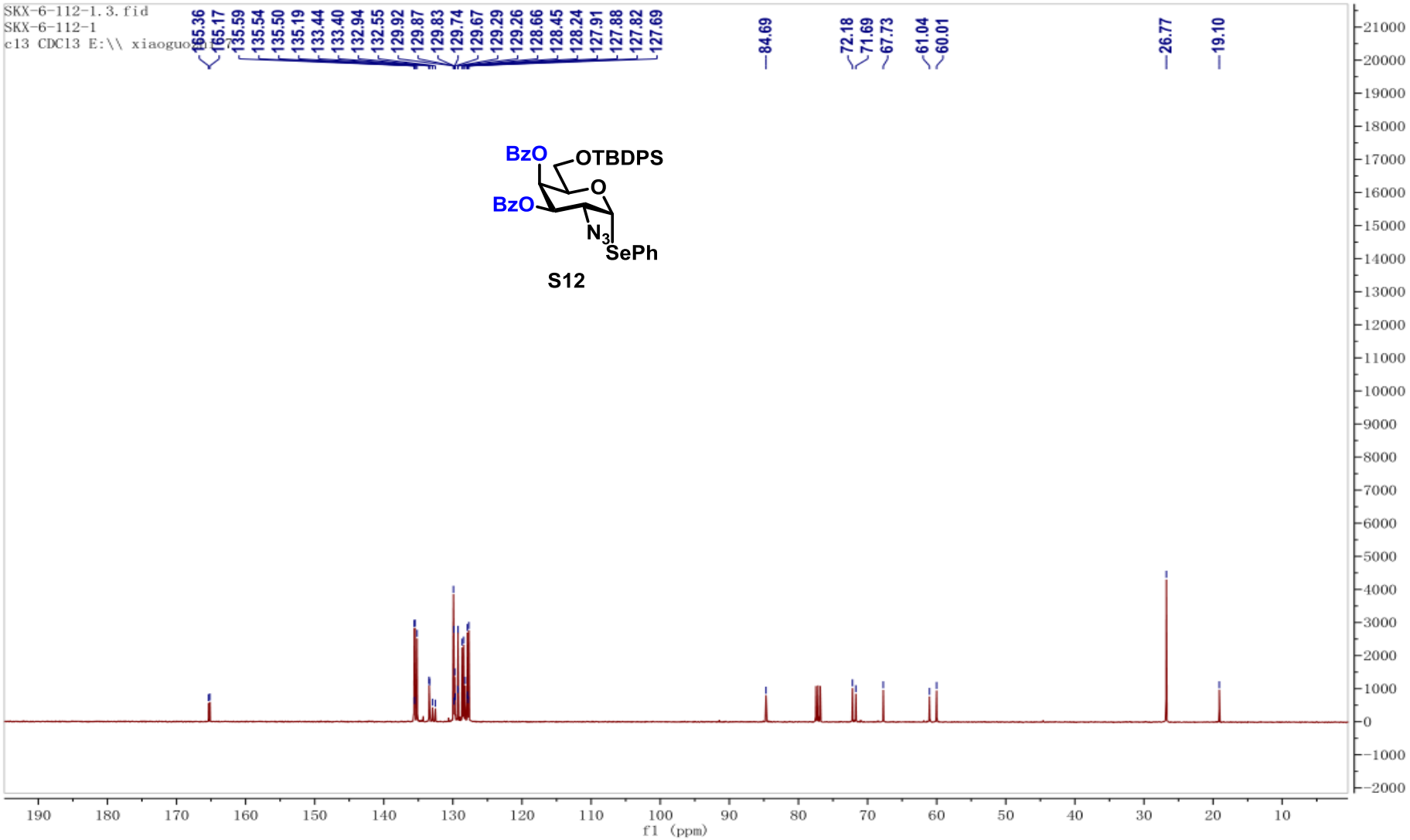

BzO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19a α/β > 20/1
f1 (ppm)

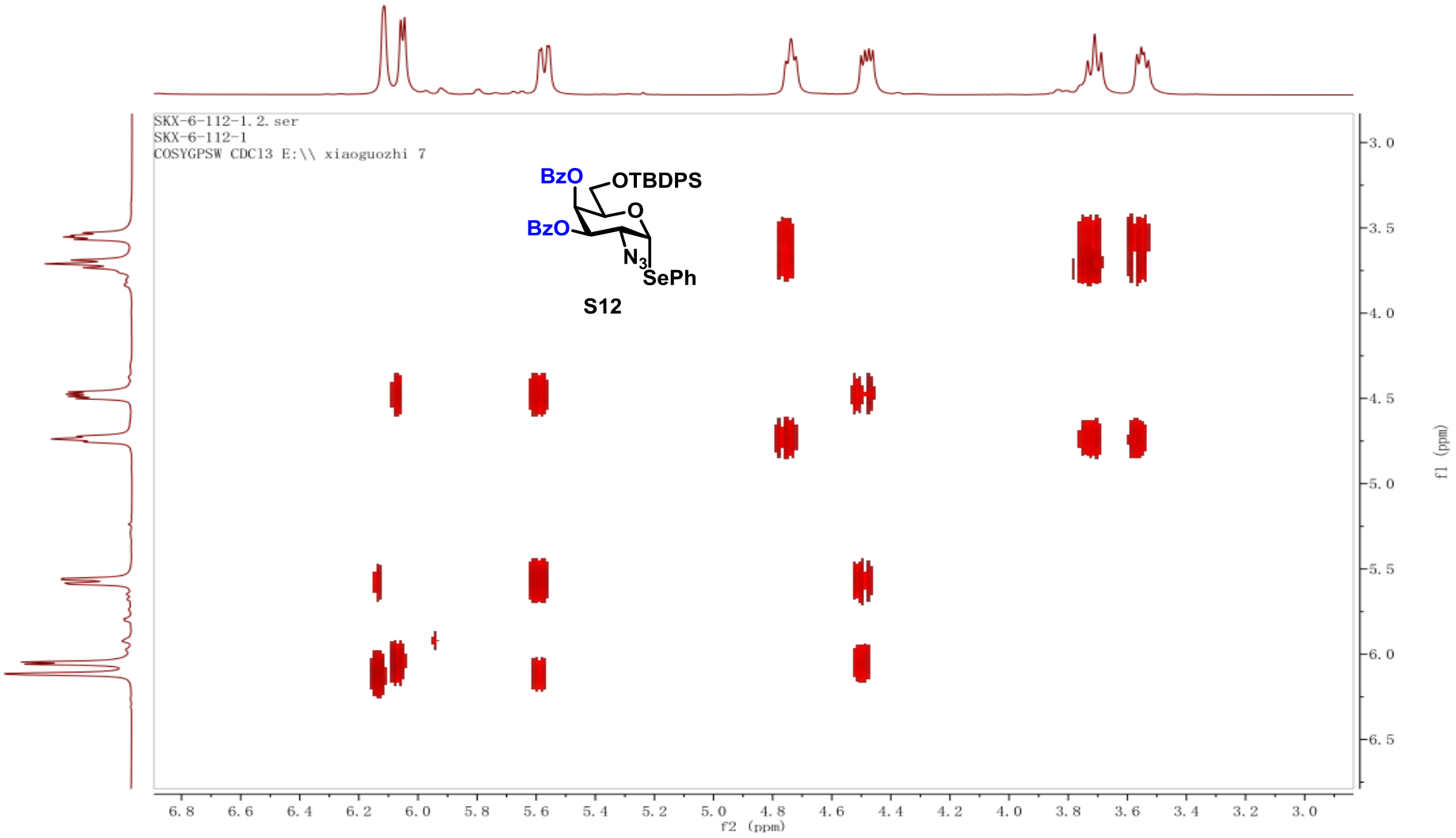

SKX-5-20.3.fid
SKX-5-20
c13 CDCl3 E:\\ xiaoguozhi
165.39
156.77
156.27
138.01
137.59
136.93
133.42
133.26
129.93
129.83
129.80
129.53
129.32
128.58
128.49
128.36
128.33
128.16
127.90
127.79
127.71
127.67
127.33
102.60
98.42
77.36
73.57
69.06
68.99
68.65
68.31
68.27
67.21
58.33
50.64
50.37
47.16
46.24
29.73
29.13
27.95
27.56
23.44
BzO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19a α/β > 20/1
f1 (ppm)

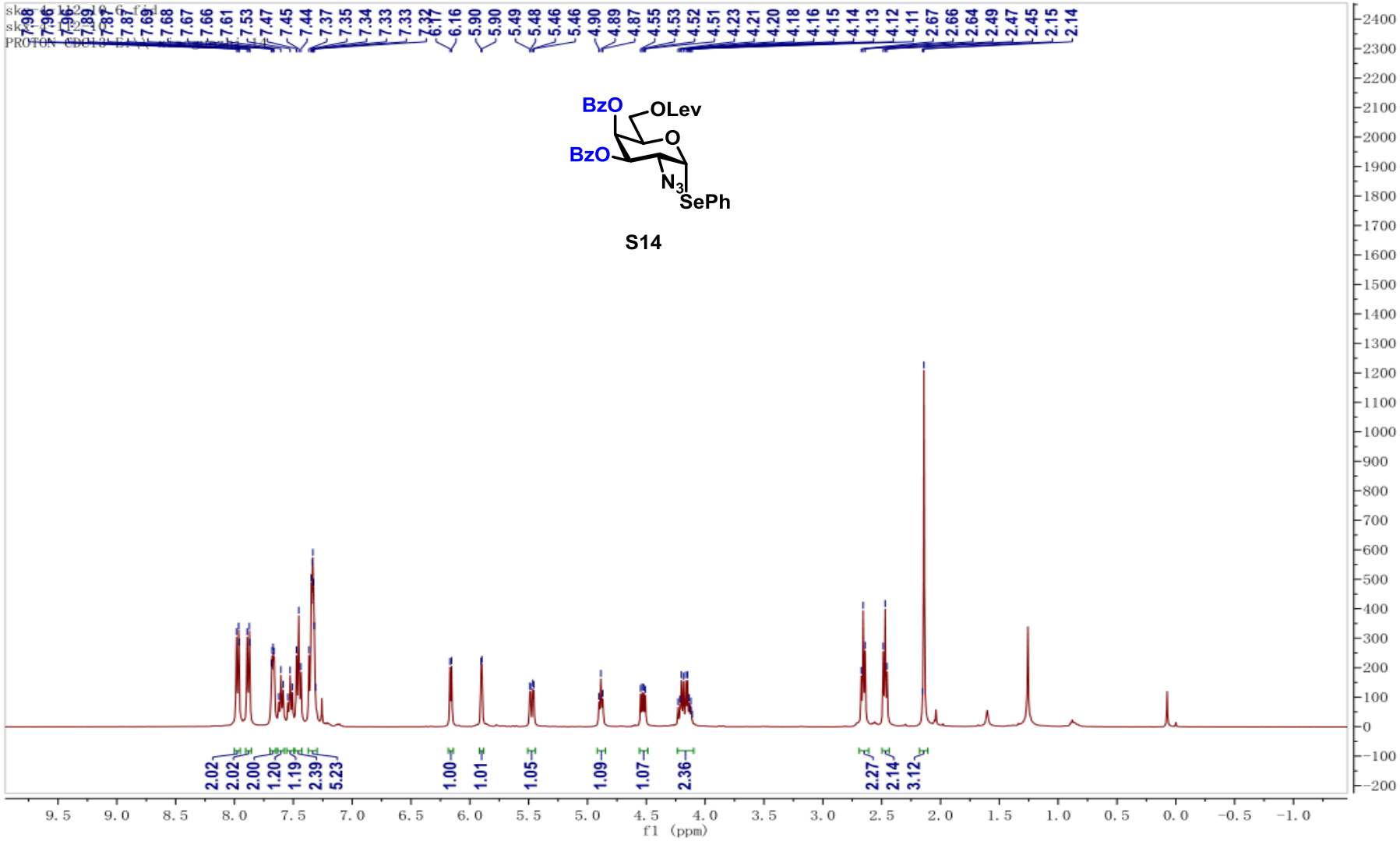

SKX-5-20-2.2.ser
SKX-5-20-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 8
BzO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19a α/β > 20/1
f2 (ppm)
f1 (ppm)

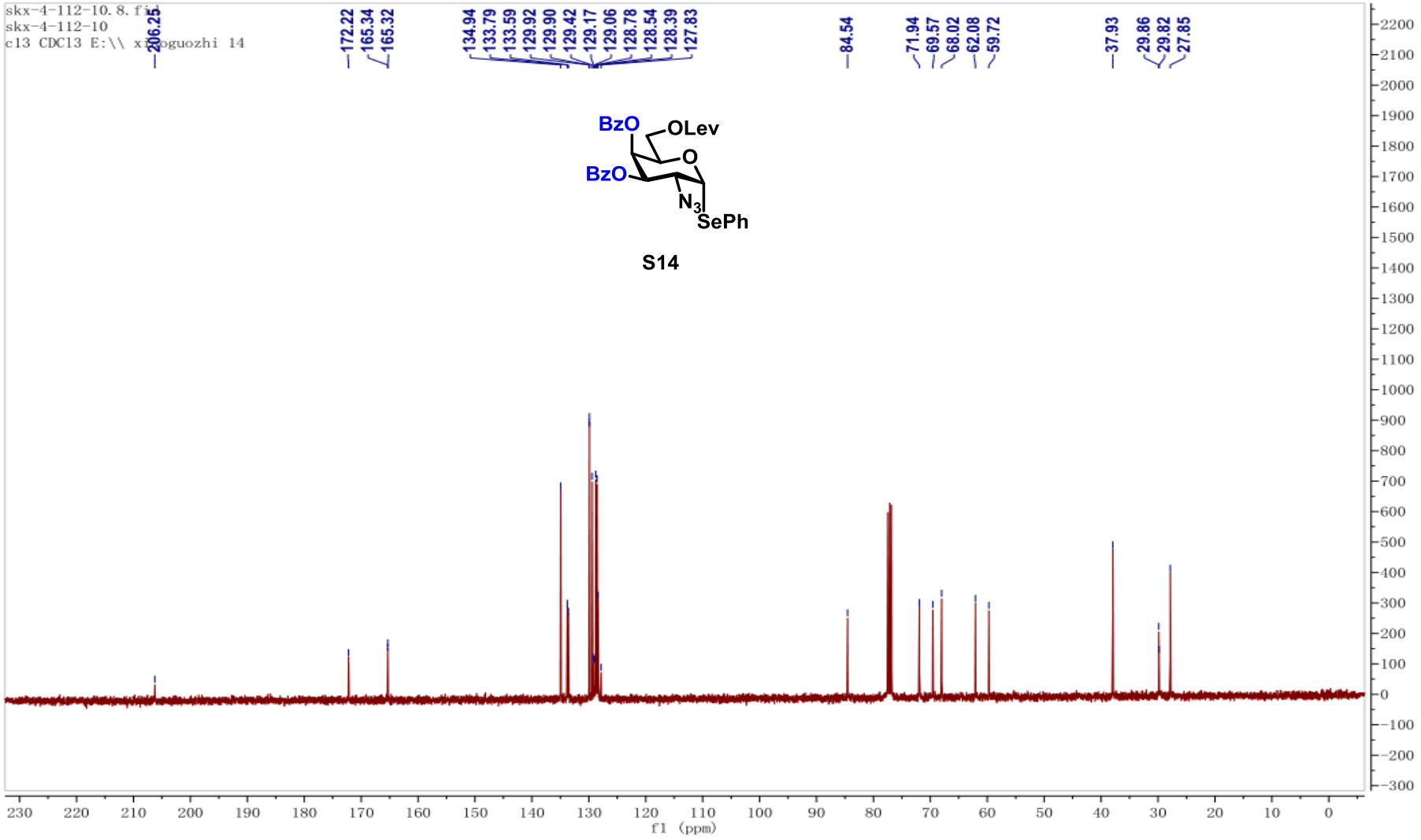

SKX-5-20.2.ser
SKX-5-20
HSQCGP CDCl3
BzO
OBn
O
BzO
N3
O(CH2)5NBnCbz
19a α/β > 20/1
f2 (ppm)
f1 (ppm)

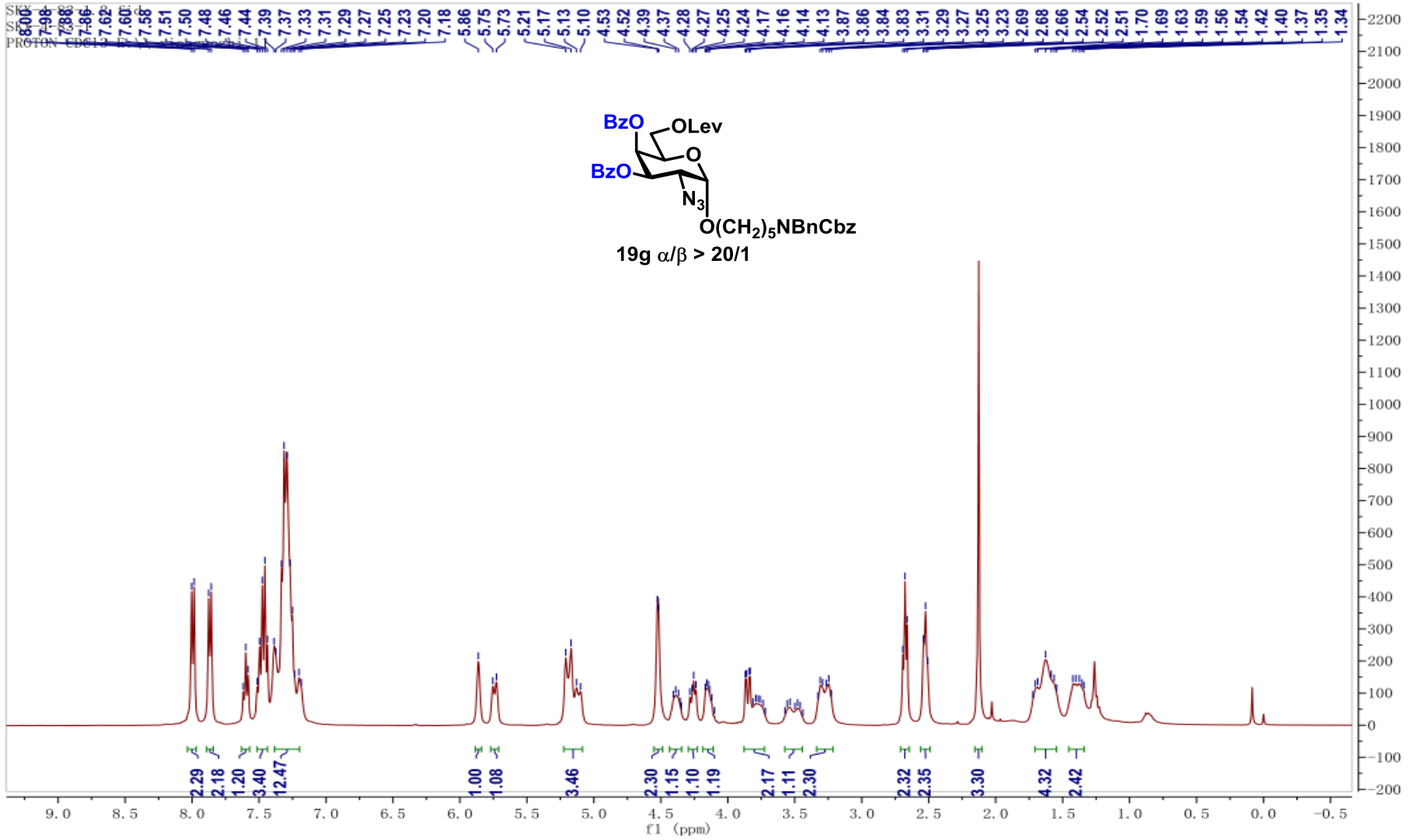

BzO
OTBDPS
O
BzO
N3
SePh
S12
f1 (ppm)

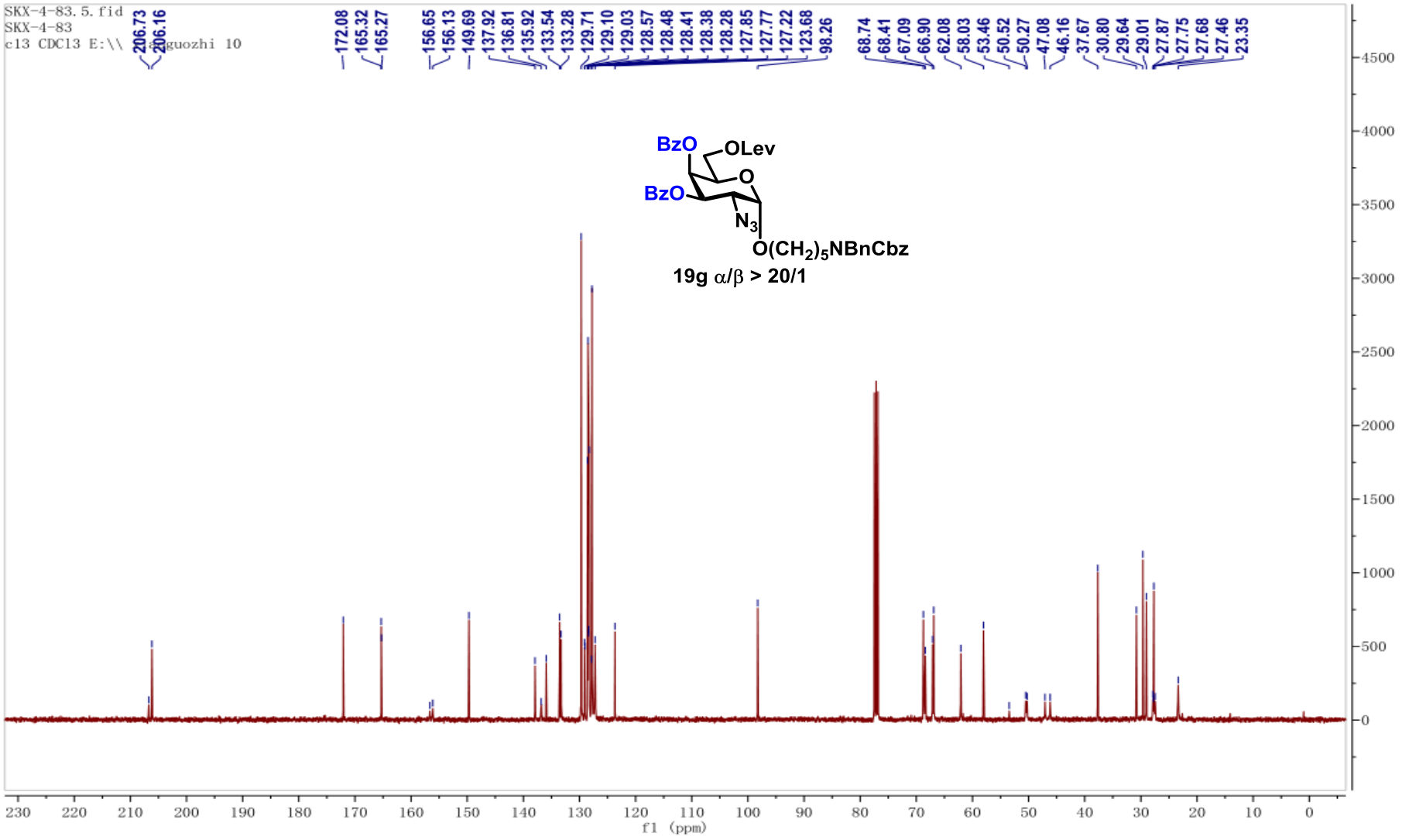

SKX-6-112-1.3.fid
SKX-6-112-1
c13 CDCl3 E:\\ xiaoguo
165.36
165.17
135.59
135.54
135.50
135.19
133.44
133.40
132.94
132.55
129.92
129.87
129.83
129.74
129.67
129.29
129.26
128.66
128.45
128.24
127.91
127.88
127.82
127.69
84.69
72.18
71.69
67.73
61.04
60.01
26.77
19.10
BzO
OTBDPS
O
BzO
N3
SePh
S12
f1 (ppm)

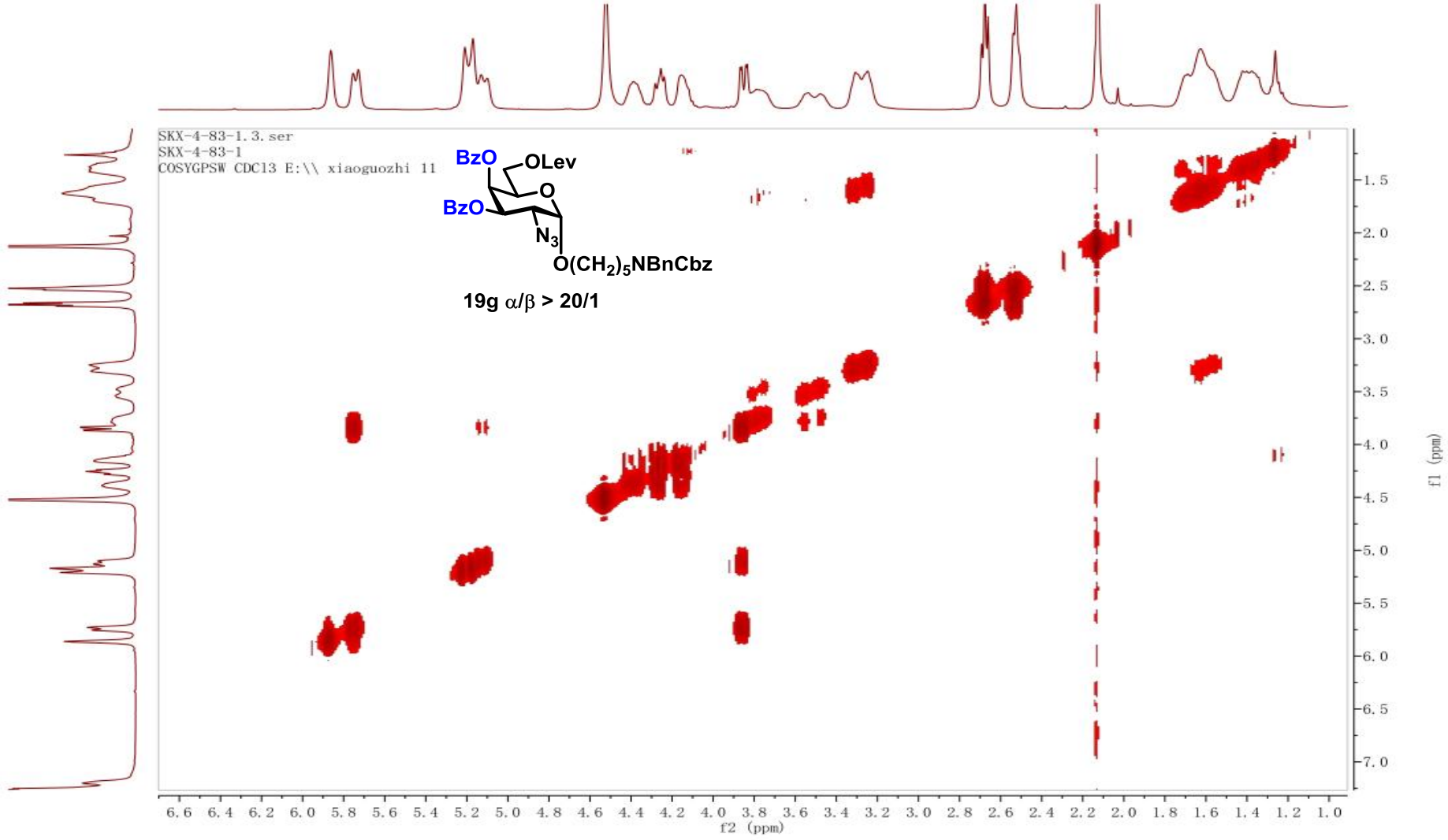

SKX-6-112-1.2.ser
SKX-6-112-1
COSYGPSW CDC13 E:\\ xiaoguozhi 7
BzO
OTBDPS
O
BzO
N3
SePh
S12
f2 (ppm)
f1 (ppm)

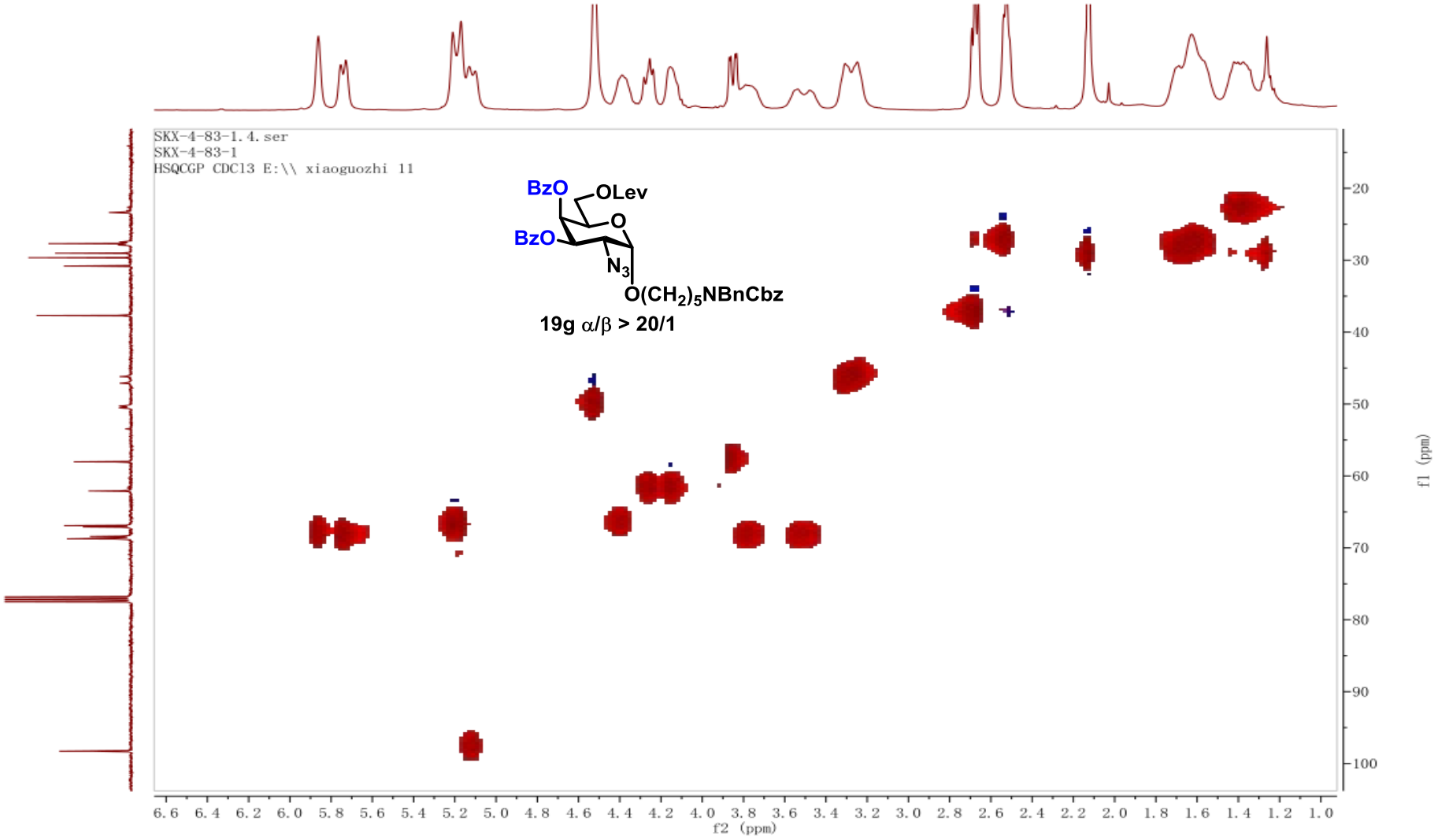

BzO
OLev
O
BzO
N3
SePh
S14
f1 (ppm)

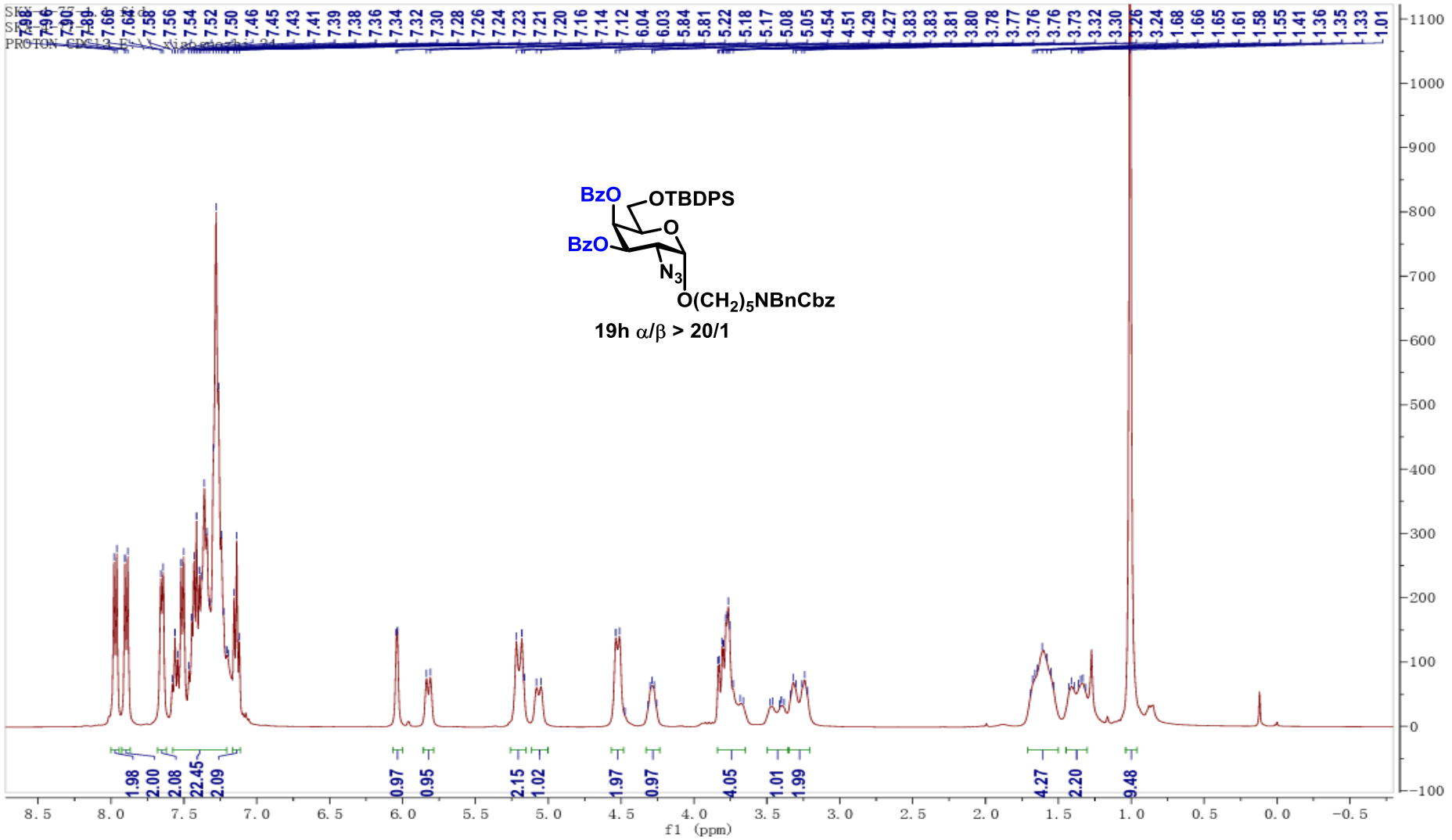

skx-4-112-10.8.fid
skx-4-112-10
c13 CDCl3 E:\\ xiaoguozhi 14
206.25
172.22
165.34
165.32
134.94
133.79
133.59
129.92
129.90
129.42
129.17
129.06
128.78
128.54
128.39
127.83
84.54
71.94
69.57
68.02
62.08
59.72
37.93
29.86
29.82
27.85
BzO
OLev
O
BzO
N3
SePh
S14
f1 (ppm)

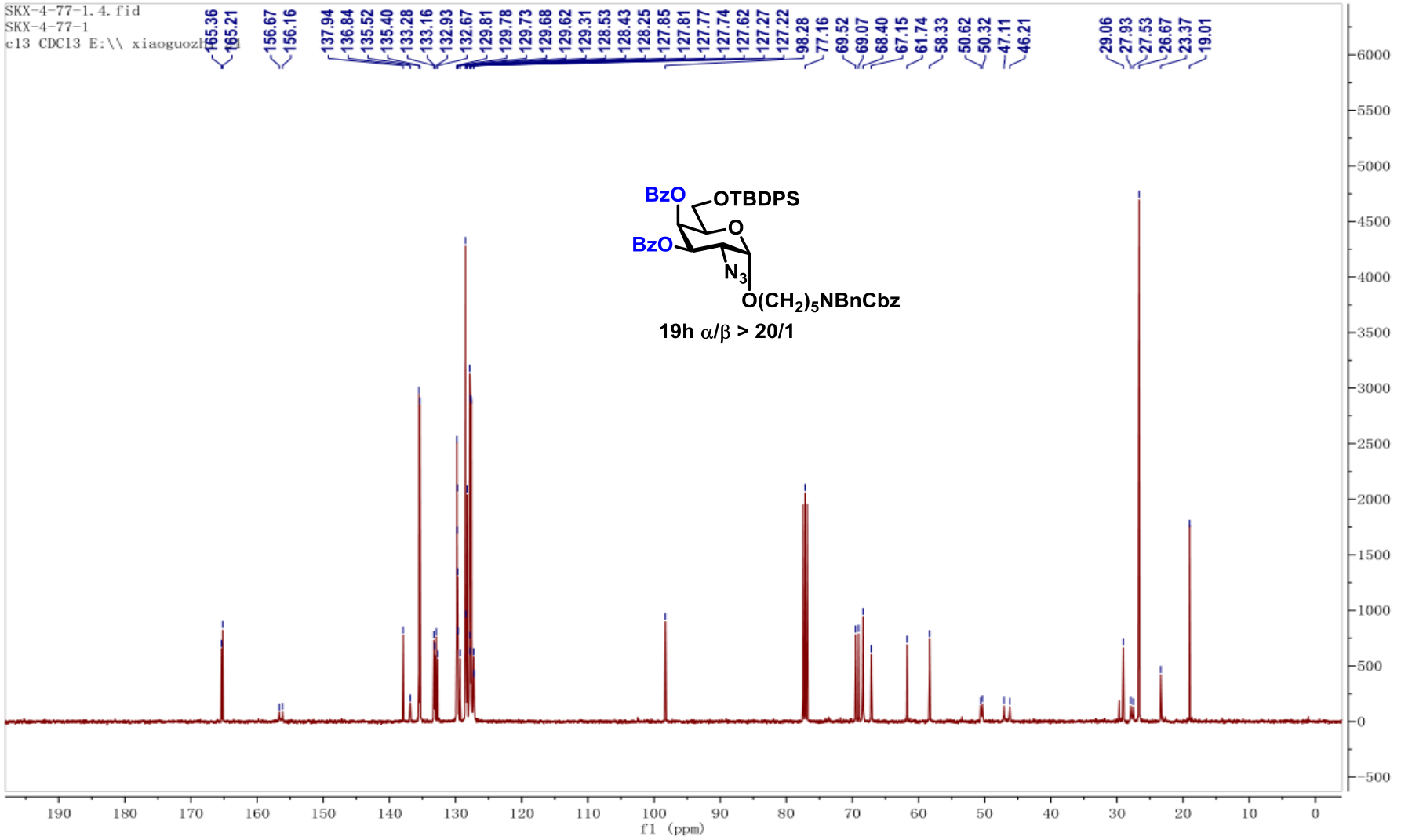

BzO
OLev
O
BzO
N3
O(CH2)5NBnCbz
19g α/β > 20/1
f1 (ppm)

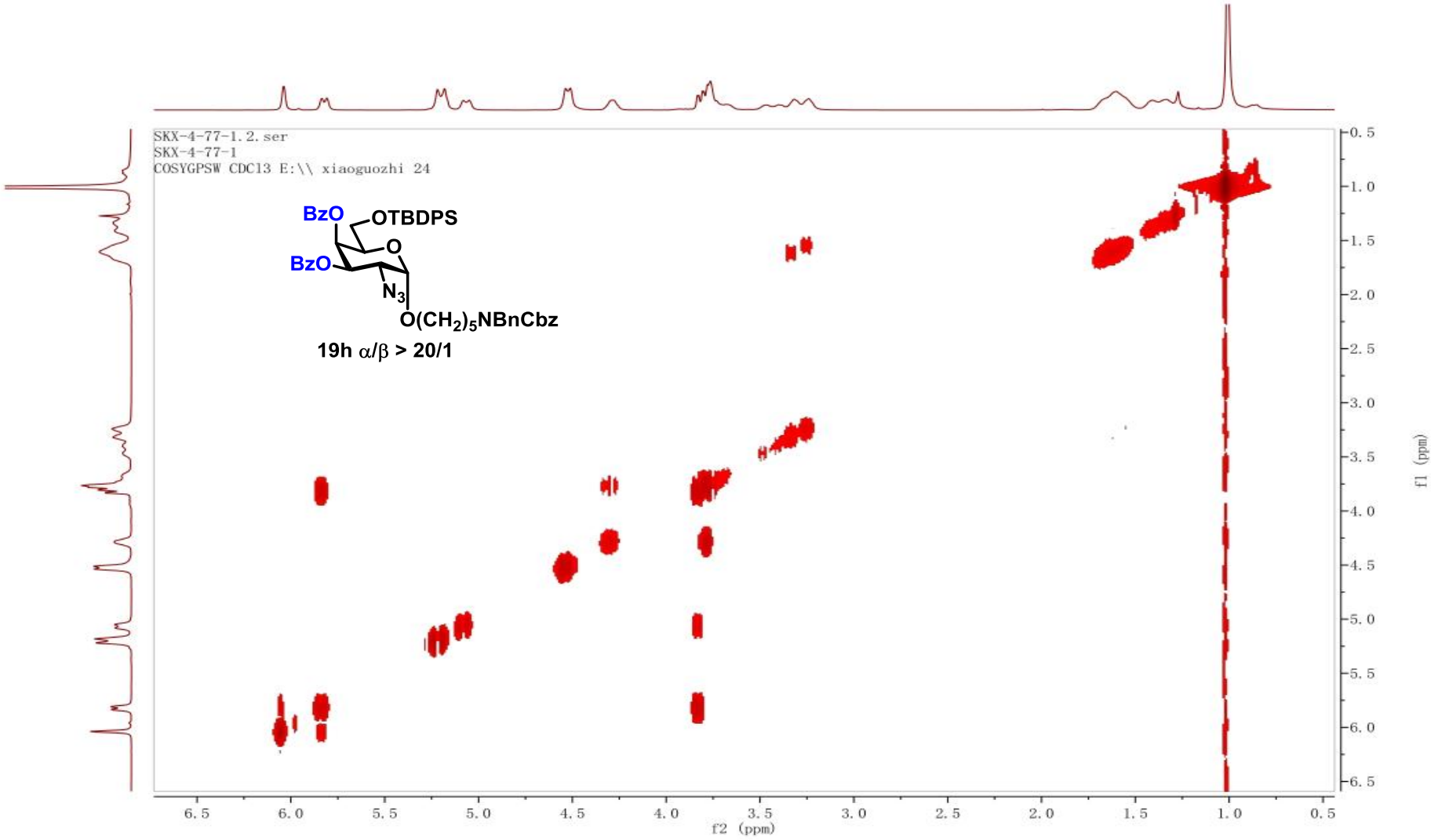

SKX-4-83.5.fid
SKX-4-83
c13 CDCl3 E:\\ ...guozhi 10
206.73
206.16
172.08
165.32
165.27
156.65
156.13
149.69
137.92
136.81
135.92
133.54
133.28
129.71
129.10
129.03
128.57
128.48
128.41
128.38
128.28
127.85
127.77
127.22
123.68
98.26
68.74
68.41
67.09
66.90
62.08
58.03
53.46
50.52
50.27
47.08
46.16
37.67
30.80
29.64
29.01
27.87
27.75
27.68
27.46
23.35
BzO
OLev
O
BzO
N3
O(CH2)5NBnCbz
19g α/β > 20/1
f1 (ppm)

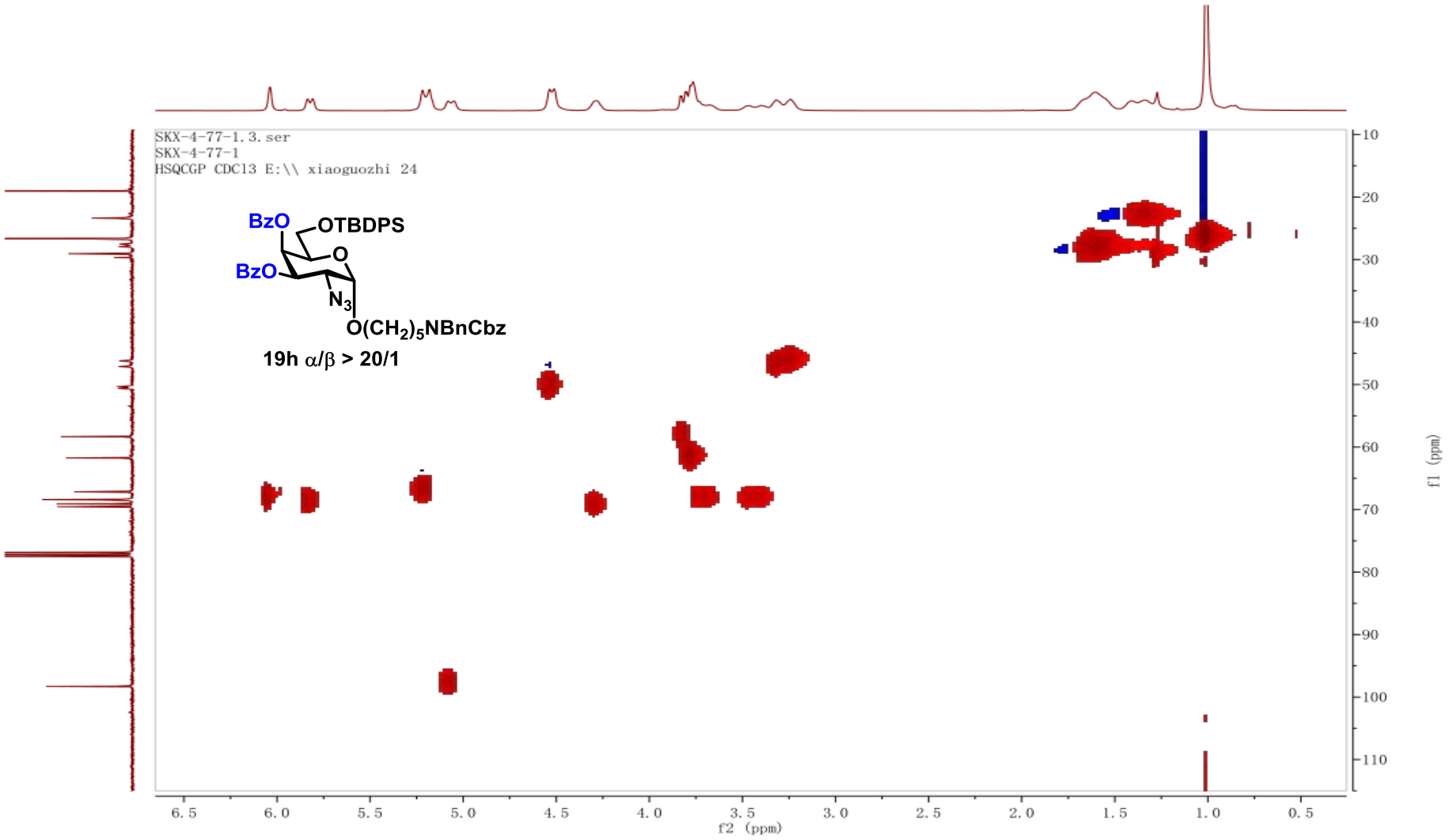

SKX-4-83-1.3.ser
SKX-4-83-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 11
BzO
OLev
O
BzO
N3
O(CH2)5NBnCbz
19g α/β > 20/1
f2 (ppm)
f1 (ppm)

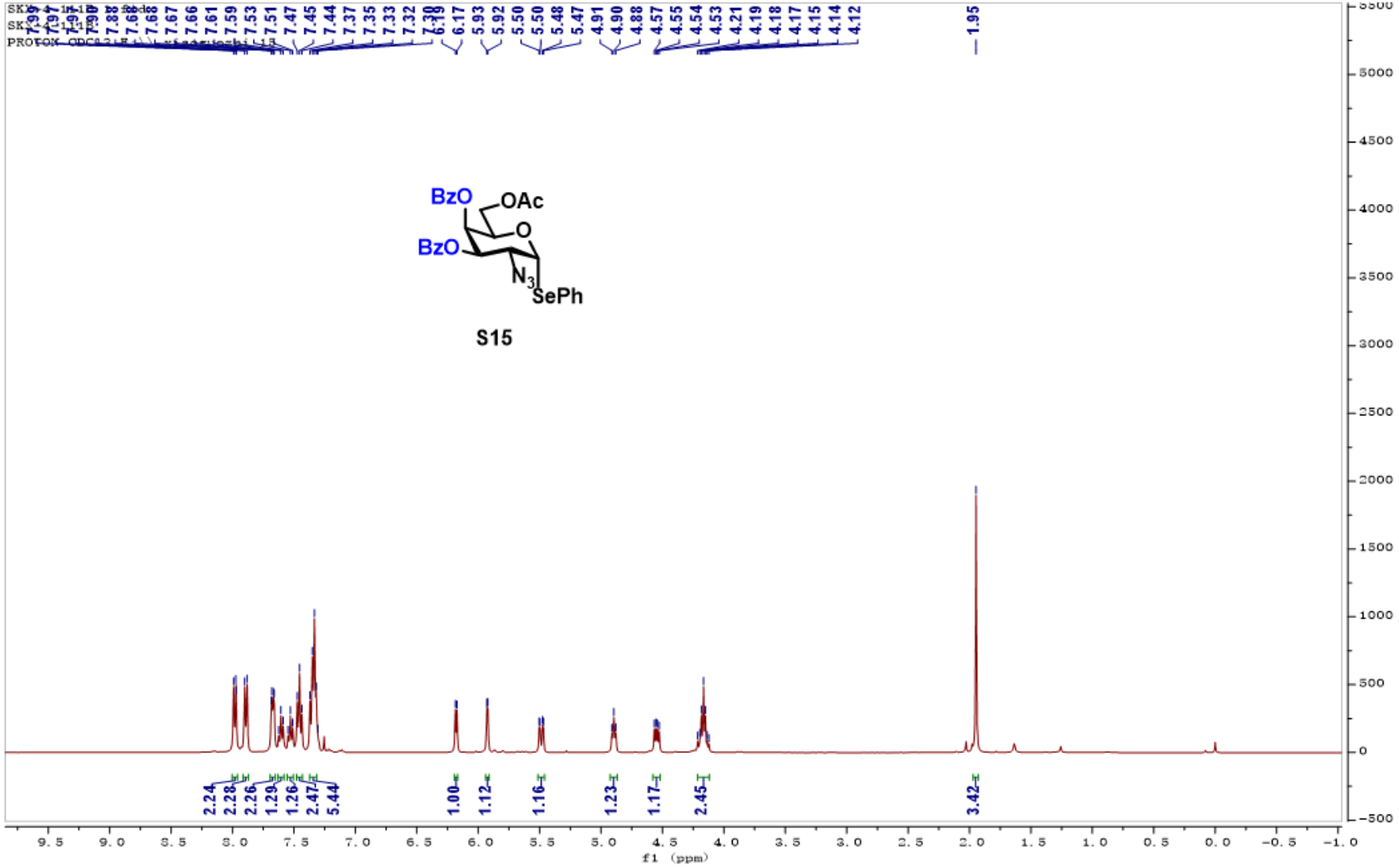

SKX-4-83-1.4.ser
SKX-4-83-1
HSQCGP CDCl3 E:\\ xiaoguozhi 11
BzO
OLev
O
BzO
N3
O(CH2)5NBnCbz
19g α/β > 20/1
f2 (ppm)
f1 (ppm)

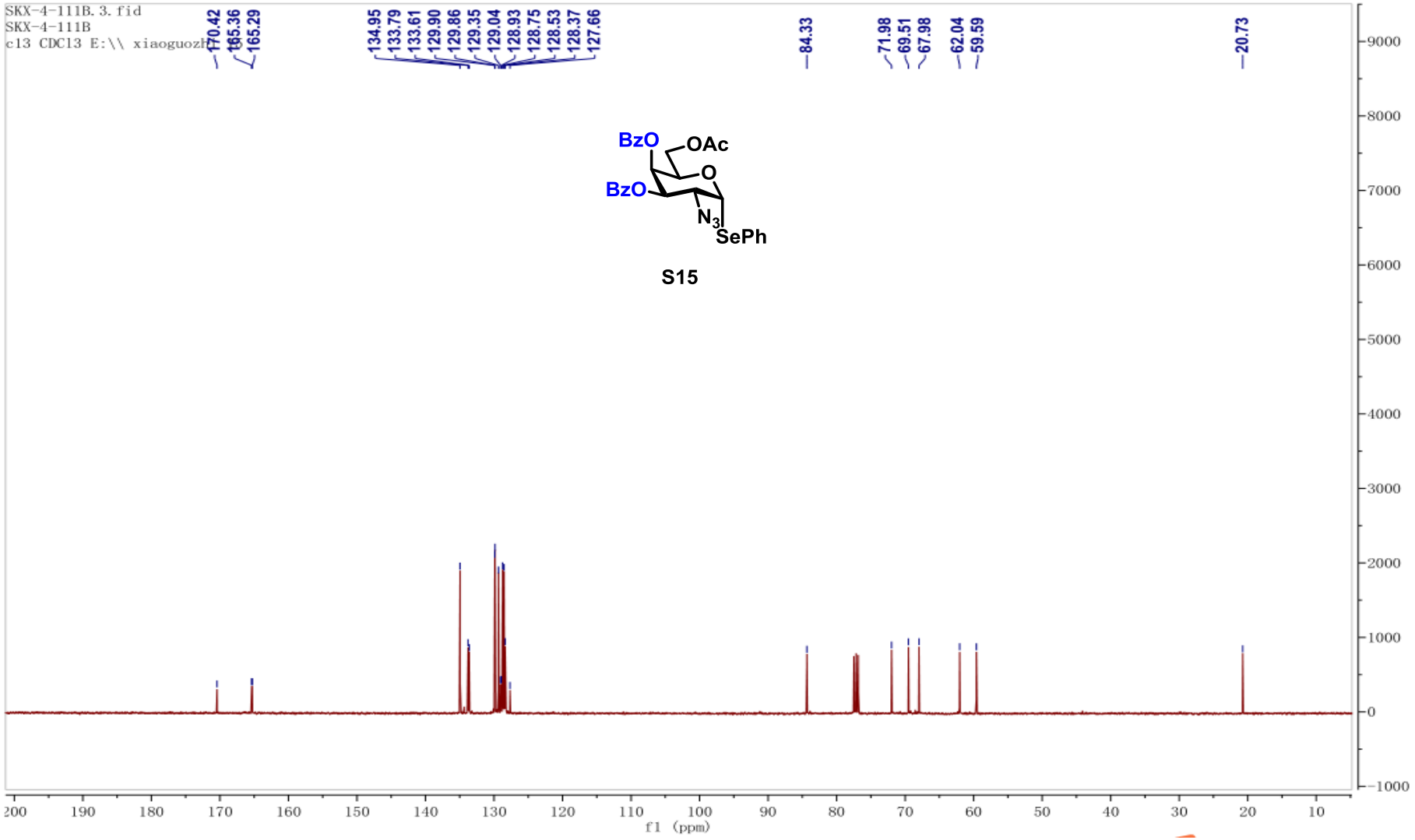

BzO
OTBDPS
O
BzO
N3
O(CH2)5NBnCbz
19h α/β > 20/1
f1 (ppm)

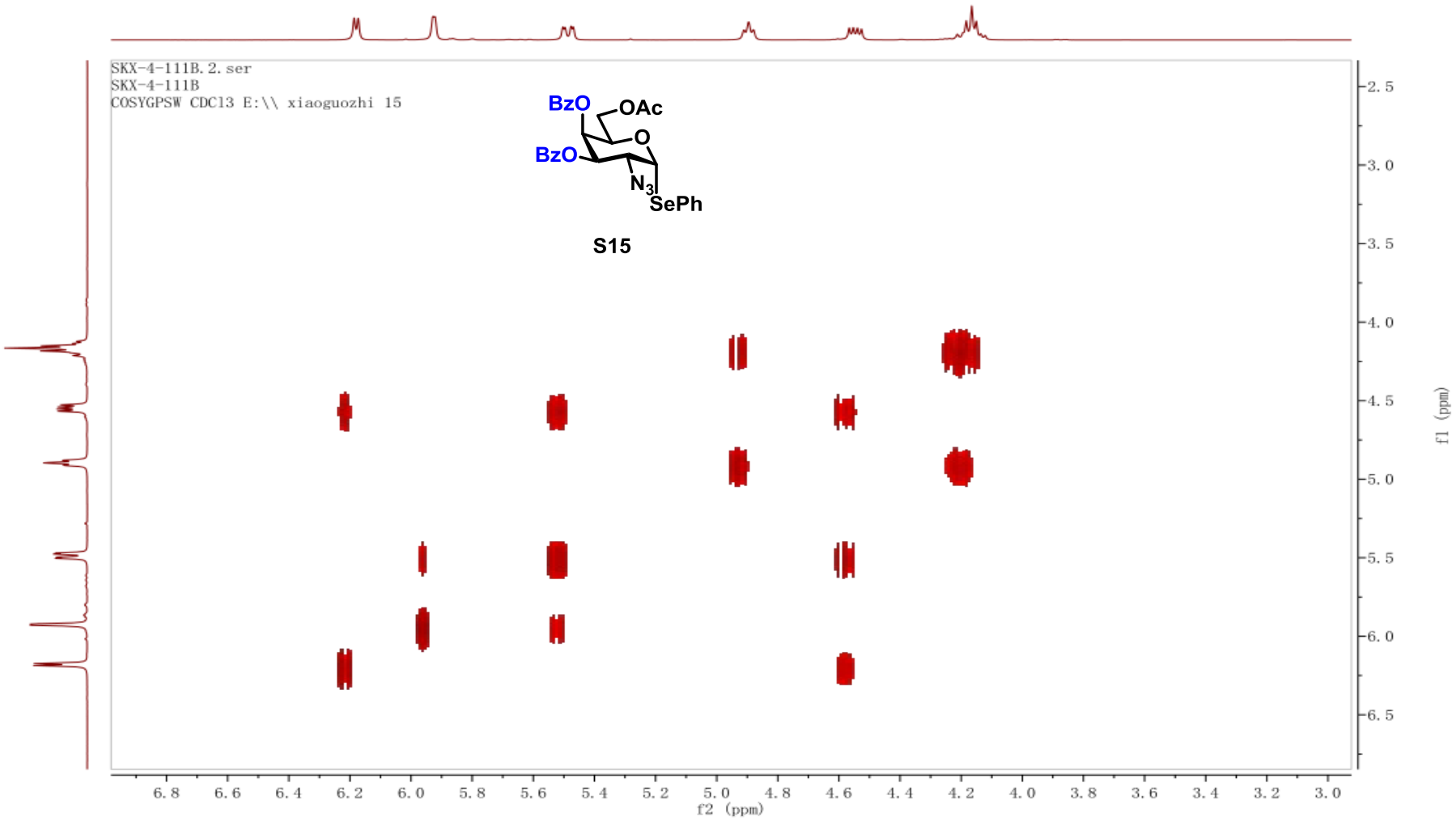

SKX-4-77-1.4.fid
SKX-4-77-1
c13 CDCl3 E:\\ xiaoguozh
165.36
165.21
156.67
156.16
137.94
136.84
135.52
135.40
133.28
133.16
132.93
132.67
129.81
129.78
129.73
129.68
129.62
129.31
128.53
128.43
128.25
127.85
127.81
127.77
127.74
127.62
127.27
127.22
98.28
77.16
69.52
69.07
68.40
67.15
61.74
58.33
50.62
50.32
47.11
46.21
29.06
27.93
27.53
26.67
23.37
19.01
BzO
OTBDPS
O
BzO
N3
O(CH2)5NBnCbz
19h α/β > 20/1
f1 (ppm)

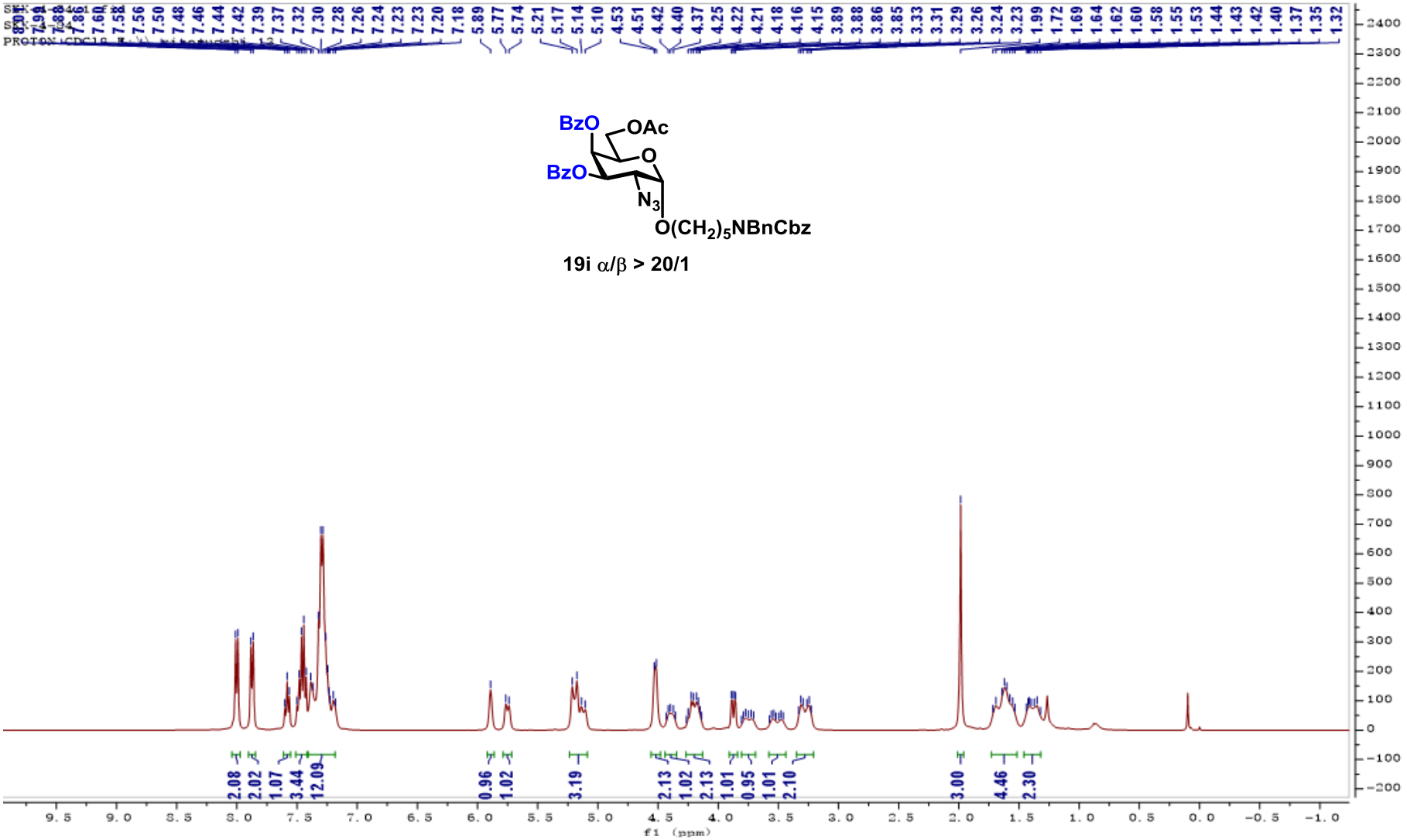

SKX-4-77-1.2.ser
SKX-4-77-1
COSYGPSW CDC13 E:\\ xiaoguozhi 24
BzO
OTBDPS
O
BzO
N3
O(CH2)5NBnCbz
19h α/β > 20/1
f2 (ppm)
f1 (ppm)


SKX-4-77-1.3.ser
SKX-4-77-1
HSQCGP CDCl3 E:\\ xiaoguozhi 24
BzO
OTBDPS
O
BzO
N3
O(CH2)5NBnCbz
19h α/β > 20/1
f2 (ppm)
f1 (ppm)

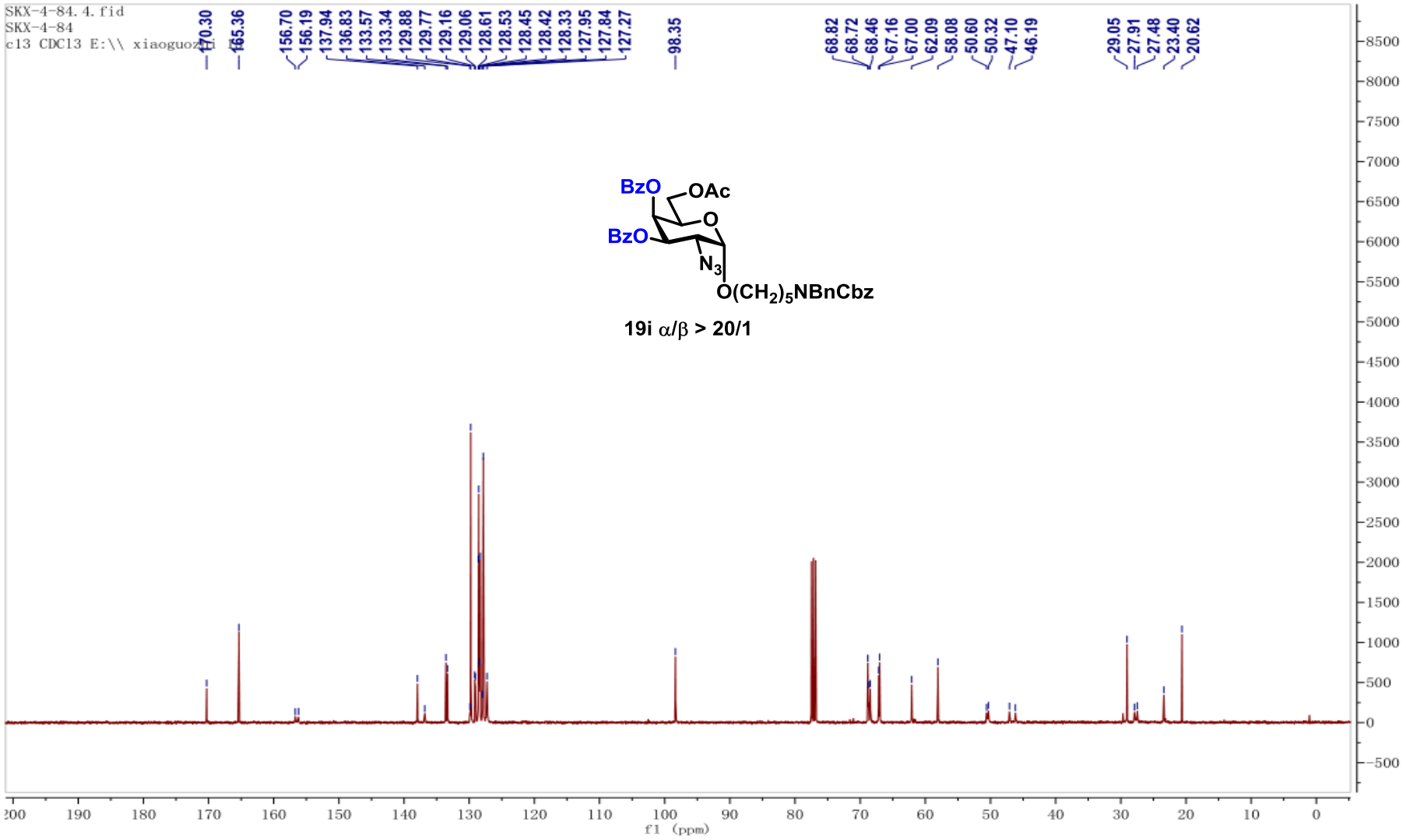

BzO
OAc
O
BzO
N3
SePh
S15
f1 (ppm)

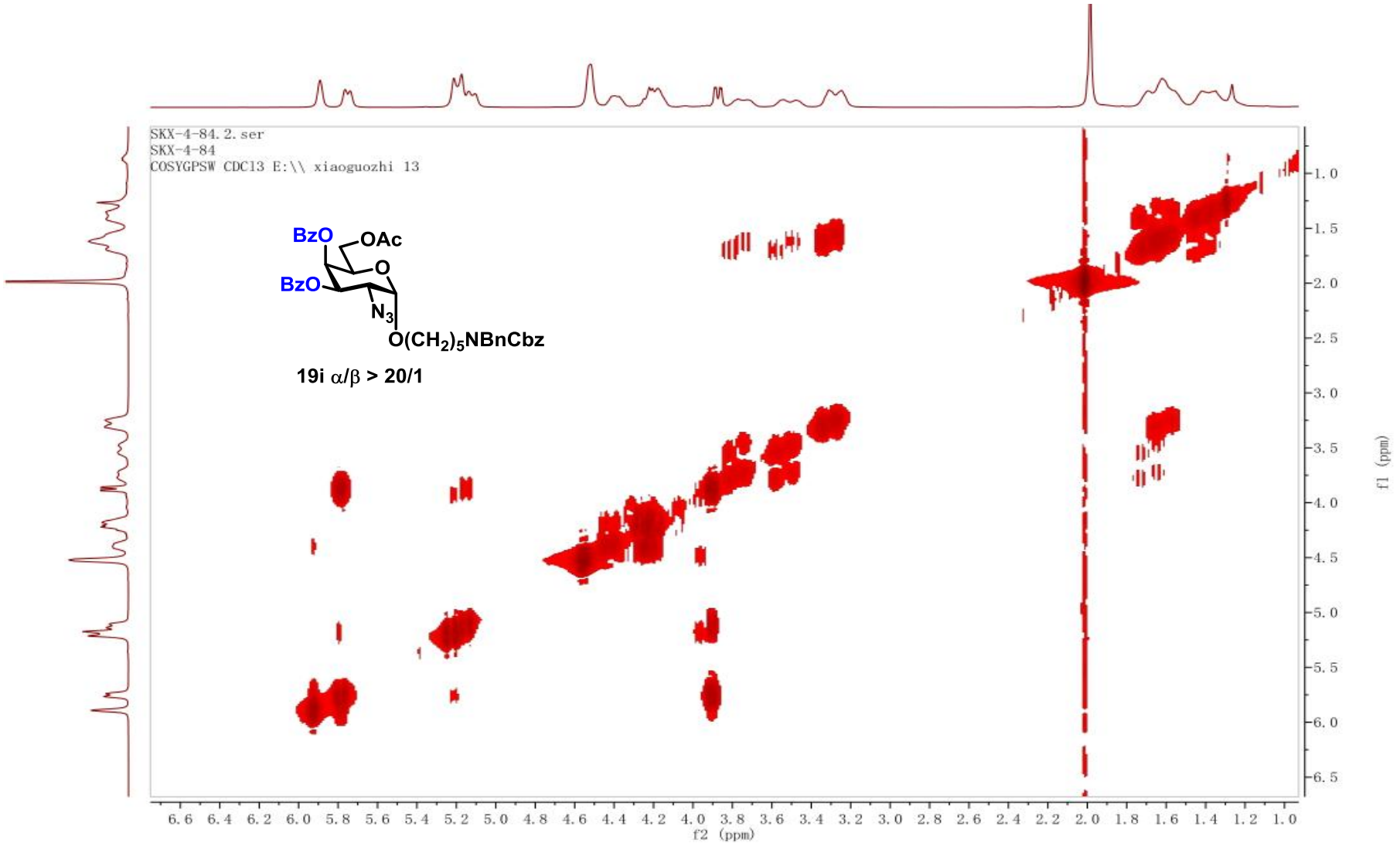

SKX-4-111B.3.fid
SKX-4-111B
c13 CDCl3 E:\\ xiaoguozh
170.42
165.36
165.29
134.95
133.79
133.61
129.90
129.86
129.35
129.04
128.93
128.75
128.53
128.37
127.66
84.33
71.98
69.51
67.98
62.04
59.59
20.73
BzO
OAc
O
BzO
N3
SePh
S15
f1 (ppm)

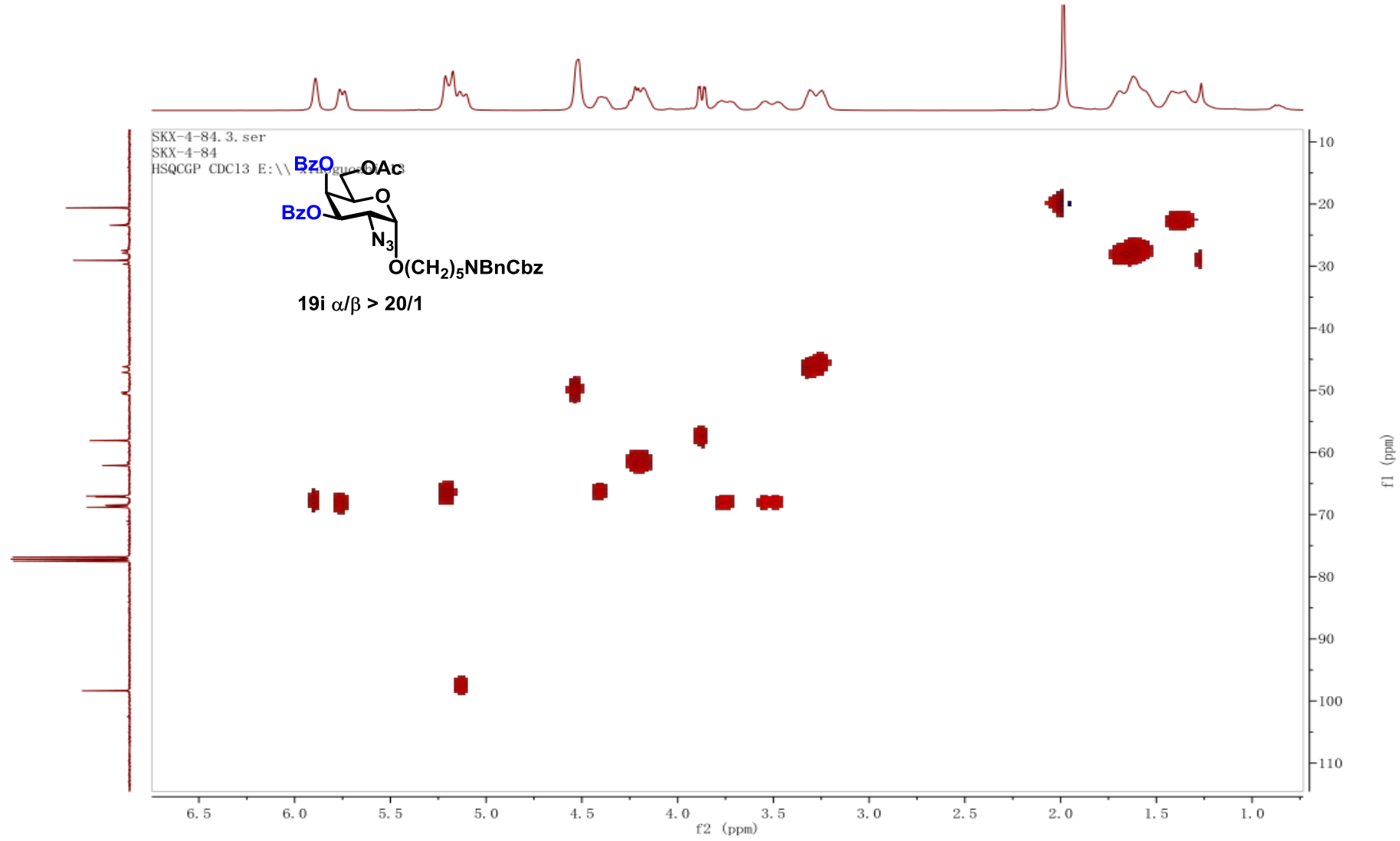

SKX-4-111B.2.ser
SKX-4-111B
COSYGPSW CDCl3 E:\\ xiaoguozhi 15
BzO
OAc
O
BzO
N3
SePh
S15
f2 (ppm)
f1 (ppm)

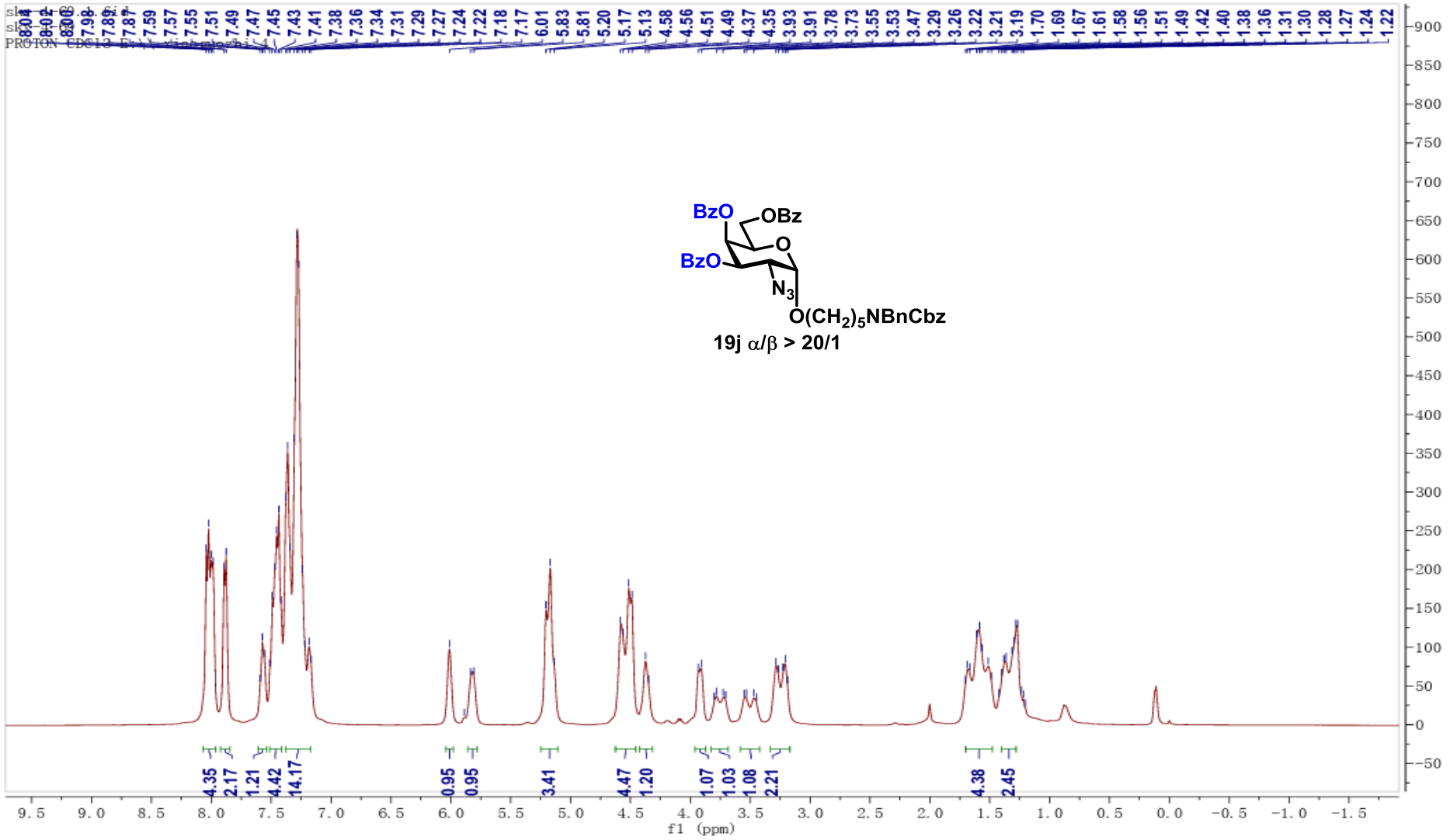


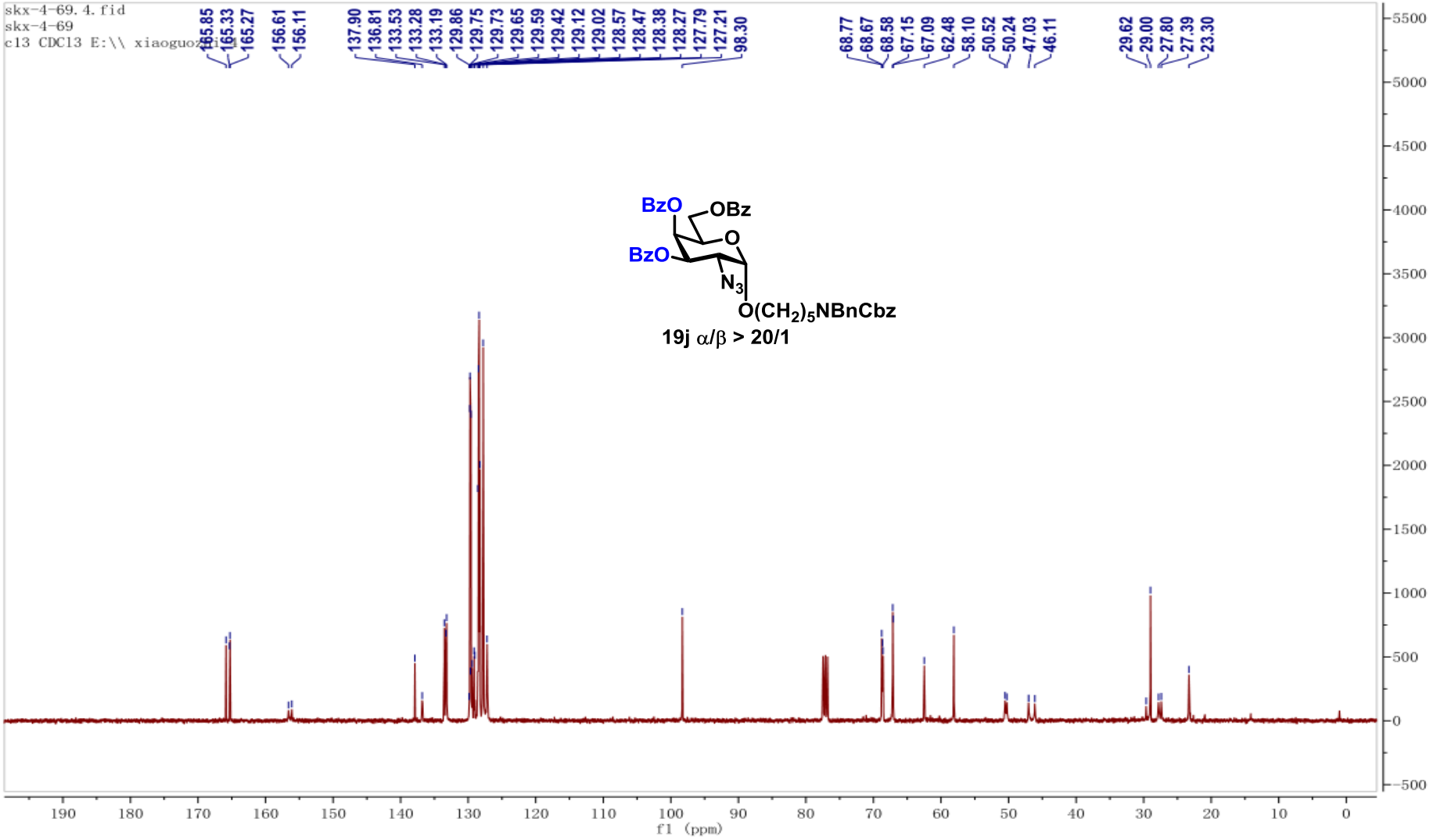
19i α/β > 20/1

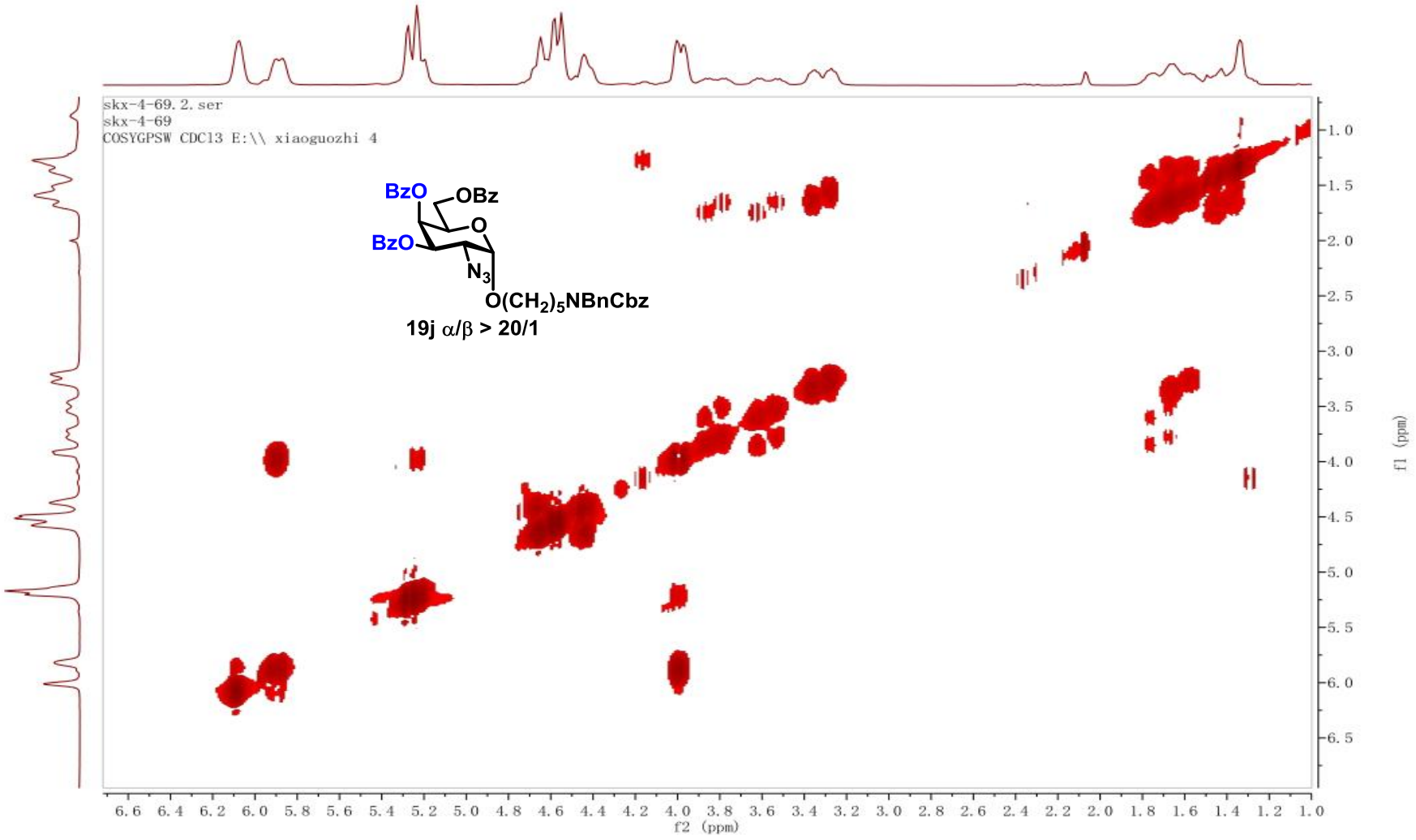

SKX-4-84.4.fid
SKX-4-84
c13 CDCl3 E:\\ xiaoguozhi
170.30
165.36
156.70
156.19
137.94
136.83
133.57
133.34
129.88
129.77
129.16
129.06
128.61
128.53
128.45
128.42
128.33
127.95
127.84
127.27
98.35
68.82
68.72
68.46
67.16
67.00
62.09
58.08
50.60
50.32
47.10
46.19
29.05
27.91
27.48
23.40
20.62
BzO
OAc
O
BzO
N3
O(CH2)5NBnCbz
19i α/β > 20/1
f1 (ppm)

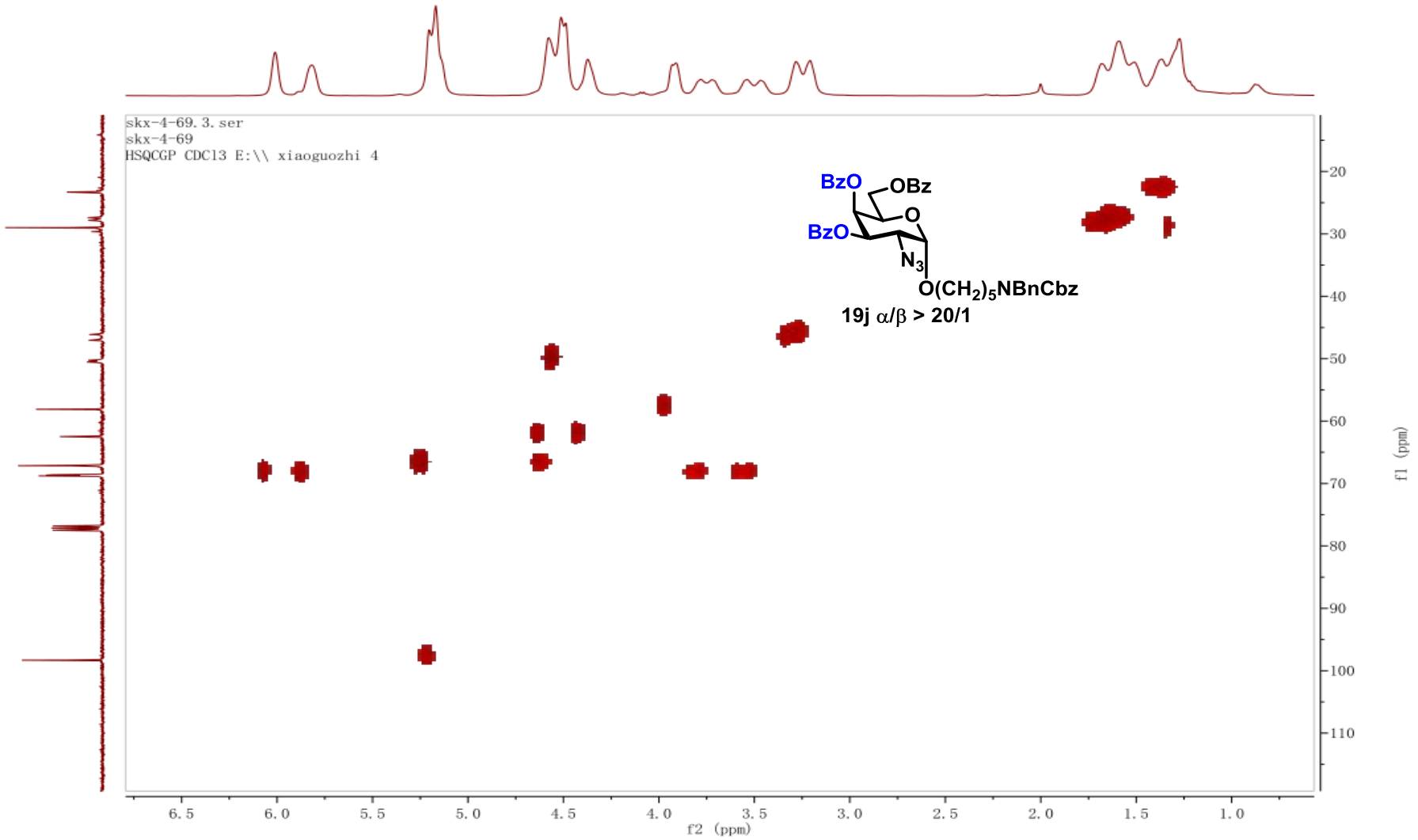

SKX-4-84.2.ser
SKX-4-84
COSYGPSW CDCl3 E:\\ xiaoguozhi 13
BzO
OAc
O
BzO
N3
O(CH2)5NBnCbz
19i α/β > 20/1
f2 (ppm)
f1 (ppm)

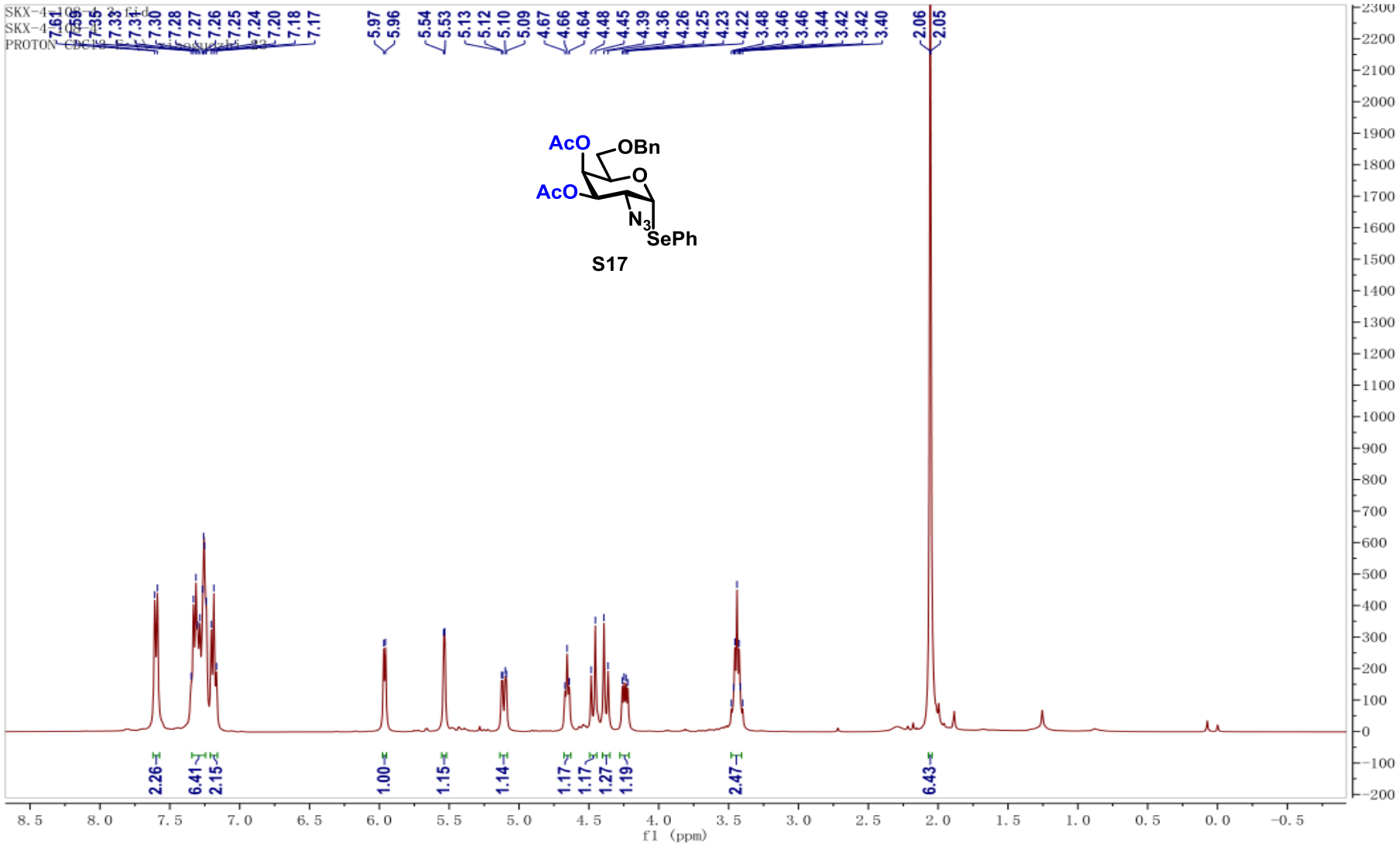

SKX-4-84.3.ser
SKX-4-84
HSQCGP CDCl3 E:\\
BzO
OAc
O
BzO
N3
O(CH2)5NBnCbz
19i α/β > 20/1
f2 (ppm)
f1 (ppm)

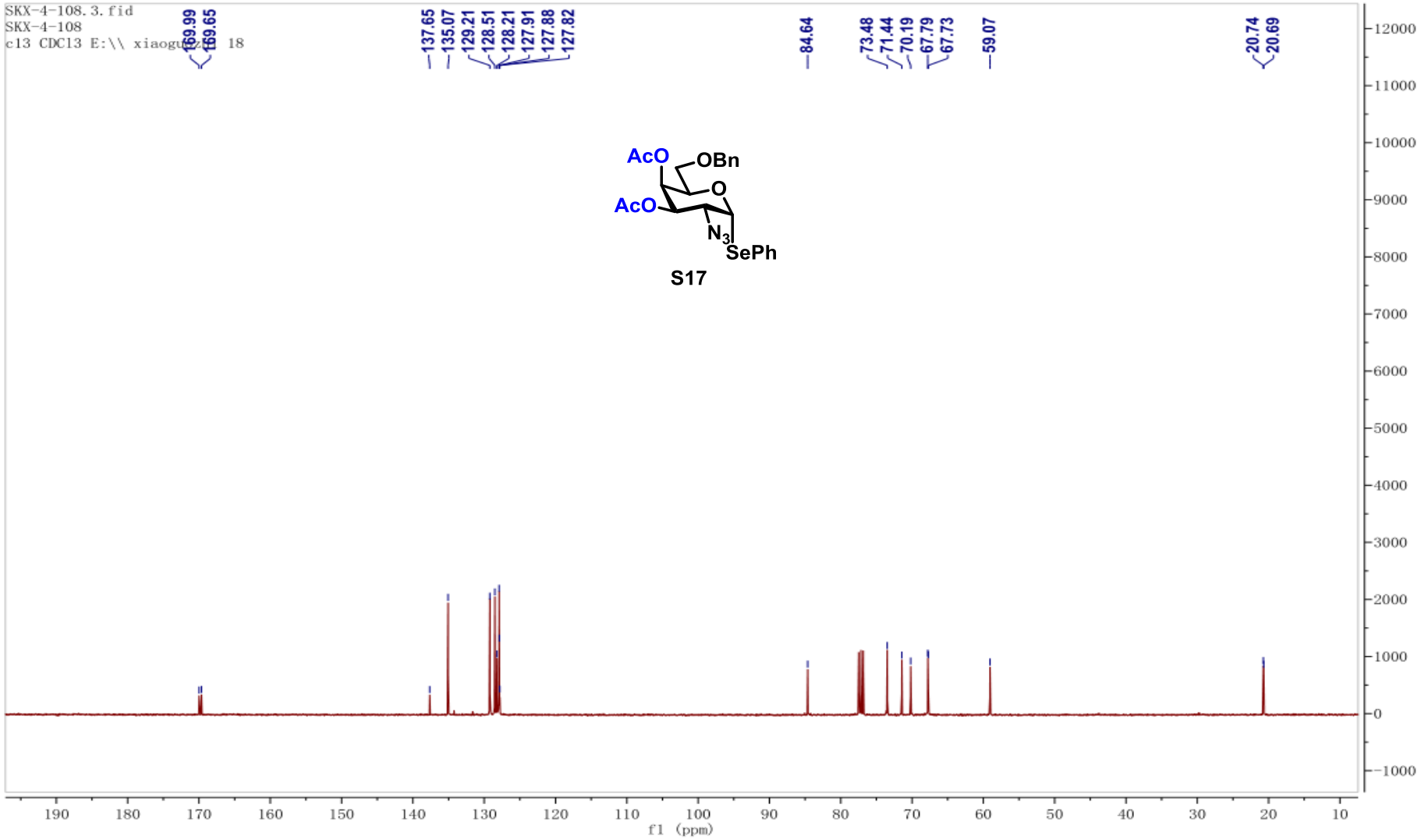

BzO
OBz
O
BzO
N3
O(CH2)5NBnCbz
19j α/β > 20/1
f1 (ppm)

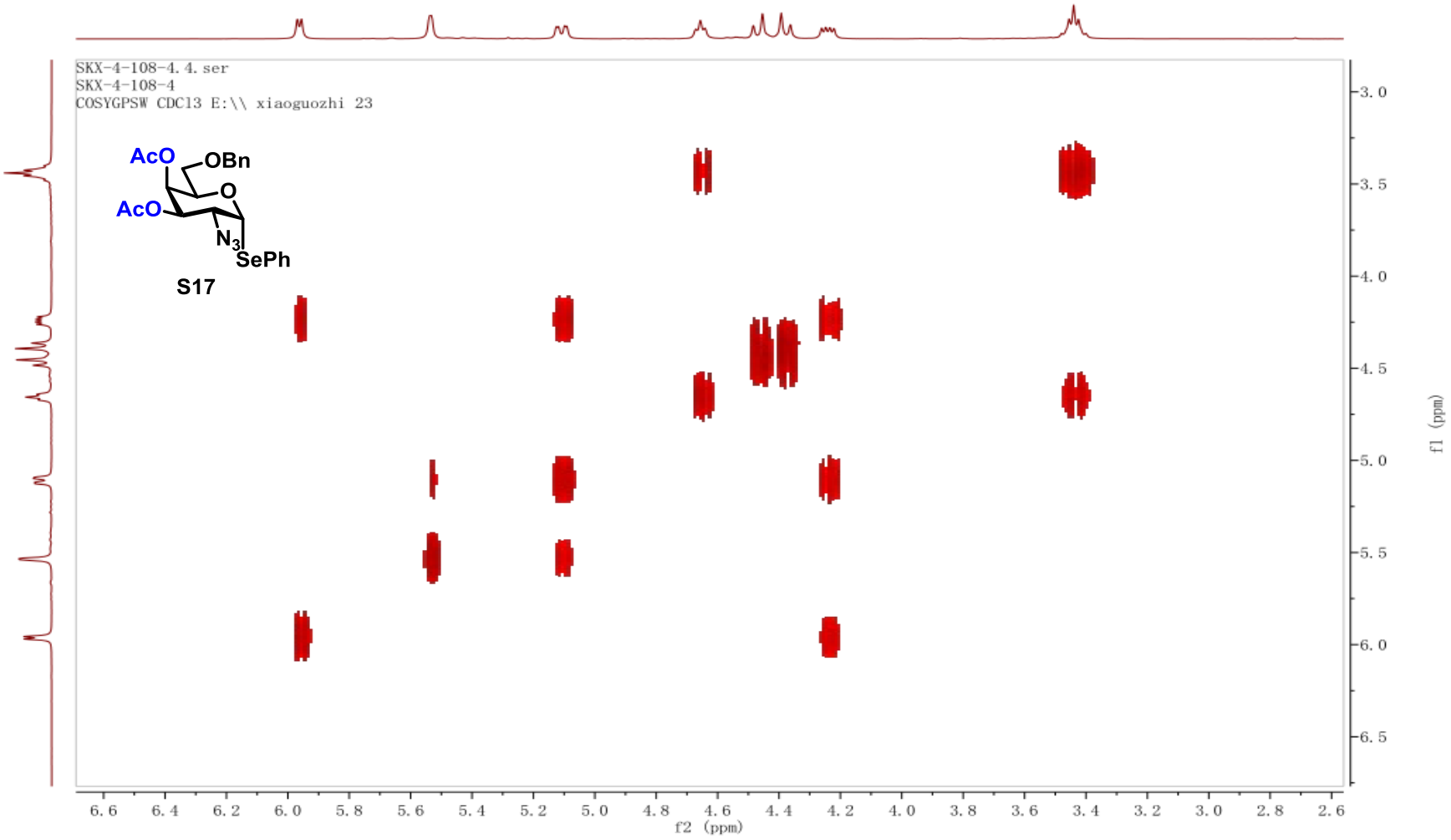

skx-4-69.4.fid
skx-4-69
c13 CDCl3 E:\\ xiaoguozi
165.85
165.33
165.27
156.61
156.11
137.90
136.81
133.53
133.28
133.19
129.86
129.75
129.73
129.65
129.59
129.42
129.12
129.02
128.57
128.47
128.38
128.27
127.79
127.21
98.30
68.77
68.67
68.58
67.15
67.09
62.48
58.10
50.52
50.24
47.03
46.11
29.62
29.00
27.80
27.39
23.30
BzO
OBz
O
BzO
N3
O(CH2)5NBnCbz
19j α/β > 20/1
f1 (ppm)

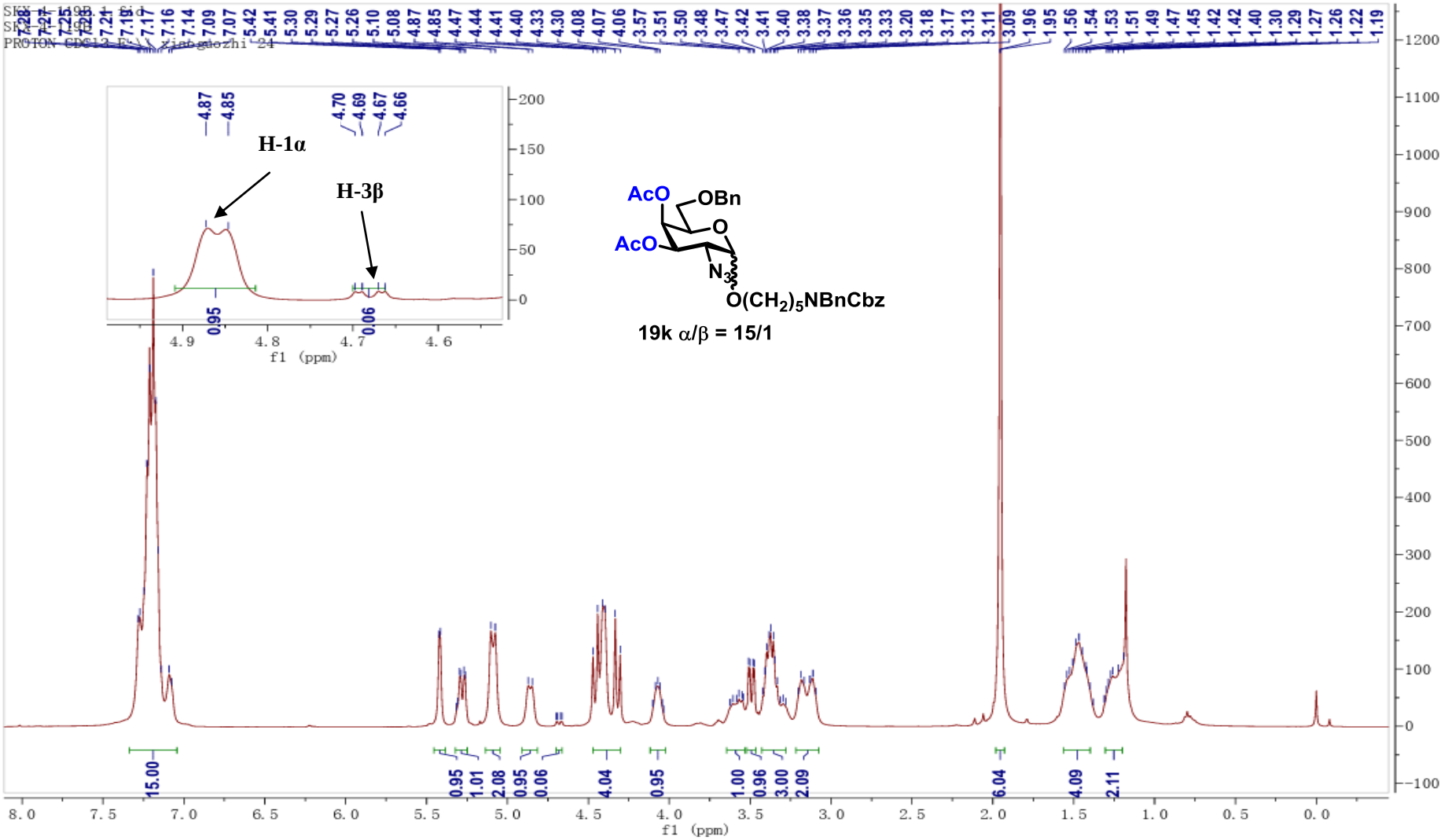

skx-4-69.2.ser
skx-4-69
COSYGPSW CDCl3 E:\\ xiaoguozhi 4
BzO
OBz
O
BzO
N3
O(CH2)5NBnCbz
19j α/β > 20/1
f2 (ppm)
f1 (ppm)

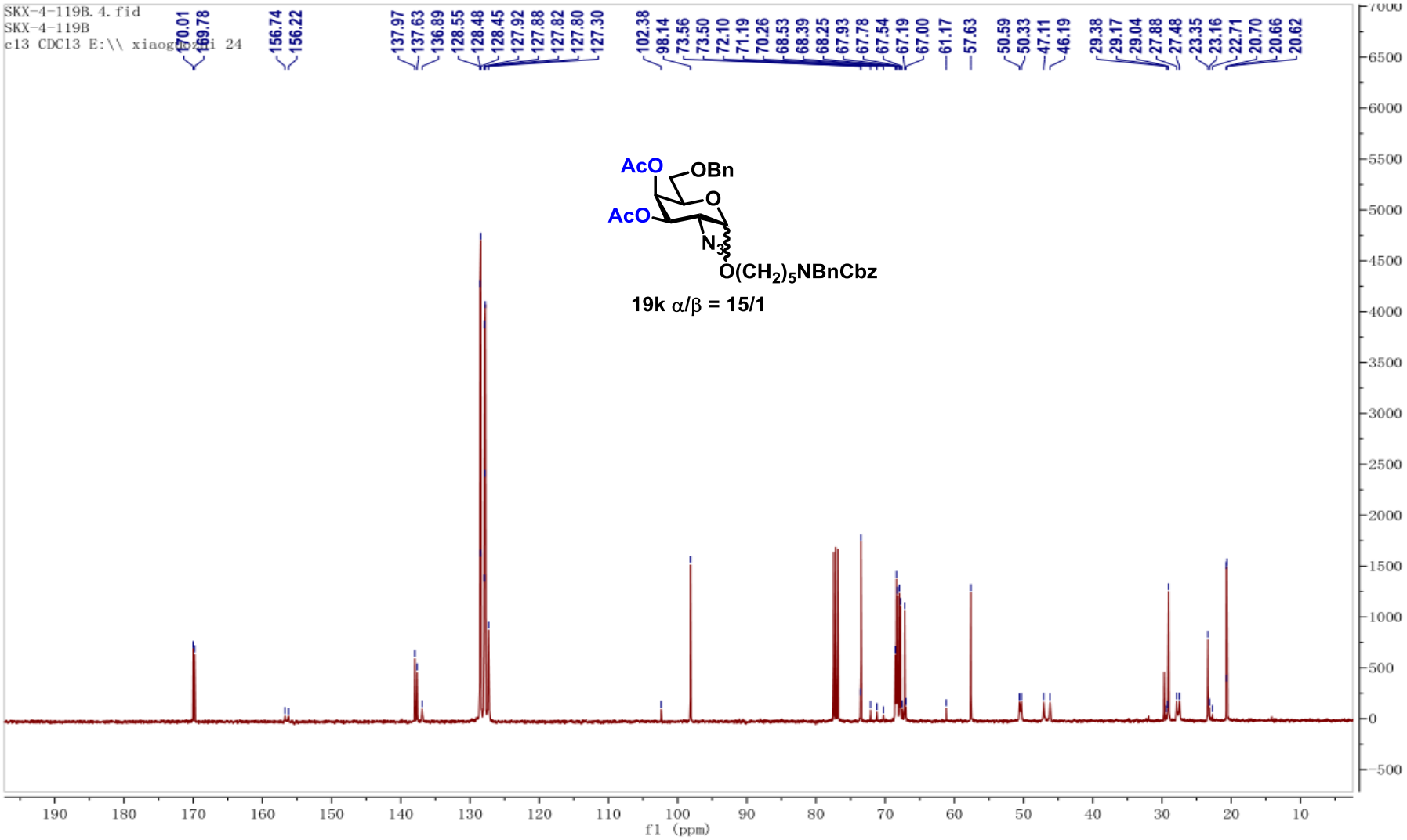

skx-4-69.3.ser
skx-4-69
HSQCGP CDCl3 E:\\ xiaoguozhi 4
BzO
OBz
O
BzO
N3
O(CH2)5NBnCbz
19j α/β > 20/1
f2 (ppm)
f1 (ppm)

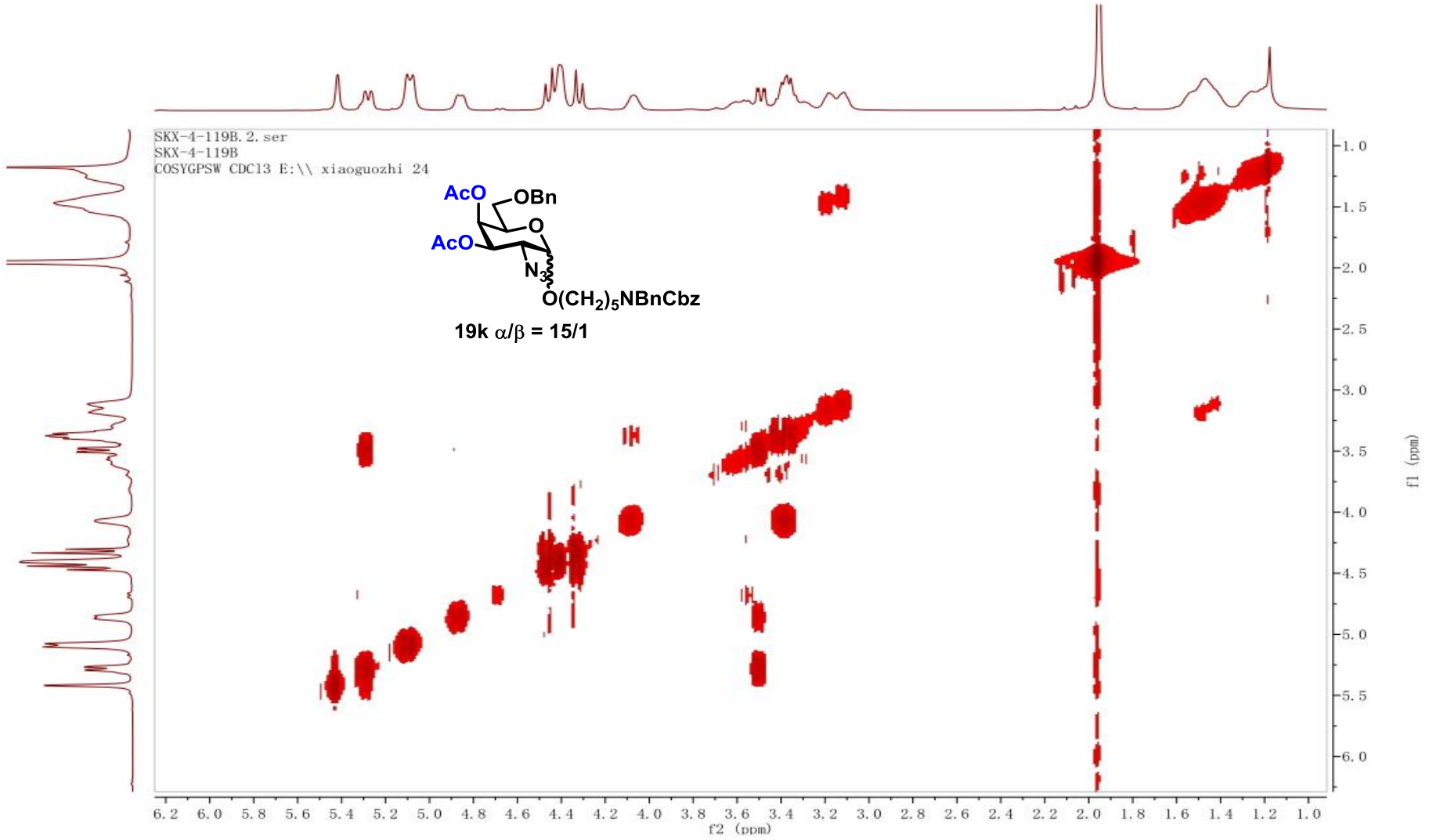

AcO
OBn
O
AcO
N3
SePh
S17
f1 (ppm)

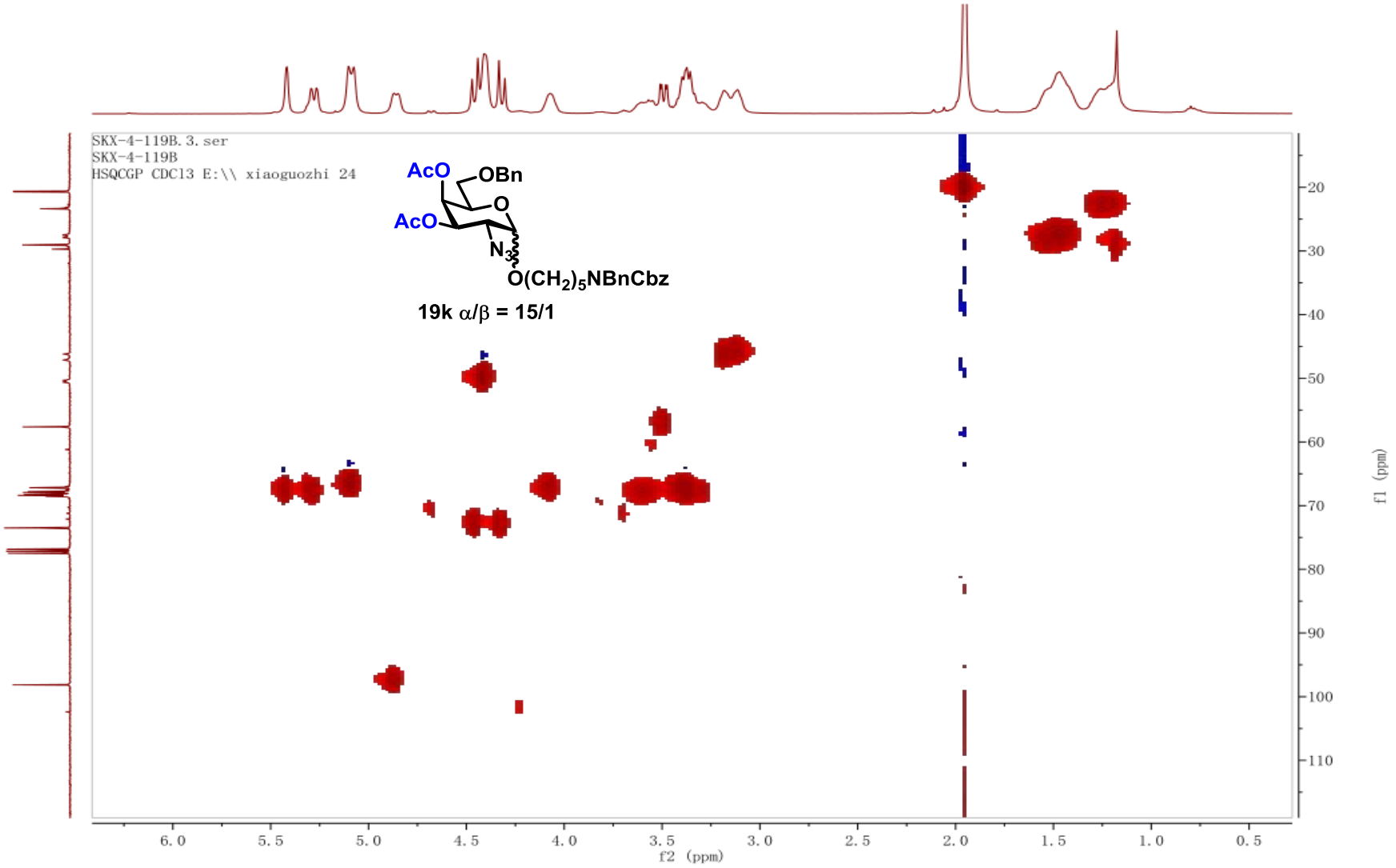

SKX-4-108.3.fid
SKX-4-108
c13 CDCl3 E:\\ xiaogu
18
169.99
169.65
137.65
135.07
129.21
128.51
128.21
127.91
127.88
127.82
84.64
73.48
71.44
70.19
67.79
67.73
59.07
20.74
20.69
AcO
OBn
O
AcO
N3
SePh
S17
f1 (ppm)

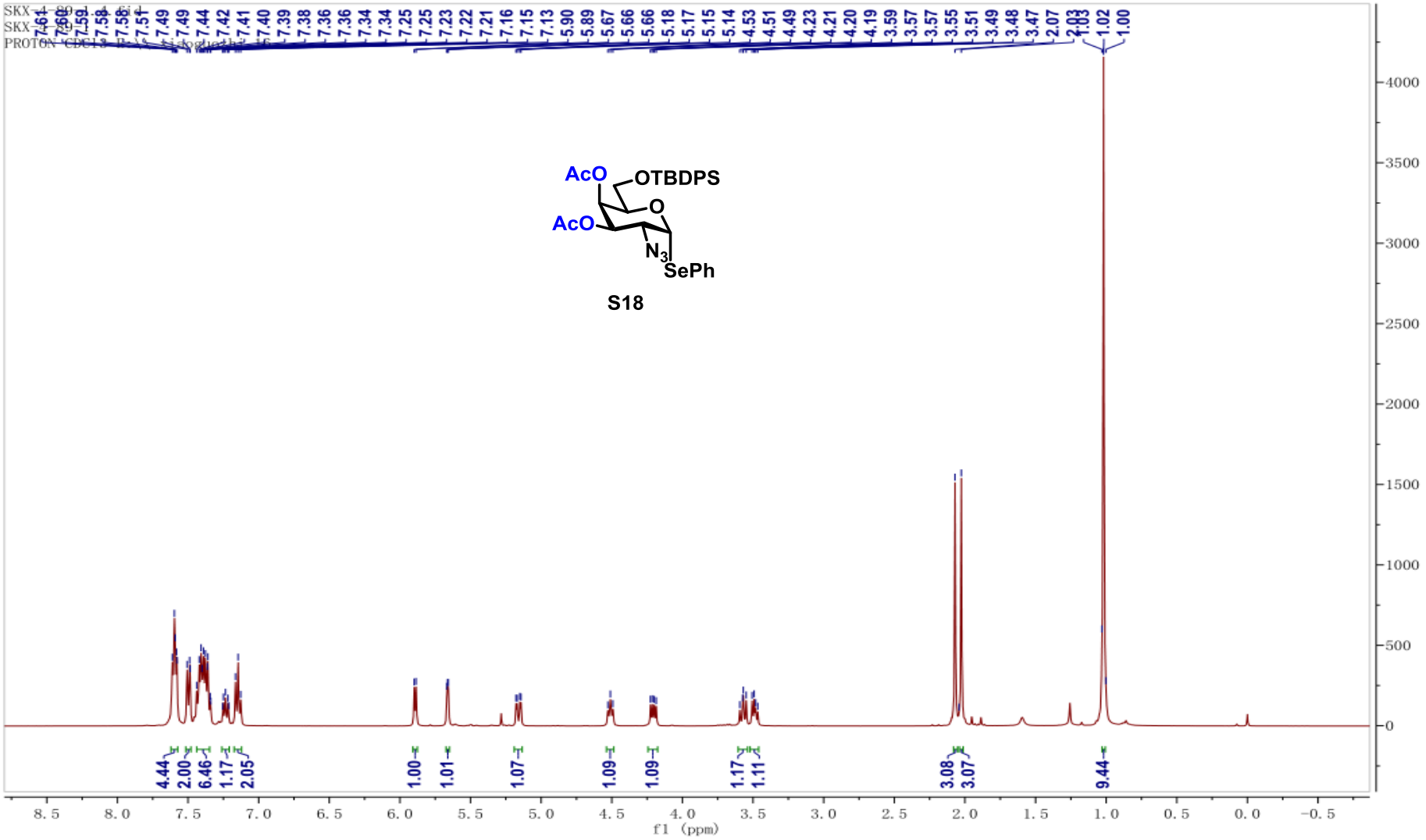

SKX-4-108-4.4.ser
SKX-4-108-4
COSYGPSW CDCl3 E:\\ xiaoguozhi 23
AcO
OBn
O
AcO
N3
SePh
S17
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f2 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

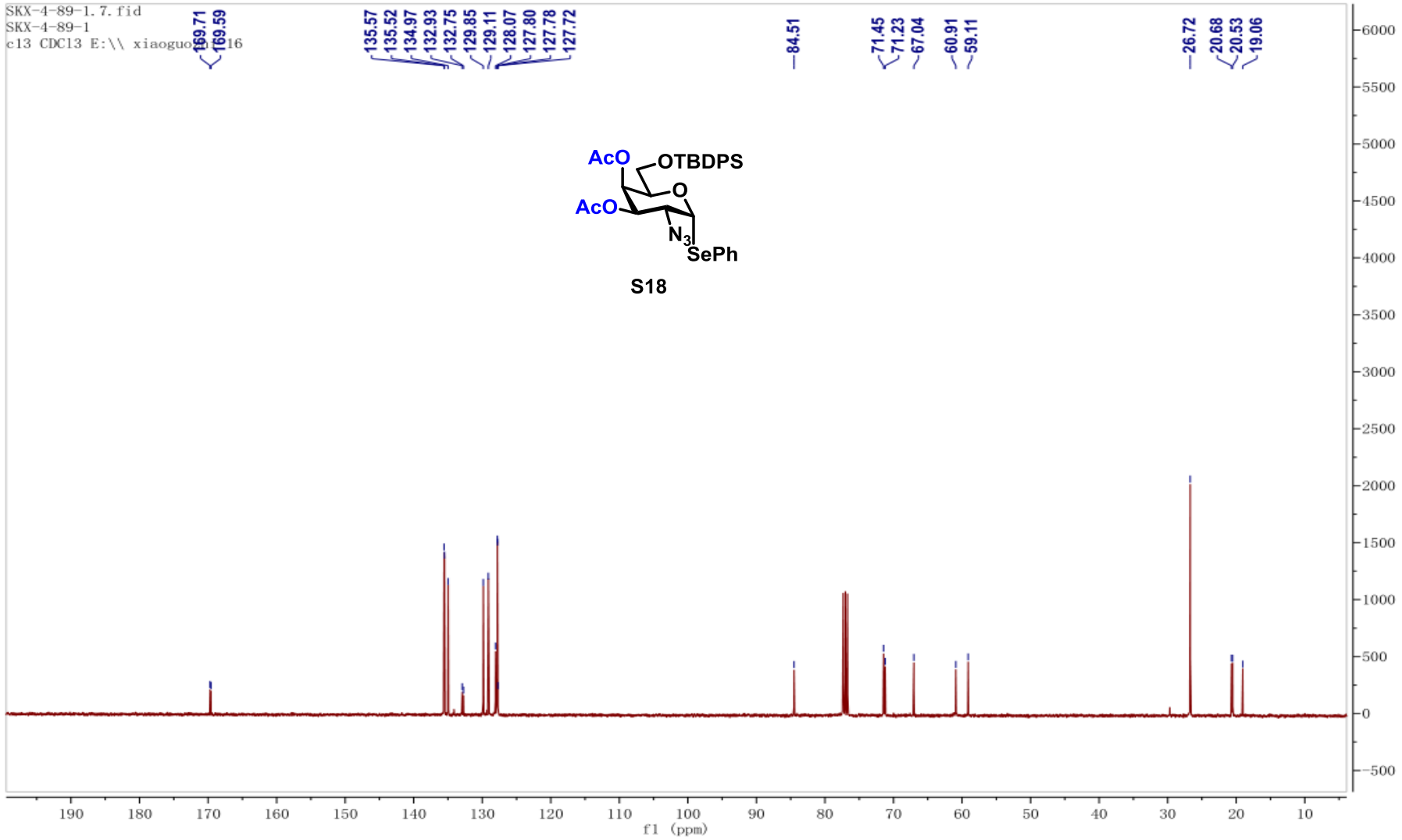

H-1α
H-3β
AcO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19k α/β = 15/1
f1 (ppm)

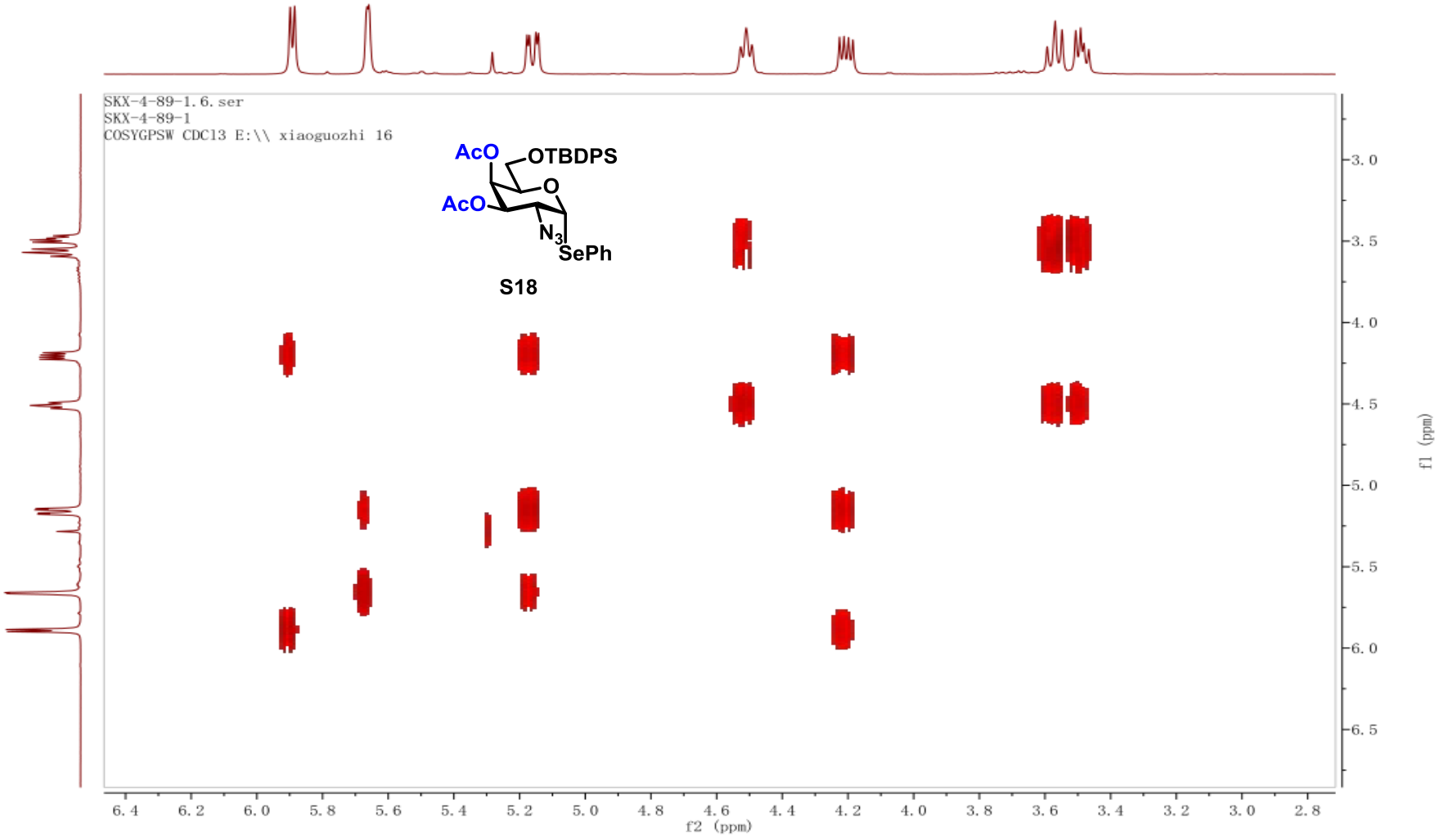

SKX-4-119B.4.fid
SKX-4-119B
c13 CDCl3 E:\\ xiaogu\zzi 24
170.01
169.78
156.74
156.22
137.97
137.63
136.89
128.55
128.48
128.45
127.92
127.88
127.82
127.80
127.30
102.38
98.14
73.56
73.50
72.10
71.19
70.26
68.53
68.39
68.25
67.93
67.78
67.54
67.19
67.00
61.17
57.63
50.59
50.33
47.11
46.19
29.38
29.17
29.04
27.88
27.48
23.35
23.16
22.71
20.70
20.66
20.62
AcO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19k α/β = 15/1
f1 (ppm)

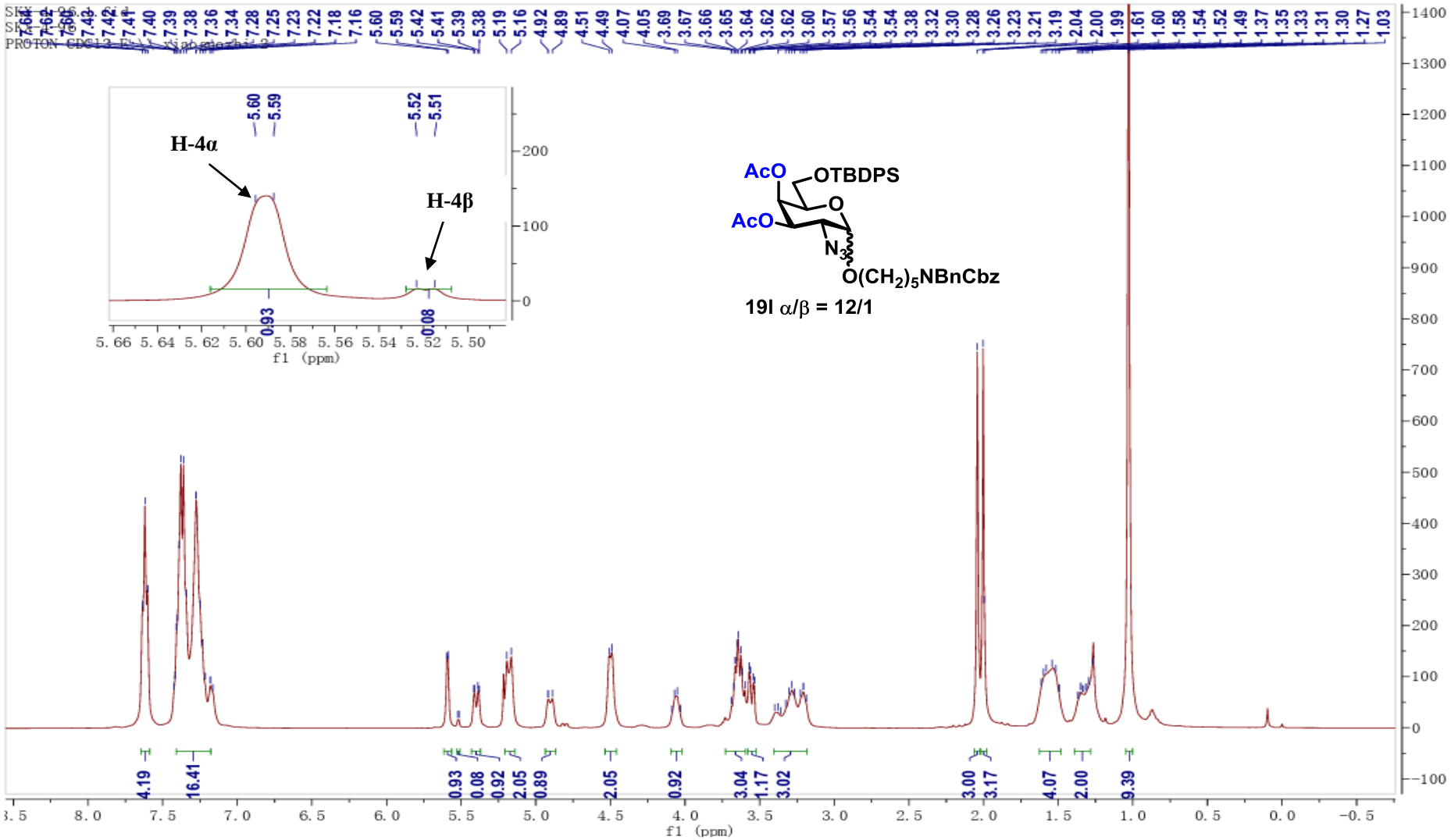

SKX-4-119B.2.ser
SKX-4-119B
COSYGPSW CDCl3 E:\\ xiaoguozhi 24
AcO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19k α/β = 15/1
f2 (ppm)
f1 (ppm)

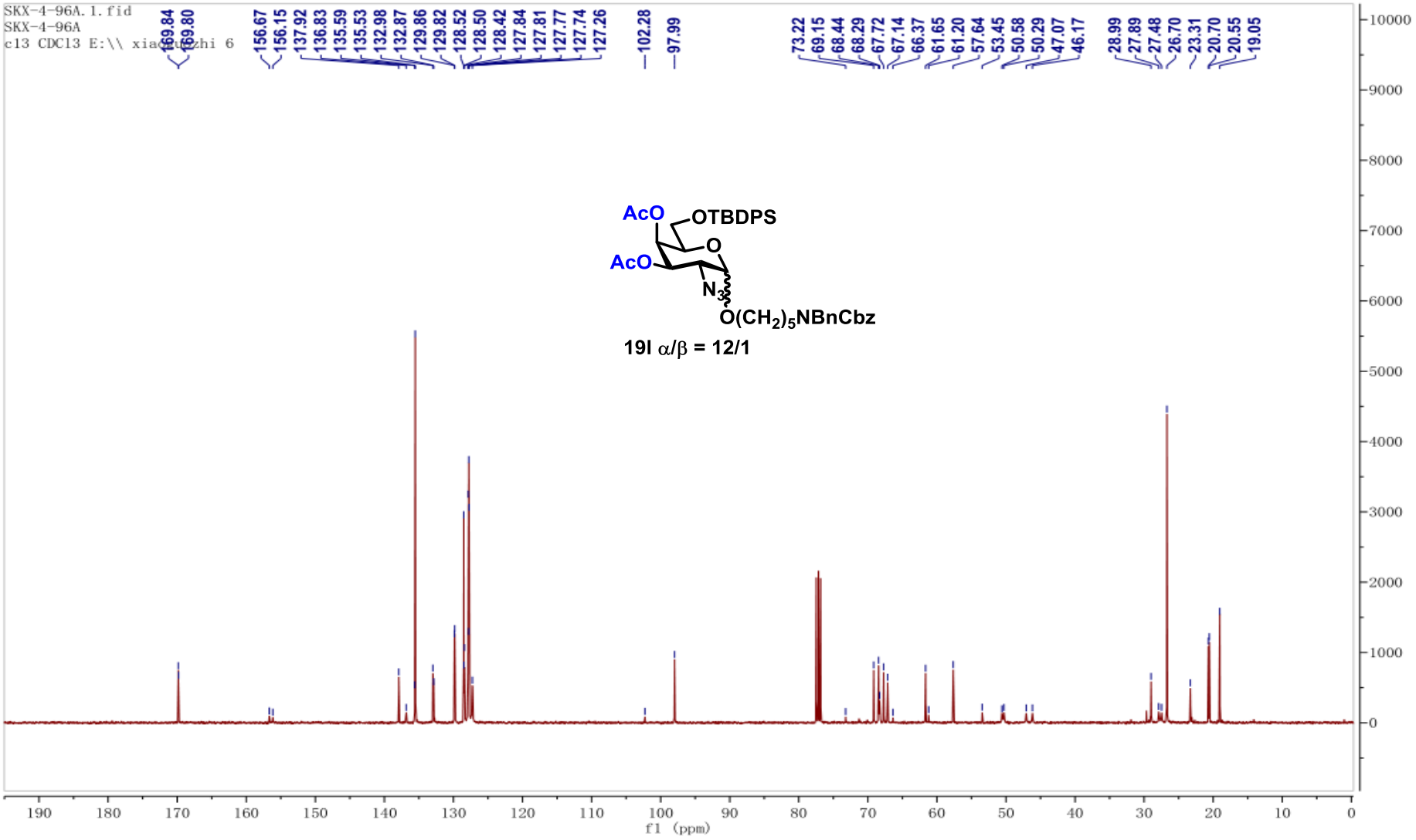

SKX-4-119B.3.ser
SKX-4-119B
HSQCGP CDCl3 E:\\ xiaoguozhi 24
AcO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19k α/β = 15/1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

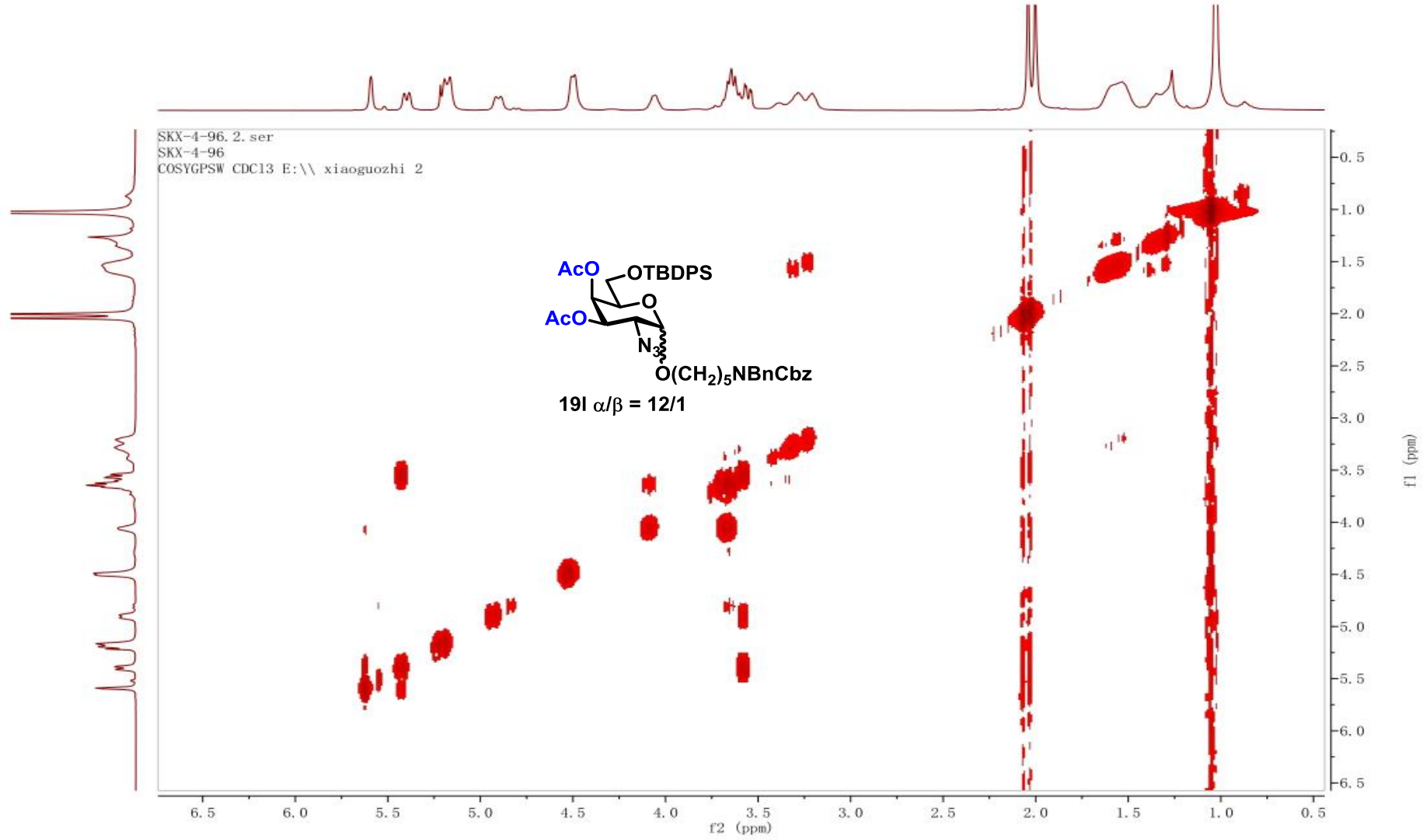

AcO
OTBDPS
O
AcO
N3
SePh
S18
f1 (ppm)

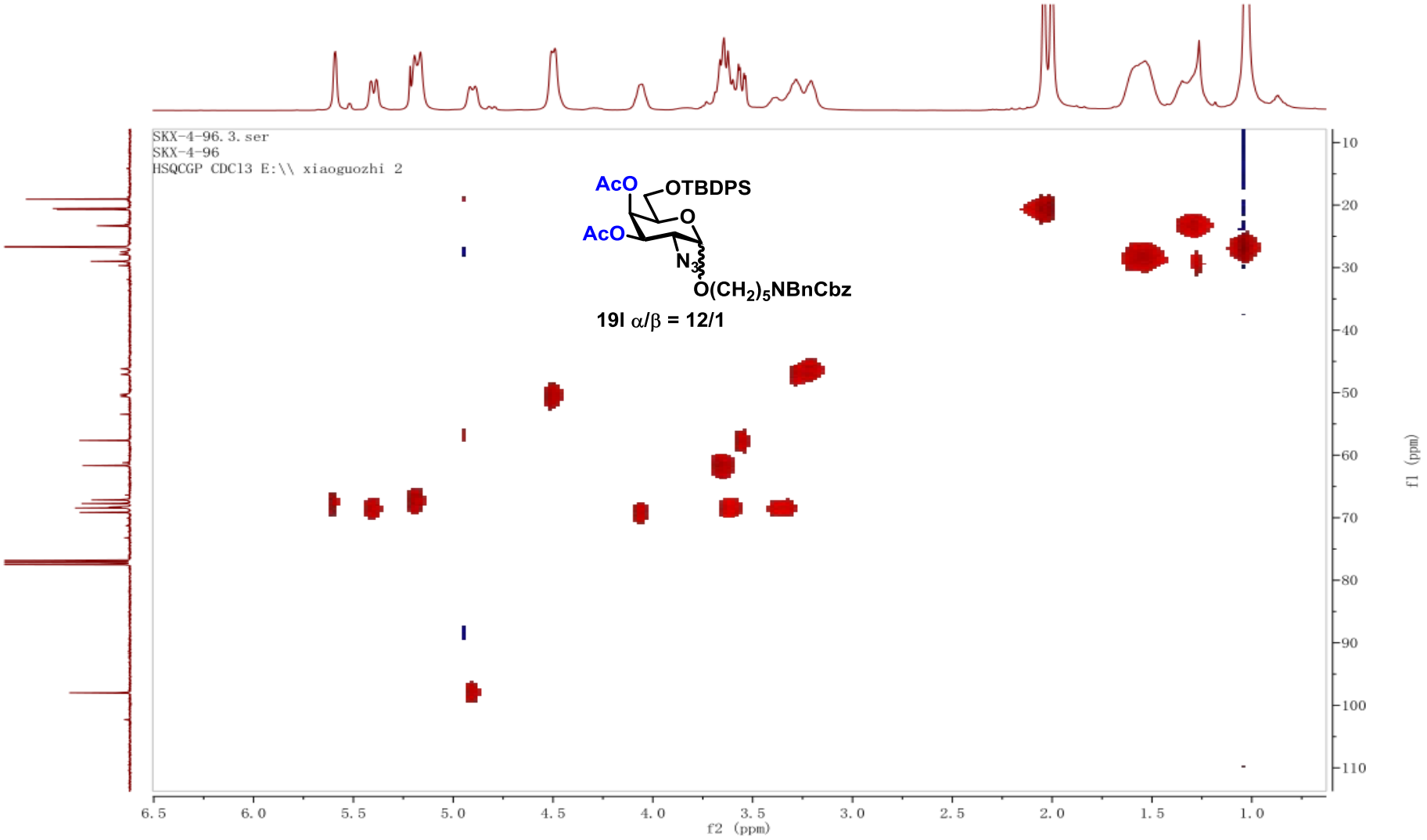

SKX-4-89-1.7.fid
SKX-4-89-1
c13 CDC13 E:\\ xiaoguo
169.71
169.59
135.57
135.52
134.97
132.93
132.75
129.85
129.11
128.07
127.80
127.78
127.72
84.51
71.45
71.23
67.04
60.91
59.11
26.72
20.68
20.53
19.06
AcO
OTBDPS
O
AcO
N3
SePh
S18
f1 (ppm)

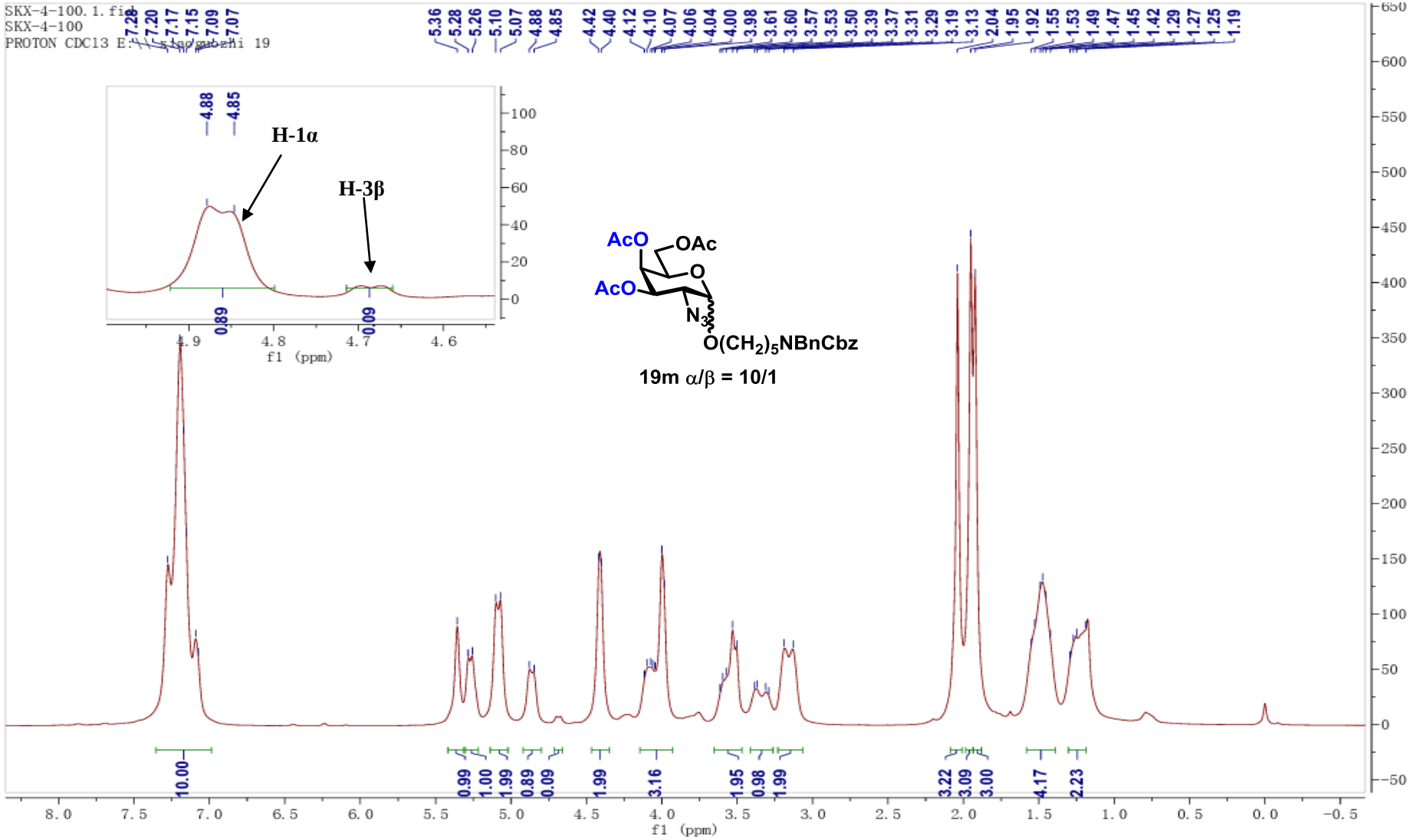

SKX-4-89-1.6.ser
SKX-4-89-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 16
AcO
OTBDPS
O
AcO
N3
SePh
S18
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f2 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

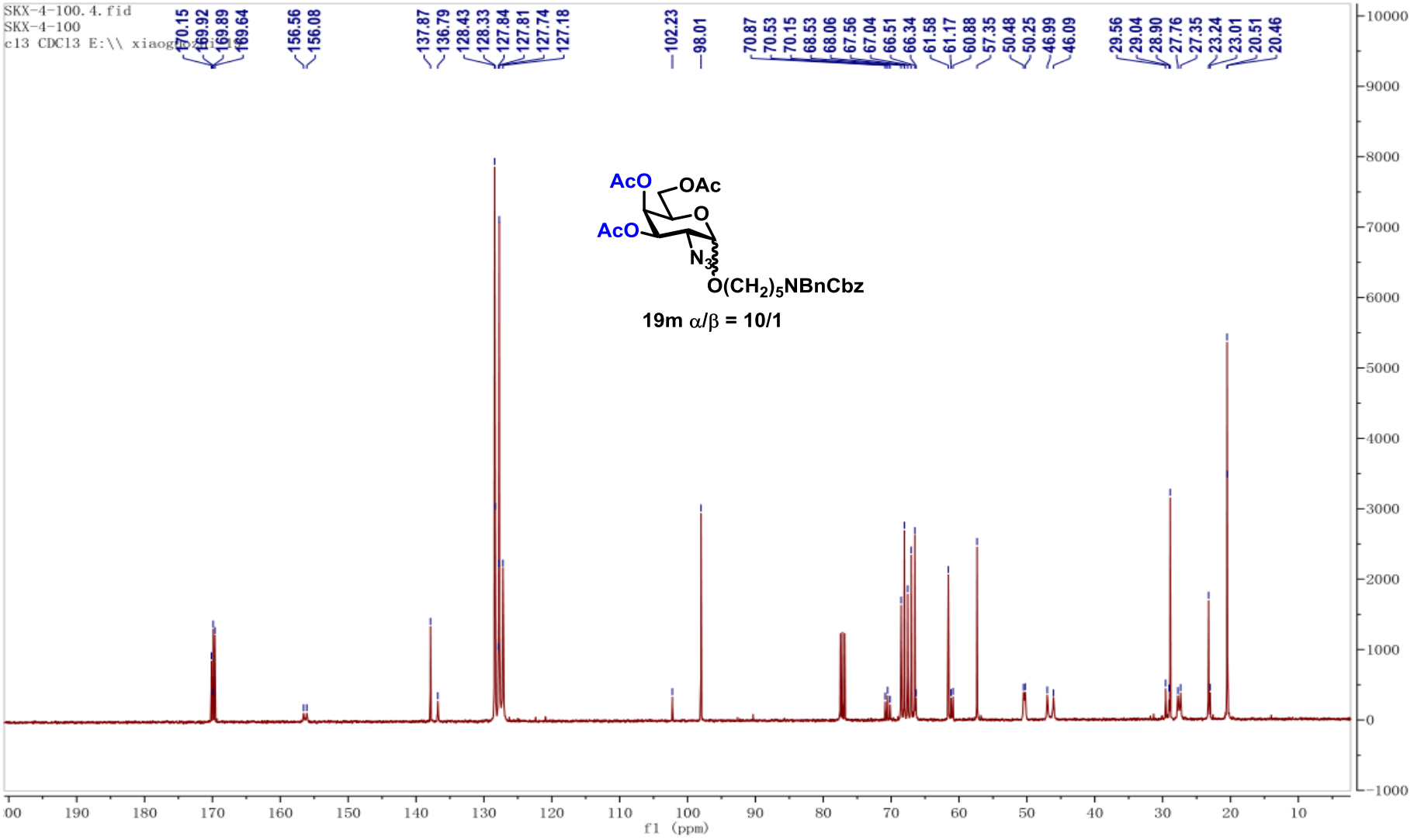

H-4α
H-4β
AcO
OTBDPS
O
AcO
N3
O(CH2)5NBnCbz
19l α/β = 12/1
f1 (ppm)

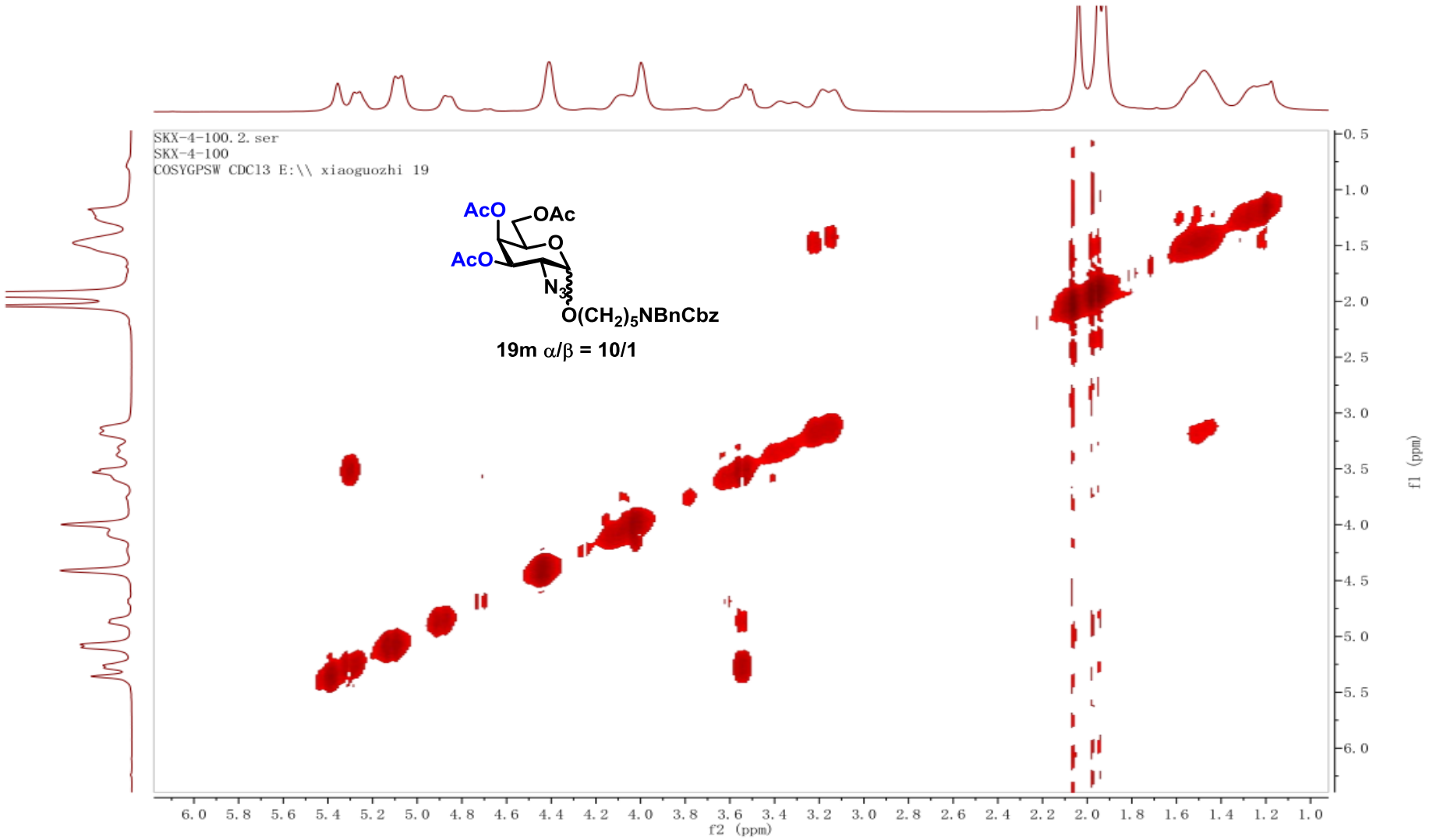

SKX-4-96A.1.fid
SKX-4-96A
c13 CDCl3 E:\\ xiaoguozhi 6
169.84
169.80
156.67
156.15
137.92
136.83
135.59
135.53
132.98
132.87
129.86
129.82
128.52
128.50
128.42
127.84
127.81
127.77
127.74
127.26
102.28
97.99
73.22
69.15
68.44
68.29
67.72
67.14
66.37
61.65
61.20
57.64
53.45
50.58
50.29
47.07
46.17
28.99
27.89
27.48
26.70
23.31
20.70
20.55
19.05
AcO
OTBDPS
O
AcO
N3
O(CH2)5NBnCbz
19l α/β = 12/1
f1 (ppm)

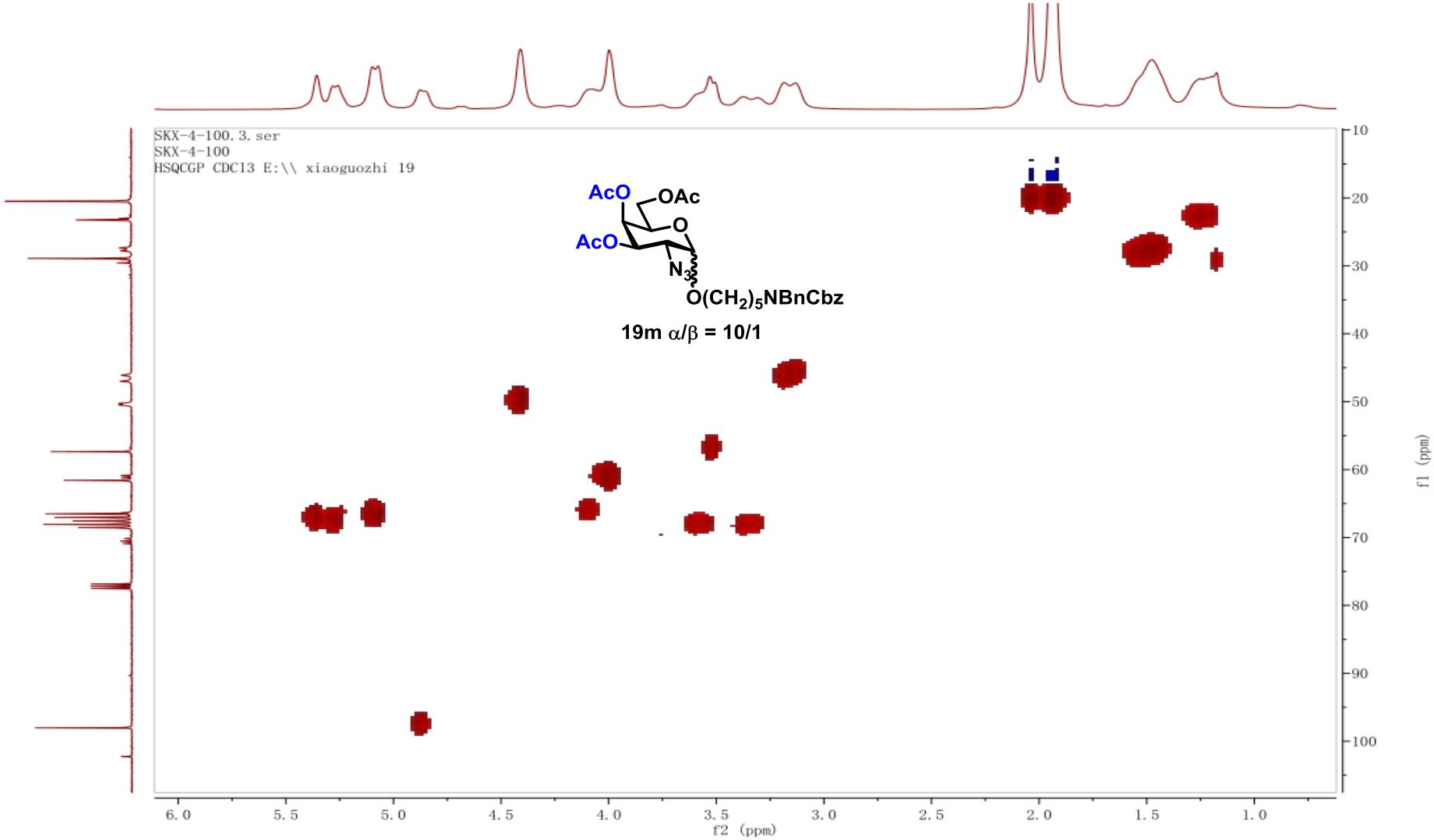

SKX-4-96.2.ser
SKX-4-96
COSYGPSW CDCl3 E:\\ xiaoguozhi 2
AcO
OTBDPS
O
AcO
N3
O(CH2)5NBnCbz
19l α/β = 12/1
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

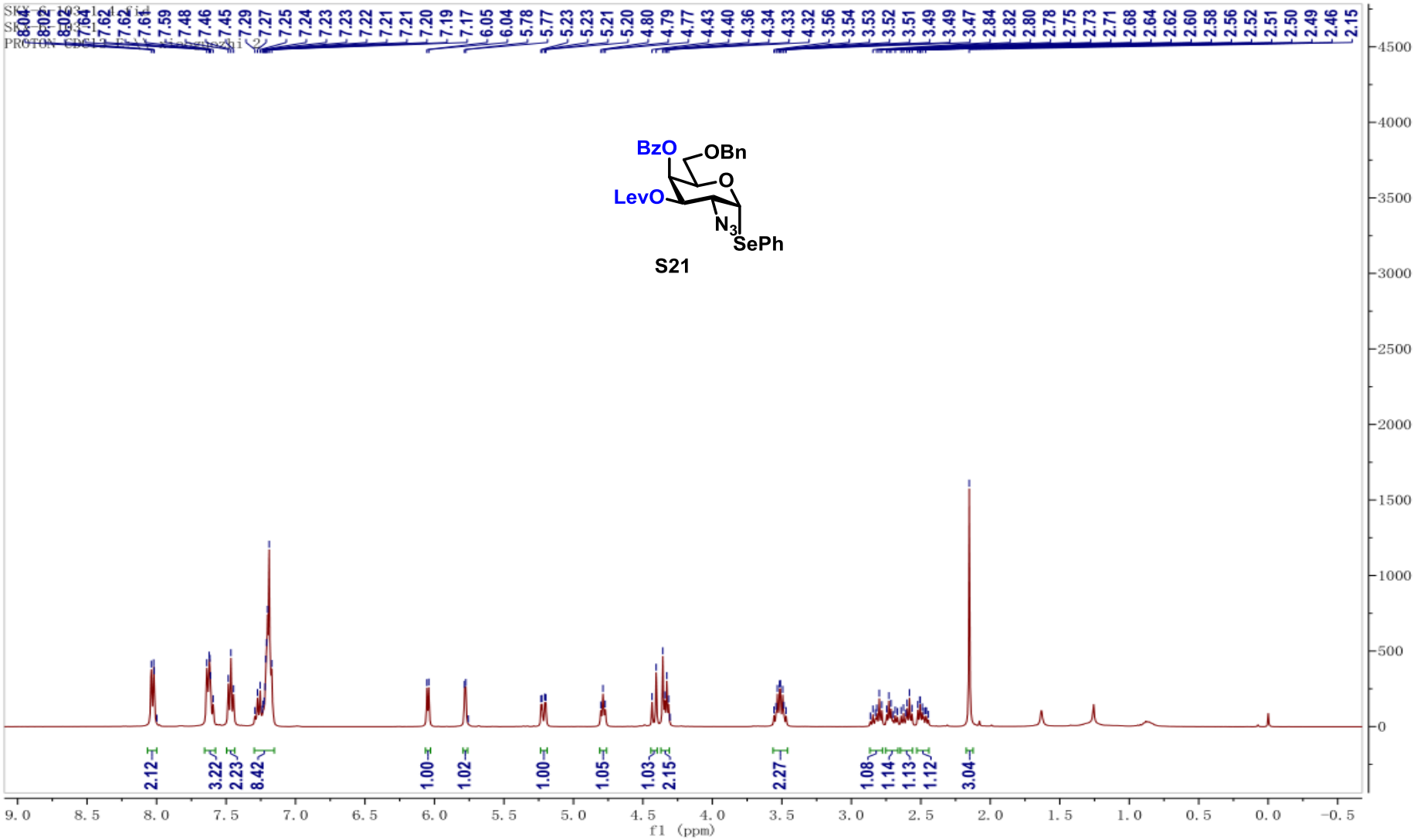

SKX-4-96.3.ser
SKX-4-96
HSQCGP CDCl3 E:\\ xiaoguozhi 2
AcO
OTBDPS
O
AcO
N3
O(CH2)5NBnCbz
19l α/β = 12/1
f2 (ppm)
f1 (ppm)

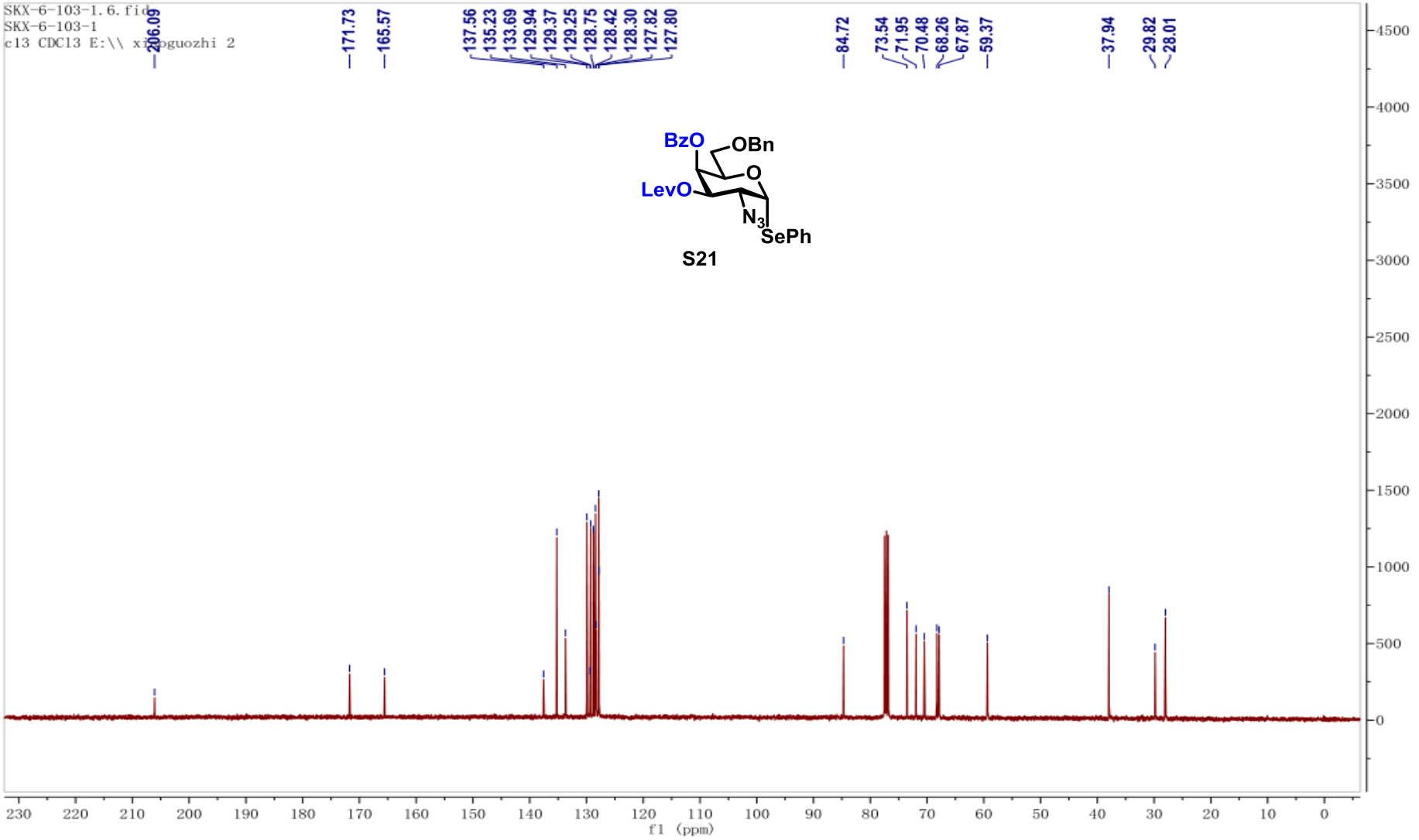

SKX-4-100.1.fid
SKX-4-100
PROTON CDCl3 E:\...\xiaogaozhi 19
H-1α
H-3β
AcO
OAc
O
AcO
N3
O(CH2)5NBnCbz
19m α/β = 10/1
f1 (ppm)

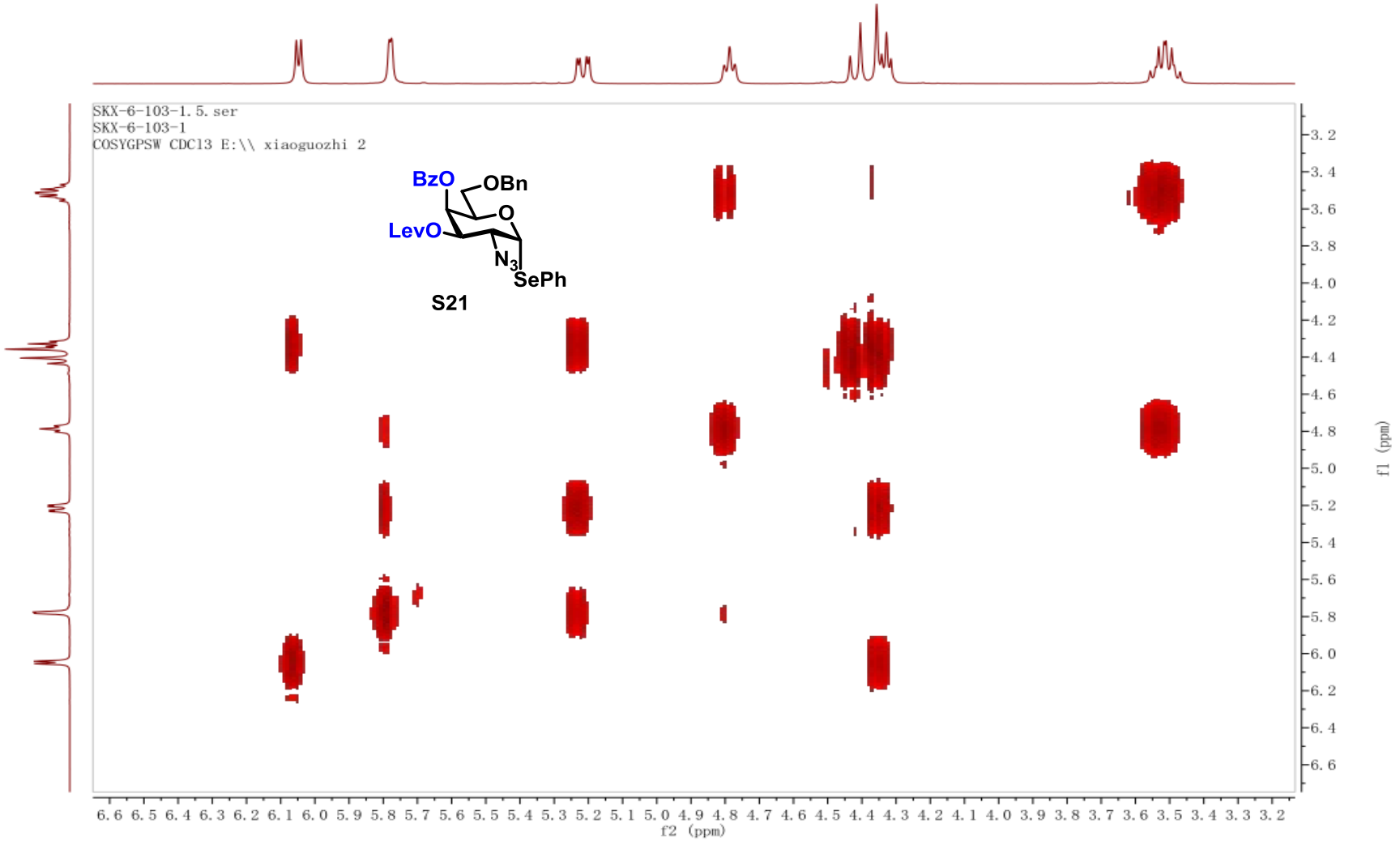

SKX-4-100.4.fid
SKX-4-100
c13 CDCl3 E:\\ xiaogu\zxi
170.15
169.92
169.89
169.64
156.56
156.08
137.87
136.79
128.43
128.33
127.84
127.81
127.74
127.18
102.23
98.01
70.87
70.53
70.15
68.53
68.06
67.56
67.04
66.51
66.34
61.58
61.17
60.88
57.35
50.48
50.25
46.99
46.09
29.56
29.04
28.90
27.76
27.35
23.24
23.01
20.51
20.46
AcO
OAc
O
AcO
N3
O(CH2)5NBnCbz
19m α/β = 10/1
f1 (ppm)

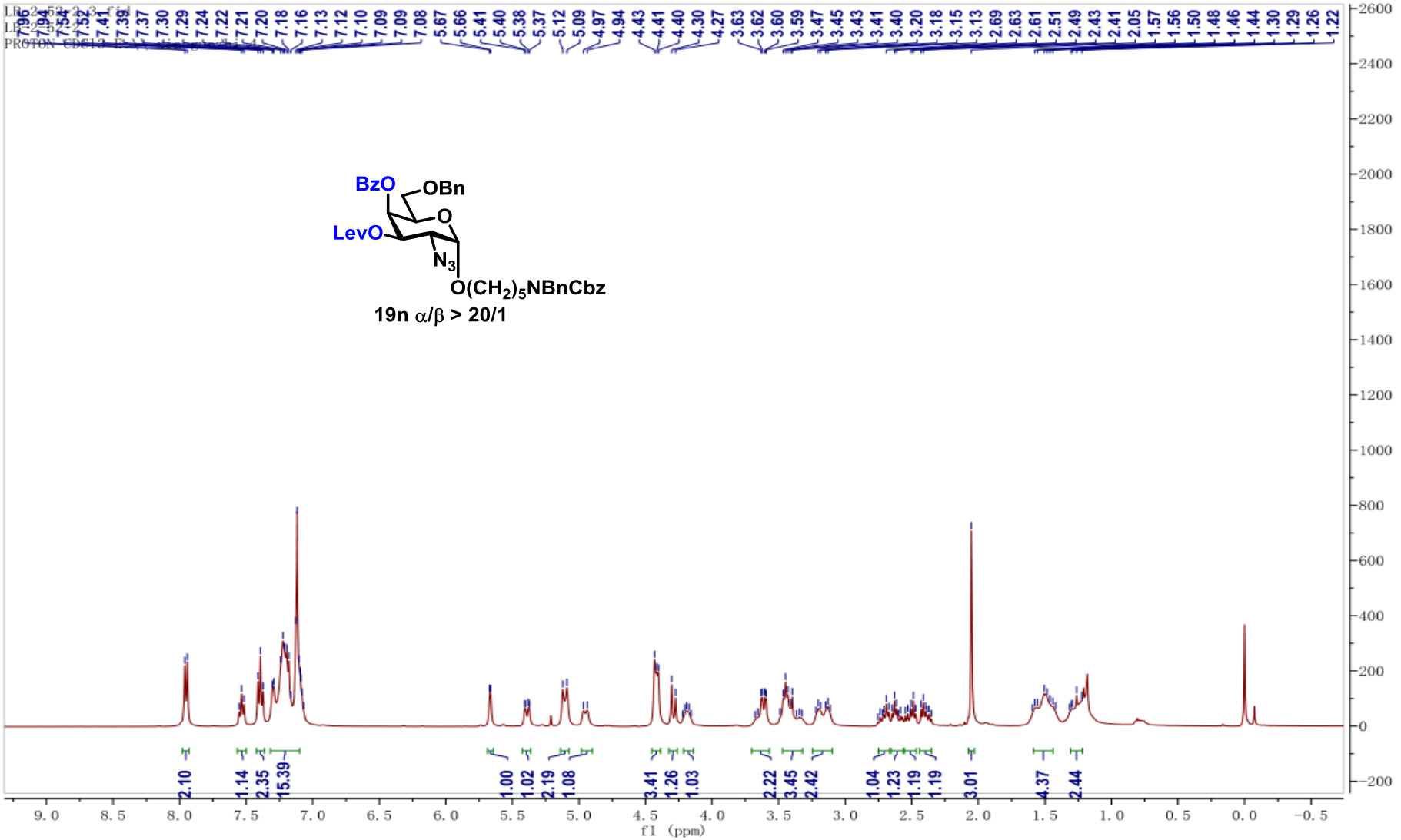

SKX-4-100.2.ser
SKX-4-100
COSYGPSW CDCl3 E:\\ xiaoguozhi 19
AcO
OAc
O
AcO
N3
O(CH2)5NBnCbz
19m α/β = 10/1
f2 (ppm)
f1 (ppm)

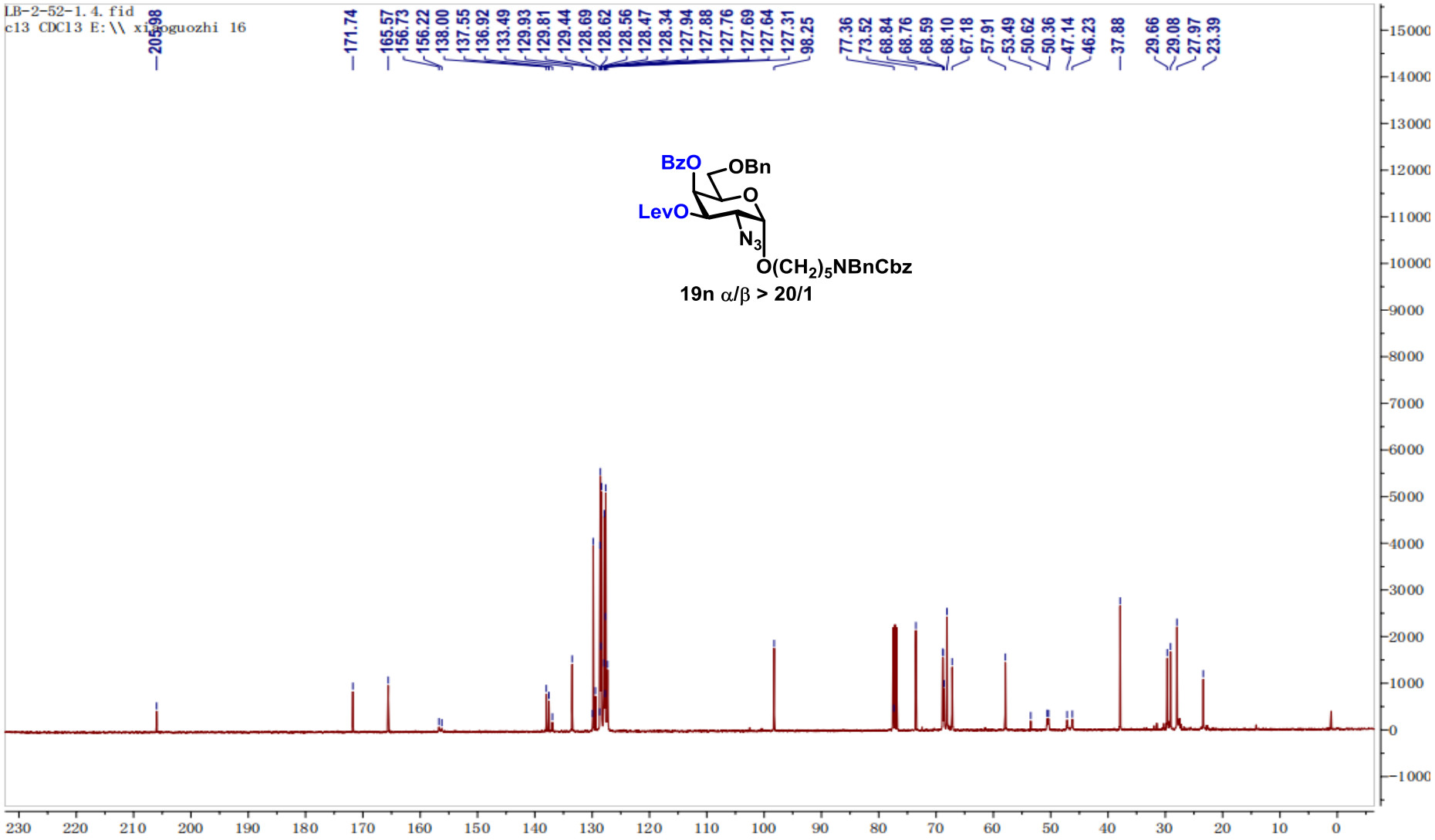

SKX-4-100.3.ser
SKX-4-100
HSQCGP CDCl3 E:\\ xiaoguozhi 19
AcO
OAc
O
AcO
N3
O(CH2)5NBnCbz
19m α/β = 10/1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)

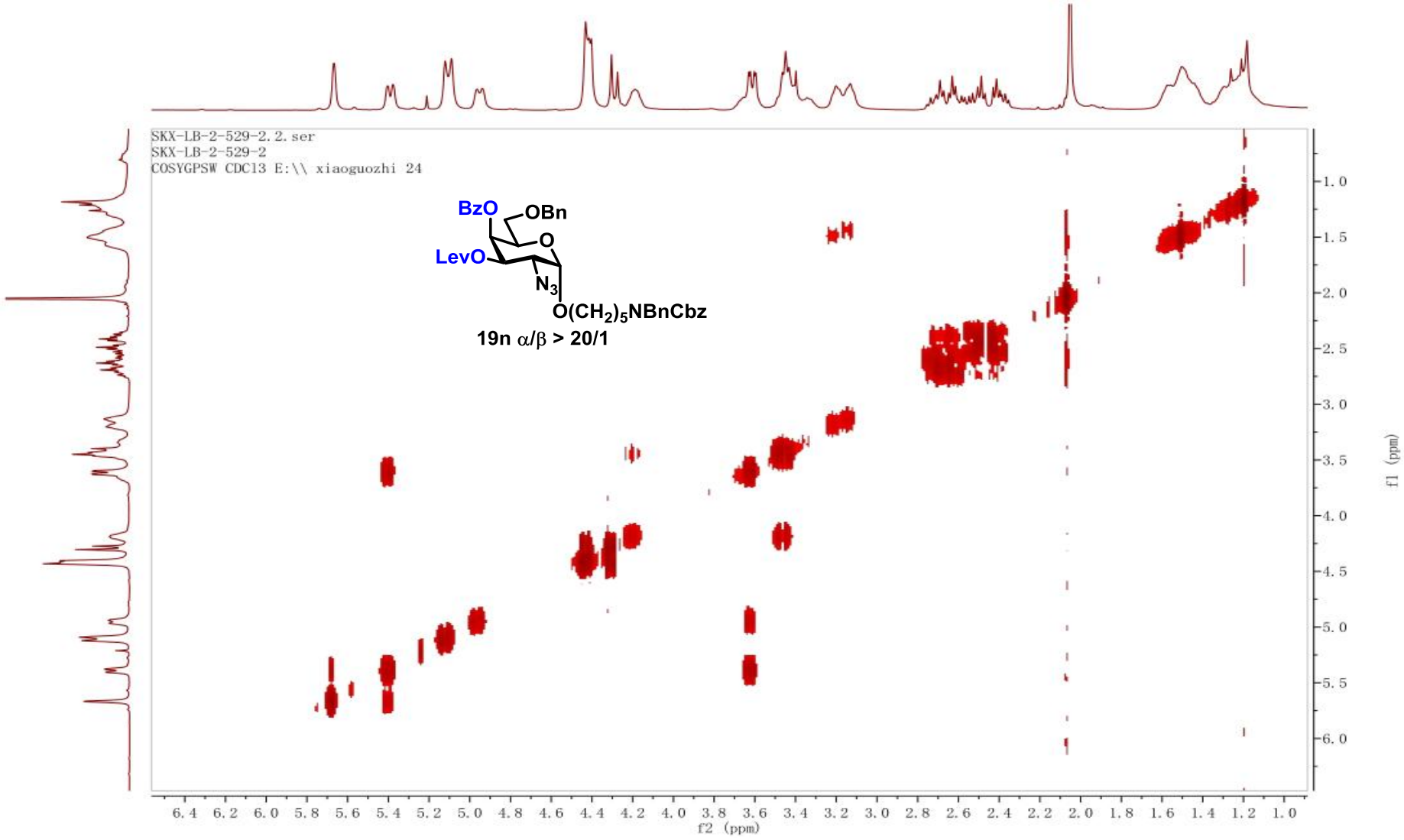

BzO
OBn
O
LevO
N3
SePh
S21
f1 (ppm)

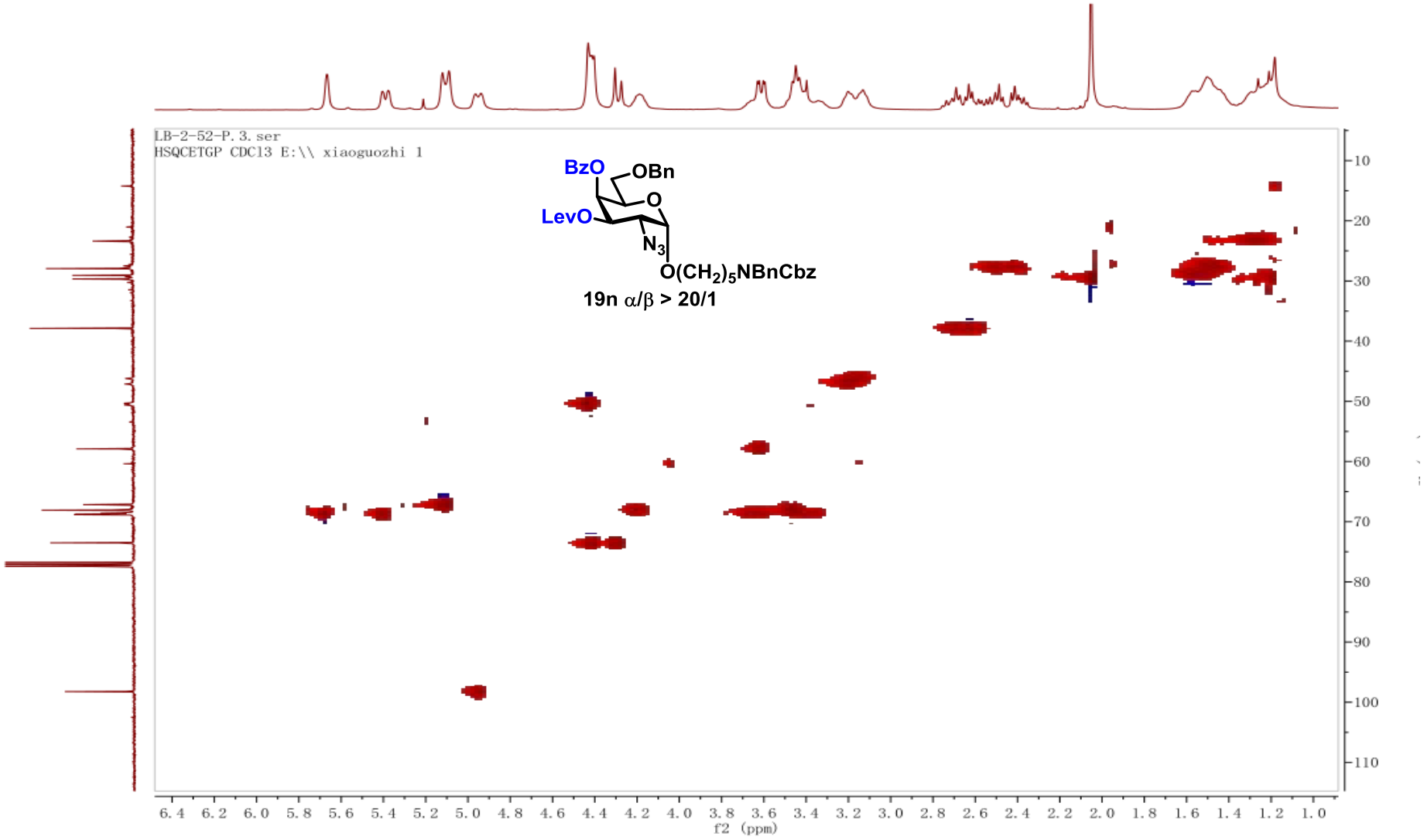

SKX-6-103-1.6.fid
SKX-6-103-1
c13 CDC13 E:\\ xiaoguozhi 2
206.09
171.73
165.57
137.56
135.23
133.69
129.94
129.37
129.25
128.75
128.42
128.30
127.82
127.80
84.72
73.54
71.95
70.48
68.26
67.87
59.37
37.94
29.82
28.01
BzO
OBn
O
LevO
N3
SePh
S21
f1 (ppm)

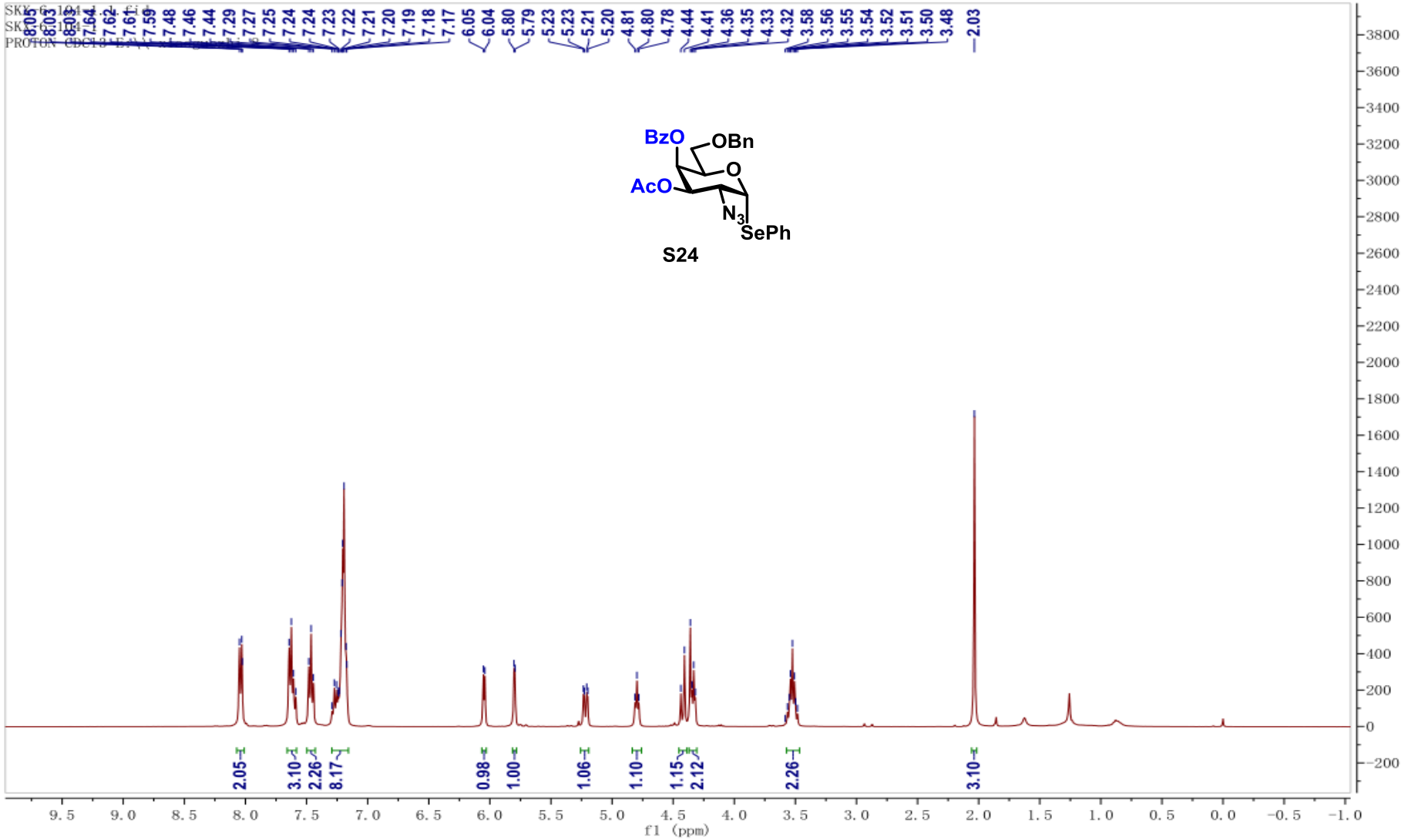

SKX-6-103-1.5.ser
SKX-6-103-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 2
BzO
OBn
O
LevO
N3
SePh
S21
f2 (ppm)
f1 (ppm)

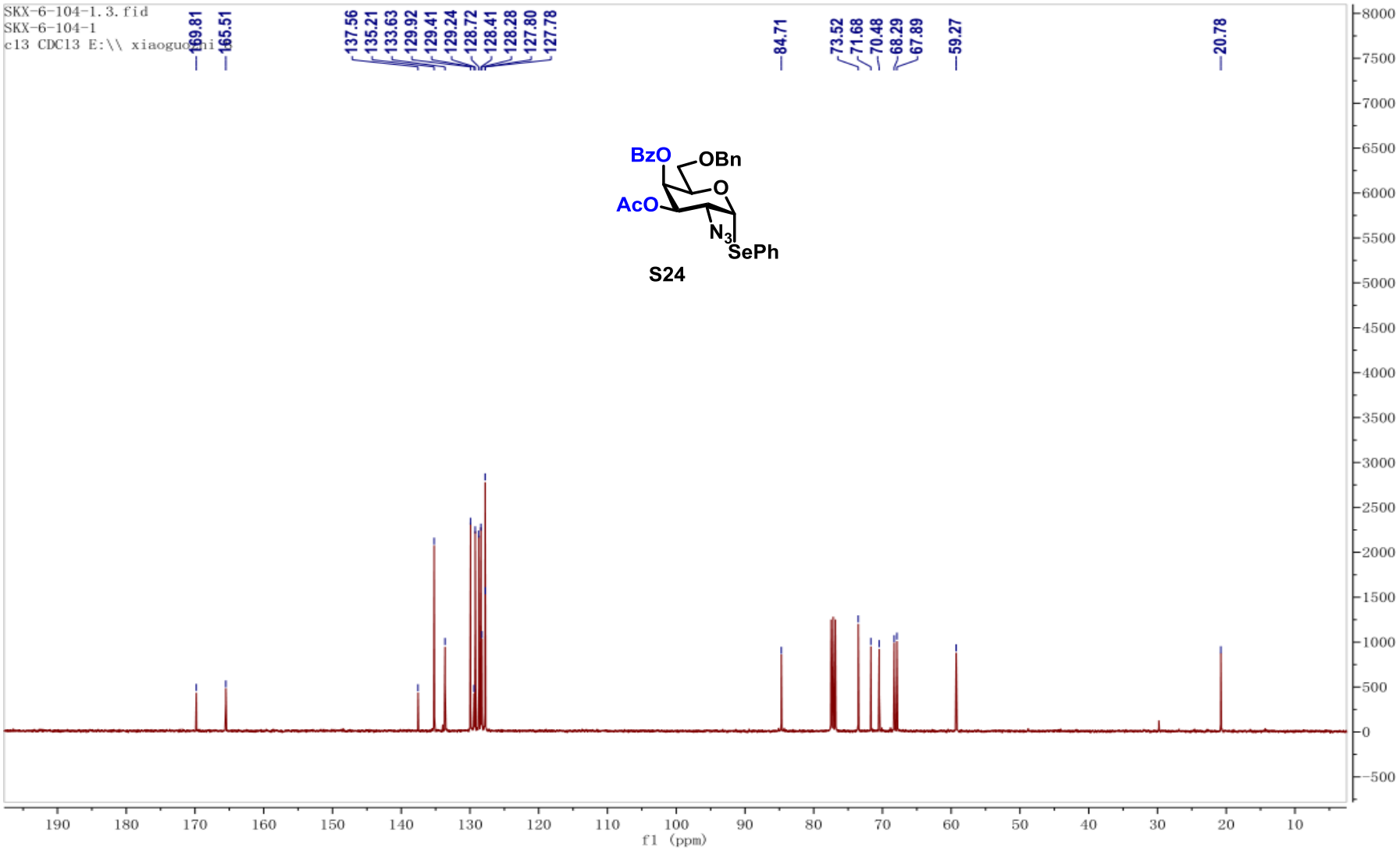

BzO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19n α/β > 20/1
f1 (ppm)

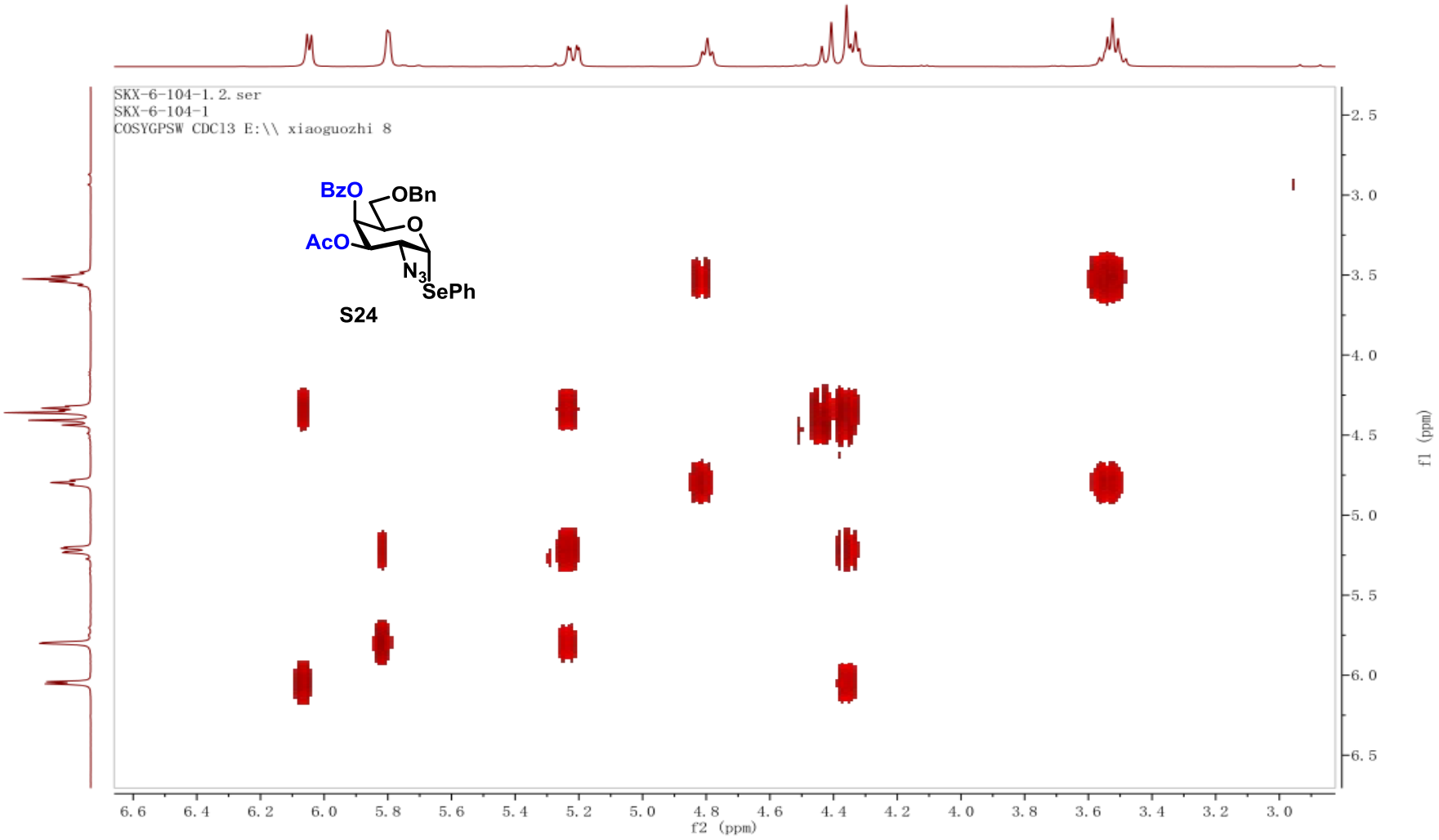

LB-2-52-1.4.fid
c13 CDCl3 E:\\ xiaoguozhi 16
205.98
171.74
165.57
156.73
156.22
138.00
137.55
136.92
133.49
129.93
129.81
129.44
128.69
128.62
128.56
128.47
128.34
127.94
127.88
127.76
127.69
127.64
127.31
98.25
77.36
73.52
68.84
68.76
68.59
68.10
67.18
57.91
53.49
50.62
50.36
47.14
46.23
37.88
29.66
29.08
27.97
23.39
BzO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19n α/β > 20/1

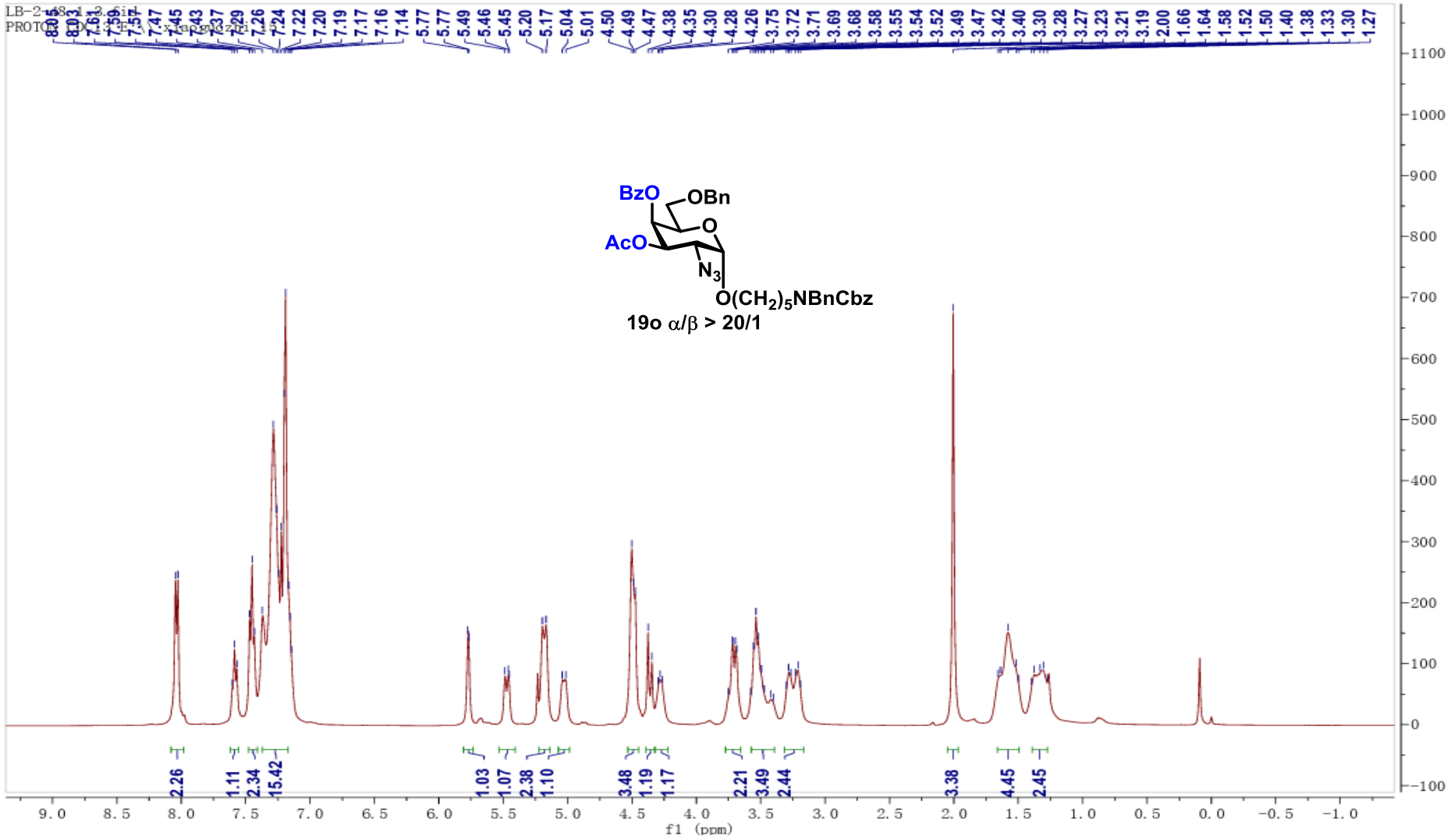

SKX-LB-2-529-2.2.ser
SKX-LB-2-529-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 24
BzO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19n α/β > 20/1
f2 (ppm)
f1 (ppm)

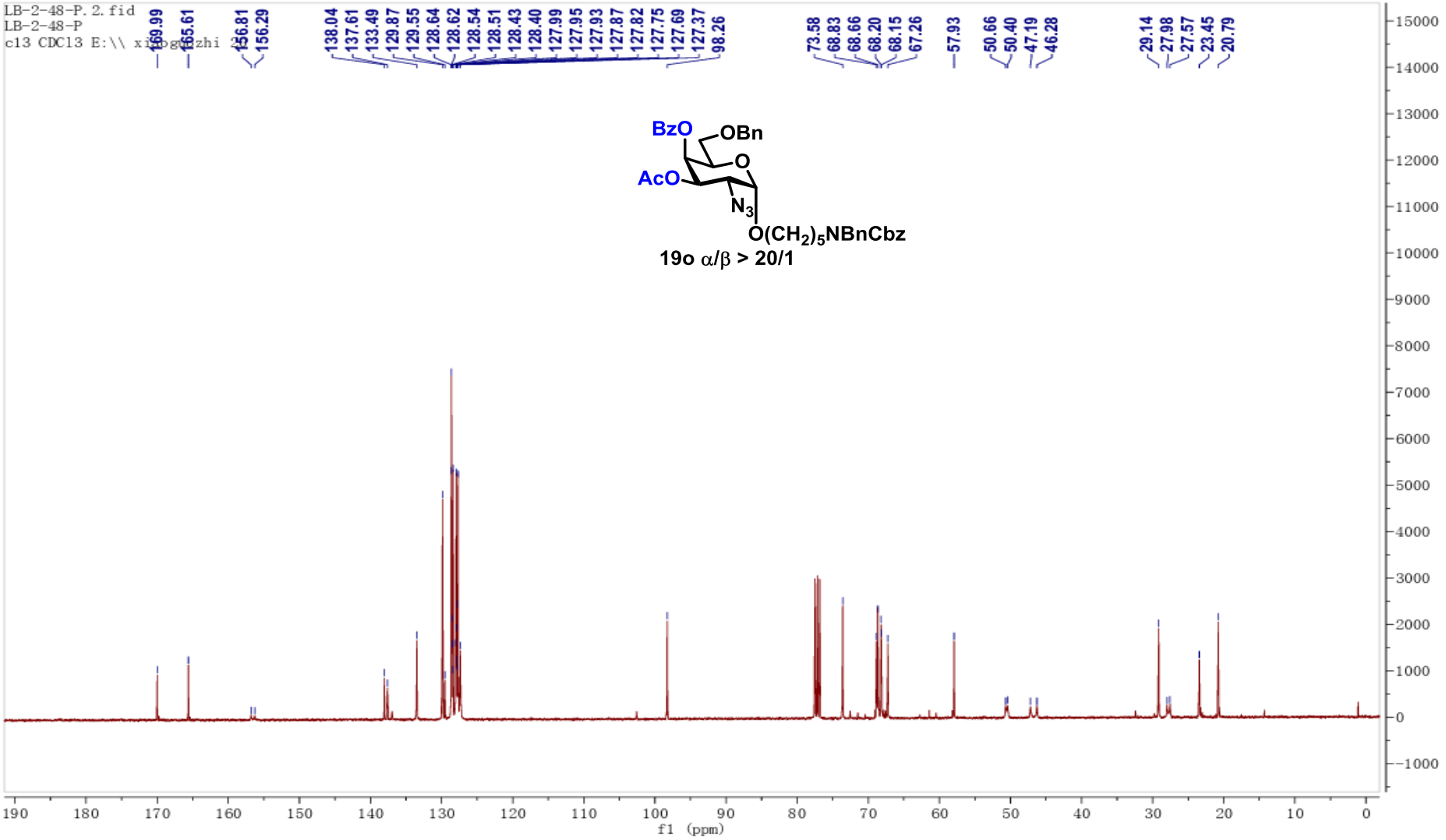

LB-2-52-P.3.ser
HSQCETGP CDCl3 E:\\ xiaoguozhi 1
BzO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19n α/β > 20/1
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110

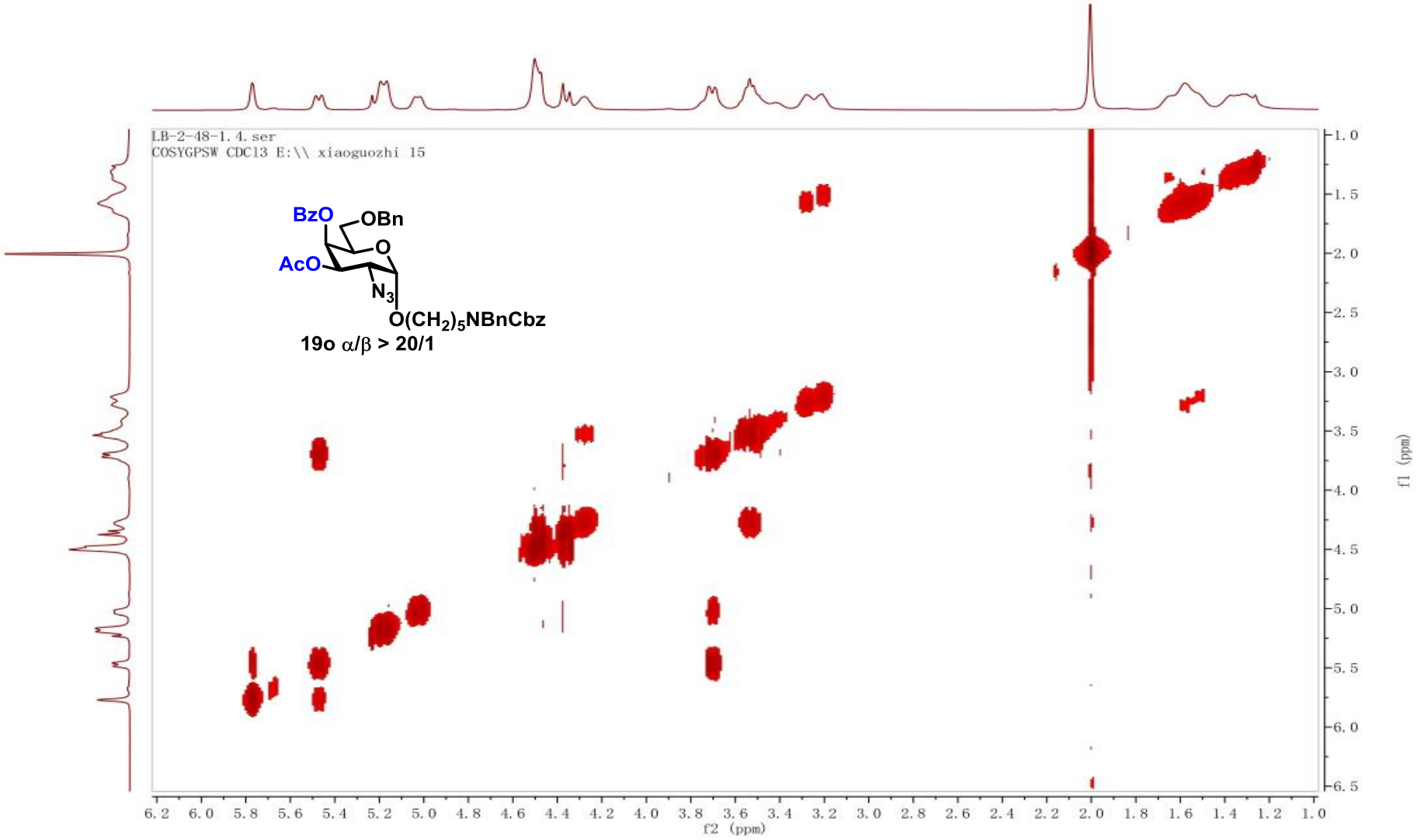

BzO
OBn
O
AcO
N3
SePh
S24
f1 (ppm)

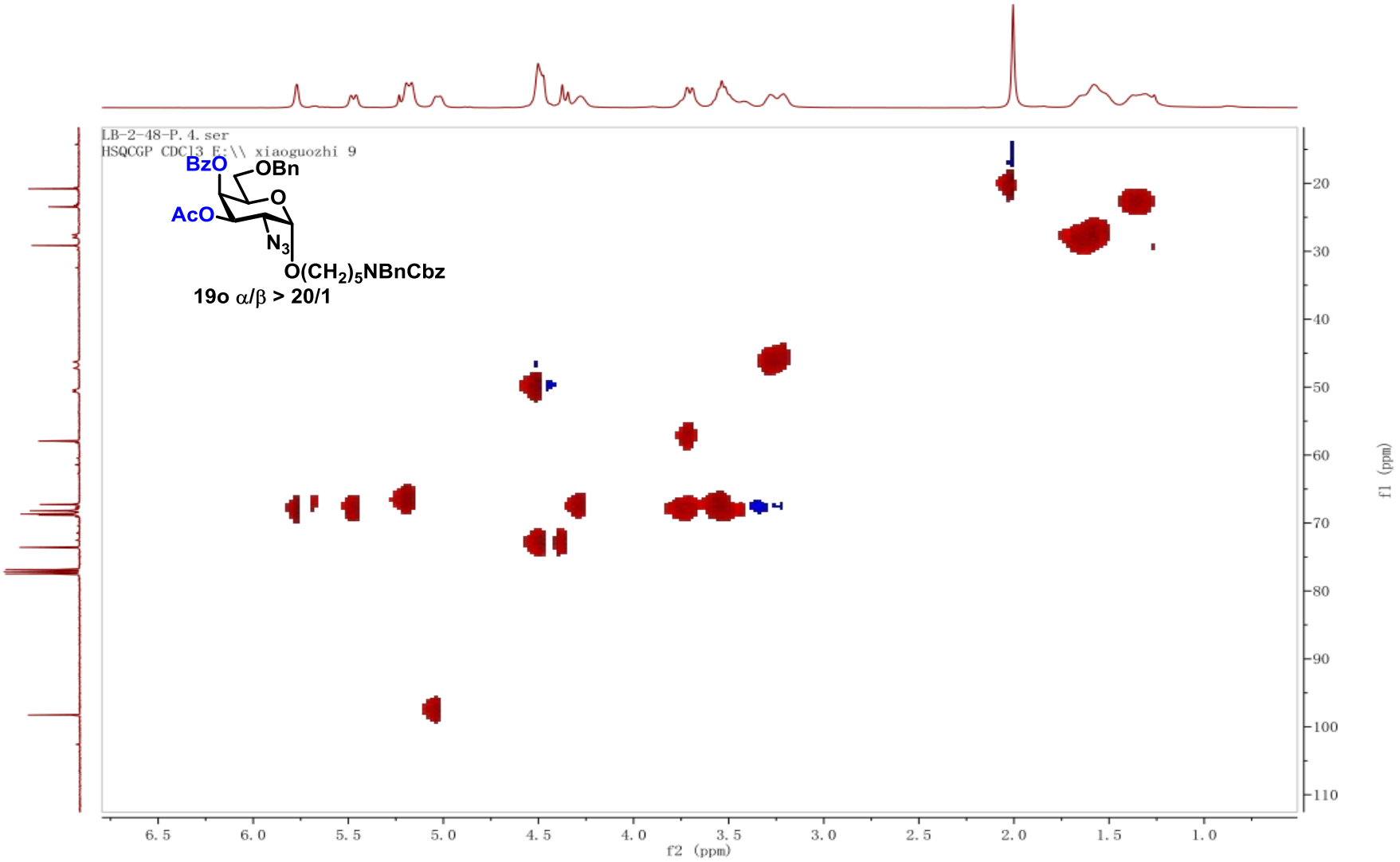

SKX-6-104-1.3.fid
SKX-6-104-1
c13 CDCl3 E:\\ xiaoguochi
169.81
165.51
137.56
135.21
133.63
129.92
129.41
129.24
128.72
128.41
128.28
127.80
127.78
84.71
73.52
71.68
70.48
68.29
67.89
59.27
20.78
BzO
OBn
O
AcO
N3
SePh
S24
f1 (ppm)

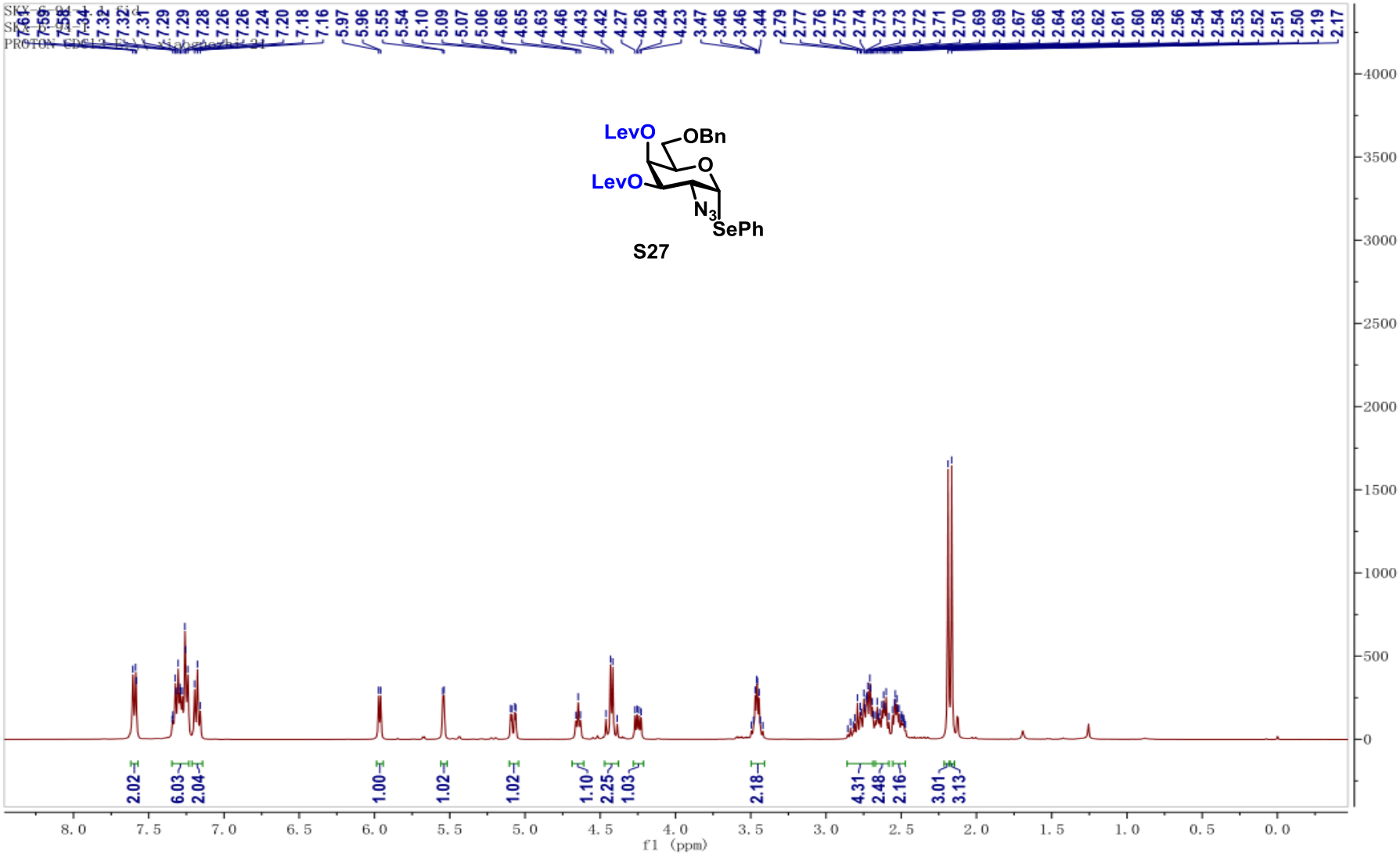

SKX-6-104-1.2.ser
SKX-6-104-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 8
BzO
OBn
O
AcO
N3
SePh
S24
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

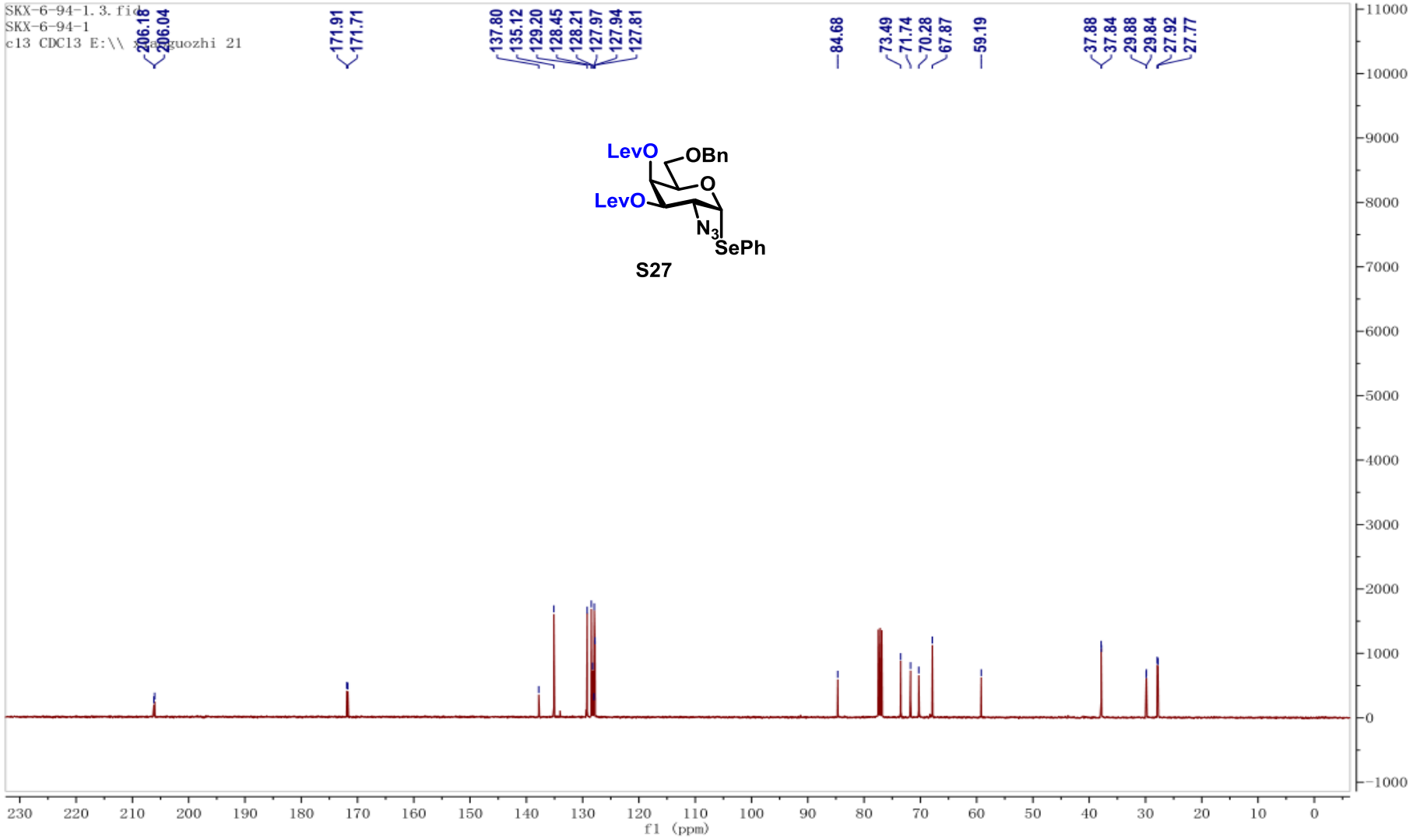

BzO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19o α/β > 20/1
f1 (ppm)

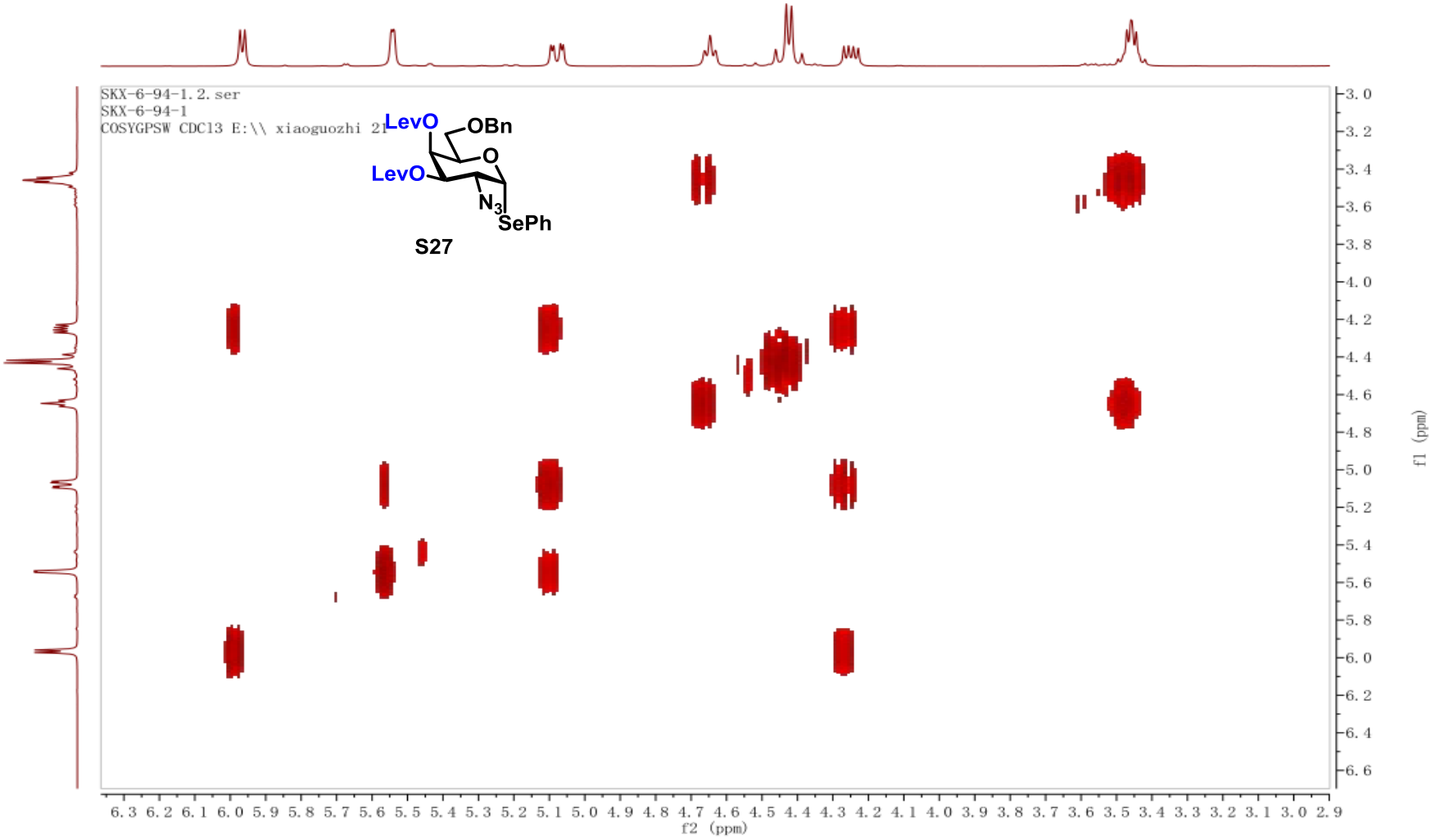

LB-2-48-P.2.fid
LB-2-48-P
c13 CDCl3 E:\\ xiaoguzhi
169.99
165.61
156.81
156.29
138.04
137.61
133.49
129.87
129.55
128.64
128.62
128.54
128.51
128.43
128.40
127.99
127.95
127.93
127.87
127.82
127.75
127.69
127.37
98.26
73.58
68.83
68.66
68.20
68.15
67.26
57.93
50.66
50.40
47.19
46.28
29.14
27.98
27.57
23.45
20.79
BzO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19o α/β > 20/1
f1 (ppm)

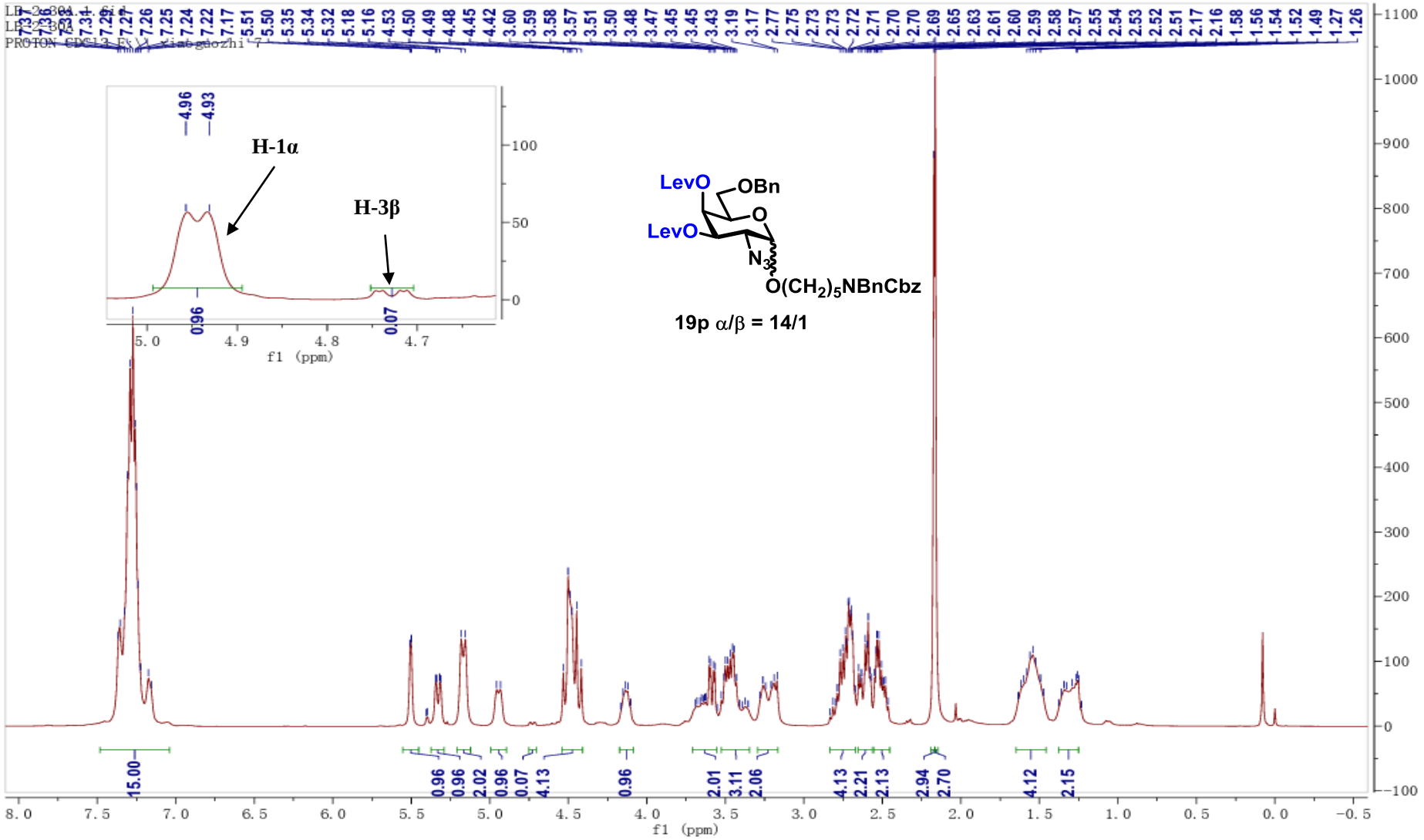

LB-2-48-1.4.ser
COSYGPSW CDC13 E:\\ xiaoguozhi 15
BzO
OBn
O
AcO
N3
O(CH2)5NBnCbz
19o α/β > 20/1
f2 (ppm)
f1 (ppm)

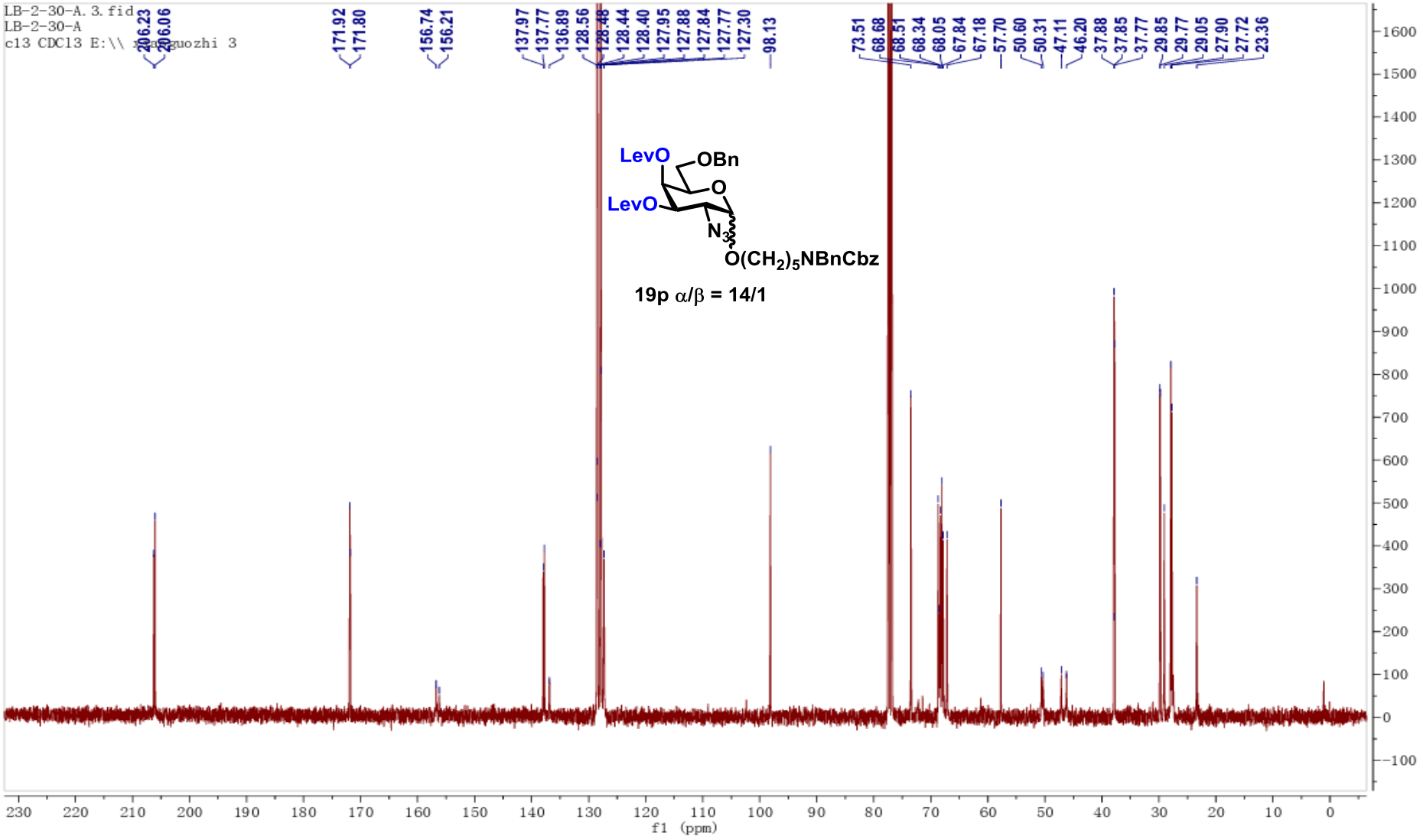

LB-2-48-P.4.ser
HSQCGP CDCl3 E:\\ xiaoguozhi 9
BzO
OBn
AcO
O
N3
O(CH2)5NBnCbz
19o α/β > 20/1
f2 (ppm)
f1 (ppm)

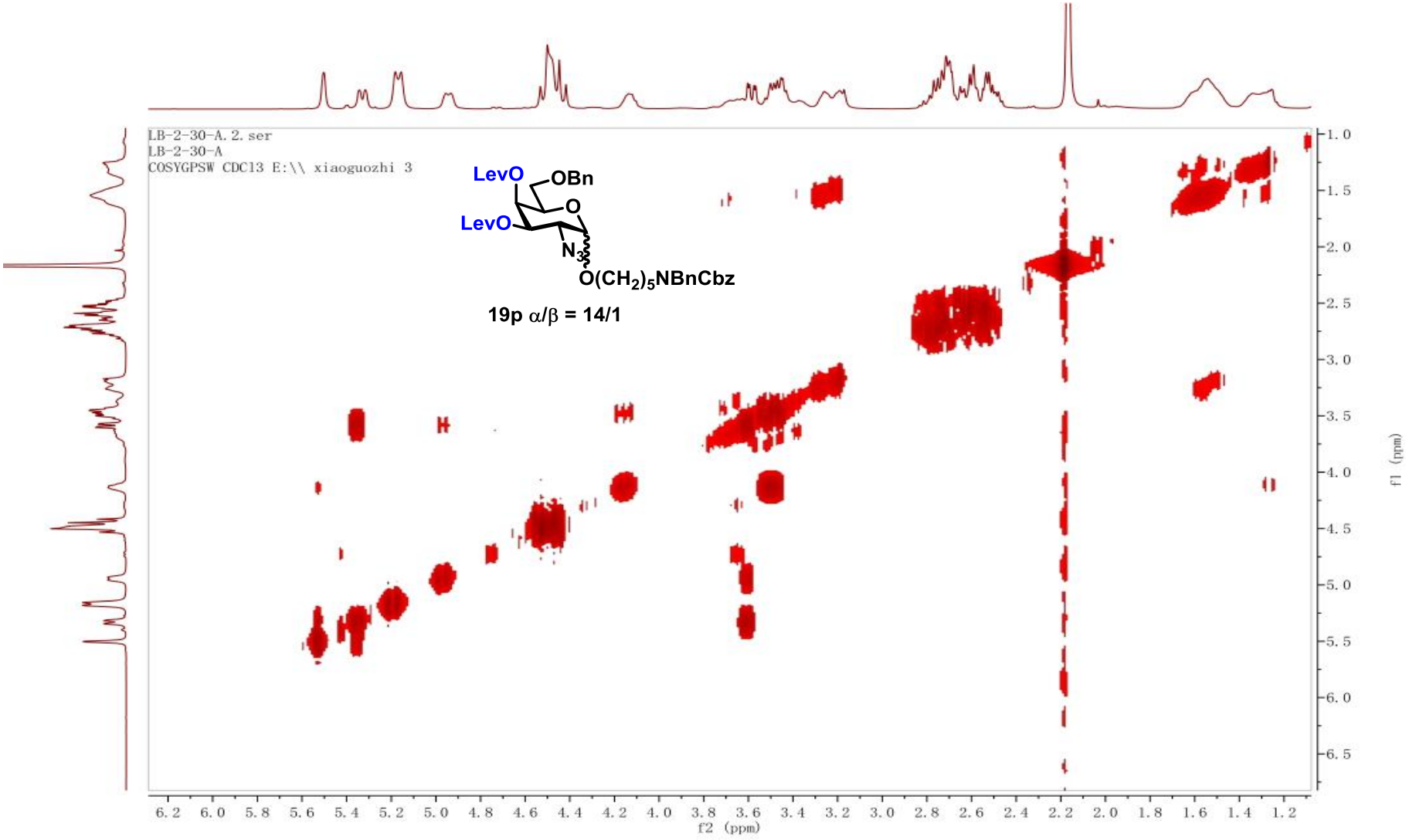

LevO
OBn
O
LevO
N3
SePh
S27
f1 (ppm)

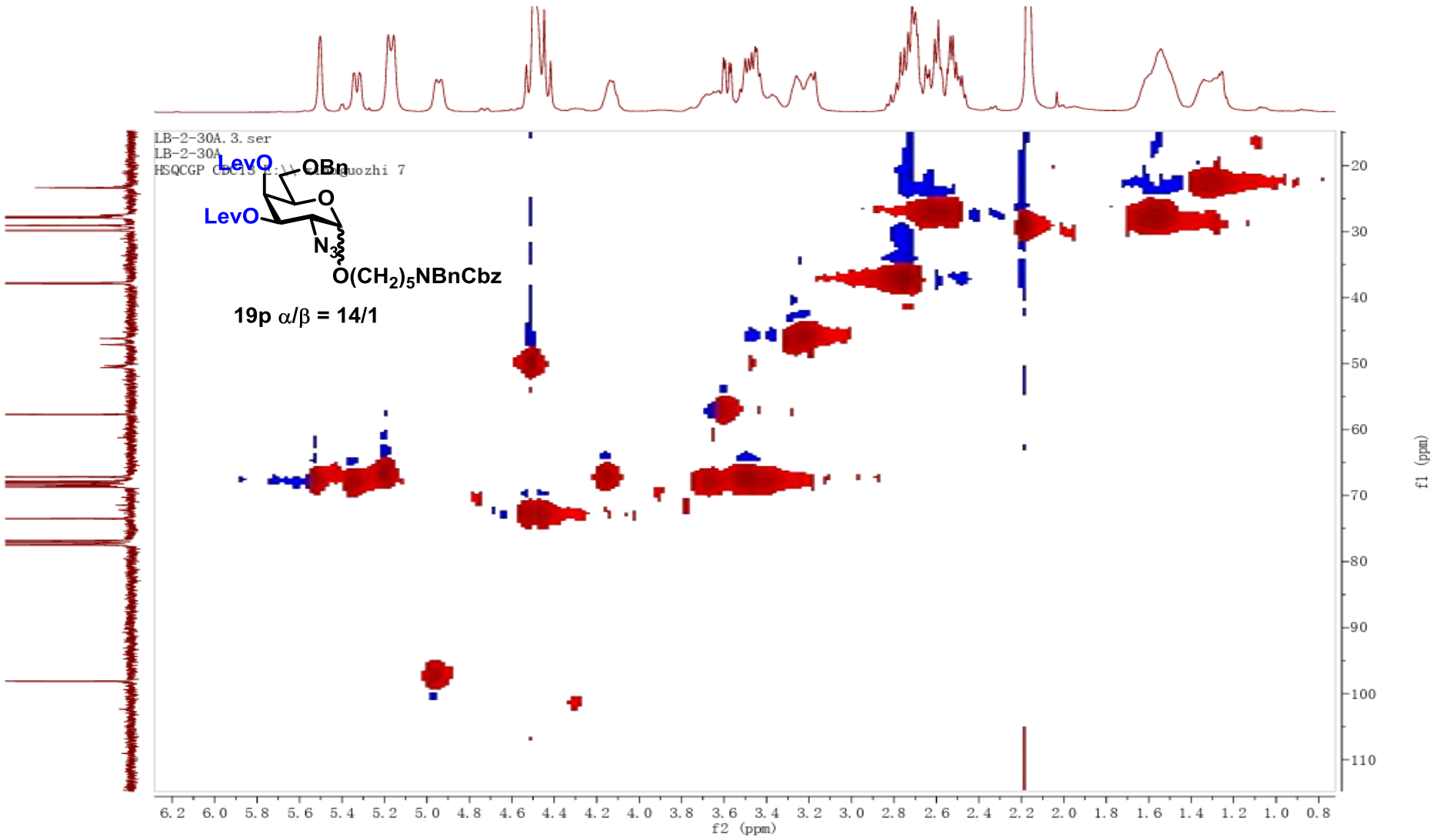

SKX-6-94-1.3.fid
SKX-6-94-1
c13 CDCl3 E:\\ zaguozhi 21
206.18
206.04
171.91
171.71
137.80
135.12
129.20
128.45
128.21
127.97
127.94
127.81
84.68
73.49
71.74
70.28
67.87
59.19
37.88
37.84
29.88
29.84
27.92
27.77
LevO
OBn
O
LevO
N3
SePh
S27
f1 (ppm)

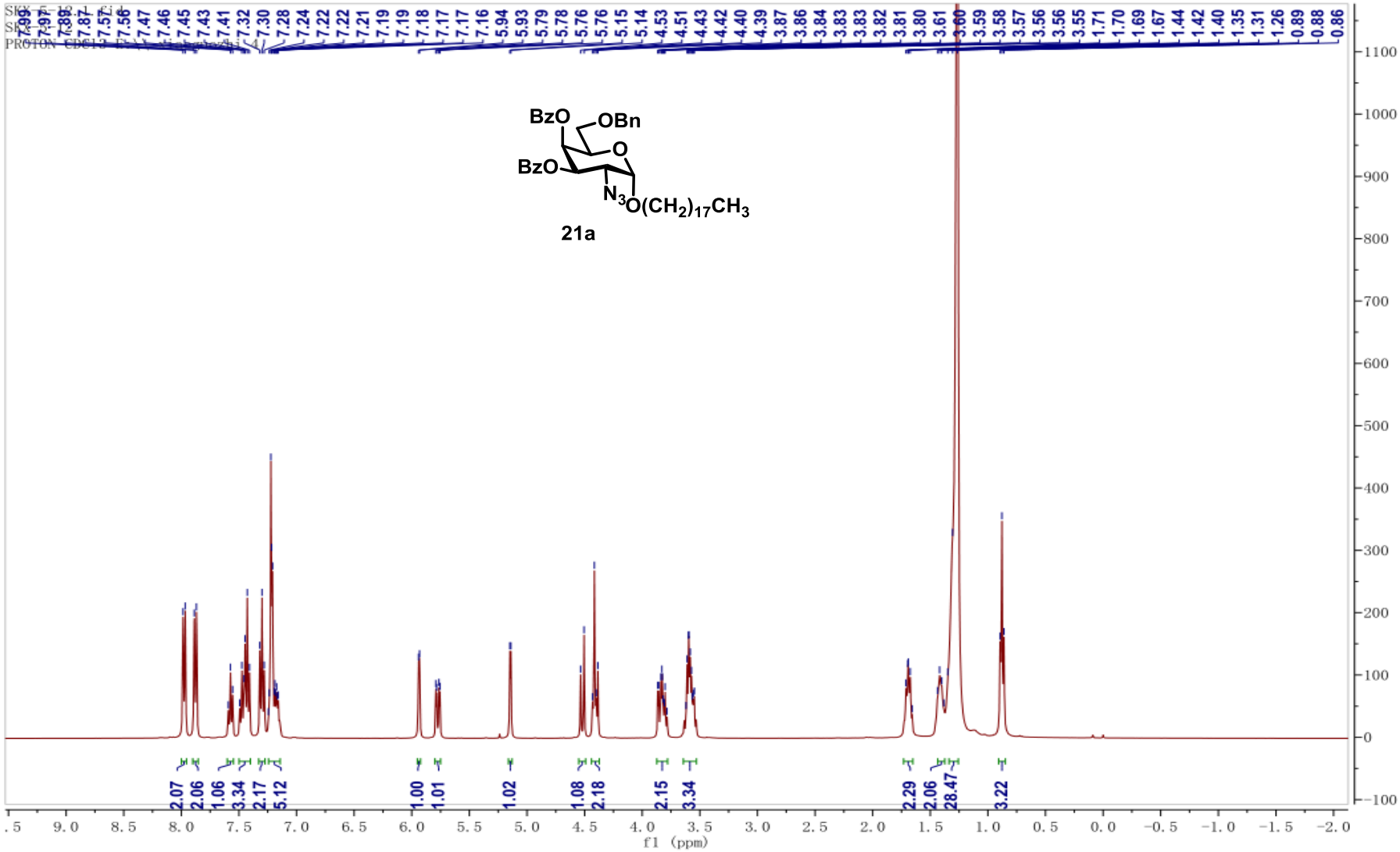

SKX-6-94-1.2.ser
SKX-6-94-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 2
LevO
OBn
O
LevO
N3
SePh
S27
f2 (ppm)
f1 (ppm)

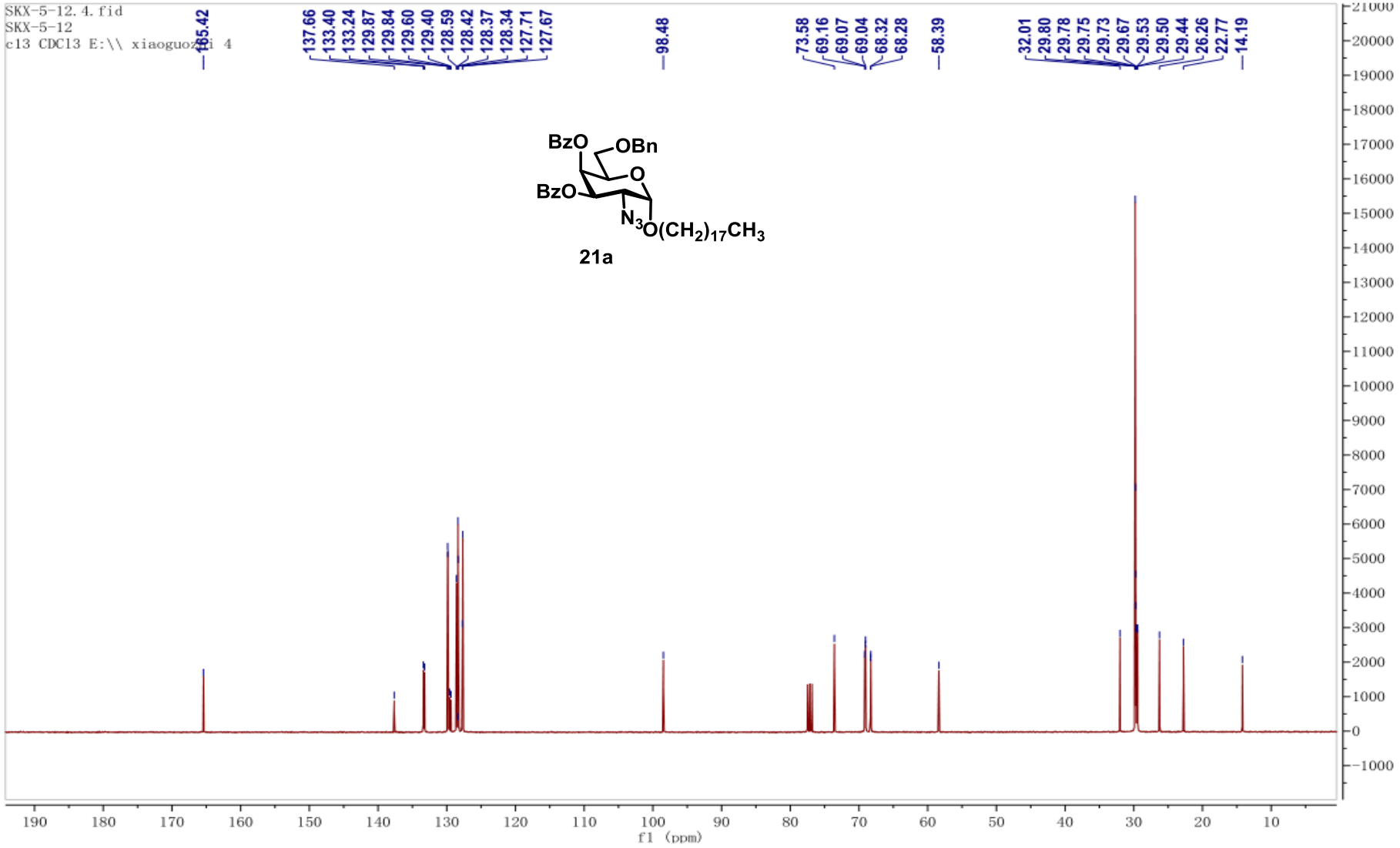

H-1α
H-3β
LevO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19p α/β = 14/1
f1 (ppm)

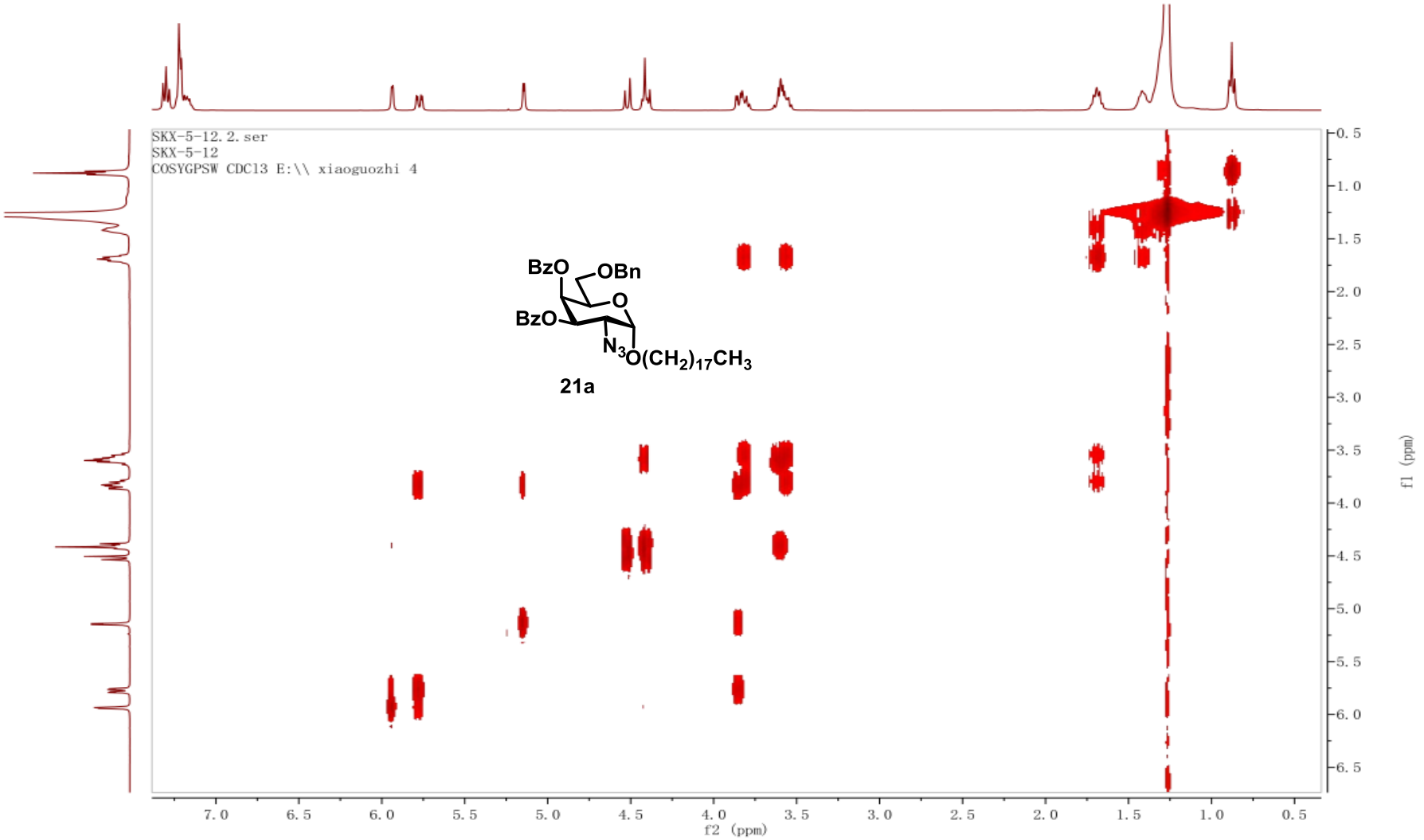

LB-2-30-A.3.fid
LB-2-30-A
c13 CDCl3 E:\\ xuguozhi 3
206.23
206.06
171.92
171.80
156.74
156.21
137.97
137.77
136.89
128.56
128.48
128.44
128.40
127.95
127.88
127.84
127.77
127.30
98.13
73.51
68.68
68.51
68.34
68.05
67.84
67.18
57.70
50.60
50.31
47.11
46.20
37.88
37.85
37.77
29.85
29.77
29.05
27.90
27.72
23.36
LevO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19p α/β = 14/1
f1 (ppm)

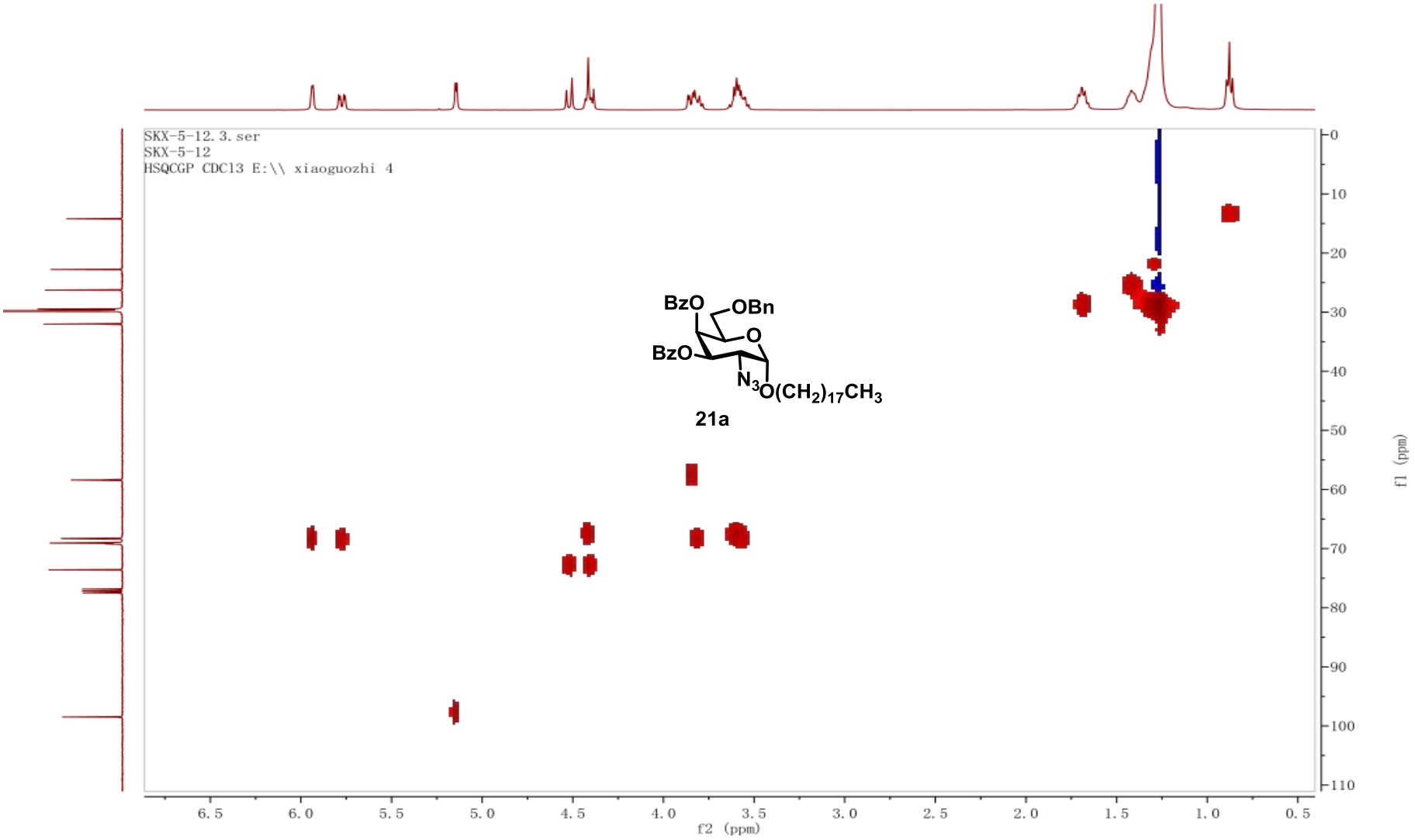

LB-2-30-A.2.ser
LB-2-30-A
COSYGPSW CDCl3 E:\\ xiaoguozhi 3
LevO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19p α/β = 14/1
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5
f1 (ppm)

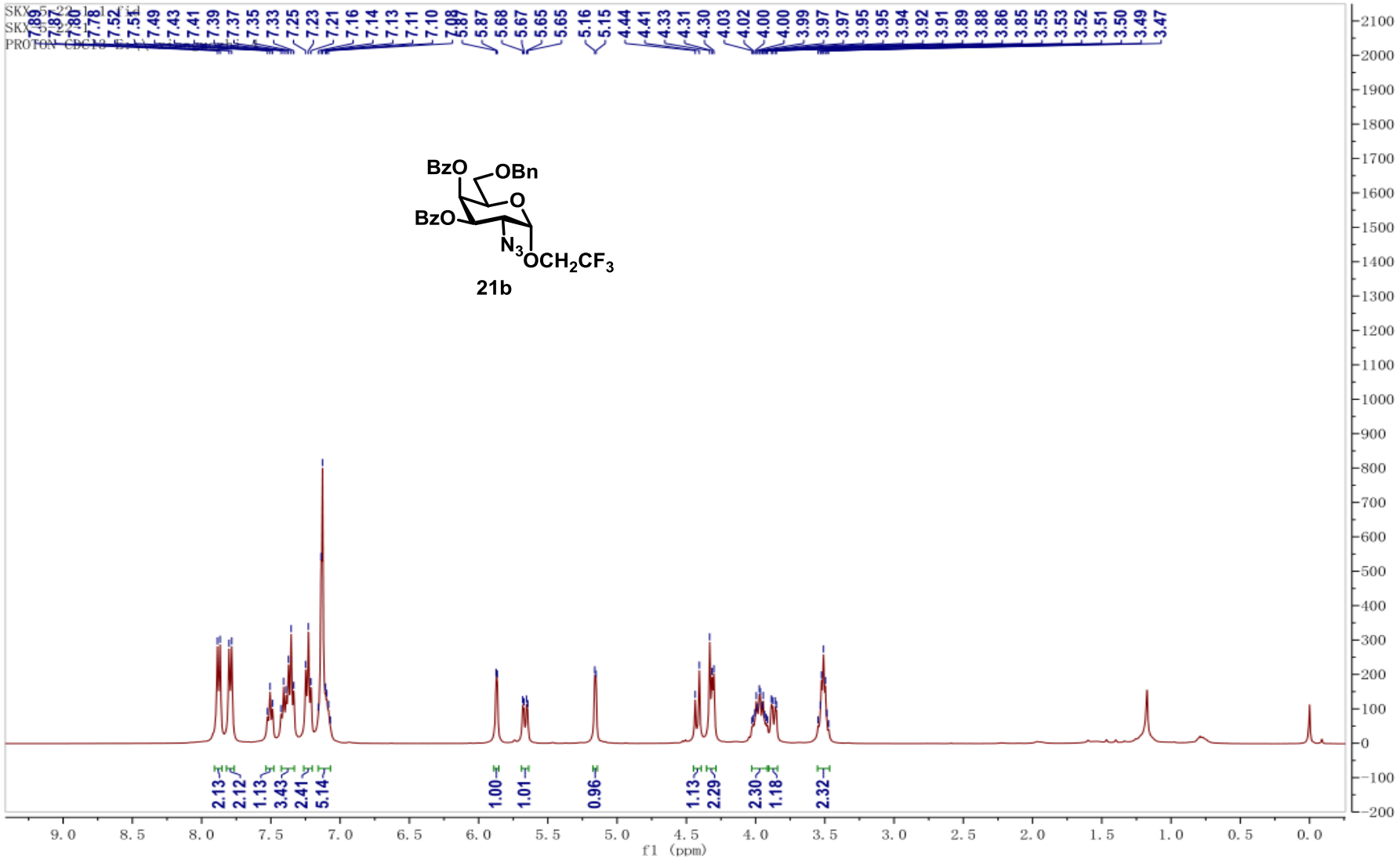

LB-2-30A.3.ser
LB-2-30A
LevO
OBn
O
LevO
N3
O(CH2)5NBnCbz
19p α/β = 14/1
f2 (ppm)
f1 (ppm)

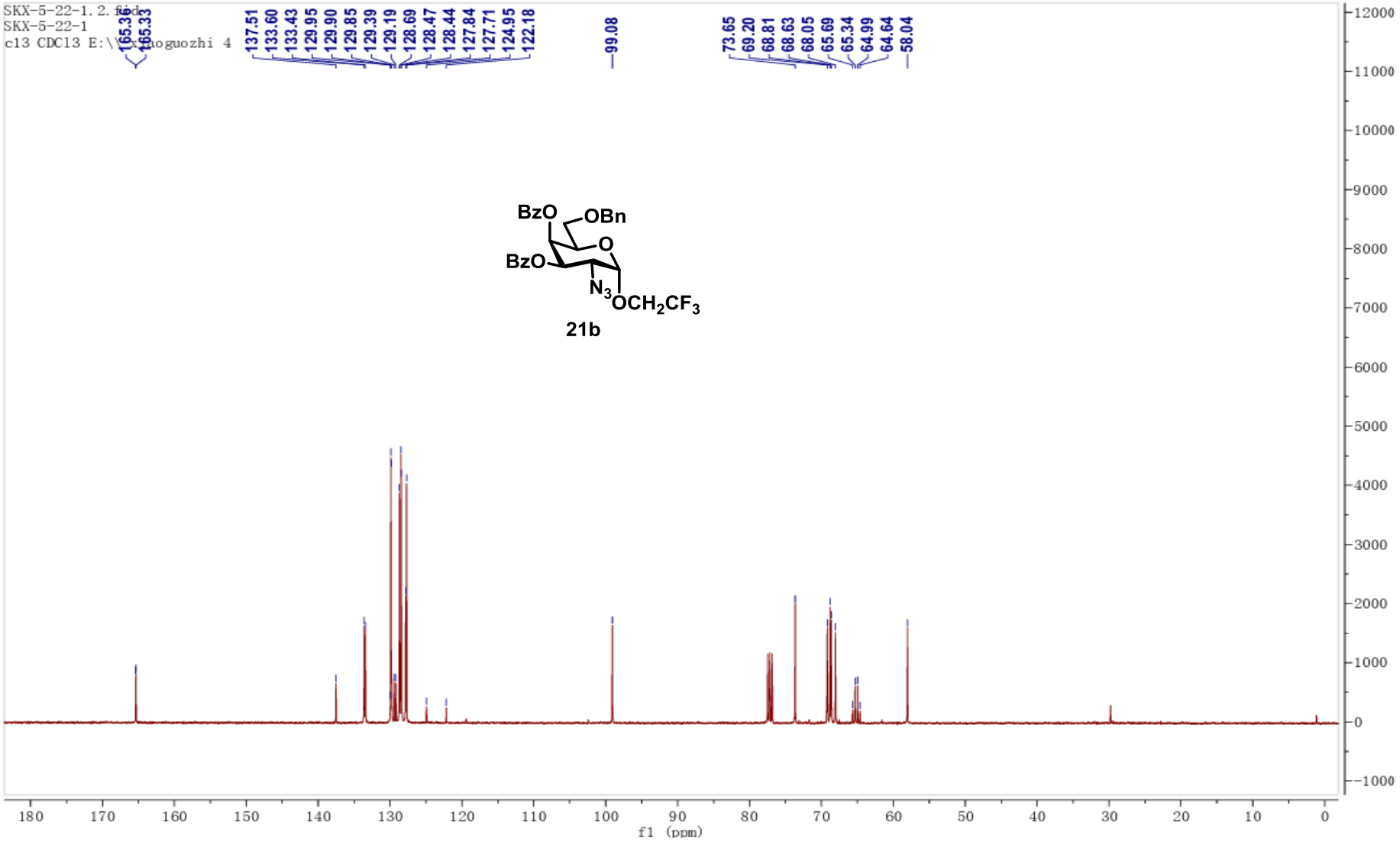

BzO
OBn
O
BzO
N3
O(CH2)17CH3
21a
f1 (ppm)

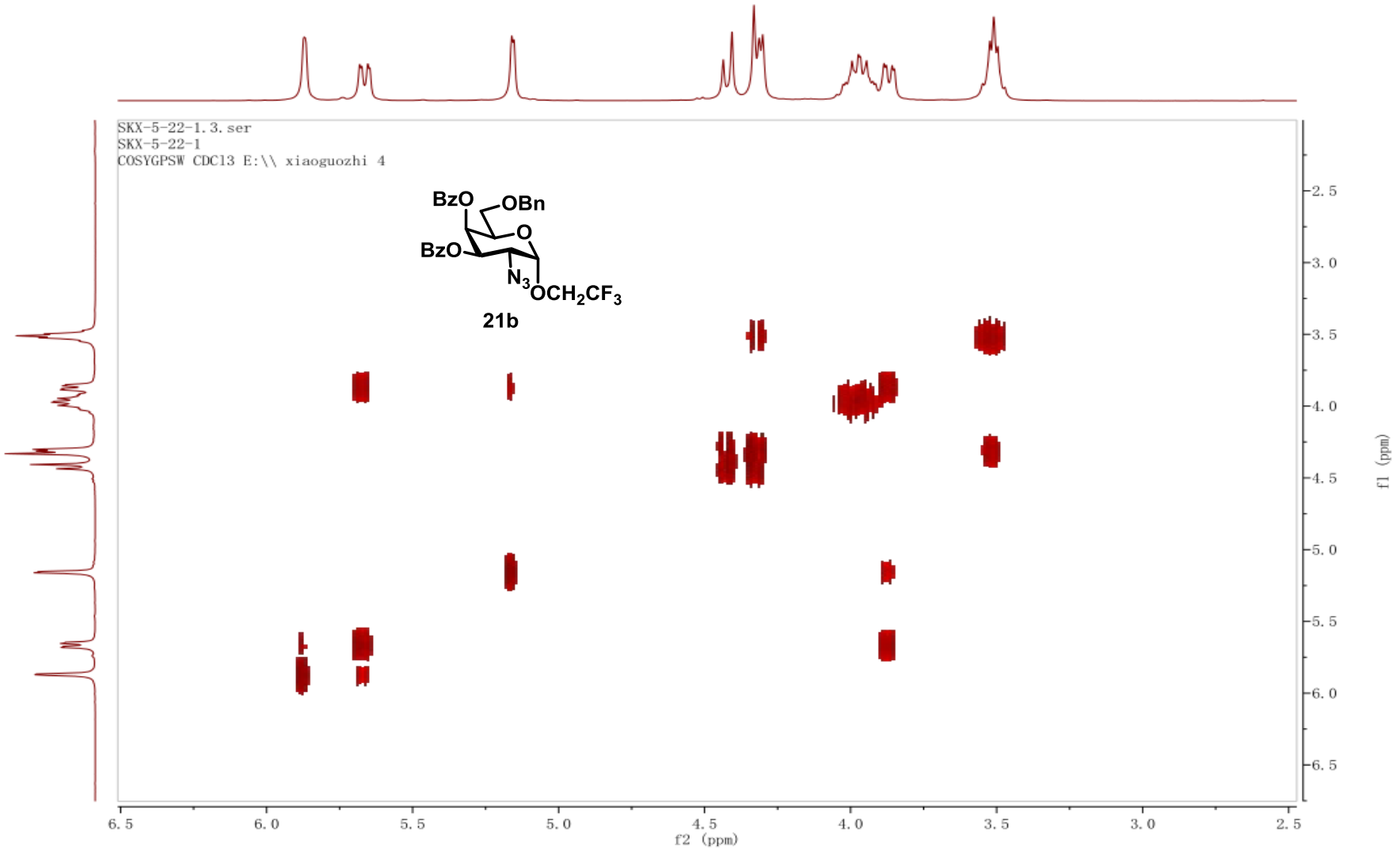

SKX-5-12.4.fid
SKX-5-12
c13 CDCl3 E:\\ xiaoguozhi 4
165.42
137.66
133.40
133.24
129.87
129.84
129.60
129.40
128.59
128.42
128.37
128.34
127.71
127.67
98.48
73.58
69.16
69.07
69.04
68.32
68.28
58.39
32.01
29.80
29.78
29.75
29.73
29.67
29.53
29.50
29.44
26.26
22.77
14.19
BzO
OBn
O
BzO
N3
O(CH2)17CH3
21a
f1 (ppm)

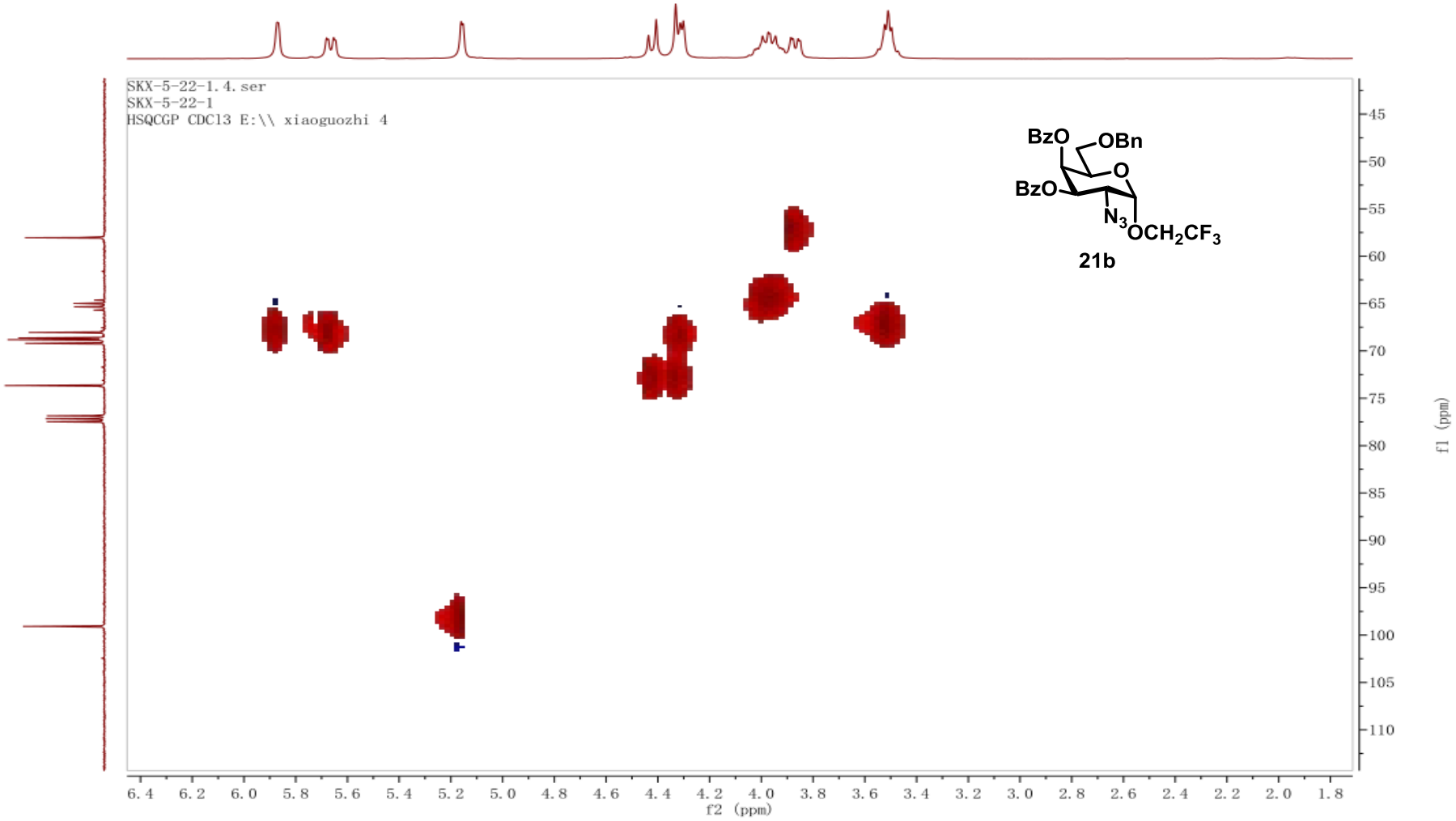

SKX-5-12.2.ser
SKX-5-12
COSYGPSW CDCl3 E:\\ xiaoguozhi 4
BzO
OBn
O
BzO
N3
O(CH2)17CH3
21a
f2 (ppm)
f1 (ppm)

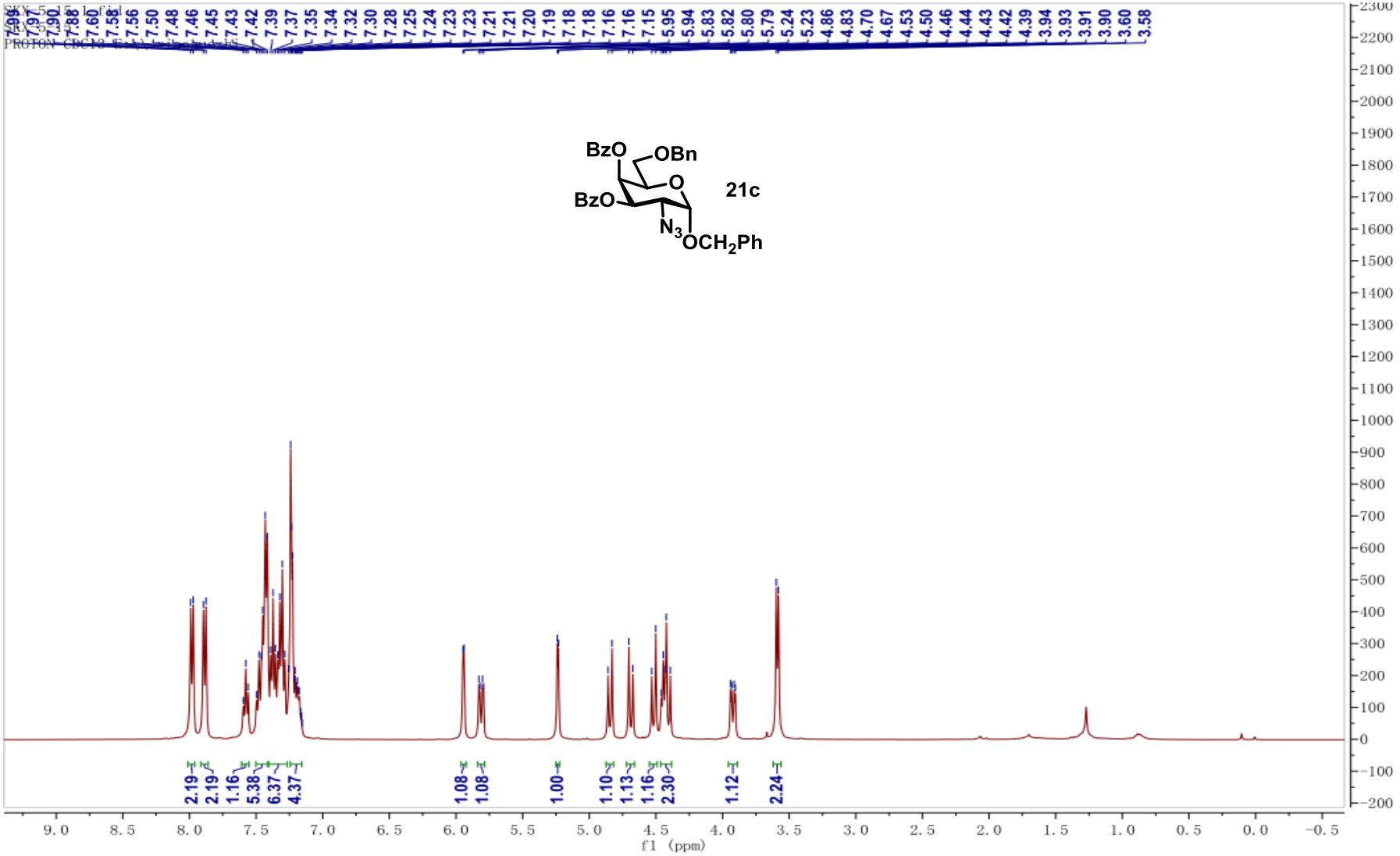

SKX-5-12.3.ser
SKX-5-12
HSQCGP CDCl3 E:\\ xiaoguozhi 4
BzO
OBn
O
BzO
N3
O(CH2)17CH3
21a
f2 (ppm)
f1 (ppm)

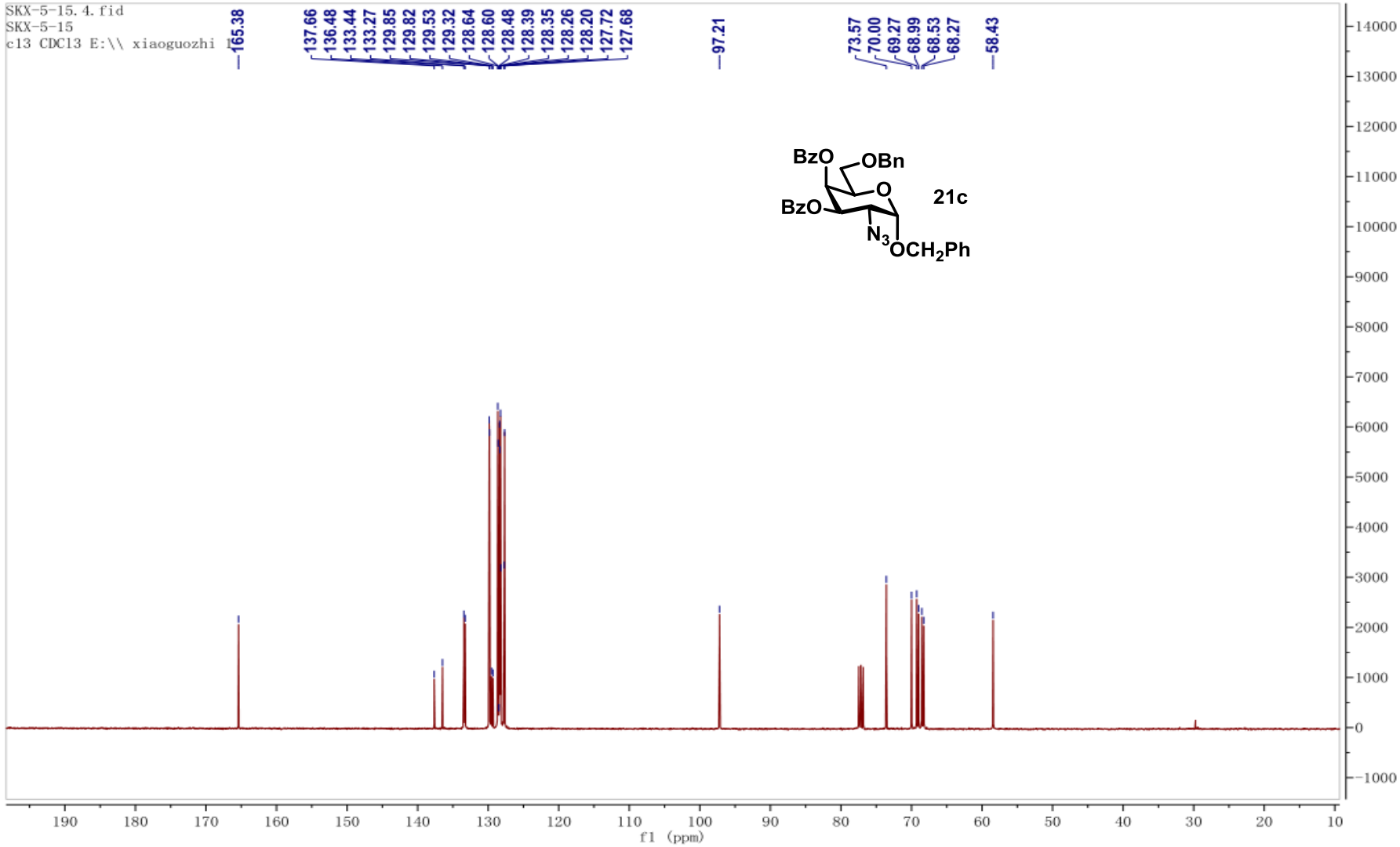

BzO
OBn
O
BzO
N3
OCH2CF3
21b
f1 (ppm)

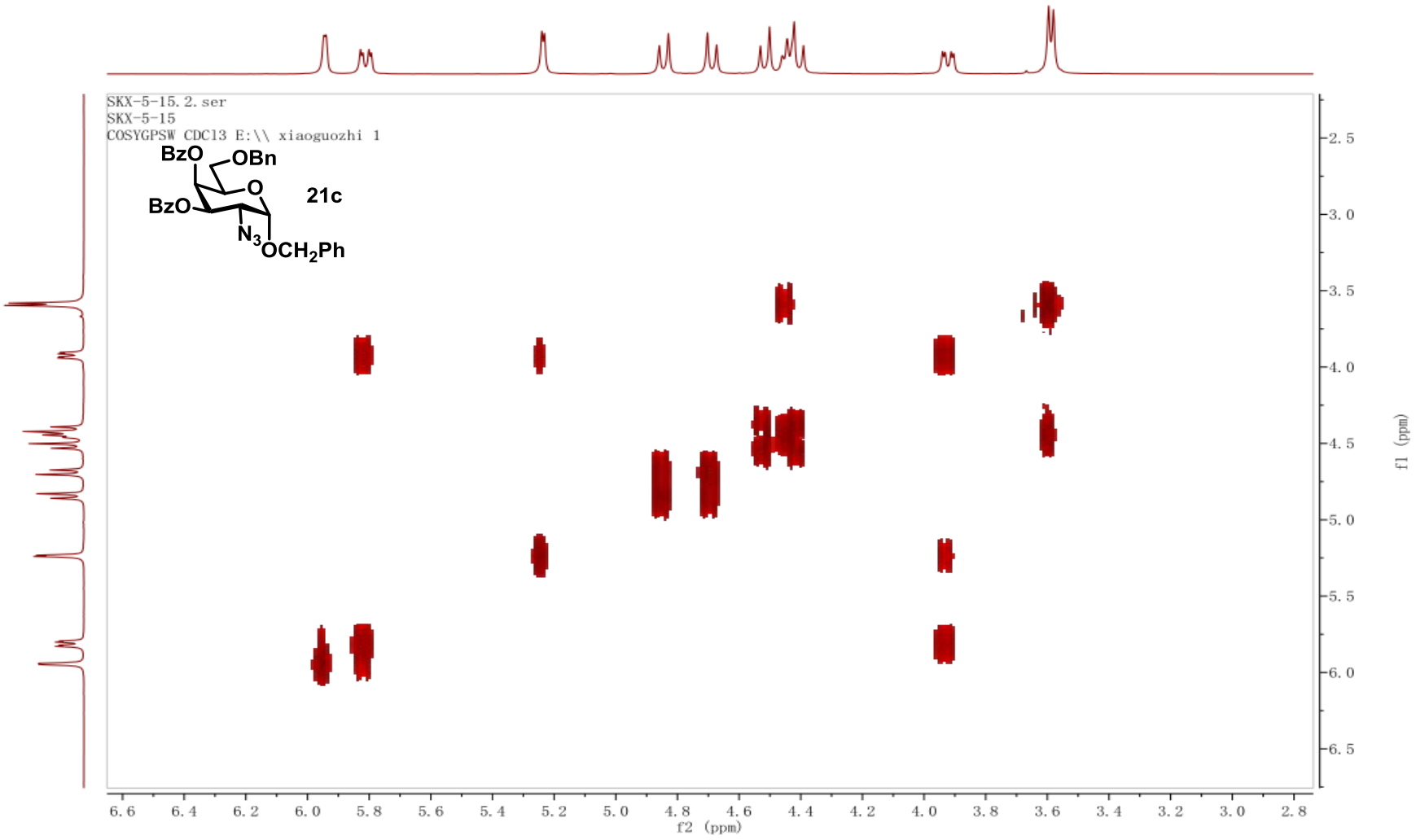

SKX-5-22-1.2.fid
SKX-5-22-1
c13 CDCl3 E:\\...\xuoguozhi 4
165.36
165.33
137.51
133.60
133.43
129.95
129.90
129.85
129.39
129.19
128.69
128.47
128.44
127.84
127.71
124.95
122.18
99.08
73.65
69.20
68.81
68.63
68.05
65.69
65.34
64.99
64.64
58.04
BzO
OBn
O
BzO
N3
OCH2CF3
21b
f1 (ppm)

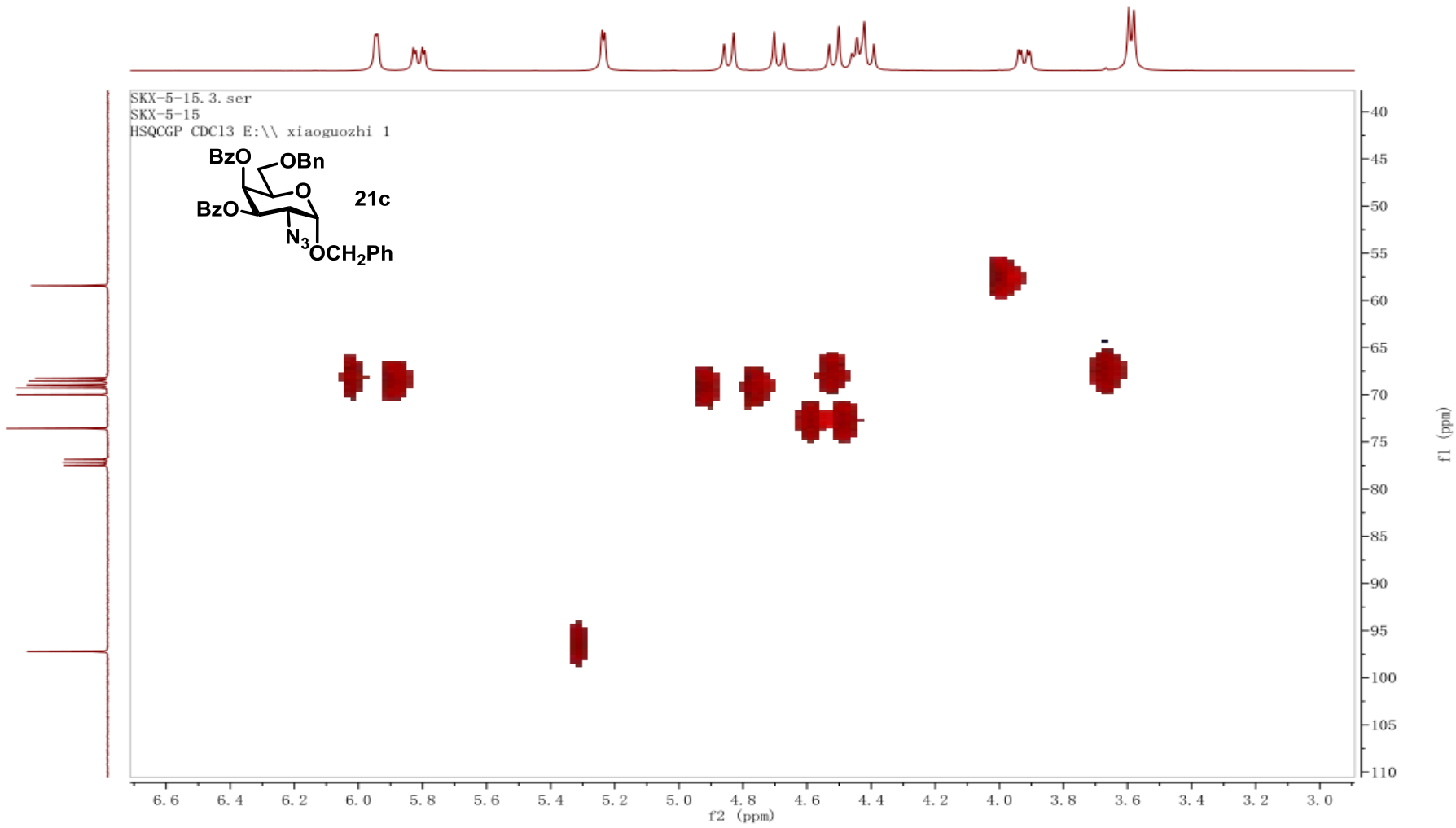

SKX-5-22-1.3.ser
SKX-5-22-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 4
BzO
OBn
O
BzO
N3
OCH2CF3
21b
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
f1 (ppm)

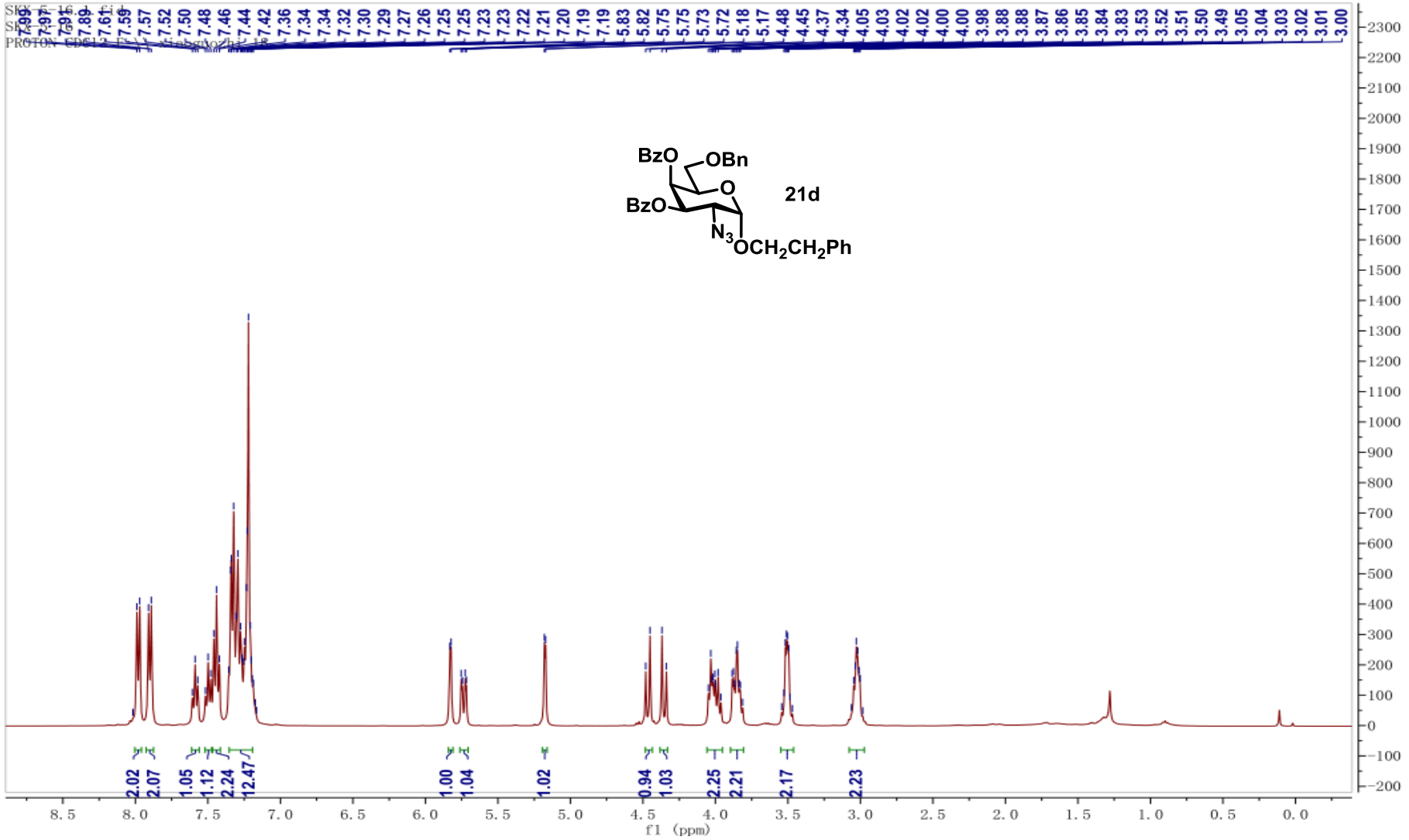

SKX-5-22-1.4.ser
SKX-5-22-1
HSQCGP CDCl3 E:\\ xiaoguozhi 4
BzO
OBn
O
BzO
N3
OCH2CF3
21b
f2 (ppm)
f1 (ppm)

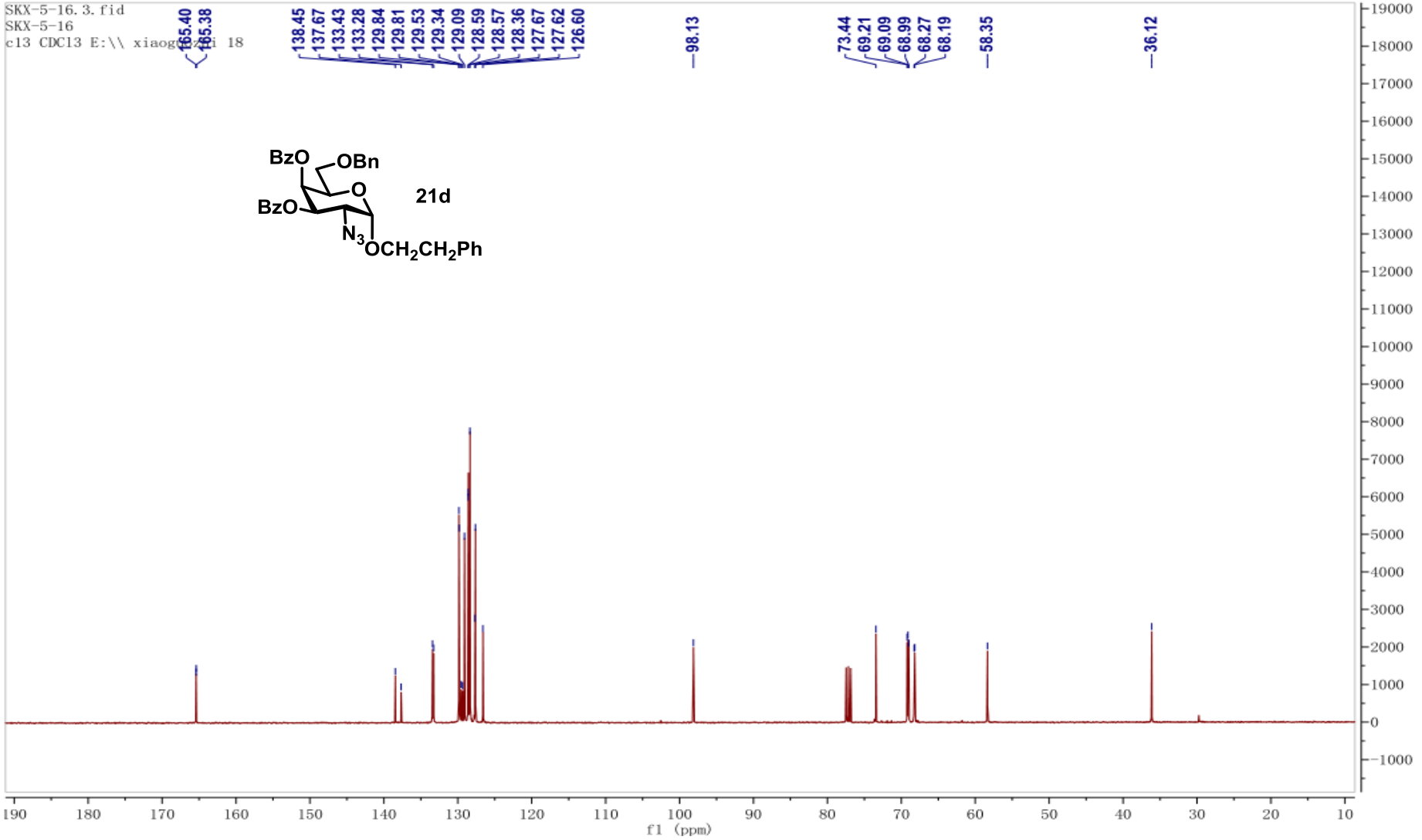

BzO
OBn
O
BzO
N3
OCH2Ph
21c
f1 (ppm)

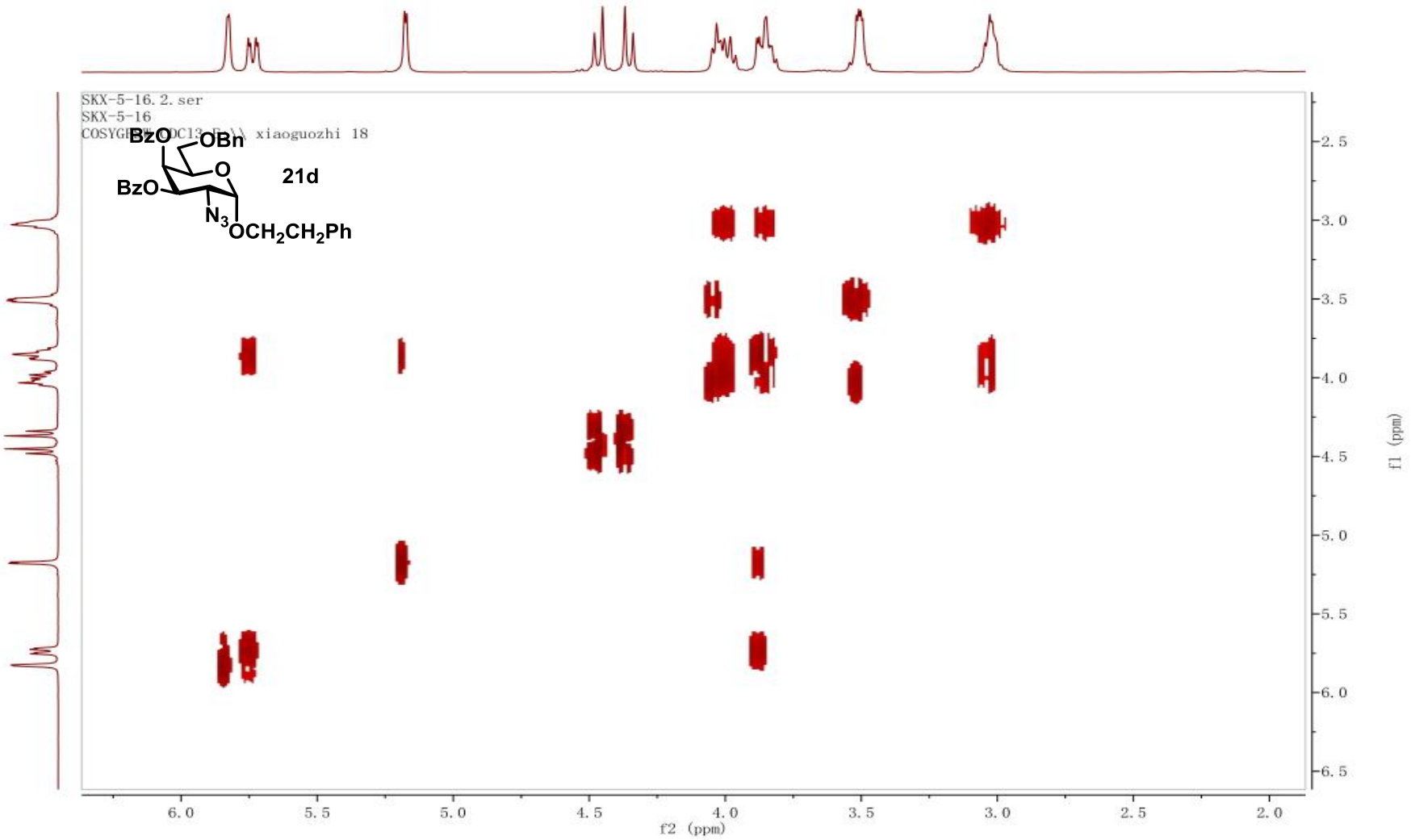

SKX-5-15.4.fid
SKX-5-15
c13 CDCl3 E:\\ xiaoguozhi
165.38
137.66
136.48
133.44
133.27
129.85
129.82
129.53
129.32
128.64
128.60
128.48
128.39
128.35
128.26
128.20
127.72
127.68
97.21
73.57
70.00
69.27
68.99
68.53
68.27
58.43
BzO
OBn
O
BzO
N3
OCH2Ph
21c
f1 (ppm)

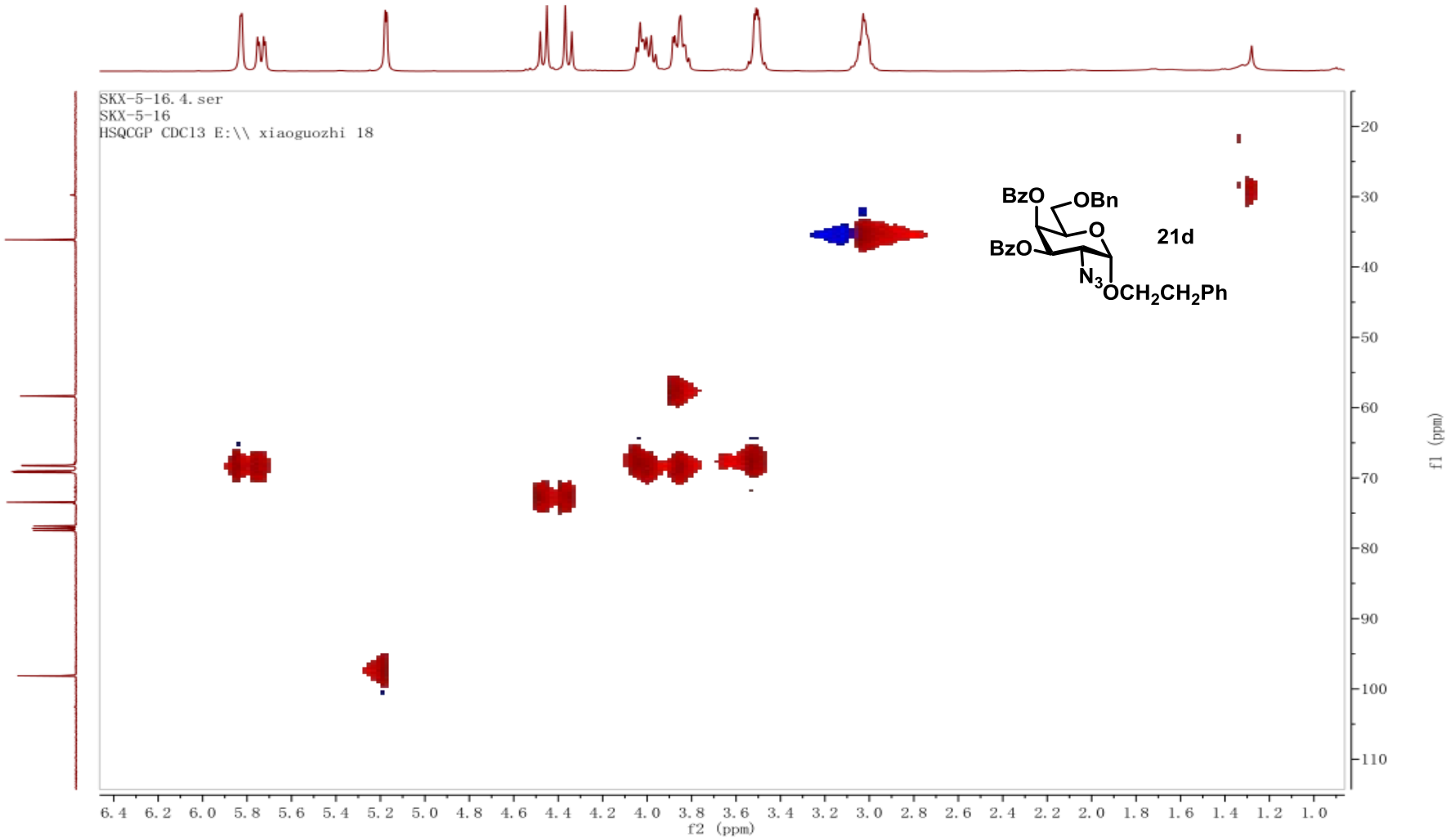

SKX-5-15.2.ser
SKX-5-15
COSYGPSW CDCl3 E:\\ xiaoguozhi 1
BzO
OBn
O
BzO
21c
N3
OCH2Ph
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8
f2 (ppm)
2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5
f1 (ppm)

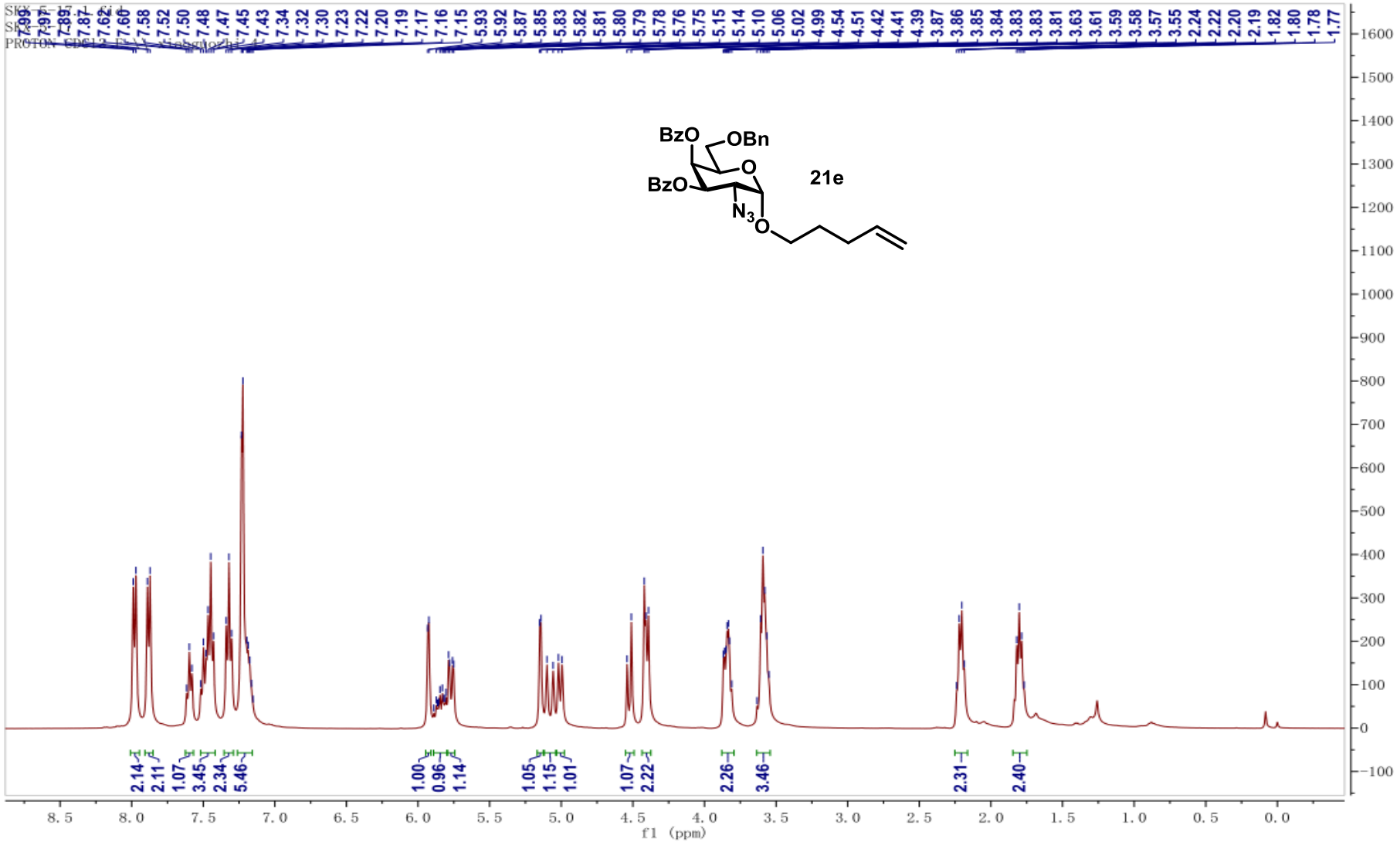

SKX-5-15.3.ser
SKX-5-15
HSQCGP CDCl3 E:\\ xiaoguozhi 1
BzO
OBn
O
BzO
21c
N3
OCH2Ph
f2 (ppm)
f1 (ppm)

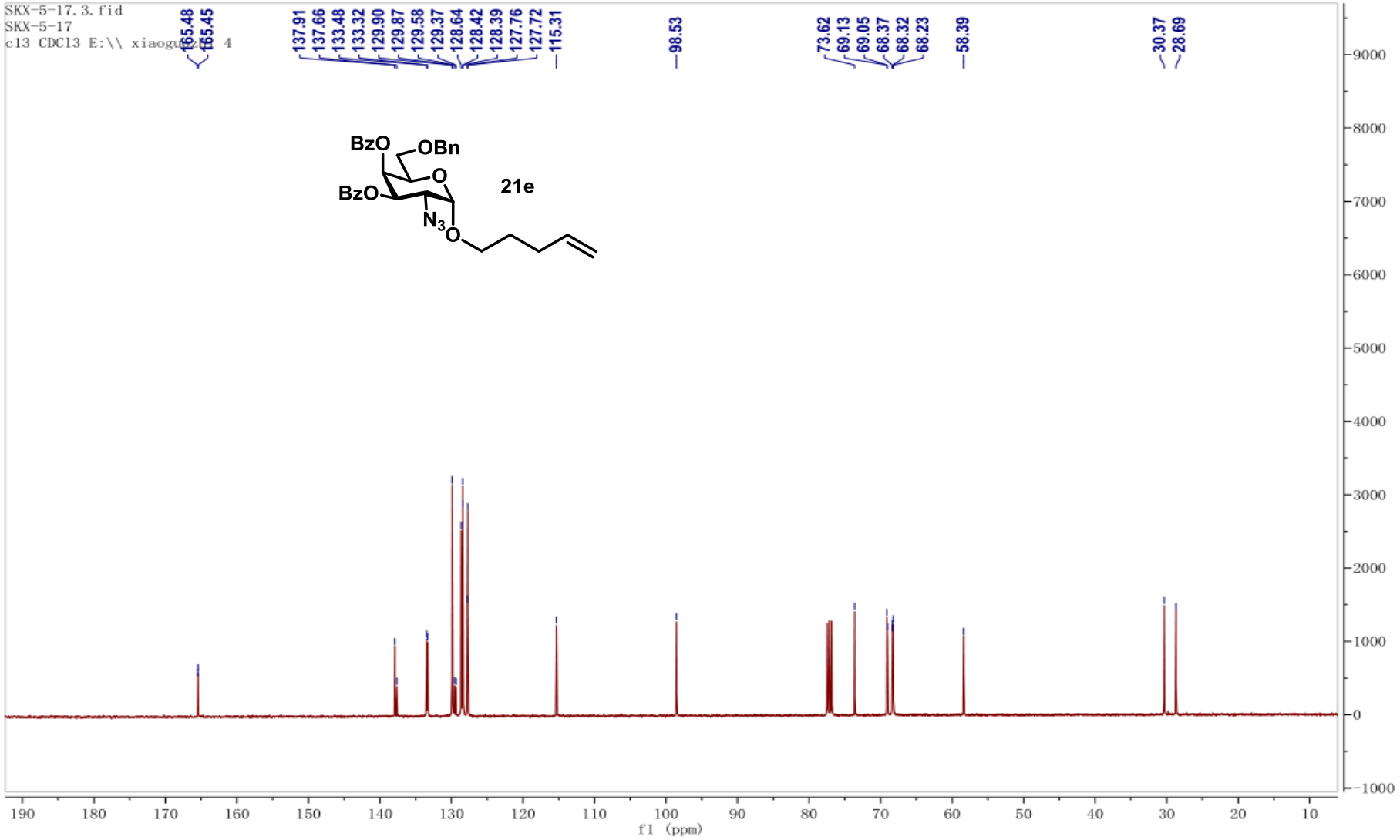

BzO
OBn
O
BzO
N3
OCH2CH2Ph
21d
f1 (ppm)

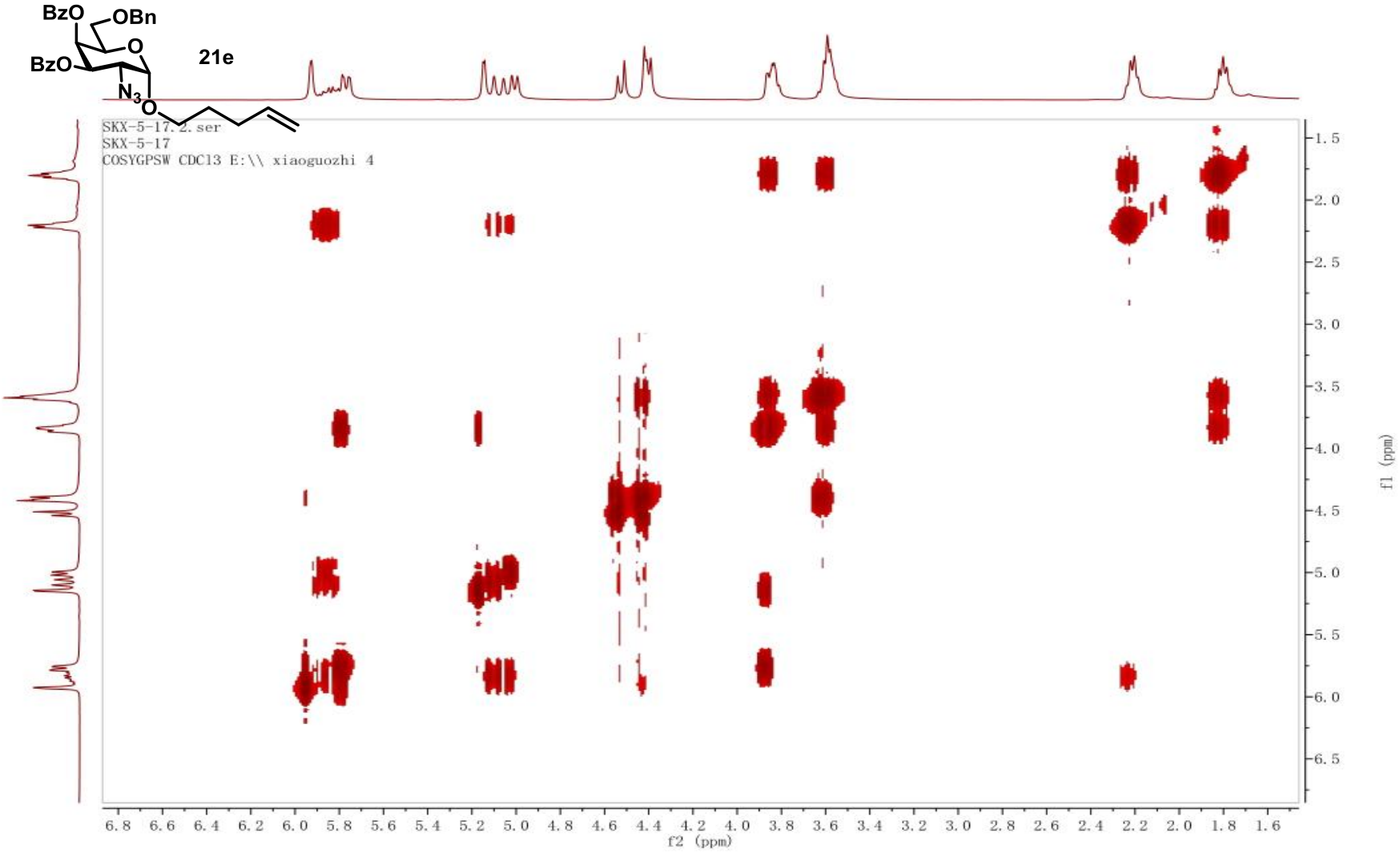

SKX-5-16.3.fid
SKX-5-16
c13 CDCl3 E:\\ xiaogu
165.40
165.38
138.45
137.67
133.43
133.28
129.84
129.81
129.53
129.34
129.09
128.59
128.57
128.36
127.67
127.62
126.60
98.13
73.44
69.21
69.09
68.99
68.27
68.19
58.35
36.12
BzO
OBn
O
BzO
N3
OCH2CH2Ph
21d
f1 (ppm)

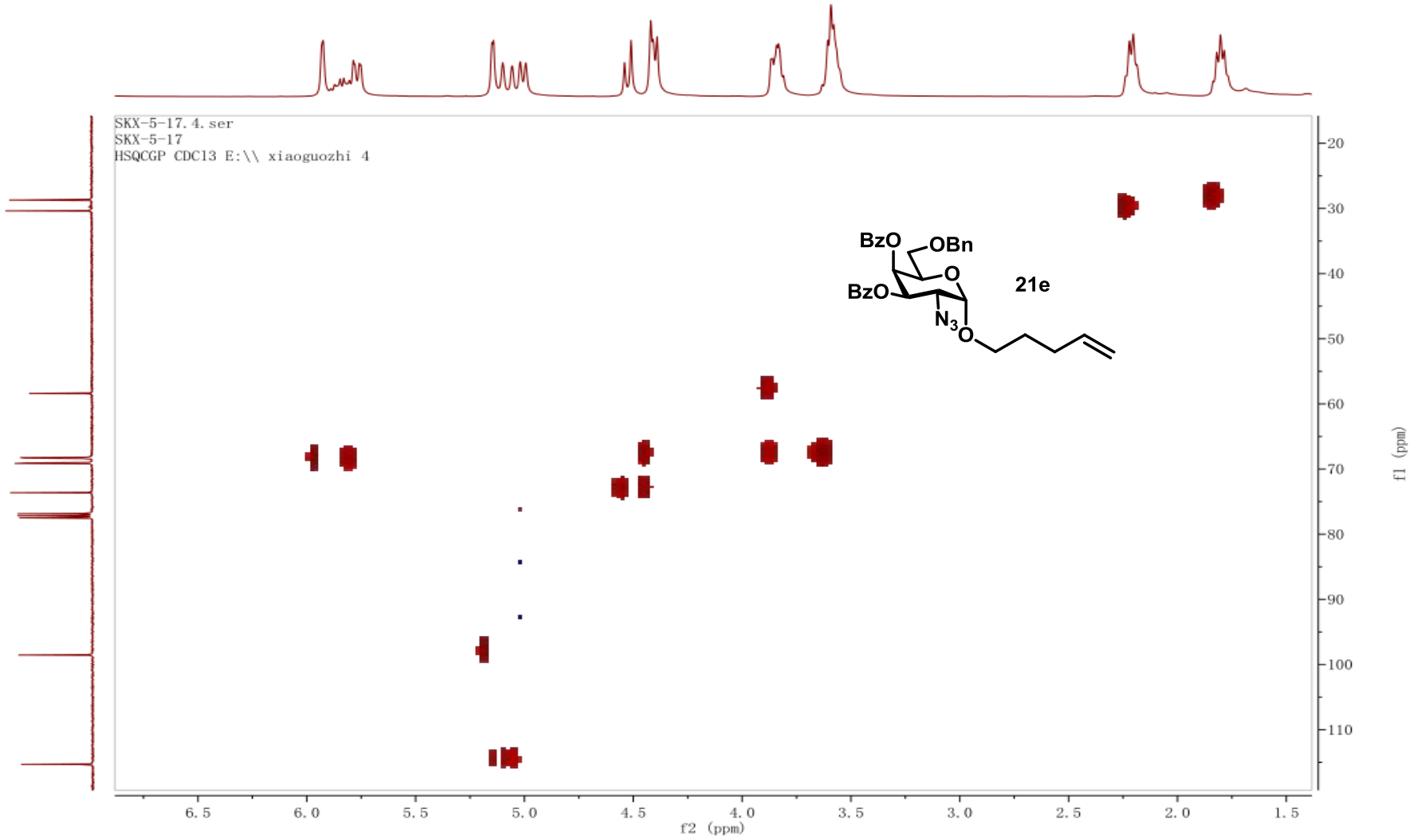

SKX-5-16.2.ser
SKX-5-16
BzO
OBn
O
BzO
21d
N3
OCH2CH2Ph
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

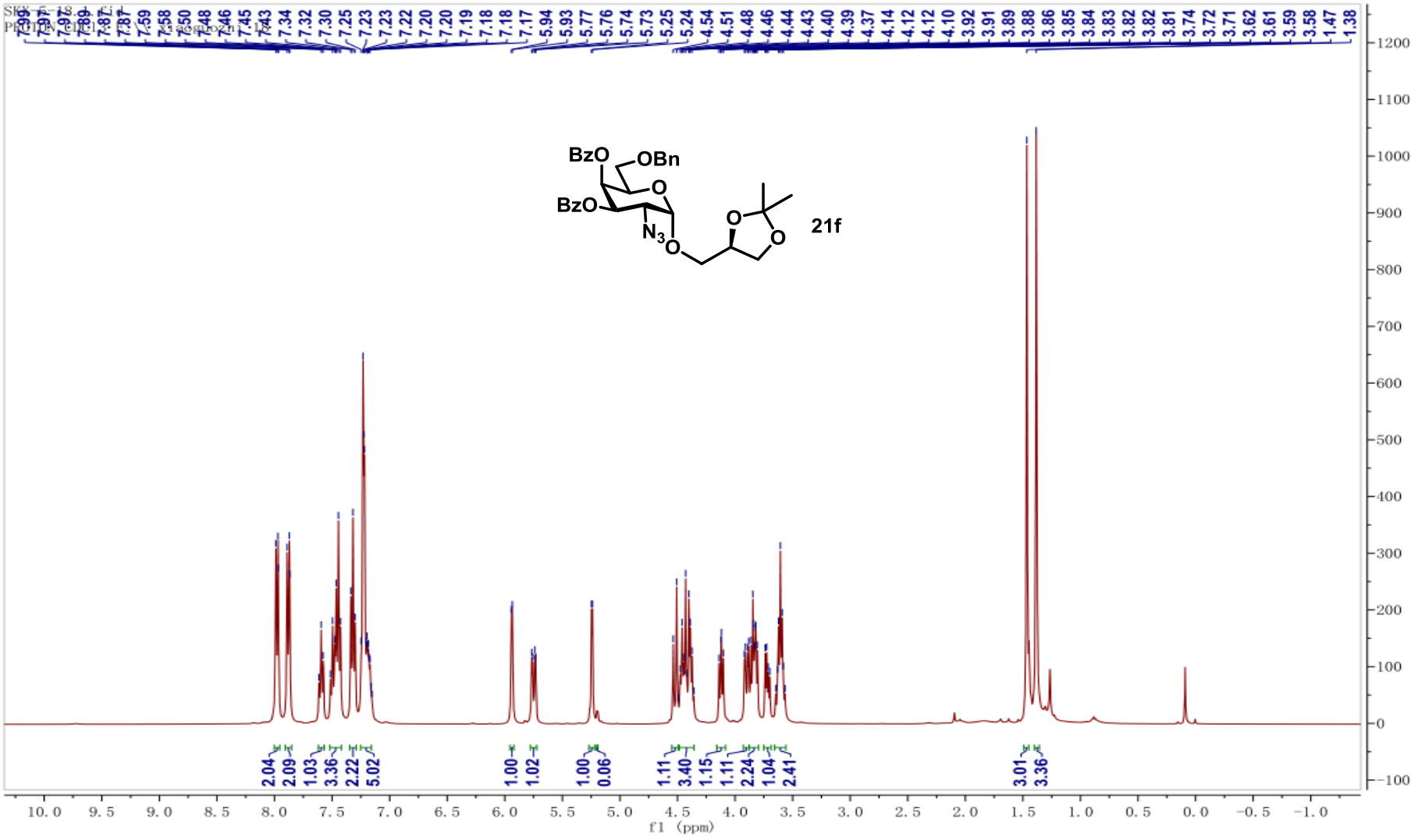

SKX-5-16.4.ser
SKX-5-16
HSQCGP CDC13 E:\\ xiaoguozhi 18
BzO
OBn
O
BzO
N3
OCH2CH2Ph
21d
f2 (ppm)
f1 (ppm)

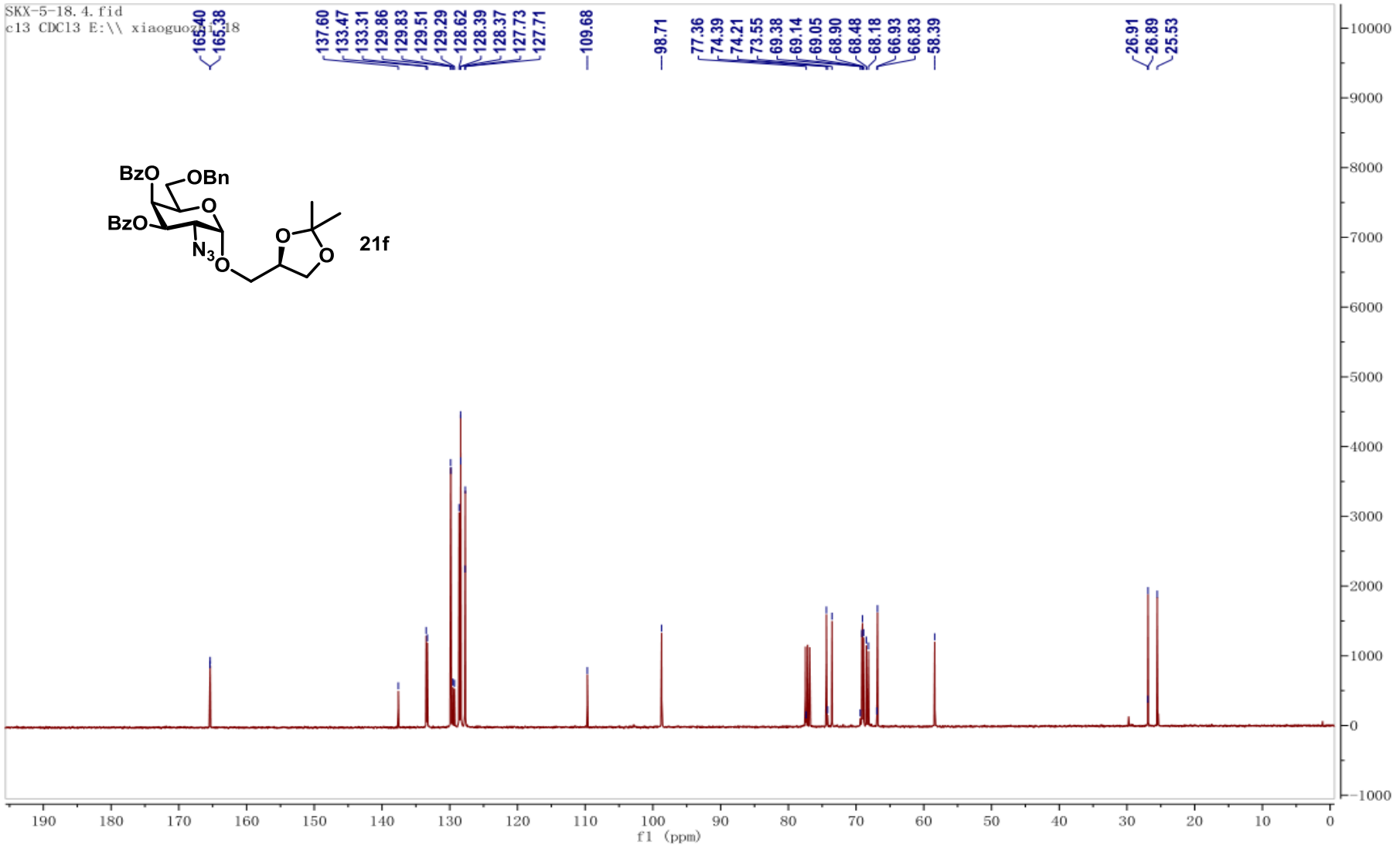

BzO
OBn
O
BzO
N3
O
21e
f1 (ppm)

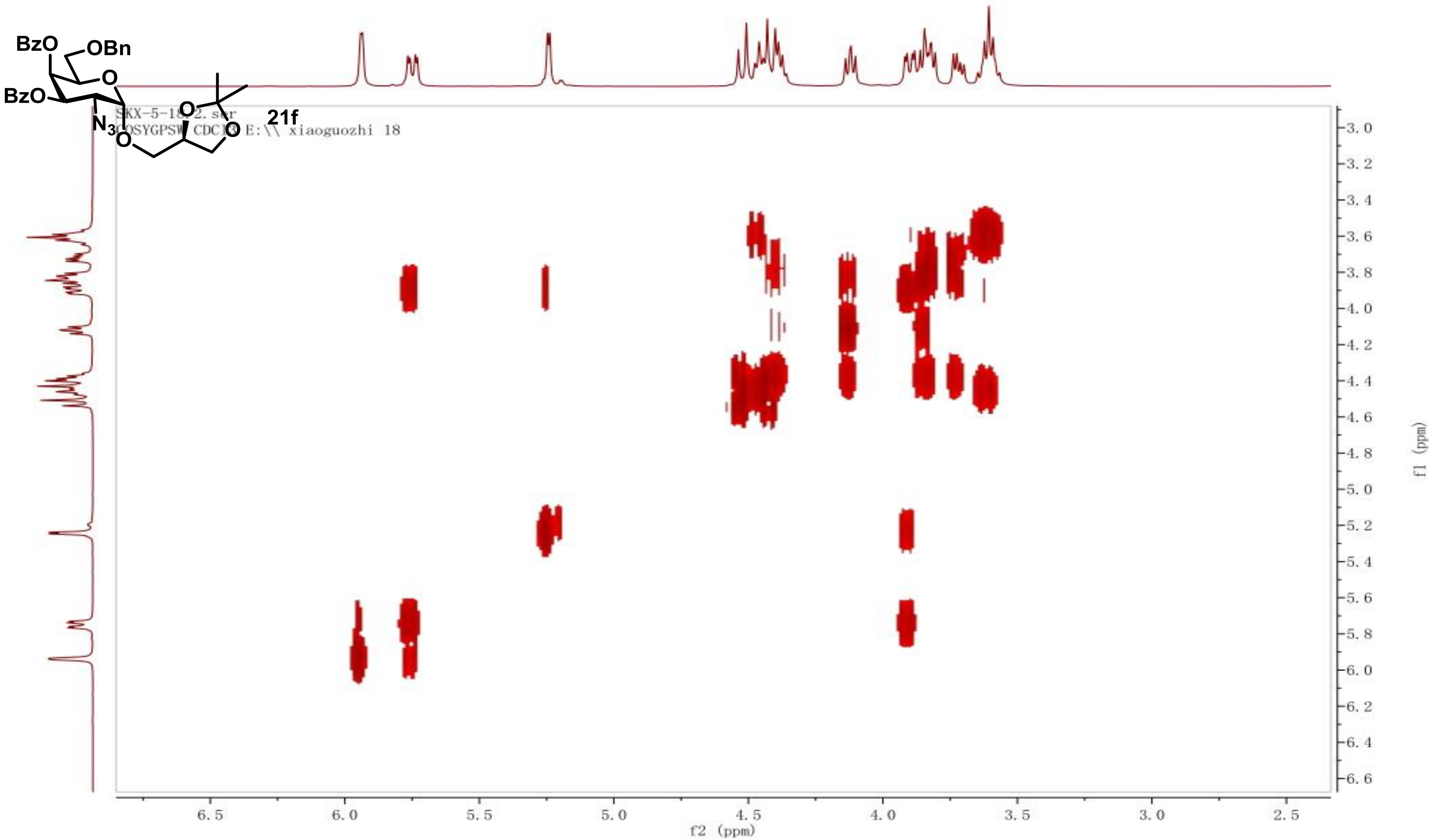

SKX-5-17.3.fid
SKX-5-17
c13 CDCl3 E:\\ xiaogu
165.48
165.45
137.91
137.66
133.48
133.32
129.90
129.87
129.58
129.37
128.64
128.42
128.39
127.76
127.72
115.31
98.53
73.62
69.13
69.05
68.37
68.32
68.23
58.39
30.37
28.69
BzO
OBn
O
BzO
N3
O
21e
f1 (ppm)

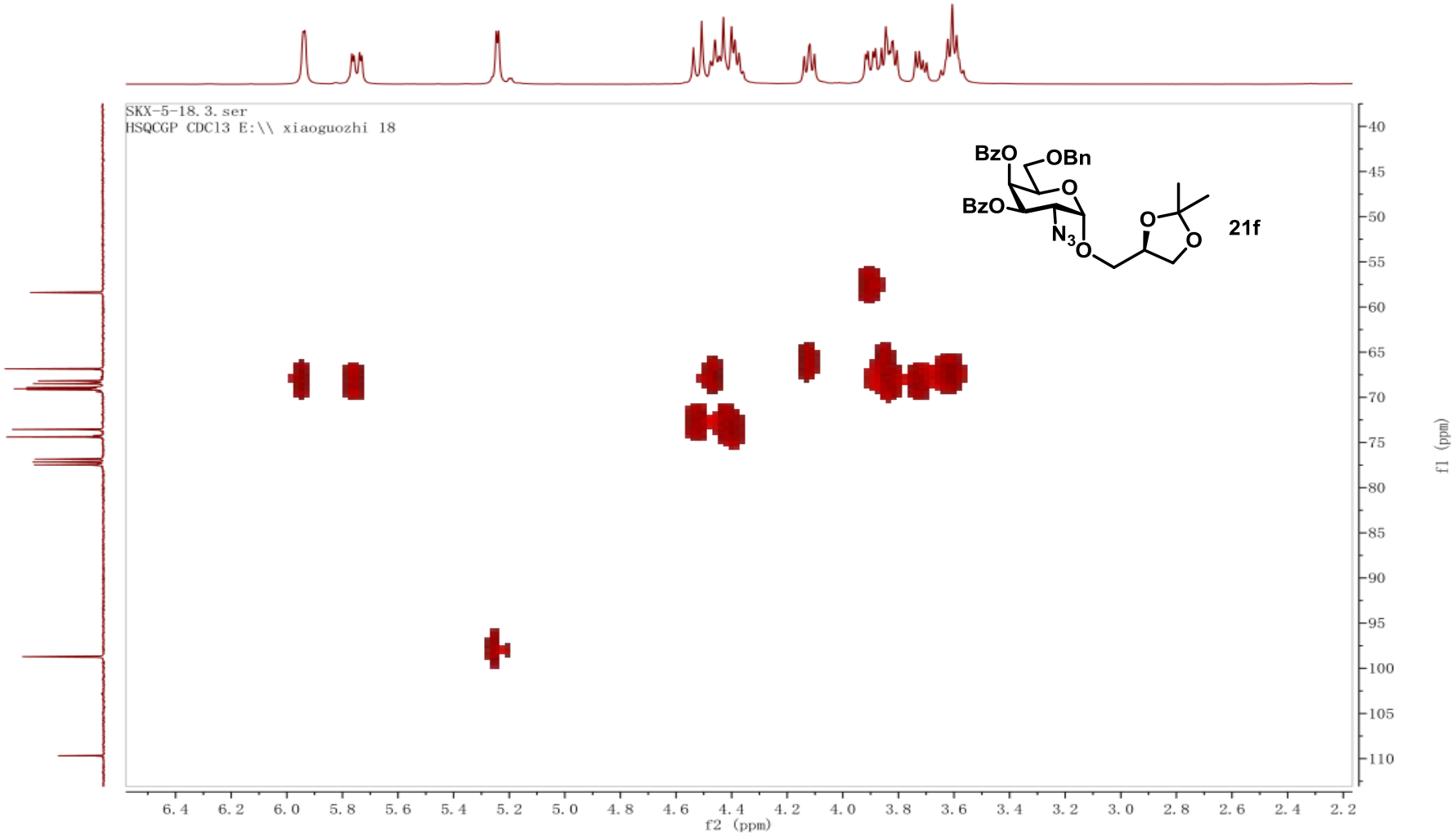

BzO
OBn
O
BzO
N3
O
21e
SKX-5-17.2.ser
SKX-5-17
COSYGPSW CDCl3 E:\\ xiaoguozhi 4
f2 (ppm)
f1 (ppm)

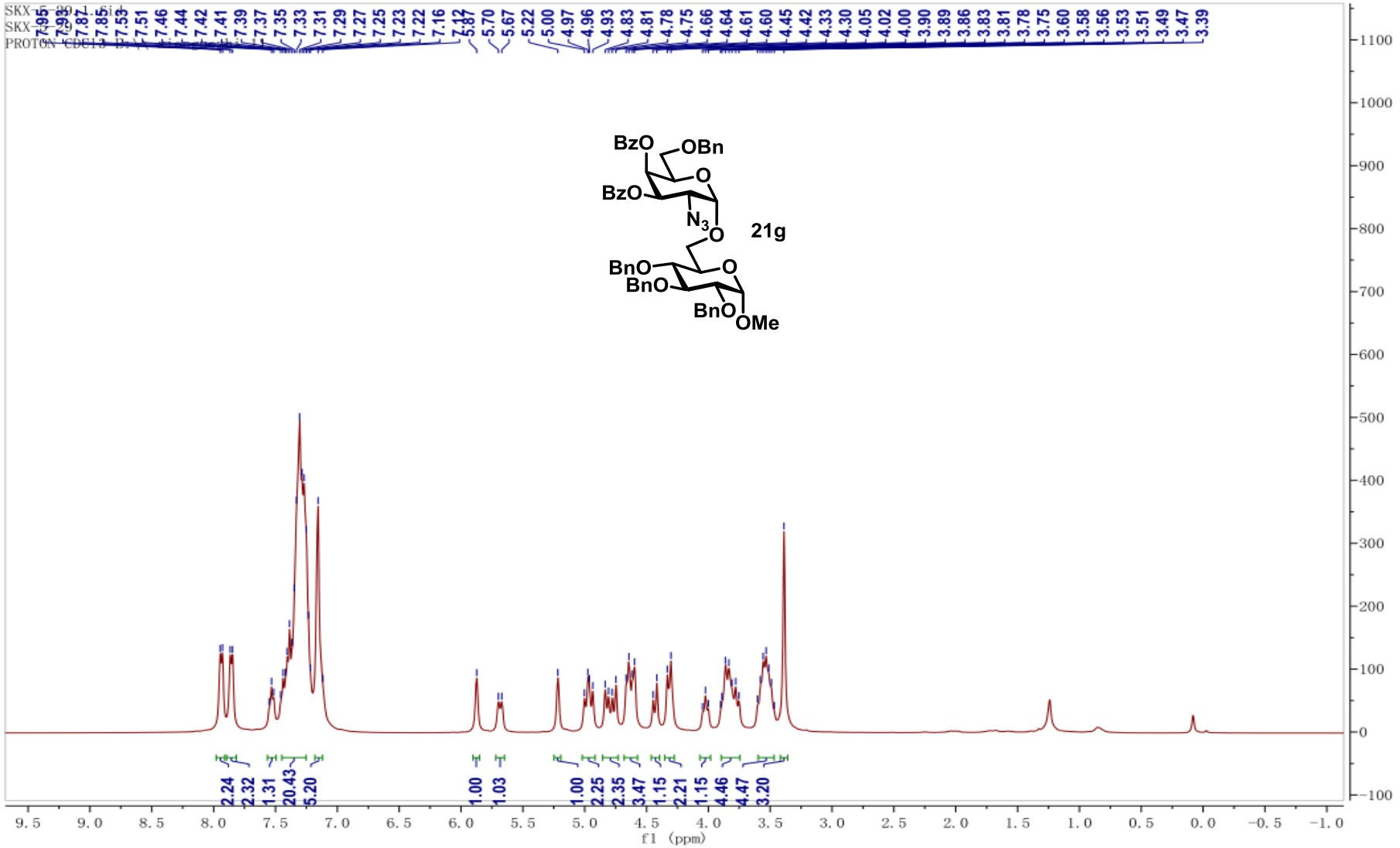

SKX-5-17.4.ser
SKX-5-17
HSQCGP CDCl3 E:\\ xiaoguozhi 4
BzO
OBn
O
BzO
N3
O
21e
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

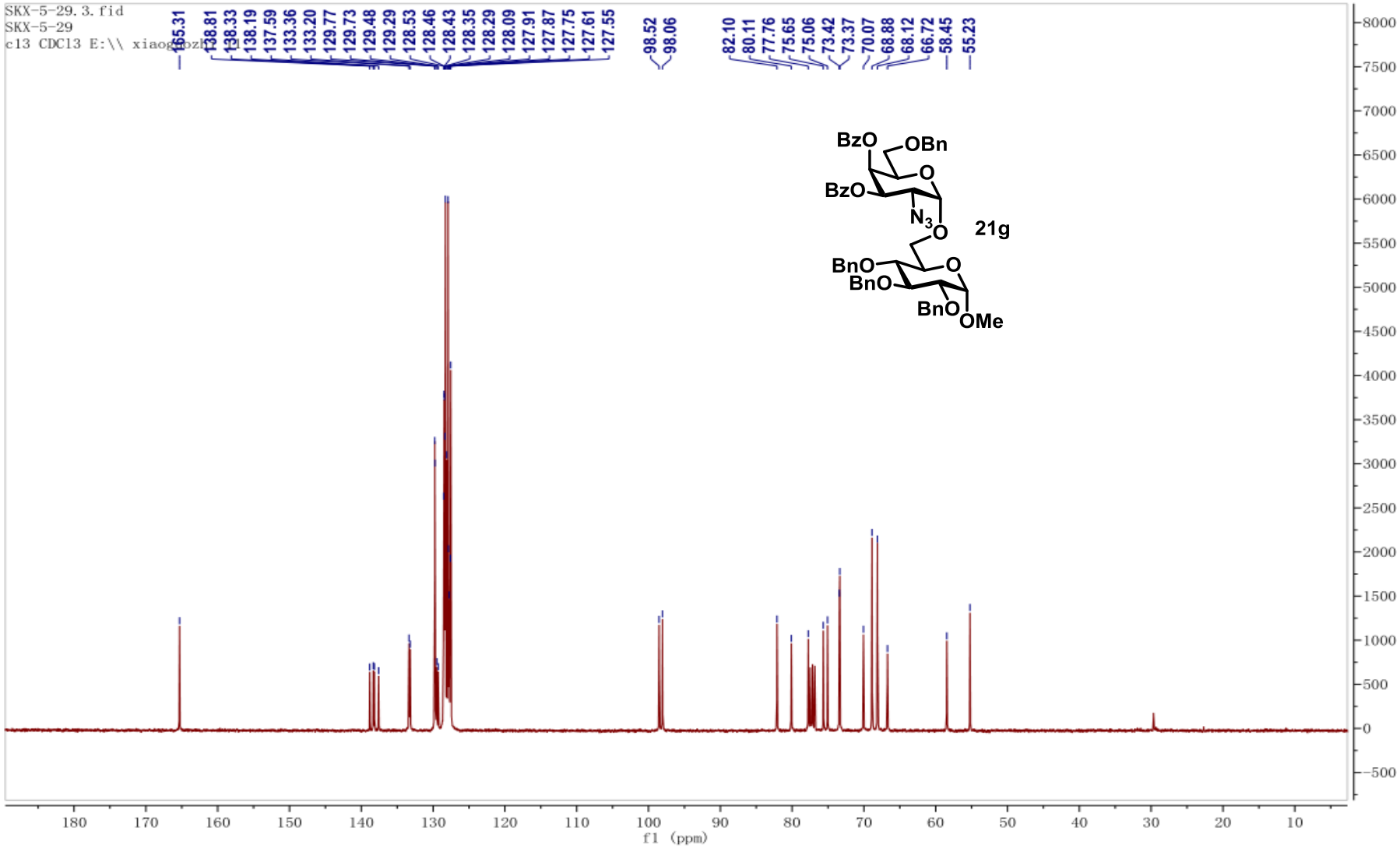

BzO
OBn
BzO
N3
O
O
O
O
21f
2.04
2.09
1.03
3.36
2.22
5.02
1.00
1.02
1.00
0.06
1.11
3.40
1.15
1.11
2.24
1.04
2.41
3.01
3.36
f1 (ppm)

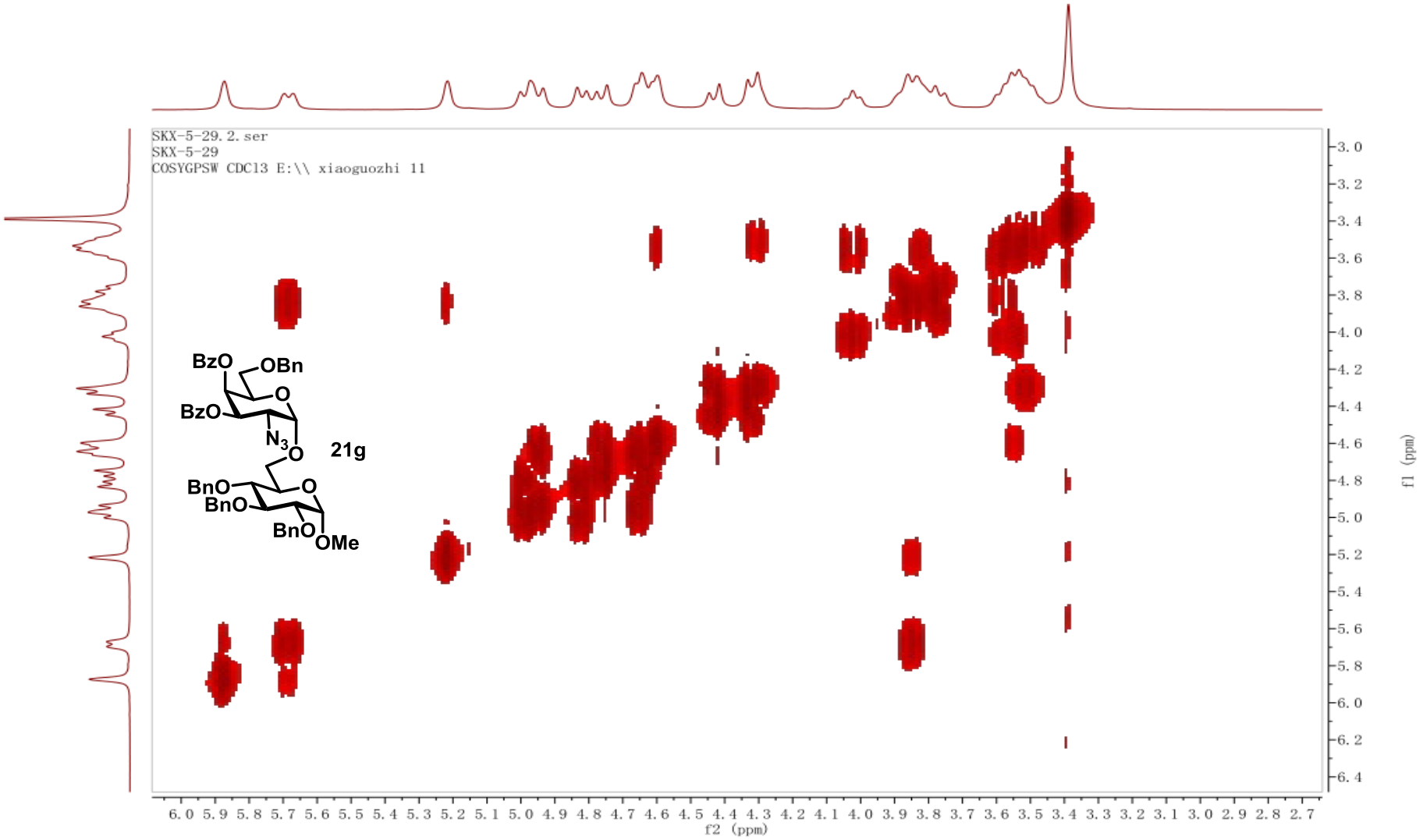

SKX-5-18.4.fid
c13 CDCl3 E:\\ xiaoguozhi\18
165.40
165.38
137.60
133.47
133.31
129.86
129.83
129.51
129.29
128.62
128.39
128.37
127.73
127.71
109.68
98.71
77.36
74.39
74.21
73.55
69.38
69.14
69.05
68.90
68.48
68.18
66.93
66.83
58.39
26.91
26.89
25.53
BzO
OBn
O
BzO
N3
O
O
O
21f
f1 (ppm)

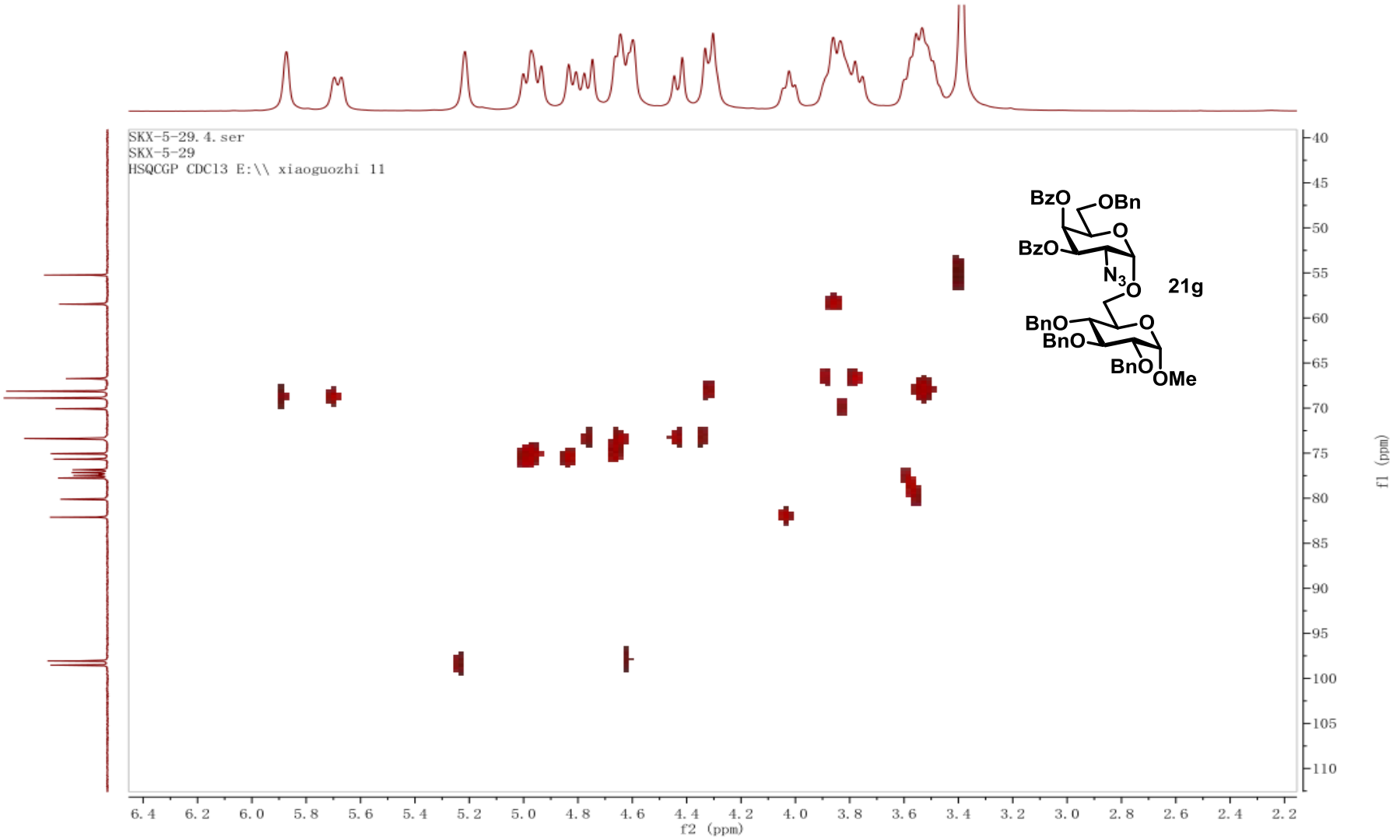

BzO
OBn
O
BzO
N3
O
O
O
21f
f2 (ppm)
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

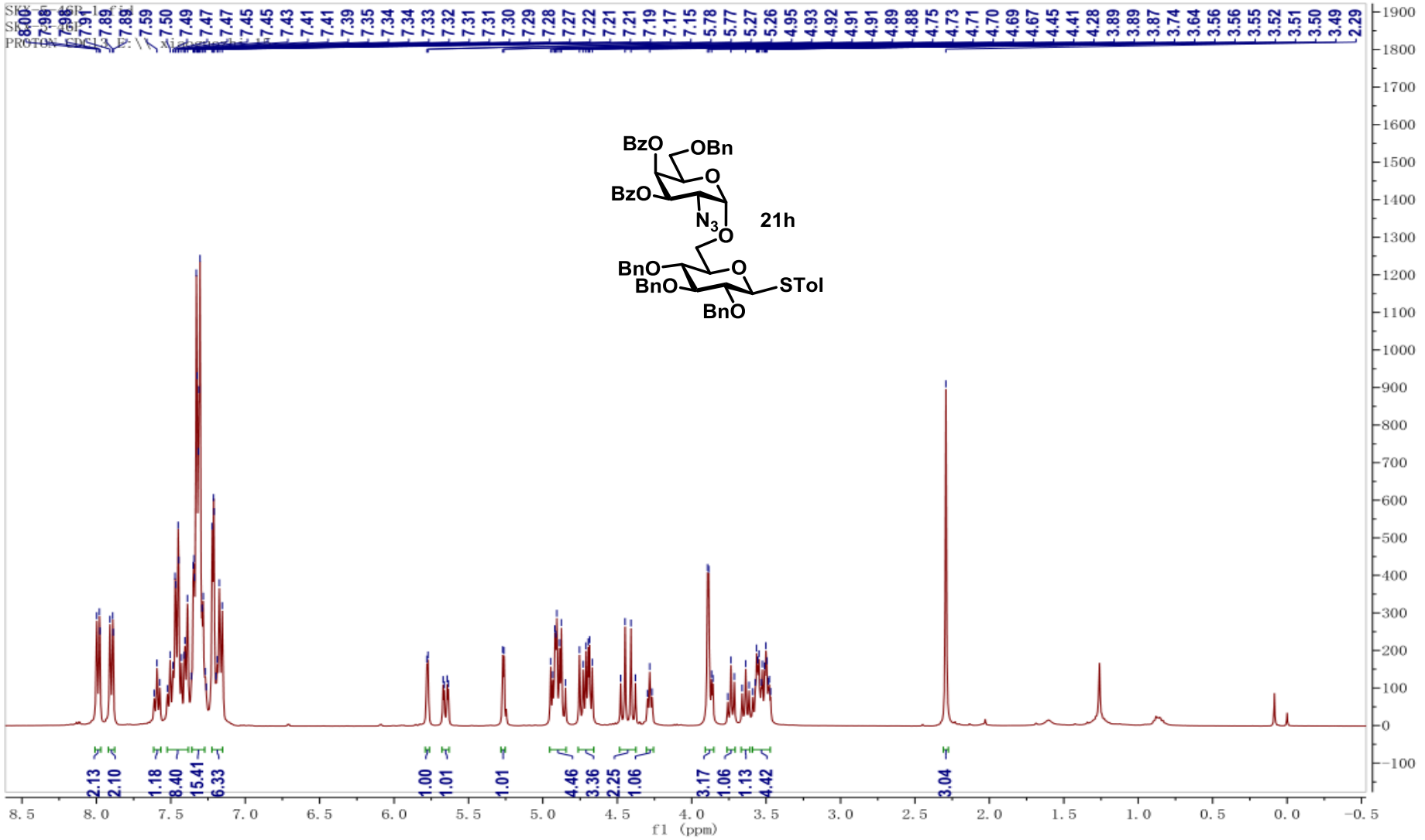

SKX-5-18.3.ser
HSQCGP CDCl3 E:\\ xiaoguozhi 18
BzO
OBn
BzO
O
N3
O
O
O
21f
f2 (ppm)
f1 (ppm)

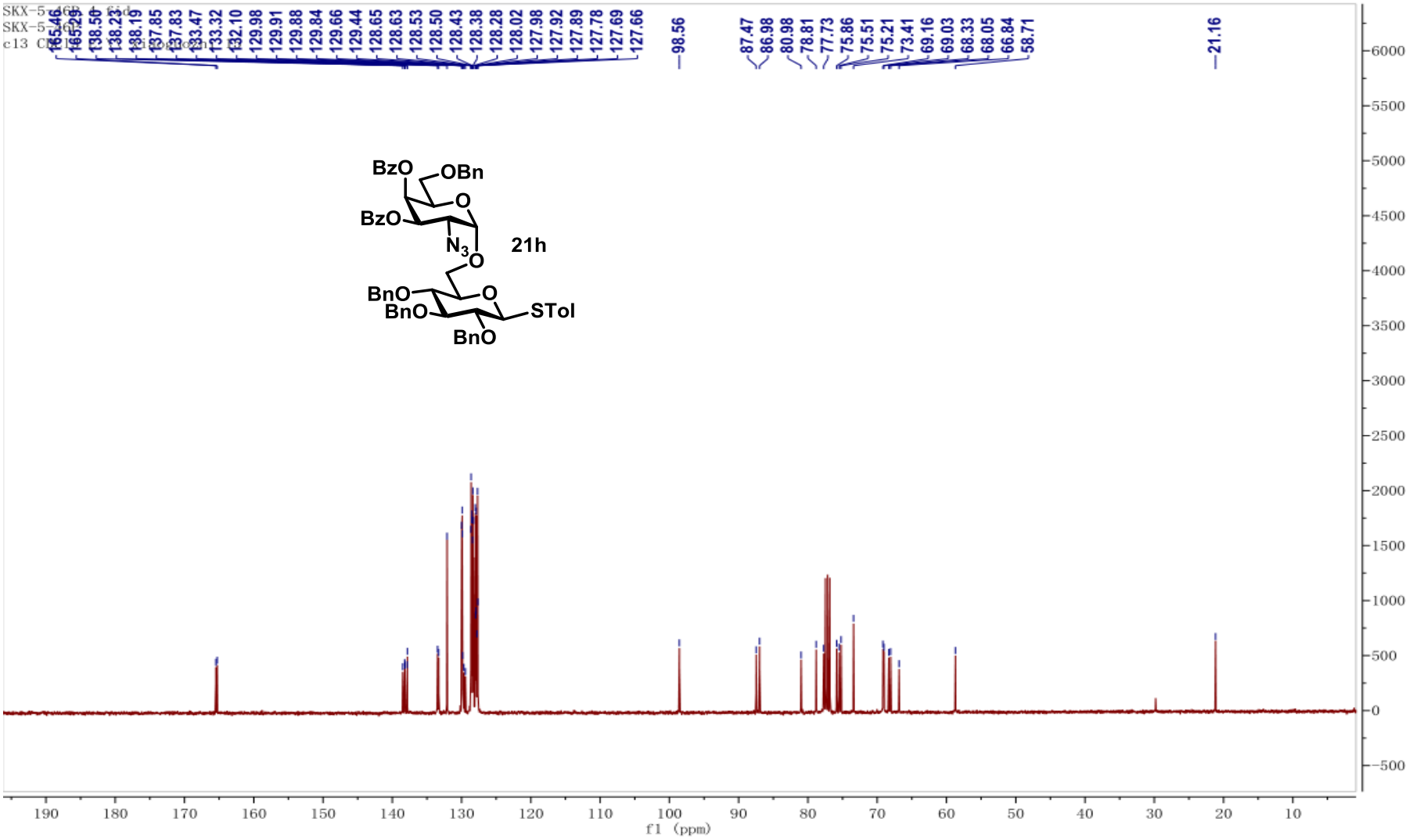

BzO
OBn
O
BzO
N3
O
21g
BnO
O
BnO
BnO
OMe
2.24
2.32
1.31
20.43
5.20
1.00
1.03
1.00
2.25
2.35
3.47
1.15
2.21
1.15
4.46
4.47
3.20
f1 (ppm)

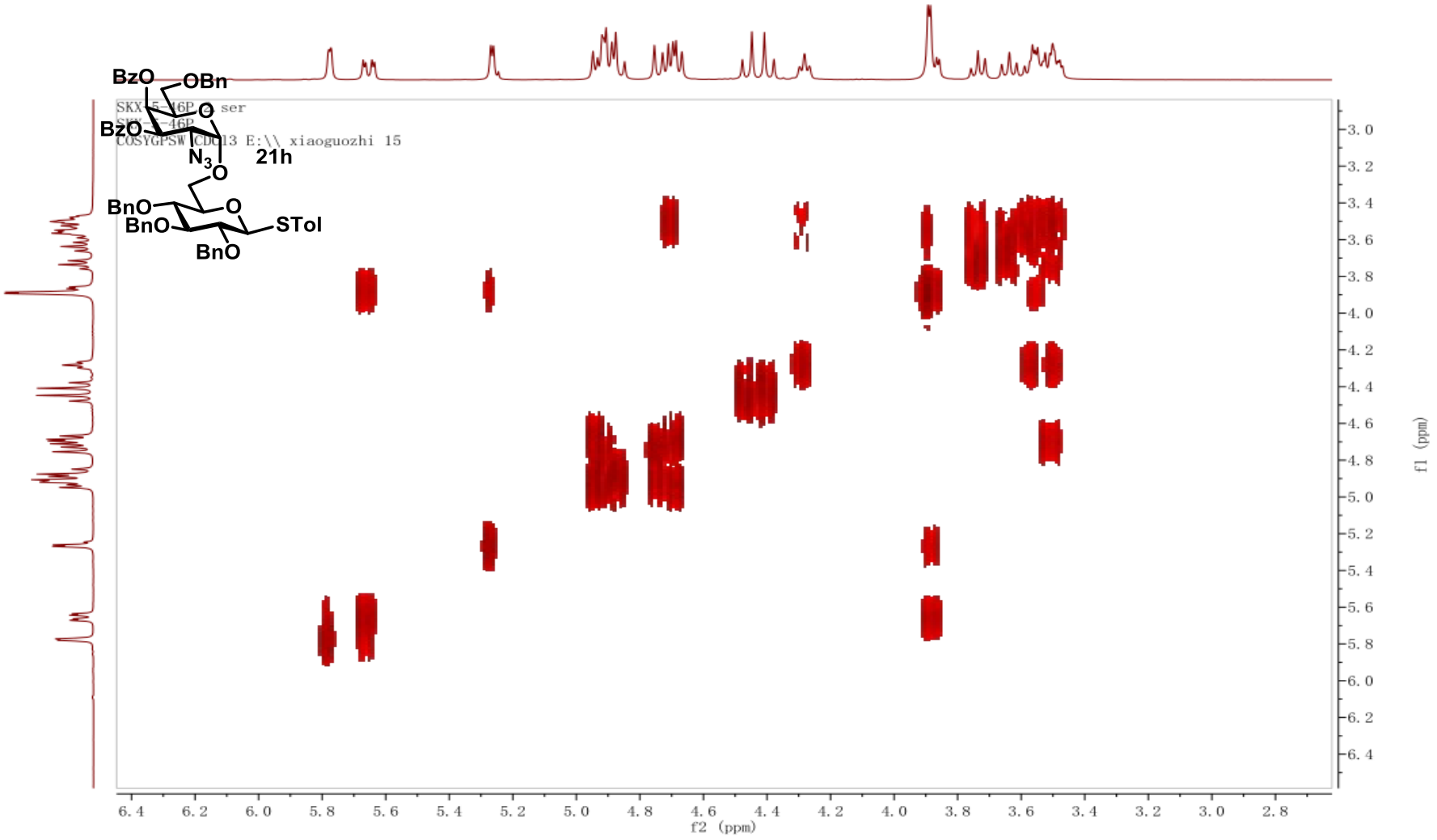

SKX-5-29.3.fid
SKX-5-29
c13 CDCl3 E:\\ xiaoguozhi
155.31
138.81
138.33
138.19
137.59
133.36
133.20
129.77
129.73
129.48
129.29
128.53
128.46
128.43
128.35
128.29
128.09
127.91
127.87
127.75
127.61
127.55
98.52
98.06
82.10
80.11
77.76
75.65
75.06
73.42
73.37
70.07
68.88
68.12
66.72
58.45
55.23
BzO
OBn
O
BzO
N3
O
21g
BnO
O
BnO
BnO
OMe
f1 (ppm)

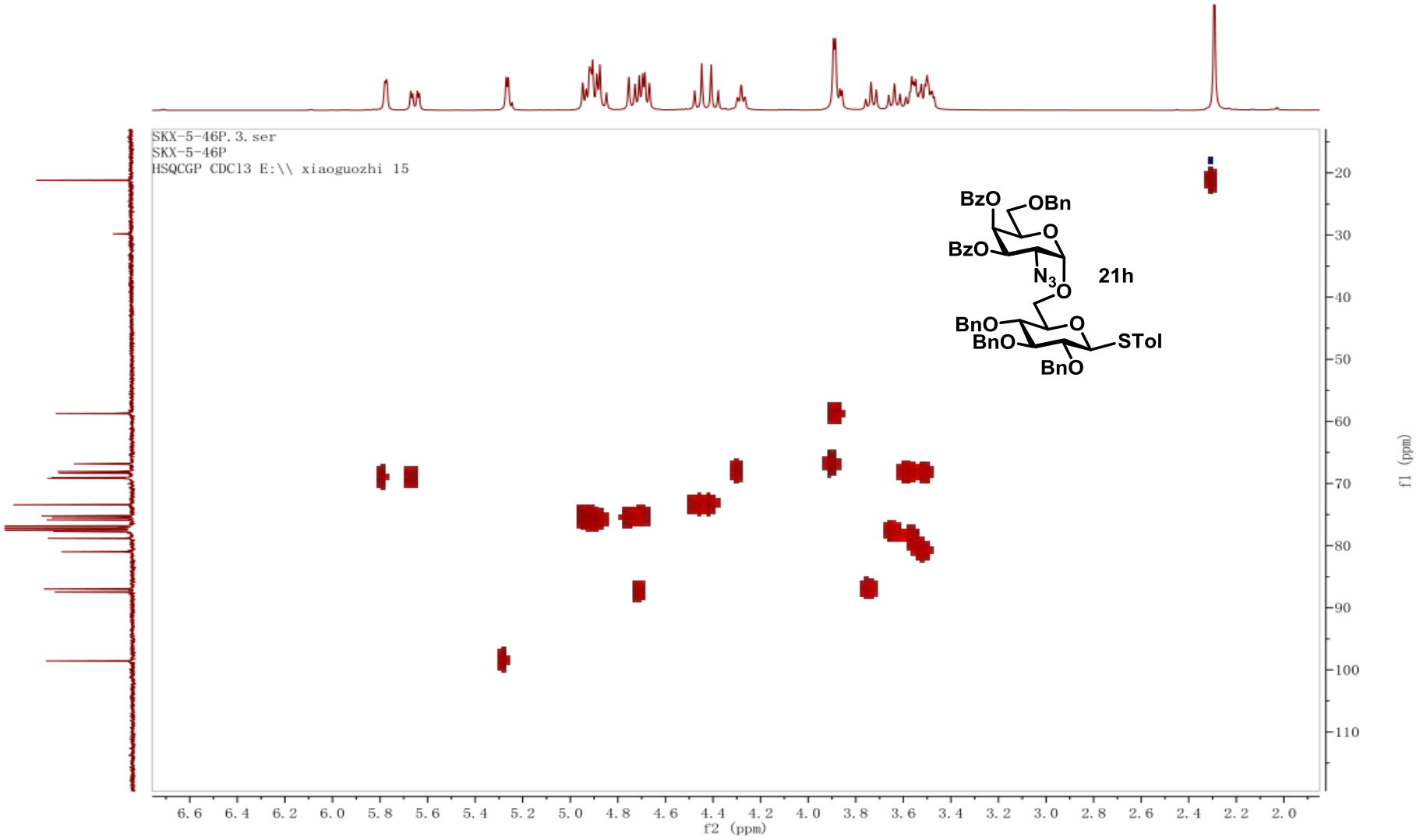

SKX-5-29.2.ser
SKX-5-29
COSYGPSW CDCl3 E:\\ xiaoguozhi 11
BzO
OBn
O
BzO
N3
O
21g
BnO
BnO
O
BnO
OMe
6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7
f2 (ppm)
3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4
f1 (ppm)

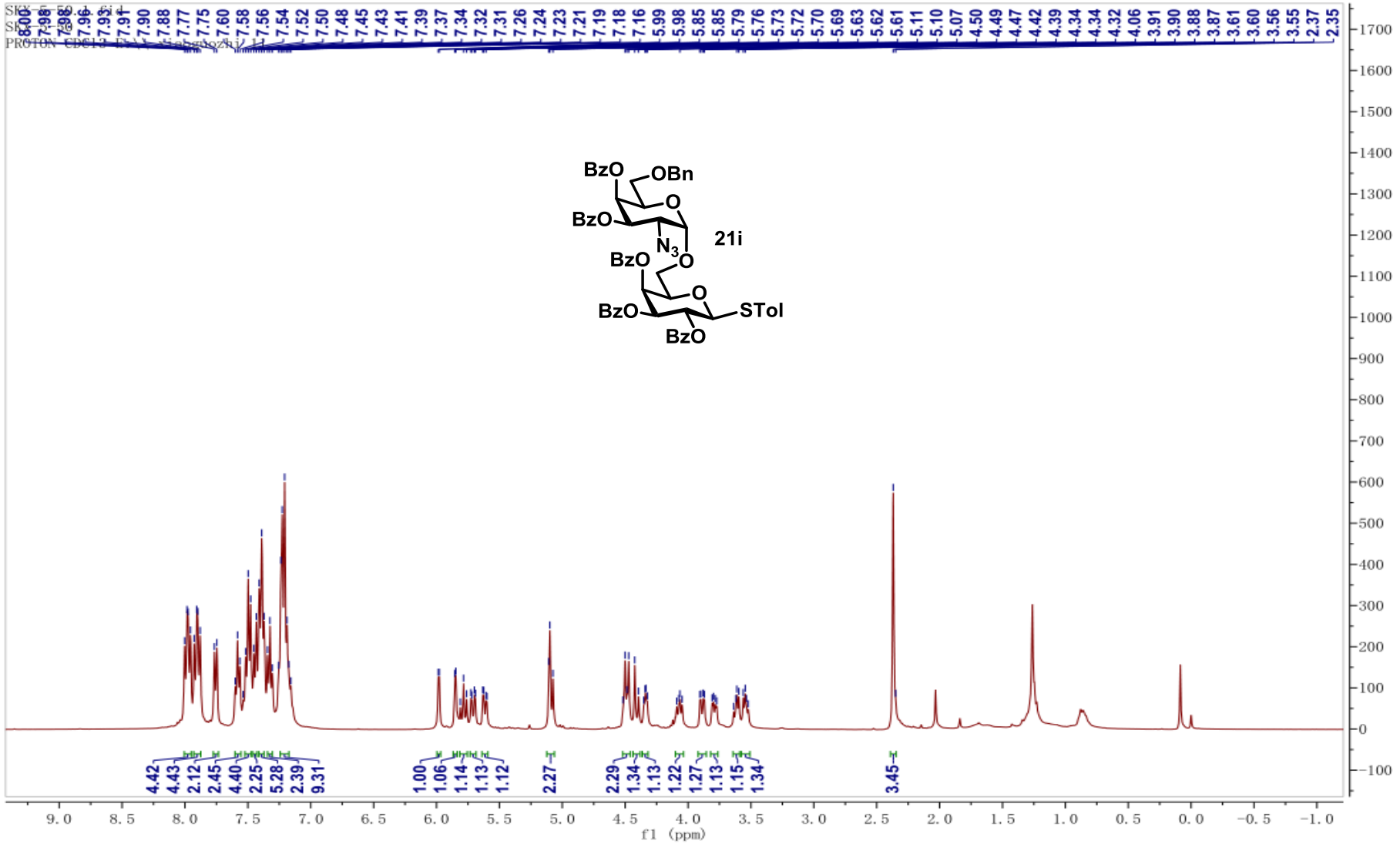

SKX-5-29.4.ser
SKX-5-29
HSQCGP CDCl3 E:\\ xiaoguozhi 11
BzO
OBn
O
BzO
N3
O
21g
BnO
BnO
O
BnO
OMe
f2 (ppm)
f1 (ppm)

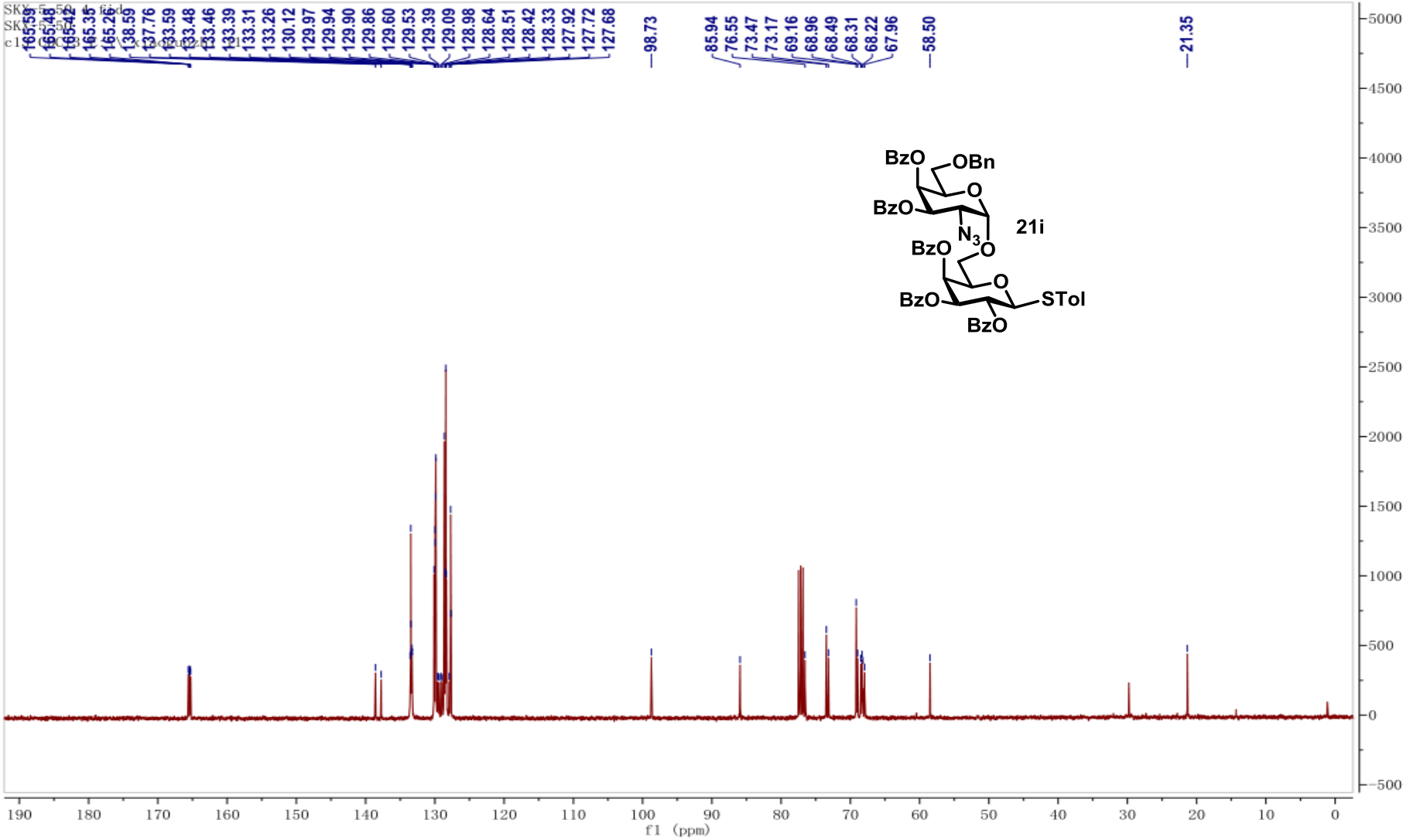

BzO
OBn
O
BzO
N3
O
21h
BnO
O
BnO
STol
BnO
f1 (ppm)

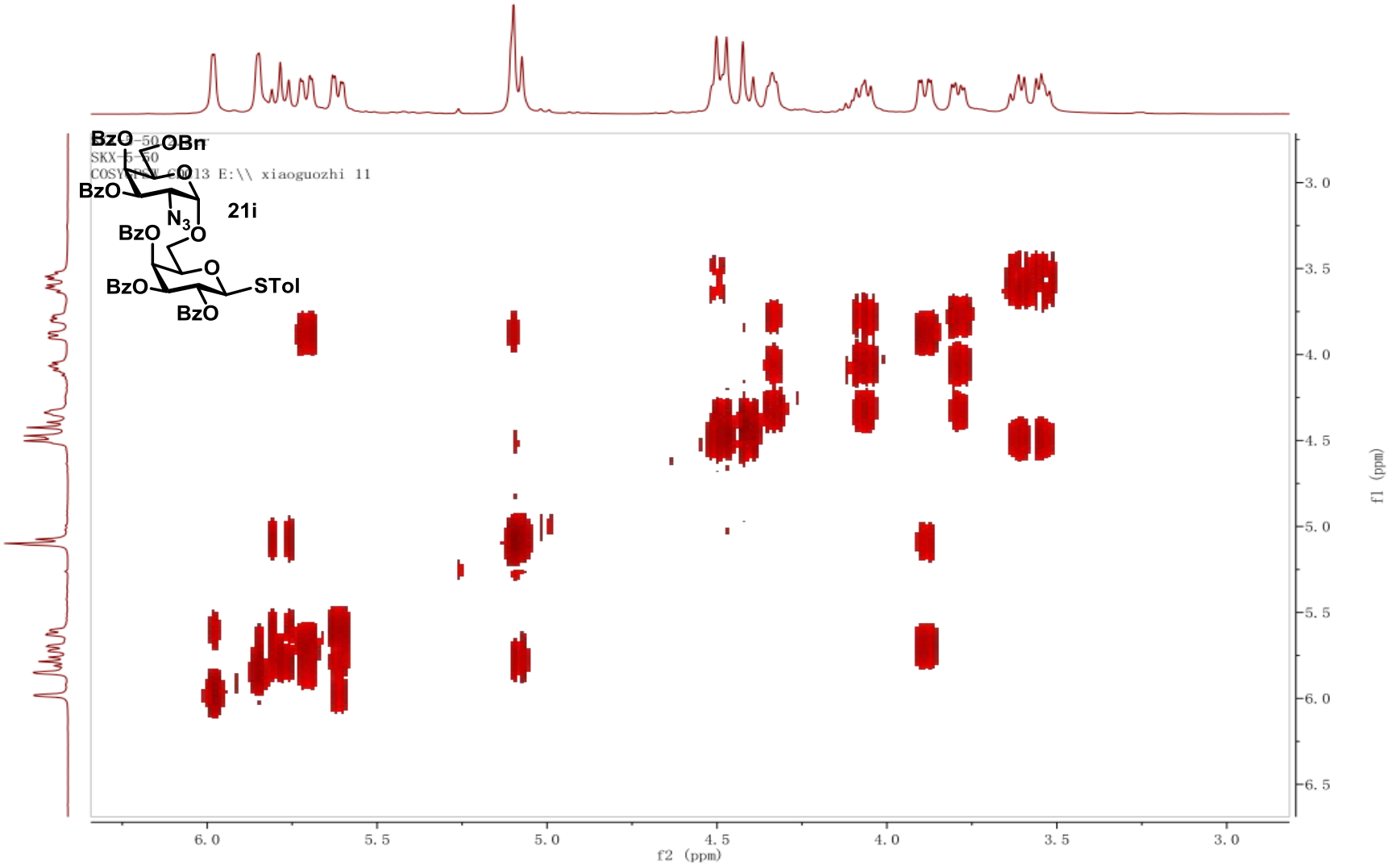

SKX-5-46b
SKX-5-46
c13 CDCl3
165.46
165.29
138.50
138.23
138.19
137.85
137.83
133.47
133.32
132.10
129.98
129.91
129.88
129.84
129.66
129.44
128.65
128.63
128.53
128.50
128.43
128.38
128.28
128.02
127.98
127.92
127.89
127.78
127.69
127.66
98.56
87.47
86.98
80.98
78.81
77.73
75.86
75.51
75.21
73.41
69.16
69.03
68.33
68.05
66.84
58.71
21.16
BzO
OBn
O
BzO
N3
O
21h
BnO
O
BnO
STol
BnO
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

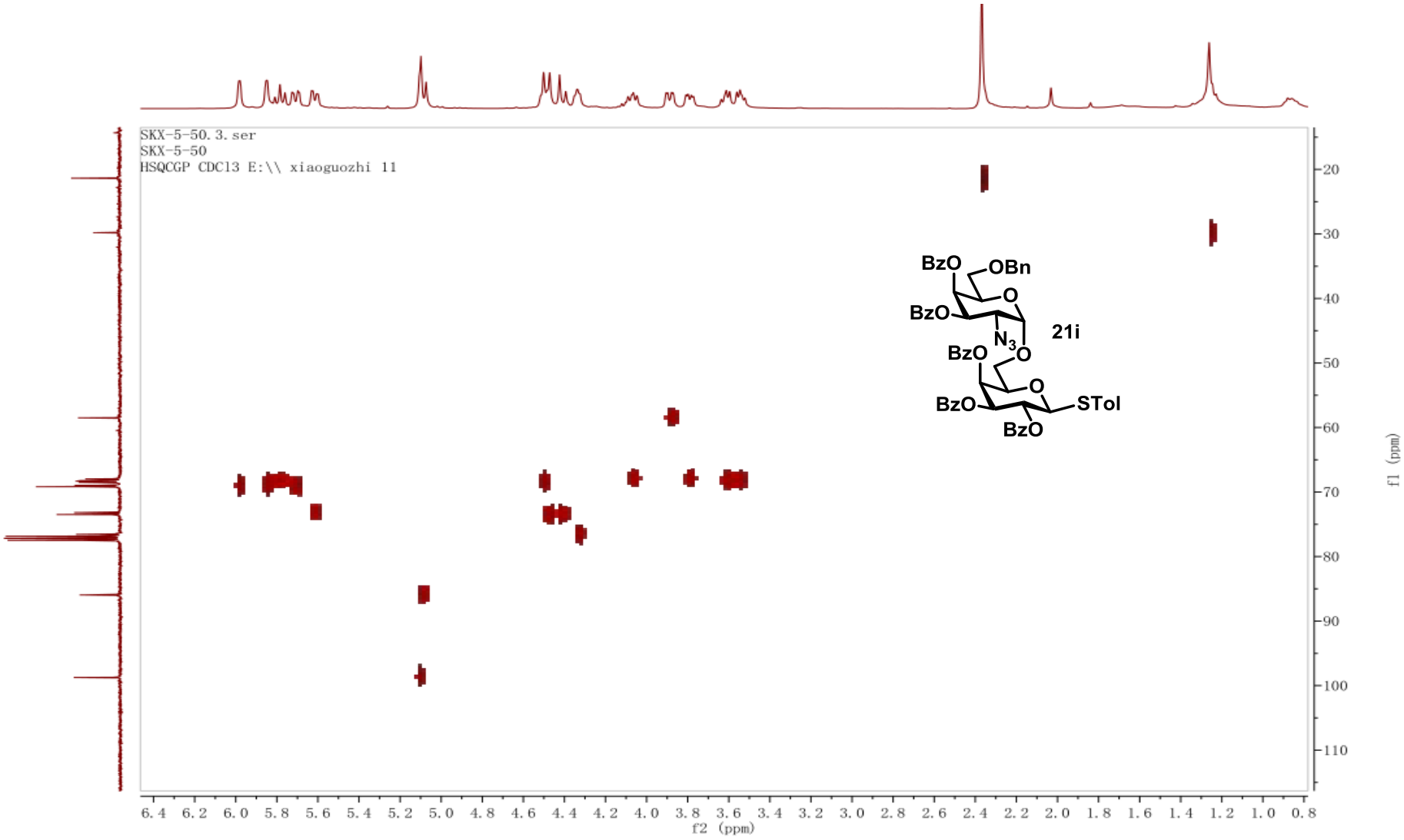

BzO
OBn
O
BzO
N3
21h
O
BnO
O
BnO
STol
BnO
f2 (ppm)
f1 (ppm)

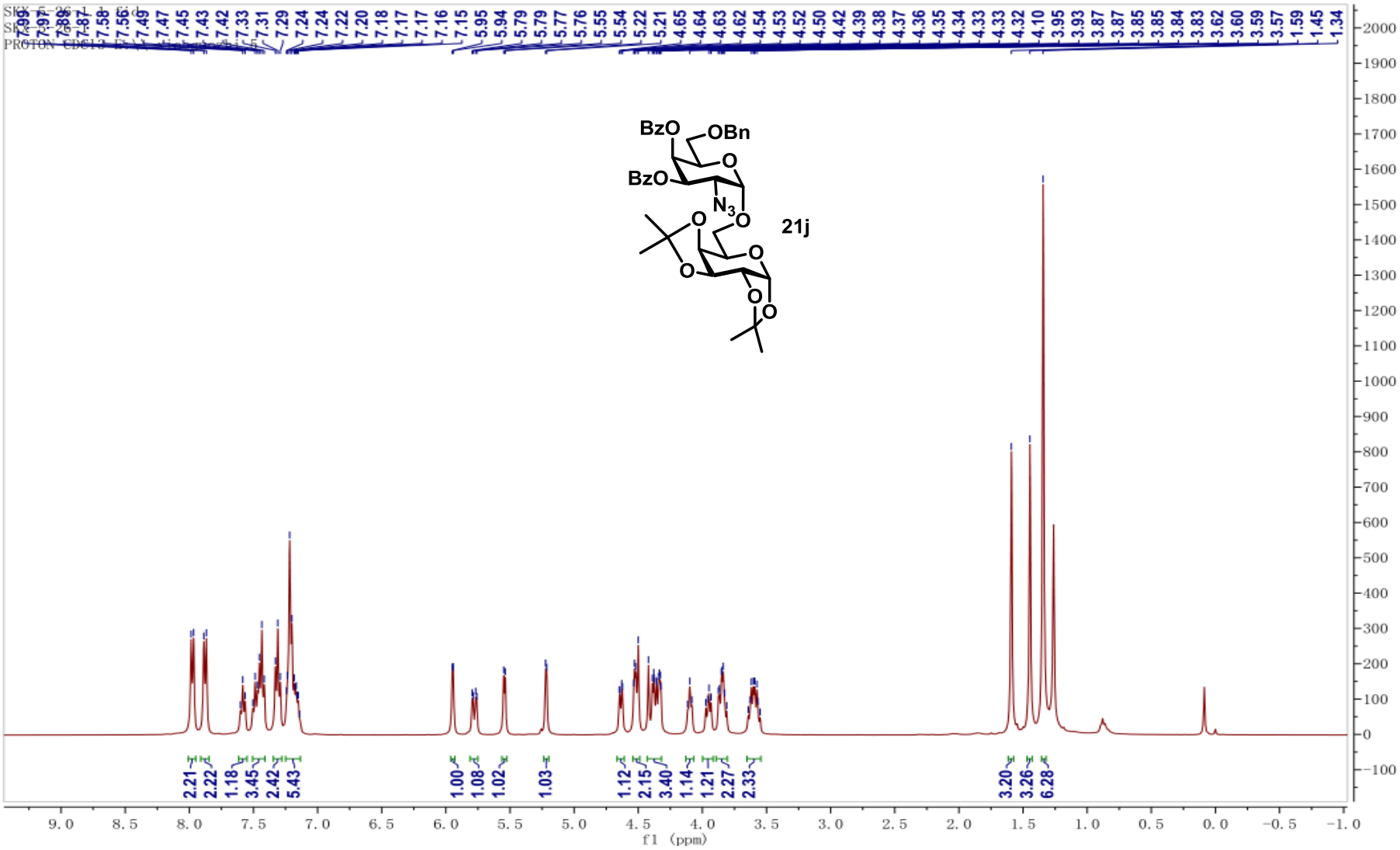

SKX-5-46P.3.ser
SKX-5-46P
HSQCGP CDCl3 E:\\ xiaoguozhi 15
BzO
OBn
O
BzO
N3
O
21h
BnO
BnO
O
STol
BnO
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f2 (ppm)
20 30 40 50 60 70 80 90 100 110
f1 (ppm)

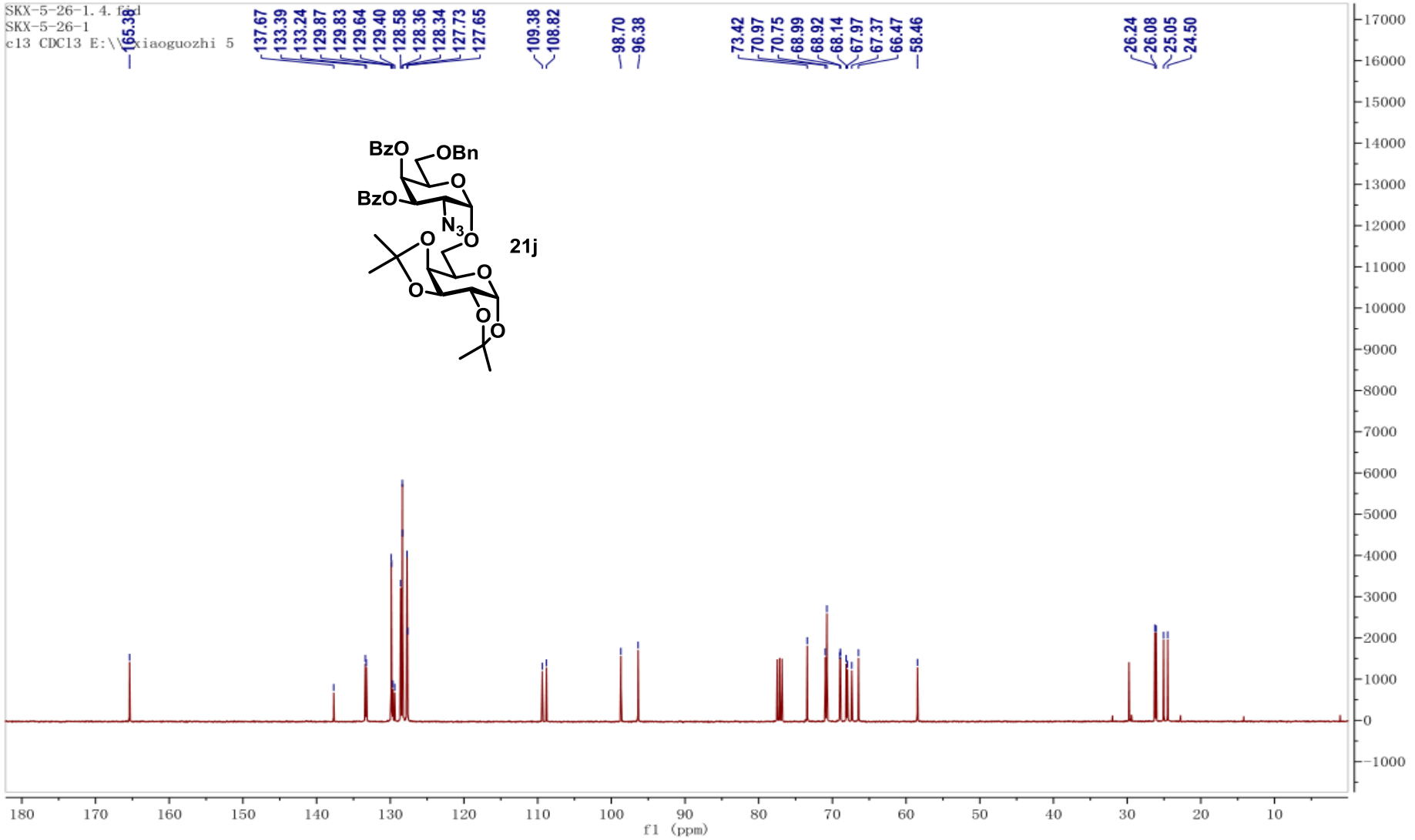

BzO
OBn
O
BzO
N3
21i
BzO
O
O
BzO
STol
BzO
4.42
4.43
2.12
2.45
4.40
2.25
5.28
2.39
9.31
1.00
1.06
1.14
1.13
1.12
2.27
2.29
1.34
1.13
1.22
1.27
1.13
1.15
1.34
3.45
f1 (ppm)

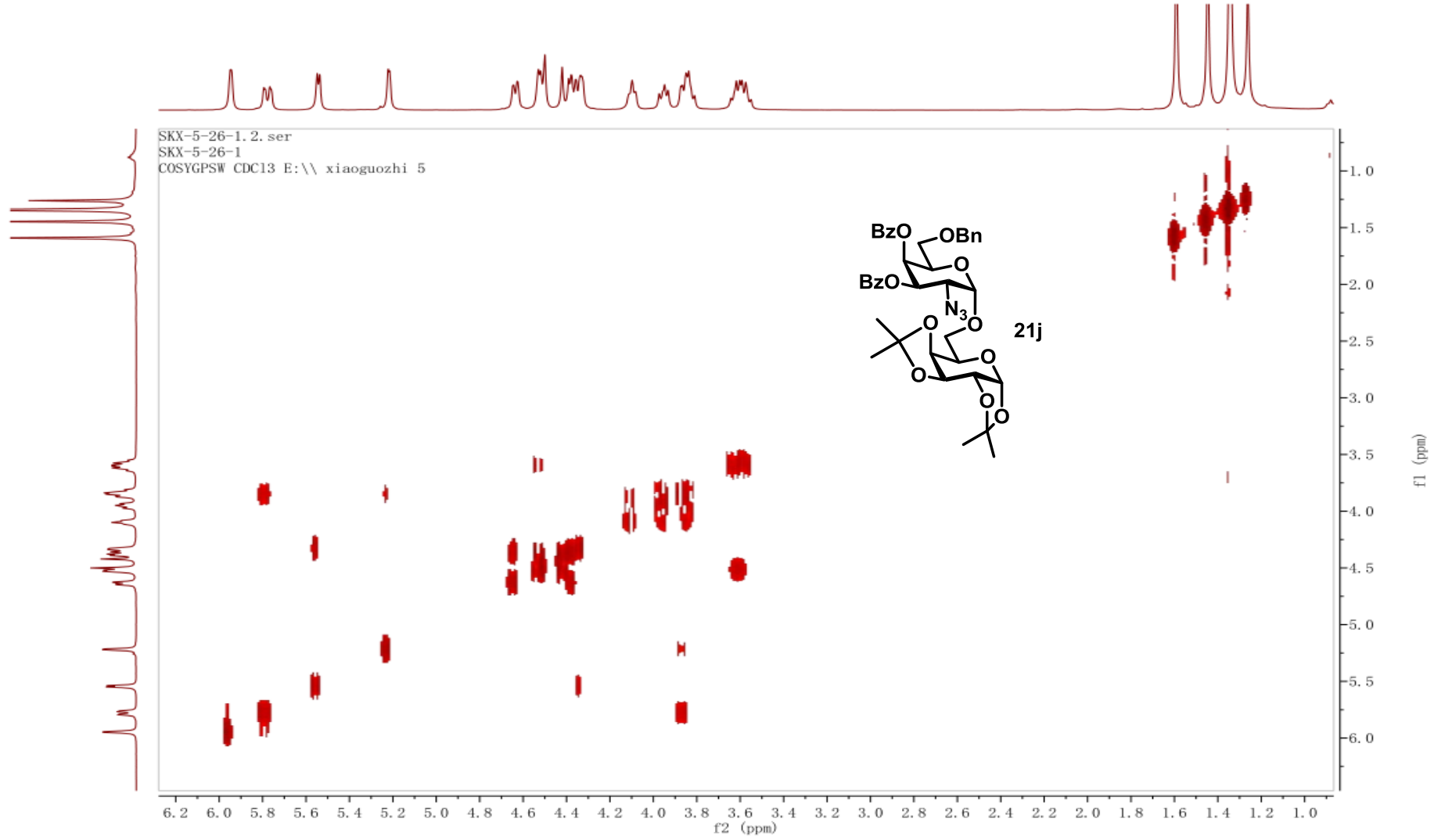

165.59
165.48
165.42
165.35
165.26
138.59
137.76
133.59
133.48
133.46
133.39
133.31
133.26
130.12
129.97
129.94
129.90
129.86
129.60
129.53
129.39
129.09
128.98
128.64
128.51
128.42
128.33
127.92
127.72
127.68
98.73
85.94
76.55
73.47
73.17
69.16
68.96
68.49
68.31
68.22
67.96
58.50
21.35
BzO
OBn
O
BzO
N3
21i
BzO
O
O
BzO
STol
BzO
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

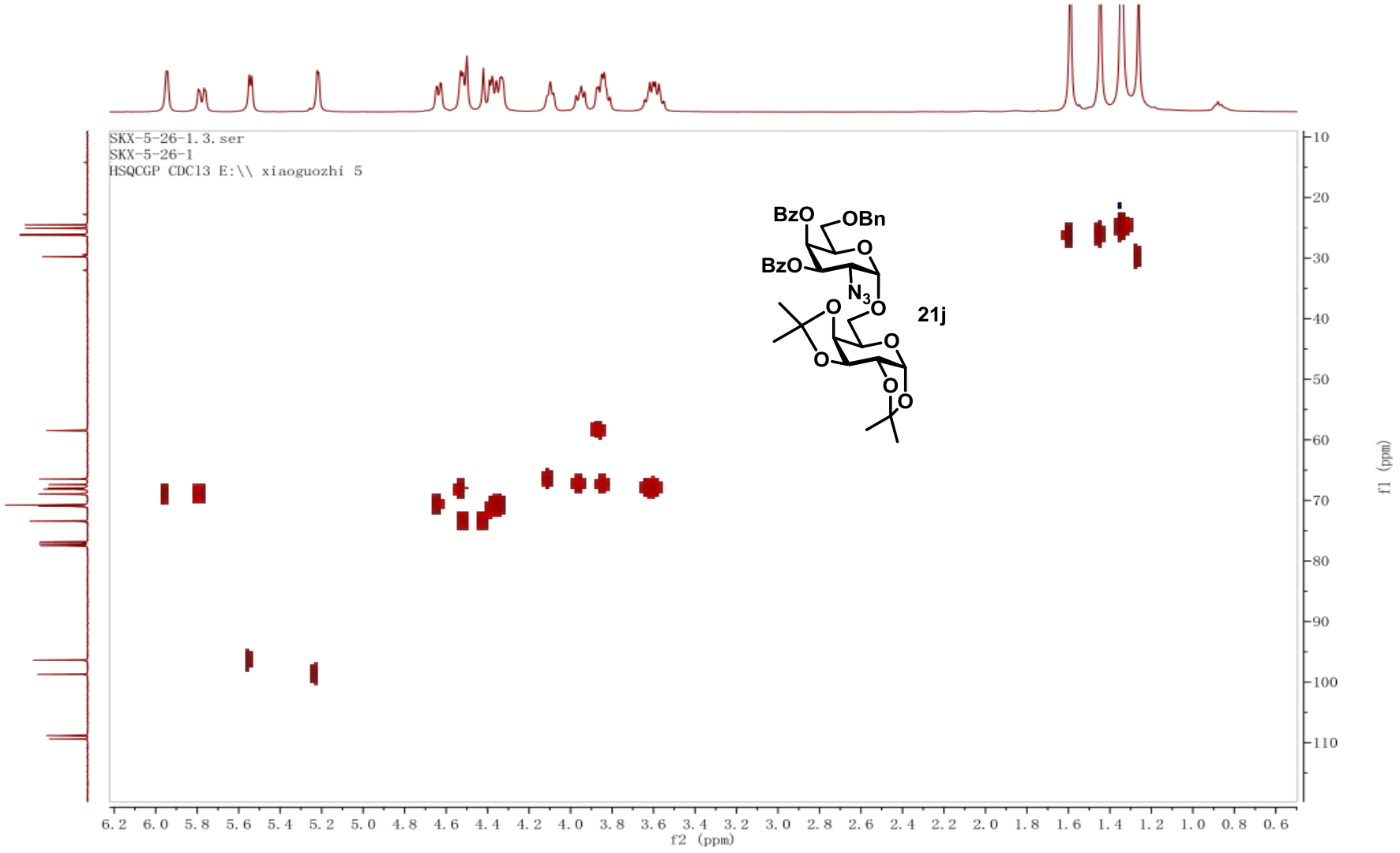

BzO
OBn
BzO
O
N3
O
21i
BzO
O
BzO
STol
BzO
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
f1 (ppm)

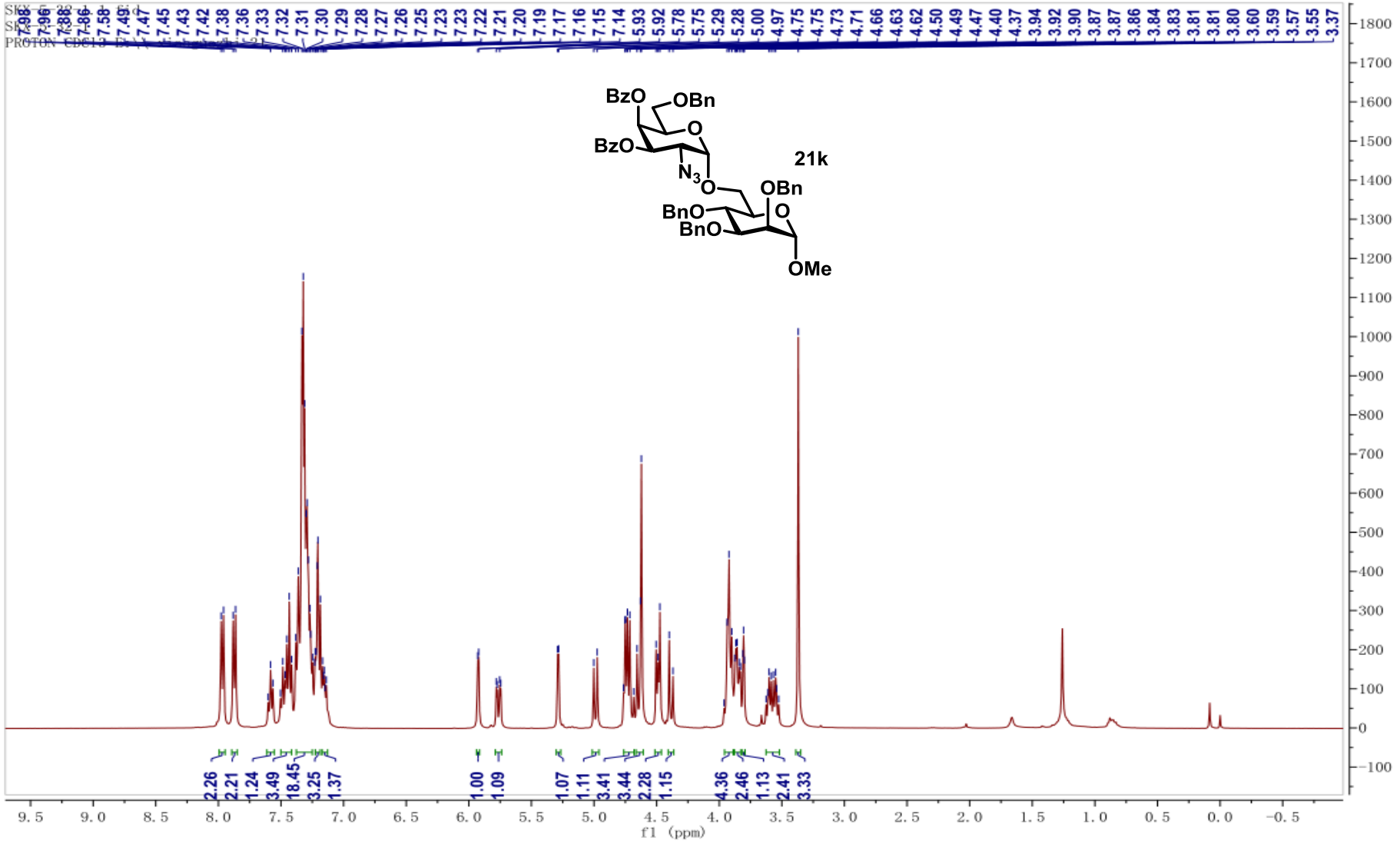

SKX-5-50.3.ser
SKX-5-50
HSQCGP CDCl3 E:\\ xiaoguozhi 11
BzO
OBn
O
BzO
N3
21i
BzO
O
O
BzO
STol
BzO
f2 (ppm)
f1 (ppm)

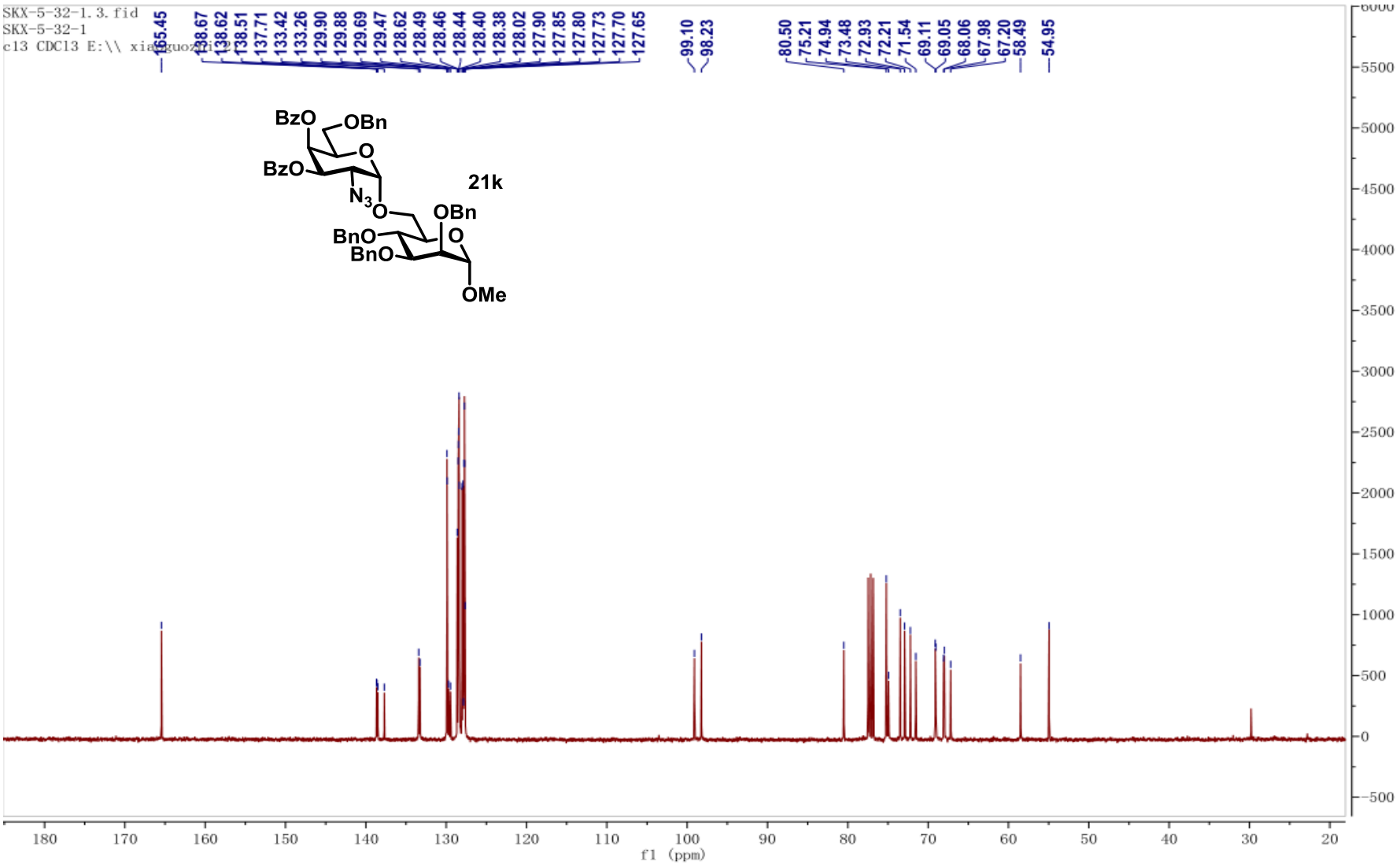

BzO
OBn
BzO
N3
21j
f1 (ppm)

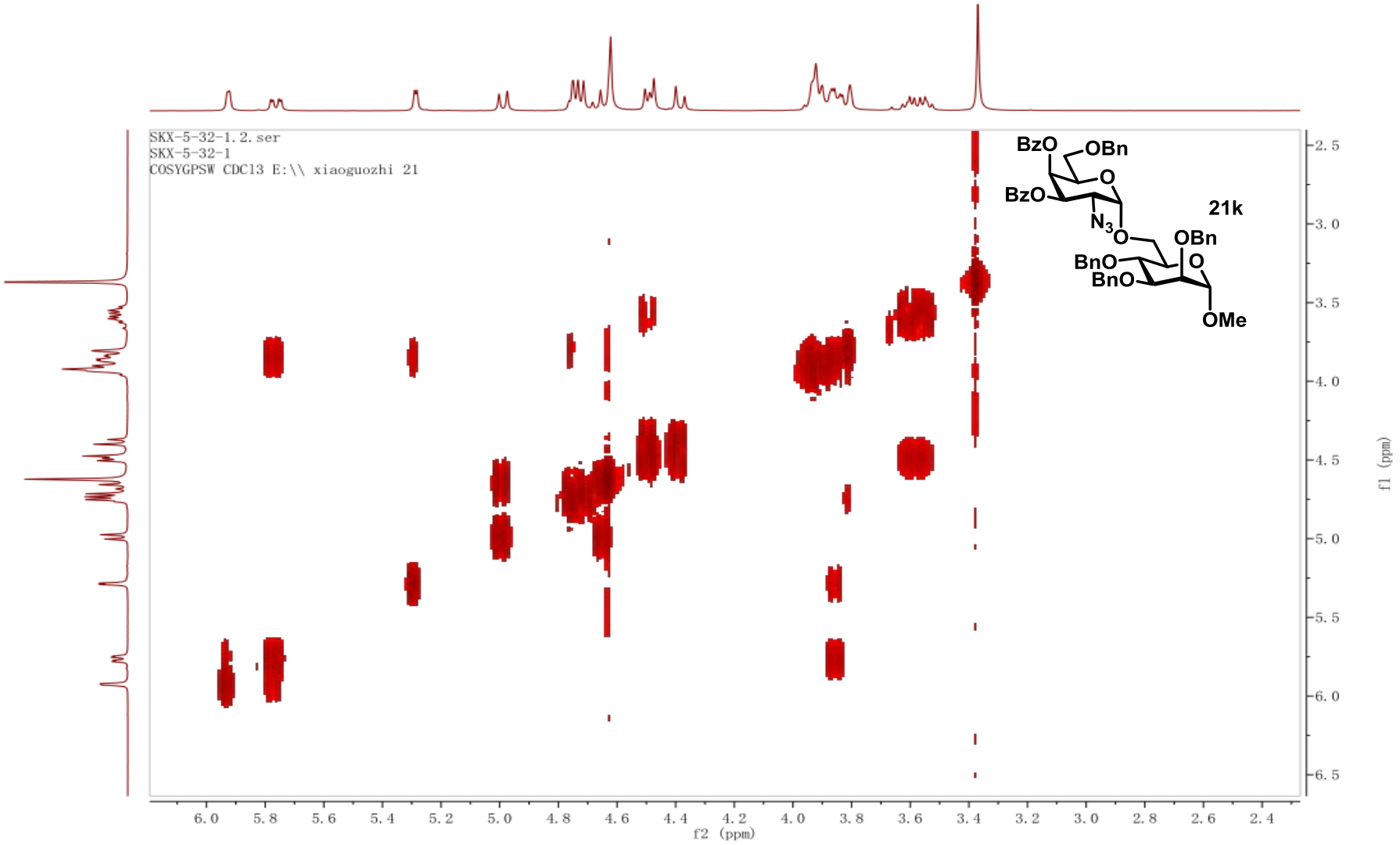

SKX-5-26-1.4.fid
SKX-5-26-1
c13 CDCl3 E:\\xiaoguozhi 5
165.38
137.67
133.39
133.24
129.87
129.83
129.64
129.40
128.58
128.36
128.34
127.73
127.65
109.38
108.82
98.70
96.38
73.42
70.97
70.75
68.99
68.92
68.14
67.97
67.37
66.47
58.46
26.24
26.08
25.05
24.50
BzO
OBn
BzO
N3
O
21j
f1 (ppm)

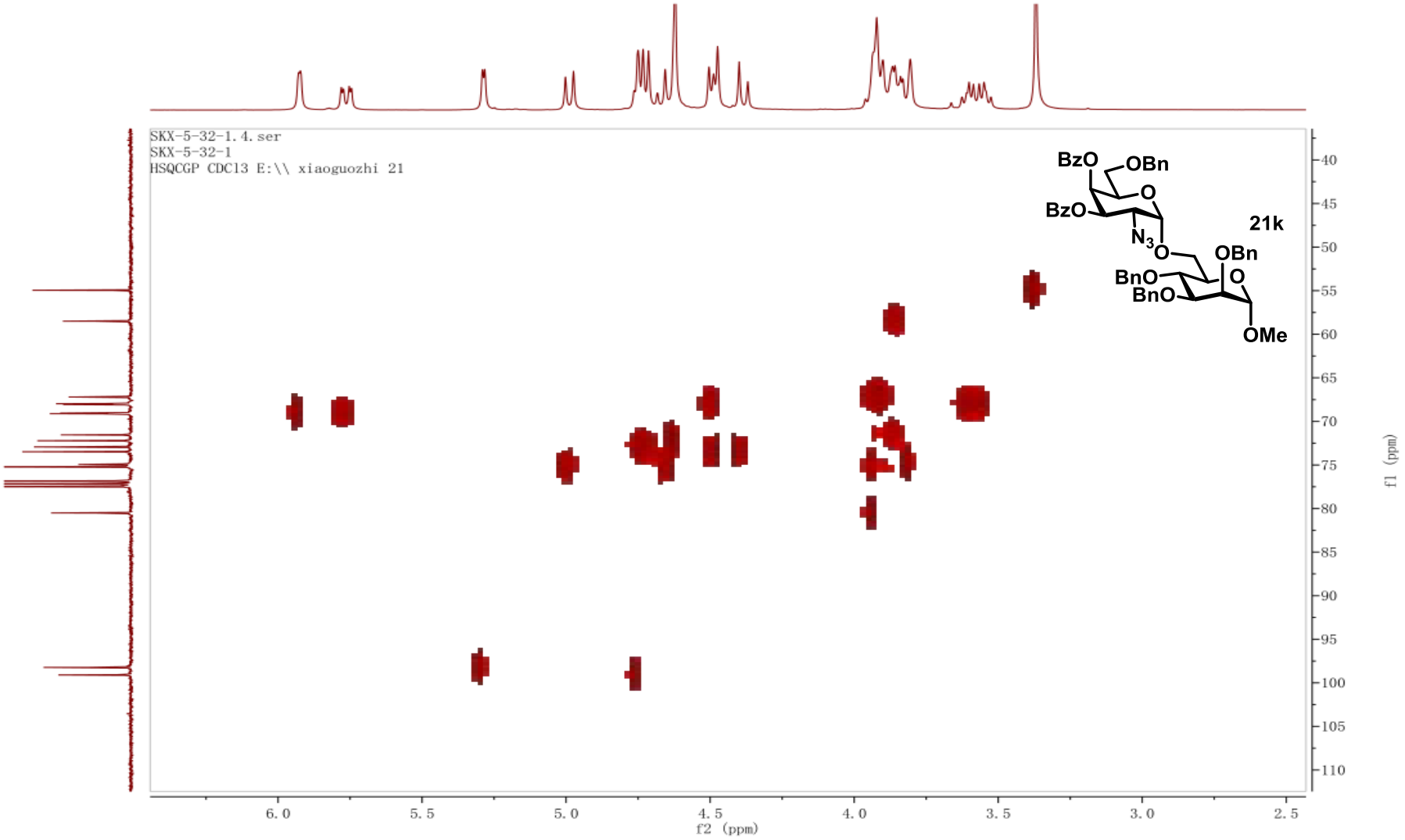

SKX-5-26-1.2.ser
SKX-5-26-1
COSYGPSW CDC13 E:\\ xiaoguozhi 5
BzO
OBn
BzO
N3
O
21j
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
f1 (ppm)

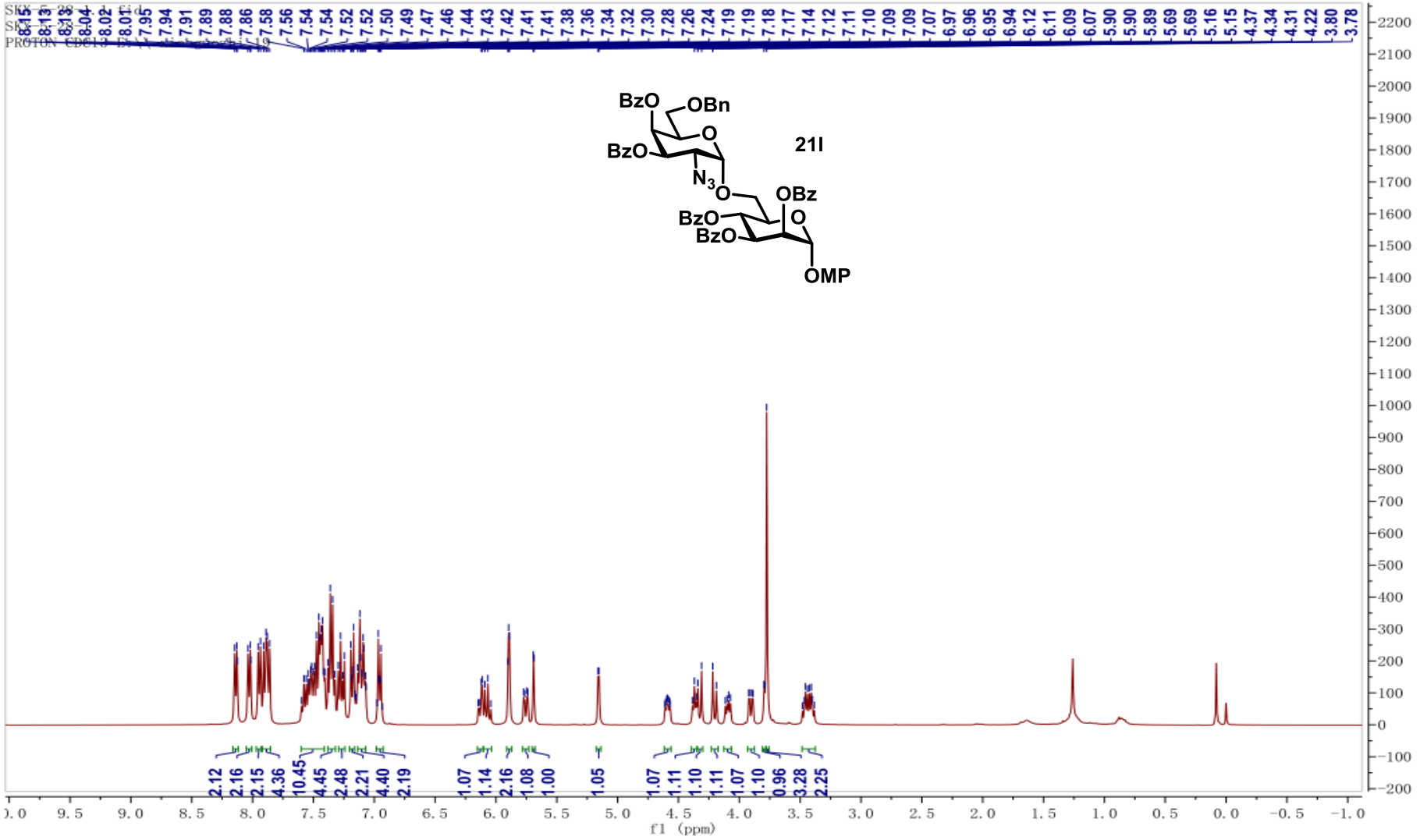

SKX-5-26-1.3.ser
SKX-5-26-1
HSQCGP CDC13 E:\\ xiaoguozhi 5
BzO
OBn
BzO
N3
O
21j
f2 (ppm)
f1 (ppm)

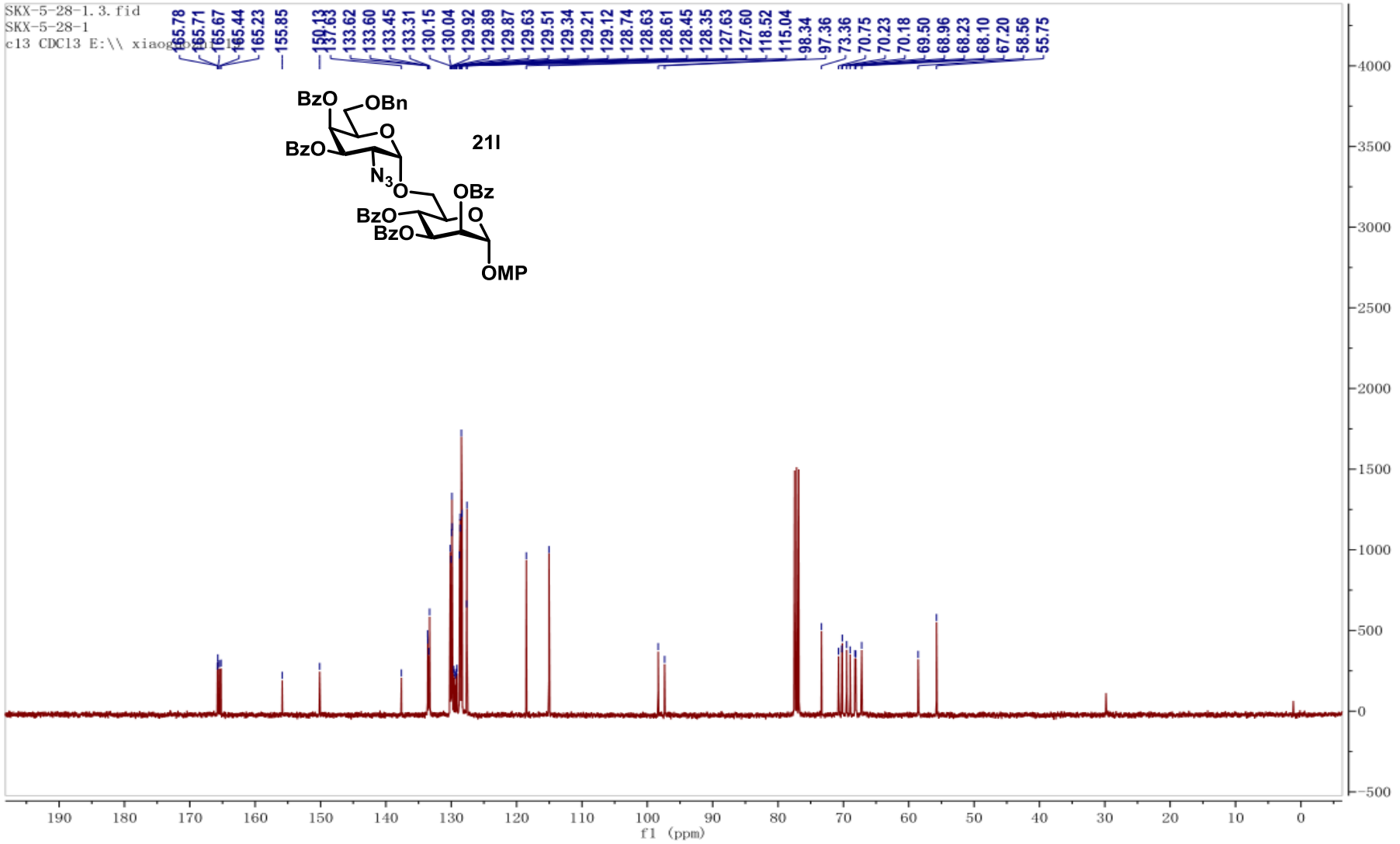

BzO
OBn
O
BzO
N3
O
21k
OBn
BnO
O
BnO
OMe
2.26
2.21
1.24
3.49
18.45
3.25
1.37
1.00
1.09
1.07
1.11
3.41
3.44
2.28
1.15
4.36
2.46
1.13
2.41
3.33
f1 (ppm)

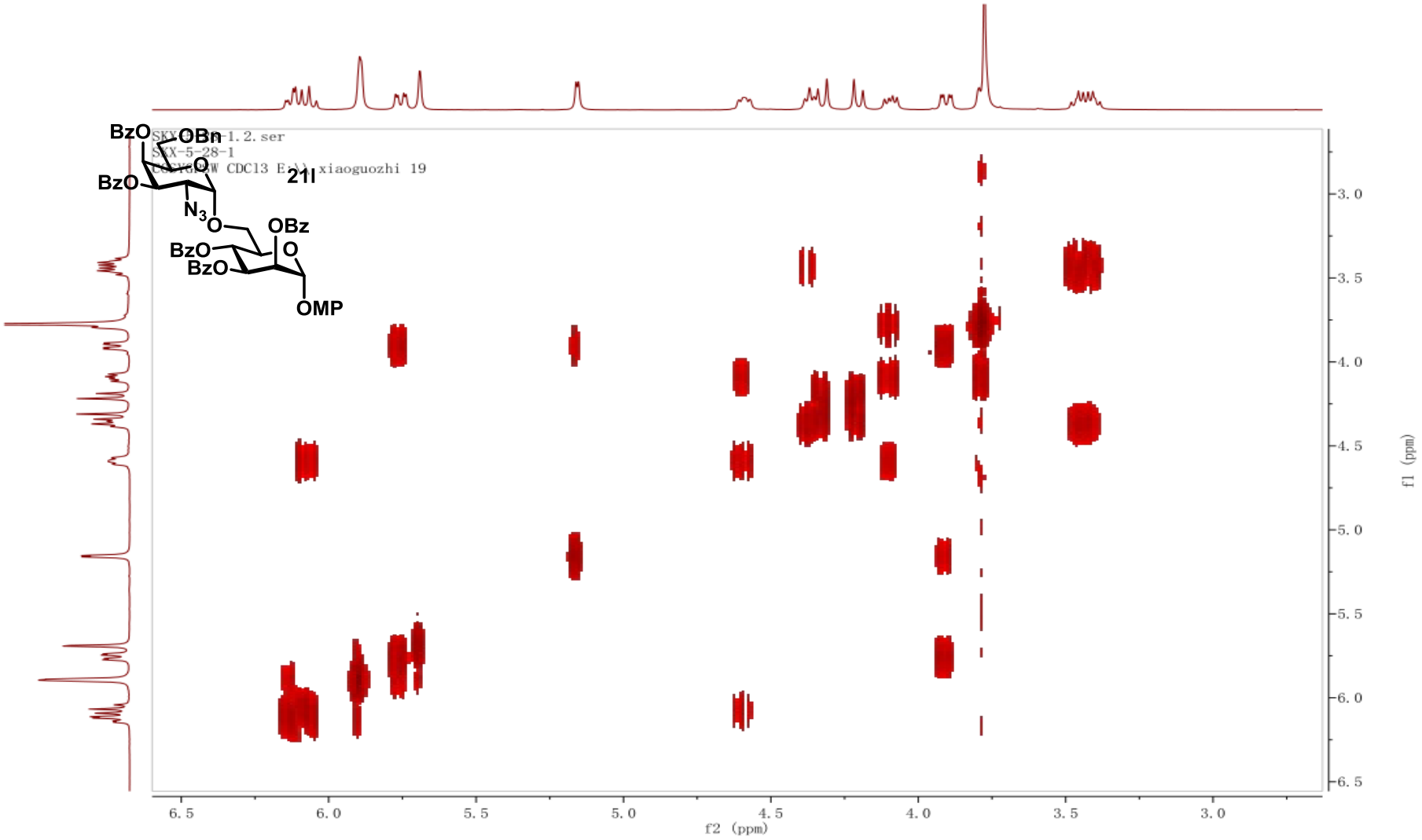

SKX-5-32-1.3.fid
SKX-5-32-1
c13 CDCl3 E:\\ xiangguozhi\data
165.45
138.67
138.62
138.51
137.71
133.42
133.26
129.90
129.88
129.69
129.47
128.62
128.49
128.46
128.44
128.40
128.38
128.02
127.90
127.85
127.80
127.73
127.70
127.65
99.10
98.23
80.50
75.21
74.94
73.48
72.93
72.21
71.54
69.11
69.05
68.06
67.98
67.20
58.49
54.95
BzO
OBn
O
BzO
N3
O
21k
OBn
BnO
O
BnO
OMe
f1 (ppm)

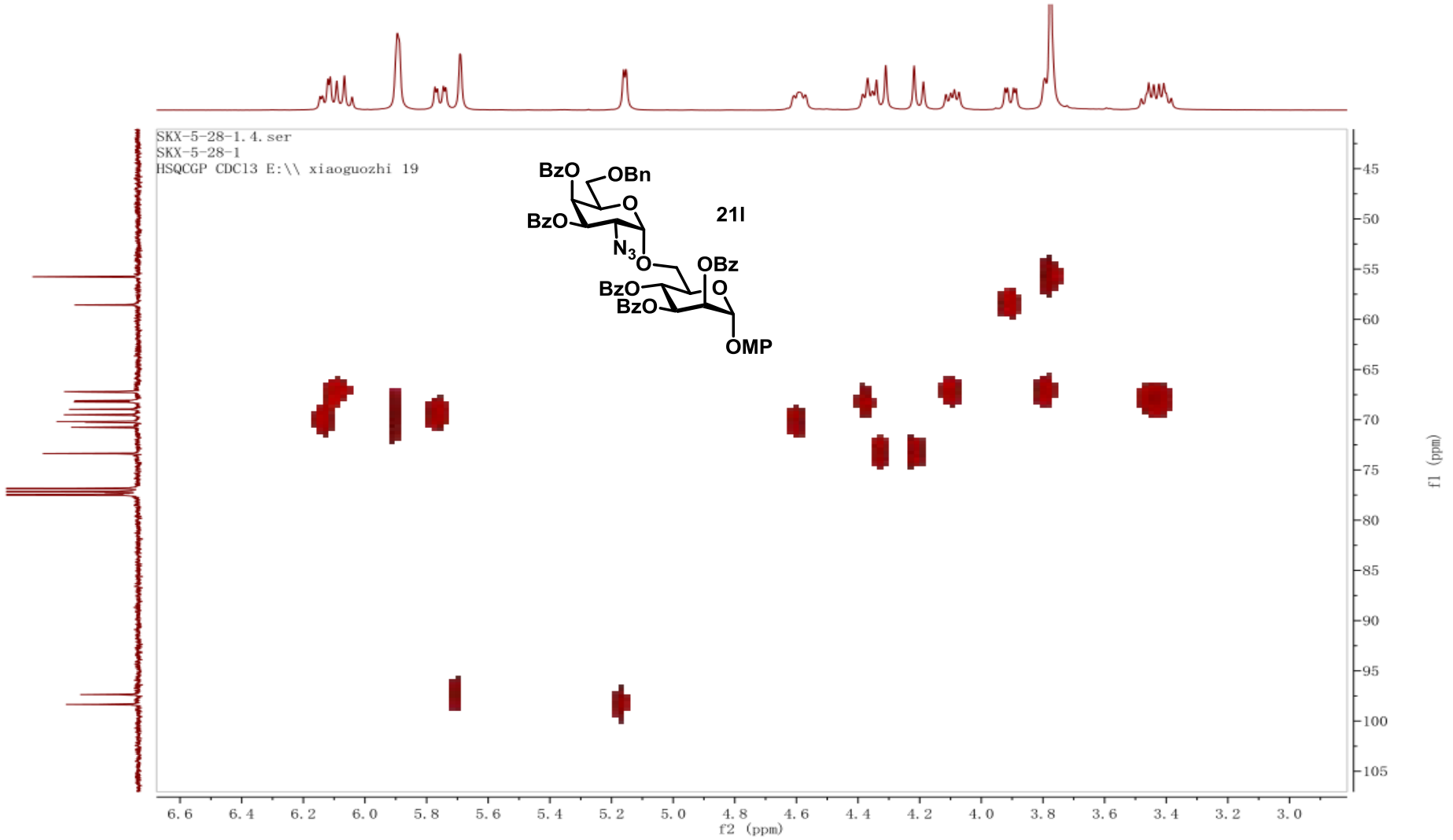

SKX-5-32-1.2.ser
SKX-5-32-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 21
BzO
OBn
O
BzO
N3
O
21k
OBn
BnO
O
BnO
OMe
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

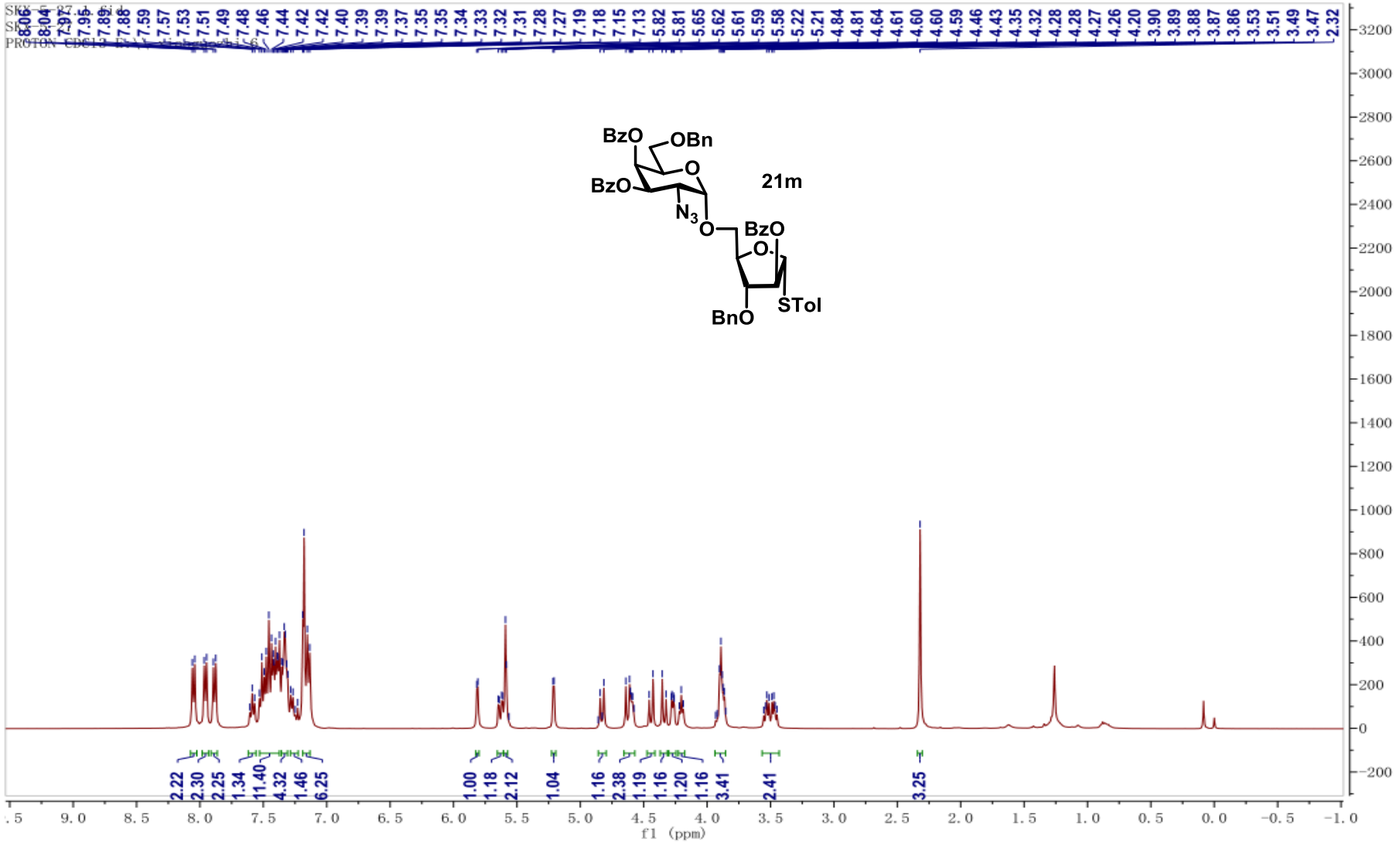

SKX-5-32-1.4.ser
SKX-5-32-1
HSQCGP CDCl3 E:\\ xiaoguozhi 21
BzO
OBn
O
BzO
N3
O
21k
OBn
BnO
O
BnO
OMe
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)

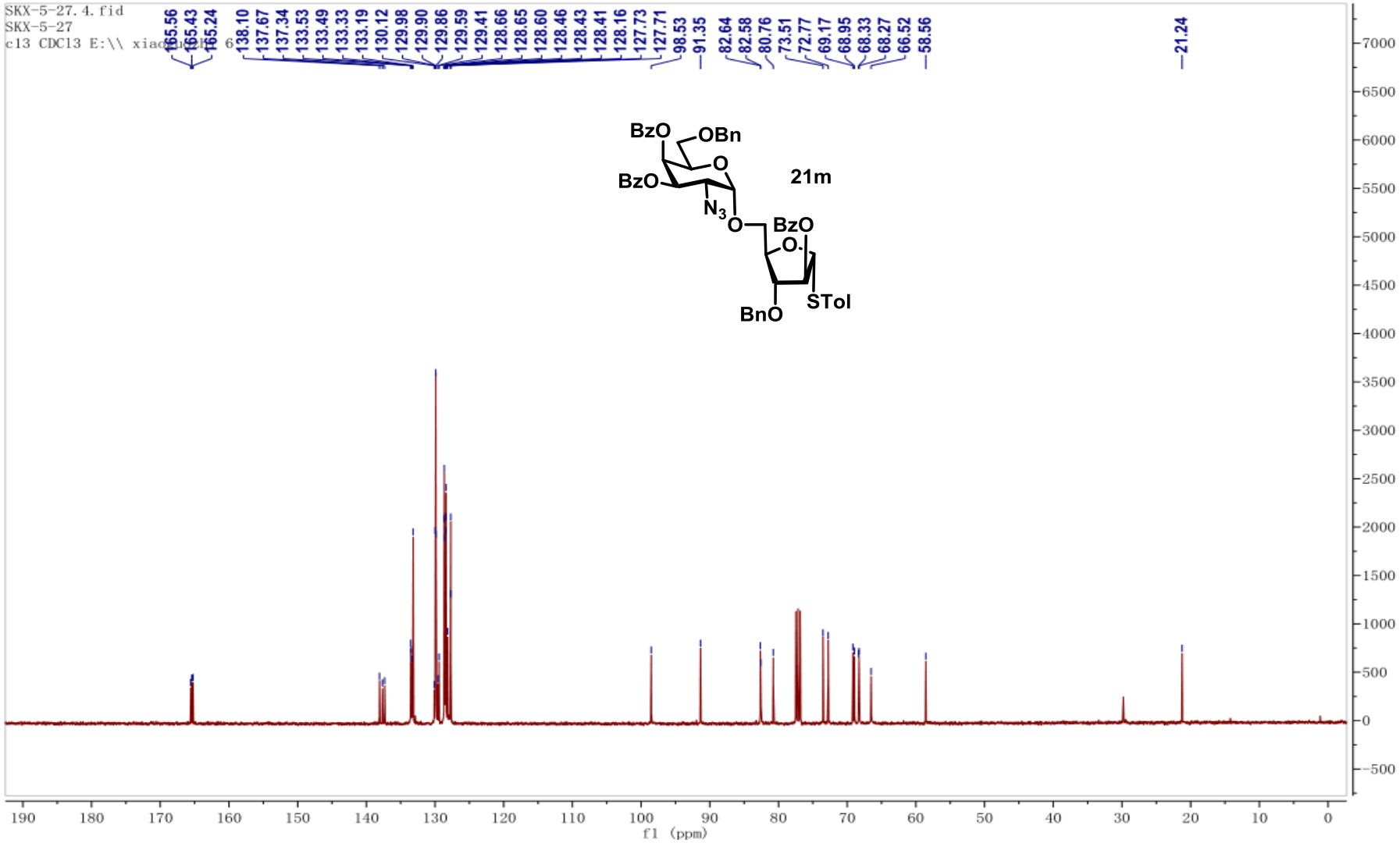

BzO
OBn
O
BzO
N3
O
OBz
BzO
O
BzO
OMP
21l
f1 (ppm)

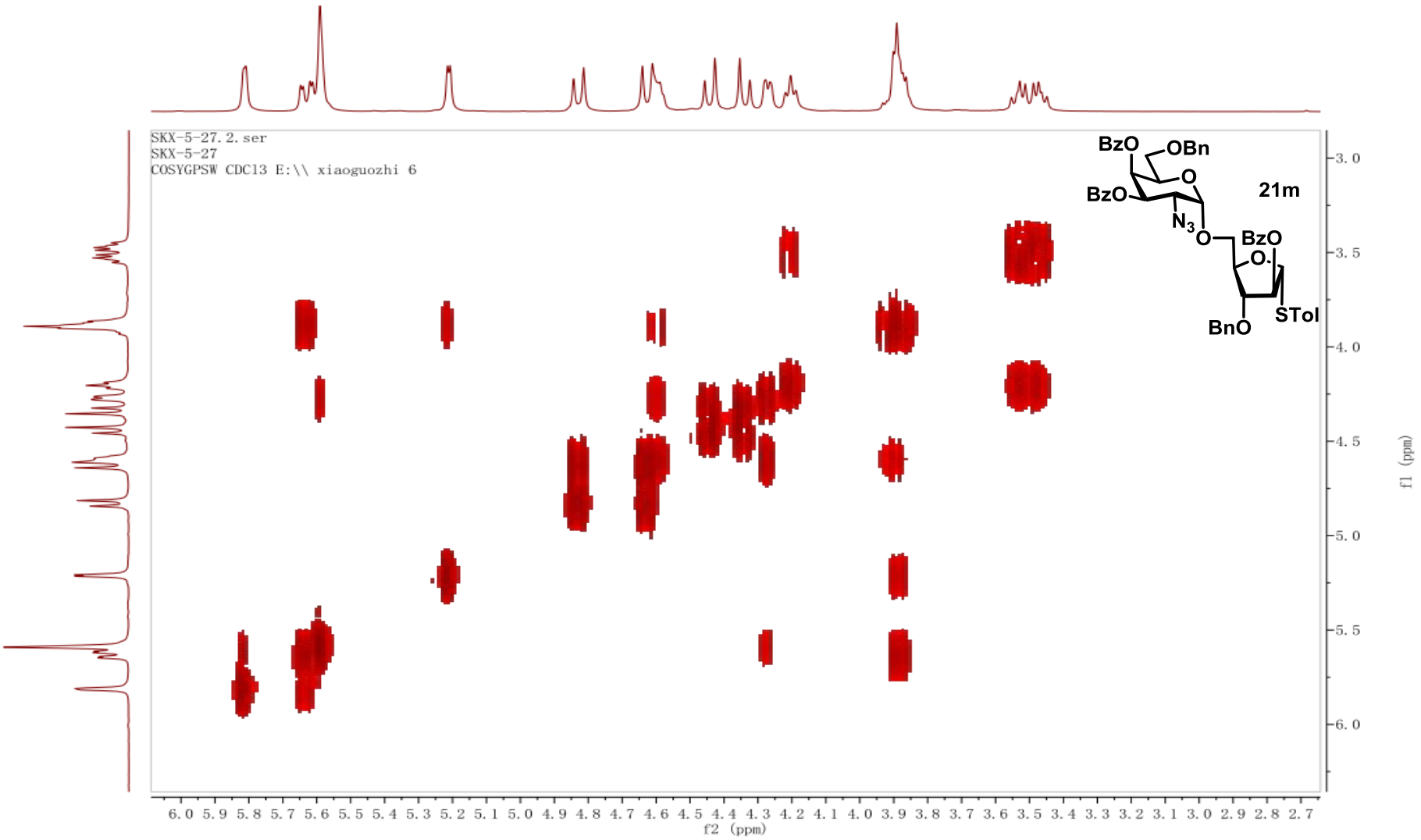

SKX-5-28-1.3.fid
SKX-5-28-1
c13 CDCl3 E:\\ xiaoguo
165.78
165.71
165.67
165.44
165.23
155.85
150.13
137.63
133.62
133.60
133.45
133.31
130.15
130.04
129.92
129.89
129.87
129.63
129.51
129.34
129.21
129.12
128.74
128.63
128.61
128.45
128.35
127.63
127.60
118.52
115.04
98.34
97.36
73.36
70.75
70.23
70.18
69.50
68.96
68.23
68.10
67.20
58.56
55.75
BzO
OBn
O
BzO
N3
O
OBz
BzO
O
BzO
OMP
21l
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

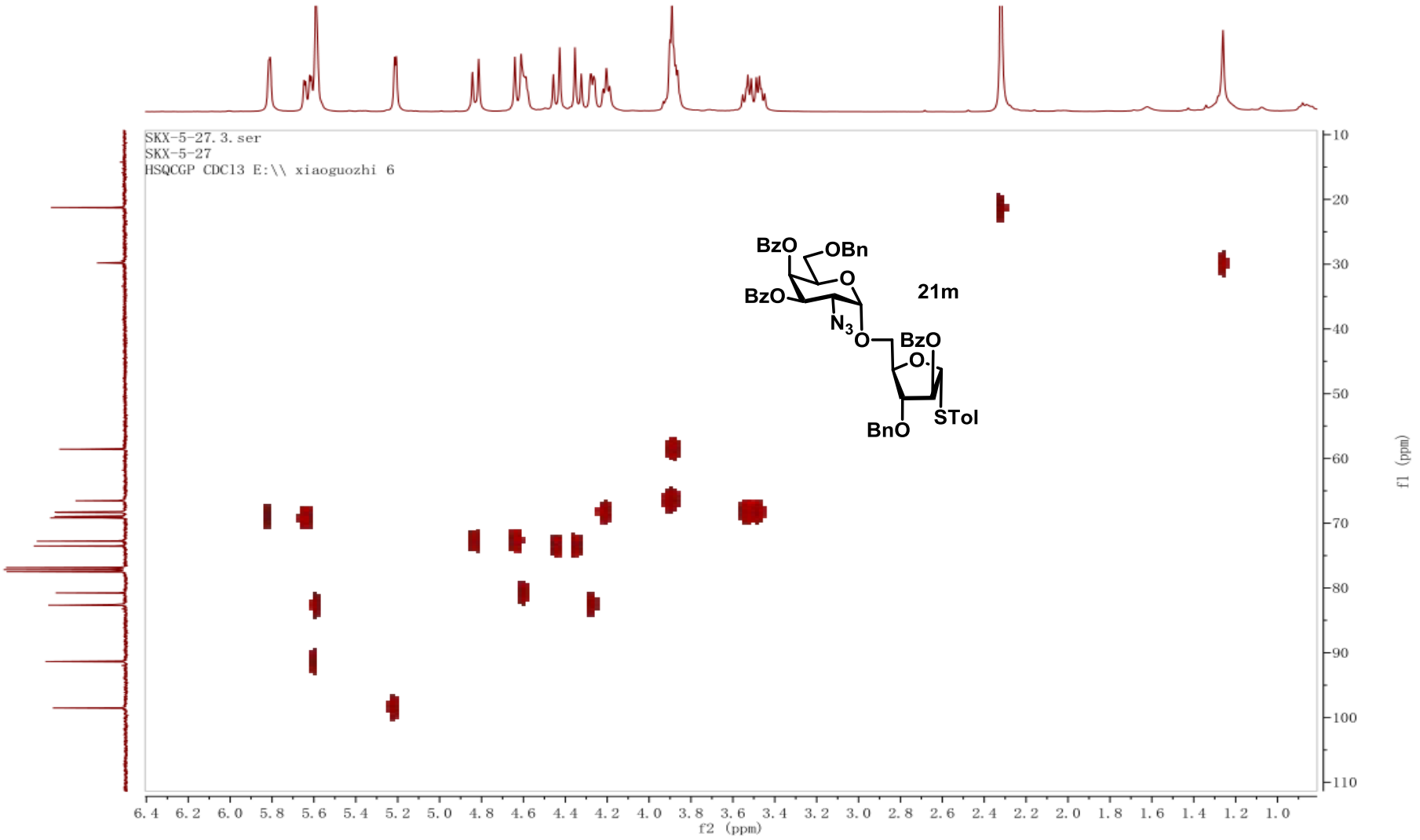

BzO
OBn
O
BzO
N3
O
OBz
BzO
O
BzO
OMP
21l
xiaoguozhi 19
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
f1 (ppm)

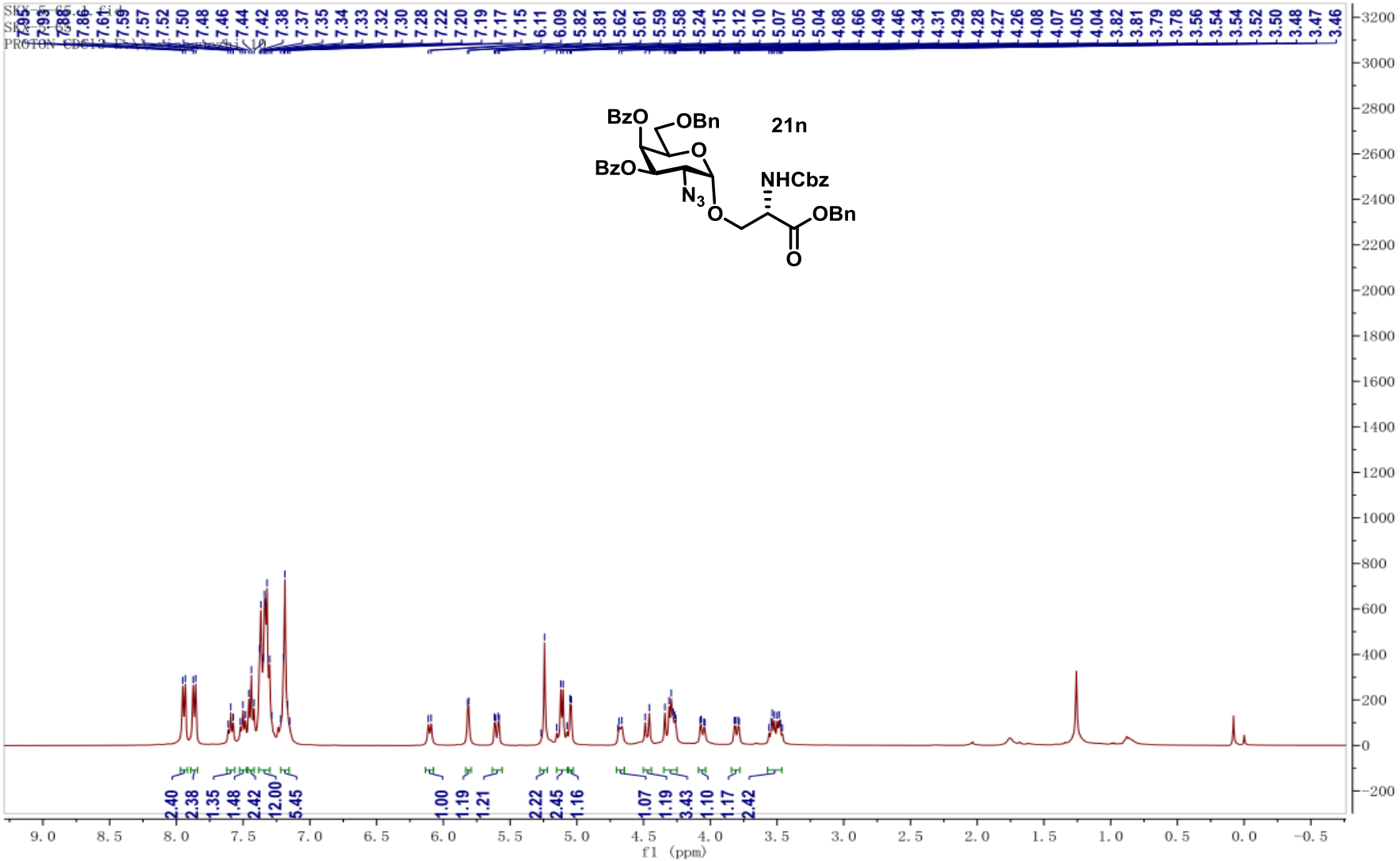

SKX-5-28-1.4.ser
SKX-5-28-1
HSQCGP CDCl3 E:\\ xiaoguozhi 19
BzO
OBn
O
BzO
N3
O
OBz
BzO
O
BzO
OMP
21l
f2 (ppm)
f1 (ppm)

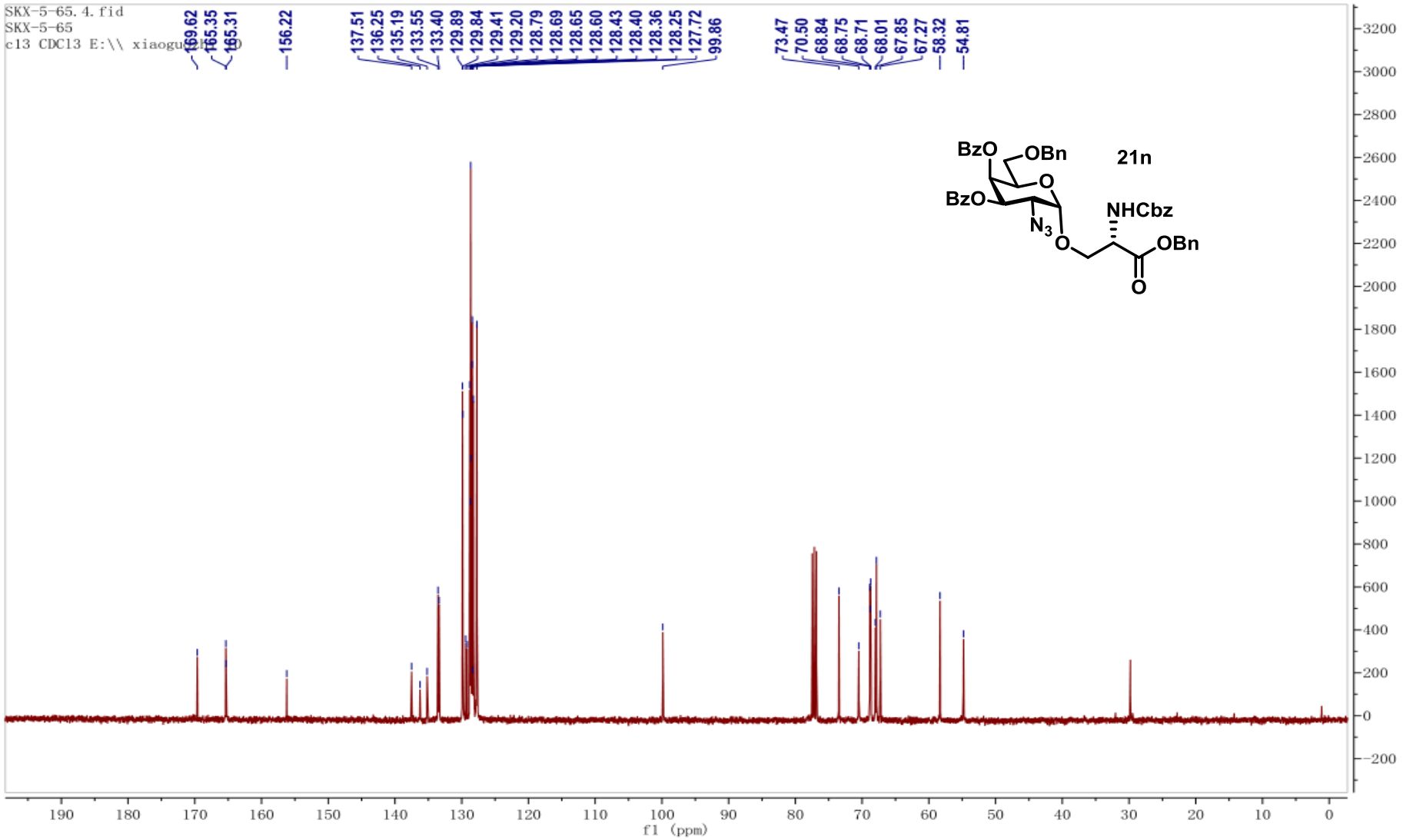

BzO
OBn
O
BzO
N3
O
BzO
O
BnO
STol
21m
f1 (ppm)

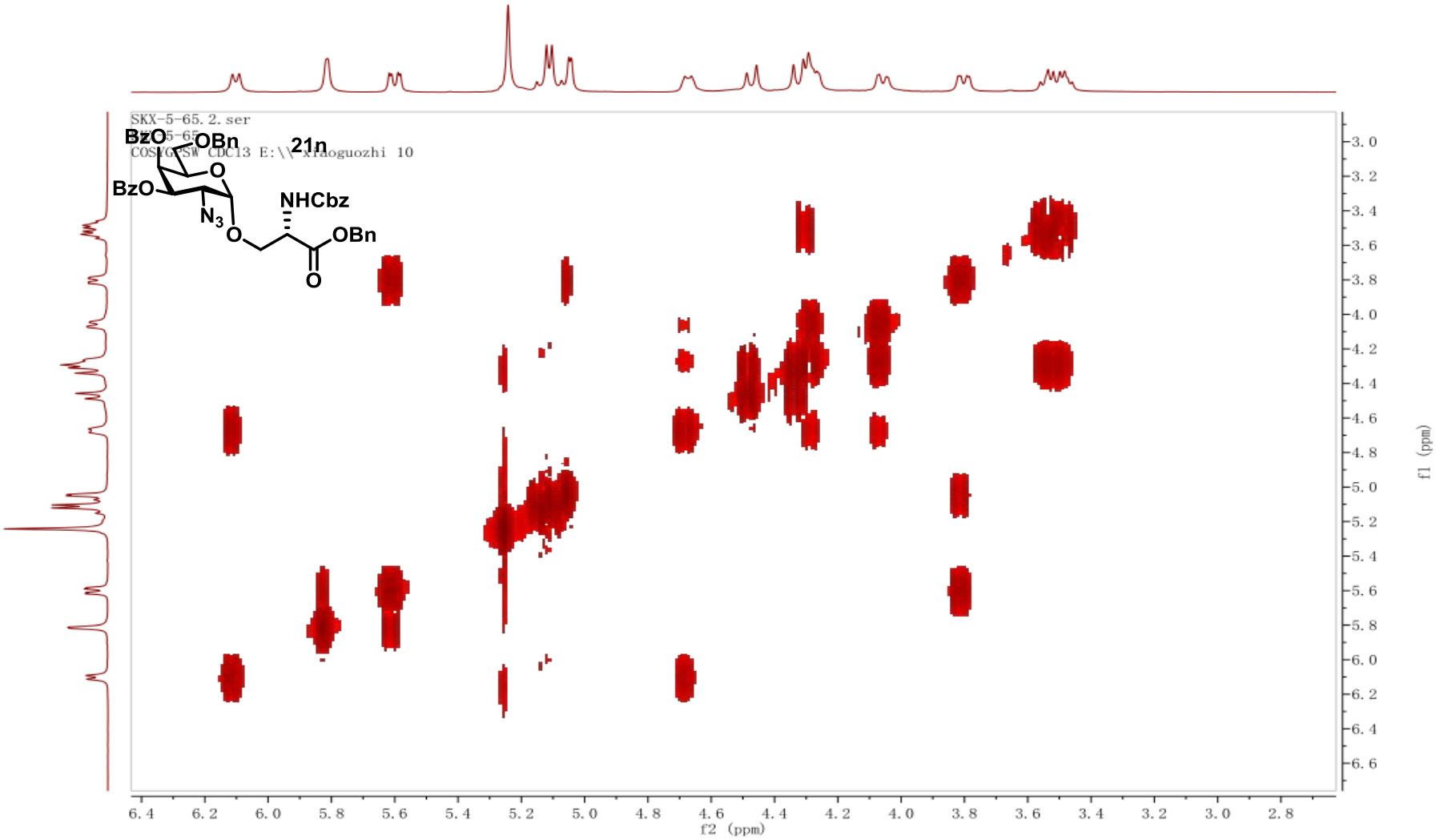

SKX-5-27.4.fid
SKX-5-27
c13 CDCl3 E:\\ xiaoguoli 6
165.56
165.43
165.24
138.10
137.67
137.34
133.53
133.49
133.33
133.19
130.12
129.98
129.90
129.86
129.59
129.41
128.66
128.65
128.60
128.46
128.43
128.41
128.16
127.73
127.71
98.53
91.35
82.64
82.58
80.76
73.51
72.77
69.17
68.95
68.33
68.27
66.52
58.56
21.24
BzO
OBn
O
BzO
N3
O
BzO
O
BnO
STol
21m
f1 (ppm)

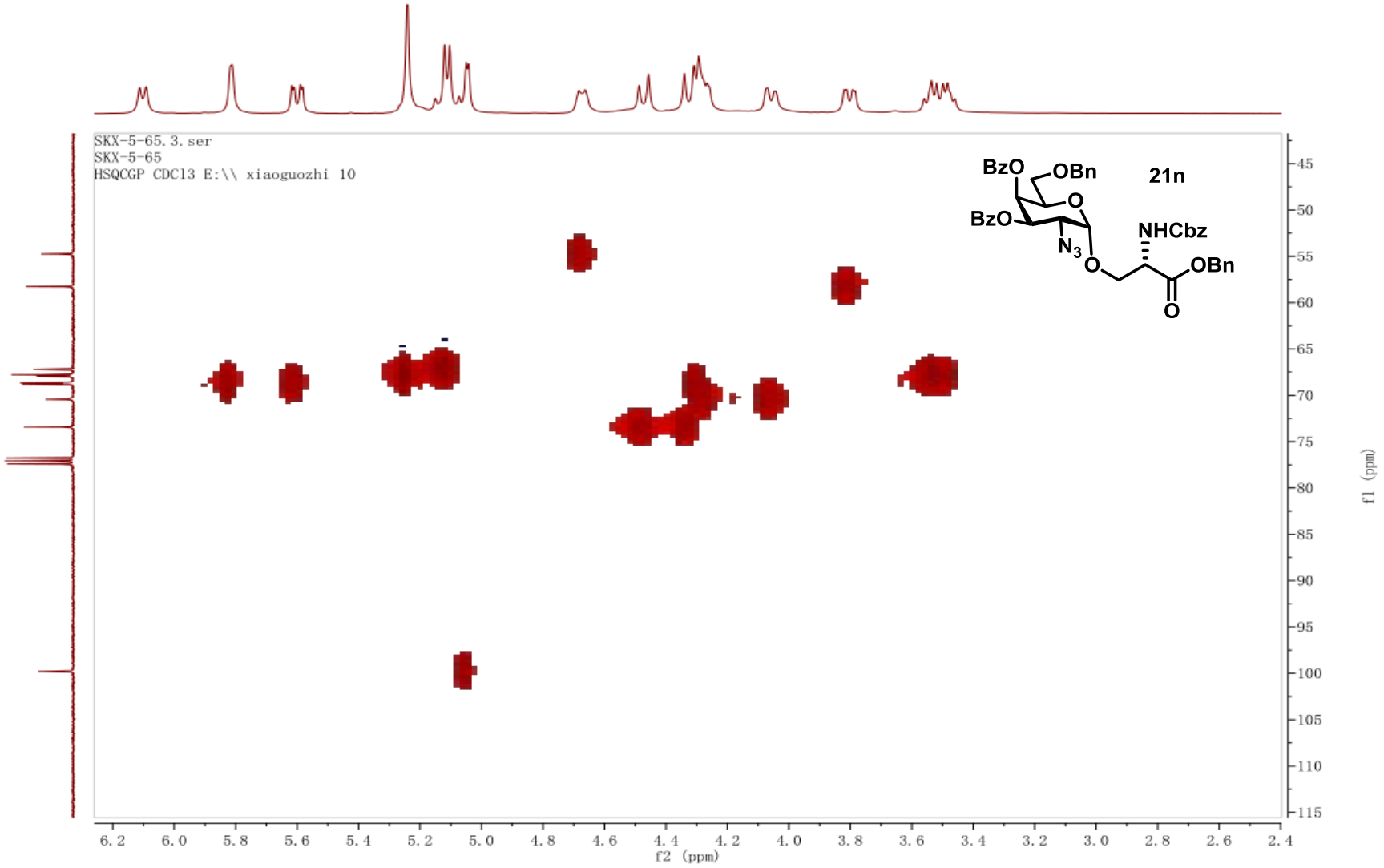

SKX-5-27.2.ser
SKX-5-27
COSYGPSW CDCl3 E:\\ xiaoguozhi 6
BzO
OBn
O
BzO
N3
O
BzO
O
BnO
STol
21m
f2 (ppm)
f1 (ppm)

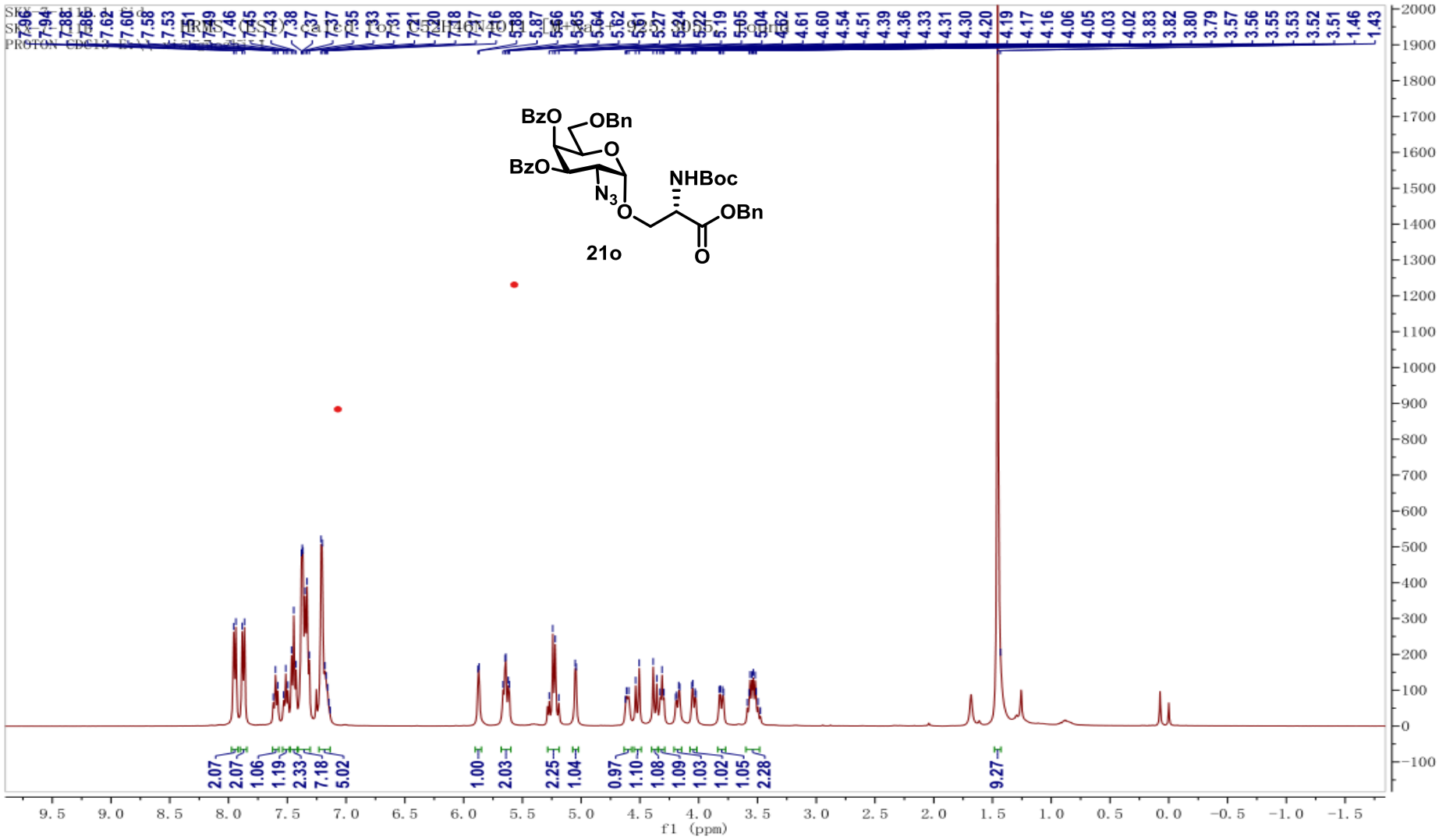

SKX-5-27.3.ser
SKX-5-27
HSQCGP CDCl3 E:\\ xiaoguozhi 6
BzO
OBn
O
BzO
N3
O
BzO
O
STol
BnO
21m
f2 (ppm)
f1 (ppm)

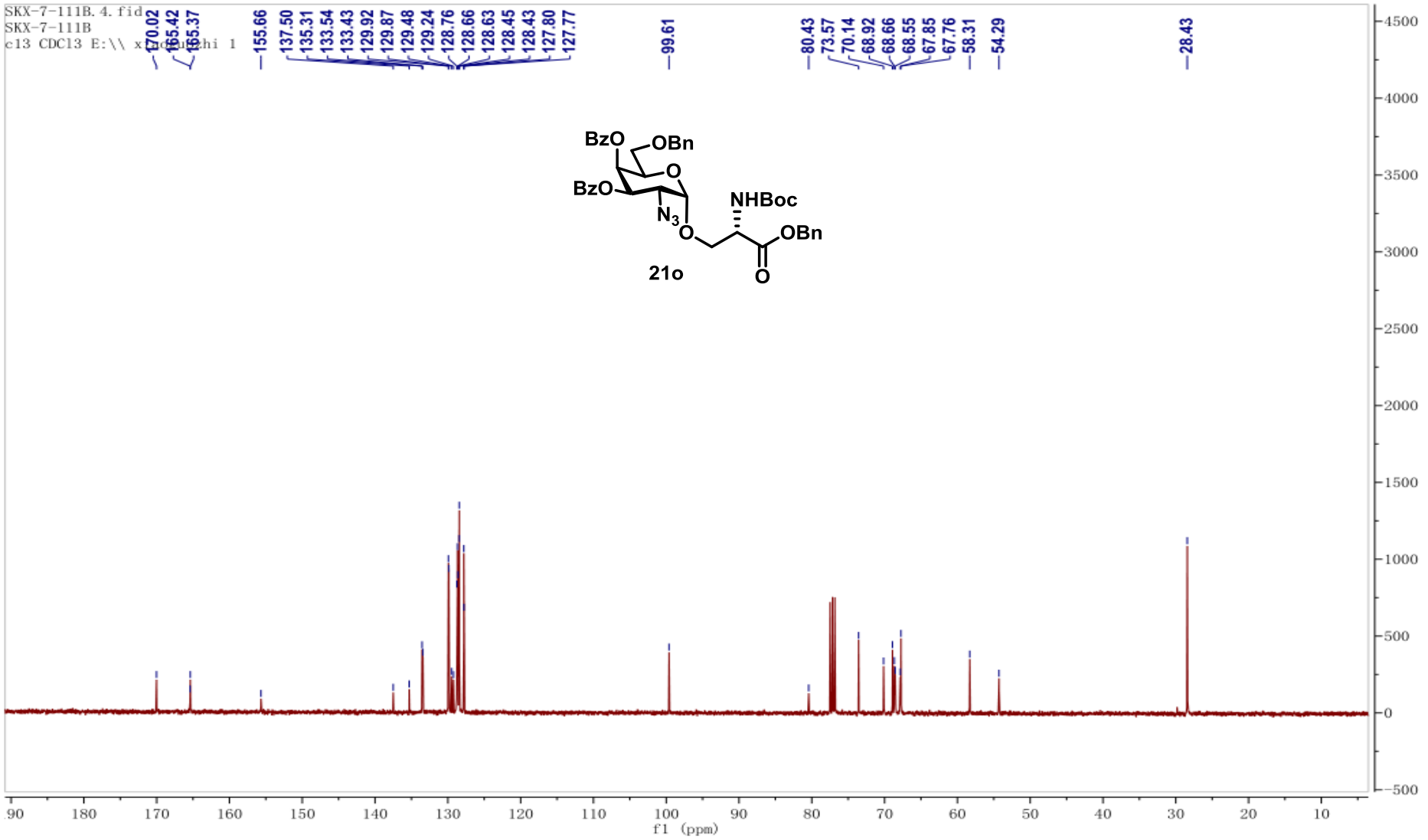

21n
BzO
OBn
O
BzO
NHCbz
N3
O
OBn
O
f1 (ppm)

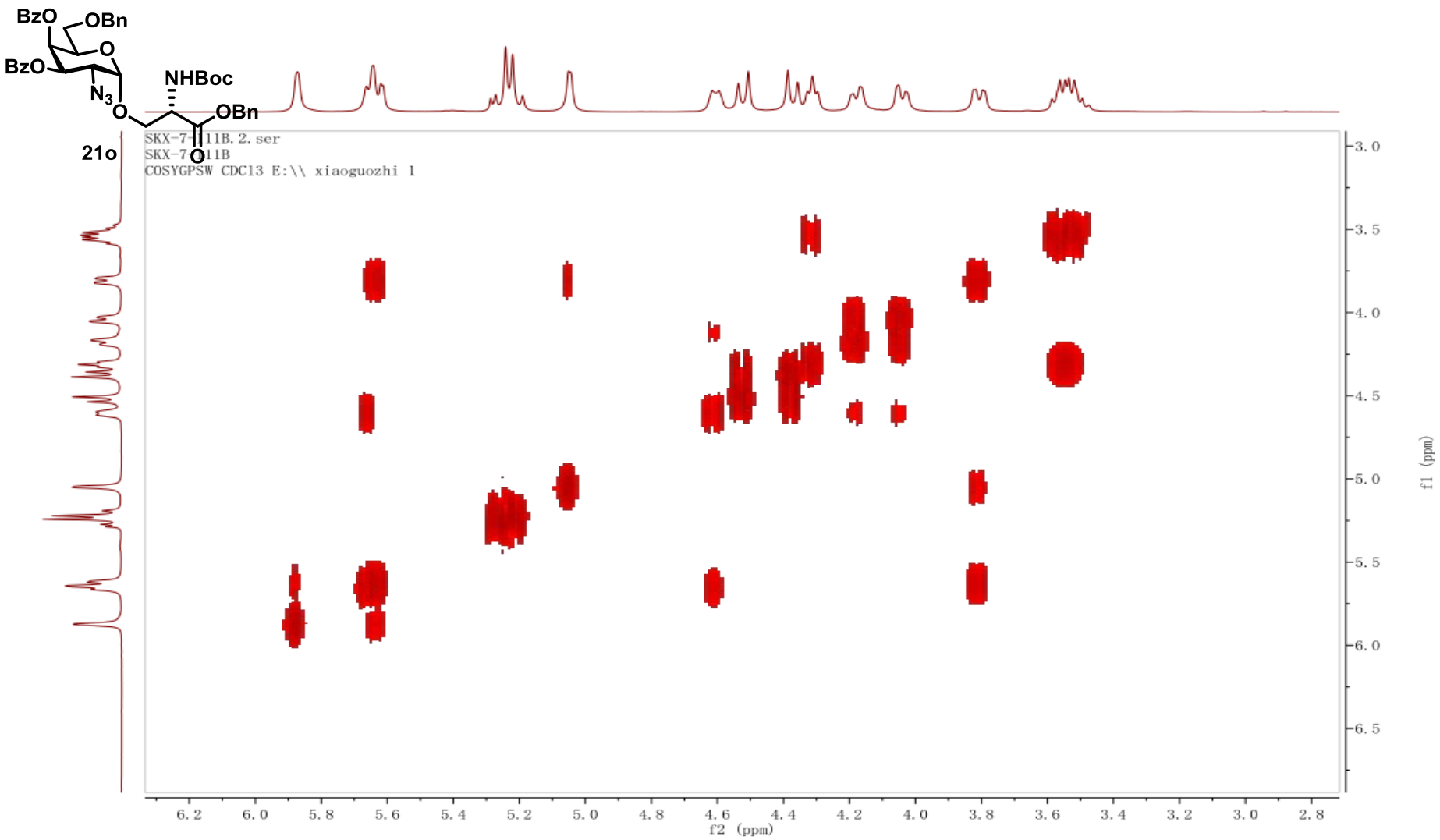

SKX-5-65.4.fid
SKX-5-65
c13 CDCl3 E:\\ xiaogu
169.62
165.35
165.31
156.22
137.51
136.25
135.19
133.55
133.40
129.89
129.84
129.41
129.20
128.79
128.69
128.65
128.60
128.43
128.40
128.36
128.25
127.72
99.86
73.47
70.50
68.84
68.75
68.71
68.01
67.85
67.27
58.32
54.81
BzO
OBn
O
BzO
N3
O
NHCbz
OBn
O
21n
f1 (ppm)

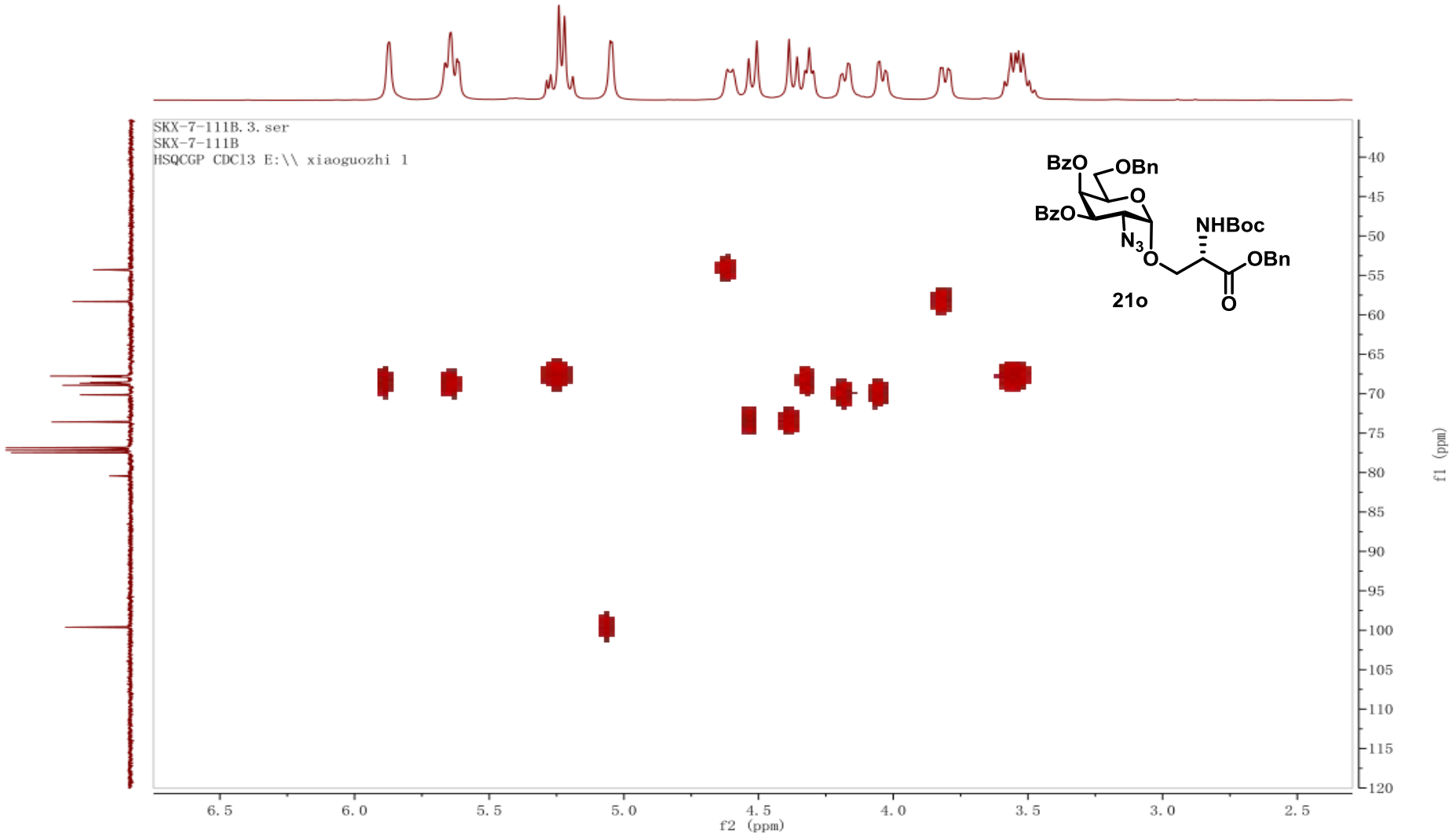

SKX-5-65.2.ser
21n
BzO
OBn
O
BzO
NHCbz
N3
O
OBn
O
f2 (ppm)
f1 (ppm)

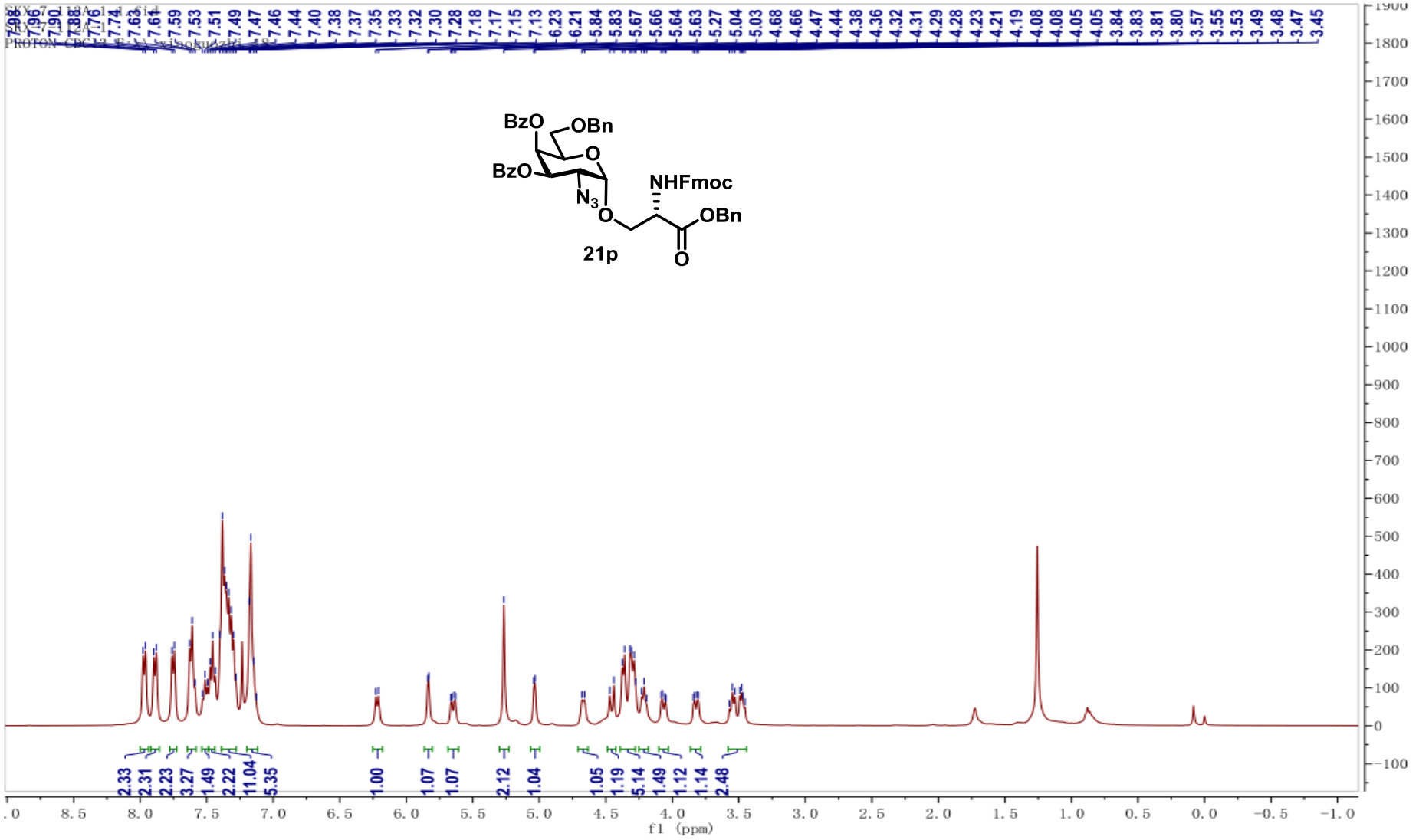

SKX-5-65.3.ser
SKX-5-65
HSQCGP CDC13 E:\\ xiaoguozhi 10
BzO
OBn
O
BzO
N3
O
NHCbz
OBn
O
21n
f2 (ppm)
f1 (ppm)

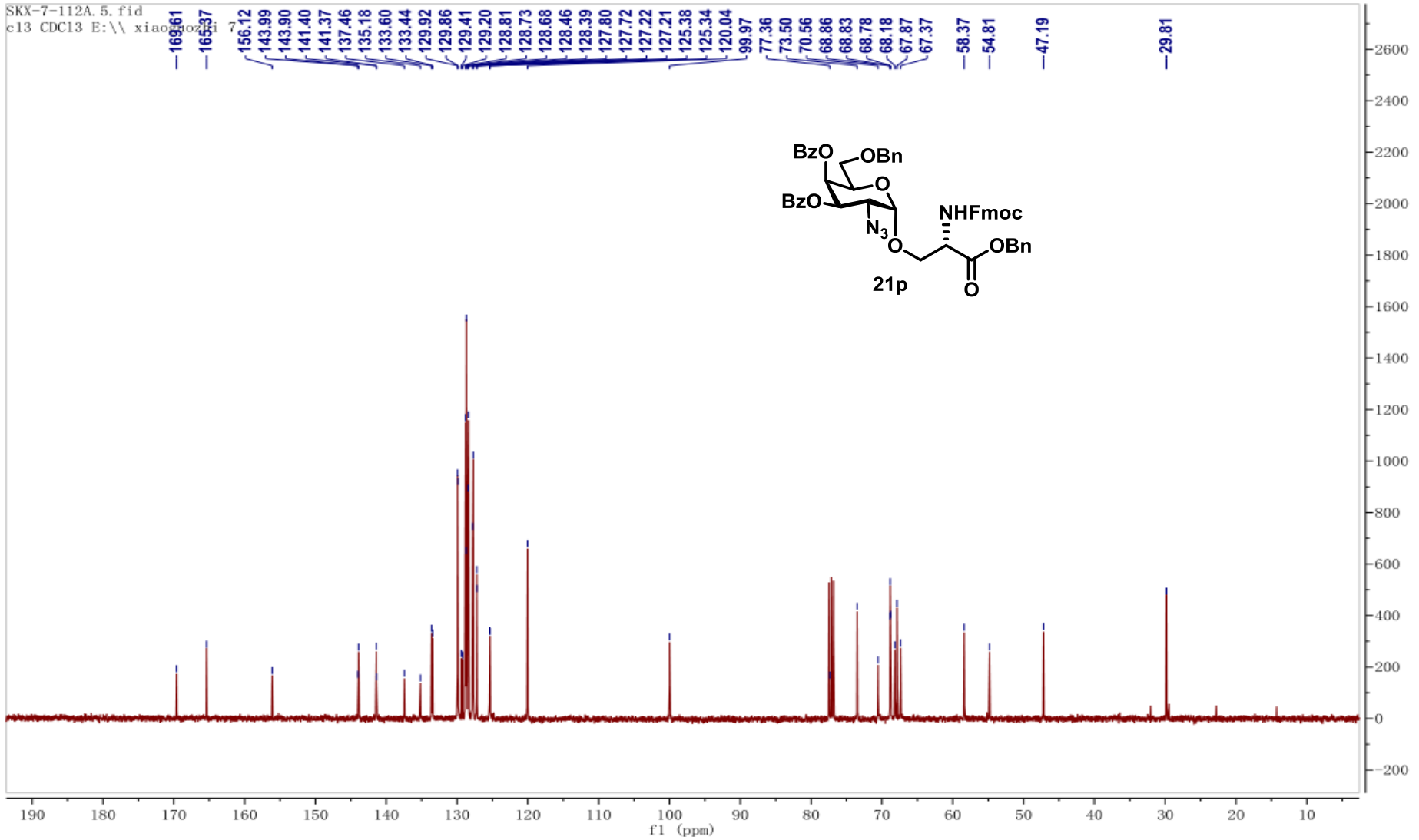

BzO
OBn
O
BzO
N3
O
NHBoc
OBn
O
21o
f1 (ppm)

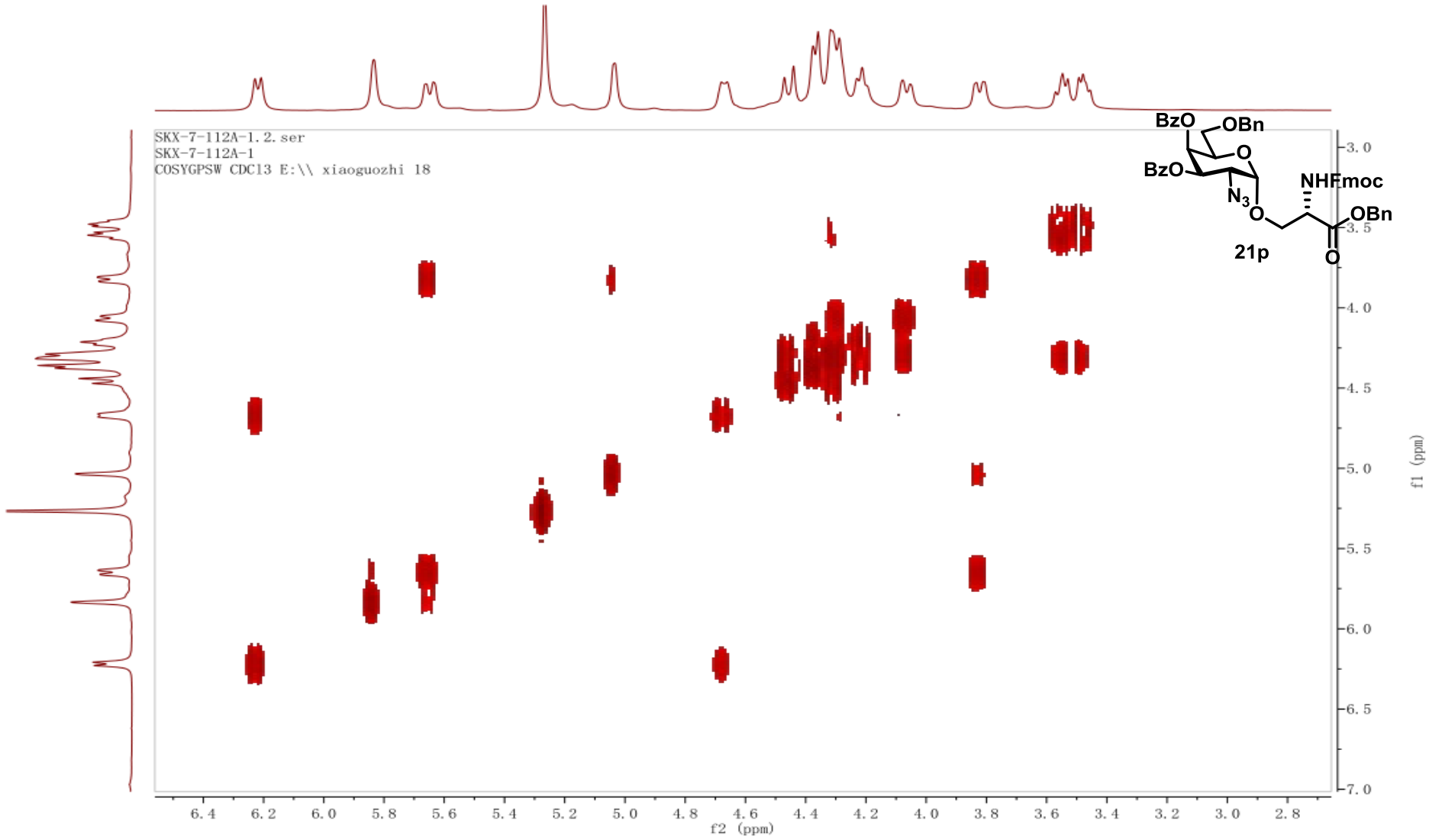

SKX-7-111B.4.fid
SKX-7-111B
c13 CDCl3 E:\\ xx\data\zhi 1
170.02
165.42
165.37
155.66
137.50
135.31
133.54
133.43
129.92
129.87
129.48
129.24
128.76
128.66
128.63
128.45
128.43
127.80
127.77
99.61
80.43
73.57
70.14
68.92
68.66
68.55
67.85
67.76
58.31
54.29
28.43
BzO
OBn
O
BzO
N3
O
NHBoc
OBn
O
21o
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

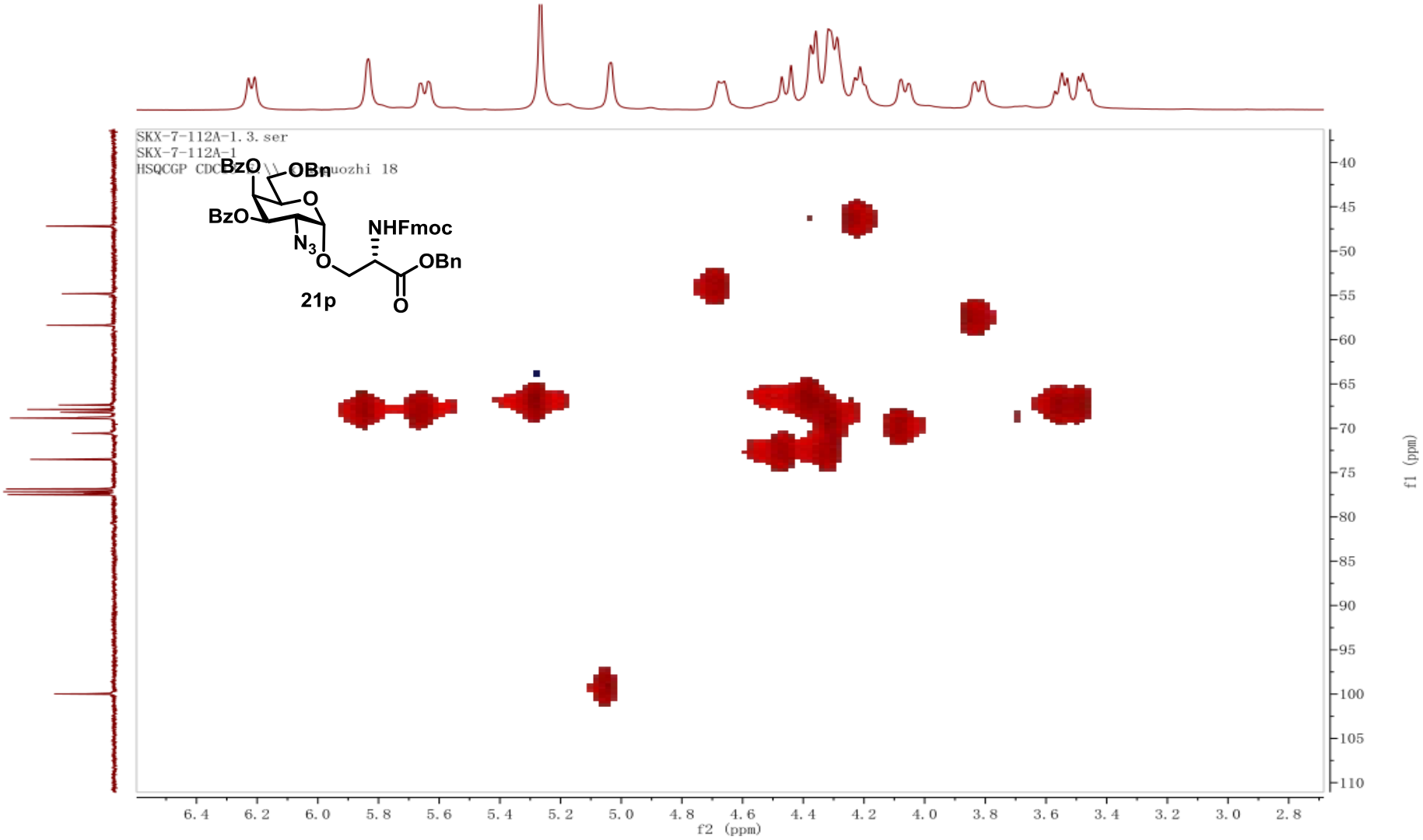

BzO
OBn
O
BzO
N3
O
NHBoc
OBn
O
21o
SKX-7-11B.2.ser
SKX-7-11B
COSYGPSW CDCl3 E:\\ xiaoguozhi 1
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f2 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

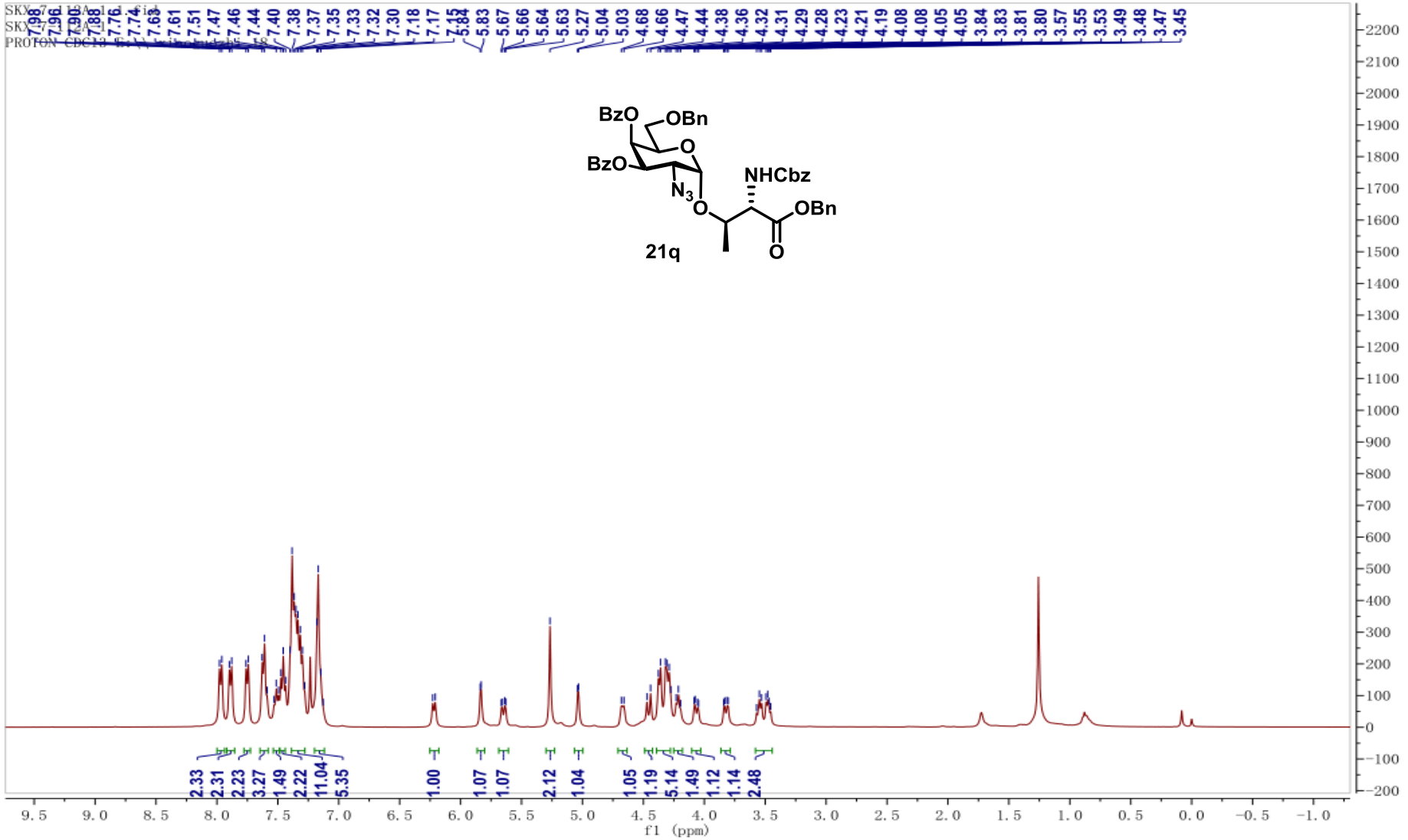

SKX-7-111B.3.ser
SKX-7-111B
HSQCGP CDCl3 E:\\ xiaoguozhi 1
BzO
OBn
O
BzO
NHBoc
N3
O
OBn
O
21o
f2 (ppm)
f1 (ppm)

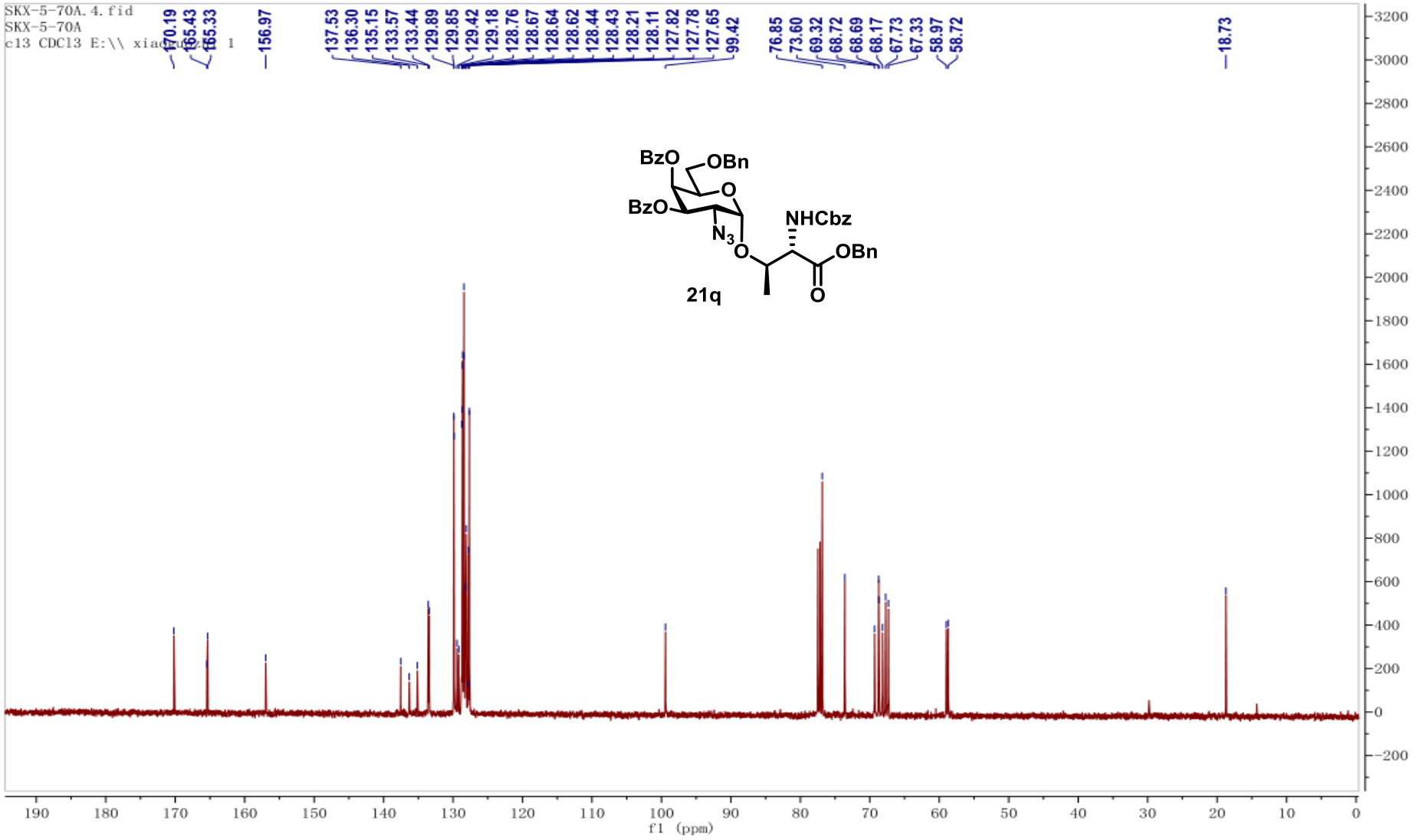

BzO
OBn
O
BzO
N3
O
NHFmoc
OBn
O
21p
f1 (ppm)

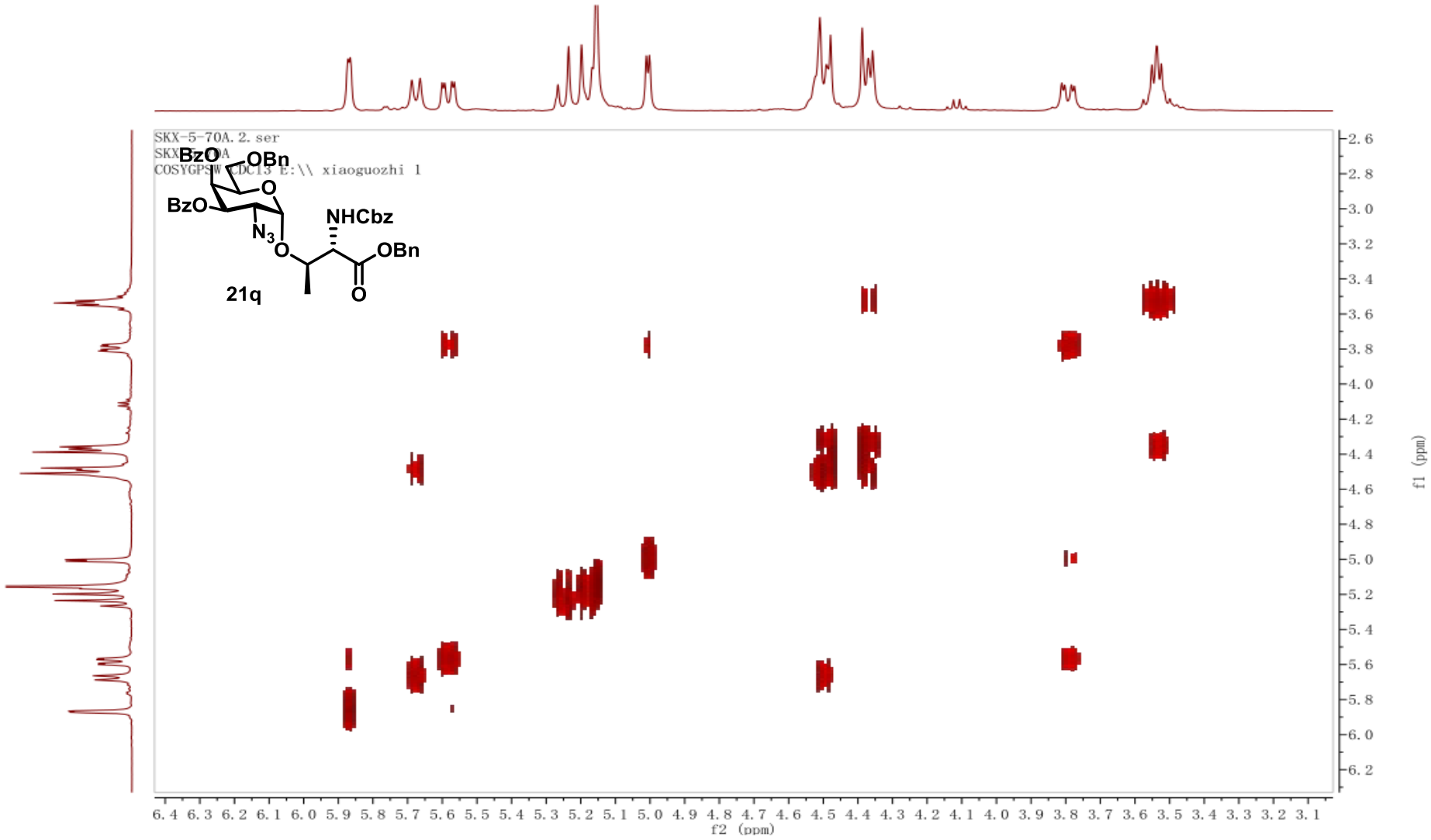

SKX-7-112A.5.fid
c13 CDCl3 E:\\ xiaoguozhi 7
169.61
165.37
156.12
143.99
143.90
141.40
141.37
137.46
135.18
133.60
133.44
129.92
129.86
129.41
129.20
128.81
128.73
128.68
128.46
128.39
127.80
127.72
127.22
127.21
125.38
125.34
120.04
99.97
77.36
73.50
70.56
68.86
68.83
68.78
68.18
67.87
67.37
58.37
54.81
47.19
29.81
BzO
OBn
O
BzO
N3
O
NHFmoc
OBn
O
21p
f1 (ppm)

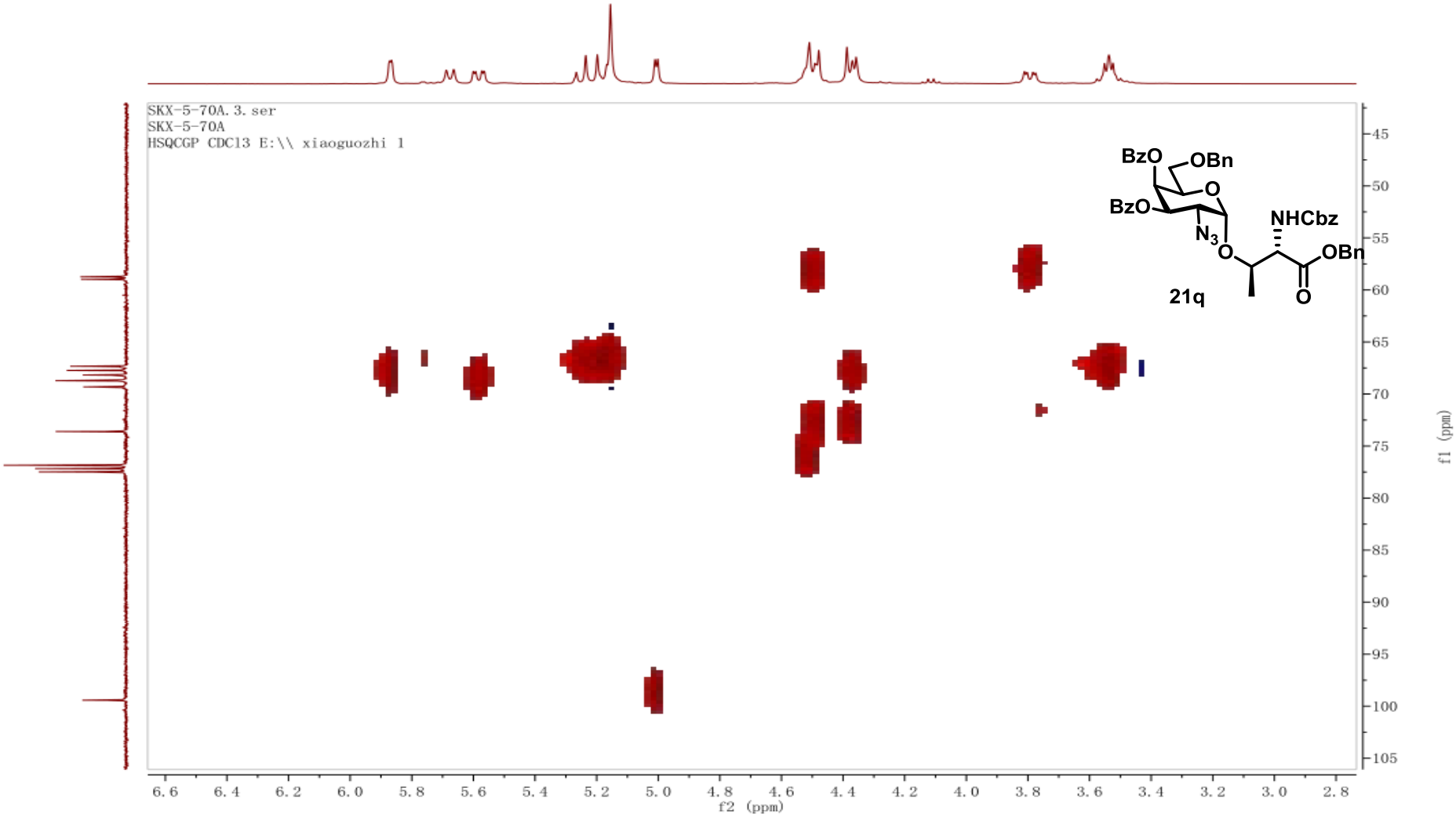

SKX-7-112A-1.2.ser
SKX-7-112A-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 18
BzO
OBn
O
BzO
N3
O
NHFmoc
OBn
O
21p
f2 (ppm)
f1 (ppm)

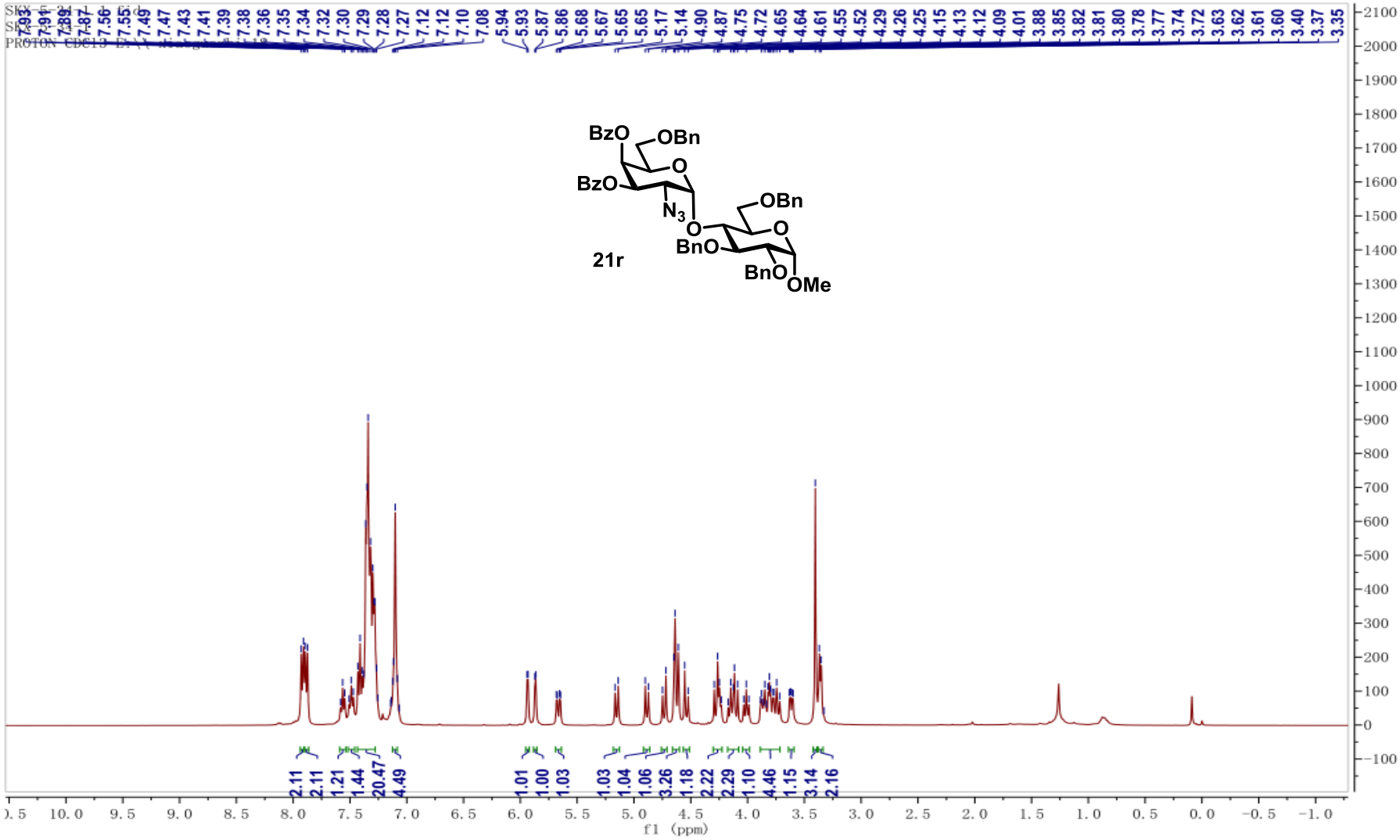

SKX-7-112A-1.3.ser
SKX-7-112A-1
BzO
OBn
O
BzO
NHFmoc
N3
O
OBn
21p
O
f2 (ppm)
f1 (ppm)

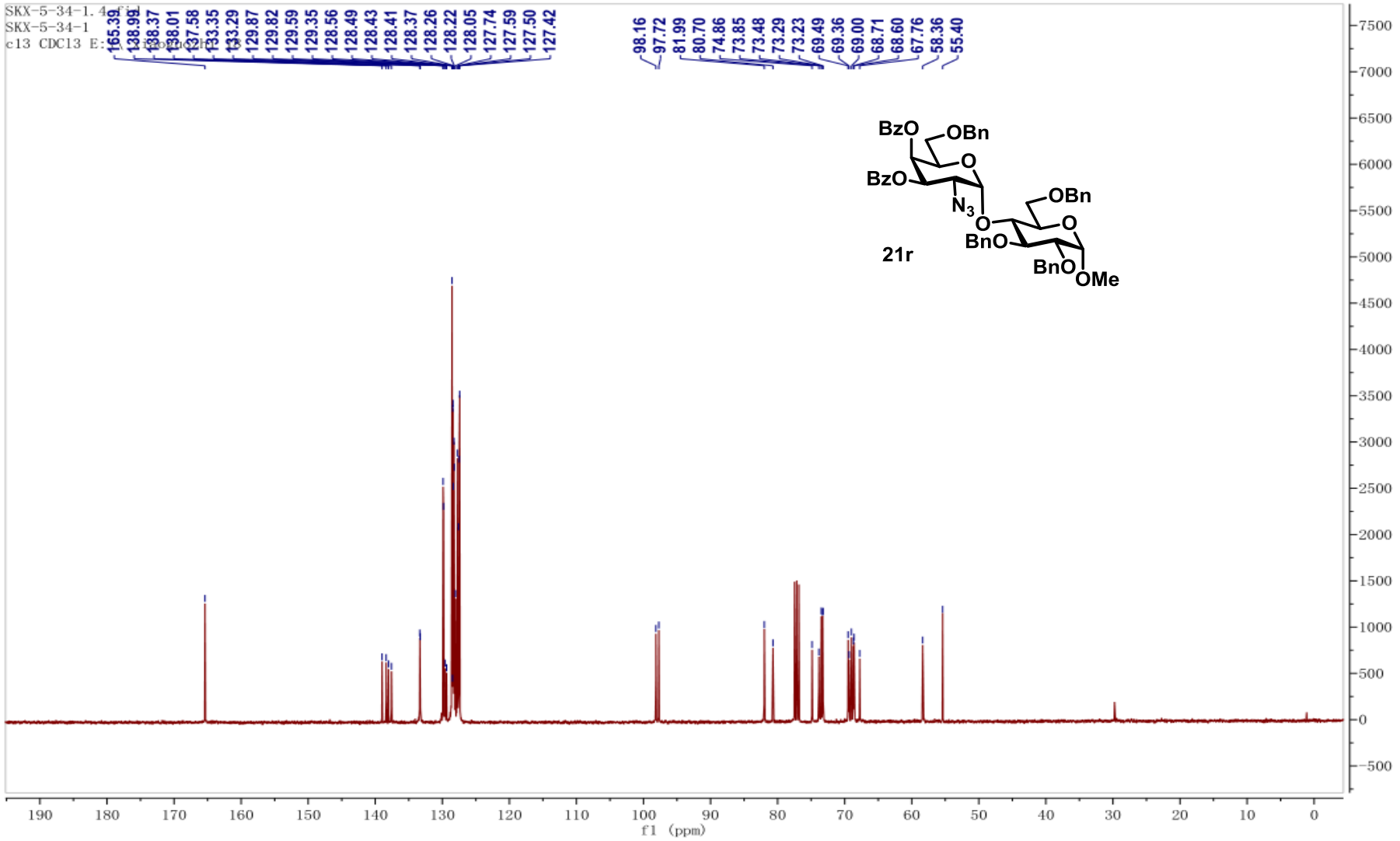

BzO
OBn
O
BzO
N3
O
NHCbz
OBn
O
21q
f1 (ppm)

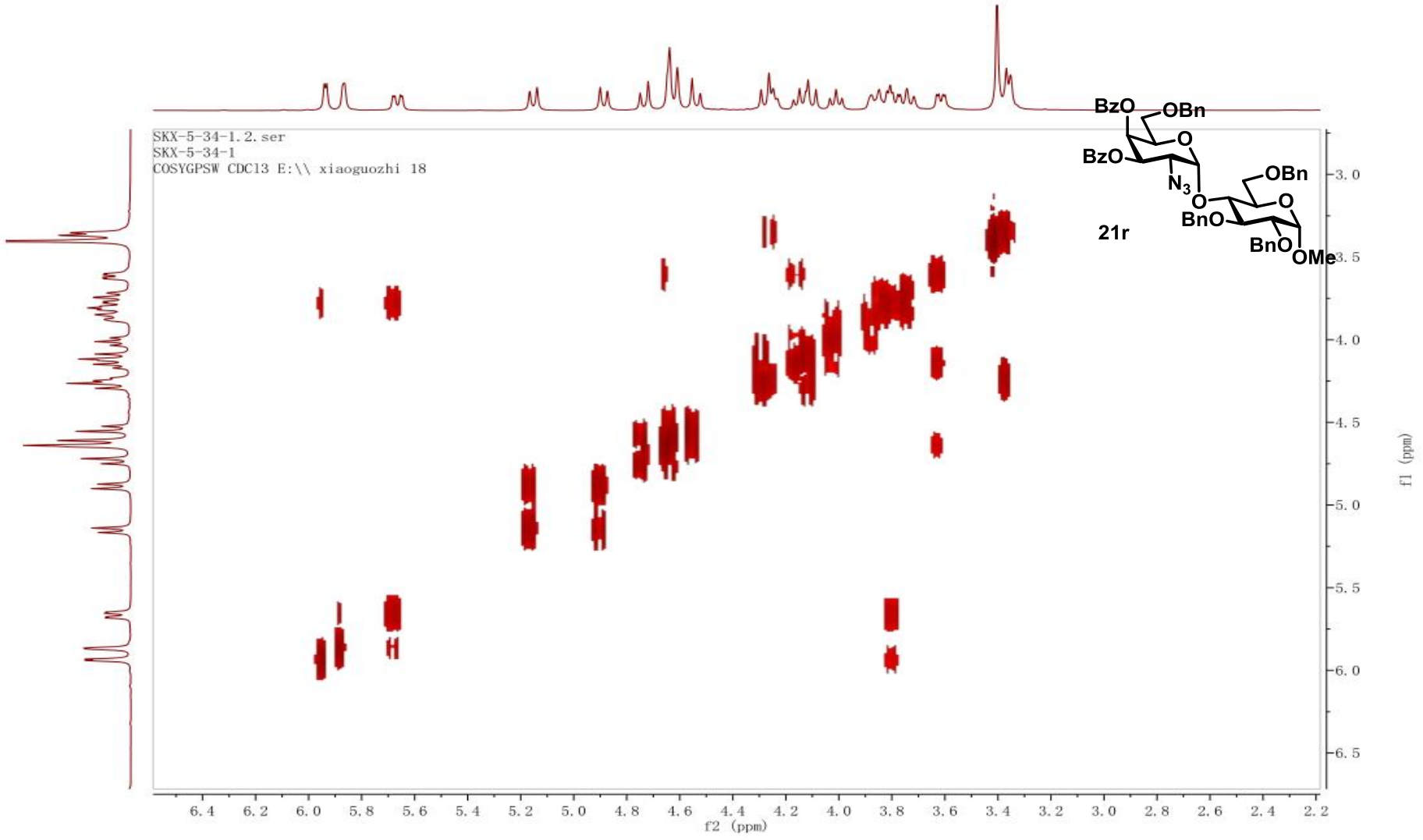

SKX-5-70A.4.fid
SKX-5-70A
c13 CDCl3 E:\\ xiaoyu
170.19
165.43
165.33
156.97
137.53
136.30
135.15
133.57
133.44
129.89
129.85
129.42
129.18
128.76
128.67
128.64
128.62
128.44
128.43
128.21
128.11
127.82
127.78
127.65
99.42
76.85
73.60
69.32
68.72
68.69
68.17
67.73
67.33
58.97
58.72
18.73
BzO
OBn
O
BzO
N3
O
NHCbz
OBn
O
21q
f1 (ppm)

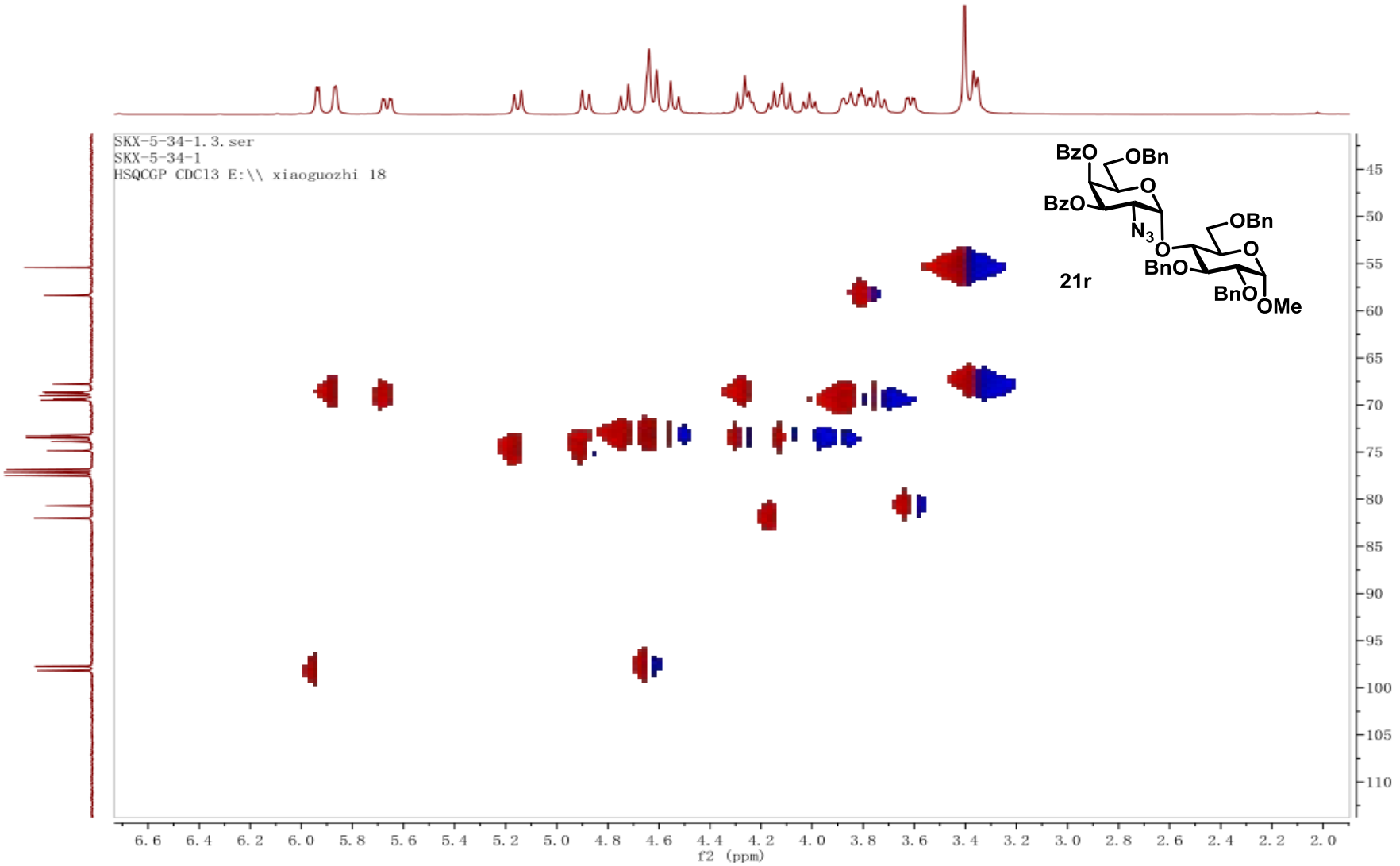

SKX-5-70A.2.ser
BzO
OBn
O
BzO
N3
O
NHCbz
OBn
O
21q
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
f1 (ppm)
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
f2 (ppm)

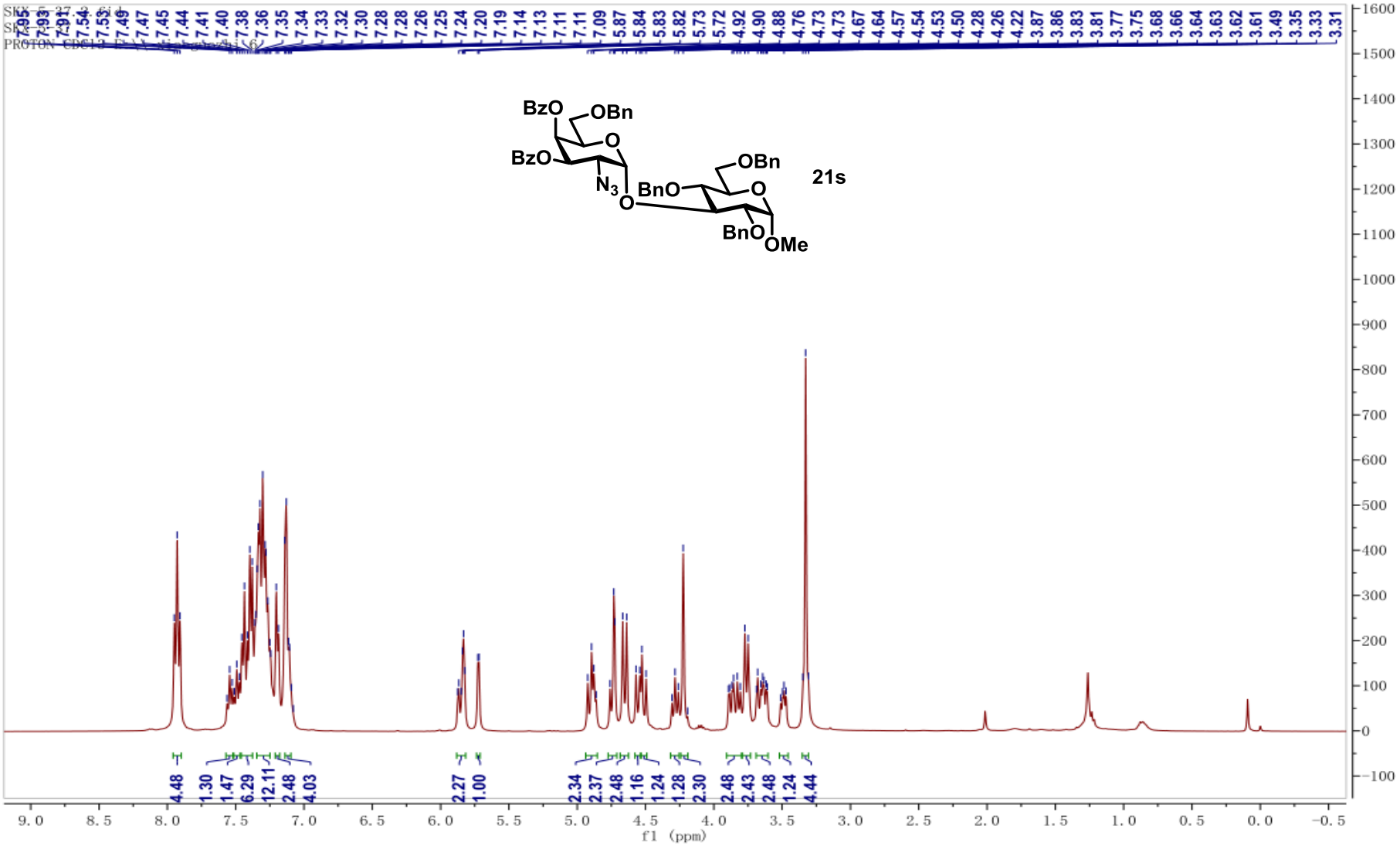

SKX-5-70A.3.ser
SKX-5-70A
HSQCGP CDC13 E:\\ xiaoguozhi 1
BzO
OBn
O
BzO
N3
O
NHCbz
OBn
O
21q
f2 (ppm)
f1 (ppm)

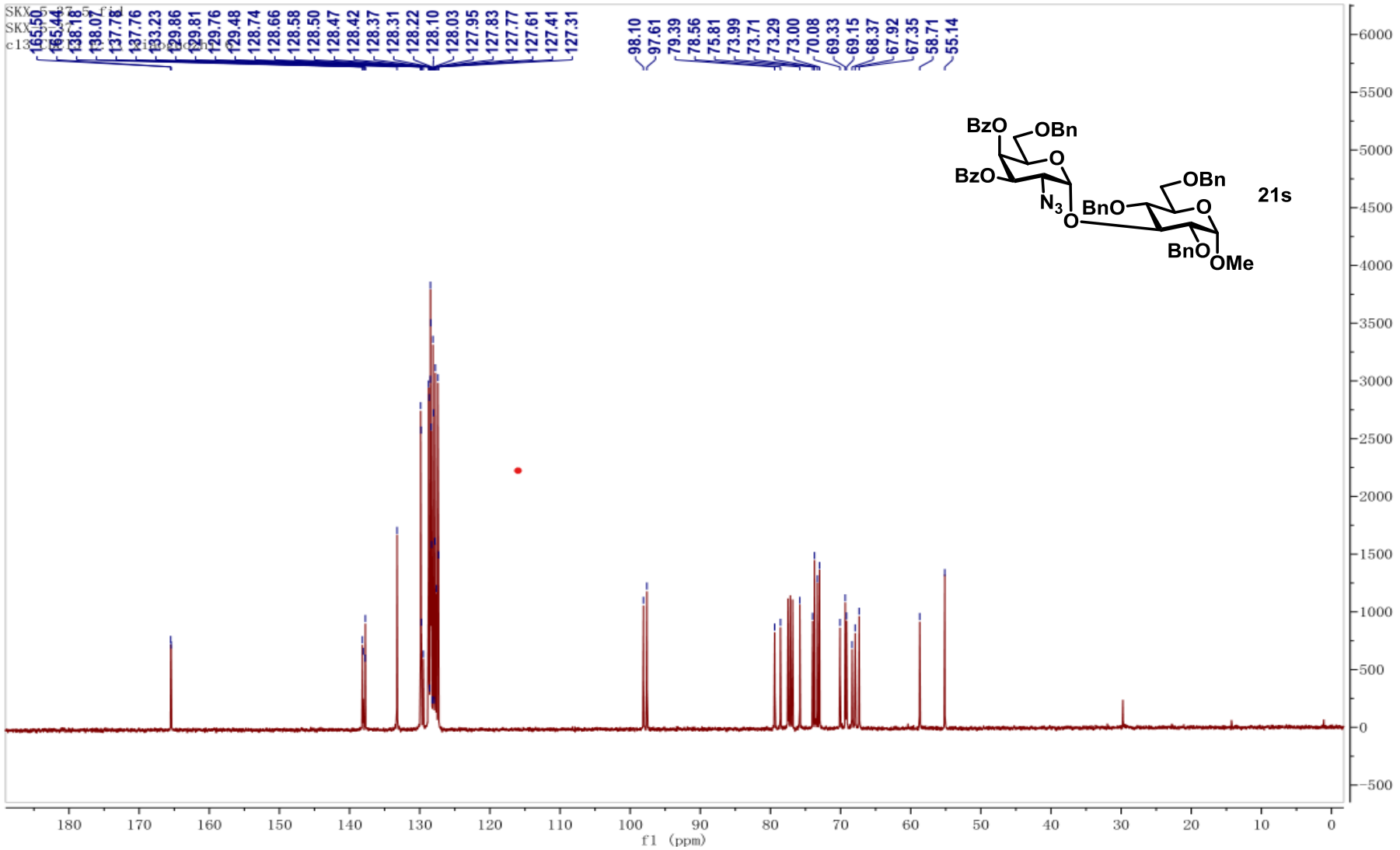

BzO
OBn
O
BzO
N3
O
OBn
O
BnO
BnO
OMe
21r
f1 (ppm)

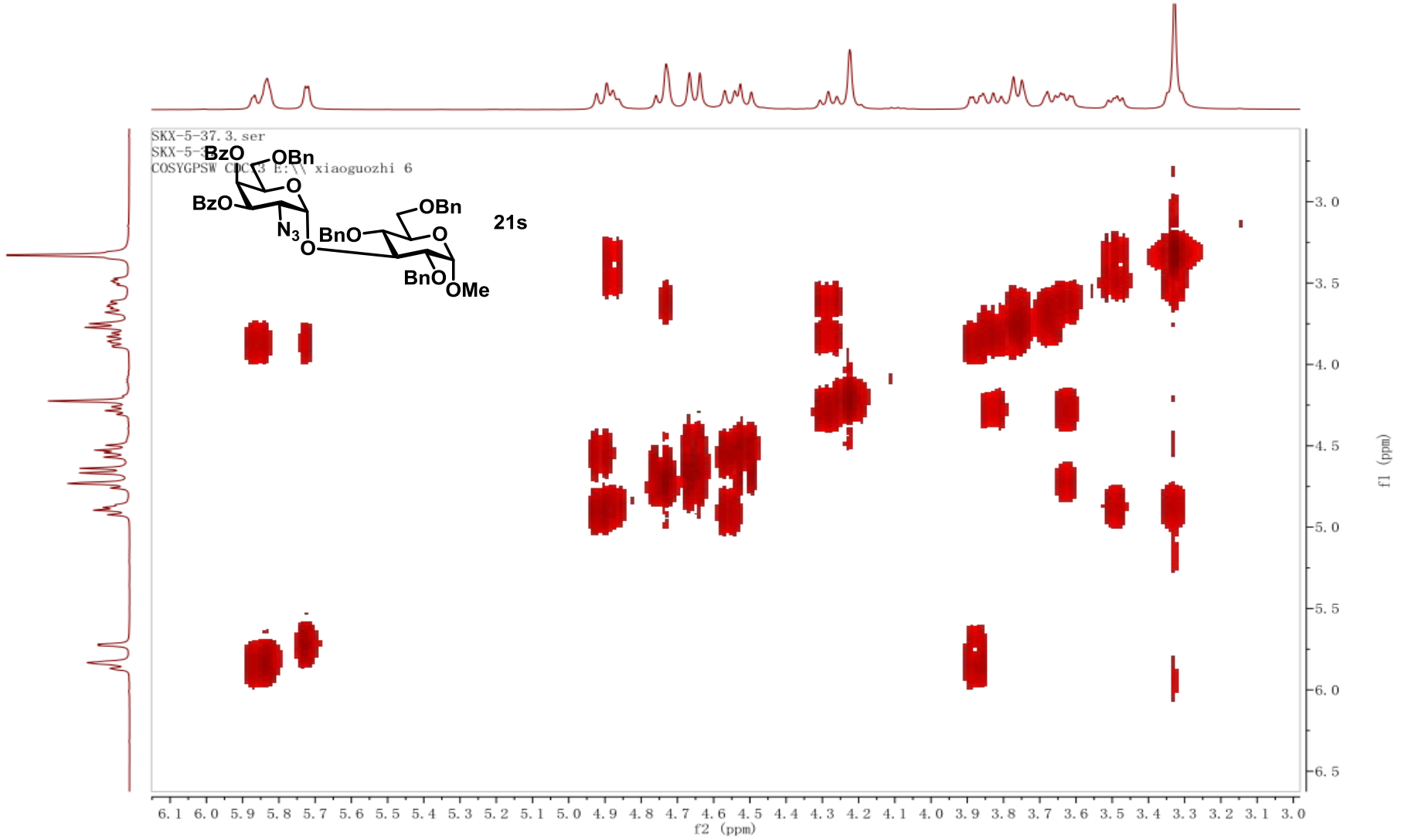

SKX-5-34-1.4.fid
SKX-5-34-1
c13 CDC13 E:
165.39
138.99
138.37
138.01
137.58
133.35
133.29
129.87
129.82
129.59
129.35
128.56
128.49
128.43
128.41
128.37
128.26
128.22
128.05
127.74
127.59
127.50
127.42
98.16
97.72
81.99
80.70
74.86
73.85
73.48
73.29
73.23
69.49
69.36
69.00
68.71
68.60
67.76
58.36
55.40
BzO
OBn
O
BzO
N3
O
OBn
O
BnO
BnO
OMe
21r
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

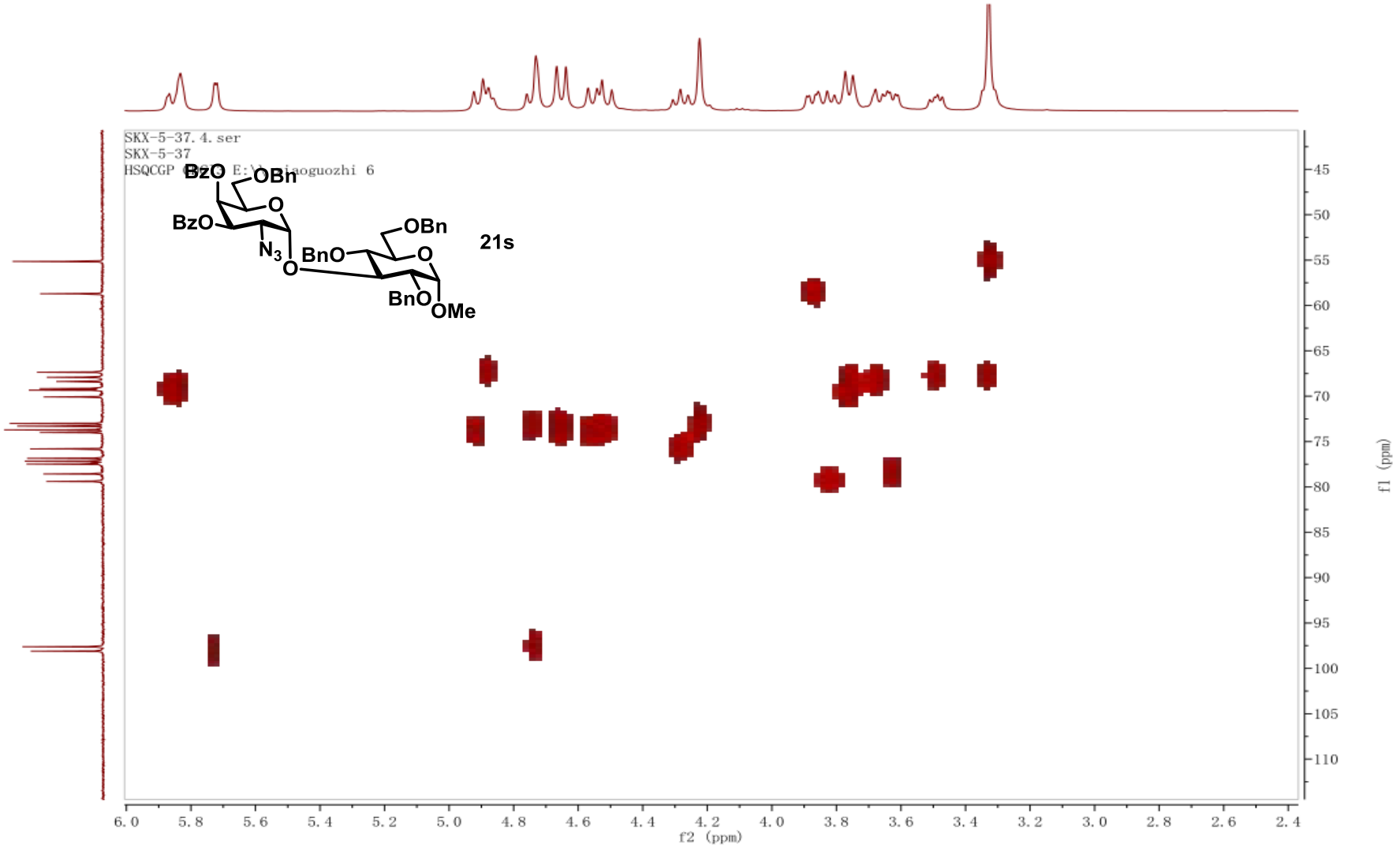

SKX-5-34-1.2.ser
SKX-5-34-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 18
BzO
OBn
O
BzO
N3
O
OBn
O
BnO
BnO
OMe
21r
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
f2 (ppm)
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5
f1 (ppm)

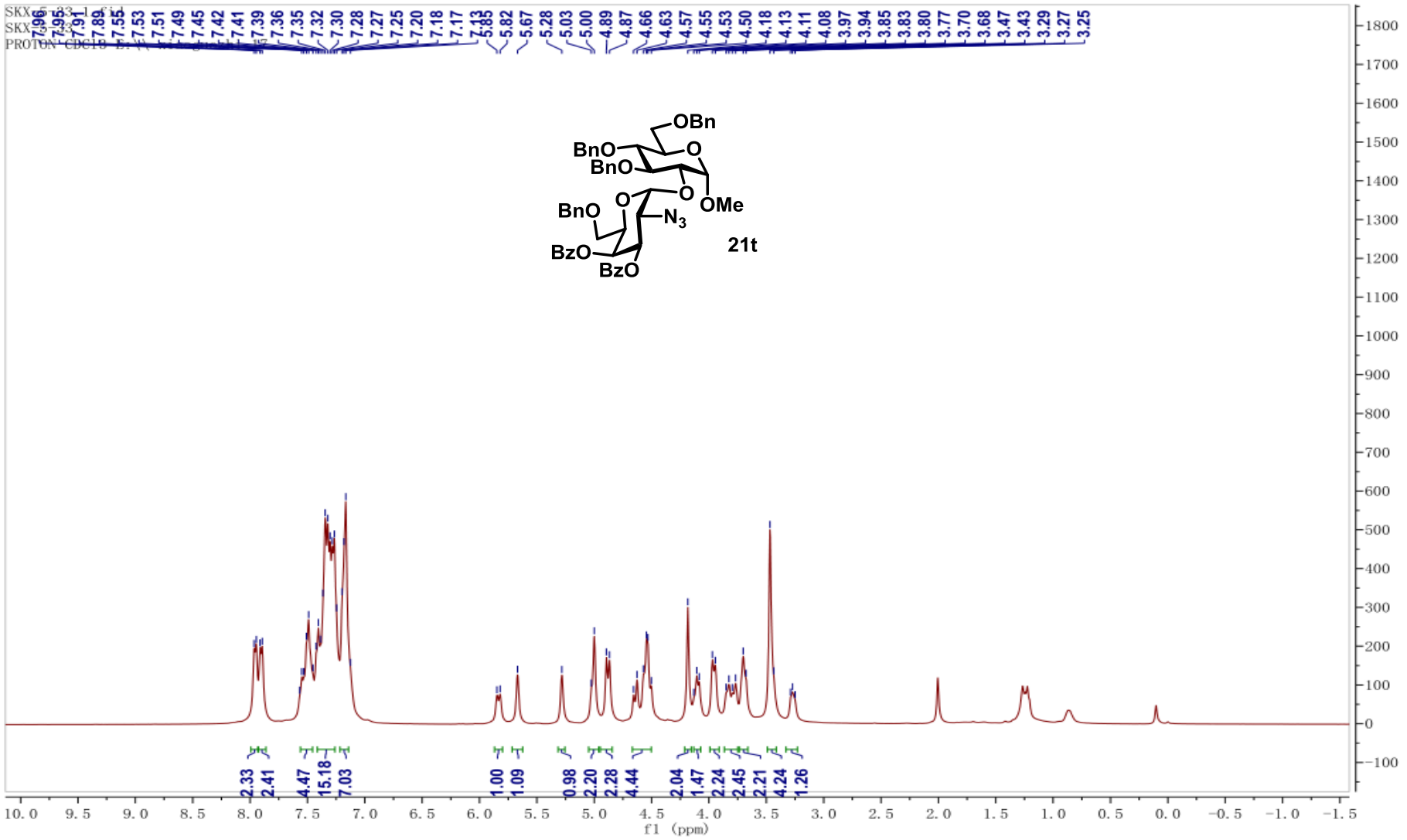

SKX-5-34-1.3.ser
SKX-5-34-1
HSQCGP CDCl3 E:\\ xiaoguozhi 18
BzO
OBn
O
BzO
N3
O
OBn
O
BnO
BnO
OMe
21r
45
50
55
60
65
70
75
80
85
90
95
100
105
110
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f2 (ppm)

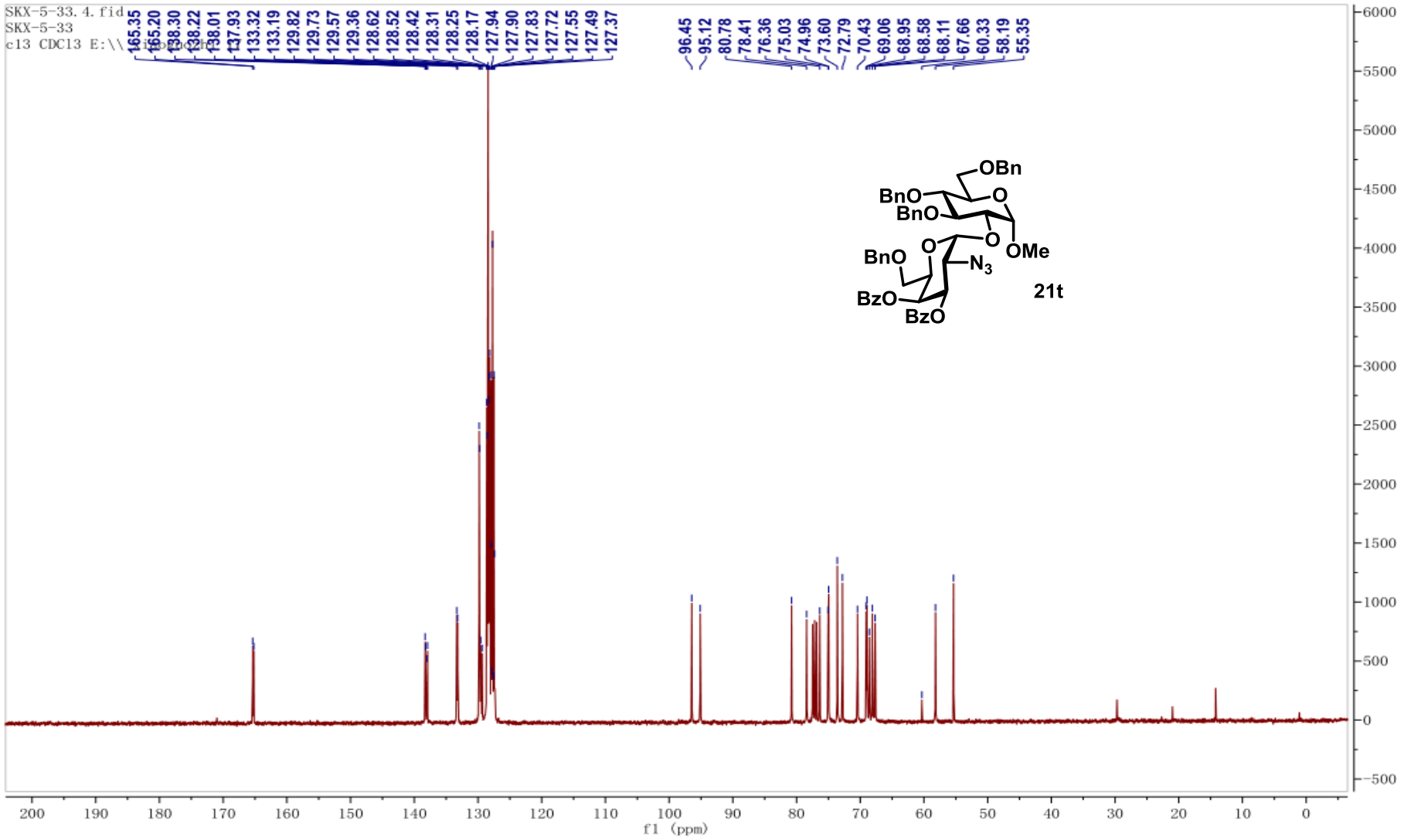

BzO
OBn
O
BzO
N3
O
BnO
OBn
O
BnO
OMe
21s
4.48
1.30
1.47
6.29
12.11
2.48
4.03
2.27
1.00
2.34
2.37
2.48
1.16
1.24
1.28
2.30
2.48
2.43
2.48
1.24
4.44
f1 (ppm)

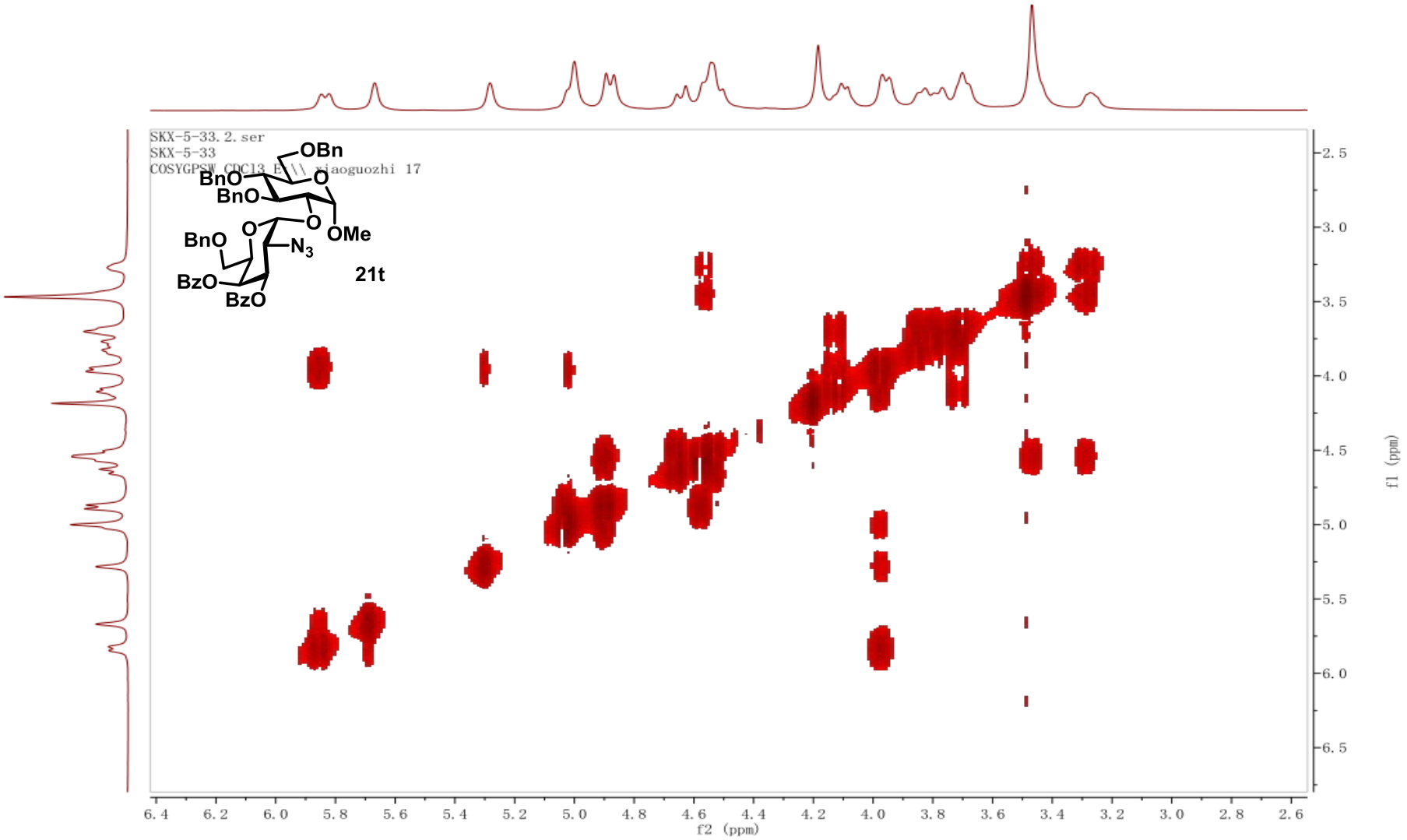

SKX
SKX
c13
165.50
165.44
138.18
138.07
137.78
137.76
133.23
129.86
129.81
129.76
129.48
128.74
128.66
128.58
128.50
128.47
128.42
128.37
128.31
128.22
128.10
128.03
127.95
127.83
127.77
127.61
127.41
127.31
98.10
97.61
79.39
78.56
75.81
73.99
73.71
73.29
73.00
70.08
69.33
69.15
68.37
67.92
67.35
58.71
55.14
BzO
OBn
O
BzO
N3
O
BnO
OBn
O
BnO
OMe
21s
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

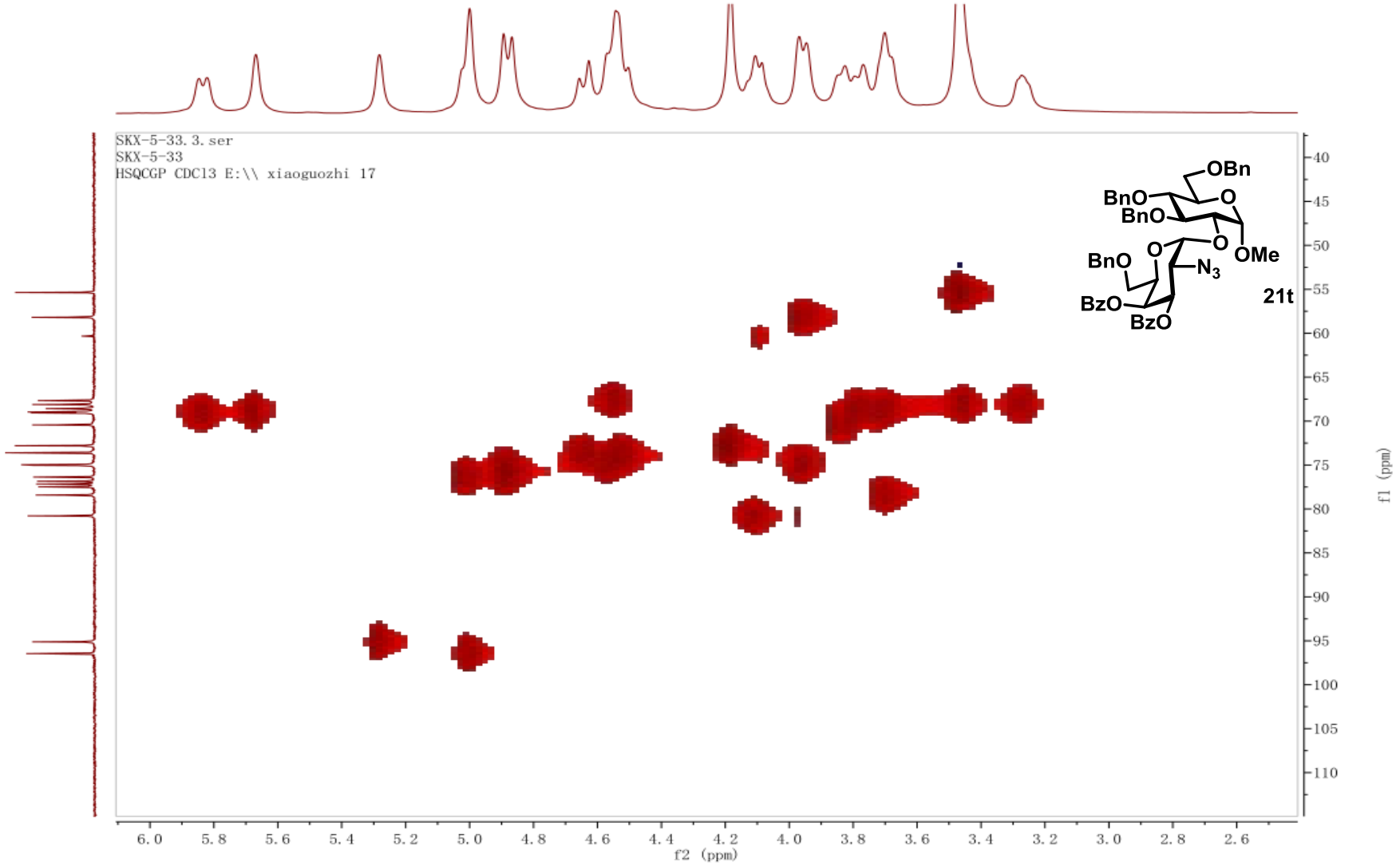

SKX-5-37.3.ser
BzO
OBn
BzO
N3
BnO
OBn
BnO
OMe
21s
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
f2 (ppm)

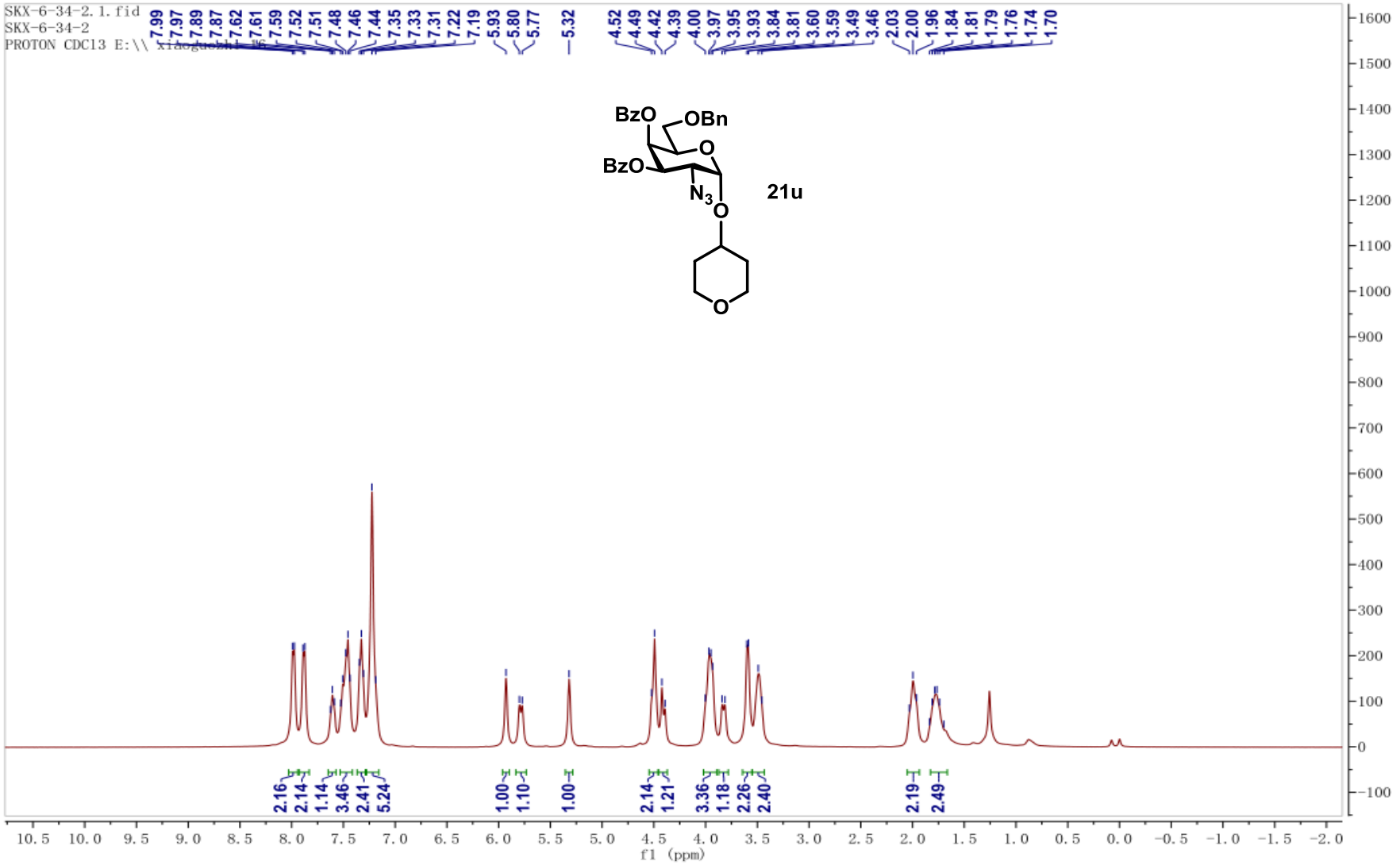

SKX-5-37.4.ser
SKX-5-37
BzO
OBn
O
BzO
N3
O
BnO
OBn
O
BnO
OMe
21s
f2 (ppm)
f1 (ppm)

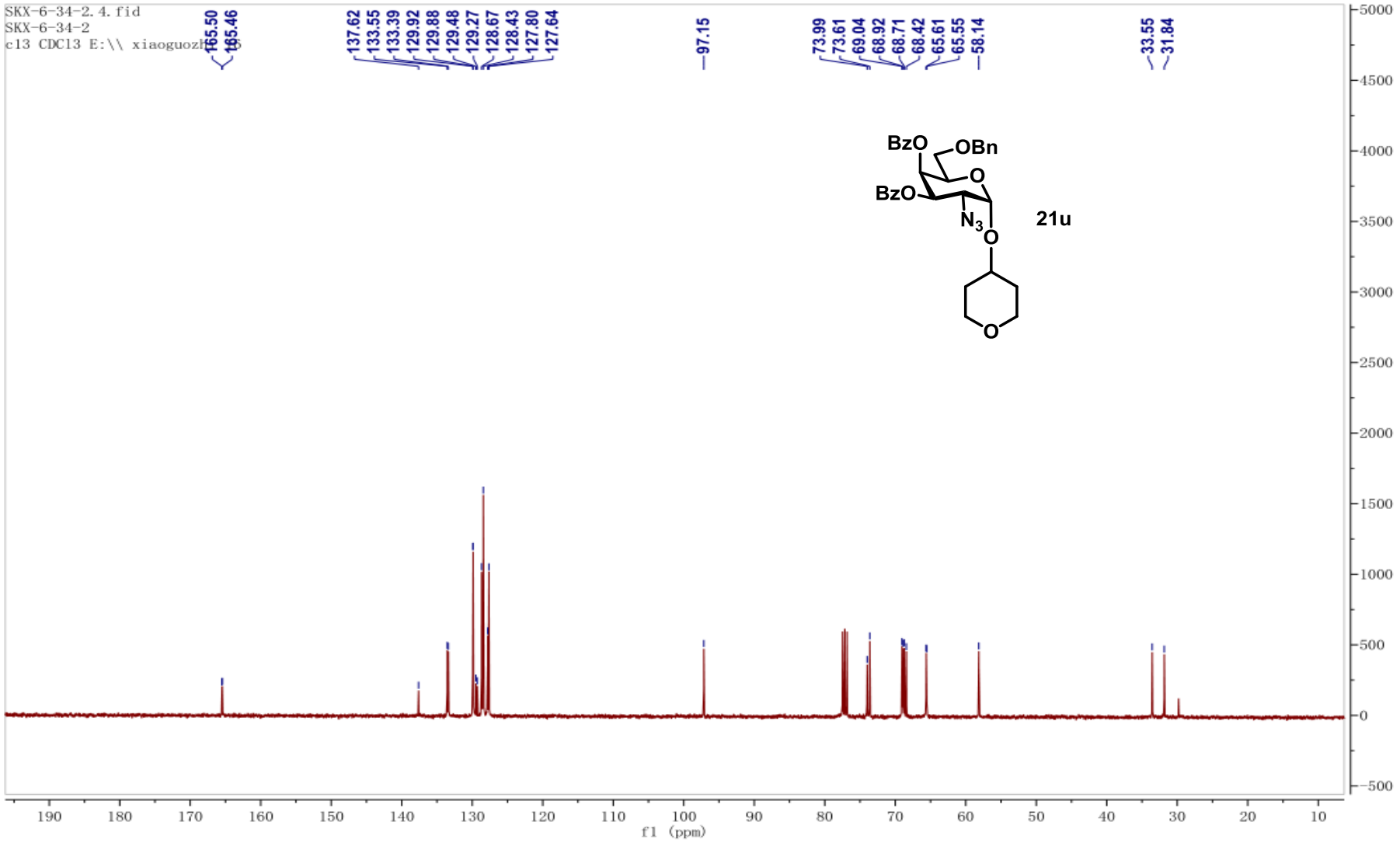

OBn
BnO
BnO
O
O
OMe
BnO
O
N3
BzO
BzO
21t
f1 (ppm)

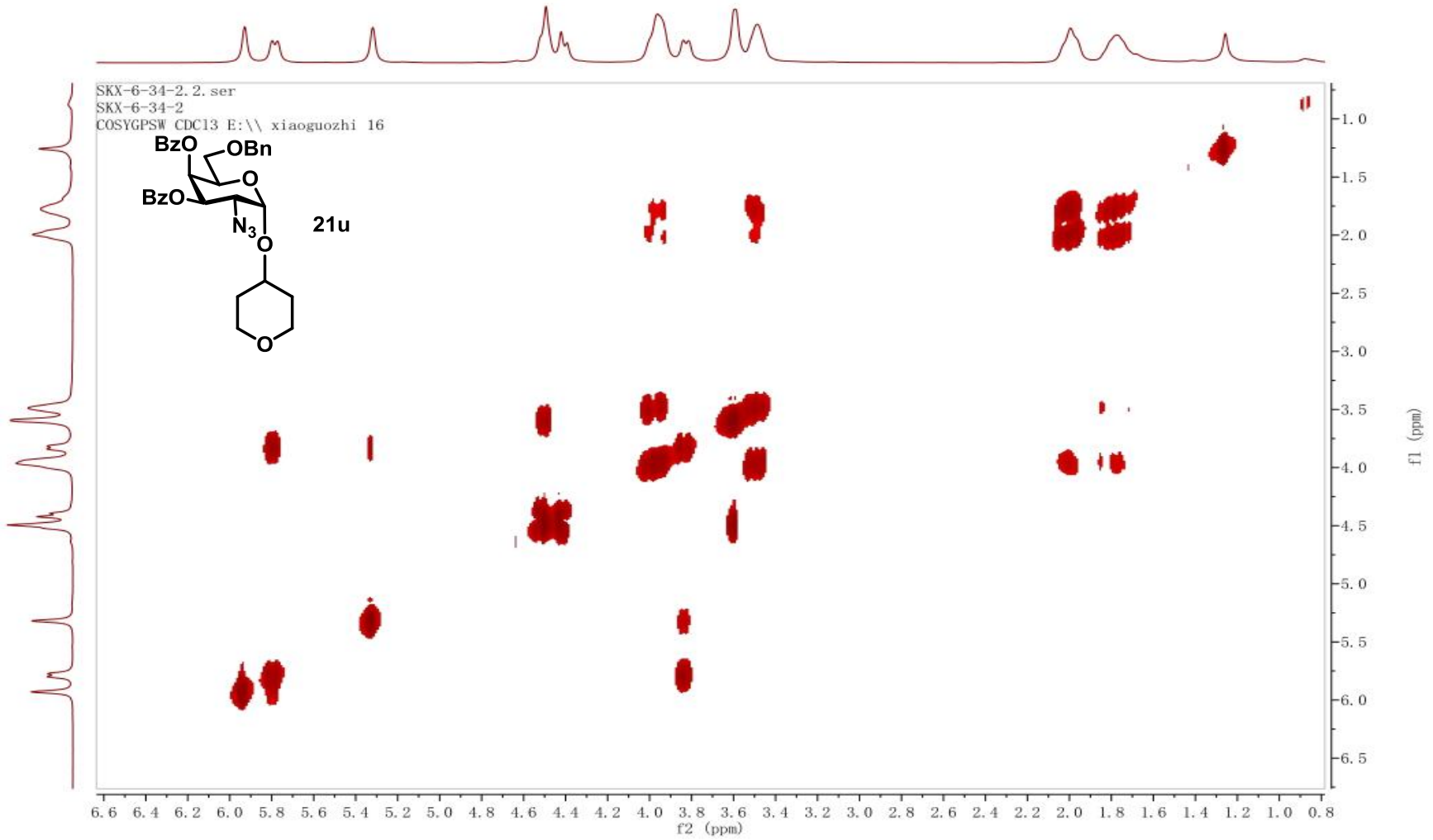

SKX-5-33.4.fid
SKX-5-33
c13 CDCl3 E:\\
165.35
155.20
138.30
138.22
138.01
137.93
133.32
133.19
129.82
129.73
129.57
129.36
128.62
128.52
128.42
128.31
128.25
128.17
127.94
127.90
127.83
127.72
127.55
127.49
127.37
96.45
95.12
80.78
78.41
76.36
75.03
74.96
73.60
72.79
70.43
69.06
68.95
68.58
68.11
67.66
60.33
58.19
55.35
OBn
BnO
BnO
O
O
OMe
BnO
O
N3
BzO
BzO
21t
f1 (ppm)

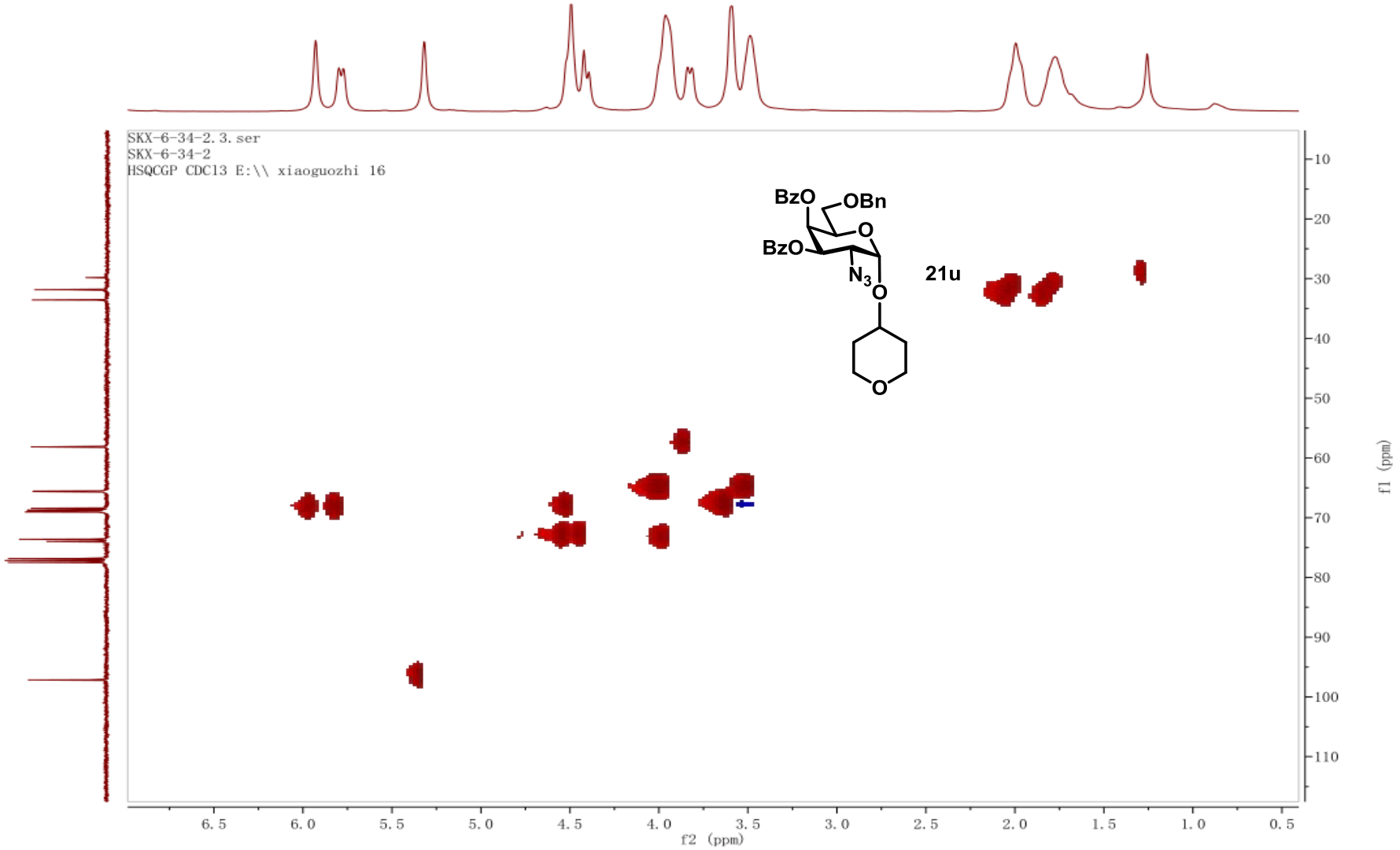

SKX-5-33.2.ser
SKX-5-33
OBn
BnO
BnO
O
O
OMe
BnO
O
N3
BzO
BzO
21t
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f2 (ppm)

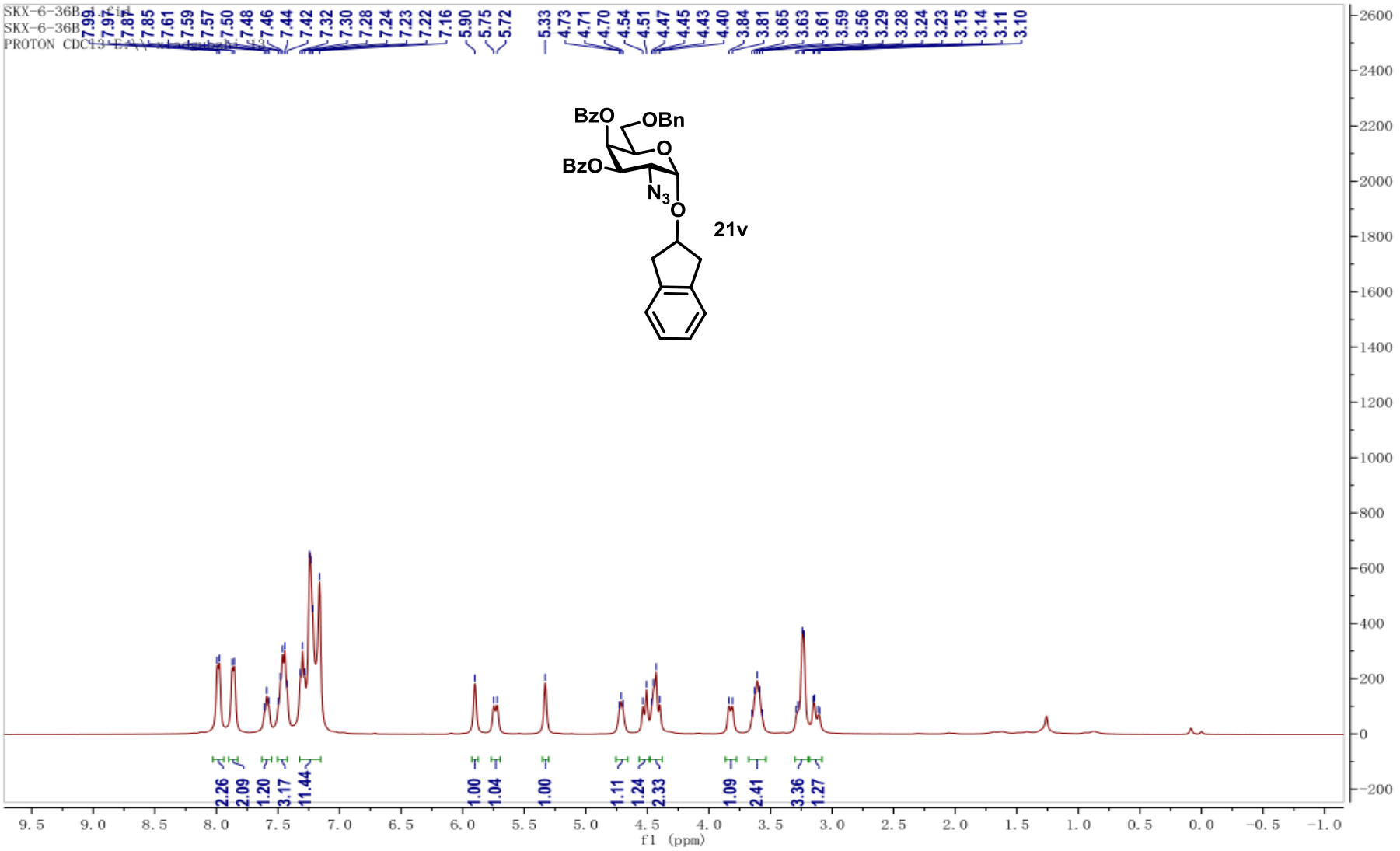

SKX-5-33.3.ser
SKX-5-33
HSQCGP CDCl3 E:\\ xiaoguozhi 17
OBn
BnO
BnO
O
O
OMe
BnO
O
N3
BzO
BzO
21t
f2 (ppm)
f1 (ppm)

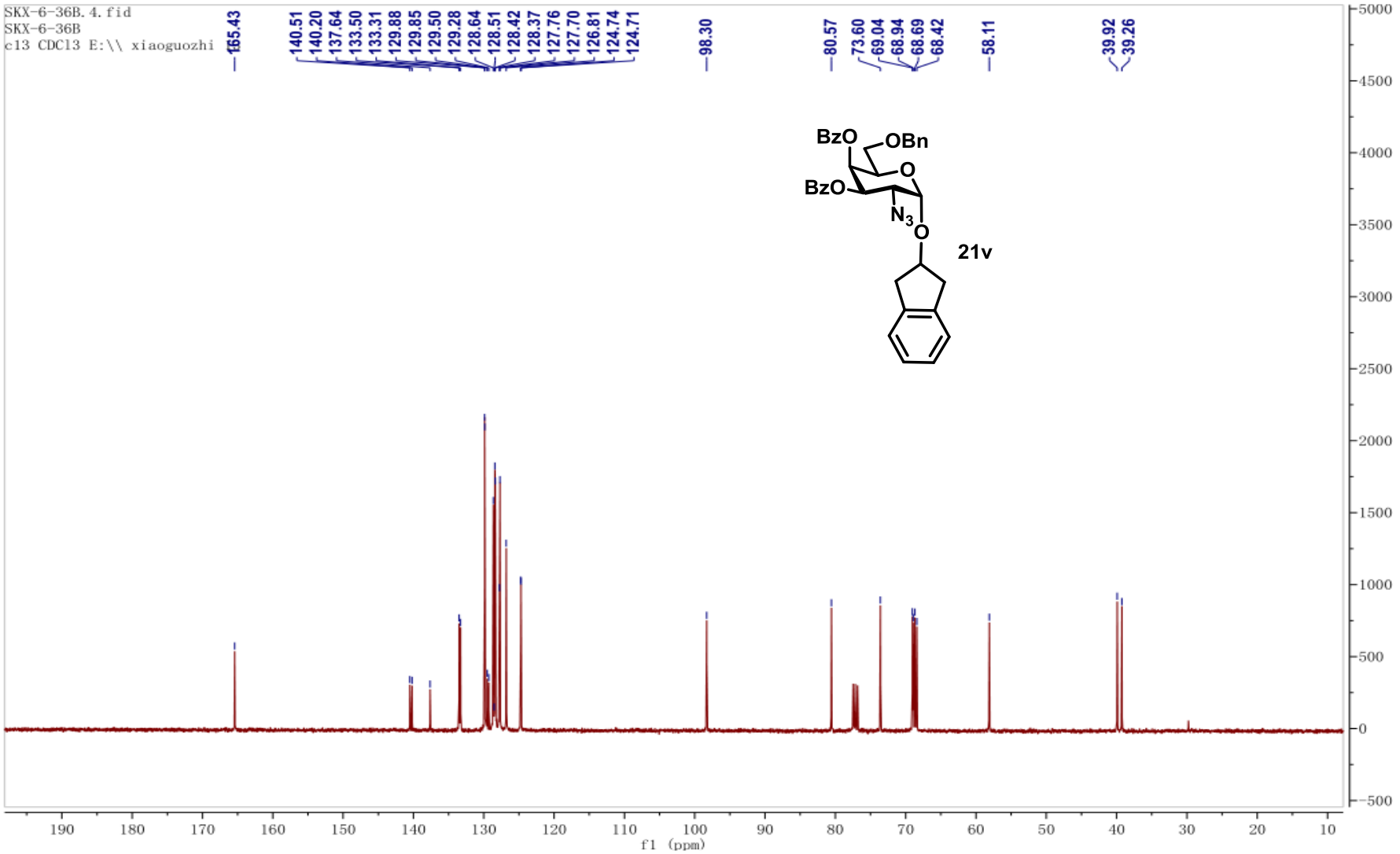

SKX-6-34-2.1.fid
SKX-6-34-2
PROTON CDCl3 E:\\
7.99 7.97 7.89 7.87 7.62 7.61 7.59 7.52 7.51 7.48 7.46 7.44 7.35 7.33 7.31 7.22 7.19 5.93 5.80 5.77 5.32 4.52 4.49 4.42 4.39 4.00 3.97 3.95 3.93 3.84 3.81 3.60 3.59 3.49 3.46 2.03 2.00 1.96 1.84 1.81 1.79 1.76 1.74 1.70
BzO
OBn
O
BzO
N3
O
O
21u
2.16 2.14 1.14 3.46 2.41 5.24 1.00 1.10 1.00 2.14 1.21 3.36 1.18 2.26 2.40 2.19 2.49
f1 (ppm)

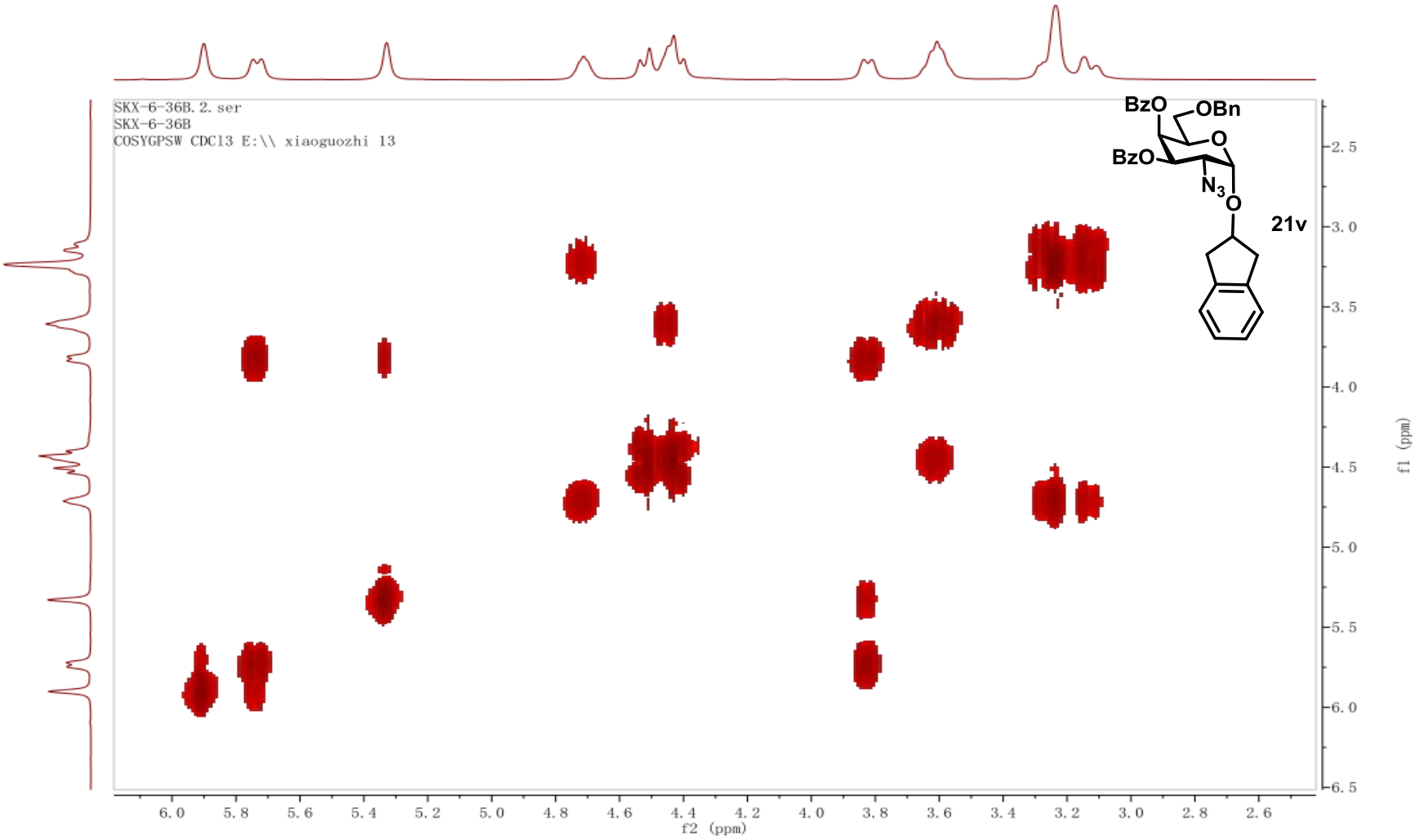

SKX-6-34-2.4.fid
SKX-6-34-2
c13 CDCl3 E:\\ xiaoguozh
165.50
165.46
137.62
133.55
133.39
129.92
129.88
129.48
129.27
128.67
128.43
127.80
127.64
97.15
73.99
73.61
69.04
68.92
68.71
68.42
65.61
65.55
58.14
33.55
31.84
BzO
OBn
O
BzO
N3
O
O
21u
f1 (ppm)

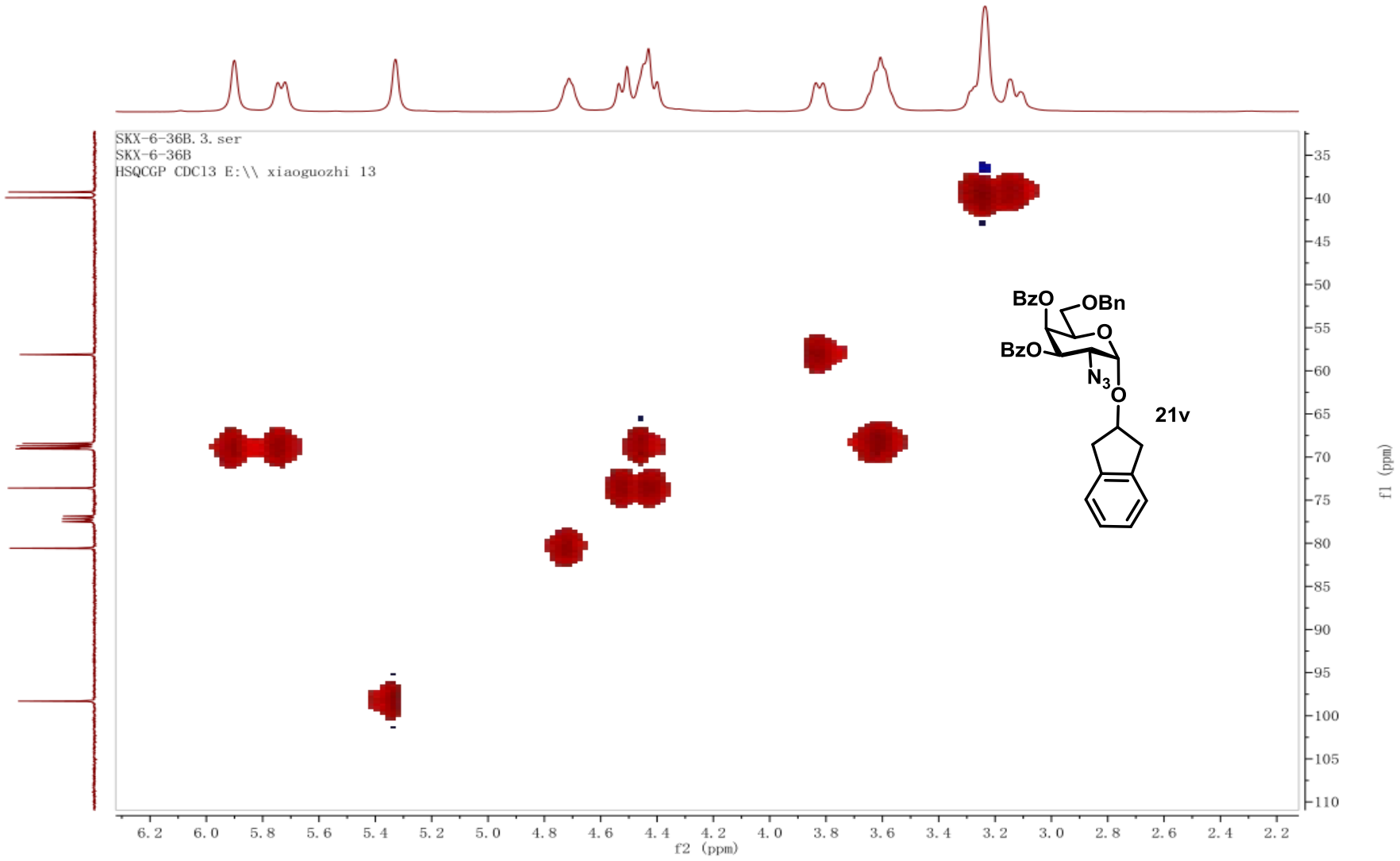

SKX-6-34-2.2.ser
SKX-6-34-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 16
BzO
OBn
O
BzO
N3
O
21u
O
f2 (ppm)
f1 (ppm)

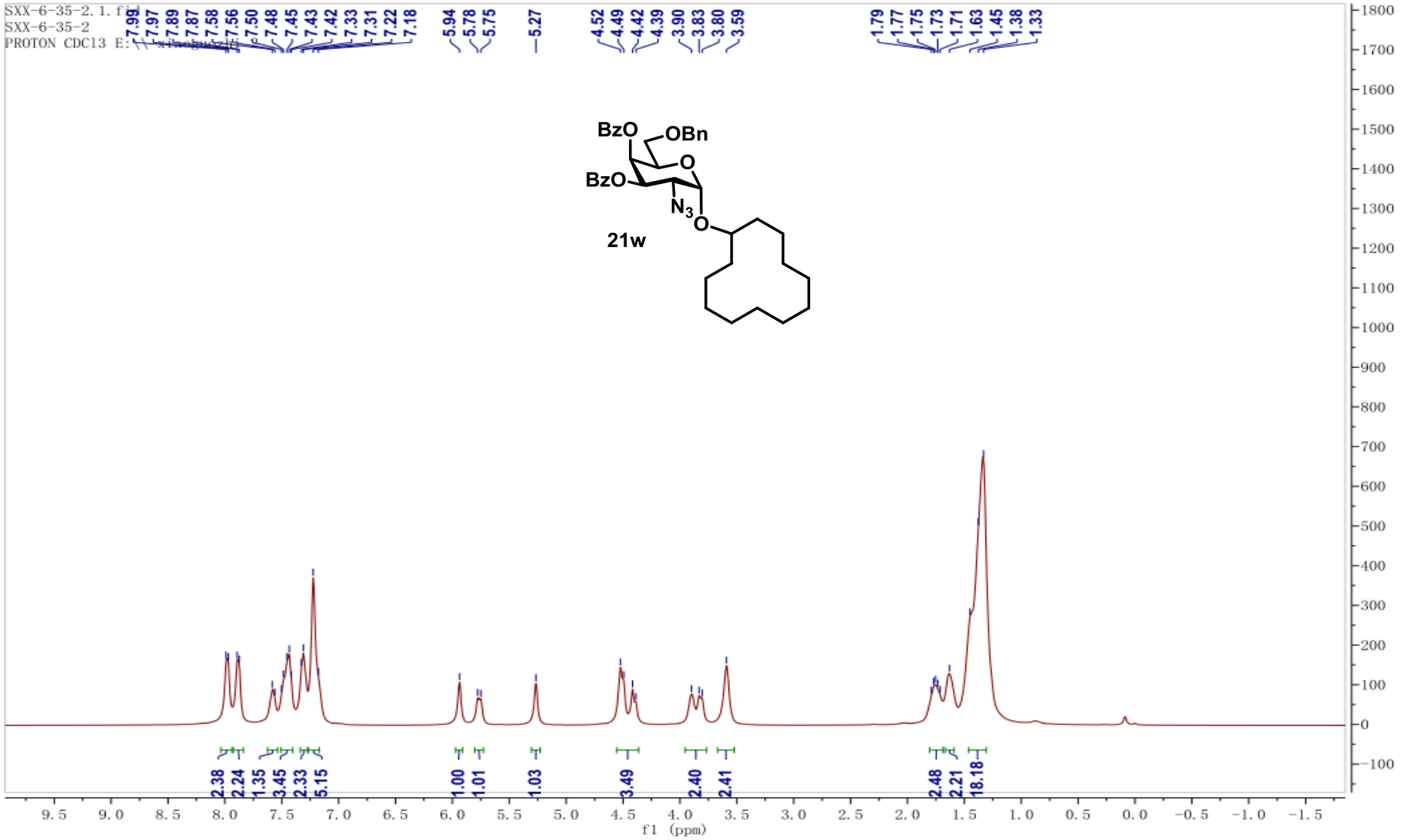

SKX-6-34-2.3.ser
SKX-6-34-2
HSQCGP CDCl3 E:\\ xiaoguozhi 16
BzO
OBn
O
BzO
N3
O
O
21u
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

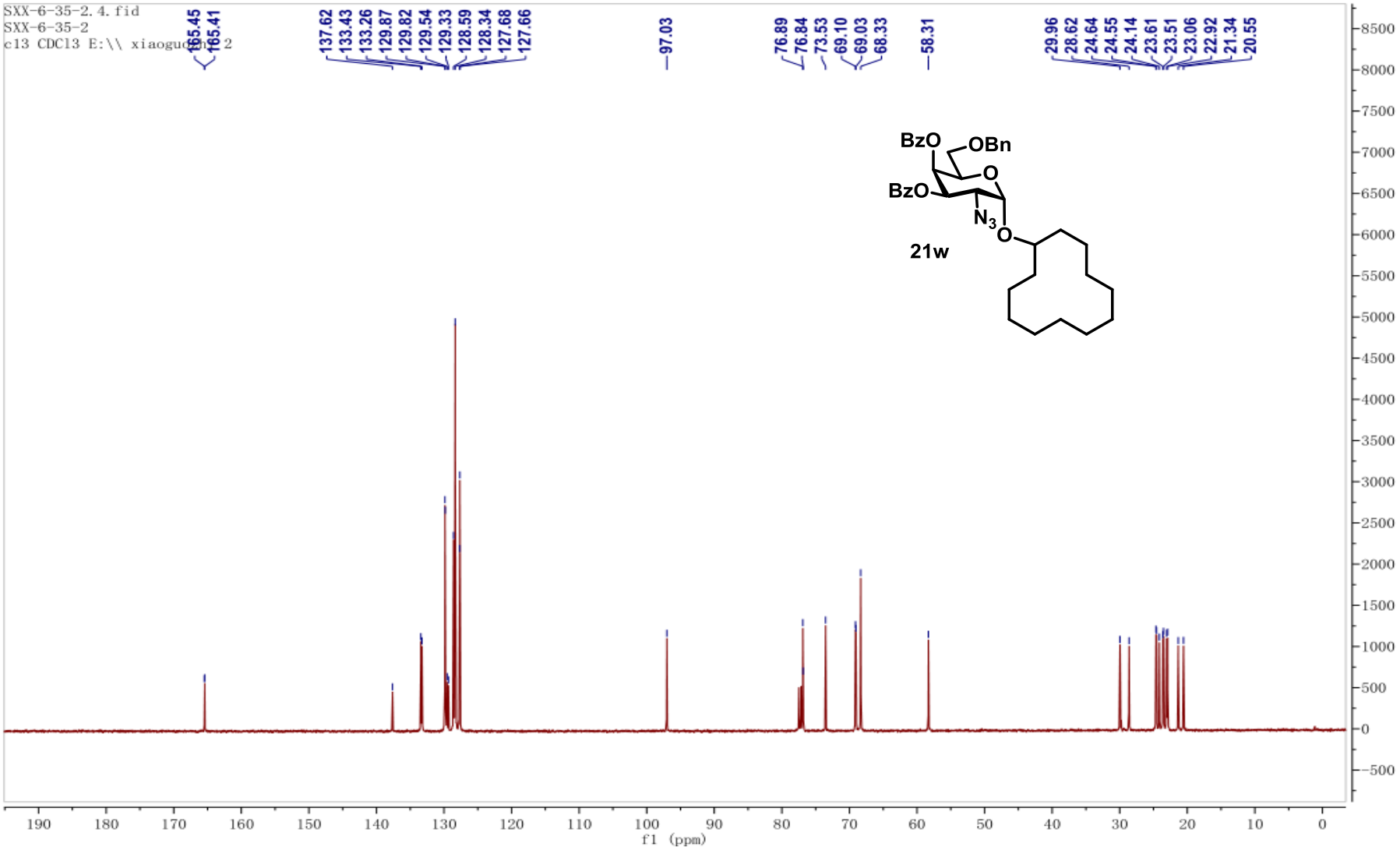

SKX-6-36B
PROTON CDCl3
BzO
OBn
O
BzO
N3
O
21v
f1 (ppm)

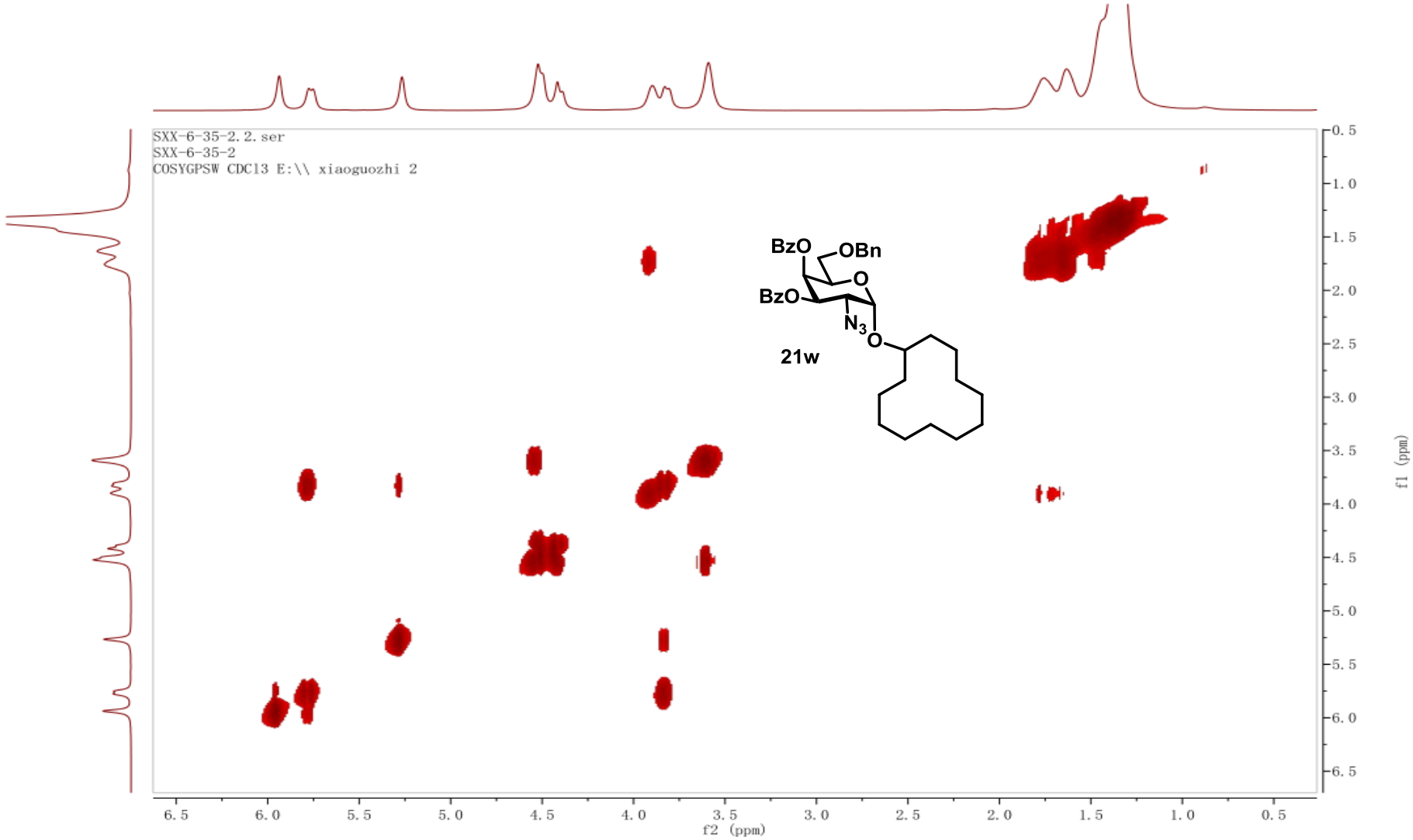

SKX-6-36B.4.fid
SKX-6-36B
c13 CDCl3 E:\\ xiaoguozhi
165.43
140.51
140.20
137.64
133.50
133.31
129.88
129.85
129.50
129.28
128.64
128.51
128.42
128.37
127.76
127.70
126.81
124.74
124.71
98.30
80.57
73.60
69.04
68.94
68.69
68.42
58.11
39.92
39.26
BzO
OBn
O
BzO
N3
O
21v
f1 (ppm)

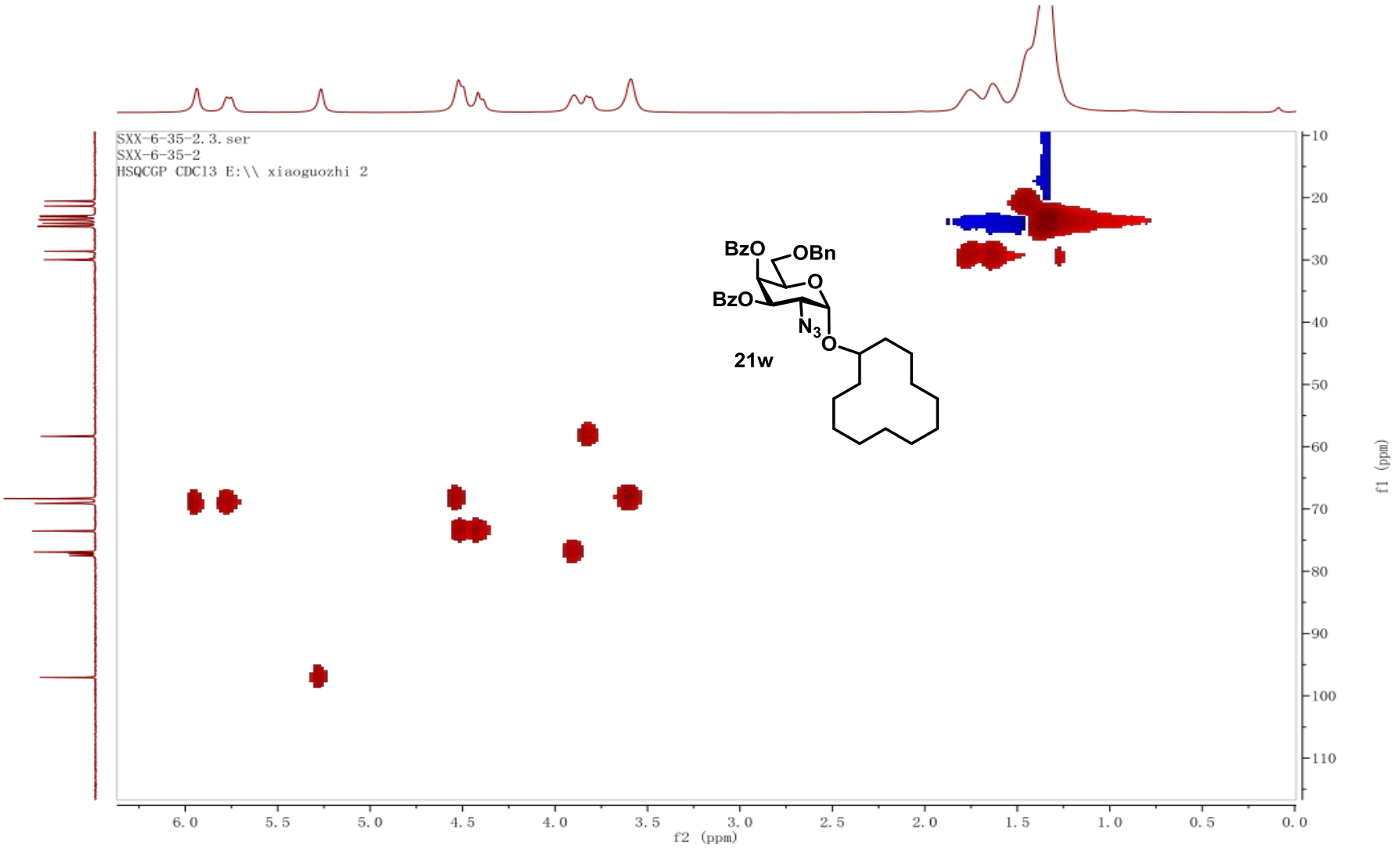

SKX-6-36B.2.ser
SKX-6-36B
COSYGPSW CDCl3 E:\\ xiaoguozhi 13
BzO
OBn
O
BzO
N3
O
21v
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

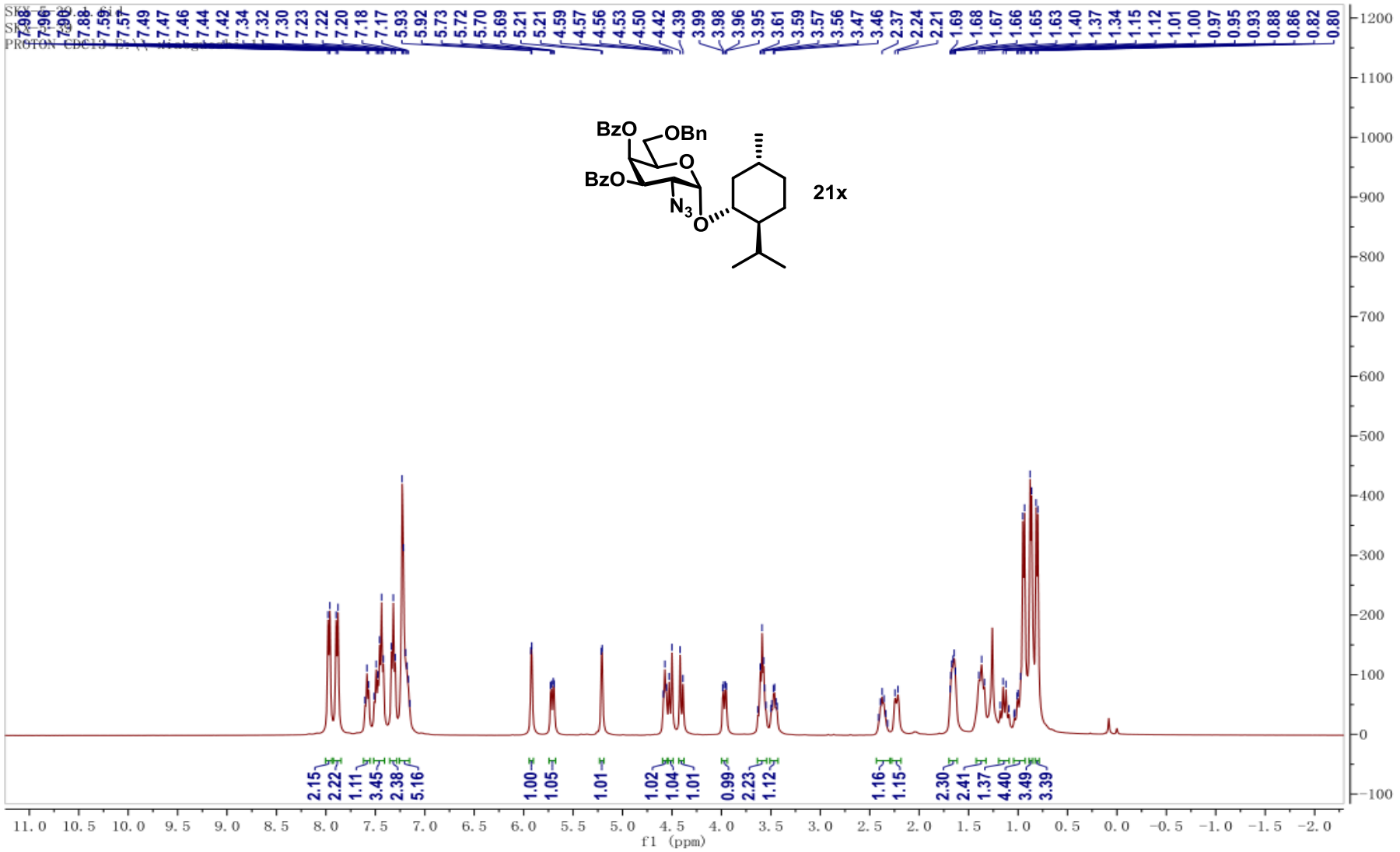

SKX-6-36B.3.ser
SKX-6-36B
HSQCGP CDCl3 E:\\ xiaoguozhi 13
BzO
OBn
O
BzO
N3
O
21v
f2 (ppm)
f1 (ppm)

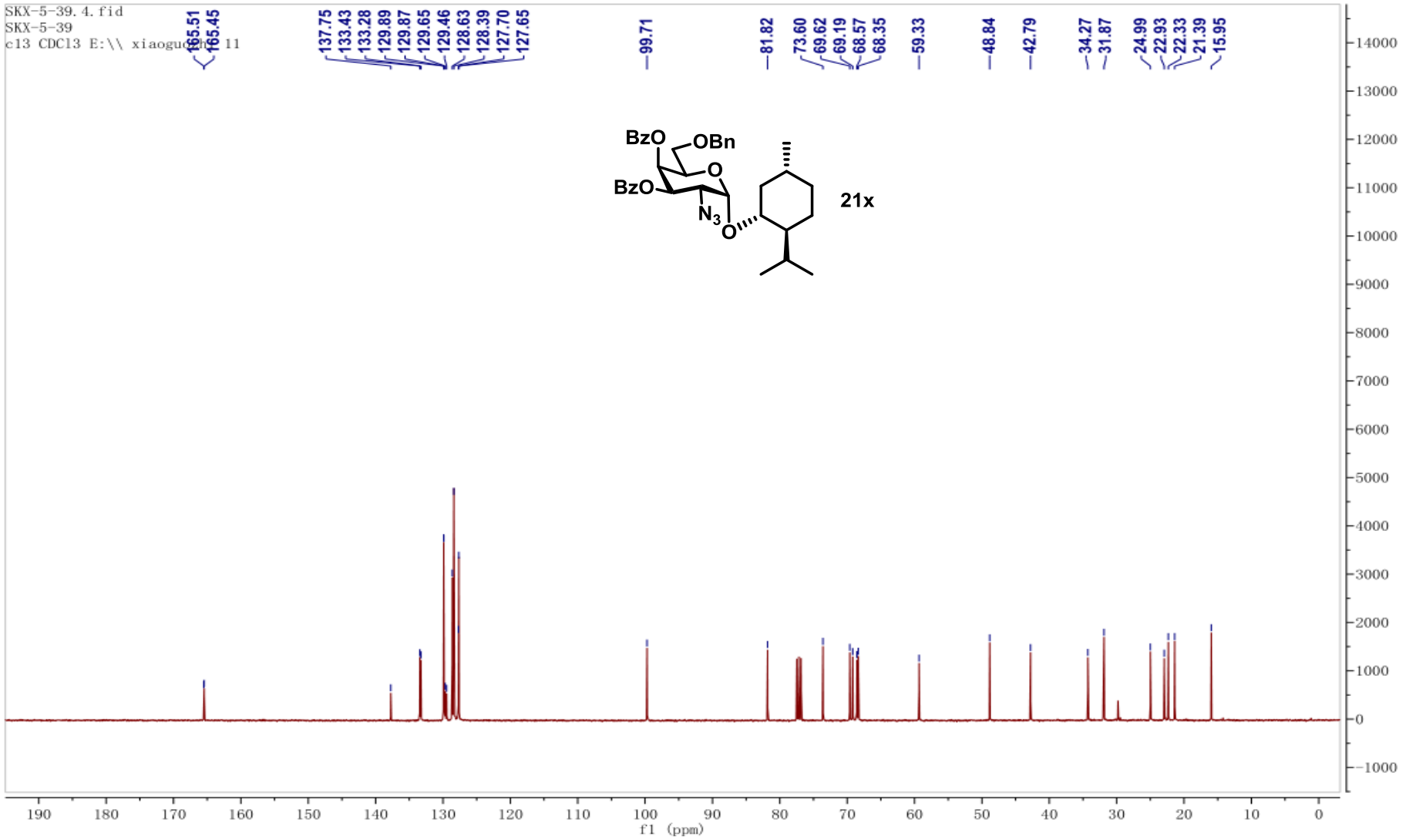

SXX-6-35-2.1.fid
SXX-6-35-2
PROTON CDC13 E:
7.99
7.97
7.89
7.87
7.58
7.56
7.50
7.48
7.45
7.43
7.42
7.33
7.31
7.22
7.18
5.94
5.78
5.75
5.27
4.52
4.49
4.42
4.39
3.90
3.83
3.80
3.59
1.79
1.77
1.75
1.73
1.71
1.63
1.45
1.38
1.33
BzO
OBn
O
BzO
N3
O
21w
2.38
2.24
1.35
3.45
2.33
5.15
1.00
1.01
1.03
3.49
2.40
2.41
2.48
2.21
18.18
f1 (ppm)

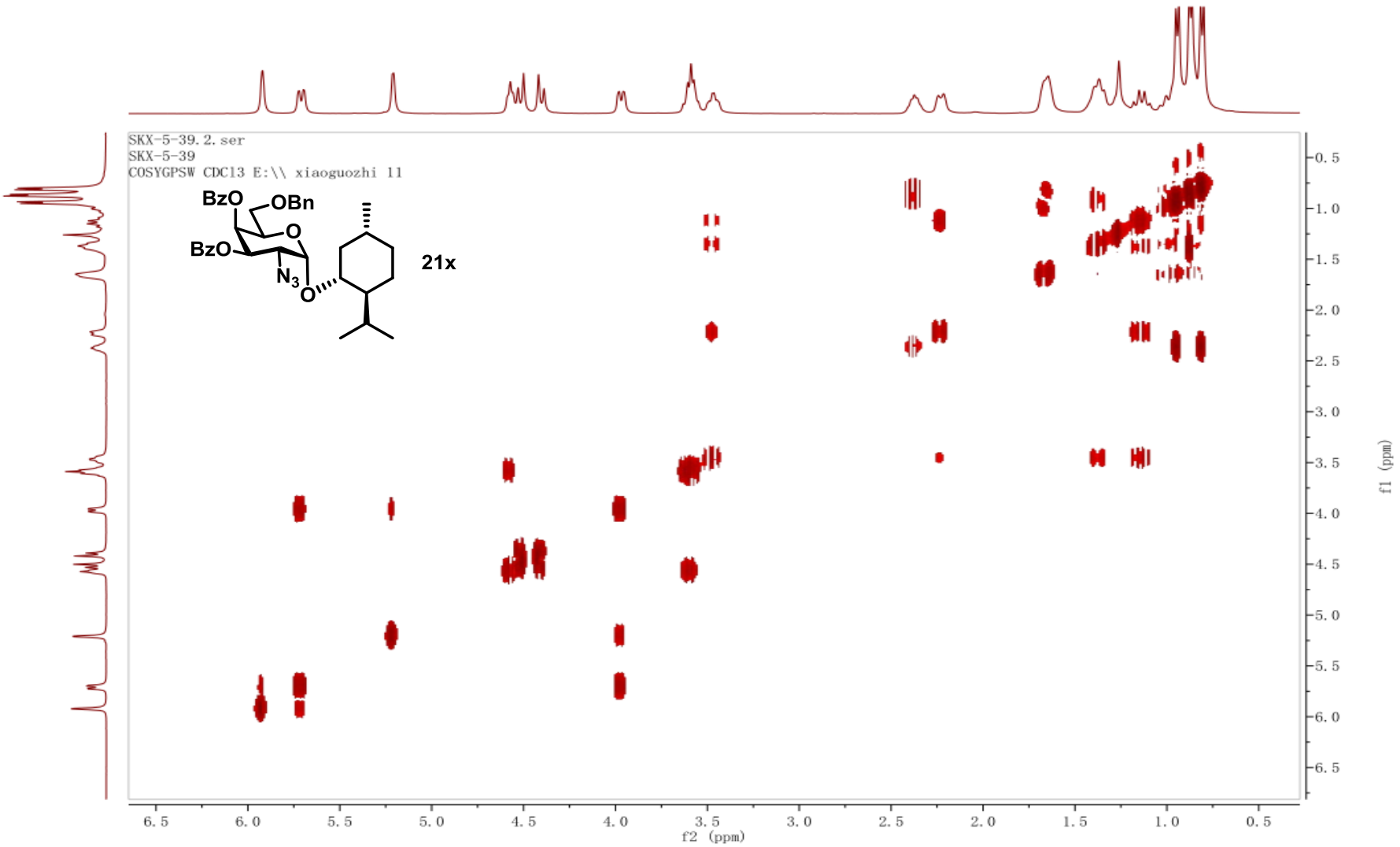

SXX-6-35-2.4.fid
SXX-6-35-2
c13 CDCl3 E:\\ xiaoguchun 2
165.45
165.41
137.62
133.43
133.26
129.87
129.82
129.54
129.33
128.59
128.34
127.68
127.66
97.03
76.89
76.84
73.53
69.10
69.03
68.33
58.31
29.96
28.62
24.64
24.55
24.14
23.61
23.51
23.06
22.92
21.34
20.55
BzO
OBn
O
BzO
N3
O
21w
f1 (ppm)

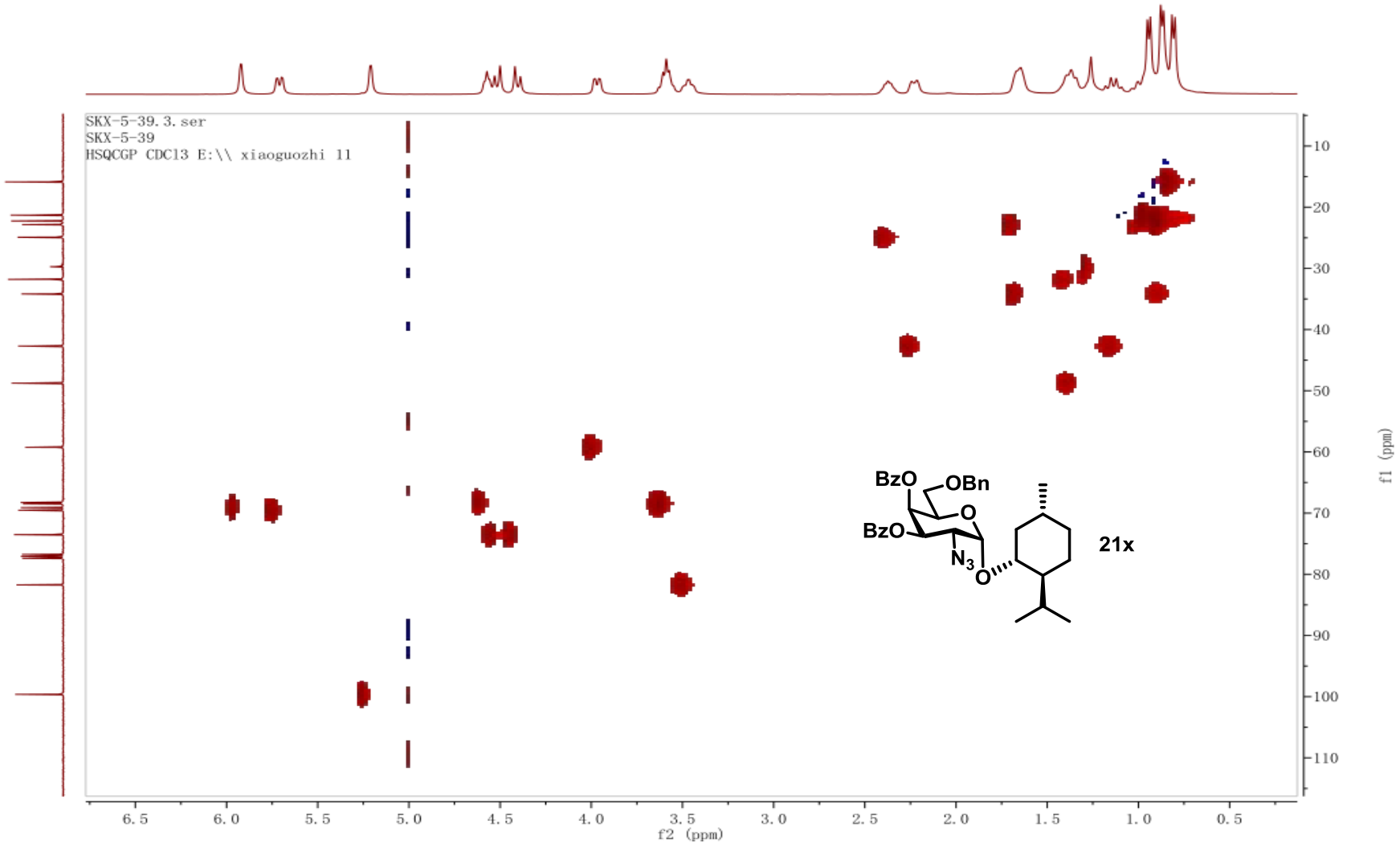

SXX-6-35-2.2.ser
SXX-6-35-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 2
BzO
OBn
O
BzO
N3
O
21w
f2 (ppm)
f1 (ppm)

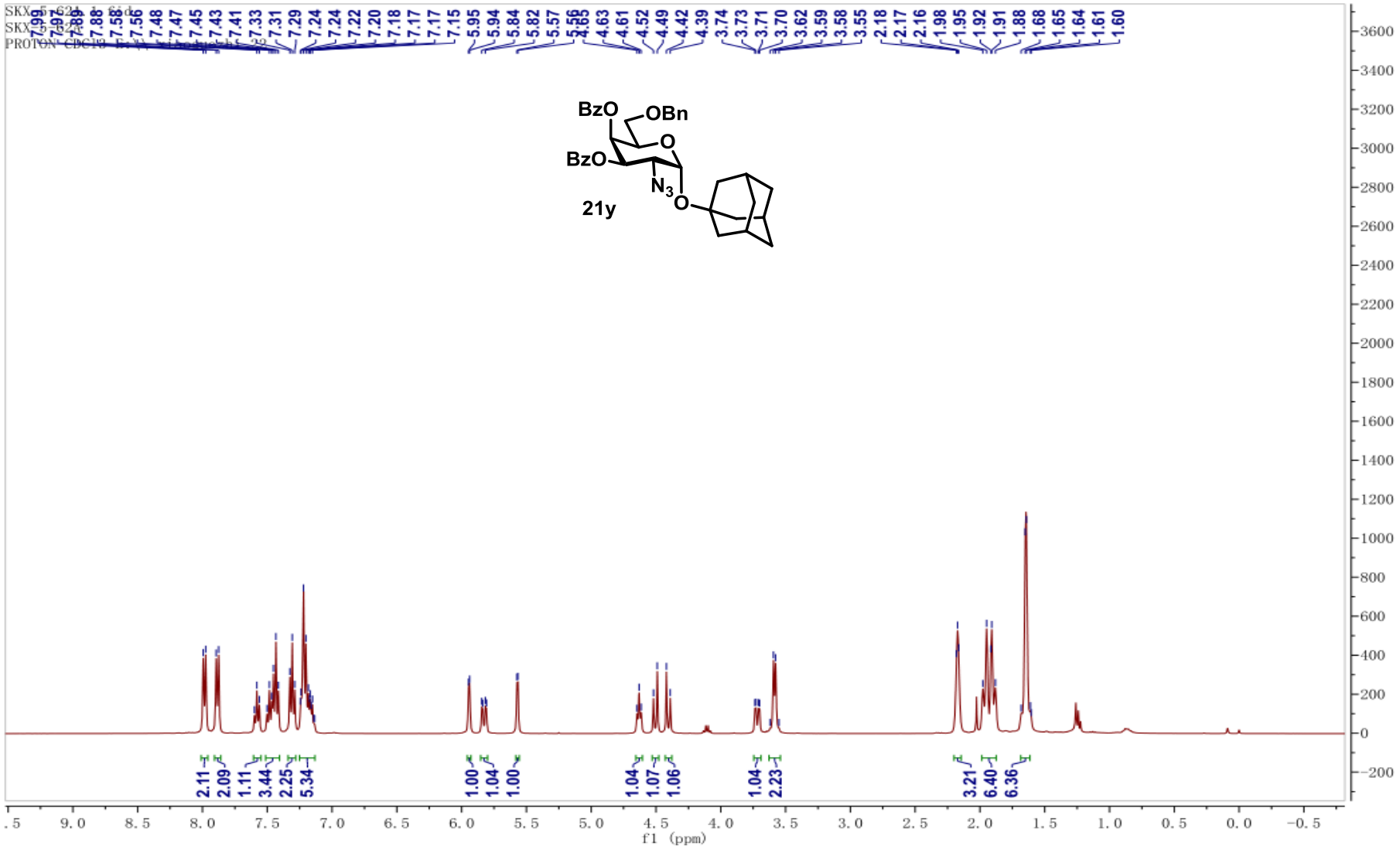

SXX-6-35-2.3.ser
SXX-6-35-2
HSQCGP CDCl3 E:\\ xiaoguozhi 2
BzO
OBn
O
BzO
N3
O
21w
f2 (ppm)
f1 (ppm)

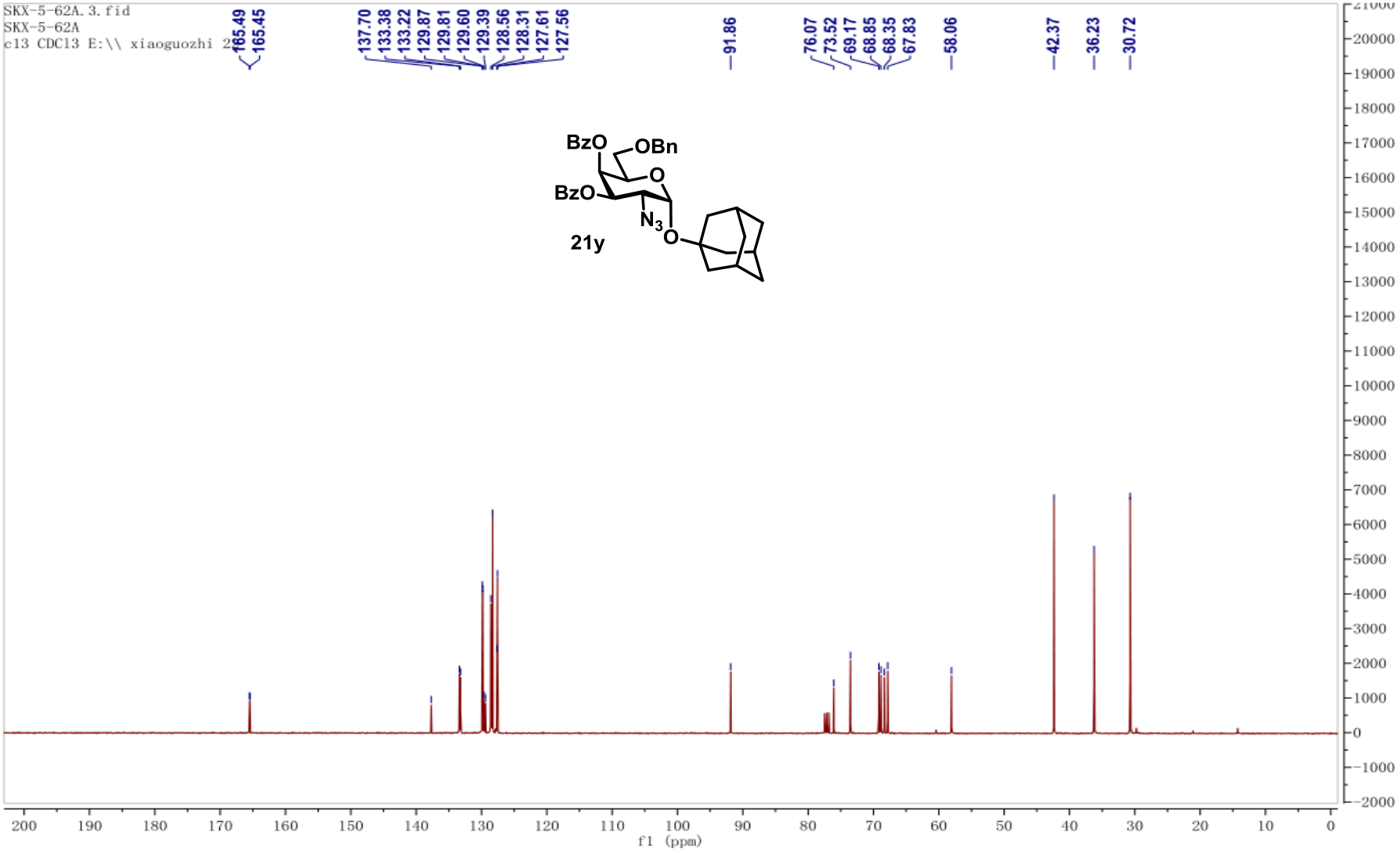

BzO
OBn
O
BzO
N3
O
21x
f1 (ppm)

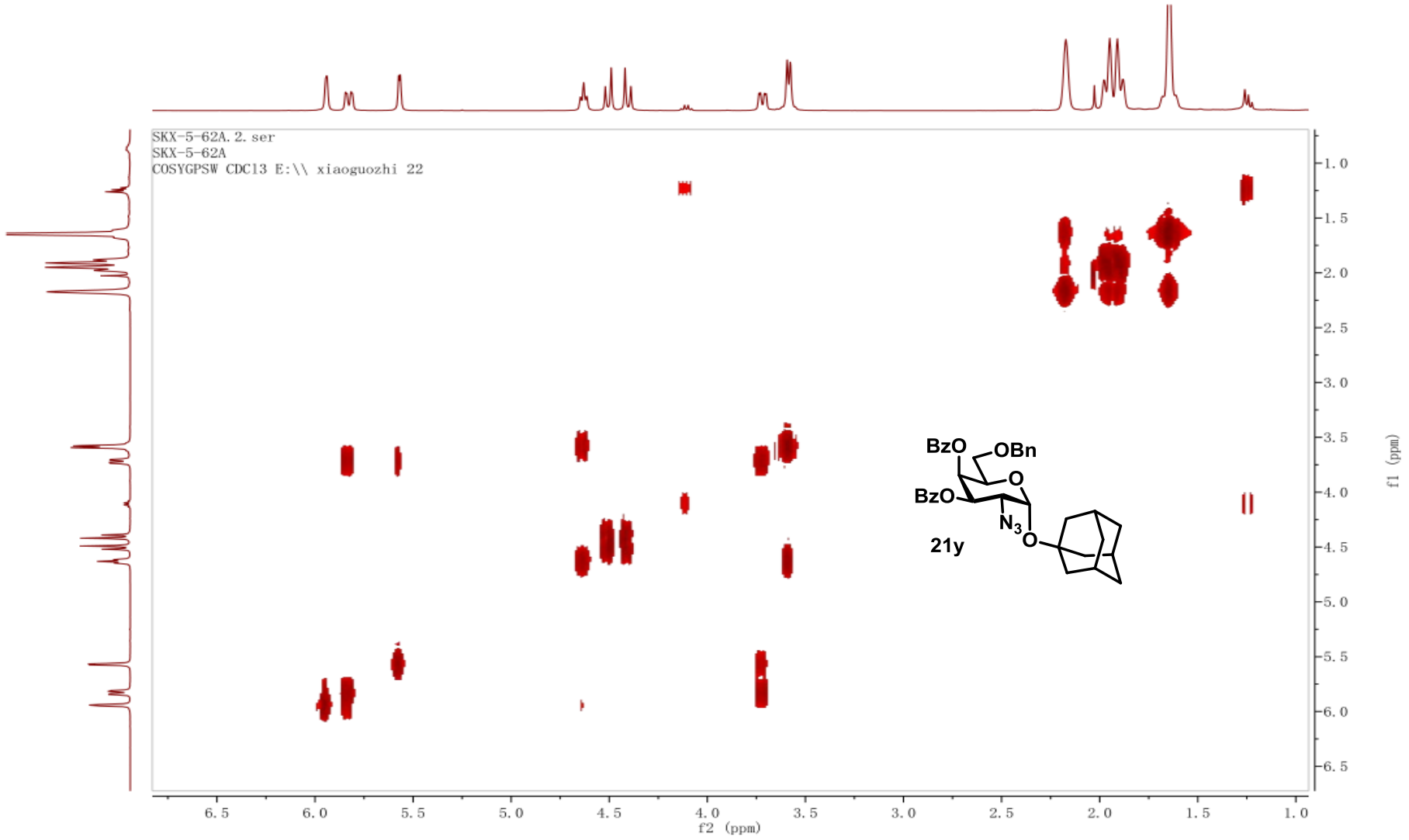

SKX-5-39.4.fid
SKX-5-39
c13 CDCl3 E:\\ xiaoguo
165.51
165.45
137.75
133.43
133.28
129.89
129.87
129.65
129.46
128.63
128.39
127.70
127.65
99.71
81.82
73.60
69.62
69.19
68.57
68.35
59.33
48.84
42.79
34.27
31.87
24.99
22.93
22.33
21.39
15.95
BzO
OBn
O
BzO
N3
O
21x
f1 (ppm)

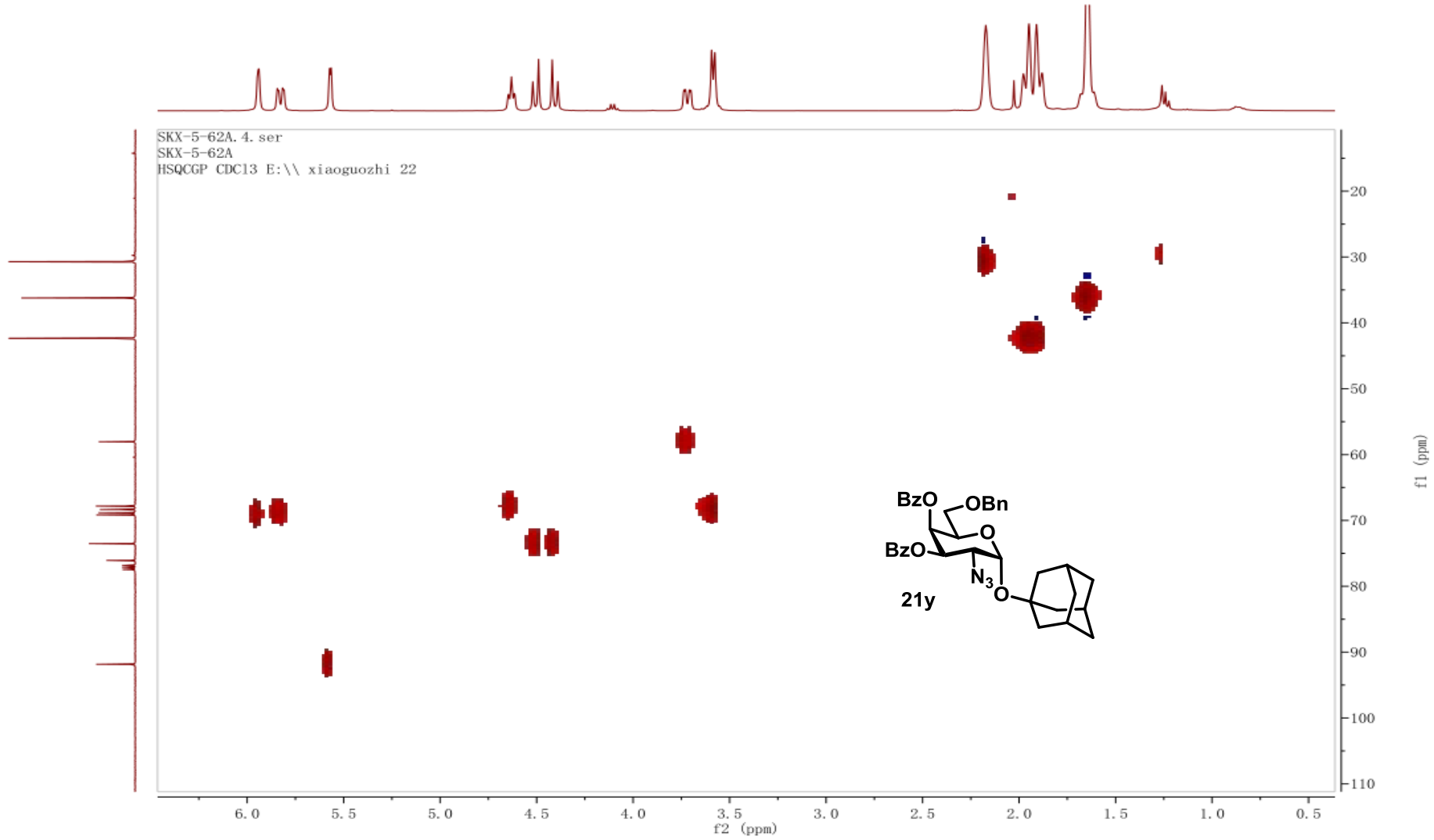

SKX-5-39.2.ser
SKX-5-39
COSYGPSW CDCl3 E:\\ xiaoguozhi 11
BzO
OBn
O
BzO
N3
O
21x
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

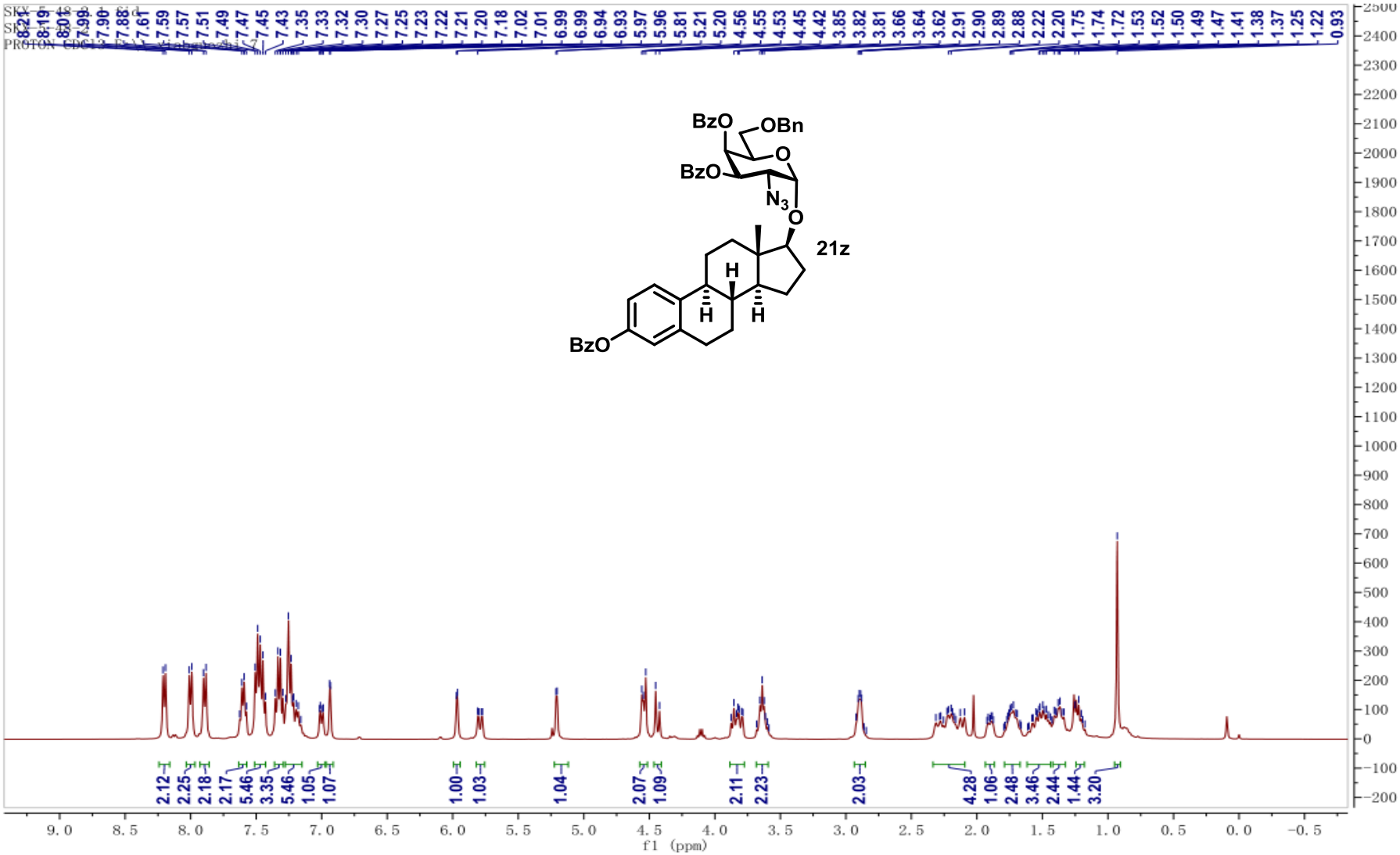

SKX-5-39.3.ser
SKX-5-39
HSQCGP CDCl3 E:\\ xiaoguozhi 11
BzO
OBn
O
BzO
N3
O
21x
f2 (ppm)
f1 (ppm)

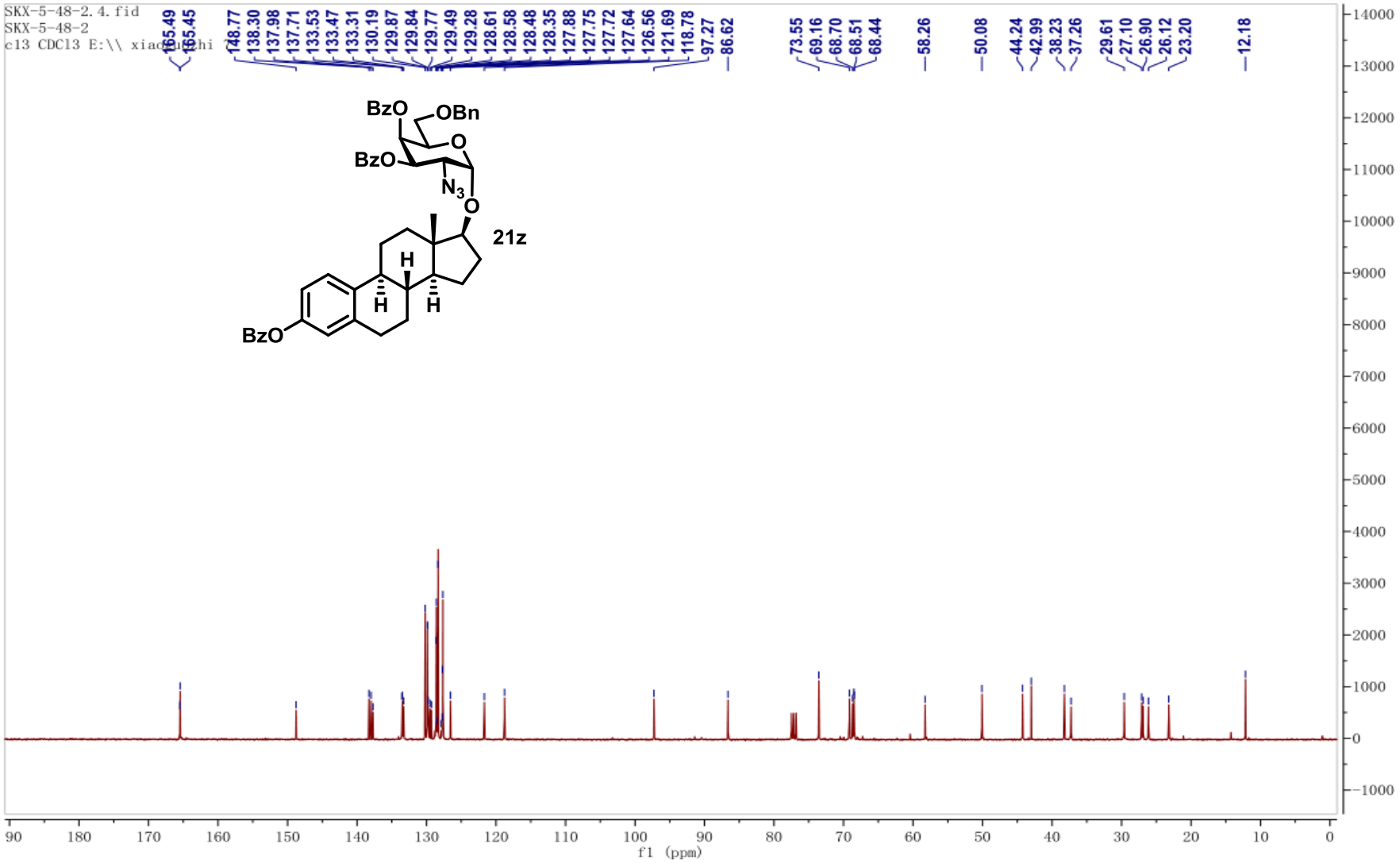

BzO
OBn
O
BzO
N3
O
21y
f1 (ppm)

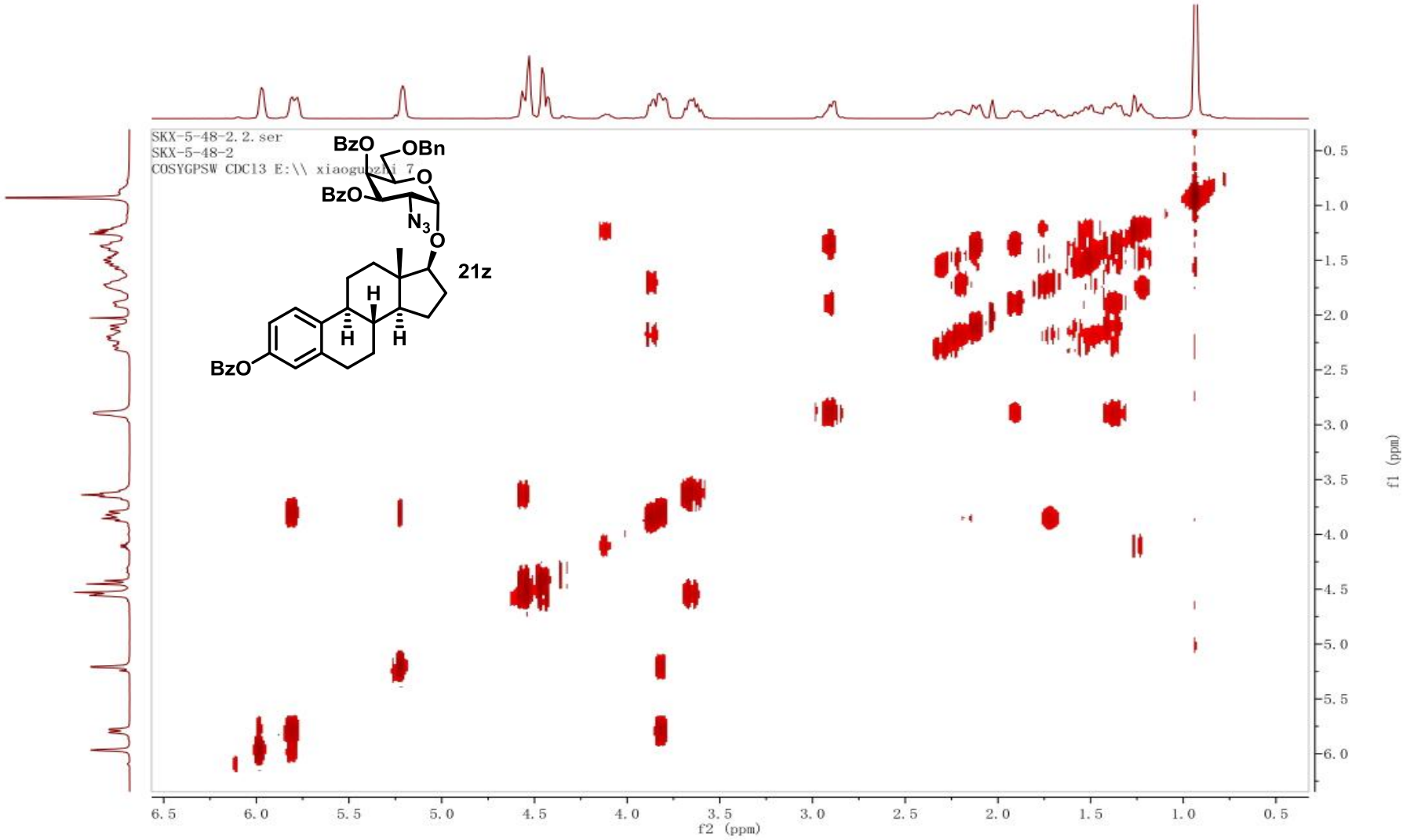

SKX-5-62A.3.fid
SKX-5-62A
c13 CDCl3 E:\\ xiaoguozhi 2
165.49
165.45
137.70
133.38
133.22
129.87
129.81
129.60
129.39
128.56
128.31
127.61
127.56
91.86
76.07
73.52
69.17
68.85
68.35
67.83
58.06
42.37
36.23
30.72
BzO
OBn
O
BzO
N3
O
21y
f1 (ppm)

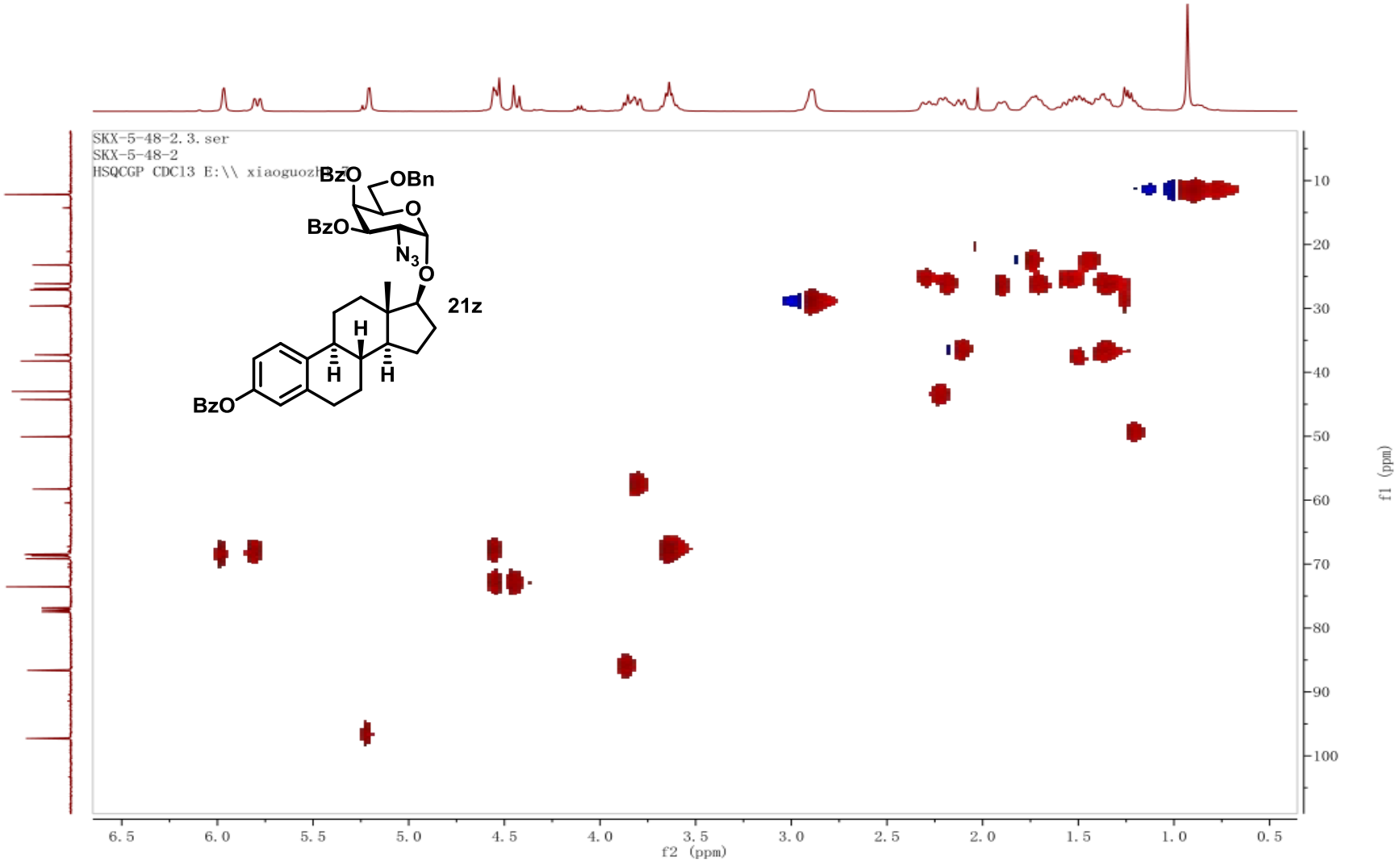

SKX-5-62A.2.ser
SKX-5-62A
COSYGPSW CDC13 E:\\ xiaoguozhi 22
BzO
OBn
O
BzO
N3
O
21y
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)

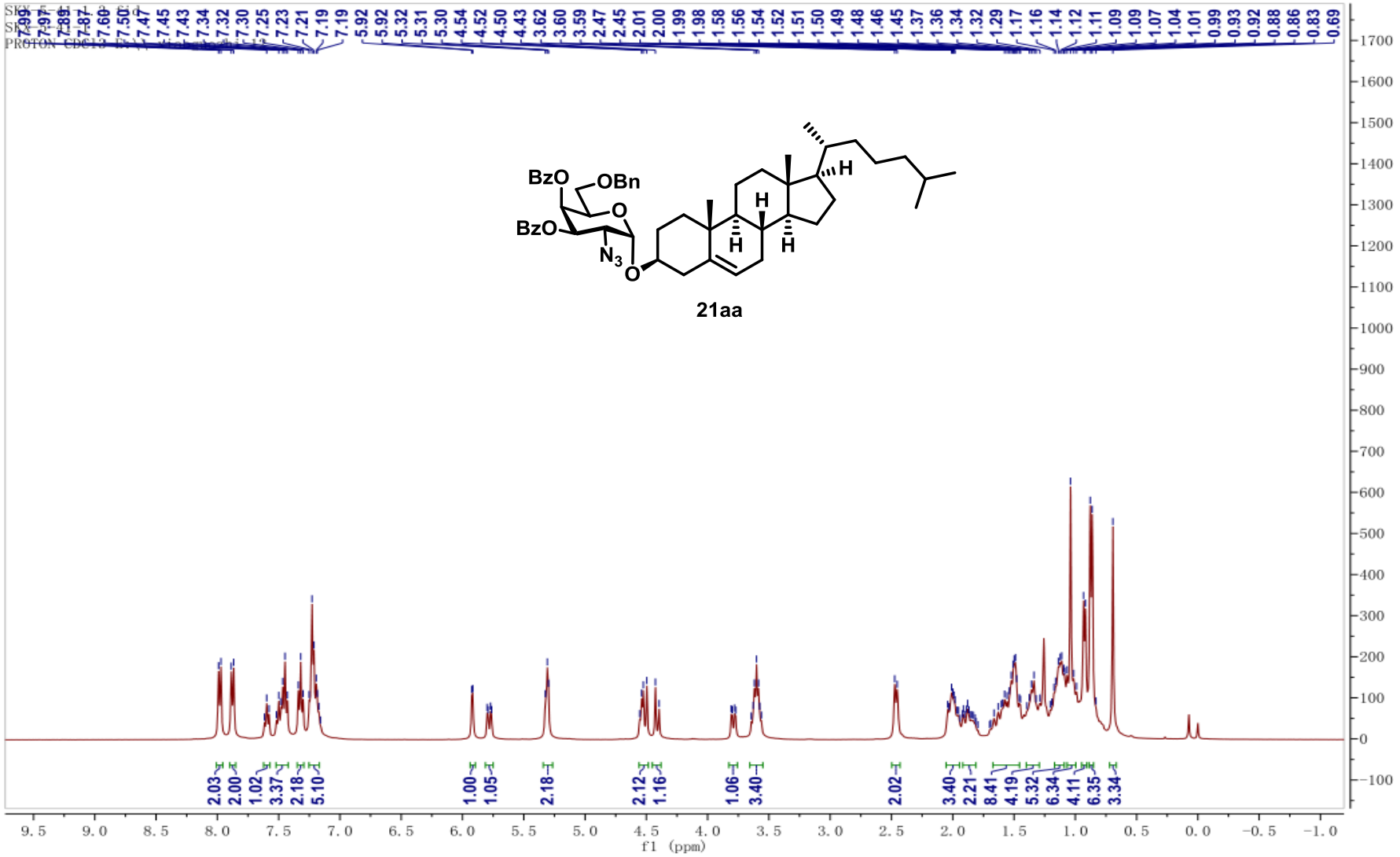

SKX-5-62A.4.ser
SKX-5-62A
HSQCGP CDCl3 E:\\ xiaoguozhi 22
BzO
OBn
O
BzO
N3
O
21y
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

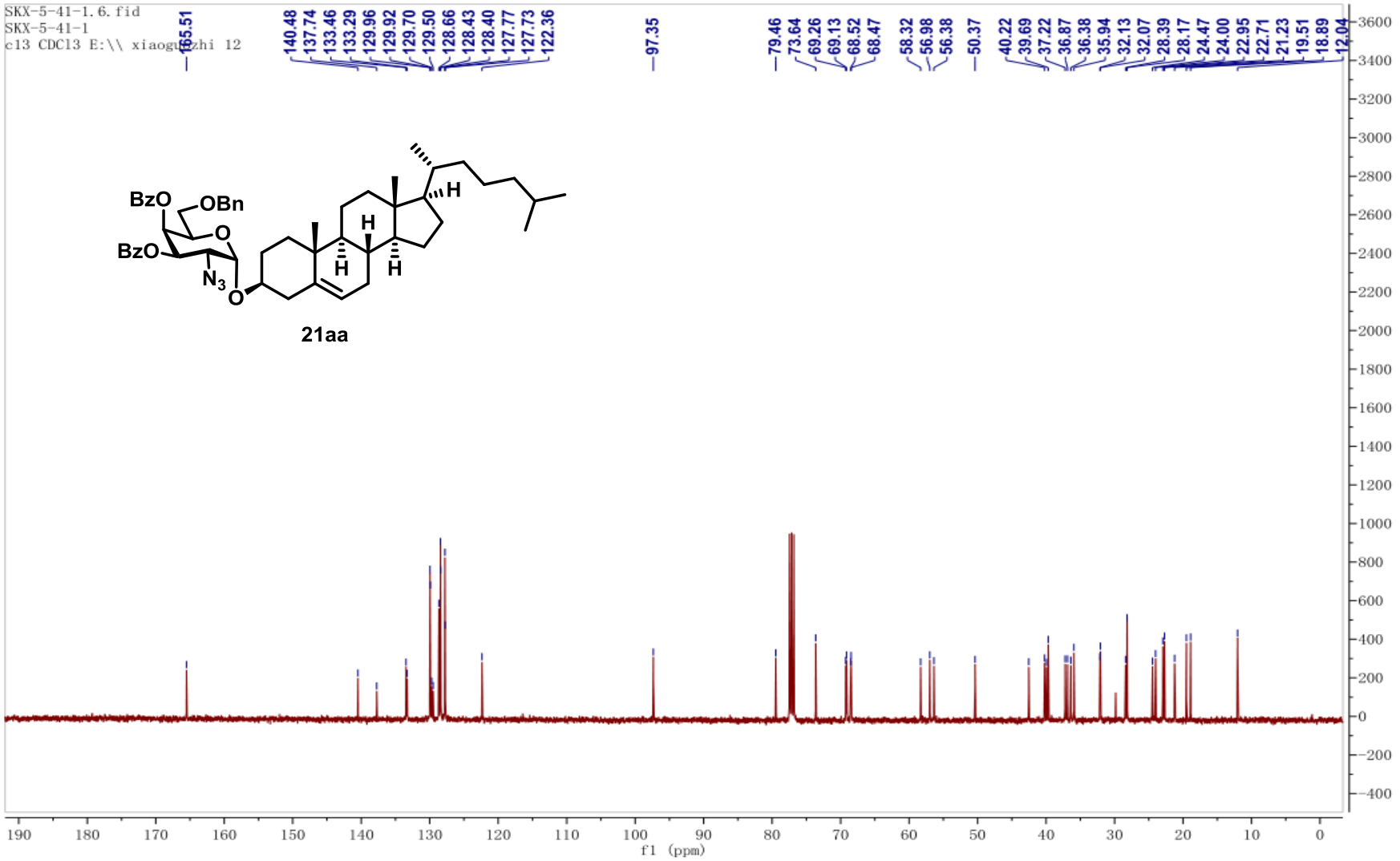

BzO
OBn
O
BzO
N3
O
21z
H
H
H
BzO
f1 (ppm)

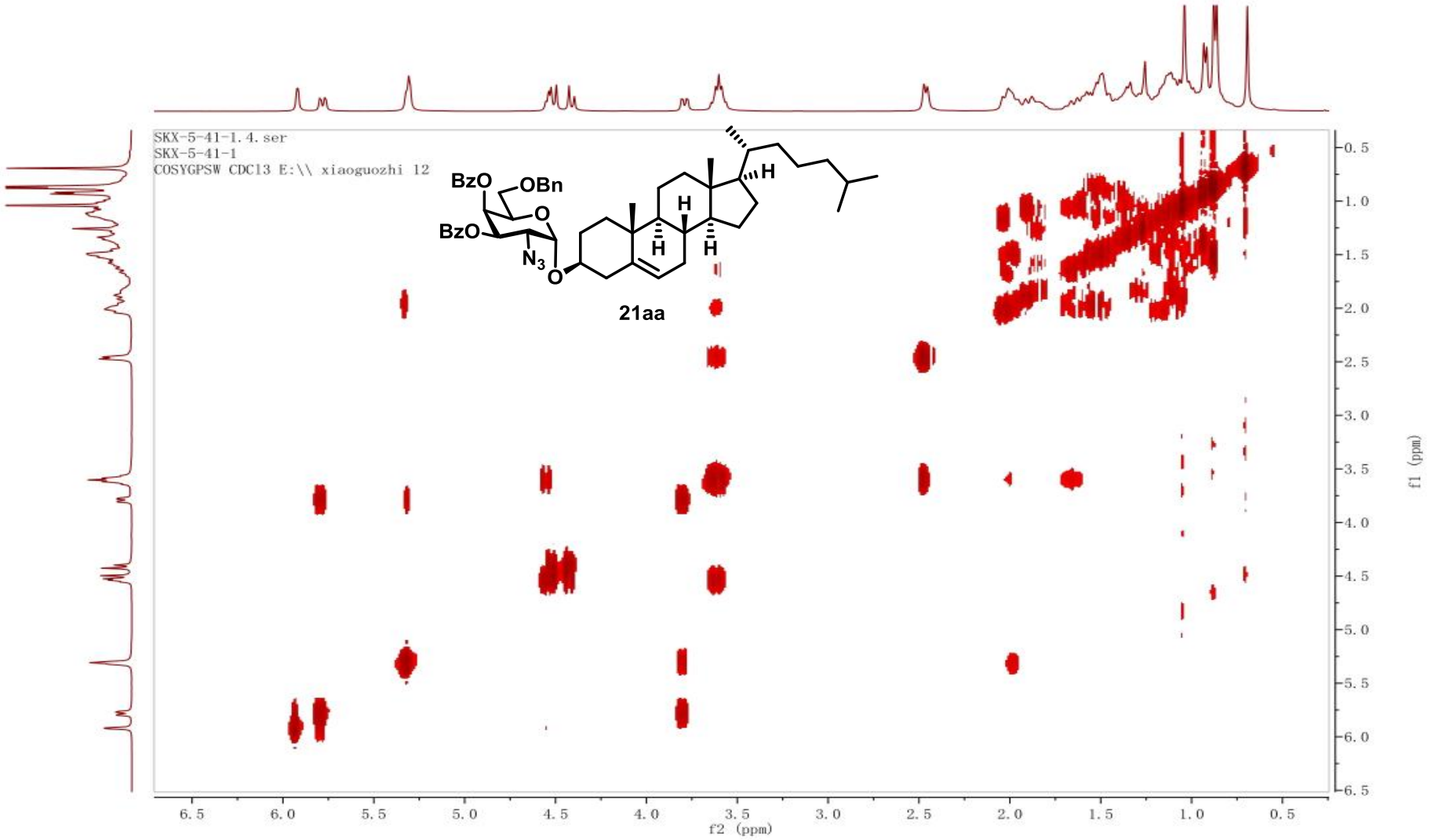

SKX-5-48-2.4.fid
SKX-5-48-2
c13 CDCl3 E:\\ xiaoguzhi
165.49
165.45
148.77
138.30
137.98
137.71
133.53
133.47
133.31
130.19
129.87
129.84
129.77
129.49
129.28
128.61
128.58
128.48
128.35
127.88
127.75
127.72
127.64
126.56
121.69
118.78
97.27
86.62
73.55
69.16
68.70
68.51
68.44
58.26
50.08
44.24
42.99
38.23
37.26
29.61
27.10
26.90
26.12
23.20
12.18
BzO
OBn
O
BzO
N3
O
21z
H
H
H
BzO
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

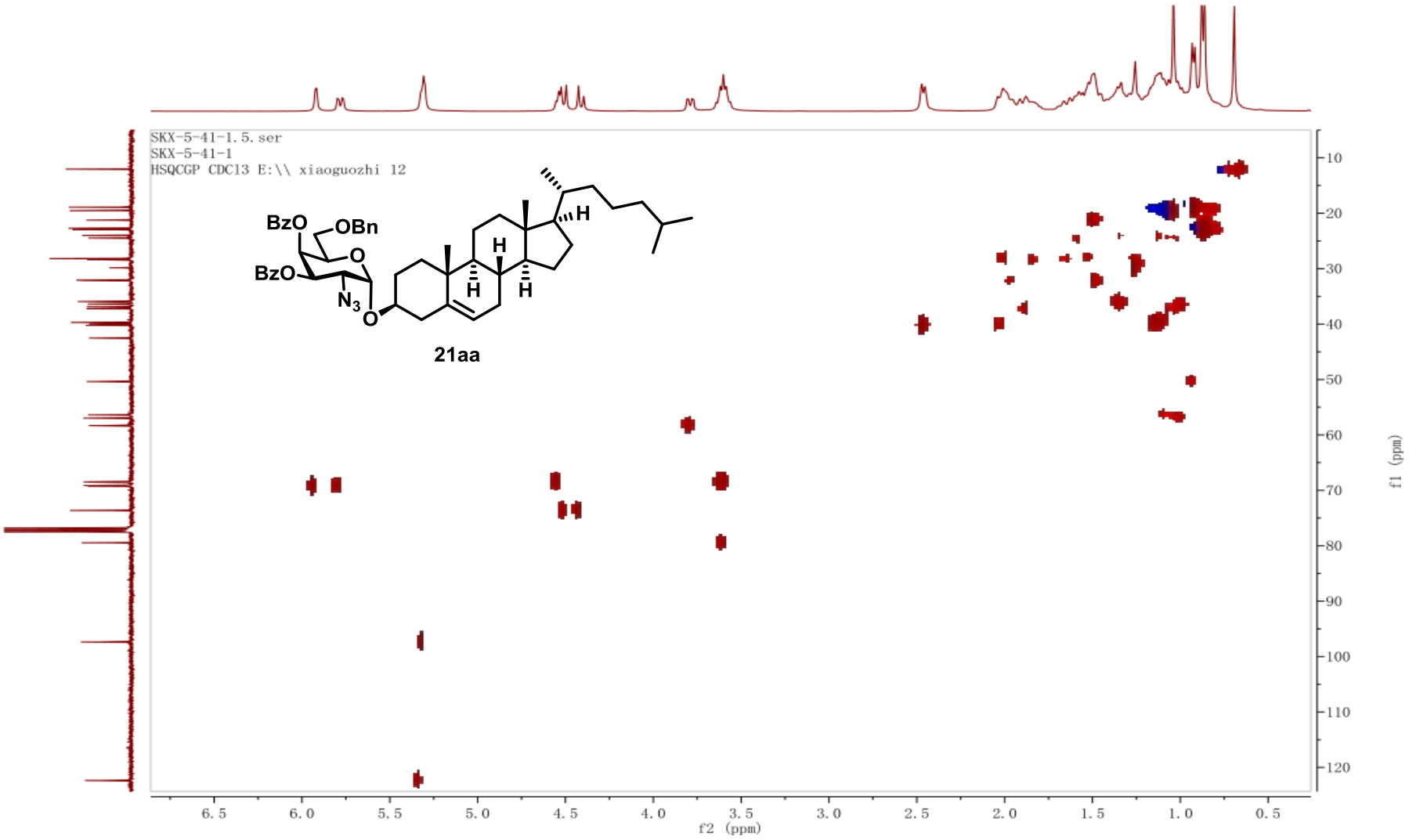

SKX-5-48-2.2.ser
SKX-5-48-2
COSYGPSW CDC13 E:\\ xiaogu
BzO
OBn
O
BzO
N3
O
21z
H
H
H
BzO
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

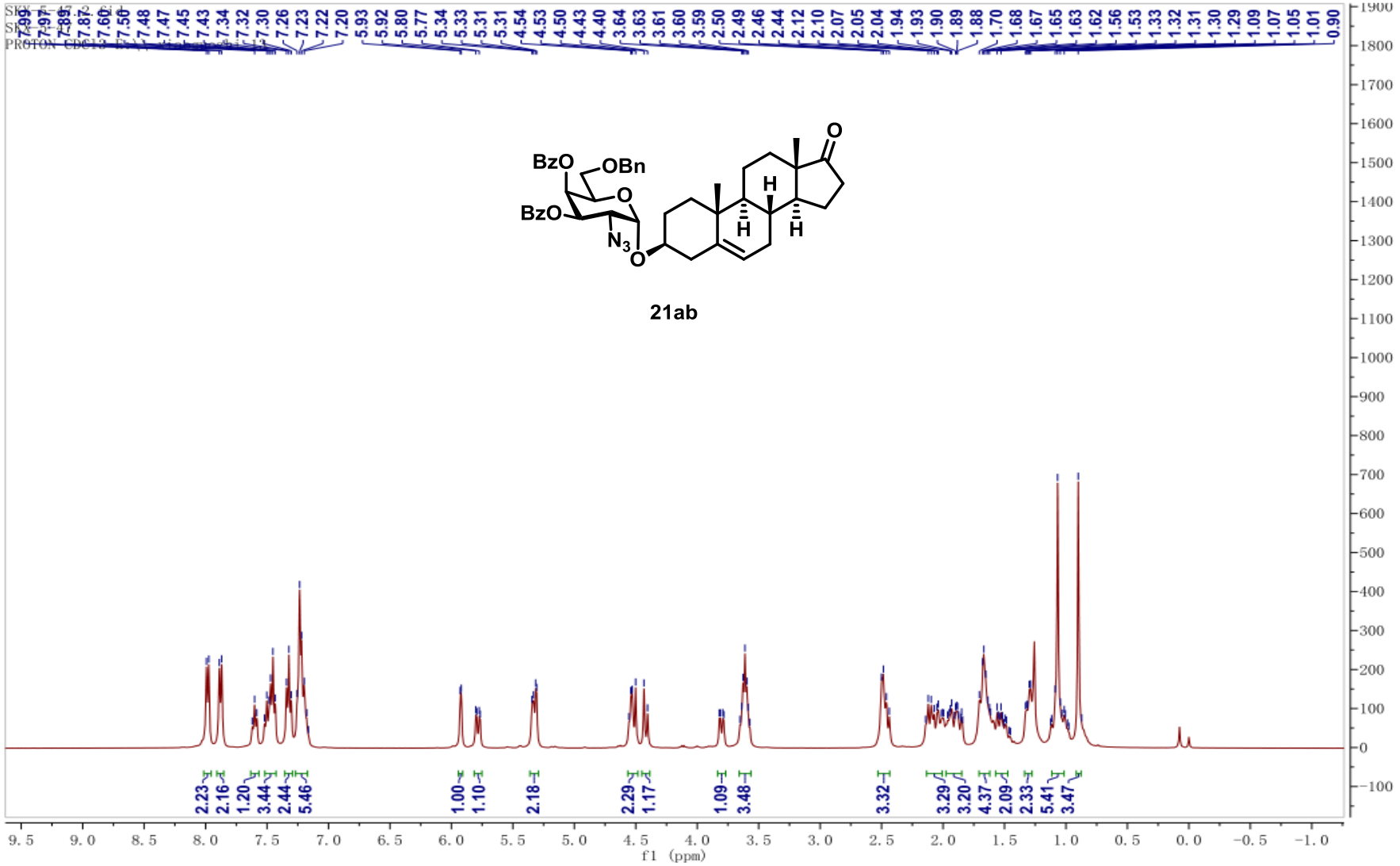

SKX-5-48-2.3.ser
SKX-5-48-2
HSQCGP CDCl3 E:\\ xiaoguozh
BzO
OBn
O
BzO
N3
O
21z
H
H
H
BzO
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)

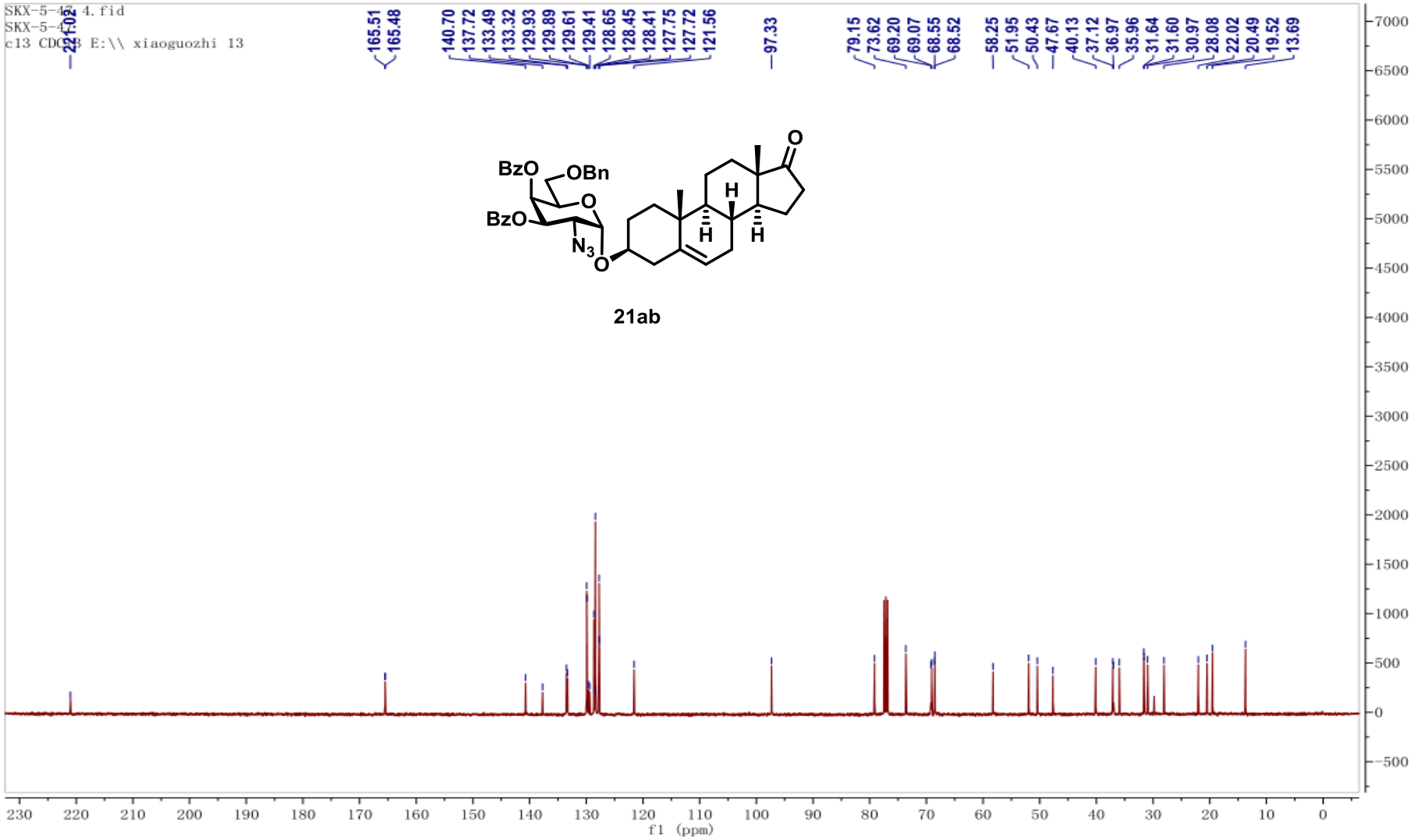

BzO
OBn
O
BzO
N3
O
H
H
H
H
21aa
f1 (ppm)

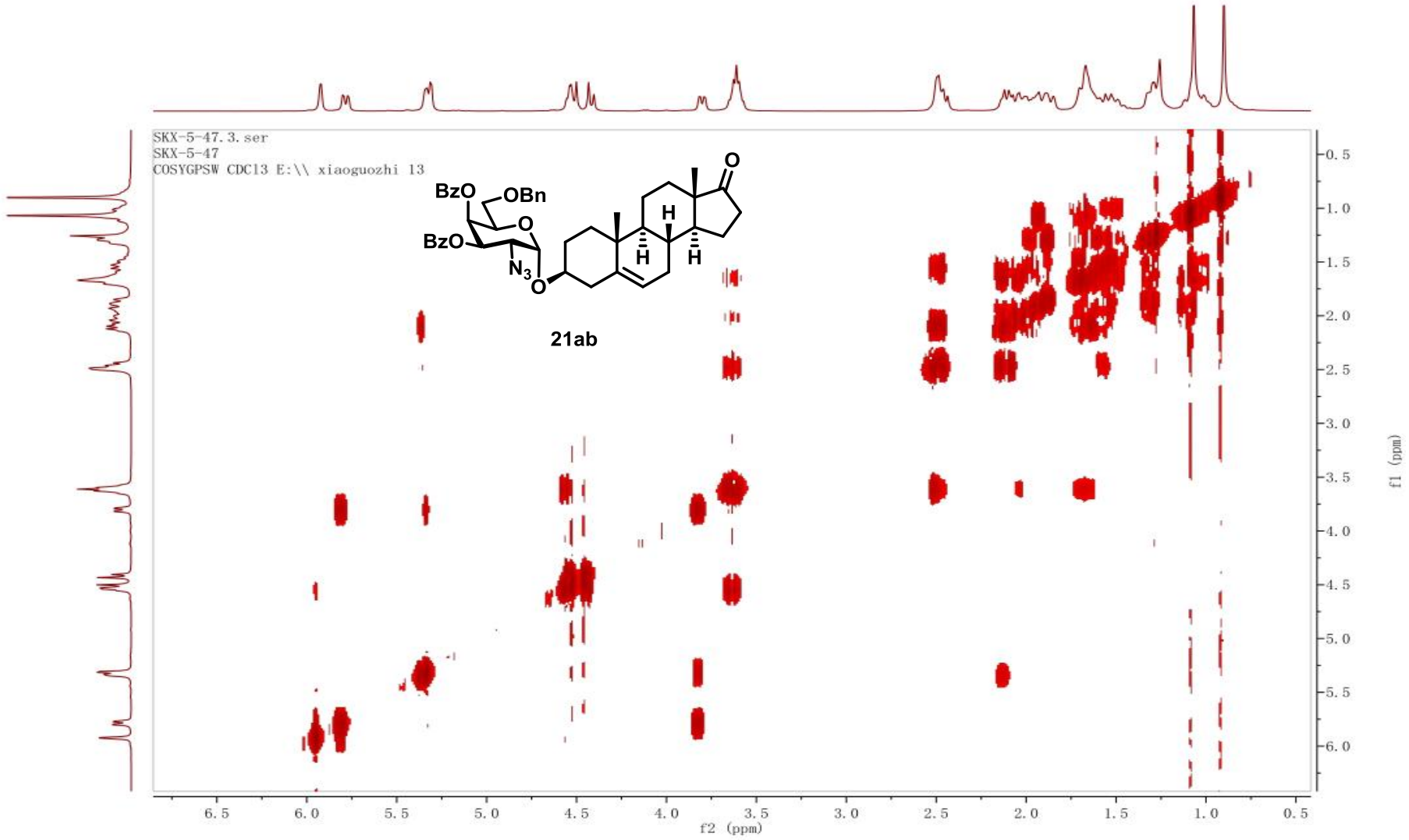

SKX-5-41-1.6.fid
SKX-5-41-1
c13 CDCl3 E:\\ xiaogu\zhi 12
165.51
140.48
137.74
133.46
133.29
129.96
129.92
129.70
129.50
128.66
128.43
128.40
127.77
127.73
122.36
97.35
79.46
73.64
69.26
69.13
68.52
68.47
58.32
56.98
56.38
50.37
40.22
39.69
37.22
36.87
36.38
35.94
32.13
32.07
28.39
28.17
24.47
24.00
22.95
22.71
21.23
19.51
18.89
12.04
BzO
OBn
O
BzO
N3
O
H
H
H
H
21aa
f1 (ppm)

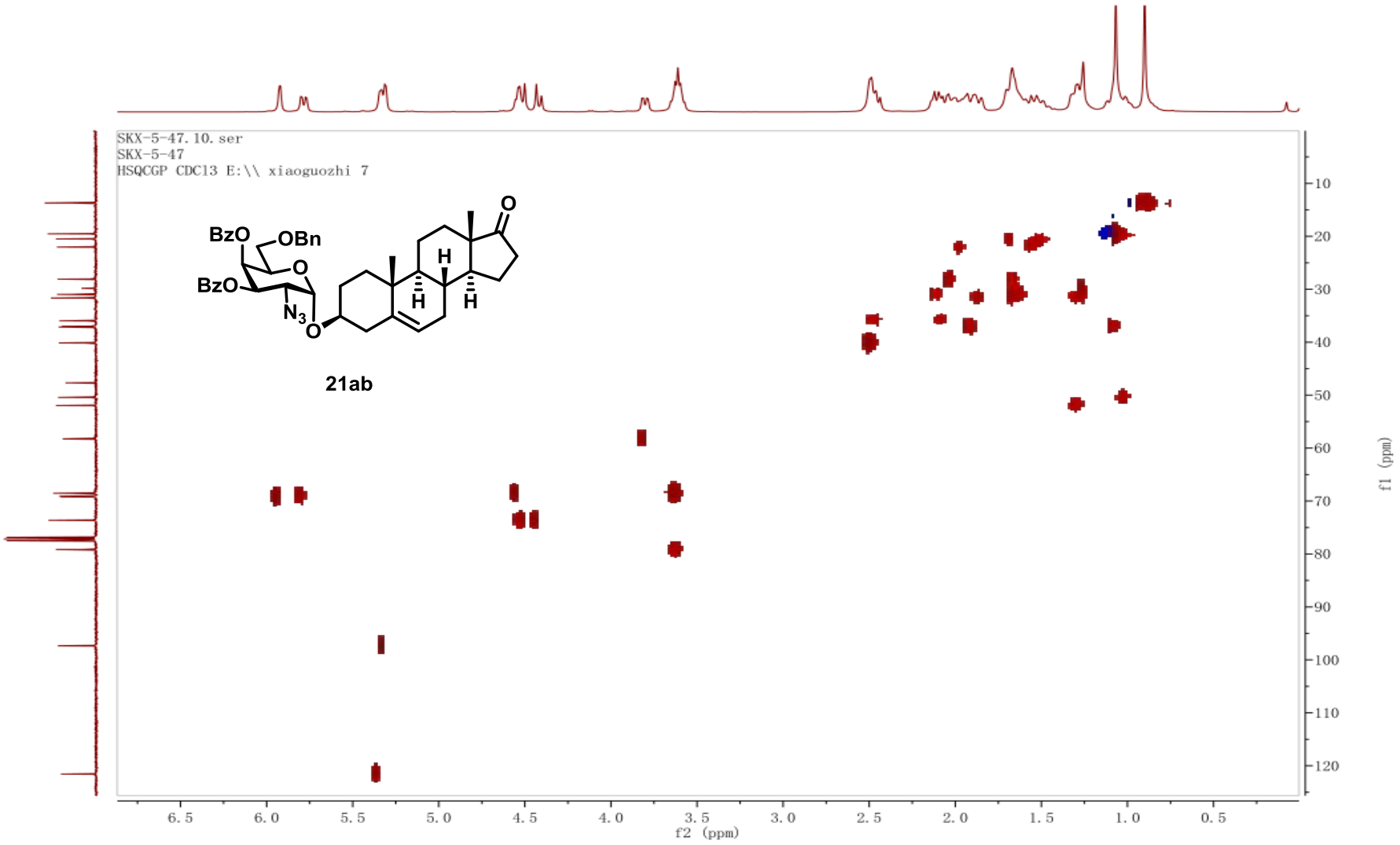

SKX-5-41-1.4.ser
SKX-5-41-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 12
BzO
OBn
O
BzO
N3
O
H
H
H
H
21aa
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

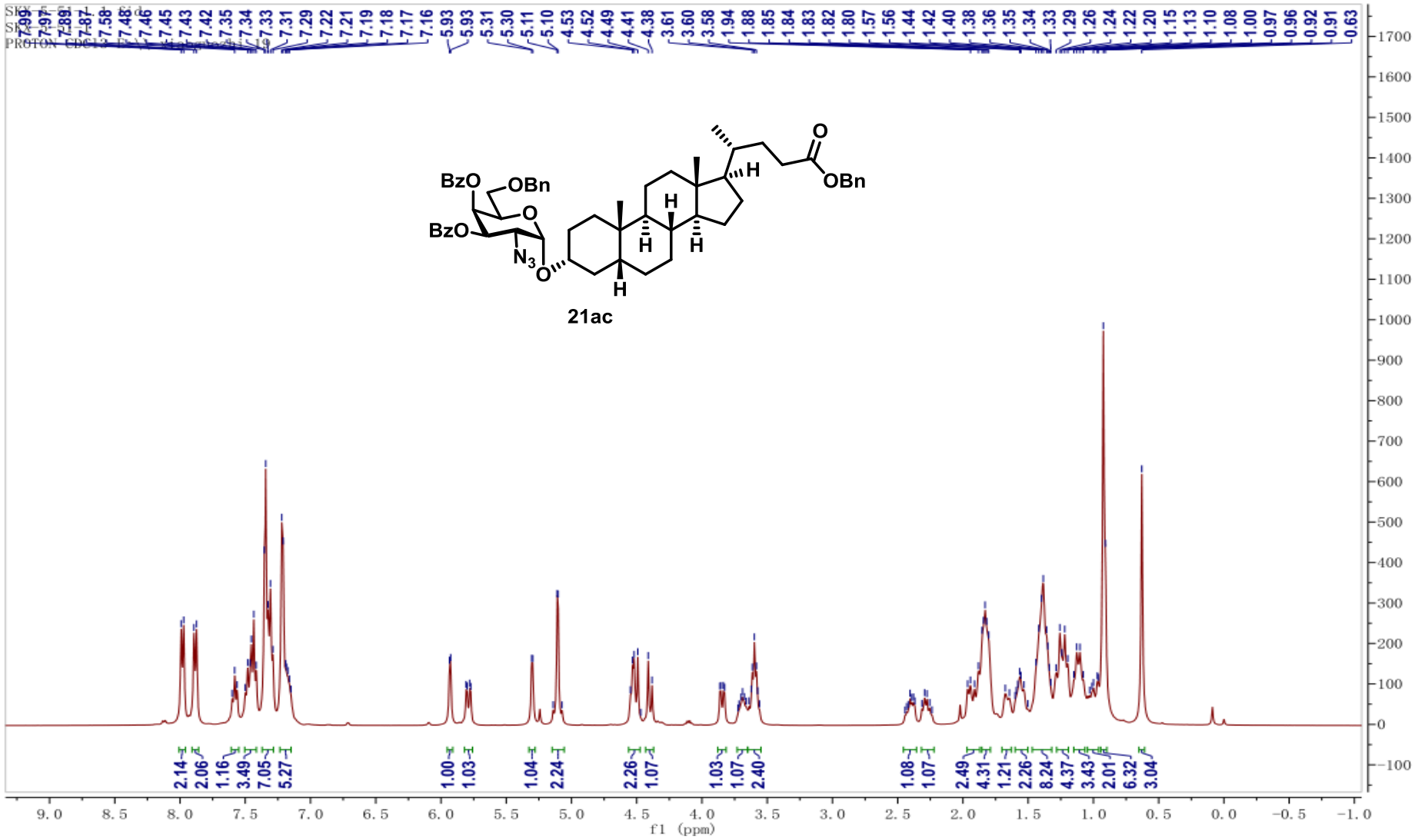

SKX-5-41-1.5.ser
SKX-5-41-1
HSQCGP CDCl3 E:\\ xiaoguozhi 12
BzO
OBn
O
BzO
N3
O
H
H
H
H
21aa
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)

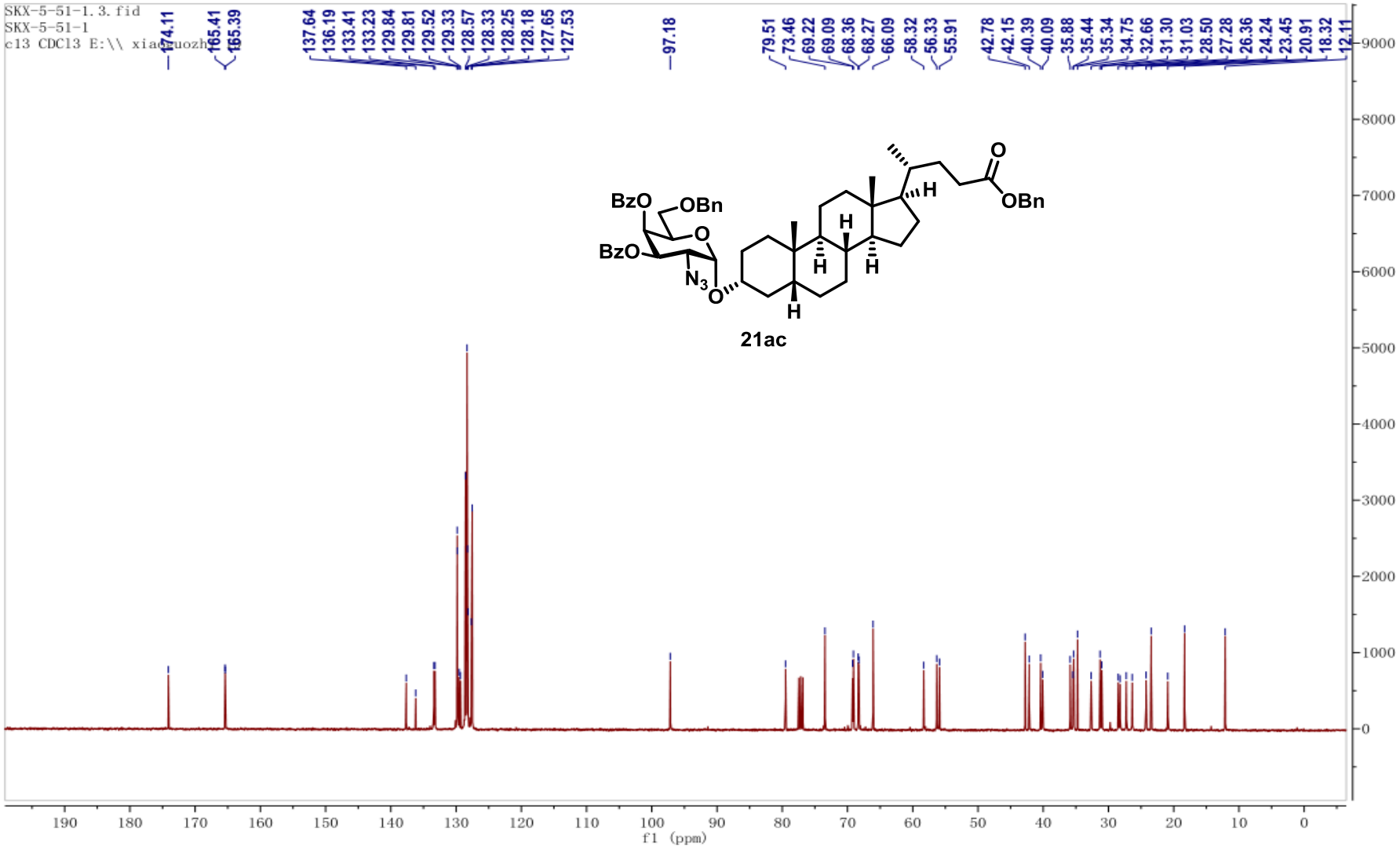

BzO
OBn
O
BzO
N3
O
H
H
H
O
21ab
f1 (ppm)

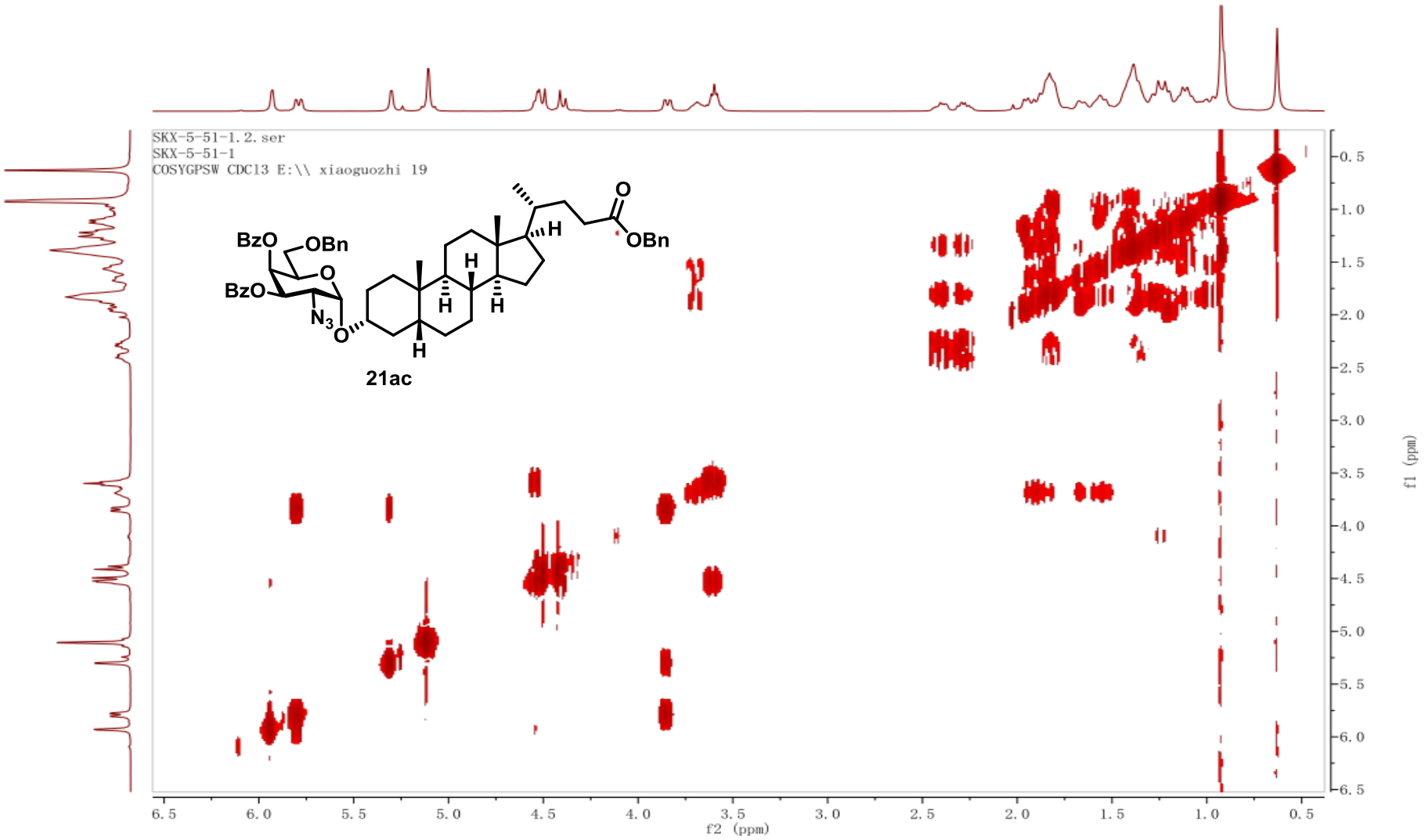

SKX-5-4 4.fid
SKX-5-4
c13 CDCl3 E:\\ xiaoguozhi 13
21.02
165.51
165.48
140.70
137.72
133.49
133.32
129.93
129.89
129.61
129.41
128.65
128.45
128.41
127.75
127.72
121.56
97.33
79.15
73.62
69.20
69.07
68.55
68.52
58.25
51.95
50.43
47.67
40.13
37.12
36.97
35.96
31.64
31.60
30.97
28.08
22.02
20.49
19.52
13.69
BzO
OBn
O
BzO
N3
O
H
H
H
O
21ab
f1 (ppm)

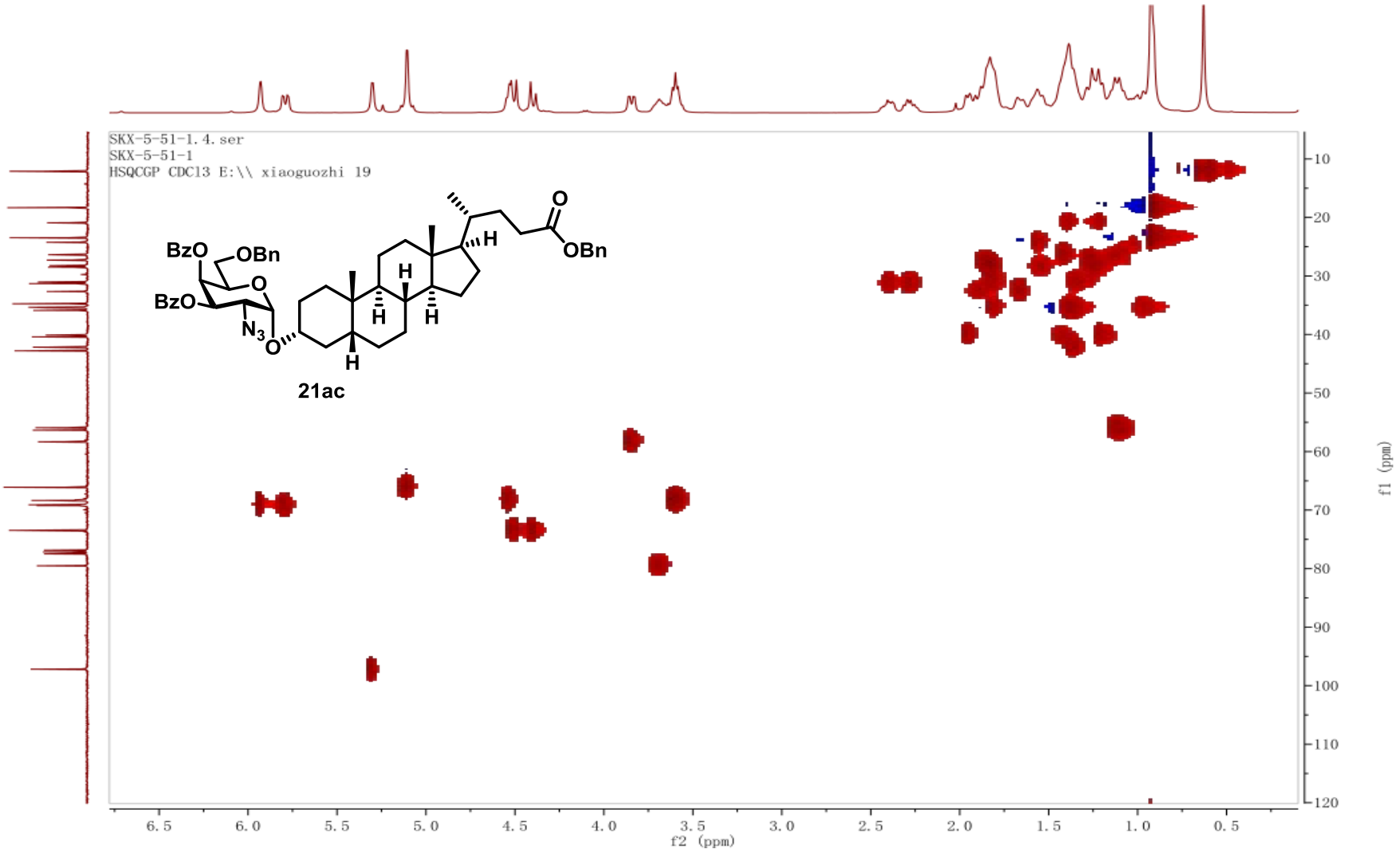

SKX-5-47.3.ser
SKX-5-47
COSYGPSW CDC13 E:\\ xiaoguozhi 13
BzO
OBn
O
BzO
N3
O
H
H
H
O
21ab
f2 (ppm)
f1 (ppm)

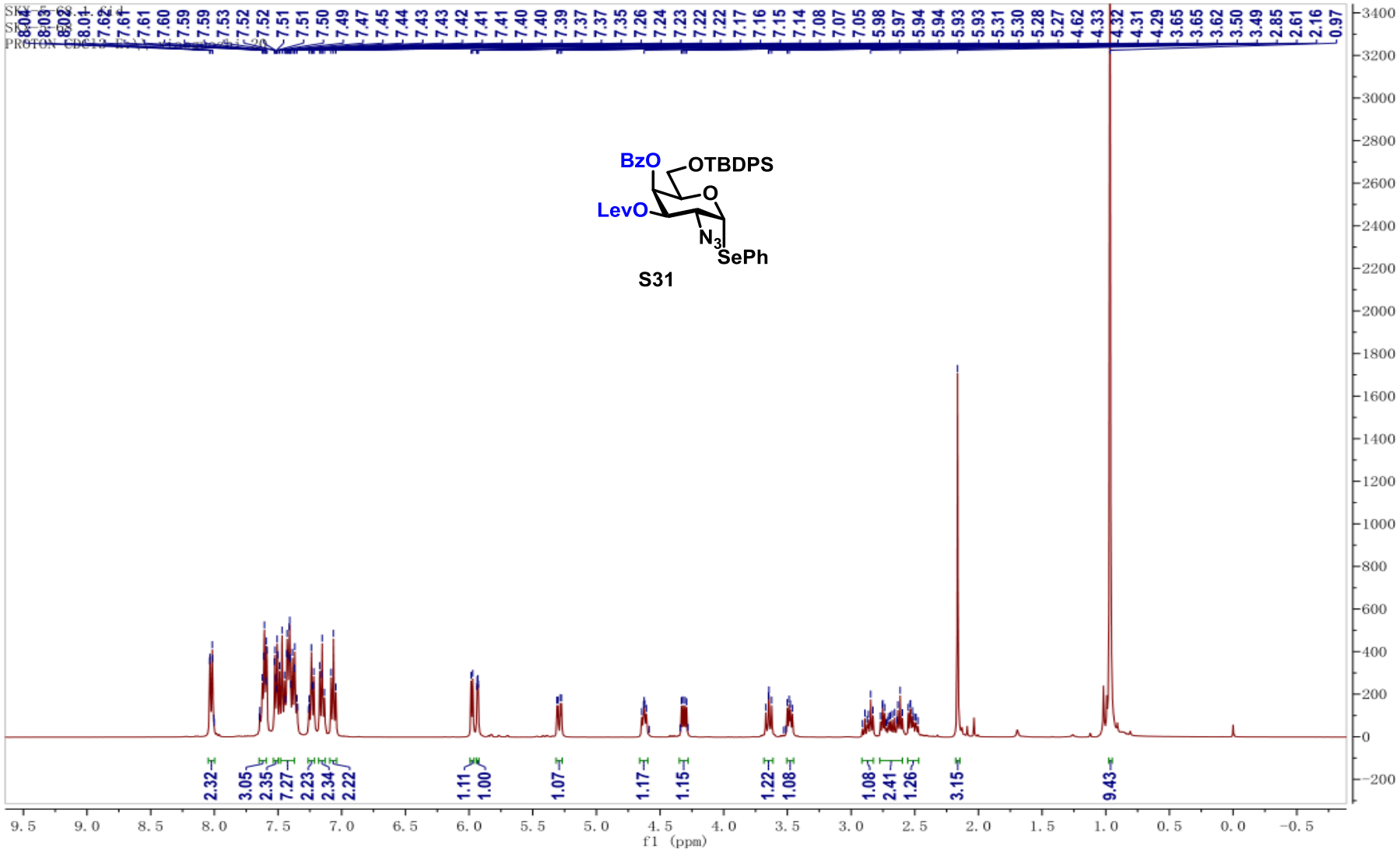

SKX-5-47.10.ser
SKX-5-47
HSQCGP CDCl3 E:\\ xiaoguozhi 7
BzO
OBn
O
BzO
N3
O
H
H
H
O
21ab
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)

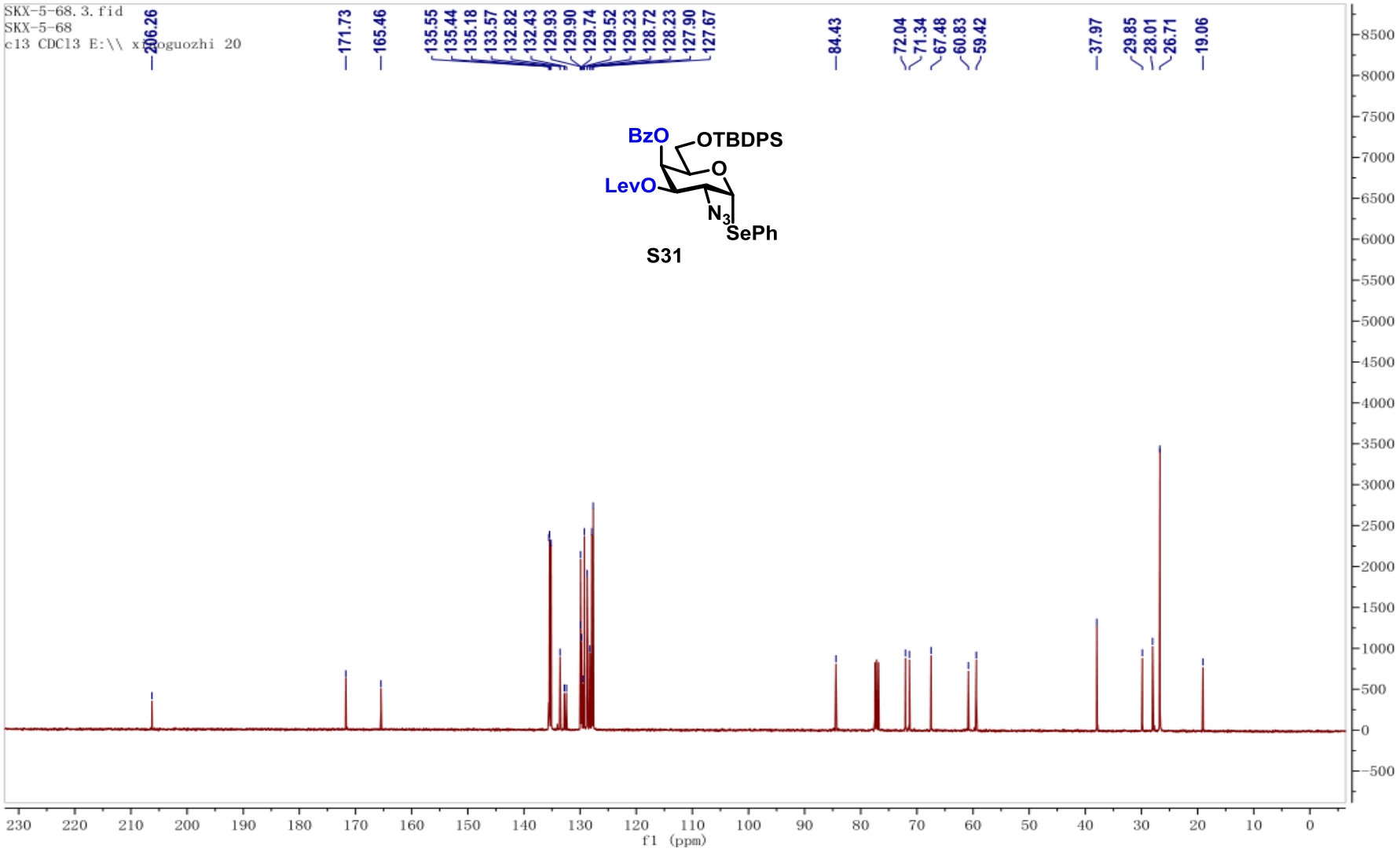

BzO
OBn
O
BzO
N3
O
H
H
H
H
O
OBn
21ac
f1 (ppm)

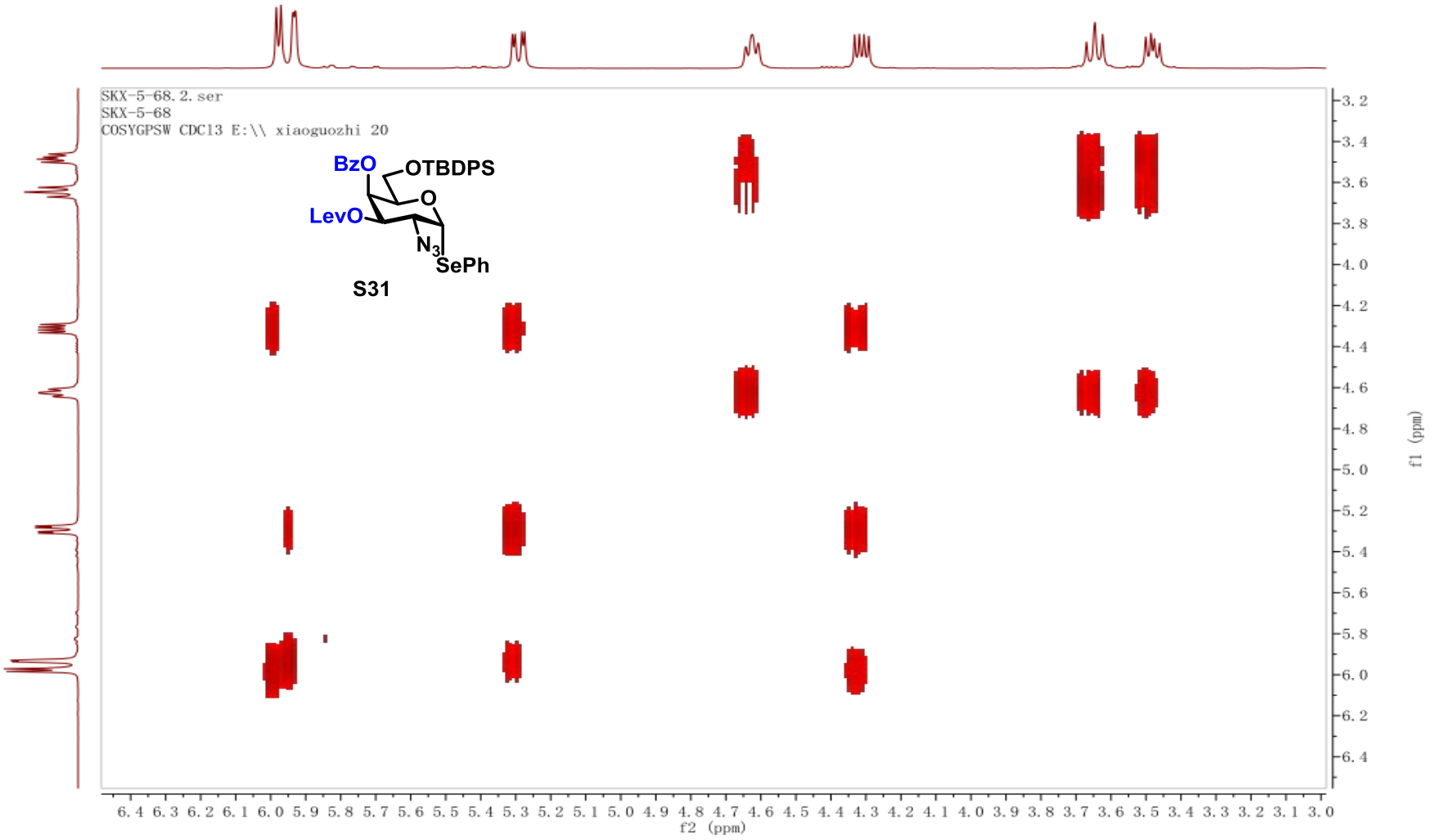

SKX-5-51-1.3.fid
SKX-5-51-1
c13 CDCl3 E:\\ xiaoguozh
174.11
165.41
165.39
137.64
136.19
133.41
133.23
129.84
129.81
129.52
129.33
128.57
128.33
128.25
128.18
127.65
127.53
97.18
79.51
73.46
69.22
69.09
68.36
68.27
66.09
58.32
56.33
55.91
42.78
42.15
40.39
40.09
35.88
35.44
35.34
34.75
32.66
31.30
31.03
28.50
27.28
26.36
24.24
23.45
20.91
18.32
12.11
BzO
OBn
BzO
N3
O
H
H
H
H
O
OBn
21ac
f1 (ppm)

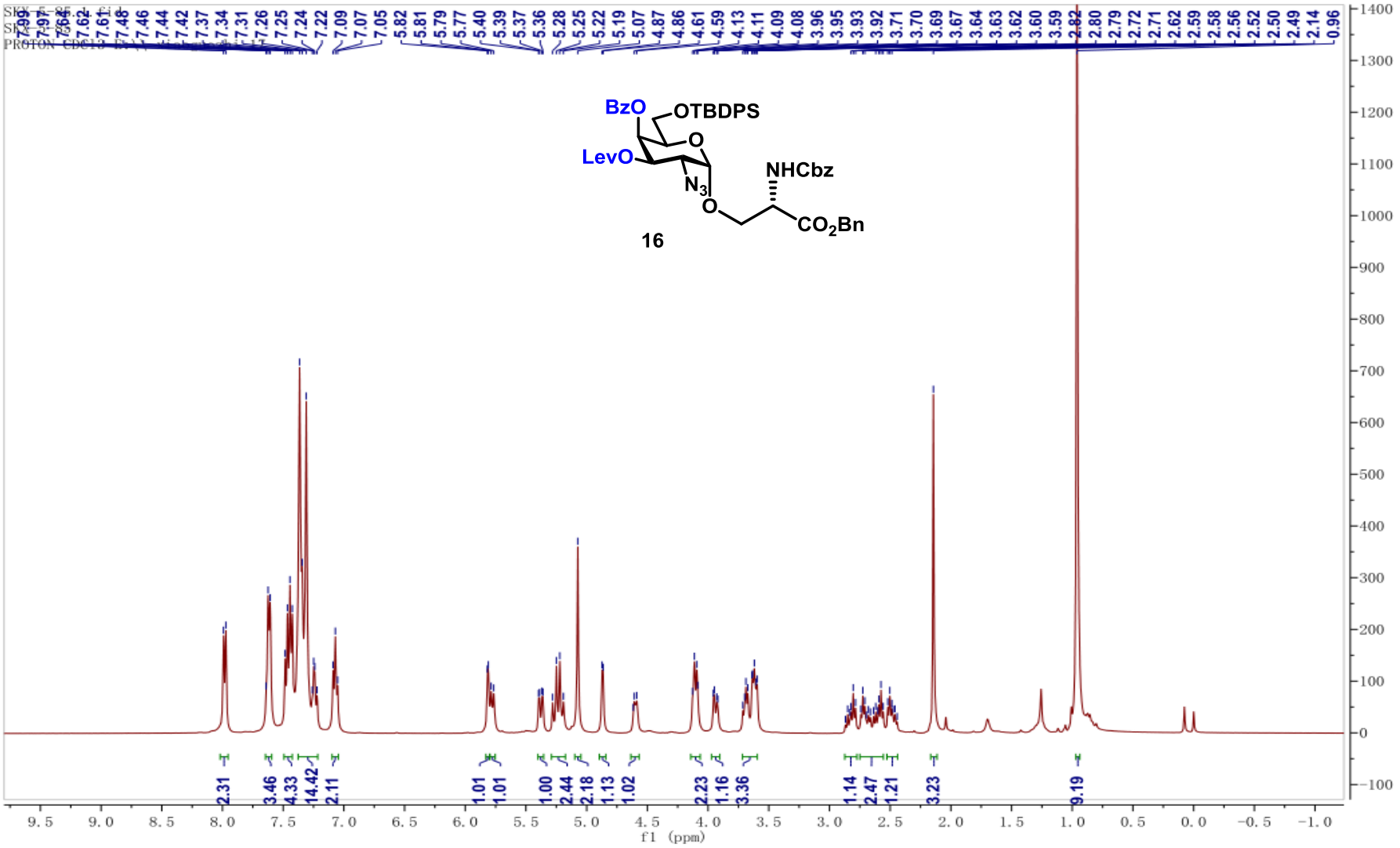

SKX-5-51-1.2.ser
SKX-5-51-1
COSYGPSW CDC13 E:\\ xiaoguozhi 19
BzO
OBn
O
BzO
N3
O
H
H
H
H
O
OBn
21ac
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

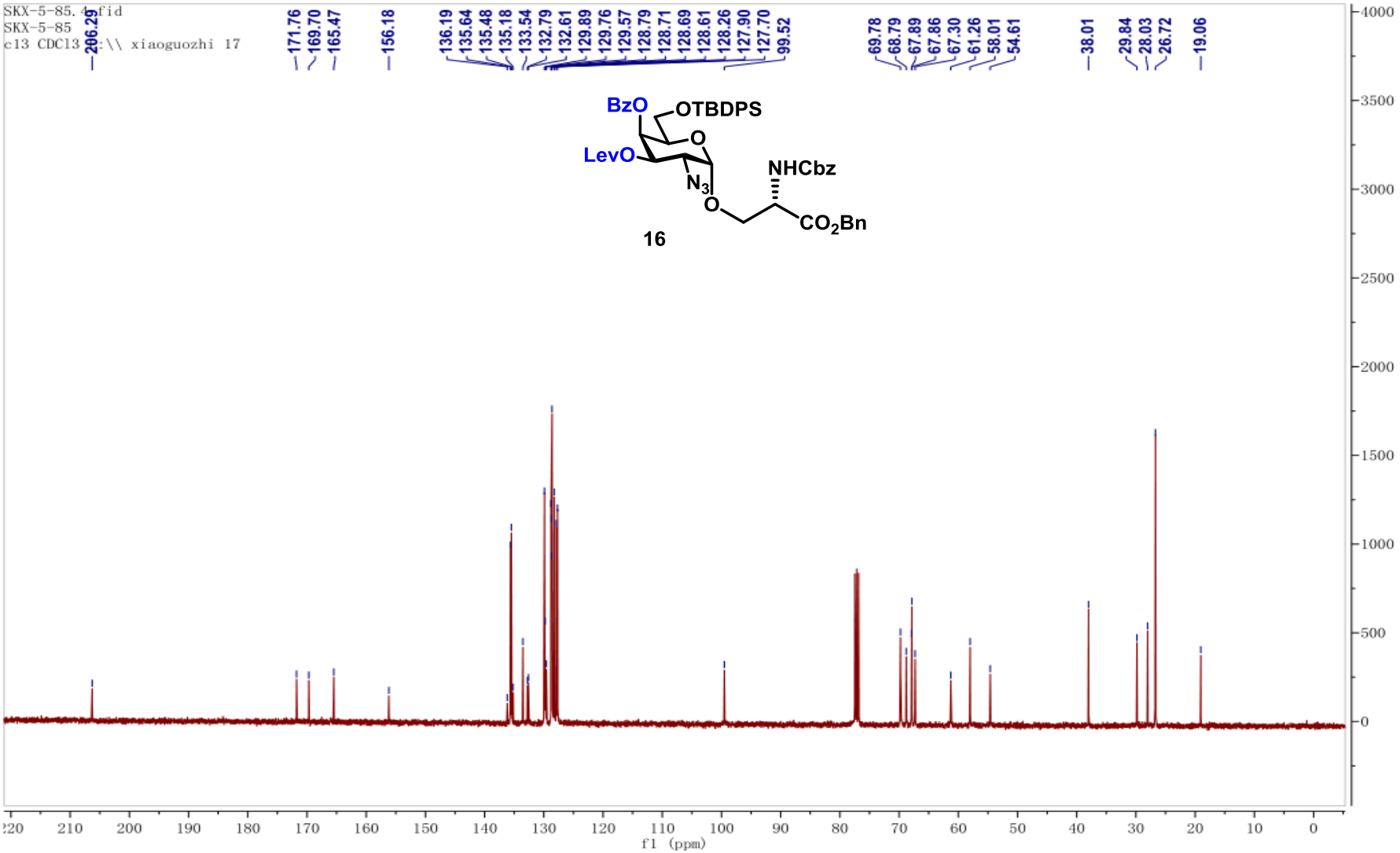

SKX-5-51-1.4.ser
SKX-5-51-1
HSQCGP CDCl3 E:\\ xiaoguozhi 19
BzO
OBn
O
BzO
N3
O
H
H
H
H
O
OBn
21ac
f2 (ppm)
f1 (ppm)

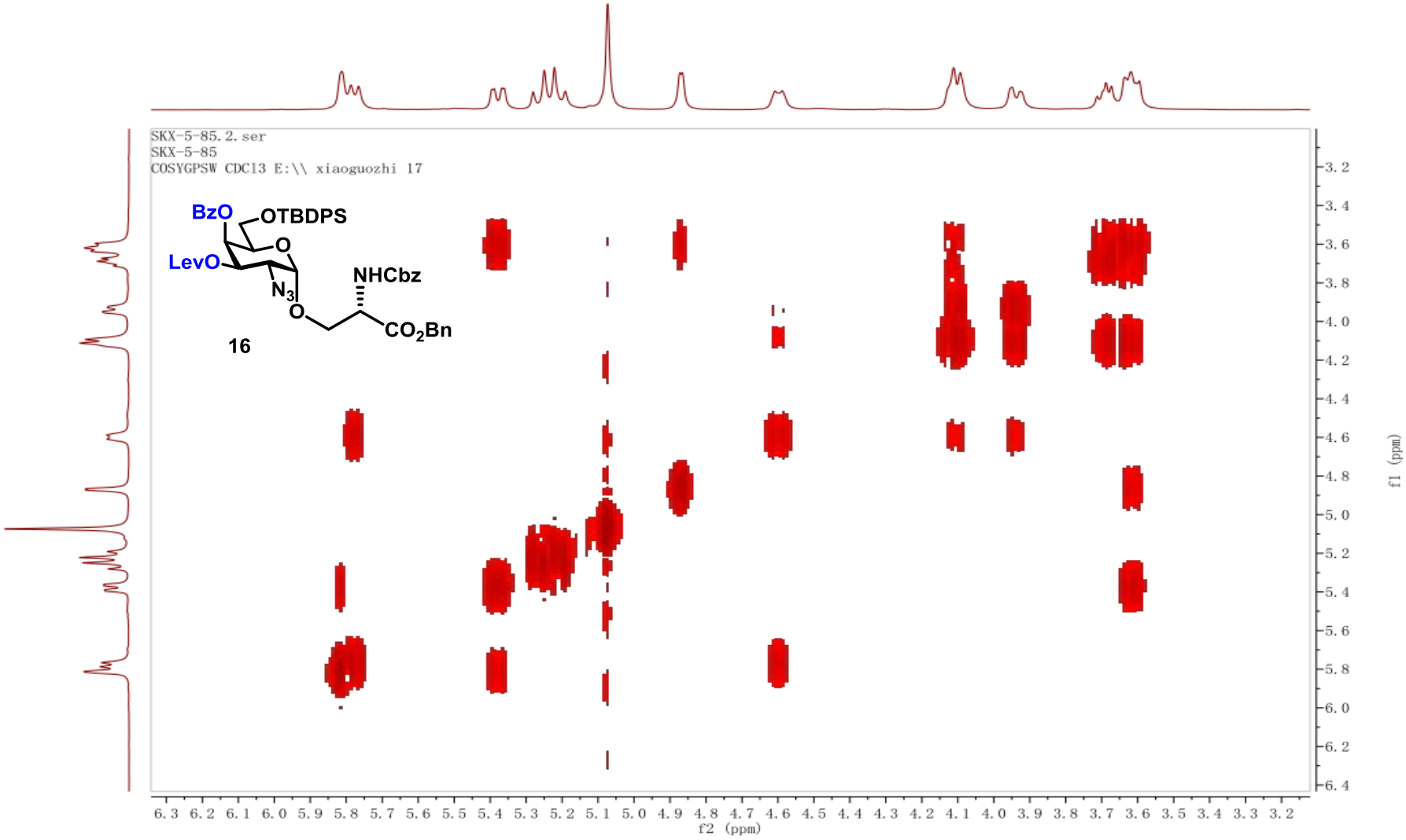

BzO
OTBDPS
O
LevO
N3
SePh
S31
f1 (ppm)

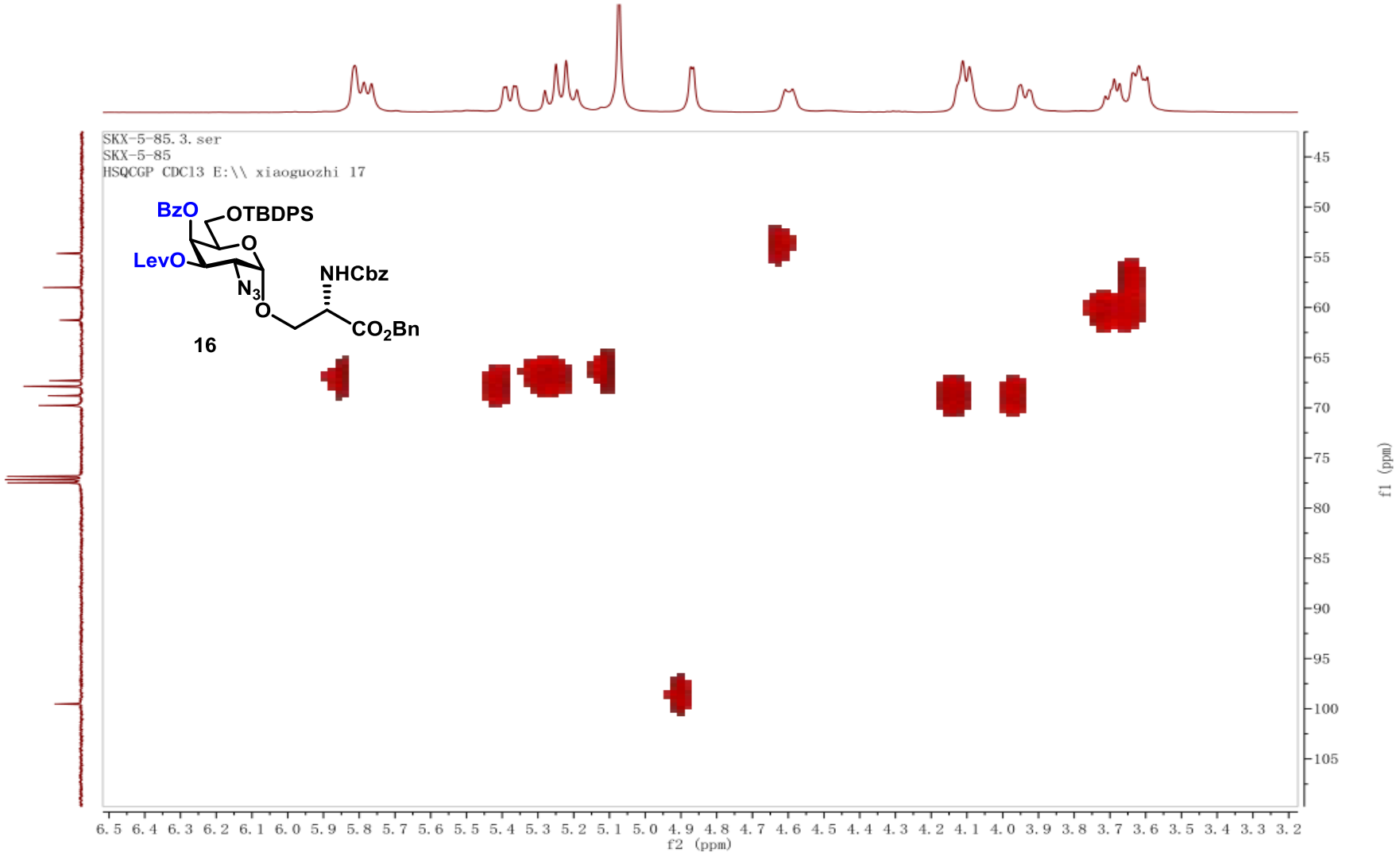

SKX-5-68.3.fid
SKX-5-68
c13 CDCl3 E:\\ xinguozhi 20
206.26
171.73
165.46
135.55
135.44
135.18
133.57
132.82
132.43
129.93
129.90
129.74
129.52
129.23
128.72
128.23
127.90
127.67
84.43
72.04
71.34
67.48
60.83
59.42
37.97
29.85
28.01
26.71
19.06
BzO
OTBDPS
O
LevO
N3
SePh
S31
f1 (ppm)

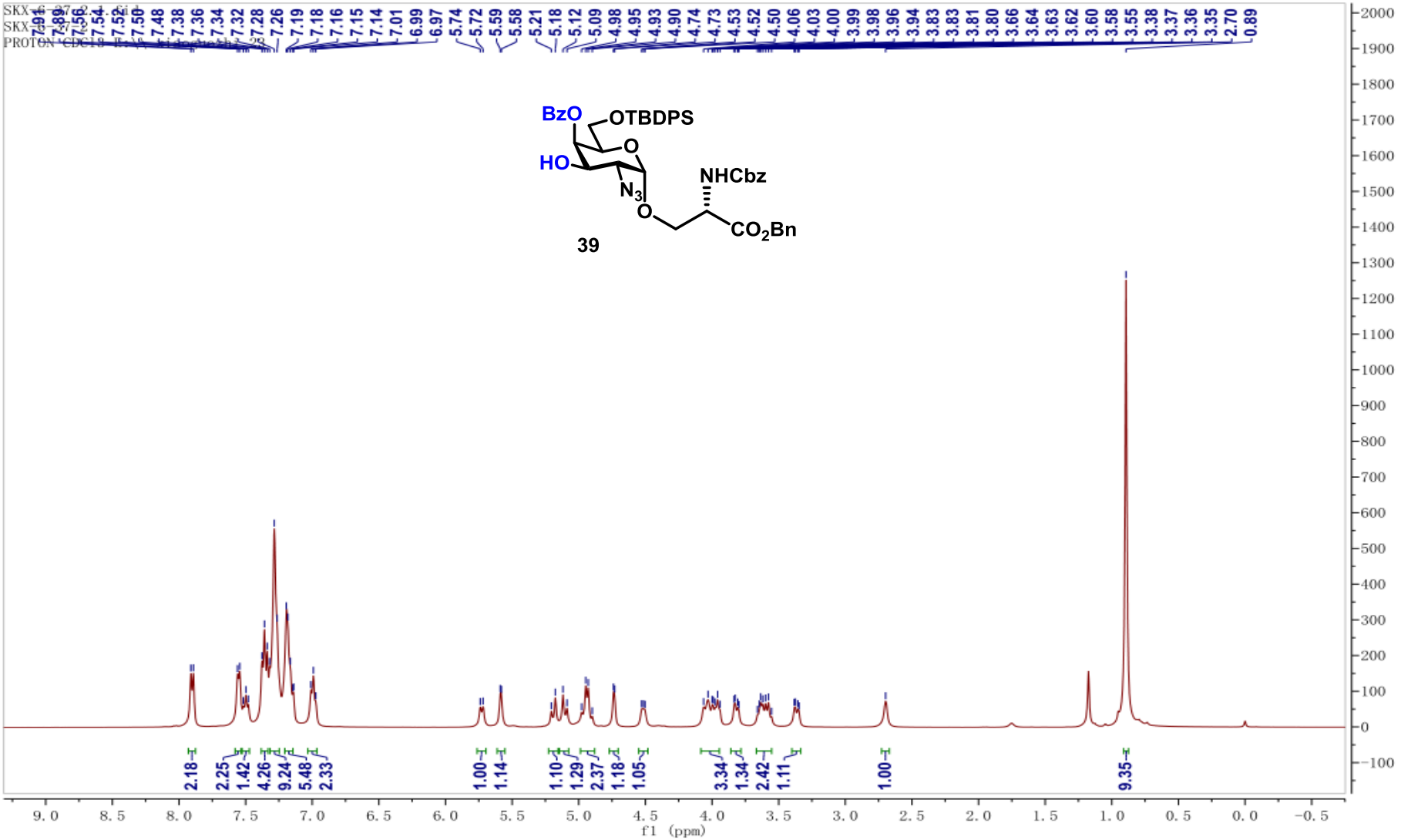

SKX-5-68.2.ser
SKX-5-68
COSYGPSW CDCl3 E:\\ xiaoguozhi 20
BzO
OTBDPS
O
LevO
N3
SePh
S31
f2 (ppm)
f1 (ppm)

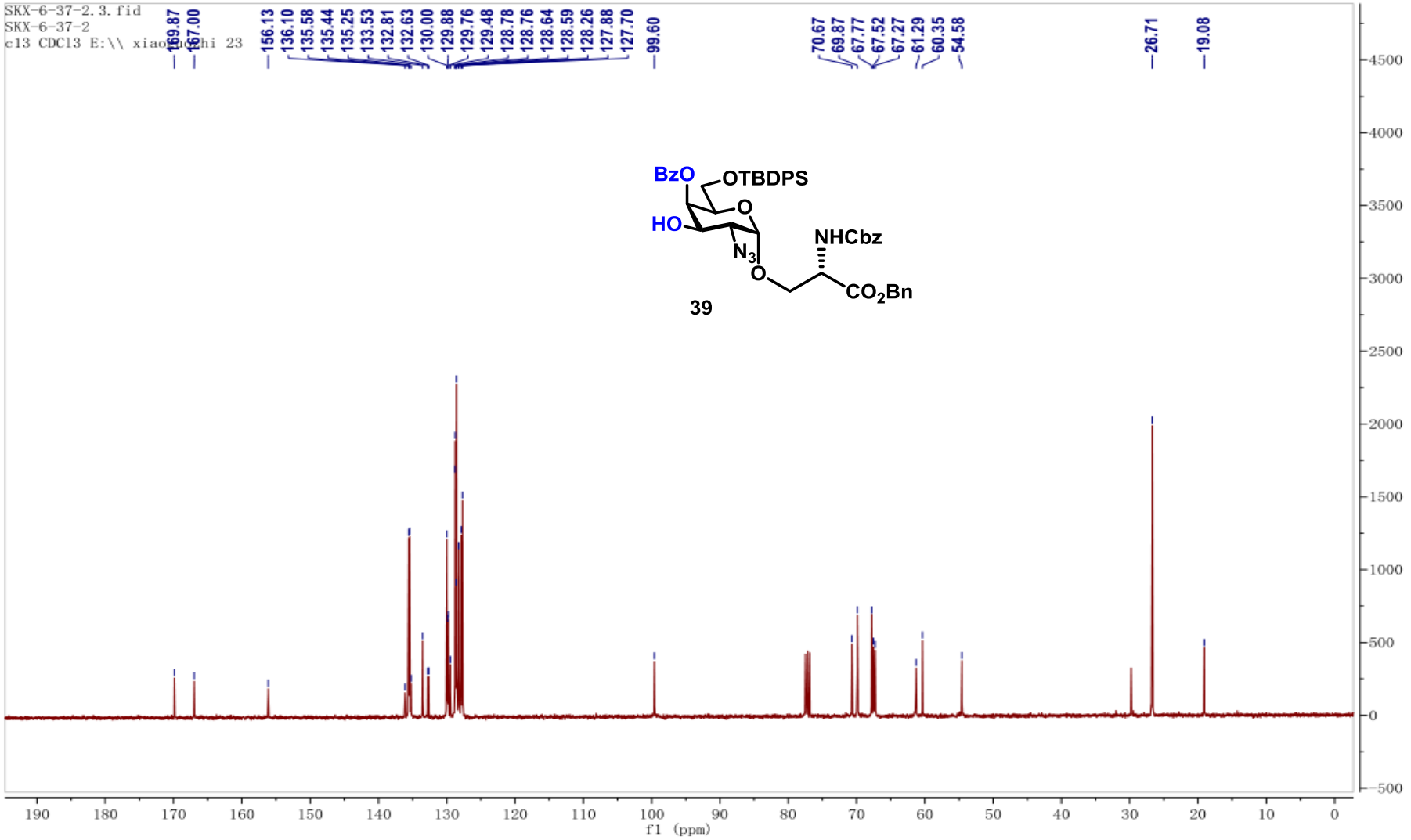

BzO
OTBDPS
LevO
O
NHCbz
N3
O
CO2Bn
16
f1 (ppm)

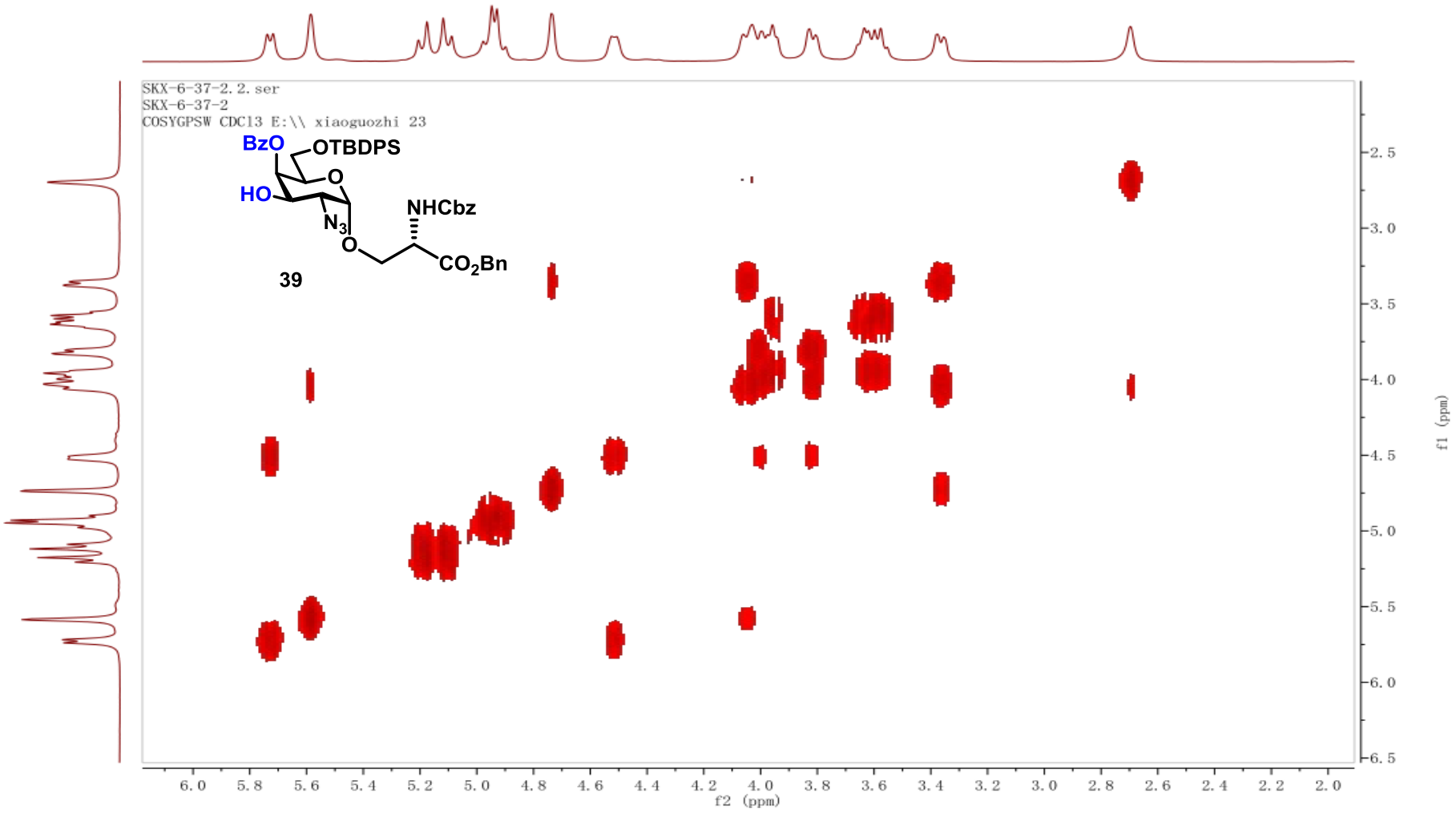

SKX-5-85.4.fid
SKX-5-85
c13 CDCl3 c:\\ xiaoguozhi 17
206.29
171.76
169.70
165.47
156.18
136.19
135.64
135.48
135.18
133.54
132.79
132.61
129.89
129.76
129.57
128.79
128.71
128.69
128.61
128.26
127.90
127.70
99.52
69.78
68.79
67.89
67.86
67.30
61.26
58.01
54.61
38.01
29.84
28.03
26.72
19.06
BzO
OTBDPS
O
LevO
N3
O
NHCbz
CO2Bn
16
f1 (ppm)

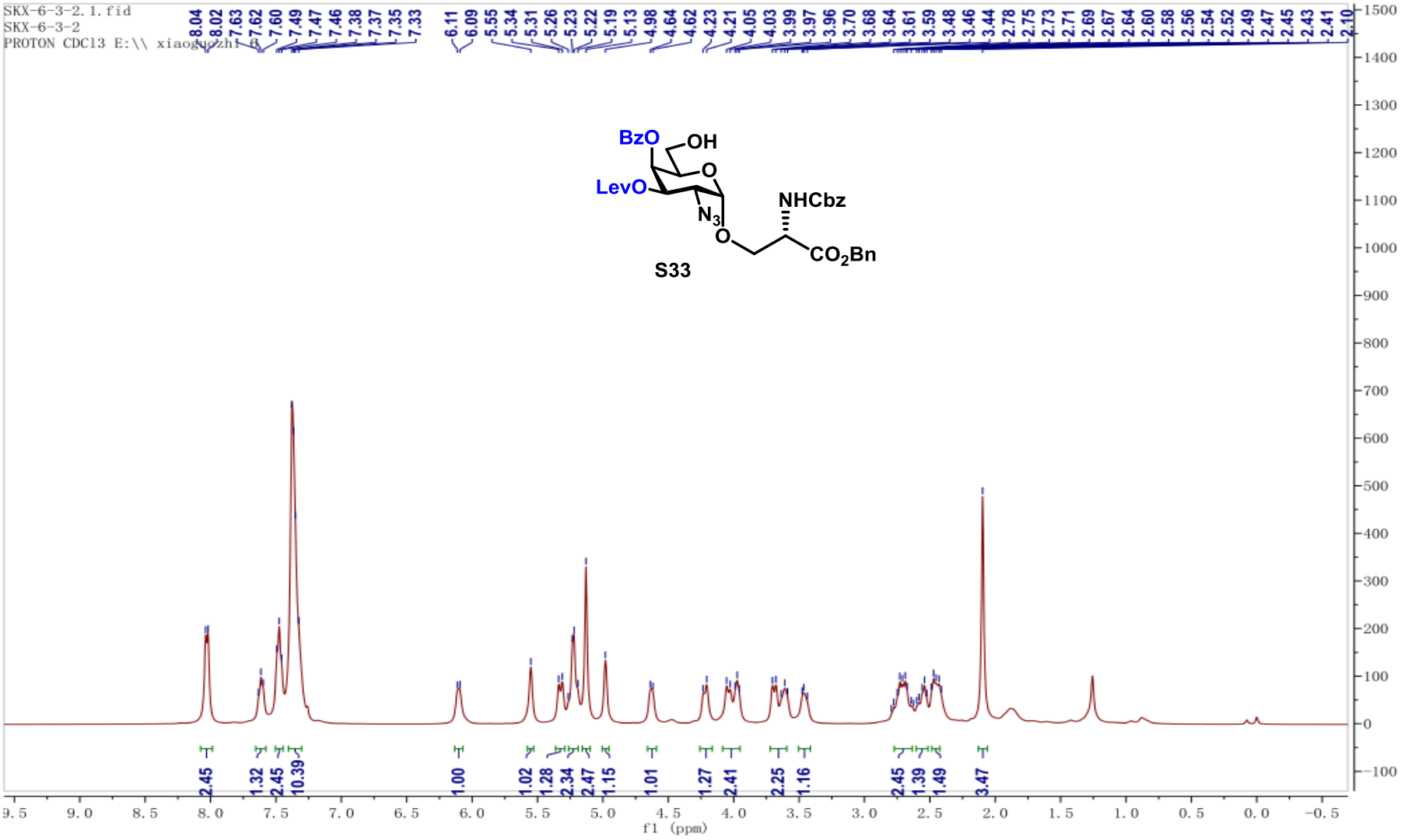

SKX-5-85.2.ser
SKX-5-85
COSYGPSW CDCl3 E:\\ xiaoguozhi 17
BzO
OTBDPS
LevO
O
N3
O
NHCbz
CO2Bn
16
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
f2 (ppm)
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4
f1 (ppm)

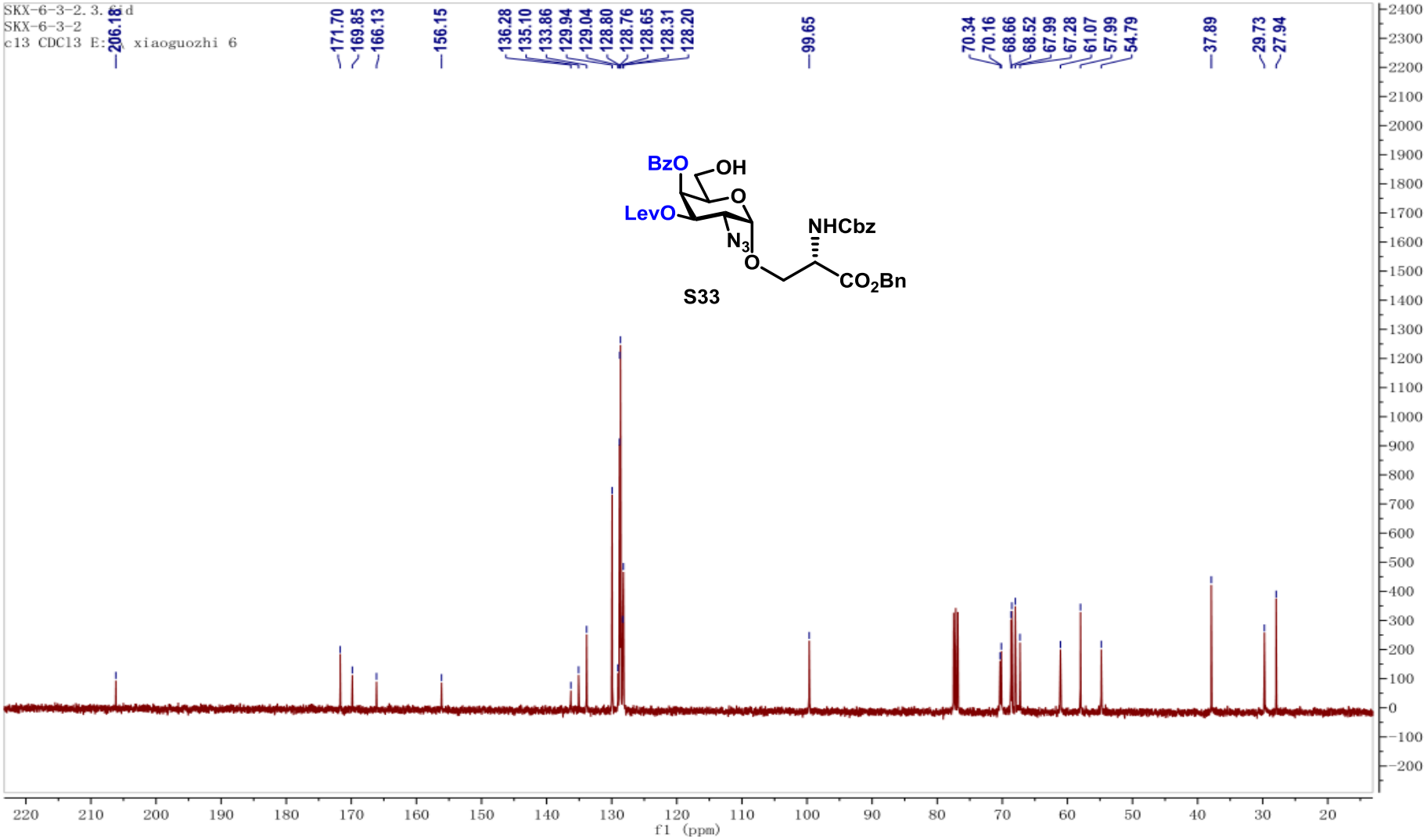

SKX-5-85.3.ser
SKX-5-85
HSQCGP CDCl3 E:\\ xiaoguozhi 17
BzO
OTBDPS
LevO
NHCbz
N3
CO2Bn
16
f2 (ppm)
f1 (ppm)

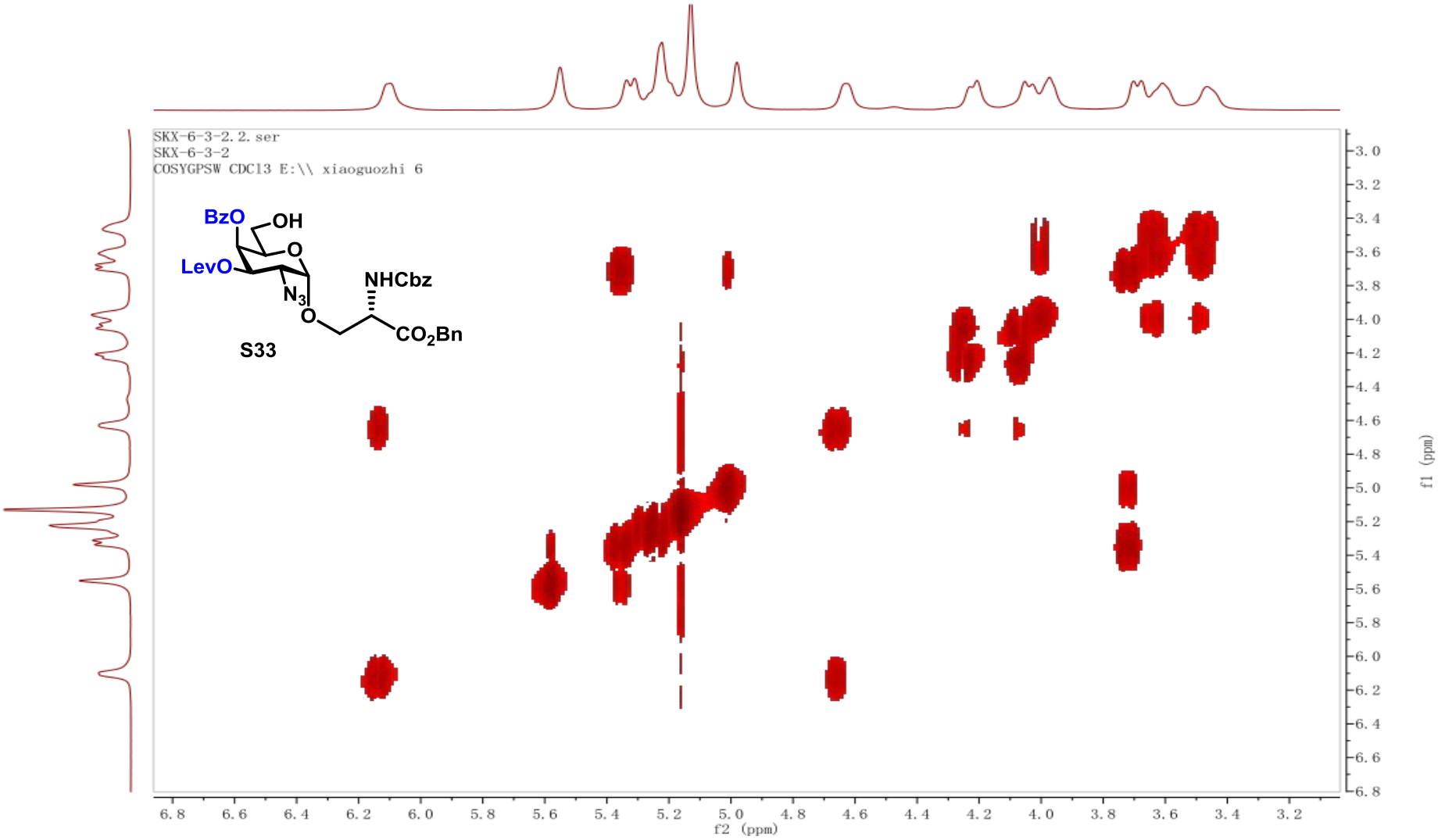

BzO
OTBDPS
HO
O
N3
O
NHCbz
CO2Bn
39
f1 (ppm)

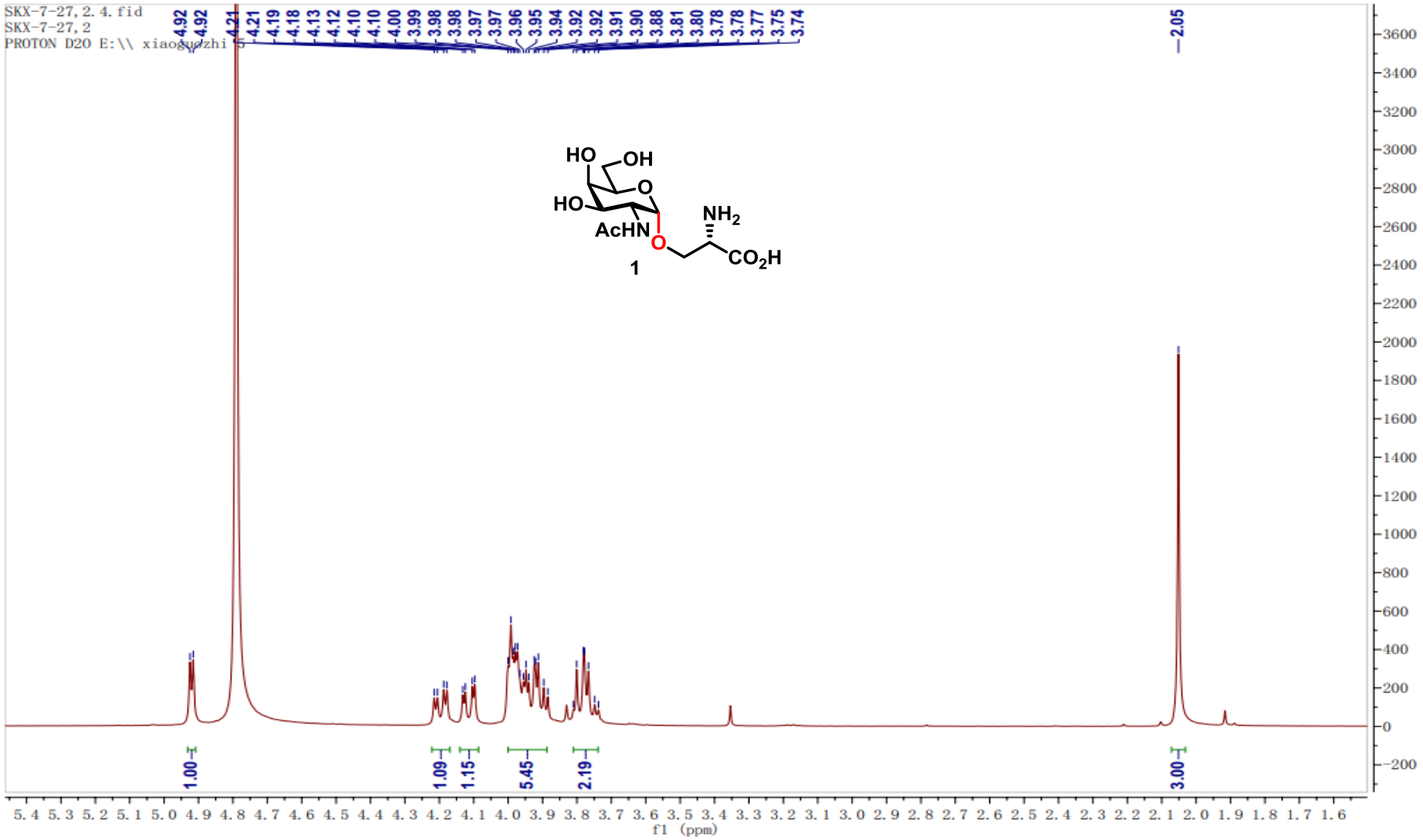

SKX-6-37-2.3.fid
SKX-6-37-2
c13 CDCl3 E:\\ xiaoqizhi 23
169.87
167.00
156.13
136.10
135.58
135.44
135.25
133.53
132.81
132.63
130.00
129.88
129.76
129.48
128.78
128.76
128.64
128.59
128.26
127.88
127.70
99.60
70.67
69.87
67.77
67.52
67.27
61.29
60.35
54.58
26.71
19.08
BzO
OTBDPS
O
HO
NHCbz
N3
O
CO2Bn
39
f1 (ppm)

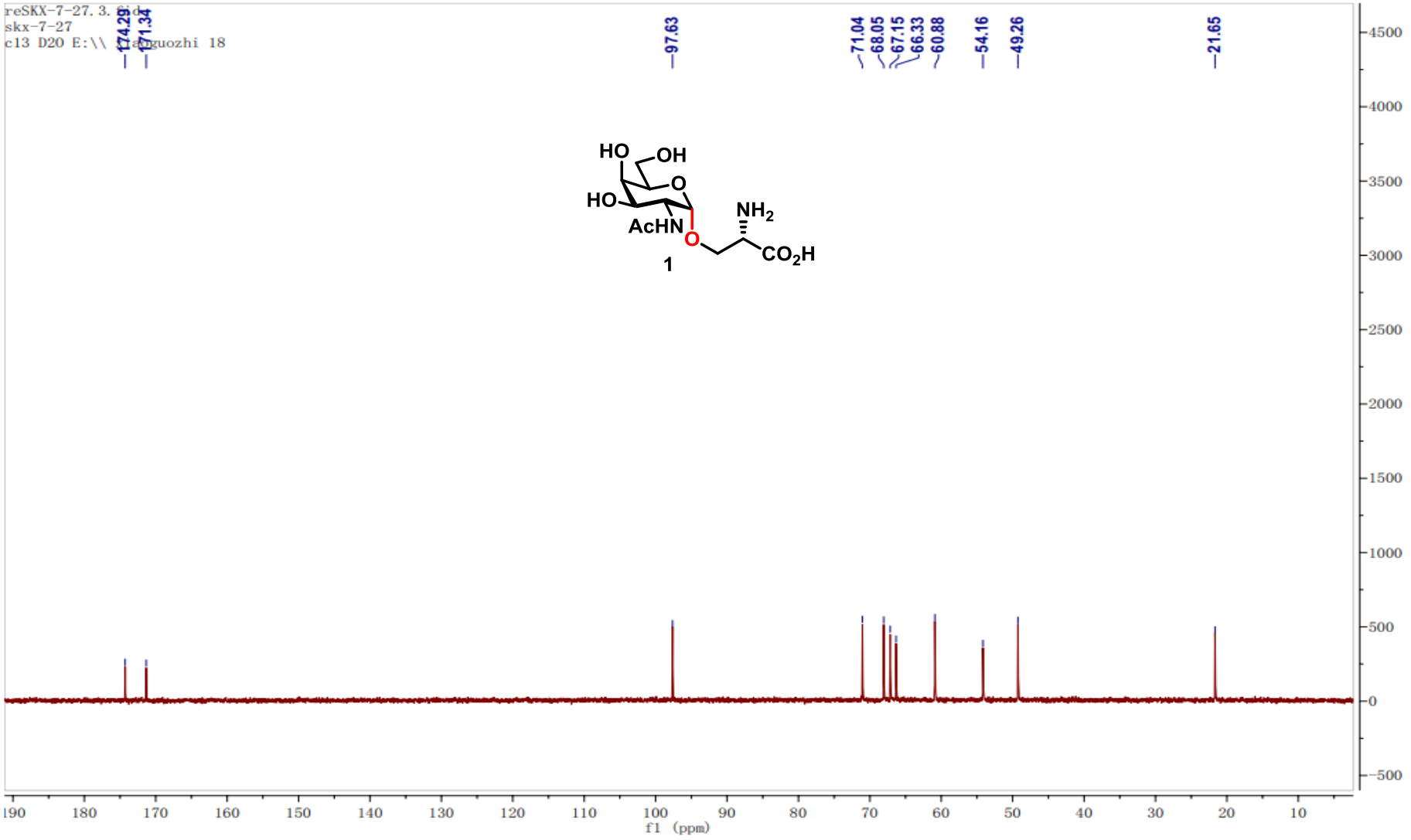

SKX-6-37-2.2.ser
SKX-6-37-2
COSYGPSW CDC13 E:\\ xiaoguozhi 23
BzO
OTBDPS
O
HO
NHCbz
N3
O
CO2Bn
39
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f2 (ppm)
2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5
f1 (ppm)

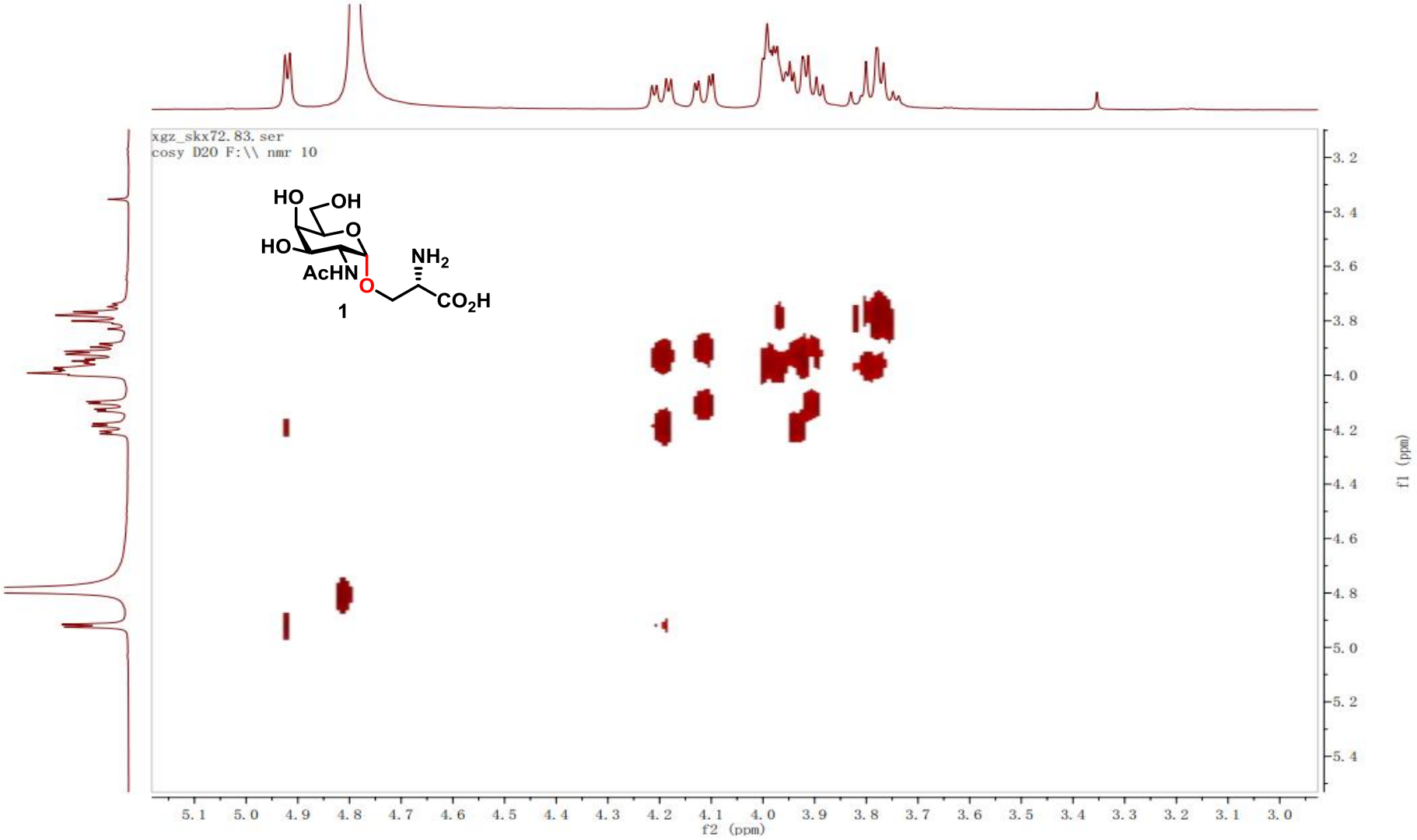

SKX-6-3-2.1.fid
SKX-6-3-2
PROTON CDCl3 E:\\ xiaoguozhi
BzO
OH
O
LevO
N3
NHCbz
O
CO2Bn
S33
f1 (ppm)

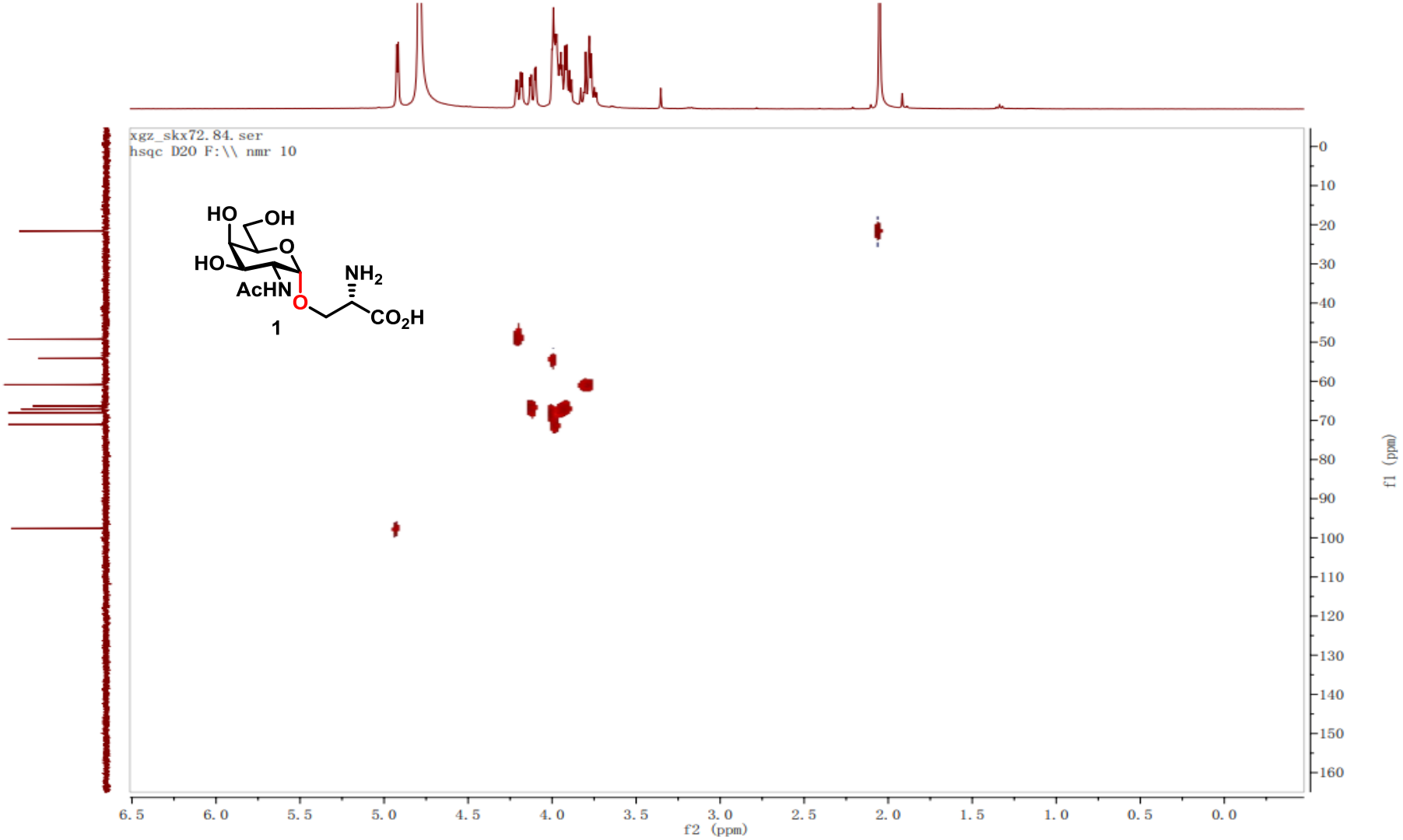

SKX-6-3-2.3.fid
SKX-6-3-2
c13 CDCl3 E:\ xiaoguozhi 6
206.18
171.70
169.85
166.13
156.15
136.28
135.10
133.86
129.94
129.04
128.80
128.76
128.65
128.31
128.20
99.65
70.34
70.16
68.66
68.52
67.99
67.28
61.07
57.99
54.79
37.89
29.73
27.94
BzO
OH
O
LevO
N3
O
NHCbz
CO2Bn
S33
f1 (ppm)

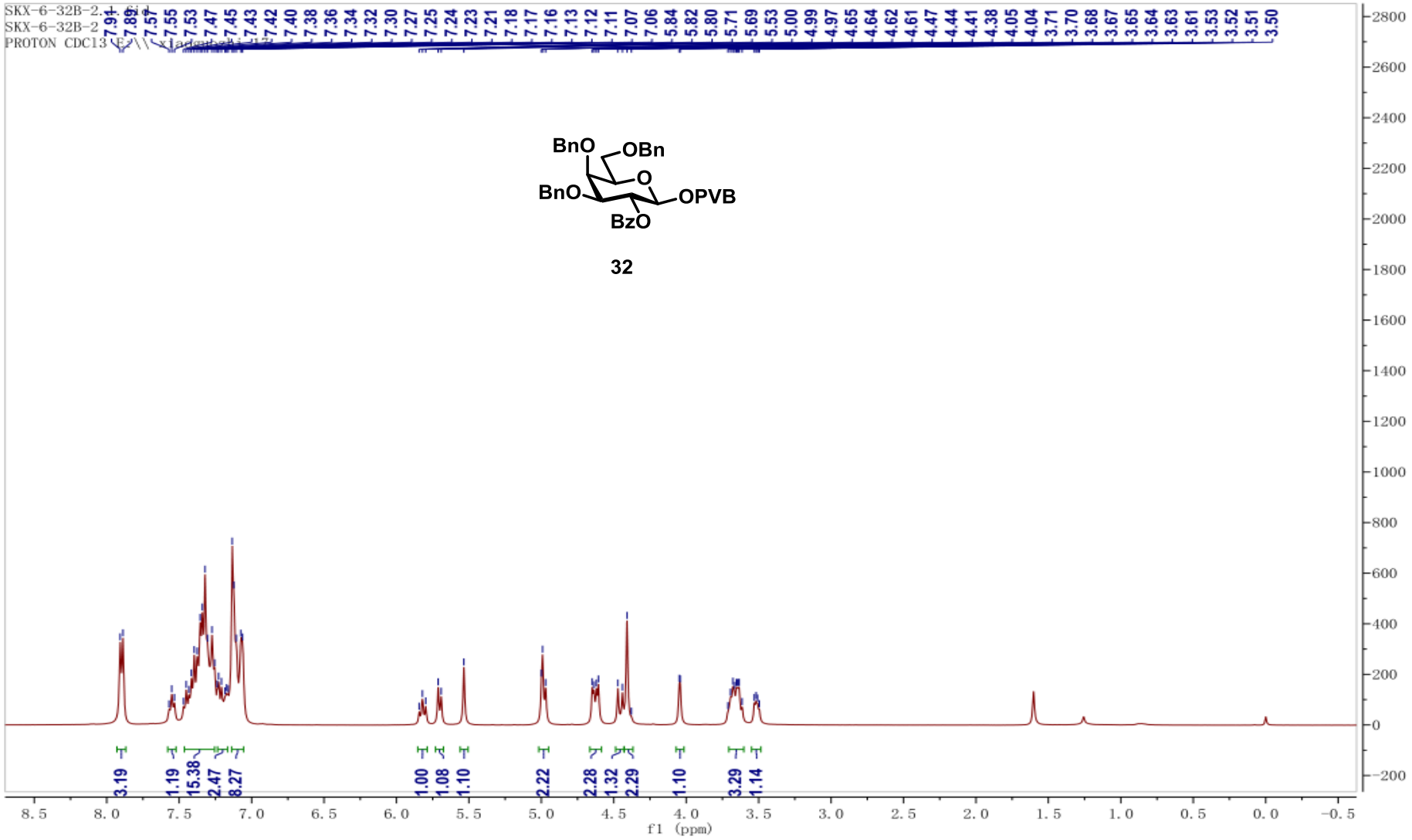

SKX-6-3-2.2.ser
SKX-6-3-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 6
BzO
OH
O
LevO
N3
O
NHCbz
CO2Bn
S33
f2 (ppm)
f1 (ppm)

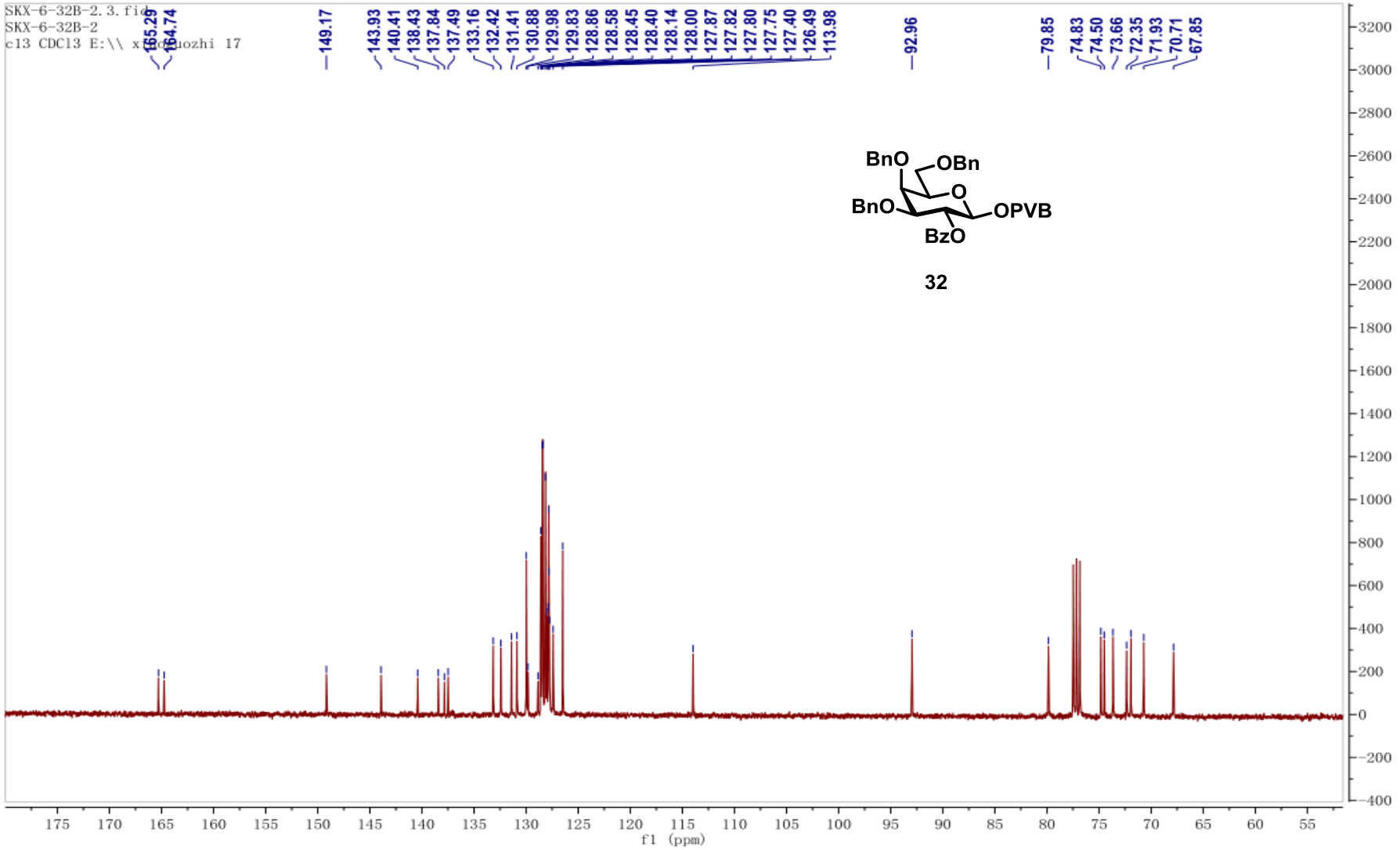

SKX-7-27, 2. 4. fid
SKX-7-27, 2
PROTON D2O E:\\ xiaoguzhi 5
4.92 4.92 4.21 4.21 4.19 4.18 4.13 4.12 4.10 4.10 4.00 3.99 3.98 3.98 3.97 3.97 3.96 3.95 3.94 3.92 3.92 3.91 3.90 3.88 3.81 3.80 3.78 3.78 3.77 3.75 3.74
2.05
HO
OH
O
HO
AcHN
O
NH2
CO2H
1
1.00
1.09
1.15
5.45
2.19
3.00
f1 (ppm)

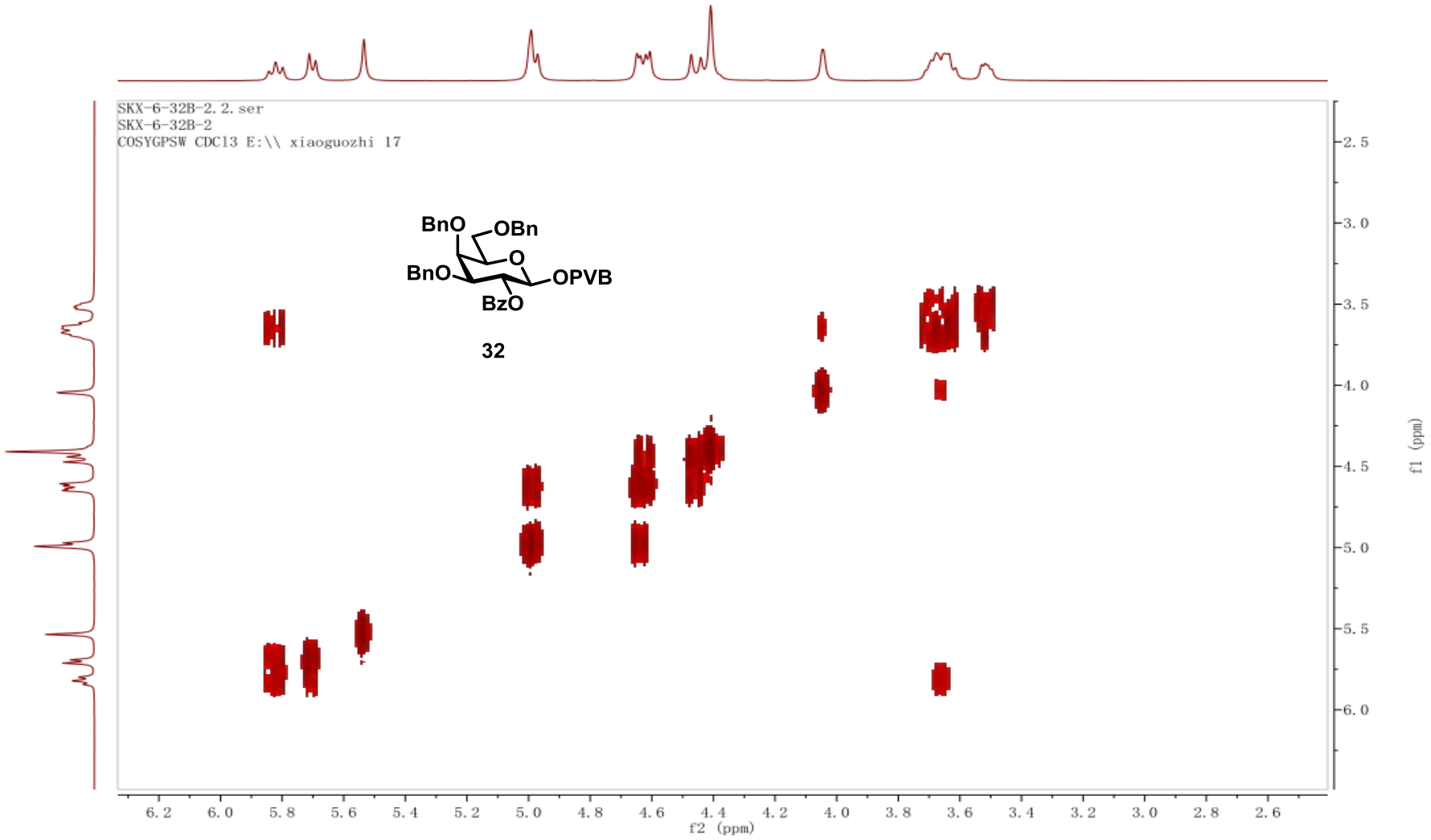

reSKX-7-27.3.fid
skx-7-27
c13 D20 E:\\ zhuguozhi 18
174.29
171.34
97.63
71.04
68.05
67.15
66.33
60.88
54.16
49.26
21.65
HO
OH
O
HO
AcHN
O
NH2
CO2H
1
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

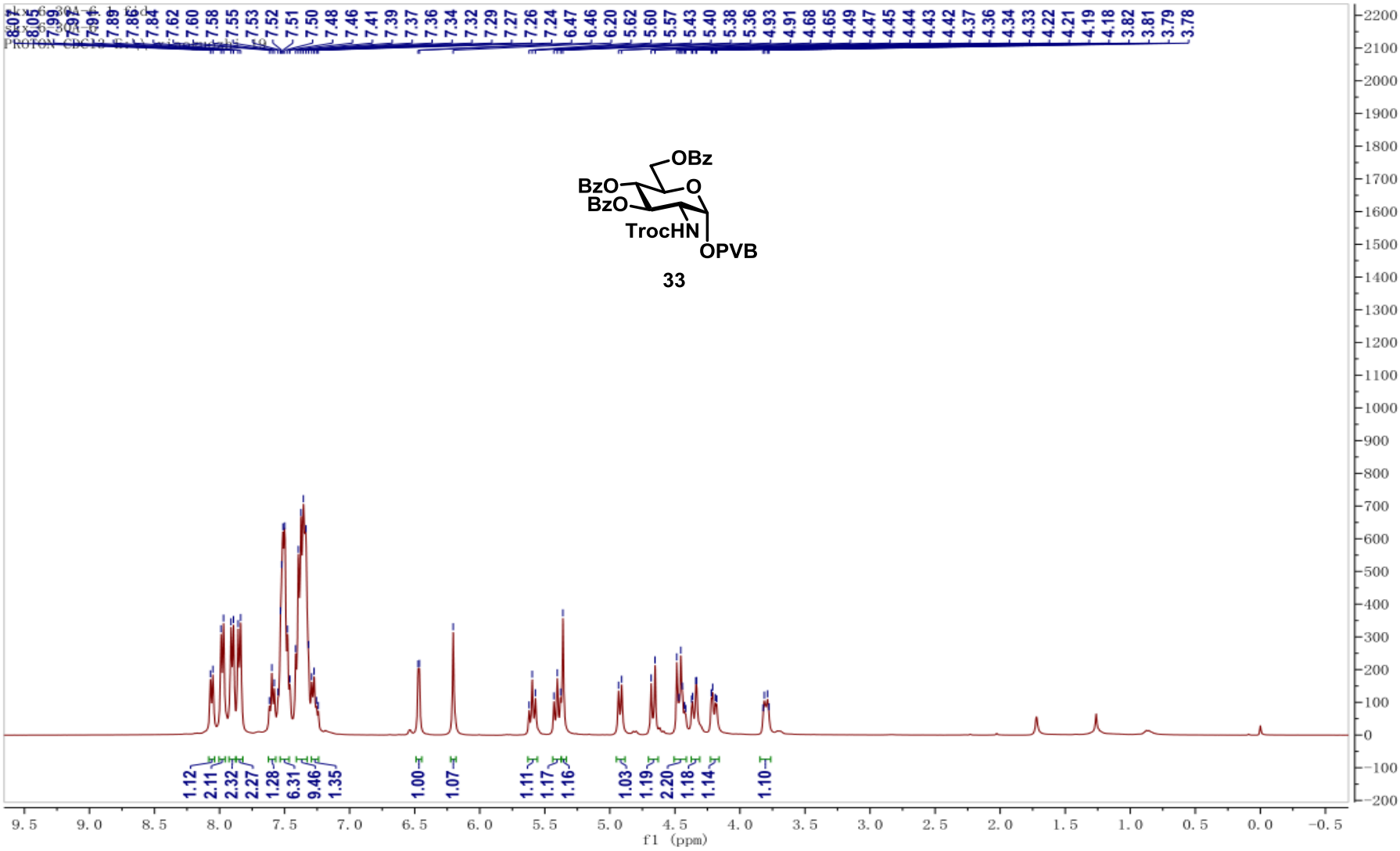

xgz_skx72.83.ser
cosy D20 F:\\ nmr 10
HO
OH
O
HO
AcHN
O
NH2
CO2H
1
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
f1 (ppm)
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
f2 (ppm)

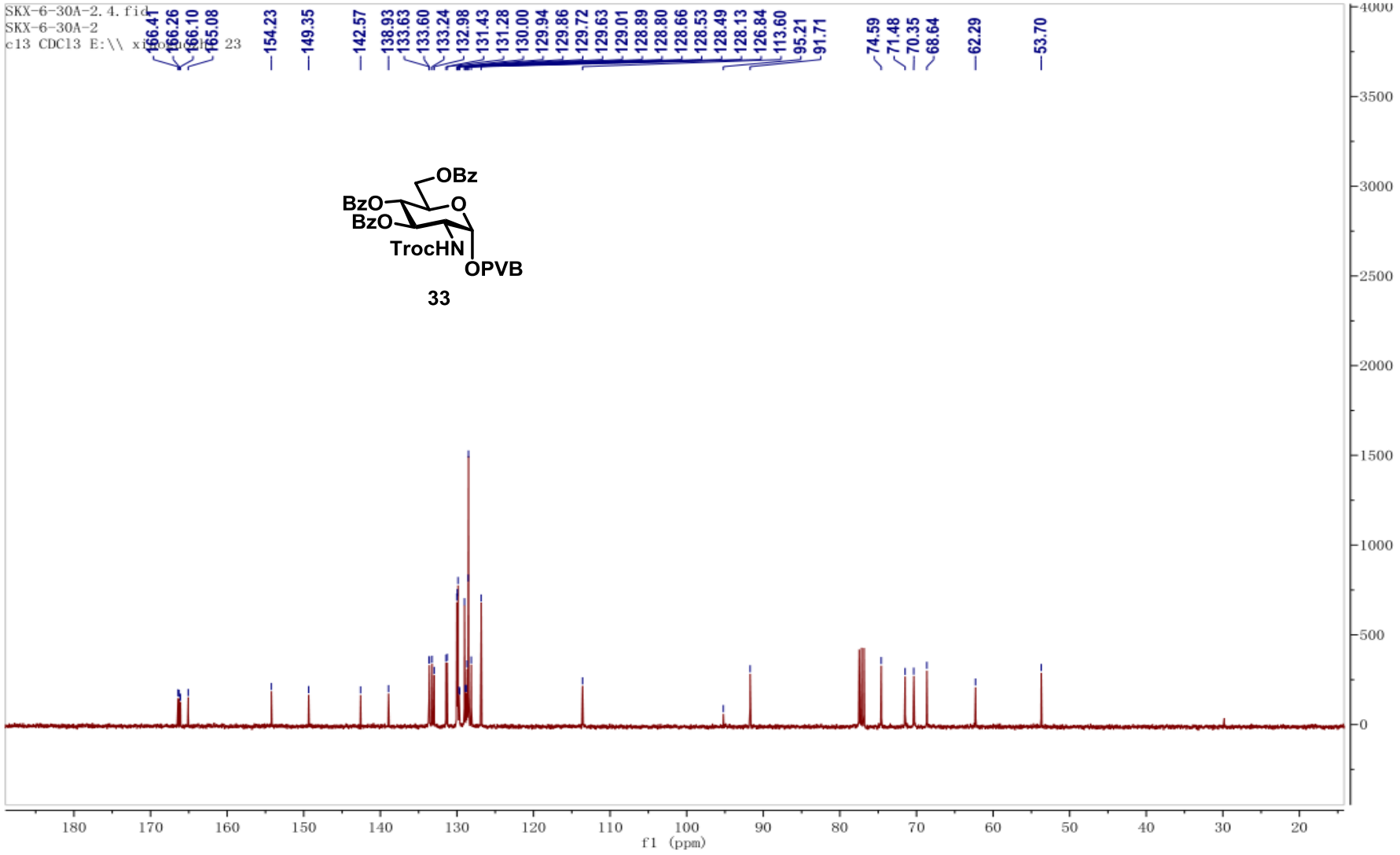

xgz_skx72.84.ser
hsqc D20 F:\\ nmr 10
HO
OH
O
HO
AcHN
O
NH2
CO2H
1
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

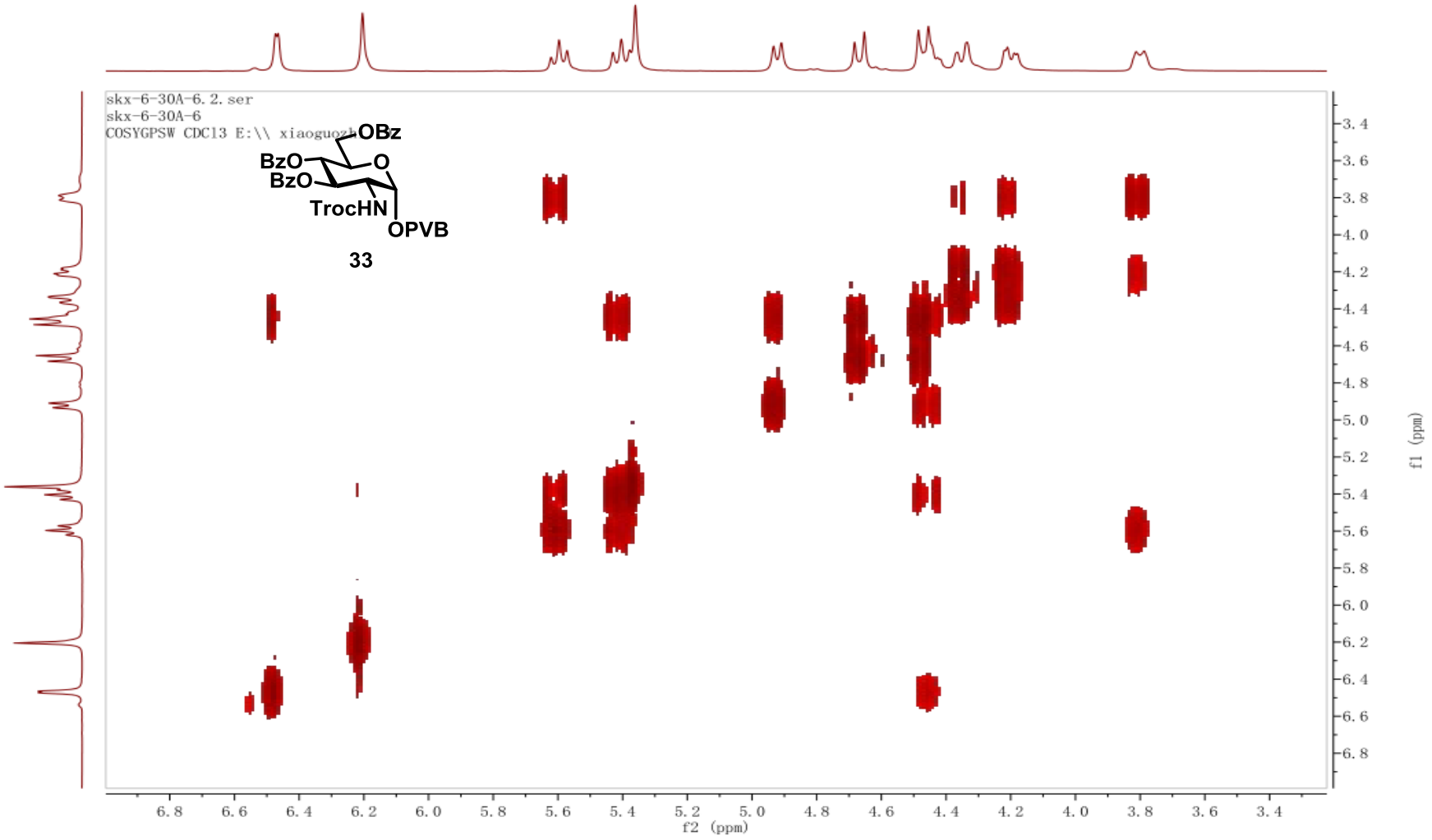

SKX-6-32B-2.1.fid
SKX-6-32B-2
PROTON CDC13
BnO
OBn
O
BnO
OPVB
BzO
32
f1 (ppm)

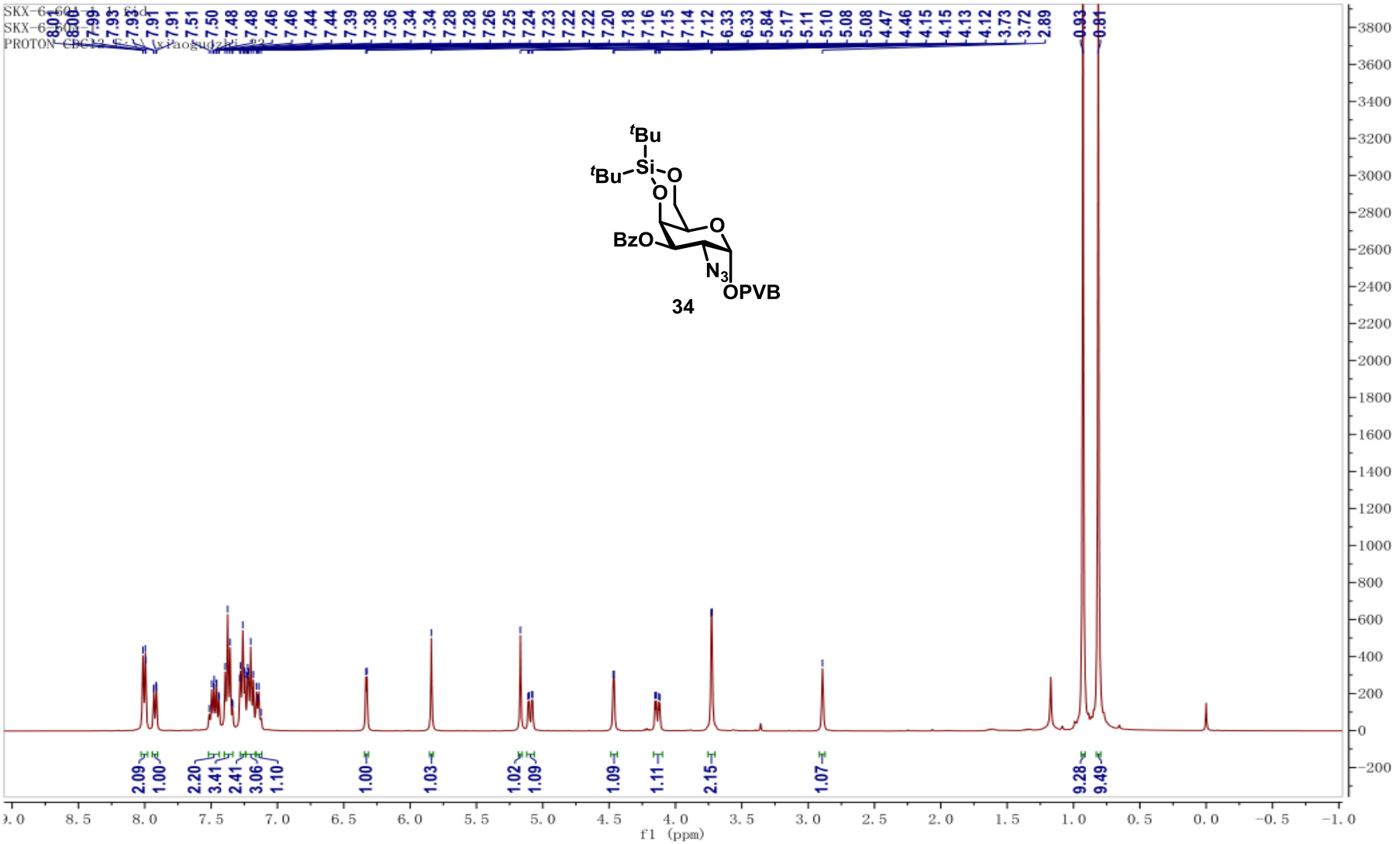

SKX-6-32B-2.3.fid
SKX-6-32B-2
c13 CDCl3 E:\\ xiaokuozhi 17
165.29
164.74
149.17
143.93
140.41
138.43
137.84
137.49
133.16
132.42
131.41
130.88
129.98
129.83
128.86
128.58
128.45
128.40
128.14
128.00
127.87
127.82
127.80
127.75
127.40
126.49
113.98
92.96
79.85
74.83
74.50
73.66
72.35
71.93
70.71
67.85
BnO
OBn
O
BnO
OPVB
BzO
32
f1 (ppm)

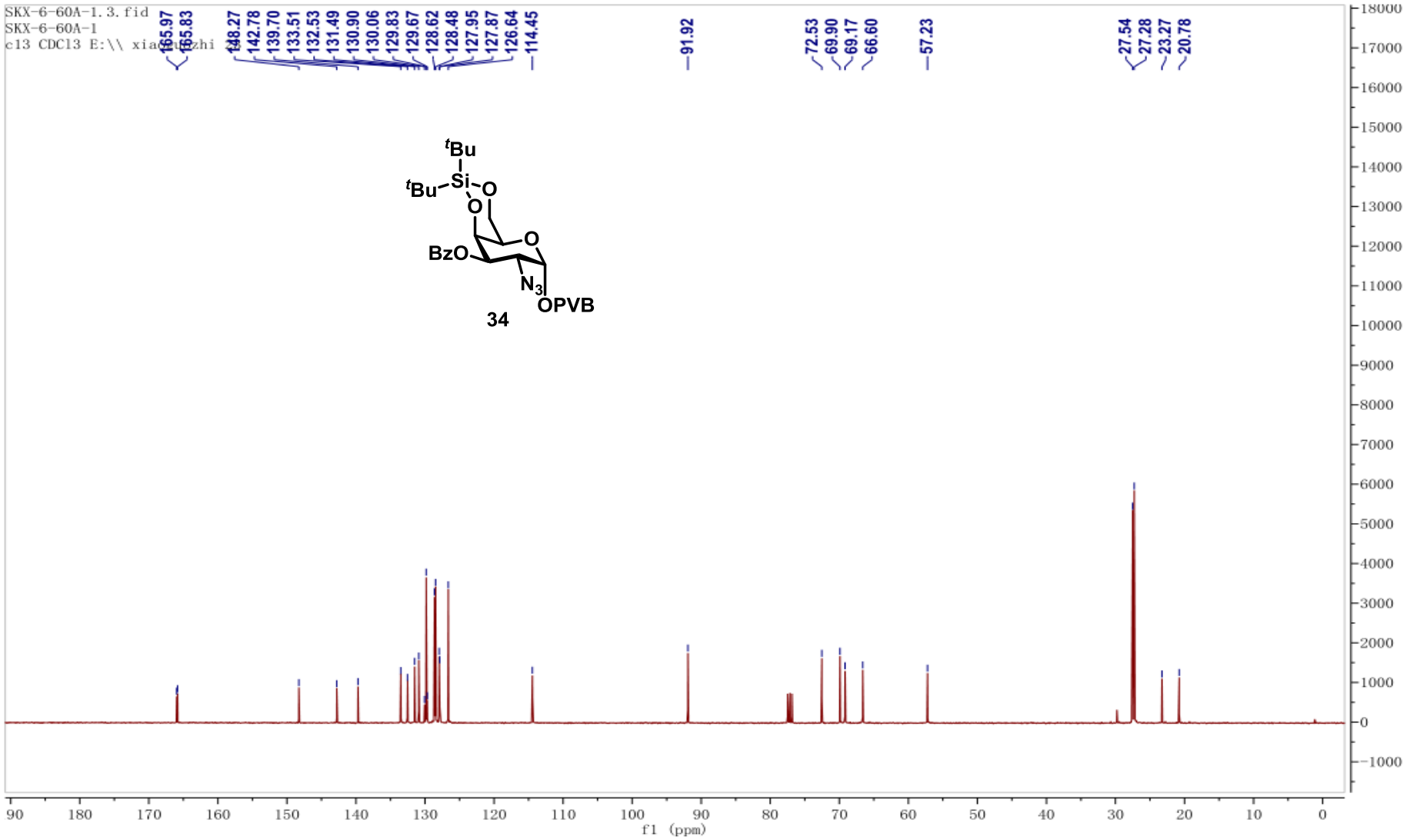

SKX-6-32B-2.2.ser
SKX-6-32B-2
COSYGPSW CDCl3 E:\\ xiaoguozhi 17
BnO
OBn
O
BnO
OPVB
BzO
32
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)

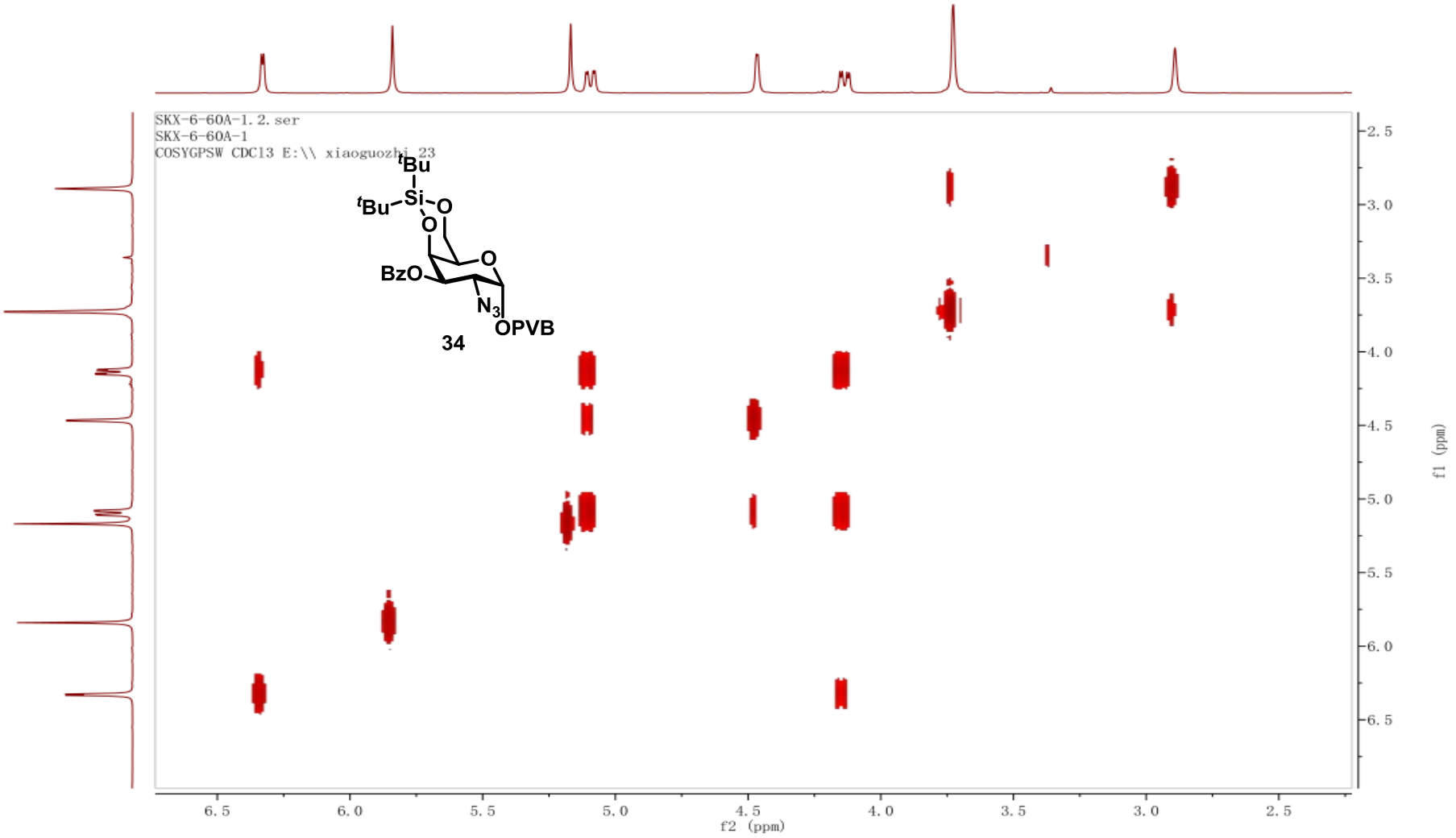

OBz
BzO
O
BzO
TrocHN
OPVB
33
f1 (ppm)

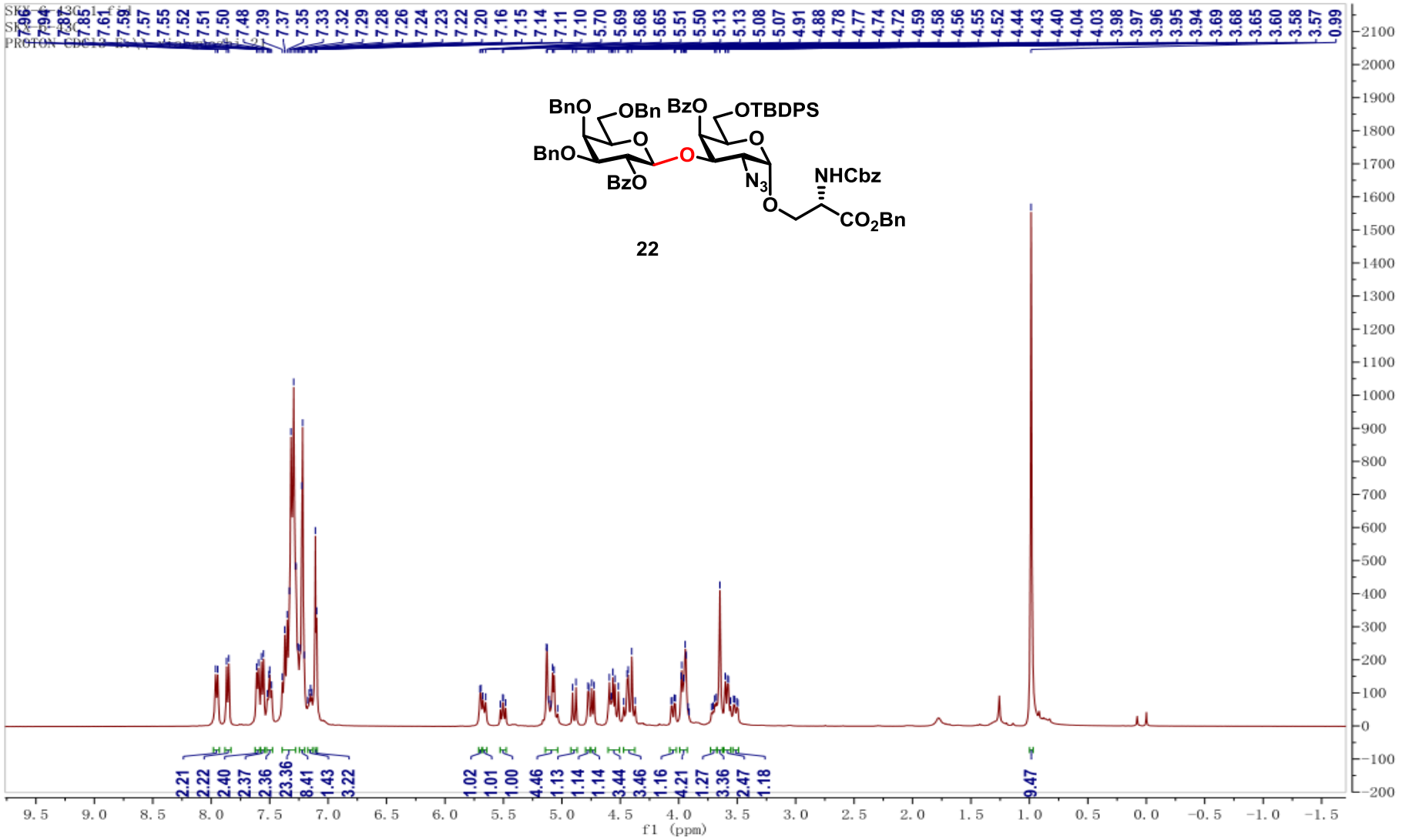

SKX-6-30A-2.4.fid
SKX-6-30A-2
c13 CDCl3 E:\\ xiaoguo
166.41
166.26
166.10
165.08
154.23
149.35
142.57
138.93
133.63
133.60
133.24
132.98
131.43
131.28
130.00
129.94
129.86
129.72
129.63
129.01
128.89
128.80
128.66
128.53
128.49
128.13
126.84
113.60
95.21
91.71
74.59
71.48
70.35
68.64
62.29
53.70
OBz
BzO
BzO
O
TrocHN
OPVB
33
4000
3500
3000
2500
2000
1500
1000
500
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

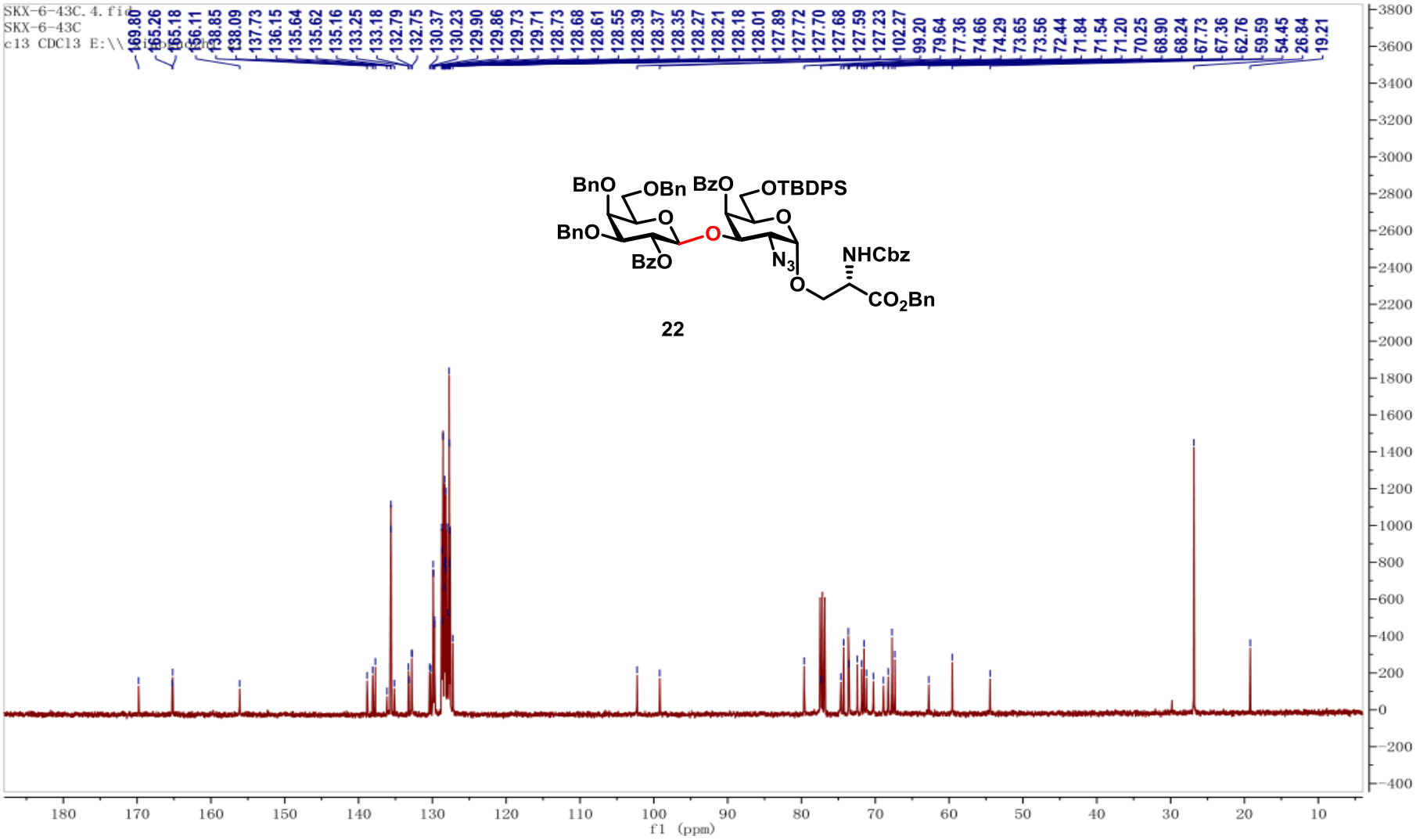

skx-6-30A-6.2.ser
skx-6-30A-6
COSYGPSW CDCl3 E:\\ xiaoguozh
OBz
BzO
O
BzO
TrocHN
OPVB
33
f2 (ppm)
f1 (ppm)

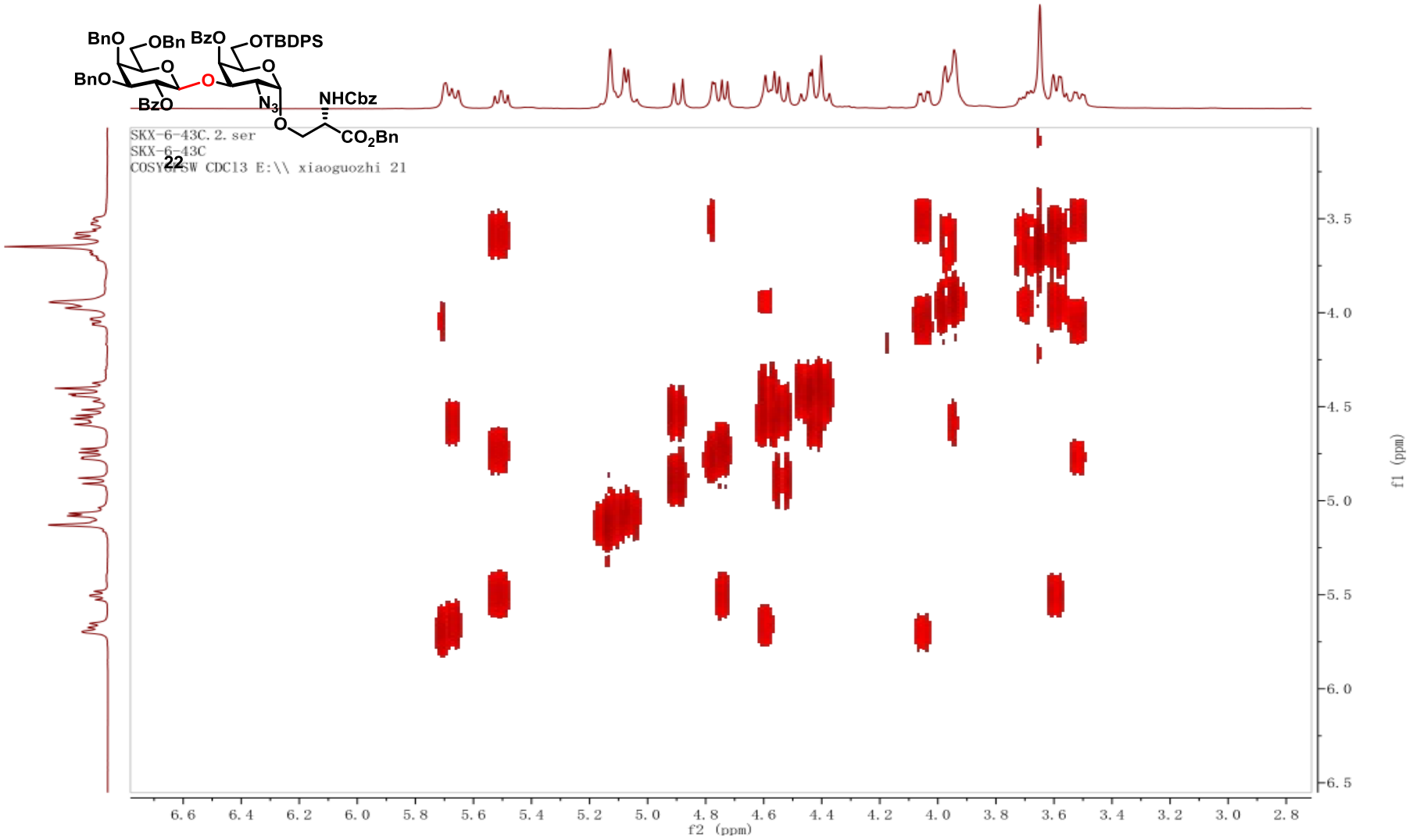

tBu
tBu
Si
O
O
O
BzO
N3
OPVB
34
f1 (ppm)

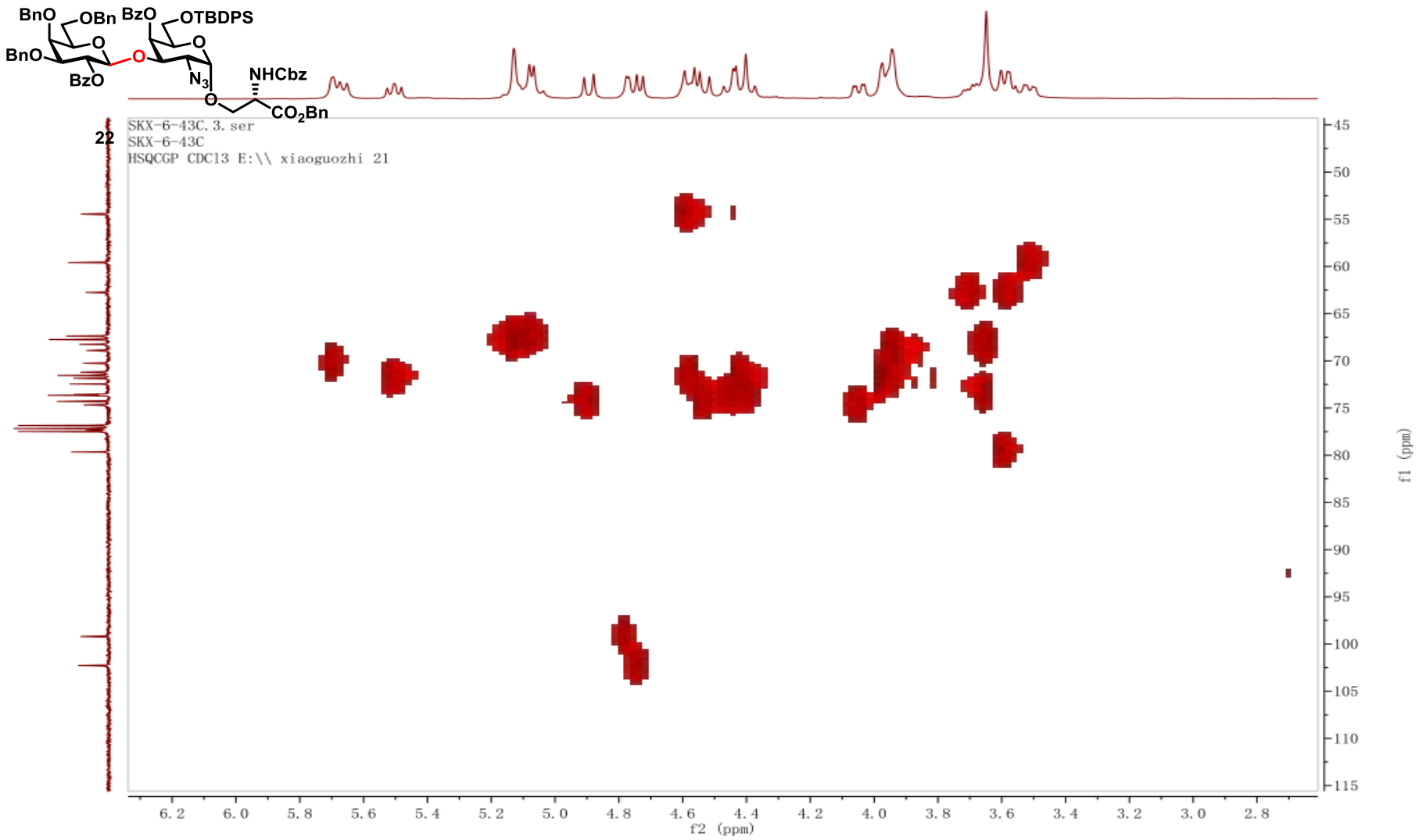

SKX-6-60A-1.3.fid
SKX-6-60A-1
c13 CDCl3 E:\\ xiaopuzhi
165.97
165.83
148.27
142.78
139.70
133.51
132.53
131.49
130.90
130.06
129.83
129.67
128.62
128.48
127.95
127.87
126.64
114.45
91.92
72.53
69.90
69.17
66.60
57.23
27.54
27.28
23.27
20.78
tBu
tBu
Si
O
O
O
BzO
N3
OPVB
34
f1 (ppm)

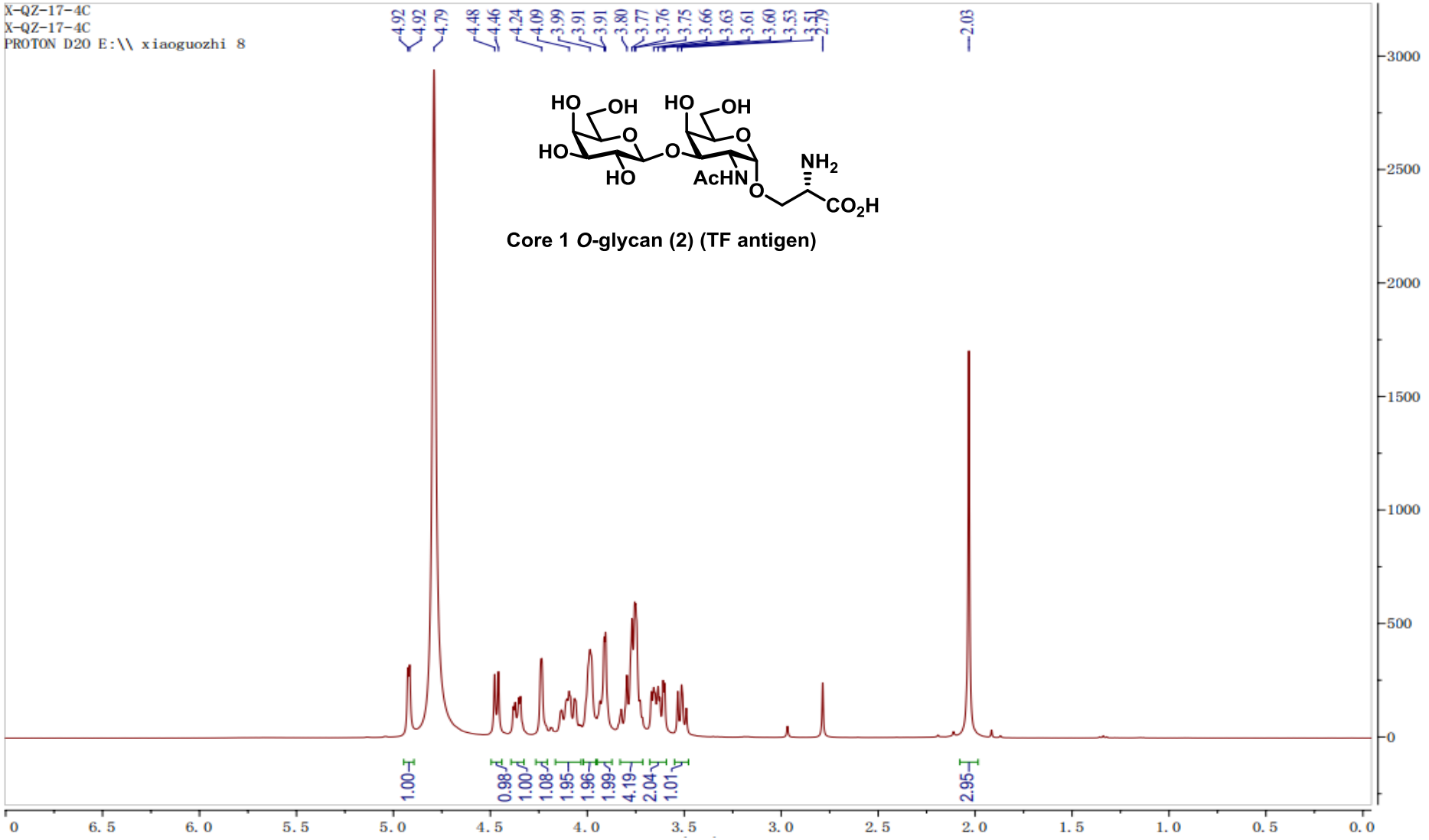

SKX-6-60A-1.2.ser
SKX-6-60A-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 23
tBu
tBu
Si
O
O
O
BzO
N3
OPVB
34
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
f1 (ppm)

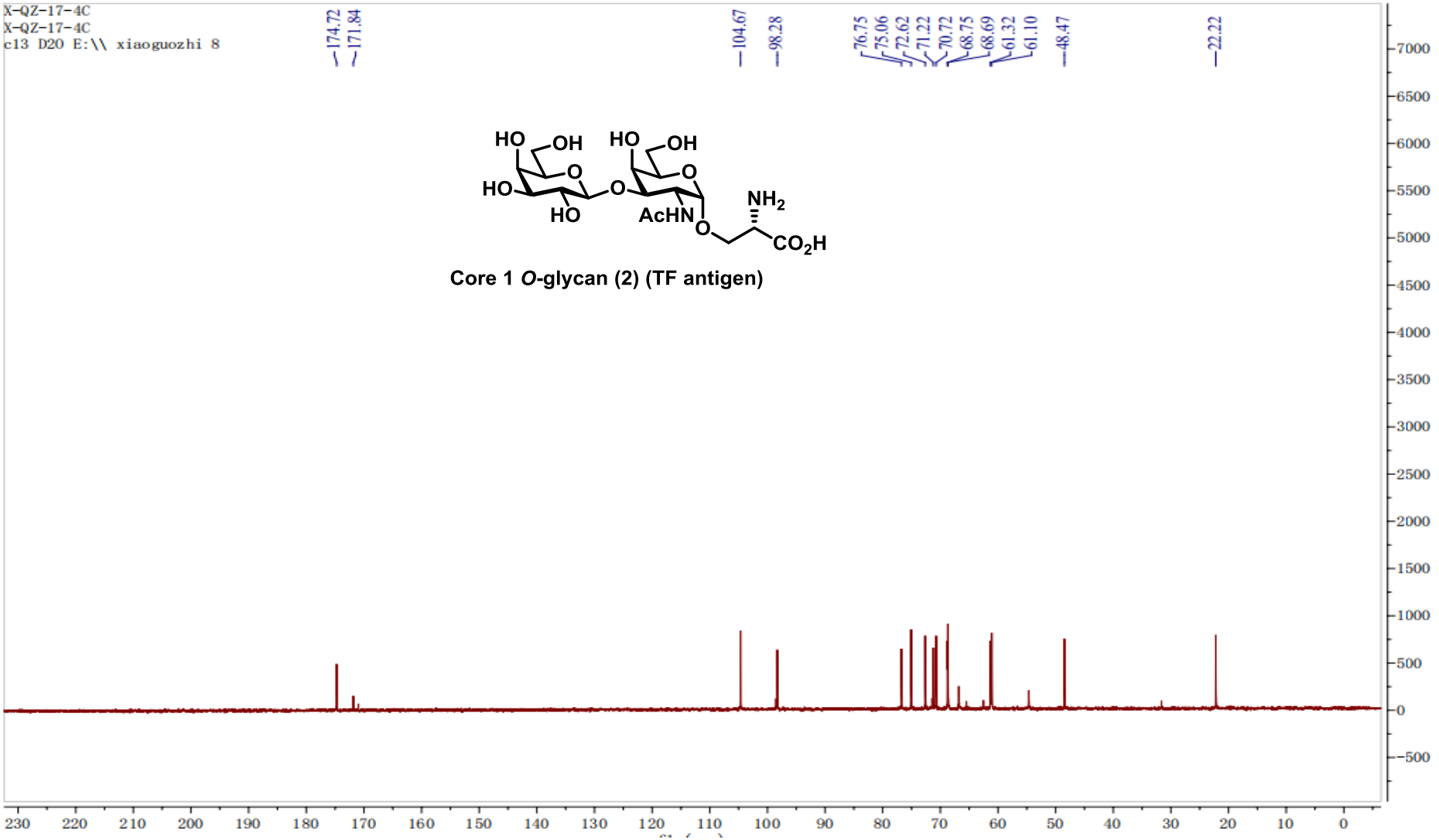

BnO
OBn
BzO
OTBDPS
BnO
O
O
O
BzO
N3
NHCbz
O
CO2Bn
22
f1 (ppm)

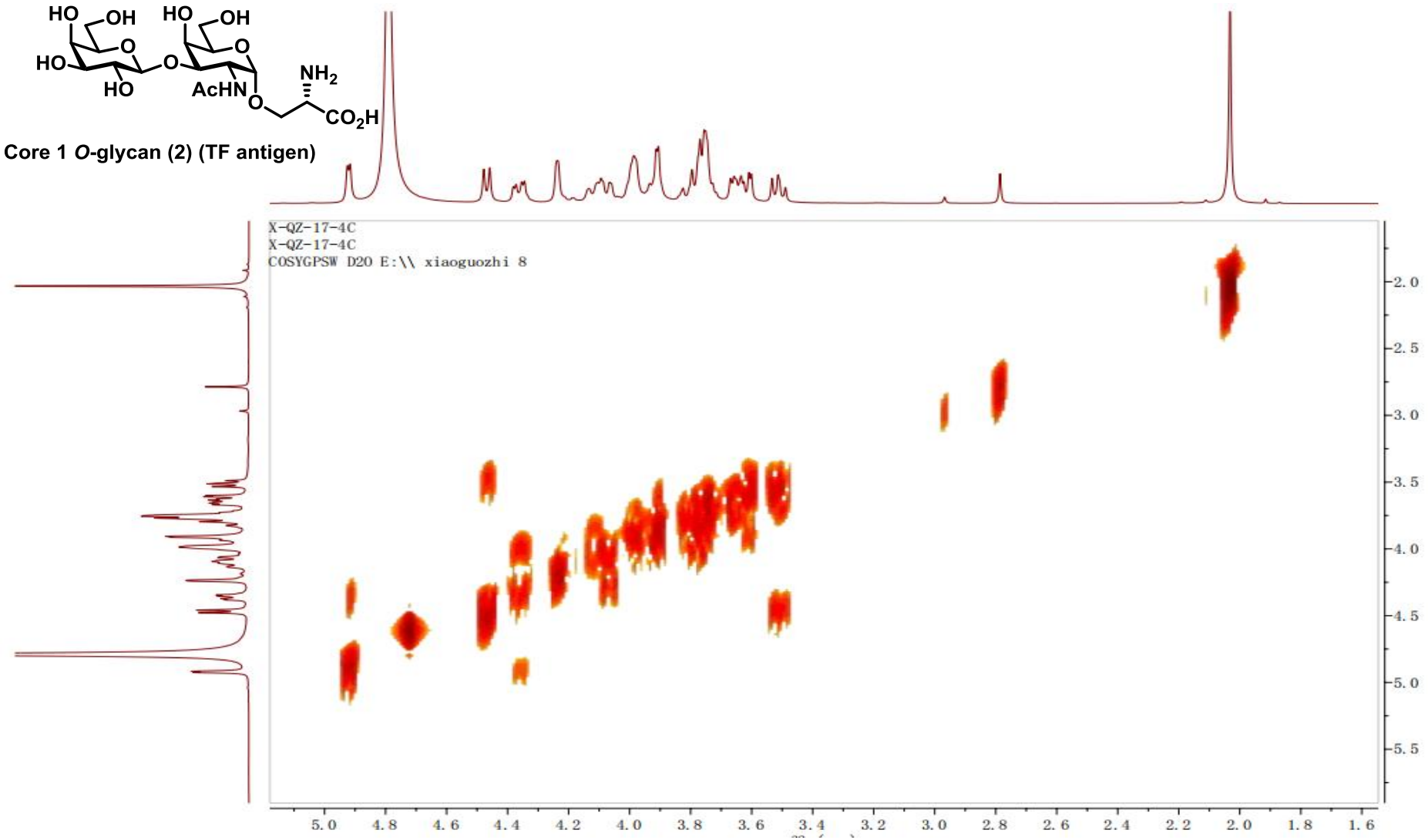

SKX-6-43C.4.fid
SKX-6-43C
c13 CDCl3 E:\\
169.80
165.26
165.18
156.11
138.85
138.09
137.73
136.15
135.64
135.62
135.16
133.25
133.18
132.79
132.75
130.37
130.23
129.90
129.86
129.73
129.71
128.73
128.68
128.61
128.55
128.39
128.37
128.35
128.27
128.21
128.18
128.01
127.89
127.72
127.70
127.68
127.59
127.23
102.27
99.20
79.64
77.36
74.66
74.29
73.65
73.56
72.44
71.84
71.54
71.20
70.25
68.90
68.24
67.73
67.36
62.76
59.59
54.45
26.84
19.21
BnO
OBn
BzO
OTBDPS
BnO
BzO
N3
NHCbz
CO2Bn
22
f1 (ppm)

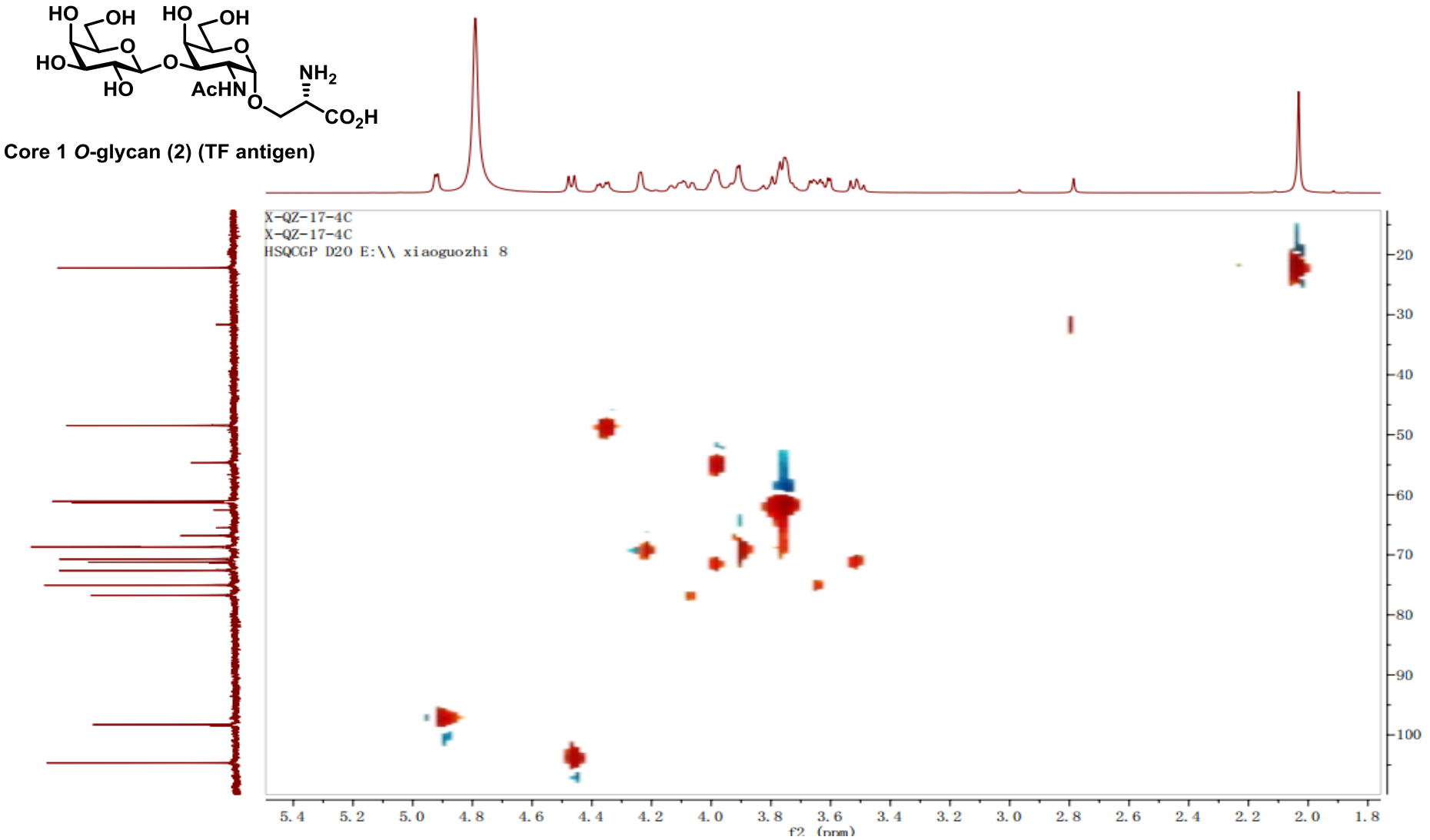

BnO
OBn
BzO
OTBDPS
BnO
O
O
O
BzO
N3
NHCbz
O
CO2Bn
22
SKX-6-43C.2.ser
SKX-6-43C
COSYGPSW CDCl3 E:\\ xiaoguozhi 21
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f2 (ppm)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)


BnO
OBn
BzO
OTBDPS
BnO
BzO
N3
NHCbz
CO2Bn
22
SKX-6-43C.3.ser
SKX-6-43C
HSQCGP CDCl3 E:\\ xiaoguozhi 21
f2 (ppm)
f1 (ppm)

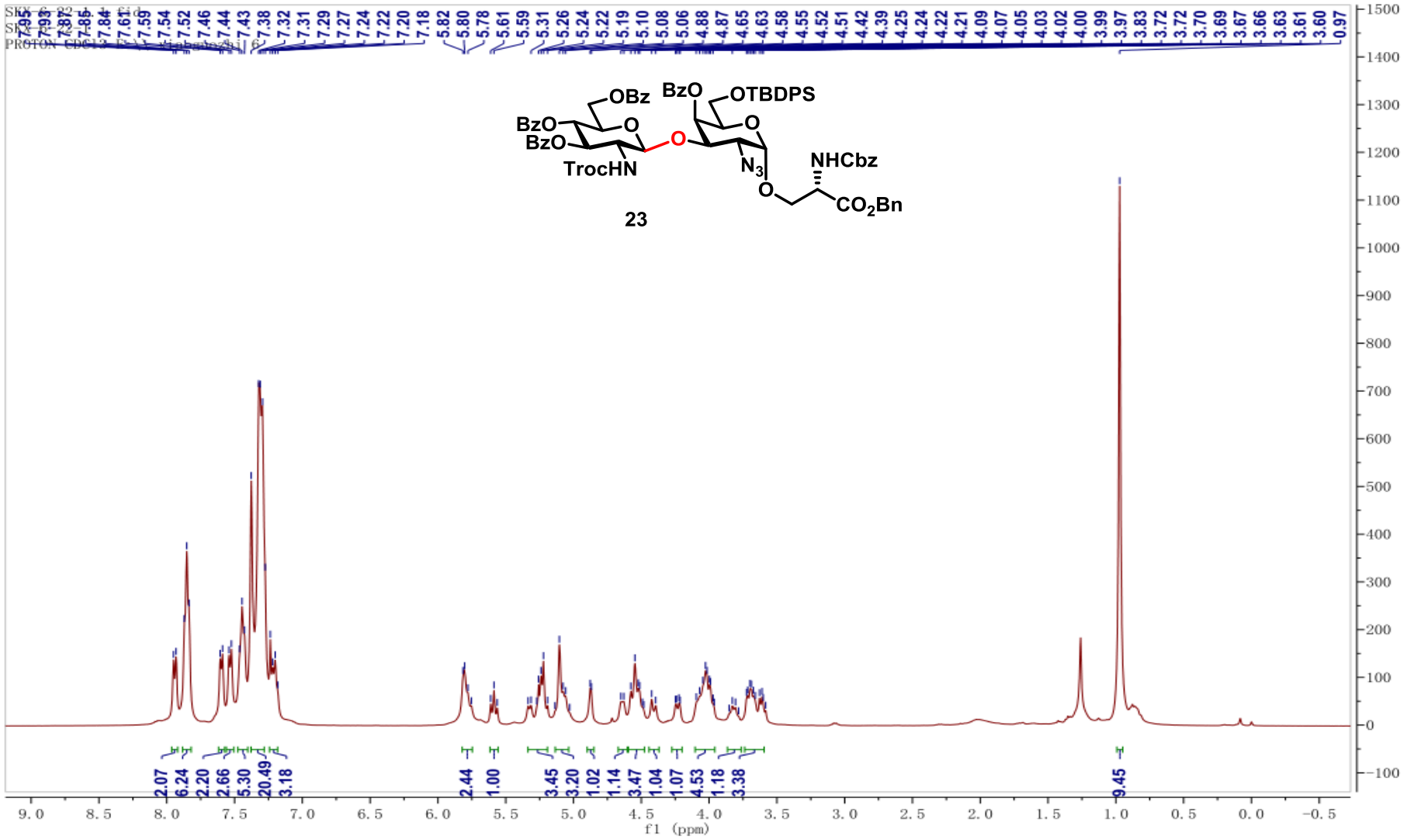

X-QZ-17-4C
X-QZ-17-4C
PROTON D20 E:\\ xiaoguozhi 8
4.92
4.92
4.79
4.48
4.46
4.24
4.09
3.99
3.91
3.91
3.80
3.77
3.76
3.75
3.66
3.63
3.61
3.60
3.53
3.51
3.50
2.03
HO
OH
HO
OH
HO
O
O
HO
AcHN
O
NH2
CO2H
Core 1 O-glycan (2) (TF antigen)
1.00
0.98
1.00
1.08
1.95
1.96
1.99
4.19
2.04
1.01
2.95
3000
2500
2000
1500
1000
500
0
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

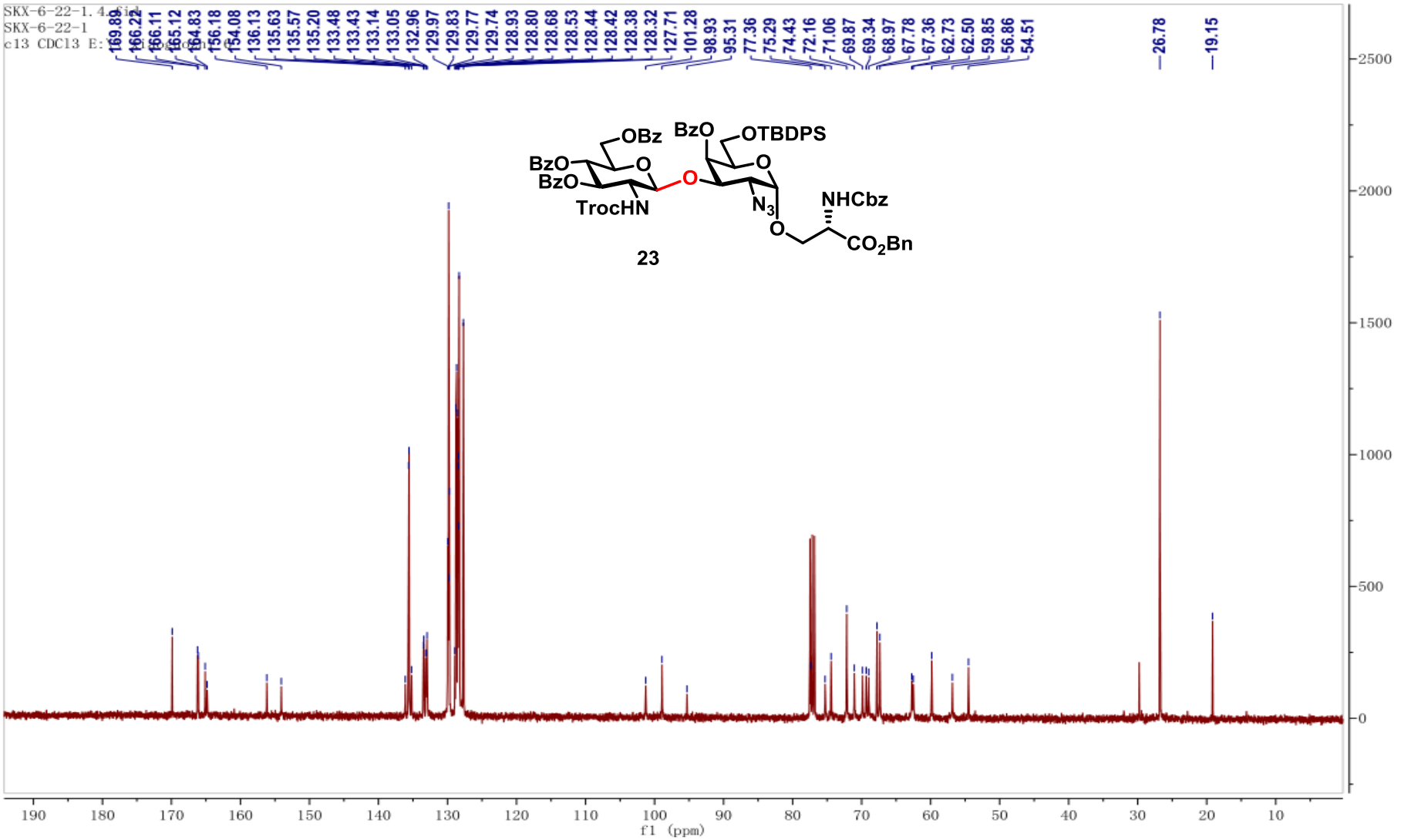

X-QZ-17-4C
X-QZ-17-4C
c13 D2O E:\\ xiaoguozhi 8
174.72
171.84
104.67
98.28
76.75
75.06
72.62
71.22
70.72
68.75
68.69
61.32
61.10
48.47
22.22
HO
OH
HO
OH
HO
O
O
O
HO
AcHN
NH2
CO2H
Core 1 O-glycan (2) (TF antigen)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

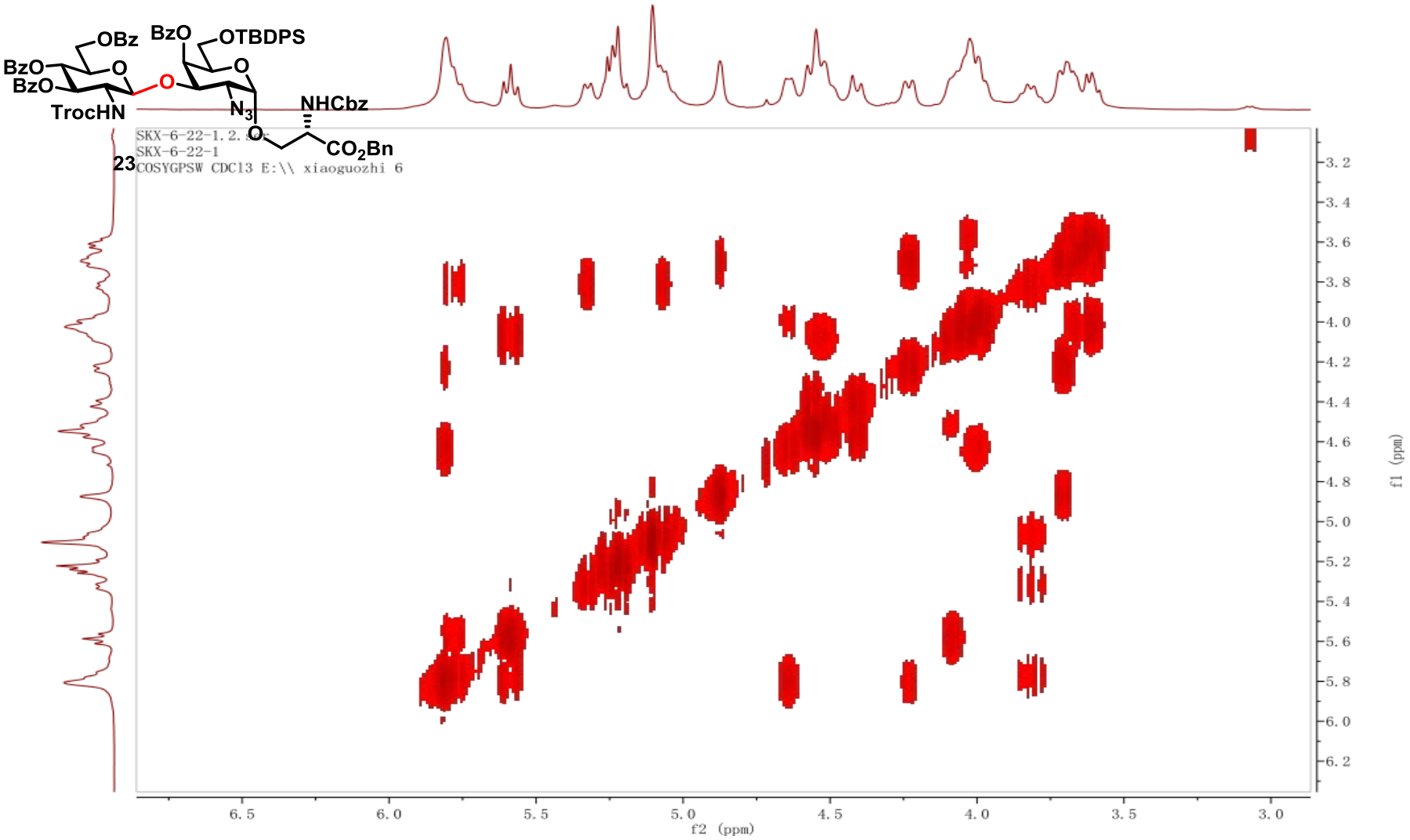

Core 1 O-glycan (2) (TF antigen)
X-QZ-17-4C
X-QZ-17-4C
COSYGPSW D2O E:\\ xiaoguozhi 8
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

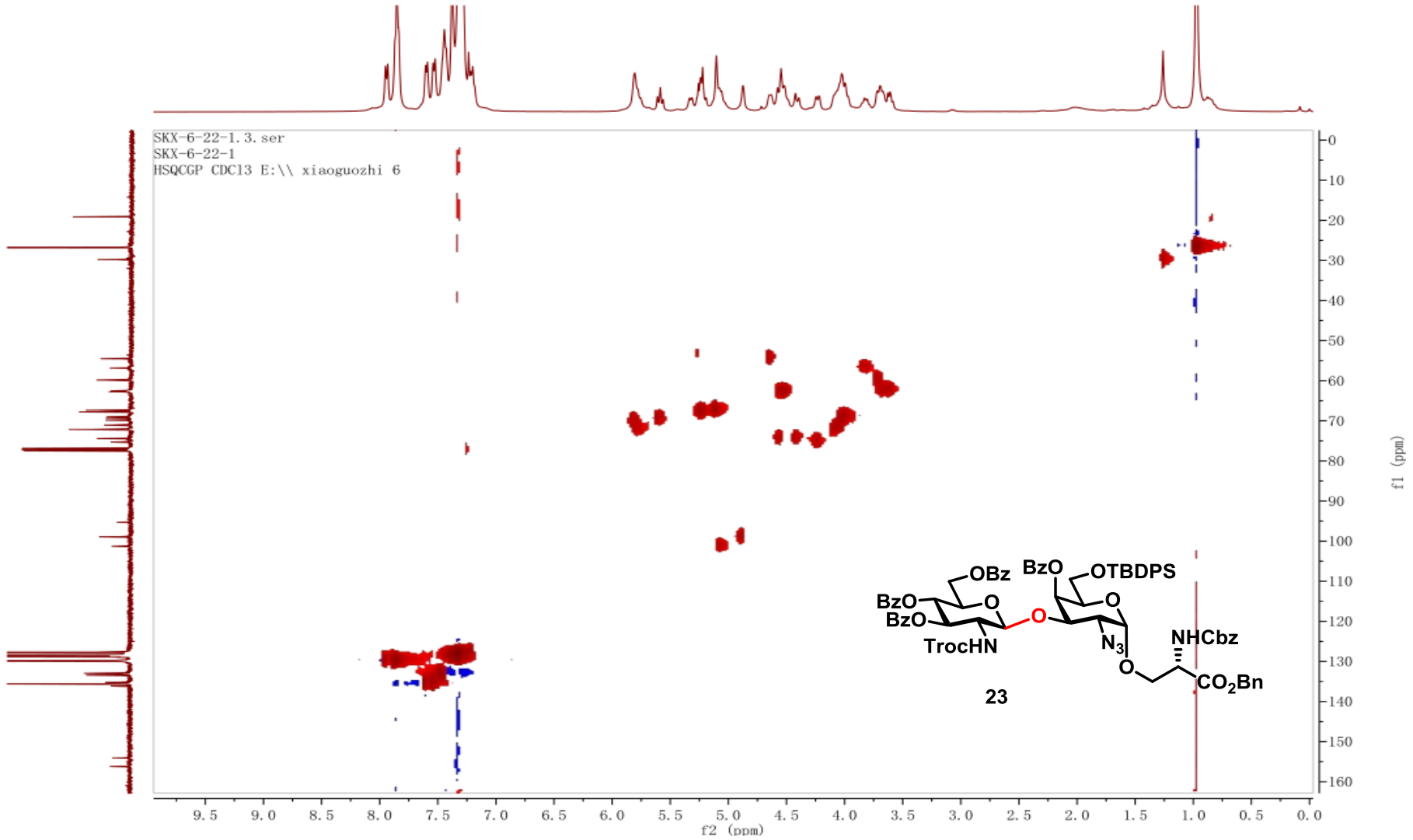


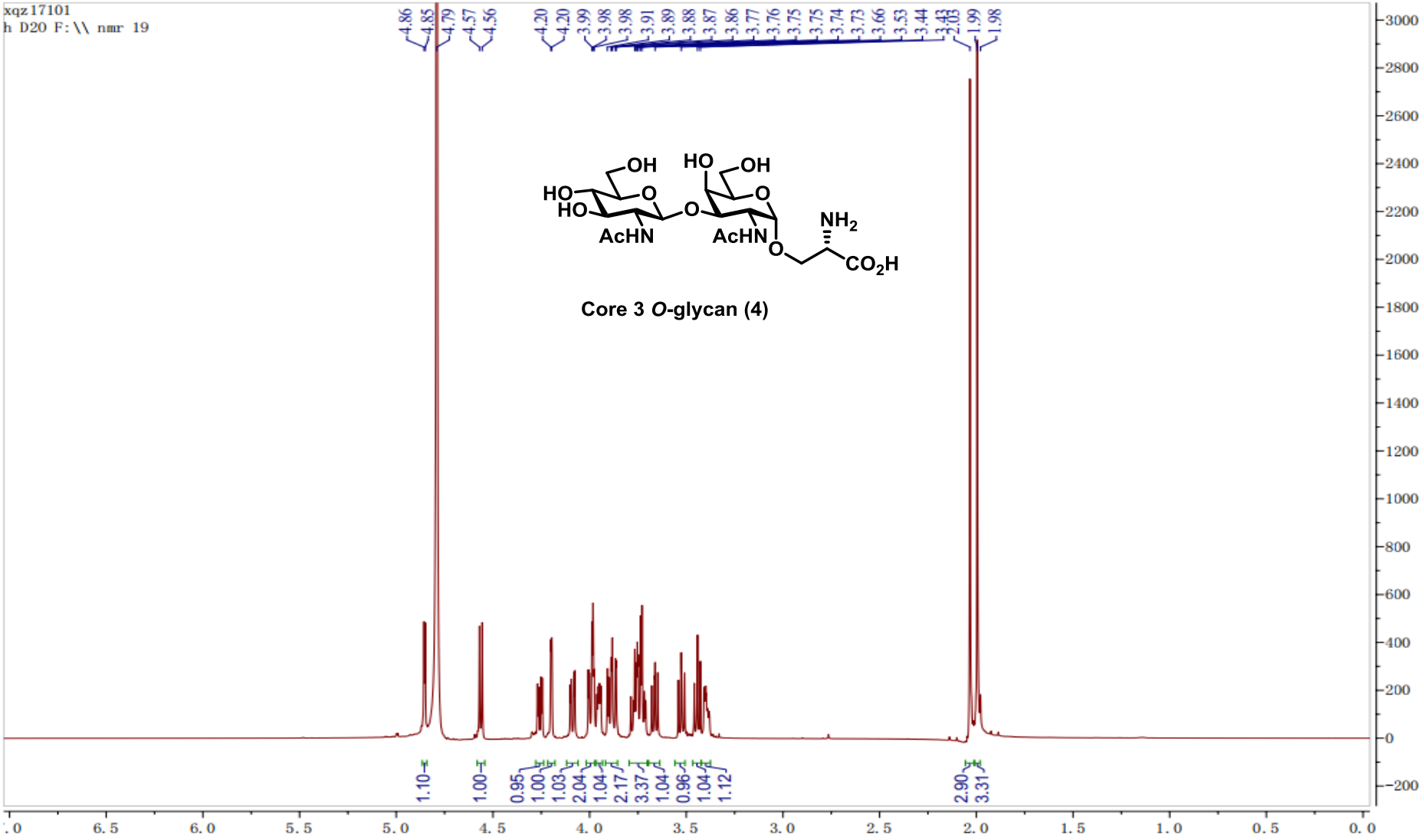
Core 1 *O*-glycan (2) (TF antigen)

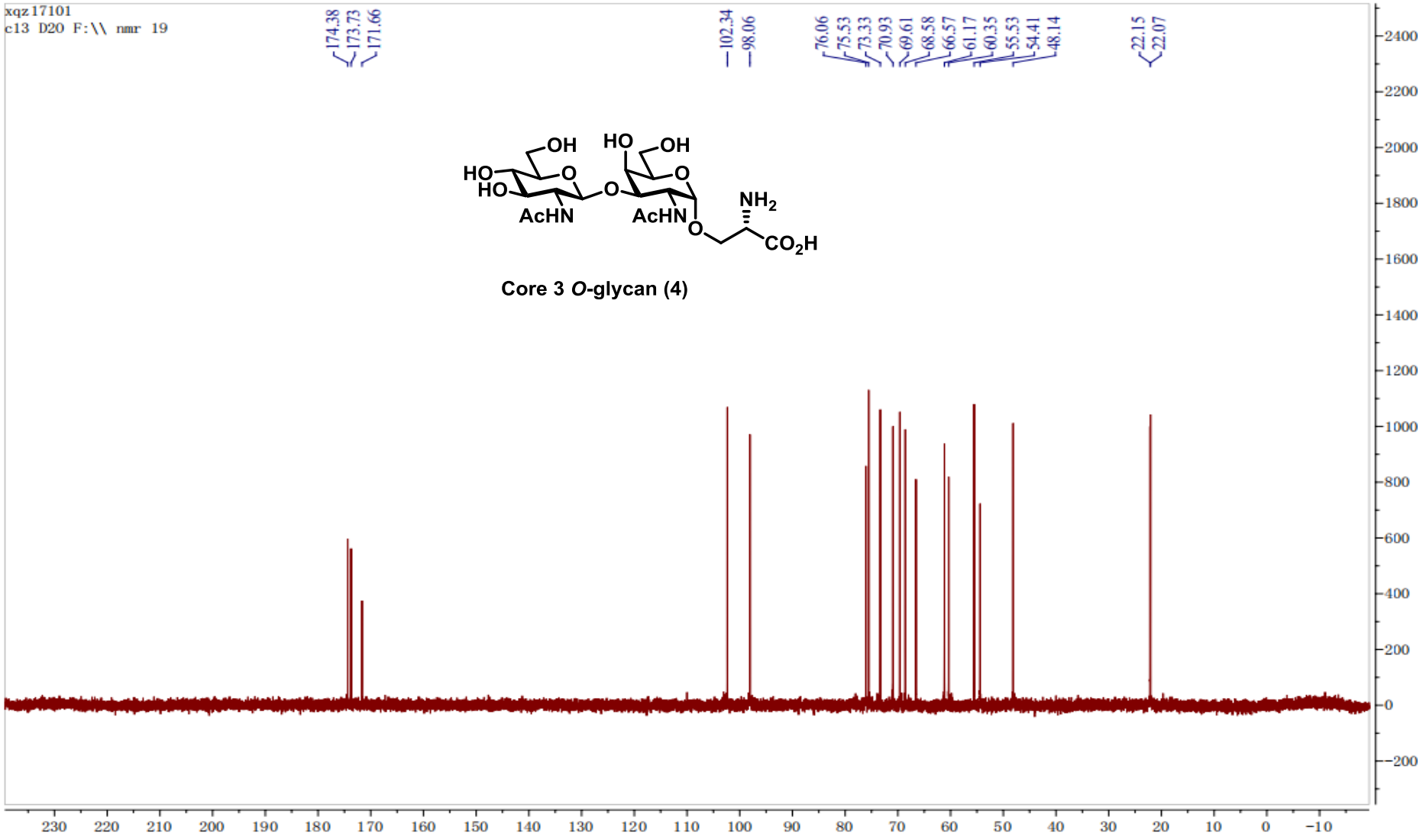

OBz
BzO
OTBDPS
BzO
BzO
O
O
O
TrocHN
N3
NHCbz
O
CO2Bn
23
f1 (ppm)


SKX-6-22-1.4.fid
SKX-6-22-1
c13 CDC13 E:
169.89
166.22
166.11
165.12
164.83
156.18
154.08
136.13
135.63
135.57
135.20
133.48
133.43
133.14
133.05
132.96
129.97
129.83
129.77
129.74
128.93
128.80
128.68
128.53
128.44
128.42
128.38
128.32
127.71
101.28
98.93
95.31
77.36
75.29
74.43
72.16
71.06
69.87
69.34
68.97
67.78
67.36
62.73
62.50
59.85
56.86
54.51
26.78
19.15
OBz
BzO
BzO
TrocHN
O
BzO
OTBDPS
O
N3
NHCbz
O
CO2Bn
23
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

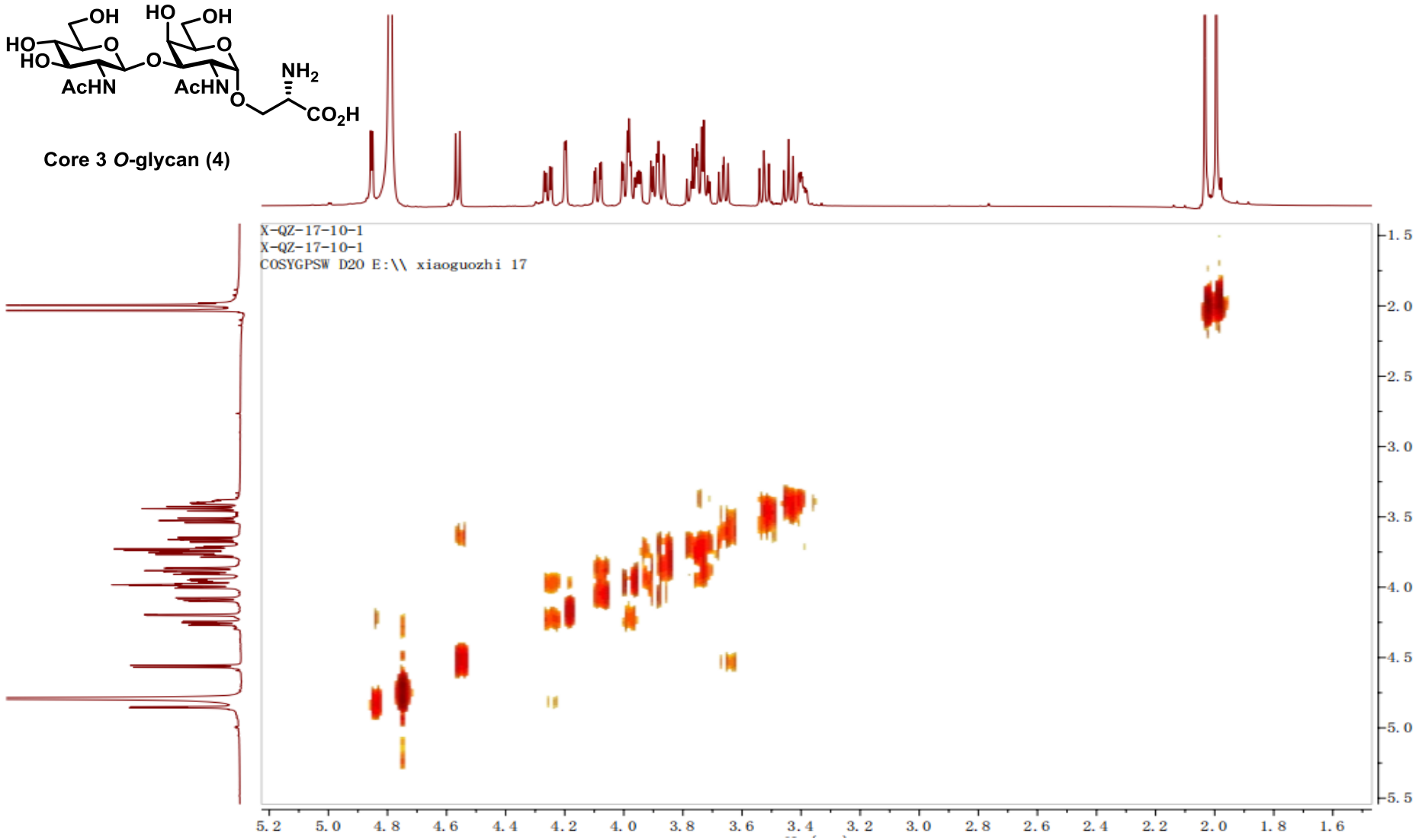

OBz
BzO
BzO
TrocHN
BzO
OTBDPS
N3
NHCbz
CO2Bn
23
SKX-6-22-1.2.
SKX-6-22-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 6
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
f1 (ppm)


SKX-6-22-1.3.ser
SKX-6-22-1
HSQCGP CDCl3 E:\\ xiaoguozhi 6
f2 (ppm)
f1 (ppm)
OBz
BzO
BzO
TrocHN
O
BzO
OTBDPS
O
N3
O
NHCbz
CO2Bn
23

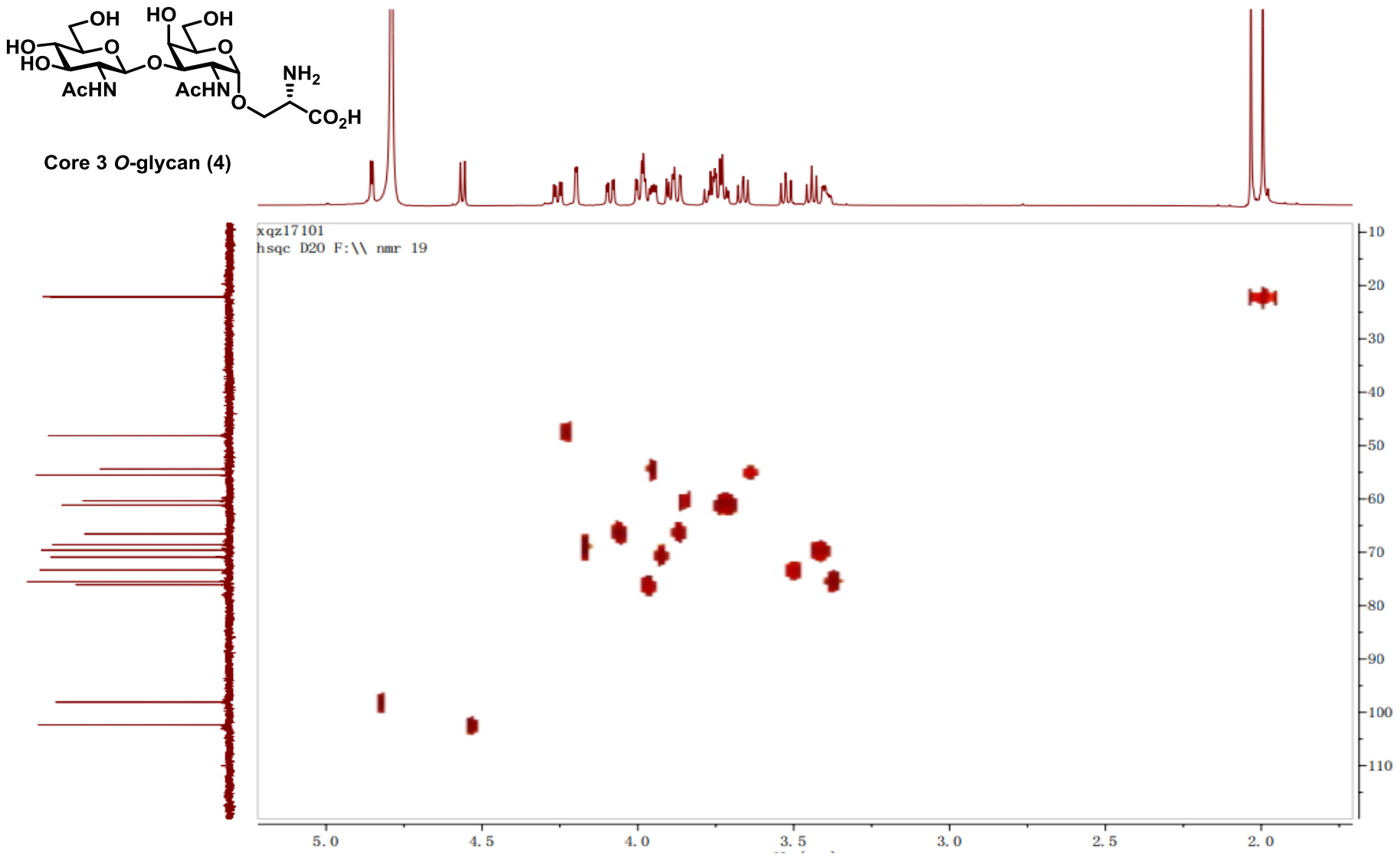

xqz17101
h D20 F:\\ nmr 19
Core 3 O-glycan (4)

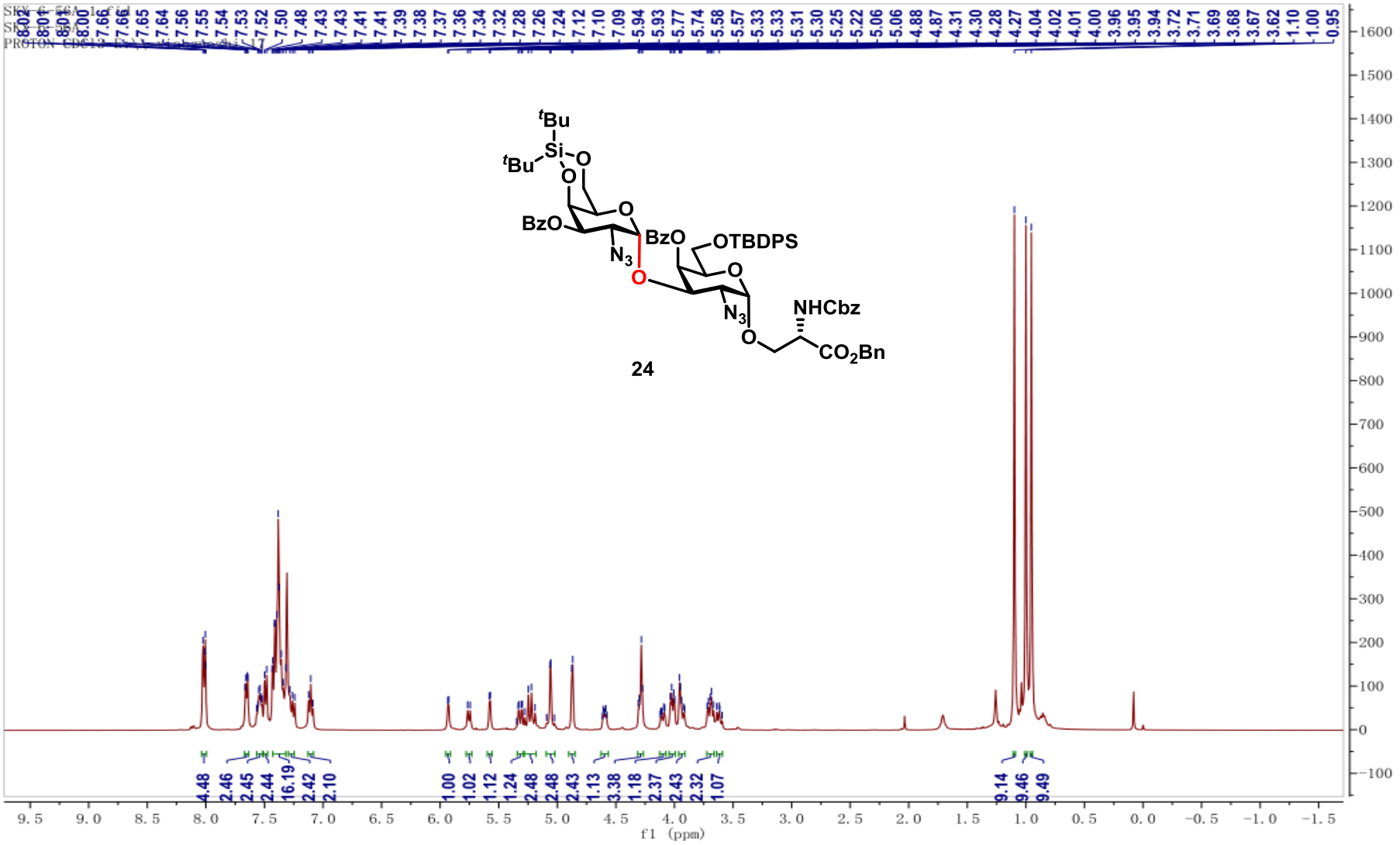


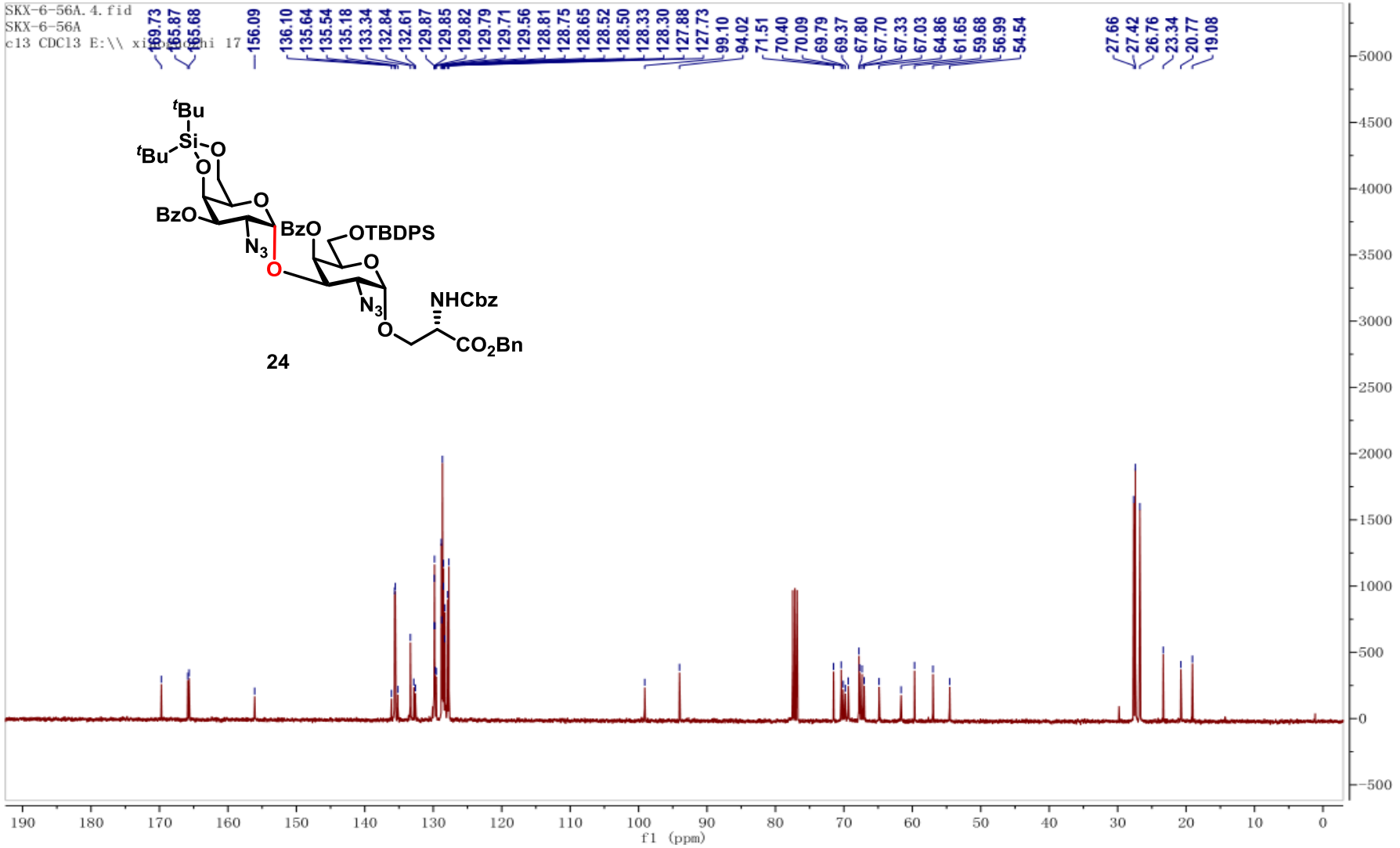
Core 3 *O*-glycan (4)

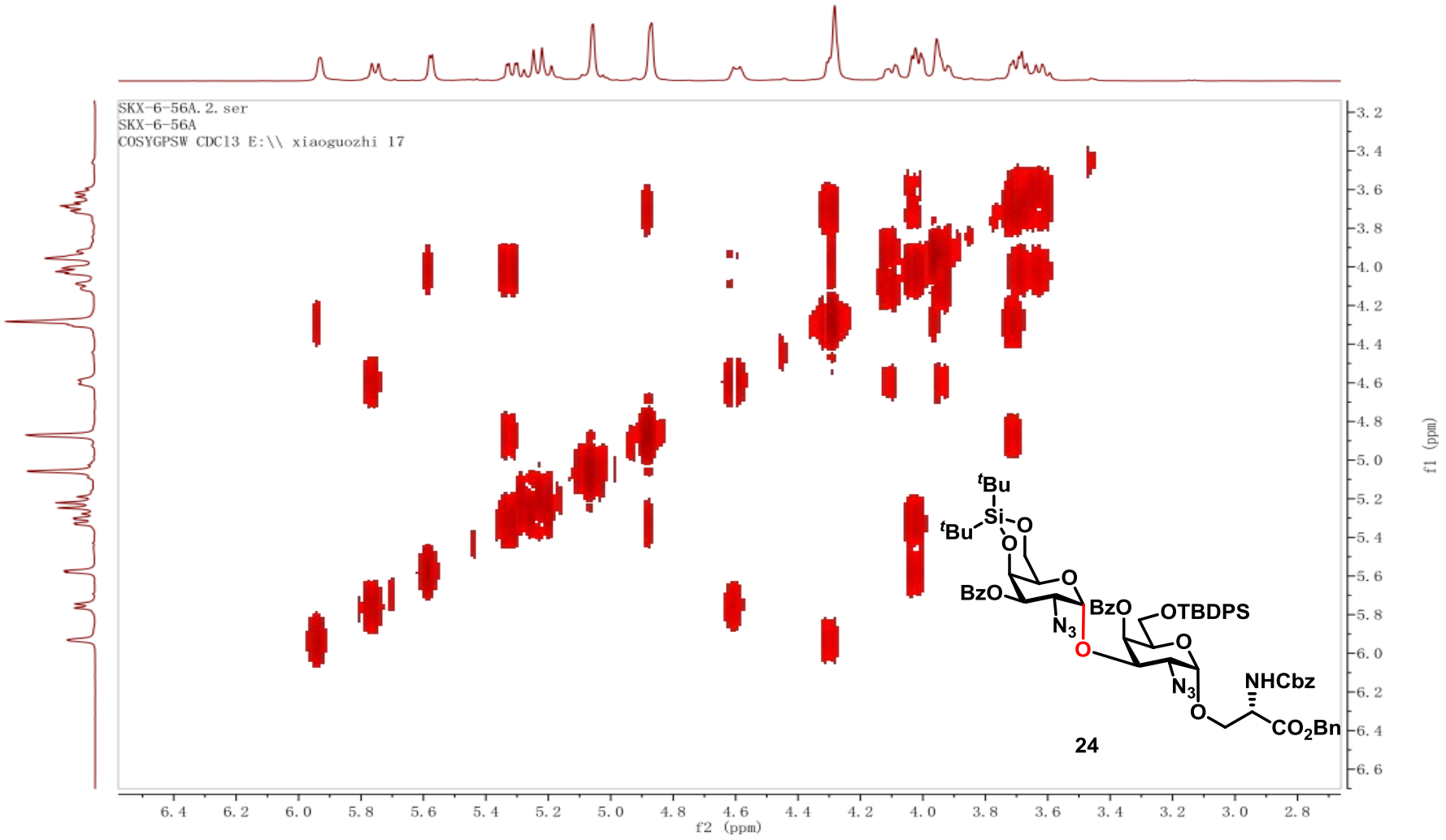


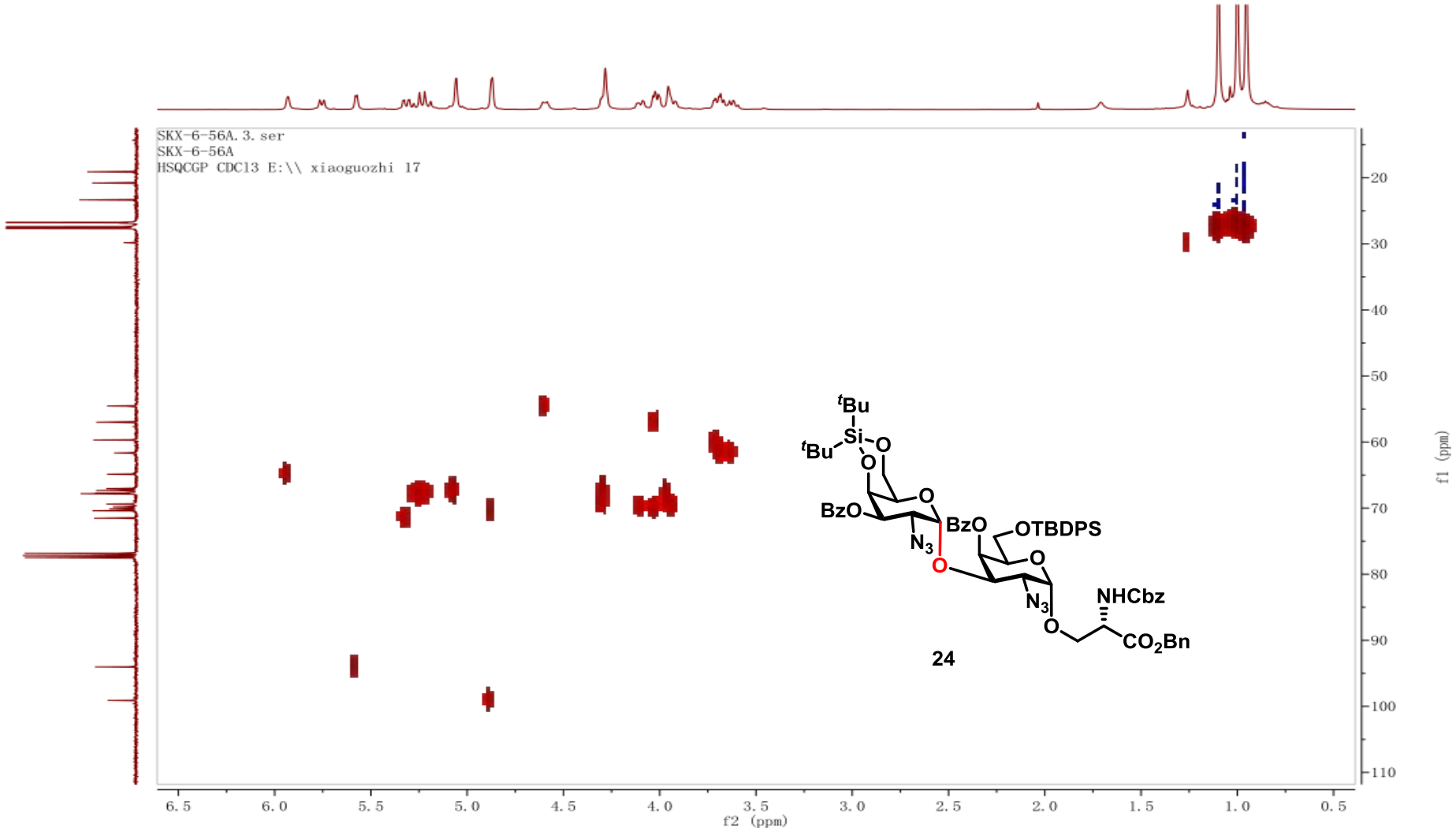
Core 3 *O*-glycan (4)

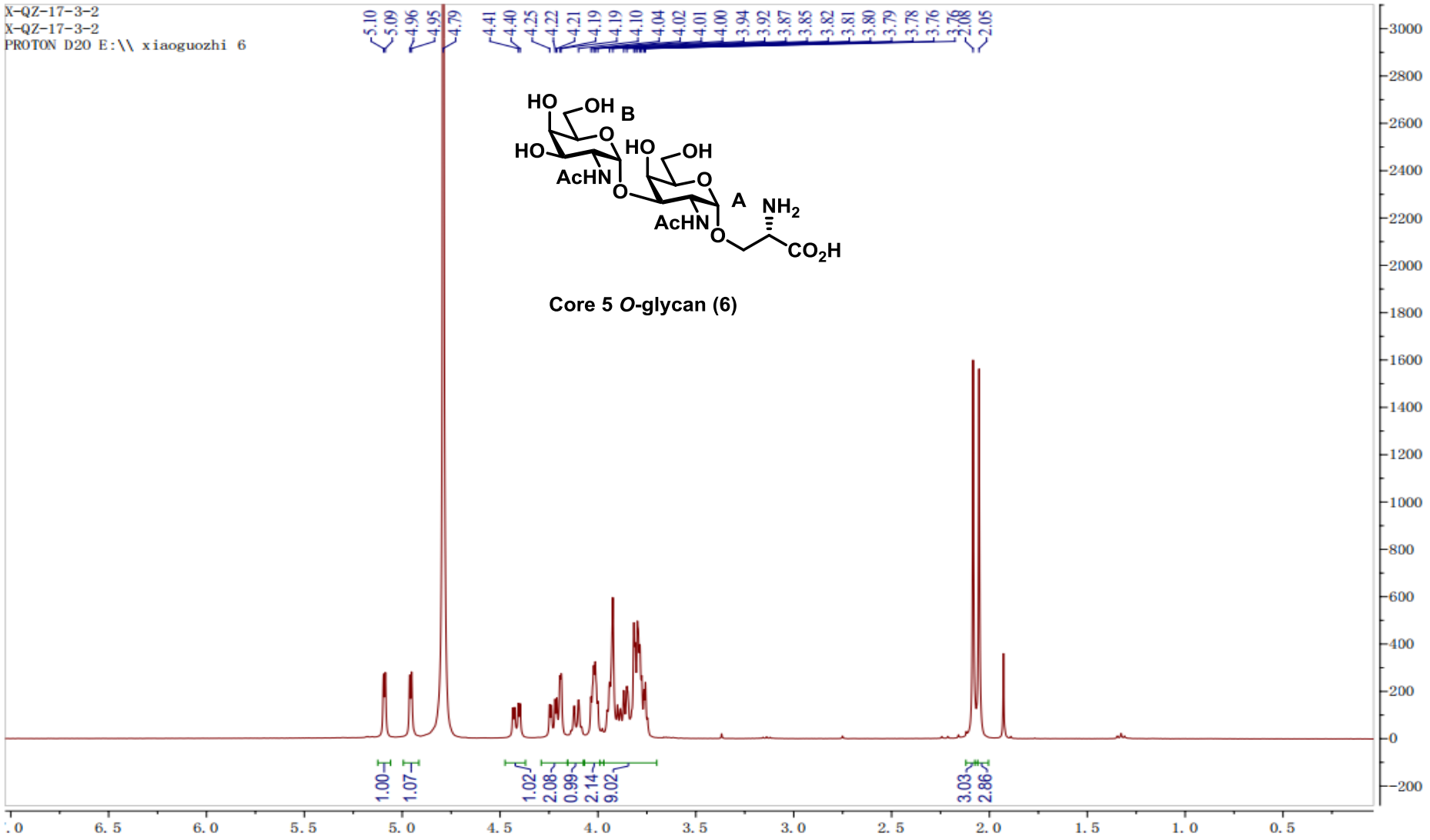

OH
HO
OH
HO
O
O
HO
HO
O
AcHN
AcHN
O
NH2
CO2H
Core 3 O-glycan (4)
xqz17101
hsqc D20 F:\\ nmr 19
10
20
30
40
50
60
70
80
90
100
110
5.0
4.5
4.0
3.5
3.0
2.5
2.0

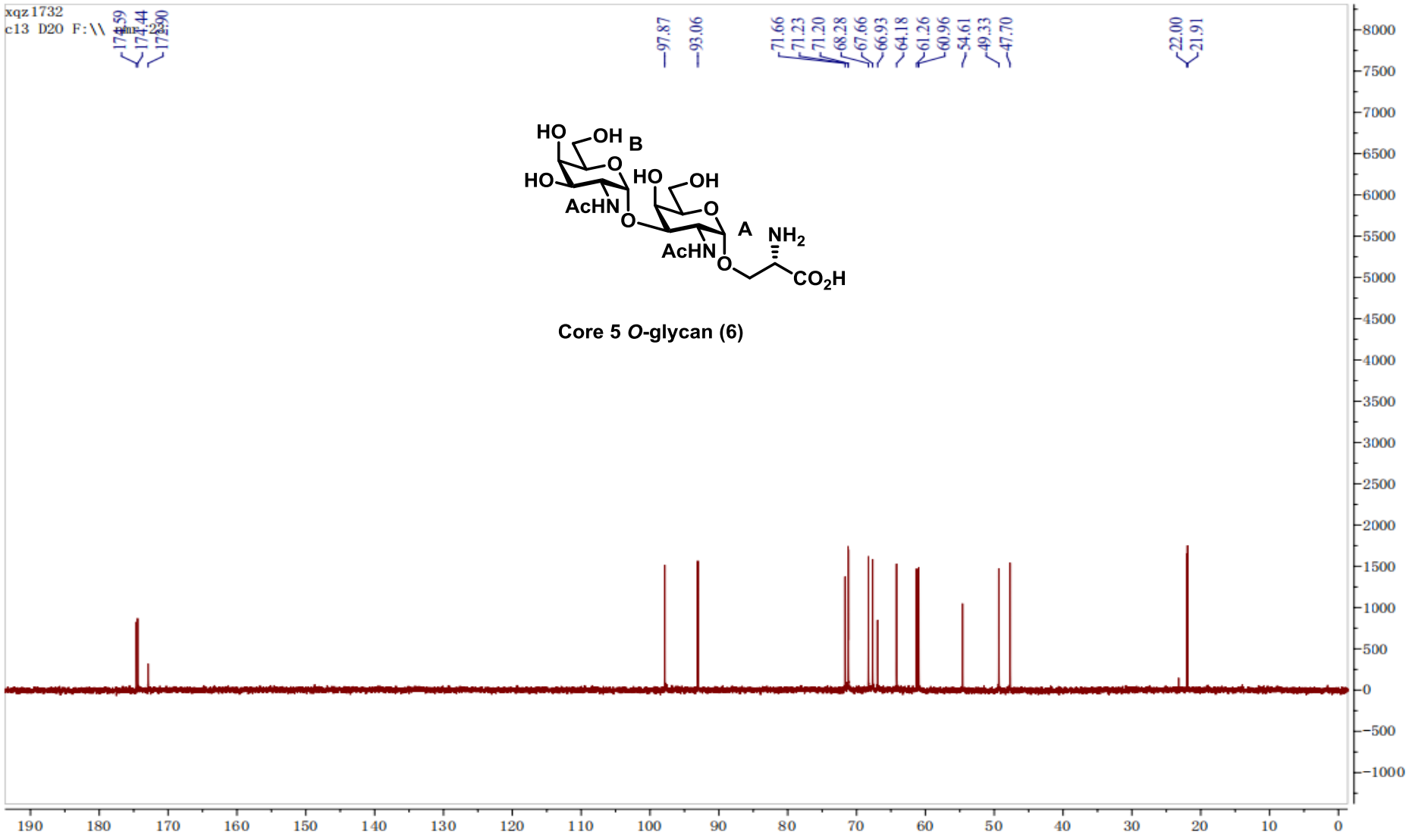

tBu
tBu
Si
O
O
O
BzO
BzO
OTBDPS
N3
O
O
N3
NHCbz
O
CO2Bn
24
f1 (ppm)


SKX-6-56A.4.fid
SKX-6-56A
c13 CDCl3 E:\\ xi
169.73
165.87
165.68
156.09
136.10
135.64
135.54
135.18
133.34
132.84
132.61
129.87
129.85
129.82
129.79
129.71
129.56
128.81
128.75
128.65
128.52
128.50
128.33
128.30
127.88
127.73
99.10
94.02
71.51
70.40
70.09
69.79
69.37
67.80
67.70
67.33
67.03
64.86
61.65
59.68
56.99
54.54
27.66
27.42
26.76
23.34
20.77
19.08
tBu
Si
tBu
O
O
BzO
O
N3
BzO
OTBDPS
O
O
N3
NHCbz
O
CO2Bn
24
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

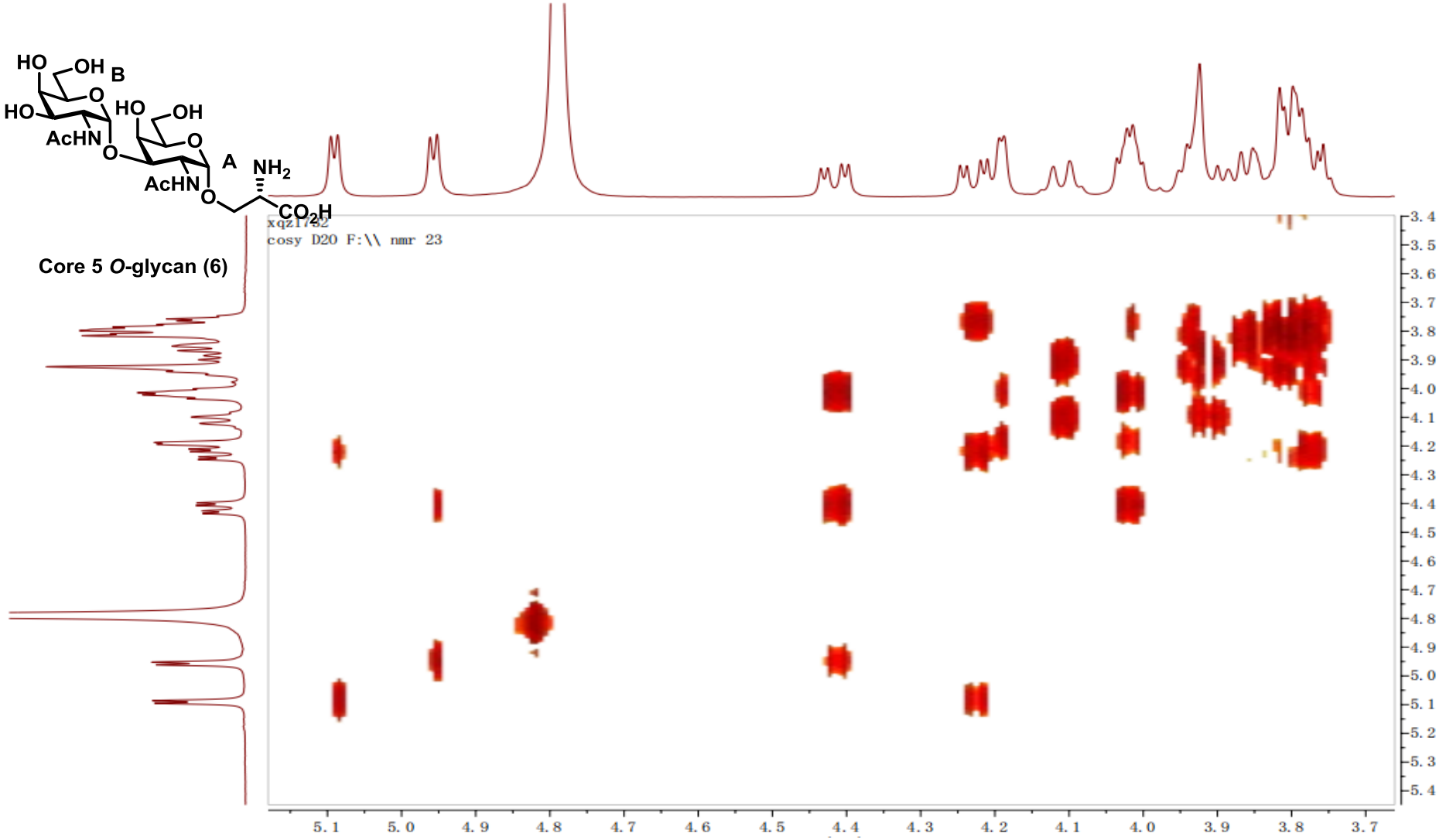

SKX-6-56A.2.ser
SKX-6-56A
COSYGPSW CDCl3 E:\\ xiaoguozhi 17
f2 (ppm)
f1 (ppm)
24

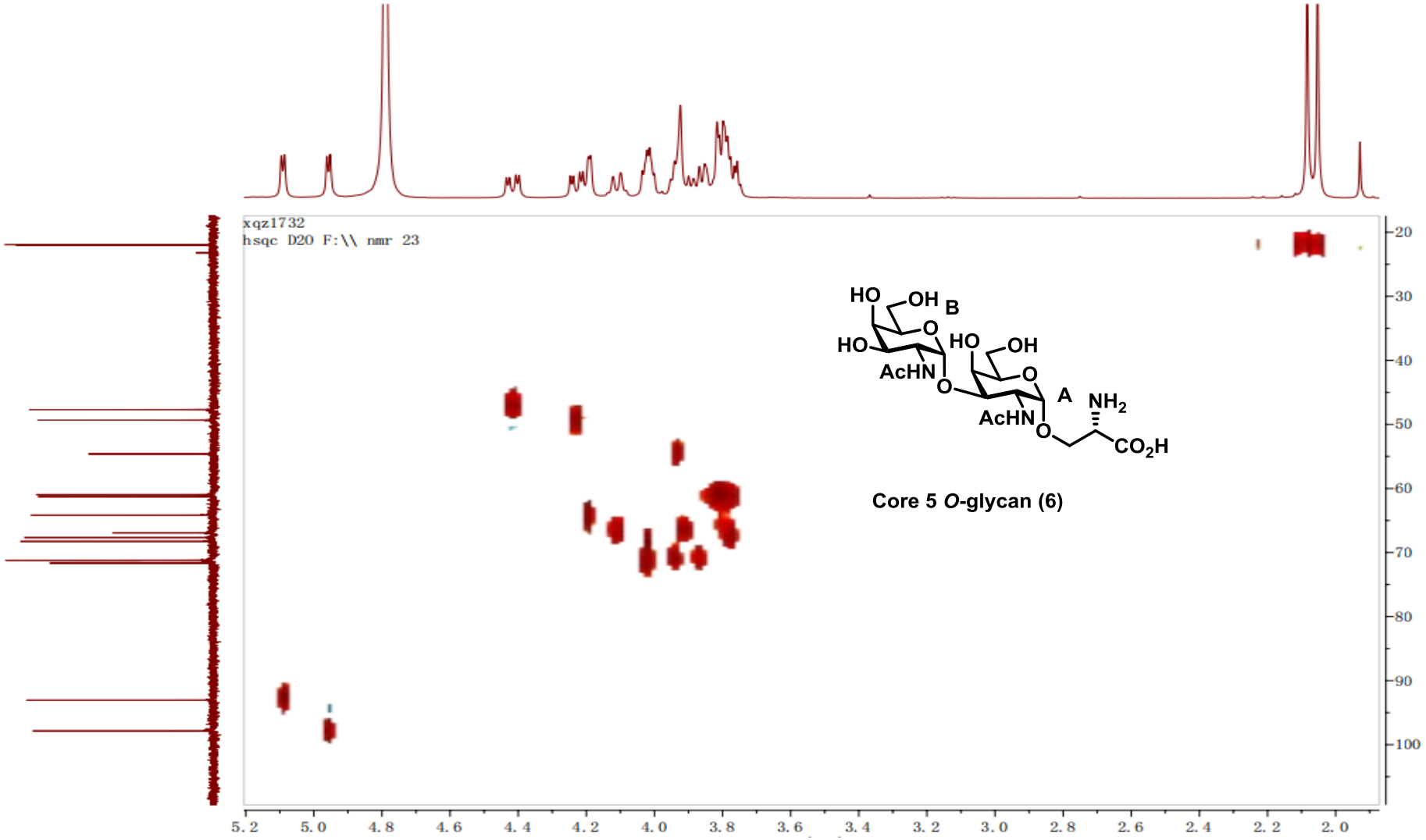

SKX-6-56A.3.ser
SKX-6-56A
HSQCGP CDC13 E:\\ xiaoguozhi 17
f2 (ppm)
f1 (ppm)
24

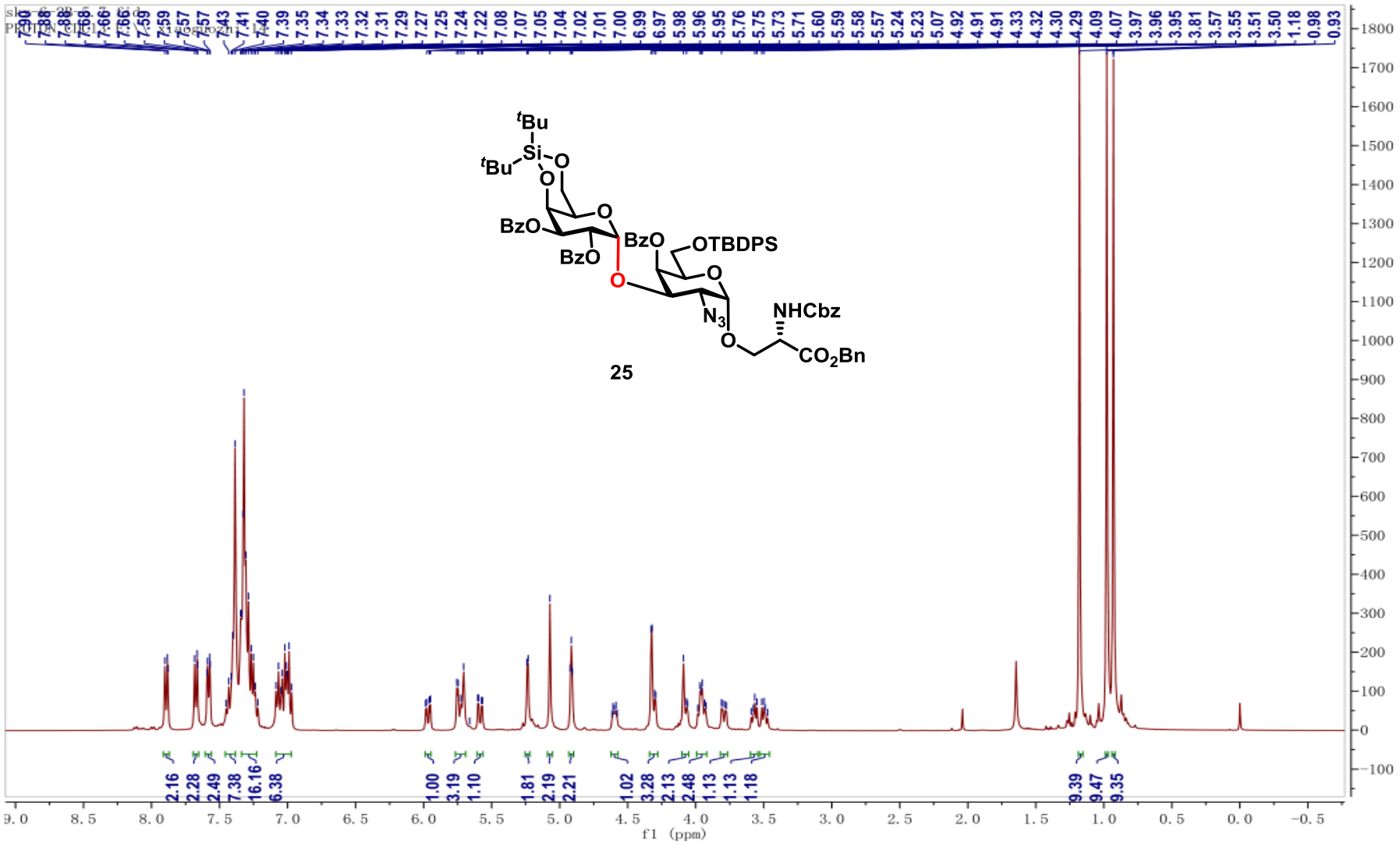

X-QZ-17-3-2
X-QZ-17-3-2
PROTON D20 E:\\ xiaoguozhi 6
5.10
5.09
4.96
4.95
4.79
4.41
4.40
4.25
4.22
4.21
4.19
4.19
4.10
4.04
4.02
4.01
4.00
3.94
3.92
3.87
3.85
3.82
3.81
3.80
3.79
3.78
3.76
3.76
2.08
2.05
HO
OH
B
O
HO
HO
OH
AcHN
O
O
A
NH2
AcHN
O
CO2H
Core 5 O-glycan (6)
1.00
1.07
1.02
2.08
0.99
2.14
9.02
3.03
2.86
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
.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

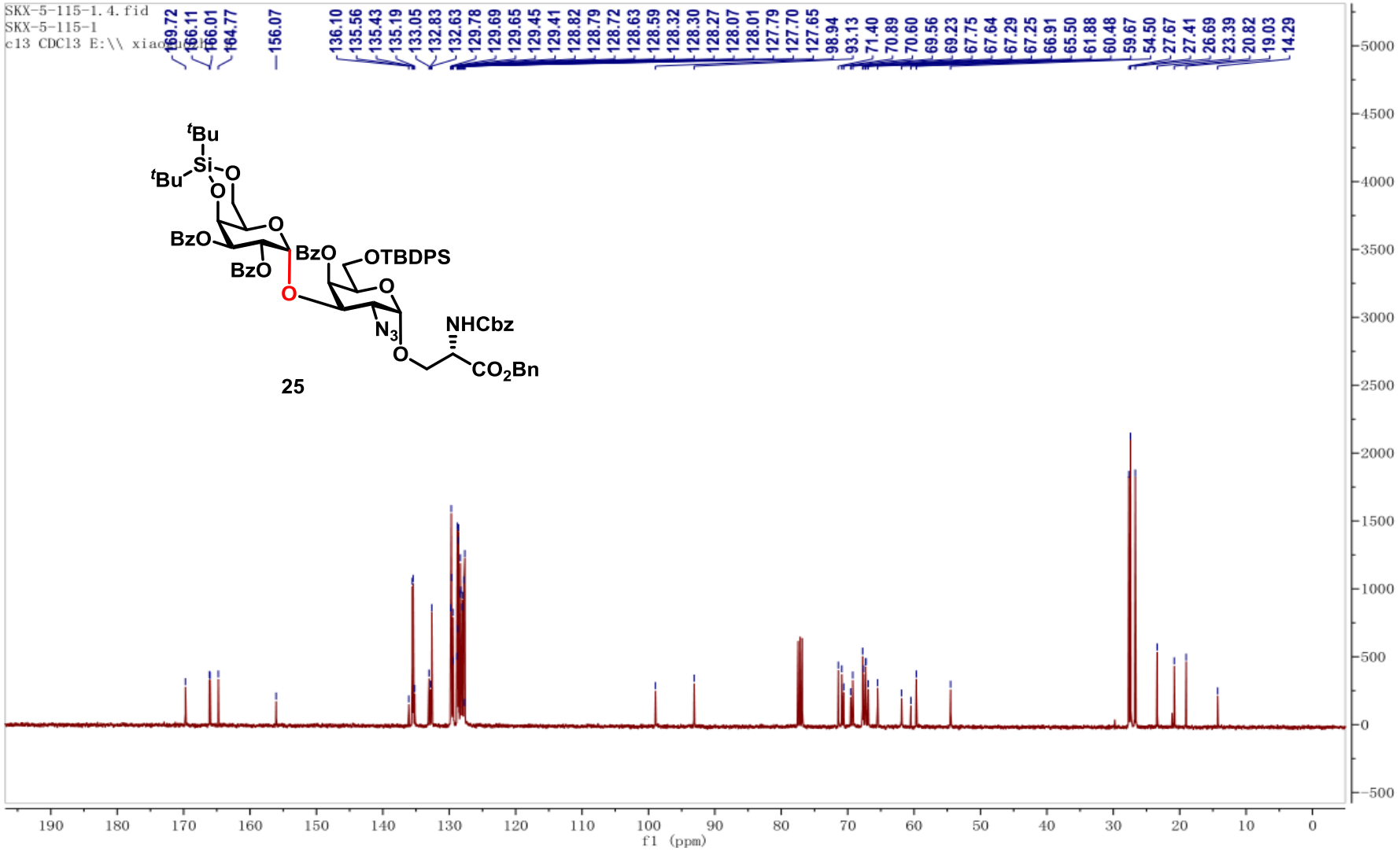


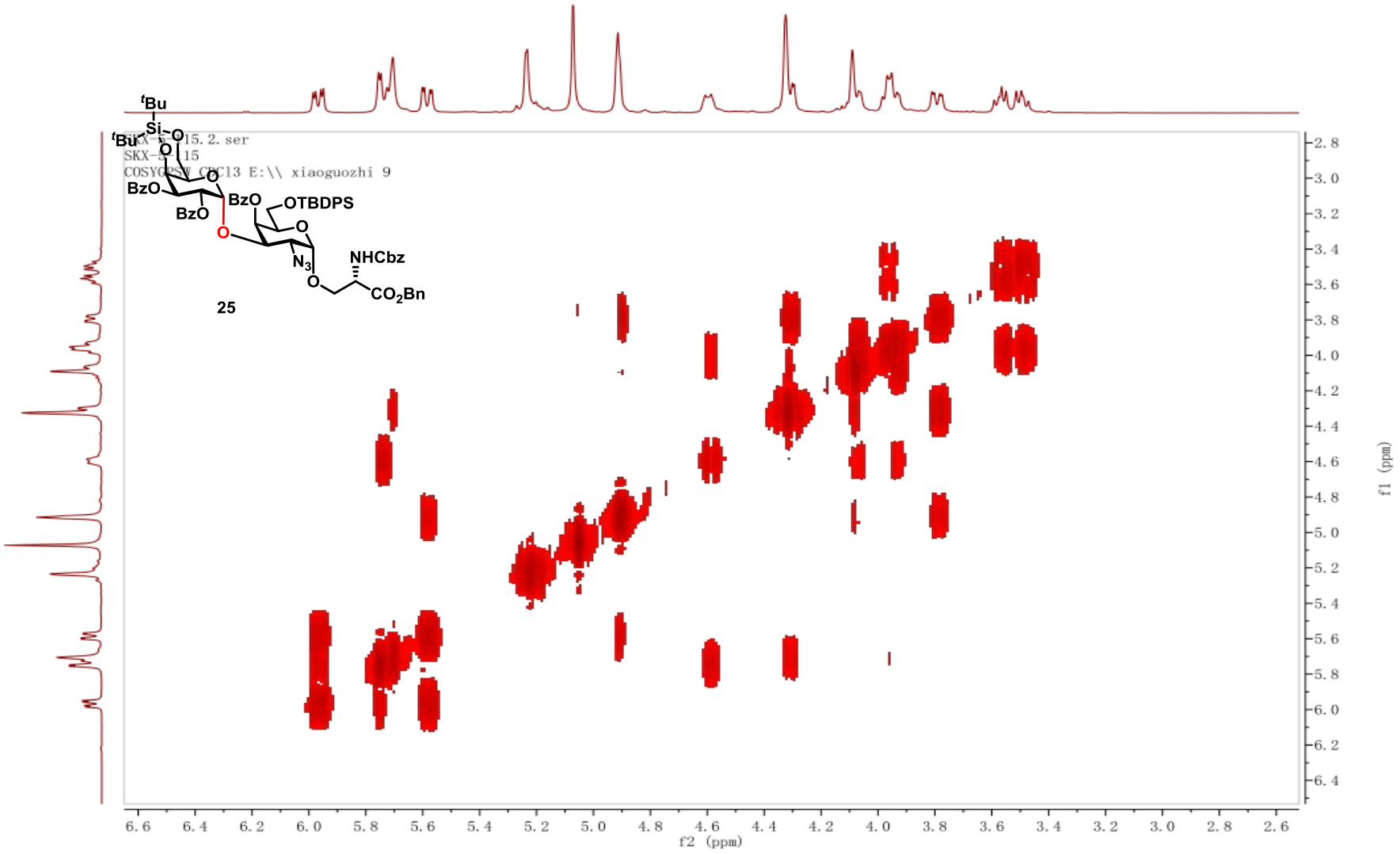
Core 5 *O*-glycan (6)

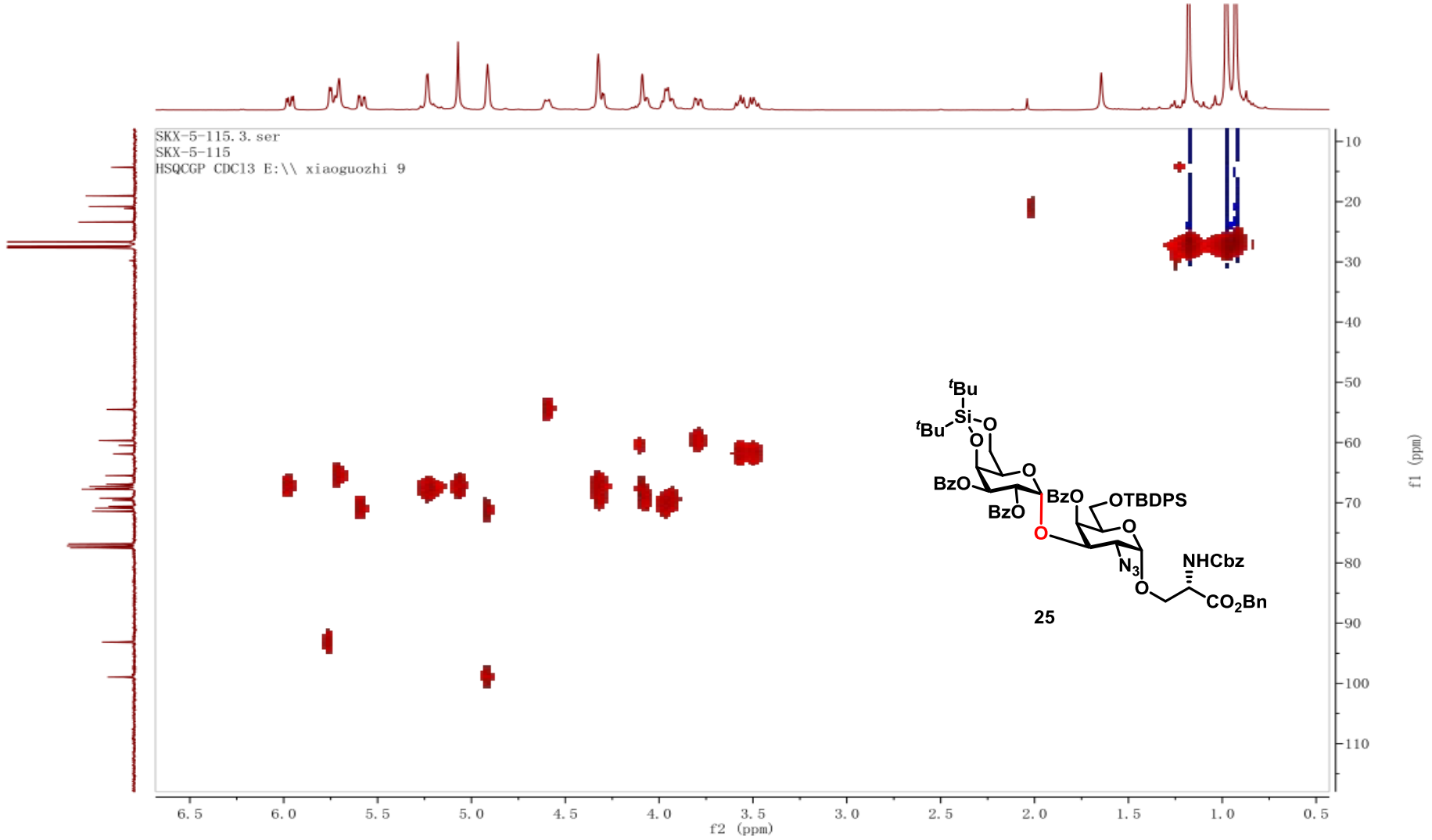

HO
OH
B
O
HO
HO
OH
AcHN
O
O
A
NH2
AcHN
O
CO2H
Core 5 O-glycan (6)
xqz1742
cosy D20 F:\\ nmr 23
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
4.8
4.9
5.0
5.1
5.2
5.3
5.4

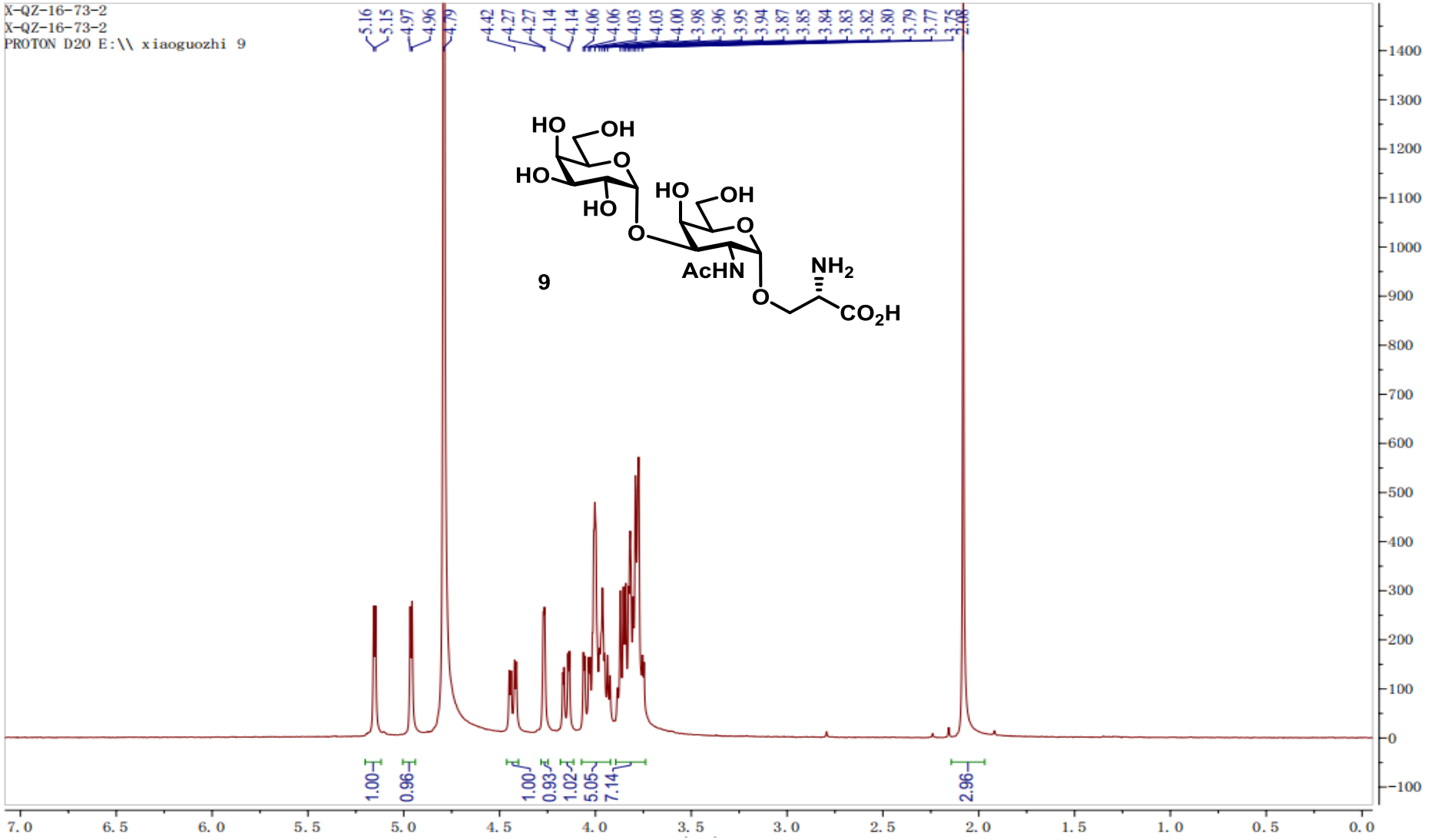

xqz1732
hsqc D20 F:\\ nmr 23
HO
OH
B
O
HO
HO
OH
AcHN
O
O
A
NH2
AcHN
O
CO2H
Core 5 O-glycan (6)
20
30
40
50
60
70
80
90
100
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0

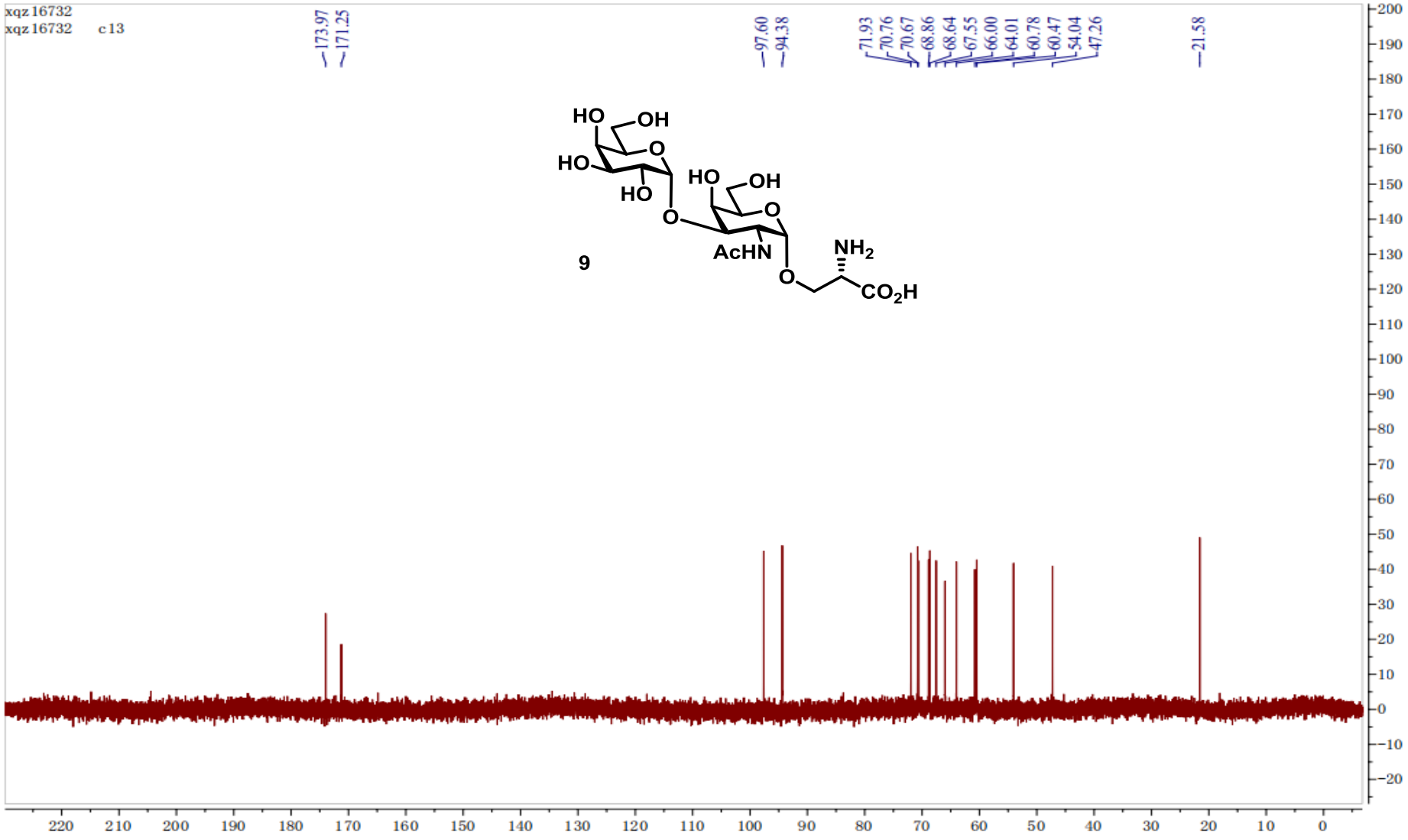

tBu
tBu
Si
O
O
O
BzO
BzO
BzO
OTBDPS
O
O
N3
NHCbz
O
CO2Bn
25
f1 (ppm)

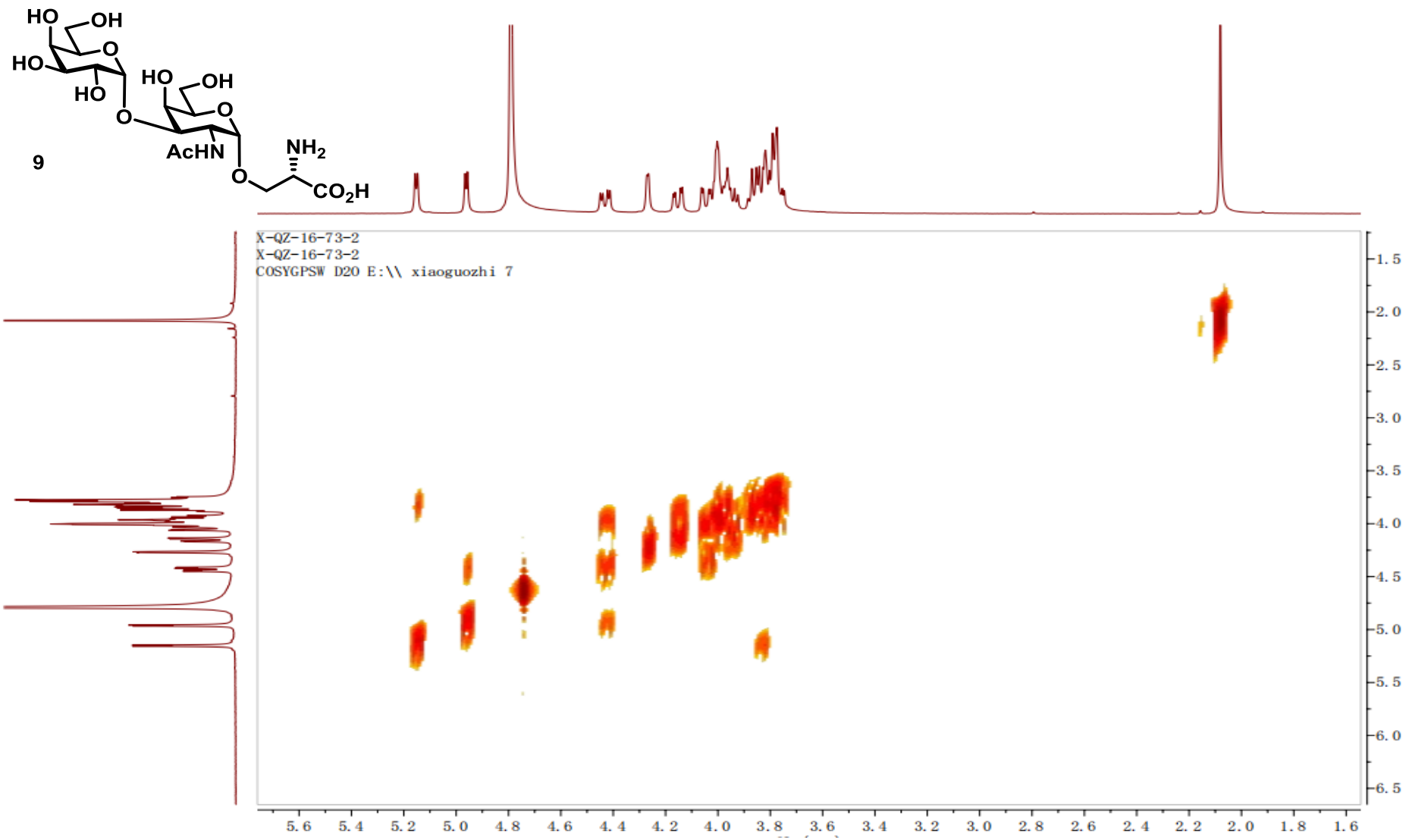

SKX-5-115-1.4.fid
SKX-5-115-1
c13 CDCl3 E:\\ xiaoxu\data
169.72
166.11
166.01
164.77
156.07
136.10
135.56
135.43
135.19
133.05
132.83
132.63
129.78
129.69
129.65
129.45
129.41
128.82
128.79
128.72
128.63
128.59
128.32
128.30
128.27
128.07
128.01
127.79
127.70
127.65
98.94
93.13
71.40
70.89
70.60
69.56
69.23
67.75
67.64
67.29
67.25
66.91
65.50
61.88
60.48
59.67
54.50
27.67
27.41
26.69
23.39
20.82
19.03
14.29
tBu
tBu
Si
O
O
O
BzO
BzO
BzO
OTBDPS
O
O
N3
NHCbz
O
CO2Bn
25
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

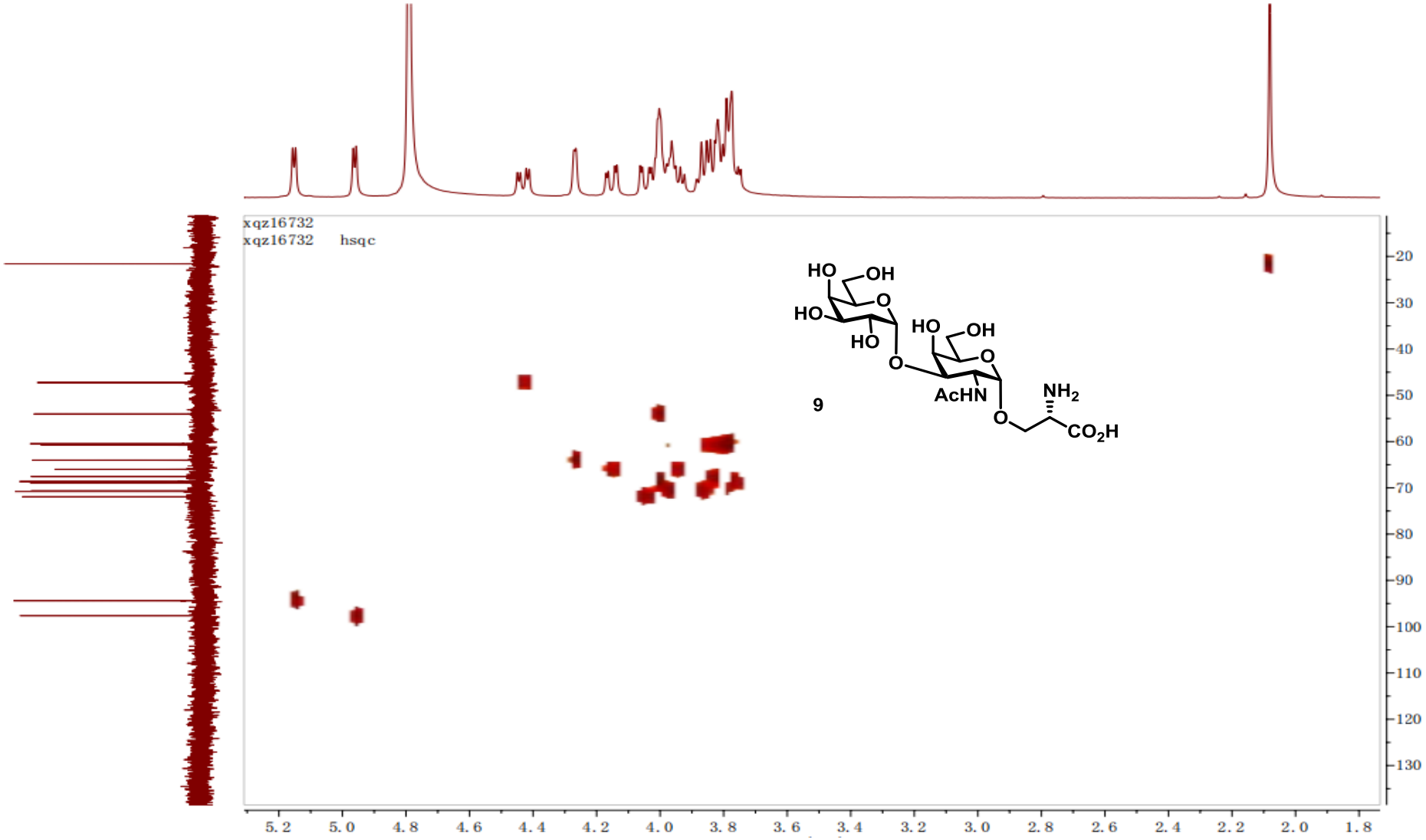

SKX-S-15.2.ser
SKX-S-15
COSYQFSW CDCl3 E:\\ xiaoguozhi 9
25
f2 (ppm)
f1 (ppm)

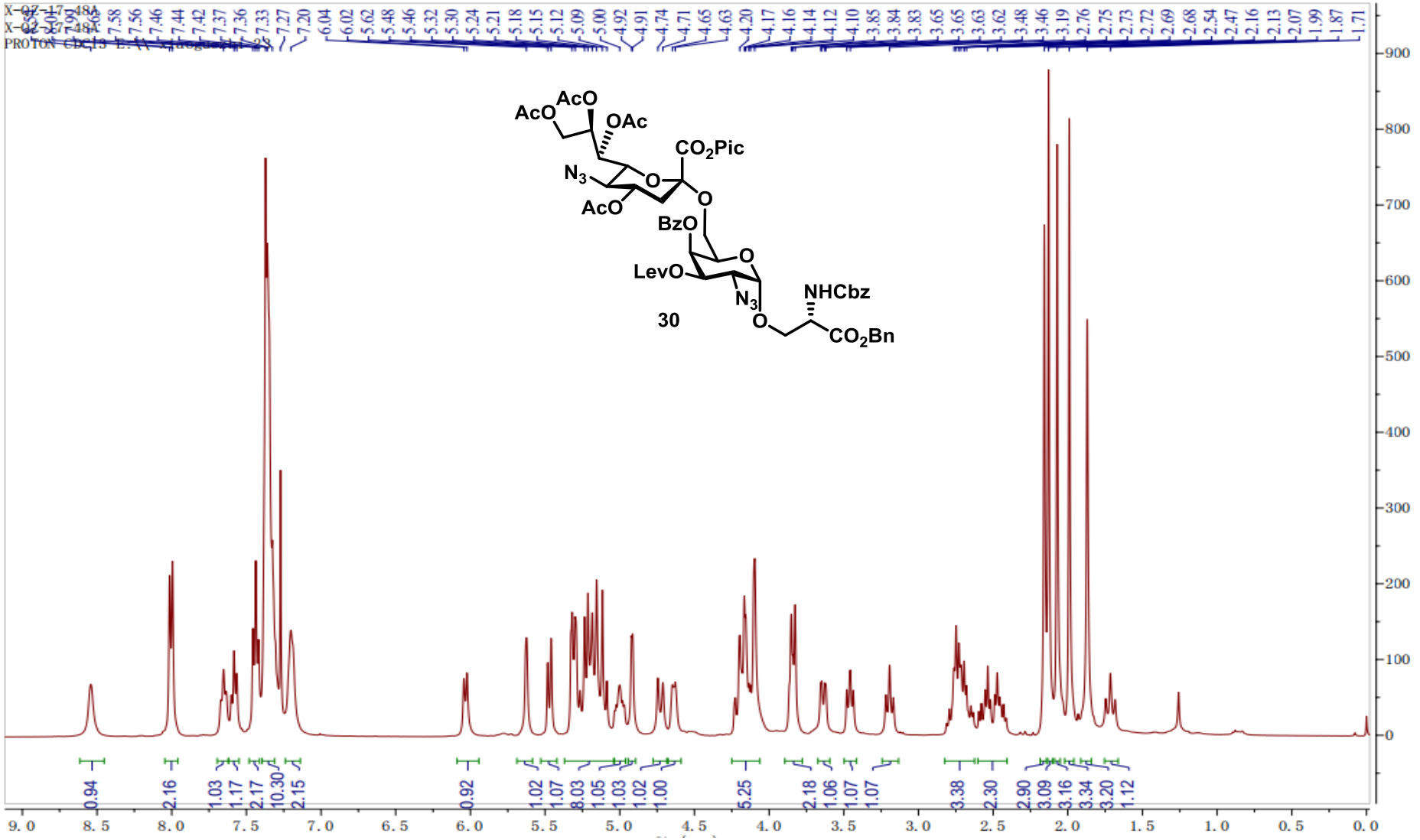

SKX-5-115.3.ser
SKX-5-115
HSQCGP CDCl3 E:\\ xiaoguozhi 9
f2 (ppm)
f1 (ppm)
25

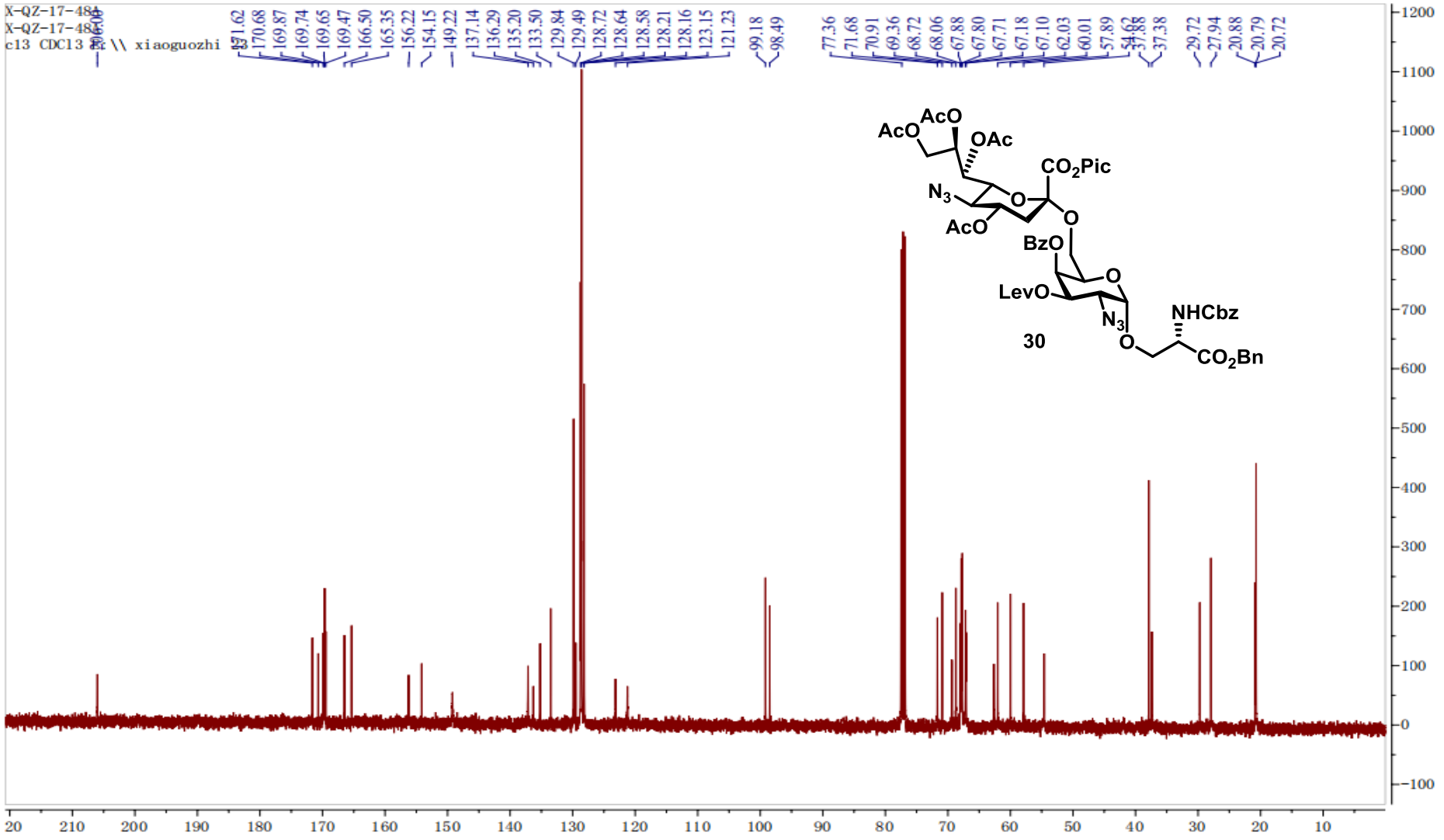

X-QZ-16-73-2
X-QZ-16-73-2
PROTON D20 E:\\ xiaoguozhi 9
5.16
5.15
4.97
4.96
4.79
4.42
4.27
4.27
4.14
4.14
4.06
4.06
4.03
4.03
4.00
3.98
3.96
3.95
3.94
3.87
3.85
3.84
3.83
3.82
3.80
3.79
3.77
3.75
2.08
HO
OH
HO
O
HO
HO
O
HO
OH
O
AcHN
NH2
O
CO2H
9
1.00
0.96
1.00
0.93
1.02
5.05
7.14
2.96
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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

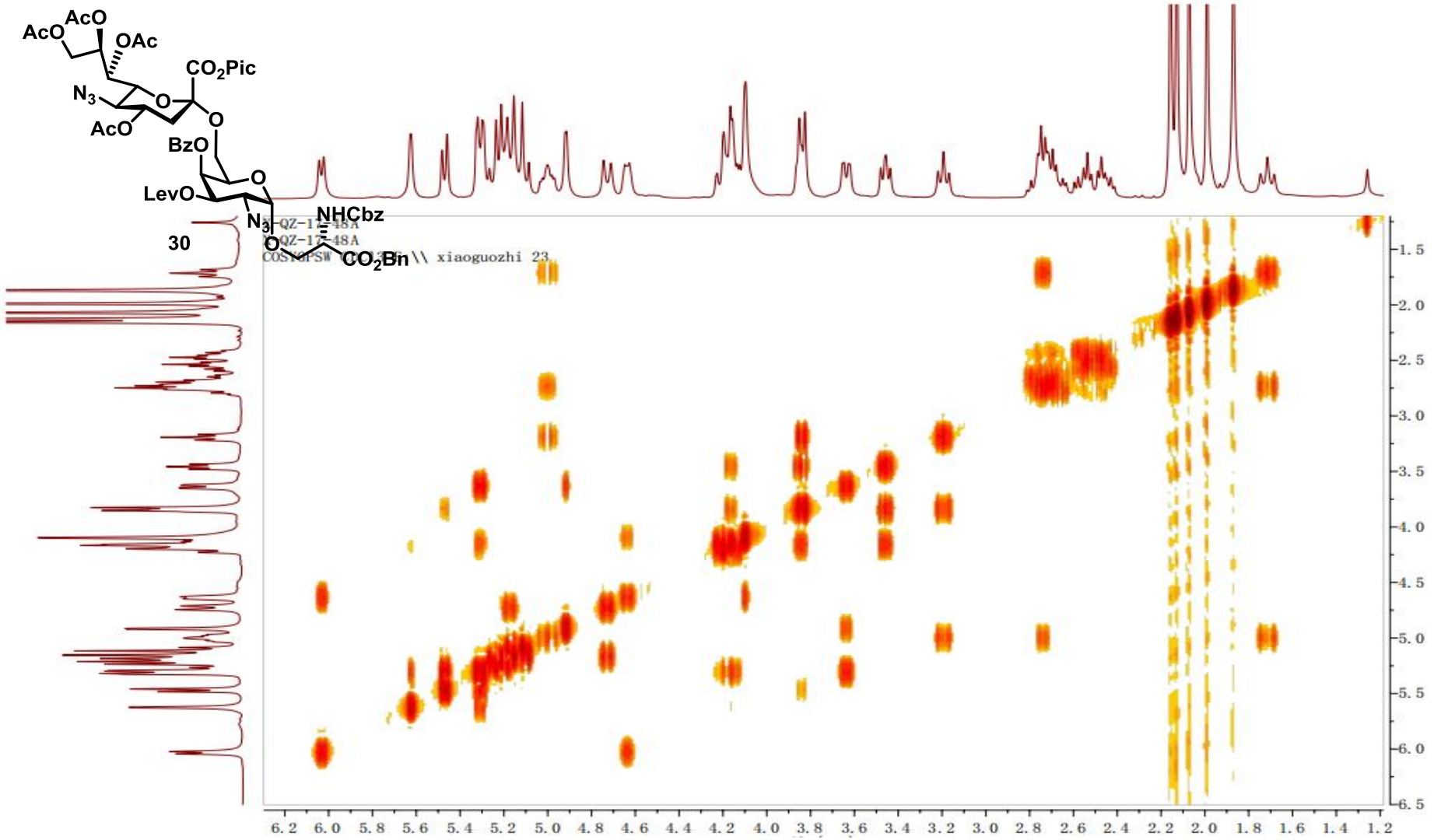

xqz 16732
xqz 16732 c13
173.97
171.25
97.60
94.38
71.93
70.76
70.67
68.86
68.64
67.55
66.00
64.01
60.78
60.47
54.04
47.26
21.58
HO
OH
O
HO
HO
HO
OH
O
O
AcHN
NH2
O
CO2H
9

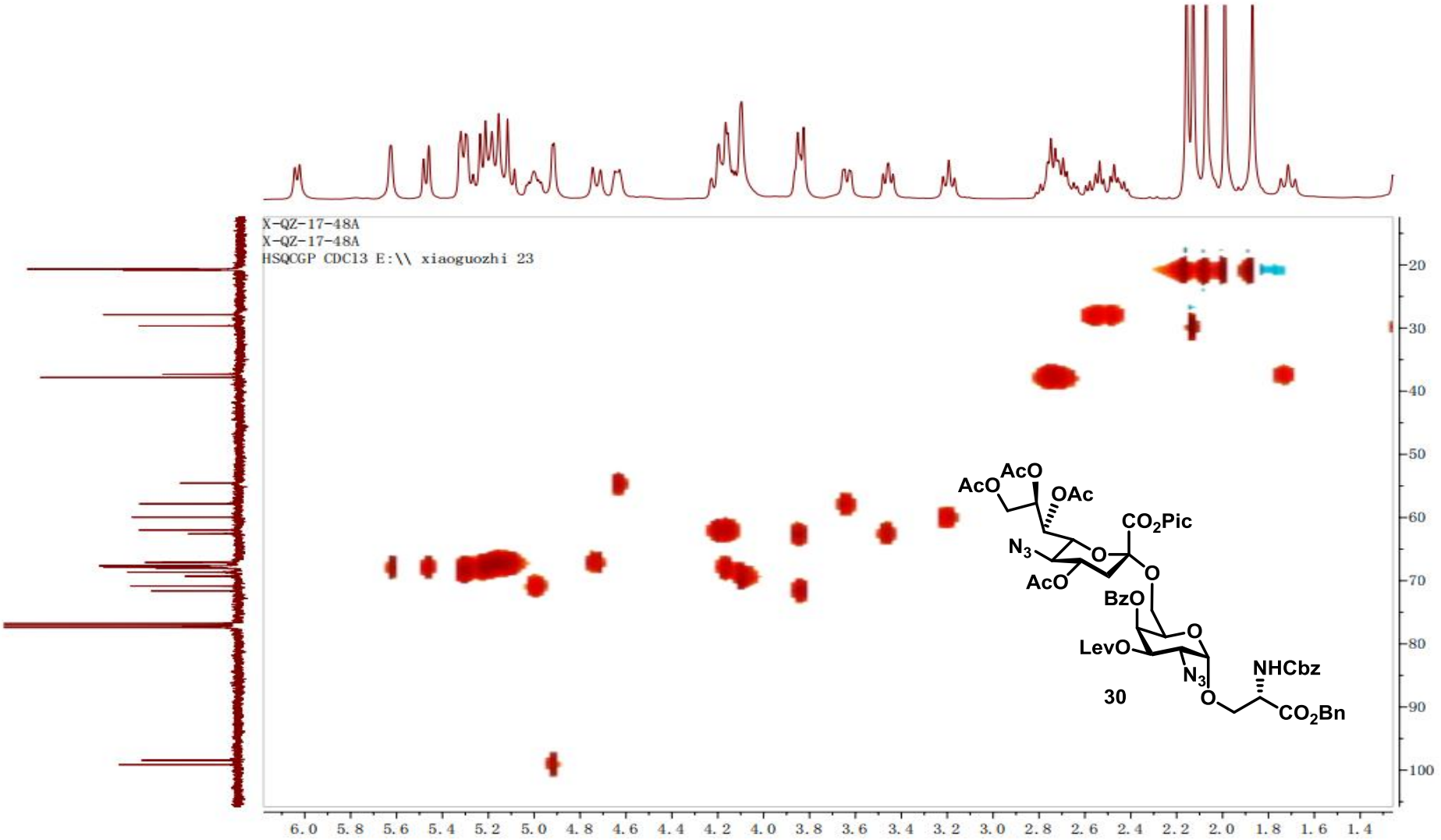

HO
OH
O
HO
HO
HO
OH
O
O
AcHN
NH2
O
CO2H
9
X-QZ-16-73-2
X-QZ-16-73-2
COSYGPSW D2O E:\\ xiaoguozhi 7
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

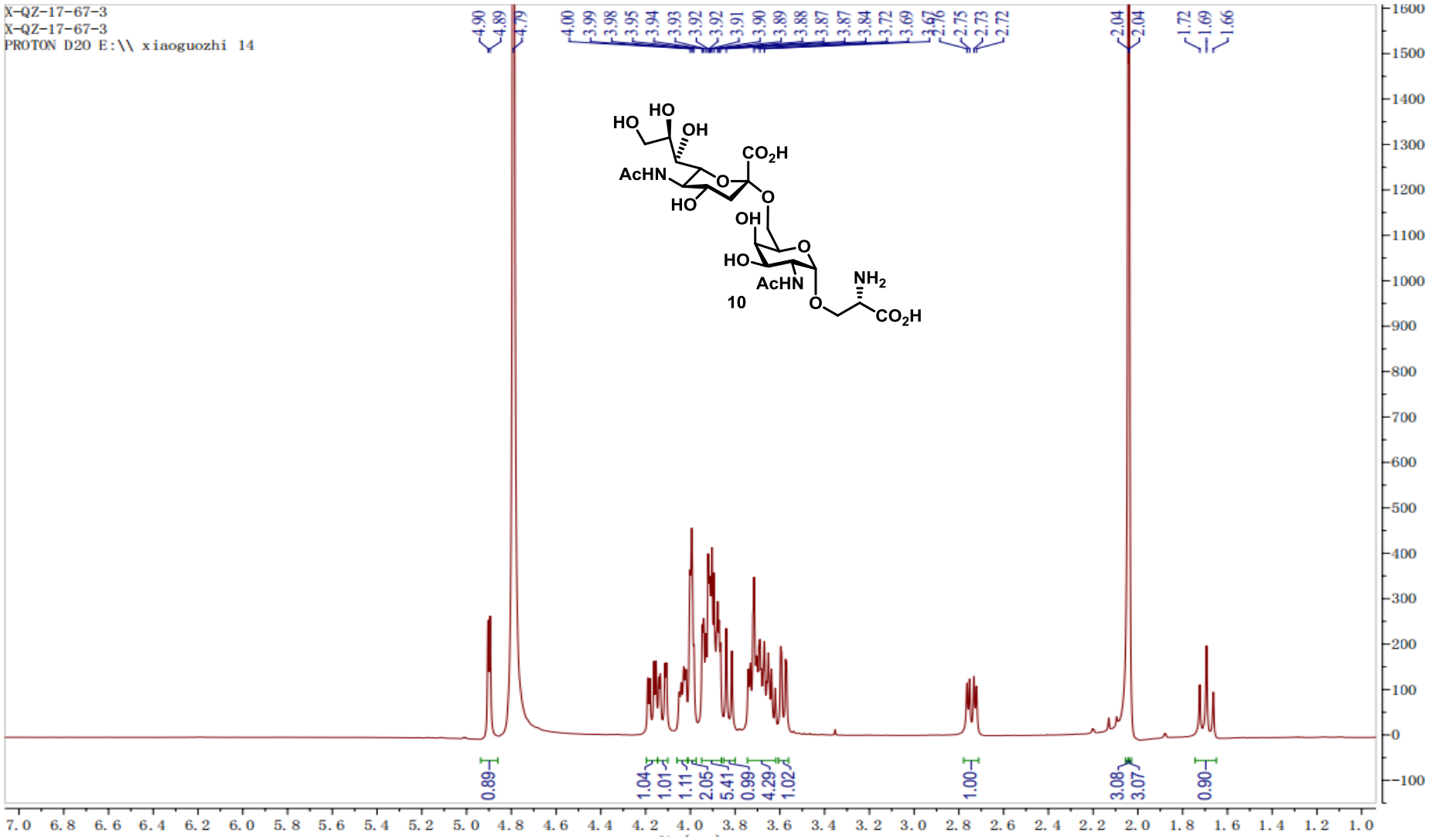

xqz16732
xqz16732 hsqc
HO
OH
O
HO
HO
HO
OH
O
O
AcHN
NH2
O
CO2H
9
20
30
40
50
60
70
80
90
100
110
120
130
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8

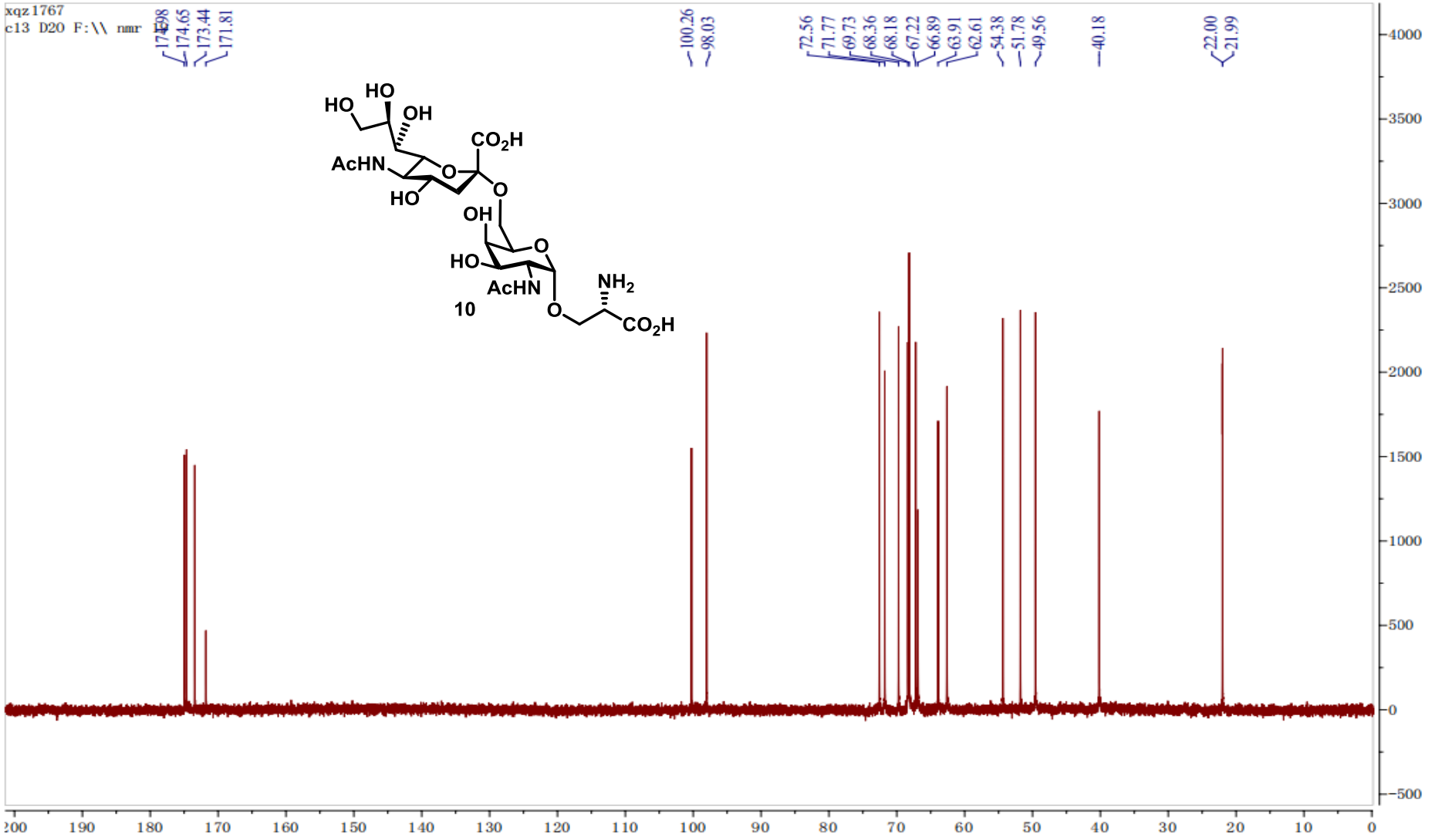

AcO
AcO
OAc
CO2Pic
N3
O
AcO
O
BzO
O
LevO
O
N3
NHCbz
O
CO2Bn
30

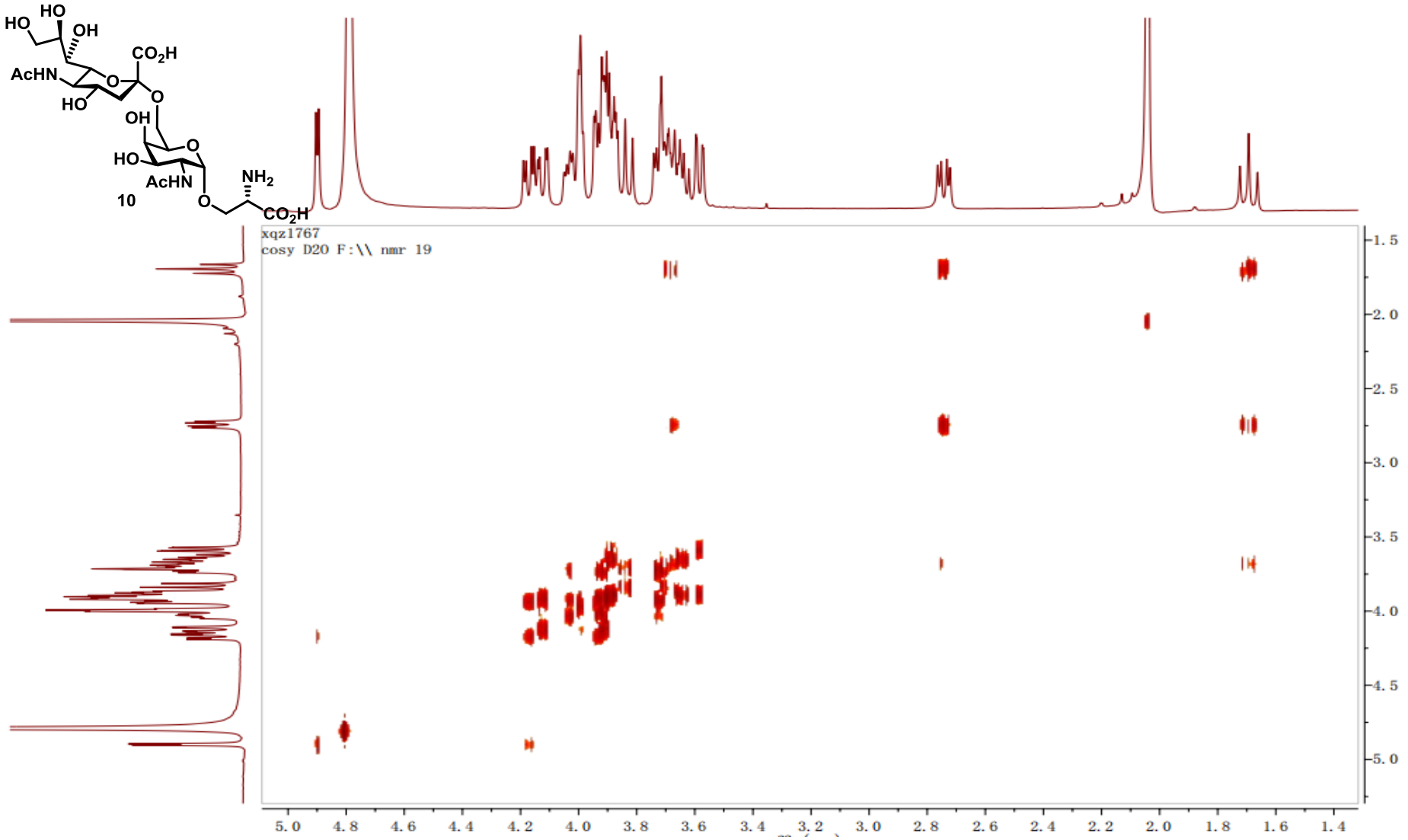

X-QZ-17-484
X-QZ-17-484
c13 CDCl3 zz \\ xiaoguozhi
171.62
170.68
169.87
169.74
169.65
169.47
166.50
165.35
156.22
154.15
149.22
137.14
136.29
135.20
133.50
129.84
129.49
128.72
128.64
128.58
128.21
128.16
123.15
121.23
99.18
98.49
77.36
71.68
70.91
69.36
68.72
68.06
67.88
67.80
67.71
67.18
67.10
62.03
60.01
57.89
37.38
29.72
27.94
20.88
20.79
20.72
AcO
AcO
OAc
CO2Pic
N3
O
O
AcO
BzO
O
LevO
N3
NHCbz
O
CO2Bn
30

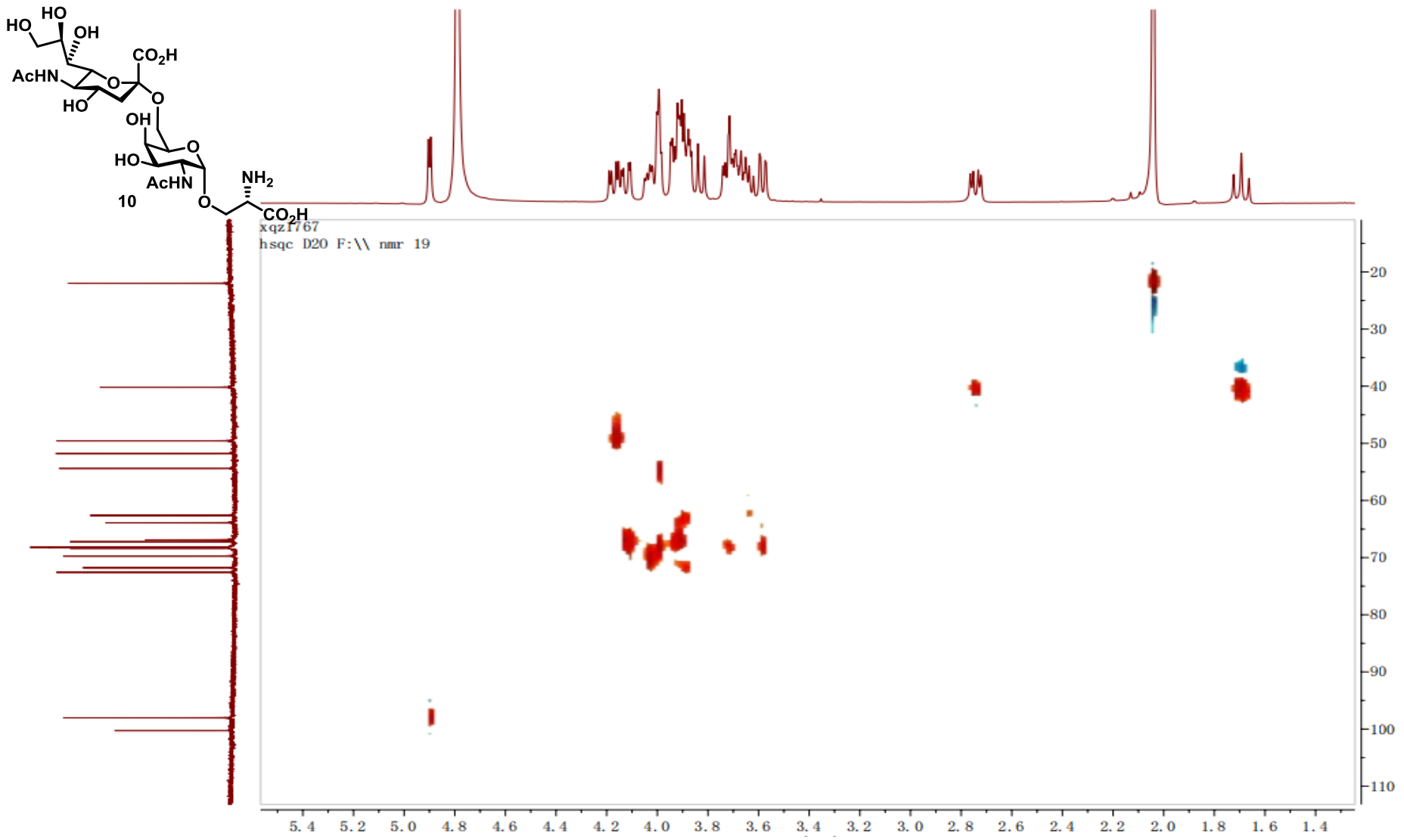

AcO
AcO
OAc
CO2Pic
N3
AcO
O
O
BzO
O
LevO
N3
NHCbz
O
CO2Bn
30
xiaoguozhi 23
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5

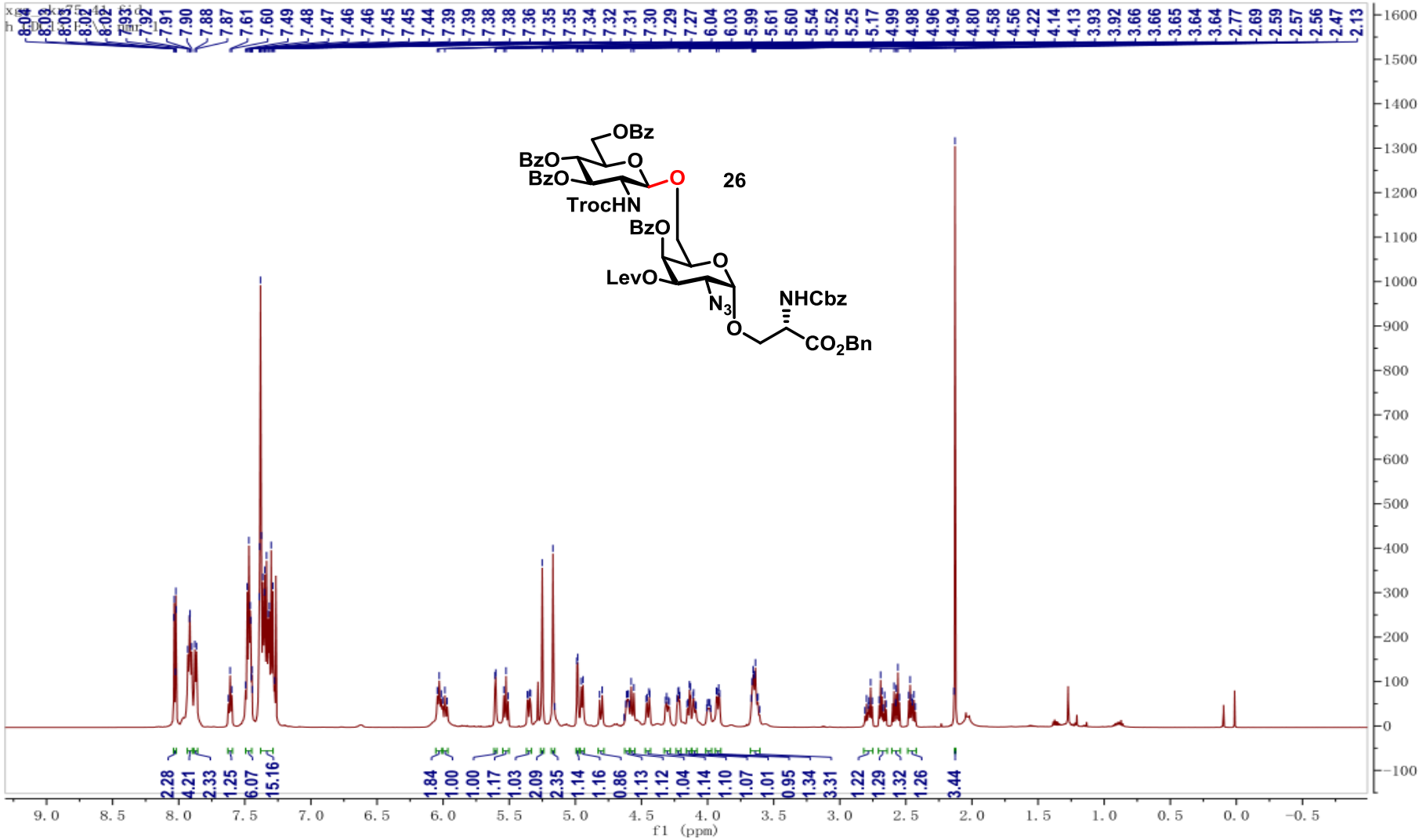

X-QZ-17-48A
X-QZ-17-48A
HSQCGP CDCl3 E:\\ xiaoguozhi 23
AcO
AcO
OAc
CO2Pic
N3
O
AcO
O
BzO
O
LevO
N3
NHCbz
O
CO2Bn
30
20
30
40
50
60
70
80
90
100
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4

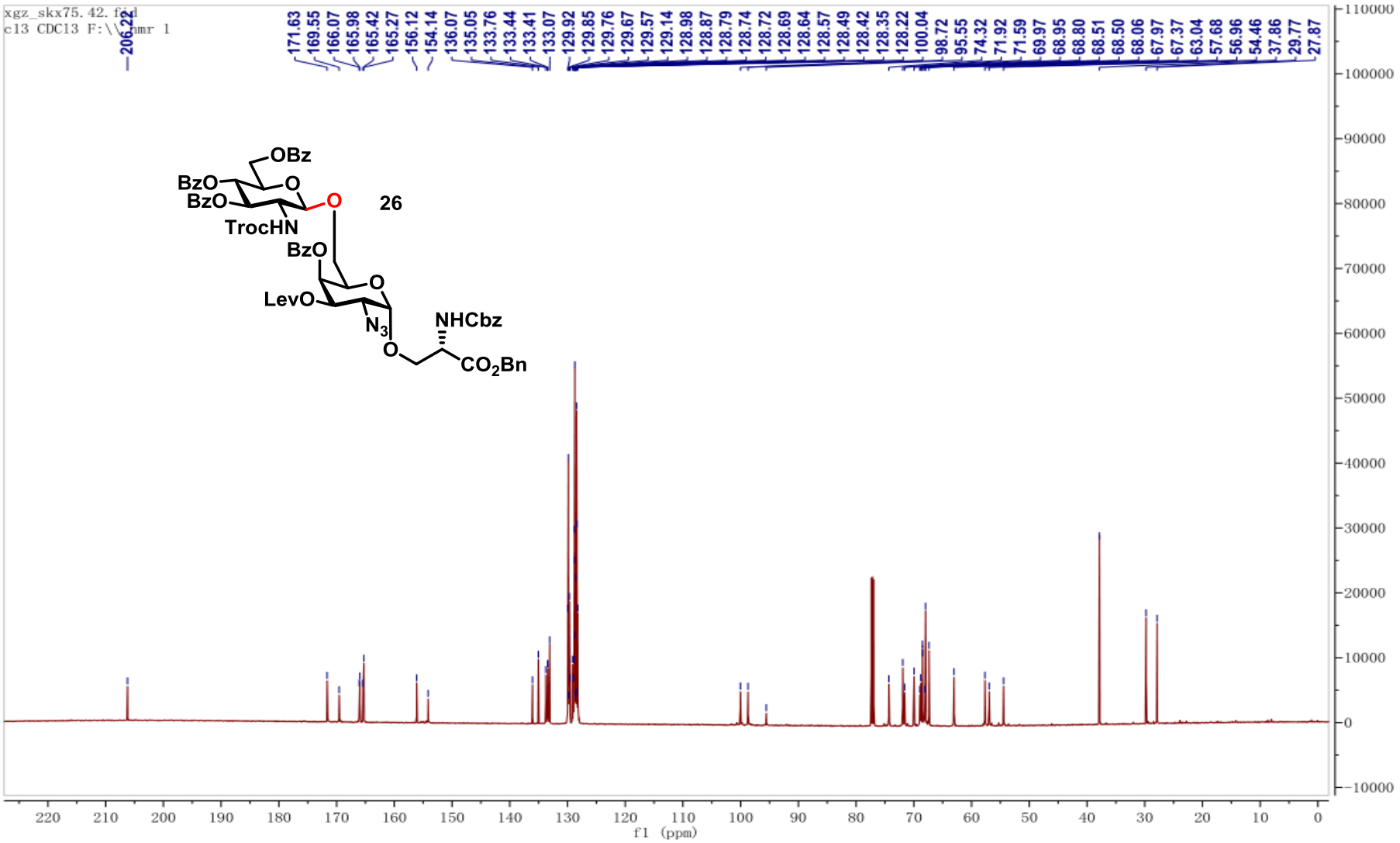

X-QZ-17-67-3
X-QZ-17-67-3
PROTON D20 E:\\ xiaoguozhi 14
10

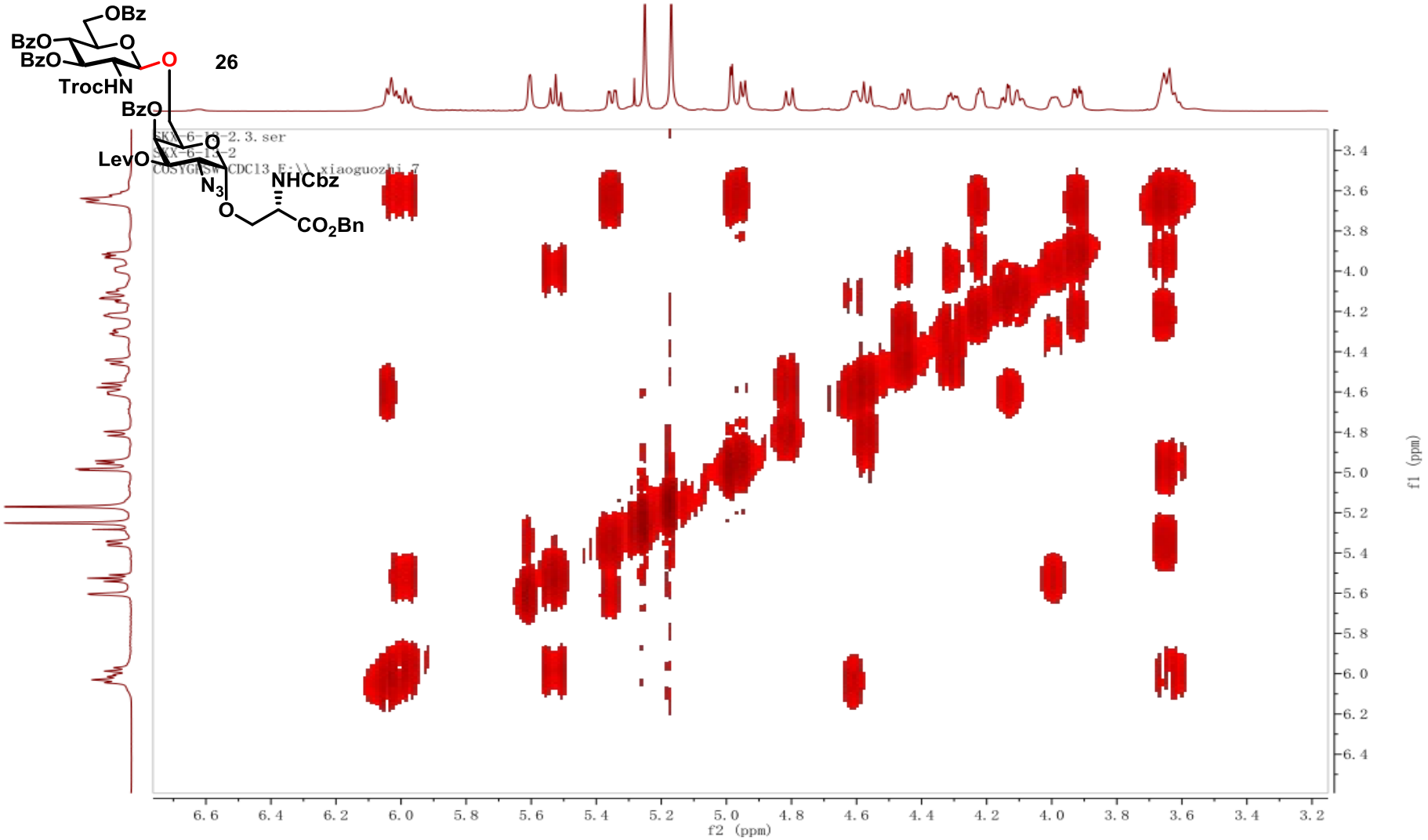

xqz 1767
c13 D20 F:\\ nmr
174.98
174.65
173.44
171.81
100.26
98.03
72.56
71.77
69.73
68.36
68.18
67.22
66.89
63.91
62.61
54.38
51.78
49.56
40.18
22.00
21.99
HO
HO
OH
CO2H
AcHN
HO
O
O
OH
HO
O
AcHN
NH2
10
O
CO2H
4000
3500
3000
2500
2000
1500
1000
500
0
−500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

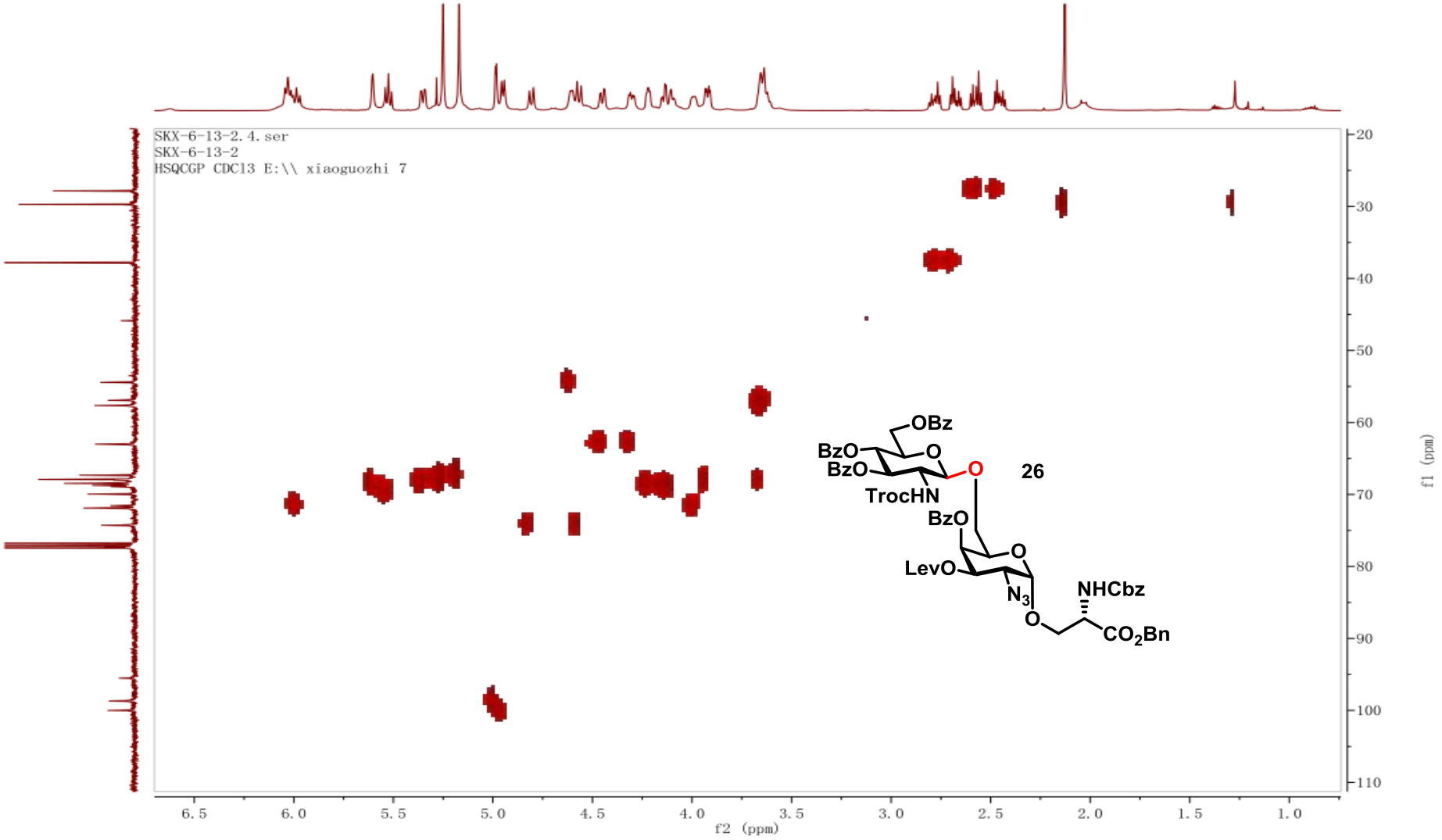

HO
HO
OH
CO2H
AcHN
O
HO
O
OH
HO
O
AcHN
NH2
10
O
CO2H
xqz1767
cosy D20 F:\\ nmr 19
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4

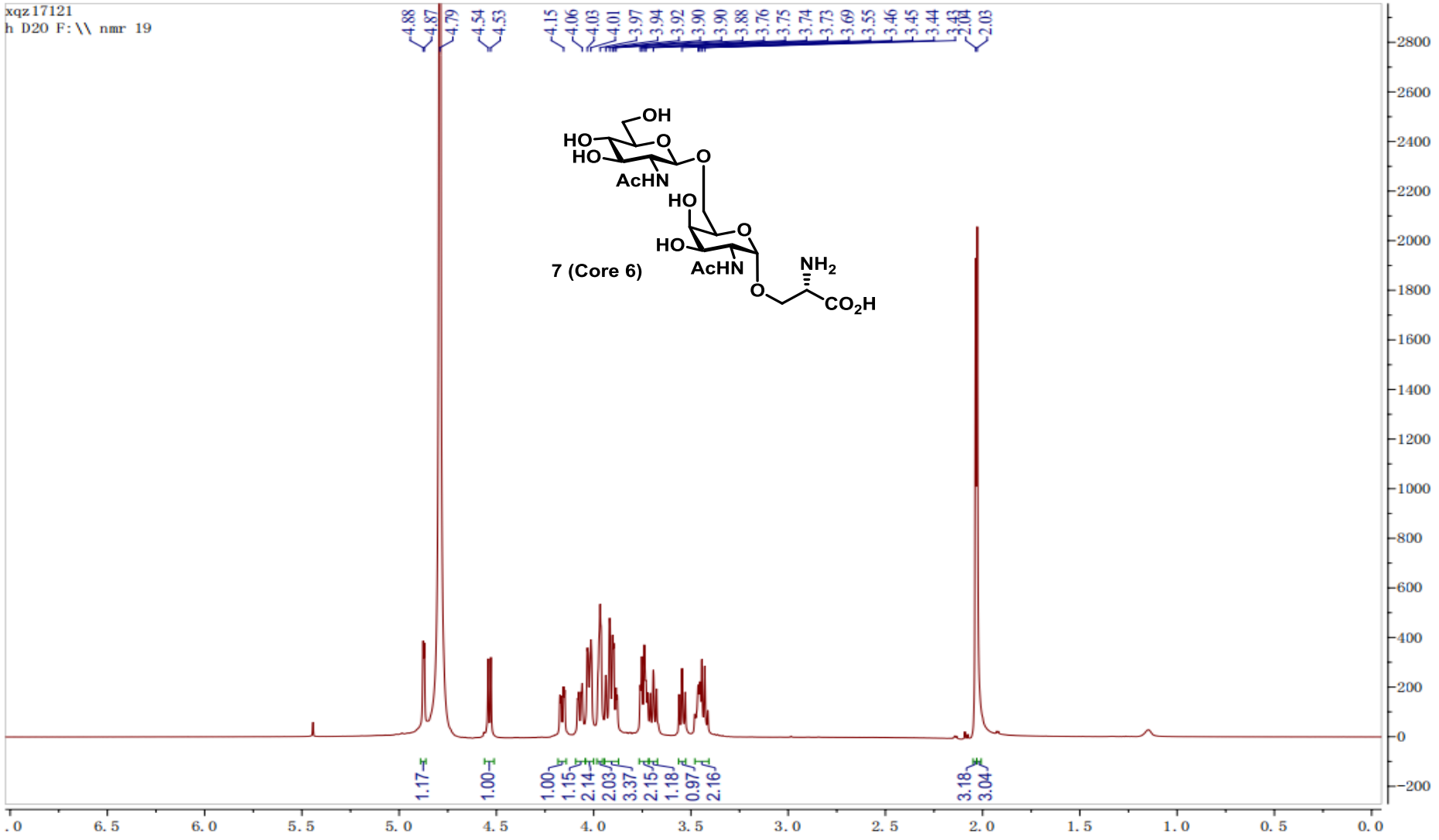

HO
HO
OH
CO2H
AcHN
O
HO
O
OH
HO
O
AcHN
NH2
O
CO2H
10
xqz1767
hsqc D20 F:\\ nmr 19
20
30
40
50
60
70
80
90
100
110
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4

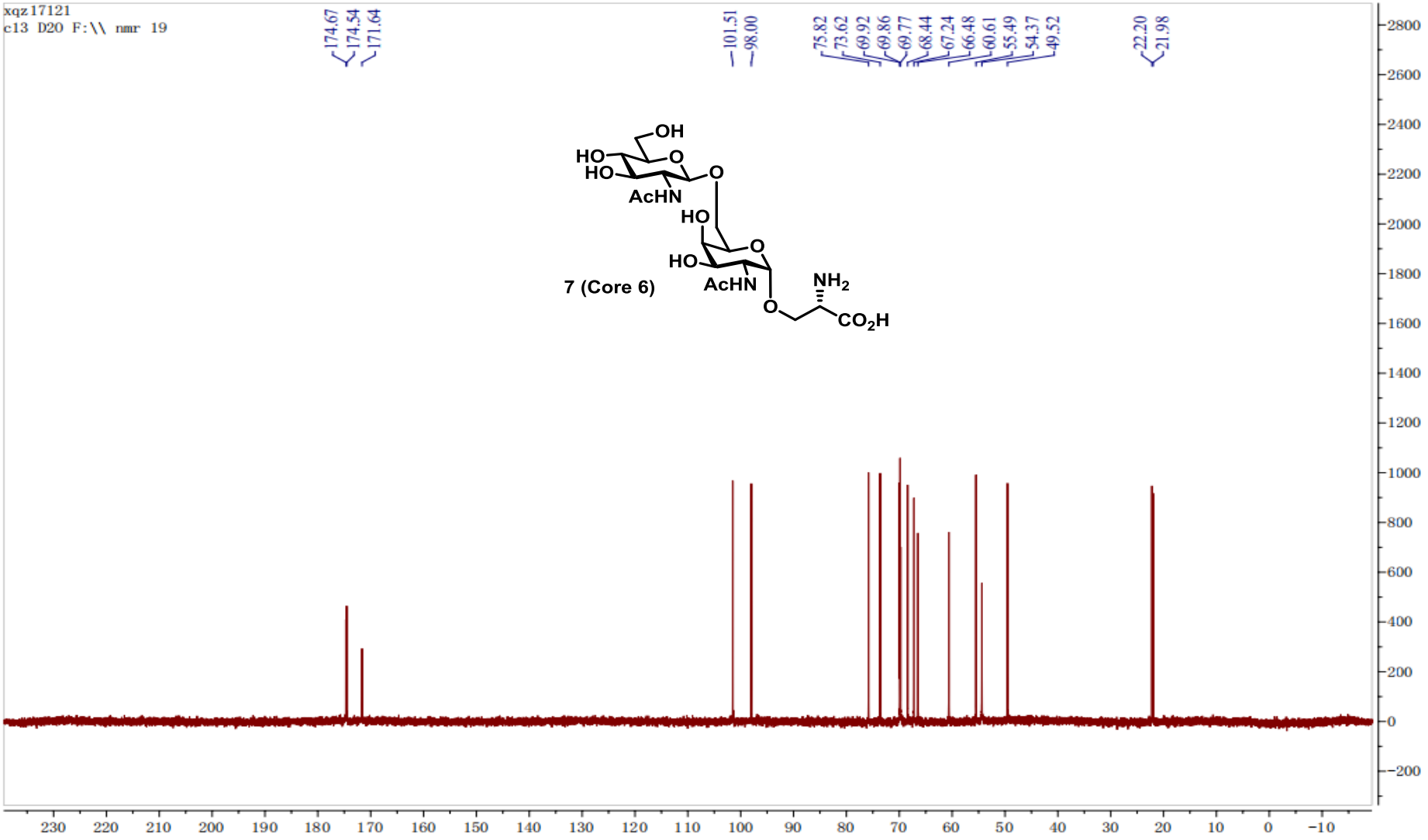

OBz
BzO
BzO
TrocHN
O
26
BzO
LevO
N3
NHCbz
CO2Bn
f1 (ppm)

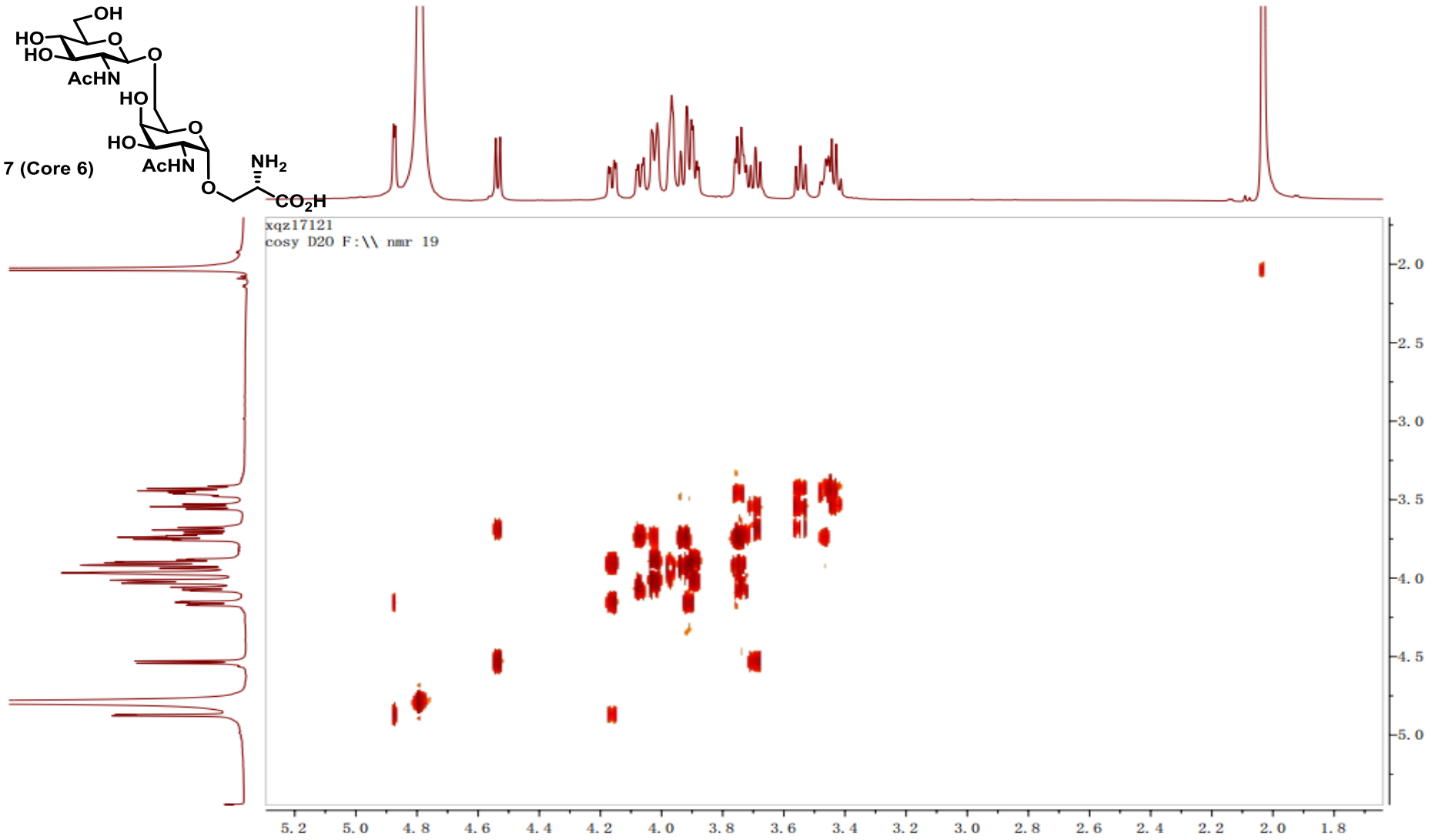

xgz_skx75. 42. fid
c13 CDCl3 F:\\ nmr 1
206.22
171.63
169.55
166.07
165.98
165.42
165.27
156.12
154.14
136.07
135.05
133.76
133.44
133.41
133.07
129.92
129.85
129.76
129.67
129.57
129.14
128.98
128.87
128.79
128.74
128.72
128.69
128.64
128.57
128.49
128.42
128.35
128.22
100.04
98.72
95.55
74.32
71.92
71.59
69.97
68.95
68.80
68.51
68.50
68.06
67.97
67.37
63.04
57.68
56.96
54.46
37.86
29.77
27.87
OBz
BzO
BzO
O
O
TrocHN
BzO
O
LevO
N3
O
NHCbz
CO2Bn
26
f1 (ppm)

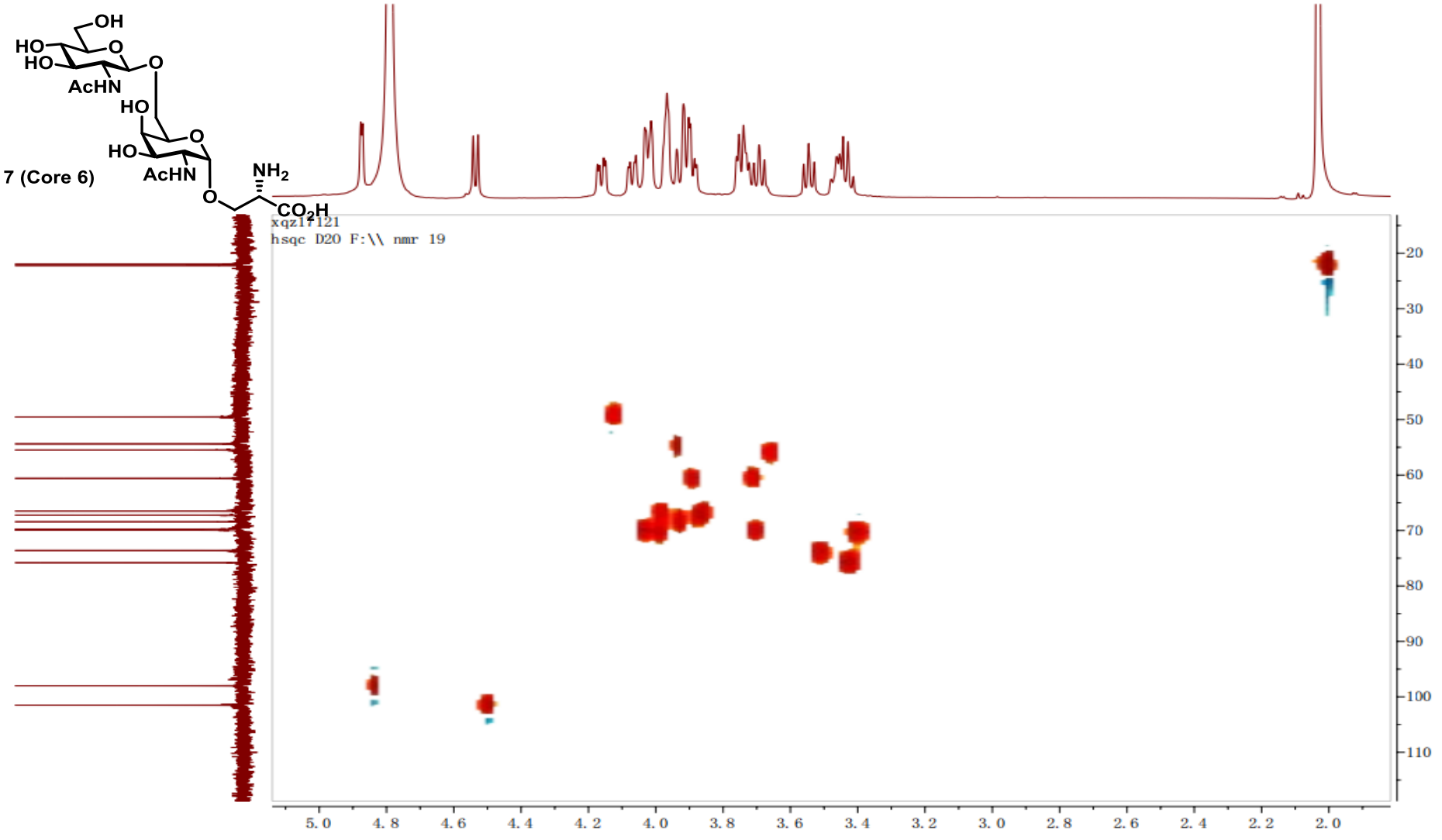

OBz
BzO
BzO
O
TrocHN
O
26
BzO
LevO
O
N3
O
NHCbz
CO2Bn
f2 (ppm)
f1 (ppm)

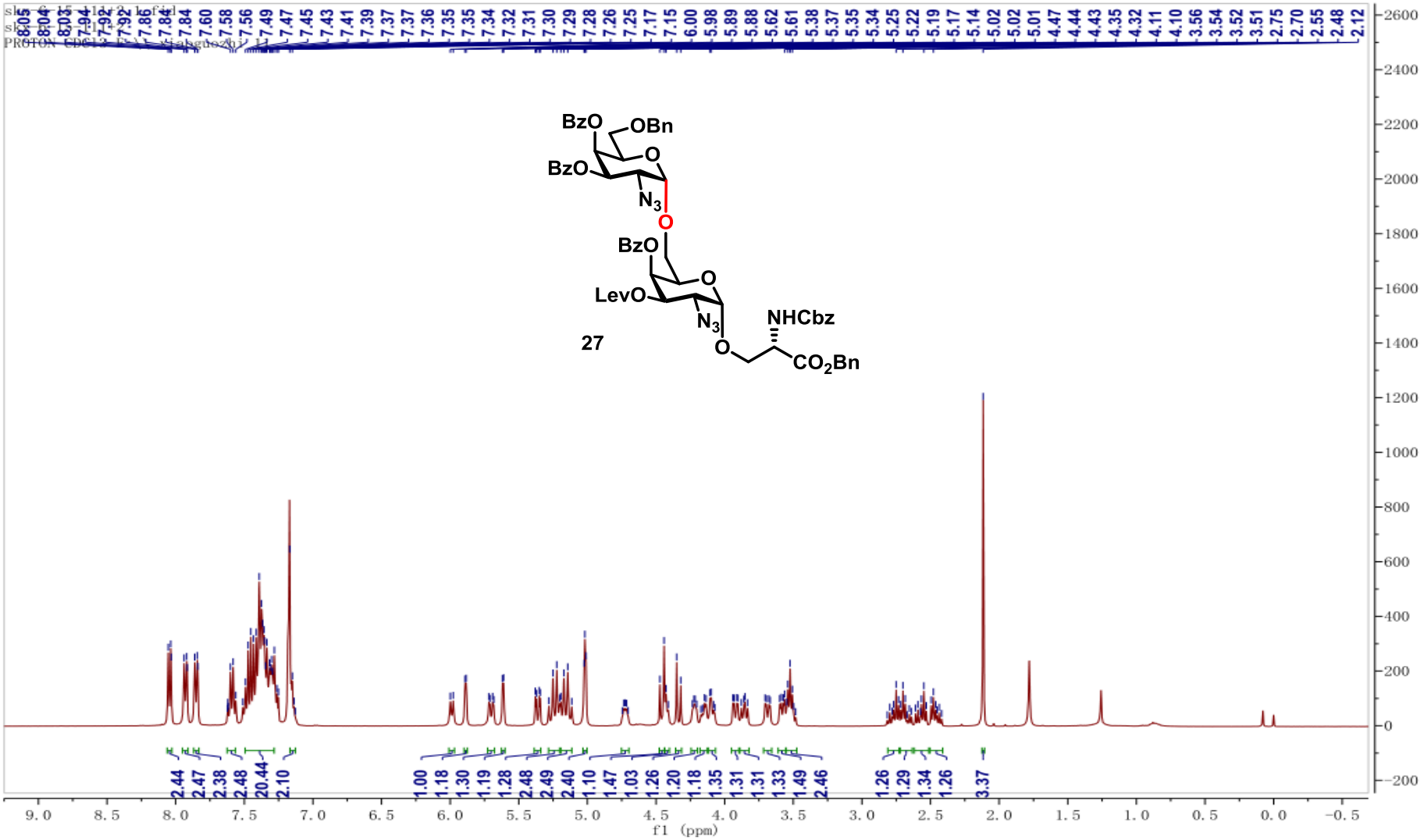

SKX-6-13-2.4.ser
SKX-6-13-2
HSQCGP CDC13 E:\\ xiaoguozhi 7
OBz
BzO
BzO
O
O
TrocHN
26
BzO
O
LevO
N3
NHCbz
O
CO2Bn
f2 (ppm)
f1 (ppm)

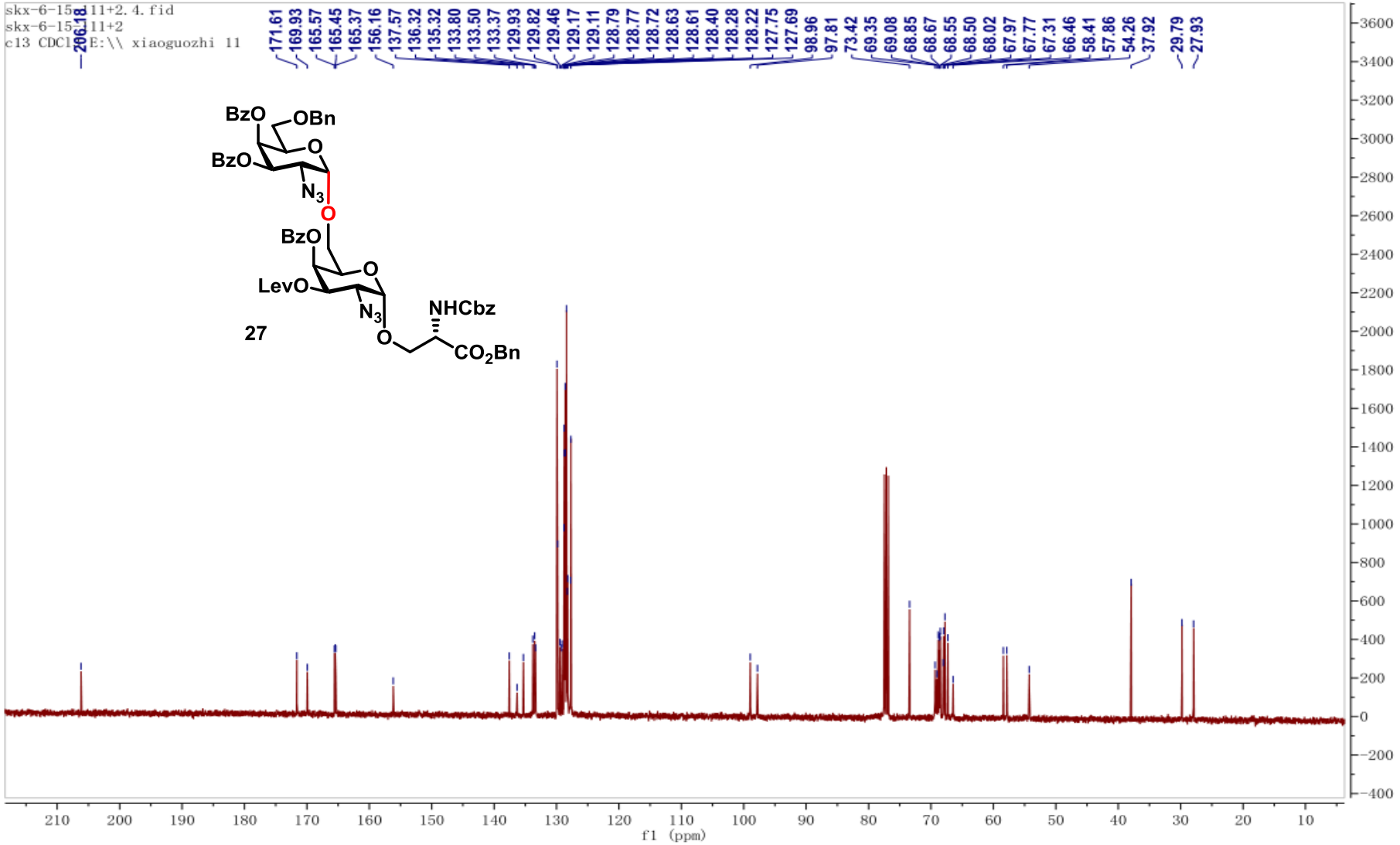

xqz17121
h D20 F:\\ nmr 19
7 (Core 6)

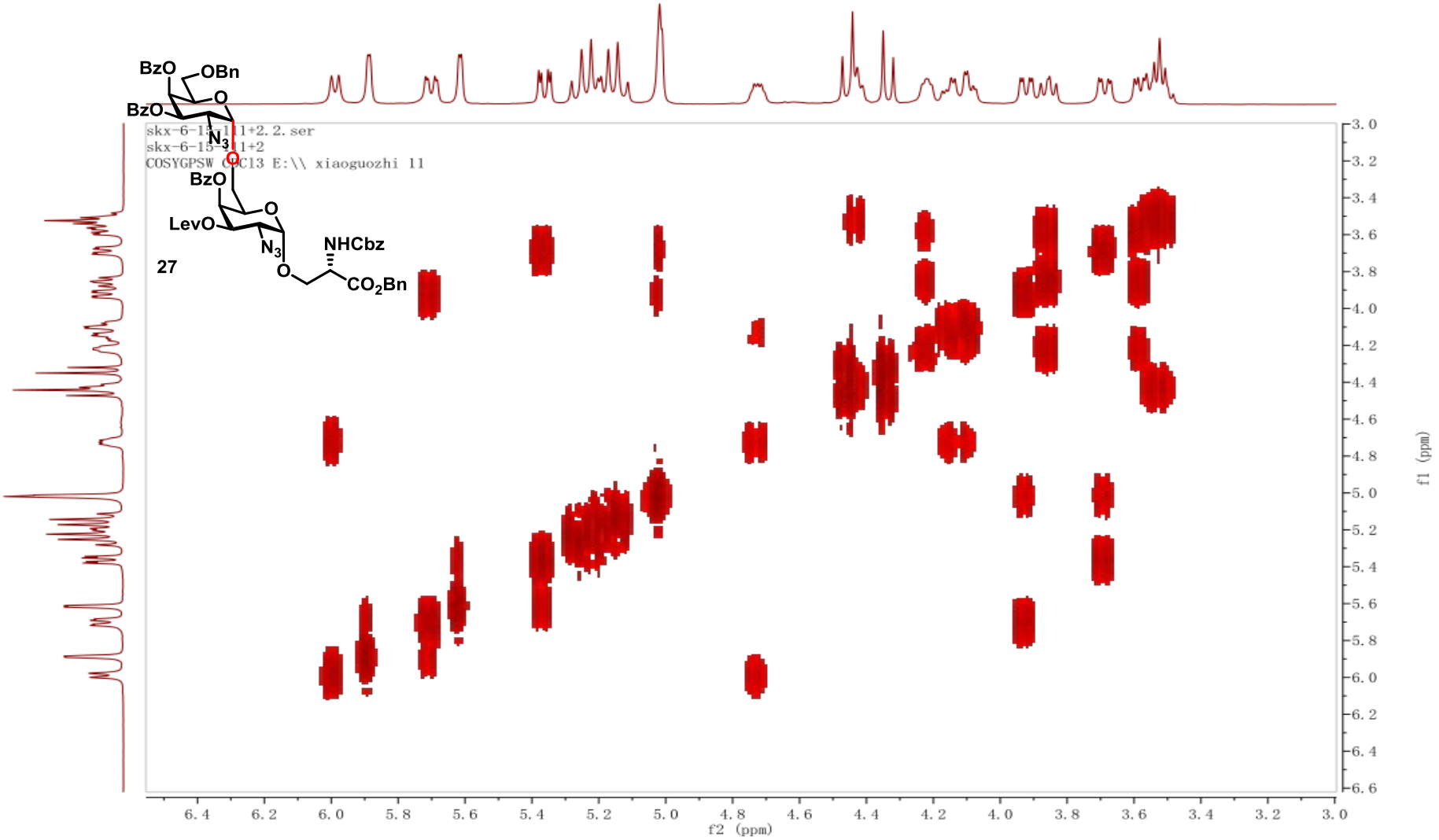

xqz17121
c13 D2O F:\\ nmr 19
174.67
174.54
171.64
101.51
98.00
75.82
73.62
69.92
69.86
69.77
68.44
67.24
66.48
60.61
55.49
54.37
49.52
22.20
21.98
OH
HO
HO
O
O
AcHN
HO
HO
O
AcHN
NH2
O
CO2H
7 (Core 6)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

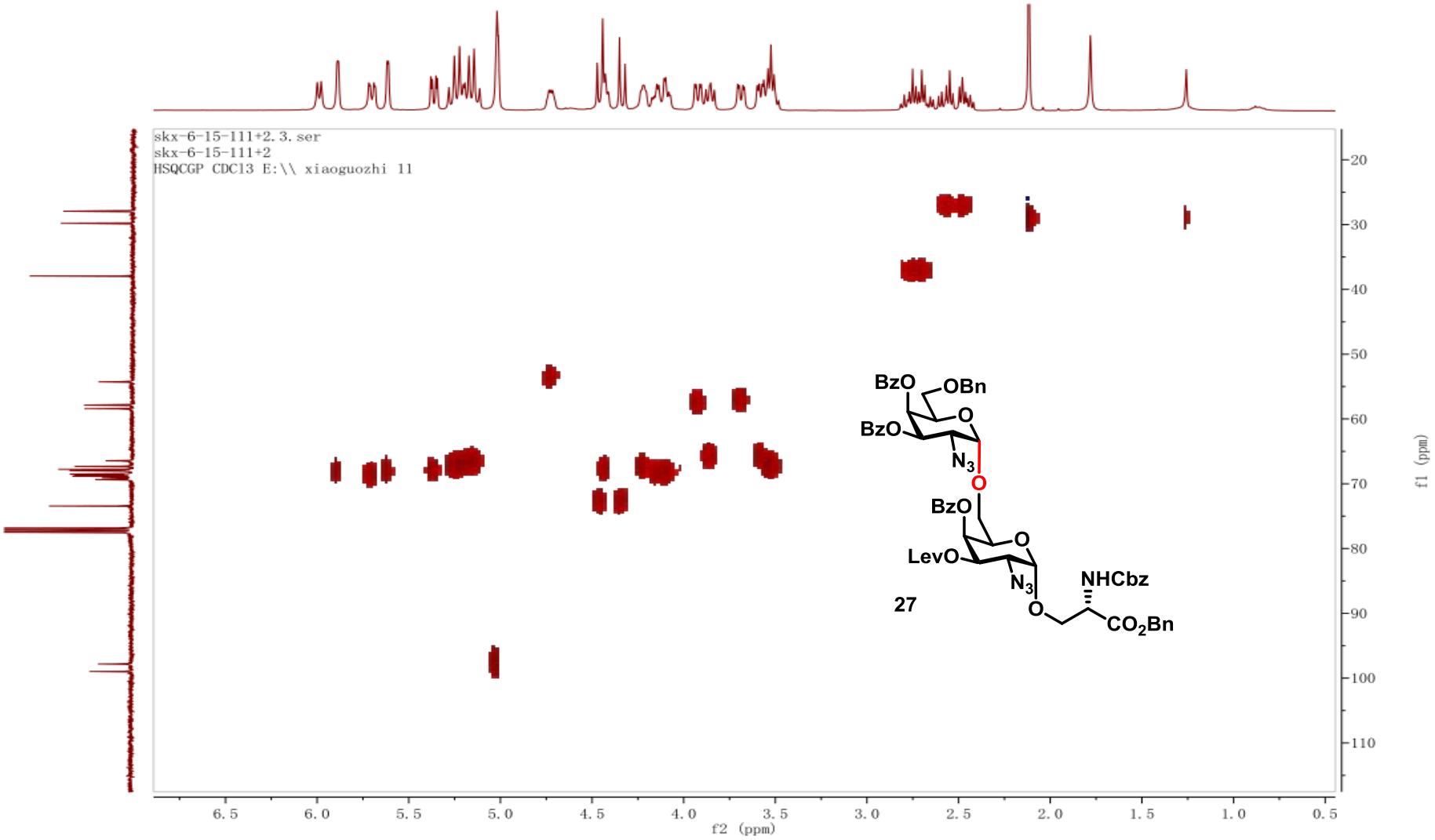

7 (Core 6)
xqz17121
cosy D20 F:\\ nmr 19
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
2.0
2.5
3.0
3.5
4.0
4.5
5.0

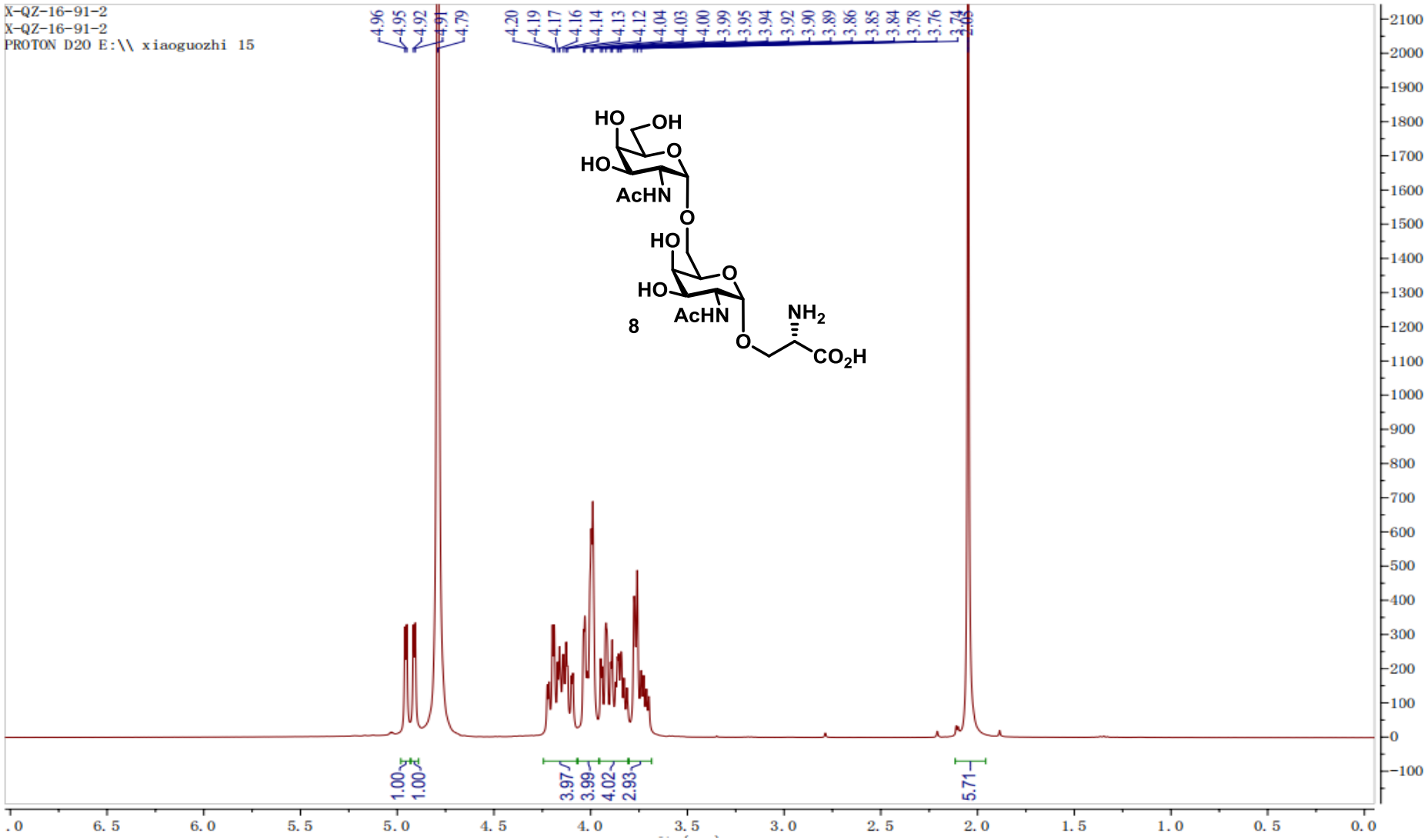

7 (Core 6)
xqz17121
hsqc D20 F:\\ nmr 19
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
20
30
40
50
60
70
80
90
100
110

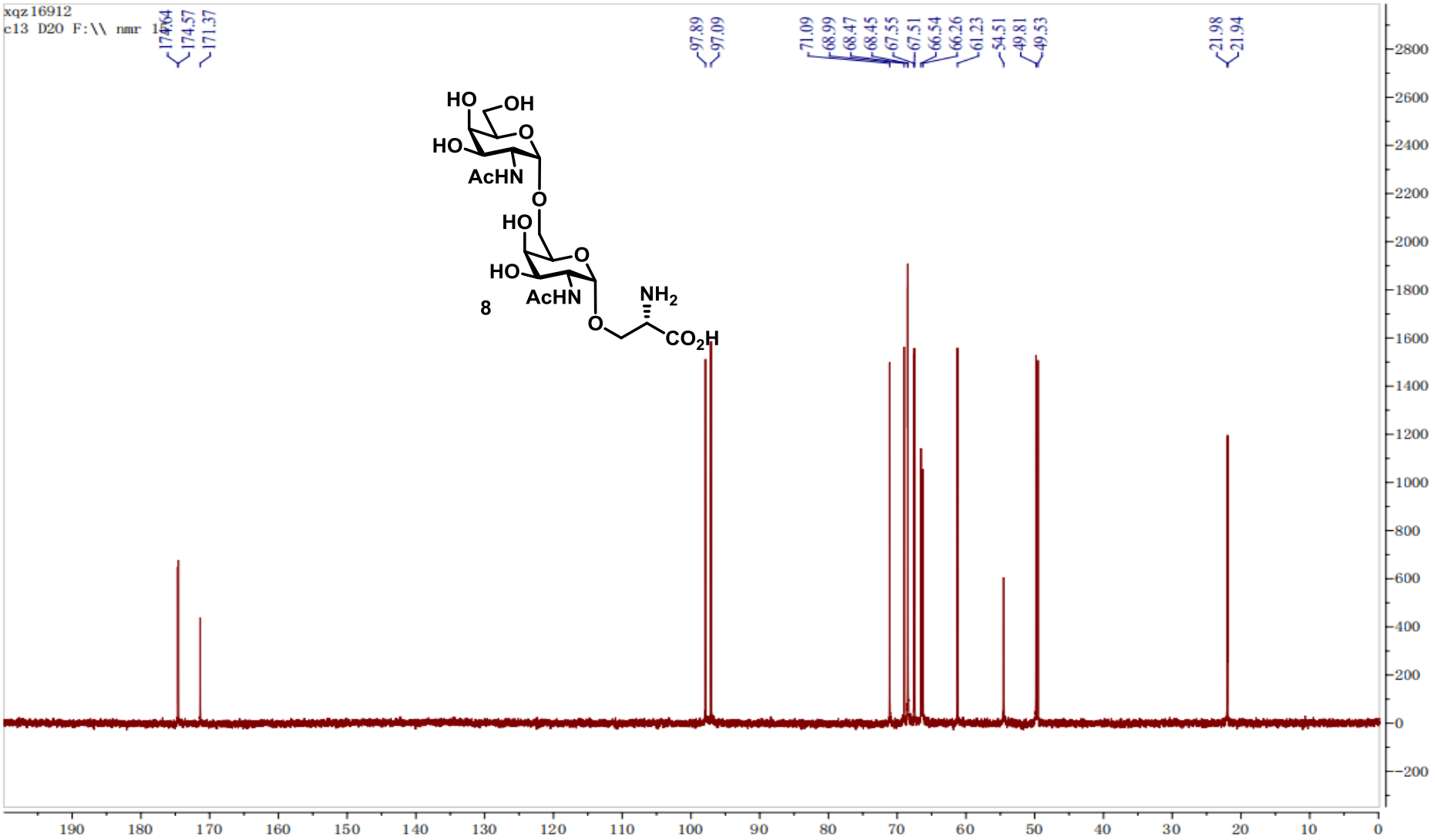

BzO
OBn
O
BzO
N3
O
BzO
O
LevO
N3
NHCbz
O
CO2Bn
27
f1 (ppm)

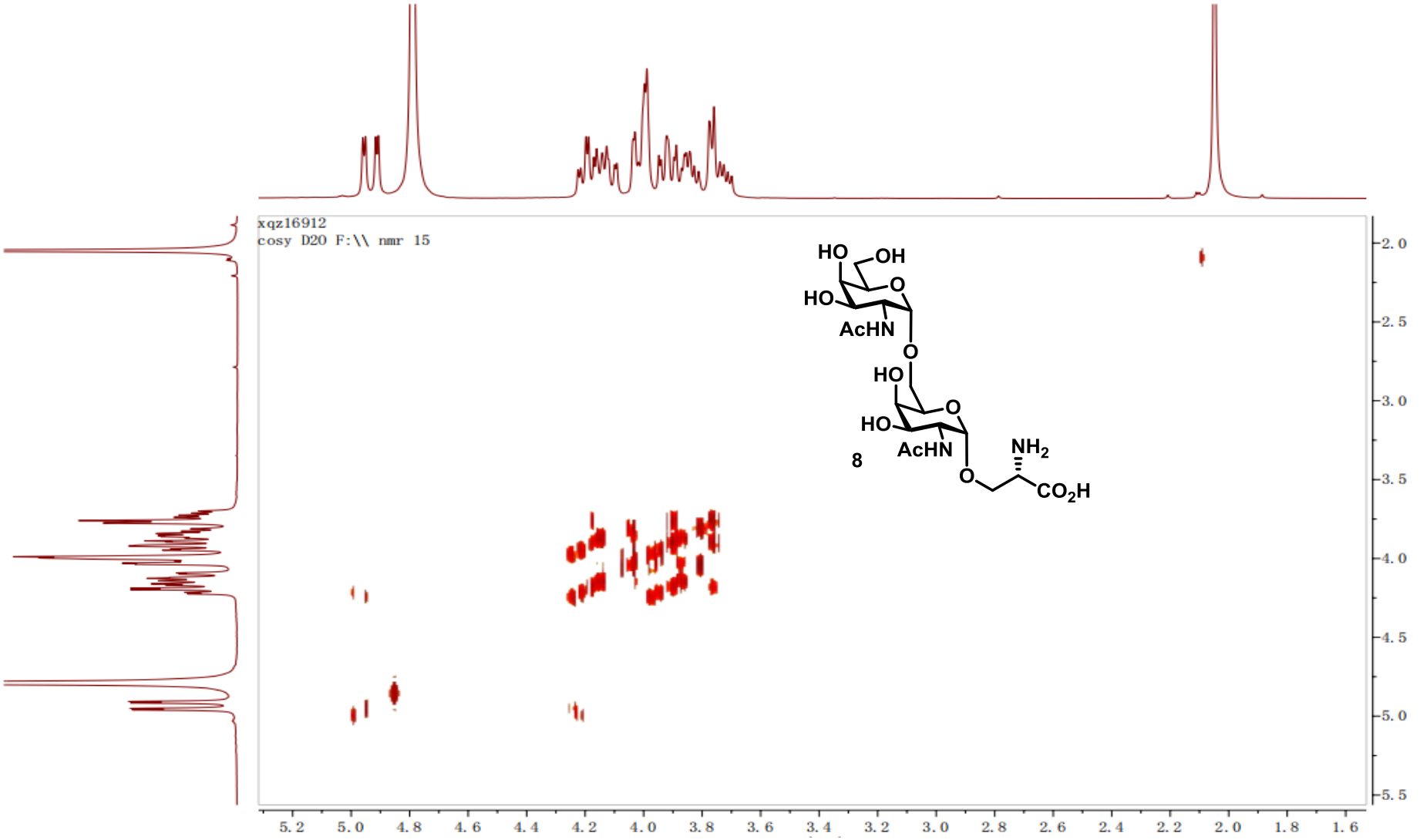

skx-6-15 11+2.4.fid
skx-6-15 11+2
c13 CDCl3 E:\\ xiaoguozhi 11
171.61
169.93
165.57
165.45
165.37
156.16
137.57
136.32
135.32
133.80
133.50
133.37
129.93
129.82
129.46
129.17
129.11
128.79
128.77
128.72
128.63
128.61
128.40
128.28
128.22
127.75
127.69
98.96
97.81
73.42
69.35
69.08
68.85
68.67
68.55
68.50
68.02
67.97
67.77
67.31
66.46
58.41
57.86
54.26
37.92
29.79
27.93
BzO
OBn
O
BzO
N3
O
BzO
O
LevO
N3
NHCbz
O
CO2Bn
27
f1 (ppm)

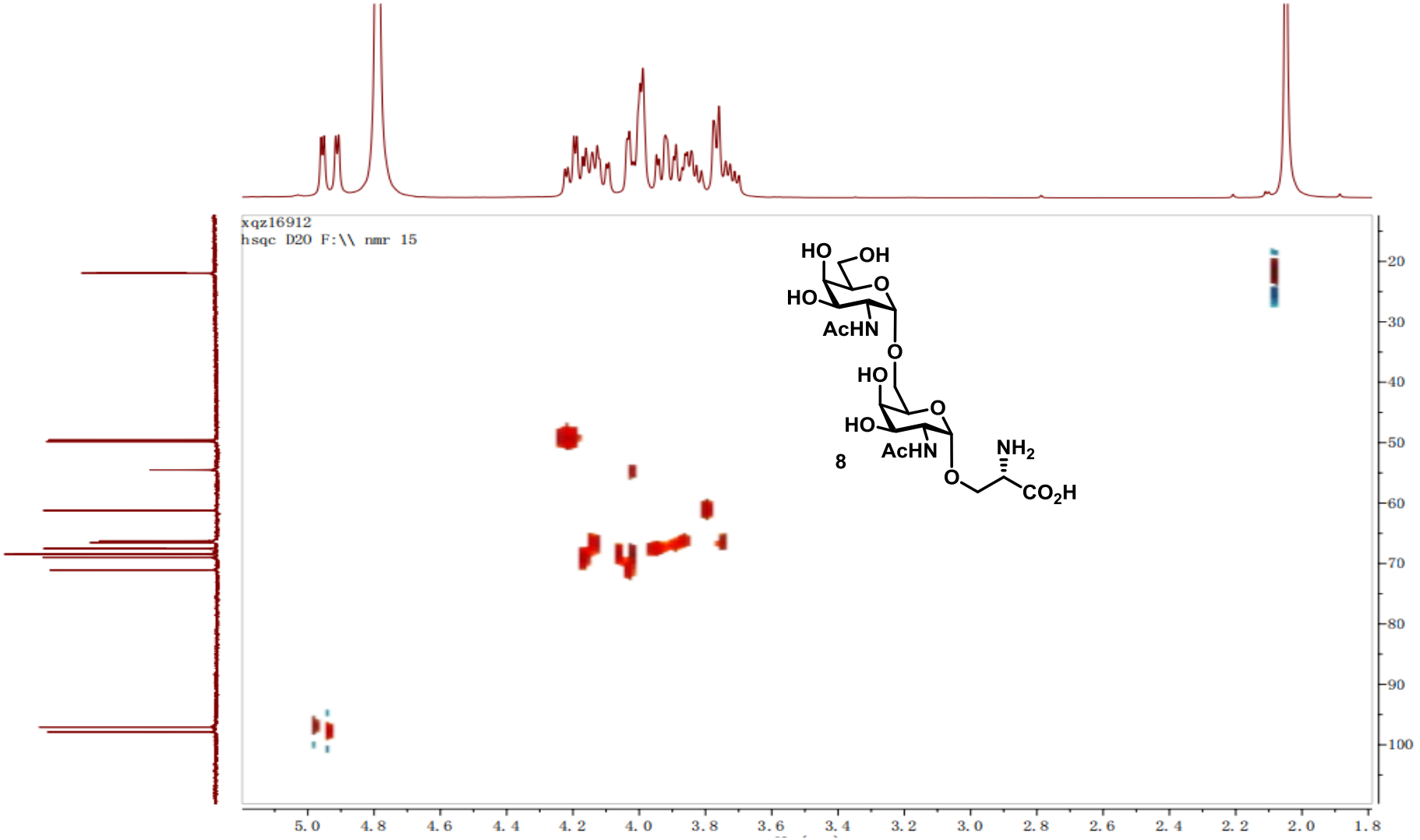

BzO
OBn
O
BzO
N3
BzO
LevO
O
N3
NHCbz
O
CO2Bn
27
skx-6-15-11+2.2.ser
skx-6-15-11+2
COSYGPSW CDCl3 E:\\ xiaoguozhi 11
f2 (ppm)
f1 (ppm)

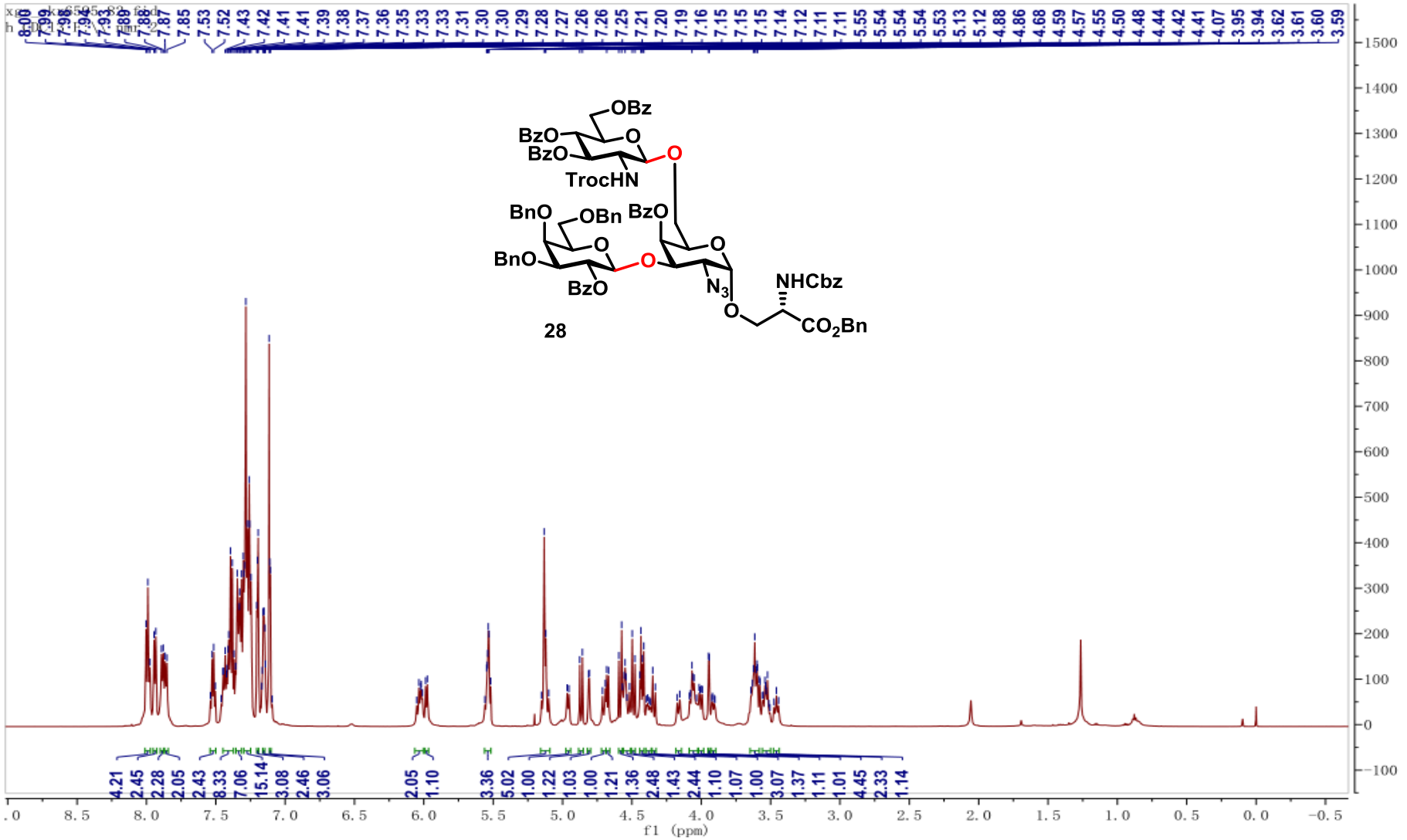

skx-6-15-111+2.3.ser
skx-6-15-111+2
HSQCGP CDCl3 E:\\ xiaoguozhi 11
BzO
OBn
O
BzO
N3
O
BzO
O
LevO
N3
NHCbz
O
CO2Bn
27
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

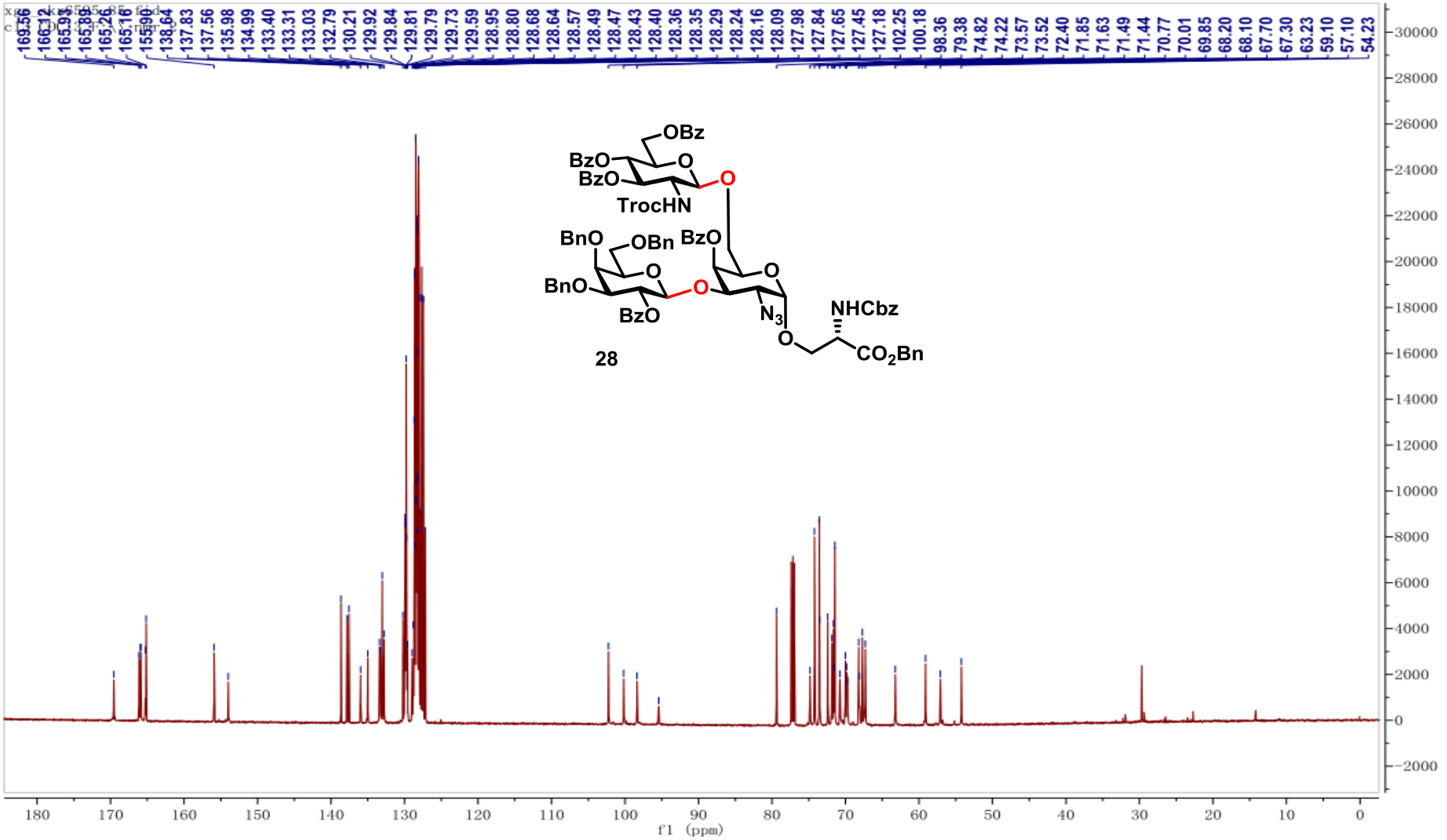

X-QZ-16-91-2
X-QZ-16-91-2
PROTON D2O E:\\ xiaoguozhi 15
4.96
4.95
4.92
4.91
4.79
4.20
4.19
4.17
4.16
4.14
4.13
4.12
4.04
4.03
4.00
3.99
3.95
3.94
3.92
3.90
3.89
3.86
3.85
3.84
3.78
3.76
3.74
2.03
HO
OH
O
HO
AcHN
O
HO
O
HO
AcHN
NH2
8
O
CO2H
1.00
1.00
3.97
3.99
4.02
2.93
5.71
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
.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

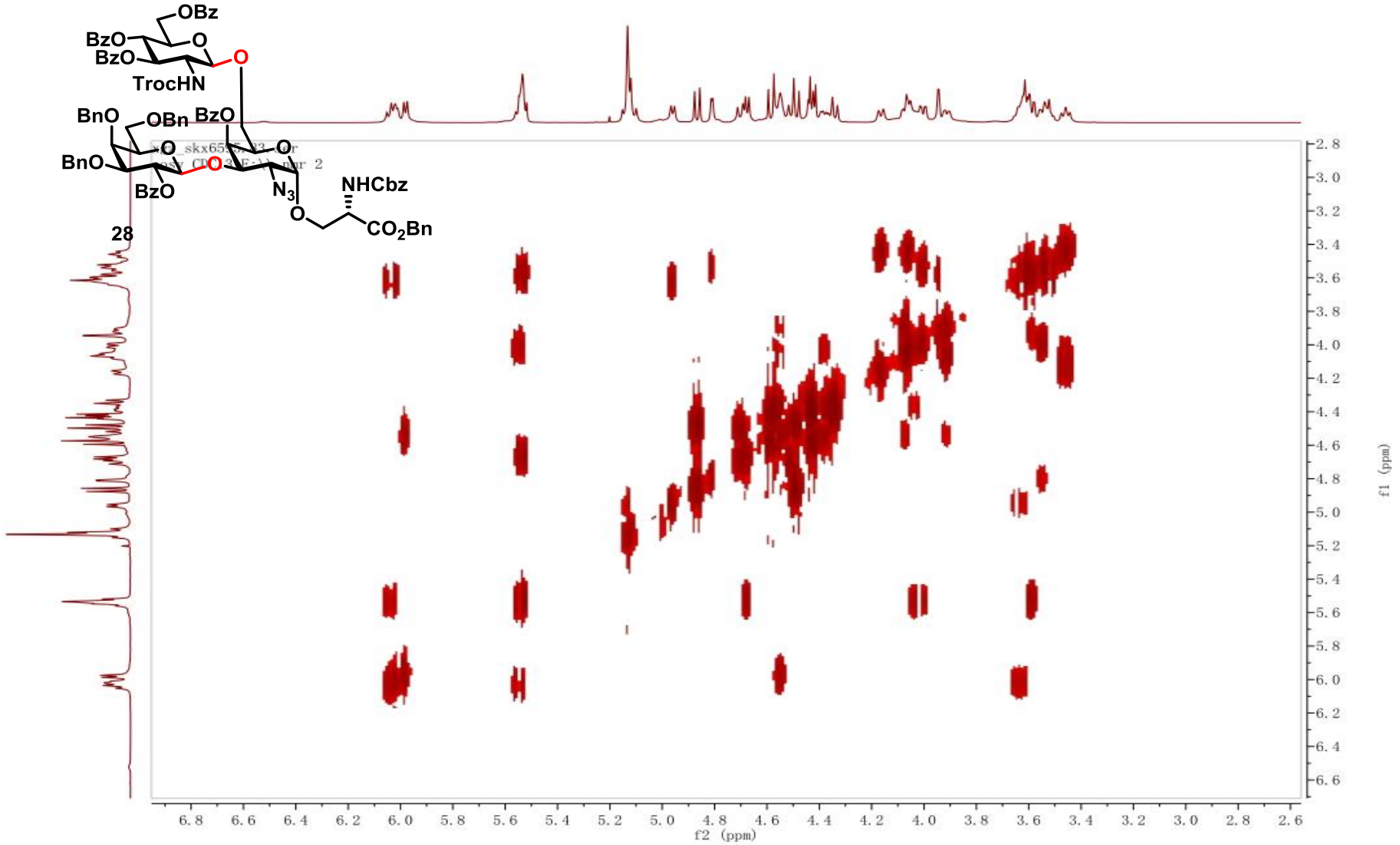

xqz16912
c13 D20 F:\\ nmr
174.64
174.57
171.37
97.89
97.09
71.09
68.99
68.47
68.45
67.55
67.51
66.54
66.26
61.23
54.51
49.81
49.53
21.98
21.94
HO
OH
O
HO
AcHN
O
HO
O
HO
AcHN
NH2
8
O
CO2H
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

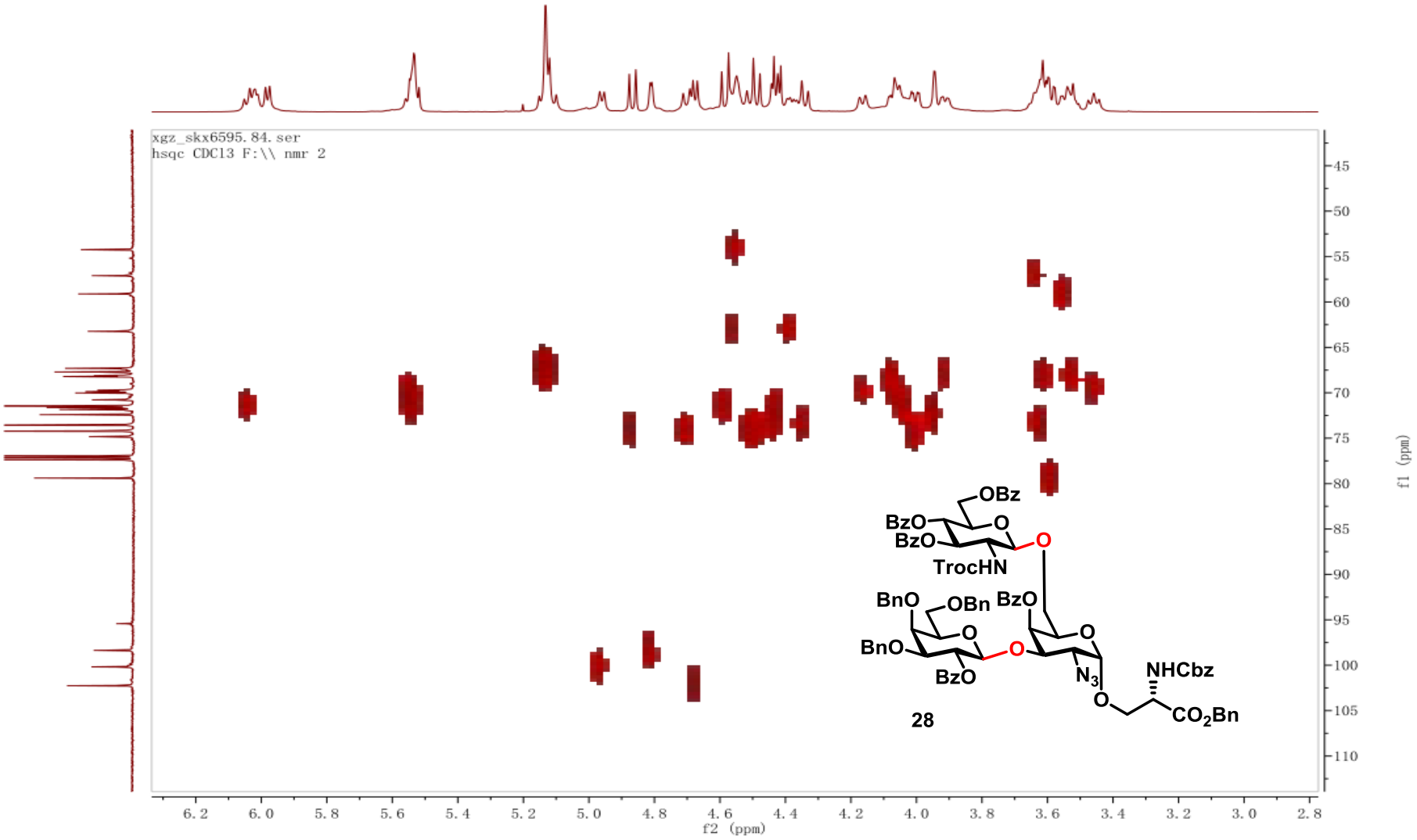

xqz16912
cosy D20 F:\\ nmr 15
HO
OH
O
HO
AcHN
O
HO
O
HO
AcHN
NH2
8
O
CO2H
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

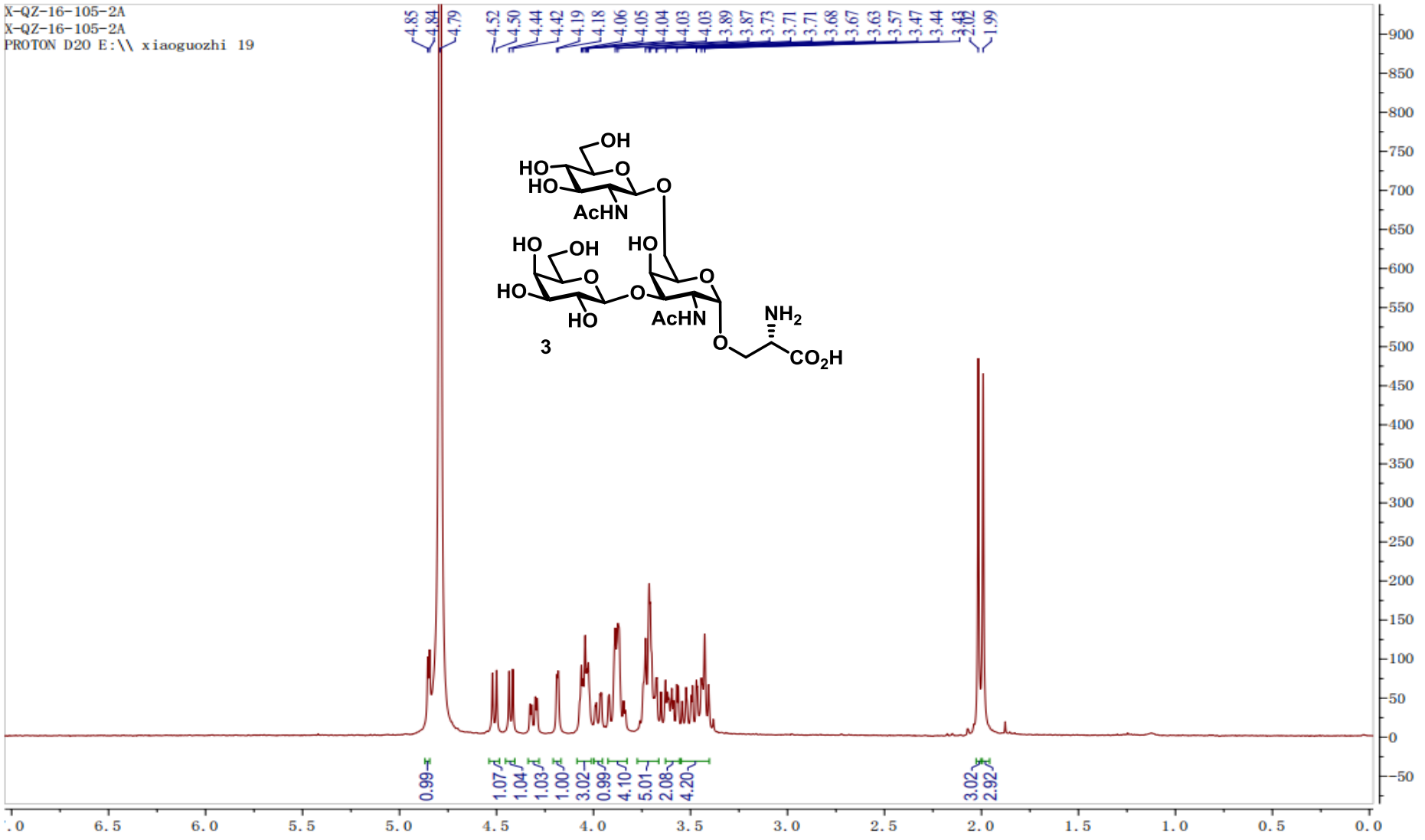

xqz16912
hsqc D2O F:\\ nmr 15
HO
OH
O
HO
AcHN
O
HO
O
HO
AcHN
NH2
8
O
CO2H
20
30
40
50
60
70
80
90
100
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8

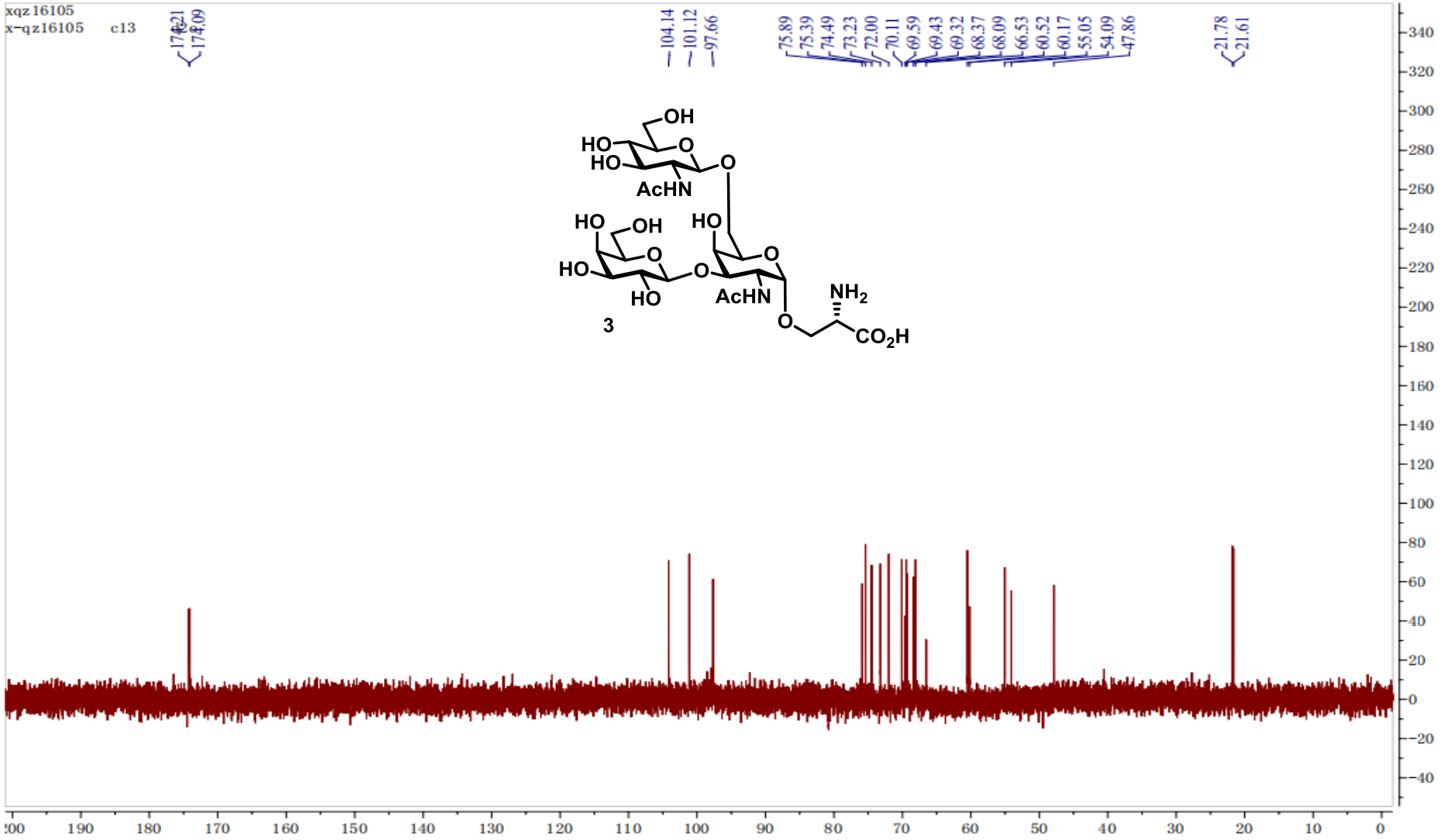

OBz
BzO
BzO
O
TrocHN
BnO
OBn
BzO
O
BnO
O
O
BzO
N3
NHCbz
O
CO2Bn
28
f1 (ppm)

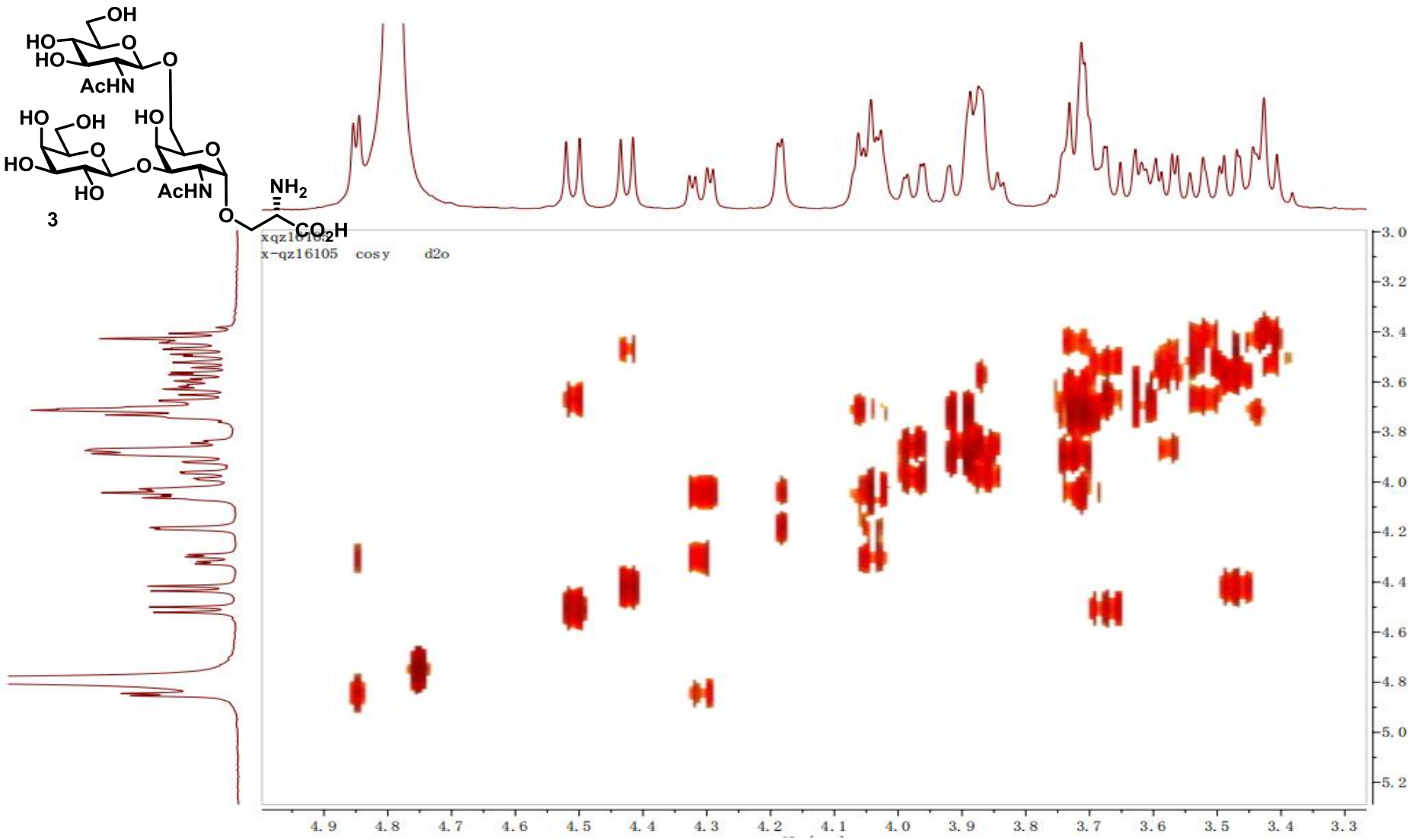

OBz
BzO
BzO
TrocHN
BnO
OBn
BzO
BnO
BzO
N3
NHCbz
CO2Bn
28
f1 (ppm)

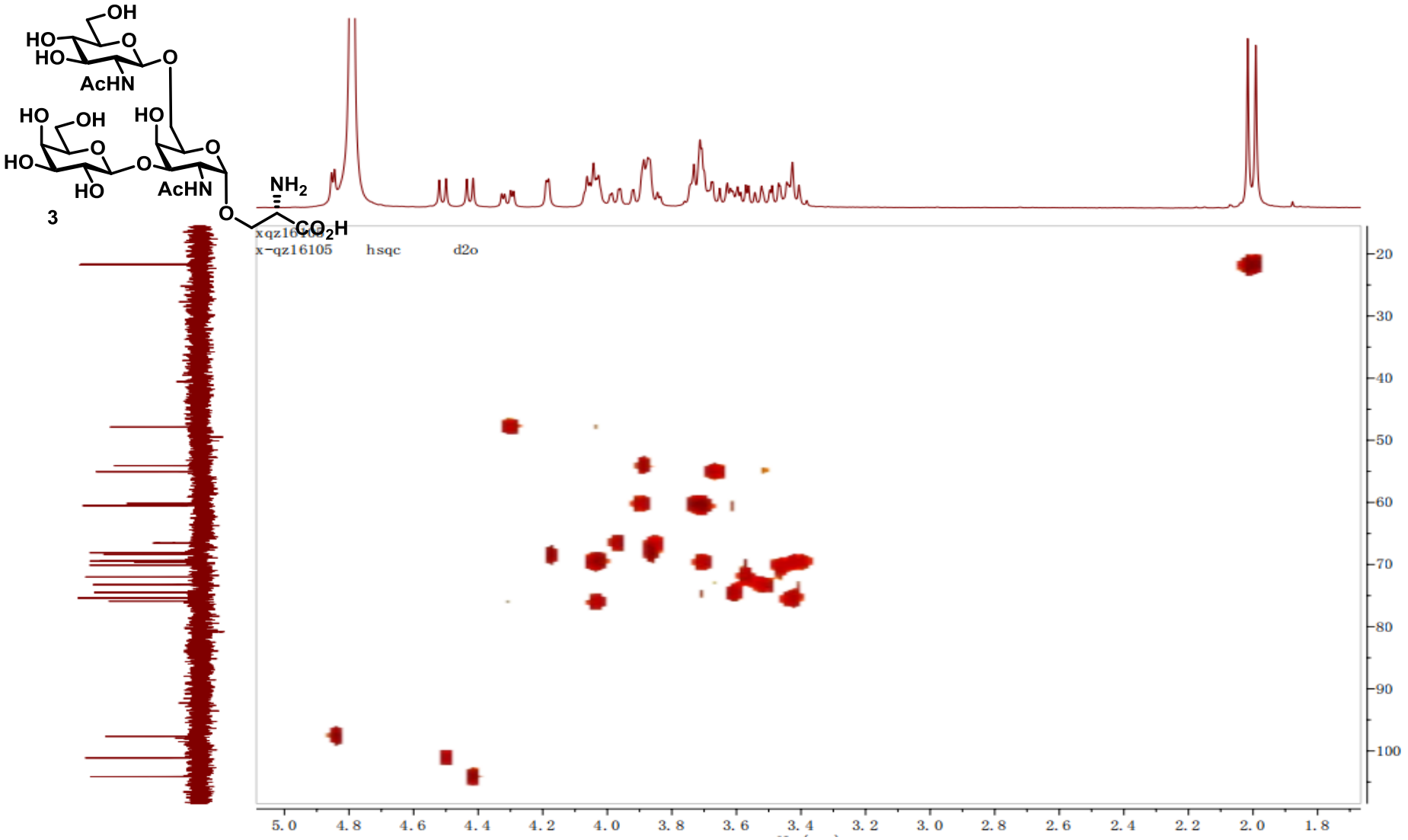

OBz
BzO
BzO
O
TrocHN
BnO
OBn
BzO
BnO
O
BzO
N3
NHCbz
O
CO2Bn
28
f2 (ppm)
f1 (ppm)

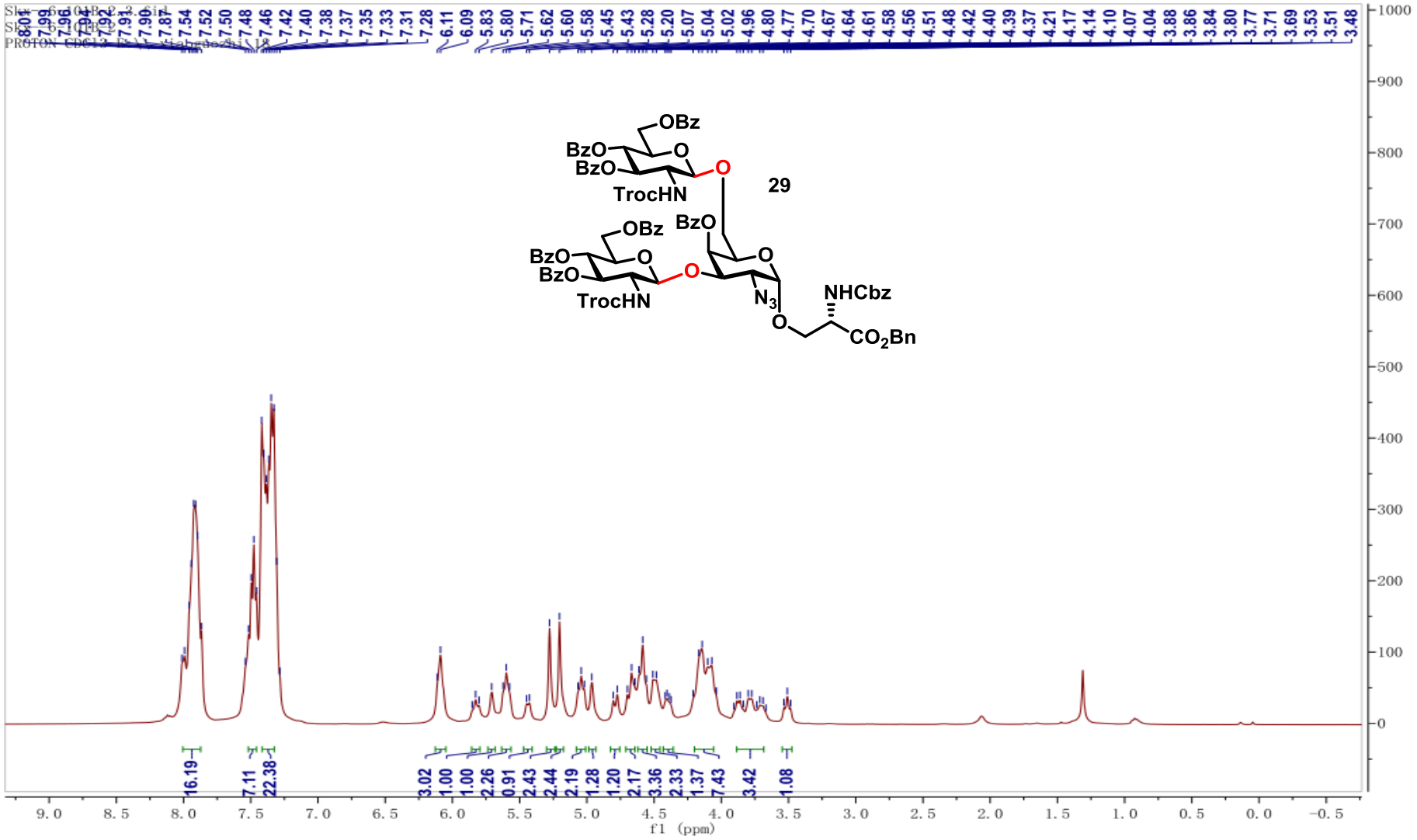

xgz_skx6595.84.ser
hsqc CDCl3 F:\\ nmr 2
f2 (ppm)
f1 (ppm)
OBz
BzO
BzO
TrocHN
BnO
OBn
BzO
BnO
BzO
N3
NHCbz
CO2Bn
28

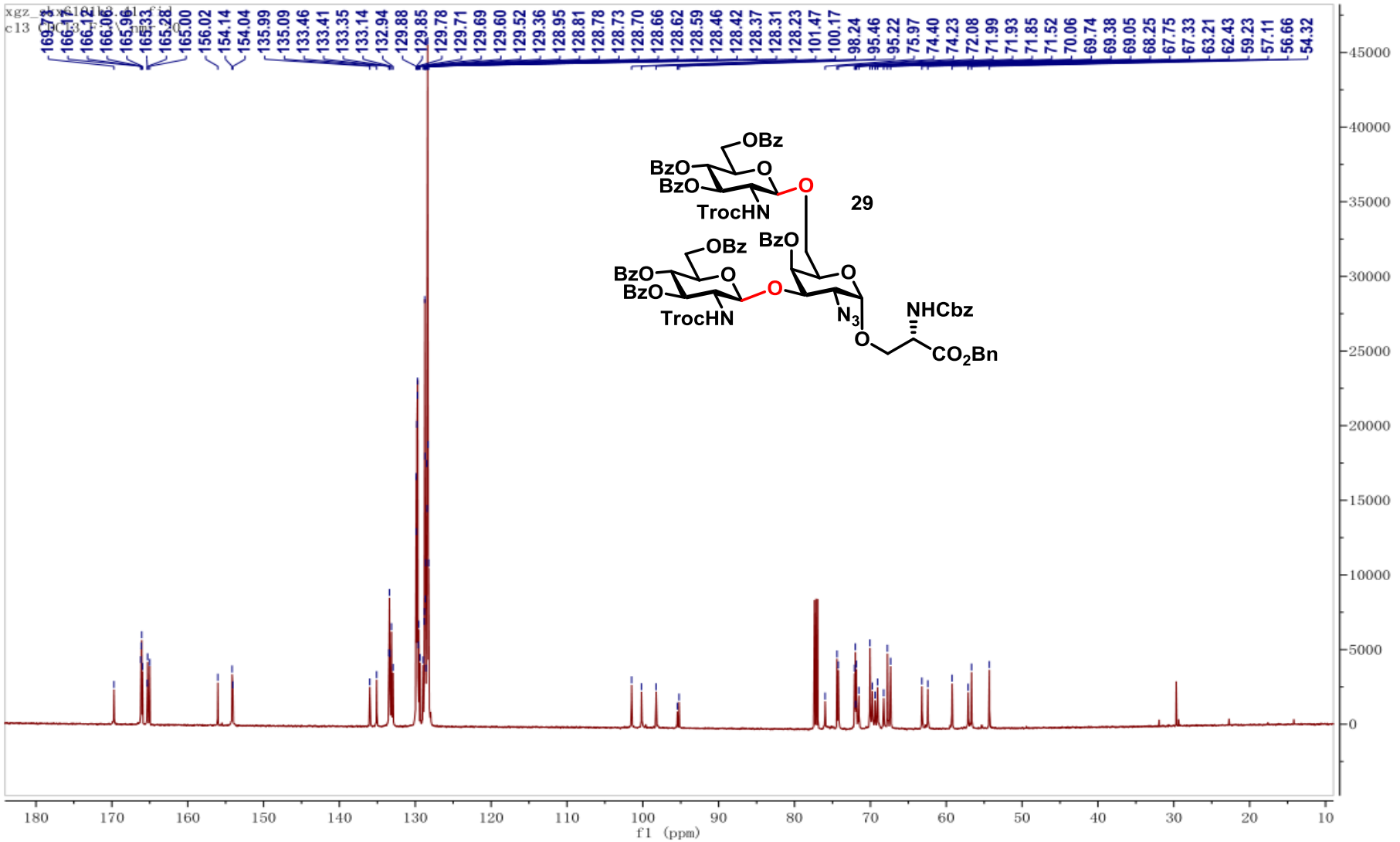

X-QZ-16-105-2A
X-QZ-16-105-2A
PROTON D20 E:\\ xiaoguozhi 19
4.85
4.84
4.79
4.52
4.50
4.44
4.42
4.19
4.18
4.06
4.05
4.04
4.03
4.03
3.89
3.87
3.73
3.71
3.71
3.68
3.67
3.63
3.57
3.47
3.44
2.02
1.99
OH
HO
HO
O
O
AcHN
HO
OH
HO
O
HO
O
O
HO
HO
AcHN
NH2
O
CO2H
3
0.99
1.07
1.04
1.03
1.00
3.02
0.99
4.10
5.01
2.08
4.20
3.02
2.92
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
.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

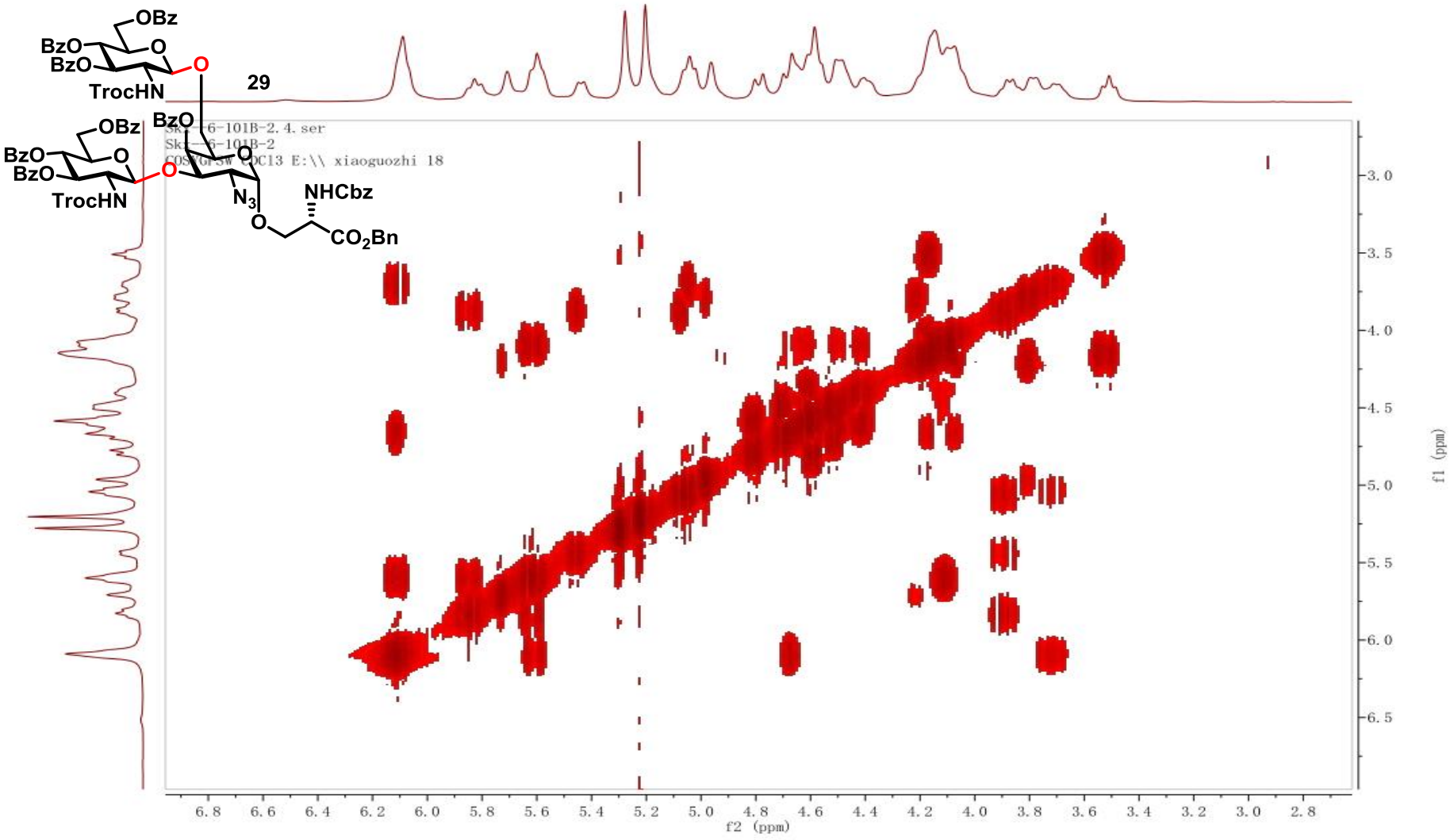

xqz16105
x-qz16105 c13
174.21
174.09
104.14
101.12
97.66
75.89
75.39
74.49
73.23
72.00
70.11
69.59
69.43
69.32
68.37
68.09
66.53
60.52
60.17
55.05
54.09
47.86
21.78
21.61
OH
HO
HO
O
O
AcHN
HO
OH
HO
HO
O
O
HO
O
AcHN
NH2
O
CO2H
3

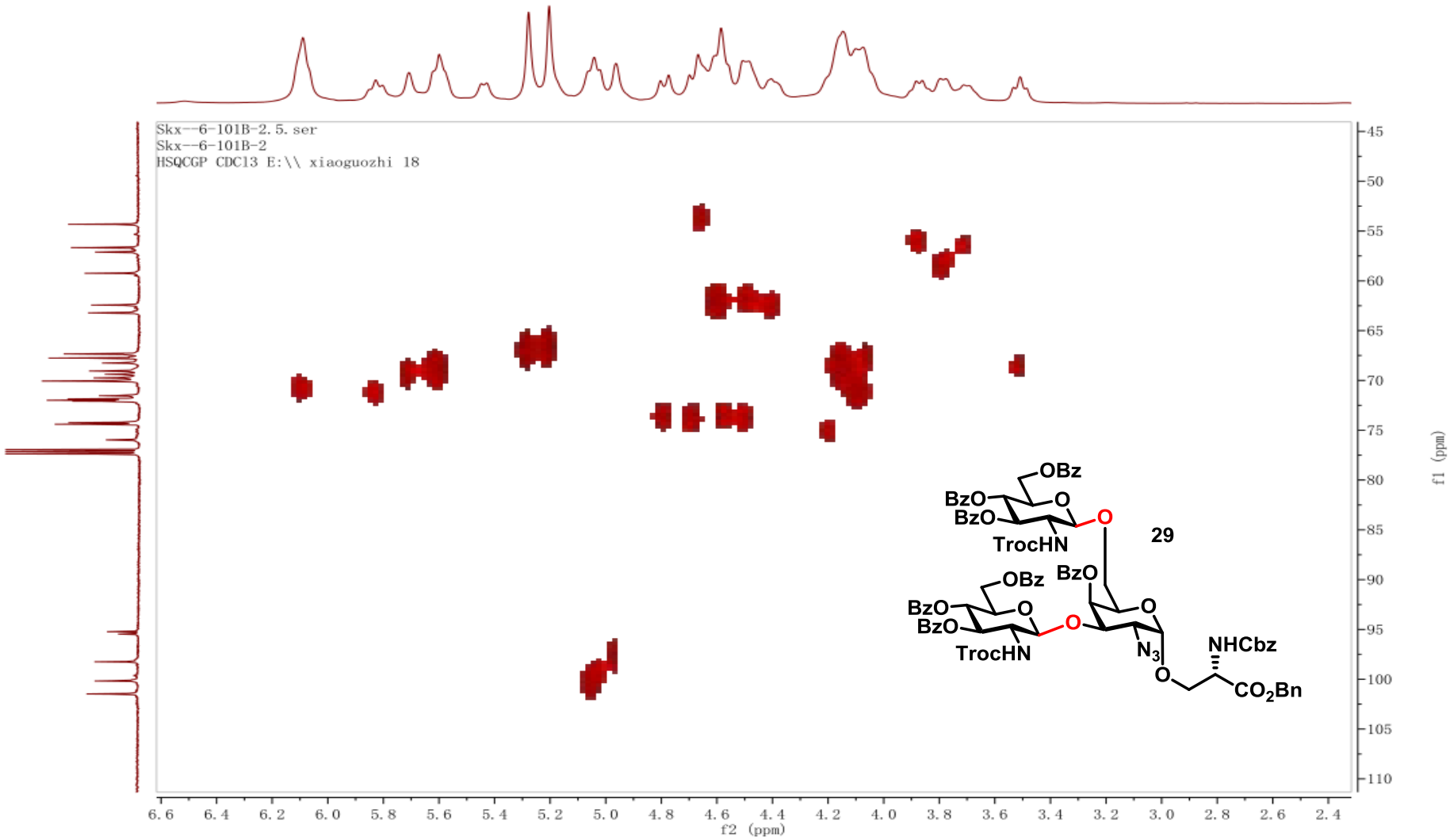

OH
HO
HO
O
O
AcHN
HO
OH
HO
O
O
HO
HO
O
AcHN
NH2
O
CO2H
3
xqz16102
x-qz16105 cosy d2o
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3

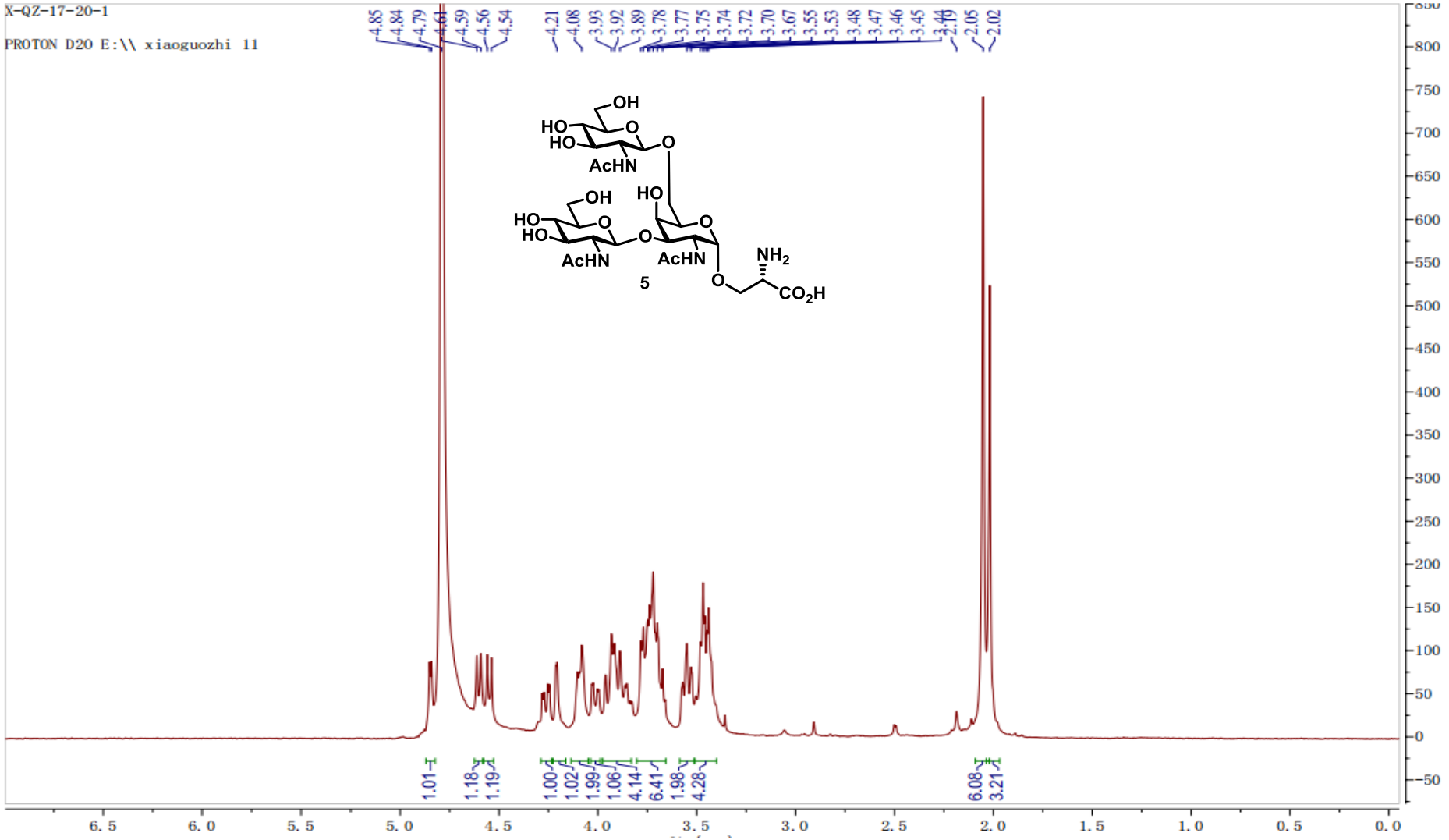

OH
HO
HO
O
AcHN
HO
OH
HO
O
HO
HO
O
AcHN
NH2
CO2H
3
xqz16105
x-qz16105 hsqc d2o
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
20
30
40
50
60
70
80
90
100

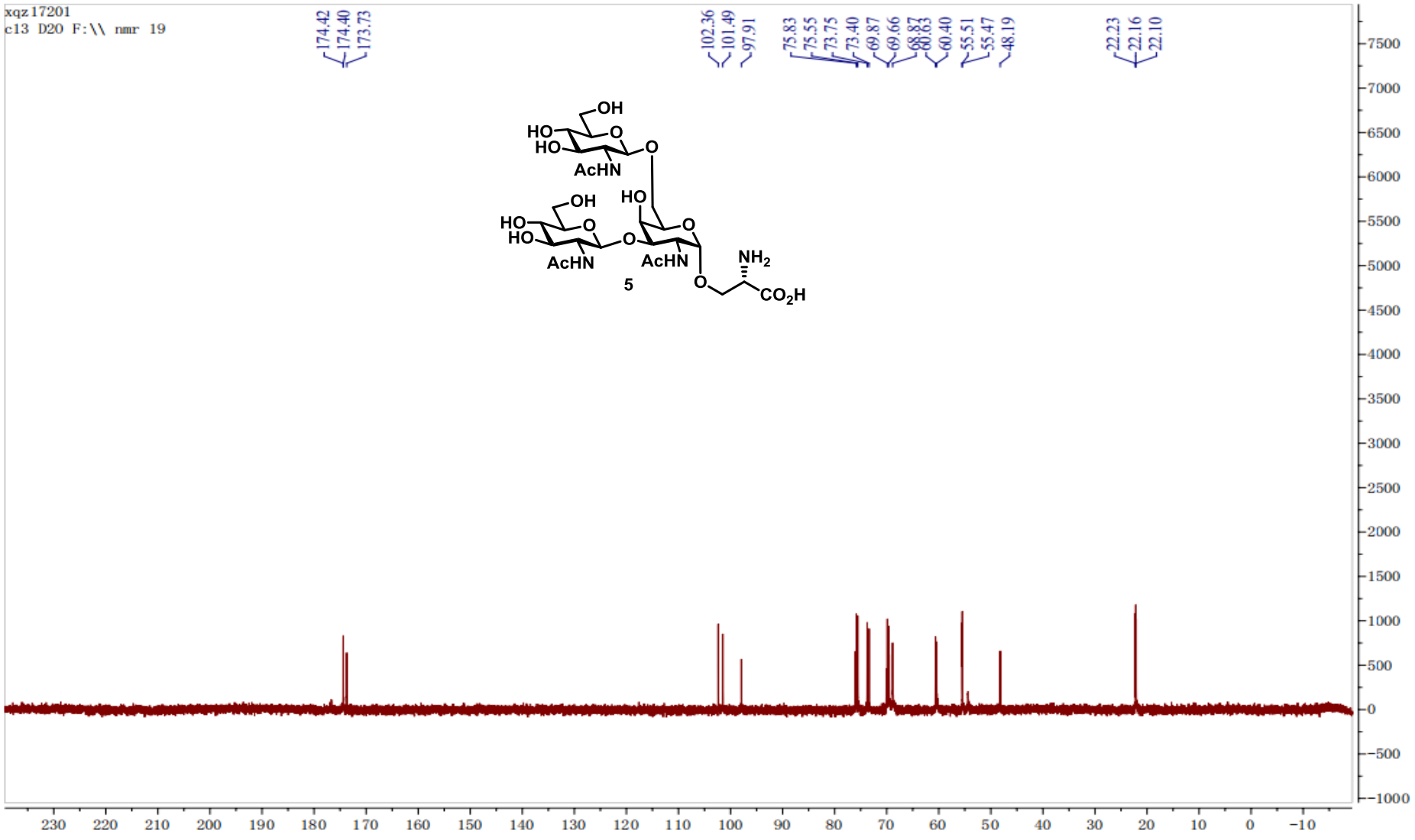

OBz
BzO
BzO
O
TrocHN
29
BzO
OBz
BzO
O
BzO
TrocHN
O
N3
NHCbz
O
CO2Bn
f1 (ppm)

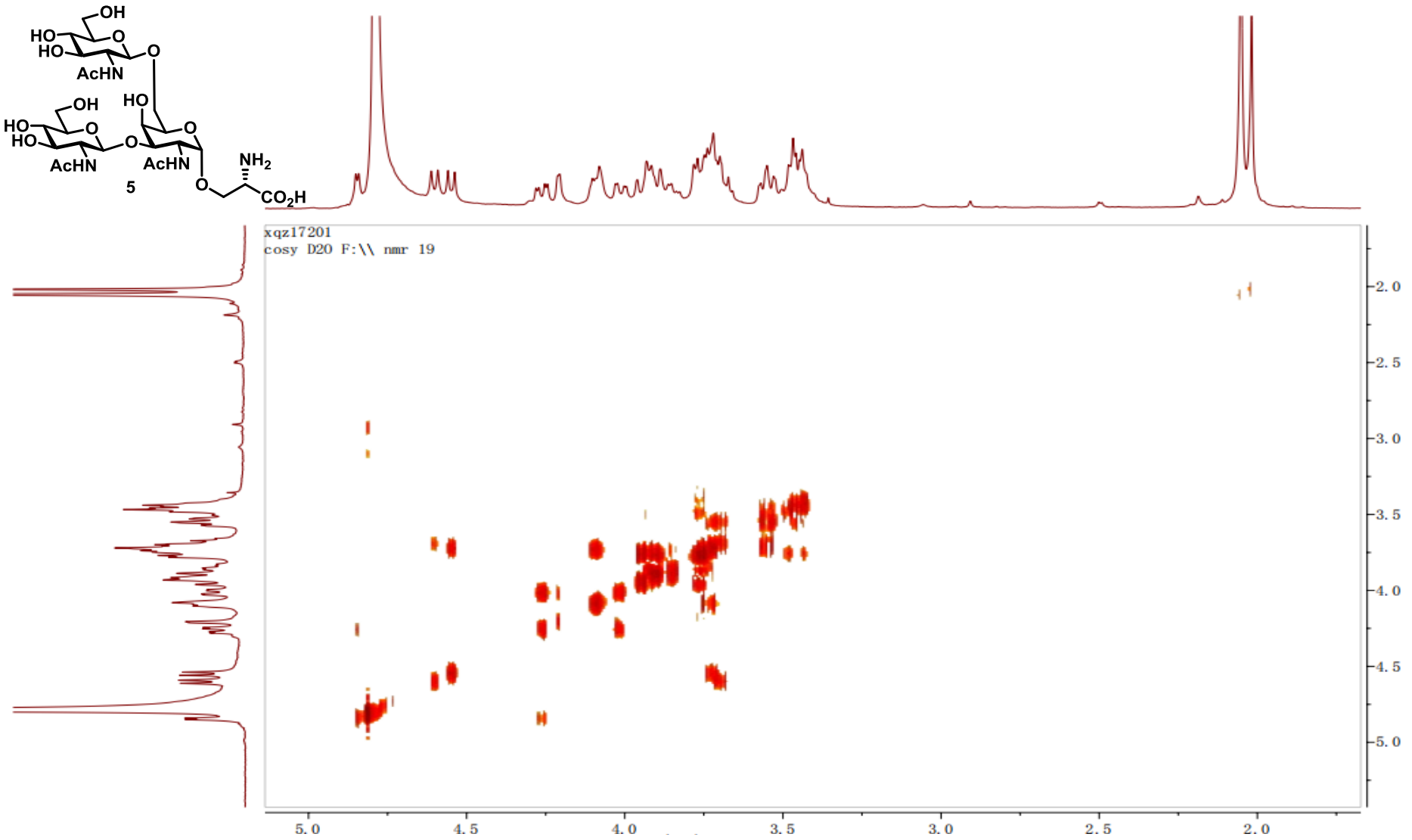

OBz
BzO
BzO
O
TrocHN
29
BzO
OBz
BzO
BzO
O
TrocHN
N3
NHCbz
CO2Bn
f1 (ppm)

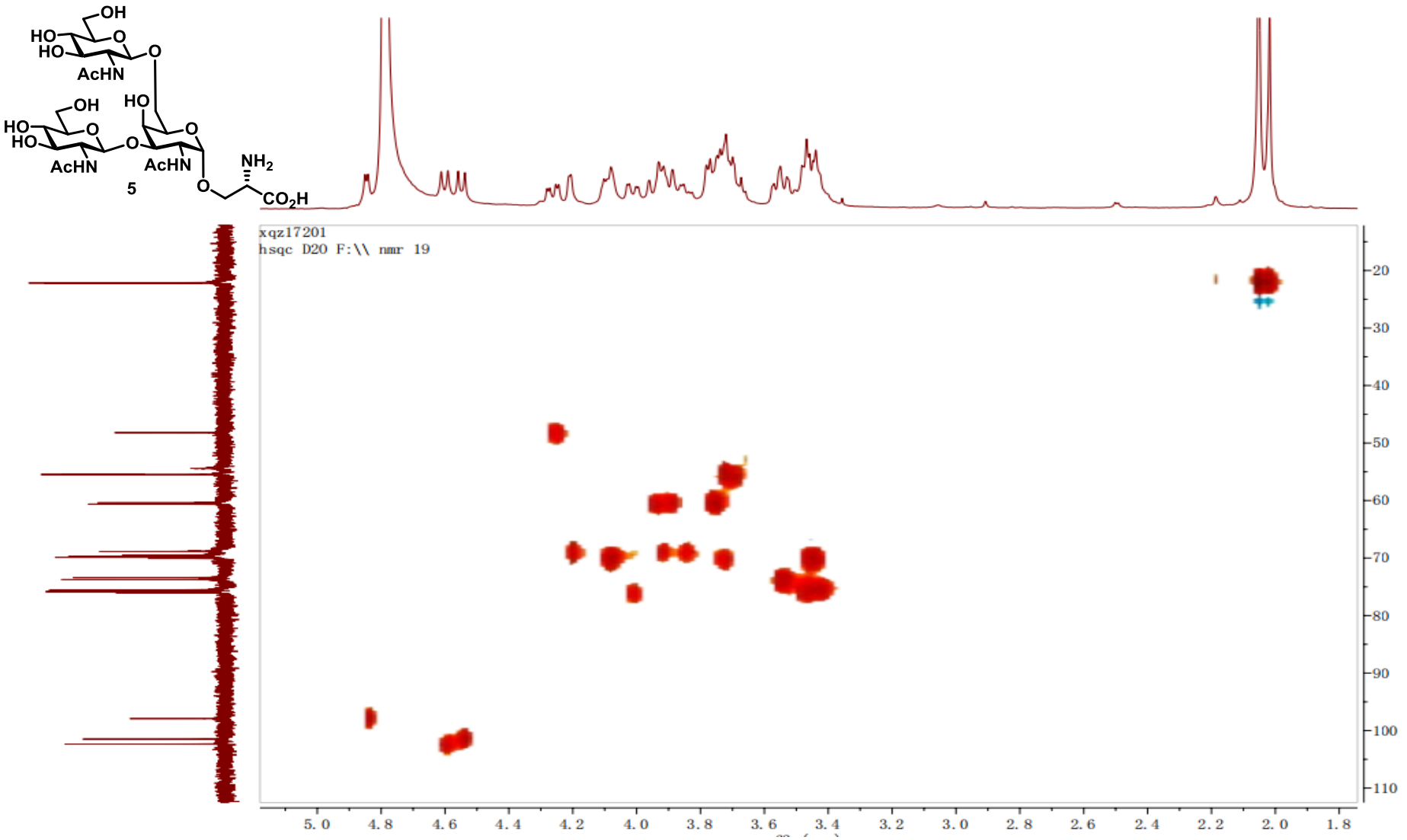

OBz
BzO
BzO
TrocHN
O
29
BzO
OBz
BzO
BzO
TrocHN
O
O
N3
NHCbz
O
CO2Bn
f2 (ppm)
f1 (ppm)

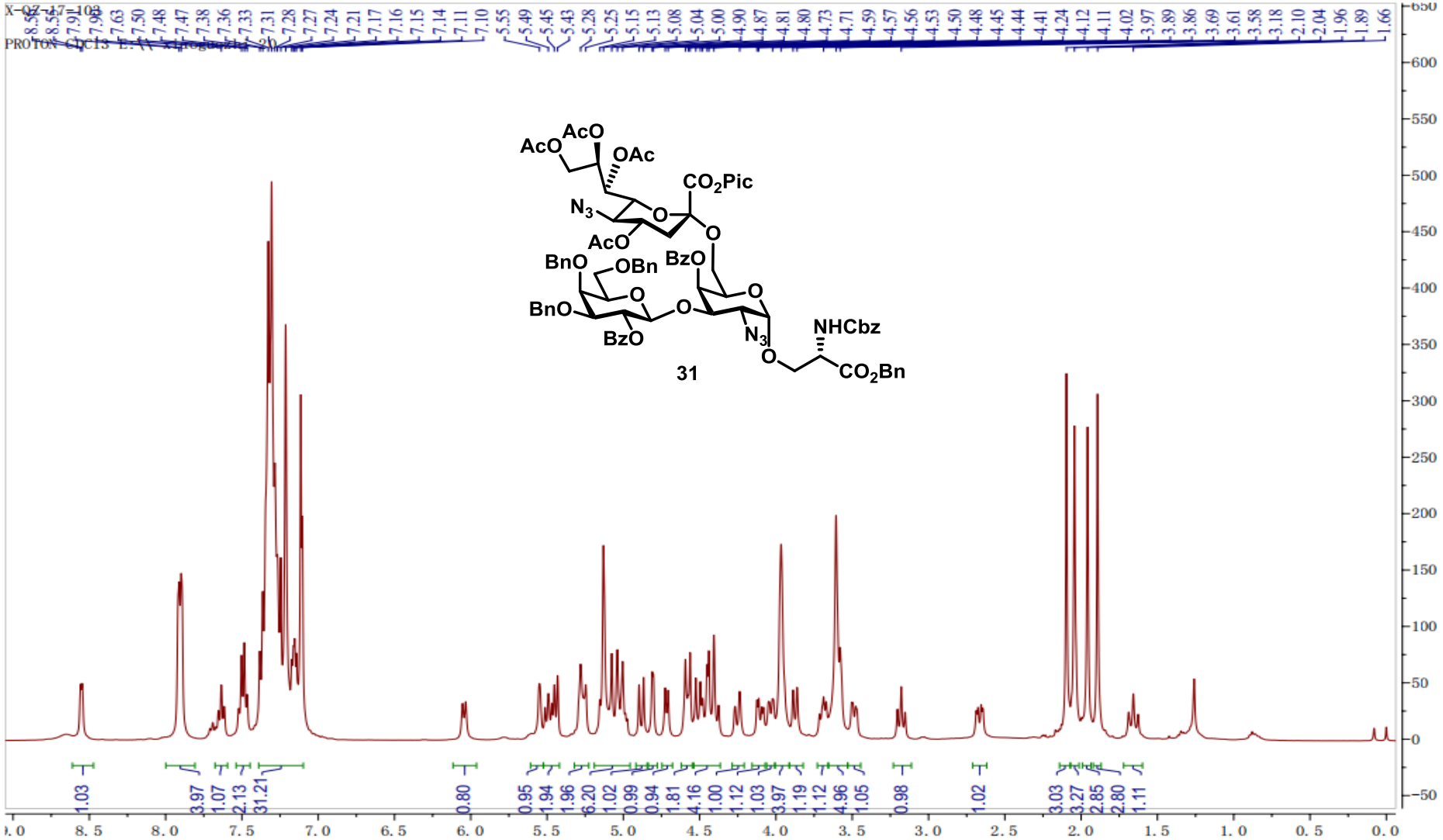

Skx--6-101B-2.5.ser
Skx--6-101B-2
HSQCGP CDCl3 E:\\ xiaoguozhi 18
OBz
BzO
O
BzO
TrocHN
O
29
BzO
OBz
BzO
O
BzO
TrocHN
O
O
N3
NHCbz
O
CO2Bn
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f2 (ppm)
45 50 55 60 65 70 75 80 85 90 95 100 105 110
f1 (ppm)

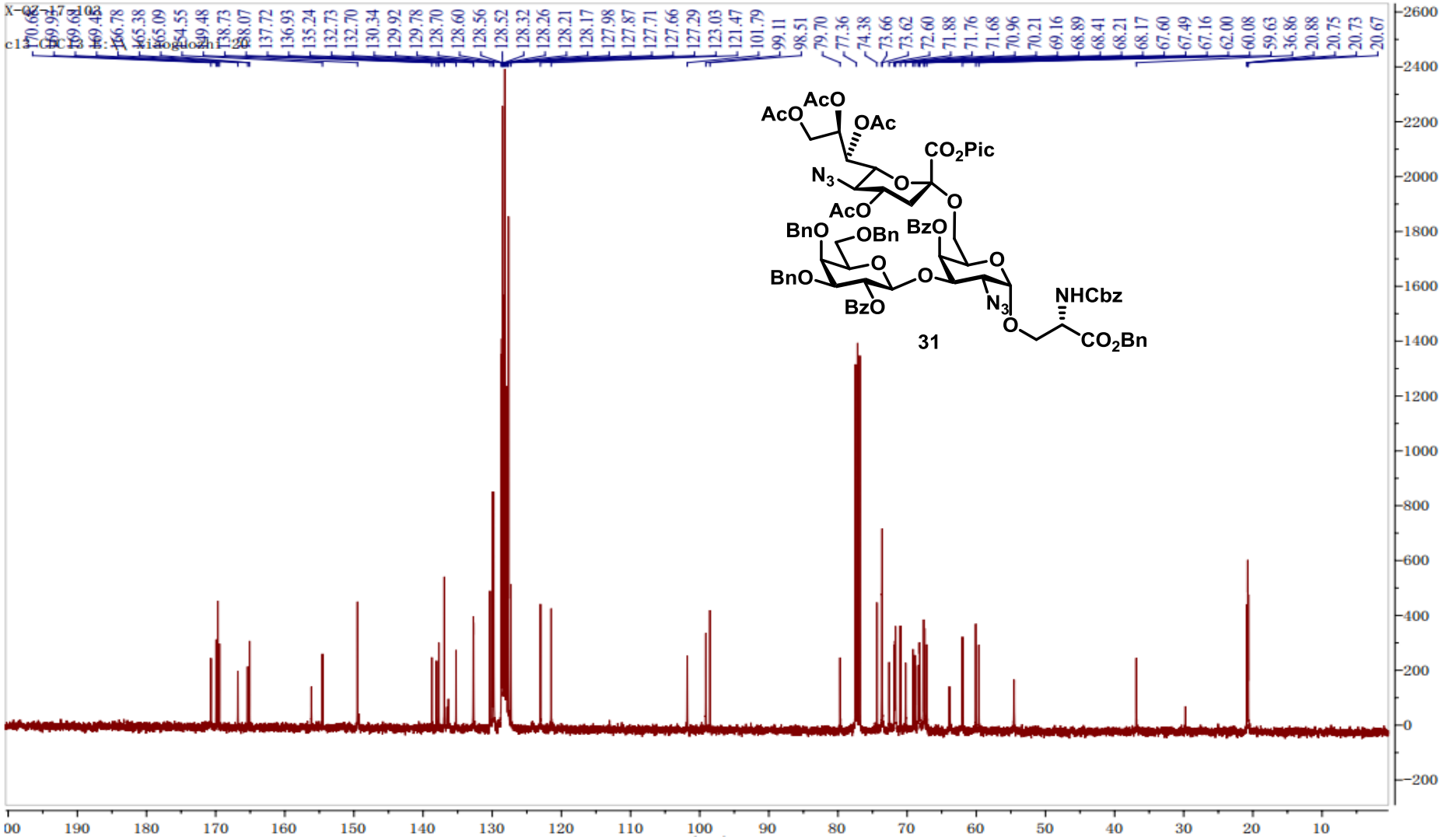

X-QZ-17-20-1
PROTON D20 E:\\ xiaoguozhi 11
4.85
4.84
4.79
4.61
4.59
4.56
4.54
4.21
4.08
3.93
3.92
3.89
3.78
3.77
3.75
3.74
3.72
3.70
3.67
3.55
3.53
3.48
3.47
3.46
3.45
2.05
2.02
OH
HO
HO
O
AcHN
HO
OH
HO
HO
O
O
AcHN
AcHN
NH2
5
O
CO2H
1.01
1.18
1.19
1.00
1.02
1.99
1.06
4.14
6.41
1.98
4.28
6.08
3.21
6.5
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

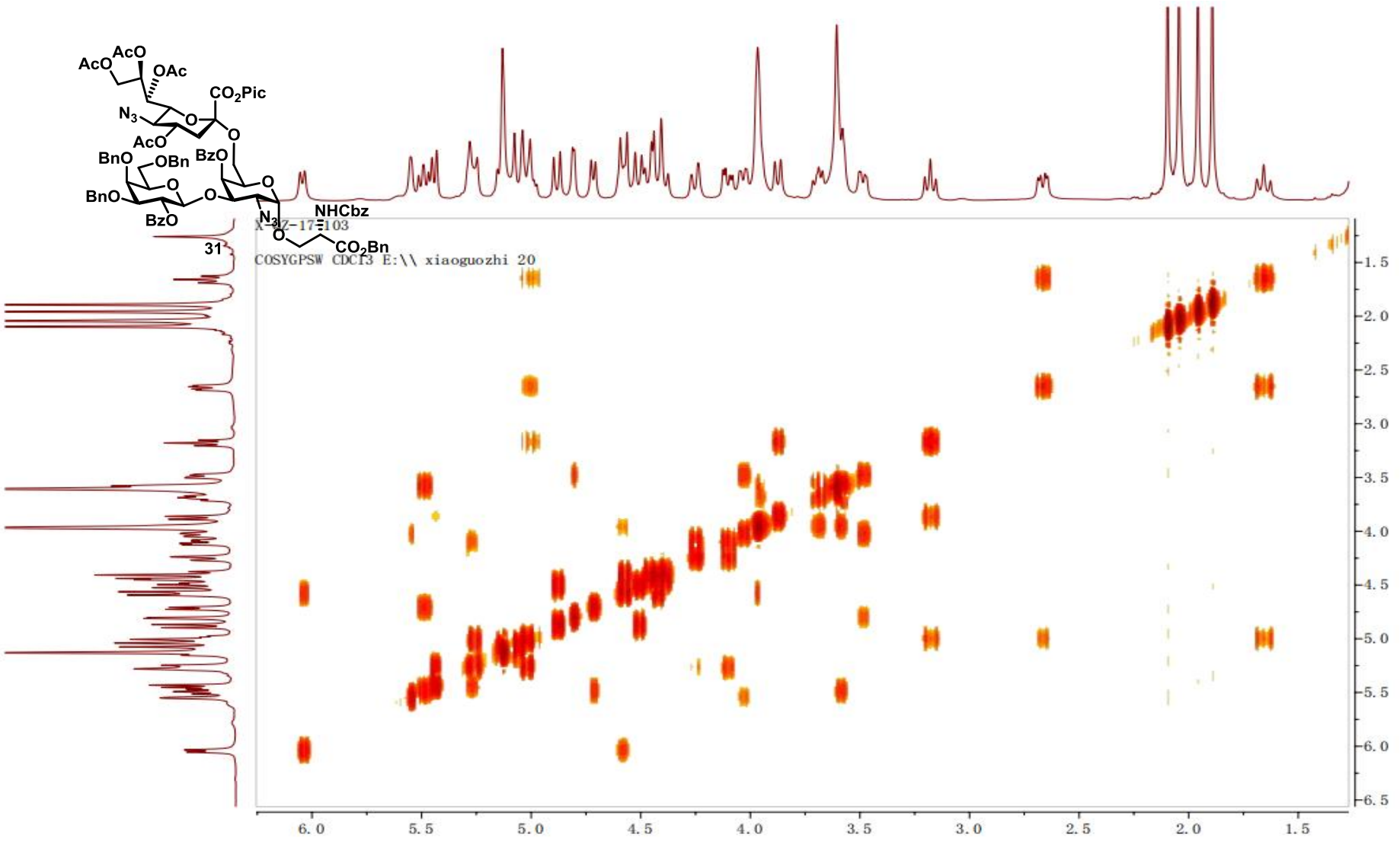

xqz17201
c13 D20 F:\\ nmr 19
174.42
174.40
173.73
102.36
101.49
97.91
75.83
75.55
73.75
73.40
69.87
69.66
68.87
60.83
60.40
55.51
55.47
48.19
22.23
22.16
22.10
OH
HO
HO
O
AcHN
HO
OH
HO
HO
O
O
O
AcHN
AcHN
NH2
5
O
CO2H
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

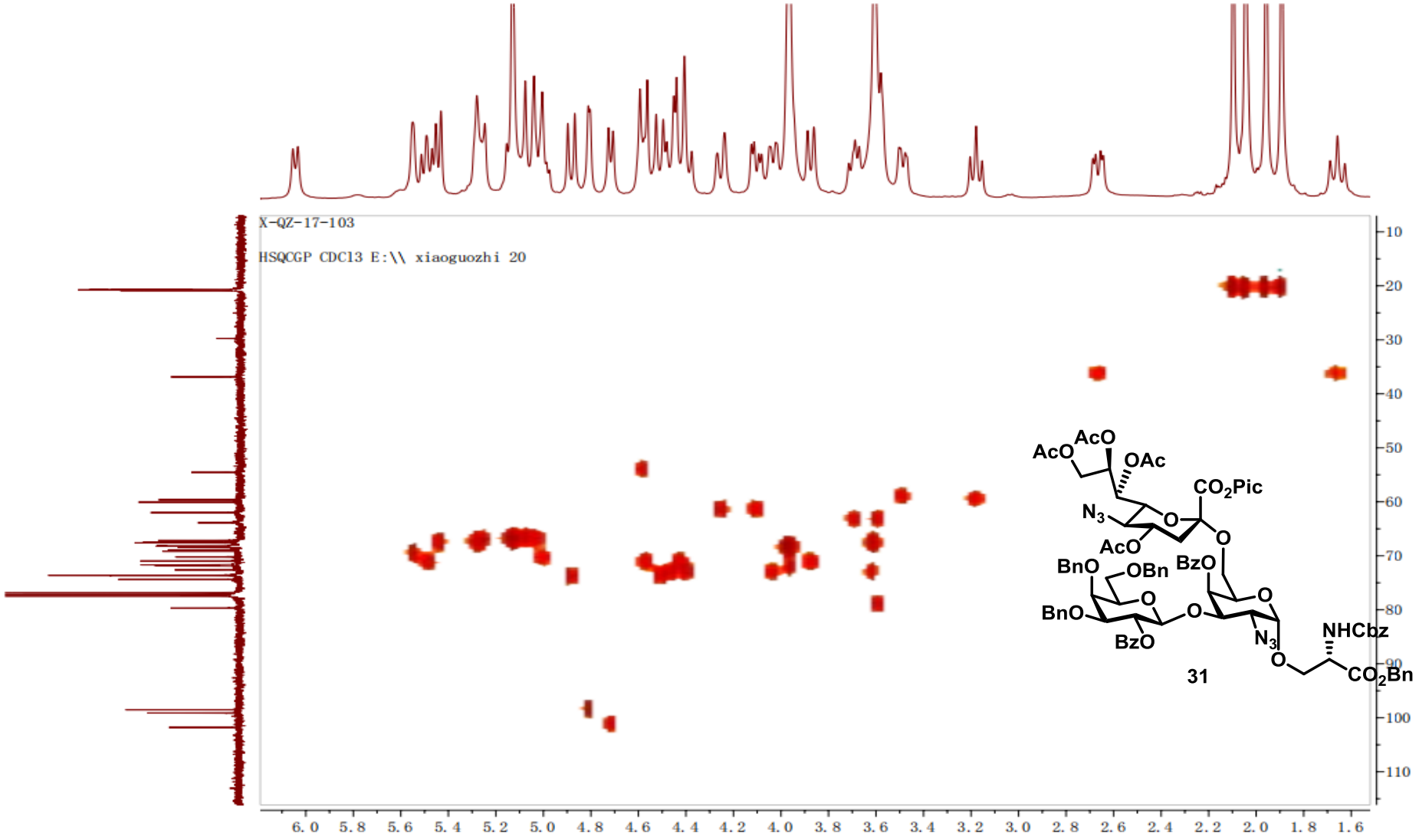

OH
HO
HO
O
AcHN
OH
HO
HO
O
O
AcHN
AcHN
O
NH2
CO2H
5
xqz17201
cosy D20 F:\\ nmr 19
5.0
4.5
4.0
3.5
3.0
2.5
2.0

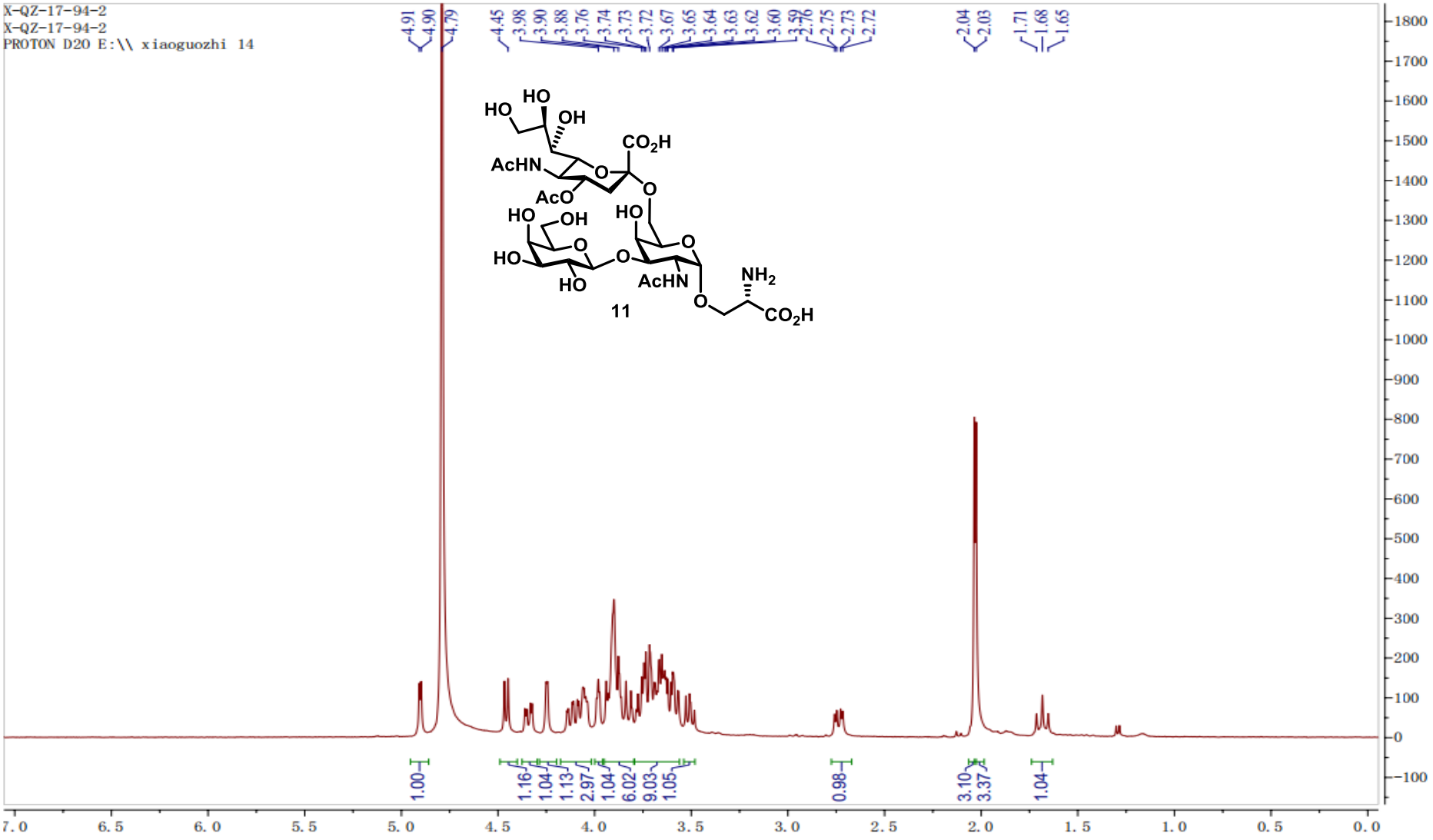

OH
HO
HO
O
O
AcHN
OH
HO
HO
O
O
AcHN
AcHN
O
NH2
CO2H
5
xqz17201
hsqc D20 F:\\ nmr 19
20
30
40
50
60
70
80
90
100
110
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8

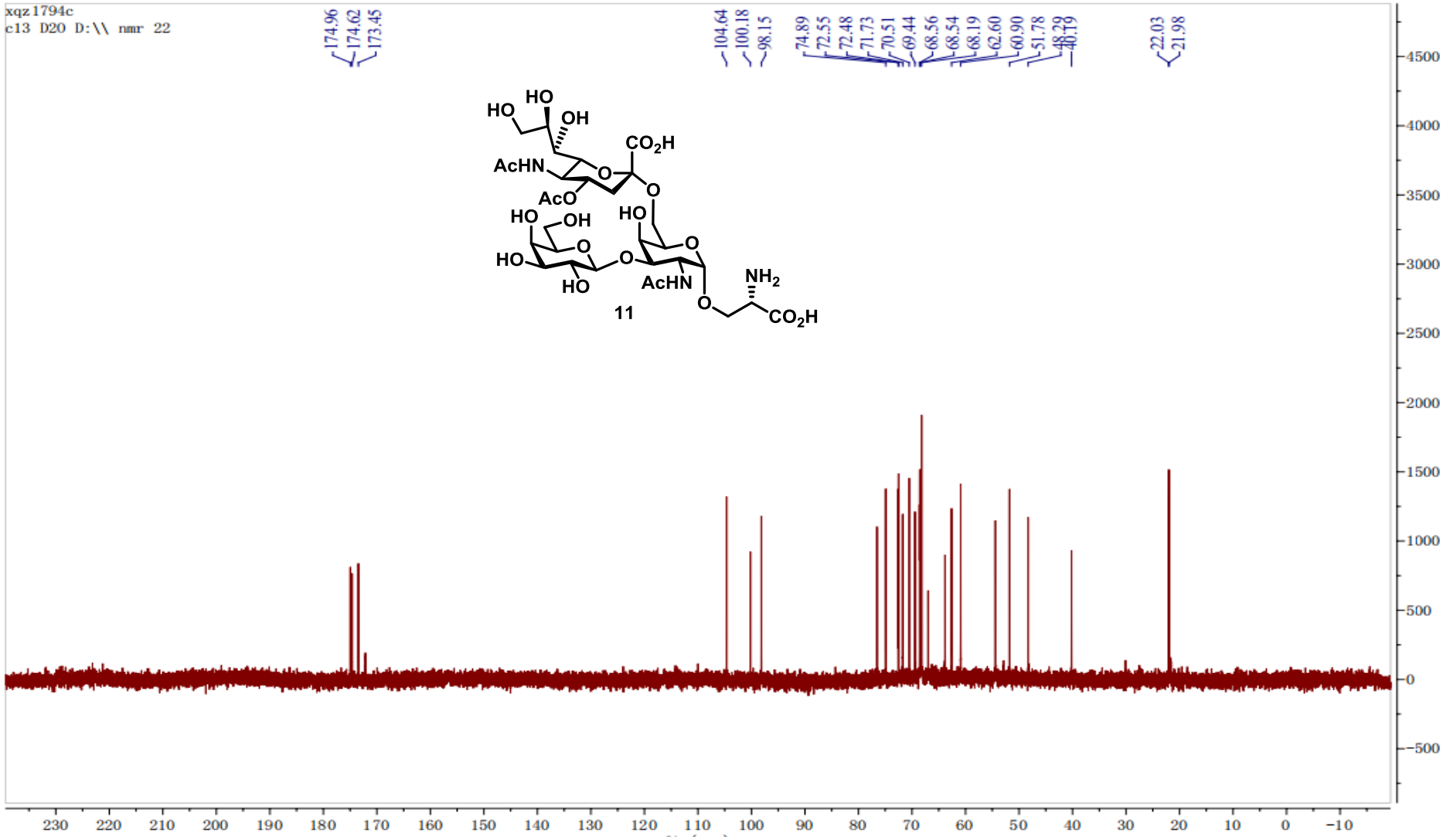

AcO
AcO
OAc
CO2Pic
N3
O
AcO
O
BnO
OBn
BzO
O
O
BnO
O
O
N3
NHCbz
O
CO2Bn
BzO
31

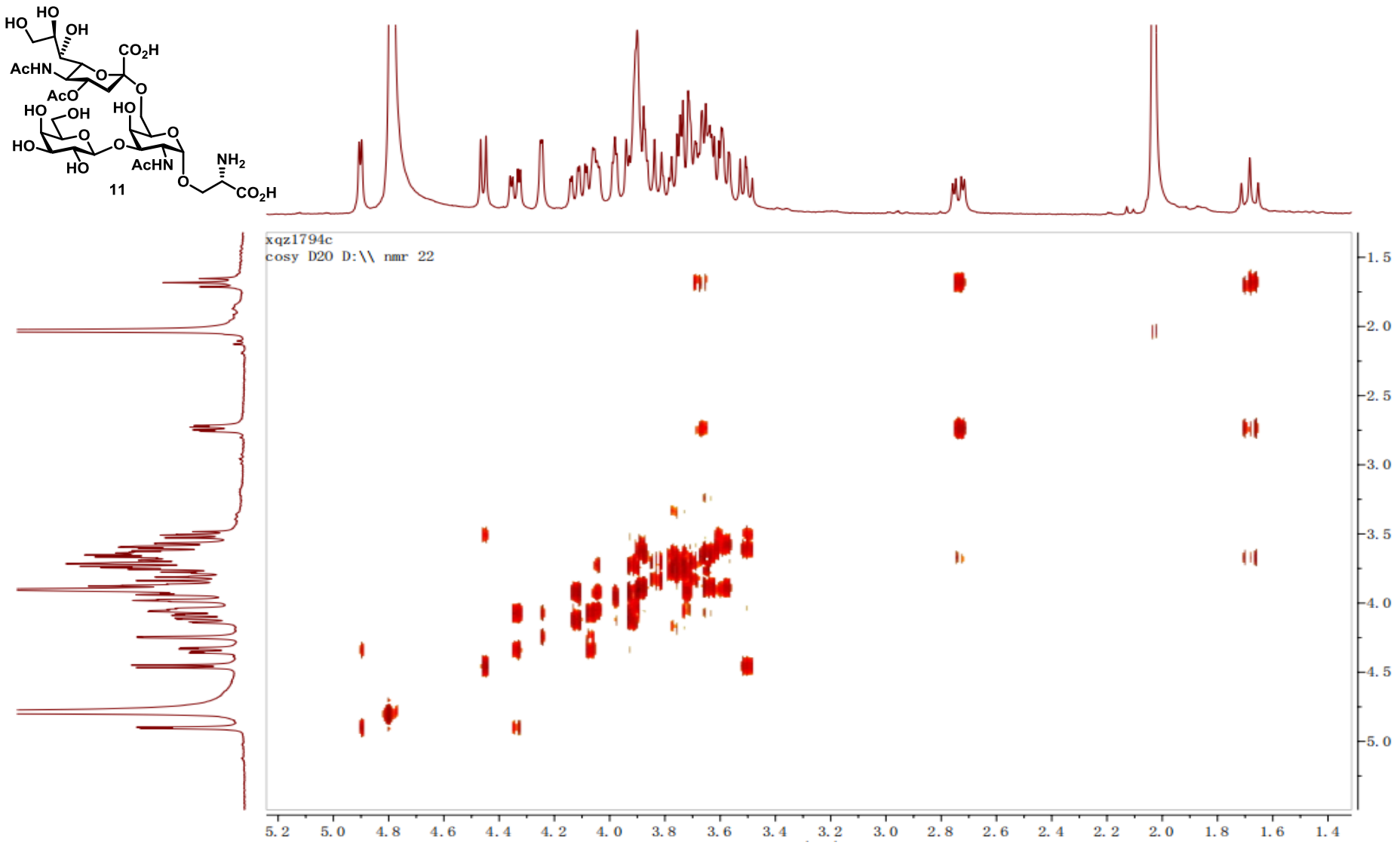

AcO
AcO
OAc
CO2Pic
N3
O
AcO
BnO
OBn
BzO
O
BnO
O
O
O
N3
NHCbz
BzO
O
CO2Bn
31

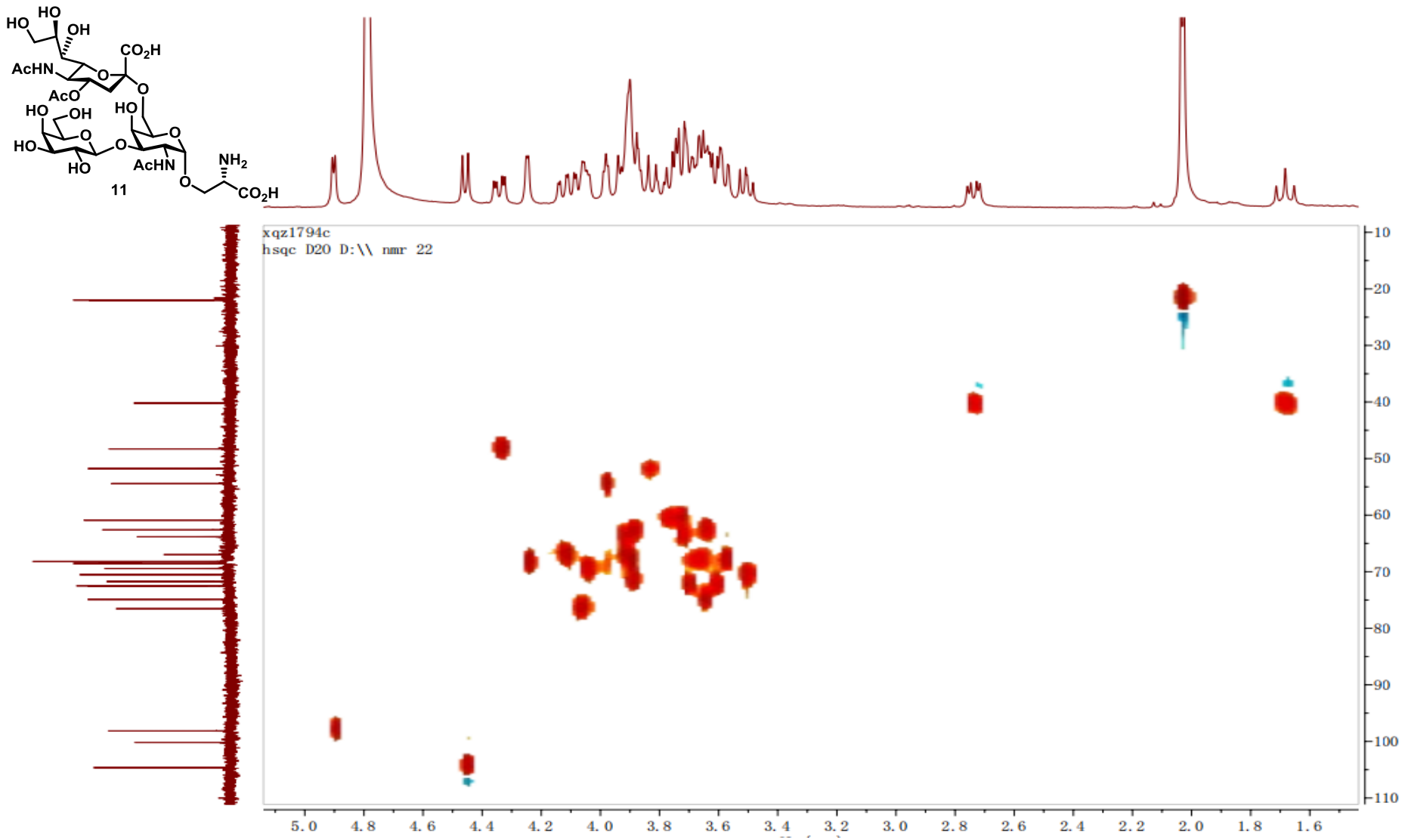

AcO
AcO
OAc
CO2Pic
N3
O
AcO
BnO
OBn
BzO
O
BnO
O
O
BzO
O
N3
NHCbz
O
CO2Bn
31
X-SZ-17-103
COSYGPSW CDCl3 E:\\ xiaoguozhi 20
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5

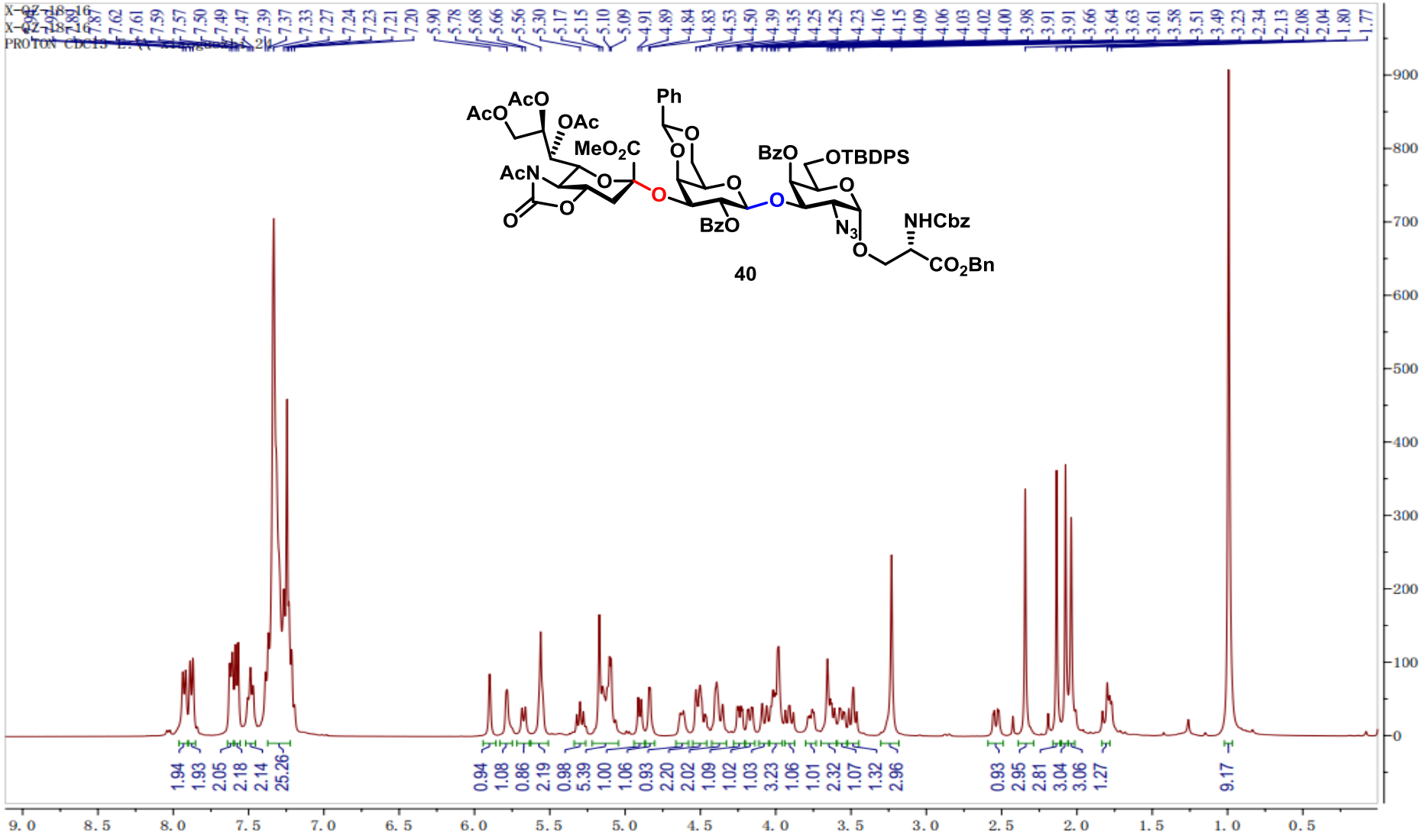

X-QZ-17-103
HSQCGP CDCl3 E:\\ xiaoguozhi 20
AcO
AcO
OAc
CO2Pic
N3
O
AcO
O
BnO
OBn
BzO
O
BnO
O
O
O
BzO
N3
NHCbz
O
CO2Bn
31
10
20
30
40
50
60
70
80
90
100
110
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

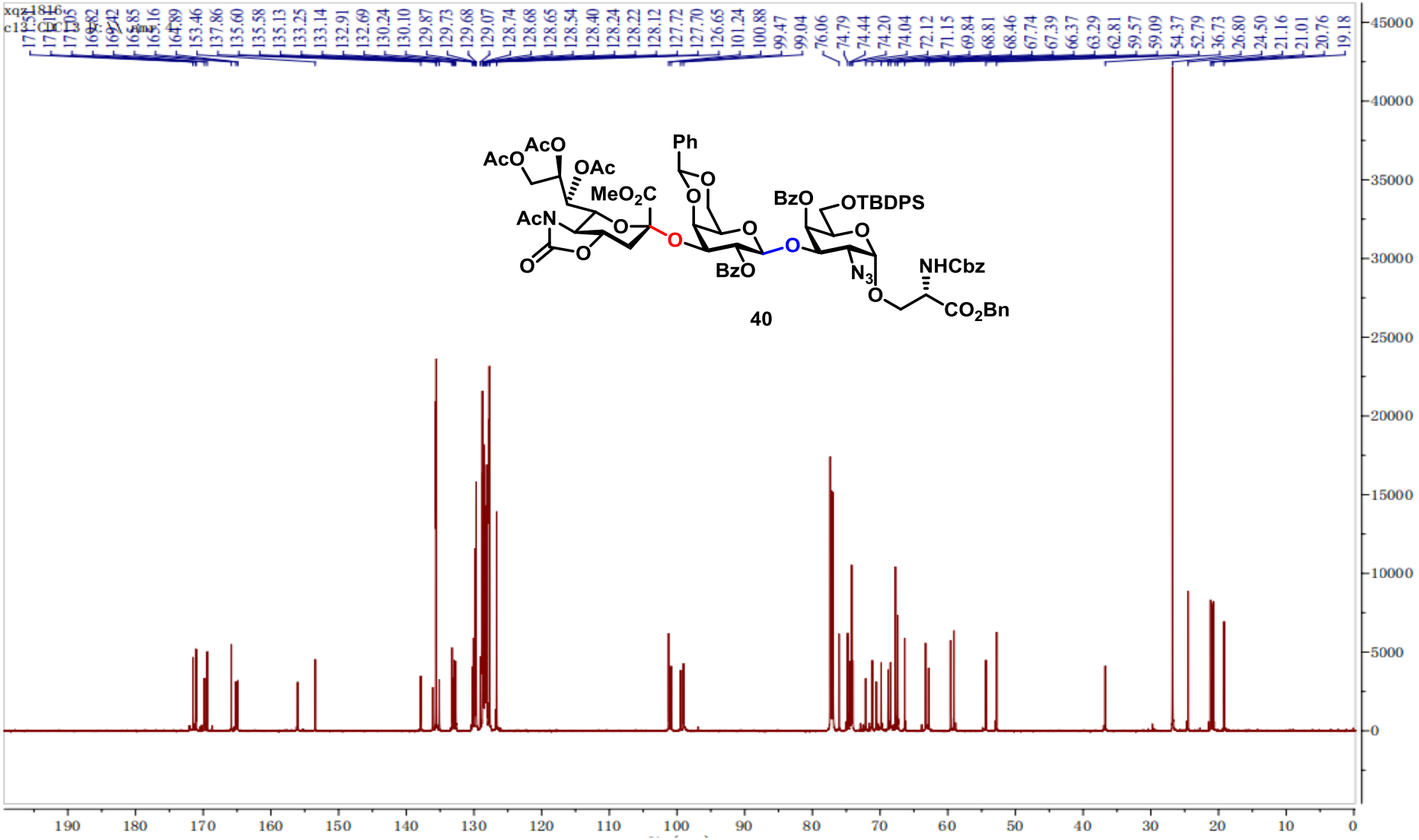

X-QZ-17-94-2
X-QZ-17-94-2
PROTON D2O E:\\ xiaoguozhi 14
4.91
4.90
4.79
4.45
3.98
3.90
3.88
3.76
3.74
3.73
3.72
3.67
3.65
3.64
3.63
3.62
3.60
3.59
2.76
2.75
2.73
2.72
2.04
2.03
1.71
1.68
1.65
HO
HO
OH
CO2H
AcHN
O
AcO
HO
OH
HO
O
HO
HO
O
AcHN
NH2
O
CO2H
11
1.00
1.16
1.04
1.13
2.97
1.04
6.02
9.03
1.05
0.98
3.10
3.37
1.04
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
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

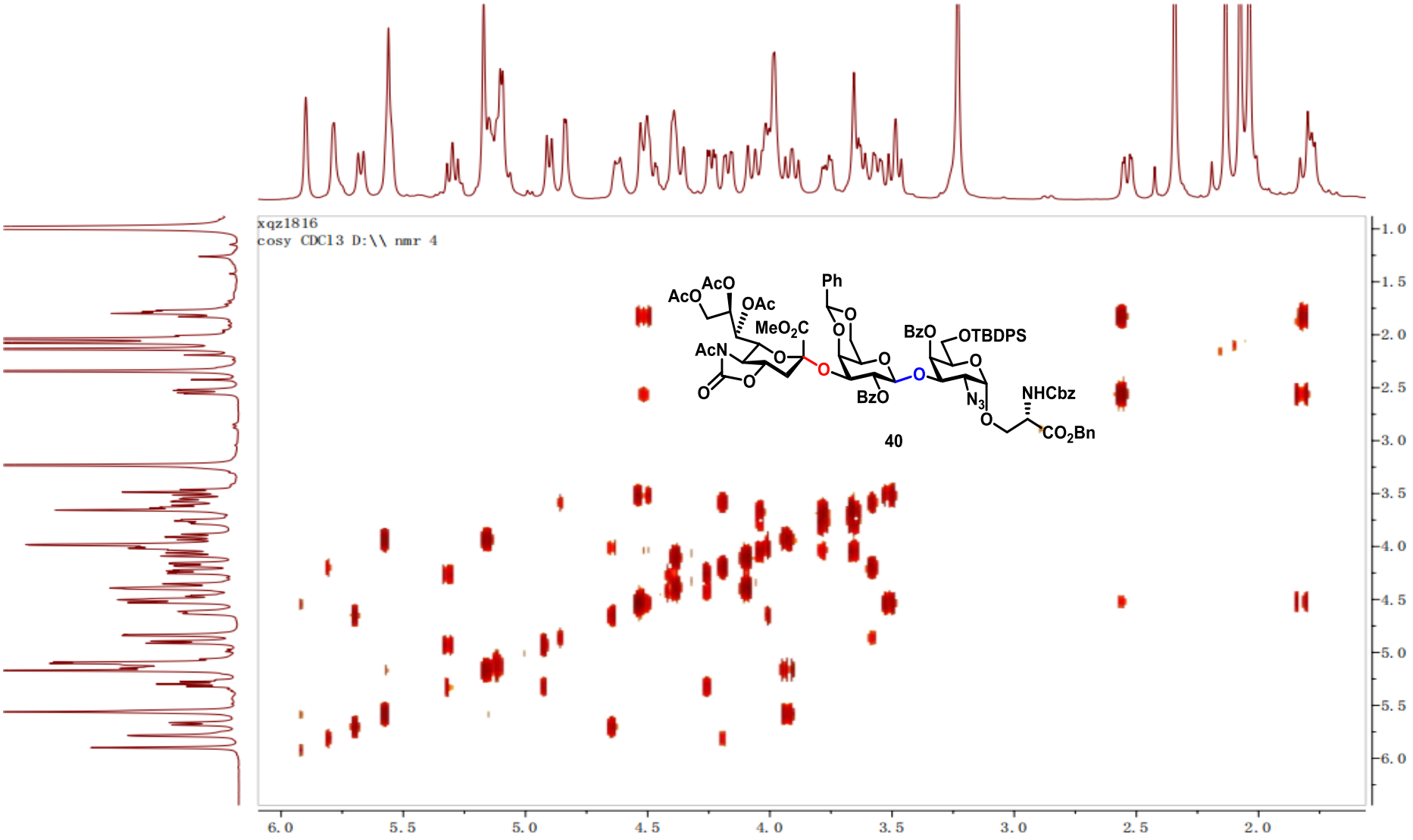

xqz1794c
c13 D20 D:\\ nmr 22
174.96
174.62
173.45
104.64
100.18
98.15
74.89
72.55
72.48
71.73
70.51
69.44
68.56
68.54
68.19
62.60
60.90
51.78
48.29
40.19
22.03
21.98
HO
HO
OH
CO2H
AcHN
O
AcO
HO
OH
HO
O
HO
HO
O
AcHN
NH2
O
CO2H
11
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

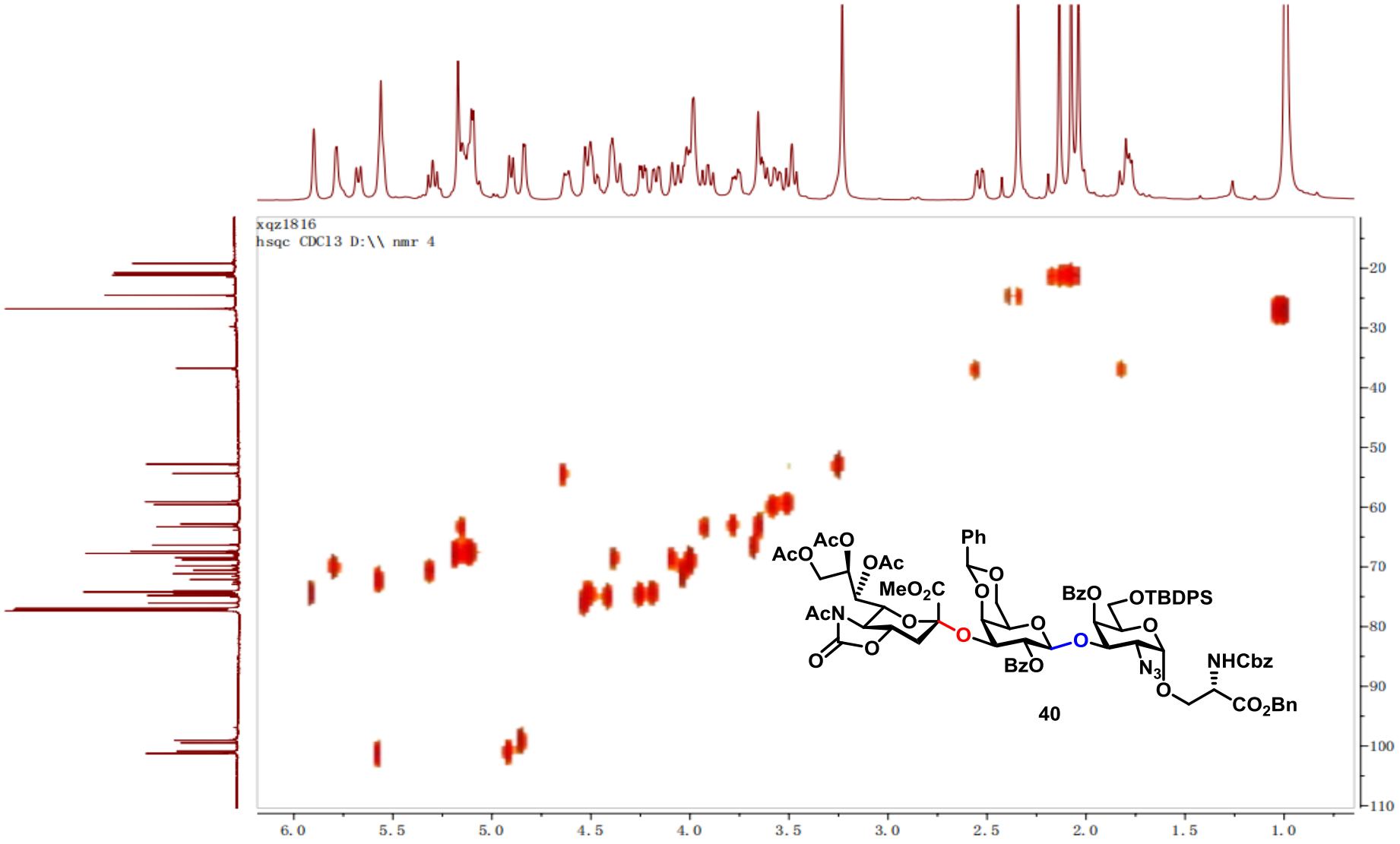

HO
HO
OH
CO2H
AcHN
AcO
HO
HO
OH
HO
HO
AcHN
NH2
CO2H
11
xqz1794c
cosy D20 D:\\ nmr 22
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

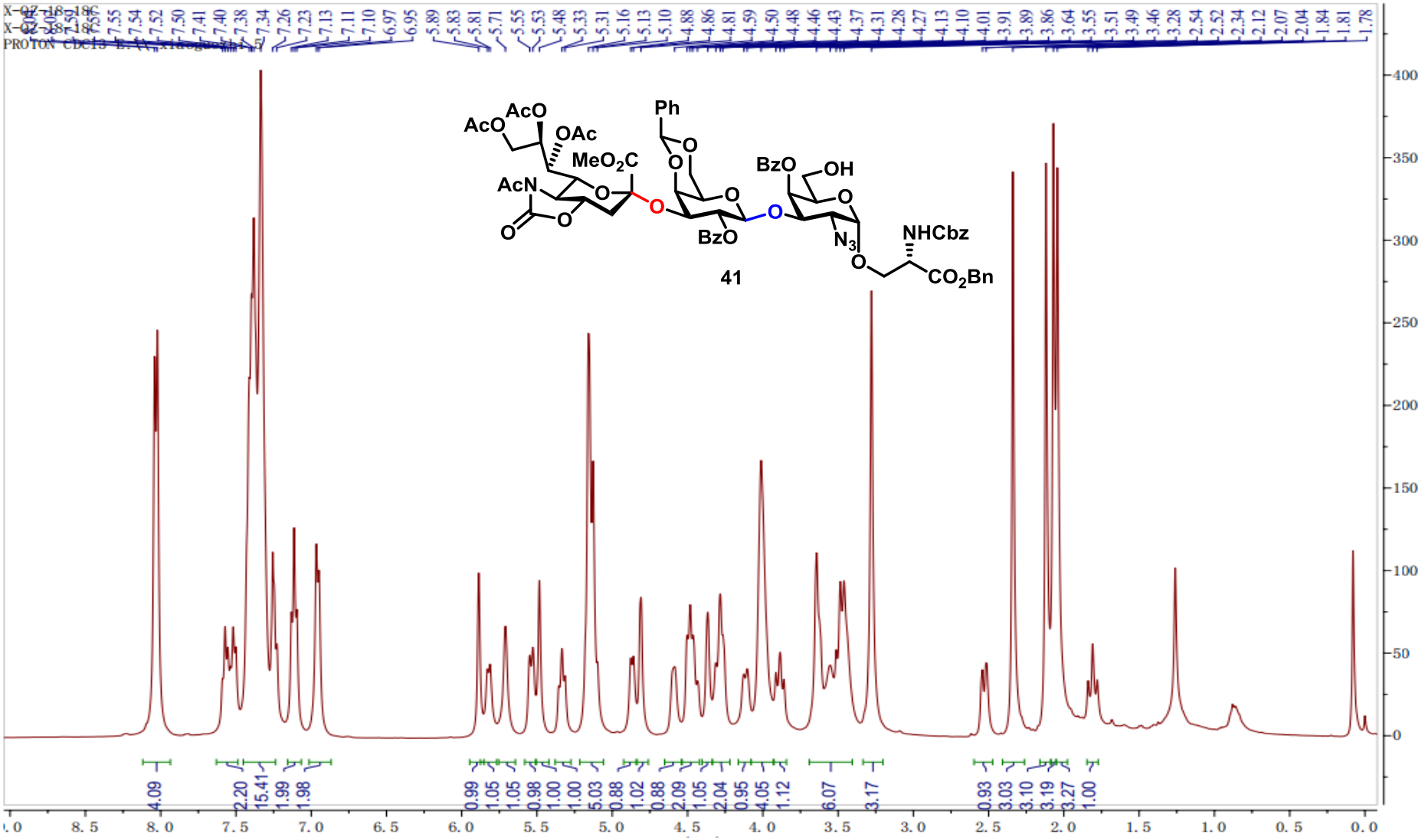

xqz1794c
hsqc D2O D:\\ nmr 22
11

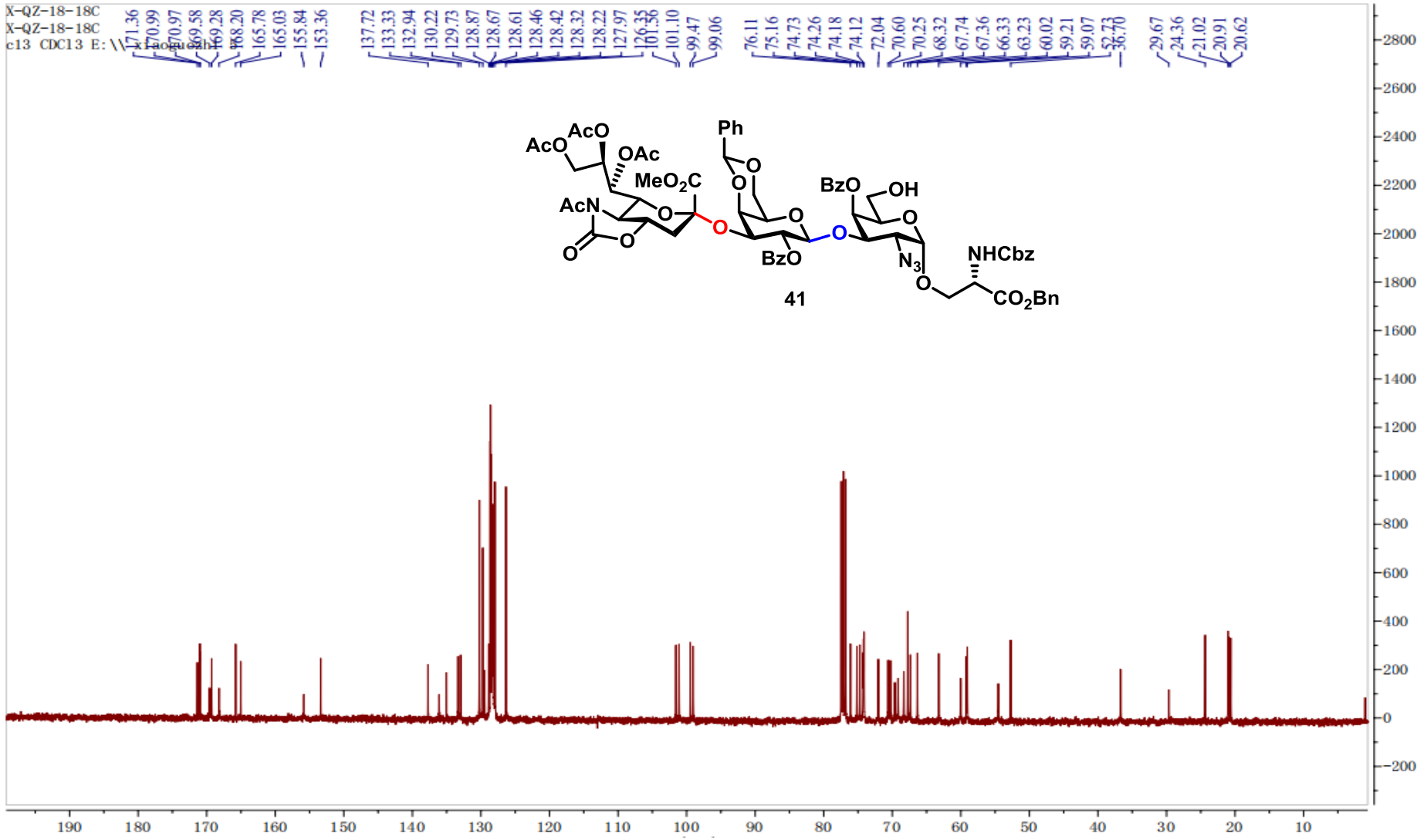

AcO
AcO
OAc
MeO2C
AcN
O
O
Ph
O
O
O
BzO
OTBDPS
O
BzO
N3
NHCbz
O
CO2Bn
40
1.94
1.93
2.05
2.18
2.14
25.26
0.94
1.08
0.86
2.19
0.98
5.39
1.00
1.06
0.93
2.20
2.02
1.09
1.02
1.03
3.23
1.06
1.01
2.32
1.07
1.32
2.96
0.93
2.95
2.81
3.04
3.06
1.27
9.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
900
800
700
600
500
400
300
200
100
0

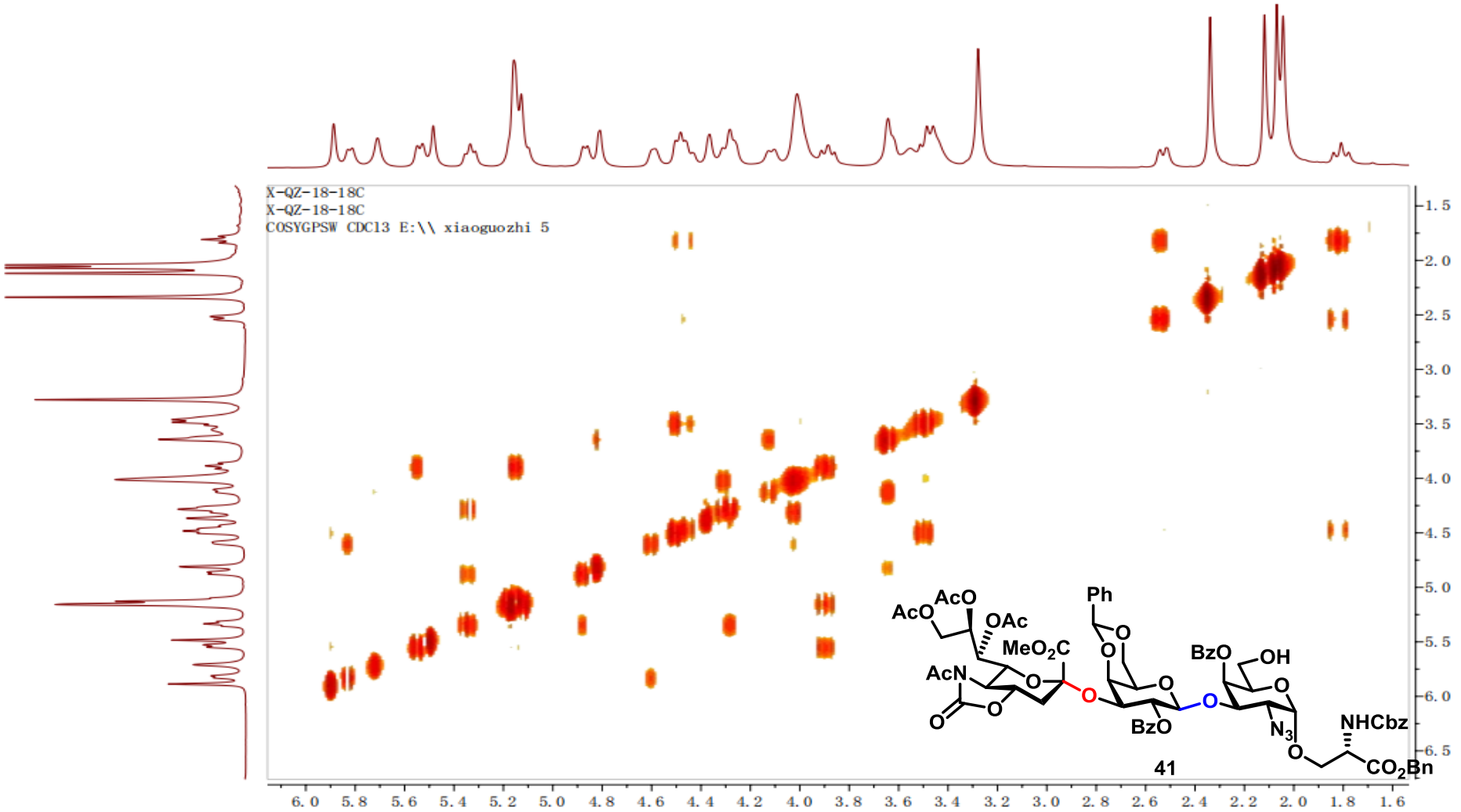

xqz-1816
c13 CDCl3
AcO
AcO
OAc
MeO2C
AcN
O
O
O
O
O
Ph
O
O
O
BzO
BzO
OTBDPS
O
O
N3
NHCbz
CO2Bn
40
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

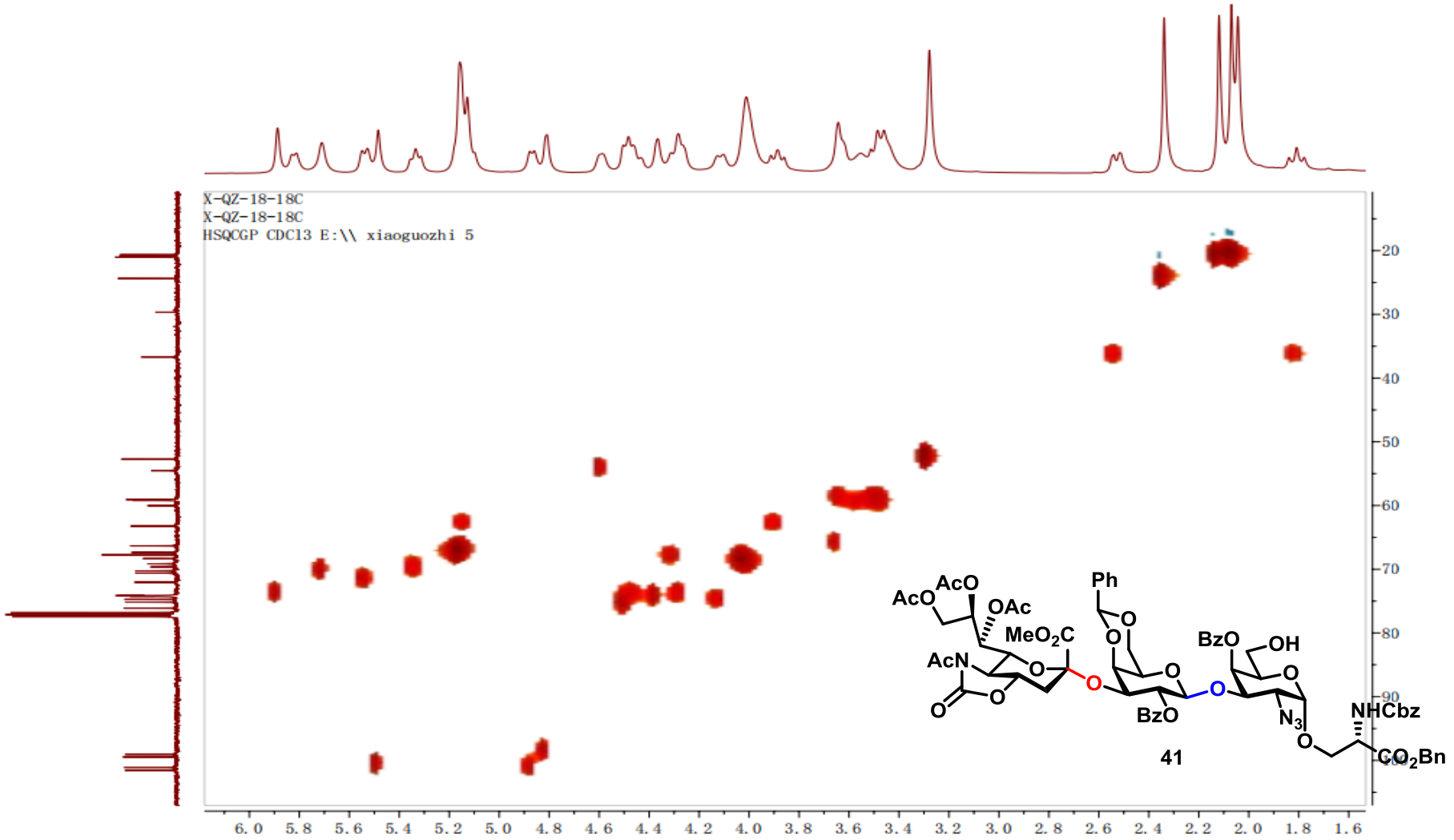

xqz1816
cosy CDCl3 D:\\ nmr 4
AcO
AcO
OAc
MeO2C
AcN
O
O
O
Ph
O
O
O
BzO
BzO
OTBDPS
O
O
N3
NHCbz
O
CO2Bn
40
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

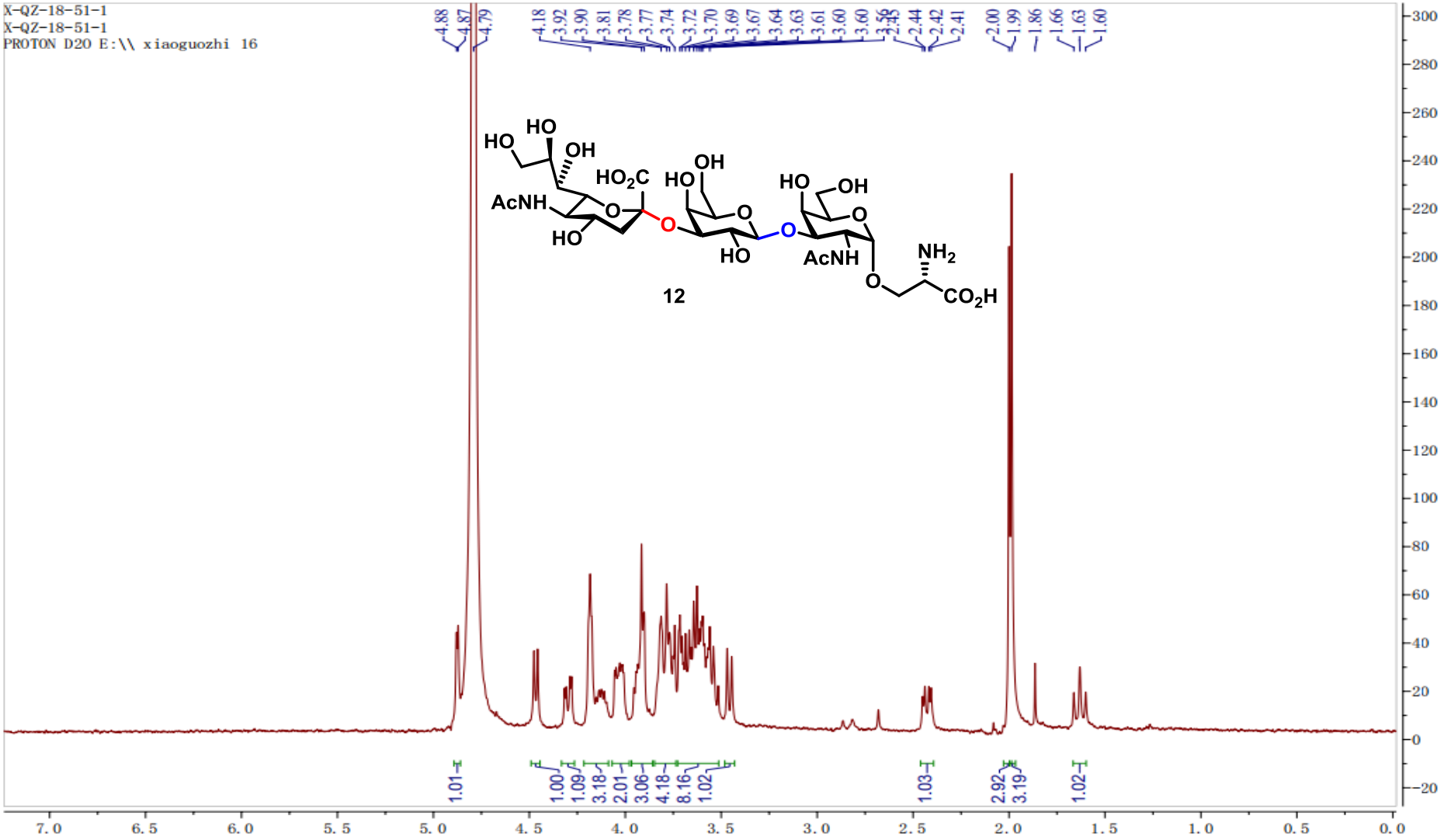

xqz1816
hsqc CDCl3 D:\\ nmr 4
AcO
AcO
OAc
MeO2C
AcN
O
O
O
Ph
O
O
O
BzO
BzO
OTBDPS
O
N3
O
NHCbz
CO2Bn
40
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

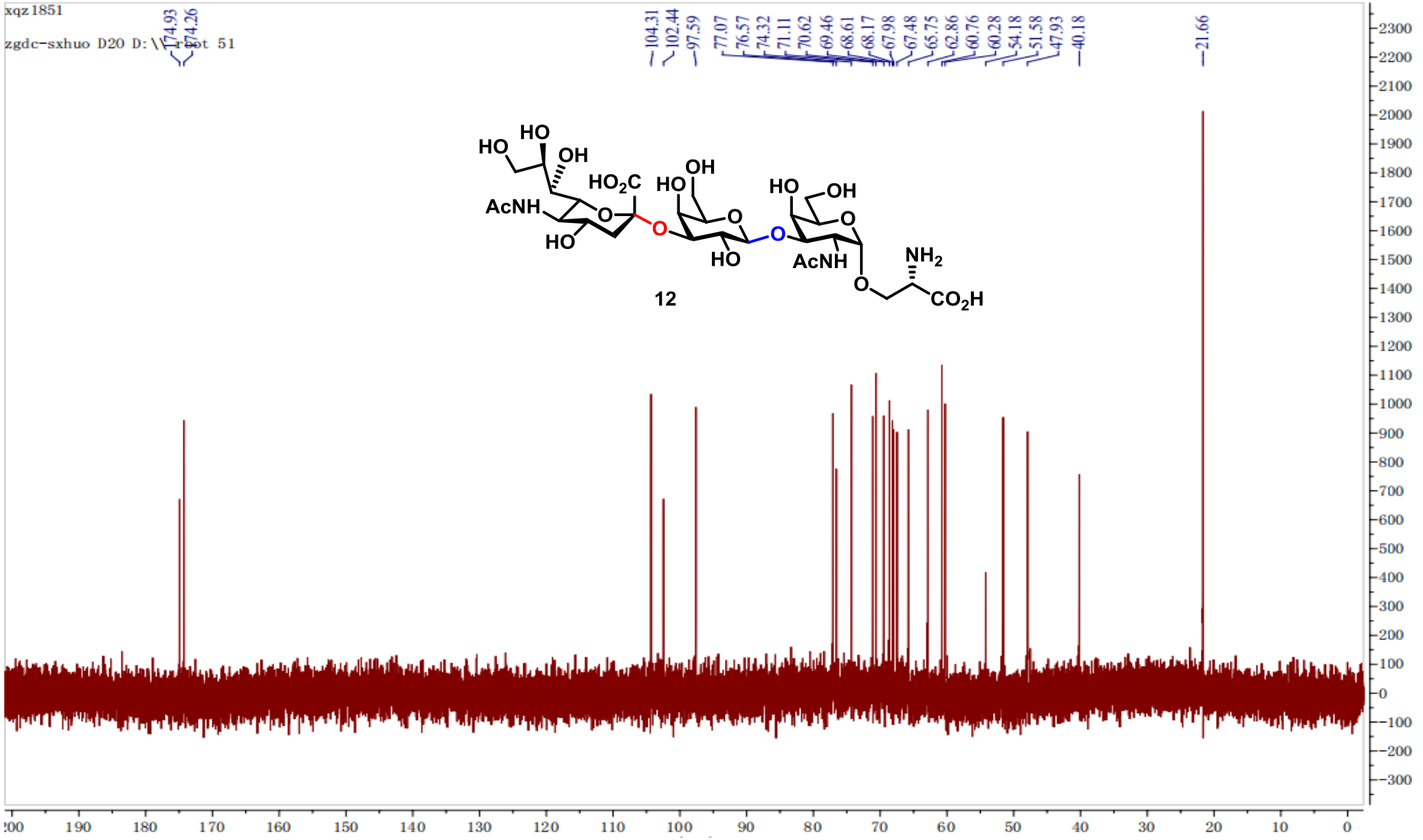

AcO
AcO
OAc
MeO2C
AcN
O
O
O
O
Ph
O
O
O
BzO
BzO
OH
O
O
N3
O
NHCbz
CO2Bn
41

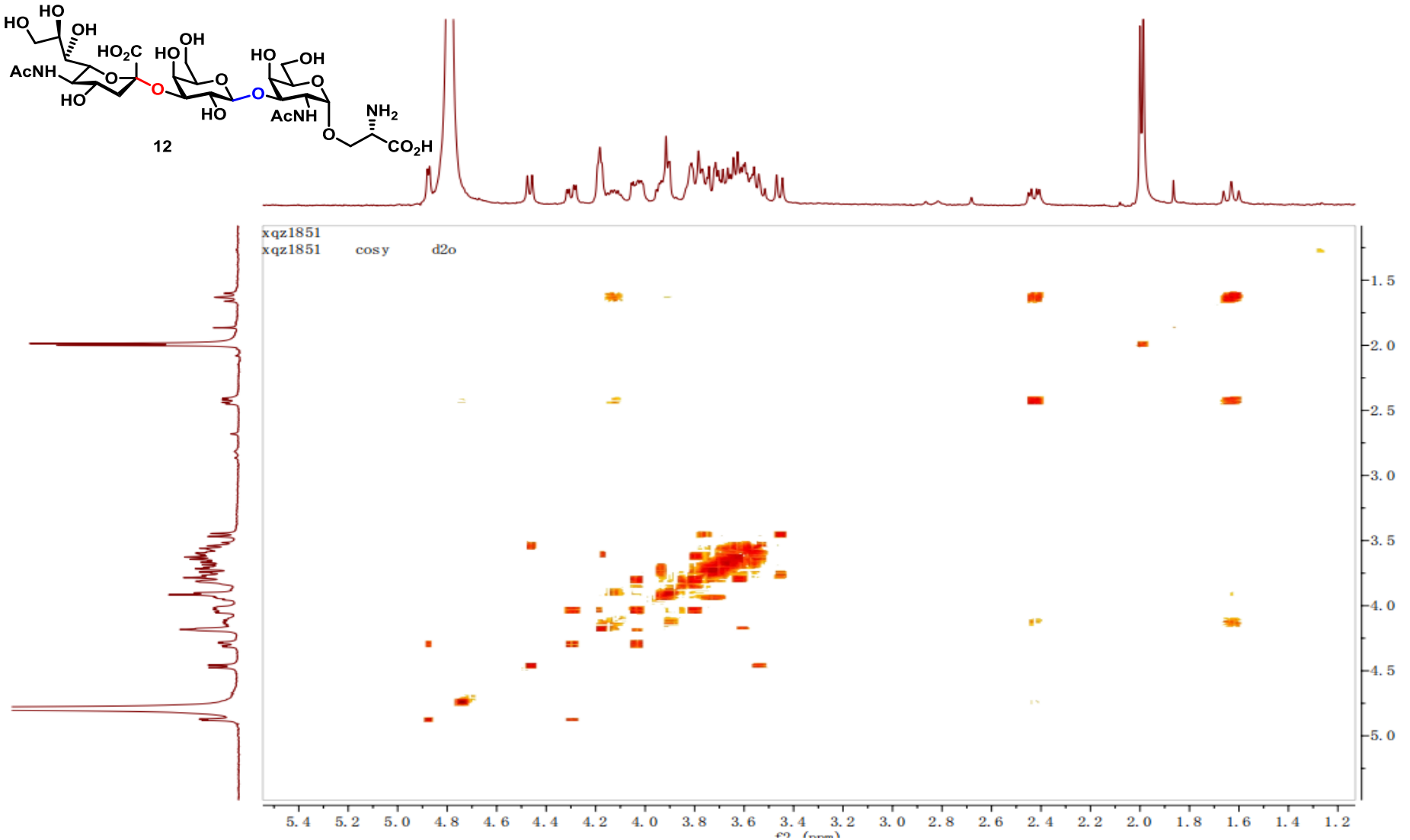

X-QZ-18-18C
X-QZ-18-18C
c13 CDC13 E:\\xiaoguoah
171.36
170.99
170.97
169.58
169.28
168.20
165.78
165.03
155.84
153.36
137.72
133.33
132.94
130.22
129.73
128.87
128.67
128.61
128.46
128.42
128.32
128.22
127.97
126.35
101.36
101.10
99.47
99.06
76.11
75.16
74.73
74.26
74.18
74.12
72.04
70.60
70.25
68.32
67.74
67.36
66.33
63.23
60.02
59.21
59.07
52.73
36.70
29.67
24.36
21.02
20.91
20.62
AcO
AcO
OAc
MeO2C
AcN
O
O
O
Ph
O
O
O
BzO
BzO
OH
O
N3
O
NHCbz
CO2Bn
41
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

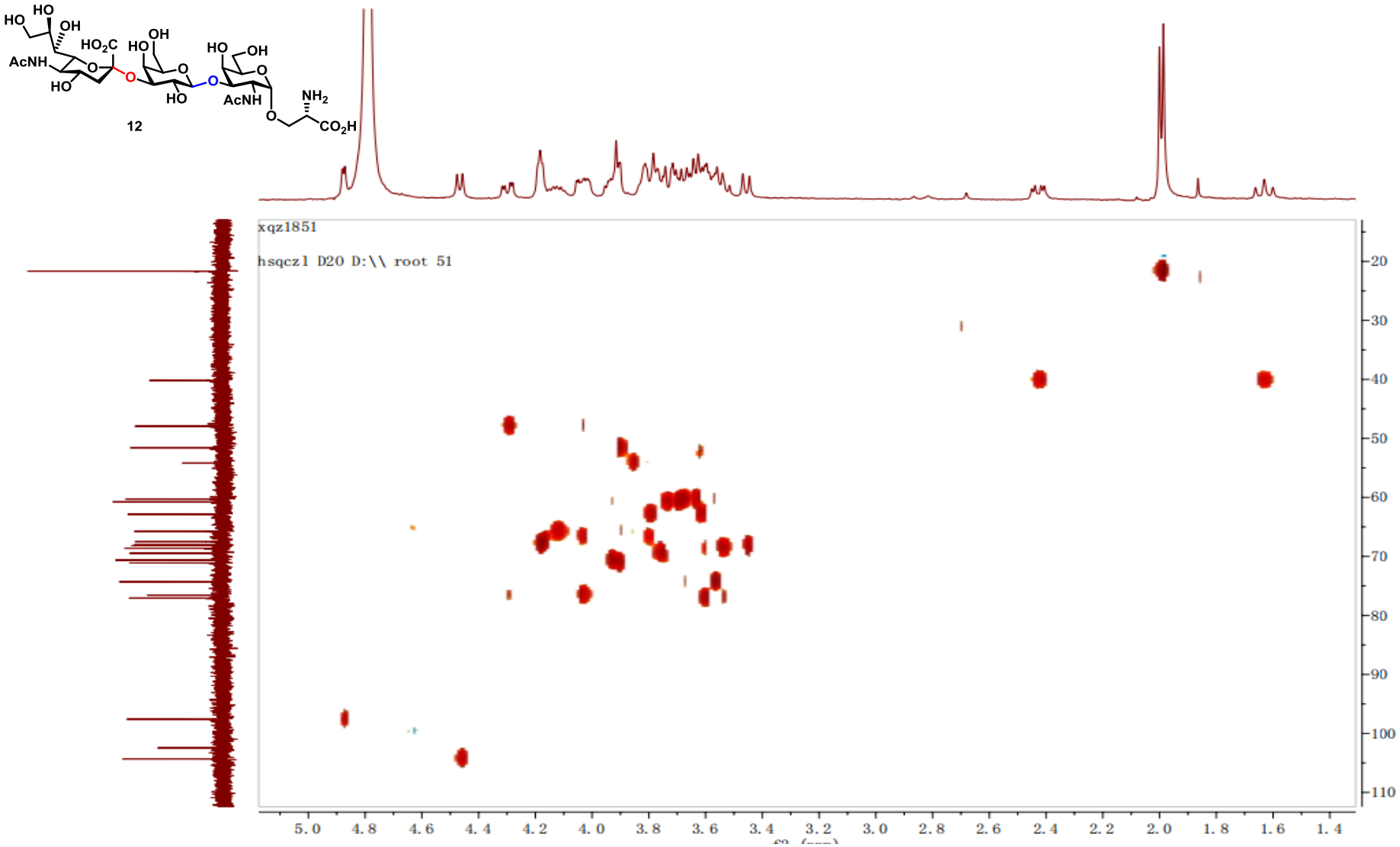

X-QZ-18-18C
X-QZ-18-18C
COSYGPSW CDC13 E:\\ xiaoguozhi 5
AcO
AcO
OAc
MeO2C
AcN
O
O
O
Ph
O
O
O
BzO
BzO
OH
O
O
N3
NHCbz
CO2Bn
41
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5

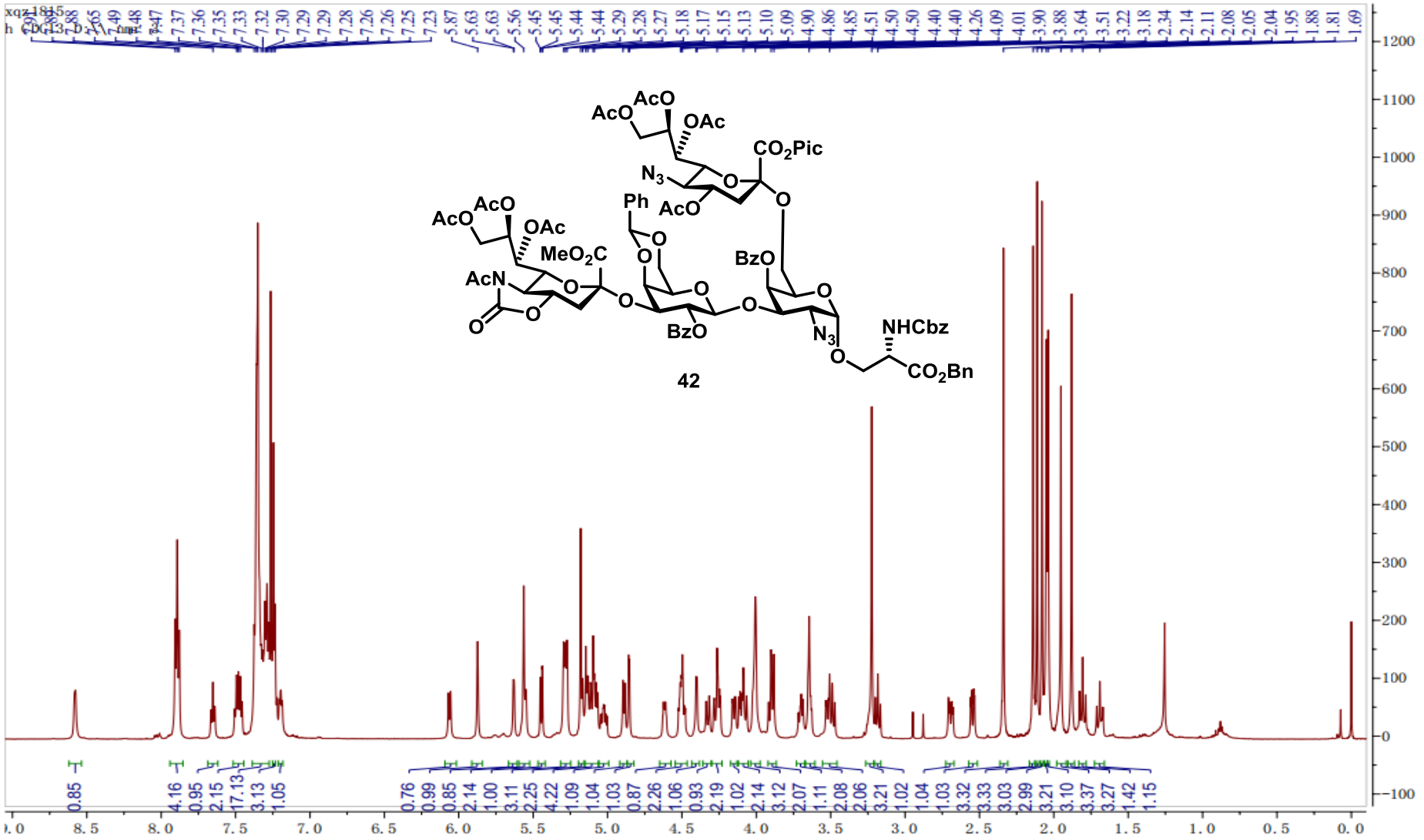

X-QZ-18-18C
X-QZ-18-18C
HSQCGP CDCl3 E:\\ xiaoguozhi 5
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
20 30 40 50 60 70 80 90
AcO
AcO
OAc
AcN
MeO2C
Ph
BzO
OH
BzO
N3
NHCbz
CO2Bn
41

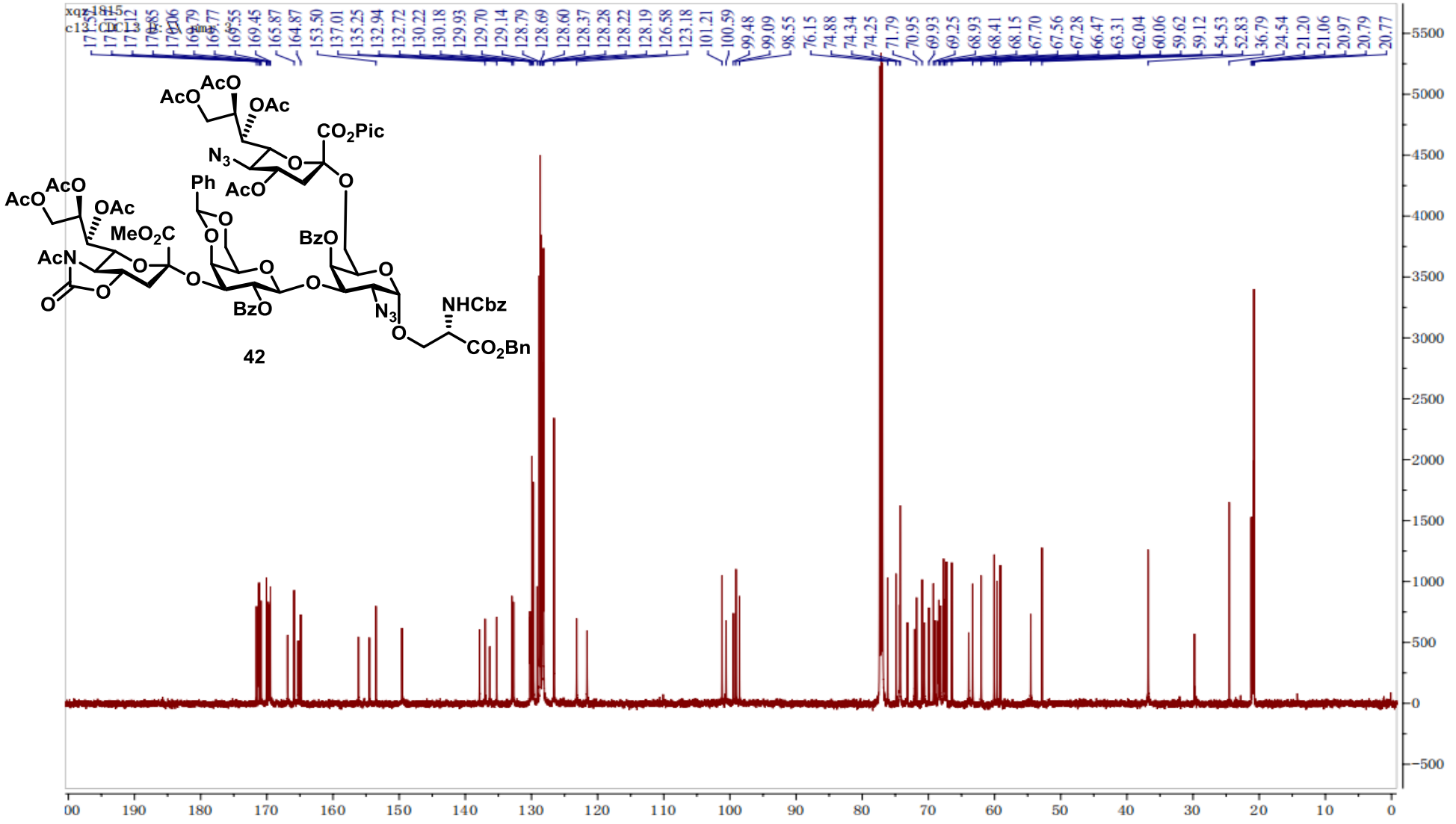

X-QZ-18-51-1
X-QZ-18-51-1
PROTON D2O E:\\ xiaoguozhi 16
12

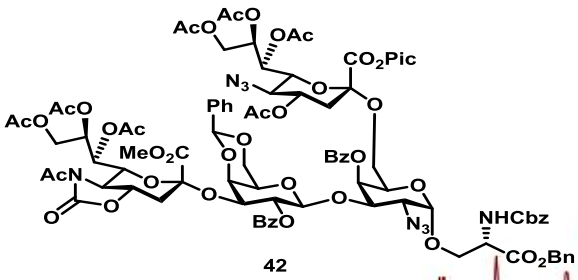

xqz1851
zgdc-sxhuo D20 D:\\ root 51
174.93
174.26
104.31
102.44
97.59
77.07
76.57
74.32
71.11
70.62
69.46
68.61
68.17
67.98
67.48
65.75
62.86
60.76
60.28
54.18
51.58
47.93
40.18
21.66
12


12
xqz1851
xqz1851 cosy d2o
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 1.8 1.6 1.4 1.2
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0


12
xqz1851
hsqcz1 D20 D:\\ root 51
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
1.8
1.6
1.4
20
30
40
50
60
70
80
90
100
110

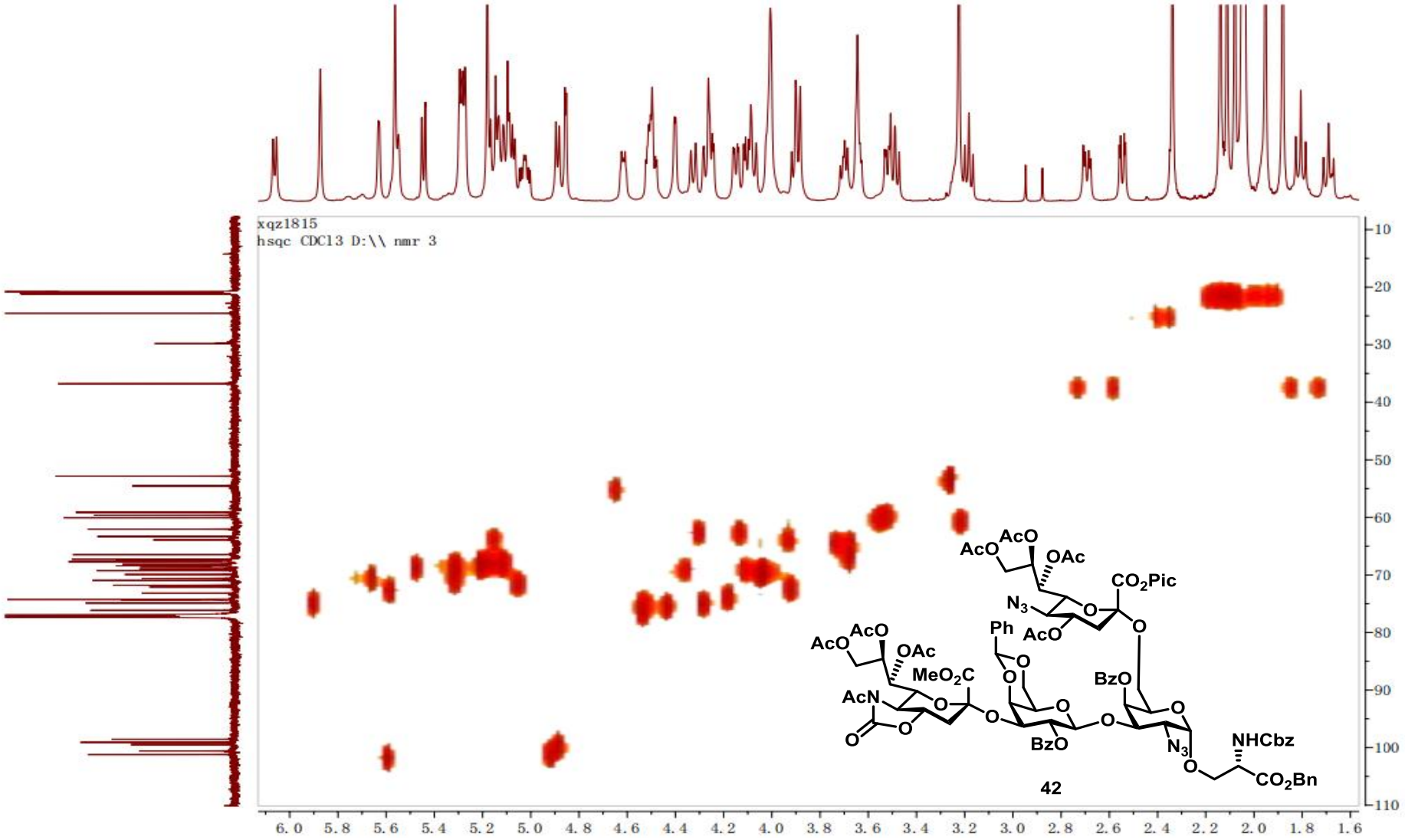

AcO
AcO
OAc
CO2Pic
N3
AcO
Ph
O
BzO
AcO
AcO
OAc
MeO2C
AcN
O
O
O
O
O
O
O
O
BzO
N3
NHCbz
O
CO2Bn
42

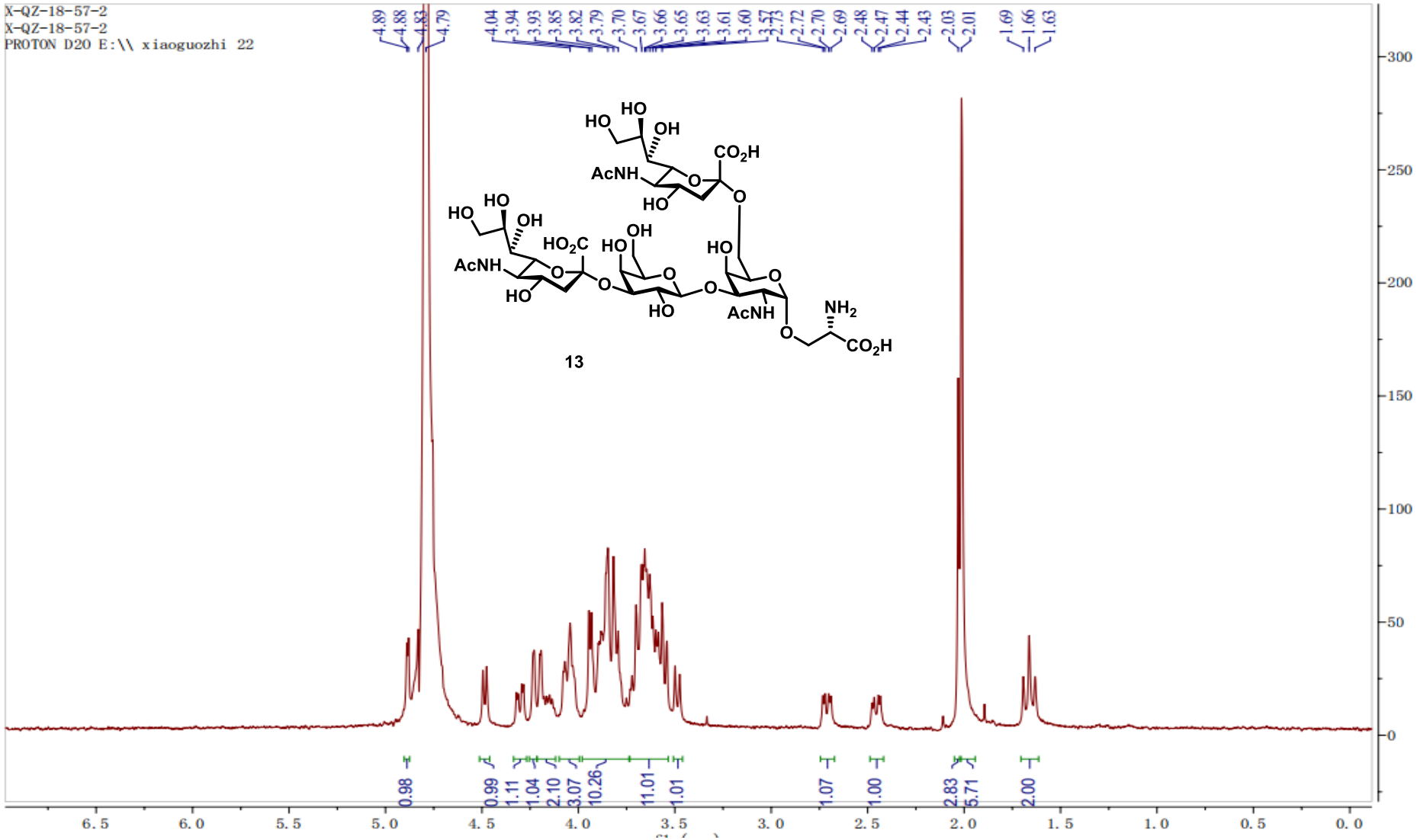

AcO
AcO
OAc
CO2Pic
N3
AcO
Ph
AcO
OAc
MeO2C
AcN
BzO
BzO
N3
NHCbz
CO2Bn
42

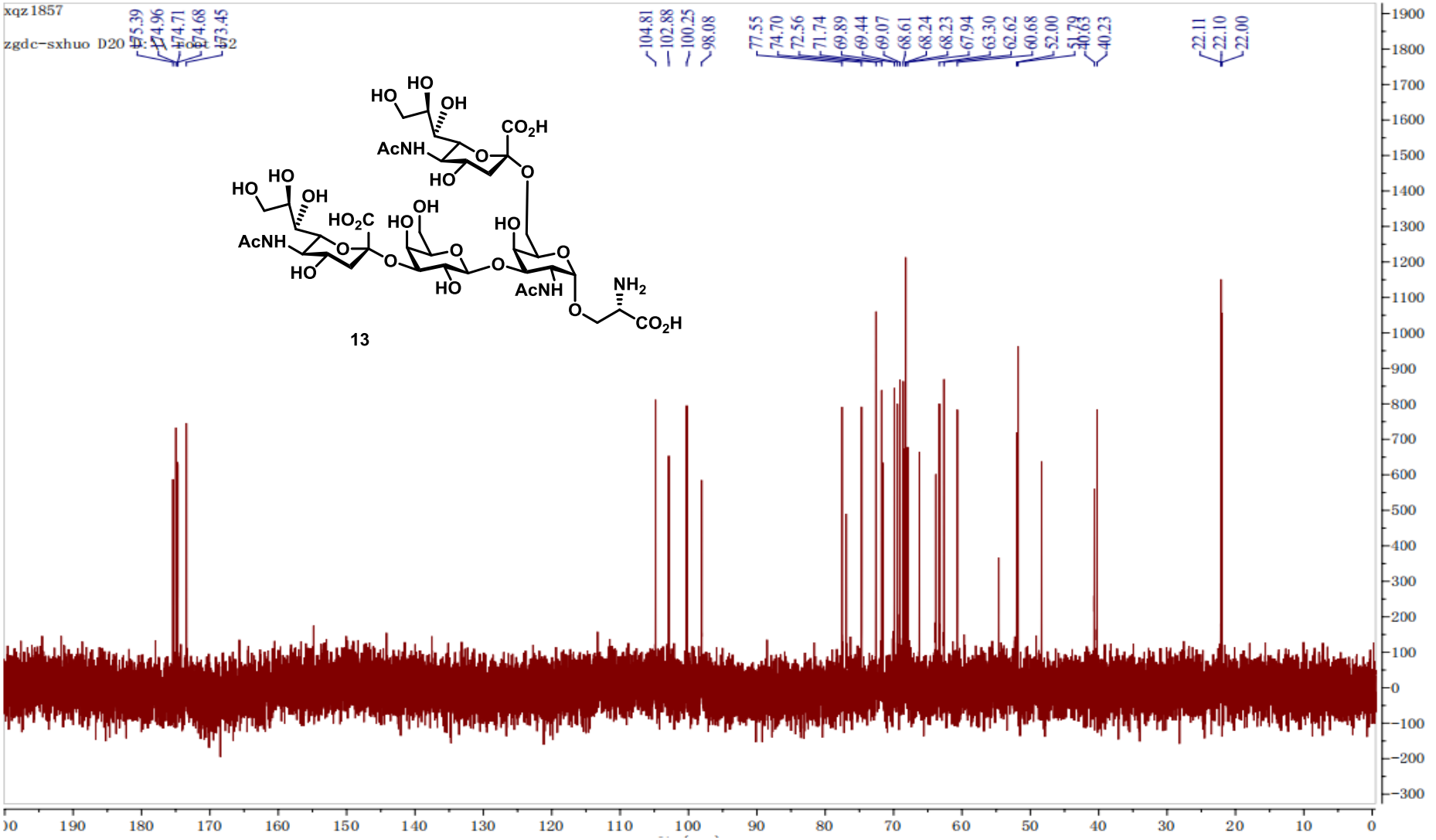

AcO
AcO
OAc
CO2Pic
N3
Ph
AcO
AcO
AcO
OAc
MeO2C
BzO
AcN
BzO
N3
NHCbz
CO2Bn

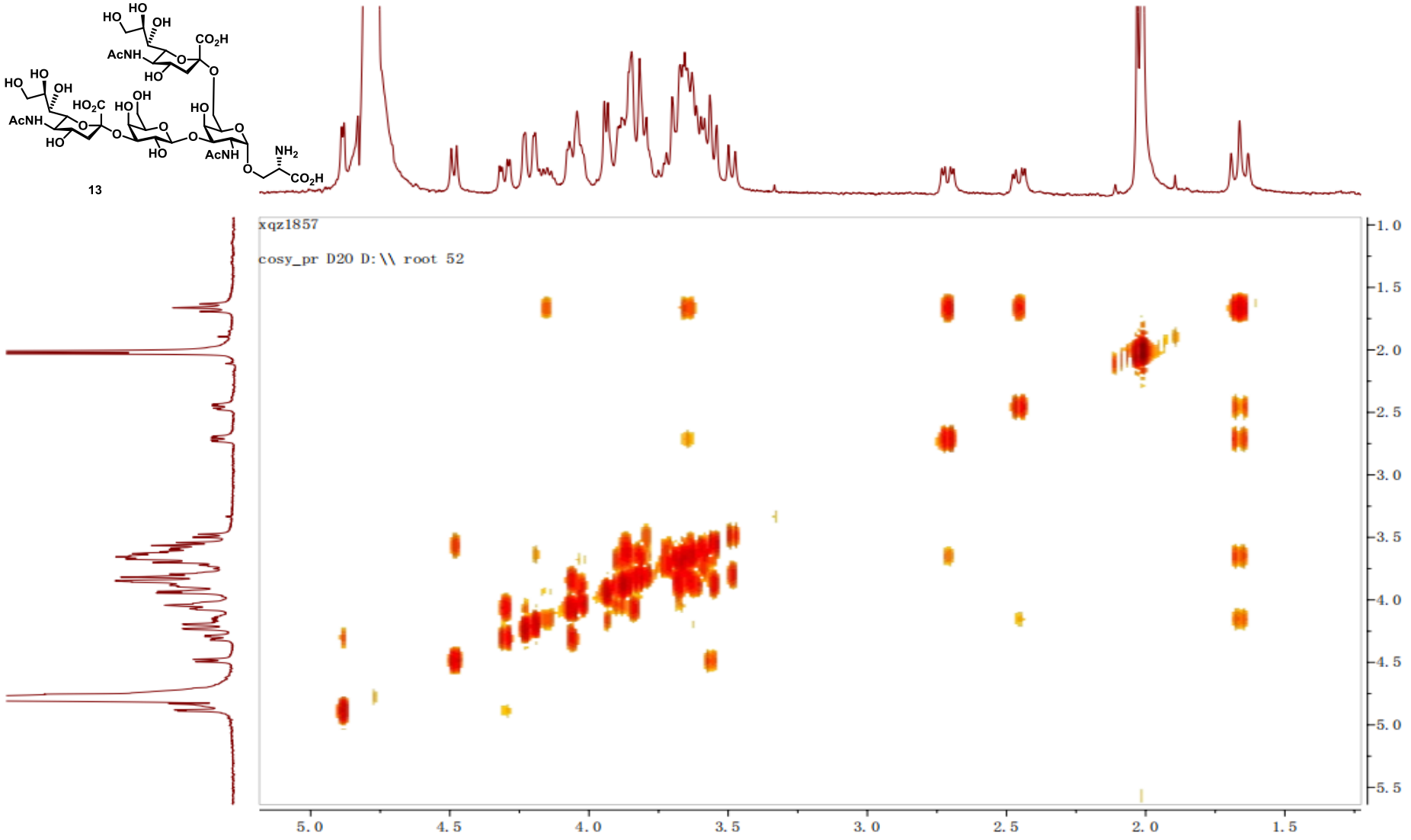
42

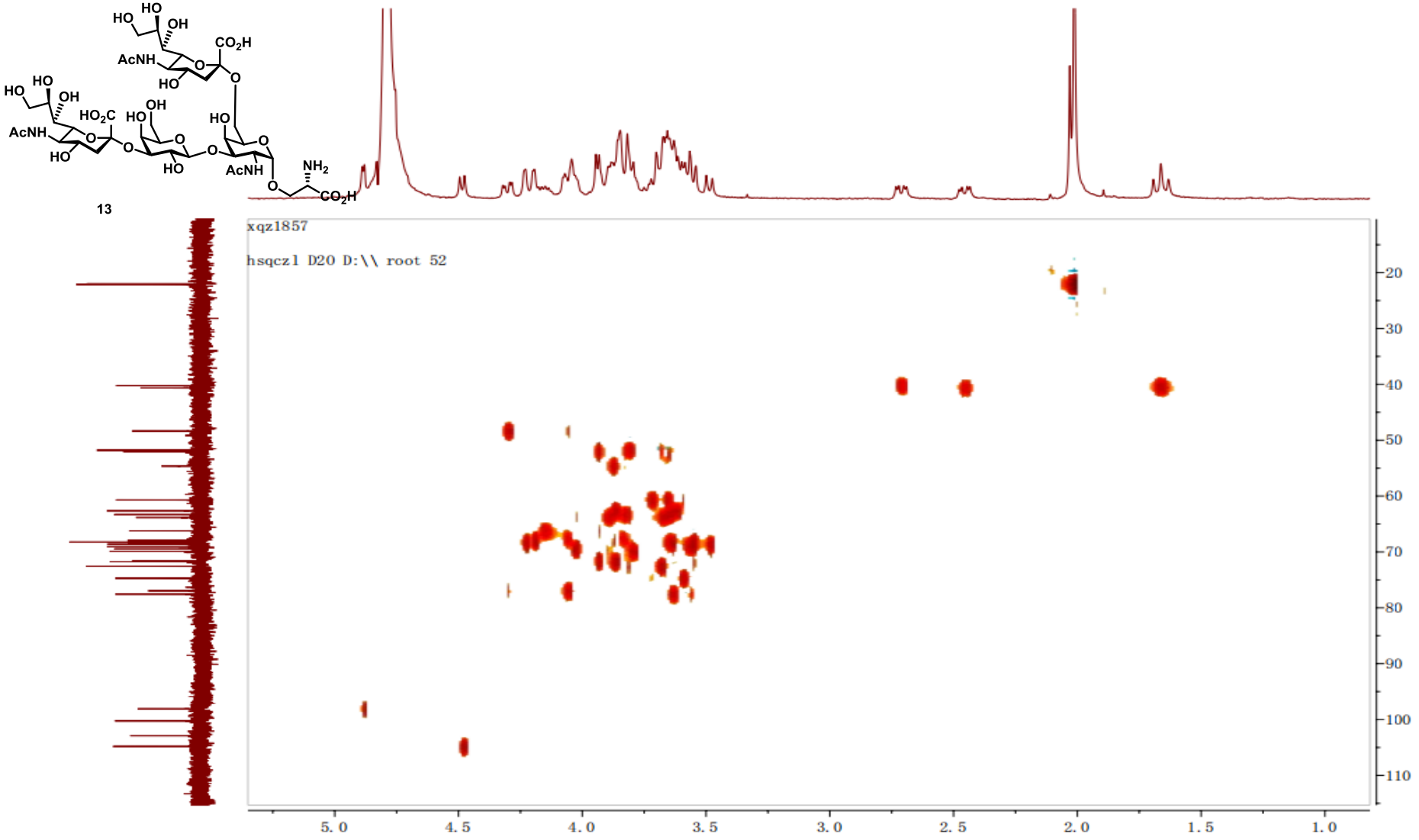
xqz1815
cosy CDCl3 D:\\ nmr 3
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

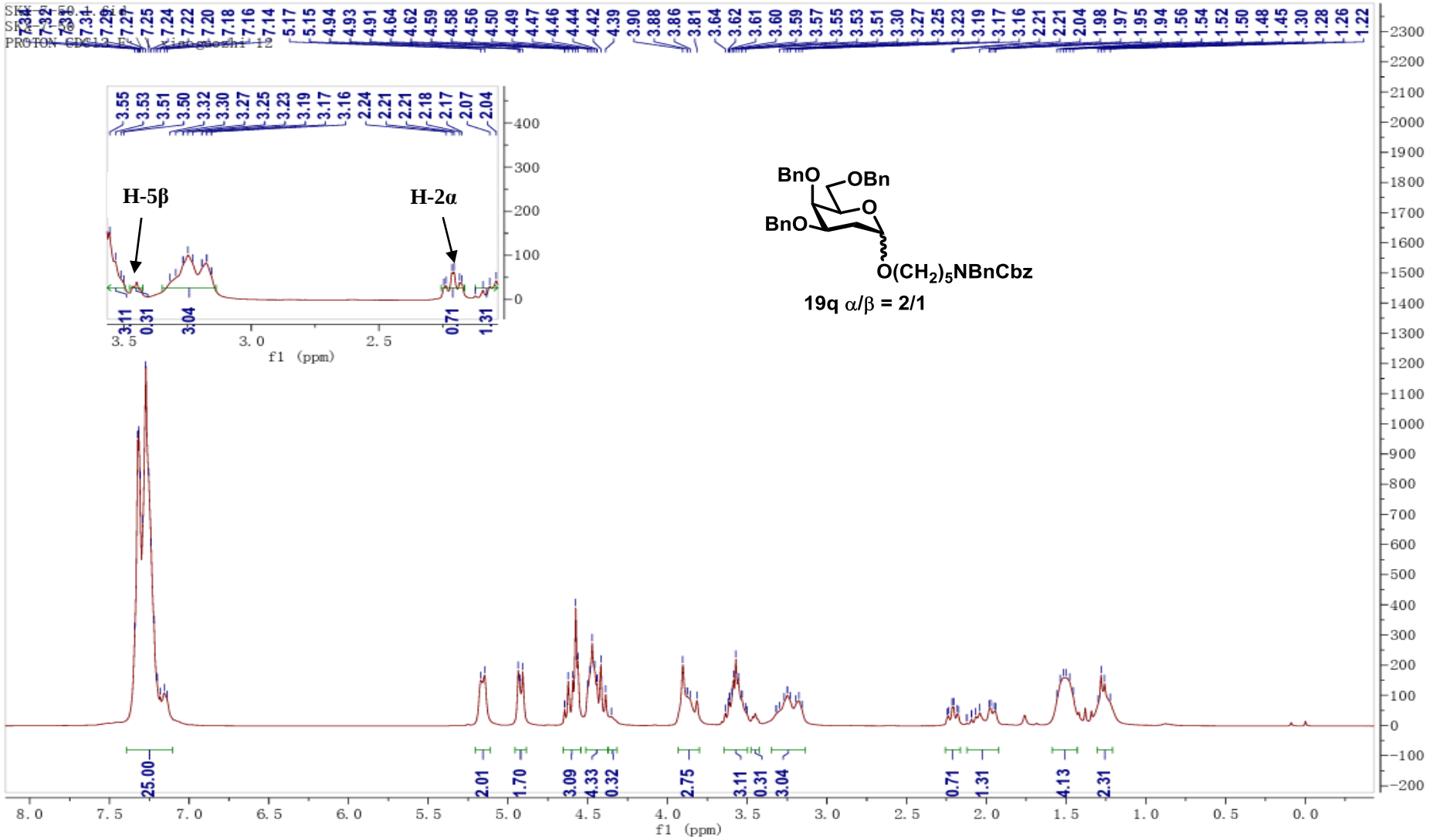

xqz1815
hsqc CDCl3 D:\\ nmr 3
42

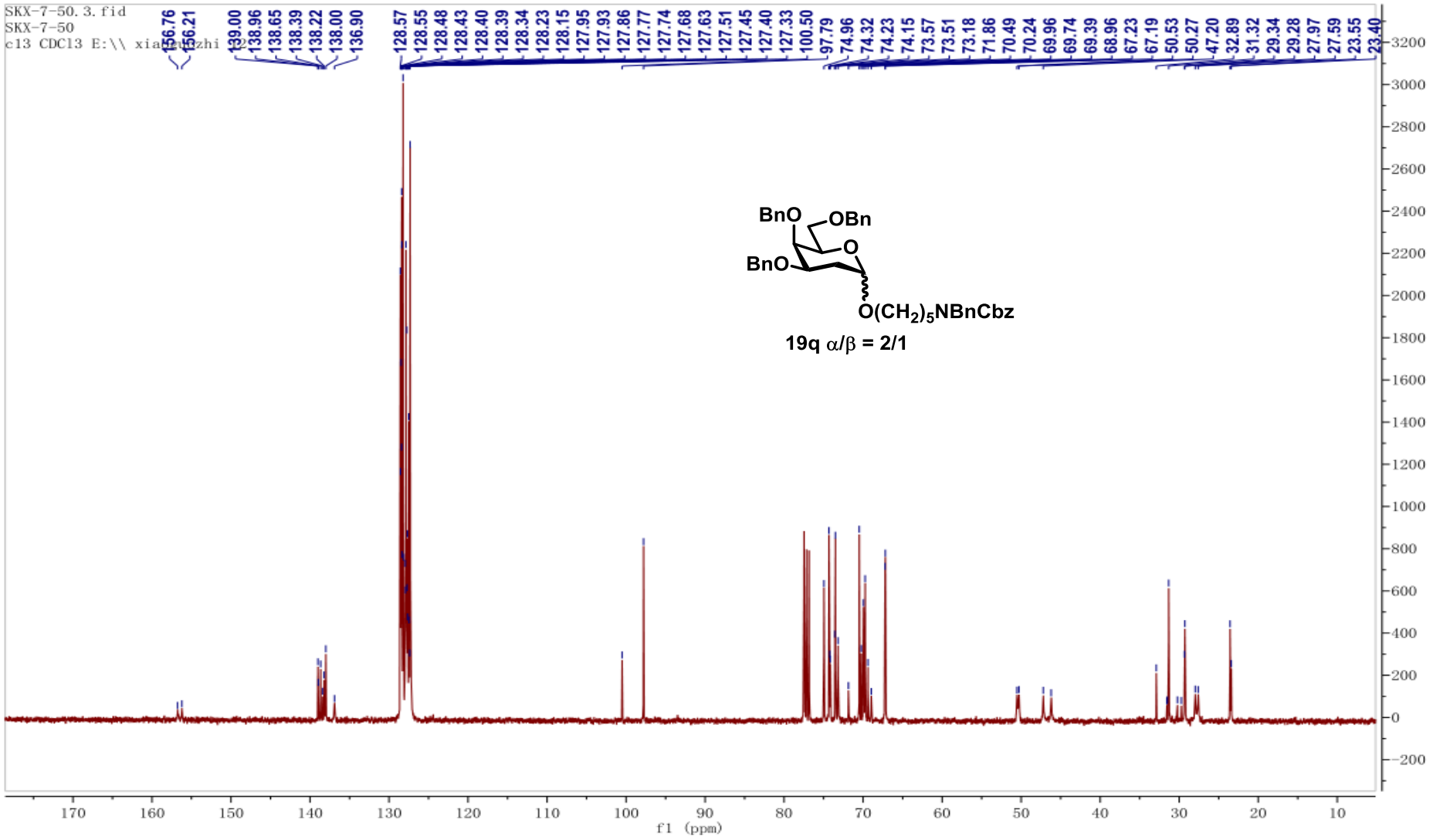

X-QZ-18-57-2
X-QZ-18-57-2
PROTON D20 E:\\ xiaoguozhi 22
4.89 4.88 4.83 4.79 4.04 3.94 3.93 3.85 3.82 3.79 3.70 3.67 3.66 3.65 3.63 3.61 3.60 3.57 3.73 2.72 2.70 2.69 2.48 2.47 2.44 2.43 2.03 2.01 1.69 1.66 1.63
13
0.98 0.99 1.11 1.04 2.10 3.07 10.26 11.01 1.01 1.07 1.00 2.83 5.71 2.00
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
300 250 200 150 100 50 0

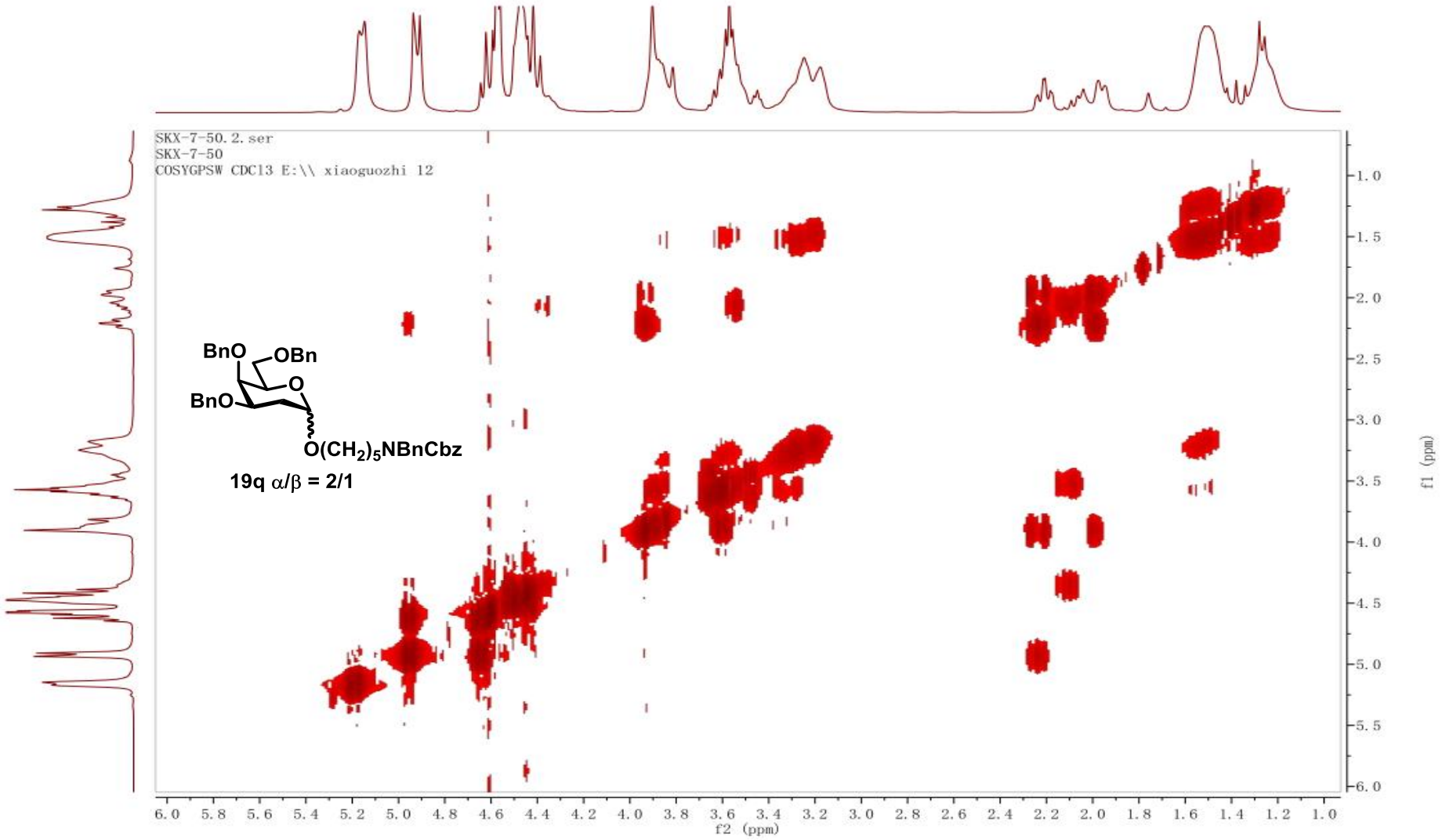

xqz1857
zgdc-sxhuo D20
175.39
174.96
174.71
174.68
173.45
104.81
102.88
100.25
98.08
77.55
74.70
72.56
71.74
69.89
69.44
69.07
68.61
68.24
68.23
67.94
63.30
62.62
60.68
52.00
51.79
40.63
40.23
22.11
22.10
22.00
HO
HO
OH
CO2H
AcNH
HO
O
HO
HO
OH
HO2C
HO
OH
HO
AcNH
O
O
O
O
HO
O
HO
AcNH
NH2
O
CO2H
13

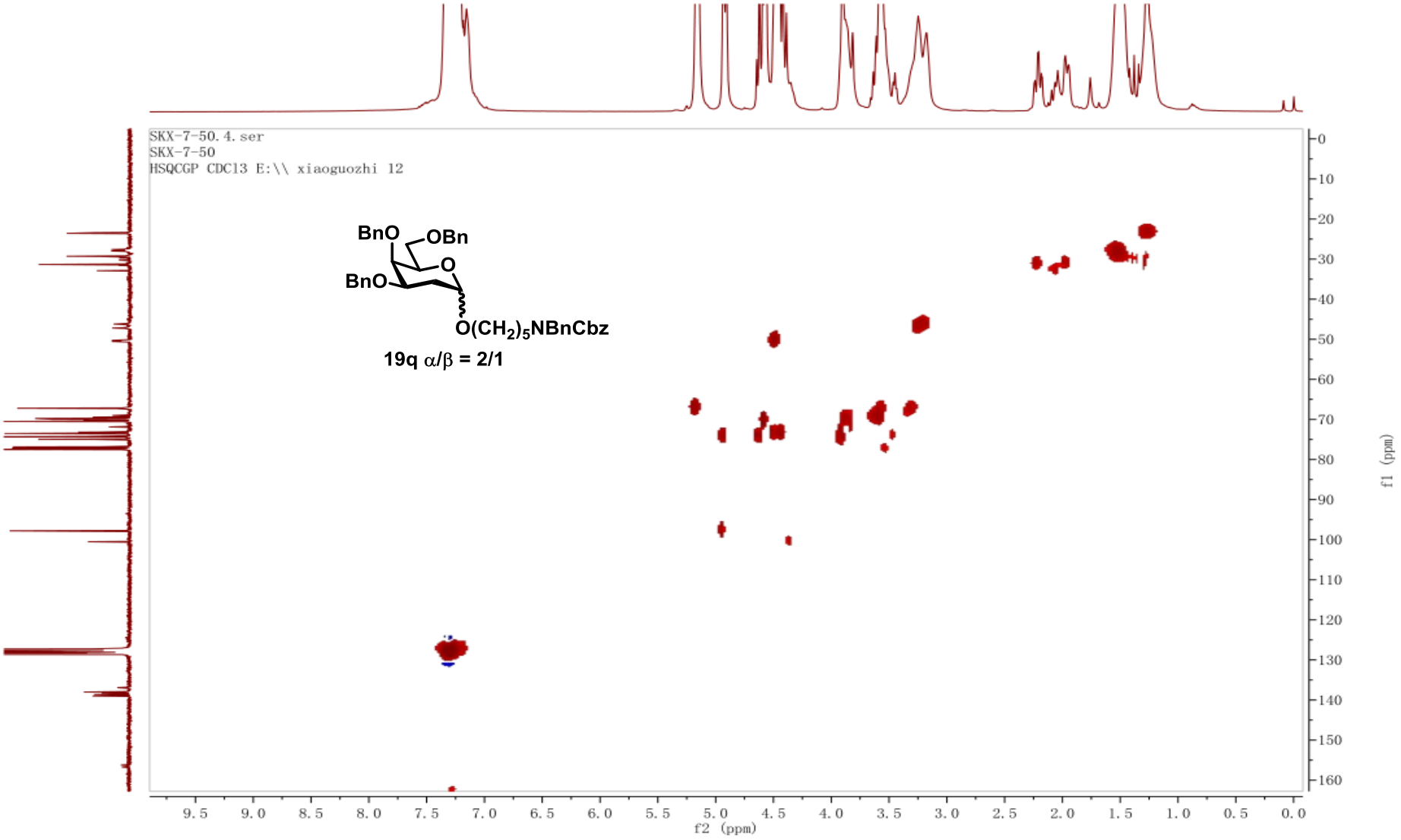

13
xqz1857
cosy_pr D20 D:\\ root 52
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

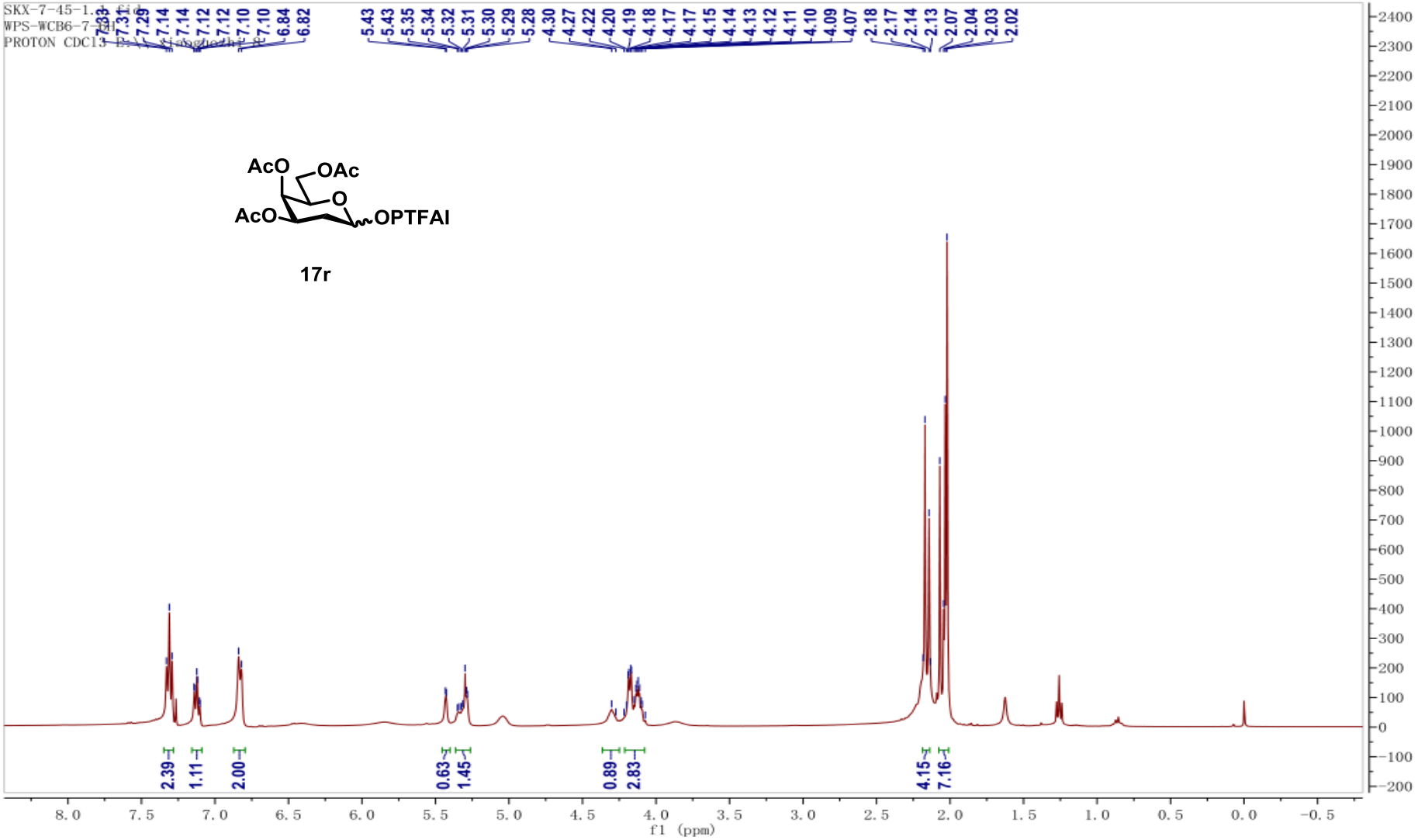

13
xqz1857
hsqcz1 D20 D:\\ root 52
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
20
30
40
50
60
70
80
90
100
110

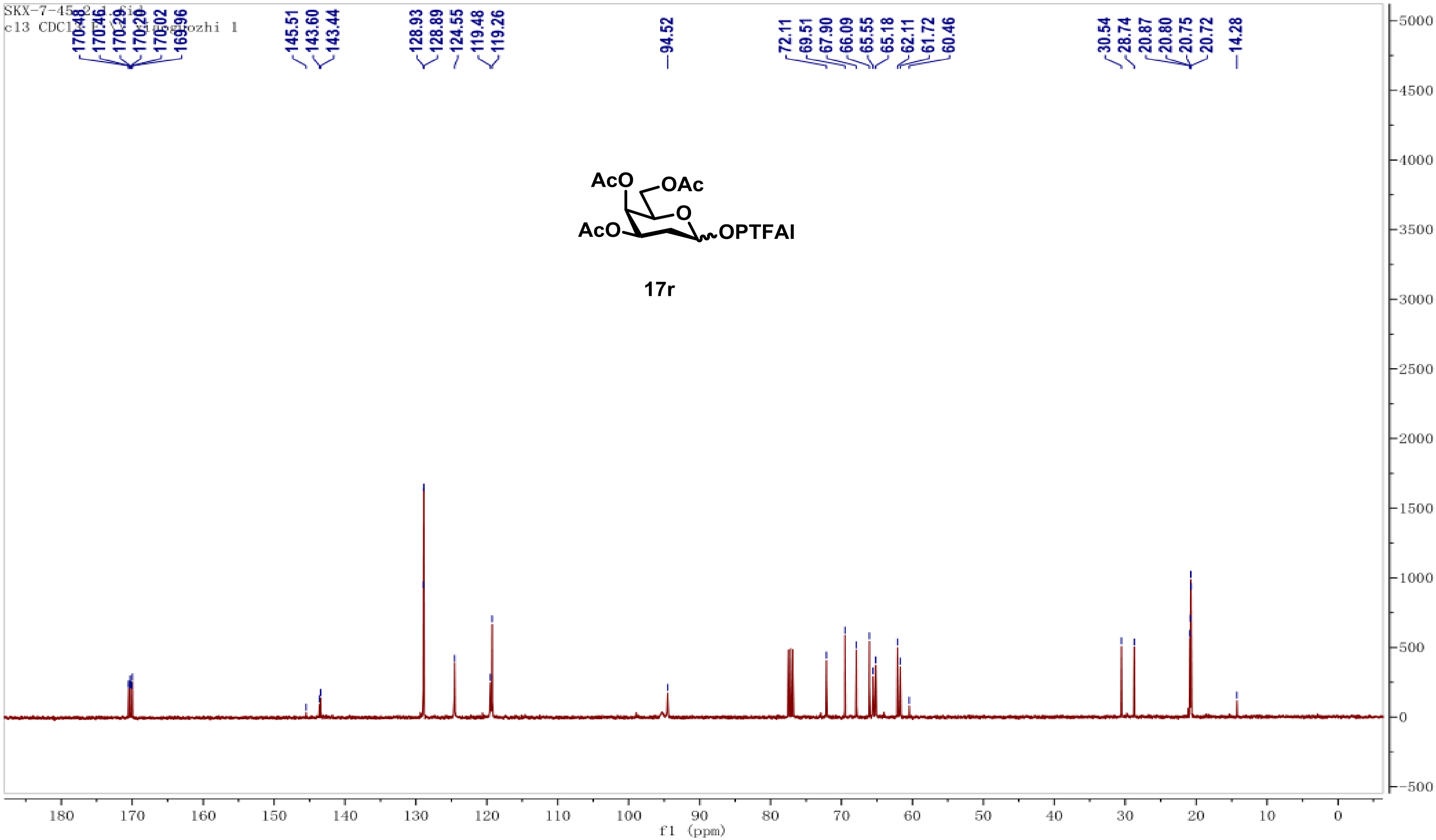

H-5β
H-2α
BnO
OBn
O
BnO
O(CH2)5NBnCbz
19q α/β = 2/1
f1 (ppm)

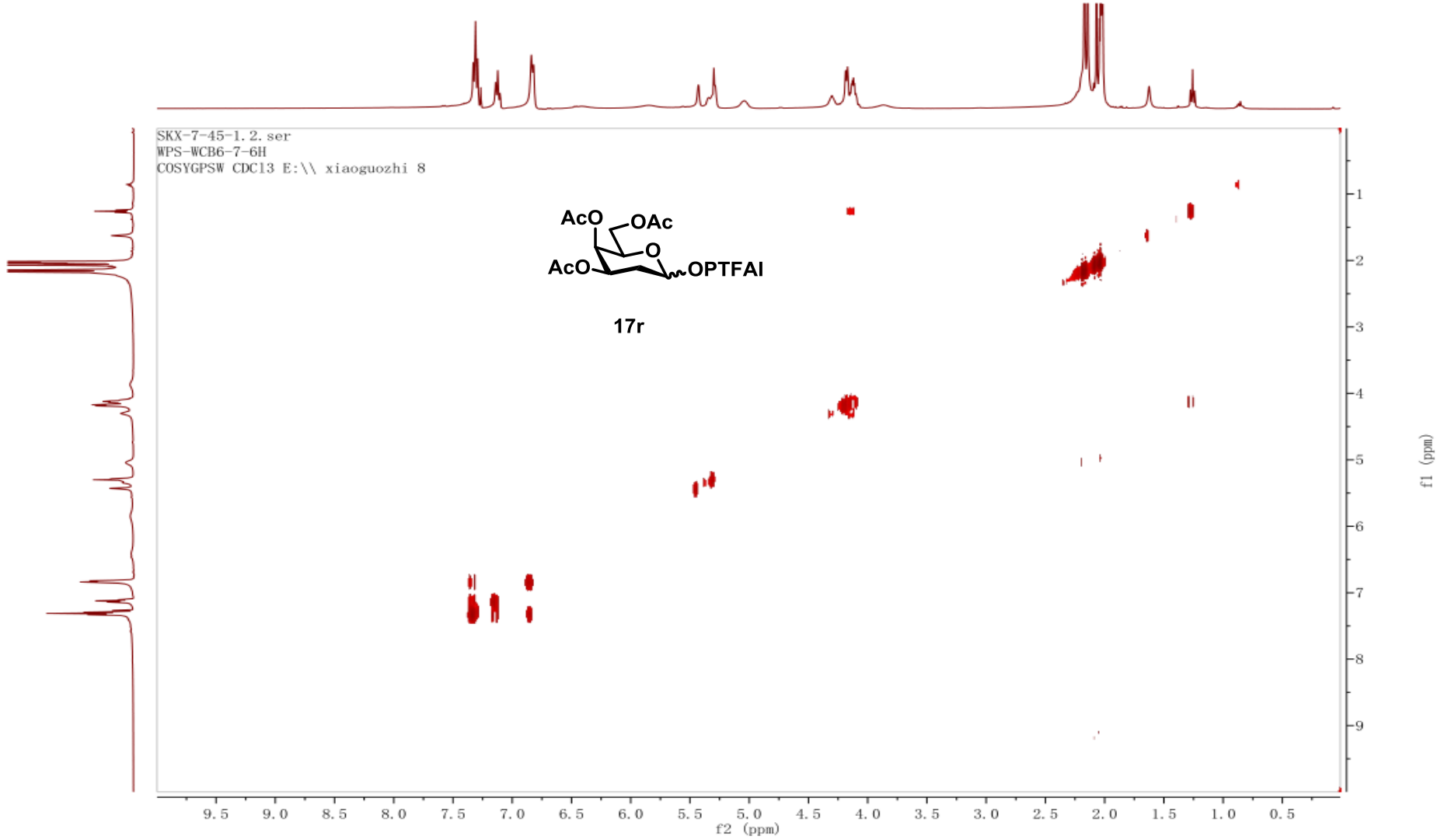

SKX-7-50.3.fid
SKX-7-50
c13 CDCl3 E:\\ xiaozhi
156.76
156.21
139.00
138.96
138.65
138.39
138.22
138.00
136.90
128.57
128.55
128.48
128.43
128.40
128.39
128.34
128.23
128.15
127.95
127.93
127.86
127.77
127.74
127.68
127.63
127.51
127.45
127.40
127.33
100.50
97.79
74.96
74.32
74.23
74.15
73.57
73.51
73.18
71.86
70.49
70.24
69.96
69.74
69.39
68.96
67.23
67.19
50.53
50.27
47.20
32.89
31.32
29.34
29.28
27.97
27.59
23.55
23.40
BnO
OBn
O
BnO
O(CH2)5NBnCbz
19q α/β = 2/1
f1 (ppm)

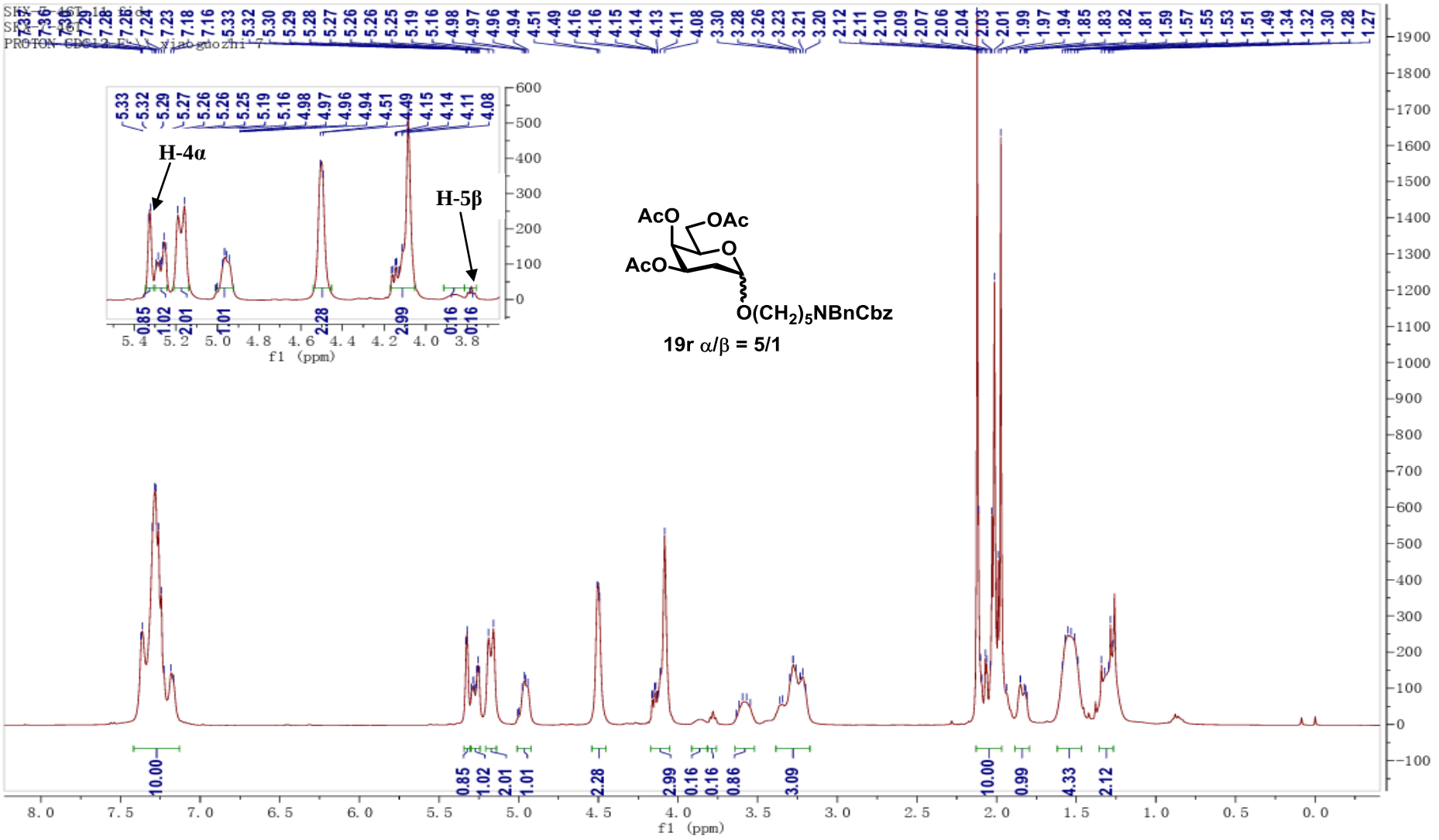

SKX-7-50.2.ser
SKX-7-50
COSYGPSW CDCl3 E:\\ xiaoguozhi 12
BnO
OBn
O
BnO
O(CH2)5NBnCbz
19q α/β = 2/1
f2 (ppm)
f1 (ppm)

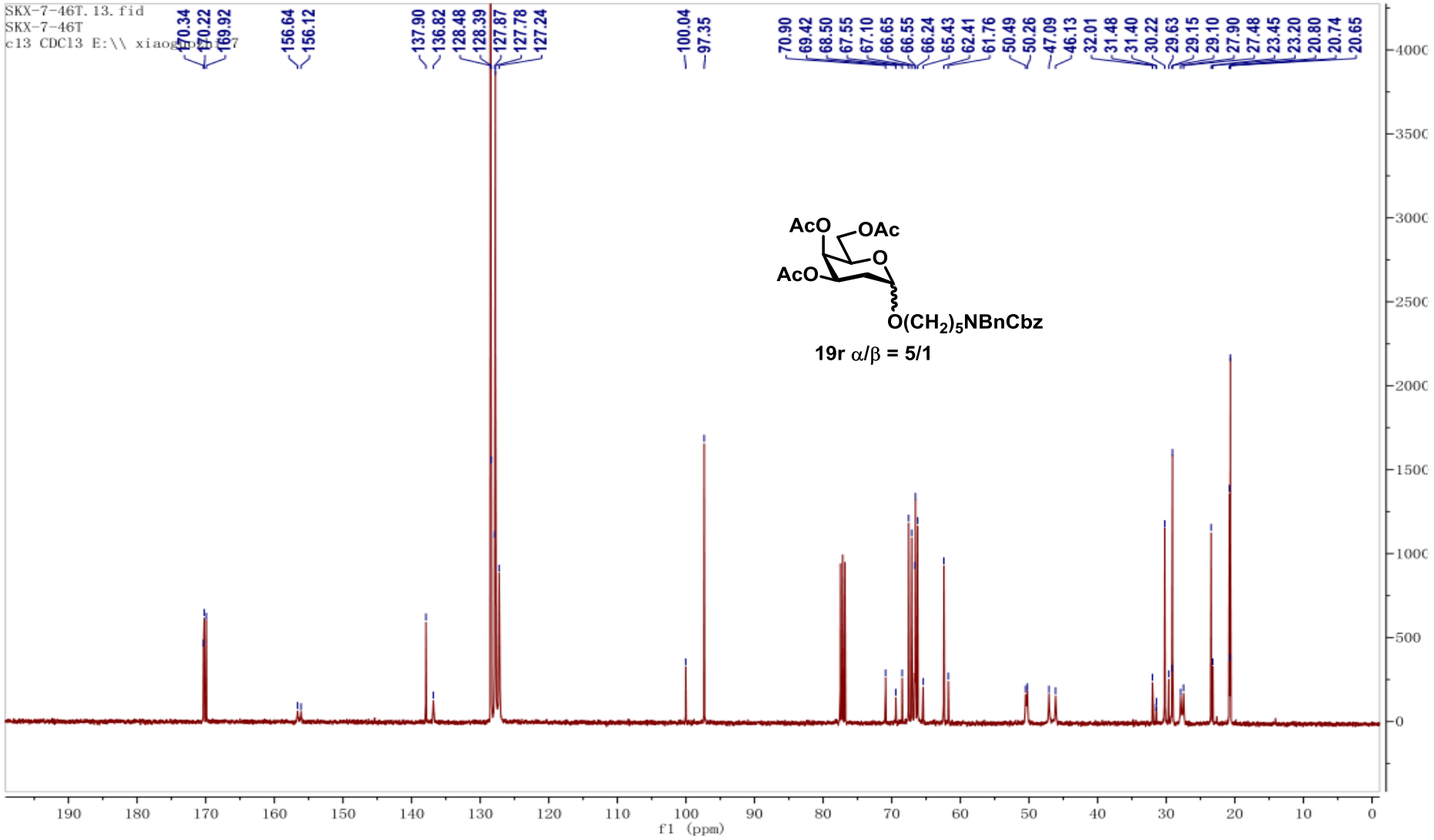

SKX-7-50.4.ser
SKX-7-50
HSQCGP CDC13 E:\\ xiaoguozhi 12
BnO
OBn
O
BnO
O(CH2)5NBnCbz
19q α/β = 2/1
f2 (ppm)
f1 (ppm)

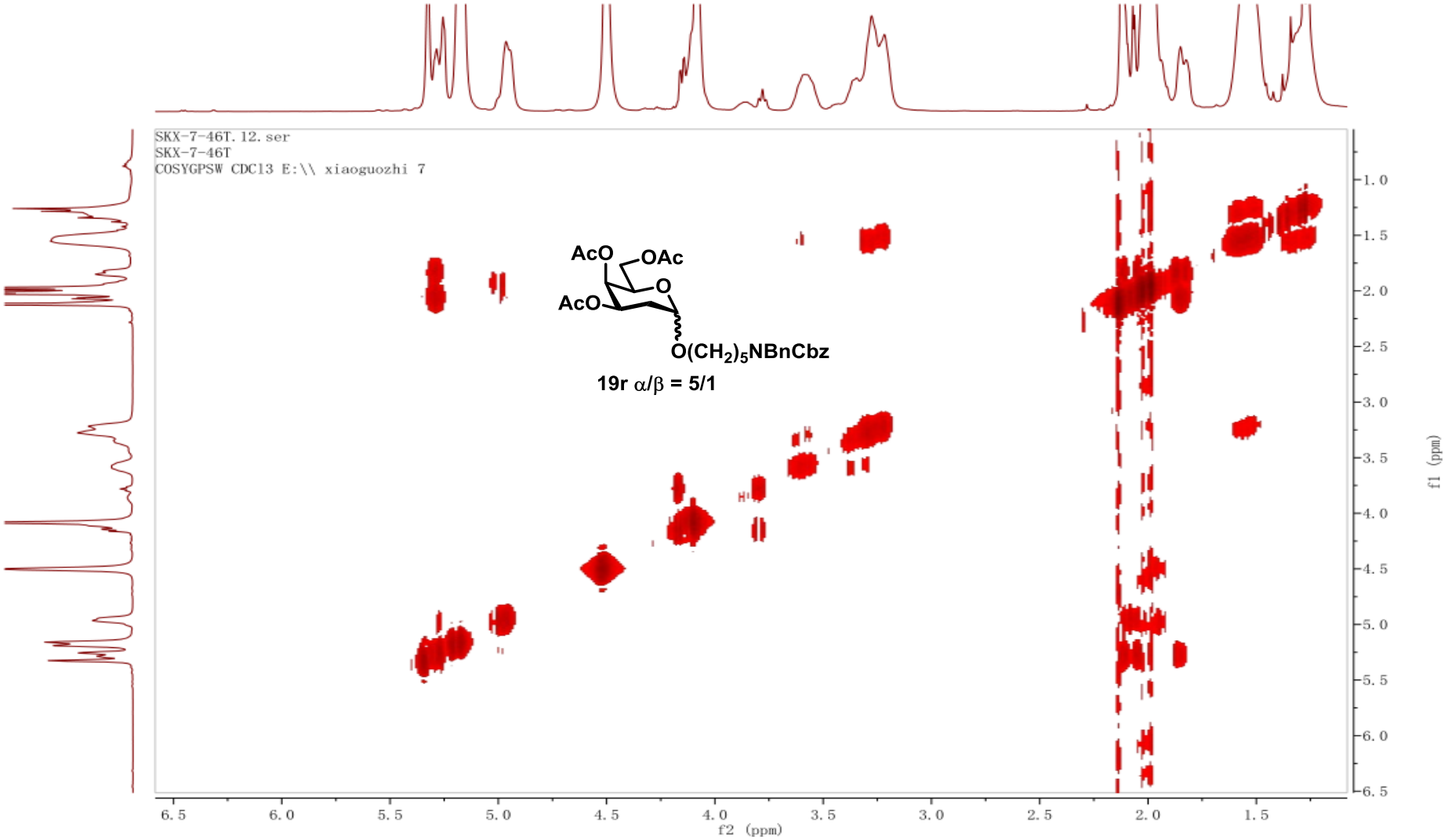

AcO
OAc
O
AcO
OPTFAI
17r
f1 (ppm)

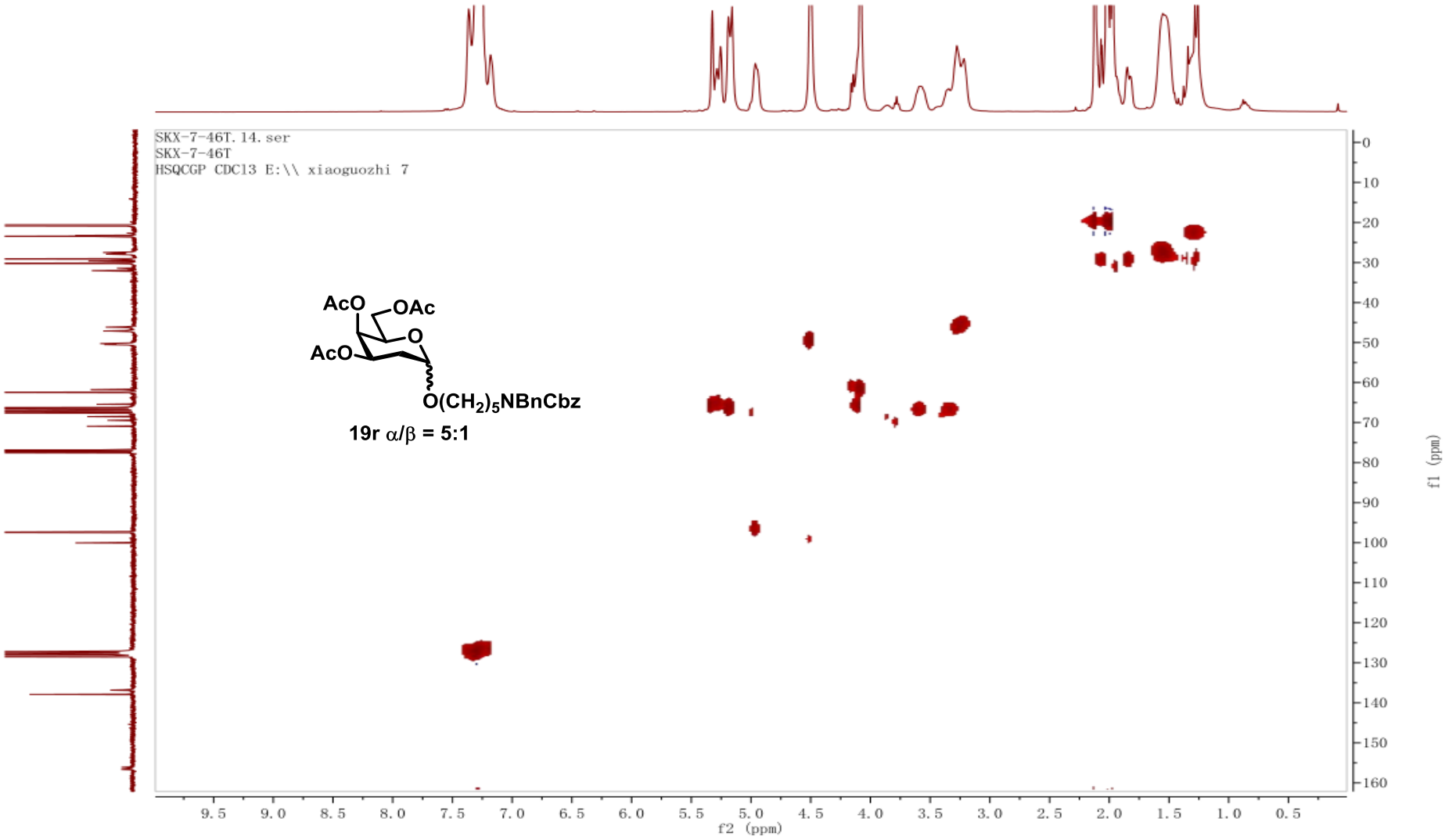

SKX-7-45-2-1.fid
c13 CDCl3 ... zhi 1
170.48
170.46
170.29
170.20
170.02
169.96
145.51
143.60
143.44
128.93
128.89
124.55
119.48
119.26
94.52
72.11
69.51
67.90
66.09
65.55
65.18
62.11
61.72
60.46
30.54
28.74
20.87
20.80
20.75
20.72
14.28
AcO
OAc
O
AcO
OPTFAI
17r
f1 (ppm)

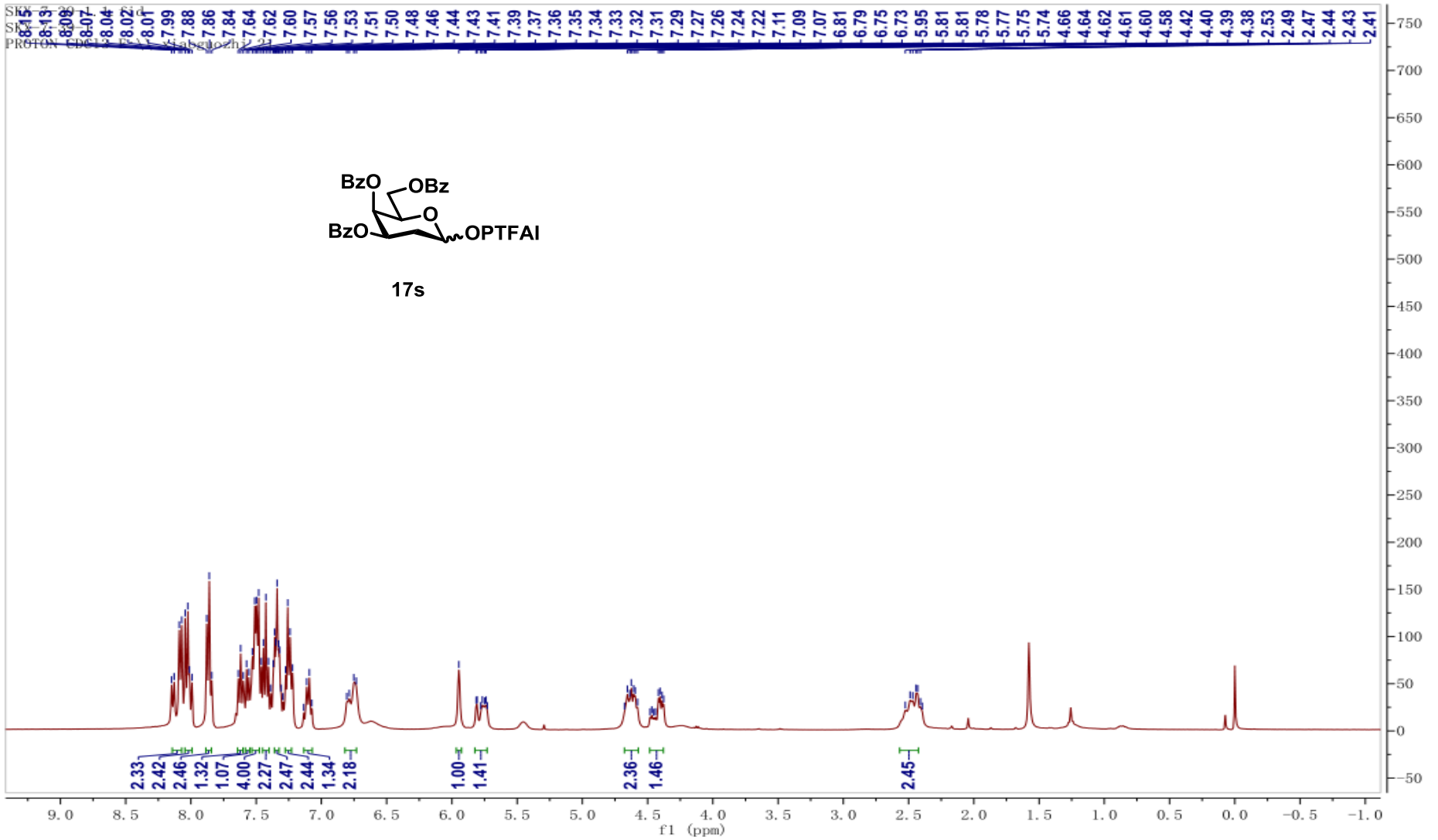

SKX-7-45-1.2.ser
WPS-WCB6-7-6H
COSYGPSW CDCl3 E:\\ xiaoguozhi 8
AcO
OAc
O
AcO
OPTFAI
17r
f2 (ppm)
f1 (ppm)

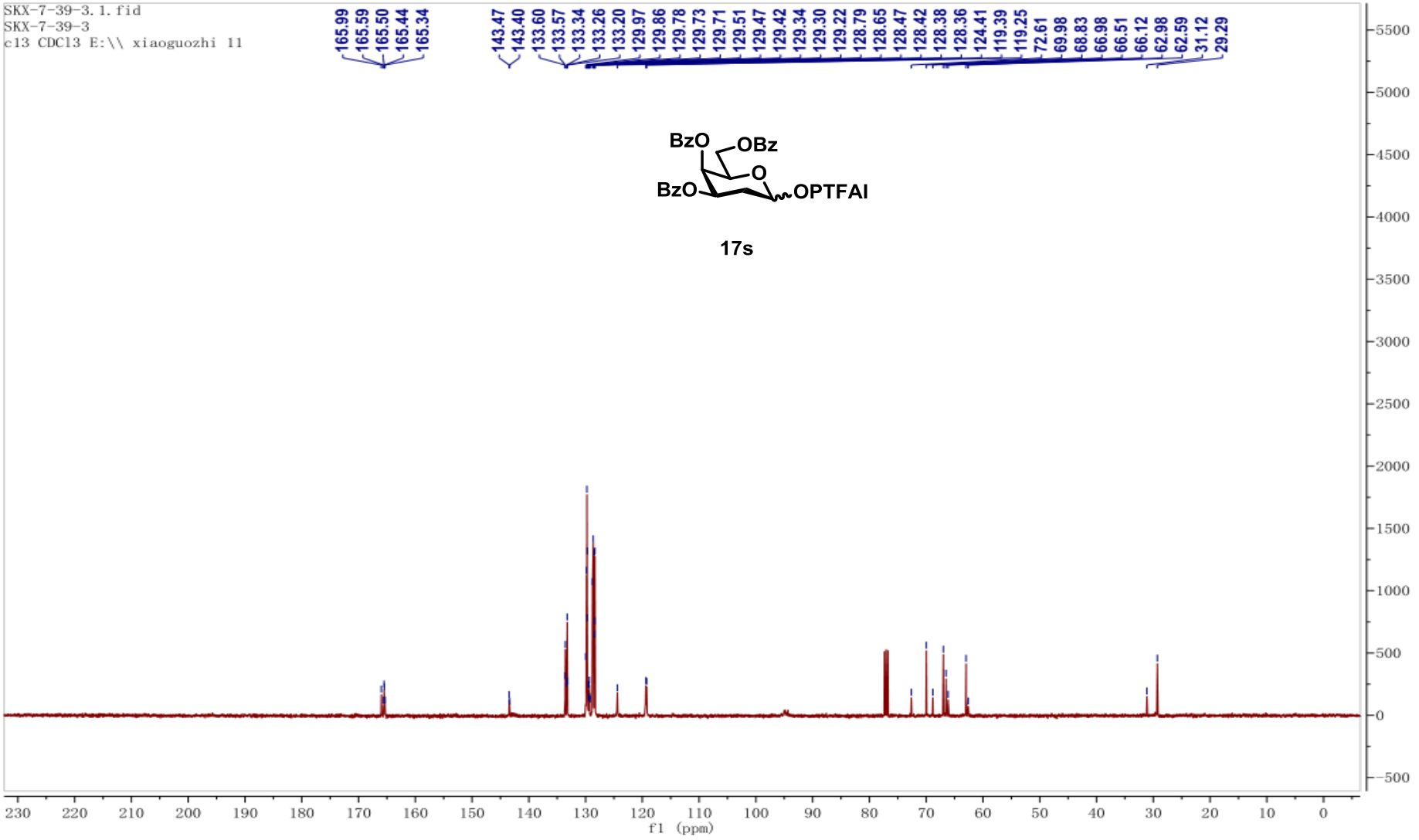

H-4α
H-5β
AcO
OAc
O
AcO
O(CH2)5NBnCbz
19r α/β = 5/1
f1 (ppm)

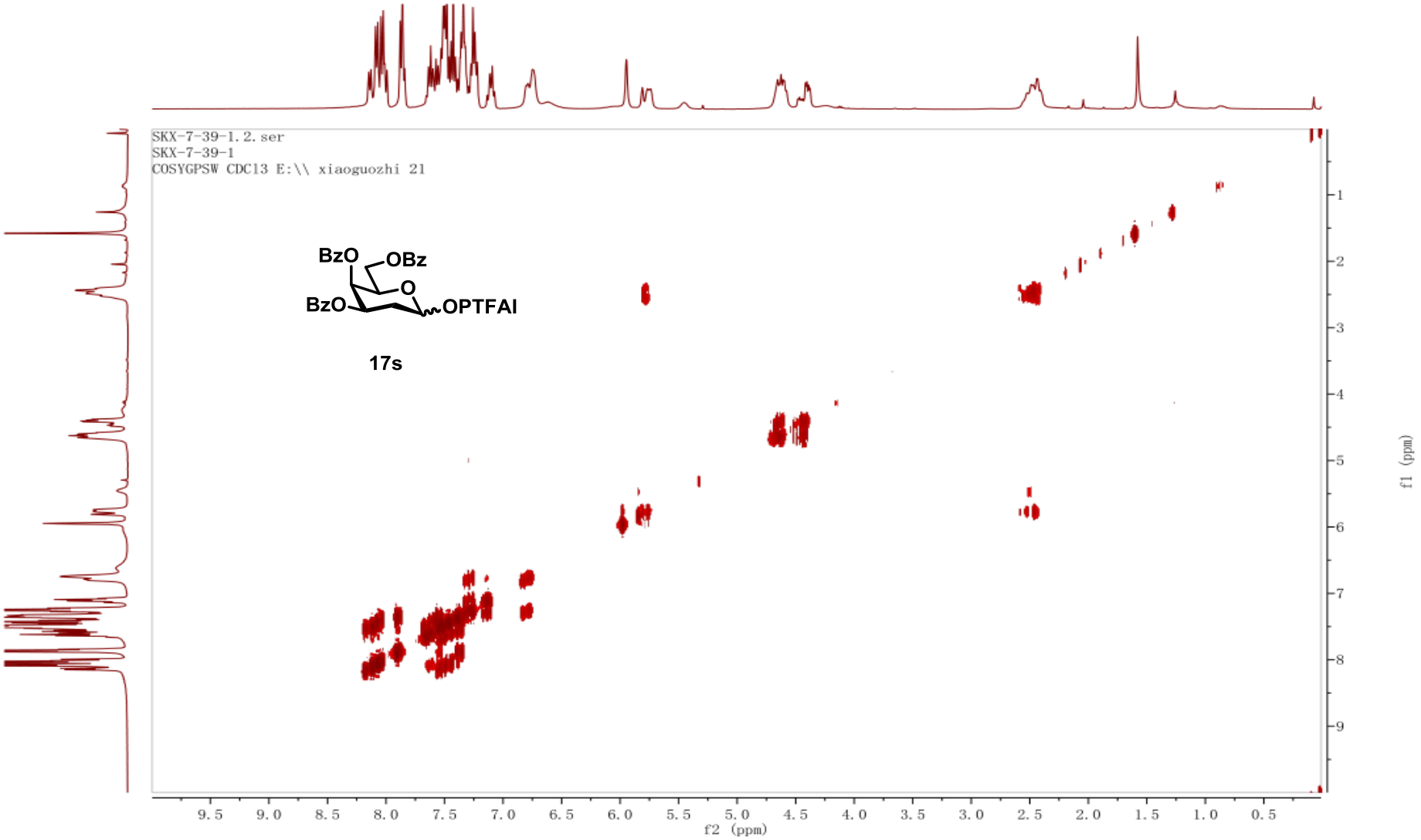

SKX-7-46T.13.fid
SKX-7-46T
c13 CDCl3 E:\\ xiaoguo
170.34
170.22
169.92
156.64
156.12
137.90
136.82
128.48
128.39
127.87
127.78
127.24
100.04
97.35
70.90
69.42
68.50
67.55
67.10
66.65
66.55
66.24
65.43
62.41
61.76
50.49
50.26
47.09
46.13
32.01
31.48
31.40
30.22
29.63
29.15
29.10
27.90
27.48
23.45
23.20
20.80
20.74
20.65
AcO
OAc
O
AcO
O(CH2)5NBnCbz
19r α/β = 5/1
f1 (ppm)

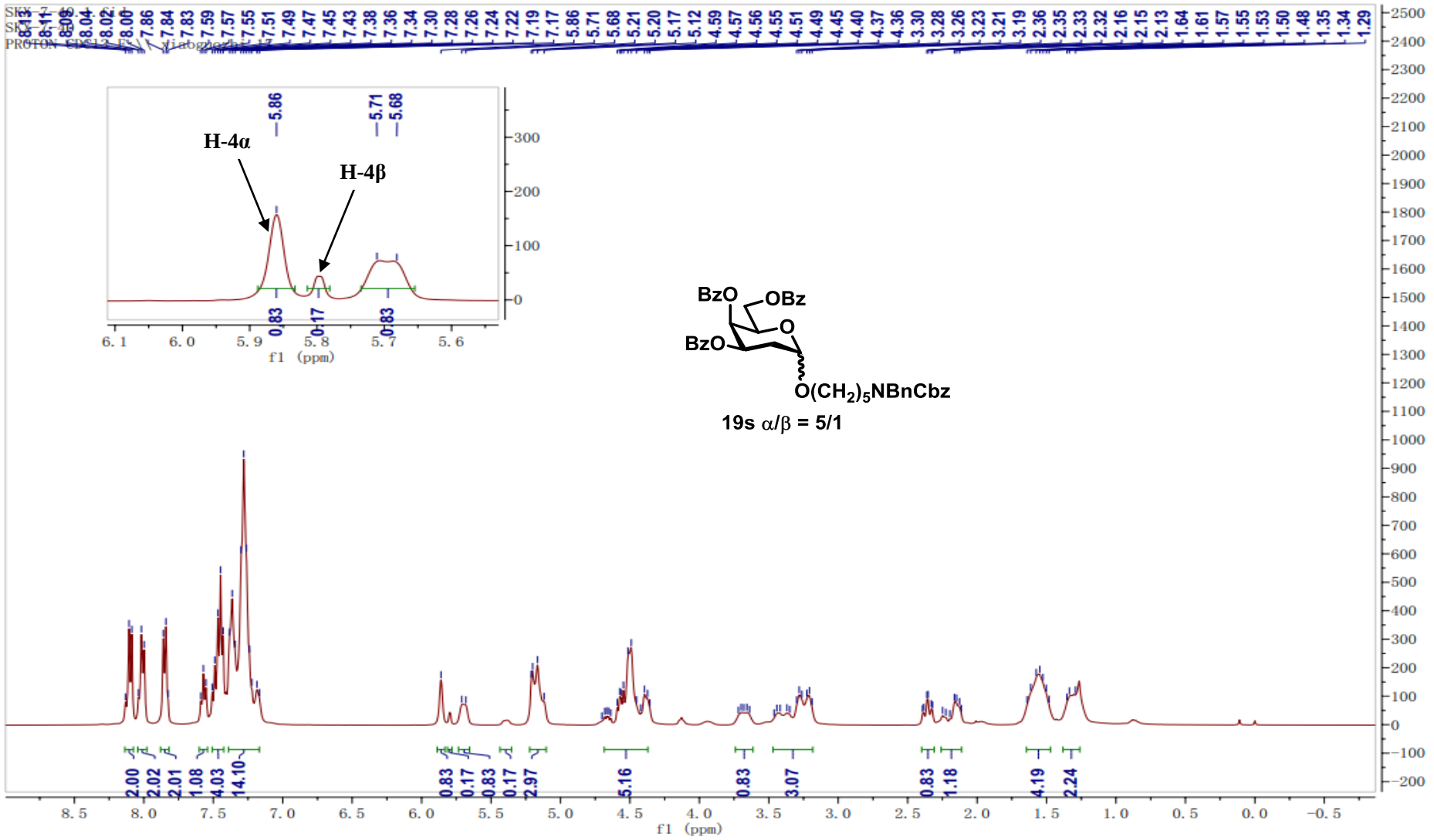

SKX-7-46T.12.ser
SKX-7-46T
COSYGPSW CDCl3 E:\\ xiaoguozhi 7
AcO
OAc
O
AcO
O(CH2)5NBnCbz
19r α/β = 5/1
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

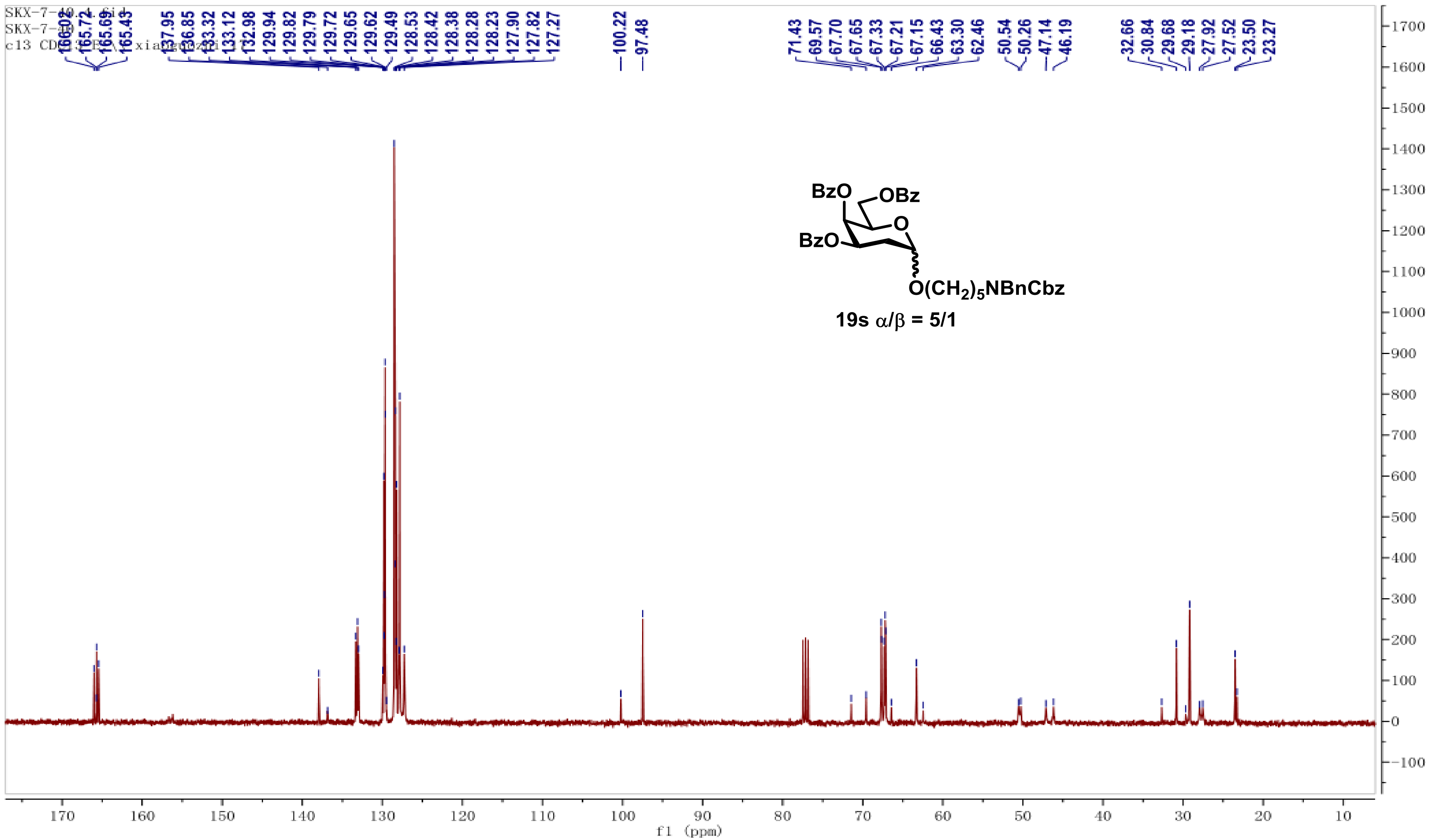

SKX-7-46T.14.ser
SKX-7-46T
HSQCGP CDC13 E:\\ xiaoguozhi 7
AcO
OAc
O
AcO
O(CH2)5NBnCbz
19r α/β = 5:1
f2 (ppm)
f1 (ppm)


BzO
OBz
O
BzO
OPTFAI
17s
f1 (ppm)

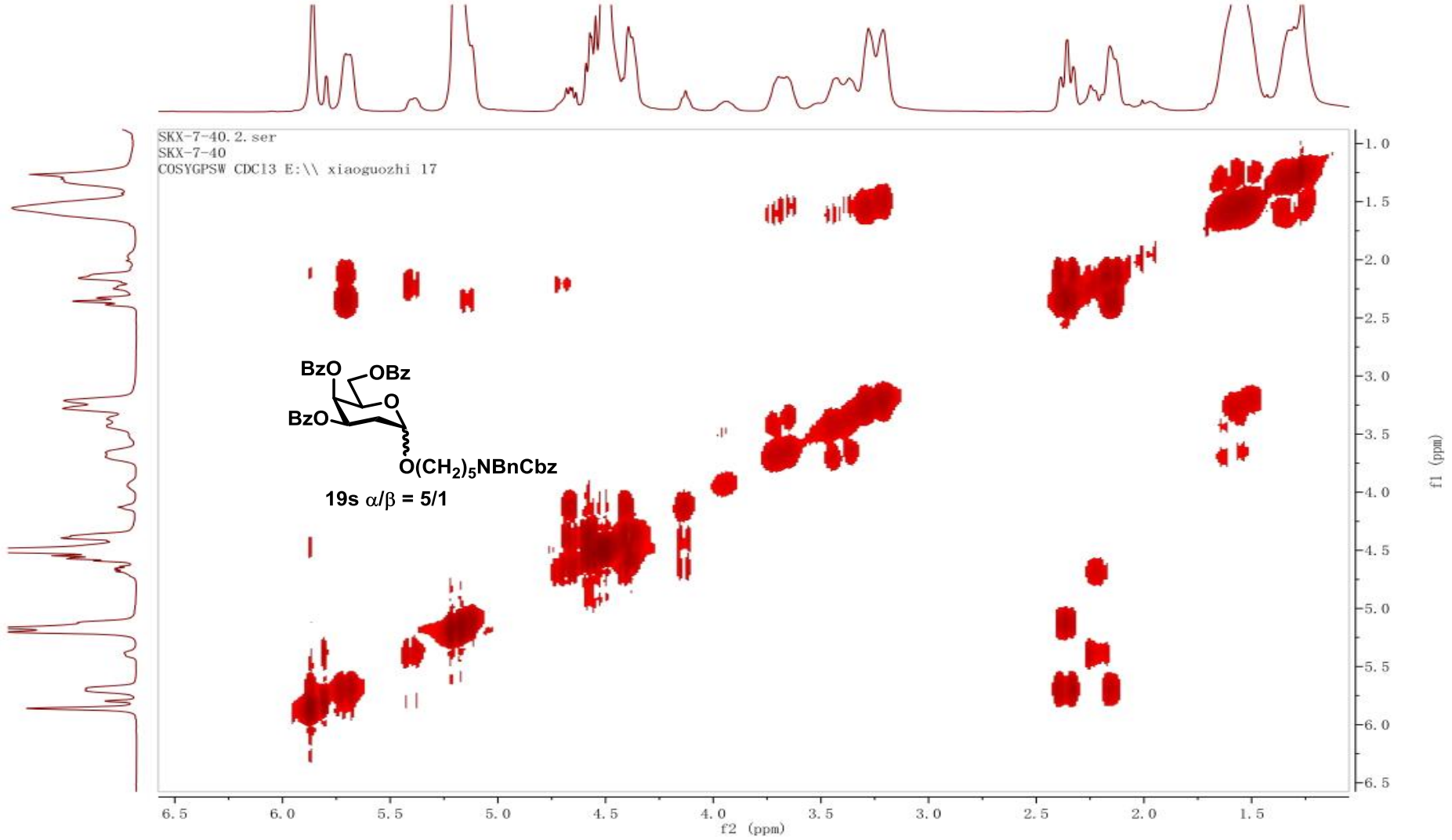

SKX-7-39-3.1.fid
SKX-7-39-3
c13 CDCl3 E:\\ xiaoguozhi 11
165.99
165.59
165.50
165.44
165.34
143.47
143.40
133.60
133.57
133.34
133.26
133.20
129.97
129.86
129.78
129.73
129.71
129.51
129.47
129.42
129.34
129.30
129.22
128.79
128.65
128.47
128.42
128.38
128.36
124.41
119.39
119.25
72.61
69.98
68.83
66.98
66.51
66.12
62.98
62.59
31.12
29.29
BzO
OBz
O
BzO
OPTFAI
17s
f1 (ppm)

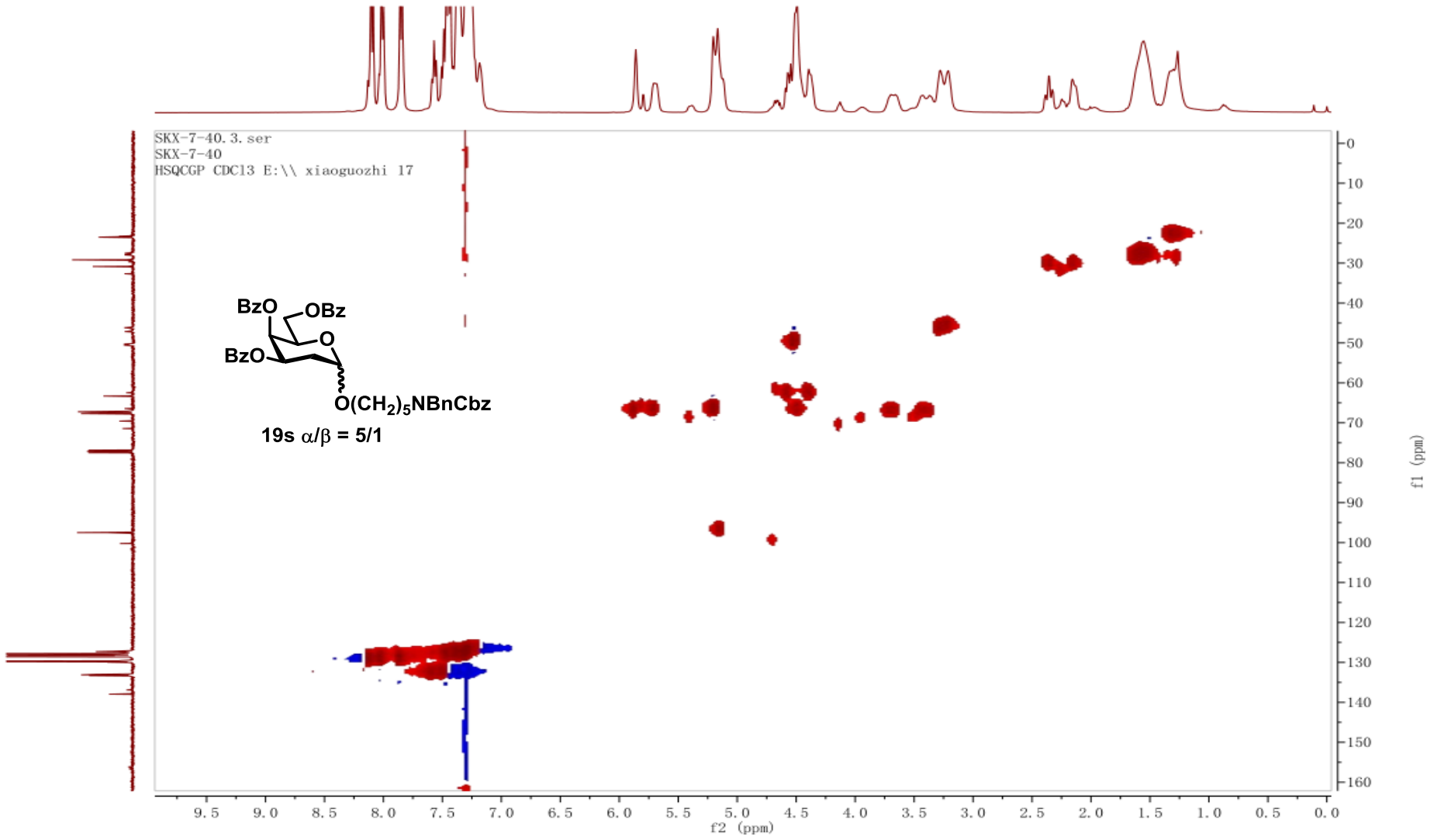

SKX-7-39-1.2.ser
SKX-7-39-1
COSYGPSW CDCl3 E:\\ xiaoguozhi 21
BzO
OBz
O
BzO
OPTFAl
17s
f2 (ppm)
f1 (ppm)


H-4α
H-4β
5.86
5.71
5.68
0.83
0.17
0.83
f1 (ppm)
BzO
OBz
O
BzO
O(CH2)5NBnCbz
19s α/β = 5/1
2.00
2.02
2.01
1.08
4.03
14.10
0.83
0.17
0.83
0.17
2.97
5.16
0.83
3.07
0.83
1.18
4.19
2.24
f1 (ppm)



166.02
165.72
165.69
165.43
137.95
136.85
133.32
133.12
132.98
129.94
129.82
129.79
129.72
129.65
129.62
129.49
128.53
128.42
128.38
128.28
128.23
127.90
127.82
127.27
100.22
97.48
71.43
69.57
67.70
67.65
67.33
67.21
67.15
66.43
63.30
62.46
50.54
50.26
47.14
46.19
32.66
30.84
29.68
29.18
27.92
27.52
23.50
23.27
BzO
OBz
BzO
O
O(CH2)5NBnCbz
19s α/β = 5/1
f1 (ppm)


SKX-7-40.2.ser
SKX-7-40
COSYGPSW CDC13 E:\\ xiaoguozhi 17
BzO
OBz
O
BzO
O(CH2)5NBnCbz
19s α/β = 5/1
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)


SKX-7-40.3.ser
SKX-7-40
HSQCGP CDCl3 E:\\ xiaoguozhi 17
BzO
OBz
O
BzO
O(CH2)5NBnCbz
19s α/β = 5/1
f2 (ppm)
f1 (ppm)