Table of Contents

General experimental procedures.....S2-3
The structure of catalysts (**C1-C10**).....S4
The structure of donors (**1a**-**1j**, **4a**-**4j**, **8a-8d**).....S5
The structure of acceptors (**2a-2u**, **6a-6j**).....S6
Synthesis of donor **1b**,**1h** and **1j**.....S7-8
Synthesis of donor **4b-4j**.....S8-14
Synthesis of donor **8d**.....S15
Synthesis of acceptor **6j**.....S16
Synthesis of **3a**-**3x**.....S17-27
The mechanism study.....S28-30
Synthesis of **5a**-**5q**.....S30-36
Synthesis of **7a**-**7t**.....S36-47
Comparison of the different imidate donors' reactivity S47-49
Synthesis of compound **9**.....S49
One-pot synthesis of trisaccharide **10**.....S50-51
References S51-53
NMR spectra S54-245

General experimental procedures

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon/nitrogen atmosphere. The solvent (DCM, toluene, DCE, CH_3CN) used in the glycosylation reactions was distilled over CaH_2 and stored on activated 4Å molecular sieves before being used. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$ (10 g/L) in 10% sulfuric acid (aq.) followed by charring at ~150 °C. Flash column chromatography was performed on silica gel (300-400 mesh). ^1H and ^{13}C spectra were recorded on a Bruker AV 400, Bruker AV 600 in $CDCl_3$, CD_3OD, CD_3COCD_3 or CD_3SOCD_3. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (^1H NMR in $CDCl_3$) or the residual signal of the deuterated solvent. Coupling constants (*J*) are given in Hz. All ^{13}C spectra are proton decoupled. Where applicable COSY, HSQC, NOESY, HMBC experiments were used to further elucidate the structure. The anomeric product ratios were analyzed through integration of proton NMR signals or seperation.

General procedure for optimization of the hydrogen bond mediated glycosylation

The correspoding donor (**1a**, **1b** or **1c**, 1.0 equiv, 0.1 mmol/0.05 mmol), acceptor **2a** (2.0 equiv) and organocatalyst **C1**-**C10** (0.1 equiv) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry solvents (83.3 mM for donor) was added to the sealed tube under N_2 atmosphere at room temperature. The reaction mixture was stirred for 16-36 h in the sealed tube under the corresponding condition and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the product.

General procedure A: Glycosyl *N*-phenyl trifluoroacetimidate donor (1.0-2.0 eq) co-evaporated twice with toluene, acceptor (1.0-1.5 equiv) co-evaporated twice with toluene and Kass catalyst **C10** (0.1 equiv-0.2 equiv) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (5-83.3 mM for acceptors) was added to the sealed tube under N_2 atmosphere at room temperature. The reaction mixture was stirred for several hours in the sealed tube under the corresponding conditions and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the product.

General procedure B: Glycosyl *N*-phenyl trifluoroacetimidate donor (2.0-2.5 equiv) co-evaporated twice with toluene, acceptor (1.0 equiv) co-evaporated twice with toluene, Kass catalyst (0.3 equiv) and activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (50 mM for acceptors) was added to the sealed tube under N_2 atmosphere at room temperature. The reaction mixture was stirred for several hours in the sealed tube under the corresponding conditions and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column

chromatography to deliver the product.

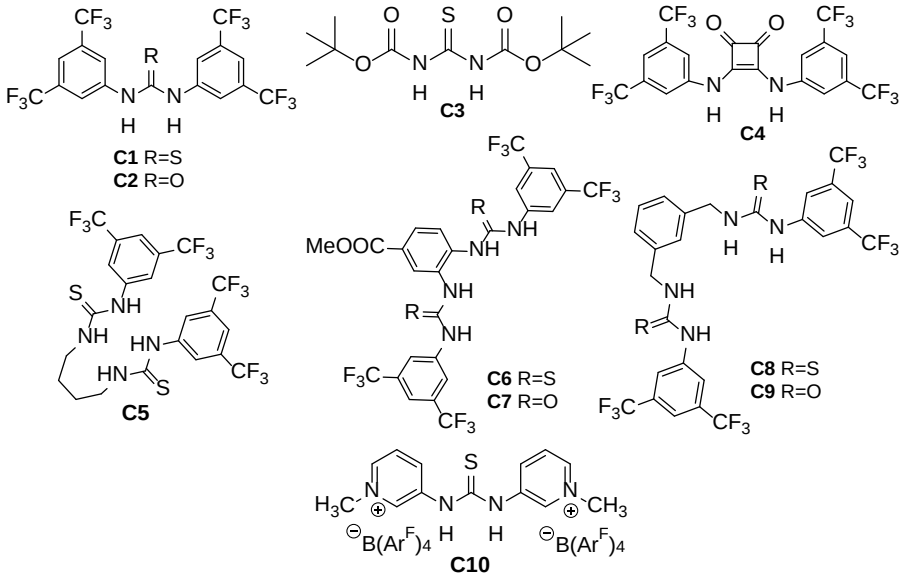
General procedure C (stereoselective glycosylation with DMF additive):
Glycosyl *N*-phenyl trifluoroacetimidate donor (1.5 eq), acceptor (1.0 equiv), Kass catalyst (0.2 equiv) and activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. The dry toluene (0.2 M for acceptors) and super-dry DMF (3.0 equiv) were added to the sealed tube under N_2 atmosphere at room temperature. The reaction mixture was stirred for 24 hours in the sealed tube under the corresponding conditions and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified size exclusion to deliver the product.

General procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor:
To a solution of the hemiacetal (1.0 equiv) in acetone (0.16 M hemiacetal in acetone) was added Cs_2CO_3 (1.5 equiv) followed by PTFACl (1.6 equiv). The mixture was stirred for several hours at 0 °C or rt, then the suspension was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate with Et_3N) to give the corresponding *N*-phenyl trifluoroacetimidates donor.

The structure of catalysts

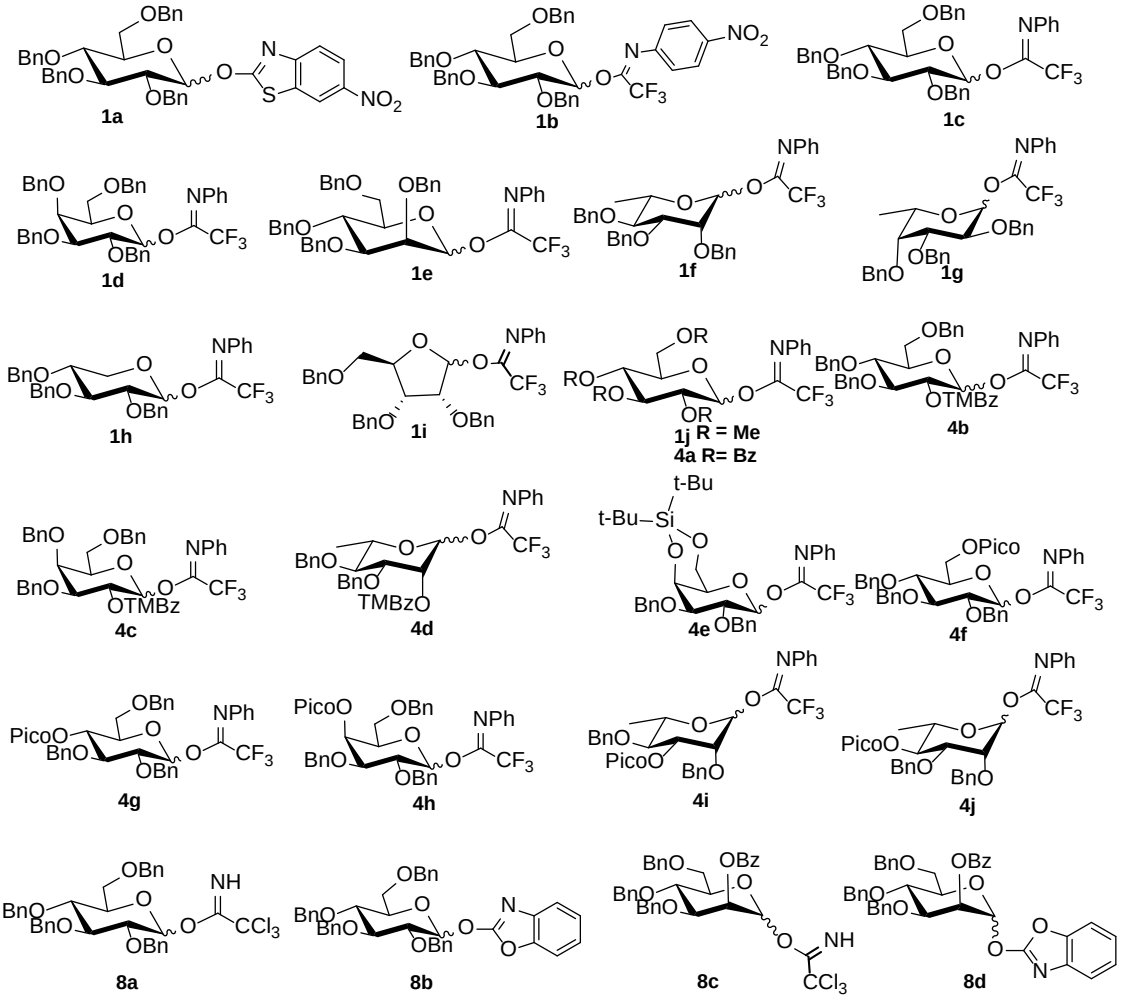
The catalysts **C1, C2, C3** were commercially available.

The catalysts **C4**[1]**, C5**[2]**, C6**[3]**, C7**[3]**, C8**[4]**, C9**[5]**, C10**[6] have been reported previously.



The structure of donors

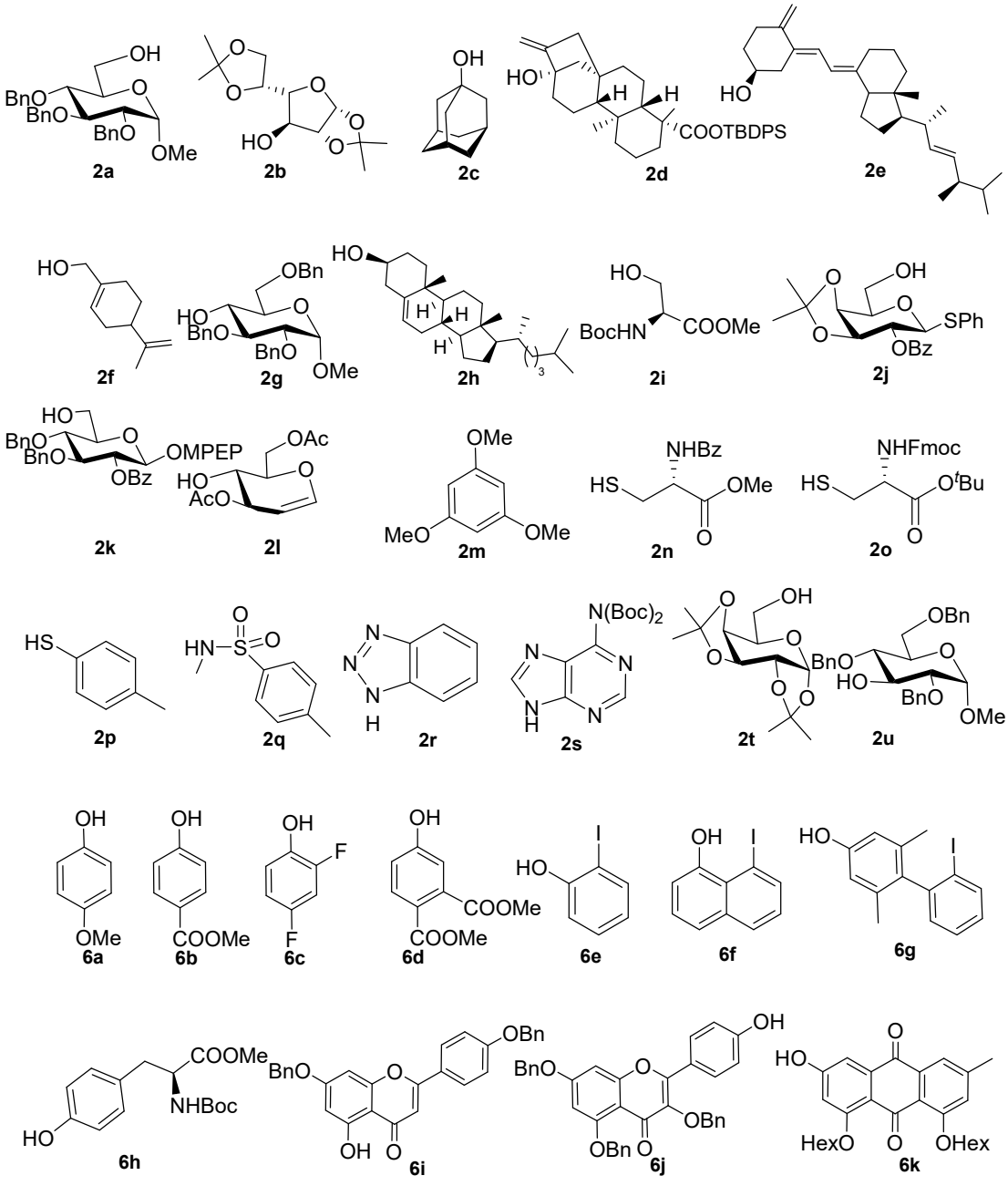
The donors **1a**[7], **1c**[8], **1d**[9], **1e**[10], **1f**[11], **1g**[11], **1i**[12], **4a**[13], **4e**[14], **8a**[15], **8b**[16], **8c**[17] are known compounds.



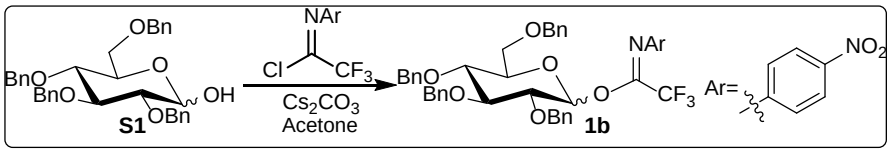
Pico: Picoloyl, TMBz: 2,4,6-trimethybenzoyl

The structure of acceptors

The acceptors **2a, 2b**, **2c**, **2e, 2f, 2g, 2h, 2i, 2m, 2p, 2q, 2r, 2t, 2u, 6a, 6b, 6c, 6d, 6e, 6f, 6h** were commercially available. The acceptors **2d**[18], **2j**[19], **2k**[20], **2l**[21], **2n**[22], **2o**[23], **2s**[24], **6g**[25], **6i**[26] and **6k**[27] have been reported previously.

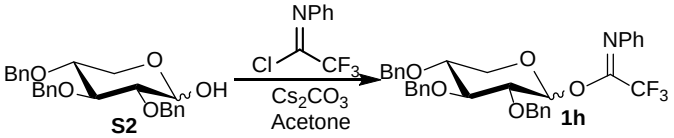


Synthesis of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl *N*-Aryl-2,2,2-trifluoroacetimidate donor (1b)



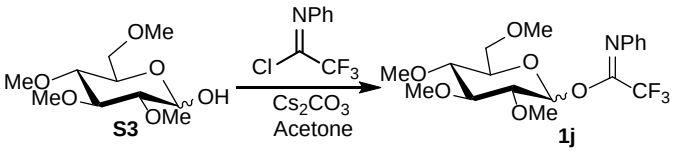
As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the corresponding hemiacetal **S1** (270 mg, 0.5 mmol) can be converted into the donor **1b** after 9 hours at 0 °C, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6:1, with Et_3N (TEA)) to yield **1b** (299 mg, 0.395 mmol, 79%) as white solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.22 – 8.14 (m, 2H), 7.45 – 7.23 (m, 20H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.47 (brs, 1H), 4.99 (t, *J* = 8.3 Hz, 1H), 4.93 – 4.84 (m, 4H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.62 – 4.57 (m, 1H), 4.56 – 4.52 (m, 1H), 4.02 – 3.92 (m, 2H), 3.87 – 3.70 (m, 4H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 150.0, 144.3, 139.0, 138.6, 138.5, 138.4, 128.3, 128.23, 128.21, 128.1, 127.9, 127.77, 127.76, 127.70, 127.65, 127.6, 127.5, 127.43, 127.36, 124.6, 120.0, 95.0, 81.4, 79.3, 76.8, 75.2, 74.8, 73.6, 73.0, 72.9, 68.5. HRMS (ESI) Calculated for $C_{34}H_{35}O_5$ [M-[OC(CF_3)=NPh]]$^+$ 523.2479, found 523.2464.

Synthesis of 2,3,4-tri-*O*-benzyl-D-Xylopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (1h)



As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the corresponding hemiacetal **S2** (211 mg, 0.5 mmol) can be converted into the donor **1h** after 9 hours at 0 °C, and purified by silica gel flash chromatography (petroleum ether/diethyl ether = 9:1, with TEA) to yield **1h** (237 mg, 0.4 mmol, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.18 (m), 7.09 (dd, *J* = 13.1, 7.2 Hz), 6.80 (t, *J* = 8.8 Hz), 6.74 (d, *J* = 7.5 Hz), 6.38 (s, 1H, H-1α), 5.73 (s, 1, H-1β), 4.95–4.59 (m), 4.01 – 3.87 (m), 3.85 – 3.55 (m).^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.5, 138.7, 138.4, 138.0, 137.9, 137.8, 128.8, 128.6, 128.5, 128.44, 128.43, 128.15, 128.04, 128.02, 128.00, 127.9, 127.77, 127.72, 127.66, 120.5, 119.4, 83.1, 81.0, 80.1, 79.0, 77.3, 77.2, 75.9, 75.5, 75.2, 73.8, 73.5, 73.3, 64.4, 62.5. HRMS (ESI) Calculated for $C_{26}H_{27}O_4$ [M-[OC(CF_3)=NPh]]$^+$ 403.1904, found 403.1890.

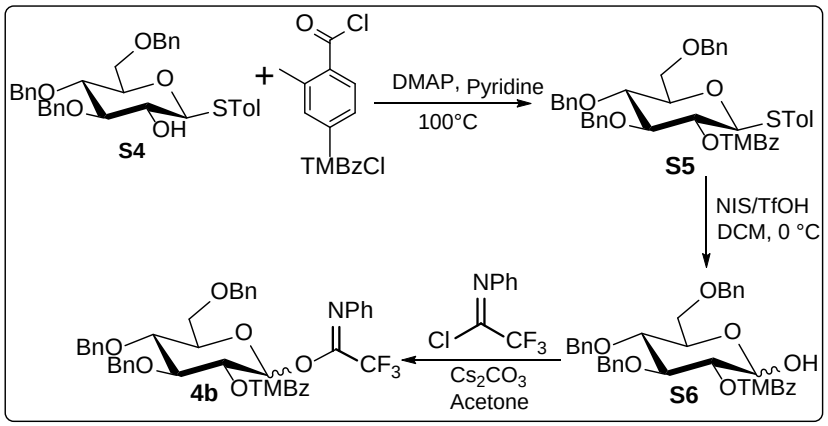
Synthesis of 2,3,4,6-tetra-*O*-methyl-D-glucopyranosyl *N*-phenyl-2,2,2-trifluoroacetimidate donor (1j)



As the general procedure for preparation of glycosyl trifluoroacetimidate (PTFAI) donor, the corresponding hemiacetal **S3** (750 mg, 3.17 mmol) can be converted into the donor **1j** after 4 hours at 0 °C, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate

= 40:1, with TEA) to yield **1j** (705 mg, 1.73 mmol, 55%) as a colorless oil. **1j-α**: ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 – 7.27 (t, *J* = 8.2 Hz, 2H), 7.20 – 7.04 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.42 (brs, 1H), 3.74 – 3.66 (m, 1H), 3.65 – 3.48 (m, 11H), 3.42 (t, *J* = 9.2 Hz, 1H), 3.34 (brs, 4H), 3.19 (t, *J* = 9.5 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 145.1, 130.2, 125.7, 120.6, 98.8, 87.5, 84.3, 80.3, 77.0, 72.3, 61.2, 61.0, 60.8, 59.7. **1j-β**: ^{1}H NMR (400 MHz, 50 °C, Acetone-d_6) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.95 – 6.78 (d, *J* = 7.8 Hz, 2H), 5.41 (brs, 1H), 3.62 – 3.49 (m, 8H), 3.47 (s, 3H), 3.34 (s, 3H), 3.23 – 3.09 (m, 4H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 144.0, 128.8, 124.2, 119.3, 93.5, 83.2, 81.0, 78.5, 73.3, 70.8, 60.1, 59.8, 58.4, 58.3. HRMS (ESI) Calculated for $C_{18}H_{24}F_3NO_6Na$ $[M+Na]^+$ 446.1193, found 446.1184.

3,4,6-Tri-*O*-benzyl-2-*O*-mesitoyl-D-glucopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4b)

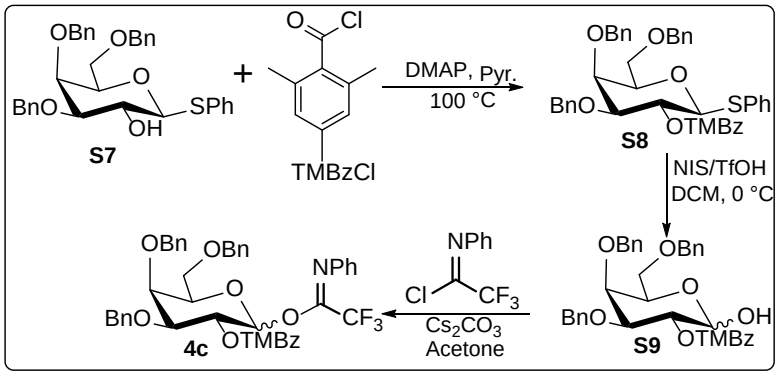


Mesitoyl chloride (1.02 ml, 6 mmol), DMAP (62 mg, 0.5 mmol), and compound **S4**[30] (557 mg, 1 mmol) were added to pyridine (5 mL), and the mixture was warmed to 100 °C and stirred for 2 d. The mixture was diluted with H_2O and extracted into CH_2Cl_2. The organic phase was washed with aqueous HCl (1 M), saturated aqueous $NaHCO_3$, and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 12:1) to afford the compound **S5** (562 mg, 0.8 mmol, 80%) as a white solid. $[\alpha]_D^{25}$ = 0.7 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 15H), 7.13 (dd, *J* = 6.8, 2.6 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 2H), 6.02 (d, *J* = 5.5 Hz, 1H), 5.27 (dd, *J* = 10.3, 5.5 Hz, 1H), 4.85 – 4.73 (m, 3H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 2H), 4.03 – 3.95 (m, 1H), 3.86 – 3.78 (m, 2H), 3.70 (dd, *J* = 10.8, 1.7 Hz, 1H), 2.31 (s, 3H), 2.28 (d, *J* = 3.4 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 139.4, 138.2, 138.1, 138.0, 137.7, 135.1, 132.3, 130.7, 129.9, 129.9, 128.5, 128.4, 128.3, 128.0, 127.89, 127.86, 127.7, 127.6, 127.4, 86.3, 80.2, 78.4, 75.4, 75.2, 74.3, 73.5, 71.4, 68.6, 21.20, 21.16, 19.9. HRMS (ESI) Calculated for $C_{44}H_{46}NaO_6S$ $[M+Na]^+$ 725.2907, found 725.2917.

To a solution of compound **S5** (562 mg, 0.8 mmol) in DCM (8 mL), TfOH (18 µl, 0.2 mmol) and NIS (221 mg, 0.96 mmol) were added to the mixture at 0 °C and stirred for 3 hours. The reaction mixture was quenched with Et_3N and saturated aqueous $Na_2S_2O_3$, and the organic phase was washed with saturated aqueous $NaHCO_3$, brine successively. The organic phases was separated and combined, and was then dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to deliver hemiacetal **S6** as a syrup.

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal **S6** can be converted into the donor **4b** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 20/1, with TEA) to yield **4b** (504 mg, 0.66 mmol, 82% for 2 steps) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.20 (m), 7.17 – 7.01 (m), 6.84 (s), 6.77 (d, *J* = 7.8 Hz), 5.81 (brs), 5.57 (brs), 4.87 (d, *J* = 11.5 Hz), 4.73 (d, *J* = 11.3 Hz), 4.66 (d, *J* = 12.2 Hz), 4.57 (d, *J* = 11.5 Hz), 3.93 (t, *J* = 9.3 Hz), 3.85 – 3.65 (m), 2.28 (s), 2.23 (s). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 143.4, 139.9, 138.0, 137.7, 135.8, 130.1, 128.9, 128.8, 128.7, 128.63, 128.56, 128.55, 128.4, 128.2, 128.1, 128.04, 127.98, 127.93, 127.87, 127.6, 127.5, 127.2, 124.6, 119.4, 95.0, 82.2, 76.0, 75.0, 74.2, 73.6, 71.9, 68.2, 21.3, 20.0. HRMS (ESI) Calculated for $C_{37}H_{39}O_6$ [M-[OC(CF_3)=NPh]]$^+$ 579.2741, found 579.2725.

3,4,6-Tri-*O*-benzyl-2-*O*-mesitoyl-D-galactopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4c)



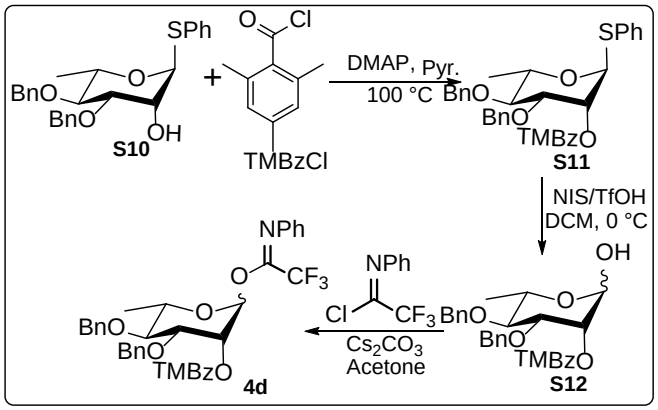
Mesitoyl chloride (1.016 ml, 6 mmol), DMAP (62 mg, 0.5 mmol), and compound **S7**[31] (543 mg, 1 mmol) were added to pyridine (5 mL), and the mixture was warmed to 100 °C and stirred for 2 d. The mixture was diluted with H_2O and extracted into CH_2Cl_2. The organic phase was washed with aq HCl (1 M), saturated aqueous $NaHCO_3$, and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 12:1) to afford the compound **S8** (544 mg, 0.79 mmol, 79%) as a white solid. $[\alpha]_D^{25}$ = 6.0 (c 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 2H), 7.40 – 7.16 (m, 18H), 6.80 (s, 2H), 5.74 (t, *J* = 9.7 Hz, 1H), 4.92 (d, *J* = 11.5 Hz, 1H), 4.85 – 4.66 (m, 2H), 4.61 – 4.34 (m, 4H), 4.07 (d, *J* = 2.6 Hz, 1H), 3.78 – 3.57 (m, 4H), 2.30 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 139.4, 138.6, 138.0, 137.6, 135.8, 133.8, 131.8, 130.8, 128.9, 128.6, 128.5, 128.4, 128.3, 128.03, 127.97, 127.9, 127.65, 127.63, 127.5, 127.1, 86.6, 82.2, 74.5, 73.7, 72.2, 71.4, 69.9, 68.9, 21.2, 20.3. HRMS (ESI) Calculated for $C_{43}H_{44}NaO_6S$ [M+Na]$^+$ 711.2751, found 711.2756.

To a solution of compound **S8** (544 mg, 0.79 mmol) in DCM (8 mL), TfOH (18 µl, 0.2 mmol) and NIS (221 mg, 0.96 mmol) were added to the mixture at 0 °C and stirred for 3 hours. The reaction mixture was quenched with Et_3N and saturated aqueous $Na_2S_2O_3$, and the organic phase was washed with saturated aqueous $NaHCO_3$, brine successively. The organic phases was separated and combined, and then dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was further purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 5/1) to deliver hemiacetal **S9** as a colorless syrup.

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal **S9** can be converted into the donor **4c** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 20/1, with TEA) to yield **4c** (510 mg, 0.664 mmol, 84% for 2 steps) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.18 (m), 7.08 (t, *J* = 7.5 Hz), 6.83 (s), 6.74 (d, *J* = 7.8 Hz), 5.92 (t, *J* = 8.9 Hz), 5.80 (s), 4.95 (d, *J* = 11.5 Hz), 4.74 (d, *J* = 11.9 Hz), 4.64 – 4.31 (m), 4.06 (d, *J* = 2.7 Hz), 3.75 – 3.49 (m), 2.27 (s), 2.21 (s). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 143.5, 139.6, 138.3, 137.8, 137.4, 135.4, 130.8, 129.5, 128.8, 128.6, 128.52, 128.49, 128.4, 128.2, 128.1, 128.04, 128.00, 127.84, 127.77, 127.2, 124.4, 119.4, 95.2, 80.8, 74.8, 74.7, 73.7, 72.0, 71.8, 70.1, 68.3, 21.3, 19.8. HRMS (ESI) Calculated for $C_{37}H_{39}O_6$ [M-[OC(CF_3)=NPh]]$^+$ 579.2741, found 579.2731.

3,4-Di-*O*-benzyl-2-*O*-mesitoyl-D-rhamnopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4d)



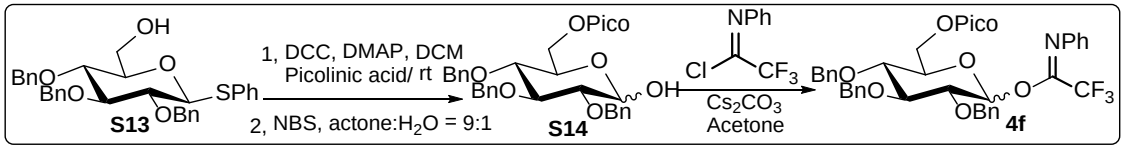
Mesitoyl chloride (0.203 ml, 1.2 mmol), DMAP (13 mg, 0.1 mmol), and compound **S10** (87 mg, 0.2 mmol) were added to pyridine (1 mL), and the mixture was warmed to 100 °C and stirred for 2 d. The mixture was diluted with H_2O and extracted into CH_2Cl_2. The organic phase was washed with aqueous HCl (1 M), saturated aqueous $NaHCO_3$, and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 15:1) to afford the compound **S11** (87 mg, 0.15 mmol, 75%). $[\alpha]_D^{25}$ = -82.3 (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (m, 2H), 7.33 – 7.16 (m, 13H), 6.76 (s, 2H), 5.77 (dd, *J* = 3.2, 1.7 Hz, 1H), 5.46 (d, *J* = 1.6 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 11.3 Hz, 1H), 4.57 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 10.8 Hz, 1H), 4.26 – 4.05 (m, 1H), 3.93 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.46 (t, *J* = 9.4 Hz, 1H), 2.20 (s, 9H), 1.22 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 139.6, 138.4, 137.8, 135.7, 134.1, 132.0, 130.6, 129.2, 128.52, 128.50, 128.49, 128.2, 128.1, 127.91, 127.87, 127.8, 86.3, 80.3, 78.5, 75.7, 72.1, 71.4, 69.3, 21.3, 20.1, 17.9. HRMS (ESI) Calculated for $C_{36}H_{39}O_5S$ [M+H]$^+$ 583.2513, found 583.2516.

To a solution of compound **S11** (410 mg, 0.704 mmol) in DCM (7 mL), TFA (52 µl, 0.7 mmol) and NIS (190 mg, 0.85 mmol) were added to the mixture at 0 °C and stirred for 30 min. The reaction mixture was quenched with Et_3N and saturated aqueous $Na_2S_2O_3$, and the organic phase was washed with saturated aqueous $NaHCO_3$, brine successively. The organic phases

was separated and combined, and was then dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to deliver hemiacetal **S12** (280 mg, 0.571 mmol, 81%) as a syrup.

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal **S12** (280 mg, 0.571 mmol) can be converted into the donor **4d** after 4 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 30/1, with TEA) to yield **4d** (267 mg, 0.403 mmol, 71%) as a syrup. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.43 (m), 7.40 – 7.26 (m), 7.19 – 7.12 (m), 6.95 (d, *J* = 7.7 Hz), 6.89 (s), 6.22 (brs), 5.86 (brs), 4.95 (d, *J* = 11.2 Hz), 4.91 (d, *J* = 11.2 Hz), 4.75 (d, 11.2 Hz), 4.70 (d, 11.2 Hz), 4.11 (dd, *J* = 9.5, 3.3 Hz), 3.99 – 3.82 (m), 3.54 (t, *J* = 9.4 Hz), 2.26 (s), 2.24 (s), 1.35 – 1.24 (m). ^{13}C NMR (100 MHz, Acetone-d_6) δ 169.2, 144.6, 140.5, 139.7, 139.0, 136.2, 131.5, 129.9, 129.3, 129.21, 129.20, 129.15, 128.9, 128.7, 128.5, 125.5, 120.4, 95.9, 80.1, 78.5, 75.9, 72.8, 71.6, 68.9, 21.2, 20.2, 18.4. HRMS (ESI) Calculated for $C_{30}H_{33}O_5$ [M-[OC(CF_3)=NPh]]$^+$ 473.2323, found 473.2287.

2,3,4-Tri-*O*-benzyl-6-*O*-picoloyl-D-glucopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4f)



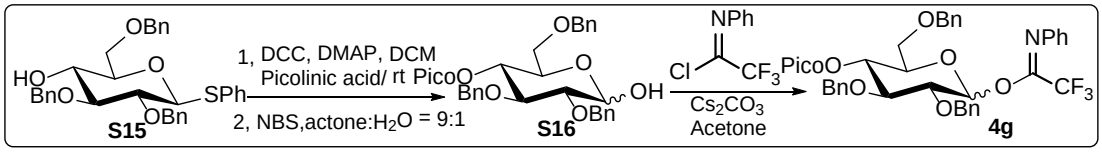
Picolinic acid (176 mg, 1.40 mmol), *N*,*N*'-dicyclohexylcarbodiimide (417 mg, 2 mmol), and 4-dimethylaminopyridine (25 mg, 0.20 mmol) were added to a solution of starting material **S13**[32] (543 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL), and the resulting mixture was stirred under N_2 for 2 hours at rt. The solid was filtered off and rinsed successively with DCM, and then the combined filtrate was washed with brine. The organic phase was separated, dried with anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude product which was used without purification in the next step.

The above obtained crude product was dissolved in acetone and H_2O (10 ml, acetone: H_2O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour at rt, and was then quenched with saturated aqueous $Na_2S_2O_3$. The organic phase was washed with saturated aqueous $NaHCO_3$ and brine successively, and the organic phases was separated and combined, and was then dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 1/2) to deliver the hemiacetal **S14** (445 mg, 0.8 mmol, 80% for 2 steps).

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal **S14** (445 mg, 0.8 mmol) can be converted into the donor **4f** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield **4f** (535 mg, 0.736 mmol, 92%) as a syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 4.5 Hz), 8.01 (d, *J* = 7.8 Hz), 7.70 (t, *J* = 7.7 Hz), 7.47 – 7.44 (m), 7.41 – 7.20 (m), 7.08 (t, *J* = 7.4 Hz), 6.74 (d, *J* = 7.6 Hz), 5.73 (brs), 4.97 (d, *J* = 10.8 Hz), 4.94 – 4.75 (m), 4.72 – 4.45 (m), 3.82 – 3.64 (m). ^{13}C NMR (100 MHz, Chloroform-*d*) δ

164.7, 150.2, 147.7, 143.4, 138.2, 137.7, 137.5, 137.0, 128.8, 128.68, 128.65, 128.36, 128.33, 128.26, 128.21, 128.19, 128.01, 127.98, 127.0, 125.4, 124.4, 119.3, 97.1, 84.6, 80.8, 76.0, 75.3, 75.2, 73.9, 64.1. HRMS (ESI) Calculated for $C_{33}H_{32}NO_6$ [M-[OC(CF_3)=NPh]]$^+$ 538.2224, found 538.2208.

2,3,6-Tri-*O*-benzyl-4-*O*-picoloyl-D-glucopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4g)

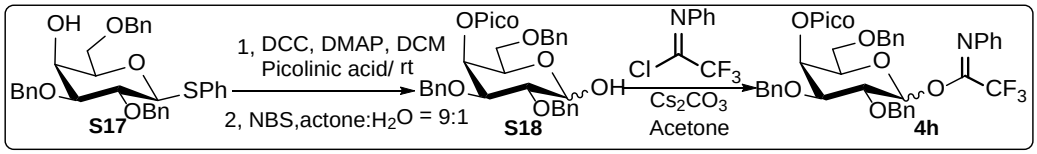


Picolinic acid (176 mg, 1.40 mmol), *N*,*N*′-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material **S15**[33] (543 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL) and the resulting mixture was stirred under N_2 for 2 hours at rt. The solid was filtered off and rinsed successively with DCM, and then the combined filtrate was washed with brine. The organic phase was separated, dried with anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude product which was used for the next step without purification.

The above obtained crude product was dissolved in acetone and H_2O (10 ml, acetone: H_2O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous $Na_2S_2O_3$. The organic phase was washed with saturated aqueous $NaHCO_3$, brine successively, and the organic phase was separated and combined, and was then dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to deliver the hemiacetal **S16** (440 mg, 0.79 mmol, 79% for 2 steps).

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal **S16** (440 mg, 0.79 mmol) can be converted into the donor **4g** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield **4g** (523 mg, 0.72 mmol, 91%) as a colorless syrup. **4g-β** isomer**:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 8.7 Hz, 1H), 7.98 (dt, *J* = 7.9 Hz, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 (m, 1H), 7.40 – 7.01 (m, 18H), 6.81 (d, *J* = 7.7 Hz, 2H), 5.70 (s, 1H), 5.47 (t, *J* = 9.6 Hz, 1H), 4.90 – 4.74 (m, 3H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 1.2 Hz, 2H), 3.86 (m, , 3H), 3.63 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 149.9, 147.5, 143.4, 137.9, 137.8, 137.7, 137.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.65, 127.58, 127.2, 125.7, 124.5, 119.4, 81.7, 80.96, 75.48, 75.46, 74.2, 73.6, 71.6, 68.8. HRMS (ESI) Calculated for $C_{33}H_{32}NO_6$ [M-[OC(CF_3)=NPh]]$^+$ 538.2224, found 538.2217.

2,3,6-Tri-*O*-benzyl-4-*O*-picoloyl-D-galactopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4h)

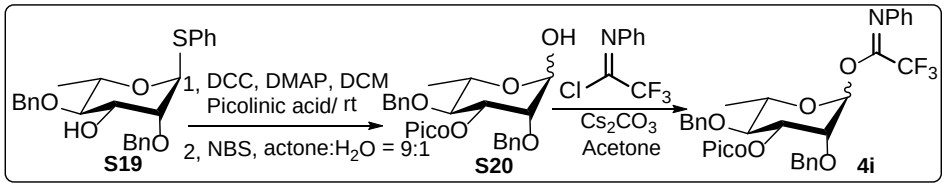


Picolinic acid (176 mg, 1.40 mmol), *N,N*′-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material **S17**[34] (543 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL) and the resulting mixture was stirred under N_2 for 2 hours at rt. The solid was filtered off and rinsed successively with DCM, and then the combined filtrate was washed with brine. The organic phase was separated, dried with anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude product which was used for next step without purification.

The above obtained crude product was dissolved in acetone and H_2O (10 ml, acetone: H_2O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous $Na_2S_2O_3$. The organic phase was washed with saturated aqueous $NaHCO_3$, brine successively, and the organic phases was separated and combined, and was then dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 1/2) to deliver the hemiacetal **S18** (456 mg, 0.82 mmol, 82% for 2 steps).

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal **S18** (456 mg, 0.82 mmol) can be converted into the donor **4h** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield **4h** (566 mg, 0.779 mmol, 95%) as a colorless syrup. **4h-β** isomer**:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 – 8.74 (m, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.82 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.40 – 7.13 (m, 17H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 2H), 5.93 (d, *J* = 3.3 Hz, 1H), 5.74 (s, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.85 – 4.71 (m, 2H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 3.93 (t, *J* = 8.9 Hz, 1H), 3.85 – 3.70 (m, 1H), 3.63 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.9, 150.3, 147.5, 143.4, 137.8, 137.44, 137.38, 137.0, 129.3, 128.8, 128.5, 128.41, 128.37, 128.33, 128.29, 128.2, 128.06, 128.0, 127.93, 127.88, 127.83, 127.78, 127.1, 125.5, 124.3, 119.3, 97.1, 79.4, 77.6, 75.7, 73.7, 73.3, 72.3, 68.0, 67.6. HRMS (ESI) Calculated for $C_{33}H_{32}NO_6$ [M-[OC(CF_3)=NPh]]$^+$ 538.2224, found 538.2216.

2,4-Di-*O*-benzyl-3-*O*-picoloyl-L-rhamnopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4i)



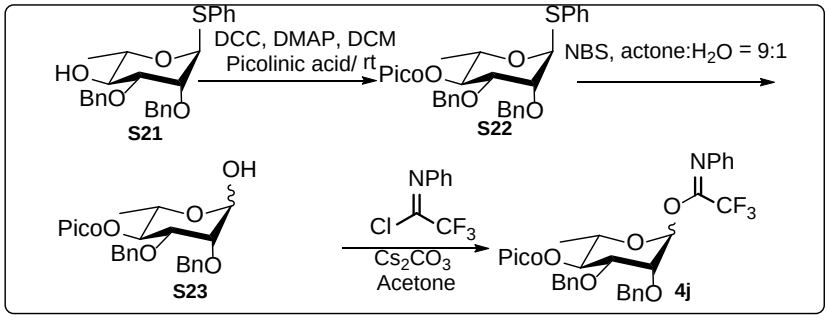
Picolinic acid (176 mg, 1.40 mmol), *N,N*′-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material **S19**[35] (437 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL) and the resulting mixture was stirred under N_2 for 2 hours at rt. The solid was filtered off and rinsed successively with CH_2Cl_2, and then the combined filtrate was washed with brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude product which was used for next step without further purification.

The above obtained crude product was dissolved in acetone and H_2O (10 ml, acetone: H_2O =

9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous $Na_2S_2O_3$. The organic phase was washed with saturated aqueous $NaHCO_3$, brine successively, and the organic phases was separated and combined, dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel chromatography (petroleum ether /ethyl acetate = 1/2) to deliver the hemiacetal **S20** (382 mg, 0.85 mmol, 85% for 2 steps).

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, hemiacetal **S20** (382 mg, 0.85 mmol) can be converted into the donor **4i** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield **4i** (497 mg, 0.8 mmol, 94%) as a colorless syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 – 8.70 (m), 8.02 (d, *J* = 7.8 Hz), 7.97 (d, *J* = 7.8 Hz), 7.82 (m), 7.50 (m), 7.37 – 7.16 (m), 7.15 – 7.00 (m), 6.84 (brs), 6.28 (brs), 5.47 (dd, *J* = 9.2, 3.4 Hz), 5.12 (s), 4.92 – 4.88 (m), 4.82 (d, *J* = 11.0 Hz), 4.69 – 4.50 (m), 4.28 (m), 4.05 (brs), 3.94 (t, *J* = 9.8 Hz), 1.43 (d, *J* = 6.0 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.3, 164.2, 150.15, 150.11, 147.8, 147.5, 143.6, 143.4, 143.3, 143.0, 137.90, 137.86, 137.5, 137.1, 137.0, 128.9, 128.8, 128.7, 128.44, 128.41, 128.33, 128.26, 128.08, 128.01, 127.9, 127.2, 127.1, 125.4, 125.3, 124.6, 119.6, 119.4, 95.4, 78.2, 77.9, 76.6, 75.4, 75.3, 74.7, 74.5, 73.8, 73.4, 72.9, 72.8, 70.9, 18.2, 18.0. HRMS (ESI) Calculated for $C_{26}H_{26}NO_5$ [M-[OC(CF_3)=NPh]]$^+$432.1805, found 432.1790.

2,3-Di-*O*-benzyl-4-*O*-picoloyl-L-rhamnopyranosyl *N*-Phenyl-2,2,2-trifluoroacetimidate donor (4j)



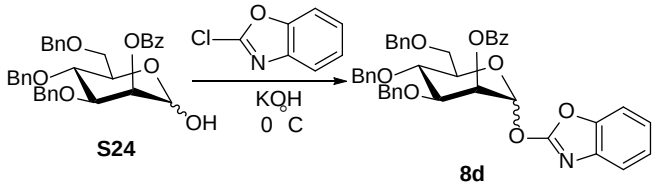
Picolinic acid (176 mg, 1.40 mmol), *N,N'*-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material **S21**[35] (437 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL) and the resulting mixture was stirred under N_2 for 2 hours at rt. The solid was filtered off and rinsed successively with CH_2Cl_2, and then the combined filtrate was washed with brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the compound **S22** (515 mg, 0.95 mmol, 95%) as a syrup. $[\alpha]_D^{25}$ = -60.0 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.0 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.5 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.43 – 7.14 (m, 15H), 5.68 – 5.60 (m, 1H), 5.54 (s, 1H), 4.77 – 4.67 (m, 2H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.51 – 4.41 (m, 2H), 4.07 – 3.99 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 164.6, 149.9, 148.0, 137.94, 137.89, 137.1, 134.4, 131.4, 129.2, 128.5, 128.3, 128.1, 127.84, 127.77, 127.67, 127.5, 127.1, 125.8, 86.2, 77.1, 76.4, 74.7, 72.5, 72.0, 68.2, 17.7. HRMS (ESI) Calculated for $C_{32}H_{32}NO_5S$ [M+H]$^+$ 542.1996, found 542.2006.

The above obtained compound **S22** was dissolved in acetone and H_2O (10 ml, acetone: H_2O =

9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous $Na_2S_2O_3$. The organic phase was washed with saturated aqueous $NaHCO_3$, brine successively, and the organic phases was separated and combined, dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to deliver the hemiacetal **S23** (372 mg, 0.83 mmol, 87%).

As the general procedure for preparation of glycosyl *N*-phenyl trifluoroacetimidate (PTFAI) donor, hemiacetal **S23** can be converted into the donor **4j** after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield **4j** (464 mg, 0.747 mmol, 90%) as a syrup. **4j-β** isomer**:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.94 – 8.68 (m, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.51 (m, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.34 (m, 2H), 7.29 (m, 6H), 7.18 (m, 5H), 5.64 (t, *J* = 9.4 Hz, 1H), 5.54 (s, 1H), 4.72 (dd, *J* = 14.8 Hz, *J* = 12.3 Hz, 2H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.51 – 4.38 (m, 2H), 4.05 – 4.00 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.6, 149.9, 148.0, 137.94, 137.89, 137.1, 134.4, 131.4, 129.2, 128.5, 128.3, 128.1, 127.84, 127.77, 127.67, 127.5, 127.1, 125.8, 86.2, 76.4, 74.7, 72.5, 72.0, 68.2, 17.7.

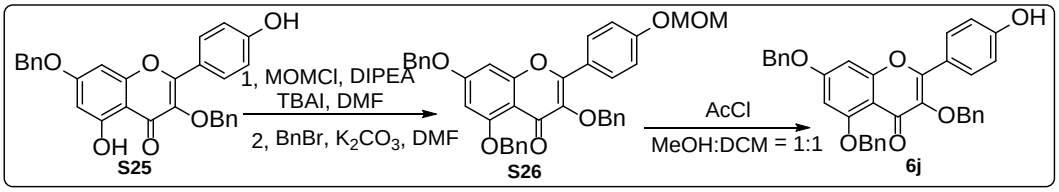
Synthesis of donor 8d



S24 **8d**

To a solution of compound **S24** (277 mg, 0.50 mmol) in dry acetone (5 mL), KOH (56 mg, 1.00 mmol) and 2-chlorobenzoxazole (230 µl, 2.00 mmol) were added to the mixture at 0 °C. The reaction mixture was stirred for another 3 hours under N_2 atmosphere. Then, the mixture was filtered off and the combined filtrate was dried over anhydrous Na_2SO_4, concentrated *in vacuo* to afford the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 12/1, with Et_3N) to afford the donor **8d** (278.8 mg, 0.415 mmol, 83%) as colorless oil. **8d-α** isomer: ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.14 – 8.07 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.41 – 7.22 (m, 17H), 6.59 (d, *J* = 1.5 Hz, 1H), 6.06 (s, 1H), 4.91 (dd, *J* = 11.2, 7.0 Hz, 2H), 4.74 – 4.65 (m, 3H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.35 – 4.25 (m, 2H), 4.17 – 4.08 (m, 1H), 3.95 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.80 (dd, *J* = 11.3, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 164.8, 161.4, 148.5, 133.5, 129.8, 128.7, 128.28, 128.23, 128.18, 128.1, 127.9, 127.4, 118.3, 109.9, 98.9, 77.6, 74.9, 74.6, 73.6, 72.9, 71.5, 68.7, 67.6. HRMS (ESI) Calculated for $C_{41}H_{37}NO_8Na$ $[M+Na]^+$ 694.2417, found 694.2413.

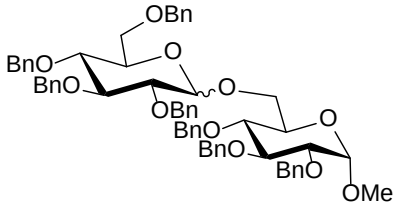
Synthesis of acceptor 6j



To a solution of compound **S25**[36] (253 mg, 0.54 mmol) in dry DMF (10 ml), tetrabutylammonium iodide (41 mg, 0.11 mmol)**,** chloromethyl methyl ether (49 µl, 0.65 mmol) and *N,N*-diisopropylethylamine (0.168 ml, 0.65 mmol) were added in sequence at 0 °C under N_2 atmosphere, and then the mixture was warmed up to rt. The reaction mixture was stirred for overnight at this temperature. The resulting mixture was diluted with DCM and washed with HCl (1 M) solution, saturated aqueous $NaHCO_3$ and brine successively. The organic phase was separated and combined, dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 20/1) to afford the intermediate (198 mg, 0.388 mmol, 72%) as a yellow solid. The above obtained intermediate (101 mg, 0.198 mmol) was dissolved in dry DMF (1ml), to which K_2CO_3 (55 mg, 0.396 mmol), Sodium iodide (6 mg, 0.0396 mmol) and BnBr (48 µl, 0.396 mmol) were added at 0 °C under N_2 atmosphere. The mixture was warmed up to rt and stirred for overnight at this temperature. The resulting mixture was diluted with DCM and washed with HCl (1 M) solution, saturated aqueous $NaHCO_3$ and brine successively. The organic phase was separated and combined, and dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford the compound **S26** (80 mg, 0.133 mmol, 67%) as a solid. $[\alpha]_D^{25}$ = -1.9 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.90 (m, 2H), 7.66 – 7.54 (m, 2H), 7.51 – 7.20 (m, 13H), 7.14 – 6.98 (m, 2H), 6.57 (d, *J* = 2.1 Hz, 1H), 6.46 (d, *J* = 2.1 Hz, 1H), 5.29 (s, 2H), 5.24 (s, 2H), 5.10 (s, 2H), 5.09 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 162.8, 159.9, 158.9, 158.8, 153.6, 139.8, 137.1, 136.5, 135.8, 130.2, 129.0, 128.9, 128.8, 128.6, 128.3, 128.0, 127.78, 127.76, 126.8, 124.5, 115.9, 110.2, 98.2, 94.3, 94.0, 74.1, 70.9, 70.6, 56.3. HRMS (ESI) Calculated for $C_{38}H_{33}O_7$ $[M+H]^+$ 601.2221, found 601.2223.

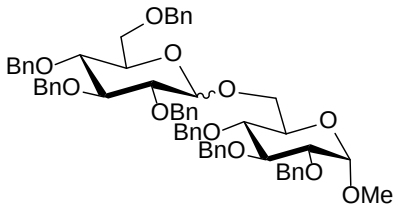
To a solution of compound **S26** (51 mg, 0.085 mmol) in mixed solvent (DCM: MeOH = 1:1, 1.7 ml), acetyl chloride (302 µl, 4.25 mmol) was added at 0 °C. The resulting reaction mixture was stirred at the same temperature for several hours, at which time TLC showed the disappearance of all starting material. The reaction mixture was diluted with ethyl acetate, and then washed with saturated aqueous $NaHCO_3$, brine successively. The organic phase was separated, combined, dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 7/1) to deliver the acceptor **6j** (42 mg, 0.0754 mmol, 89%) as a pale yellow solid. $[\alpha]_D^{25}$= -2.1 (c 0.25, Acetone); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.27 (m, 13H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 2.2 Hz, 1H), 5.26 (s, 2H), 5.23 (s, 2H), 5.00 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.4, 162.6, 159.6, 159.2, 158.2, 153.1, 138.7, 137.1, 136.9, 136.2, 130.0, 128.6, 128.5, 128.32, 128.27, 128.1, 128.0, 127.6, 127.0, 121.0, 115.4, 109.0, 97.9, 94.2, 72.9, 70.1, 70.0. HRMS (ESI) Calculated for $C_{36}H_{29}O_6$ $[M+H]^+$ 557.1959, found 557.1962.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3a)



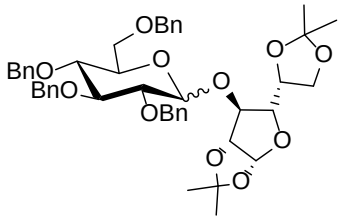
As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **3a** in the sealed tube at 27 °C after 20 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3a** (46 mg, 0.0466 mmol, 93%, α/β = 1/1) as a white amorphous solid. Analytical data for **3a** was in accordance with that reported previously.[38]

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3a, gram-scale synthesis)



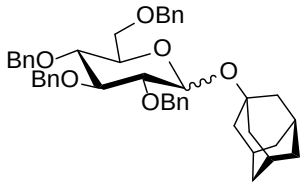
As the general procedure A, donor **1c** (1158 mg, 1.625 mmol) and acceptor **2a** (581 mg, 1.25 mmol) can be converted into the product **3a** in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3a** (1099 mg, 1.11 mmol, 89%, α/β = 2/1) as a white amorphous solid. Analytical data for **3a** was in accordance with that reported previously.[38]

3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-1,2:5,6-*O*-diisopropylidene-α-D-galactofuranose (3b)



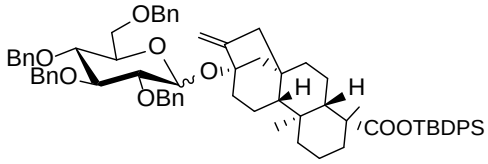
As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2b** (13 mg, 0.05 mmol) can be converted into the product **3b** in the sealed tube at 30°C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3b** (34.4 mg, 0.044 mmol, 88%, α/β = 3/1) as a syrup. Analytical data for **3b** was in accordance with that reported previously.[39]

1-Adamantanyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside (3c)



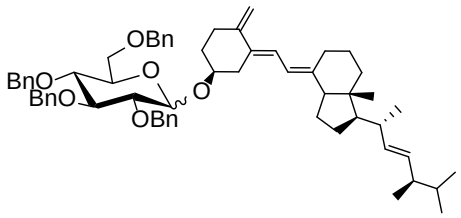
As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2c** (7.8 mg, 0.05 mmol) can be converted into the product **3c** in the sealed tube at 30 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver **3c** (31 mg, 0.046 mmol, 92%, α/β = 1.2/1) as a white solid. Analytical data for **3c** was in accordance with that reported previously.[25]

13-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)stevioltert-Butyldiphenylsilyl Ester (3d)



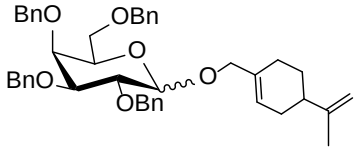
As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2d** (28 mg, 0.05 mmol) can be converted into the product **3d** in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to deliver **3d** (43.7 mg, 0.0405 mmol, 81%, α/β = 1/1.4) as a white solid. The α and β isomer cannot be separated. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m), 7.44 – 7.14 (m), 7.12 – 7.05 (m, 2H), 5.21 (d, *J* = 3.4 Hz, 1H), 5.15 (s, 1.4H), 5.13 (s, 1H), 5.04 – 4.96 (m), 4.93 – 4.53 (m), 4.44 – 4.40 (m, 2.4H), 4.31 (d, *J* = 12.1 Hz, 1H), 4.07 (t, *J* = 9.3 Hz, 1H), 3.92 (dt, *J* = 10.0, 2.3 Hz, 1H), 3.81 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.76 (t, *J* = 9.4 Hz, 1H), 3.70 – 3.55 (m), 3.56 – 3.43 (m), 3.34 (m, 1H), 2.29 – 1.30 (m), 1.26 (s), 1.14 (s), 1.12 (s), 1.03 (m), 0.94 (t, *J* = 8.1 Hz, 2H), 0.75 (s). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.0, 176.7, 153.0, 151.7, 139.2, 138.8, 138.52, 138.50, 138.44, 138.42, 138.2, 138.0, 135.73, 135.70, 135.68, 132.20, 132.17, 130.11, 130.09, 130.06, 128.55, 128.52, 128.47, 128.45, 128.43, 128.3, 128.25, 128.22, 128.17, 128.0, 127.94, 127.90, 127.84, 127.82, 127.76, 127.74, 127.71, 127.65, 127.56, 127.5, 105.2, 104.9, 98.6, 92.5, 86.4, 86.0, 85.3, 82.4, 82.2, 80.4, 78.2, 75.8, 75.6, 75.31, 75.26, 75.0, 74.9, 73.6, 73.5, 70.1, 69.2, 68.3, 57.21, 57.19, 54.0, 53.8, 47.96, 47.91, 45.30, 45.28, 43.9, 43.7, 42.5, 41.8, 41.7, 41.5, 40.8, 40.7, 39.6, 39.5, 39.1, 38.8, 38.7, 37.6, 29.8, 29.43, 29.35, 27.33, 27.28, 22.4, 22.2, 20.4, 20.2, 19.5, 19.42, 19.40, 16.3, 16.2. HRMS (ESI) Calculated for $C_{70}H_{83}O_8Si$ $[M+H]^+$ 1079.5852, found 1079.5873.

9,10-secoergosta-5,7,10,22-tetraen-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside) (3e)



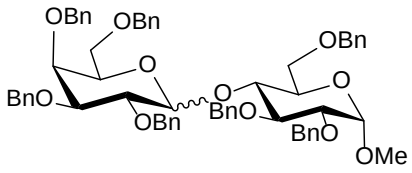
As the general procedure A, donor **1c** (39.2 mg, 0.055 mmol) and acceptor **2e** (20.3 mg, 0.05 mmol) can be converted into the product **3e** in the sealed tube wrapped in tin foil with freshly activated 4Å MS at 3 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 18/1) to deliver **3e** (28 mg, 0.0305 mmol, 61%, α/β = 1.2/1) as a colorless oil. **3e-β:** $[\alpha]_D^{25}$= 47.1 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.48 – 7.20 (m, 20H), 6.28 (d, *J* = 11.2 Hz, 1H), 6.09 (d, *J* = 11.2 Hz, 1H), 5.24 (t, *J* = 5.8 Hz, 2H), 5.08 (brs, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 11.1 Hz, 1H), 4.82 – 4.77 (m, 2H), 4.73 – 4.54 (m, 5H), 4.09 – 4.03 (m, 1H), 3.84 – 3.52 (m, 4H), 3.34 (dd, *J* = 9.0, 7.8 Hz, 1H), 2.69 – 2.58 (m, 1H), 2.54 – 2.42 (m, 2H), 2.24 – 2.11 (m, 1H), 2.03 – 1.96 (m, 2H), 1.94 – 1.22 (m, 16H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 6H), 0.58 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 146.8, 142.1, 140.21, 140.19, 139.85, 139.8, 136.73, 136.67, 132.8, 129.2, 129.12, 129.06, 129.0, 128.8, 128.7, 128.6, 128.45, 128.36, 128.3, 128.2, 128.1, 122.9, 118.8, 112.6, 102.8, 85.6, 83.3, 79.1, 76.7, 76.0, 75.6, 75.4, 75.0, 73.8, 70.1, 57.3, 57.2, 46.5, 43.8, 43.2, 41.4, 41.3, 34.8, 33.9, 33.0, 28.6, 24.3, 23.0, 21.7, 20.4, 20.1, 18.2, 12.7. HRMS (ESI) Calculated for $C_{62}H_{78}NaO_6$ $[M+Na]^+$ 941.5691, found 941.5689.

(4-Isopropenyl-1-cyclohexen-1-yl)methyl-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside) (3f)



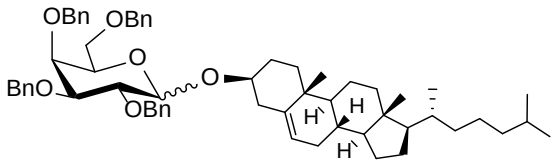
As the general procedure A, donor **1d** (46.3 mg, 0.065 mmol) and acceptor **2f** (7.8 mg, 0.05 mmol) can be converted into the product **3f** in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 14/1) to deliver **3f** (29 mg, 0.043 mmol, 86%, α/β = 1/1) as a colorless oil. The α and β isomer cannot be separated. ^{1}H NMR (400 MHz, Acetone-d_6) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.04 (m), 5.73 (d), 4.99 – 4.90 (), 4.89 – 4.85 (m), 4.82 (d), 4.79 – 4.66 (m), 4.66 – 4.52 (m), 4.51 – 4.35 (m), 4.25 (d), 4.09 – 3.78 (m), 3.63 – 3.45 (m), 2.46 – 1.89 (m), 1.85 – 1.55 (m), 1.55 – 1.32 (m). δ ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.0, 149.9, 139.0, 138.81, 138.80, 138.75, 138.7, 138.6, 138.1, 138.0, 134.0, 133.5, 128.52, 128.48, 128.45, 128.43, 128.39, 128.36, 128.31, 128.29, 128.27, 128.24, 128.01, 127.98, 127.88, 127.84, 127.80, 127.64, 127.62, 127.60, 127.5, 125.8, 124.9, 108.8, 108.7, 102.6, 95.3, 82.5, 79.7, 79.4, 76.4, 75.4, 75.1, 74.8, 74.6, 73.62, 73.55, 73.52, 73.46, 73.4, 73.2, 73.1, 70.9, 69.4, 69.1, 68.9, 41.09, 41.05, 30.58, 30.56, 27.54, 27.50, 26.6, 26.3, 20.93, 20.89.HRMS (ESI) Calculated for $C_{44}H_{50}NaO_6$ $[M+Na]^+$ 697.3500, found 697.3503.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galacotopyranosyl)-α-D-glucopyranoside (3g)



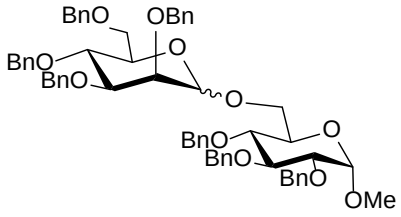
As the general procedure A, donor **1d** (46.3 mg, 0.065 mmol) and acceptor **2g** (23.3 mg, 0.05 mmol) can be converted into the product **3g** in the sealed tube at 30 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3g** (42 mg, 0.0425 mmol, 85%, α/β = 2.2/1) as a syrup. Analytical data for **3g** was in accordance with that reported previously.[40]

(3β)-Cholest-5-en-3-yl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (3h)



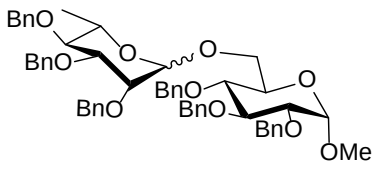
As the general procedure A, donor **1d** (46.3 mg, 0.065 mmol) and acceptor **2h** (19.4 mg, 0.05 mmol) can be converted into the product **3h** in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver **3h** (44 mg, 0.0484 mmol, 97%, α/β = 1/1.5) as a white solid. Analytical data for **3h** was in accordance with that reported previously.[41]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl)-α-D-glucopyranoside (3i)



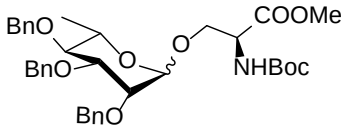
As the general procedure A, donor **1e** (46.3 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **3i** in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3i** (45 mg, 0.0456 mmol, 91%, α/β = 1.6/1) as a syrup. Analytical data for **3i** was in accordance with that reported previously.[41]

Methyl 6-*O*-(2,3,4-tri-*O*-benzyl-L-rhamnopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3j)



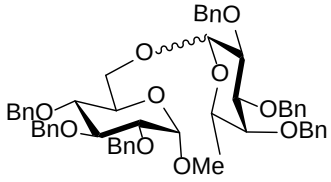
As the general procedure A, donor **1f** (45.5 mg, 0.075 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **3j** in the sealed tube at 19 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3j** (43.6 mg, 0.0494 mmol, 99%, α/β = 1/1) as a white foam. Analytical data for **3j** was in accordance with that reported previously.[21]

***N*-[(1,1-Dimethylethoxy)carbonyl]-*O*-(2,3,4-tri-*O*-benzyl-L-rhamnopyranosyl)-L-serine methyl ester (3k)**



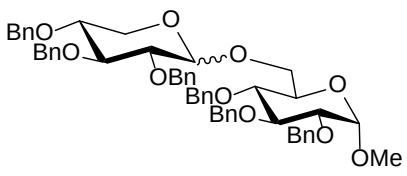
As the general procedure A, donor **1f** (45.5 mg, 0.075 mmol) and acceptor **2i** (11 mg, 0.05 mmol) can be converted into the product **3k** in the sealed tube at 19 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3k** (28 mg, 0.044 mmol, 88%, α/β = 1.5/1) as a syrup. **3k-α** isomer:$[\alpha]_D^{25}$= -7.0 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.15 (m, 15H), 5.24 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.81 – 4.52 (m, 6H), 4.47 (m, 1H), 4.03 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.76 – 3.60 (m, 5H), 3.63 – 3.39 (m, 3H), 1.30 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 155.4, 138.8, 138.5, 138.4, 128.5, 128.4, 128.0, 127.95, 127.92, 127.8, 127.74, 127.66, 98.2, 80.3, 80.2, 79.9, 75.3, 75.0, 72.9, 72.6, 68.6, 67.6, 53.7, 52.6, 28.5, 18.0. HRMS (ESI) Calculated for $C_{36}H_{45}NNaO_9$ $[M+Na]^+$ 658.2987, found 658.2986. **3k-β** isomer: $[\alpha]_D^{25}$= 34.1 (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.38 (m, 2H), 7.36 – 7.24 (m, 13H), 5.72 (d, *J* = 9.0 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.90 (d, *J* = 12.5 Hz, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 4.64 (d, *J* = 10.8 Hz, 1H), 4.46 (q, *J* = 11.9 Hz, 3H), 4.31 (s, 1H), 4.18 – 3.95 (m, 2H), 3.84 (d, *J* = 3.0 Hz, 1H), 3.73 (s, 3H), 3.61 (t, *J* = 9.3 Hz, 1H), 3.42 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.32 (m, 1H), 1.46 (s, 9H), 1.40 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.1, 155.7, 138.7, 138.5, 138.2, 128.52, 128.48, 128.3, 128.2, 127.9, 127.74, 127.69, 127.6, 101.8, 82.1, 80.0, 75.6, 74.1, 74.0, 72.3, 71.6, 71.0, 54.10, 52.6, 28.5, 17.9. HRMS (ESI) Calculated for $C_{36}H_{45}NNaO_9$ $[M+Na]^+$ 658.2987, found 658.2981.

Methyl 6-*O*-(2,3,4-tri-*O*-benzyl-L-fucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3l)



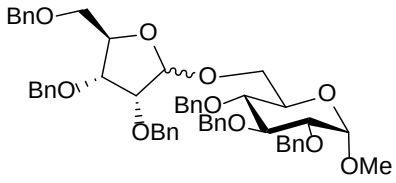
As the general procedure A, donor **1g** (45.5 mg, 0.075 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **3l** in the sealed tube at 25 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3l** (34 mg, 0.0386 mmol, 77%, α/β = 1/1.4) as a syrup. Analytical data for **3l** was in accordance with that reported previously.[40]

Methyl 6-*O*-(2,3,4-tri-*O*-benzyl-D-xylopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3m)



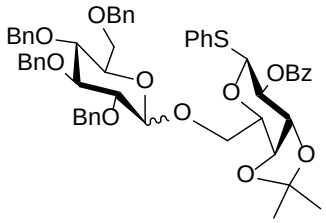
As the general procedure A, donor **1h** (38.5 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **3m** in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3m** (40.3 mg, 0.0465 mmol, 93%, α/β = 1/1.5) as a syrup. Analytical data for **3m** was in accordance with that reported previously.[42]

Methyl 6-*O*-(2,3,5-tri-*O*-benzyl-D-ribofuranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3n)



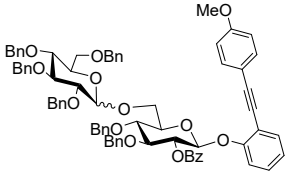
As the general procedure A, donor **1i** (38.5 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **3n** in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3n** (38 mg, 0.0438 mmol, 88%, α/β = 1/1) as a syrup. Analytical data for **3n** was in accordance with that reported previously.[43]

Synthesis of compound 3o



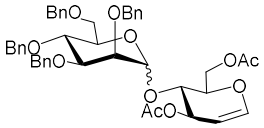
As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2j** (20.8 mg, 0.05 mmol) can be converted into the product **3o** in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3o** (39.9 mg, 0.0425 mmol, 85%, α/β = 1/1) as a syrup. The α and β isomer cannot be separated. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.03 (m), 7.62 – 7.51 (m), 7.50 – 7.03 (m), 5.33 – 5.25 (m), 4.97 – 4.92 (m), 4.88 – 4.73 (m), 4.70 – 4.41 (m), 4.37 – 4.25 (m), 4.24 – 4.21 (m), 4.18 – 3.95 (m), 3.78 – 3.58 (m), 3.50 – 3.45 (m), 1.56 (s), 1.32 (s). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.51, 165.46, 139.0, 138.7, 138.54, 138.51, 138.3, 138.18, 138.16, 138.1, 133.9, 133.6, 133.3, 132.2, 131.3, 130.1, 130.013, 129.912, 129.1, 128.9, 128.6, 128.52, 128.50, 128.48, 128.46, 128.42, 128.37, 128.35, 128.3, 128.09, 128.05, 128.00, 127.95, 127.9, 127.81, 127.77, 127.75, 127.72, 127.66, 127.6, 127.4, 110.9, 110.8, 104.2, 97.4, 86.3, 85.6, 84.7, 82.4, 82.2, 80.0, 77.8, 76.1, 75.9, 75.8, 75.2, 75.1, 75.0, 74.9, 74.8, 74.1, 74.0, 73.60, 73.56, 73.4, 72.0, 71.9, 70.4, 69.6, 69.0, 68.6, 67.5, 27.77, 27.75, 26.54, 26.51. HRMS (ESI) Calculated for $C_{56}H_{58}NaO_{11}S$ $[M+Na]^+$961.3592, found 961.3603.

Synthesis of compound 3p



As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2k** (33.6 mg, 0.05 mmol) can be converted into the product **3p** in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **3p** (50 mg, 0.0419 mmol, 84%, α/β = 2.2/1) as a colorless syrup. **3p-α** isomer: $[\alpha]_D^{25}$= 2.4 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.49 – 6.98 (m, 38H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 5.69 (dd, *J* = 9.4, 7.9 Hz, 1H), 5.20 (d, *J* = 7.9 Hz, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.87 – 4.62 (m, 8H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.37 (t, *J* = 11.9 Hz, 2H), 4.04 – 3.73 (m, 10H), 3.65 – 3.47 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.1, 159.4, 157.3, 138.9, 138.6, 138.3, 138.05, 138.01, 137.8, 133.4, 133.2, 132.9, 129.9, 129.6, 128.63, 128.61, 128.5, 128.43, 128.38, 128.29, 128.24, 128.18, 128.15, 128.04, 128.02, 127.9, 127.8, 127.7, 127.5, 122.4, 115.8, 115.0, 114.0, 113.7, 99.4, 97.4, 93.9, 83.6, 83.0, 82.0, 80.0, 78.1, 75.8, 75.3, 75.22, 75.16, 74.9, 73.4, 73.2, 70.1, 68.4, 66.6, 55.4. HRMS (ESI) calcd for $C_{76}H_{72}NaO_{13}$ $[M+Na]^+$ 1215.4865, found 1215.4849. **3p-β** isomer: $[\alpha]_D^{25}$= -1.0 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.37 (m, 3H), 7.34 – 7.10 (m, 34H), 7.02 (t, *J* = 8.2 Hz, 1H), 6.86 – 6.36 (m, 3H), 5.71 (t, *J* = 9.0 Hz, 1H), 5.19 (d, *J* = 7.8 Hz, 1H), 4.92 (dd, *J* = 10.9, 5.7 Hz, 2H), 4.87 – 4.36 (m, 12H), 4.20 (d, *J* = 11.3 Hz, 1H), 3.91 (q, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.82 – 3.24 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.2, 159.4, 157.2, 138.6, 138.5, 138.23, 138.16, 137.8, 133.4, 133.1, 133.0, 129.9, 129.8, 129.3, 128.63, 128.55, 128.53, 128.48, 128.43, 128.40, 128.3, 128.22, 128.20, 128.12, 128.07, 127.9, 127.8, 127.7, 122.3, 115.9, 114.8, 114.0, 113.7, 103.9, 98.9, 94.0, 84.7, 83.5, 82.9, 82.5, 78.2, 77.9, 75.9, 75.2, 75.1, 74.8, 73.6, 73.2, 68.9, 55.5. HRMS (ESI) calcd for $C_{76}H_{72}NaO_{13}$ $[M+Na]^+$ 1215.4865, found 1215.4853.

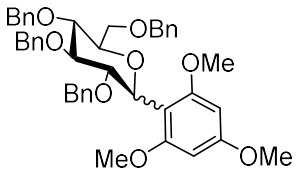
Synthesis of compound 3q



As the general procedure A, donor **1e** (71.3 mg, 0.1 mmol) and acceptor **2l** (11.5 mg, 0.05 mmol) can be converted into the product **3q** in the sealed tube at 25 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **3q** (28.2 mg, 0.0375 mmol, 75%, α/β = 2.5/1) as a syrup. **3q-α** isomer: $[\alpha]_D^{25}$= 9.5 (c 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.23 (m, 18H), 7.17 – 7.12 (m, 2H), 6.41 (dd, *J* = 6.2, 1.1 Hz, 1H), 5.14 (d, *J* = 2.2 Hz, 1H), 5.12 (t, *J* = 4.2 Hz, 1H), 4.87 – 4.77 (m, 2H), 4.77 – 4.56 (m, 6H), 4.49 (dd, *J* = 16.3, 11.4 Hz, 2H), 4.08 – 3.96 (m, 2H), 3.88 – 3.63 (m, 5H), 2.03 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 170.2, 145.6, 138.4, 138.34, 138.31, 138.2, 128.39, 128.37, 128.33, 128.30, 128.0, 127.74, 127.70, 127.68, 127.66, 127.63, 127.5, 98.7, 98.1, 79.6, 75.5, 75.0, 74.7, 74.6, 73.4, 72.9, 72.8, 72.4, 71.8, 69.0, 67.6, 62.0, 21.1, 20.8. HRMS

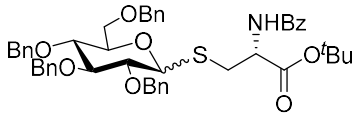
(ESI) calcd for $C_{44}H_{48}NaO_{11}$ $[M+Na]^+$ 775.3089, found 775.3071.

Synthesis the C-glycoside 3r



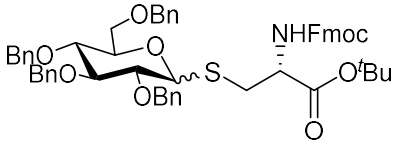
As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2m** (8.6 mg, 0.05 mmol) can be converted into the product **3r** in the sealed tube with freshly activated 4Å MS at 50 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver **3r** (23 mg, 0.033 mmol, 66%, α/β = 1/1.3) as a syrup. Analytical data for **3r** was in accordance with that reported previously.[38]

Synthesis the S-glycoside 3s



As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2n** (12 mg, 0.05 mmol) can be converted into the product **3s** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **3s** (25 mg, 0.033 mmol, 66%, α/β = 2/1) as a white solid. The α and β isomer cannot be separated. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.46 (m, 1.5H), 7.42 – 7.17 (m, 31H), 7.09 (m, 3H), 5.26 (d, *J* = 5.4 Hz, 1H), 5.20 (m, 1H), 5.10 (m, 0.5H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.90 – 4.71 (m, 4.5H), 4.67 (t, *J* = 12.5 Hz, 1.5H), 4.51 – 4.40 (m, 3.5H), 4.36 (d, *J* = 12.1 Hz, 0.5H), 4.27 (m, *J* = 12.0 Hz, 1H), 4.13 (m, 1H), 3.84 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.76 (s, 4.5H), 3.74 – 3.57 (m, 5H), 3.53 (t, *J* = 8.8 Hz, 0.5H), 3.44 – 3.32 (m, 3H), 2.97 (dd, *J* = 14.6, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 171.1, 167.3, 167.1, 138.7, 138.5, 138.1, 138.0, 137.9, 137.8, 137.74, 137.72, 133.72, 133.68, 131.9, 131.8, 128.65, 128.60, 128.56, 128.52, 128.49, 128.48, 128.14, 128.08, 128.06, 127.99, 127.95, 127.90, 127.84, 127.81, 127.76, 127.74, 127.51, 127.48, 86.6, 86.1, 86.0, 82.3, 81.6, 79.6, 79.0, 77.7, 77.2, 75.9, 75.8, 75.3, 75.2, 73.5, 73.4, 72.8, 71.7, 68.6, 68.4, 53.0, 52.85, 52.76, 52.69, 35.0, 32.9, 29.8. HRMS (ESI) calcd for $C_{45}H_{48}NO_8S$ $[M+H]^+$ 762.3095, found 762.3075.

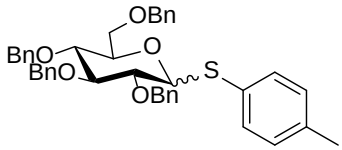
Synthesis the S-glycoside 3t



As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2o** (20 mg, 0.05 mmol) can be converted into the product **3t** in the sealed tube at 50 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **3t** (37.3 mg, 0.0404 mmol, 81%, α/β = 2/1) as a syrup. The α and β isomer cannot be separated.

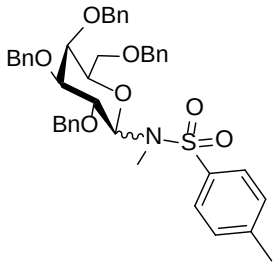
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.6), 7.61 (m), 7.41 – 7.18 (m), 7.12 (m), 6.23 (d, *J* = 8.6 Hz), 6.15 (d, *J* = 7.6 Hz), 5.27 (d, *J* = 5.1 Hz), 4.99 – 4.74 (m), 4.73 –4.13 (m), 3.84 – 3.61 (m), 3.44 (t, *J* = 8.9 Hz), 3.35 – 3.20 (m), 3.08 (dd, *J* = 14.2, 6.5 Hz), 2.89 (dd, *J* = 14.2, 4.0 Hz), 1.48 (d, *J* = 5.4 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.6, 169.5, 156.1, 156.0, 144.1, 144.0, 141.4, 138.7, 138.5, 138.4, 138.34, 138.26, 138.1, 138.0, 137.9, 137.8, 128.6, 128.53, 128.50, 128.48, 128.46, 128.4, 128.36, 128.18, 128.13, 128.09, 128.06, 128.01, 127.99, 127.97, 127.94, 127.87, 127.82, 127.80, 127.77, 127.74, 127.71, 127.66, 127.62, 127.2, 125.5, 125.3, 120.05, 120.02, 99.4, 86.7, 85.8, 85.2, 82.62, 82.58, 82.44, 82.3, 81.8, 79.7, 79.2, 77.92, 77.85, 75.9, 75.8, 75.6, 75.2, 75.10 73.6, 72.7, 71.6, 68.9, 68.7, 67.3, 67.1, 55.1, 54.6, 47.3, 47.2, 34.8, 32.8, 29.8, 28.2, 28.1. HRMS (ESI) Calculated for $C_{56}H_{60}NO_9S$ $[M+H]^+$ 922.3983, found 922.3990.

Synthesis the S-glycoside 3u



As the general procedure A, donor **1c** (46.3 mg, 0.065 mmol) and acceptor **2p** (6.4 mg, 0.05 mmol) can be converted into the product **3u** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 18/1) to deliver **3u** (31.7 mg, 0.049 mmol, 98%, α/β = 1.3/1) as a syrup. Analytical data for **3u** was in accordance with that reported previously.[44]

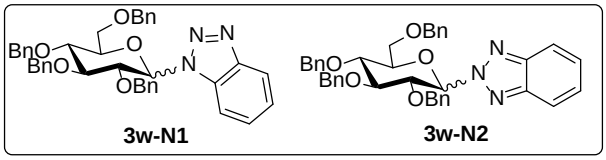
Synthesis the *N*-glycoside 3v



As the general procedure A, donor **1d** (46.3 mg, 0.065 mmol) and acceptor **2q** (9.5 mg, 0.05 mmol) can be converted into the product **3v** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver **3v** (33.3 mg, 0.047 mmol, 94%, α/β = 1.5/1) as a syrup. **3v-α** isomer: $[\alpha]_D^{25}$= -7.7 (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.17 (m, 20H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.87 (d, *J* = 2.5 Hz, 1H), 4.67 – 4.37 (m, 8H), 4.27 (m, 1H), 4.11 (dd, *J* = 11.4, 8.6 Hz, 1H), 3.98 (dd, *J* = 5.9, 2.8 Hz, 1H), 3.85 – 3.68 (m, 3H), 2.88 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.2, 138.5, 138.2, 138.1, 137.6, 135.3, 129.5, 128.6, 128.5, 128.4, 128.1, 128.02, 127.99, 127.86, 127.82, 127.77, 127.68, 127.67, 80.0, 76.8, 75.6, 75.2, 73.6, 73.4, 73.0, 72.6, 72.0, 66.7, 31.1, 21.5. HRMS (ESI) Calculated for $C_{42}H_{45}NNaO_7S$ $[M+Na]^+$ 730.2809, found 730.2806. **3v-β** isomer: $[\alpha]_D^{25}$= 9.1 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.22 (m, 20H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.17 (d, *J* = 8.9 Hz, 1H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.87 – 4.69 (m, 4H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.37 (s, 2H), 3.94 – 3.86 (m, 2H), 3.66 (dd, *J* = 9.3, 2.7 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 1H), 3.40 (dd, *J* = 9.2,

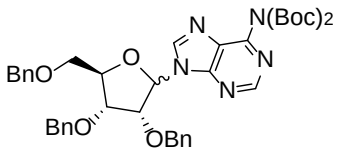
7.1 Hz, 1H), 3.30 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.63 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.2, 138.8, 138.4, 138.2, 137.9, 136.0, 129.3, 128.59, 128.57, 128.55, 128.4, 128.3, 128.0, 127.94, 127.88, 127.81, 127.78, 127.73, 127.6, 86.6, 83.5, 74.8, 74.7, 74.6, 73.7, 73.4, 73.1, 68.4, 28.9, 21.6. HRMS (ESI) Calculated for $C_{42}H_{45}NNaO_7S$ $[M+Na]^+$ 730.2809, found 730.2801.

Synthesis the *N*-glycoside 3w



As the general procedure A, donor **1c** (92.6 mg, 0.13 mmol) and acceptor **2r** (12 mg, 0.1 mmol) can be converted into the product **3w** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver **3w** (**N1**: 37.9 mg, 0.059 mmol, 59%, α/β = 1/4.7; **N2**: 23.7 mg, 0.037 mmol, 37%, α/β = 1/3) as a syrup. Analytical data for **7w-N1** was in accordance with that reported previously.[45] **3w-N1-β** isomer: HRMS (ESI) Calculated for $C_{40}H_{40}N_3O_5$ $[M+H]^+$ 642.2962, found 642.2966. **3w-N2-β** isomer: $[\alpha]_D^{25}$= -21.9 (c 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.40 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.35 – 7.22 (m, 14H), 7.17 (m, 2H), 7.11 – 6.99 (m, 3H), 6.80 – 6.69 (m, 2H), 5.92 (d, *J* = 9.1 Hz, 1H), 4.99 – 4.89 (m, 2H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.59 – 4.42 (m, 4H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.97 – 3.84 (m, 2H), 3.78 (dd, *J* = 22.8, 3.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6, 128.58, 128.57, 128.5, 128.2, 128.04, 128.02, 127.88, 127.85, 127.83, 127.78, 127.76, 127.3, 118.8, 92.3, 85.8, 81.0, 78.4, 77.5, 75.9, 75.3, 74.9, 73.7, 68.7. HRMS (ESI) Calculated for $C_{40}H_{40}N_3O_5$ $[M+H]^+$ 642.2962, found 642.2968.

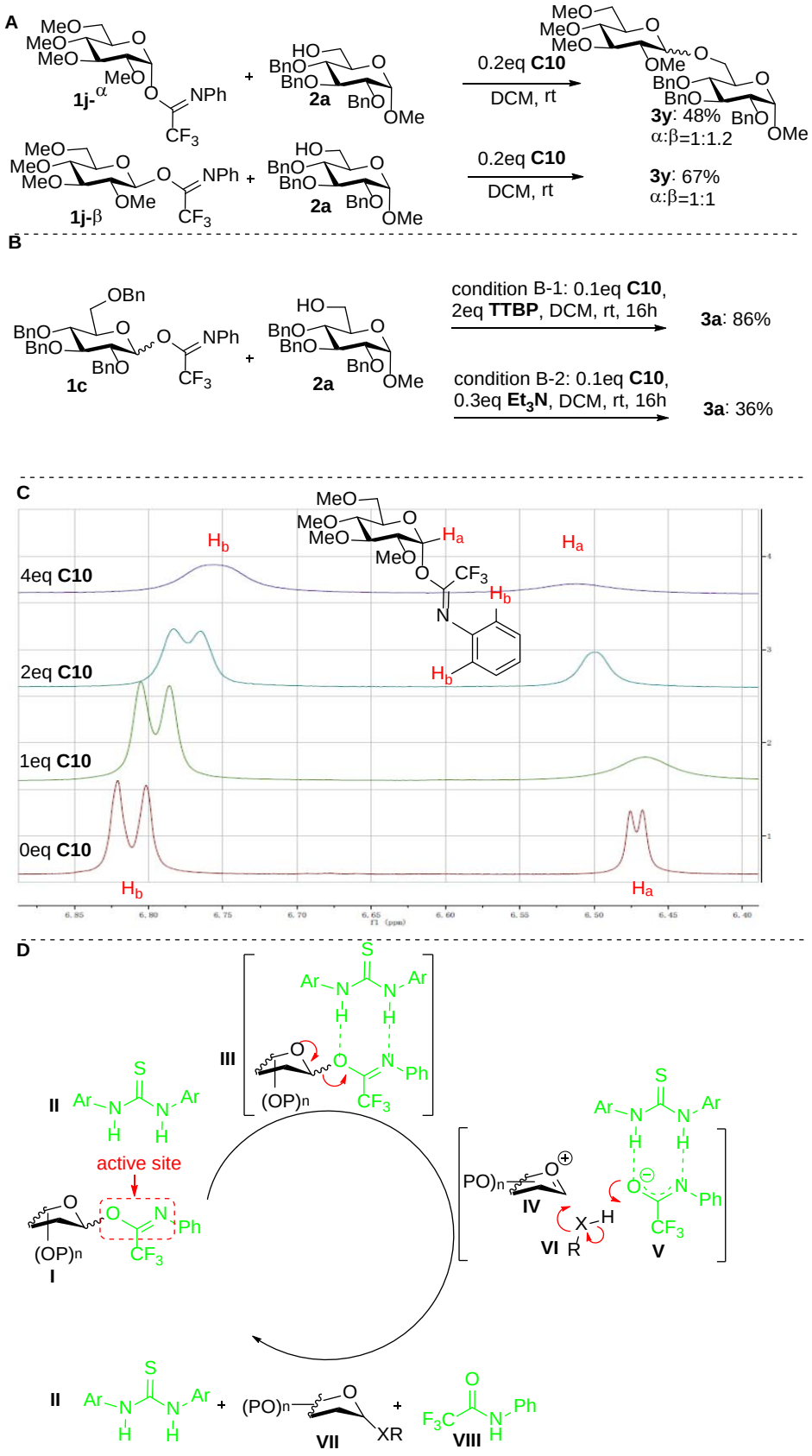
Synthesis the *N*-glycoside 3x



As the general procedure A, donor **1i** (88.9 mg, 0.15 mmol) and acceptor **2s** (33.6 mg, 0.1 mmol) can be converted into the product **3x** in the sealed tube with freshly activated 4Å MS at 40 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **3x** (45.8 mg, 0.062 mmol, 62%, α/β = 1.5/1) as a syrup. **3x-α** isomer: $[\alpha]_D^{25}$= 23.3 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 8.41 (s, 1H), 7.35 – 7.22 (m, 15H), 6.35 (d, *J* = 2.8 Hz, 1H), 4.73 (s, 2H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.56 – 4.46 (m, 2H), 4.42 (m, 3H), 4.25 (t, *J* = 5.5 Hz, 1H), 3.85 (dd, *J* = 10.9, 2.9 Hz, 1H), 3.63 (dd, *J* = 10.8, 2.8 Hz, 1H), 1.47 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.8, 152.1, 150.7, 150.3, 143.5, 137.5, 137.4, 137.0, 129.5, 128.7, 128.61, 128.59, 128.45, 128.38, 128.35, 128.15, 128.12, 128.05, 127.98, 127.8, 87.8, 84.0, 82.0, 79.4, 75.5, 73.7, 72.5, 72.4, 68.5, 28.0. HRMS (ESI) Calculated for $C_{41}H_{48}N_5O_8$ $[M+H]^+$ 738.3497, found 738.3491. **3x-β** isomer: $[\alpha]_D^{25}$= 26.0 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.79 (s, 1H), 7.39 – 7.24 (m, 10H), 7.21 – 7.15 (m, 3H), 7.00 (dd, *J* = 7.2, 1.7 Hz, 2H), 6.58 (d, *J* = 6.0 Hz,

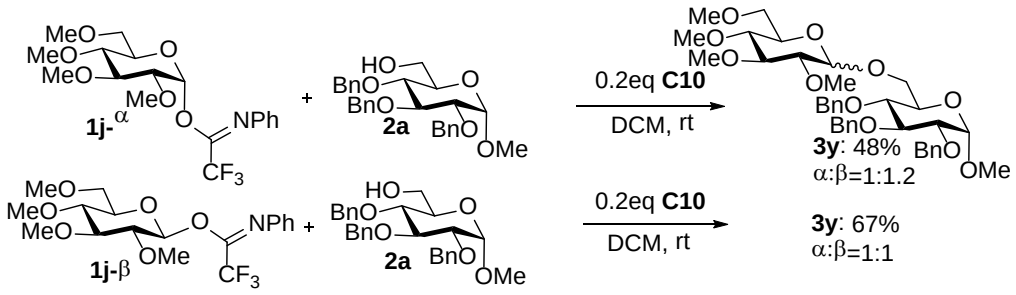
1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.63 – 4.44 (m, 6H), 4.32 (d, *J* = 11.7 Hz, 1H), 4.23 (dd, *J* = 5.4, 3.2 Hz, 1H), 3.60 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.53 (dd, *J* = 10.6, 3.0 Hz, 1H), 1.41 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.8, 151.8, 150.4, 150.0, 146.4, 137.6, 137.2, 136.5, 128.6, 128.54, 128.49, 128.42, 128.16, 128.13, 128.0, 127.9, 127.8, 127.7, 83.6, 83.0, 82.7, 73.7, 73.4, 73.2, 70.0, 27.8. HRMS (ESI) Calculated for $C_{41}H_{48}N_5O_8$ $[M+H]^+$ 738.3497, found 738.3497.

Mechanism studies



Mechanism studies and proposed catalytic cycle.

In order to gain a deeper understanding of the mechanism of thiourea catalyzed glycosylation, a serious of experiments were carried out. Under the new catalysis condition, the pure α conformation donor **1j-α** coupled with acceptor **2a** producing disaccharide **3y** with α/β mixture (α:β = 1:1.2) and the pure β conformation donor **1j-β** coupled with acceptor **2a** producing disaccharide **3y** with α/β mixture (α:β = 1:1) as well, which revealed that the reaction was not S_N2 process. In present of two equivalent hindered base 2,4,6-tri-tert-butylpyrimidine (TTBP), the glycosylation of the donor **1c** with acceptor **2a** catalyzed by Kass catalyst **C10** still works and produce the disaccharide product in 86% yield; exceptionally, the donor **1c** was activated by 0.1 equivalent **C10** even in present of 0.3 equivalent Et_3N producing disaccharide in 36% yield (donor **1c** was recovered in 55%). The results revealed that thiourea **C10** not as Brønsted acid/Lewis acid activated glycosyl donor **1c**. The interaction of glycosyl donor **1j** with **C10** was monitored by ^1H NMR and we found the anomer position proton H_a of glycosyl donor **1j** shift to downfield and the aryl proton H_b of glycosyl donor **1j** shift to upfield upon addition of thiourea **C10** (from 0 equiv to 4 equiv), which support that the hydrogen bond existence on donor **1j** and thiourea **C10**. All together, we brought up a plausible mechanism. Glycosyl imidate donor and thiourea catalyst form the donor-catalyst complex thought hydrogen bond and then generate the glycosyl oxocarbenium species **IV** and the complex of departing species of leaving group and catalyst species **V**. Combination with various stereoselective glycosylation strategies, the oxocabenium species **IV** can form special intermediate which can be selectively attacked by nucleophiles to produce glycosides **VII** and H^+. Protonation of departing species of leaving group can regenerate catalyst **II**, which can undergo the next catalytic cycle.

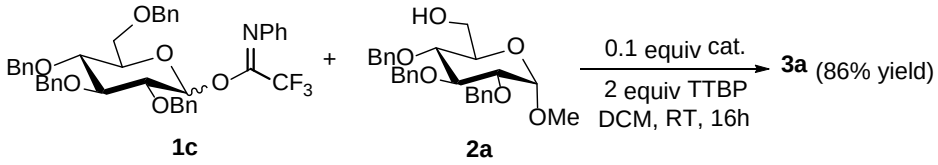


As the general procedure A, donor **1j-α** (41 mg, 0.1 mmol) was reacted with acceptor **2a** (59 mg, 0.12 mmol) catalyzed by Kass catalyst (39 mg, 0.02 mmol) in 1 ml DCM at rt for 30 hours to deliver **3t** (33 mg, 0.0483 mmol, 48%, α/β = 1:1.2) as a syrup. Analytical data for **5a** was in accordance with that reported previously.[46]

As the general procedure A, donor **1j-β** (41 mg, 0.1 mmol) was reacted with acceptor **2a** (59 mg, 0.12 mmol) catalyzed by Kass catalyst (39 mg, 0.02 mmol) in 1 ml DCM at rt for 30 hours to deliver **3t** (46 mg, 0.0673 mmol, 67%, α/β = 1:1) as a syrup. Analytical data for **5a** was in accordance with that reported previously. [46]

The glycosylation of the donor **1c** with acceptor **2a** catalyzed by Kass catalyst in the presence

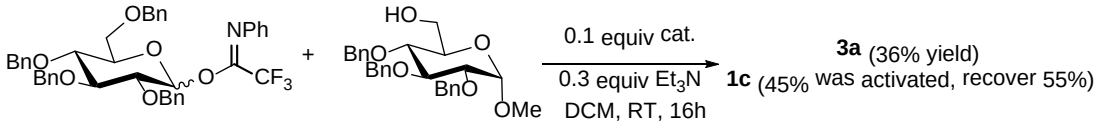
of 2,4,6-tri-tert-butylpyrimidine (TTBP)



1c **2a**

As the general procedure A, donor **1c** (35.7 mg, 0.05 mmol), acceptor **2a** (46.5 mg, 0.1 mmol), Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol), TTBP (2 equiv, 25mg, 0.1 mmol) and 0.6 ml DCM can be converted into the product **3a** in the sealed tube at rt. after 16 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3a** (42.4 mg, 0.043 mmol, 86%, α/β = 1.6:1) as a syrup.

The glycosylation of the donor **1c** with acceptor **2a** catalyzed by Kass catalyst in the presence of Et_3N



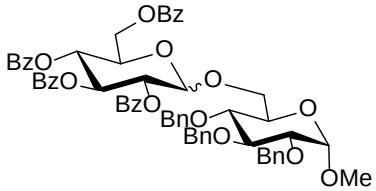
1c **2a**

As the general procedure A, donor **1c** (35.7 mg, 0.05 mmol), acceptor **2a** (46.5 mg, 0.1 mmol), Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol), Et_3N (0.3 equiv, 2.1 µl, 0.015 mmol) and 0.6 ml DCM can be converted into the product **3a** in the sealed tube at rt. after 16 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **3a** (42.4 mg, 0.043 mmol, 36%) as a syrup. Note: donor **1c** was recovered in 55% yield (19.6 mg, 0.0275 mmol).

^{1}H NMR studies for the interaction of Kass catalyst C10 with donor 1j-α

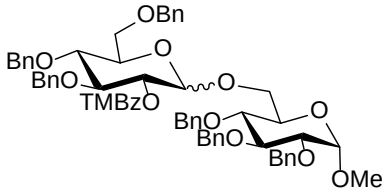
The interaction of glycosyl donor **1j-α** with **C10** was monitored by ^{1}H NMR at -60 °C in CD_2Cl_2 and we found the anomer position proton H_a of glycosyl donor **1j-α** shift to downfield and the aryl proton H_b of glycosyl donor **1j-α** shift to upfield upon addition of thiourea **C10** (from 0 to 4 equiv), which support that the hydrogen bond existence on donor **1j-α** and thiourea **C10**.

Neighboring group participation strategy for synthesis of the compound 5a



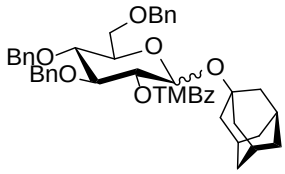
As the general procedure A, donor **4a** (38.4 mg, 0.05 mmol) and acceptor **2a** (46.5 mg, 0.1 mmol) can be converted into the product **5a** in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **5a** (42.7 mg, 0.041 mmol, 82%, α/β = 1/7.2) as a white foam. Analytical data for **5a** was in accordance with that reported previously.[25]

Neighboring group participation strategy for synthesis of the compound 5b



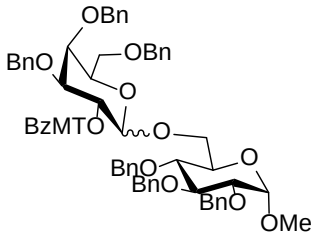
As the general procedure A, donor **4b** (49.9 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **5b** in the sealed tube at 50 °C after 48 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **5b** (44.3 mg, 0.0425 mmol, 85%, β/α > 20/1) as a white foam. **5b-β** isomer: $[\alpha]_D^{25}$= 14.3 (c 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.19 (m, 26H), 7.13 (dd, *J* = 7.0, 2.5 Hz, 4H), 6.72 (s, 2H), 5.34 (dd, *J* = 9.1, 7.9 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.79 – 4.70 (m, 4H), 4.68 (d, *J* = 7.2 Hz, 1H), 4.62 (dd, *J* = 11.1, 2.7 Hz, 2H), 4.58 (s, 1H), 4.57 – 4.48 (m, 3H), 4.39 (d, *J* = 11.3 Hz, 1H), 4.08 (dd, *J* = 10.7, 1.9 Hz, 1H), 3.95 (t, *J* = 9.2 Hz, 1H), 3.88 – 3.65 (m, 5H), 3.59 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.50 (m, 2H), 3.34 (dd, *J* = 10.0, 9.0 Hz, 1H), 3.26 (s, 3H), 2.23 (s, 6H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 139.5, 139.0, 138.5, 138.24, 138.21, 137.9, 136.2, 130.2, 128.7, 128.6, 128.52, 128.49, 128.43, 128.35, 128.2, 128.04, 128.02, 128.00, 127.9, 127.8, 127.72, 127.70, 127.62, 127.61, 127.5, 127.1, 101.2, 97.8, 82.6, 82.1, 79.9, 78.11, 78.08, 75.8, 75.4, 74.9, 74.7, 73.8, 73.6, 73.3, 72.8, 70.0, 68.9, 68.0, 55.2, 21.2, 20.4. HRMS (ESI) Calculated for $C_{65}H_{70}NaO_{12}$ $[M+Na]^+$ 1065.4759, found 1065.4804.

Neighboring group participation strategy for synthesis of the compound 5c



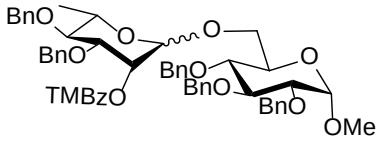
As the general procedure A, donor **4b** (57.6 mg, 0.075 mmol) and acceptor **2c** (7.8 mg, 0.05 mmol) can be converted into the product **5c** in the sealed tube at 50 °C after 48 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 13/1) to deliver **5c** (33.6 mg, 0.046 mmol, 92%, β/α > 20/1) as a syrup. **5c-β** isomer: $[\alpha]_D^{25}$= 14.0 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.07 (m, 15H), 6.80 (s, 2H), 5.30 (t, *J* = 8.2 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 7.8 Hz, 1H), 4.72 (dd, *J* = 13.2, 11.2 Hz, 2H), 4.60 (dd, *J* = 11.4, 7.8 Hz, 3H), 3.88 – 3.64 (m, 4H), 3.53 (tt, *J* = 5.5, 2.1 Hz, 1H), 2.28 (s, 6H), 2.25 (s, 3H), 2.15 – 2.02 (m, 3H), 1.92 – 1.71 (m, 6H), 1.58 (q, *J* = 12.5 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 139.2, 138.32, 138.29, 137.9, 135.7, 130.6, 128.52, 128.49, 128.42, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.3, 127.0, 94.6, 82.6, 78.3, 75.6, 74.7, 74.6, 73.5, 73.3, 73.1, 69.2, 42.6, 36.3, 30.7, 21.2, 21.1, 20.54, 20.50. HRMS (ESI) Calculated for $C_{47}H_{54}NaO_7$ $[M+Na]^+$ 753.3762, found 753.3795.

Neighboring group participation strategy for synthesis of the compound 5d



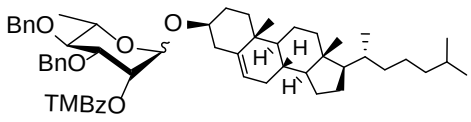
As the general procedure A, donor **4c** (57.6 mg, 0.075 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **5d** in the sealed tube at 50 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **5d** (40 mg, 0.0383 mmol, 77%, α/β = 1/10) as a white foam. **5d-β** isomer: $[\alpha]_D^{25}$= 11.9 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.16 (m, 28H), 7.12 – 7.06 (m, 2H), 6.71 (s, 2H), 5.72 (dd, *J* = 10.0, 7.9 Hz, 1H), 4.92 (t, *J* = 11.4 Hz, 2H), 4.80 – 4.69 (m, 3H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.56 – 4.30 (m, 7H), 4.11 – 4.01 (m, 2H), 3.93 (t, *J* = 9.3 Hz, 1H), 3.84 – 3.78 (m, 1H), 3.67 – 3.52 (m, 5H), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.34 (dd, *J* = 10.1, 8.9 Hz, 1H), 3.25 (s, 3H), 2.20 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 139.2, 139.1, 138.60, 138.55, 138.3, 137.9, 137.7, 135.8, 130.9, 128.56, 128.55, 128.52, 128.47, 128.42, 128.3, 128.2, 128.05, 128.03, 127.97, 127.8, 127.61, 127.57, 127.53, 126.9, 101.4, 97.8, 82.2, 81.3, 80.0, 78.1, 75.8, 74.8, 74.5, 73.6, 73.3, 72.0, 71.3, 70.9, 70.0, 68.5, 67.2, 55.2, 21.2, 20.1. HRMS (ESI) Calculated for $C_{65}H_{70}NaO_{12}$ $[M+Na]^+$ 1065.4759, found 1065.4779.

Neighboring group participation strategy for synthesis of the compound 5e



As the general procedure A, donor **4d** (99.3 mg, 0.15 mmol) and acceptor **2a** (46.5 mg, 0.1 mmol) can be converted into the product **5e** in the sealed tube at 30 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **5e** (76 mg, 0.81 mmol, 81%, α/β = 17/1) as a colorless oil. **5e-α** isomer: $[\alpha]_D^{25}$= 28.0 (c 4.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.24 (m, 25H), 6.84 (s, 2H), 5.56 (brs, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.96 – 4.72 (m, 6H), 4.73 – 4.46 (m, 5H), 3.99 (m, 2H), 3.85 (d, *J* = 10.9 Hz, 1H), 3.81 – 3.69 (m, 2H), 3.60 – 3.48 (m, 2H), 3.44 (t, *J* = 9.5 Hz, 2H), 3.35 (s, 3H), 2.28 (s, 3H), 2.26 (s, 6H), 1.24 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.4, 139.5, 138.8, 138.5, 138.3, 138.2, 138.1, 135.6, 130.8, 128.61, 128.55, 128.48, 128.45, 128.40, 128.24, 128.15, 128.0, 127.9, 127.83, 127.78, 127.75, 98.0, 82.2, 80.2, 80.1, 78.0, 77.8, 76.0, 75.6, 75.2, 73.5, 72.0, 70.2, 69.8, 68.0, 66.4, 55.3, 21.3, 20.0, 17.9. HRMS (ESI) Calculated for $C_{58}H_{64}NaO_{11}$ $[M+Na]^+$ 959.4341, found 959.4349.

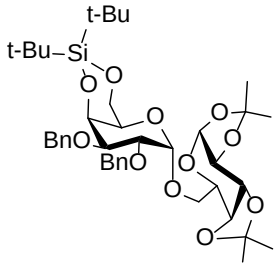
Neighboring group participation strategy for synthesis of the compound 5f



As the general procedure A, donor **4d** (99.3 mg, 0.15 mmol) and acceptor **2h** (38.8 mg, 0.1

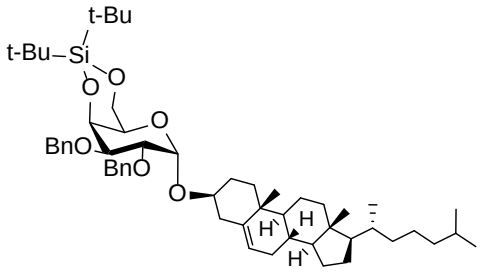
mmol) can be converted into the product **5f** in the sealed tube at 30 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver **5f** (83.3 mg, 0.097 mmol, 97%, α/β = 13/1) as a white solid. **5f-α** isomer: $[\alpha]_D^{25}$= -6.4 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.23 (m, 10H), 6.84 (s, 2H), 5.58 (brs, 1H), 5.36 (brs, 1H), 5.01 (d, *J* = 1.9 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.07 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.86 (m, 1H), 3.57 – 3.36 (m, 2H), 2.40 – 2.18 (m, 11H), 2.05 – 1.92 (m, 2H), 1.93 – 1.77 (m, 3H), 1.68 – 0.81 (m, 36H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.6, 140.4, 139.4, 138.6, 138.3, 135.6, 131.0, 128.48, 128.46, 128.4, 128.2, 128.0, 127.8, 127.6, 122.1, 96.2, 80.4, 78.4, 77.6, 75.6, 71.9, 70.3, 68.0, 56.9, 56.3, 50.3, 42.5, 39.9, 39.7, 38.7, 37.4, 36.8, 36.3, 35.9, 32.1, 32.0, 29.6, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.3, 21.2, 20.1, 19.5, 18.9, 18.0, 12.0. HRMS (ESI) Calculated for $C_{57}H_{78}NaO_6$ $[M+Na]^+$ 881.5691, found 881.5691.

Conformation-restrained strategy for synthesis of the compound 5g



As the general procedure A, donor **4e** (50.4 mg, 0.075 mmol) and acceptor **2t** (13.1 mg, 0.05 mmol) can be converted into the product **5g** in the sealed tube at 23 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver **5g** (30.8 mg, 0.0415 mmol, 83%, α only) as a syrup. $[\alpha]_D^{25}$= 23.9 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.22 (m, 10H), 5.48 (d, *J* = 5.0 Hz, 1H), 4.57 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.51 (d, *J* = 3.0 Hz, 1H), 4.28 (dt, *J* = 7.4, 2.2 Hz, 2H), 4.20 (dd, *J* = 12.5, 2.1 Hz, 1H), 4.10 (dd, *J* = 12.5, 1.7 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.83 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.74 (d, *J* = 6.4 Hz, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.31 (s, 6H), 1.05 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.2, 138.8, 128.41, 128.37, 128.2, 127.73, 127.66, 127.5, 109.4, 108.6, 98.2, 96.5, 77.7, 74.4, 73.3, 71.3, 71.2, 71.0, 70.8, 70.7, 67.4, 67.3, 67.1, 66.7, 27.8, 27.5, 26.2, 25.1, 24.7, 23.6, 20.8. HRMS (ESI) Calculated for $C_{40}H_{58}NaO_{11}Si$ $[M+Na]^+$ 765.3641, found 765.3643.

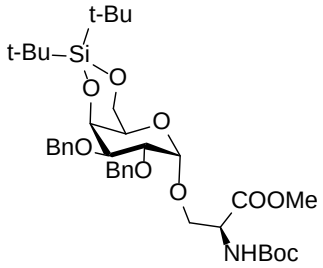
Conformation-restrained strategy for synthesis of the compound 5h



As the general procedure A, donor **4e** (50.4 mg, 0.075 mmol) and acceptor **2h** (19.4 mg, 0.05 mmol) can be converted into the product **5h** in the sealed tube at 23 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver

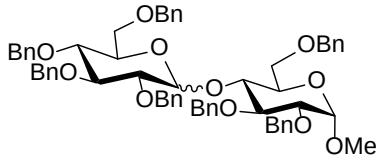
5h (35.6 mg, 0.041 mmol, 82%, α only) as a syrup. $[\alpha]_D^{25}$ = 36.8 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.20 (m, 10H), 5.30 (brs, 1H), 4.88 (d, *J* = 3.7 Hz, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.73 (s, 2H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.52 (d, *J* = 3.1 Hz, 1H), 4.22 (d, *J* = 13.4 Hz, 1H), 4.09 (d, *J* = 13.4 Hz, 1H), 3.96 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.83 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.70 (d, *J* = 2.1 Hz, 1H), 3.45 (m, 1H), 2.38 (td, *J* = 12.2, 11.3, 2.9 Hz, 1H), 2.16 (ddd, *J* = 13.3, 5.0, 2.2 Hz, 1H), 2.06 – 1.74 (m, 5H), 1.60 – 0.81 (m, 51H), 0.67 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.0, 139.3, 138.9, 128.4, 128.3, 127.73, 127.71, 127.5, 121.8, 96.0, 78.0, 76.7, 74.4, 73.6, 71.4, 71.2, 67.4, 67.3, 56.9, 56.3, 50.2, 42.4, 40.1, 39.9, 39.7, 37.2, 36.9, 36.3, 35.9, 32.05, 32.02, 31.6, 30.3, 29.8, 28.4, 28.2, 27.8, 27.7, 27.5, 24.4, 24.0, 23.6, 23.0, 22.7, 21.2, 20.8, 19.6, 18.9, 12.0. HRMS (ESI) Calculated for $C_{55}H_{84}NaO_6Si$ $[M+Na]^+$ 891.5929, found 891.5932.

Conformation-restrained strategy for synthesis of the compound 5i



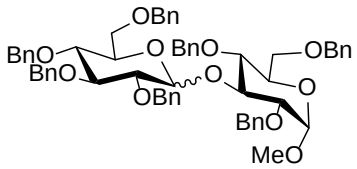
As the general procedure A, donor **4e** (50.4 mg, 0.075 mmol) and acceptor **2i** (11 mg, 0.05 mmol) can be converted into the product **5i** in the sealed tube at 23 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver **5i** (20.3 mg, 0.029 mmol, 58%, α only) as a colorless syrup. $[\alpha]_D^{25}$= 53.0 (c 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.20 (m, 10H), 5.69 (d, *J* = 8.6 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.78 – 4.58 (m, 4H), 4.52 (d, *J* = 2.9 Hz, 1H), 4.39 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.26 – 4.03 (m, 3H), 3.98 (dd, *J* = 10.1, 3.7 Hz, 1H), 3.77 (m, 2H), 3.64 (d, *J* = 8.6 Hz, 4H), 1.44 (s, 9H), 1.05 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.1, 155.6, 139.0, 138.7, 128.4, 128.2, 127.8, 127.7, 127.6, 99.9, 80.1, 74.4, 73.6, 71.04, 71.02, 70.2, 68.0, 67.2, 54.3, 52.6, 29.8, 28.4, 27.8, 27.43, 27.39, 23.5, 20.8. HRMS (ESI) Calculated for $C_{37}H_{55}NNaO_{10}Si$ $[M+Na]^+$ 724.3487, found 734.3482.

Additives-controlled strategy for synthesis of the compound 5j



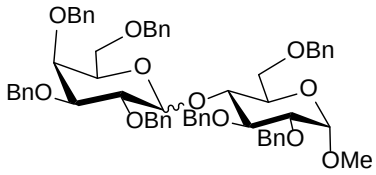
As the general procedure C, donor **1c** (105 mg, 0.15 mmol), acceptor **2g** (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.30 mmol) and 0.5 mL toluene can be converted into the product **5j** in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver **5j** (69.3 mg, 73%, α/β > 20/1) as a colorless syrup. Analytical data for 9l was in accordance with that reported previously.[47]

Additives-controlled strategy for synthesis of the compound 5k



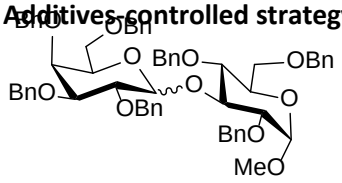
As the general procedure C, donor **1c** (105 mg, 0.15 mmol), acceptor **2u** (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.3 mmol) and 0.6 mL DCM can be converted into the product **5k** in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver **5k** (60 mg, 61%, α/β > 20/1) as a colorless syrup. Analytical data for 9l was in accordance with that reported previously.[47]

Additives-controlled strategy for synthesis of the compound 3g



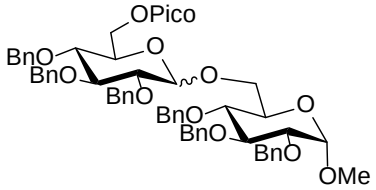
As the general procedure C, donor **1d** (105 mg, 0.15 mmol), acceptor **2g** (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.30 mmol) and 0.5 mL toluene can be converted into the product **3g** in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver **3g** (71 mg, 75%, α/β > 20/1) as a colorless syrup. Analytical data for 7g was in accordance with that reported previously.[40]

Additives-controlled strategy for synthesis of the compound 5l



Under the general procedure C, donor **1d** (105 mg, 0.15 mmol), acceptor **2u** (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.30 mmol) and 0.5 mL toluene can be converted into the product **5l** in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver **5l** (76 mg, 80%, α/β = 11/1) as a colorless syrup. Analytical data for 9n was in accordance with that reported previously.[48]

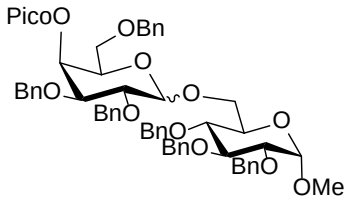
Synthesis of the compound 5m



As the general procedure A, donor **4f** (36.4 mg, 0.05 mmol) and acceptor **2a** (35 mg, 0.075 mmol) can be converted into the product **5m** in the sealed tube at 29 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver

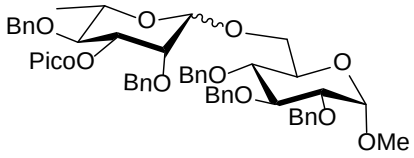
5m (40.5 mg, 0.0404 mmol, 81%, α/β = 1/7.5) as a colorless syrup. Analytical data for **5m** was in accordance with that reported previously.[29]

Synthesis of the compound 5n



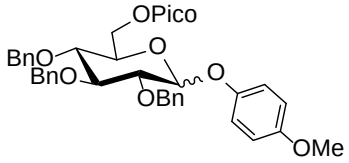
As the general procedure A, donor **4h** (47.3 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **5n** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver **5n** (41.6 mg, 0.0415 mmol, 83%, α/β = 1/11) as a colorless syrup. Analytical data for **5n** was in accordance with that reported previously.[29]

Synthesis of the compound 5o



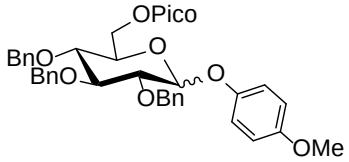
As the general procedure A, donor **4i** (40.4 mg, 0.065 mmol) and acceptor **2a** (23.3 mg, 0.05 mmol) can be converted into the product **5o** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver **5o** (39 mg, 0.0435 mmol, 87%, α/β = 1/3) as a colorless syrup. Analytical data for **5o** was in accordance with that reported previously.[29]

Synthesis of the compound 7a



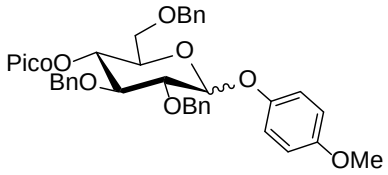
As the general procedure A, donor **4f** (54.6 mg, 0.075 mmol) and acceptor **6a** (6.4 mg, 0.05 mmol) can be converted into the product **7a** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver **7a** (31 mg, 0.047 mmol, 94%, α/β = 1/8) as a colorless syrup. Analytical data for **7a** was in accordance with that reported previously. [49]

TfOH-catalyzed glycosylation for synthesis of the compound 7a



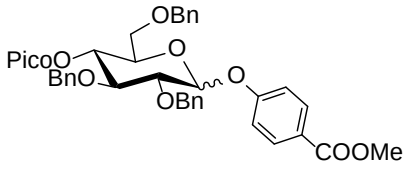
Donor **4f** (43.7 mg, 0.06 mmol), acceptor **6a** (6.4 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt. The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 µl, 0.025 mmol) was added. The mixture was warmed up to 0 °C and stirred for 5 hours at this temperature, and then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 3/1) to deliver the product **7a** (22.2 mg, 0.0335 mmol, 67%, α/β = 1/3) as a colorless syrup. Analytical data for **7a** was in accordance with that reported previously. [49]

Synthesis of the compound 7b



As the general procedure A, donor **4g** (54.6 mg, 0.075 mmol) and acceptor **6a** (6.4 mg, 0.05 mmol) can be converted into the product **7b** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver **7b** (28.1 mg, 0.0425 mmol, 84%, α/β > 20/1) as a colorless syrup. **7b-α** isomer: $[\alpha]_D^{25}$= 43.1 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 4.6 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.79 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (m, 1H), 7.40 – 7.03 (m, 18H), 6.88 – 6.70 (m, 2H), 5.54 (dd, *J* = 10.3, 9.4 Hz, 1H), 5.36 (d, *J* = 3.5 Hz, 1H), 4.92 (d, *J* = 11.3 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.73 – 4.68 (m, 2H), 4.55 – 4.21 (m, 4H), 3.81 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.77 (s, 3H), 3.67 – 3.45 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 155.3, 150.9, 149.9, 147.8, 138.5, 138.0, 137.8, 137.0, 128.6, 128.2, 128.2, 128.1, 128.0, 127.8, 127.49, 127.46, 127.0, 125.7, 118.5, 114.6, 96.8, 79.7, 79.3, 73.6, 75.6, 73.5, 71.8, 69.3, 68.7, 55.7. HRMS (ESI) Calculated for $C_{40}H_{40}NO_8$ $[M+H]^+$ 662.2748, found 662.2744.

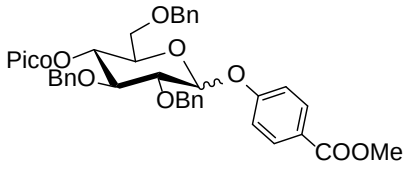
Synthesis of the compound 7c



As the general procedure A, donor **4g** (54.6 mg, 0.075 mmol) and acceptor **6b** (7.8 mg, 0.05 mmol) can be converted into the product **7c** in the sealed tube at 50 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2/1) to deliver **7c** (24 mg, 0.0348 mmol, 70%, α/β > 20/1) as a colorless syrup. **7c-α** isomer: $[\alpha]_D^{25}$= 65.5 (c 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 4.9 Hz, 1H), 8.10 – 7.95 (m, 3H), 7.80 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 (m, 1H), 7.37 – 7.00 (m, 17H), 5.58 (t, *J* = 9.9 Hz, 1H), 5.48 (d, *J* = 3.5 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 12.1 Hz, 1H), 4.73 (d, *J* = 11.4 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.48 – 4.29 (m, 3H), 4.16 (dt, *J* = 10.3, 3.5 Hz, 1H), 3.90 (s, 3H), 3.84 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.52 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 164.1, 160.3, 149.9, 147.6, 138.3, 137.9, 137.6, 137.0, 131.6, 128.6, 128.24, 128.19, 128.17, 128.0, 127.8, 127.6,

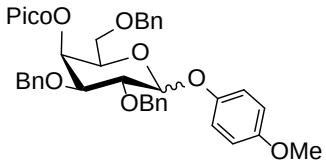
127.5, 127.1, 125.7, 124.4, 116.4, 95.5, 79.5, 79.1, 75.6, 73.8, 73.6, 71.4, 69.6, 68.3, 52.1. HRMS (ESI) Calculated for $C_{41}H_{40}NO_9$ $[M+H]^+$ 690.2698, found 690.2710.

TfOH-catalyzed glycosylation for synthesis of the compound 7c



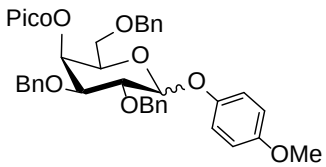
Donor **4g** (43.7 mg, 0.06 mmol) and acceptor **6b** (7.8 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt. The mixture was stirred for 10 min at -20 °C, and then TfOH (2.3 µl, 0.025 mmol) was added. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to deliver the product **7c** (17.0 mg, 0.025 mmol, 50%, α/β > 20/1) as a colorless syrup.

Synthesis of the compound 7d



As the general procedure A, donor **4h** (54.6 mg, 0.075 mmol) and acceptor **6a** (6.4 mg, 0.05 mmol) can be converted into the product **7d** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7d** (30.4 mg, 0.046 mmol, 92%, α/β = 1/7) as a colorless syrup. The α and β isomer cannot be separated. **7d-β**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 4.6 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.38 – 7.16 (m, 15H), 7.09 – 7.05 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.93 (d, *J* = 3.3 Hz, 1H), 4.97 (t, *J* = 9.2 Hz, 2H), 4.85 (dd, *J* = 18.5, 11.2 Hz, 2H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.55 – 4.40 (m, 2H), 3.99 – 3.92 (m, 2H), 3.76 (s, 3H), 3.67 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 155.4, 151.6, 150.2, 147.5, 138.4, 137.7, 137.6, 137.1, 128.42, 128.39, 128.36, 128.32, 128.30, 128.2, 128.01, 127.98, 127.80, 127.75, 127.1, 125.7, 118.5, 114.64, 114.62, 103.1, 79.4, 78.8, 75.6, 73.8, 72.7, 72.4, 68.38, 68.35, 55.7. HRMS (ESI) Calculated for $C_{40}H_{40}NO_8$ $[M+H]^+$ 662.2748, found 662.2766.

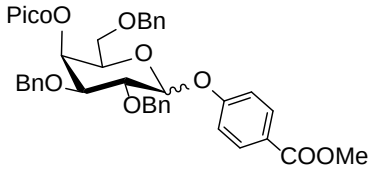
TfOH-catalyzed glycosylation for synthesis of the compound 7d



Donor **4h** (43.7 mg, 0.06 mmol), acceptor **6a** (6.4 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt.

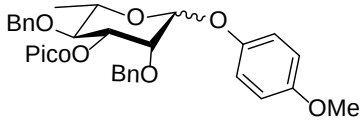
The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 µl, 0.025 mmol) was added to the stirred solution. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to deliver the product **7d** (27.1 mg, 0.041 mmol, 82%, α/β = 1/3.5) as a colorless syrup.

Synthesis of the compound 7e



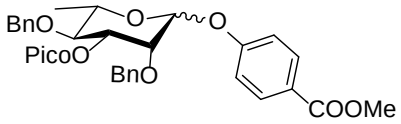
As the general procedure A, donor **4h** (54.6 mg, 0.075 mmol), acceptor **6b** (7.8 mg, 0.05 mmol), Kass catalyst (0.2 equiv, 20 mg, 0.01 mmol) and 2.5 ml DCM can be converted into the product **7e** in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver **7e** (27.2 mg, 0.0394 mmol, 79%, α/β = 1/10) as a colorless syrup. **7e-β** isomer: $[\alpha]_D^{25}$= 1.6 (c 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (brs, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.47 (brs, 1H), 7.42 – 7.15 (m, 15H), 7.11 (d, *J* = 8.6 Hz, 2H), 5.94 (d, *J* = 3.3 Hz, 1H), 5.14 (d, *J* = 7.7 Hz, 1H), 5.00 – 4.76 (m, 3H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.57 – 4.37 (m, 2H), 4.09 – 3.96 (m, 2H), 3.89 (s, 3H), 3.81 (m, 1H), 3.67 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.7, 164.0, 160.8, 150.3, 147.5, 138.2, 137.54, 137.48, 137.1, 131.7, 128.5, 128.42, 128.38, 128.3, 128.2, 128.0, 127.9, 127.8, 127.1, 125.6, 124.6, 116.2, 101.1, 79.2, 78.5, 75.7, 73.8, 73.1, 72.4, 68.3, 68.2, 52.0. HRMS (ESI) Calculated for $C_{41}H_{40}NO_9$ $[M+H]^+$ 690.2698, found 690.2721.

Synthesis of the compound 7f



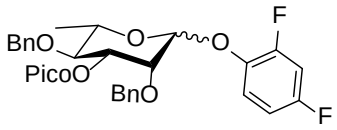
As the general procedure A, donor **4i** (46.6 mg, 0.075 mmol) and acceptor **6a** (6.4 mg, 0.05 mmol) can be converted into the product **7f** in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7f** (27.1 mg, 0.049 mmol, 98%, α/β = 1/9.6) as a colorless syrup. **7f-β** isomer: $[\alpha]_D^{25}$= 54.0 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (brs, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.50 (m, 1H), 7.40 – 7.31 (m, 2H), 7.24 – 7.15 (m, 5H), 7.06 – 7.03 (m, 2H), 6.99 (d, *J* = 9.1 Hz, 2H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.17 (dd, *J* = 9.8, 3.2 Hz, 1H), 5.09 (s, 1H), 5.03 (d, *J* = 12.3 Hz, 1H), 4.83 (dd, *J* = 13.9, 11.7 Hz, 2H), 4.70 (d, *J* = 11.0 Hz, 1H), 4.33 (d, *J* = 3.2 Hz, 1H), 3.94 (t, *J* = 9.5 Hz, 1H), 3.77 (s, 3H), 3.58 (m, 1H), 1.47 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.2, 155.3, 151.3, 150.1, 147.6, 138.1, 138.0, 136.9, 128.6, 128.4, 128.1, 128.0, 127.8, 127.6, 127.1, 125.4, 118.2, 114.6, 100.0, 78.4, 77.0, 75.5, 75.4, 75.0, 72.0, 55.7, 18.2. HRMS (ESI) Calculated for $C_{33}H_{34}NO_7$ $[M+H]^+$ 556.2330, found 556.2320.

Synthesis of the compound 7g



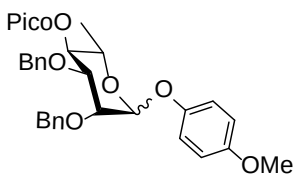
As the general procedure A, donor **4i** (46.6 mg, 0.075 mmol) and acceptor **6b** (7.8 mg, 0.05 mmol) can be converted into the product **7g** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver **7g** (28.3 mg, 0.0485 mmol, 97%, α/β = 1/15) as a colorless syrup. **7g-β** isomer: $[\alpha]_D^{25}$= 56.0 (c 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8. 82 (d, *J* = 4.2 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.59 – 7.44 (m, 1H), 7.39 – 7.30 (m, 2H), 7.25 – 7.14 (m, 5H), 7.11 – 7.05 (m, 3H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.30 (s, 1H), 5.20 (dd, *J* = 9.8, 3.2 Hz, 1H), 5.02 (d, *J* = 12.2 Hz, 1H), 4.93 – 4.78 (m, 2H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.36 (d, *J* = 3.1 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.89 (s, 3H), 3.67 (m, 1H), 1.48 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 164.2, 160.6, 150.2, 147.6, 138.0, 137.9, 137.0, 131.7, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.2, 125.4, 124.4, 115.8, 98.1, 78.2, 75.5, 75.2, 72.3, 52.1, 18.2. HRMS (ESI) Calculated for $C_{34}H_{34}NO_8$ $[M+H]^+$ 584.2279, found 584.2276.

Synthesis of the compound 7h



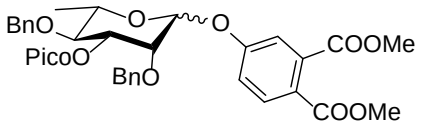
As the general procedure A, donor **4i** (46.6 mg, 0.075 mmol) and acceptor **6c** (6.7 mg, 0.05 mmol) can be converted into the product **7h** in the sealed tube at 40 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver **7h** (23 mg, 0.041 mmol, 82%, α/β = 1/12) as a colorless syrup. **7h-β** isomer: $[\alpha]_D^{25}$= 56.4 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (d, *J* = 4.5 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.24 – 6.97 (m, 8H), 6.94 – 6.73 (m, 2H), 5.15 (dd, *J* = 9.8, 3.3 Hz, 1H), 5.12 (d, *J* = 0.8 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 4.92 – 4.79 (m, 2H), 4.70 (d, *J* = 10.9 Hz, 1H), 4.46 – 4.29 (m, 1H), 3.95 (t, *J* = 9.5 Hz, 1H), 3.62 – 3.52 (m, 1H), 1.46 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 159.3 (dd, *J* = 243.9, 10.7 Hz), 154.4 (dd, *J* = 250.2, 11.8 Hz), 150.1, 147.6 (dd, *J* = 10.7, 3.6 Hz), 138.0 (d, *J* = 5.2 Hz), 137.0, 128.8, 128.4, 128.25, 128.16, 128.1, 127.9, 127.7, 127.1, 125.4, 119.5 (dd, *J* = 9.5, 1.9 Hz), 111.0 (dd, *J* = 22.6, 3.9 Hz), 105.3 (dd, *J* = 26.9, 22.0 Hz), 100.5, 78.1, 76.7, 75.4, 75.0, 74.8, 72.3, 18.2. HRMS (ESI) Calculated for $C_{32}H_{29}F_2NNaO_6$ $[M+Na]^+$ 584.1855, found 584.1854.

Synthesis of the compound7i



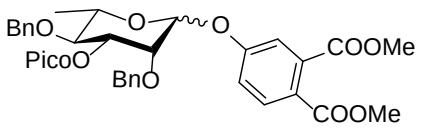
As the general procedure A, donor **4j** (62.2 mg, 0.1 mmol) and acceptor **6a** (6.4 mg, 0.05 mmol) can be converted into the product **7i** in the sealed tube at 30 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7i** (27.5 mg, 0.0495 mmol, 99%, α/β > 20/1) as a colorless syrup. **7i-α** isomer: $[\alpha]_D^{25}$= -27.7 (c 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 4.6 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.84 (td, *J* = 7.8, 1.8 Hz, 1H), 7.49 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.43 – 7.13 (m, 10H), 6.93 – 6.80 (m, 4H), 5.65 (t, *J* = 9.8 Hz, 1H), 5.43 (d, *J* = 1.9 Hz, 1H), 4.87 (d, *J* = 12.4 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.71 – 4.51 (m, 2H), 4.28 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.15 (m, 1H), 4.00 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 3H), 1.26 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7, 155.0, 150.2, 149.9, 148.0, 138.2, 138.2, 137.1, 128.5, 128.3, 128.1, 127.8, 127.61, 127.56, 127.0, 125.7, 117.5, 114.7, 97.3, 74.8, 74.6, 73.3, 72.3, 67.5, 55.7, 17.8. HRMS (ESI) Calculated for $C_{33}H_{34}NO_7$ $[M+H]^+$ 556.2330, found 556.2324.

Synthesis of the compound 7j



As the general procedure A, donor **4i** (46.6 mg, 0.075 mmol) and acceptor **6d** (11 mg, 0.05 mmol) can be converted into the product **7j** in the sealed tube with freshly activated 4Å MS at 50 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7j** (32 mg, 0.05 mmol, quant, α/β = 1/10) as a colorless syrup. **7j-β** isomer: $[\alpha]_D^{25}$= 61.3 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 4.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.91 – 7.74 (m, 2H), 7.51 (m, 1H), 7.33 (m, 2H), 7.25 – 7.16 (m, 6H), 7.15 – 7.03 (m, 4H), 5.29 (s, 1H), 5.19 (dd, *J* = 9.7, 3.2 Hz, 1H), 5.00 (d, *J* = 12.2 Hz, 1H), 4.91 – 4.77 (m, 2H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.36 (d, *J* = 3.0 Hz, 1H), 3.96 (t, *J* = 9.5 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.66 (m, 1H), 1.47 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.3, 167.0, 164.2, 159.2, 150.2, 147.5, 138.0, 137.8, 137.0, 135.3, 131.5, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.2, 125.4, 124.7, 117.8, 116.6, 98.3, 98.2, 78.1, 76.8, 75.4, 75.2, 72.4, 52.94, 52.90, 52.64, 52.59, 18.2. HRMS (ESI) Calculated for $C_{36}H_{36}NO_6$ $[M+H]^+$ 642.2334, found 642.2333.

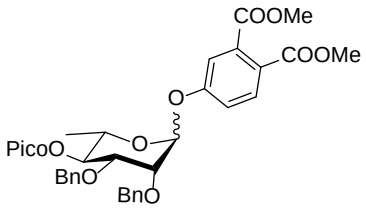
TfOH-catalyzed glycosylation for synthesis of the compound 7j



Donor **4i** (37.3 mg, 0.06 mmol) and acceptor **6d** (11 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt. The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 µl, 0.025 mmol) was added to the stirred solution. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to deliver the product **7j** (26.0 mg, 0.0405 mmol, 81%, α/β = 1/5.5) as a colorless

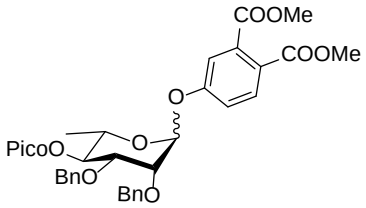
syrup.

Synthesis of the compound 7k



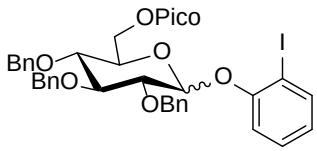
As the general procedure A, donor **4j** (62.1 mg, 0.10 mmol) and acceptor **6d** (11 mg, 0.05 mmol) can be converted into the product **7k** in the sealed tube with freshly activated 4Å MS at 55 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7k** (27.2 mg, 0.0425 mmol, 85%, α/β > 20/1) as a brown syrup. **7k-α** isomer: $[\alpha]_D^{25}$= -46.3 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 4.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.91 – 7.74 (m, 2H), 7.51 (m, 1H), 7.33 (m, 2H), 7.25 – 7.16 (m, 6H), 7.15 – 7.03 (m, 4H), 5.29 (s, 1H), 5.19 (dd, *J* = 9.7, 3.2 Hz, 1H), 5.00 (d, *J* = 12.2 Hz, 1H), 4.91 – 4.77 (m, 2H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.36 (d, *J* = 3.0 Hz, 1H), 3.96 (t, *J* = 9.5 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.66 (m, 1H), 1.24 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.3, 167.0, 164.6, 158.3, 149.9, 147.7, 138.0, 137.8, 137.2, 135.4, 131.6, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.2, 125.4, 124.7, 117.8, 116.6, 996.4, 76.8, 74.3, 74.1, 73.4, 72.4, 68.0, 53.0, 52.6, 52.59, 17.7. HRMS (ESI) Calculated for $C_{36}H_{36}NO_6$ $[M+H]^+$ 642.2339, found 642.2344.

TfOH-catalyzed glycosylation for synthesis of the compound 7k



Donor **4j** (46.6 mg, 0.075 mmol), acceptor **6d** (11 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt. The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 µl, 0.025 mmol) was added to the stirred solution. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to deliver the product **7k** (17.0 mg, 0.0265 mmol, 53%, α/β > 20/1) as a brown syrup.

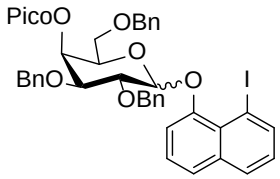
Synthesis of the compound 7l



As the general procedure A, donor **4f** (54.6 mg, 0.075 mmol) and acceptor **6e** (11.2 mg, 0.05

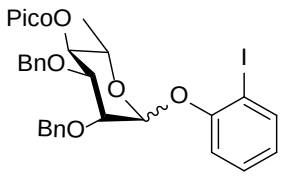
mmol) can be converted into the product **7l** in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3.5/1) to deliver **7l** (28.3 mg, 0.0374 mmol, 75%, α/β = 1/10) as a colorless syrup. **7l-β** isomer: $[\alpha]_D^{25}$= 14.8 (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.73 (m, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.46 (ddd, *J* = 7.6, 4.7, 1.3 Hz, 1H), 7.40 – 7.00 (m, 17H), 6.78 (td, *J* = 7.6, 1.4 Hz, 1H), 5.57 (t, *J* = 9.8 Hz, 1H), 5.48 (d, *J* = 3.4 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.57 – 4.32 (m, 3H), 4.20 (dt, *J* = 10.3, 3.5 Hz, 1H), 3.83 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.58 – 4.32 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 155.8, 150.0, 147.8, 139.6, 138.31, 138.29, 137.7, 137.0, 129.6, 128.5, 128.4, 128.3, 128.24, 128.19, 127.91, 127.89, 127.84, 127.54, 127.49, 127.0, 125.6, 124.2, 115.2, 96.8, 87.3, 80.0, 78.4, 75.3, 73.6, 73.4, 71.3, 70.1, 68.5. HRMS (ESI) Calculated for $C_{39}H_{37}INO_7$ $[M+H]^+$ 758.1609, found 758.1617.

Synthesis of the compound 7m



As the general procedure A, donor **4h** (54.6 mg, 0.075 mmol) and acceptor **6f** (13.5 mg, 0.05 mmol) can be converted into the product **7m** in the sealed tube at 40°C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3.5/1) to deliver **7m** (35.5 mg, 0.044 mmol, 88%, α/β = 1/10) as a syrup. **7m-β** isomer: $[\alpha]_D^{25}$= 46.2 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.85 (d, *J* = 4.4 Hz, 1H), 8.30 – 8.20 (m, 2H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.12 (m, 24H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.00 (d, *J* = 3.1 Hz, 1H), 5.49 (d, *J* = 7.6 Hz, 1H), 5.14 (d, *J* = 10.7 Hz, 1H), 5.00 – 4.90 (m, 2H), 4.62 (d, *J* = 11.1 Hz, 1H), 4.53 (t, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.6 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 1H), 3.89 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.62 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.8, 151.1, 150.4, 147.5, 141.7, 138.5, 137.51, 137.49, 137.3, 136.4, 129.2, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.2, 127.1, 126.3, 126.0, 125.7, 123.5, 110.3, 100.7, 85.8, 80.4, 77.8, 75.7, 73.8, 72.8, 72.3, 68.2, 67.8. HRMS (ESI) Calculated for $C_{43}H_{39}INO_7$ $[M+H]^+$ 808.1766, found 808.1770.

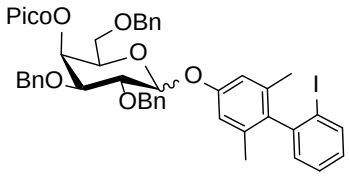
Synthesis of the compound 7n



As the general procedure A, donor **4j** (62.2 mg, 0.1 mmol) and acceptor **6e** (11.2 mg, 0.05 mmol) can be converted into the product **7n** in the sealed tube at 40 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3.5/1) to deliver **7n** (30 mg, 0.046 mmol, 92%, α/β > 20/1) as a white foam. **7n-α** isomer: $[\alpha]_D^{25}$= -16.0 (c 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.11 (d, *J* = 7.8 Hz,

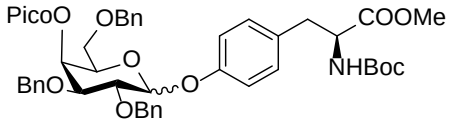
1H), 7.86 (td, *J* = 7.7, 1.6 Hz, 1H), 7.74 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (ddd, *J* = 7.7, 4.7, 1.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.14 (m, 9H), 7.09 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.77 (td, *J* = 7.6, 1.4 Hz, 1H), 5.68 (t, *J* = 9.9 Hz, 1H), 5.48 (d, *J* = 2.0 Hz, 1H), 4.89 (d, *J* = 12.3 Hz, 1H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.38 (dd, *J* = 9.9, 3.0 Hz, 1H), 4.21 – 4.03 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.5, 155.3, 149.9, 147.8, 139.4, 138.10, 138.08, 137.2, 129.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.1, 125.7, 124.2, 115.4, 97.9, 87.4, 76.5, 74.9, 74.4, 73.5, 72.3, 68.2, 17.8. HRMS (ESI) Calculated for $C_{32}H_{31}INO_6$ $[M+H]^+$ 652.1191, found 652.1180.

Synthesis of the compound 7o



As the general procedure A, donor **4g** (54.6 mg, 0.075 mmol) and acceptor **6g** (16.2 mg, 0.05 mmol) can be converted into the product **7o** in the sealed tube at 40°C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7o** (37.9 mg, 0.044 mmol, 88%, α/β = 1/10) as a syrup. **7o-β** isomer: $[\alpha]_D^{25}$= 12.6 (c 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (d, *J* = 4.6 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.83 (td, *J* = 7.8, 1.5 Hz, 1H), 7.50 (dd, *J* = 7.7, 4.5 Hz, 1H), 7.44 – 7.08 (m, 19H), 7.03 (td, *J* = 7.6, 1.7 Hz, 1H), 6.91 – 6.81 (m, 2H), 5.95 (d, *J* = 3.3 Hz, 1H), 5.14 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 17.1, 11.2 Hz, 2H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.81 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.71 (dd, *J* = 6.3, 4.1 Hz, 2H), 1.91 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 156.6, 150.3, 147.6, 145.8, 139.2, 138.9, 138.5, 137.72, 137.65, 137.4, 137.2, 130.0, 128.65, 128.63, 128.49, 128.45, 128.41, 128.39, 128.32, 128.26, 128.2, 128.13, 128.07, 127.95, 127.86, 127.83, 127.77, 127.74, 127.7, 127.2, 125.8, 115.64, 115.60, 101.9, 101.3, 79.4, 79.0, 75.6, 73.9, 73.0, 72.4, 68.6, 68.5, 20.7. HRMS (ESI) Calculated for $C_{47}H_{45}INO_7$ $[M+H]^+$ 862,2235, found 862.2279.

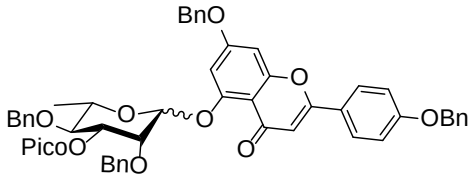
Synthesis of the compound 7p



As the general procedure A, donor **4g** (54.6 mg, 0.075 mmol) and acceptor **6h** (15 mg, 0.05 mmol) can be converted into the product **7p** in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7p** (36.6 mg, 0.044 mmol, 88%, α/β = 1/10) as a syrup. **7p-β** isomer: $[\alpha]_D^{25}$= 22.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.6 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.82 (t, *J* = 7.3 Hz, 1H), 7.49 (dd, *J* = 7.7, 4.6 Hz, 1H), 7.38 – 7.16 (m, 15H), 7.08 – 6.99 (m, 4H), 5.94 (d, *J* = 3.3 Hz, 1H), 5.04 (d, *J* = 7.7 Hz, 1H), 4.99 – 4.92 (m, 2H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.53 (m, 2H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.00 – 3.93 (m, 2H), 3.78 (dd, *J*

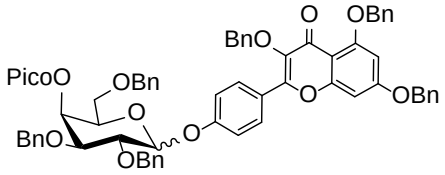
= 9.6, 3.4 Hz, 1H), 3.71 – 3.64 (m, 5H), 3.04 (m, 2H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.4, 163.9, 156.5, 155.2, 150.2, 147.4, 138.3, 137.65, 137.55, 137.3, 130.5, 130.4, 128.7, 128.5, 128.43, 128.38, 128.34, 128.30, 128.25, 128.21, 128.1, 127.88, 127.86, 127.8, 127.2, 125.7, 117.1, 102.0, 80.1, 79.3, 78.7, 75.6, 73.9, 72.8, 72.4, 68.3, 54.6, 52.35, 52.32, 37.6, 28.4. HRMS (ESI) Calculated for $C_{48}H_{53}N_2O_{11}$ $[M+H]^+$ 833.3644, found 833.3679.

Synthesis of the compound 7q



As the general procedure B, donor **4i** (62.2 mg, 0.1 mmol) and acceptor **6i** (22.6 mg, 0.05 mmol) can be converted into the product **7q** in the sealed tube with freshly activated 4Å MS at 60°C after 60 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1/1) to deliver **7q** (40.5 mg, 0.046 mmol, 92%, α/β = 1/13) as a white foam. **7q-β** isomer: $[\alpha]_D^{25}$= -42.8 (c 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.80 (m, 3H), 7.60 – 7.30 (m, 13H), 7.29 – 7.11 (m, 8H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.59 (s, 1H), 5.93 (dd, *J* = 9.4, 3.4 Hz, 1H), 5.61 (d, *J* = 2.0 Hz, 1H), 5.14 (s, 4H), 4.90 (d, *J* = 11.1 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.61 (dd, *J* = 3.4, 2.0 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.97 (t, *J* = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.9, 164.0, 162.5, 161.3, 161.1, 159.5, 156.7, 149.8, 148.0, 138.4, 138.2, 137.1, 136.3, 135.8, 128.9, 128.8, 128.6, 128.4, 128.32, 128.26, 128.0, 127.8, 127.7, 127.6, 126.9, 125.6, 124.1, 115.3, 111.0, 107.6, 104.6, 98.8, 97.5, 78.9, 75.8, 75.0, 74.9, 73.2, 70.6, 70.3, 69.5, 18.2. HRMS (ESI) Calculated for $C_{55}H_{47}NNaO_{10}$ $[M+Na]^+$ 904.3092, found 904.3128.

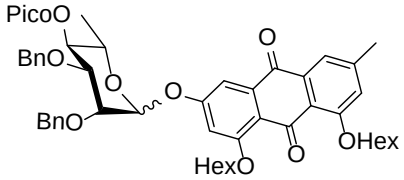
Synthesis of the compound 7r



As the general procedure B, donor **4g** (90.9 mg, 0.125 mmol) and acceptor **6j** (28 mg, 0.05 mmol) can be converted into the product **11r** in the sealed tube with freshly activated 4Å MS at 60 °C after 64 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver **7r** (44.2 mg, 0.0404 mmol, 81%, β/α > 20/1) as a syrup. **7r-β** isomer: $[\alpha]_D^{25}$= -4.4 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.05 (m, 29H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.48 (d, *J* = 2.2 Hz, 1H), 5.97 (d, *J* = 3.3 Hz, 1H), 5.29 (s, 2H), 5.19 – 5.03 (m, 6H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.88 (dd, *J* = 17.2, 11.1 Hz, 2H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.58 – 4.41 (m, 2H), 4.07 – 3.98 (m, 2H), 3.83 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.69 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 163.9, 162.8, 159.9, 158.9, 158.7, 153.4, 150.2, 147.3, 139.9, 138.2, 137.6, 137.5, 137.3, 137.0, 136.5, 135.8, 130.3, 129.0, 128.9, 128.7,

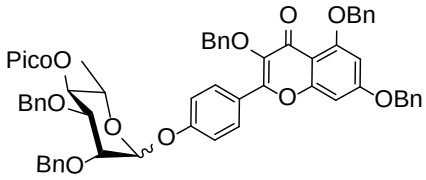
128.6, 128.50, 128.47, 128.45, 128.39, 128.26, 128.24, 128.1, 127.92, 127.90, 127.8, 127.7, 127.2, 126.8, 125.7, 125.4, 116.4, 110.2, 101.4, 98.3, 94.0, 79.3, 78.6, 75.8, 74.1, 73.9, 73.0, 72.4, 70.9, 70.6, 68.28, 68.24. HRMS (ESI) Calculated for $C_{69}H_{60}NO_{12}$ $[M+H]^+$ 1094.4110, found 1094.4154.

Synthesis of the compound 7s



As the general procedure B, donor **4j** (77.6 mg, 0.125 mmol) and acceptor **6k** (23.4 mg, 0.05 mmol) can be converted into the product **7s** in the sealed tube with freshly activated 4Å MS at 50 °C after 72 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver **7s** (37.6 mg, 0.042 mmol, 84%, α/β = 8/1) as a yellow syrup. **7s-α** isomer: $[\alpha]_D^{25}$= -30.4 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 4.5 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 1.7 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 2.6 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.44 – 7.18 (m, 12H), 7.00 (d, *J* = 2.7 Hz, 1H), 5.74 – 5.55 (m, 2H), 4.88 (d, *J* = 12.2 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.61 (q, *J* = 12.1 Hz, 2H), 4.25 (dd, *J* = 9.7, 3.1 Hz, 1H), 4.08 – 3.94 (m, 2H), 2.74 – 2.69 (m, 4H), 2.49 (s, 3H), 1.89 – 1.78 (m, 4H), 1.51 – 1.34 (m, 8H), 1.32 – 1.20 (m, 7H), 1.01 – 0.93 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.1, 179.6, 172.3, 172.1, 164.4, 160.2, 152.4, 150.4, 149.9, 147.7, 145.9, 138.0, 137.8, 137.3, 136.1, 134.3, 131.0, 128.6, 128.4, 128.2, 128.1, 127.75, 127.73, 127.2 126.0, 125.8, 123.5, 120.7, 117.6, 112.4, 96.8, 74.4, 74.2, 73.6, 72.5, 68.4, 34.5, 34.4, 31.6, 24.4, 24.3, 22.6, 21.8, 17.8, 14.1. HRMS (ESI) Calculated for $C_{53}H_{56}NO_{12}$ $[M+H]^+$ 898.3797, found 898.3819.

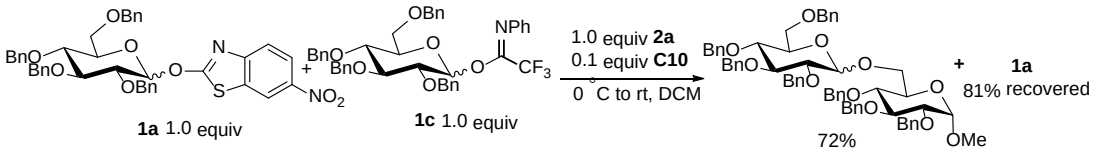
Synthesis of the compound 7t



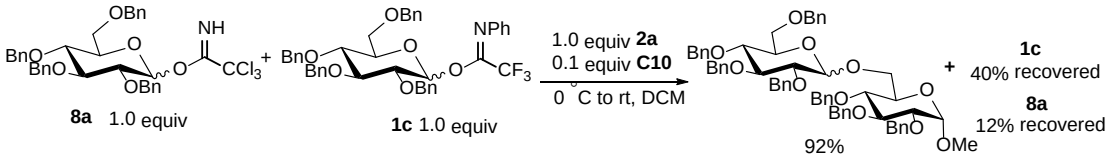
As the general procedure B, donor **4j** (77.6 mg, 0.125 mmol) and acceptor **6j** (28 mg, 0.05 mmol) can be converted into the product **7t** in the sealed tube with freshly activated 4Å MS at 55 °C after 72 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2/1) to deliver **7t** (40.5 mg, 0.041 mmol, 82%, α/β > 20/1) as a syrup. **7t-α** isomer: $[\alpha]_D^{25}$= -34.0 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 4.7 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.88 (td, *J* = 7.7, 1.6 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 2H), 7.52 (m, 1H), 7.48 – 7.13 (m, 24H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 2.2 Hz, 1H), 6.47 (d, *J* = 2.2 Hz, 1H), 5.68 (t, *J* = 9.8 Hz, 1H), 5.60 (d, *J* = 1.9 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 5.09 (s, 2H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.79 (d, *J* = 12.4 Hz, 1H), 4.75 – 4.53 (m, 2H), 4.33 (dd, *J* = 9.8, 3.0 Hz, 1H), 4.12 (m, 1H), 4.07 – 3.99 (m, 1H), 1.28 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 164.5, 162.8, 159.88, 158.86, 157.4, 153.4, 149.7, 147.6, 139.8, 138.1, 138.0, 137.5, 137.0, 136.5, 135.7, 130.3, 129.1, 128.9, 128.7, 128.63, 128.57, 128.56, 128.34,

128.26, 128.2, 128.1, 128.0, 127.8, 127.73, 127.66, 127.6, 127.3, 126.7, 125.9, 124.9, 115.8, 110.2, 98.2, 96.4, 93.9, 74.7, 74.3, 74.2, 73.5, 72.5, 70.8, 70.6, 67.8, 17.8. HRMS (ESI) Calculated for $C_{62}H_{53}NO_{11}$ $[M+H]^+$ 988.3691, found 988.3726.

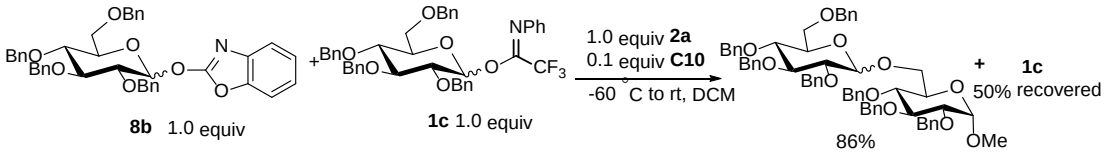
Comparison of the different imidate donors' reactivity under Kass catalyst-catalyzed conditions



Donor **1a** (36.0 mg, 0.05 mmol) and **1c** (35.6 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst **C10** (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.6 ml) was added to the sealed tube under N_2 atmosphere at 0 °C. The reaction mixture was stirred for 10 hours in the sealed tube and gradually warmed up to rt. for several hours, and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the donor **1a** (29 mg, 0.0405 mmol, 81% recovered) and product **3a** (35.5 mg, 0.036 mmol, 72%).

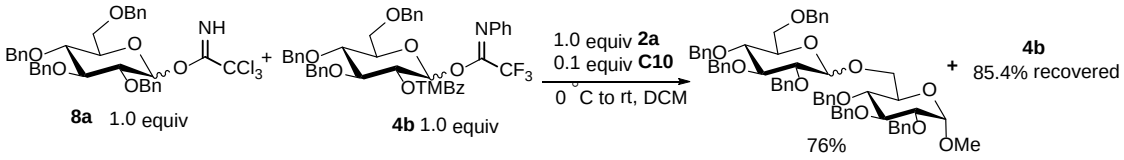


Donor **8a** (34.3 mg, 0.05 mmol) and **1c** (35.6 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.6 ml) was added to the sealed tube under N_2 atmosphere at 0 °C. The reaction mixture was stirred for 12 hours in the sealed tube and gradually warmed up to rt. for several hours, and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the donor **8a** (4.1 mg, 0.006 mmol, 12% recovered), **1c** (14.3 mg, 0.02 mmol, 40% recovered) and product **3a** (45.4 mg, 0.046 mmol, 92%).

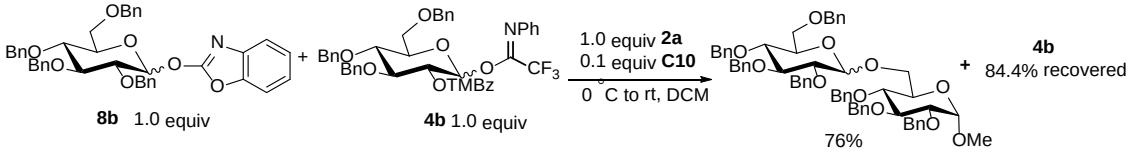


Donor **8b** (32.9 mg, 0.05 mmol) and **1c** (35.6 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.6 ml) was added to the sealed tube under N_2 atmosphere at -60 °C. The reaction mixture was stirred for 10 hours in the sealed

tube and gradually warmed up to rt. for several hours, and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the donor **8b** (16.4 mg, 0.025 mmol, 50% recovered) and product **3a** (42.4 mg, 0.043 mmol, 86%).

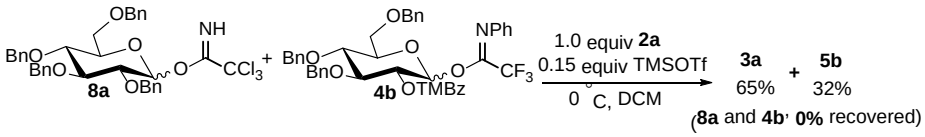


Donor **8a** (34.3 mg, 0.05 mmol) and **4b** (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.6 ml) was added to the sealed tube under N_2 atmosphere at 0 °C. The reaction mixture was stirred for 12 hours in the sealed tube and gradually warmed up to rt and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the donor **4b** (32.7 mg, 0.0427 mmol, 85.4% recovered) and product **3a** (37.5 mg, 0.038 mmol, 76%).



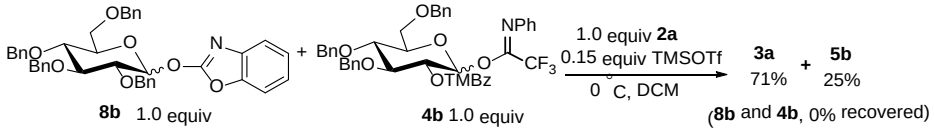
Donor **8b** (32.9 mg, 0.05 mmol) and **4b** (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.6 ml) was added to the sealed tube under N_2 atmosphere at 0 °C. The reaction mixture was stirred for 12 hours in the sealed tube and gradually warmed up to rt and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to deliver the donor **4b** (32.3 mg, 0.0422 mmol, 84.4% recovered) and product **3a** (37.5 mg, 0.038 mmol, 76%).

Comparison of the different imidate donors' reactivity under TMSOTf catalyst-catalyzed conditions



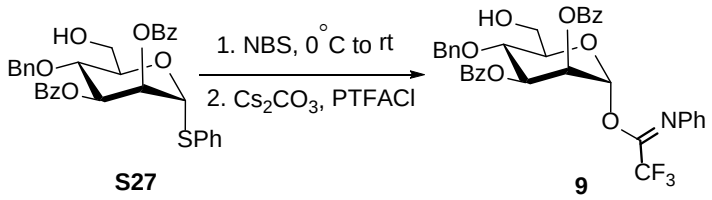
Donor **8a** (34.3 mg, 0.05 mmol) and **4b** (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene, freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt. The mixture was stirred for 10 min at 0 °C and then TMSOTf (1.4 µl, 0.0075 mmol) was added to the stirred solution. The mixture was stirred for 1.5 hours at this temperature, and

then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography to deliver the product **3a** (32.1 mg, 0.0325 mmol, 65%) and **5b** (16.7 mg, 0.016 mmol, 32%).



Donor **8b** (32.9 mg, 0.05 mmol) and **4b** (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor **2a** (23.3 mg, 0.05 mmol) co-evaporated twice with toluene, freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N_2 atmosphere at rt. The mixture was stirred for 10 min at 0 °C and then TMSOTf (1.4 µl, 0.0075 mmol) was added to the stirred solution. The mixture was stirred for 1.5 hours at this temperature, and then quenched with Et_3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography to deliver the product **3a** (35.0 mg, 0.0355 mmol, 71%) and **5b** (13 mg, 0.0125 mmol, 25%).

Synthesis of compound 9



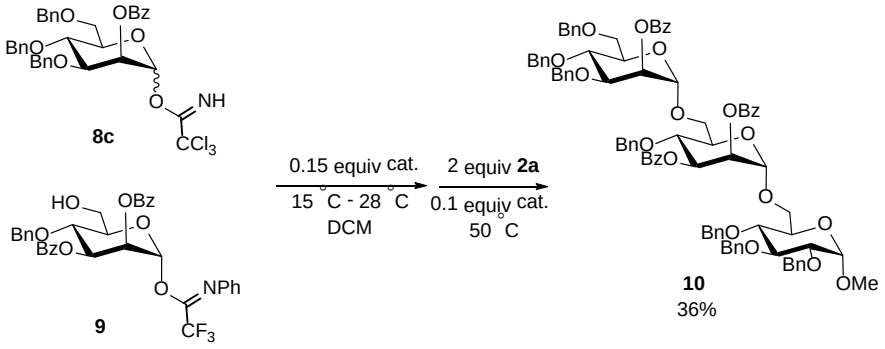
S27 **9**

The compound **S27**[37] (570.7 mg, 1 mmol) was dissolved in acetone and H_2O (10 ml, acetone: H_2O = 8:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous $Na_2S_2O_3$. The organic phase was washed with saturated aqueous $NaHCO_3$, brine successively, and the organic phases was separated and combined, dried over anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to deliver the hemiacetal intermediate (354.1 mg, 0.74 mmol, 74%; brsm: 90%).

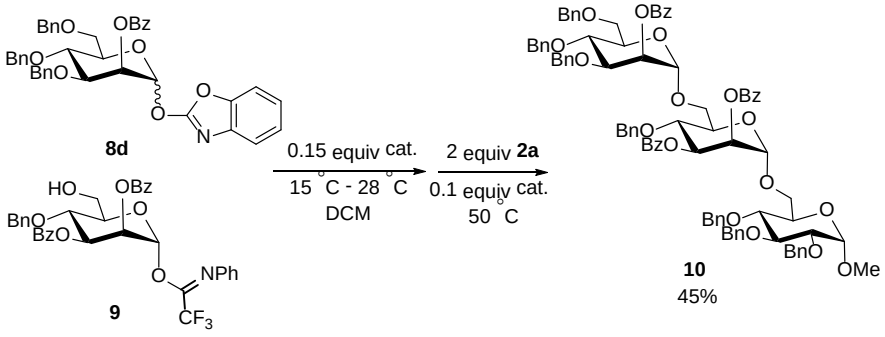
Cs_2CO_3 (265.2 mg, 0.814 mmol) followed by PTFACl (228 mg, 1.1 mmol) was added to a solution of the above hemiacetal intermediate (354.1 mg, 0.74 mmol) in acetone (7 ml). The mixture was stirred for 4 hours at 0 °C, and then the suspension was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 8/1 to 4/1, with Et_3N) to give the compound **9** (270.4 mg, 0.555 mmol, 75%) as a colorless syrup. **9-α** isomer: $[\alpha]_D^{25}$ = -23.5 (c 1.0, acetone); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.58 (dt, *J* = 15.5, 7.5 Hz, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.18 (m, 5H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.48 (s, 1H), 5.89 (s, 1H), 5.75 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.55 (t, *J* = 9.7 Hz, 1H), 4.23 (dd, *J* = 7.1, 5.4 Hz, 1H), 4.06 – 3.92 (m, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 165.1, 164.9, 143.6, 138.2, 133.7, 129.7, 129.5, 129.4, 128.9, 128.7, 128.5, 128.2, 127.9, 127.6, 124.4, 119.3, 94.7, 75.6,

74.7, 72.1, 72.0, 69.0, 60.5. HRMS (ESI) Calculated for $C_{35}H_{30}F_3NO_8Na$ $[M+Na]^+$ 672.1821, found 672.1809.

One-pot synthesis of trisaccharide:



Donor **8c** (69.9 mg, 0.1 mmol) co-evaporated twice with toluene, compound **9** (32.5 mg, 0.05 mmol) co-evaporated twice with toluene, Kass catalyst (0.15 equiv, 15 mg, 0.075 mmol) and freshly activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.8 ml) was added to the sealed tube under N_2 atmosphere at 15 °C. The reaction mixture was stirred and gradually warmed up to rt. The reaction was monitored by TLC analysis. When TLC shows that the donor **9c** is consumed completely (around 17h), the acceptor **2a** (0.1 mmol, 46.5 mg), 0.1 equiv. Kass catalyst were added to the reaction mixture, and the mixture was gradually warmed up to 50 °C and stirred for another several hours (about 2 d.). The resulting mixture was cooled to rt and then transferred into round-bottomed flask and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to deliver the product **10** (26.3 mg, 0.018 mmol, 36%) as a colorless oil. **10**: $[\alpha]_D^{25}$ = 25 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 12.5, 4.7 Hz, 4H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.57 – 7.47 (m, 5H), 7.39 – 7.07 (m, 39H), 5.80 (s, 1H), 5.71 (m, 2H), 5.16 (d, *J* = 1.6 Hz, 1H), 5.04 – 4.93 (m, 3H), 4.79 (m, 5H), 4.67 – 4.57 (m, 4H), 4.55 – 4.41 (m, 4H), 4.17 – 4.07 (m, 3H), 4.03 – 3.64 (m, 10H), 3.61 – 3.52 (m, 2H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.40, 165.37, 138.9, 138.46, 138.42, 138.34, 138.26, 137.9, 137.7, 130.1, 129.8, 129.7, 128.7, 128.46, 128.43, 128.39, 128.37, 128.31, 128.29, 128.2, 128.1, 128.0, 127.9, 127.7, 127.66, 127.63, 127.6, 98.1, 98.0, 97.9, 82.2, 80.4, 78.0, 77.8, 75.7, 75.4, 75.1, 74.9, 74.3, 73.51, 73.46, 73.2, 72.8, 72.0, 71.3, 70.7, 70.6, 69.9, 68.9, 68.6, 66.3, 55.2. HRMS (ESI) Calculated for $C_{89}H_{88}O_{29}Na$ $[M+Na]^+$ 1483.5818, found 1483.5827.



Donor **8d** (67.2 mg, 0.1 mmol) co-evaporated twice with toluene, compound **9** (32.5 mg, 0.05

mmol) co-evaporated twice with toluene, Kass catalyst (0.15 equiv, 15 mg, 0.075 mmol) and freshly activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N_2 for three times. Dry DCM (0.8 ml) was added to the sealed tube under N_2 atmosphere at 15 °C. The reaction mixture was stirred and gradually warmed up to rt. The reaction was monitored by TLC analysis. When TLC shows that the donor **8d** is consumed completely (around 17h), the acceptor **2a** (0.1 mmol, 46.5 mg), 0.1 equiv. Kass catalyst were added to the reaction mixture, and the mixture was gradually warmed up to 50 °C and stirred for another several hours (about 2d). The resulting mixture was cooled to rt, transferred into round-bottomed flask and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to deliver the product **10** (32.9 mg, 0.0225 mmol, 45%) as a colorless oil.

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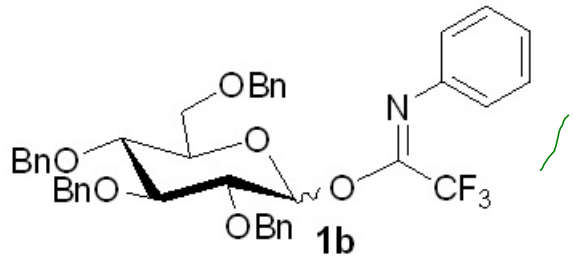
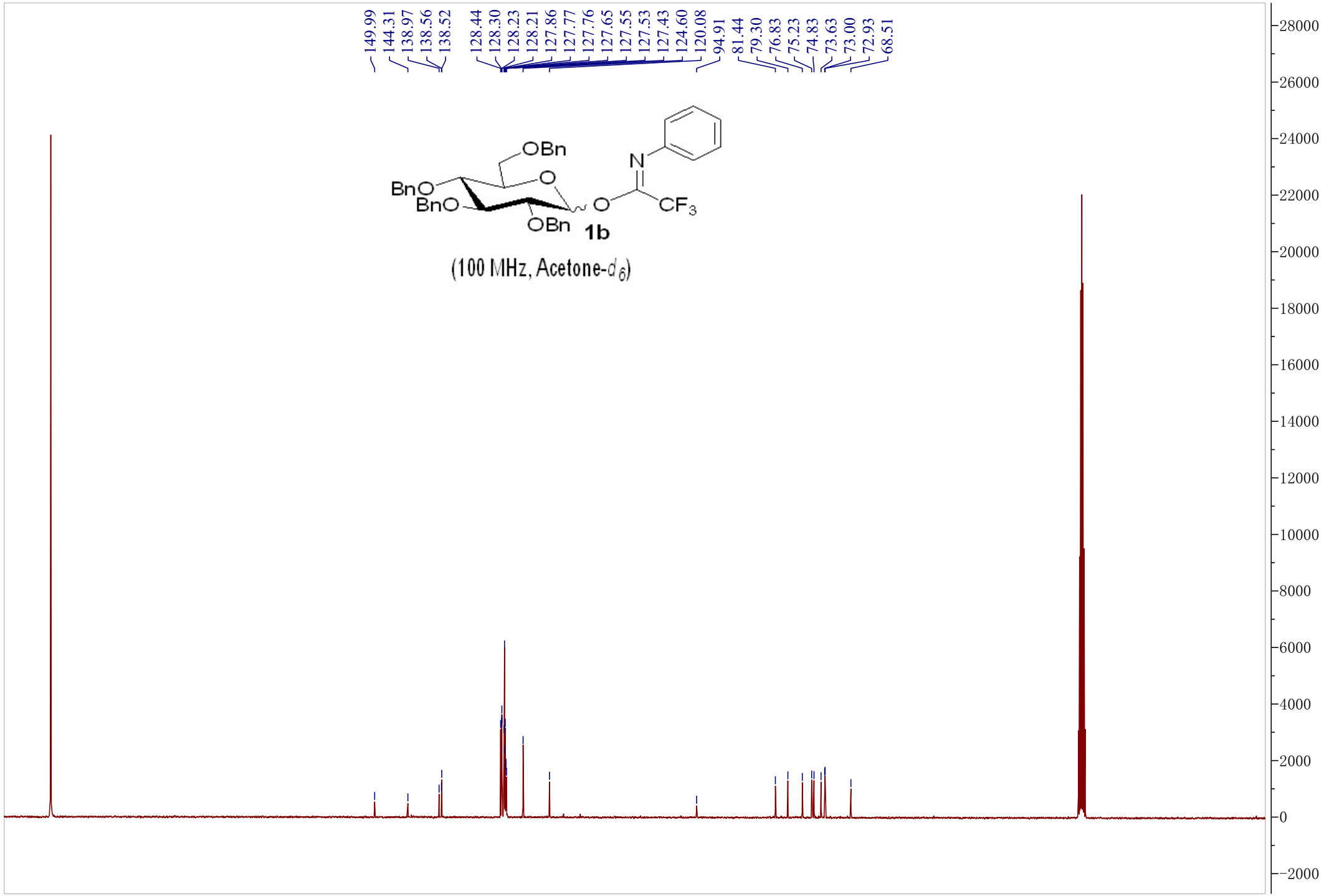
^{1}H-NMR, ^{13}C-NMR, of **1b**



1b

(400 MHz, Acetone-d_6)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144.31
138.97
138.56
138.52
128.44
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128.23
128.21
127.86
127.77
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127.65
127.55
127.53
127.43
124.60
120.08
94.91
81.44
79.30
76.83
75.23
74.83
73.63
73.00
72.93
68.51
OBn
BnO
BnO
O
OBn
O
N
CF3
1b
(100 MHz, Acetone-d6)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210
200
190
180
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110
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90
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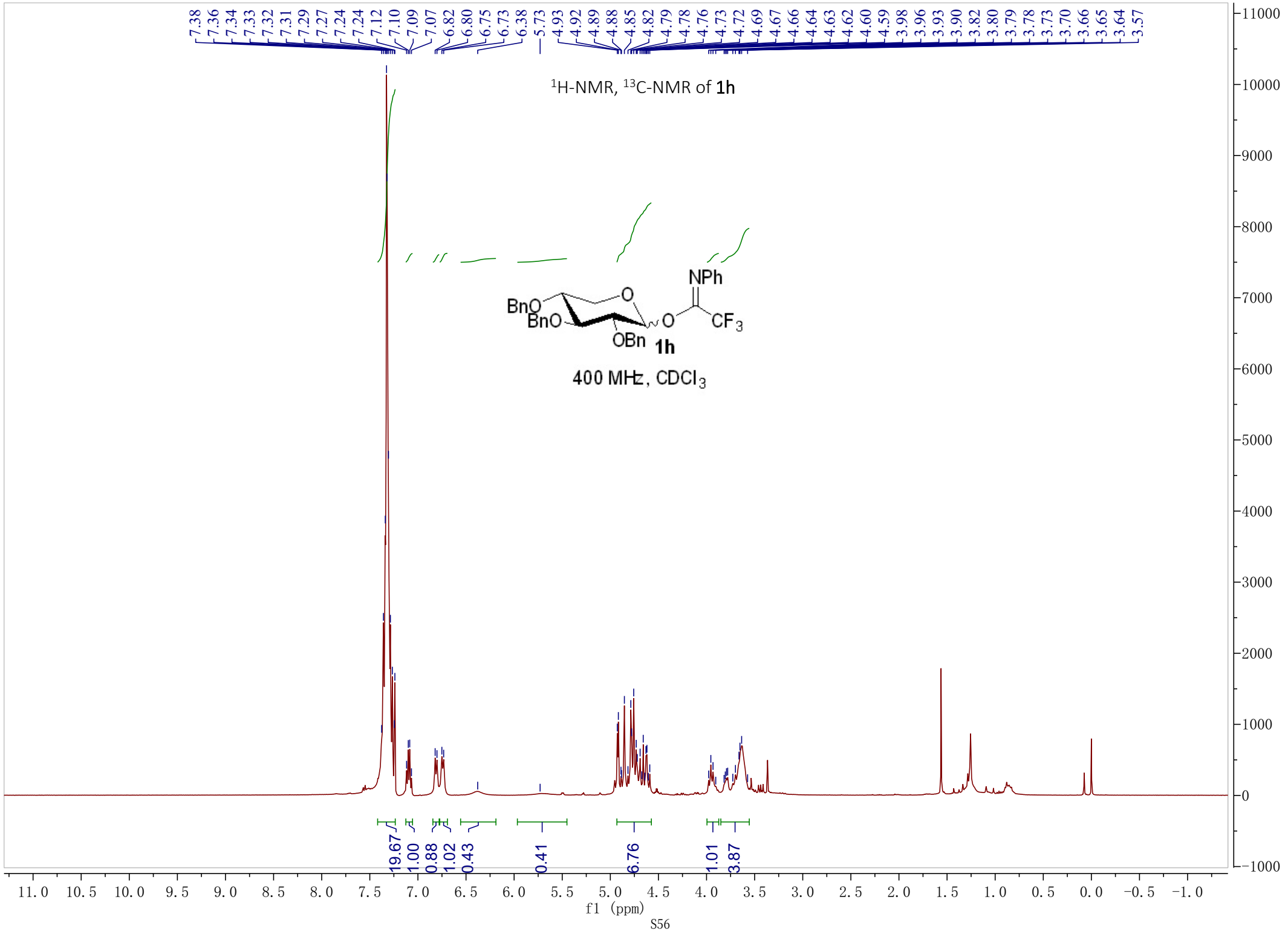
f1 (ppm)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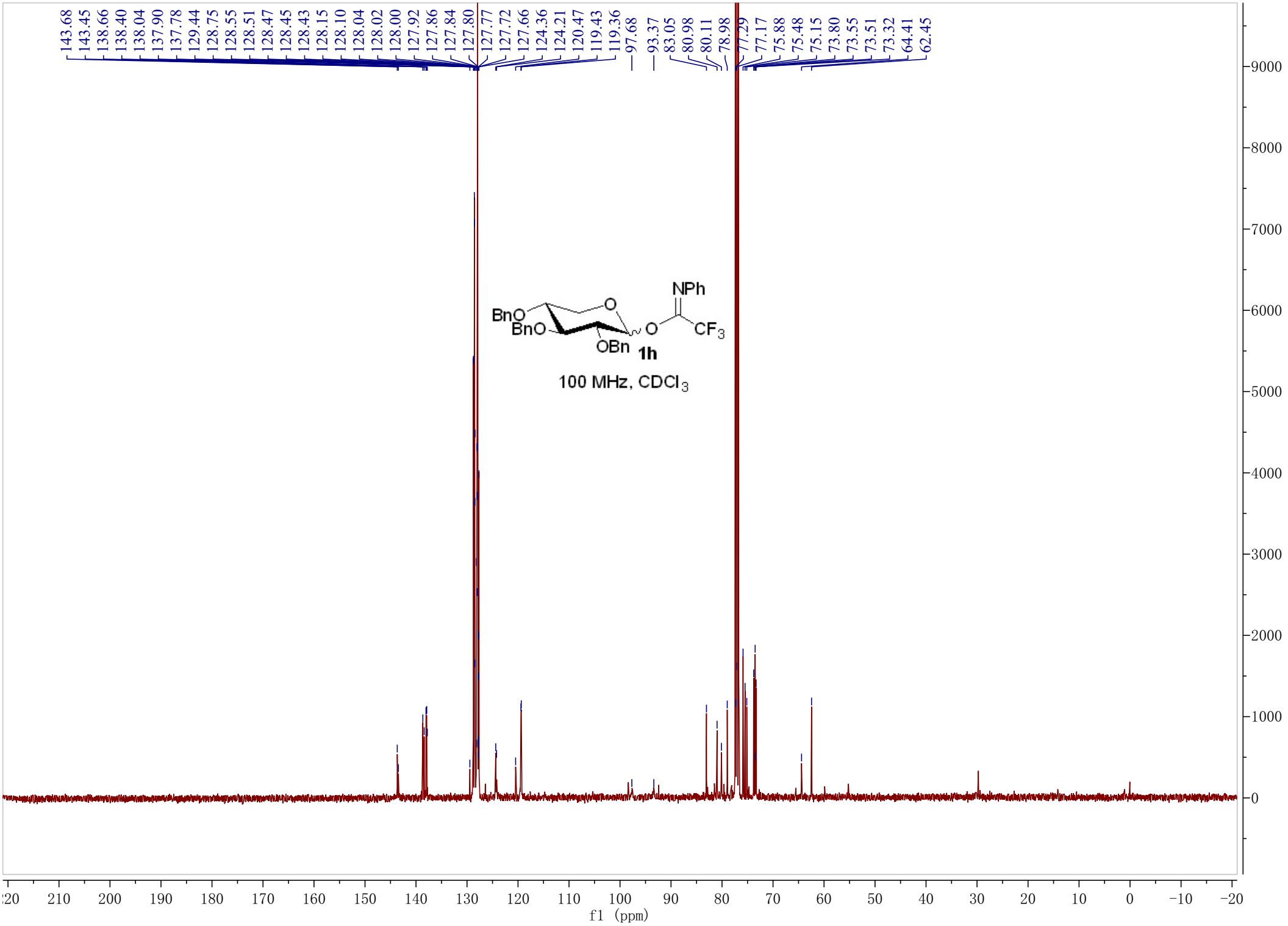
1H-NMR, 13C-NMR of 1h
NPh
BnO
BnO
O
O
CF3
OBn
1h
400 MHz, CDCl3
19.67 1.00 0.88 1.02 0.43 0.41 6.76 1.01 3.87
11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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127.84
127.80
127.77
127.72
127.66
124.36
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120.47
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119.36
97.68
93.37
83.05
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80.11
78.98
77.29
77.17
75.88
75.48
75.15
73.80
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73.32
64.41
62.45
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BnO
BnO
OBn
O
O
CF3
1h
100 MHz, CDCl3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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200
190
180
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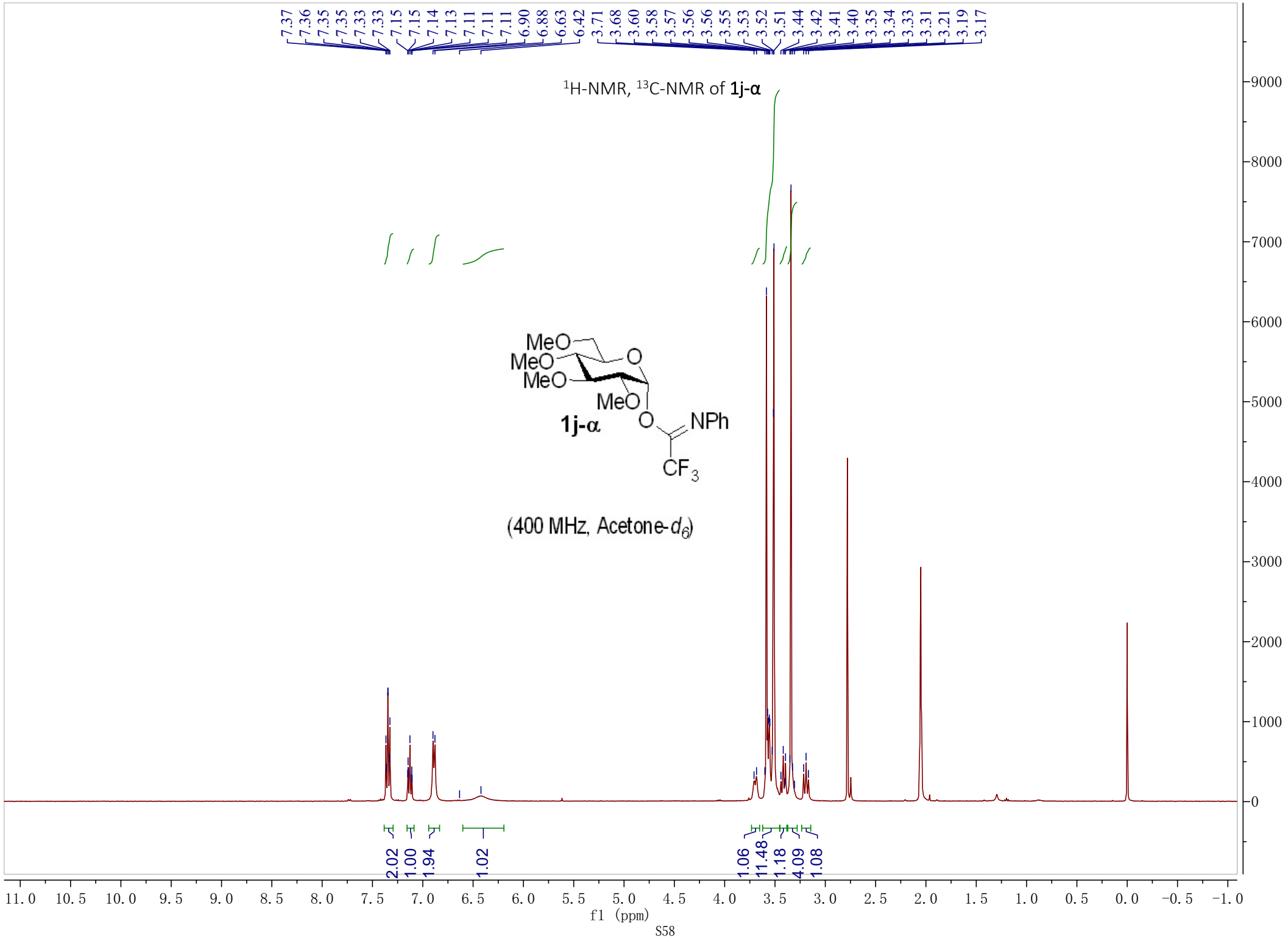
f1 (ppm)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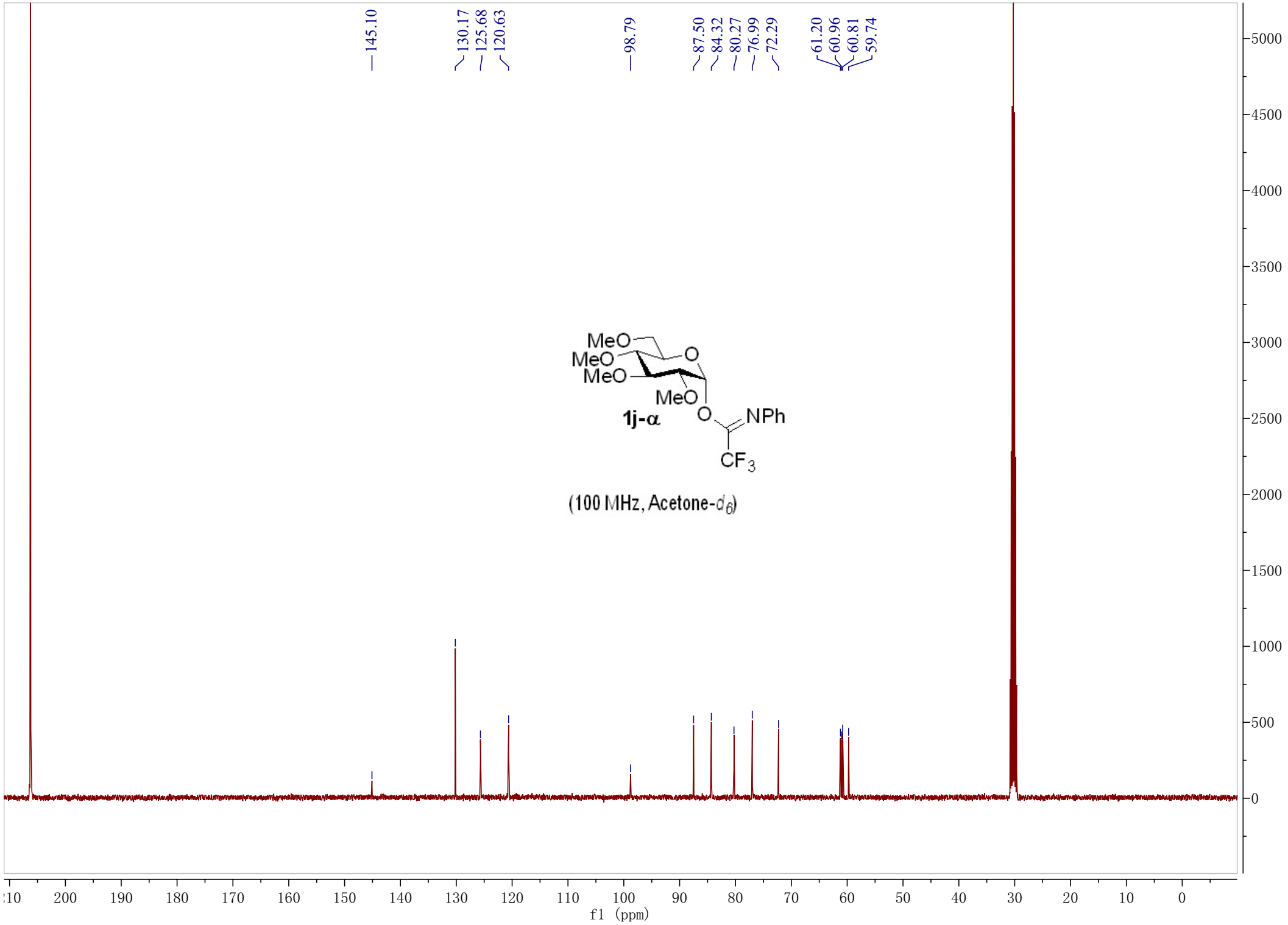
^{1}H-NMR, ^{13}C-NMR of **1j-α**
MeO
MeO
MeO
MeO
O
O
NPh
CF3
1j-α
(400 MHz, Acetone-d_6)
2.02 1.00 1.94 1.02 1.06 11.48 1.18 4.09 1.08
f1 (ppm)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72.29
61.20
60.96
60.81
59.74
MeO
MeO
MeO
MeO
O
O
NPh
CF3
1j-α
(100 MHz, Acetone-d6)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
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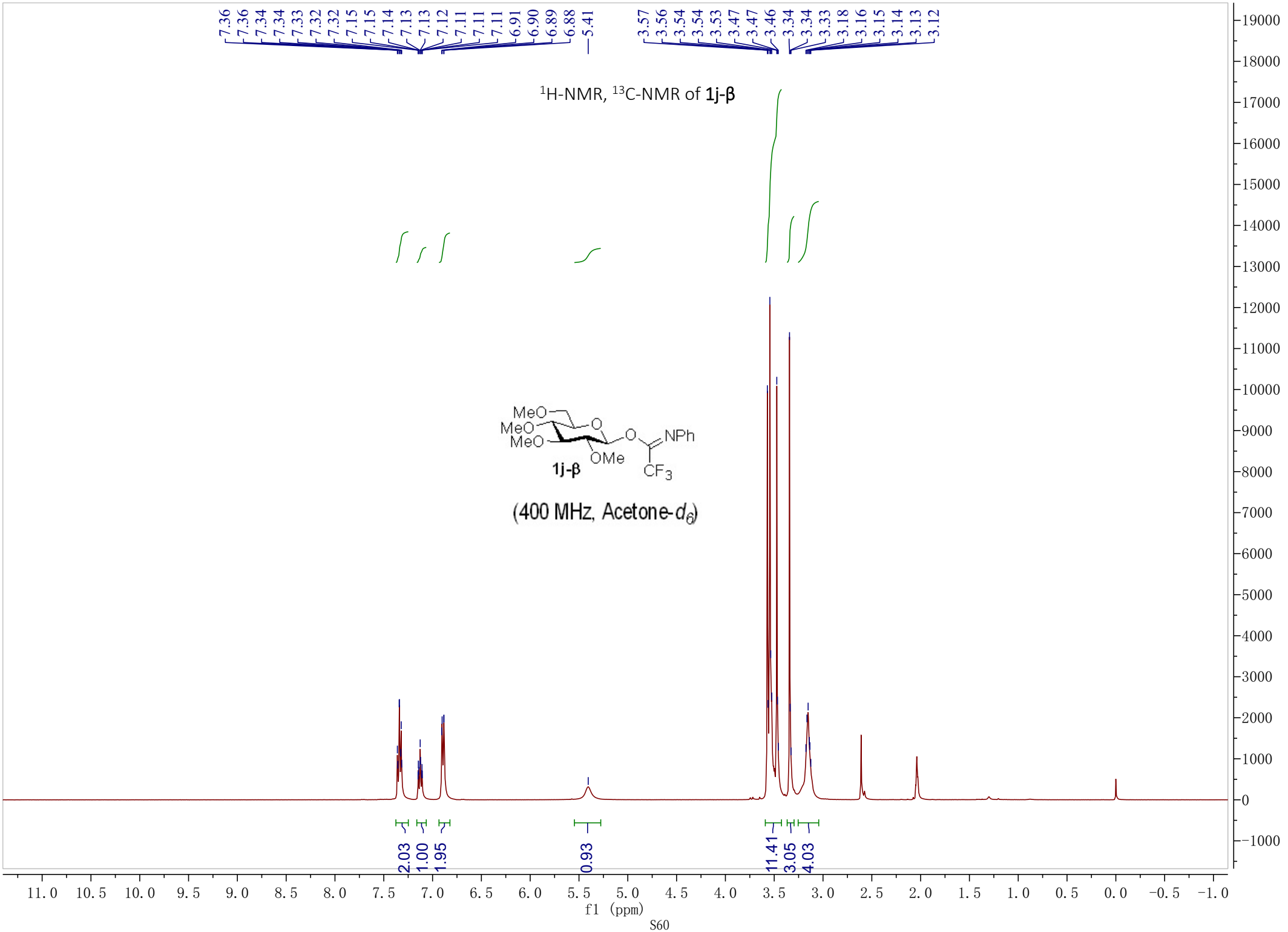
f1 (ppm)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3.57 3.56 3.54 3.54 3.53 3.47 3.47 3.46 3.34 3.34 3.33 3.18 3.16 3.15 3.14 3.13 3.12
^{1}H-NMR, ^{13}C-NMR of **1j-β**
MeO
MeO
MeO
OMe
O
O
NPh
CF$_3$
1j-β
(400 MHz, Acetone-d_6)
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1.95
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11.41
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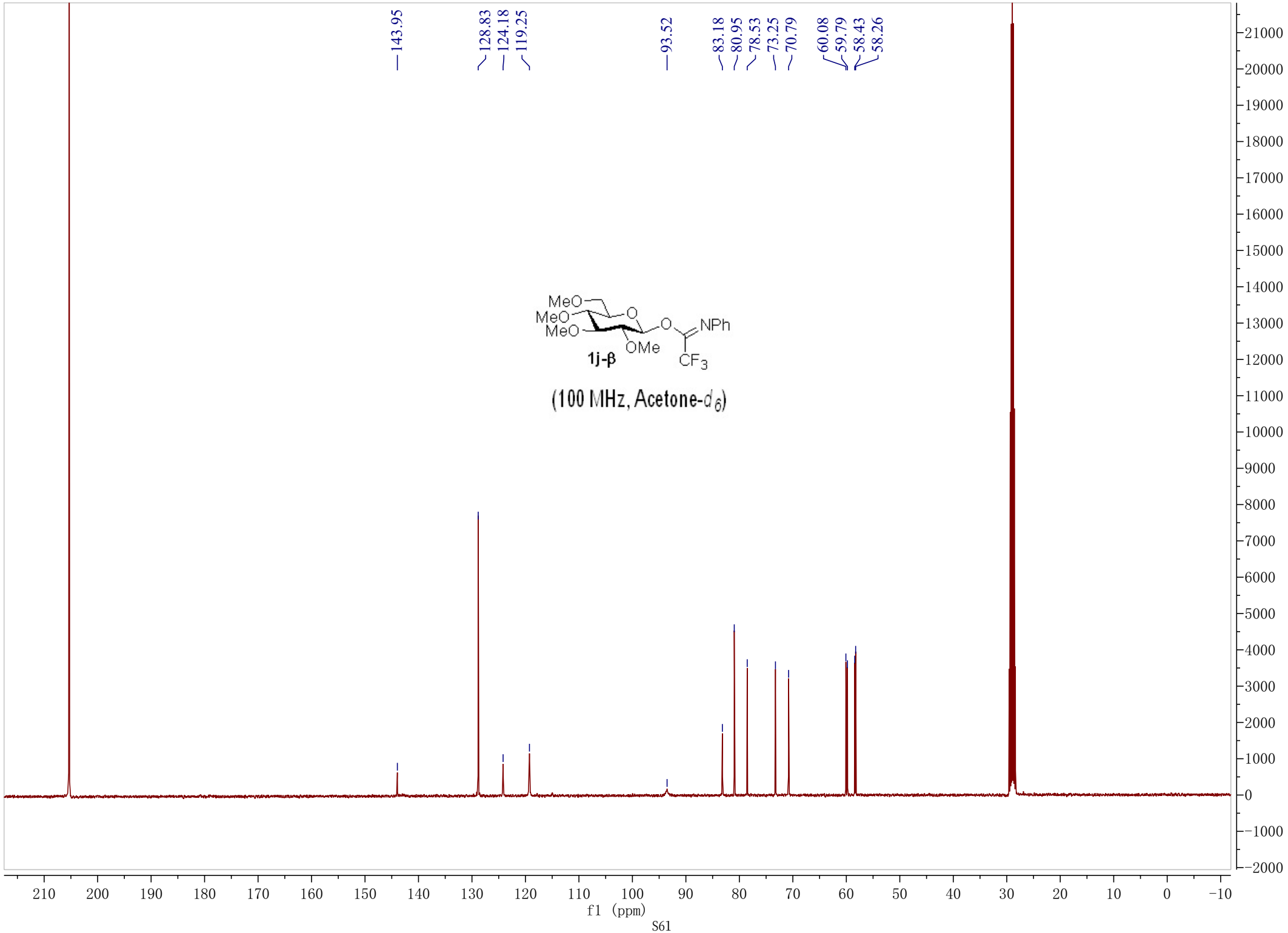
4.03
f1 (ppm)


143.95
128.83
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60.08
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58.43
58.26
MeO
MeO
MeO
OMe
O
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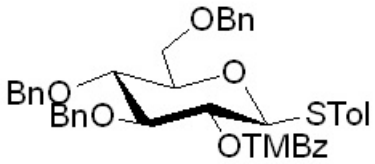
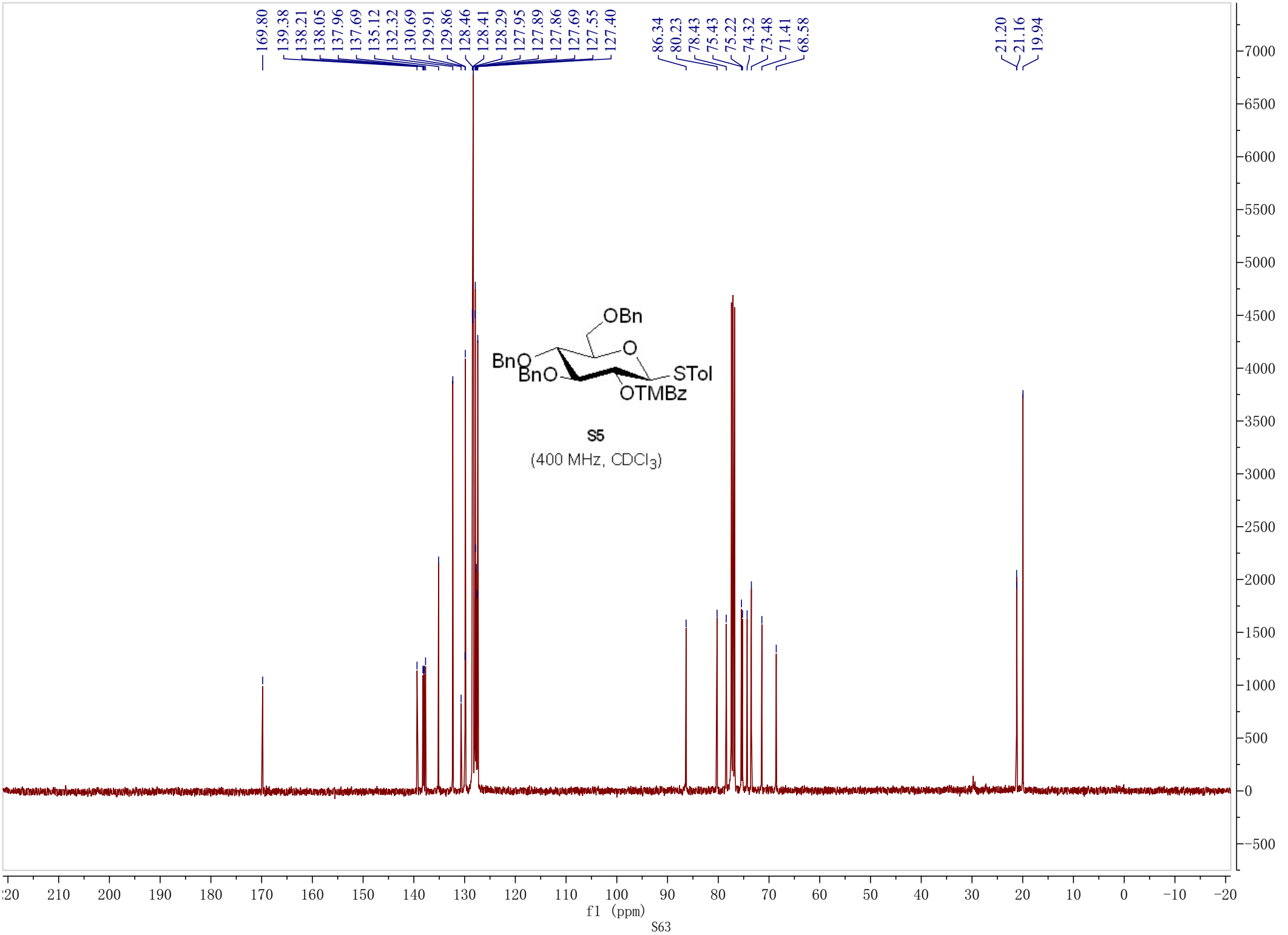
CF3
1j-β
(100 MHz, Acetone-d6)
f1 (ppm)

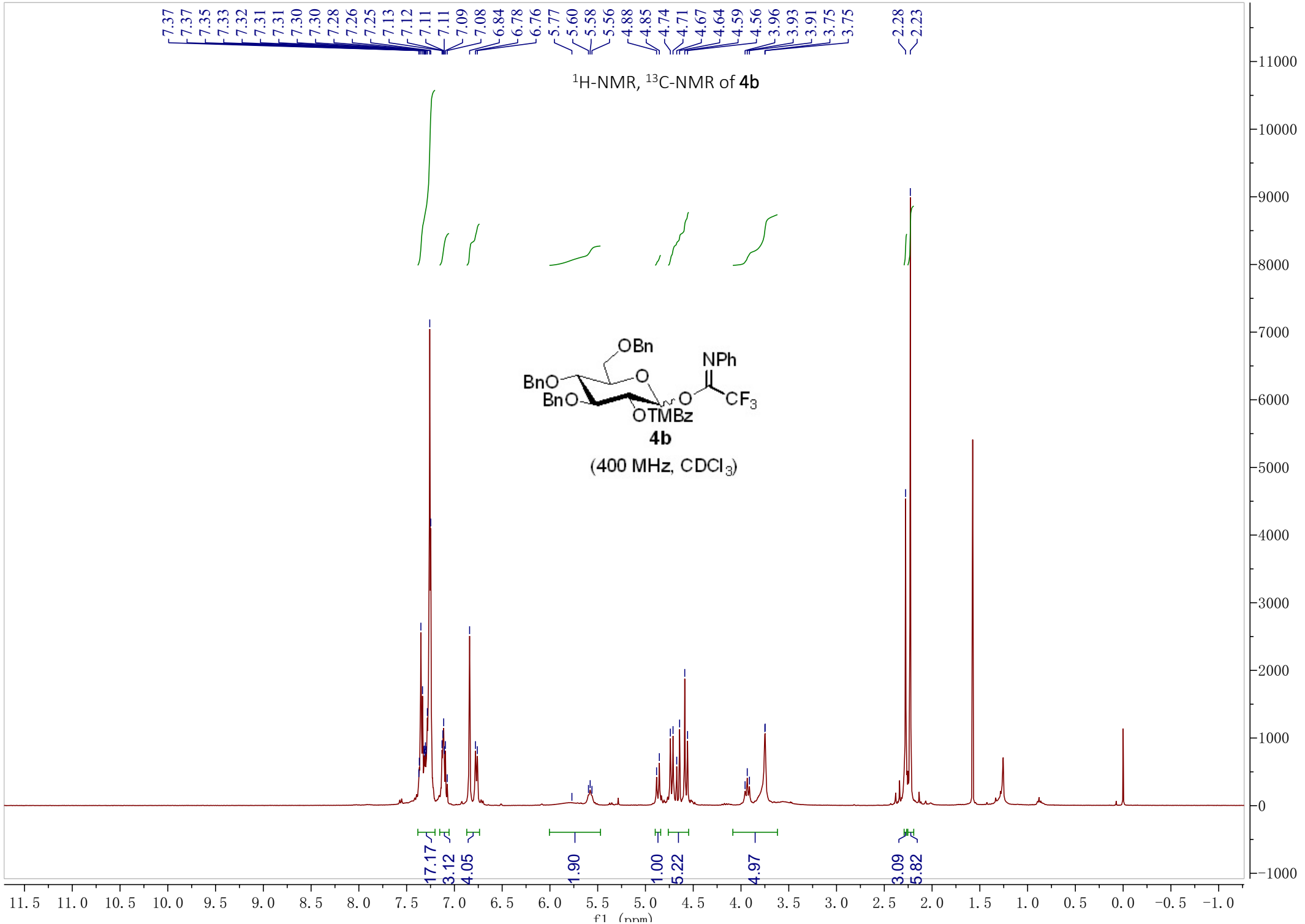
^{1}H-NMR, ^{13}C-NMR of **S5**

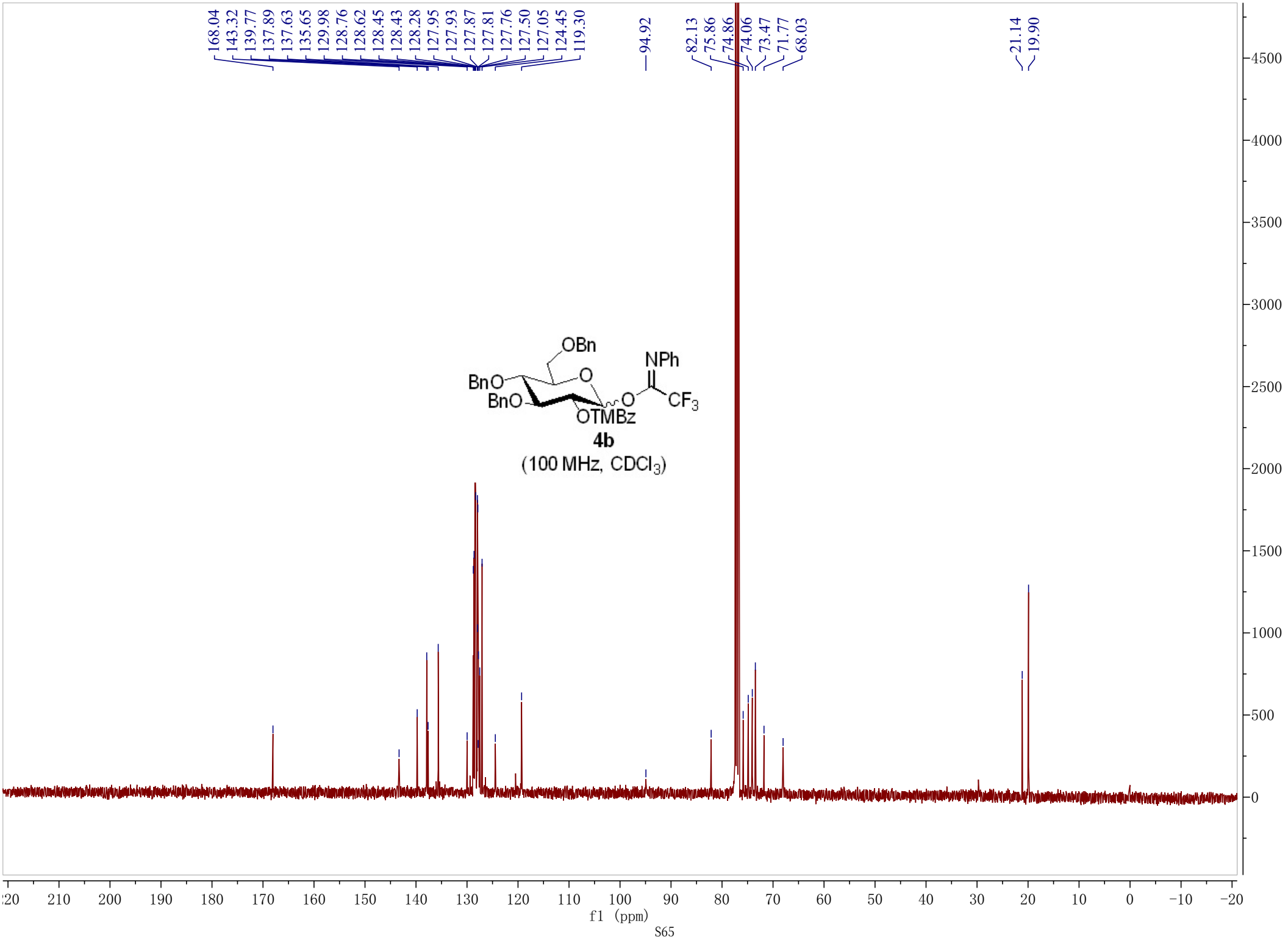


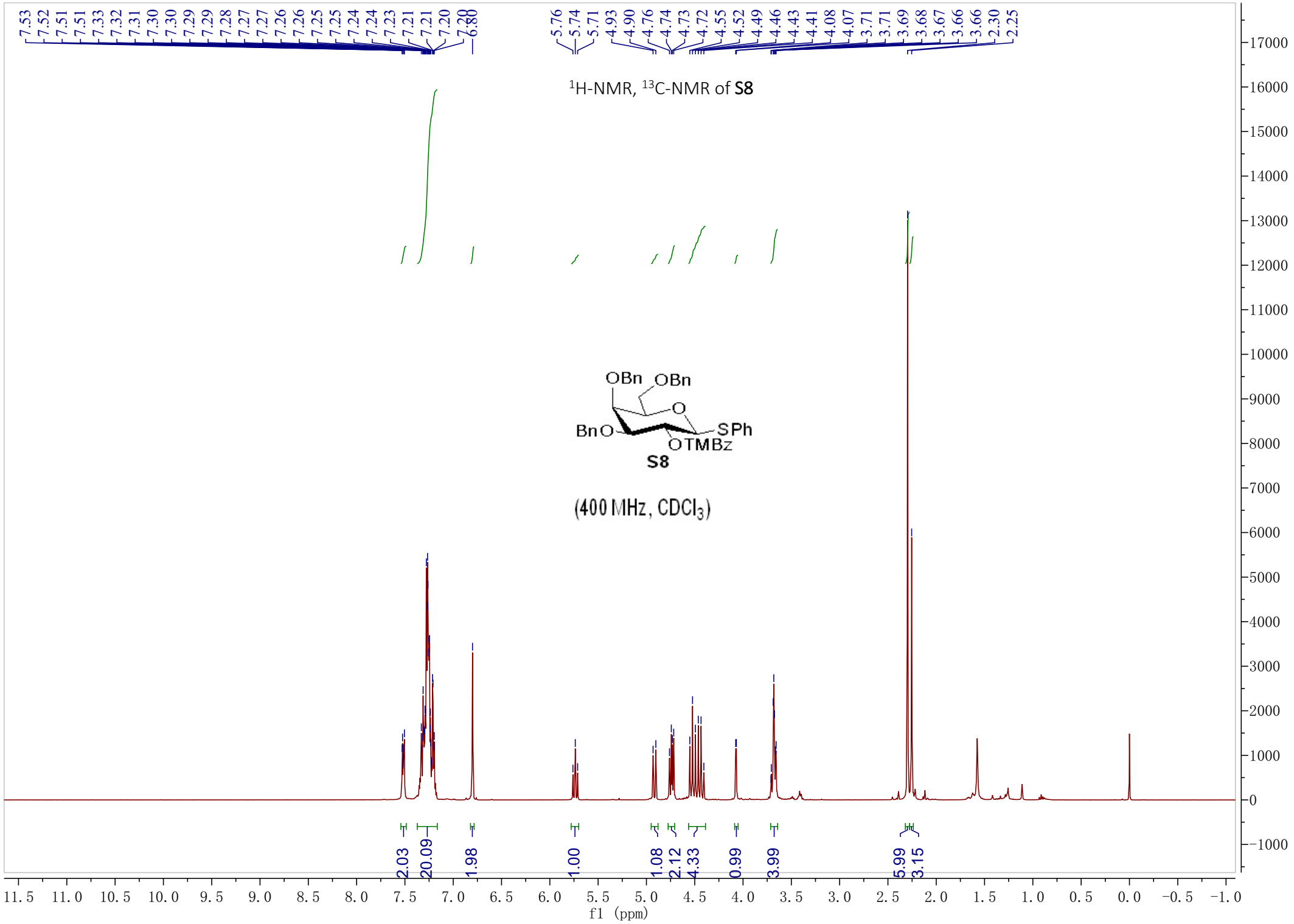
S5

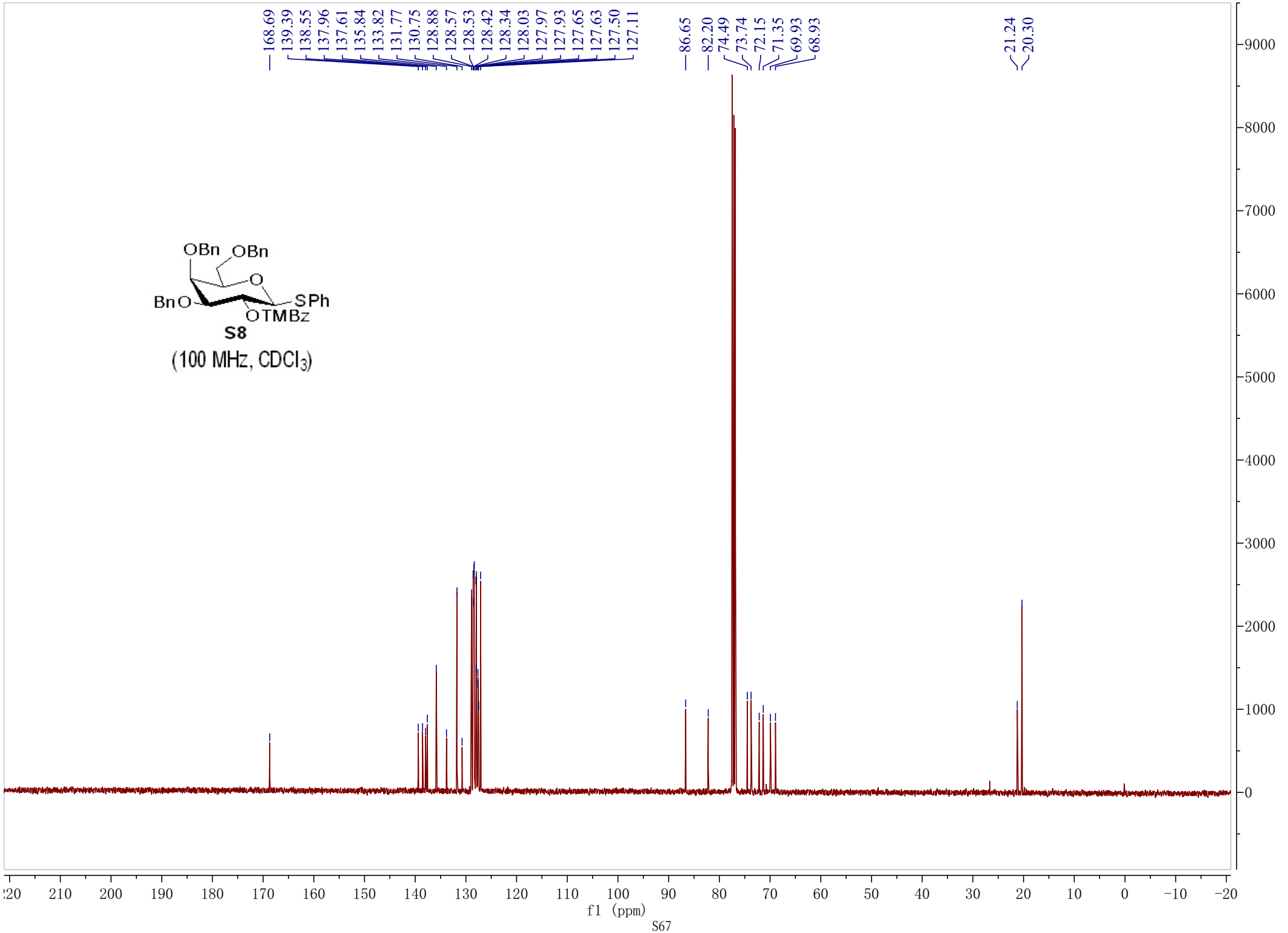
(400 MHz, $CDCl_3$)

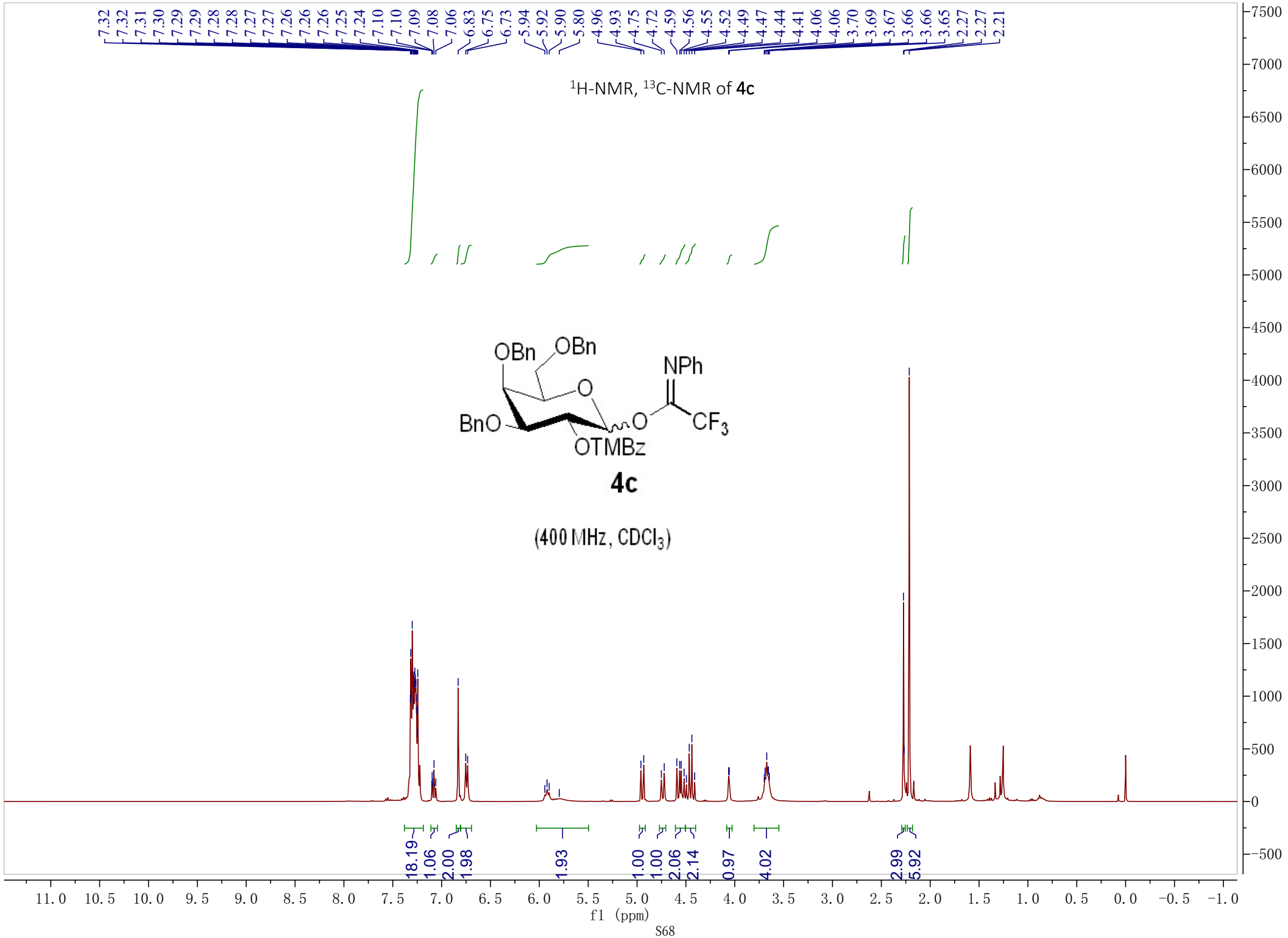

169.80
139.38
138.21
138.05
137.96
137.69
135.12
132.32
130.69
129.91
129.86
128.46
128.41
128.29
127.95
127.89
127.86
127.69
127.55
127.40
86.34
80.23
78.43
75.43
75.22
74.32
73.48
71.41
68.58
21.20
21.16
19.94
OBn
O
BnO
BnO
STol
OTMBz
S5
(400 MHz, CDCl3)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

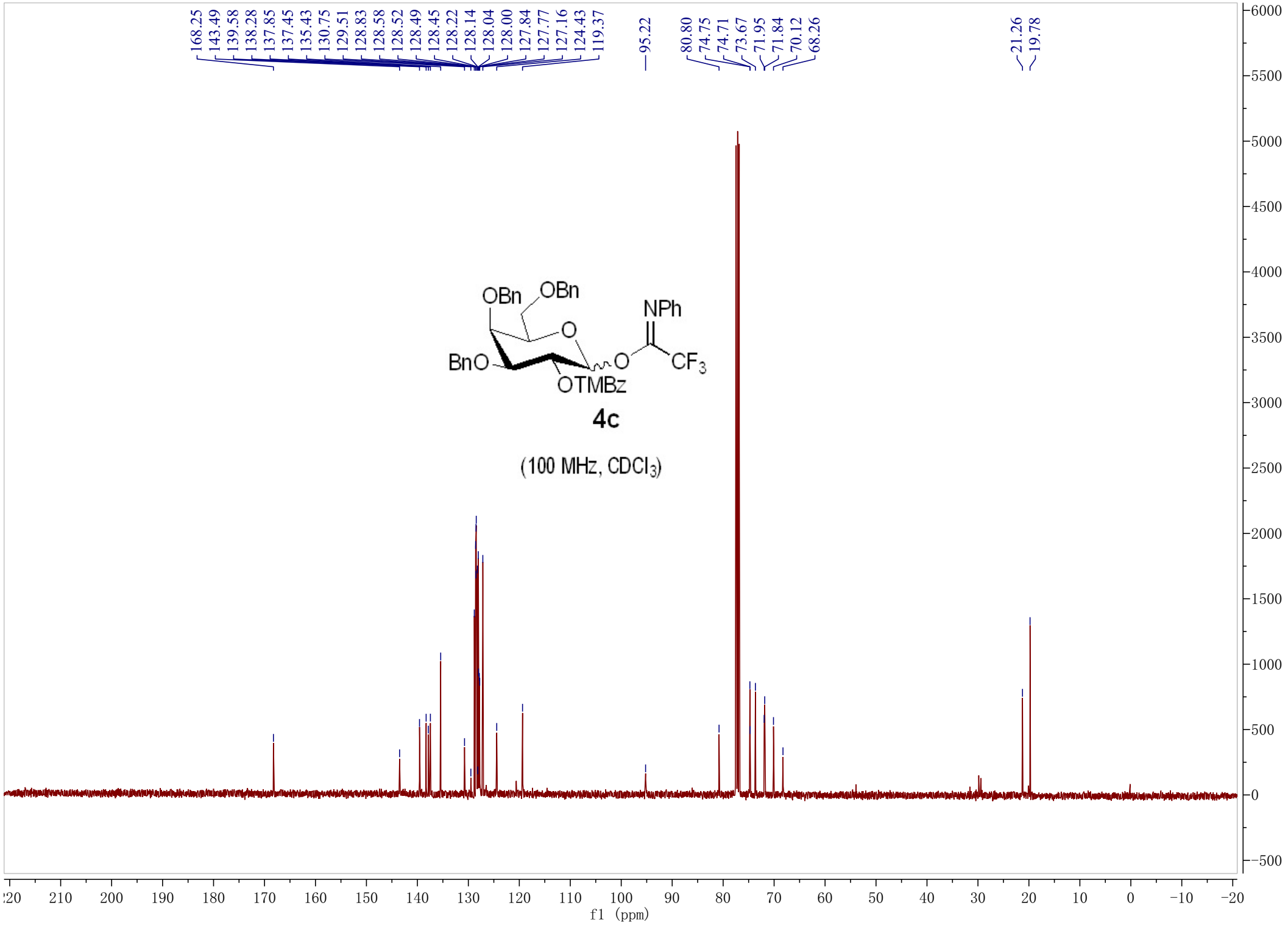

7.37 7.37 7.35 7.33 7.32 7.31 7.31 7.30 7.30 7.28 7.26 7.25 7.13 7.12 7.11 7.11 7.09 7.08 6.84 6.78 6.76 5.77 5.60 5.58 5.56 4.88 4.85 4.74 4.71 4.67 4.64 4.59 4.56 3.96 3.93 3.91 3.75 3.75 2.28 2.23
1H-NMR, 13C-NMR of 4b
OBn
NPh
BnO
O
BnO
O
CF3
OTMBz
4b
(400 MHz, CDCl3)
17.17 3.12 4.05 1.90 1.00 5.22 4.97 3.09 5.82
f1 (ppm)

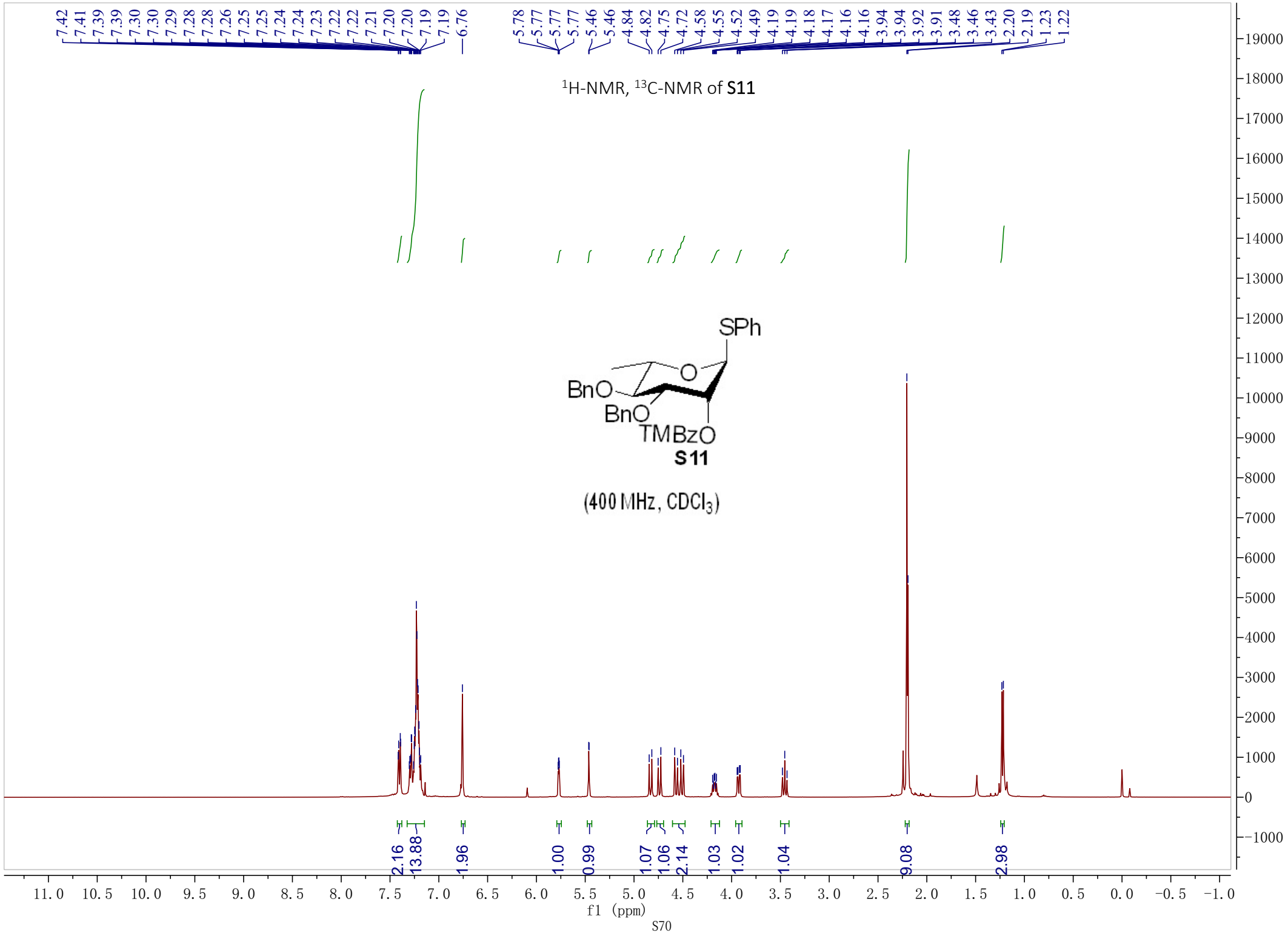

168.04
143.32
139.77
137.89
137.63
135.65
129.98
128.76
128.62
128.45
128.43
128.28
127.95
127.93
127.87
127.81
127.76
127.50
127.05
124.45
119.30
94.92
82.13
75.86
74.86
74.06
73.47
71.77
68.03
21.14
19.90
OBn
BnO
BnO
O
O
OTMBz
NPh
CF3
4b
(100 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

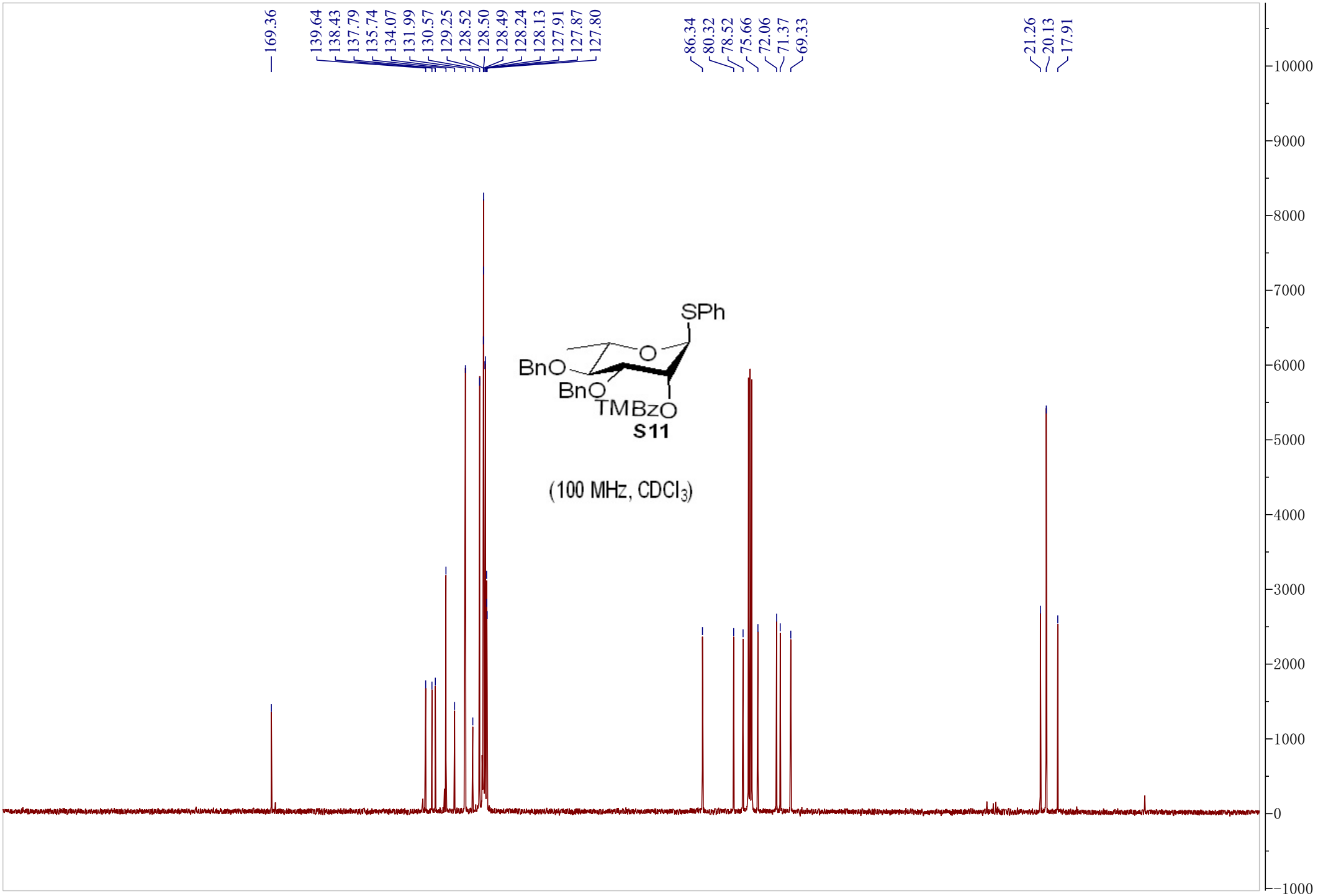

7.53 7.52 7.51 7.51 7.33 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.23 7.21 7.21 7.20 7.20 6.80
5.76 5.74 5.71 4.93 4.90 4.76 4.74 4.73 4.72 4.55 4.52 4.49 4.46 4.43 4.41 4.08 4.07 3.71 3.71 3.69 3.68 3.67 3.66 3.66 2.30 2.25
1H-NMR, 13C-NMR of S8
OBn OBn
O
BnO
SPh
OTMBz
S8
(400 MHz, CDCl3)
2.03 20.09 1.98 1.00 1.08 2.12 4.33 0.99 3.99 5.99 3.15
f1 (ppm)

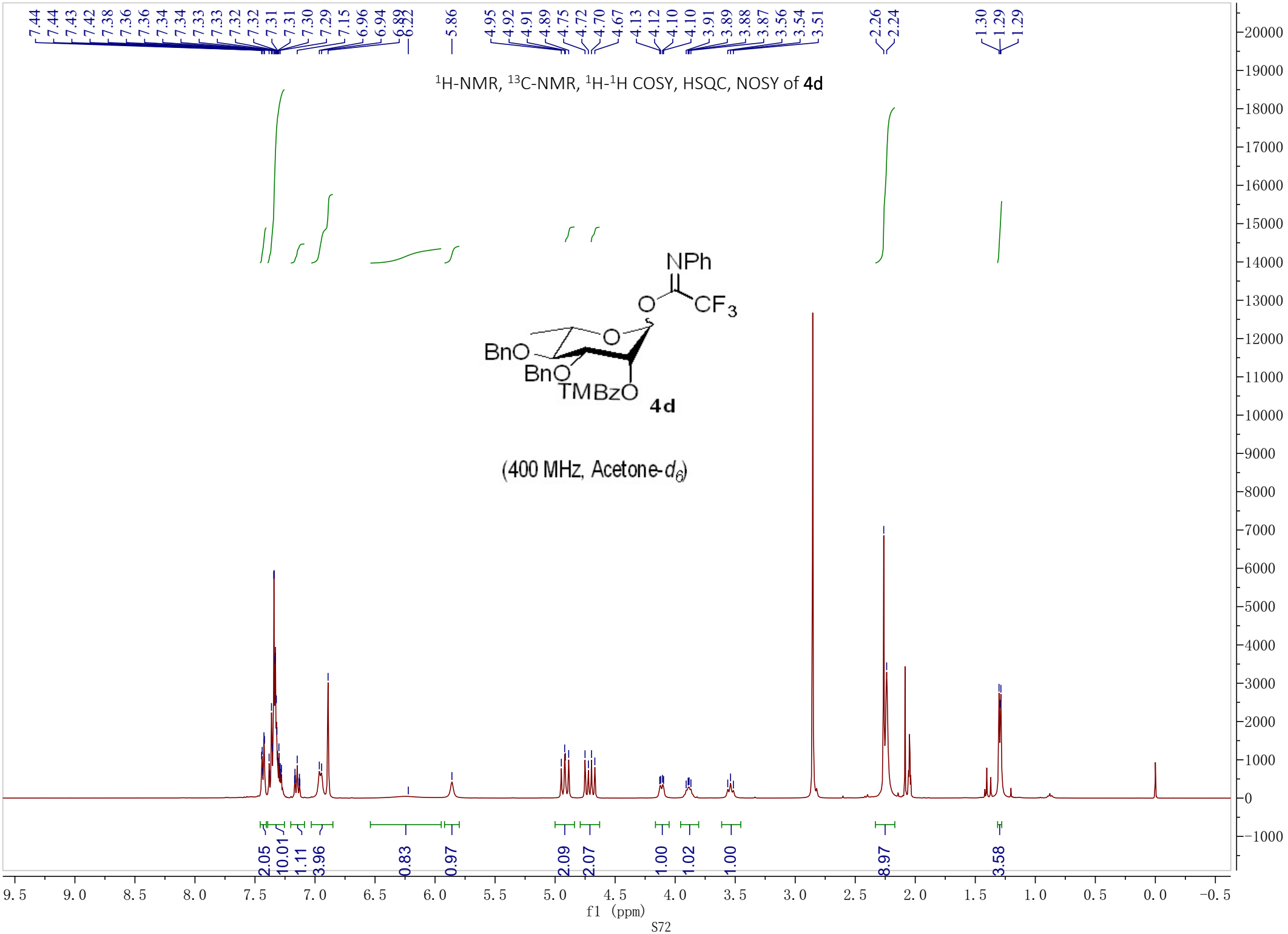

168.69
139.39
138.55
137.96
137.61
135.84
133.82
131.77
130.75
128.88
128.57
128.53
128.42
128.34
128.03
127.97
127.93
127.65
127.63
127.50
127.11
86.65
82.20
74.49
73.74
72.15
71.35
69.93
68.93
21.24
20.30
OBn
OBn
O
BnO
SPh
OTMBz
S8
(100 MHz, CDCl3)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

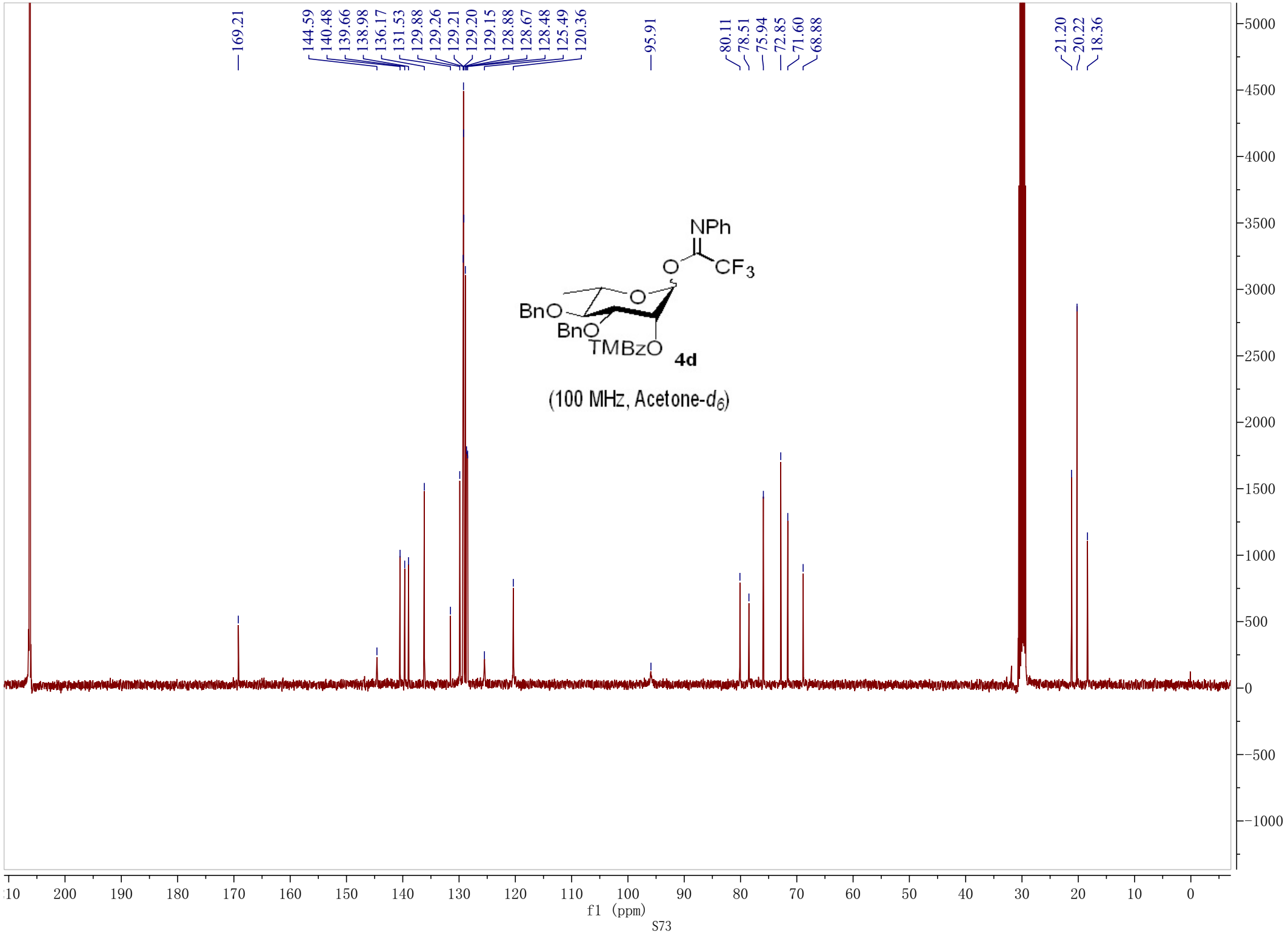

7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.24 7.10 7.10 7.09 7.08 7.06 6.83 6.75 6.73 5.94 5.92 5.90 5.80 4.96 4.93 4.75 4.72 4.59 4.56 4.55 4.52 4.49 4.47 4.44 4.41 4.06 4.06 3.70 3.69 3.67 3.66 3.66 3.65 2.27 2.27 2.21
1H-NMR, 13C-NMR of 4c
OBn
OBn
O
NPh
BnO
O
CF3
OTMBz
4c
(400 MHz, CDCl3)
18.19
1.06
2.00
1.98
1.93
1.00
1.00
2.06
2.14
0.97
4.02
2.99
5.92
f1 (ppm)

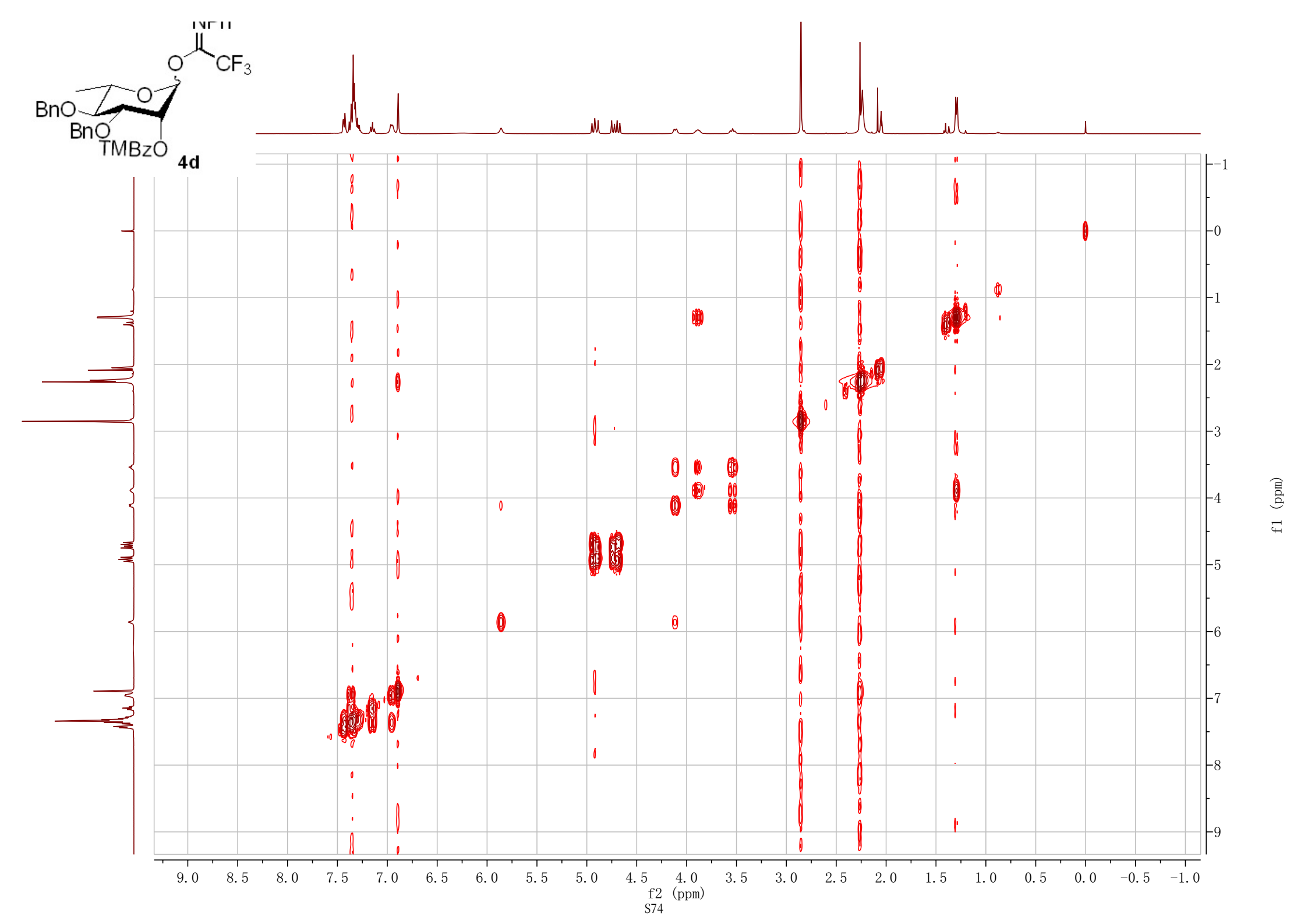

168.25
143.49
139.58
138.28
137.85
137.45
135.43
130.75
129.51
128.83
128.58
128.52
128.49
128.45
128.22
128.14
128.04
128.00
127.84
127.77
127.16
124.43
119.37
95.22
80.80
74.75
74.71
73.67
71.95
71.84
70.12
68.26
21.26
19.78
OBn
OBn
O
NPh
BnO
O
CF3
OTMBz
4c
(100 MHz, CDCl3)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

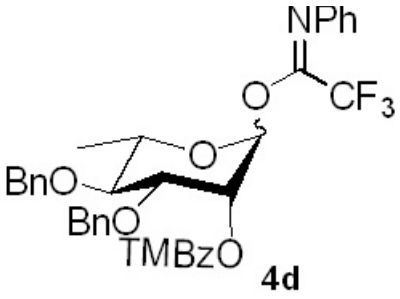

7.42 7.41 7.39 7.39 7.30 7.30 7.29 7.28 7.28 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 6.76
5.78 5.77 5.77 5.77 5.46 5.46 4.84 4.82 4.75 4.72 4.58 4.55 4.52 4.49 4.19 4.19 4.18 4.17 4.16 4.16 3.94 3.94 3.92 3.91 3.48 3.46 3.43 2.20 2.19 1.23 1.22
1H-NMR, 13C-NMR of S11
SPh
O
BnO
BnO
TMBzO
S11
(400 MHz, CDCl3)
2.16 13.88 1.96 1.00 0.99 1.07 1.06 2.14 1.03 1.02 1.04 9.08 2.98
f1 (ppm)


169.36
139.64
138.43
137.79
135.74
134.07
131.99
130.57
129.25
128.52
128.50
128.49
128.24
128.13
127.91
127.87
127.80
86.34
80.32
78.52
75.66
72.06
71.37
69.33
21.26
20.13
17.91
SPh
O
BnO
BnO
TMBzO
S11
(100 MHz, CDCl3)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


7.44 7.44 7.43 7.42 7.38 7.36 7.36 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.15 6.96 6.94 6.89 6.22
5.86
4.95 4.92 4.91 4.89 4.75 4.72 4.70 4.67 4.13 4.12 4.10 4.10 3.91 3.89 3.88 3.87 3.56 3.54 3.51
2.26 2.24
1.30 1.29 1.29
1H-NMR, 13C-NMR, 1H-1H COSY, HSQC, NOSY of 4d
NPh
O
CF3
O
BnO
BnO
TMBzO
4d
(400 MHz, Acetone-d6)
2.05 10.01 1.11 3.96 0.83 0.97 2.09 2.07 1.00 1.02 1.00 8.97 3.58
f1 (ppm)

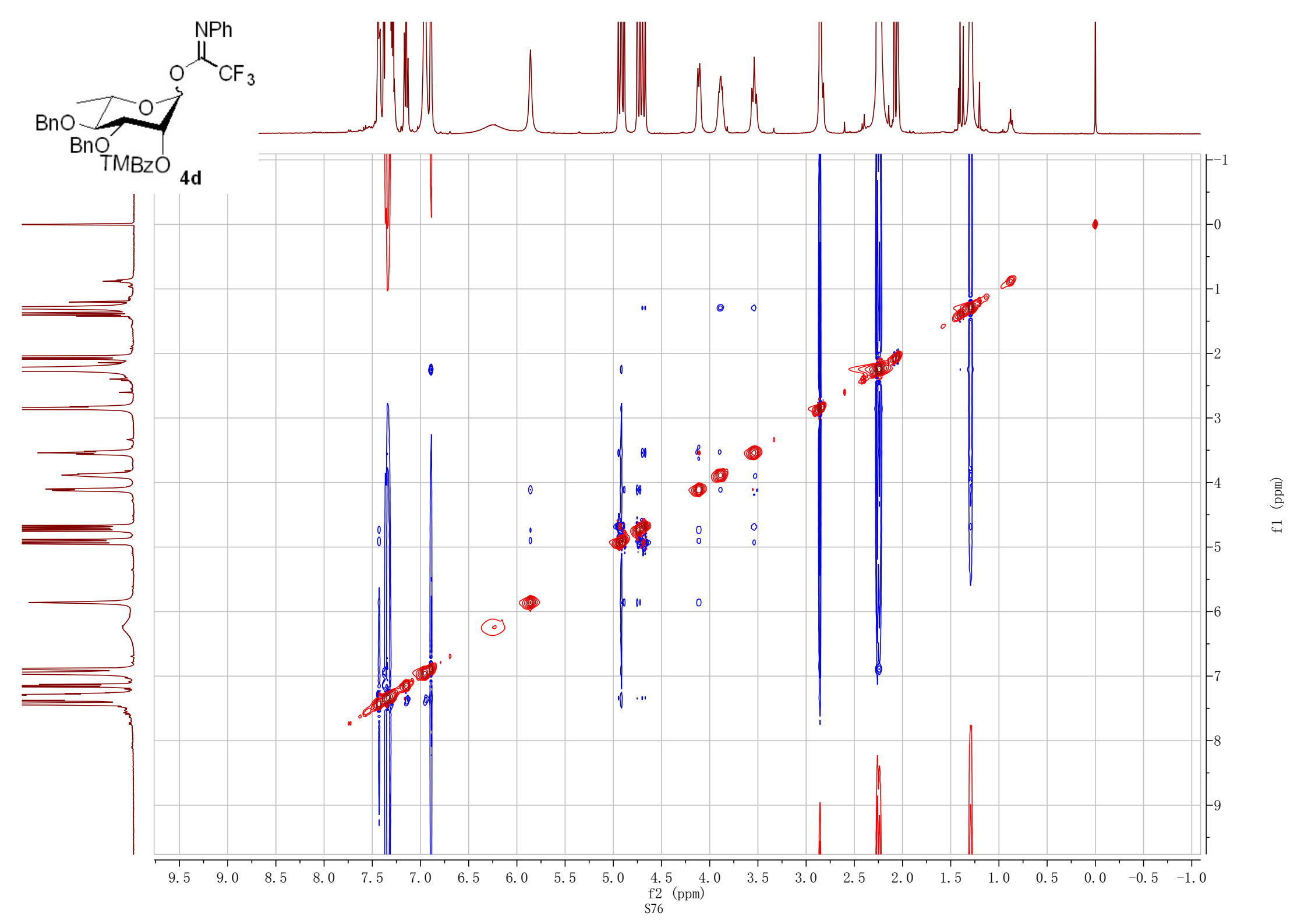

169.21
144.59
140.48
139.66
138.98
136.17
131.53
129.88
129.26
129.21
129.20
129.15
128.88
128.67
128.48
125.49
120.36
95.91
80.11
78.51
75.94
72.85
71.60
68.88
21.20
20.22
18.36
NPh
O
CF3
O
BnO
BnO
TMBzO
4d
(100 MHz, Acetone-d6)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
f1 (ppm)

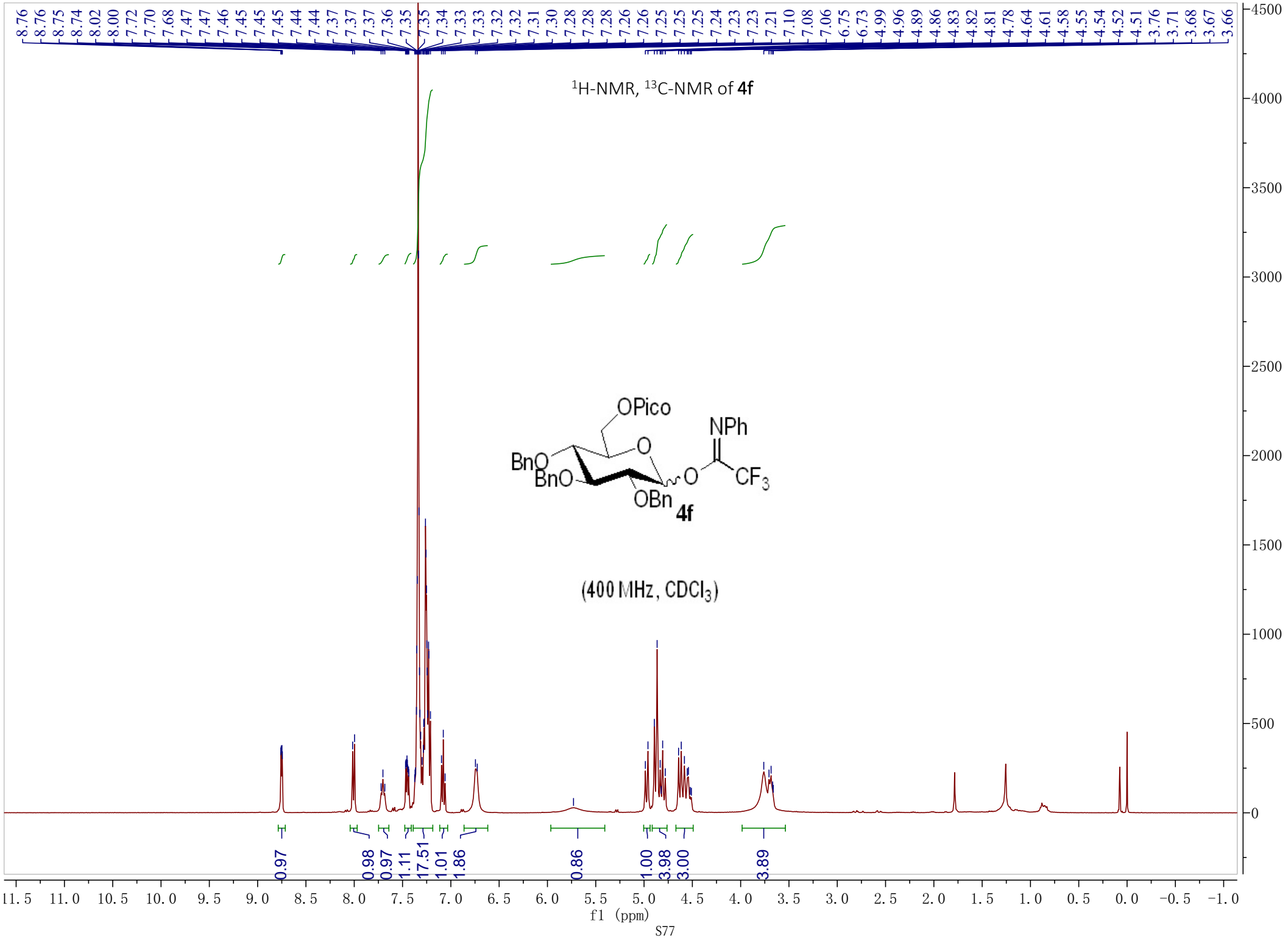

NPH
O
CF3
O
BnO
BnO
TMBzO
4d
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8
9

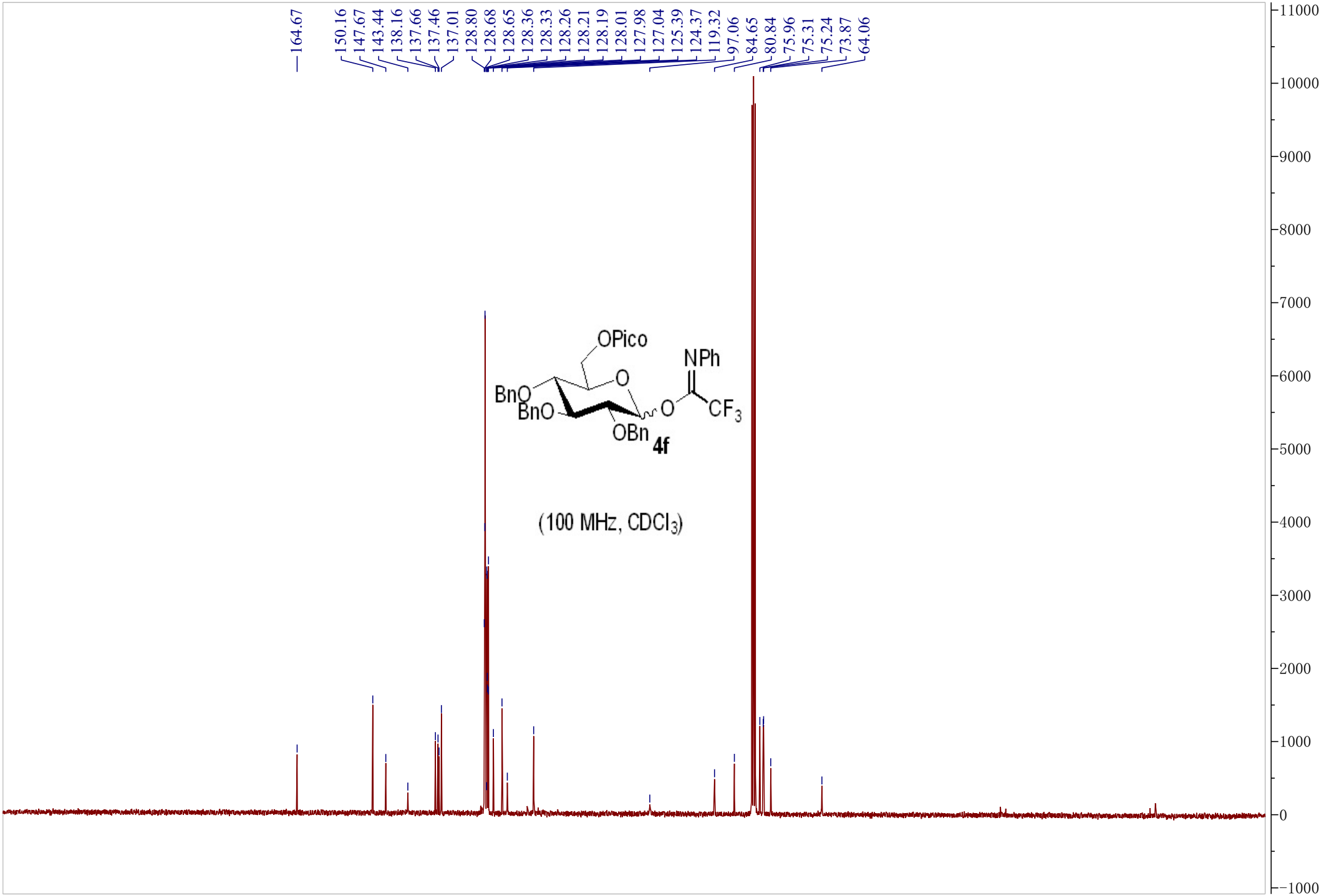

NPh
O
CF3
O
BnO
BnO
TMBzO

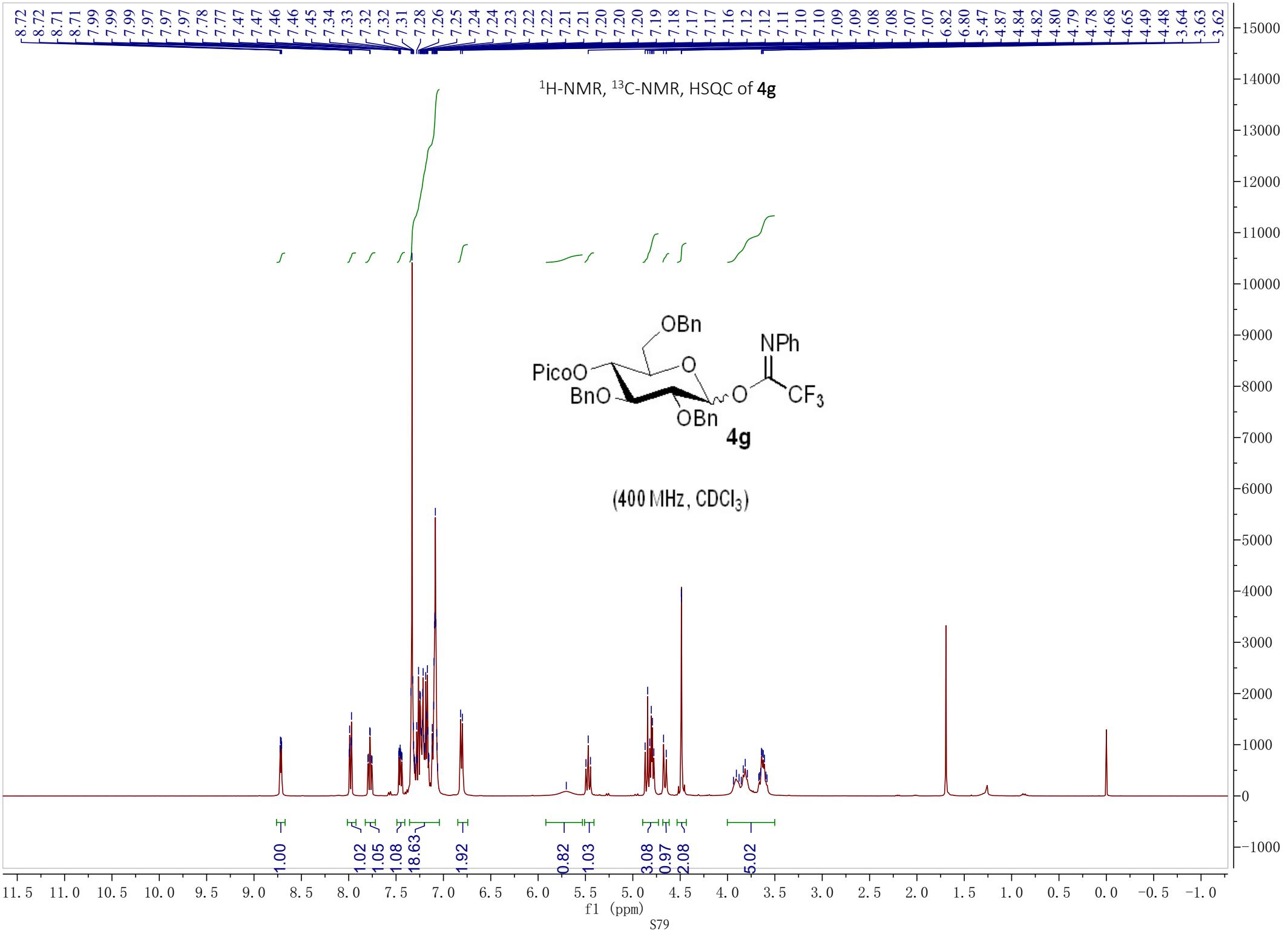
4d

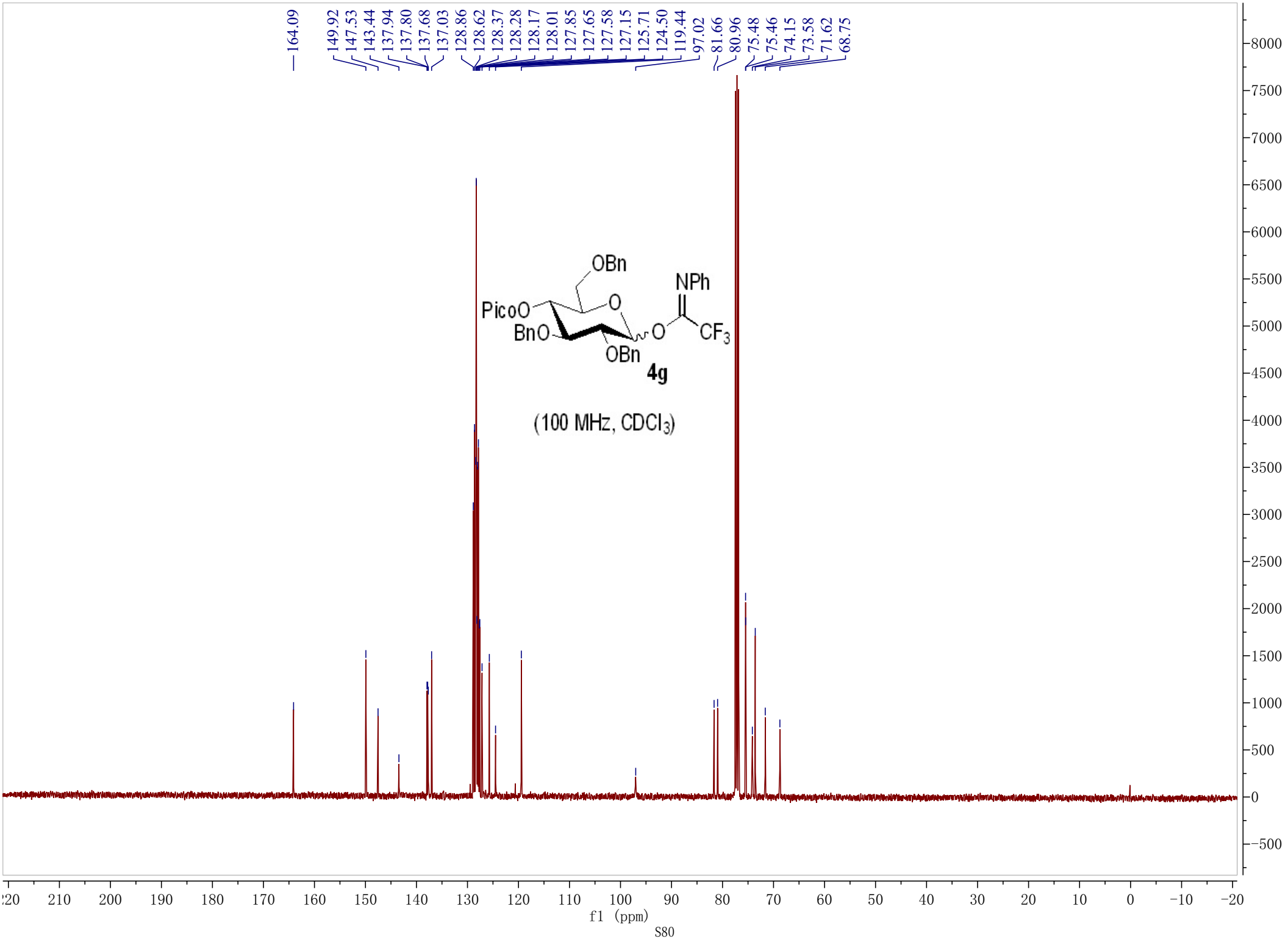
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)

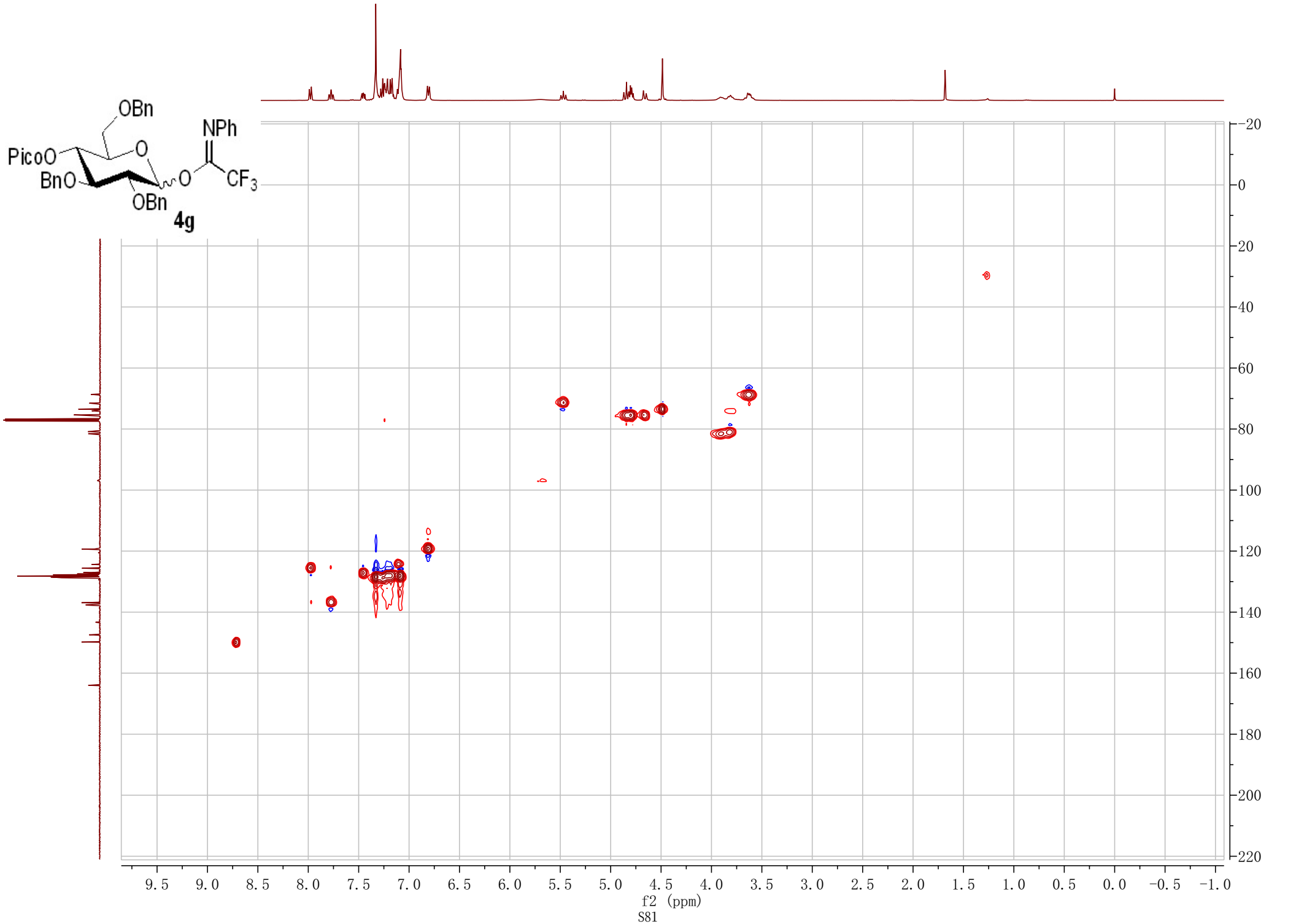

NPh
O
CF3
O
BnO
BnO
TMBzO
4d
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
-1 0 1 2 3 4 5 6 7 8 9

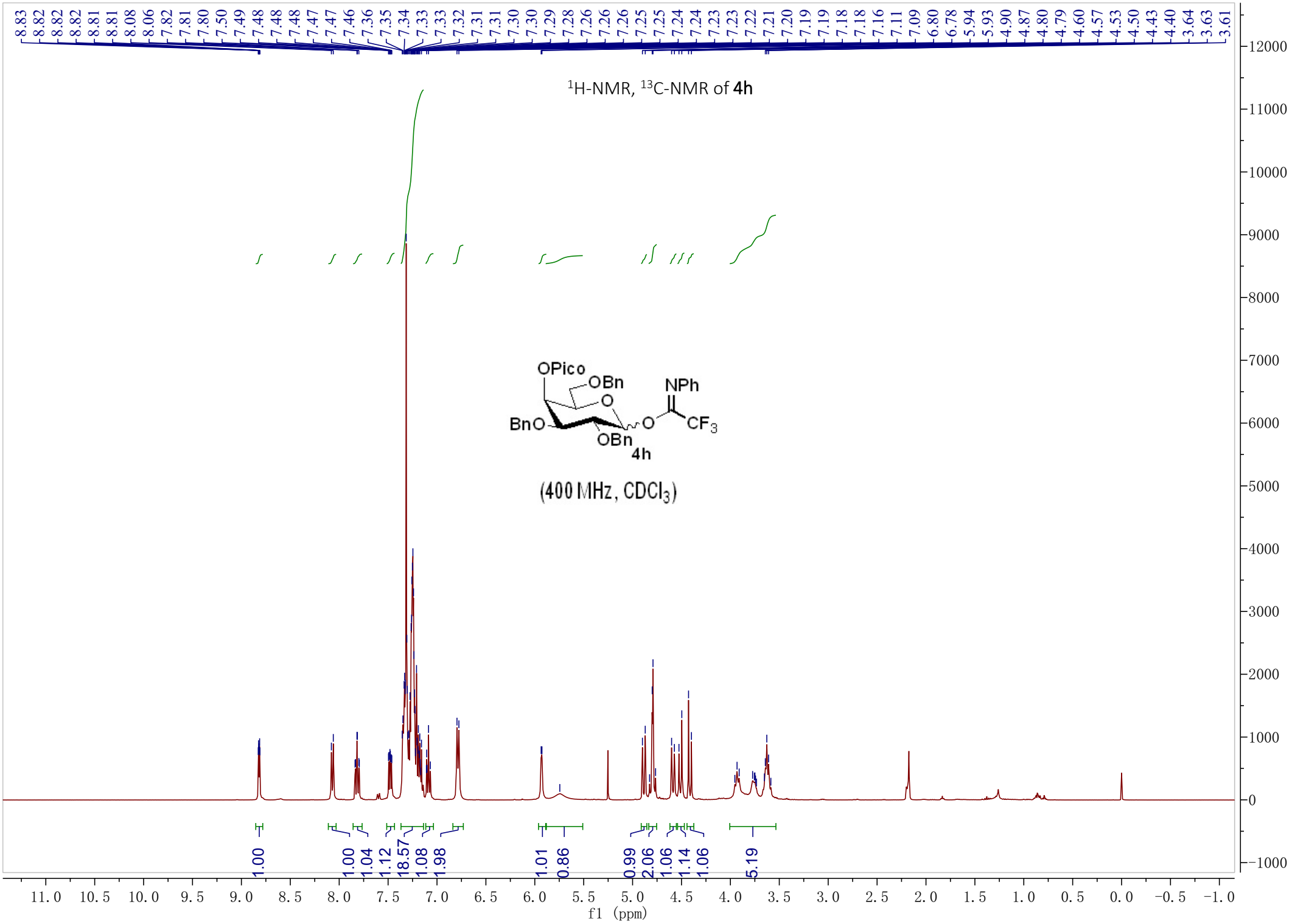

^{1}H-NMR, ^{13}C-NMR of **4f**
OPico
NPh
BnO
BnO
O
O
CF$_3$
OBn
4f
(400 MHz, CDCl$_3$)
f1 (ppm)

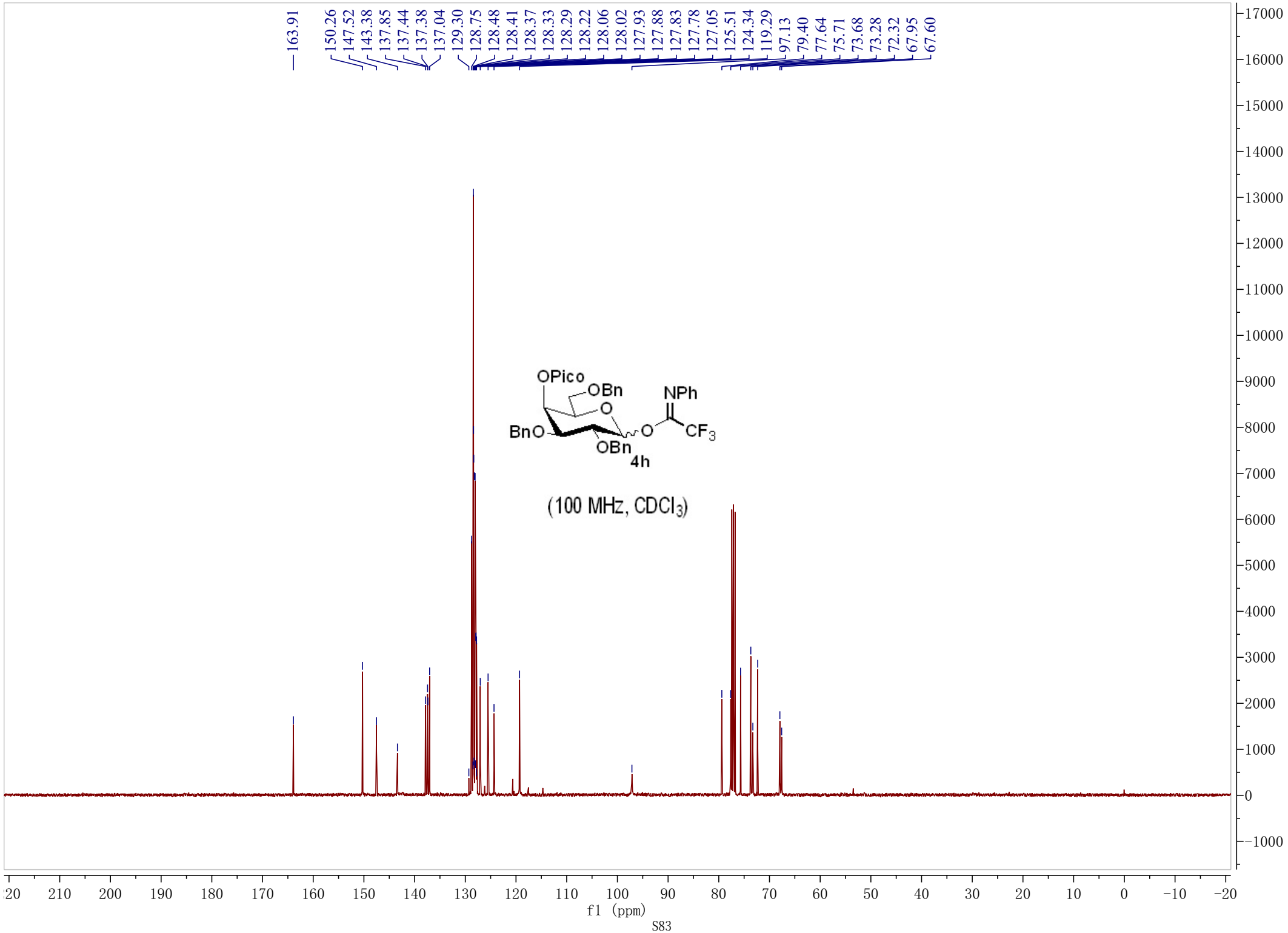

164.67
150.16
147.67
143.44
138.16
137.66
137.46
137.01
128.80
128.68
128.65
128.36
128.33
128.26
128.21
128.19
128.01
127.98
127.04
125.39
124.37
119.32
97.06
84.65
80.84
75.96
75.31
75.24
73.87
64.06
OPico
NPh
O
BnO
BnO
O
CF3
OBn
4f
(100 MHz, CDCl3)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20

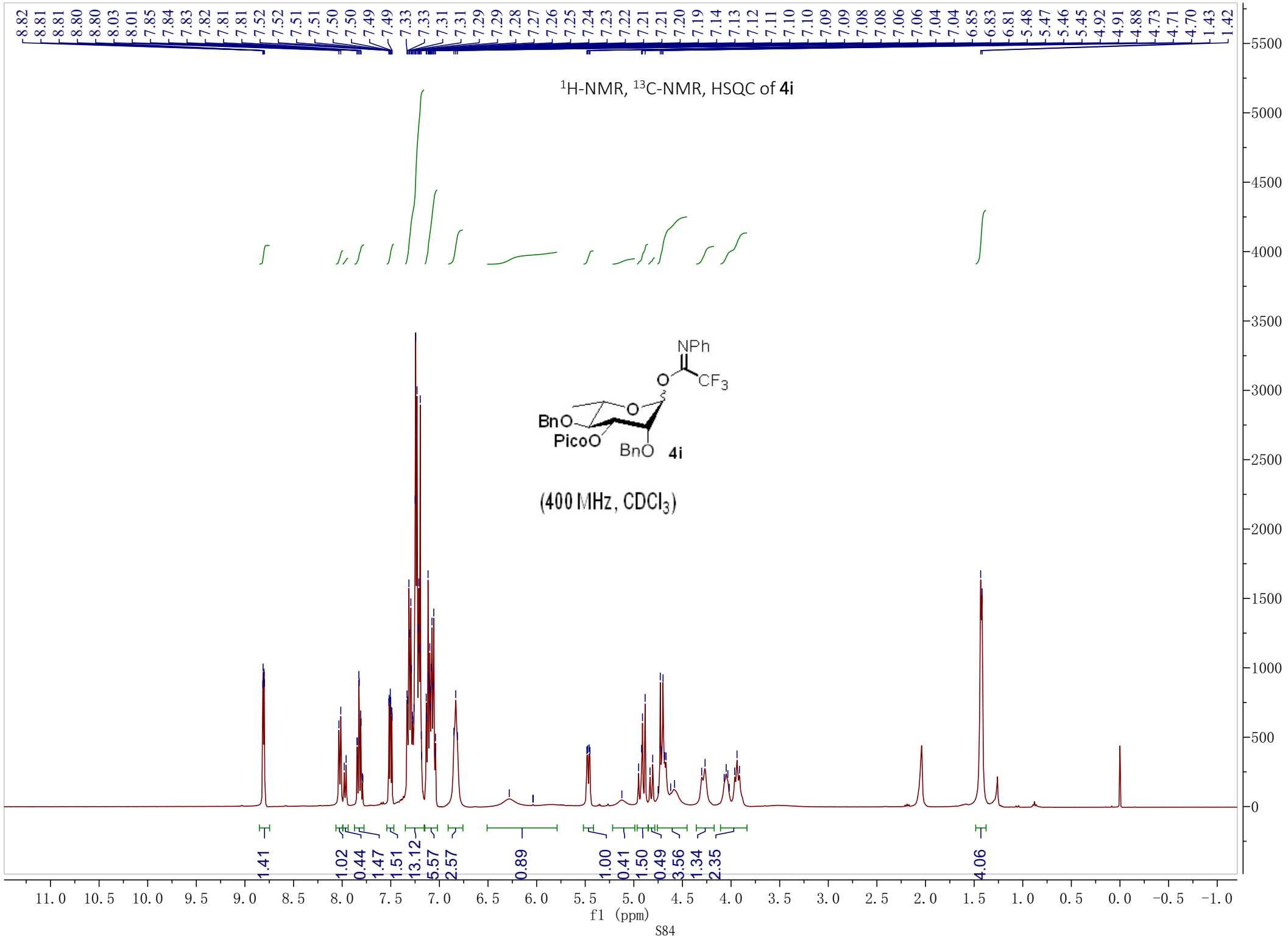

^{1}H-NMR, ^{13}C-NMR, HSQC of **4g**
OBn
NPh
PicoO
O
BnO
O
CF$_3$
OBn
4g
(400 MHz, CDCl$_3$)
f1 (ppm)

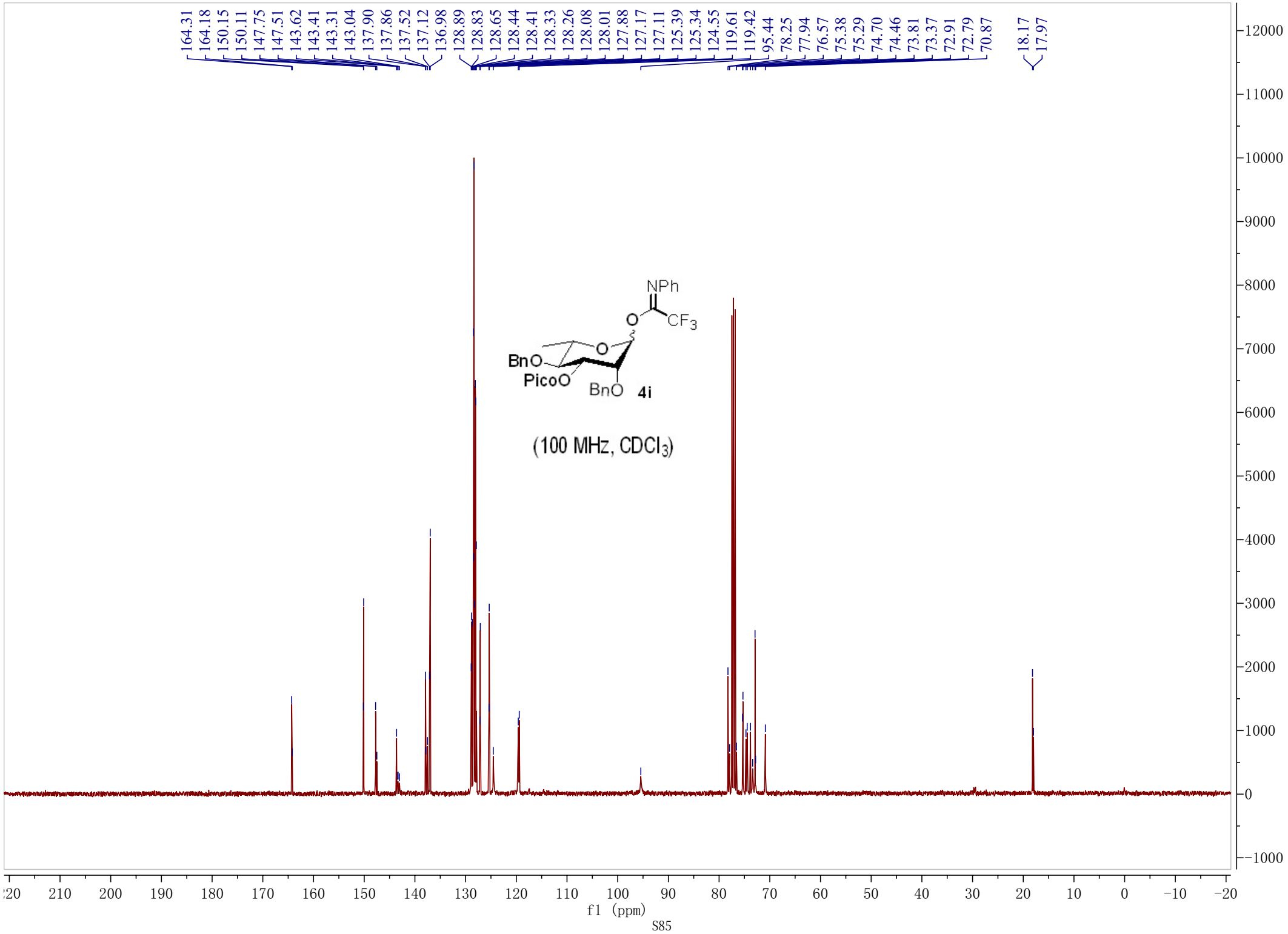

164.09
149.92
147.53
143.44
137.94
137.80
137.68
137.03
128.86
128.62
128.37
128.28
128.17
128.01
127.85
127.65
127.58
127.15
125.71
124.50
119.44
97.02
81.66
80.96
75.48
75.46
74.15
73.58
71.62
68.75
OBn
NPh
PicoO
O
BnO
O
CF3
OBn
4g
(100 MHz, CDCl3)
f1 (ppm)

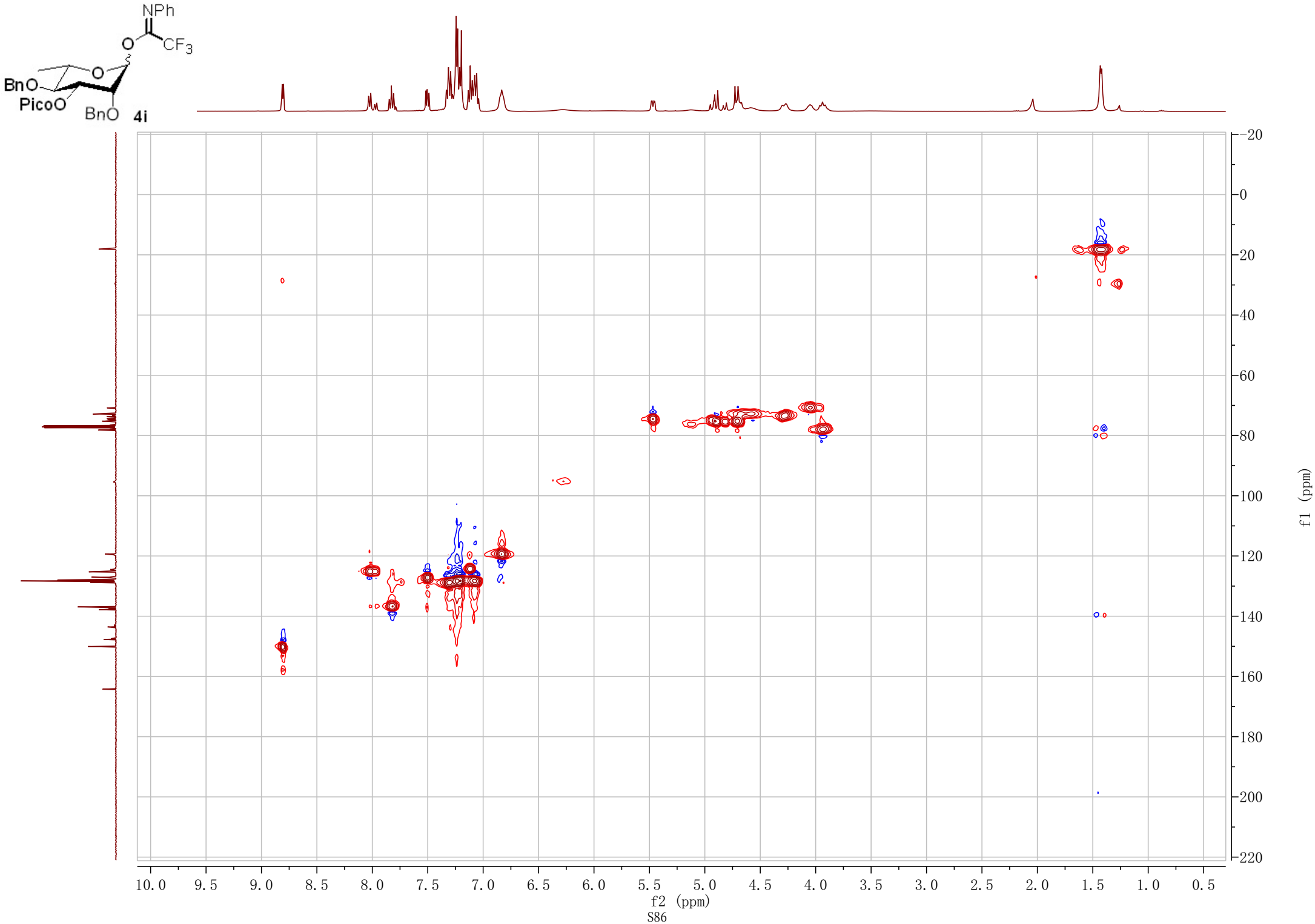

OBn
NPh
PicoO
O
BnO
O
CF3
OBn
4g
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
-20 0 20 40 60 80 100 120 140 160 180 200 220


^{1}H-NMR, ^{13}C-NMR of **4h**
OPico
OBn
O
NPh
BnO
O
CF_3
OBn
4h
(400 MHz, $CDCl_3$)
f1 (ppm)

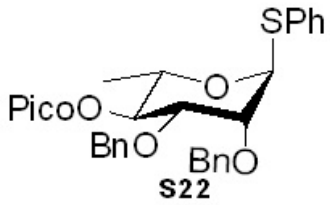

163.91
150.26
147.52
143.38
137.85
137.44
137.38
137.04
129.30
128.75
128.48
128.41
128.37
128.33
128.29
128.22
128.06
128.02
127.93
127.88
127.83
127.78
127.05
125.51
124.34
119.29
97.13
79.40
77.64
75.71
73.68
73.28
72.32
67.95
67.60
OPico
OBn
O
NPh
BnO
O
CF3
OBn
4h
(100 MHz, CDCl3)
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


8.82 8.81 8.81 8.80 8.80 8.03 8.01 7.85 7.84 7.83 7.82 7.81 7.81 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.33 7.33 7.31 7.31 7.29 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.19 7.14 7.13 7.12 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.06 7.06 7.04 7.04 6.85 6.83 6.81 5.48 5.47 5.46 5.45 4.92 4.91 4.88 4.73 4.71 4.70 1.43 1.42
1H-NMR, 13C-NMR, HSQC of 4i
NPh
O
CF3
O
BnO
PicoO
BnO
4i
(400 MHz, CDCl3)
1.41 1.02 0.44 1.47 1.51 13.12 5.57 2.57 0.89 1.00 0.41 1.50 0.49 3.56 1.34 2.35 4.06
f1 (ppm)


164.31
164.18
150.15
150.11
147.75
147.51
143.62
143.41
143.31
143.04
137.90
137.86
137.52
137.12
136.98
128.89
128.83
128.65
128.44
128.41
128.33
128.26
128.08
128.01
127.88
127.17
127.11
125.39
125.34
124.55
119.61
119.42
95.44
78.25
77.94
76.57
75.38
75.29
74.70
74.46
73.81
73.37
72.91
72.79
70.87
18.17
17.97
NPh
O
CF3
O
BnO
PicoO
BnO
4i
(100 MHz, CDCl3)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


NPh
O
CF3
BnO
PicoO
O
BnO
4i
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)

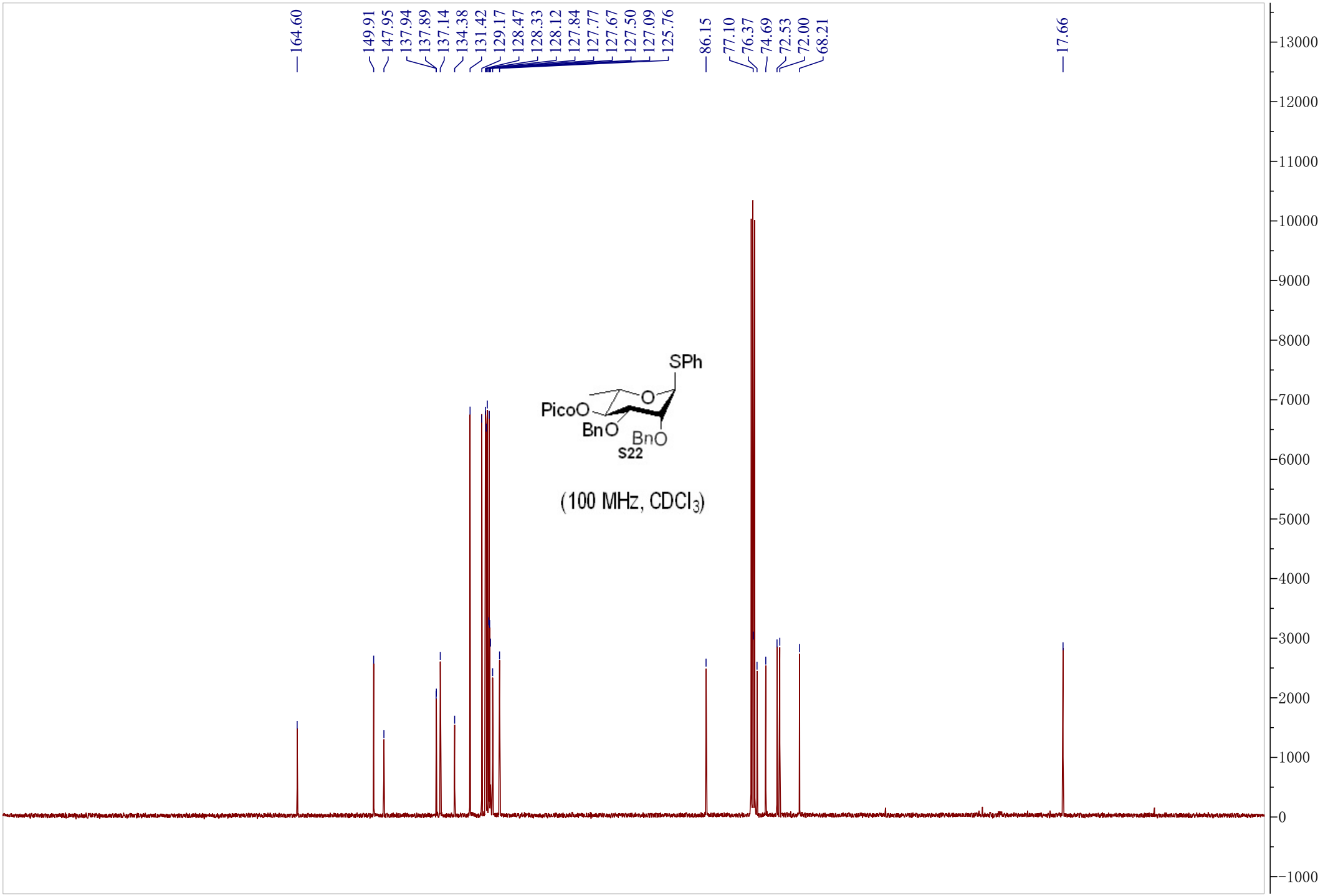
^{1}H-NMR, ^{13}C-NMR of **S22**

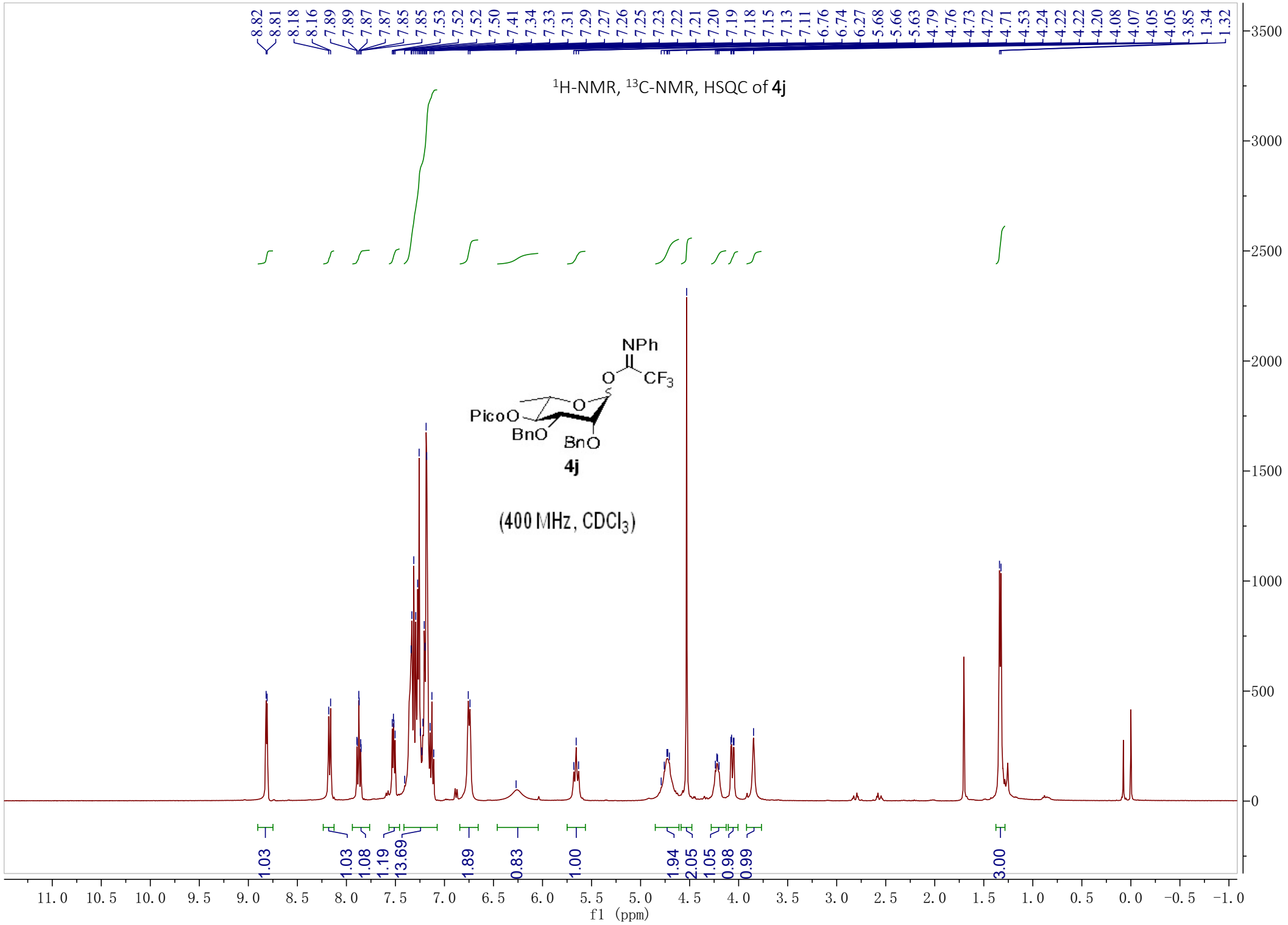


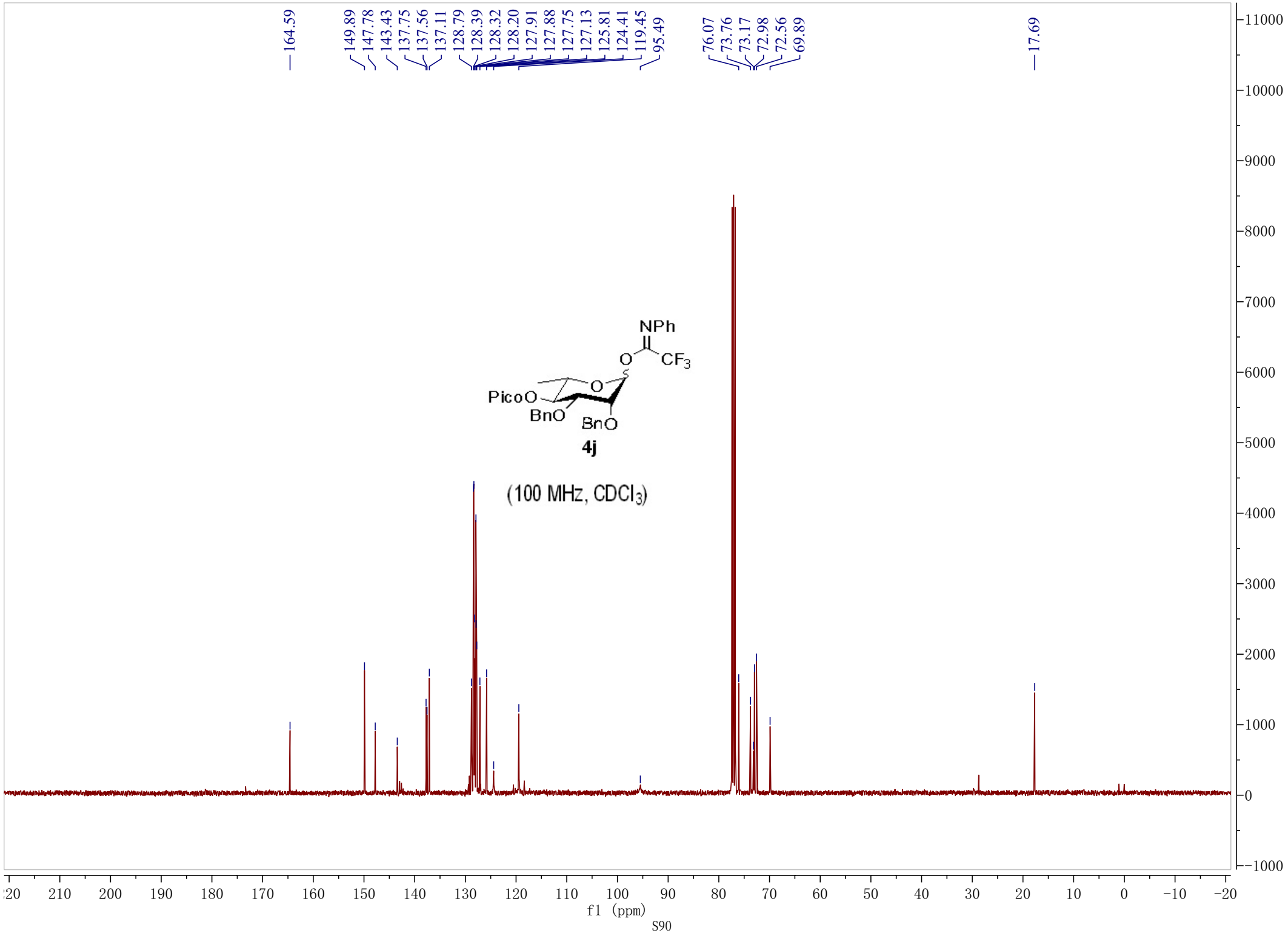
S22

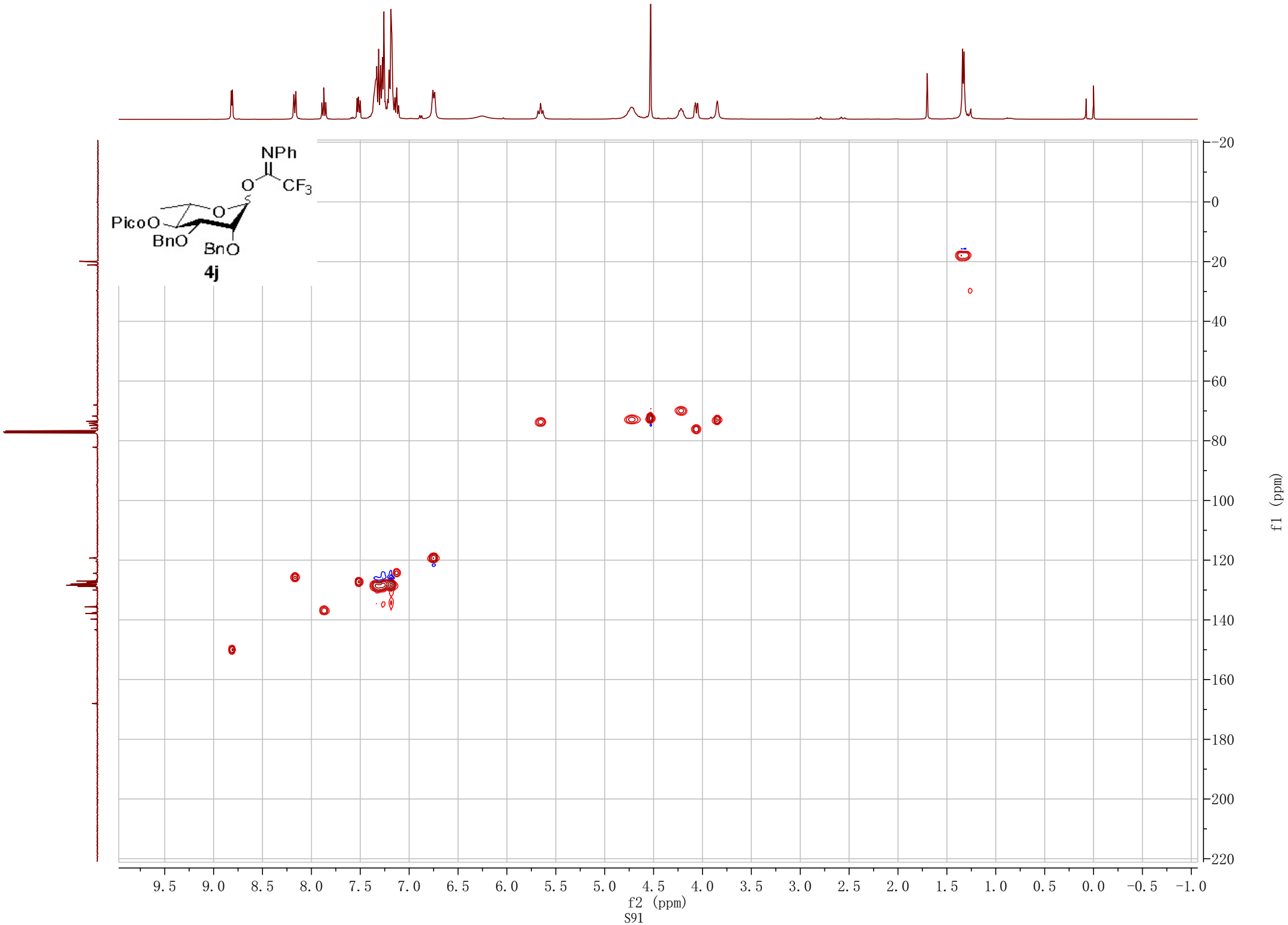
(400 MHz, $CDCl_3$)

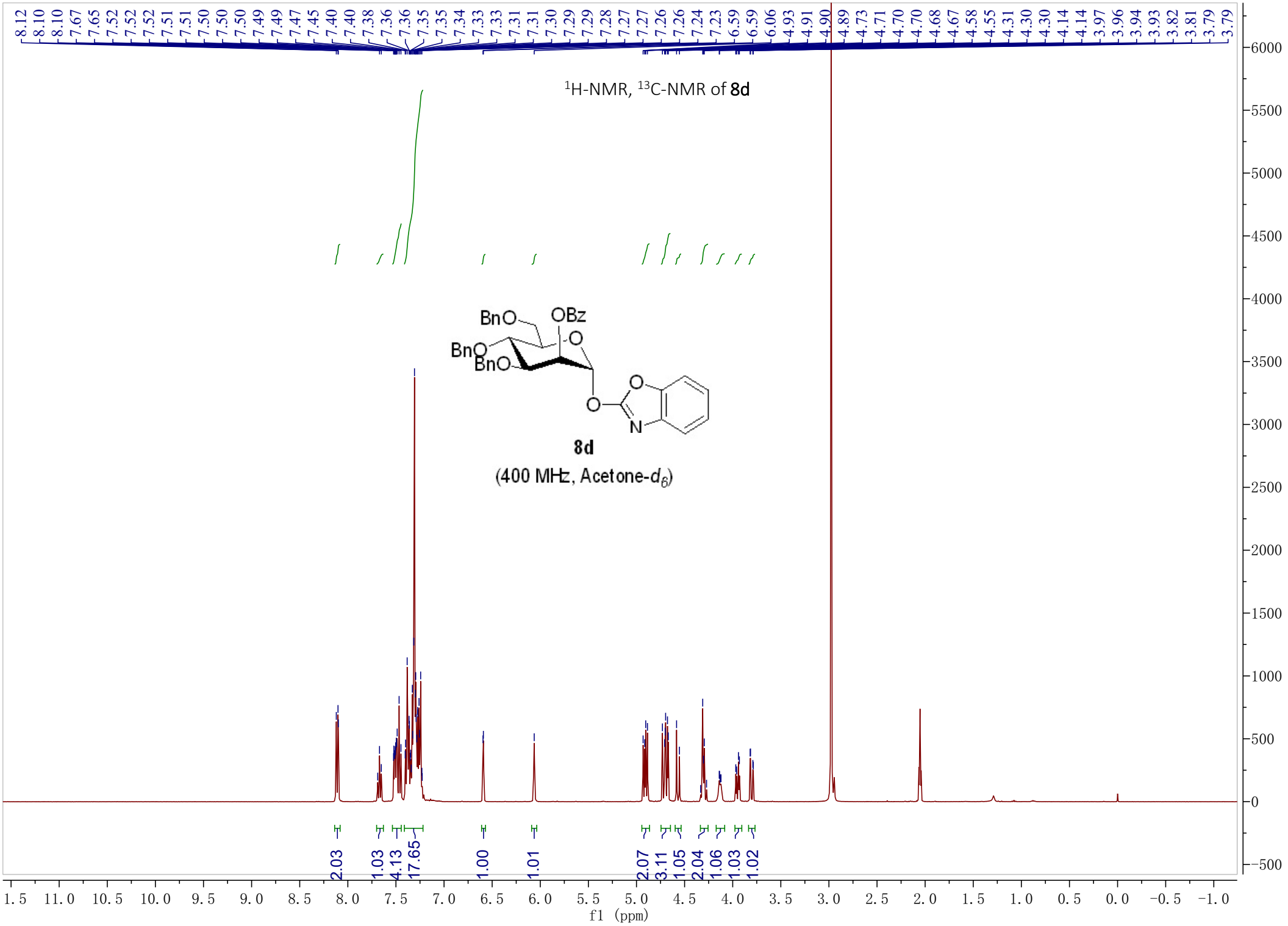
f1 (ppm)

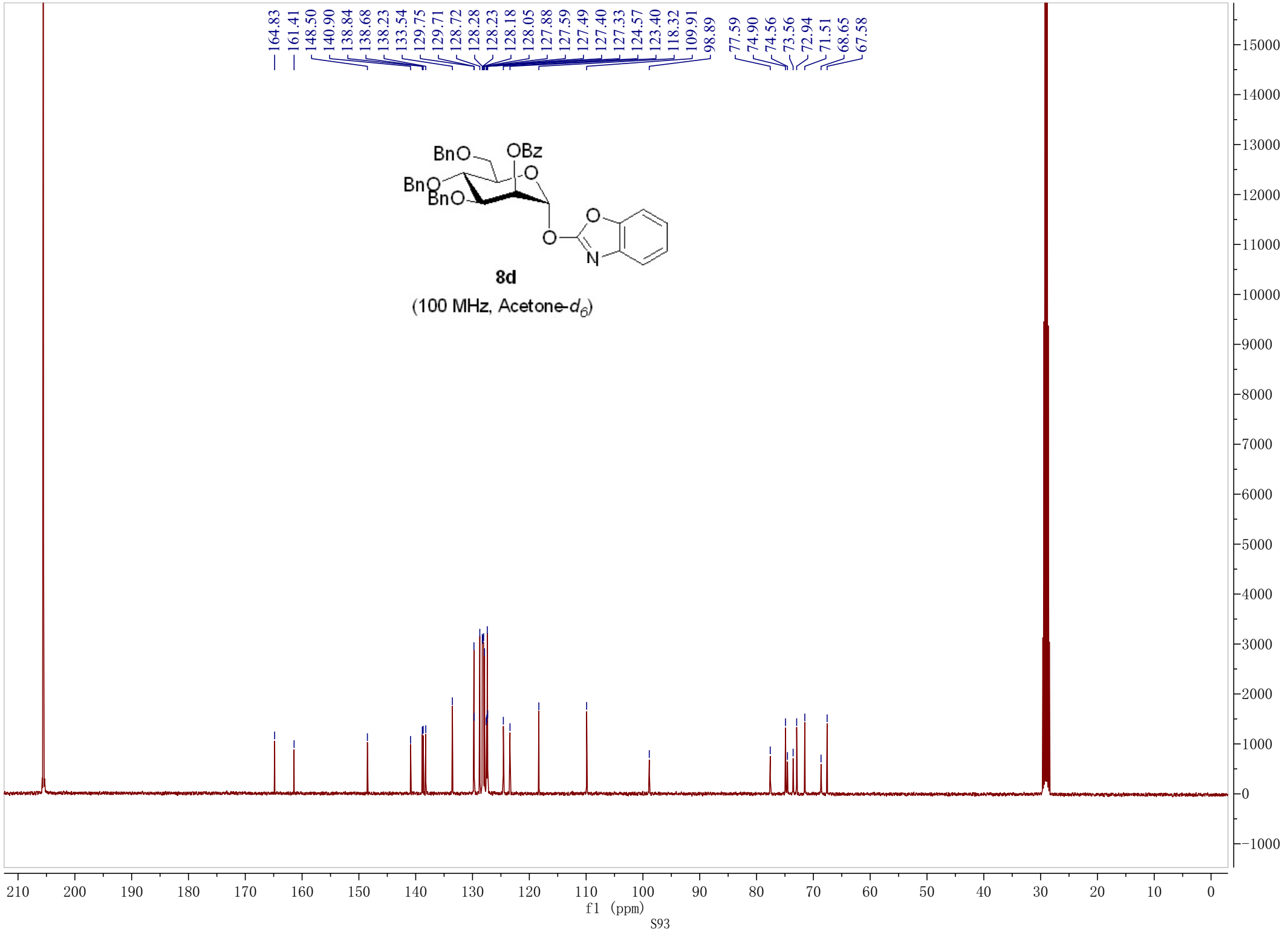

164.60
149.91
147.95
137.94
137.89
137.14
134.38
131.42
129.17
128.47
128.33
128.12
127.84
127.77
127.67
127.50
127.09
125.76
86.15
77.10
76.37
74.69
72.53
72.00
68.21
17.66
SPh
O
PicoO
BnO
BnO
S22
(100 MHz, CDCl3)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

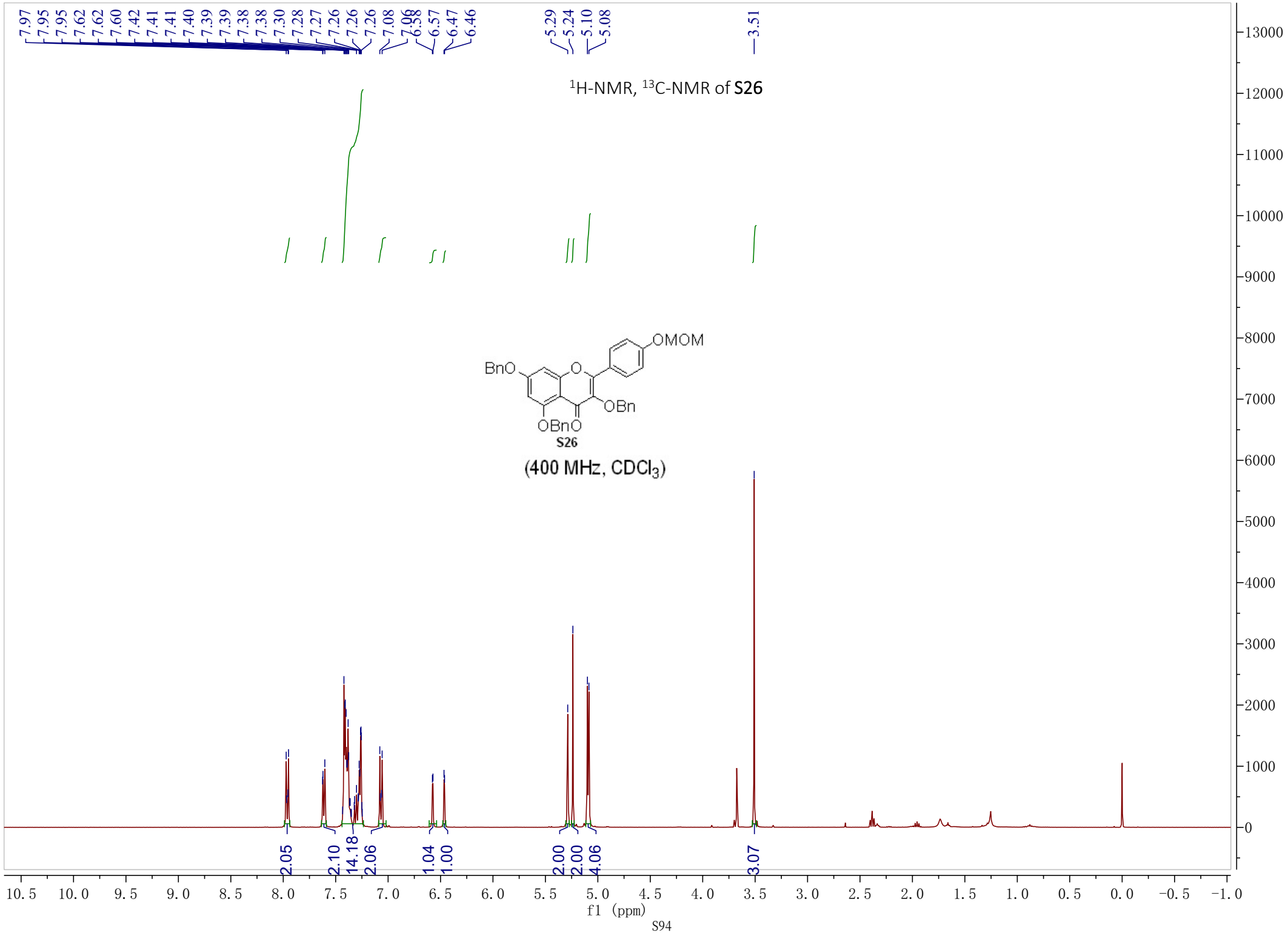

8.82 8.81 8.18 8.16 7.89 7.89 7.87 7.87 7.85 7.85 7.53 7.52 7.52 7.50 7.41 7.34 7.33 7.31 7.29 7.27 7.26 7.25 7.23 7.22 7.21 7.20 7.19 7.18 7.15 7.13 7.11 6.76 6.74 6.27 5.68 5.66 5.63 4.79 4.76 4.73 4.72 4.71 4.53 4.24 4.22 4.22 4.20 4.08 4.07 4.05 4.05 3.85 1.34 1.32
1H-NMR, 13C-NMR, HSQC of 4j
NPh
O
CF3
PicoO
O
BnO
BnO
4j
(400 MHz, CDCl3)
1.03 1.03 1.08 1.19 13.69 1.89 0.83 1.00 1.94 2.05 1.05 0.98 0.99 3.00
3500 3000 2500 2000 1500 1000 500 0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

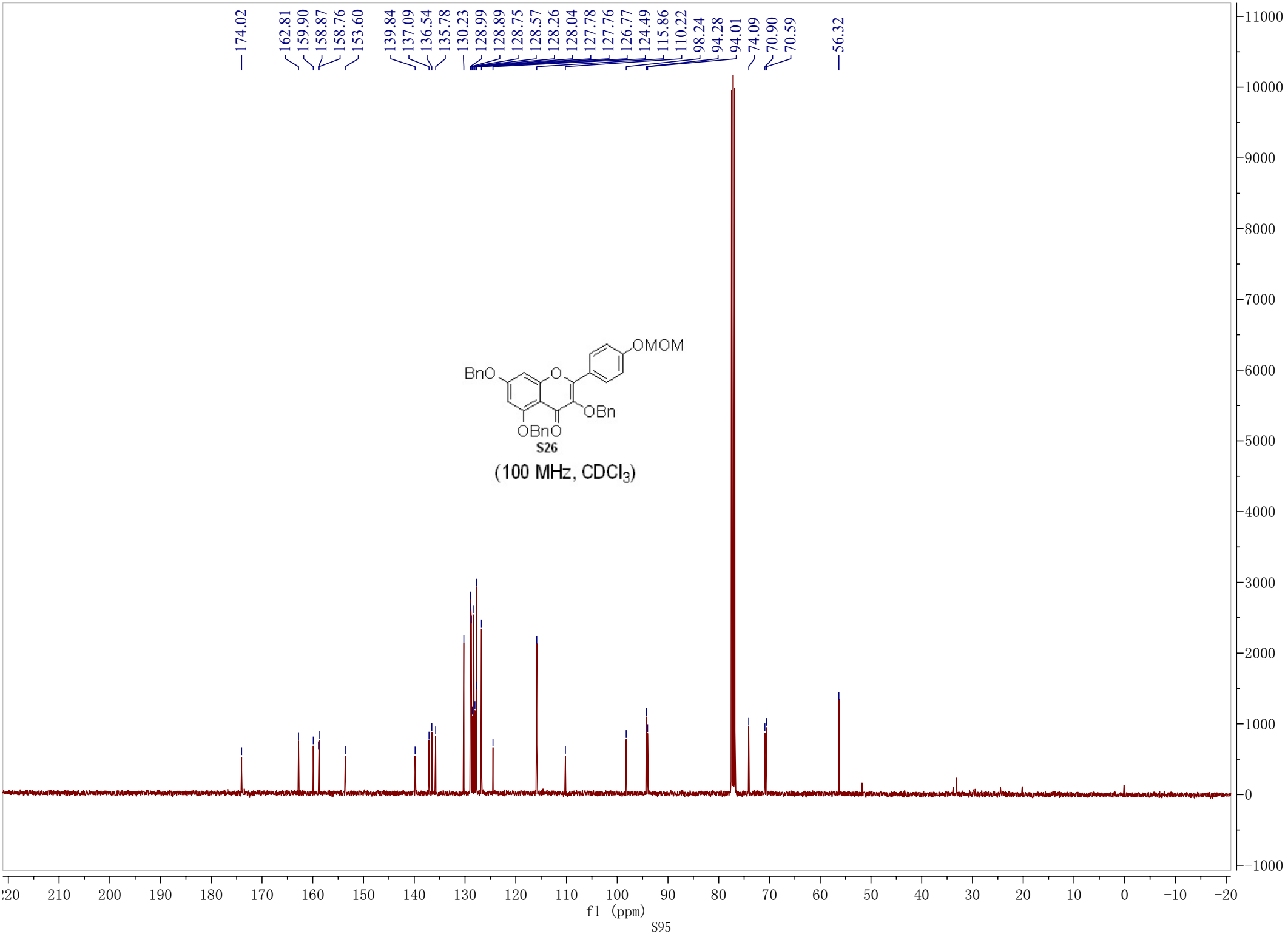

164.59
149.89
147.78
143.43
137.75
137.56
137.11
128.79
128.39
128.32
128.20
127.91
127.88
127.75
127.13
125.81
124.41
119.45
95.49
76.07
73.76
73.17
72.98
72.56
69.89
17.69
NPh
O
CF3
PicoO
O
BnO
BnO
4j
(100 MHz, CDCl3)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

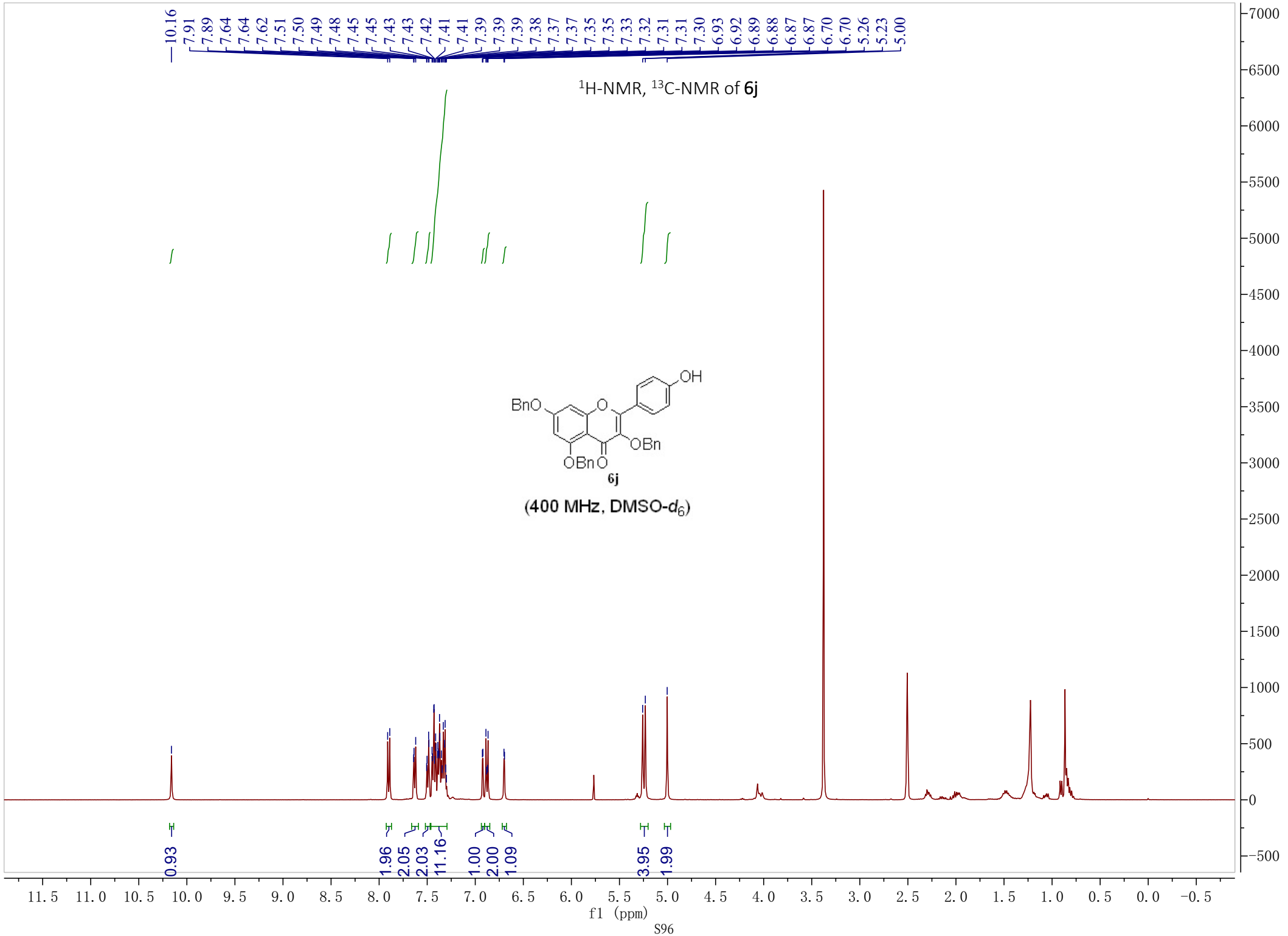

NPh
O
CF3
O
PicoO
BnO
BnO
4j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)

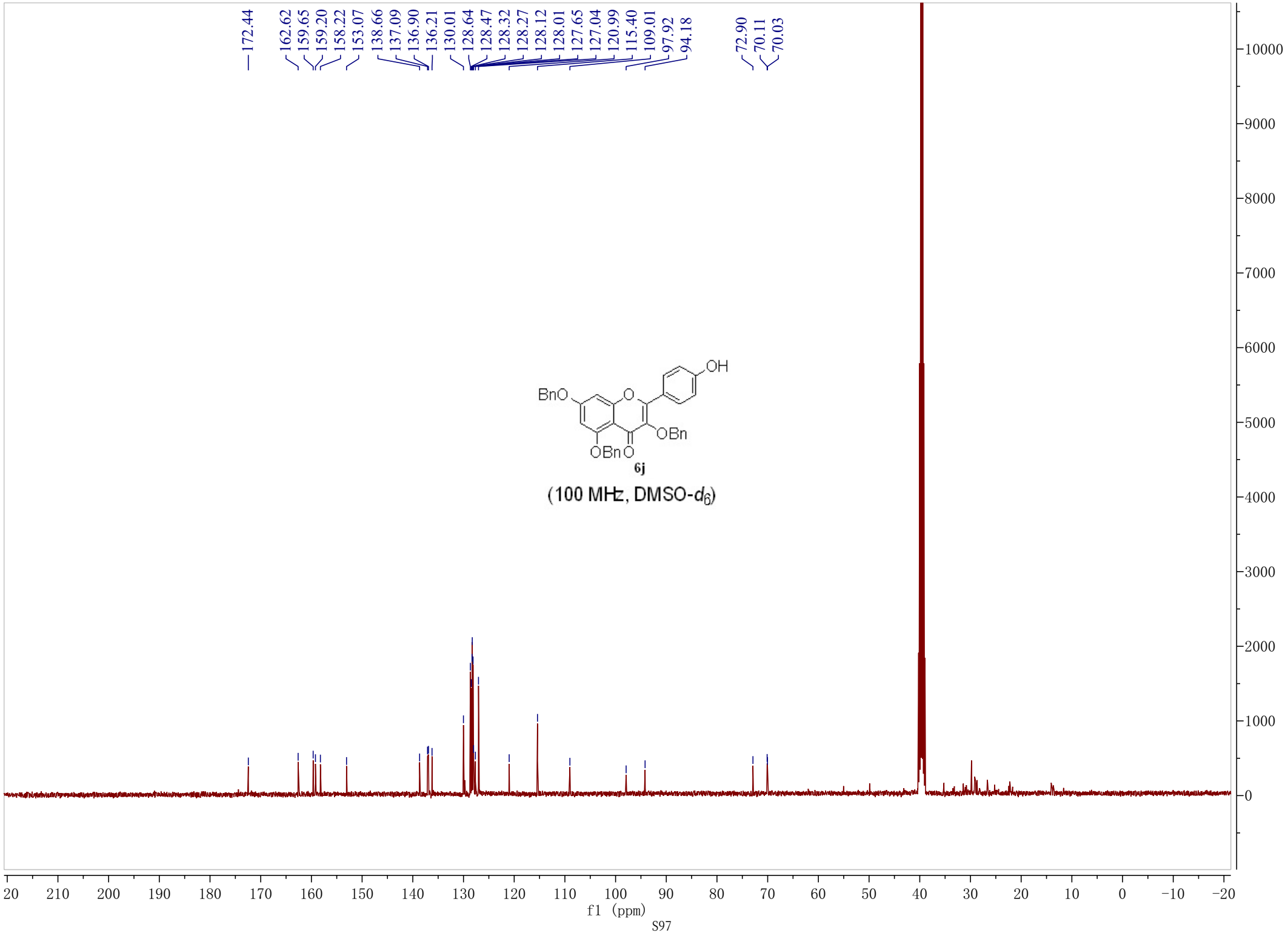

8.12 8.10 8.10 7.67 7.65 7.52 7.52 7.52 7.51 7.51 7.50 7.50 7.50 7.49 7.49 7.47 7.45 7.40 7.40 7.38 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.23 6.59 6.59 6.06 4.93 4.91 4.90 4.89 4.73 4.71 4.70 4.70 4.68 4.67 4.58 4.55 4.31 4.30 4.30 4.14 4.14 3.97 3.96 3.94 3.93 3.82 3.81 3.79 3.79
1H-NMR, 13C-NMR of 8d
BnO
OBz
BnO
BnO
O
O
O
N
8d
(400 MHz, Acetone-d6)
2.03 1.03 4.13 17.65 1.00 1.01 2.07 3.11 1.05 2.04 1.06 1.03 1.02
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

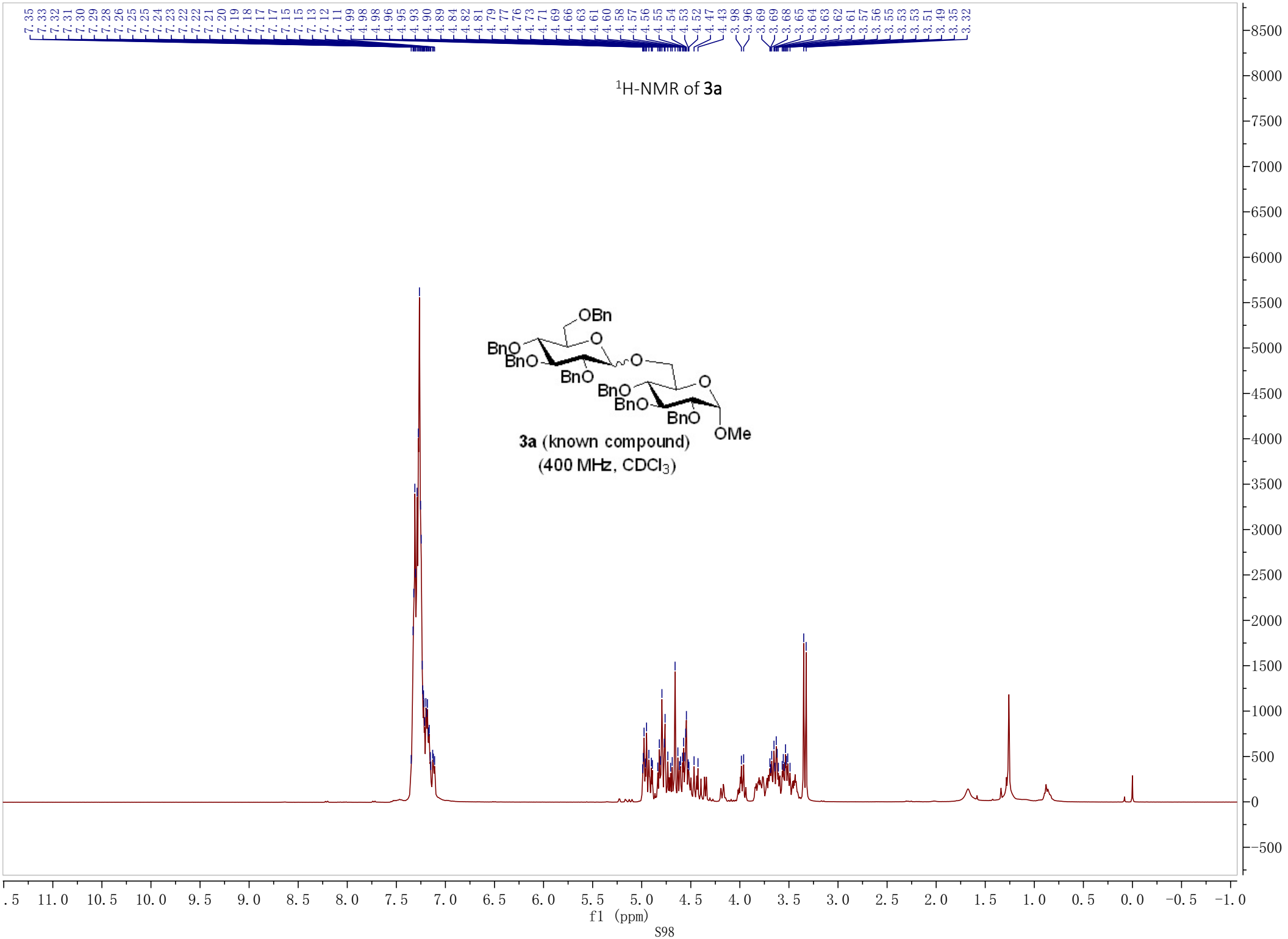

164.83
161.41
148.50
140.90
138.84
138.68
138.23
133.54
129.75
129.71
128.72
128.28
128.23
128.18
128.05
127.88
127.59
127.49
127.40
127.33
124.57
123.40
118.32
109.91
98.89
77.59
74.90
74.56
73.56
72.94
71.51
68.65
67.58
BnO
OBz
O
BnO
BnO
O
O
N
8d
(100 MHz, Acetone-d_6)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.97
7.95
7.95
7.62
7.62
7.60
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.30
7.28
7.27
7.26
7.26
7.26
7.08
7.06
6.58
6.57
6.47
6.46
5.29
5.24
5.10
5.08
3.51
1H-NMR, 13C-NMR of S26
BnO
OMOM
OBn
OBnO
S26
(400 MHz, CDCl3)
2.05
2.10
14.18
2.06
1.04
1.00
2.00
2.00
4.06
3.07
f1 (ppm)


174.02
162.81
159.90
158.87
158.76
153.60
139.84
137.09
136.54
135.78
130.23
128.99
128.89
128.75
128.57
128.26
128.04
127.78
127.76
126.77
124.49
115.86
110.22
98.24
94.28
94.01
74.09
70.90
70.59
56.32
OMOM
BnO
OBn
OBnO
S26
(100 MHz, CDCl3)
f1 (ppm)

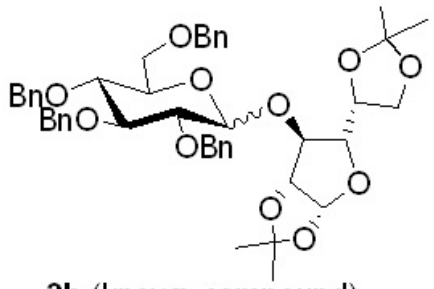

10.16
7.91
7.89
7.64
7.64
7.62
7.51
7.50
7.49
7.48
7.45
7.45
7.43
7.43
7.42
7.41
7.41
7.39
7.39
7.39
7.38
7.37
7.37
7.35
7.35
7.33
7.32
7.31
7.31
7.30
6.93
6.92
6.89
6.88
6.87
6.87
6.70
6.70
5.26
5.23
5.00
1H-NMR, 13C-NMR of 6j
BnO
O
OH
OBn
OBn
O
6j
(400 MHz, DMSO-d6)
0.93
1.96
2.05
2.03
11.16
1.00
2.00
1.09
3.95
1.99
f1 (ppm)


172.44
162.62
159.65
159.20
158.22
153.07
138.66
137.09
136.90
136.21
130.01
128.64
128.47
128.32
128.27
128.12
128.01
127.65
127.04
120.99
115.40
109.01
97.92
94.18
72.90
70.11
70.03
BnO
OH
OBn
OBn
O
O
6j
(100 MHz, DMSO-d_6)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


7.35 7.33 7.32 7.31 7.30 7.29 7.28 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.18 7.17 7.17 7.15 7.15 7.13 7.12 7.11 4.99 4.98 4.98 4.96 4.95 4.93 4.90 4.89 4.84 4.82 4.81 4.79 4.77 4.76 4.73 4.71 4.69 4.66 4.63 4.61 4.60 4.58 4.57 4.56 4.55 4.54 4.53 4.52 4.47 4.43 3.98 3.96 3.69 3.69 3.68 3.65 3.64 3.63 3.62 3.61 3.57 3.56 3.55 3.53 3.53 3.51 3.49 3.35 3.32
1H-NMR of 3a
OBn
BnO
BnO
BnO
BnO
BnO
BnO
OMe
3a (known compound)
(400 MHz, CDCl3)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

XK200924.1.fid
XK200924

^{1}H-NMR of **3b**

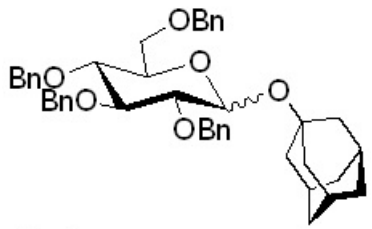


3b (known compound)
(400 MHz, $CDCl_3$)

f1 (ppm)

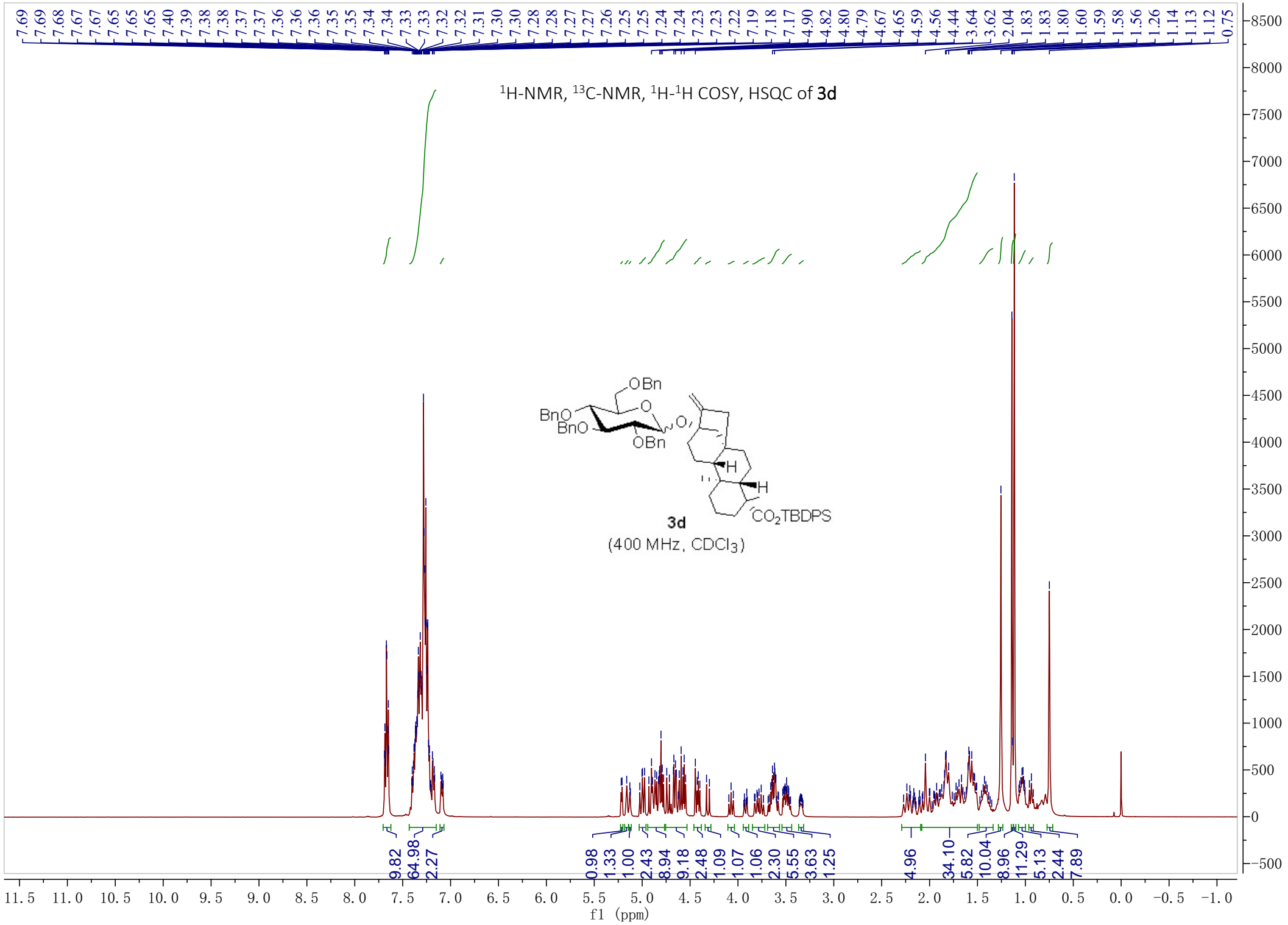
XK190809-2.1.fid
XK190809-2

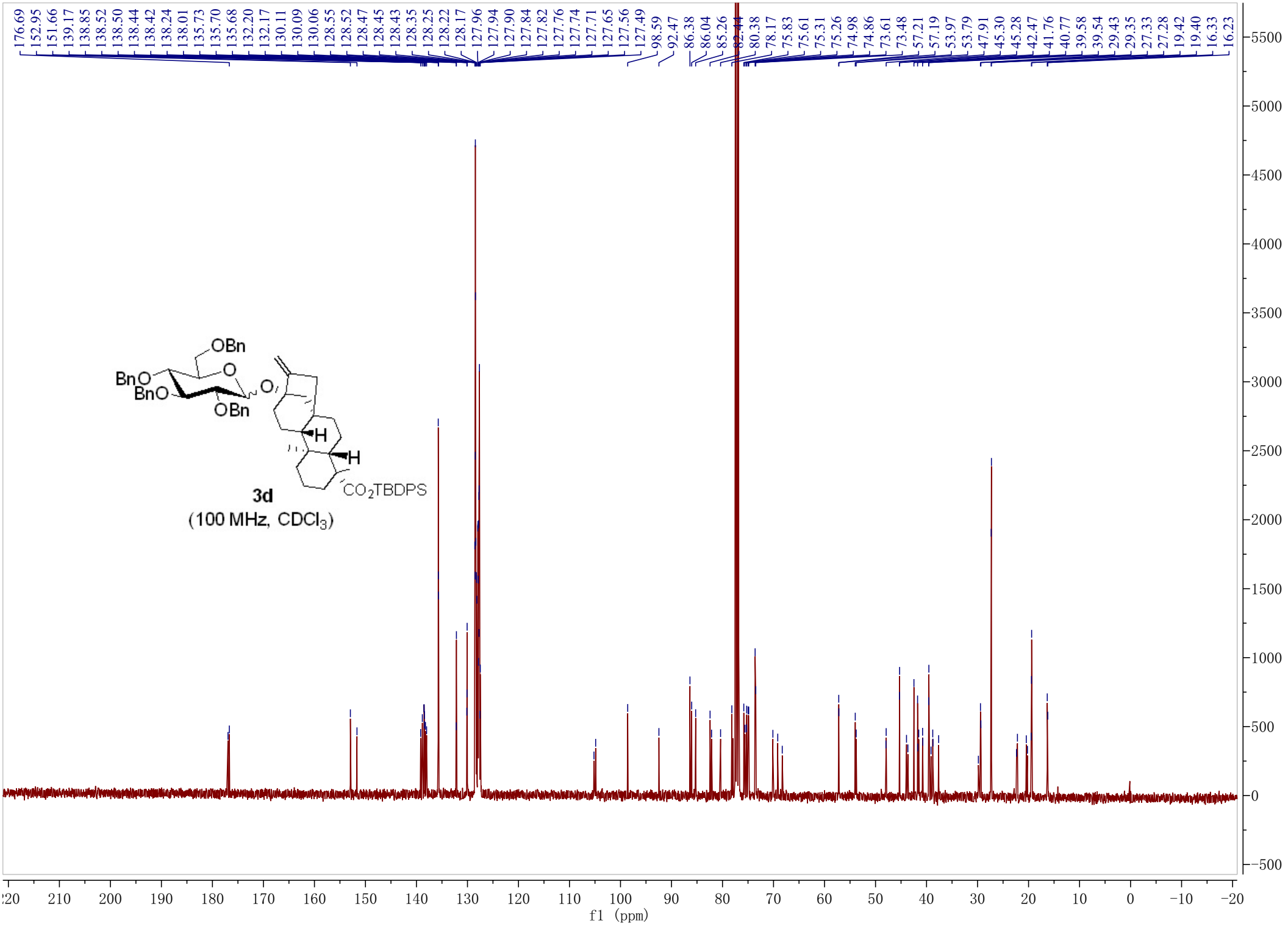
^{1}H-NMR of **3c**

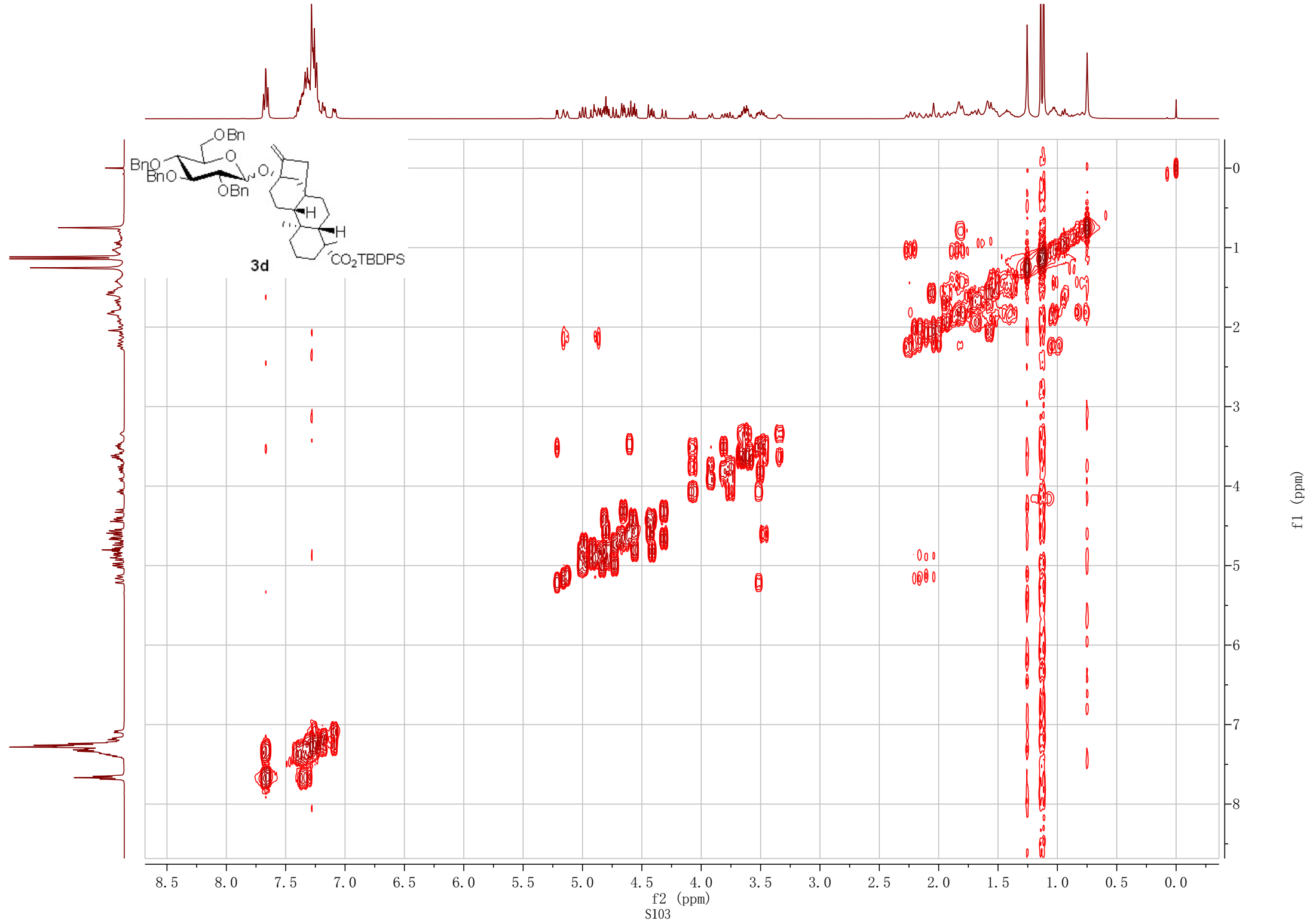


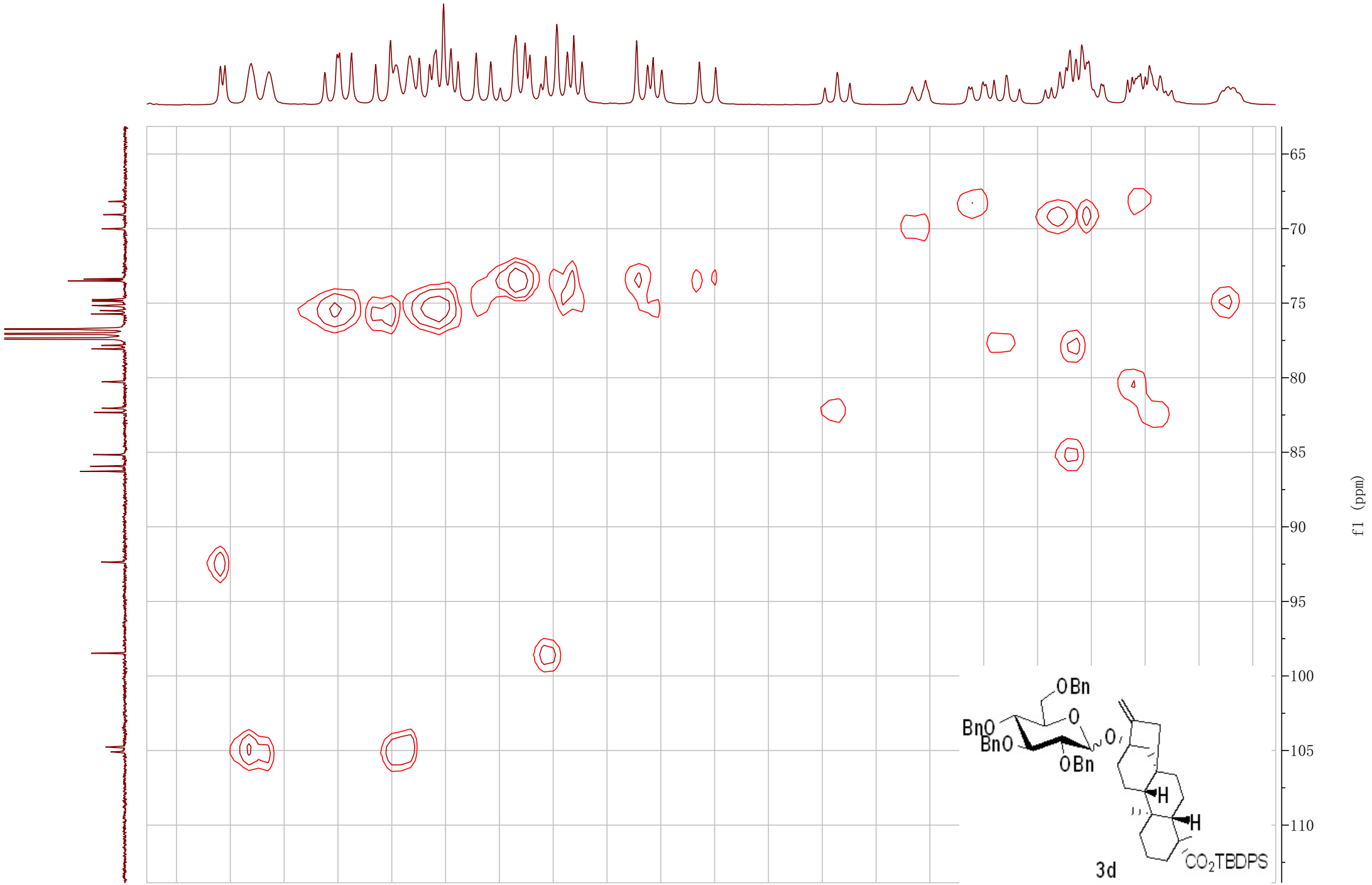
3c (known compound)
(400 MHz, $CDCl_3$)

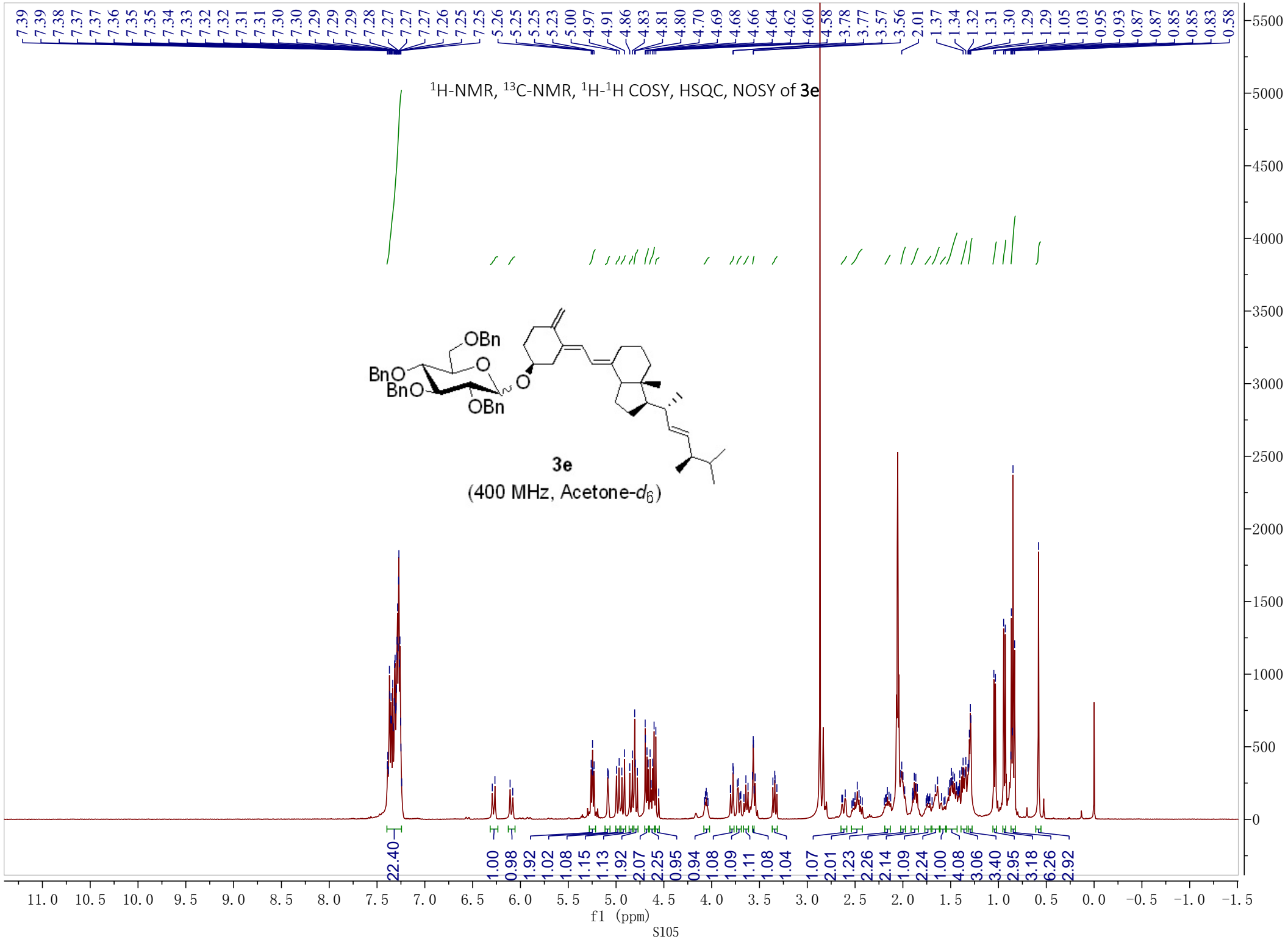
f1 (ppm)

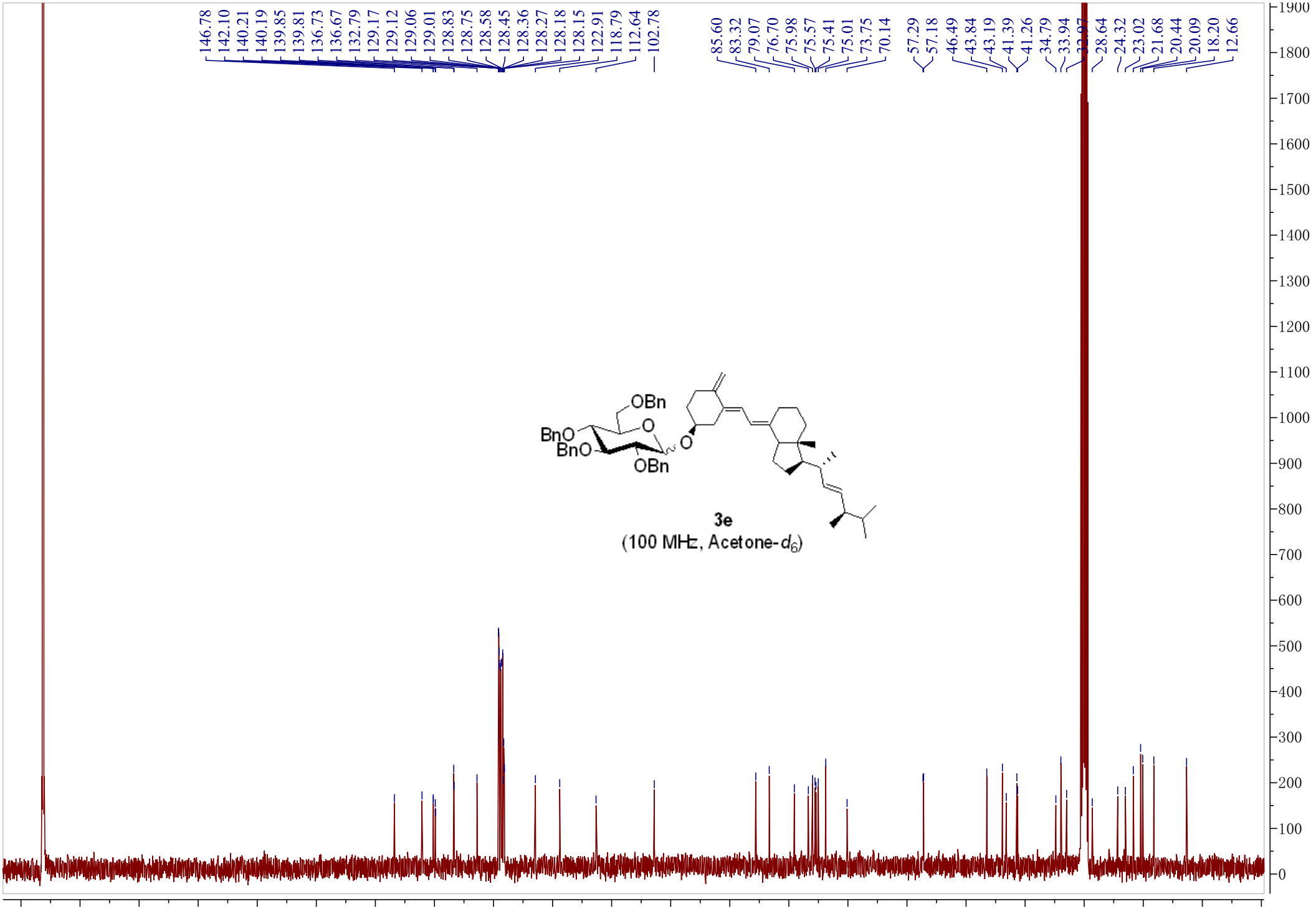

^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC of **3d**
OBn
BnO
BnO
OBn
O
O
H
H
CO_2TBDPS
3d
(400 MHz, $CDCl_3$)
f1 (ppm)

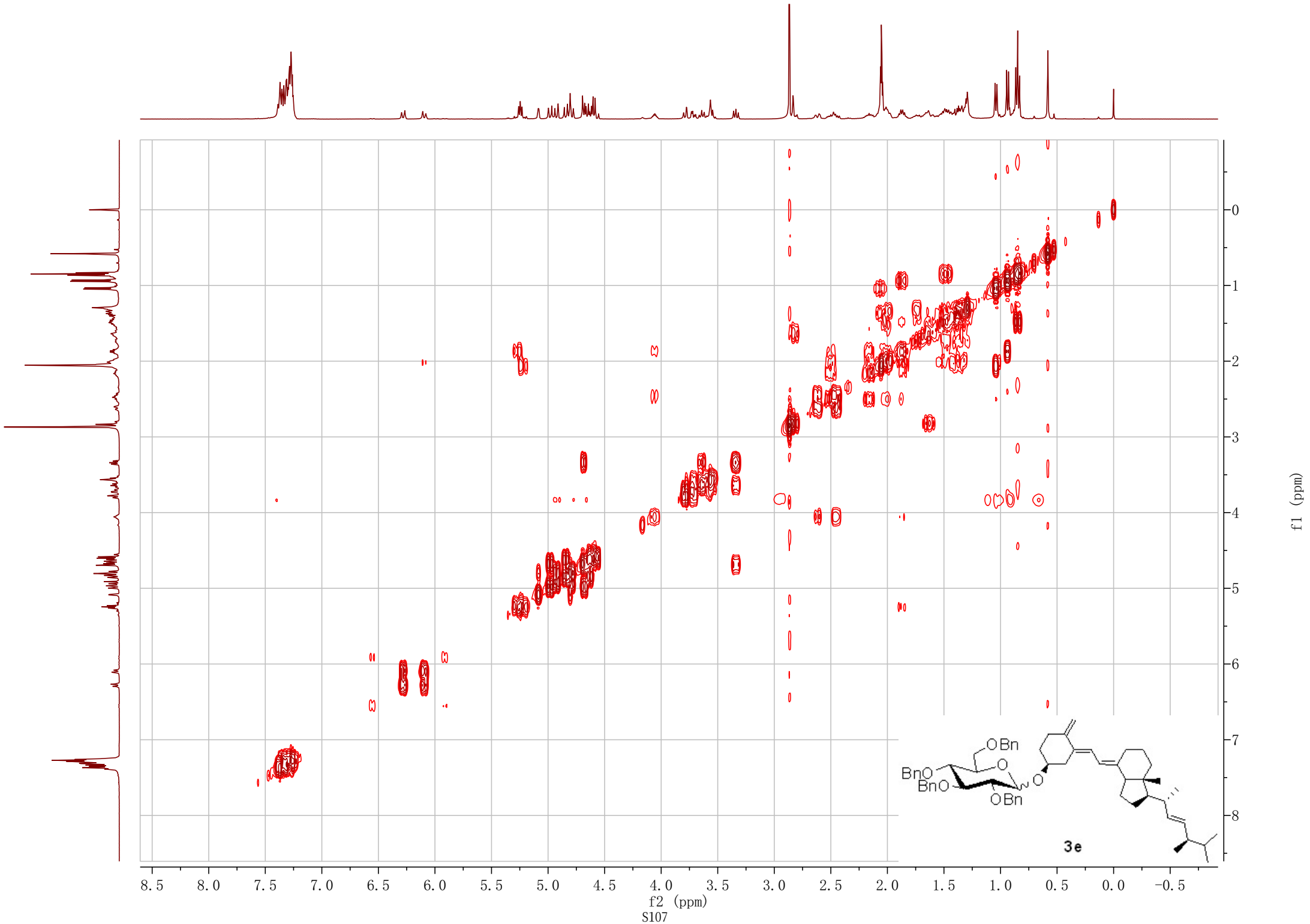

176.69
152.95
151.66
139.17
138.85
138.52
138.50
138.44
138.42
138.24
138.01
135.73
135.70
135.68
132.20
132.17
130.11
130.09
130.06
128.55
128.52
128.47
128.45
128.43
128.35
128.25
128.22
128.17
127.96
127.94
127.90
127.84
127.82
127.76
127.74
127.71
127.65
127.56
127.49
98.59
92.47
86.38
86.04
85.26
82.44
80.38
78.17
75.83
75.61
75.31
75.26
74.98
74.86
73.61
73.48
57.21
57.19
53.97
53.79
47.91
45.30
45.28
42.47
41.76
40.77
39.58
39.54
29.43
29.35
27.33
27.28
19.42
19.40
16.33
16.23
OBn
BnO
BnO
OBn
O
O
H
H
CO2TBDPS
3d
(100 MHz, CDCl3)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

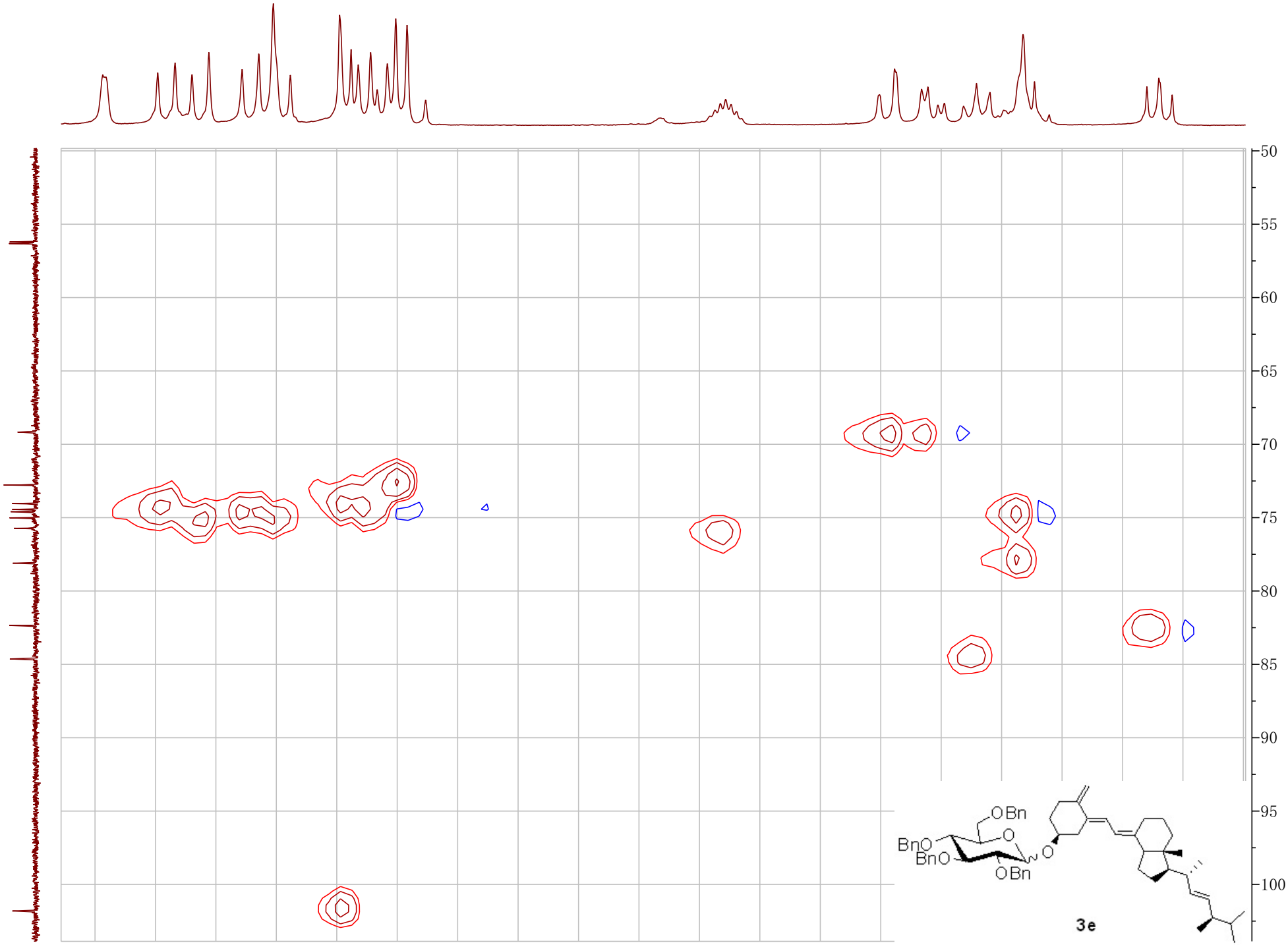

OBn
BnO
BnO
OBn
O
O
H
H
CO2TBDPS
3d
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

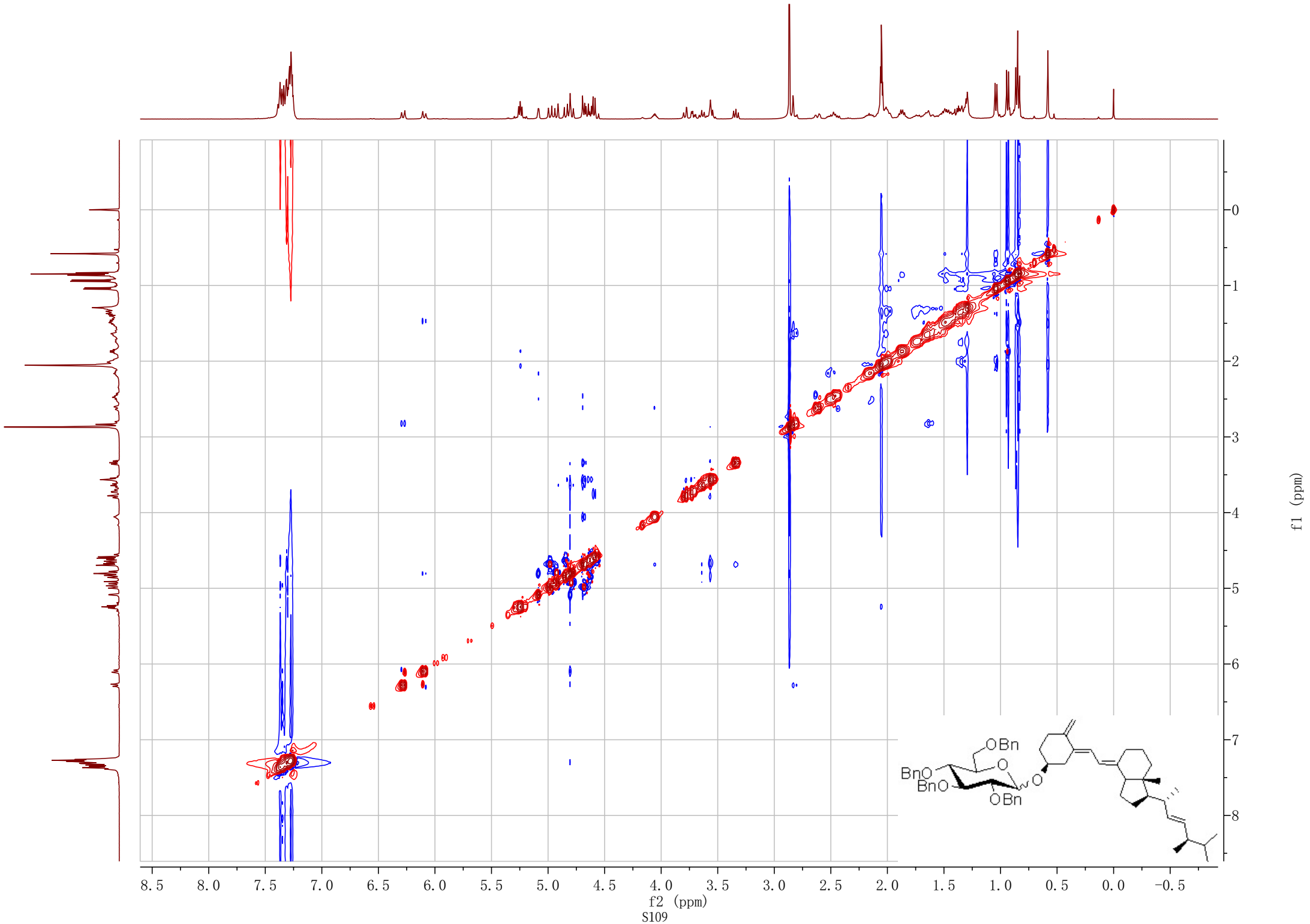

OBn
O
BnO
BnO
O
OBn
H
H
CO2TBDPS
3d
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
65
70
75
80
85
90
95
100
105
110
f1 (ppm)

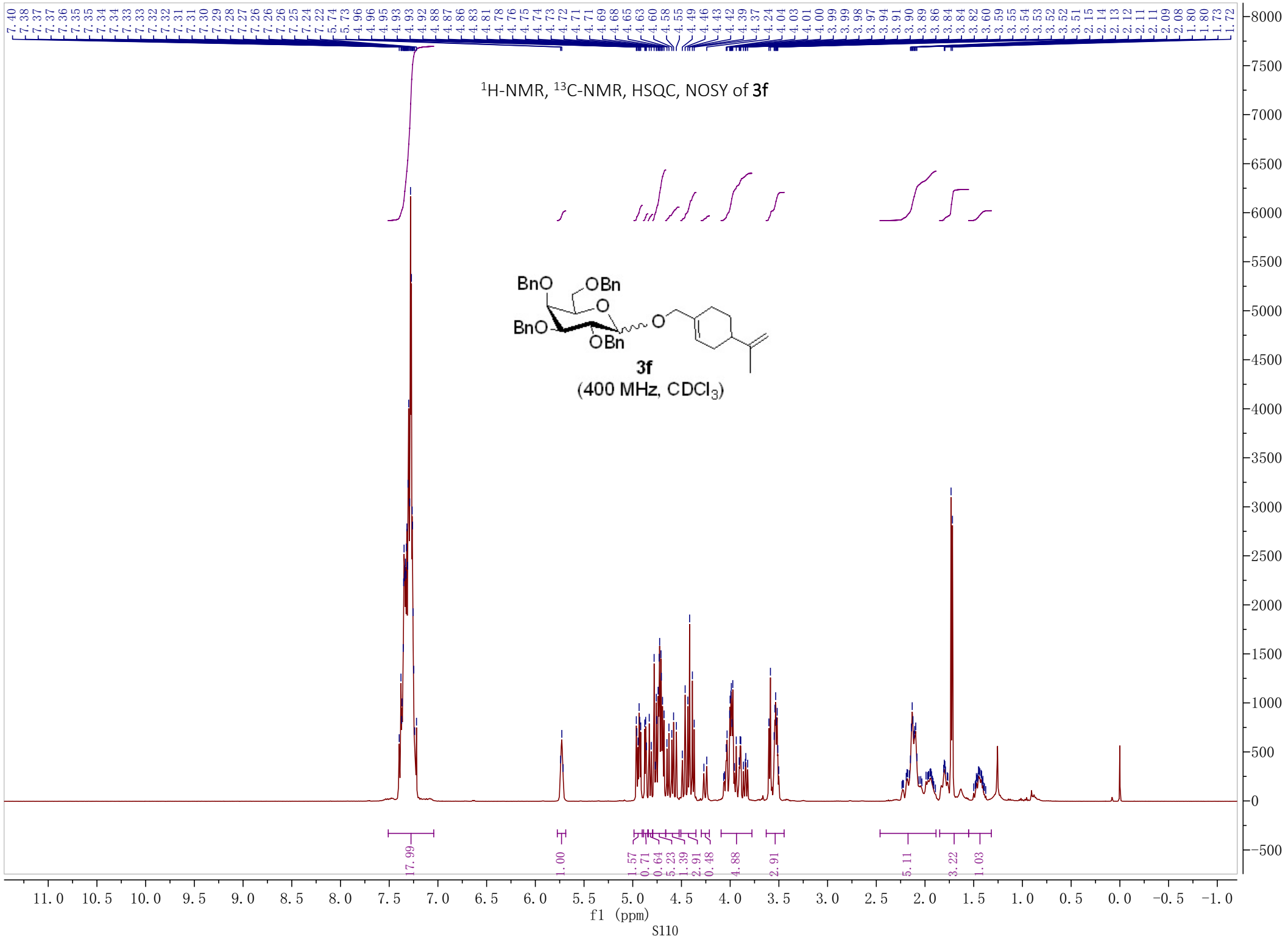

^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC, NOSY of **3e**
OBn
BnO
BnO
OBn
O
O
3e
(400 MHz, Acetone-d_6)
f1 (ppm)

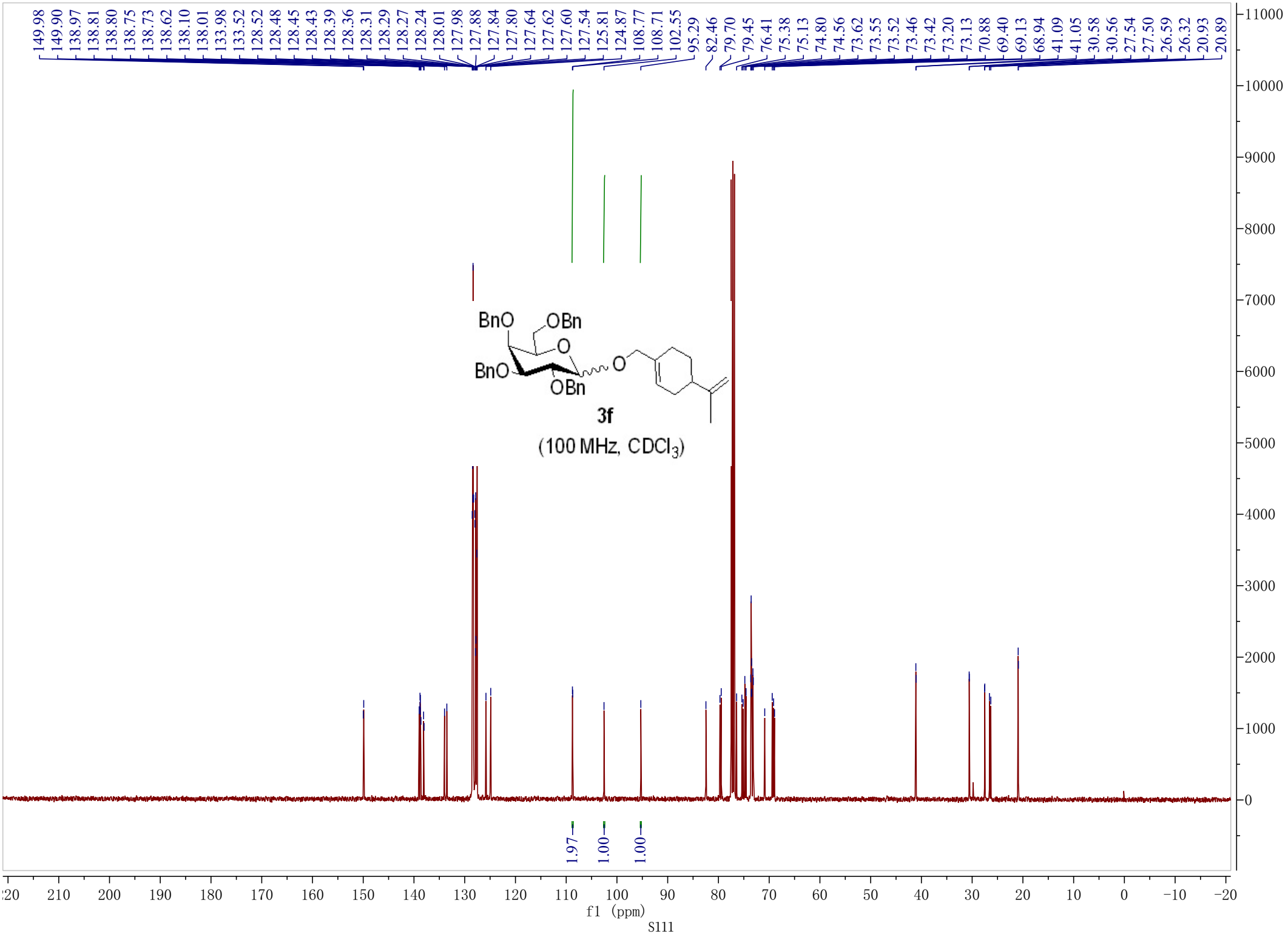

146.78
142.10
140.21
140.19
139.85
139.81
136.73
136.67
132.79
129.17
129.12
129.06
129.01
128.83
128.75
128.58
128.45
128.36
128.27
128.18
128.15
122.91
118.79
112.64
102.78
85.60
83.32
79.07
76.70
75.98
75.57
75.41
75.01
73.75
70.14
57.29
57.18
46.49
43.84
43.19
41.39
41.26
34.79
33.94
32.97
28.64
24.32
23.02
21.68
20.44
20.09
18.20
12.66
OBn
BnO
BnO
O
O
OBn
3e
(100 MHz, Acetone-d_6)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

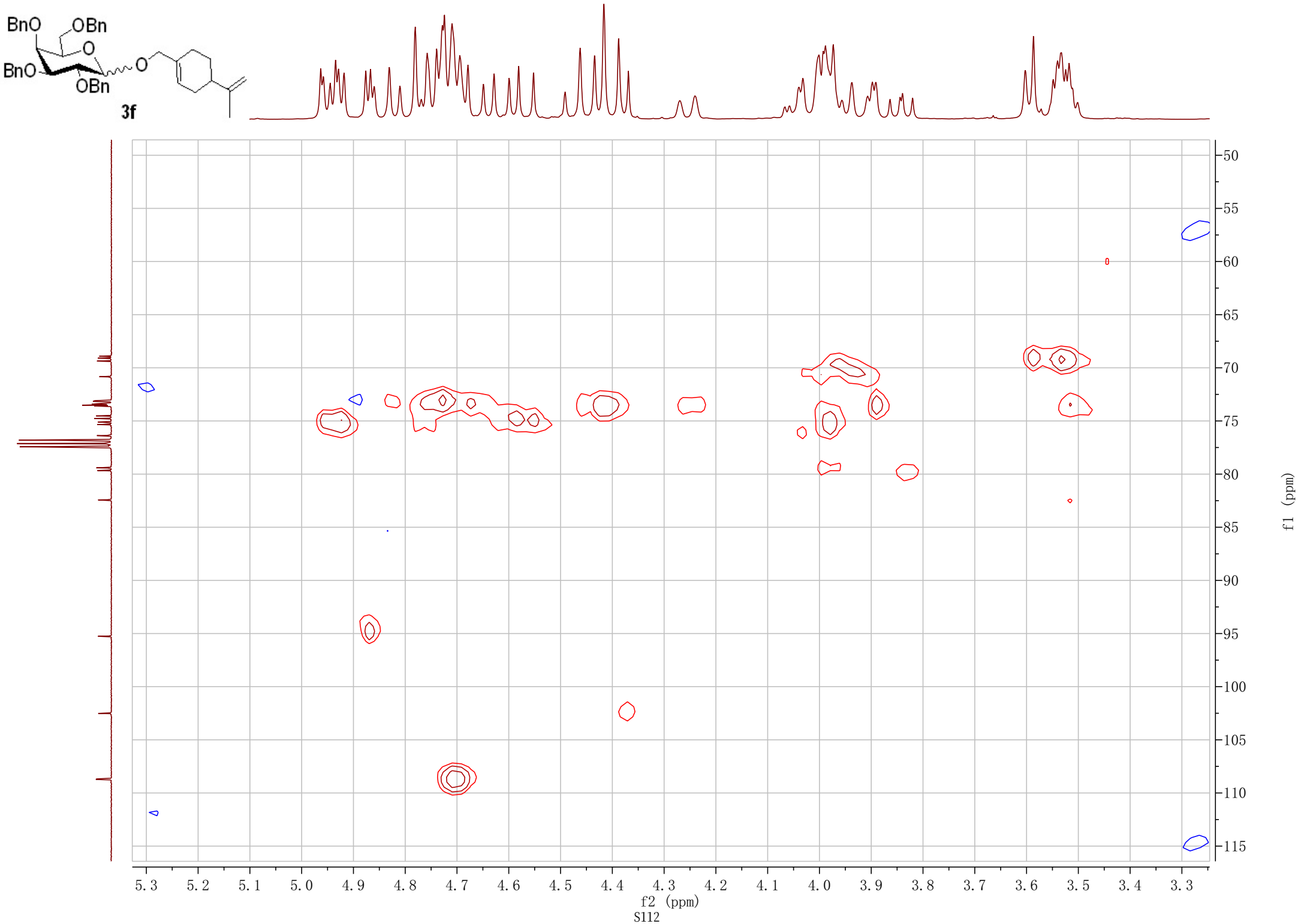

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)
OBn
BnO
BnO
OBn
O
O
3e

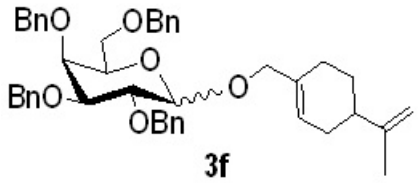

50
55
60
65
70
75
80
85
90
95
100
f1 (ppm)
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f2 (ppm)
OBn
BnO
BnO
OBn
O
O
3e


OBn
BnO
BnO
O
O
OBn
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

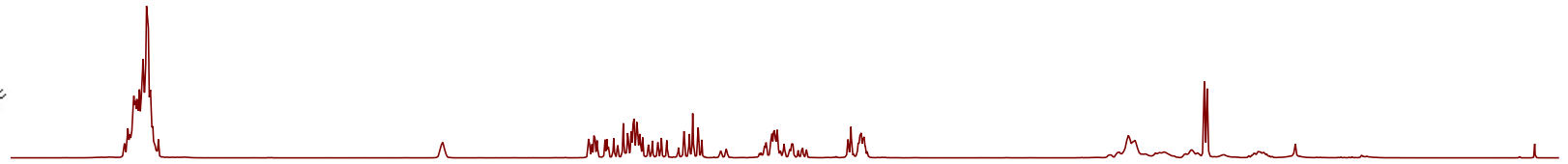

^{1}H-NMR, ^{13}C-NMR, HSQC, NOSY of **3f**
BnO
OBn
O
BnO
O
OBn
3f
(400 MHz, $CDCl_3$)
f1 (ppm)

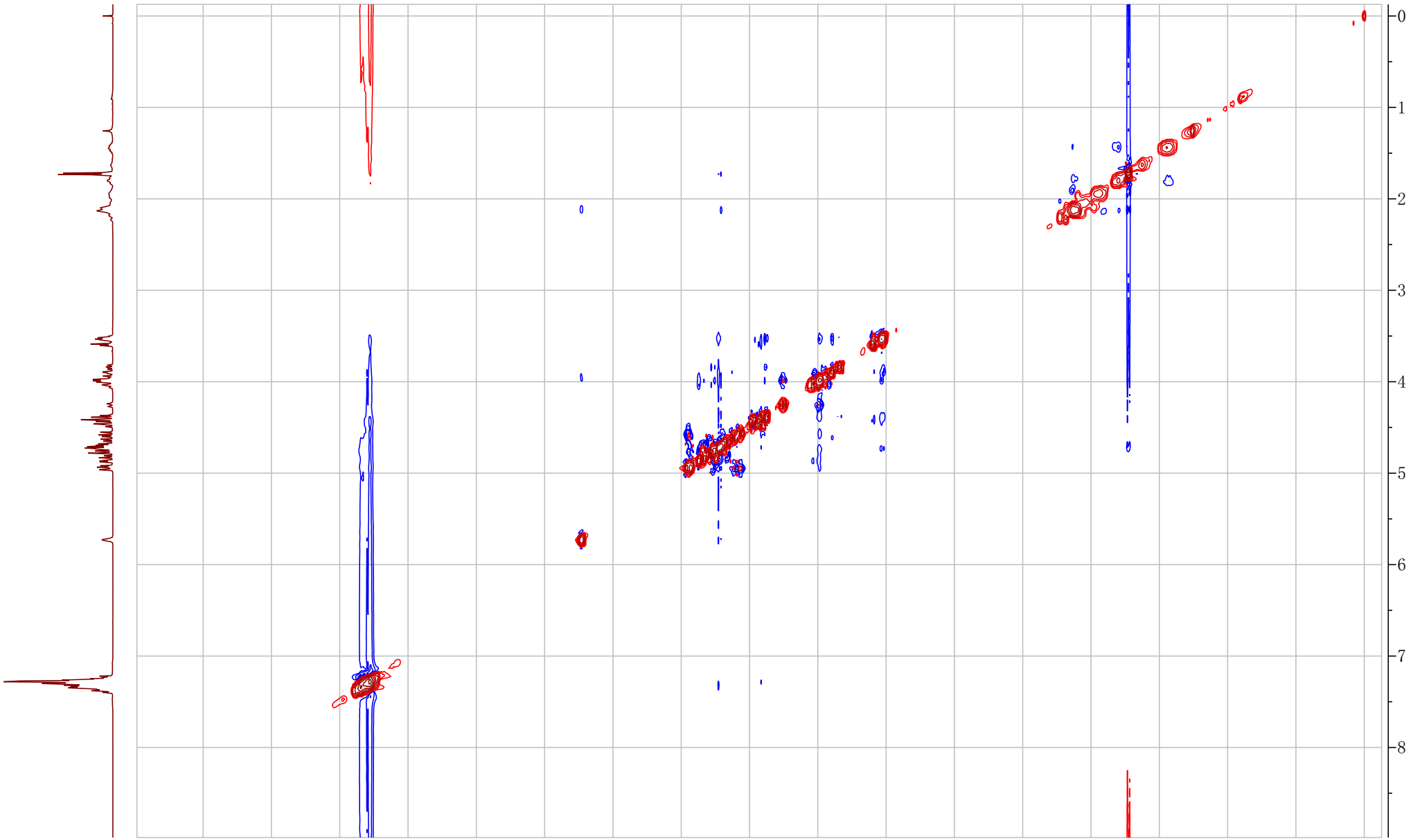

149.98
149.90
138.97
138.81
138.80
138.75
138.73
138.62
138.10
138.01
133.98
133.52
128.52
128.48
128.45
128.43
128.39
128.36
128.31
128.29
128.27
128.24
128.01
127.98
127.88
127.84
127.80
127.64
127.62
127.60
127.54
125.81
124.87
108.77
108.71
102.55
95.29
82.46
79.70
79.45
76.41
75.38
75.13
74.80
74.56
73.62
73.55
73.52
73.46
73.42
73.20
73.13
70.88
69.40
69.13
68.94
41.09
41.05
30.58
30.56
27.54
27.50
26.59
26.32
20.93
20.89
BnO
OBn
O
BnO
O
OBn
3f
(100 MHz, CDCl3)
1.97
1.00
1.00
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


BnO
OBn
O
BnO
O
OBn
3f
50
55
60
65
70
75
80
85
90
95
100
105
110
115
f1 (ppm)
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)


BnO
OBn
O
BnO
O
OBn

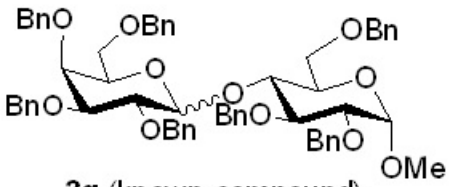
3f




0
1
2
3
4
5
6
7
8
f1 (ppm)
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)

XK190916-3.1.fid
XK190916-3

^{1}H-NMR of **3g**

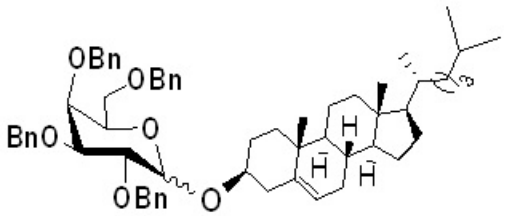


3g (known compound)
(400 MHz, $CDCl_3$)

f1 (ppm)

XK190902.1.fid
XK190902

^{1}H-NMR of **3h**

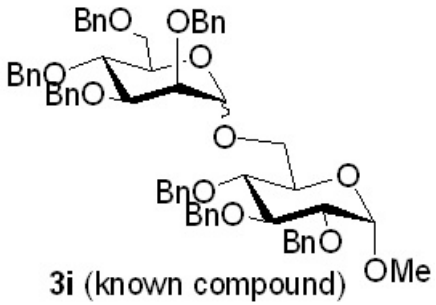


3h (known compound)
(400 MHz, $CDCl_3$)

f1 (ppm)

XK200108-3.1.fid
XK200108-3

^{1}H-NMR of **3i**



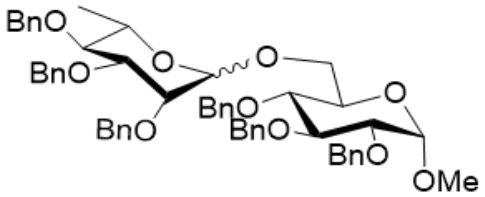
3i (known compound)
(400 MHz, $CDCl_3$)

f1 (ppm)

XK200116-1.1.fid
XK200116-1

7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.29 7.29 7.28 7.27 7.25 7.23 7.22 7.21 7.21 7.20 7.19 7.19 4.99 4.96 4.93 4.80 4.79 4.77 4.76 4.71 4.70 4.70 4.68 4.67 4.65 4.64 4.62 4.60 4.52 4.51 4.37 4.34 3.97 3.95 3.92 3.84 3.84 3.83 3.82 3.81 3.81 3.80 3.70 3.69 3.68 3.67 3.67 3.66 3.65 3.63 3.61 3.48 3.47 3.46 3.45 3.44 3.42 3.41 3.36 3.34 3.31 3.26 1.31 1.29

^{1}H-NMR of **3j-α**



3j-alfa known compound
(400 MHz, $CDCl_3$)

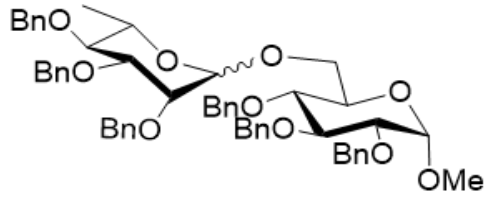
9000 8000 7000 6000 5000 4000 3000 2000 1000 0

1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

f1 (ppm)

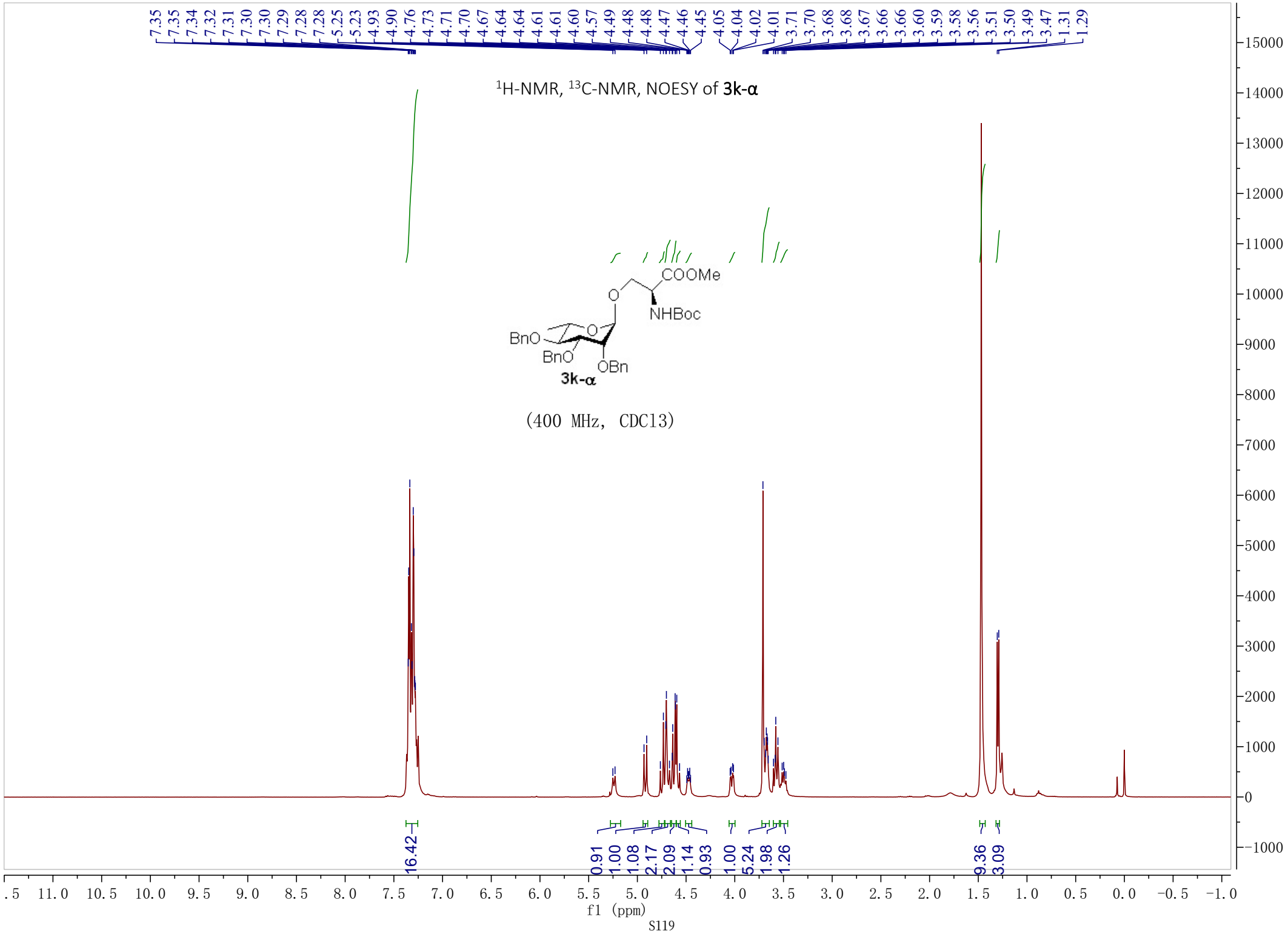
XK200116-2.1.fid
XK200116-2

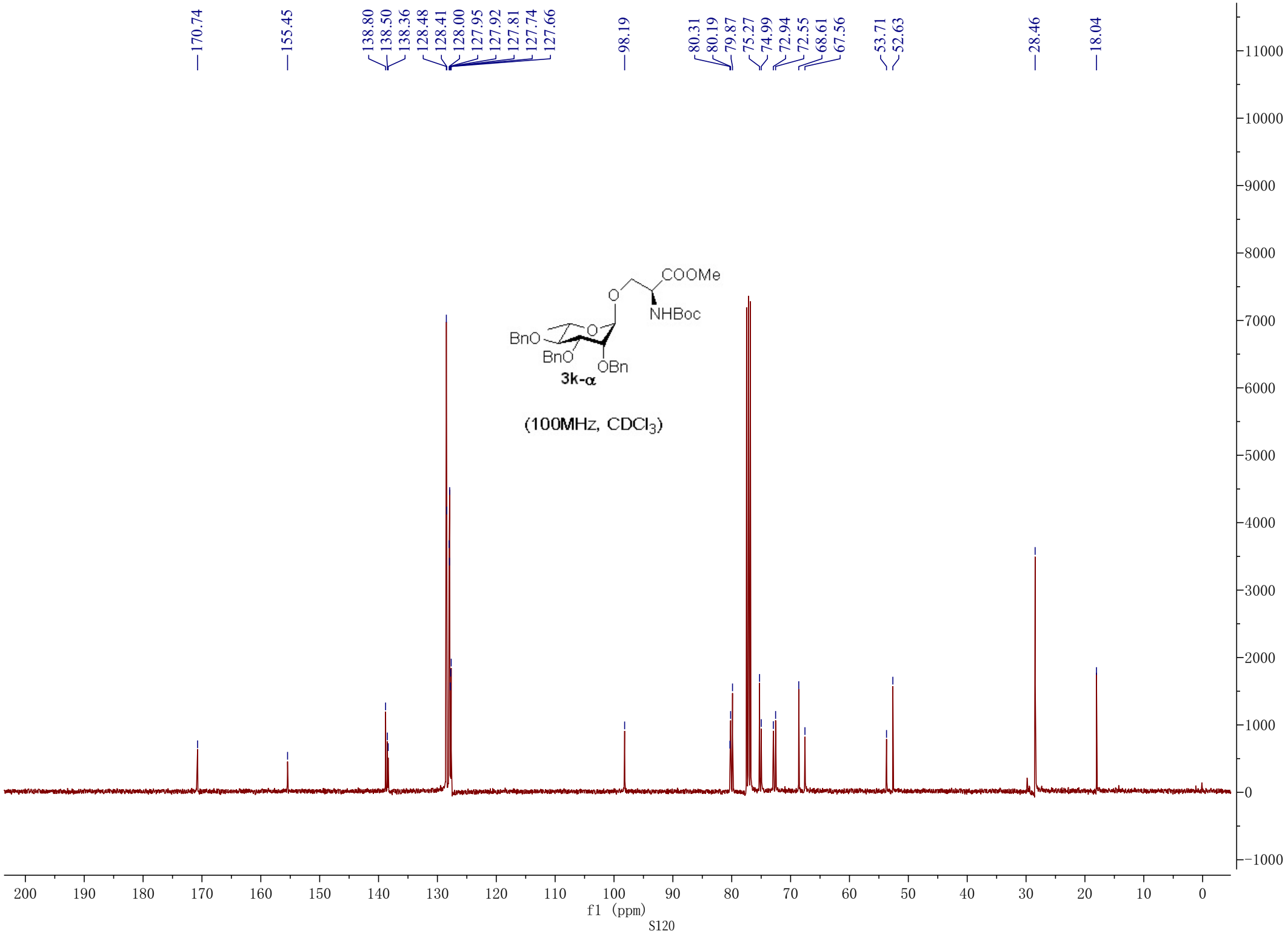
^{1}H-NMR of **3j-β**

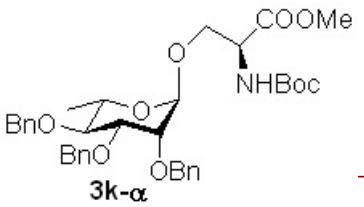


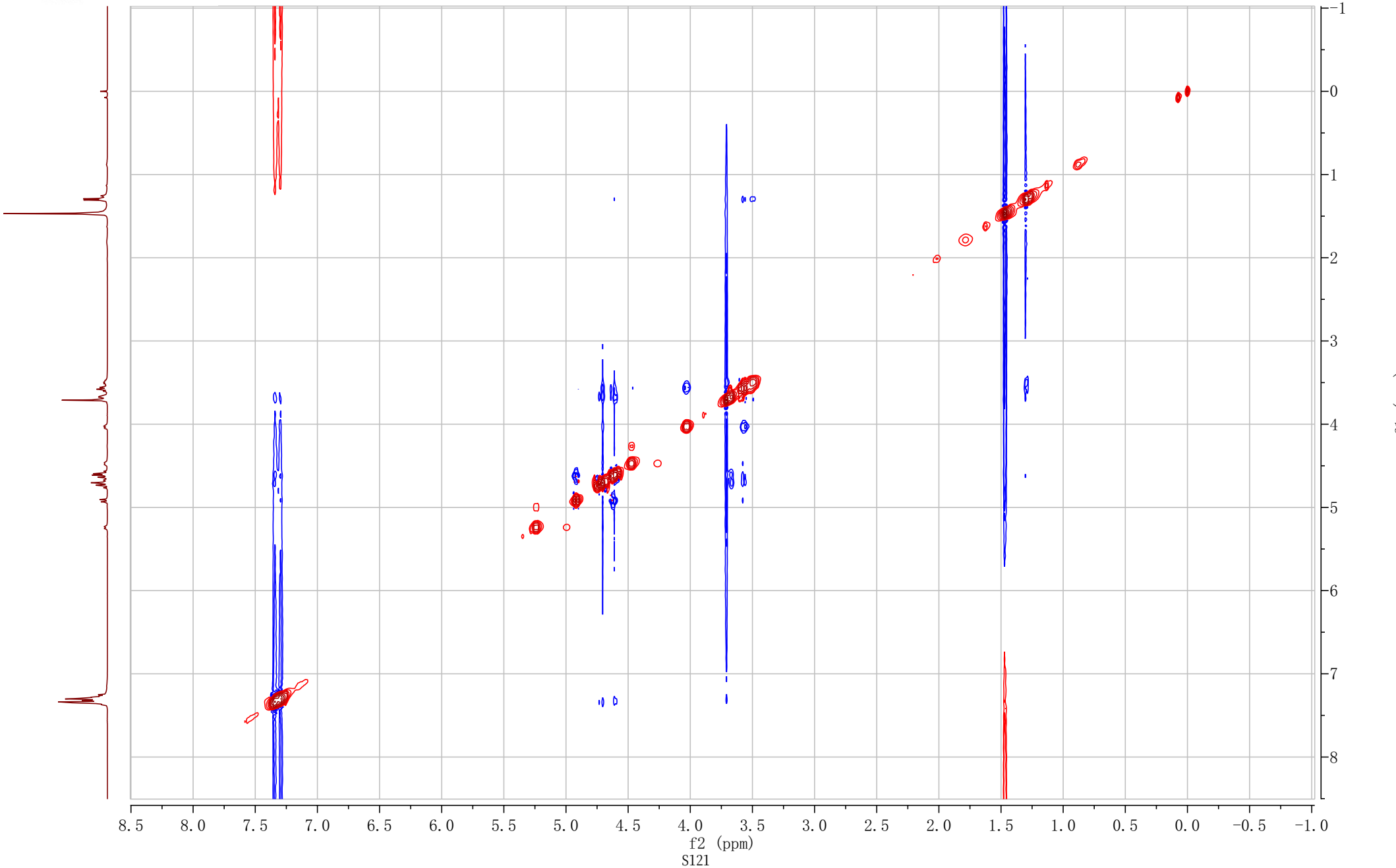
3j-beta known compound
(400 MHz, CDCl3)

f1 (ppm)

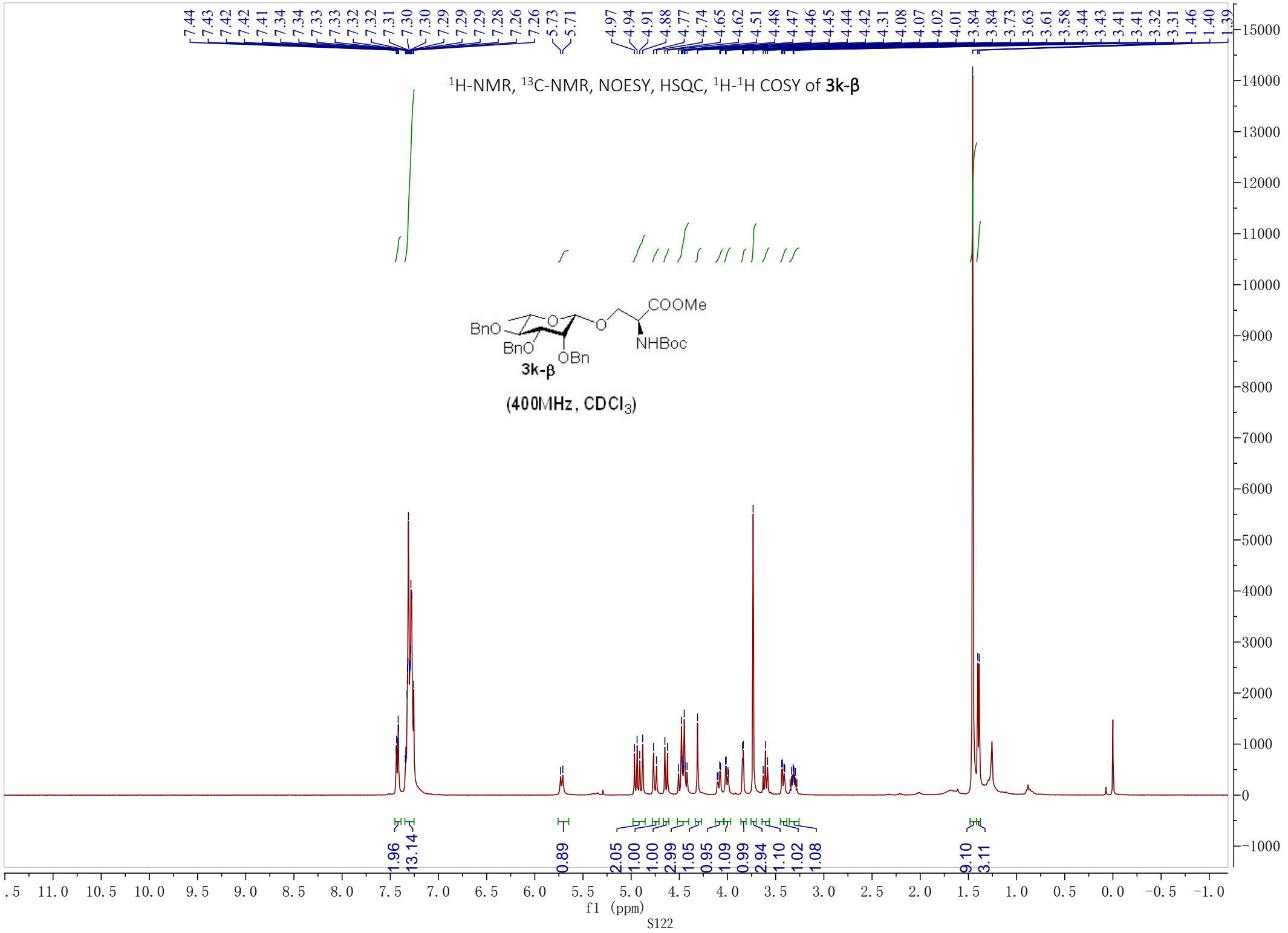

7.35 7.35 7.34 7.32 7.31 7.30 7.30 7.29 7.28 7.28 5.25 5.23 4.93 4.90 4.76 4.73 4.71 4.70 4.67 4.64 4.64 4.61 4.61 4.60 4.57 4.49 4.48 4.48 4.47 4.46 4.45 4.05 4.04 4.02 4.01 3.71 3.70 3.68 3.68 3.67 3.66 3.66 3.60 3.59 3.58 3.56 3.51 3.50 3.49 3.47 1.31 1.29
1H-NMR, 13C-NMR, NOESY of 3k-α
COOMe
NHBoc
BnO
BnO
OBn
3k-α
(400 MHz, CDC13)
16.42
0.91
1.00
1.08
2.17
2.09
1.14
0.93
1.00
5.24
1.98
1.26
9.36
3.09
f1 (ppm)

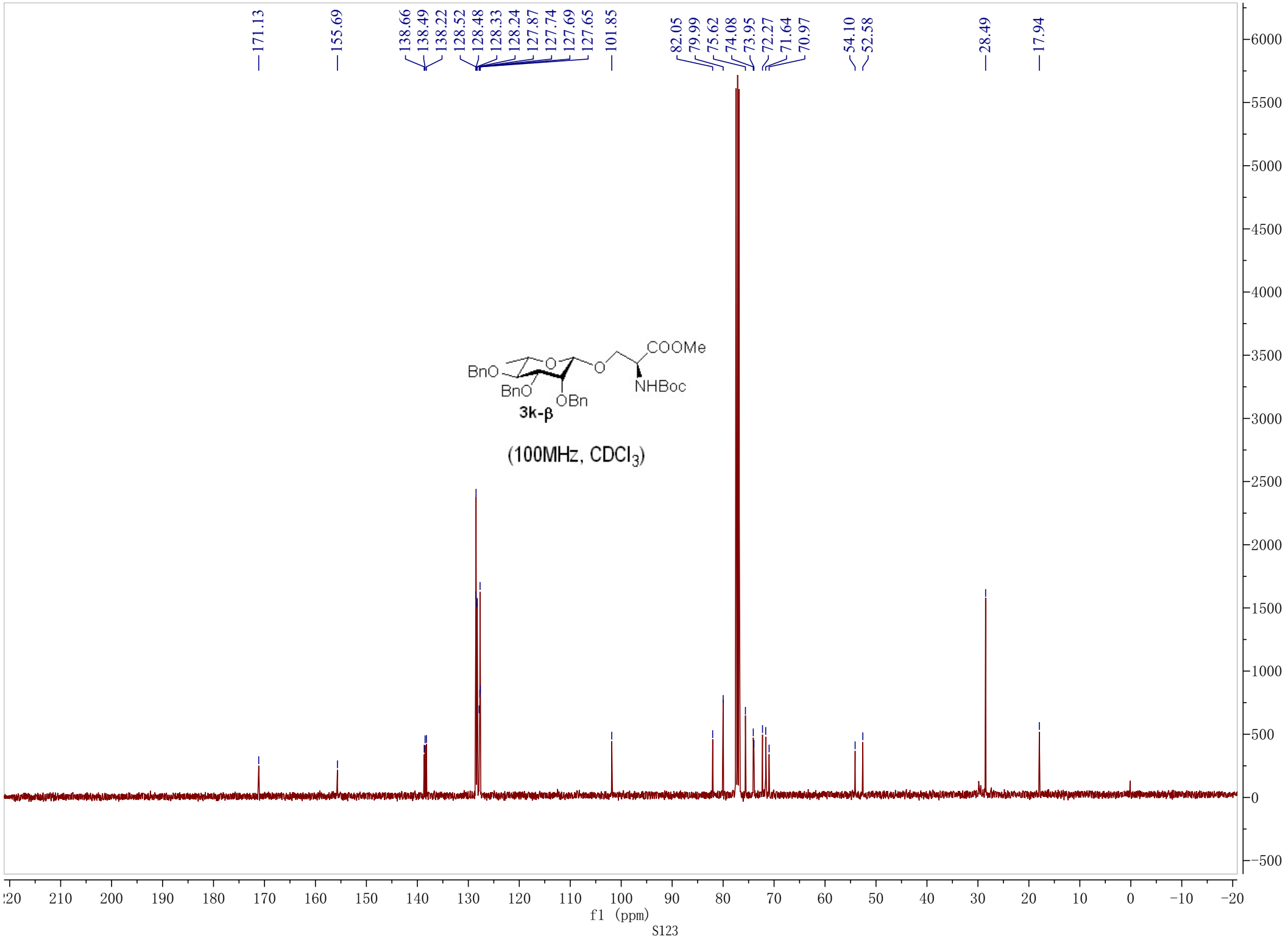

170.74
155.45
138.80
138.50
138.36
128.48
128.41
128.00
127.95
127.92
127.81
127.74
127.66
98.19
80.31
80.19
79.87
75.27
74.99
72.94
72.55
68.61
67.56
53.71
52.63
28.46
18.04
COOMe
NHBoc
O
BnO
BnO
OBn
3k-α
(100MHz, CDCl3)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

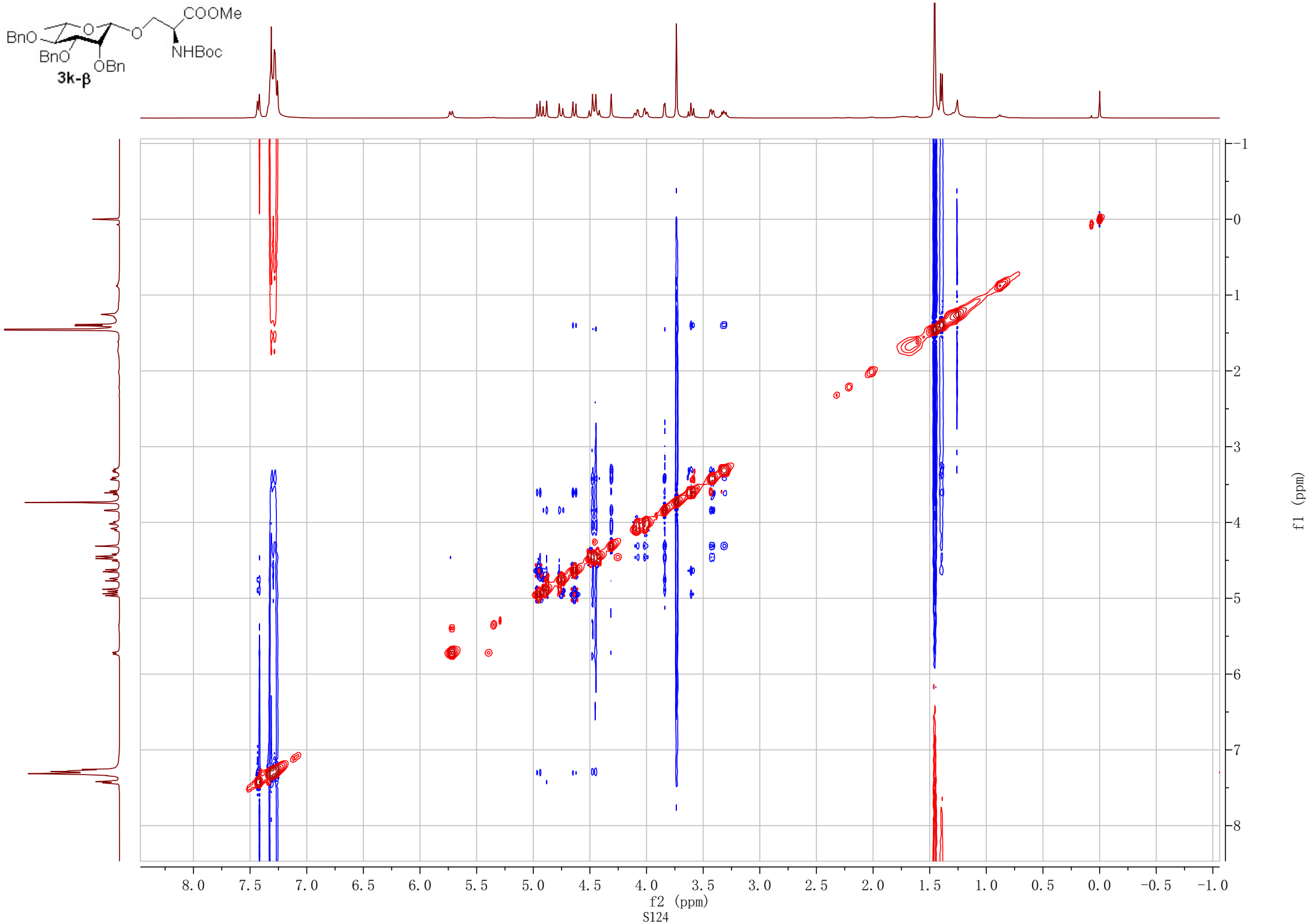

COOMe
NHBoc
BnO
BnO
OBn
3k-α

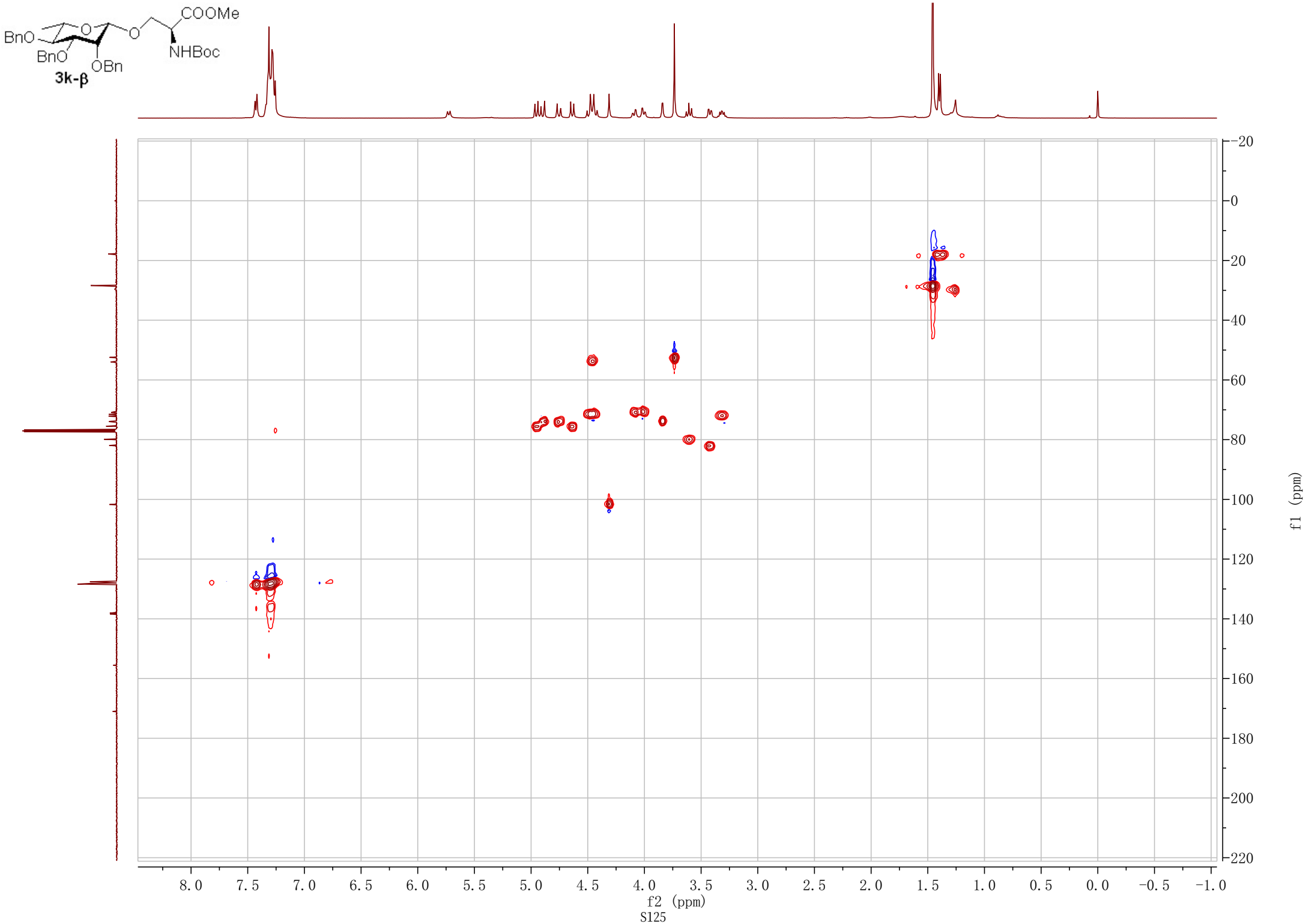

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)

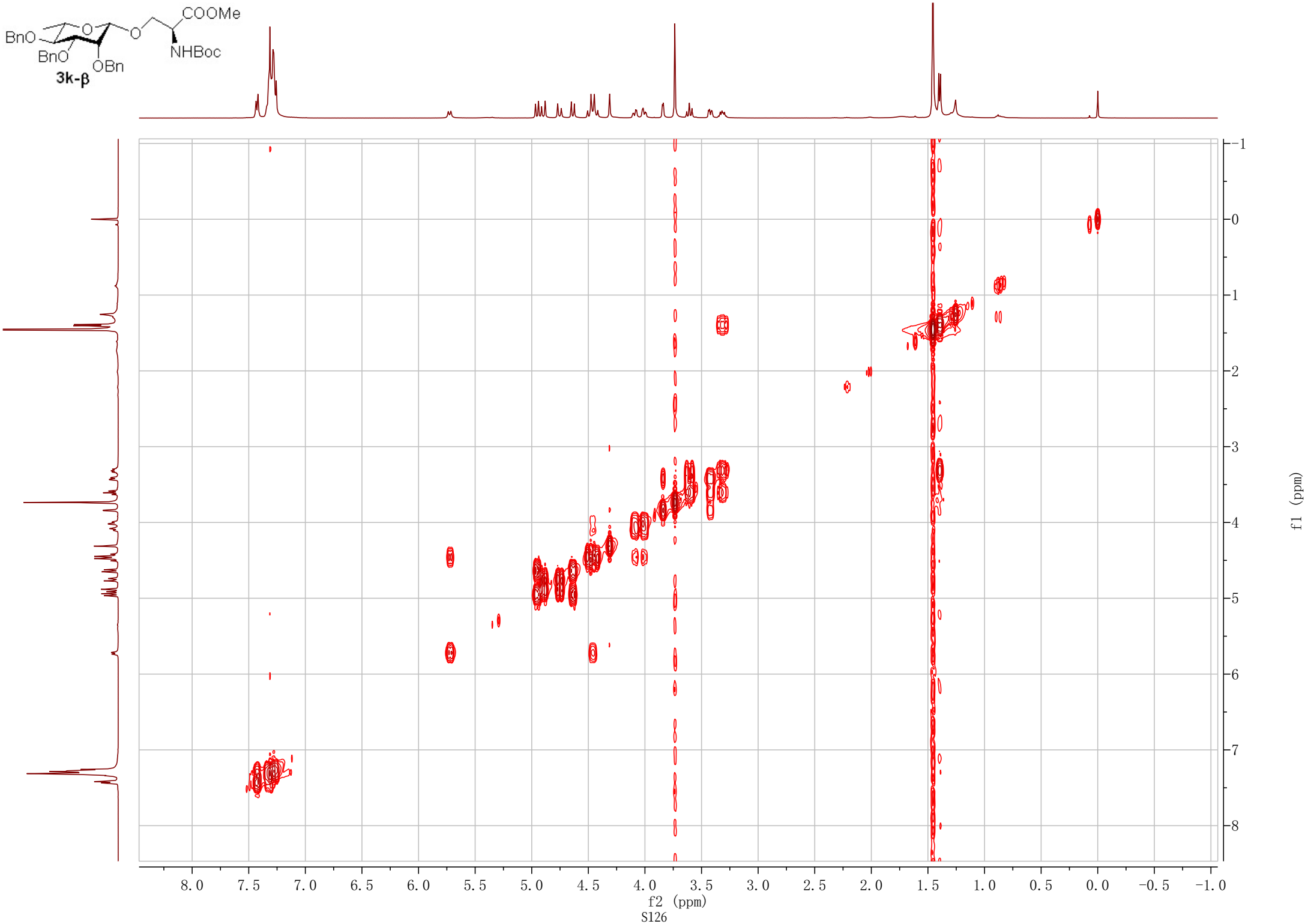
S121


^{1}H-NMR, ^{13}C-NMR, NOESY, HSQC, ^{1}H-^{1}H COSY of **3k-β**
BnO
BnO
OBn
O
O
COOMe
NHBoc
3k-β
(400MHz, $CDCl_3$)
f1 (ppm)


171.13
155.69
138.66
138.49
138.22
128.52
128.48
128.33
128.24
127.87
127.74
127.69
127.65
101.85
82.05
79.99
75.62
74.08
73.95
72.27
71.64
70.97
54.10
52.58
28.49
17.94
BnO
BnO
OBn
O
O
COOMe
NHBoc
3k-β
(100MHz, CDCl3)
f1 (ppm)


COOMe
BnO
BnO
OBn
NHBoc
3k-β
f2 (ppm)
f1 (ppm)

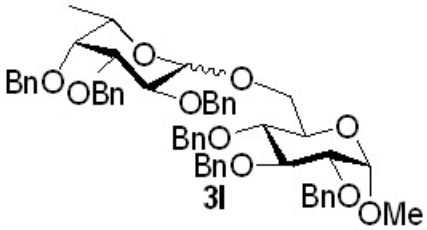

COOMe
BnO
BnO
OBn
NHBoc
3k-β
f2 (ppm)
f1 (ppm)
S125


COOMe
BnO
O
O
NHBoc
BnO
OBn
3k-β
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)

XK200628-2.1.fid
XK200628-2

7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.30 7.28 7.28 7.27 7.25 7.25 7.24 7.23 7.23 4.97 4.97 4.96 4.95 4.94 4.82 4.82 4.81 4.79 4.79 4.78 4.75 4.74 4.72 4.69 4.66 4.65 4.63 4.59 4.59 4.58 4.41 4.39 4.03 4.02 3.98 3.97 3.95 3.83 3.81 3.80 3.74 3.66 3.65 3.59 3.54 3.52 3.50 3.45 3.32 3.31 1.17 1.16 1.11 1.09

^{1}H-NMR of **3l**



3l

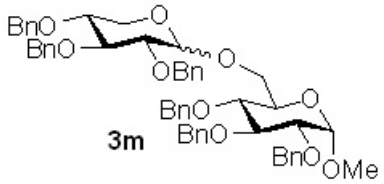
known compound
(400MHz, $CDCl_3$)

8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500

1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0

f1 (ppm)

^{1}H-NMR of **3m**



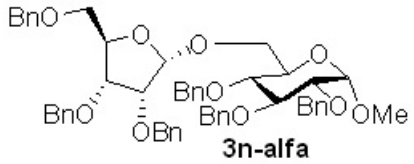
3m

known compound
(400 MHz, $CDCl_3$)

f1 (ppm)

XK200109-2.1.fid
XK200109-2

^{1}H-NMR of **3n-α**

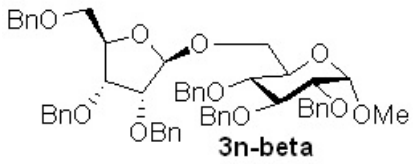


3n-alfa

known compound
(400 MHz, $CDCl_3$)

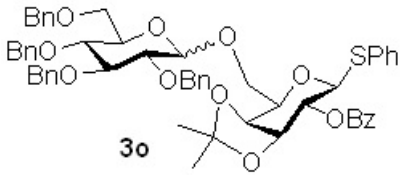
XK200109-1.1.fid
XK200109-1

^{1}H-NMR of **3n-β**



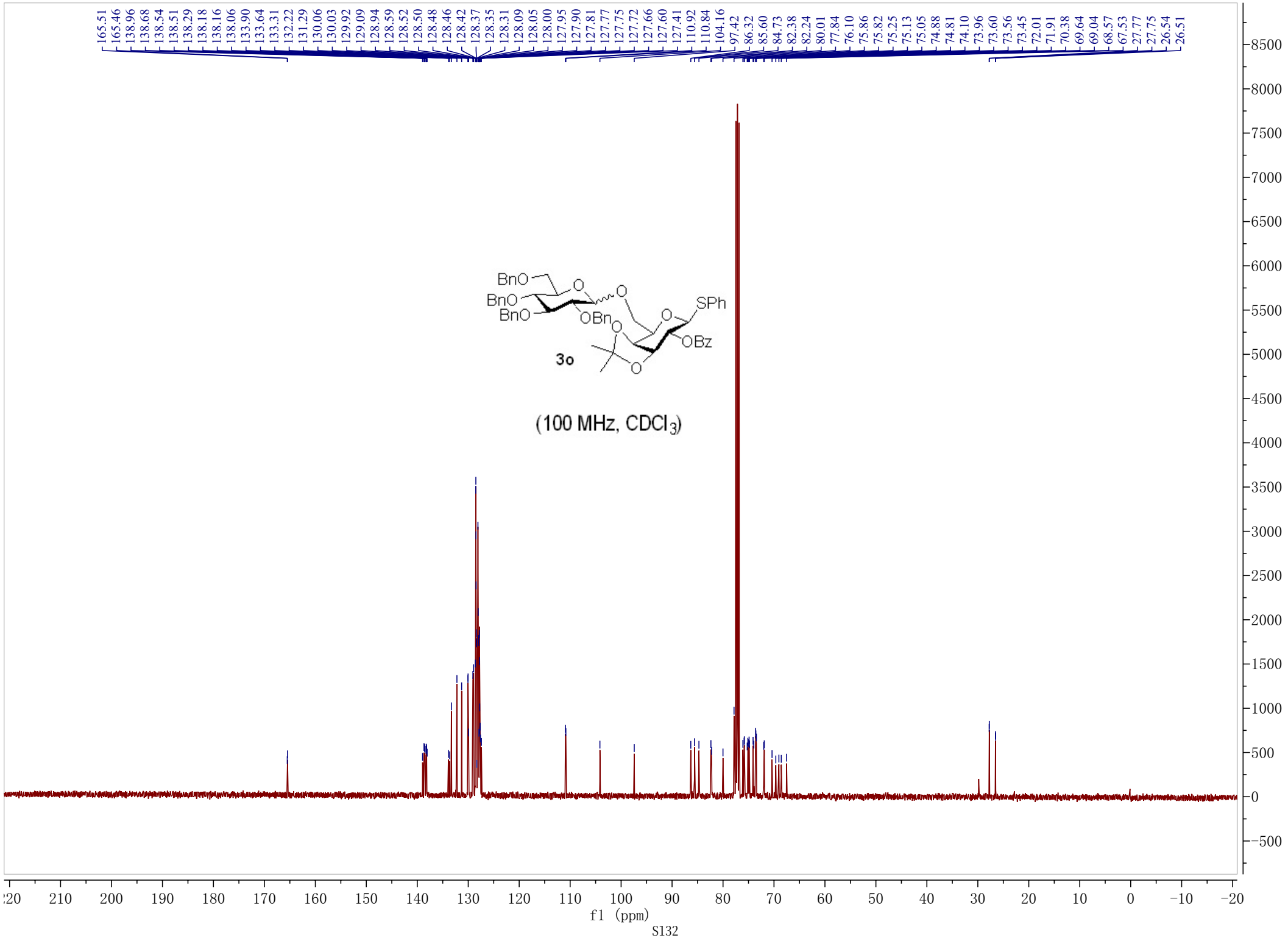
3n-beta

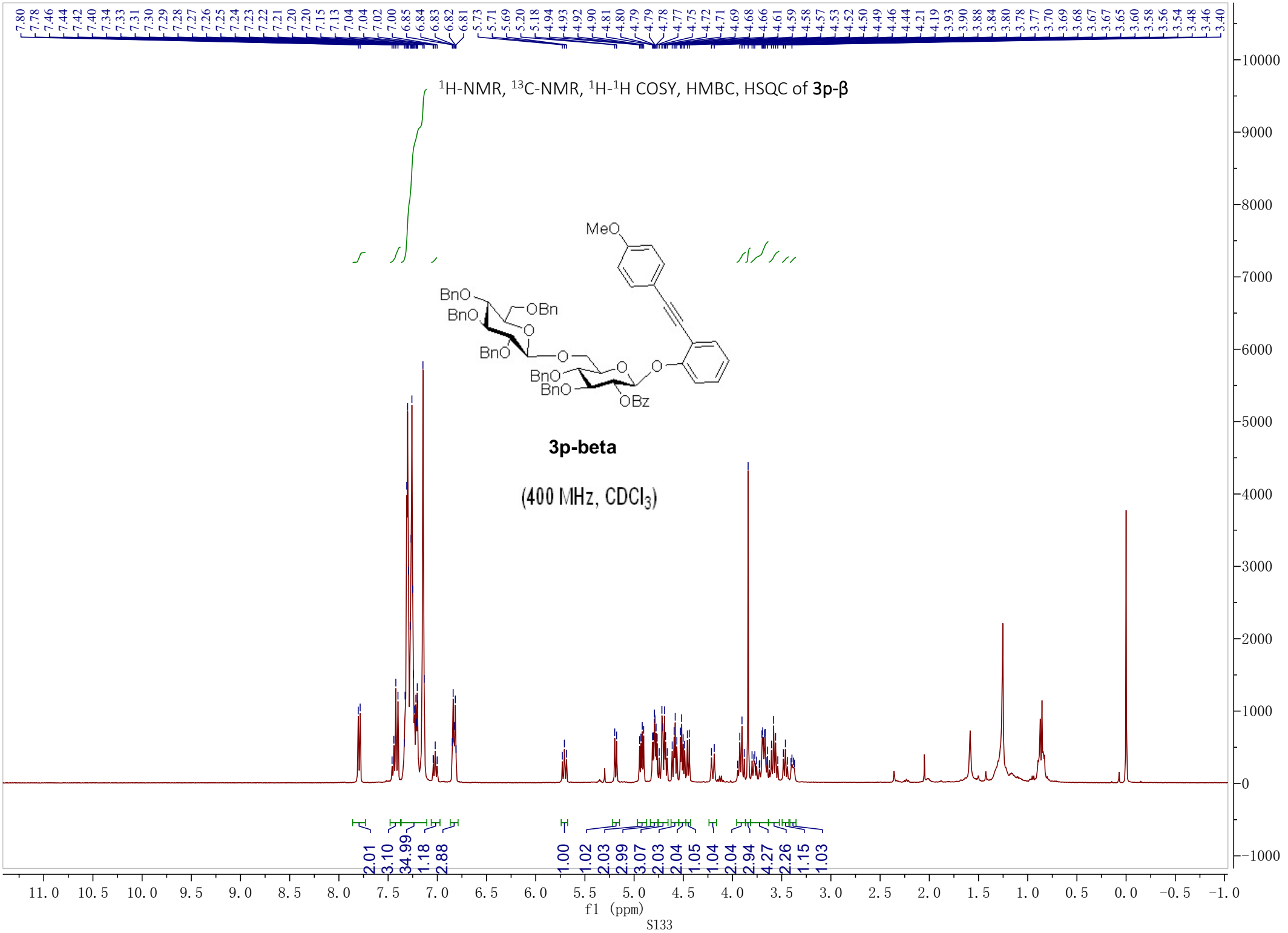
^{1}H-NMR, ^{13}C-NMR of **3o**

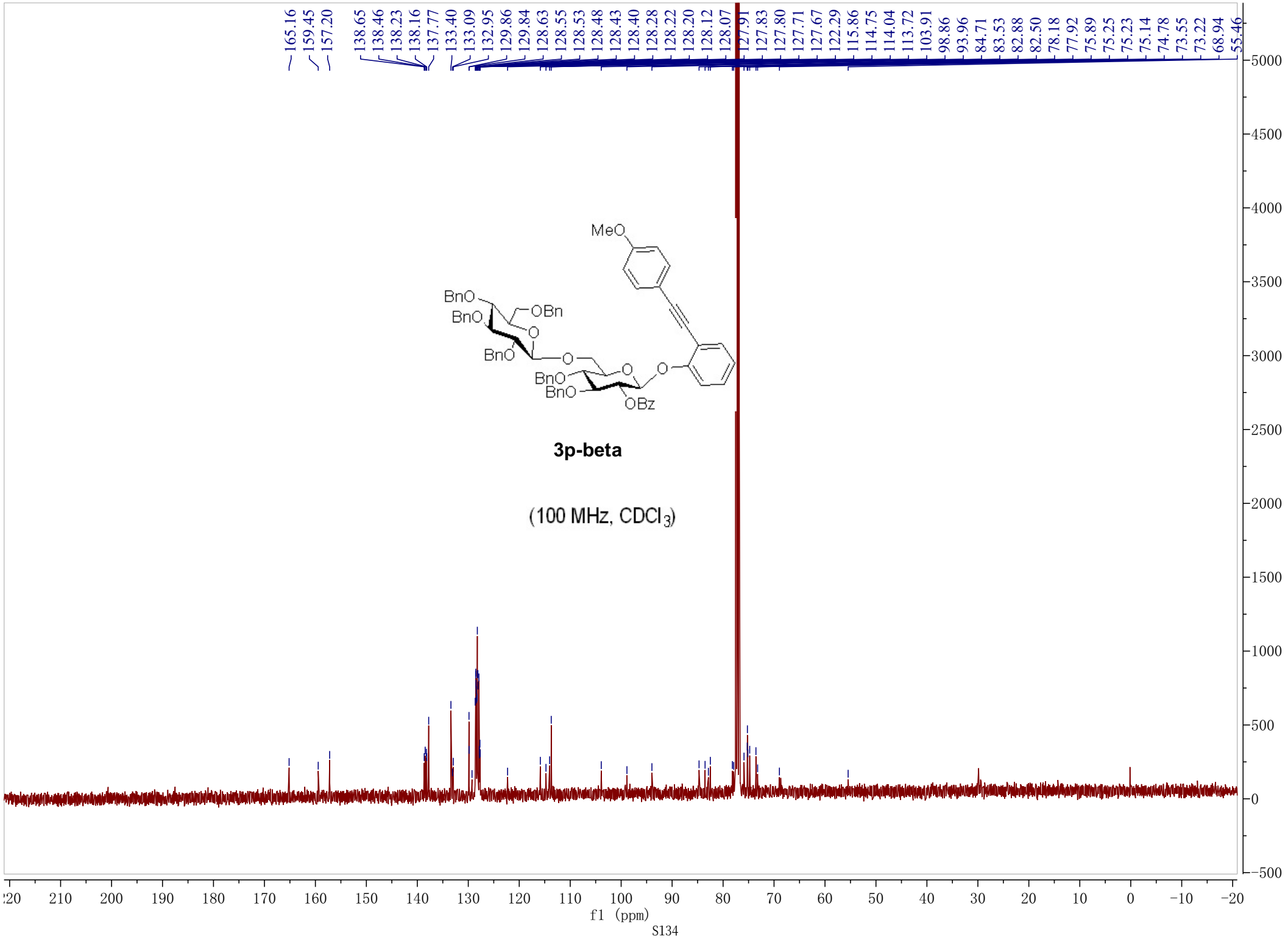


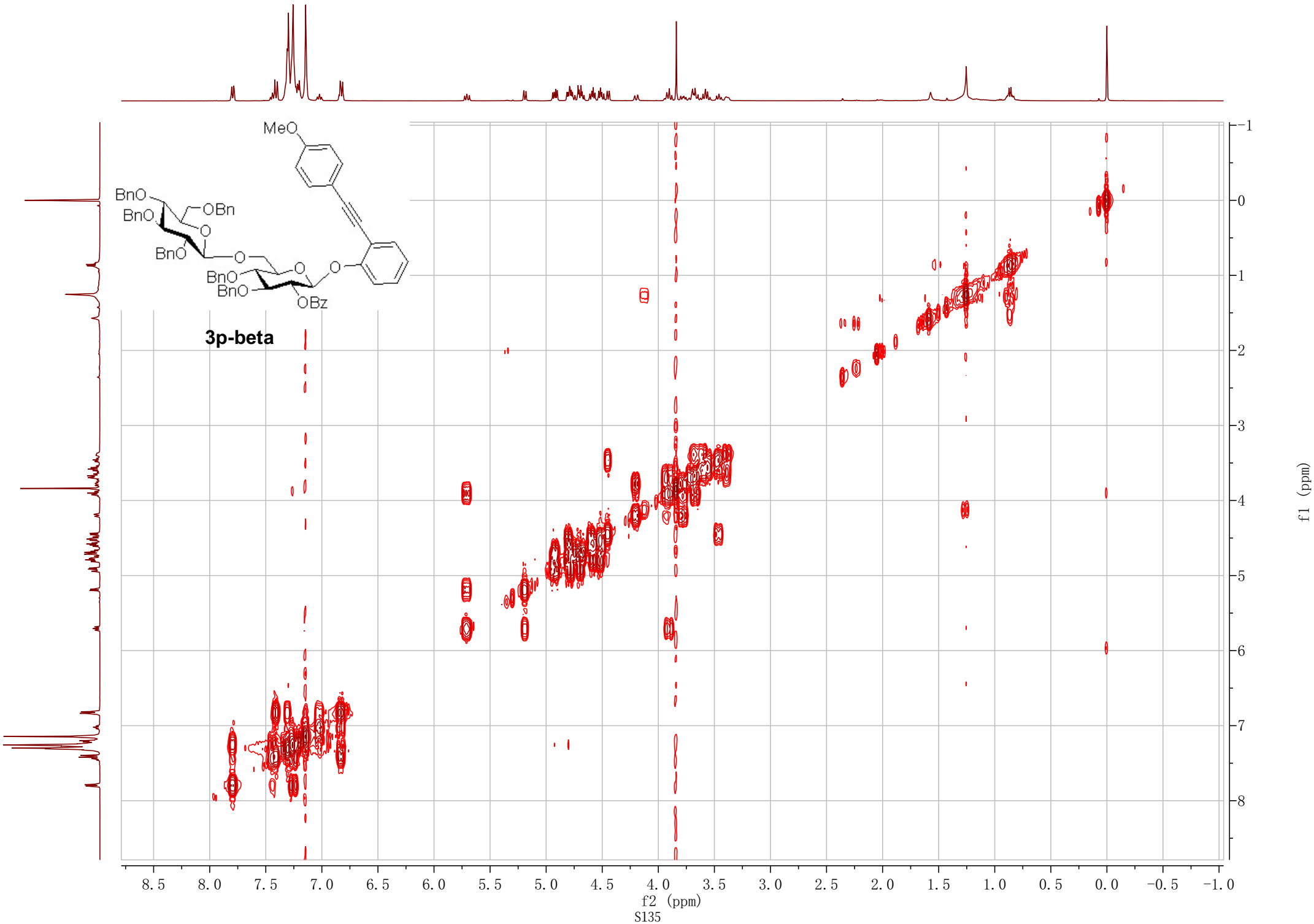
3o

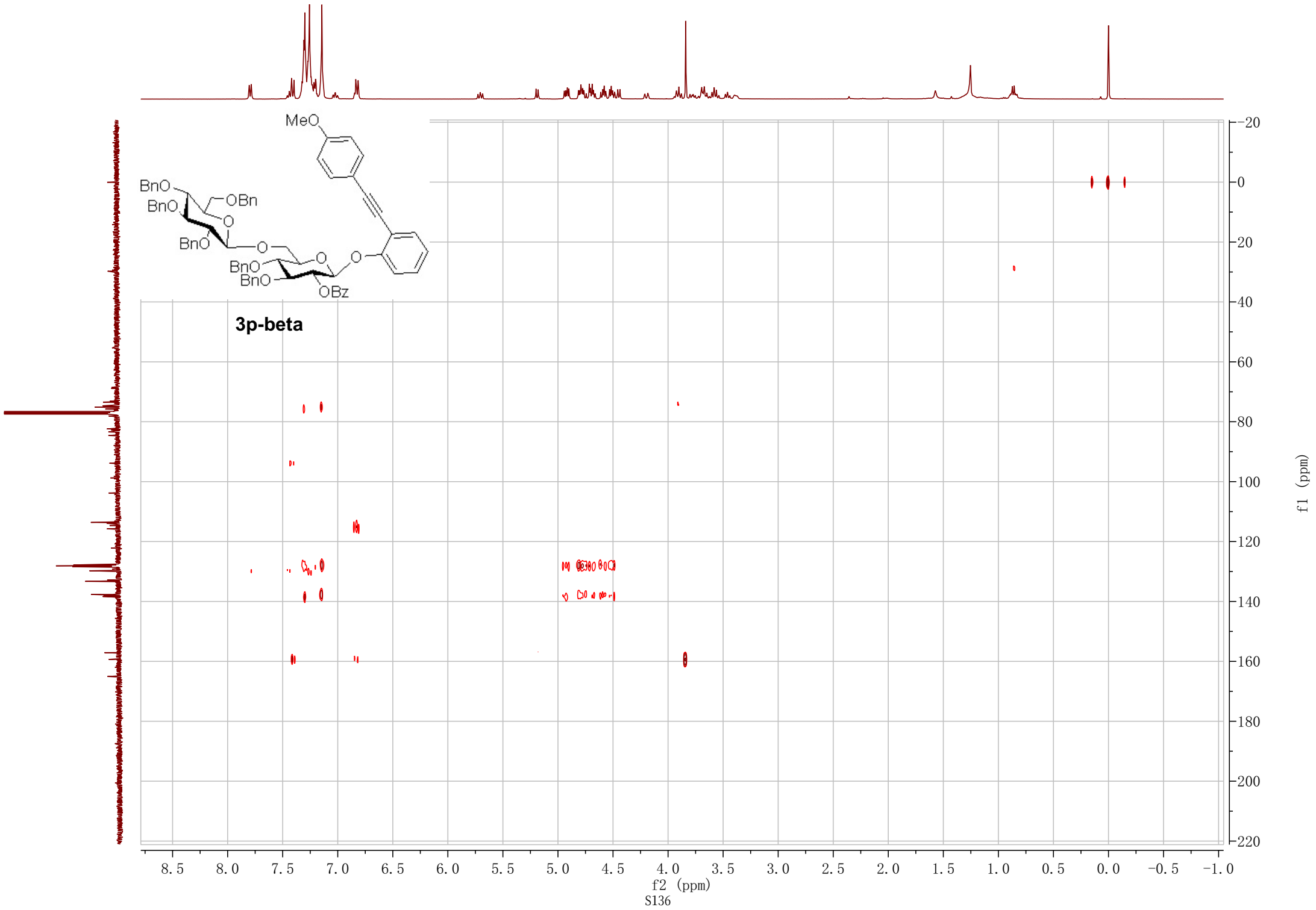
(400 MHz, $CDCl_3$)

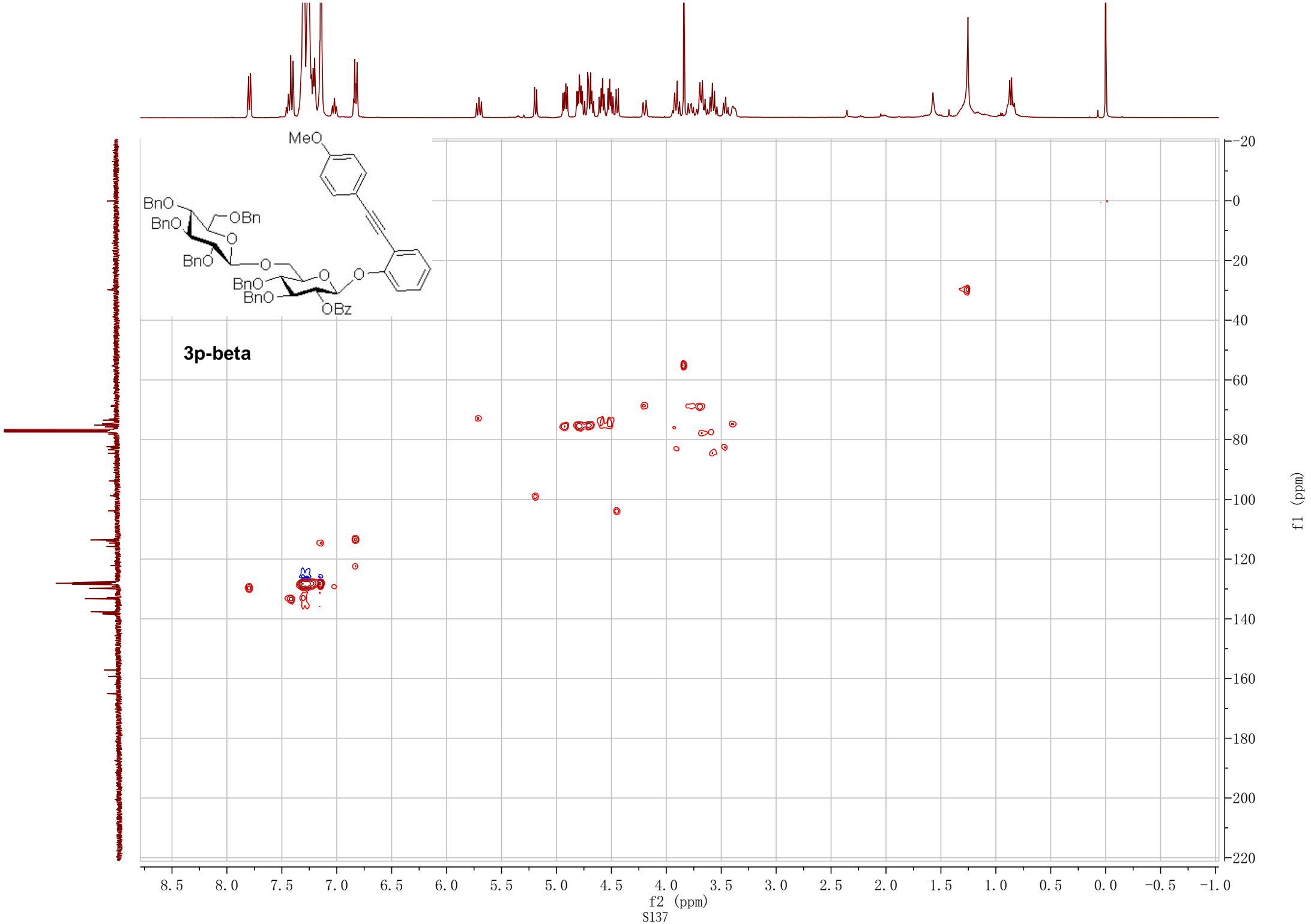

165.51
165.46
138.96
138.68
138.54
138.51
138.29
138.18
138.16
138.06
133.90
133.64
133.31
132.22
131.29
130.06
130.03
129.92
129.09
128.94
128.59
128.52
128.50
128.48
128.46
128.42
128.37
128.35
128.31
128.09
128.05
128.00
127.95
127.90
127.81
127.77
127.75
127.72
127.66
127.60
127.41
110.92
110.84
104.16
97.42
86.32
85.60
84.73
82.38
82.24
80.01
77.84
76.10
75.86
75.82
75.25
75.13
75.05
74.88
74.81
74.10
73.96
73.60
73.56
73.45
72.01
71.91
70.38
69.64
69.04
68.57
67.53
27.77
27.75
26.54
26.51
BnO
BnO
BnO
OBn
SPh
OBz
3o
(100 MHz, CDCl3)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

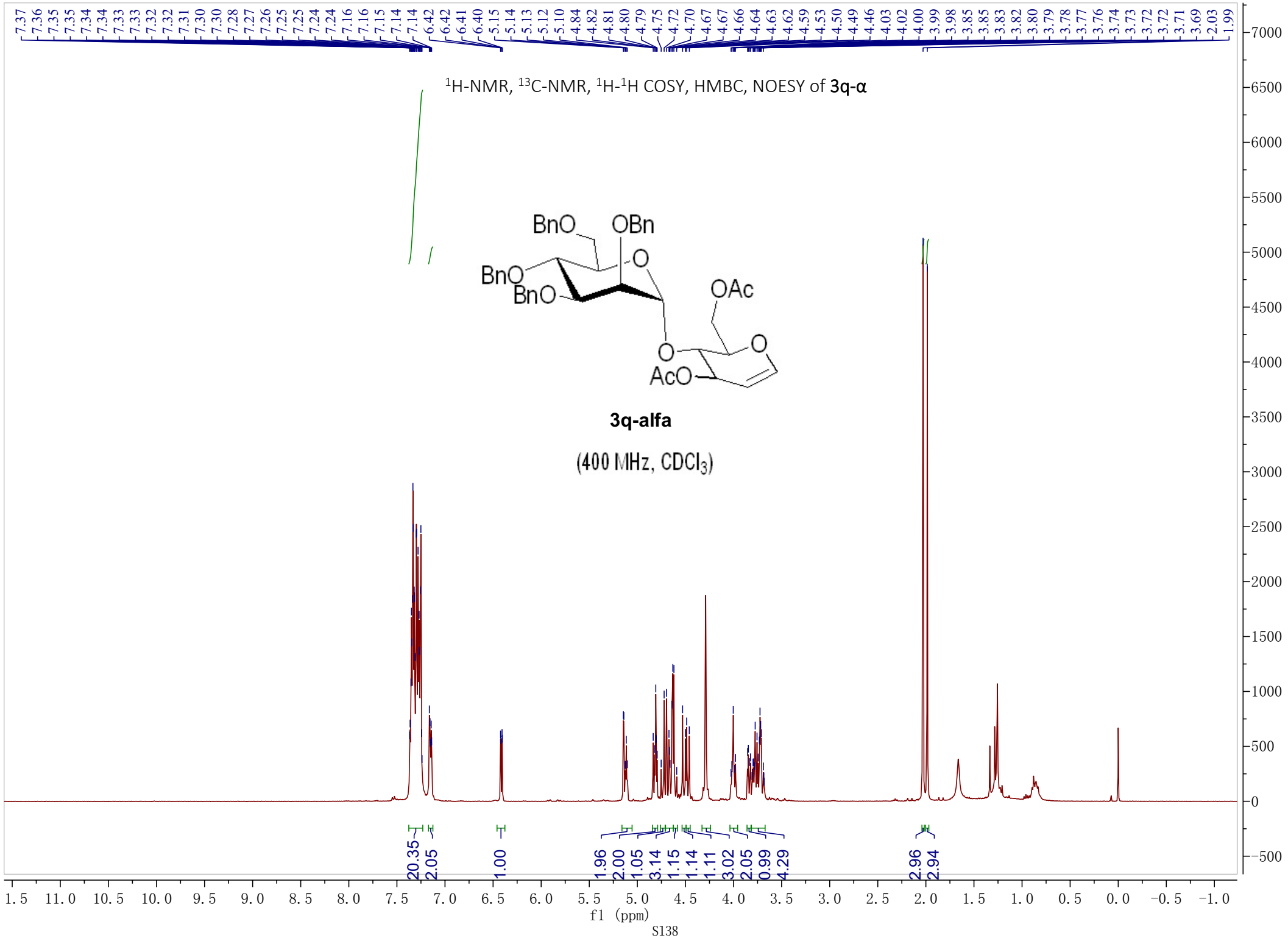

^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HMBC, HSQC of **3p-β**
MeO
BnO
BnO
OBn
O
BnO
O
BnO
BnO
O
O
OBz
3p-beta
(400 MHz, $CDCl_3$)
f1 (ppm)

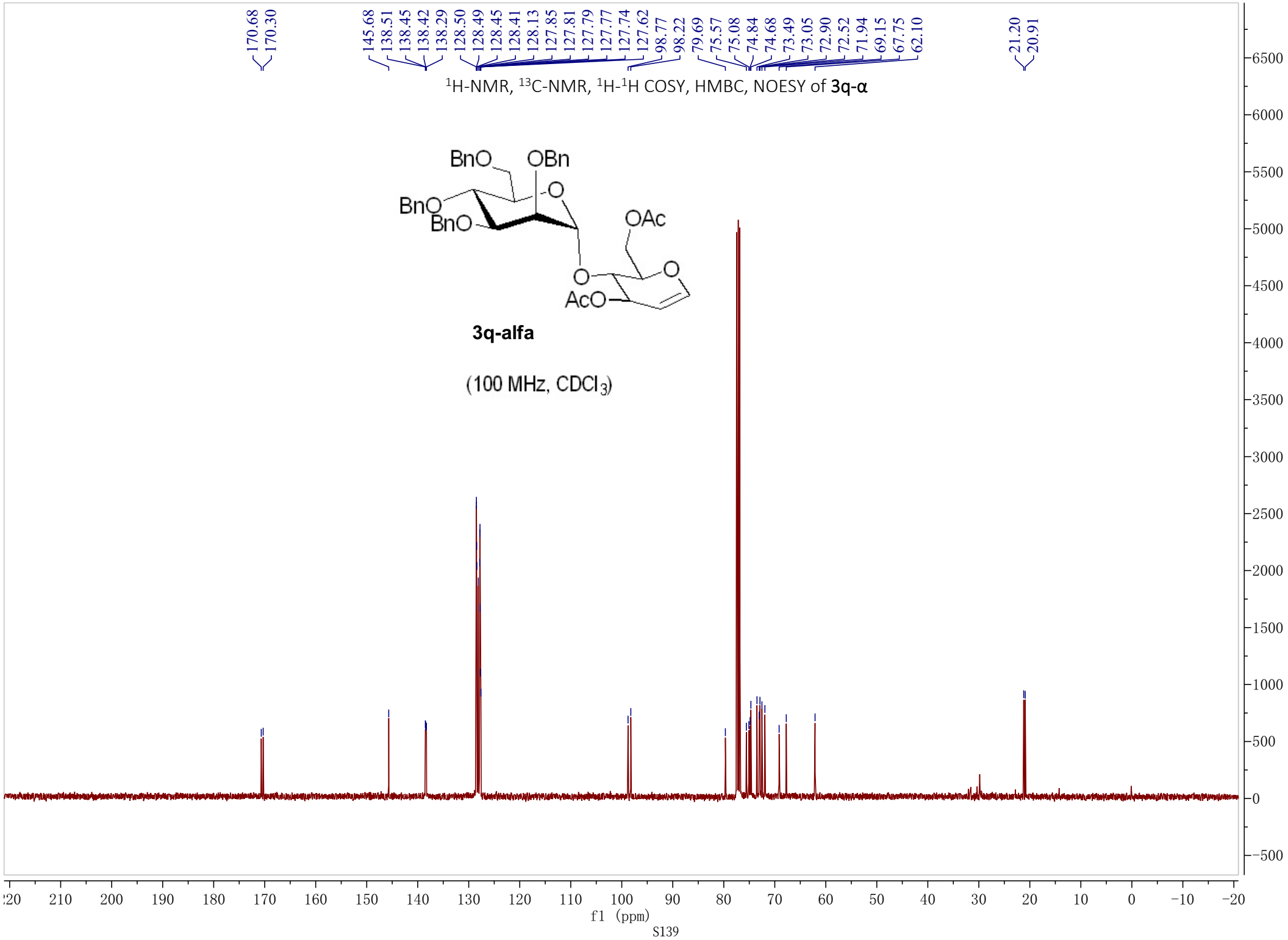

165.16
159.45
157.20
138.65
138.46
138.23
138.16
137.77
133.40
133.09
132.95
129.86
129.84
128.63
128.55
128.53
128.48
128.43
128.40
128.28
128.22
128.20
128.12
128.07
127.91
127.83
127.80
127.71
127.67
122.29
115.86
114.75
114.04
113.72
103.91
98.86
93.96
84.71
83.53
82.88
82.50
78.18
77.92
75.89
75.25
75.23
75.14
74.78
73.55
73.22
68.94
55.46
MeO
BnO
BnO
OBn
O
BnO
O
O
BnO
BnO
O
OBz
3p-beta
(100 MHz, CDCl3)
f1 (ppm)

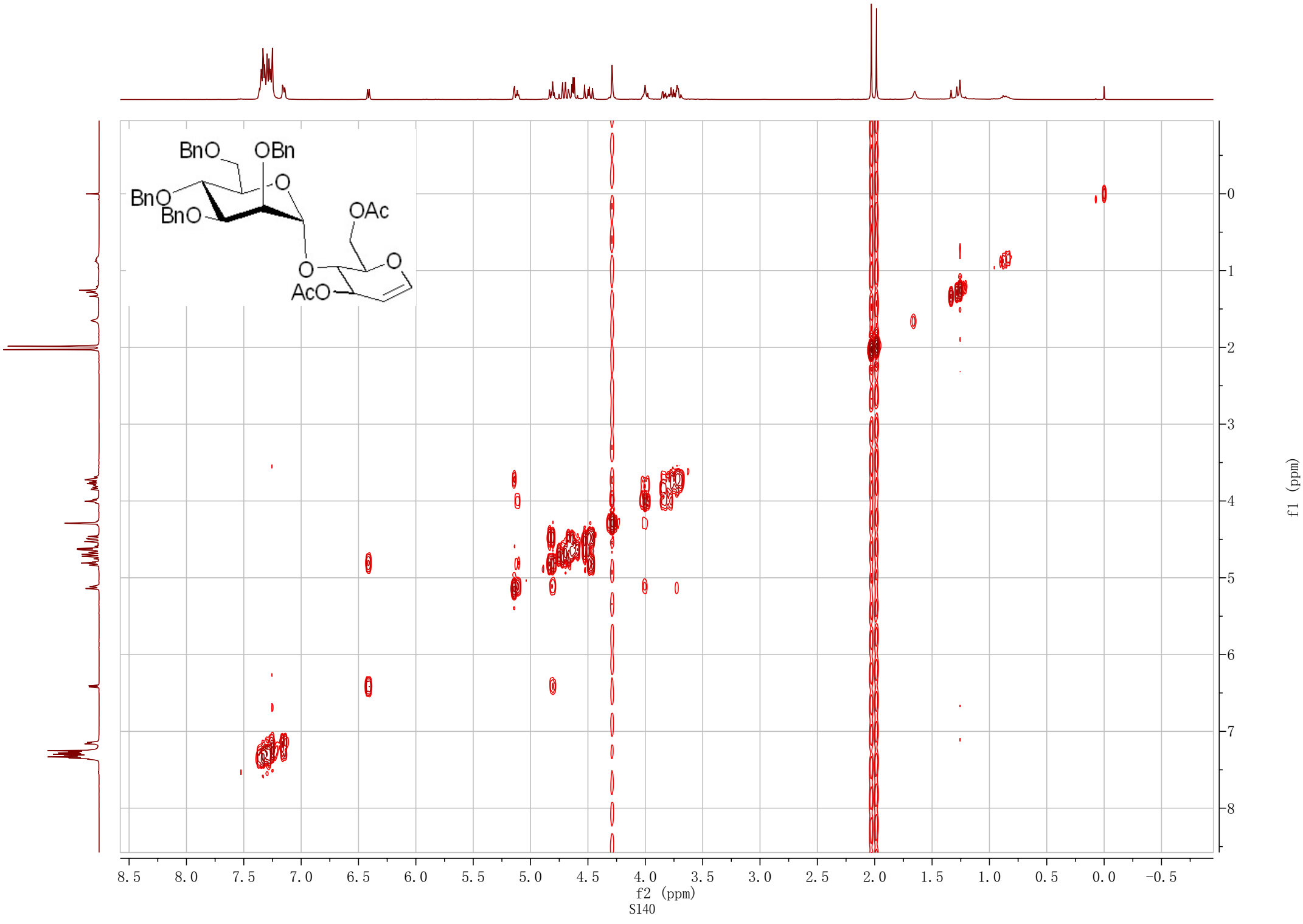

MeO
BnO
BnO
OBn
O
BnO
O
O
BnO
BnO
OBz
3p-beta
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8

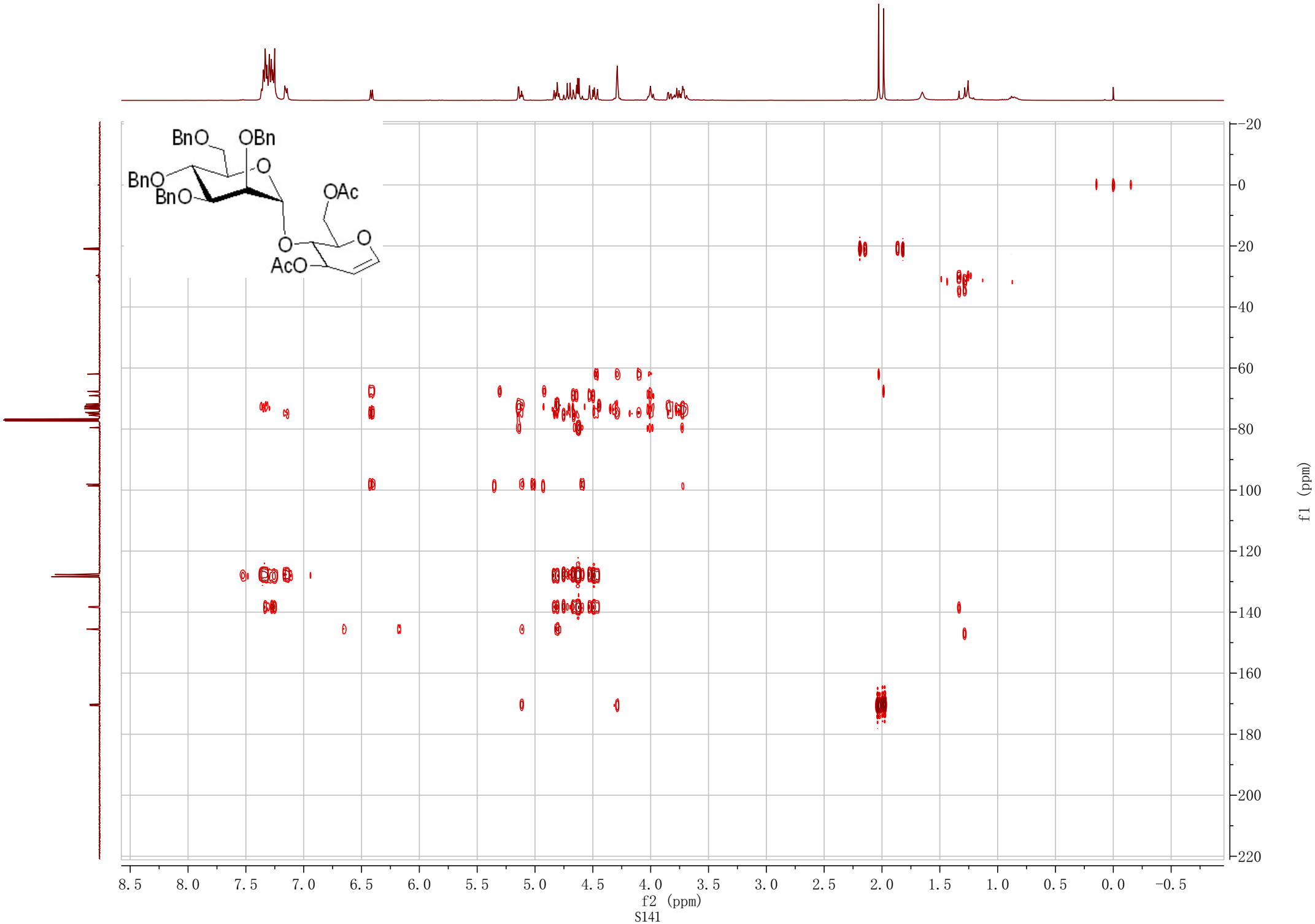

MeO
BnO
BnO
OBn
O
BnO
O
O
BnO
BnO
OBz
3p-beta
f2 (ppm)
f1 (ppm)

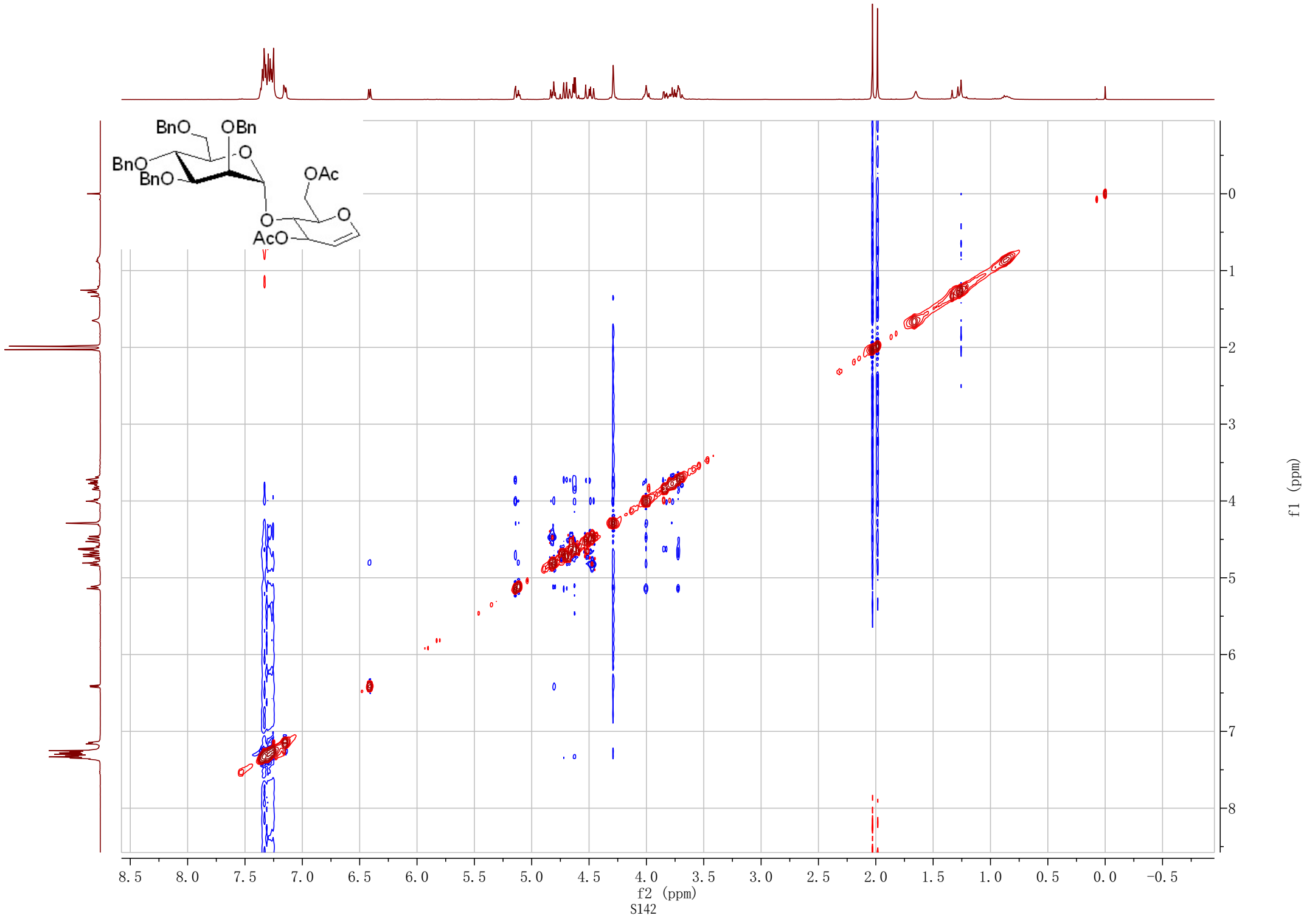

MeO
BnO
BnO
OBn
O
BnO
O
BnO
BnO
O
O
OBz
3p-beta
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-20
0
20
40
60
80
100
120
140
160
180
200
220


^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HMBC, NOESY of **3q-α**
BnO
OBn
O
BnO
BnO
OAc
O
O
AcO
3q-alfa
(400 MHz, $CDCl_3$)
20.35
2.05
1.00
1.96
2.00
1.05
3.14
1.15
1.14
1.11
3.02
2.05
0.99
4.29
2.96
2.94
f1 (ppm)


170.68
170.30
145.68
138.51
138.45
138.42
138.29
128.50
128.49
128.45
128.41
128.13
127.85
127.81
127.79
127.77
127.74
127.62
98.77
98.22
79.69
75.57
75.08
74.84
74.68
73.49
73.05
72.90
72.52
71.94
69.15
67.75
62.10
21.20
20.91
1H-NMR, 13C-NMR, 1H-1H COSY, HMBC, NOESY of 3q-α
BnO
OBn
O
BnO
BnO
OAc
O
O
AcO
3q-alfa
(100 MHz, CDCl3)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


BnO
OBn
O
BnO
BnO
OAc
O
O
AcO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

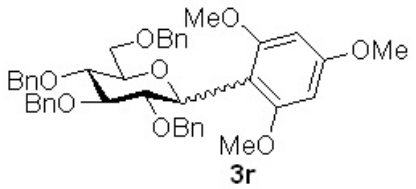

BnO
OBn
BnO
BnO
O
OAc
O
O
AcO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)


BnO
OBn
BnO
BnO
O
OAc
O
O
AcO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

XK210128-1.1.fid
XK210128-1

7.36 7.36 7.35 7.34 7.33 7.32 7.31 7.29 7.29 7.27 7.26 7.25 6.93 6.93 6.92 6.91 6.17 6.16 6.10 6.09 4.97 4.94 4.94 4.92 4.91 4.90 4.90 4.88 4.80 4.77 4.73 4.70 4.54 4.53 4.51 4.50 4.39 4.37 4.34 4.11 4.09 3.93 3.92 3.90 3.89 3.86 3.84 3.82 3.78 3.76 3.74 3.73 3.70 3.58 3.57 3.55 3.54

^{1}H-NMR of **3r**



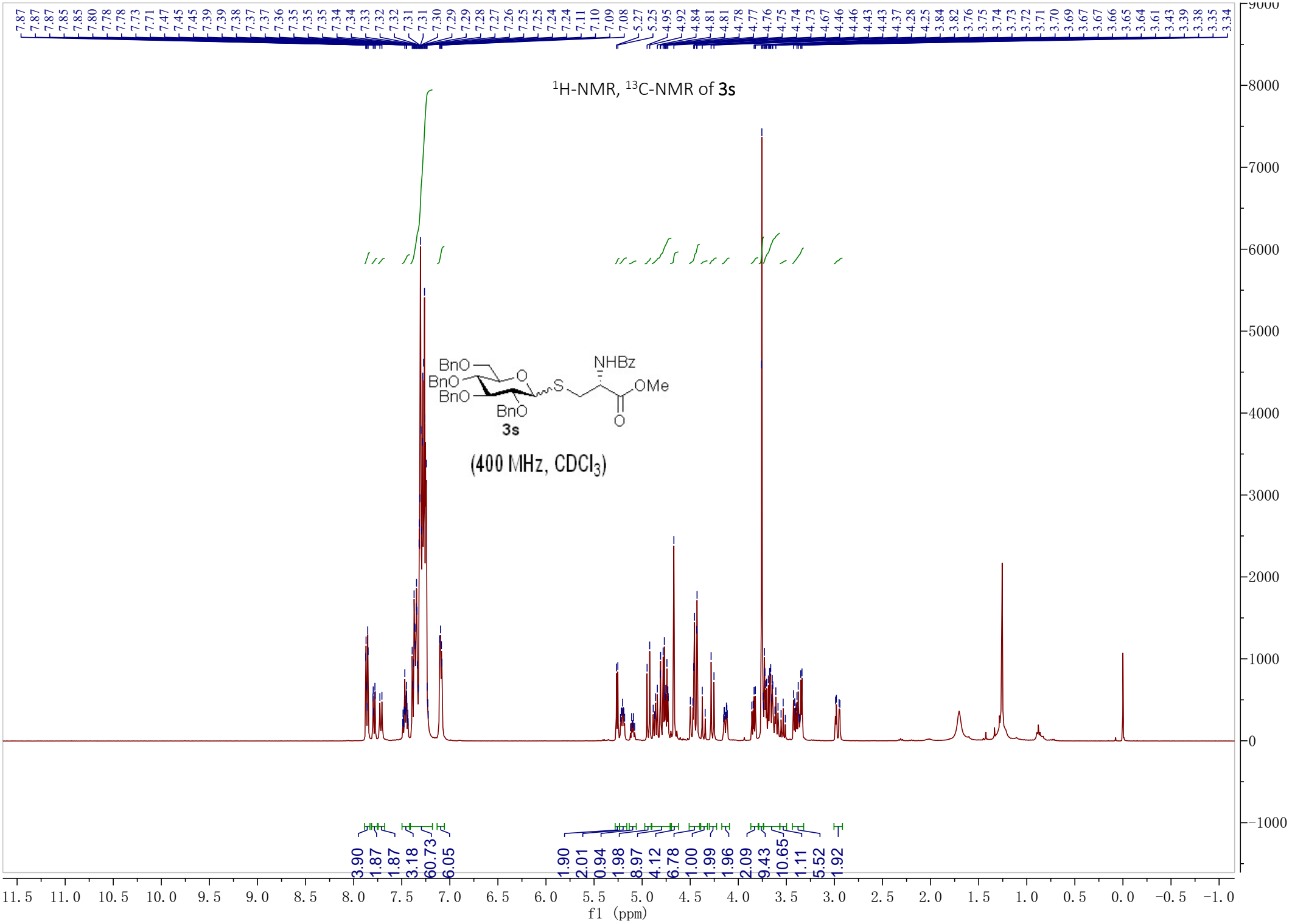
3r

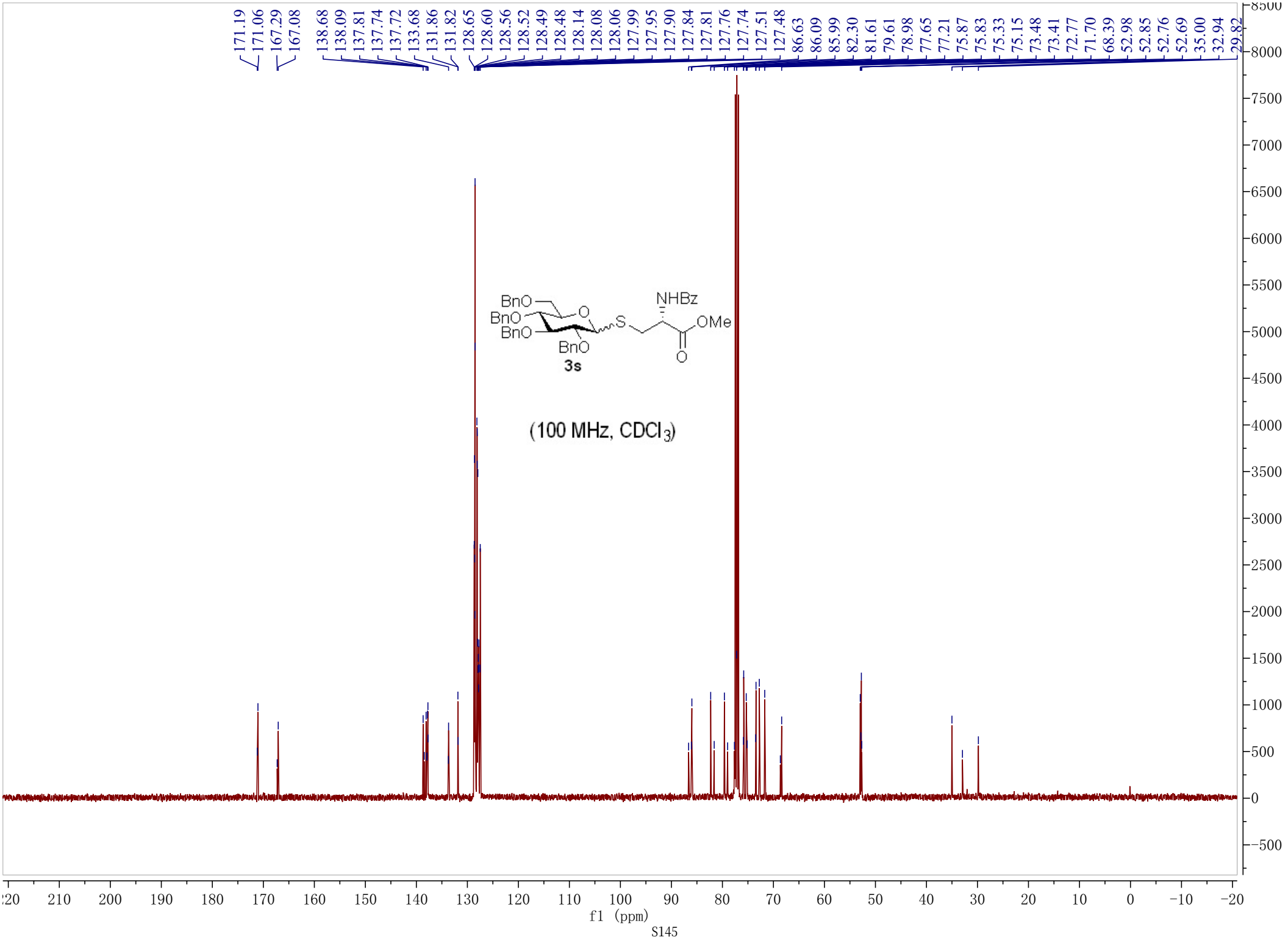
Known compound
(400 MHz, CDC13)

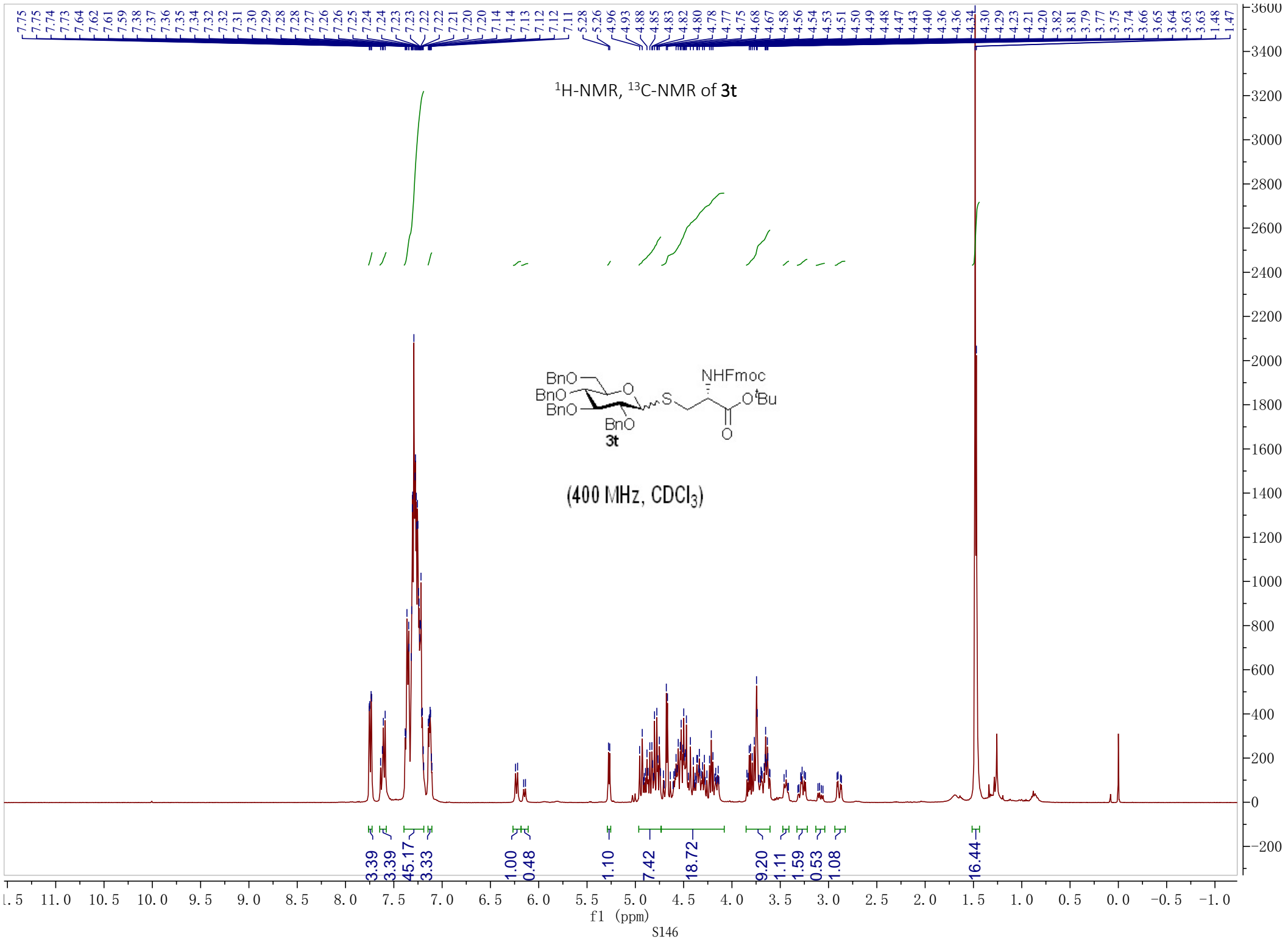
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0

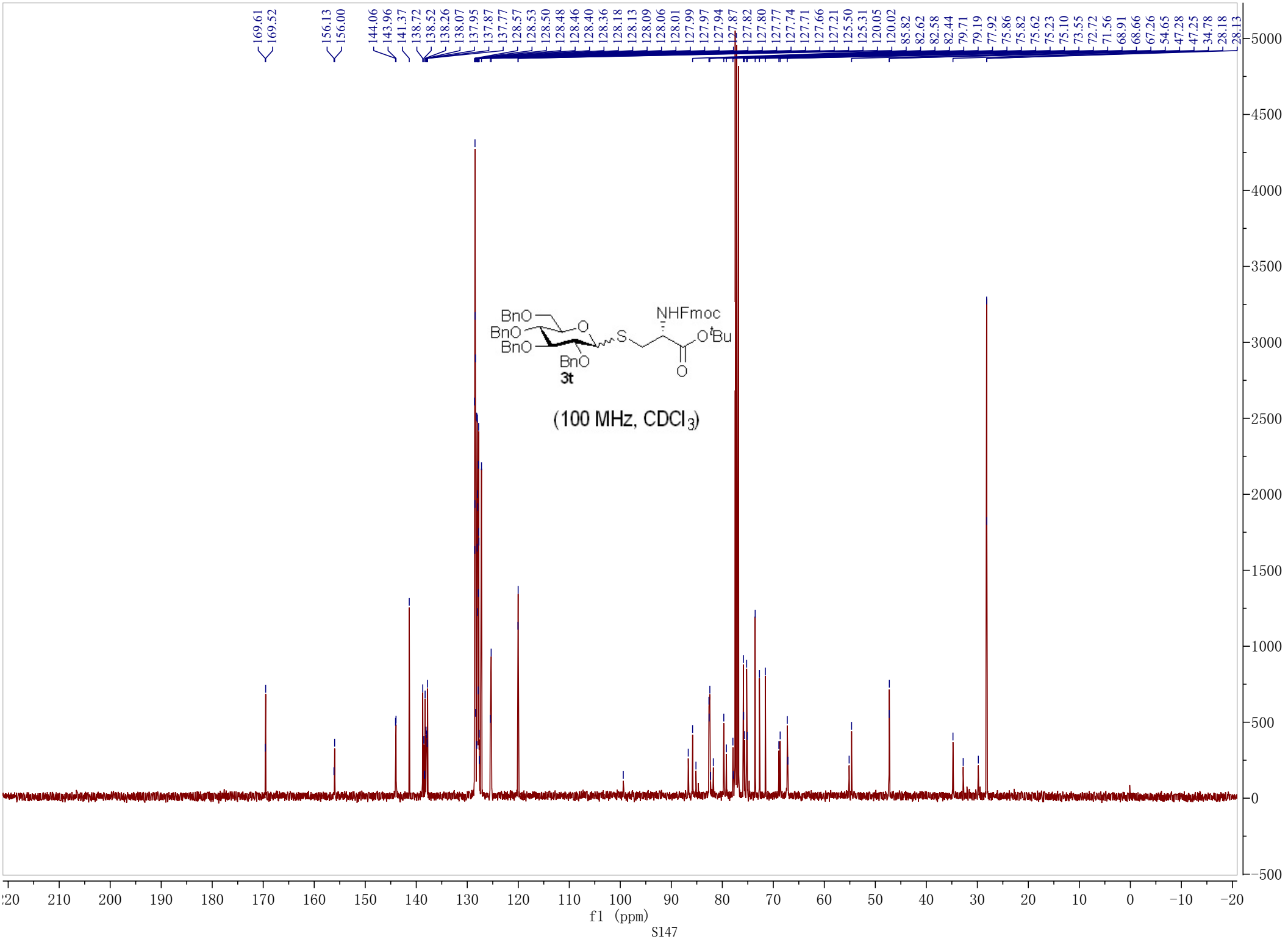
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

f1 (ppm)

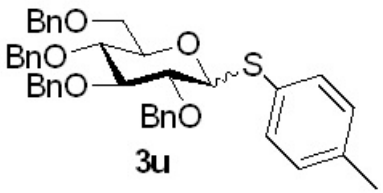

^{1}H-NMR, ^{13}C-NMR of **3s**
BnO
BnO
BnO
BnO
O
S
NHBz
OMe
O
3s
(400 MHz, $CDCl_3$)
f1 (ppm)


171.19
171.06
167.29
167.08
138.68
138.09
137.81
137.74
137.72
133.68
131.86
131.82
128.65
128.60
128.56
128.52
128.49
128.48
128.14
128.08
128.06
127.99
127.95
127.90
127.84
127.81
127.76
127.74
127.51
127.48
86.63
86.09
85.99
82.30
81.61
79.61
78.98
77.65
77.21
75.87
75.83
75.33
75.15
73.48
73.41
72.77
71.70
68.39
52.98
52.85
52.76
52.69
35.00
32.94
29.82
BnO
BnO
BnO
BnO
O
S
NHBz
OMe
O
3s
(100 MHz, CDCl3)
f1 (ppm)


^{1}H-NMR, ^{13}C-NMR of **3t**
BnO
BnO
BnO
BnO
O
S
NHFmoc
O
^{t}Bu
O
3t
(400 MHz, $CDCl_3$)
3.39
3.39
45.17
3.33
1.00
0.48
1.10
7.42
18.72
9.20
1.11
1.59
0.53
1.08
16.44
f1 (ppm)

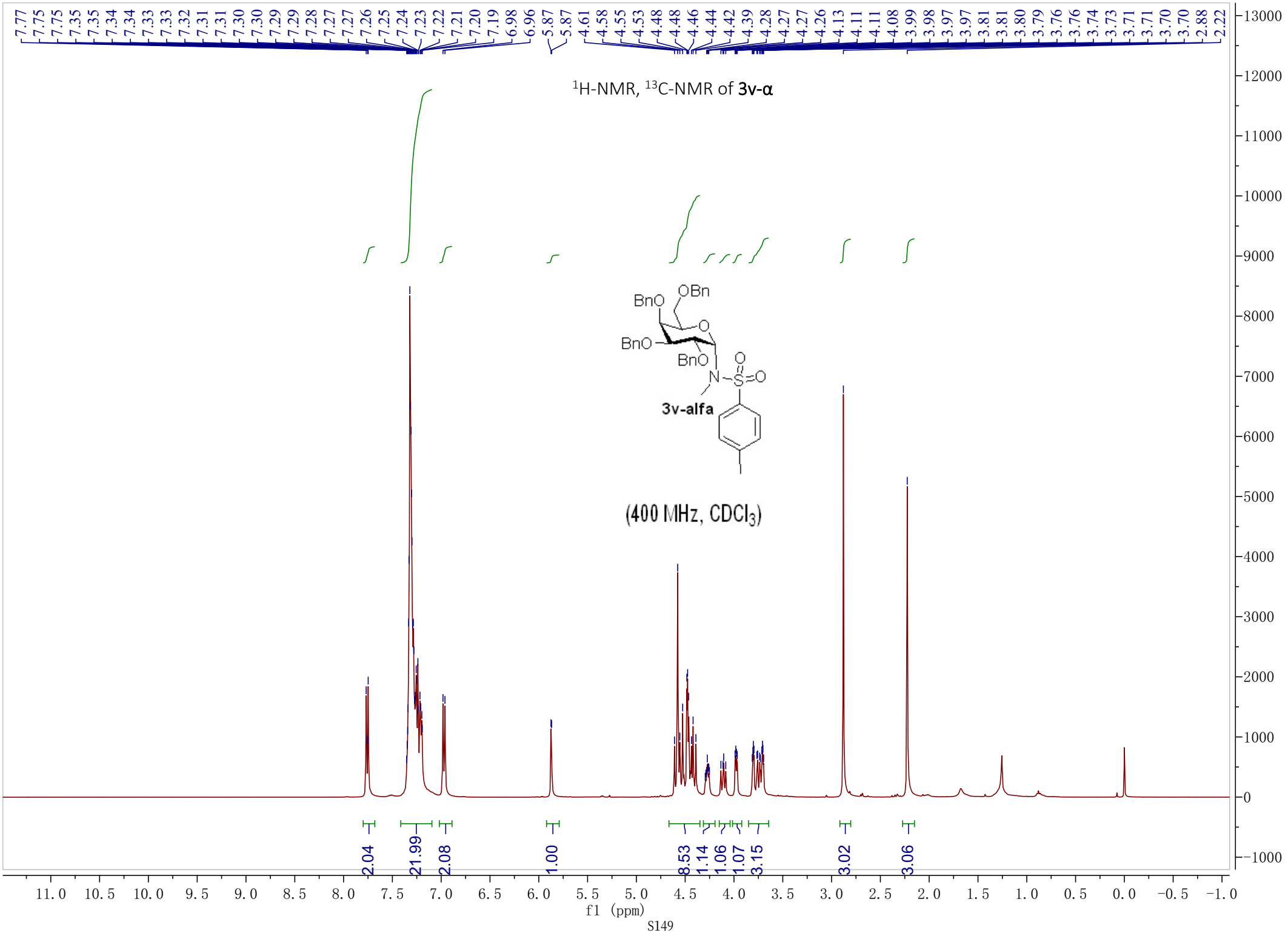

169.61
169.52
156.13
156.00
144.06
143.96
141.37
138.72
138.52
138.26
138.07
137.95
137.87
137.77
128.57
128.53
128.50
128.48
128.46
128.40
128.36
128.18
128.13
128.09
128.06
128.01
127.99
127.97
127.94
127.87
127.82
127.80
127.77
127.74
127.71
127.66
127.21
125.50
125.31
120.05
120.02
85.82
82.62
82.58
82.44
79.71
79.19
77.92
75.86
75.82
75.62
75.23
75.10
73.55
72.72
71.56
68.91
68.66
67.26
54.65
47.28
47.25
34.78
28.18
28.13
BnO
BnO
BnO
BnO
O
S
NHFmoc
O
O
tBu
3t
(100 MHz, CDCl3)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

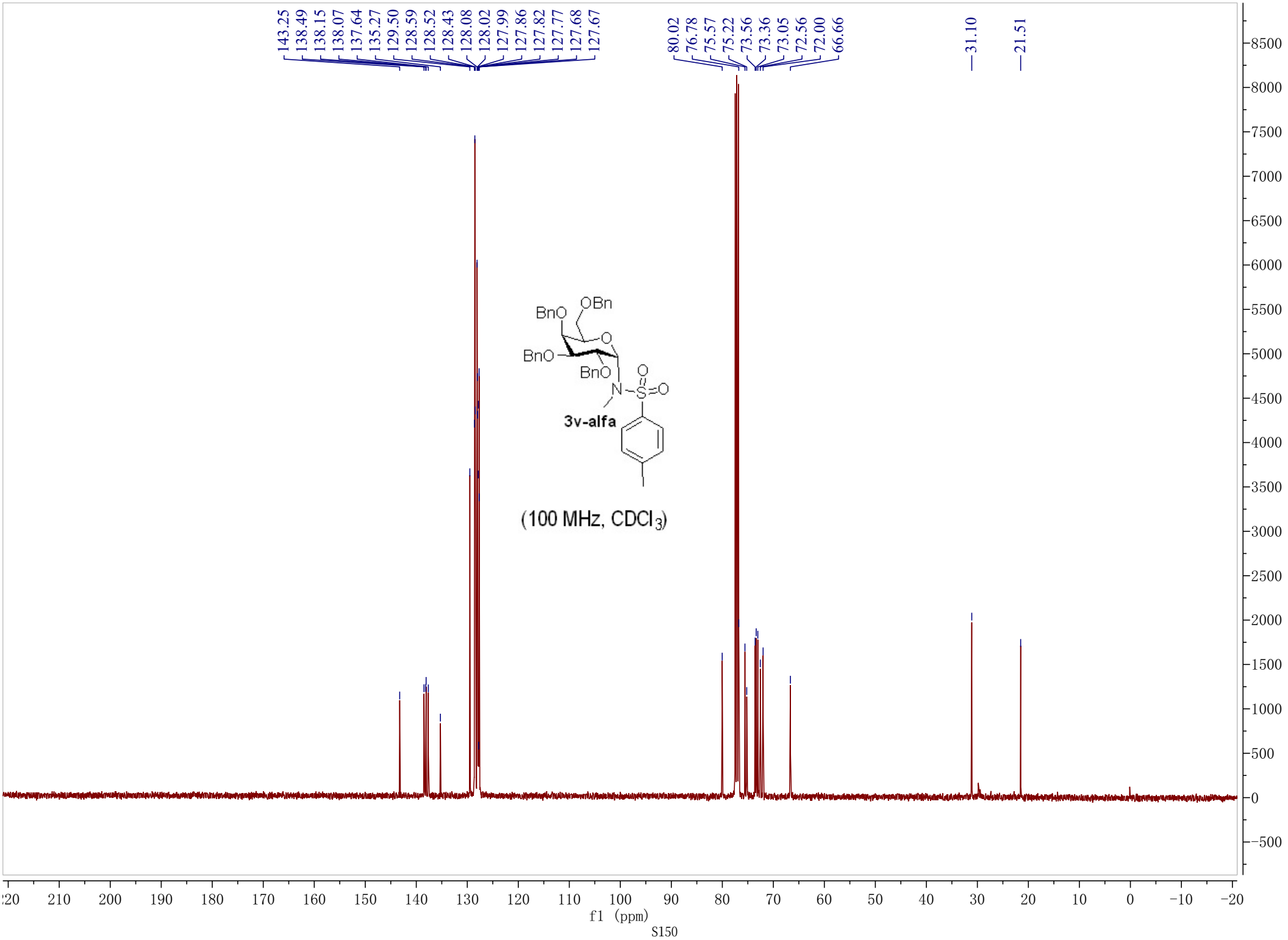
^{1}H-NMR of **3u**

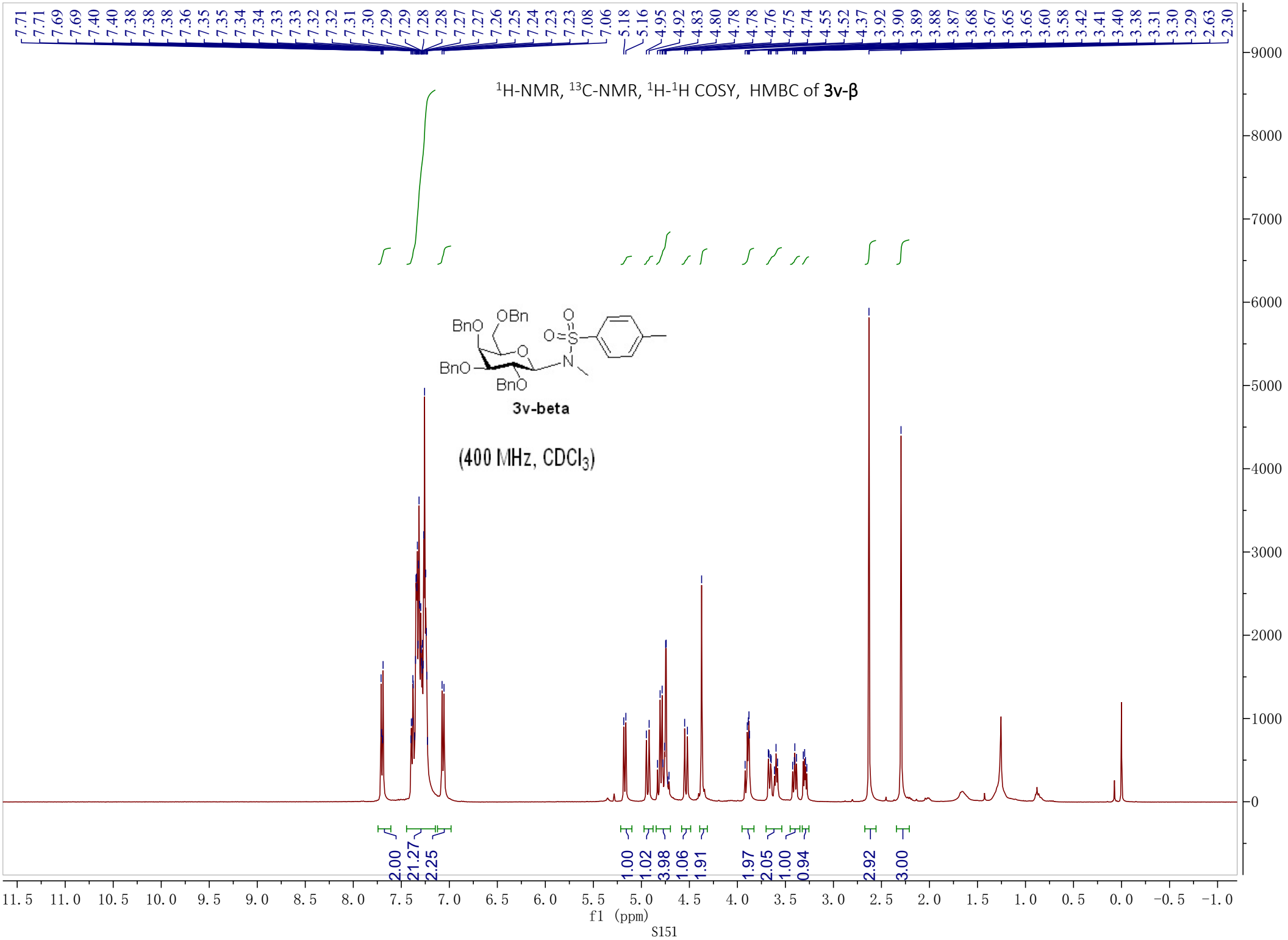


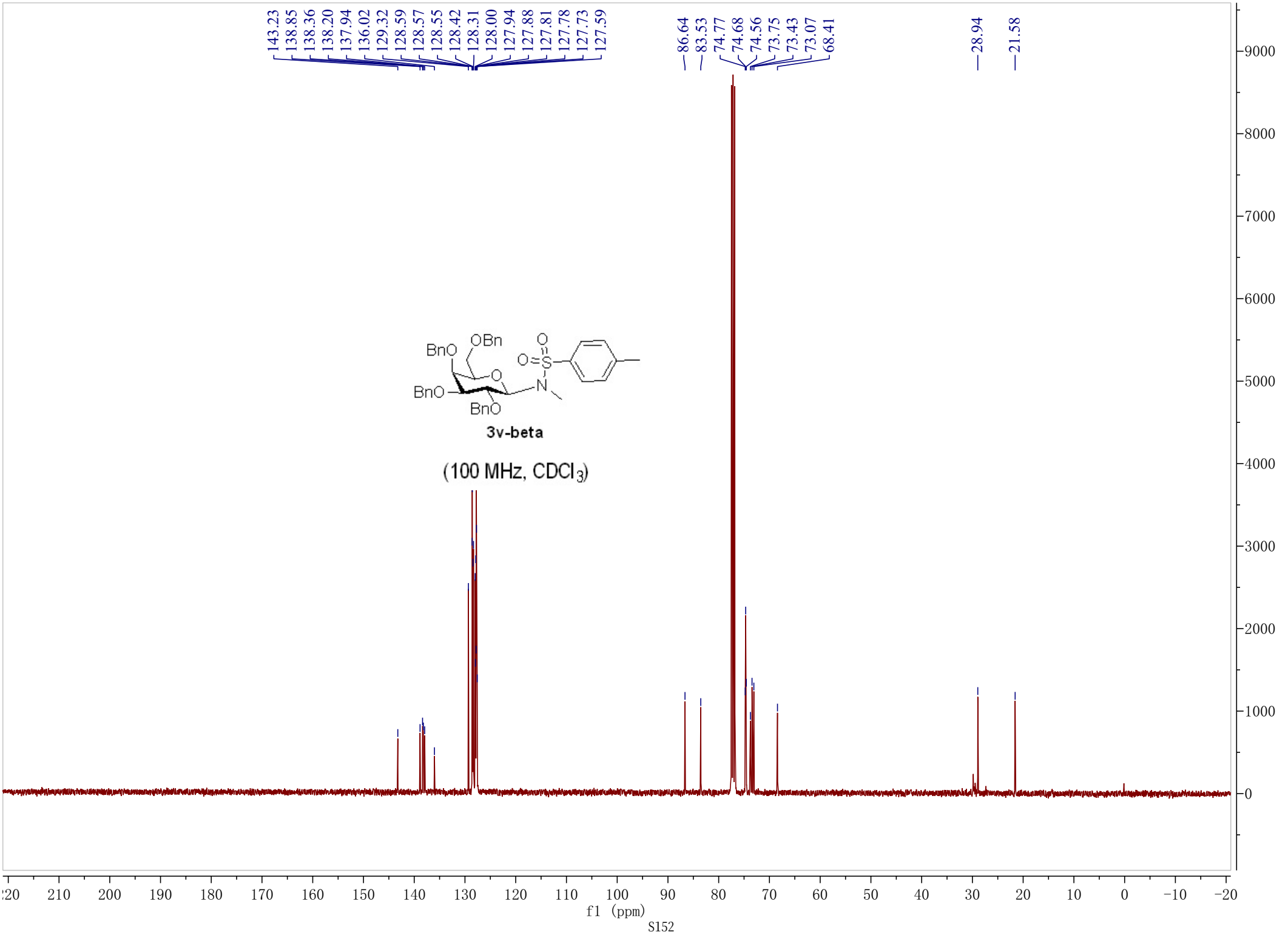
3u

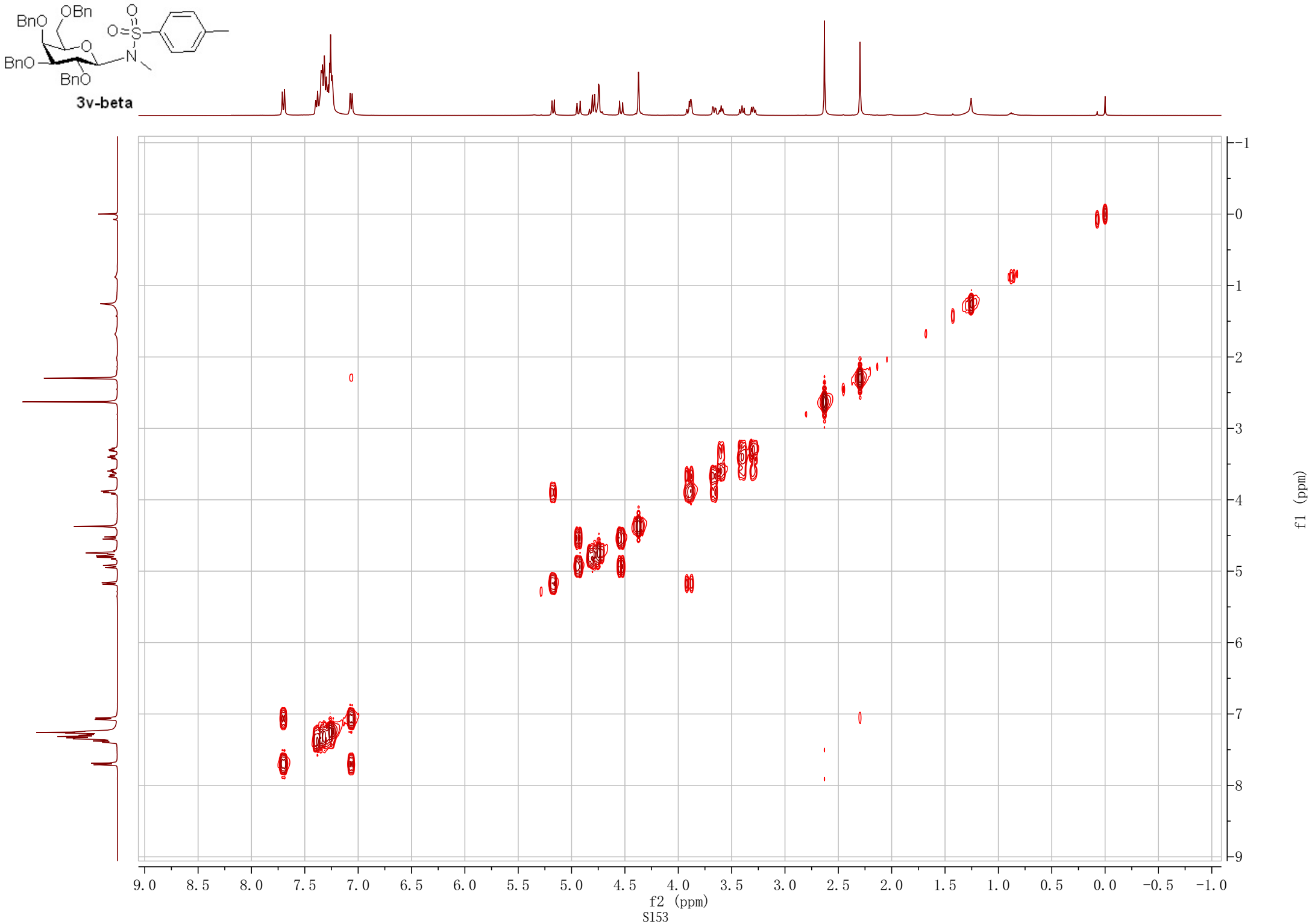
Known compound
(400 MHz, CDCl3)

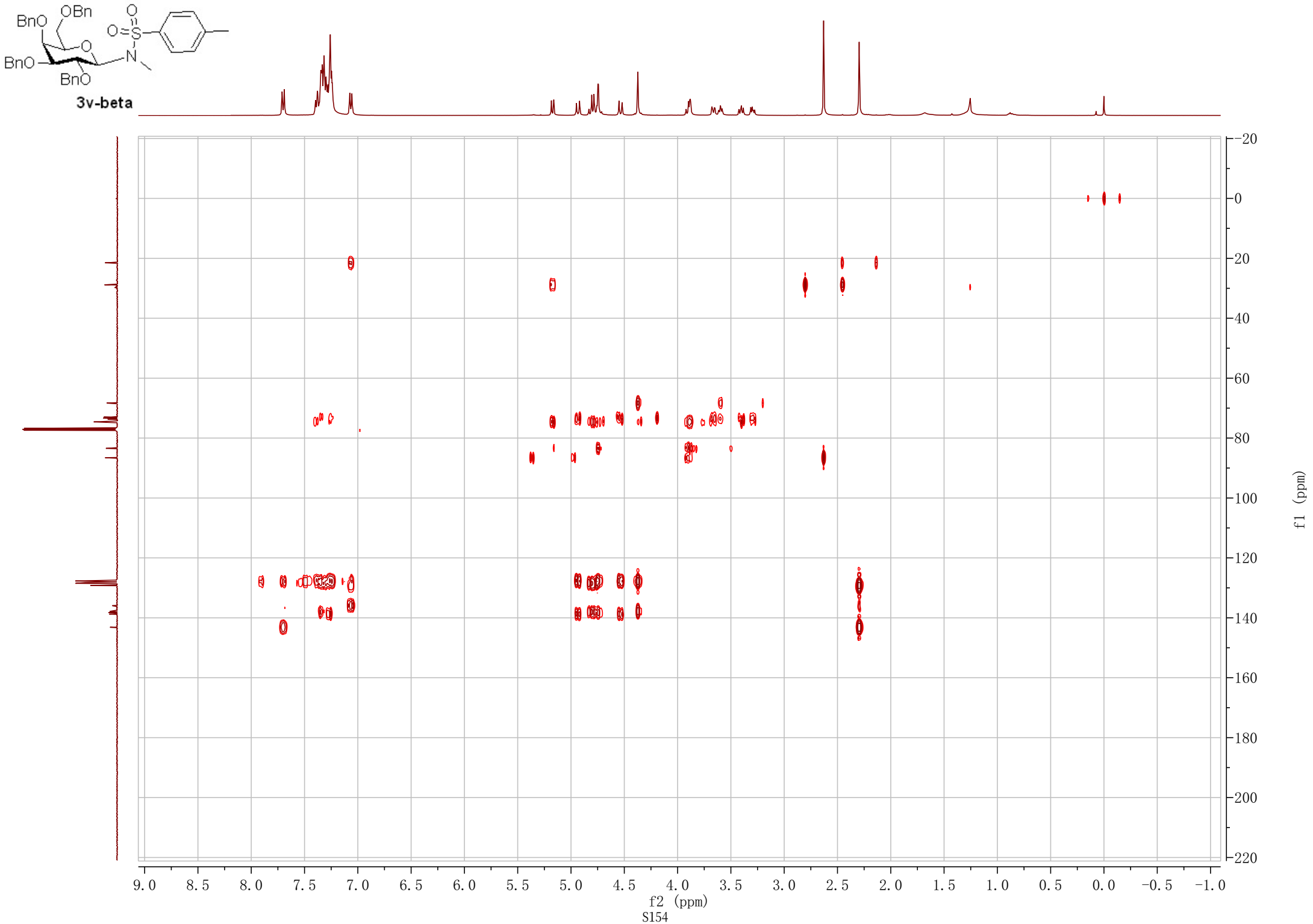

7.77 7.75 7.75 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.20 7.19 6.98 6.96 5.87 5.87 4.61 4.58 4.55 4.53 4.48 4.48 4.46 4.44 4.42 4.39 4.28 4.27 4.27 4.26 4.13 4.11 4.11 4.08 3.99 3.98 3.97 3.97 3.81 3.81 3.80 3.79 3.76 3.76 3.74 3.73 3.71 3.71 3.70 3.70 2.88 2.22
1H-NMR, 13C-NMR of 3v-α
BnO
OBn
O
BnO
BnO
N
S
O
O
3v-alfa
(400 MHz, CDCl3)
2.04
21.99
2.08
1.00
8.53
1.14
1.06
1.07
3.15
3.02
3.06
f1 (ppm)

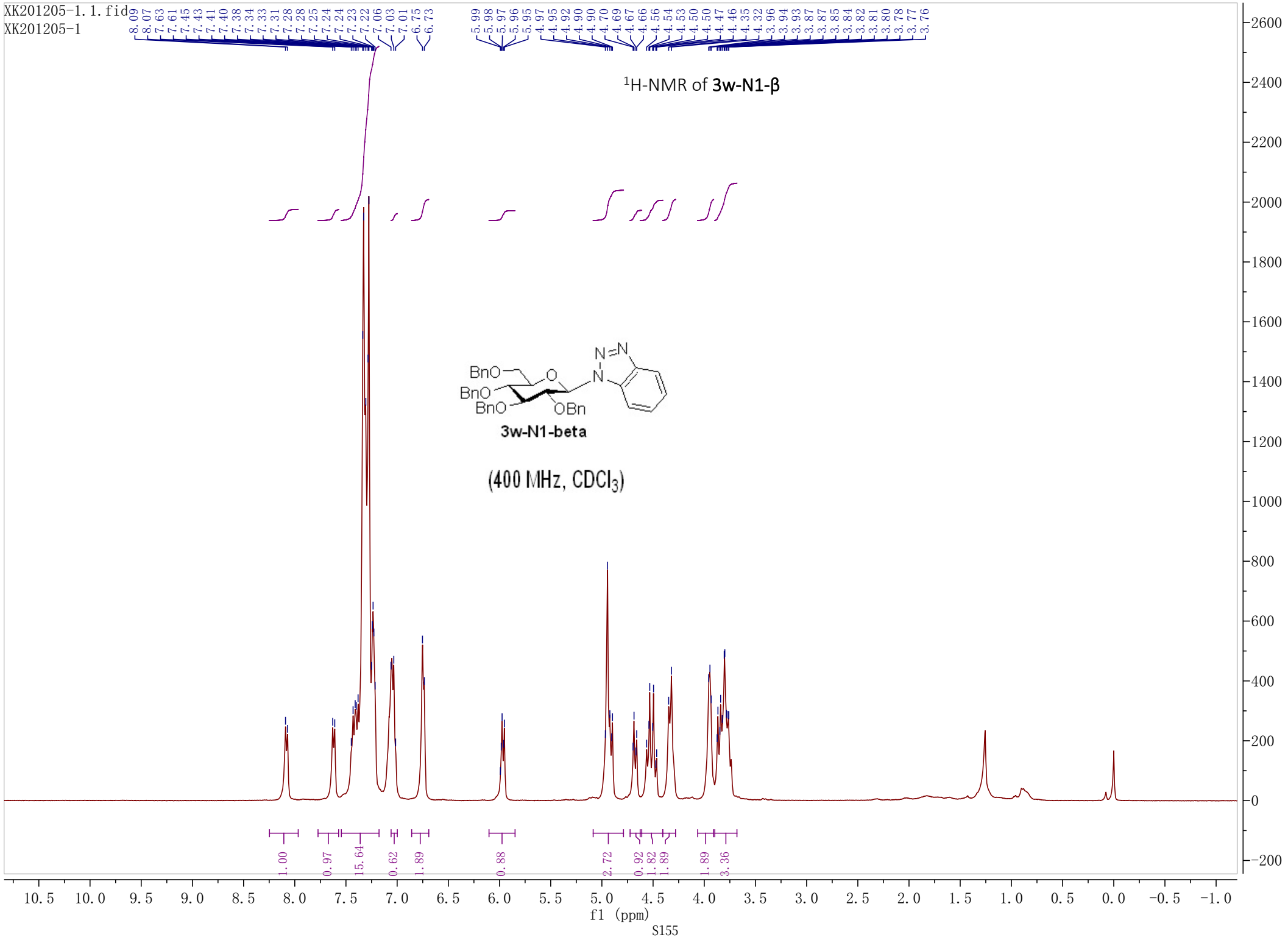

143.25
138.49
138.15
138.07
137.64
135.27
129.50
128.59
128.52
128.43
128.08
128.02
127.99
127.86
127.82
127.77
127.68
127.67
80.02
76.78
75.57
75.22
73.56
73.36
73.05
72.56
72.00
66.66
31.10
21.51
BnO
OBn
BnO
BnO
O
N
S
O
O
3v-alfa
(100 MHz, CDCl3)
f1 (ppm)

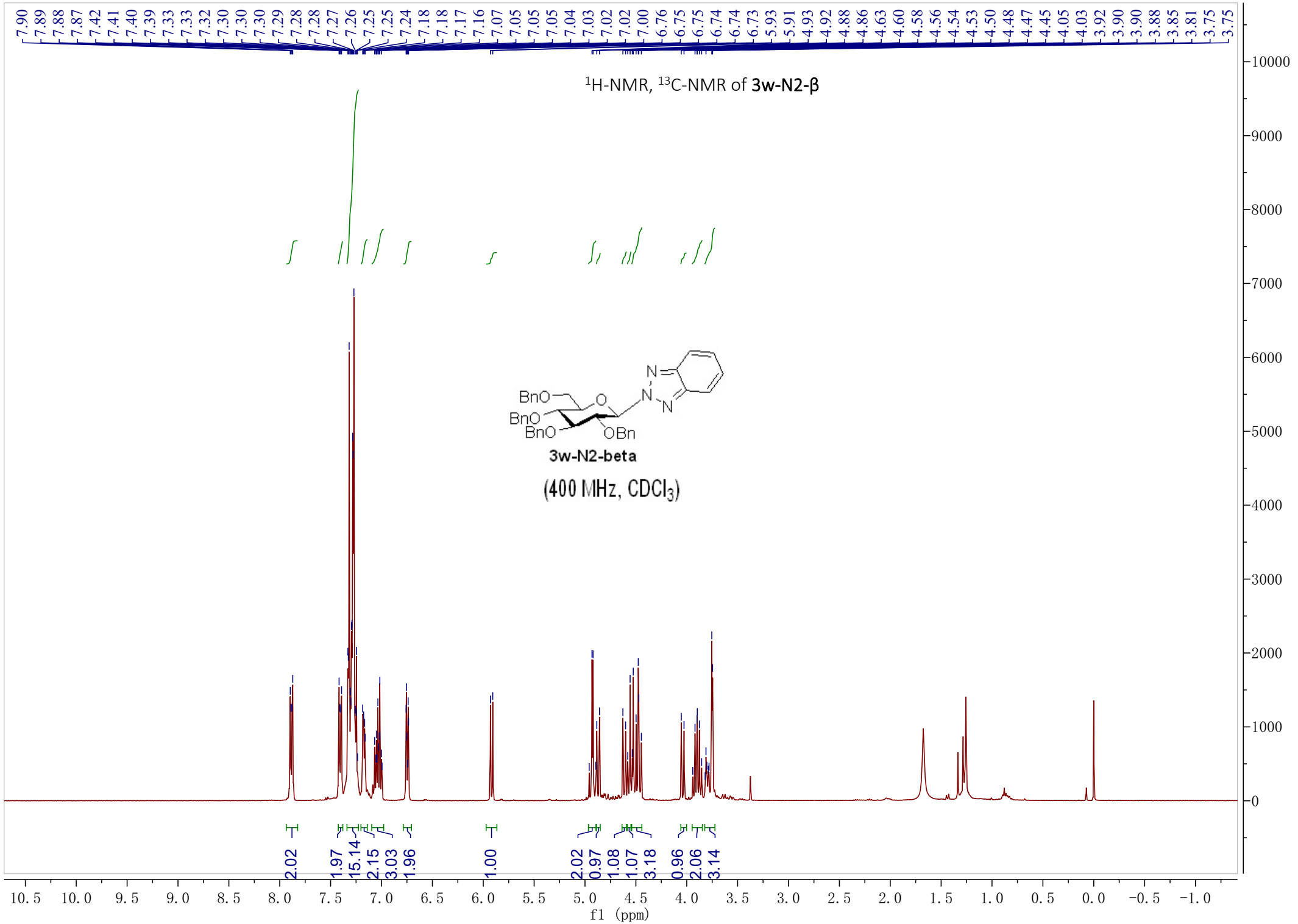

7.71 7.71 7.69 7.69 7.40 7.40 7.38 7.38 7.38 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.23 7.08 7.06 5.18 5.16 4.95 4.92 4.83 4.80 4.78 4.78 4.76 4.75 4.74 4.55 4.52 4.37 3.92 3.90 3.89 3.88 3.87 3.68 3.67 3.65 3.65 3.60 3.58 3.42 3.41 3.40 3.38 3.31 3.30 3.29 2.63 2.30
^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HMBC of 3v-β
BnO
OBn
BnO
BnO
O
O=S
N
3v-beta
(400 MHz, CDCl$_3$)
2.00 21.27 2.25 1.00 1.02 3.98 1.06 1.91 1.97 2.05 1.00 0.94 2.92 3.00
f1 (ppm)

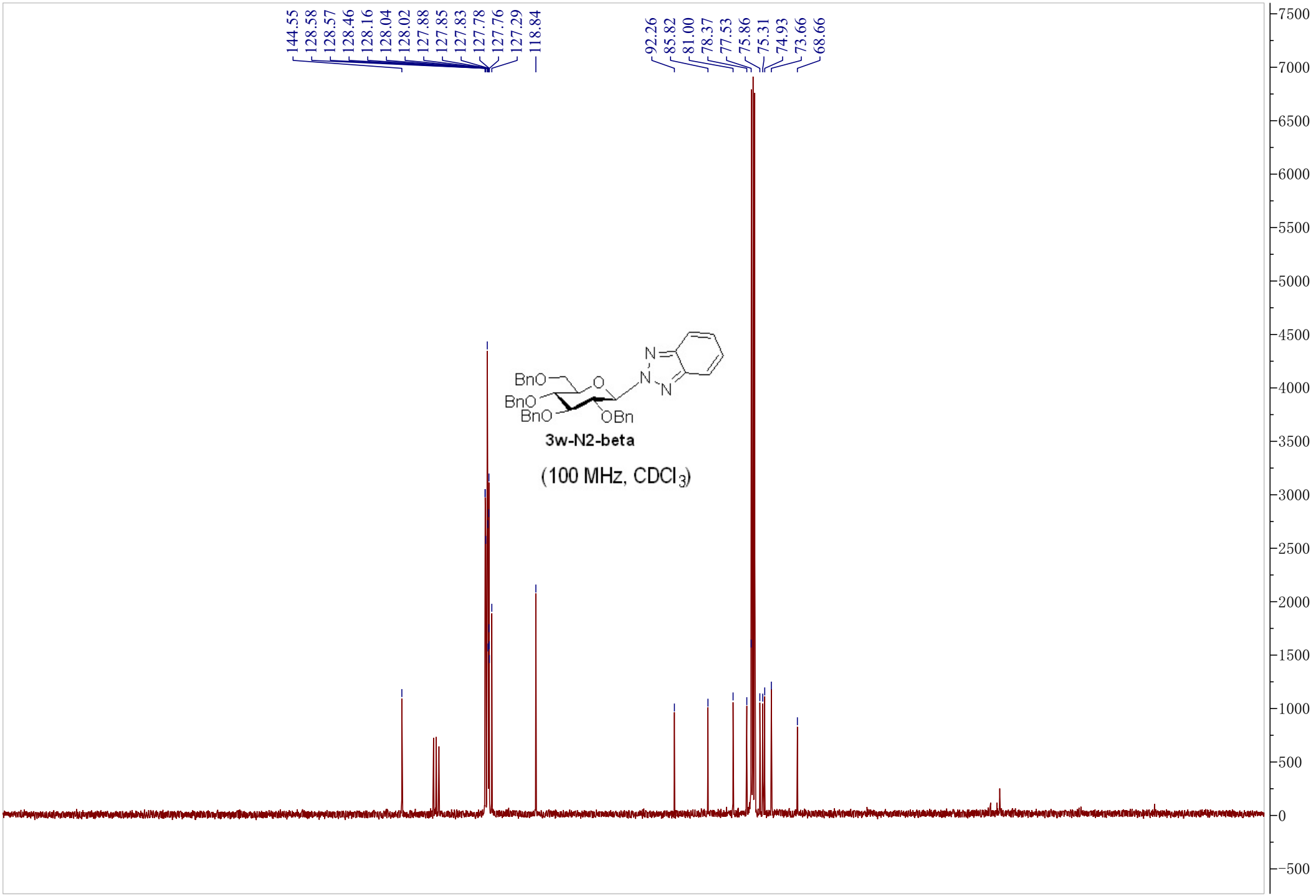

143.23
138.85
138.36
138.20
137.94
136.02
129.32
128.59
128.57
128.55
128.42
128.31
128.00
127.94
127.88
127.81
127.78
127.73
127.59
86.64
83.53
74.77
74.68
74.56
73.75
73.43
73.07
68.41
28.94
21.58
BnO
OBn
BnO
BnO
O
O
S
N
3v-beta
(100 MHz, CDCl3)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

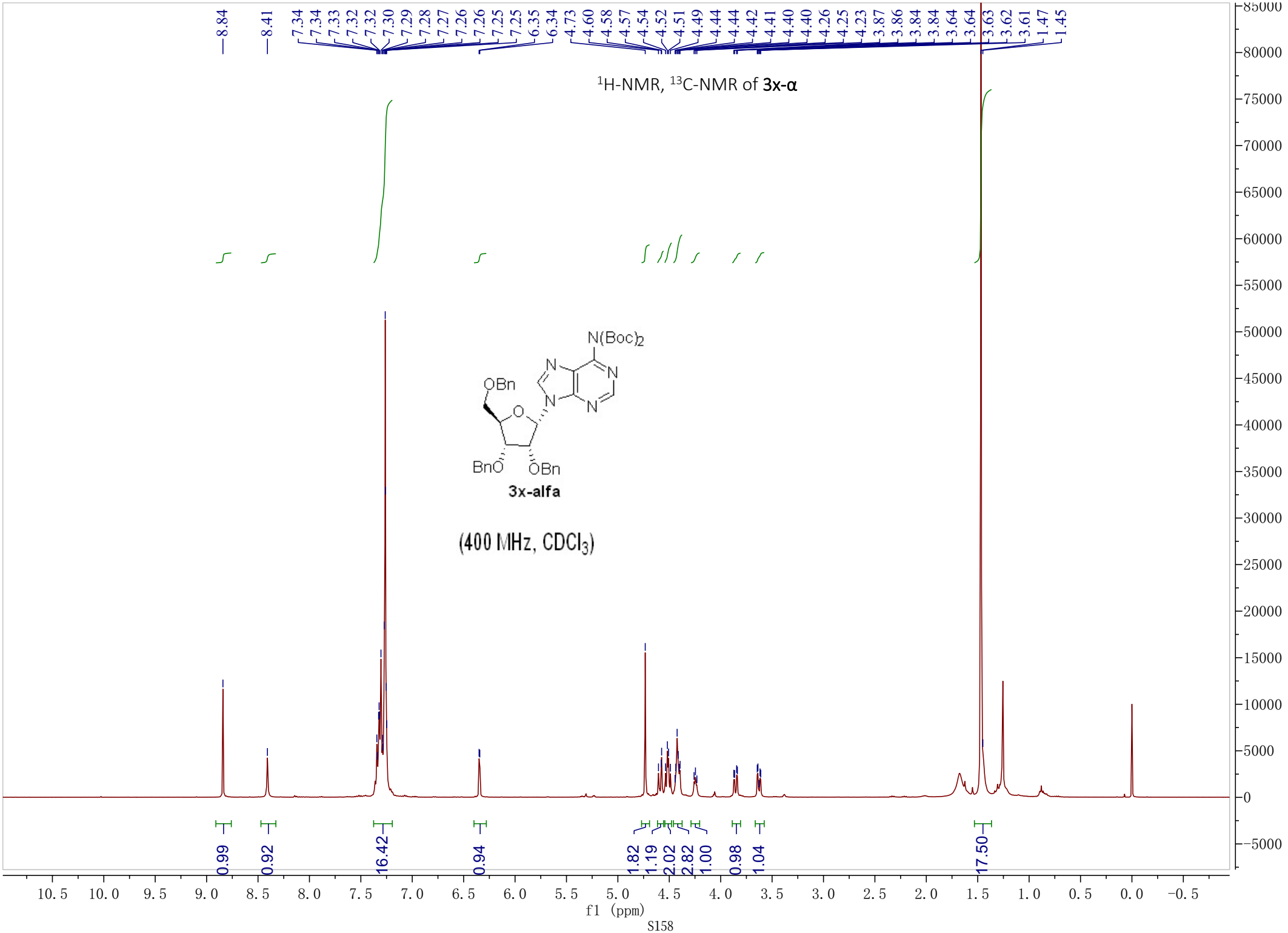

BnO
OBn
BnO
BnO
O
O
S
O
N
3v-beta
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8
9

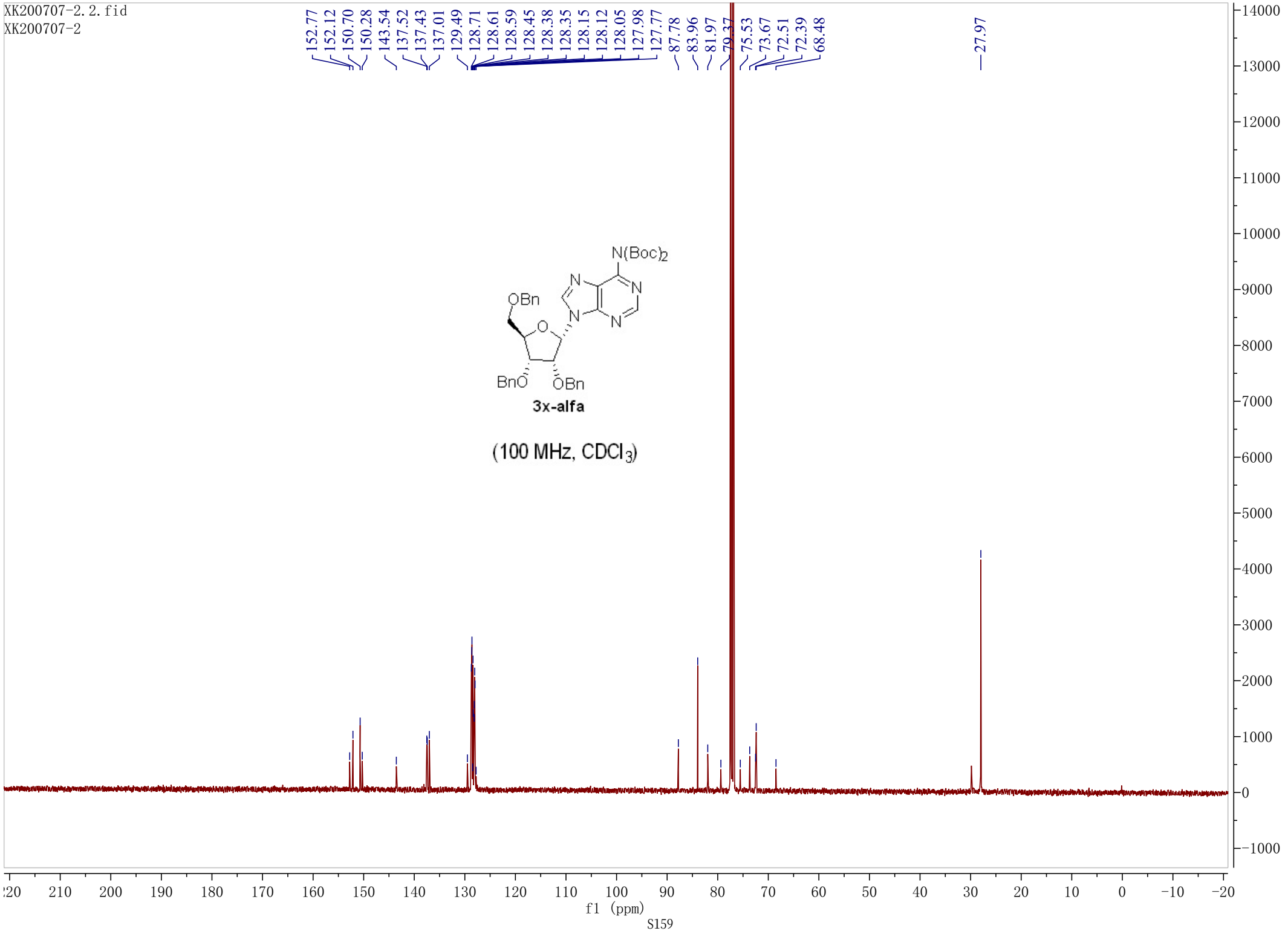

BnO
OBn
BnO
BnO
O
O=S=O
N
3v-beta
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-20
0
20
40
60
80
100
120
140
160
180
200
220

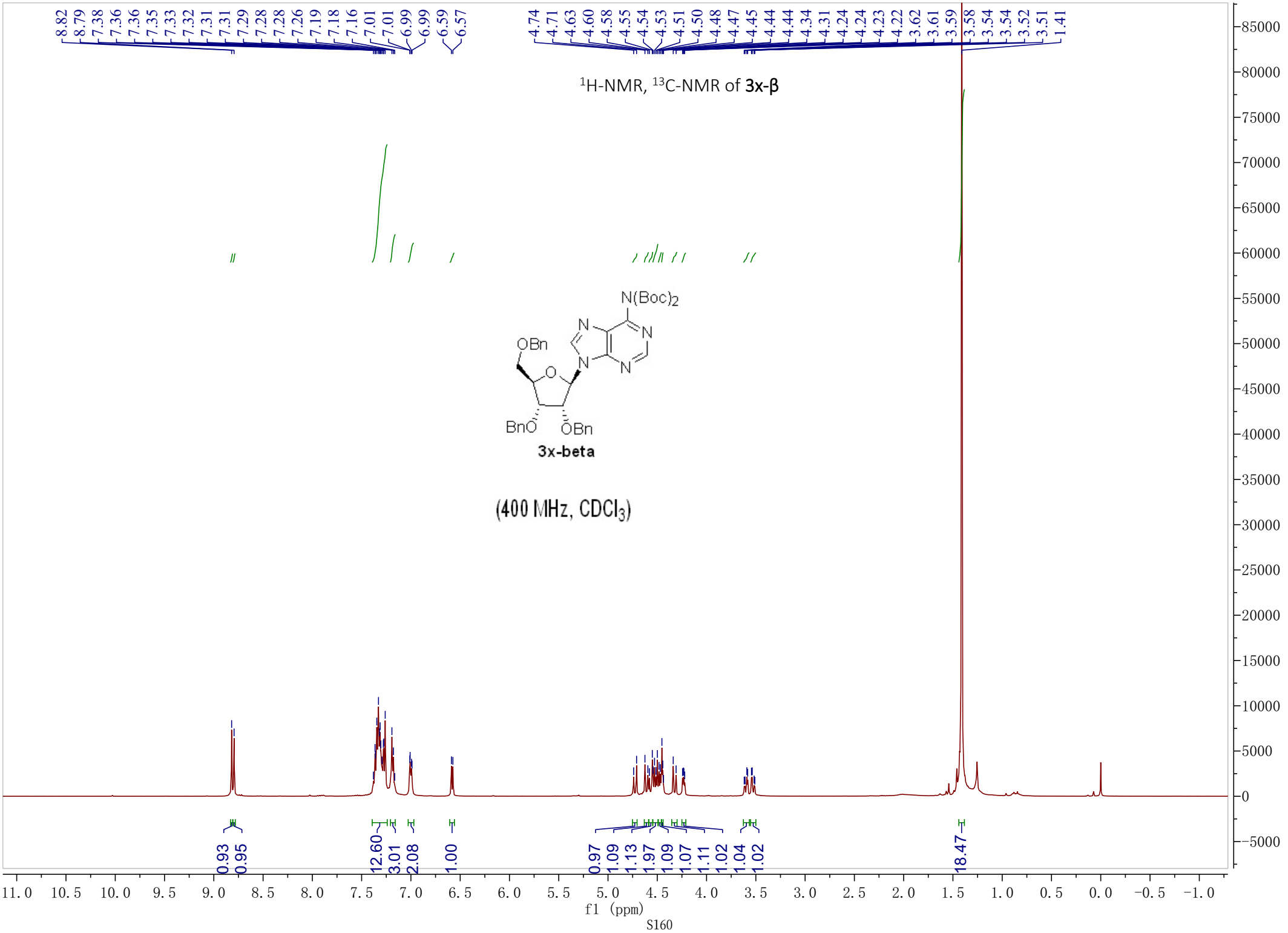

XK201205-1.1.fid
XK201205-1
8.09 8.07 7.63 7.61 7.45 7.43 7.41 7.40 7.38 7.34 7.33 7.31 7.28 7.28 7.25 7.24 7.24 7.23 7.22 7.06 7.03 7.01 6.75 6.73
5.99 5.98 5.97 5.96 5.95 4.97 4.95 4.92 4.90 4.90 4.70 4.69 4.67 4.66 4.56 4.54 4.53 4.50 4.50 4.47 4.46 4.35 4.32 3.96 3.94 3.93 3.87 3.87 3.85 3.84 3.82 3.81 3.80 3.78 3.77 3.76
1H-NMR of 3w-N1-β
BnO
BnO
BnO
O
OBn
N
N
3w-N1-beta
(400 MHz, CDCl3)
1.00 0.97 15.64 0.62 1.89 0.88 2.72 0.92 1.82 1.89 1.89 3.36
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

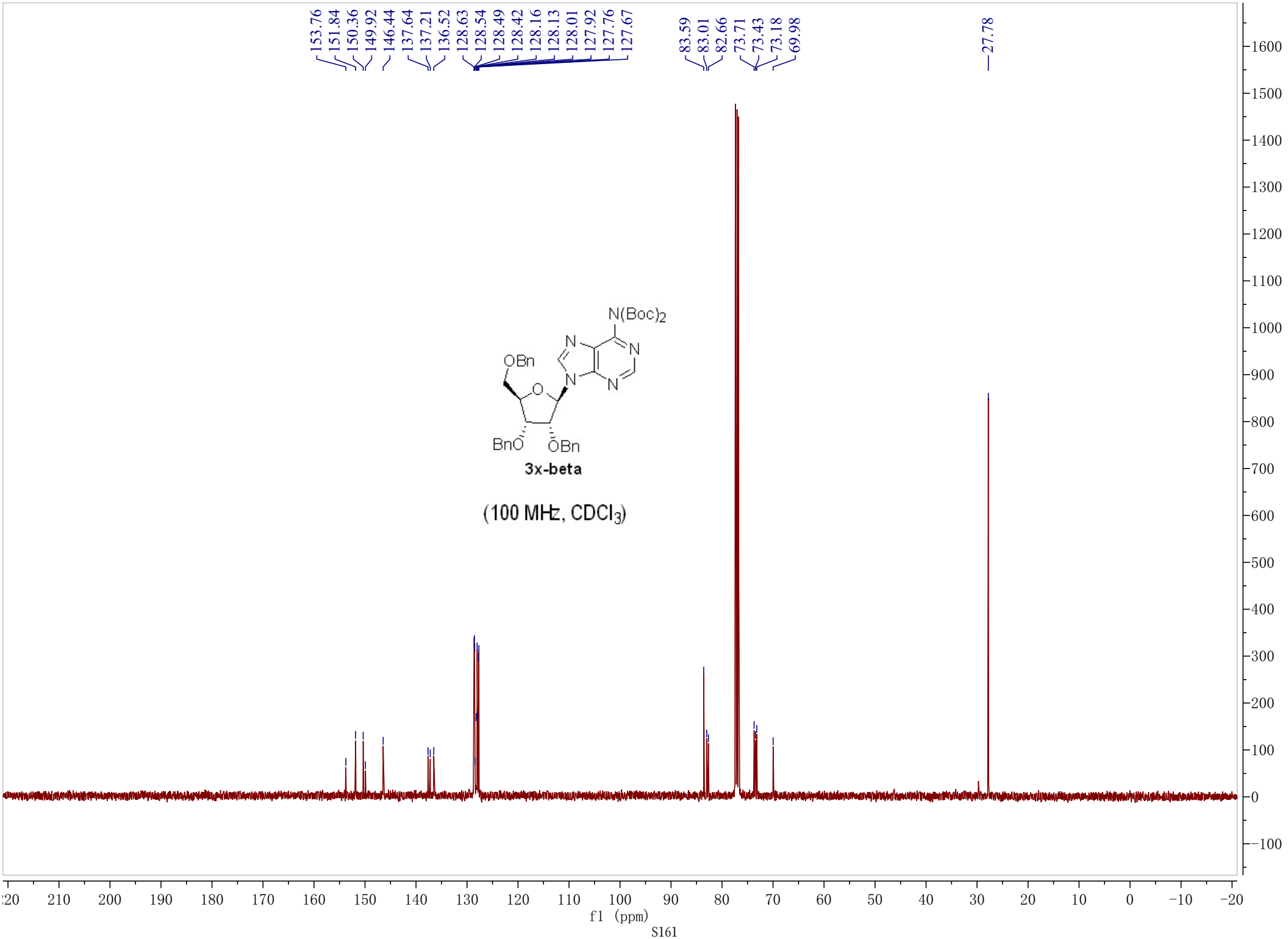

7.90 7.89 7.88 7.87 7.42 7.41 7.40 7.39 7.33 7.33 7.32 7.30 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.25 7.25 7.24 7.18 7.18 7.17 7.16 7.07 7.05 7.05 7.05 7.04 7.03 7.02 7.02 7.00 6.76 6.75 6.75 6.74 6.74 6.73 5.93 5.91 4.93 4.92 4.88 4.86 4.63 4.60 4.58 4.56 4.54 4.53 4.50 4.48 4.47 4.45 4.05 4.03 3.92 3.90 3.90 3.88 3.85 3.81 3.75 3.75
1H-NMR, 13C-NMR of 3w-N2-β
BnO
BnO
BnO
O
OBn
N
N
N
3w-N2-beta
(400 MHz, CDCl3)
2.02 1.97 15.14 2.15 3.03 1.96 1.00 2.02 0.97 1.08 1.07 3.18 0.96 2.06 3.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0

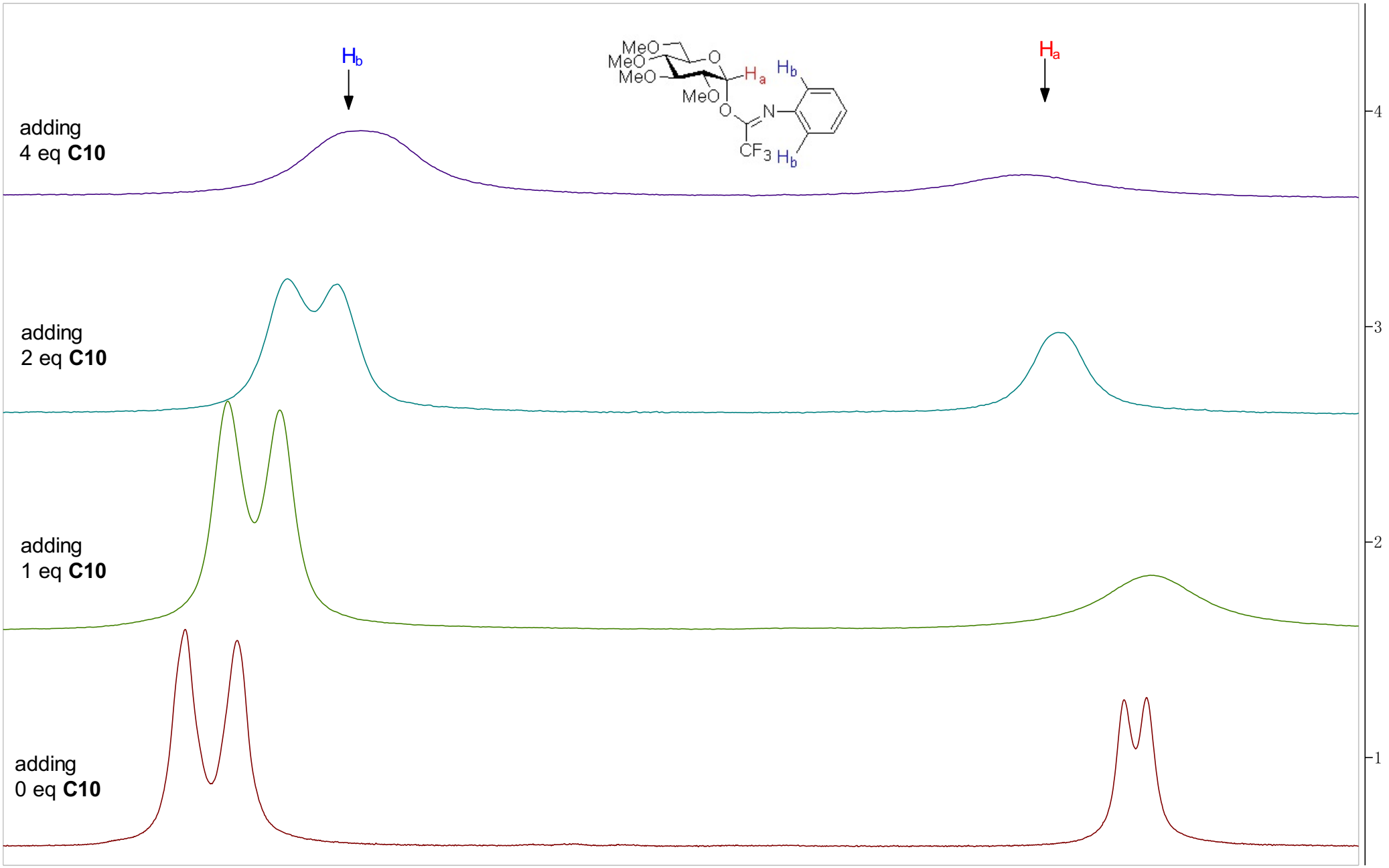

144.55
128.58
128.57
128.46
128.16
128.04
128.02
127.88
127.85
127.83
127.78
127.76
127.29
118.84
92.26
85.82
81.00
78.37
77.53
75.86
75.31
74.93
73.66
68.66
BnO
BnO
BnO
O
OBn
N
N
N
3w-N2-beta
(100 MHz, CDCl3)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


8.84
8.41
7.34
7.34
7.33
7.32
7.32
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.25
6.35
6.34
4.73
4.60
4.58
4.57
4.54
4.52
4.51
4.49
4.44
4.44
4.42
4.41
4.40
4.40
4.26
4.25
4.23
3.87
3.86
3.84
3.84
3.64
3.64
3.63
3.62
3.61
1.47
1.45
1H-NMR, 13C-NMR of 3x-α
N(Boc)2
OBn
BnO
OBn
3x-alfa
(400 MHz, CDCl3)
0.99
0.92
16.42
0.94
1.82
1.19
2.02
2.82
1.00
0.98
1.04
17.50
f1 (ppm)


XK200707-2.2.fid
XK200707-2
152.77
152.12
150.70
150.28
143.54
137.52
137.43
137.01
129.49
128.71
128.61
128.59
128.45
128.38
128.35
128.15
128.12
128.05
127.98
127.77
87.78
83.96
81.97
79.37
75.53
73.67
72.51
72.39
68.48
27.97
N(Boc)2
OBn
BnO
OBn
3x-alfa
(100 MHz, CDCl3)
f1 (ppm)


8.82 8.79 7.38 7.36 7.36 7.35 7.33 7.32 7.31 7.31 7.29 7.28 7.28 7.26 7.19 7.18 7.16 7.01 7.01 6.99 6.99 6.59 6.57
4.74 4.71 4.63 4.60 4.58 4.55 4.54 4.53 4.51 4.50 4.48 4.47 4.45 4.44 4.44 4.34 4.31 4.24 4.24 4.23 4.22 3.62 3.61 3.59 3.58 3.54 3.54 3.52 3.51 1.41
1H-NMR, 13C-NMR of 3x-β
N(Boc)2
OBn
BnO
OBn
3x-beta
(400 MHz, CDCl3)
0.93 0.95 12.60 3.01 2.08 1.00 0.97 1.09 1.13 1.97 1.09 1.07 1.11 1.02 1.04 1.02 18.47
f1 (ppm)

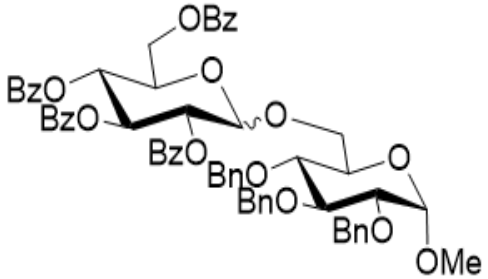

153.76
151.84
150.36
149.92
146.44
137.64
137.21
136.52
128.63
128.54
128.49
128.42
128.16
128.13
128.01
127.92
127.76
127.67
83.59
83.01
82.66
73.71
73.43
73.18
69.98
27.78
N(Boc)2
OBn
BnO
OBn
3x-beta
(100 MHz, CDCl3)
f1 (ppm)


H_b
H_a
adding
4 eq **C10**
adding
2 eq **C10**
adding
1 eq **C10**
adding
0 eq **C10**
MeO
MeO
MeO
MeO
O
H_a
H_b
N
CF_3
H_b
4
3
2
1
6.85
6.80
6.75
6.70
6.65
6.60
6.55
6.50
6.45
6.40
f1 (ppm)

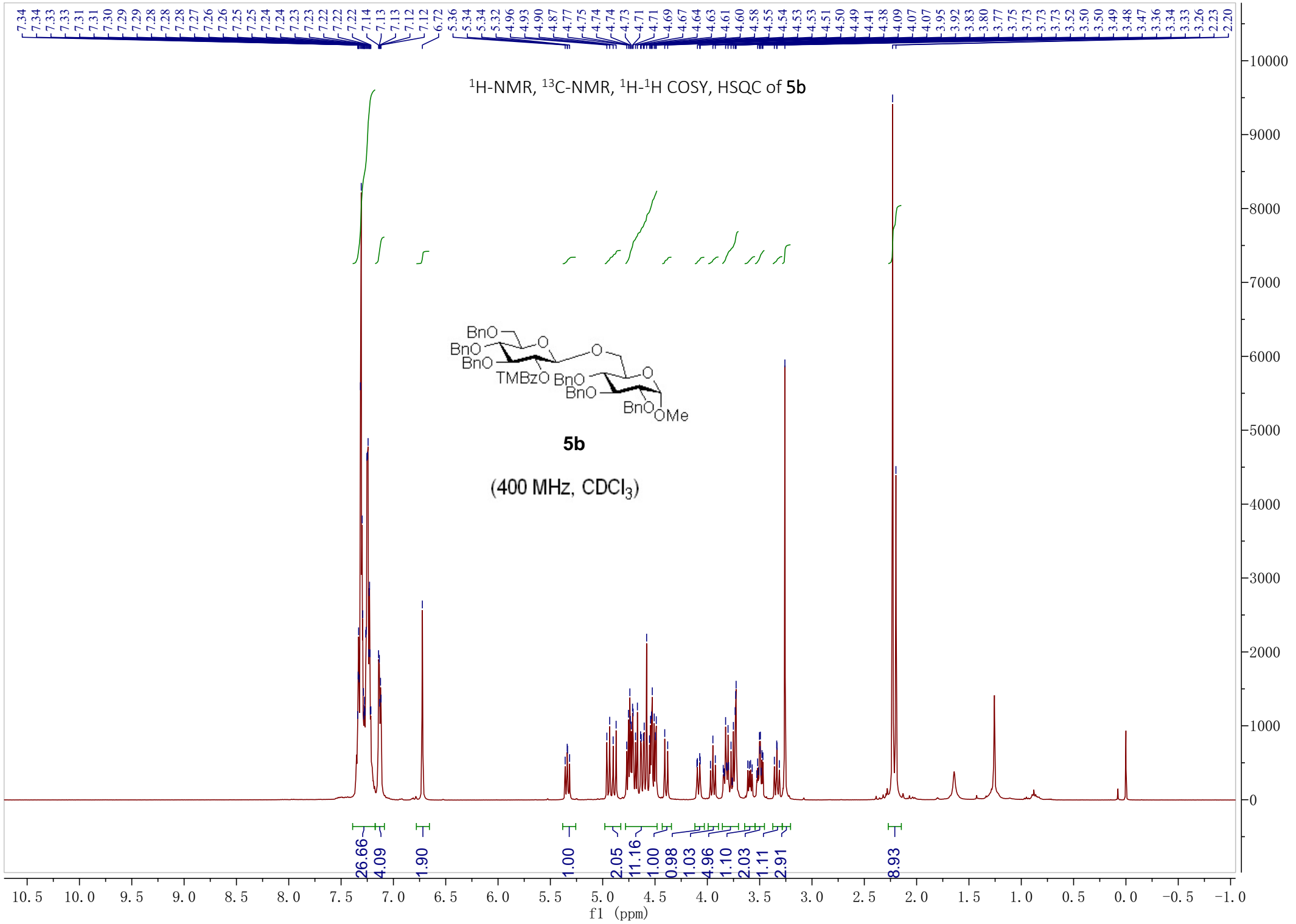
XK190702-1.1.fid
XK190702-1

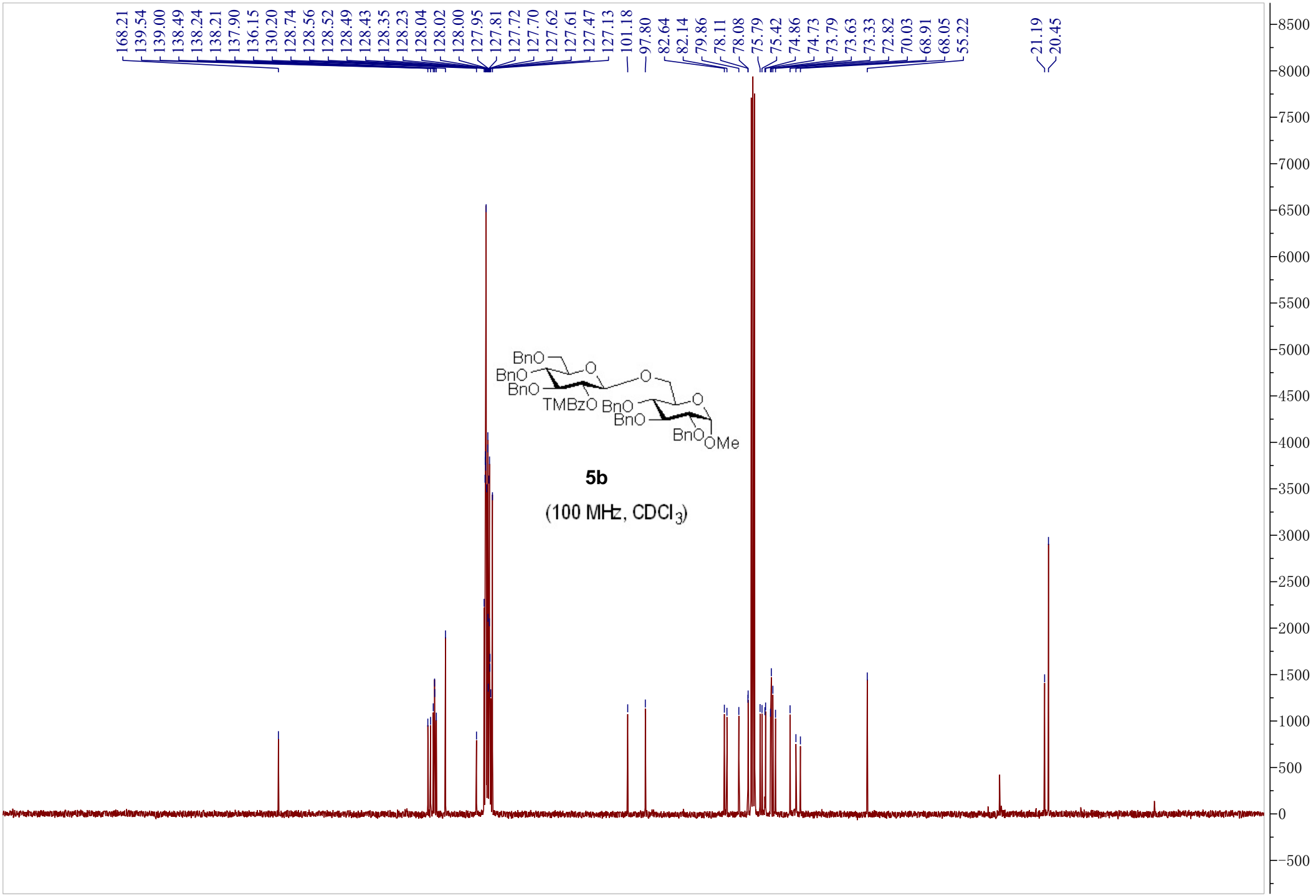
8.07 8.05 7.94 7.92 7.83 7.82 7.62 7.57 7.49 7.47 7.36 7.35 7.35 7.33 7.32 7.29 7.27 7.27 7.25 7.25 7.15 7.15 7.13 6.06 6.03 6.01 5.81 5.78 5.76 5.60 5.58 5.58 5.56 5.21 5.19 4.89 4.86 4.68 4.67 4.66 4.65 4.61 4.60 4.55 4.53 4.45 4.42 4.22 4.22 4.20 4.19 3.86 3.85 3.83 3.82 3.80 3.78 3.72 3.70 3.69 3.43 3.41 3.40 3.39 3.38 3.20 2.85

^{1}H-NMR of **5a**

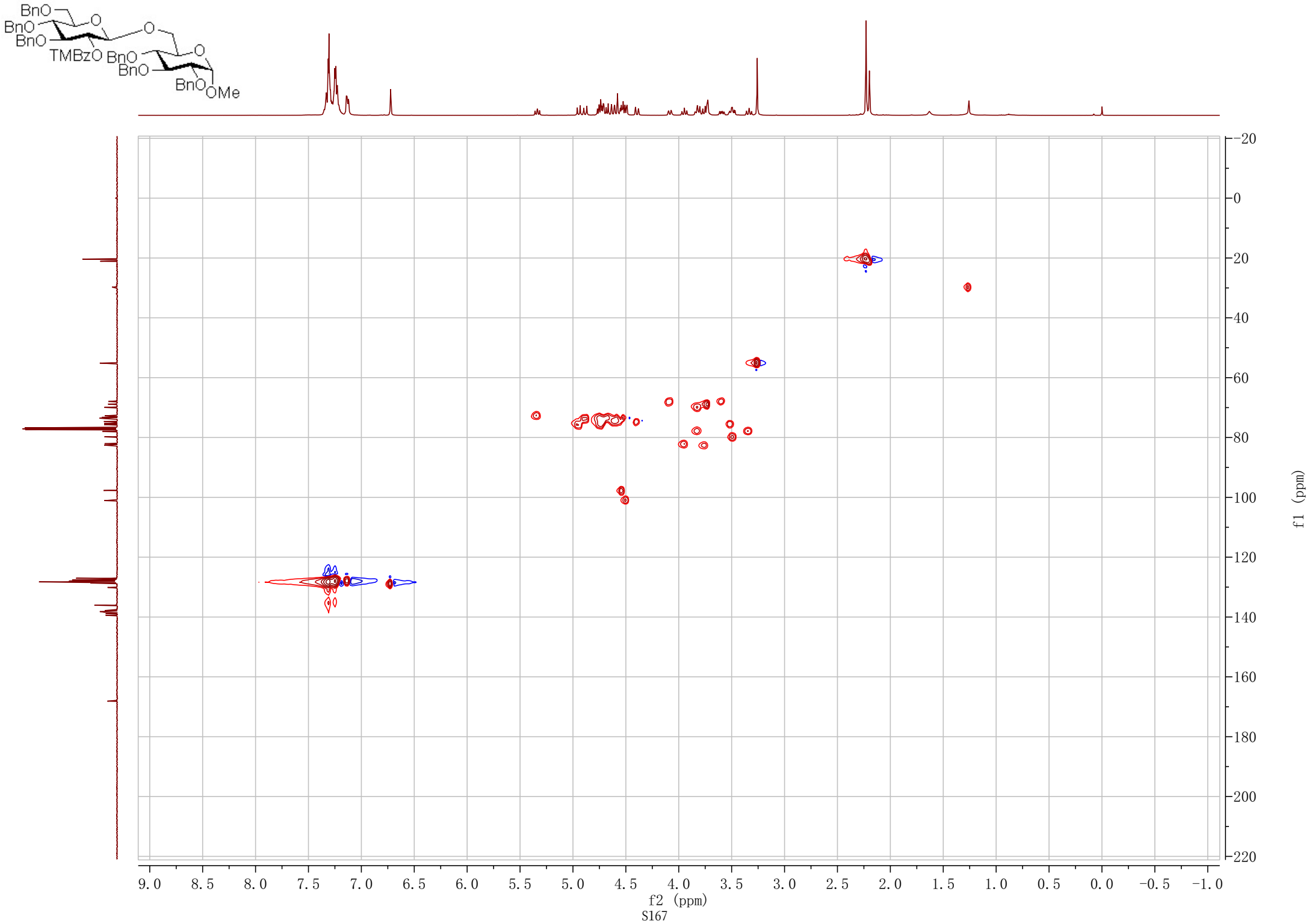


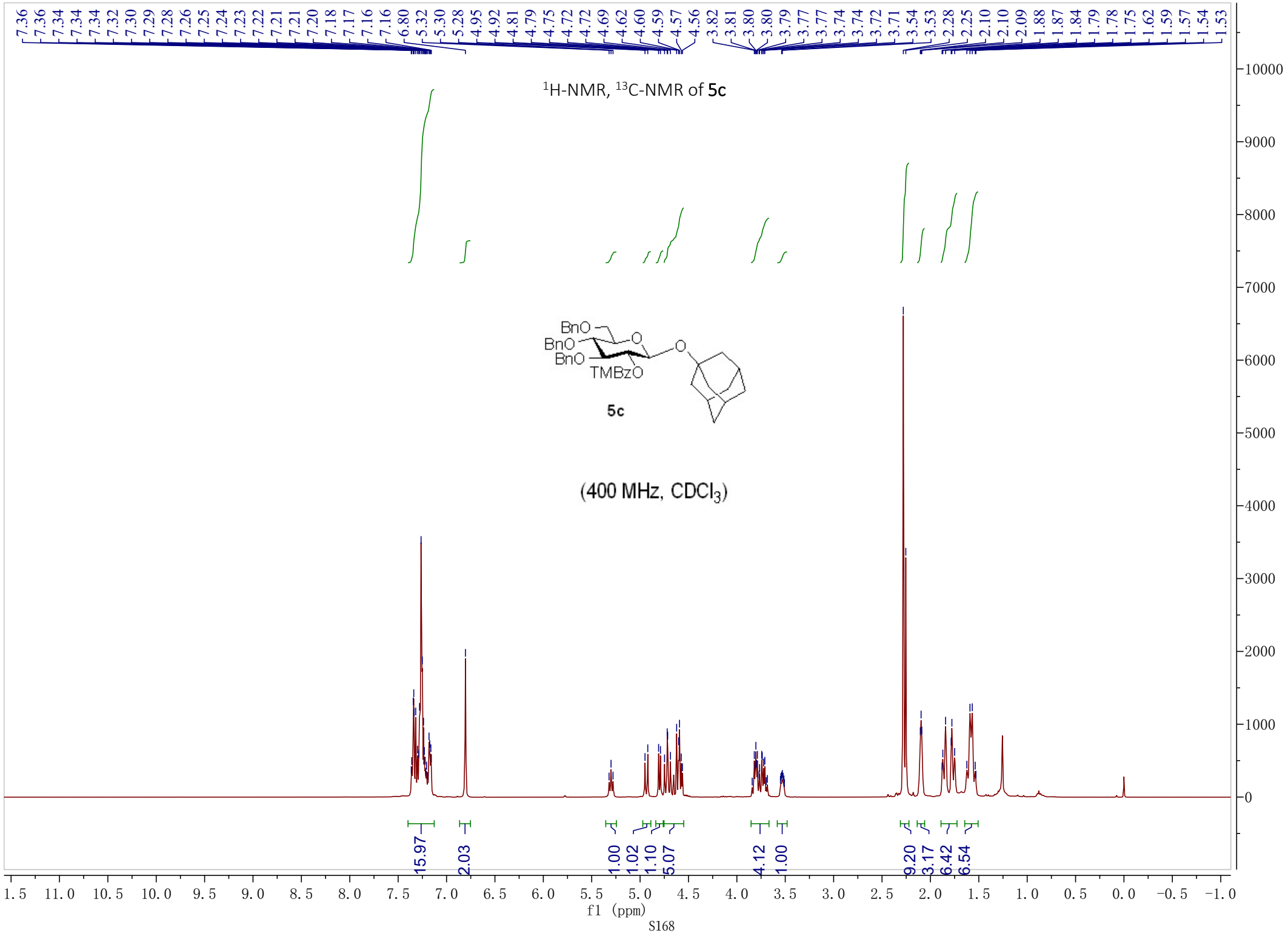
5a known compound
(400 MHz, acetone-d_6)

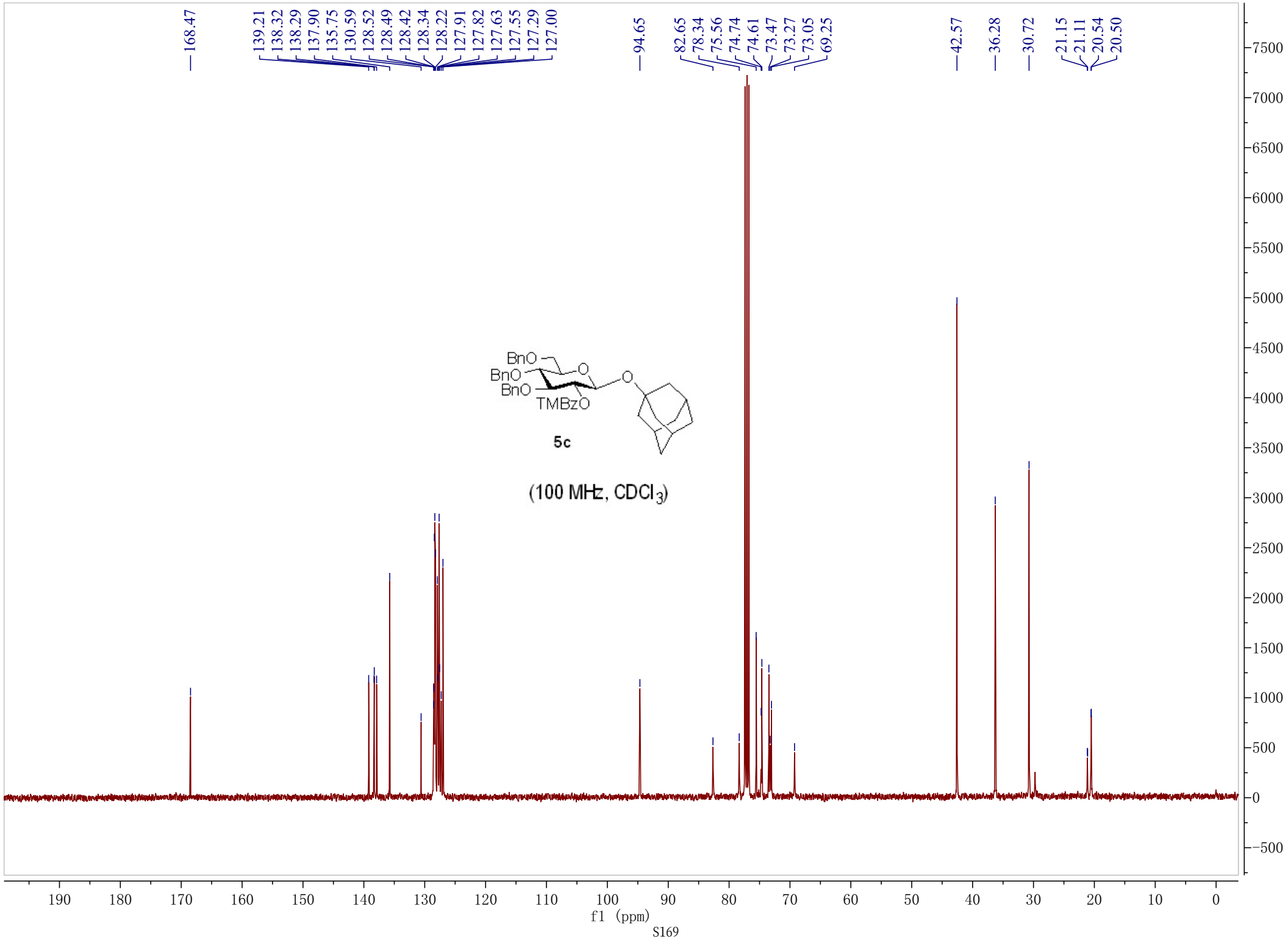

^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC of **5b**
BnO
BnO
BnO
TMBzO
BnO
BnO
BnO
OMe
5b
(400 MHz, $CDCl_3$)
f1 (ppm)

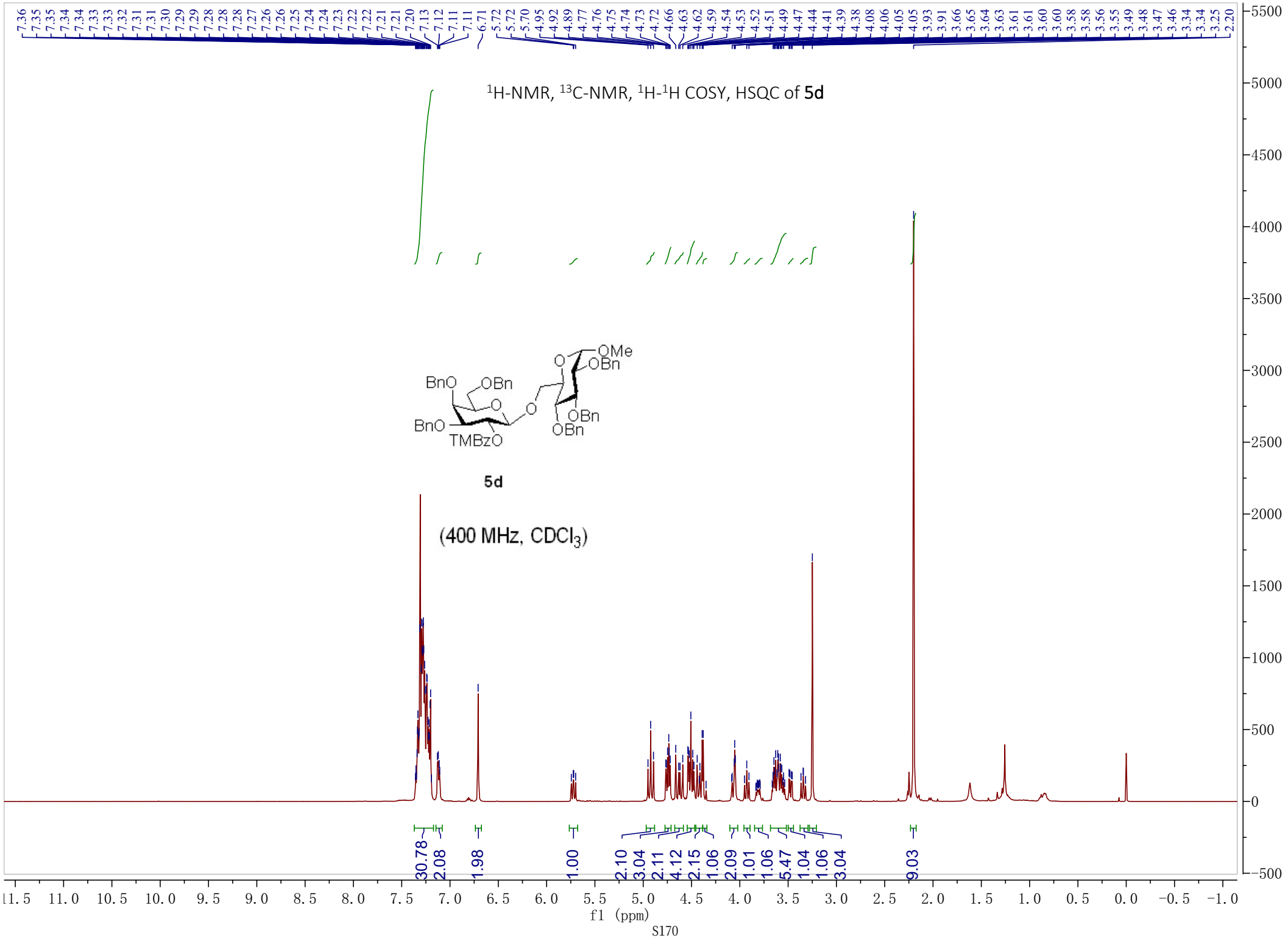

168.21
139.54
139.00
138.49
138.24
138.21
137.90
136.15
130.20
128.74
128.56
128.52
128.49
128.43
128.35
128.23
128.04
128.02
128.00
127.95
127.81
127.72
127.70
127.62
127.61
127.47
127.13
101.18
97.80
82.64
82.14
79.86
78.11
78.08
75.79
75.42
74.86
74.73
73.79
73.63
73.33
72.82
70.03
68.91
68.05
55.22
21.19
20.45
BnO
BnO
BnO
TMBzO
BnO
BnO
BnO
OMe
5b
(100 MHz, CDCl3)
f1 (ppm)

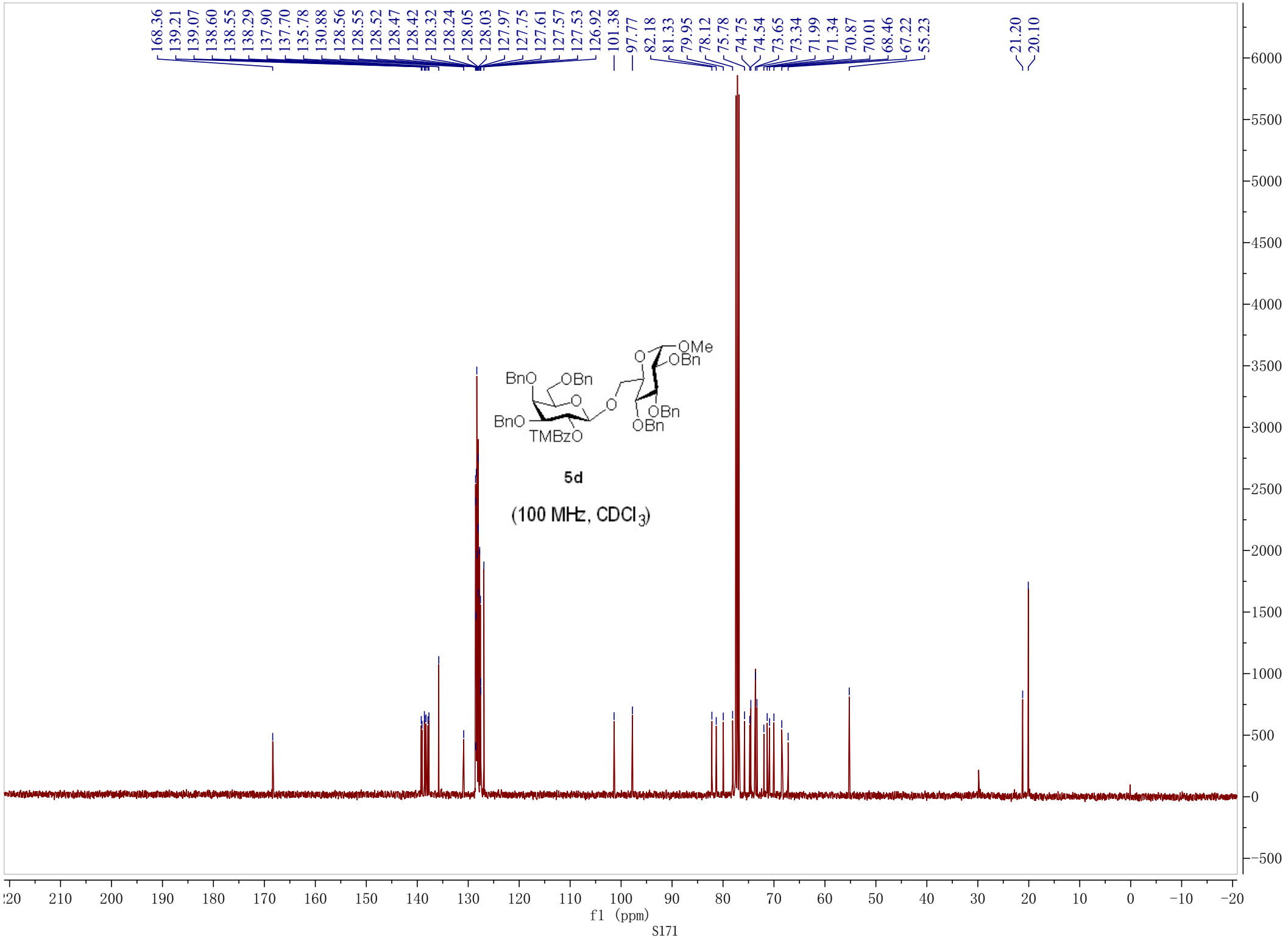

BnO
BnO
BnO
O
O
TMBzO
BnO
BnO
O
BnO
OMe
XK200804-1.4.ser
XK200804-1
f2 (ppm)
f1 (ppm)

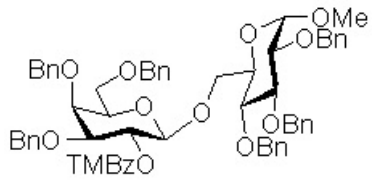

BnO
BnO
BnO
O
O
TMBzO
BnO
O
BnO
BnO
OMe
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-20
0
20
40
60
80
100
120
140
160
180
200
220


^{1}H-NMR, ^{13}C-NMR of **5c**
BnO
BnO
BnO
TMBzO
O
O
5c
(400 MHz, $CDCl_3$)
15.97
2.03
1.00
1.02
1.10
5.07
4.12
1.00
9.20
3.17
6.42
6.54
f1 (ppm)


168.47
139.21
138.32
138.29
137.90
135.75
130.59
128.52
128.49
128.42
128.34
128.22
127.91
127.82
127.63
127.55
127.29
127.00
94.65
82.65
78.34
75.56
74.74
74.61
73.47
73.27
73.05
69.25
42.57
36.28
30.72
21.15
21.11
20.54
20.50
BnO
BnO
BnO
TMBzO
O
O
5c
(100 MHz, CDCl3)
f1 (ppm)


^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC of **5d**
BnO
OBn
BnO
TMBzO
OMe
OBn
OBn
OBn
5d
(400 MHz, $CDCl_3$)
30.78
2.08
1.98
1.00
2.10
3.04
2.11
4.12
2.15
1.06
2.09
1.01
1.06
5.47
1.04
1.06
3.04
9.03
f1 (ppm)

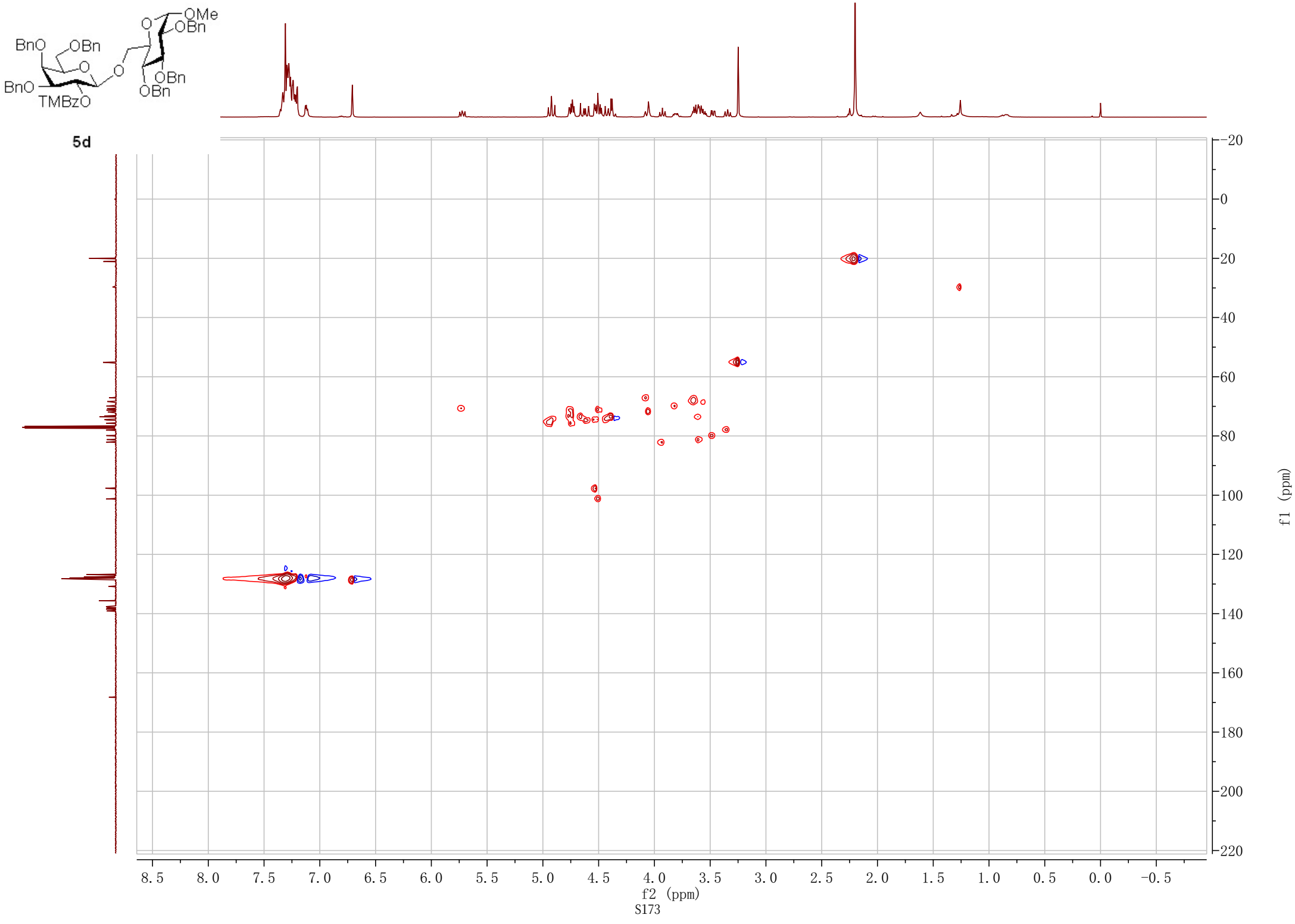

168.36
139.21
139.07
138.60
138.55
138.29
137.90
137.70
135.78
130.88
128.56
128.55
128.52
128.47
128.42
128.32
128.24
128.05
128.03
127.97
127.75
127.61
127.57
127.53
126.92
101.38
97.77
82.18
81.33
79.95
78.12
75.78
74.75
74.54
73.65
73.34
71.99
71.34
70.87
70.01
68.46
67.22
55.23
21.20
20.10
BnO
OBn
BnO
TMBzO
OMe
OBn
OBn
OBn
5d
(100 MHz, CDCl3)
f1 (ppm)



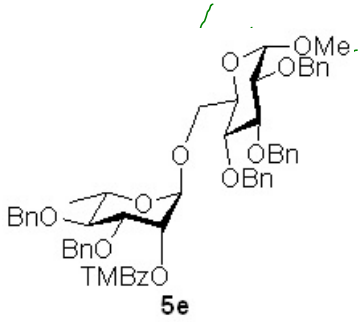
5d

f2 (ppm)

f1 (ppm)


OMe
OBn
BnO
OBn
O
O
OBn
BnO
OBn
TMBzO
5d
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-20
0
20
40
60
80
100
120
140
160
180
200
220

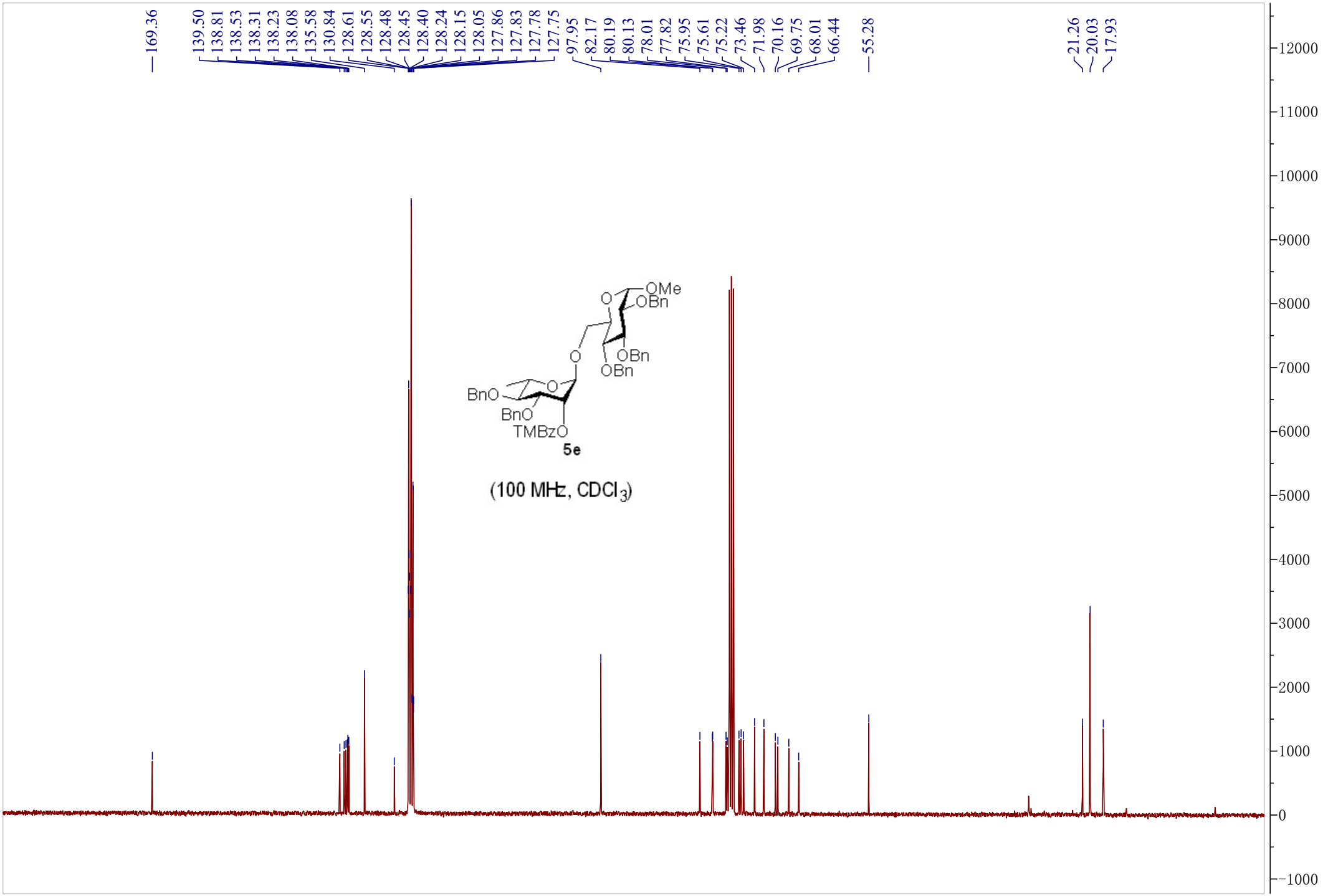
^{1}H-NMR, ^{13}C-NMR, HSQC, NOESY of **5e**

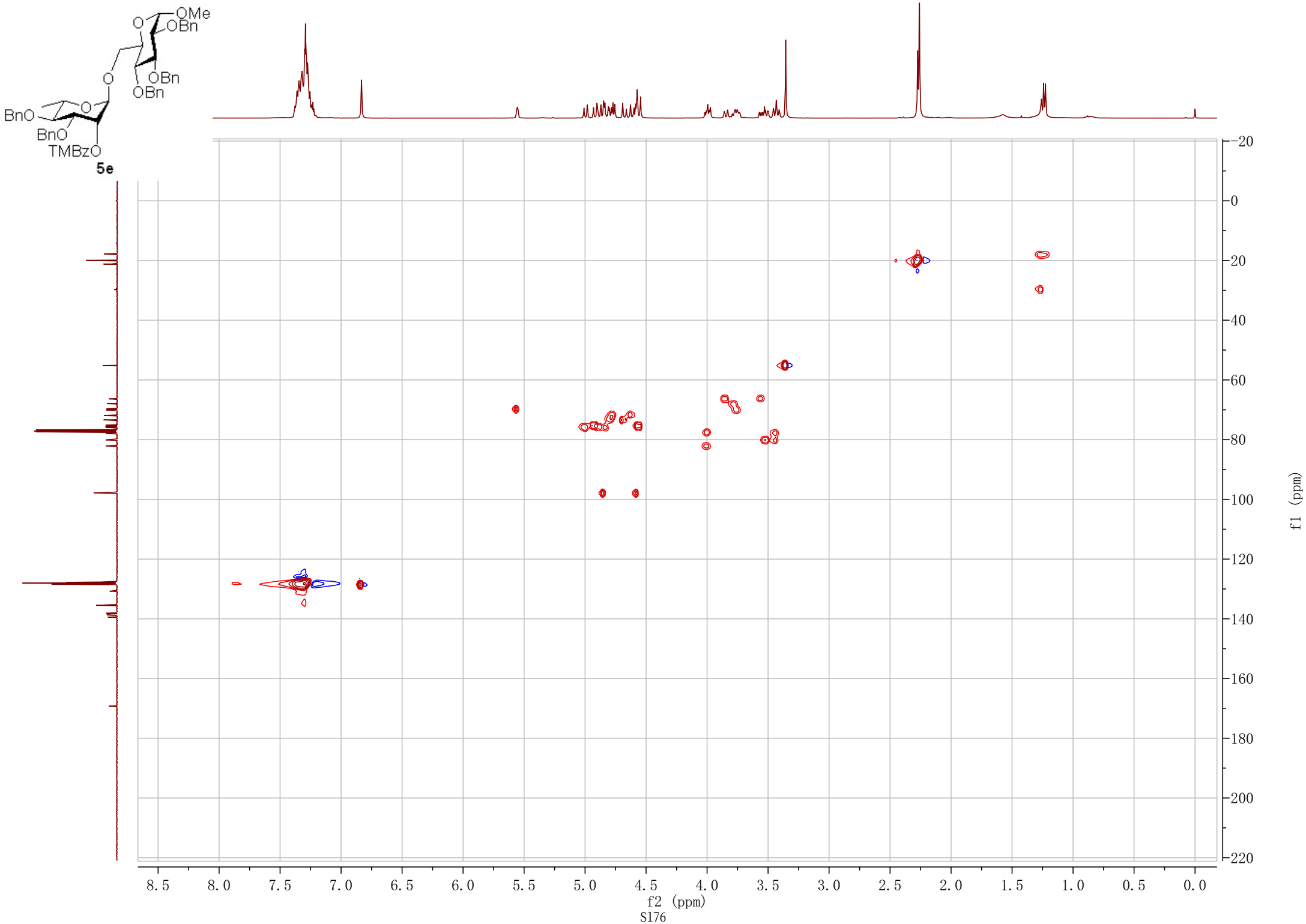


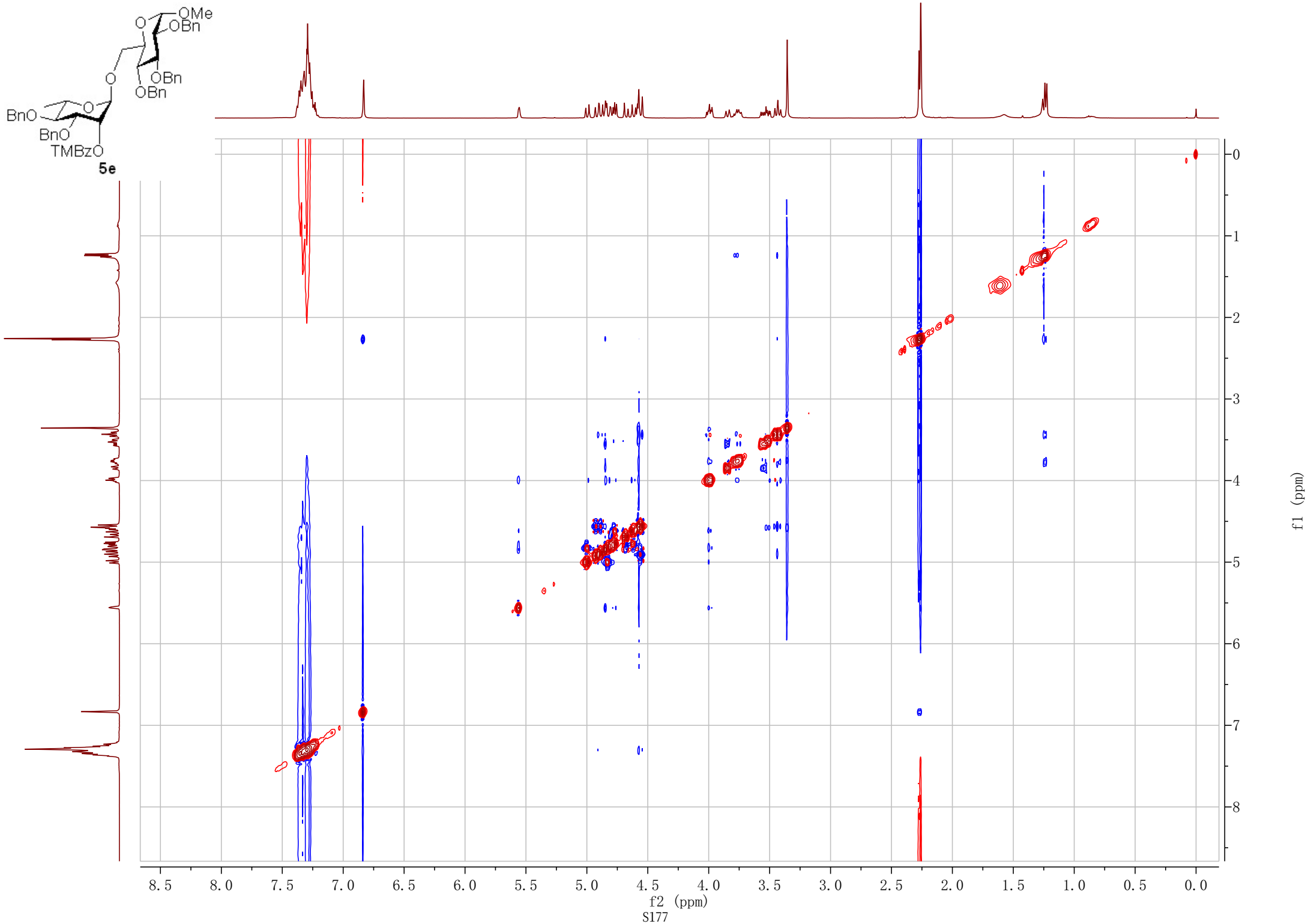
5e

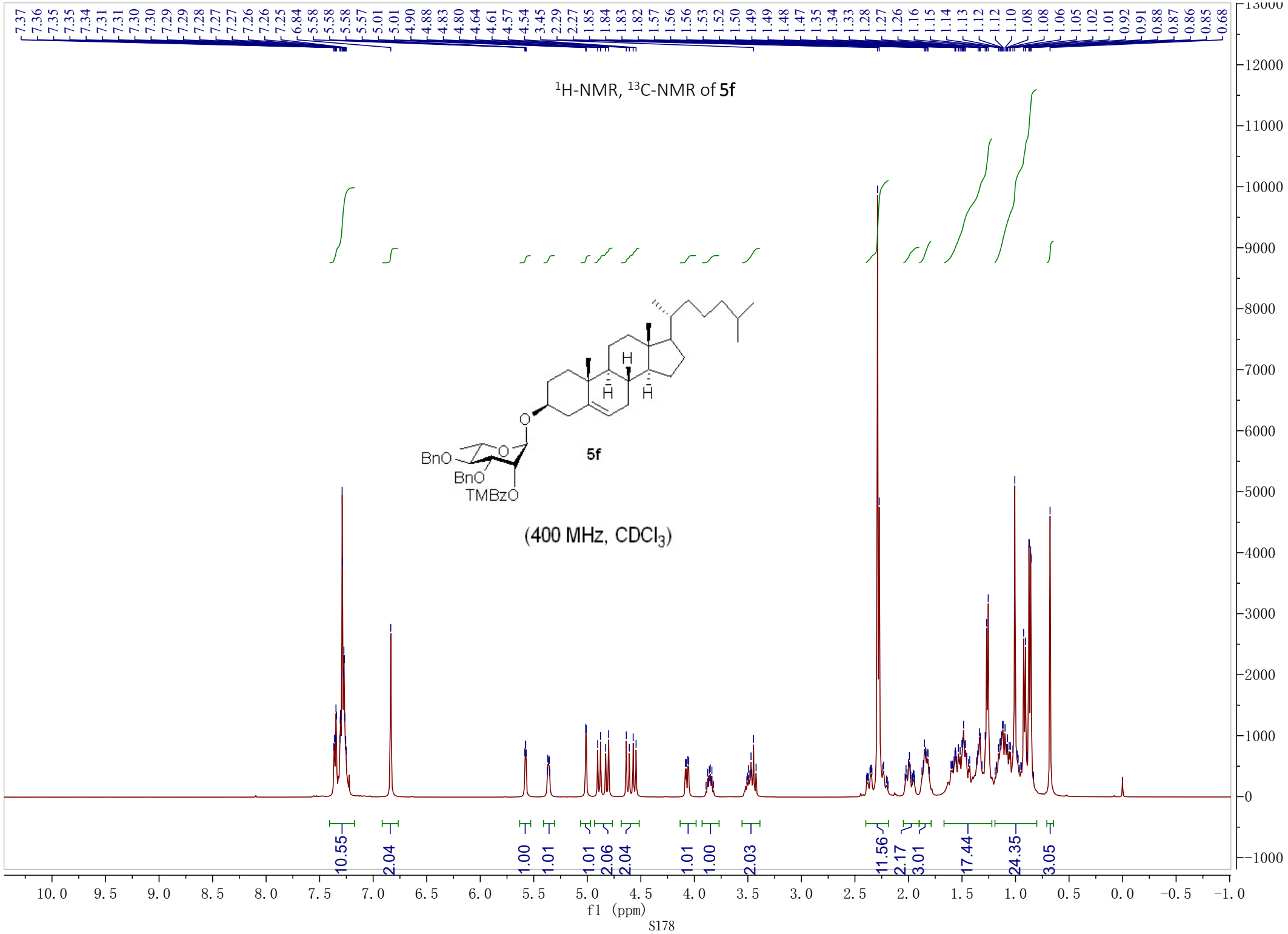
(400 MHz, $CDCl_3$)

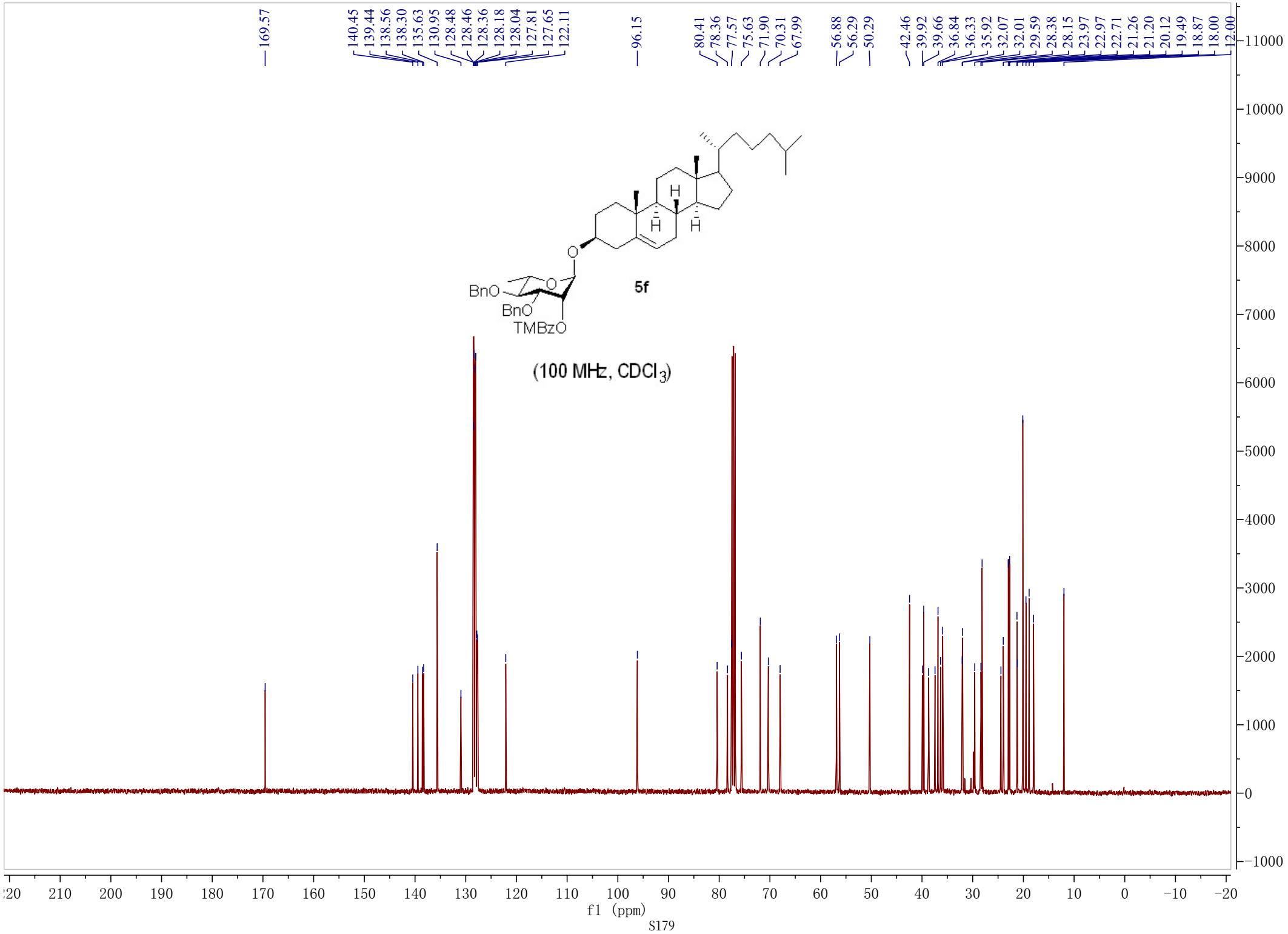
f1 (ppm)


169.36
139.50
138.81
138.53
138.31
138.23
138.08
135.58
130.84
128.61
128.55
128.48
128.45
128.40
128.24
128.15
128.05
127.86
127.83
127.78
127.75
97.95
82.17
80.19
80.13
78.01
77.82
75.95
75.61
75.22
73.46
71.98
70.16
69.75
68.01
66.44
55.28
21.26
20.03
17.93
OMe
OBn
OBn
OBn
BnO
BnO
TMBzO
5e
(100 MHz, CDCl3)
f1 (ppm)

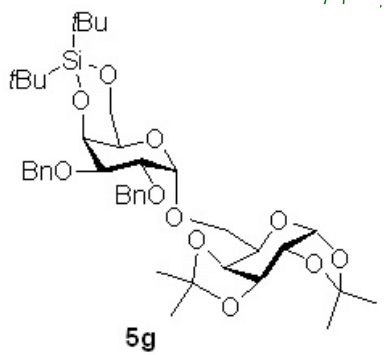

OMe
OBn
OBn
OBn
BnO
BnO
TMBzO
5e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)


OMe
OBn
OBn
OBn
BnO
BnO
TMBzO
5e
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8


^{1}H-NMR, ^{13}C-NMR of **5f**
BnO
BnO
TMBzO
O
O
H
H
H
5f
(400 MHz, $CDCl_3$)
10.55
2.04
1.00
1.01
1.01
2.06
2.04
1.01
1.00
2.03
11.56
2.17
3.01
17.44
24.35
3.05
f1 (ppm)

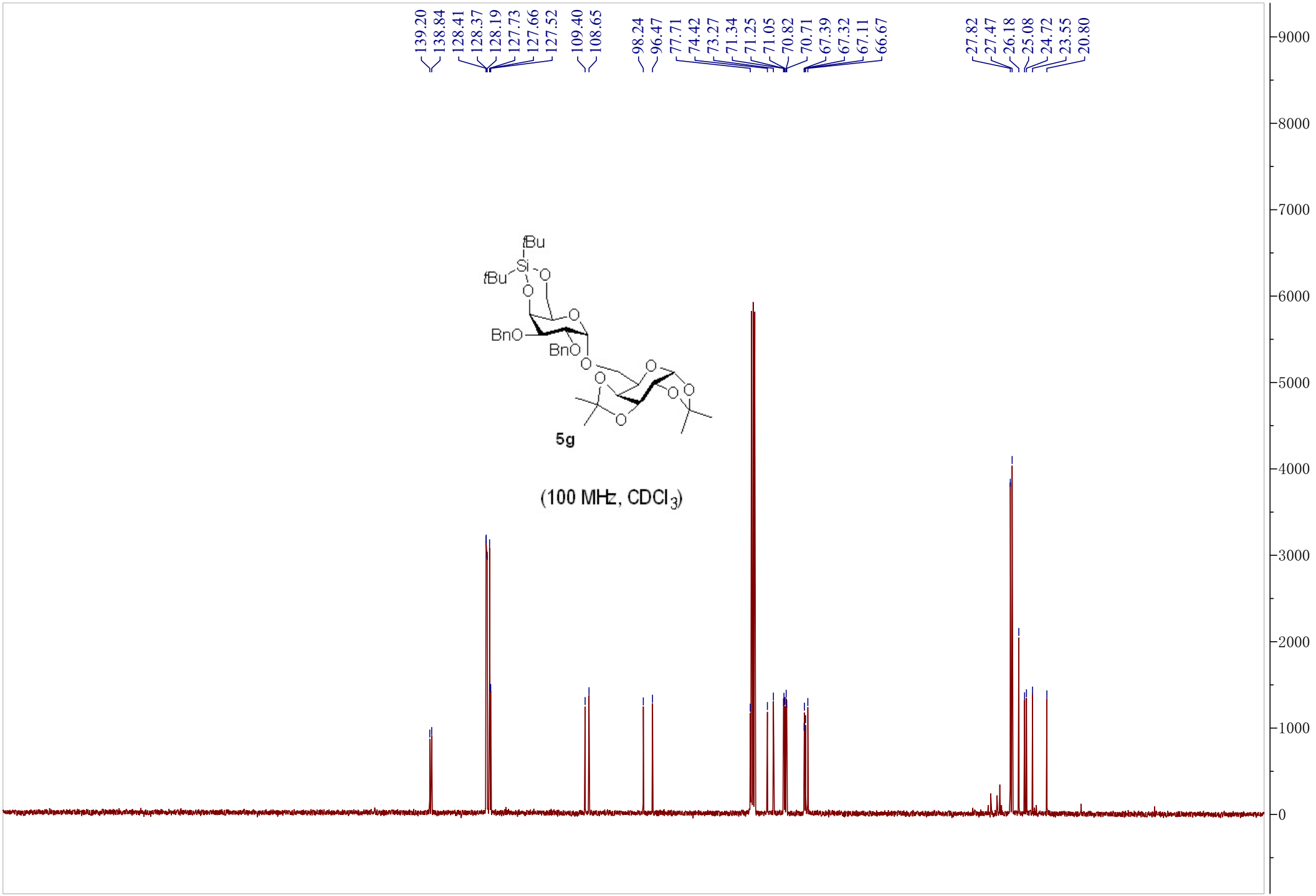

169.57
140.45
139.44
138.56
138.30
135.63
130.95
128.48
128.46
128.36
128.18
128.04
127.81
127.65
122.11
96.15
80.41
78.36
77.57
75.63
71.90
70.31
67.99
56.88
56.29
50.29
42.46
39.92
39.66
36.84
36.33
35.92
32.07
32.01
29.59
28.38
28.15
23.97
22.97
22.71
21.26
21.20
20.12
19.49
18.87
18.00
12.00
BnO
BnO
TMBzO
5f
(100 MHz, CDCl3)
f1 (ppm)

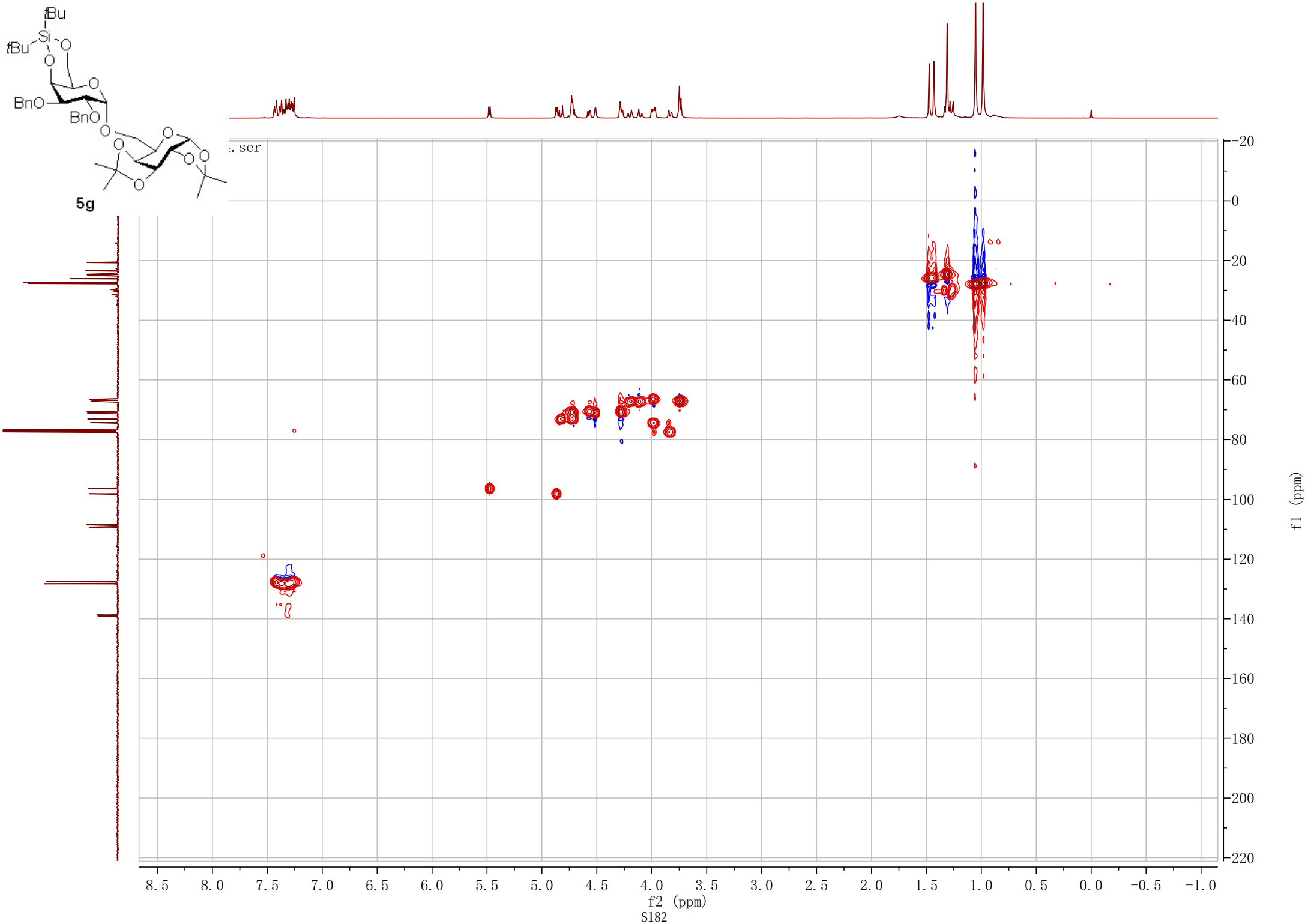
^{1}H-NMR, ^{13}C-NMR, HSQC of **5g**



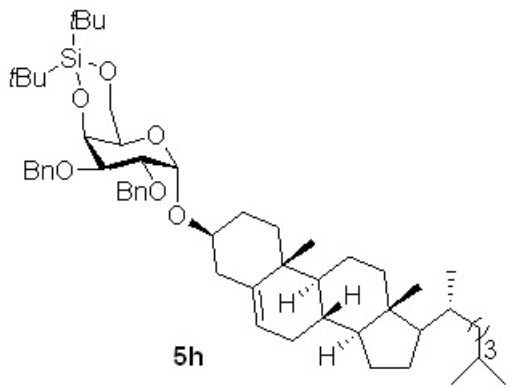
5g

(400 MHz, $CDCl_3$)

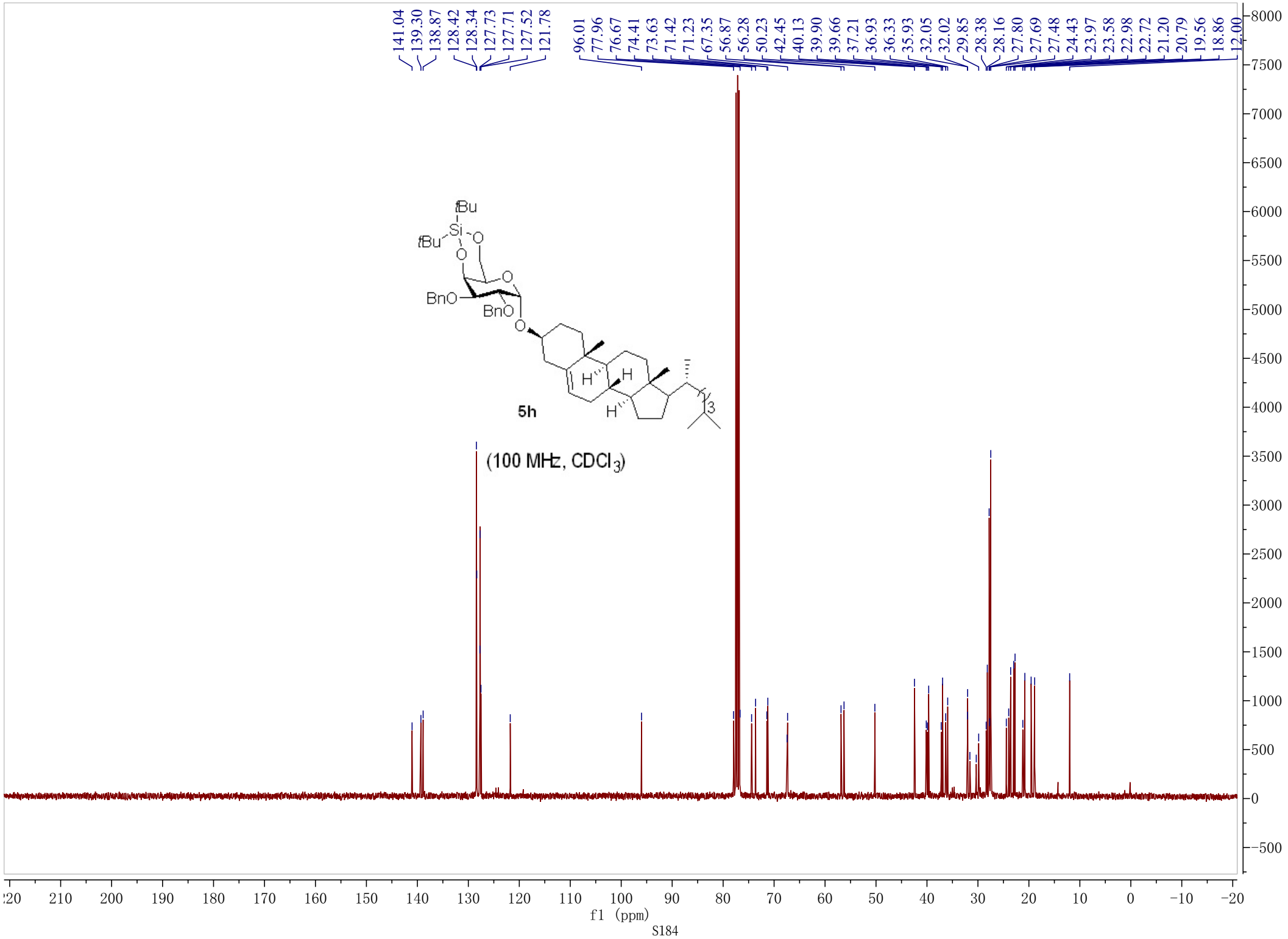

139.20
138.84
128.41
128.37
128.19
127.73
127.66
127.52
109.40
108.65
98.24
96.47
77.71
74.42
73.27
71.34
71.25
71.05
70.82
70.71
67.39
67.32
67.11
66.67
27.82
27.47
26.18
25.08
24.72
23.55
20.80
tBu
Si
tBu
O
BnO
BnO
5g
(100 MHz, CDCl3)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

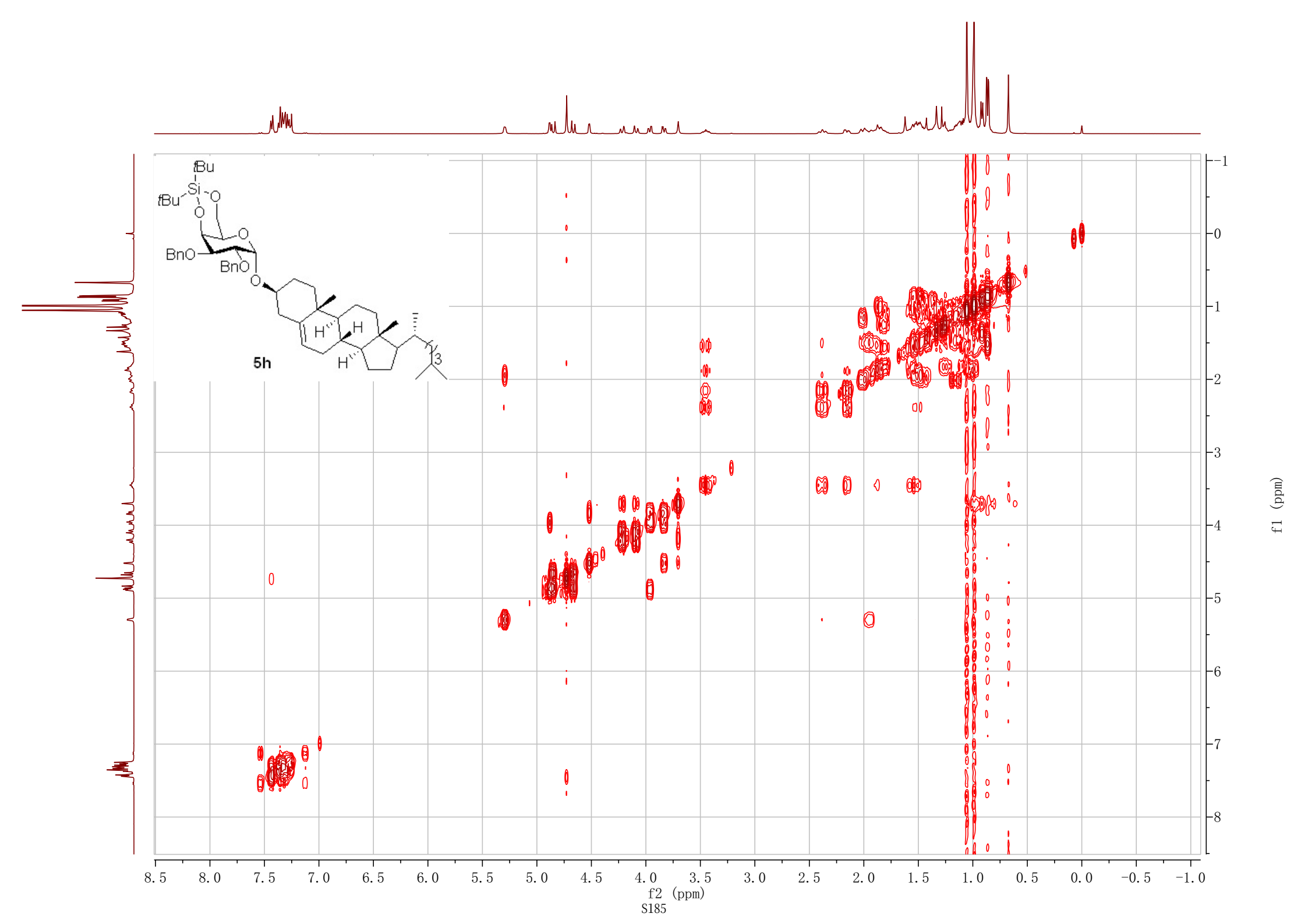

tBu
tBu
Si
O
BnO
BnO
5g
. ser
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)

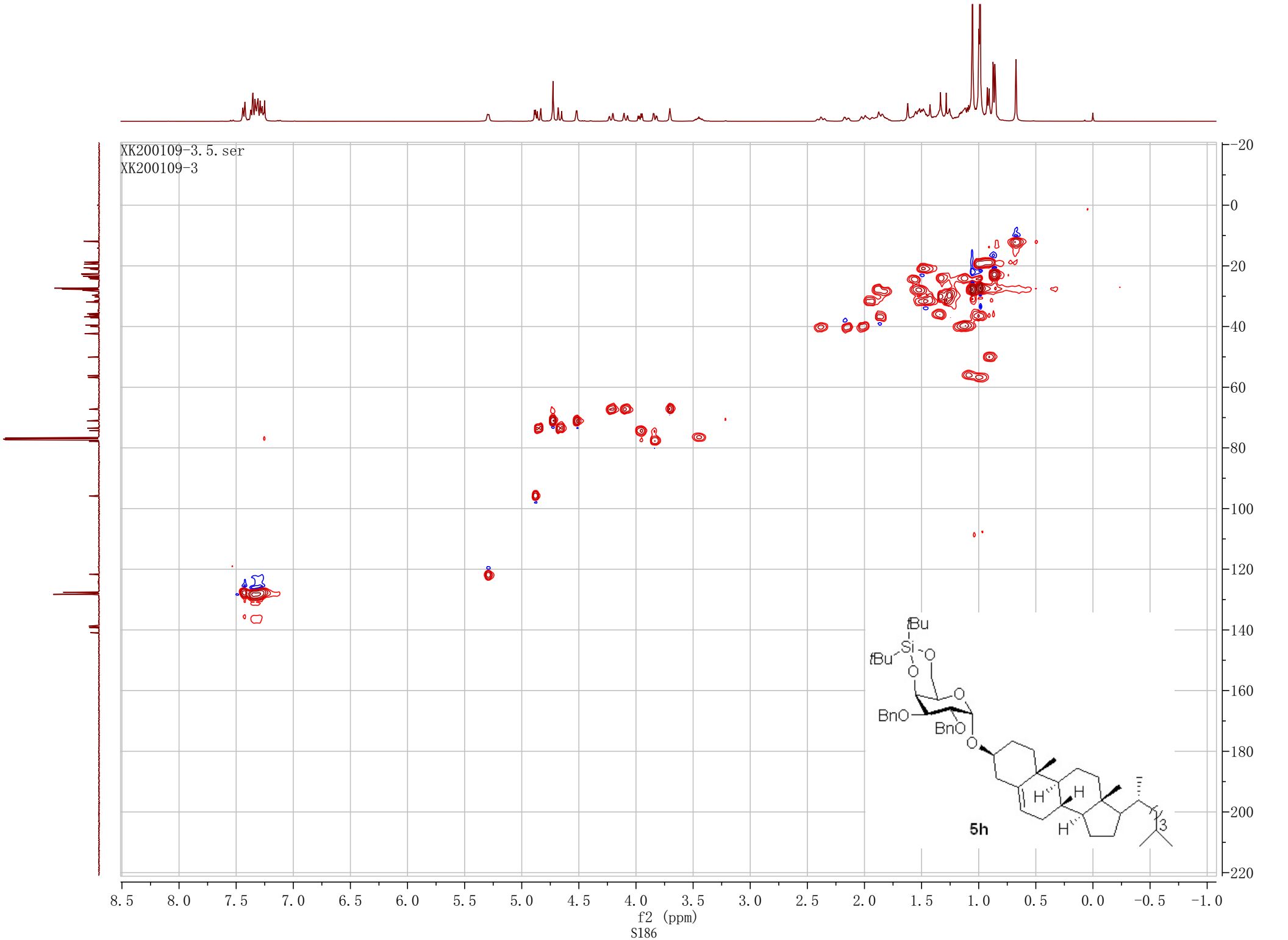
^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC of **5h**

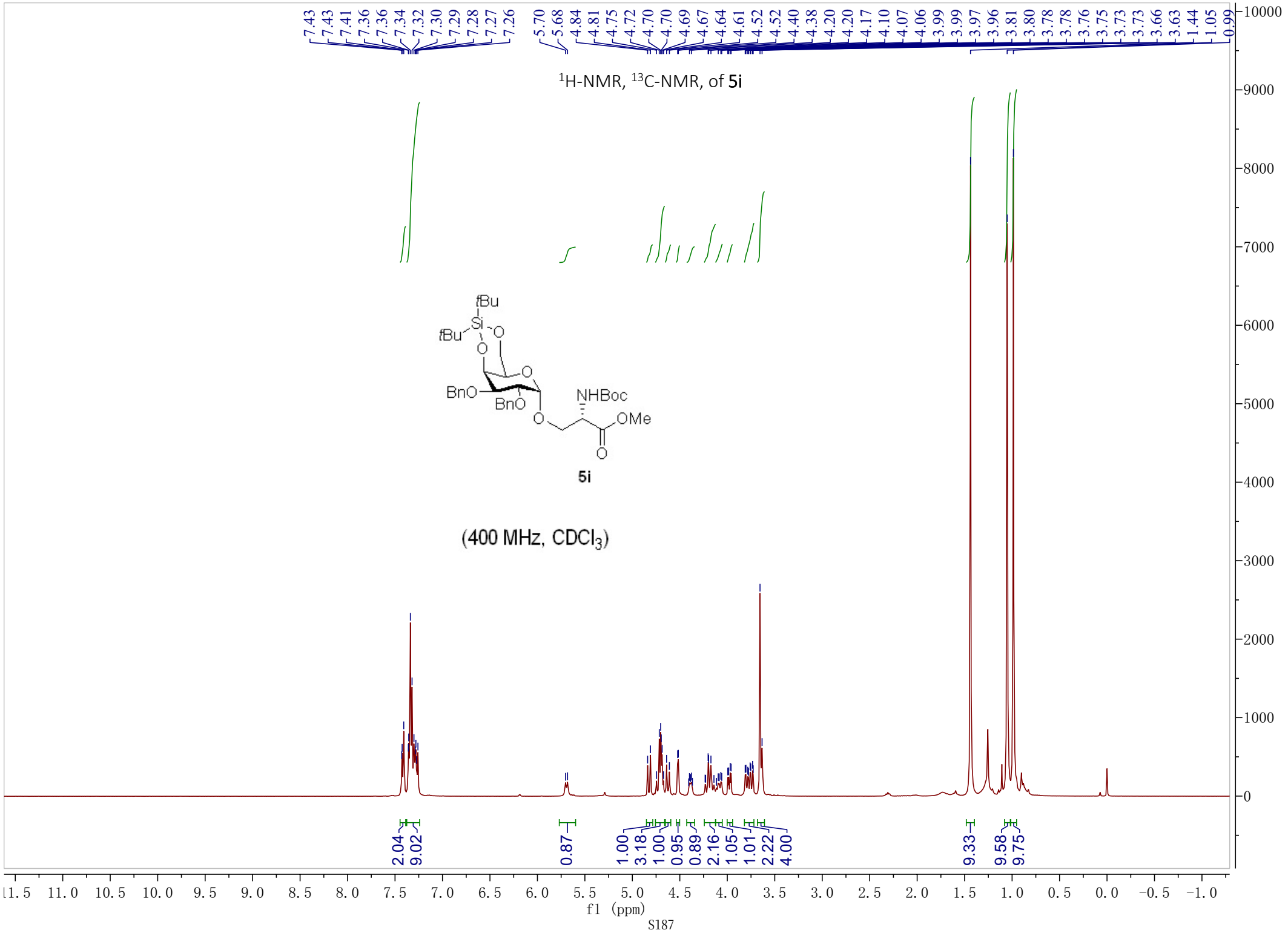


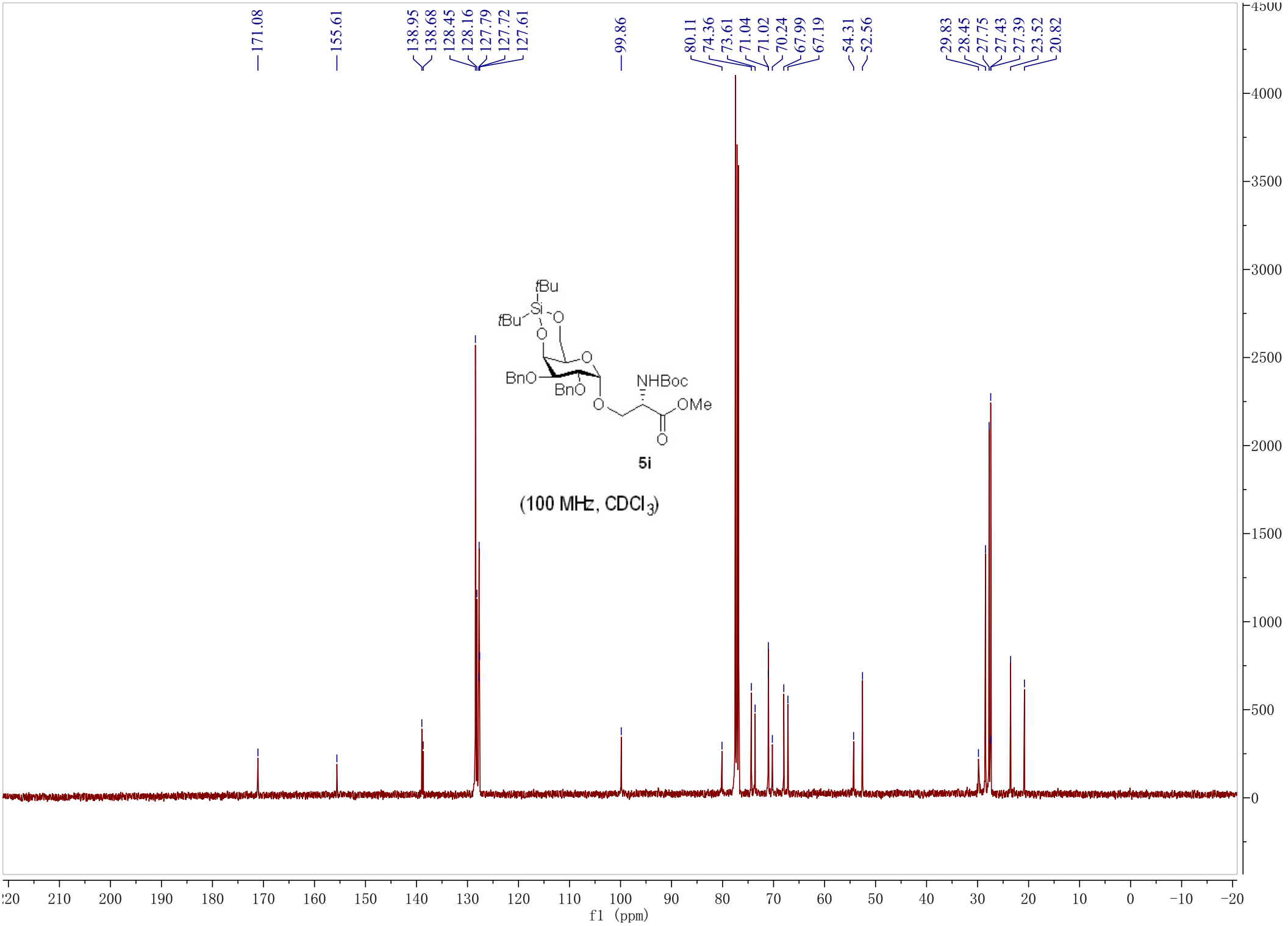
(400 MHz, $CDCl_3$)

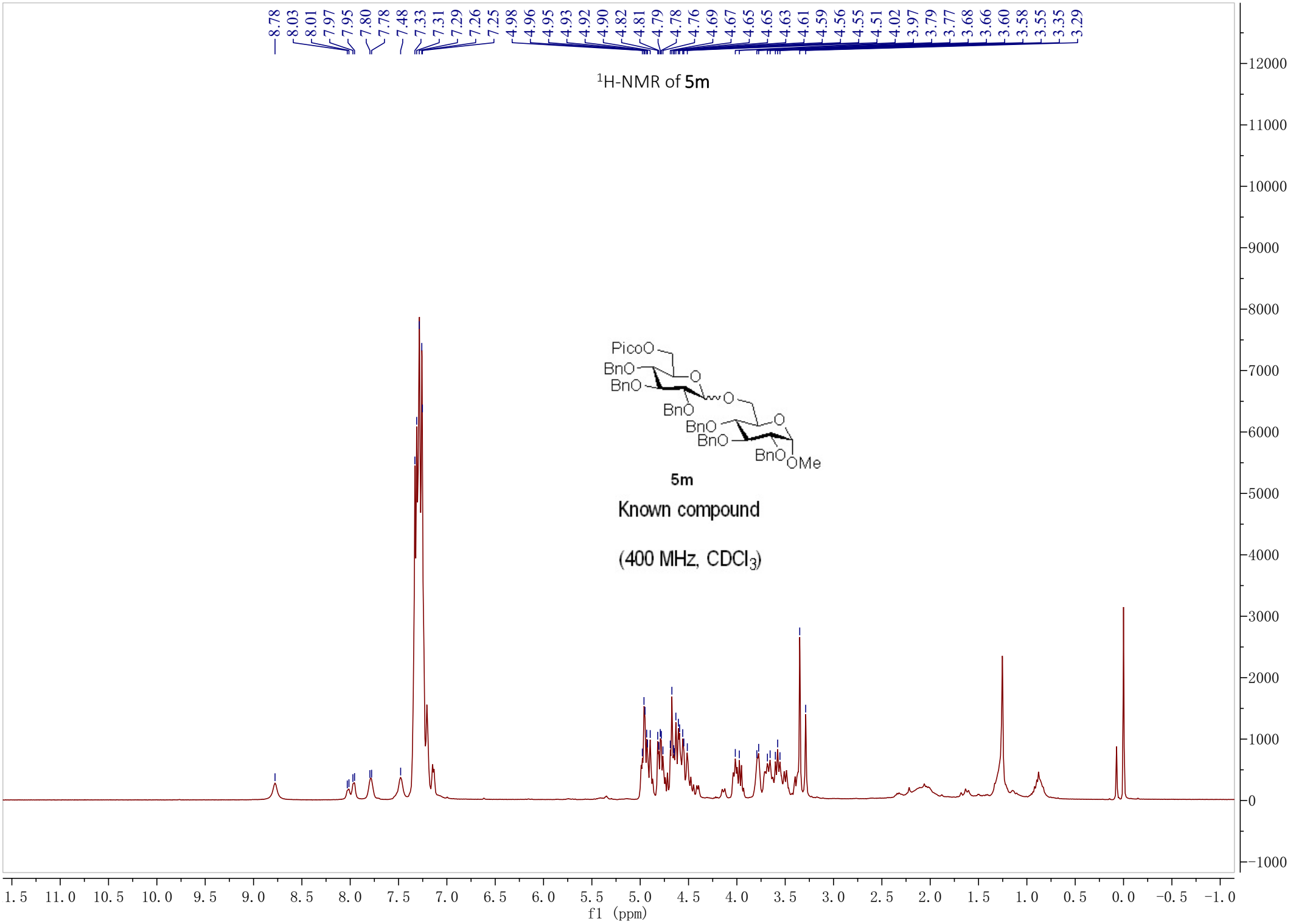

141.04
139.30
138.87
128.42
128.34
127.73
127.71
127.52
121.78
96.01
77.96
76.67
74.41
73.63
71.42
71.23
67.35
56.87
56.28
50.23
42.45
40.13
39.90
39.66
37.21
36.93
36.33
35.93
32.05
32.02
29.85
28.38
28.16
27.80
27.69
27.48
24.43
23.97
23.58
22.98
22.72
21.20
20.79
19.56
18.86
12.00
tBu
Si
tBu
O
BnO
BnO
H
H
H
3
5h
(100 MHz, CDCl3)
f1 (ppm)


tBu
Si
tBu
O
O
O
BnO
BnO
O
H
H
H
3
5h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)


XK200109-3.5.ser
XK200109-3
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-20
0
20
40
60
80
100
120
140
160
180
200
220
tBu
tBu
Si
O
O
O
O
BnO
BnO
O
H
H
H
3
5h

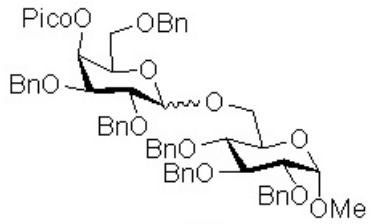

7.43 7.43 7.41 7.36 7.36 7.34 7.32 7.30 7.29 7.28 7.27 7.26
5.70 5.68 4.84 4.81 4.75 4.72 4.70 4.70 4.69 4.67 4.64 4.61 4.52 4.52 4.40 4.38 4.20 4.20 4.17 4.10 4.07 4.06 3.99 3.99 3.97 3.96 3.81 3.80 3.78 3.78 3.76 3.75 3.73 3.73 3.66 3.63 1.44 1.05 0.99
1H-NMR, 13C-NMR, of 5i
fBu
Si
fBu
O
O
O
BnO
BnO
NHBoc
OMe
O
O
5i
(400 MHz, CDCl3)
2.04 9.02 0.87 1.00 3.18 1.00 0.95 0.89 2.16 1.05 1.01 2.22 4.00 9.33 9.58 9.75
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


171.08
155.61
138.95
138.68
128.45
128.16
127.79
127.72
127.61
99.86
80.11
74.36
73.61
71.04
71.02
70.24
67.99
67.19
54.31
52.56
29.83
28.45
27.75
27.43
27.39
23.52
20.82
tBu
tBu
Si
O
O
O
O
BnO
BnO
NHBoc
OMe
O
O
5i
(100 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
f1 (ppm)


8.78
8.03
8.01
7.97
7.95
7.80
7.78
7.48
7.33
7.31
7.29
7.26
7.25
4.98
4.96
4.95
4.93
4.92
4.90
4.82
4.81
4.79
4.78
4.76
4.69
4.67
4.65
4.65
4.63
4.61
4.59
4.56
4.55
4.51
4.02
3.97
3.79
3.77
3.68
3.66
3.60
3.58
3.55
3.35
3.29
1H-NMR of 5m
PicoO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
OMe
5m
Known compound
(400 MHz, CDCl3)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
1.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

XK200102-4.1.fid
XK200102-4

^{1}H-NMR of **5n**



5n

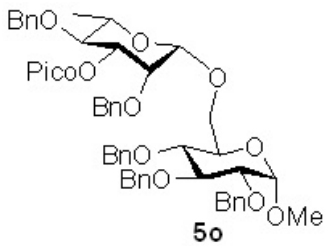
Known compound

(400 MHz, $CDCl_3$)

f1 (ppm)

XK200115-1.fid

^{1}H-NMR of **5o**



5o

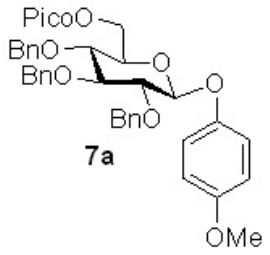
Known compound

(400 MHz, $CDCl_3$)

f1 (ppm)

XK201118.1.fid
XK201118

^{1}H-NMR, ^{13}C-NMR of **7a**

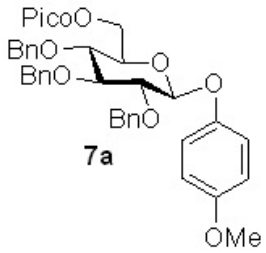


7a

(400 MHz, $CDCl_3$)

XK201118.2.fid
XK201118

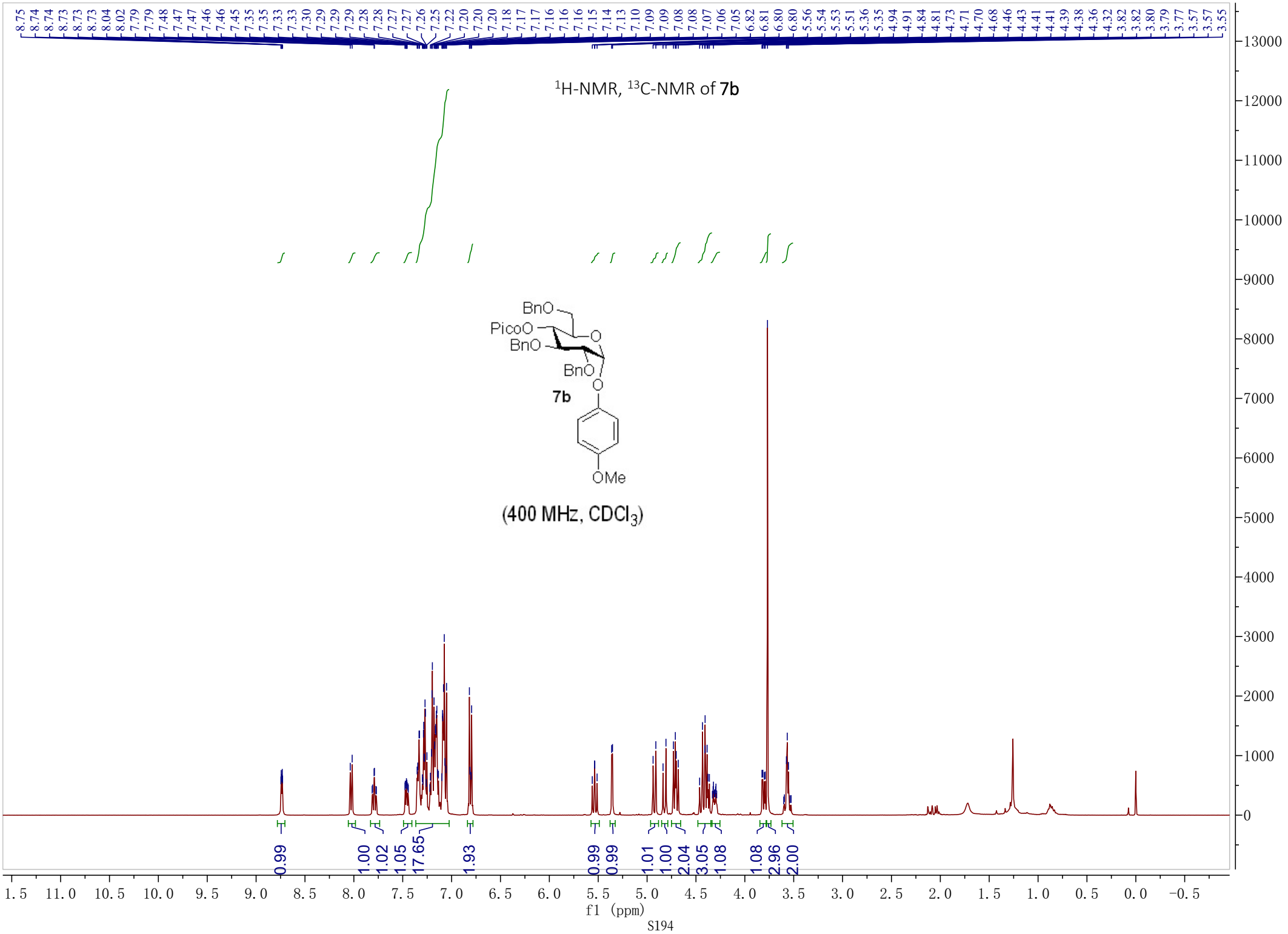
164.56
155.34
151.31
149.96
147.73
138.32
138.19
137.62
136.99
128.54
128.49
128.48
128.23
128.13
128.03
128.00
127.98
127.86
127.81
126.98
125.34
118.59
114.46
102.79
84.74
82.04
77.74
75.92
75.10
75.08
73.05
64.43
55.61

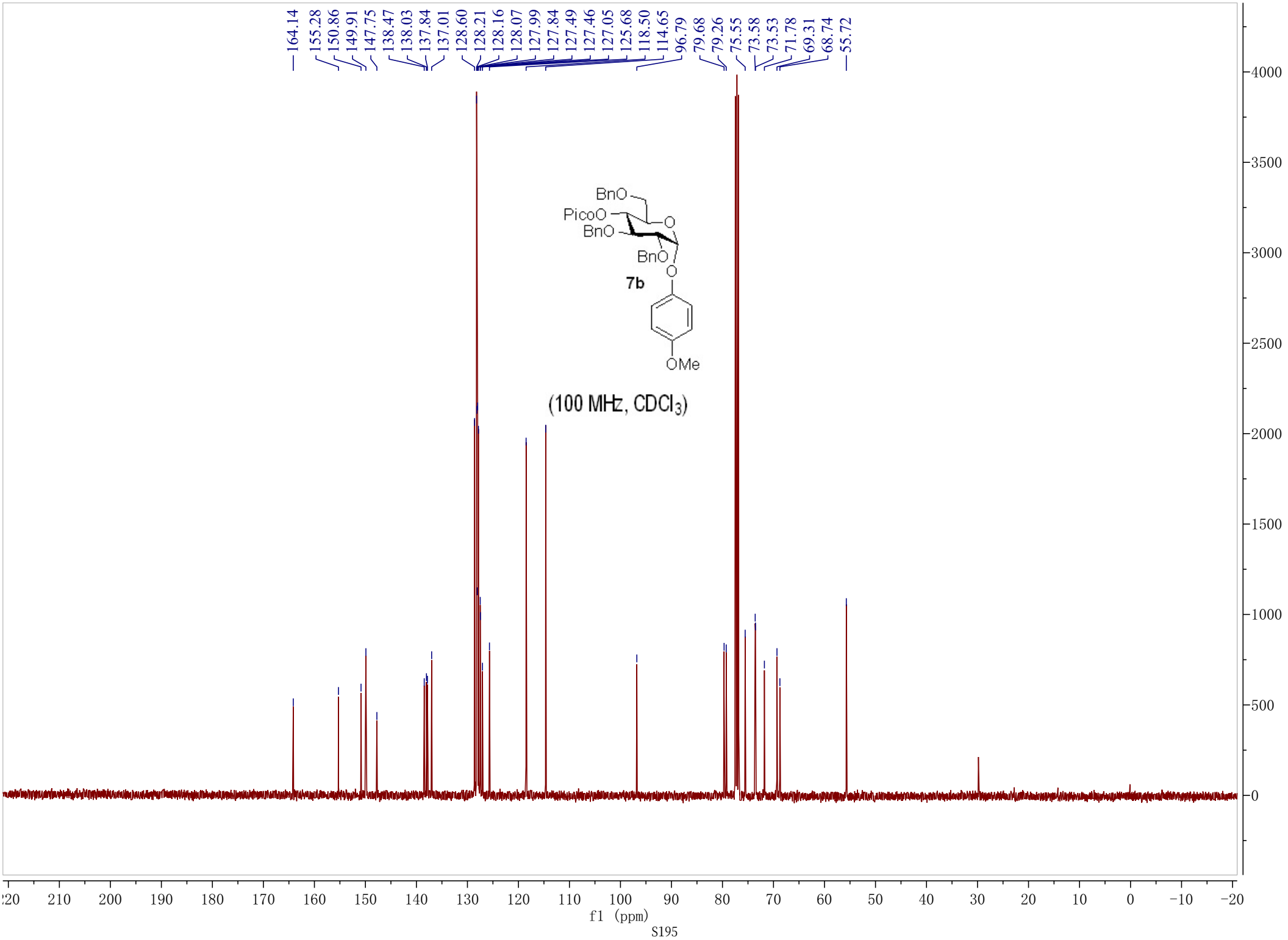


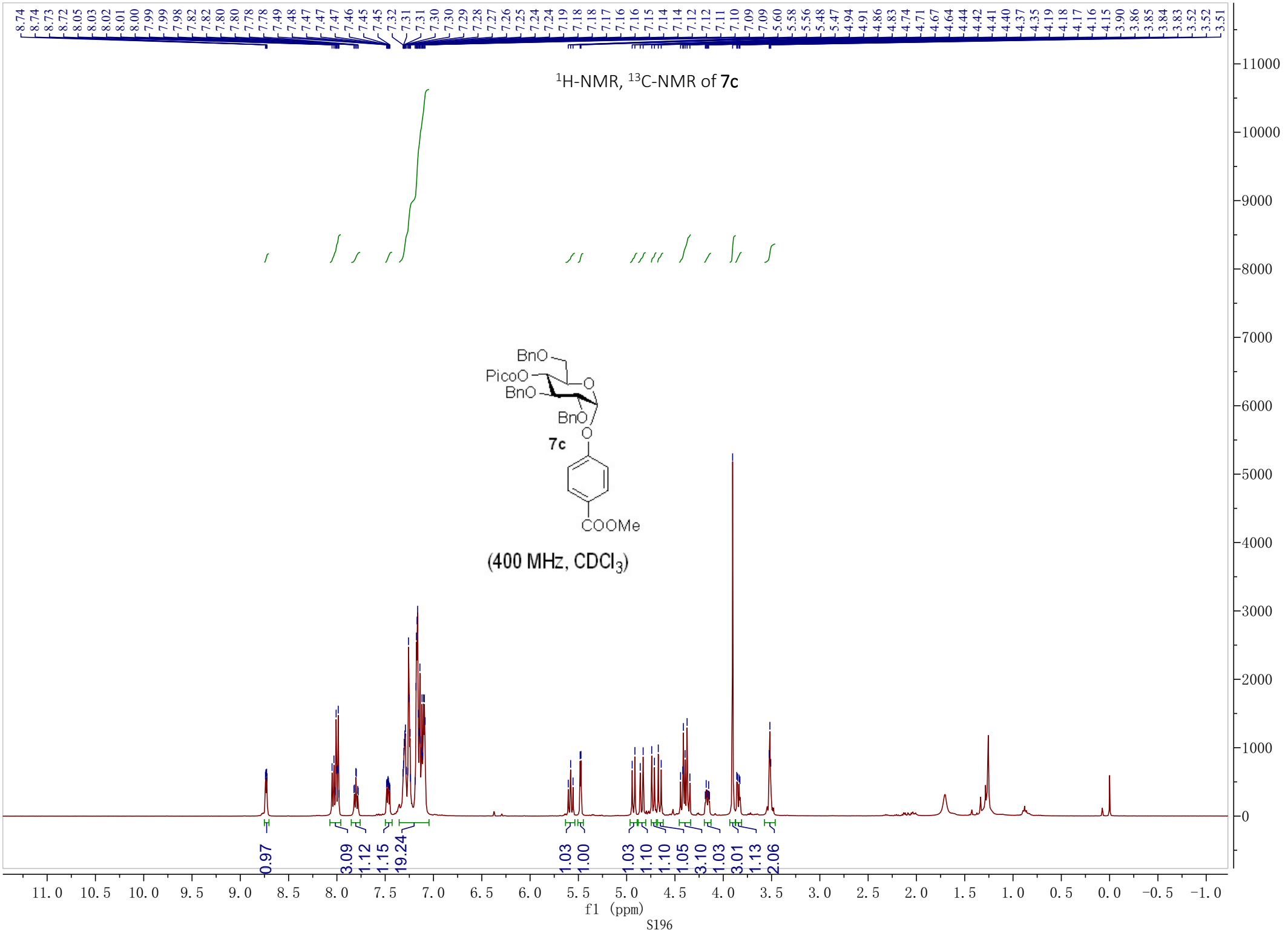
7a

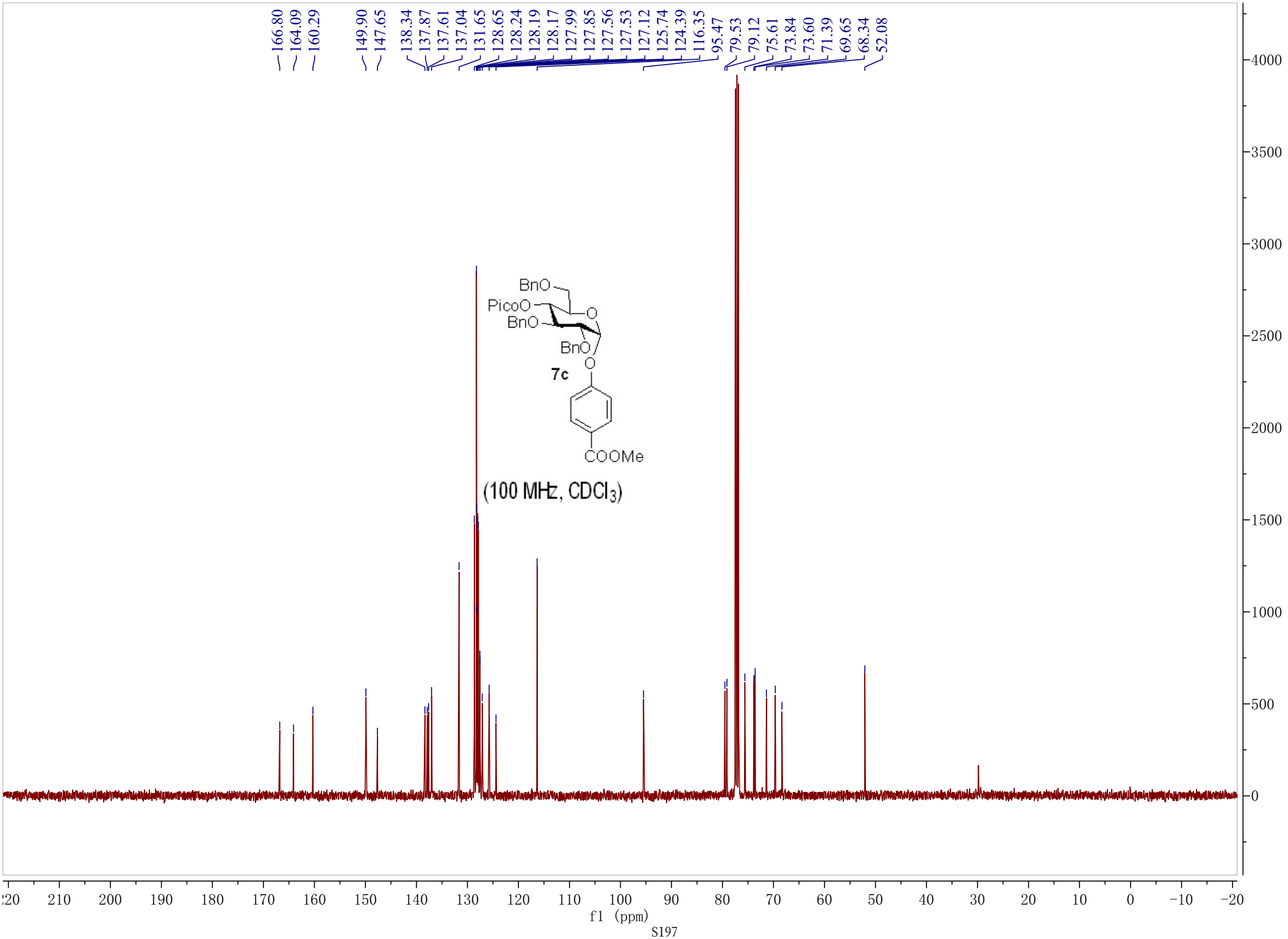
(100 MHz, $CDCl_3$)

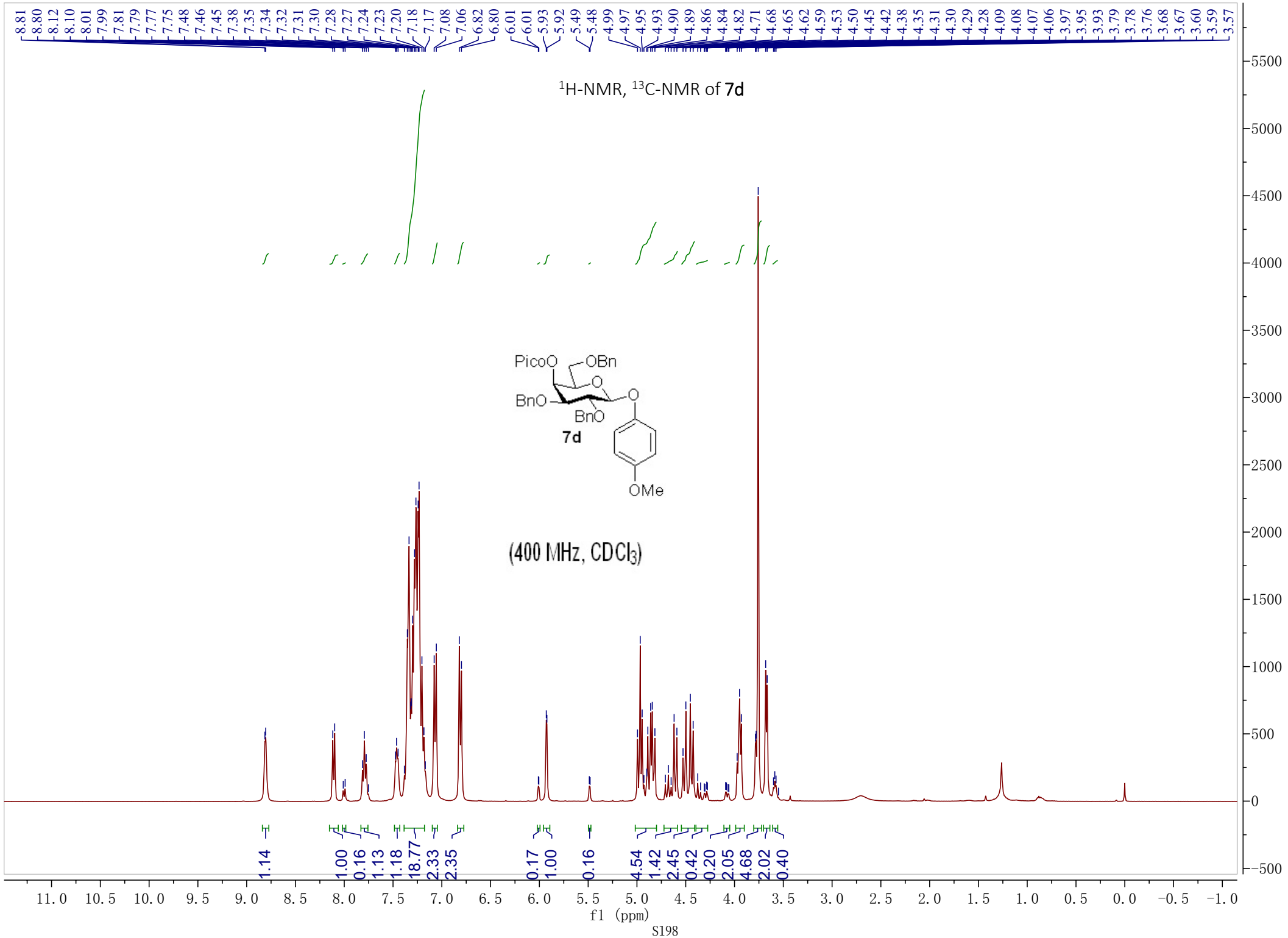
f1 (ppm)

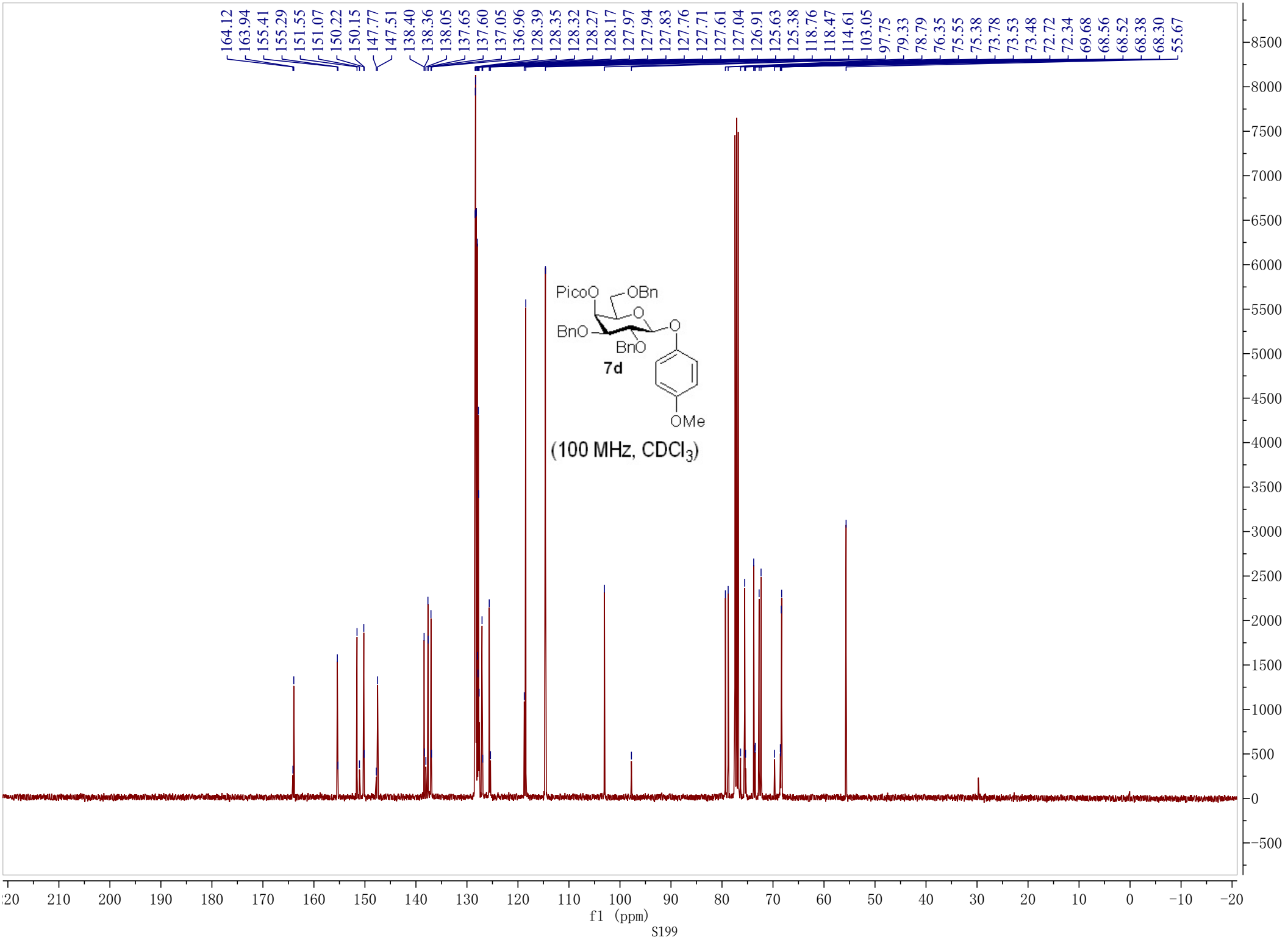

^{1}H-NMR, ^{13}C-NMR of **7b**
BnO
PicoO
BnO
BnO
O
O
7b
OMe
(400 MHz, $CDCl_3$)
0.99
1.00
1.02
1.05
17.65
1.93
0.99
0.99
1.01
1.00
2.04
3.05
1.08
1.08
2.96
2.00
f1 (ppm)


164.14
155.28
150.86
149.91
147.75
138.47
138.03
137.84
137.01
128.60
128.21
128.16
128.07
127.99
127.84
127.49
127.46
127.05
125.68
118.50
114.65
96.79
79.68
79.26
75.55
73.58
73.53
71.78
69.31
68.74
55.72
BnO
PicoO
BnO
BnO
O
O
OMe
7b
(100 MHz, CDCl3)
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

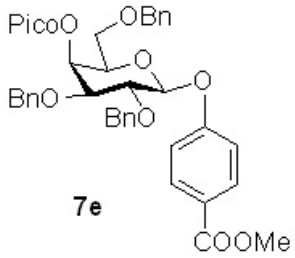

^{1}H-NMR, ^{13}C-NMR of **7c**
BnO
PicoO
BnO
BnO
O
O
7c
COOMe
(400 MHz, $CDCl_3$)
0.97
3.09
1.12
1.15
19.24
1.03
1.00
1.03
1.10
1.10
1.05
3.10
1.03
3.01
1.13
2.06
f1 (ppm)


166.80
164.09
160.29
149.90
147.65
138.34
137.87
137.61
137.04
131.65
128.65
128.24
128.19
128.17
127.99
127.85
127.56
127.53
127.12
125.74
124.39
116.35
95.47
79.53
79.12
75.61
73.84
73.60
71.39
69.65
68.34
52.08
BnO
PicoO
BnO
BnO
O
O
7c
COOMe
(100 MHz, CDCl3)
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


^{1}H-NMR, ^{13}C-NMR of **7d**
PicoO
OBn
BnO
BnO
OMe
7d
(400 MHz, $CDCl_3$)
f1 (ppm)

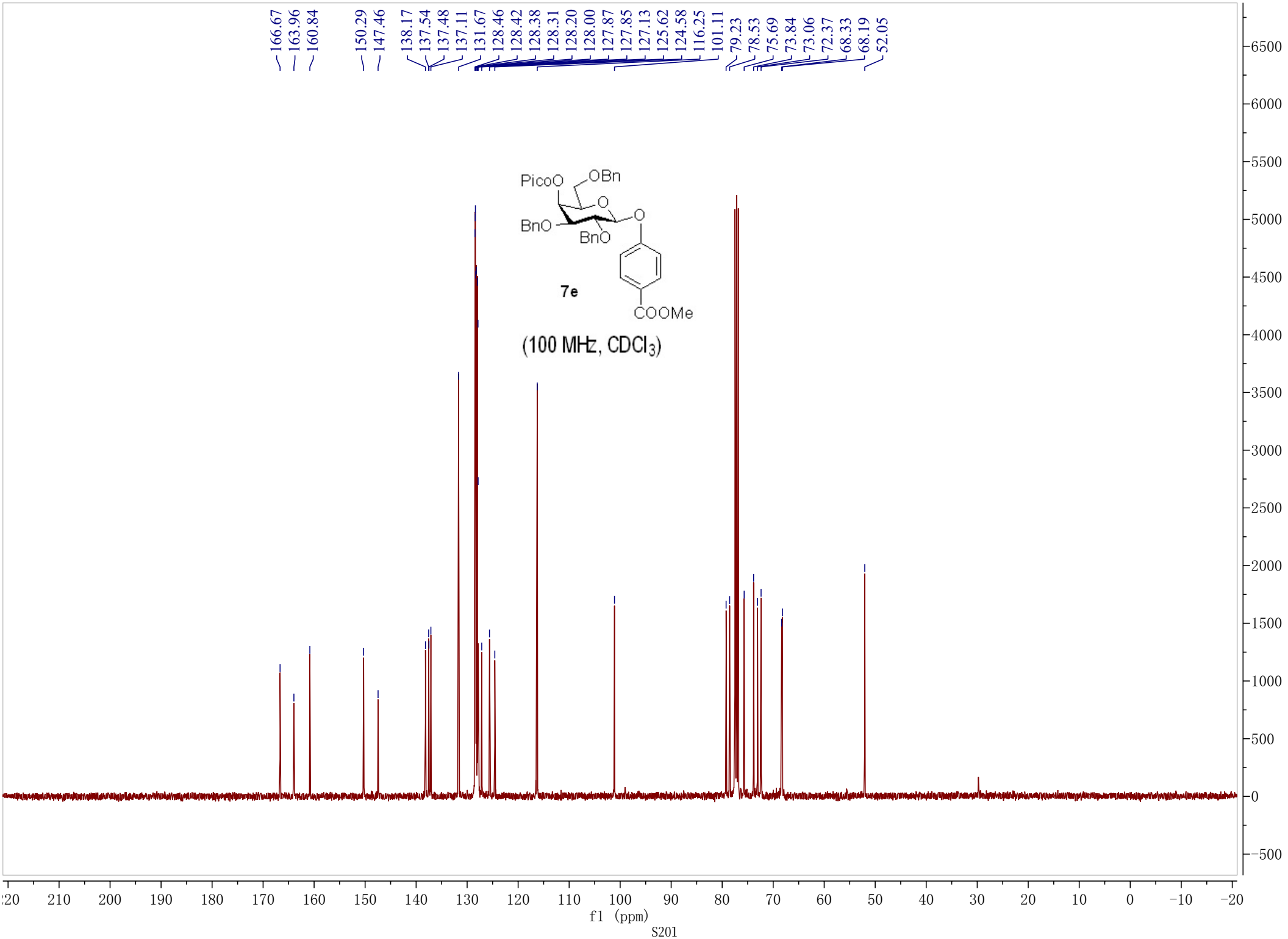

164.12
163.94
155.41
155.29
151.55
151.07
150.22
150.15
147.77
147.51
138.40
138.36
138.05
137.65
137.60
137.05
136.96
128.39
128.35
128.32
128.27
128.17
127.97
127.94
127.83
127.76
127.71
127.61
127.04
126.91
125.63
125.38
118.76
118.47
114.61
103.05
97.75
79.33
78.79
76.35
75.55
75.38
73.78
73.53
73.48
72.72
72.34
69.68
68.56
68.52
68.38
68.30
55.67
PicoO
OBn
O
BnO
O
BnO
7d
OMe
(100 MHz, CDCl3)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

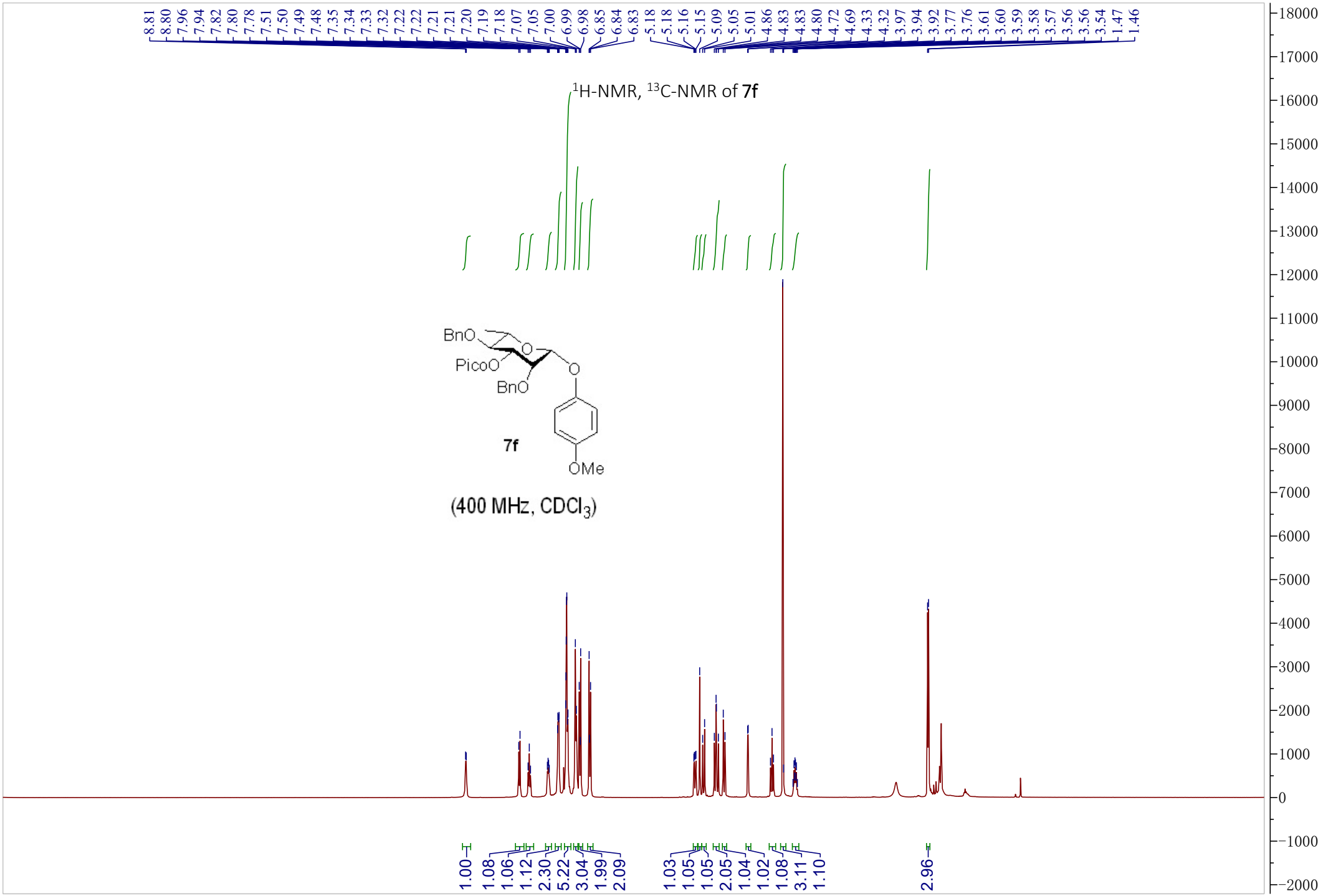
^{1}H-NMR, ^{13}C-NMR of **7e**

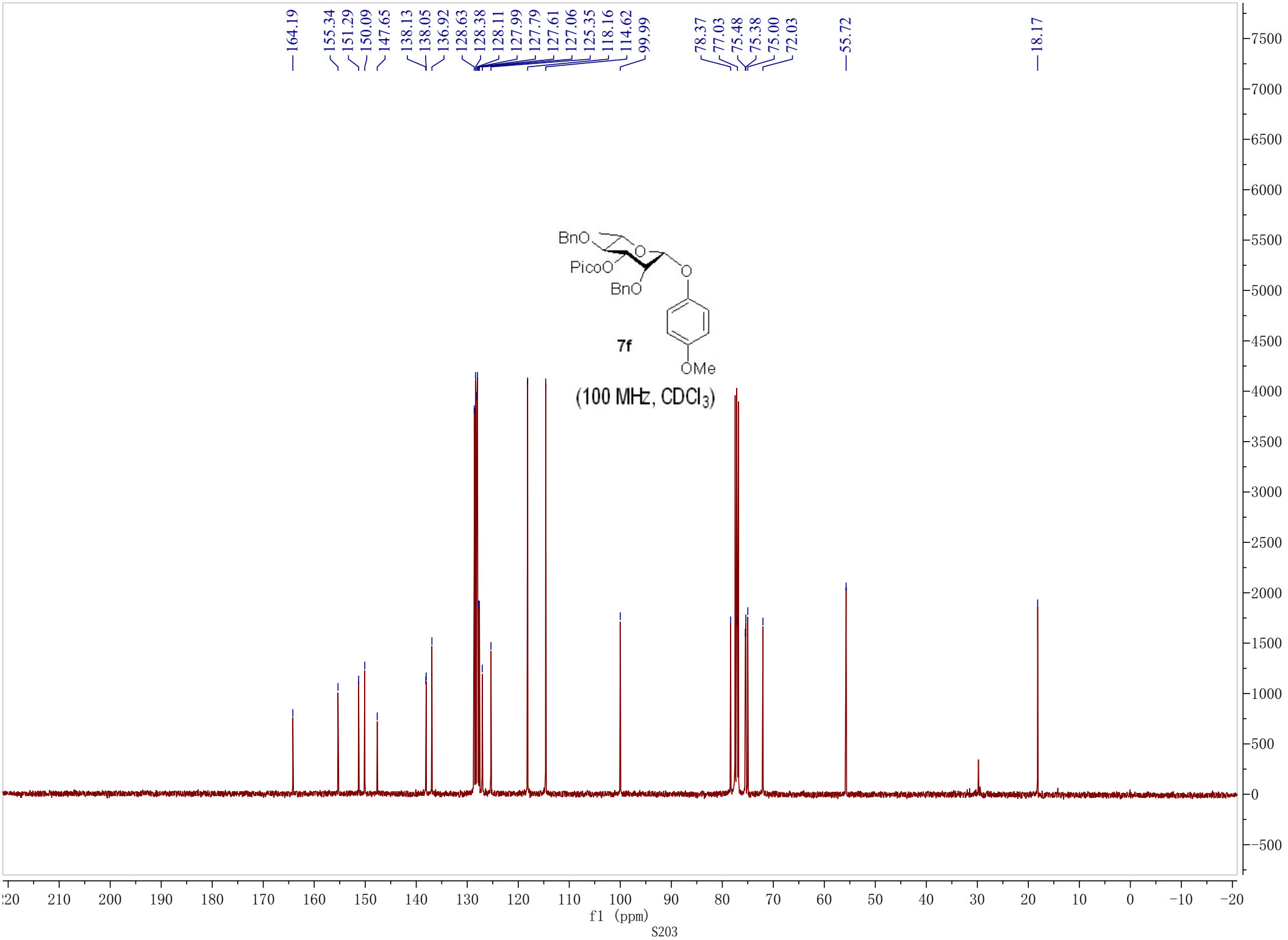


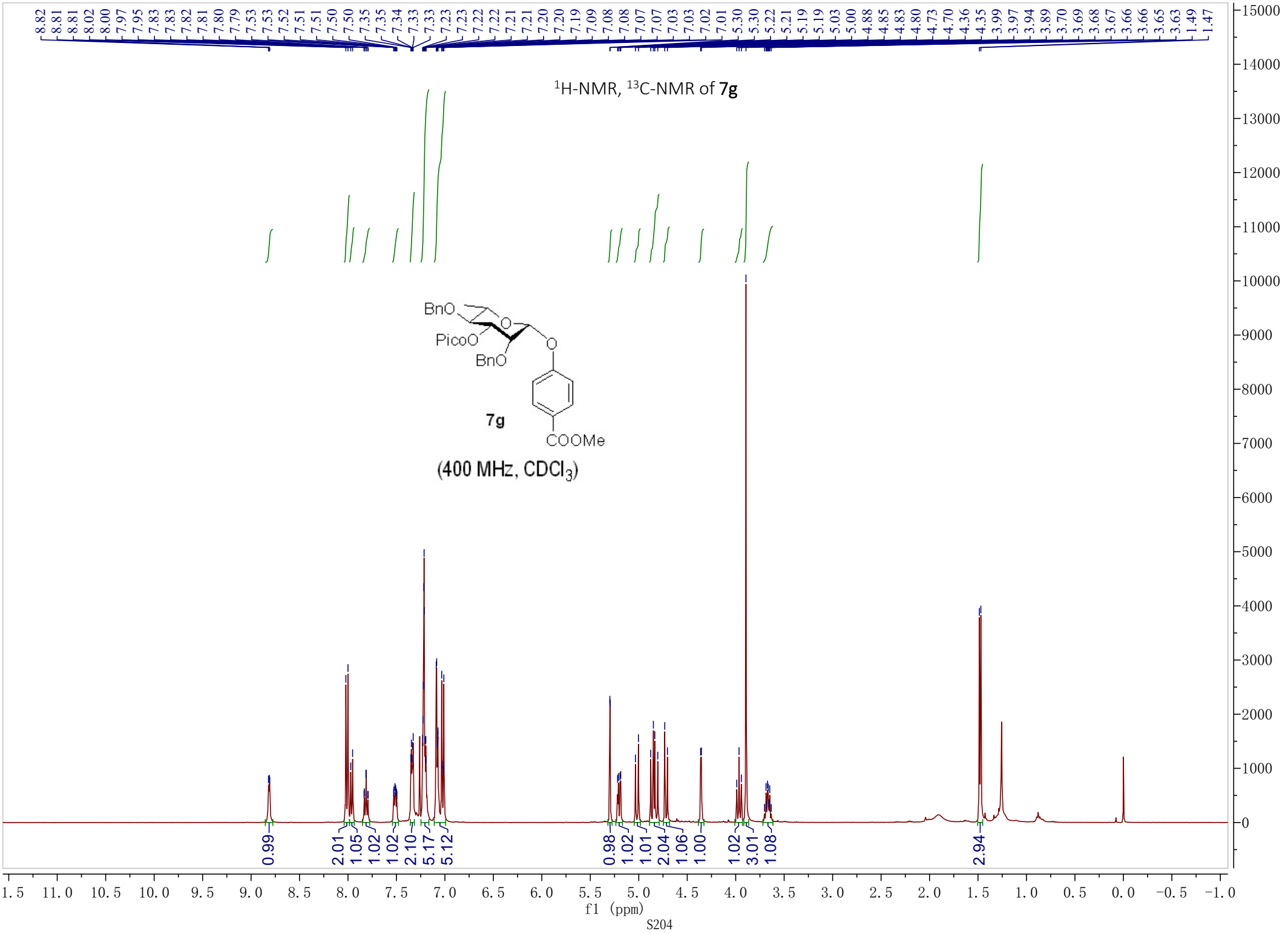
7e

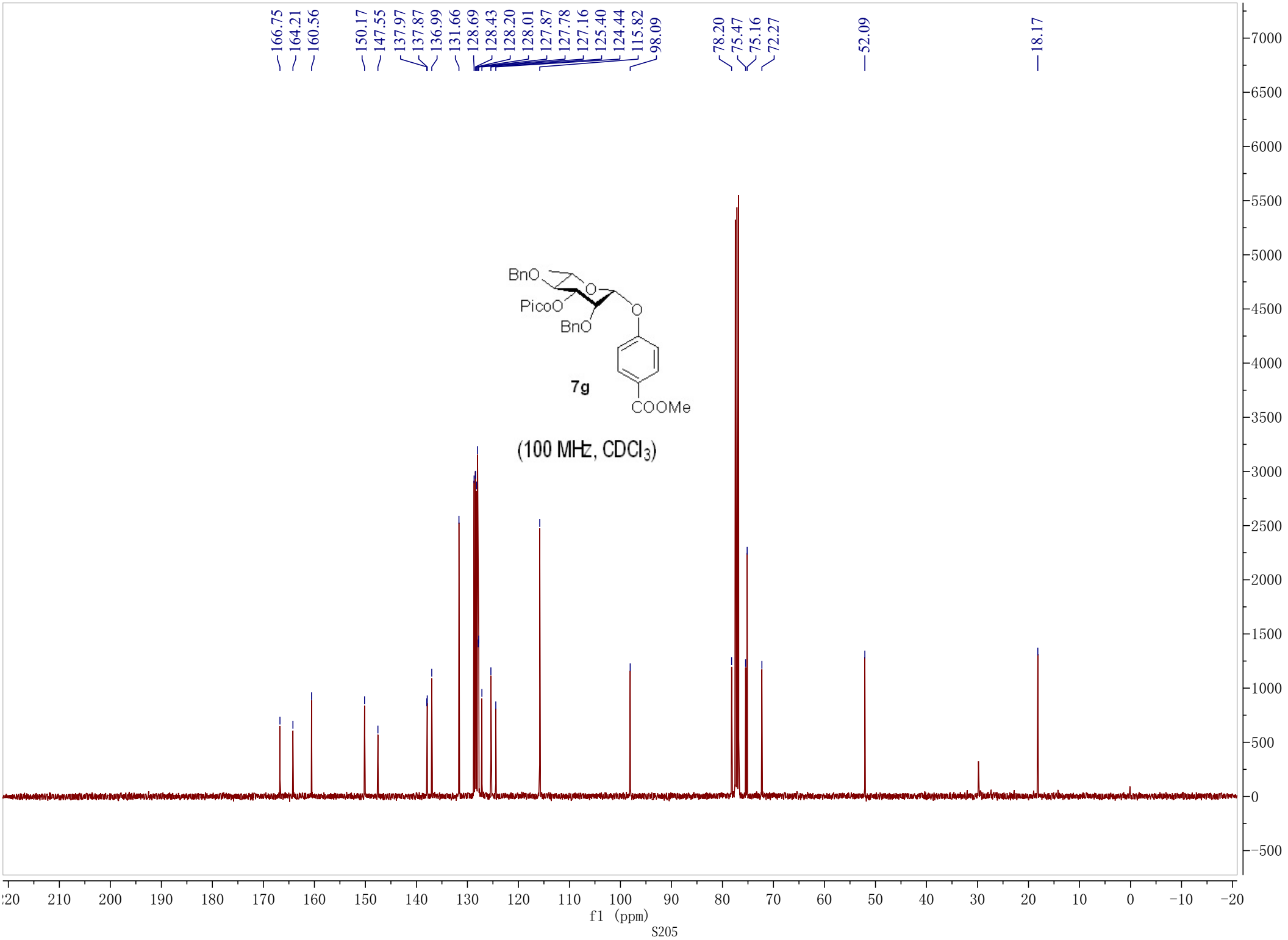
(400 MHz, $CDCl_3$)


166.67
163.96
160.84
150.29
147.46
138.17
137.54
137.48
137.11
131.67
128.46
128.42
128.38
128.31
128.20
128.00
127.87
127.85
127.13
125.62
124.58
116.25
101.11
79.23
78.53
75.69
73.84
73.06
72.37
68.33
68.19
52.05
PicoO
OBn
O
O
BnO
BnO
7e
COOMe
(100 MHz, CDCl3)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

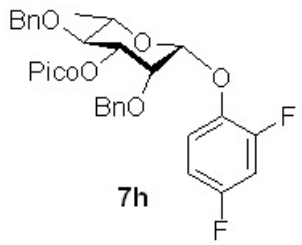

8.81 8.80 7.96 7.94 7.82 7.80 7.78 7.51 7.50 7.49 7.48 7.35 7.34 7.33 7.32 7.22 7.22 7.21 7.21 7.20 7.19 7.18 7.07 7.05 7.00 6.99 6.98 6.85 6.84 6.83
5.18 5.18 5.16 5.15 5.09 5.05 5.01 4.86 4.83 4.83 4.80 4.72 4.69 4.33 4.32 3.97 3.94 3.92 3.77 3.76 3.61 3.60 3.59 3.58 3.57 3.56 3.56 3.54 1.47 1.46
1H-NMR, 13C-NMR of 7f
BnO
PicoO
BnO
O
O
OMe
7f
(400 MHz, CDCl3)
1.00 1.08 1.06 1.12 2.30 5.22 3.04 1.99 2.09
1.03 1.05 1.05 2.05 1.04 1.02 1.08 3.11 1.10
2.96
f1 (ppm)


164.19
155.34
151.29
150.09
147.65
138.13
138.05
136.92
128.63
128.38
128.11
127.99
127.79
127.61
127.06
125.35
118.16
114.62
99.99
78.37
77.03
75.48
75.38
75.00
72.03
55.72
18.17
BnO
PicoO
BnO
O
O
OMe
7f
(100 MHz, CDCl3)
f1 (ppm)


^{1}H-NMR, ^{13}C-NMR of **7g**
BnO
PicoO
BnO
O
O
COOMe
7g
(400 MHz, $CDCl_3$)
f1 (ppm)


166.75
164.21
160.56
150.17
147.55
137.97
137.87
136.99
131.66
128.69
128.43
128.20
128.01
127.87
127.78
127.16
125.40
124.44
115.82
98.09
78.20
75.47
75.16
72.27
52.09
18.17
BnO
PicoO
BnO
O
O
7g
COOMe
(100 MHz, CDCl3)
f1 (ppm)

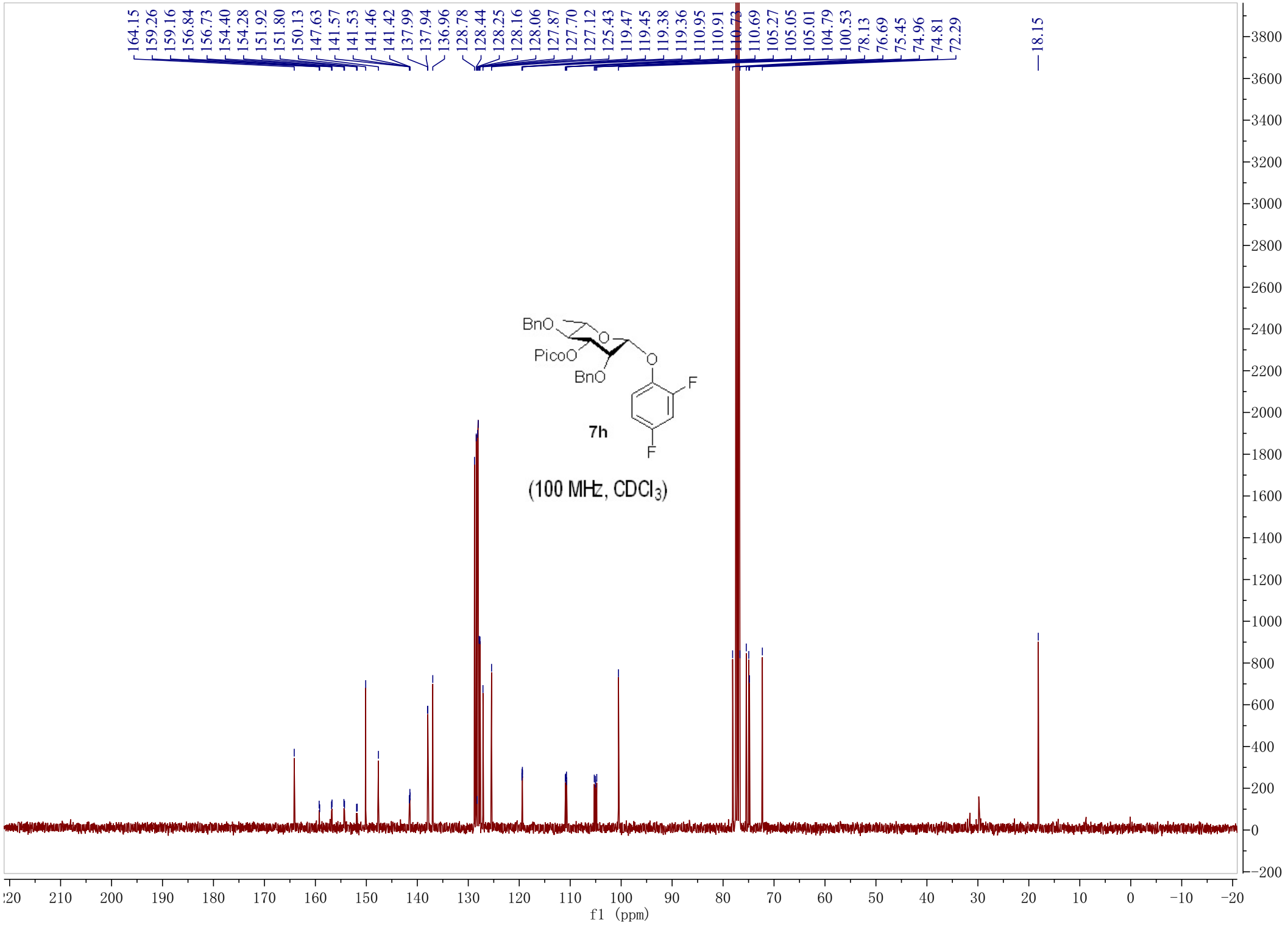
^{1}H-NMR, ^{13}C-NMR of **7h**

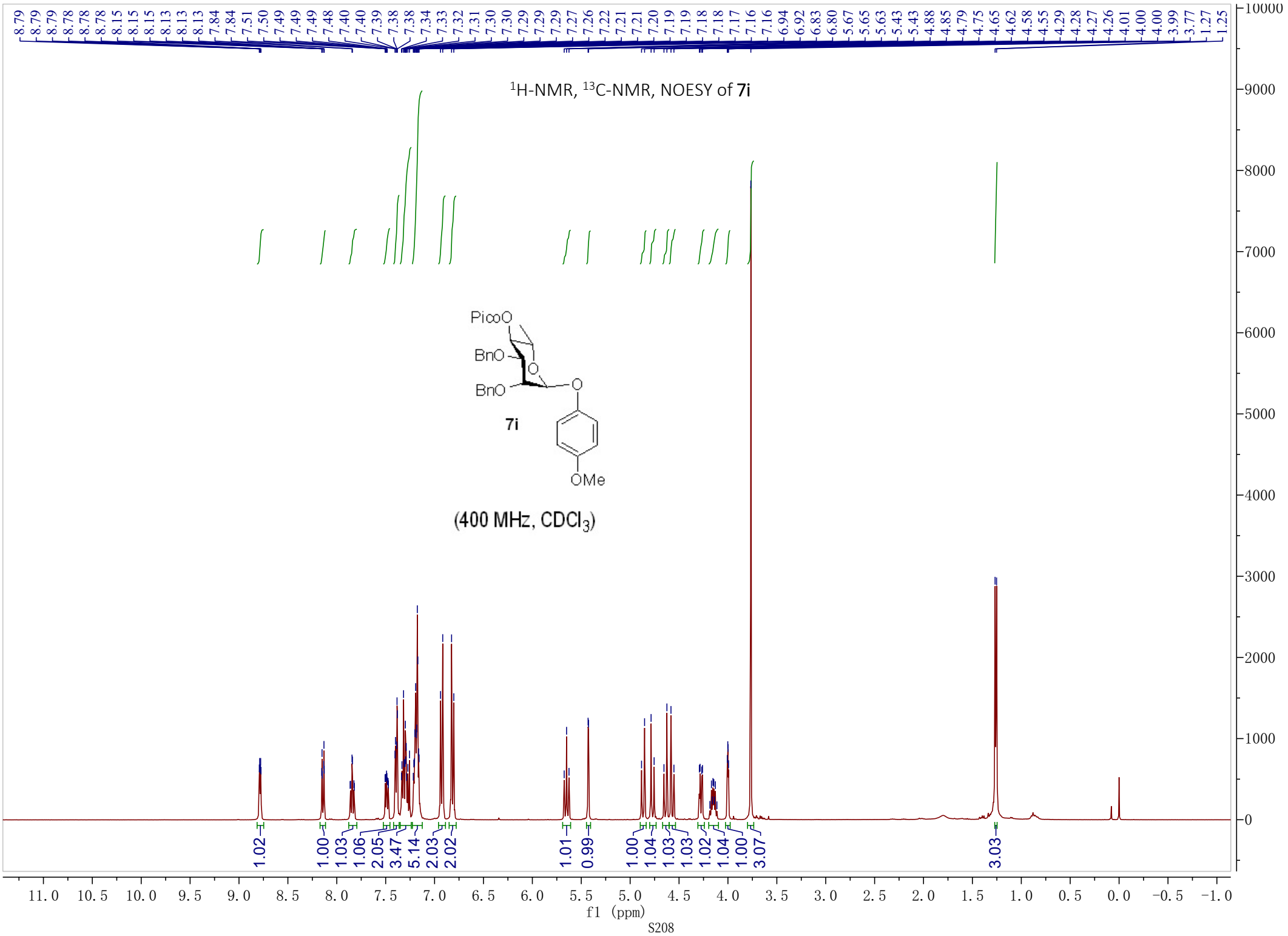


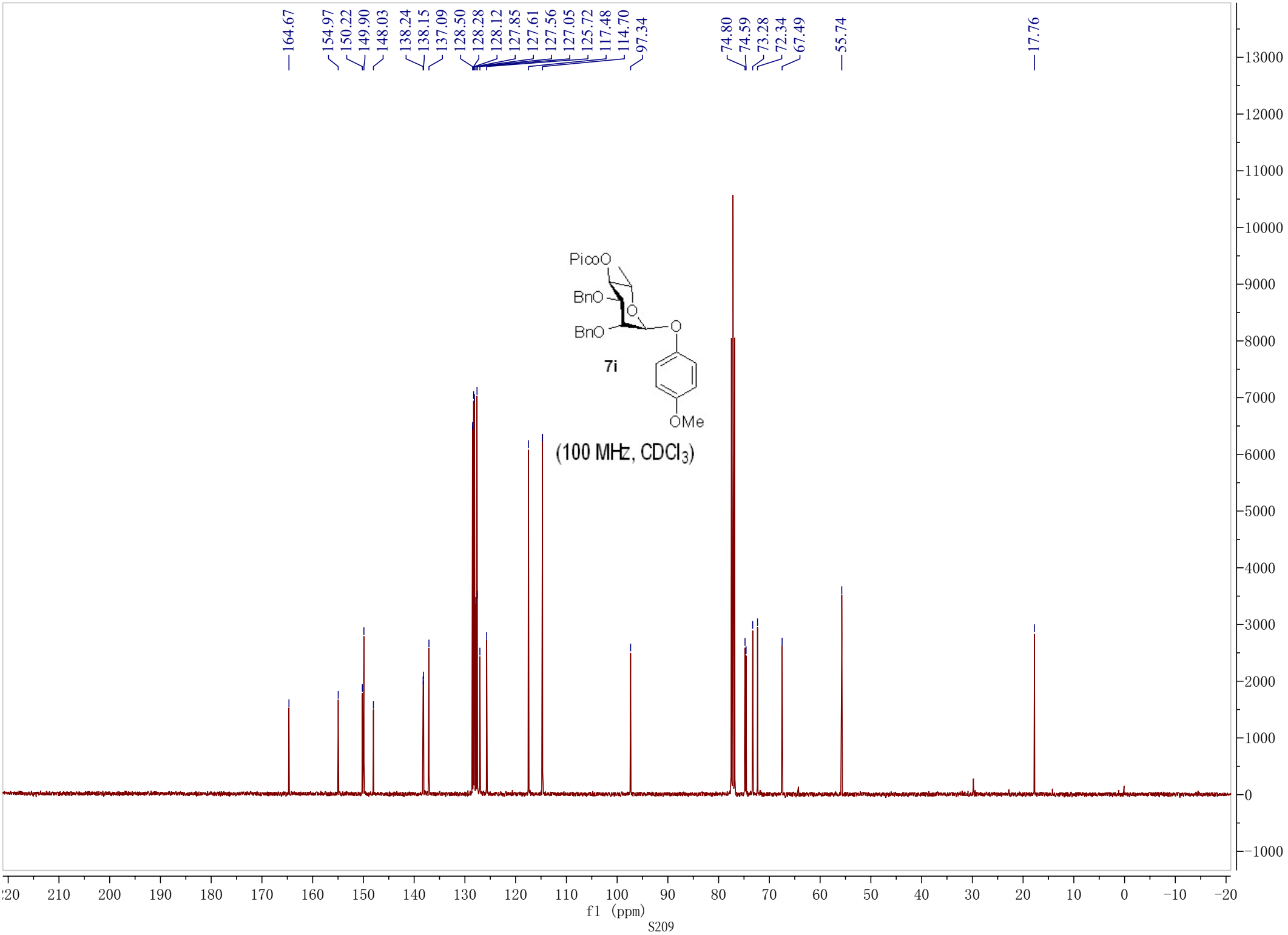
7h

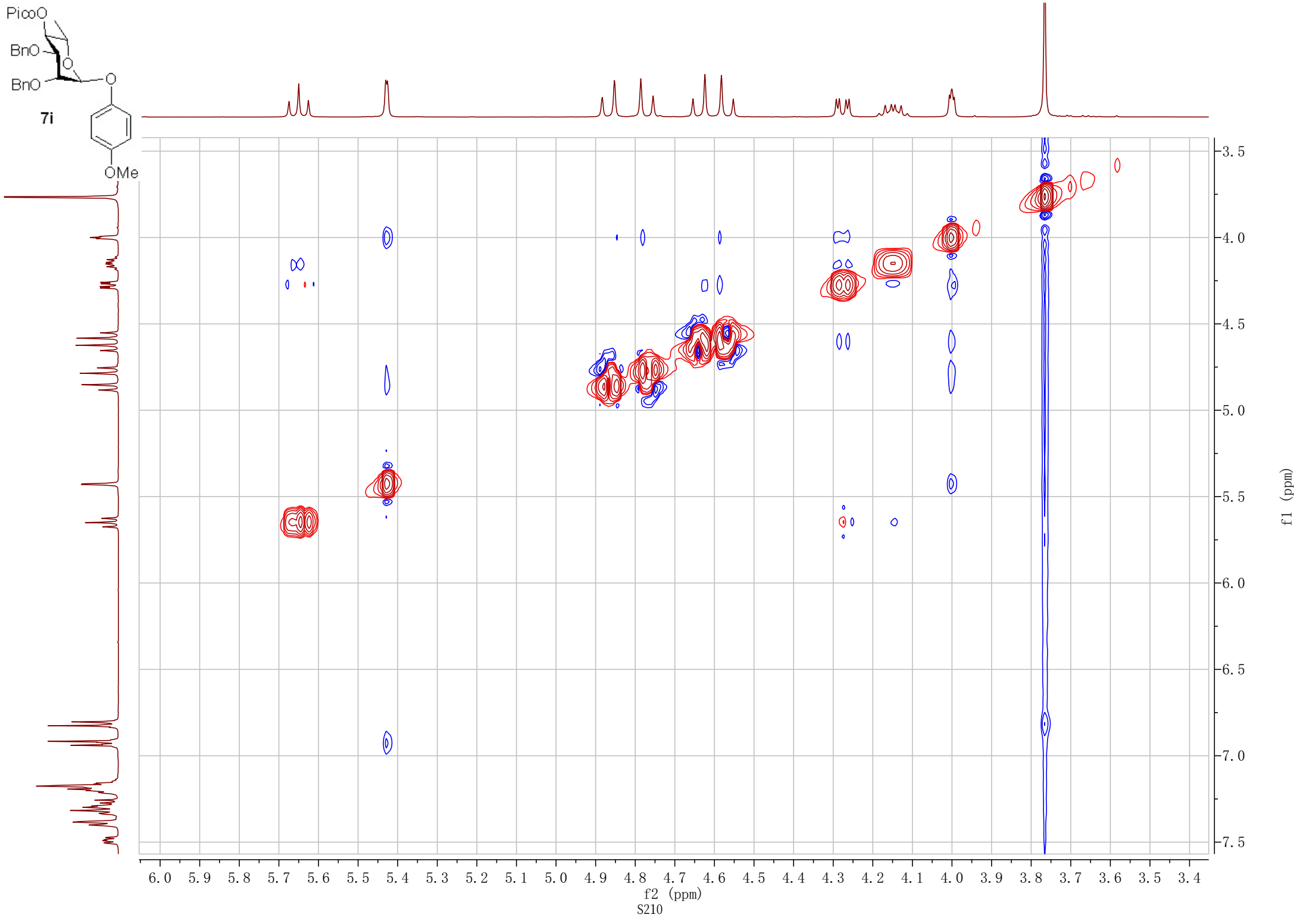
(400 MHz, $CDCl_3$)

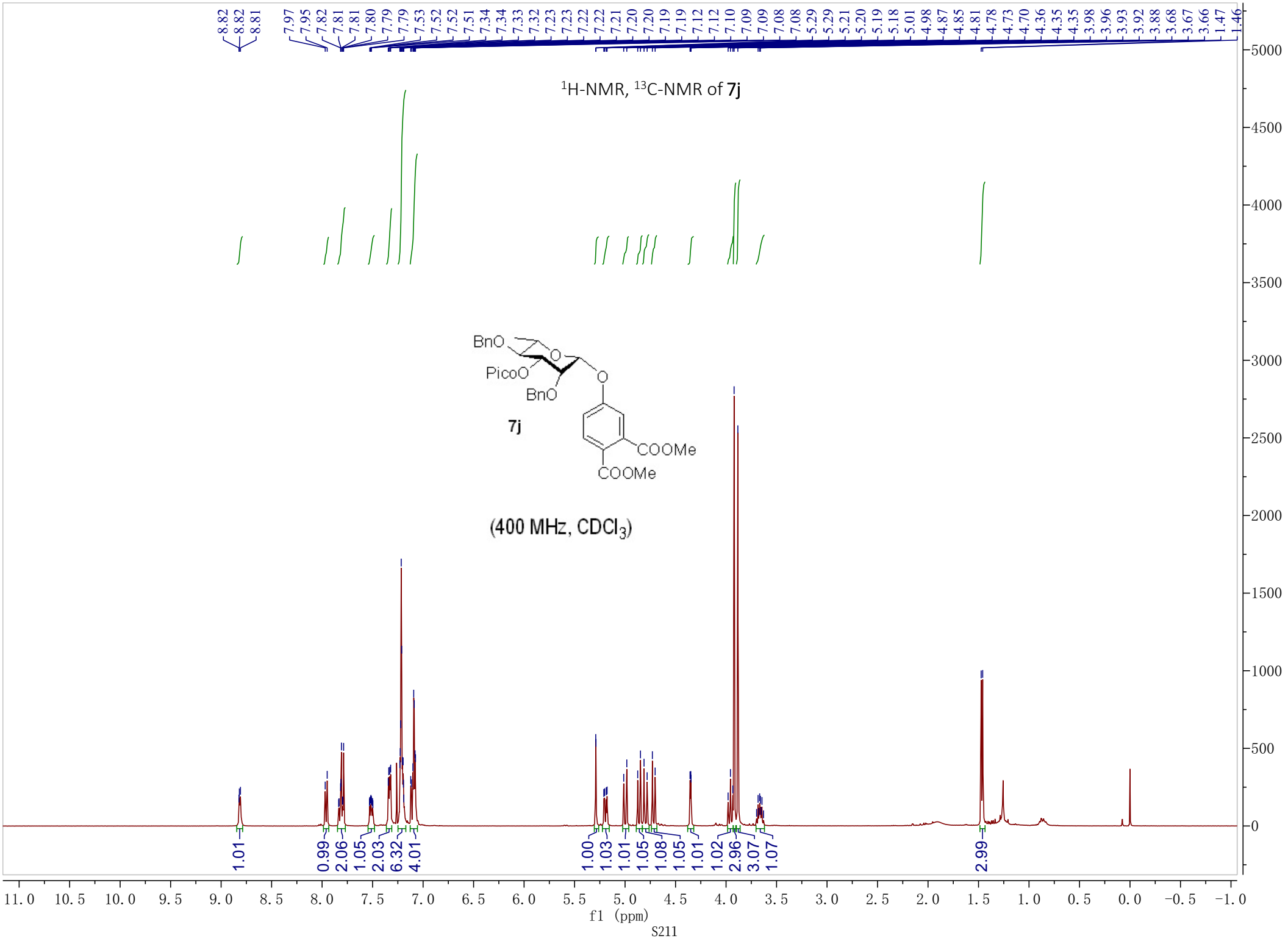
f1 (ppm)

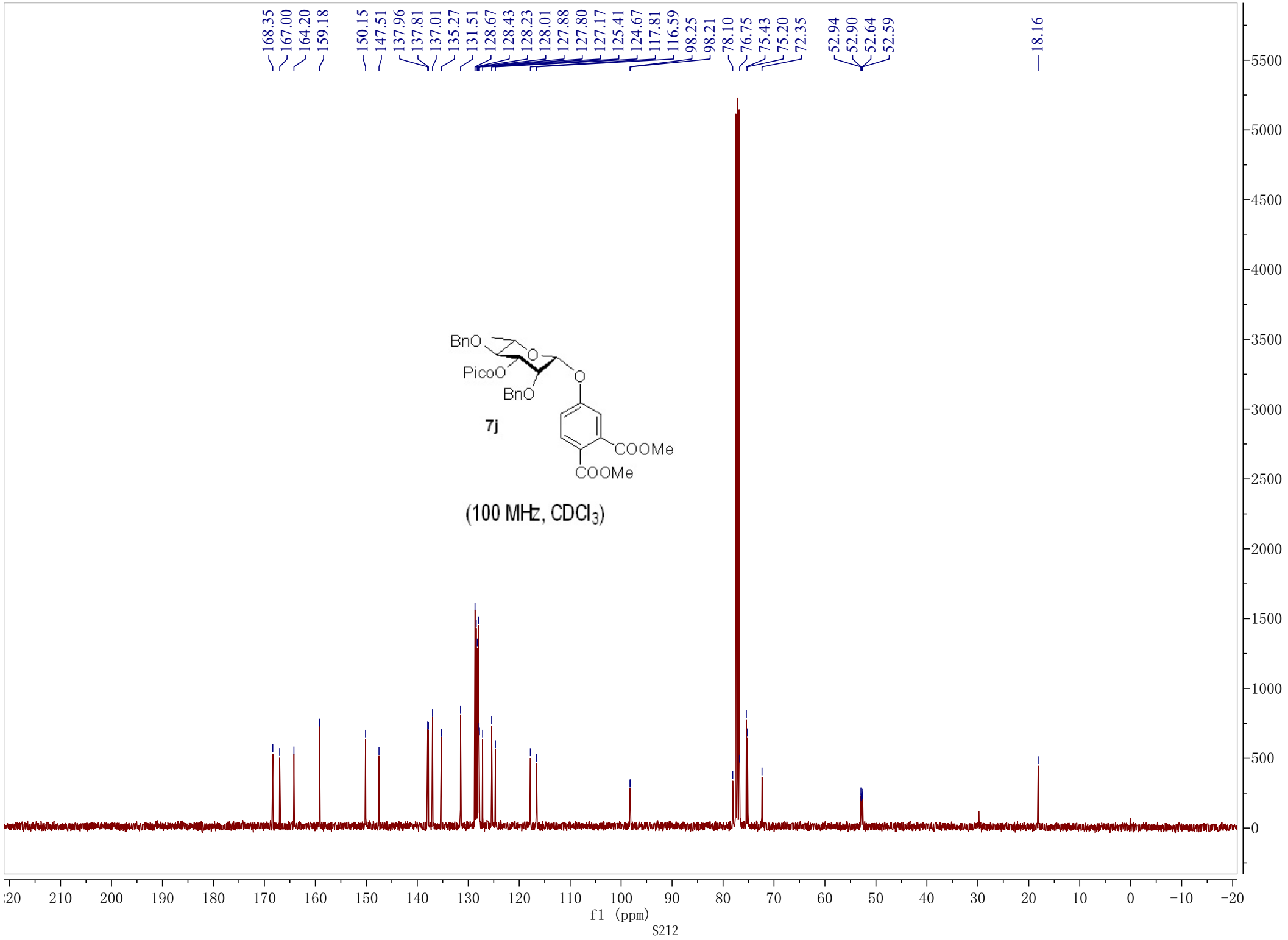

164.15
159.26
159.16
156.84
156.73
154.40
154.28
151.92
151.80
150.13
147.63
141.57
141.53
141.46
141.42
137.99
137.94
136.96
128.78
128.44
128.25
128.16
128.06
127.87
127.70
127.12
125.43
119.47
119.45
119.38
119.36
110.95
110.91
110.73
110.69
105.27
105.05
105.01
104.79
100.53
78.13
76.69
75.45
74.96
74.81
72.29
18.15
BnO
PicoO
BnO
O
O
F
F
7h
(100 MHz, CDCl3)
f1 (ppm)

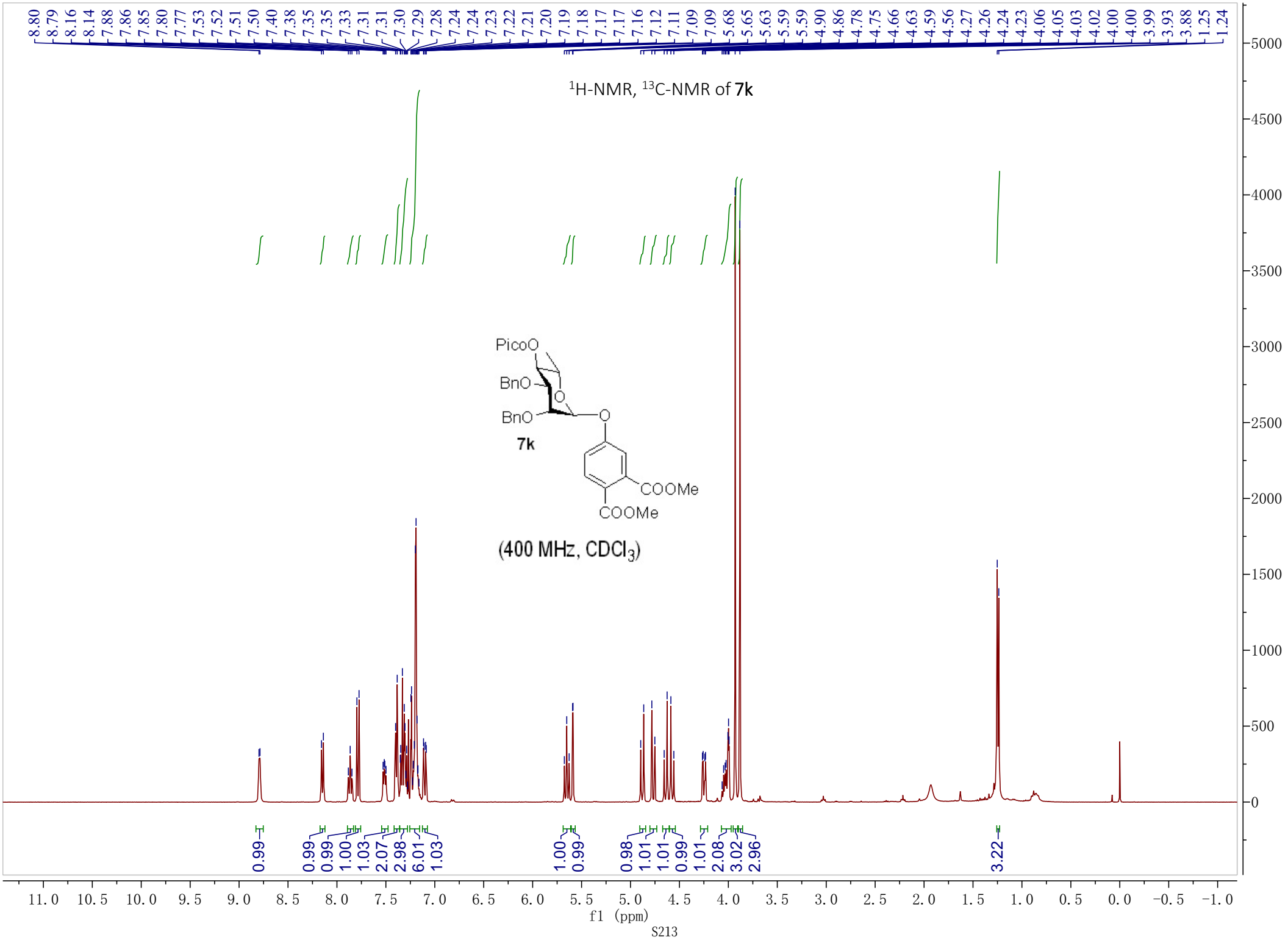

^{1}H-NMR, ^{13}C-NMR, NOESY of **7i**
PicoO
BnO
BnO
O
O
OMe
7i
(400 MHz, $CDCl_3$)
f1 (ppm)

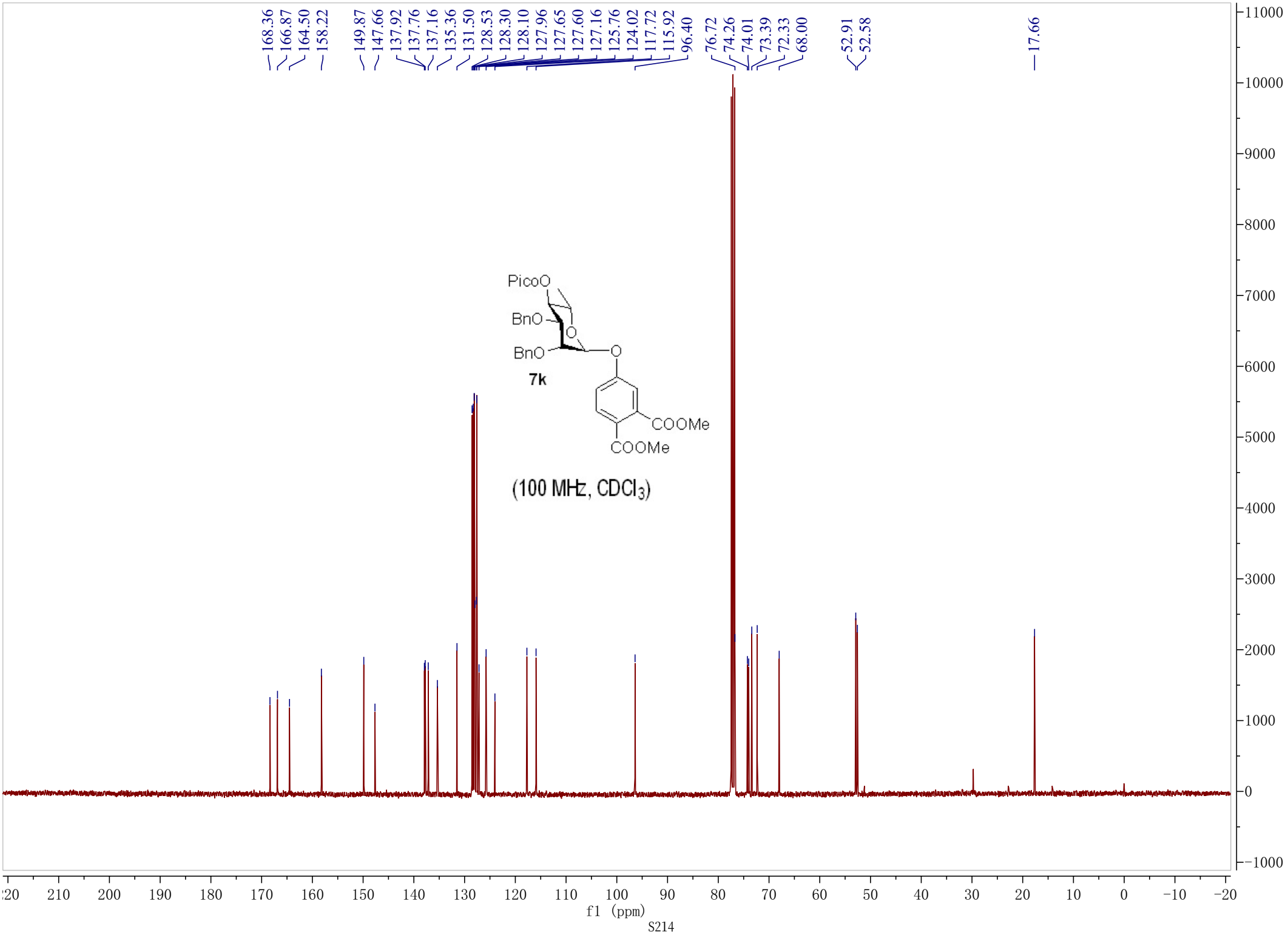

164.67
154.97
150.22
149.90
148.03
138.24
138.15
137.09
128.50
128.28
128.12
127.85
127.61
127.56
127.05
125.72
117.48
114.70
97.34
74.80
74.59
73.28
72.34
67.49
55.74
17.76
PicoO
BnO
BnO
O
O
OMe
7i
(100 MHz, CDCl3)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

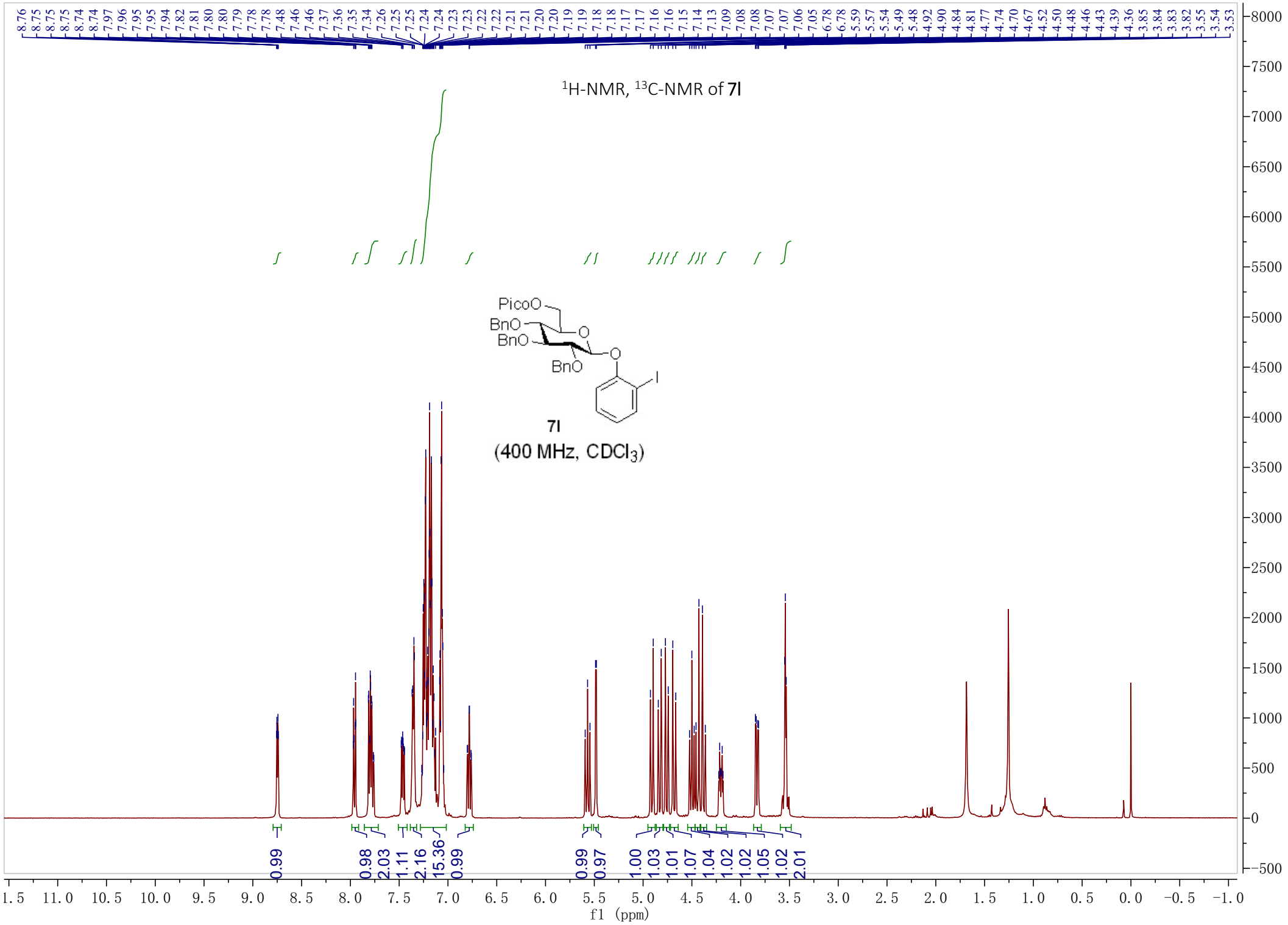

PicoO
BnO
BnO
O
O
OMe
7i
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4
f2 (ppm)

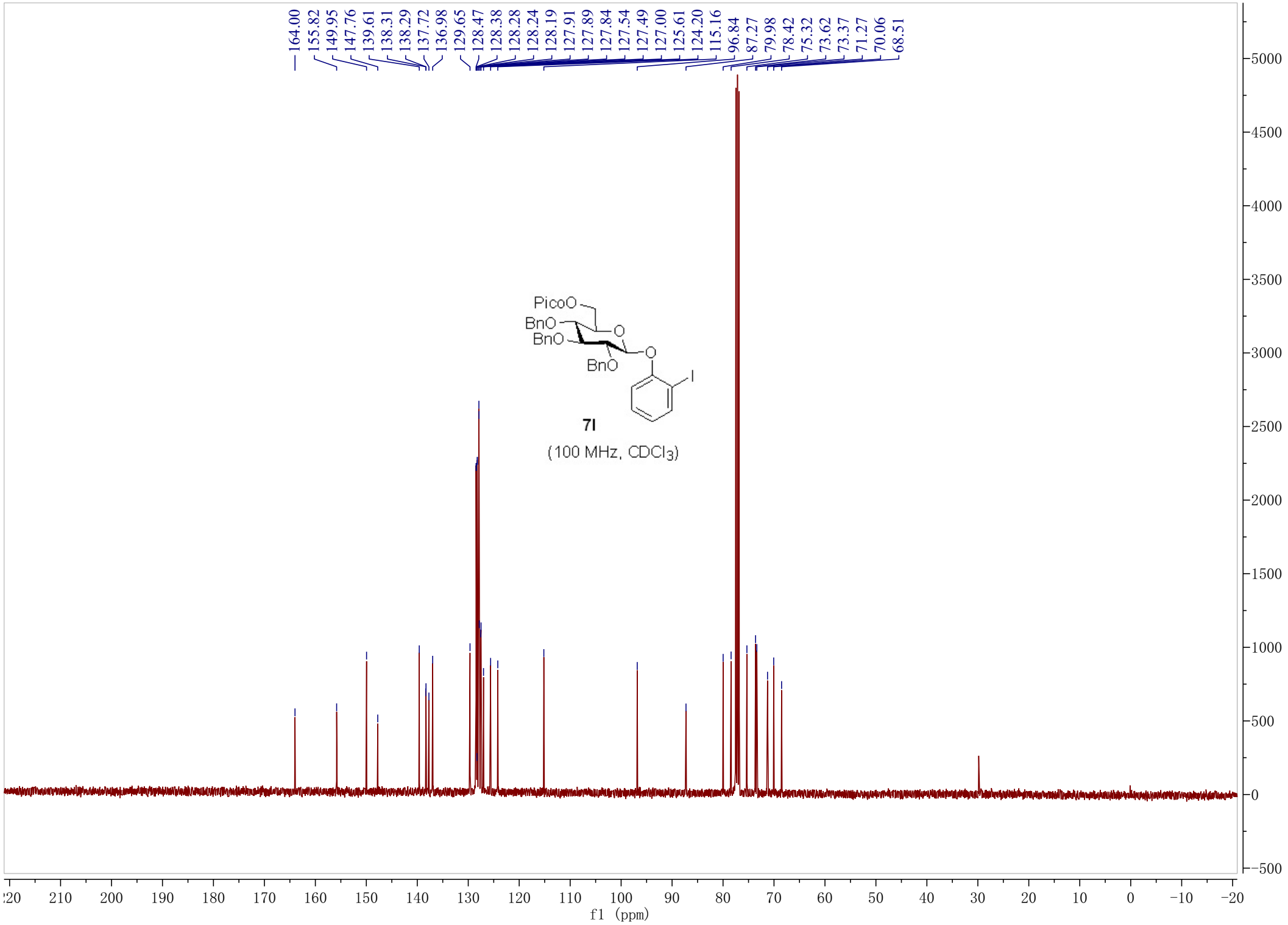

8.82 8.82 8.81 7.97 7.95 7.82 7.81 7.81 7.80 7.79 7.79 7.53 7.52 7.52 7.51 7.34 7.34 7.33 7.32 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.12 7.12 7.10 7.09 7.09 7.08 7.08 5.29 5.29 5.21 5.20 5.19 5.18 5.01 4.98 4.87 4.85 4.81 4.78 4.73 4.70 4.36 4.35 4.35 3.98 3.96 3.93 3.92 3.88 3.68 3.67 3.66 1.47 1.46
1H-NMR, 13C-NMR of 7j
BnO
PicoO
BnO
O
O
COOMe
COOMe
7j
(400 MHz, CDCl3)
1.01 0.99 2.06 1.05 2.03 6.32 4.01 1.00 1.03 1.01 1.05 1.08 1.05 1.01 1.02 2.96 3.07 1.07 2.99
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.35
167.00
164.20
159.18
150.15
147.51
137.96
137.81
137.01
135.27
131.51
128.67
128.43
128.23
128.01
127.88
127.80
127.17
125.41
124.67
117.81
116.59
98.25
98.21
78.10
76.75
75.43
75.20
72.35
52.94
52.90
52.64
52.59
18.16
BnO
PicoO
BnO
O
O
COOMe
COOMe
7j
(100 MHz, CDCl3)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

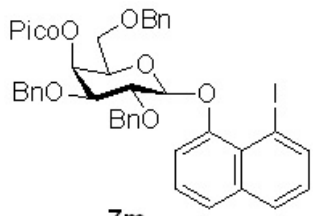

^{1}H-NMR, ^{13}C-NMR of **7k**
PicoO
BnO
BnO
O
O
COOMe
COOMe
7k
(400 MHz, $CDCl_3$)
f1 (ppm)


168.36
166.87
164.50
158.22
149.87
147.66
137.92
137.76
137.16
135.36
131.50
128.53
128.30
128.10
127.96
127.65
127.60
127.16
125.76
124.02
117.72
115.92
96.40
76.72
74.26
74.01
73.39
72.33
68.00
52.91
52.58
17.66
PicoO
BnO
BnO
O
O
7k
COOMe
COOMe
(100 MHz, CDCl3)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


^{1}H-NMR, ^{13}C-NMR of 7l
PicoO
BnO
BnO
BnO
O
O
I
7l
(400 MHz, $CDCl_3$)
f1 (ppm)

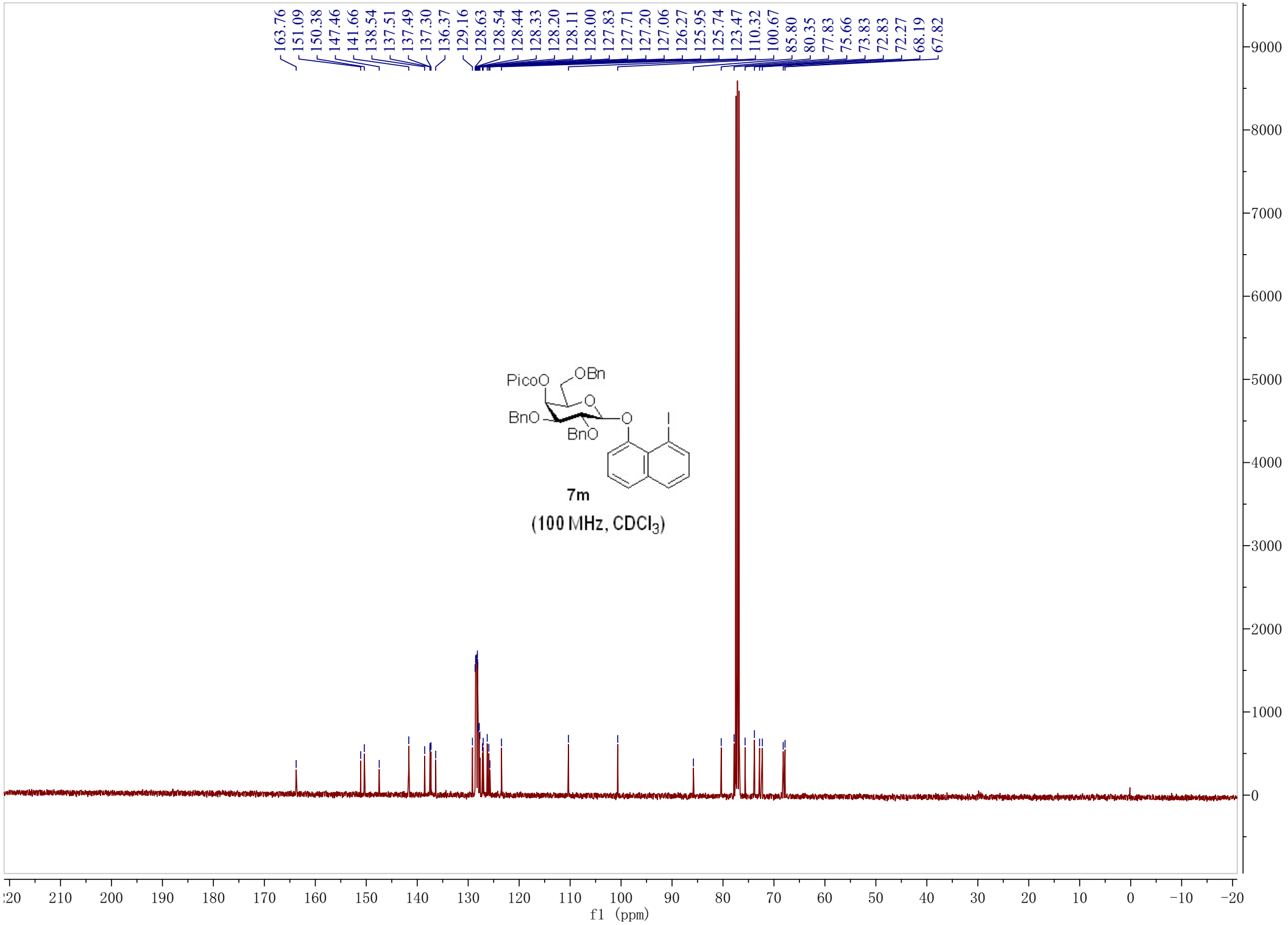

164.00
155.82
149.95
147.76
139.61
138.31
138.29
137.72
136.98
129.65
128.47
128.38
128.28
128.24
128.19
127.91
127.89
127.84
127.54
127.49
127.00
125.61
124.20
115.16
96.84
87.27
79.98
78.42
75.32
73.62
73.37
71.27
70.06
68.51
PicoO
BnO
BnO
BnO
O
O
I
7l
(100 MHz, CDCl3)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

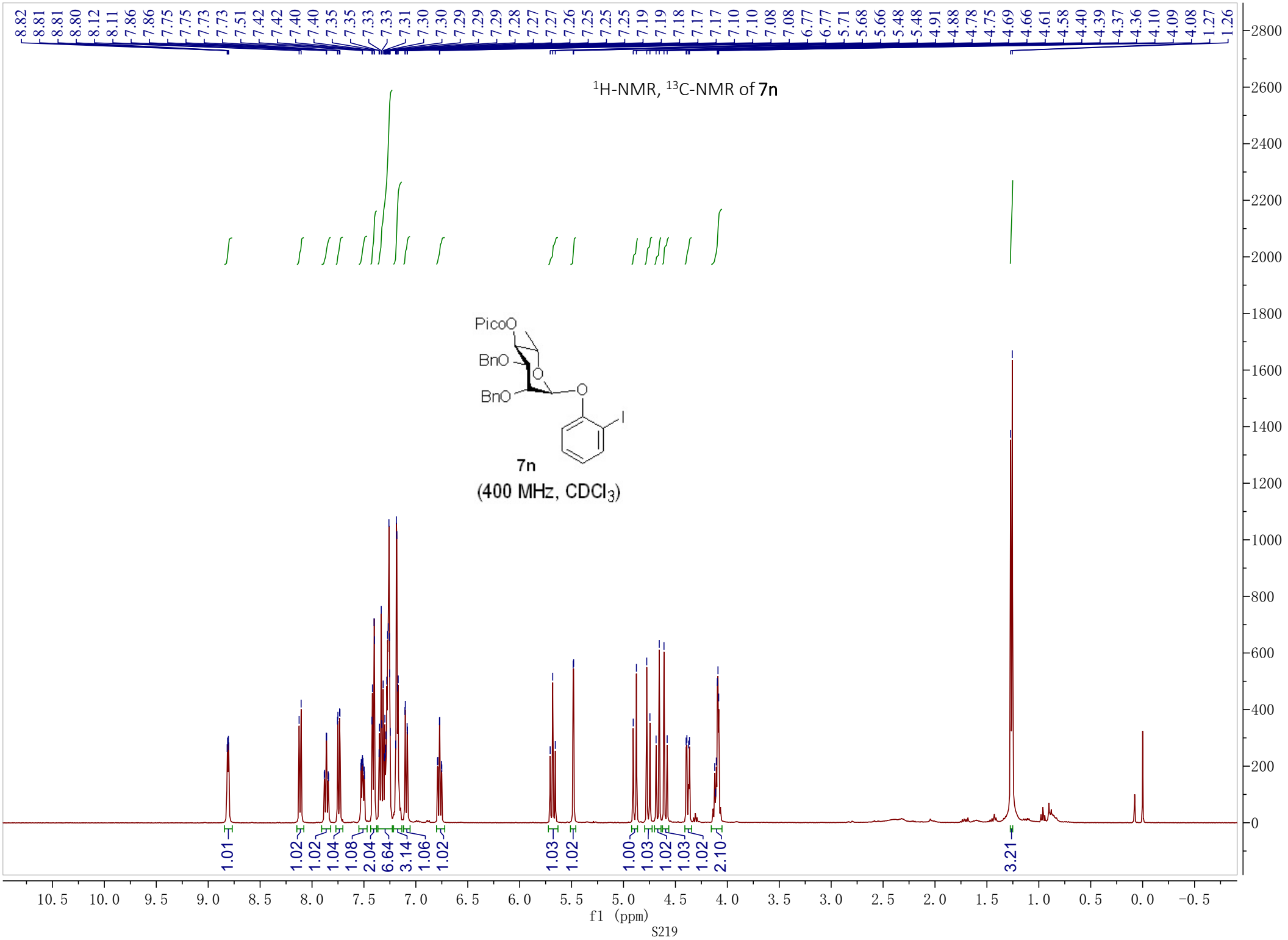
^{1}H-NMR, ^{13}C-NMR of **7m**

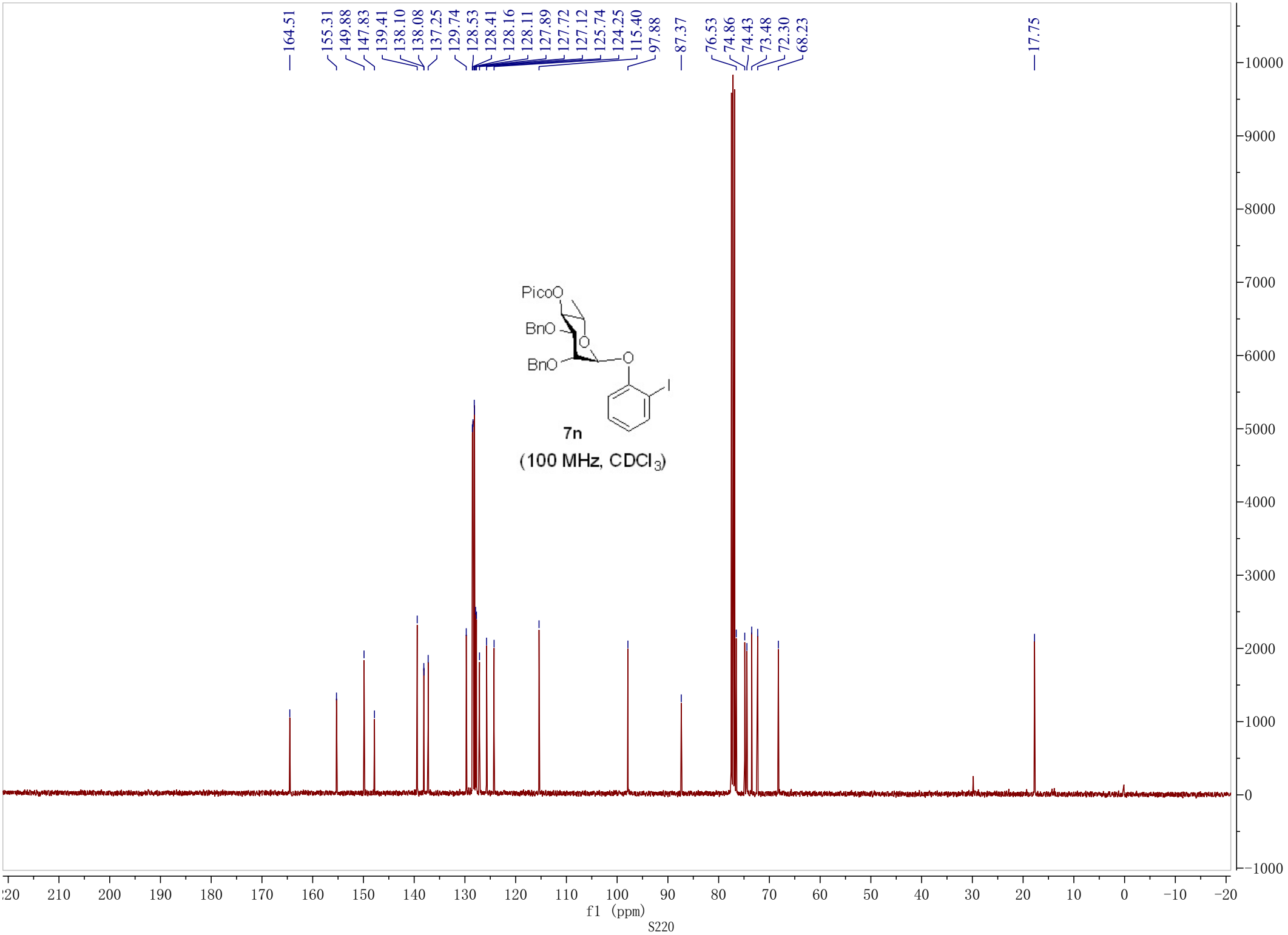


7m

(400 MHz, $CDCl_3$)

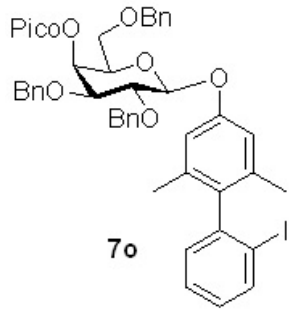

163.76
151.09
150.38
147.46
141.66
138.54
137.51
137.49
137.30
136.37
129.16
128.63
128.54
128.44
128.33
128.20
128.11
128.00
127.83
127.71
127.20
127.06
126.27
125.95
125.74
123.47
110.32
100.67
85.80
80.35
77.83
75.66
73.83
72.83
72.27
68.19
67.82
PicoO
OBn
O
BnO
O
BnO
I
7m
(100 MHz, CDCl3)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


^{1}H-NMR, ^{13}C-NMR of **7n**
PicoO
BnO
BnO
O
O
I
7n
(400 MHz, $CDCl_3$)
f1 (ppm)


164.51
155.31
149.88
147.83
139.41
138.10
138.08
137.25
129.74
128.53
128.41
128.16
128.11
127.89
127.72
127.12
125.74
124.25
115.40
97.88
87.37
76.53
74.86
74.43
73.48
72.30
68.23
17.75
PicoO
BnO
BnO
O
O
I
7n
(100 MHz, CDCl3)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

XK210116_1.fid
XK210116

^{1}H-NMR, ^{13}C-NMR of **7o**

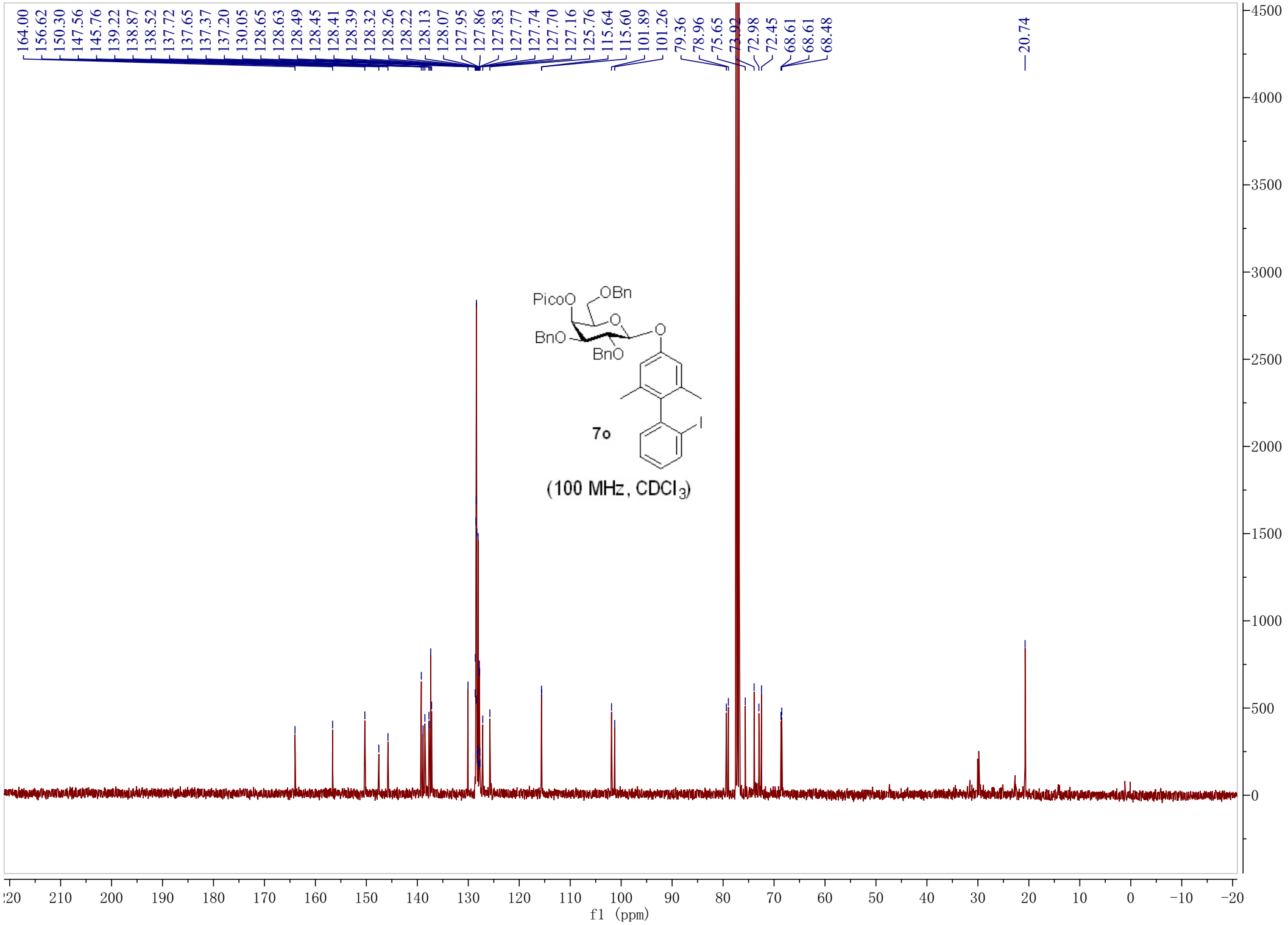


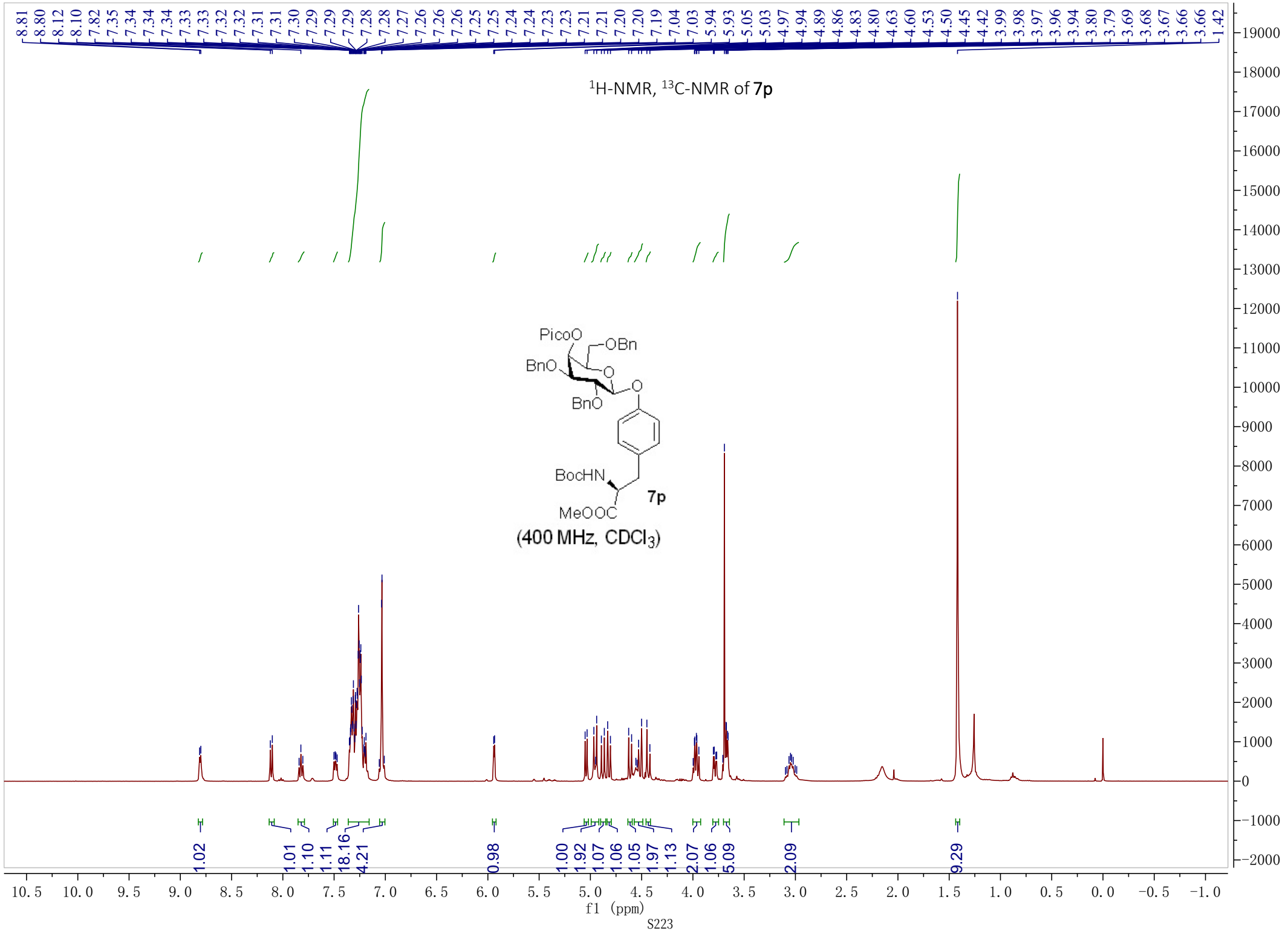
7o

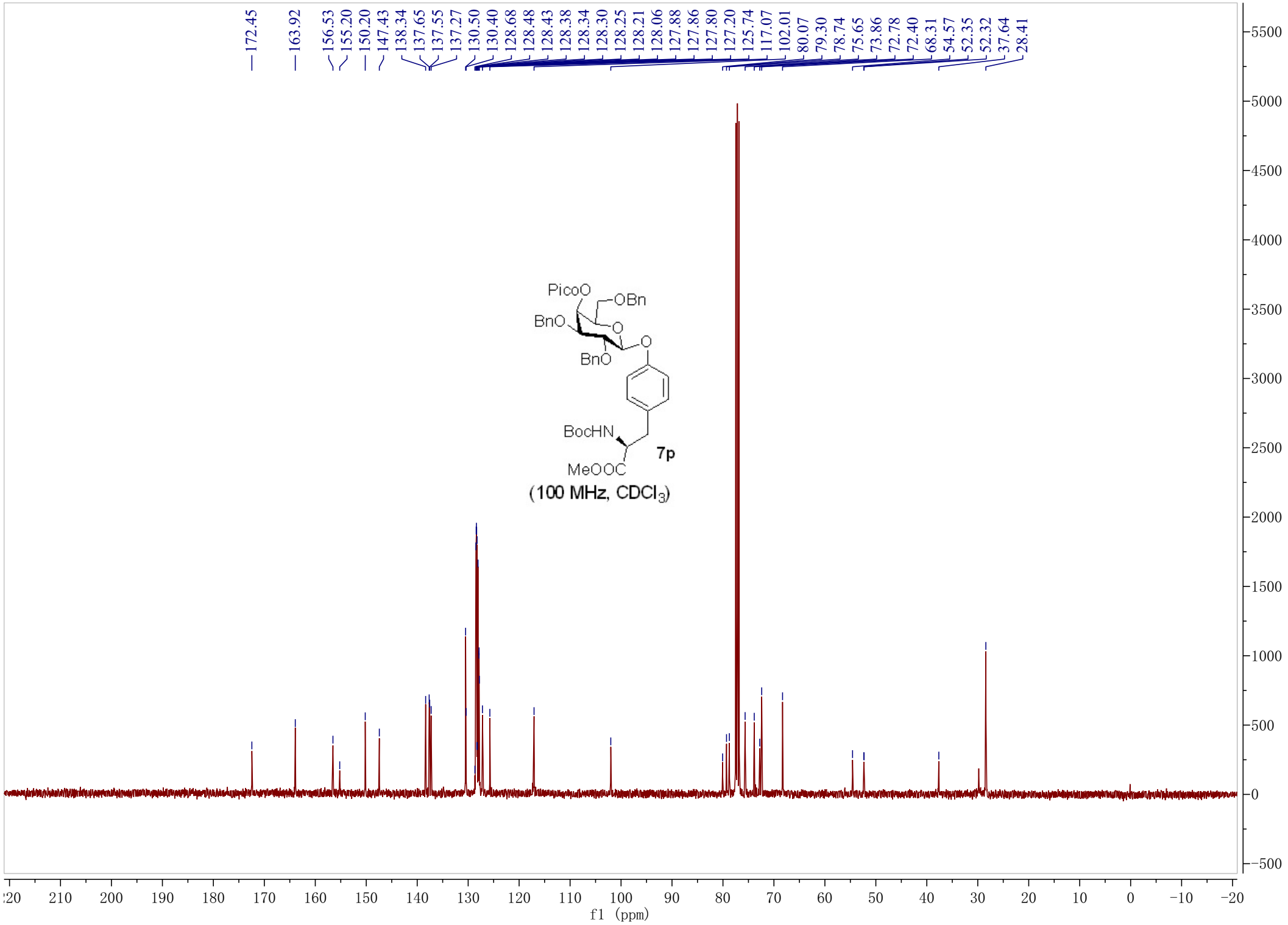
(400 MHz, $CDCl_3$)

1.03 0.99 1.04 1.05 1.17 20.35 1.19 2.12 1.00 0.99 1.00 2.14 1.02 1.01 1.10 2.14 1.08 2.06 6.07

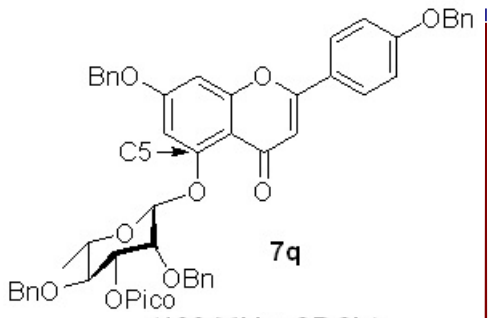
f1 (ppm)


164.00
156.62
150.30
147.56
145.76
139.22
138.87
138.52
137.72
137.65
137.37
137.20
130.05
128.65
128.63
128.49
128.45
128.41
128.39
128.32
128.26
128.22
128.13
128.07
127.95
127.86
127.83
127.77
127.74
127.70
127.16
125.76
115.64
115.60
101.89
101.26
79.36
78.96
75.65
73.92
72.98
72.45
68.61
68.61
68.48
20.74
PicoO
OBn
BnO
BnO
O
O
I
7o
(100 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


8.81 8.80 8.12 8.10 7.82 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.21 7.21 7.20 7.20 7.19 7.04 7.03 5.94 5.93 5.05 5.03 4.97 4.94 4.89 4.86 4.83 4.80 4.63 4.60 4.53 4.50 4.45 4.42 3.99 3.98 3.97 3.96 3.94 3.80 3.79 3.69 3.68 3.67 3.66 3.66 1.42
1H-NMR, 13C-NMR of 7p
PicoO
OBn
BnO
O
O
BnO
BocHN
MeOOC
7p
(400 MHz, CDCl3)
1.02 1.01 1.10 1.11 18.16 4.21 0.98 1.00 1.92 1.07 1.06 1.05 1.97 1.13 2.07 1.06 5.09 2.09 9.29
f1 (ppm)

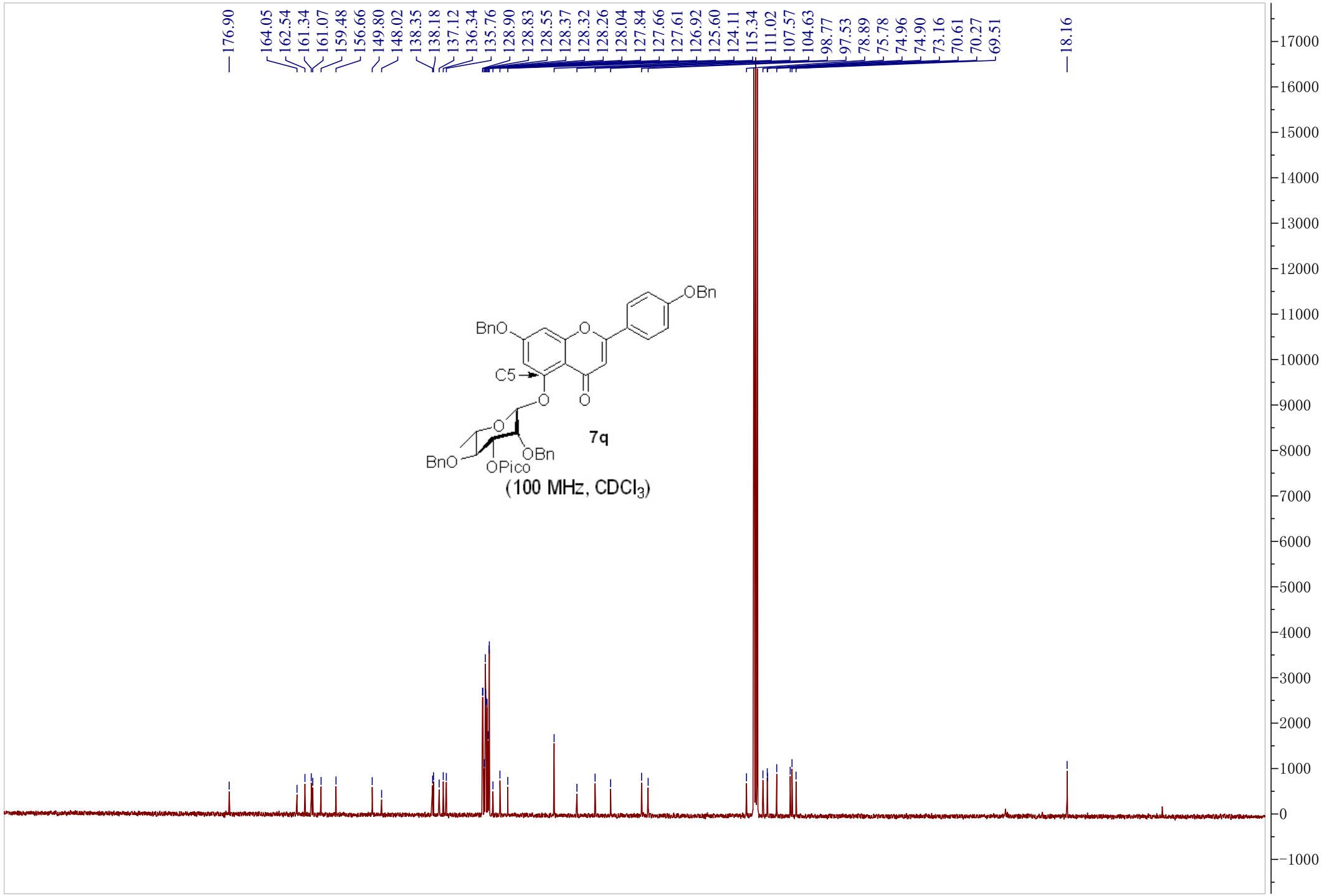

172.45
163.92
156.53
155.20
150.20
147.43
138.34
137.65
137.55
137.27
130.50
130.40
128.68
128.48
128.43
128.38
128.34
128.30
128.25
128.21
128.06
127.88
127.86
127.80
127.20
125.74
117.07
102.01
80.07
79.30
78.74
75.65
73.86
72.78
72.40
68.31
54.57
52.35
52.32
37.64
28.41
PicoO
OBn
BnO
O
O
BnO
BocHN
MeOOC
7p
(100 MHz, CDCl3)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

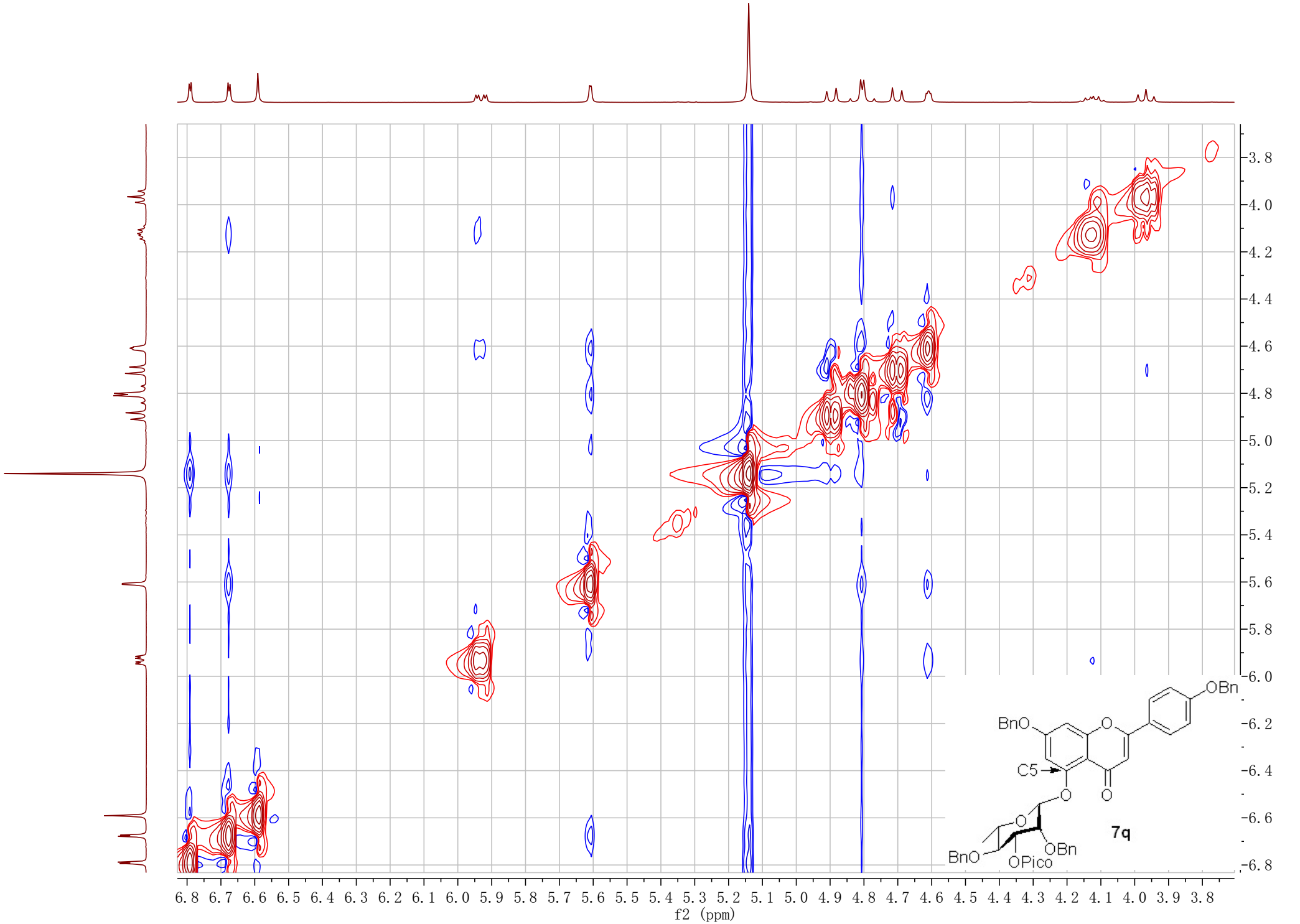
^{1}H-NMR, ^{13}C-NMR, NOESY of **7q**

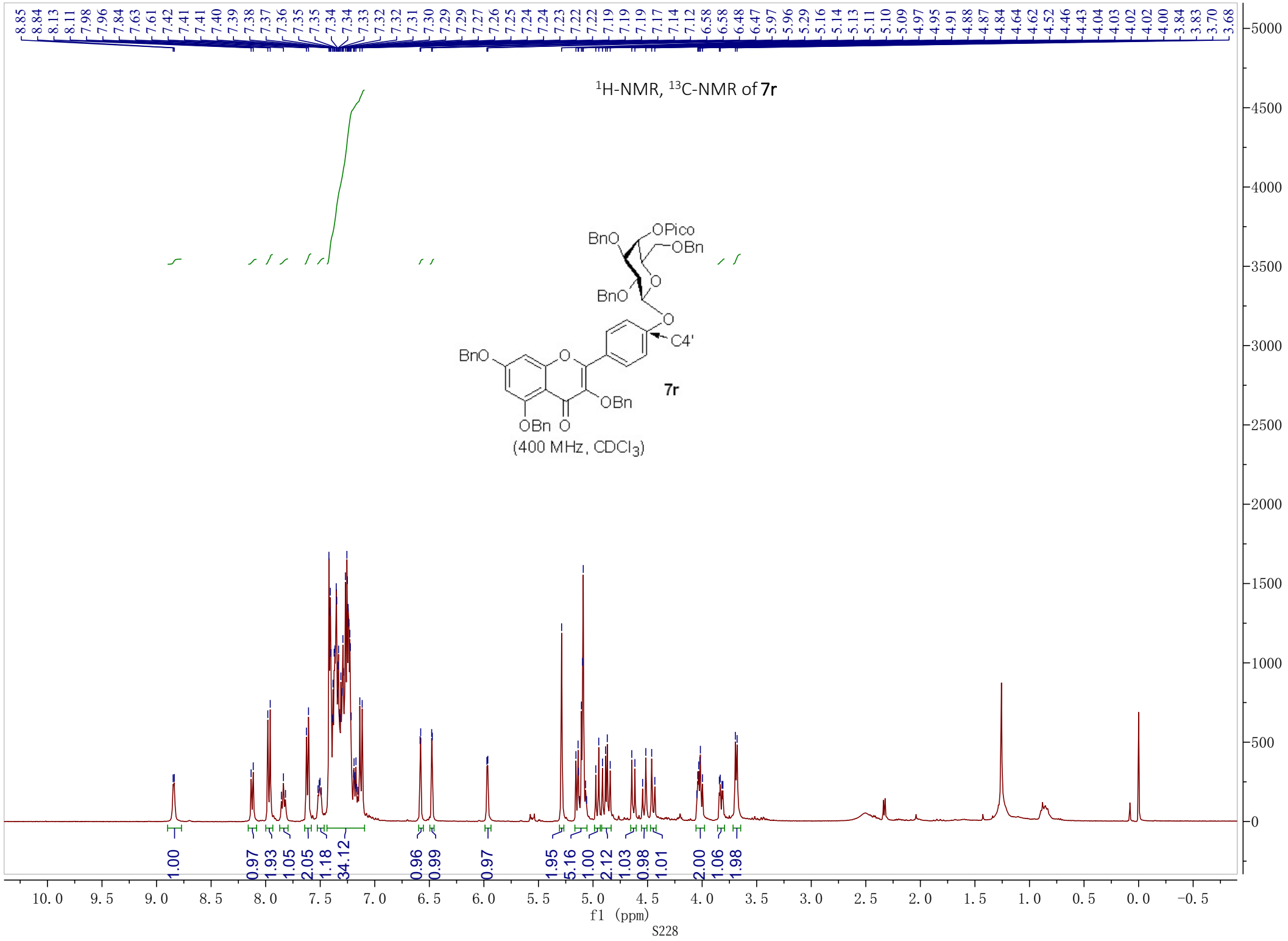


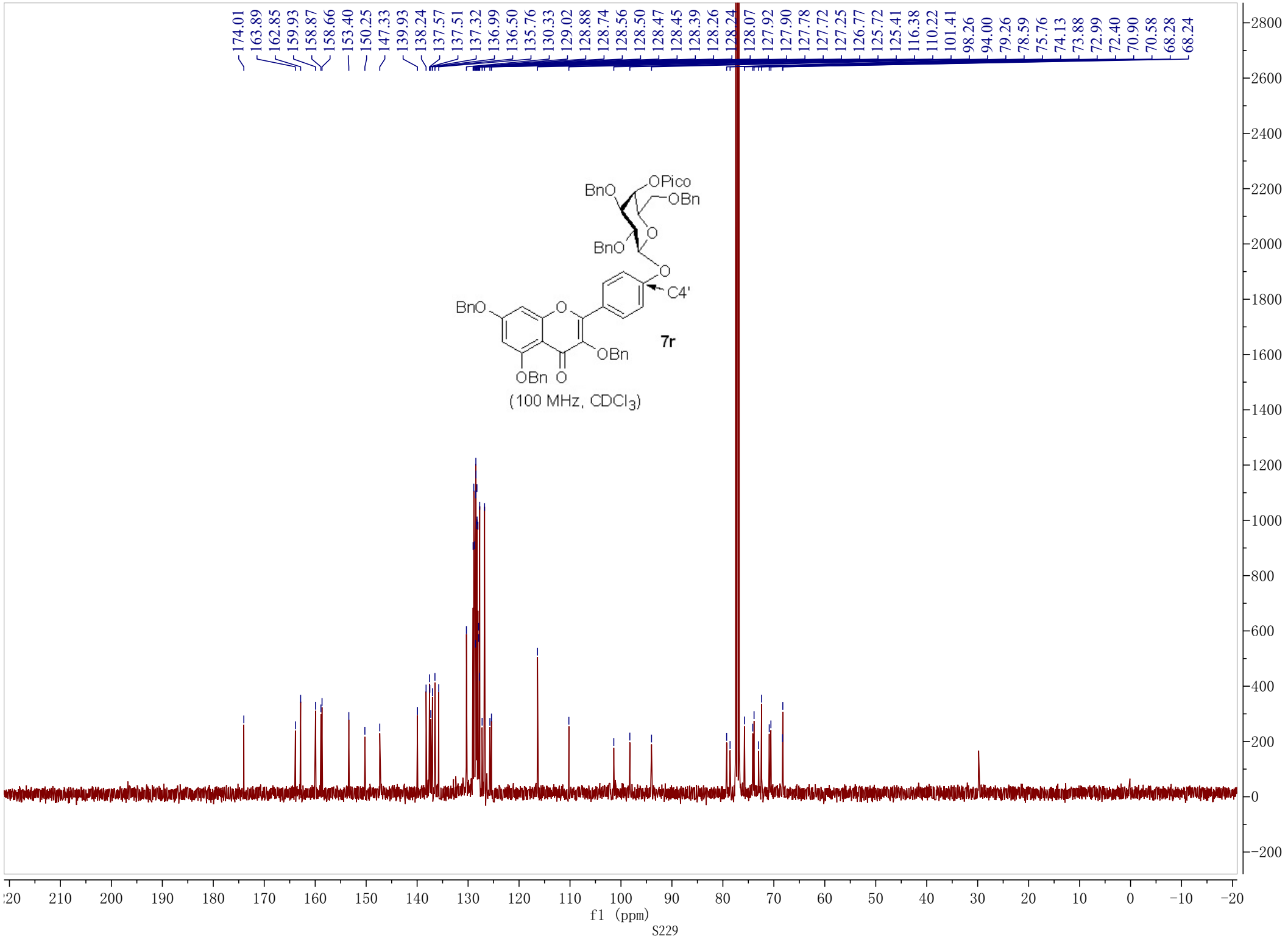
7q

(400 MHz, $CDCl_3$)

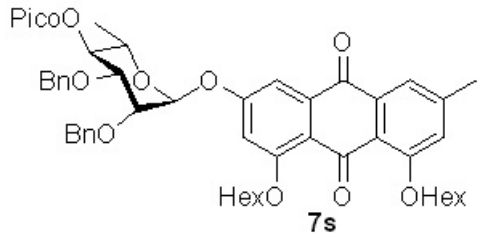

176.90
164.05
162.54
161.34
161.07
159.48
156.66
149.80
148.02
138.35
138.18
137.12
136.34
135.76
128.90
128.83
128.55
128.37
128.32
128.26
128.04
127.84
127.66
127.61
126.92
125.60
124.11
115.34
111.02
107.57
104.63
98.77
97.53
78.89
75.78
74.96
74.90
73.16
70.61
70.27
69.51
18.16
OBn
BnO
O
C5
O
O
O
BnO
OPico
OBn
7q
(100 MHz, CDCl3)
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8
f2 (ppm)
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 6.6 6.8
f1 (ppm)
OBn
BnO
O
C5
O
O
O
BnO
OPico
OBn
7q


^{1}H-NMR, ^{13}C-NMR of **7r**
BnO
OPico
OBn
BnO
O
O
C4'
BnO
O
OBn
OBn O
7r
(400 MHz, $CDCl_3$)
f1 (ppm)

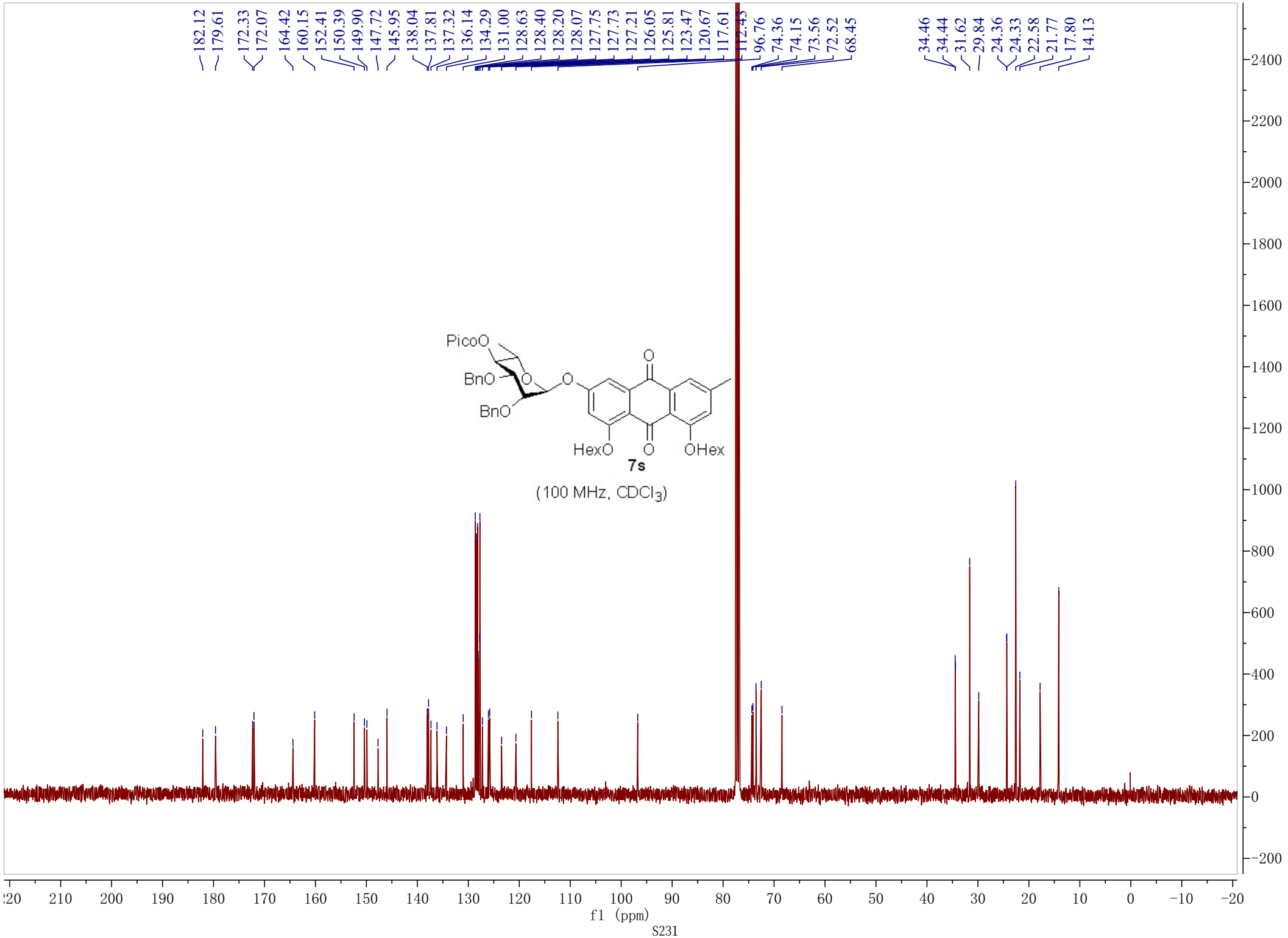

174.01
163.89
162.85
159.93
158.87
158.66
153.40
150.25
147.33
139.93
138.24
137.57
137.51
137.32
136.99
136.50
135.76
130.33
129.02
128.88
128.74
128.56
128.50
128.47
128.45
128.39
128.26
128.24
128.07
127.92
127.90
127.78
127.72
127.25
126.77
125.72
125.41
116.38
110.22
101.41
98.26
94.00
79.26
78.59
75.76
74.13
73.88
72.99
72.40
70.90
70.58
68.28
68.24
BnO
OPico
OBn
BnO
O
O
C4'
BnO
O
OBn
OBn
O
7r
(100 MHz, CDCl3)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

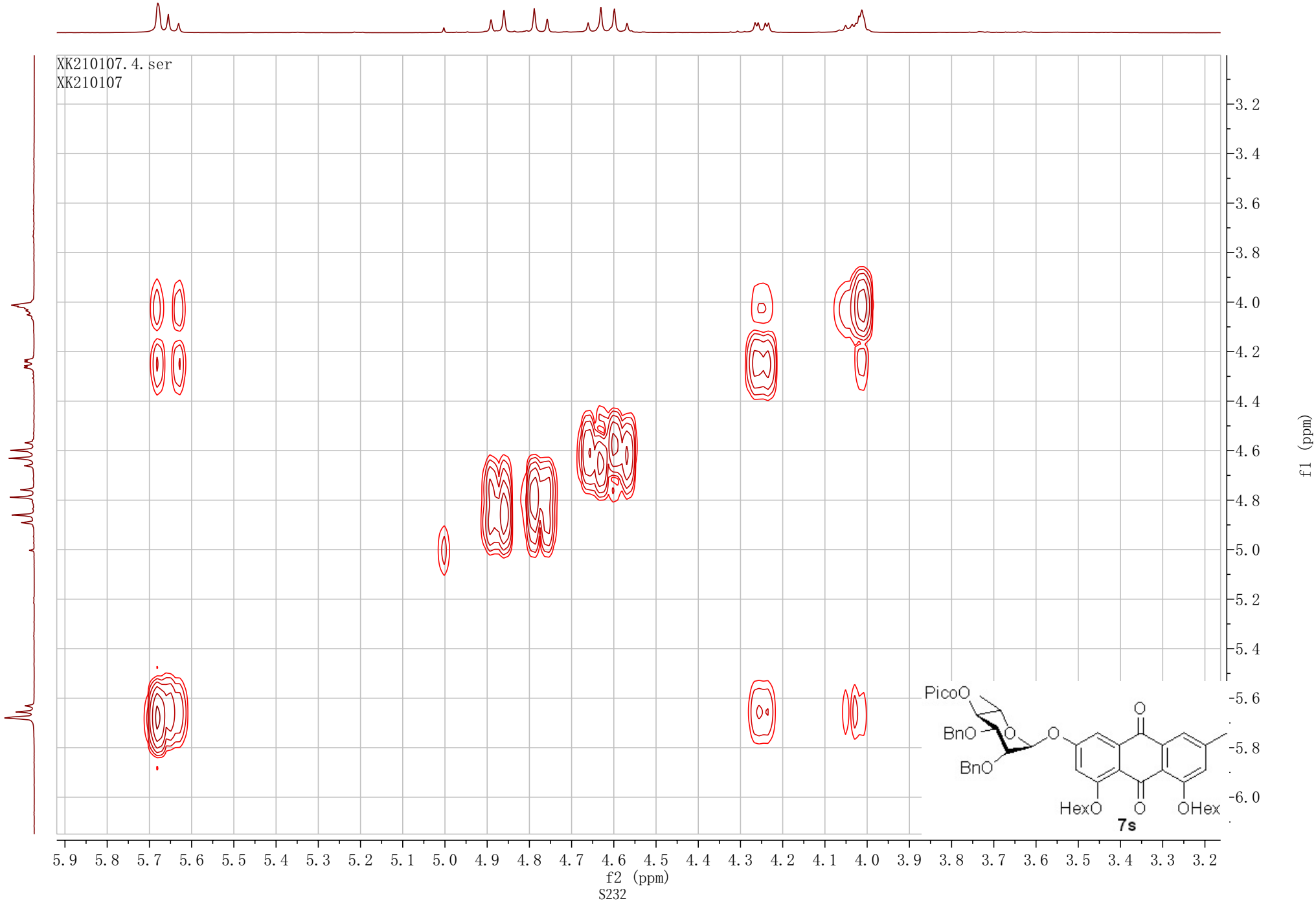
^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC, NOESY of **7s**

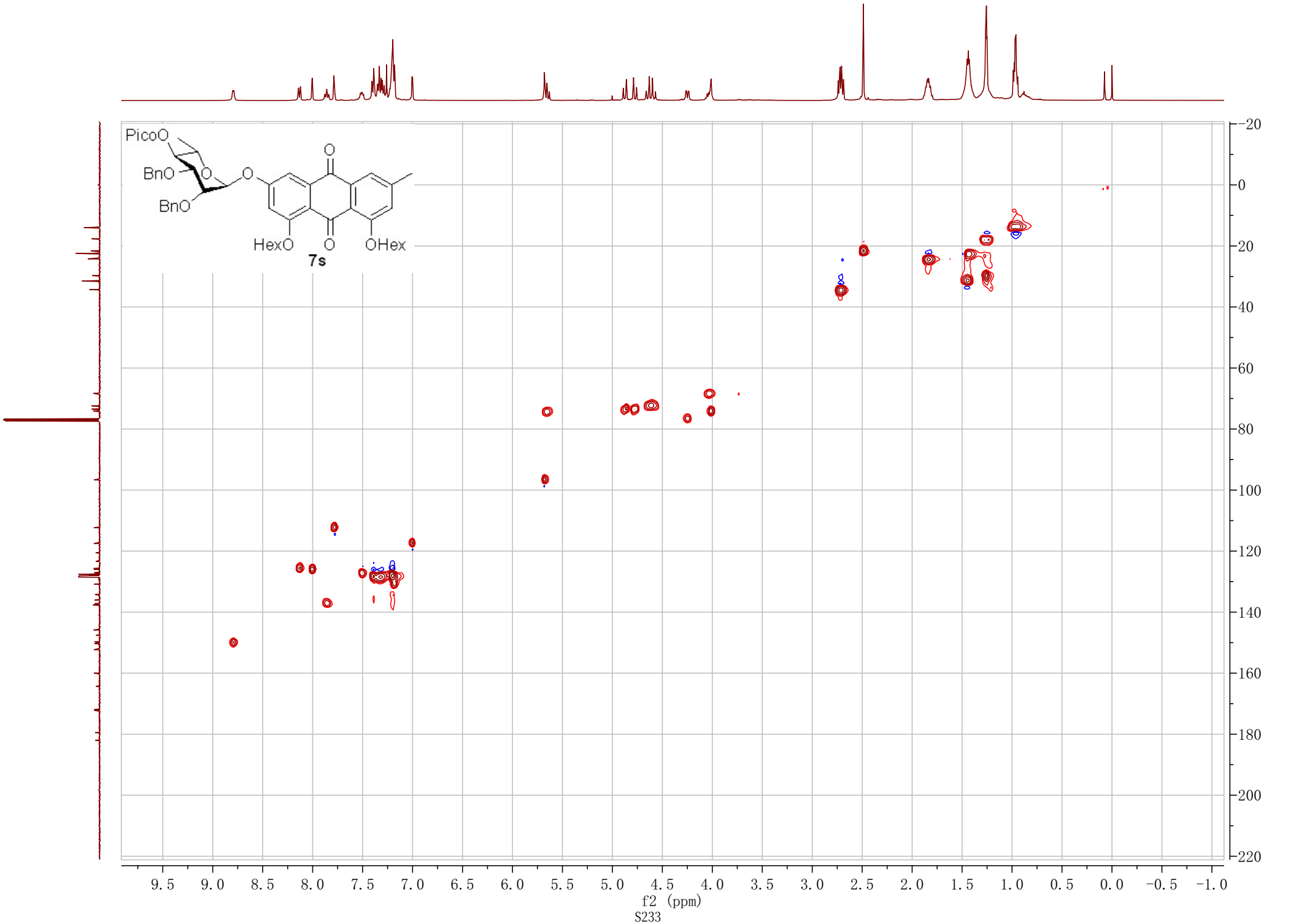


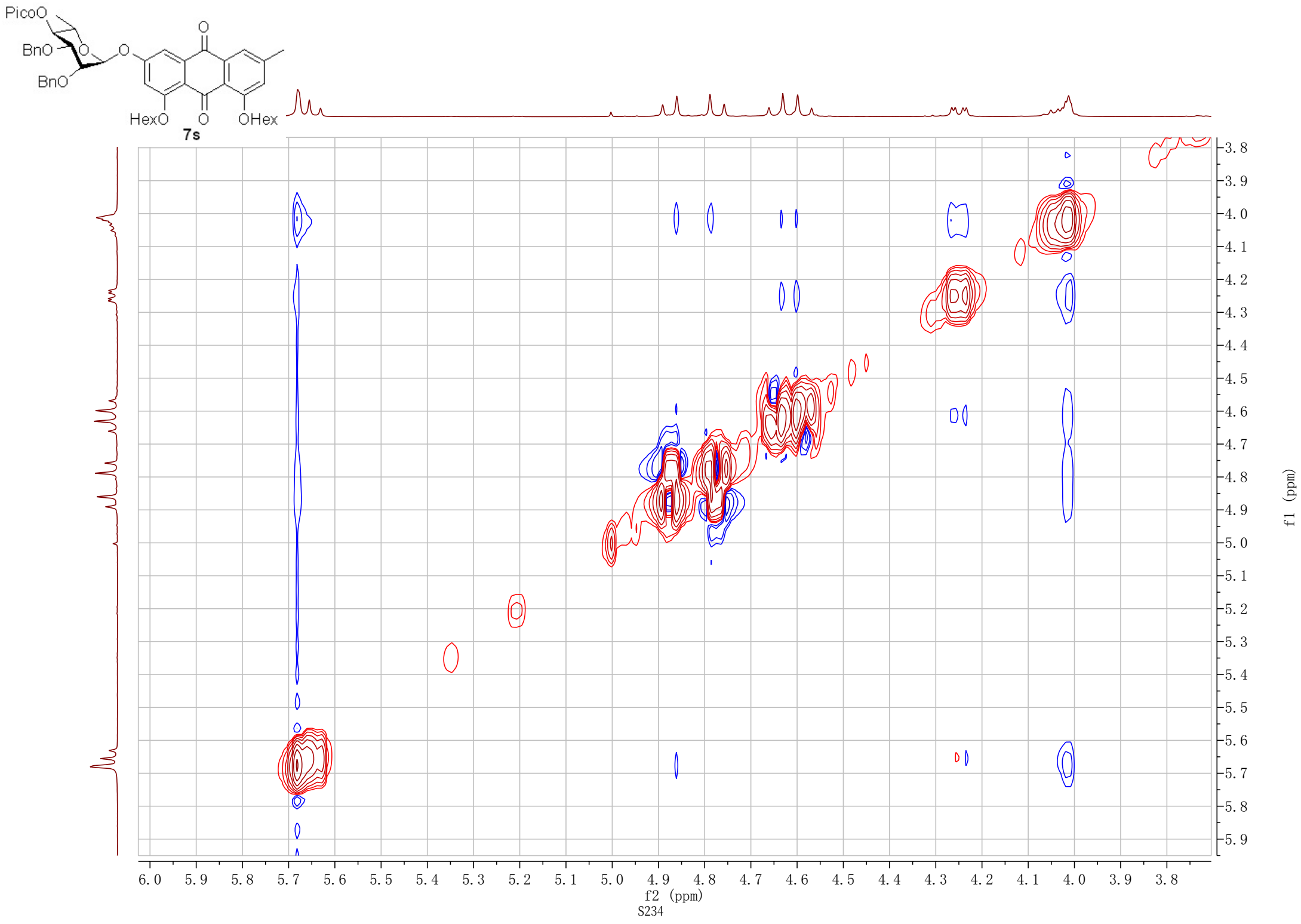
7s

(400 MHz, $CDCl_3$)

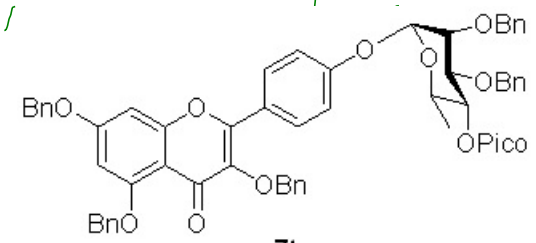

182.12
179.61
172.33
172.07
164.42
160.15
152.41
150.39
149.90
147.72
145.95
138.04
137.81
137.32
136.14
134.29
131.00
128.63
128.40
128.20
128.07
127.75
127.73
127.21
126.05
125.81
123.47
120.67
117.61
112.43
96.76
74.36
74.15
73.56
72.52
68.45
34.46
34.44
31.62
29.84
24.36
24.33
22.58
21.77
17.80
14.13
PicoO
BnO
BnO
O
O
HexO
O
OHex
7s
(100 MHz, CDCl3)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


XK210107.4.ser
XK210107
f2 (ppm)
f1 (ppm)
PicoO
BnO
BnO
HexO
OHex
7s


PicoO
BnO
BnO
O
HexO
O
OHex
7s
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-20 0 20 40 60 80 100 120 140 160 180 200 220
f1 (ppm)

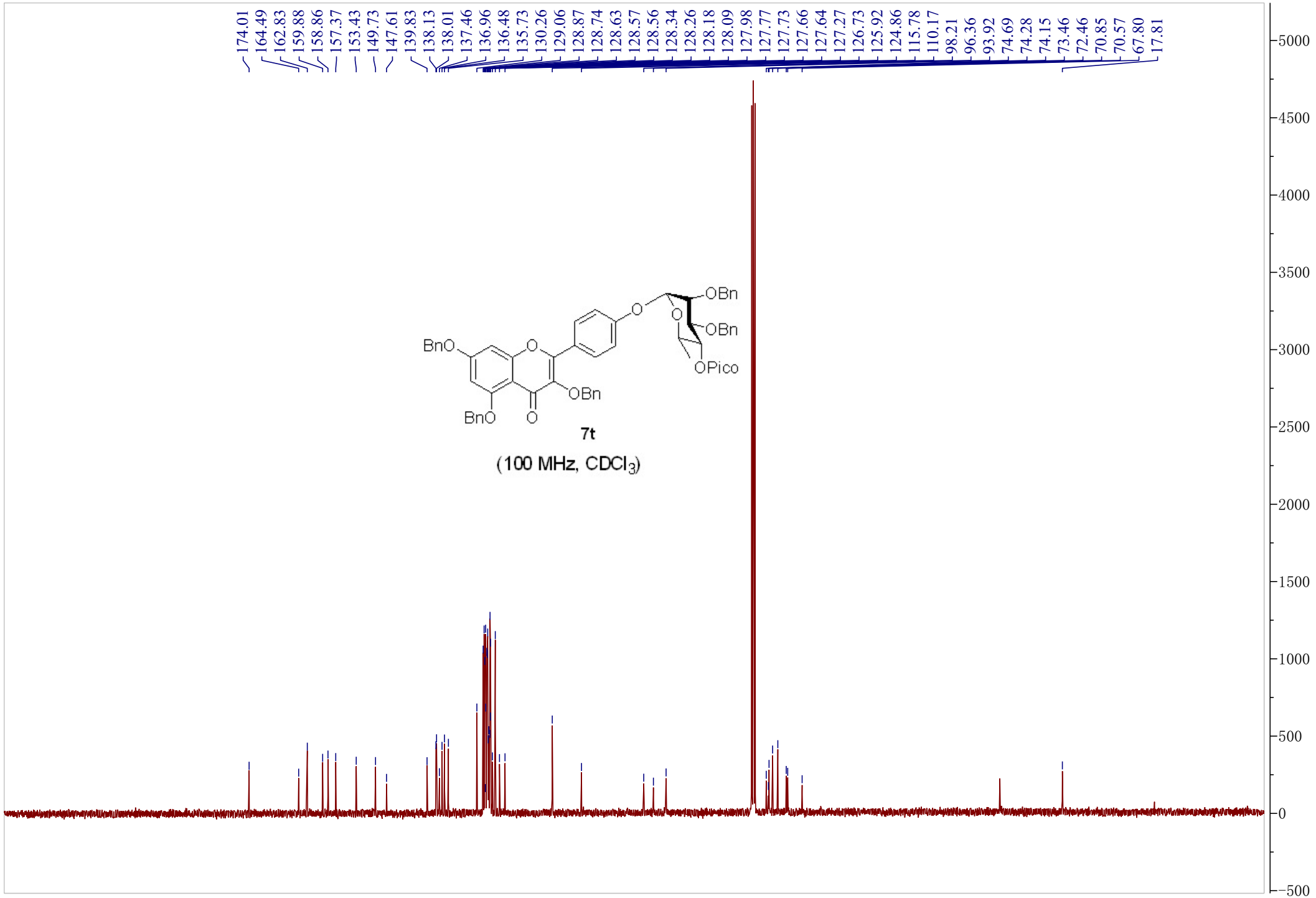

PicoO
BnO
BnO
O
O
HexO
OHex
7s
f2 (ppm)
f1 (ppm)
S234

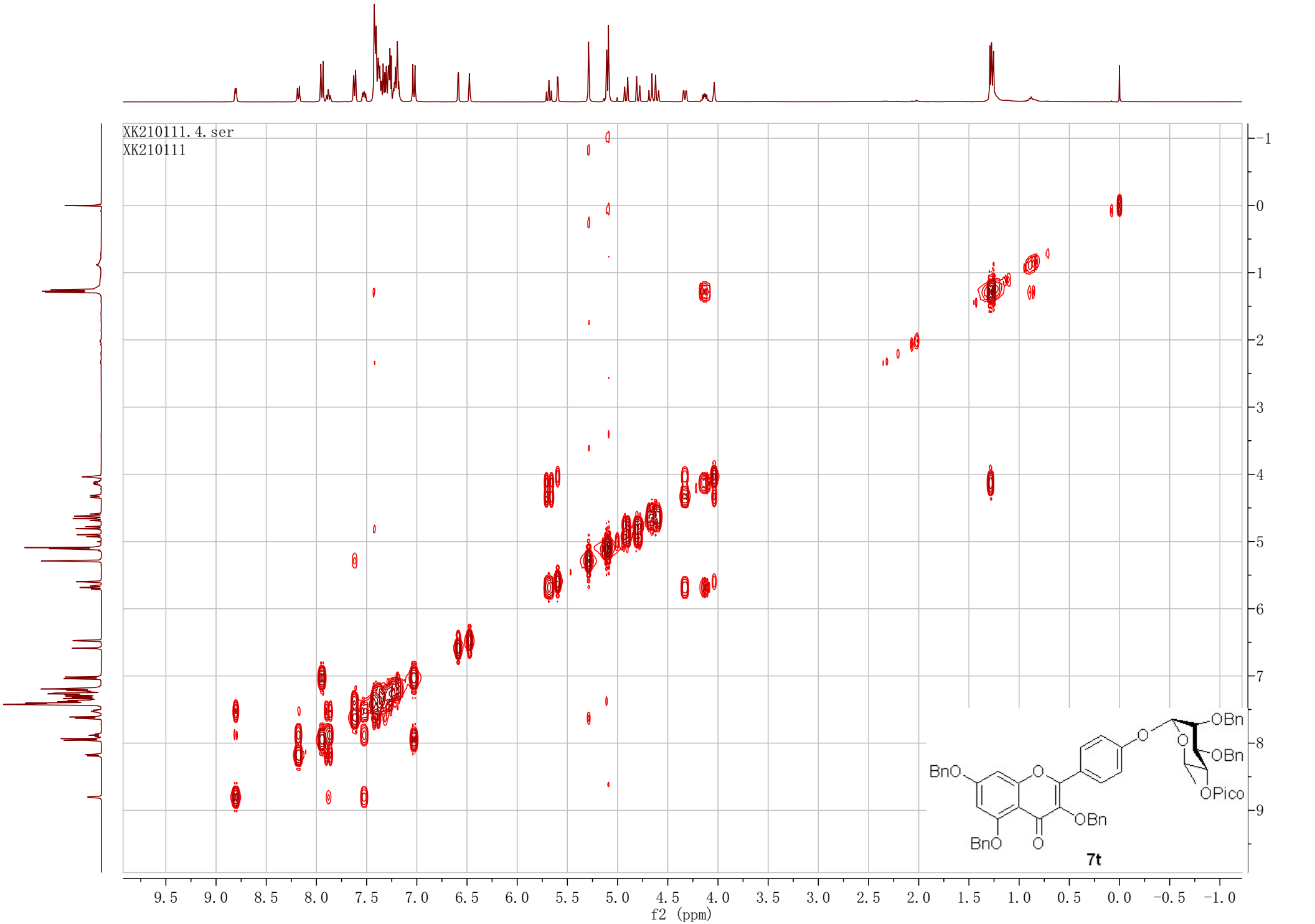
^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HSQC, NOESY of **7t**

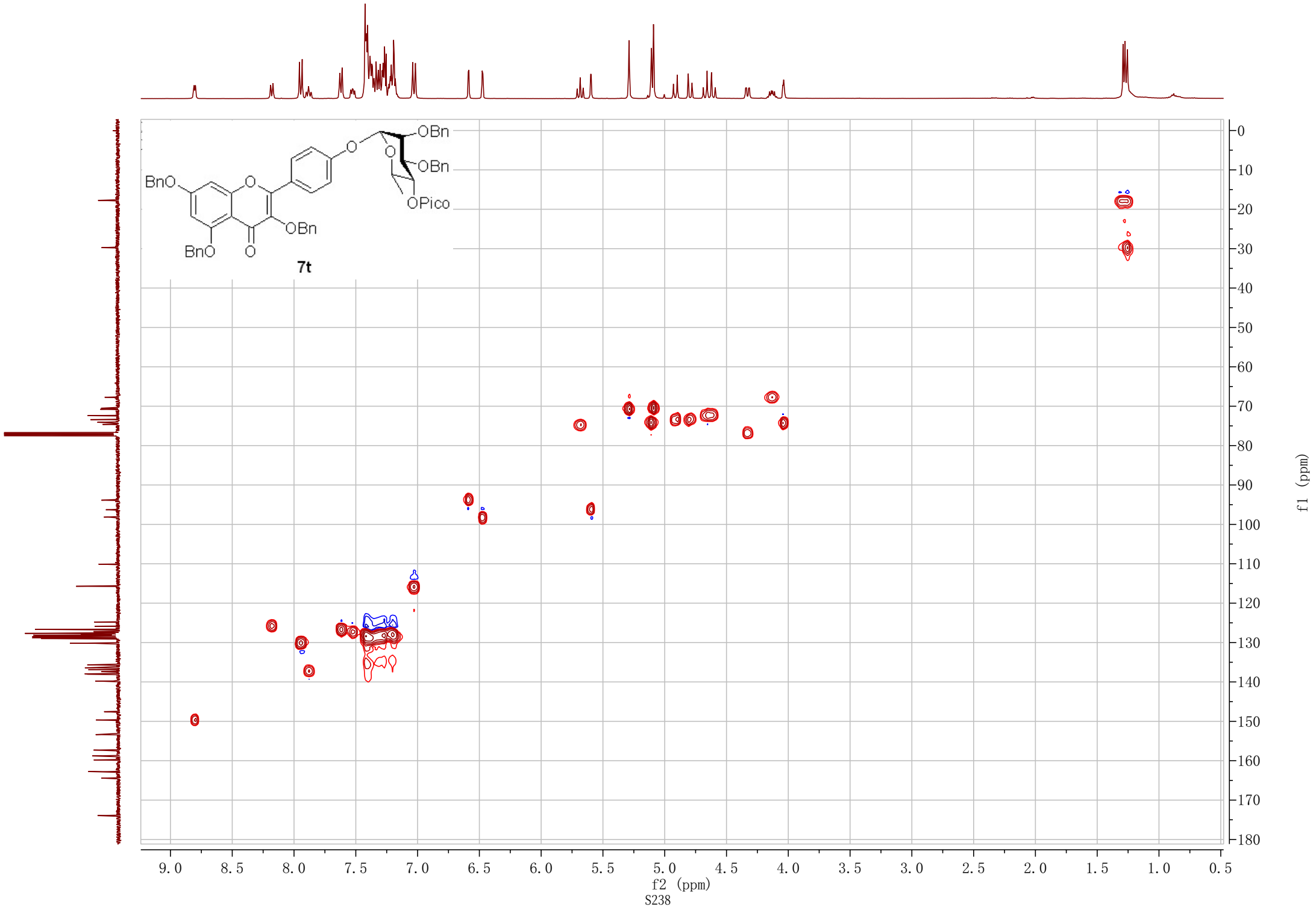


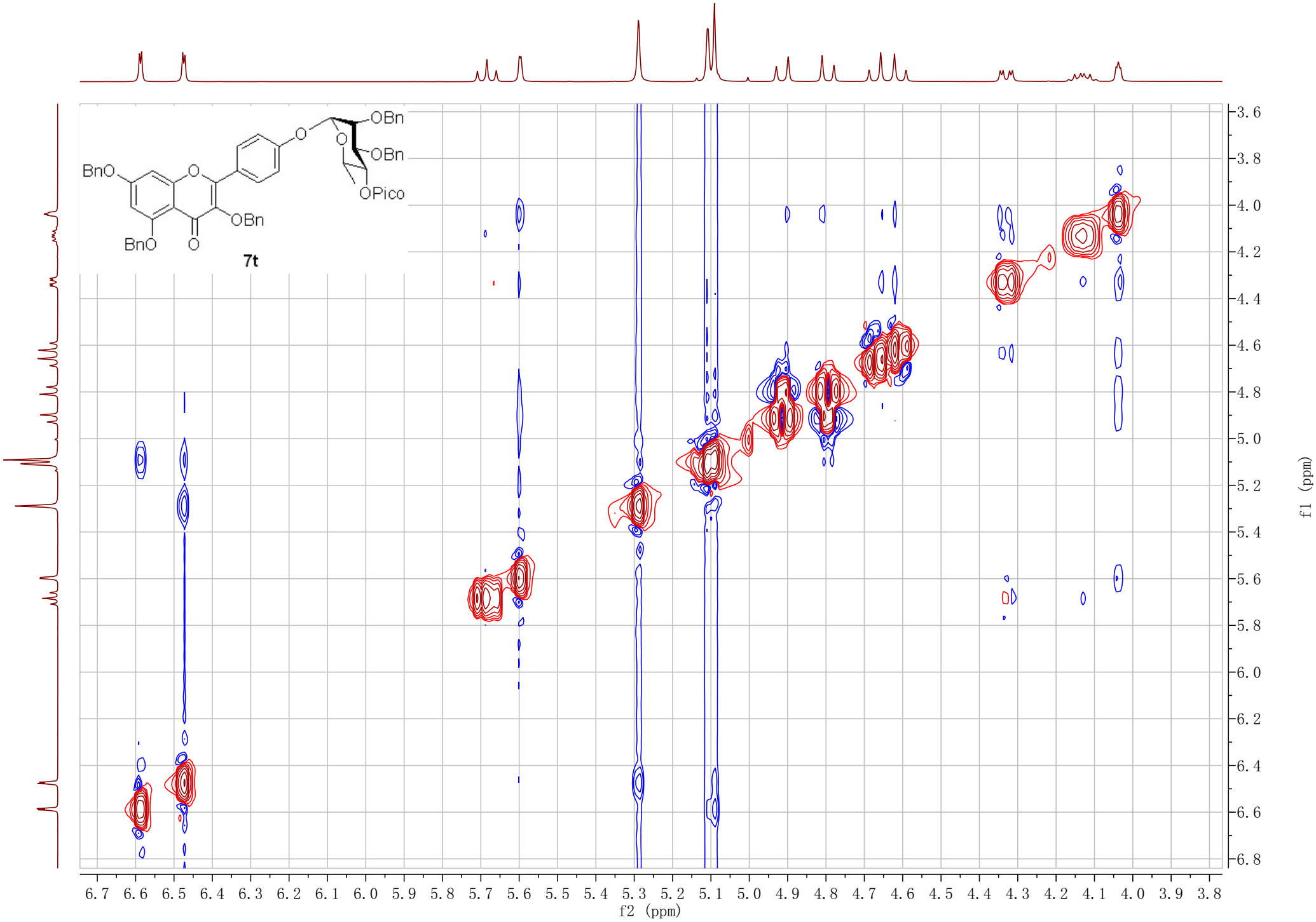
7t

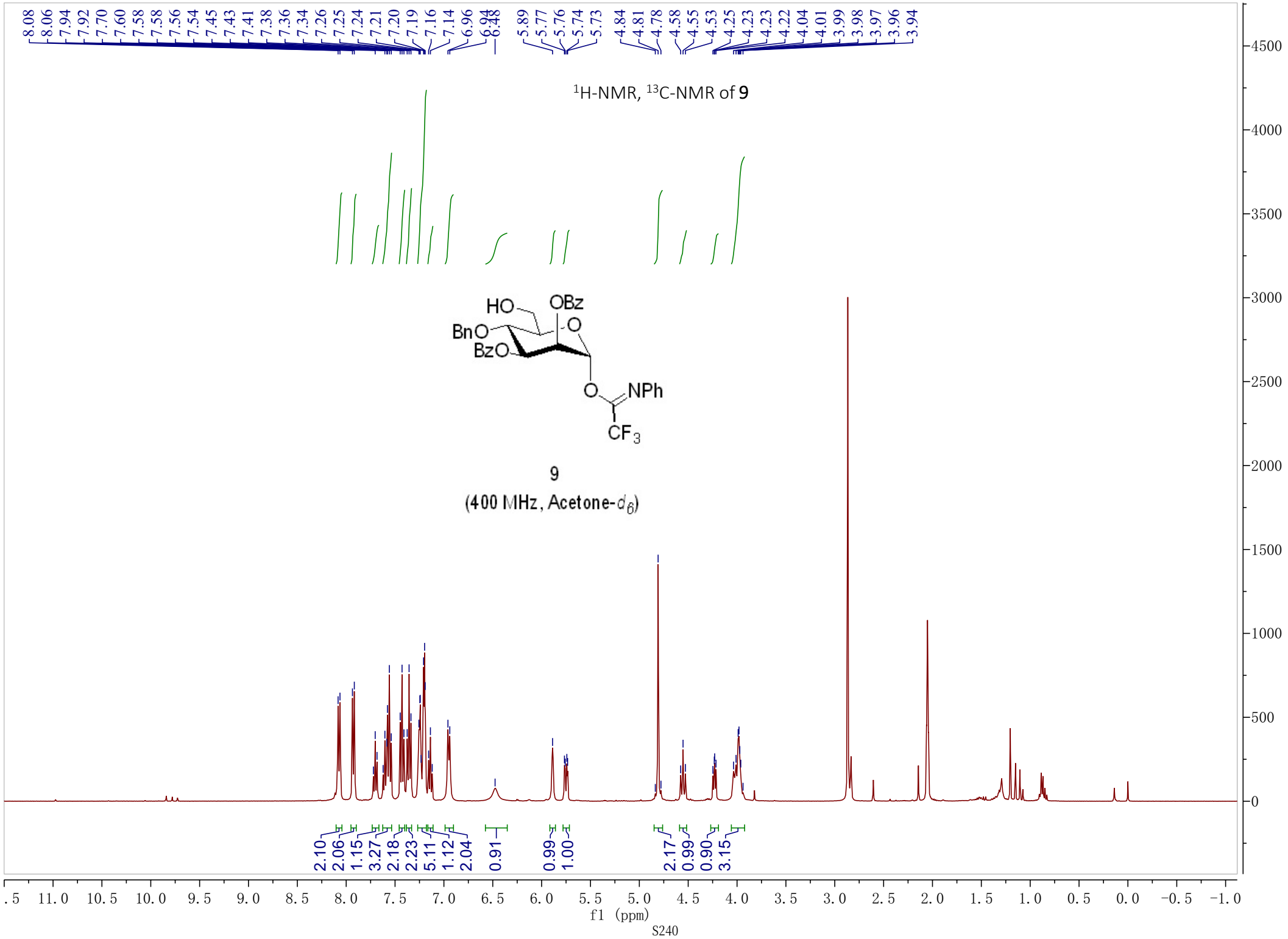
(400 MHz, $CDCl_3$)

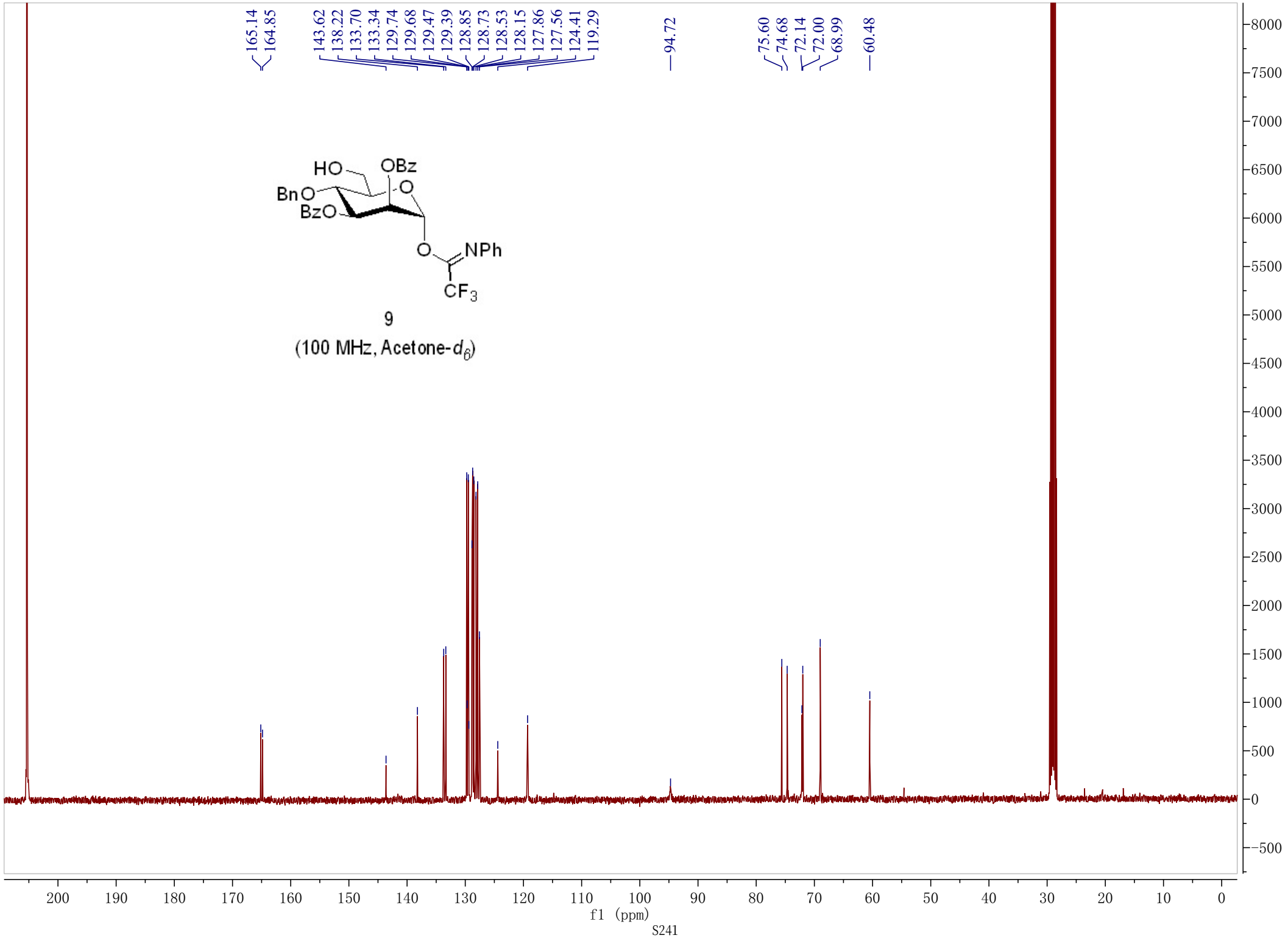

174.01
164.49
162.83
159.88
158.86
157.37
153.43
149.73
147.61
139.83
138.13
138.01
137.46
136.96
136.48
135.73
130.26
129.06
128.87
128.74
128.63
128.57
128.56
128.34
128.26
128.18
128.09
127.98
127.77
127.73
127.66
127.64
127.27
126.73
125.92
124.86
115.78
110.17
98.21
96.36
93.92
74.69
74.28
74.15
73.46
72.46
70.85
70.57
67.80
17.81
BnO
OBn
OBn
OPico
OBn
BnO
7t
(100 MHz, CDCl3)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

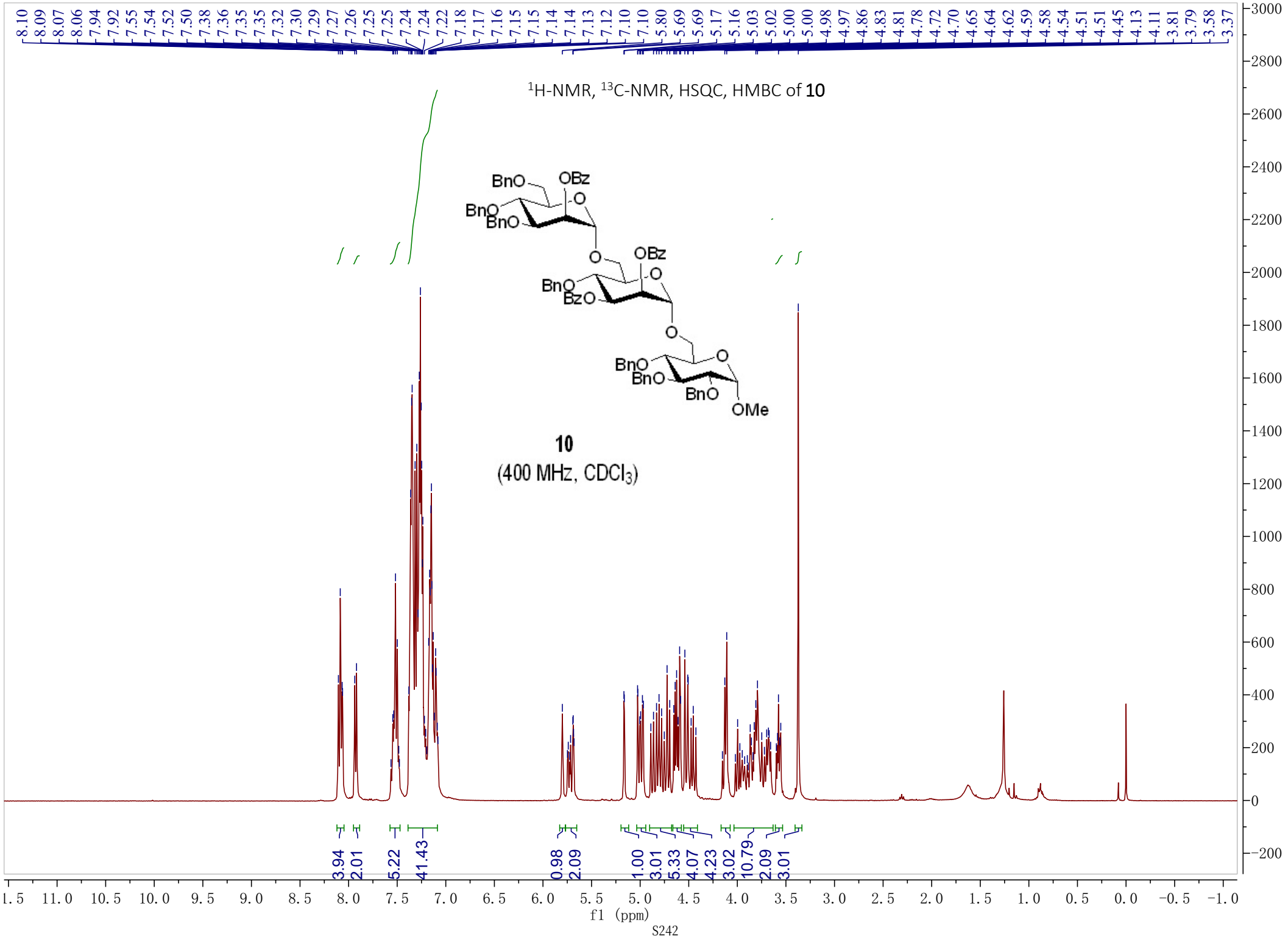

XK210111.4.ser
XK210111
f2 (ppm)
f1 (ppm)
BnO
OBn
OBn
OPico
BnO
OBn
O
7t

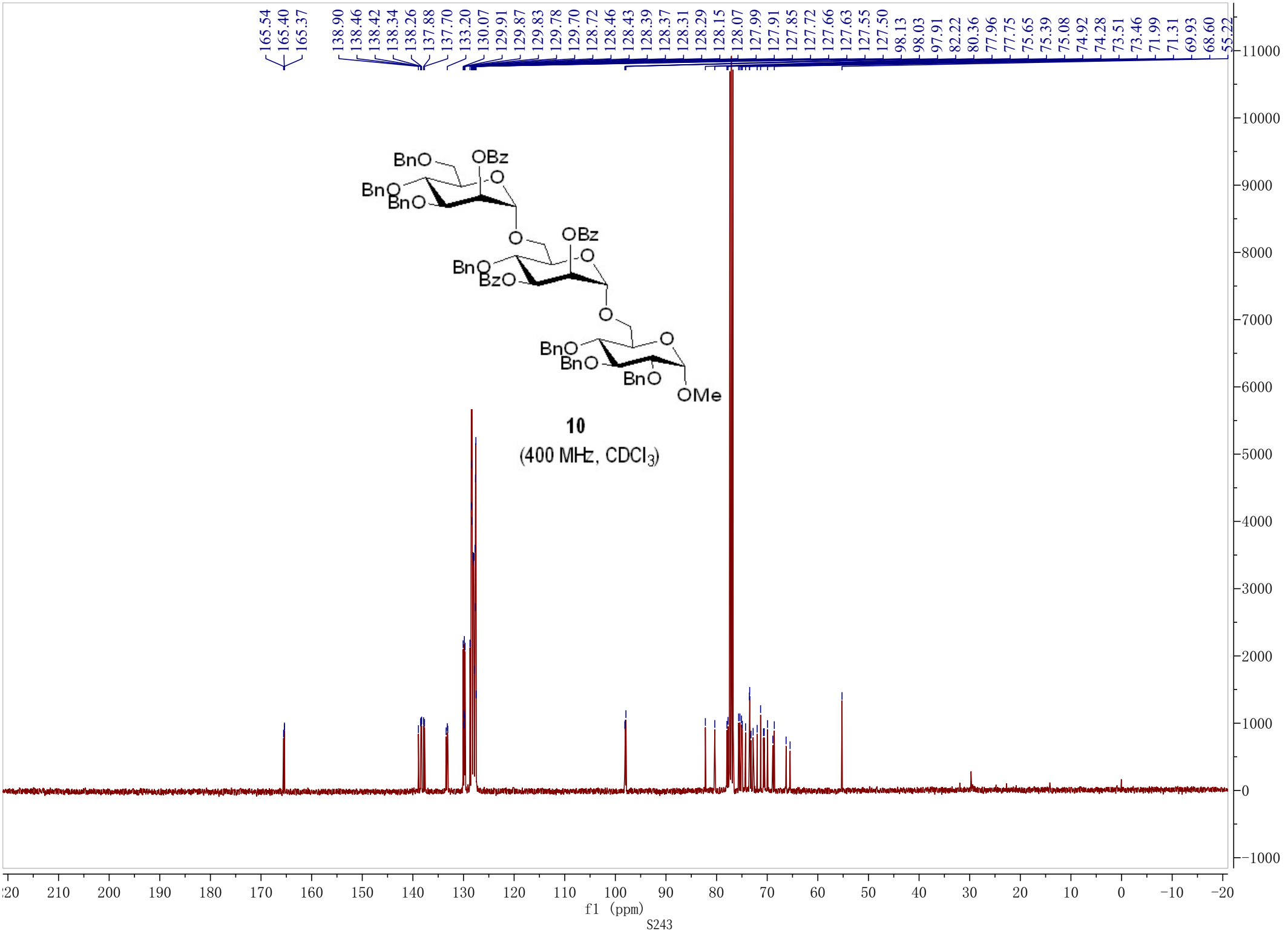

OBn
OBn
OPico
BnO
OBn
BnO
O
O
O
O
7t
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

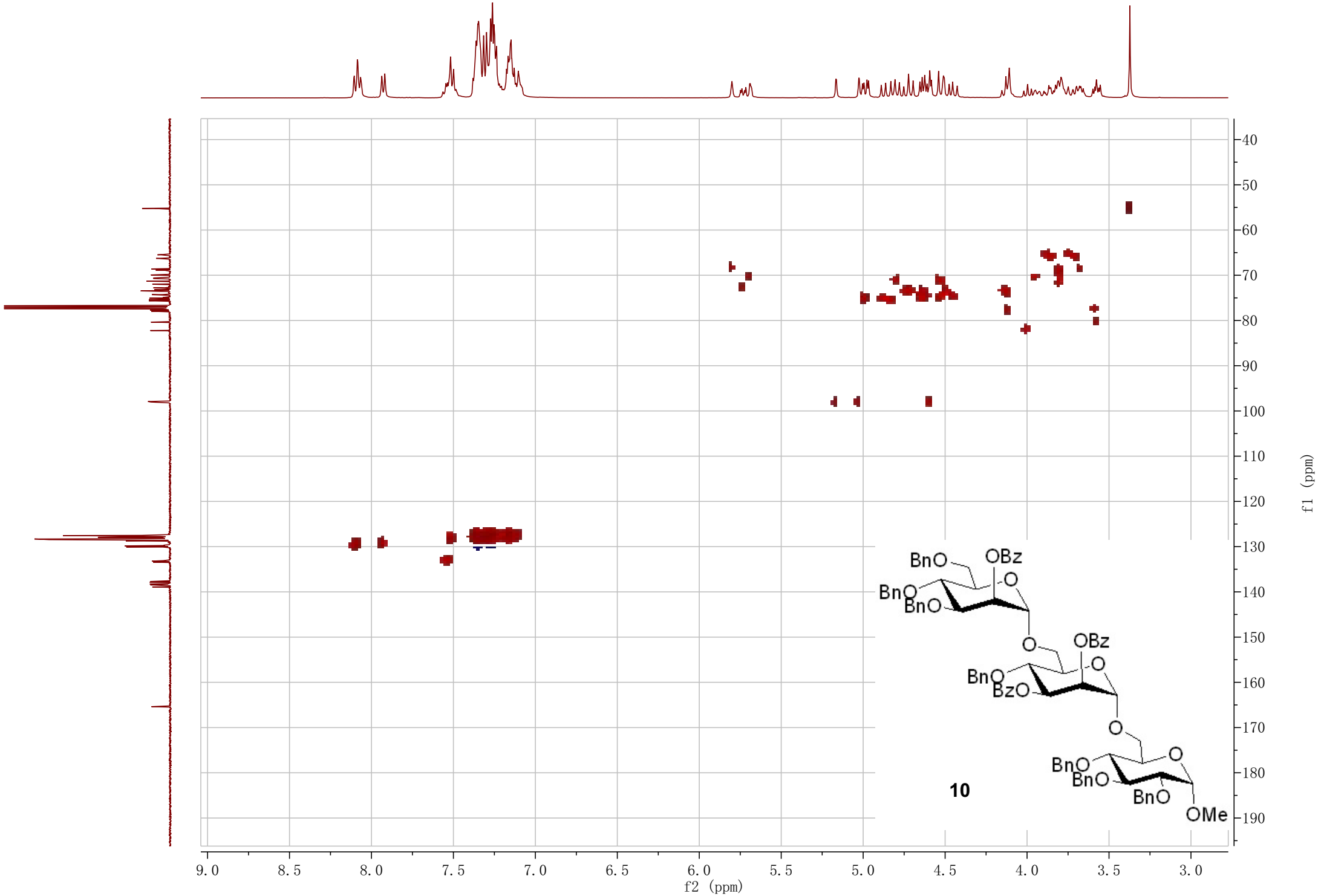

OBn
OBn
OPico
BnO
OBn
BnO
O
7t
f2 (ppm)
f1 (ppm)

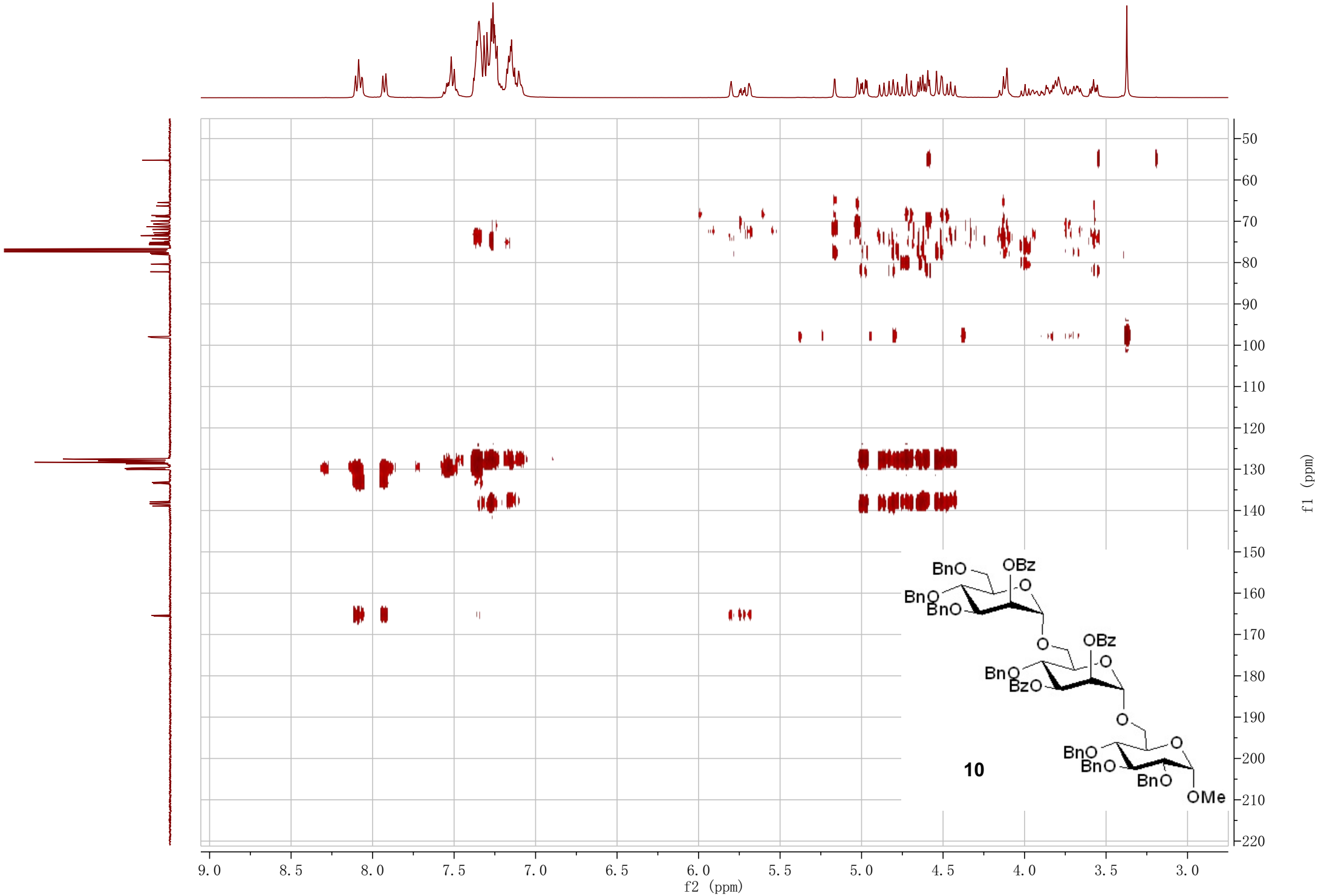

8.08 8.06 7.94 7.92 7.70 7.60 7.58 7.58 7.56 7.54 7.45 7.43 7.41 7.38 7.36 7.34 7.26 7.25 7.24 7.21 7.20 7.19 7.16 7.14 6.96 6.94 6.48
5.89 5.77 5.76 5.74 5.73
4.84 4.81 4.78 4.58 4.55 4.53 4.25 4.23 4.23 4.22 4.04 4.01 3.99 3.98 3.97 3.96 3.94
1H-NMR, 13C-NMR of 9
HO
OBz
BnO
BzO
O
O
NPh
CF3
9
(400 MHz, Acetone-d6)
2.10 2.06 1.15 3.27 2.18 2.23 5.11 1.12 2.04 0.91 0.99 1.00 2.17 0.99 0.90 3.15
f1 (ppm)


165.14
164.85
143.62
138.22
133.70
133.34
129.74
129.68
129.47
129.39
128.85
128.73
128.53
128.15
127.86
127.56
124.41
119.29
94.72
75.60
74.68
72.14
72.00
68.99
60.48
HO
OBz
BnO
BzO
O
O
NPh
CF3
9
(100 MHz, Acetone-d6)
8000
7500
7000
6500
6000
5500
5000
4500
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
f1 (ppm)


8.10 8.09 8.07 8.06 7.94 7.92 7.55 7.54 7.52 7.50 7.38 7.36 7.35 7.35 7.32 7.30 7.29 7.27 7.26 7.25 7.25 7.24 7.24 7.22 7.18 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.12 7.10 7.10 5.80 5.69 5.69 5.17 5.16 5.03 5.02 5.00 5.00 4.98 4.97 4.86 4.83 4.81 4.78 4.72 4.70 4.65 4.64 4.62 4.59 4.58 4.54 4.51 4.51 4.45 4.13 4.11 3.81 3.79 3.58 3.37
1H-NMR, 13C-NMR, HSQC, HMBC of 10
BnO
OBz
O
BnO
BnO
OBz
O
BnO
BzO
O
O
BnO
BnO
BnO
OMe
10
(400 MHz, CDCl3)
3.94 2.01 5.22 41.43 0.98 2.09 1.00 3.01 5.33 4.07 4.23 3.02 10.79 2.09 3.01
f1 (ppm)


165.54
165.40
165.37
138.90
138.46
138.42
138.34
138.26
137.88
137.70
133.20
130.07
129.91
129.87
129.83
129.78
129.70
128.72
128.46
128.43
128.39
128.37
128.31
128.29
128.15
128.07
127.99
127.91
127.85
127.72
127.66
127.63
127.55
127.50
98.13
98.03
97.91
82.22
80.36
77.96
77.75
75.65
75.39
75.08
74.92
74.28
73.51
73.46
71.99
71.31
69.93
68.60
55.22
BnO
OBz
BnO
BnO
O
OBz
BnO
BzO
O
BnO
BnO
BnO
OMe
10
(400 MHz, CDCl3)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


BnO
OBz
O
BnO
BnO
O
OBz
BnO
O
BzO
O
BnO
BnO
BnO
OMe
10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)


f2 (ppm)
f1 (ppm)
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
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
BnO
OBz
O
BnO
BnO
O
OBz
BnO
BzO
O
O
BnO
BnO
BnO
OMe
10