SUPPORTING INFORMATION

Stereoselective Alkyl C-Glycosylation of Glycosyl Esters *via* Anomeric C-O Bonds Homolysis: Efficient Access to *C*-Glycosyl Amino Acids and *C*-Glycosyl Peptides

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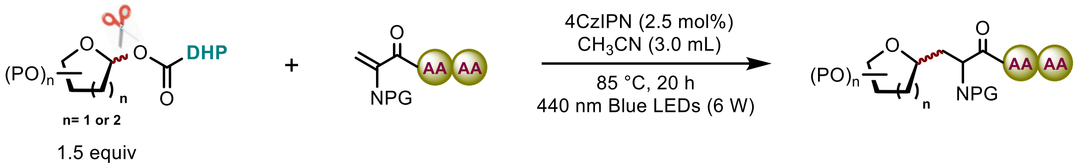
1. General Information

Commercially available materials were used as received without further purification unless otherwise noted. All reactions were carried out under anhydrous N_2 in oven-dried glassware. Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (95% purity) were purchased from Leyan, Anhydrous CH_3CN (99.5% purity), anhydrous 1,4-dioxane (99.5% purity) were purchased from Adamas. Aldrich® Micro Photochemical Reactors (6 W blue LED strips) were purchased from Sigma-Aldrich. Visualizations were performed with UV light and/or Hanessian stain and/or sulfuric acid stain (5% H_2SO_4 in MeOH). Column chromatography was performed on silica gel (200-400 mesh). Automated column chromatography was performed on a Biotage Selekt using Silicycle high-resolution SiO_2 cartridges unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400/500 MHz instruments and were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. The residual solvent reference peaks were used from published literature. 2D NMR experiments were performed using standard parameters (*200 and More NMR Experiments,* S. Berger, S. Braun, Wiley-VCH, **2004**). High-resolution mass spectra (HR-MS) were recorded on a Waters Micromass Q-Tof Premier mass spectrometer. Optical rotations were measured on JASCO P-1030 and were reported as average of five data points. Optical rotations were measured on an Anton Paar MCP100 automatic polarimeter using a 100 mm path-length cell at 589 nm. Thin layer chromatography was used to monitor reaction progress and analyze fractions from column chromatography.

2. General Procedures

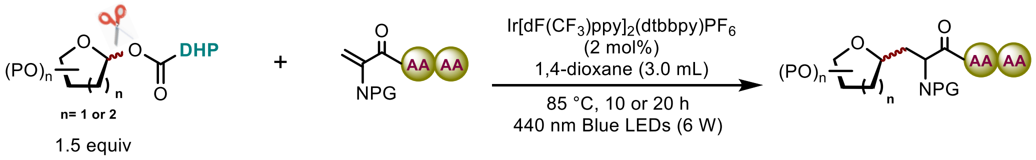
2.1 General Procedure for the Coupling of Glycosyl Esters with Chiral Dehydroalanines

Procedure A:



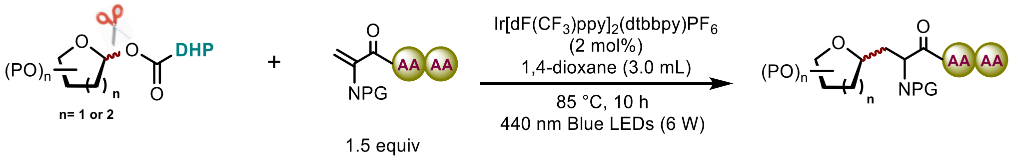
Glycosyl esters (1.50 equiv), chiral dehydroalanines (1.00 equiv), 4CzIPN (2.5 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3×). Anhydrous CH_3CN (3.00 mL) were added, and the reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h, cooled to rt, filtered through a pad of Celite®, and concentrated. It is worth noting that the upper edge of the heating block submerges up 1/3 of the reaction mixture. ^1H NMR spectra were recorded using this mixture to evaluate diastereoselectivity. The crude material was purified by column chromatography on SiO_2.

Procedure B:



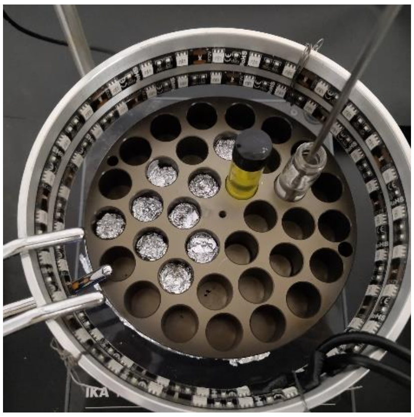
Glycosyl esters (1.50 equiv), chiral dehydroalanines (1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3×). Anhydrous 1,4-dioxane (3.00 mL) were added, and the reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 10 h or 20 h, cooled to rt, filtered through a pad of Celite®, and concentrated. It is worth noting that the upper edge of the heating block submerges up 1/3 of the reaction mixture. ^1H NMR spectra were recorded using this mixture to evaluate diastereoselectivity. The crude material was purified by column chromatography on SiO_2.

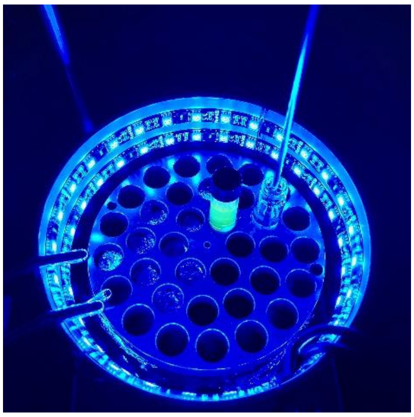
Procedure C:



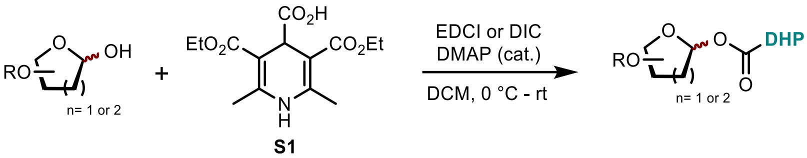
Glycosyl esters (1.00 equiv), chiral dehydroalanines (1.50 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3×). Anhydrous 1,4-dixoane (3.00 mL) were added, and the reaction mixture was stirred at 85 °C for 10 h under 6W blue LED irradiation, cooled to rt, filtered through a pad of Celite®, and concentrated. It is worth noting that the upper edge of the heating block submerges up 1/3 of the reaction mixture. ^1H NMR spectra were recorded using this mixture to evaluate diastereoselectivity. The crude material was purified by column chromatography on SiO_2.

Reaction Set-up for the Radical Addition of Glycosyl Esters with Chiral Dehydroalanines:





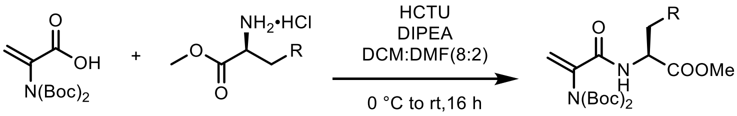
2.2 General Procedure D for Preparation of Glycosyl 4-Formate-1,4-dihydropyridine[1]



In a round bottom flask, carboxylic acid **S1**, EDCI (EDCI = 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride) and DMAP (DMAP = 4-dimethylaminopyridine) (0.100 equiv) were added to a solution of protected-furanose or -pyranose (1.00 equiv) in DCM (0.200 M) at 0 °C. After stirring for 30 minutes, the resulting yellow reaction mixture was warmed up to rt and stirred for 12 h to 18 h. After solvent removal *in vacuo*, the residue was purified by flash column chromatography to afford the corresponding glycosyl ester. Replacing EDCI with DIC (DIC = *N*, *N*'-diisopropylcarbodiimide) resulted in higher conversion to the ester in a shorter time.

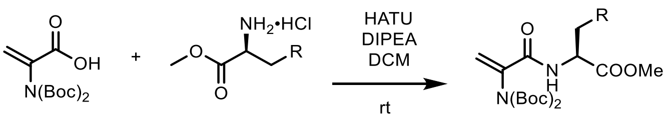
2.3 General Procedure for Preparation of Dehydroalanine Derivatives

General Procedure E:[2]



HCTU (*O*-(6-Chlorobenzotriazol-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate) (1.07 g, 2.61 mmol, 1.50 equiv) was added to a solution of 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] (0.500 g, 1.74 mmol, 1.00 equiv) in anhydrous DCM:DMF (16:4). The solution was cooled to 0 °C and stirred under N_2 for 0.5 h, then glycine methyl ester (1.74 mmol, 1.00 equiv) and DIPEA (*N*,*N*-Diisopropylethylamine) (0.454 mL, 2.61 mmol, 1.50 equiv) was added. After stirring at rt for another 16 hours, the crude material was quenched with water, extracted with EtOAc (3 × 20.0 mL) and washed with 1.0 M HCl solution (2 × 20.0 mL), sat. aq. $NaHCO_3$ solution (2 × 20.0 mL) and brine (20.0 mL). The organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on SiO_2.

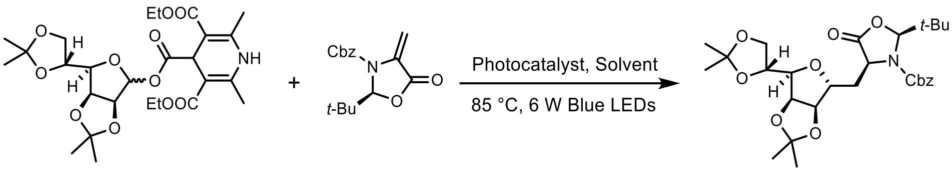
General Procedure F:[3]



2-(Di(*tert*-butoxycarbonyl)amino)acrylic acid[2] (5.00 mmol, 1.00 equiv) was dissolved in anhydrous DCM

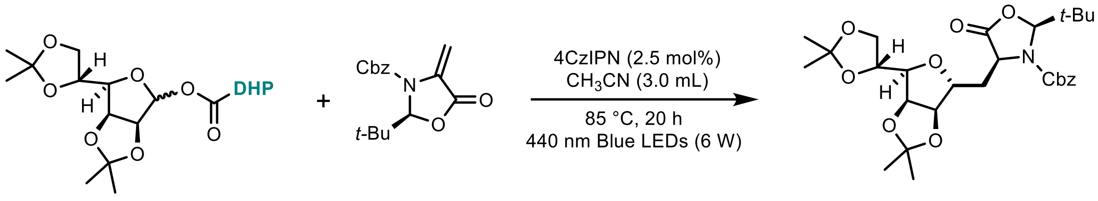
(10.0 mL), then glycine methyl ester (6.00 mmol, 1.20 equiv), HATU (2-(7-Aza-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) (3.80 g, 10.00 mmol, 2.00 equiv), and DIPEA (1.75 mL, 10.00 mmol, 2.00 equiv) were subsequently added. After stirring for 4 h, the mixture was diluted with DCM (10.0 mL) and washed with brine (20.0 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on SiO_2.

3. Additional Reaction Optimization Conditions



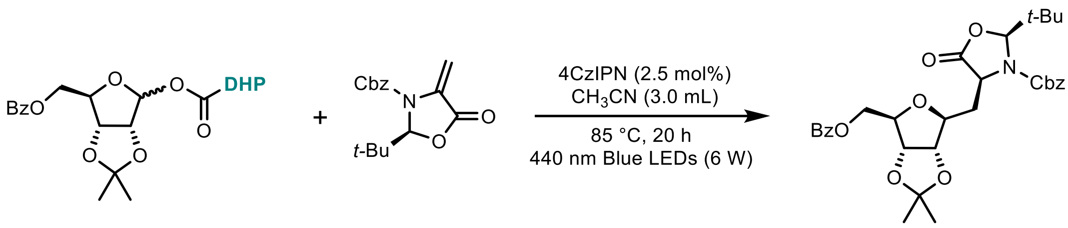
Entry	Catalyst	17a (equiv)	18 (equiv)	Solvent	Time	Temperature	Yield
1	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	1.50	1.00	MeCN (2.0 mL)	10 h	85 °C	52%
2	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	1.50	1.00	DMSO (2.0 mL)	10 h	85 °C	ND
3	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	1.50	1.00	Dioxane (2.0 mL)	10 h	85 °C	69%
4	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	1.50	1.00	DMA (2.0 mL)	10 h	85 °C	7%
5	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	1.50	1.00	DMF (2.0 mL)	10 h	85 °C	9%
6	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)-	1.50	1.00	THF (2.0 mL)	10 h	85 °C	33%
7	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)-	1.00	1.50	Dioxane (2.0 mL)	10 h	85 °C	36%
8	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)-	1.50	1.00	Dioxane (2.0 mL)	10 h	60 °C	35%
9	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)-	1.50	1.00	Dioxane (2.0 mL)	10 h	75 °C	63%
10	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)-	1.50	1.00	Dioxane (2.0 mL)	10 h	100 °C	60%
11	Ir(ppy)$_3$	1.50	1.00	Dioxane (2.0 mL)	10 h	85 °C	ND
12	Ru(bpy)$_3$$Cl_2$	1.50	1.00	Dioxane (2.0 mL)	10 h	85 °C	NR
13	9,10-Diphenylanthracene	1.50	1.00	Dioxane (2.0 mL)	10 h	85 °C	NR
14	4CzIPN (2.0 mol%)-	1.50	1.00	Dioxane (2.0 mL)	10 h	85 °C	7%
15	4CzIPN (2.0 mol%)	1.50	1.00	MeCN (2.0 mL)	10 h	85 °C	64%
16	4CzIPN (2.5 mol%)	1.50	1.00	MeCN (2.0 mL)	10 h	85 °C	70%
17	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	1.50	1.00	Dioxane (1.0 mL)	10 h	85 °C	54%
18	**Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)**	**1.50**	**1.00**	**Dioxane (3.0 mL)**	**10 h**	**85 °C**	**80%**
19	4CzIPN (2.5 mol%)	1.50	1.00	MeCN (2.0 mL)	20 h	85 °C	82%
20	**4CzIPN (2.5 mol%)**	**1.50**	**1.00**	**MeCN (3.0 mL)**	**20 h**	**85 °C**	**85%**
21	4CzIPN (2.5 mol%)	1.50	1.00	MeCN : H_2O=2:1 (3.0 mL)	20 h	85 °C	78%

4. Detailed Experimental Procedures for the Coupling of Glycosyl Esters with Chiral Dehydroalanines



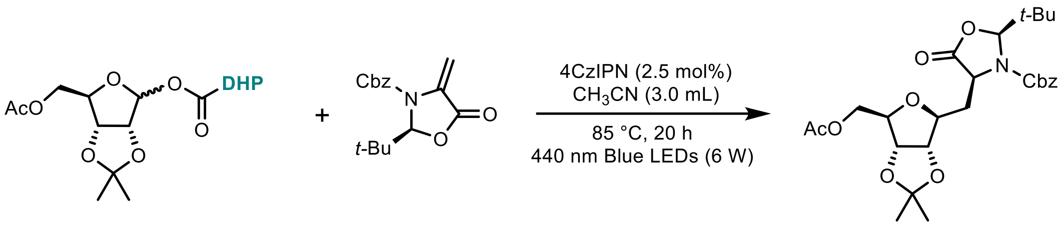
17a, 0.3 mmol **18**, 0.2 mmol **19a**

Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-4-(((3*aR*,4*S*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-5-oxooxazolidine-3-carboxylate (19a). According to the general procedure A, 4-((3a*S*,4*R*,6*R*,6a*S*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19a** (90.8 mg, 85%, d.r. >20:1) as a colorless oil: $[\alpha]_D^{25}$ = +16.6 (c = 0.740, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 5.54 (s, 1H), 5.21 (d, *J* = 1.9 Hz, 2H), 4.77 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.57 (d, *J* = 6.0 Hz, 2H), 4.54 – 4.45 (m, 1H), 4.45 – 4.36 (m, 1H), 4.14 – 4.01 (m, 2H), 3.83 (dd, *J* = 7.7, 3.7 Hz, 1H), 2.06 – 1.87 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 0.94 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 155.8, 135.7, 128.8, 128.7, 112.9, 109.3, 96.4, 85.1, 80.7, 80.6, 80.5, 73.4, 68.4, 67.1, 54.0, 37.2, 33.9, 27.0, 26.2, 25.3, 24.9, 24.8; **HRMS** (ESI) *m/z* calcd for $C_{28}H_{39}O_9NNa$ $[M + Na]^+$ 556.2517, found 556.2522.



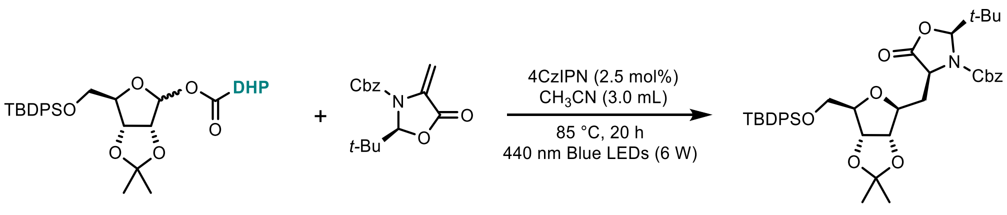
17b, 0.3 mmol **18**, 0.2 mmol **19b**

Benzyl (2*S*,4*S*)-4-(((3*aS*,4*S*,6*R*,6*aR*)-6-((benzoyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19b). According to the general protocol A, 4-((*3aR,6R,6aR*)-6-((benzoyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17b**[1] (172 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv), 4CzlPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **19b** (89.0 mg, 78%, d.r. = 5.3:1, major β) as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 2H), 7.59 – 7.55 (m, 1H), 7.48 – 7.43 (m, 2H), 7.39 – 7.32 (m, 5H), 5.58 – 5.57 (m, 1H), 5.16 – 5.13 (m, 2H), 4.61 – 4.51 (m, 2H), 4.49 – 4.33 (m, 3.20H), 4.25 – 4.22 (m, 1H), 4.09 – 4.05 (m, 0.80H), 2.29 – 2.22 (m, 1.20H), 2.07 – 2.00 (m, 0.80H), 1.52 (s, 2.40H), 1.45 (s, 0.60H), 1.30 – 1.26 (m, 3H), 0.98 (s, 1.80H), 0.95 (s, 7.20H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 166.4, 156.0, 135.2, 133.3, 129.9(2), 129.8, 128.9(2), 128.8, 128.7, 128.6, 115.1, 113.0, 96.6, 84.6, 83.3, 82.2, 81.8, 81.6, 80.7, 68.8, 64.6, 54.0, 37.6, 37.2, 27.6, 26.4, 25.8, 25.2, 25.1, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{31}H_{37}NNaO_9$ [M + Na]$^+$ 590.2361, found 590.2364.



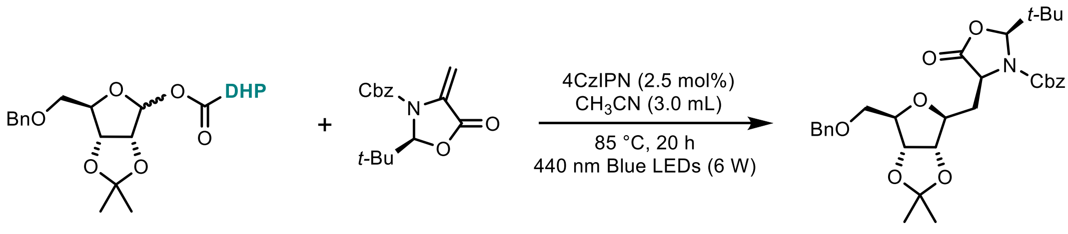
17c, 0.3 mmol **18**, 0.2 mmol **19c**

Benzyl (2*S*,4*S*)-4-(((3*aS*,4*S*,6*R*,6*aR*)-6-(acetoxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19c). According to the general protocol A, 4-((*3aR,6R,6aR*)-6-(acetoxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17c** (153.3 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv), 4CzlPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **19c** (80.0 mg, 79%, d.r. = 5.3:1, major β) as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H), 5.58 (s, 1H), 5.19 - 5.17 (m, 2H), 4.67 – 4.31 (m, 3.17H), 4.23 – 4.13 (m, 1.83H), 4.09 – 3.95 (m, 2H), 2.28 – 2.21 (m, 1H), 2.07 – 2.06 (m, 3H), 2.04 – 1.97 (m, 1H), 1.50 (s, 2.5H), 1.43 (s, 0.5H), 1.30 – 1.28 (m, 3H), 0.98 – 0.96 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 170.9, 156.1, 135.2, 128.9, 128.9, 115.1, 96.6, 84.7, 82.1, 81.7, 80.7, 68.7, 64.3, 54.0, 37.5, 37.2, 27.5, 25.7, 25.0, 21.0; **HRMS** (ESI) *m/z* calcd for $C_{26}H_{35}NNaO_9$ [M + Na]$^+$ 528.2204, found 528.2202.



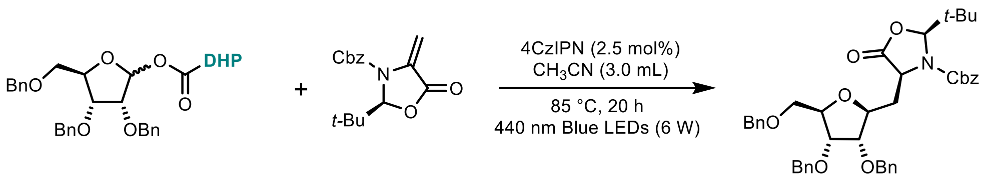
17d, 0.3 mmol **18**, 0.2 mmol **19d**

Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-4-(((3*aS*,4*S*,6*R*,6*aR*)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-5-oxooxazolidine-3-carboxylate (19d). According to the general procedure A. 4-((3a*R*,6*R*,6a*R*)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17d** (212 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19d** (77.6 mg, 57%, d.r. = 3.2:1, major β) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.46 – 7.30 (m, 11H), 5.59 (d, *J* = 2.7 Hz, 1H), 5.21 – 5.11 (m, 2H), 4.83 (d, *J* = 5.9 Hz, 0.24H), 4.70 – 4.61 (m, 1H), 4.53 (t, *J* = 6.6 Hz, 1H), 4.30 (t, *J* = 6.0 Hz, 0.68H), 4.18 (q, *J* = 6.6 Hz, 0.78H), 4.11 (t, *J* = 4.4 Hz, 0.27H), 3.88 (d, *J* = 4.1 Hz, 0.74H), 3.75 – 3.62 (m, 2H), 2.27 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.04 (dt, *J* = 13.5, 6.6 Hz, 1H), 1.47 (d, *J* = 26.7 Hz, 3H), 1.32 (d, *J* = 9.6 Hz, 3H), 1.07 (d, *J* = 3.8 Hz, 9H), 0.98 (d, *J* = 7.5 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 172.4, 156.1 (2), 135.8, 135.7, 135.3, 135.2, 133.5, 133.3, 133.1, 132.9, 130.0, 129.9(2), 129.8, 128.8 (2), 128.5, 128.2, 127.9, 127.8 (2), 114.4, 112.5, 96.6, 96.4, 84.8, 84.2, 84.1, 83.5, 82.0 (2), 80.5, 68.6, 68.3, 65.1, 64.2, 54.7, 54.1, 37.8, 37.1, 33.5, 29.8, 27.6, 27.0, 26.4, 25.8, 25.2, 25.0 (2), 19.4, 19.2; **HRMS** (ESI) *m/z* calcd for $C_{40}H_{51}O_8NNaSi$ $[M + Na]^+$ 724.3276, found 724.3283.



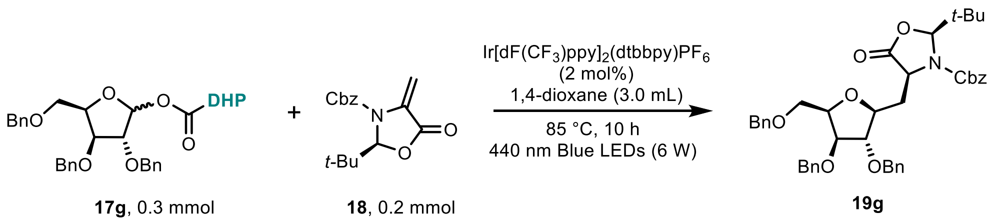
17e, 0.3 mmol **18**, 0.2 mmol **19e**

Benzyl (*2S,4S*)-4-(((*3aS,4S,6R,6aR*)-6-((benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19e). According to the general protocol A, 4-((*3aR,6R,6aR*)-6-((benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17e** (158.7 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.20 mmol, 1.00 equiv), 4CzlPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19e** (82.0 mg, 75%, d.r. = 4.3:1, major β) as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 5.59 (s, 0.11H), 5.57 (s, 0.89H), 5.18 – 5.11 (m, 2H), 4.62 – 4.47 (m, 4.11H), 4.31 – 4.16 (m, 2H), 4.01 – 3.98 (m, 0.91H), 3.53 – 3.49 (m, 2H), 2.32 – 2.20 (m, 1.11H), 2.05 – 1.99 (m, 0.89H), 1.49 (s, 2.67H), 1.42 (s, 0.33H), 1.27 (s, 3H), 0.99 (s, 0.99H), 0.96 (s, 8.01H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 156.0, 138.1, 135.3, 128.9, 128.8, 128.5, 128.0, 127.8, 114.6, 96.5, 84.8, 83.3, 82.6, 81.0, 73.7, 70.6, 68.6, 54.1, 37.7, 37.2, 27.5, 25.7, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{31}H_{39}NNaO_8$ $[M + Na]^+$ 576.2568, found 576.2573.

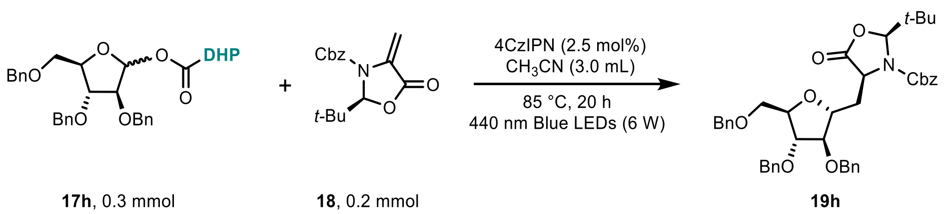


17f, 0.3 mmol **18**, 0.2 mmol **19f**

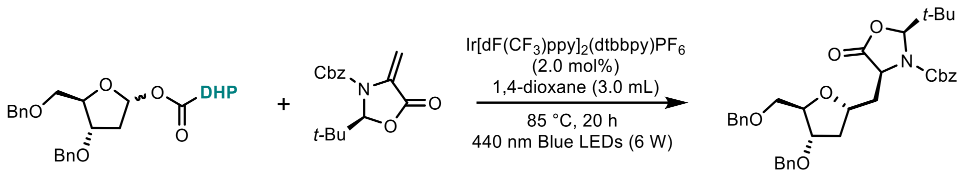
Benzyl (2*S*,4*S*)-4-(((2*S*,3*S*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19f). According to the general procedure A, 4-((3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17f** (210 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19f** (120 mg, 87%, d.r. = 3.5:1, major β) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 20H), 5.58 (s, 1H), 5.13 (q, *J* = 12.0 Hz, 2.22H), 4.61 (t, *J* = 6.7 Hz, 1H), 4.57 (d, *J* = 2.6 Hz, 0.84H), 4.56 – 4.48 (m, 4.35H), 4.46 (d, *J* = 5.4 Hz, 0.65H), 4.36 (d, *J* = 11.8 Hz, 1H), 4.24 (q, *J* = 6.9 Hz, 1H), 3.95 (s, 1H), 3.89 (dd, *J* = 5.5, 3.3 Hz, 1H), 3.57 (dd, *J* = 7.3, 5.4 Hz, 1H), 3.43 (dd, *J* = 10.3, 3.9 Hz, 1H), 3.38 (dd, J = 10.3, 4.9 Hz, 1H), 2.04 (d, J = 6.2 Hz, 2H), 0.96 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 156.3, 138.3, 138.0, 137.9, 135.4, 128.8, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.0, 127.9, 127.9, 127.8, 96.8, 81.9, 81.3, 76.5, 73.6, 72.2, 71.7, 70.6, 68.6, 54.5, 37.9, 37.0, 29.8, 25.1, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{42}H_{47}O_8NNa$ [M + Na]$^+$ 716.3194, found 716.3198.



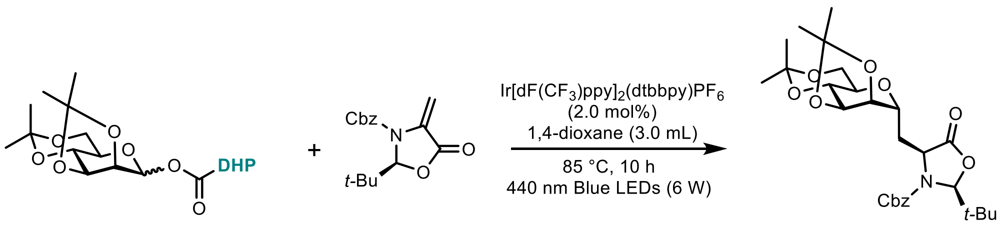
Benzyl (2*S*,4*S*)-4-(((2*S*,3*S*,4*S*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19g). According to the general procedure B, 4-((3*R*,4*S*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17g** (210 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)(ppy)$_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19g** (114 mg, 82%, d.r. = 3.5:1, major β) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 20H), 5.57 (d, J = 7.1 Hz, 1H), 5.22 – 5.07 (m, 2H), 4.63 – 4.38 (m, 7H), 4.37 – 4.28 (m, 0.3H), 4.28 – 4.10 (m, 1.76H), 4.07 – 3.88 (m, 2H), 3.83 – 3.66 (m, 2H), 2.36 (dt, J = 14.1, 7.1 Hz, 0.84H), 2.31 – 2.21 (m, 0.29H), 2.06 (dt, J = 13.5, 6.4 Hz, 0.83H), 0.97 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 172.5, 156.1, 156.0, 138.4, 138.3, 138.0, 137.9 (2), 135.4, 128.7 (3), 128.5 (2), 128.4, 127.9 (2), 127.8 (2), 127.7 (2), 127.6, 96.5, 96.4, 86.4, 82.6, 81.5, 80.0, 79.8, 78.6, 73.6, 72.3, 72.0, 71.8, 71.7, 68.5, 68.4, 68.2, 54.9, 54.4, 38.1, 37.1, 37.0, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{42}H_{47}O_8NNa$ [M + Na]$^+$ 716.3194, found 716.3195.



Benzyl (2*S*,4*S*)-4-(((2*S*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19h). According to the general procedure A, 4-((3*S*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17h** (210 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19h** (114.6 mg, 80%, d.r. >20:1) as a colorless oil: $[\alpha]_D^{25}$ = +30.9 (c = 1.10, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 20H), 5.59 (s, 1H), 5.26 – 5.11 (m, 2H), 4.70 – 4.47 (m, 8H), 4.23 – 4.13 (m, 1H), 4.06 (dd, J = 3.6, 2.0 Hz, 1H), 3.89 (t, J = 2.5 Hz, 1H), 3.62 – 3.49 (m, 2H), 2.41 – 2.27 (m, 1H), 2.10 – 1.98 (m, 1H), 1.00 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 155.8, 138.3, 137.9, 137.8, 135.5, 128.7 (2), 128.5(3), 128.4, 127.8 (3), 127.6, 96.2, 87.5, 85.2, 81.9, 79.0, 73.5, 72.1, 71.8, 71.5, 70.4, 68.2, 53.9, 37.2, 36.4, 24.9, 24.8; **HRMS** (ESI) *m/z* calcd for $C_{42}H_{47}O_8NNa$ [M + Na]$^+$ 716.3194, found 716.3198.

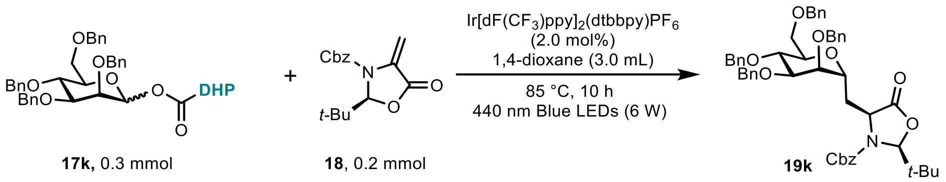


Benzyl (2*S*,4*S*)-4-(((2*S*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19i). According to the general procedure B, 4-((4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17i** (178 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)($ppy)_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **19i** (68.0 mg, 58%, d.r. = 1.9:1, major α) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 15H), 5.57 (s, 1H), 5.19 (dd, *J* = 12.0, 2.8 Hz, 1H), 5.11 (dd, *J* = 12.0, 5.3 Hz, 1H), 4.62 – 4.38 (m, 6H), 4.13 – 3.95 (m, 2H), 3.53 – 3.36 (m, 2H), 2.42 – 2.22 (m, 1.46H), 2.13 – 2.02 (m, 0.85H), 2.00 – 1.88 (m, 0.41H), 1.76 (d, *J* = 11.6 Hz, 1H), 0.97 – 0.96 (d, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 172.6, 156.1, 156.0, 138.3 (3), 135.4, 135.3, 128.8 (2), 128.7, 128.6, 128.5 (2), 127.8, 127.7 (2), 96.7, 96.4, 83.4, 82.5, 81.3, 80.9, 75.3, 75.2, 73.6, 73.5, 71.5, 71.1 (2), 70.8, 68.6, 68.4, 55.0, 54.5, 39.5 (2), 38.2, 37.7, 37.2, 37.1, 25.0 (2); **HRMS** (ESI) *m/z* calcd for $C_{35}H_{41}O_7NNa$ [M + Na]$^+$ 610.2775, found 610.2777.

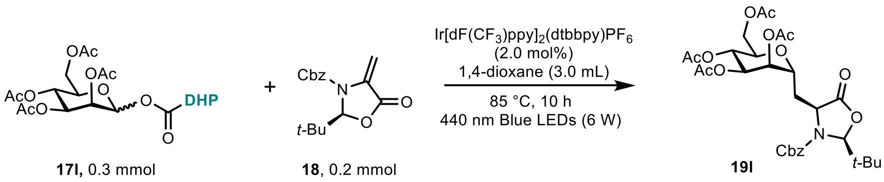


Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-5-oxo-4-(((3*aR*,4*R*,5*aR*,9*aR*,9*bR*)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-*d*][1,3]dioxin-4-yl)methyl)oxazolidine-3-carboxylate (19j). According to the general procedure B, 3,5-diethyl 4-((3*aS*,5*aR*,9*aR*,9*bS*)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-*d*][1,3]dioxin-4-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17j** (162 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)($ppy)_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **19j** (48.4 mg, 45%, d.r. > 20:1) as a colorless oil: $[\alpha]_D^{25}$ = +7.6 (c = 0.380, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 5.55 (s, 1H), 5.21 (d, *J* = 1.9 Hz, 2H), 4.62 (dd, *J* = 10.3, 4.1 Hz, 1H), 4.52 – 4.43 (m, 1H), 4.15 (dd, *J* = 7.6, 6.3 Hz, 1H), 4.02 (dd, *J* = 6.3, 4.9 Hz, 1H), 3.96 (dd, *J* = 10.6, 7.6 Hz, 1H), 3.81 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.69 (t, *J* = 10.4 Hz, 1H), 3.53 – 3.39 (m, 1H), 2.25 – 2.12 (m, 1H), 2.14 – 2.03 (m, 1H), 1.52 (d, *J* = 4.8 Hz, 6H), 1.45 (s, 3H), 1.34 (s, 3H), 0.96 (s, 9H); **^{13}C NMR** (101 MHz,

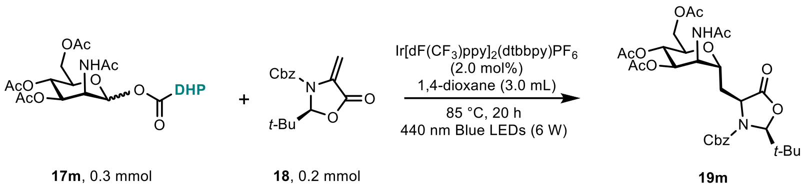
$CDCl_3$) δ 172.2, 155.7, 135.5, 128.8 (2), 128.6, 109.9, 99.7, 96.3, 76.7, 75.4, 72.6, 70.2, 68.4, 64.1, 62.9, 53.2, 37.3, 35.3, 29.2, 27.9, 25.7, 25.0, 19.1; **HRMS** (ESI) *m/z* calcd for $C_{28}H_{39}O_9NNa$ $[M + Na]^+$ 556.2517, found 556.2523.



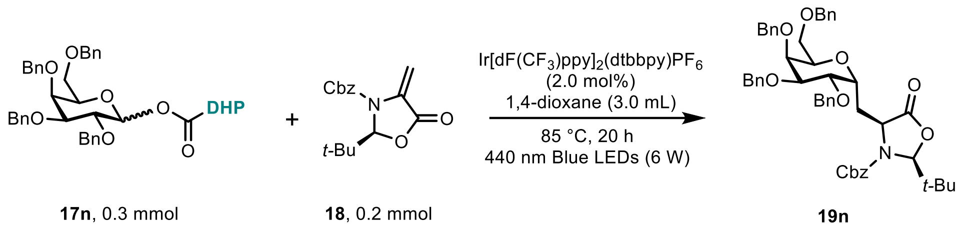
Benzyl (*2S,4S*)-2-(*tert*-butyl)-5-oxo-4-(((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (19k). According to the general protocol B, 3,5-diethyl 4-((*3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17k** (246 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **19k** (104 mg, 63%, d.r. > 20:1) as a light yellow oil: $[\alpha]_D^{25}$ = +21.1 (c = 0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 25H), 5.43 (s, 1H), 5.05 (d, *J* = 1.8 Hz, 2H), 4.63 (d, *J* = 11.3 Hz, 1H), 4.57 – 4.39 (m, 10H), 3.85 (t, *J* = 6.8 Hz, 1H), 3.79 – 3.76 (m, 1H), 3.68 – 3.64 (m, 2H), 3.61 – 3.58 (m, 1H), 3.49 (t, *J* = 3.8 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.87 – 1.80 (m, 1H), 0.84 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 155.7, 138.6, 138.5, 138.3, 138.2, 135.5, 128.8, 128.6, 128.4 (3), 128.0 (2), 127.9 (2), 127.7 (2), 127.5, 96.1, 76.2, 74.9, 74.0, 73.50, 72.16, 71.31, 69.25, 68.17, 53.36, 52.76, 37.17, 33.54, 24.94; **HRMS** (ESI) *m/z* calcd for $C_{50}H_{55}NNaO_9$ $[M + Na]^+$ 836.3769, found 836.3773.



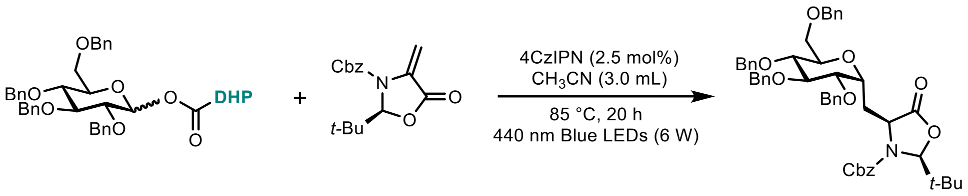
(*2R,3R,4R,5R,6R*)-2-(Acetoxymethyl)-6-(((*2S,4S*)-3-((benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (19l). According to the general protocol B, 3,5-diethyl 4-((*3S,4S,5R,6R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17l** (188 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **19l** (59.6 mg, 48%, d.r. > 20:1) as a light yellow oil: $[\alpha]_D^{25}$ = +21.1 (c = 2.44, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.53 (s, 1H), 5.23 – 5.12 (m, 5H), 4.57 – 4.52 (m, 2H), 4.16 – 4.01 (m, 3H), 2.45 – 2.37 (m, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.98 – 1.93 (m, 1H), 0.93 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 170.8, 170.2, 170.2, 169.6, 155.5, 135.1, 128.9, 128.6, 96.2, 70.6, 70.2, 68.9, 68.6, 66.5, 62.2, 52.6, 37.2, 31.8, 24.9, 20.9 (2), 20.8; **HRMS** (ESI) *m/z* calcd for $C_{30}H_{39}NNaO_{13}$ $[M + Na]^+$ 644.2314, found 644.2314.



(2*R*,3*S*,4*R*,5*R*,6*R*)-5-Acetamido-2-(acetoxymethyl)-6-(((2*S*,4*S*)-3-((benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (19m). According to the general procedure B, 4-((3*S*,4*R*,5*S*,6*R*)-3-acetamido-4,5-diacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[5] **17m** (188 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv), and Ir[dF(CF_3)($ppy)_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 1:3) **19m** (84.0 mg, 68%, d.r. > 20:1) as a light yellow oil: $[\alpha]_D^{25}$ = +38.5 (c = 0.460, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 5H), 5.96 (s, 1H), 5.55 (s, 1H), 5.18 (s, 2H), 5.13 – 5.01 (m, 2H), 4.56 – 4.36 (m, 3H), 4.32 – 3.90 (m, 3H), 2.56 – 2.41 (m, 1H), 2.09 – 1.99 (m, 13H), 0.94 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 170.7, 170.3, 170.0, 169.8, 155.6, 135.1, 128.9, 128.5, 96.4, 70.7, 69.7, 68.6, 66.4, 62.0, 52.9, 49.3, 37.3, 33.0, 24.9, 24.8, 23.4, 21.0 (2), 20.9; **HRMS** (ESI) *m/z* calcd for $C_{30}H_{40}O_{12}N_2Na$ $[M + Na]^+$ 643.2473, found 643.2477.

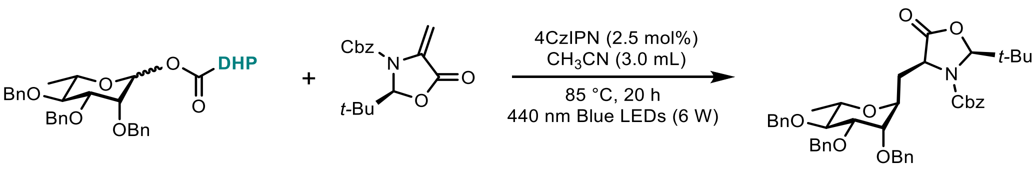


Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-5-oxo-4-(((2*R*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (19n). According to the general procedure B, 3,5-diethyl 4-((3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17n** (246 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)($ppy)_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19n** (83.0 mg, 51%, d.r. = 10.1:1, major α) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 25H), 5.50 (s, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.02 (d, *J* = 12.1 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.76 – 4.67 (m, 3H), 4.66 – 4.53 (m, 3H), 4.52 – 4.40 (m, 3H), 4.00 (s, 1H), 3.87 – 3.63 (m, 3H), 3.61 – 3.45 (m, 2H), 2.33 – 2.20 (m, 1H), 2.10 – 1.96 (m, 1H), 0.94 – 0.89 (s, 9H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 155.6, 138.8, 138.7, 138.6, 138.3, 135.7, 128.7, 128.6, 128.5 (3), 128.4 (2), 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (2), 127.6, 127.5, 95.9, 76.3, 74.4, 73.8, 73.5, 73.1 (2), 68.8, 68.4, 68.1, 53.2, 51.4, 37.3, 29.8, 24.9; **HRMS** (ESI) *m/z* calcd for $C_{50}H_{55}O_9NNa$ $[M + Na]^+$ 836.3769, found 836.3777.



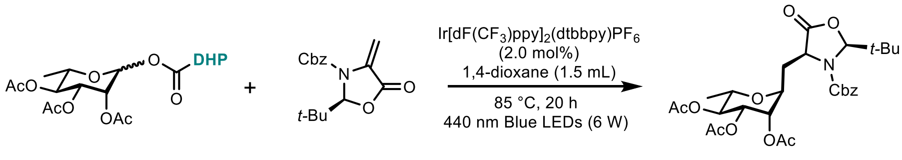
17o, 0.3 mmol   **18**, 0.2 mmol   **19o**

Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-5-oxo-4-(((2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (19o). According to the general procedure A, 3-ethyl 4-((3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl) 5-((ethylperoxy)-l2-methyl)-2,6-dimethyl-1,4-dihydropyridine-3,4-dicarboxylate[1] **17o** (246 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5.7:1) **19o** (114 mg, 70%, d.r. = 5:1, major α) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 25H), 5.58 (d, *J* = 13.6 Hz, 1H), 5.14 (s, 2H), 4.99 – 4.76 (m, 4H), 4.68 – 4.52 (m, 4H), 4.48 (d, *J* = 10.9 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 3.87 – 3.34 (m, 6H), 2.40 – 1.96 (m, 1H), 0.94 (d, *J* = 22.3 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 172.5, 156.6 (2), 138.9, 138.7, 138.6, 138.3, 138.0, 137.9, 135.4, 135.3, 128.92 (2), 128.8 (2), 128.7, 128.6, 128.5 (2), 128.4 (2), 128.3, 128.1, 128.0 (2), 127.9 (4), 127.8 (2), 127.7 (2), 97.0, 96.1, 87.5, 82.3, 82.0, 79.3, 78.8, 78.6, 77.9, 75.6, 75.2, 74.9, 73.6, 73.5, 72.8, 71.7, 69.9, 68.8, 68.5, 68.4, 54.2, 52.9, 37.3, 36.9, 29.8, 28.4, 25.2, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{50}H_{55}O_9NNa$ $[M + Na]^+$ 836.3769, found 836.3780.



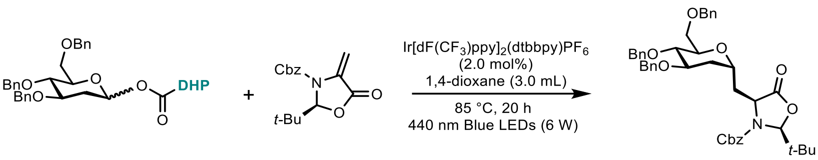
17p, 0.3 mmol   **18**, 0.2 mmol   **19p**

Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-5-oxo-4-(((2*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (19p). According to the general protocol A, 3,5-diethyl 4-((*3R,4R,5S,6S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17p** (214 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzlPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) **19p** (102 mg, 72%, d.r. > 20:1) as a light yellow oil: $[\alpha]_D^{25}$ = +19.9 (c = 1.42, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 20H), 5.56 (s, 1H), 5.22 – 5.11 (m, 2H), 4.78 (d, *J* = 11.3 Hz, 1H), 4.63 – 4.54 (m, 5H), 4.49 (dd, *J* = 6.8, 5.0 Hz, 1H), 4.39 – 4.35 (m, 1H), 3.85 – 3.79 (m, 1H), 3.74 (dd, *J* = 7.4, 3.1 Hz, 1H), 3.62 – 3.58 (m, 2H), 2.30 – 2.23 (m, 1H), 1.92 – 1.85 (m, 1H), 1.36 (d, *J* = 6.3 Hz, 3H), 0.93 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 156.1, 138.6, 138.5, 138.3, 135.5, 128.8, 128.7(2), 128.5(2), 128.4, 128.1, 128.0, 127.9, 127.8(2), 96.6, 80.0, 77.9, 76.1, 74.3, 72.3, 71.6, 69.9, 69.8, 68.4, 54.5, 37.1, 34.6, 25.0, 18.1; **HRMS** (ESI) *m/z* calcd for $C_{43}H_{49}NNaO_8$ $[M + Na]^+$ 730.3350, found 730.3353.



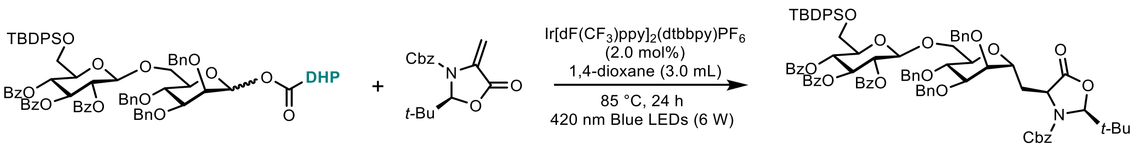
17q, 0.15 mmol **18**, 0.1 mmol **19q**

(2*S*,3*S*,4*R*,5*S*,6*S*)-2-(((2*S*,4*S*)-3-((Benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate (19q). According to the general procedure B, 3,5-diethyl 4-((3*R*,4*R*,5*S*,6*S*)-3,4,5-triacetoxy-6-methyltetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17q** (85.5 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv) and Ir[dF(CF_3)($ppy)_2$](dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (1.50 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **19q** (16.0 mg, 28%, d.r. > 20:1) as a colorless oil:$[\alpha]_D^{25}$ = +14.9 (c = 0.770, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 5H), 5.58 (s, 1H), 5.24 – 5.02 (m, 5H), 4.52 (dd, J = 6.2, 4.3 Hz, 1H), 4.31 – 4.24 (m, 1H), 3.96 – 3.84 (m, 1H), 2.60 – 2.47 (m, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.97 – 1.90 (m, 1H), 1.23 (d, J = 6.1 Hz, 3H), 0.95 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 170.4, 170.3, 170.1, 156.0, 135.2, 128.8 (2), 96.8, 73.0, 71.3, 70.6, 69.4, 68.8, 68.1, 54.4, 37.2, 33.6, 29.8, 24.9, 21.1, 21.0, 20.8, 17.8; **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{37}O_{11}NNa$ 586.2259; found 586.2260.



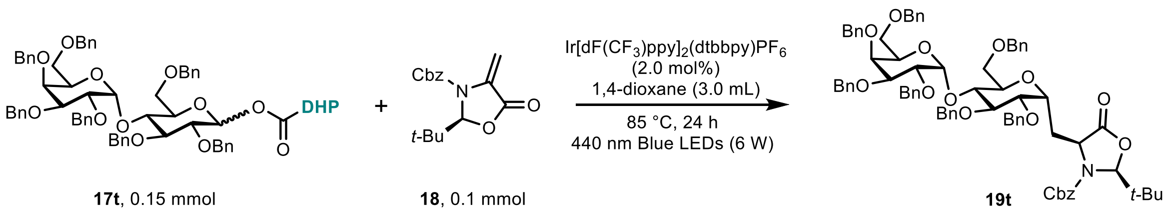
17r, 0.3 mmol **18**, 0.2 mmol **19r**

Benzyl (2*S*,4*S*)-4-(((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19r). According to the general procedure B, 3-ethyl 4-((3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl) 5-((ethylperoxy)-l2-methyl)-2,6-dimethyl-1,4-dihydropyridine-3,4-dicarboxylate[1] **17r** (214 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)($ppy)_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ^{o}C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) to afford **19r** (84.0 mg, 59%, d.r. >20:1) as a colorless oil:$[\alpha]_D^{25}$ = +32.9 (c = 0.770, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 20H), 5.55 (s, 1H), 5.23 – 5.06 (m, 2H), 4.82 (d, *J* = 11.1 Hz, 1H), 4.69 – 4.44 (m, 7H), 3.84 – 3.73 (m, 2H), 3.74 – 3.52 (m, 3H), 2.39 – 2.26 (m, 1H), 2.02 – 1.90 (m, 1H), 1.94 – 1.78 (m, 2H), 0.96 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 155.7, 138.7, 138.6, 138.5, 135.4, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0 (2), 127.9 (2), 127.7 (2), 127.6, 96.2, 74.3, 73.6, 72.9, 71.6, 69.2, 68.4, 67.4, 53.6, 37.2, 35.6, 33.4, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{43}H_{49}O_8NNa$ $[M + Na]^+$ 730.3350, found 730.3356.



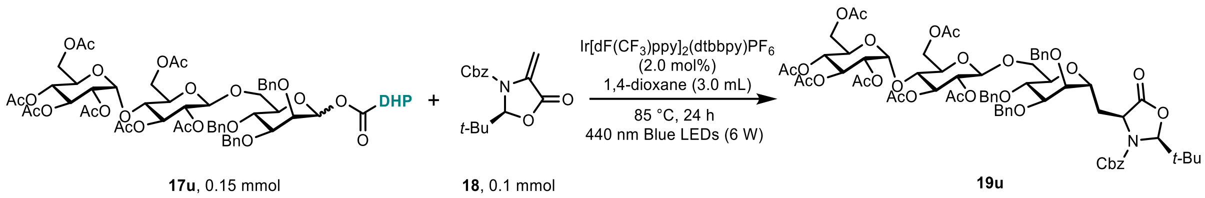
17s, 0.15 mmol **18**, 0.1 mmol **19s**

(*2R,3R,4S,5R,6R*)-2-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-6-(((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((*2S,4S*)-3-((benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)tetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (19s). According to the general protocol B, 3,5-diethyl 4-((*2R,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((((*2R,3R,5R,6R*)-3,4,5-tris(benzoyloxy)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)tetrahydro-2H-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17s** (214 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **19s** (103 mg, 72%, d.r. > 20:1) as a foam: $[\alpha]_D^{25}$ = +1.4 (c = 2.21, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 4H), 7.81 – 7.79 (m, 2H), 7.71 – 7.69 (m, 2H), 7.60 – 7.57 (m, 2H), 7.55 – 7.51 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.17 (m, 33H), 5.85 (t, *J* = 9.7 Hz, 1H), 5.69 – 5.62 (m, 1H), 5.58 – 5.52 (m, 1H), 5.29 – 5.21 (m, 2H), 5.01 – 4.96 (m, 2H), 4.60 – 4.45 (m, 7H), 4.23 – 4.20 (m, 2H), 4.02 – 3.85 (m, 5H), 3.68 – 3.63 (m, 2H), 3.45 (dd, *J* = 5.4, 2.3 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.87 – 1.80 (m, 1H), 1.01 (s, 9H), 0.90 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 165.9, 165.1, 164.9, 155.0, 138.3, 138.1, 138.0, 135.6, 135.5, 133.2, 133.1, 133.0, 129.8 (2), 129.7, 129.6, 129.3, 129.1, 128.6, 128.6, 128.4 (2), 128.3, 128.2, 127.9 (2), 127.7 (2), 127.6, 127.6, 101.3, 95.6, 76.3, 75.3, 75.0, 73.5, 73.4, 73.2, 72.3, 72.0, 71.2, 69.4, 68.8, 67.7, 62.9, 37.1, 33.6,7 26.7, 24.7, 19.2; **HRMS** (ESI) *m/z* calcd for $C_{86}H_{89}NNaO_{17}Si$ [M + Na]$^+$ 1458.5792, found 1458.5794.

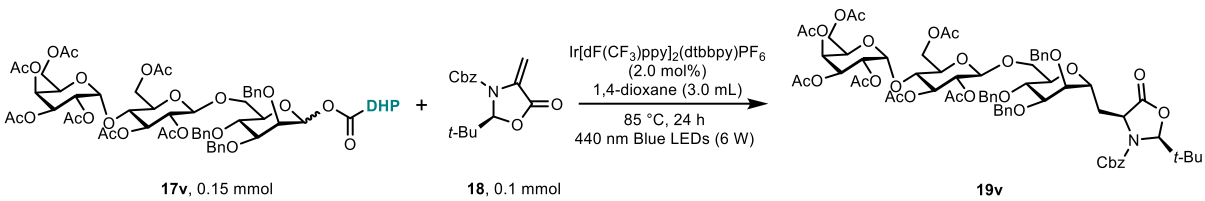


17t, 0.15 mmol **18**, 0.1 mmol **19t**

Benzyl (*2S,4S*)-4-(((*2S,3S,4R,5R,6R*)-3,4-bis(benzyloxy)-6-((benzyloxy)methyl)-5-(((*2R,3R,4S,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19t). According to the general protocol B, 4-((*3R,4S,5R,6R*)-3,4-bis(benzyloxy)-6-((benzyloxy)methyl)-5-(((*2R,3R,4S,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17t** (188 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **19t** (80.2 mg, 64%, d.r. = 5:1, major α) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 1H), 5.56 – 5.49 (m, 1H), 5.20 – 5.17 (m, 0.20H), 5.14 – 5.08 (m, 0.30H), 5.03 – 4.93 (m, 3H), 4.85 – 4.79 (m, 1.80H), 4.76 – 4.72 (m, 1H), 4.70 – 4.65 (m, 3.60H), 4.60 – 4.53 (m, 3.60H), 4.50 (s, 0.10H), 4.48 – 4.45 (m, 0.20H), 4.41 – 4.32 (m, 2.90H), 4.29 – 4.23 (m, , 1H), 4.17 (dd, *J* = 8.8, 6.2 Hz, 0.10H), 4.09 – 4.06 (m, 0.10H), 4.05 – 3.97 (m, 1H), 3.94 – 3.88 (m, 1.80H), 3.86 – 3.82 (m, 0.20H), 3.79 – 3.50 (m, 5.40H), 3.47 – 3.45 (m, 0.10H), 3.43 – 3.42 (m, 0.10H), 3.40 – 3.32 (m, 2.90H), 3.25 – 3.16 (m, 0.30H), 2.88 (dd, *J* = 16.0, 6.8 Hz, 0.10H), 2.71 (dd, *J* = 16.1, 5.7 Hz, 0.10H), 2.38 – 2.14 (m, 1.80H), 2.07 – 1.93 (m, 0.20H), 0.95 – 0.88 (m, , 9H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 172.5, 156.6, 155.5, 139.4, 139.2, 139.0, 138.6, 138.4, 138.3, 138.2, 135.5, 128.8 (2), 128.7, 128.5 (2), 128.4 (2), 128.3 (3), 128.2, 128.1 (2), 128.0 (2), 127.9 (3), 127.8 (3), 127.7, 127.6 (3), 127.5 (2), 127.2, 103.1, 102.7, 96.0, 82.6, 80.1, 80.0, 78.5, 77.0, 75.2, 74.8, 73.7, 73.5, 73.3, 73.1, 72.7, 71.9, 69.9, 68.6, 68.3, 54.3, 53.0, 37.3, 36.8, 28.8, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{77}H_{83}NNaO_{14}$ $[M + Na]^+$ 1268.5706, found 1268.5718.

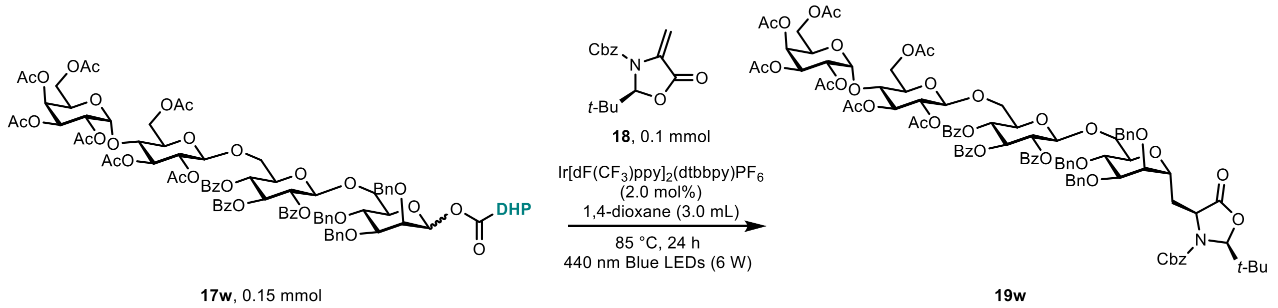


(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(((*2R,3R,4S,5R,6R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((*2S,4S*)-3-((benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)tetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (19u). According to the general protocol B, 3,5-diethyl 4-((*2R,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((((*2R,3R,4S,5R,6R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((*2R,3R,4S,5R,6R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17u** (202 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 1.5:1) **19u** (101 mg, 75%, d.r. > 20:1) as a foam: $[\alpha]_D^{25}$ = +24.1 (c = 1.84, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 20H), 5.61 (s, 1H), 5.41 – 5.33 (m, 3H), 5.22 (t, *J* = 9.3 Hz, 1H), 5.08 – 5.03 (m, 2H), 4.86 – 4.77 (m, 2H), 4.74 – 4.39 (m, 10H), 4.26 – 4.18 (m, 2H), 4.05 – 3.63 (m, 9H), 3.53 – 3.51 (m, 1H), 2.16 – 1.94 (m, 20H), 1.90 (s, 3H), 0.94 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 170.7(2), 170.6, 170.1(3), 169.6, 138.4, 138.2, 138.1, 135.6, 128.8, 128.7, 128.6, 128.5(2), 128.1, 128.0, 127.9(3), 127.8, 100.6, 96.1, 95.5, 76.3, 75.2, 75.0, 72.5, 72.3, 72.0, 71.6, 70.1, 69.5, 68.8, 68.5, 68.1, 62.9, 61.6, 37.2, 25.0, 21.0, 20.8(3), 20.7(2), 20.6; **HRMS** (ESI) *m/z* calcd for $C_{69}H_{83}NNaO_{26}$ $[M + Na]^+$ 1364.5096, found 1364.5105.

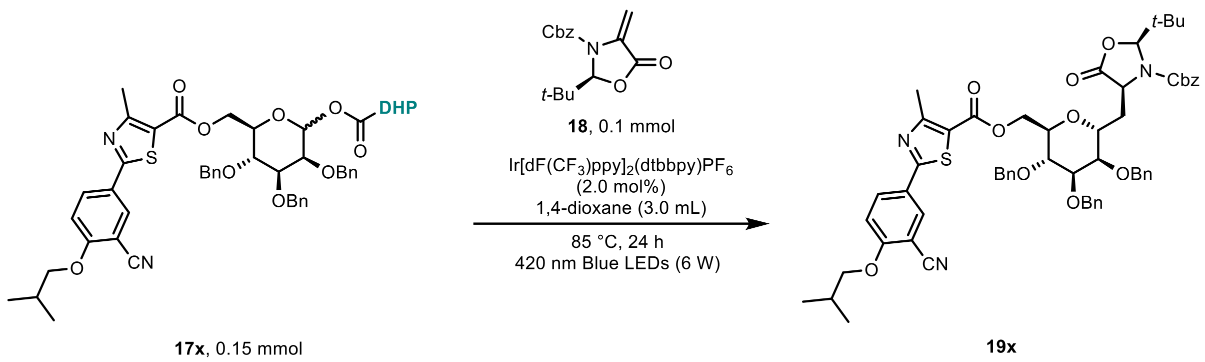


(*2R,3S,4S,5R,6R*)-2-(Acetoxymethyl)-6-(((*2R,3R,4S,5R,6R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((*2S,4S*)-3-((benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)tetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (19v). According to the general protocol B, 3,5-diethyl 4-((*2R,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((*2R,3R,4S,5S,6R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17v** (202 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether:

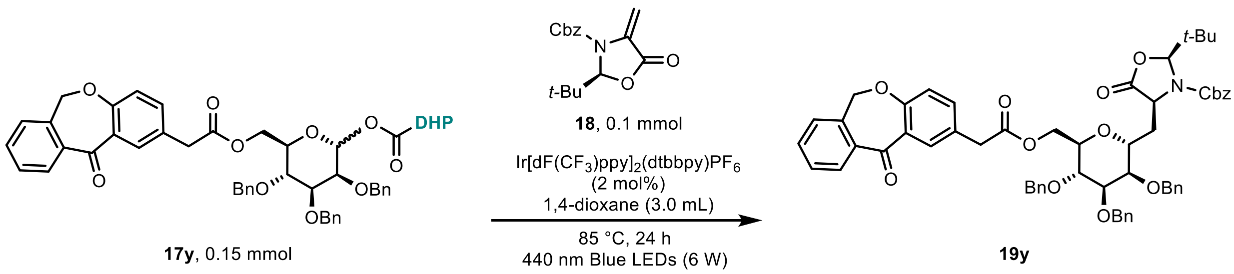
EtOAc = 1.5:1) **19v** (90.5 mg, 67%, d.r. > 20:1) as a foam:$[\alpha]_D^{25}$ = -5.1 (c = 0.965, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 20H), 5.64 (s, 1H), 5.34 – 5.32 (m, 2H), 5.20 – 5.03 (m, 3H), 4.95 – 4.85 (m, 2H), 4.70 – 4.46 (m, 11H), 4.15 – 4.05 (m, 4H), 3.91 – 3.62 (m, 7H), 3.52 (d, *J* = 4.6 Hz, 1H), 2.16 – 1.92 (m, 23H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 170.5(2), 170.3, 170.2(2), 169.8, 169.1, 156.0, 138.4, 138.1(2), 135.7, 128.8, 128.7, 128.5(3), 128.0(2), 127.9(2), 127.8(2), 100.7, 96.2, 76.2, 75.2, 72.5, 72.3, 72.0, 71.7, 71.6, 71.2, 70.7, 69.1, 68.7, 67.9, 66.8, 62.1, 60.9, 37.2, 31.5, 29.8, 24.9, 20.9, 20.8(2), 20.6(2); **HRMS** (ESI) *m/z* calcd for $C_{69}H_{83}NNaO_{26}$ $[M + Na]^+$ 1364.5096, found 1364.5109.



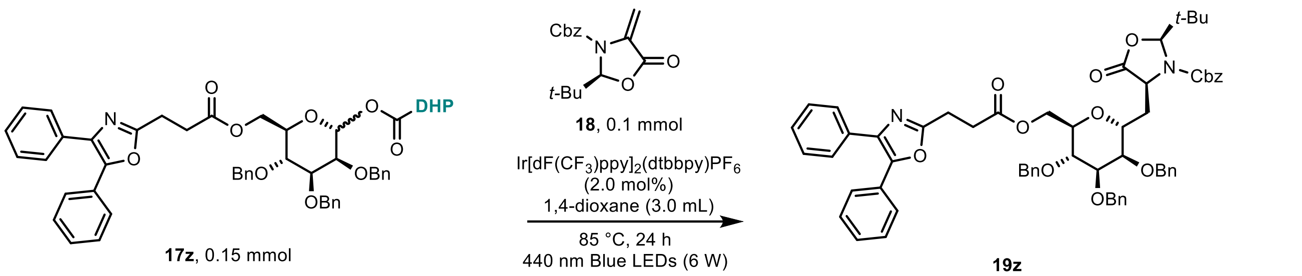
(*2R,3R,5R,6R*)-2-((((*2R,3R,4S,5R,6R*)-3,4-Diacetoxy-6-(acetoxymethyl)-5-(((*2R,3R,4S,5S,6R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-6-(((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((*2S,4S*)-3-((benzyloxy)carbonyl)-2-(*tert*-butyl)-5-oxooxazolidin-4-yl)methyl)tetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (19w). According to the general protocol B, 3,5-diethyl 4-((*2R,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((((*2R,3R,4S,5R,6R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((*2R,3R,4S,5R,6R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17w** (202 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 1:1) **19w** (118 mg, 65%, d.r. > 20:1) as a foam: $[\alpha]_D^{25}$ = -7.3 (c = 0.78, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 3H), 7.77 – 7.75 (m, 2H), 7.55 – 7.50 (m, 1H), 7.46 – 7.17 (m, 29H), 5.83 (t, *J* = 9.6, 9.6 Hz, 1H), 5.50 – 5.39 (m, 2H), 5.33 (d, *J* = 3.4 Hz, 1H), 5.25 – 5.20 (m, 2H), 5.12 – 5.05 (m, 2H), 5.00 – 4.83 (m, 4H), 4.58 – 4.19 (m, 12H), 4.12 – 3.94 (m, 6H), 3.89 – 3.84 (m, 2H), 3.75 – 3.65 (m, 3H), 3.60 (t, *J* = 9.4, 9.4 Hz, 1H), 3.54 – 3.43 (m, 2H), 2.14 (s, 3H), 2.06 – 1.84 (m, 20H), 0.89 (s, 9H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 170.5 (2), 170.3, 170.2, 169.8, 169.2, 165.8, 165.2, 165.0, 155.2, 138.6, 138.3, 138.2, 133.6, 133.2, 129.9, 129.8, 129.1, 129.0, 128.7, 128.6, 128.5 (2), 128.4, 128.3, 128.1, 127.9, 127.8, 127.7 (3), 101.2, 101.0, 100.8, 95.8, 76.4, 76.3, 73.5, 73.2, 72.8, 72.6, 72.1, 72.0, 71.7, 71.2, 71.1, 70.7, 69.7, 69.1, 68.7, 68.3, 66.7, 62.3, 60.9, 37.1, 25.0, 20.9 (2), 20.8 (3), 20.7 (2); **HRMS** (ESI) *m/z* calcd for $C_{96}H_{105}NNaO_{34}$ $[M + Na]^+$ 1838.6410, found 1838.6412.



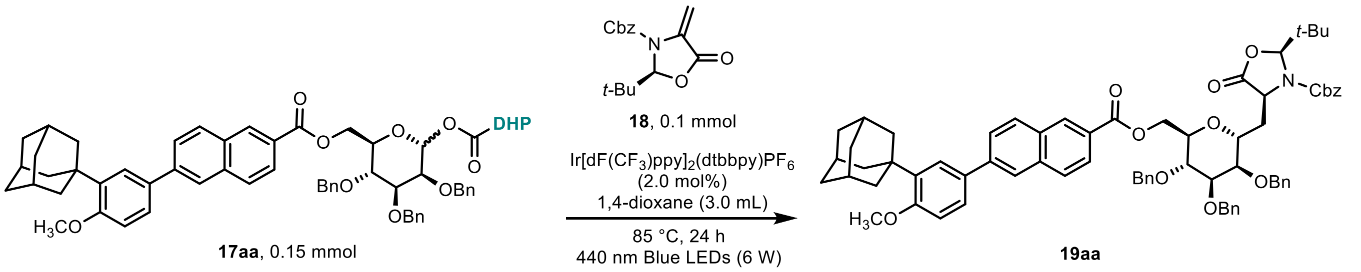
Benzyl (*2S,4S*)-2-(*tert*-butyl)-5-oxo-4-(((*2S,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((5-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-2-carbonyl)oxy)methyl)tetrahydro-2*H*-pyran-2 yl)methyl)oxazolidine-3-carboxylate (19x). According to the general protocol B, 3,5-diethyl 4-((*2S,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)oxy)methyl)tetrahydro-2H-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17x** (154 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **19x** (52.0 mg, 51%, d.r. > 20:1) as a foam: $[\alpha]_D^{25}$ = +11.4 (c = 1.40, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.98 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.38 – 7.24 (m, 23H), 6.97 (d, *J* = 8.9 Hz, 1H), 5.55 (s, 1H), 5.14 (s, 2H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.70 – 4.57 (m, 7H), 4.50 – 4.45 (m, 1H), 3.98 – 3.87 (m, 4H), 3.78 (dd, *J* = 7.7, 2.9 Hz, 1H), 3.61 (t, *J* = 3.4, 3.4 Hz, 1H), 2.71 (s, 4H), 2.26 – 2.16 (m, 2H), 1.93 – 1.86 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 6H), 0.95 (s, 9H). . **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 167.3, 162.6, 161.8, 161.4, 155.6, 138.2, 138.1 (2), 135.1, 132.7, 132.1, 128.8 (2), 128.6, 128.5 (2), 128.4, 128.2, 128.0 (2), 127.9 (2), 127.7, 126.0, 121.8, 115.5, 112.6, 103.0, 96.1, 76.2, 75.7, 74.5, 74.4, 72.4, 71.9, 71.5, 68.5, 63.9, 53.3, 37.2, 33.0, 28.2, 24.9, 19.2, 17.6. **HRMS** (ESI) *m/z* calcd for $C_{59}H_{63}N_3NaO_{11}S$ $[M + Na]^+$ 1044.4076, found 1044.4087.



Benzyl (*2S,4S*)-2-(*tert*-butyl)-5-oxo-4-(((*2S,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetoxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (19y). According to the general protocol B, 3,5-diethyl 4-((*3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetoxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17y** (147 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **19y** (55.0 mg, 56%, d.r. > 20:1) as a foam: $[\alpha]_D^{25}$ = +15.6 (c = 1.17, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.49 – 7.45 (m, 1H), 7.41 – 7.26 (m, 22H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.51 (s, 1H), 5.15 – 5.12 (m, 4H), 4.46 – 4.72 (m, 8H), 4.40 – 4.29 (m, 2H), 3.93 – 3.88 (m, 2H), 3.80 – 3.73 (m, 2H), 3.67 – 3.56 (m, 3H), 2.18 – 2.11 (m, 1H), 1.93 – 1.86 (m, 1H), 0.93 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 172.2, 171.2, 160.5, 155.6, 140.5, 138.2(2), 136.6, 135.8, 135.4, 132.8, 132.7, 129.8, 129.3, 128.8, 128.7, 128.5(3), 128.1, 128.0, 127.9(2), 127.8(2), 125.2, 121.1, 96.1, 76.0, 75.0, 74.1, 73.7, 72.3, 72.1, 71.4, 68.3(2), 53.2, 40.4, 37.1, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{59}H_{59}NNaO_{12}$ [M + Na]$^+$ 996.3929, found 996.3937.

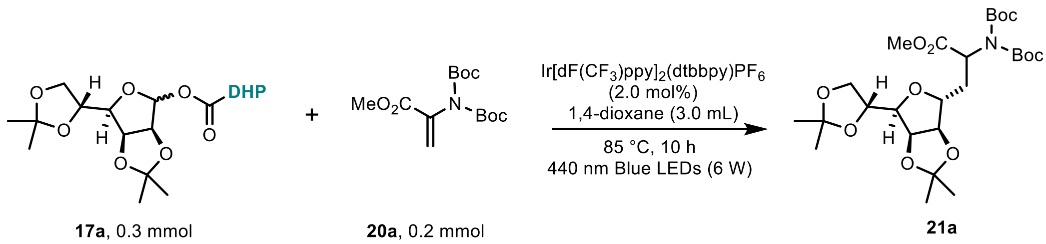


Benzyl (*2S,4S*)-2-(*tert*-butyl)-5-oxo-4-(((*2S,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (19z). According to the general protocol B, 3,5-diethyl 4-((*2S,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17z** (154 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **19z** (50.0 mg, 50%, d.r. > 20:1) as a foam: $[\alpha]_D^{25}$ = +14.0 (c = 1.67, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.57 – 7.54 (m, 2H), 7.37 7.24 (m, 26H), 5.5 (s, 1H), 5.18 – 5.11 (m, 2H), 4.7 (d, *J* = 11.2 Hz, 1H), 4.66 – 4.54 (m, 6H), 4.41 – 4.27 (m, 2H), 3.88 – 3.81 (m, 3H), 3.59 – 3.57 (m, 1H), 3.1 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.9 (dd, *J* = 9.0, 6.6 Hz, 2H), 2.19 – 2.12 (m, 1H), 1.93 – 1.86 (m, 1H), 0.9 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 171.9, 161.9, 155.7, 145.5, 138.2(2), 135.2, 132.6, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5(2), 128.2, 128.1, 128.0(2), 127.9(2), 127.8, 126.6, 96.2, 76.0, 74.8, 72.3, 71.4, 68.4, 63.6, 53.4, 37.2, 31.2, 25.0, 23.6; **HRMS** (ESI) *m/z* calcd for $C_{61}H_{62}N_2NaO_{11}$ [M + Na]$^+$ 1021.4246, found 1021.4255.

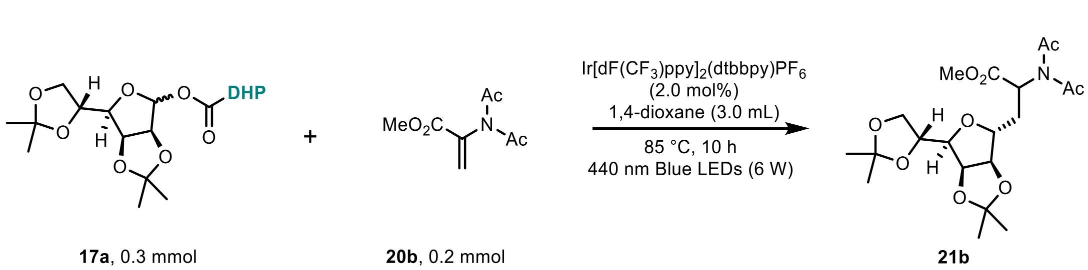


Benzyl (*2S,4S*)-4-(((*2S,3R,4R,5R,6R*)-6-(((6-(3-((*3r,5r,7r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)methyl)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl)methyl)-2-(*tert*-butyl)-5-oxooxazolidine-3-carboxylate (19aa). According to the general protocol B, 4-((*2S,3S,4S,5R,6R*)-6-(((6-(3-((*3r,5r,7r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)methyl)-3,4,5-tris(benzyloxy)tetrahydro-

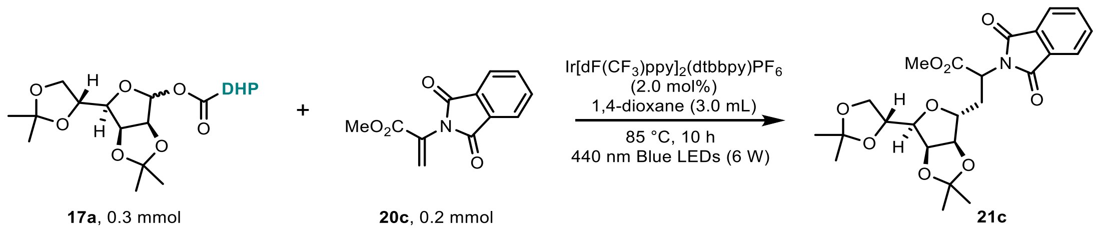
2*H*-pyran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **17aa** (149 mg, 0.150 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[4] **18** (29.0 mg, 0.100 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **19aa** (52.0 mg, 46%, d.r. = 16:1, major α) as a foam **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 – 8.55 (m, 1H), 8.38 (d, *J* = 8.9 Hz, 0.10H), 8.13 (d, *J* = 9.2 Hz, 0.10H), 8.06 – 8.00 (m, 1.90H), 7.91 – 7.83 (m, 1.90H), 7.78 – 7.73 (m, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 0.20H), 7.43 – 7.27 (m, 19.80H), 7.03 – 6.98 (m, 1H), 5.54 (s, 0.95H), 5.47 (s, 0.05H), 5.13 (s, 1.90H), 5.01 (s, 0.10H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.78 – 4.51 (m, 9H), 4.10 – 4.01 (m, 2H), 3.92 (s, 3H), 3.82 (dd, *J* = 7.6, 3.0 Hz, 1H), 3.65 (t, *J* = 3.5, 3.5 Hz, 1H), 2.27 – 2.17 (m, 7H), 2.13 – 2.09 (m, 3H), 1.96 – 1.89 (m, 1H), 1.86 – 1.79 (m, 6H), 0.95 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 166.7, 159.0, 155.6, 141.4, 139.1, 138.3, 138.2, 136.0, 135.2, 132.7, 131.3, 131.1, 129.9, 128.9, 128.8(2), 128.6(2), 128.5(2), 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.0, 126.5, 126.1, 125.9, 125.8, 124.8, 112.2, 96.1, 76.3, 74.7, 74.4, 72.4, 72.2, 71.5, 68.5, 63.8, 55.3, 53.4, 40.7, 37.3, 37.2(2), 31.6, 29.2, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{71}H_{75}NNaO_{11}$ $[M + Na]^+$ 1140.5232, found 1140.5241.



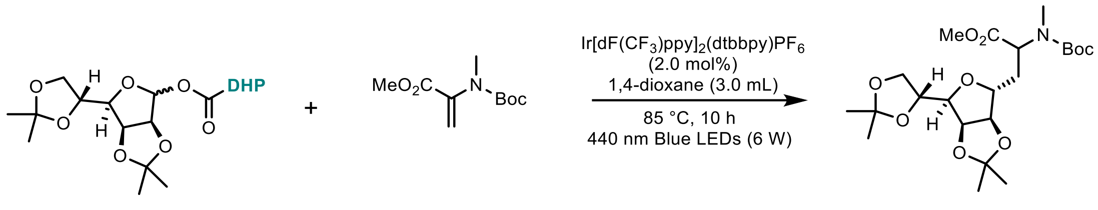
Methyl 2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoate (21a). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), *N,N-tert*-butoxycarbonyldehydroalanine[2] **20a** (60.2 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred in 6W Blue LEDs irradiation under N_2 at 85 ºC for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **21a** (73.0 mg, 67%, d.r. = 1.5:1) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.12 (t, *J* = 6.6, 6.6 Hz, 0.77H), 4.96 (dd, *J* = 10.0, 4.0 Hz, 0.23H), 4.80 – 4.74 (m, 1H), 4.53 (dd, *J* = 6.2, 2.8 Hz, 1H), 4.38 – 4.29 (m, 1.77H), 4.12 – 4.00 (m, 2.23H), 3.76 – 3.70 (m, 3.23H), 3.65 (dd, *J* = 8.4, 3.7 Hz, 0.77H), 2.31 – 2.25 (m, 0.77H), 2.02 – 1.95 (m, 0.46H), 1.90 – 1.82 (m, 0.77H), 1.49 – 1.47 (m, 18H), 1.43 – 1.33 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 171.0, 152.2, 151.9, 112.8, 112.7, 109.4, 109.3, 85.7, 85.4, 83.5, 83.3, 82.5, 81.0, 80.9, 80.8, 80.5, 80.2, 73.4, 73.3, 67.3(2), 55.6, 55.4, 52.5, 52.4, 31.6, 30.9, 28.1(2), 27.1, 27.0, 26.3, 25.4, 25.3, 24.9(2); **HRMS** (ESI) *m/z* calcd for $C_{26}H_{43}NNaO_{11}$ $[M + Na]^+$ 568.2728, found 568.2727.



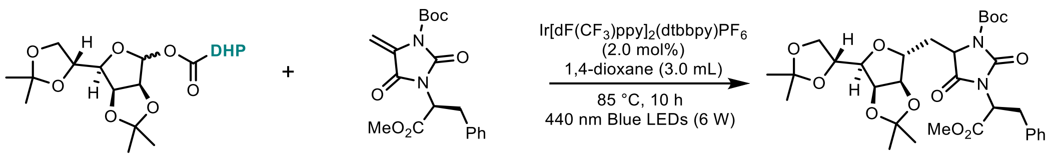
Methyl 2-(*N*-acetylacetamido)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoate (21b). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), methyl 2-(*N*-acetylacetamido)acrylate[6] **20b** (39.8 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **21b** (75.0 mg, 87%, d.r. = 1.1:1) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.77 (dd, *J* = 6.1, 3.9 Hz, 0.53H), 4.70 (dd, *J* = 6.1, 3.8 Hz, 0.47H), 4.56 (dd, *J* = 7.1, 4.5 Hz, 0.47H), 4.51 – 4.48 (m, 1H), 4.46 – 4.42 (m, 0.53H), 4.40 – 4.32 (m, 1.47H), 4.07 – 3.88 (m, 3H), 3.76 (dd, *J* = 6.0, 3.8 Hz, 0.47H), 3.70 – 3.69 (m, 3H), 2.59 – 2.53 (m, 0.53H), 2.42 – 2.41 (m, 6H), 2.21 – 2.16 (m, 1H), 1.70 – 1.62 (m, 0.47H), 1.45 (s, 3H), 1.40 (- 1.38 (s, 3H), 1.34 -1.33 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 173.1, 170.4, 170.0, 112.9, 112.8, 109.0, 108.8, 85.2, 85.1, 82.7, 80.6, 80.5, 80.3, 79.9, 79.8, 73.6, 73.5, 66.5, 66.2, 56.6, 56.2, 52.8(2), 31.9, 29.1, 26.9(2), 26.6, 26.4, 26.0(2), 25.2, 25.1, 24.5, 24.4; **HRMS** (ESI) *m/z* calcd for $C_{20}H_{31}NNaO_9$ $[M + Na]^+$ 452.1891, found 452.1888.



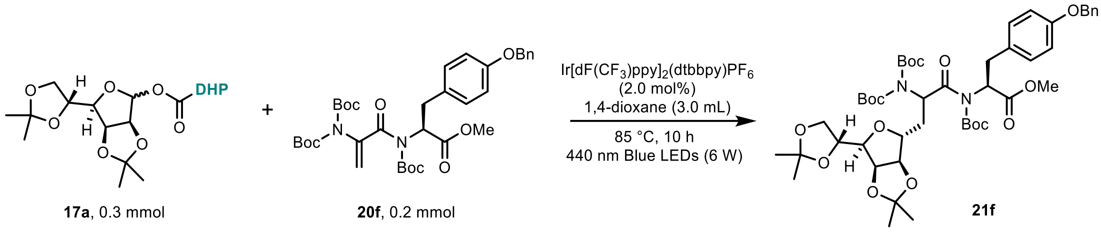
Methyl 3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2-(1,3-dioxoisoindolin-2-yl)propanoate (21c). According to the general protocol B, 4-((3*aS*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), methyl 2-phthalimidoacrylate[7] **20c** (46.0 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred under 6W Blue LEDs irradiation at 85 ºC for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **21c** (82.0 mg, 86%, d.r. = 1.1:1) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.76 – 7.72 (m, 2H), 5.04 – 5.00 (m, 1H), 4.81 (dd, *J* = 6.0, 3.8 Hz, 0.50H), 4.71 (dd, *J* = 6.0, 3.8 Hz, 0.50H), 4.53 (dd, *J* = 6.0, 1.4 Hz, 1H), 4.40 – 4.36 (m, 0.50H), 4.25 (dd, *J* = 10.4, 4.0 Hz, 0.50H), 4.21 – 4.08 (m, 1.50H), 3.91 (dd, *J* = 12.4, 3.6 Hz, 0.50H), 3.78 (dd, *J* = 8.1, 3.8 Hz, 0.50H), 3.74 – 3.73 (s, 3H), 3.67 (dd, *J* = 8.6, 6.2 Hz, 0.50H), 3.60 (dd, *J* = 8.2, 3.8 Hz, 0.50H), 3.46 (dd, *J* = 8.6, 5.2 Hz, 0.50H), 2.49 – 2.42 (m, 0.50H), 2.39 – 2.28 (m, 1.50H), 1.48 (s, 1H), 1.44 (s, 2H), 1.42 (s, 2H), 1.37 (s, 1H), 1.32 – 1.26 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 169.5, 167.6(2), 134.4, 132.1, 132.0, 123.8, 113.0, 112.9, 109.5, 109.3, 85.9, 85.3, 83.0, 80.7(2), 80.6, 80.3, 80.2, 73.4, 73.1, 67.2, 67.0, 53.1, 49.9, 48.9, 29.8, 28.9, 27.2, 26.9, 26.3, 26.1, 25.5, 25.4, 24.8, 24.5; **HRMS** (ESI) *m/z* calcd for $C_{24}H_{29}NNaO_9$ $[M + Na]^+$ 498.1735, found 498.1732.



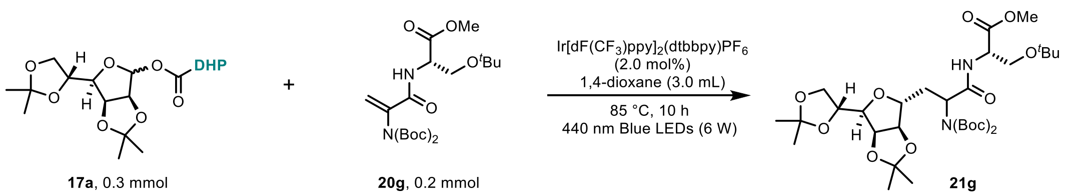
Methyl 2-((*tert*-butoxycarbonyl)(methyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoate (21d). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), methyl 2-((*tert*-butoxycarbonyl)(methyl)amino)acrylate[8] **20d** (43.0 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 4:1) **21d** (44.6 mg, 49%, d.r. = 1.1:1) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.80 – 4.76 (m, 1H), 4.55 (dd, *J* = 6.2, 2.2 Hz, 1H), 4.40 – 4.35 (m, 1.50H), 4.18 – 4.14 (m, 1H), 4.10 – 3.97 (m, 2.5H), 3.77 – 3.71 (m, 4H), 2.90 – 2.83 (m, 3H), 2.15 – 1.95 (m, 1H), 1.90 – 1.73 (m, 1H), 1.49 – 1.41 (m, 15H), 1.36 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0, 140.9, 140.1, 138.9, 138.4, 138.2, 128.9, 128.7, 128.6(2), 128.3, 128.1(2), 127.8, 127.4, 127.1, 126.8, 126.4, 98.2, 82.5, 80.0, 77.8, 77.5, 77.2, 76.8, 76.0, 75.3, 73.6(2), 70.7, 55.0, 29.8; **HRMS** (ESI) *m/z* calcd for $C_{22}H_{37}NNaO_9$ $[M + Na]^+$ 482.2361, found 482.2358.



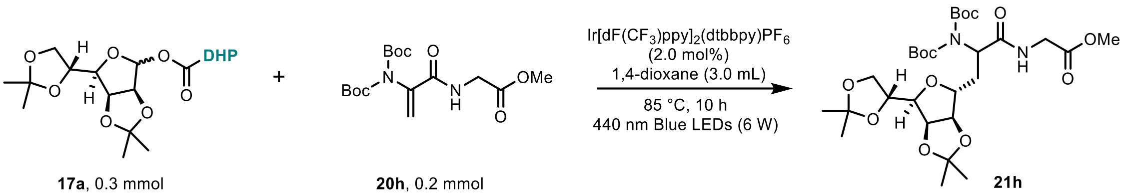
***tert*-Butyl 5-(((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-3-((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4-dioxoimidazolidine-1-carboxylate (21e).** According to the general procedure C, 3,5-diethyl 4-((3*aS*,5*aR*,9*aR*,9*bS*)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-*d*][1,3]dioxin-4-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (108 mg, 0.200 mmol, 1.00 equiv), *tert*-butyl (*S*)-3-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-5-methylene-2,4-dioxoimidazolidine-1-carboxylate **20e** (112 mg, 0.300 mmol, 1.50 equiv) and Ir[dF(CF_3)(ppy)$_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **21e** (55.0 mg, 44%, d.r. = 1.1:1) as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 5H), 5.07 – 4.96 (m, 1H), 4.72 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.47 – 4.13 (m, 4H), 4.03 – 3.87 (m, 2H), 3.77 (d, *J* = 6.1 Hz, 3H), 3.68 (dd, *J* = 8.3, 3.7 Hz, 0.52H), 3.60 (dd, *J* = 8.1, 3.8 Hz, 0.54H), 3.57 – 3.41 (m, 2H), 2.19 – 1.92 (m, 1H), 1.87 – 1.72 (m, 0.57H), 1.63 – 1.30 (m, 21H), 1.20 – 1.13 (m, 0.61H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 169.9, 168.6, 168.5, 151.1, 151.0, 148.7, 148.4, 136.5, 136.4, 129.2, 128.9, 128.8, 127.1 (2), 112.9 (2), 109.3, 109.2, 85.5, 85.3, 85.0, 84.9, 80.7 (2), 80.6 (2), 80.5, 79.6, 77.2, 73.2, 73.1, 67.3, 66.8, 57.2, 56.4, 54.0, 53.5, 53.1 (2), 33.9, 33.8, 31.1, 30.3, 28.2, 28.1, 27.0, 26.9, 26.2, 25.4, 25.2, 24.9, 24.7; **HRMS** (ESI) *m/z* calcd for $C_{31}H_{42}O_{11}N_2Na$ $[M + Na]^+$ 641.2681, found 641.2684.



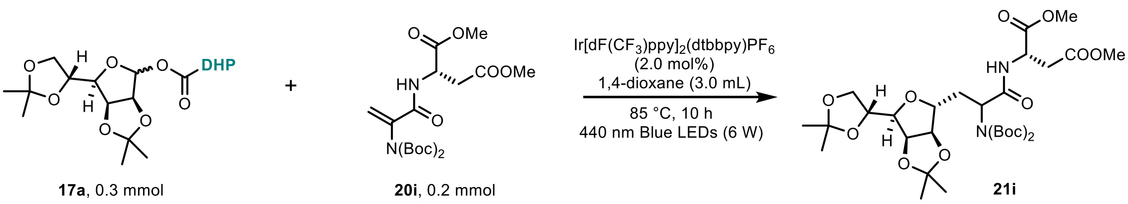
Methyl (2*S*)-3-(4-(benzyloxy)phenyl)-2-(2-(bis(*tert*-butoxycarbonyl)amino)-*N*-(*tert*-butoxycarbonyl)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanamido)propanoate (21f). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), *N,N-tert*-butoxycarbonyldehydroalanine **20f** (131 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Toluene: EtOAc = 5:1) **21f** (146 mg, 81%, d.r. = 1.8:1) as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.28 – 7.27 (m, 0.53H), 7.18 – 7.16 (m, 0.47H), 7.12 – 7.06 (m, 1H), 6.91 – 6.88 (m, 2H), 5.89 (dd, *J* = 11.0, 4.5 Hz, 0.47H), 5.63 (t, *J* = 6.7, 6.7 Hz, 0.53H), 5.40 – 5.35 (m, 1H), 5.03 – 5.01 (m, 2H), 4.77 (dd, *J* = 6.0, 3.7 Hz, 0.53H), 4.70 (dd, *J* = 6.0, 3.8 Hz, 0.47H), 4.59 (d, *J* = 6.0 Hz, 0.53H), 4.40 – 4.30 (m, 2H), 4.17 – 4.04 (m, 2.47H), 3.82 (dd, *J* = 8.4, 3.8 Hz, 0.53H), 3.76 (dd, *J* = 8.7, 3.8 Hz, 0.47H), 3.70 – 3.66 (m, 3H), 3.44 – 3.36 (m, 1H), 3.08 (dd, *J* = 14.1, 9.5 Hz, 0.47H), 2.84 (dd, *J* = 14.0, 3.6 Hz, 0.53H), 2.32 – 2.25 (m, 0.53H), 2.03 – 1.97 (m, 0.47H), 1.49 – 1.47 (m, 20H), 1.45 – 1.42 (m, 11H), 1.38 (d, *J* = 2.6 Hz, 3H), 1.33 (d, *J* = 1.4 Hz, 3H), 1.29 – 1.27 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 172.6, 171.1, 170.8, 157.9, 157.6, 153.2, 152.6, 151.6, 151.3, 137.3, 137.0, 131.6, 130.8, 130.6, 130.0, 129.2, 128.7, 128.4, 128.1, 128.0, 127.7, 127.6, 115.0, 114.8, 112.6, 109.4, 109.3, 85.8, 85.4, 84.5, 84.0, 83.1, 82.4, 82.3, 80.8, 80.5, 80.4, 73.4, 73.3, 70.3, 70.1, 67.7, 67.4, 58.8 (2), 58.4, 52.4, 52.3, 36.9, 35.6, 34.7, 31.6, 31.1, 30.3, 29.8, 28.1 (2), 28.0 (3), 27.0, 26.9, 26.3, 26.2, 25.6, 25.5, 25.0, 24.8; **HRMS** (ESI) *m/z* calcd for $C_{47}H_{66}N_2NaO_{15}$ $[M + Na]^+$921.4355, found 921.4369.



Methyl *N*-(2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*O*-(*tert*-butyl)-*L*-serinate (21g). According to the general procedure B, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), (2-(di(*tert*-butoxycarbonyl)amino)acrylic-L-methionine **20g** (89.0 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)(ppy)$_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 2:1) **21g** (70.5 mg, 51%, d.r. = 1:1) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.1 Hz, 0.29H), 6.58 (d, *J* = 8.1 Hz, 0.73H), 4.93 – 4.87 (m, 0.77H), 4.79 – 4.69 (m, 1.25H), 4.69 – 4.60 (m, 0.34H), 4.62 – 4.54 (m, 0.78H), 4.52 (d, *J* = 6.1 Hz, 1H), 4.39 – 4.30 (m, 1H), 4.22 (dd, *J* = 10.0, 5.1 Hz, 0.74H), 4.09 – 3.95 (m, 2.22H), 3.82 – 3.73 (m, 1.11H), 3.69 (d, J = 7.3 Hz, 3H), 3.65 (dd, J = 8.4, 3.7 Hz, 0.69H), 3.53 (dd, J = 9.0, 3.4 Hz, 0.33H), 3.45 (dd, J = 9.0, 3.5 Hz, 0.64H), 2.41 – 2.25 (m, 0.78H), 2.22 – 2.01 (m, 0.58H), 1.91 – 1.78 (m, 0.78H), 1.51 – 1.29 (m, 30H), 1.10 (d, J = 2.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 170.7, 170.1, 169.9, 152.4, 152.0, 112.7, 112.6, 109.3, 109.2, 85.5, 85.4, 83.7, 83.6, 82.7, 80.9, 80.8, 80.7, 80.5, 80.1, 73.6, 73.5, 73.4, 73.3, 67.3, 67.2, 62.1, 61.8, 57.0, 56.6, 53.1, 53.0, 52.4, 52.3, 30.5, 30.3, 29.8, 29.5, 28.0(2), 27.3, 27.0, 26.2(2), 25.3(2), 24.9, 24.8; **HRMS** (ESI) *m/z* calcd for $C_{33}H_{56}O_{13}N_2Na$ $[M + Na]^+$ 711.3675, found 711.3678.

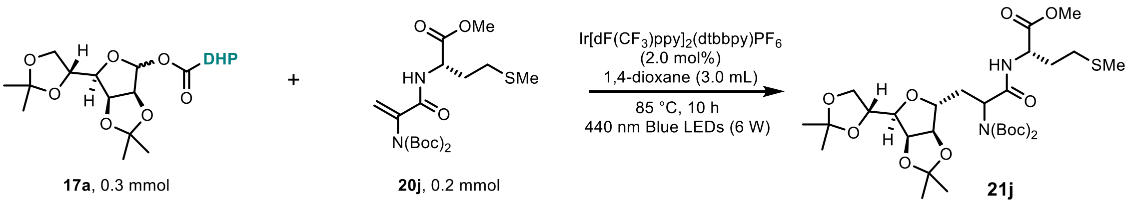


Methyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)glycinate (21h). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), *N,N*-tert-butoxycarbonyldehydroalanine[3] **20h** (71.6 mg, 0.200 mmol, 1.00 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.02 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred in 6W Blue LEDs under N_2 at 85 ºC for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **21h** (59.0 mg, 49%, d.r. = 1.1:1) as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.62 (t, J = 5.2 Hz, 0.62H), 6.39 (t, J = 5.2 Hz, 0.38H), 4.94 (t, J = 6.6 Hz, 0.38H), 4.79 – 4.74 (m, 1.28H), 4.55 (d, J = 6.0 Hz, 1.01H), 4.38 – 4.32 (m, 1H), 4.25 (dd, J = 10.3, 4.8 Hz, 0.38H), 4.13 – 3.93 (m, 4.29H), 3.77 – 3.74 (m, 3.38H), 3.67 (dd, J = 8.3, 3.7 Hz, 0.38H), 2.40 – 2.32 (m, 0.39H), 2.27 – 2.20 (m, 0.62H), 2.13 – 2.05 (m, 0.62H), 1.93 – 1.85 (m, 0.39H), 1.50 – 1.49 (m, 19.03H), 1.42 – 1.41 (m, 2.62H), 1.36 – 1.25 (m, 7.99H), 1.14 (d, J = 6.4 Hz, 0.38H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 170.2, 152.6, 152.2, 112.8(2), 109.3, 85.7, 85.5, 84.1, 83.8, 82.9, 81.1, 80.9, 80.8, 80.5, 80.0, 73.4, 67.3, 67.1, 57.0, 56.8, 52.5(2), 41.5(2), 30.8, 30.2, 28.1, 28.0, 27.1, 27.0, 26.3, 26.2, 25.4, 25.0, 24.9. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{46}NNaO_{12}$ $[M + Na]^+$ 625.2943, found 625.2945.

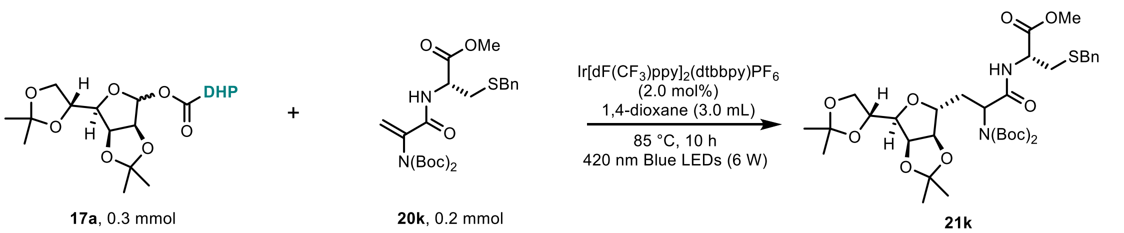


Dimethyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*L*-aspartate (21i). According to the general procedure B, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), (2-(di(*tert*-butoxycarbonyl)amino)acrylic-*L*-dimethyl-asparate **20i** (86.0 mg, 0.200 mmol, 1.00 equiv) and $Ir[dF(CF_3)(ppy)_2](dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **21i** (70.0 mg, 52%, d.r. = 1.2:1) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, J =

7.8 Hz, 0.67H), 6.85 (d, J = 8.1 Hz, 0.29H), 4.92 – 4.68 (m, 3H), 4.54 (d, J = 6.1 Hz, 1H), 4.41 – 4.30 (m, 1H), 4.24 (dd, J = 10.2, 4.9 Hz, 0.35H), 4.12 – 3.98 (m, 2.60H), 3.75 – 3.63 (m, 7H), 3.03 (d, J = 4.2 Hz, 0.33H), 2.99 (d, J = 4.2 Hz, 0.55H), 2.89 (d, J = 4.8 Hz, 0.37H), 2.85 (d, J = 4.7 Hz, 0.20H), 2.77 (d, J = 4.7 Hz, 0.19H), 2.72 (d, J = 4.7 Hz, 0.13H), 2.43 – 2.30 (m, 0.42H), 2.24 – 2.04 (m, 1.41H), 1.53 – 1.29 (m, 30H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 171.3, 171.1, 171.0, 170.2, 169.8, 152.5, 152.1, 112.8, 112.7, 109.4, 109.3, 85.6, 85.5, 84.0, 83.9, 83.7, 82.8, 80.9, 80.8, 80.7, 80.5, 80.1, 73.4, 67.2, 56.9, 56.6, 52.9, 52.8, 52.1, 52.0, 48.8, 48.7, 36.3, 36.1, 31.0, 30.5, 29.5, 28.0(2), 27.1, 27.0, 26.3, 26.2, 25.3, 24.9, 24.8; **HRMS** (ESI) *m/z* calcd for $C_{31}H_{50}O_{14}N_2Na$ $[M + Na]^+$ 697.3154, found 697.3162.

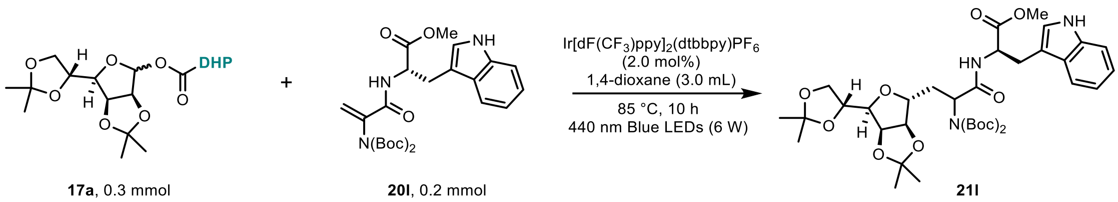


Methyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*L*-methioninate (21j). According to the general procedure B, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), (2-(di(*tert*-butoxycarbonyl)amino)acrylic-L-methionine **20j** (86.5 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)(ppy)$_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **21j** (46.5 mg, 34%, d.r. = 1:1) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 (d, J = 7.7 Hz, 0.43H), 6.62 (d, J = 7.5 Hz, 0.44H), 4.90 – 4.63 (m, 3H), 4.53 (dd, J = 6.1, 2.5 Hz, 1H), 4.39 – 4.29 (m, 1H), 4.22 (dd, J = 10.2, 4.9 Hz, 0.53H), 4.12 – 3.98 (m, 2H), 3.80 – 3.68 (m, 4H), 3.65 (dd, J = 8.3, 3.7 Hz, 0.45H), 2.54 – 2.44 (m, 2H), 2.42 – 2.34 (m, 0.43H), 2.21 – 2.04 (m, 5.37H), 2.03 – 1.92 (m, 1H), 1.91 – 1.80 (m, 0.57H), 1.55 – 1.23 (m, 30H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 172.2, 170.3, 169.8, 152.6, 152.2, 112.8, 112.7, 109.4, 109.3, 85.6, 85.5, 84.1, 83.8, 82.9, 80.9, 80.8, 80.7, 80.5, 80.1, 73.4, 67.2(2), 57.1, 56.7, 52.7, 52.6, 51.9, 51.8, 31.9, 31.7, 30.5, 30.0, 29.9, 29.6, 28.1, 28.0, 27.1(2), 26.3, 26.2, 25.3(2), 24.9(2), 15.6, 15.4; **HRMS** (ESI) *m/z* calcd for $C_{31}H_{52}O_{12}N_2SNa$ $[M + Na]^+$ 699.3133, found 699.3135.



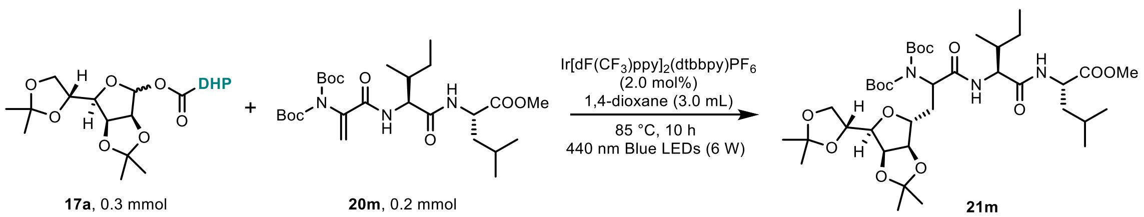
Methyl *S*-benzyl-*N*-(2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*L*-cysteinate (21k). According to the general procedure B, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), (2-(di(*tert*-butoxycarbonyl)amino)acrylic-L-*S*-benzyl-cysteine **20k** (86.5 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)(ppy)$_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 °C under

6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **21k** (78.3 mg, 53%, d.r. = 1:1) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 5H), 6.83 (d, *J* = 7.7 Hz, 0.52H), 6.65 (d, *J* = 7.6 Hz, 0.41H), 4.89 (t, *J* = 6.5 Hz, 0.48H), 4.82 – 4.71 (m, 2.69H), 4.54 (dd, *J* = 6.2, 2.1 Hz, 1H), 4.39 – 4.32 (m, 1H), 4.23 (dd, *J* = 10.2, 4.8 Hz, 0.47H), 4.12 – 3.98 (m, 2.63H), 3.77 – 3.64 (m, 7H), 2.92 – 2.76 (m, 2.22H), 2.42 – 2.34 (m, 0.52H), 2.26 – 2.06 (m, 1.23H), 1.91 – 1.81 (m, 0.52H), 1.49 (d, *J* = 1.9 Hz, 21H), 1.41 (d, *J* = 5.8 Hz, 3H), 1.35 (d, *J* = 3.1 Hz, 3H), 1.32 (d, *J* = 4.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 171.0, 170.2, 169.8, 152.5, 152.2, 137.6(2), 129.0(2), 128.6, 127.3, 127.3, 112.7(2), 109.3(2), 85.5, 85.4, 84.0, 83.7, 82.8, 80.9, 80.8, 80.7, 80.5, 80.1, 73.3, 67.2, 56.9, 56.7, 52.7, 52.6, 52.0, 51.9, 36.6, 36.5, 33.4, 33.3, 30.6, 29.7, 28.1, 28.0, 27.0, 26.2(2), 25.3(2), 24.9, 24.8; **HRMS** (ESI) *m/z* calcd for $C_{36}H_{54}O_{12}N_2NaS$ $[M + Na]^+$ 761.3290, found 761.3293.



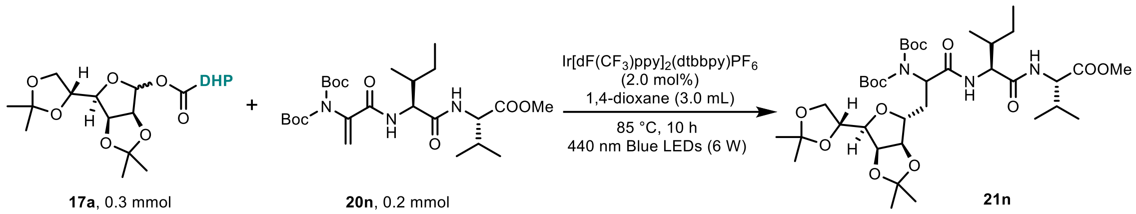
17a, 0.3 mmol **20l**, 0.2 mmol **21l**

Methyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*D*-tryptophanate (21l). According to the general procedure B, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), (2-(di(*tert*-butoxycarbonyl)amino)acryloyl)-*L*-tryptophanate[2] **20l** (86.5 mg, 0.200 mmol, 1.00 equiv) and Ir[dF(CF_3)(ppy)$_2$](dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ^{o}C under 6W blue LED irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **21l** (94.7 mg, 65%, d.r. = 1.2:1) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 19.7 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.20 – 7.06 (m, 2H), 7.01 (t, *J* = 3.5 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 4.93 – 4.83 (m, 2H), 4.75 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.53 (d, *J* = 6.1 Hz, 1H), 4.42 – 4.32 (m, 1H), 4.28 – 4.18 (m, 1H), 4.15 – 4.00 (m, 2H), 3.72 – 3.59 (m, 4H), 3.30 (d, *J* = 5.4 Hz, 2H), 2.45 – 2.29 (m, 1H), 1.92 – 1.80 (m, 1H), 1.49 – 1.32 (m, 30H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 169.4, 152.1, 136.2, 127.6, 123.0, 122.3, 119.8, 118.7, 112.7, 111.3, 110.0, 109.3, 85.6, 83.9, 82.8, 80.8, 80.5, 73.5, 67.2, 57.0, 53.1, 52.4, 30.7, 28.1, 28.0, 27.1, 26.3, 25.3, 25.0; **HRMS** (ESI) *m/z* calcd for $C_{37}H_{53}O_{12}N_3Na$ $[M + Na]^+$ 754.3521, found 754.3530.

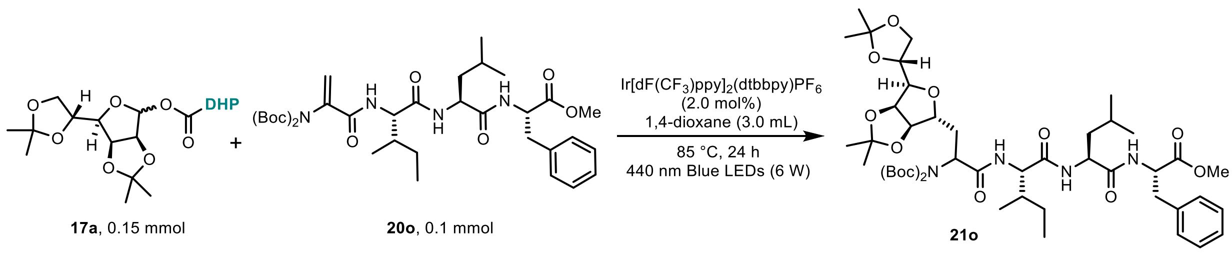


17a, 0.3 mmol **20m**, 0.2 mmol **21m**

Methyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*L*-alloisoleucyl-*L*-leucinate (21m). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), methyl (2-(bis(*tert*-butoxycarbonyl)amino)acryloyl)-*L*-alloisoleucyl-*L*-leucinate **20m** (105 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 1:1) **21m** (87.9 mg, 57%, d.r. = 1.4:1) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.57 (d, *J* = 8.4 Hz, 0.39H), 6.49 (d, *J* = 8.4 Hz, 0.61H), 6.41 (d, *J* = 8.1 Hz, 0.39H), 6.17 (d, *J* = 8.0 Hz, 0.61H), 4.83 – 4.72 (m, 2H), 4.59 – 4.49 (m, 2H), 4.38 – 4.31 (m, 1H), 4.30 – 4.19 (m, 1.61H), 4.08 – 3.99 (m, 2.39H), 3.75 – 3.70 (m, 3.39H), 3.65 (dd, *J* = 8.3, 3.7 Hz, 0.61H), 2.45 – 2.38 (m, 0.61H), 2.29 – 2.21 (m, 0.39H), 2.09 – 1.93 (m, 1H), 1.82 – 1.77 (m, 1H), 1.76 – 1.53 (m, 4H), 1.50 – 1.48 (m, 18H), 1.45 – 1.40 (m, 5.61H), 1.35 – 1.31 (m, 6.39H), 1.15 – 1.06 (m, 1H), 0.93 – 0.86 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 173.0, 170.7(2), 170.4, 169.9, 152.7, 152.4, 112.8, 112.7, 109.4, 109.3, 85.6, 85.5, 84.1, 83.9, 82.8, 80.9, 80.8, 80.6, 80.5, 80.2, 73.4, 67.3(2), 58.0, 57.9, 57.0, 56.9, 52.4, 52.3, 50.9(2), 41.4, 41.3, 37.4, 37.1, 30.6, 29.8, 29.4, 28.1, 28.0, 27.1, 27.0, 26.2(2), 25.3(2), 25.0, 24.9, 24.8, 22.9, 22.8, 22.0, 21.9, 15.6, 15.4, 11.6, 11.5; **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{38}H_{65}N_3NaO_{13}$ 794.4410; found 794.4406.



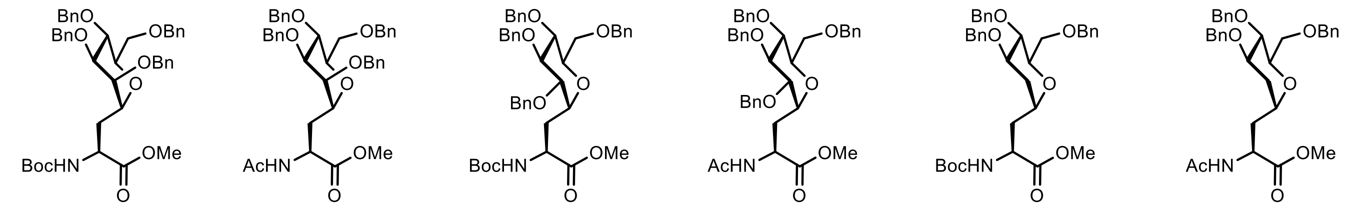
Methyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*L*-alloisoleucyl-*L*-valinate (21n). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), methyl (2-(bis(*tert*-butoxycarbonyl)amino)acryloyl)-*L*-alloisoleucyl-*L*-valinate **20n** (103 mg, 0.200 mmol, 1.00 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 1:1) **21n** (80.2 mg, 53%, d.r. = 1.2:1) as a foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.65 (d, *J* = 8.4 Hz, 0.48H), 6.51 (d, *J* = 8.3 Hz, 0.52H), 6.43 (d, *J* = 8.6 Hz, 0.48H), 6.29 (d, *J* = 8.6 Hz, 0.52H), 4.82 – 4.72 (m, 2H), 4.54 – 4.43 (m, 2H), 4.37 – 4.25 (m, 2H), 4.20 (dd, *J* = 10.3, 4.8 Hz, 0.52H), 4.07 – 3.99 (m, 2.48H), 3.75 – 3.71 (m, 3.52H), 3.64 (dd, *J* = 8.3, 3.7 Hz, 0.48H), 2.44 – 2.38 (m, 0.52H), 2.27 – 2.03 (m, 2H), 1.93 (s, 2H), 1.87 – 1.79 (m, 1H), 1.49 – 1.39 (m, 25.52H), 1.35 – 1.30 (m, 6.52H), 1.20 – 1.05 (m, 1.48H), 0.92 – 0.86 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1(2), 170.9, 170.8, 170.5, 169.9, 152.7, 152.4, 112.7(2), 109.4, 109.3, 85.6, 85.5, 84.1, 83.8, 82.9, 80.9, 80.8, 80.6, 80.5, 80.2, 73.4, 67.3, 67.2, 58.0(2), 57.4, 57.3, 57.1, 56.9, 52.3, 52.2, 37.3, 37.2, 31.2, 31.0, 30.5, 29.5, 28.1, 28.0, 27.1, 27.0, 26.3, 26.2, 25.3(2), 25.0, 24.9(2), 24.8, 19.1, 18.1, 17.9, 15.6, 15.5, 11.6, 11.5; **HRMS** (ESI) *m/z* calcd for $C_{37}H_{63}N_3NaO_{13}$ $[M + Na]^+$ 780.4253, found 780.4260.



Methyl (2-(bis(*tert*-butoxycarbonyl)amino)-3-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl)-*L*-alloisoleucyl-*L*-leucyl-*L*-

phenylalaninate (21o). According to the general protocol B, 4-((*3aS,6R,6aS*)-6-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (81.0 mg, 0.150 mmol, 1.50 equiv), methyl (2-(bis(*tert*-butoxycarbonyl)amino)acryloyl)-*L*-alloisoleucyl-*L*-leucyl-*L*-phenylalaninate **20o** (67.4 mg, 0.100 mmol, 1.0 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.3 mg, 0.002 mmol, 0.02 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs for 24 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: Acetone = 1:1) **21o** (57.0 mg, 62%, d.r. = 1.2:1) as a foam: **^{1}H NMR** (400 MHz, CD_3CN) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 0.55H), 6.99 (d, *J* = 7.7 Hz, 0.45H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 7.0 Hz, 0.55H), 6.56 (d, *J* = 7.4 Hz, 0.45H), 4.89 (dd, *J* = 7.6, 5.8 Hz, 0.45H), 4.73 (dd, *J* = 10.3, 4.4 Hz, 0.55H), 4.68 – 4.64 (m, 1H), 4.59 – 4.55 (m, 1H), 4.53 – 4.52 (m, 0.55H), 4.47 (dd, *J* = 6.0, 0.9 Hz, 0.55H), 4.31 – 4.21 (m, 2H), 4.16 – 4.06 (m, 1.55H), 4.00 – 3.97 (m, 1.45H), 3.93 – 3.88 (m, 1H), 3.74 – 3.71 (m, 0.45H), 3.64 – 3.61 (m, 3.55H), 3.12 – 3.05 (m, 1H), 3.02 – 2.95 (m, 1H), 2.24 – 2.22 (m, 0.55H), 1.91 – 1.87 (m, 0.45H), 1.51 – 1.47 (m, 20H), 1.40 – 1.38 (m, 3.35H), 1.35 – 1.34 (m, 3H), 1.28 – 1.26 (m, 6.65H), 0.90 – 0.82 (m, 15H); **^{13}C NMR** (101 MHz, CD_3CN) δ 172.8, 172.7, 171.9, 171.8, 171.6, 171.2, 153.7, 153.3, 138.0, 137.8, 130.3, 130.3, 129.4, 129.3, 127.8, 127.7, 112.9, 112.7, 109.6(2), 86.4, 86.0, 84.4, 84.2, 84.0, 82.0, 81.7, 81.6, 81.2, 81.0, 74.0, 67.8, 67.8, 59.2, 58.1, 57.6, 54.7, 52.6(2), 52.5(2), 42.4, 41.4, 41.3, 38.2, 38.1, 37.9, 37.8, 36.9, 30.9, 30.8, 29.8, 29.1, 28.2(2), 27.1(2), 26.4, 25.7, 25.6, 25.4(2), 25.3, 24.9(2), 23.5, 23.3(2), 22.9, 21.7, 21.6, 19.7, 16.1, 11.8, 11.7; **HRMS** (ESI) *m/z* calcd for $C_{47}H_{74}N_4NaO_{14}$ $[M + Na]^+$ 941.5094, found 941.5104.

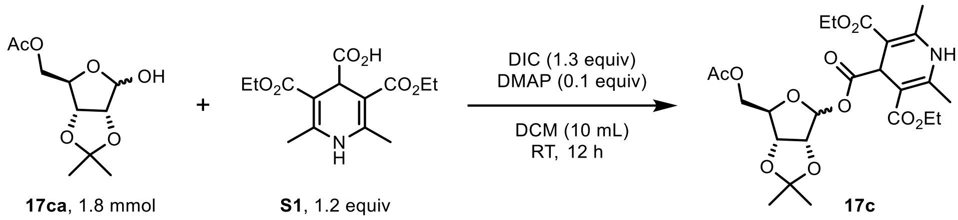
Unsuccessful examples



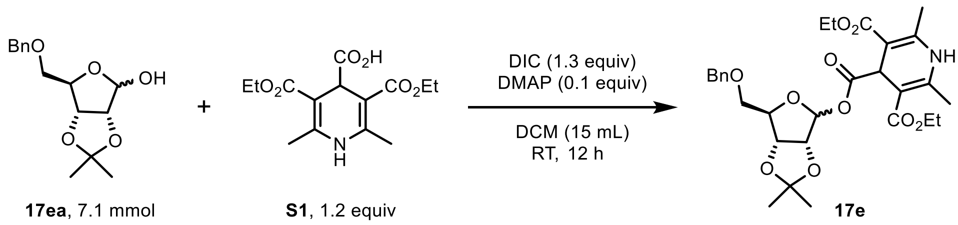
17a', N.D. **17b'**, trace **17a''**, N.D. **17b''**, trace **17a'''**, N.D. **17b'''**, trace

Glycosyl esters (1.50 equiv), chiral dehydroalanines (1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3×). Anhydrous 1,4-dioxane (3.00 mL) were added, and the reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 10 h or 20 h, cooled to rt. It is worth noting that the upper edge of the heating block submerges up 1/3 of the reaction mixture. The experimental results showed that no target compounds (**17a', 17a'', 17a'''**) were detected, there are some residual raw materials and by-products of the protonation of glycosyl esters; At the same time, only trace of product (**17b', 17b'', 17b'''**) formation can be detected in HRMS, the by-product is also the protonation of glycosyl esters.

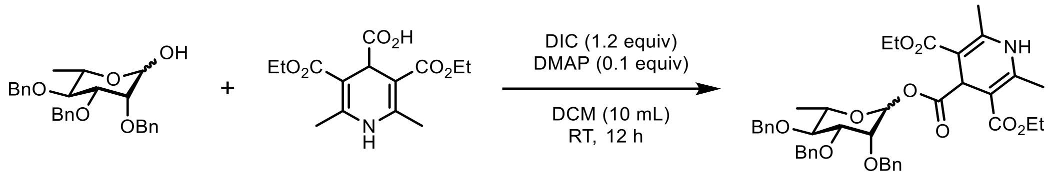
5. Detailed Experimental Procedures for Preparation of Glycosyl 4-Formate-1,4-dihydropyridine



4-((*3aR,6R,6aR*)-6-(Acetoxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17c). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (653 mg, 2.20 mmol, 1.20 equiv), DIC (290 mg, 2.30 mmol, 1.30 equiv) and DMAP (24.4 mg, 0.180 mmol, 0.100 equiv) were added to a solution of ((*3aR,4R,6aR*)-6-hydroxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl (*2S*)-2-(6-methoxynaphthalen-2-yl)propanoate[9] **17ca** (410 mg, 1.80 mmol, 1.00 equiv) in DCM (10.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated *in vacuo* and afforded after flash column chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 2:1) **17c** (653 mg, β and α mixture, 71%) as a light-yellow foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 6.08 (s, 1H), 4.85 (s, 1H), 4.66 (d, J = 5.9 Hz, 1H), 4.60 (d, J = 5.9 Hz, 1H), 4.43 – 4.35 (m, 1H), 4.23 – 4.17 (m, 4H), 4.02 – 3.94 (m, 2H), 2.31 (d, J = 2.9 Hz, 6H), 2.09 (s, 3H), 1.47 (s, 3H), 1.32 – 1.27 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 170.8, 167.1, 167.0, 146.1, 146.0, 113.3, 102.3, 98.4, 98.1, 85.2, 85.1, 82.0, 64.2, 60.3(2), 40.6, 26.5, 25.2, 20.9, 19.5, 19.4, 14.5; **HRMS** (ESI) *m/z* calcd for $C_{24}H_{33}NNaO_{11}$ $[M + Na]^+$ 534.1946, found 534.1944.

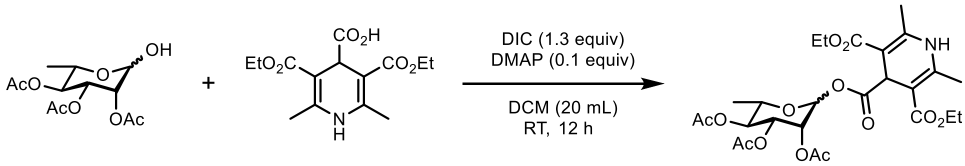


4-((*3aR,6R,6aR*)-6-((Benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17e). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (2.50 g, 8.50 mmol, 1.20 equiv), DIC (1.20 g, 9.30 mmol, 1.30 equiv) and DMAP (86.0 mg, 0.710 mmol, 0.100 equiv) were added to a solution of (3*aR,6R,6aR*)-6-((benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol[10] **17ea** (2.00 g, 7.10 mmol, 1.00 equiv) in DCM (15.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated *in vacuo* and afforded after flash column chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **17e** (2.20 g, β and α mixture, 56%) as a light-yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 4H), 7.29 – 7.26 (m, 1H), 6.32 (s, 1H), 6.11 (s, 1H), 4.84 (s, 1H), 4.74 (d, *J* = 5.9 Hz, 1H), 4.60 (d, *J* = 6.0 Hz, 1H), 4.57 (s, 2H), 4.41 (dd, *J* = 9.3, 5.6 Hz, 1H), 4.21 – 4.10 (m, 4H), 3.50 – 3.39 (m, 2H), 2.25 – 2.24 (m, 6H), 1.47 (s, 3H), 1.30 – 1.23 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 167.1, 167.0, 146.3, 146.1, 138.1, 128.5, 127.8, 127.6, 113.0, 102.6, 98.1, 97.7, 86.1, 85.1, 82.2, 73.2, 70.3, 60.2, 60.1, 40.4, 26.5, 25.1, 19.2(2), 14.5(2); **HRMS** (ESI) *m/z* calcd for $C_{29}H_{37}NNaO_{10}$ $[M + Na]^+$ 582.2310, found 582.2309.



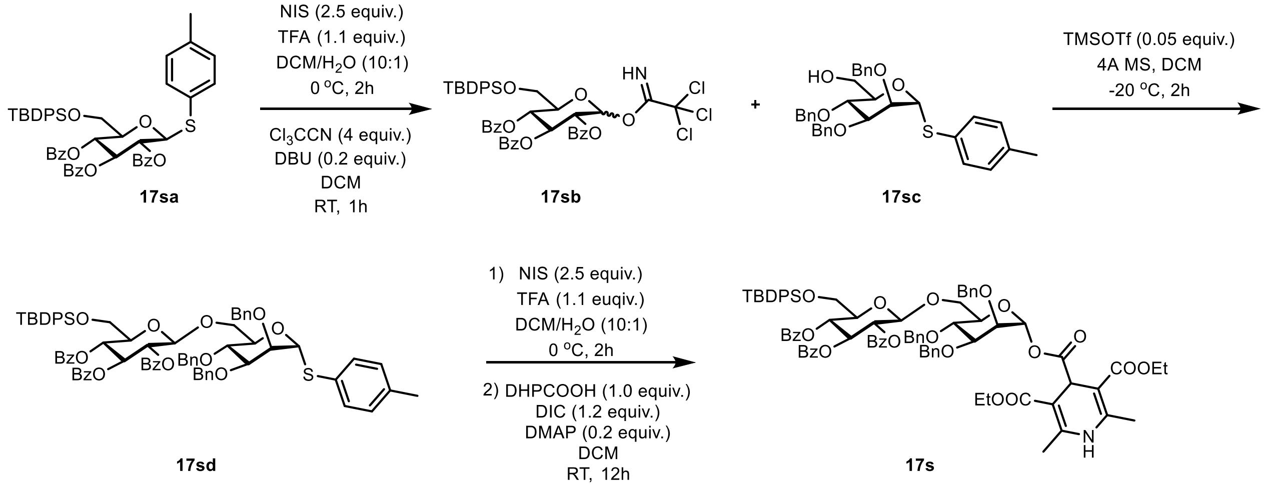
17pa, 5 mmol　**S1**, 5.5 mmol　**17p**

3,5-Diethyl 4-((*3R,4R,5S,6S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17p). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (1.64 g, 5.50 mmol, 1.10 equiv), DIC (756 mg, 6.00 mmol, 1.20 equiv) and DMAP (61.0 mg, 0.500 mmol, 0.100 equiv) were added to a solution of (*3R,4R,5S,6S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-ol[11] **17pa** (2.17 g, 5.00 mmol, 1.00 equiv) in DCM (10.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated *in vacuo* and afforded after flash column chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **17p** (2.0 g, β and α mixture, 56%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.34 – 7.23 (m, 13H), 5.95 (s, 1H), 5.52 (s, 1H), 5.01 (s, 1H), 4.91 (dd, *J* = 11.5, 4.5 Hz, 2H), 4.63 (dd, *J* = 18.3, 11.5 Hz, 2H), 4.49 – 4.42 (m, 2H), 4.21 – 4.12 (m, 4H), 3.91 (d, *J* = 2.8 Hz, 1H), 3.60 – 3.50 (m, 2H), 3.45 – 3.38 (m, 1H), 2.28 – 2.27 (m, 6H), 1.34 – 1.24 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 167.1, 146.1, 139.0, 138.5, 138.2, 128.5(2), 128.3, 128.2, 128.1, 127.8, 127.7(2), 127.6, 98.5, 98.3, 94.3, 81.8, 79.7, 75.5, 74.6, 74.2, 72.9, 71.5, 60.4, 60.3, 40.8, 19.5(2), 18.0, 14.5(2); **HRMS** (ESI) *m/z* calcd for $C_{41}H_{47}NNaO_{10}$ $[M + Na]^+$ 736.3092, found 736.3094.



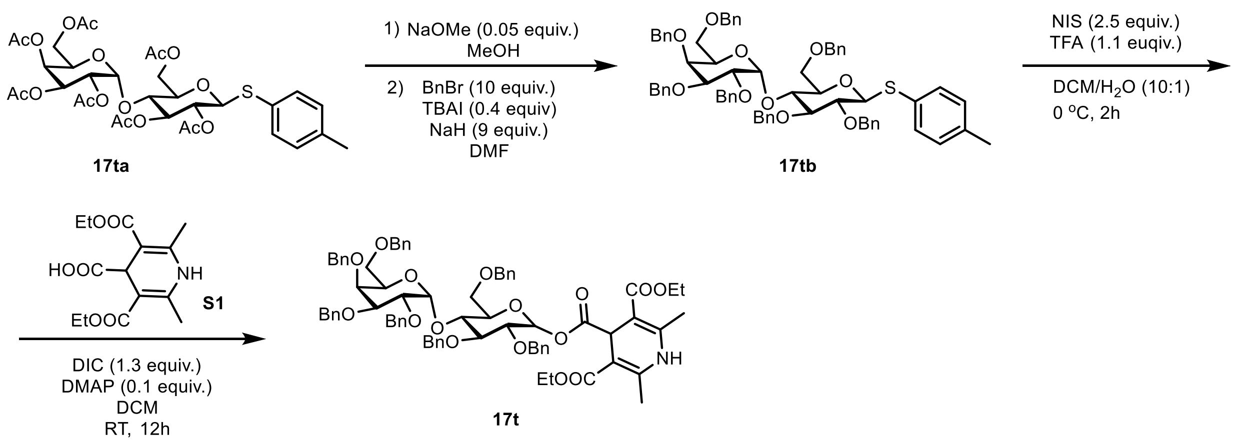
17qa, 3.4 mmol　**S1**, 1.2 equiv　**17q**

3,5-Diethyl 4-((*3R,4R,5S,6S*)-3,4,5-triacetoxy-6-methyltetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17q). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (1.12 g, 4.08 mmol, 1.20 equiv), DIC (557 mg, 4.42 mmol, 1.30 equiv) and DMAP (42.0 mg, 0.340 mmol, 0.100 equiv) were added to a solution of (*3R,4R,5S,6S*)-2-hydroxy-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate[6] **17qa** (1.00 g, 3.40 mmol, 1.00 equiv) in DCM (20.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated *in vacuo* and afforded after flash column chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 1:1) **17q** (420 mg, β and α mixture, 22%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 6.06 (s, 1H), 5.91 (d, *J* = 1.9 Hz, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 5.39 (dd, *J* = 2.9, 1.2 Hz, 1H), 5.21 – 5.16 (m, 2H), 5.10 – 4.98 (m, 3H), 4.98 – 4.94 (m, 2H), 4.28 – 4.12 (m, 10H), 3.88 – 3.81 (m, 1H), 3.62 – 3.55 (m, 1H), 2.36 – 2.28 (m, 14H), 2.20 (s, 4H), 2.14 (s, 3H), 2.06 – 2.04 (m, 7H), 1.98 – 1.97 (m, 3H), 1.33 – 1.23 (m, 18H), 1.18 (d, J = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 170.6, 170.4, 170.1, 170.0, 167.0, 166.9, 146.0(2), 98.2, 97.9, 90.8, 71.5, 71.0, 70.6, 70.4, 69.0, 68.7, 68.4, 60.4, 60.2(2), 40.5, 40.2, 20.9, 20.8, 20.7, 19.4(3), 19.3, 17.5, 17.4, 14.5, 14.4; **HRMS** (ESI) *m/z* calcd for $C_{26}H_{35}NNaO_{13}$ $[M + Na]^+$ 592.2001, found 592.1998.



3,5-Diethyl 4-((*2R,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((((*2R,3R,5R,6R*)-3,4,5-tris(benzoyloxy)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17s). NIS (9.30 g, 41.25 mmol, 2.50 equiv) and TFA (673 mg, 5.90 mmol, 1.10 equiv) were added to a solution of **17sa**[12] (13.8 g, 16.5 mmol, 1.00 equiv) in a mixture of DCM/H_2O (88.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to proceed under stirring for 2 h at rt and quenched with Et_3N. The mixture was washed with 20% (w/w) aqueous $Na_2S_2O_3$ (30.0 mL) and saturated aqueous $NaHCO_3$ (80.0 mL). The organic layer was separated, and the aqueous layer was reextracted with DCM (2 × 80.0 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed. The crude product was purified by short column on SiO_2 (petroleum ether: EtOAc = 5:1) to give the hemiacetal (9.50 g, 79%). The hemiacetal (9.50 g, 13.0 mmol, 1.00 equiv) was treated with trichloroacetonitrile (7.488 g, 52.0 mmol, 4.00 equiv) in anhydrous DCM (30.0 mL) in the presence of DBU (395.2 mg, 2.60 mmol, 0.200 equiv). After stirring at rt for 2 h, the reaction mixture was concentrated and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) the trichloroacetimidate glycosyl donor **7sb** as a white foam. Freshly activated 4Å MS (3.00 g), the above **17sb**, ((*2R,3R,4S,5S,6R*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-2-yl)methanol[13] **17sc** (6.60 g, 12.2 mmol, 1.00 equiv) and anhydrous DCM (60.0 mL) were successively added into a flame dried glassware. The mixture was cooled to -20 °C and TMSOTf (135.4 mg, 0.610 mmol, 0.050 equiv) was added. After stirring at this temperature for 2 h, the resulting mixture was filtered through a pad of silica, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 5:1) to afford **17sd** (10.2 g, 74%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 6H), 7.80 – 7.78 (m, 2H), 7.67 – 7.65 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 – 7.30 (m, 26H), 7.29 – 7.27 (m, 3H), 7.25 – 7.24 (m, 1H), 7.18 – 7.16 (m, 2H), 5.90 (t, *J* = 9.6, 9.6 Hz, 1H), 5.73 – 5.64 (m, 3H), 4.91 (d, *J* = 7.9 Hz, 1H), 4.79 (d, *J* = 12.7 Hz, 1H), 4.68 – 4.61 (m, 2H), 4.57 (s, 2H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.06 – 3.97 (m, 3H), 3.93 – 3.82 (m, 4H), 2.39 (s, 3H), 1.10 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 165.1, 165.0, 138.6, 138.3, 138.1, 137.5, 135.7, 135.6, 133.3, 133.1, 133.0, 132.8, 131.6, 130.9, 130.0, 129.9, 129.8 (2), 129.7 (2), 129.6, 129.3, 129.1, 128.4, 128.3 (3), 128.0, 127.7 (3), 127.6, 101.3, 86.2, 80.2, 75.9, 75.3, 74.8, 74.5, 73.5, 72.8, 72.1, 71.8, 71.7, 69.4, 68.3, 62.8, 26.7, 21.2, 19.2; **HRMS** (ESI) *m/z* calcd for $C_{77}H_{76}NaO_{13}SSi$ $[M + Na]^+$ 1291.4668, found 1291.4689.

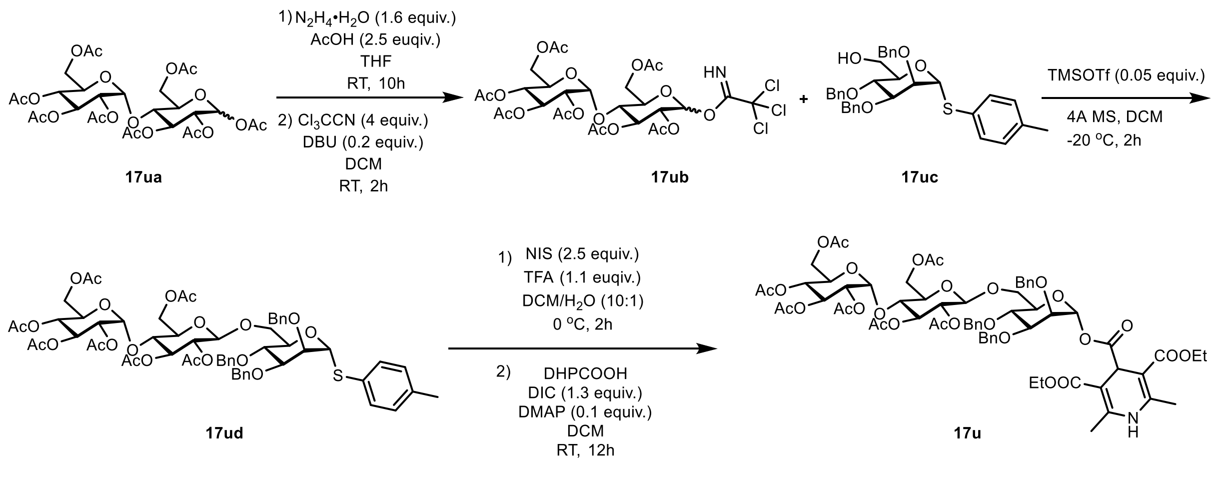
NIS (1.20 g, 5.00 mmol, 2.50 equiv) and TFA (250 mg, 2.20 mmol, 1.10 equiv) were added to a solution of **17sd** (2.30 g, 2.00 mmol, 1.00 equiv) in a mixture of DCM/H_2O (22.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to stir at rt for 2 h and quenched with Et_3N. The mixture was washed with 20% (w/w) aqueous $Na_2S_2O_3$ (20.0 mL) and saturated aqueous $NaHCO_3$ (20.0 mL). The organic layer was separated, reextracted with DCM (2 × 20 mL), dried over anhydrous Na_2SO_4, and contracted. The crude product was purified by short column on SiO_2 to obtain the hemiacetal (1.15 g, 50%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (297 mg, 1.00 mmol, 1.00 equiv), DIC (151 mg, 1.20 mmol, 1.20 equiv) and DMAP (24.4 mg, 0.200 mmol, 0.200 equiv) were added to a solution of the above hemiacetal (1.15 g, 1.00 mmol, 1.00 equiv) in DCM (10.0 mL) at rt and stirred for 12 h. The reaction mixture was concentrated and afforded after chromatographic purification on SiO_2 (Toluene: ether: EtOAc = 3:1) **17s** (620 mg, β and α mixture , 44%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 6H), 7.78 – 7.75 (m, 2H), 7.64 – 7.55 (m, 6H), 7.53 – 7.47 (m, 2H), 7.42 (t, *J* = 7.8, 7.8 Hz, 2H), 7.38 – 7.29 (m, 16H), 7.27 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 5.82 – 5.72 (m, 2H), 5.56 – 5.52 (m, 2H), 5.33 (s, 1H), 5.16 (d, *J* = 8.0 Hz, 1H), 5.03 (d, *J* = 12.2 Hz, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.51 – 4.43 (m, 2H), 4.39 – 4.29 (m, 4H), 4.23 (dd, *J* = 10.8, 7.1 Hz, 1H), 4.19 – 4.13 (m, 1H), 4.12 – 4.07 (m, 1H), 4.04 (d, *J* = 2.8 Hz, 1H), 4.01 – 3.95 (m, 2H), 3.90 – 3.82 (m, 2H), 3.64 – 3.60 (m, 1H), 3.52 – 3.47 (m, 2H), 2.66 (s, 3H), 2.21 (s, 3H), 1.39 (t, *J* = 7.1, 7.1 Hz, 3H), 1.27 (t, *J* = 7.1, 7.1 Hz, 3H), 1.08 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 167.2, 167.2, 167.1, 165.2, 164.9, 147.1, 146.3, 138.7, 138.0, 137.9, 135.8, 135.6, 133.7, 133.4, 133.3, 133.0, 130.0, 129.9, 129.7, 129.7, 129.3, 129.1, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.6, 101.0, 98.6, 97.7, 94.5, 81.7, 78.4, 75.2, 74.9, 74.4, 74.4, 74.0, 73.4, 71.6, 71.3, 69.4, 66.9, 62.7, 60.3, 60.2, 39.8, 26.7, 19.6, 19.3, 18.7, 14.6, 14.5. **HRMS** (ESI) *m/z* calcd for $C_{84}H_{87}NNaO_{19}Si$ $[M + Na]^+$ 1464.5534, found 1464.5540.



4-((*3R,4S,5R,6R*)-3,4-Bis(benzyloxy)-6-((benzyloxy)methyl)-5-(((*2R,3R,4S,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17t). 30% NaOMe in MeOH (58 mg, 0.31 mmol, 0.1 equiv) was added a solution of (*2R,3S,4S,5R,6R*)-2-(acetoxymethyl)-6-(((*2R,3R,4S,5R,6S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate[14] **17ta** (2.30 g, 3.10 mmol, 1.00 equiv) in anhydrous MeOH (20.0 mL) at rt. The reaction mixture was stirred at 2 h, concentrated, and azeotroped with toluene (2×). A solution of the crude heptol (3.00 mmol, 1.00 equiv) and TBAI (443 mg, 1.20 mmol, 0.400 equiv) in anhydrous DMF (30.0 mL) was added NaH (60% in oil) (1.10 g, 27.0 mmol, 9.00 equiv) at 0 °C and stirred for 10 minutes. BnBr (5.13 g, 30.0 mmol, 10.0 equiv) was added dropwise to the resulting mixture at 0 °C. After warming up to rt and stirring overnight, the reaction mixture was poured into ice-water and extracted with EtOAc (3×). The combined organic extracts were washed with H_2O (3×), brine (2×), dried over Na_2SO_4, and filtered. After solvent removal *in vacuo*, the residue afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) the corresponding the benzylated lactopyranoside **17tb** (1.50 g, 47%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.48

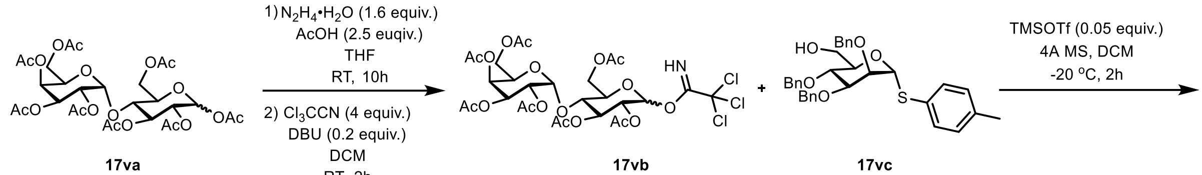
– 7.45 (m, 2H), 7.41 – 7.27 (m, 30H), 7.25 – 7.21 (m, 1H), 7.18 – 7.14 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.14 (d, *J* = 10.4 Hz, 1H), 5.03 (d, *J* = 11.4 Hz, 1H), 4.88 – 4.81 (m, 4H), 4.80 – 4.71 (m, 3H), 4.64 – 4.56 (m, 2H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 11.8 Hz, 1H), 4.29 (d, *J* = 11.8 Hz, 1H), 4.02 – 3.98 (m, 2H), 3.90 – 3.80 (m, 3H), 3.66 (t, *J* = 8.9, 8.9 Hz, 1H), 3.58 (t, *J* = 7.8, 7.8 Hz, 1H), 3.51 – 3.37 (m, 5H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 139.0, 138.8, 138.6, 138.6, 138.5, 138.2, 137.7, 132.9, 129.7, 129.7, 128.5, 128.5, 128.5, 128.3, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 127.3, 102.9, 87.6, 85.1, 82.7, 80.1, 80.1, 79.5, 76.6, 75.7, 75.6, 75.4, 74.8, 73.7, 73.5, 73.1, 73.1, 72.7, 68.5, 68.1, 21.2; **HRMS** (ESI) *m/z* calcd for $C_{68}H_{70}NaO_{10}S$ $[M + Na]^+$ 1101.4582, found 1101.4580.

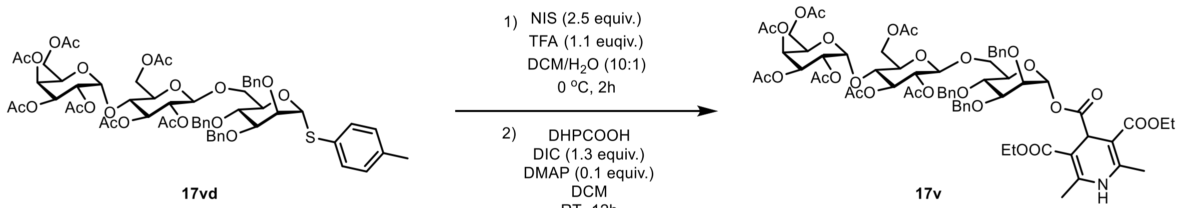
NIS (788 mg, 3.50 mmol, 2.50 equiv) and TFA (182 mg, 1.60 mmol, 1.10 equiv) were added to a solution of **17tb** (1.50 g, 1.40 mmol, 1.00 equiv) in a mixture of DCM/H_2O (22.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to stir at rt for 2 h and quenched with Et_3N. After solvent removal in *vacuo*, the residue was dissolved in DCM (20.0 mL) and washed with 20% (w/w) aqueous $Na_2S_2O_3$ (20.0 mL) and saturated aqueous $NaHCO_3$ (20.0 mL). The organic layer was separated, and the aqueous layer was reextracted with DCM (2 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 to obtain the hemiacetal (1.10 g, 73%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (386 mg, 1.30 mmol, 1.30 equiv), DIC (189 mg, 1.50 mmol, 1.50 equiv) and DMAP (24.4 mg, 0.200 mmol, 0.200 equiv) were added to a solution of the above hemiacetal (972 mg, 1.00 mmol, 1.00 equiv) in DCM (15.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Toluene: EtOAc = 3:1) **17t** (620 mg, β and α mixture, 49%) as a light-yellow foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 31H), 7.25 – 7.19 (m, 2H), 7.16 – 7.12 (m, 2H), 6.22 – 6.21 (m, 1H), 5.63 (d, *J* = 7.9 Hz, 1H), 5.09 (s, 1.45H), 5.06 (d, *J* = 6.6 Hz, 1H), 5.02 (s, 0.55H), 4.86 – 4.79 (m, 3H), 4.78 – 4.74 (m, 3H), 4.72 – 4.69 (m, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.56 (s, 0.45H), 4.52 (d, *J* = 4.2 Hz, 1H), 4.50 (s, 0.55H), 4.42 – 4.37 (m, 2H), 4.31 (d, *J* = 11.8 Hz, 1H), 4.26 – 4.16 (m, 3H), 4.15 – 4.08 (m, 2H), 3.97 (d, *J* = 2.9 Hz, 1H), 3.89 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.81 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.66 – 3.58 (m, 3H), 3.55 – 3.51 (m, 1H), 3.48 – 3.39 (m, 4H), 2.27 (s, 3H), 2.18 (s, 3H), 1.28 – 1.23 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 167.1, 167.1, 146.2, 146.0, 139.1, 138.9, 138.7, 138.7, 138.6, 138.3, 138.1, 128.5, 128.4, 128.3 (3), 128.2, 128.0 (2), 127.9, 127.8, 127.7, 127.6 (2), 127.5 (3), 127.4, 127.2, 102.6, 98.0, 97.8, 94.8, 83.0, 82.6, 80.6, 80.0, 76.0, 75.7, 75.6, 75.4, 74.8, 74.7, 73.7, 73.5, 73.1, 73.0, 72.7, 68.1, 67.6, 60.1 (2), 40.4, 19.2, 19.1, 14.5; **HRMS** (ESI) *m/z* calcd for $C_{75}H_{81}NNaO_{16}$ $[M + Na]^+$ 1274.5448, found 1274.5453.



3,5-Diethyl 4-((2*R*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17u). $N_2H_4 \cdot H_2O$ (43.8 mmol, 1.60 equiv) and AcOH (43.8 mmol, 2.50 equiv) were added to a solution of acetylated maltose **17ua** (17.5 mmol, 1.00 equiv) in THF (80.0 mL). The reaction was allowed to stir at rt for 10 h. The reaction mixture was concentrated, poured into ice-water and extracted with EtOAc (3×). The combined organic layer were dried over Na_2SO_4, filtered, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc, 1:1) to give the acetylated maltosyl hemiacetal (4.35 g, 39%). The resulted hemiacetal (5.00 mmol, 1.00 equiv) was treated with trichloroacetonitrile (20.0 mmol, 4.00 equiv) in anhydrous DCM (30.0 mL) in the presence of DBU (1.00 mmol, 0.200 equiv). After stirring at rt for 2 h, the reaction mixture was concentrated and purified by short column on SiO_2 (Petroleum ether: EtOAc, 1:1) to afford the curde **17ub**. Freshly activated 4Å MS, the above trichloroacetimidate glycosyl donor **17ub** (5.00 mmol, 1.00 equiv), ((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-2-yl)methanol[13] **17uc** (4.00 mmol, 0.800 equiv) and anhydrous DCM (30.0 mL) were successively added into a flame dried glassware. The mixture was cooled to -20 °C and TMSOTf (0.25 mmol, 0.05 equiv.) was added. The resulting mixture was stirred at this temperature for 2 h, filtered through a pad of silica and concentrated. The residue was purified by column chromatography on SiO_2 (petroleum ether: EtOAc = 10:1) to afford **17ud** (1.45 g, 24%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.06 (m, 19H), 5.48 (d, *J* = 1.7 Hz, 1H), 5.43 – 5.34 (m, 2H), 5.19 (t, *J* = 9.1 Hz, 1H), 5.06 (t, *J* = 9.9 Hz, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 4.91 – 4.81 (m, 2H), 4.71 (d, *J* = 12.3 Hz, 1H), 4.63 – 4.53 (m, 4H), 4.49 (d, *J* = 7.9 Hz, 1H), 4.43 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.17 (dd, *J* = 12.1, 4.3 Hz, 1H), 4.07 – 3.92 (m, 5H), 3.91 – 3.81 (m, 3H), 3.50 – 3.44 (m, 1H), 2.34 (s, 3H), 2.09 (d, *J* = 6.4 Hz, 9H), 2.04 – 1.98 (m, 9H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5 (2), 170.3, 169.9, 169.6, 169.4, 138.4, 138.0, 137.8, 137.7, 132.0, 130.7, 130.4, 129.9, 128.5, 128.4(2), 128.2(2), 128.0, 127.9, 127.8(3), 100.3, 95.5, 86.3, 80.0, 76.0, 75.5, 75.1, 74.6, 73.0, 72.7, 72.1, 71.9(2), 71.8, 70.0, 69.3, 68.4(2), 68.0, 62.8, 61.5, 60.4, 21.1, 20.9, 20.8, 20.7, 20.6(3), 14.2; **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{60}H_{70}NaSO_{22}$ 1197.3972; found 1197.3991.

NIS (652 mg, 2.90 mmol, 2.00 equiv) and TFA (182 mg, 1.60 mmol, 1.10 equiv) were added to a solution of **17ud** (1.70 g, 1.45 mmol, 1.00 equiv) in a mixture of DCM/H_2O (22.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to stir at rt for 2 h and quenched with Et_3N. The mixture was washed with 20% (w/w) aqueous $Na_2S_2O_3$ (20 mL) and saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated, and the aqueous layer was reextracted with DCM (2 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc, 1:1) to afford the hemiacetal (1.35 g, 90%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1**(357 mg, 1.20 mmol, 1.00 equiv), DIC (190 mg, 1.56 mmol, 1.30 equiv) and DMAP (0.240 mmol, 0.200 equiv) were added to a solution of the above hemiacetal (1.30 g, 1.20 mmol, 1.00 equiv) in DCM (15.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Hexane: Toluene: THF = 3:1:1) to afford **17u** (850 mg, β and α mixture, 53%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.35 – 7.22 (m, 13H), 6.78 (s, 1H), 5.54 (s, 1H), 5.38 – 5.33 (m, 2H), 5.13 (t, *J* = 9.3, 9.3 Hz, 1H), 5.07 – 5.02 (m, 2H), 4.95 – 4.89 (m, 2H), 4.85 (dd, *J* = 10.5, 3.9 Hz, 1H), 4.77 (dd, *J* = 9.6, 7.9 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.56 – 4.44 (m, 4H), 4.38 (d, *J* = 11.8 Hz, 1H), 4.26 – 4.11 (m, 6H), 4.04 – 3.90 (m, 5H), 3.76 (dd, *J* = 12.3, 6.9 Hz, 1H), 3.66 (t, *J* = 9.3, 9.3 Hz, 1H), 3.55 – 3.45 (m, 3H), 2.36 (s, 6H), 2.11 – 2.09 (m, 6H), 2.05 – 2.01 (m, 12H), 1.92 (s, 3H), 1.29 – 1.22 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 171.0, 170.7, 170.5, 170.2, 170.1, 169.5, 167.1, 146.7, 145.8, 138.7, 138.2, 137.9, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7 (2) 100.3, 98.2, 97.9, 95.7, 93.6, 81.7, 77.1, 75.7, 75.1, 74.3, 74.0, 73.7, 73.1, 72.0, 71.9, 71.4, 70.3, 69.4, 68.6, 68.1, 68.0, 62.7, 61.6, 60.4, 60.2, 40.1, 21.2, 21.0, 20.8, 20.7 (2), 20.5, 19.6, 19.1, 14.5 (2); **HRMS** (ESI) *m/z* calcd for $C_{67}H_{81}NNaO_{28}$ $[M + Na]^+$ 1370.4837, found 1370.4844.

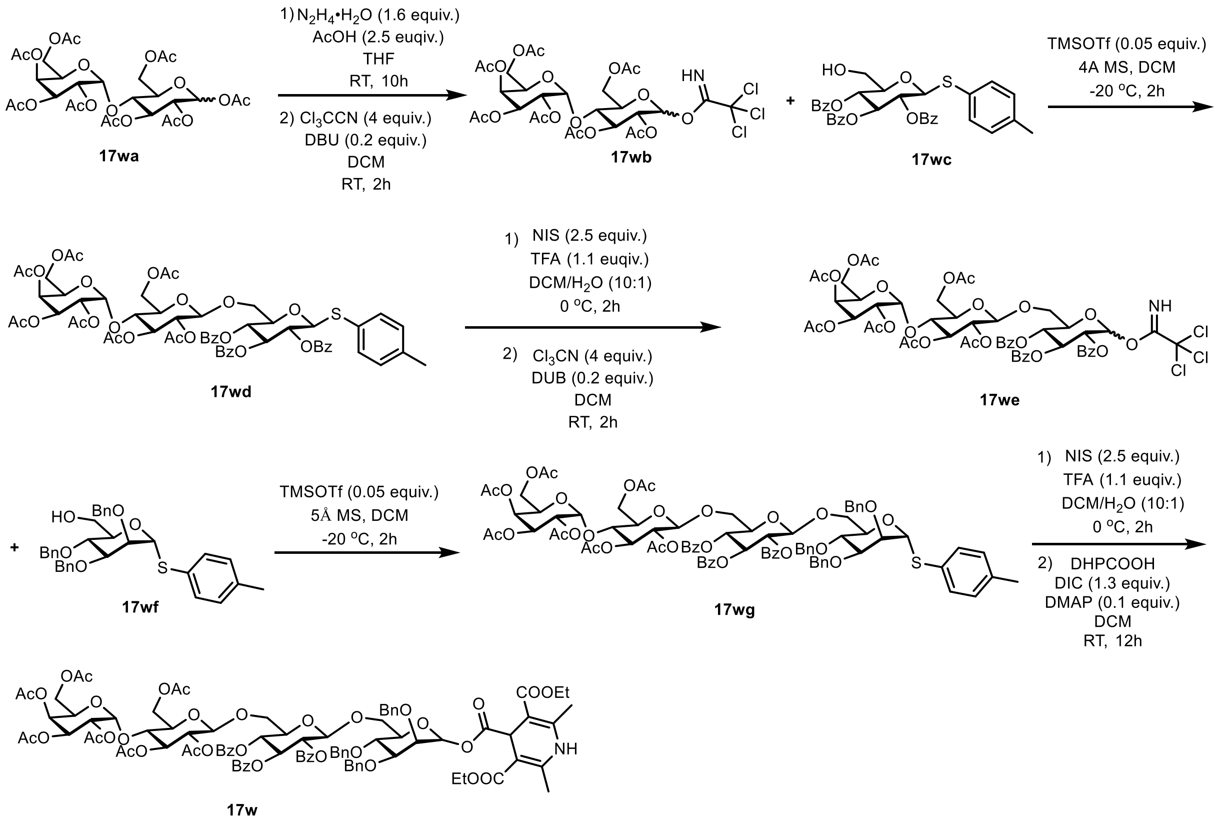




3,5-Diethyl 4-((2*R*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17v). $N_2H_4·H_2O$ (1.60 g, 32.0 mmol, 1.60 equiv) and AcOH (3.00 g, 50.0 mmol, 2.50 equiv) were added to a solution of acetylated lactose **17va** (13.5 g, 20.0 mmol, 1.00 equiv) in THF (80.0 mL). After stirring at rt for 10 h, the mixture was concentrated, poured into ice-water, and extracted with EtOAc (3×). The combined organic layer were dried over Na_2SO_4, filtered, concentrated, purified by short column on SiO_2 (Petroleum ether: EtOAc, 1:2) to give the acetylated lactosyl hemiacetal (7.80 g, 62%). The resulted hemiacetal (3.82 g, 6.00 mmol, 1.00 equiv) was treated with trichloroacetonitrile (3.46 g, 24.0 mmol, 4.00 equiv) in anhydrous DCM (15.0 mL) in the presence of DBU (182 mg, 1.20 mmol, 0.200 equiv). After stirring at rt for 2 h, the reaction mixture was concentrated and purified by short column on SiO_2 (Petroleum ether: EtOAc = 1:1) to afford trichloroacetimidate glycosyl donor **17vb** as a white foam. Freshly activated 4Å MS, the above trichloroacetimidate glycosyl donor **17vb**, ((*2R,3R,4S,5S,6R*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio) tetrahydro-2*H*-pyran-2-yl) methanol[13] **17vc** (2.78 g, 5.00 mmol, 1.00 equiv) and anhydrous DCM (30.0 mL) were successively added into a flame dried glassware. The mixture was cooled to -20 °C and TMSOTf (111 mg, 0.500 mmol, 0.100 equiv) was added. After stirring at this temperature for 2 h, the resulting mixture was filtered through a pad of silica, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 1.5:1) to afford **17vd** (3.20 g, 54%) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 17H), 7.16 – 7.13 (m, 2H), 5.47 (d, *J* = 1.8 Hz, 1H), 5.34 (dd, *J* = 3.4, 1.2 Hz, 1H), 5.14 – 5.08 (m, 2H), 4.98 – 4.89 (m, 3H), 4.72 – 4.69 (m, 1H), 4.59 – 4.56 (m, 4H), 4.47 – 4.42 (m, 3H), 4.25 – 4.21 (m, 1H), 4.15 – 3.98 (m, 5H), 3.87 – 3.73 (m, 5H), 3.43 – 3.39 (m, 1H), 2.35 (s, 3H), 2.15 (s, 3H), 2.05 – 2.03 (m, 11H), 1.97 – 1.93 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5 (2), 170.3, 170.2, 169.9, 169.7, 169.2, 138.4, 138.1, 137.9 (2), 132.0, 130.8, 130.1, 128.6 (2), 128.5 (2), 128.1, 128.0, 127.9 (4) 101.3, 100.6, 86.4, 80.1, 76.5, 76.1, 75.2, 74.8, 73.3, 73.1, 72.5, 72.0, 71.9, 71.8, 71.1, 70.7, 69.2, 68.4, 66.7, 62.1, 60.9, 21.2, 21.0, 20.9, 20.8, 20.7 (2), 20.6; **HRMS** (ESI) *m/z* calcd for $C_{60}H_{70}NaO_{22}S$ $[M + Na]^+$ 1197.3972, found 1197.3982.

NIS (956 mg, 4.25 mmol, 2.50 equiv) and TFA (213 mg, 1.87 mmol, 1.10 equiv) were added to a solution of

17vd (2.00 g, 1.70 mmol, 1.00 equiv) in a mixture of DCM/H_2O (22.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to stir at rt for 2 h and quenched with Et_3N. The mixture was washed with 20% (w/w) aqueous $Na_2S_2O_3$ (20.0 mL) and saturated aqueous $NaHCO_3$ (20.0 mL). The organic layer was separated, and the aqueous layer was reextracted with DCM (2 × 20.0 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated, purified by short column on SiO_2 (Petroleum ether: EtOAc = 1:1) to give the hemiacetal (1.60 g, 88%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1**(445 mg, 1.50 mmol, 1.00 equiv), DIC (227 mg, 1.80 mmol, 1.20 equiv) and DMAP (36.6 mg, 0.300 mmol, 0.200 equiv) were added to a solution of the above hemiacetal (1.60 g, 1.50 mmol, 1.00 equiv) in DCM (15.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Hexane: Toluene: THF = 3:1:1) to afford **17v** (850 mg, α and β mixture, 42% yield) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1.35H), 7.35 – 7.27 (m, 10H), 7.26 – 7.25 (m, 1H), 7.23 – 7.20 (m, 2.65H), 5.55 (s, 0.65H), 5.35 – 5.33 (m, 1H), 5.24 (d, J = 1.8 Hz, 0.35H), 5.18 – 5.05 (m, 2H), 4.98 – 4.87 (m, 3.65H), 4.85 – 4.80 (m, 1H), 4.72 – 4.69 (m, 1.35H), 4.60 – 4.40 (m, 6H), 4.36 – 4.33 (m, 0.65H), 4.26 – 4.04 (m, 6H), 4.03 – 3.94 (m, 2H), 3.91 – 3.68 (m, 5.35H), 3.59 – 3.48 (m, 2.35H), 3.45 – 3.41 (m, 0.65H), 2.35 – 2.33 (m, 4H), 2.14 (s, 3.35H), 2.11 (s, 2H), 2.07 – 2.03 (m, 11H), 1.99 – 1.95 (m, 6.65H), 1.42 (s, 0.65H), 1.33 – 1.21 (m, 5.35H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 170.9, 170.7, 170.5, 170.4 (2), 170.2, 170.1 (3), 170.0, 169.8, 169.1, 167.2, 167.1, 147.1, 146.3, 138.6, 138.4 (2), 138.3, 137.9, 137.8, 128.5 (2), 128.4, 128.3 (2), 128.0, 127.9 (3), 127.8, 127.7 (4), 101.2, 101.1, 100.9, 100.7, 97.9, 97.2, 93.3, 92.6, 81.7, 79.8, 77.8, 76.0, 75.6, 75.2 (2), 75.0, 74.8, 74.4, 73.8, 73.5, 73.4, 72.9, 72.8, 72.7, 72.4, 72.0, 71.9, 71.3 (2), 71.0 (2), 70.9, 70.8, 70.7, 70.4, 69.2, 69.1, 67.4, 66.7 (2), 61.8, 61.7, 60.8, 60.2, 60.1, 39.5, 30.4, 21.0, 21.0 (2), 20.9, 20.8, 20.7 (2), 20.6 (3), 20.5, 19.5, 18.8, 14.5, 14.4; **HRMS** (ESI) *m/z* calcd for $C_{67}H_{81}NNaO_{28}$ $[M + Na]^+$ 1370.4837; found 1370.4841.



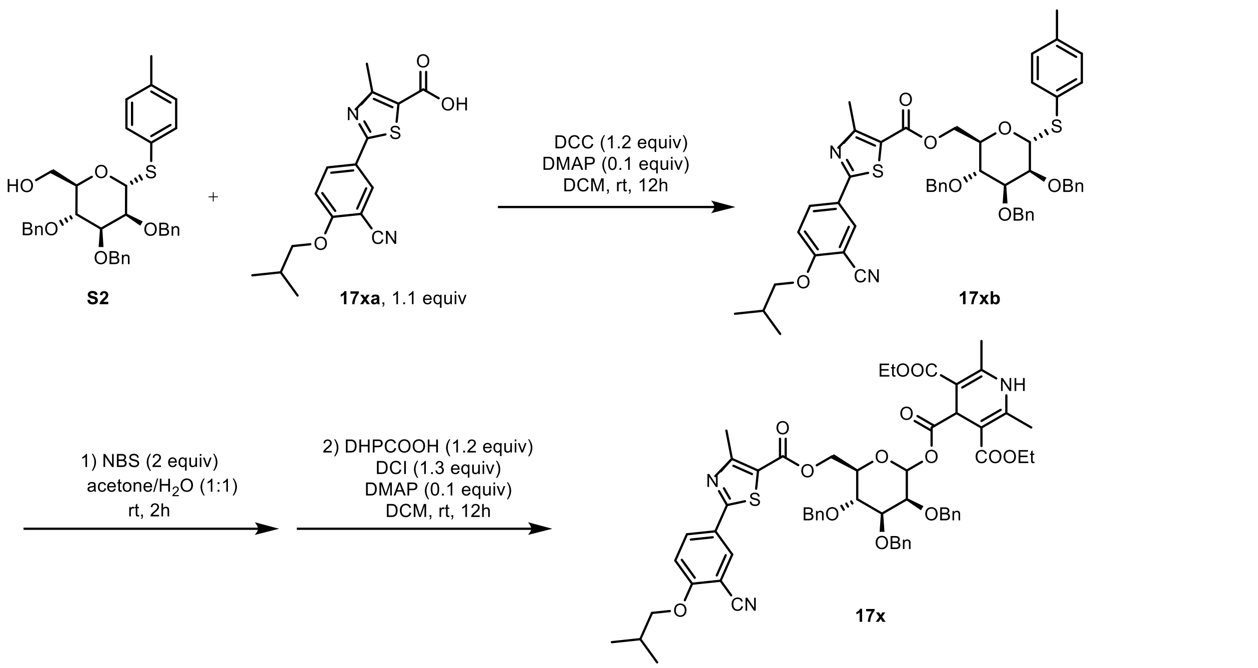
3,5-Diethyl 4-((*3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((((*2R,3R,5R,6R*)-3,4,5-tris(benzoyloxy)-6-((((*2R,3R,4S,5R,6R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((*2R,3R,4S,5S,6R*)-3,4,5-triacetoxy-6-

(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17w). $N_2H_4 \cdot H_2O$ (1.60 g, 32.0 mmol, 1.60 equiv) and AcOH (3.00 g, 50.0 mmol, 2.50 equiv) were added to a solution of acetylated lactose **17wa** (13.5 g, 20.0 mmol, 1.00 equiv) in THF (80.0 mL). The reaction was allowed to stir at rt for 10 h. The mixture was concentrated under reduced pressure and the residue was poured into ice-water and extracted with EtOAc (3x). The combined organic layer were dried over Na_2SO_4, filtered, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc, 1:2) to give the acetylated lactosyl hemiacetal (7.80 g, 62%). The above acetylated lactosyl hemiacetal (5.10 g, 8.00 mmol, 1.00 equiv) was treated with trichloroacetonitrile (4.60 g, 32.0 mmol, 4.00 equiv) in anhydrous DCM (20.0 mL) in the presence of DBU (243 mg, 1.60 mmol, 0.200 equiv). After stirring at rt for 2 h, the reaction mixture was concentrated and purified by short column on SiO_2 (Petroleum ether: EtOAc, 1:1) to afford trichloroacetimidate glycosyl donor **17wb** as a white foam. Freshly activated 4Å MS (5.00 g), the aboved glycosyl donor **17wb** (8.00 mmol, 1.15 equiv), (*2R,3R,4S,5R,6S*)-2-(hydroxymethyl)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate[13] **17wc** (4.20 g, 7.00 mmol, 1.00 equiv) and anhydrous DCM (50.0 mL) were successively added into a flame dried glassware. The mixture was cooled to -20°C and TMSOTf (155 mg, 0.7 mmol, 0.100 equiv) was added. After stirring at this temperature for 2 h, the reaction mixture was filtered through a pad of silica, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 1.5:1) to afford **17wd** (4.50 g, 53%) as a white foam: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 – 7.81 (m, 4H), 7.68 – 7.61 (m, 4H), 7.50 (dtd, *J* = 20.3, 7.6, 7.5, 5.3 Hz, 5H), 7.38 (t, *J* = 7.8, 7.8 Hz, 2H), 7.33 – 7.31 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.97 (t, *J* = 9.4, 9.4 Hz, 1H), 5.49 (d, *J* = 9.9 Hz, 1H), 5.36 – 5.30 (m, 1H), 5.28 – 5.22 (m, 1H), 5.16 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.13 – 5.08 (m, 1H), 4.83 (dd, *J* = 10.2, 8.0 Hz, 1H), 4.77 – 4.72 (m, 3H), 4.38 – 4.34 (m, 1H), 4.26 – 4.21 (m, 2H), 4.04 – 3.99 (m, 3H), 3.88 (d, *J* = 11.1 Hz, 1H), 3.80 – 3.74 (m, 2H), 3.68 – 3.63 (m, 1H), 2.31 (s, 3H), 2.09 (s, 3H), 2.00 – 1.98 (m, 9H), 1.93 – 1.89 (m, 9H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.6, 170.4, 170.3, 170.0, 169.8, 169.7, 169.5, 165.5, 165.0, 164.9, 137.8, 134.3, 131.8, 130.3, 129.7, 129.4, 129.3 (2), 129.2, 129.1, 129.0, 128.9, 100.4, 99.6, 84.3, 74.7, 72.9, 72.1, 70.7, 70.1, 69.3, 61.3, 21.1, 20.9, 20.9, 20.8 (2), 20.7; **HRMS** (ESI) *m/z* calcd for $C_{60}H_{64}NaO_{25}S$ $[M + Na]^+$ 1239.3350, found 1239.3357.

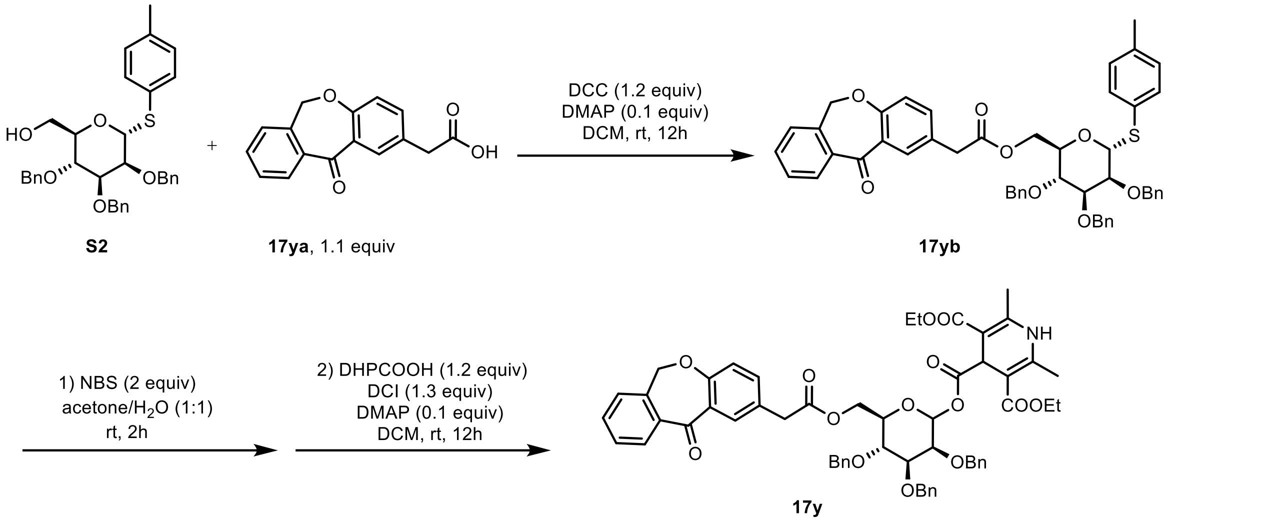
NIS (2.08 g, 9.25 mmol, 2.50 equiv) and TFA (464 mg, 4.07 mmol, 1.10 equiv) were added to a solution of **17wd** (4.50 g, 3.70 mmol, 1.00 equiv) in a mixture of DCM/H_2O (44.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to stir at rt for 2 h and quenched with Et_3N. The mixture was washed with 20% (w/w) aqueous $Na_2S_2O_3$ (30 mL) and saturated aqueous $NaHCO_3$ (30.0 mL). The organic layer was separated, and the aqueous layer was reextracted with DCM (2 × 30.0 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 1:1) to give the hemiacetal (3.46 g, 84%). The resulted hemiacetal (3.33 g, 3.00 mmol, 1.00 equiv) was treated with trichloroacetonitrile (1.30 g, 9.00 mmol, 4.00 equiv) in anhydrous DCM (20.0 mL) in the presence of DBU (91.2 mg, 0.600 mmol, 0.200 equiv). After stirring at rt for 2 h, the reaction mixture was concentrated and purified by short column on SiO_2 (Petroleum ether: EtOAc = 1:1) to afford trichloroacetimidate glycosyl donor **17we** as a white foam. Freshly activated 5Å MS (4.00 g), the above glycosyl donor **17we**, ((*2R,3R,4S,5S,6R*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-2-yl)methanol[13] **17wf** (1.67 g, 3.00 mmol, 1.00 equiv) and anhydrous DCM (30.0 mL) were successively added into a flame dried glassware. The reaction mixture was cooled to -20 °C and TMSOTf (66.6 mg, 0.300 mmol, 0.100 equiv) was added. After stirring at this temperature for 2 h, the resulting mixture was filtered through a pad of silica, concentrated and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 1:1) to afford **17wg** (3.00 g, 61%) as a white foam: **^{1}H NMR** (400 MHz,

CD_3CN) δ 7.91 – 7.89 (m, 2H), 7.82 – 7.79 (m, 1.82H), 7.75 – 7.71 (m, 2.18H), 7.62 – 7.58 (m, 1H), 7.52 – 7.43 (m, 4H), 7.38 – 7.24 (m, 18H), 7.20 – 7.18 (m, 2H), 7.13 – 7.07 (m, 2H), 5.82 – 5.76 (m, 1H), 5.57 (d, *J* = 1.7 Hz, 0.91H), 5.45 – 5.34 (m, 2.09H), 5.30 – 5.29 (m, 1H), 5.12 – 5.08 (m, 1H), 5.03 (dd, *J* = 10.5, 3.6 Hz, 1H), 4.96 – 4.89 (m, 2H), 4.81 (dd, *J* = 9.9, 8.0 Hz, 1H), 4.74 (d, *J* = 2.3 Hz, 0.09H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.61 – 4.52 (m, 4H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.42 – 4.33 (m, 2H), 4.28 (d, *J* = 10.8 Hz, 0.91H), 4.25 – 4.24 (m, 0.09H), 4.12 – 4.02 (m, 7H), 4.01 – 3.96 (m, 2H), 3.86 (dd, *J* = 10.7, 3.5 Hz, 1H), 3.82 – 3.76 (m, 1.92H), 3.72 – 3.61 (m, 3H), 3.42 (dd, *J* = 9.1, 4.3 Hz, 0.09H), 2.34 (s, 2.73H), 2.30 (s, 0.27H), 2.07 (s, 3H), 2.01 – 1.97 (m, 15.27H), 1.90 (s, 2.73H); **^{13}C NMR** (101 MHz, CD_3CN) δ 171.3, 171.1, 170.7(2), 170.5, 170.3, 166.3, 165.9, 165.8, 139.5, 139.4(2), 138.9, 134.6, 134.5, 134.4, 133.0, 131.3, 131.1, 130.9, 130.4, 130.3, 130.1, 130.0, 129.8, 129.6, 129.5(2), 129.3, 129.2, 129.1, 128.8, 128.7, 128.6, 128.5(2), 128.4, 101.5, 101.4, 101.2, 87.0, 80.6, 77.1, 75.4, 75.0, 74.6, 73.7, 73.4, 73.2, 73.1, 72.9, 72.7, 72.1, 72.0, 71.6, 71.4, 70.1, 69.9, 69.2, 68.6, 68.1, 62.9, 62.0, 21.1(3), 21.0, 20.9, 20.8, 20.7; **HRMS** (ESI) *m/z* calcd for $C_{87}H_{92}NaO_{30}S$ $[M + Na]^+$ 1671.5286, found 1671.5292.

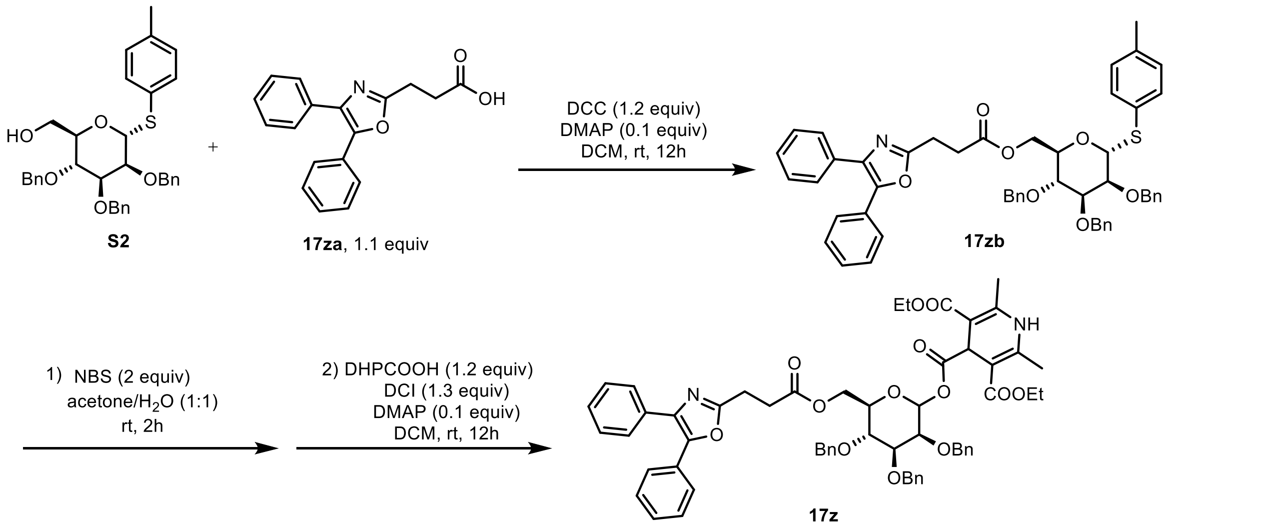
NIS (956 mg, 4.25 mmol, 2.50 equiv) and TFA (213 mg, 1.87 mmol, 1.10 equiv) were added to a solution of **17wg** (2.96 g, 1.70 mmol, 1.00 equiv) in a mixture of DCM/H_2O (33.0 mL, 10:1 v/v) at 0 °C. The reaction was allowed to stir for 2 h and quenched with Et_3N. The mixture was washed with 20% (w/w) aqueous $Na_2S_2O_3$ (20.0 mL) and saturated aqueous $NaHCO_3$ (20.0 mL). The organic layer was separated, and the aqueous layer was reextracted with DCM (2 × 30.0 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 1:1) to afford the hemiacetal (1.80 g, 72%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (326 mg, 1.10 mmol, 1.10 equiv), DIC (164 mg, 1.30 mmol, 1.30 equiv) and DMAP (36.6 mg, 0.300 mmol, 0.200 equiv) were added to a solution of the above hemiacetal (1.50 g, 1.00 mmol, 1.00 equiv) in DCM (15.0 mL) at rt. After stirring for 12 h, the reaction mixture was concentrated, and purified by column chromatography on SiO_2 (Hexane: Toluene: THF = 3:1:1) to afford the corresponding trisaccharide ester **17w** (605mg, α and β mixture, 33% yield) as a white foam and recovered the hemiacetal material (950 mg, 62% yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.90 (m, 0.16H), 7.89 – 7.88 (m, 0.16H), 7.86 – 7.78 (m, 5.16H), 7.56 – 7.44 (m, 5.32H), 7.41 – 7.22 (m, 15.16H), 7.20 – 7.16 (m, 3.52H), 7.13 – 7.08 (m, 0.32H), 6.83 – 6.81 (m, 0.16H), 5.88 (t, *J* = 9.7, 9.7 Hz, 5.88H), 5.68 (t, *J* = 9.8, 9.8 Hz, 0.84H), 5.58 (dd, *J* = 10.0, 8.0 Hz, 0.16H), 5.46 (s, 1H), 5.44 – 5.41 (m, 1.16H), 5.38 (s, 0.16H), 5.35 – 5.31 (m, 1H), 5.26 (s, 0.84H), 5.24 – 5.23 (m, 0.16H), 5.21 – 5.15 (m, 1H), 5.12 – 5.07 (m, 1.68H), 4.95 – 4.76 (m, 4H), 4.68 – 4.61 (m, 1.84H), 4.54 (d, *J* = 2.9 Hz, 0.16H), 4.51 – 4.43 (m, 2H), 4.41 – 4.34 (m, 1.68H), 4.33 – 4.31(m, 1H), 4.30 (d, *J* = 2.1 Hz, 0.84H), 4.28 – 4.25 (m, 1H), 4.24 – 4.23 (m, 0.32H), 4.21 (d, *J* = 3.5 Hz, 0.16H), 4.19 – 4.14 (m, 0.84H), 4.12 – 3.96 (m, 6.64H), 3.93 – 3.88 (m, 1H), 3.86 – 3.82 (m, 1H), 3.78 – 3.70 (m, 1.84H), 3.64 – 3.58 (m, 1.68H), 3.52 – 3.49 (m, 0.16H), 3.42 – 3.37 (m, 1.68H), 2.63 (s, 2.52H), 2.16 (s, 2.52H), 2.12 (s, 33H), 2.07 – 2.01 (m, 12.96H), 1.97 – 1.95 (m, 2.52H), 1.36 – 1.25 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 170.6, 170.5, 170.3, 170.2, 170.1, 169.7, 169.2, 167.3, 167.3, 167.0, 165.1, 147.0, 146.3, 138.6, 138.1, 137.9, 133.9, 133.8, 133.6, 130.0, 129.8, 129.8, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.0, 127.8, 127.7, 127.7, 101.2, 101.1, 100.7, 98.8, 97.7, 94.7, 81.6, 78.6, 76.4, 75.3, 74.3, 74.1, 74.0, 73.9, 73.2, 72.9, 72.7, 71.5, 71.4, 71.1, 70.8, 69.7, 69.2, 66.7, 62.3, 60.9, 60.5, 60.3, 39.9, 29.8, 21.0, 20.9, 20.8, 20.8, 20.7, 19.7, 18.8, 14.7, 14.6. **HRMS** (ESI) *m/z* calcd for $C_{94}H_{103}NNaO_{36}$ $[M + Na]^+$ 1844.6152, found 1844.6158.



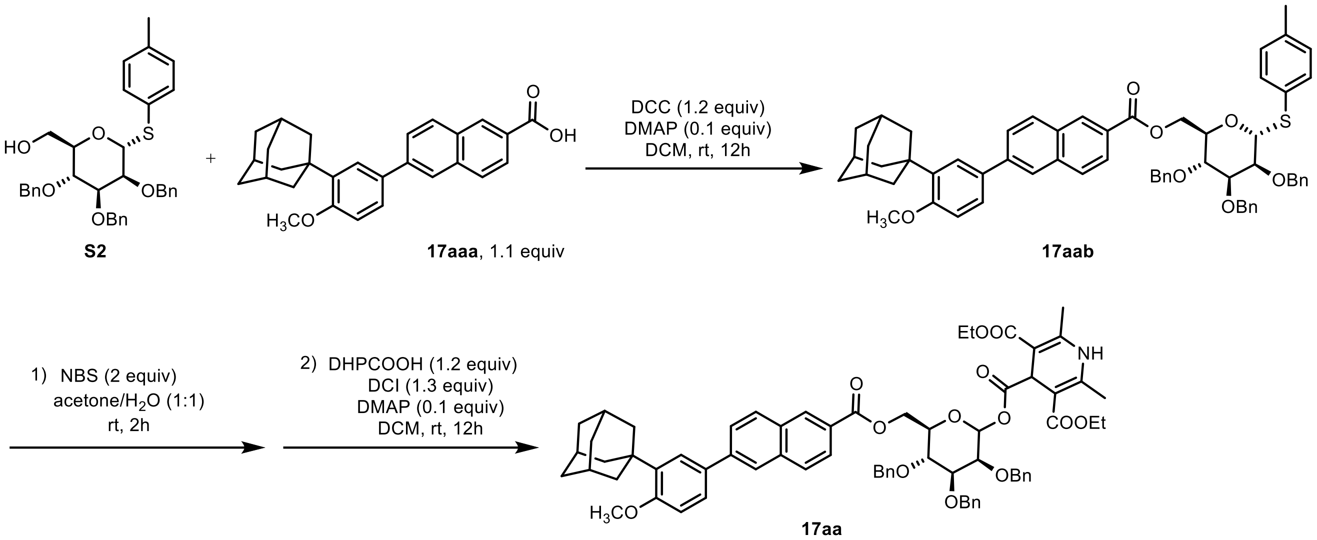
3,5-Diethyl 4-((*2S,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17x). To the solution of ((*2R,3R,4S,5S*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio) tetrahydro-2*H*-pyran-2-yl) methanol[13] **S2** (3.30 g, 6.00 mmol, 1.00 equiv) in anhydrous DCM (20.0 mL), 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylic acid **17xa** (2.10 g, 6.60 mmol, 1.10 equiv), DCC (1.48 g, 7.20 mmol, 1.20 equiv) and DMAP (73.2 mg, 0.60 mmol, 0.100 equiv) were added. After stirring at rt for 12 h, the reaction was completed by TLC. The reaction mixture was filtered, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **17xb** (4.82 g, 92 %) as a white foam. A mixture of compounds **17xb** (4.80 g, 5.50 mmol, 1.00 equiv), NBS (1.96 g, 11.0 mmol, 2.00 equiv) and acetone–H_2O (50.0 mL, 1:1 v/v) was stirred at rt for 2 h. NBS (979 mg, 5.50 mmol, 1.00 equiv) was added and the solution was stirred for another 1 h. The reaction mixture was concentrated, extracted with DCM, dried over anhydrous Na_2SO_4, purified by short column on SiO_2 (Petroleum ether: EtOAc = 2:1) to give the hemiacetal (2.87 g, 70%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (713 mg, 2.40 mmol, 1.20 equiv), DIC (328 mg, 2.60 mmol, 1.30 equiv) and DMAP (24.4 mg, 0.200 mmol, 0.100 equiv) were added to a solution of the above hemiacetal (1.50 g, 2.00 mmol, 1.00 equiv) in anhydrous DCM (20.0 mL) at rt. After stirring for 12 h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Toluene: EtOAc = 3:1) to afford **17x** (1.10 g, 52%, α and β mixture) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.3 Hz, 1H), 7.97 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.33 – 7.29 (m, 6H), 7.28 – 7.25 (m, 5H), 7.24 – 7.18 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.09 (s, 1H), 5.62 (s, 1H), 4.97 (s, 1H), 4.92 (dd, *J* = 11.4, 6.7 Hz, 2H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.62 – 4.59 (m, 2H), 4.53 (d, *J* = 11.9 Hz, 2H), 4.41 (dd, *J* = 11.8, 4.0 Hz, 1H), 4.16 – 3.99 (m, 5H), 3.97 (d, *J* = 2.8 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.67 – 3.61 (m, 2H), 2.67 (s, 3H), 2.26 – 2.17 (m, 7H), 1.23 – 1.15 (m, 6H), 1.10 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 167.5, 167.0, 166.9, 162.5, 161.7, 161.4, 146.2, 146.1, 138.9, 137.9 (2), 132.8, 132.1, 128.5, 128.5, 128.3 (2), 128.2, 127.9 (2), 127.8, 127.7, 127.5, 126.0, 121.9, 115.5, 112.6, 102.9, 98.2, 98.1, 94.0, 81.7, 75.7, 75.1, 74.3, 74.1, 74.0, 73.4, 71.6, 63.7, 60.2, 60.2, 40.8, 28.2, 19.4, 19.3, 19.1, 17.6, 14.5, 14.4; **HRMS** (ESI) *m/z* calcd for $C_{57}H_{61}N_3NaO_{13}S$ $[M + Na]^+$ 1050.3817, found 1050.3835.



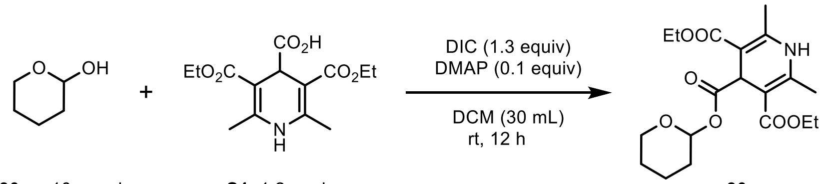
3,5-Diethyl 4-((*3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetoxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17y). To the solution of ((*2R,3R,4S,5S*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio) tetrahydro-2*H*-pyran-2-yl) methanol[13] **S2** (3.83 g, 7.00 mmol, 1.00 equiv) in anhydrous DCM (20.0 mL), 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetic acid **17ya** (2.10 g, 7.70 mmol, 1.10 equiv), DCC (1.80 g, 8.40 mmol, 1.20 equiv) and DMAP (85.4 mg, 0.700 mmol, 0.100 equiv) were added and the reaction was stirred under N_2 at rt. After stirring for 12 h, the reaction was filtered, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **17yb** (4.30 g, 76%) as a white foam. A mixture of compounds **17yb** (4.30 g, 5.30 mmol, 1.00 equiv), NBS (1.89 g, 10.6 mmol, 2.00 equiv) and acetone–H_2O (40.0 mL, 1:1 v/v) was stirred at rt for 2 h. After removal the solvent, the resulting residue was poured onto DCM and extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to give the hemiacetal (2.70 g, 89%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (713 mg, 2.40 mmol, 1.20 equiv), DIC (328 mg, 2.60 mmol, 1.3 equiv) and DMAP (24.4 mg, 0.200 mmol, 0.100 equiv) were added to a solution of the hemiacetal (1.40 g, 2.00 mmol, 1.00 equiv) in DCM (20.0 mL) at rt. After stirring for 12 h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Toluene: EtOAc = 3:1) to afford **17y** (700 mg, 51%,α and β mixture) as a white foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 2.3 Hz, 1H), 7.84 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.50 – 7.43 (m, 3H), 7.39 (dd, J = 8.5, 2.4 Hz, 1H), 7.36 – 7.27 (m, 9H), 7.26 – 7.24 (m, 3H), 7.20 – 7.17 (m, 2H), 6.99 (d, J = 8.4 Hz, 1H), 6.44 (s, 1H), 5.59 (d, J = 0.9 Hz, 1H), 5.13 (s, 2H), 5.03 (s, 1H), 4.90 (d, J = 11.9 Hz, 1H), 4.80 (d, J = 10.9 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.52 – 4.38 (m, 4H), 4.26 (dd, J = 11.8, 5.3 Hz, 1H), 4.21 – 4.08 (m, 4H), 3.94 (dd, J = 2.9, 0.9 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.64 – 3.54 (m, 4H), 2.31 (s, 3H), 2.28 (s, 3H), 1.28 – 1.21 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.1, 172.0, 171.2, 167.1 (2), 160.7, 146.4, 140.4, 138.9, 138.0 (2), 137.0, 135.7, 133.0, 132.5, 129.6, 129.4, 128.5 (2), 128.3, 128.2, 128.0 (2), 127.9, 127.8, 127.7, 127.6, 125.1, 121.3, 98.3, 98.1, 93.9, 81.4, 75.1, 74.3, 74.0, 73.9 (2), 73.7, 71.5, 63.7, 60.3 (2), 40.7, 40.0, 19.4 (2), 14.5 (2); **HRMS** (ESI) m/z calcd for $C_{57}H_{57}NNaO_{14}$ $[M + Na]^+$ 1002.3671, found 1002.3678.



3,5-Diethyl 4-((*2S,3S,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-(((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17z). To the solution of ((*2R,3R,4S,5S*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio) tetrahydro-2*H*-pyran-2-yl) methanol[13] **S2** (3.30 g, 6.00 mmol, 1.00 equiv) in anhydrous DCM (20.0 mL), 3-(4,5-diphenyloxazol-2-yl) propanoic acid **17za** (1.94 g, 6.60 mmol, 1.10 equiv), DCC (1.48 g, 7.20 mmol, 1.20 equiv) and DMAP (73.2 mg, 0.600 mmol, 0.100 equiv) was added at rt. After stirring for12 h, the reaction was filtered and concentrated under reduced pressure. The resulting residue was purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **17zb** (4.21 g, 85% yield) as a light-yellow foam. A mixture of compounds **17zb** (4.20 g, 5.00 mmol, 1.00 equiv), NBS (1.78 g, 10.0 mmol, 2.00 equiv) and acetone/H_2O (50.0 mL, 1:1 v/v) was stirred at rt for 2 h. NBS (890 mg, 5.00 mmol, 1.00 equiv) was added and the solution was stirred for another 1 h. After the removal of the volatile solvents, the resulting residue was poured onto DCM and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to give the hemiacetal (2.00 g, 55%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (980 mg, 3.30 mmol, 1.20 equiv), DIC (454 mg, 3.60 mmol, 1.30 equiv) and DMAP (36.6 mg, 0.275 mmol, 0.100 equiv) were added to a solution of the hemiacetal (2.00 g, 2.75 mmol, 1.00 equiv) in DCM (20.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Toluene: EtOAc = 3:1) to afford **17z** (1.20 g, 44%, α and β mixture) as a light-yellow foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.57 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.38 – 7.28 (m, 15H), 7.26 (s, 2H), 7.25 – 7.20 (m, 3H), 6.81 (s, 1H), 5.60 (d, *J* = 0.9 Hz, 1H), 5.02 (s, 1H), 4.89 (dd, *J* = 11.4, 9.7 Hz, 2H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.56 – 4.42 (m, 4H), 4.32 – 4.28 (m, 1H), 4.20 – 4.08 (m, 4H), 3.95 – 3.93 (m, 1H), 3.88 (t, *J* = 9.1, 9.1 Hz, 1H), 3.61 – 3.56 (m, 2H), 3.16 – 3.12 (m, 2H), 2.89 – 2.85 (m, 2H), 2.24 – 2.23 (m, 6H), 1.28 – 1.21 (m, 7H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 171.6, 167.1, 167.0, 161.9, 146.6, 146.5, 145.6, 138.8, 138.0, 135.0, 132.4, 128.9, 128.7 (2), 128.6, 128.5 (2), 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 126.5, 98.1, 97.8, 93.8, 81.4, 75.1, 74.1, 73.9, 73.7, 73.7, 71.5, 63.4, 60.2, 60.2, 40.5, 31.2, 23.6, 19.2, 19.1, 14.5, 14.4; **HRMS** (ESI) *m/z* calcd for $C_{59}H_{60}N_2NaO_{13}$ $[M + Na]^+$ 1027.3988, found 1027.3990.

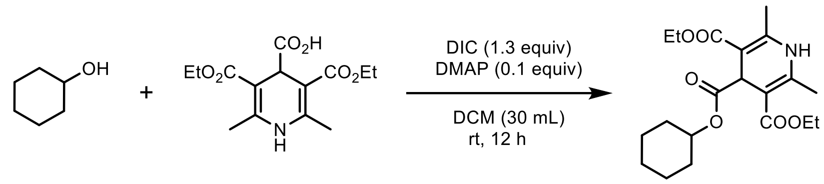


4-((*2S,3S,4S,5R,6R*)-6-(((6-(3-((*3r,5r,7r*)-Adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)methyl)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (17aa). To the solution of ((*2R,3R,4S,5S*)-3,4,5-tris(benzyloxy)-6-(*p*-tolylthio) tetrahydro-2*H*-pyran-2-yl) methanol[13] **S2** (2.74 g, 5.00 mmol, 1.00 equiv) was dissolved in anhydrous DCM (20.0 mL), 6-(3-((*3r,5r,7r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid **17aaa** (1.61 g, 5.50 mmol, 1.10 equiv), DCC (1.24 g, 6.00 mmol, 1.20 equiv) and DMAP (61.0 mg, 0.500 mmol, 0.100 equiv) were added and the reaction at rt. After stirring for 12 h, the reaction mixture was filtered, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **17aab** (3.40 g, 82%) as a white foam. A mixture of compounds **17aab** (3.40 g, 4.00 mmol, 1.00 equiv), NBS (1.41 g, 8.00 mmol, 2.00 equiv) and acetone/H_2O (40.0 mL, 1:1 v/v) was stirred at rt for 2 h. NBS (712 mg, 4.00 mmol, 1.00 equiv) was added and the solution was stirred for another 1 h. After the removal of the volatile solvents, the resulting residue was poured onto DCM and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by short column on SiO_2 (Petroleum ether: EtOAc = 3:1) to give the hemiacetal (2.16 g, 75%). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (1.10 g, 3.60 mmol, 1.20 equiv), DIC (492 mg, 3.90 mmol, 1.30 equiv) and DMAP (73.2 mg, 0.300 mmol, 0.100 equiv) were added to a solution of the hemiacetal (2.16 g, 3.00 mmol, 1.00 equiv) in DCM (20.0 mL) at rt. After stirring for 12h, the reaction mixture was concentrated and purified by column chromatography on SiO_2 (Toluene: EtOAc = 3:1) to afford **17aa** (1.60 g, α and β mixture, 53%) as a yellow foam: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 1.7 Hz, 0.88H), 8.50 (d, *J* = 1.7 Hz, 0.12H), 8.35 (d, *J* = 9.0 Hz, 0.12H), 8.09 (dd, *J* = 8.9, 1.7 Hz, 0.12H), 8.02 – 7.99 (m, 1.76H), 7.82 – 7.74 (m, 2.64H), 7.68 (d, *J* = 8.4 Hz, 0.12H), 7.64 (d, *J* = 2.4 Hz, 0.88H), 7.59 – 7.56 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 0.12H), 7.42 (d, *J* = 2.3 Hz, 0.12H), 7.37 – 7.28 (m, 10.76H), 7.24 – 7.16 (m, 2.24H), 7.03 – 6.99 (m, 1H), 6.24 – 6.23 (m, 1H), 5.71 (d, *J* = 2.5 Hz, 1H), 5.01 – 4.94 (m, 3H), 4.75 (d, *J* = 11.8 Hz, 1H), 4.68 – 4.55 (m, 5H), 4.21 – 4.11 (m, 3H), 4.10 – 3.97 (m, 3H), 3.93 – 3.92 (m, 3H), 3.79 – 3.71 (m, 2H), 2.23 – 2.15 (m, 15H), 1.87 – 1.81 (m, 6H), 1.24 – 1.20 (m, 3H), 1.13 (t, *J* = 7.1, 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 167.0, 166.9, 166.6, 159.0, 146.1, 146.0, 141.4, 139.1, 138.0, 137.9, 136.0, 132.7, 131.2 (2), 130.0, 128.6, 128.5, 128.4 (3), 128.2, 128.0, 127.9, 127.8 (2), 127.5, 126.8, 126.5, 126.1, 125.9, 125.8, 124.8, 112.2, 98.2 (2), 94.0, 81.6, 75.2, 74.4, 74.3, 74.1, 73.6, 71.8, 63.6, 60.3, 60.2, 55.3, 40.9, 40.7, 37.3, 37.2, 29.2, 19.5, 19.3, 14.5, 14.4; **HRMS** (ESI) *m/z* calcd for $C_{69}H_{73}NNaO_{13}$ $[M + Na]^+$ 1146.4974, found 1146.4975.



30aa, 10 mmol **S1**, 1.2 equiv **30a**

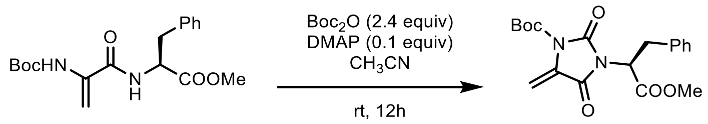
3,5-Diethyl 4-(tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (30a). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (3.50 g, 12.0 mmol, 1.20 equiv), DIC (1.64 g, 13.0 mmol, 1.30 equiv) and DMAP (122 mg, 1.00 mmol, 0.100 equiv) were added to a solution of tetrahydro-2*H*-pyran-2-ol **30aa** (1.02 g, 10.0 mmol, 1.00 equiv) in DCM (30.0 mL) at rt and stirred for 12 h. After solvent removal *in vacuo*, the residue was purified by flash column chromatography on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **30a** (2.00 g, 52%) as a light-yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.48 (s, 1H), 5.94 (s, 1H), 4.92 (s, 1H), 4.23 – 4.14 (m, 4H), 3.79 – 3.72 (m, 1H), 3.63 – 3.58 (m, 1H), 2.27 (s, 6H), 1.78 – 1.59 (m, 5H), 1.55 – 1.51 (m, 1H), 1.30 – 1.26 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 167.4, 146.1, 145.9, 98.3, 98.2, 92.6, 62.3, 60.1, 40.5, 29.1, 25.1, 19.1, 19.1, 18.0, 14.5; **HRMS** (ESI) *m/z* calcd for $C_{19}H_{27}NNaO_7$ $[M + Na]^+$ 404.1680, found 404.1678.



30ba, 10 mmol **S1**, 1.2 equiv **30b**

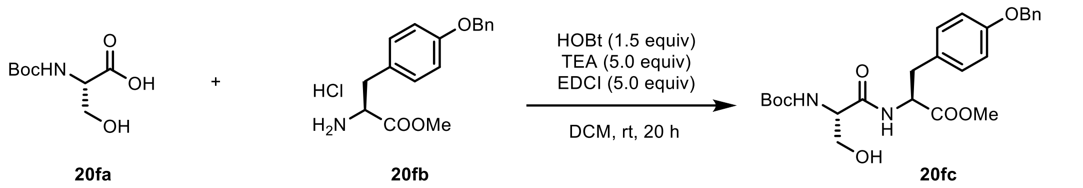
4-Cyclohexyl 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate (30b). According to the general protocol D, 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid[1] **S1** (3.50 g, 12.0 mmol, 1.20 equiv), DIC (1.64 g, 13.0 mmol, 1.300 equiv) and DMAP (122 mg, 1.0 mmol, 0.100 equiv) were added to a solution of cyclohexanol **30ba** (1.00 g, 10.0 mmol, 1.00 equiv) in DCM (30.0 mL) at rt and stirred for 12 h. After solvent removal *in vacuo*, the residue was purified by flash column chromatography on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **30b** (1.40 g, 37%) as a light-yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.77 (s, 1H), 4.79 (s, 1H), 4.70 – 4.64 (m, 1H), 4.19 – 4.11 (m, 4H), 2.23 (s, 6H), 1.73 – 1.61 (m, 4H), 1.47 – 1.34 (m, 3H), 1.33 – 1.22 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 167.5, 145.9, 98.4, 72.8, 60.0, 40.8, 31.4, 25.5, 23.3, 18.9, 14.5. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{29}NNaO_6$ $[M + Na]^+$ 402.1887, found 402.1884.

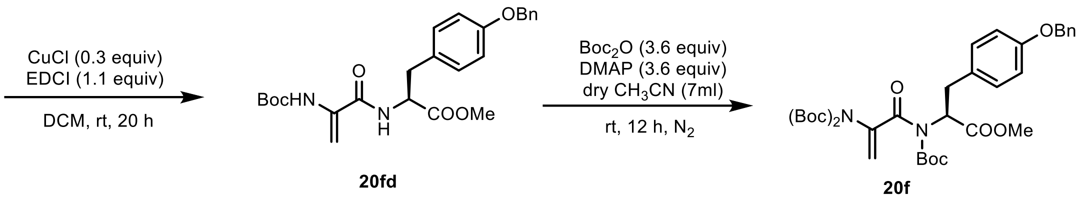
6. Detailed Experimental Procedures for Dehydroalanine Derivatives



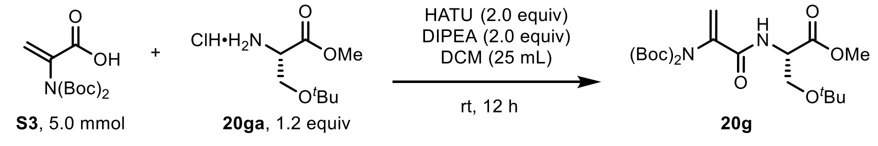
20ea **20e**

***tert*-Butyl (*S*)-3-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-5-methylene-2,4-dioxoimidazolidine-1-carboxylate (20e).** To a solution of methyl (2-((*tert*-butoxycarbonyl)amino)acryloyl)-*L*-phenylalaninate **20ea** (2.06 g, 5.90 mmol, 1.00 equiv) in CH_3CN (50.0 mL), DMAP (72.0 mg, 0.590 mmol, 0.100 equiv) and Boc_2O (1.55 g, 7.08 mmol, 2.40 equiv) were added and the solution was stirred under the air at rt for 12 h. After removal of volatiles *in vacuo*, the residue was diluted with EtOAc (20.0 mL), washed with 10% aqueous solution of citric acid (5.00 mL) and brine (10.0 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated and purified by flash column chromatography on SiO_2 (Petroleum ether: EtOAc = 10: 1) to afford **20e** as colorless oil (1.11 g, 36%): $[\alpha]_D^{25}$ = -91.3 (c = 2.23, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.11 (m, 5H), 5.95 (d, *J* = 1.1 Hz, 1H), 5.77 (d, *J* = 1.1 Hz, 1H), 5.06 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.78 (s, 3H), 3.61 – 3.43 (m, 2H), 1.57 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 160.4, 149.5, 147.7, 136.2, 131.5, 128.8 (2), 127.1, 105.7, 85.6, 54.2, 53.1, 33.9, 28.0; **HRMS** (ESI) *m/z* calcd for $C_{19}H_{22}O_6N_2Na$ $[M + Na]^+$ 397.1370, found 397.1370.

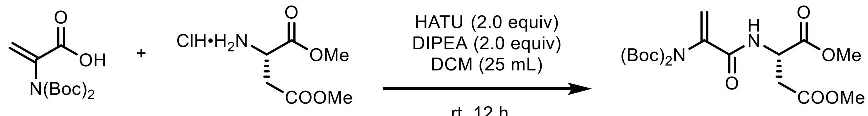




Methyl (*S*)-3-(4-(benzyloxy)phenyl)-2-(2-(bis(tert-butoxycarbonyl)amino)-*N*-(*tert*-butoxycarbonyl)acrylamido)propanoate (20f). *O*-Benzyl-*L*-tyrosine methyl ester hydrochloride **20fb** (3.86 mg, 12.0 mmol) and *N*-Boc-*L*-serine **20fa** (2.46 mg, 12.0 mmol) were dissolved in anhydrous DCM (60.0 mL). The reaction mixture was cooled to 0 °C before addition of HOBt hydrate (2.40 g, 18.0 mmol) and TEA (8.40 mL, 15.0 mmol). The reaction mixture was kept at 0 °C for 15 min before EDCI (2.88 g, 3.75 mmol) was added. The reaction mixture was worm up to rt and stirred for 20 h. An additional DCM (60.0 mL) was added, and the organic layer was washed successively with citric acid (1.6 M, 100 mL), saturated $NaHCO_3$ (100 mL), and saturated NaCl (80.0 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was dissolved in anhydrous DCM (100 mL) under N_2, copper(I) chloride (360 mg, 3.60 mmol) and EDCI (2.52 g, 13.2 mmol) were subsequently added, and the resultant suspension was stirred at rt for 20 h. The reaction mixture was filtered under Celite and washed with saturated NaCl (20 mL). The organic phase was dried over Na_2SO_4, concentrated and purified by short column on SiO_2 to afford **20fd**. To a solution of **20fd** (2.46 g, 5.50 mmol, 1.00 equiv.) and DMAP (2.42 g, 19.8 mmol, 3.60 equiv) in anhydrous CH_3CN (15.0 mL), Boc_2O (4.30 g, 19.8 mmol, 3.60 equiv) were added at rt. After stirring for 12 h, the reaction mixture was concentrated and purified by flash column chromatography on SiO_2 (Petroleum ether: EtOAc = 8: 1) to afford **20f** as a light yellow oil (0.300 g, 8.3%): $[\alpha]_D^{25}$ = -31.3 (c = 0.800, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 7.19 – 7.14 (m, 2H), 6.91 – 6.85 (m, 2H), 5.41 (d, *J* = 1.4 Hz, 1H), 5.25 (dd, *J* = 9.0, 6.2 Hz, 1H), 5.19 (d, *J* = 1.4 Hz, 1H), 5.02 (s, 2H), 3.72 (s, 3H), 3.44 (dd, *J* = 14.3, 6.2 Hz, 1H), 3.14 (dd, *J* = 14.3, 9.0 Hz, 1H), 1.47 (s, 18H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 168.1, 157.6, 151.7, 151.0, 138.2, 137.2, 130.6, 130.4, 130.0, 128.6, 128.0, 127.5 (2), 118.5, 114.9, 84.7, 83.9, 83.4, 70.0, 59.0, 52.3, 35.2, 27.9, 27.8; **HRMS** (ESI) *m/z* calcd for $C_{35}H_{46}O_{10}N_2Na$ $[M + Na]^+$ 677.3045, found 677.3050.

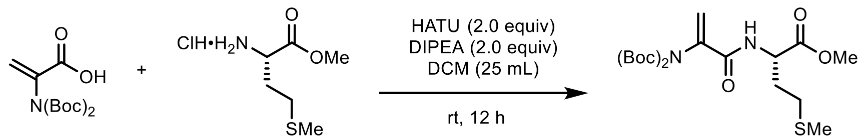


2-(Di(*tert*-butoxycarbonyl)amino)acrylic-*L*-*O*-*tert*-Butyl-serine (20g). According to the general protocol F, 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.400 g, 5.00 mmol, 1.00 equiv) was dissolved in DCM (25.0 mL) and *O*-*tert*-butyl-*L*-serine methyl ester hydrochloride **20ga** (1.27 g, 6.00 mmol, 1.20 equiv), HATU (3.80 g, 10.0 mmol, 2.00 equiv), and DIPEA (1.75 mL, 10.0 mmol, 2.00 equiv) were subsequently added. After stirring at rt for 12 h, the mixture was diluted with DCM (10.0 mL) and washed with brine (20.0 mL). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 3:1) to afford **20g** (358 mg, 16%) as a colorless oil: $[\alpha]_D^{25}$ = +9.6 (c = 1.50, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.73 (d, *J* = 8.2 Hz, 1H), 6.19 (s, 1H), 5.47 (s, 1H), 4.81 – 4.65 (m, 1H), 3.86 – 3.77 (m, 1H), 3.71 (s, 3H), 3.59 – 3.48 (m, 1H), 1.45 (s, 18H), 1.10 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 163.3, 150.5, 138.8, 121.4, 83.6, 73.6, 62.0, 53.3, 52.5, 52.4, 28.3, 27.9, 27.8, 27.4; **HRMS** (ESI) *m/z* calcd for $C_{21}H_{36}O_8N_2Na$ [M + Na]$^+$ 467.2364, found 467.2363.



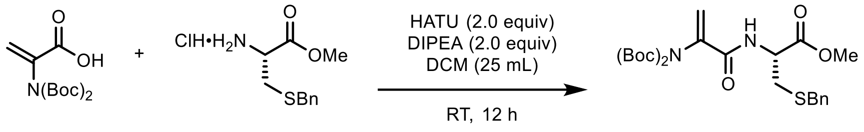
S3, 5.0 mmol **20ia**, 1.2 equiv **20i**

2-(Di(*tert*-butoxycarbonyl)amino)acrylic-*L*-dimethyl-asparate (20i). According to the general protocol F, 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.40 g, 5.00 mmol, 1.00 equiv) was dissolved in DCM (25.0 mL) and methyl *L*-aspartate hydrochloride **20ia** (1.27 g, 6.00 mmol, 1.20 equiv), HATU (3.80 g, 10.0 mmol, 2.00 equiv), and DIPEA (1.75 mL, 10.0 mmol, 2.00 equiv) were subsequently added. After stirring at rt for 12 h, the mixture was diluted with DCM (10.0 mL) and washed with brine (20.0 mL). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 2:1) to afford **20i** (419 mg, 19%) as a colorless oil: $[\alpha]_D^{25}$ = +23.8 (c = 1.30, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 7.9 Hz, 1H), 6.18 – 6.12 (m, 1H), 5.47 (s, 1H), 4.85 (dt, *J* = 8.3, 4.4 Hz, 1H), 3.72 (s, 3H), 3.63 (s, 3H), 3.03 (dd, *J* = 17.4, 4.3 Hz, 1H), 2.83 (dd, *J* = 17.4, 4.5 Hz, 1H), 1.42 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 170.7, 169.0, 163.2, 150.5, 138.6, 121.5, 83.6, 52.9, 52.1, 48.8, 36.0, 28.3, 27.8, 27.7; **HRMS** (ESI) *m/z* calcd for $C_{19}H_{30}O_9N_2Na$ [M + H]$^+$ 453.1844, found 453.1841.



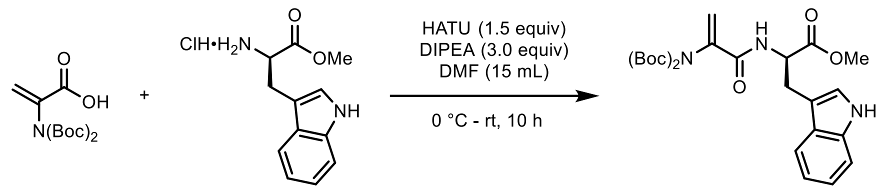
S3, 5.0 mmol **20ja**, 1.2 equiv **20j**

2-(Di(*tert*-butoxycarbonyl)amino)acrylic-*L*-methionine (20j). According to the general protocol F, 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.40 g, 5.00 mmol, 1.00 equiv) was dissolved in DCM (25.0 mL) and *L*-Methionine methyl ester hydrochloride **20ja** (1.2 g, 6.0 mmol, 1.2 equiv), HATU (3.8 g, 10.0 mmol, 2.0 equiv), and DIPEA (1.75 mL, 10.0 mmol, 2.0 equiv) were subsequently added. After stirring at rt for 12 h, the mixture was diluted with DCM (10 mL) and washed with brine (20 mL). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 3:1) **20j** (770 mg, 36% yield) as a colorless oil: $[\alpha]_D^{25}$ = +7.8 (c = 1.46, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 7.8 Hz, 1H), 6.17 (d, *J* = 0.7 Hz, 1H), 5.45 (d, *J* = 0.7 Hz, 1H), 4.75 – 4.69 (m, 1H), 3.71 (s, 3H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.23 – 2.07 (m, 1H), 2.03 (s, 3H), 2.02 – 1.89 (m, 1H), 1.42 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 163.2, 150.5, 138.6, 121.4, 83.7, 82.9, 52.6, 51.8, 31.5, 29.8, 28.3, 27.8, 27.7, 15.4; **HRMS** (ESI) *m/z* calcd for $C_{19}H_{32}O_7N_2NaS$ [M + Na]$^+$ 455.1822, found 455.1816.



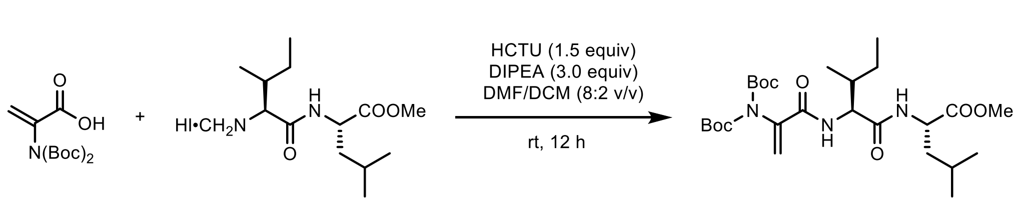
S3, 5.0 mmol **20ka**, 1.2 equiv **20k**

2-(Di(*tert*-butoxycarbonyl)amino)acrylic-*L*-S-benzyl-cysteine (20k). According to the general protocol F, 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.40 g, 5.00 mmol, 1.00 equiv) was dissolved in DCM (25.0 mL) and benzyl-*L*-cysteine methyl ester hydrochloeide **20ka** (1.57g, 6.00 mmol, 1.20 equiv), HATU (3.80 g, 10.0 mmol, 2.00 equiv) and DIPEA (1.75 mL, 10.0 mmol, 2.00 equiv) were subsequently added. After stirring at rt for 12 h, the mixture was diluted with DCM (10.0 mL) and washed with brine (20.0 mL). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 4:1) to afford **20k** (1.35 g, 56%) as a colorless oil: $[\alpha]_D^{25}$ = -0.9 (c = 0.650, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 5H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.20 (s, 1H), 5.50 (s, 1H), 4.92 – 4.77 (m, 1H), 3.72 (s, 3H), 3.68 (s, 2H), 2.92 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.82 (dd, *J* = 13.9, 5.7 Hz, 1H), 1.45 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 169.1, 169.0, 163.3, 150.6, 138.6, 137.5, 129.0, 128.6, 127.3, 121.6, 83.8, 82.9, 52.7, 52.0, 36.7, 36.5, 33.3, 33.1, 28.3, 27.9, 27.7 (2); **HRMS** (ESI) *m/z* calcd for $C_{24}H_{34}O_7N_2NaS$ $[M + Na]^+$ 517.1979, found 527.1978.



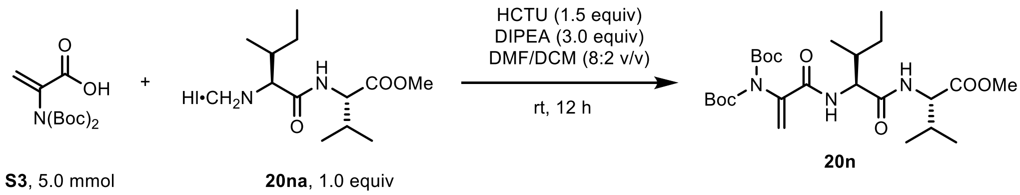
S3, 5.0 mmol **20la**, 1.2 equiv **20l**

Methyl (2-(di(*tert*-butoxycarbonyl)amino)acryloyl)-*D*-tryptophanate (20l). According to the general protocol F, 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.40 g, 5.00 mmol, 1.00 equiv) and HATU (2.85 g, 7.50 mmol, 1.50 equiv) were dissolved in anhydrous DMF (15.0 mL). The reaction was cooled to 0 °C before addition of DIPEA (2.60 mL, 15.0 mmol, 3.00 equiv). After stirring at 0 °C for 0.5 h, *D*-tryptophan methyl ester hydrochloride **20la** (1.53 g, 6.00 mmol, 1.20 equiv) was added and the reaction mixture was warmed up to rt. After stirring for 10 h, the reaction mixture was diluted with H_2O and extracted with EtOAc (3x). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Petroleum ether: EtOAc = 1:1) to afford **20l** (480 mg, 20%) as a white foam. Characterization data matched the literature report[2].

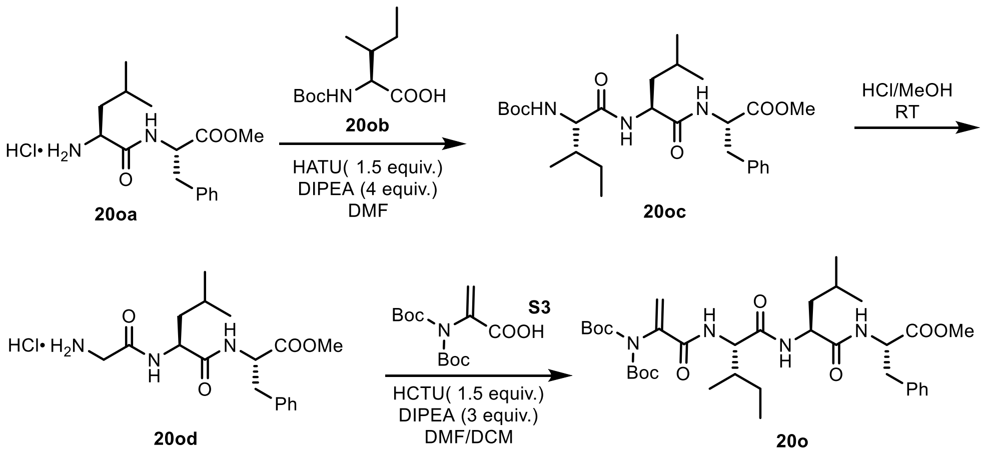


S3, 2.5 mmol **20ma**, 1.0 equiv **20m**

Methyl (2-(bis(*tert*-butoxycarbonyl)amino)acryloyl)-*D*-isoleucylleucinate (20m). According to the general protocol E, HCTU (1.55 g, 3.75 mmol, 1.50 equiv) and DIPEA (1.30 mL, 7.50 mmol, 3.00 equiv) was added to a solution of 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.55 g, 2.50 mmol, 1.00 equiv) in anhydrous DMF/DCM (18.0 mL, 2:8 v/v). The solution was cooled to 0 °C and stirred under N_2 for 0.5h, then **20ma**[15] (0.610 g, 2.50 mmol, 1.00 equiv) was added. After stirring at rt for 12 hours, the reaction mixture was diluted with H_2O (25.0 mL) and EtOAc (50.0 mL), washed with 1.0 M HCl solution (2 × 30 mL), sat. aq. $NaHCO_3$ solution (2 × 30.0 mL) and brine (2 × 30.0 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography on SiO_2 (Petroleum ether: EtOAc = 1.5:1) to afford **20m** (138 mg, 17%) as a white solid: $[\alpha]_D^{25}$ = -18.2 (c = 0.71, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72 (dd, *J* = 12.8, 8.8 Hz, 2H), 6.26 (s, 1H), 5.46 (s, 1H), 4.50 – 4.43 (m, 2H), 3.70 (s, 3H), 2.18 – 2.09 (m, 1H), 1.85 – 1.77 (m, 1H), 1.41 (s, 18H), 1.30 – 1.21 (m, 1H), 1.15 – 1.05 (m, 1H), 0.90 – 0.83 (m, 14H). ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 170.9, 170.8, 163.3, 150.7, 138.8, 121.8, 83.8, 67.9, 58.3, 58.0, 57.4, 57.3, 52.4, 52.3 (2), 37.8, 37.4, 31.1 (2), 28.3, 28.2, 27.9, 25.0, 19.1 (2), 18.0, 17.9, 15.5, 15.4, 11.4, 11.3; **HRMS** (ESI) *m/z* calcd for $C_{26}H_{45}N_3NaO_8$ $[M + Na]^+$ 550.3099, found 550.3097.

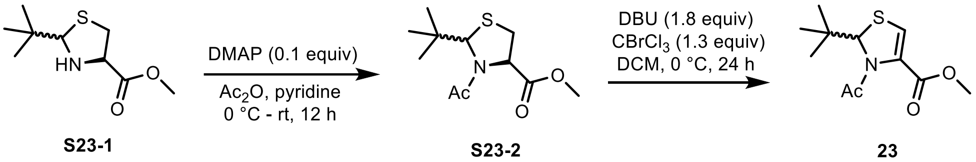


Methyl (2-(bis(*tert*-butoxycarbonyl)amino)acryloyl)-D-isoleucylvalinate (20n). According to the general protocol E, HCTU (3.10 g, 7.50 mmol, 1.50 equiv) and DIPEA (2.60 mL, 15.0 mmol, 3.00 equiv) was added to a solution of 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid[2] **S3** (1.44 g, 5.00 mmol, 1.00 equiv) in anhydrous DMF/DCM (18.0 mL, 2:8 v/v). The solution was cooled to 0 °C and stirred under N_2 for 0.5 h, then **20na**[16] (1.925 g. 5.0 mmol, 1.0 equiv) was added. After stirring at rt for 12 h, the reaction mixture was diluted with H_2O (25.0 mL) and EtOAc (50.0 mL), washed with 1.0 M HCl solution (2 × 30 mL), sat. aq. $NaHCO_3$ solution (2 × 30.0 mL) and brine (2 × 30.0 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography on SiO_2 (Petroleum ether:EtOAc = 1.5:1) to afford **20n** (331 mg, 27%) as a white solid: $[\alpha]_D^{25}$ = -25.7 (c = 0.58, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 8.7 Hz, 1H), 6.22 (s, 1H), 6.19 (d, *J* = 8.2 Hz, 1H), 5.49 (s, 1H), 4.61 – 4.56 (m, 1H), 4.36 (dd, *J* = 8.7, 6.9 Hz, 1H), 3.73 (s, 3H), 1.91 – 1.84 (m, 1H), 1.58 – 1.46 (m, 20H), 1.41 (d, *J* = 2.3 Hz, 1H), 0.95 – 0.89 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 170.6, 163.4, 150.7, 138.9, 121.7, 83.9, 57.9, 52.5, 50.9, 41.5, 37.9, 27.9, 25.0, 24.9, 22.9, 22.0, 15.4, 11.4; **HRMS** (ESI) *m/z* calcd for $C_{25}H_{43}N_3NaO_8$ $[M + Na]^+$ 536.2942, found 536.2943.



Methyl (2-(bis(*tert*-butoxycarbonyl)amino)acryloyl)-*L*-alloisoleucyl-*L*-leucyl-*L*-phenylalaninate (20o). **20oa** was prepared by following the previously reported procedure[17]. To a solution of **20oa** (1.4 g, 8mmol, 1.0 equiv), HATU (4.56 g, 12.0 mmol, 1.50 equiv) in anhydrous DMF (30.0 mL) and DIPEA (3.10 g, 24.0 mmol, 3.00 equiv) was added. After the mixture was stirred at 0 ºC for 30 min. **20ob** (3.50 g, 8.80 mmol, 1.10 equiv) was added. The resulting mixture was warmed to rt and stirred for 12 h, after which time the reaction mixture was diluted with H_2O (50.0 mL) and EtOAc (100.0 mL). The crude material was washed with 1 M HCl solution (2 × 50.0 mL), sat. aq. $NaHCO_3$ solution (2 × 50.0 mL) and brine (2 × 50.0 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica (Petroleum ether: EtOAc = 1.5:1) to afford the corresponding **20oc** (3.30 g, 91%) as a white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.10 – 7.08 (m, 2H), 6.52 (d, J = 7.8 Hz, 0H), 6.35 (d, J = 8.1 Hz, 1H), 5.02 – 5.00 (m, 1H), 4.83 – 4.78 (m, 1H), 4.45 – 4.40 (m, 1H), 3.89 (dd, J = 8.6, 6.8 Hz, 1H), 3.69 (s, 3H), 3.14 – 3.05 (m, 1H), 1.86 – 1.84 (m, 1H), 1.66 – 1.57 (m, 2H), 1.52 – 1.42 (m, 11H), 1.15 – 1.07 (m, 1H), 0.91 – 0.87 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 171.7, 171.4, 135.8, 129.4, 128.8, 127.3, 80.2, 59.5, 53.4, 52.5, 51.7, 41.2, 38.0, 36.9, 28.4, 24.9, 24.7, 23.0, 22.0, 15.7, 11.4. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{43}N_3NaO_6$ $[M + Na]^+$ 528.3044, found 528.3038.

20of was dissolved in sat. HCl soln in MeOH (20 mL) and stirred at rt for 2 h. The mixture was then evaporated and dried under high vacuum to give **20od**. According to the general protocol E, HCTU (3.10 g, 7.50 mmol, 1.50 equiv) and DIPEA (2.60 mL, 15.0 mmol, 3.00 equiv) was added to a solution of 2-(di(*tert*-butoxycarbonyl)amino)acrylic acid **S3** (1.44 g, 5.00 mmol, 1.00 equiv) in anhydrous DCM:DMF (18.0 mL, 2:8). The solution was cooled to 0 °C and stirred under N_2 for 30 min. **20od** (2.10 g, 5.00 mmol, 1.00 equiv) was added to the first solution and the mixture was stirred at rt for 12 h, after which time the reaction mixture was diluted with H_2O (25.0 mL) and EtOAc (50.0 mL). The crude material was washed with 1 M HCl solution (2 × 30.0 mL), sat. aq. $NaHCO_3$ solution (2 × 30.0 mL) and brine (2 × 30.0 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The product was purified by flash column chromatography with an eluent Petroleum ether: EtOAc = 1.5:1 to afford the corresponding **20o** (662 mg, 19%) as a white solid: $[\alpha]_D^{25}$ = -2.2 (c = 0.09, $CHCl_3$); **^{1}H NMR** (400 MHz, CD_3CN) δ 7.32 – 7.16 (m, 5H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.06 (d, *J* = 1.1 Hz, 1H), 5.52 (d, *J* = 1.1 Hz, 1H), 4.60 – 4.54 (m, 1H), 4.32 – 4.22 (m, 2H), 3.61 (s, 3H), 3.08 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.97 (dd, *J* = 13.9, 7.8 Hz, 1H), 1.83 (m, 1H), 1.62 – 1.55 (m, 1H), 1.50 – 1.40 (m, 21H), 1.14 – 1.08 (m, 1H), 0.90 – 0.83 (m, 12H). **^{13}C NMR** (101 MHz, CD_3CN) δ 172.7, 172.6, 171.6, 164.6, 151.7, 140.0, 137.7, 130.2, 129.3, 127.7, 121.0, 83.9, 58.8, 54.6, 52.6, 52.4, 41.5, 38.0, 37.9, 28.0, 25.6, 25.2, 23.2, 21.8, 15.9, 11.4; **HRMS** (ESI) *m/z* calcd for $C_{35}H_{54}N_4NaO_9$ $[M + Na]^+$ 697.3783, found 697.3791.

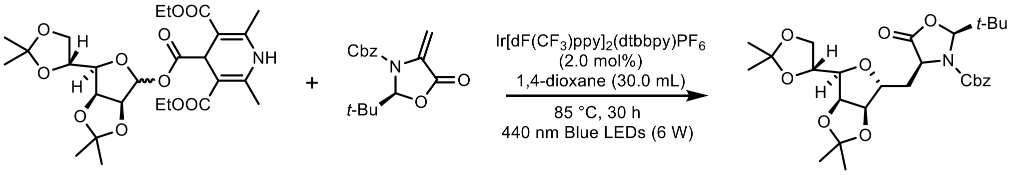


Methyl ®-3-acetyl-2-(*tert*-butyl)-2,3-dihydrothiazole-4-carboxylate (23).S23-1 was prepared by following the previously reported procedure.[18] To a solution of crude **S23-1** (4.58 g, 20.0 mmol, 1.00 equiv) in pyridine (20.0 mL) and Ac_2O (20.0 mL), DMAP (0.244 g, 2.00 mol, 0.10 equiv.) was added. The mixture was stirred at 0 ºC for 10 min. The reaction mixture was stirred at 25 ºC for 12 h before the solvent was removed under reduced pressure. The obtained residue was treated with 1 M HCl and extracted with ethyl acetate (3 × 100.0 mL). The combined organic layers were washed with brine dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica (petroleum ether: EtOAc = 3:1) to give product **S23-2** as a yellow oil (3.60 g, 71% yield over two steps).

To a solution of **S23-2** (3.60 g, 15.6 mmol, 1.00 equiv.) in DCM (50.0 mL) the DBU (4.20 mL, 28.0 mmol, 1.80 equiv.) was added. The mixture was stirred at 0 ºC for 10 min, then $CBrCl_3$ (2.00 mL, 20.3 mmol, 1.30 equiv.) was added, and the reaction mixture was stirred at 0 ºC for 24 h. After the reaction completed, saturated aqueous $NaHCO_3$ (50.0 mL) was added at 0 ºC, and the reaction mixture was warmed to 25 ºC. After the two layers separated, the aqueous phase was extracted with DCM (100.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered off, and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica (EaOAc: Petroleum ether = 1/3) to give product **23** as light yellow oil (0.420 g, 1.70 mmol, 12%): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 5.77 (s, 1H), 3.74 (s, 3H), 2.01 (s, 3H), 0.83 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 160.2, 131.4, 129.5, 78.3, 52.2, 38.7, 24.4, 22.3; **HRMS** (ESI) m/z calcd for $C_{11}H_{17}NNaO_3S^+$ $[M + Na]^+$ 266.0821; found 266.0821.

7. Synthetic Applications and Transformation

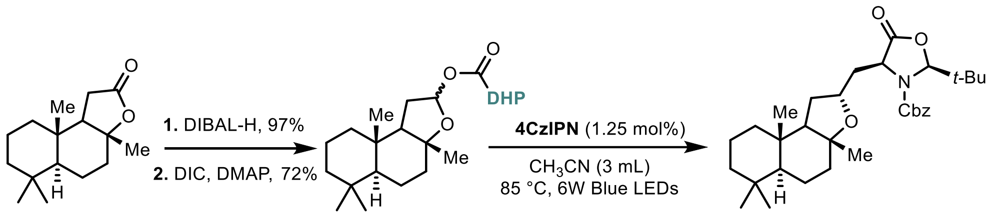
7.1 Gram Scale Reaction



17a, 1.62 g, 3.0 mmol **18**, 1.0 equiv **19a**, 0.78 g

According to the general protocol B, **17a** (1.62 g, 3.00 mmol, 1.50 equiv), **18** (580 mg, 2.00 mmol, 1.00 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (20.0 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (30.0 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs for 30 h and afforded after chromatographic purification on SiO_2 (Petroleum ether:EtOAc = 6:1) **19a** (0.78 g, 77%) as a yellow foam.

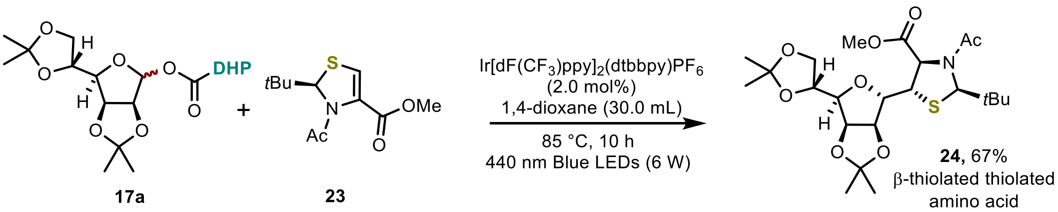
7.2 Derivation of (+)-Sclareolide from Deoxygenative Radical Addition



22a-1, (+)-Sclareolide **22a** **22b**, 61% (dr 4:1)

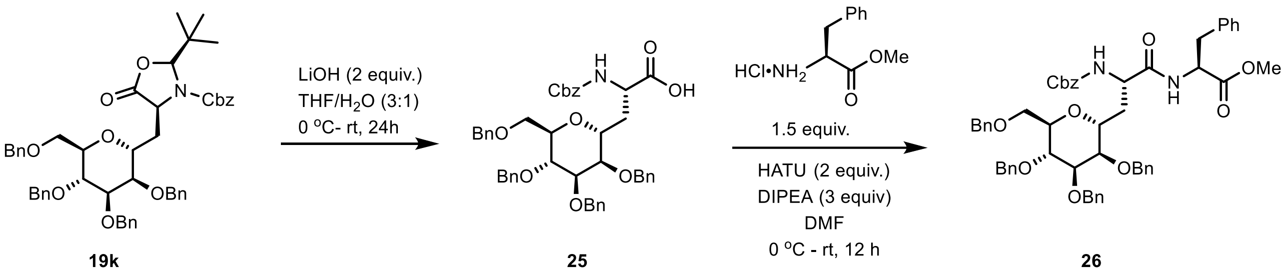
Benzyl (*2S,4S*)-2-(*tert*-butyl)-5-oxo-4-(((*3aR,5aS,9aS,9bR*)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl)methyl)oxazolidine-3-carboxylate (22b). According to the reported method[1], **22a** was prepared from **22a-1** over two steps. According to the general protocol A, **22a** (167 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate **18** (58.0 mg, 0.200 mmol, 1.00 equiv), 4CzIPN (4.0 mg, 0.005 mmol, 0.025 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 5:1) **22b** (62.0 mg, 61%, d.r. = 4:1) as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 5H), 5.57 (s, 1H), 5.22 – 5.15 (m, 2H), 4.55 (dd, J = 8.4, 5.9 Hz, 0H), 4.41 – 4.35 (m, 2H), 2.23 – 2.13 (m, 1H), 2.08 – 2.01 (m, 0H), 1.92 – 1.82 (m, 2H), 1.80 – 1.69 (m, 2H), 1.66 – 1.61 (m, 1H), 1.50 – 1.35 (m, 5H), 1.33 – 1.11 (m, 9H), 1.03 (s, 3H), 0.96 – 0.93 (m, 1H), 0.91 – 0.89 (m, 0H), 0.87 – 0.85 (m, 4H), 0.81 – 0.81 (m, 3H), 0.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 156.1, 135.4, 128.9, 128.8, 128.8, 128.7, 96.6, 80.8, 72.6, 68.4, 59.0, 57.4, 55.1, 42.5, 40.5, 40.0, 39.9, 37.1, 36.1, 33.7, 33.2, 27.5, 25.1, 21.7, 21.2, 20.7, 18.5, 15.1; **HRMS** (ESI) *m/z* calcd for $C_{32}H_{47}NNaO_5$ [M + Na]$^+$ 548.3346, found 548.3348.

7.3 Selectivitive Glycosylation of Thiazoline under Photoredox Conditons

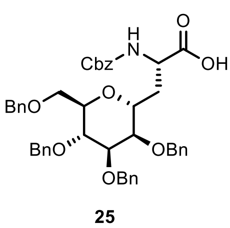


Methyl (2*R*,4*R*)-3-acetyl-2-(*tert*-butyl)-5-((3*aS*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)thiazolidine-4-carboxylate (24). According to the general protocol B, methyl 3-acetyl-2-(*tert*-butyl)-2,3-dihydrothiazole-4-carboxylate **23** (162 mg, 0.300 mmol, 1.50 equiv), methyl 2-phthalimidoacrylate[1] **17a** (46.0 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6 W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO$_2$ (Petroleum ether: EtOAc = 3:1) **24** (65.0 mg, 67%) as a colorless foam. The NMR data supports that **24** exists as a mixture of rotamers. It was recorded at DMSO-*d$_6$* (25 ºC and 80 ºC), respectively. Both solvent and temperature affect the ratio of isomers. **^{1}H NMR** (400 MHz, DMSO-*d$_6$*, 25 ºC) δ 5.41 (s, 0.80H), 5.16 (d, *J* = 2.7 Hz, 1H), 4.99 (d, *J* = 6.9 Hz, 0.20H), 4.79 – 4.73 (m, 2H), 4.25 (dd, *J* = 4.5, 1.8 Hz, 0.80H), 4.21 – 4.03 (m, 3.20H), 3.99 – 3.90 (m, 1H), 3.80 (dd, *J* = 8.5, 5.3 Hz, 1H), 3.72 (s, 2.40H), 3.67 (s, 0.60H), 2.20 (s, 0.60H), 2.11 (s, 2.40H), 1.39 (s, 2.40H), 1.32 – 1.31 (m, 3H), 1.27 – 1.23 (m, 6.60H), 0.97 (s, 1.80H), 0.82 (s, 7.20H).; **^{13}C NMR** (101 MHz, DMSO-*d$_6$*, 25 ºC) δ 171.5, 170.4, 111.8, 108.1, 86.6, 84.1, 83.3, 80.9, 72.8, 71.9, 67.2, 66.1, 52.7, 49.9, 37.8, 26.6 (2), 26.3, 25.2, 24.6, 23.4.; **^{1}H NMR** (500 MHz, DMSO-*d$_6$*, 80 ºC) δ 5.09 (d, *J* = 3.9 Hz, 1H), 4.81 (dd, *J* = 6.0, 3.8 Hz, 1H), 4.76 (dd, *J* = 6.0, 1.8 Hz, 1H), 4.22 – 4.12 (m, 4H), 3.96 (dd, *J* = 8.4, 6.3 Hz, 1H), 3.84 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.74 (s, 3H), 2.15 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H), 0.91 (s, 9H); **HRMS** (ESI) *m/z* calcd for $C_{23}H_{37}NNaO_8S$ [M + Na]$^+$ 510.2132, found 510.2135.

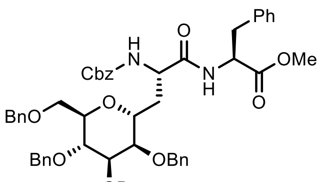
7.4 Deprotection and Peptide Coupling



(*S*)-2-(((Benzyloxy)carbonyl)amino)-3-((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoic acid (25)



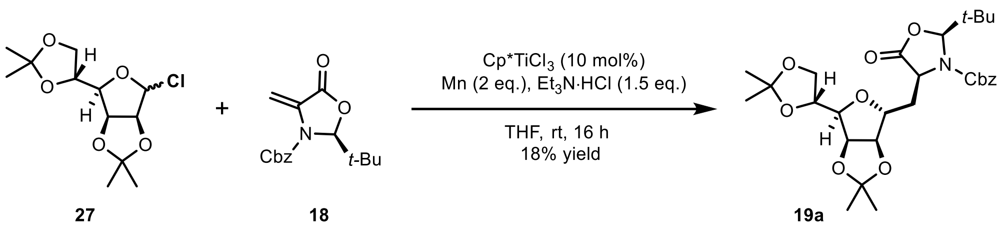
A solution of **19k** (405 mg, 0.500 mmol, 1.00 equiv) in THF/H$_2$O (12.0 mL, 3:1 v/v) was cooled to 0 °C and treated with lithium hydroxide monohydrate (42.0 mg, 1.00 mmol, 2.00 equiv). After stirring at 0 °C for 1h and at rt for another 24 h, the mixture was added H$_2$O (10.0 mL) and concentrated *in vacuum*. The resulted solution was acidified to pH 2-3 by careful addition of 1.0 M hydrochloric acid, and the mixture was extracted with EtOAc (2 × 10.0 mL). The combined organic layers were dried over Na$_2$SO$_4$, concentrated, and purified by flash column chromatography on SiO_2 (Petroleum ether: acetone = 4:1) to afford **25** (258 mg, 70%) as a white foam: $[\alpha]_D^{25}$ = +10.7 (c = 1.20, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 23H), 7.18 – 7.16 (m, 2H), 6.14 (d, *J* = 6.3 Hz, 1H), 5.06 (s, 2H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.57 – 4.43 (m, 7H), 4.36 (t, *J* = 6.1, 6.1 Hz, 1H), 4.23 – 4.19 (m, 1H), 3.91 – 3.87 (m, 1H), 3.77 – 3.68 (m, 3H), 3.59 (dd, *J* = 6.6, 3.3 Hz, 2H), 2.19 – 2.15 (m, 1H), 2.10 – 2.03 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1, 156.3, 138.2, 138.1, 137.9, 136.5, 128.6, 128.5(2), 128.2, 128.1(2), 128.0(2), 127.9(2), 127.8, 76.3, 74.9, 73.7, 73.3, 72.3, 71.9, 69.7, 68.9, 66.9, 52.3, 34.7; **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{45}H_{47}NNaO_9$ 768.3143; found 768.3143.



26

Methyl ((*S*)-2-(((benzyloxy)carbonyl)amino)-3-((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl)-*L*-phenylalaninate (26). (*S*)-2-(((Benzyloxy)carbonyl)amino)-3-((*2R,3R,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoic acid **25** (89.4 mg, 0.120 mmol, 1.00 equiv), HATU (91.2 mg, 0.240 mmol, 2.00 equiv) and DIPEA (46.4 mg, 0.360 mmol, 3.00 equiv) were added anhydrous DMF (3.00 mL) at 0 ºC. After stirring for 0.5 h, *L*-phenylalanine methyl ester hydrochloride (38.9 mg, 0.180 mmol, 1.50 equiv) was added. After stirring at rt for 12 h, the reaction mixture was diluted with H_2O (5.00 mL) and EtOAc (10.0 mL), washed with 1.0 M HCl solution (2 × 5.00 mL), sat. aq. $NaHCO_3$ solution (2 × 5.00 mL) and brine (2 × 5.00 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography on SiO_2 (Toluene: EtOAc = 5:1) to afford **26** (64.0 mg, 59%) as a white solid: $[\alpha]_D^{25}$ = +6.3 (c = 0.62, $CHCl_3$); **^{1}H NMR** (400 MHz, CD_3CN) δ 7.35 – 7.24 (m, 25H), 7.22 – 7.15 (m, 3H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.07 (d, *J* = 7.4 Hz, 1H), 5.04 (s, 2H), 4.66 – 4.43 (m, 9H), 4.21 (q, *J* = 7.4, 7.4, 7.3 Hz, 1H), 4.12 – 4.08 (m, 1H), 3.87 – 3.78 (m, 3H), 3.69 (t, *J* = 6.0, 6.0 Hz, 1H), 3.63 – 3.54 (m, 5H), 3.03 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.85 (dd, *J* = 13.9, 7.7 Hz, 1H), 1.93 – 1.90 (m, 1H), 1.85 – 1.78 (m, 1H); **^{13}C NMR** (101 MHz, CD_3CN) δ 172.6, 172.1, 156.8, 139.6, 139.5, 139.4, 138.0, 137.7, 130.2, 129.4, 129.3, 129.3, 129.2 (2), 128.9, 128.8 (4), 128.7, 128.5 (2), 127.7, 77.2, 75.6, 74.1, 74.0, 73.3, 72.7, 72.1, 70.1, 69.2, 67.1, 54.5, 53.5, 52.7, 38.0, 33.3, 31.5, 30.4; **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{55}H_{58}N_2NaO_{10}$ 929.3984, found 929.3985.

7.5 Comparision with the Reported Method

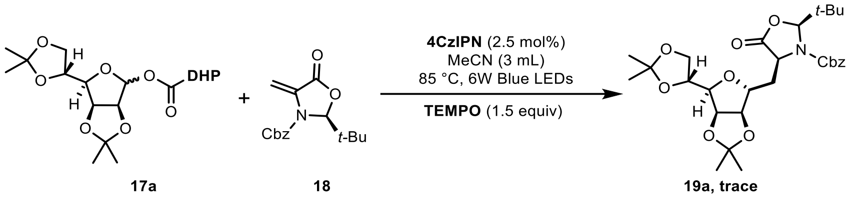


27 18 19a

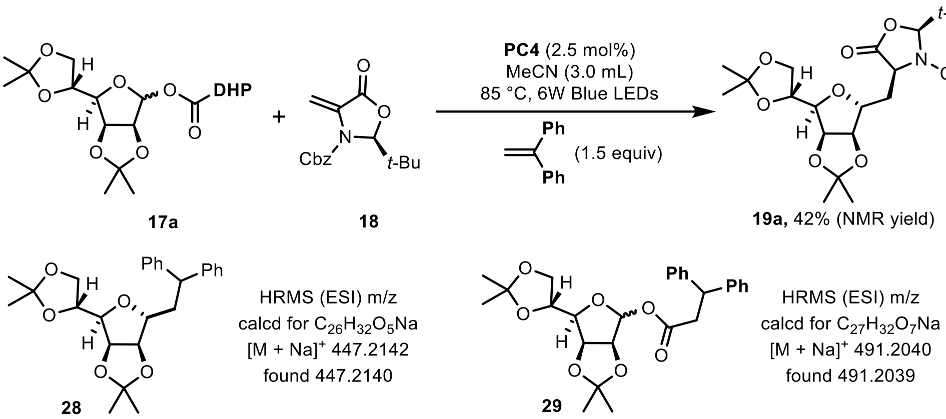
According to the reported protocol,[19] (3*aS*,6*R*,6*aS*)-4-Chloro-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole **27** (55.6 mg, 0.200 mmol, 1.00 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate **18** (83.0 mg, 0.300 mmol, 1.50 equiv), $CpTiCl_3$ (4.4 mg, 0.0200 mmol, 0.010 equiv), Mn (22.0 mg, 0.400 mmol, 2.00 equiv), $Et_3N{\cdot}HCl$(41.3 mg, 0.300 mmol, 1.50 equiv) were added to THF (2.00 mL). The reaction mixture was stirred under N_2 at rt for 16 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 3:1) **19a** (17.0 mg, 18% yield).

8. Mechanistic Studies

8.1 Radical Trapping Experiments

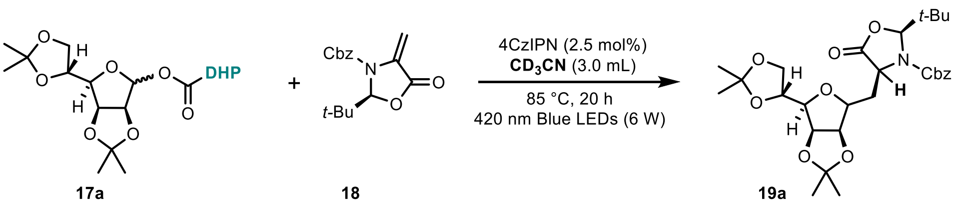


According to the general protocol A, **17a** (162 mg, 0.300 mmol, 1.50 equiv), **18** (58.0 mg, 0.200 mmol, 1.00 equiv), 4CzIPN (4.0 mg, 0.005 mmol, 0.025 equiv) and TEMPO (46.8 mg, 0.200 mmol, 1.00 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 ^{o}C under 6W blue LED irradiation for 20 h. Trace of **19a** was detected.

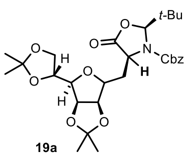


According to the general protocol A, **17a** (162 mg, 0.300 mmol, 1.50 equiv), **18** (58.0 mg, 0.200 mmol, 1.00 equiv), 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) and 1,1-diphenylethylene (54.0 mg, 0.200 mmol, 1.00 equiv) were added to anhydrous CH_3CN (3.00 mL). The reaction mixture was stirred at 85 ^{o}C under 6W blue LED irradiation for 20 h. The yield of **19a** was calculated by using the NMR internal standard. Radical cross-coupling product **30** and **31** were detected by HRMS.

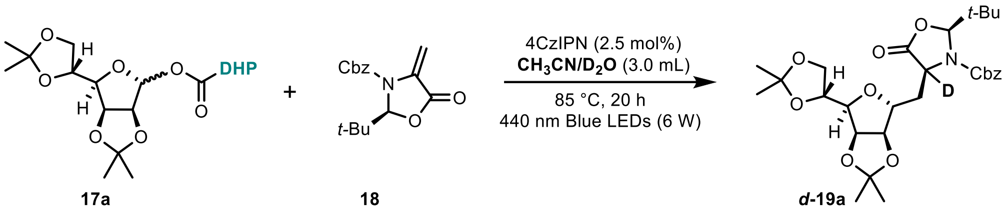
8.2 Deuterium Labeling Studies



Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-4-(((3a*R*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-5-oxooxazolidine-3-carboxylate (19a).

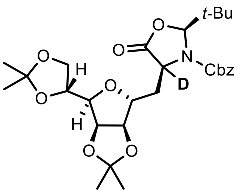

19a

According to the general procedure A, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] (162 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[2] (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.025 equiv) were added to anhydrous CD_3CN (3.00 mL). The reaction mixture was stirred at 85 ^{o}C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) to afford product **19a** (70.7 mg, 67% yield) as a colorless oil.



17a 18 d-19a

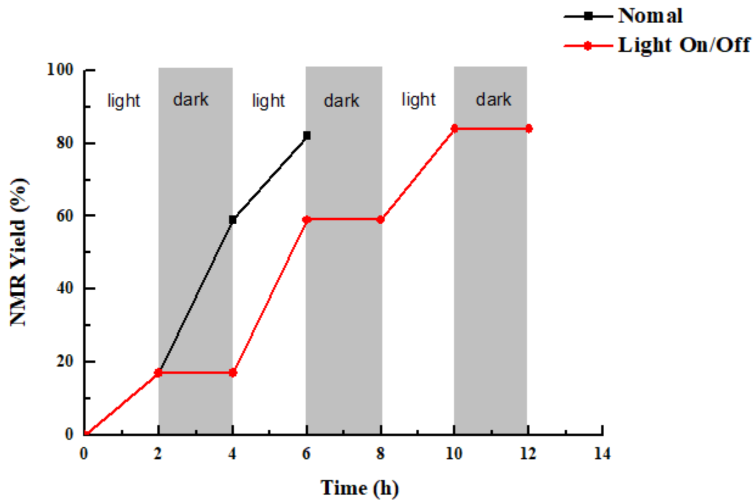
Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-4-(((3*aR*,4*S*,6*R*,6*aS*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)-5-oxooxazolidine-3-carboxylate-4-d (*d*-19a).



d-19a

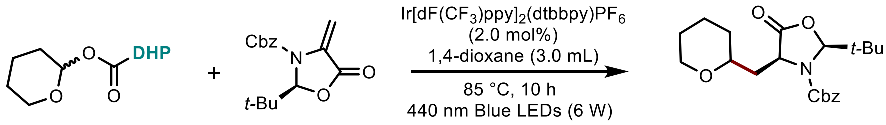
According to the general procedure A, 4-((3*aS*,4*R*,6*R*,6*aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl) 3,5-diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate[1] **17a** (162 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[2] **18** (58.0 mg, 0.200 mmol, 1.00 equiv) and 4CzIPN (4.0 mg, 0.005 mmol, 0.0250 equiv) were added to anhydrous CH_3CN:D_2O (3.0 mL, 2:1 v/v). The reaction mixture was stirred at 85 °C under 6W blue LED irradiation for 20 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 6:1) to afford ***d*-19a** (87.0 mg, 82%) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 5.54 (s, 1H), 5.26 – 5.14 (m, 2H), 4.77 (dd, *J* = 6.0, 3.8 Hz, 1H), 4.56 (dd, *J* = 9.3, 5.8 Hz, 2H), 4.45 – 4.35 (m, 1H), 4.14 – 4.01 (m, 2H), 3.83 (dd, *J* = 7.8, 3.7 Hz, 1H), 2.06 – 1.88 (m, 2H), 1.50 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 0.94 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 155.8, 128.8, 128.7, 112.9, 109.3, 96.5, 85.1, 80.7, 80.5, 80.5, 76.9, 76.8, 73.4, 68.4, 67.1, 54.0, 37.2, 33.8, 27.1, 26.2, 25.3, 24.9, 24.8; **HRMS** (ESI) m/z calcd for $C_{28}H_{38}DO_9NNa$ $[M + Na]^+$ 557.2580, found 557.2581.

8.3 Light on-off Experiments



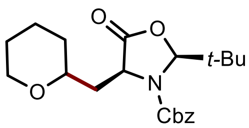
According to the general protocol A, During the light off time, the reaction device is moved into a completely black environment, and during the light on time, the reaction device is in the normal environment. Calculate the yield over each time period by using the NMR internal standard.

8.4 The Role of α-Heteroatoms



30a 18 31a

Benzyl (*2S,4S*)-2-(*tert*-butyl)-5-oxo-4-(((*S*)-tetrahydro-2*H*-pyran-2-yl)methyl)oxazolidine-3-carboxylate (30a).



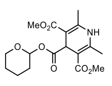
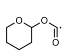
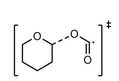
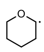
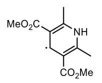
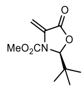
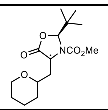
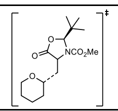
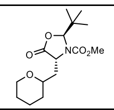
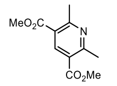
31a

According to the general protocol B, 3,5-diethyl 4-(tetrahydro-2*H*-pyran-2-yl) 2,6-dimethyl-1,4-dihydropyridine-3,4,5-tricarboxylate **30a** (115.0 mg, 0.300 mmol, 1.50 equiv), benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate **18** (58.0 mg, 0.200 mmol, 1.00 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 0.004 mmol, 0.020 equiv) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 85 ºC under 6W Blue LEDs irradiation for 10 h and afforded after chromatographic purification on SiO_2 (Petroleum ether: EtOAc = 8:1) to afford **31a** (36.0 mg, 48%) as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 5H), 5.58 (s, 1H), 5.23 – 5.13 (m, 2H), 4.56 (dd, *J* = 7.2, 5.3 Hz, 1H), 3.85 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.55 – 3.49 (m, 1H), 3.17 (t, *J* = 11.5 Hz, 1H), 2.14 – 2.07 (m, 1H), 1.83 – 1.74 (m, 2H), 1.58 – 1.47 (m, 2H), 1.45 – 1.33 (m, 2H), 1.26 – 1.19 (m, 2H), 0.95 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 156.4, 135.4, 96.6, 73.9, 68.6, 68.4, 54.2, 40.8, 37.1, 31.9, 26.0, 25.1, 23.4; **HRMS** (ESI) *m/z* calcd for $C_{21}H_{29}NNaO_5$ $[M + Na]^+$ 398.1938, found 398.1937.

9. Computational Details

All DFT calculations were performed with Gaussian09[20] or Gaussian16 software packages.[21] Geometry optimizations of all the minima were performed at B97XD/6-31+G(d,p) (SDM DCM). Vibrational frequencies were computed at the same level to evaluate thermal corrections at 298 K. All structures in Figure 4 were characterized by NIMAG=0 or NIMAG=1 for transition states. The single-point energies were computed at B97XD/6-311+G(d,p) (SDM DCM). SMD solvation model was used for DCM to optimize all structures.[22] To correct the Gibbs free energies under pressure of 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_S/c_g)$ (about 1.89 kcal/mol) is added to energies of all species. c_S is the standard molar concentration in solution (1 mol/L), c_g is the standard molar concentration in gas phase (0.0446 mol/L), and *R* is the gas constant. Electronic energies and Gibbs free energy corrections reported in Hartrees.

Summary of Thermodynamic Parameters for Structures

				CO_2							
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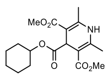
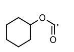
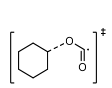
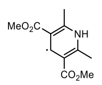
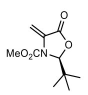
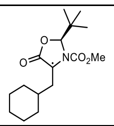
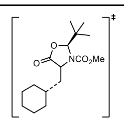
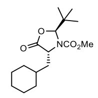
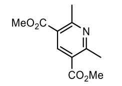
DG corr	0.2888	0.115437	0.109748	-0.008997	0.10451	0.142052	0.206813	0.337034	0.332054	0.351262	0.134907
DH corr	0.365946	0.158788	0.154901	0.015282	0.140278	0.19946	0.265201	0.410377	0.406975	0.423192	0.190427
DG	-1164.077629	-459.552143	-459.529218	-188.58946	-271.002337	-704.443596	-745.548494	-1016.589088	-1016.536969	-1017.218319	-703.880035
DH	-1164.000483	-459.508792	-459.484065	-188.565181	-270.966569	-704.386188	-745.490106	-1016.515745	-1016.462048	-1017.146389	-703.824515

				CO_2							
EE	-1128.469864	-423.77043	-423.731266	-188.580463	-235.209204	-704.585648	-745.755307	-981.03045	-980.969123	-981.672656	-704.014942
DG corr	0.312638	0.138966	0.133686	-0.008997	0.126539	0.142052	0.206813	0.360506	0.35587	0.373426	0.134907
DH corr	0.390007	0.182824	0.178207	0.015282	0.16326	0.19946	0.265201	0.434519	0.430259	0.447271	0.190427
DG	-1128.157226	-423.631464	-423.59758	-188.58946	-235.082665	-704.443596	-745.548494	-980.669944	-980.613253	-981.29923	-703.880035
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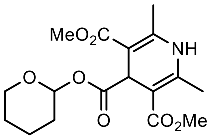
Cartesian Coordinates



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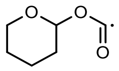

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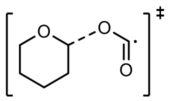

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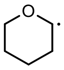

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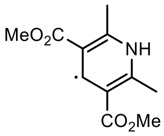

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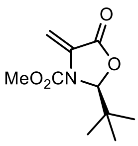

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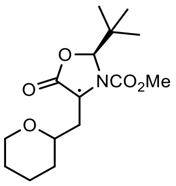

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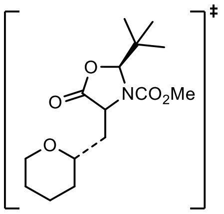

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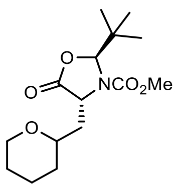

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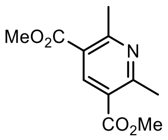

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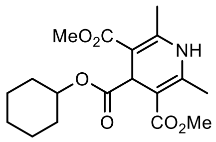

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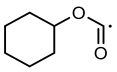

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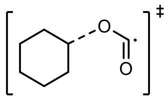

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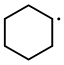

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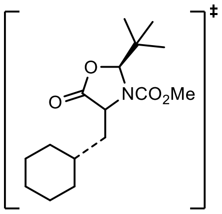

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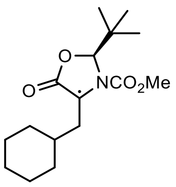

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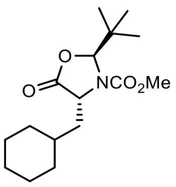

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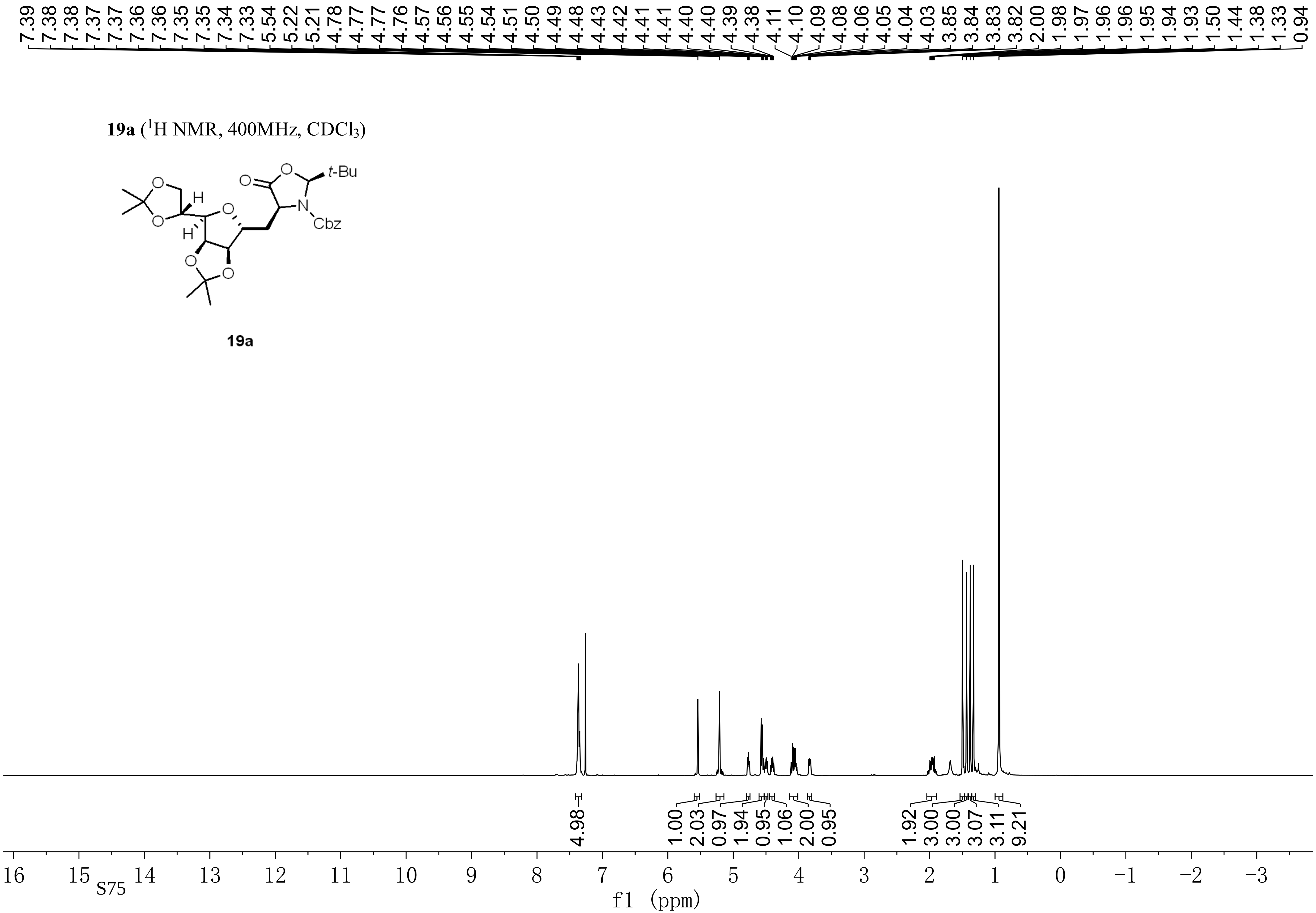
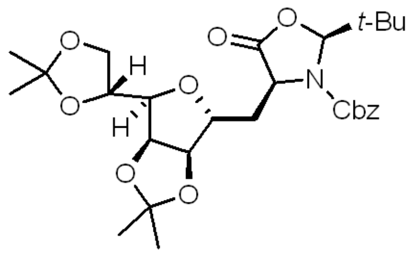
22. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009,** *113* (18), 6378-6396.

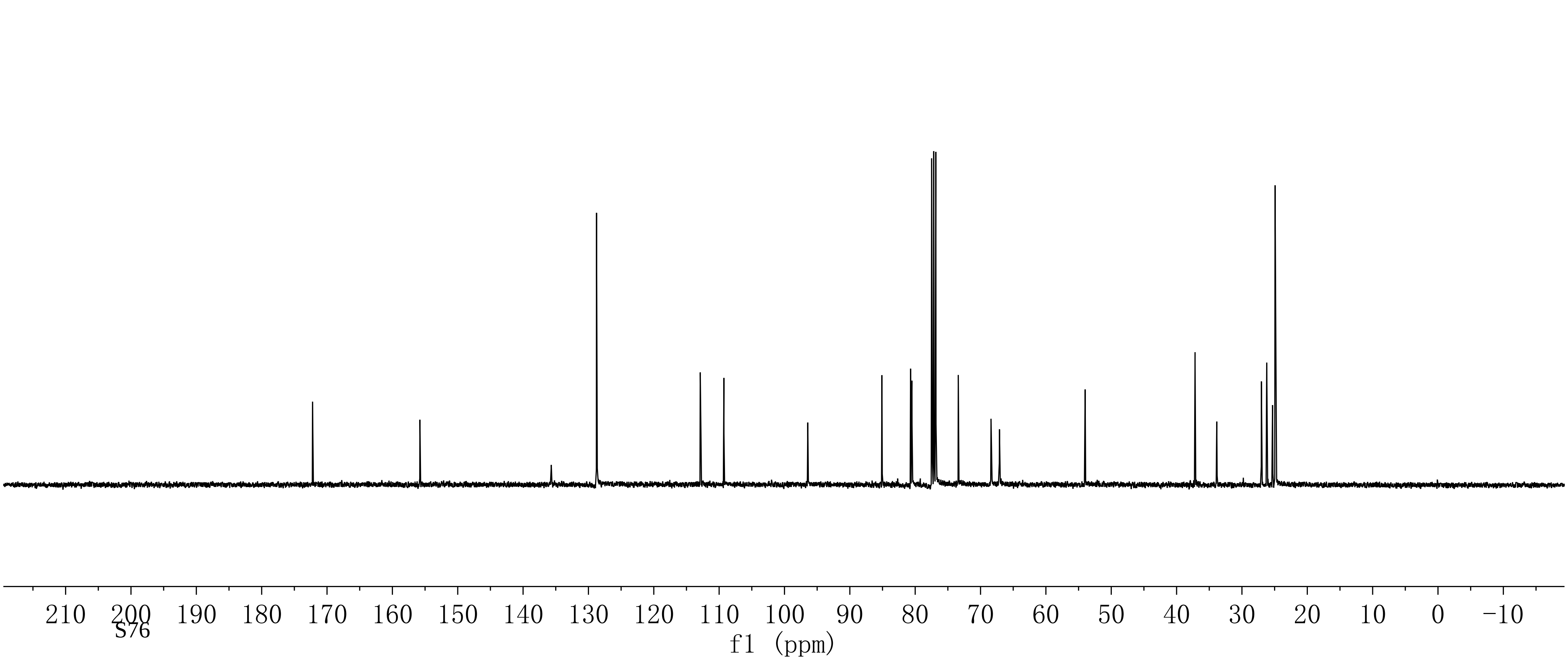
11. Copies of 1D and 2D NMR spectra

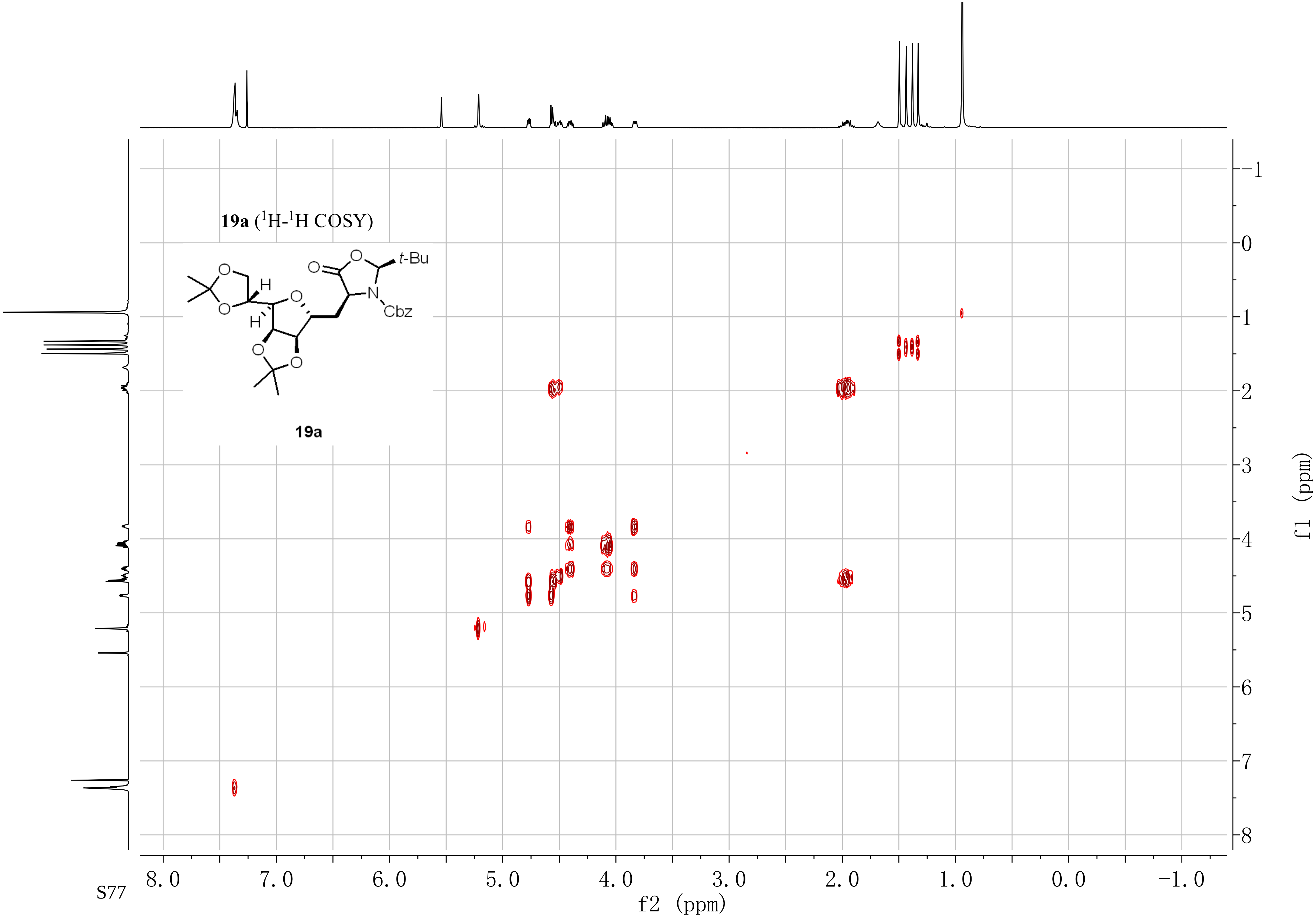

7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.33 5.54 5.22 5.21 4.78 4.77 4.77 4.76 4.57 4.56 4.55 4.54 4.51 4.50 4.49 4.48 4.43 4.42 4.41 4.41 4.40 4.40 4.39 4.38 4.11 4.10 4.09 4.08 4.06 4.05 4.04 4.03 3.85 3.84 3.83 3.82 2.00 1.98 1.97 1.96 1.96 1.95 1.94 1.93 1.50 1.44 1.38 1.33 0.94
19a (^{1}H NMR, 400MHz, $CDCl_3$)
O
t-Bu
N
Cbz
H
19a
4.98
1.00
2.03
0.97
1.94
0.95
1.06
2.00
0.95
1.92
3.00
3.00
3.07
3.11
9.21
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

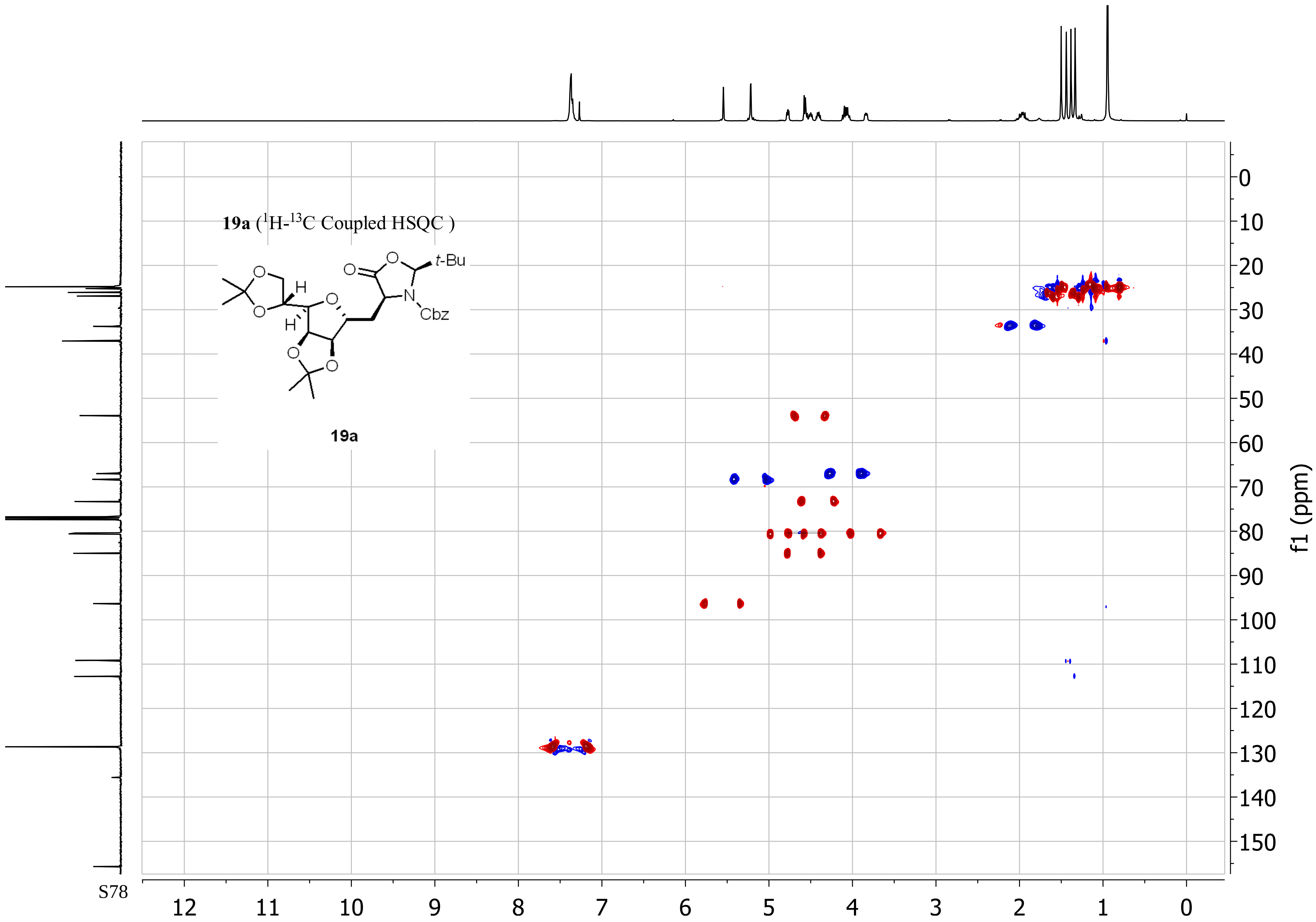
19a (^{13}C NMR, 101MHz, $CDCl_3$)



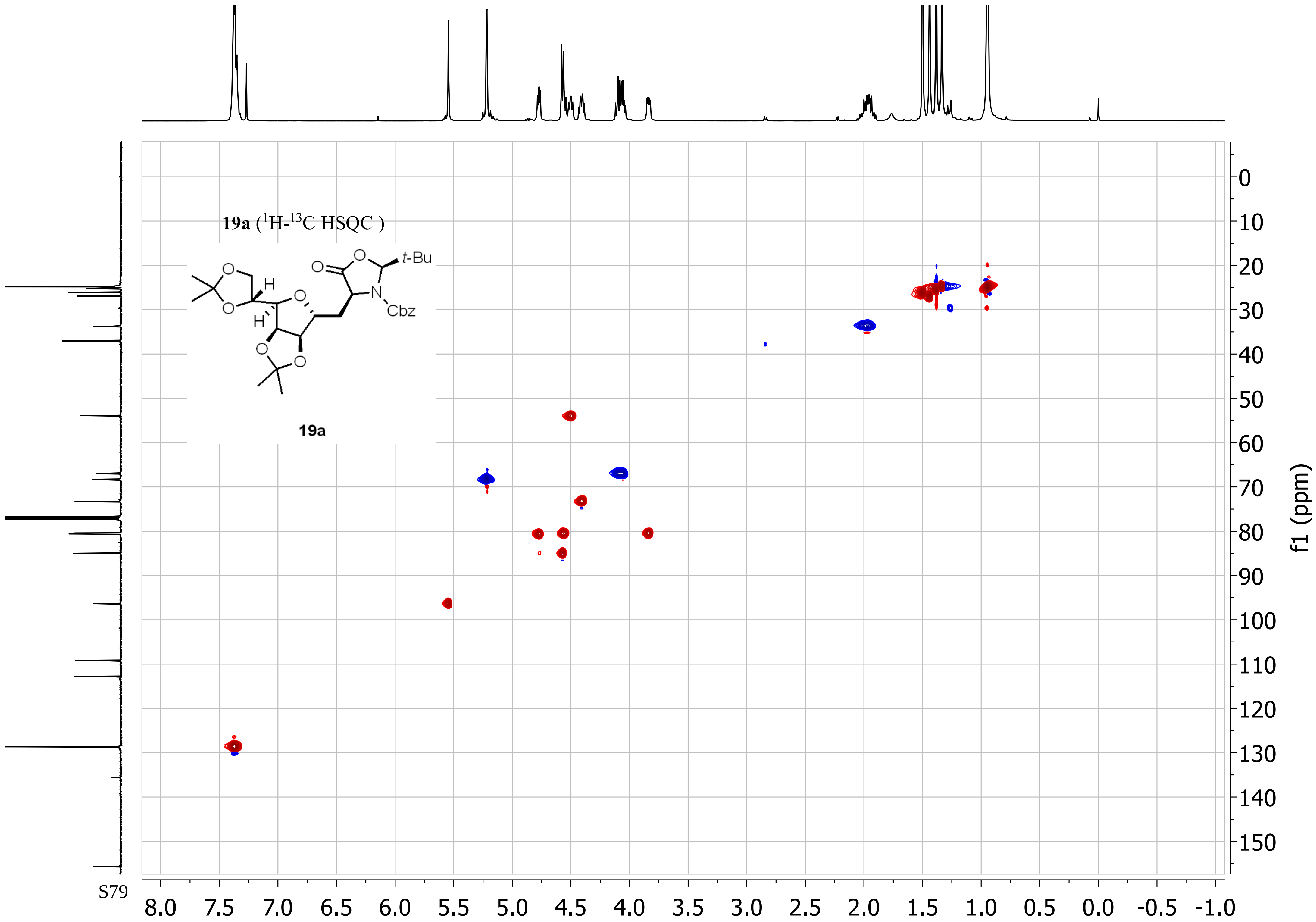
19a




19a (1H-1H COSY)
O
O
t-Bu
N
Cbz
H
H
19a
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f2 (ppm)
f1 (ppm)

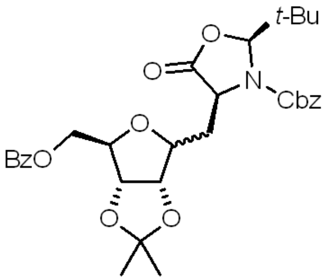


19a (1H-13C Coupled HSQC)
t-Bu
N
Cbz
H
19a
12 11 10 9 8 7 6 5 4 3 2 1 0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

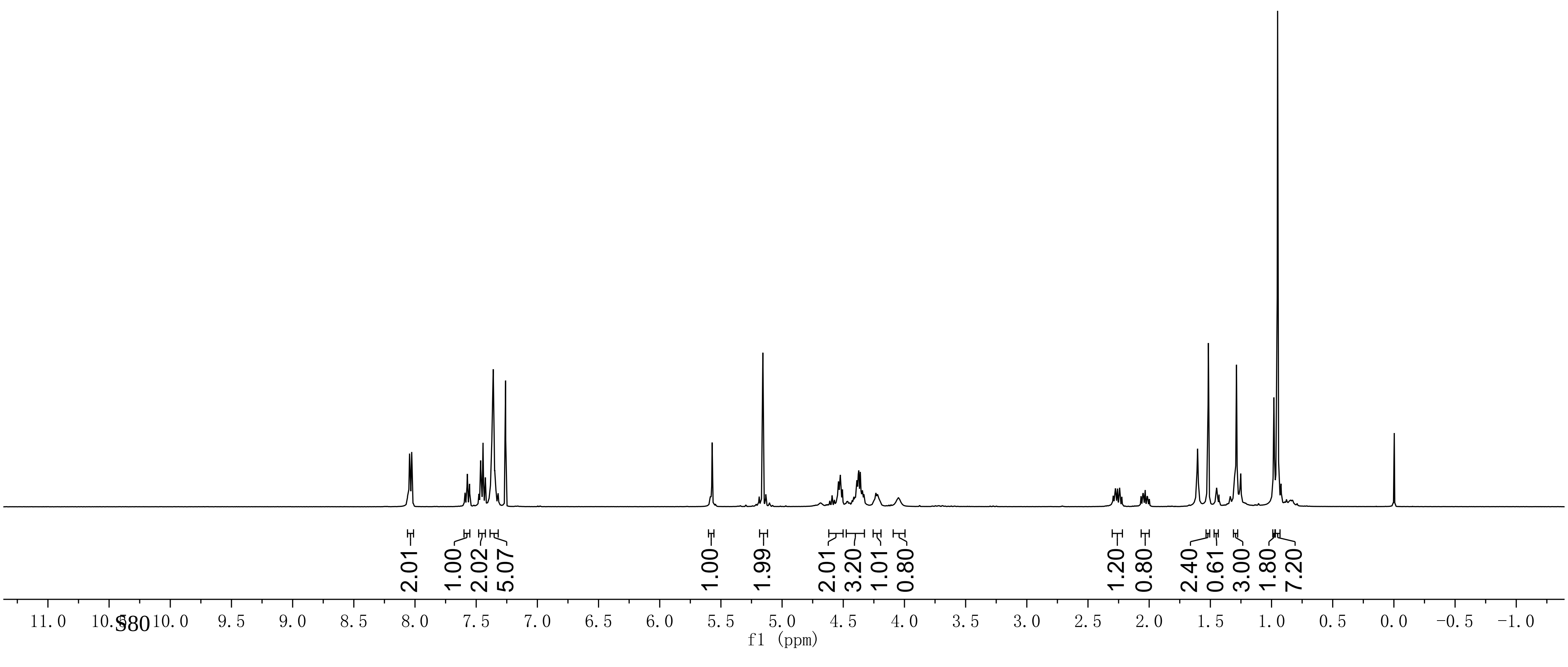


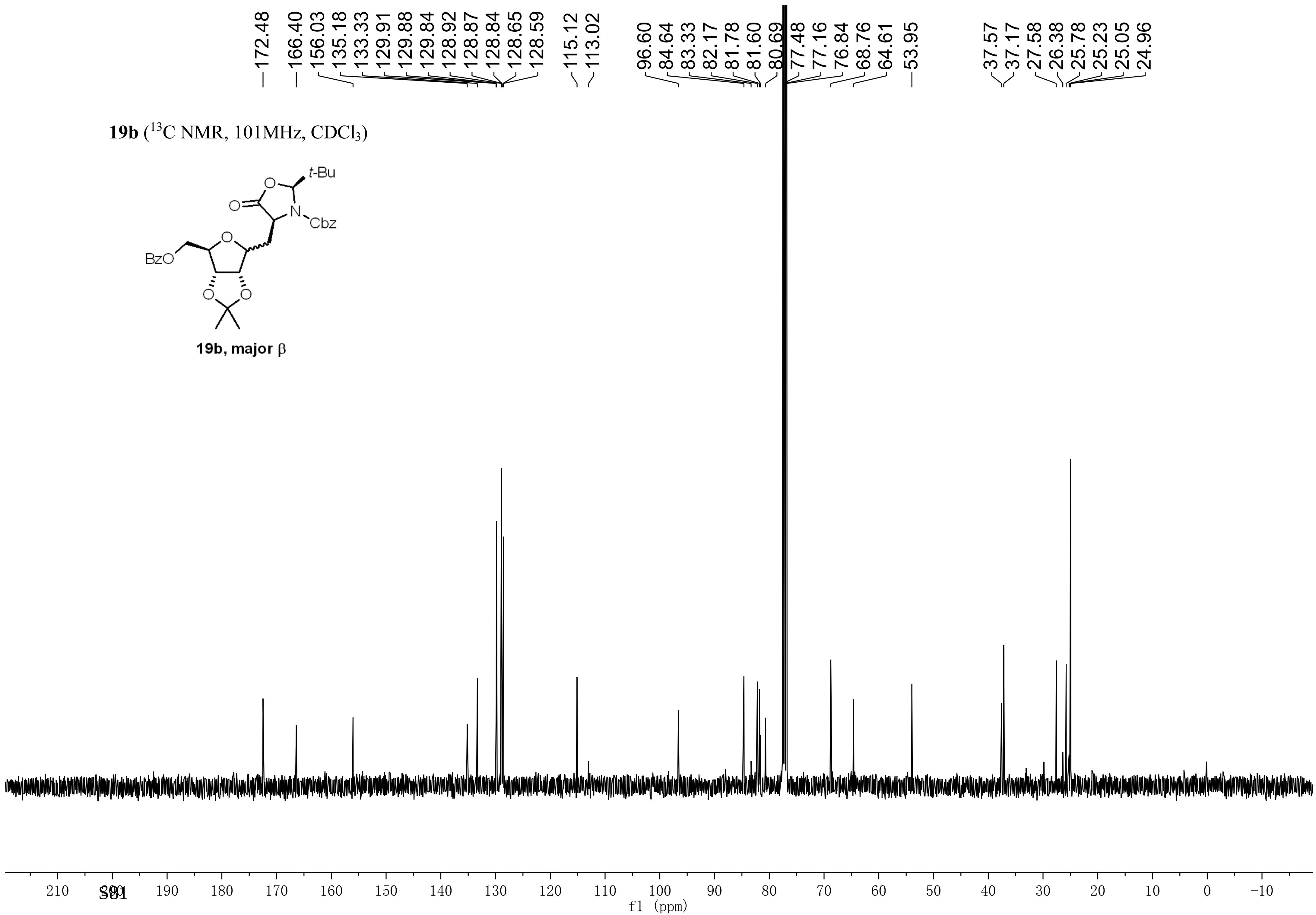
19a (1H-13C HSQC)
t-Bu
N
Cbz
H
O
19a
f1 (ppm)

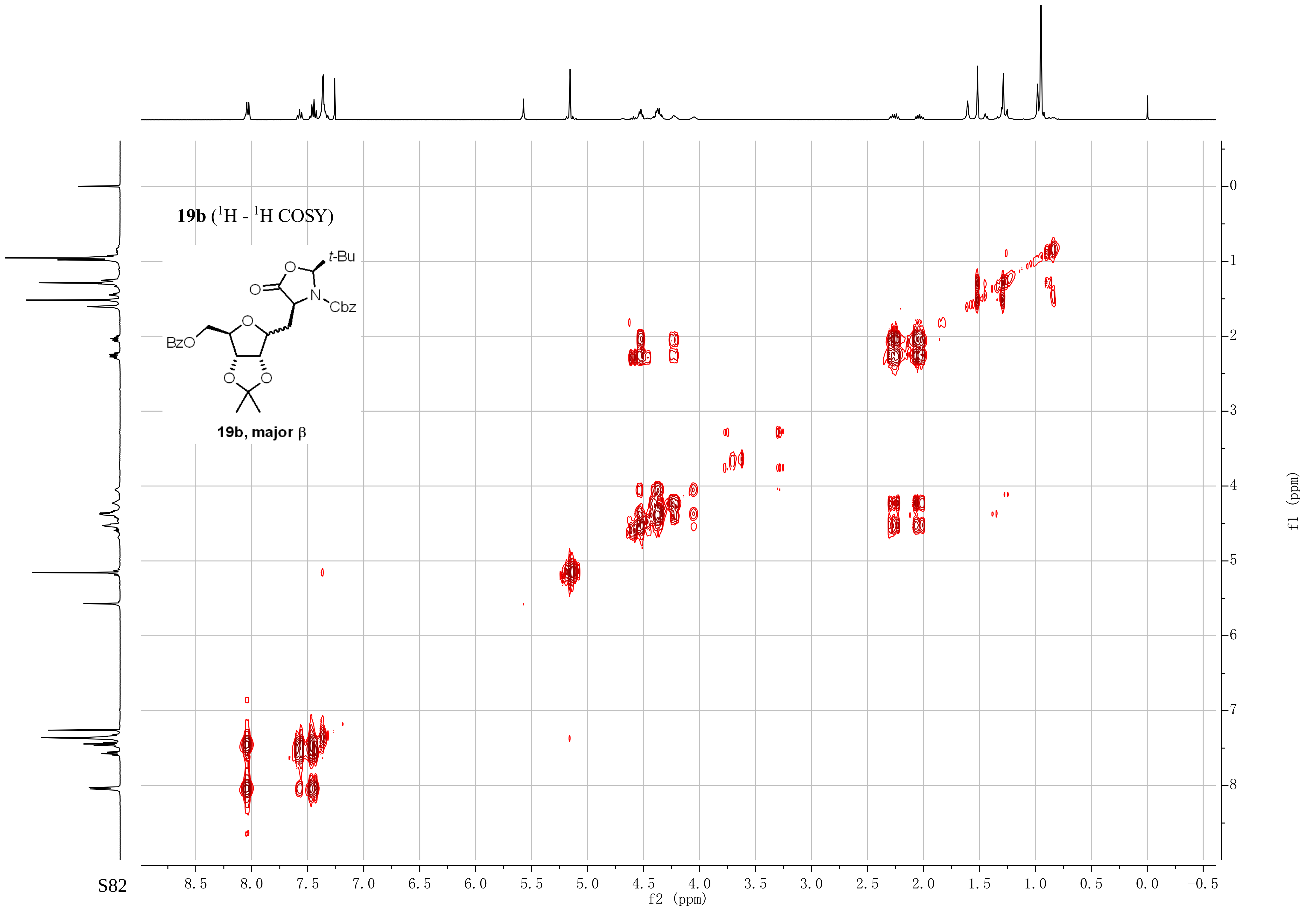
19b (^{1}H NMR, 400MHz, $CDCl_3$)

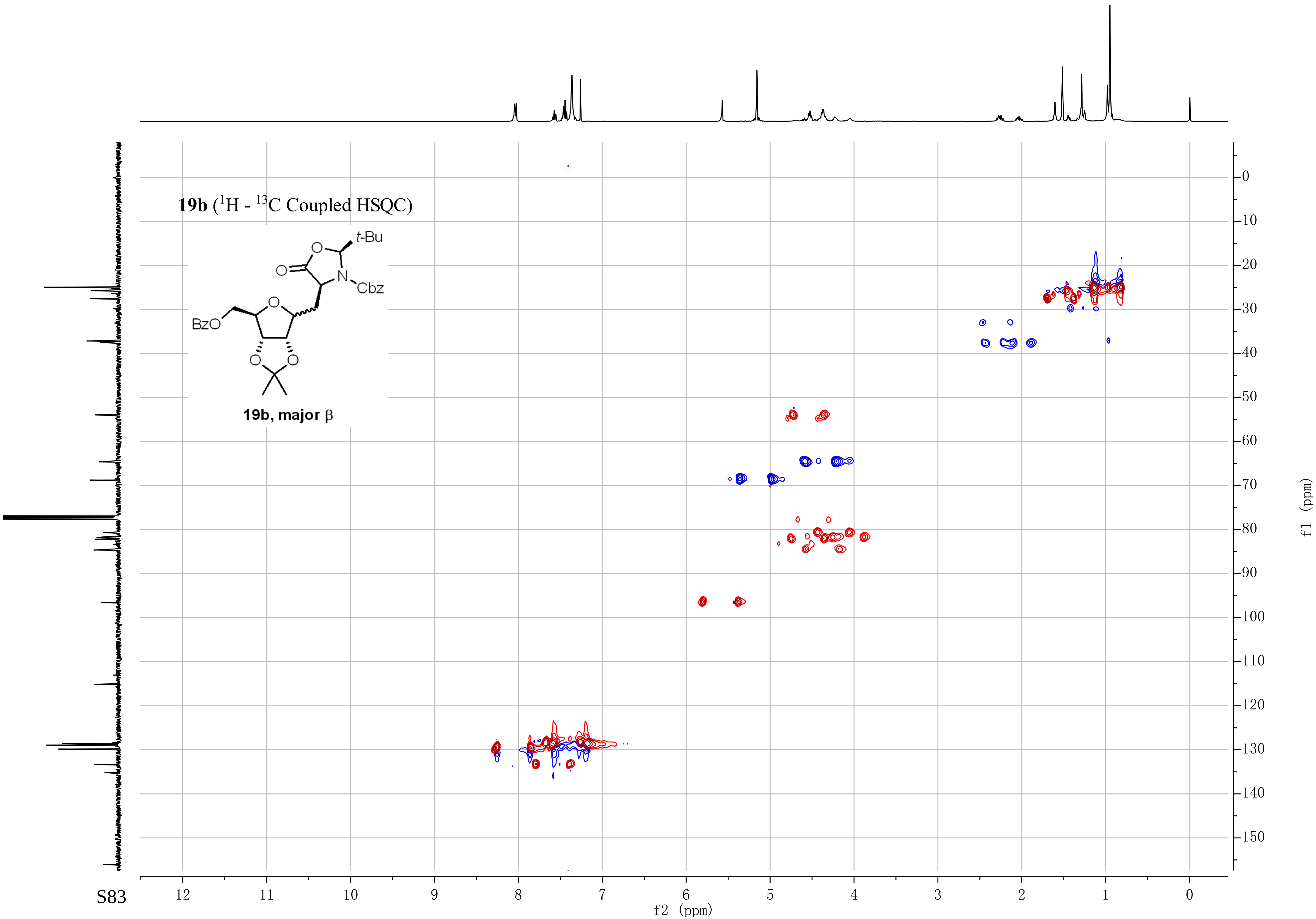


19b, major β

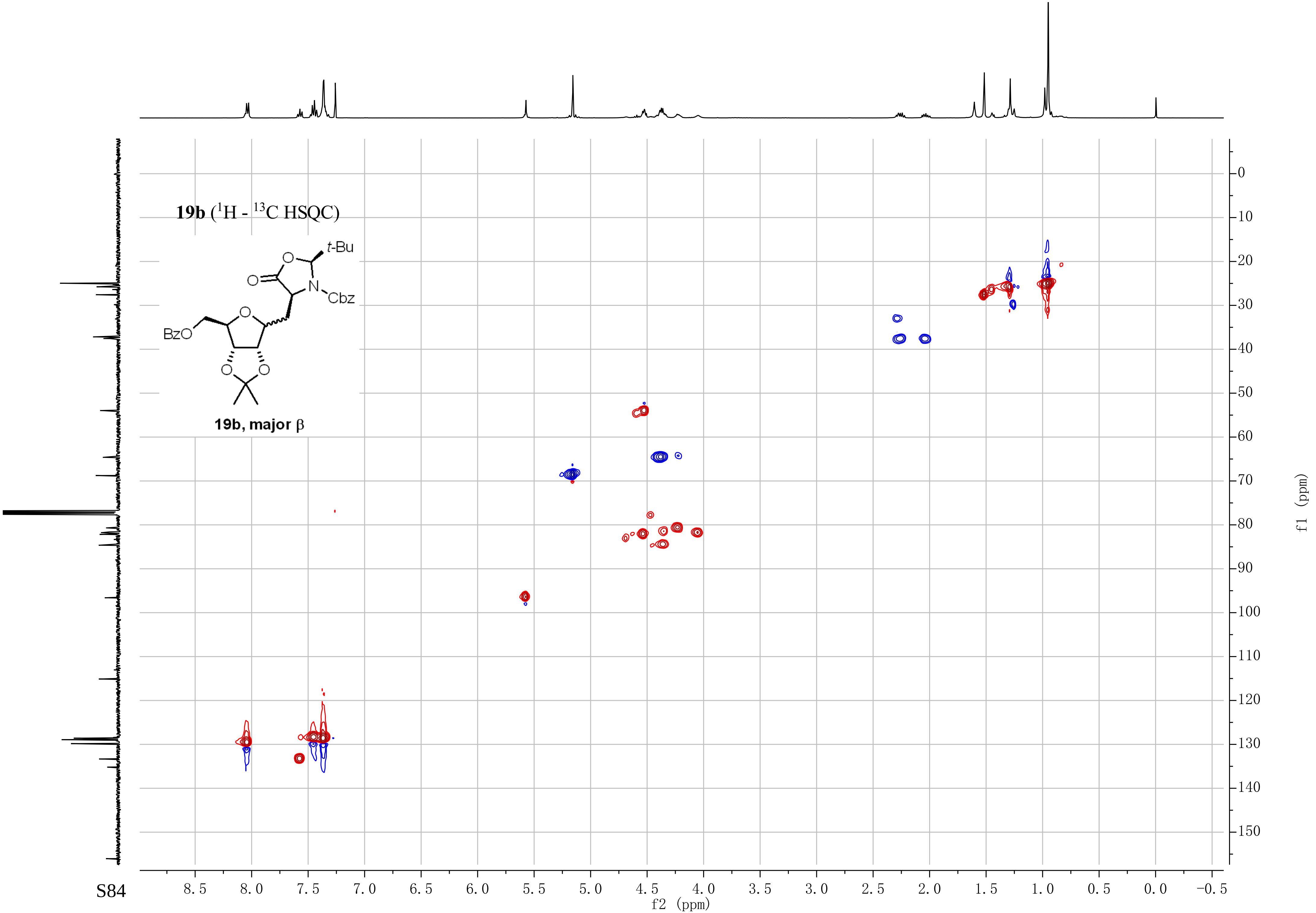



172.48
166.40
156.03
135.18
133.33
129.91
129.88
129.84
128.92
128.87
128.84
128.65
128.59
115.12
113.02
96.60
84.64
83.33
82.17
81.78
81.60
80.69
77.48
77.16
76.84
68.76
64.61
53.95
37.57
37.17
27.58
26.38
25.78
25.23
25.05
24.96
19b (13C NMR, 101MHz, CDCl3)
t-Bu
O
O
N
Cbz
BzO
19b, major β
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

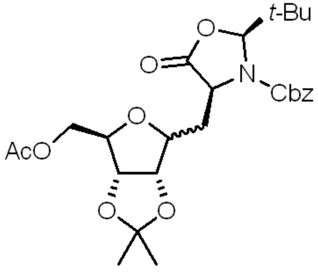

19b (¹H - ¹H COSY)
t-Bu
O
O
N
Cbz
BzO
O
O
O
19b, major β
f2 (ppm)
f1 (ppm)



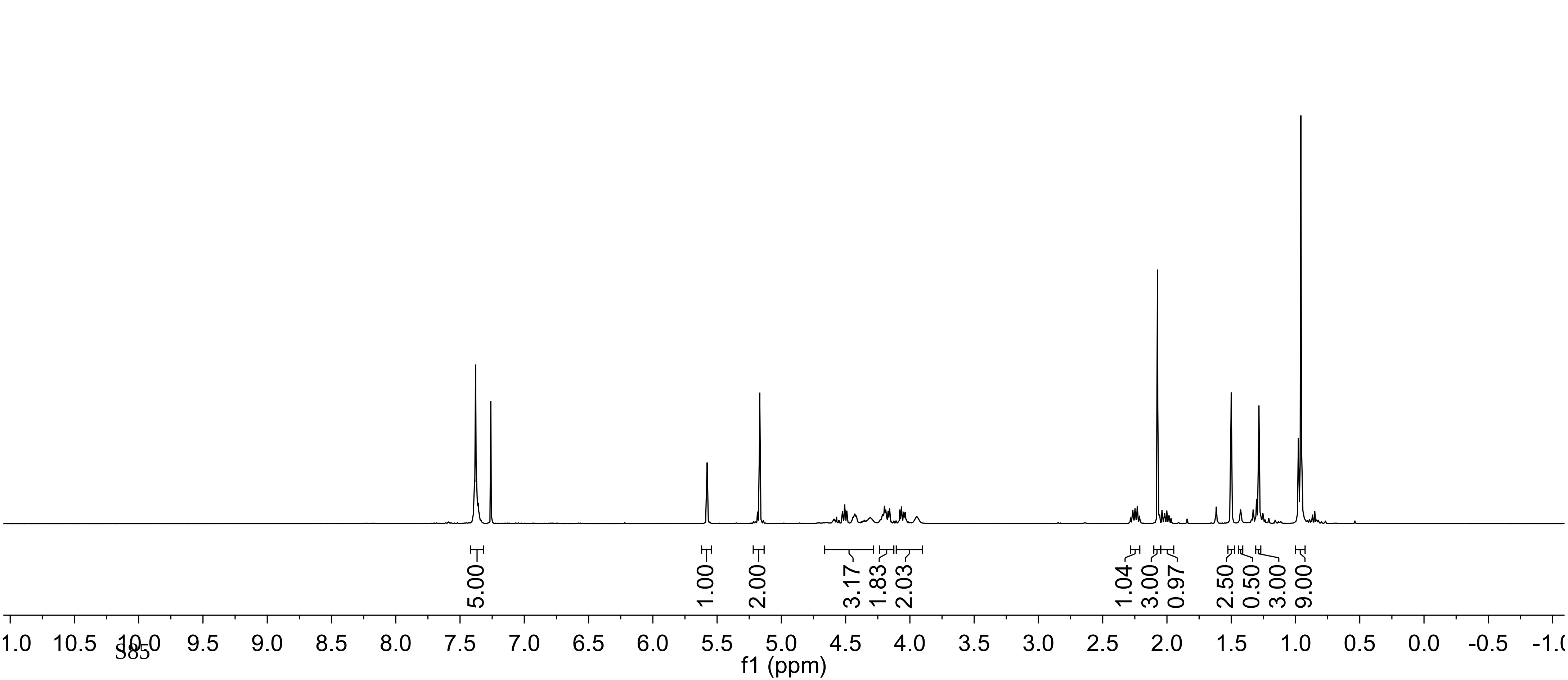
19b (^{1}H - ^{13}C Coupled HSQC)
t-Bu
O
N
Cbz
BzO
19b, major β
f2 (ppm)
f1 (ppm)

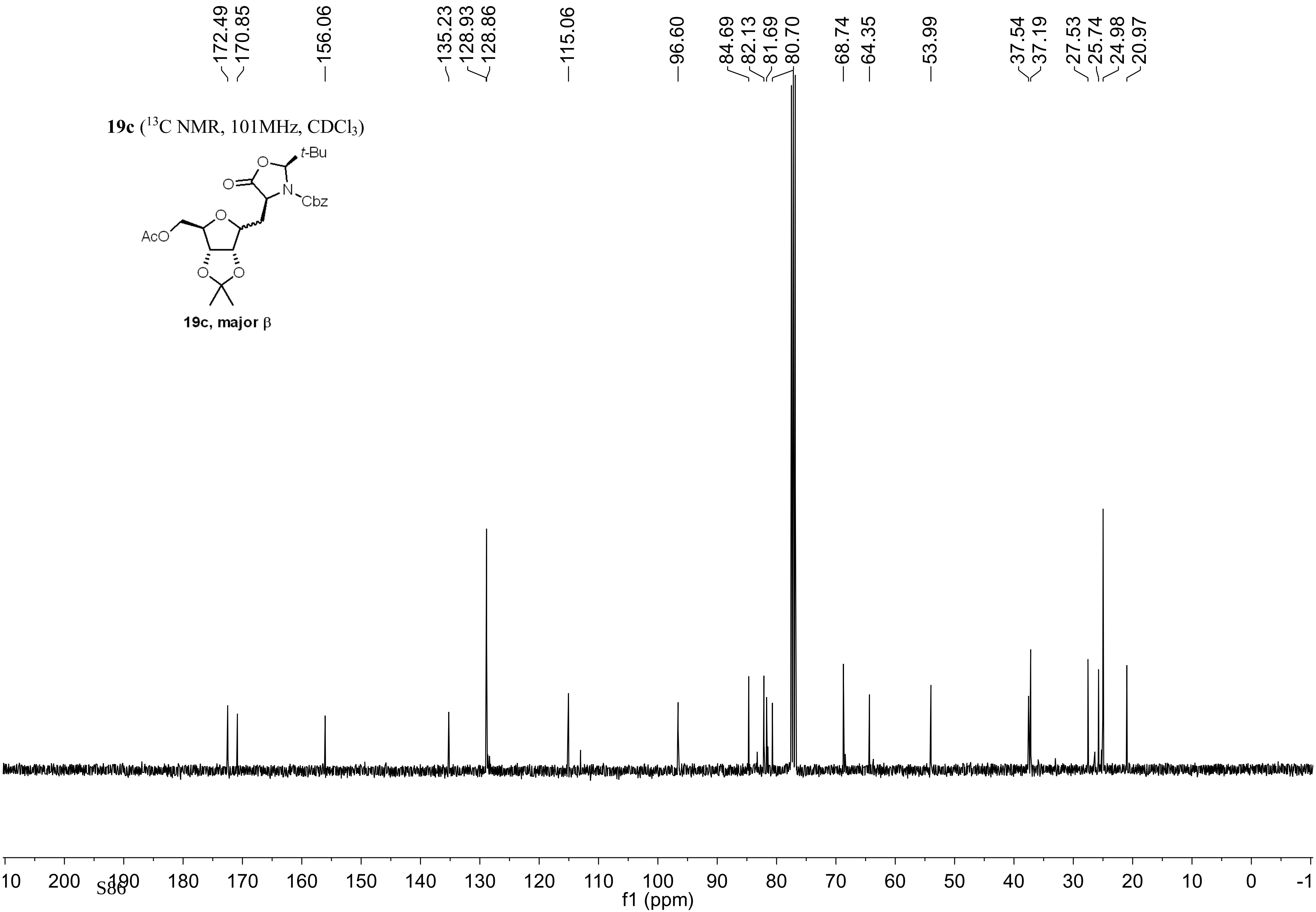

19b (¹H - ¹³C HSQC)
t-Bu
O
N
Cbz
BzO
19b, major β
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

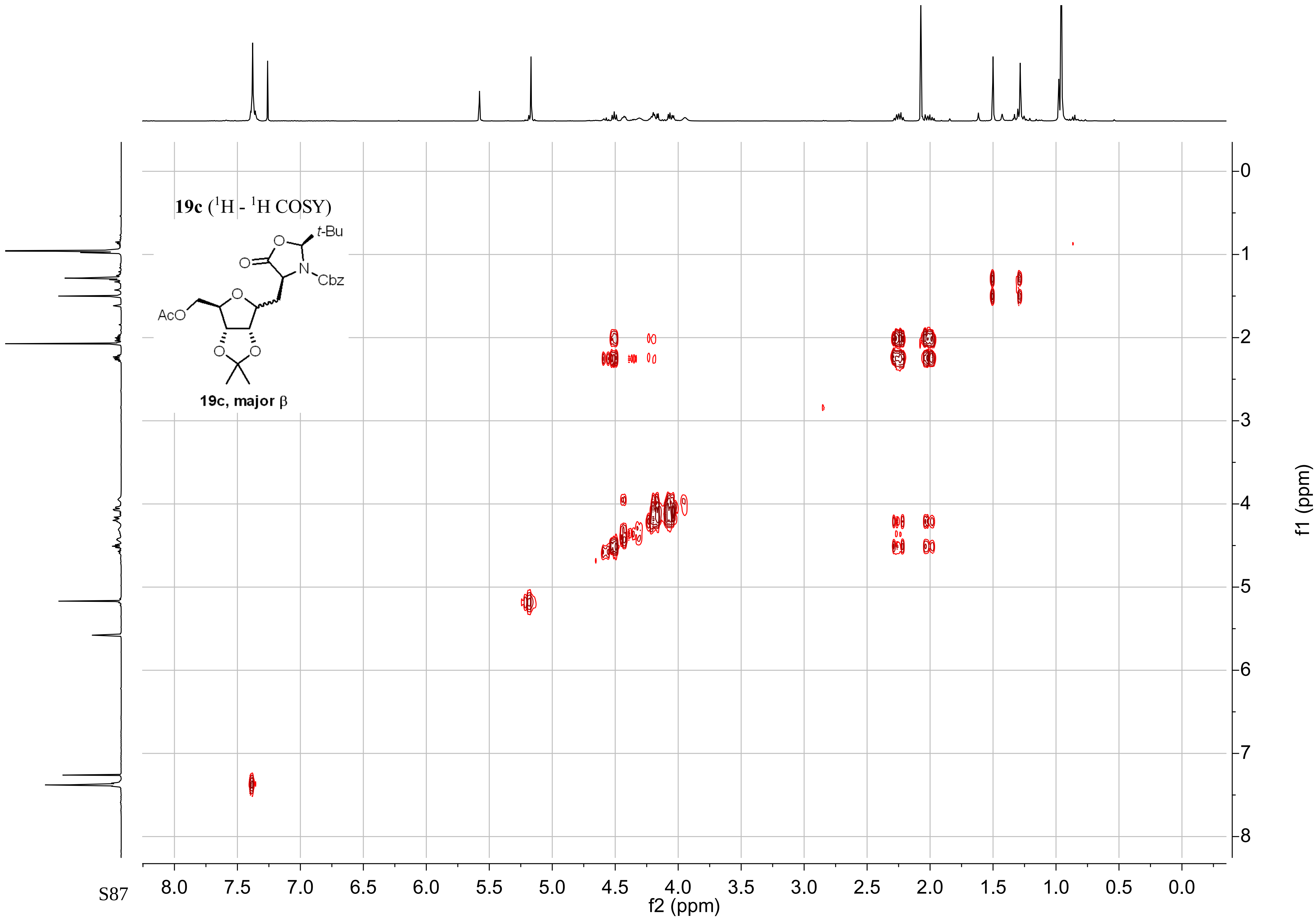
19c (^{1}H NMR, 400MHz, $CDCl_3$)

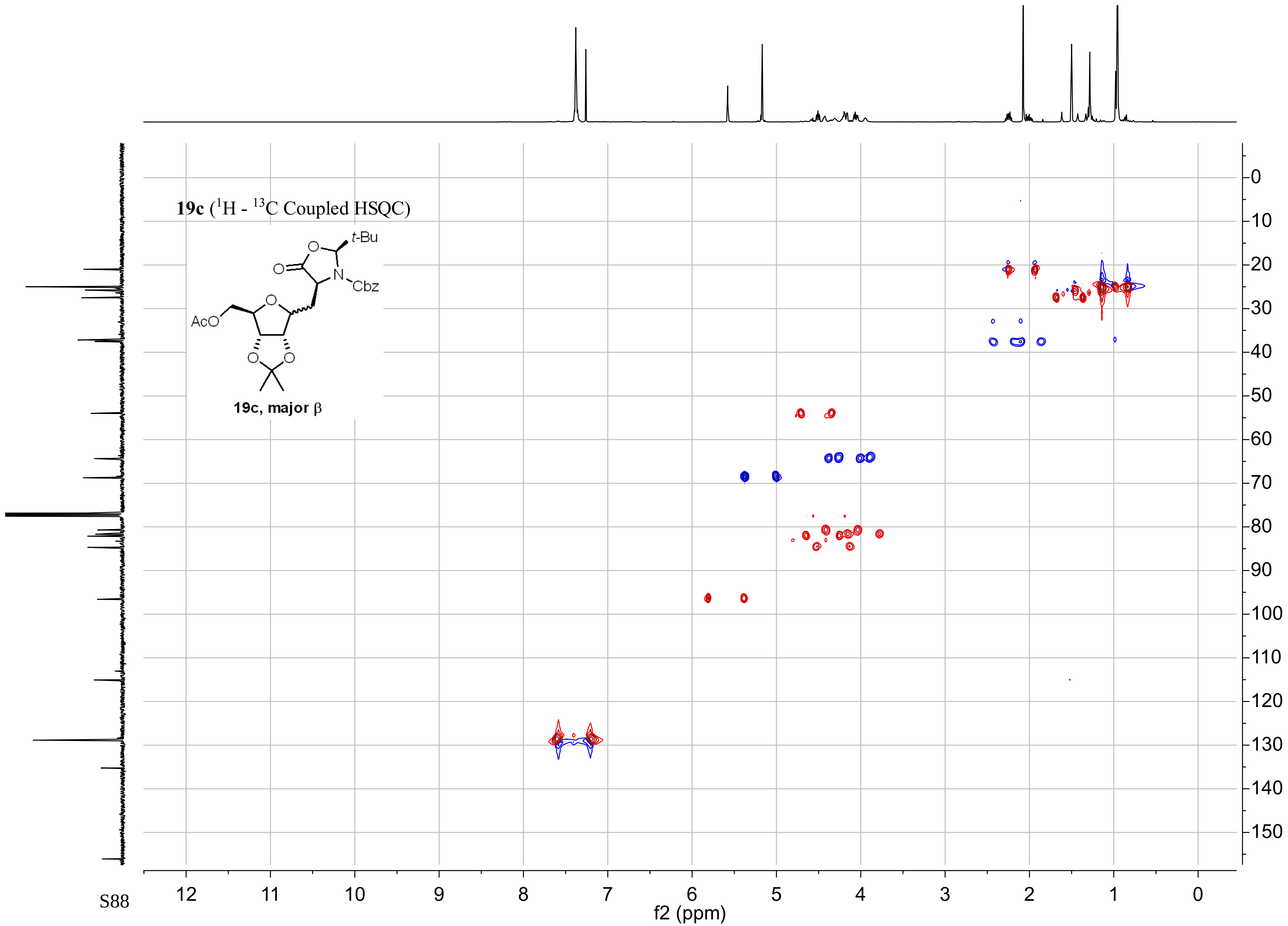


19c, major β

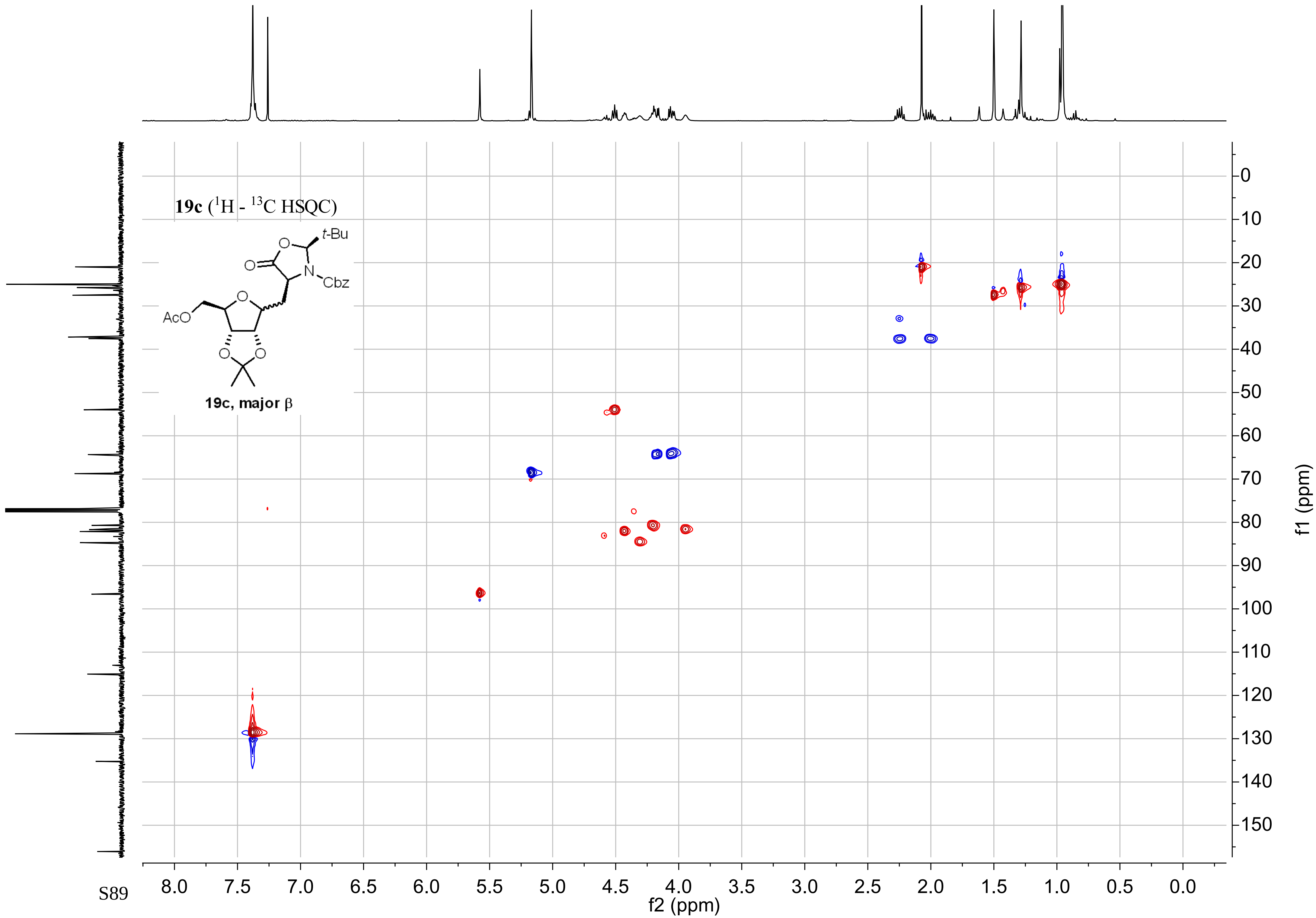



172.49
170.85
156.06
135.23
128.93
128.86
115.06
96.60
84.69
82.13
81.69
80.70
68.74
64.35
53.99
37.54
37.19
27.53
25.74
24.98
20.97
19c (13C NMR, 101MHz, CDCl3)
t-Bu
O
O
N
Cbz
AcO
19c, major β
f1 (ppm)

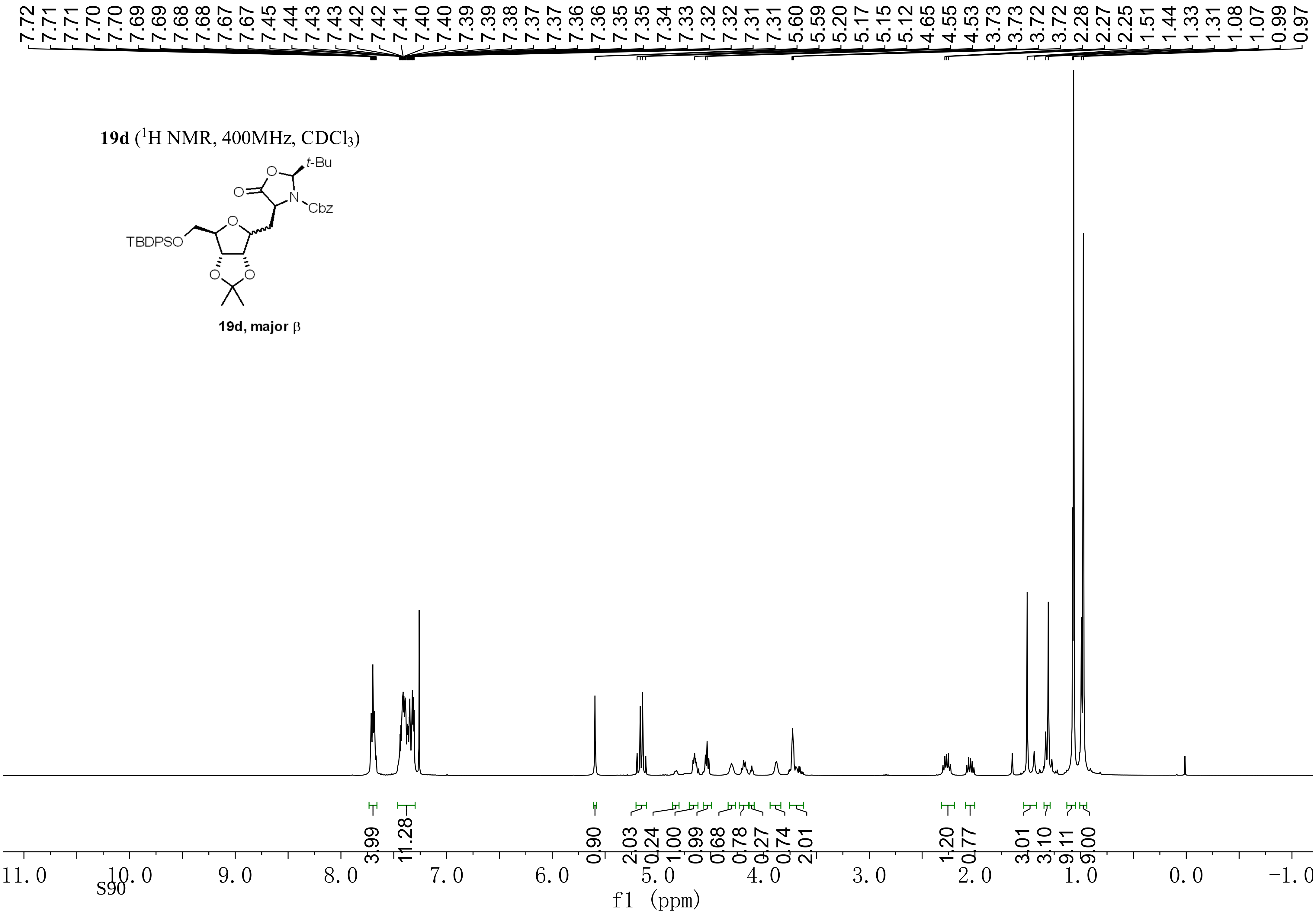

19c (1H - 1H COSY)
t-Bu
Cbz
AcO
19c, major β
f2 (ppm)
f1 (ppm)

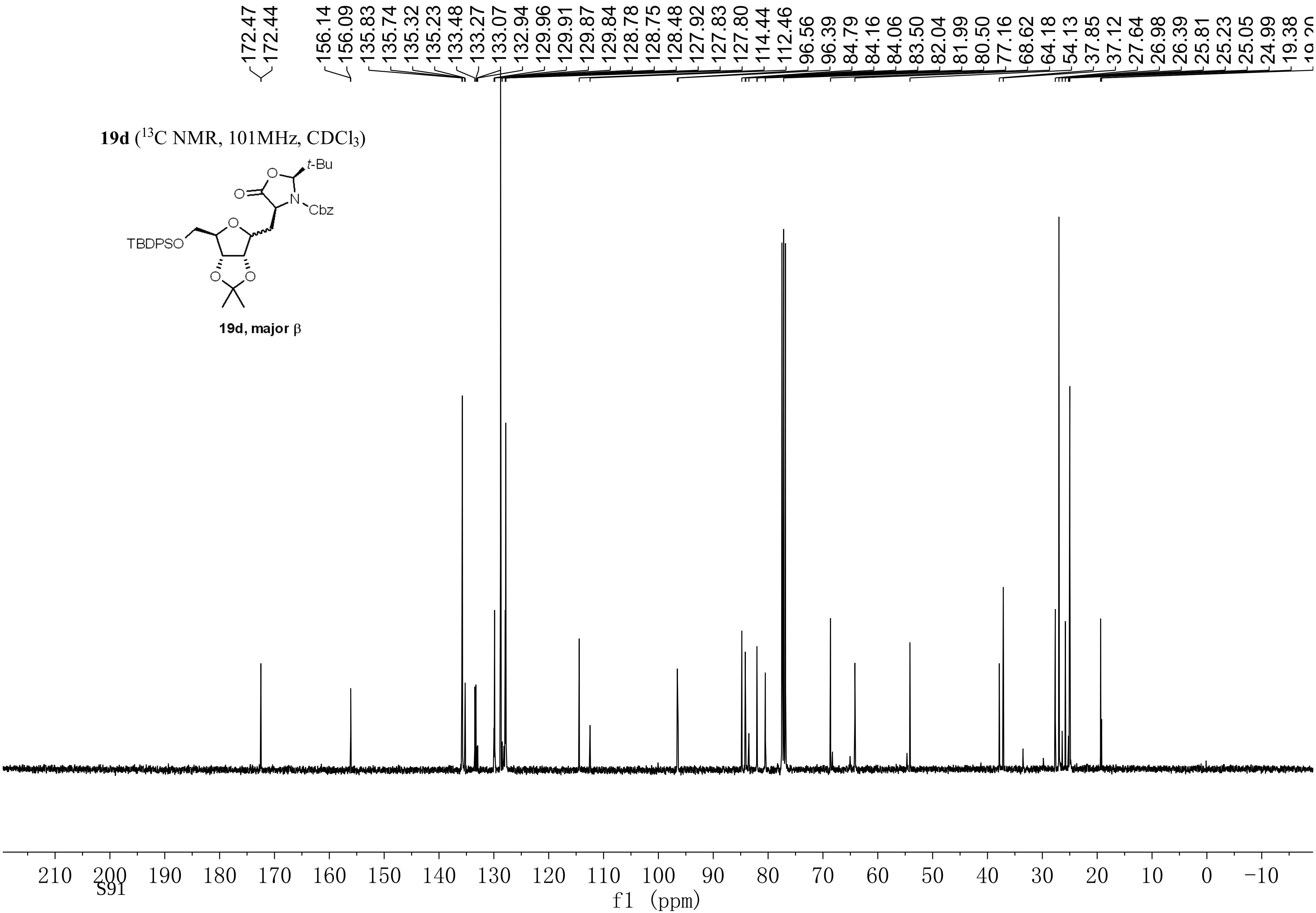


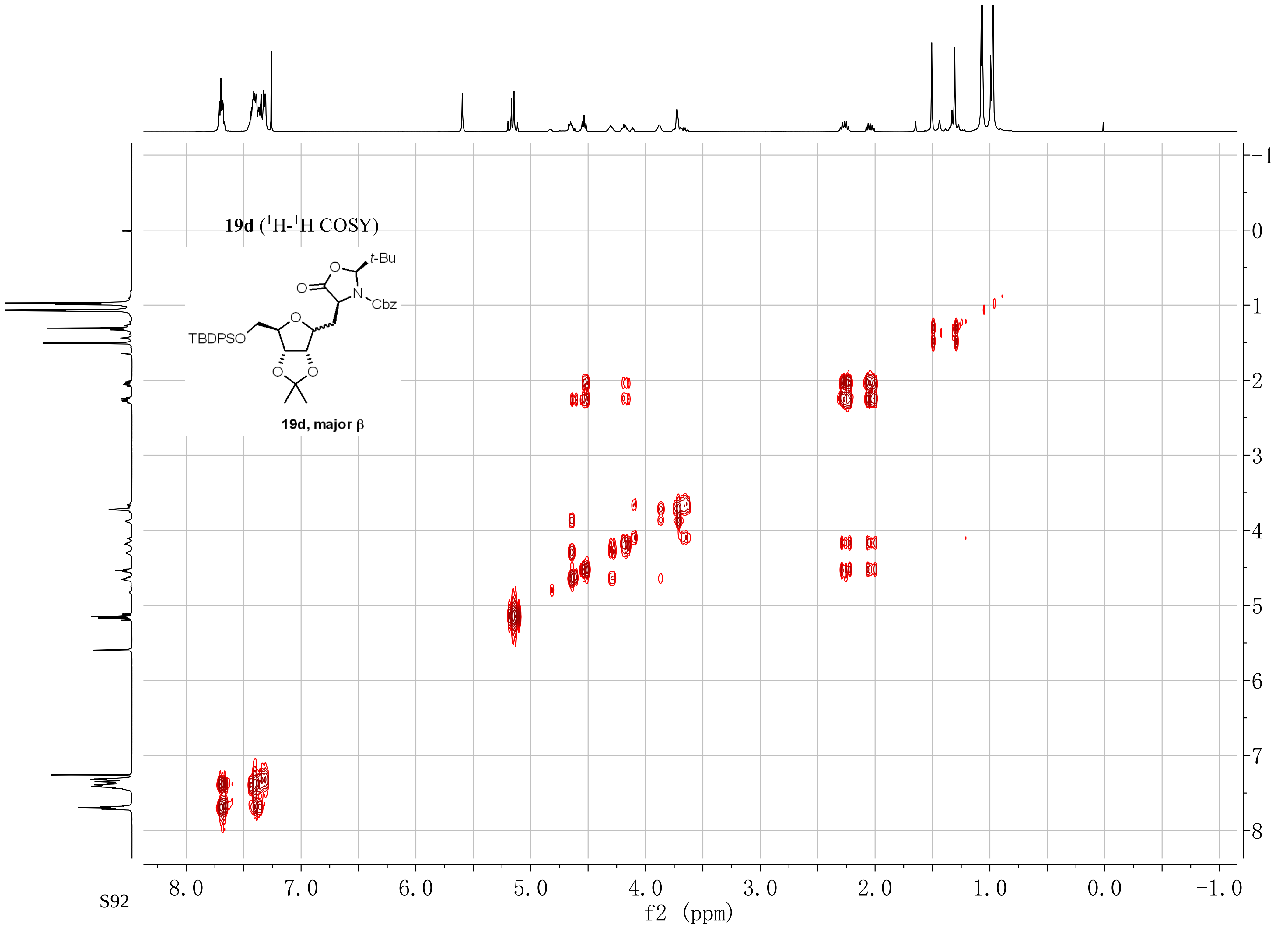
19c (1H - 13C Coupled HSQC)
t-Bu
O
O
N
Cbz
AcO
O
O
O
19c, major β
f2 (ppm)
f1 (ppm)

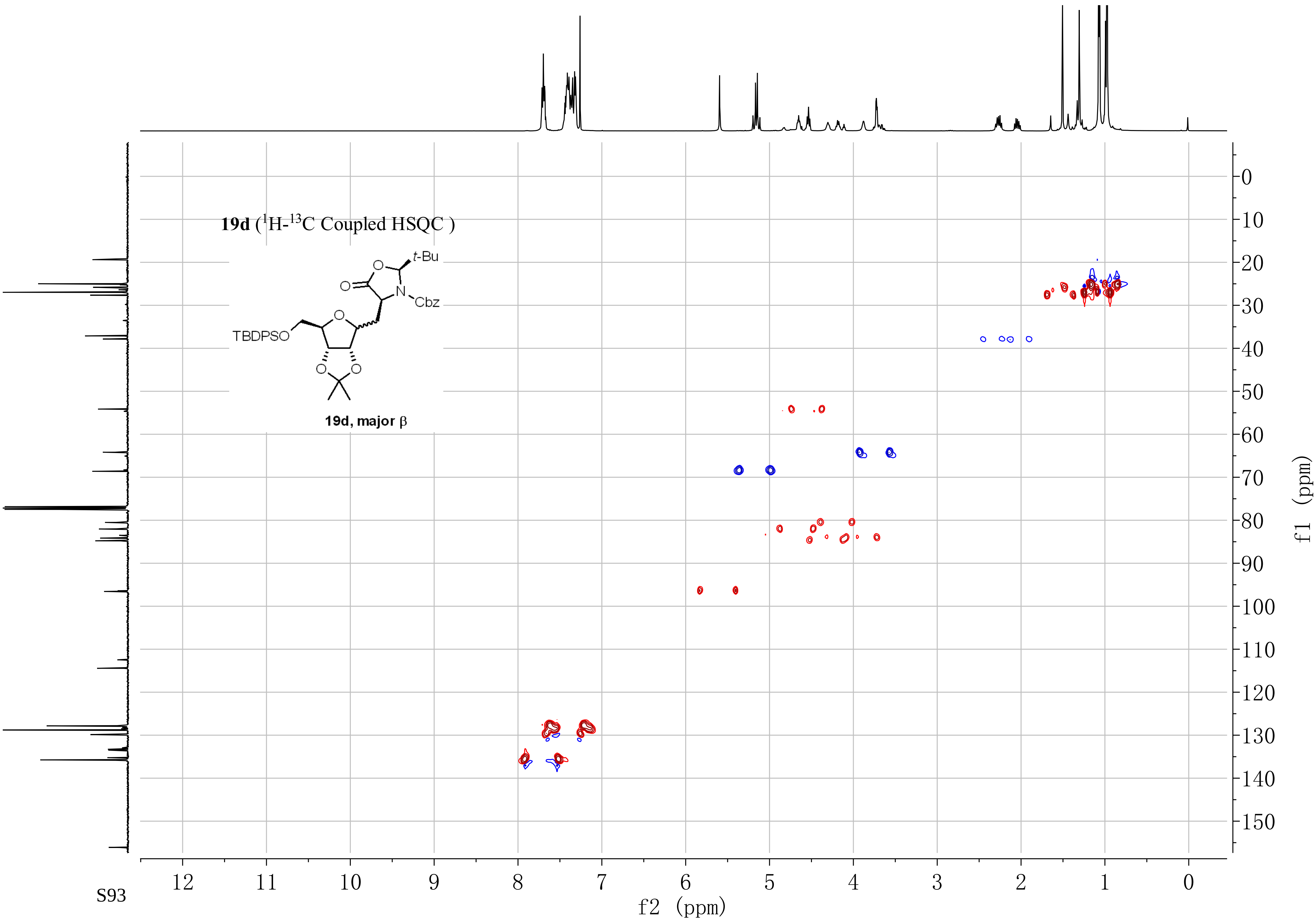


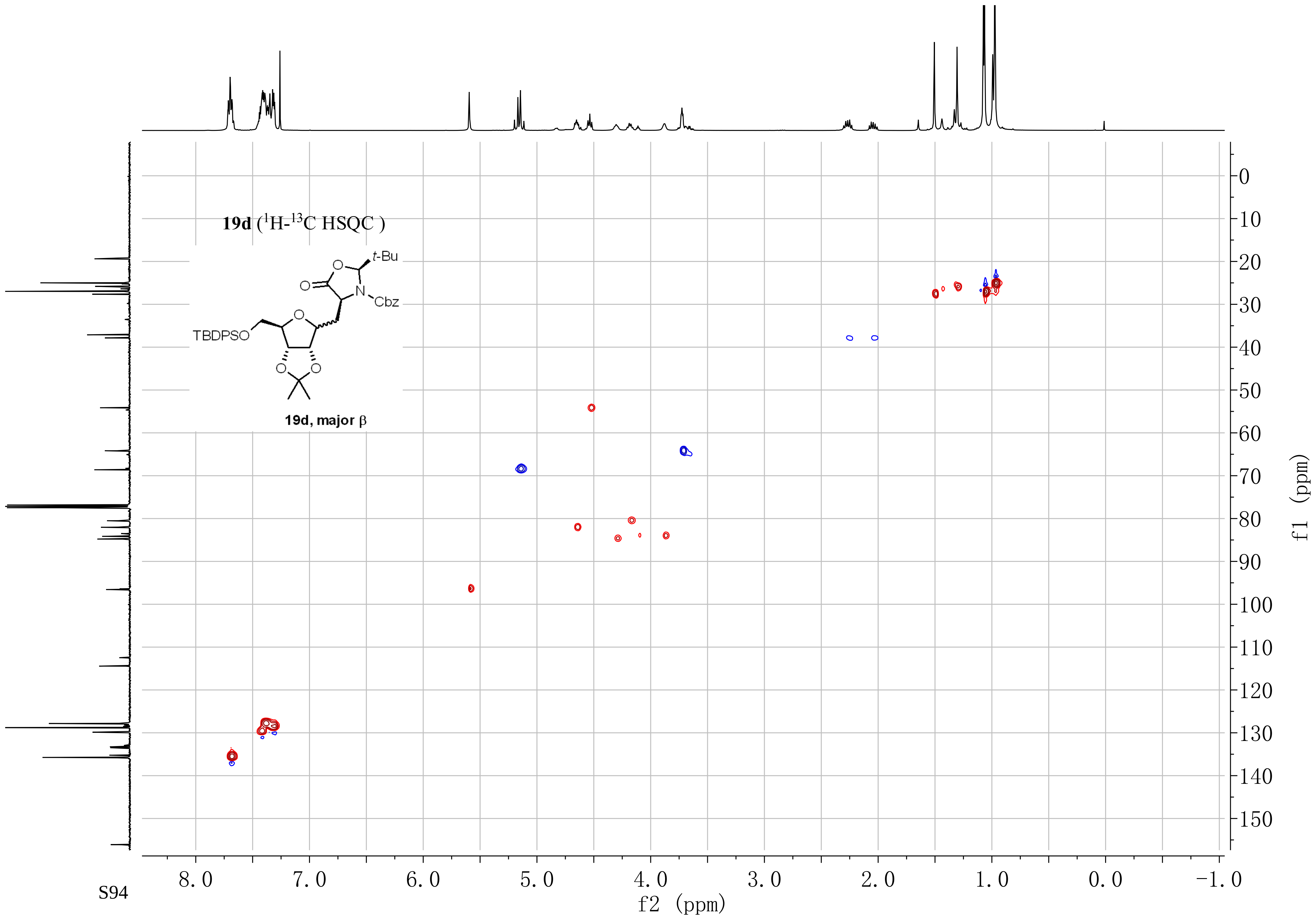
19c (1H - 13C HSQC)
t-Bu
Cbz
AcO
19c, major β
f2 (ppm)
f1 (ppm)


7.72 7.71 7.71 7.70 7.70 7.69 7.69 7.68 7.68 7.67 7.67 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.31 5.60 5.59 5.20 5.17 5.15 5.12 4.65 4.55 4.53 3.73 3.73 3.72 3.72 2.28 2.27 2.25 1.51 1.44 1.33 1.31 1.08 1.07 0.99 0.97
19d (^{1}H NMR, 400MHz, $CDCl_3$)
O
t-Bu
O
N
Cbz
O
TBDPSO
O
O
19d, major β
3.99
11.28
0.90
2.03
0.24
1.00
0.99
0.68
0.78
0.27
0.74
2.01
1.20
0.77
3.01
3.10
9.11
9.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)

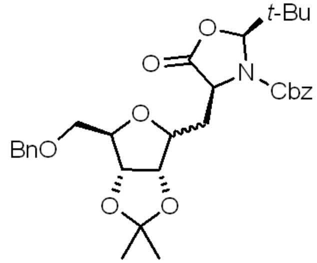

172.47
172.44
156.14
156.09
135.83
135.74
135.32
135.23
133.48
133.27
133.07
132.94
129.96
129.91
129.87
129.84
128.78
128.75
128.48
127.92
127.83
127.80
114.44
112.46
96.56
96.39
84.79
84.16
84.06
83.50
82.04
81.99
80.50
77.16
68.62
64.18
54.13
37.85
37.12
27.64
26.98
26.39
25.81
25.23
25.05
24.99
19.38
19d (13C NMR, 101MHz, CDCl3)
t-Bu
O
O
N
Cbz
O
TBDPSO
O
O
19d, major β
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)


19d (1H-1H COSY)
t-Bu
O
N
Cbz
TBDPSO
19d, major β
f2 (ppm)
f1 (ppm)

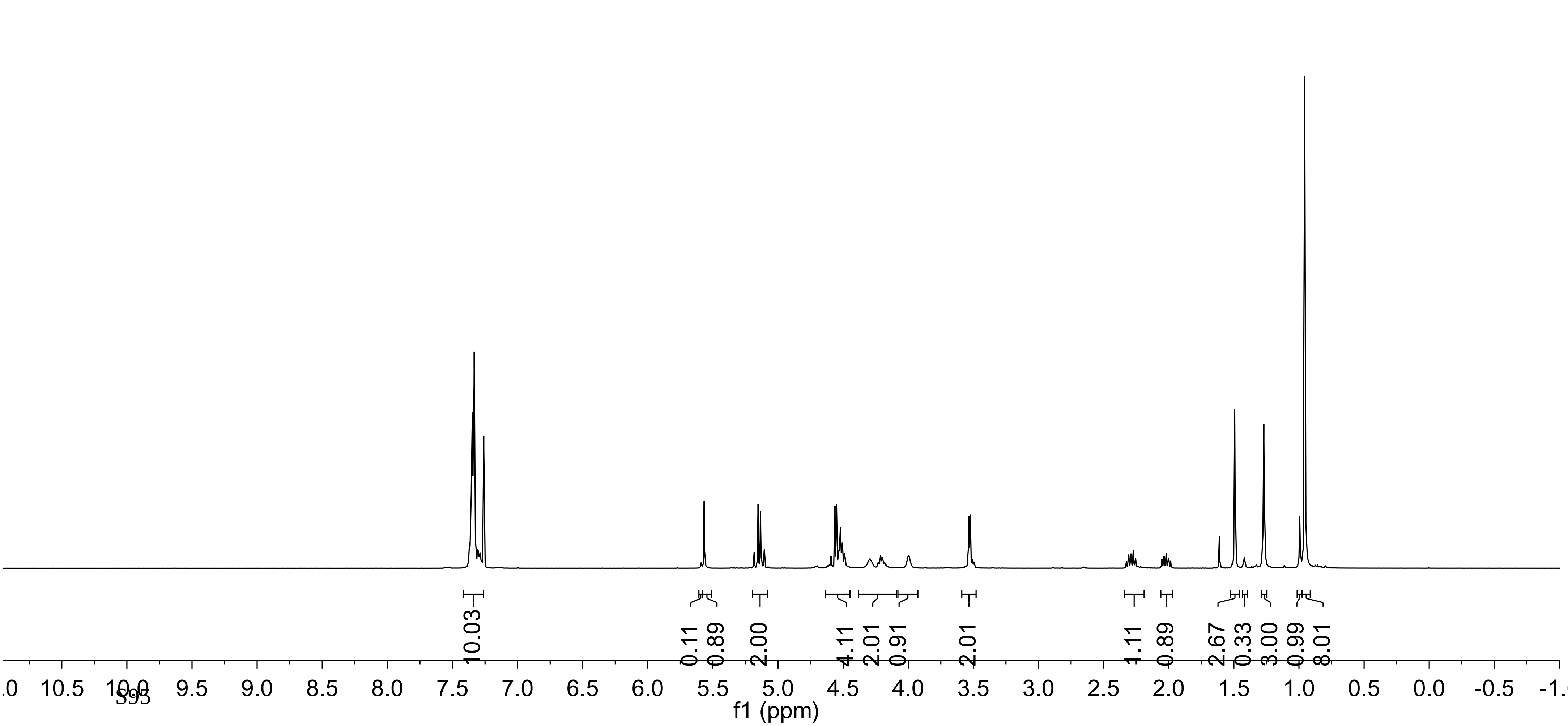

19d (^{1}H-^{13}C Coupled HSQC)
t-Bu
O
N
Cbz
TBDPSO
19d, major β
f2 (ppm)
f1 (ppm)


19d (1H-13C HSQC)
t-Bu
O
N
Cbz
TBDPSO
19d, major β
f2 (ppm)
f1 (ppm)

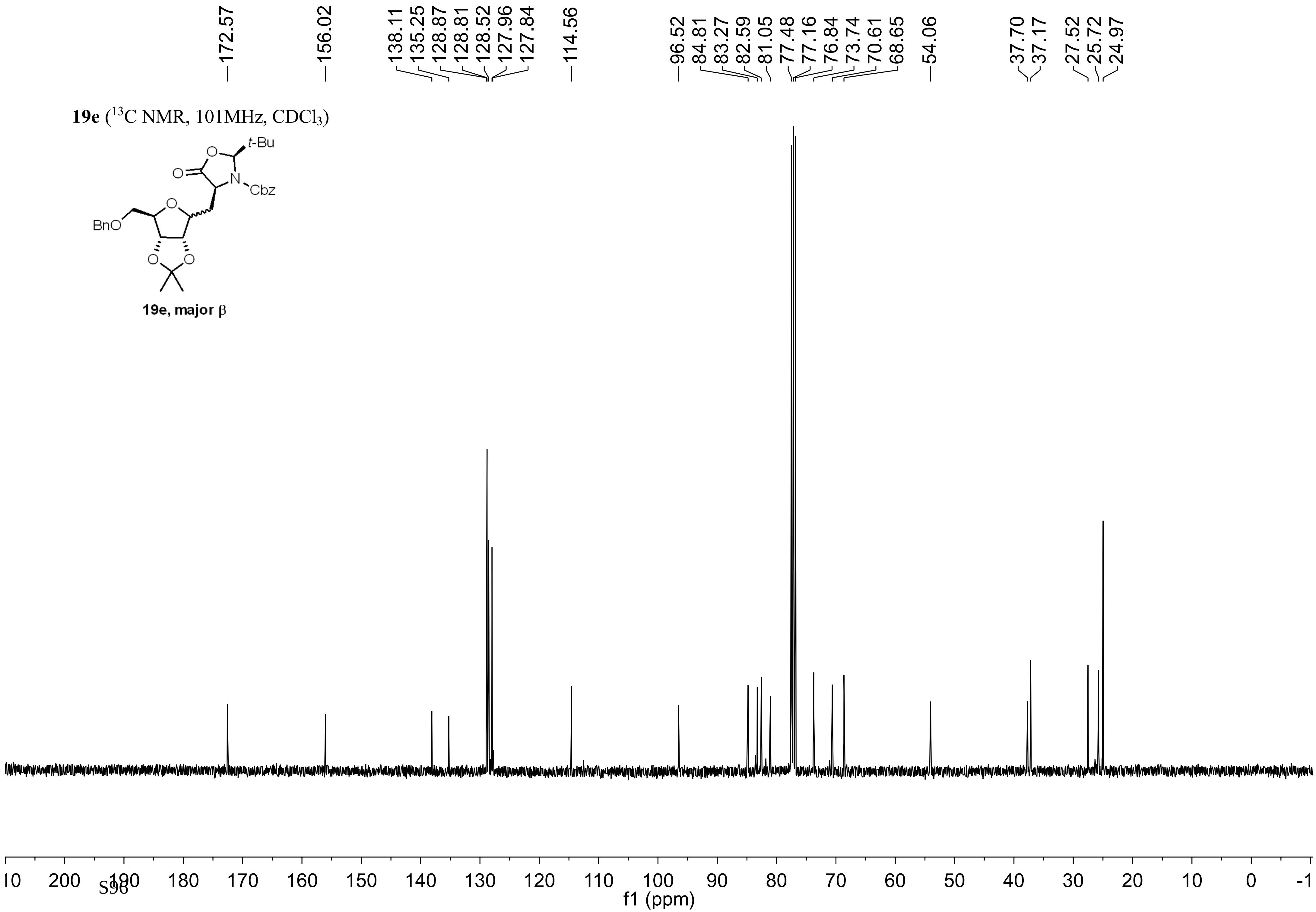
19e (^{1}H NMR, 400MHz, $CDCl_3$)



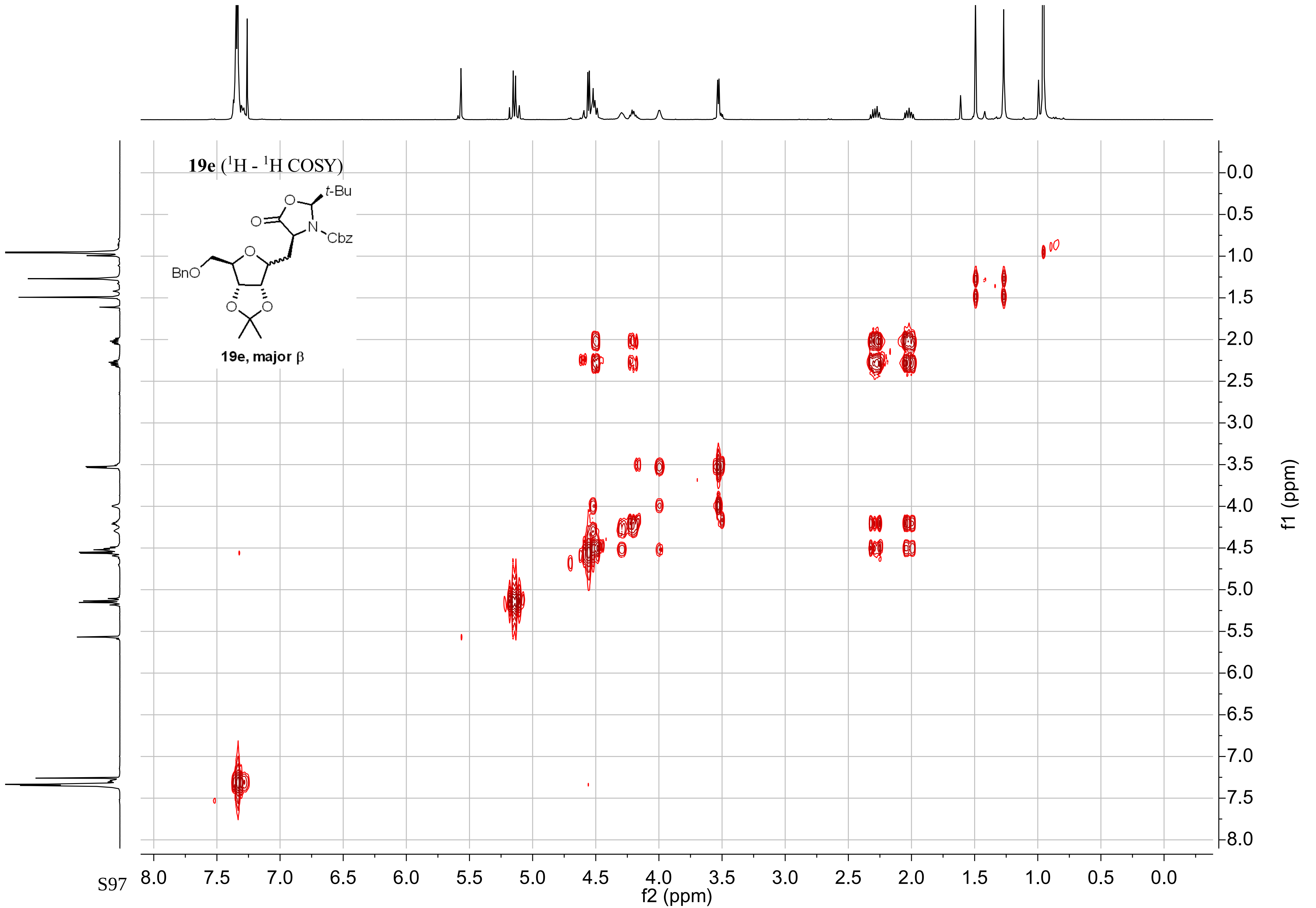
19e, major β

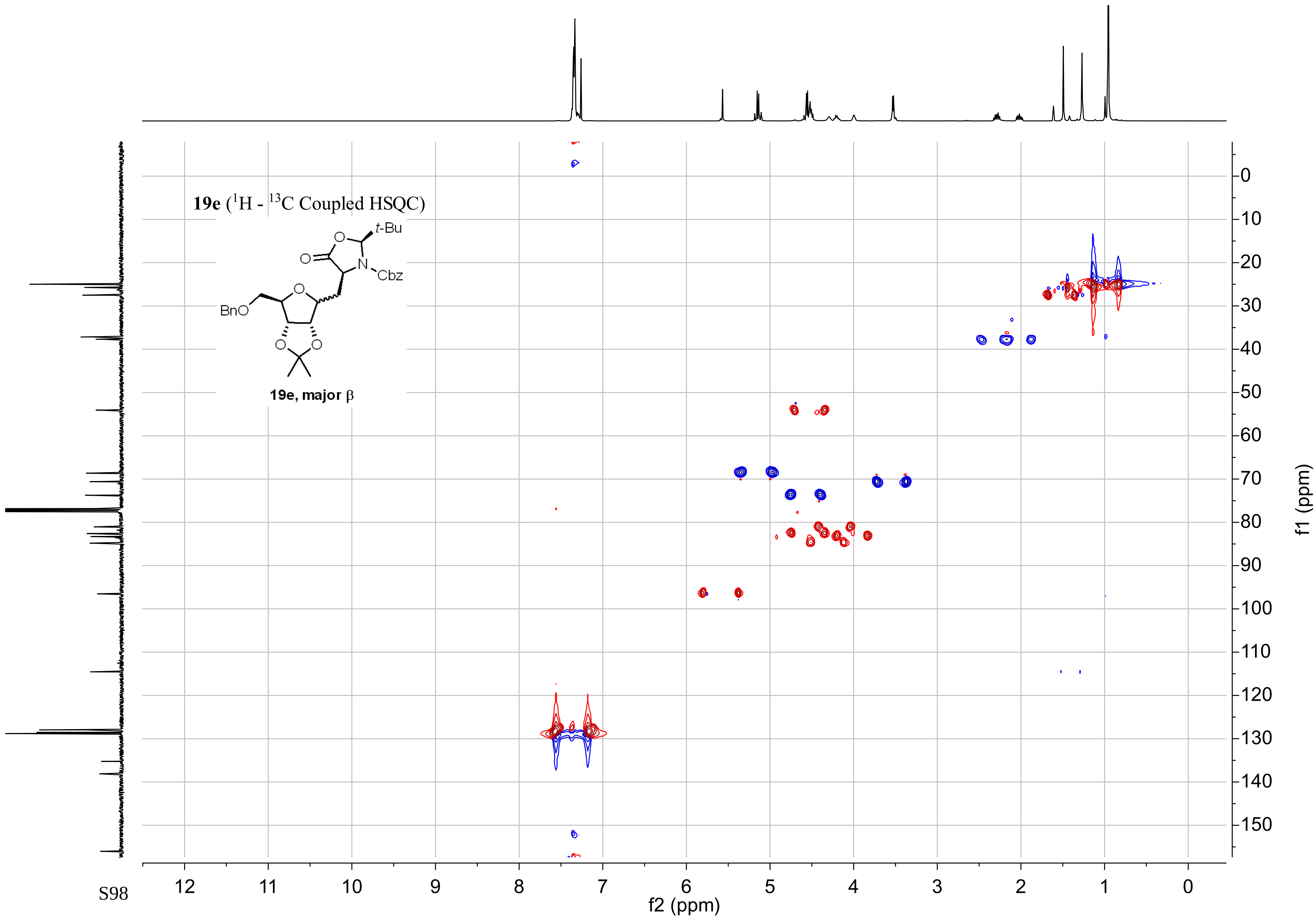


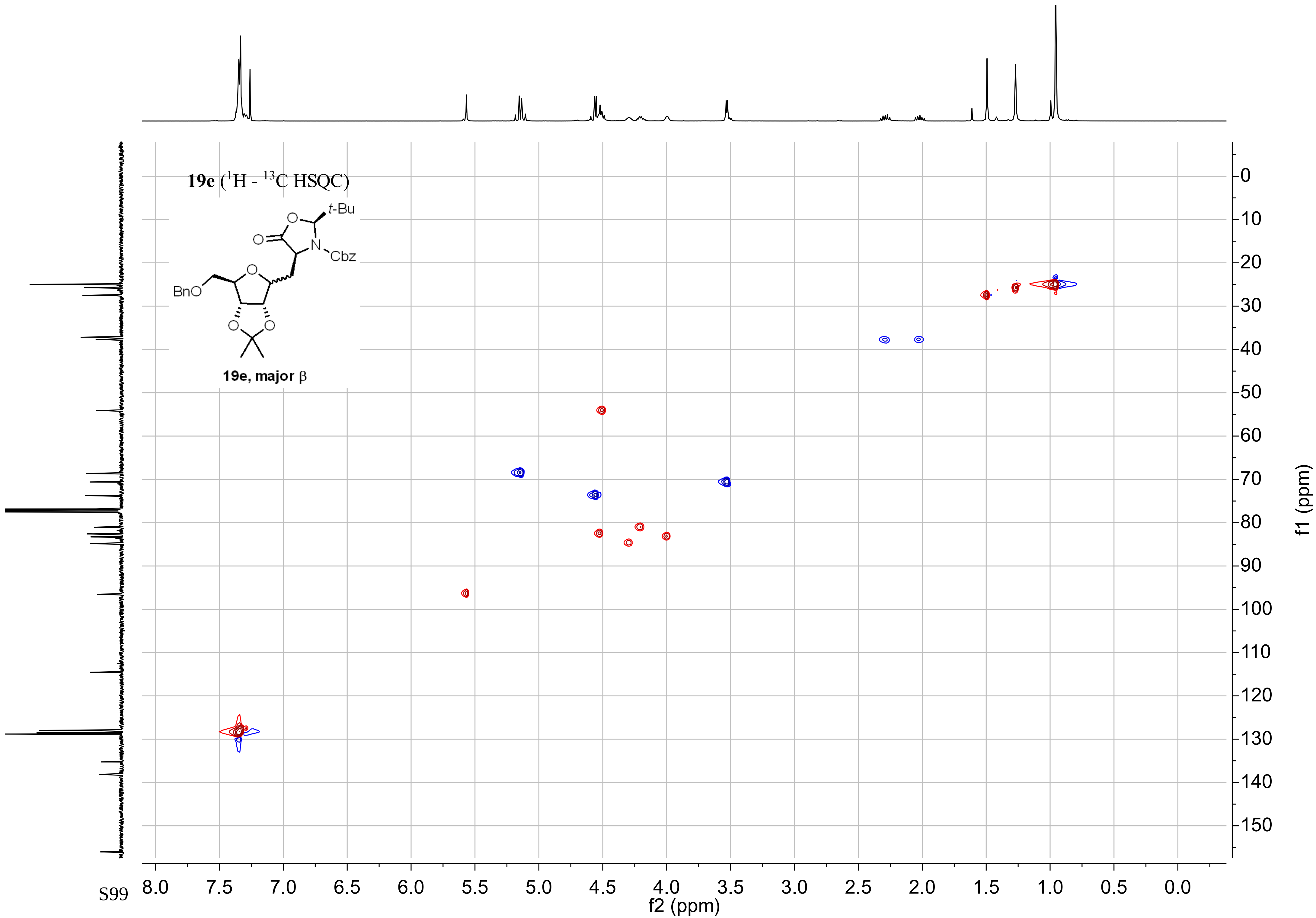
19e (^{13}C NMR, 101MHz, $CDCl_3$)

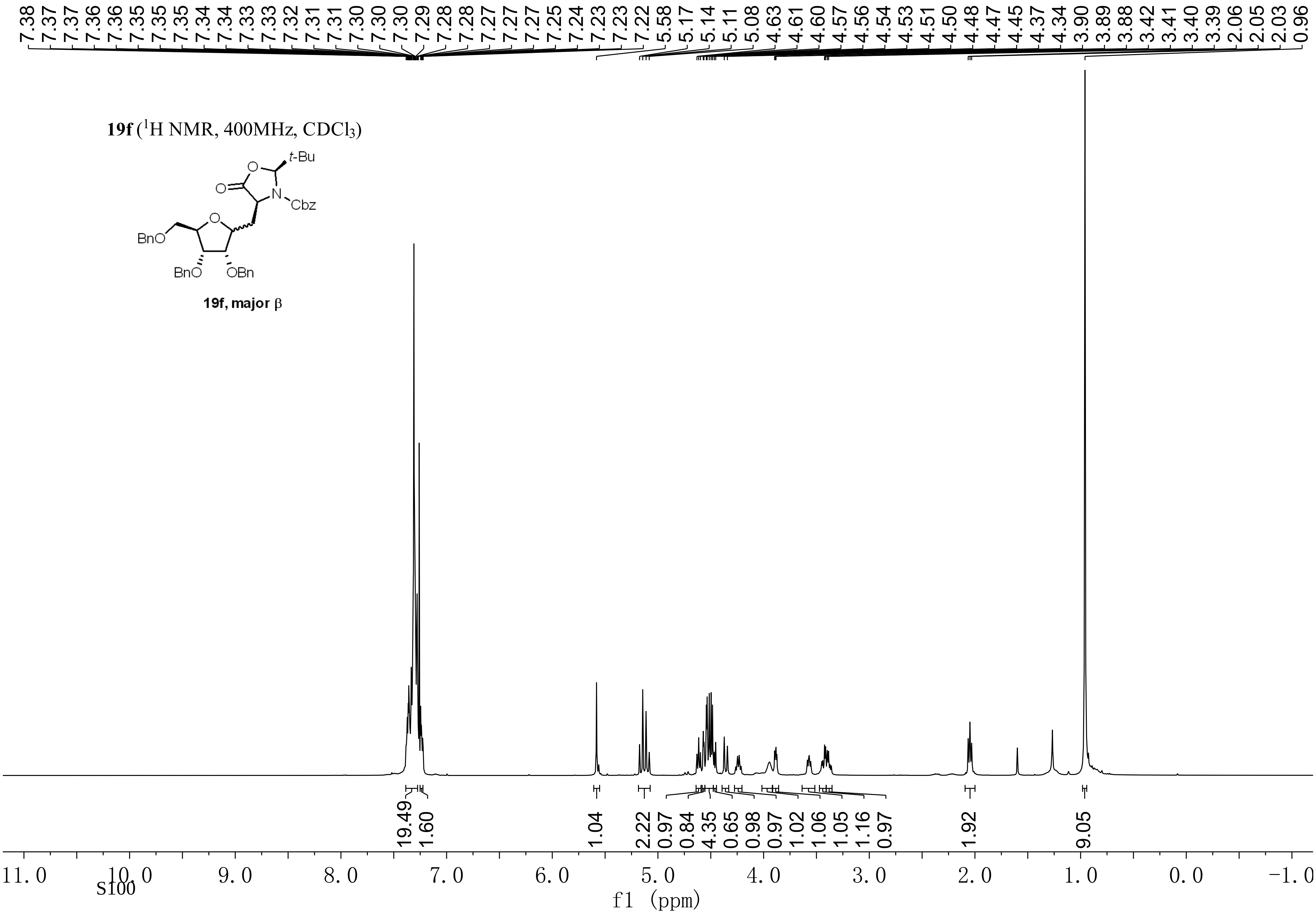


19e, major β

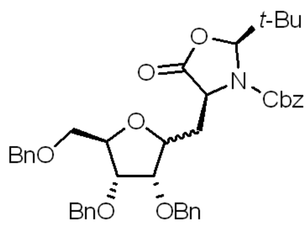

19e (^{1}H - ^{1}H COSY)
t-Bu
O
N
Cbz
BnO
19e, major β
f2 (ppm)
f1 (ppm)


19e (¹H - ¹³C Coupled HSQC)
t-Bu
O
O
N
Cbz
BnO
O
O
O
19e, major β
f2 (ppm)
f1 (ppm)

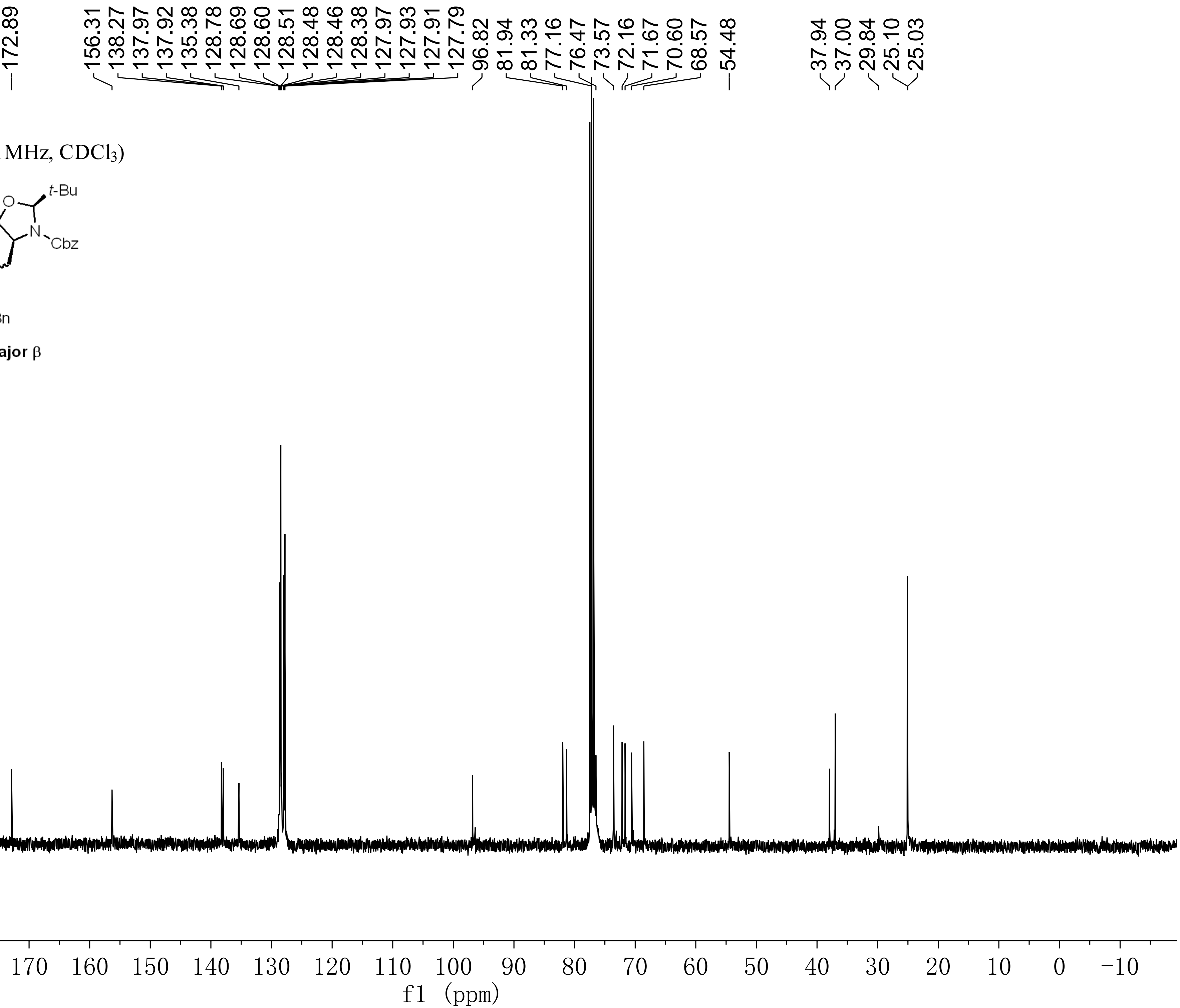

19e (1H - 13C HSQC)
t-Bu
N
Cbz
O
BnO
19e, major β
f2 (ppm)
f1 (ppm)

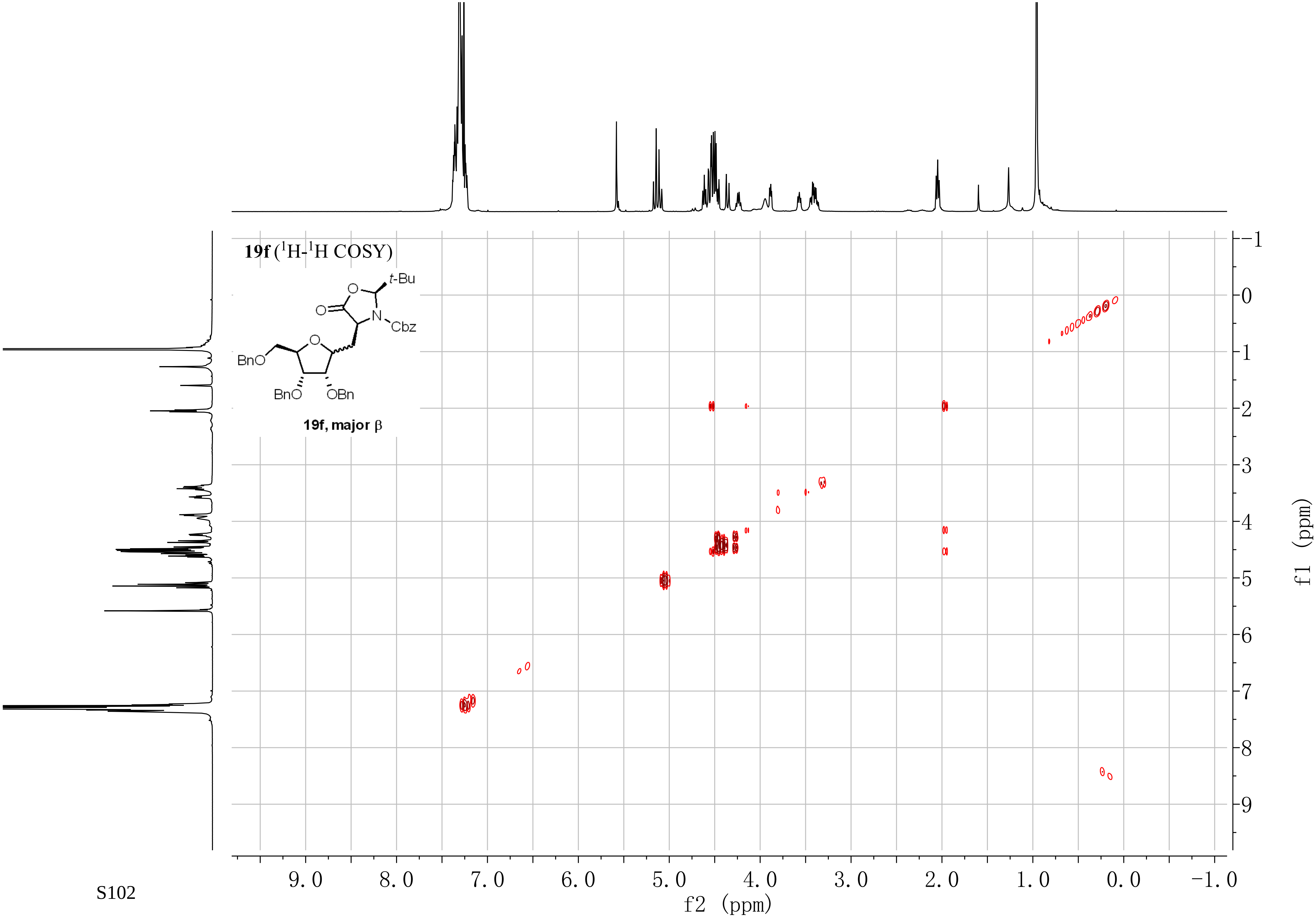

19f (1H NMR, 400MHz, CDCl3)
t-Bu
O
O
N
Cbz
BnO
O
BnO
OBn
19f, major β
7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.27 7.25 7.24 7.23 7.23 7.22 5.58 5.17 5.14 5.11 5.08 4.63 4.61 4.60 4.57 4.56 4.54 4.53 4.51 4.50 4.48 4.47 4.45 4.37 4.34 3.90 3.89 3.88 3.42 3.41 3.40 3.39 2.06 2.05 2.03 0.96
19.49 1.60 1.04 2.22 0.97 0.84 4.35 0.65 0.98 0.97 1.02 1.06 1.05 1.16 0.97 1.92 9.05
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

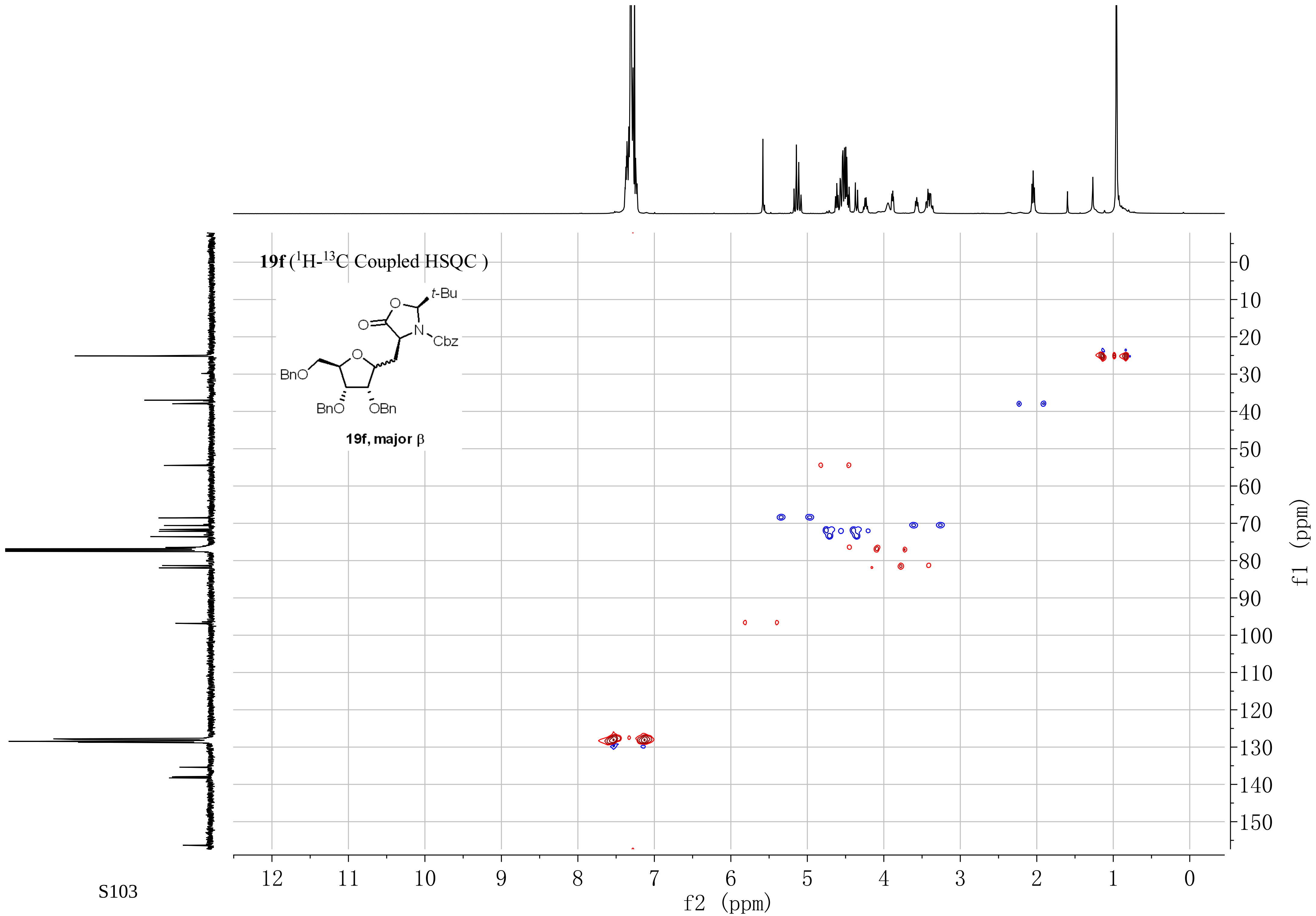
19f (^{13}C NMR, 101MHz, $CDCl_3$)



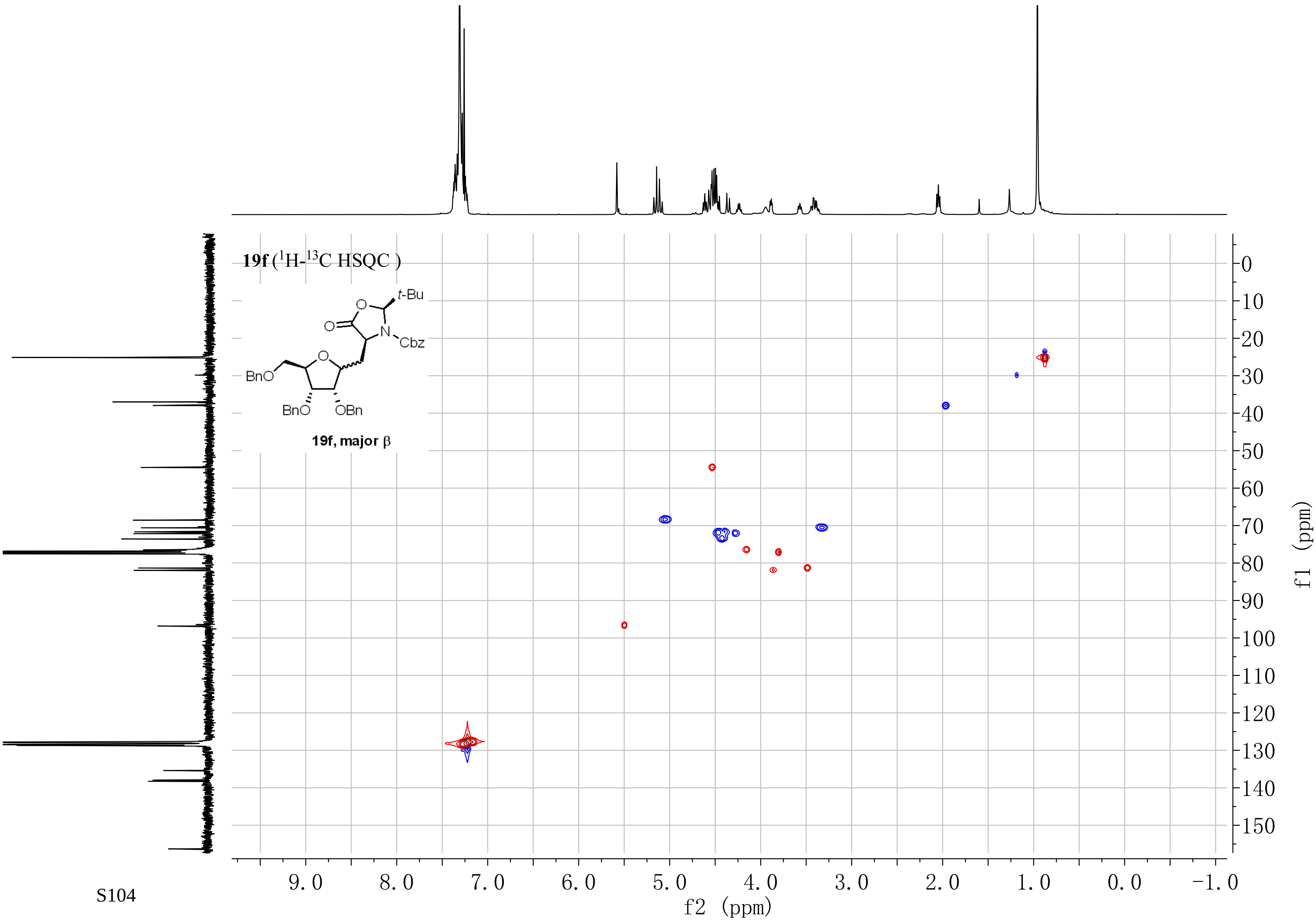
19f, major β

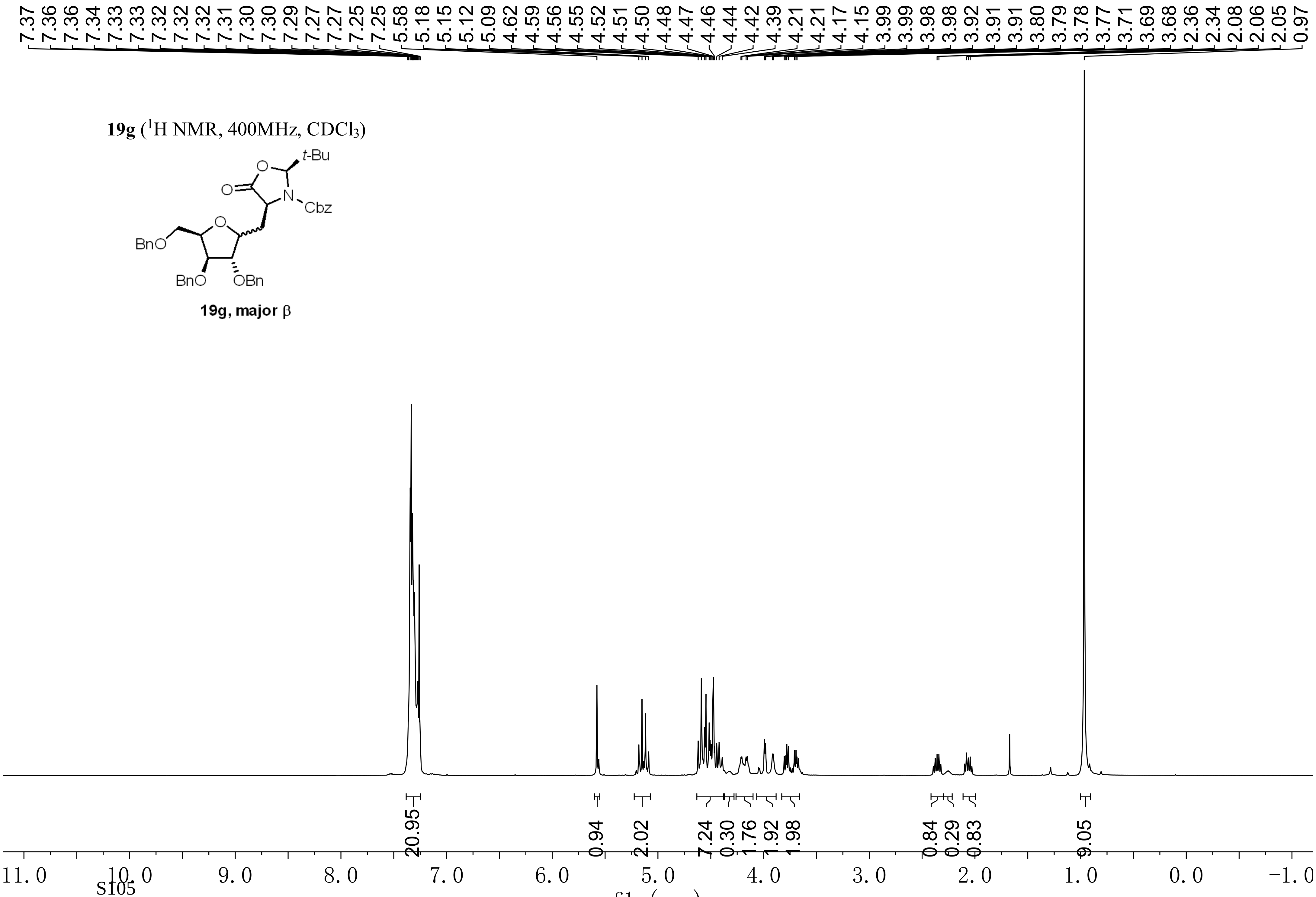



19f (¹H-¹H COSY)
t-Bu
Cbz
BnO
BnO
OBn
19f, major β
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)



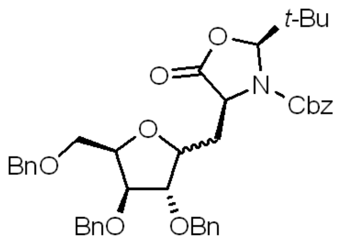
19f (1H-13C Coupled HSQC)
t-Bu
O
O
N
Cbz
BnO
BnO
OBn
19f, major β
f2 (ppm)
f1 (ppm)


19f (1H-13C HSQC)
t-Bu
Cbz
BnO
BnO
OBn
19f, major β
f2 (ppm)
f1 (ppm)

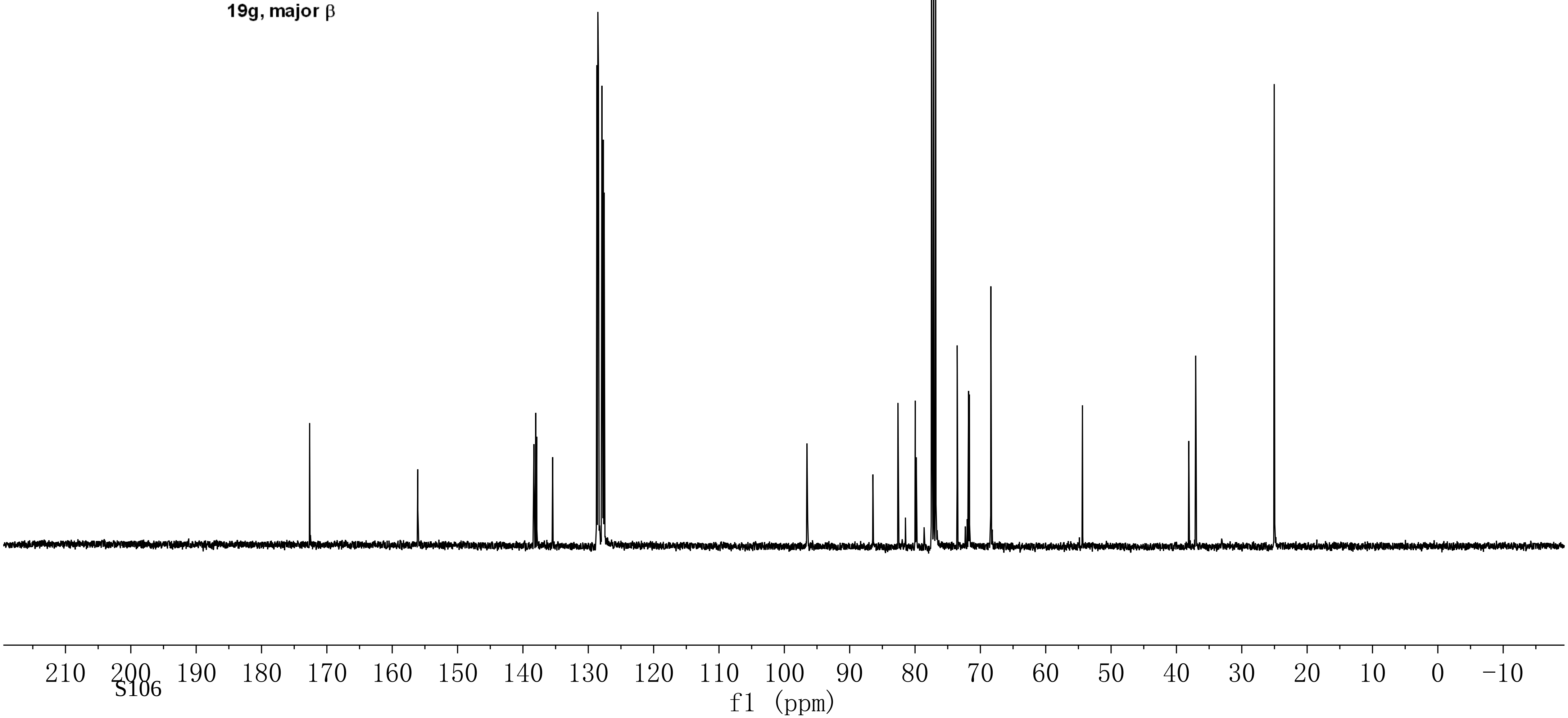


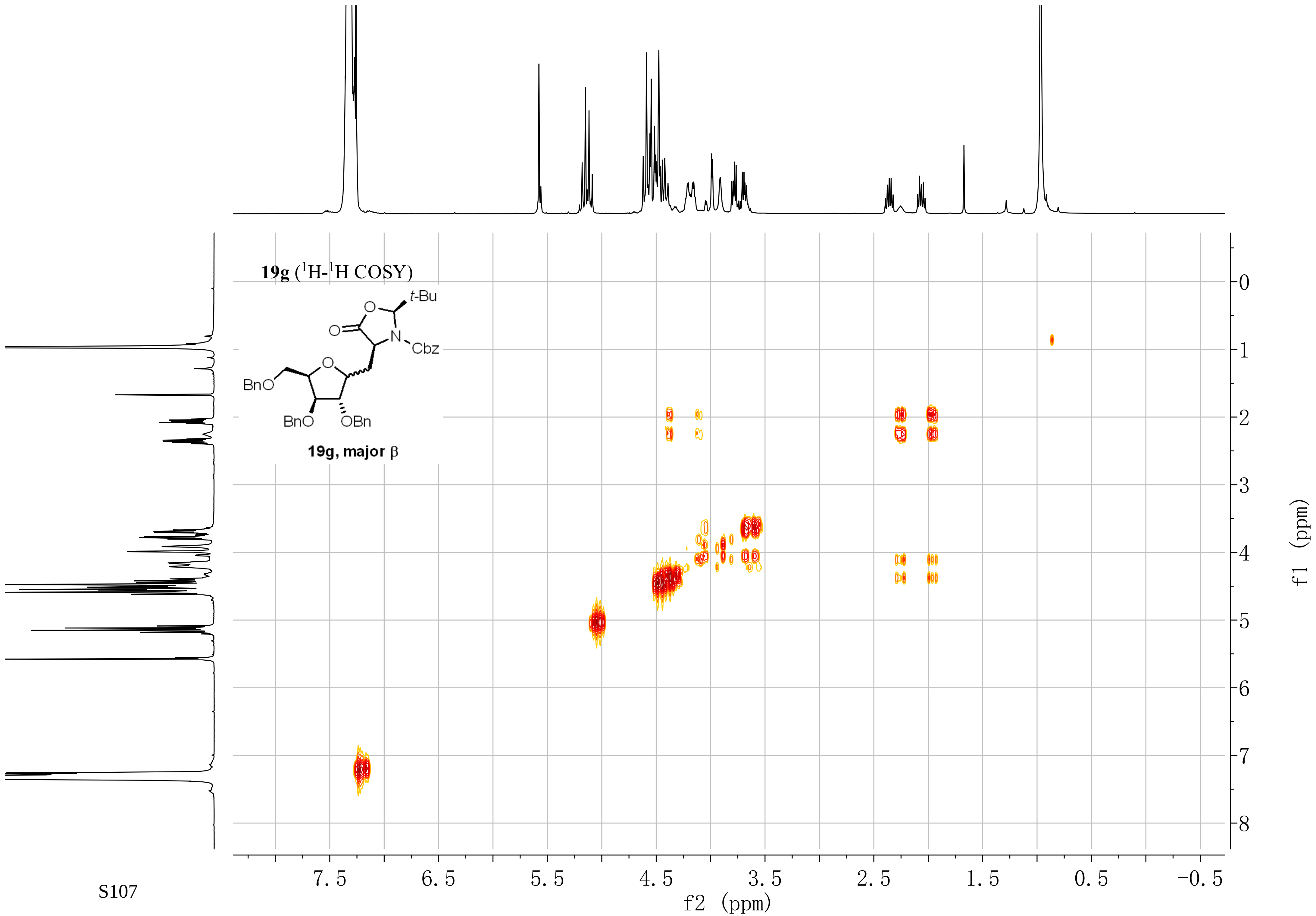
7.37 7.36 7.36 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.27 7.27 7.25 7.25 5.58 5.18 5.15 5.12 5.09 4.62 4.59 4.56 4.55 4.52 4.51 4.50 4.48 4.47 4.46 4.44 4.42 4.39 4.21 4.21 4.17 4.15 3.99 3.99 3.98 3.98 3.92 3.91 3.91 3.80 3.79 3.78 3.77 3.71 3.69 3.68 2.36 2.34 2.08 2.06 2.05 0.97
19g (^{1}H NMR, 400MHz, $CDCl_3$)
t-Bu
O
O
N
Cbz
O
BnO
BnO
OBn
19g, major β
20.95
0.94
2.02
7.24
0.30
1.76
1.92
1.98
0.84
0.29
0.83
9.05
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

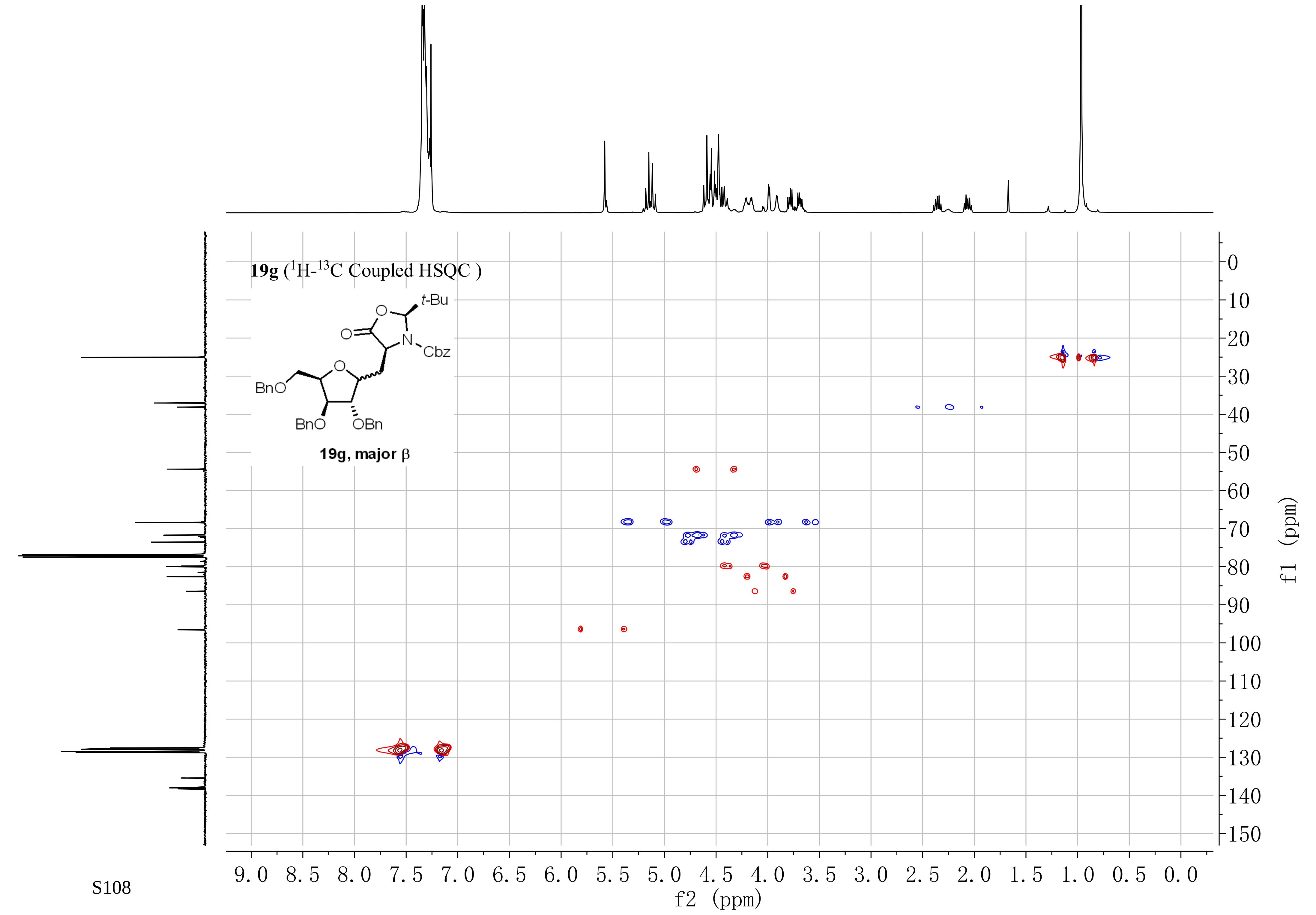
19g (^{13}C NMR, 101MHz, $CDCl_3$)



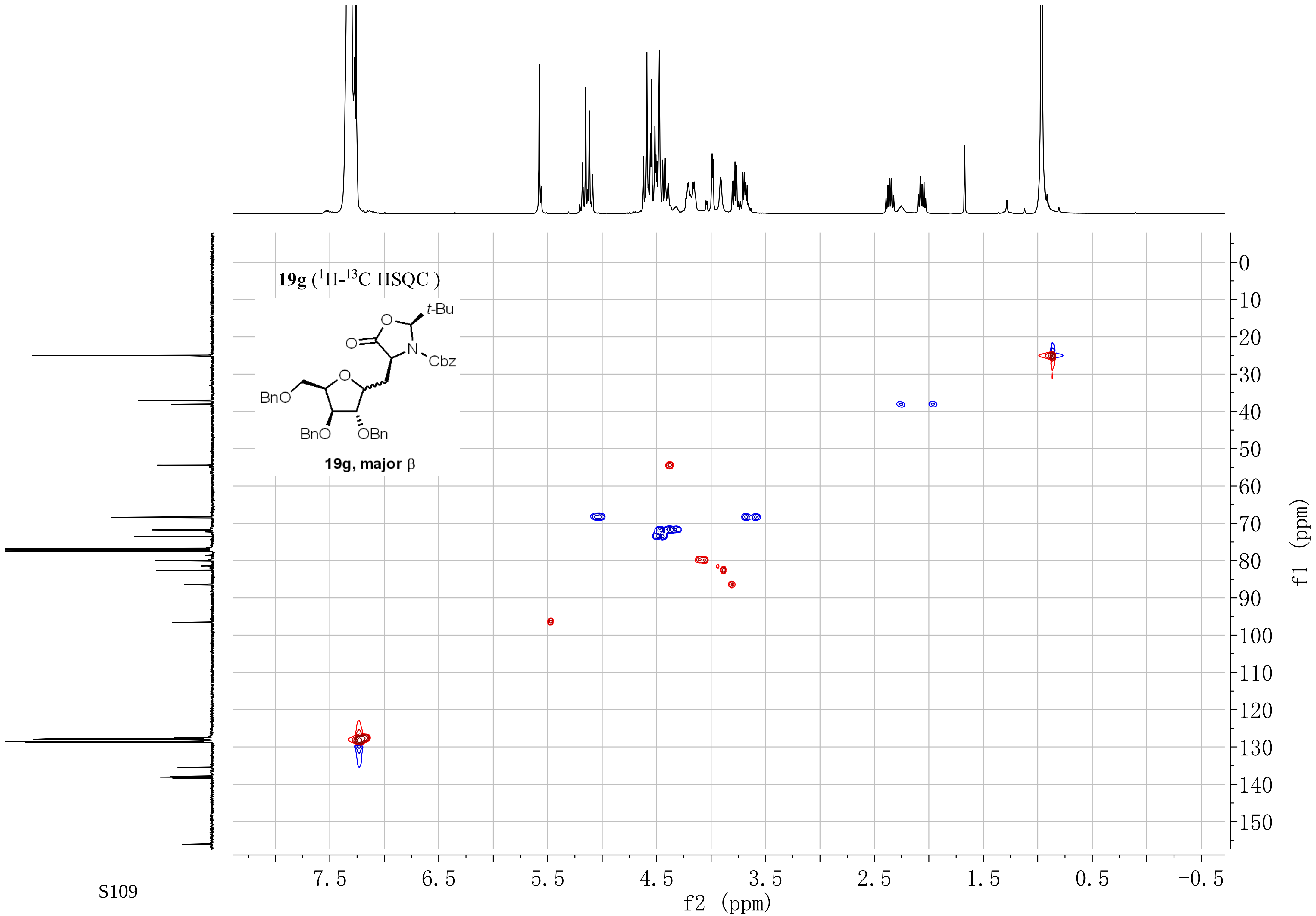
19g, major β



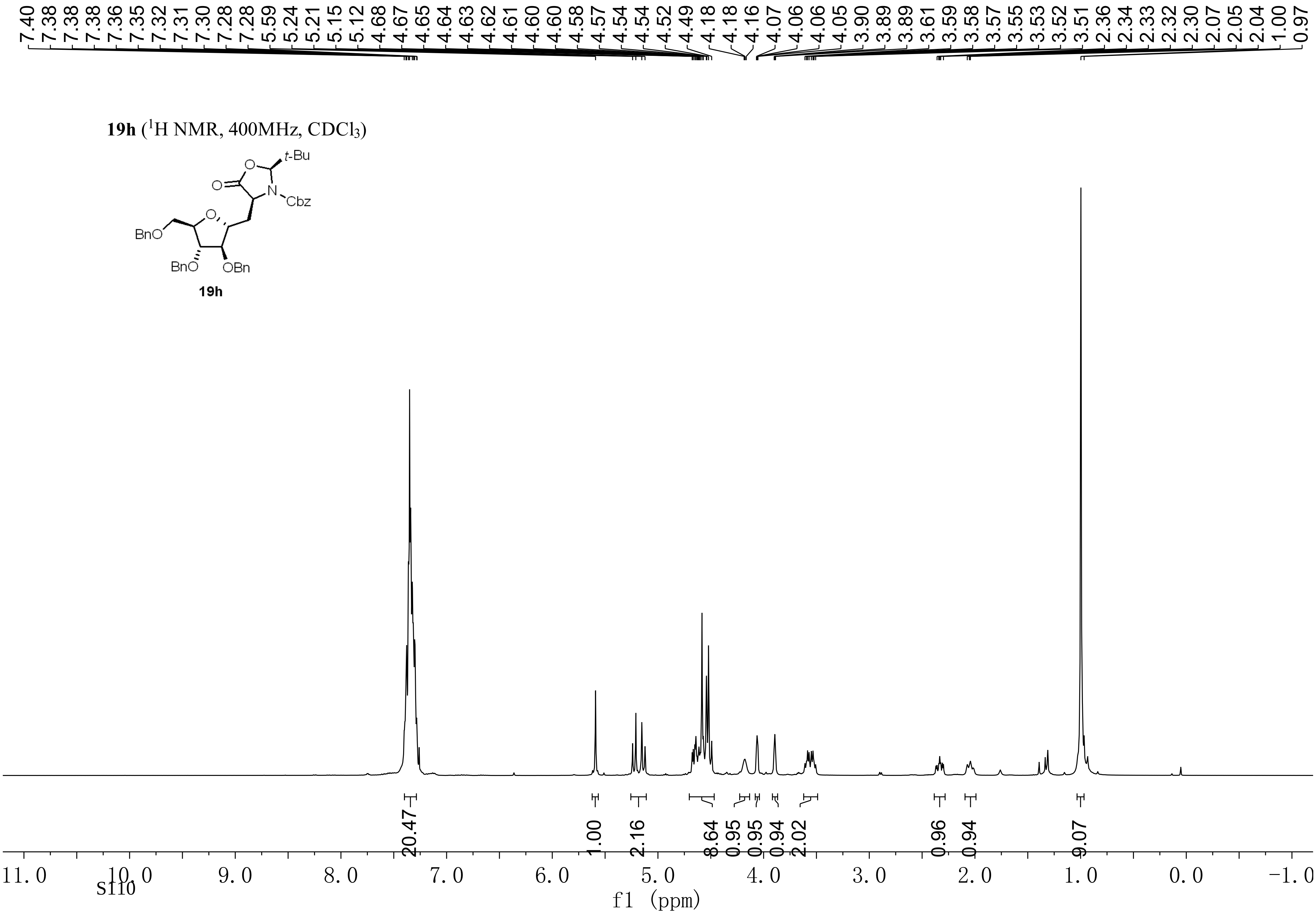

19g (1H-1H COSY)
t-Bu
O
O
N
Cbz
BnO
BnO
OBn
19g, major β
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

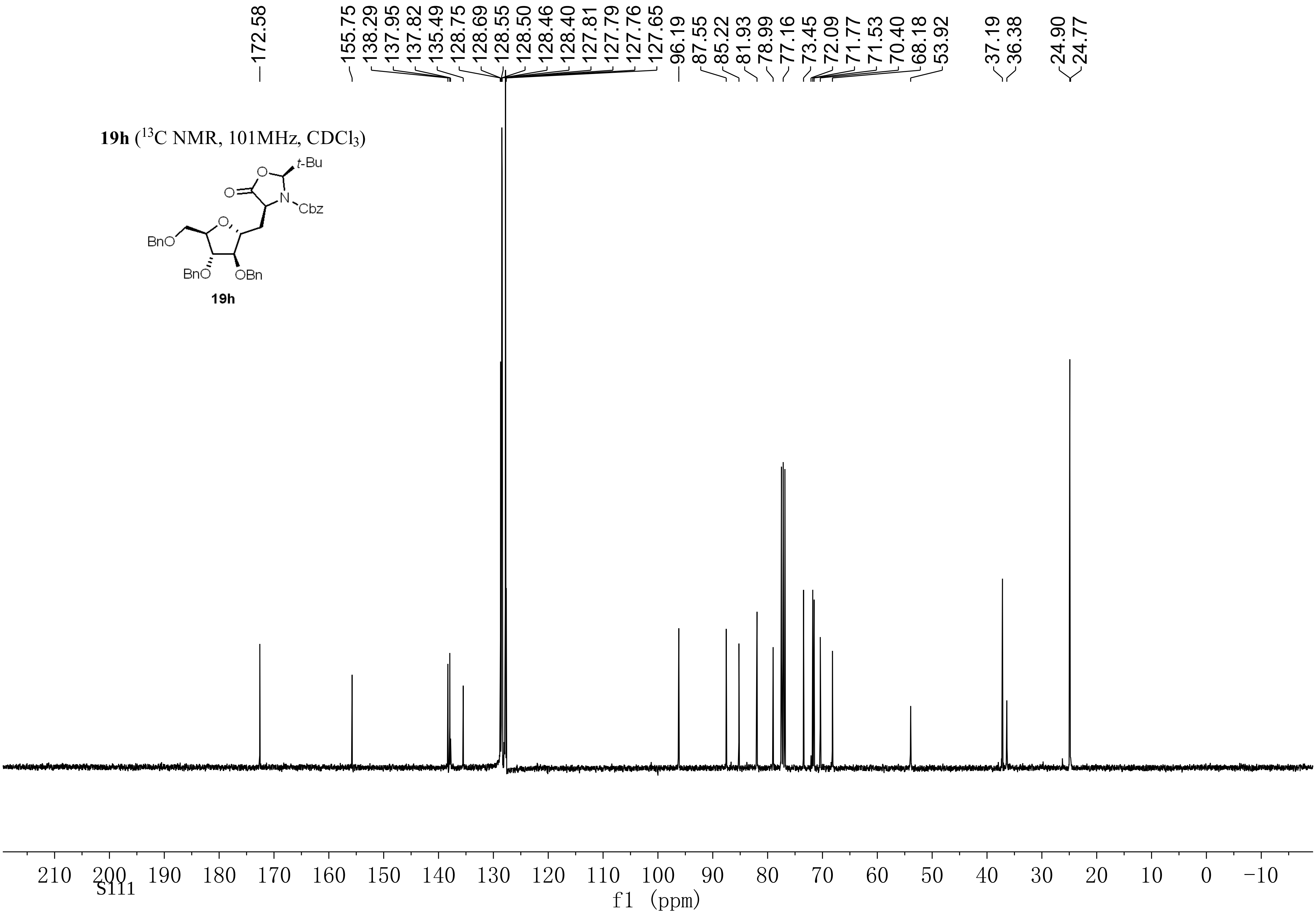


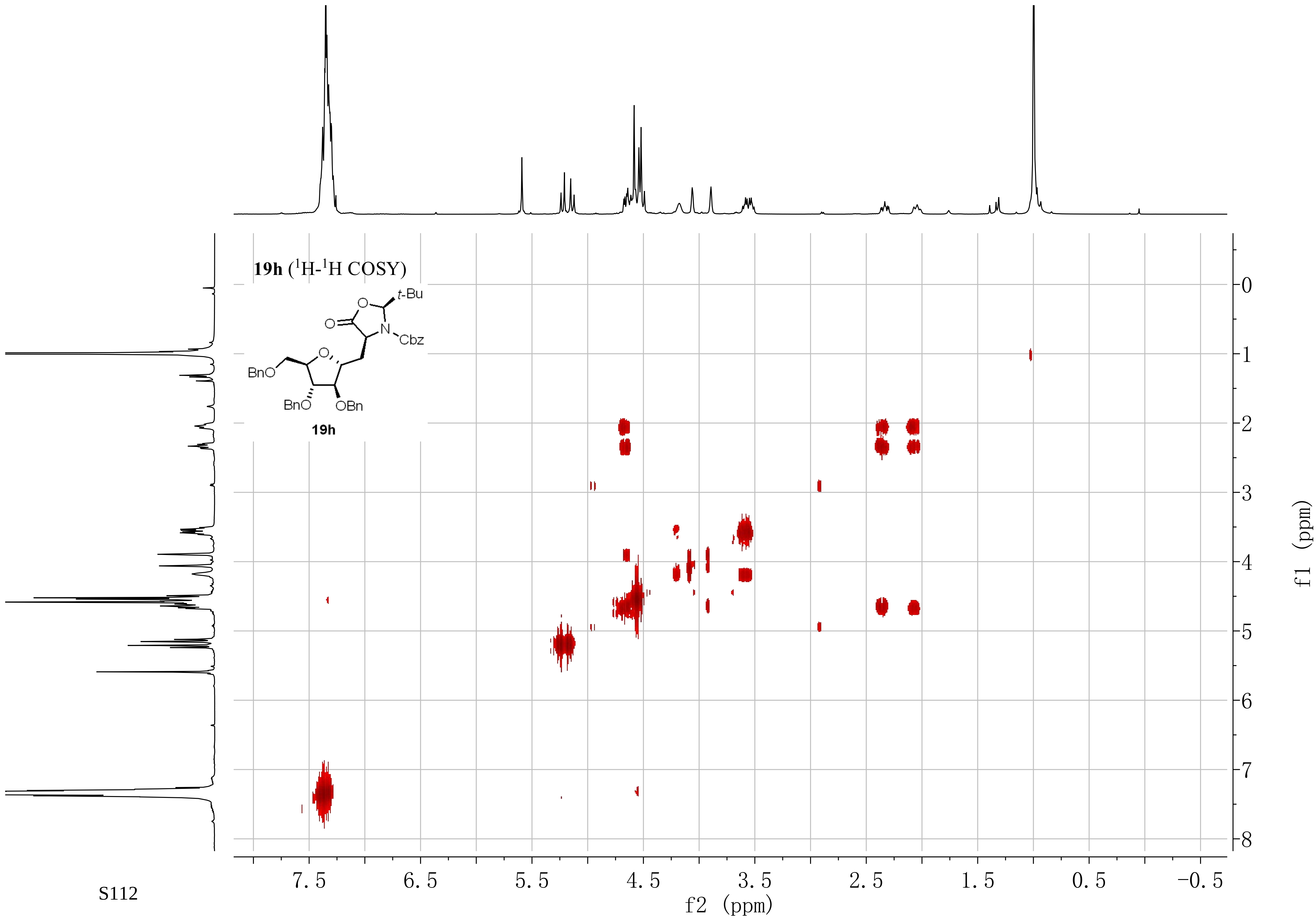
19g (1H-13C Coupled HSQC)
t-Bu
O
O
N
Cbz
BnO
O
BnO
OBn
19g, major β
f2 (ppm)
f1 (ppm)



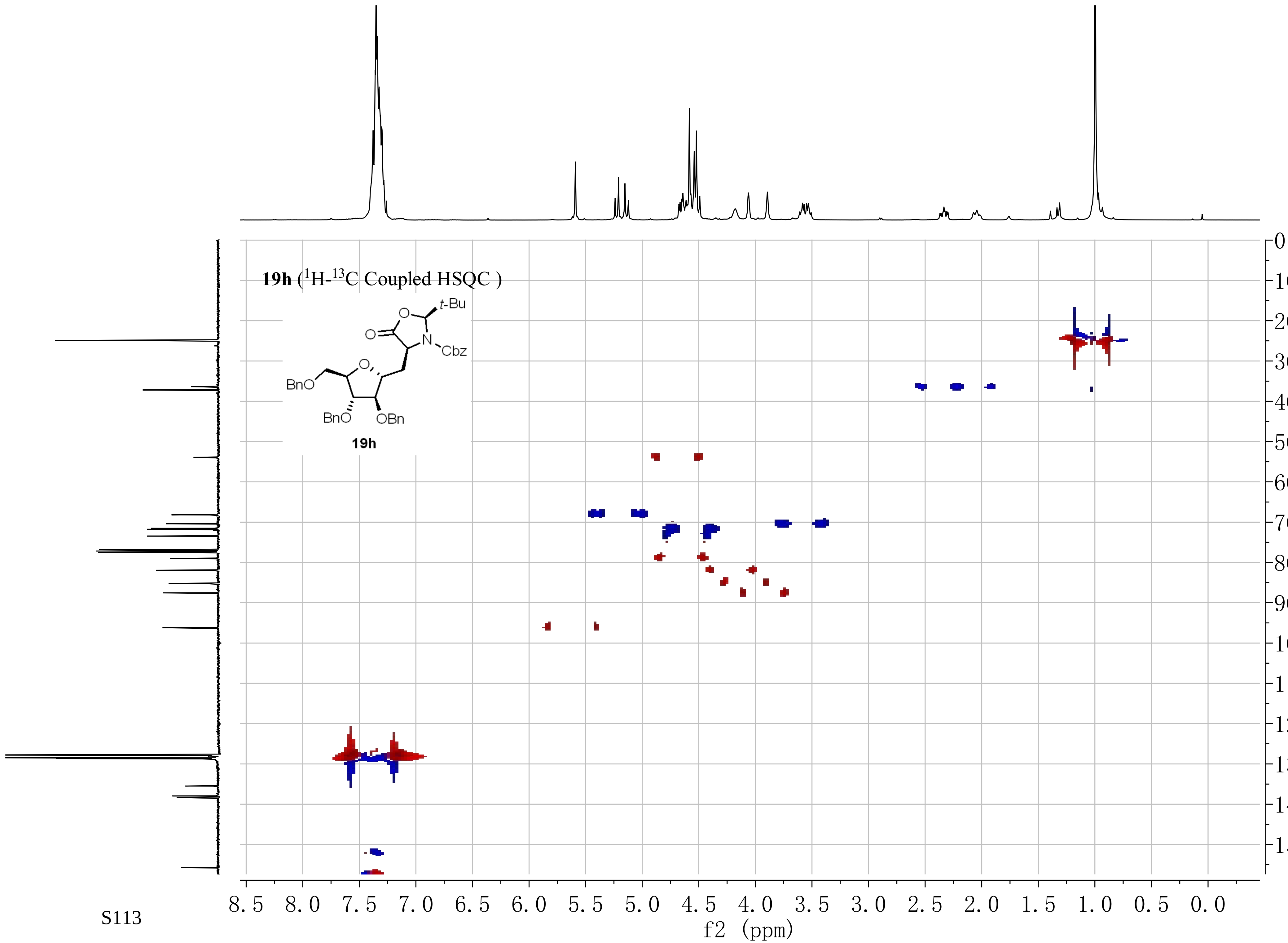
19g (1H-13C HSQC)
t-Bu
O
O
N
Cbz
O
BnO
BnO
OBn
19g, major β
f1 (ppm)
f2 (ppm)


7.40 7.38 7.38 7.38 7.36 7.35 7.32 7.31 7.30 7.28 7.28 5.59 5.24 5.21 5.15 5.12 4.68 4.67 4.65 4.64 4.63 4.62 4.61 4.60 4.60 4.58 4.57 4.54 4.54 4.52 4.49 4.18 4.18 4.16 4.07 4.06 4.06 4.05 3.90 3.89 3.89 3.61 3.59 3.58 3.57 3.55 3.53 3.52 3.51 2.36 2.34 2.33 2.32 2.30 2.07 2.05 2.04 1.00 0.97
19h (^{1}H NMR, 400MHz, $CDCl_3$)
t-Bu
O
O
N
Cbz
BnO
BnO
OBn
19h
20.47
1.00
2.16
8.64
0.95
0.95
0.94
2.02
0.96
0.94
9.07
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

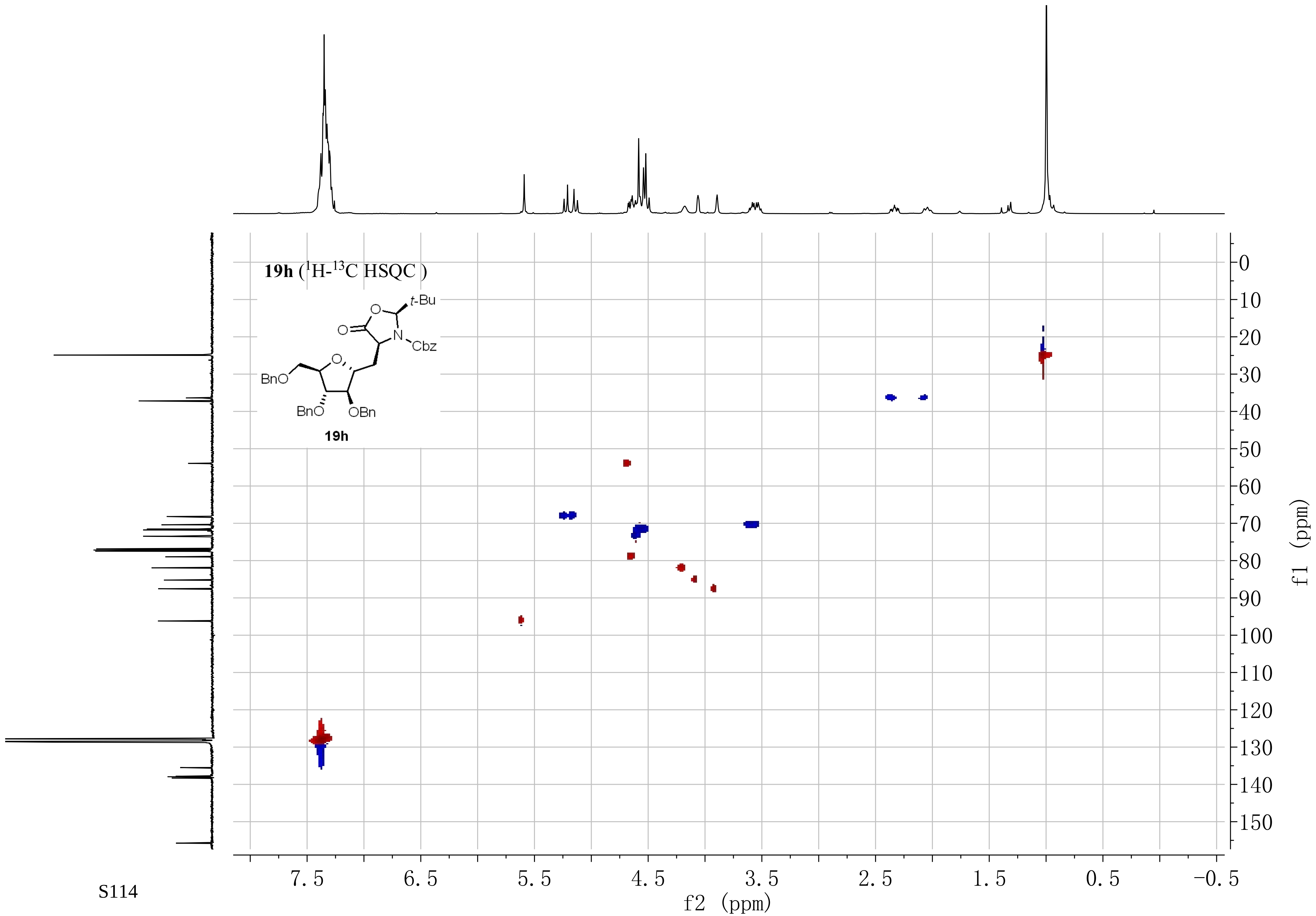

172.58
155.75
138.29
137.95
137.82
135.49
128.75
128.69
128.55
128.50
128.46
128.40
127.81
127.79
127.76
127.65
96.19
87.55
85.22
81.93
78.99
77.16
73.45
72.09
71.77
71.53
70.40
68.18
53.92
37.19
36.38
24.90
24.77
19h (^{13}C NMR, 101MHz, $CDCl_3$)
t-Bu
O
O
N
Cbz
O
BnO
BnO
OBn
19h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



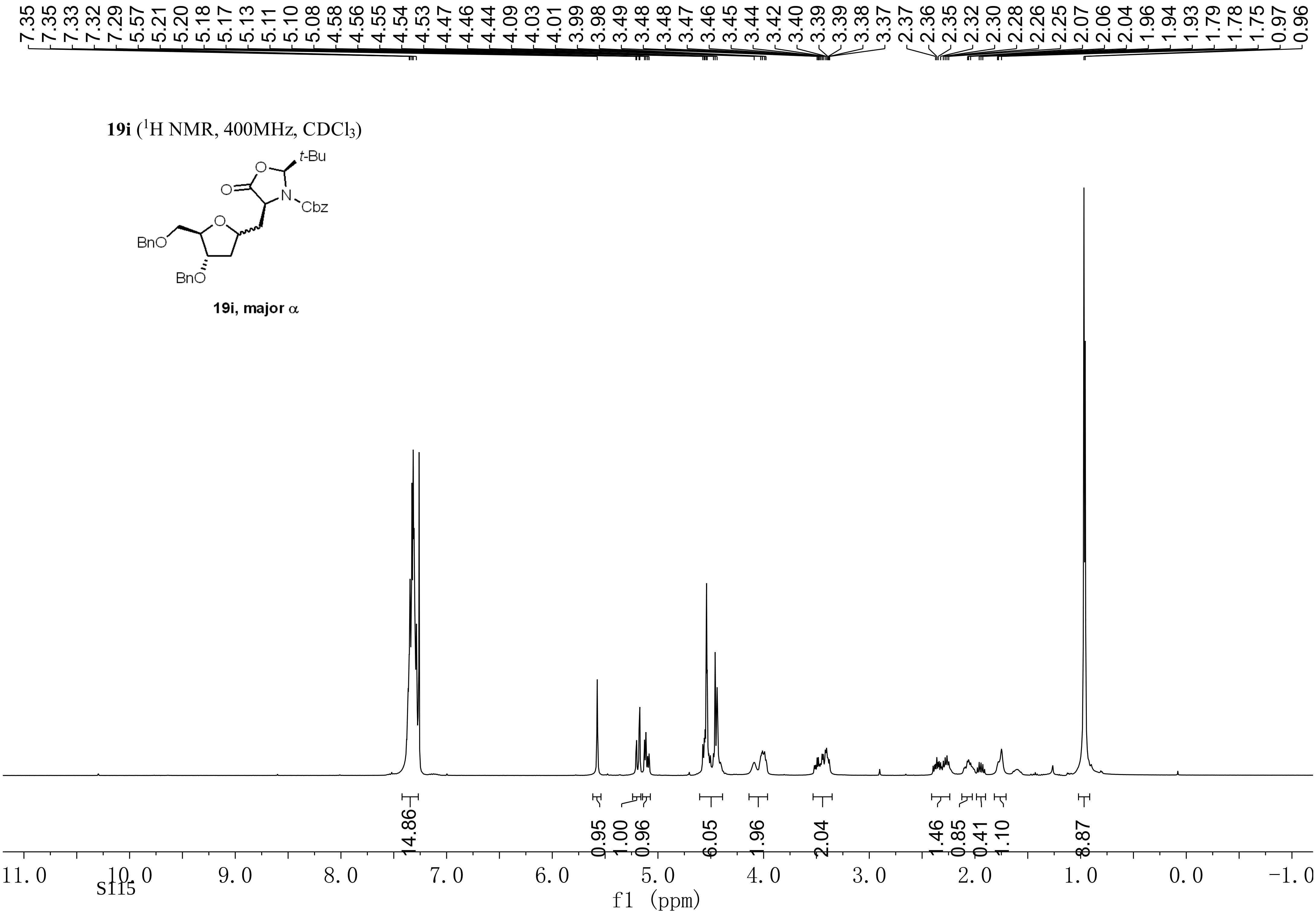
19h (1H-1H COSY)
t-Bu
O
O
N
Cbz
O
BnO
BnO
OBn
19h
f2 (ppm)
f1 (ppm)
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
0
1
2
3
4
5
6
7
8



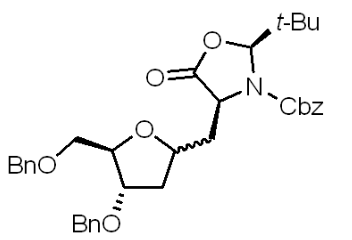
19h (1H-13C Coupled HSQC)
t-Bu
O
O
N
Cbz
O
BnO
BnO
OBn
19h
f2 (ppm)
f1 (ppm)



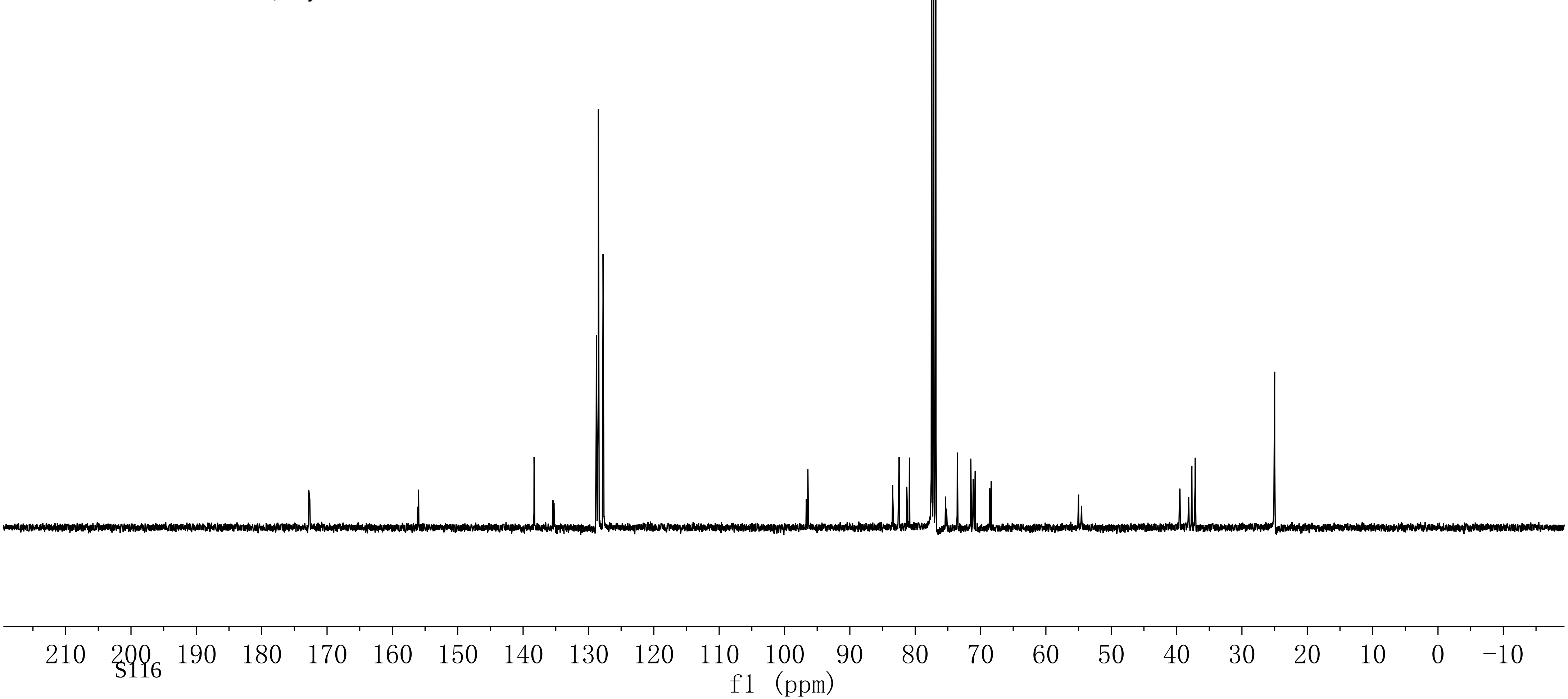
19h (^{1}H-^{13}C HSQC)
t-Bu
O
O
N
Cbz
O
BnO
BnO
OBn
19h
f1 (ppm)
f2 (ppm)

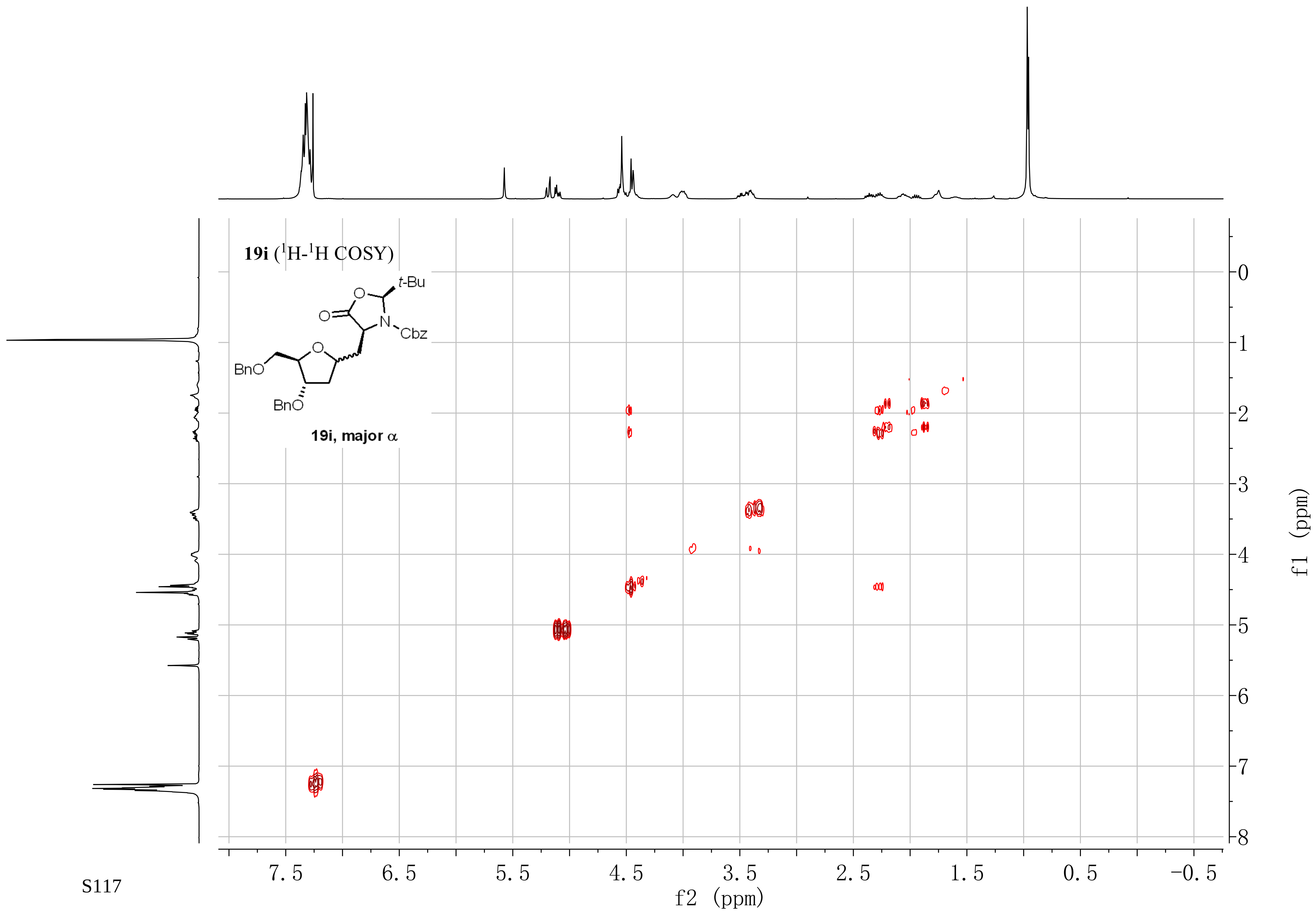

7.35 7.35 7.33 7.32 7.29 5.57 5.21 5.20 5.18 5.17 5.13 5.11 5.10 5.08 4.58 4.56 4.55 4.54 4.53 4.47 4.46 4.44 4.09 4.03 4.01 3.99 3.98 3.49 3.48 3.48 3.47 3.46 3.45 3.44 3.42 3.40 3.39 3.39 3.38 3.37 2.37 2.36 2.35 2.32 2.30 2.28 2.26 2.25 2.07 2.06 2.04 1.96 1.94 1.93 1.79 1.78 1.75 0.97 0.96
19i (1H NMR, 400MHz, CDCl3)
t-Bu
O
O
N
Cbz
O
BnO
BnO
19i, major α
14.86 0.95 1.00 0.96 6.05 1.96 2.04 1.46 0.85 0.41 1.10 8.87
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

19i (^{13}C NMR, 101MHz, $CDCl_3$)

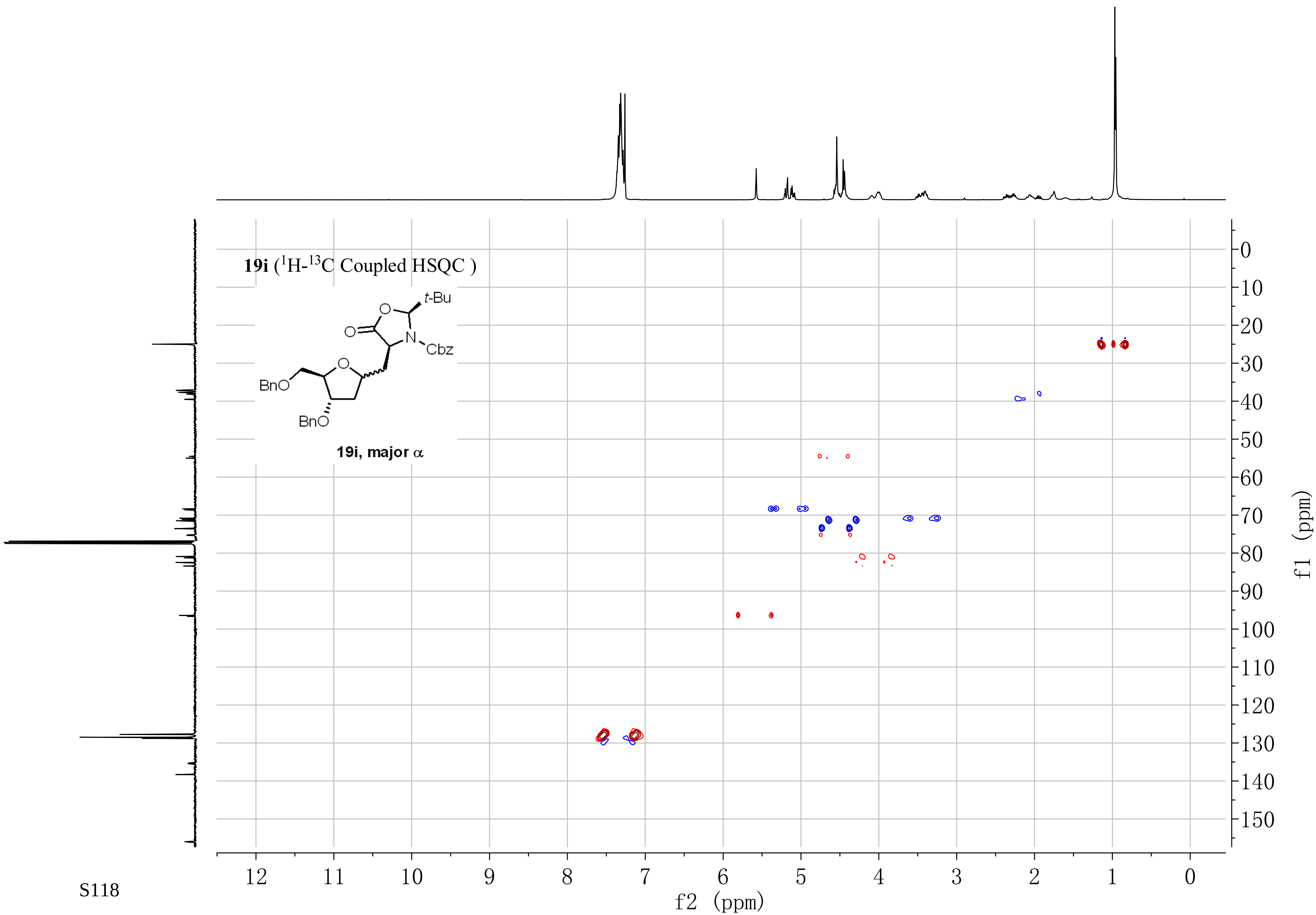


19i, major α

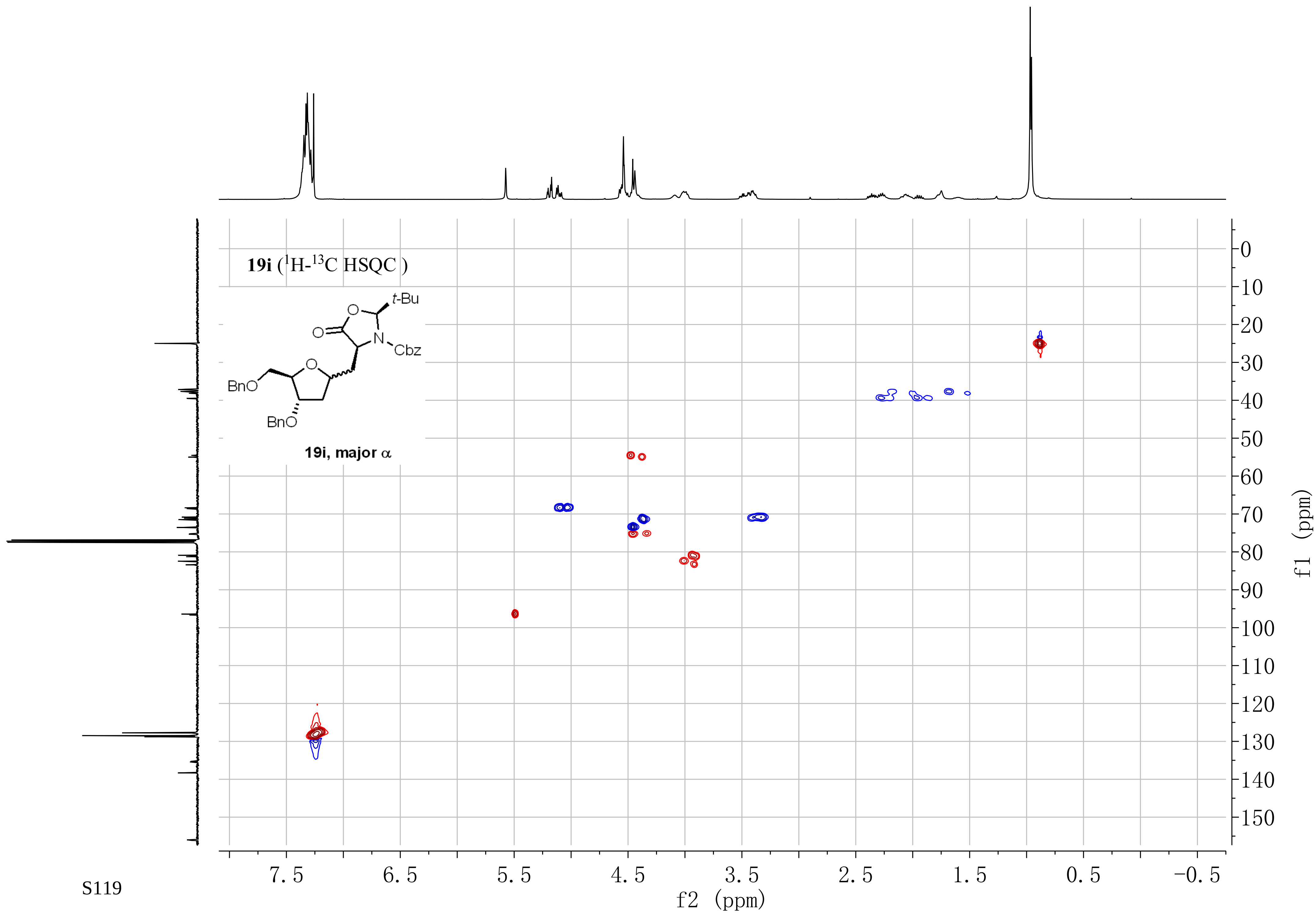


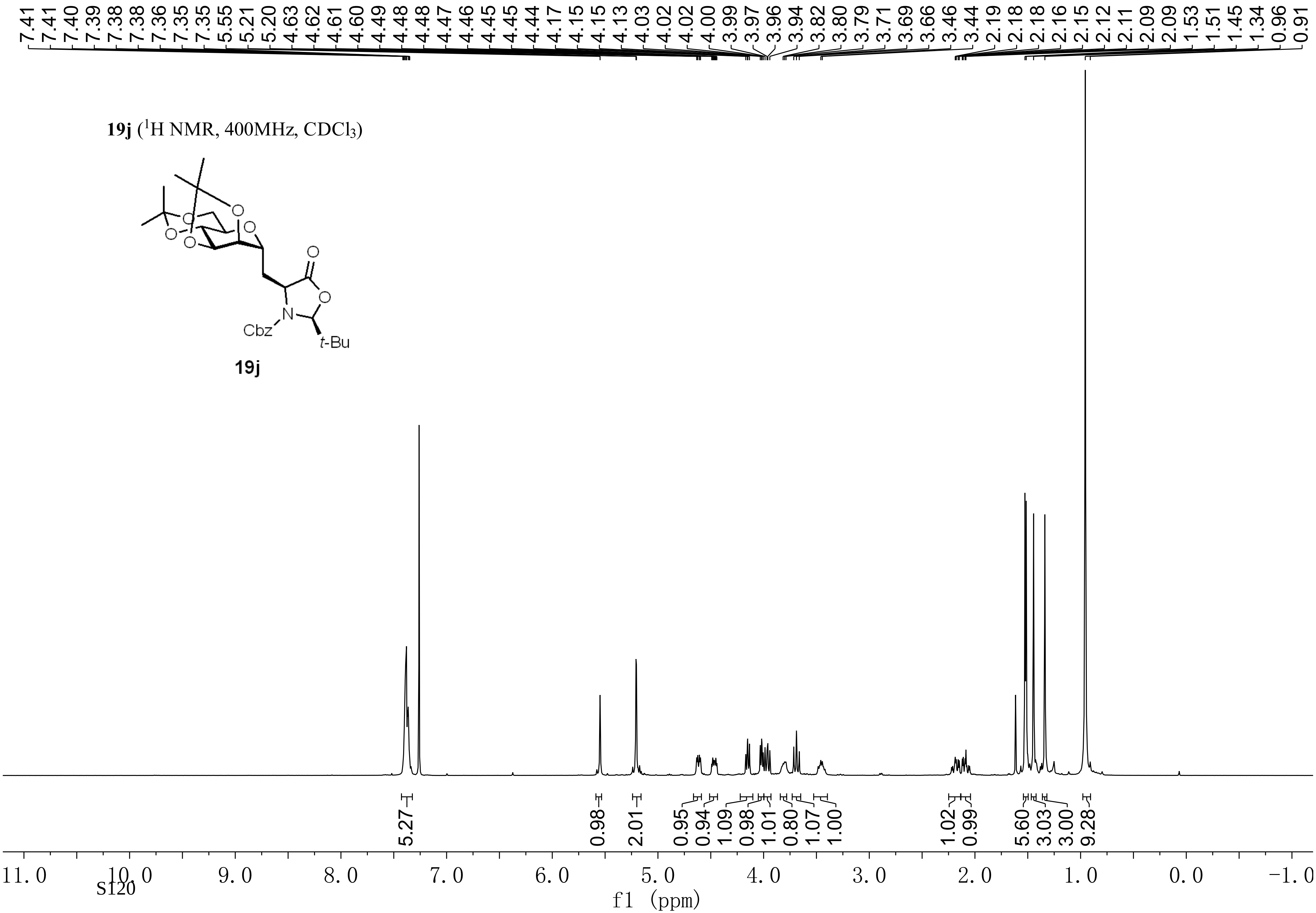


19i (1H-1H COSY)
t-Bu
O
O
N
Cbz
O
BnO
BnO
19i, major α
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)



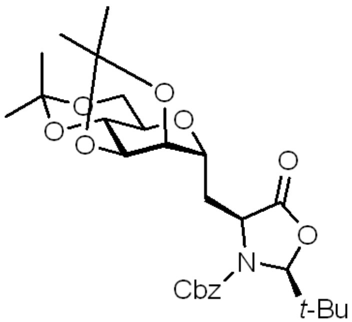
19i (^{1}H-^{13}C Coupled HSQC)
t-Bu
O
O
N
Cbz
O
BnO
BnO
19i, major α
f2 (ppm)
f1 (ppm)


19i (¹H-¹³C HSQC)
t-Bu
O
O
N
Cbz
O
BnO
BnO
19i, major α
f2 (ppm)
f1 (ppm)

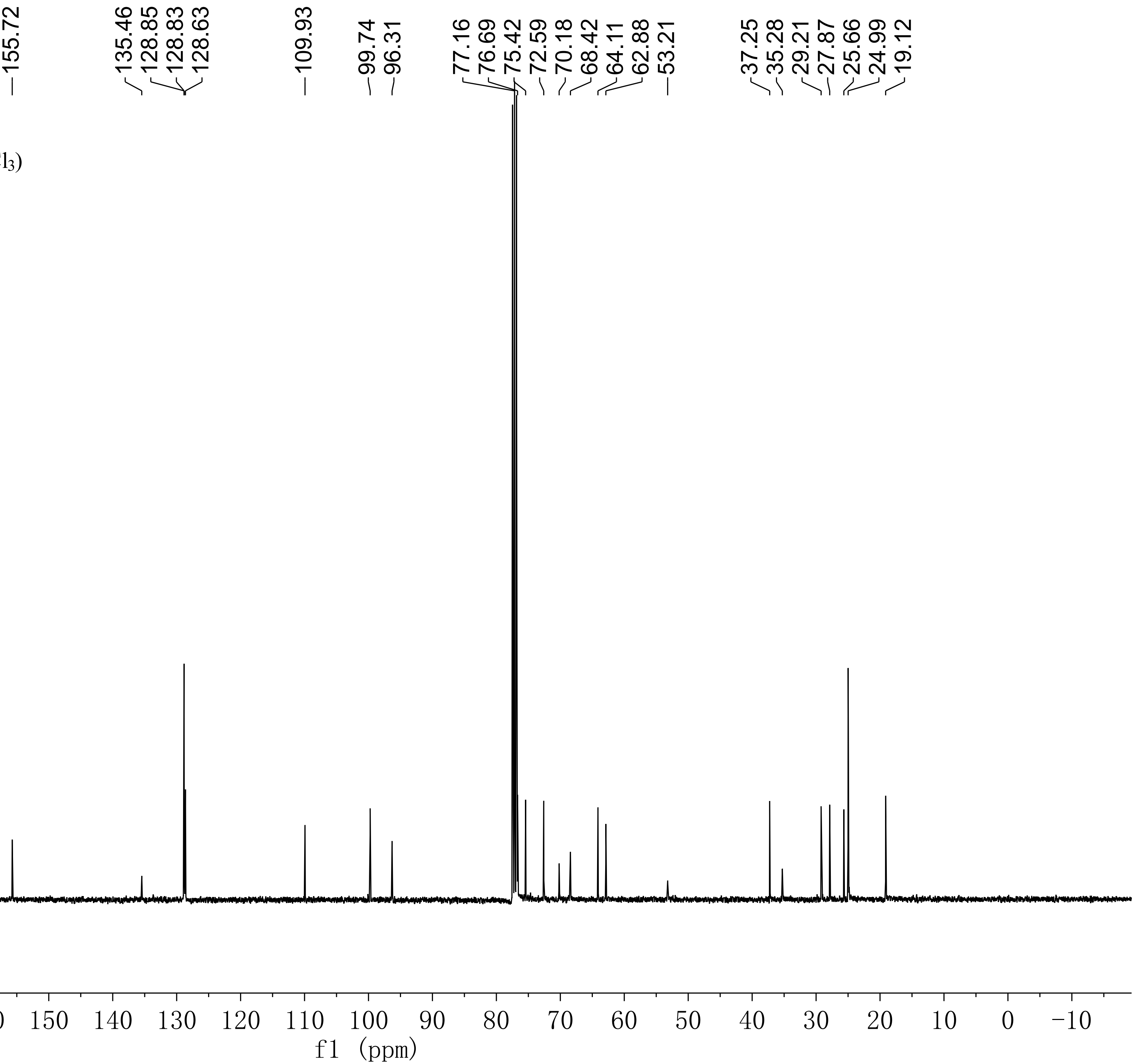


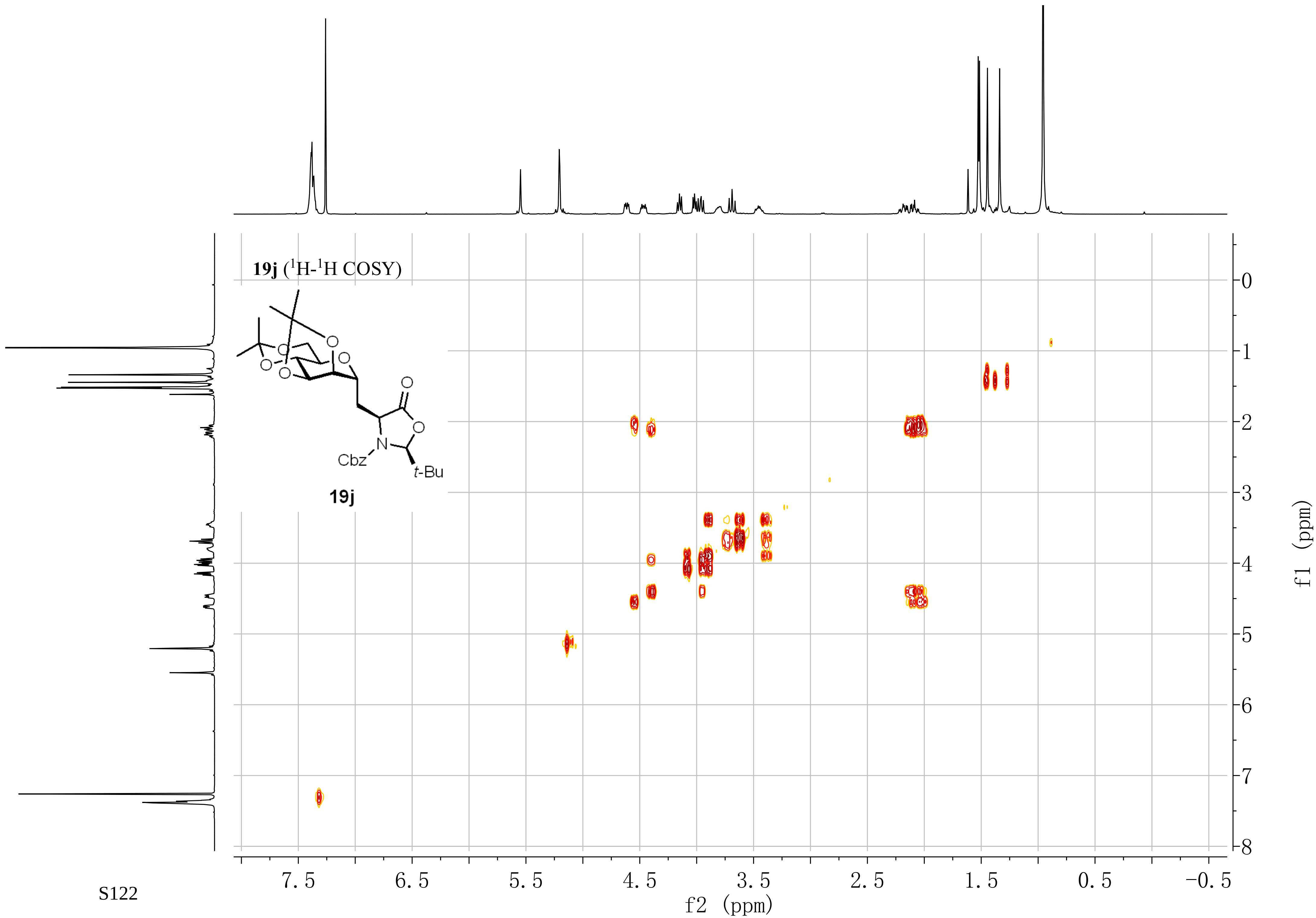
19j (1H NMR, 400MHz, CDCl3)
Cbz
t-Bu
19j
7.41 7.41 7.40 7.39 7.38 7.38 7.36 7.35 7.35 5.55 5.21 5.20 4.63 4.62 4.61 4.60 4.49 4.48 4.48 4.47 4.46 4.45 4.45 4.44 4.17 4.15 4.15 4.13 4.03 4.02 4.02 4.00 3.99 3.97 3.96 3.94 3.82 3.80 3.79 3.71 3.69 3.66 3.46 3.44 2.19 2.18 2.18 2.16 2.15 2.12 2.11 2.09 2.09 1.53 1.51 1.45 1.34 0.96 0.91
5.27 0.98 2.01 0.95 0.94 1.09 0.98 1.01 0.80 1.07 1.00 1.02 0.99 5.60 3.03 3.00 9.28
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

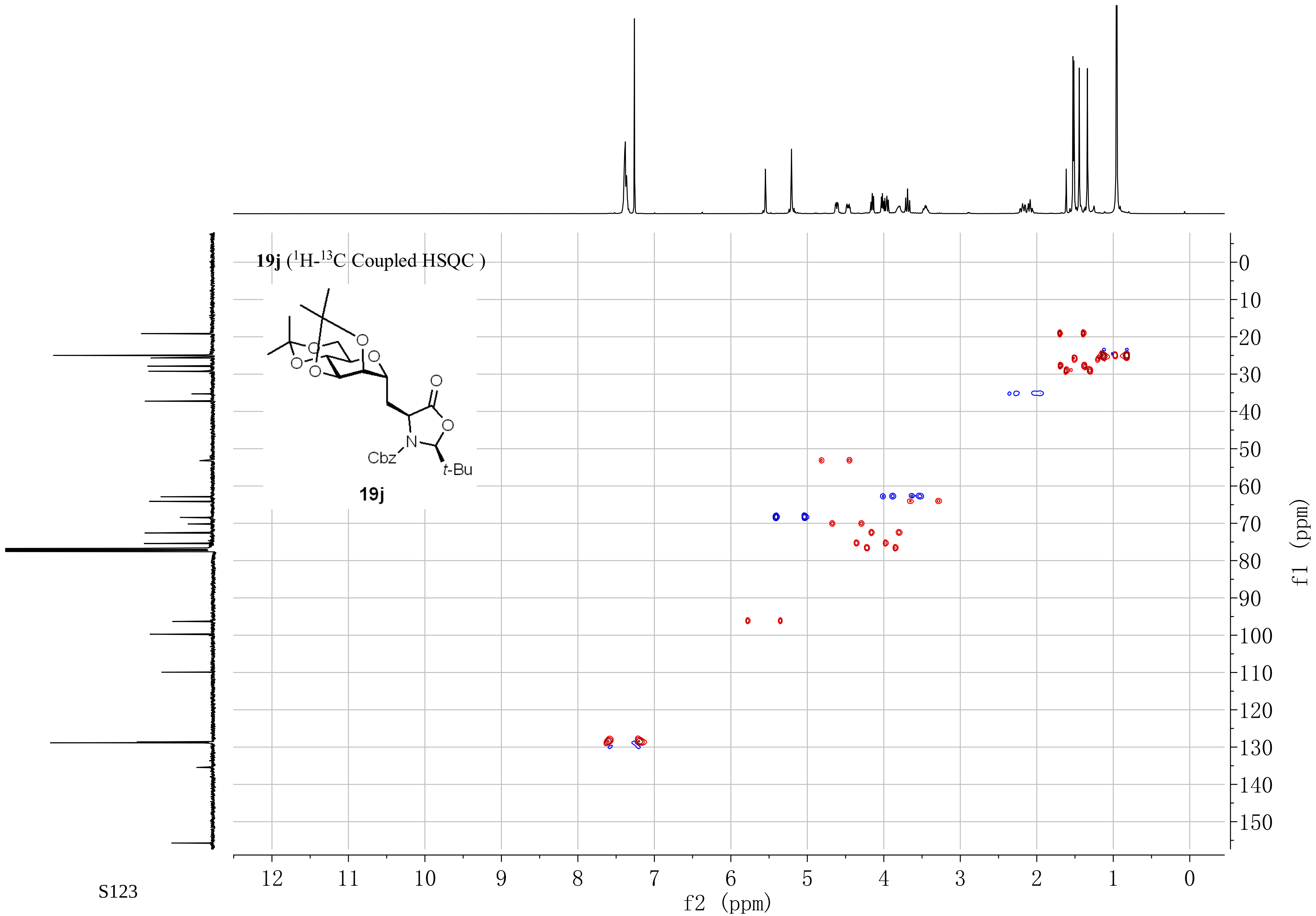
19j (^{13}C NMR, 101MHz, $CDCl_3$)

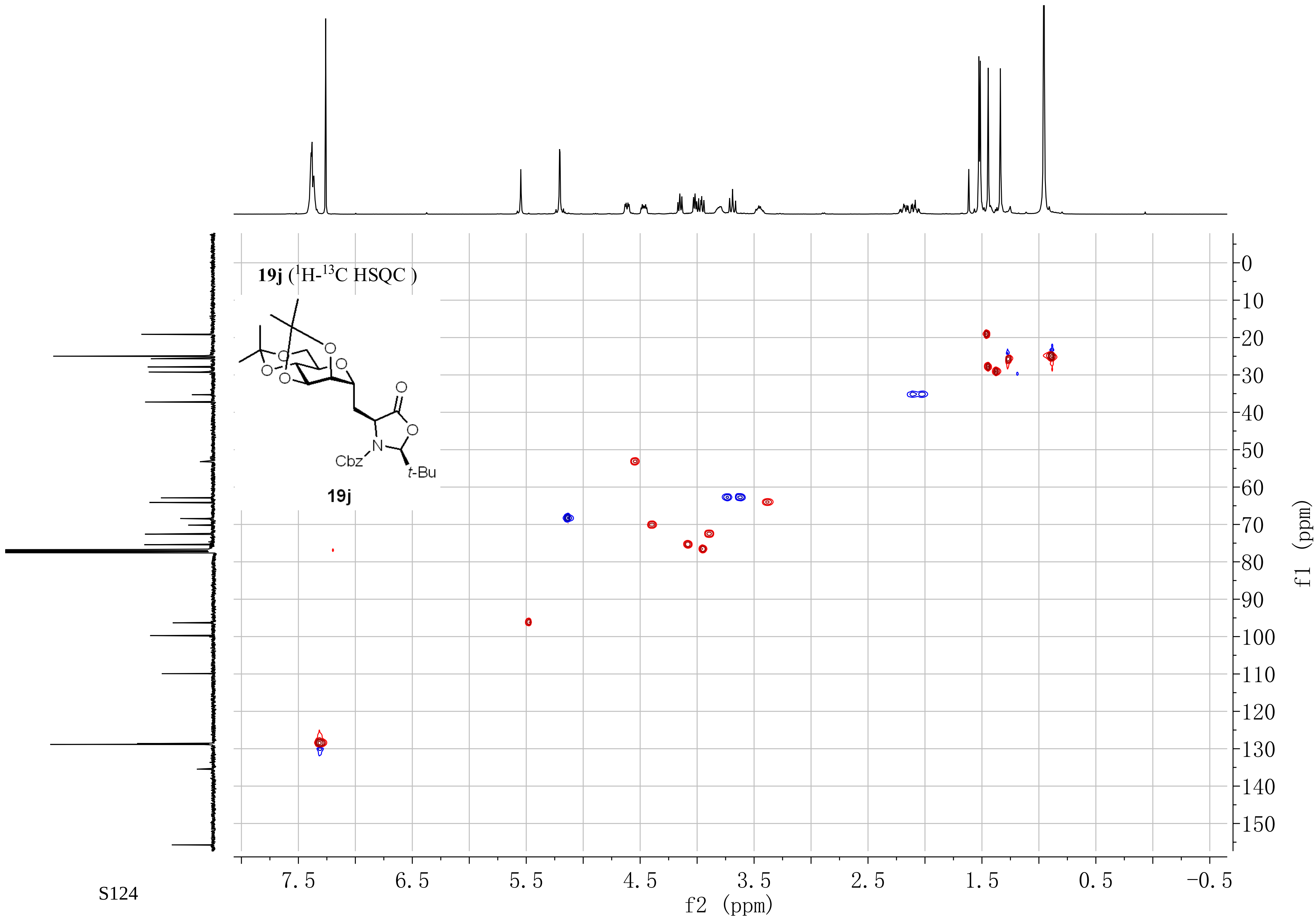


19j



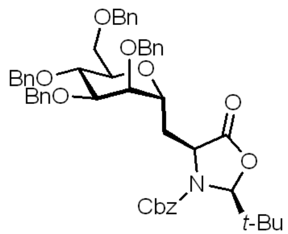

19j (1H-1H COSY)
Cbz
N
t-Bu
19j
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


19j (1H-13C Coupled HSQC)
Cbz
N
O
O
t-Bu
19j
f2 (ppm)
f1 (ppm)

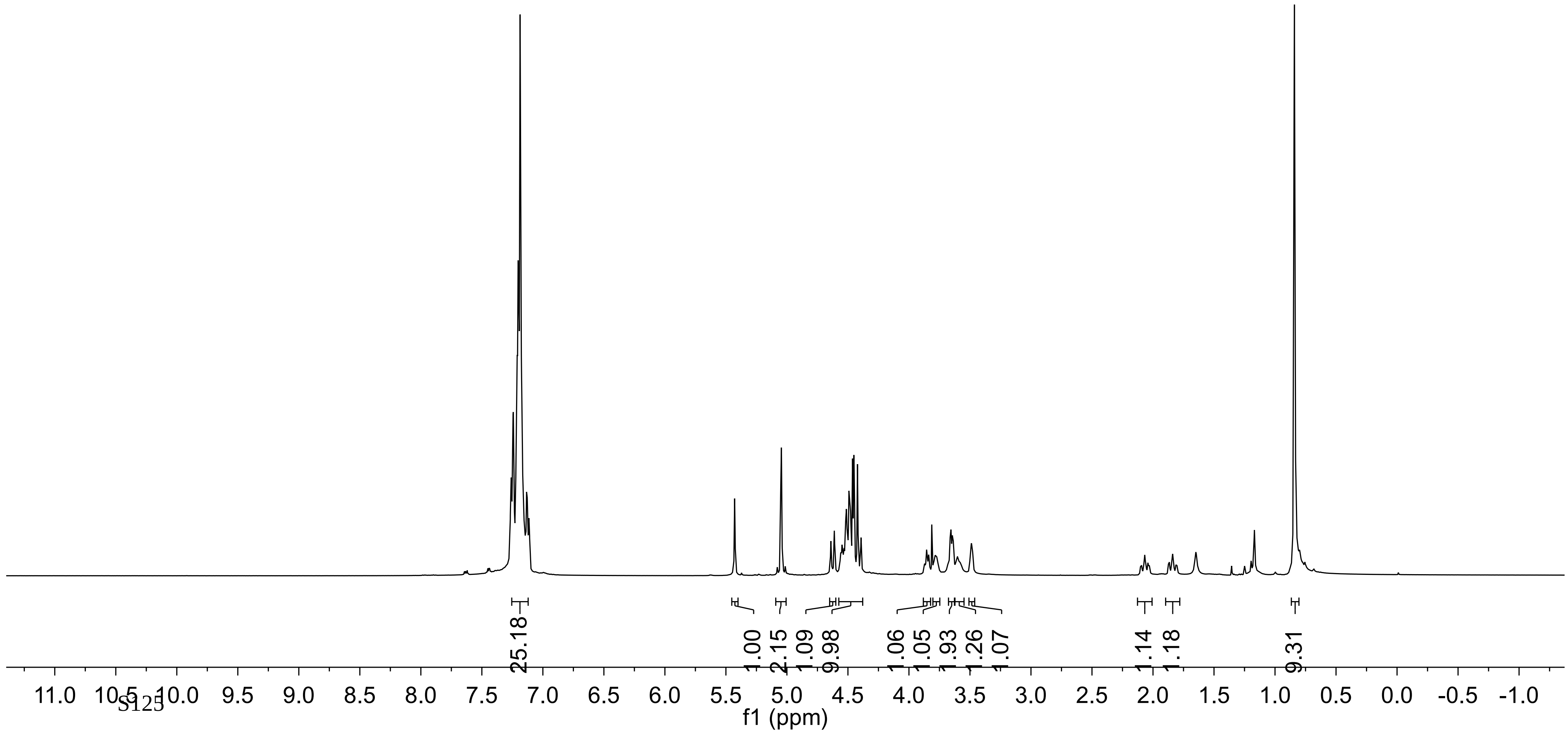


19j (^{1}H-^{13}C HSQC)
Cbz
N
O
t-Bu
19j
f2 (ppm)
f1 (ppm)
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

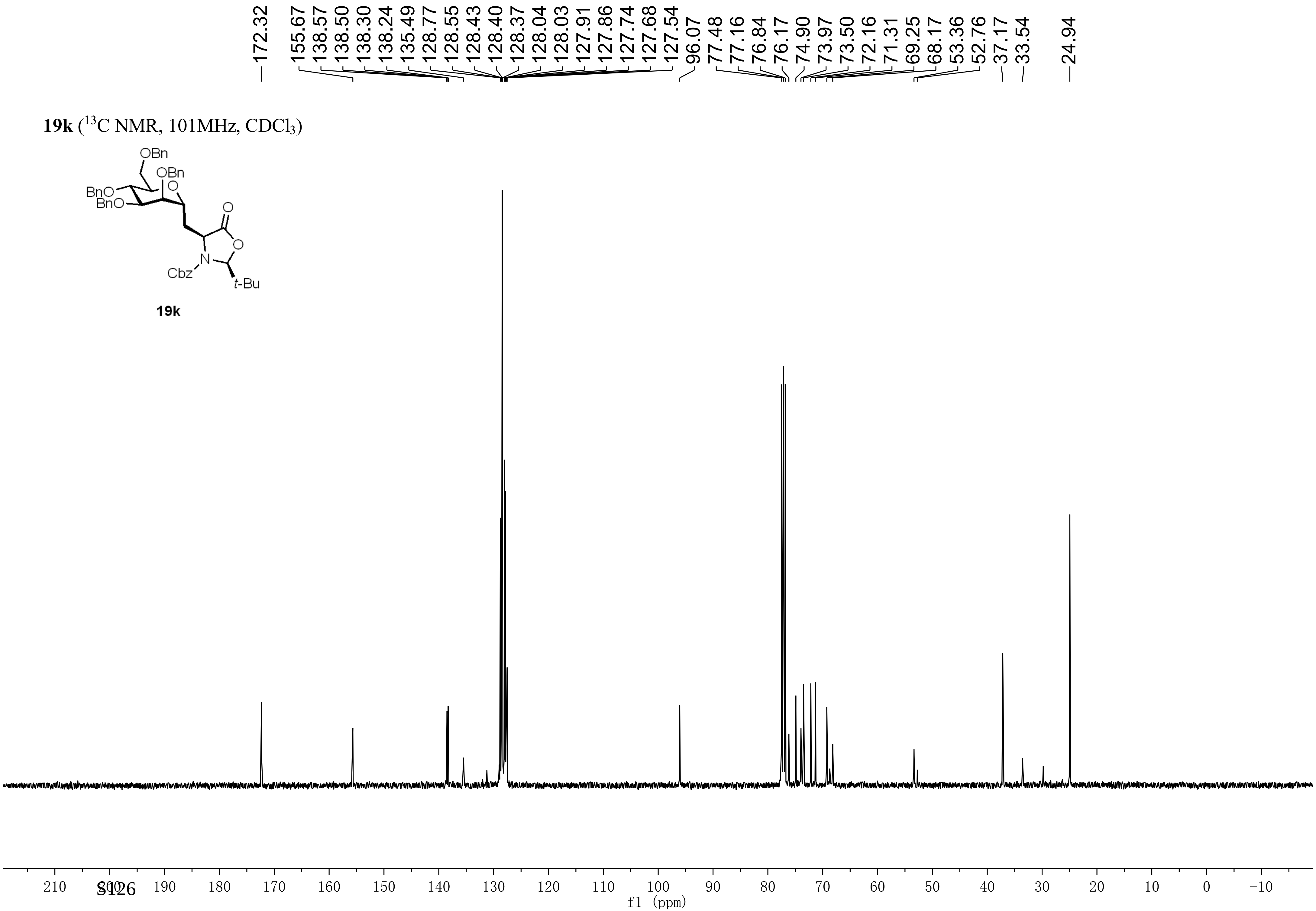
19k (^{1}H NMR, 400MHz, $CDCl_3$)



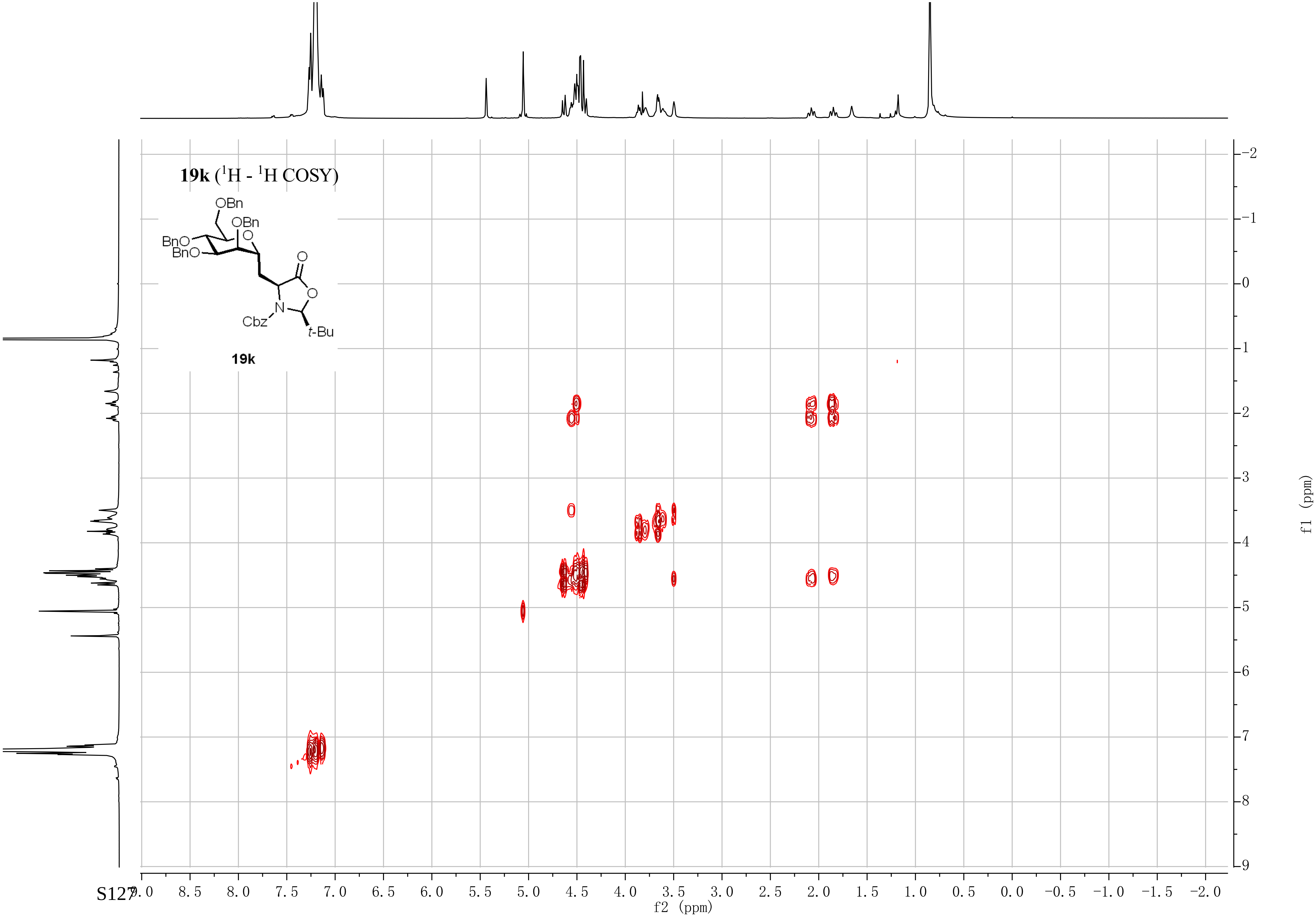
19k

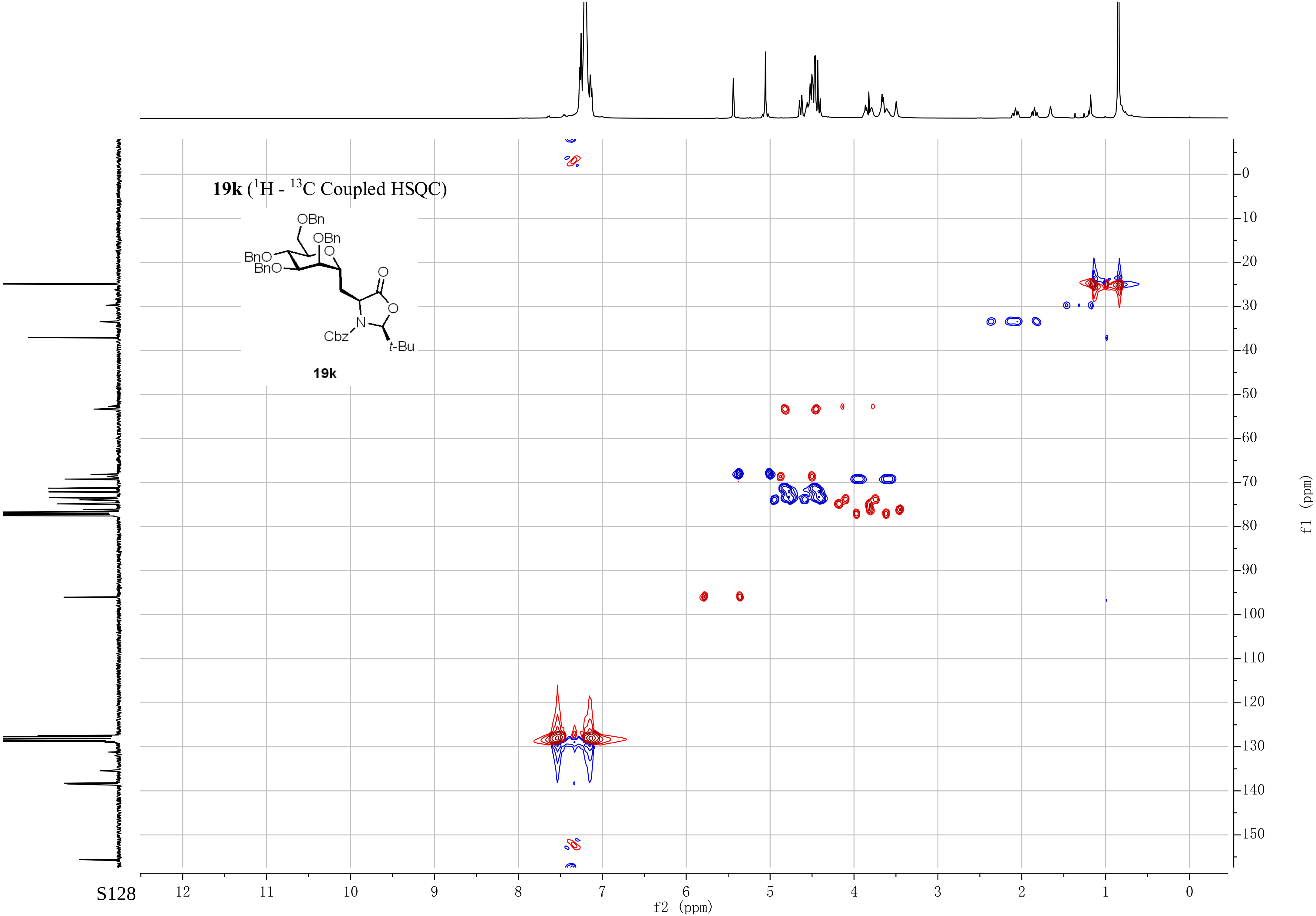


19k (^{13}C NMR, 101MHz, $CDCl_3$)

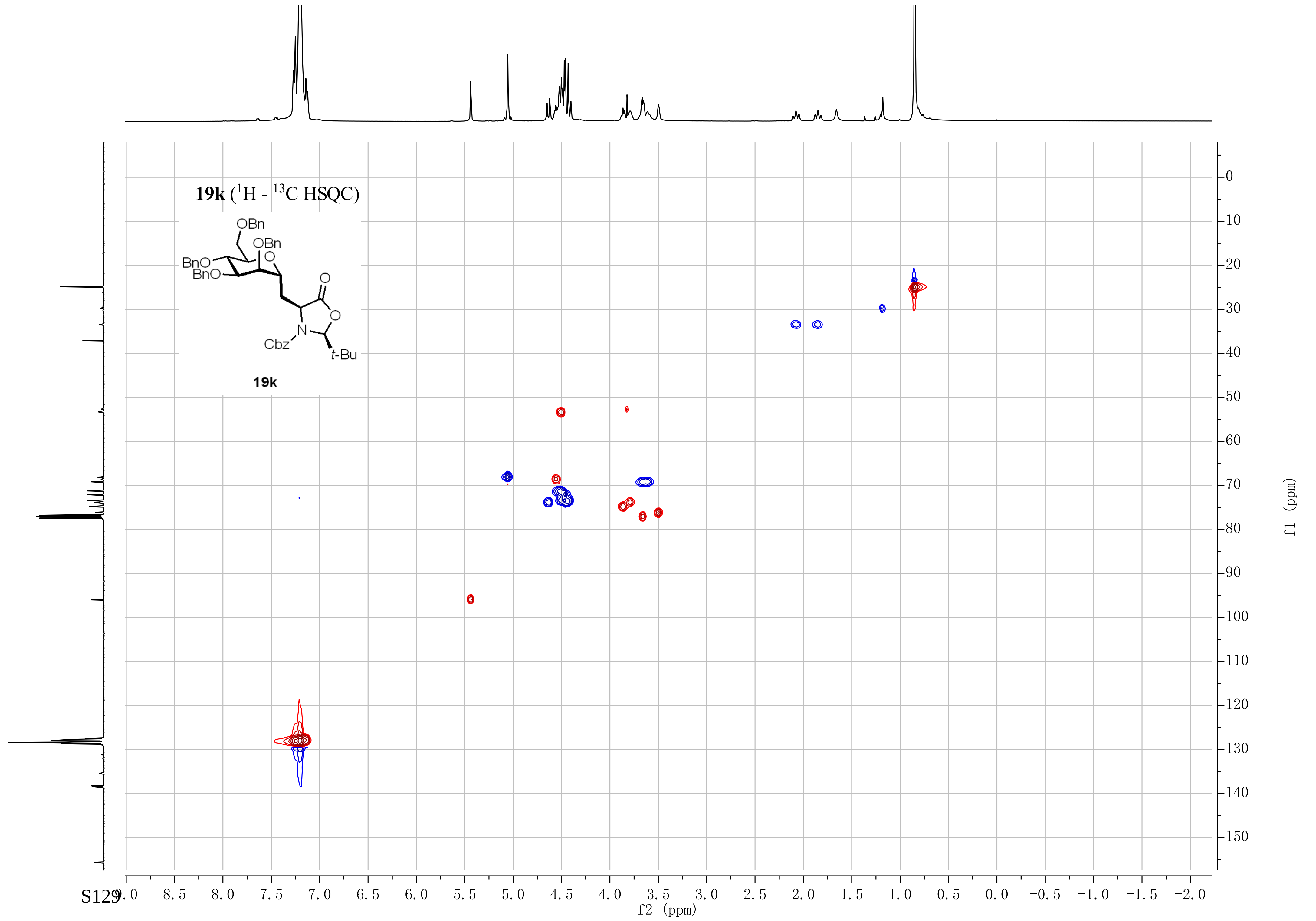


19k


19k (¹H - ¹H COSY)
OBn
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19k
f2 (ppm)
f1 (ppm)

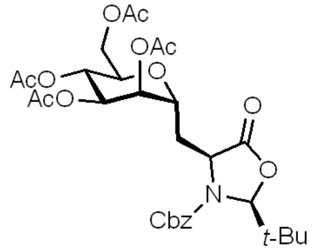


19k (^{1}H - ^{13}C Coupled HSQC)
OBn
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19k
f2 (ppm)
f1 (ppm)

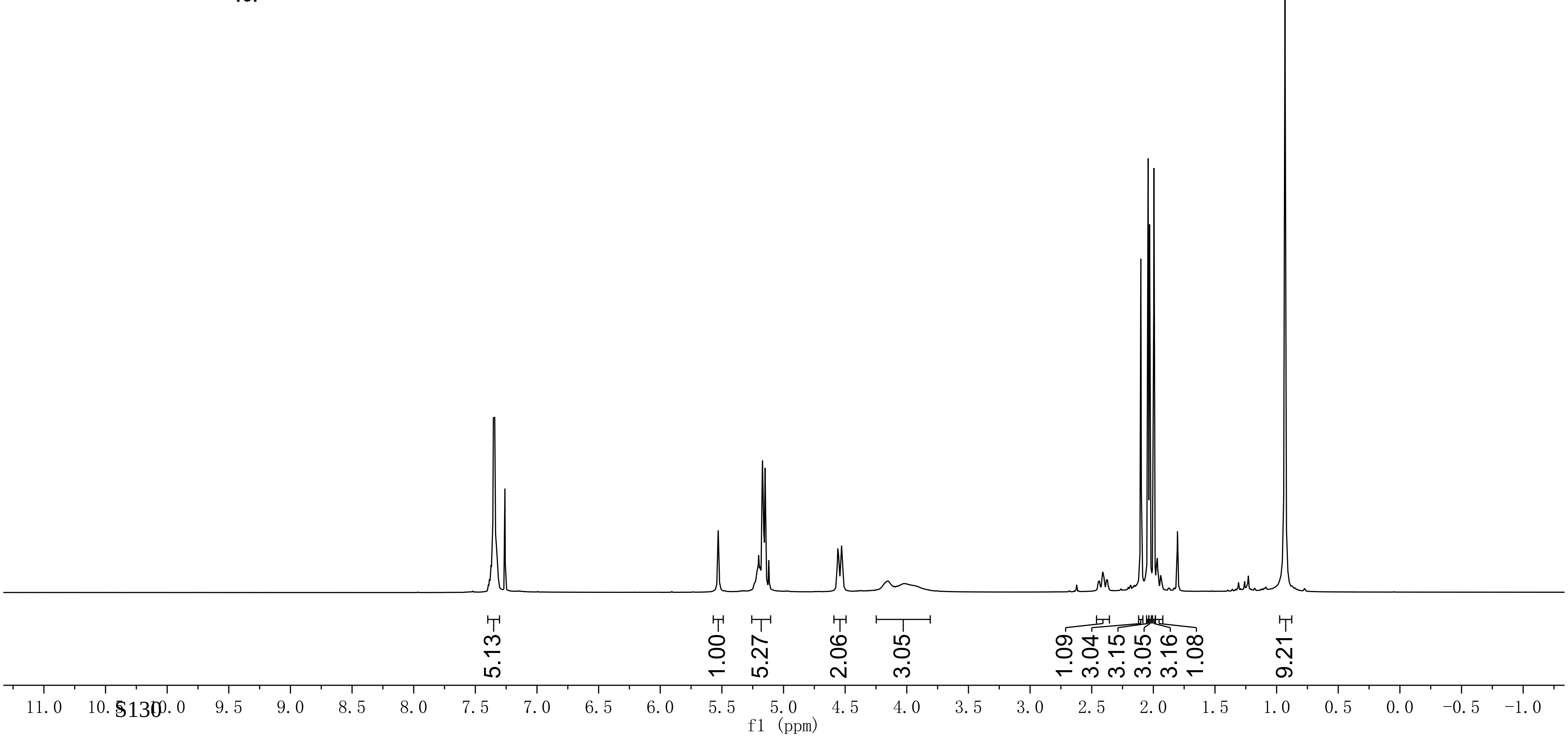


19k (1H - 13C HSQC)
OBn
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19k
f1 (ppm)
f2 (ppm)

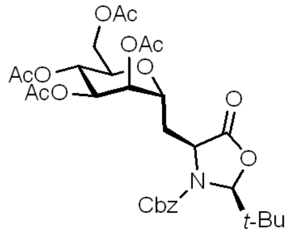
19l (^{1}H NMR, 400MHz, $CDCl_3$)



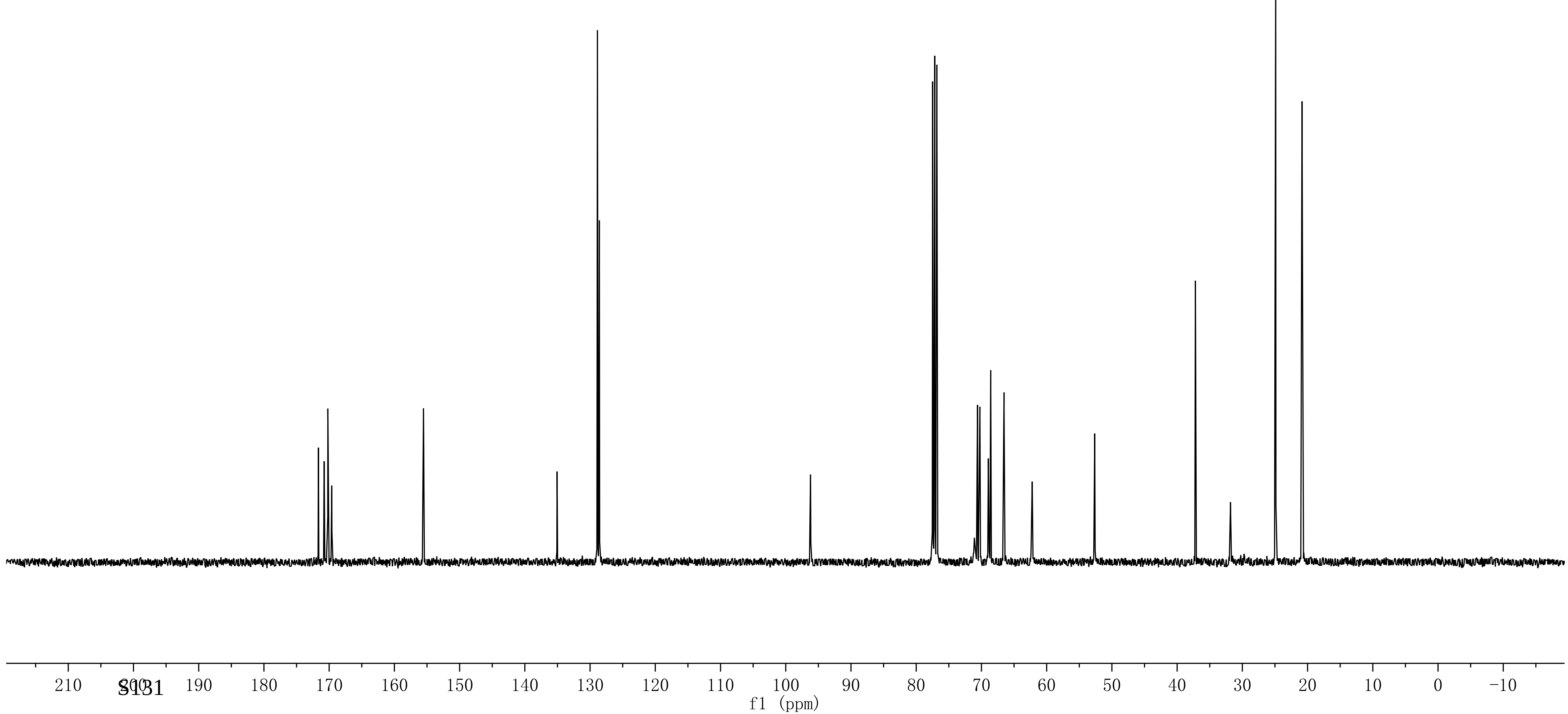
19l

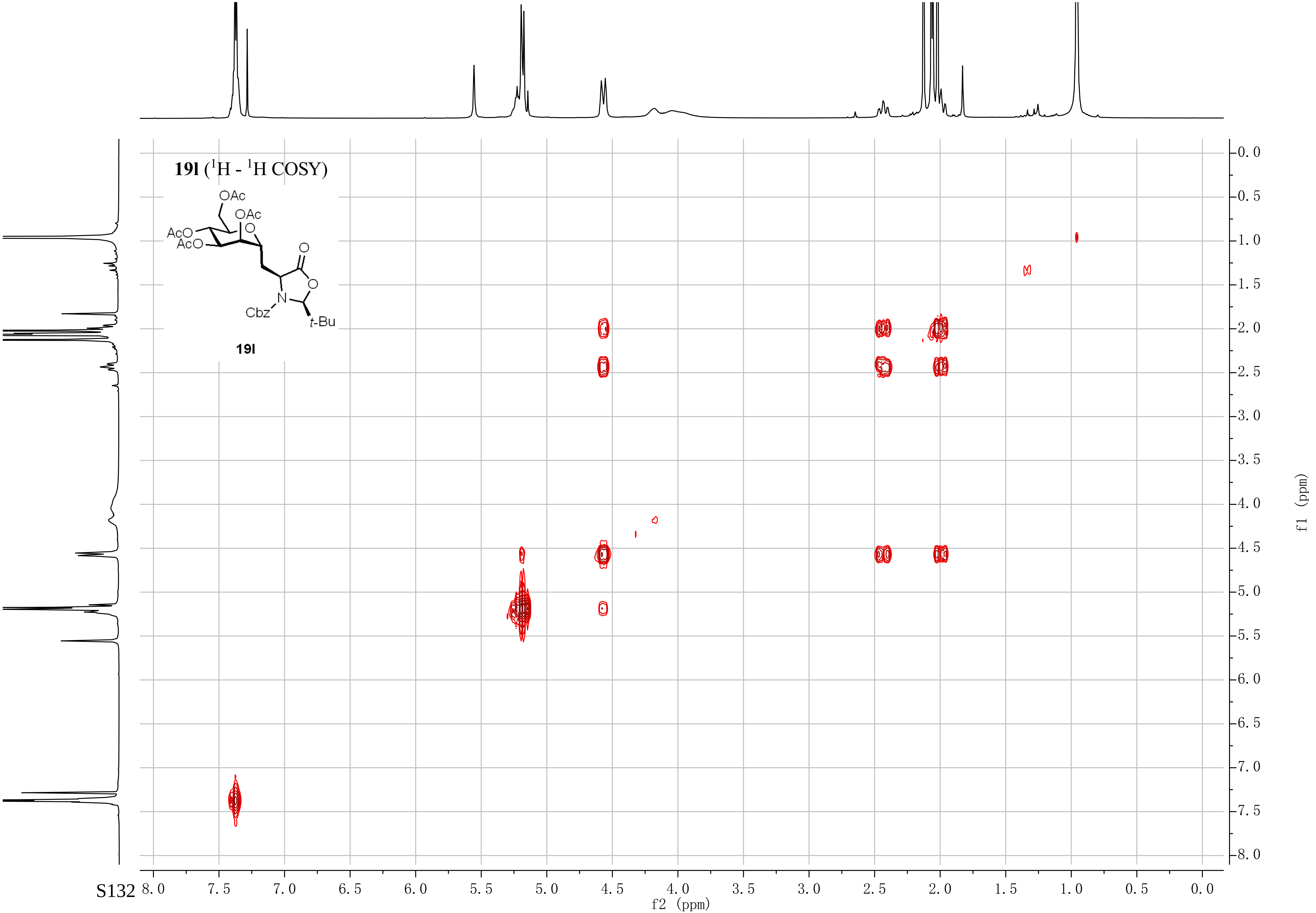


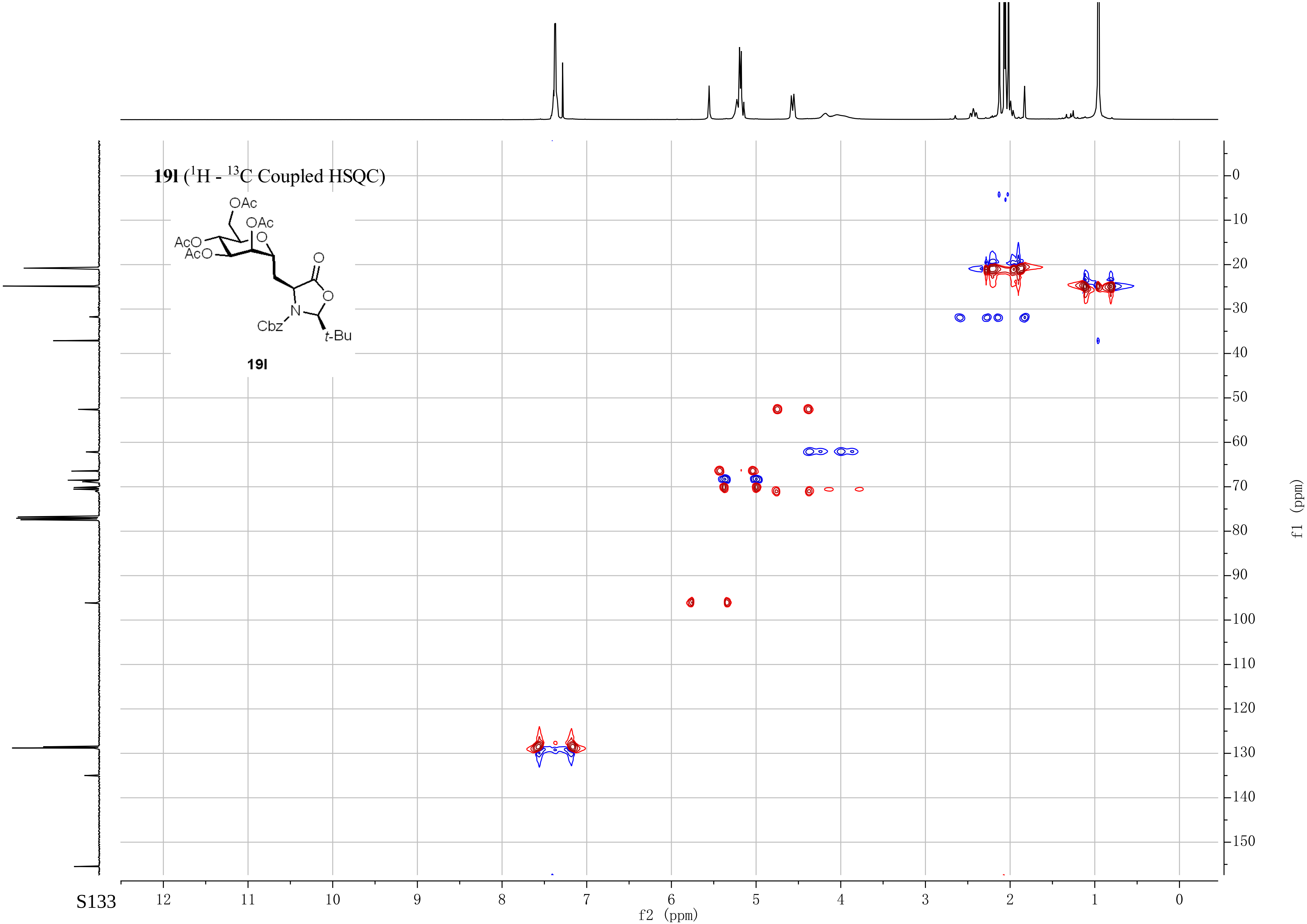
19l (^{13}C NMR, 101MHz, $CDCl_3$)



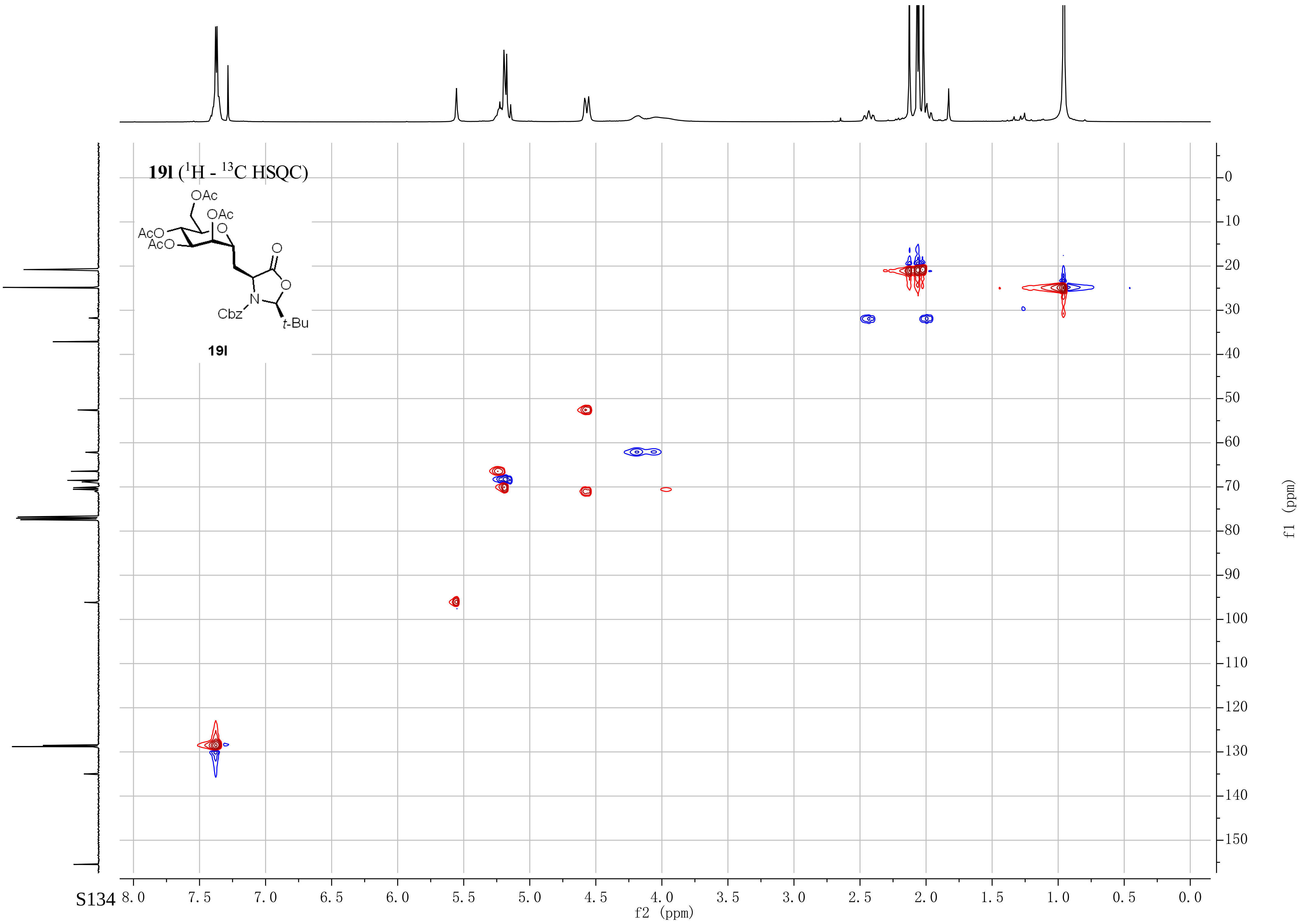
19l




19l (^{1}H - ^{1}H COSY)
OAc
OAc
AcO
AcO
O
O
O
N
Cbz
t-Bu
19l
f2 (ppm)
f1 (ppm)

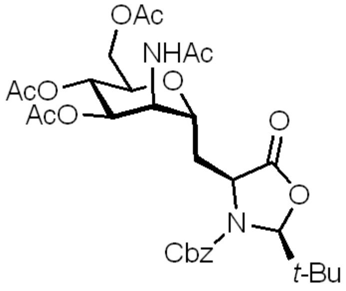


19l (1H - 13C Coupled HSQC)
OAc
OAc
AcO
AcO
O
O
O
N
Cbz
t-Bu
19l
f2 (ppm)
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

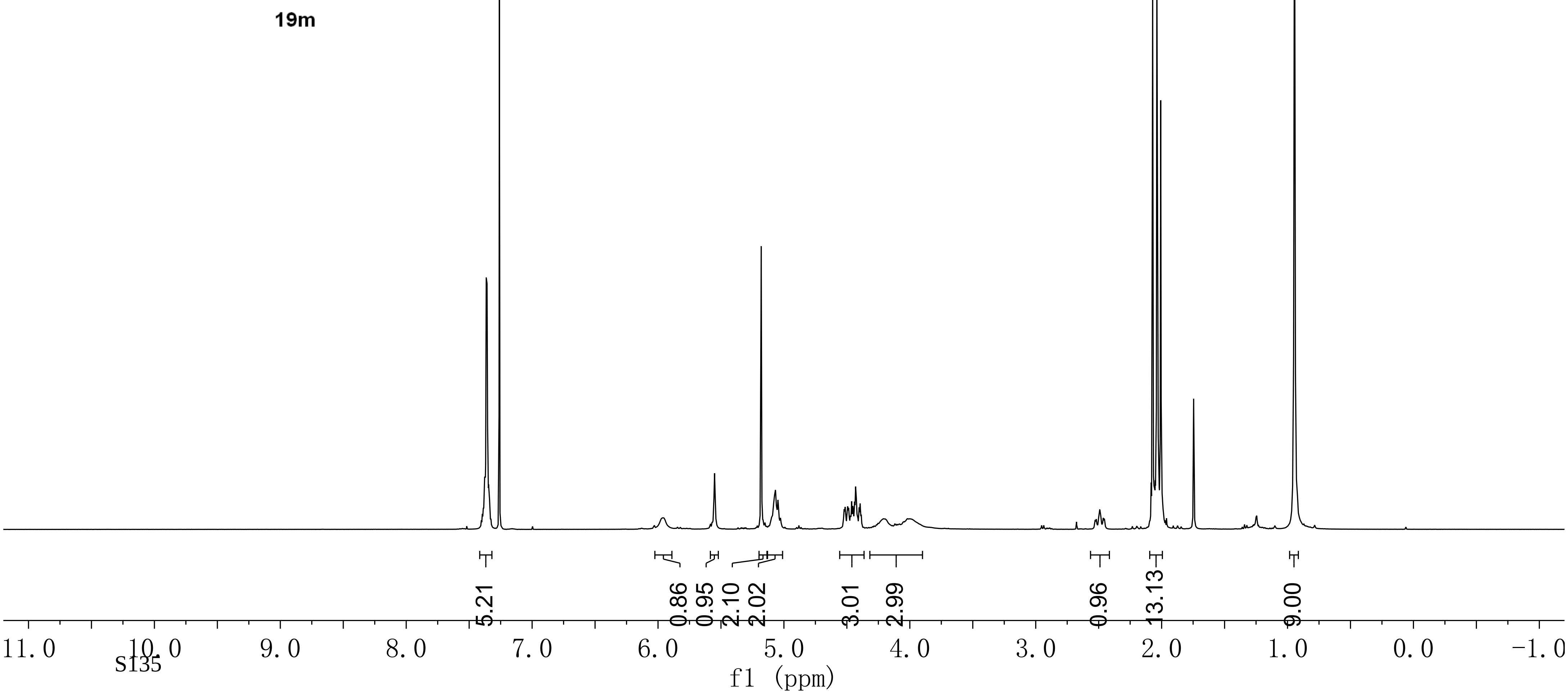


19l (^{1}H - ^{13}C HSQC)
OAc
OAc
AcO
AcO
O
O
O
N
Cbz
t-Bu
19l
f2 (ppm)
f1 (ppm)

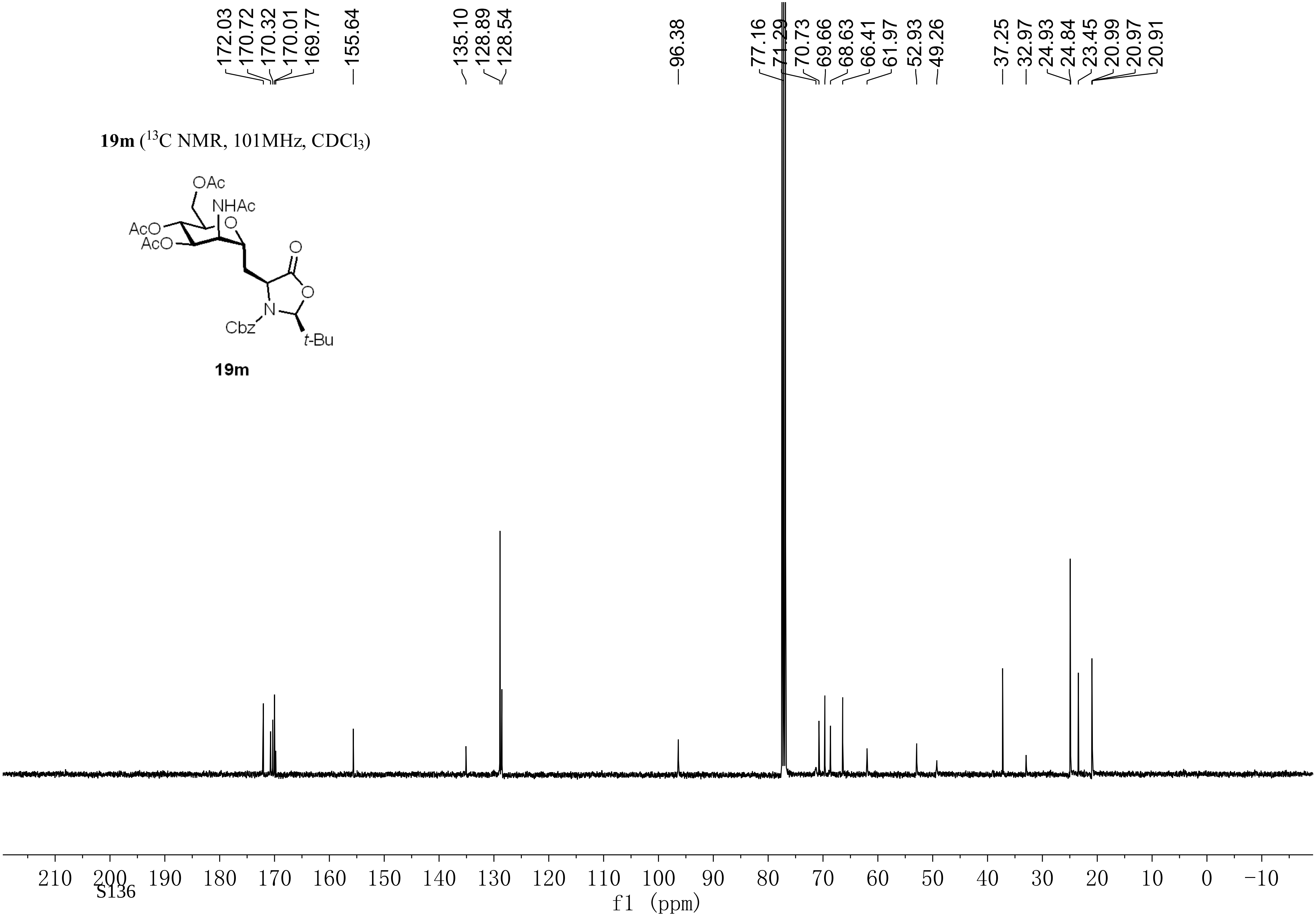
19m (^{1}H NMR, 400MHz, $CDCl_3$)

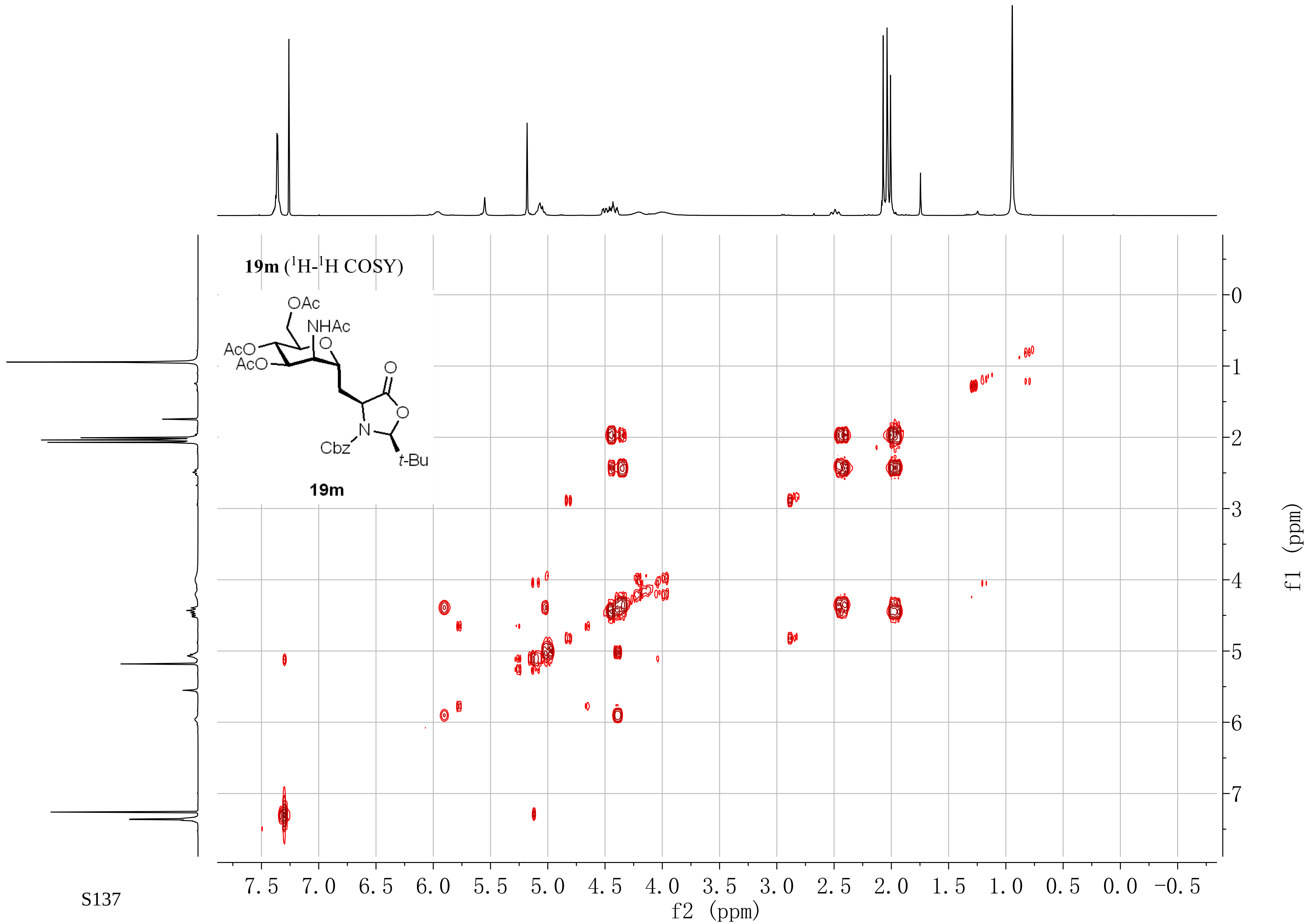


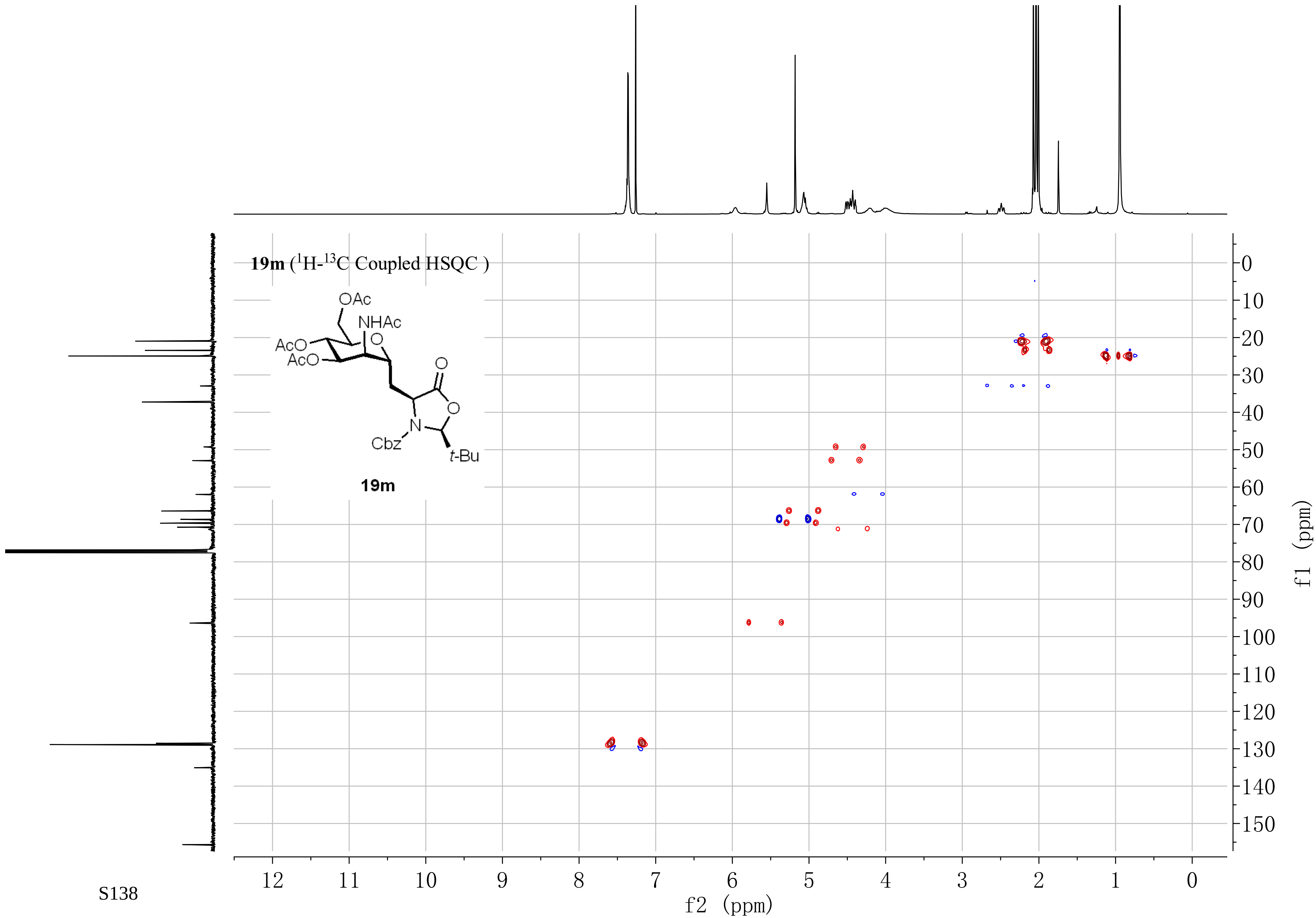
19m



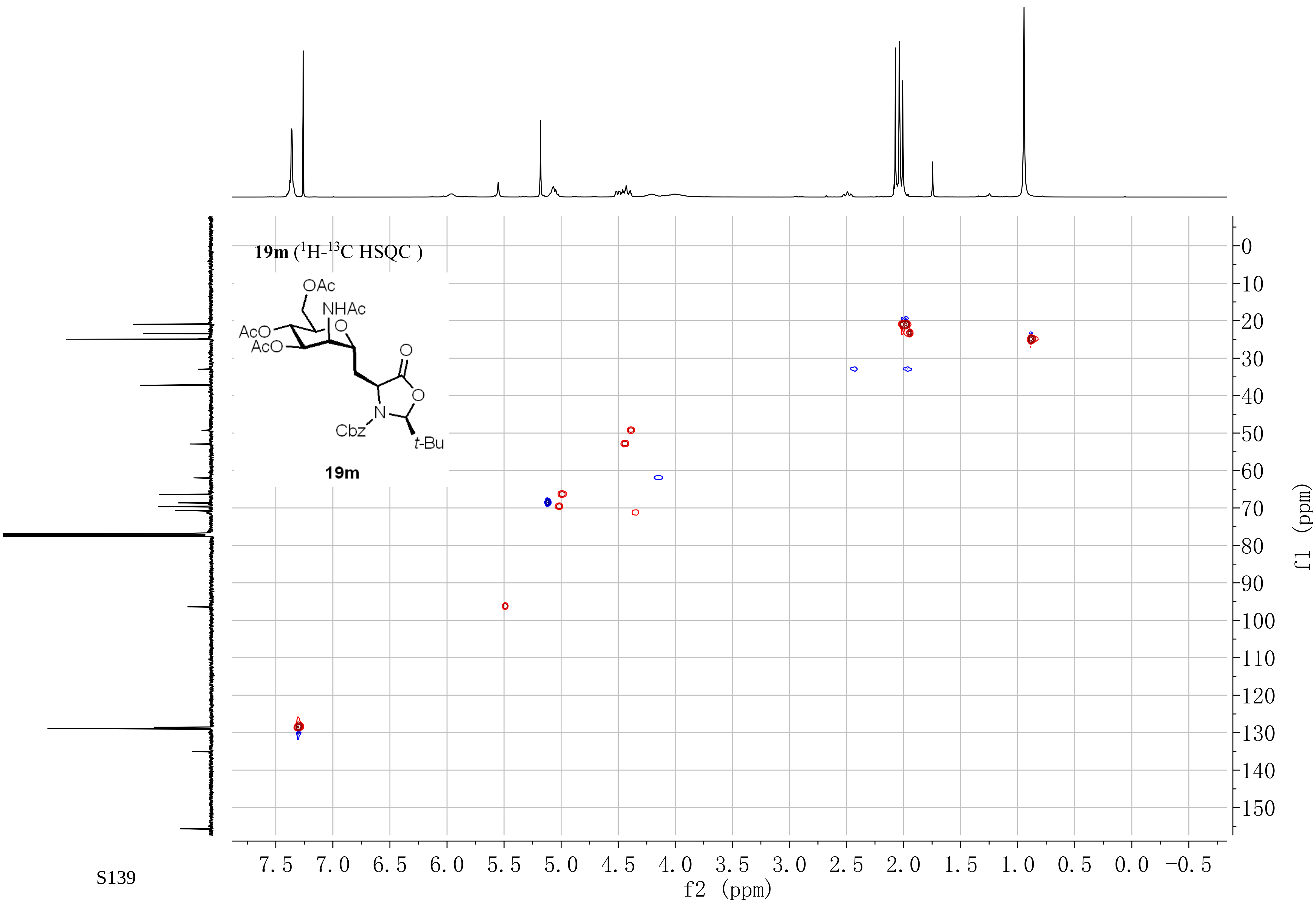
19m (^{13}C NMR, 101MHz, $CDCl_3$)



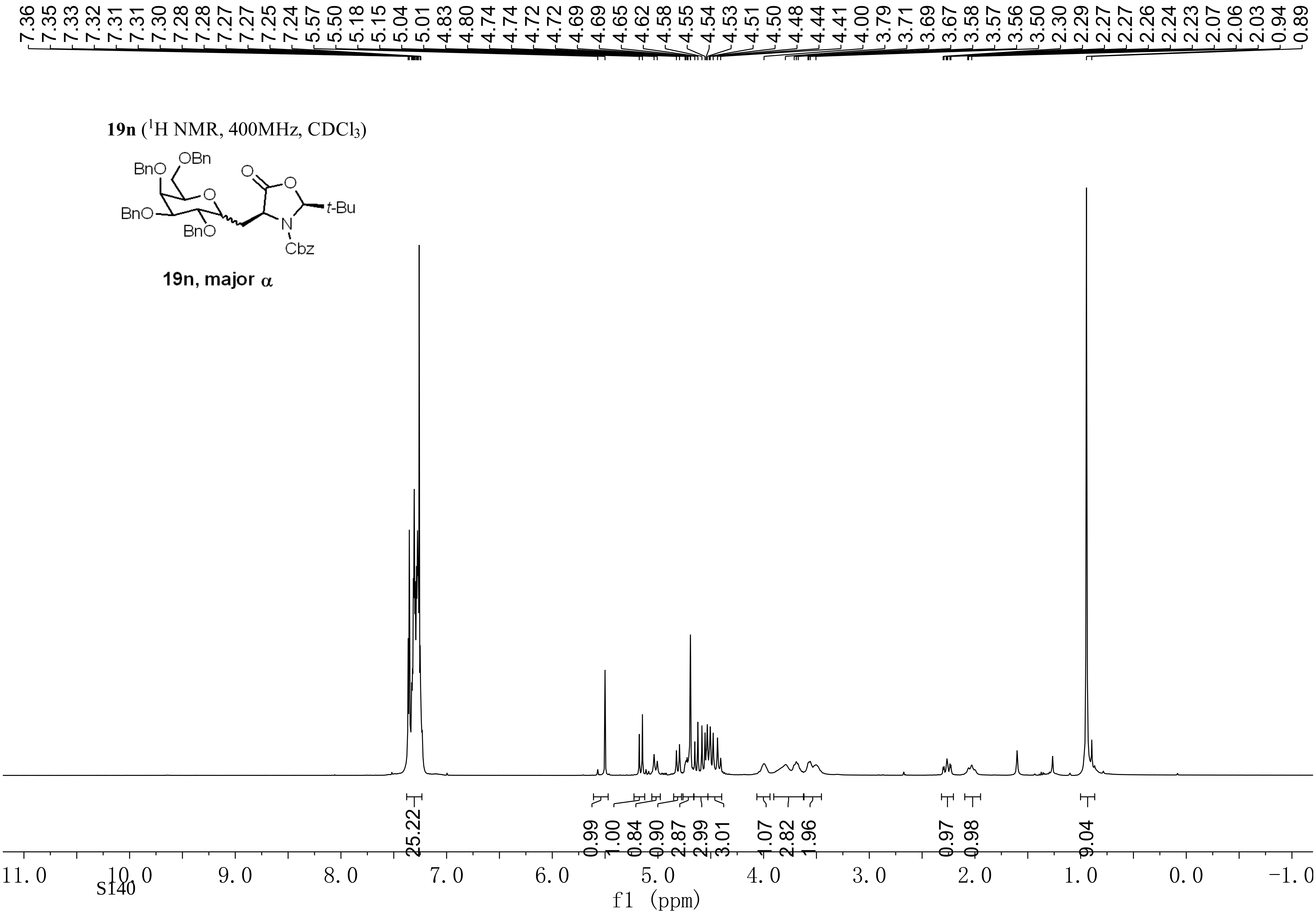

19m (1H-1H COSY)
OAc
NHAc
AcO
AcO
O
O
O
N
Cbz
t-Bu
19m
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f2 (ppm)
0 1 2 3 4 5 6 7
f1 (ppm)

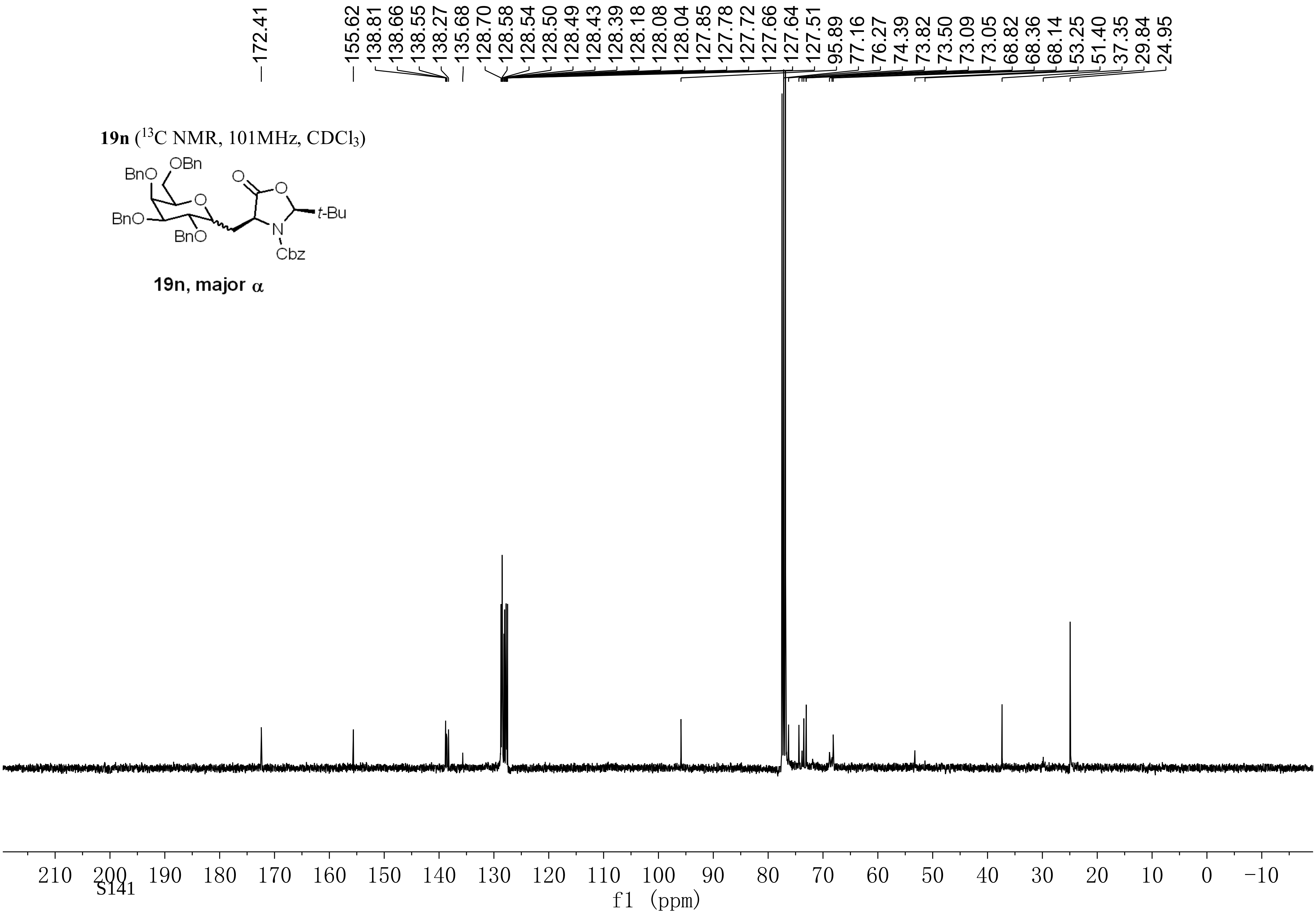


19m (1H-13C Coupled HSQC)
OAc
NHAc
AcO
AcO
O
O
O
N
Cbz
t-Bu
19m
f2 (ppm)
f1 (ppm)



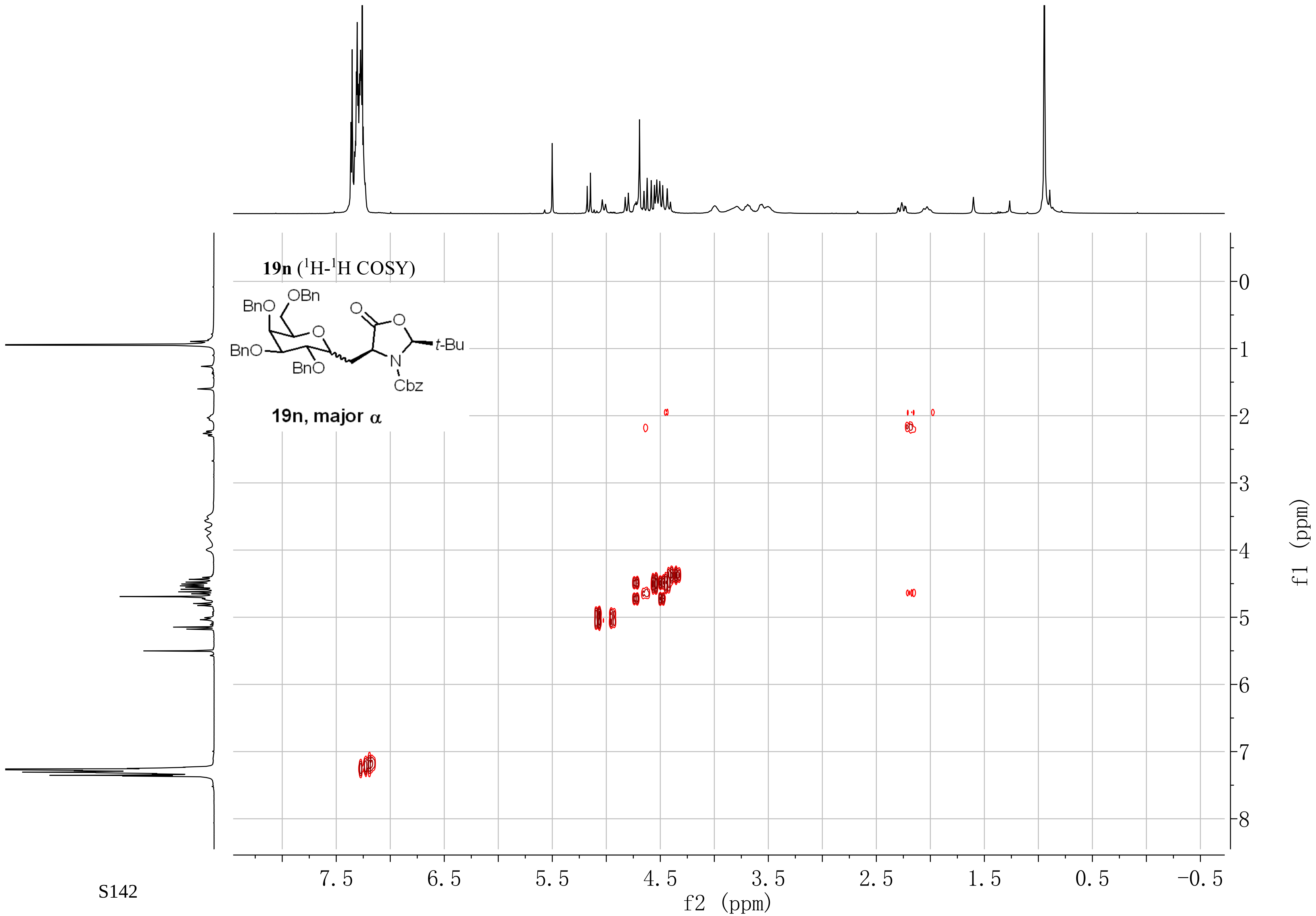
19m (^{1}H-^{13}C HSQC)
OAc
NHAc
AcO
AcO
O
O
O
N
Cbz
t-Bu
19m
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)


7.36 7.35 7.33 7.32 7.31 7.31 7.30 7.28 7.28 7.27 7.27 7.25 7.24 5.57 5.50 5.18 5.15 5.04 5.01 4.83 4.80 4.74 4.74 4.72 4.72 4.69 4.65 4.62 4.58 4.55 4.54 4.53 4.51 4.50 4.48 4.44 4.41 4.00 3.79 3.71 3.69 3.67 3.58 3.57 3.56 3.50 2.30 2.29 2.27 2.27 2.26 2.24 2.23 2.07 2.06 2.03 0.94 0.89
19n (1H NMR, 400MHz, CDCl3)
BnO
OBn
O
O
O
t-Bu
BnO
N
BnO
Cbz
19n, major α
25.22
0.99 1.00 0.84 0.90 2.87 2.99 3.01
1.07 2.82 1.96
0.97 0.98
9.04
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

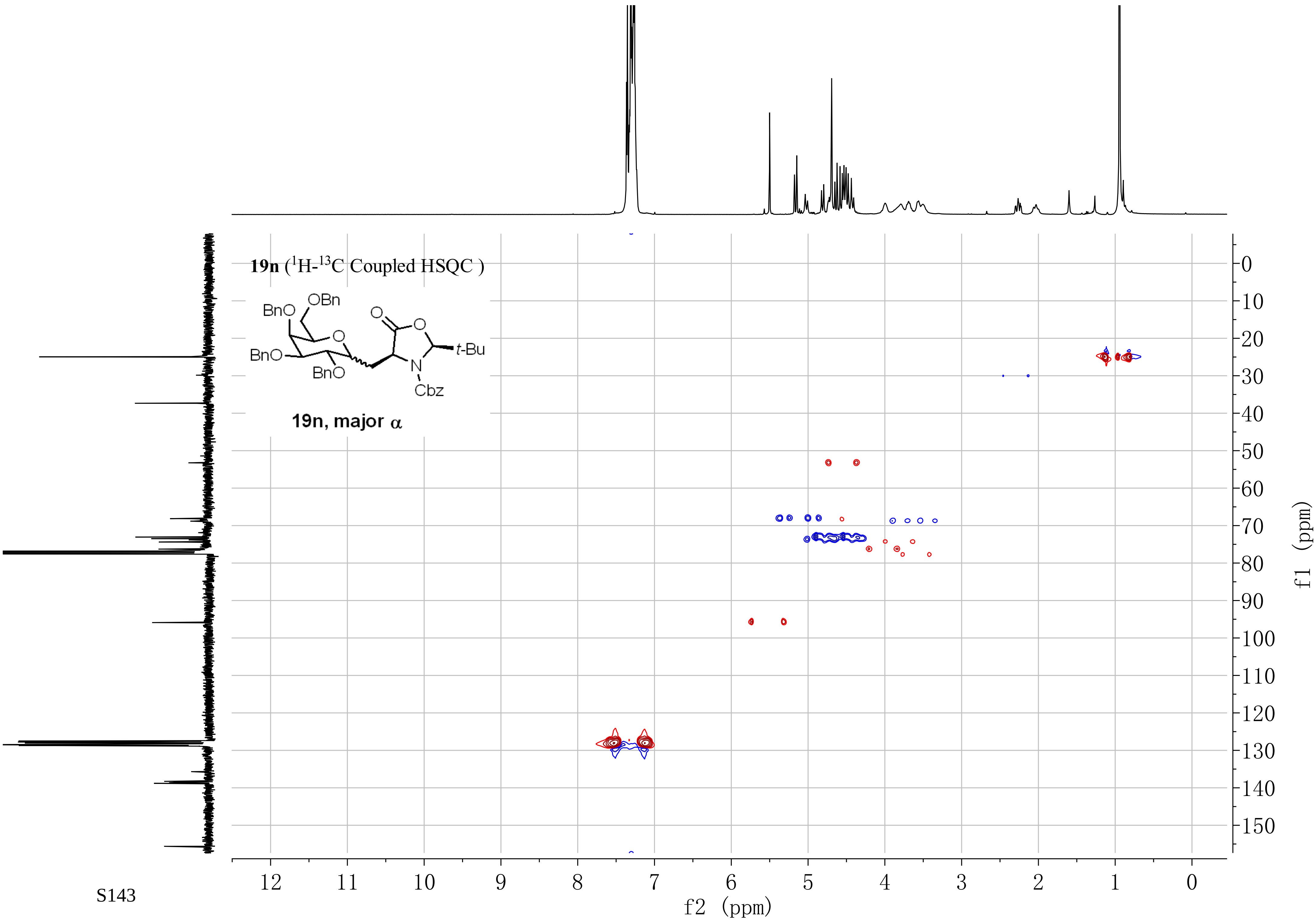


19n (^{13}C NMR, 101MHz, $CDCl_3$)

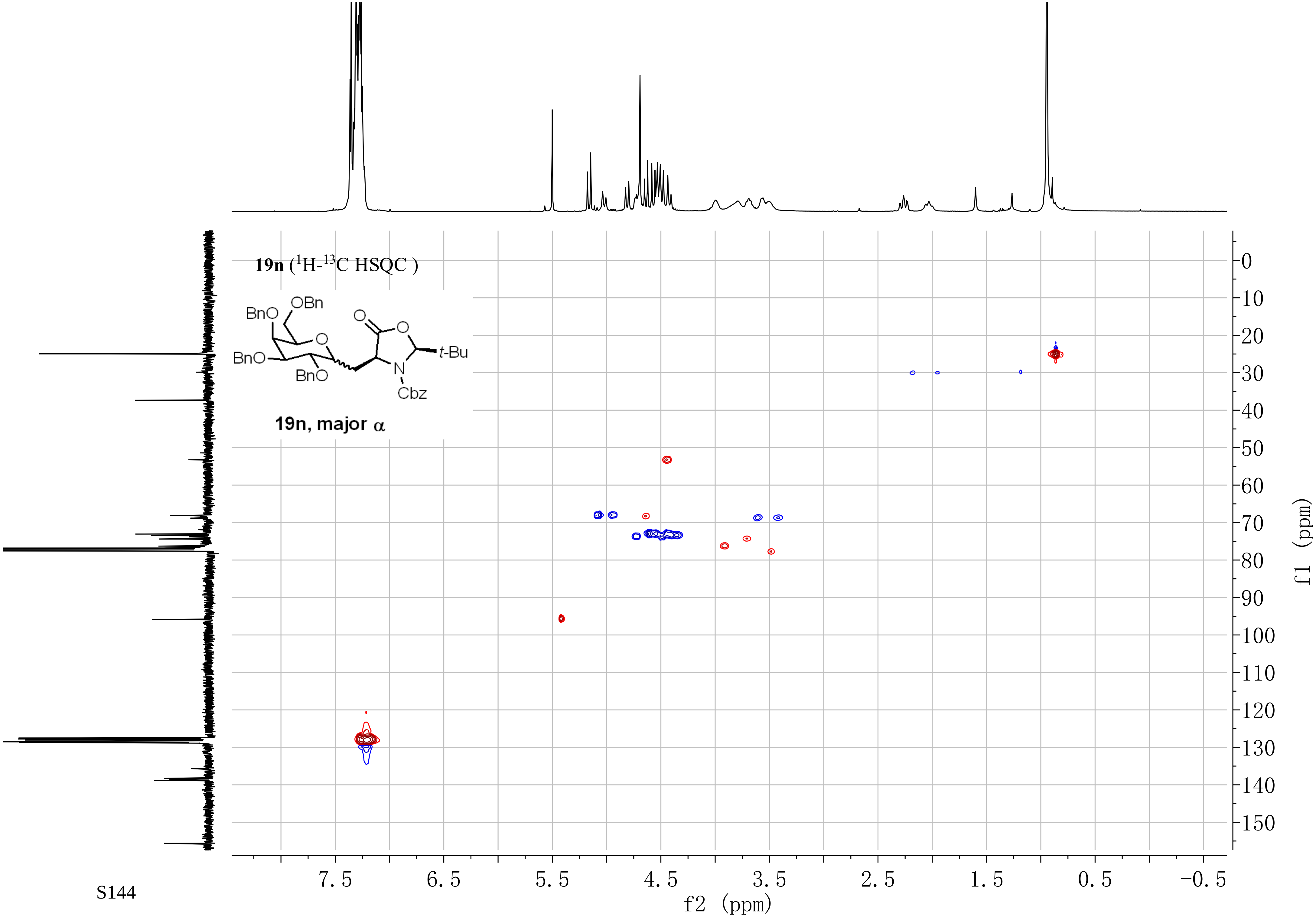
19n, major α



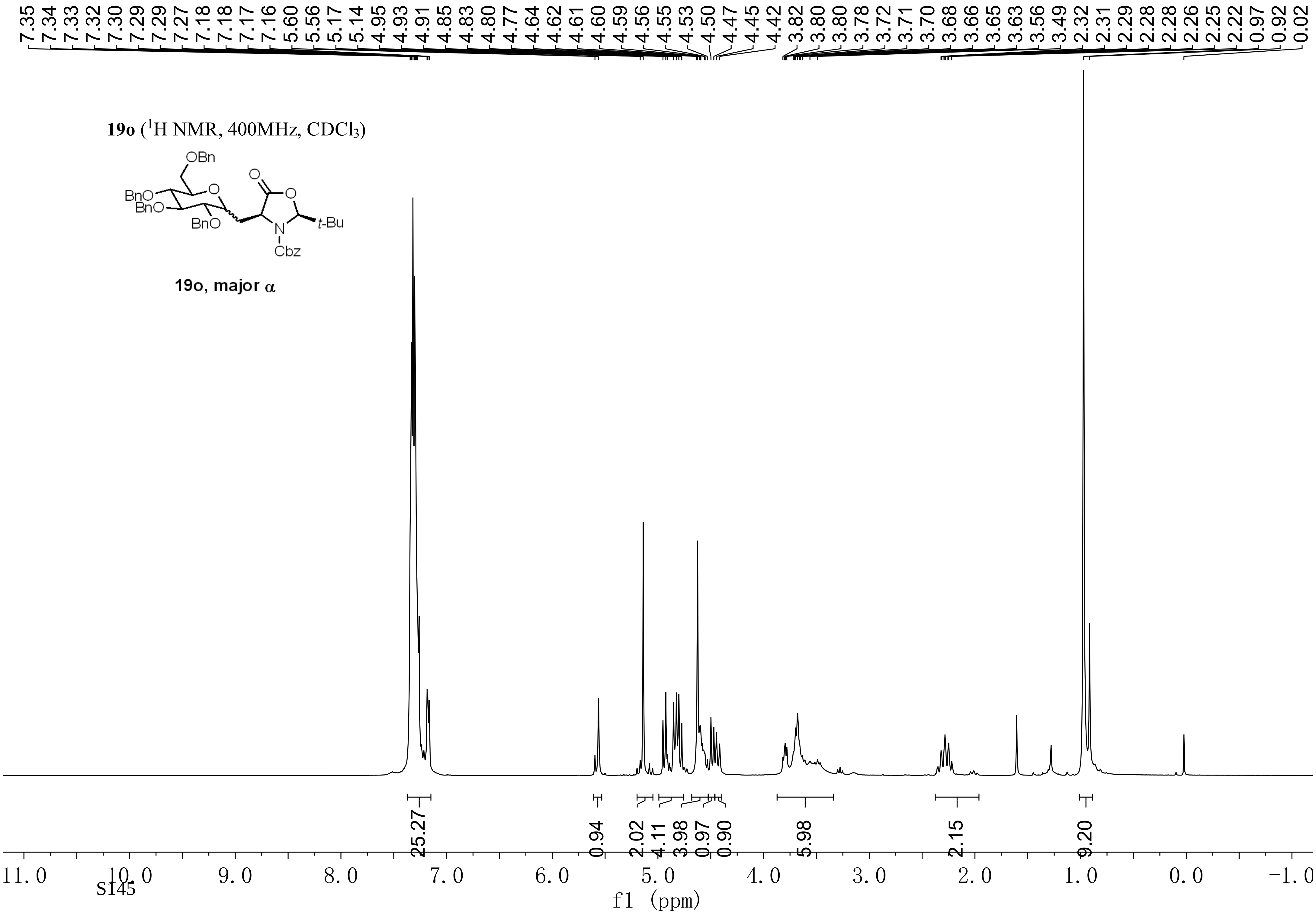
19n (1H-1H COSY)
OBn
BnO
O
O
O
t-Bu
BnO
N
BnO
Cbz
19n, major α
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)



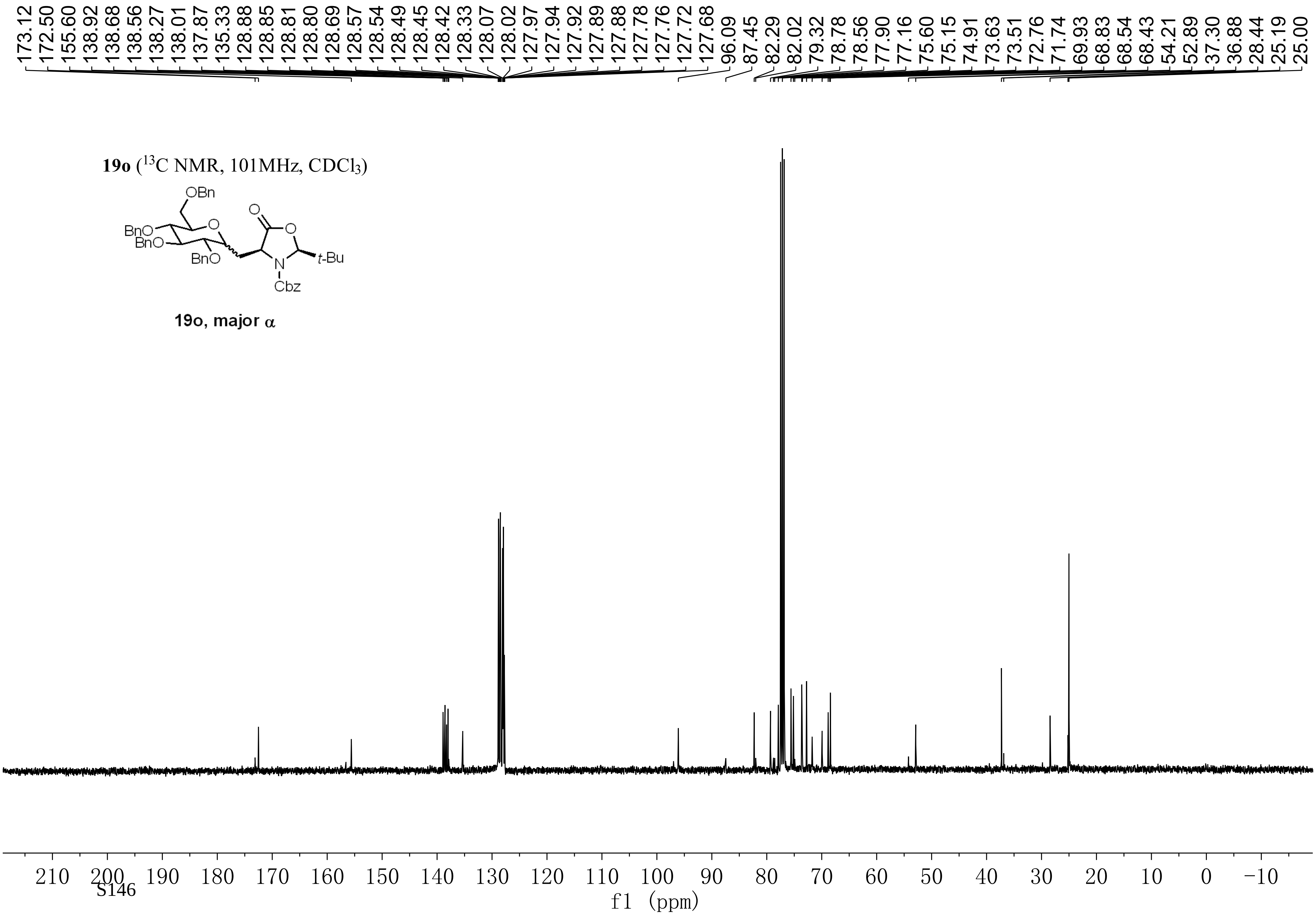
19n (1H-13C Coupled HSQC)
BnO
OBn
O
t-Bu
N
Cbz
19n, major α
f2 (ppm)
f1 (ppm)

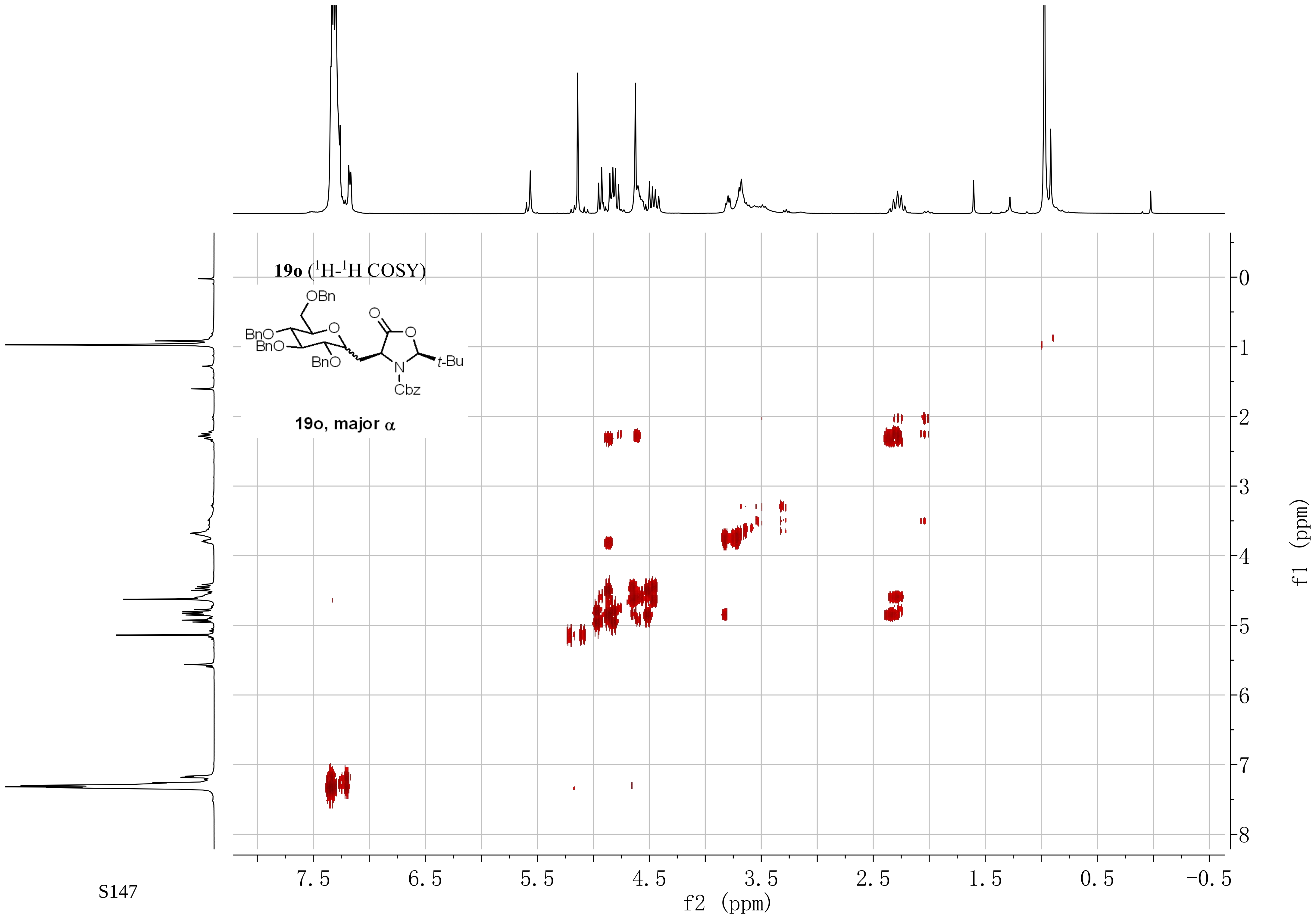

19n (1H-13C HSQC)
BnO
OBn
O
O
O
BnO
t-Bu
N
BnO
Cbz
19n, major α
f2 (ppm)
f1 (ppm)

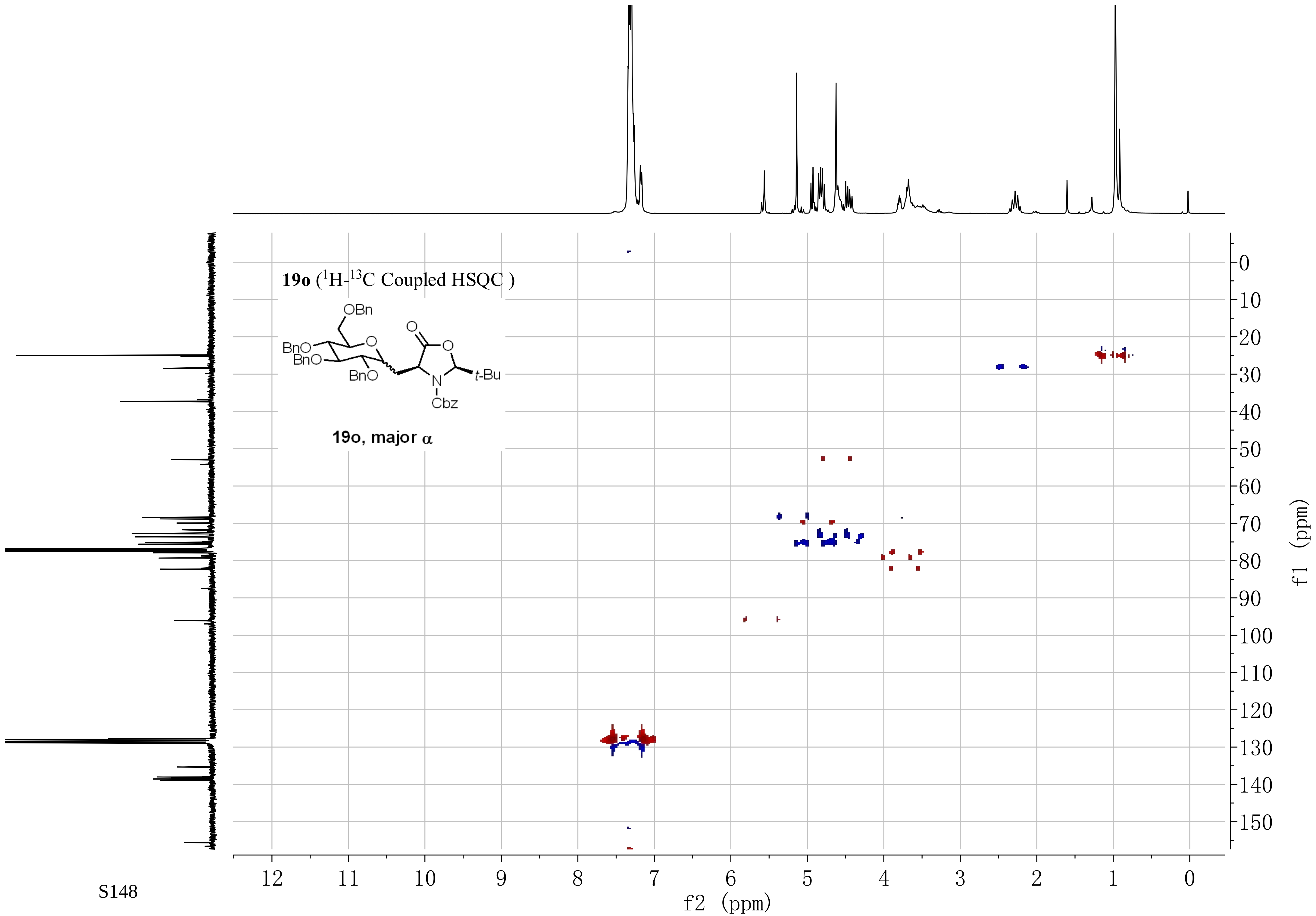
19o (^{1}H NMR, 400MHz, $CDCl_3$)



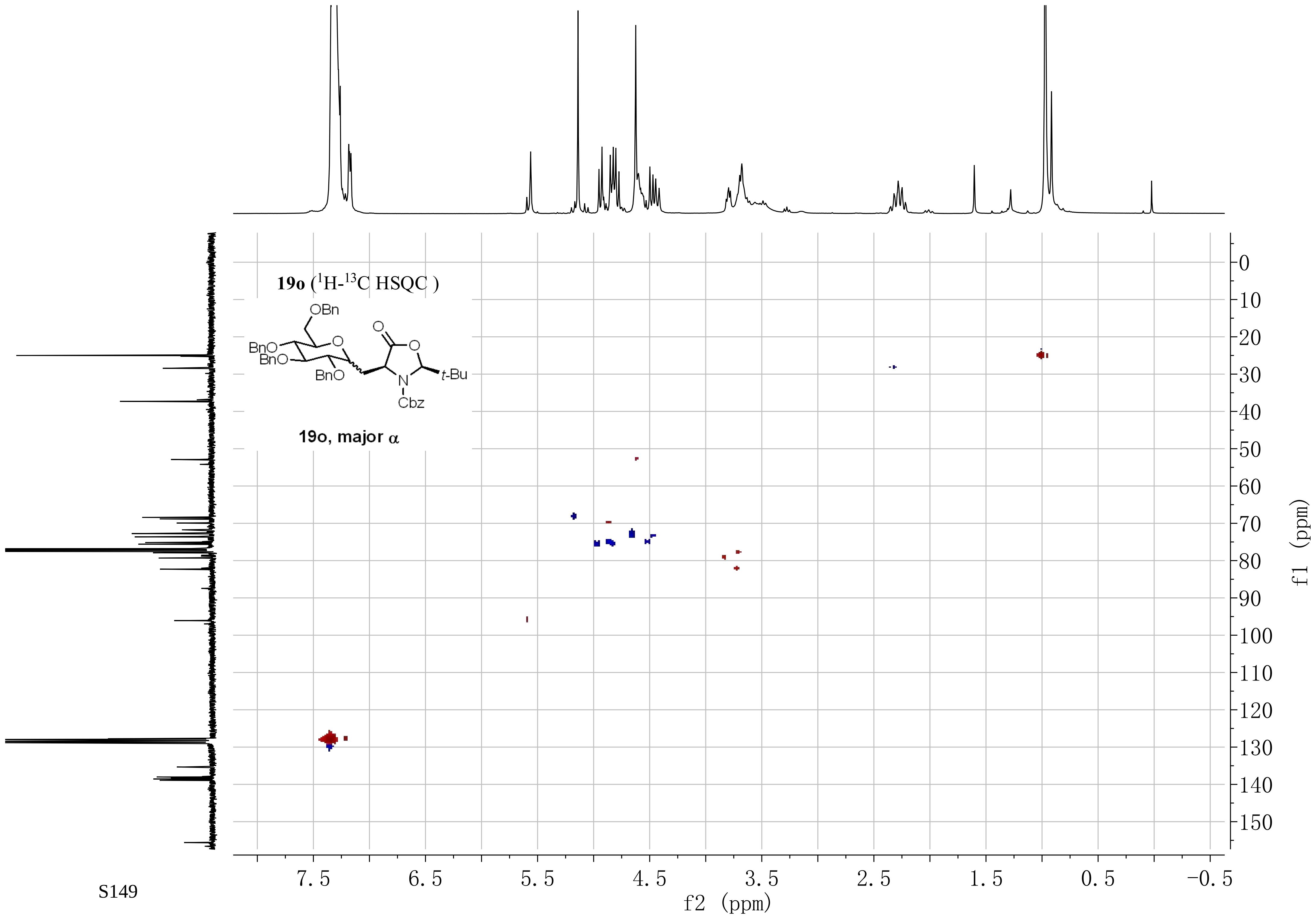
19o, major α


173.12 172.50 155.60 138.92 138.68 138.56 138.27 138.01 137.87 135.33 128.88 128.85 128.81 128.80 128.69 128.57 128.54 128.49 128.45 128.42 128.33 128.07 128.02 127.97 127.94 127.92 127.89 127.88 127.78 127.76 127.72 127.68 96.09 87.45 82.29 82.02 79.32 78.78 78.56 77.90 77.16 75.60 75.15 74.91 73.63 73.51 72.76 71.74 69.93 68.83 68.54 68.43 54.21 52.89 37.30 36.88 28.44 25.19 25.00
19o (13C NMR, 101MHz, CDCl3)
OBn
BnO
BnO
BnO
O
N
Cbz
t-Bu
19o, major α
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)

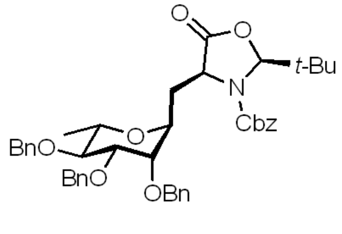

19o (1H-1H COSY)
OBn
BnO
BnO
BnO
O
O
O
N
Cbz
t-Bu
19o, major α
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f2 (ppm)
f1 (ppm)



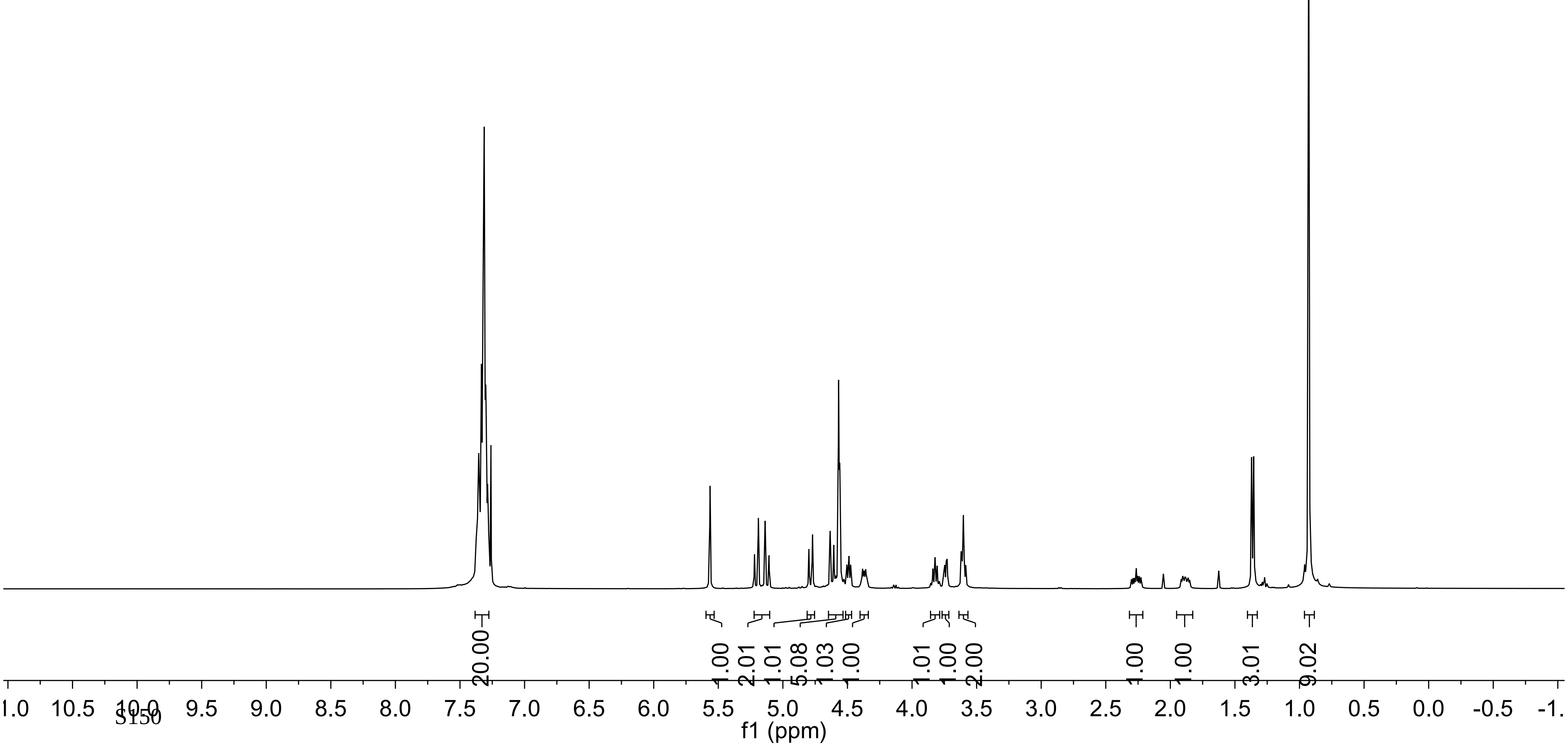
19o (1H-13C Coupled HSQC)
OBn
BnO
BnO
BnO
O
O
O
N
Cbz
t-Bu
19o, major α
f2 (ppm)
f1 (ppm)

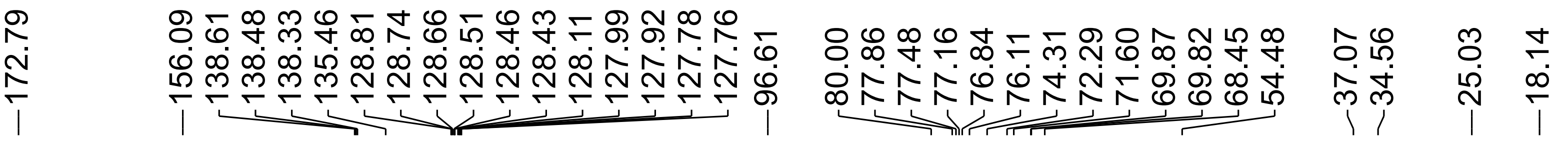

19o (1H-13C HSQC)
OBn
BnO
BnO
BnO
O
O
O
N
Cbz
t-Bu
19o, major α
f2 (ppm)
f1 (ppm)

19p (^{1}H NMR, 400MHz, $CDCl_3$)

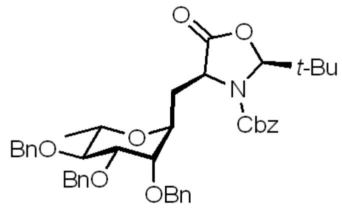


19p

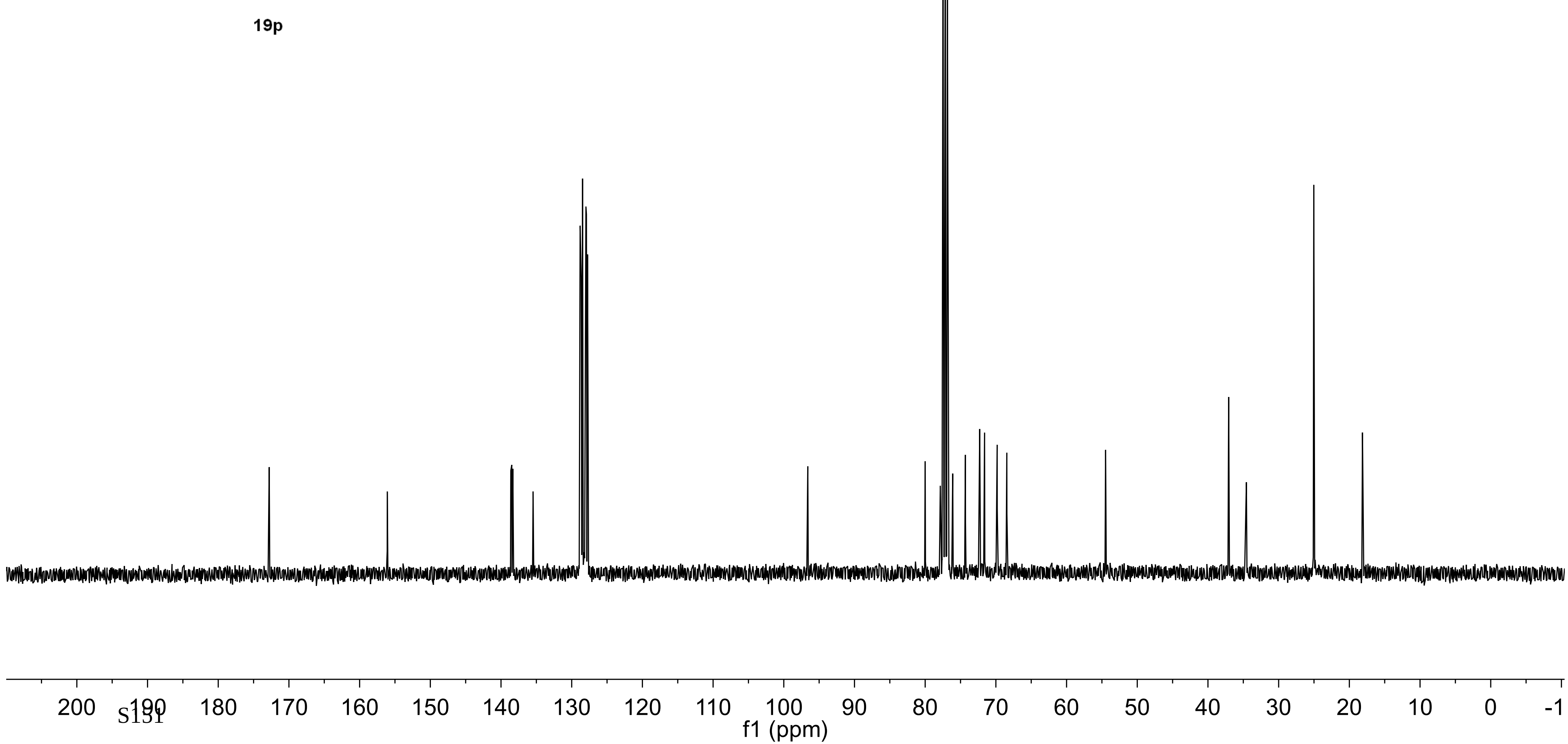


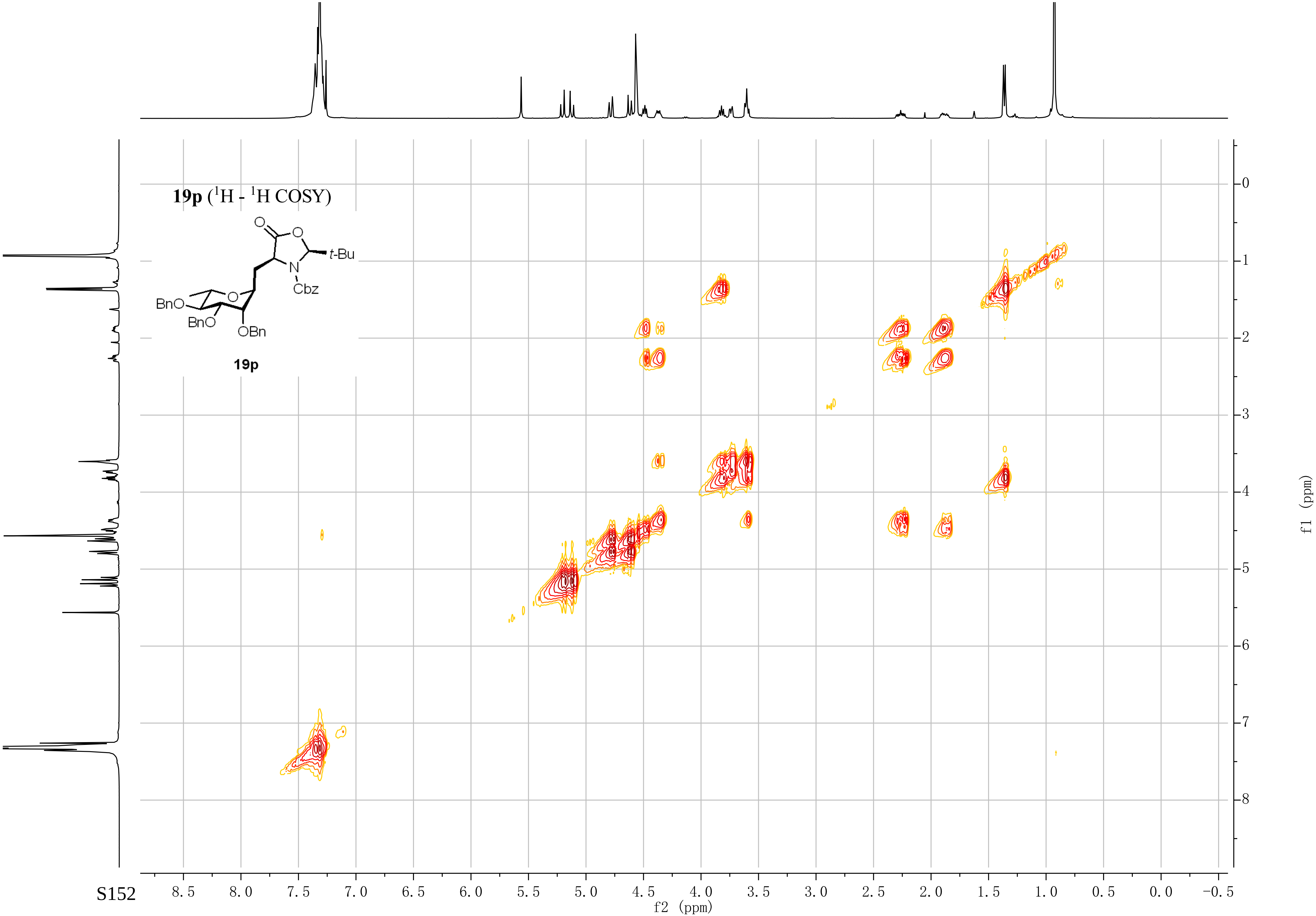


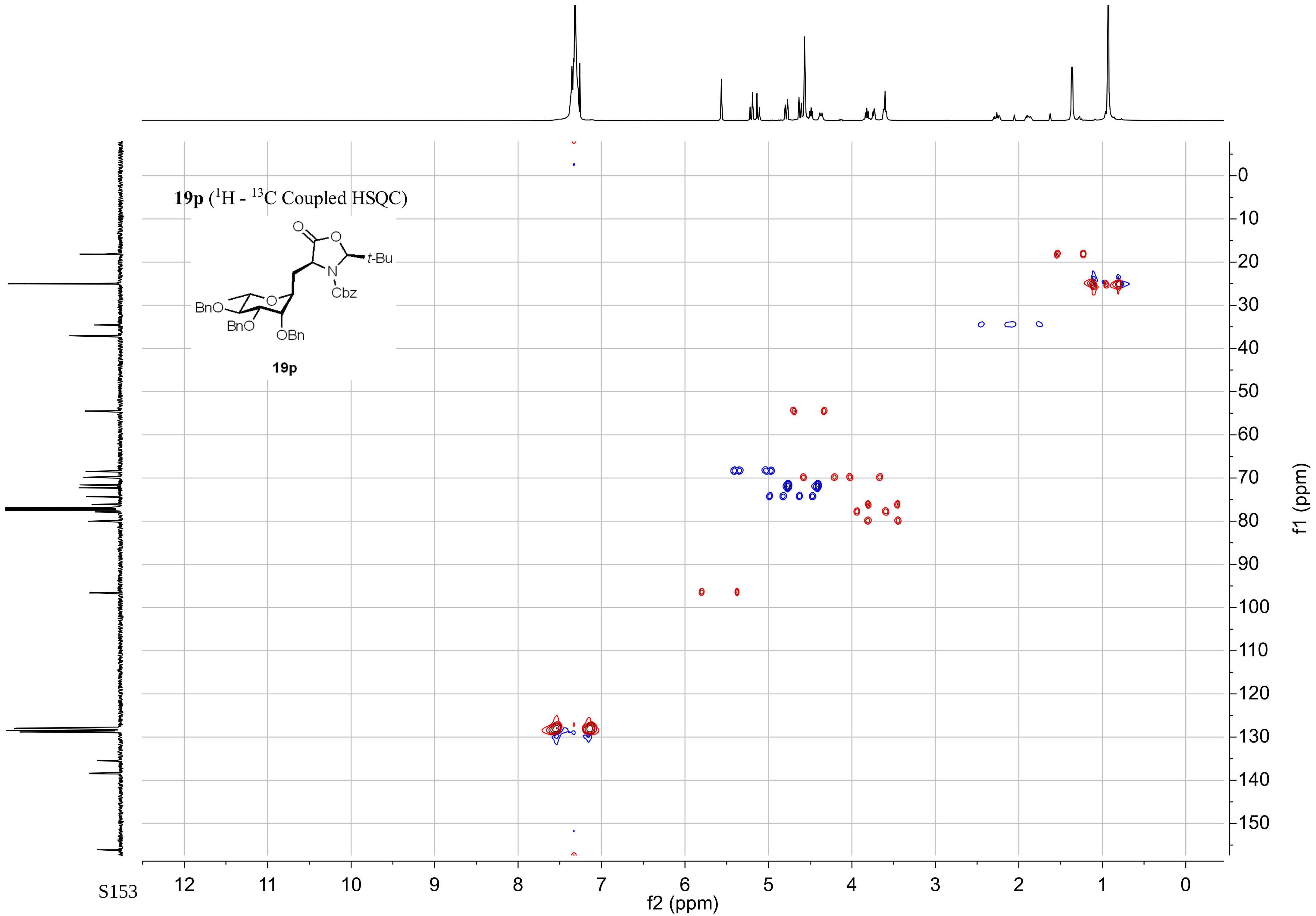
19p (^{13}C NMR, 101MHz, $CDCl_3$)

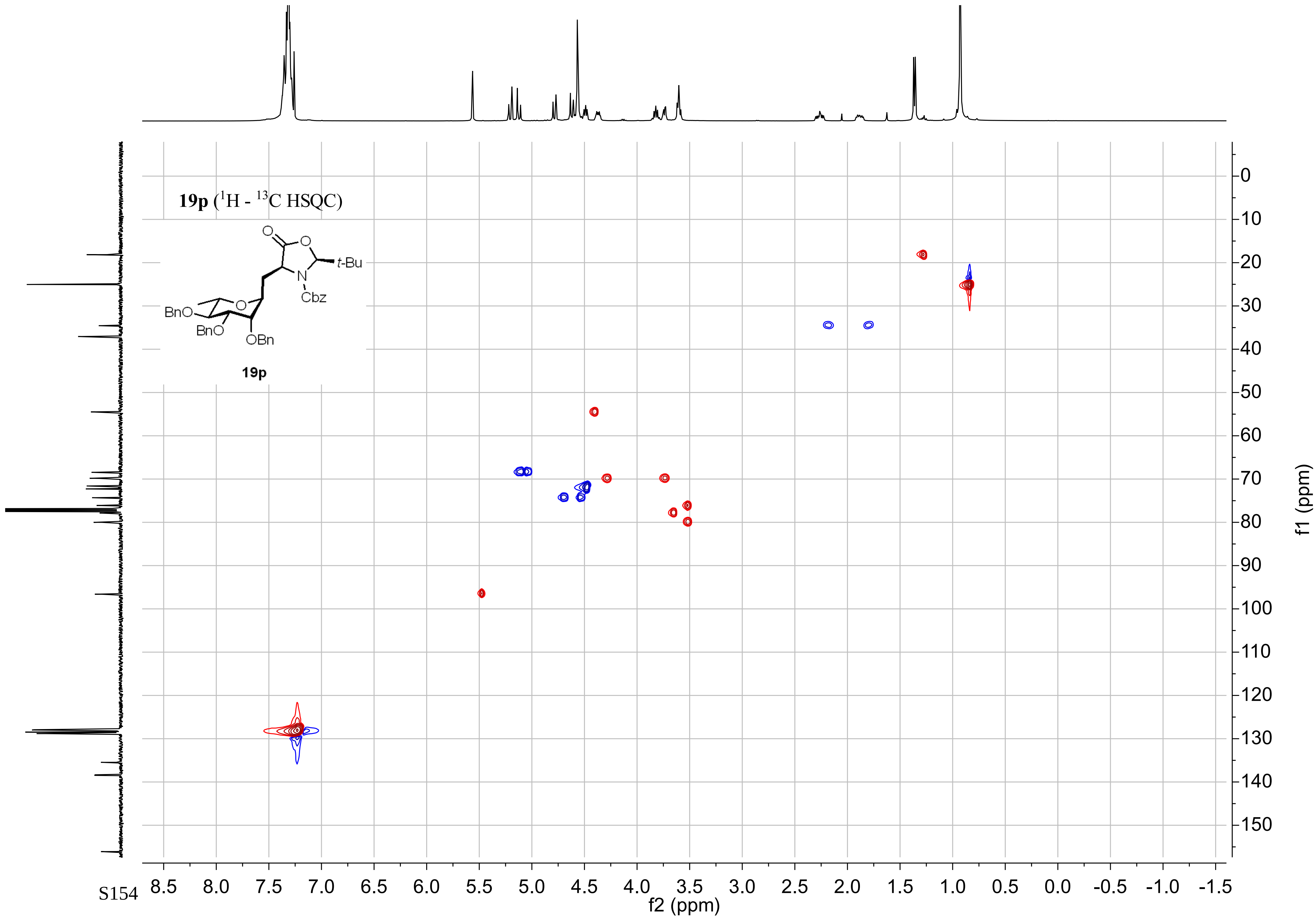


19p



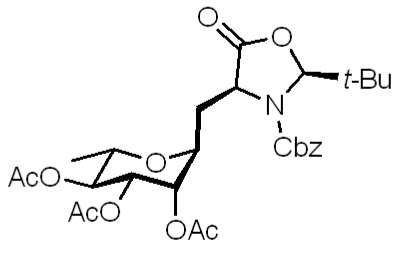

19p (^{1}H - ^{1}H COSY)
O
O
t-Bu
N
Cbz
BnO
O
BnO
OBn
19p
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
7
8


19p (^{1}H - ^{13}C Coupled HSQC)
O
O
t-Bu
N
Cbz
BnO
O
BnO
OBn
19p
f2 (ppm)
f1 (ppm)

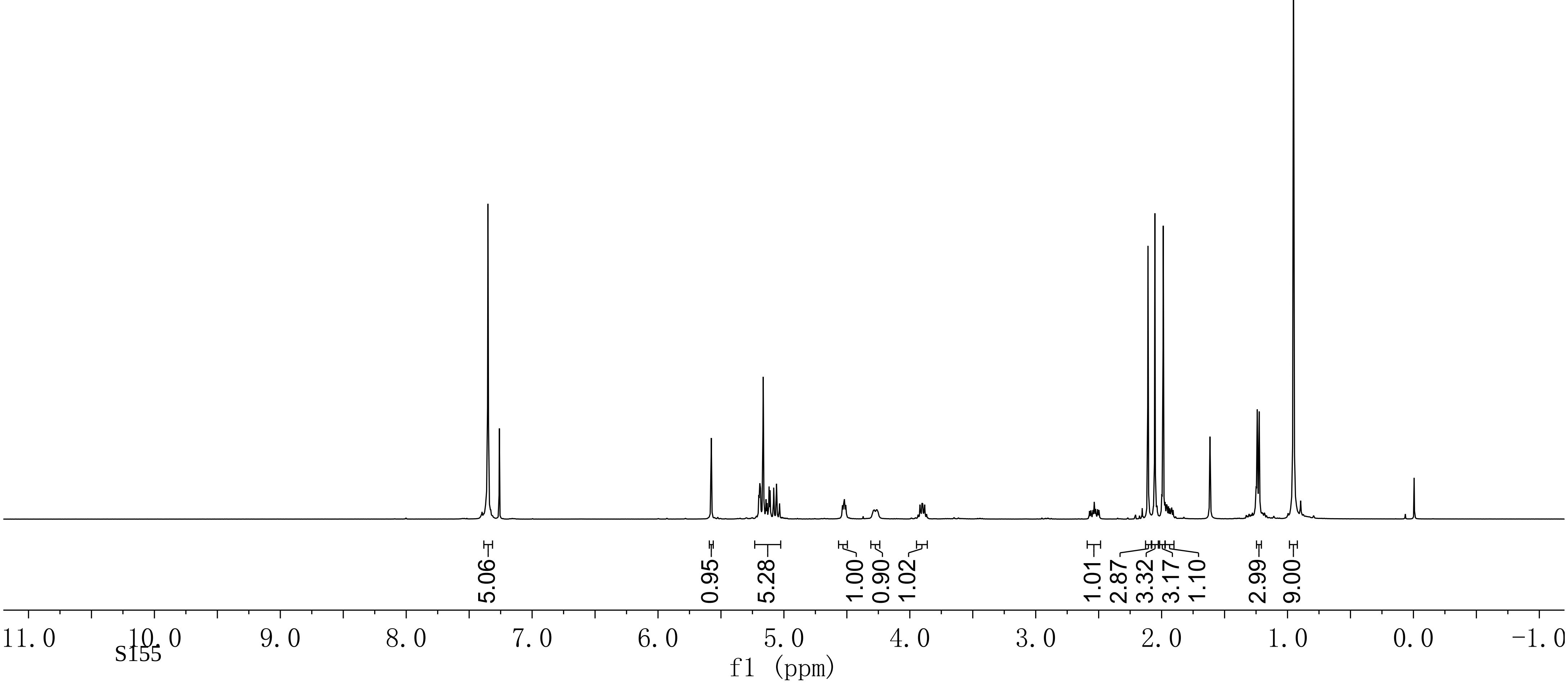


19p (1H - 13C HSQC)
O
O
t-Bu
N
Cbz
BnO
O
BnO
OBn
19p
f2 (ppm)
f1 (ppm)

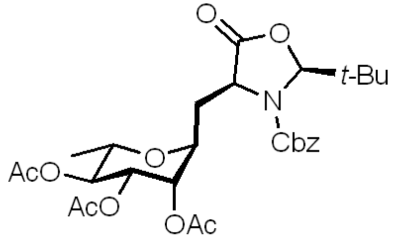
19q (^{1}H NMR, 400MHz, $CDCl_3$)



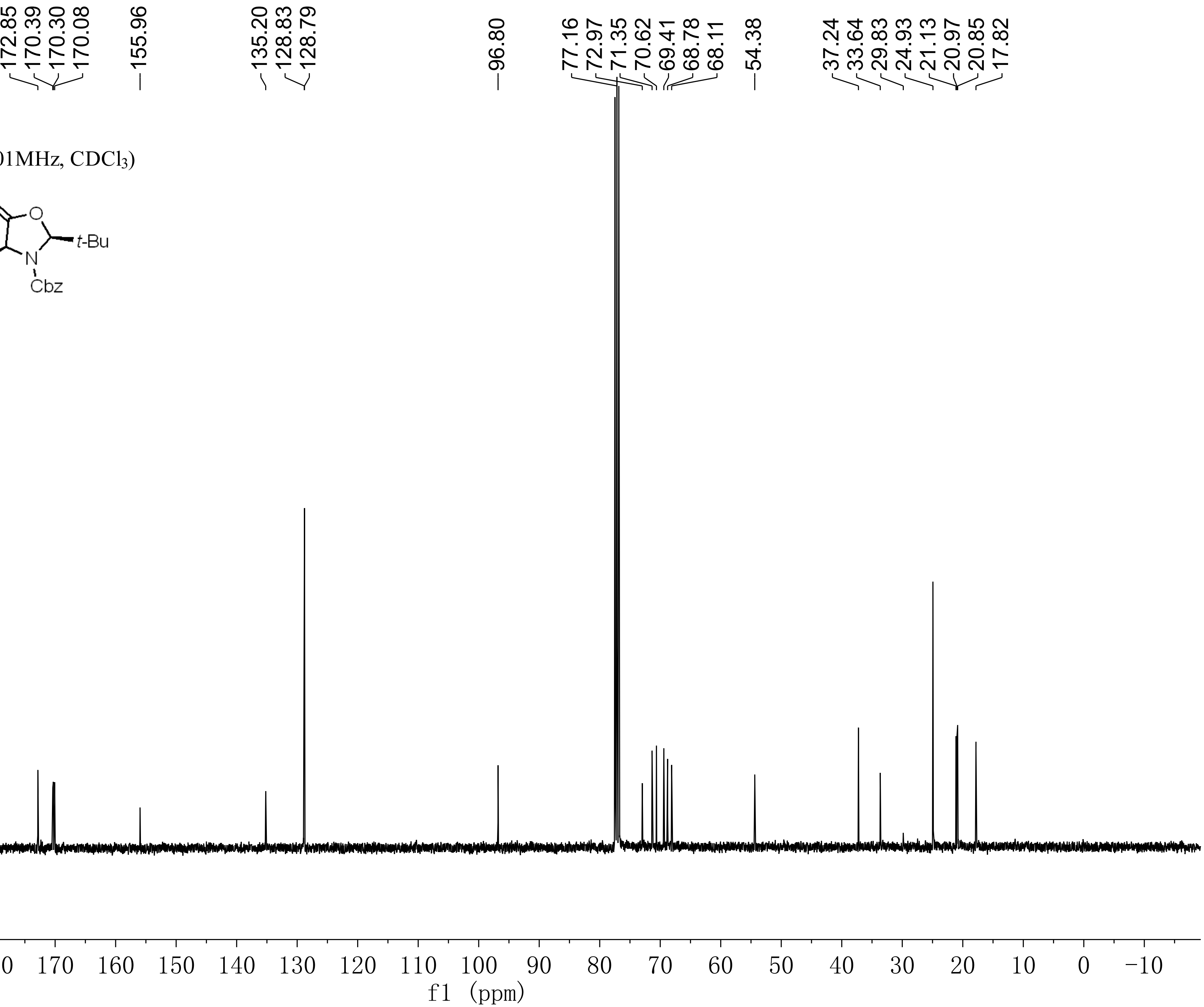
19q

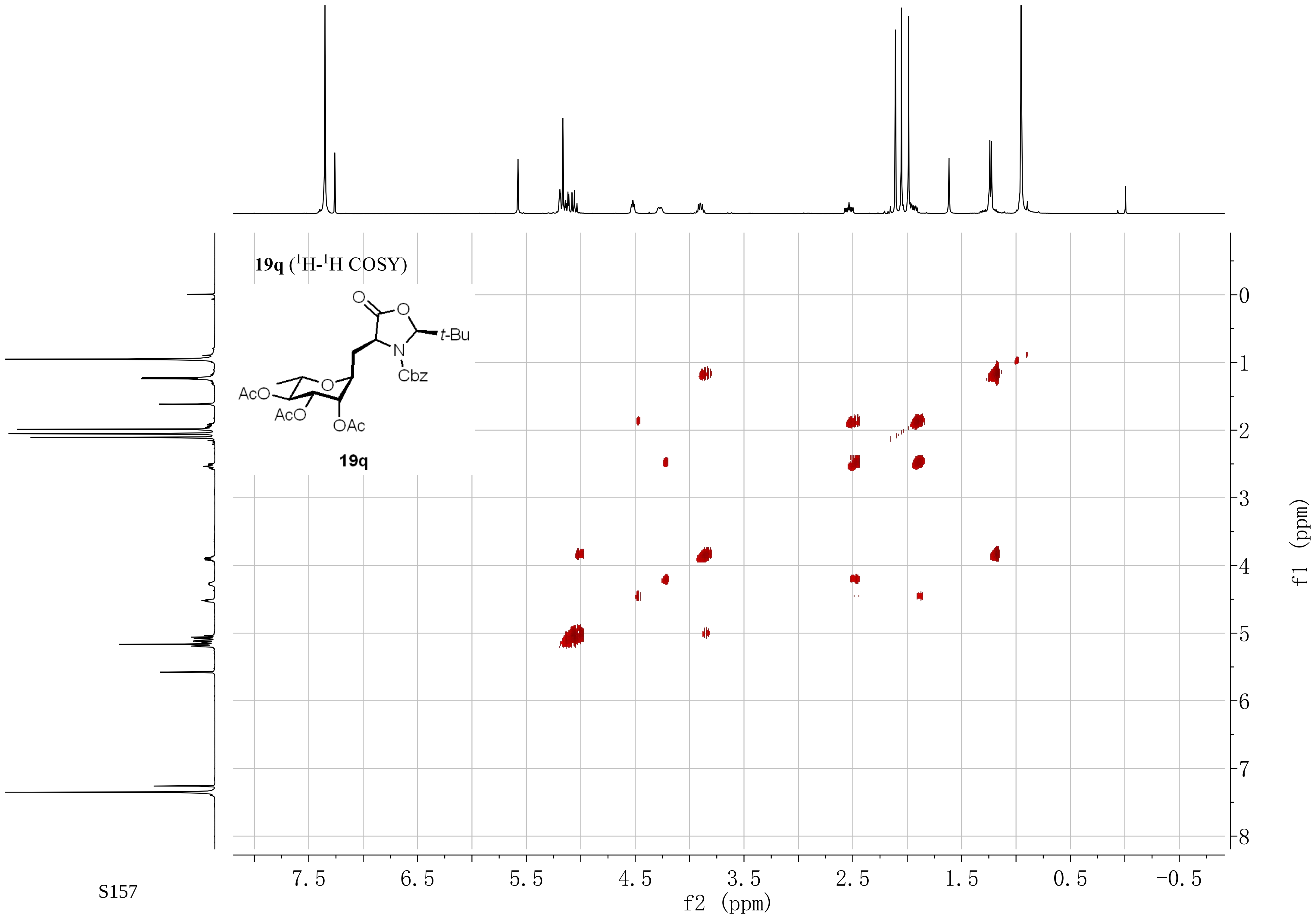


19q (^{13}C NMR, 101MHz, $CDCl_3$)

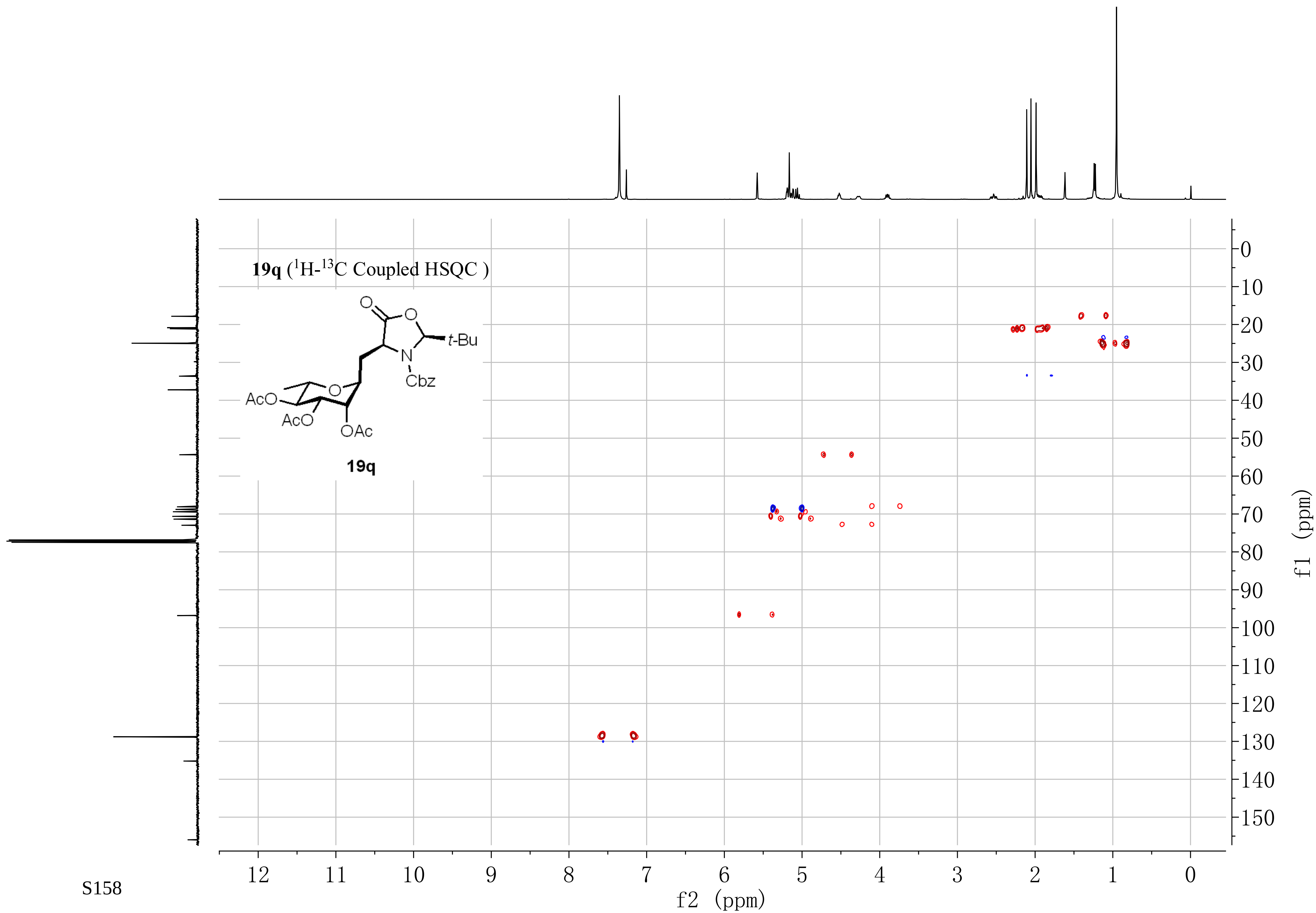


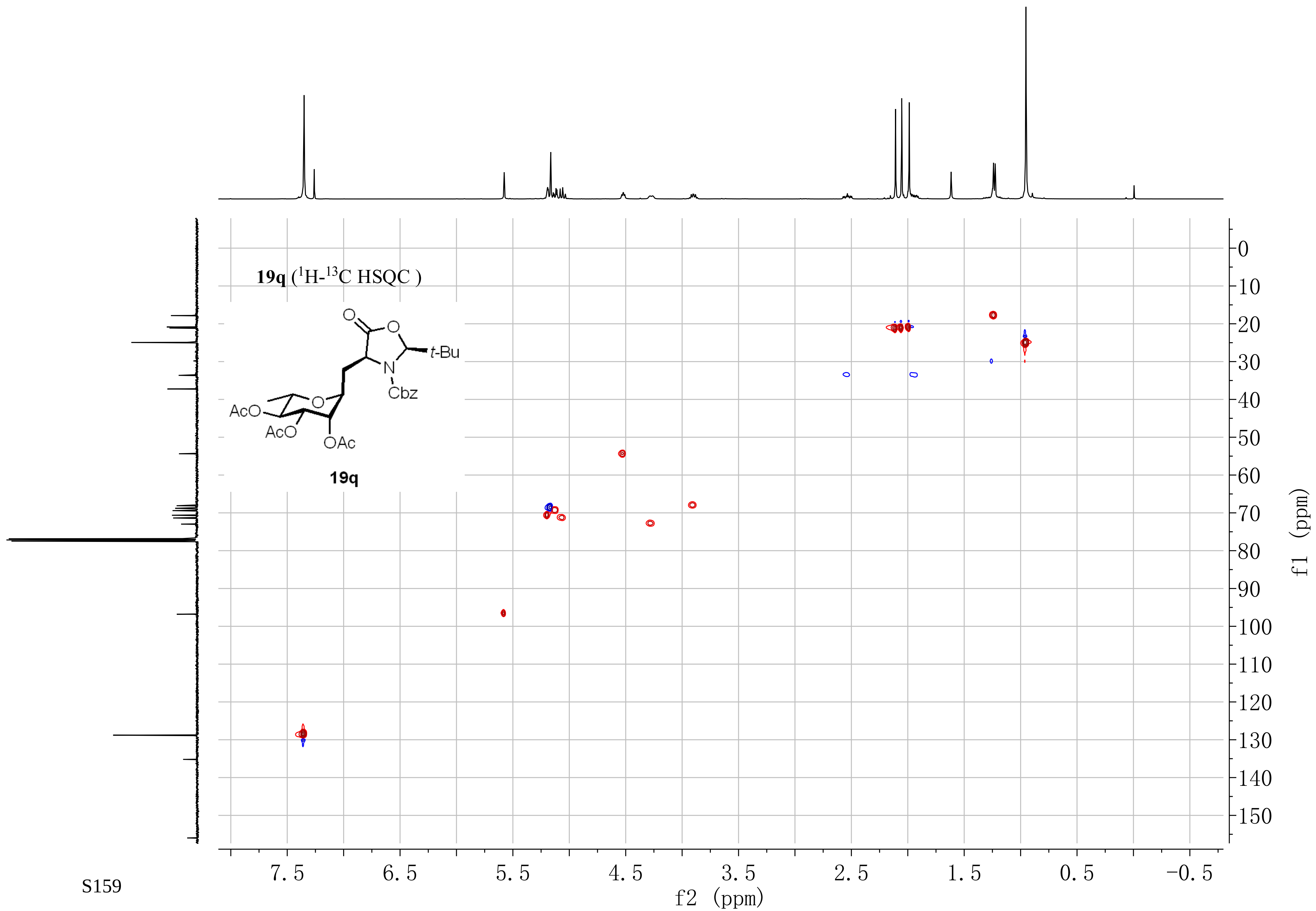
19q

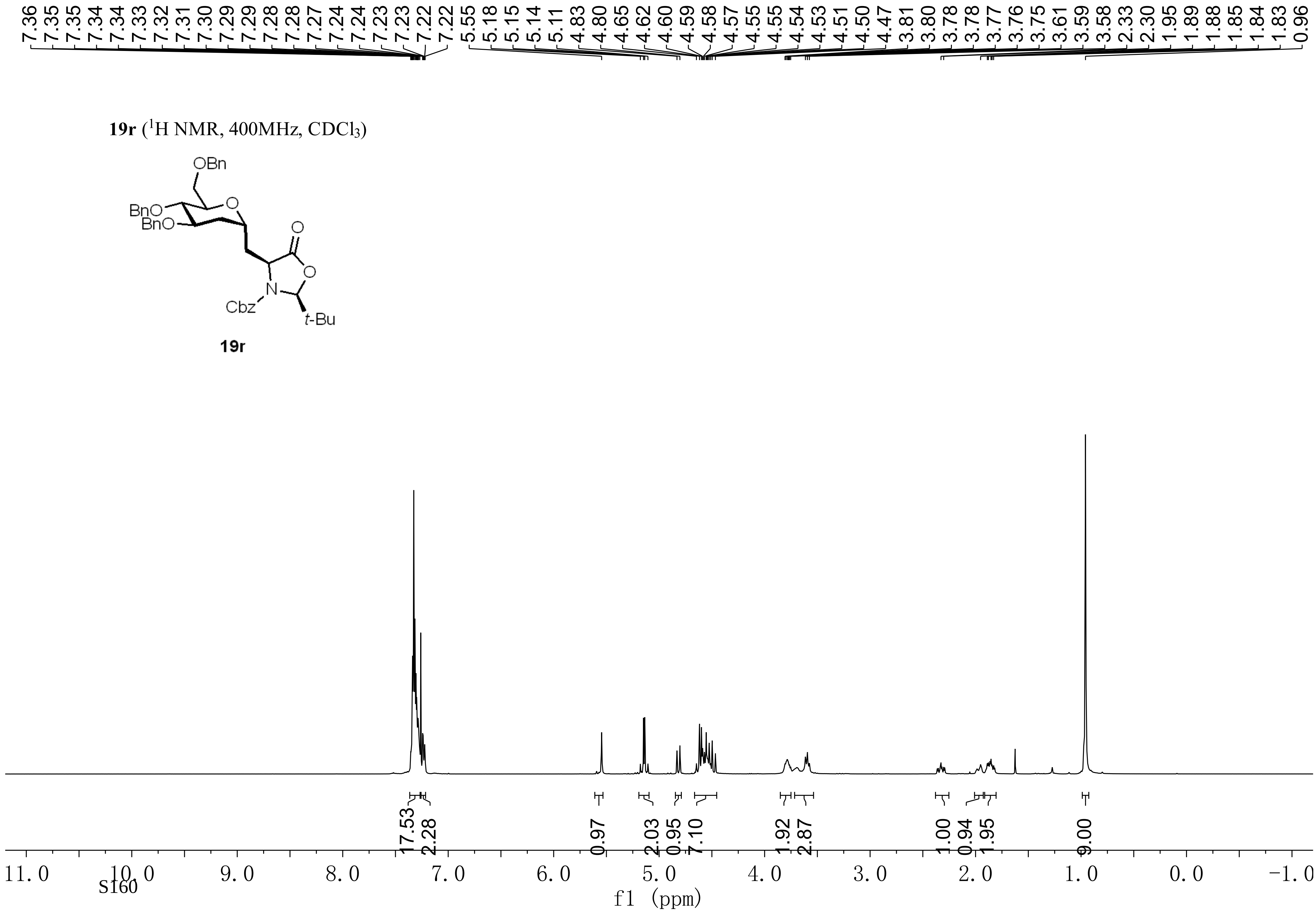




19q (1H-1H COSY)
O
O
t-Bu
N
Cbz
O
AcO
AcO
OAc
19q
f2 (ppm)
f1 (ppm)
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
0
1
2
3
4
5
6
7
8

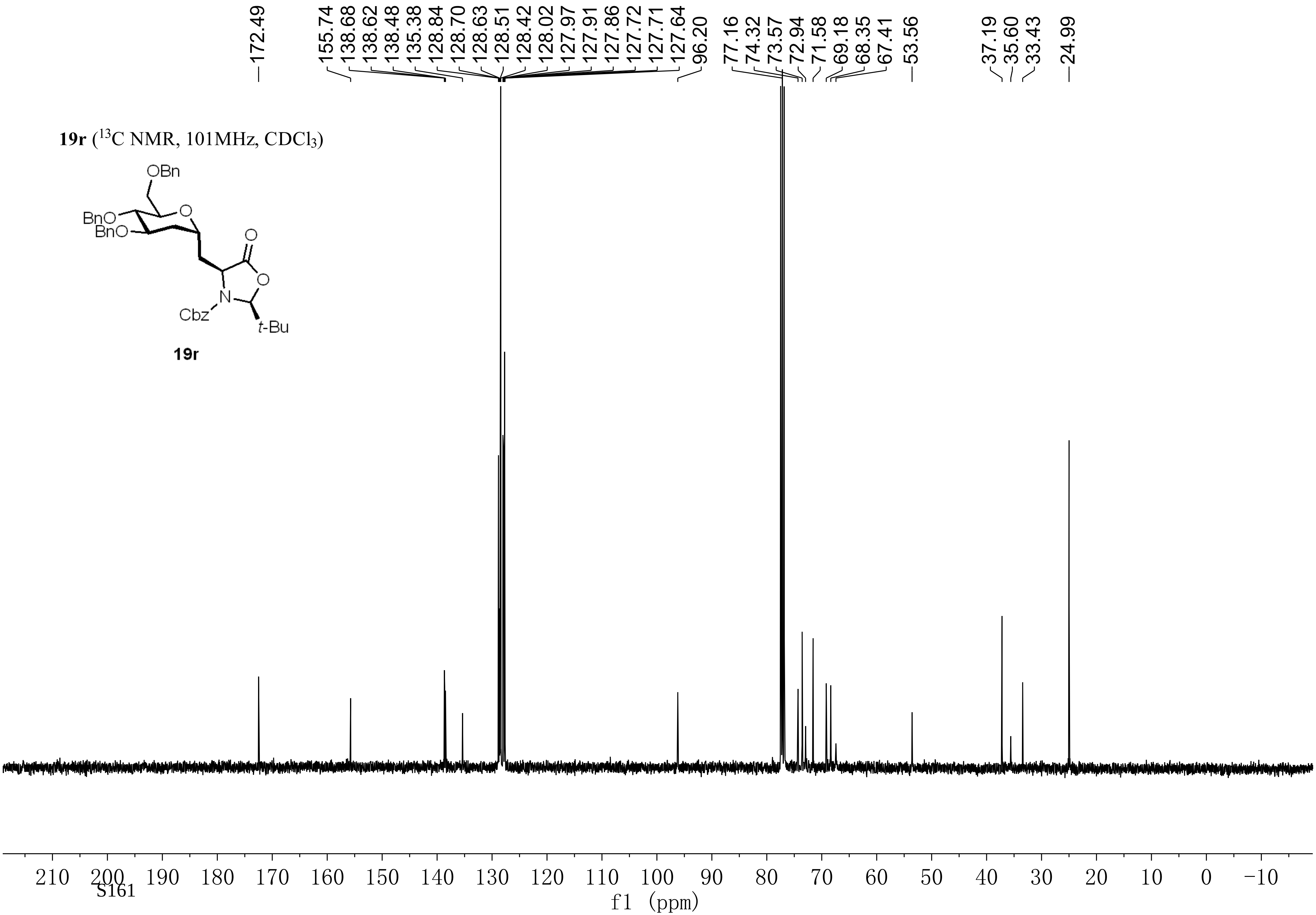

19q (^{1}H-^{13}C Coupled HSQC)
O
O
t-Bu
N
Cbz
O
AcO
AcO
OAc
19q
f1 (ppm)
f2 (ppm)

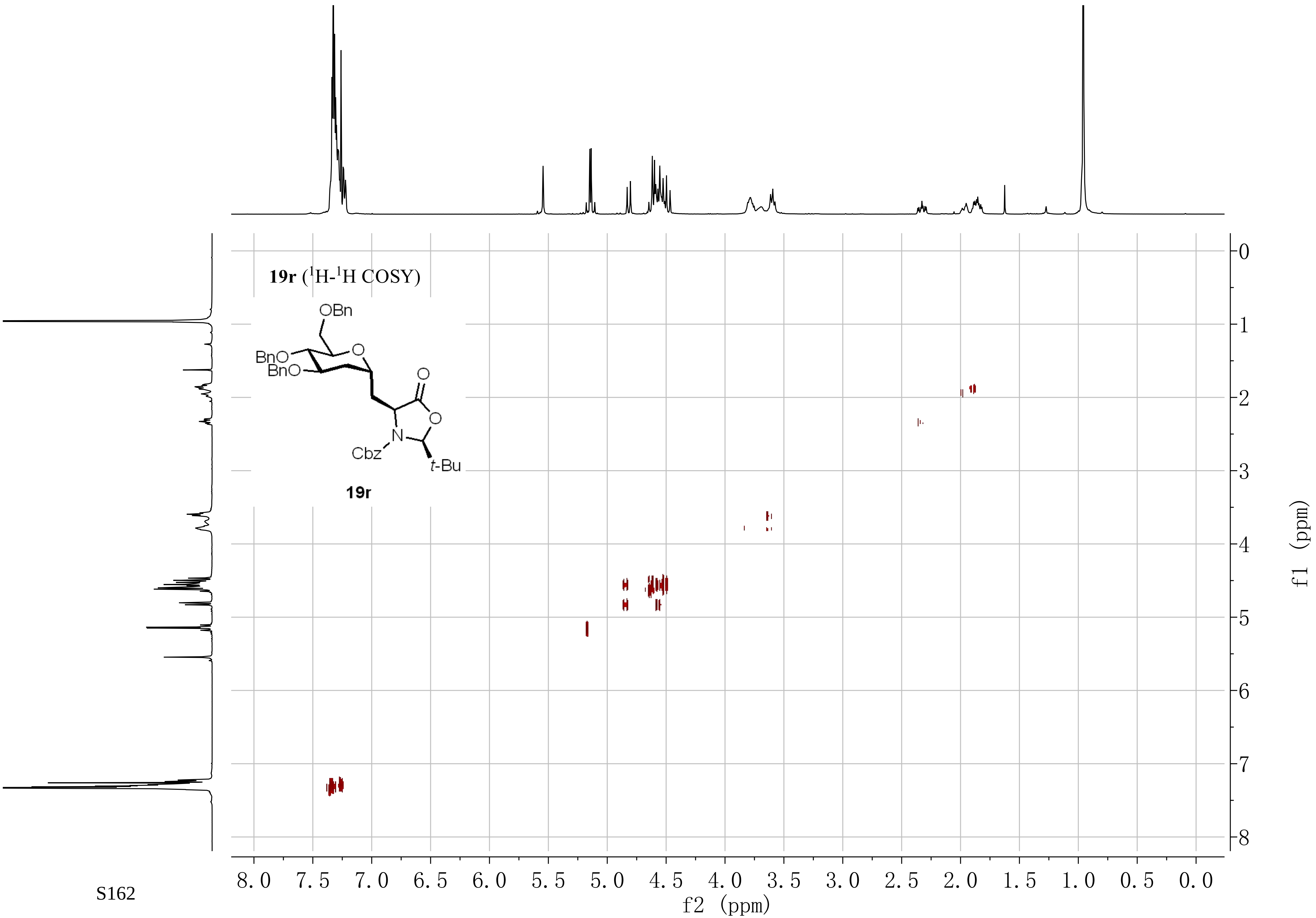

19q (1H-13C HSQC)
O
O
t-Bu
N
Cbz
O
AcO
AcO
OAc
19q
f2 (ppm)
f1 (ppm)



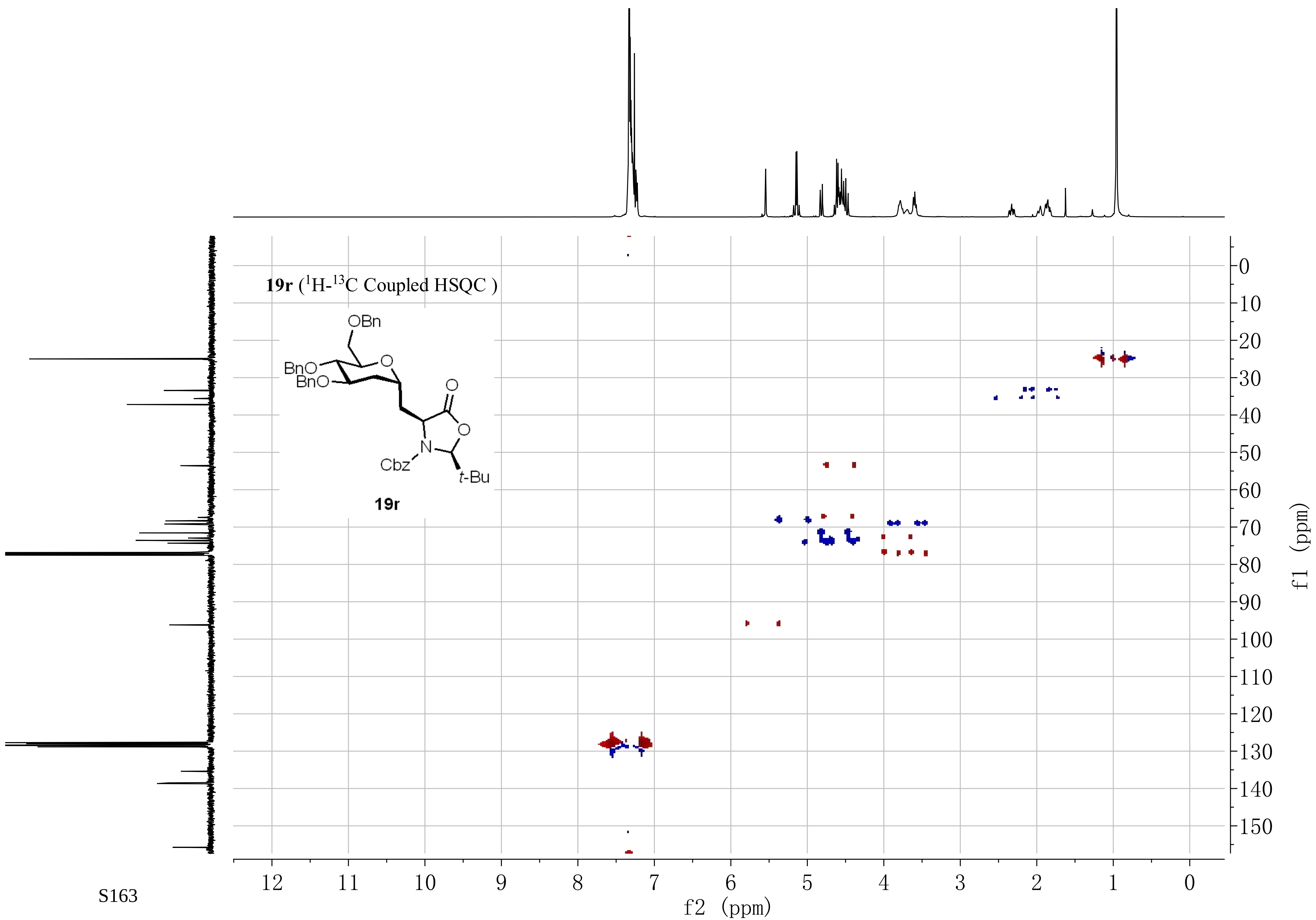
7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.24 7.24 7.23 7.23 7.22 7.22 5.55 5.18 5.15 5.14 5.11 4.83 4.80 4.65 4.62 4.60 4.59 4.58 4.57 4.55 4.55 4.54 4.53 4.51 4.50 4.47 3.81 3.80 3.78 3.78 3.77 3.76 3.75 3.61 3.59 3.58 2.33 2.30 1.95 1.89 1.88 1.85 1.84 1.83 0.96
19r (^{1}H NMR, 400MHz, $CDCl_3$)
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19r
17.53
2.28
0.97
2.03
0.95
7.10
1.92
2.87
1.00
0.94
1.95
9.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)

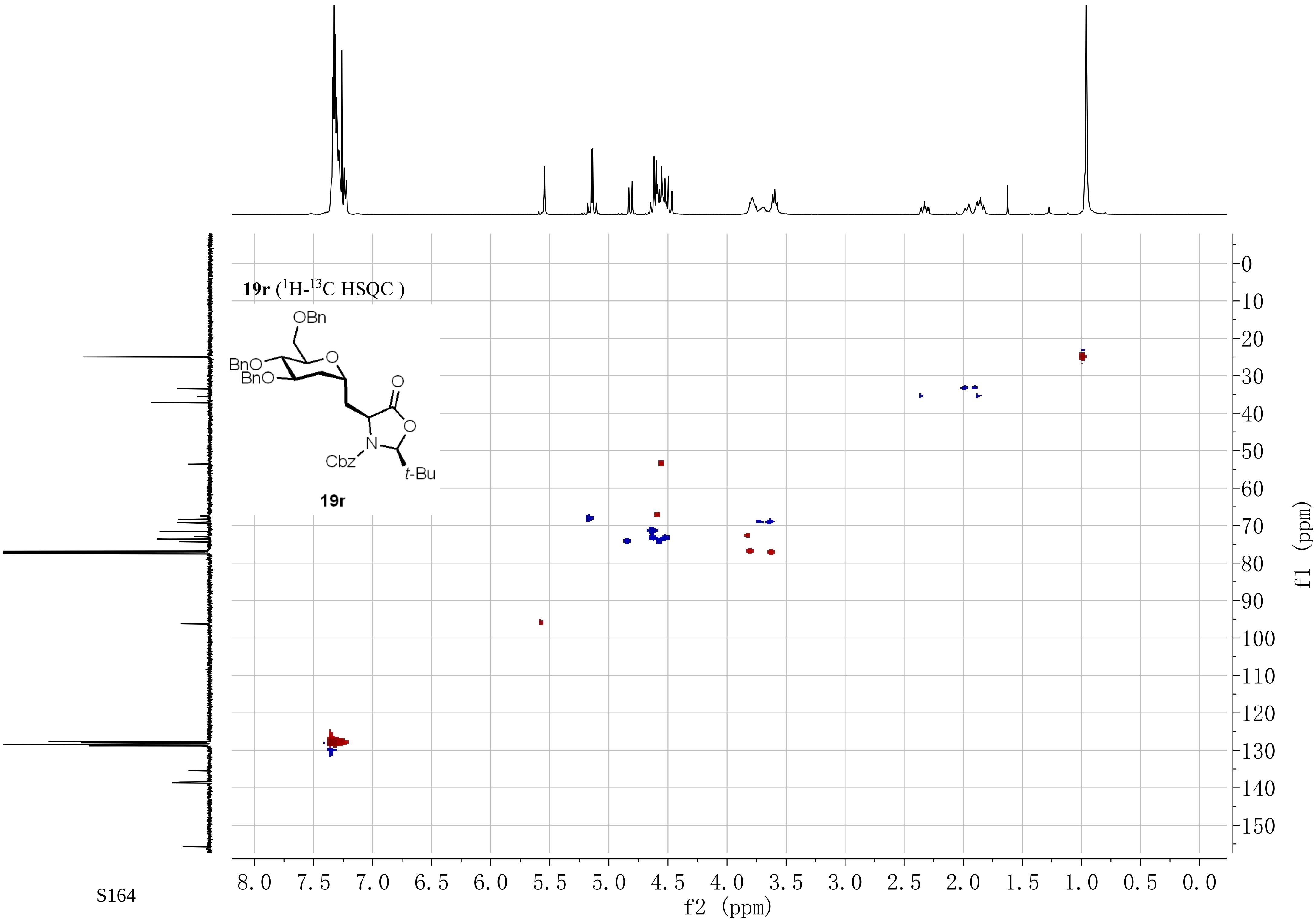
19r (^{13}C NMR, 101MHz, $CDCl_3$)



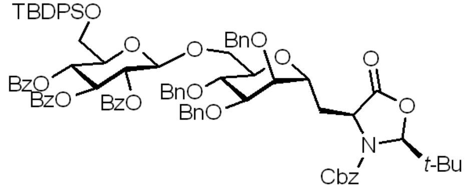


19r (1H-1H COSY)
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19r
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

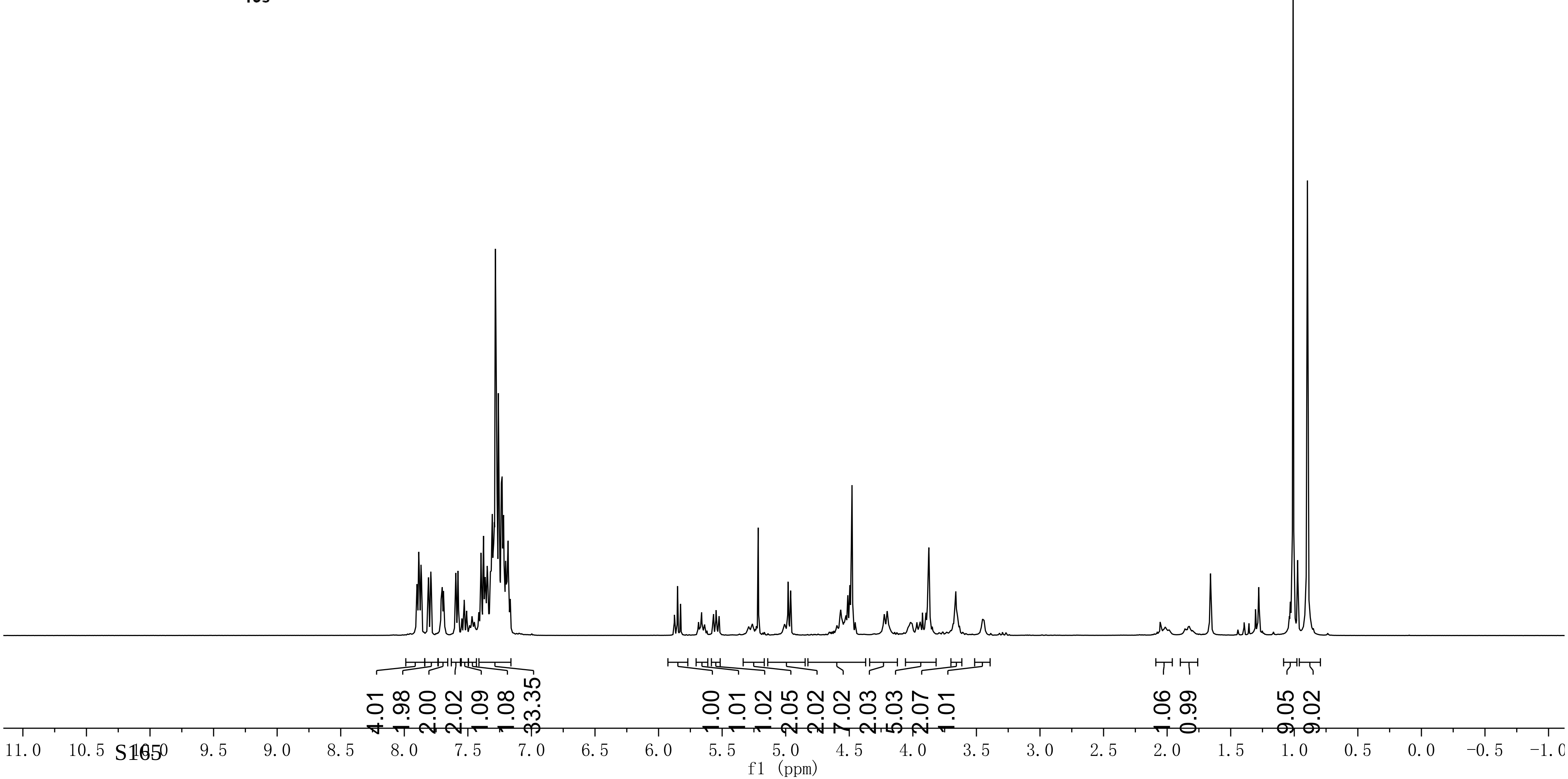

19r (1H-13C Coupled HSQC)
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19r
f2 (ppm)
f1 (ppm)


19r (¹H-¹³C HSQC)
OBn
BnO
BnO
O
O
O
N
Cbz
t-Bu
19r
f2 (ppm)
f1 (ppm)
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
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

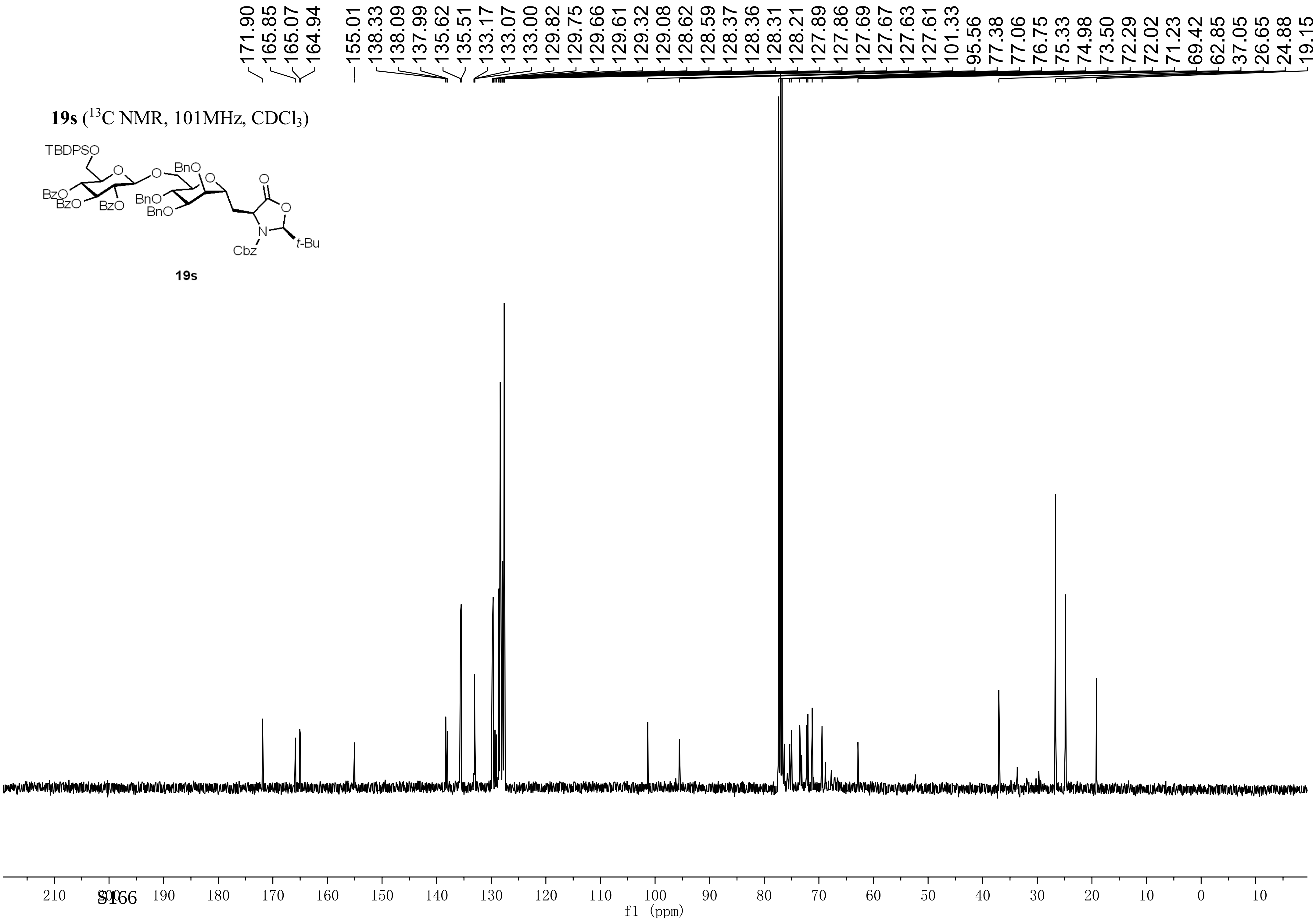
19s (^{1}H NMR, 400MHz, $CDCl_3$)

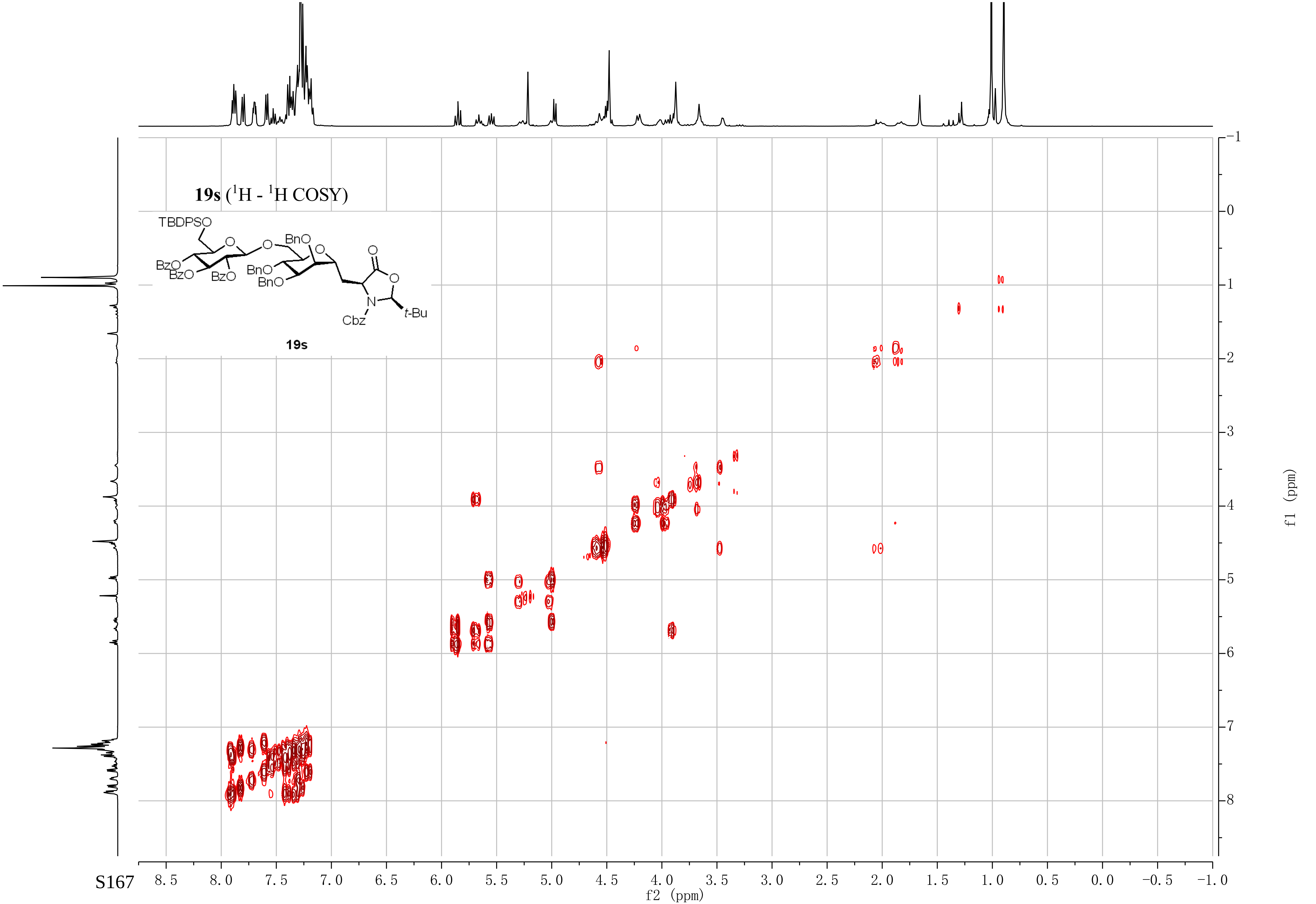


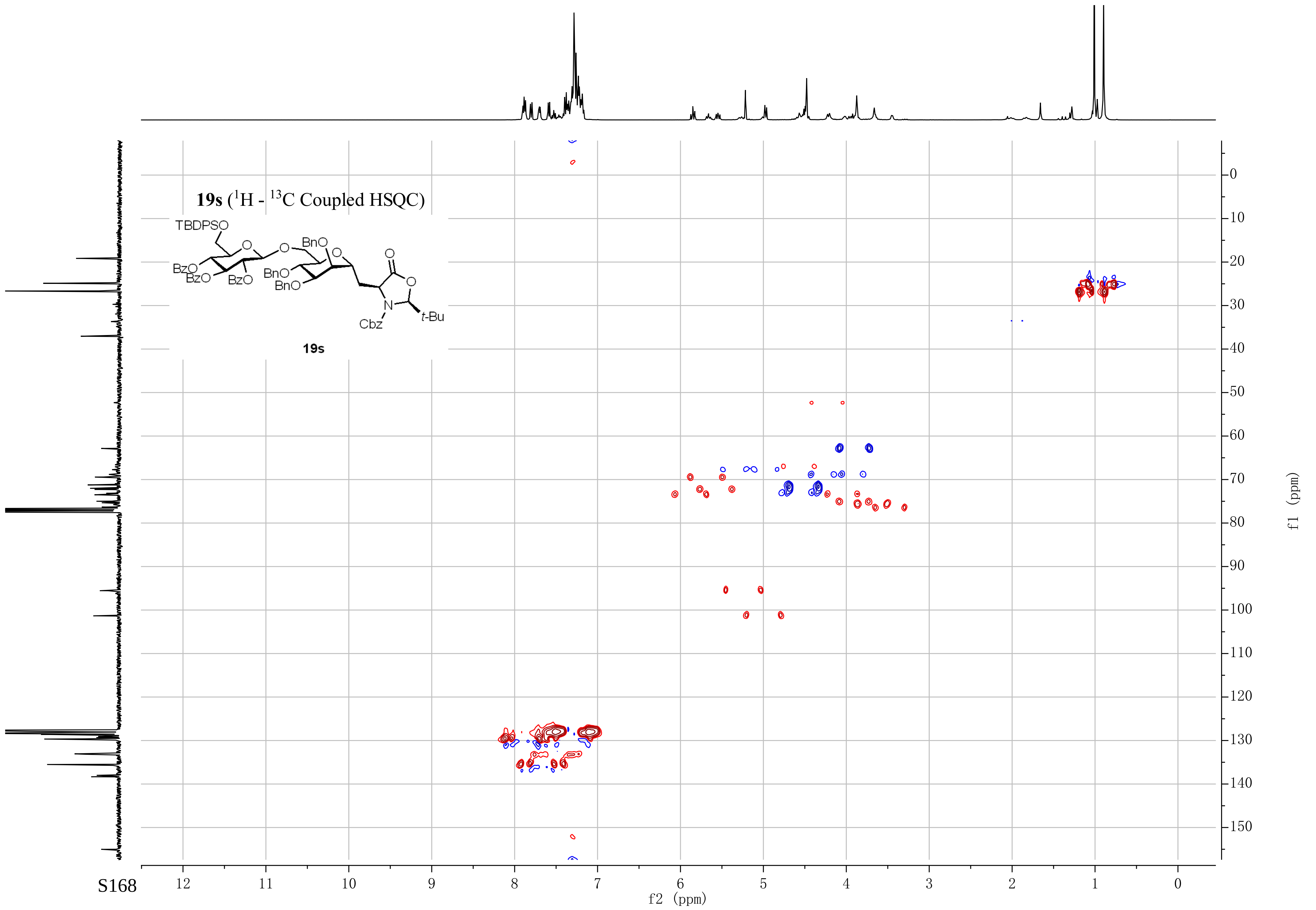
19s

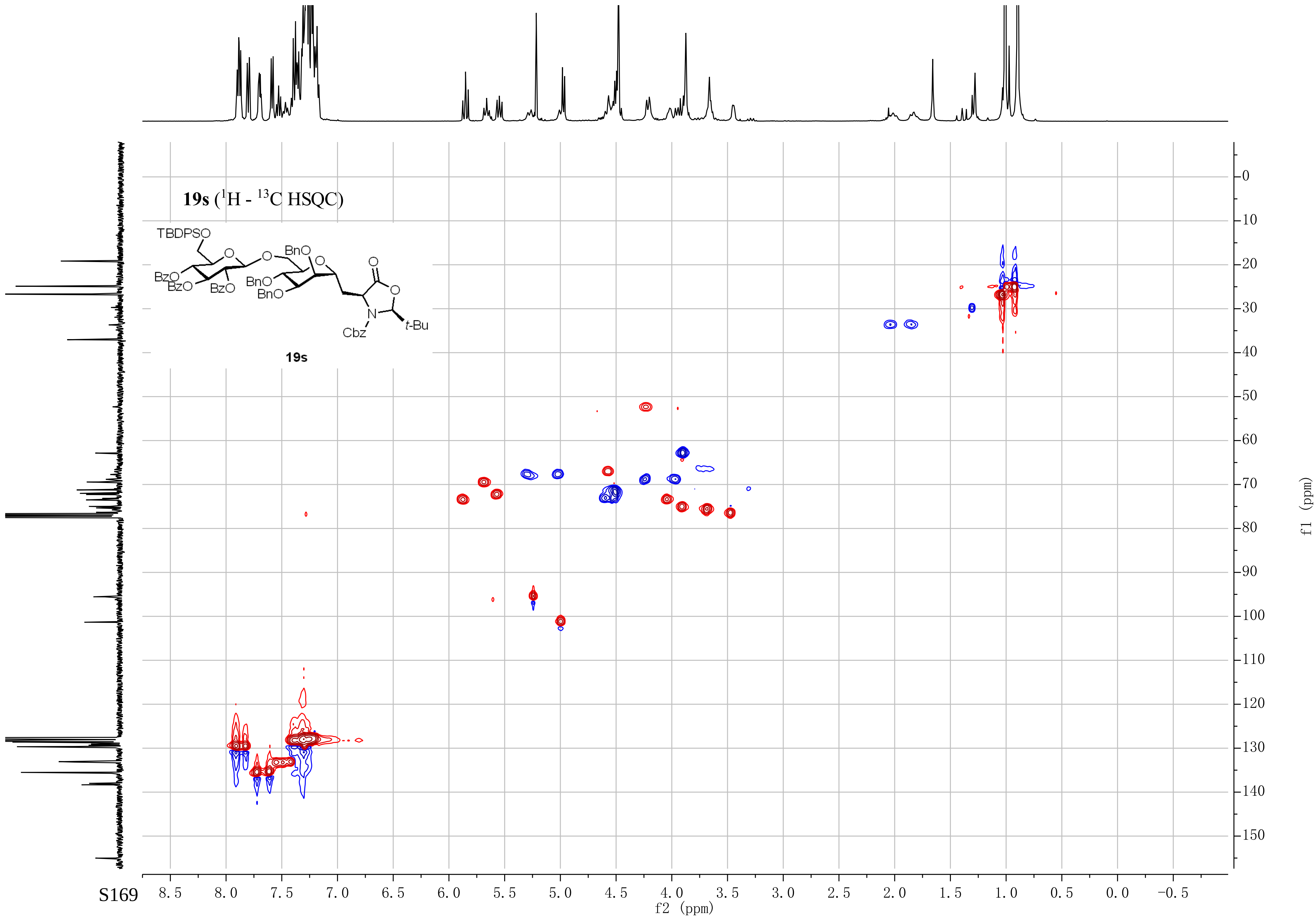


19s (^{13}C NMR, 101MHz, $CDCl_3$)

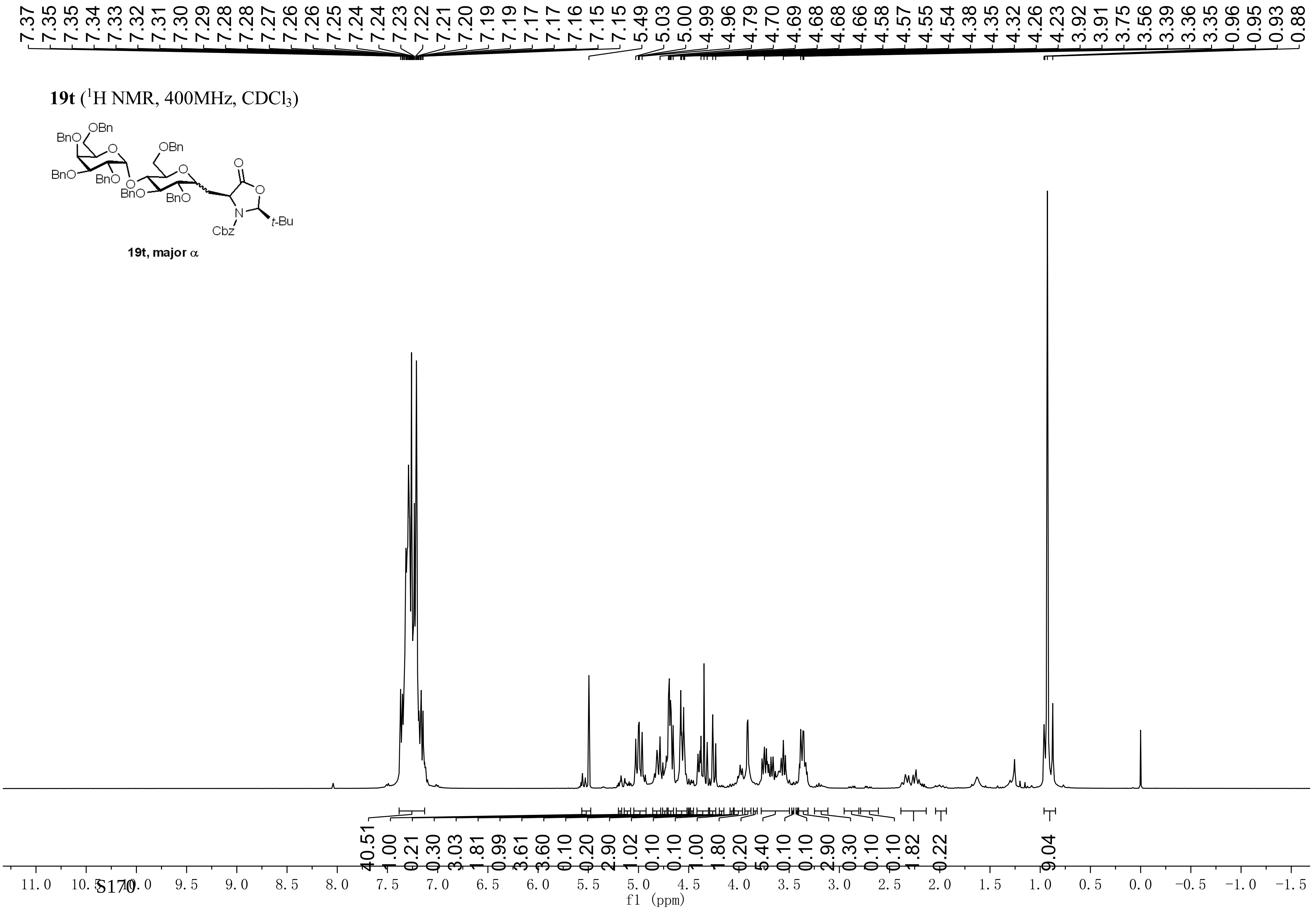



19s (1H - 1H COSY)
TBDPSO
BzO
BzO
BzO
BnO
BnO
BnO
O
N
Cbz
t-Bu
19s
f2 (ppm)
f1 (ppm)

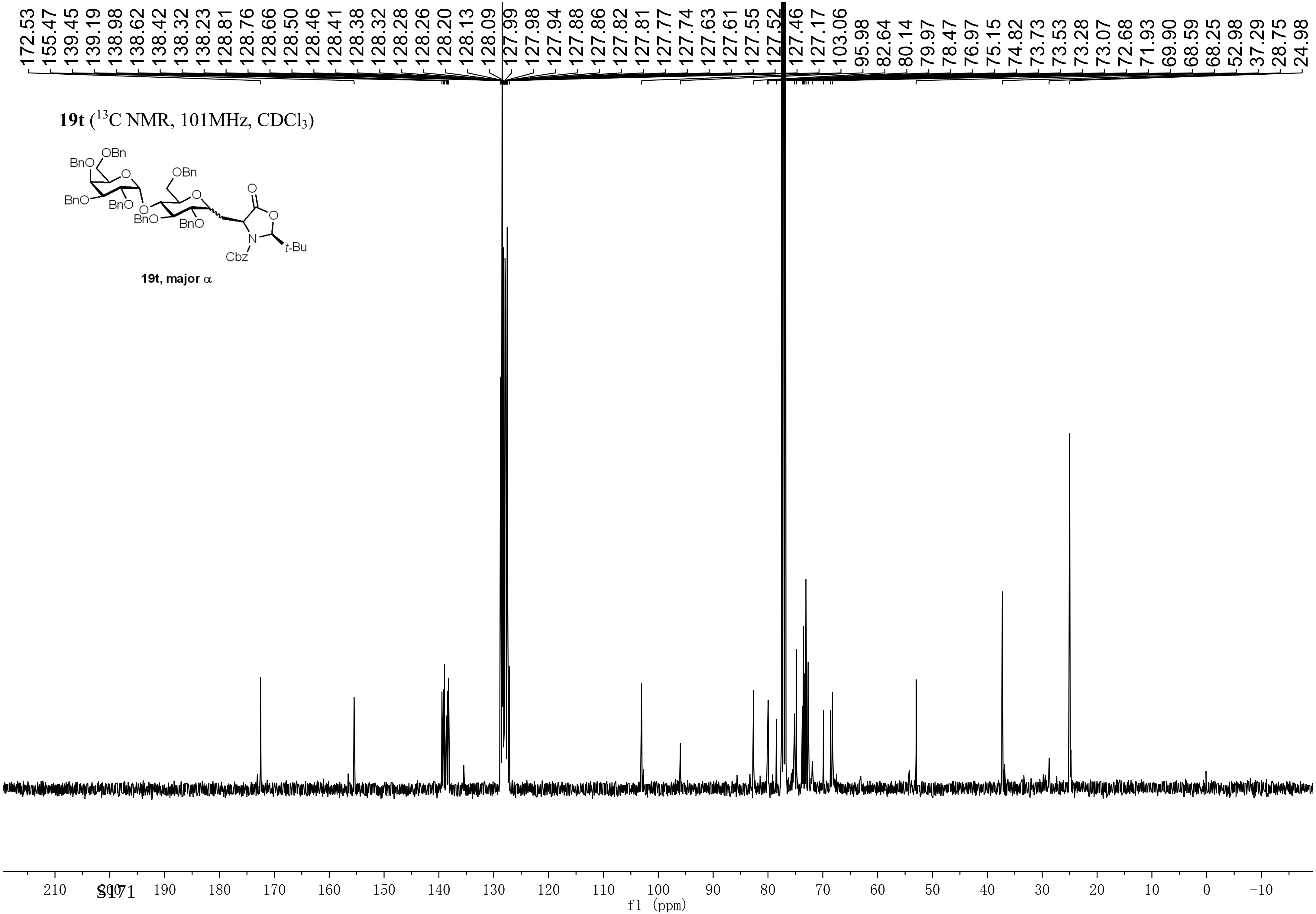

19s (^{1}H - ^{13}C Coupled HSQC)
TBDPSO
BzO
BzO
BzO
BnO
BnO
BnO
O
N
Cbz
t-Bu
19s
f2 (ppm)
f1 (ppm)



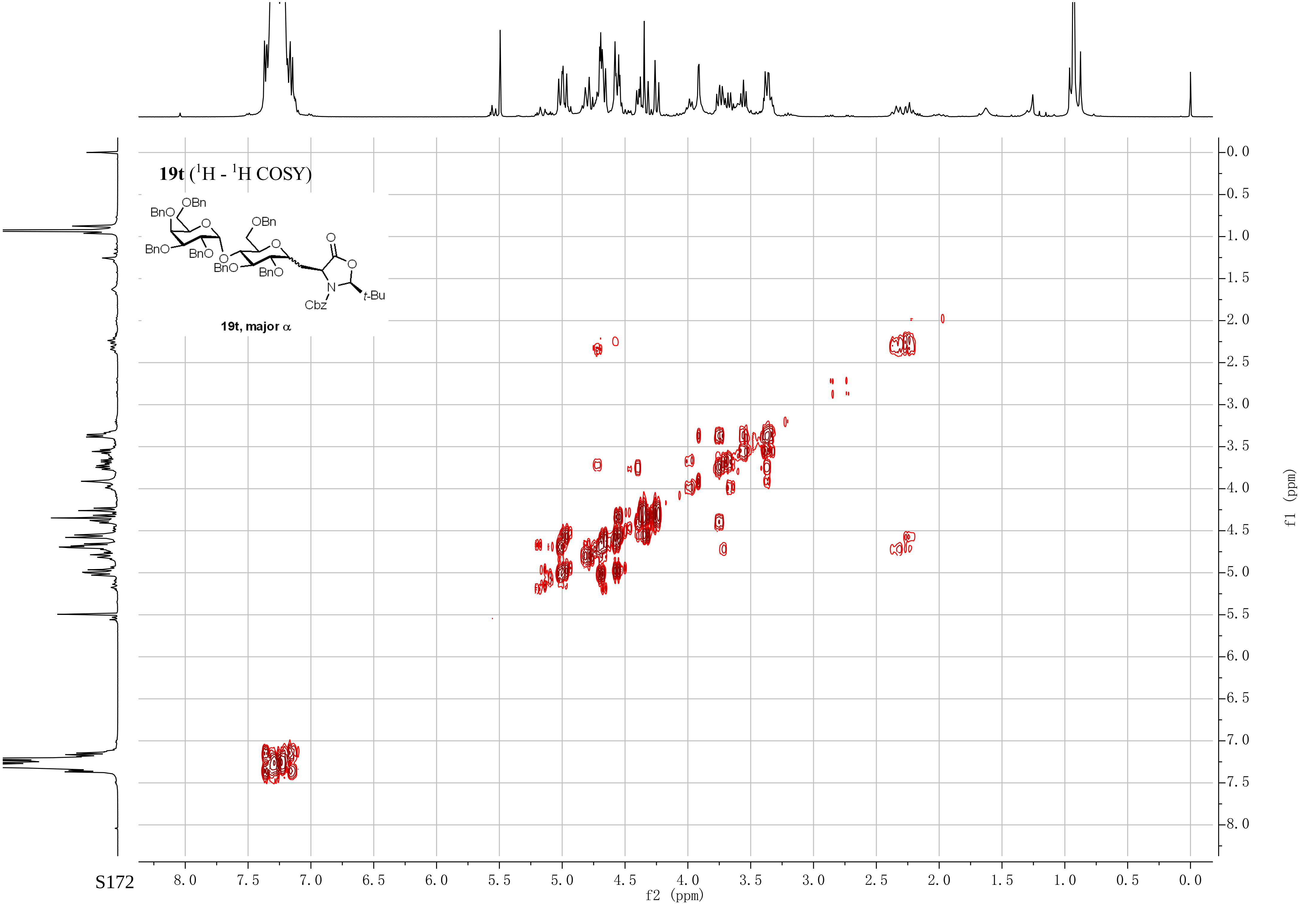
19s (1H - 13C HSQC)
TBDPSO
BzO
BzO
BzO
BnO
BnO
BnO
O
N
Cbz
t-Bu
19s
f2 (ppm)
f1 (ppm)

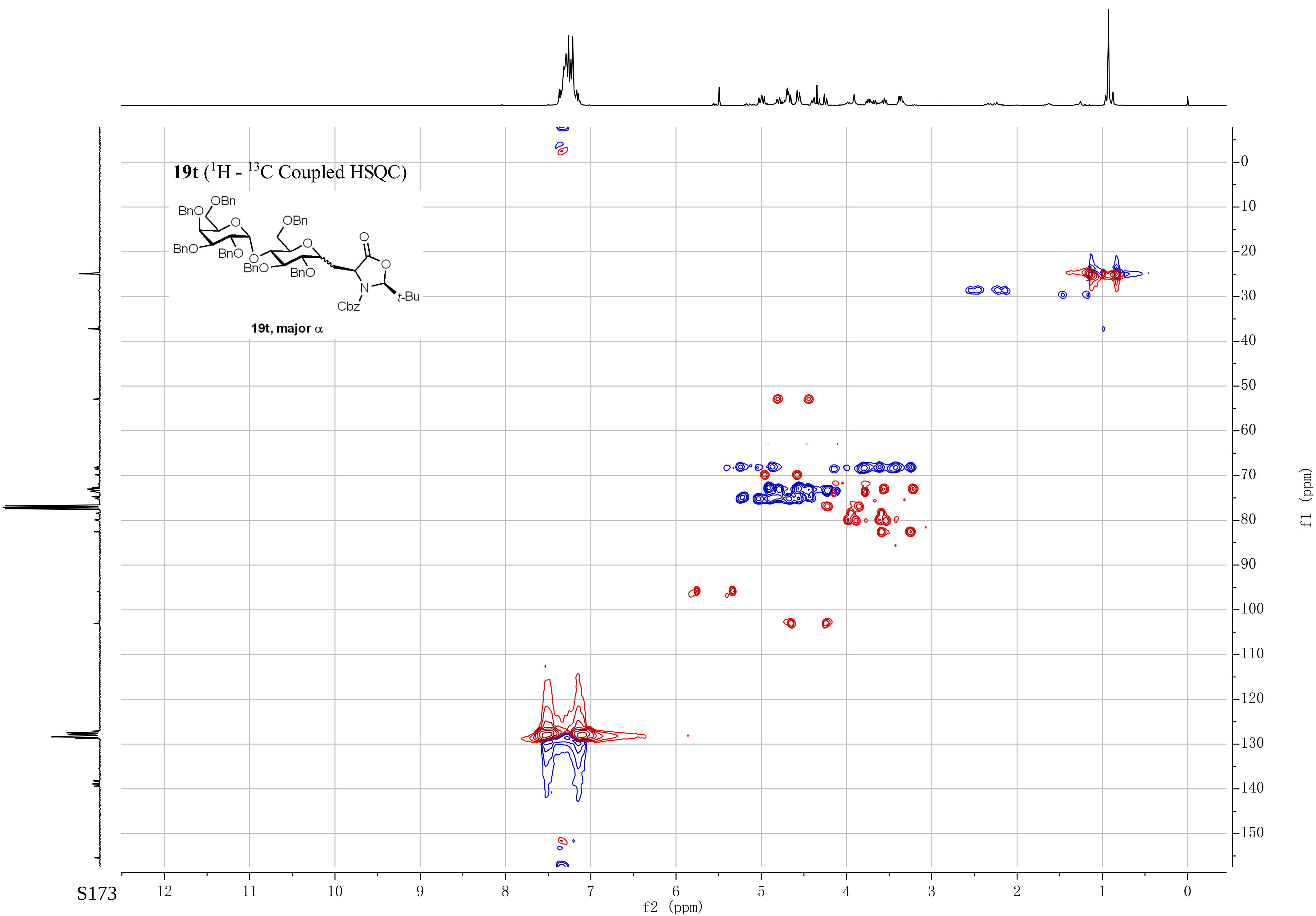


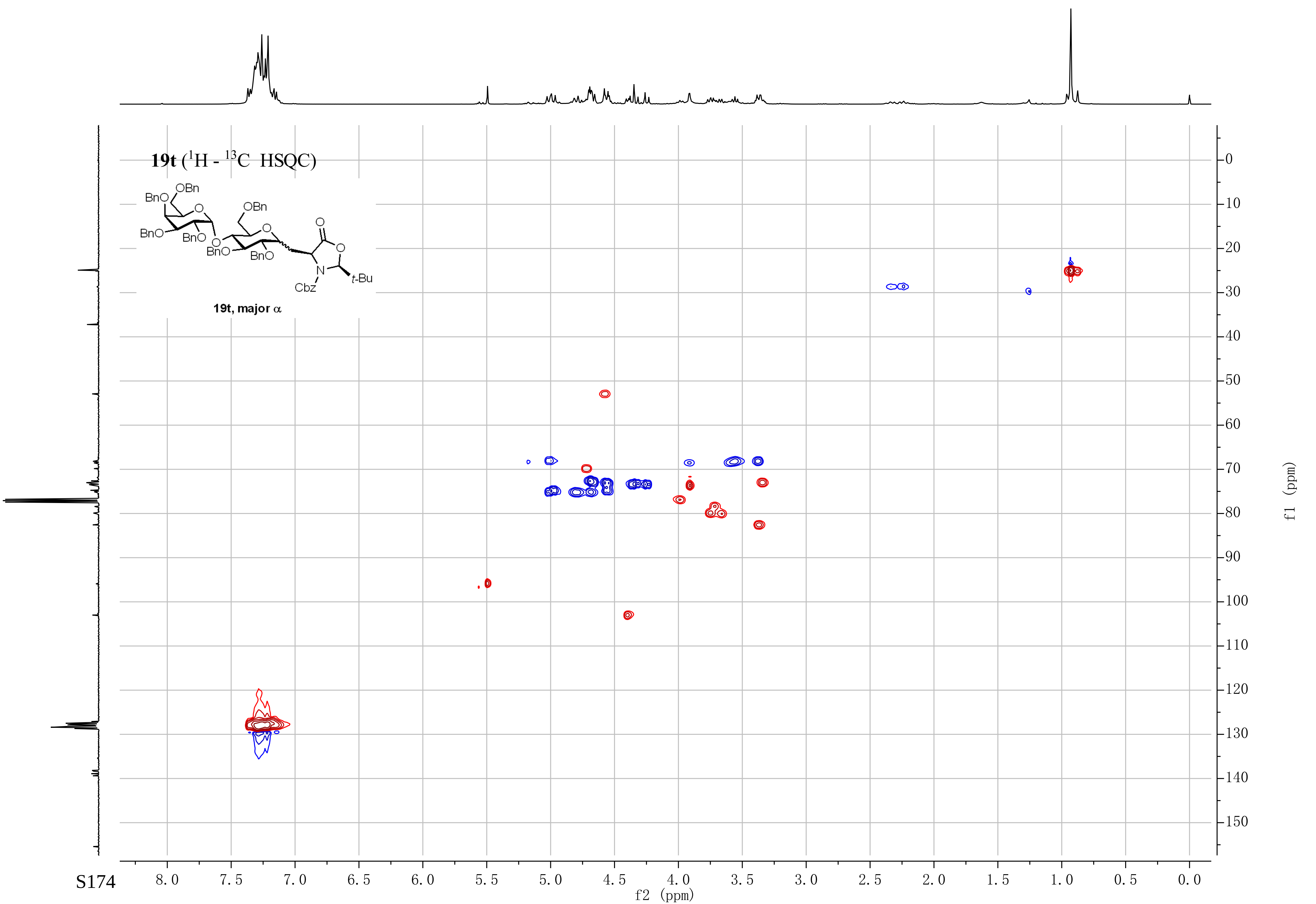
7.37 7.35 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.19 7.17 7.17 7.16 7.15 7.15 5.49 5.03 5.00 4.99 4.96 4.79 4.70 4.69 4.68 4.68 4.66 4.58 4.57 4.55 4.54 4.38 4.35 4.32 4.26 4.23 3.92 3.91 3.75 3.56 3.39 3.36 3.35 0.96 0.95 0.93 0.88
19t (^{1}H NMR, 400MHz, $CDCl_3$)
OBn
BnO
BnO
BnO
O
BnO
BnO
BnO
N
Cbz
t-Bu
19t, major α
40.51 1.00 0.21 0.30 3.03 1.81 0.99 3.61 3.60 0.10 0.20 2.90 1.02 0.10 0.10 1.00 1.80 0.20 5.40 0.10 0.10 2.90 0.30 0.10 0.10 1.82 0.22 9.04
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 −1.5
f1 (ppm)



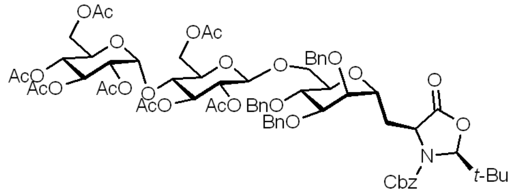
172.53
155.47
139.45
139.19
138.98
138.62
138.42
138.32
138.23
128.81
128.76
128.66
128.50
128.46
128.41
128.38
128.32
128.28
128.26
128.20
128.13
128.09
127.99
127.98
127.94
127.88
127.86
127.82
127.81
127.77
127.74
127.63
127.61
127.55
127.52
127.46
127.17
103.06
95.98
82.64
80.14
79.97
78.47
76.97
75.15
74.82
73.73
73.53
73.28
73.07
72.68
71.93
69.90
68.59
68.25
52.98
37.29
28.75
24.98
19t (^{13}C NMR, 101MHz, CDCl$_3$)
BnO
OBn
O
BnO
BnO
O
OBn
O
BnO
BnO
O
O
N
Cbz
t-Bu
19t, major α
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)


19t (^{1}H - ^{1}H COSY)
OBn
BnO
O
BnO
BnO
O
OBn
O
BnO
BnO
O
O
N
Cbz
t-Bu
19t, major α
f2 (ppm)
f1 (ppm)

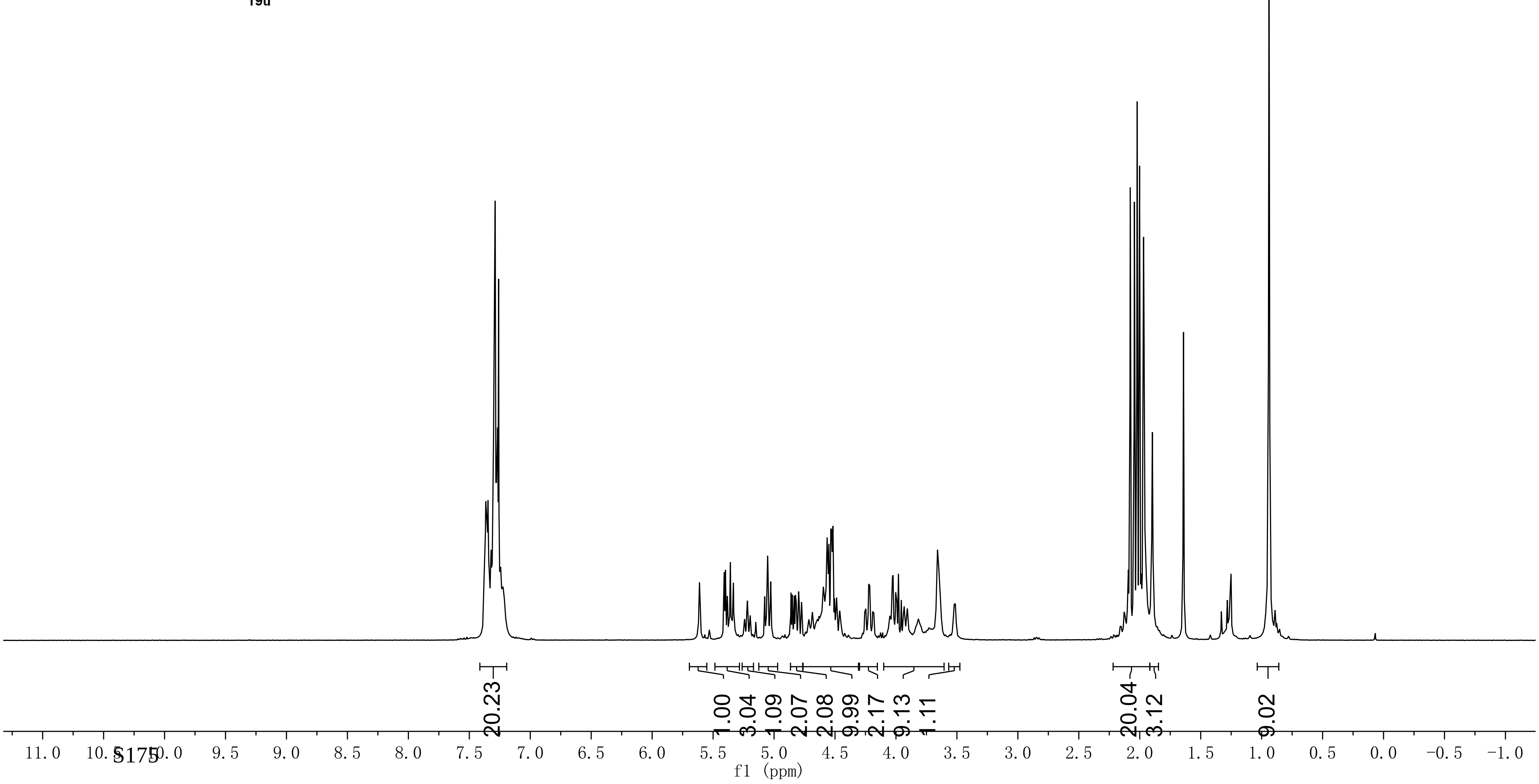

19t (1H - 13C Coupled HSQC)
BnO
OBn
O
BnO
BnO
O
OBn
O
BnO
BnO
O
O
N
t-Bu
Cbz
19t, major α
f2 (ppm)
f1 (ppm)


19t (1H - 13C HSQC)
BnO
OBn
O
BnO
BnO
O
OBn
O
BnO
BnO
O
O
N
t-Bu
Cbz
19t, major α
f2 (ppm)
f1 (ppm)

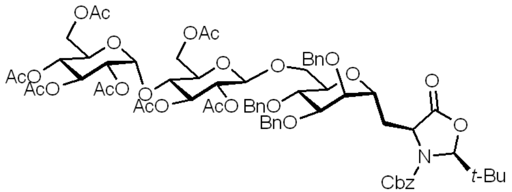
19u (^{1}H NMR, 400MHz, $CDCl_3$)



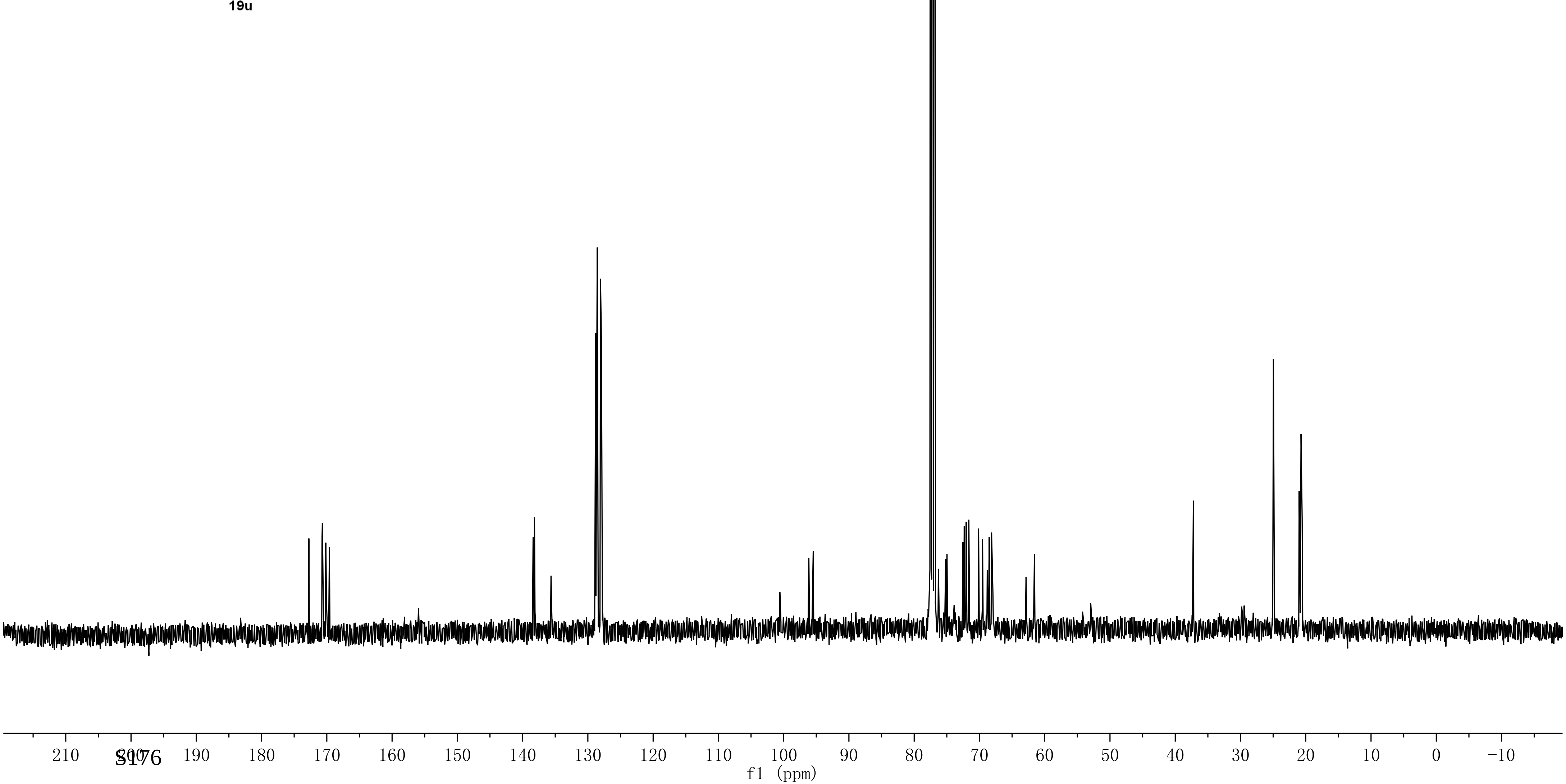
19u

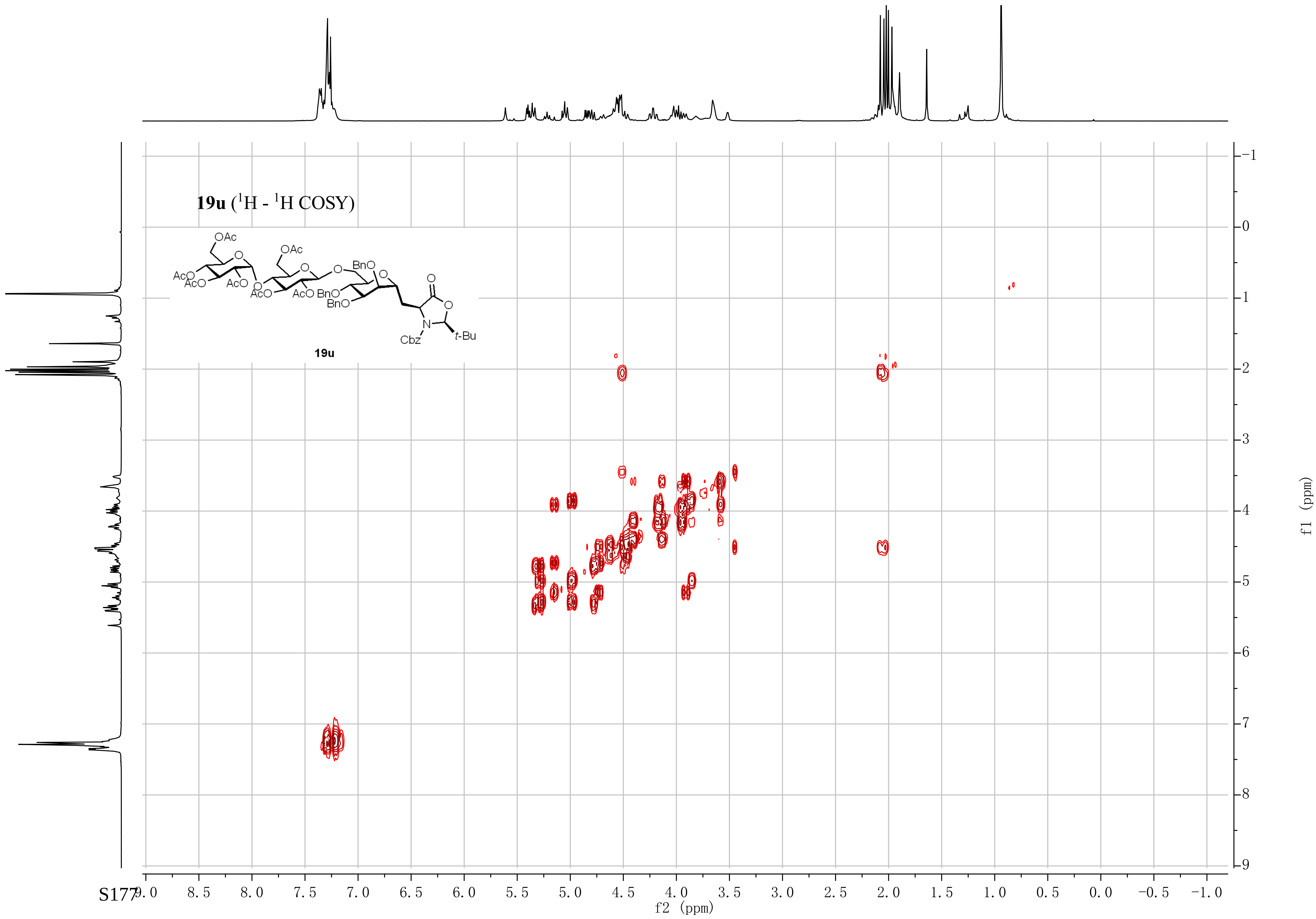


19u (^{13}C NMR, 101MHz, $CDCl_3$)

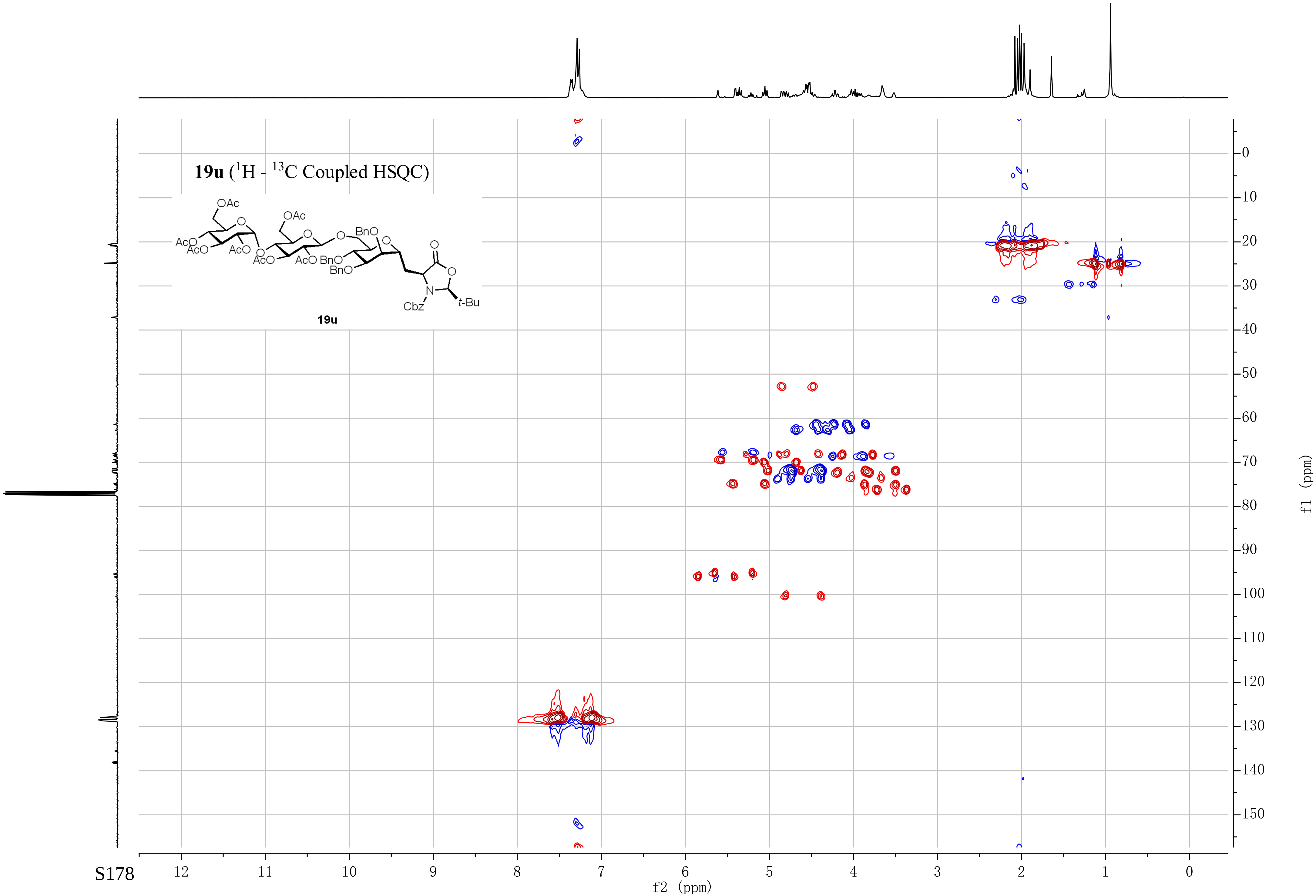


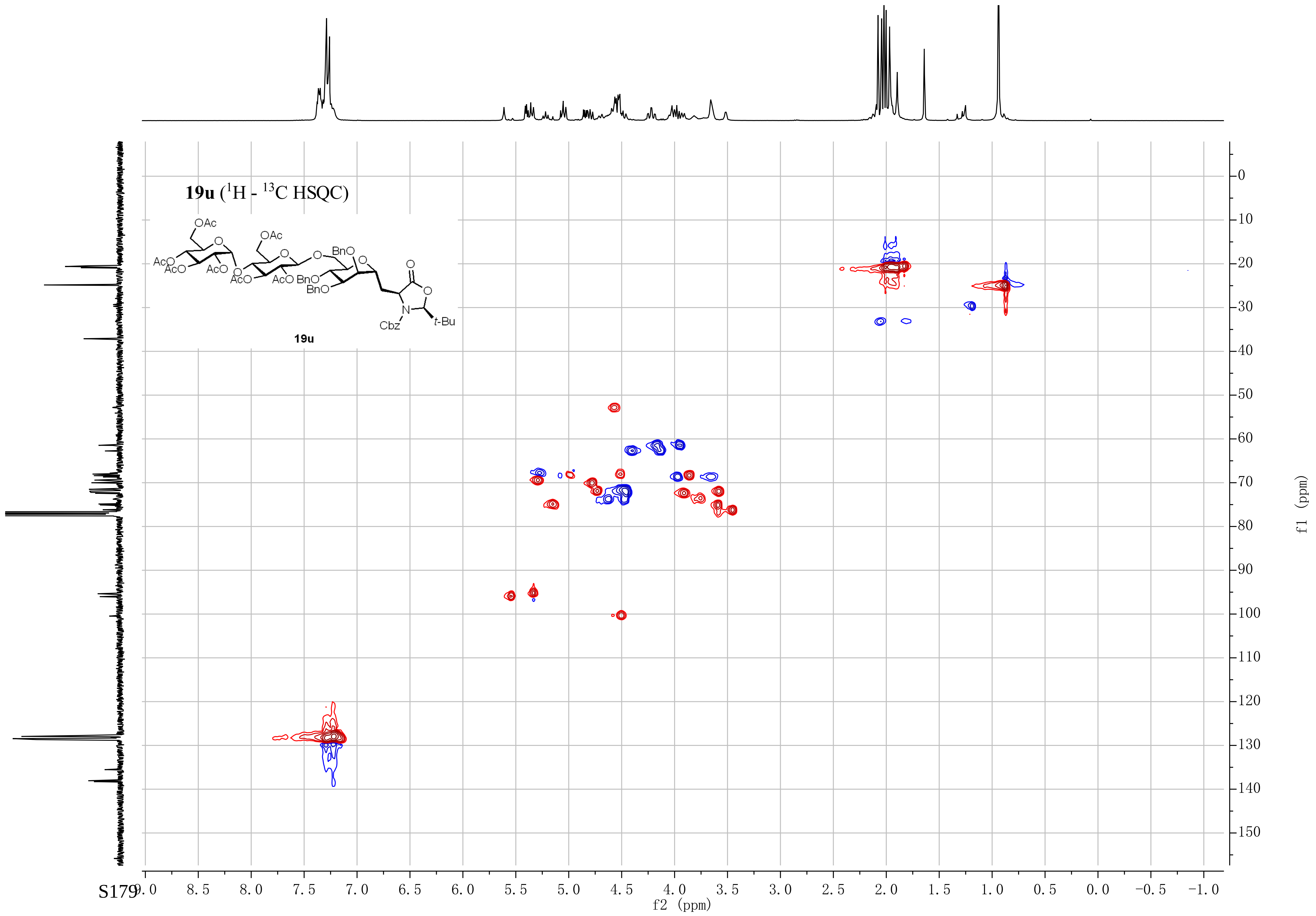
19u

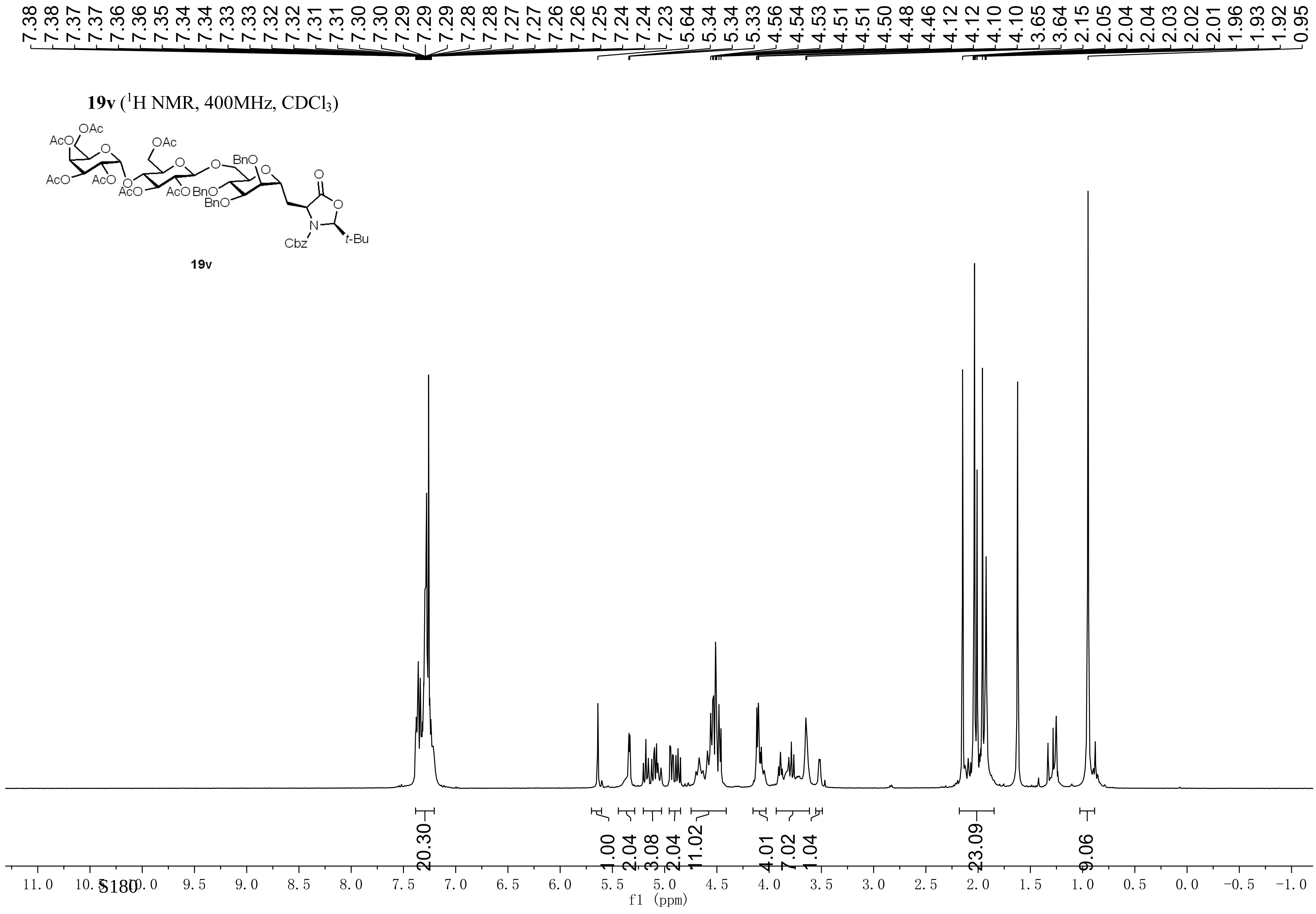




19u (1H - 1H COSY)
OAc
AcO
AcO
AcO
AcO
OAc
AcO
BnO
BnO
BnO
N
Cbz
t-Bu
19u
f2 (ppm)
f1 (ppm)

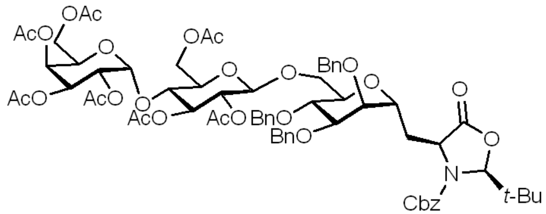

19u (1H - 13C Coupled HSQC)
OAc
AcO
AcO
AcO
OAc
AcO
AcO
BnO
BnO
BnO
N
Cbz
t-Bu
19u
f2 (ppm)
f1 (ppm)


19u (¹H - ¹³C HSQC)
OAc
OAc
AcO
AcO
AcO
AcO
AcO
BnO
BnO
BnO
O
N
Cbz
t-Bu
19u
f2 (ppm)
f1 (ppm)

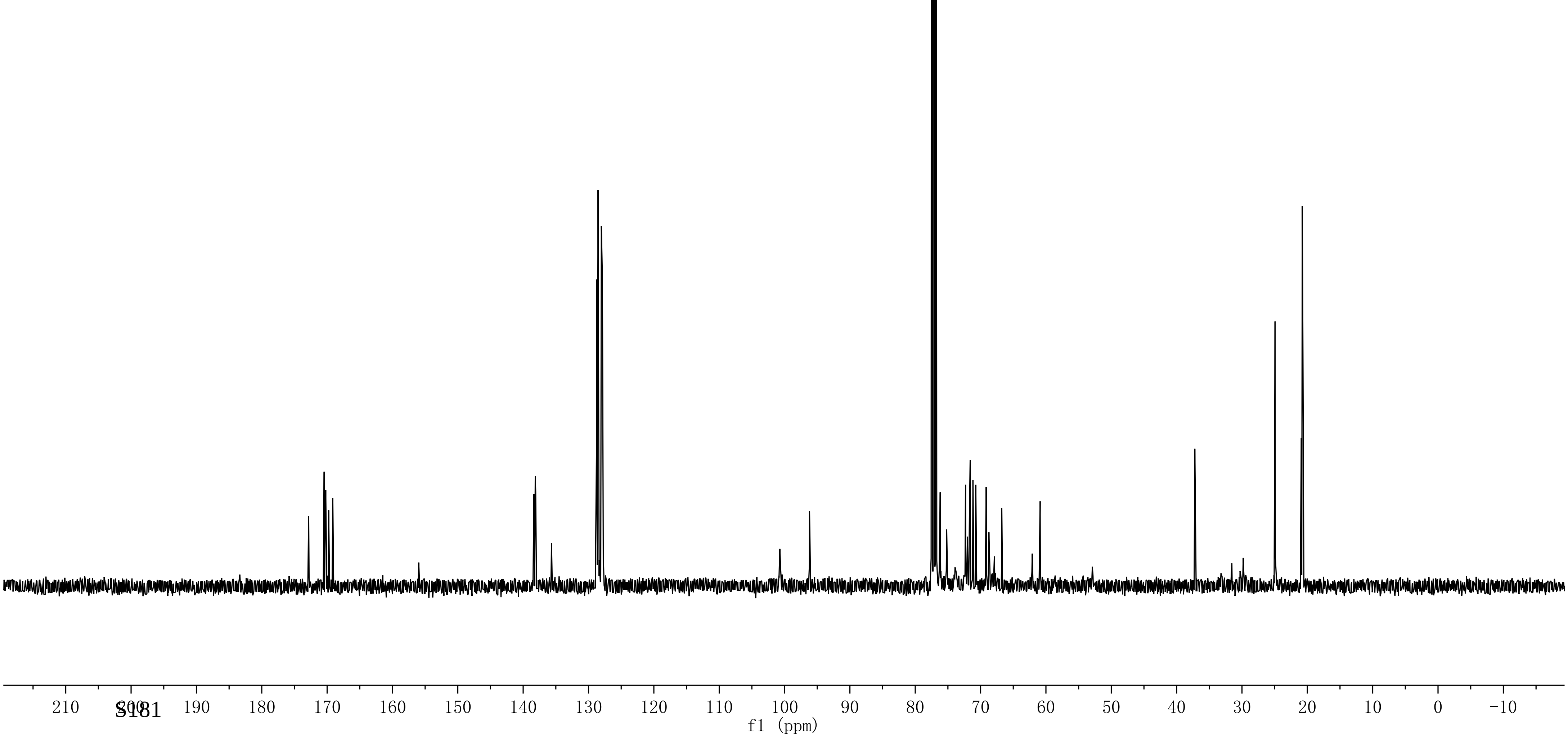


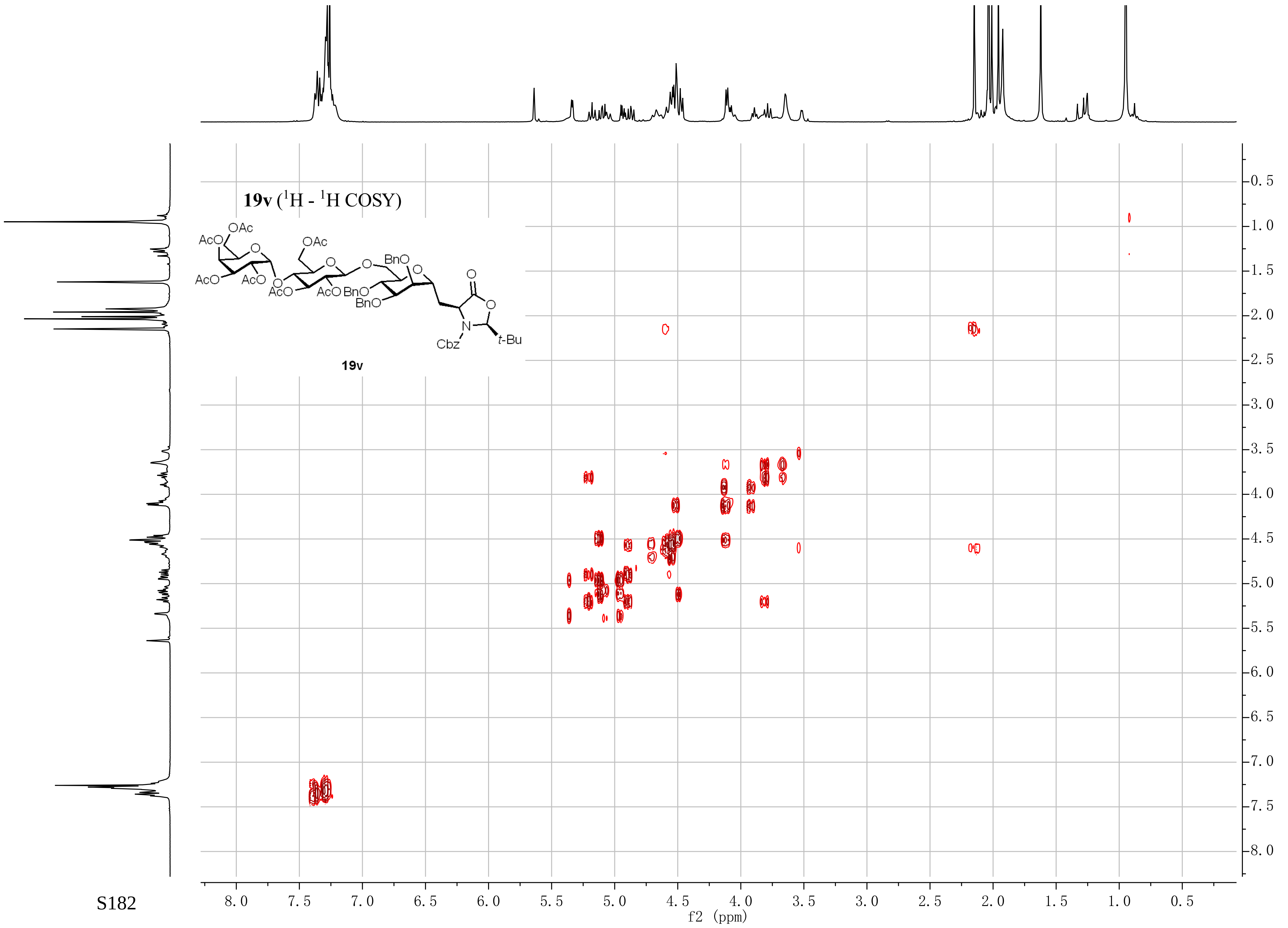
7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 5.64 5.34 5.34 5.33 4.56 4.54 4.53 4.51 4.51 4.50 4.48 4.46 4.12 4.12 4.10 4.10 3.65 3.64 2.15 2.05 2.04 2.04 2.03 2.02 2.01 1.96 1.93 1.92 0.95
19v (^{1}H NMR, 400MHz, CDCl$_3$)
AcO OAc
OAc
AcO AcO AcO AcO AcO BnO BnO BnO BnO
O
N
Cbz
t-Bu
19v
20.30
1.00 2.04 3.08 2.04 11.02
4.01 7.02 1.04
23.09
9.06
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)

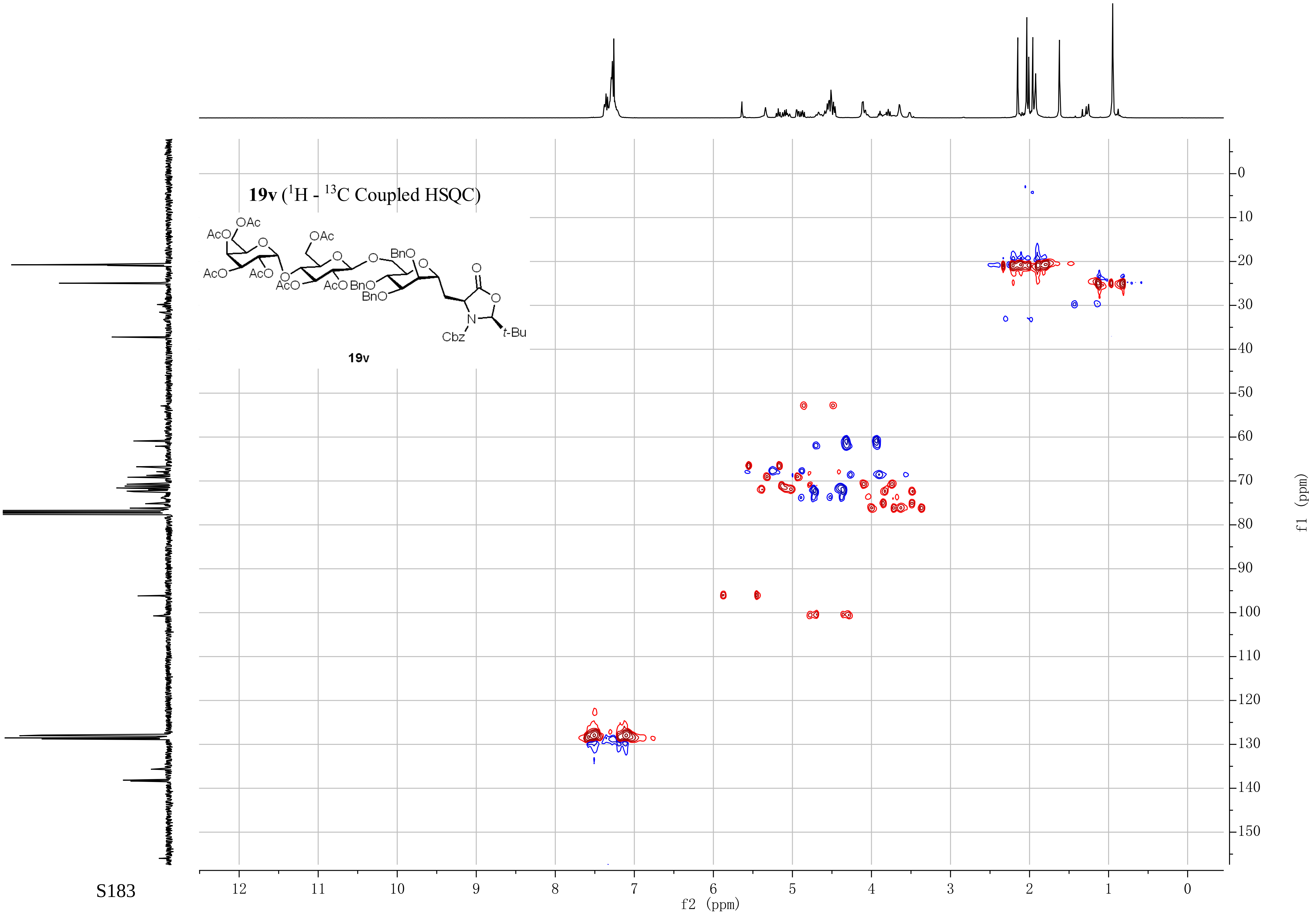
19v (^{13}C NMR, 101MHz, CDCl$_3$)

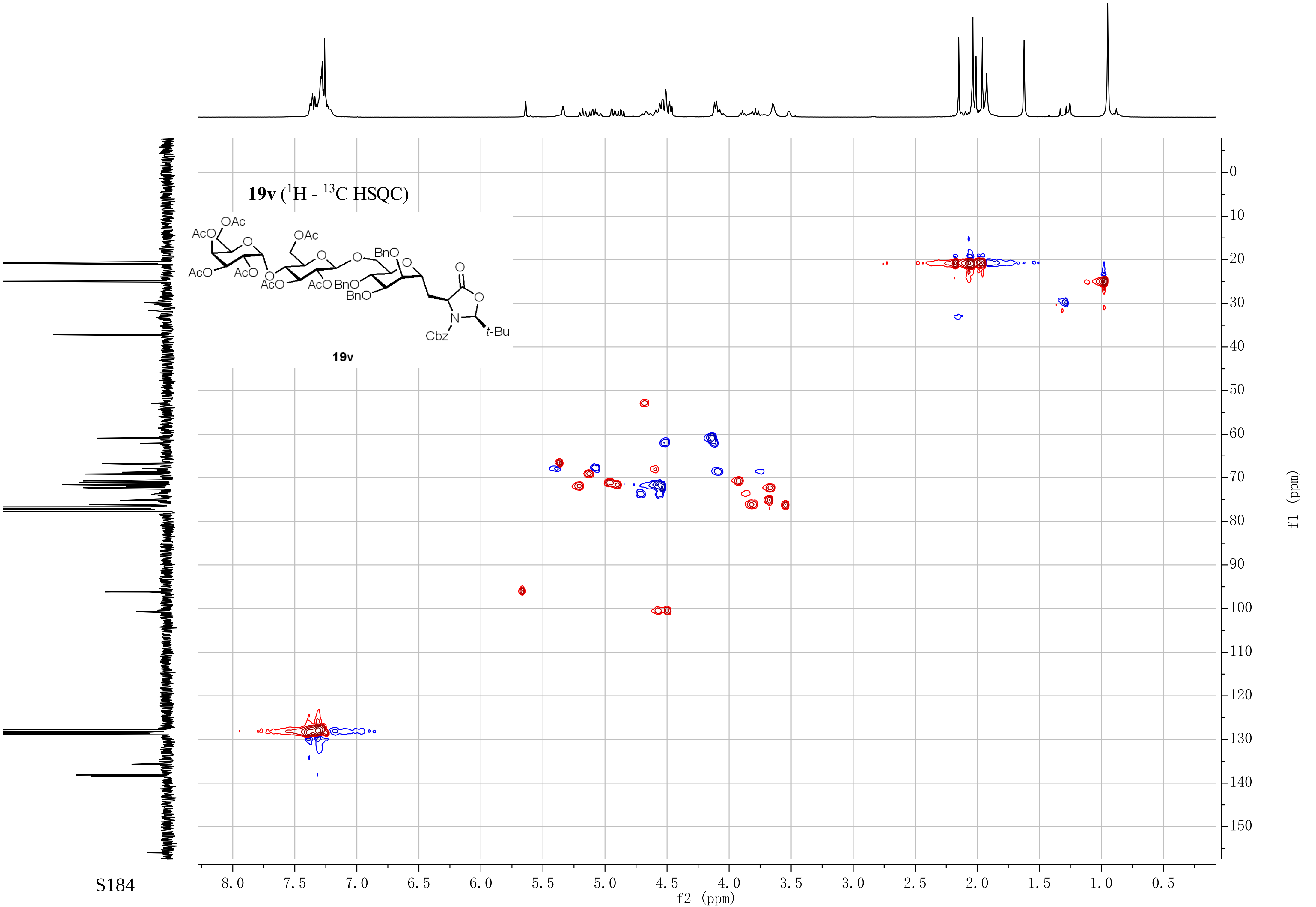


19v



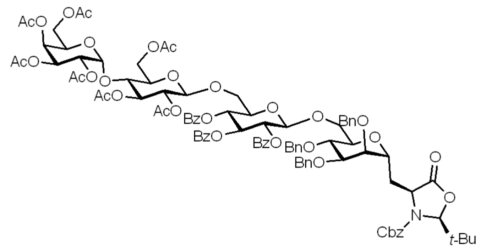

19v (1H - 1H COSY)
OAc
AcO
OAc
AcO
AcO
AcO
AcO
BnO
BnO
BnO
N
Cbz
t-Bu
19v
f2 (ppm)
f1 (ppm)


19v (1H - 13C Coupled HSQC)
OAc
AcO
OAc
AcO
AcO
AcO
AcO
BnO
BnO
BnO
Cbz
t-Bu
19v
f2 (ppm)
f1 (ppm)

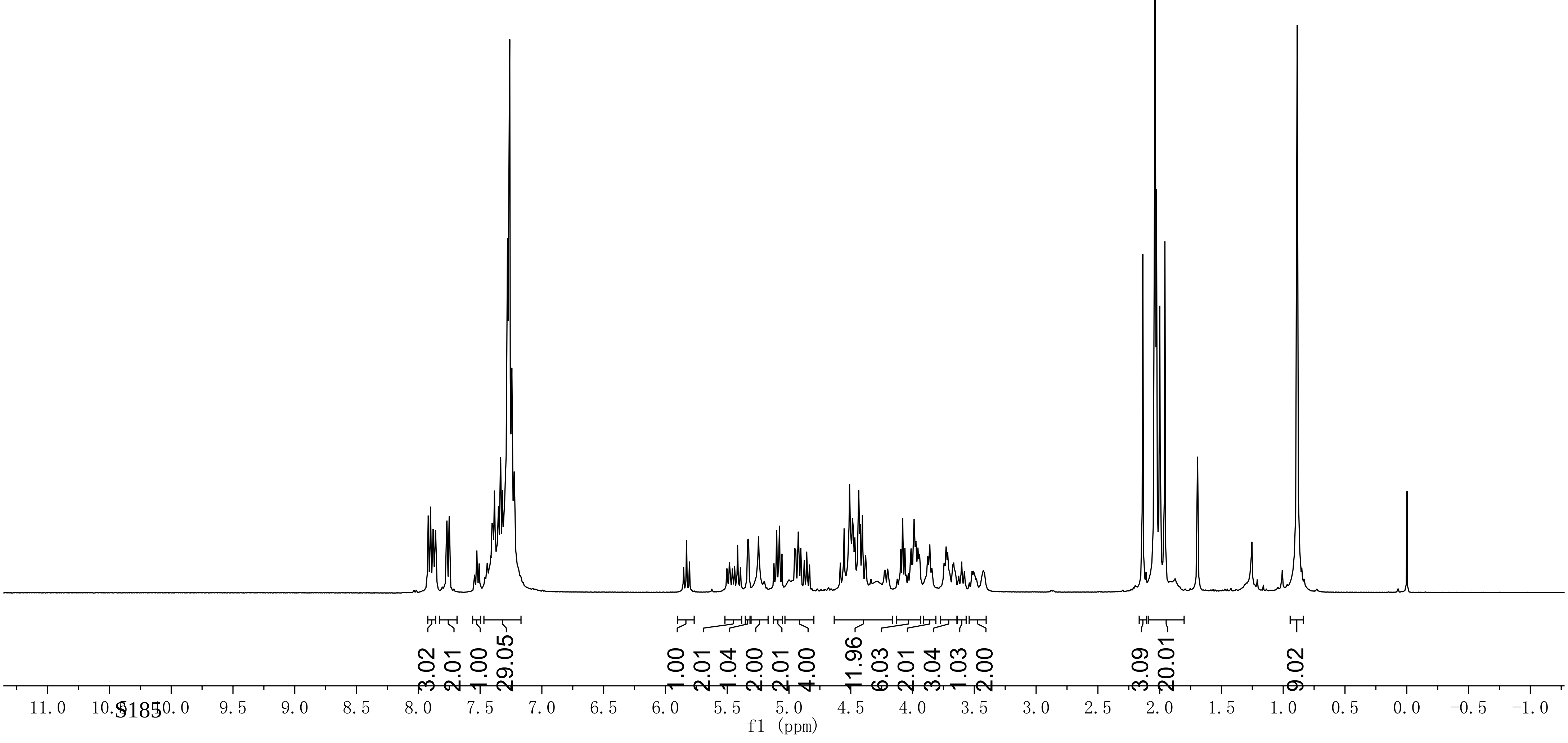


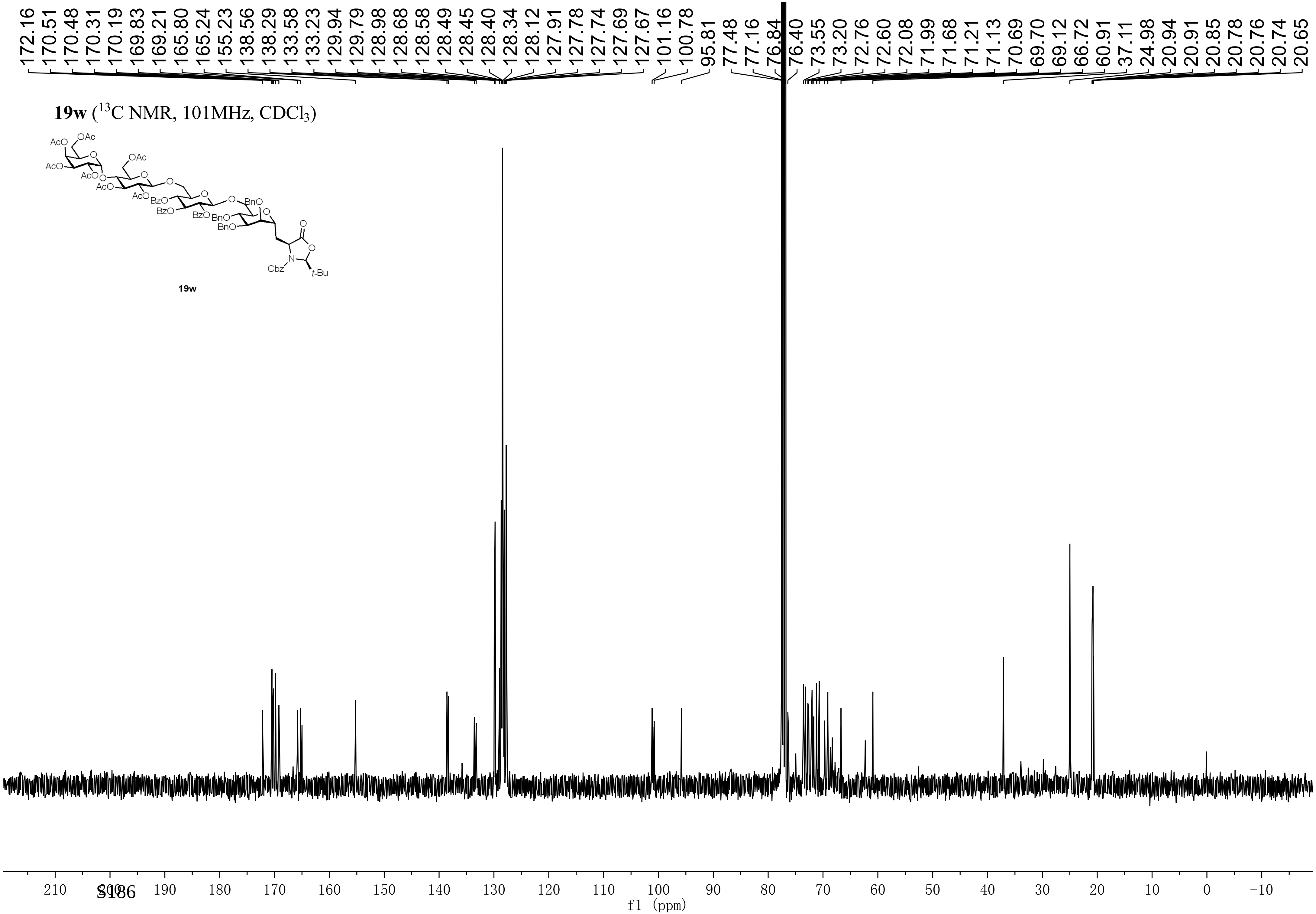
19v (1H - 13C HSQC)
OAc
AcO
OAc
AcO
AcO
O
AcO
AcO
BnO
BnO
BnO
O
N
Cbz
t-Bu
19v
f2 (ppm)
f1 (ppm)

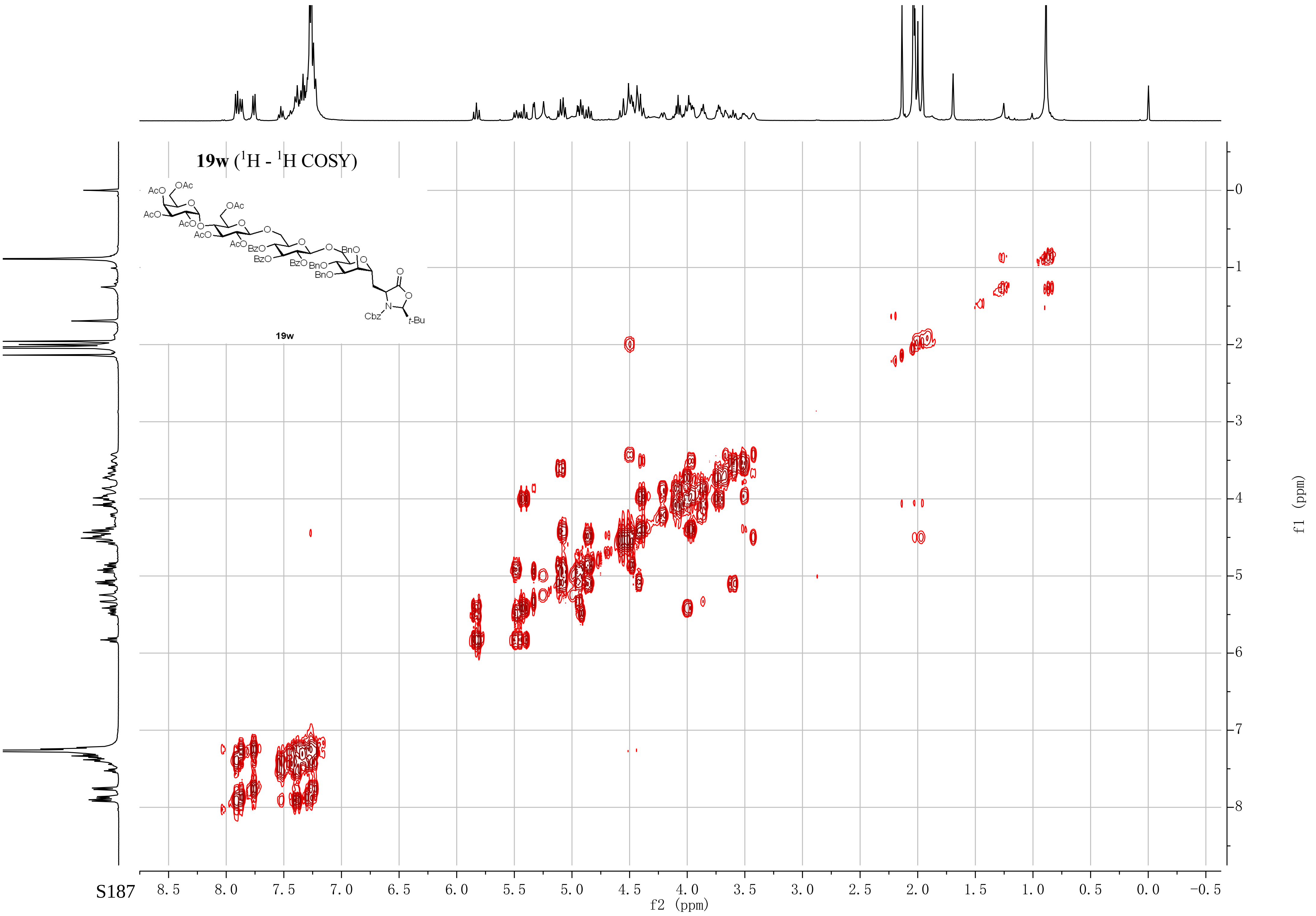
19w (^{1}H NMR, 400MHz, $CDCl_3$)



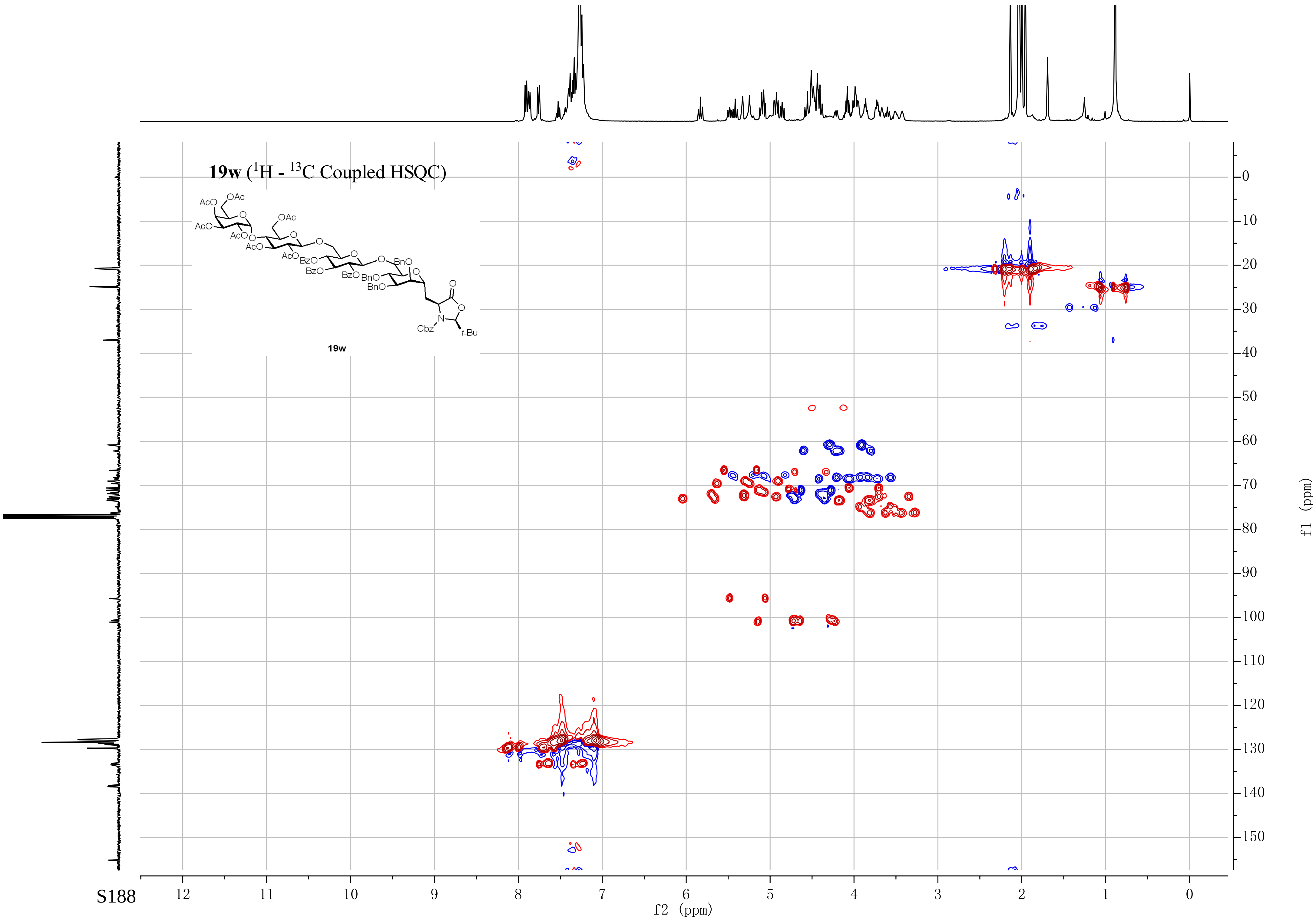
19w

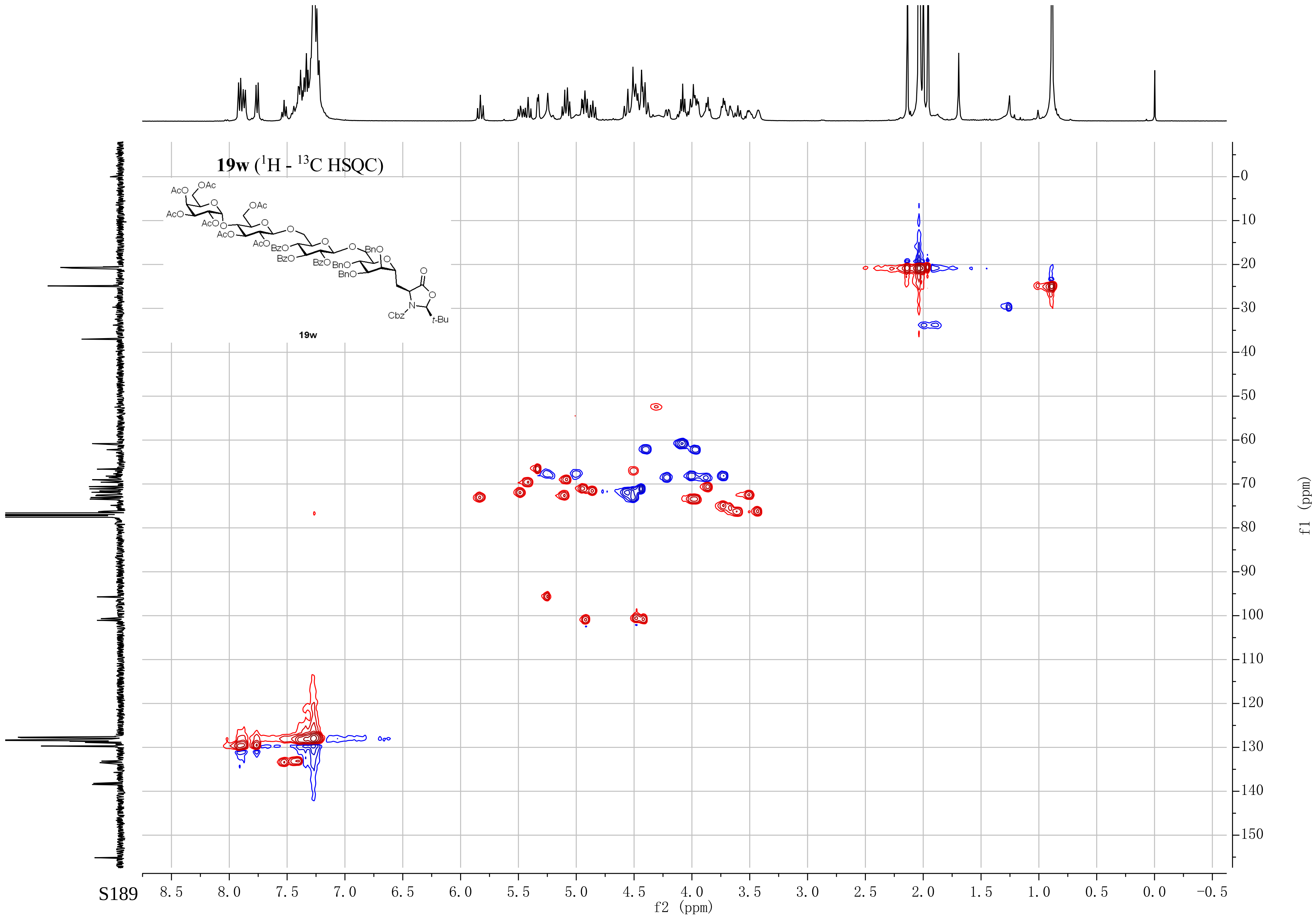



172.16
170.51
170.48
170.31
170.19
169.83
169.21
165.80
165.24
155.23
138.56
138.29
133.58
133.23
129.94
129.79
128.98
128.68
128.58
128.49
128.45
128.40
128.34
128.12
127.91
127.78
127.74
127.69
127.67
101.16
100.78
95.81
77.48
77.16
76.84
76.40
73.55
73.20
72.76
72.60
72.08
71.99
71.68
71.21
71.13
70.69
69.70
69.12
66.72
60.91
37.11
24.98
20.94
20.91
20.85
20.78
20.76
20.74
20.65
19w (^{13}C NMR, 101MHz, $CDCl_3$)
19w
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)

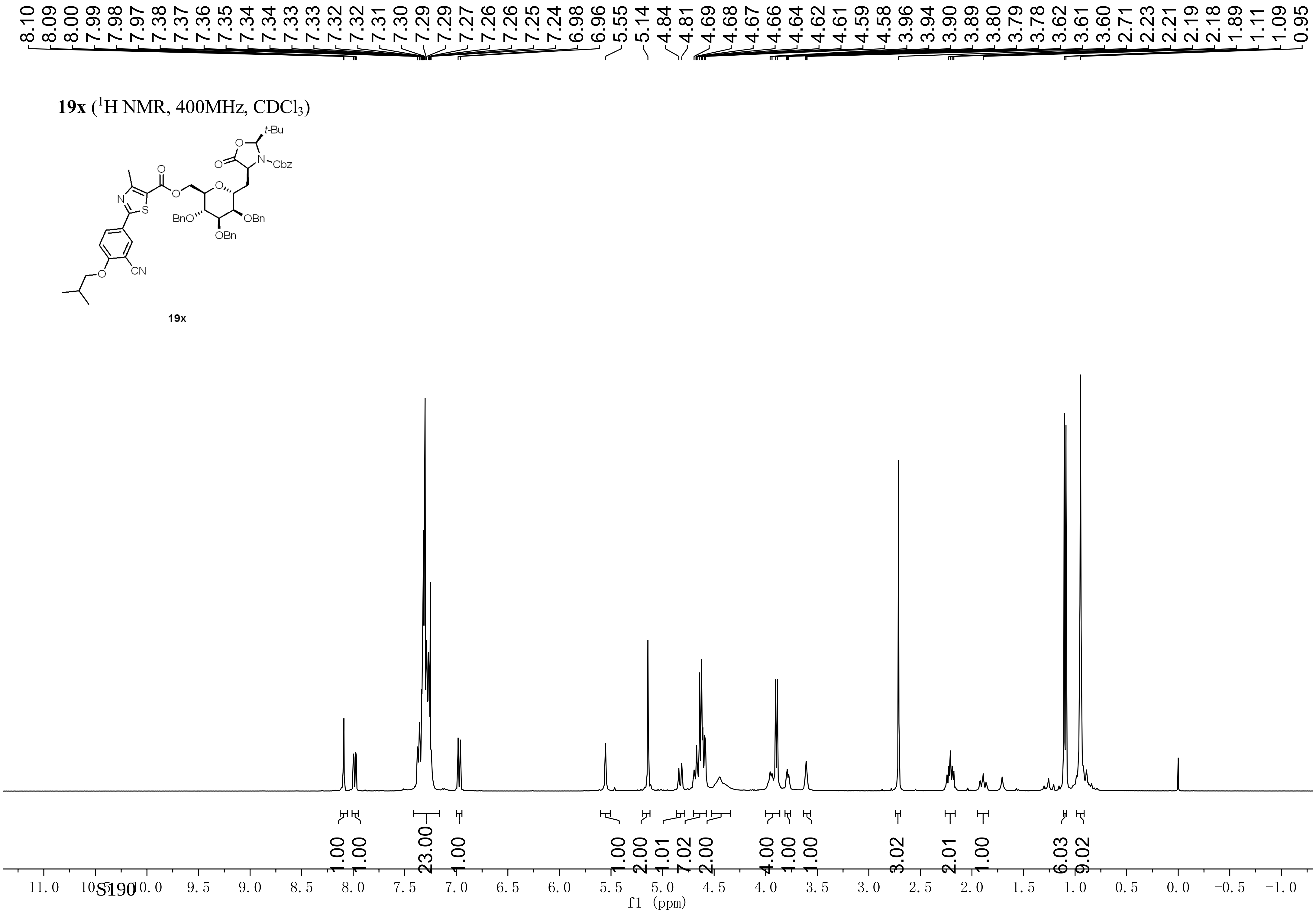


19w (1H - 1H COSY)
AcO
OAc
AcO
AcO
OAc
AcO
AcO
BzO
BzO
BzO
BnO
BnO
BnO
Cbz
N
t-Bu
19w
f1 (ppm)
f2 (ppm)


19w (1H - 13C Coupled HSQC)
AcO
OAc
AcO
AcO
AcO
OAc
AcO
AcO
BzO
BzO
BzO
BnO
BnO
BnO
Cbz
N
t-Bu
19w
f2 (ppm)
f1 (ppm)

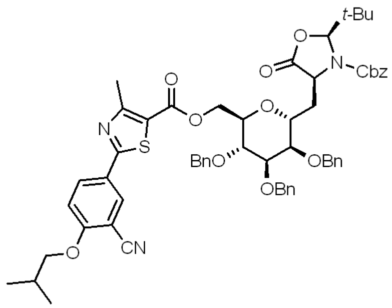

19w (1H - 13C HSQC)
AcO
OAc
AcO
AcO
AcO
OAc
AcO
BzO
BzO
BzO
BnO
BnO
BnO
N
Cbz
t-Bu
19w
f2 (ppm)
f1 (ppm)

19x (^{1}H NMR, 400MHz, $CDCl_3$)

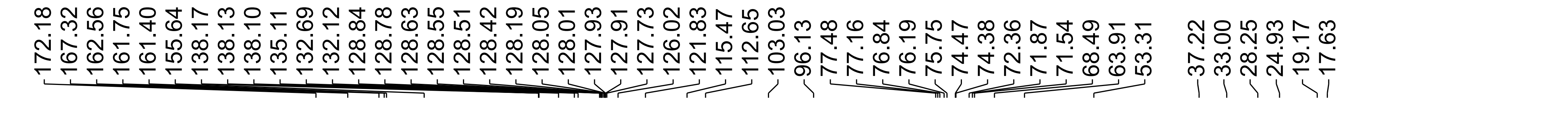


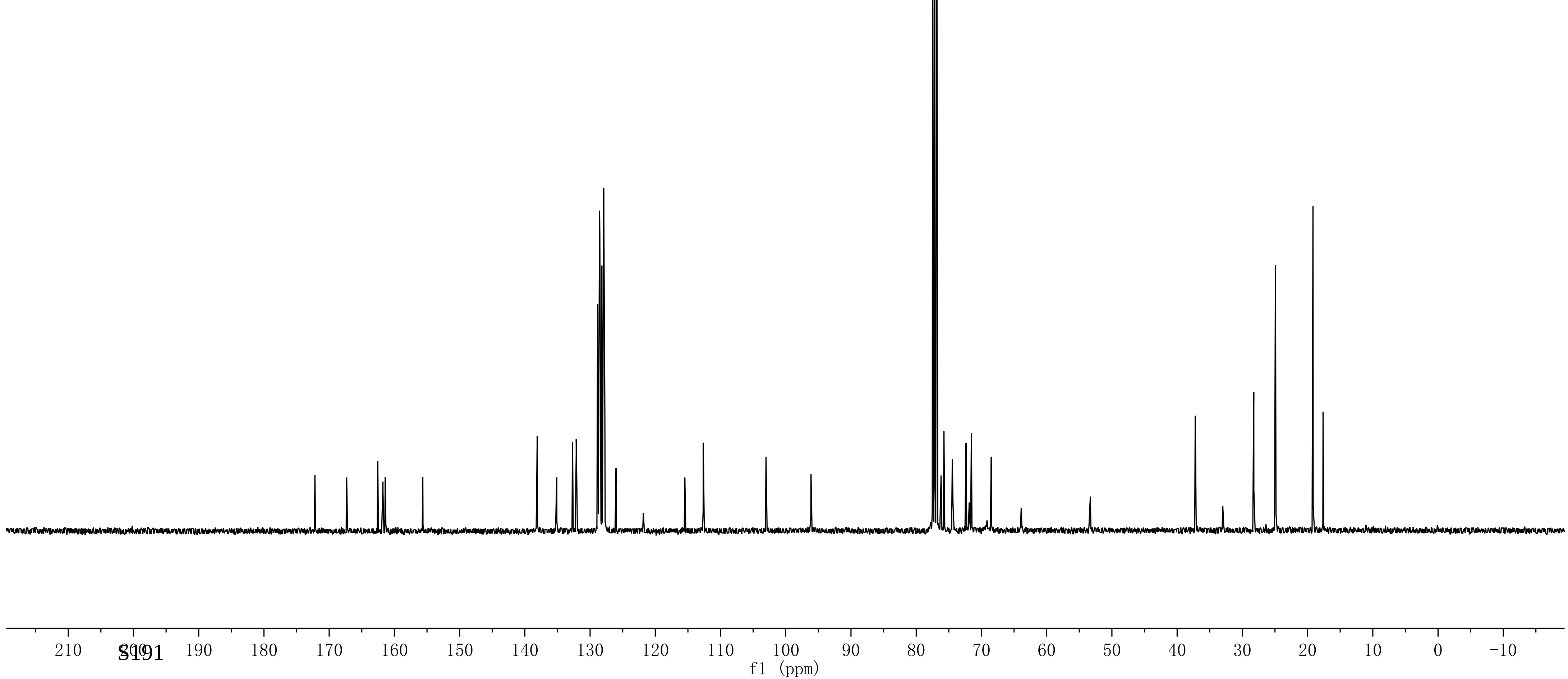
19x

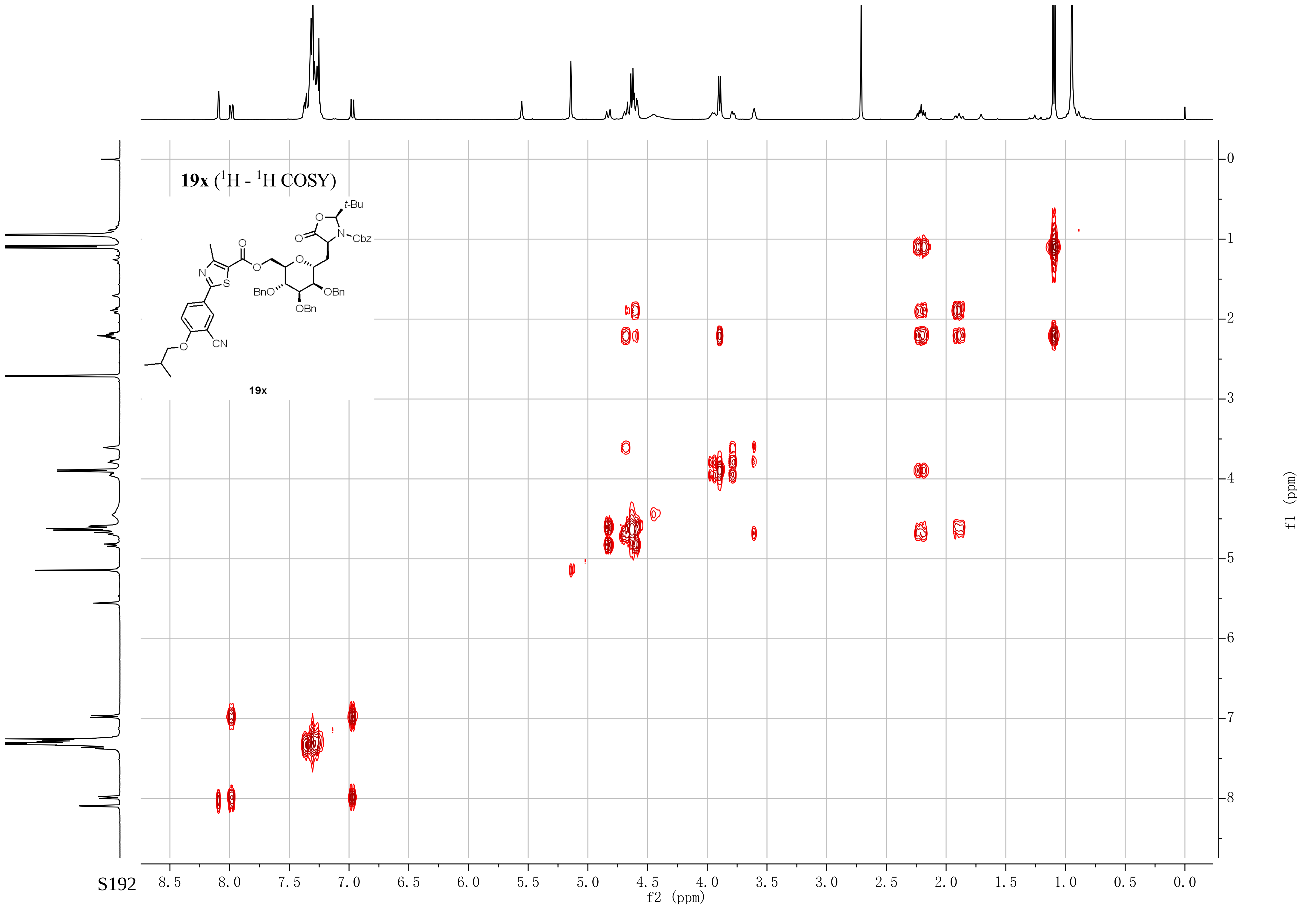
19x (^{13}C NMR, 101MHz, $CDCl_3$)

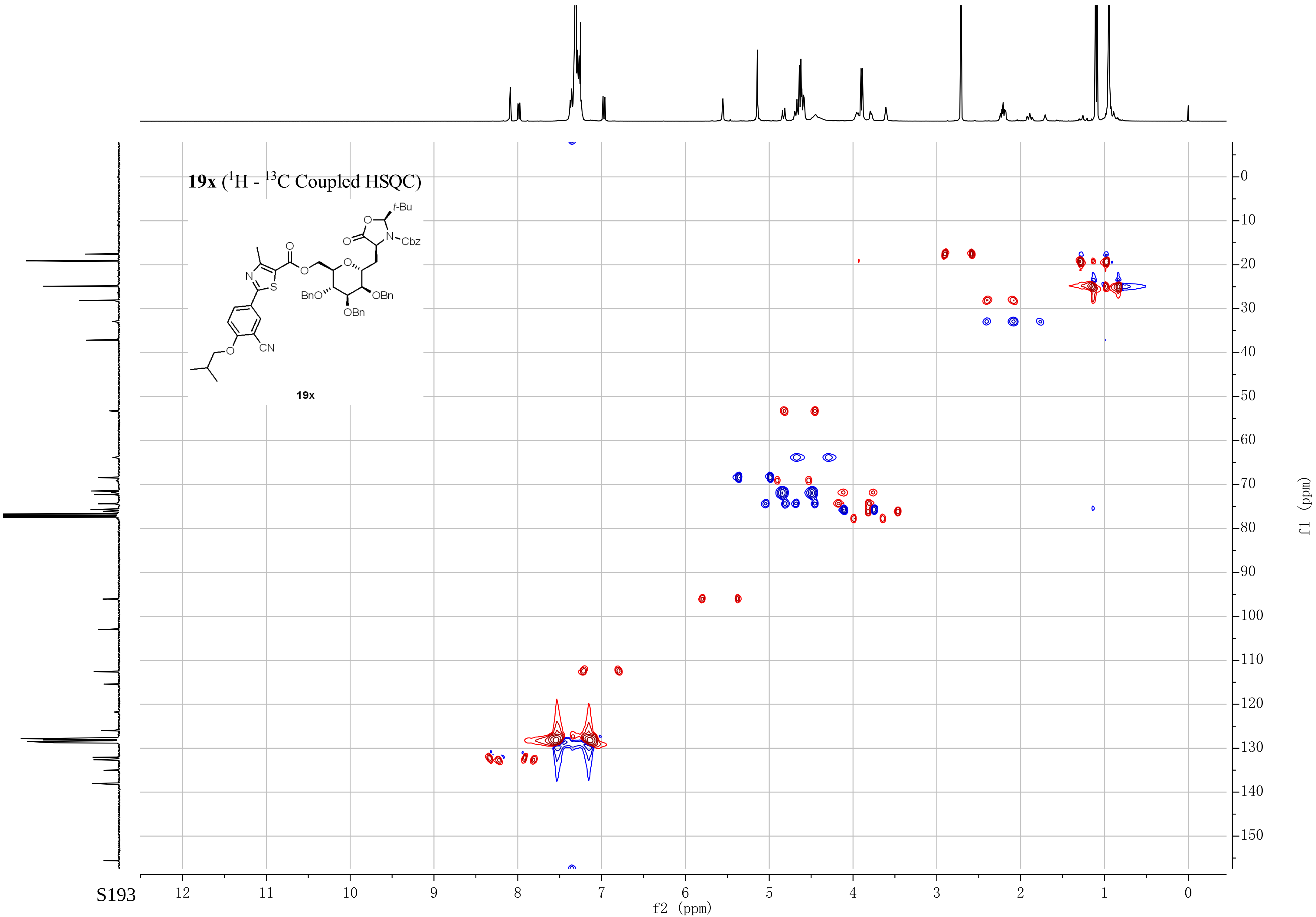


19x

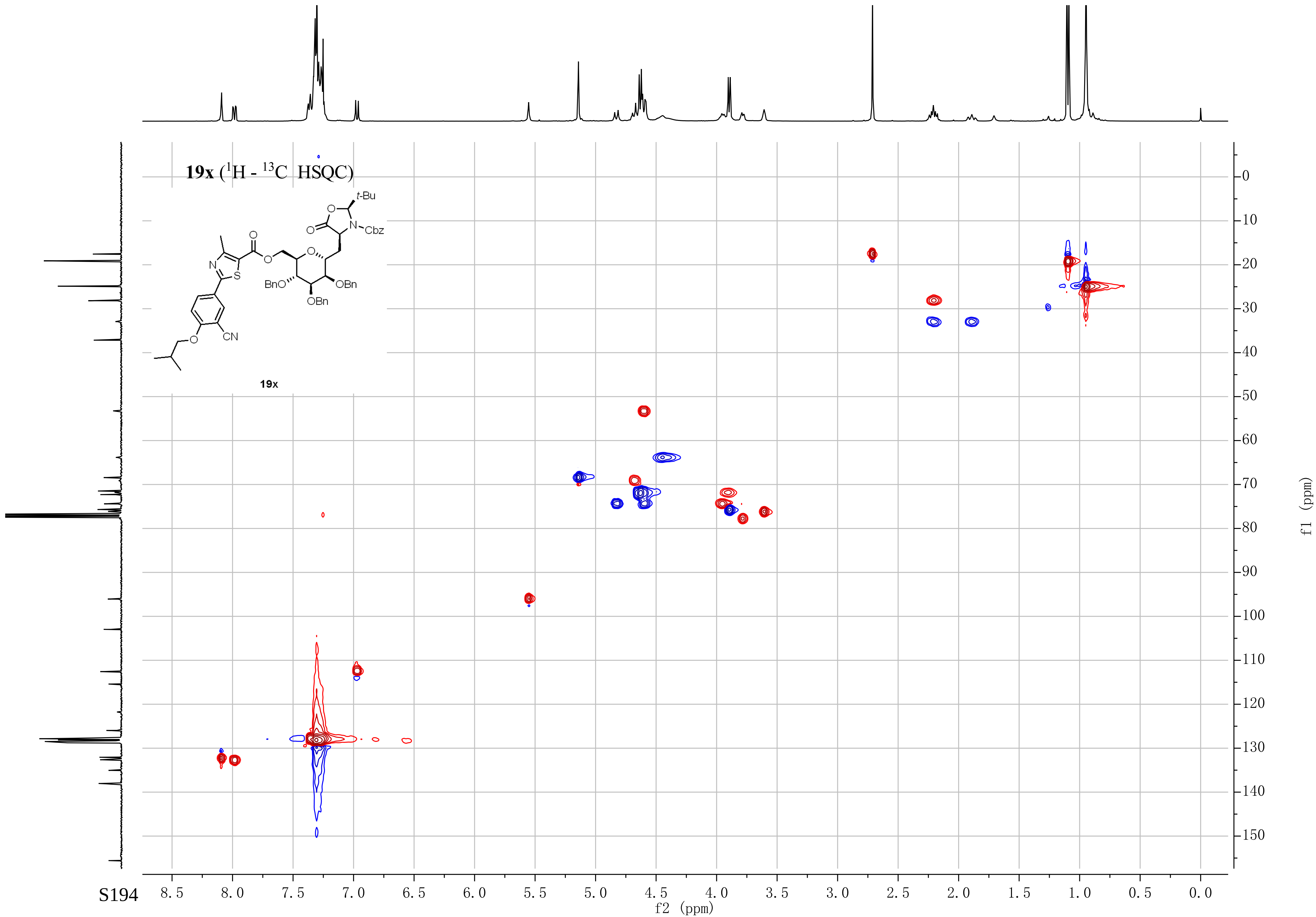




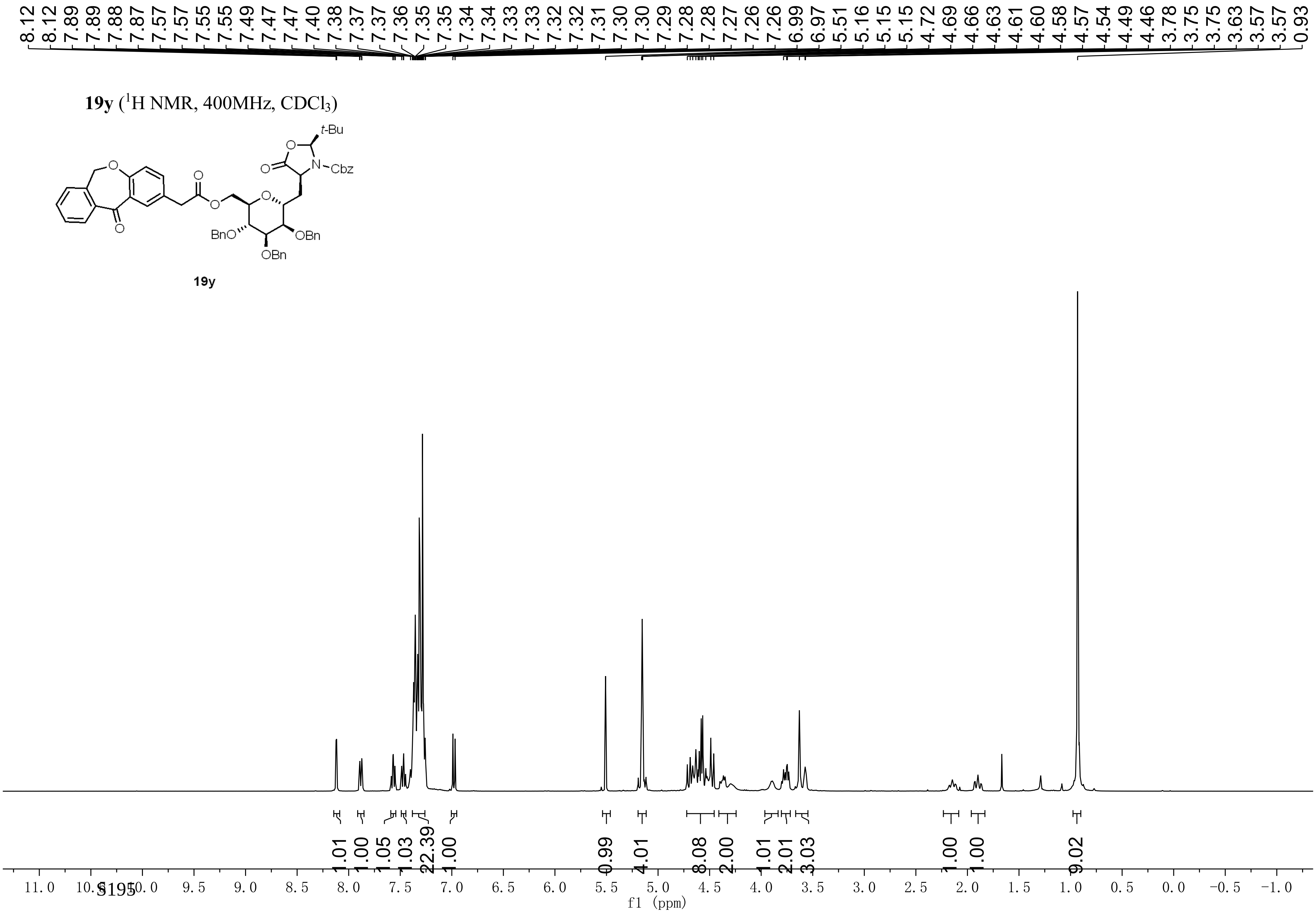

19x (1H - 1H COSY)
t-Bu
O
N
Cbz
BnO
OBn
OBn
S
CN
19x
f2 (ppm)
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8



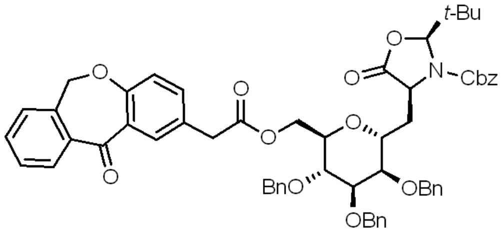
19x (^{1}H - ^{13}C Coupled HSQC)
t-Bu
O
N
Cbz
O
O
N
S
O
O
BnO
OBn
OBn
CN
O
19x
f2 (ppm)
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


19x (¹H - ¹³C HSQC)
t-Bu
O
N
Cbz
BnO
OBn
OBn
N
S
CN
19x
f1 (ppm)
f2 (ppm)

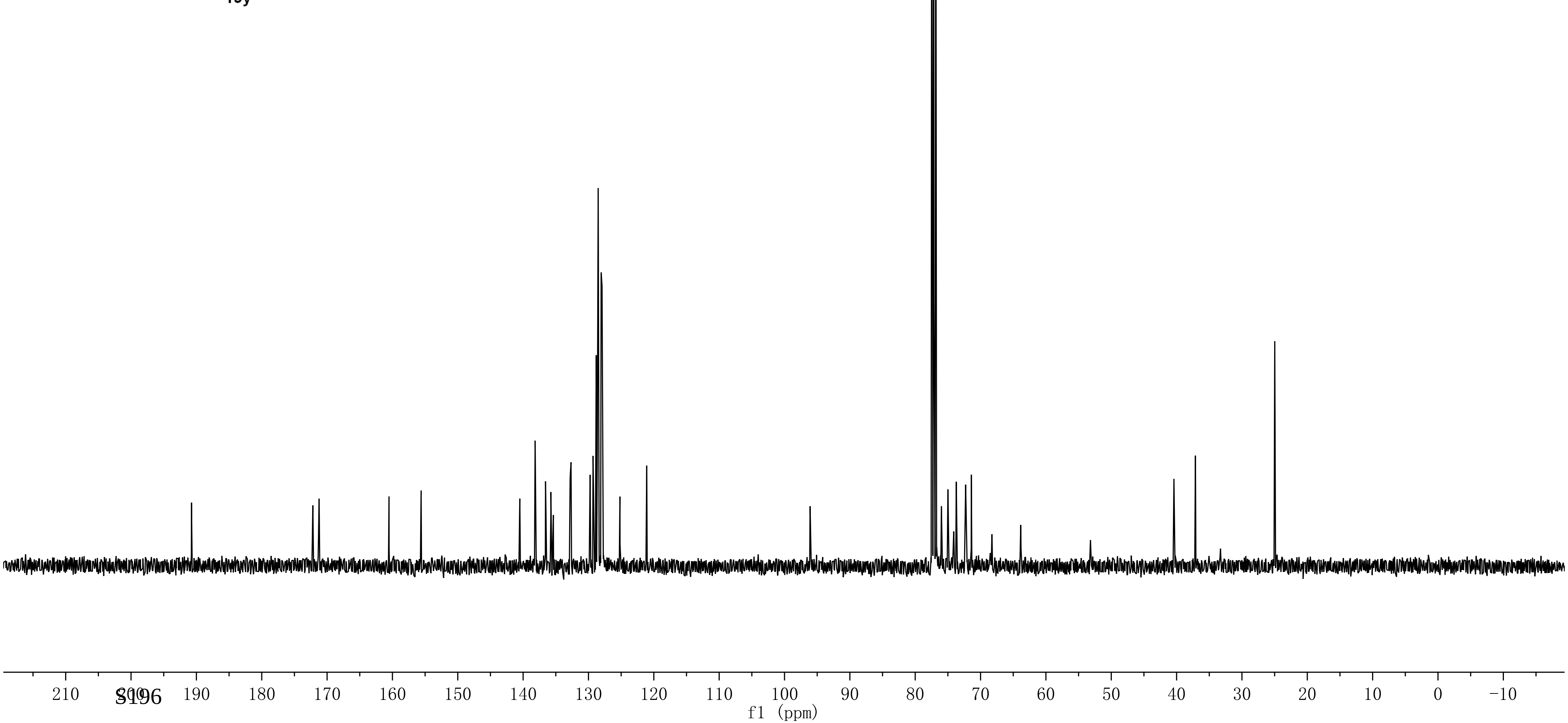
19y (^{1}H NMR, 400MHz, $CDCl_3$)

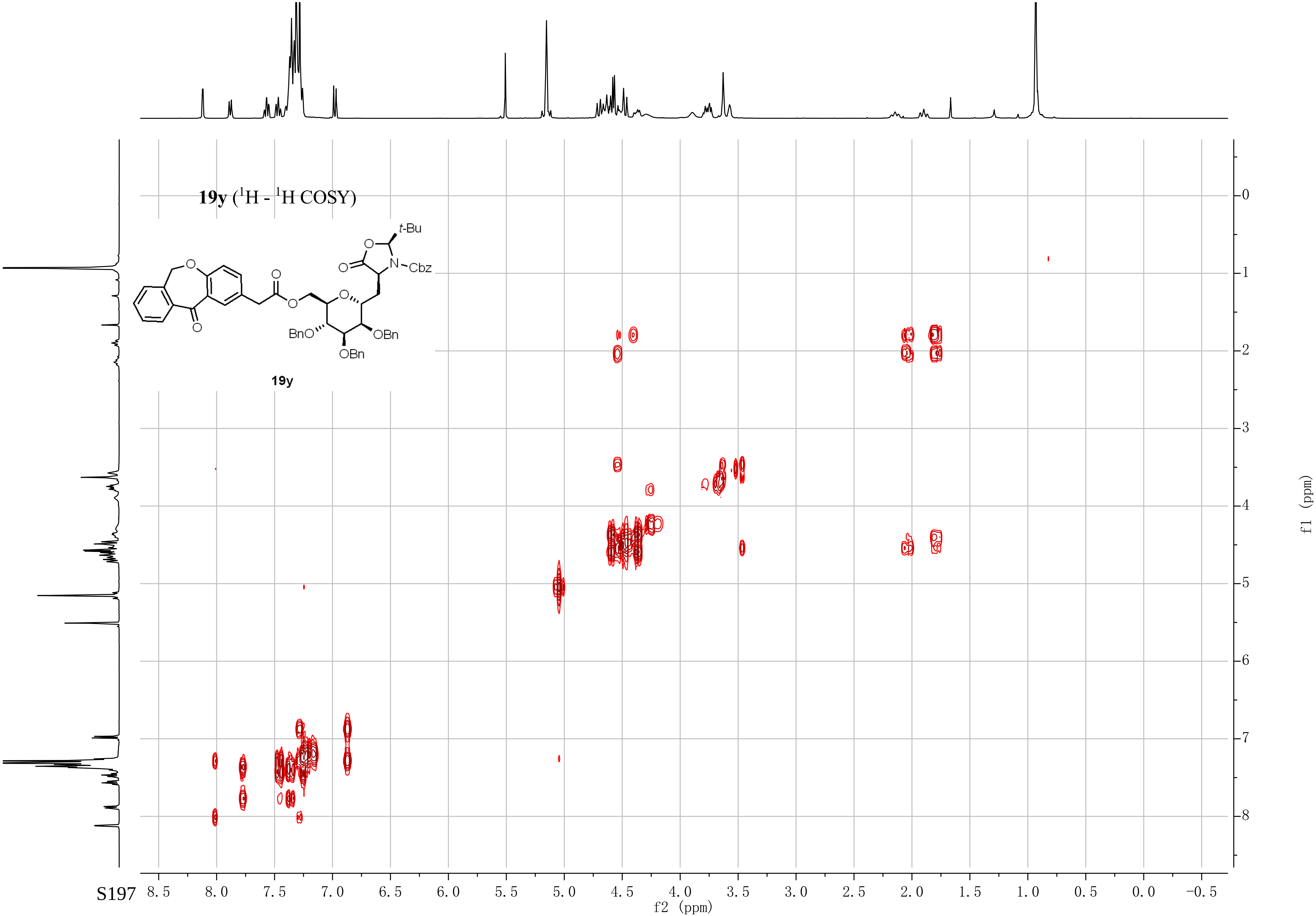


19y (^{13}C NMR, 101MHz, $CDCl_3$)

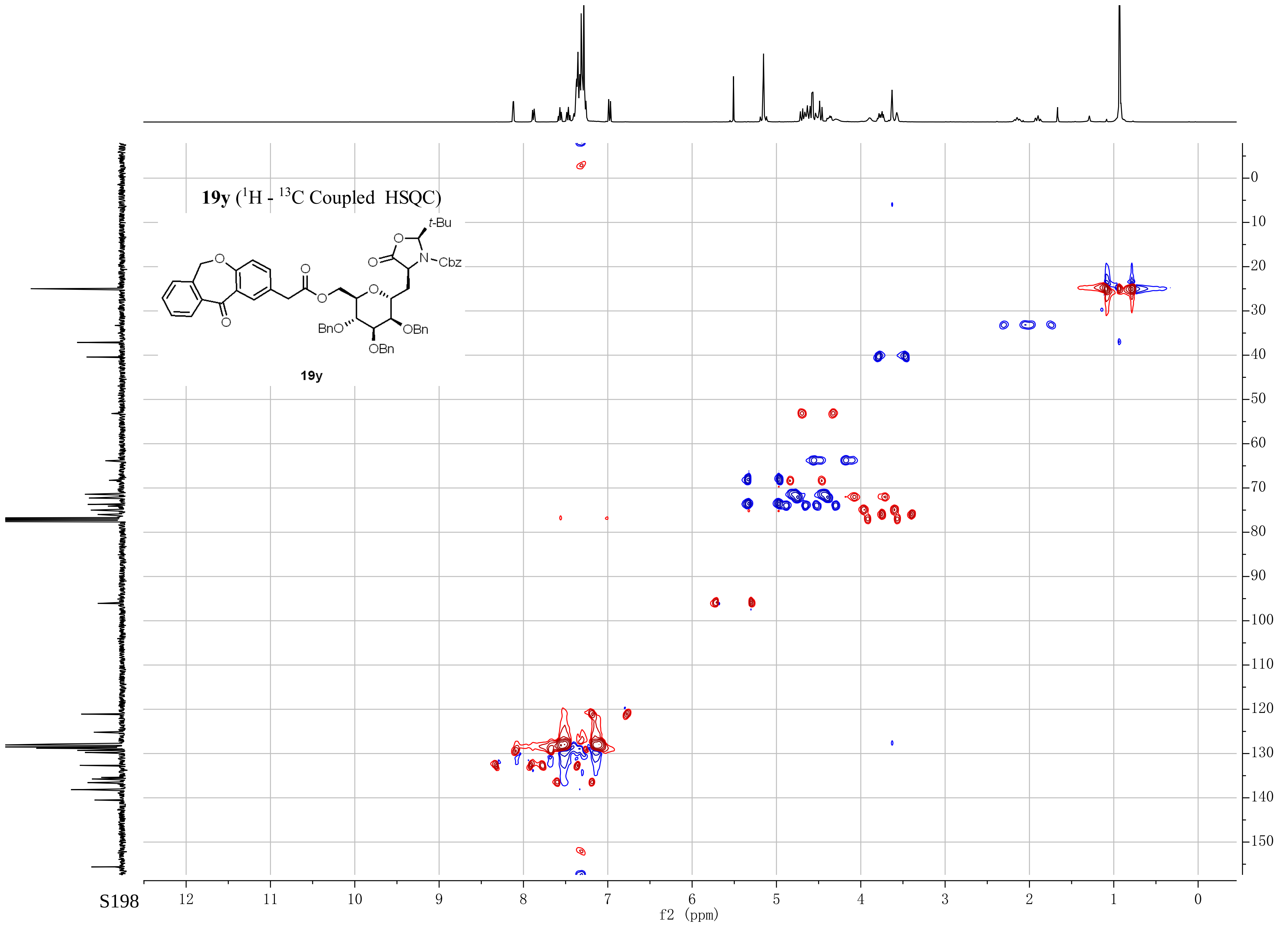


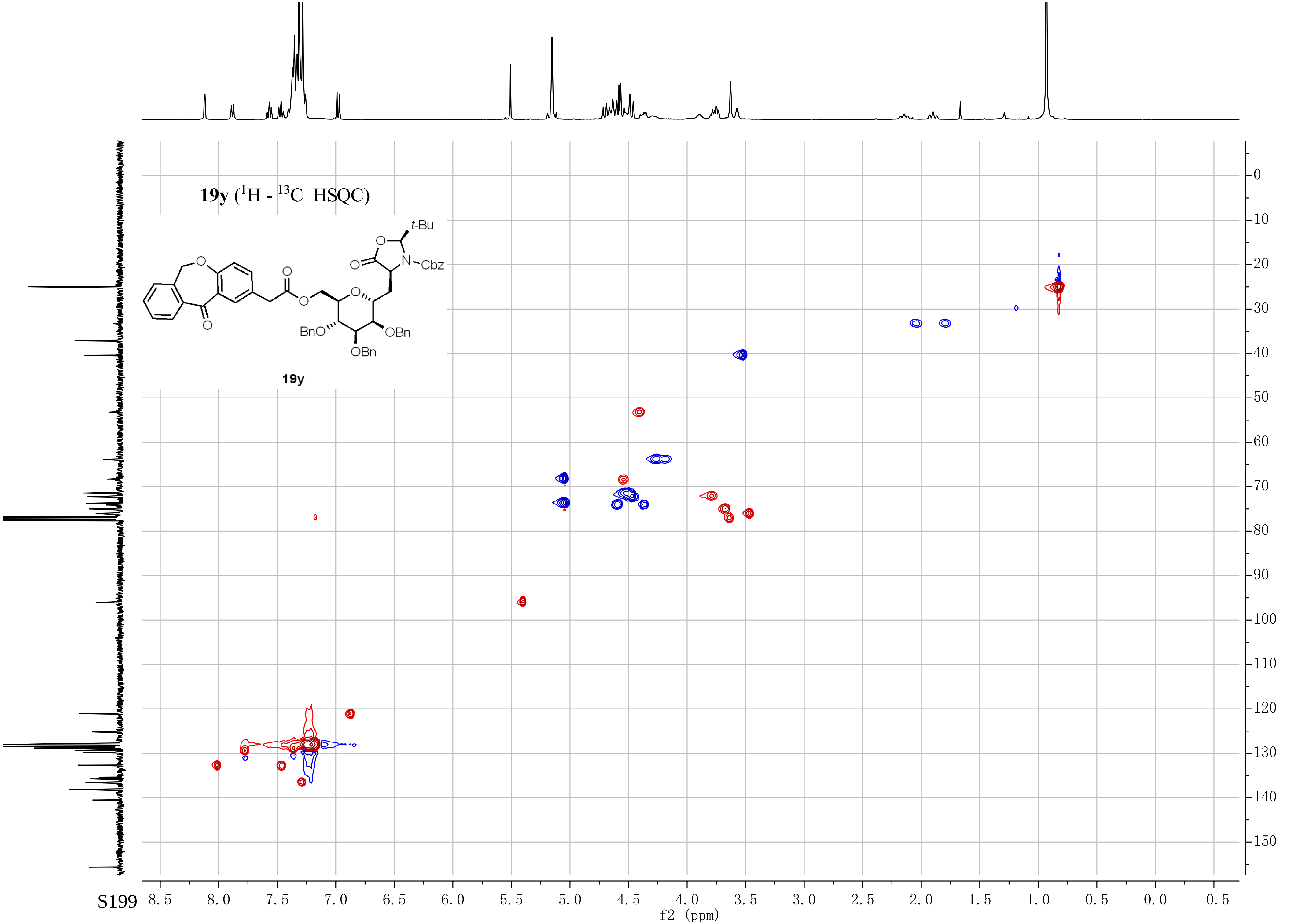
19y




19y (1H - 1H COSY)
t-Bu
O
N
Cbz
BnO
OBn
OBn
19y
f2 (ppm)
f1 (ppm)

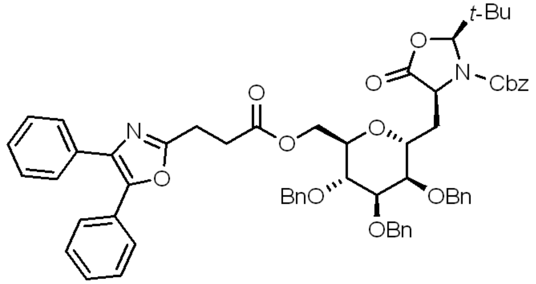
19y (^{1}H - ^{13}C Coupled HSQC)



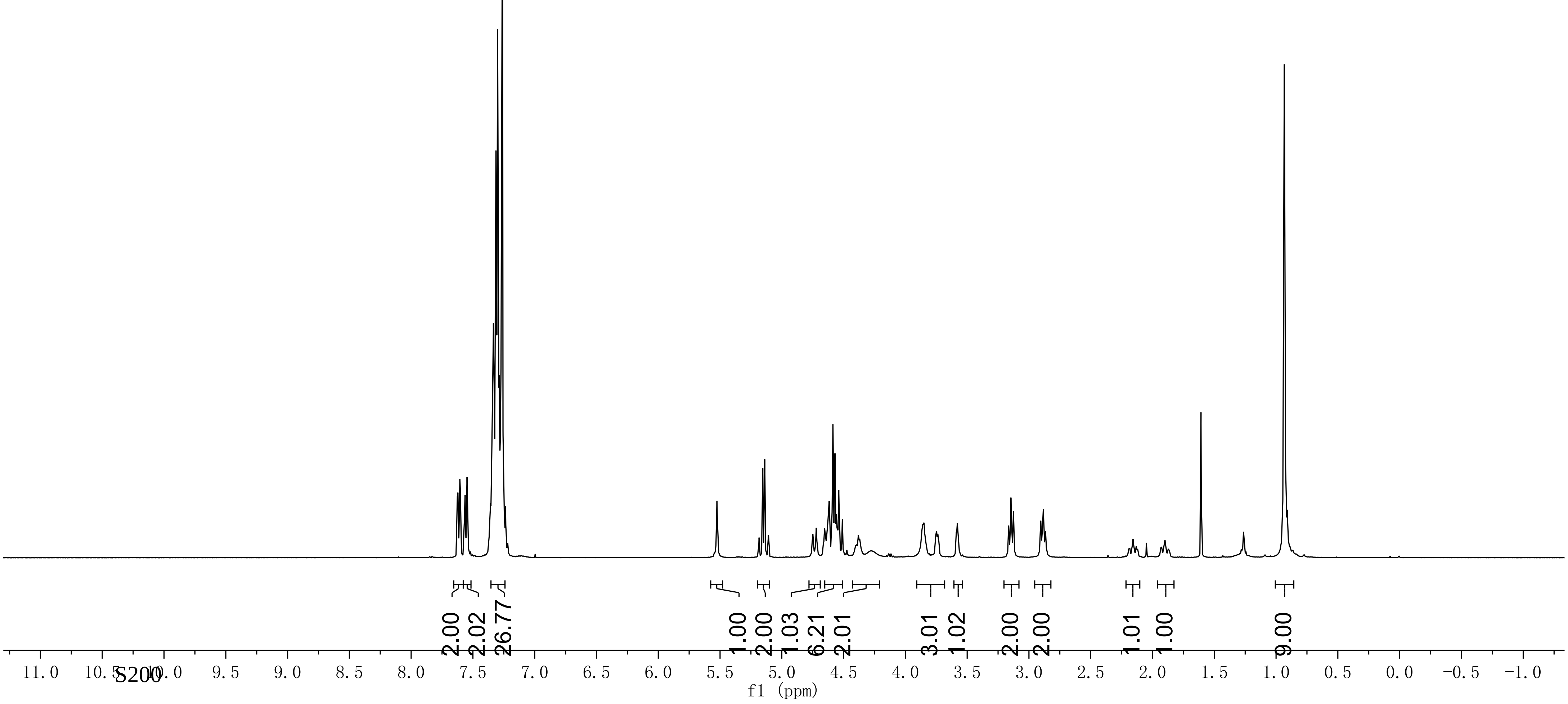


19y (1H - 13C HSQC)
t-Bu
N
Cbz
BnO
OBn
OBn
19y
f2 (ppm)
f1 (ppm)

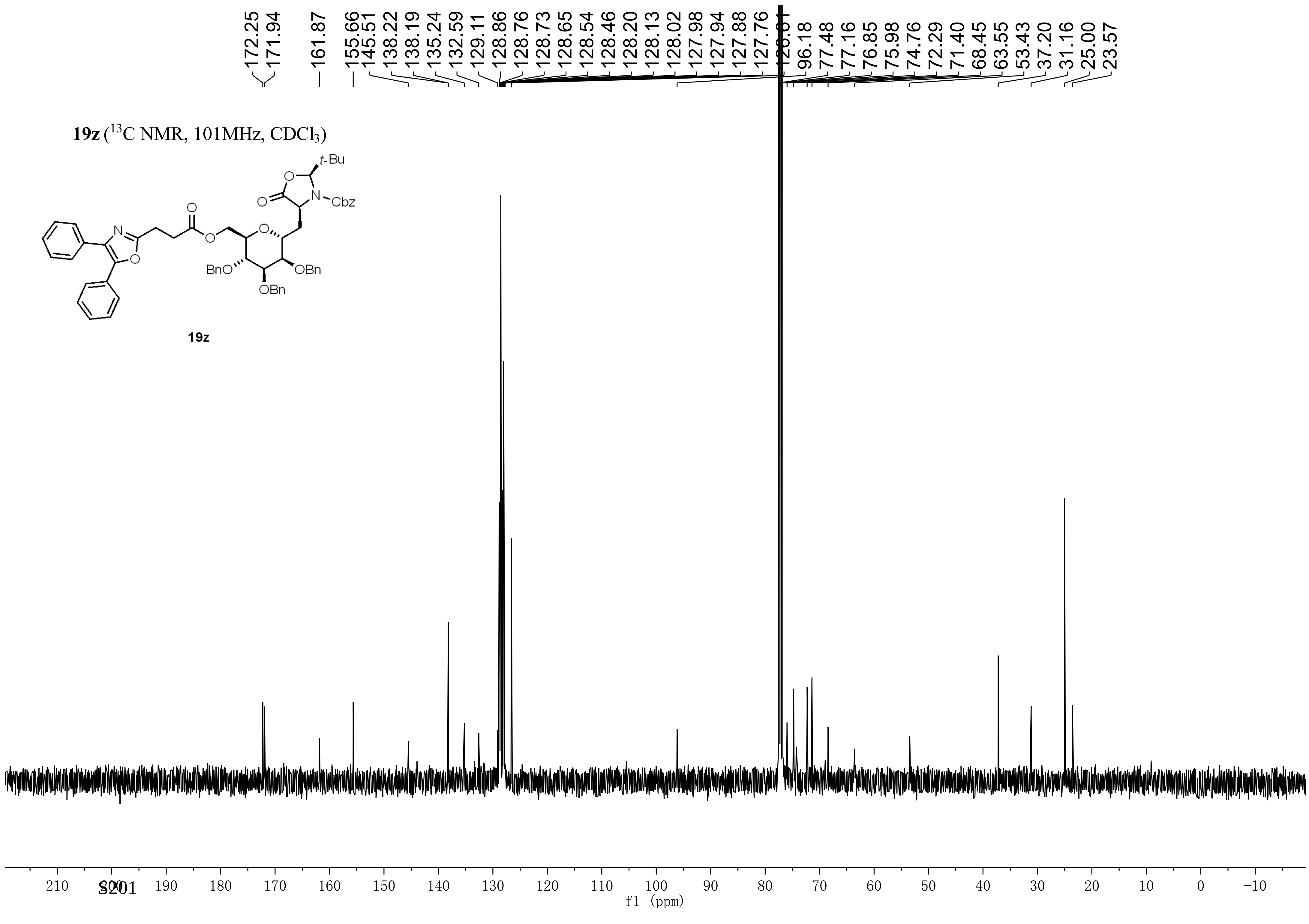
19z (^{1}H NMR, 400MHz, $CDCl_3$)

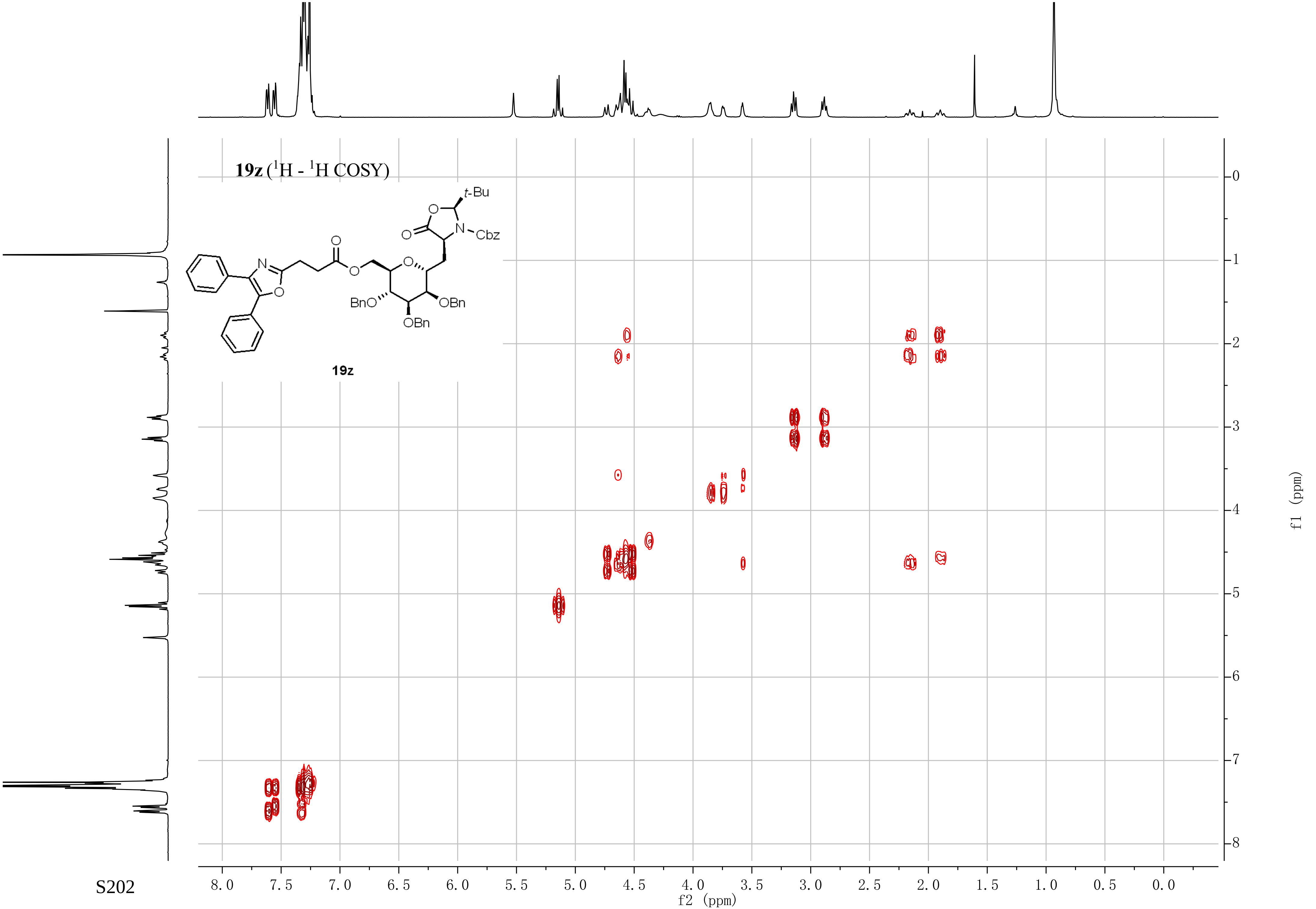


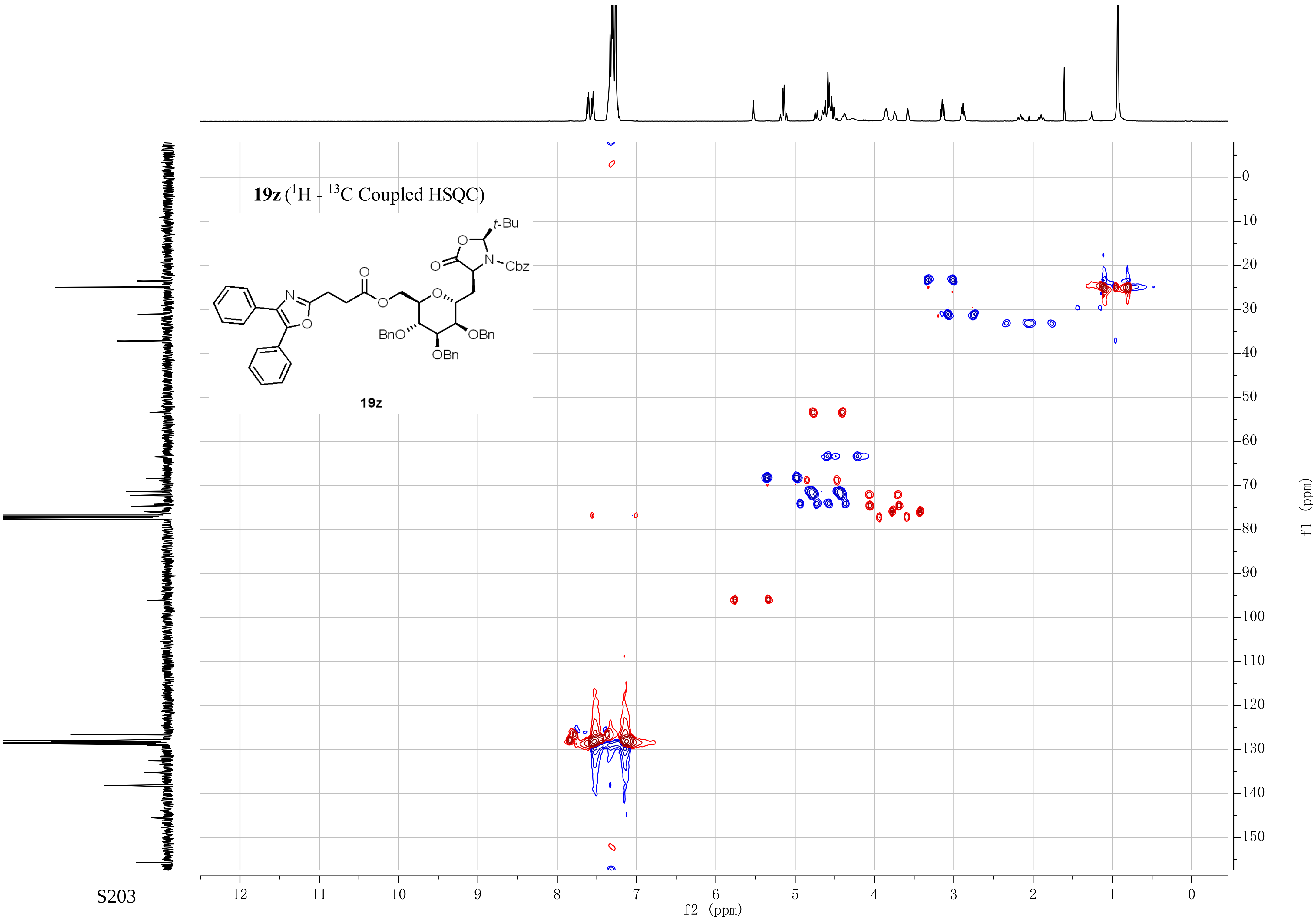
19z

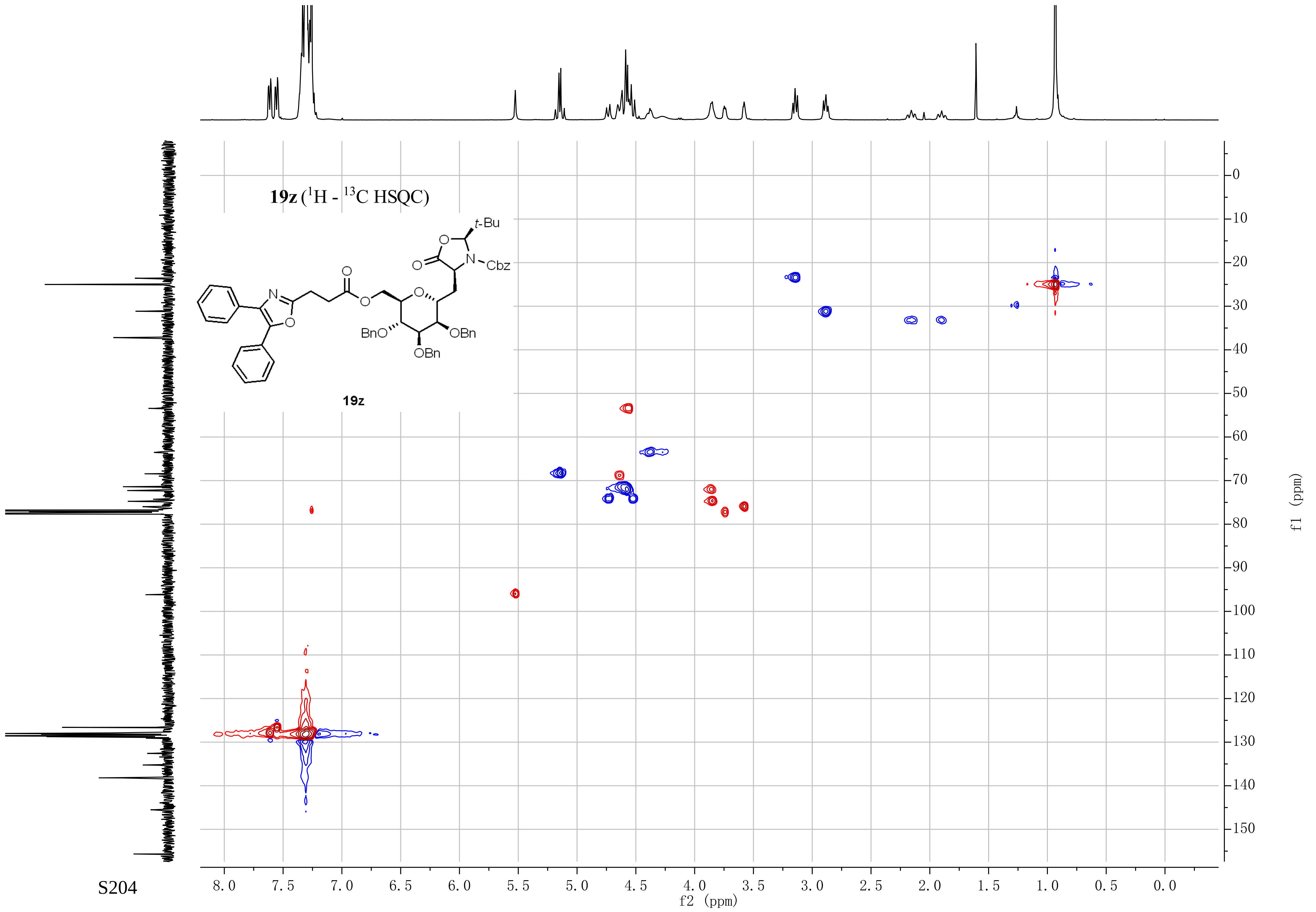


19z (^{13}C NMR, 101MHz, $CDCl_3$)

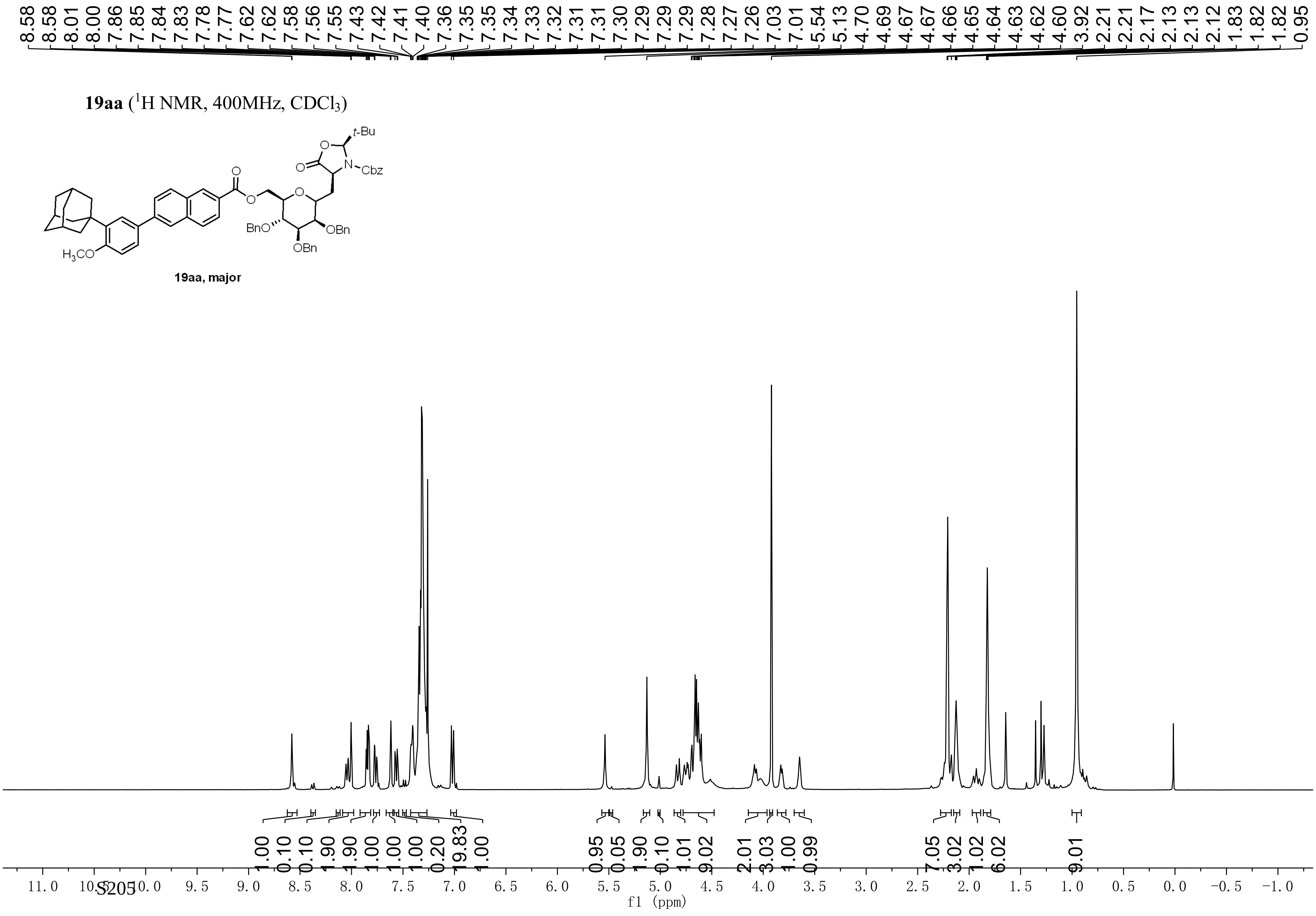



19z (1H - 1H COSY)
t-Bu
O
N
Cbz
O
O
N
O
O
BnO
OBn
OBn
19z
f1 (ppm)
f2 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8


19z (1H - 13C Coupled HSQC)
t-Bu
O
N
Cbz
O
N
O
O
O
O
BnO
OBn
OBn
19z
f2 (ppm)
f1 (ppm)
12 11 10 9 8 7 6 5 4 3 2 1 0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150

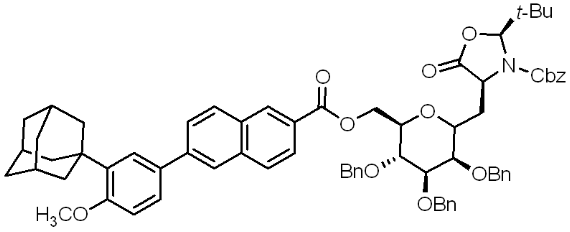


19z (¹H - ¹³C HSQC)
t-Bu
O
N
Cbz
O
N
O
O
O
O
BnO
OBn
OBn
19z
f2 (ppm)
f1 (ppm)

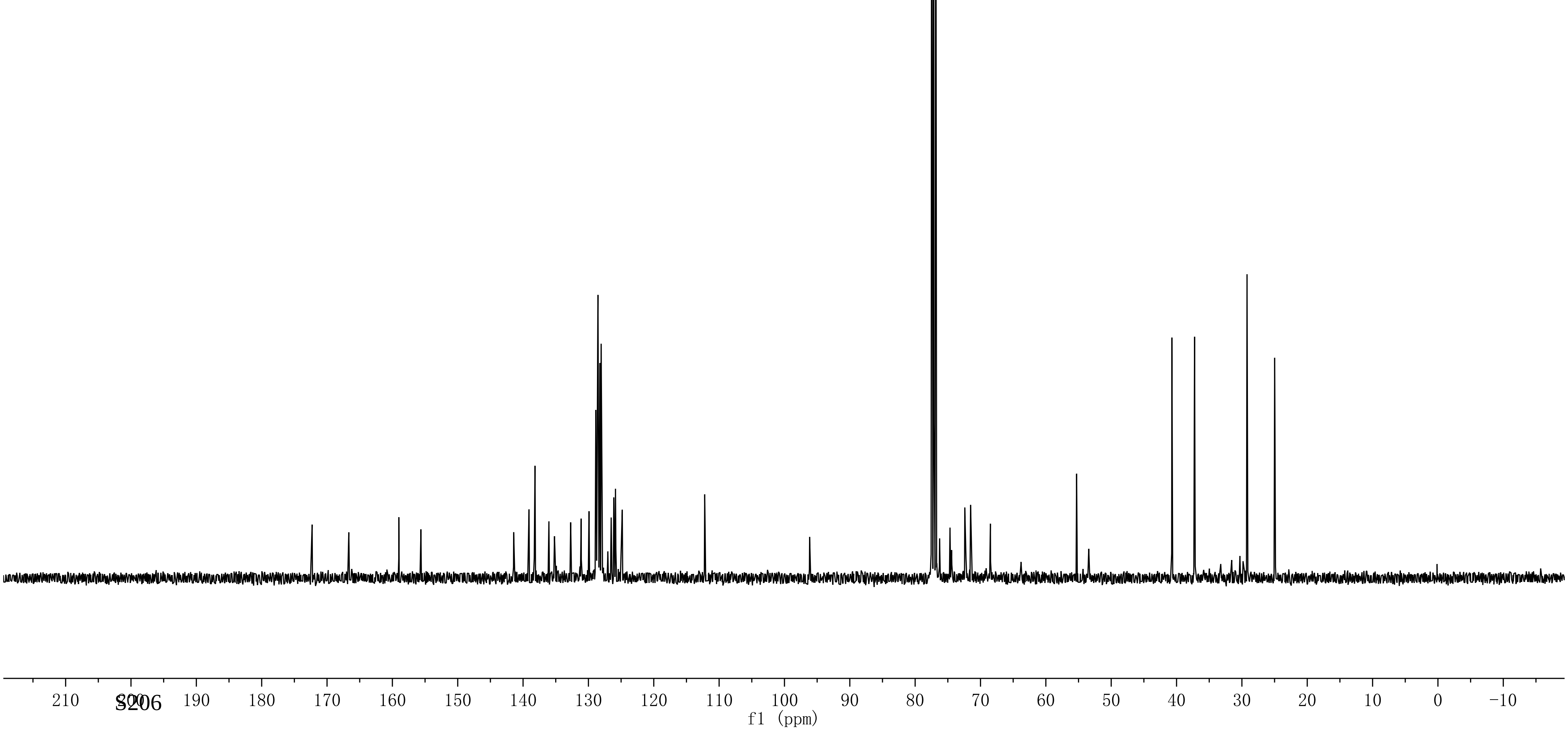


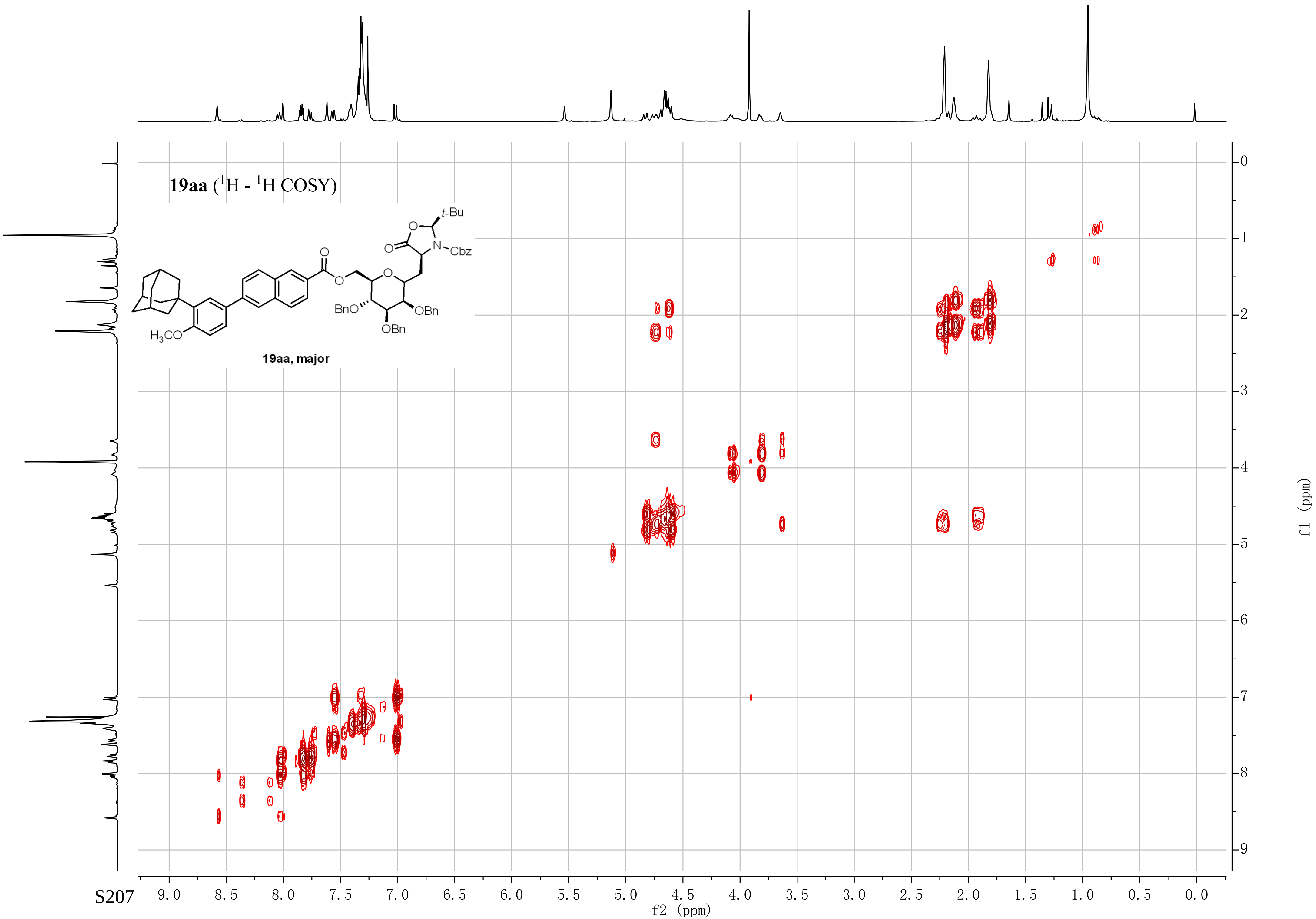
8.58 8.58 8.01 8.00 7.86 7.85 7.84 7.83 7.78 7.77 7.62 7.62 7.58 7.56 7.55 7.43 7.42 7.41 7.40 7.36 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.26 7.03 7.01 5.54 5.13 4.70 4.69 4.67 4.67 4.66 4.65 4.64 4.63 4.62 4.60 3.92 2.21 2.21 2.17 2.13 2.13 2.12 1.83 1.82 1.82 0.95
19aa (^{1}H NMR, 400MHz, $CDCl_3$)
t-Bu
O
N
Cbz
BnO
OBn
OBn
H_3CO
19aa, major
1.00 0.10 0.10 1.90 1.90 1.00 1.00 1.00 0.20 19.83 1.00 0.95 0.05 1.90 0.10 1.01 9.02 2.01 3.03 1.00 0.99 7.05 3.02 1.02 6.02 9.01
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)

19aa (^{13}C NMR, 101MHz, $CDCl_3$)

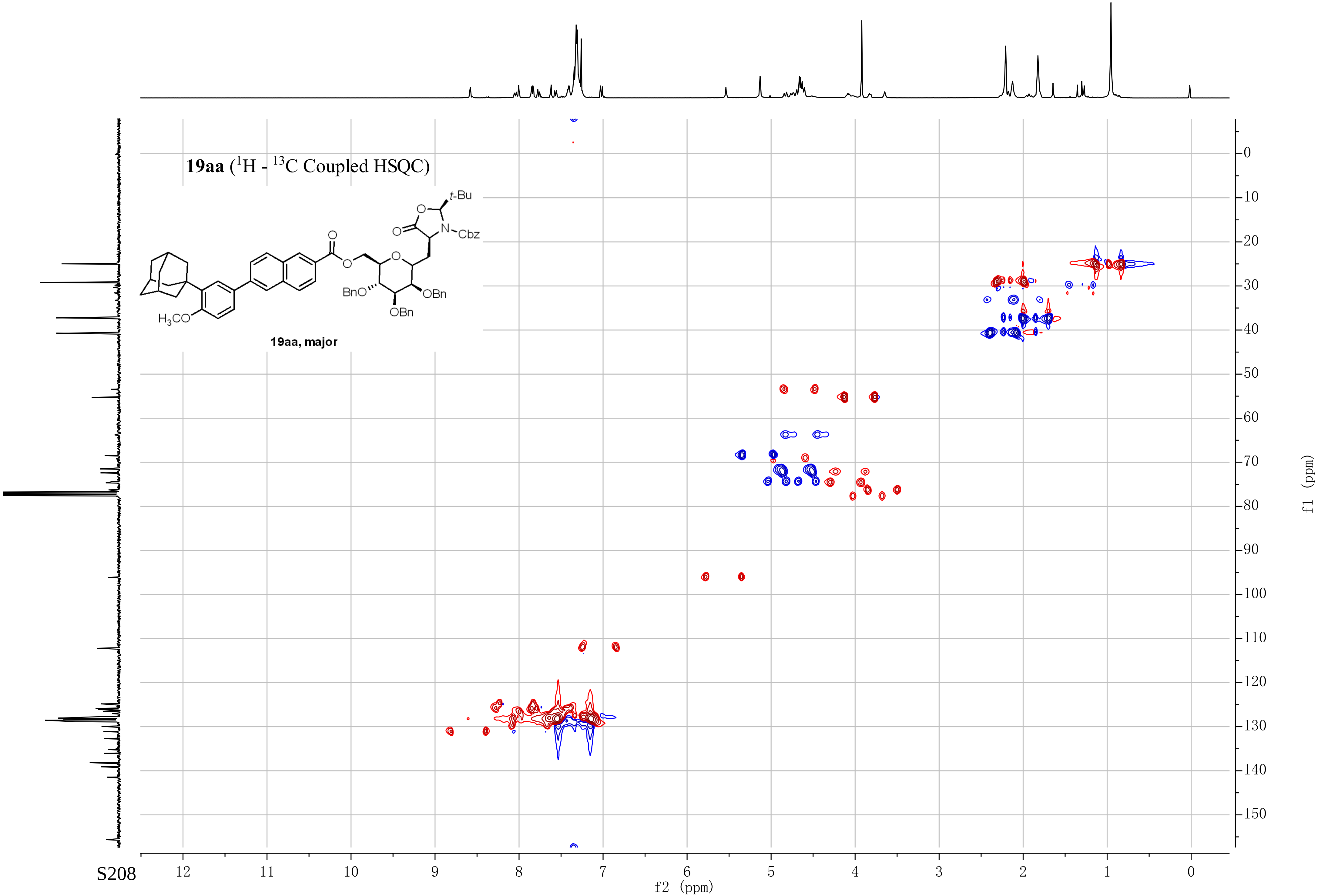


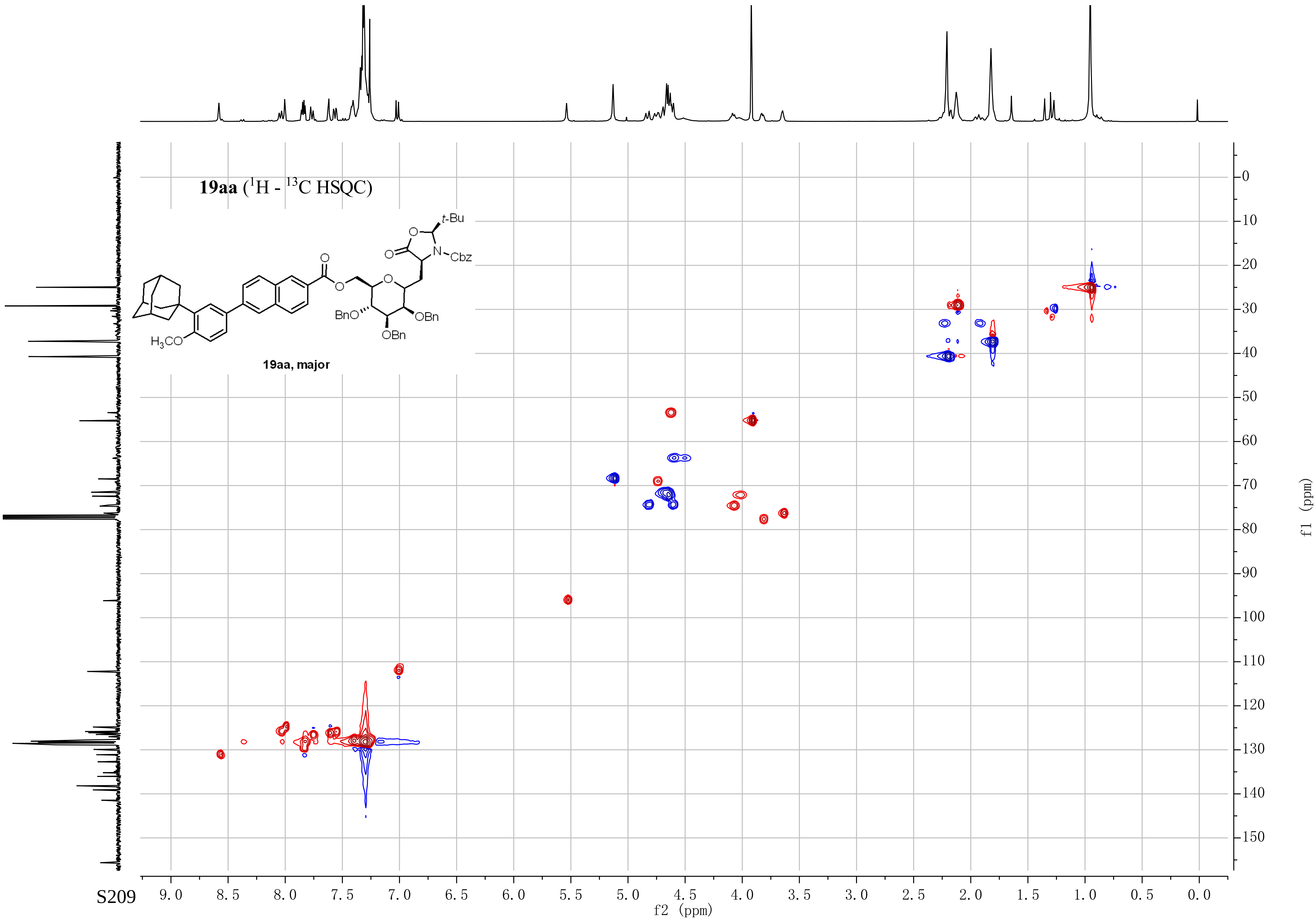
19aa, major



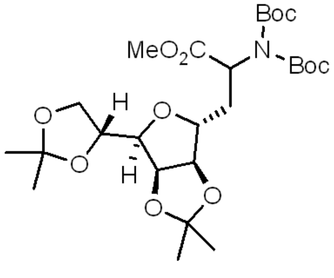

19aa (¹H - ¹H COSY)
t-Bu
O
N
Cbz
O
O
O
O
BnO
OBn
OBn
H3CO
19aa, major
f2 (ppm)
f1 (ppm)

19aa (^{1}H - ^{13}C Coupled HSQC)

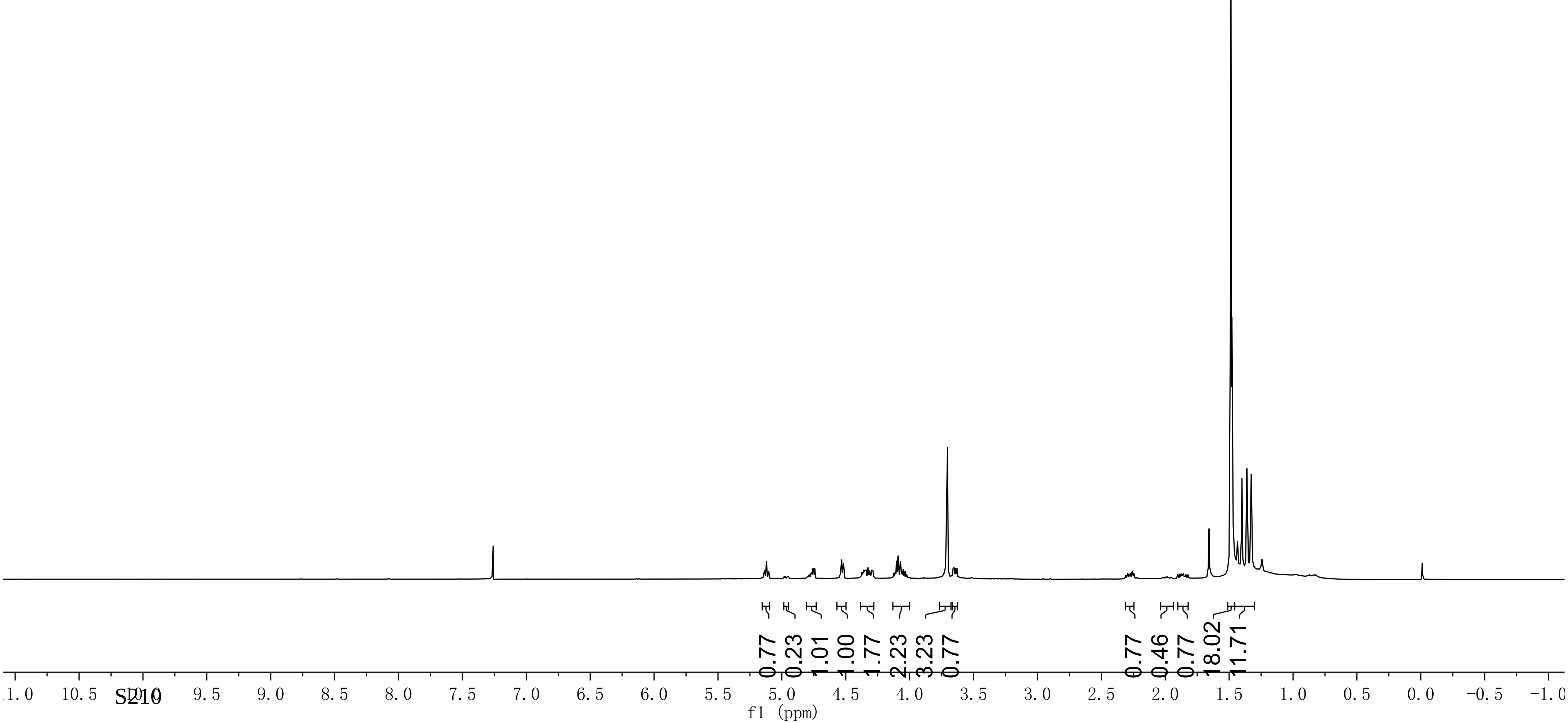



19aa (^{1}H - ^{13}C HSQC)
t-Bu
O
O
N
Cbz
O
O
O
BnO
OBn
OBn
H$_3$CO
19aa, major
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

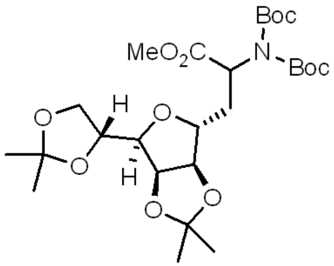
21a (^1H NMR, 400MHz, $CDCl_3$)



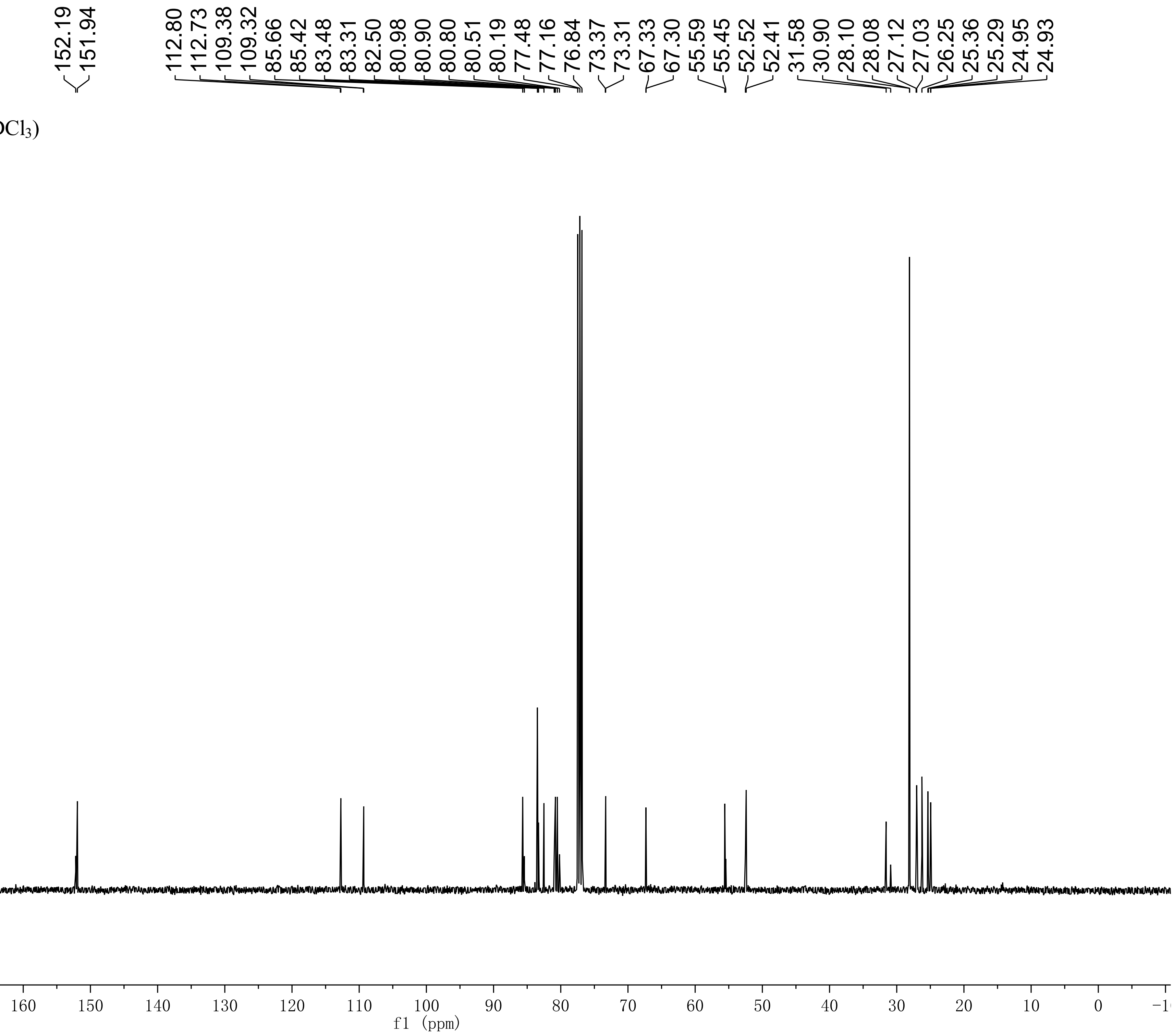
21a

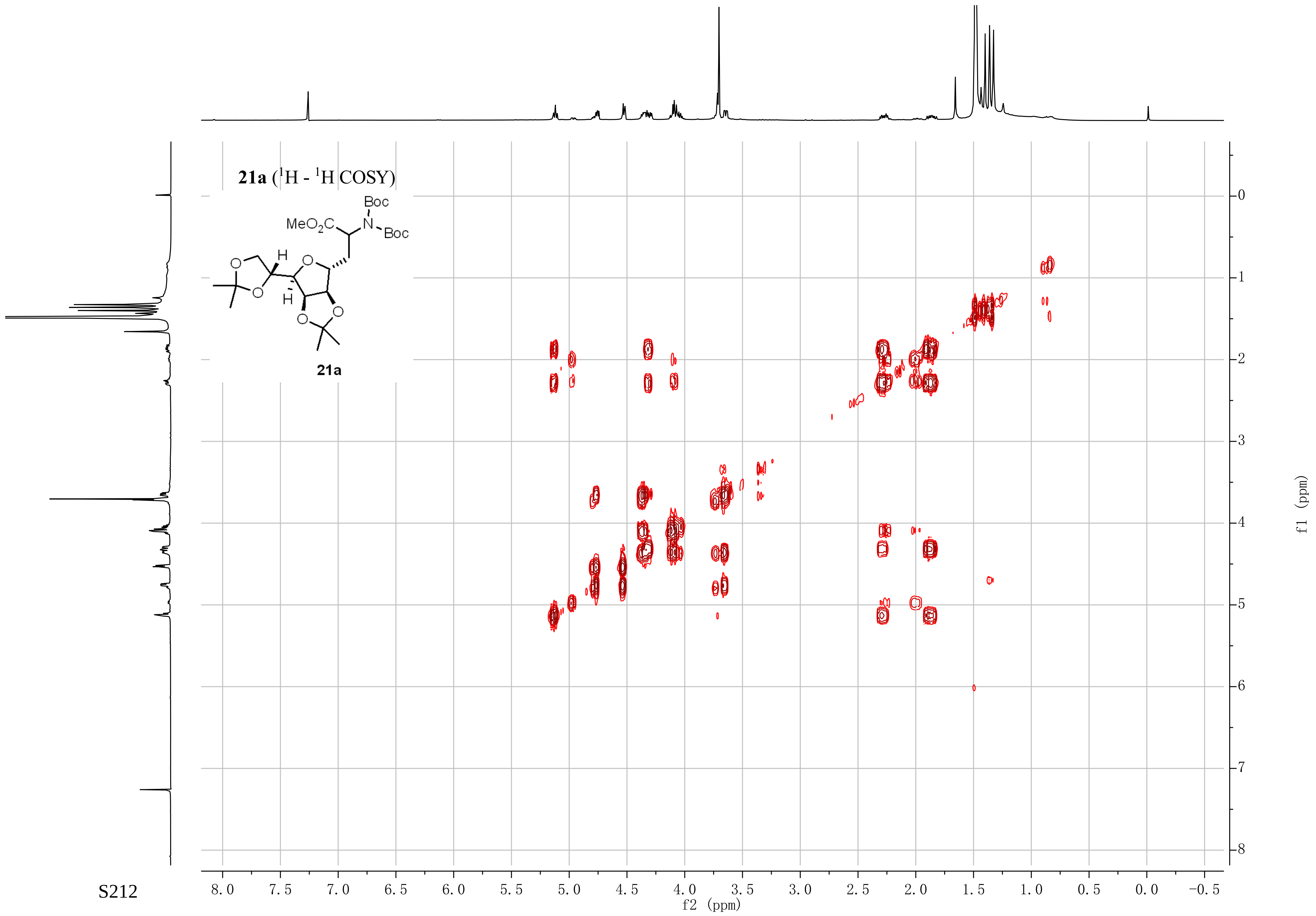


21a (^{13}C NMR, 101MHz, $CDCl_3$)

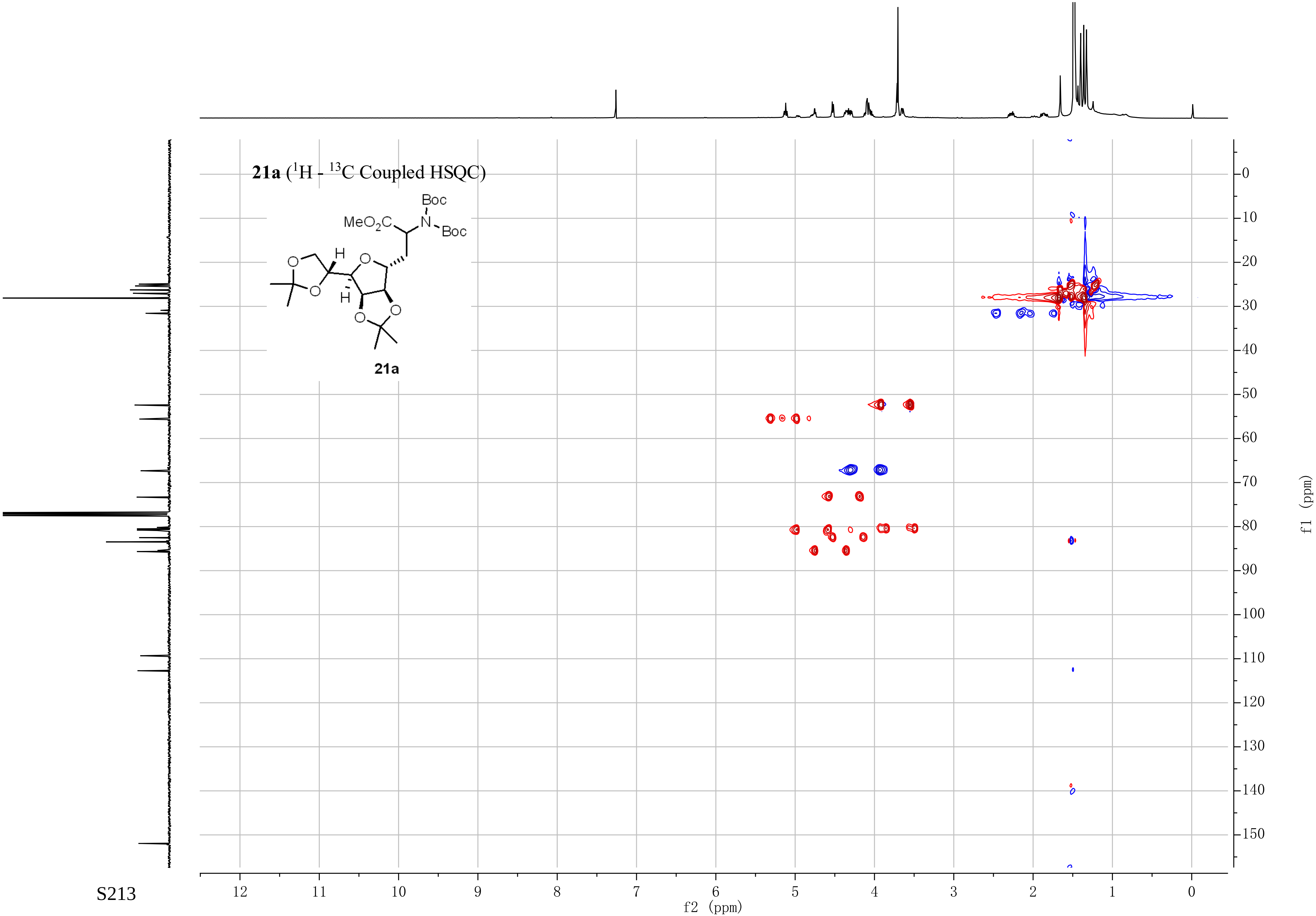


21a

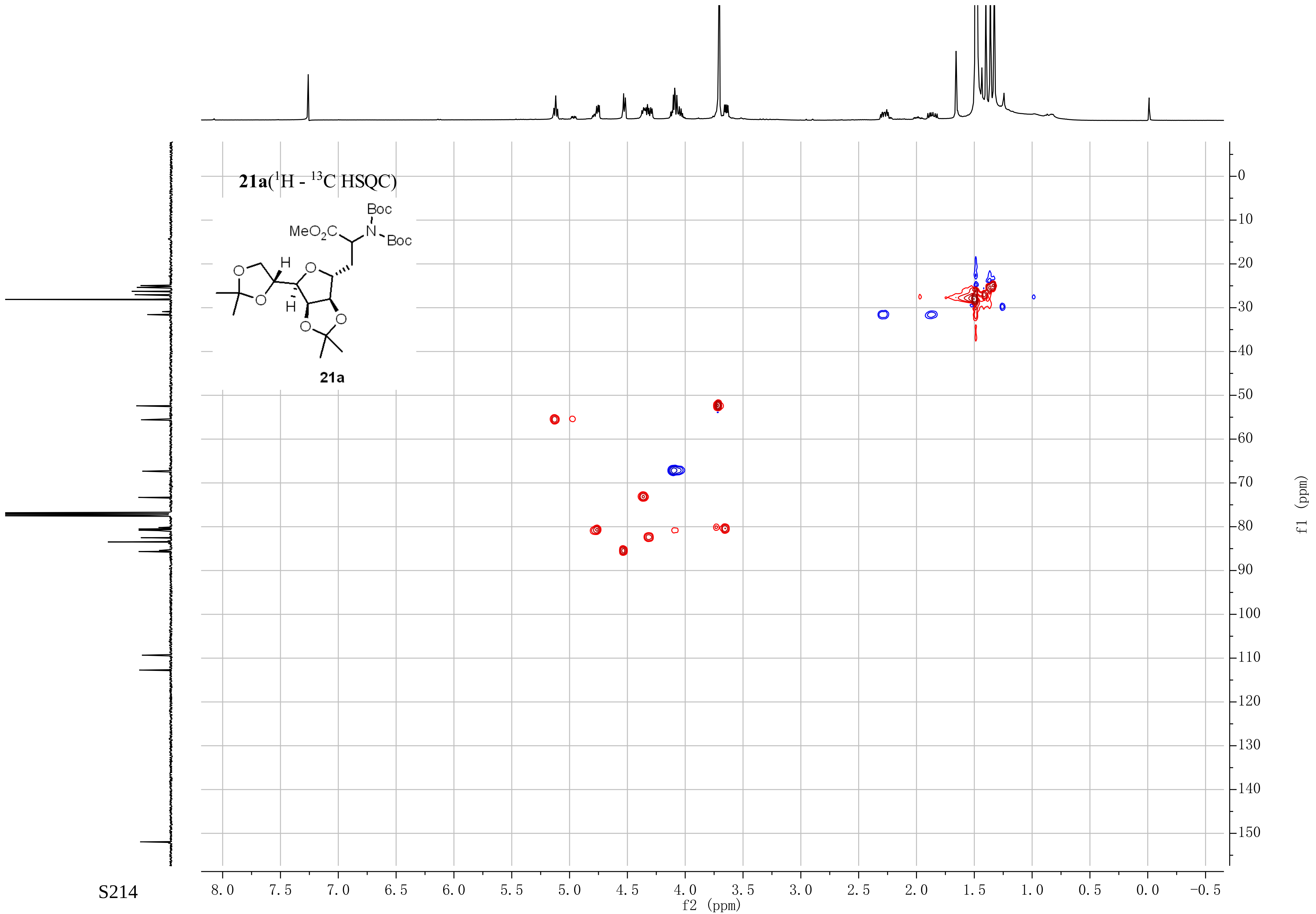




21a (^{1}H - ^{1}H COSY)
Boc
MeO$_2$C
N
Boc
H
O
O
O
H
O
O
21a
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)

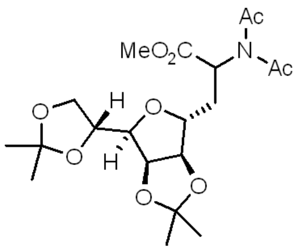


21a (1H - 13C Coupled HSQC)
MeO2C
Boc
N
Boc
H
O
O
O
H
O
O
21a
f2 (ppm)
f1 (ppm)

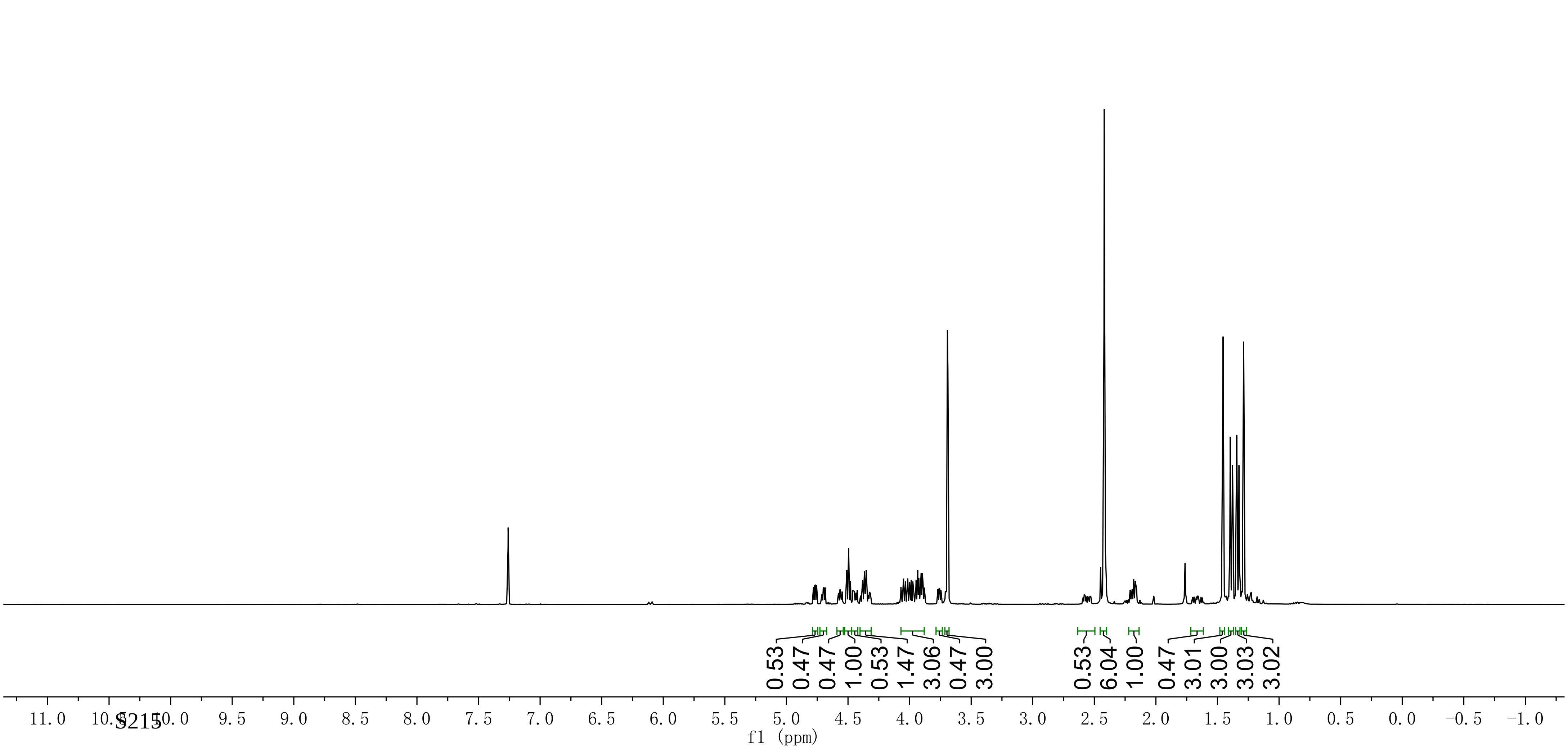


21a(¹H - ¹³C HSQC)
Boc
MeO2C
N
Boc
H
O
O
O
H
O
O
21a
f2 (ppm)
f1 (ppm)

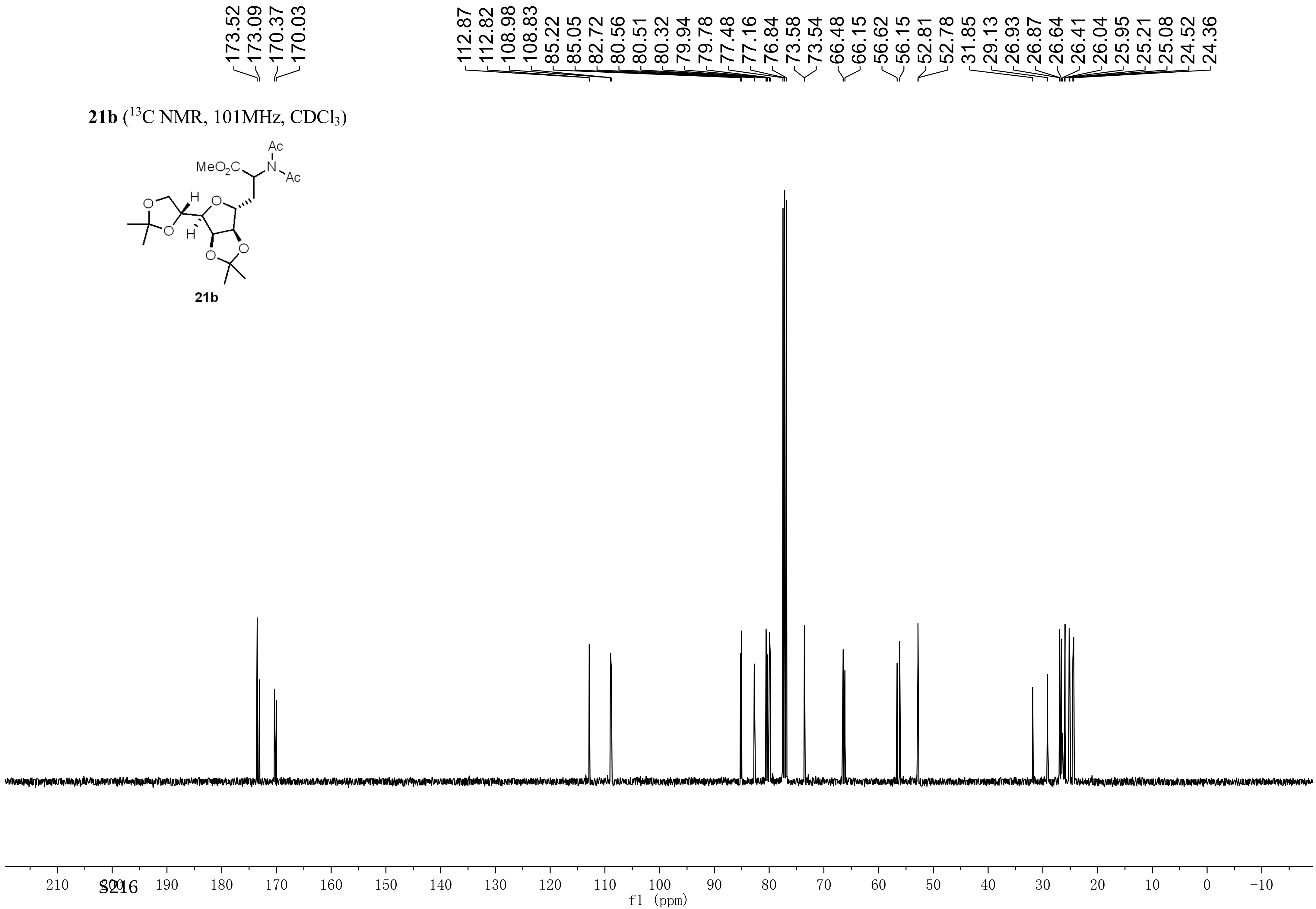
21b (^{1}H NMR, 400MHz, $CDCl_3$)

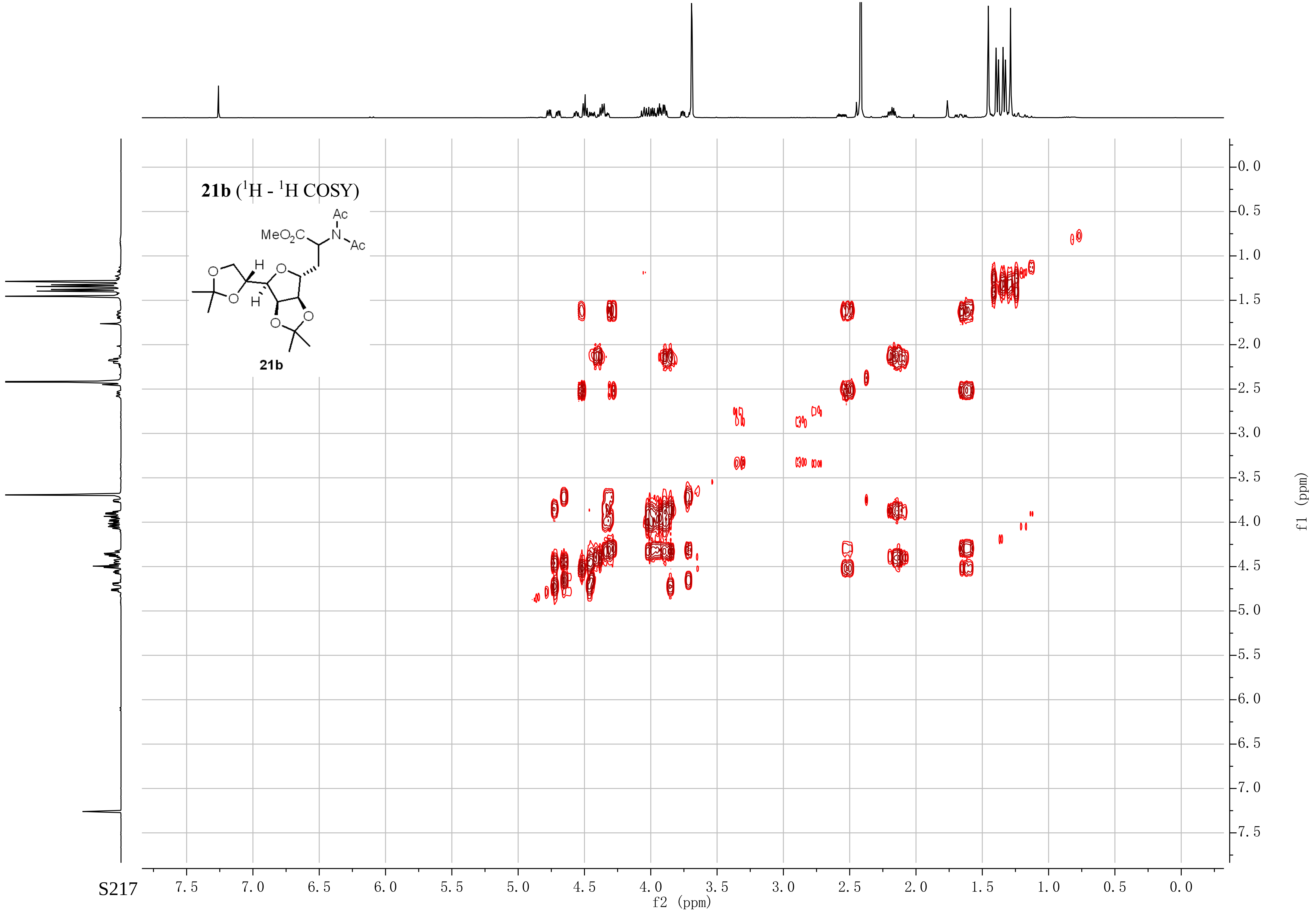


21b

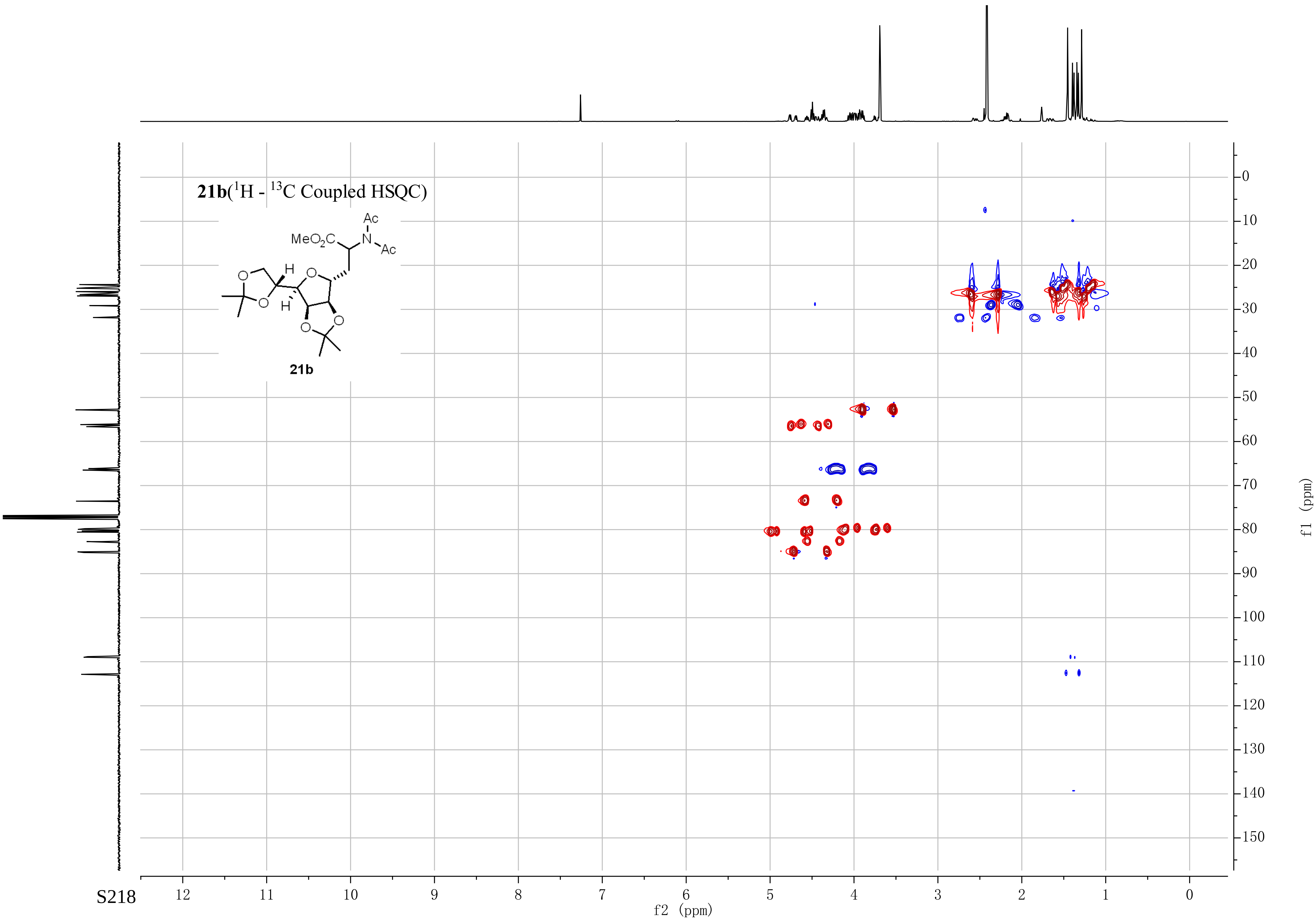


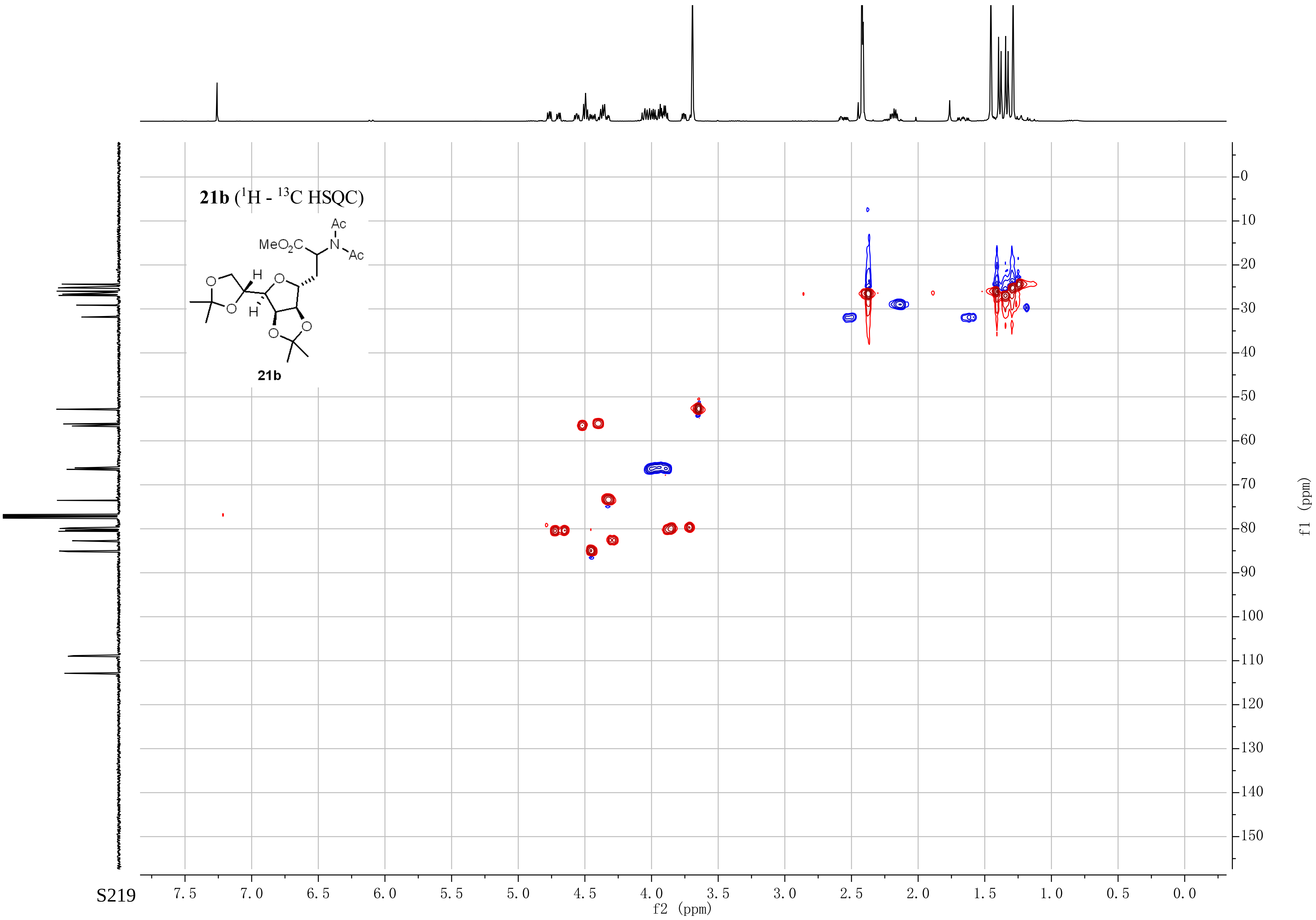
21b (^{13}C NMR, 101MHz, $CDCl_3$)



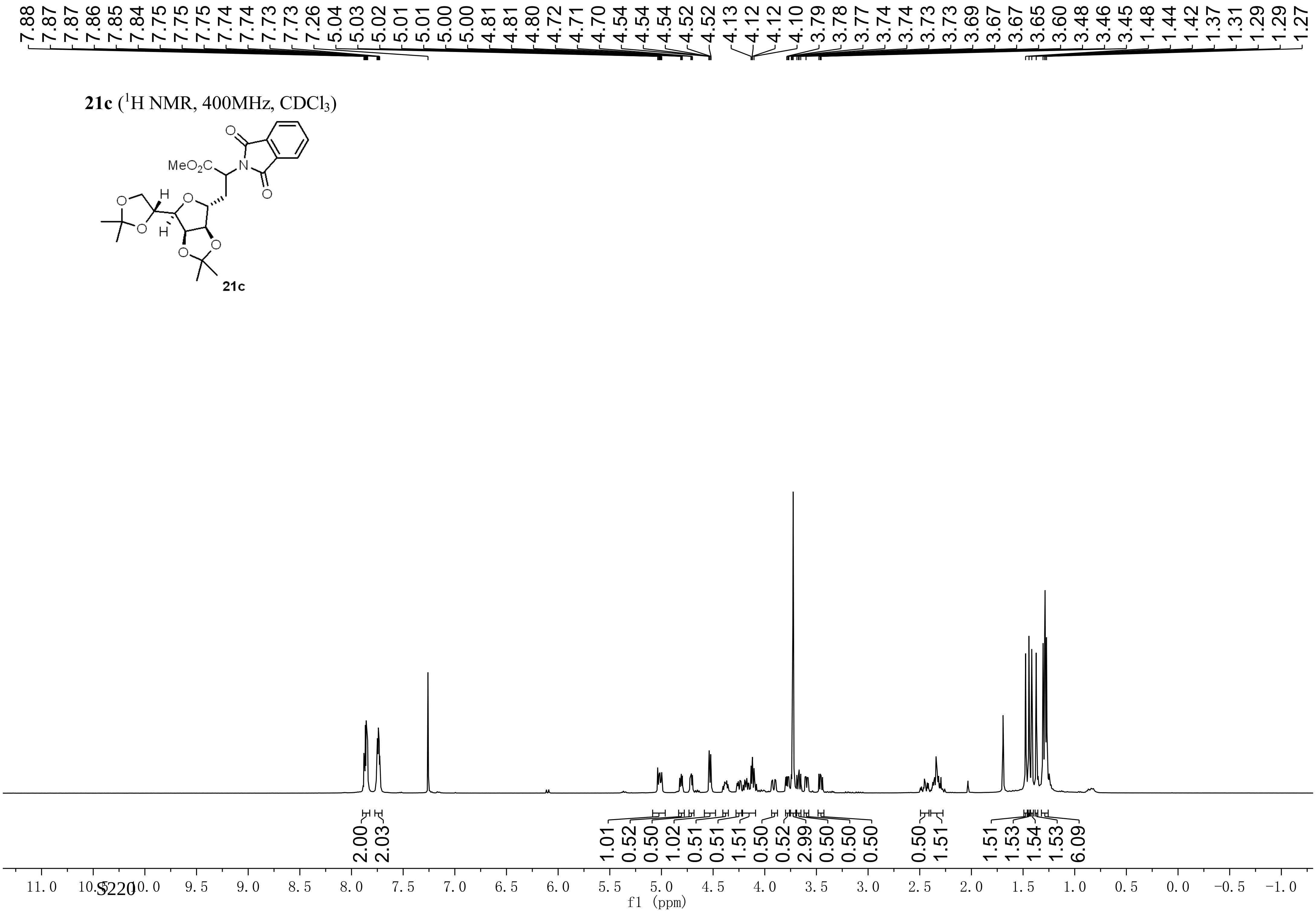


21b (^{1}H - ^{1}H COSY)
21b
f2 (ppm)
f1 (ppm)

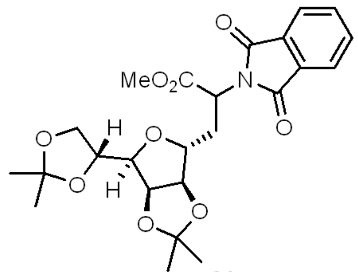

21b(1H - 13C Coupled HSQC)
MeO2C
Ac
N
Ac
H
O
H
21b
f2 (ppm)
f1 (ppm)


21b (1H - 13C HSQC)
MeO2C
N
Ac
Ac
O
H
21b
f2 (ppm)
f1 (ppm)
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 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150

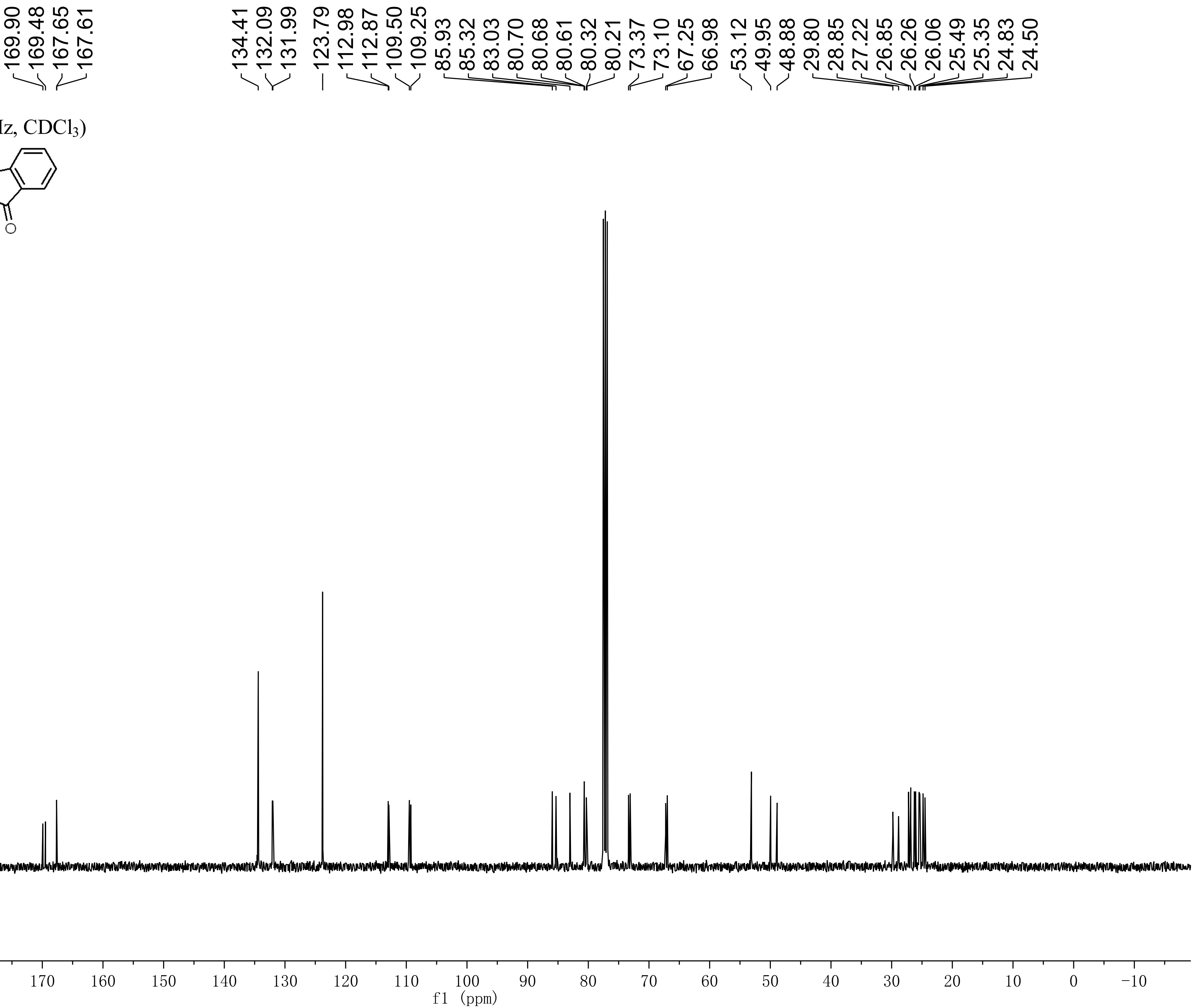
21c (^{1}H NMR, 400MHz, $CDCl_3$)

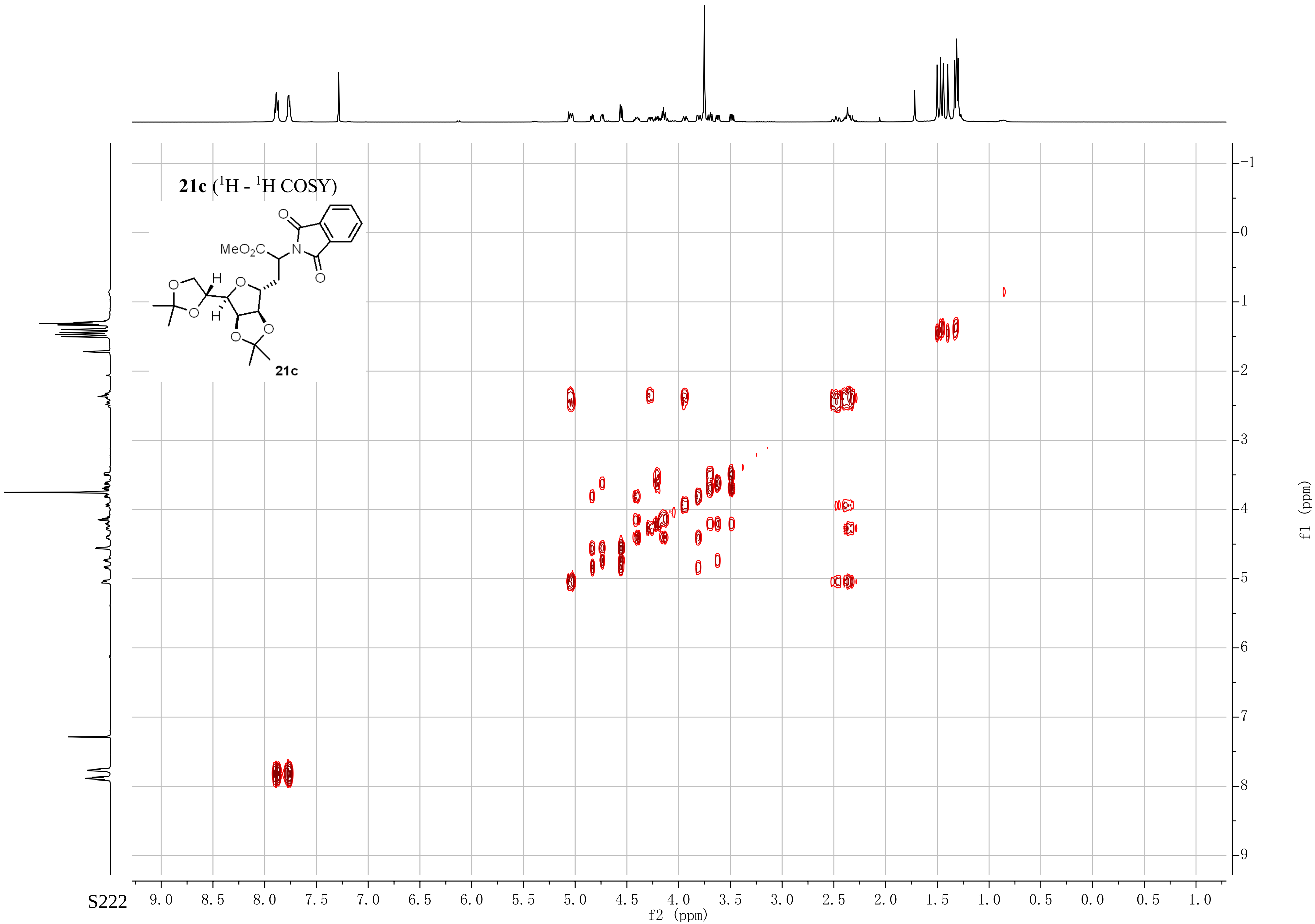


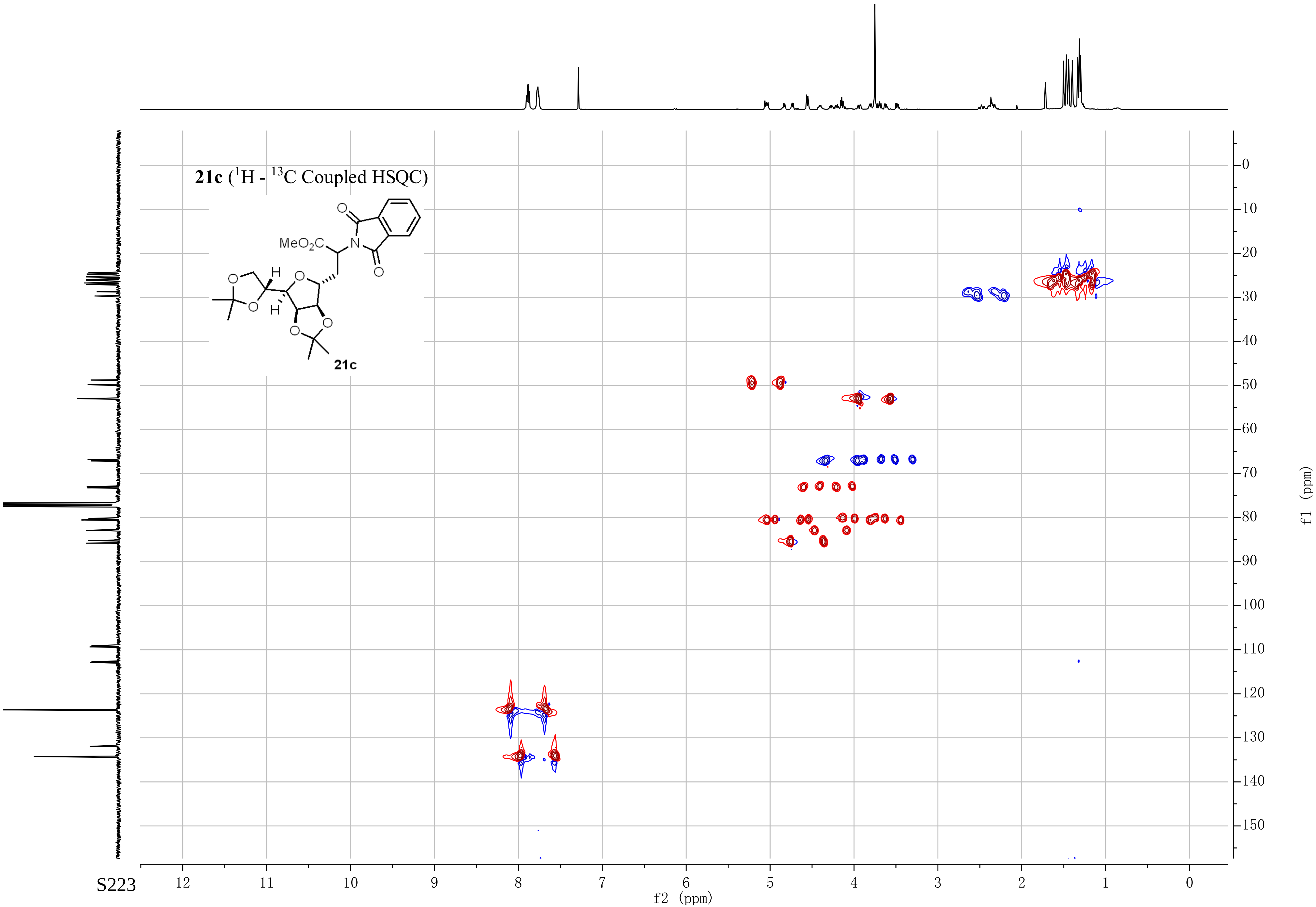
21c (^{13}C NMR, 101MHz, $CDCl_3$)

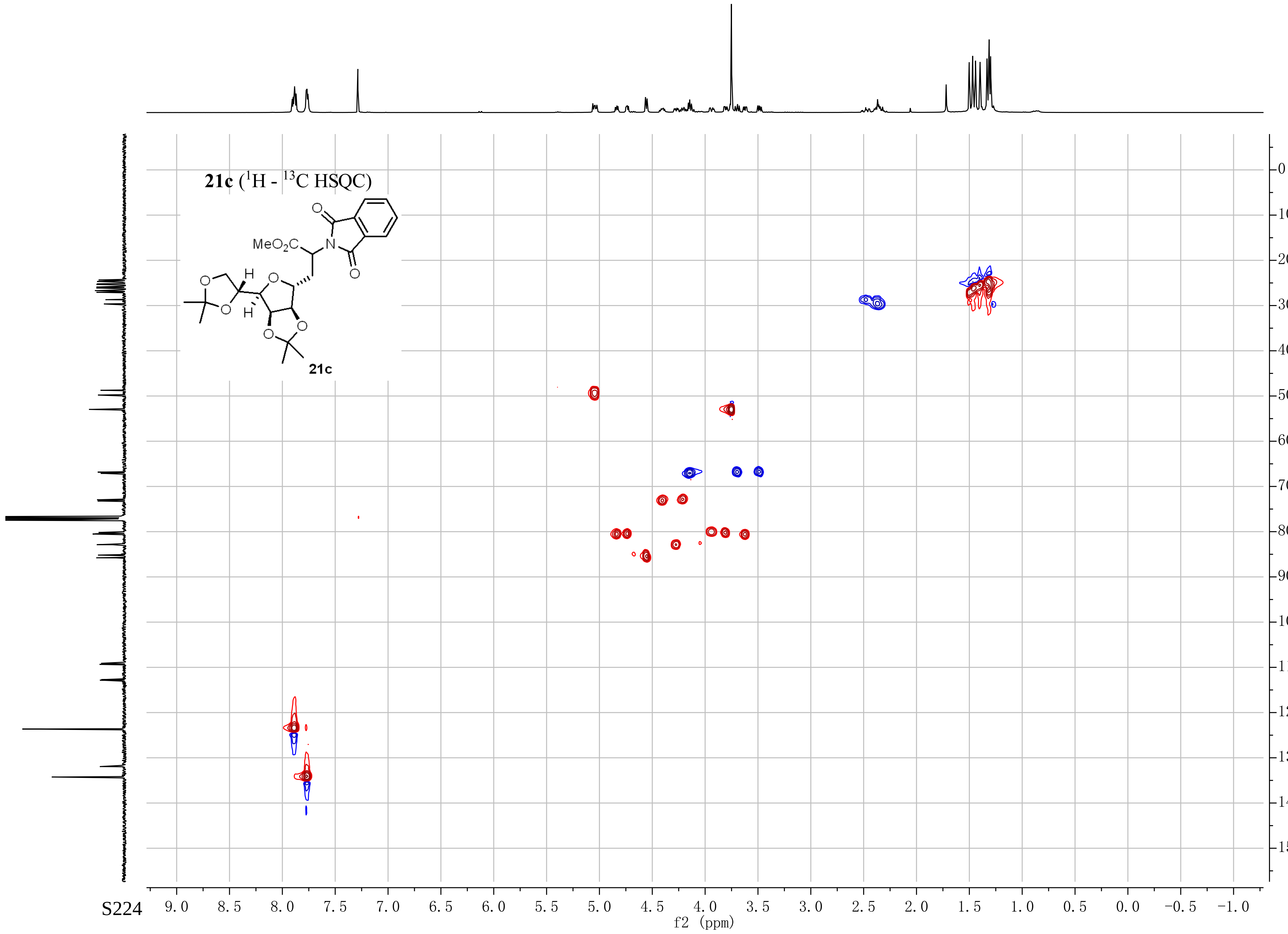


21c

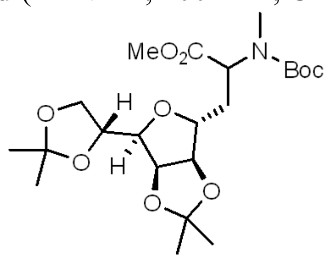



21c (¹H - ¹H COSY)
MeO2C
N
O
H
21c
f2 (ppm)
f1 (ppm)

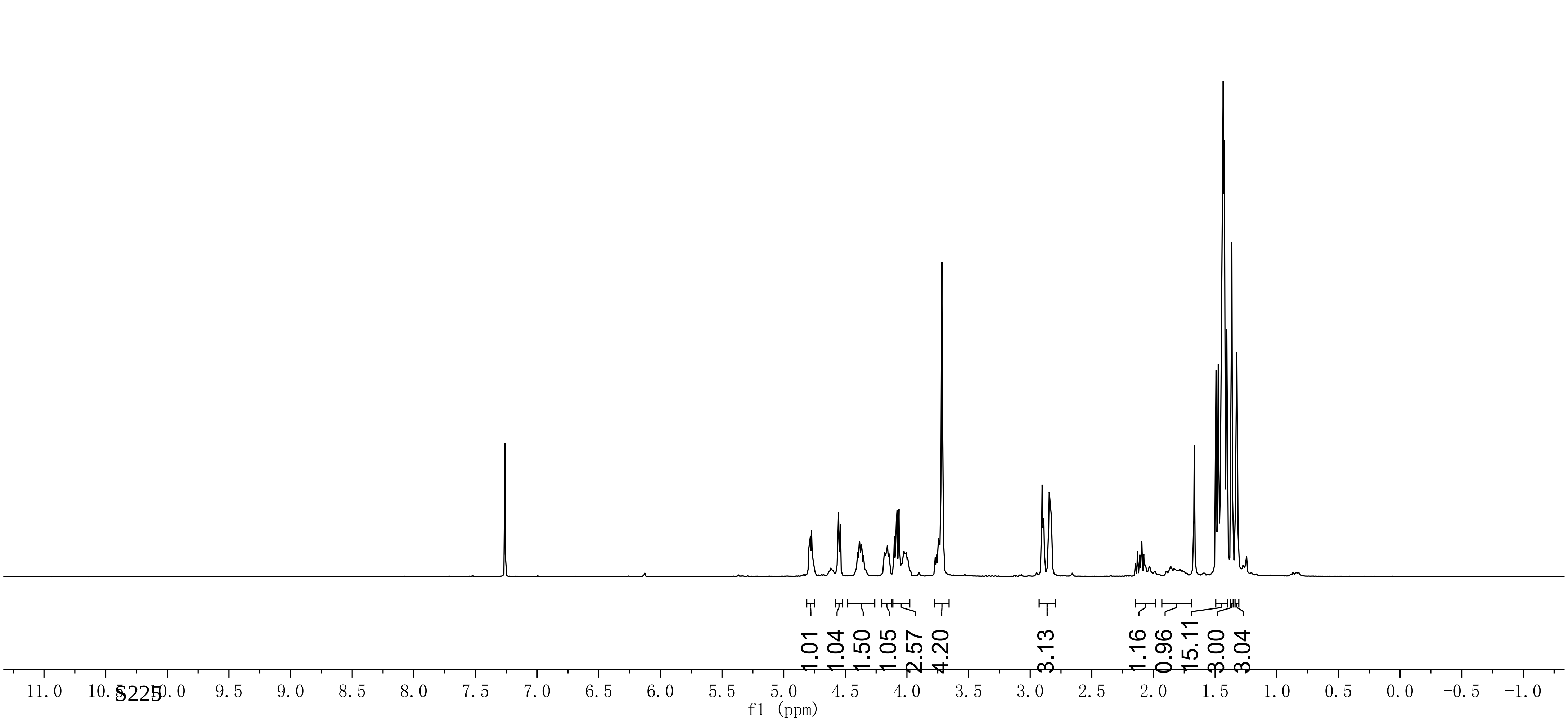

21c (1H - 13C Coupled HSQC)
MeO2C
N
O
O
H
H
21c
f2 (ppm)
f1 (ppm)


21c (¹H - ¹³C HSQC)
MeO2C
N
21c
f2 (ppm)
f1 (ppm)

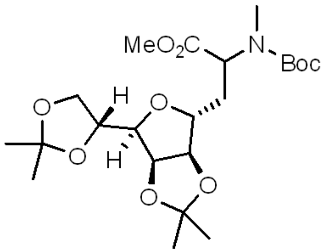
21d (^{1}H NMR, 400MHz, $CDCl_3$)



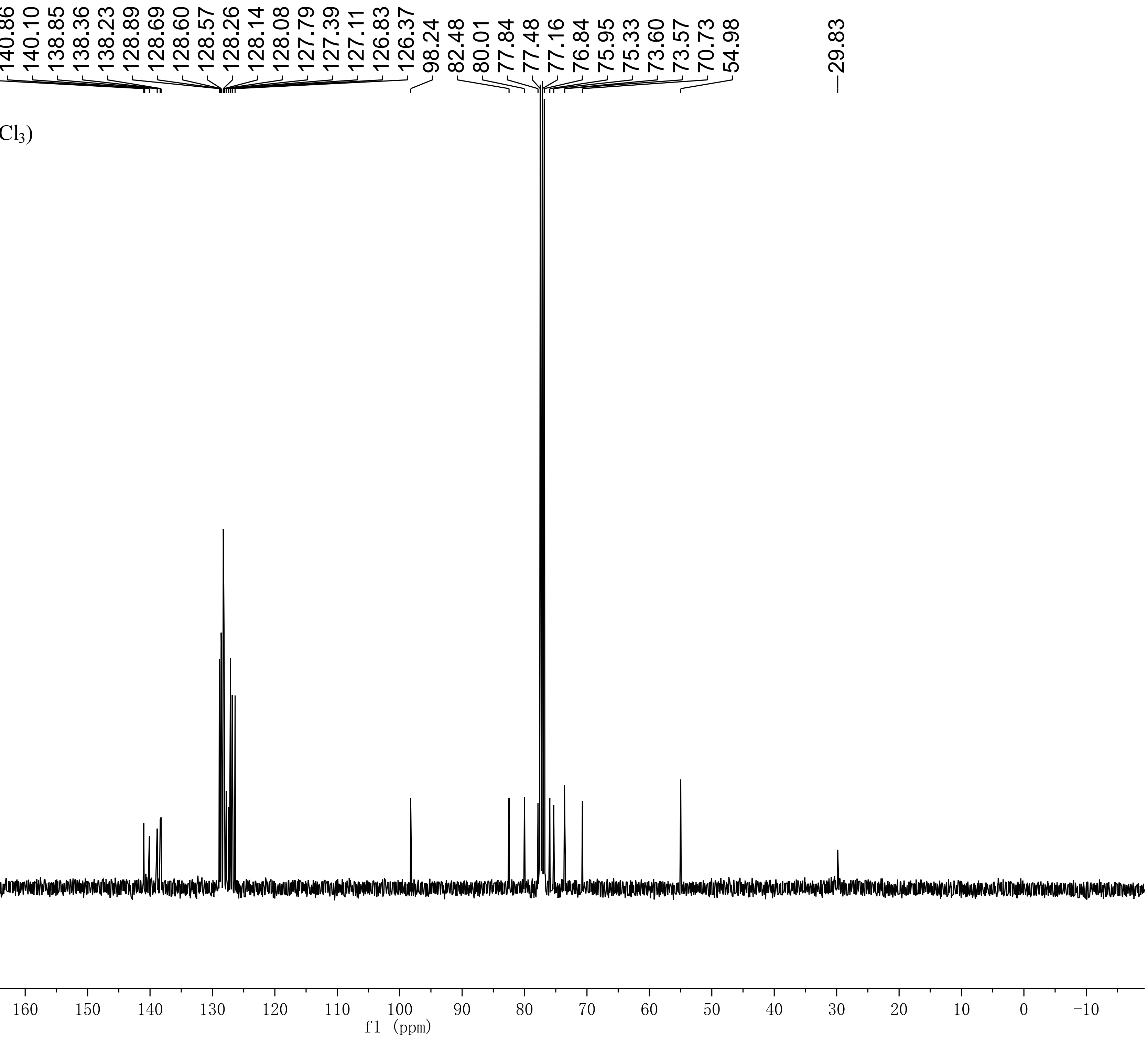
21d

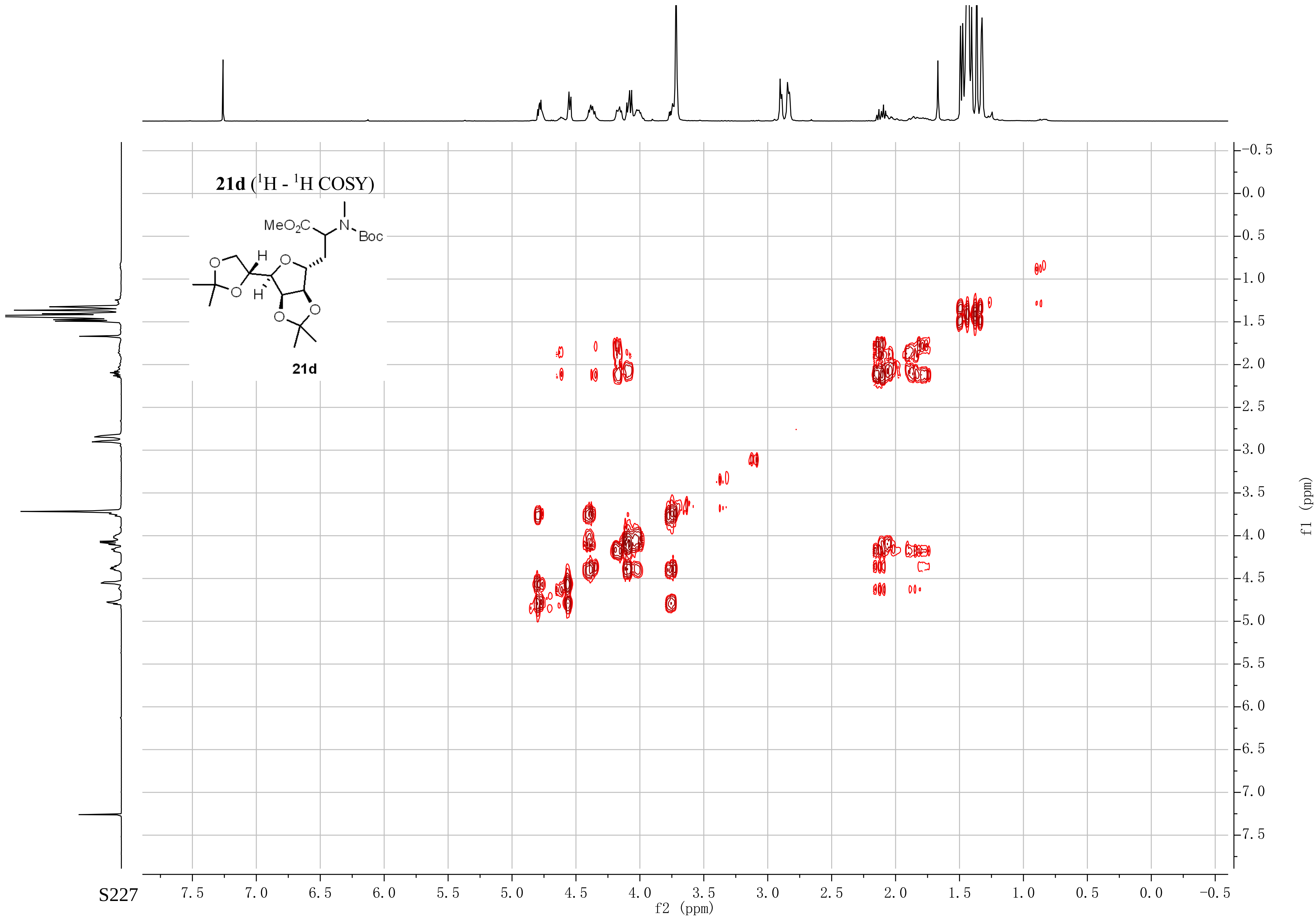


21d (^{13}C NMR, 101MHz, $CDCl_3$)



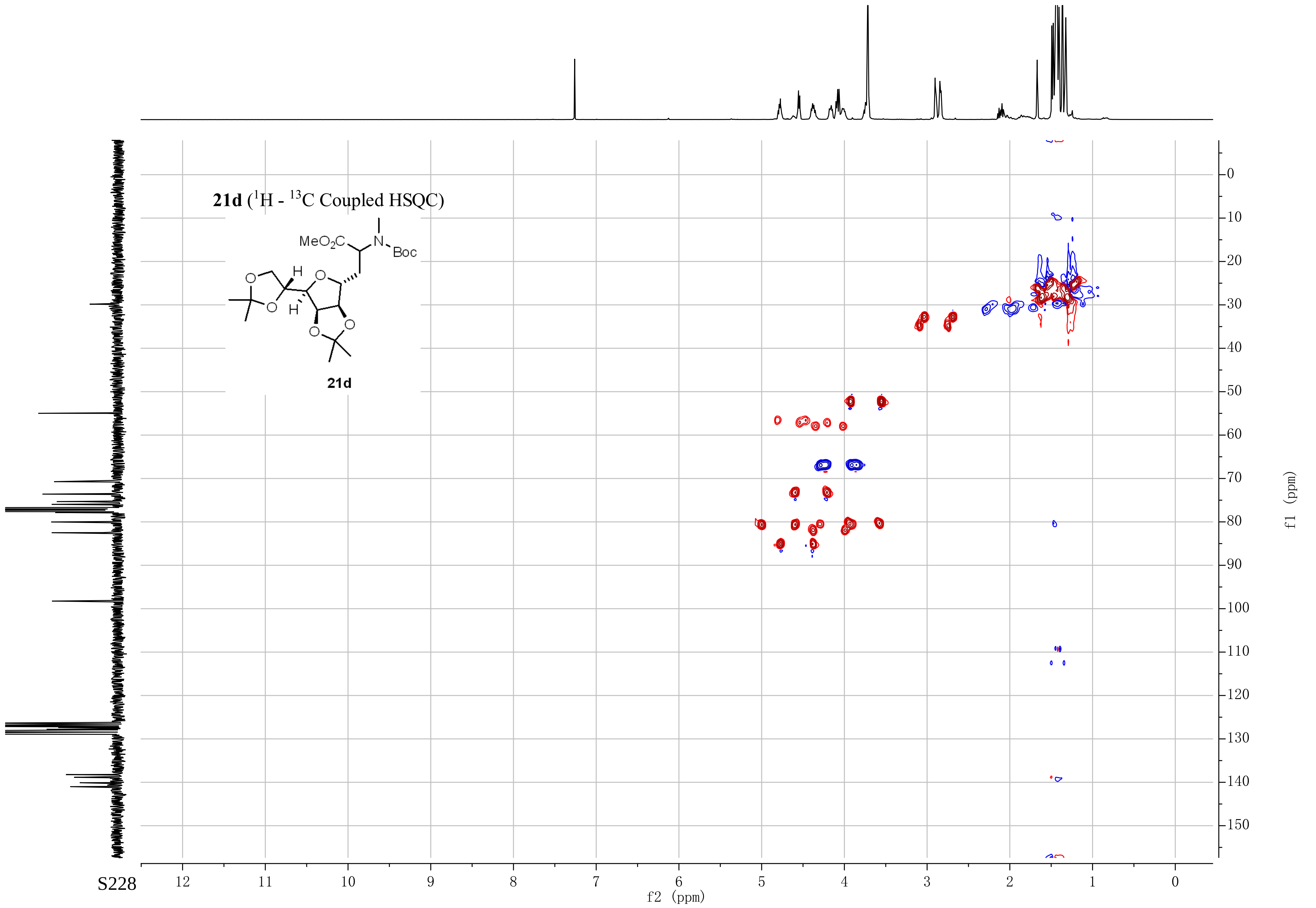
21d



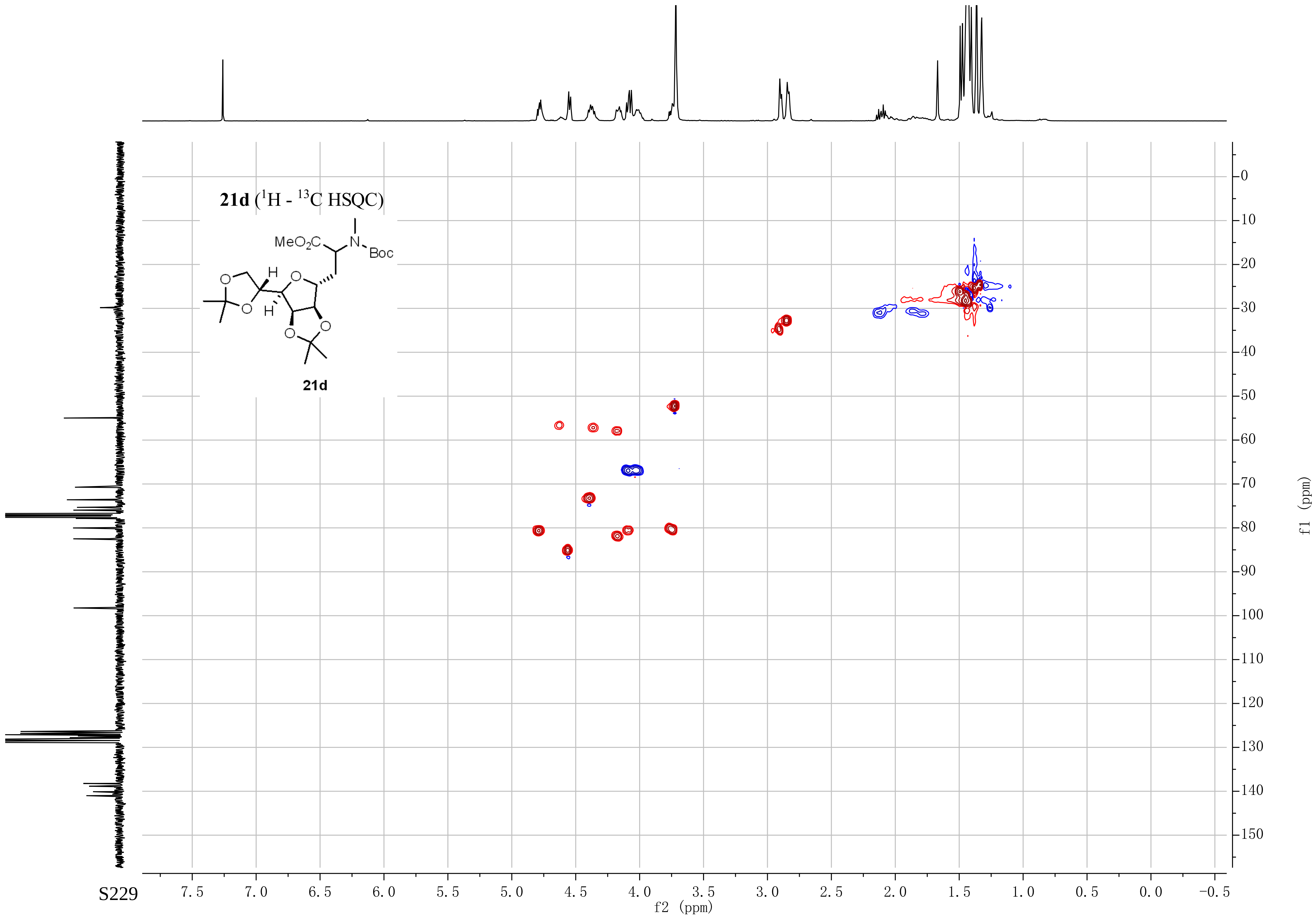


21d (^{1}H - ^{1}H COSY)
MeO2C
N
Boc
H
O
H
21d
f2 (ppm)
f1 (ppm)

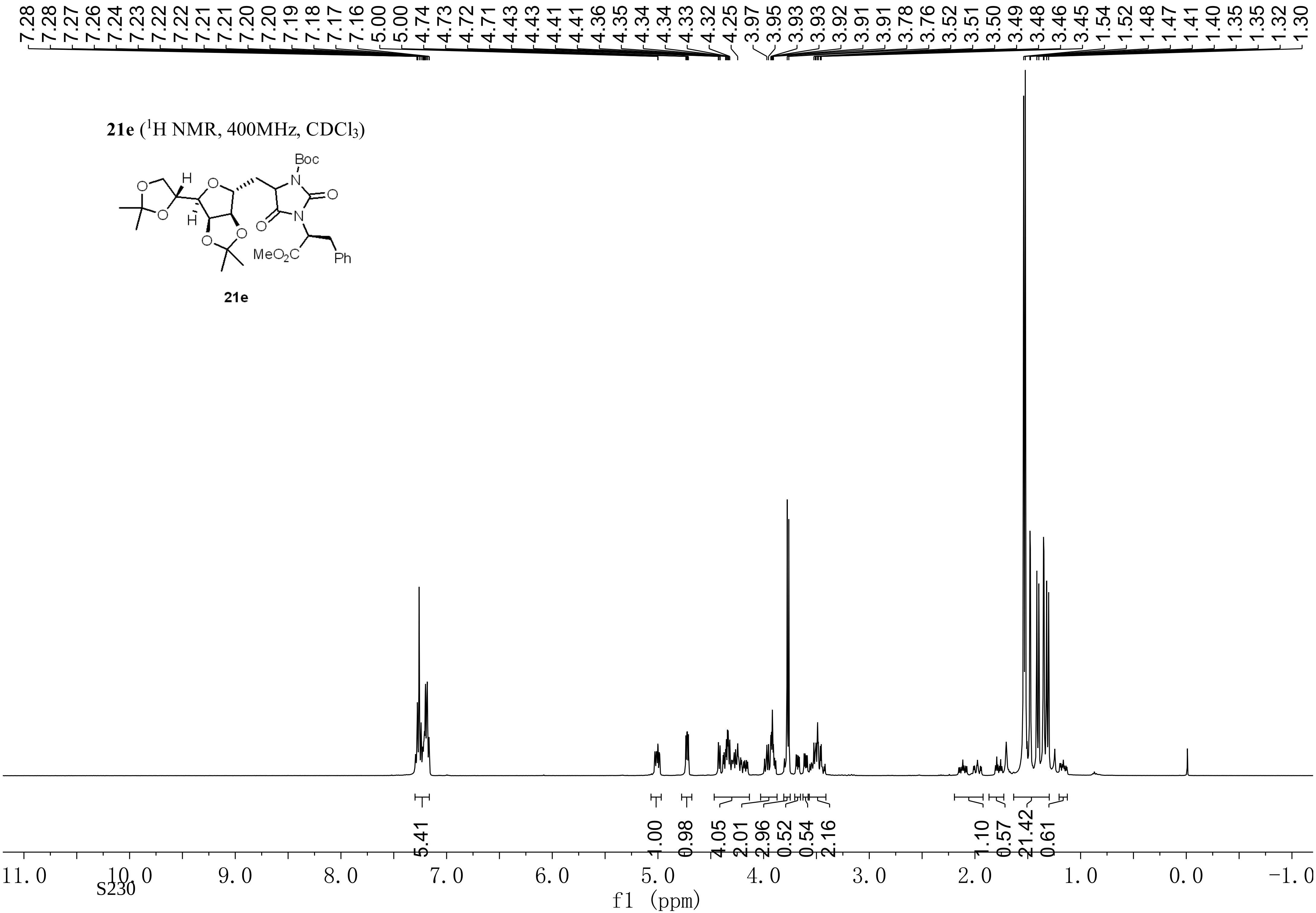
21d (^{1}H - ^{13}C Coupled HSQC)



21d

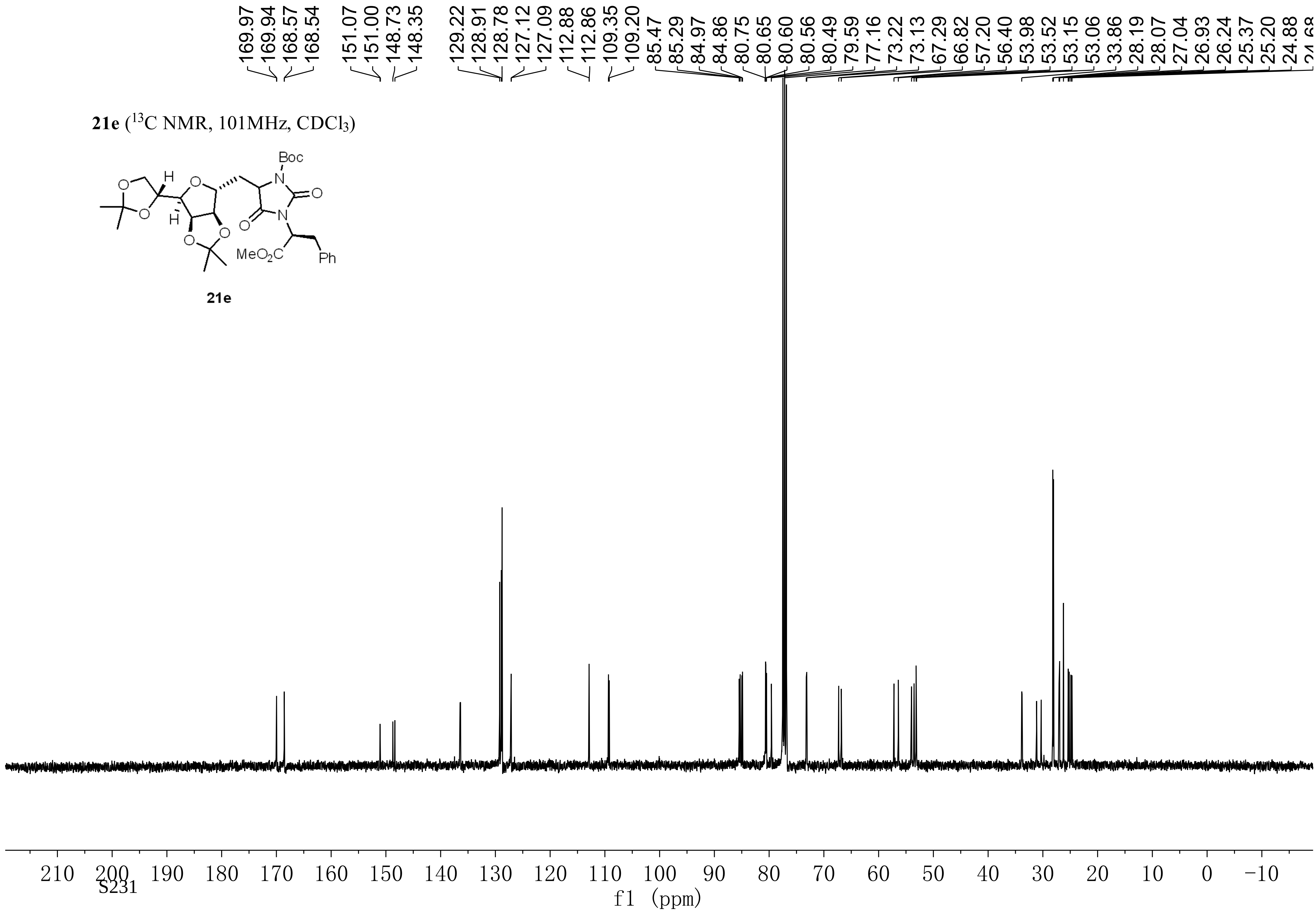


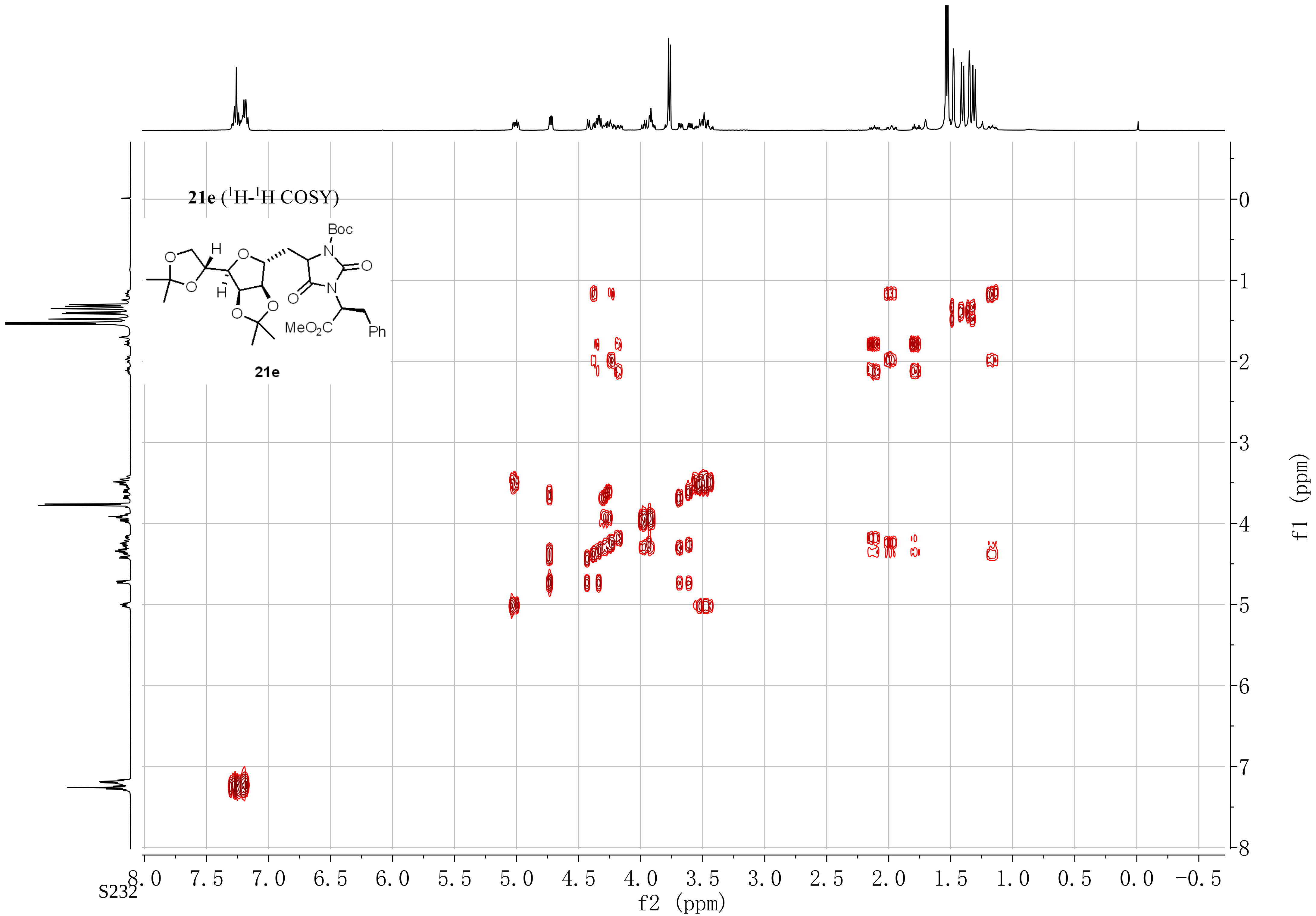
21d (1H - 13C HSQC)
MeO2C
N
Boc
H
O
21d
f2 (ppm)
f1 (ppm)


7.28 7.28 7.27 7.26 7.24 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.17 7.16 5.00 5.00 4.74 4.73 4.72 4.71 4.43 4.43 4.41 4.41 4.36 4.35 4.34 4.34 4.33 4.32 4.25 3.97 3.95 3.93 3.93 3.92 3.91 3.91 3.78 3.76 3.52 3.51 3.50 3.49 3.48 3.46 3.45 1.54 1.52 1.48 1.47 1.41 1.40 1.35 1.35 1.32 1.30
21e (^{1}H NMR, 400MHz, $CDCl_3$)
Boc
N
O
N
O
H
H
MeO$_2$C
Ph
21e
5.41
1.00
0.98
4.05
2.01
2.96
0.52
0.54
2.16
1.10
0.57
21.42
0.61
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

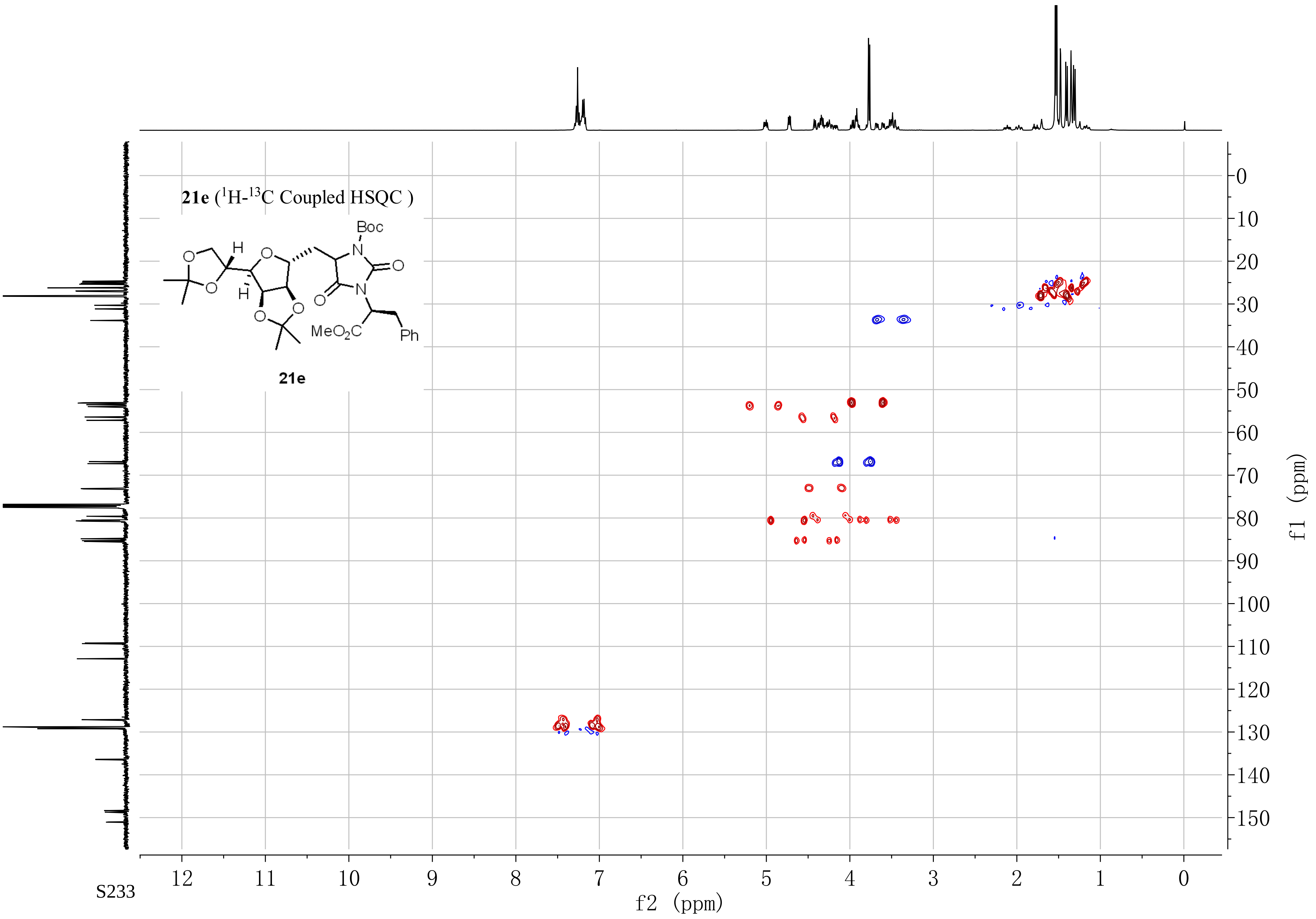
21e (^{13}C NMR, 101MHz, $CDCl_3$)

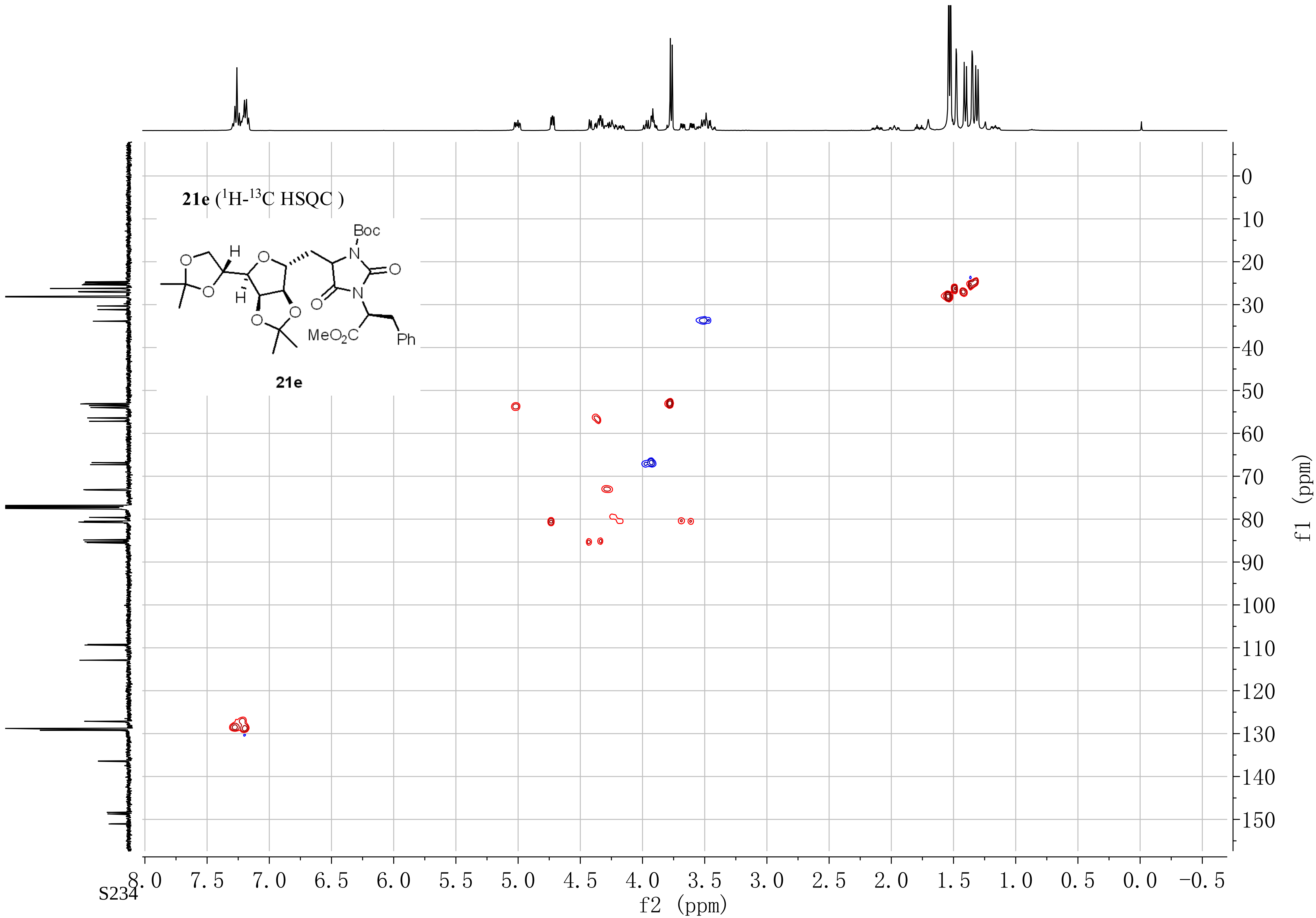
21e



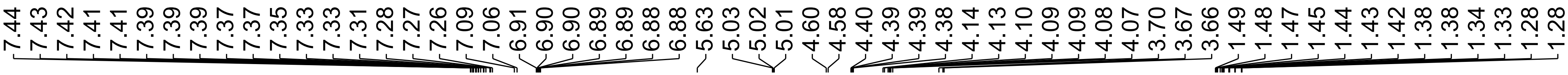


21e (1H-1H COSY)
Boc
N
O
MeO2C
Ph
H
21e
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7 8

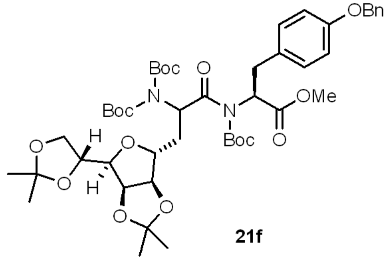

21e (^{1}H-^{13}C Coupled HSQC)
Boc
N
O
N
O
O
O
O
O
O
H
H
MeO$_2$C
Ph
21e
f1 (ppm)
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
12
11
10
9
8
7
6
5
4
3
2
1
0



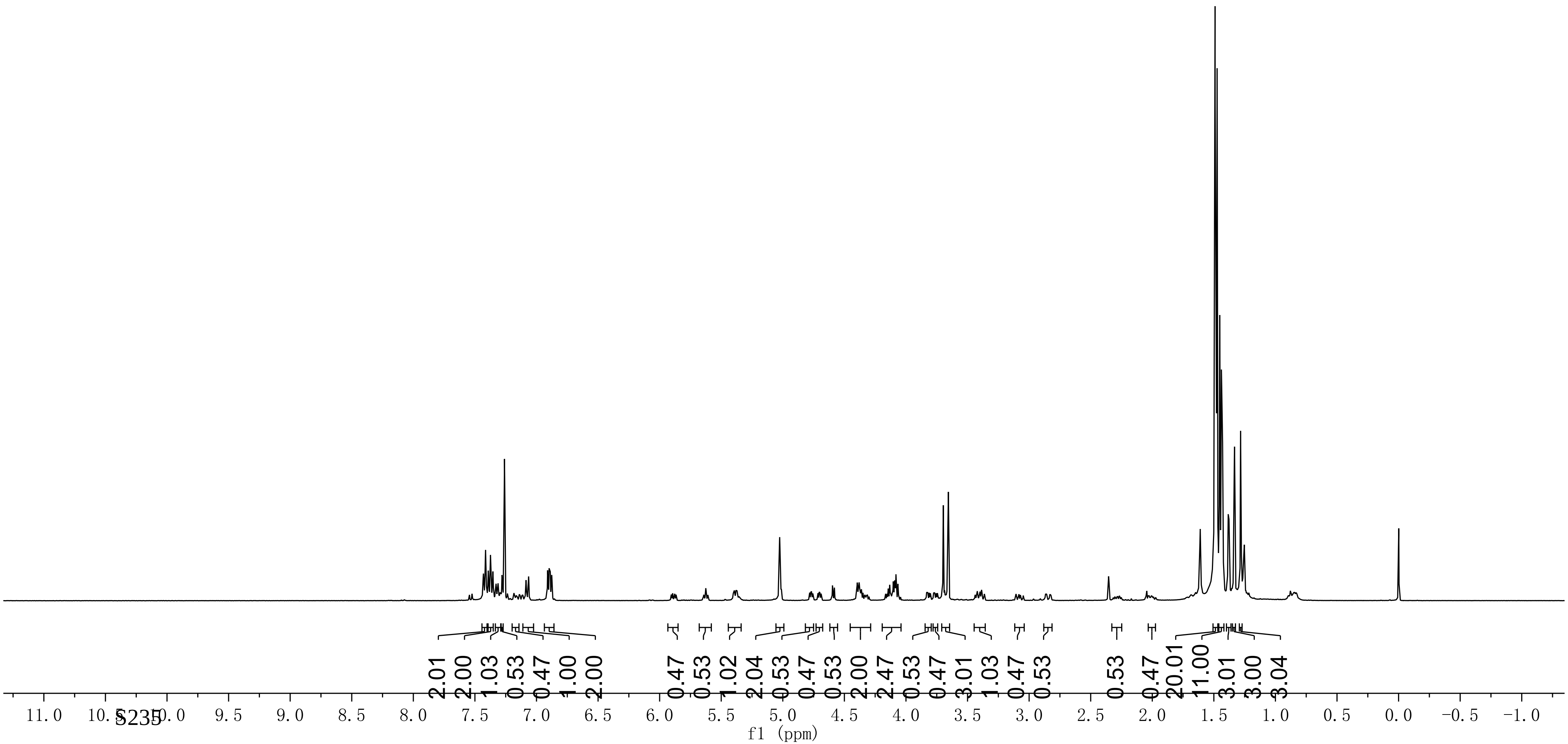
21e (¹H-¹³C HSQC)
Boc
H
H
MeO2C
Ph
21e
f2 (ppm)
f1 (ppm)



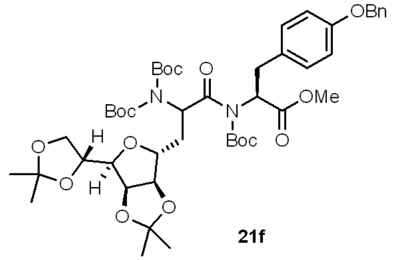
21f (^{1}H NMR, 400MHz, $CDCl_3$)



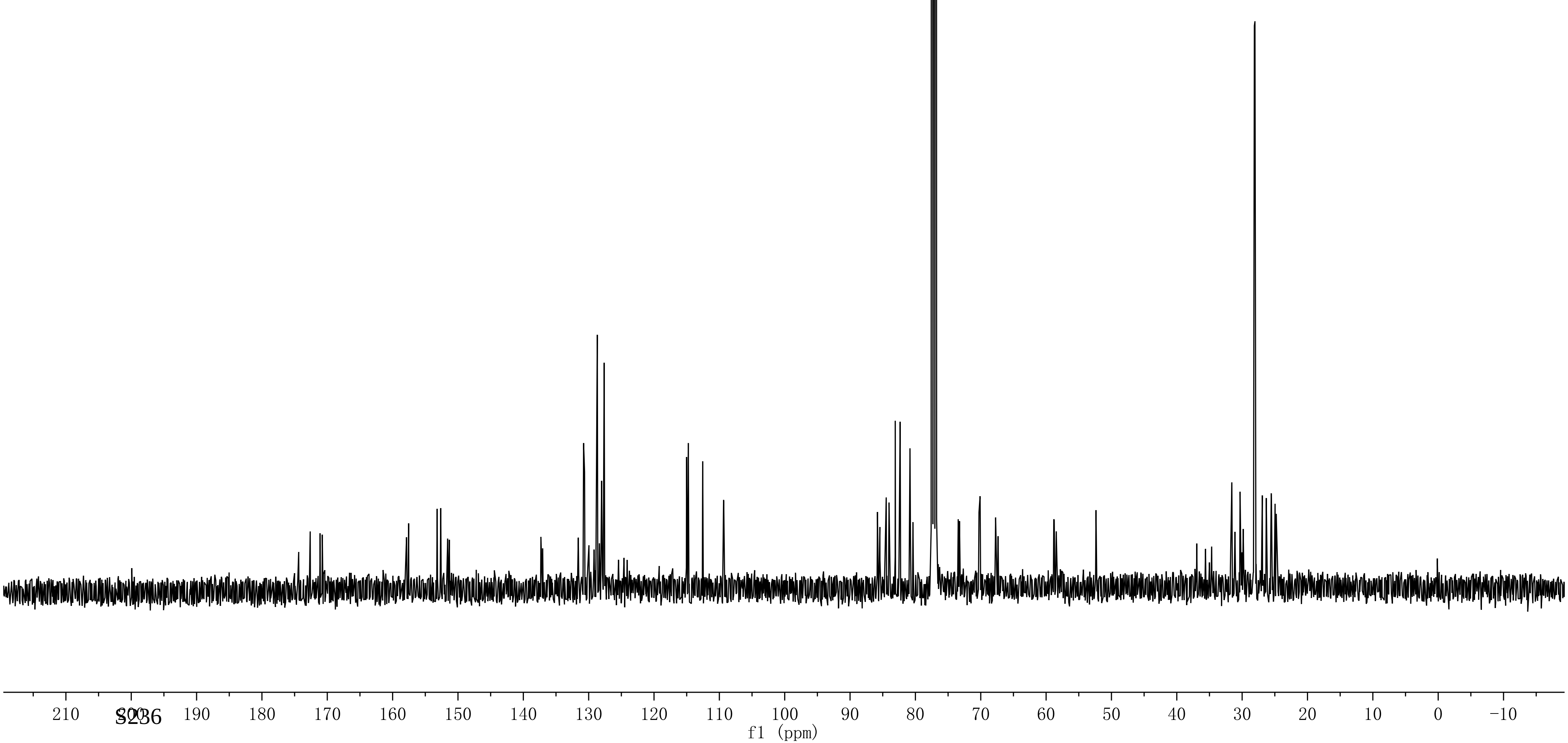
21f

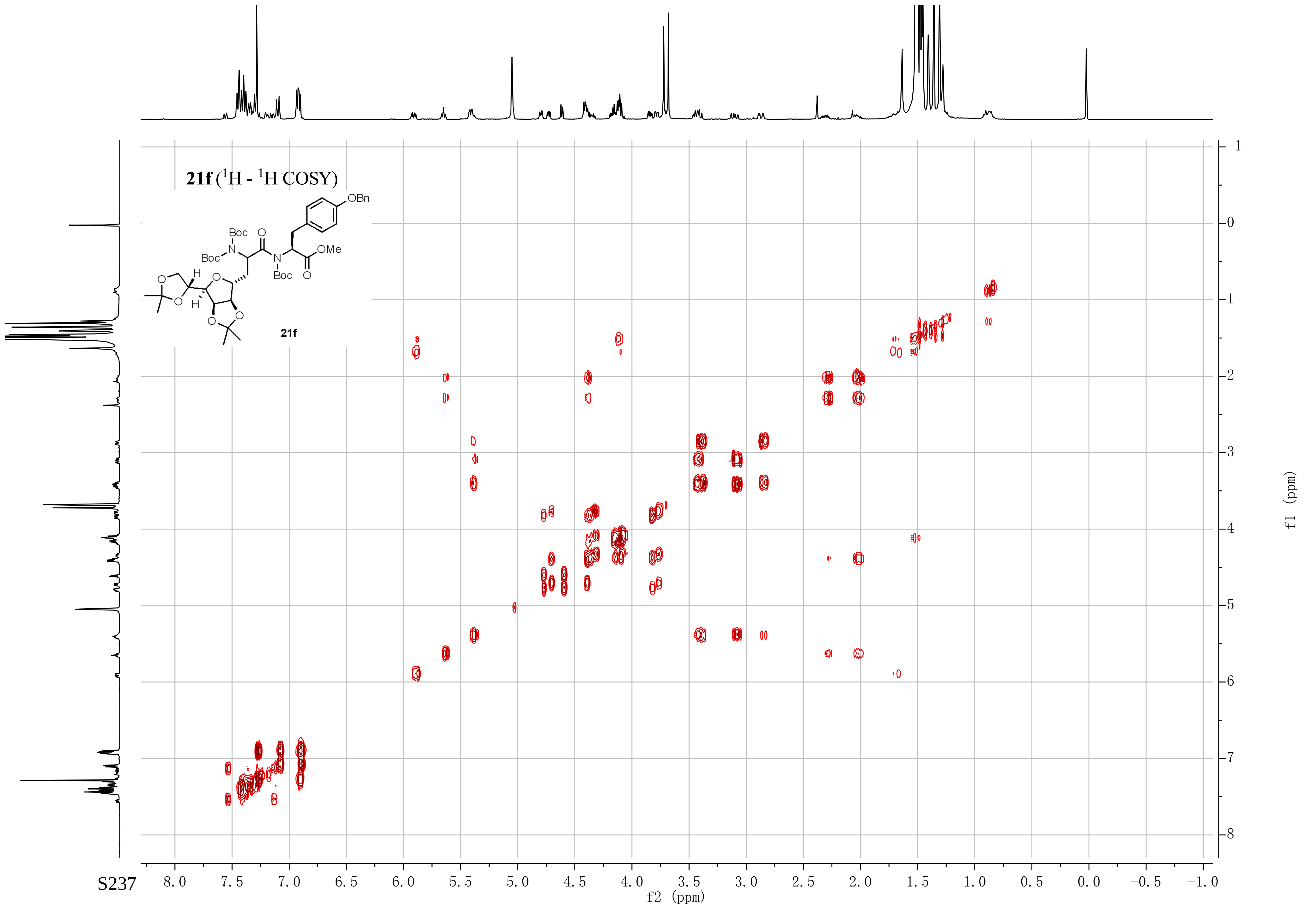


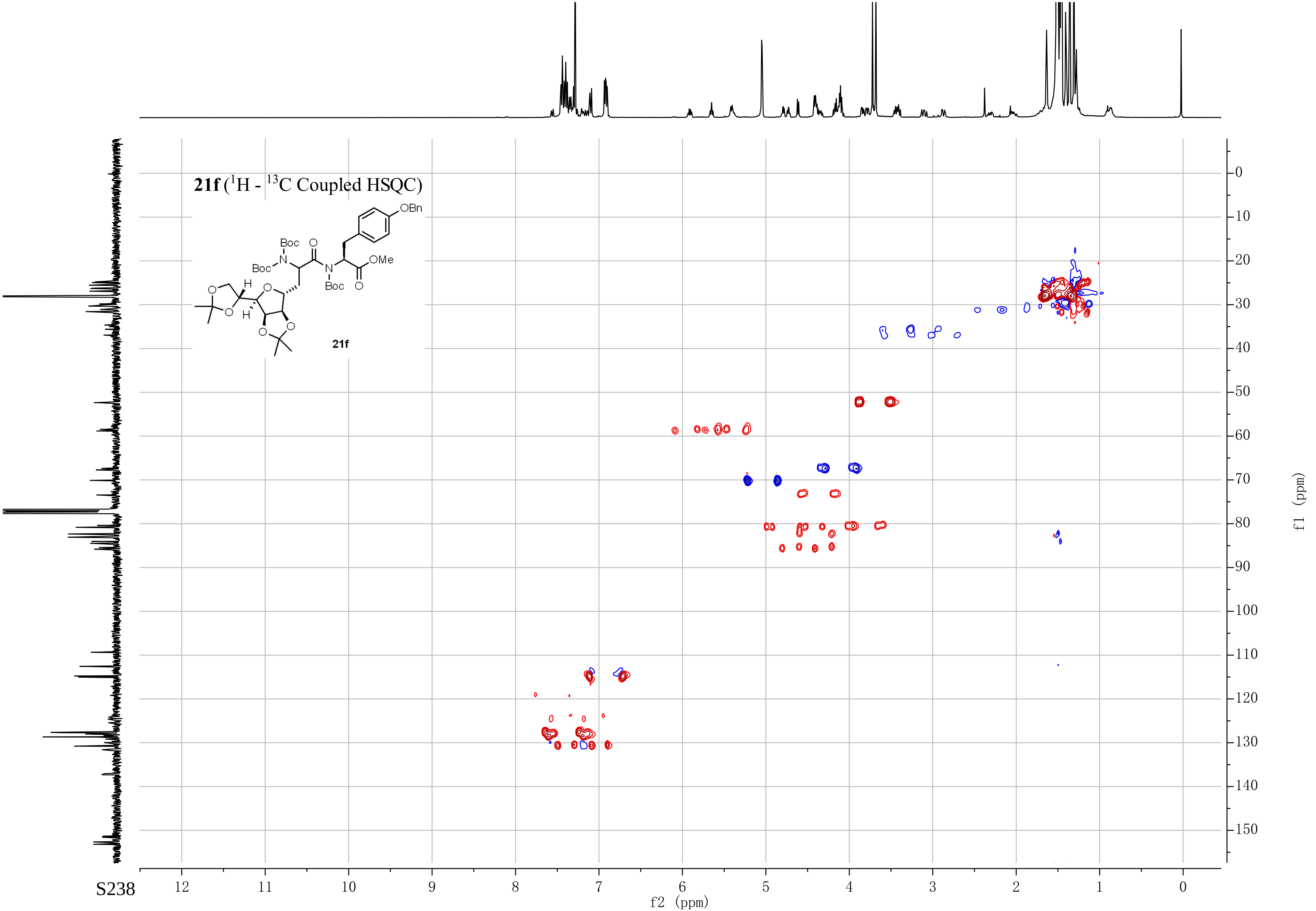
21f (^{13}C NMR, 101MHz, $CDCl_3$)



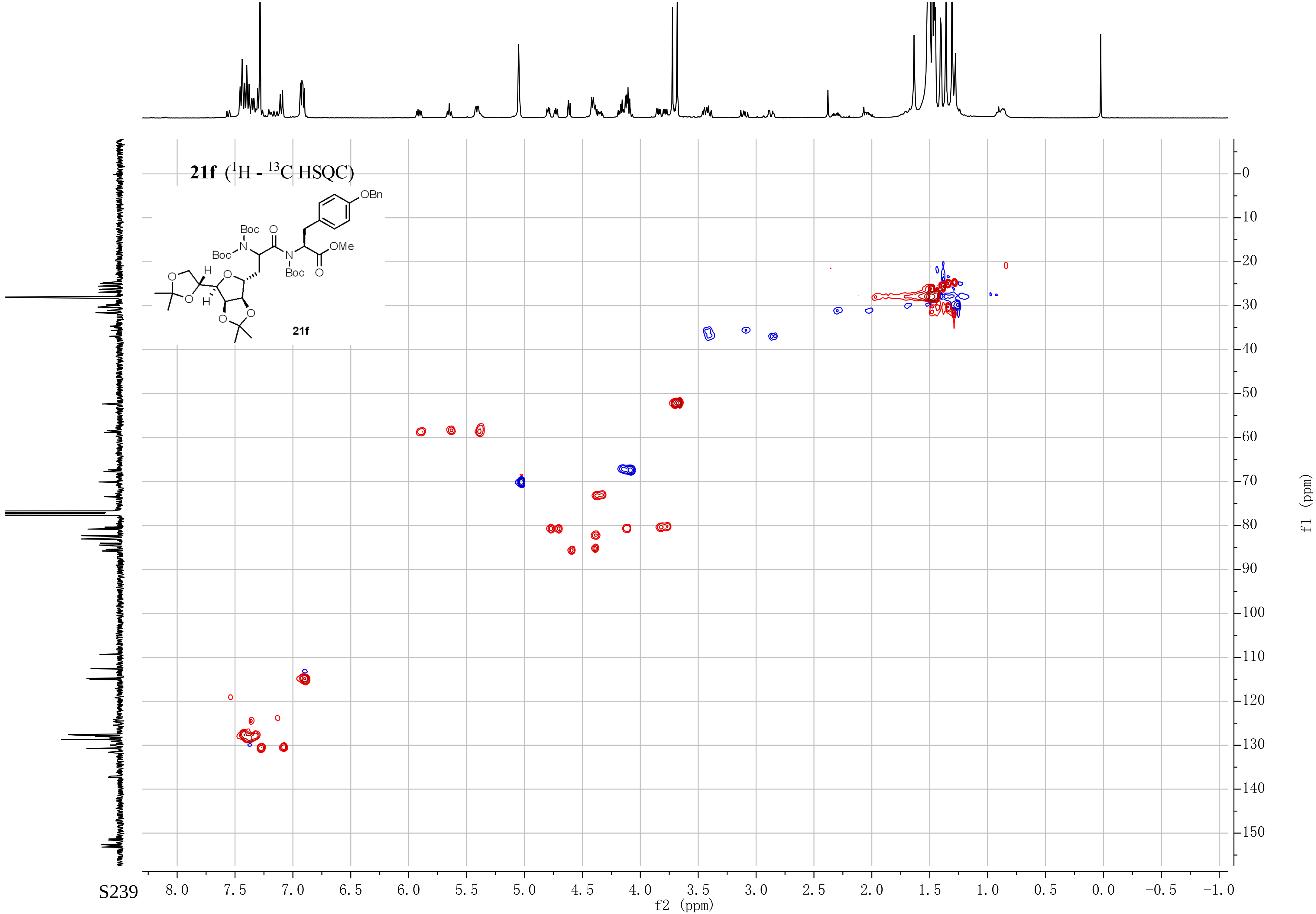
21f



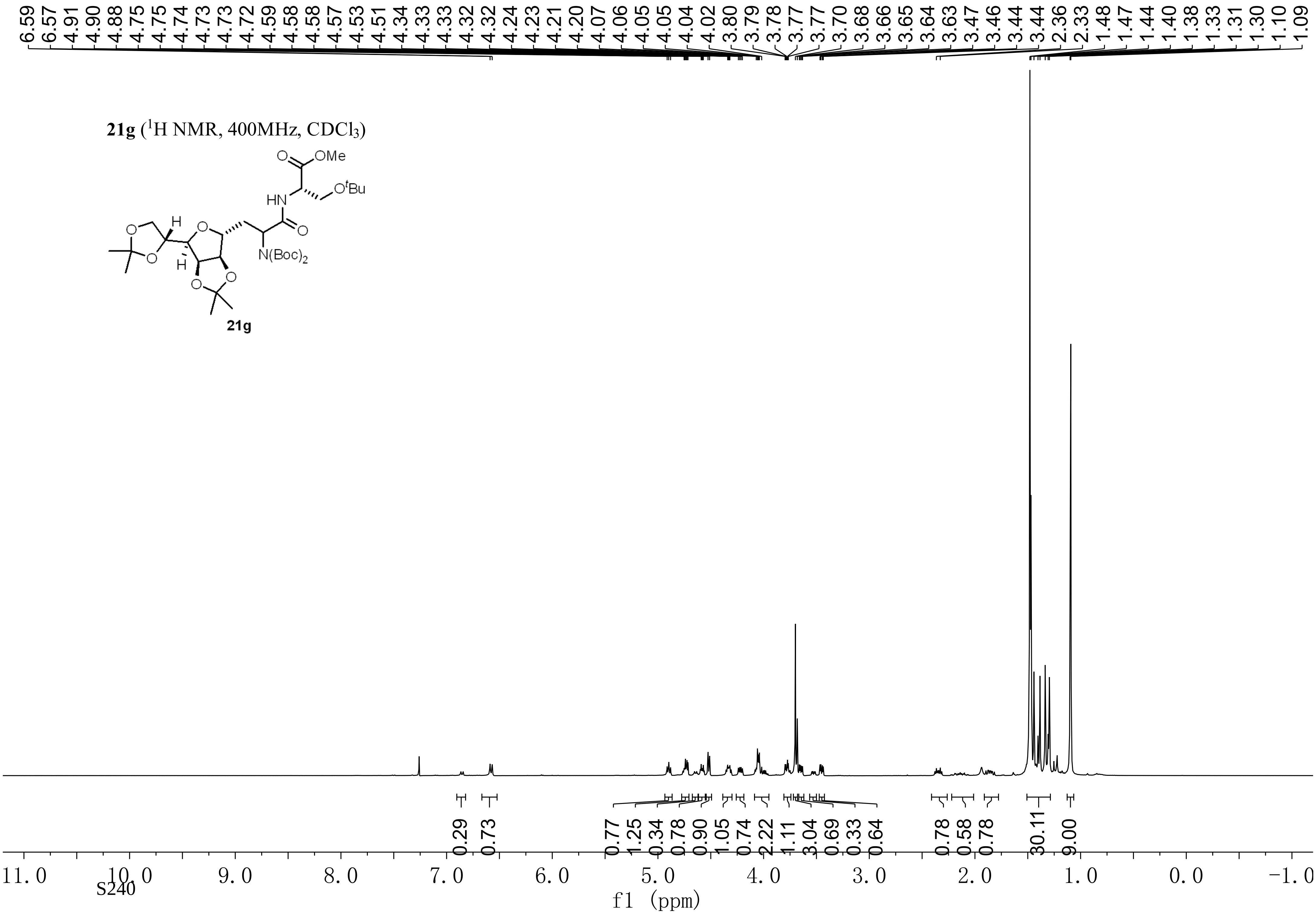

21f (1H - 1H COSY)
OBn
Boc
O
Boc
N
N
OMe
Boc
O
H
O
O
O
H
O
O
21f
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8



21f (¹H - ¹³C Coupled HSQC)
OBn
Boc
O
N
OMe
H
21f
f2 (ppm)
f1 (ppm)
12 11 10 9 8 7 6 5 4 3 2 1 0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150

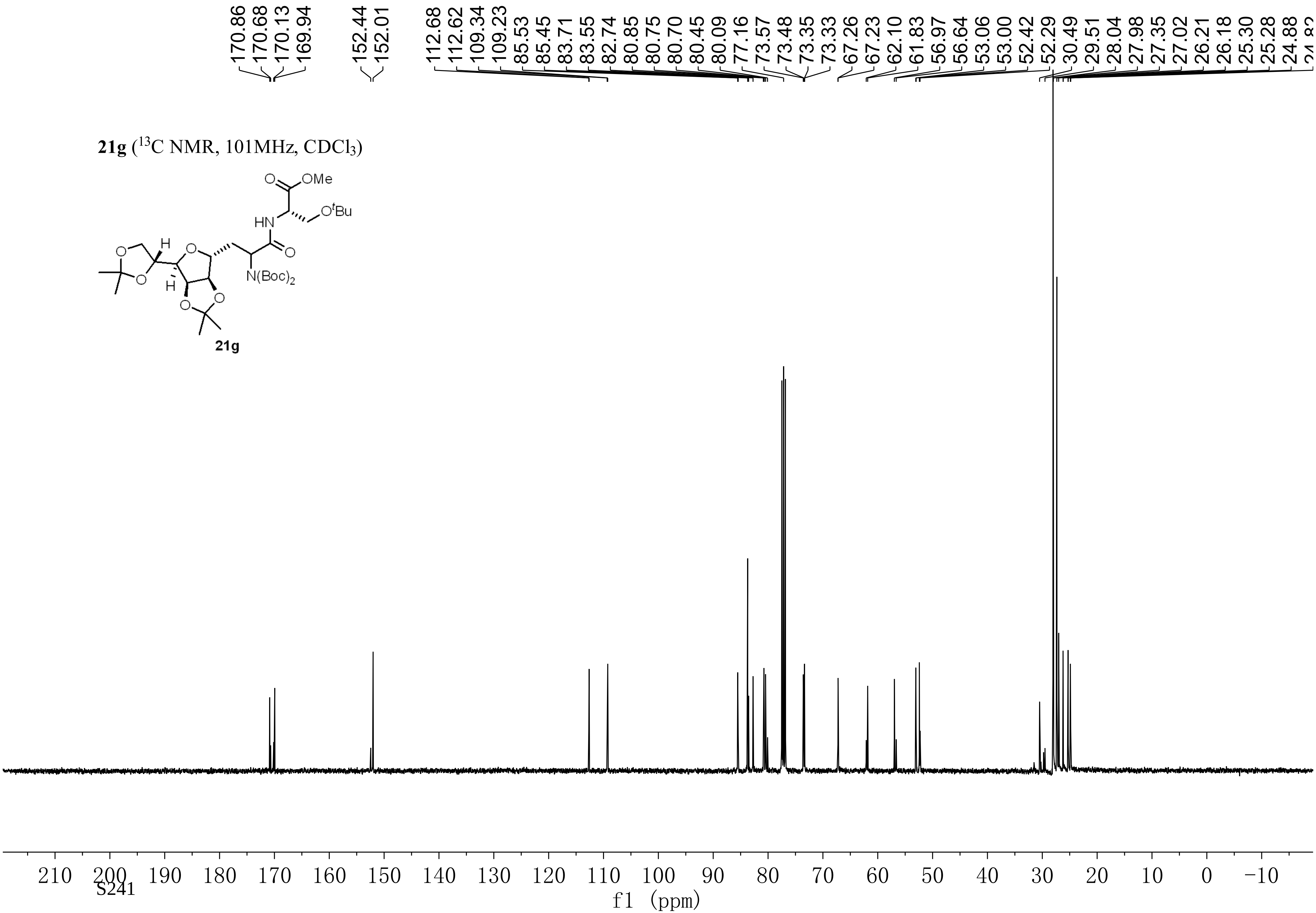


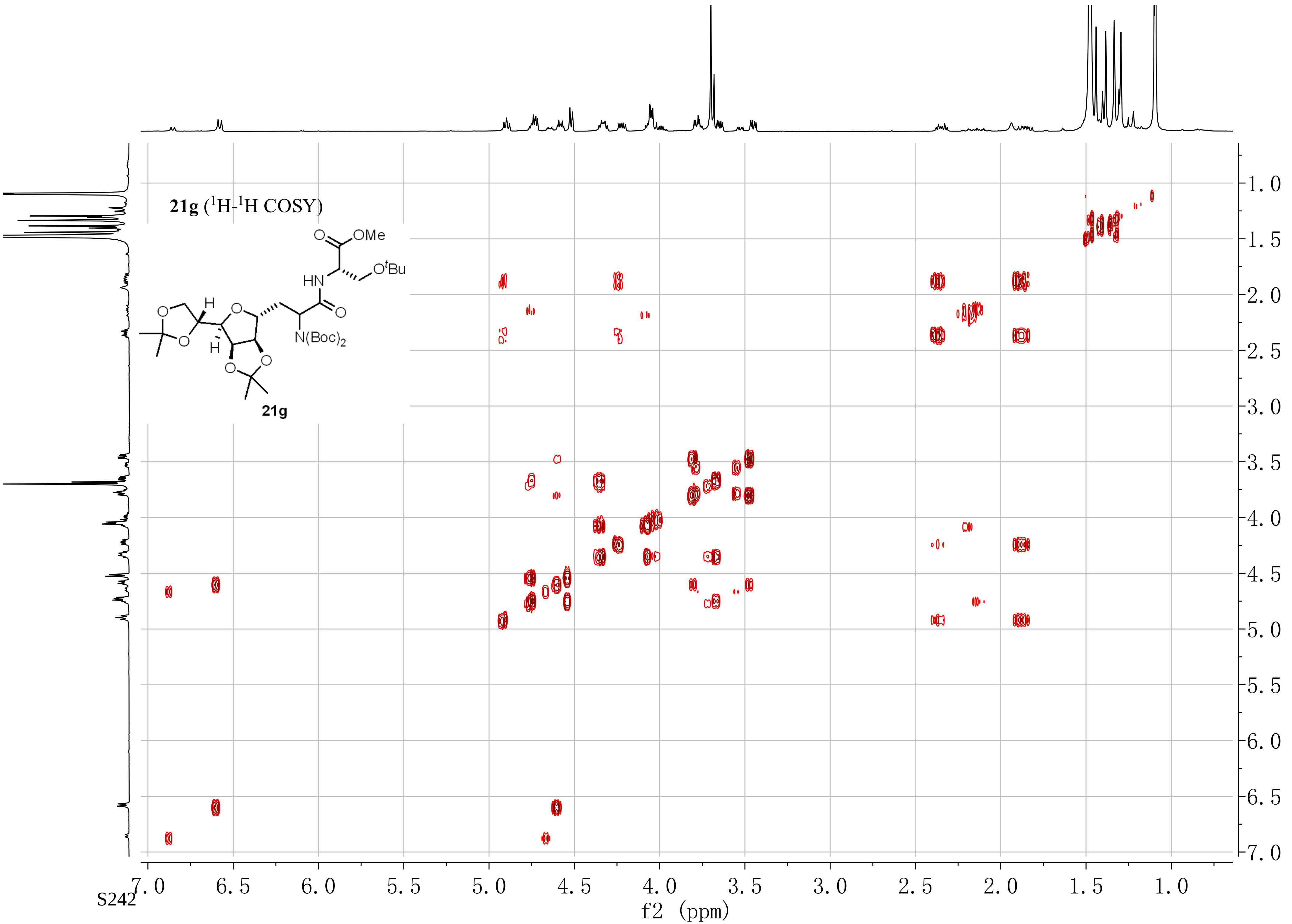
21f (1H - 13C HSQC)
OBn
Boc
O
Boc
N
N
OMe
Boc
O
H
O
O
H
O
O
21f
f2 (ppm)
f1 (ppm)



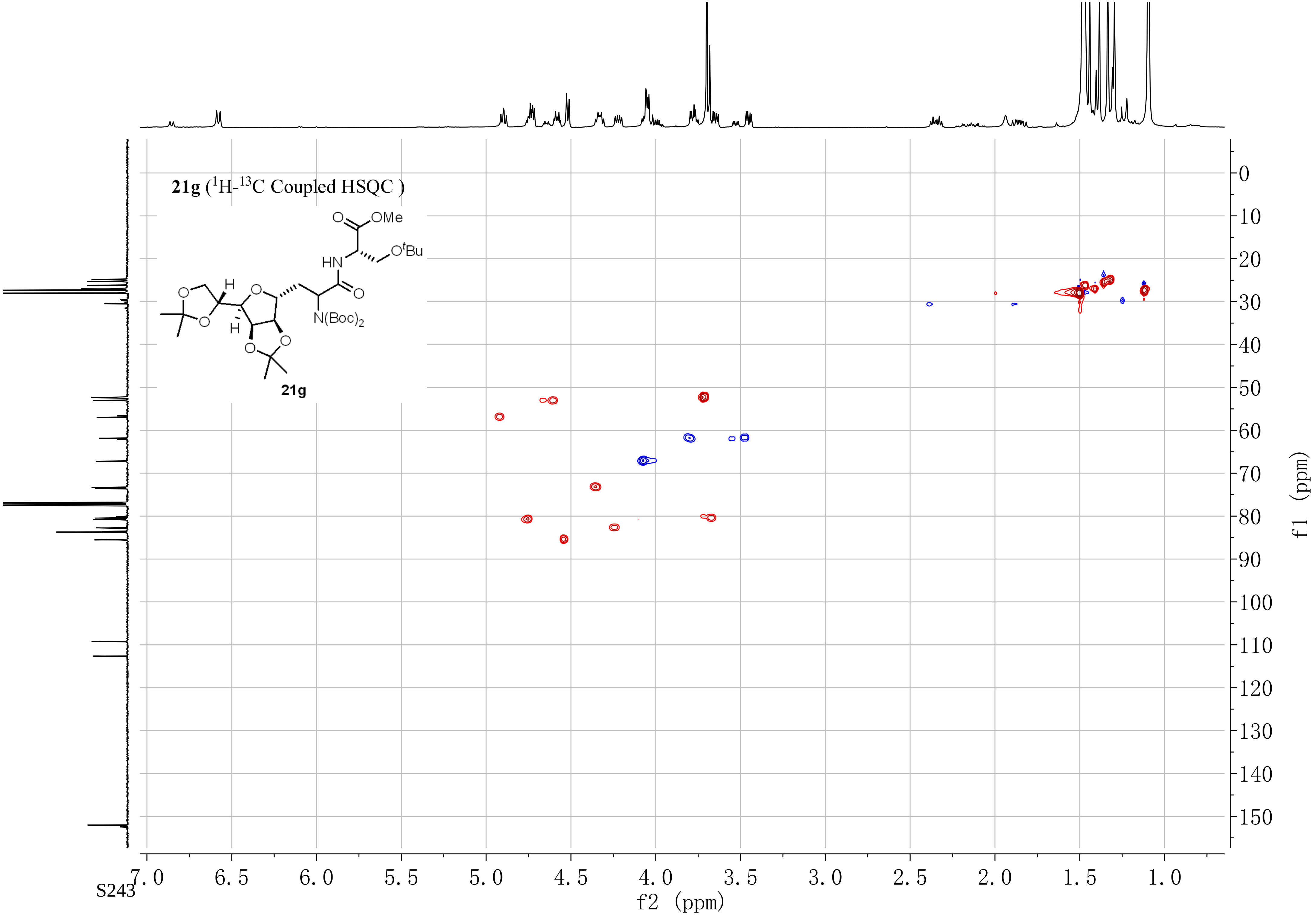
21g (^{1}H NMR, 400MHz, $CDCl_3$)
6.59 6.57 4.91 4.90 4.88 4.75 4.75 4.74 4.73 4.73 4.72 4.59 4.58 4.58 4.57 4.53 4.51 4.34 4.33 4.33 4.32 4.32 4.24 4.23 4.21 4.20 4.07 4.06 4.05 4.05 4.04 4.02 3.80 3.79 3.78 3.77 3.77 3.70 3.68 3.66 3.65 3.64 3.63 3.47 3.46 3.44 3.44 2.36 2.33 1.48 1.47 1.44 1.40 1.38 1.33 1.31 1.30 1.10 1.09
OMe
O
O^{t}Bu
HN
H
O
O
N(Boc)$_2$
H
21g
0.29 0.73 0.77 1.25 0.34 0.78 0.90 1.05 0.74 2.22 1.11 3.04 0.69 0.33 0.64 0.78 0.58 0.78 30.11 9.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

21g (^{13}C NMR, 101MHz, $CDCl_3$)

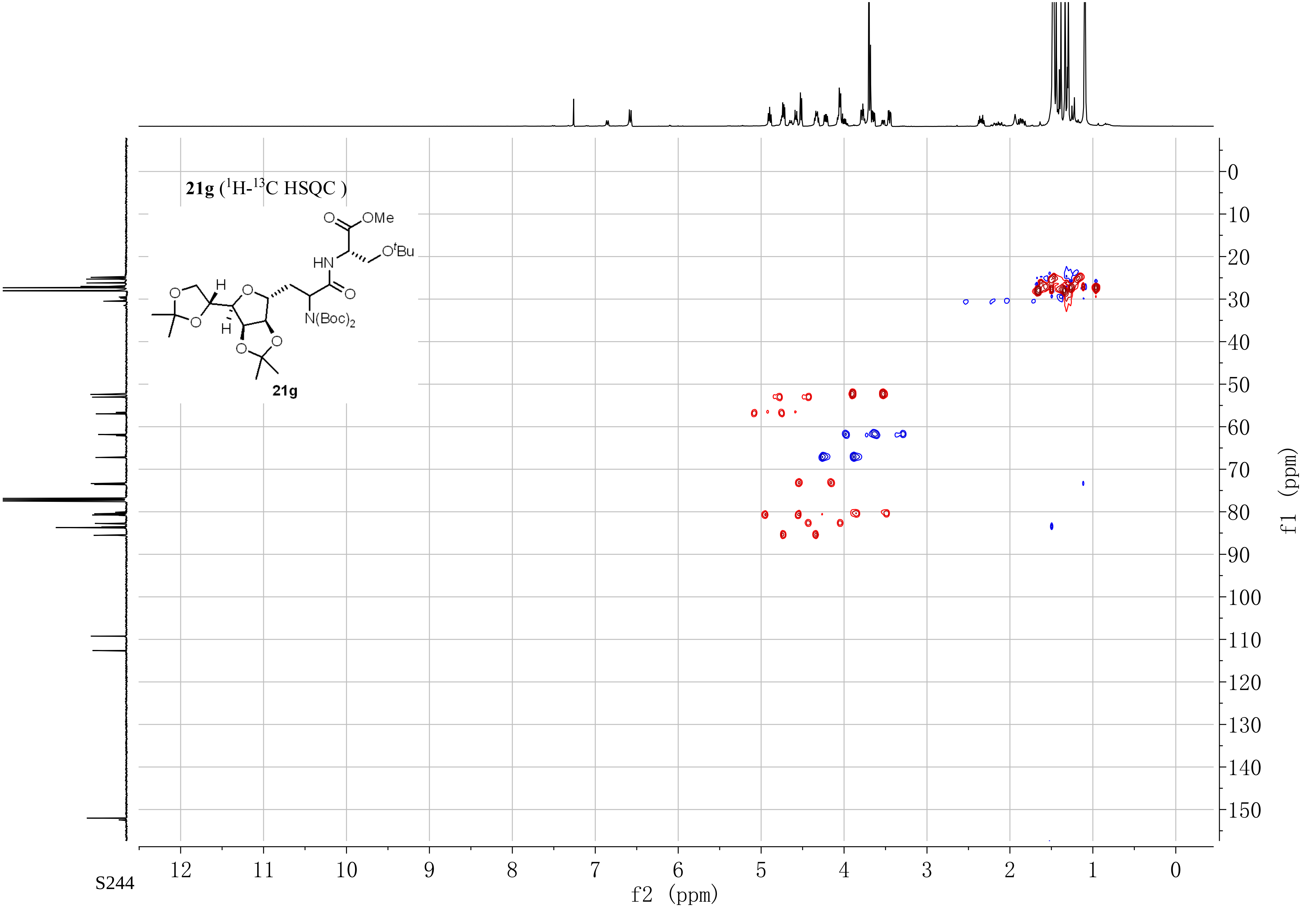


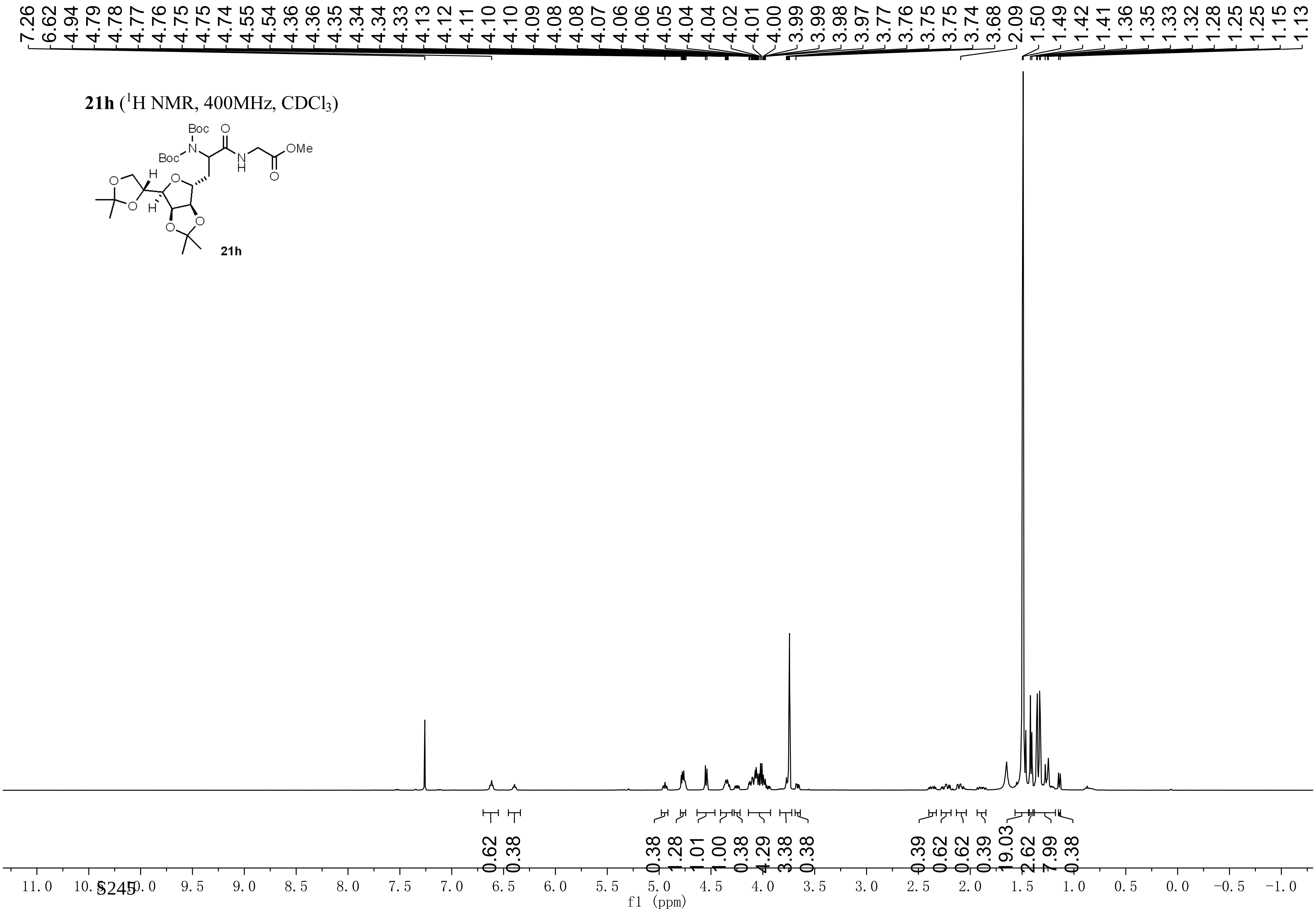


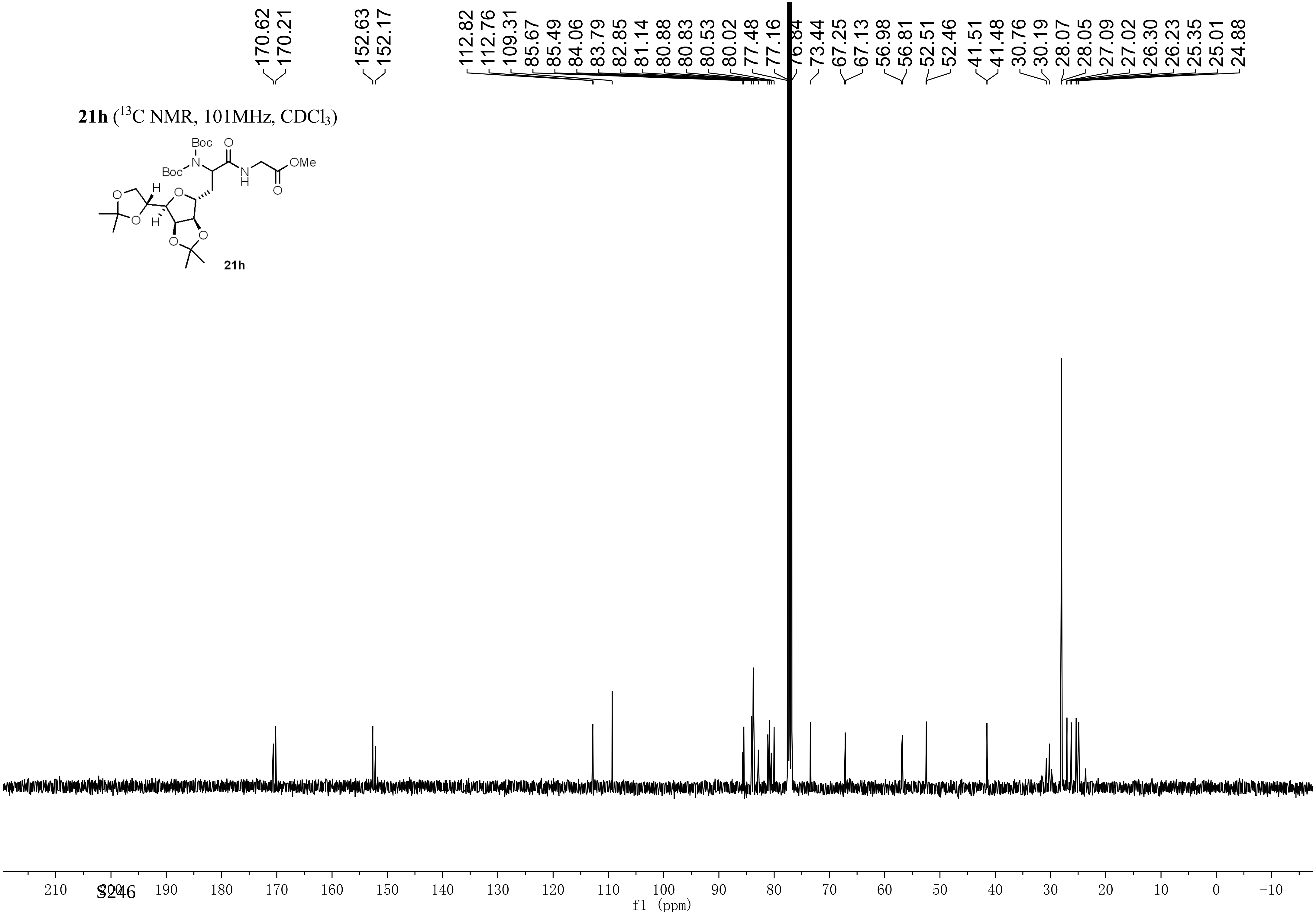
21g (^{1}H-^{1}H COSY)
OMe
O^{t}Bu
HN
H
O
N(Boc)$_2$
21g
f2 (ppm)
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

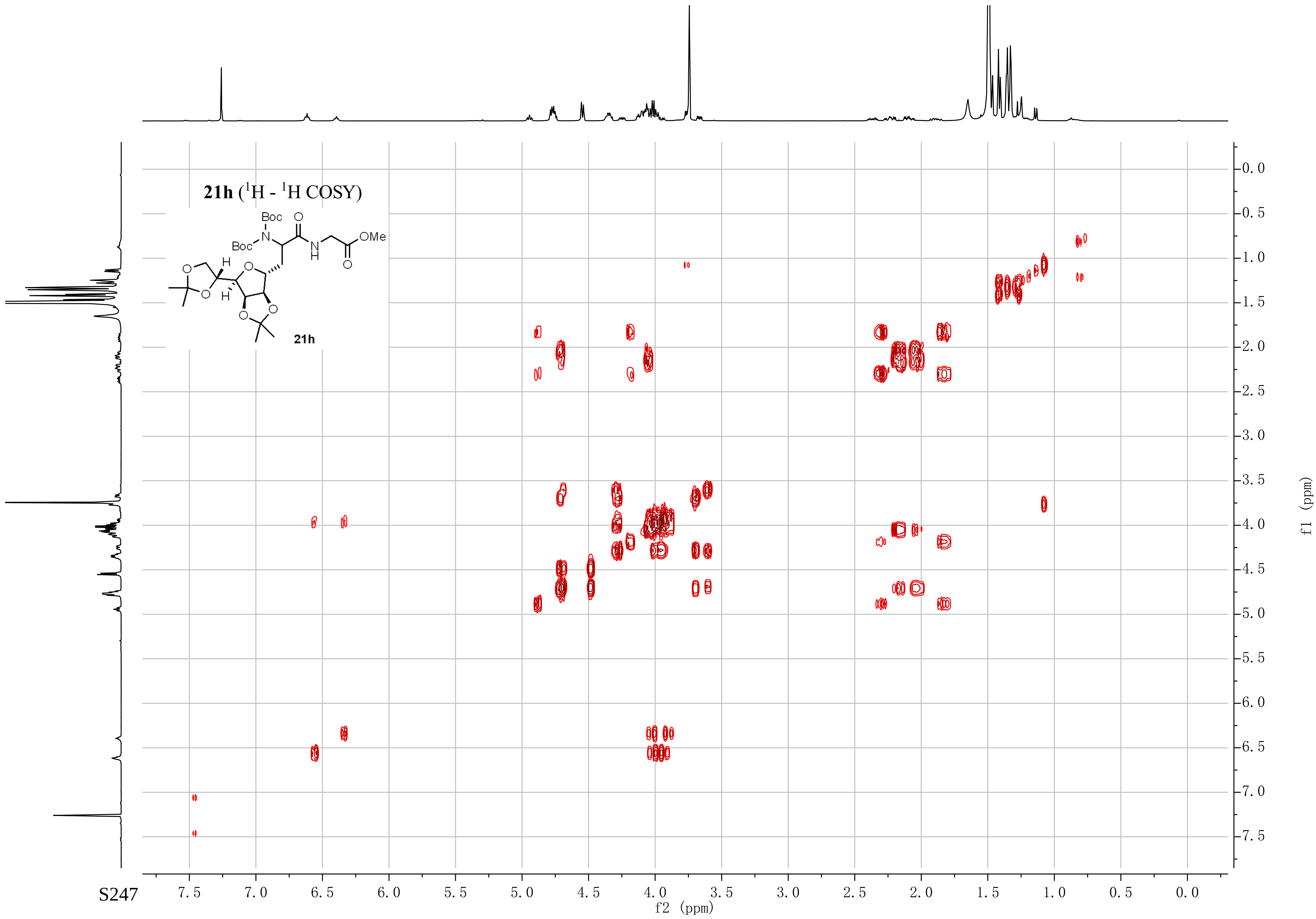


21g (^{1}H-^{13}C Coupled HSQC)
OMe
O^{t}Bu
HN
N(Boc)$_2$
21g
f2 (ppm)
f1 (ppm)

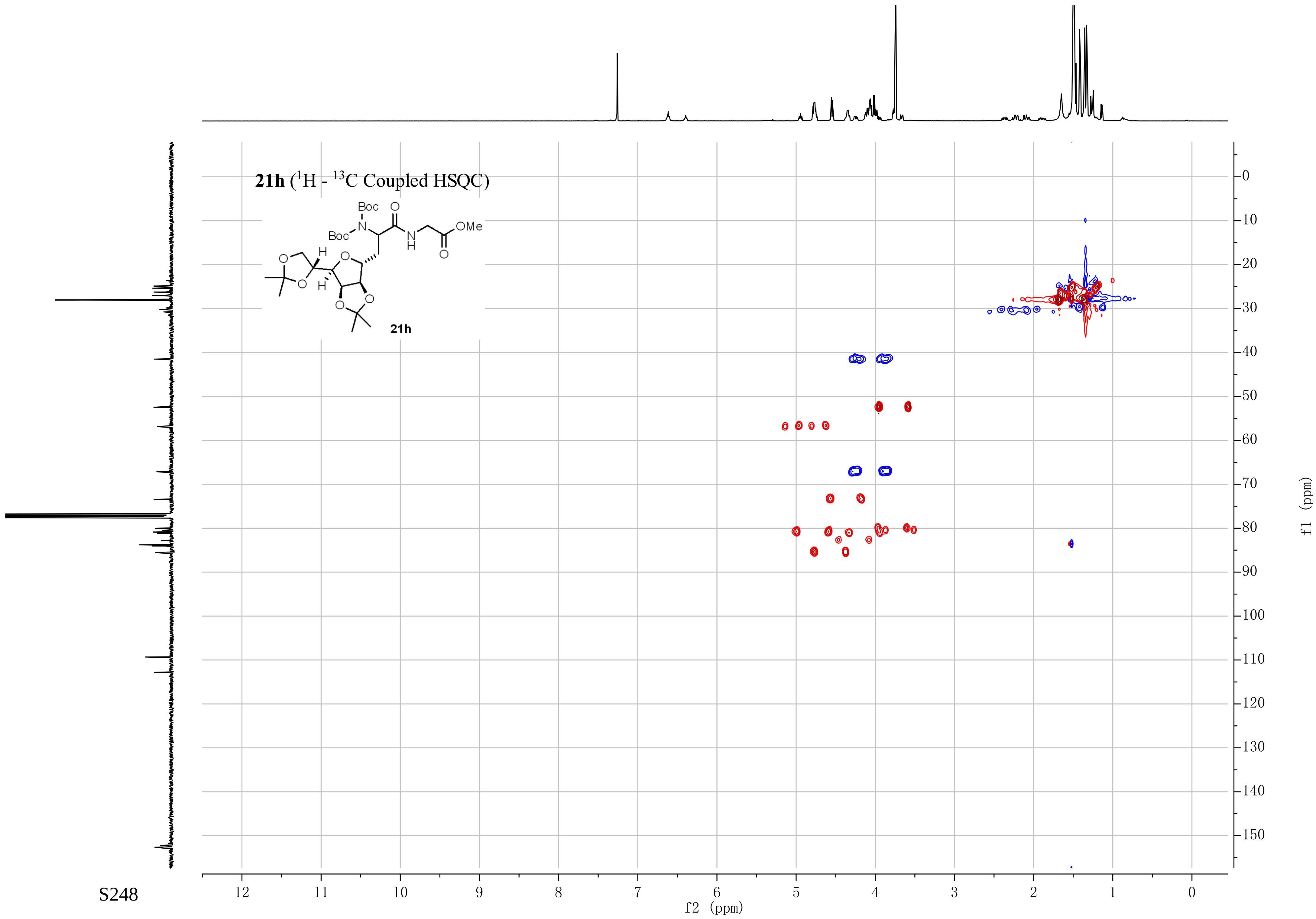

21g (1H-13C HSQC)
OMe
O
HN
O'Bu
H
N(Boc)2
21g
f2 (ppm)
f1 (ppm)
12 11 10 9 8 7 6 5 4 3 2 1 0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150


21h (^{1}H NMR, 400MHz, $CDCl_3$)
Boc
Boc
N
O
OMe
N
H
O
H
O
O
O
H
O
O
21h
7.26 6.62 4.94 4.79 4.78 4.77 4.76 4.75 4.75 4.74 4.55 4.54 4.36 4.36 4.35 4.34 4.34 4.33 4.13 4.12 4.11 4.10 4.10 4.09 4.08 4.08 4.07 4.06 4.06 4.05 4.04 4.04 4.02 4.01 4.00 3.99 3.99 3.98 3.97 3.77 3.76 3.75 3.75 3.74 3.68 2.09 1.50 1.49 1.42 1.41 1.36 1.35 1.33 1.32 1.28 1.25 1.25 1.15 1.13
0.62 0.38 0.38 1.28 1.01 1.00 0.38 4.29 3.38 0.38 0.39 0.62 0.62 0.39 19.03 2.62 7.99 0.38
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)

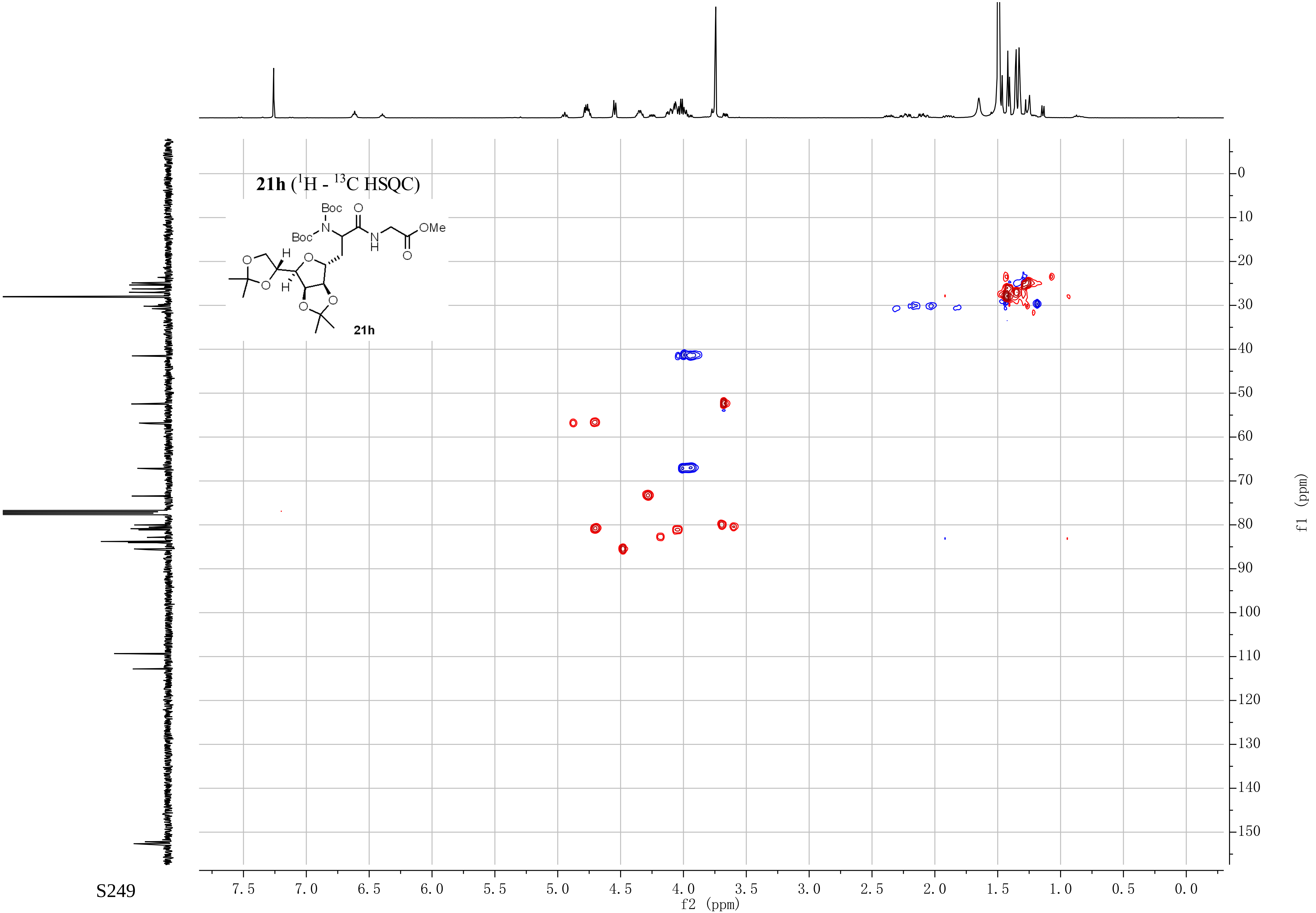

170.62
170.21
152.63
152.17
112.82
112.76
109.31
85.67
85.49
84.06
83.79
82.85
81.14
80.88
80.83
80.53
80.02
77.48
77.16
76.84
73.44
67.25
67.13
56.98
56.81
52.51
52.46
41.51
41.48
30.76
30.19
28.07
28.05
27.09
27.02
26.30
26.23
25.35
25.01
24.88
21h (^{13}C NMR, 101MHz, $CDCl_3$)
Boc
Boc
N
O
N
H
OMe
O
O
O
O
O
O
H
H
21h
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)

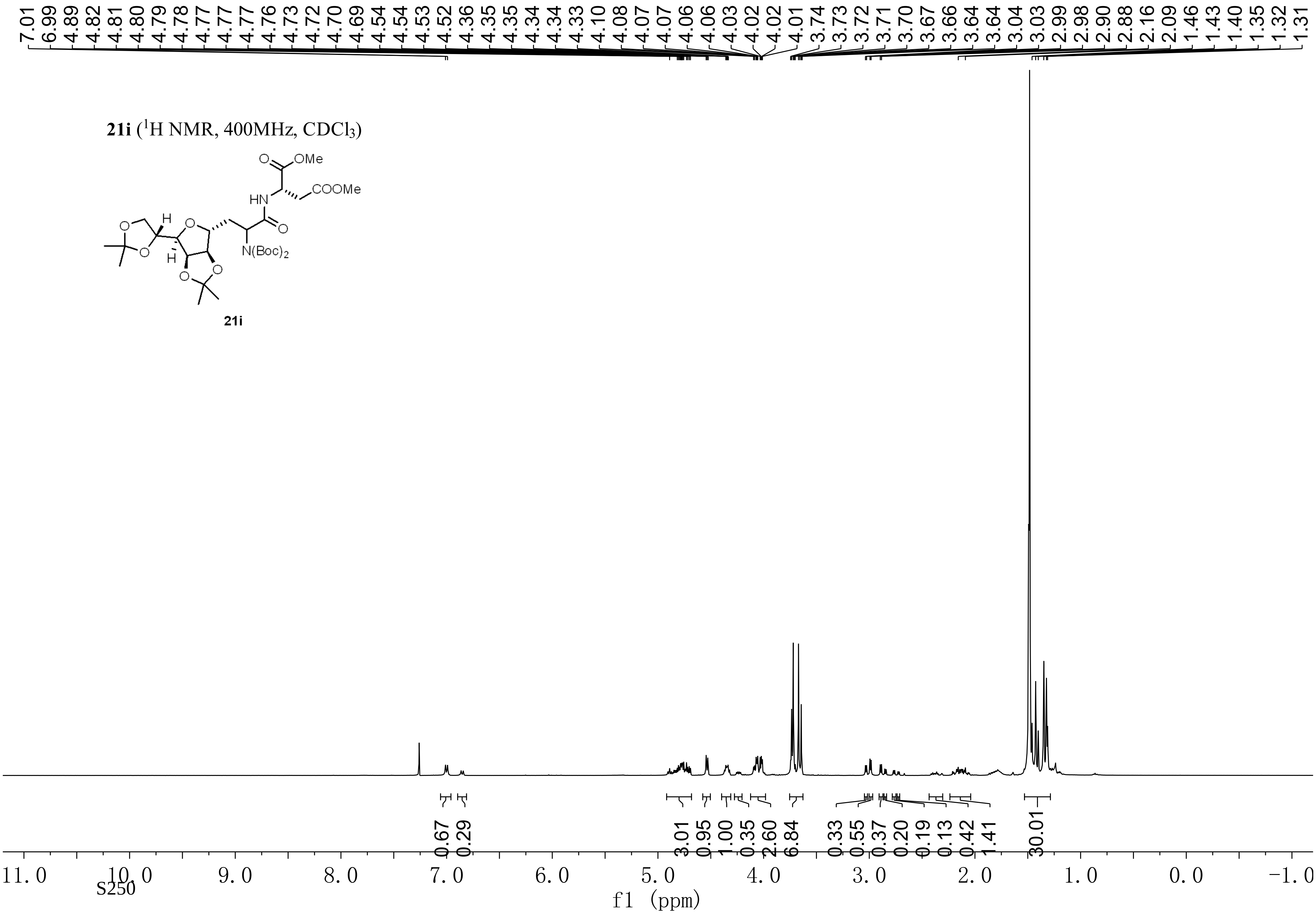


21h (^{1}H - ^{1}H COSY)
Boc
Boc
N
O
N
H
OMe
O
H
O
O
O
H
O
O
21h
f2 (ppm)
f1 (ppm)

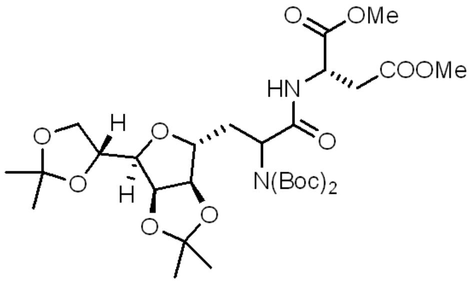


21h (¹H - ¹³C Coupled HSQC)
Boc
Boc
N
O
N
H
OMe
O
O
O
H
H
O
O
O
21h
f2 (ppm)
f1 (ppm)

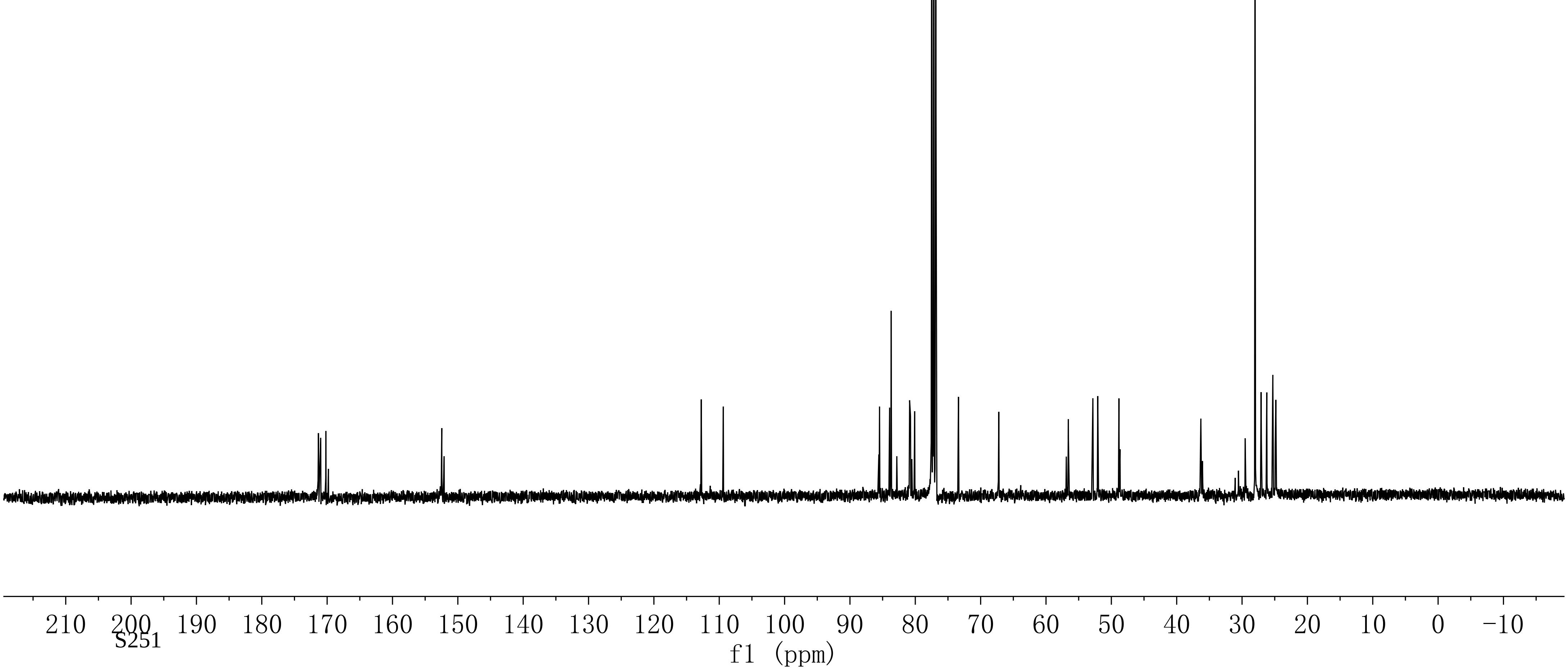

21h (1H - 13C HSQC)
Boc
Boc
N
O
N
H
OMe
O
O
O
H
O
H
O
O
21h
f1 (ppm)
f2 (ppm)

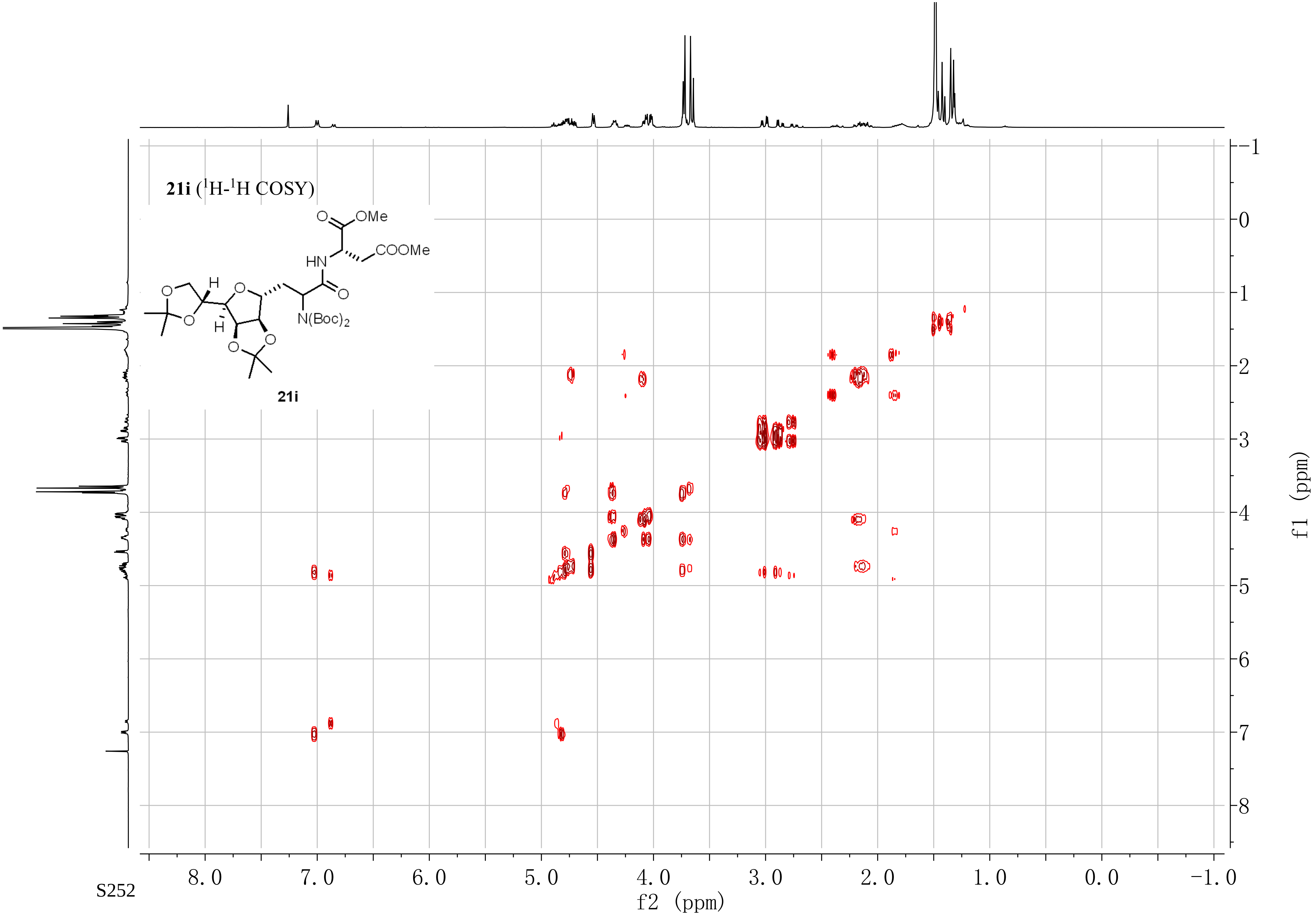

7.01 6.99 4.89 4.82 4.81 4.80 4.79 4.78 4.77 4.77 4.77 4.76 4.73 4.72 4.70 4.69 4.54 4.54 4.53 4.52 4.36 4.35 4.35 4.34 4.34 4.33 4.10 4.08 4.07 4.07 4.06 4.06 4.03 4.02 4.02 4.01 3.74 3.73 3.72 3.71 3.70 3.67 3.66 3.64 3.64 3.04 3.03 2.99 2.98 2.90 2.88 2.16 2.09 1.46 1.43 1.40 1.35 1.32 1.31
21i (1H NMR, 400MHz, CDCl3)
OMe
COOMe
HN
H
N(Boc)2
H
21i
0.67 0.29 3.01 0.95 1.00 0.35 2.60 6.84 0.33 0.55 0.37 0.20 0.19 0.13 0.42 1.41 30.01
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

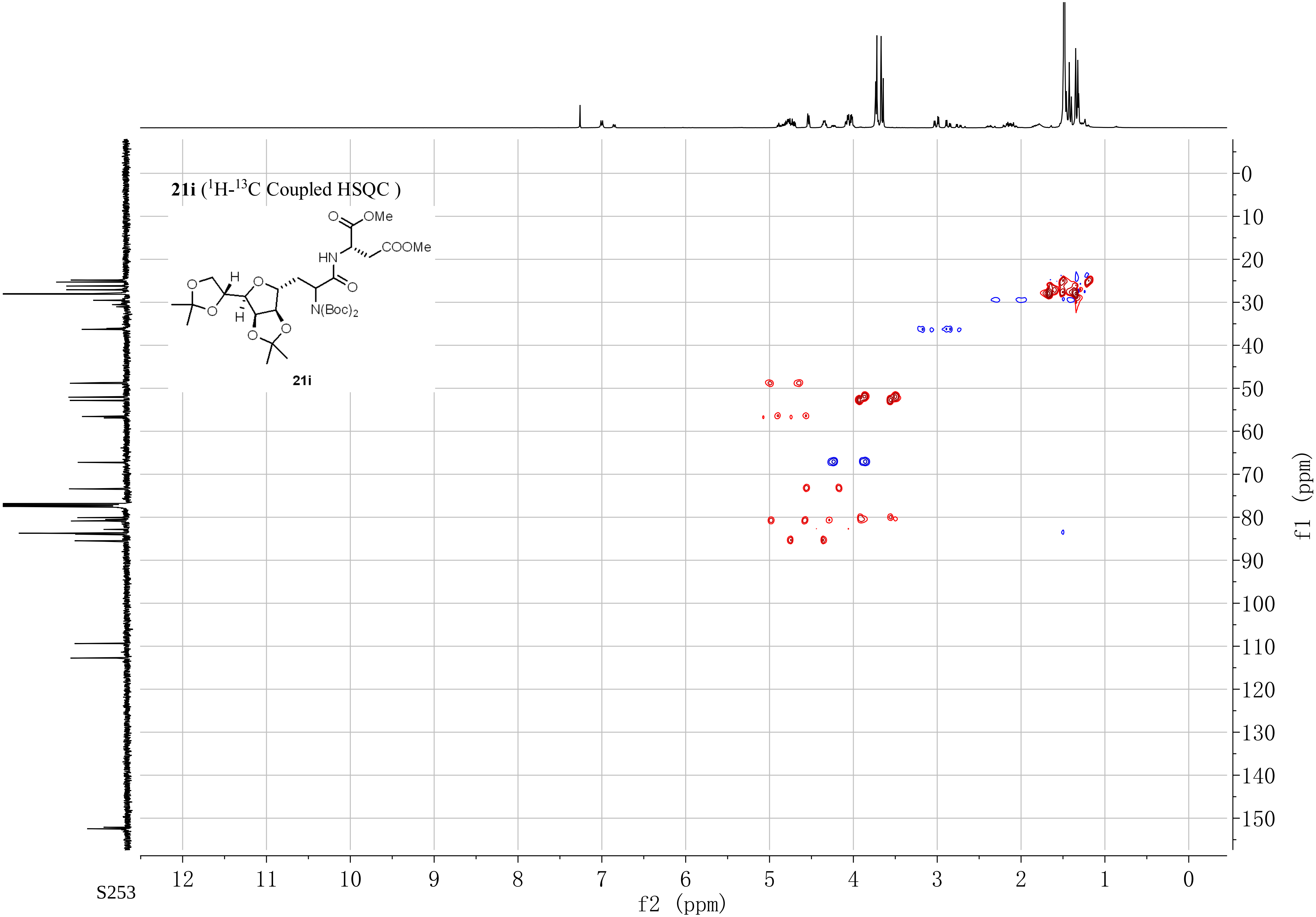
21i (^{13}C NMR, 101MHz, $CDCl_3$)

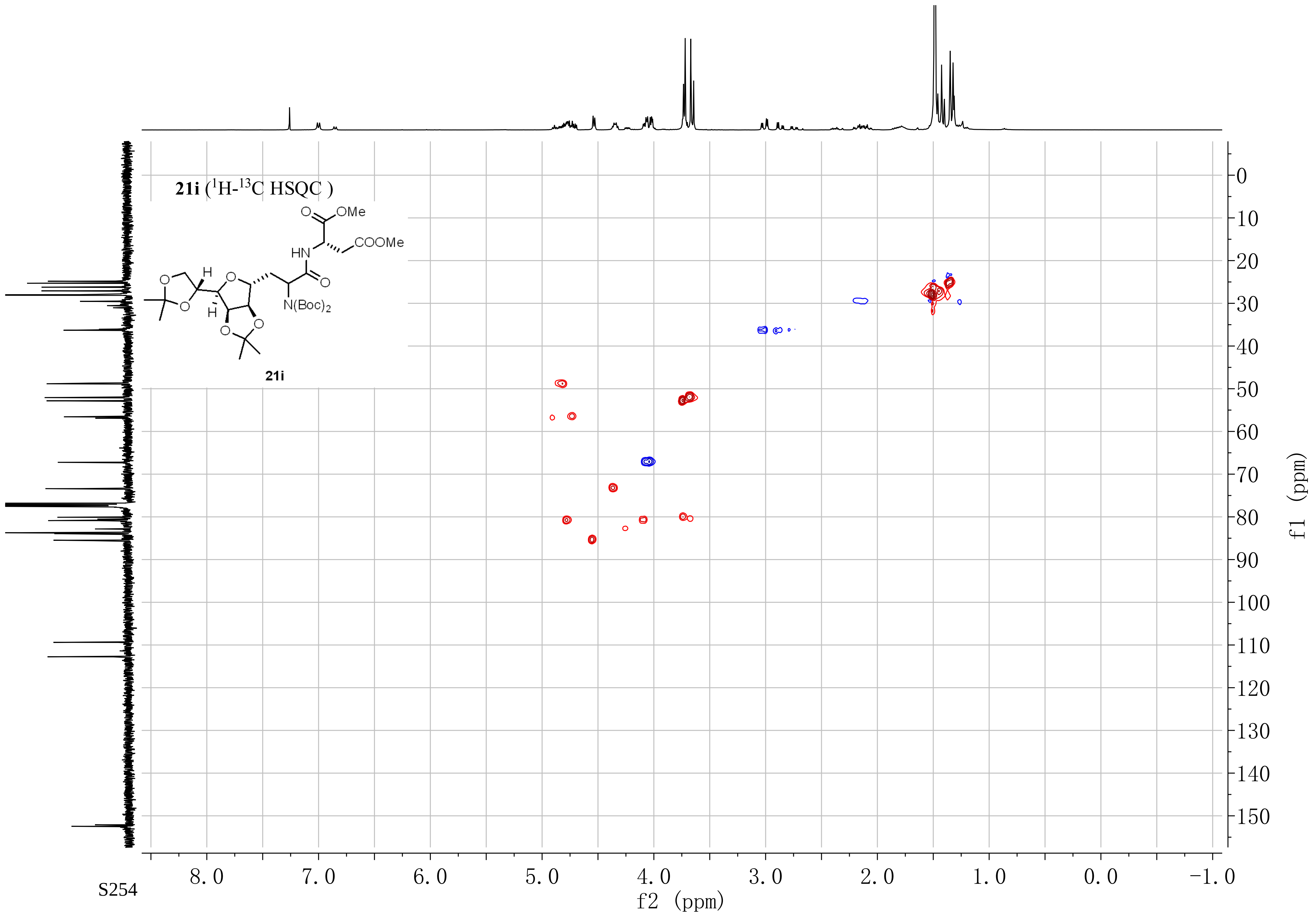


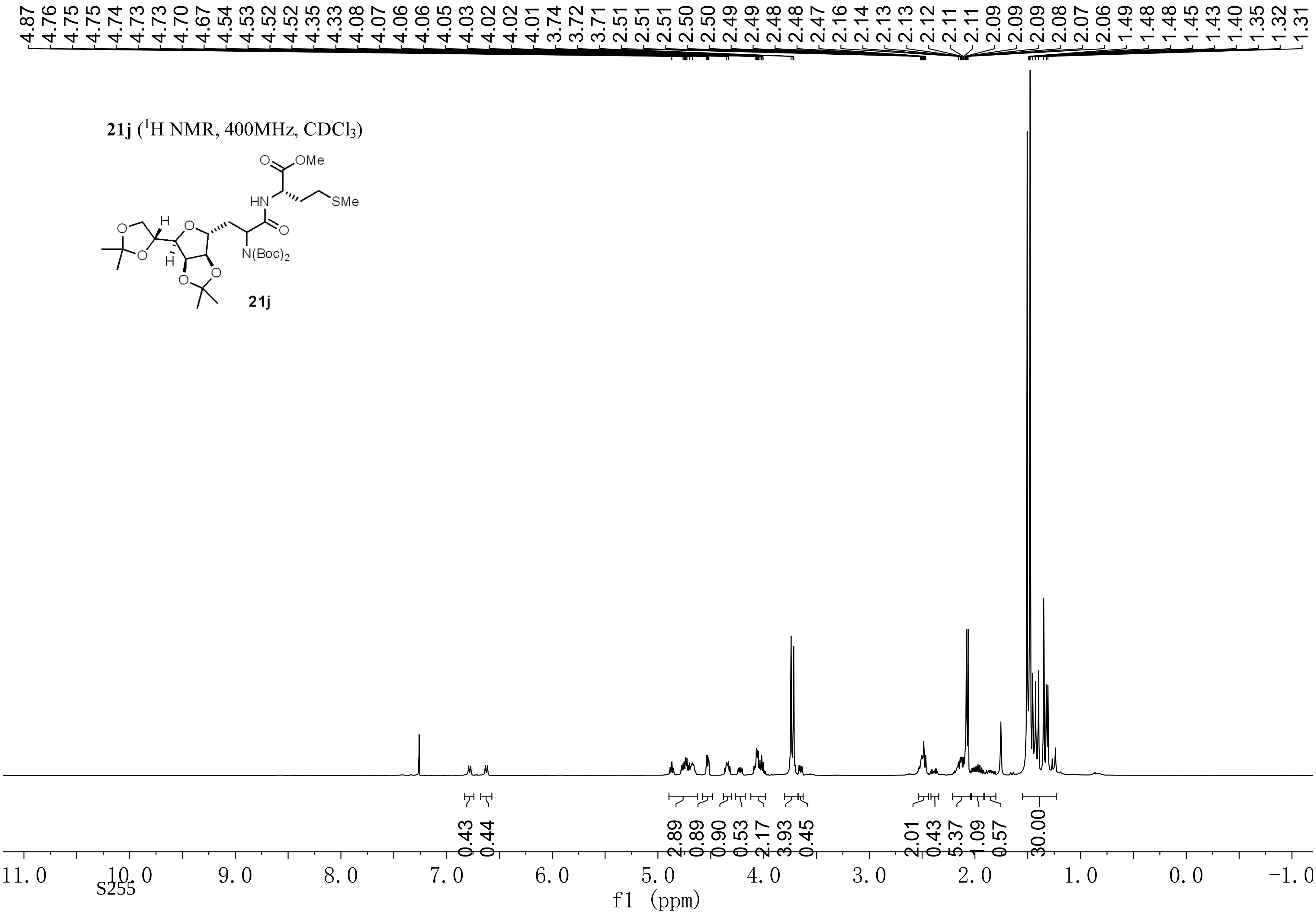
21i




21i (1H-1H COSY)
OMe
COOMe
HN
H
O
H
N(Boc)2
21i
f2 (ppm)
f1 (ppm)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-1
0
1
2
3
4
5
6
7
8

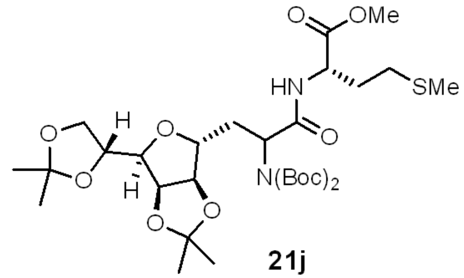

21i (1H-13C Coupled HSQC)
OMe
COOMe
HN
N(Boc)2
21i
f2 (ppm)
f1 (ppm)

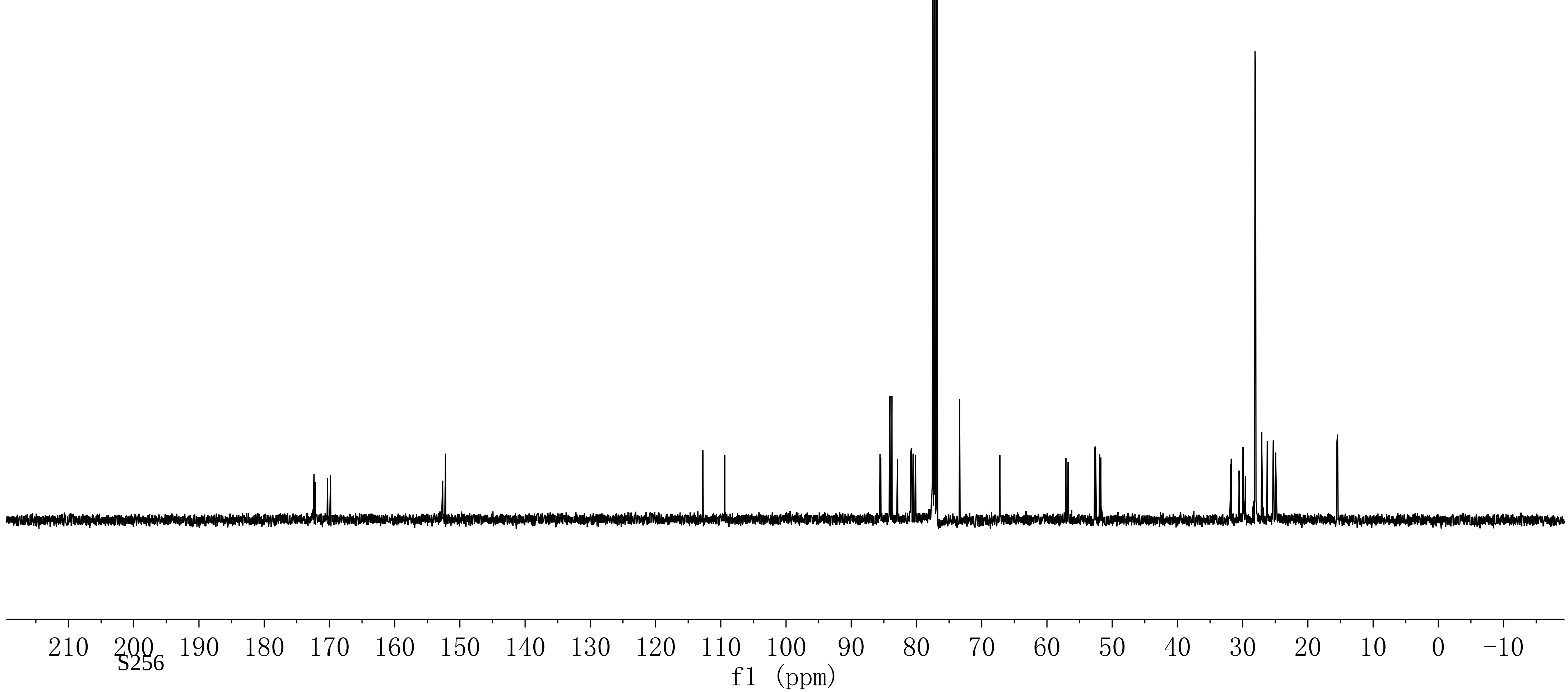

21i (1H-13C HSQC)
OMe
COOMe
HN
O
N(Boc)2
H
21i
f2 (ppm)
f1 (ppm)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

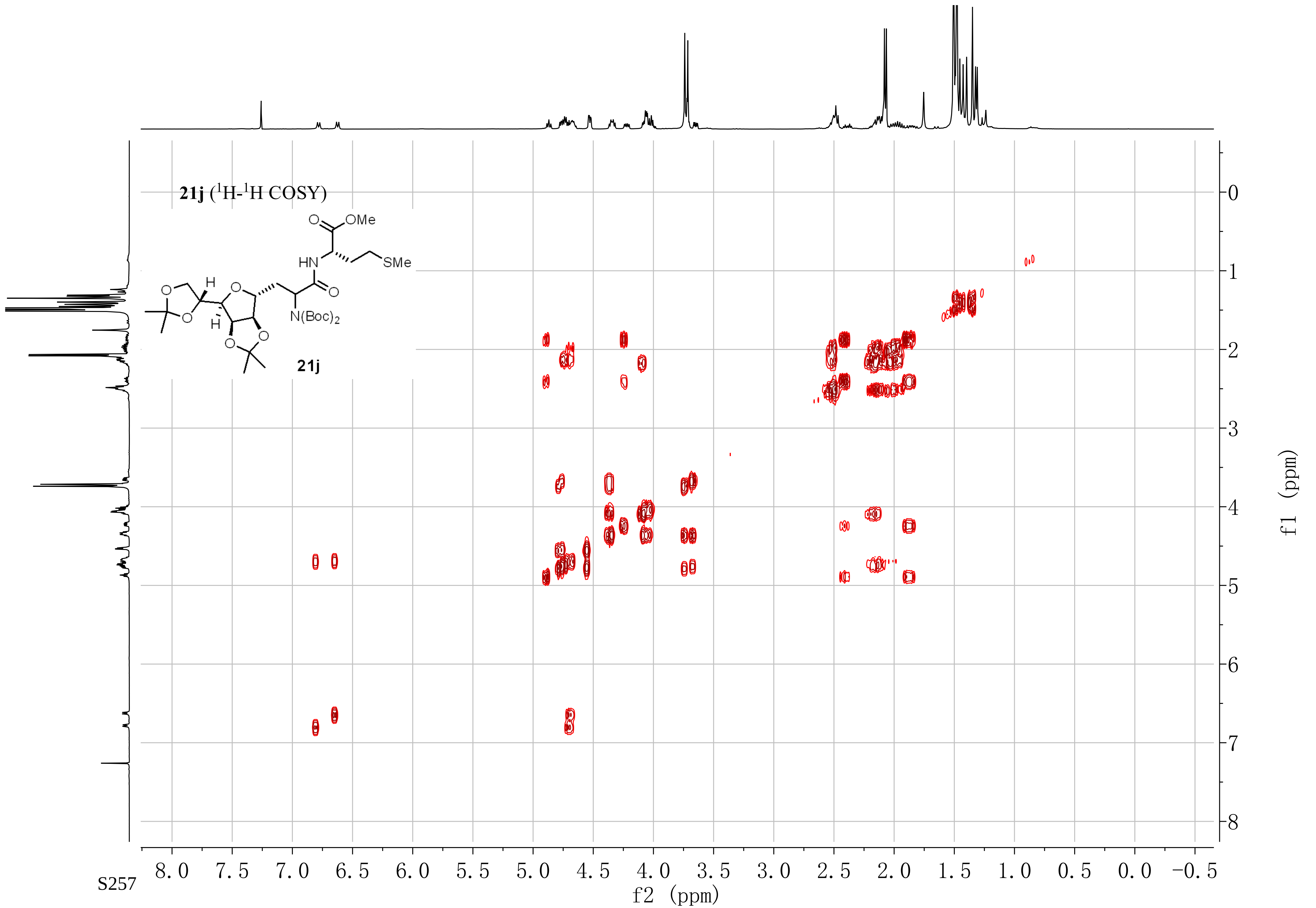


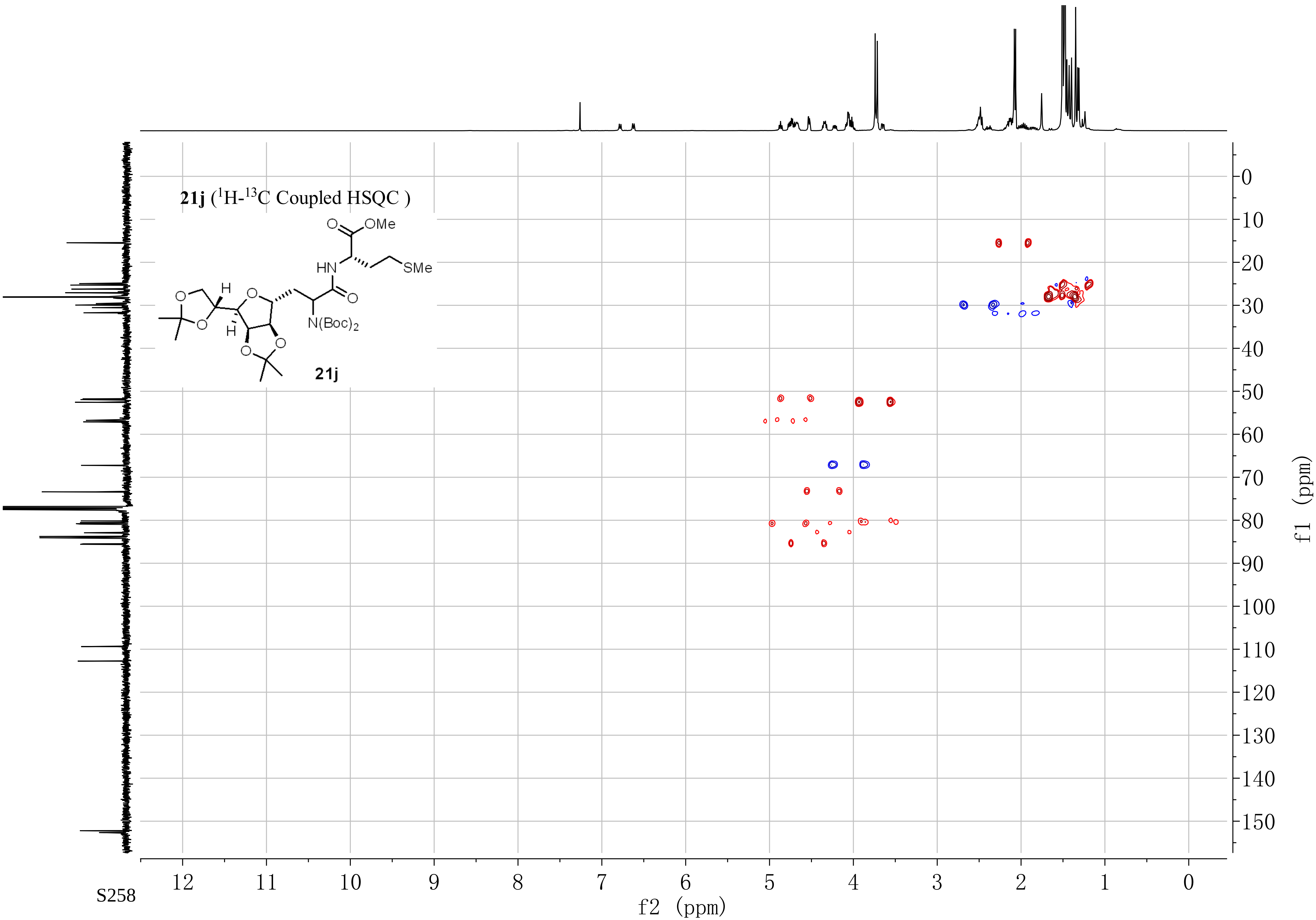
4.87 4.76 4.75 4.75 4.74 4.73 4.73 4.70 4.67 4.54 4.53 4.52 4.52 4.35 4.33 4.08 4.07 4.06 4.06 4.05 4.03 4.02 4.02 4.01 3.74 3.72 3.71 2.51 2.51 2.51 2.50 2.50 2.49 2.49 2.48 2.48 2.47 2.16 2.14 2.13 2.13 2.12 2.11 2.11 2.09 2.09 2.09 2.08 2.07 2.06 1.49 1.48 1.48 1.45 1.43 1.40 1.35 1.32 1.31
21j (^{1}H NMR, 400MHz, $CDCl_3$)
OMe
HN
SMe
H
O
N(Boc)$_2$
H
21j
0.43 0.44 2.89 0.89 0.90 0.53 2.17 3.93 0.45 2.01 0.43 5.37 1.09 0.57 30.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)

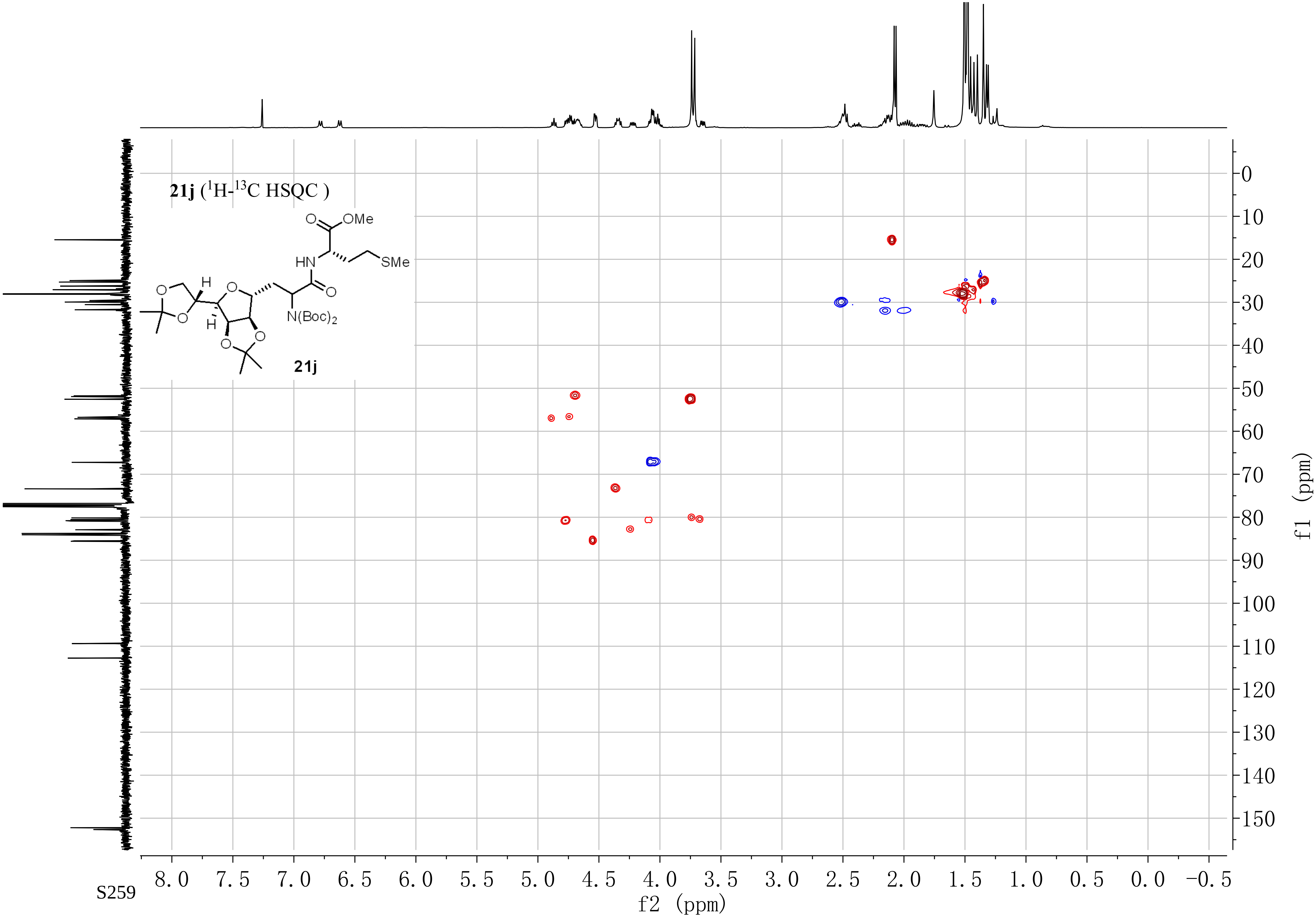
21j (^{13}C NMR, 101MHz, $CDCl_3$)





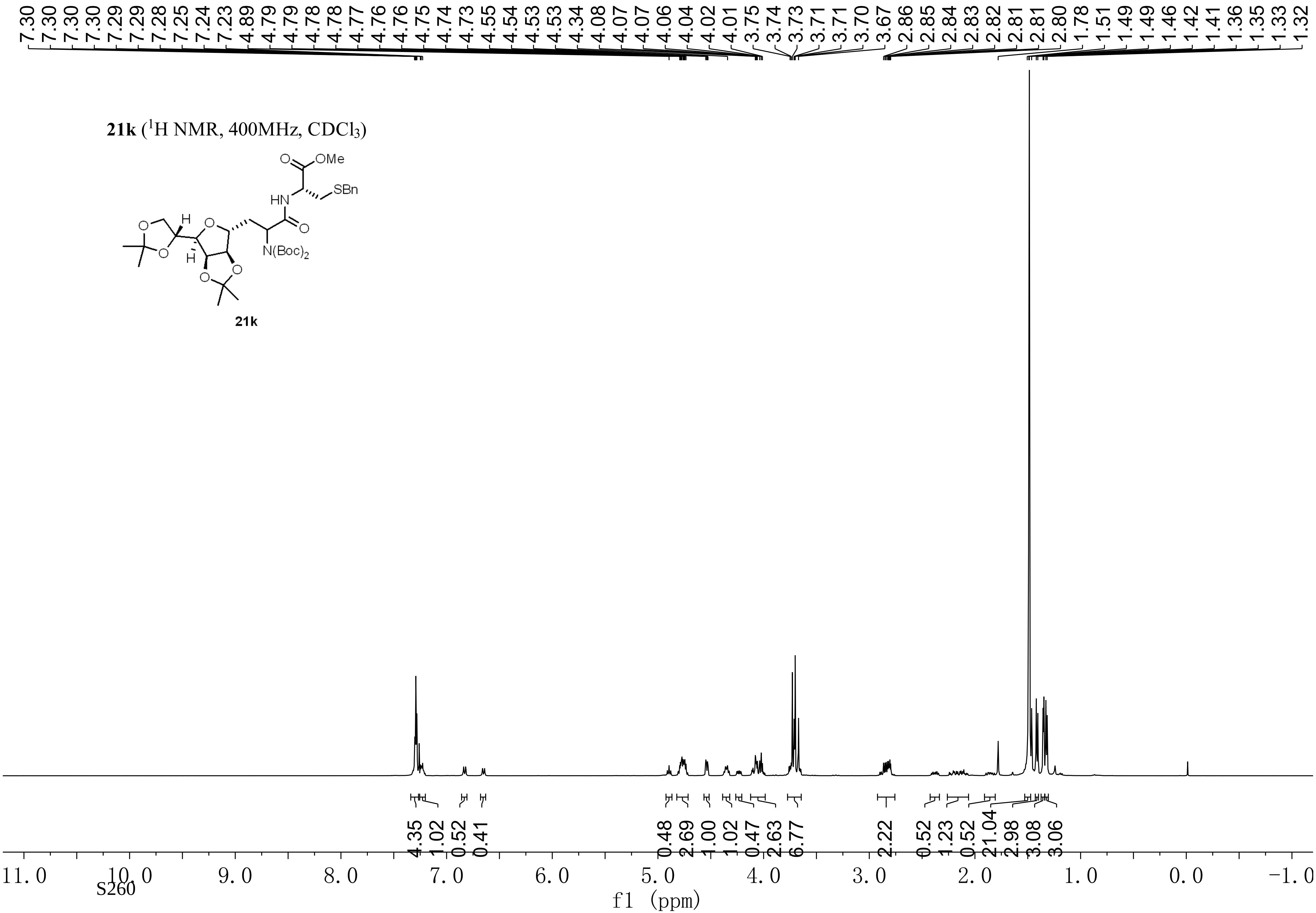

21j (^{1}H-^{1}H COSY)
OMe
HN
SMe
H
N(Boc)$_2$
H
21j
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7 8

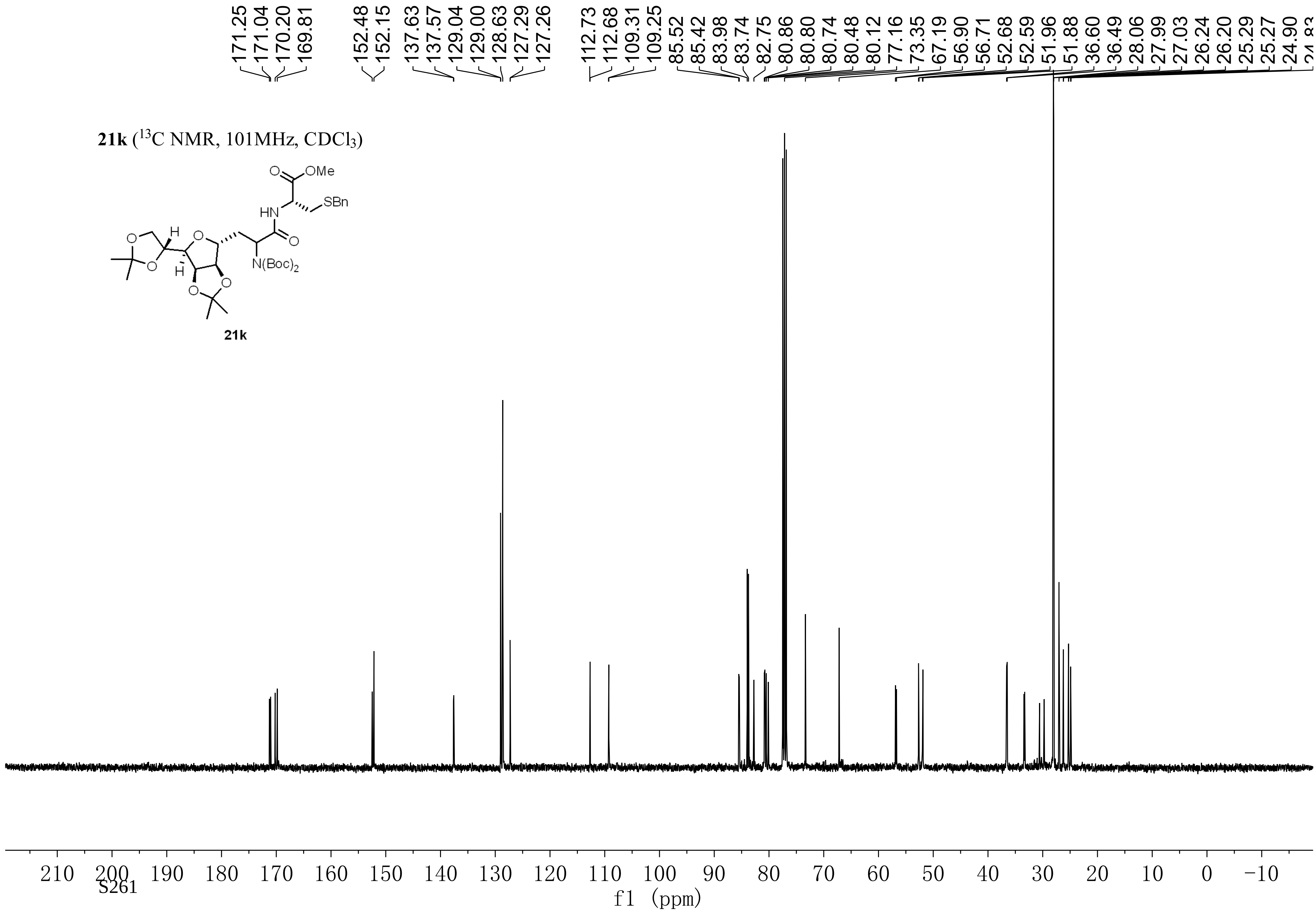

21j (1H-13C Coupled HSQC)
OMe
HN
SMe
H
N(Boc)2
21j
f2 (ppm)
f1 (ppm)

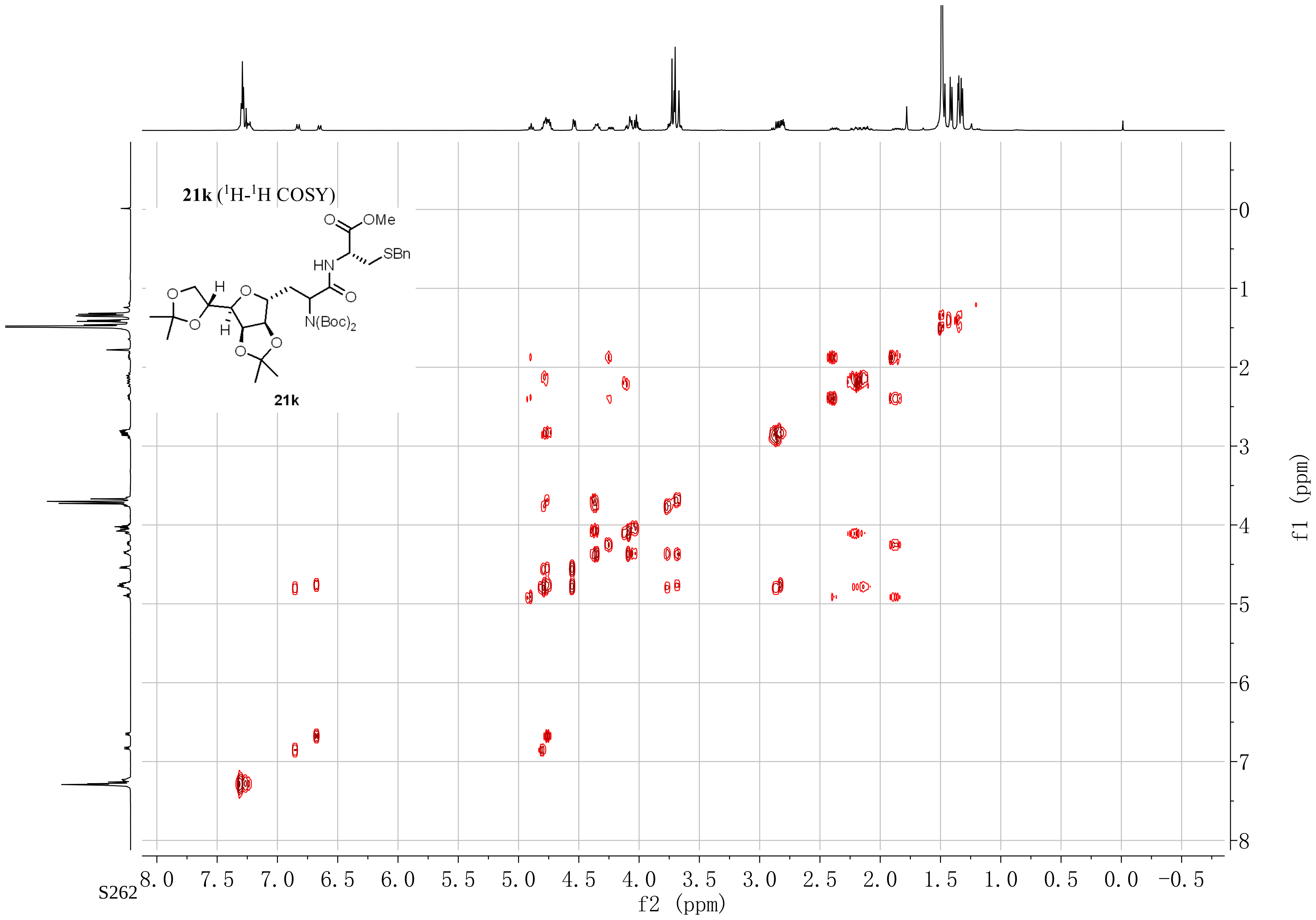

21j (1H-13C HSQC)
OMe
HN
SMe
N(Boc)2
21j
f2 (ppm)
f1 (ppm)

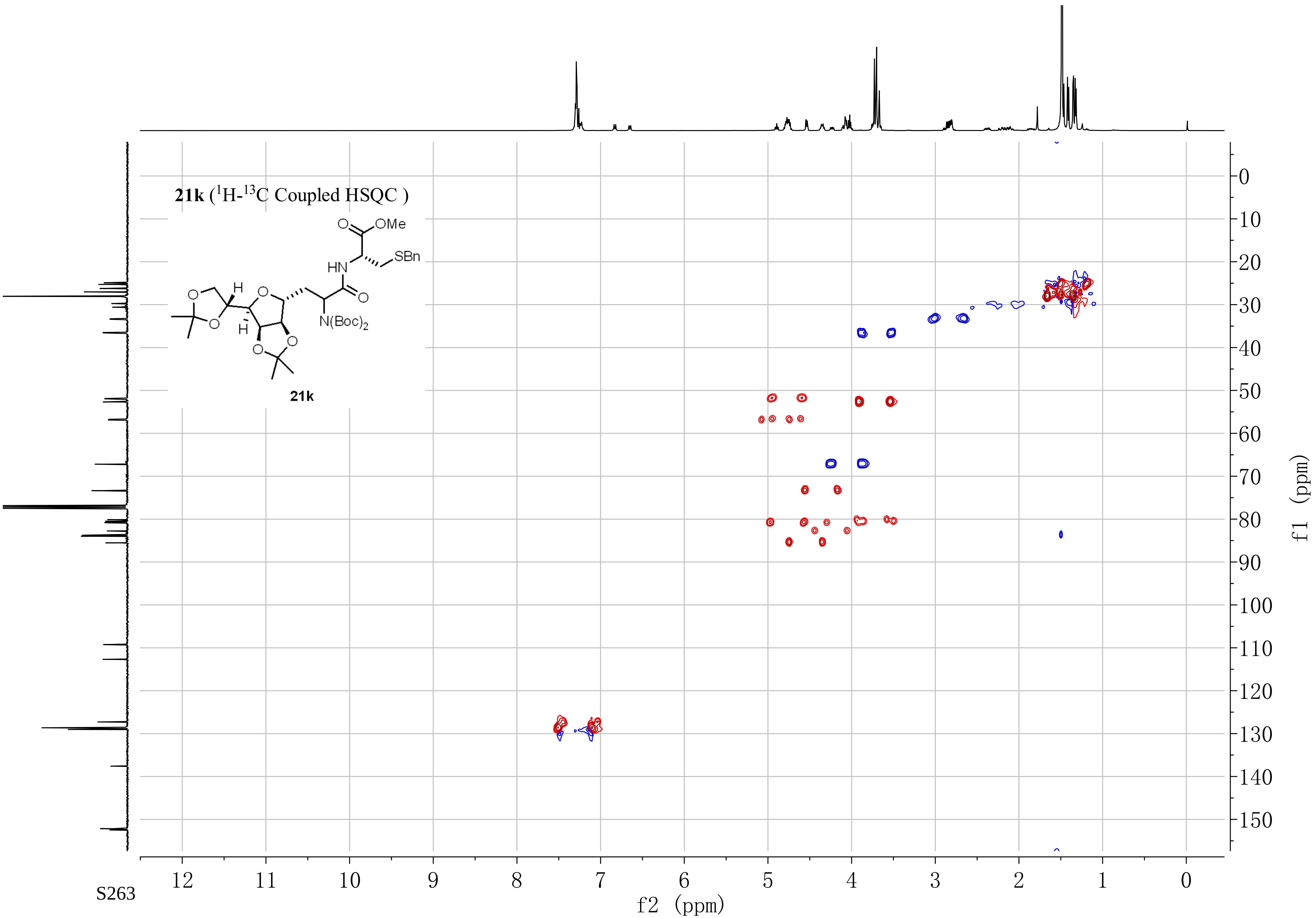
21k (^{1}H NMR, 400MHz, $CDCl_3$)

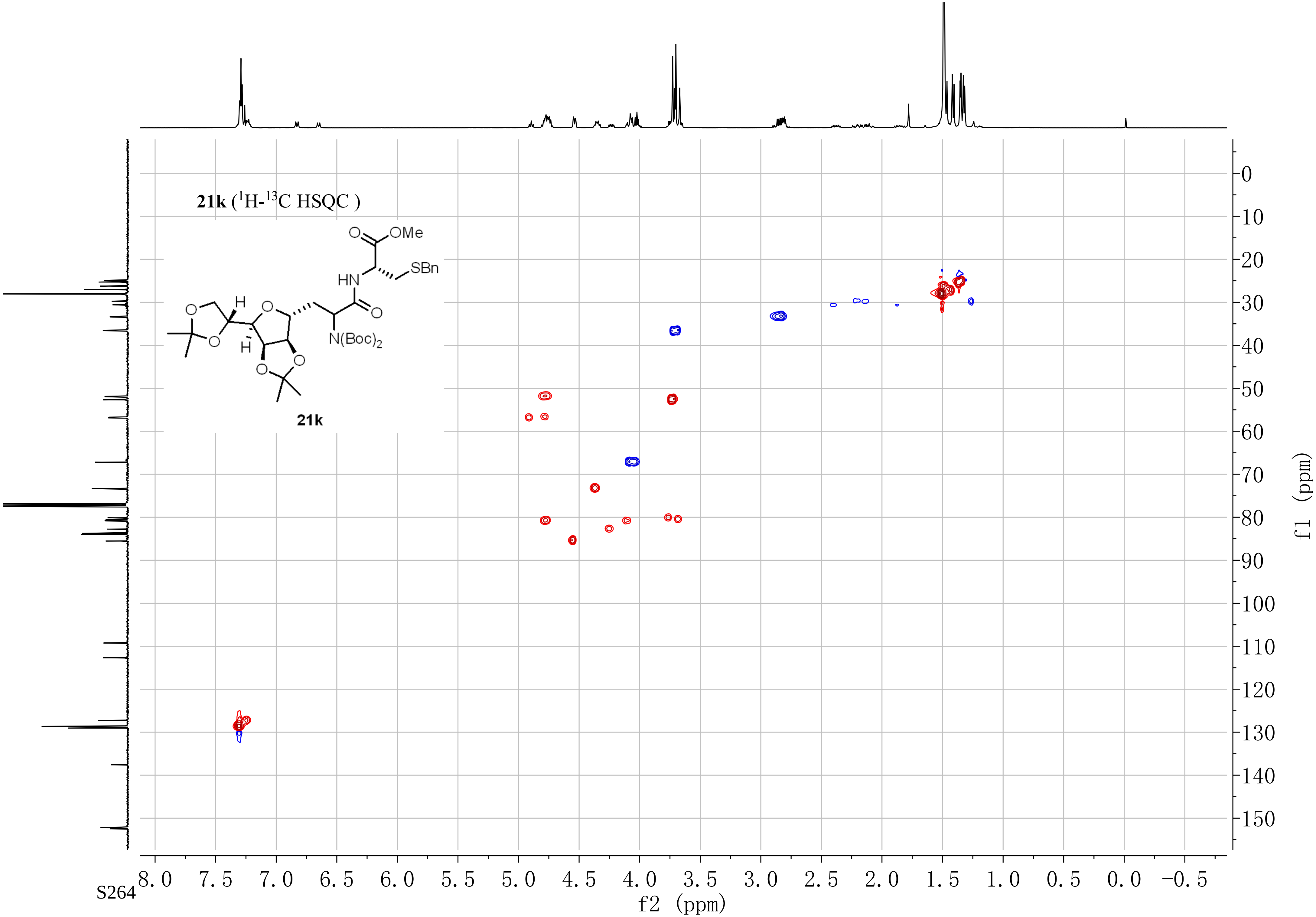
21k

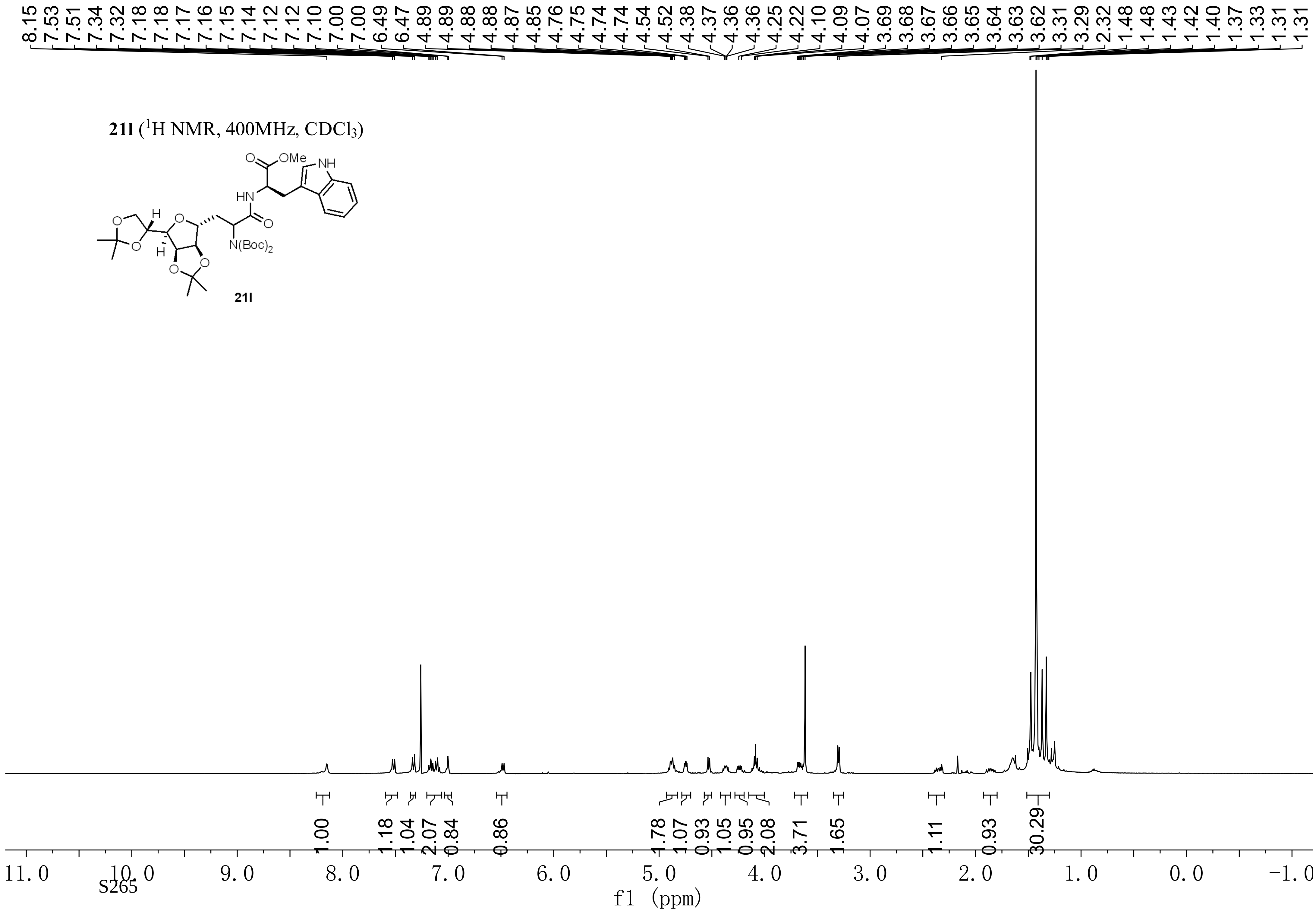


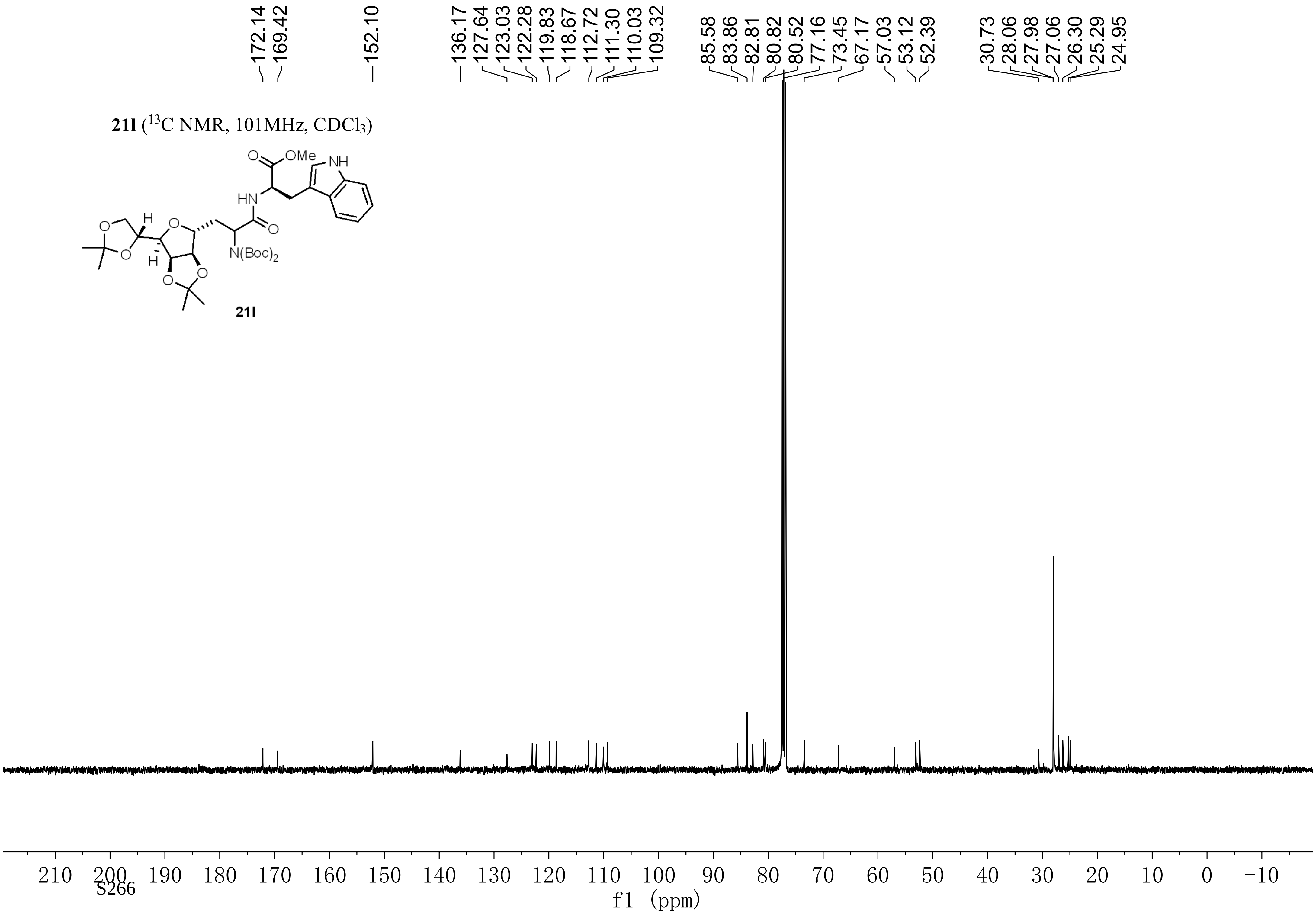

171.25
171.04
170.20
169.81
152.48
152.15
137.63
137.57
129.04
129.00
128.63
127.29
127.26
112.73
112.68
109.31
109.25
85.52
85.42
83.98
83.74
82.75
80.86
80.80
80.74
80.48
80.12
77.16
73.35
67.19
56.90
56.71
52.68
52.59
51.96
51.88
36.60
36.49
28.06
27.99
27.03
26.24
26.20
25.29
25.27
24.90
21k (13C NMR, 101MHz, CDCl3)
OMe
SBn
HN
N(Boc)2
21k
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)


21k (¹H-¹H COSY)
OMe
SBn
HN
N(Boc)2
H
21k
f2 (ppm)
f1 (ppm)
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
0 1 2 3 4 5 6 7 8

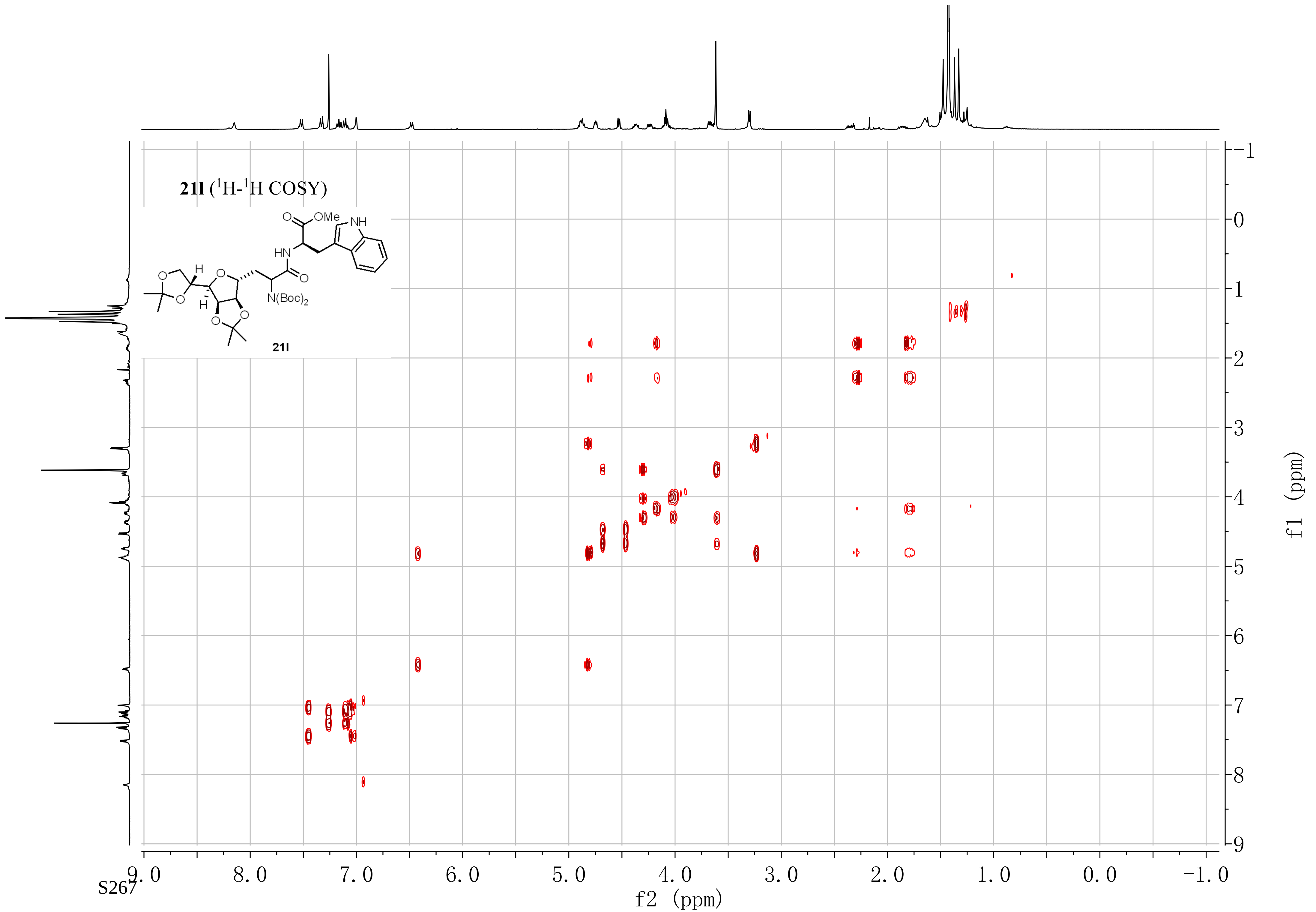

21k (1H-13C Coupled HSQC)
OMe
SBn
HN
H
N(Boc)2
21k
f2 (ppm)
f1 (ppm)

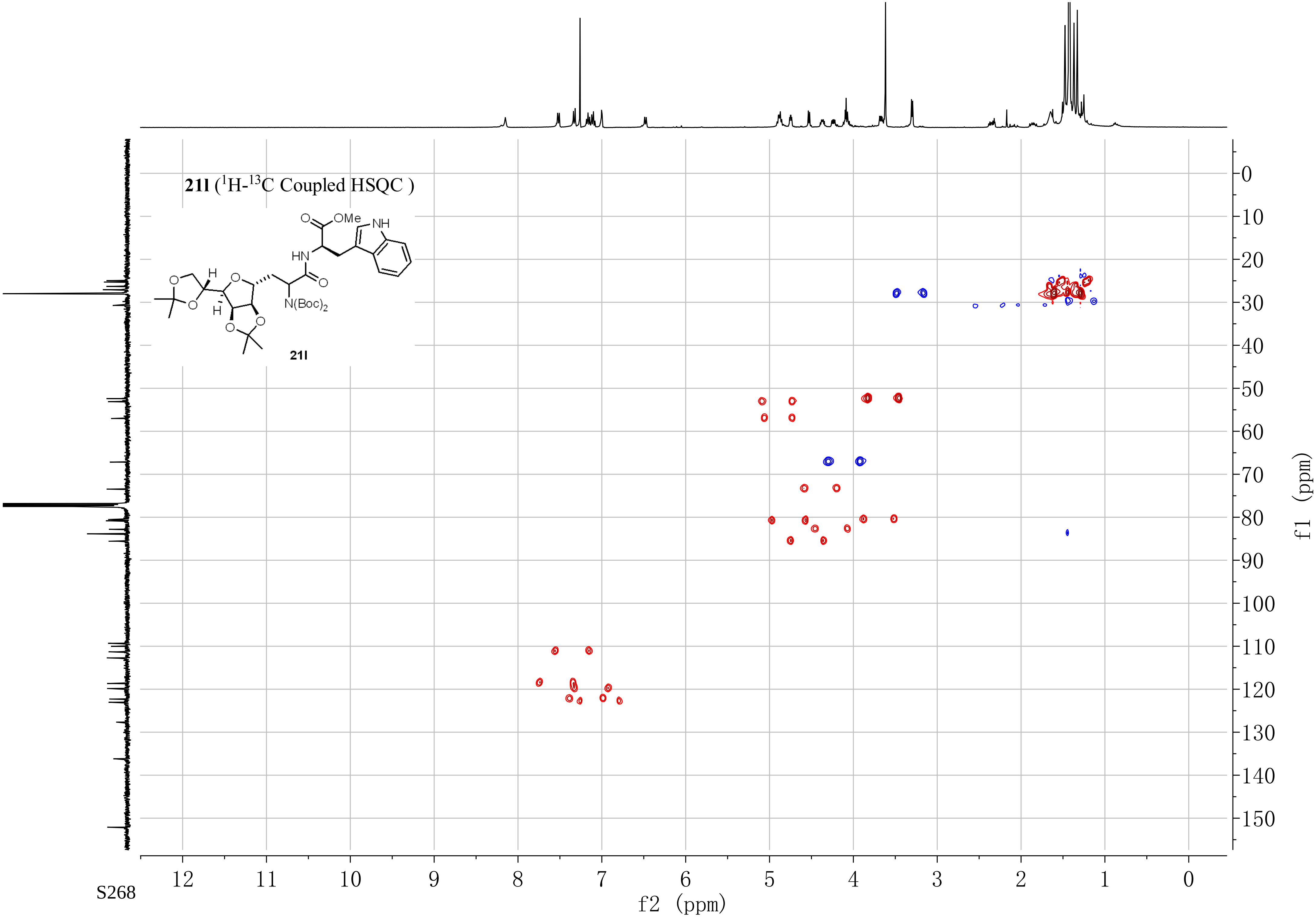

21k (1H-13C HSQC)
OMe
SBn
HN
H
N(Boc)2
21k
f2 (ppm)
f1 (ppm)


8.15 7.53 7.51 7.34 7.32 7.18 7.18 7.17 7.16 7.15 7.14 7.12 7.12 7.10 7.00 7.00 6.49 6.47 4.89 4.89 4.88 4.88 4.87 4.85 4.76 4.75 4.74 4.74 4.54 4.52 4.38 4.37 4.36 4.36 4.25 4.22 4.10 4.09 4.07 3.69 3.68 3.67 3.66 3.65 3.64 3.63 3.62 3.31 3.29 2.32 1.48 1.48 1.43 1.42 1.40 1.37 1.33 1.31 1.31
21l (1H NMR, 400MHz, CDCl3)
OMe
NH
HN
H
O
N(Boc)2
21l
1.00 1.18 1.04 2.07 0.84 0.86 1.78 1.07 0.93 1.05 0.95 2.08 3.71 1.65 1.11 0.93 30.29
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

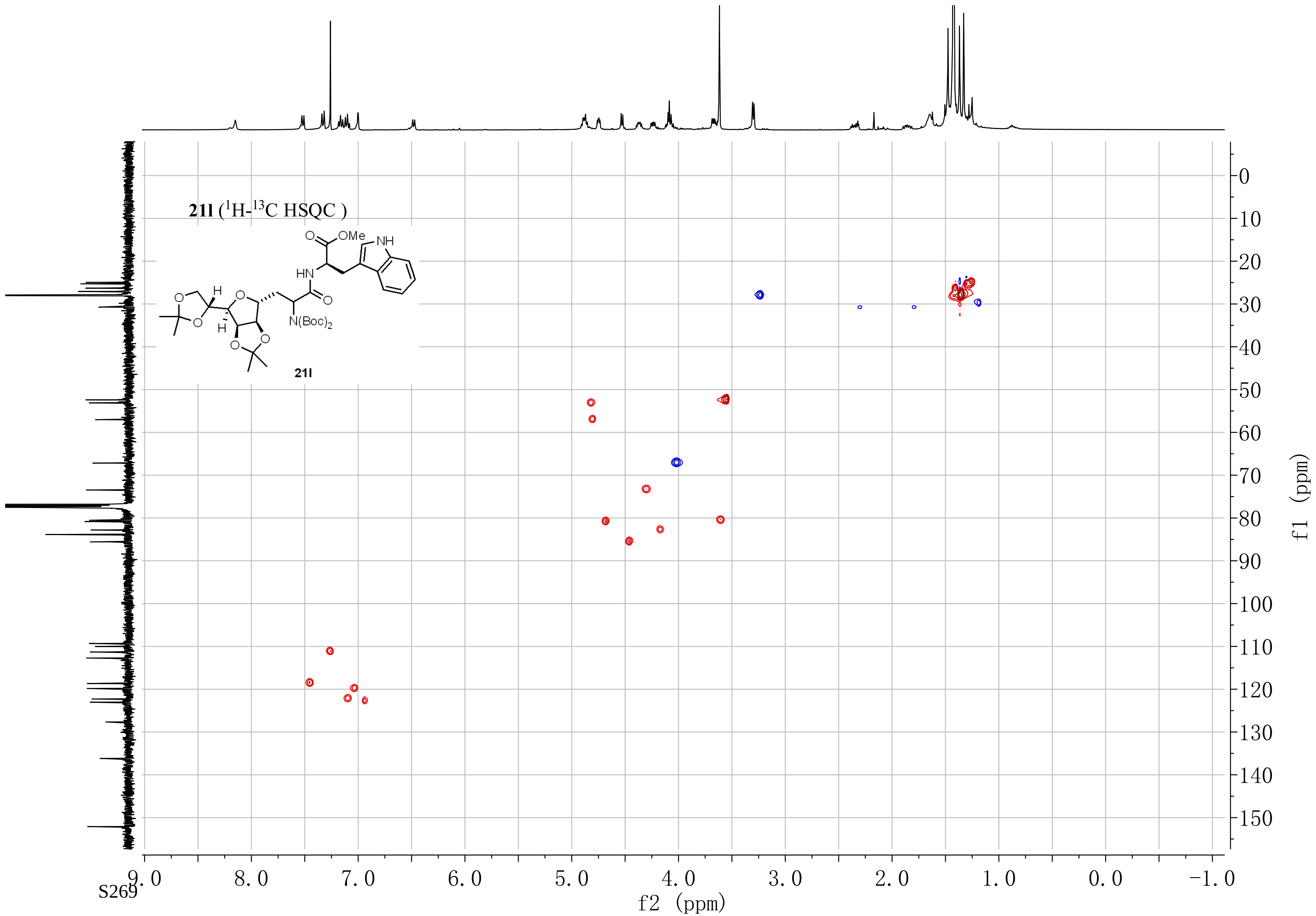

172.14
169.42
152.10
136.17
127.64
123.03
122.28
119.83
118.67
112.72
111.30
110.03
109.32
85.58
83.86
82.81
80.82
80.52
77.16
73.45
67.17
57.03
53.12
52.39
30.73
28.06
27.98
27.06
26.30
25.29
24.95
21l (13C NMR, 101MHz, CDCl3)
OMe
NH
HN
N(Boc)2
21l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

21l (^{1}H-^{1}H COSY)

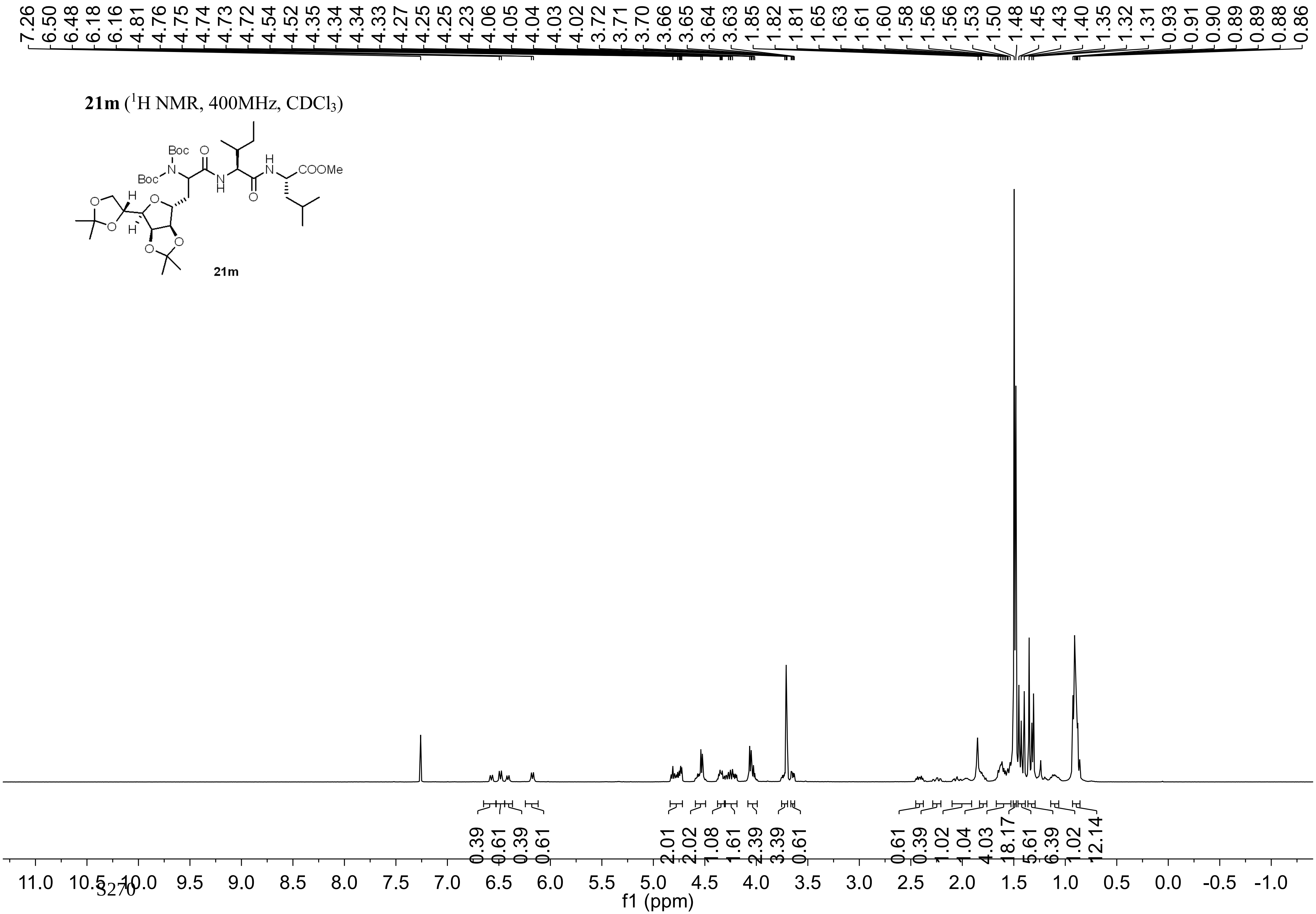




21l (^{1}H-^{13}C Coupled HSQC)
O
OMe
NH
HN
H
O
O
O
O
N(Boc)$_2$
H
O
O
21l
f1 (ppm)
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
12
11
10
9
8
7
6
5
4
3
2
1
0

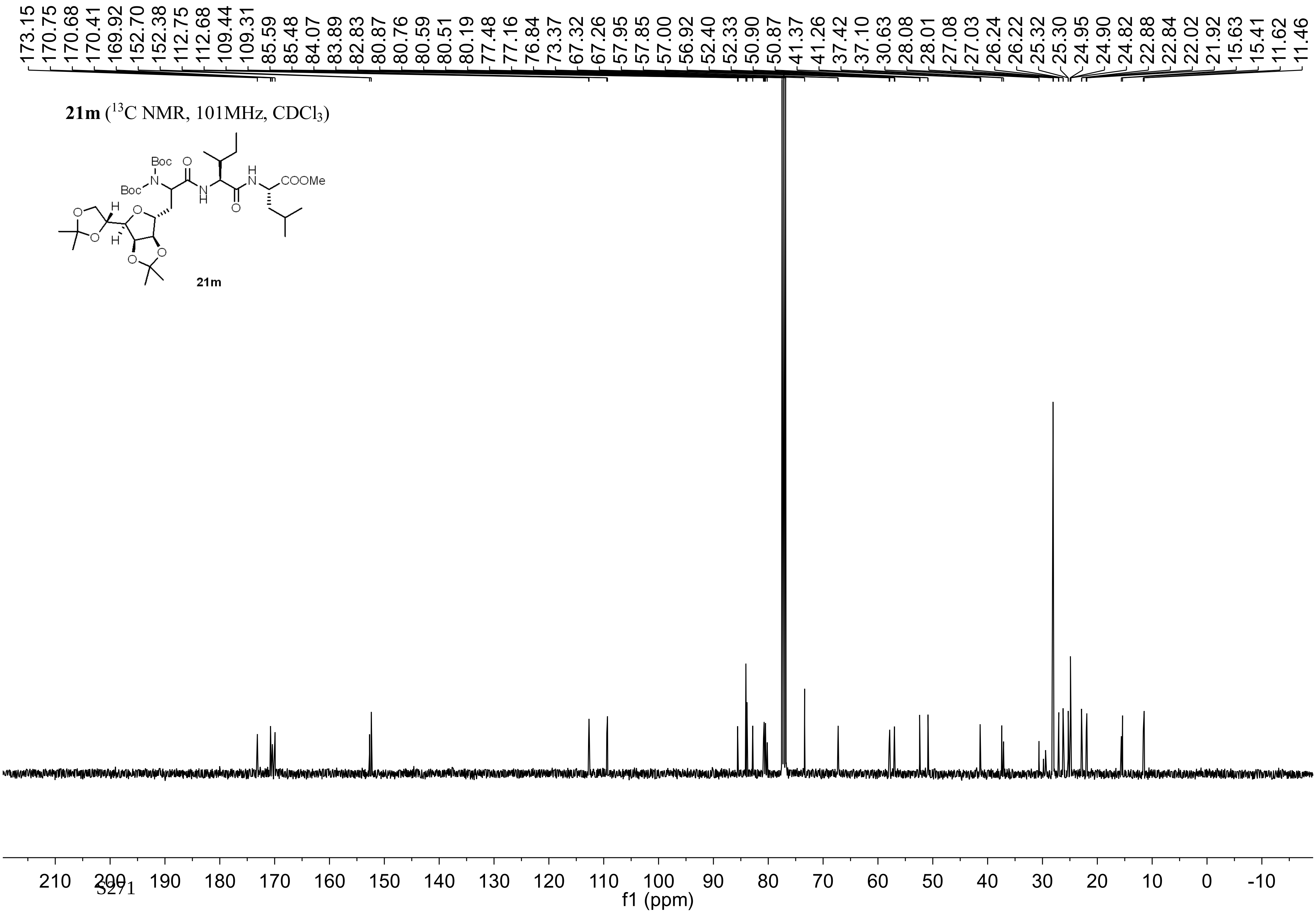

21l (1H-13C HSQC)
OMe
NH
HN
N(Boc)2
21l
f2 (ppm)
f1 (ppm)

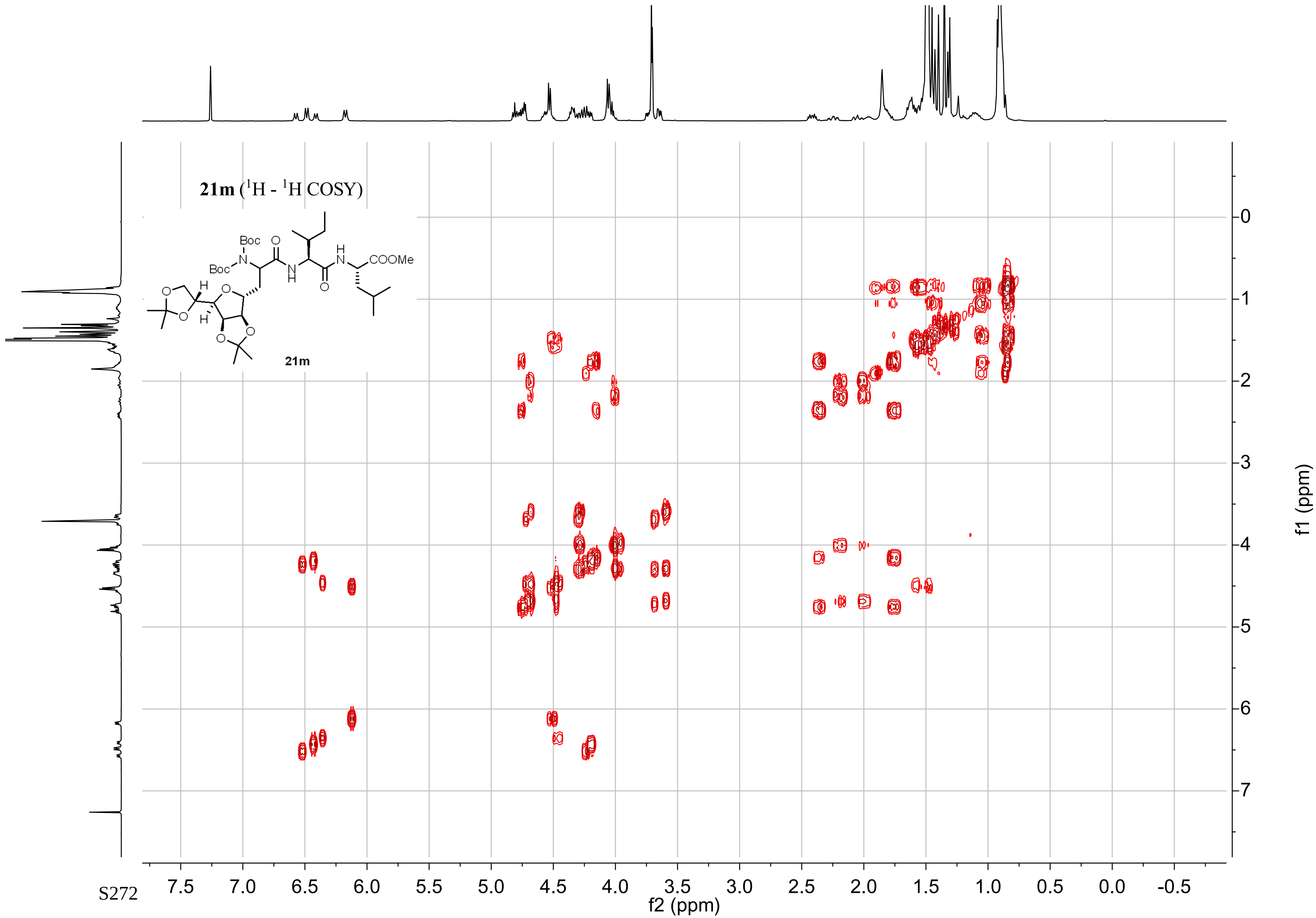
21m (^{1}H NMR, 400MHz, $CDCl_3$)



21m (^{13}C NMR, 101MHz, $CDCl_3$)

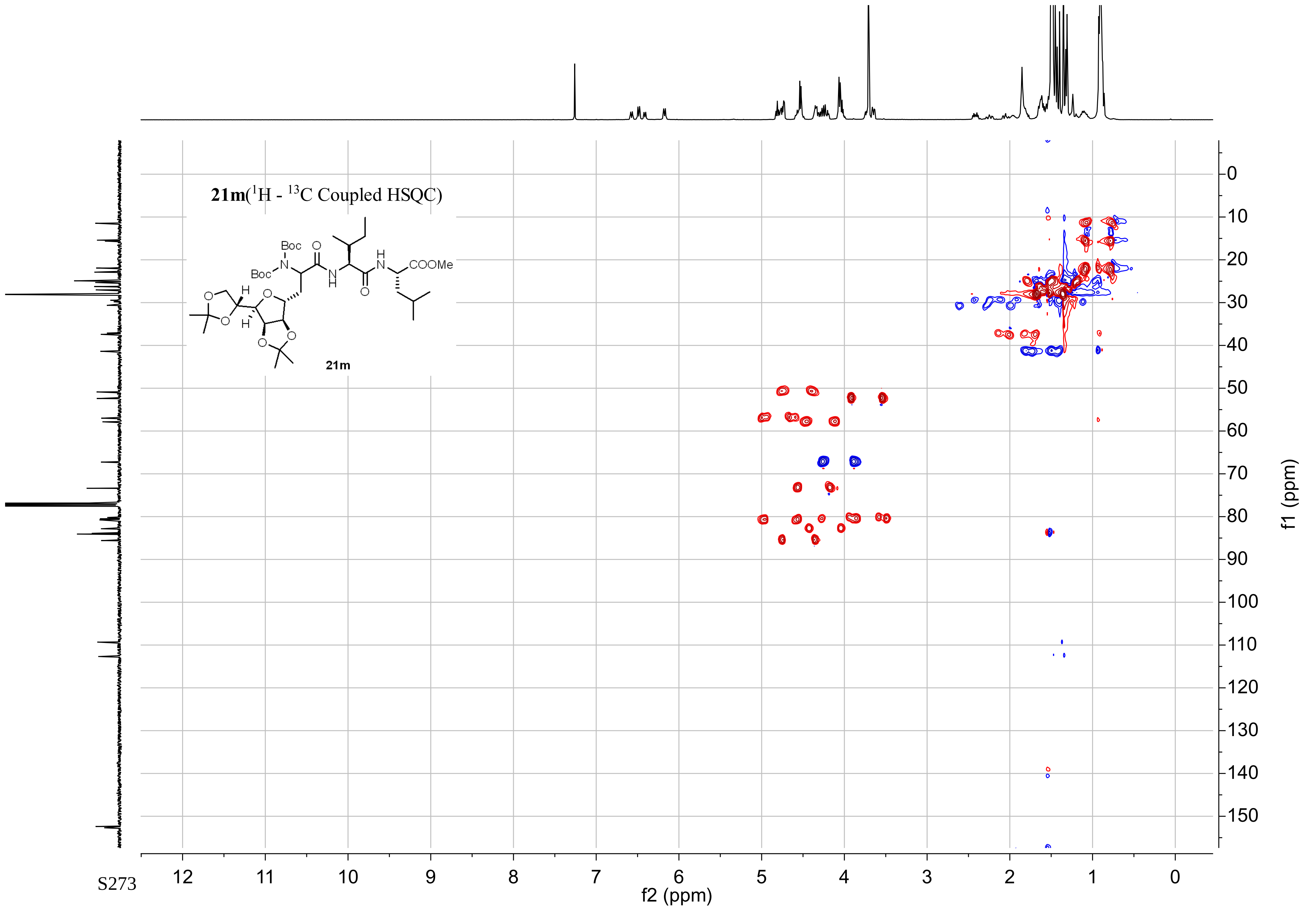
21m

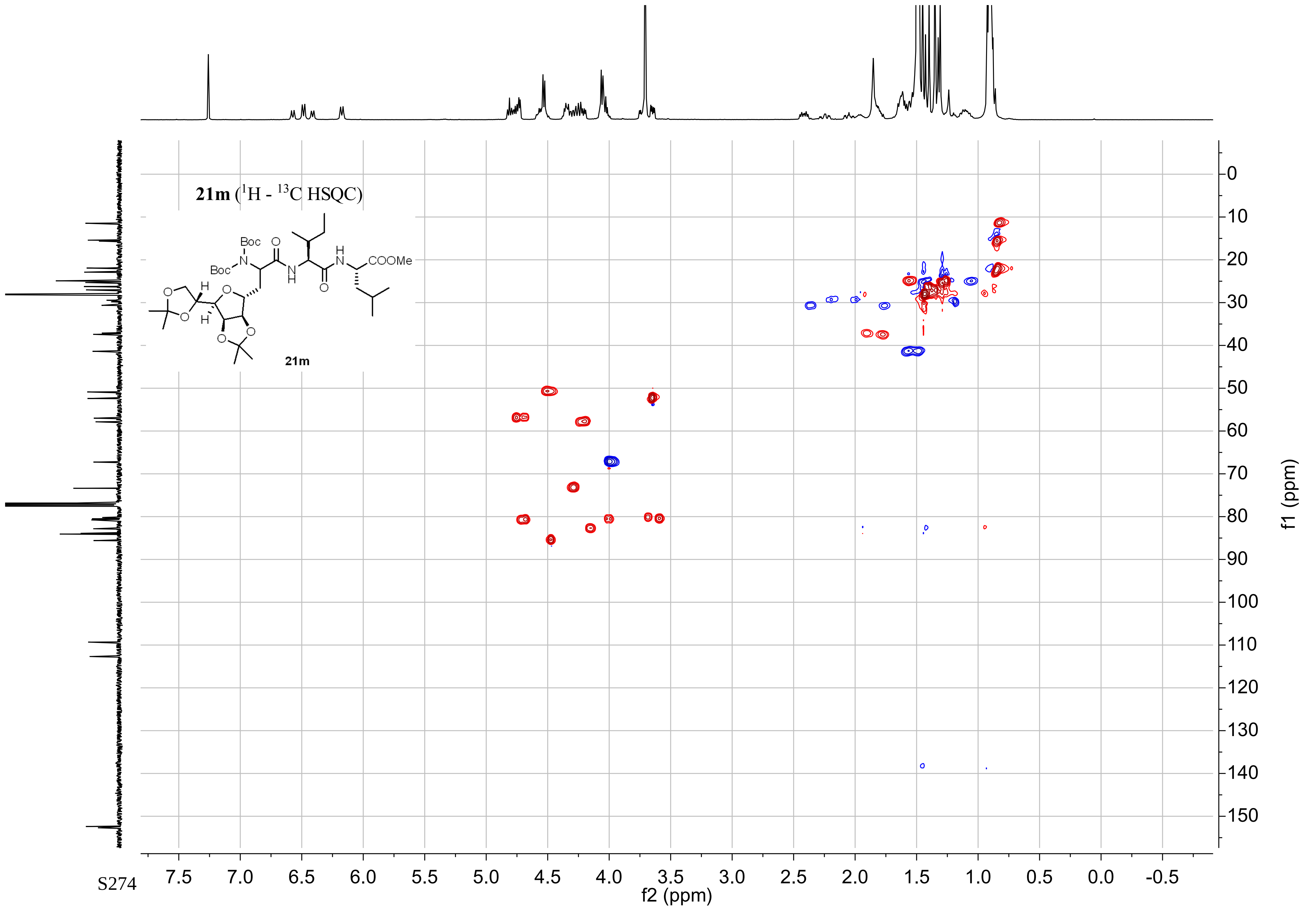


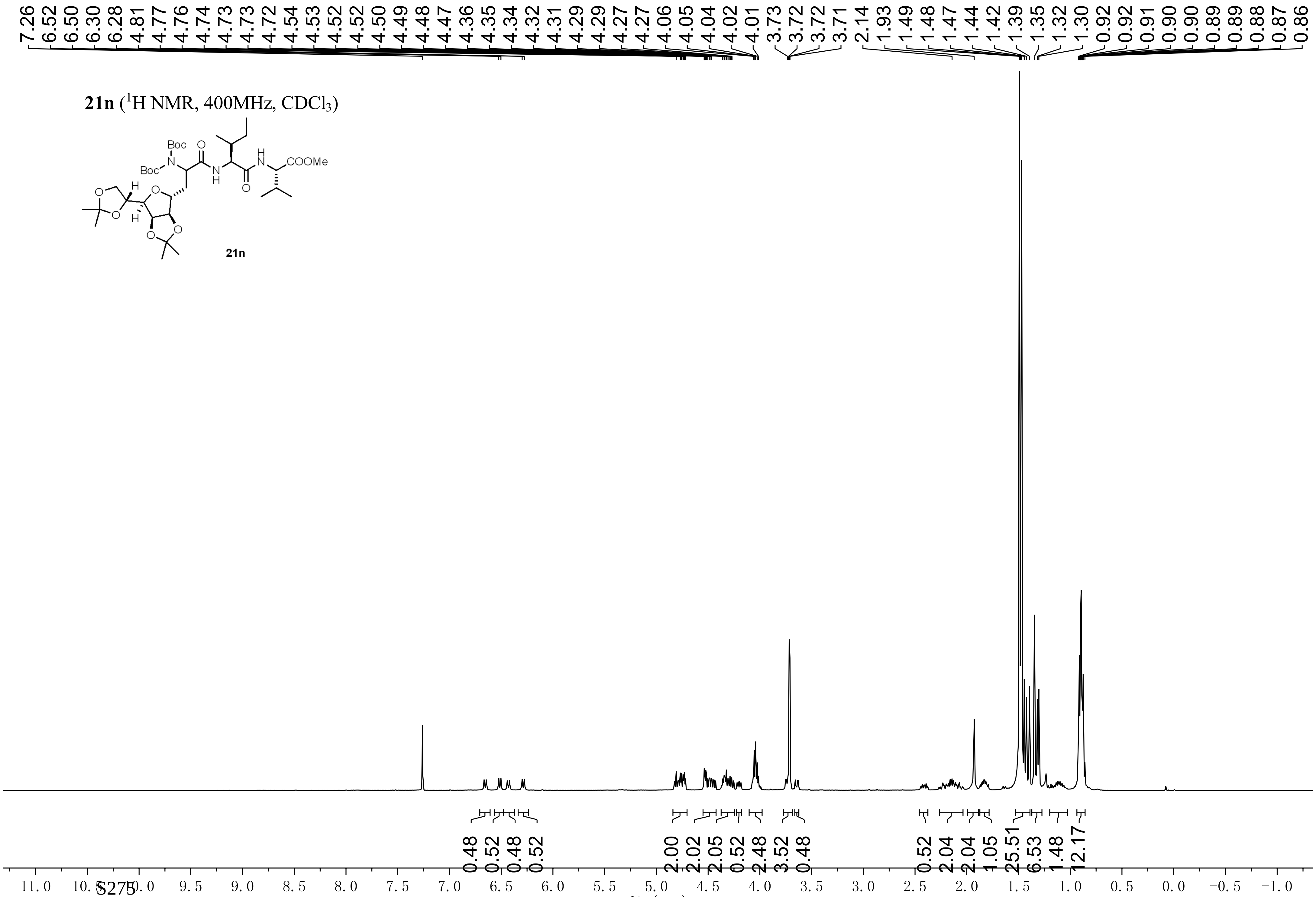


21m (1H - 1H COSY)
Boc
Boc
N
O
H
N
H
N
COOMe
O
H
O
O
O
H
O
O
21m
f2 (ppm)
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7

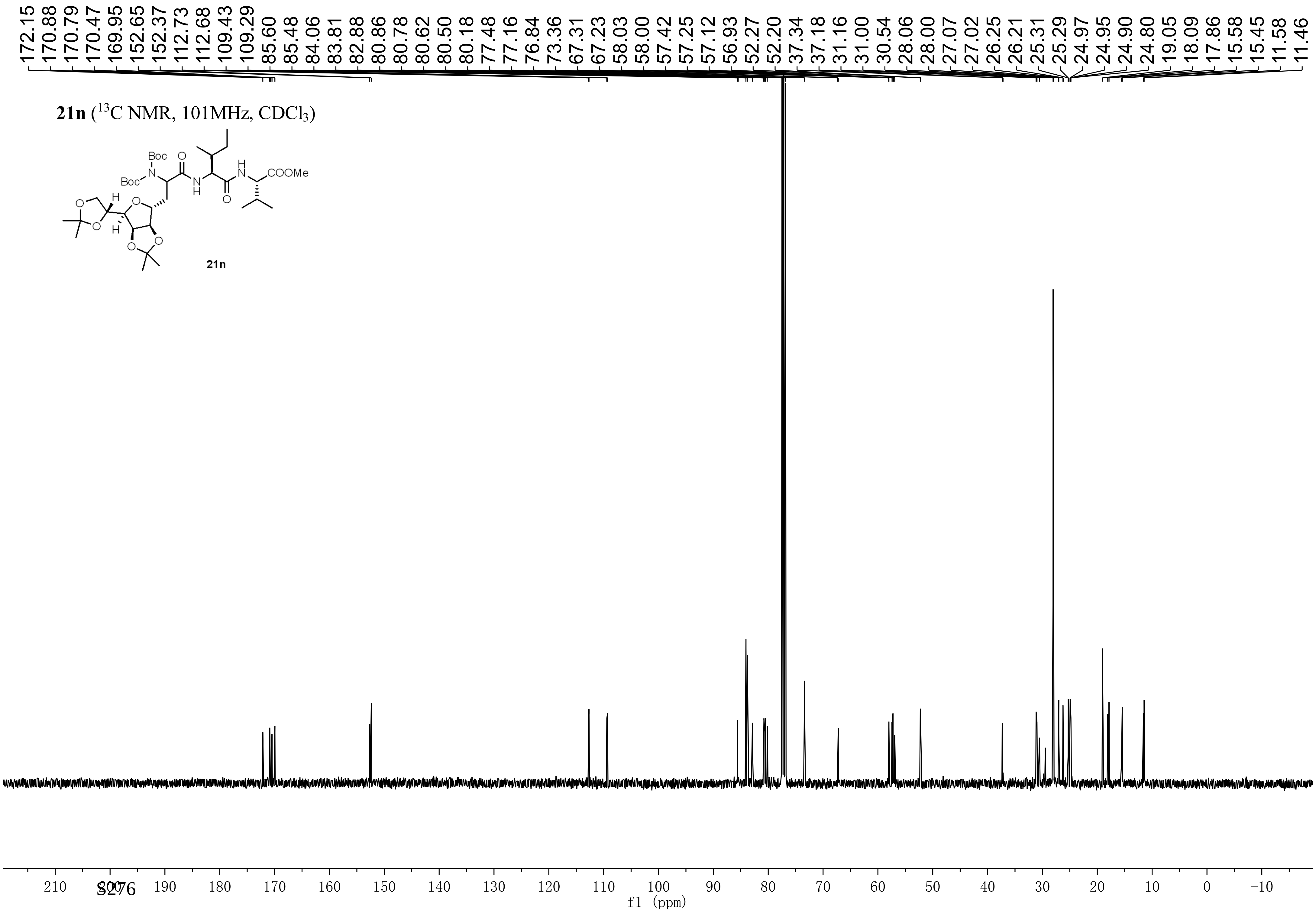
21m(^{1}H - ^{13}C Coupled HSQC)

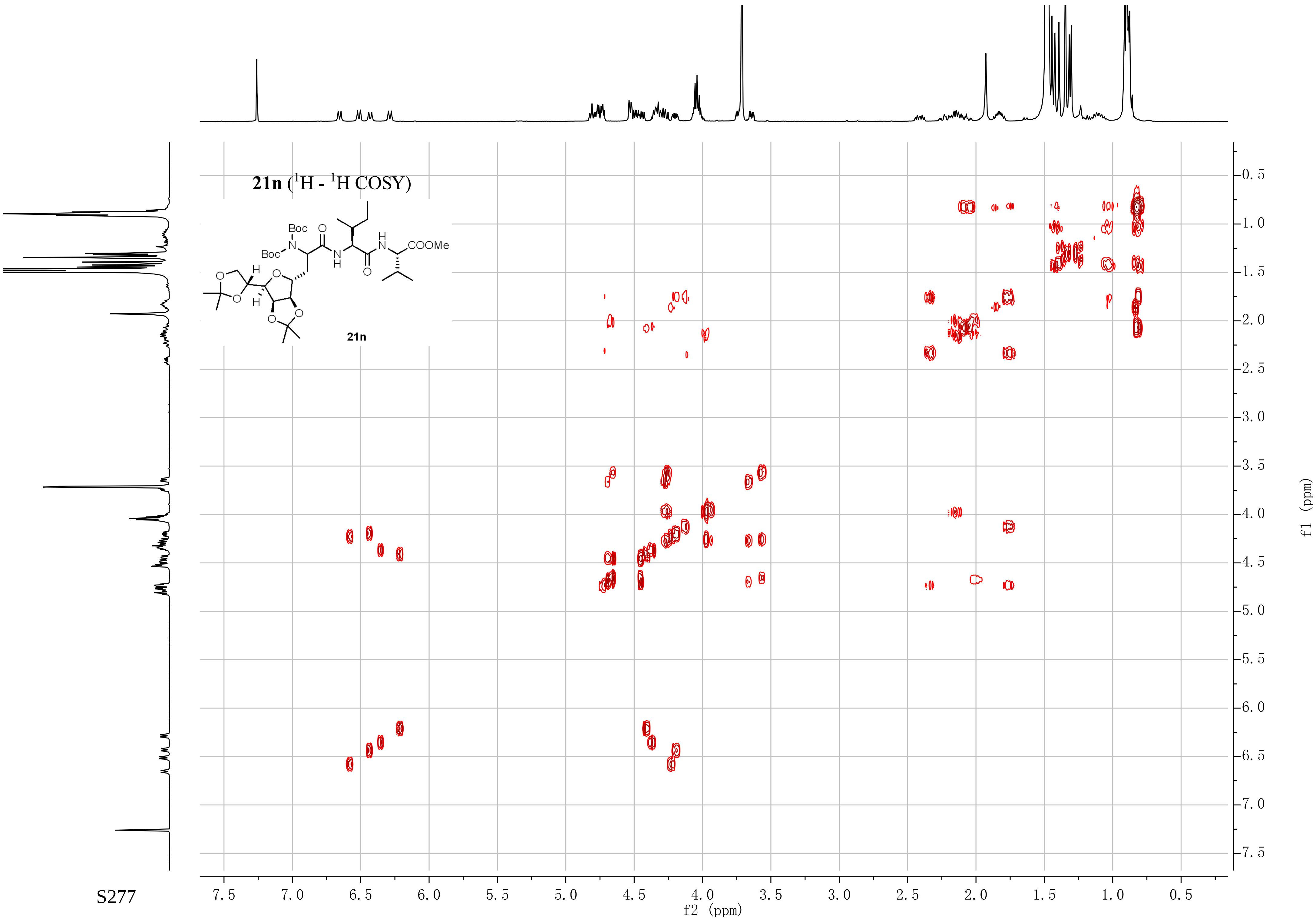


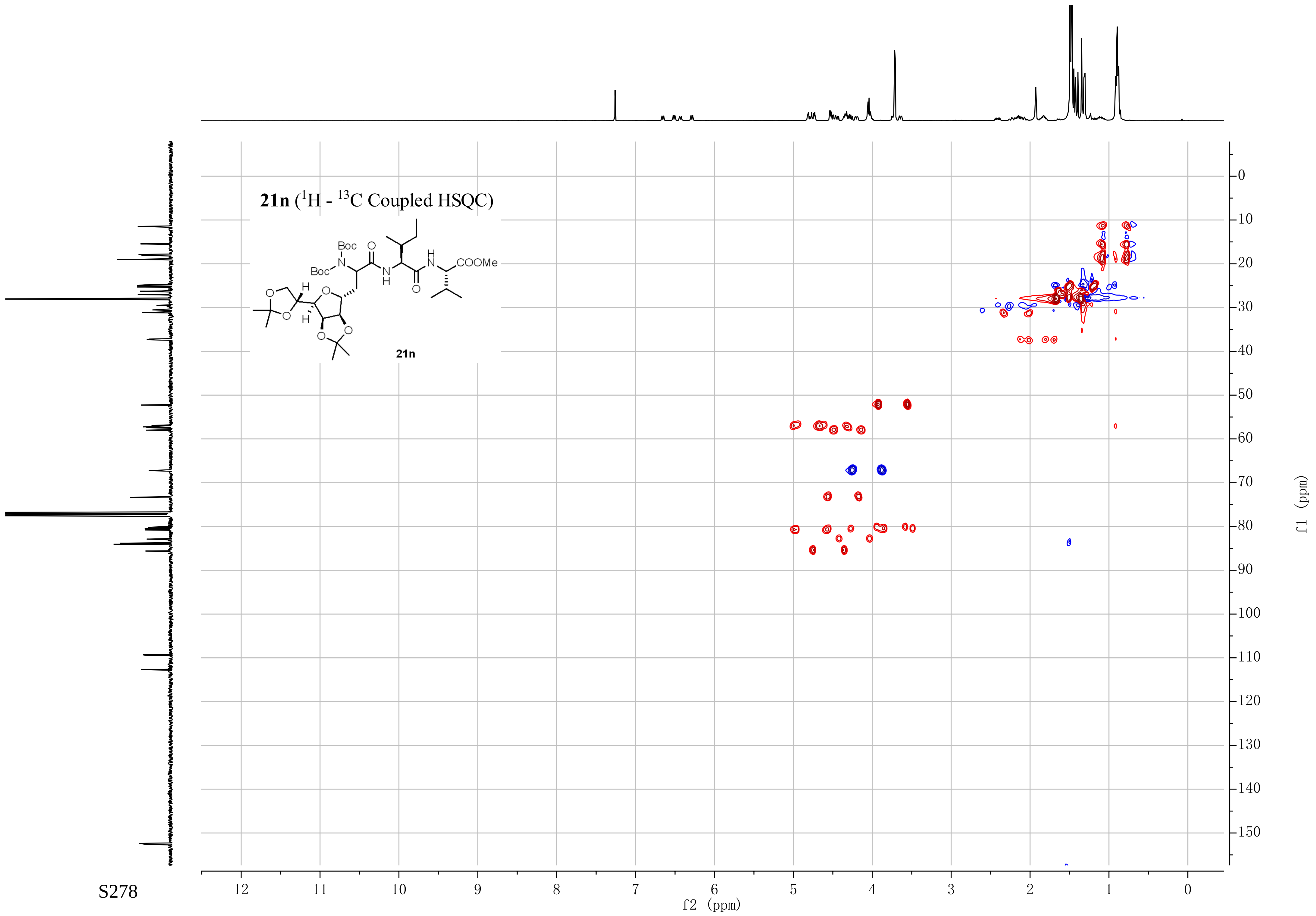

21m (1H - 13C HSQC)
Boc
Boc
N
O
H
N
H
H
COOMe
O
O
O
O
O
O
O
21m
f2 (ppm)
f1 (ppm)

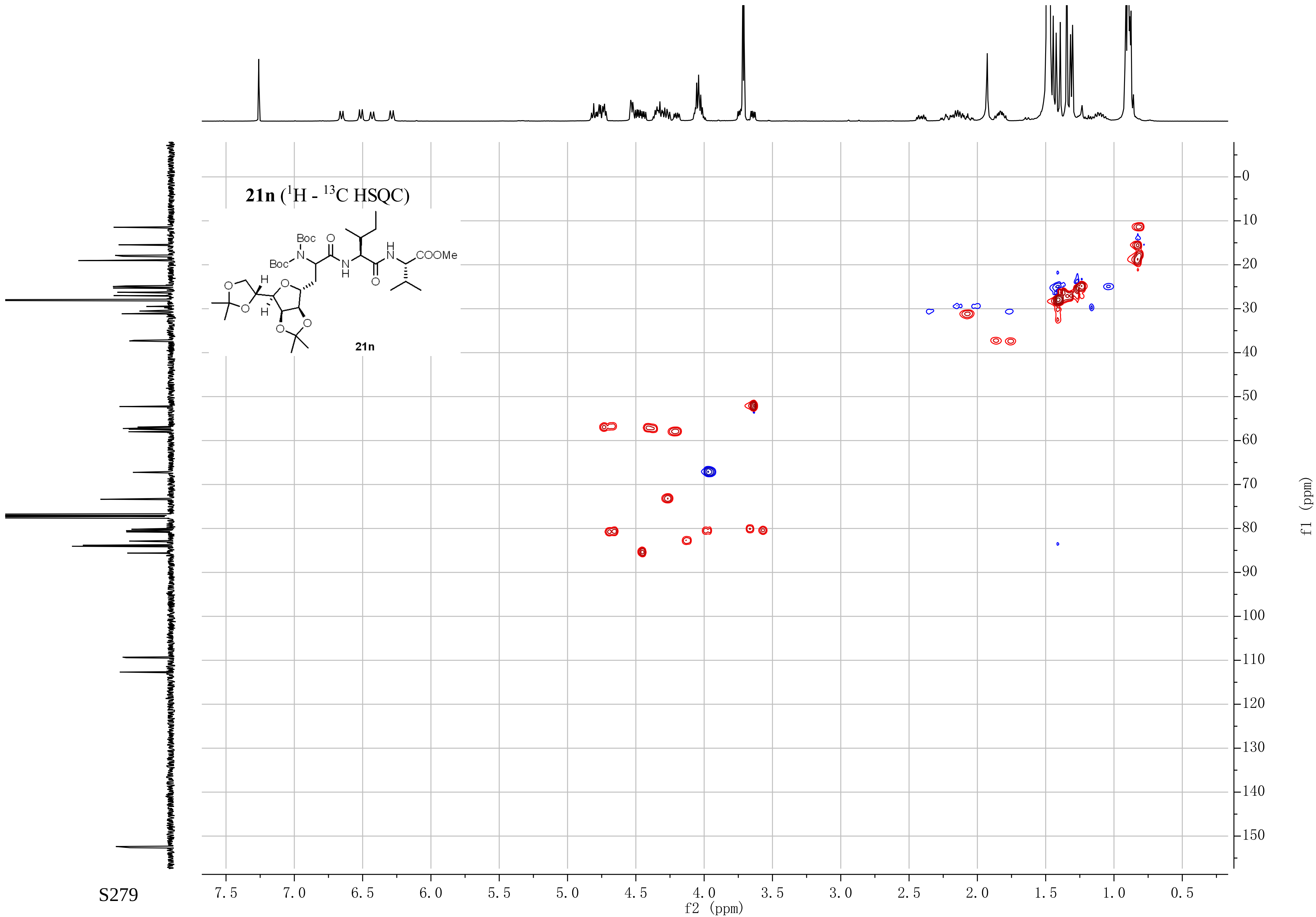

21n (¹H NMR, 400MHz, CDCl₃)
Boc
Boc
N
O
N
H
H
N
COOMe
O
H
O
O
O
H
O
O
21n
7.26 6.52 6.50 6.30 6.28 4.81 4.77 4.76 4.74 4.73 4.73 4.72 4.54 4.53 4.52 4.52 4.50 4.49 4.48 4.47 4.36 4.35 4.34 4.32 4.31 4.29 4.29 4.27 4.27 4.06 4.05 4.04 4.02 4.01 3.73 3.72 3.72 3.71 2.14 1.93 1.49 1.48 1.47 1.44 1.42 1.39 1.35 1.32 1.30 0.92 0.92 0.91 0.90 0.90 0.89 0.89 0.88 0.87 0.86
0.48 0.52 0.48 0.52 2.00 2.02 2.05 0.52 2.48 3.52 0.48 0.52 2.04 2.04 1.05 25.51 6.53 1.48 12.17
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)

21n (^{13}C NMR, 101MHz, $CDCl_3$)

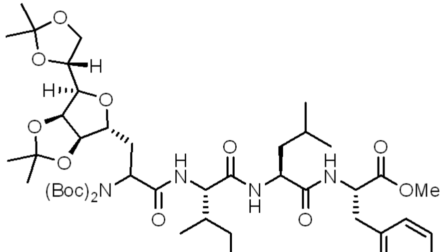


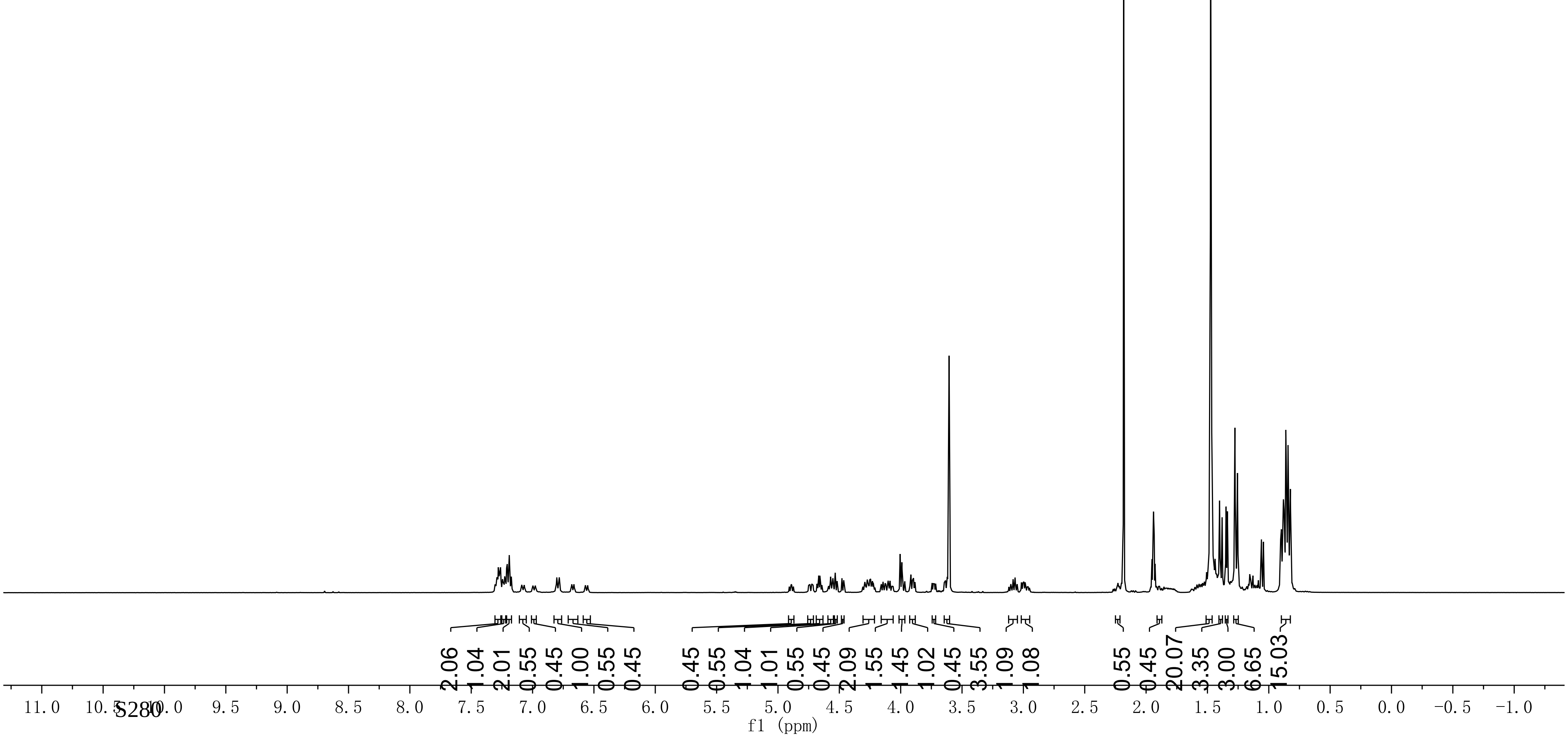

21n (1H - 1H COSY)
Boc
N
Boc
O
H
N
H
COOMe
21n
f2 (ppm)
f1 (ppm)

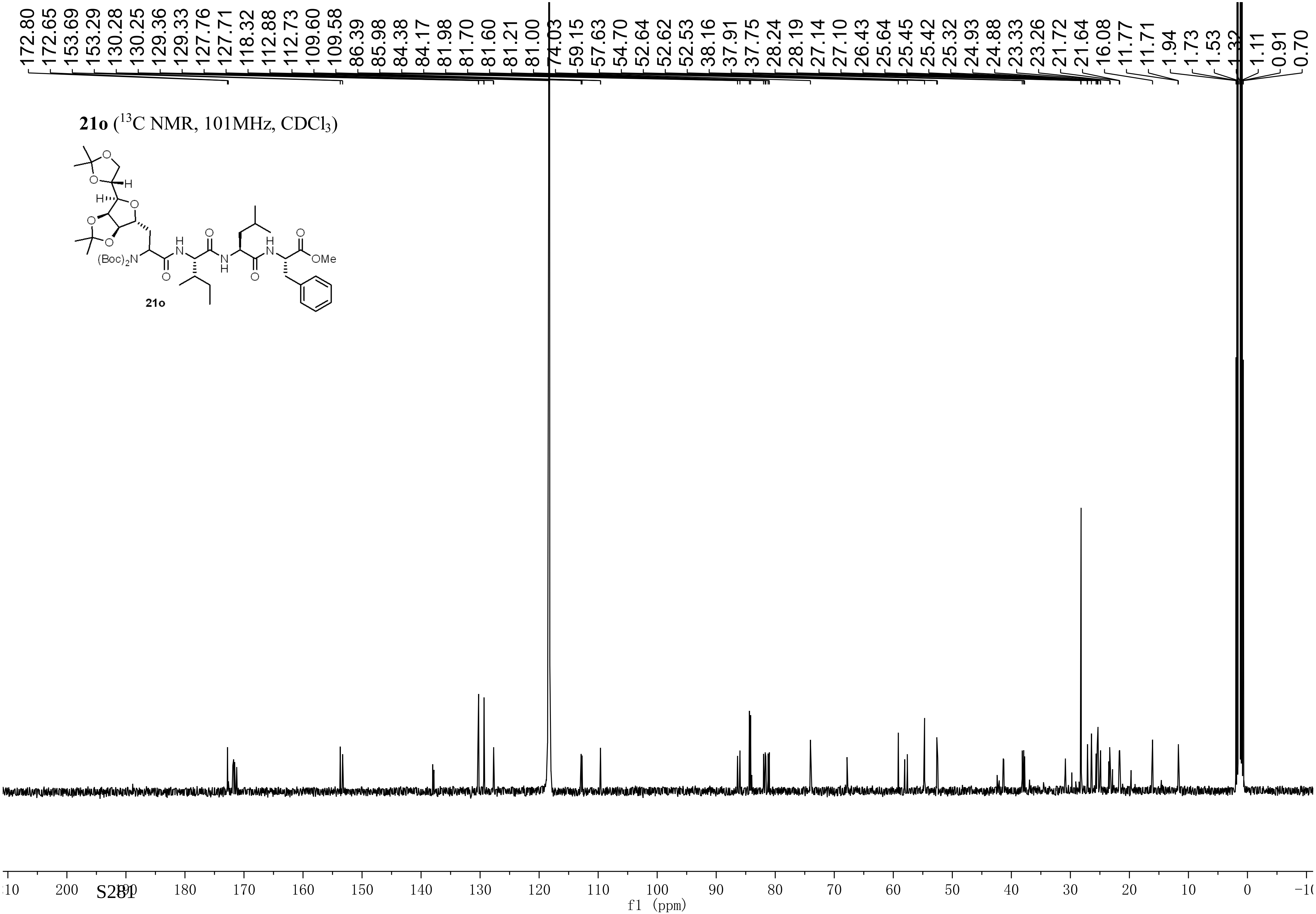

21n (1H - 13C Coupled HSQC)
Boc
Boc
N
O
N
H
H
N
COOMe
O
O
O
H
H
O
O
O
O
21n
f2 (ppm)
f1 (ppm)

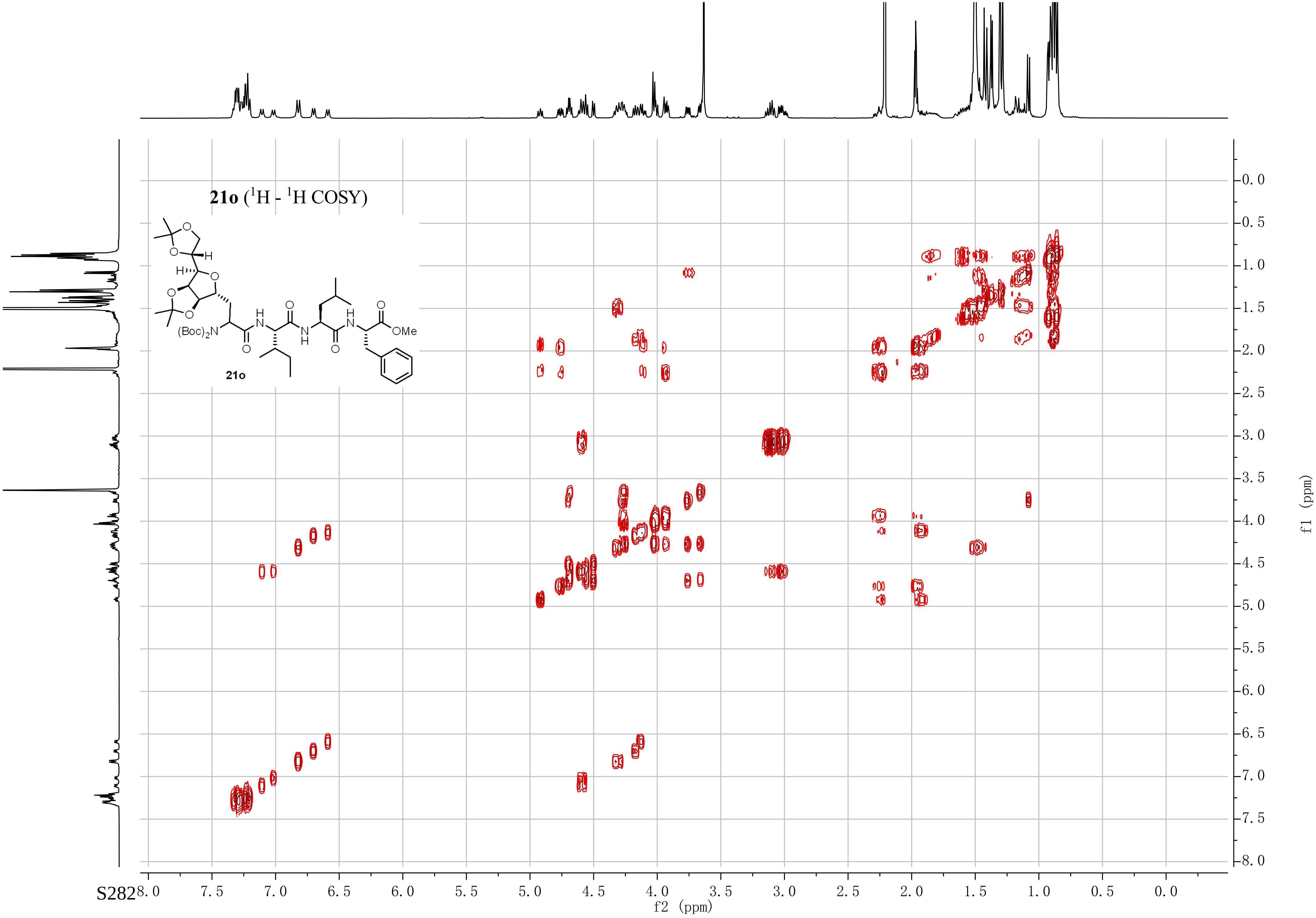

21n (1H - 13C HSQC)
Boc
Boc
COOMe
21n
f2 (ppm)
f1 (ppm)

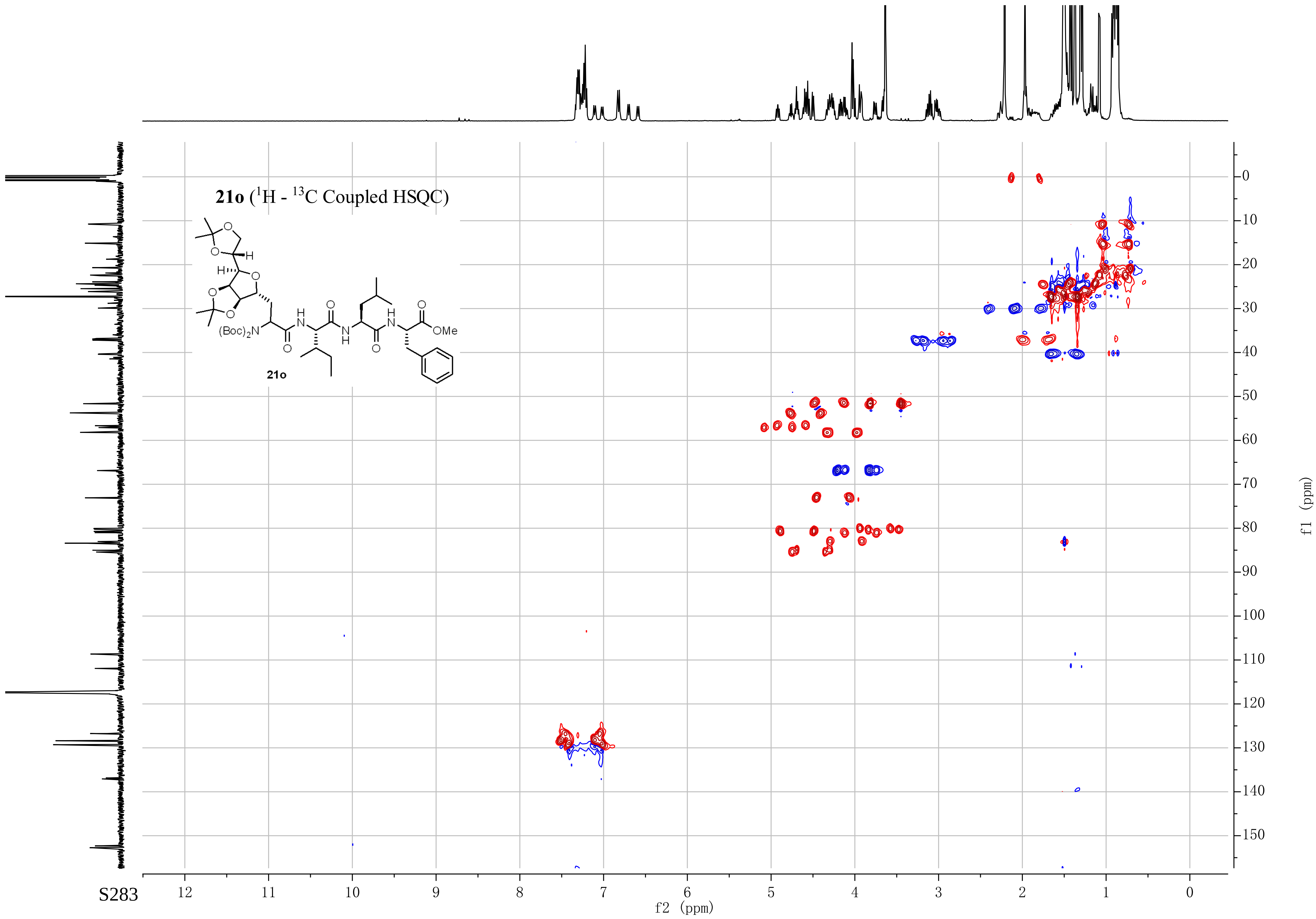
21o (^{1}H NMR, 400MHz, $CDCl_3$)



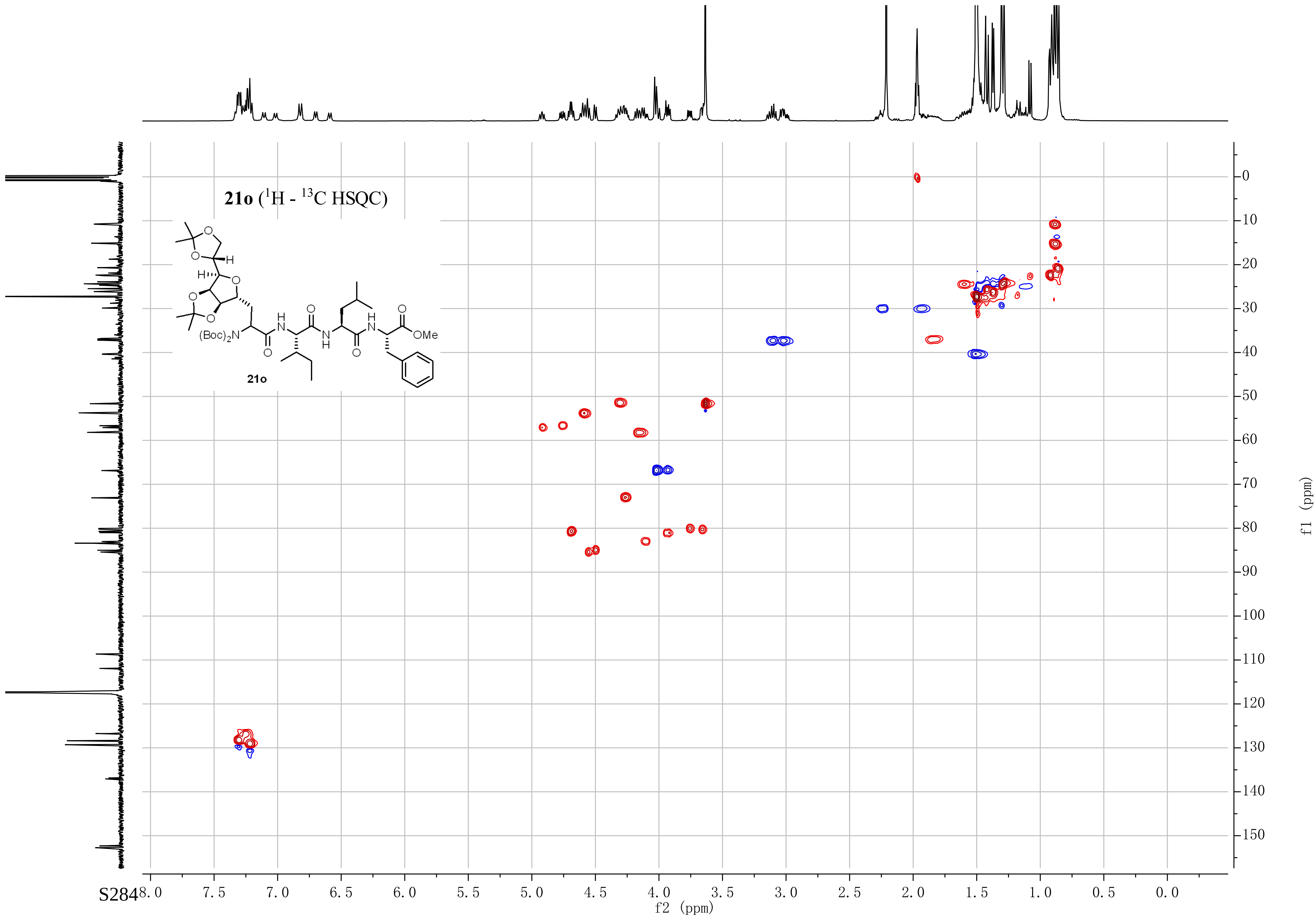



172.80
172.65
153.69
153.29
130.28
130.25
129.36
129.33
127.76
127.71
118.32
112.88
112.73
109.60
109.58
86.39
85.98
84.38
84.17
81.98
81.70
81.60
81.21
81.00
74.03
59.15
57.63
54.70
52.64
52.62
52.53
38.16
37.91
37.75
28.24
28.19
27.14
27.10
26.43
25.64
25.45
25.42
25.32
24.93
24.88
23.33
23.26
21.72
21.64
16.08
11.77
11.71
1.94
1.73
1.53
1.32
1.11
0.91
0.70
21o (^{13}C NMR, 101MHz, $CDCl_3$)
(Boc)$_2$N
OMe
21o
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)


21o (1H - 1H COSY)
(Boc)2N
OMe
21o
f2 (ppm)
f1 (ppm)

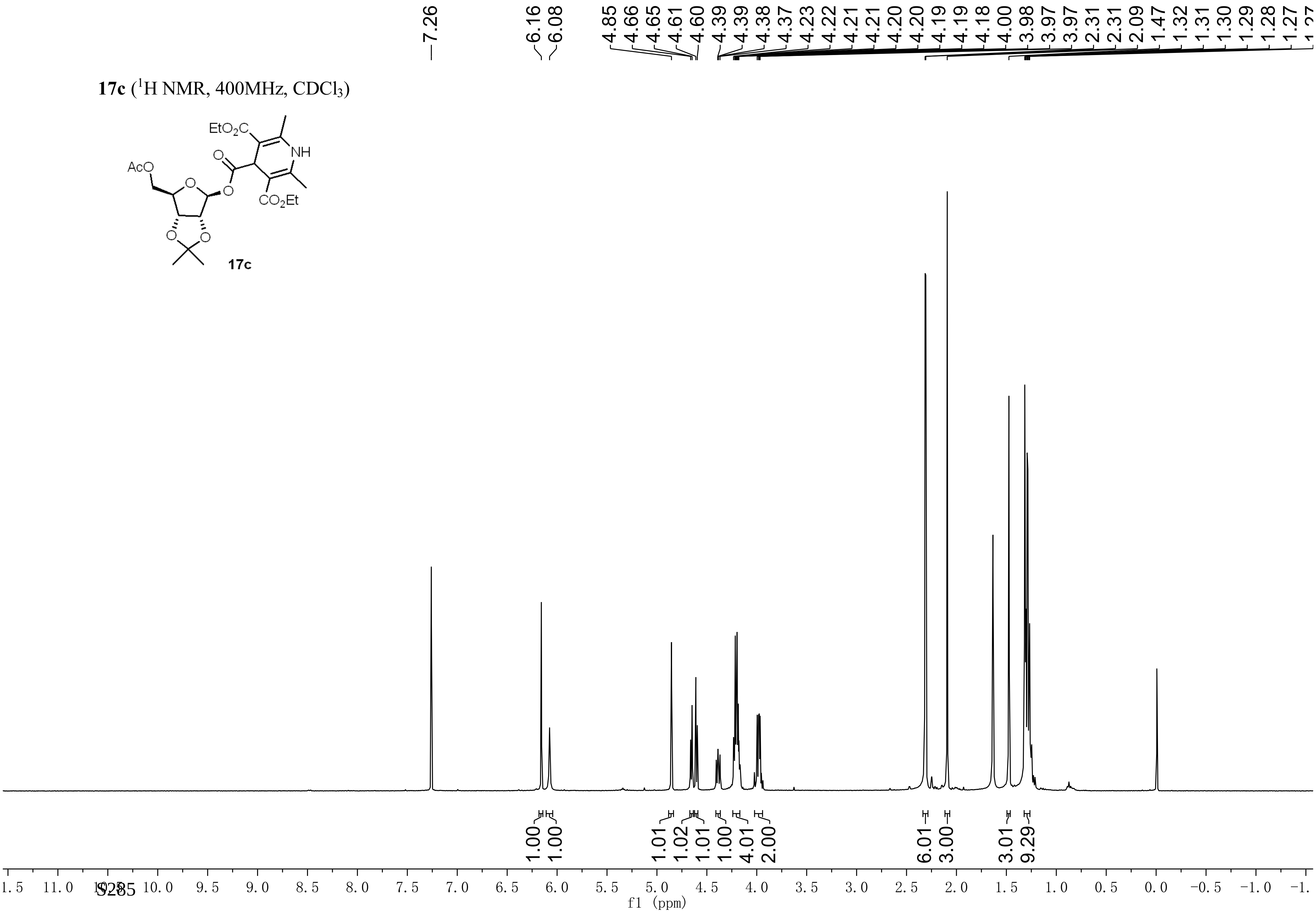


21o (^{1}H - ^{13}C Coupled HSQC)
21o
(Boc)$_2$N
OMe
f2 (ppm)
f1 (ppm)

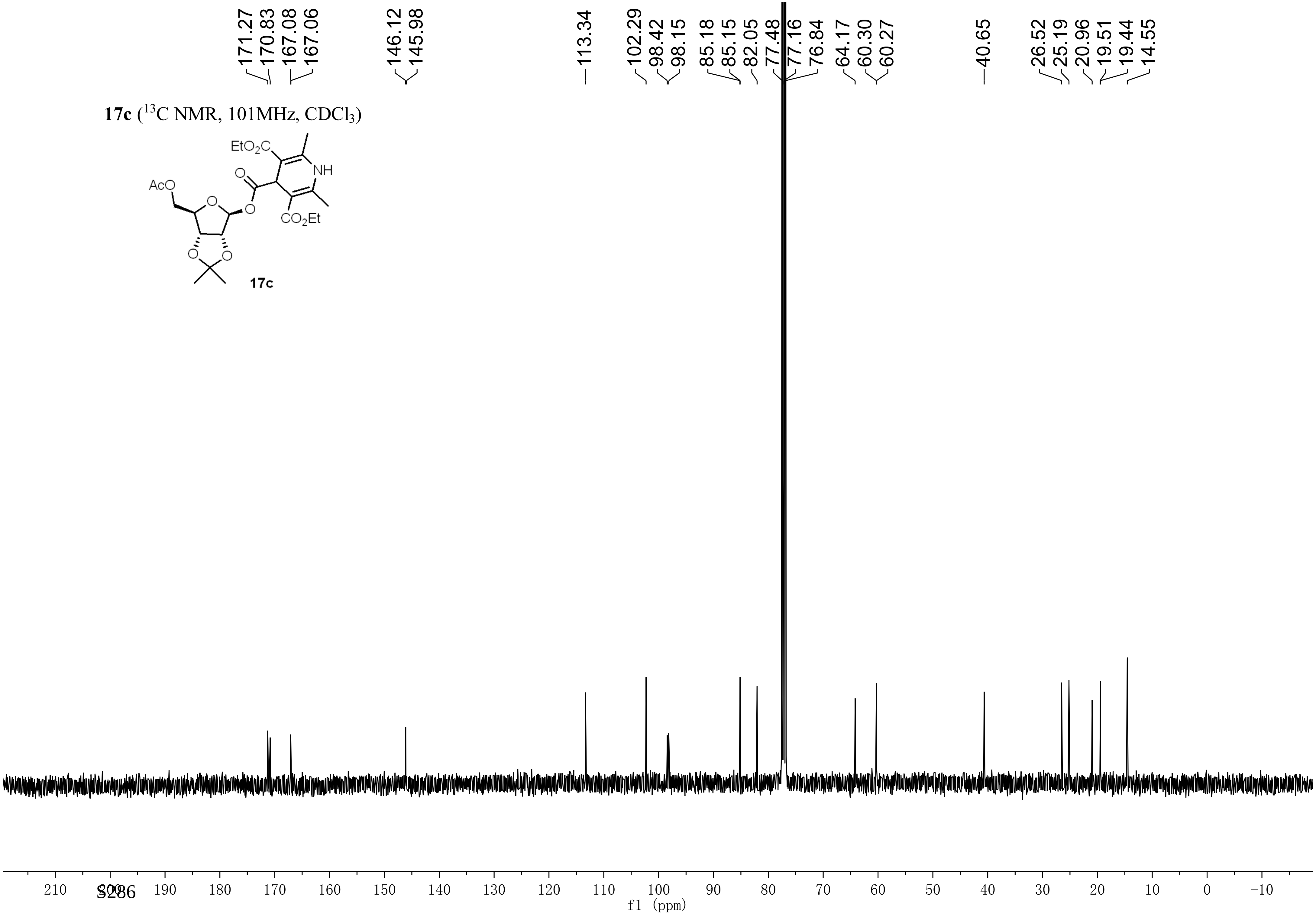


21o (1H - 13C HSQC)
(Boc)2N
OMe
21o
f2 (ppm)
f1 (ppm)

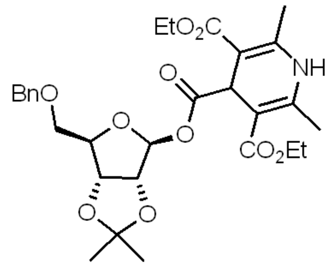
17c (^{1}H NMR, 400MHz, $CDCl_3$)

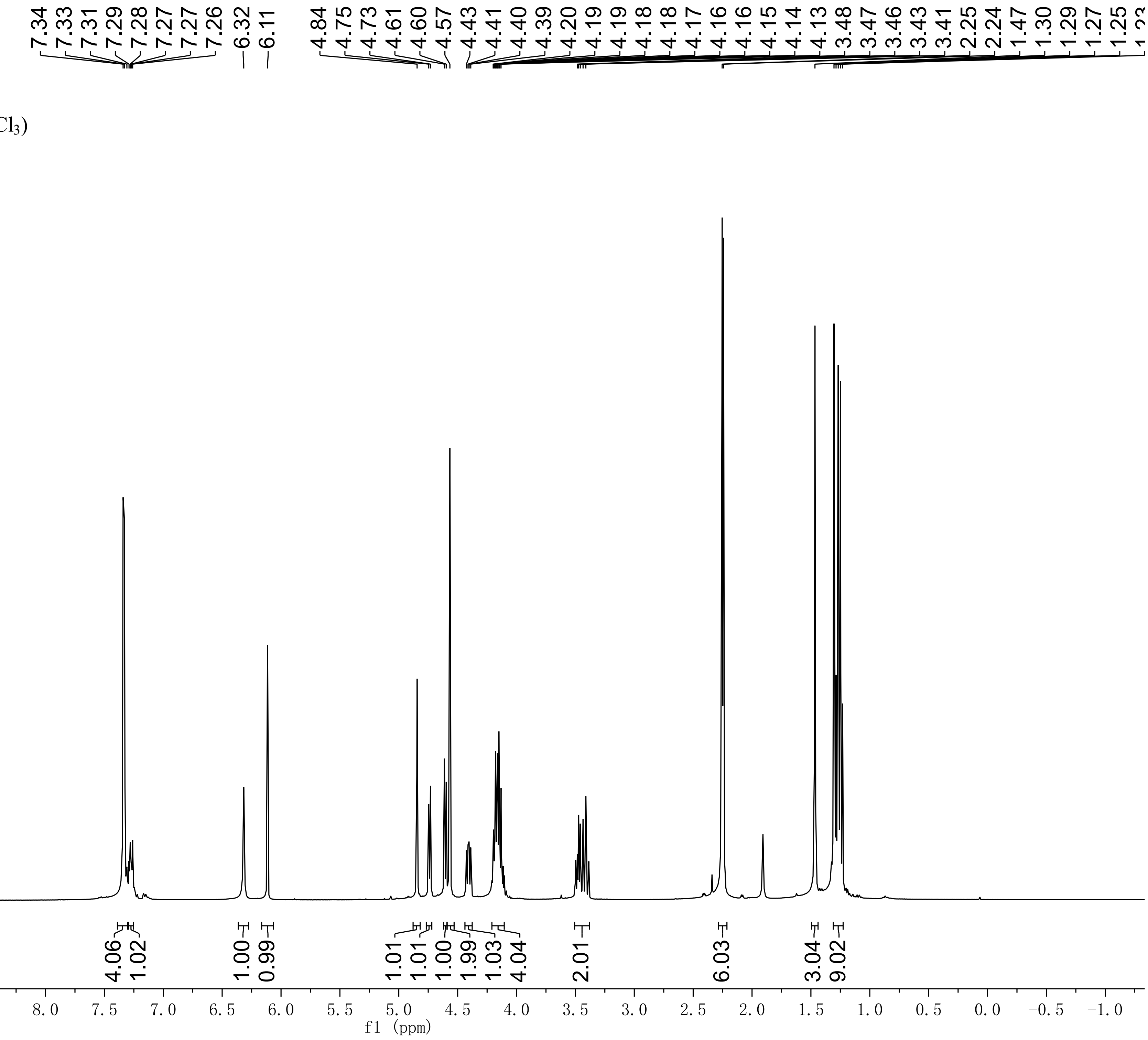


17c

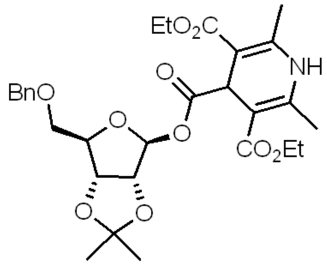

171.27
170.83
167.08
167.06
146.12
145.98
113.34
102.29
98.42
98.15
85.18
85.15
82.05
77.48
77.16
76.84
64.17
60.30
60.27
40.65
26.52
25.19
20.96
19.51
19.44
14.55
17c (^{13}C NMR, 101MHz, $CDCl_3$)
EtO_2C
NH
O
AcO
O
O
CO_2Et
O
O
17c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

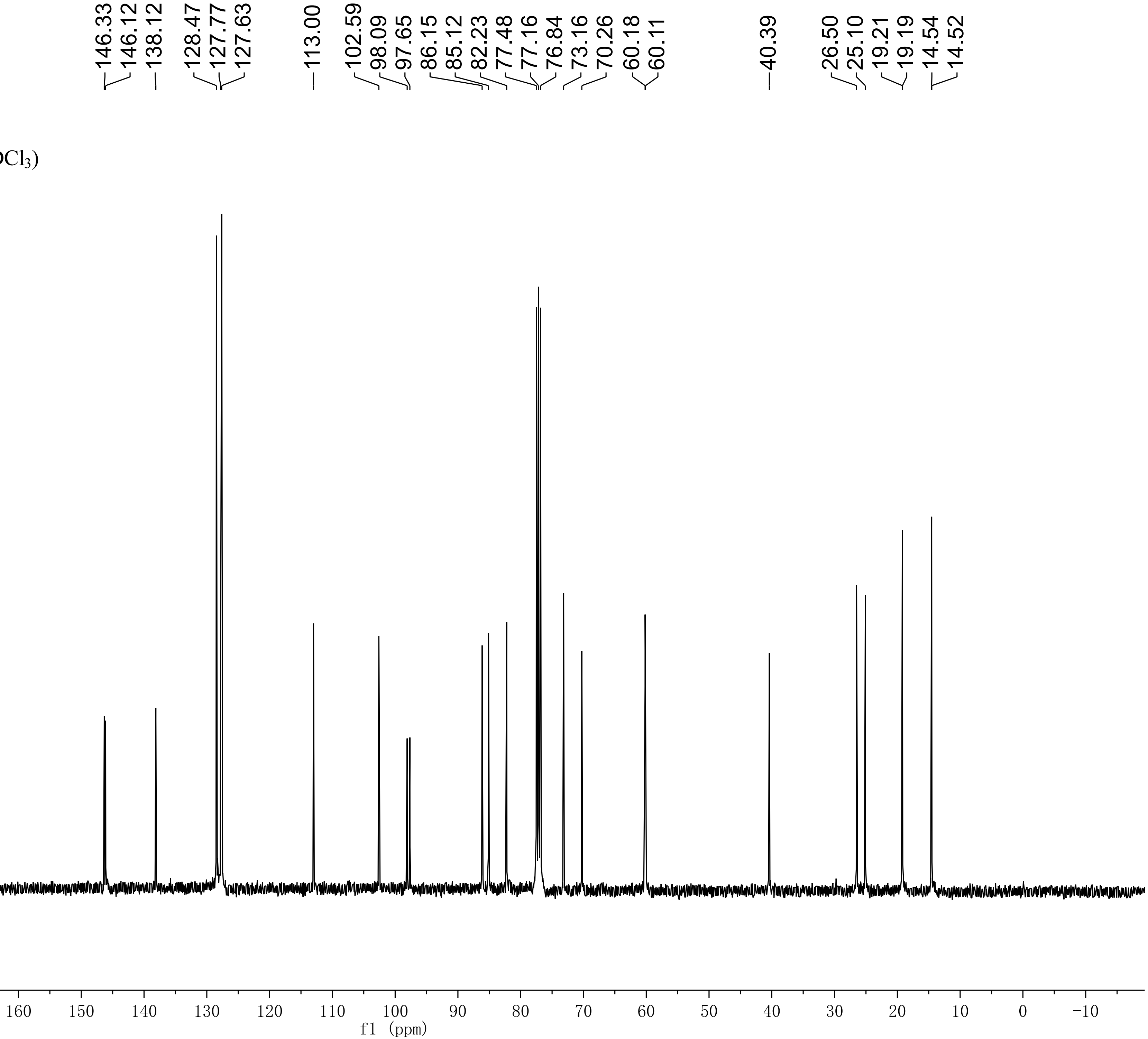
17e (^{1}H NMR, 400MHz, $CDCl_3$)



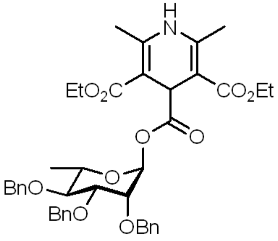


17e (^{13}C NMR, 101MHz, $CDCl_3$)

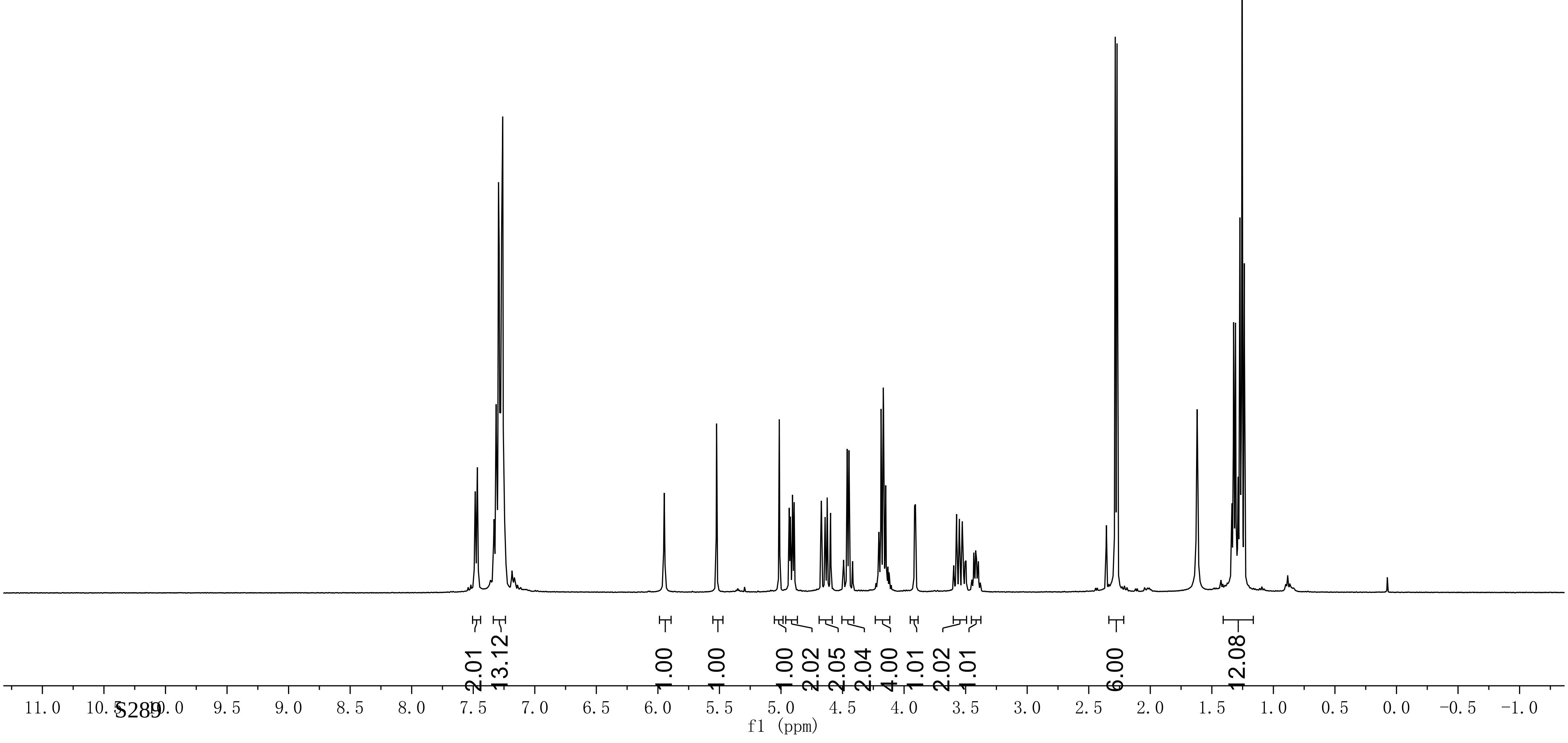




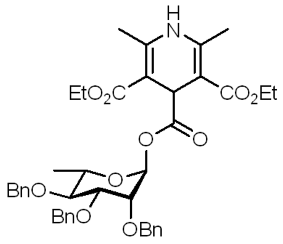
17p (^{1}H NMR, 400MHz, $CDCl_3$)



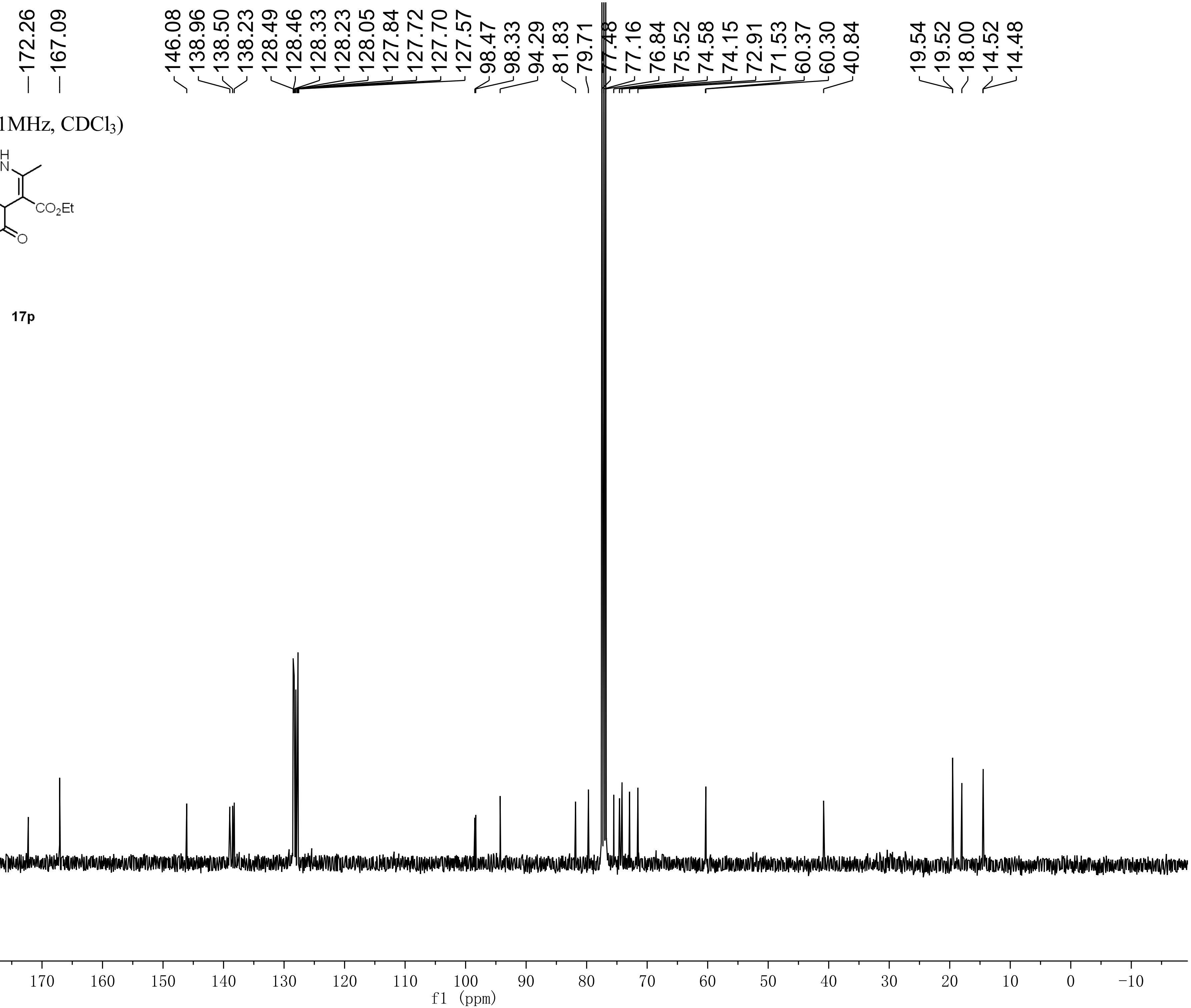
17p



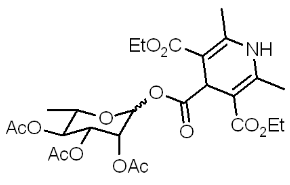
17p (^{13}C NMR, 101MHz, $CDCl_3$)



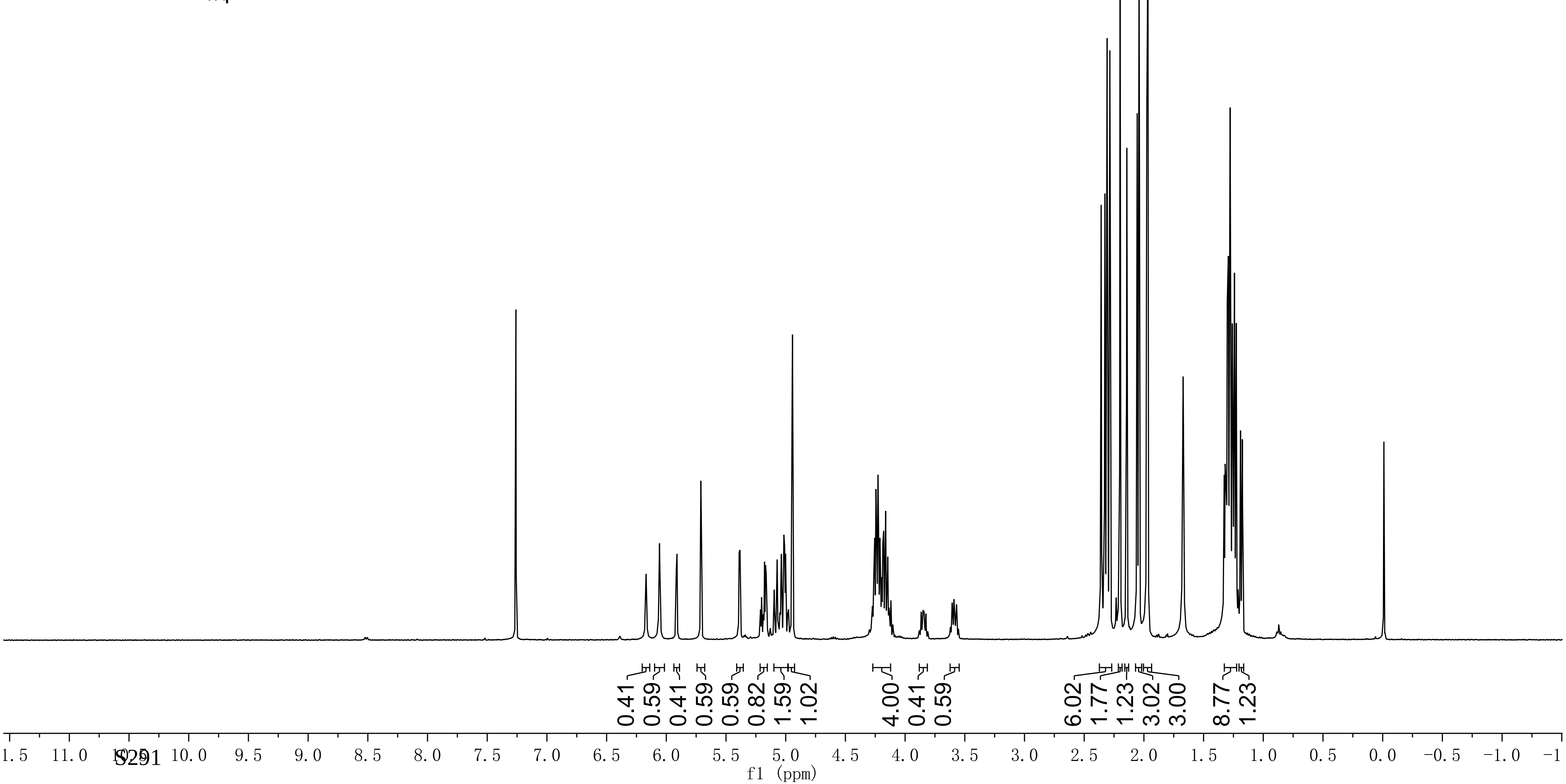
17p



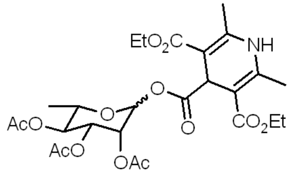
17q (^{1}H NMR, 400MHz, $CDCl_3$)



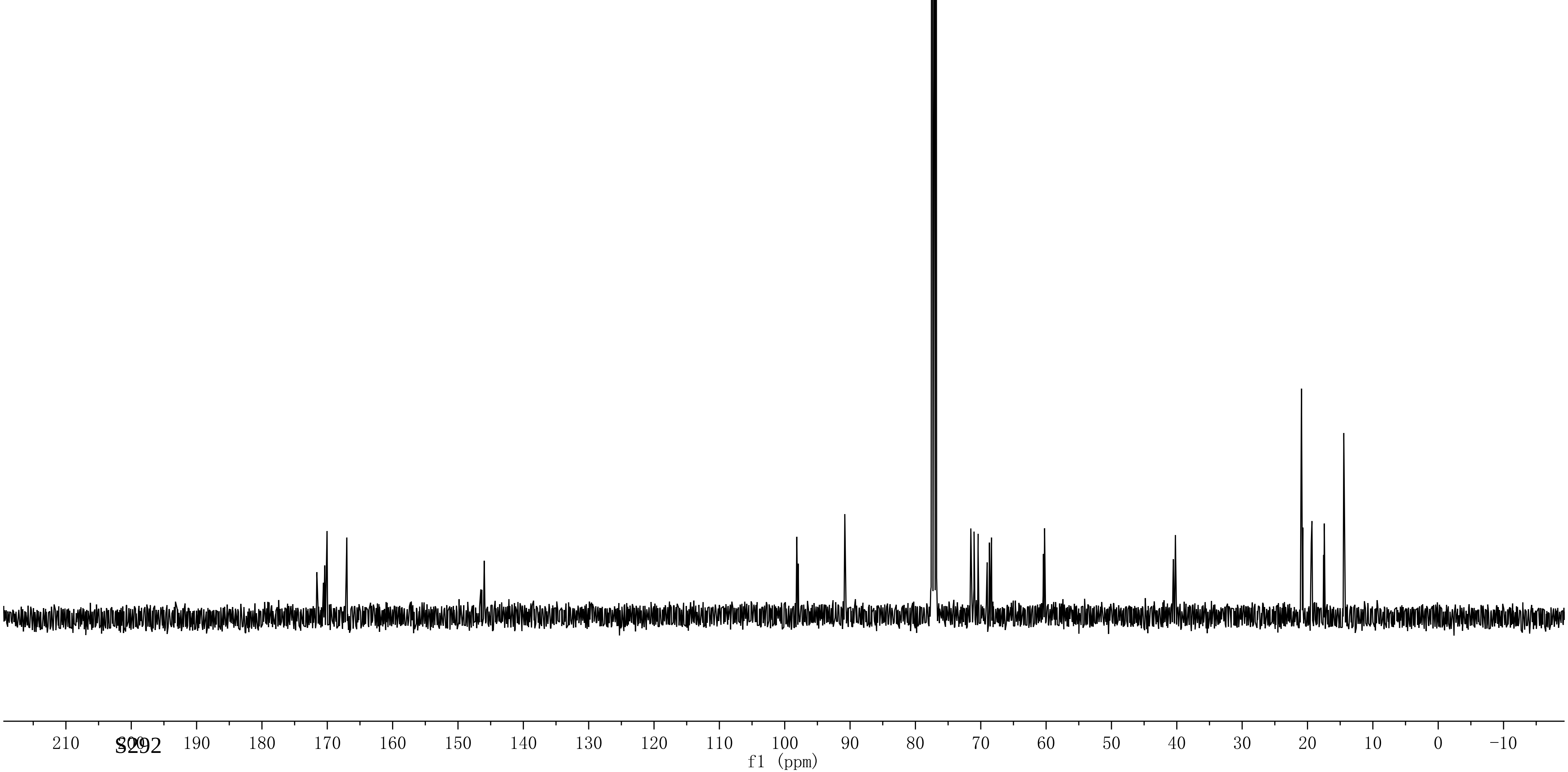
17q

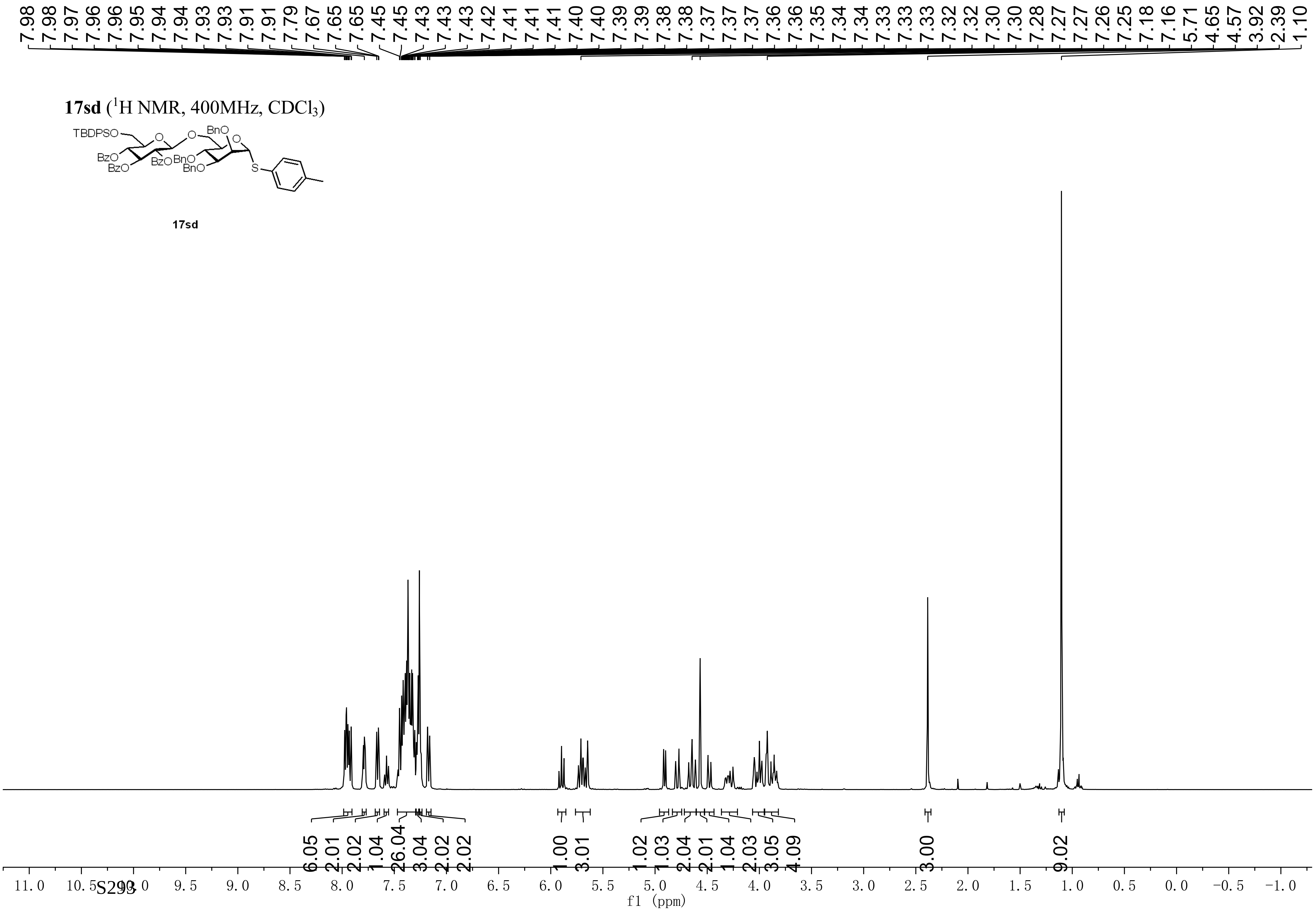


17q (^{13}C NMR, 101MHz, $CDCl_3$)



17q

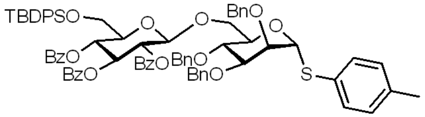




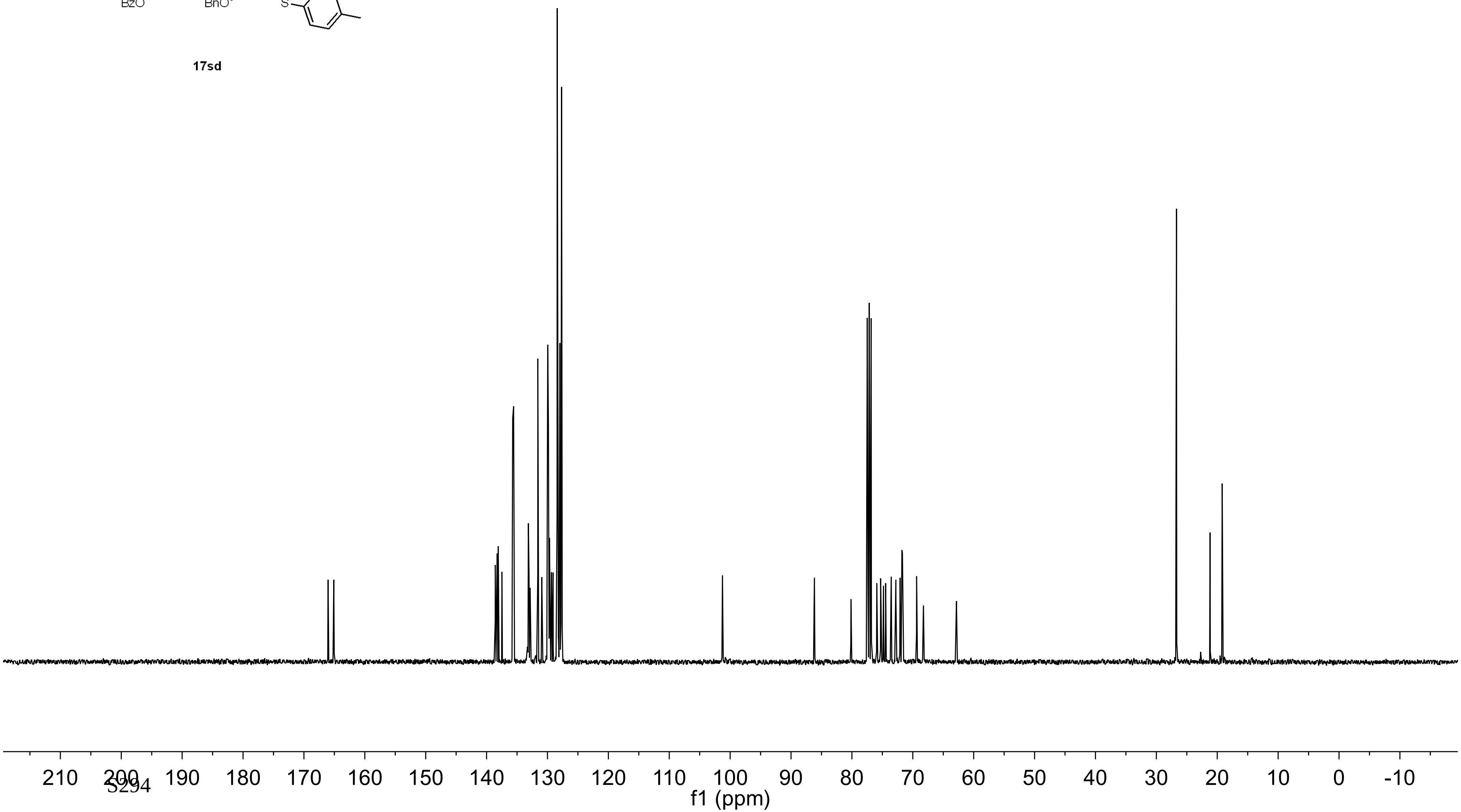
7.98 7.98 7.97 7.96 7.96 7.95 7.94 7.94 7.93 7.93 7.91 7.91 7.79 7.67 7.65 7.65 7.45 7.45 7.43 7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.30 7.30 7.28 7.27 7.27 7.26 7.25 7.18 7.16 5.71 4.65 4.57 3.92 2.39 1.10
17sd (1H NMR, 400MHz, CDCl3)
TBDPSO
BzO
BzO
BzO
BnO
BnO
BnO
S
17sd
6.05 2.01 2.02 1.04 26.04 3.04 2.02 2.02 1.00 3.01 1.02 1.03 2.04 2.01 1.04 2.03 3.05 4.09 3.00 9.02
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)

166.04
165.10
165.05
138.57
138.27
138.08
137.47
135.71
135.56
133.26
133.14
133.03
132.84
131.58
130.93
129.96
129.90
129.84
129.81
129.70
129.67
129.65
129.33
129.07
128.40
128.35
128.30
128.26
127.95
127.75
127.72
127.68
127.61
101.26
86.16
80.15
77.48
77.16
76.84
75.91
75.28
74.82
74.46
73.54
72.78
72.09
71.79
71.71
69.37
68.25
62.83
26.70
21.18
19.19

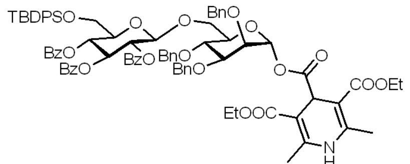
17sd (^{13}C NMR, 101MHz, $CDCl_3$)



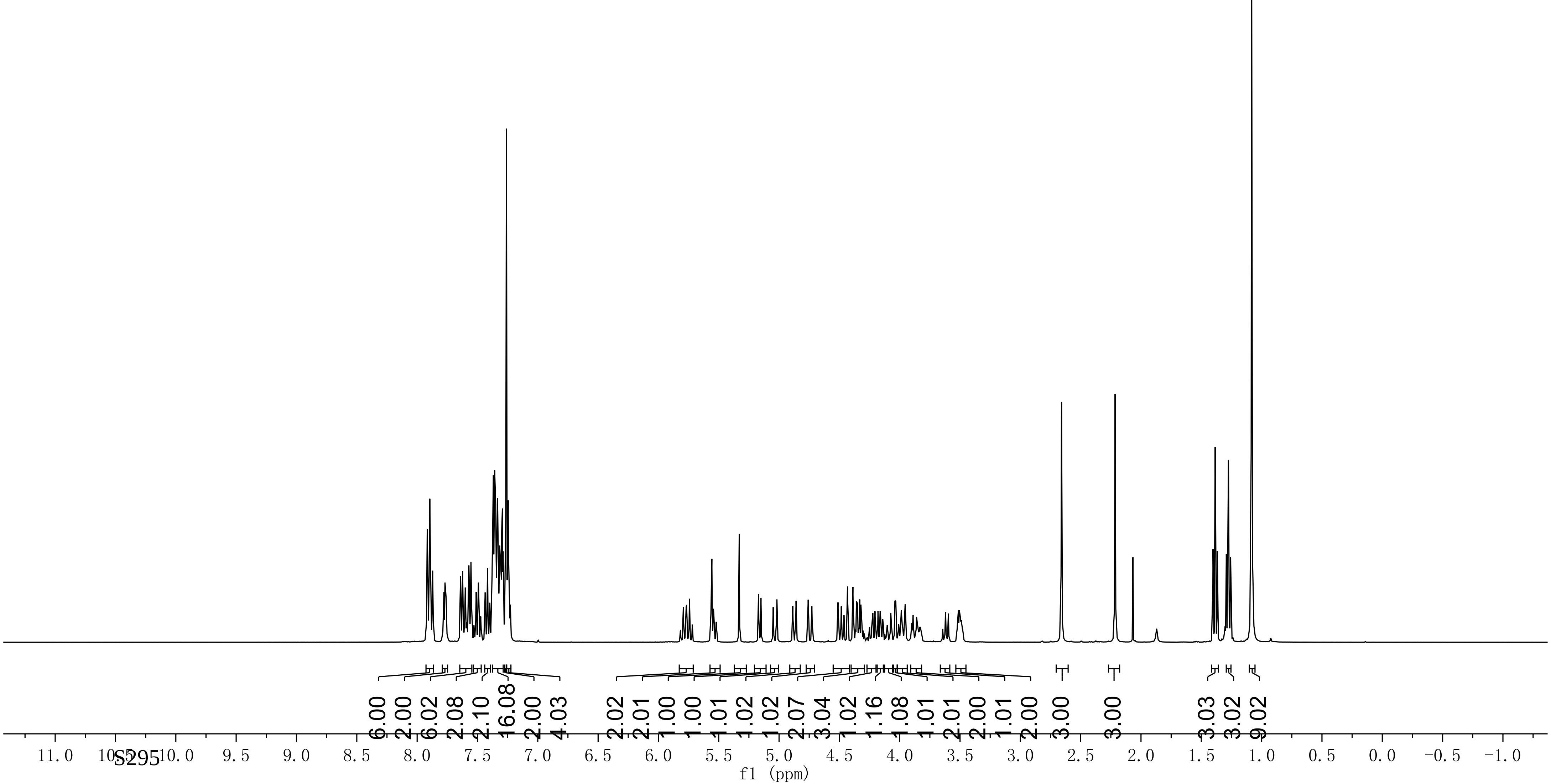
17sd



17s (^{1}H NMR, 400MHz, $CDCl_3$)

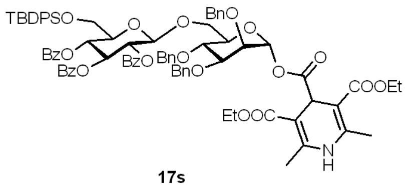


17s

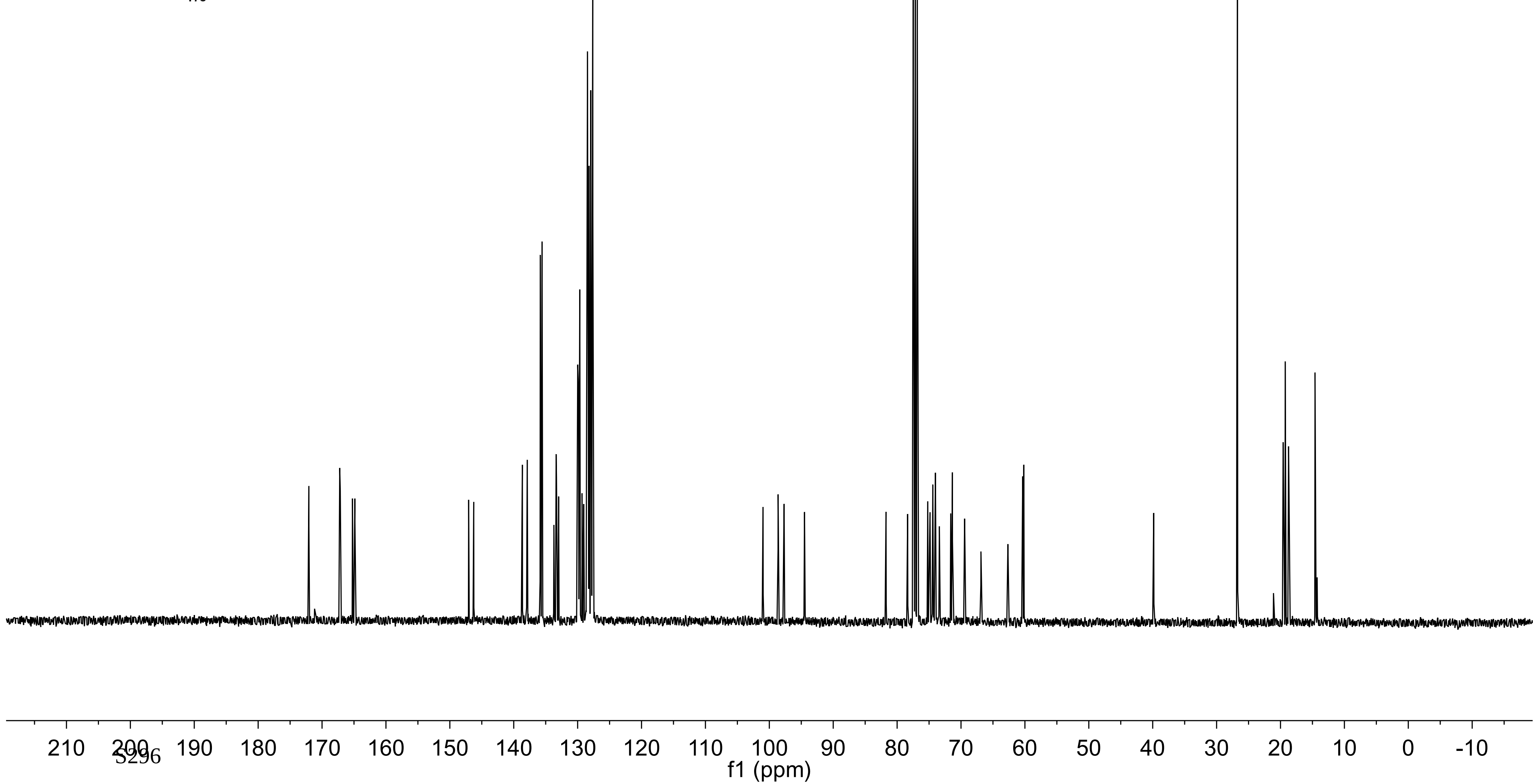


172.06, 167.23, 167.22, 167.15, 165.24, 164.86, 147.05, 146.26, 138.65, 137.96, 137.89, 135.85, 135.57, 133.36, 133.31, 132.97, 129.99, 129.87, 129.74, 129.67, 129.31, 129.05, 128.59, 128.53, 128.51, 128.50, 128.47, 128.40, 128.32, 128.21, 127.95, 127.85, 127.71, 127.69, 127.63, 100.98, 98.63, 97.69, 94.49, 81.74, 77.48, 77.16, 76.84, 75.20, 74.85, 74.44, 74.41, 74.00, 71.61, 71.35, 60.35, 60.17, 39.84, 26.74, 19.59, 19.26, 18.73, 14.60, 14.52

17s (^{13}C NMR, 101MHz, $CDCl_3$)

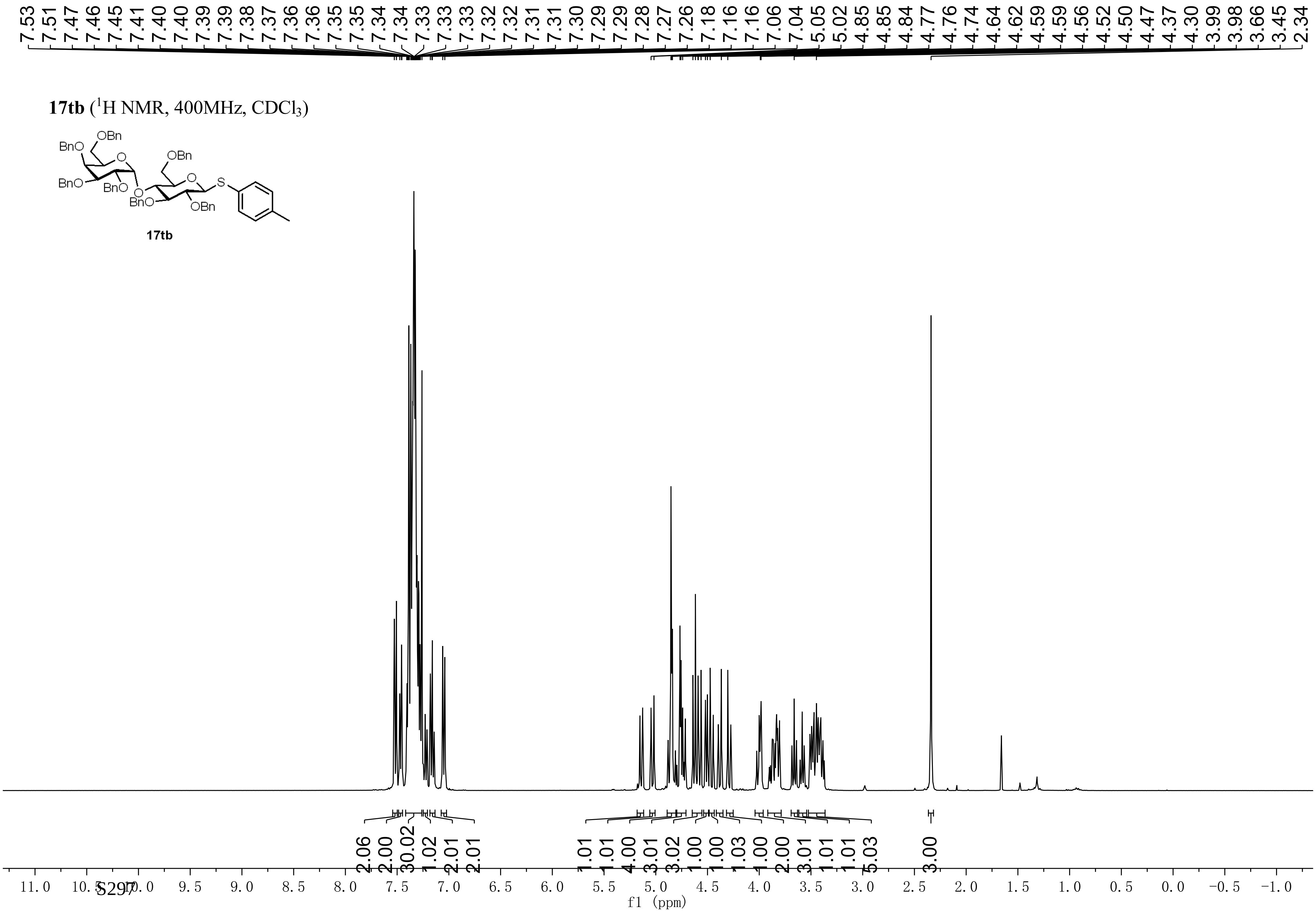


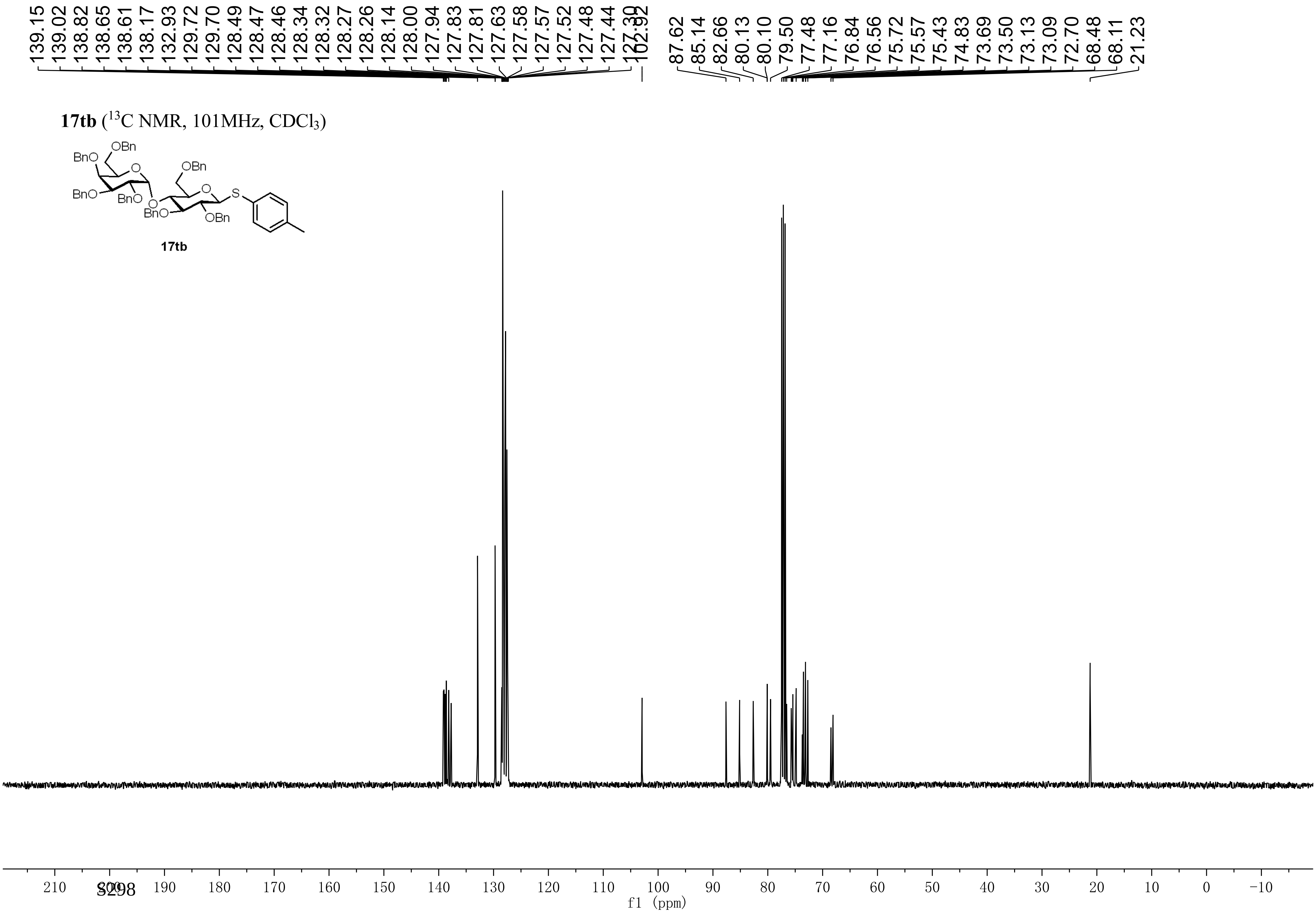
17s



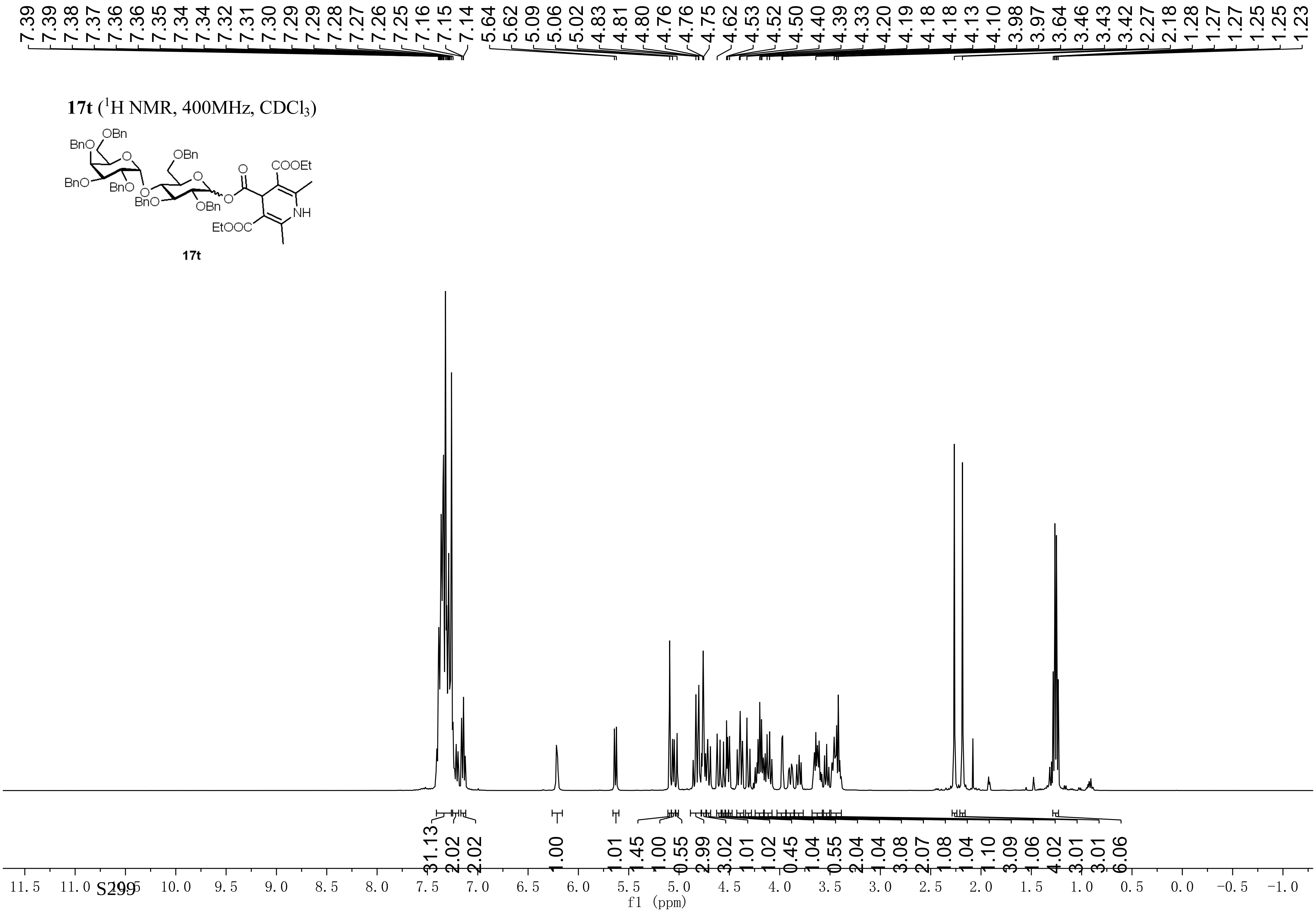
17tb (^{1}H NMR, 400MHz, $CDCl_3$)

17tb

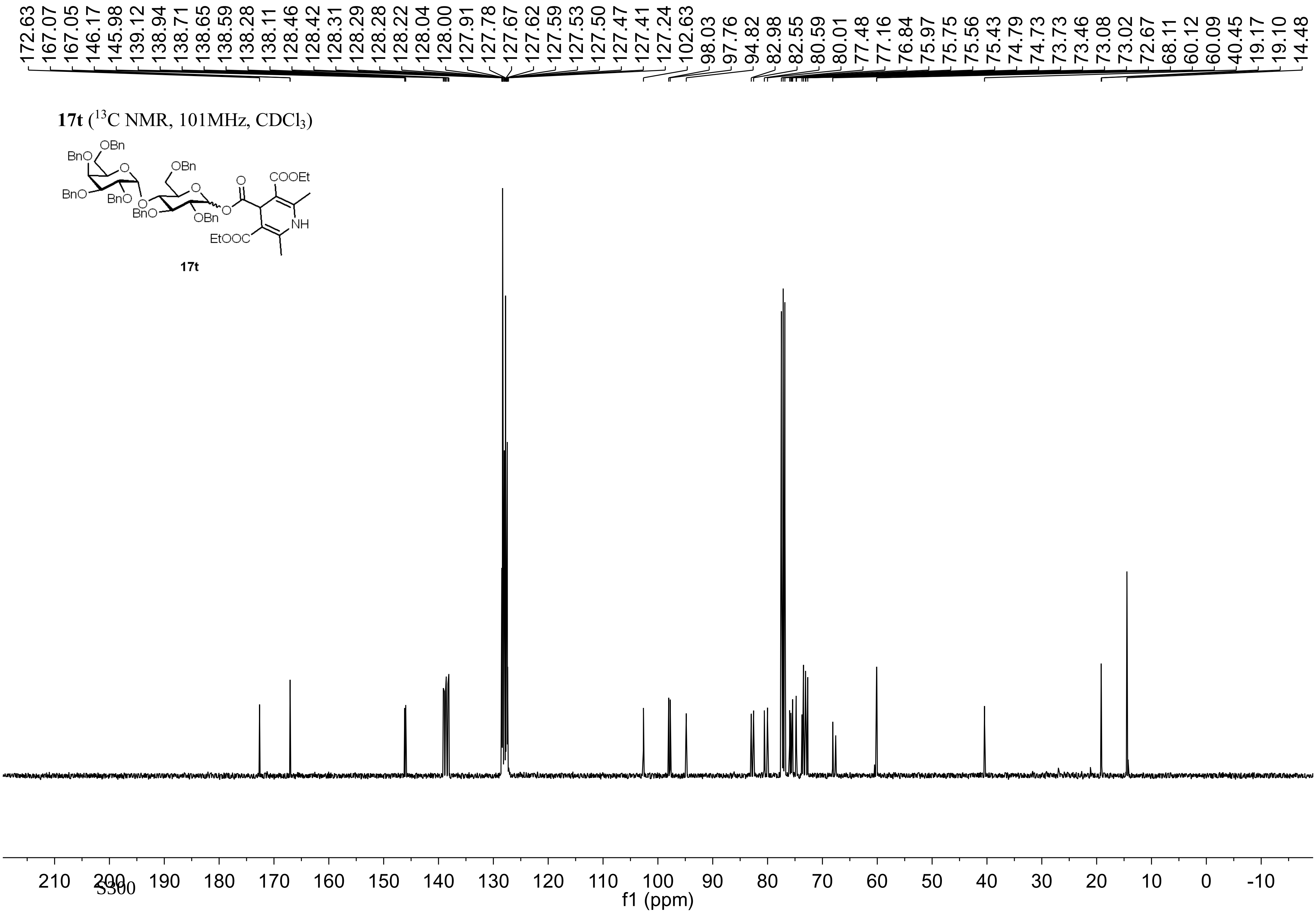



139.15
139.02
138.82
138.65
138.61
138.17
132.93
129.72
129.70
128.49
128.47
128.46
128.34
128.32
128.27
128.26
128.14
128.00
127.94
127.83
127.81
127.63
127.58
127.57
127.52
127.48
127.44
127.30
102.92
87.62
85.14
82.66
80.13
80.10
79.50
77.48
77.16
76.84
76.56
75.72
75.57
75.43
74.83
73.69
73.50
73.13
73.09
72.70
68.48
68.11
21.23
17tb (^{13}C NMR, 101MHz, $CDCl_3$)
OBn
BnO
O
OBn
O
S
BnO
BnO
O
BnO
OBn
17tb
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)

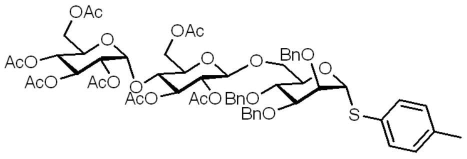
17t (^{1}H NMR, 400MHz, $CDCl_3$)



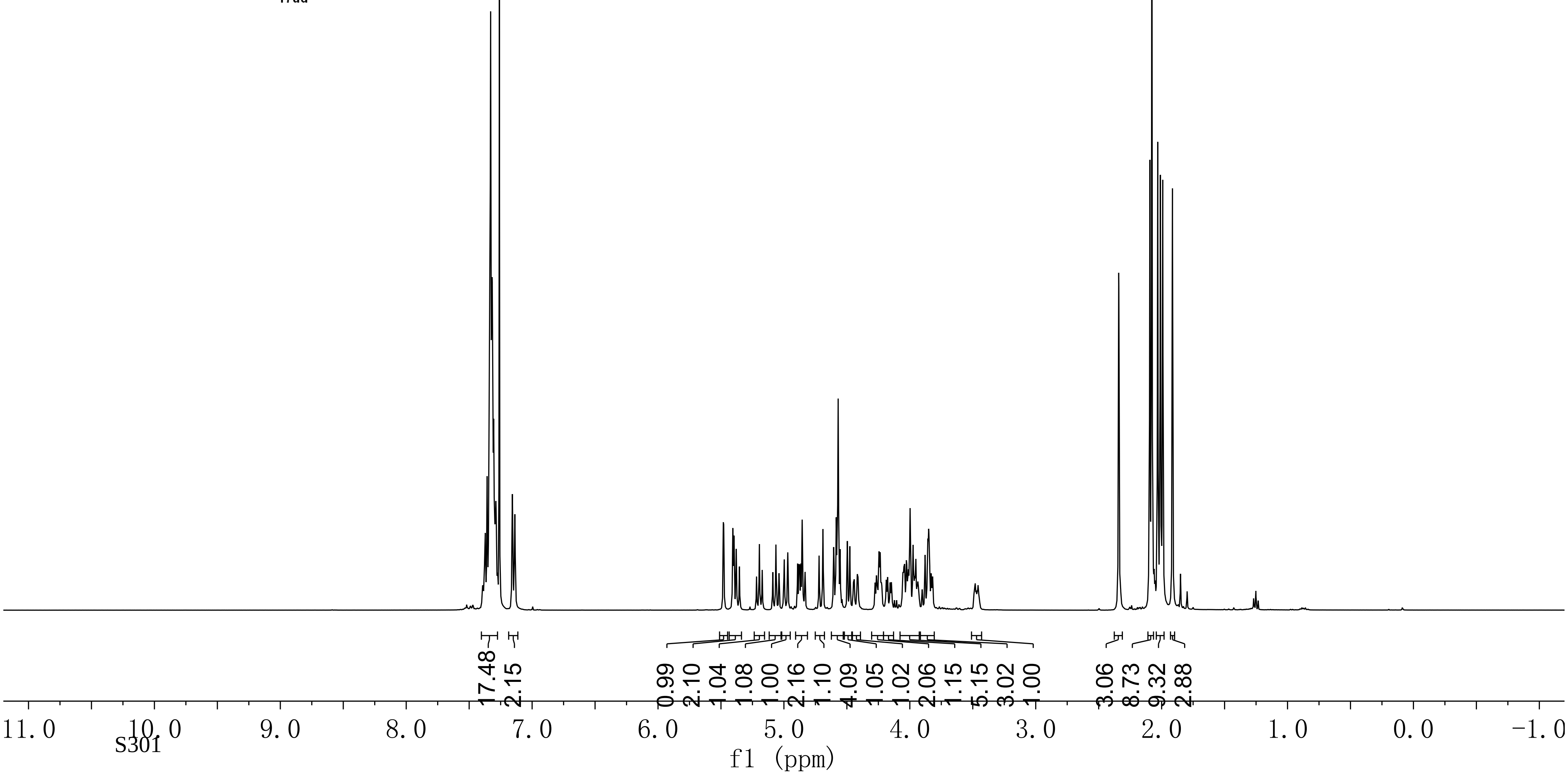
17t (^{13}C NMR, 101MHz, $CDCl_3$)



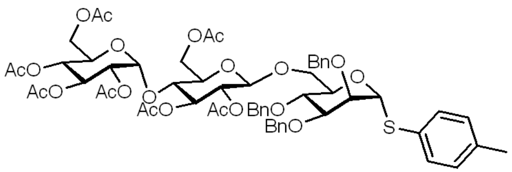
17ud (^1H NMR, 400MHz, $CDCl_3$)



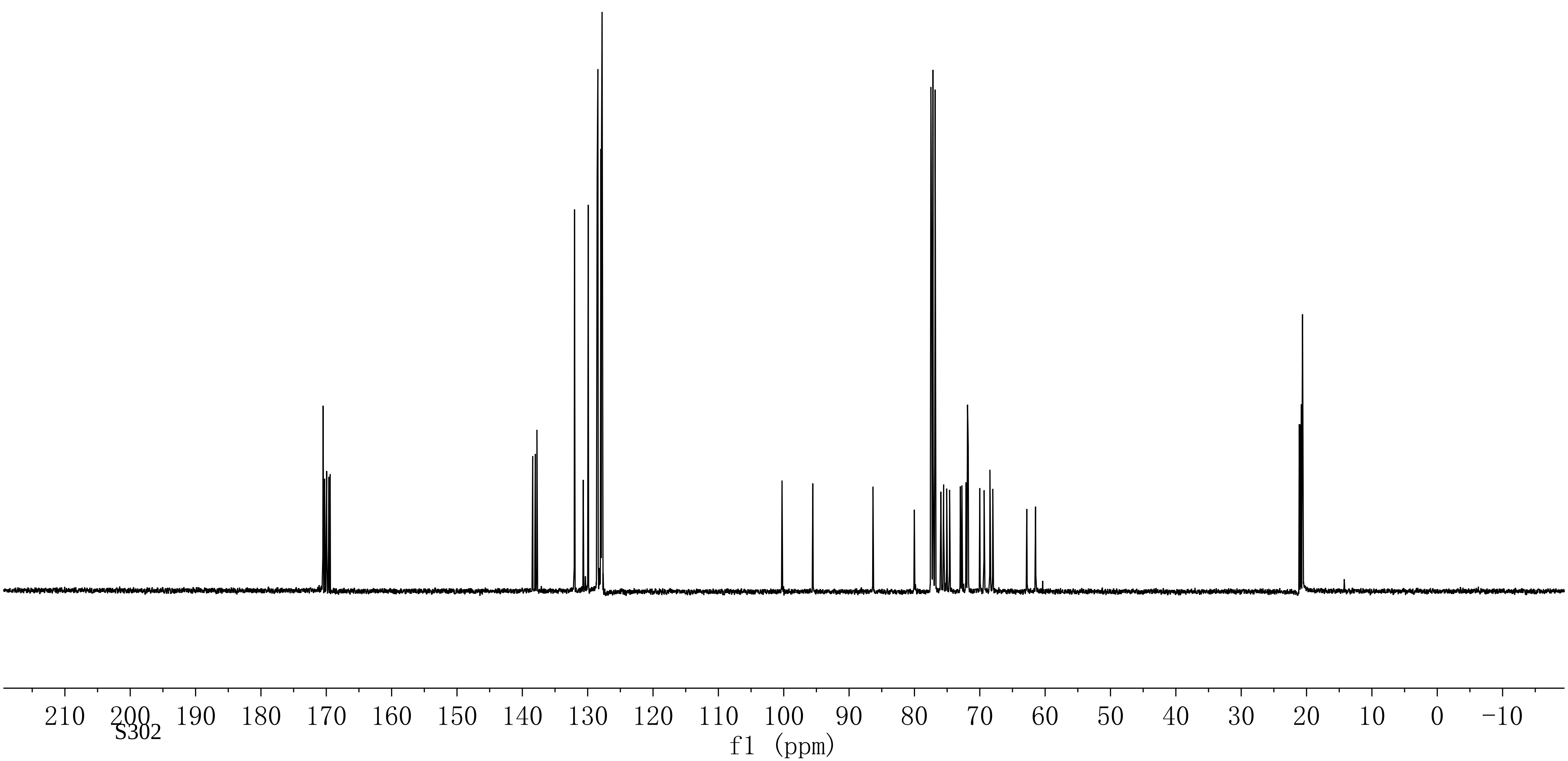
17ud



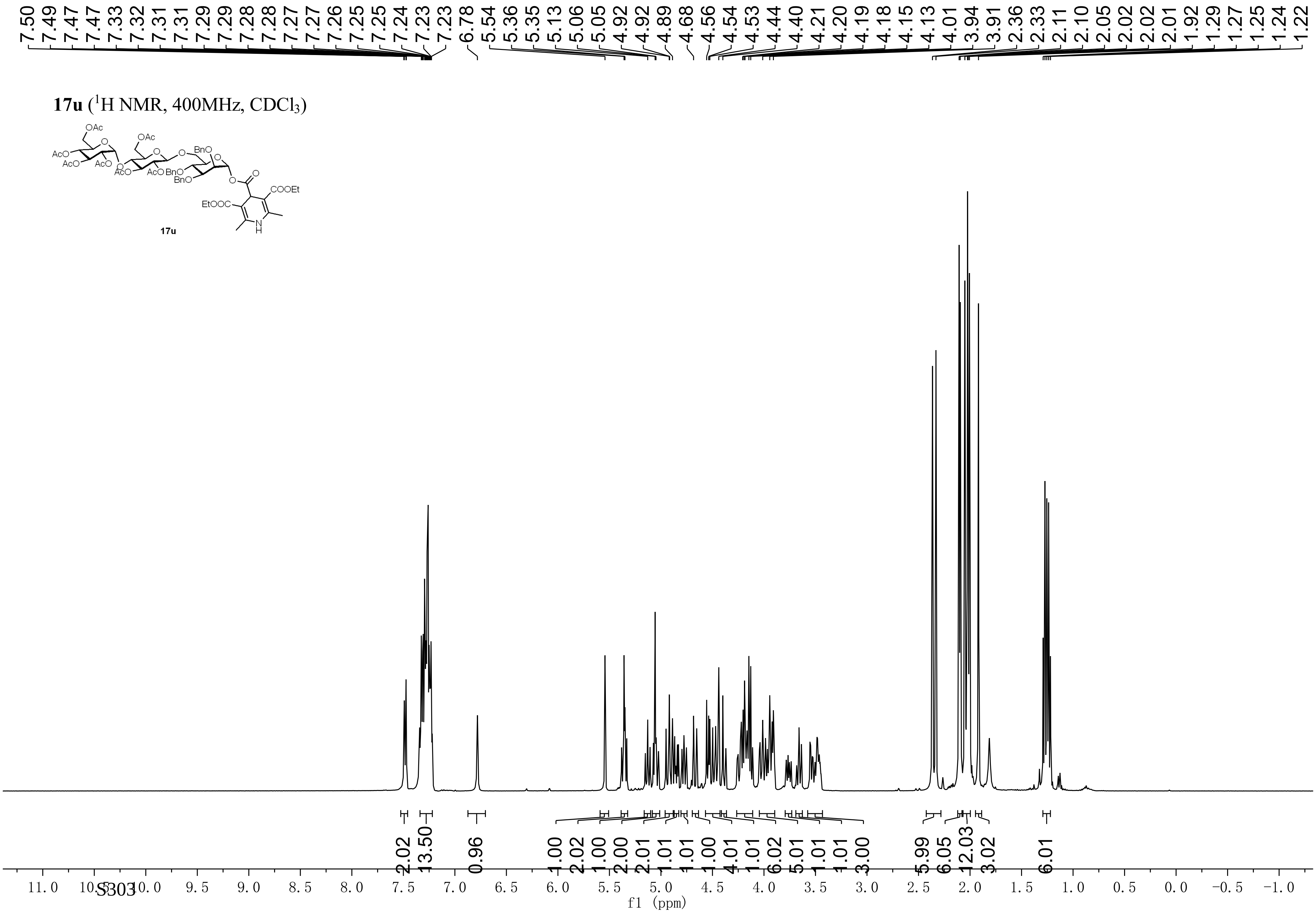
17ud (^{13}C NMR, 101MHz, $CDCl_3$)

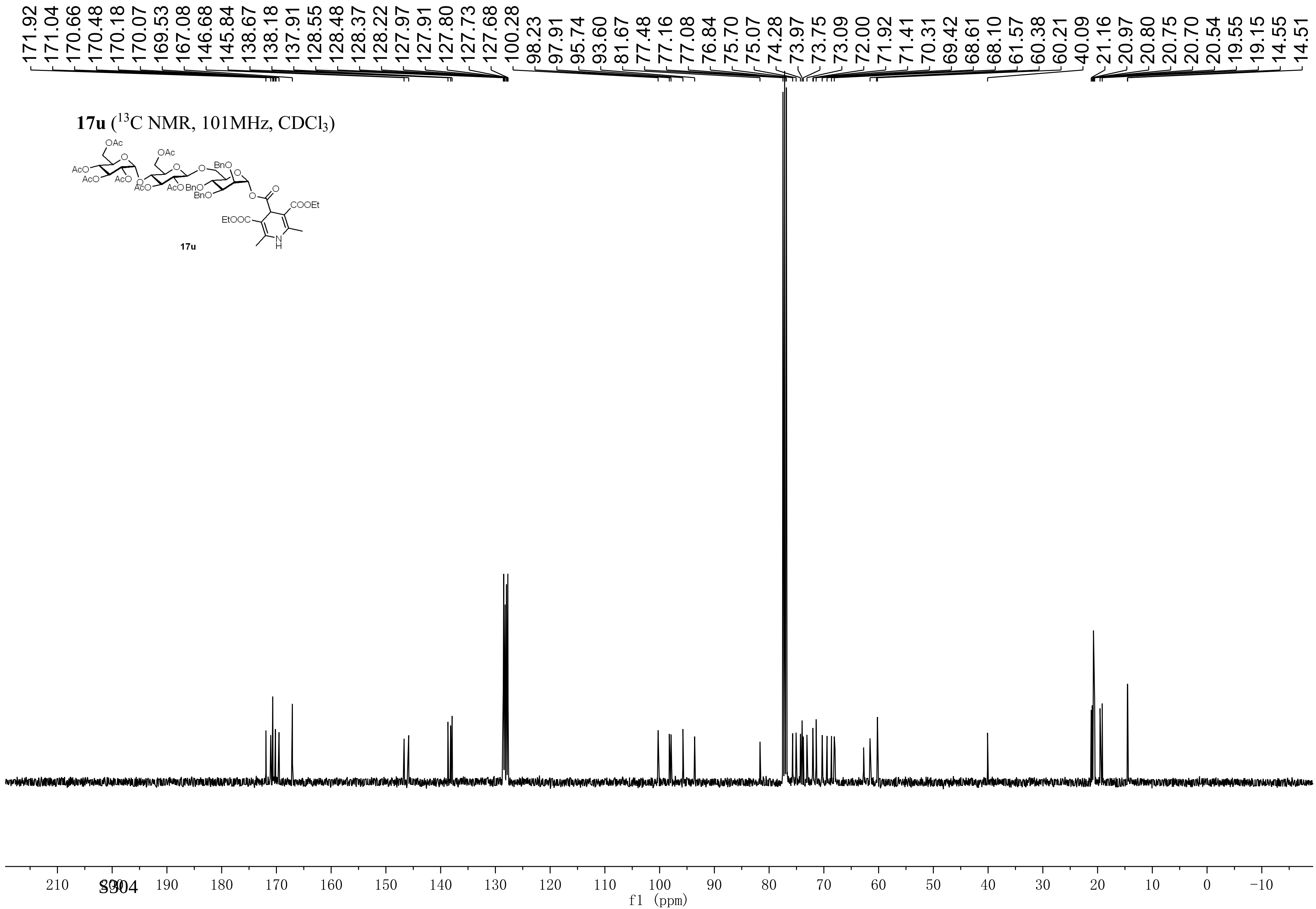


17ud

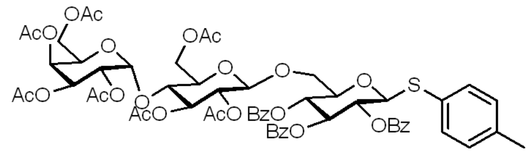


17u (^{1}H NMR, 400MHz, $CDCl_3$)

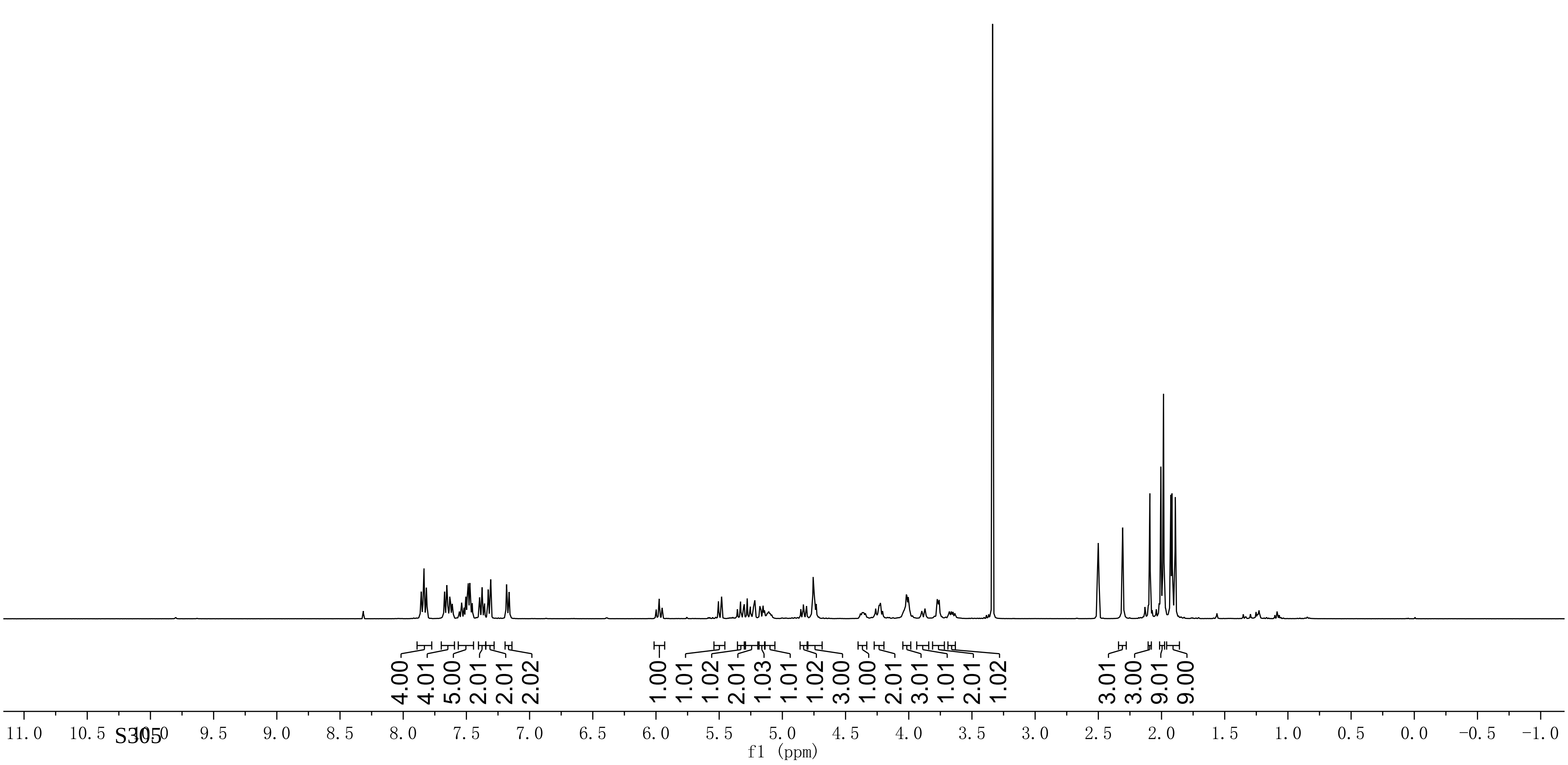



171.92
171.04
170.66
170.48
170.18
170.07
169.53
167.08
146.68
145.84
138.67
138.18
137.91
128.55
128.48
128.37
128.22
127.97
127.91
127.80
127.73
127.68
100.28
98.23
97.91
95.74
93.60
81.67
77.48
77.16
77.08
76.84
75.70
75.07
74.28
73.97
73.75
73.09
72.00
71.92
71.41
70.31
69.42
68.61
68.10
61.57
60.38
60.21
40.09
21.16
20.97
20.80
20.75
20.70
20.54
19.55
19.15
14.55
14.51
17u (13C NMR, 101MHz, CDCl3)
OAc
AcO
AcO
AcO
OAc
O
AcO
AcO
BnO
BnO
BnO
BnO
O
COOEt
EtOOC
N
H
17u
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)

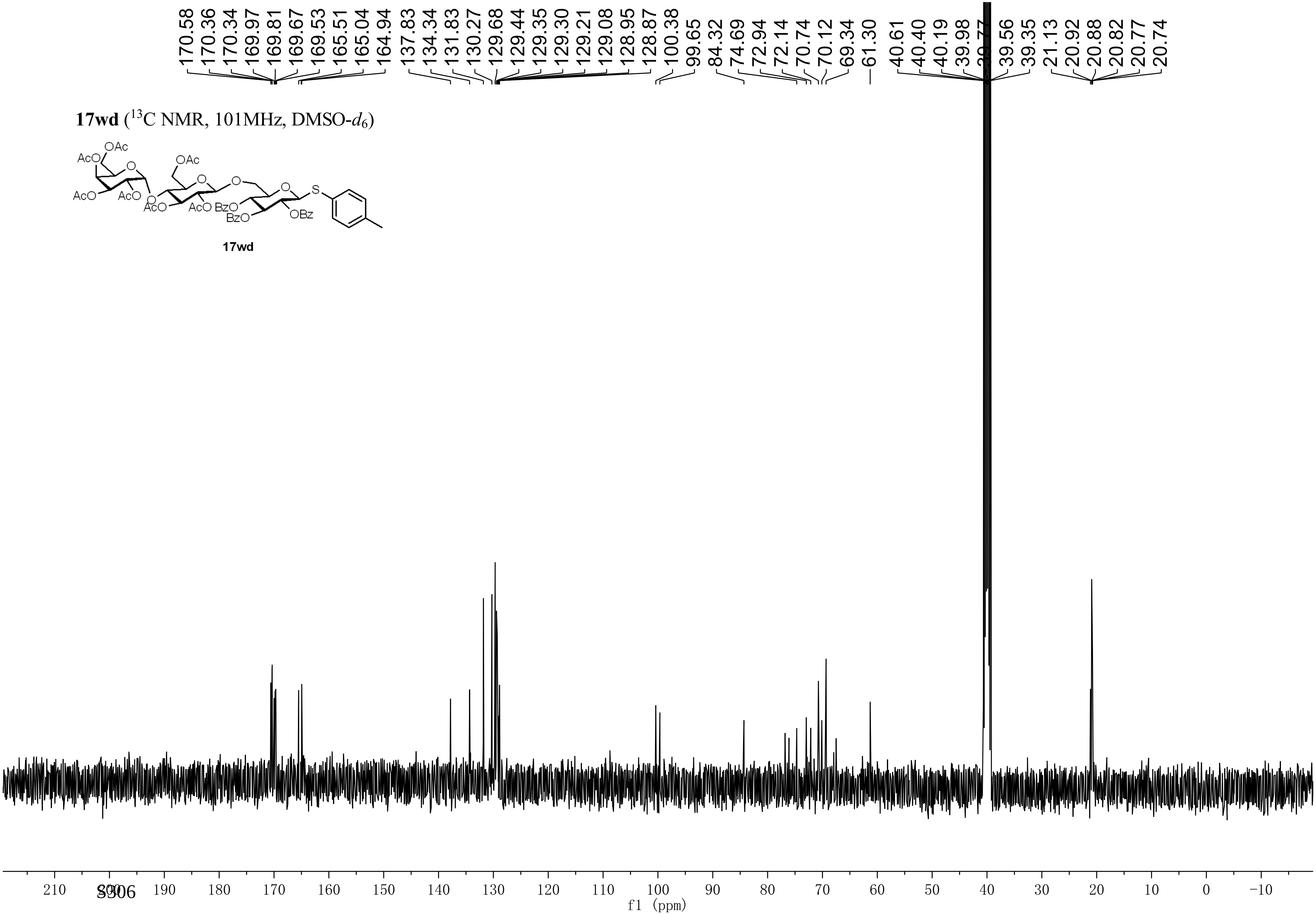
17wd (^{1}H NMR, 400MHz, DMSO-d_6)



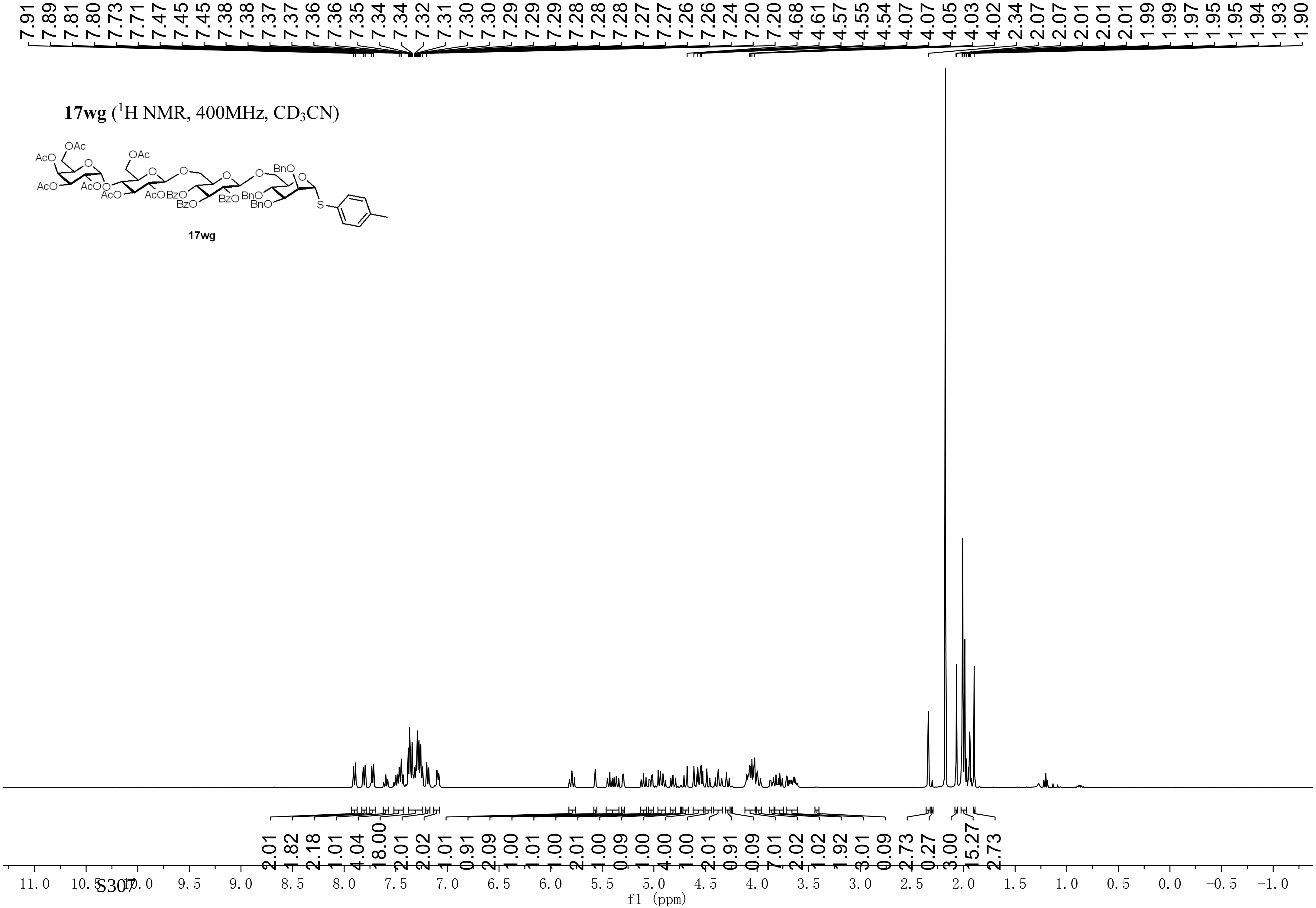
17wd



17wd (^{13}C NMR, 101MHz, DMSO-d_6)



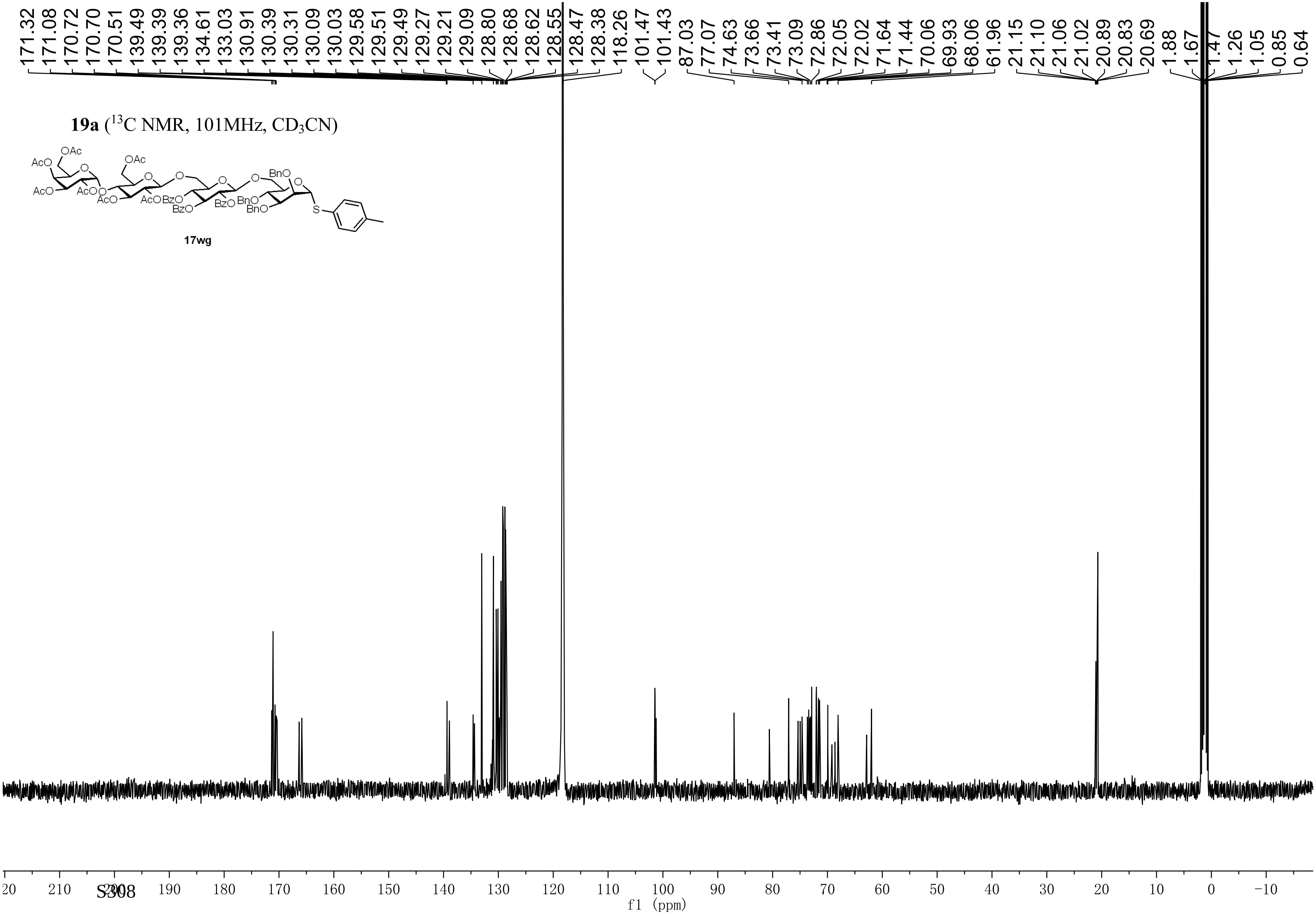
17wg (^{1}H NMR, 400MHz, CD_3CN)



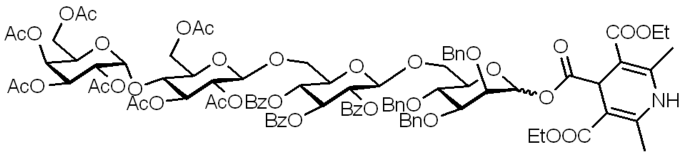
17wg

19a (^{13}C NMR, 101MHz, CD_3CN)

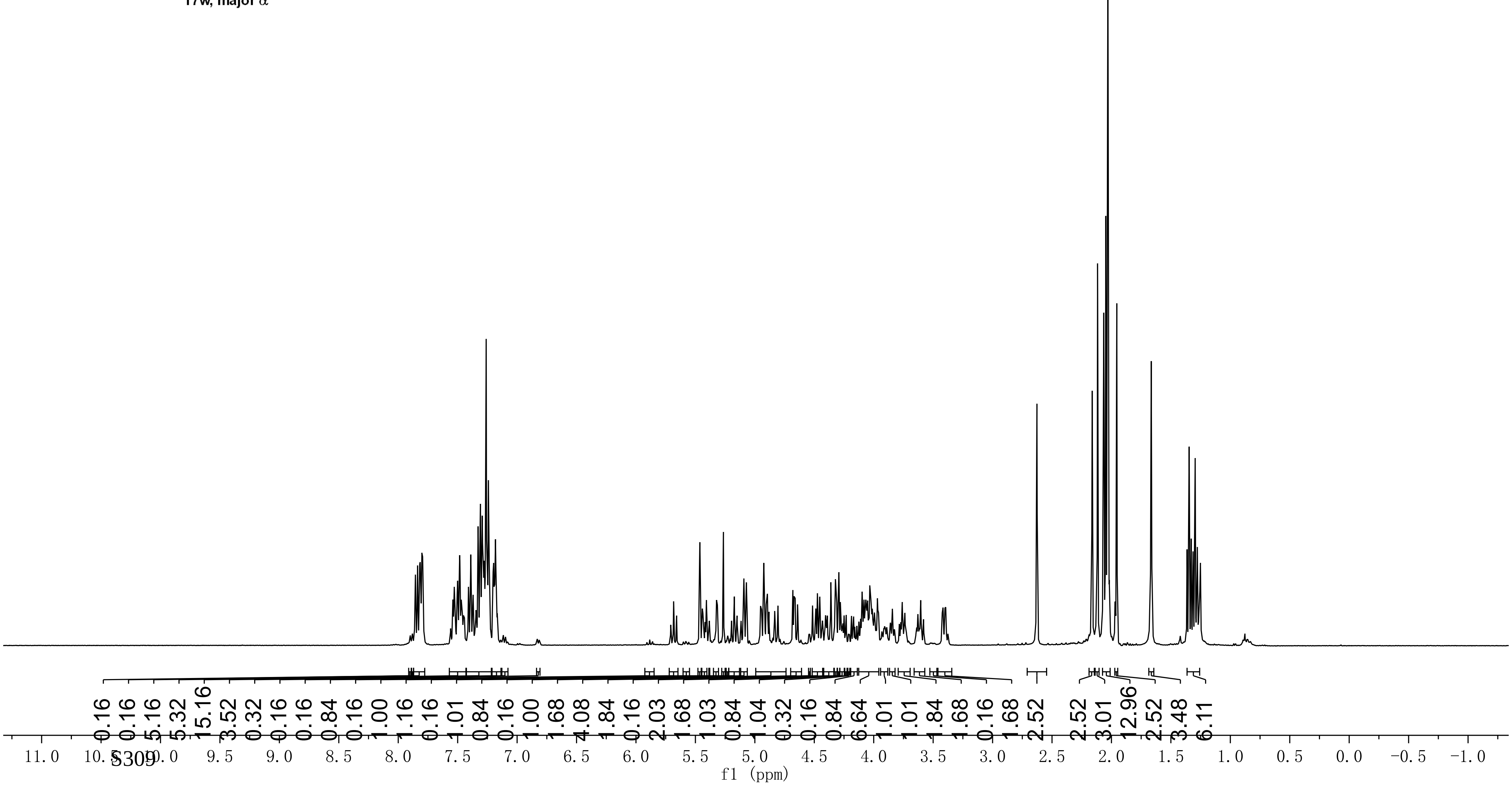
17wg



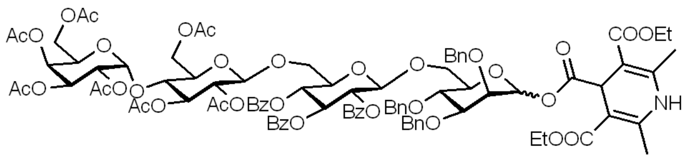
17w ([1]H NMR, 400MHz, $CDCl_3$)



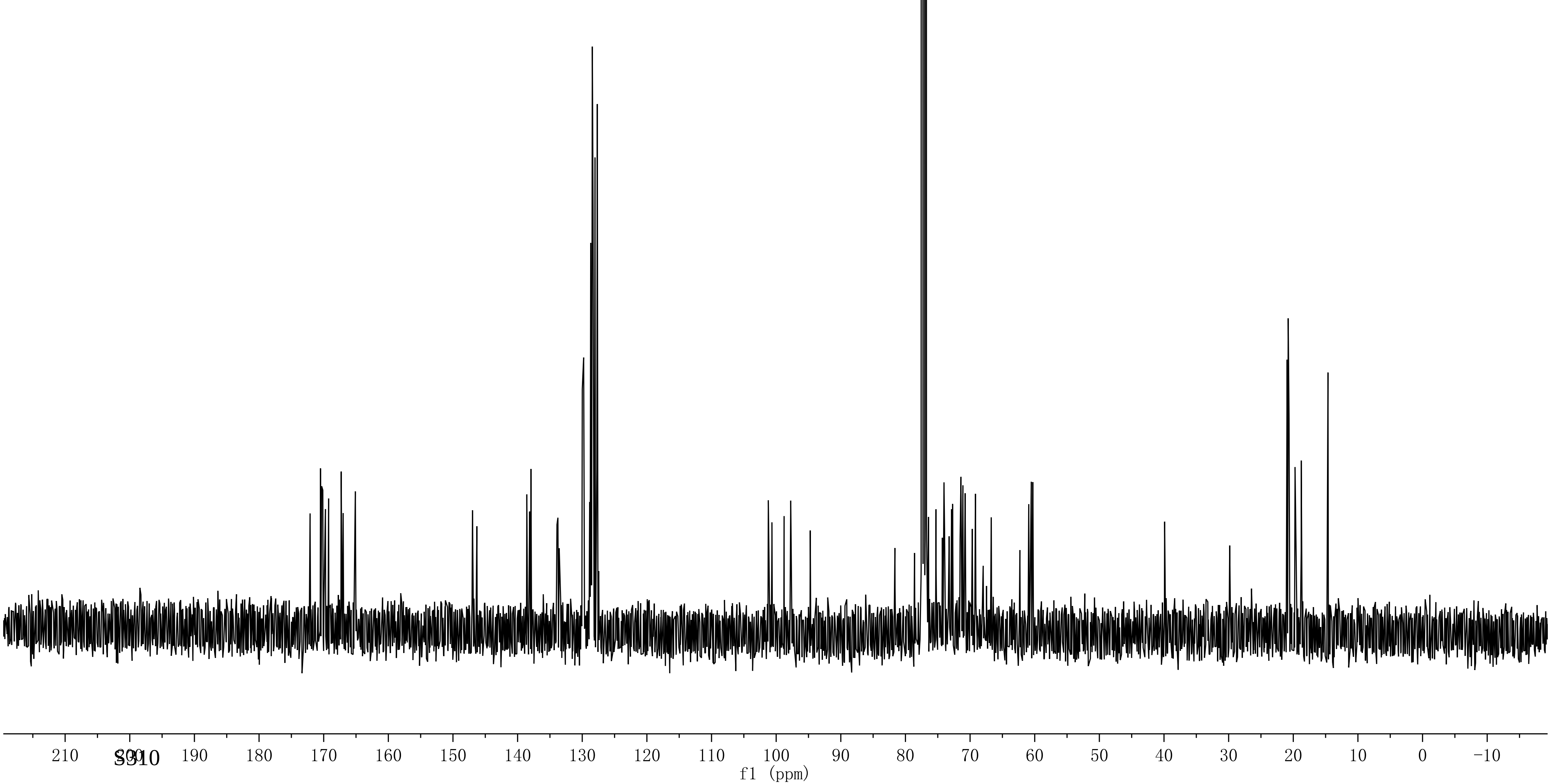
17w, major α



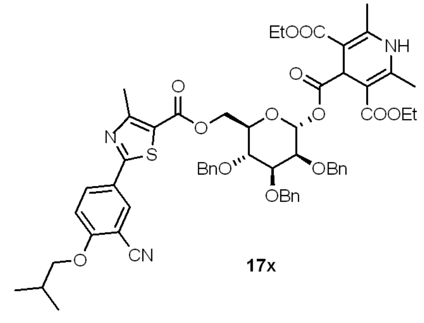
17w (^{13}C NMR, 101MHz, $CDCl_3$)



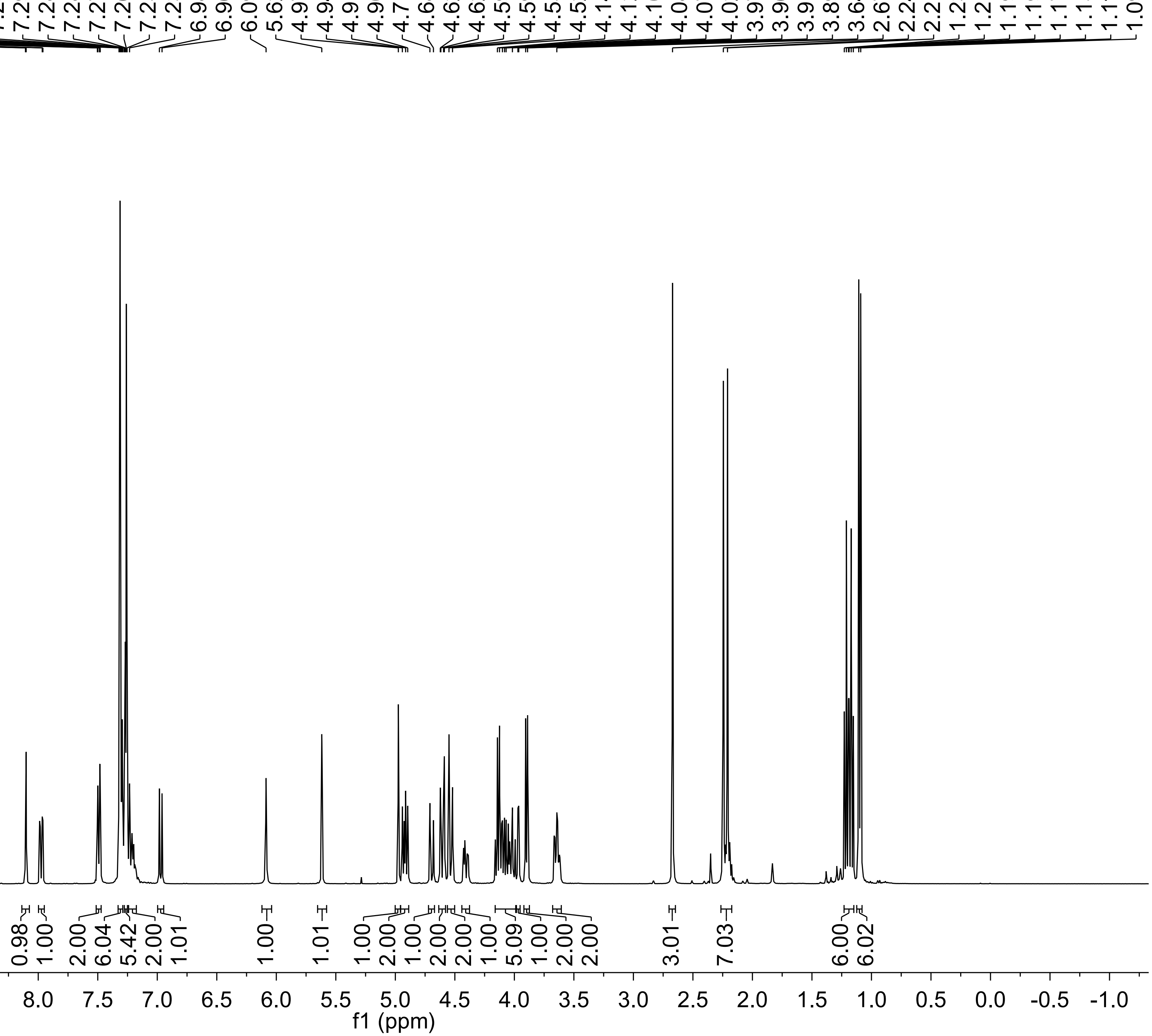
17w, major α

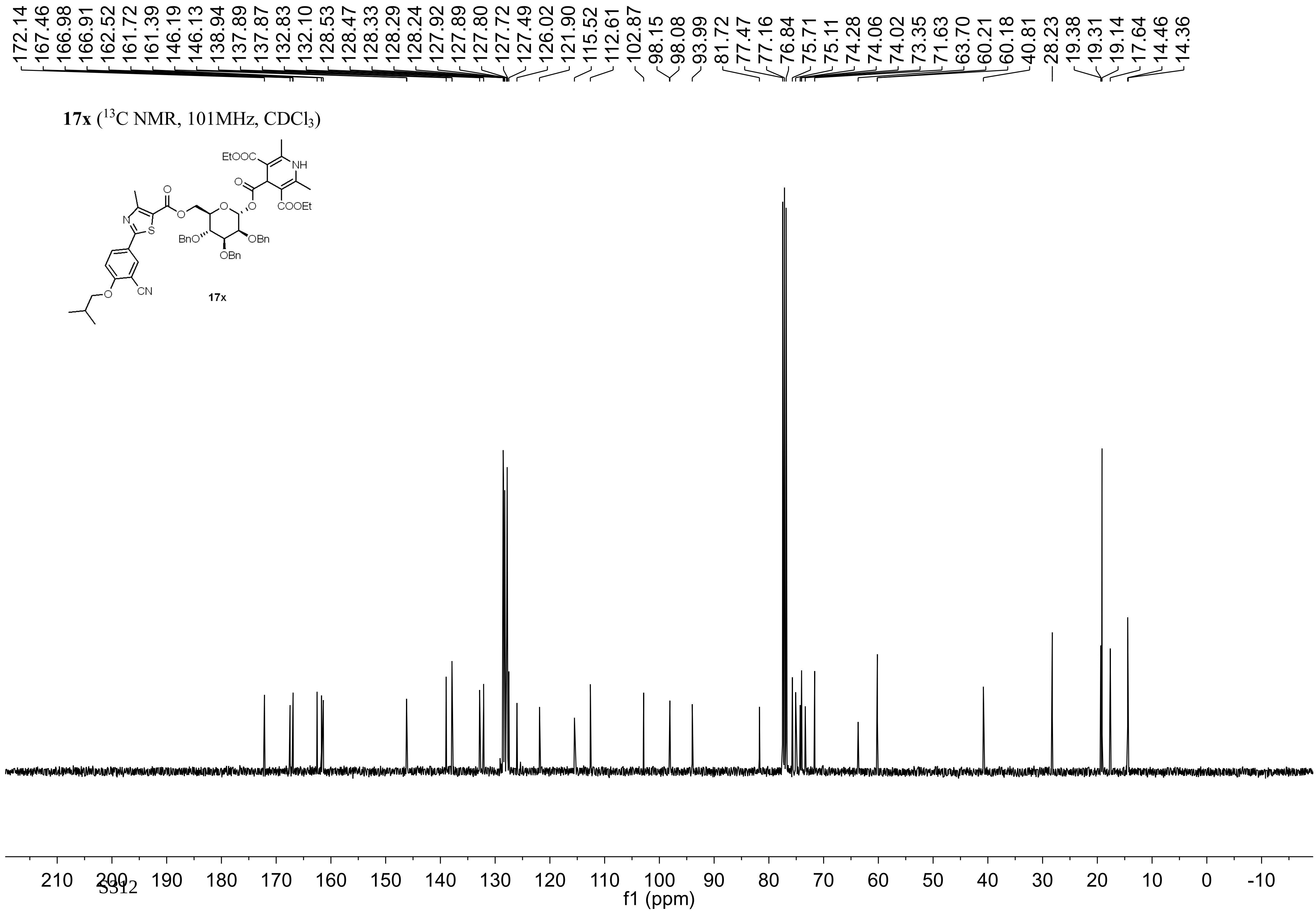


17x (^{1}H NMR, 400MHz, $CDCl_3$)

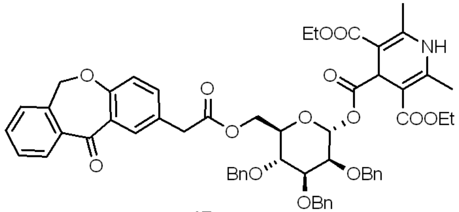


17x

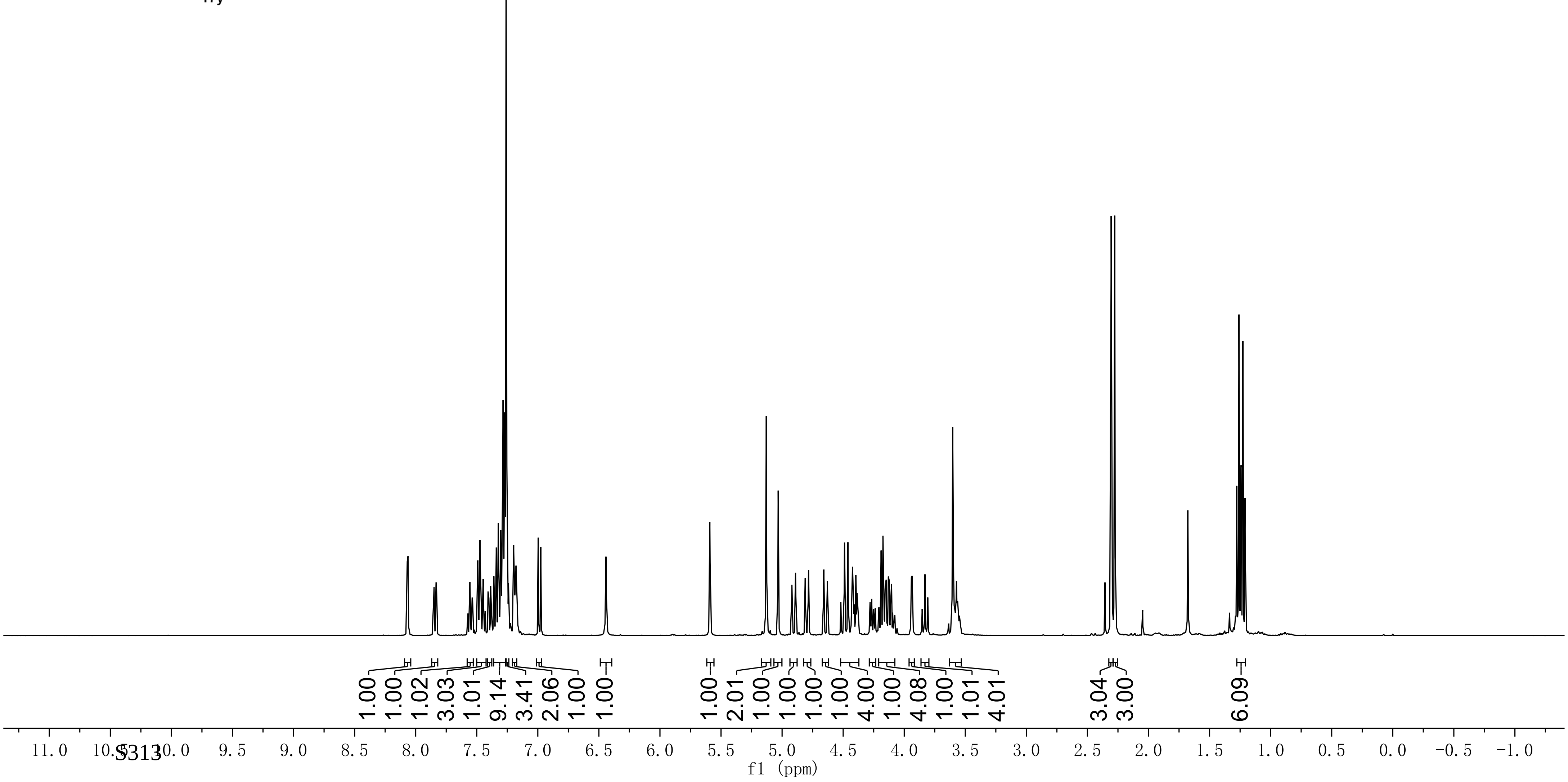



172.14
167.46
166.98
166.91
162.52
161.72
161.39
146.19
146.13
138.94
137.89
137.87
132.83
132.10
128.53
128.47
128.33
128.29
128.24
127.92
127.89
127.80
127.72
127.49
126.02
121.90
115.52
112.61
102.87
98.15
98.08
93.99
81.72
77.47
77.16
76.84
75.71
75.11
74.28
74.06
74.02
73.35
71.63
63.70
60.21
60.18
40.81
28.23
19.38
19.31
19.14
17.64
14.46
14.36
17x (^{13}C NMR, 101MHz, CDCl$_3$)
EtOOC
NH
COOEt
O
N
S
CN
BnO
OBn
OBn
17x
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)

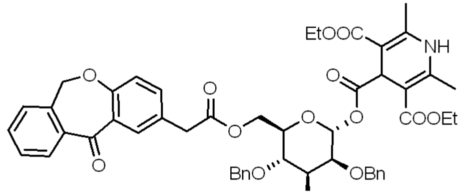
17y (^{1}H NMR, 400MHz, $CDCl_3$)



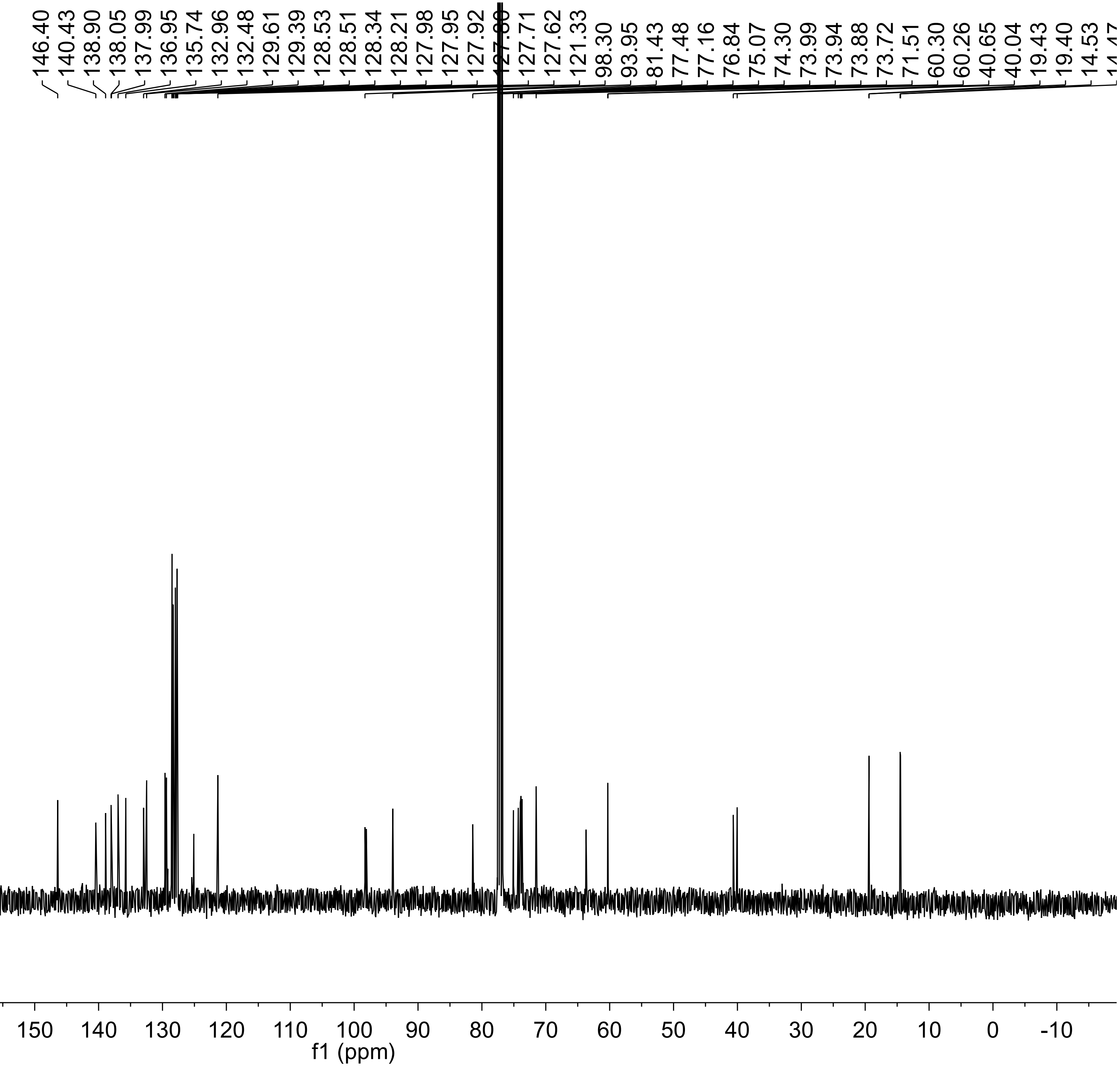
17y

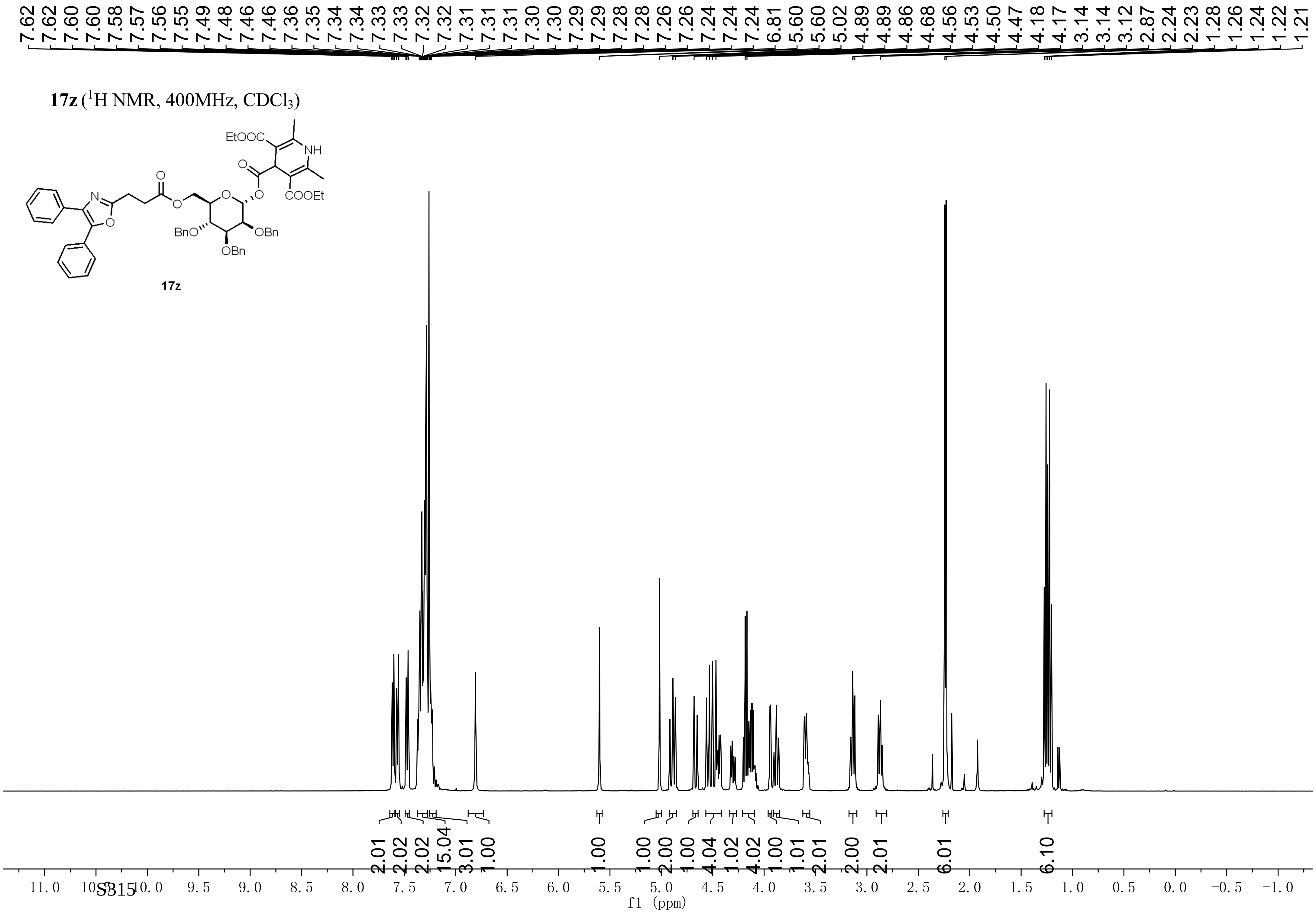


17y (^{13}C NMR, 101MHz, $CDCl_3$)

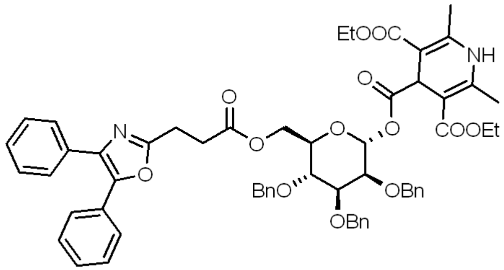


17y

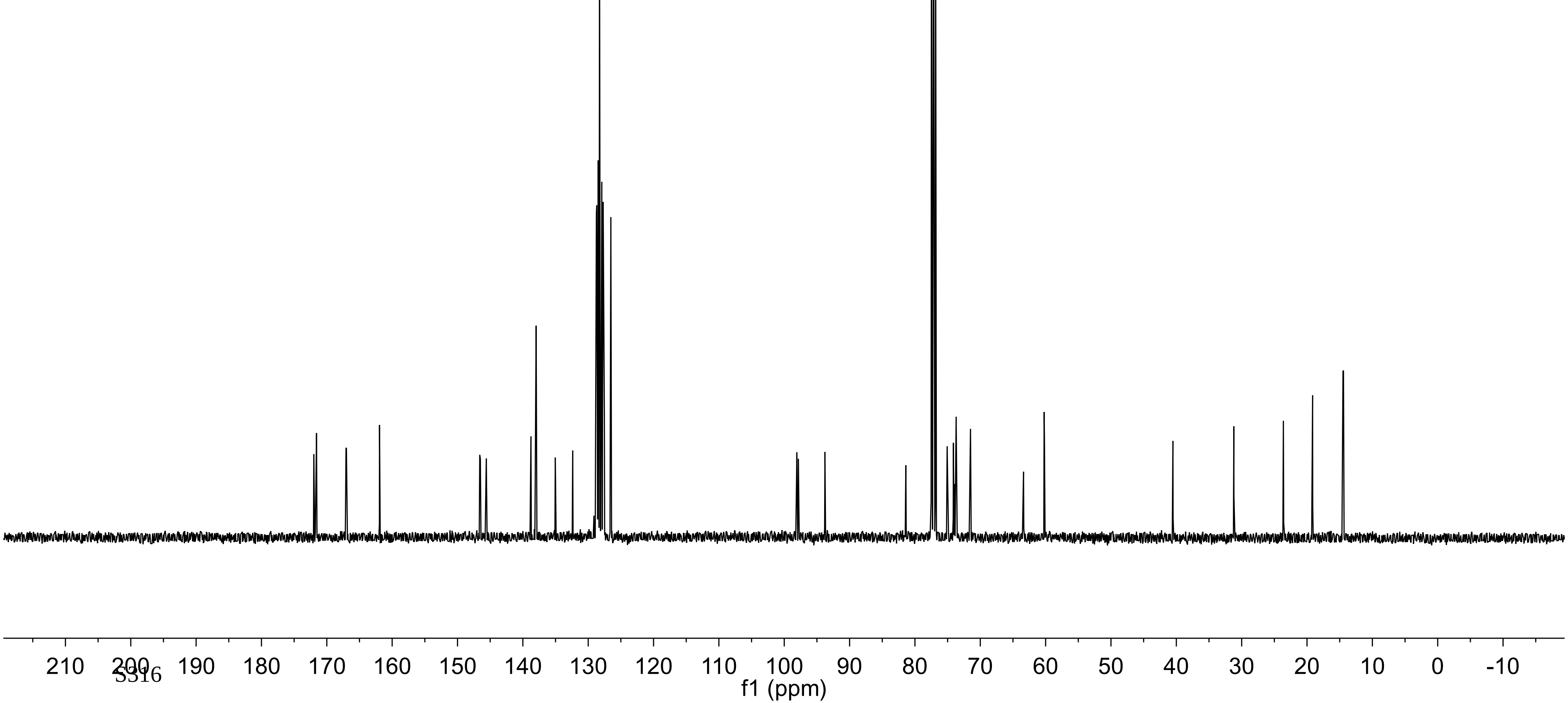



7.62 7.62 7.60 7.60 7.58 7.57 7.56 7.55 7.49 7.48 7.46 7.46 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.26 7.26 7.24 7.24 7.24 6.81 5.60 5.60 5.02 4.89 4.89 4.86 4.68 4.56 4.53 4.50 4.47 4.18 4.17 3.14 3.14 3.12 2.87 2.24 2.23 1.28 1.26 1.24 1.22 1.21
17z (^{1}H NMR, 400MHz, $CDCl_3$)
EtOOC
NH
COOEt
BnO
OBn
OBn
17z
2.01 2.02 2.02 15.04 3.01 1.00 1.00 1.00 2.00 1.00 4.04 1.02 4.02 1.00 1.01 2.01 2.00 2.01 6.01 6.10
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)

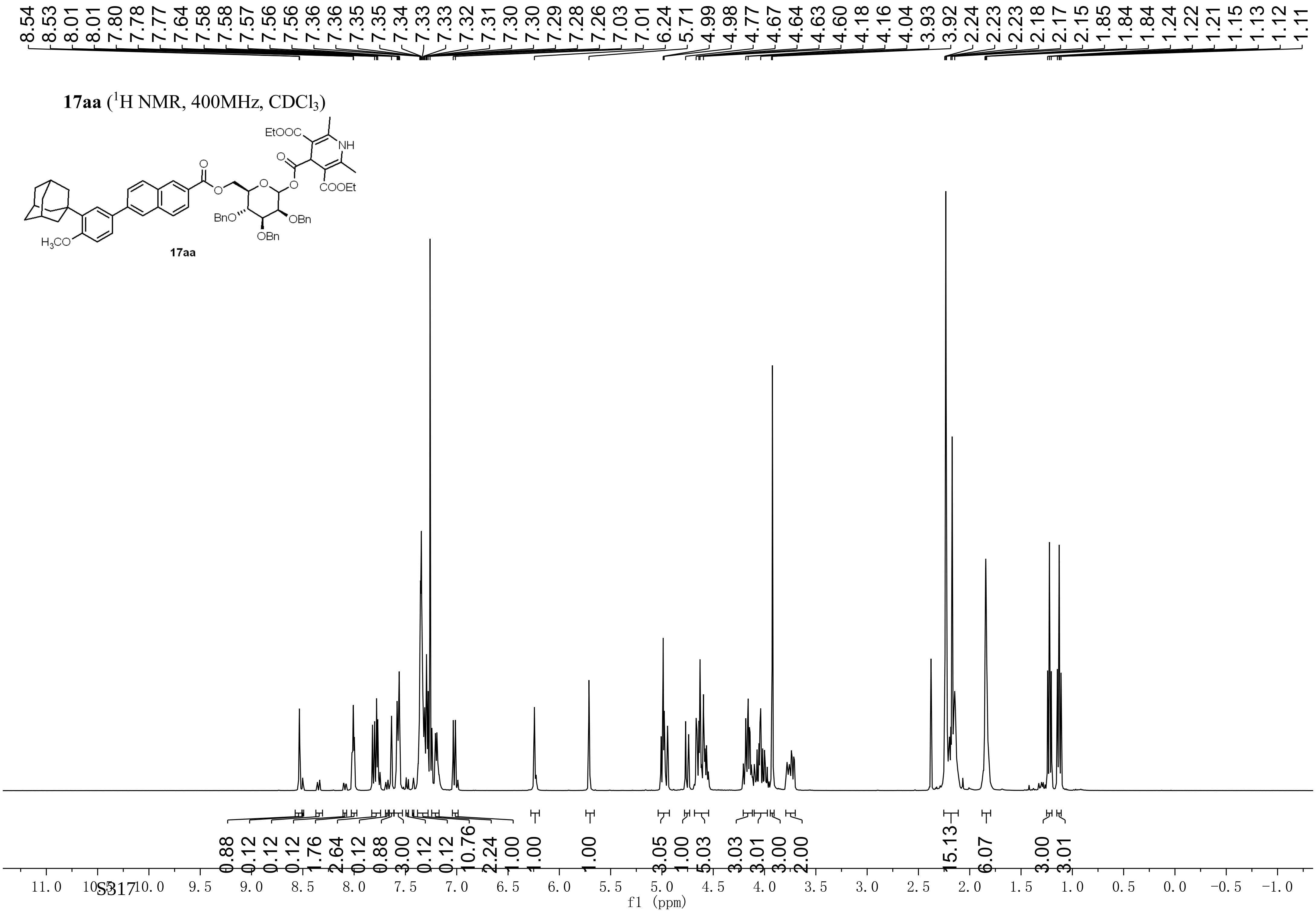
17z (^{13}C NMR, 101MHz, $CDCl_3$)

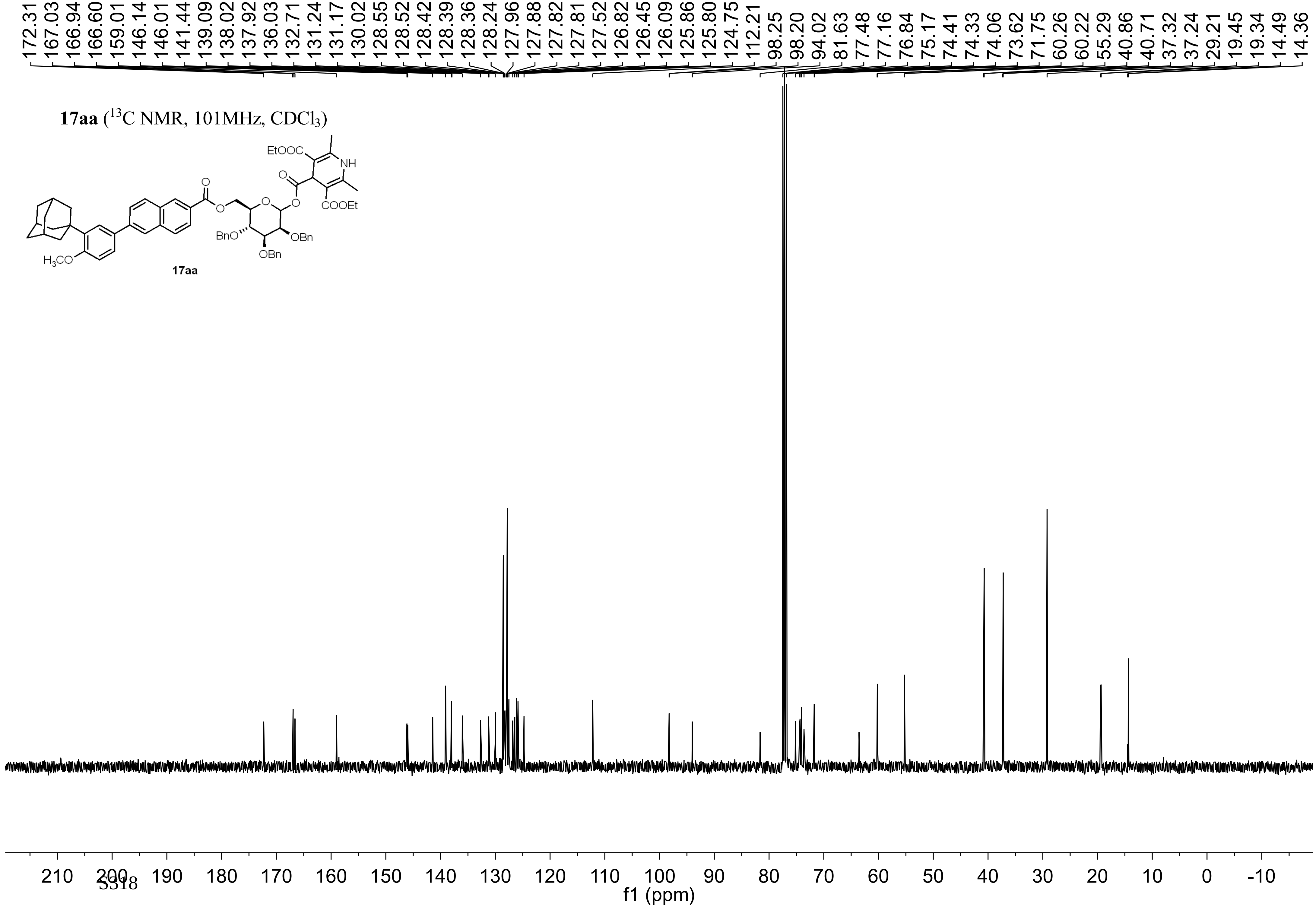


17z

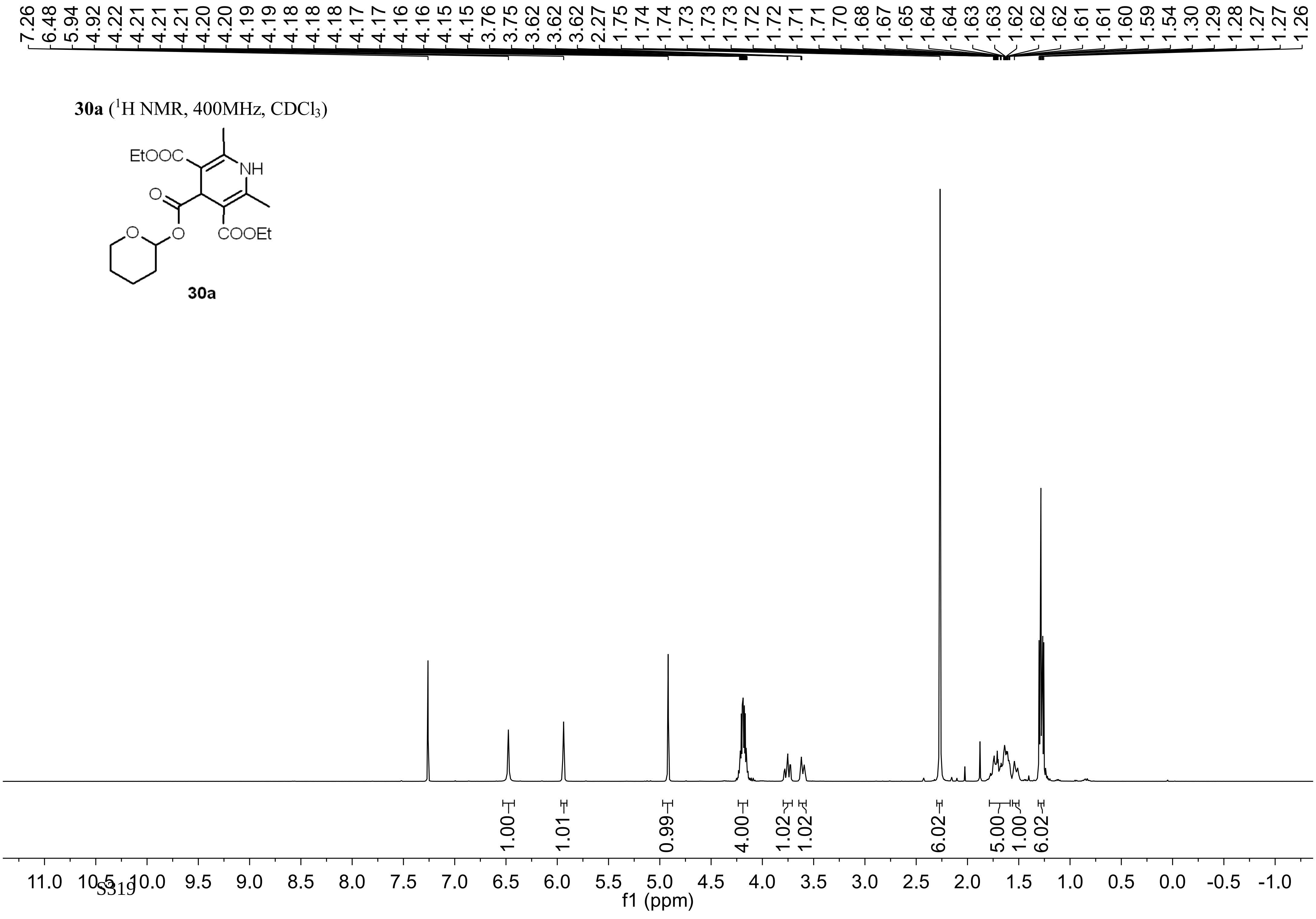


17aa (^{1}H NMR, 400MHz, $CDCl_3$)

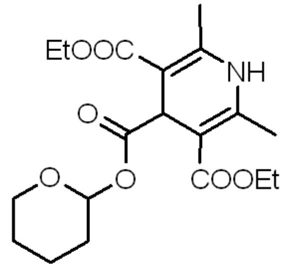



172.31
167.03
166.94
166.60
159.01
146.14
146.01
141.44
139.09
138.02
137.92
136.03
132.71
131.24
131.17
130.02
128.55
128.52
128.42
128.39
128.36
128.24
127.96
127.88
127.82
127.81
127.52
126.82
126.45
126.09
125.86
125.80
124.75
112.21
98.25
98.20
94.02
81.63
77.48
77.16
76.84
75.17
74.41
74.33
74.06
73.62
71.75
60.26
60.22
55.29
40.86
40.71
37.32
37.24
29.21
19.45
19.34
14.49
14.36
17aa (13C NMR, 101MHz, CDCl3)
EtOOC
NH
COOEt
BnO
OBn
OBn
H3CO
17aa
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)

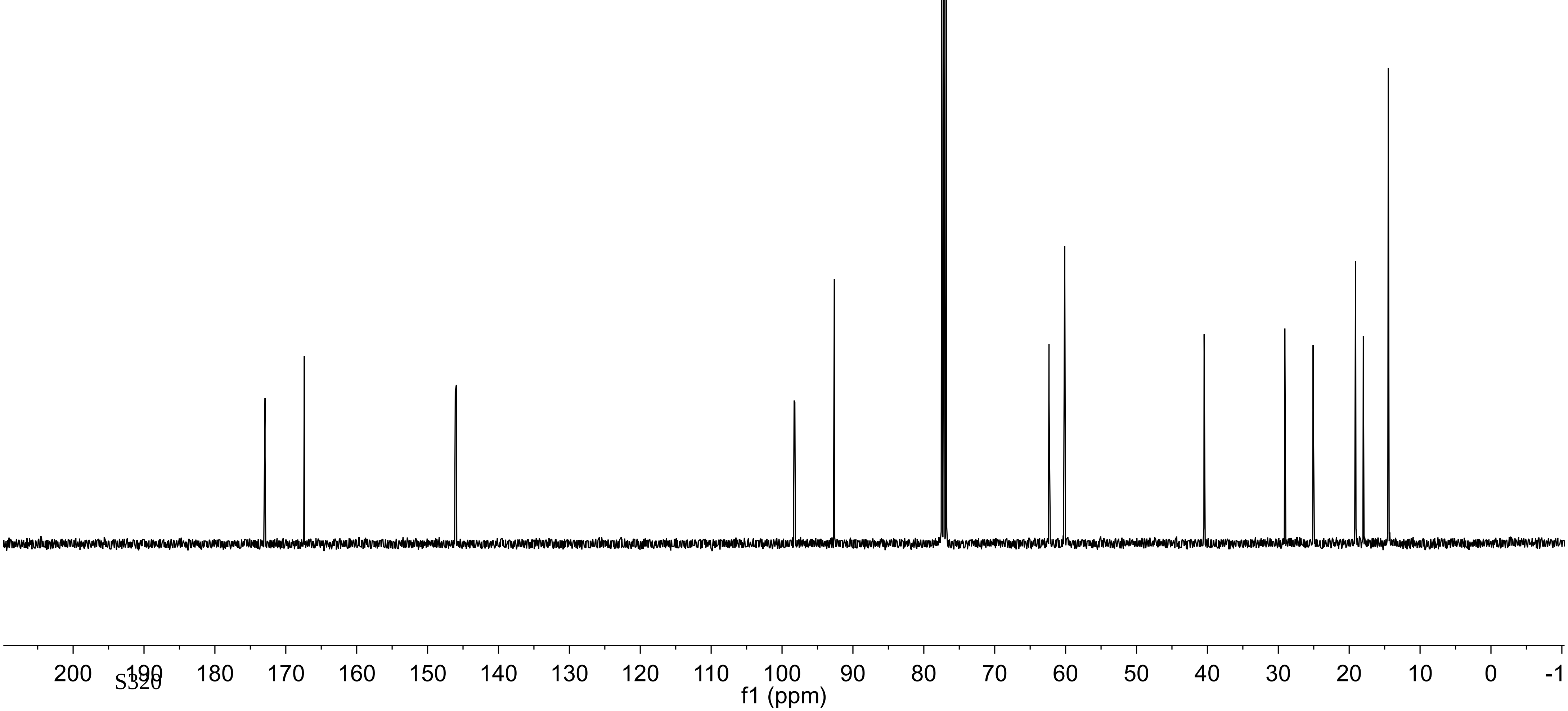
30a (^{1}H NMR, 400MHz, $CDCl_3$)



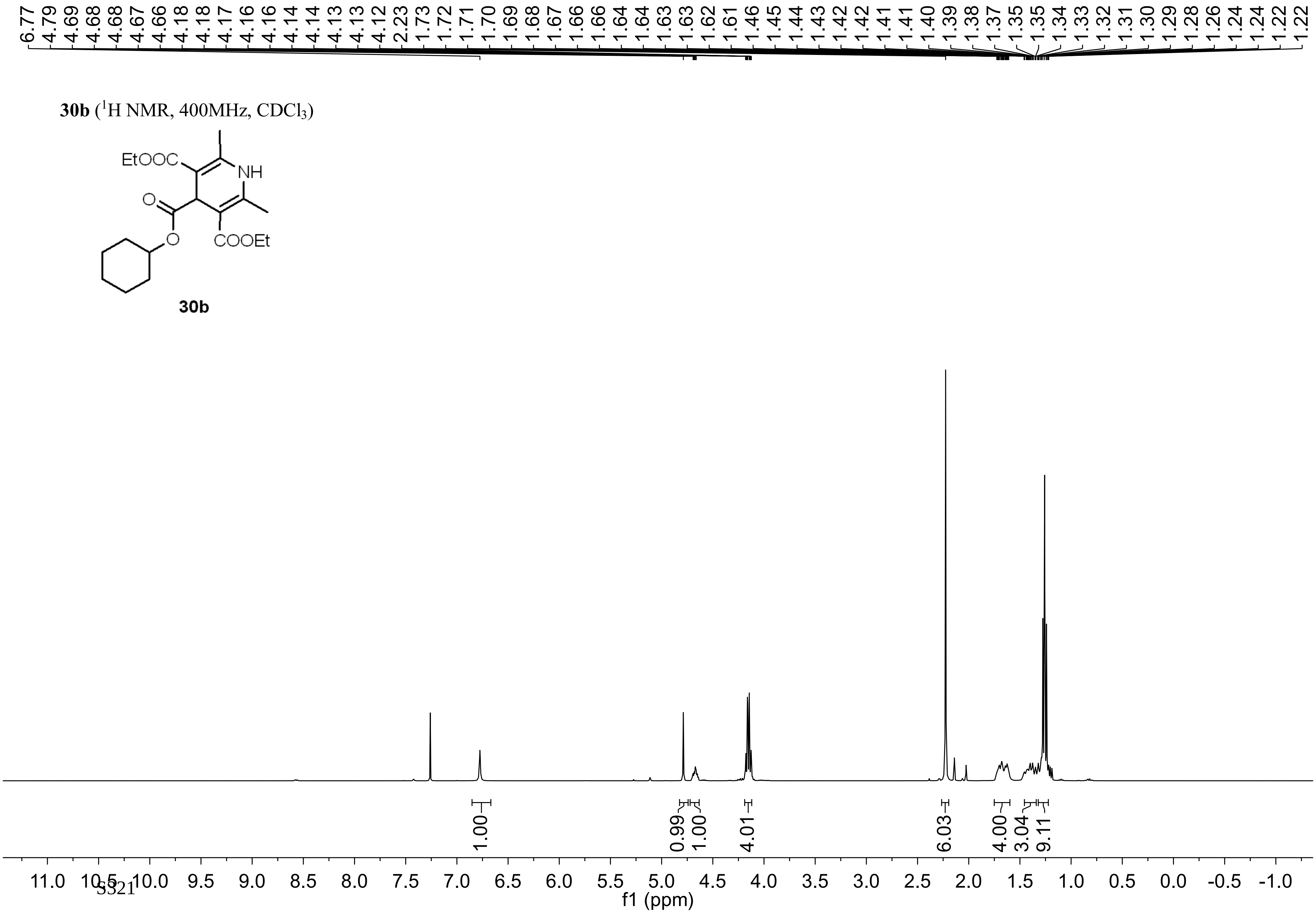
30a (^{13}C NMR, 101MHz, $CDCl_3$)



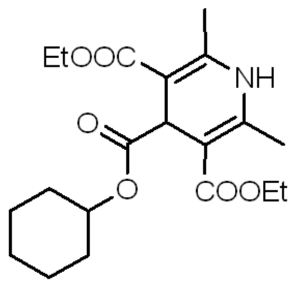
30a



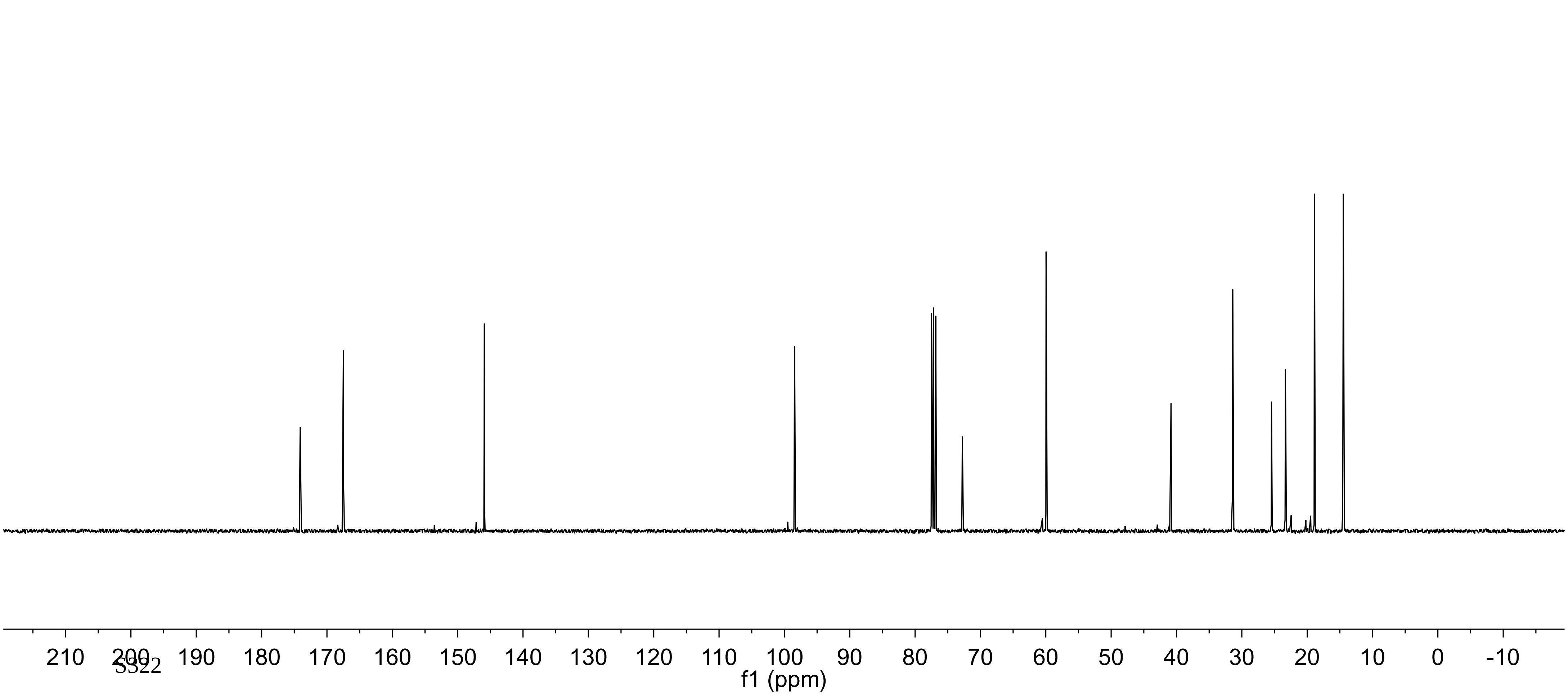
30b (^{1}H NMR, 400MHz, $CDCl_3$)

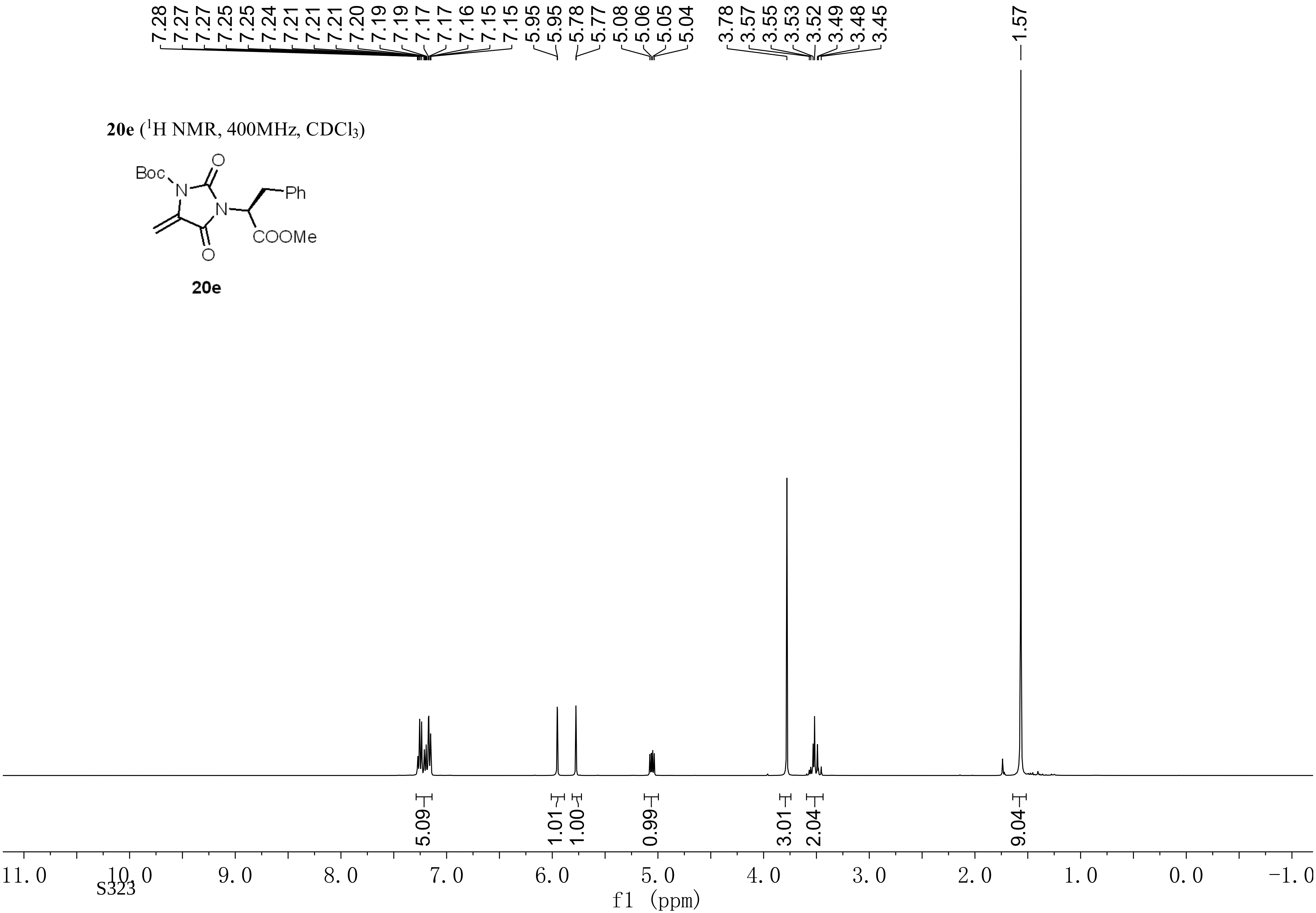


30b (^{13}C NMR, 101MHz, $CDCl_3$)



30b

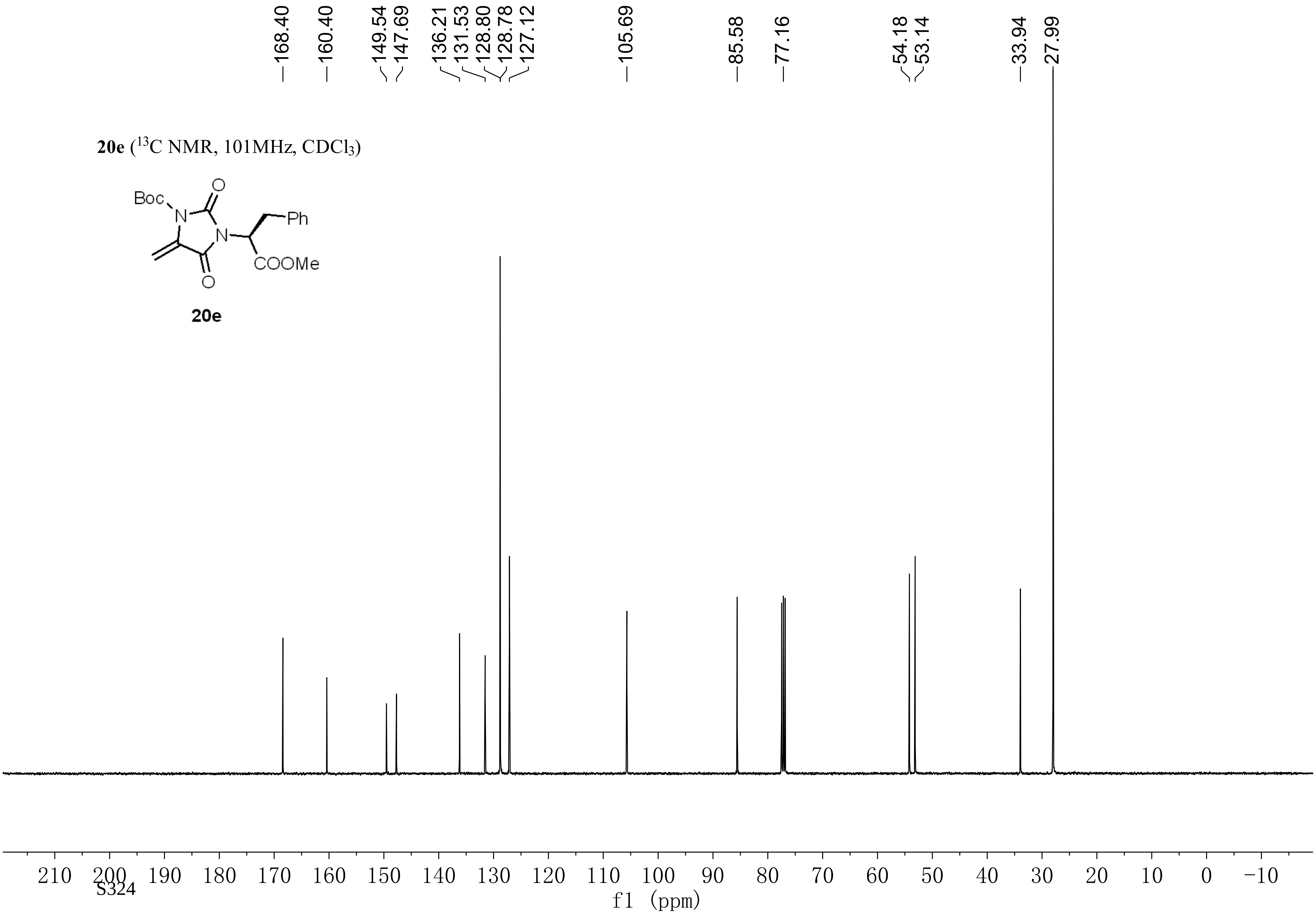


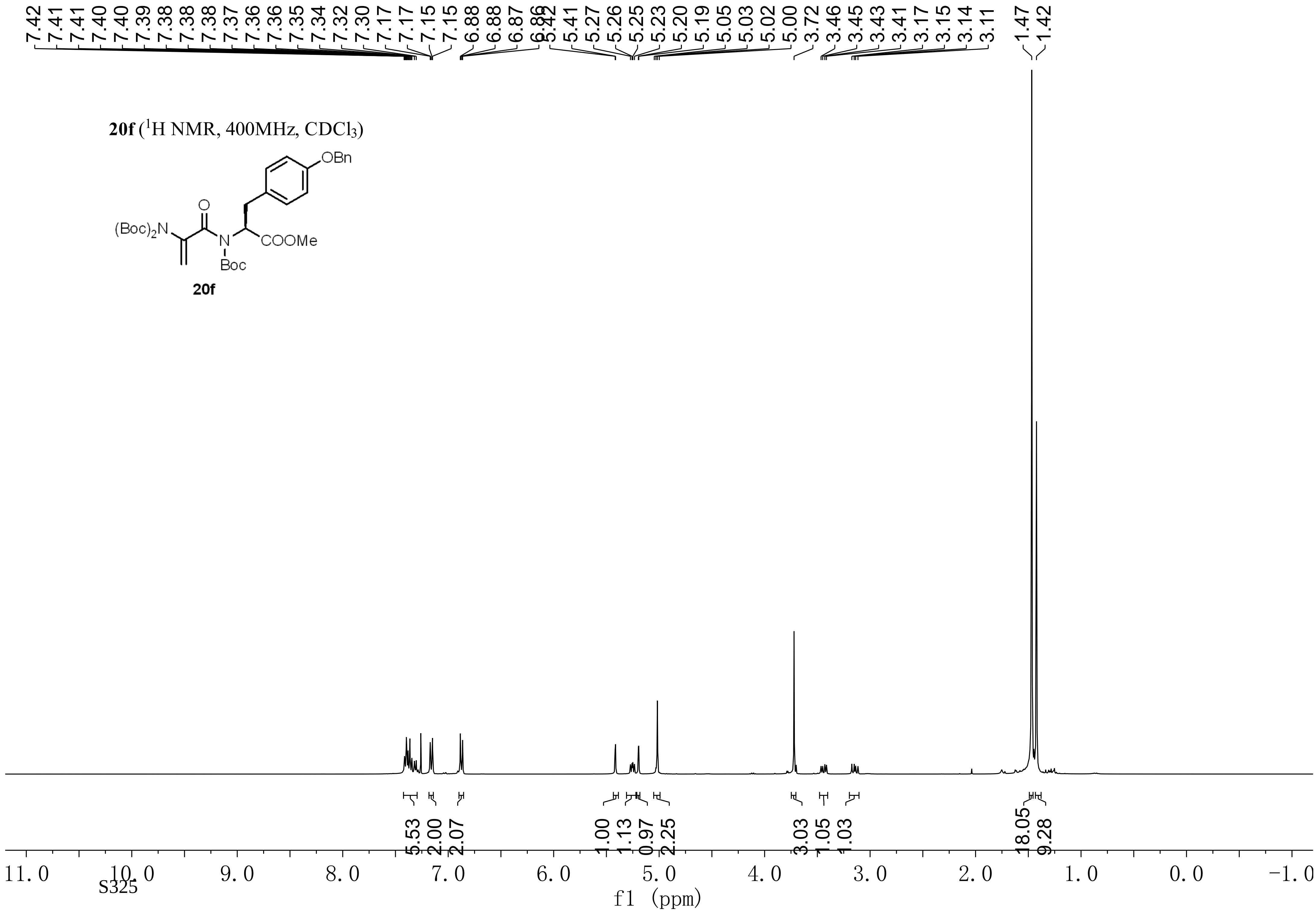


7.28 7.27 7.27 7.25 7.25 7.24 7.21 7.21 7.21 7.20 7.19 7.19 7.17 7.17 7.16 7.15 7.15 5.95 5.95 5.78 5.77 5.08 5.06 5.05 5.04 3.78 3.57 3.55 3.53 3.52 3.49 3.48 3.45 1.57
20e (1H NMR, 400MHz, CDCl3)
Boc
N
O
N
Ph
COOMe
O
20e
5.09
1.01
1.00
0.99
3.01
2.04
9.04
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

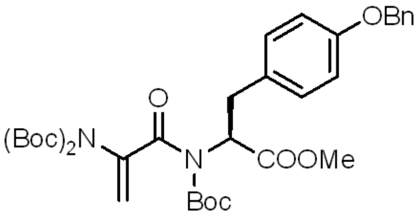
20e (^{13}C NMR, 101MHz, $CDCl_3$)

20e

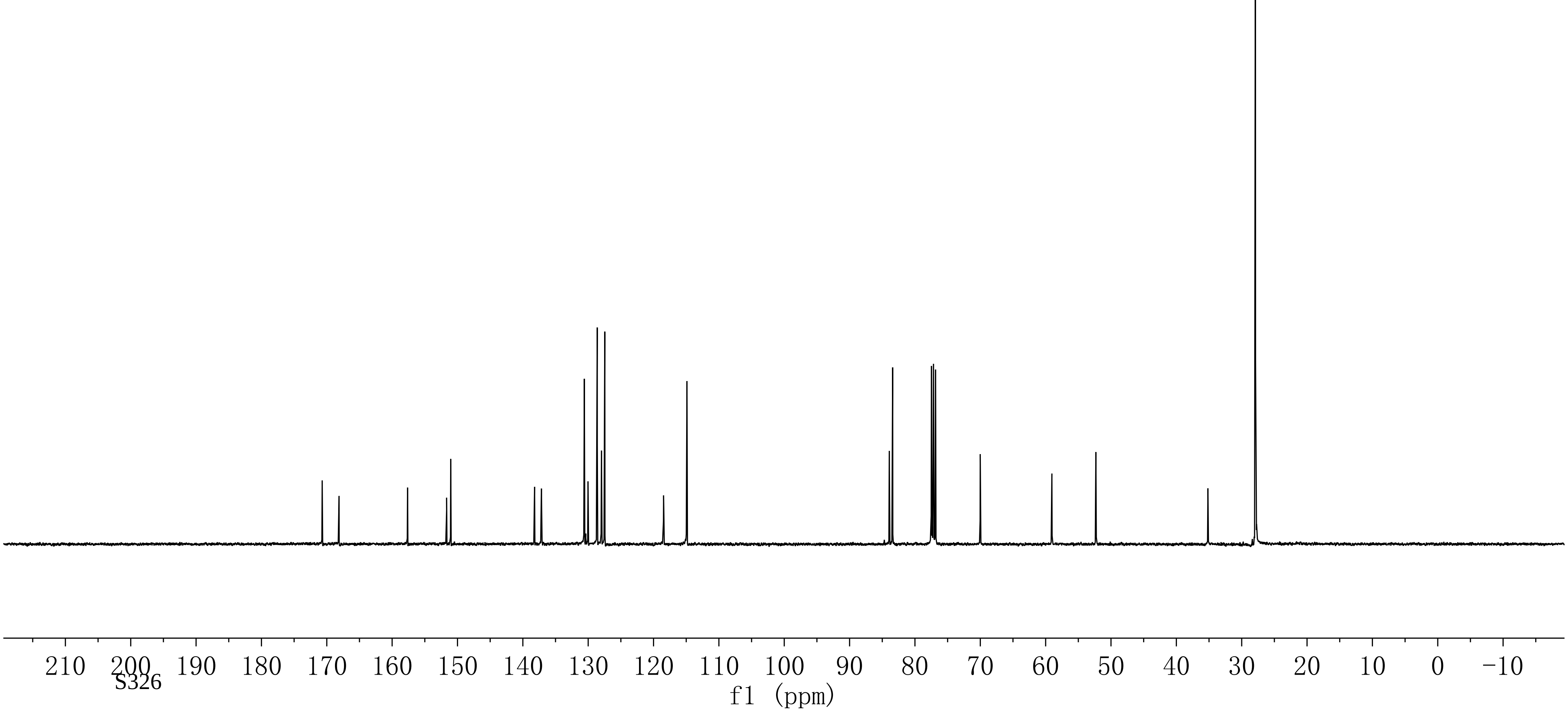



7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.34 7.32 7.30 7.17 7.17 7.15 7.15 6.88 6.88 6.87 6.86 5.42 5.41 5.27 5.26 5.25 5.23 5.20 5.19 5.05 5.03 5.02 5.00 3.72 3.46 3.45 3.43 3.41 3.17 3.15 3.14 3.11 1.47 1.42
20f (1H NMR, 400MHz, CDCl3)
OBn
O
(Boc)2N
N
COOMe
Boc
20f
5.53 2.00 2.07 1.00 1.13 0.97 2.25 3.03 1.05 1.03 18.05 9.28
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)

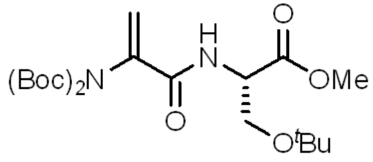
20f (^{13}C NMR, 101MHz, $CDCl_3$)



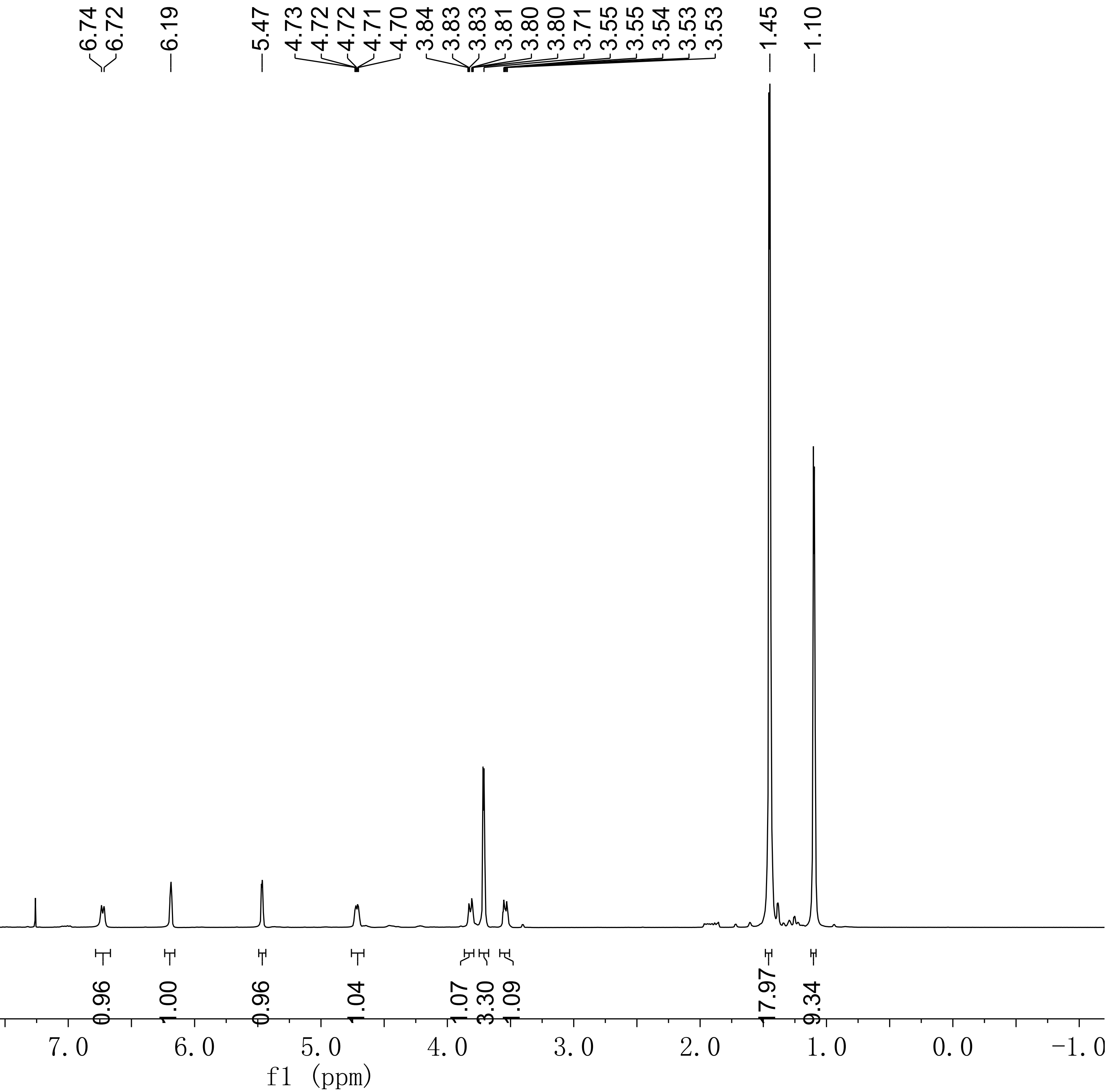
20f



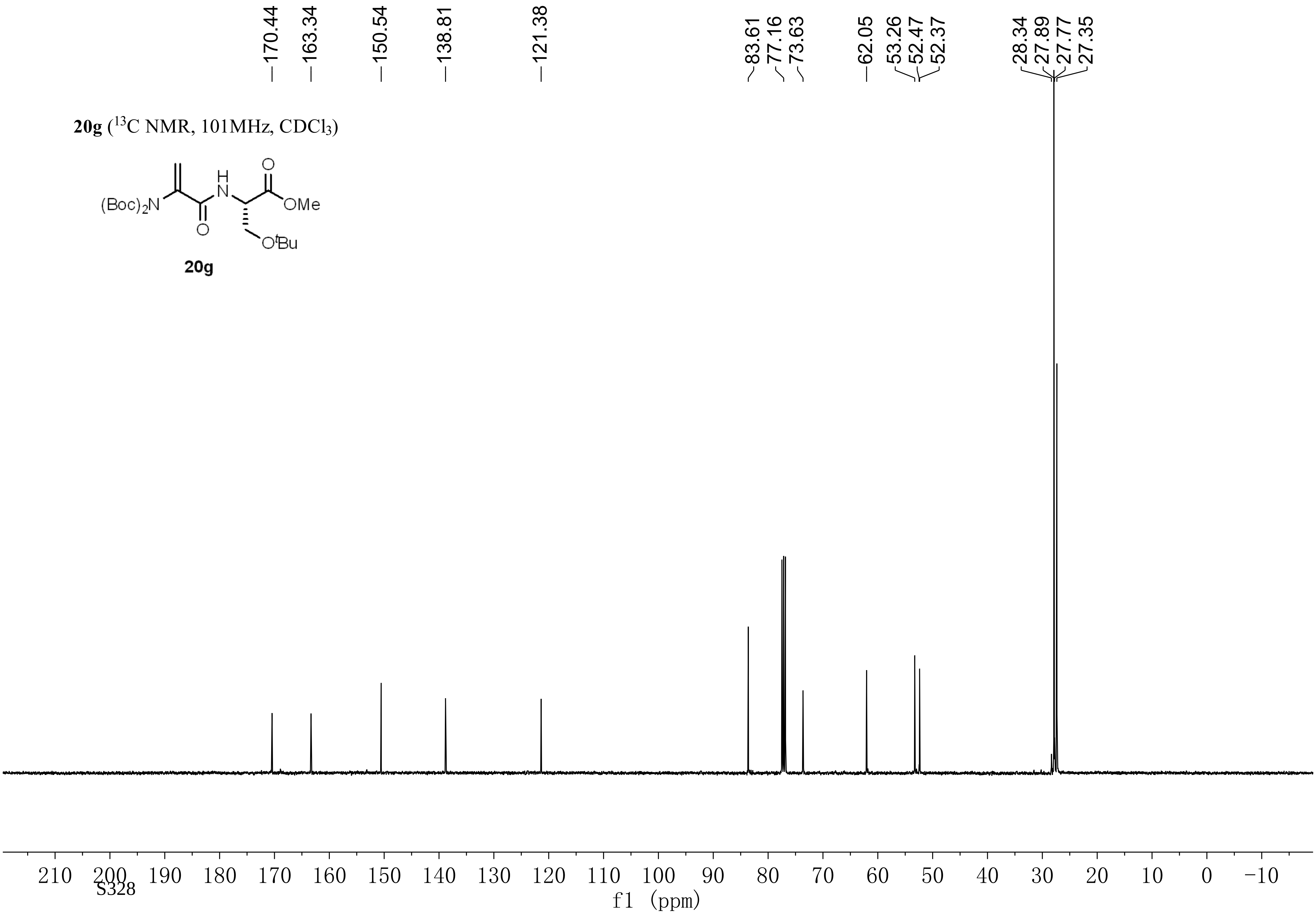
20g (^{1}H NMR, 400MHz, $CDCl_3$)



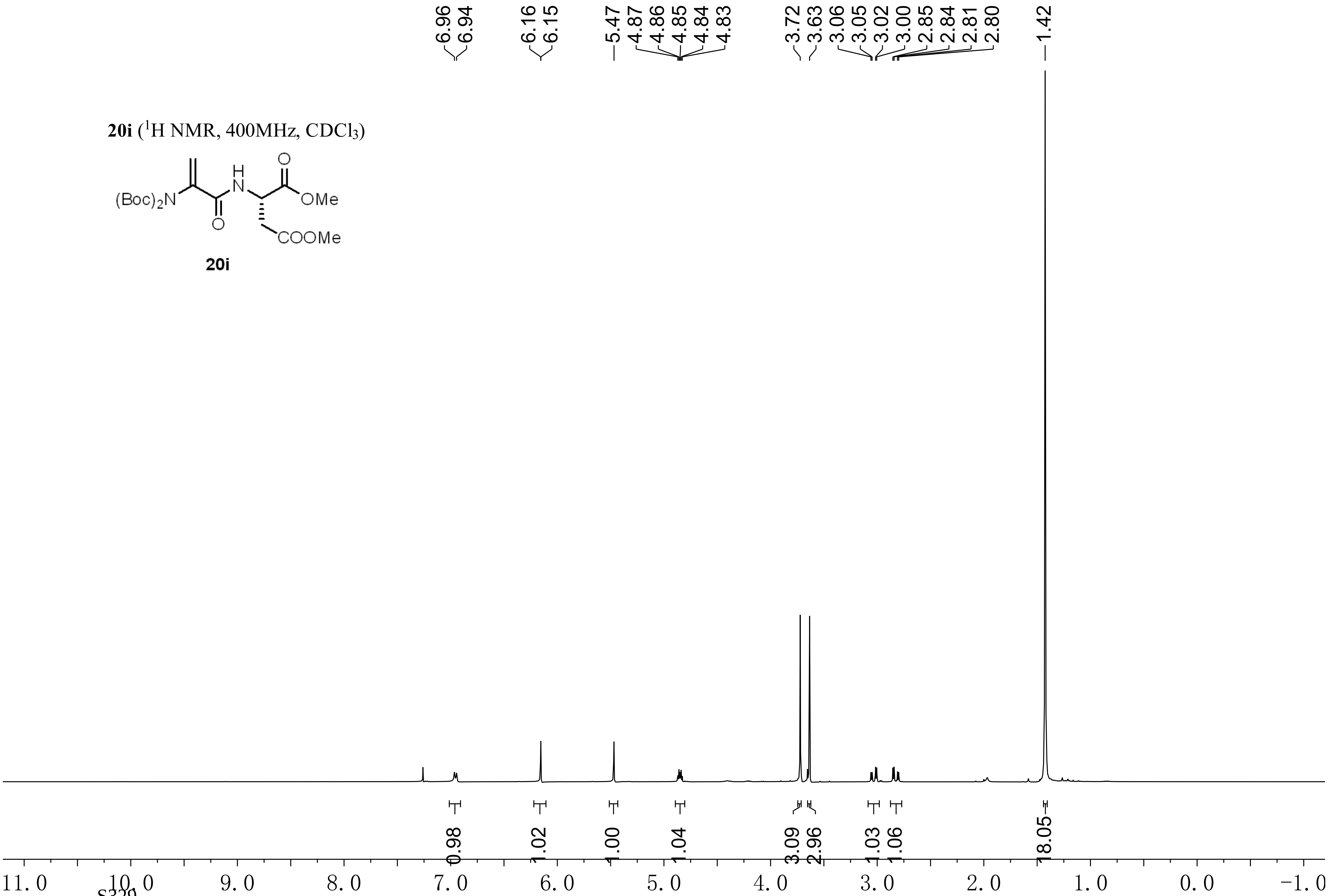
20g



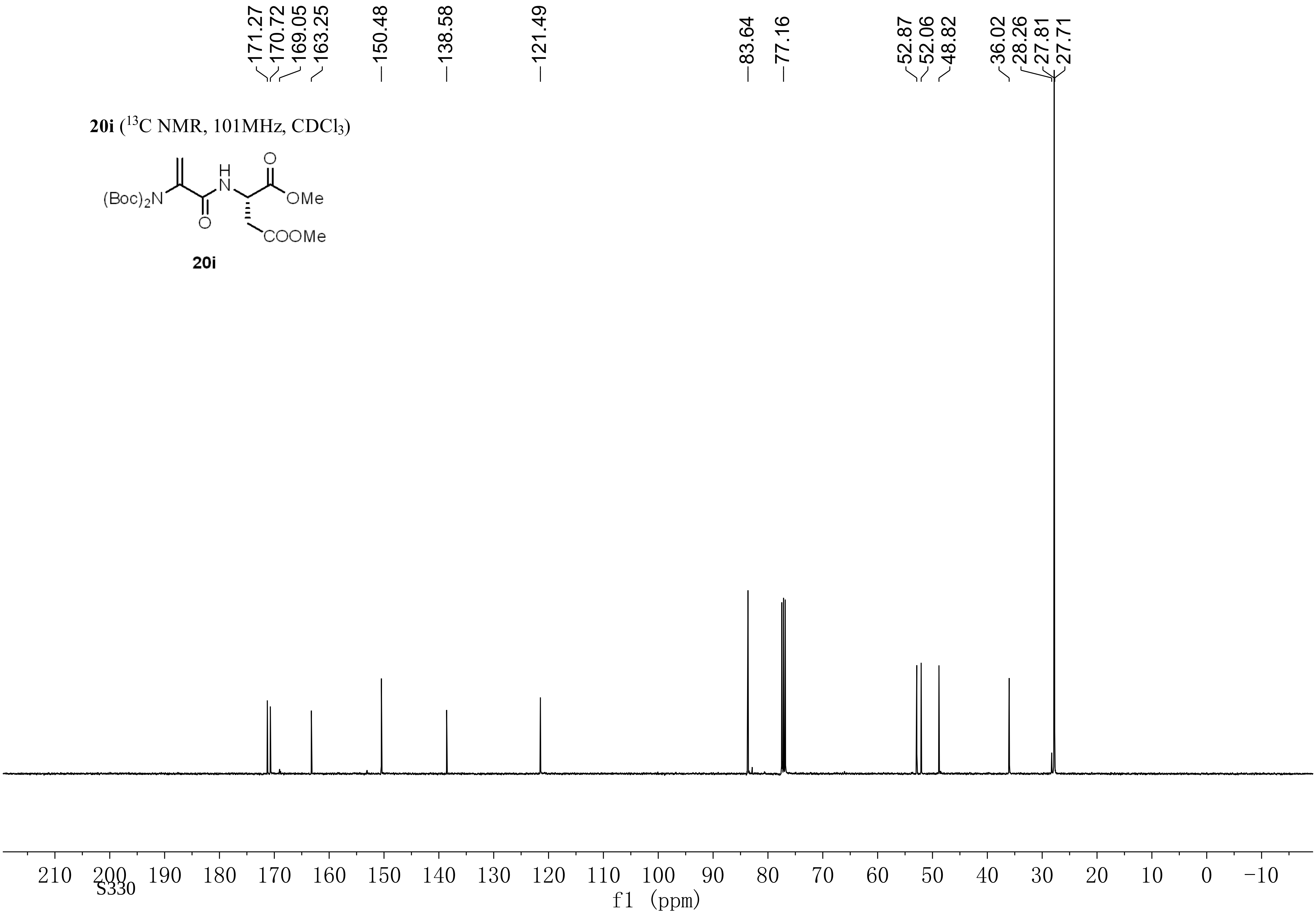
20g (^{13}C NMR, 101MHz, $CDCl_3$)



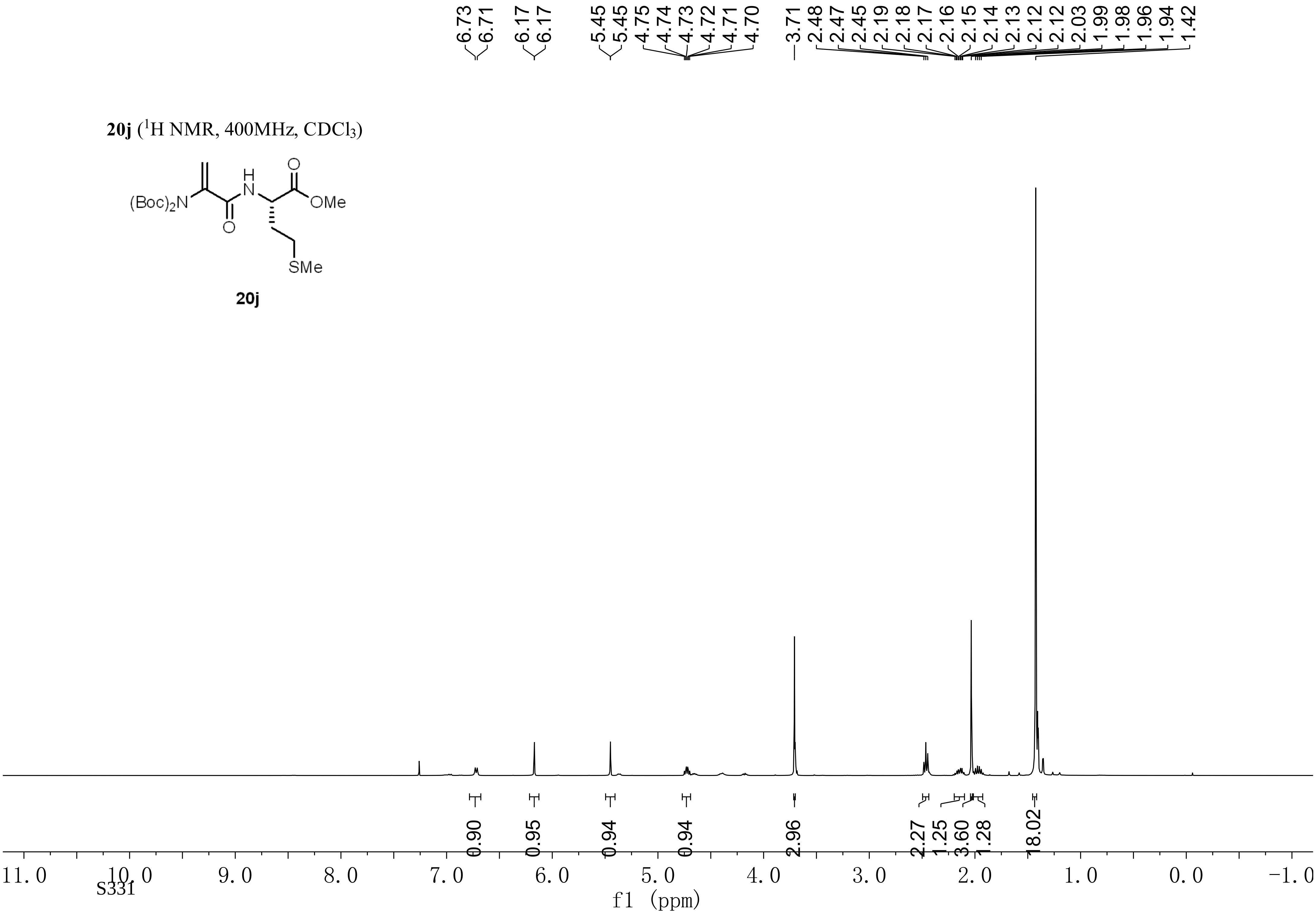
20i (^{1}H NMR, 400MHz, $CDCl_3$)



20i

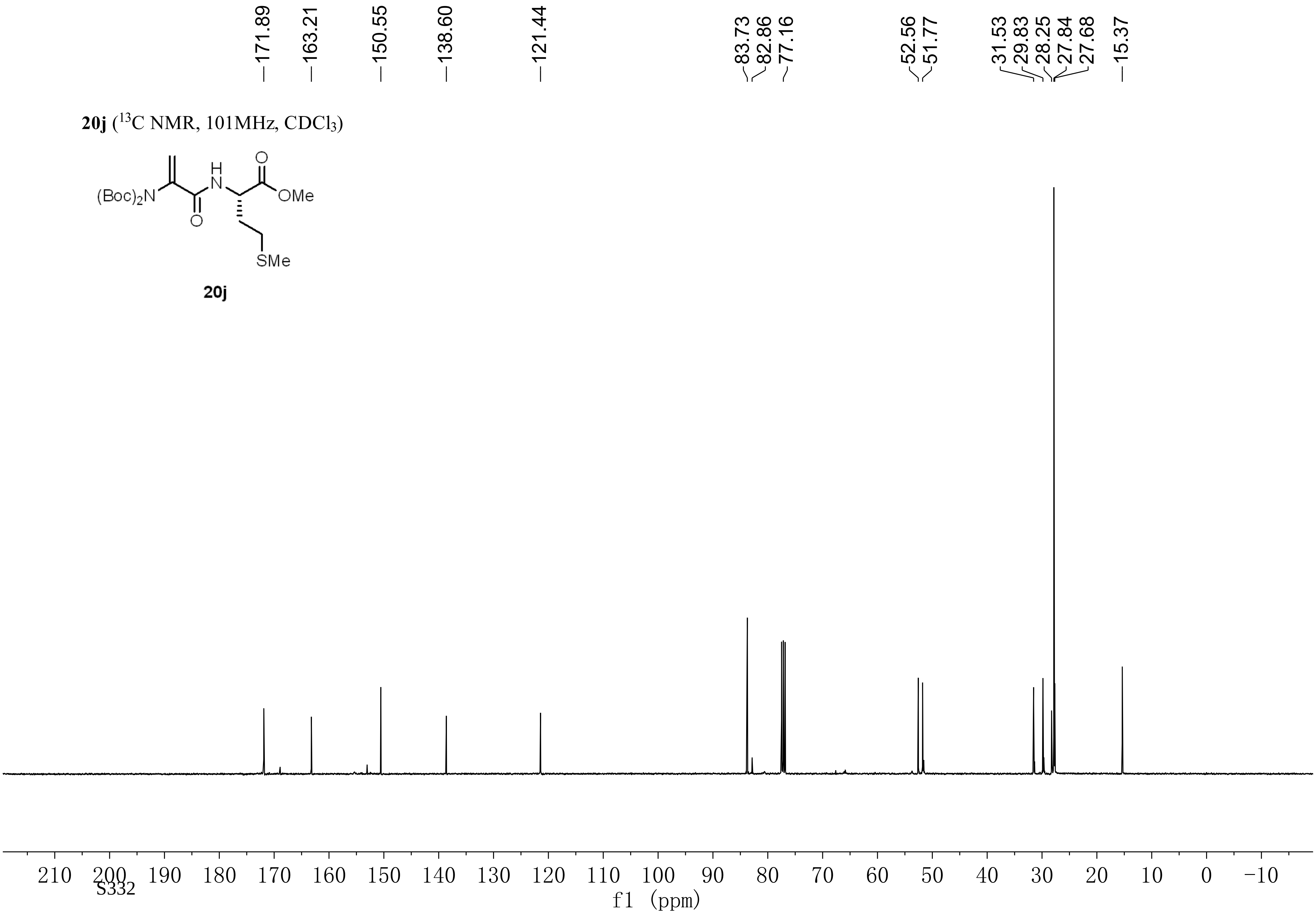

171.27
170.72
169.05
163.25
150.48
138.58
121.49
83.64
77.16
52.87
52.06
48.82
36.02
28.26
27.81
27.71
20i (^{13}C NMR, 101MHz, $CDCl_3$)
(Boc)$_2$N
H
N
O
OMe
O
COOMe
20i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

20j (^{1}H NMR, 400MHz, $CDCl_3$)

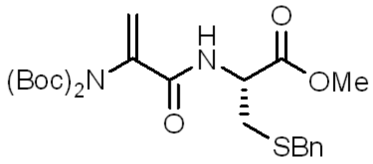


20j

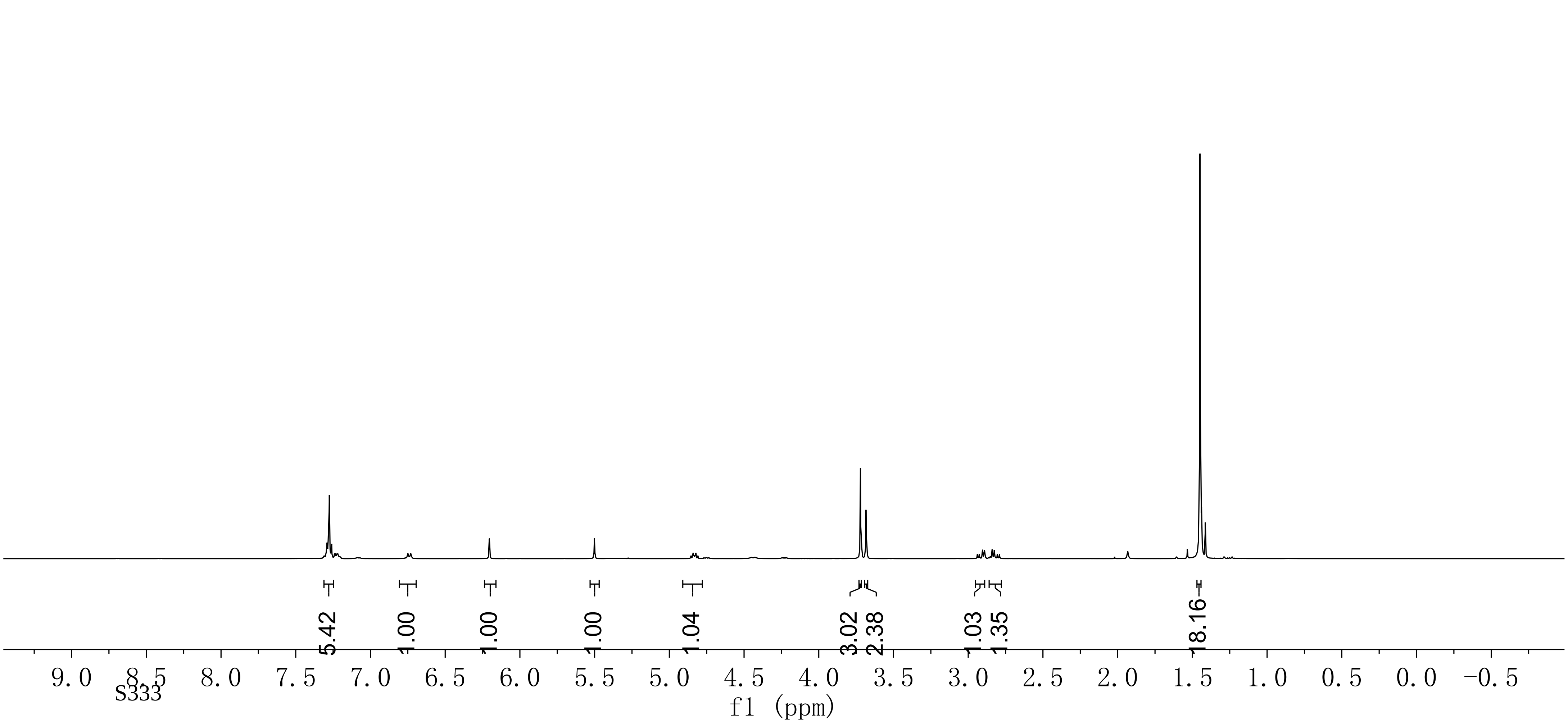
20j (^{13}C NMR, 101MHz, $CDCl_3$)



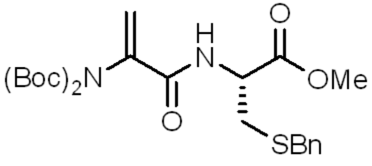
20k (^{1}H NMR, 400MHz, $CDCl_3$)



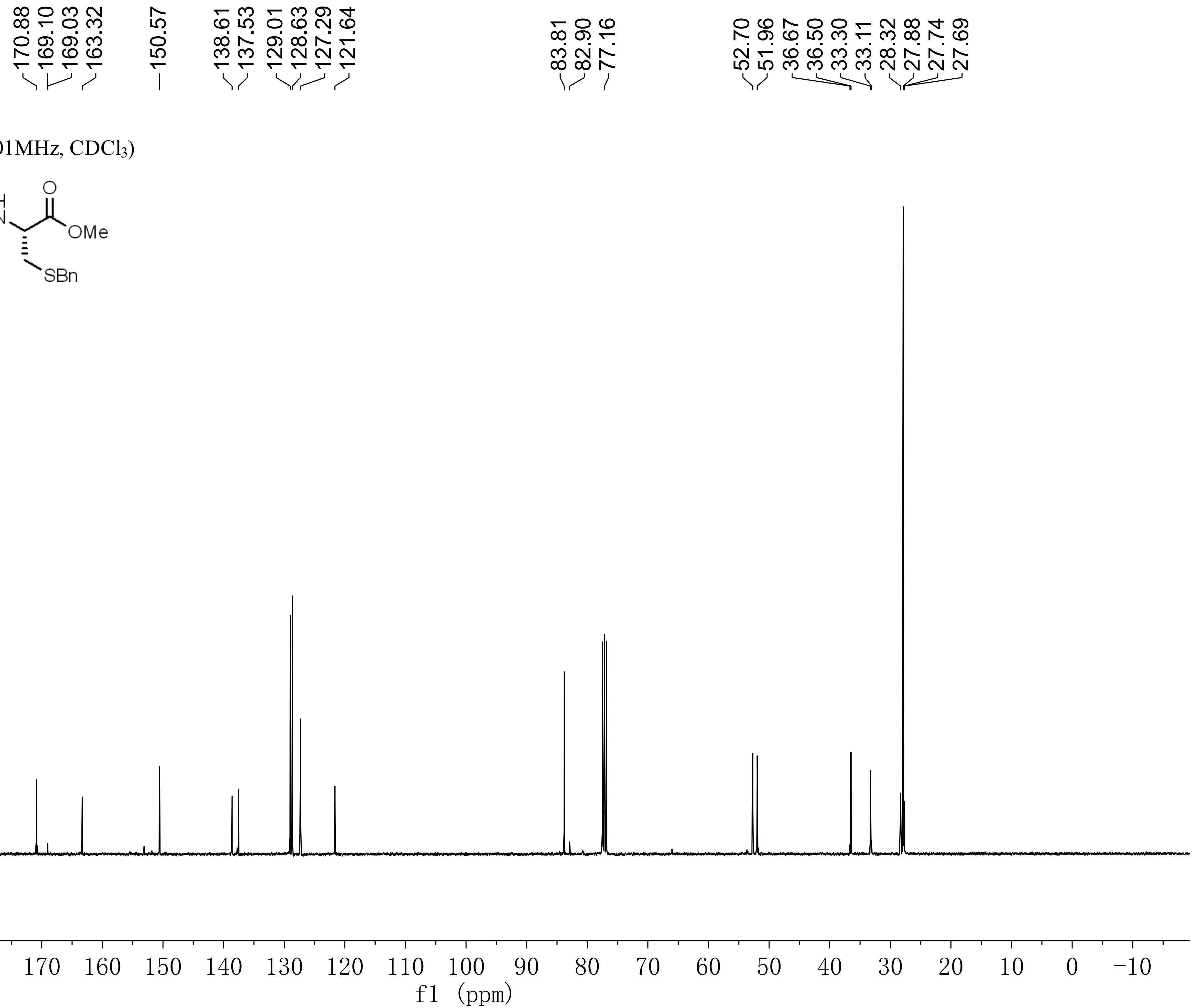
20k



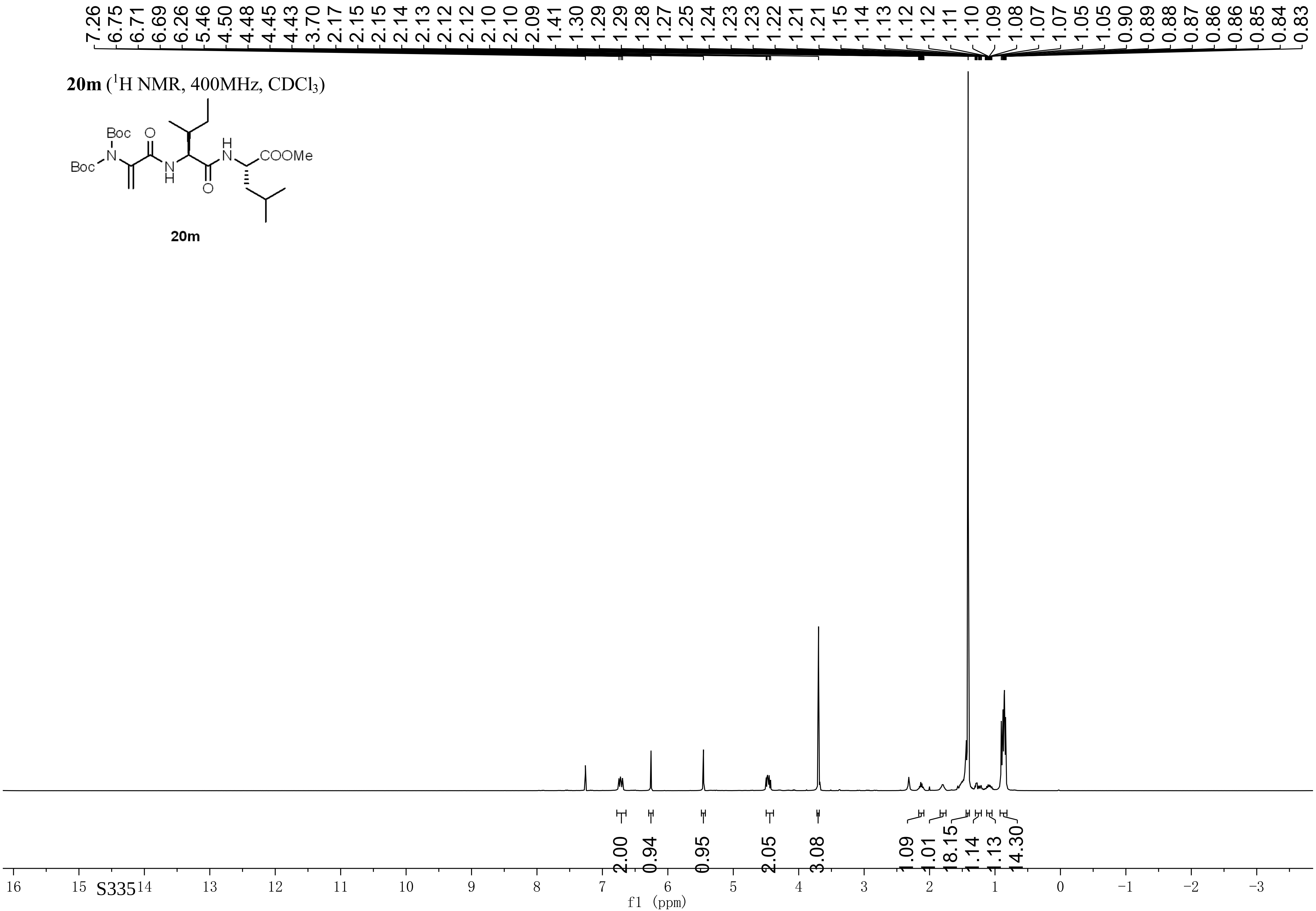
20k (^{13}C NMR, 101MHz, $CDCl_3$)



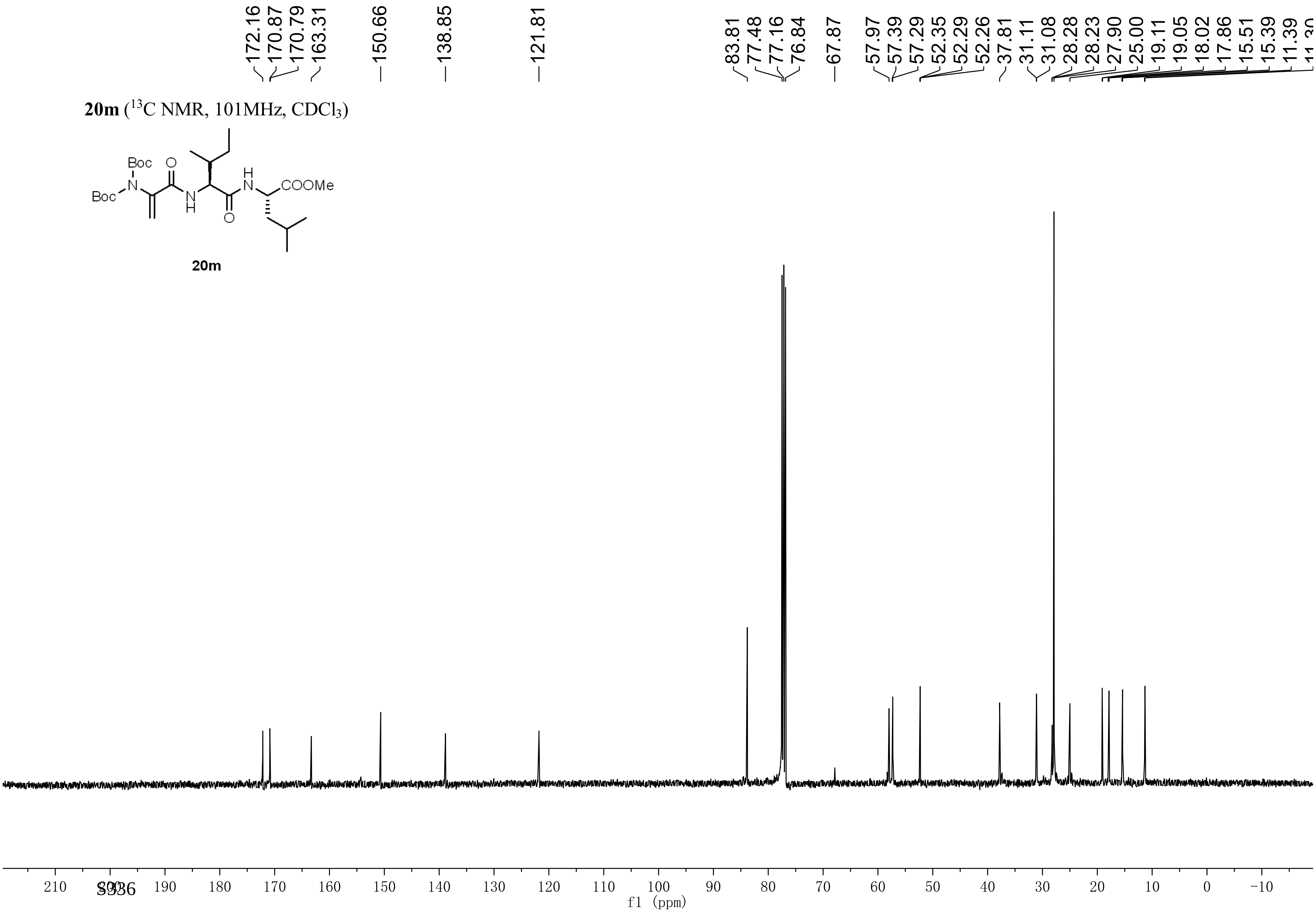
20k



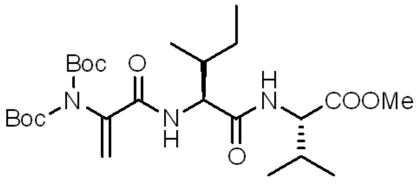
20m (^{1}H NMR, 400MHz, $CDCl_3$)



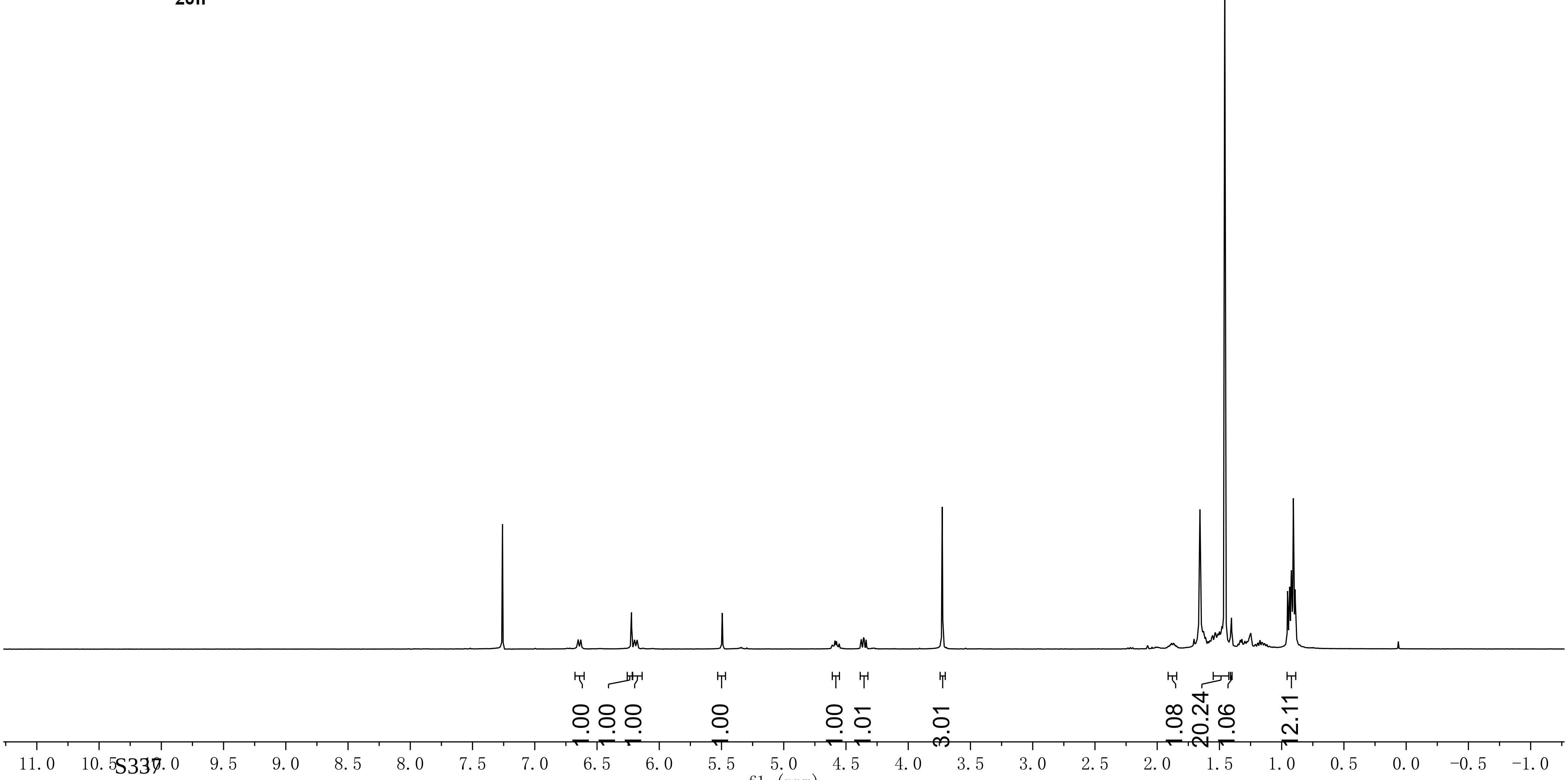
20m (^{13}C NMR, 101MHz, $CDCl_3$)



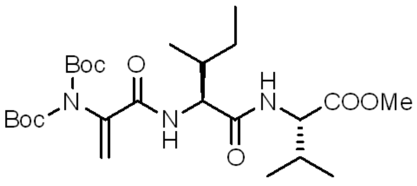
20n (^{1}H NMR, 400MHz, $CDCl_3$)



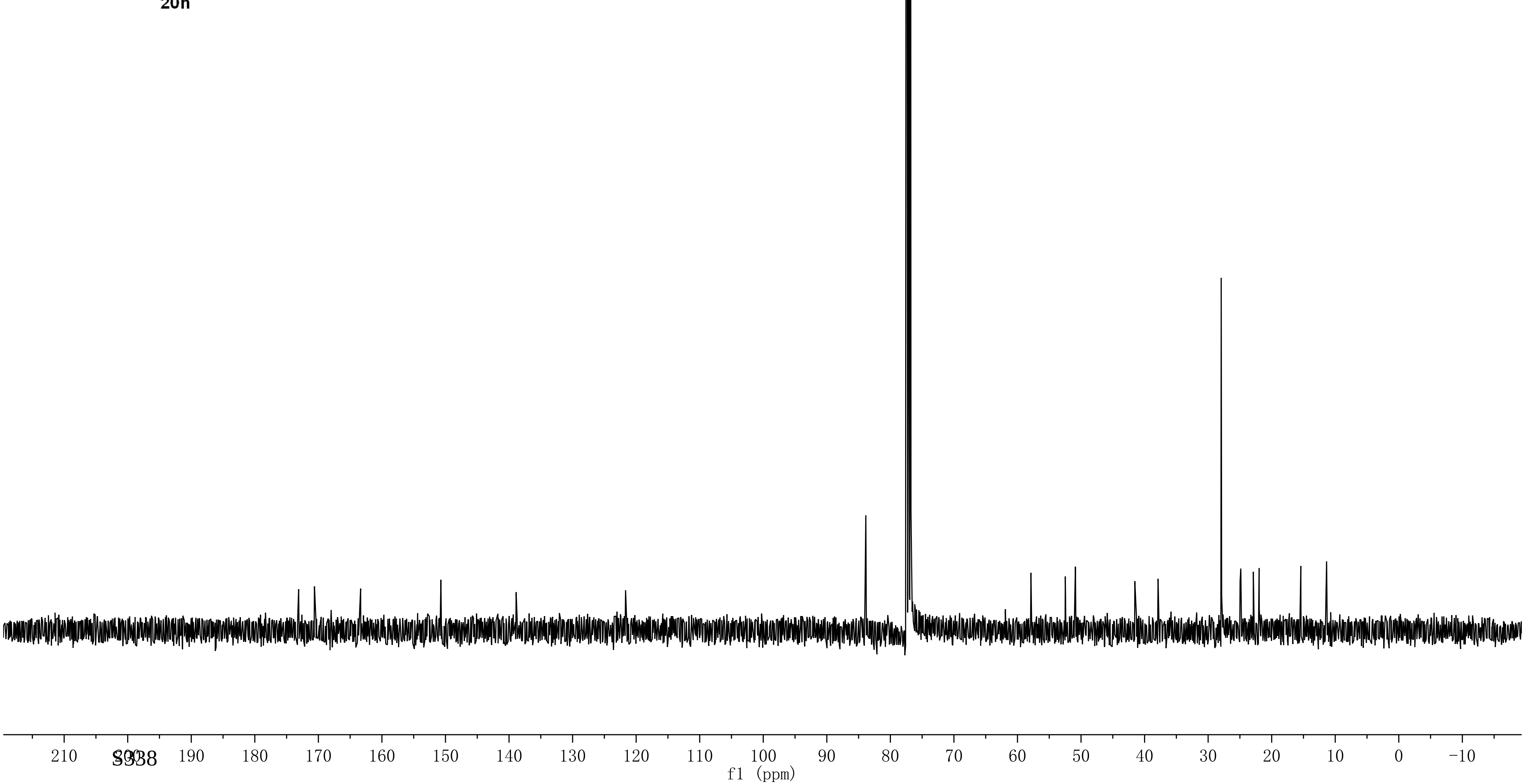
20n

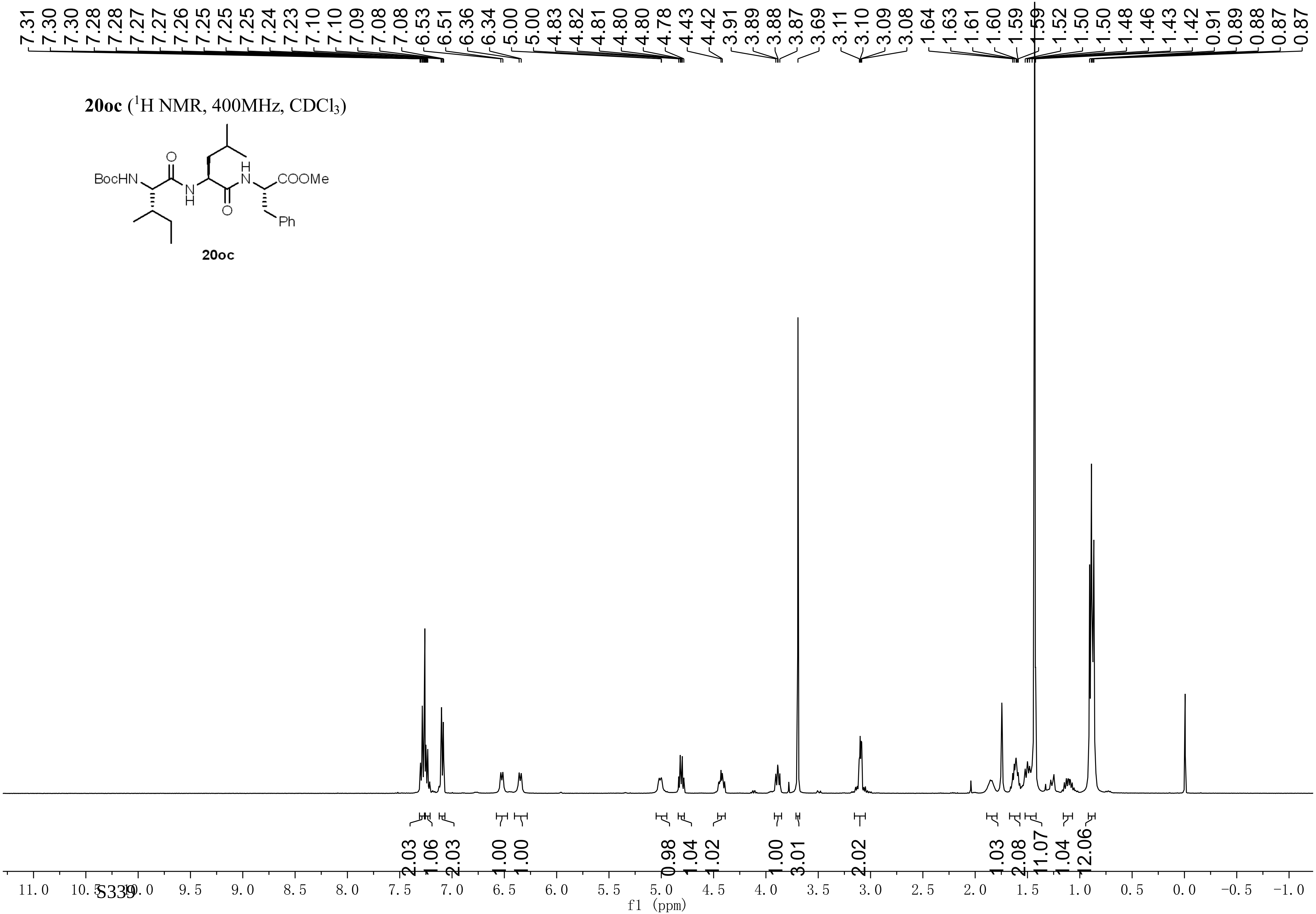


20n (^{13}C NMR, 101MHz, $CDCl_3$)

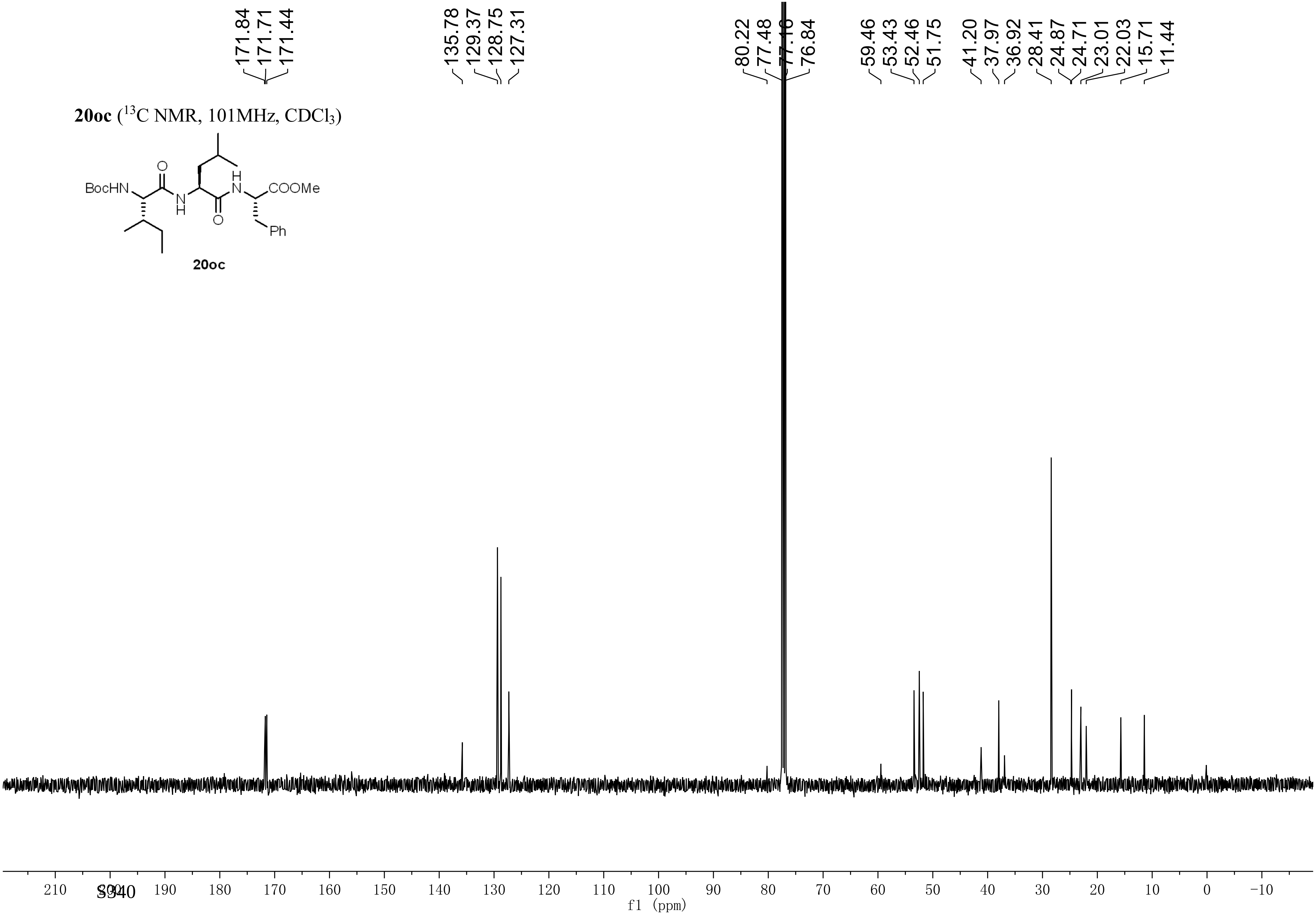


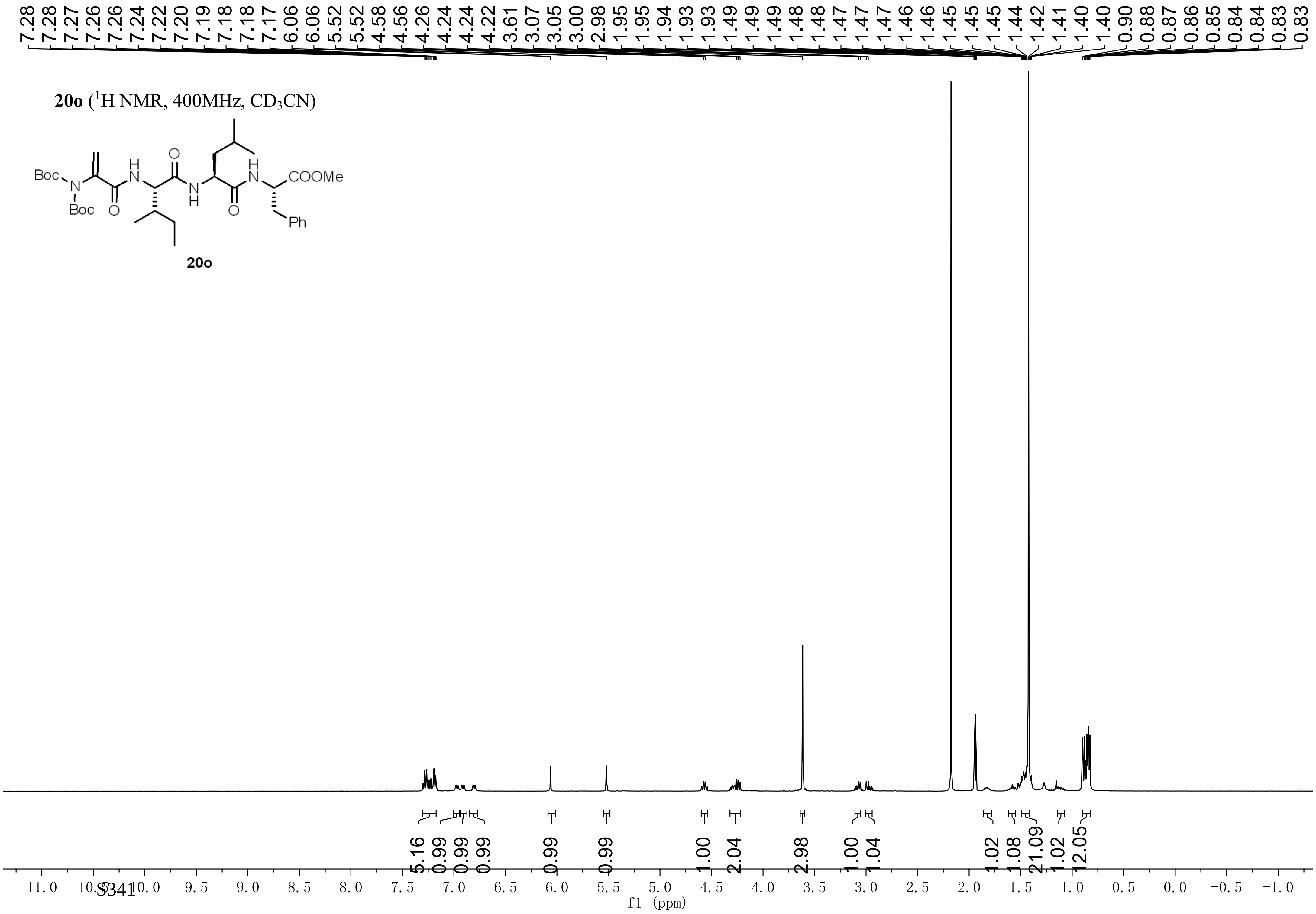
20n



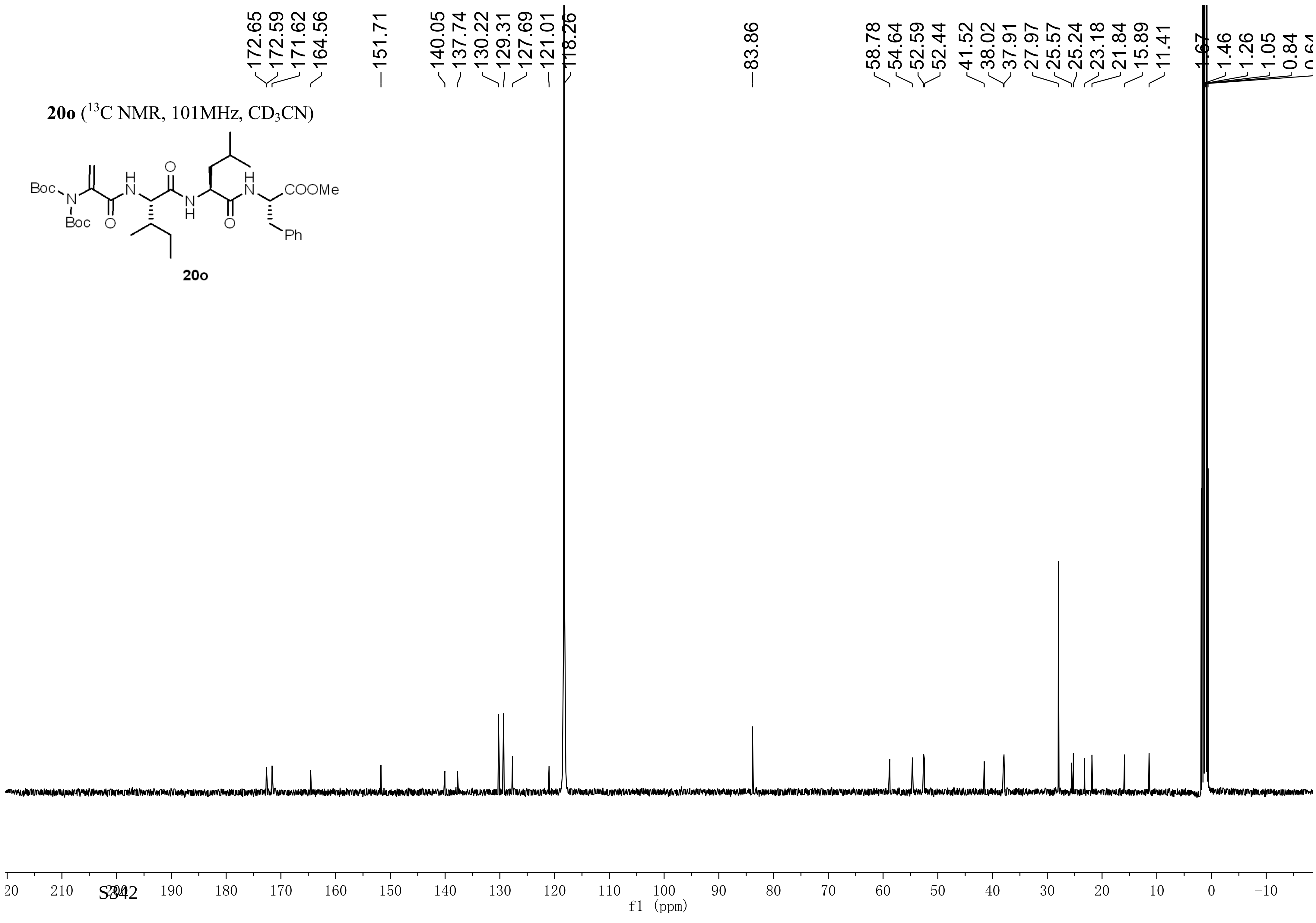

7.31 7.30 7.30 7.28 7.28 7.27 7.27 7.26 7.25 7.25 7.25 7.24 7.23 7.10 7.10 7.09 7.08 7.08 6.53 6.51 6.36 6.34 5.00 5.00 4.83 4.82 4.81 4.80 4.80 4.78 4.43 4.42 3.91 3.89 3.88 3.87 3.69 3.11 3.10 3.09 3.08 1.64 1.63 1.61 1.60 1.59 1.59 1.52 1.50 1.50 1.48 1.46 1.43 1.42 0.91 0.89 0.88 0.87 0.87
20oc (1H NMR, 400MHz, CDCl3)
BocHN
O
N
H
H
N
COOMe
O
Ph
20oc
2.03 1.06 2.03 1.00 1.00 0.98 1.04 1.02 1.00 3.01 2.02 1.03 2.08 11.07 1.04 12.06
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)

20oc (^{13}C NMR, 101MHz, CDCl$_3$)

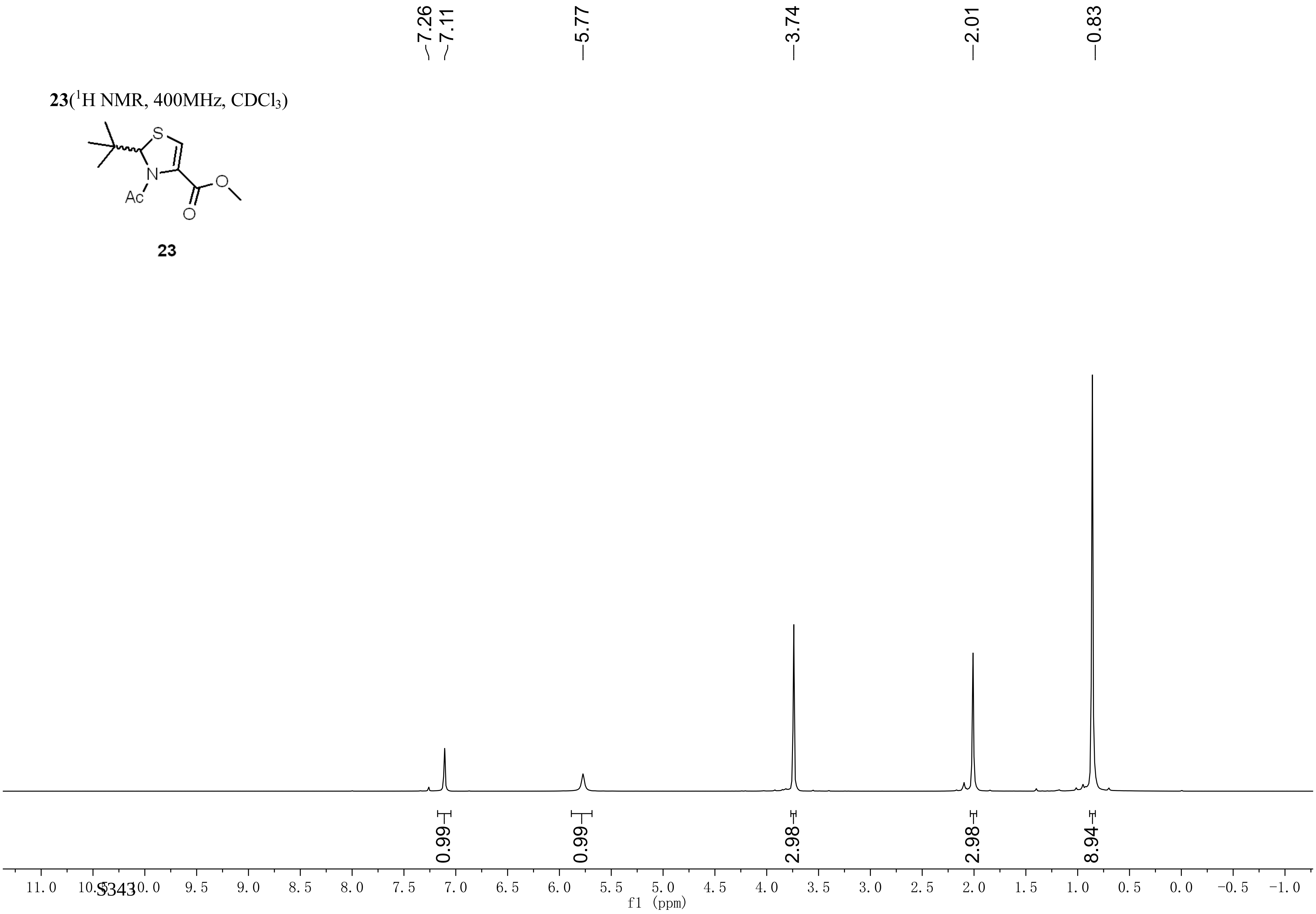



20o (^{1}H NMR, 400MHz, CD_3CN)
Boc
N
Boc
O
H
N
O
N
H
O
H
N
COOMe
O
Ph
20o
7.28 7.28 7.27 7.26 7.26 7.24 7.22 7.20 7.19 7.18 7.18 7.17 6.06 6.06 5.52 5.52 4.58 4.56 4.26 4.24 4.24 4.22 3.61 3.07 3.05 3.00 2.98 1.95 1.95 1.94 1.93 1.49 1.49 1.49 1.48 1.48 1.47 1.47 1.47 1.46 1.46 1.45 1.45 1.45 1.44 1.42 1.41 1.40 1.40 0.90 0.88 0.87 0.86 0.85 0.84 0.84 0.83 0.83
5.16 0.99 0.99 0.99 0.99 0.99 1.00 2.04 2.98 1.00 1.04 1.02 1.08 21.09 1.02 12.05
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)

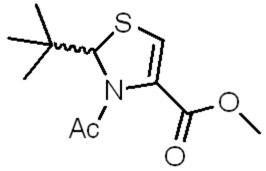
20o (^{13}C NMR, 101MHz, CD_3CN)



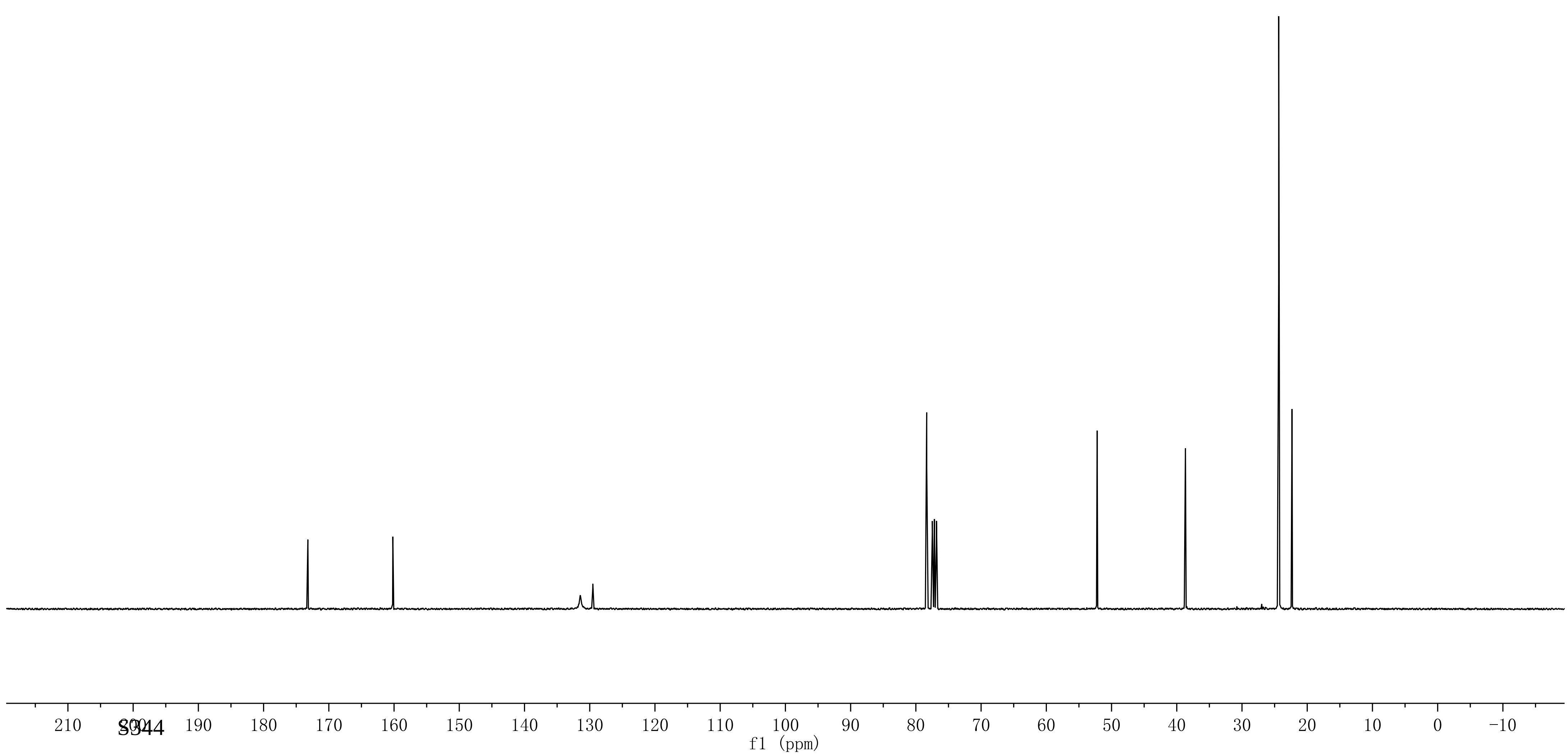
23(^{1}H NMR, 400MHz, $CDCl_3$)



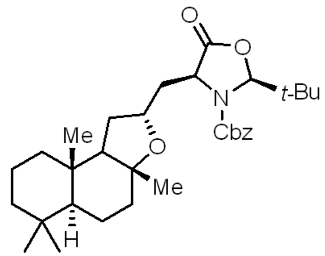
23 (^{13}C NMR, 101MHz, $CDCl_3$)



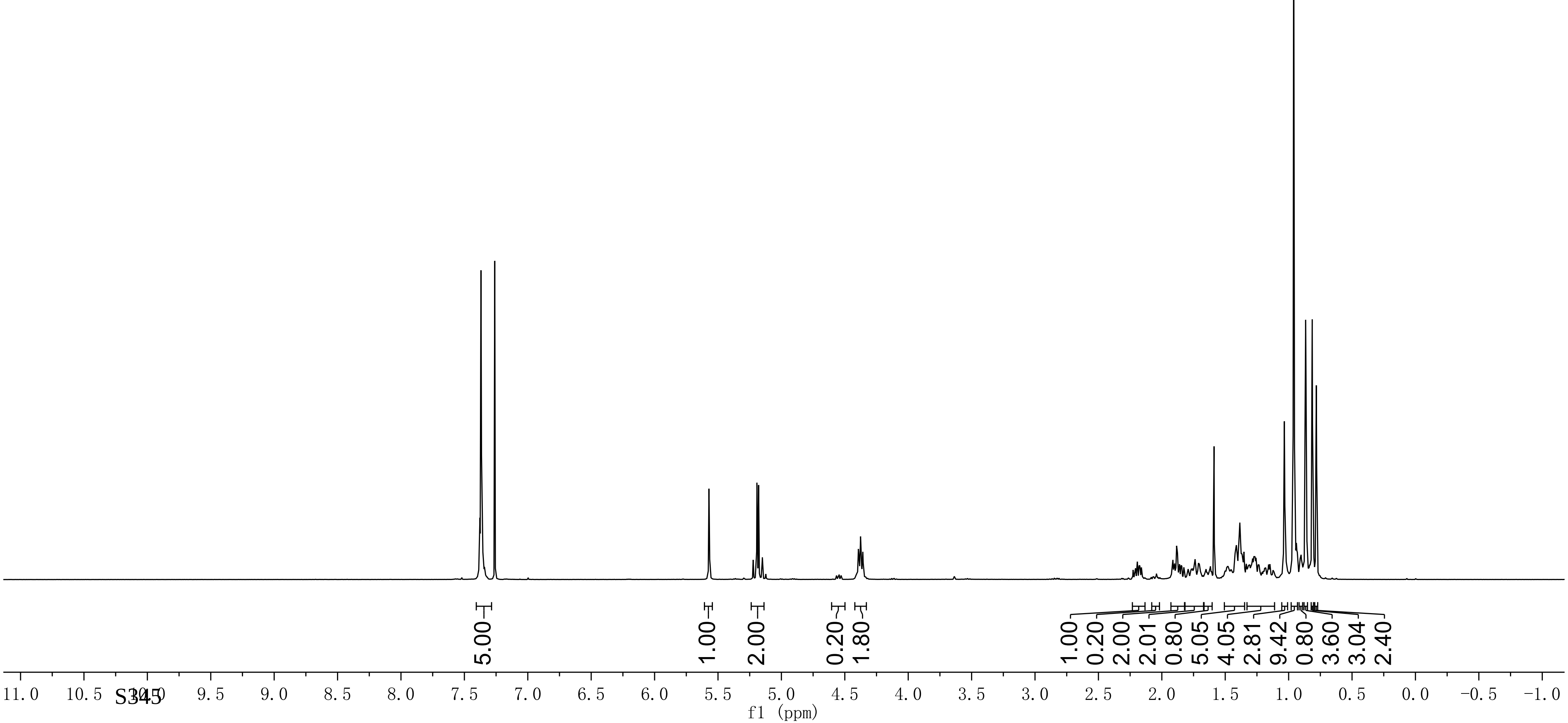
23



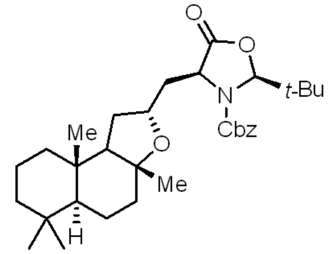
22b (^{1}H NMR, 400MHz, $CDCl_3$)



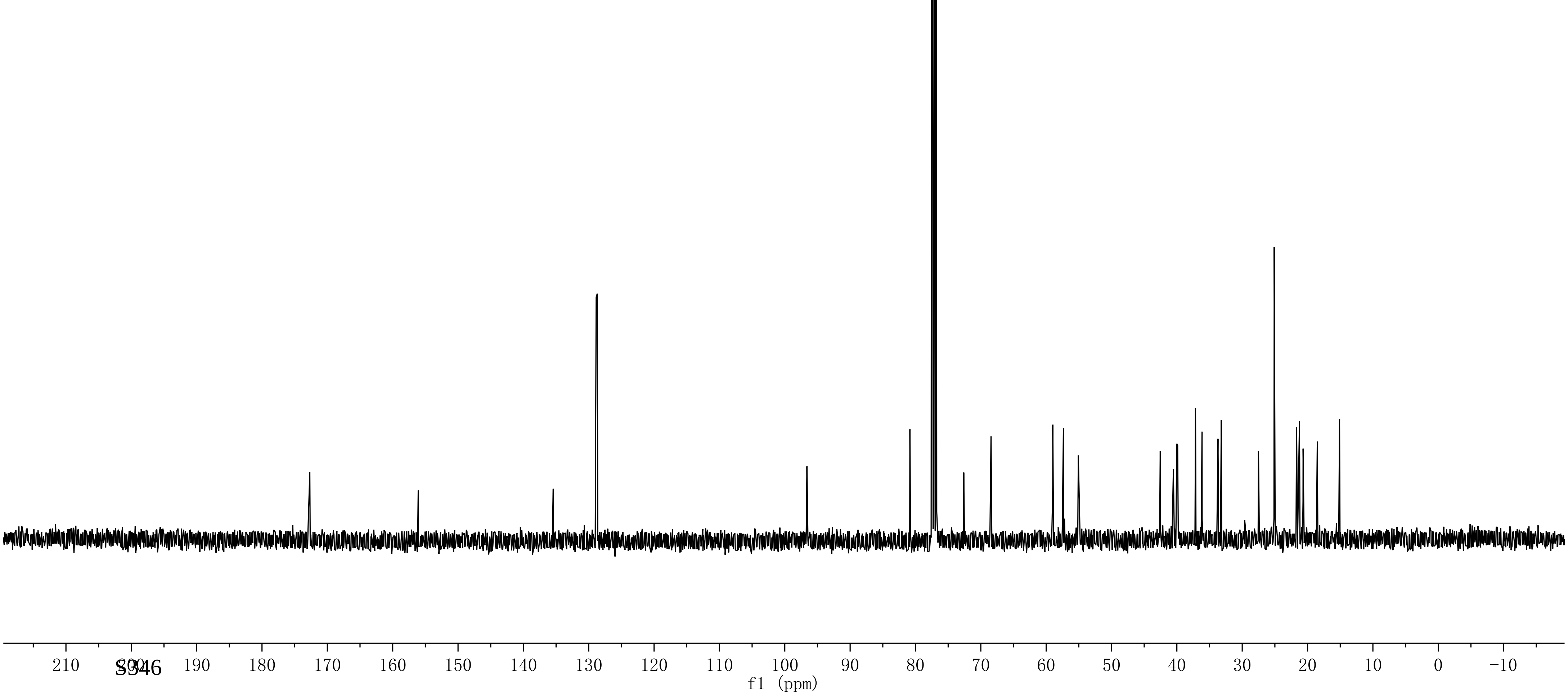
22b

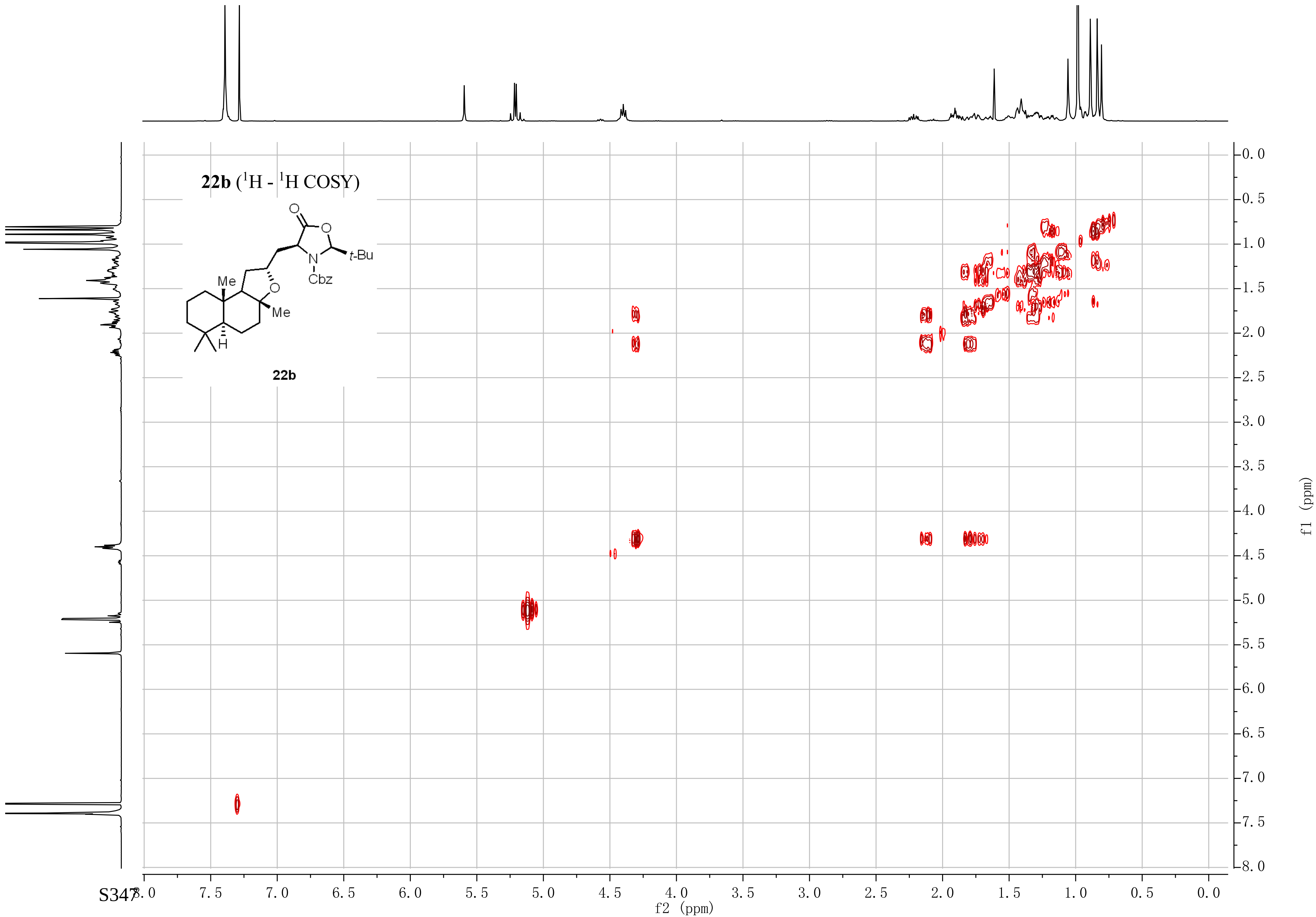


22b (^{13}C NMR, 101MHz, $CDCl_3$)

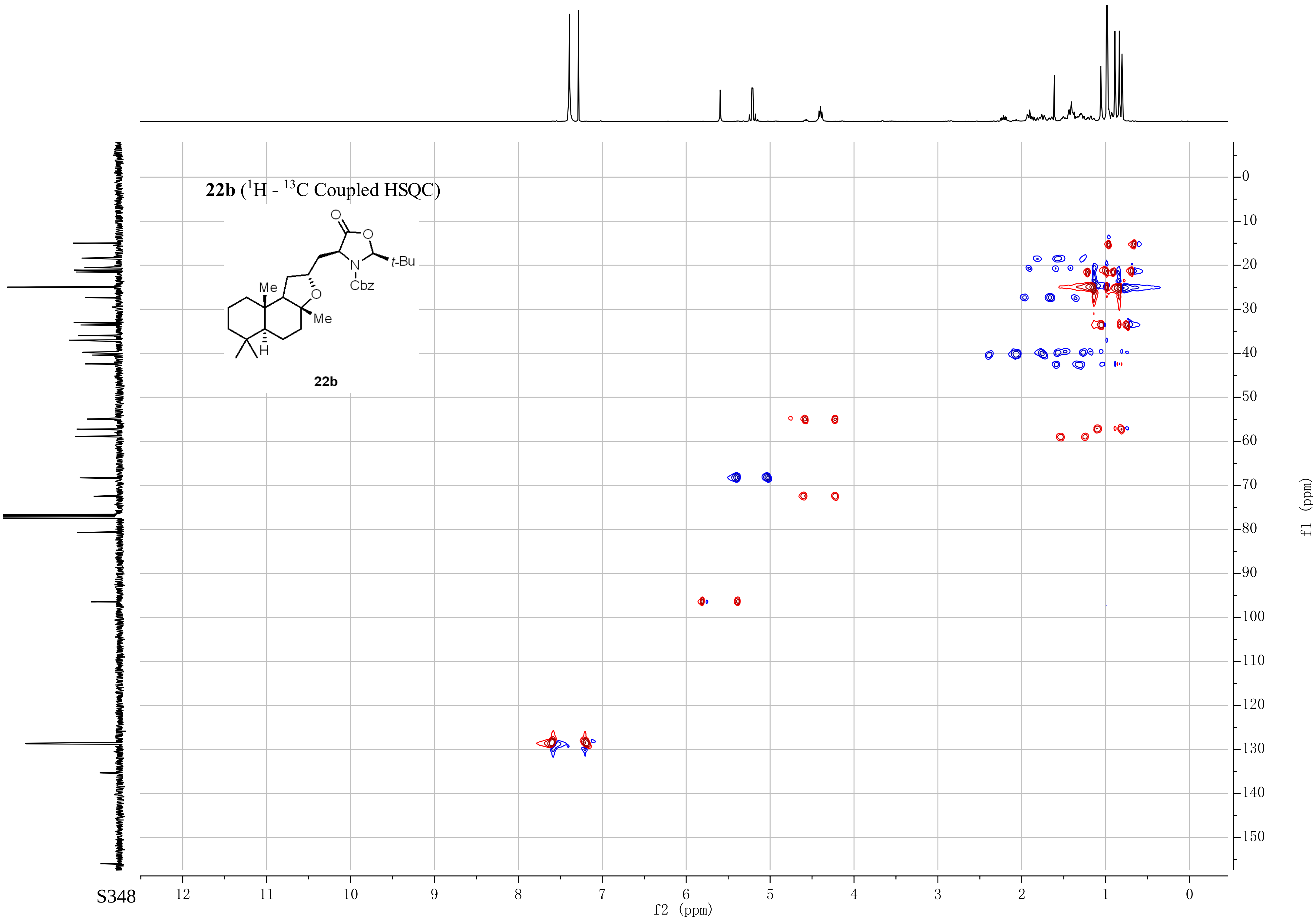


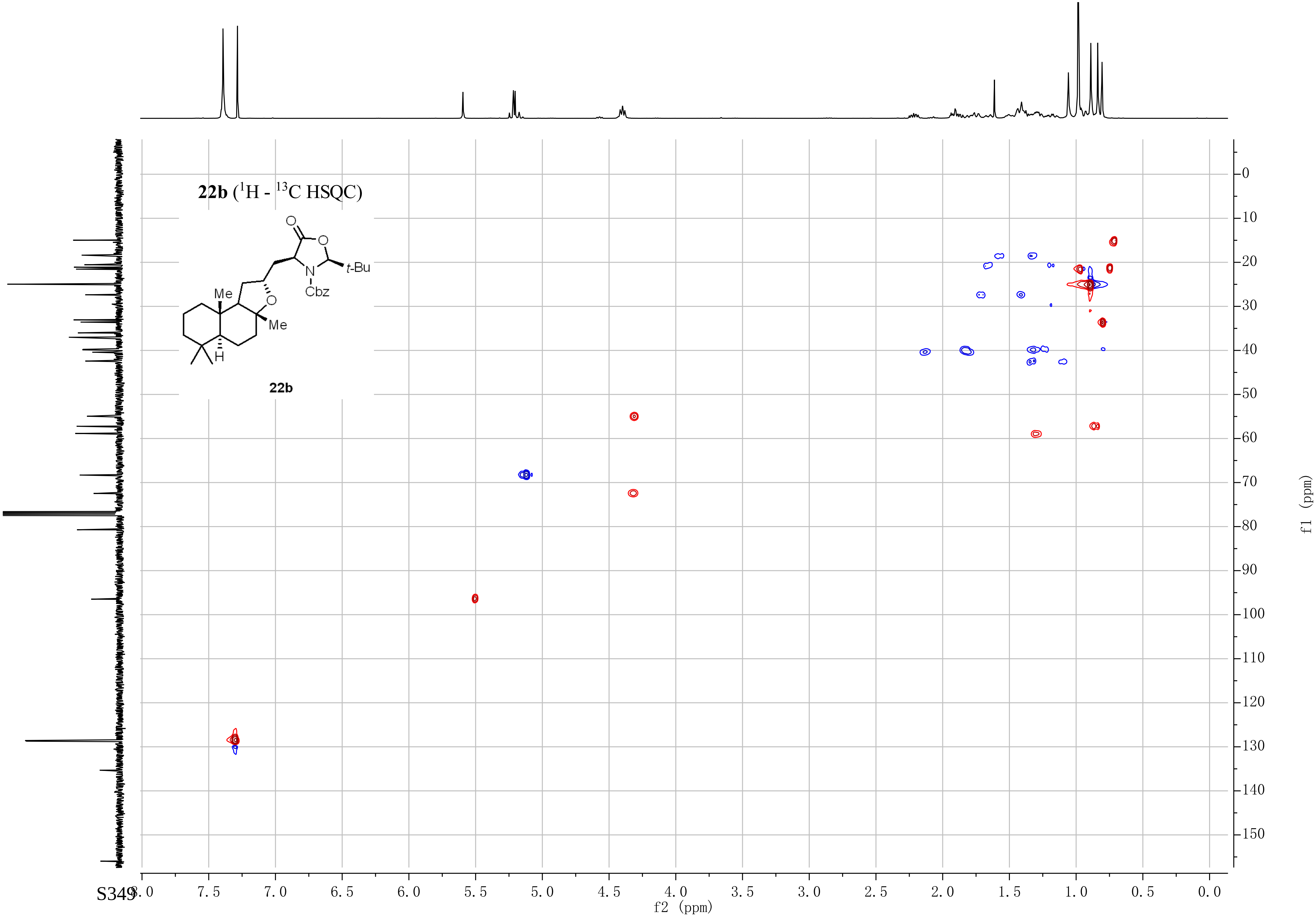
22b



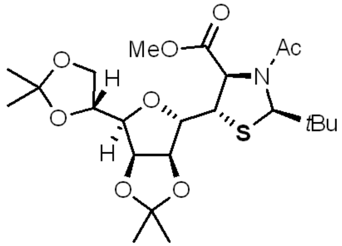


22b (^{1}H - ^{1}H COSY)
O
O
N
t-Bu
Cbz
Me
O
Me
H
22b
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

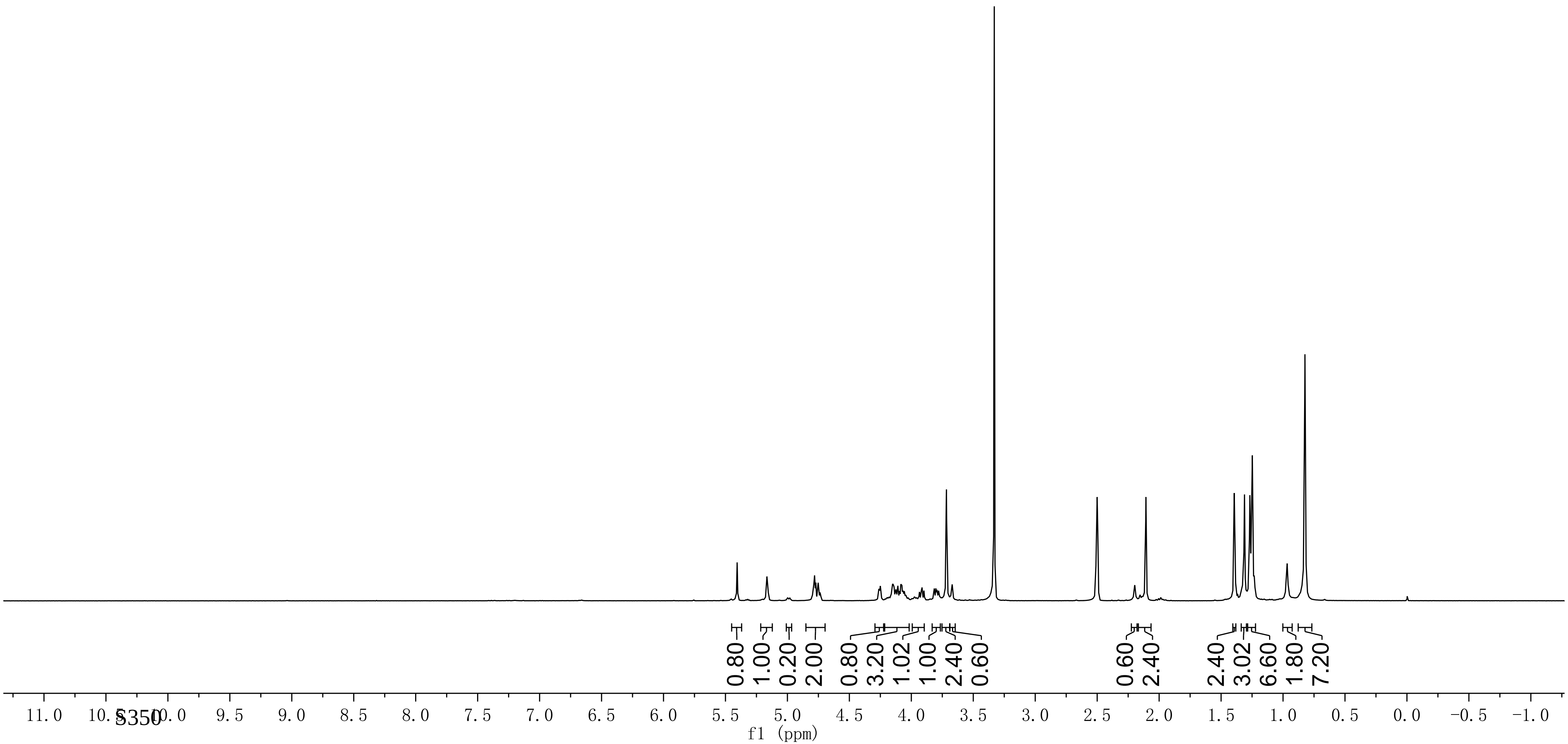

22b (¹H - ¹³C Coupled HSQC)
O
O
N
Cbz
t-Bu
Me
O
Me
H
22b
f2 (ppm)
f1 (ppm)


22b (1H - 13C HSQC)
t-Bu
Cbz
Me
Me
H
22b
f2 (ppm)
f1 (ppm)

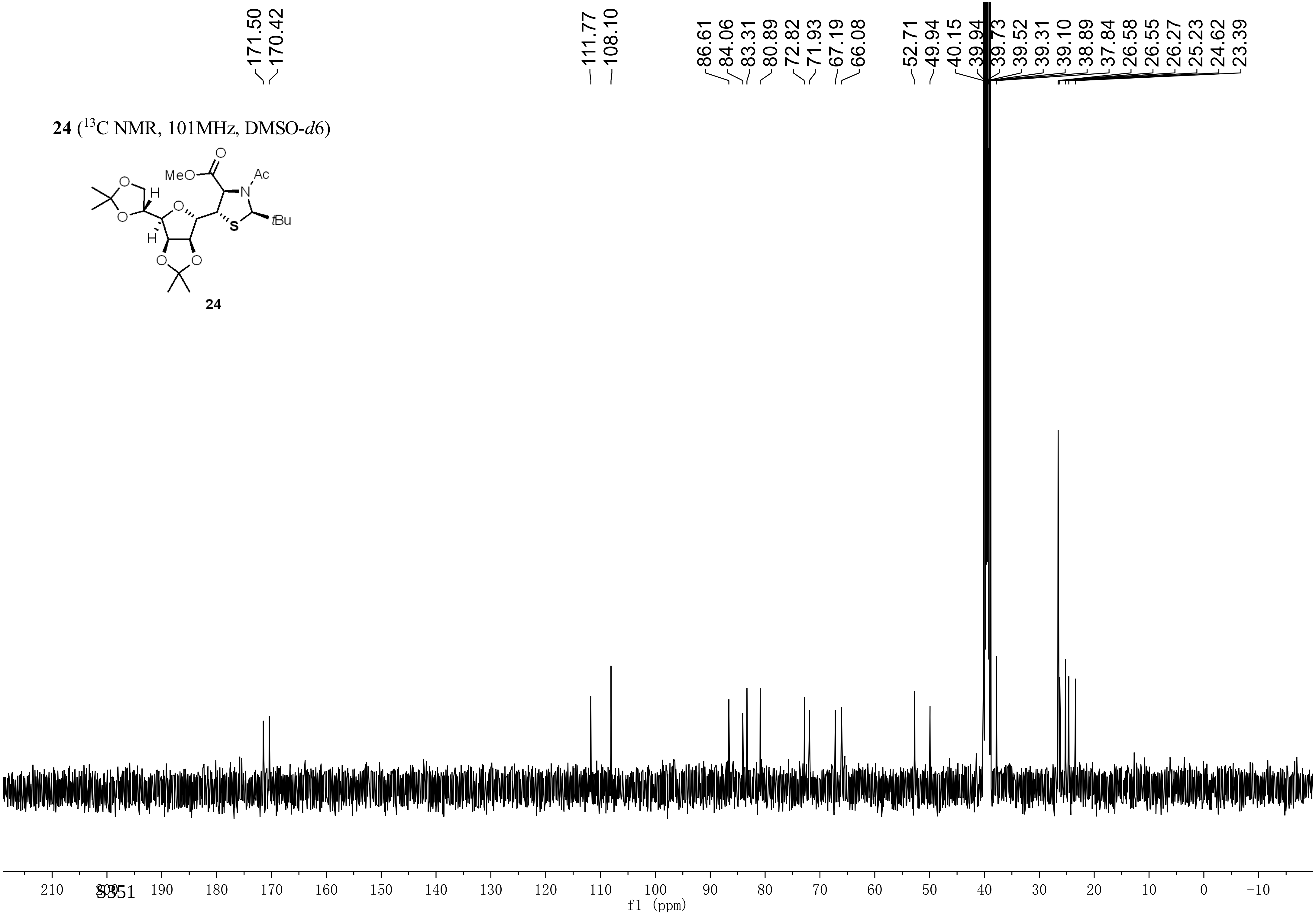
24 ([1]H NMR, 400MHz, DMSO-*d6*)

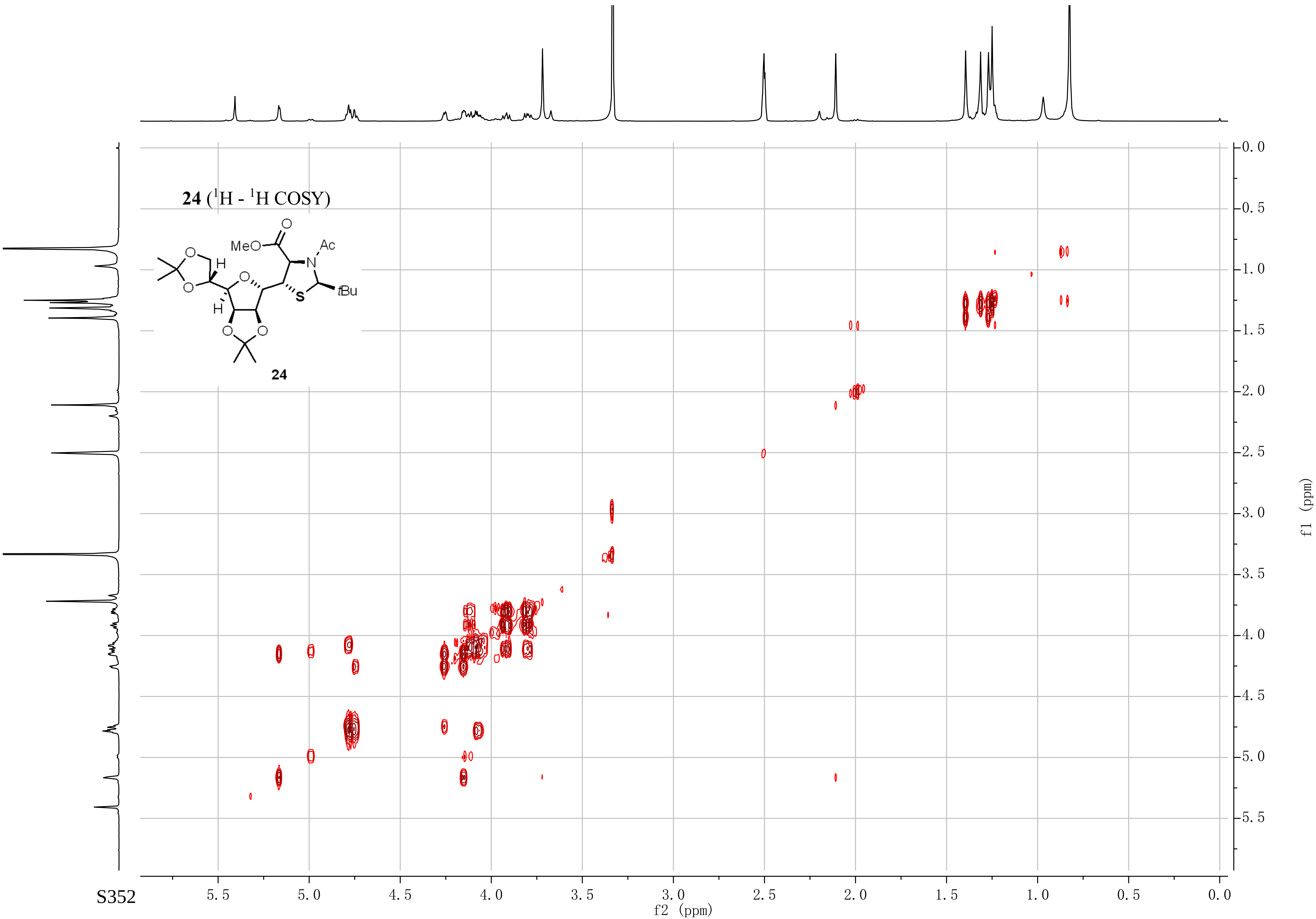


24

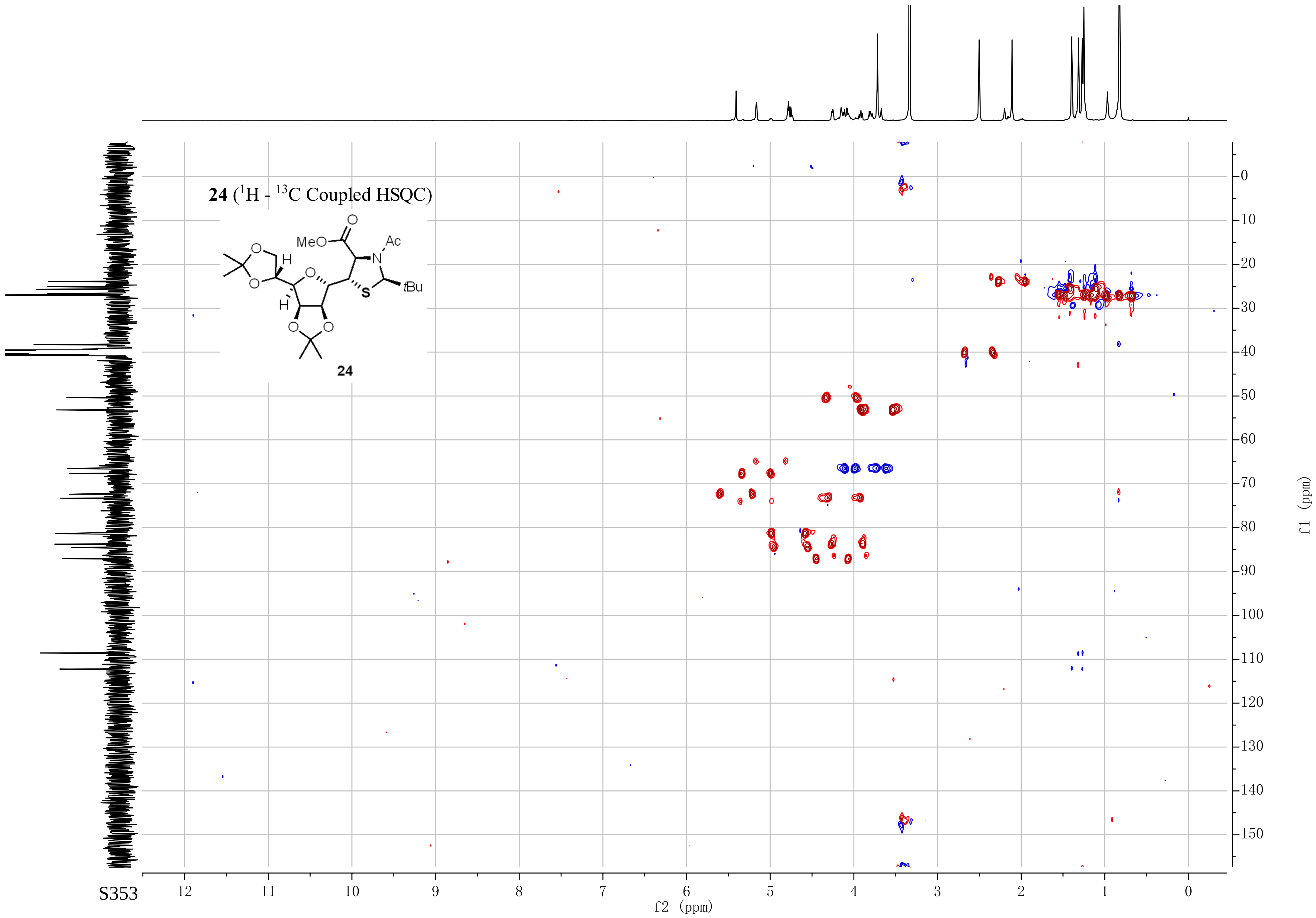


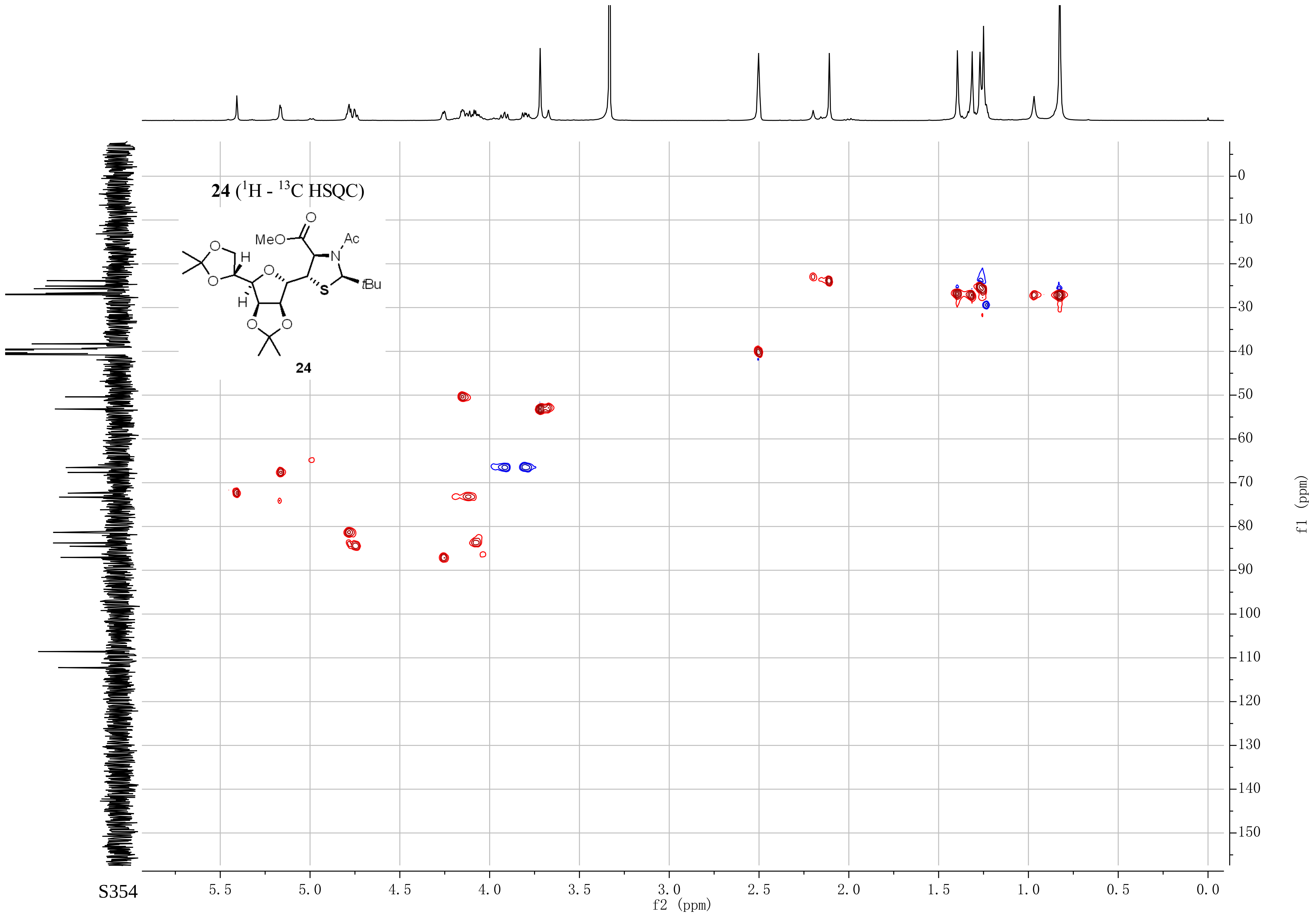
24 (^{13}C NMR, 101MHz, DMSO-*d6*)





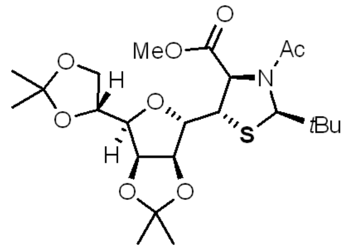
24 (1H - 1H COSY)
MeO
O
Ac
N
O
H
O
O
S
tBu
O
H
O
O
24
f2 (ppm)
f1 (ppm)


24 (^{1}H - ^{13}C Coupled HSQC)
MeO
O
N
Ac
O
H
O
O
S
*t*Bu
H
O
O
24
f2 (ppm)
f1 (ppm)

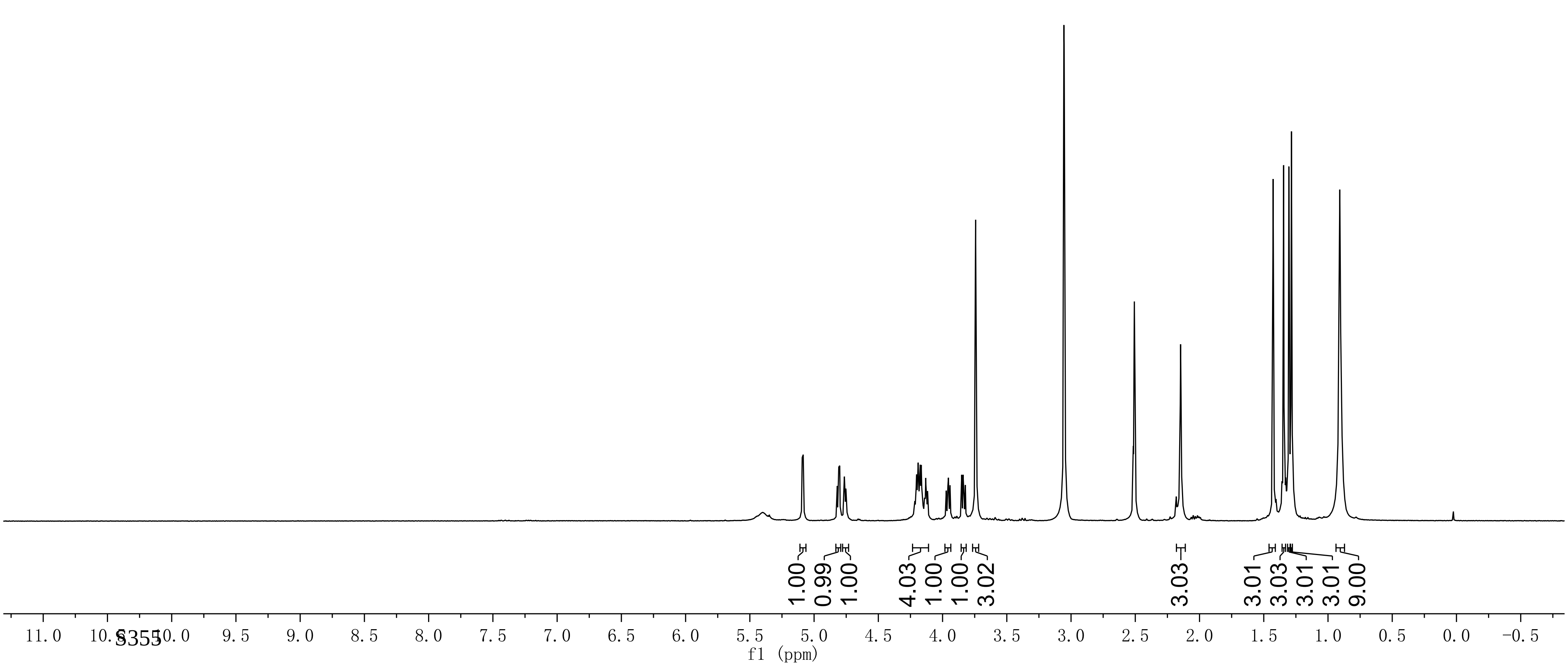


24 (1H - 13C HSQC)
MeO
O
Ac
N
H
O
O
O
S
tBu
H
O
O
24
f2 (ppm)
f1 (ppm)

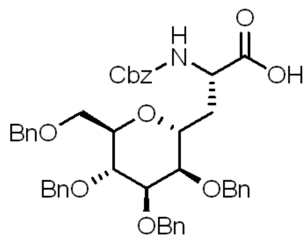
24 (^{1}H NMR, 500MHz, DMSO-*d6*, 85ºC)



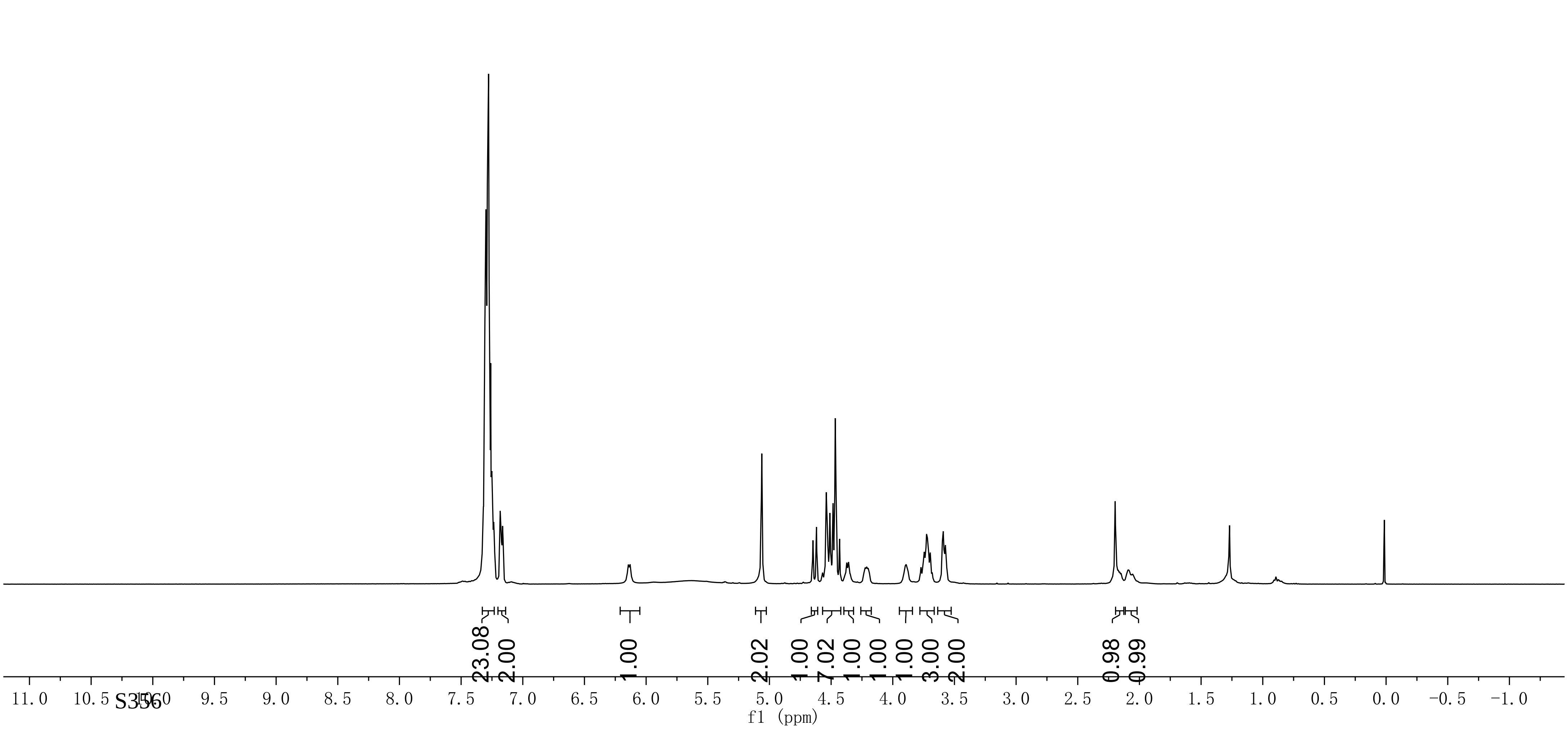
24



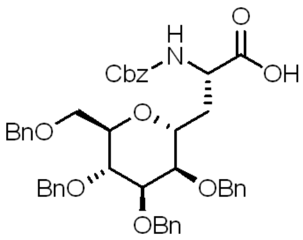
25 (^{1}H NMR, 400MHz, $CDCl_3$)



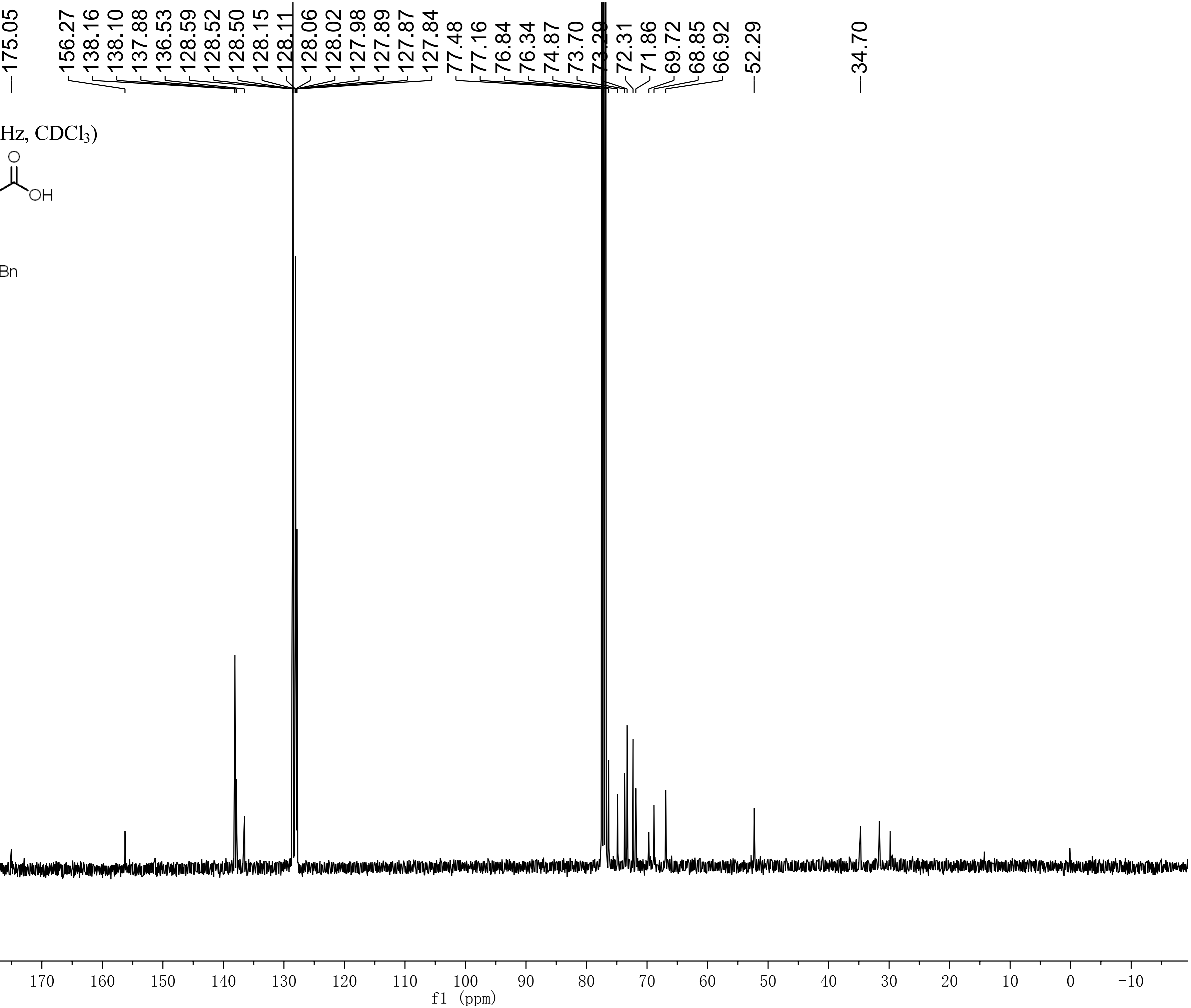
25



25 (^{13}C NMR, 101MHz, $CDCl_3$)

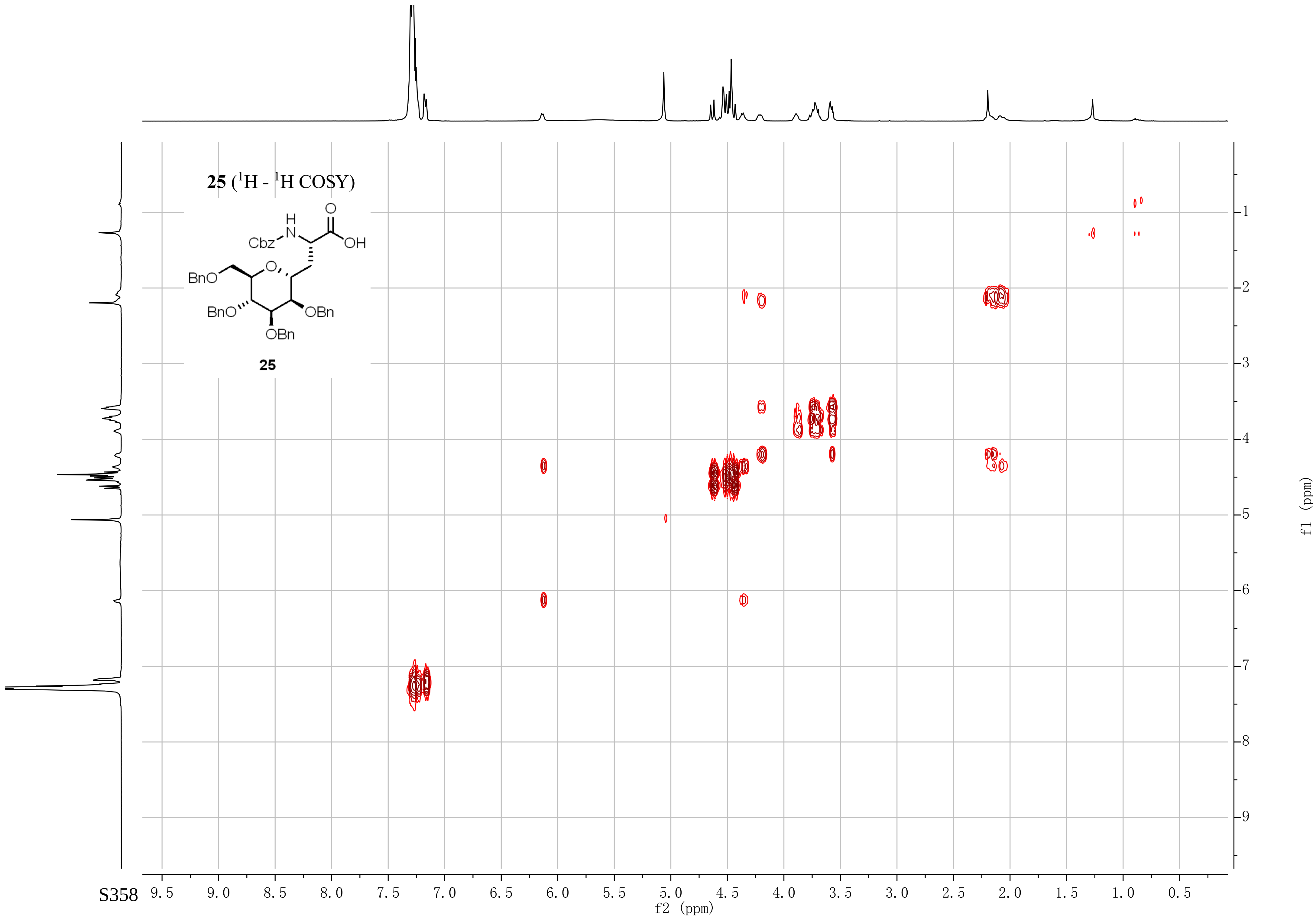


25

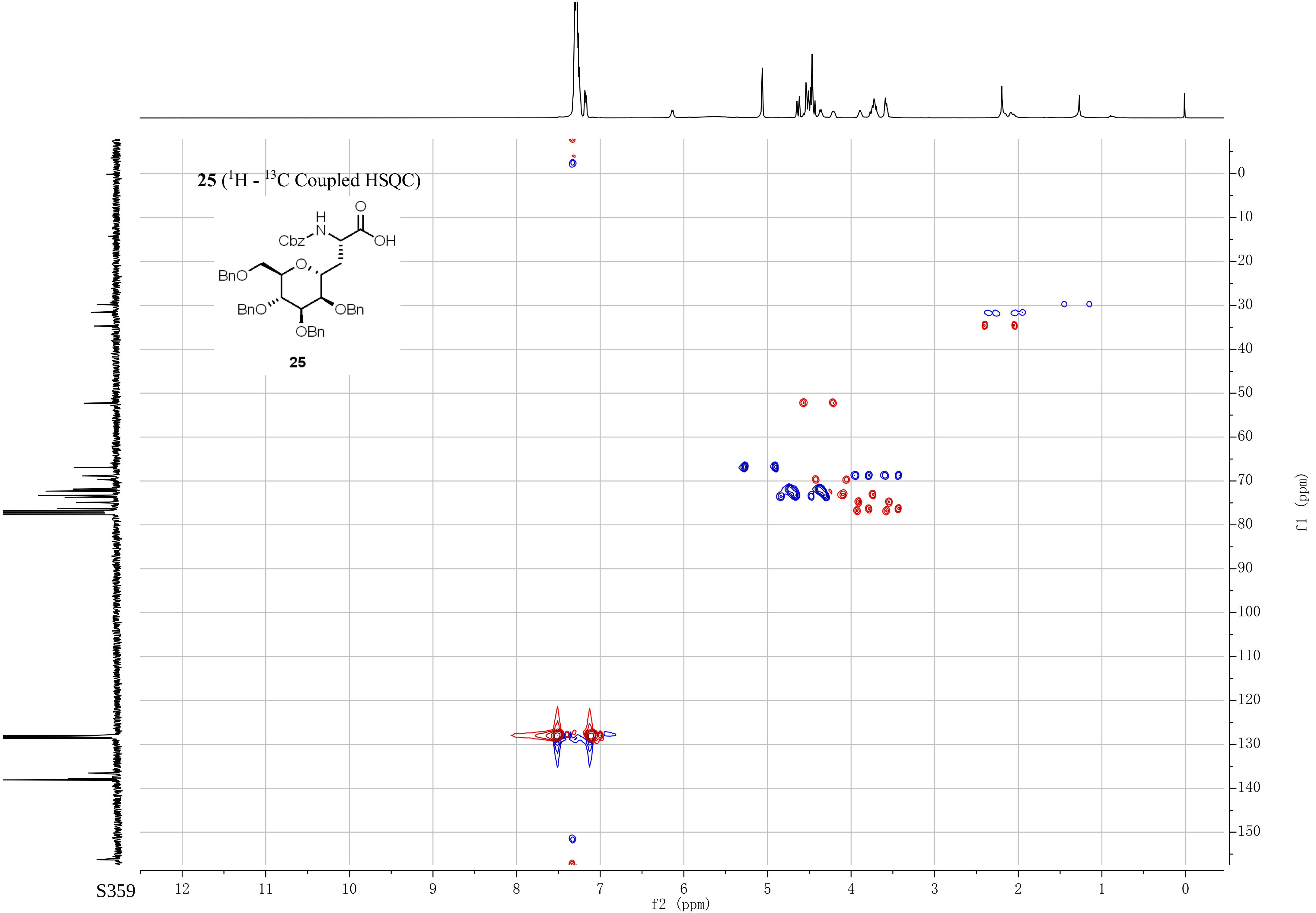


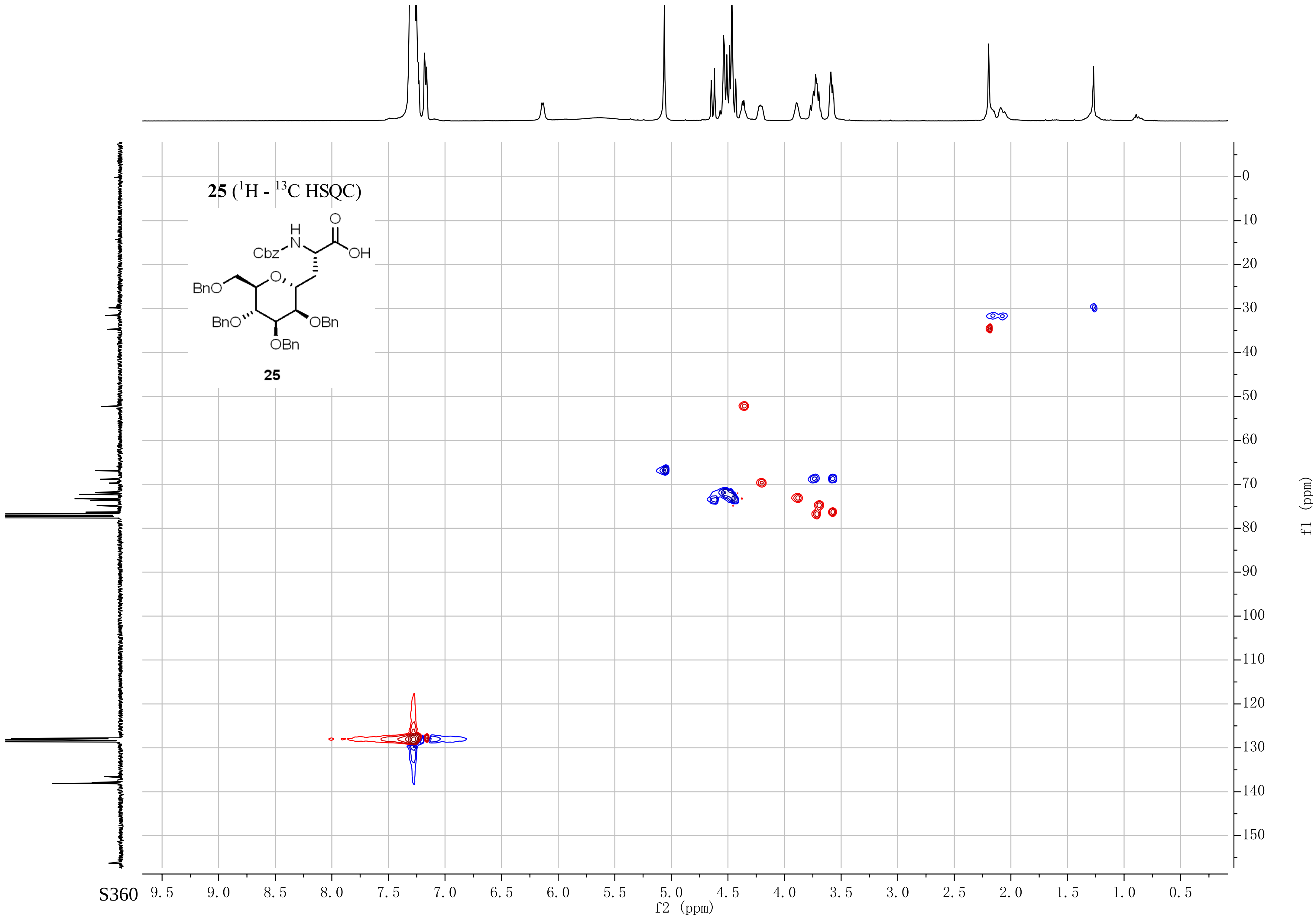
25 (^{1}H - ^{1}H COSY)

25



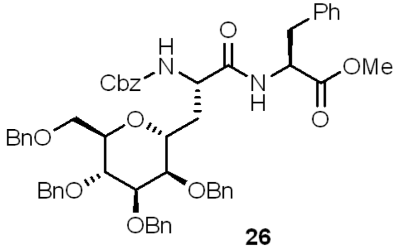
25 (^{1}H - ^{13}C Coupled HSQC)



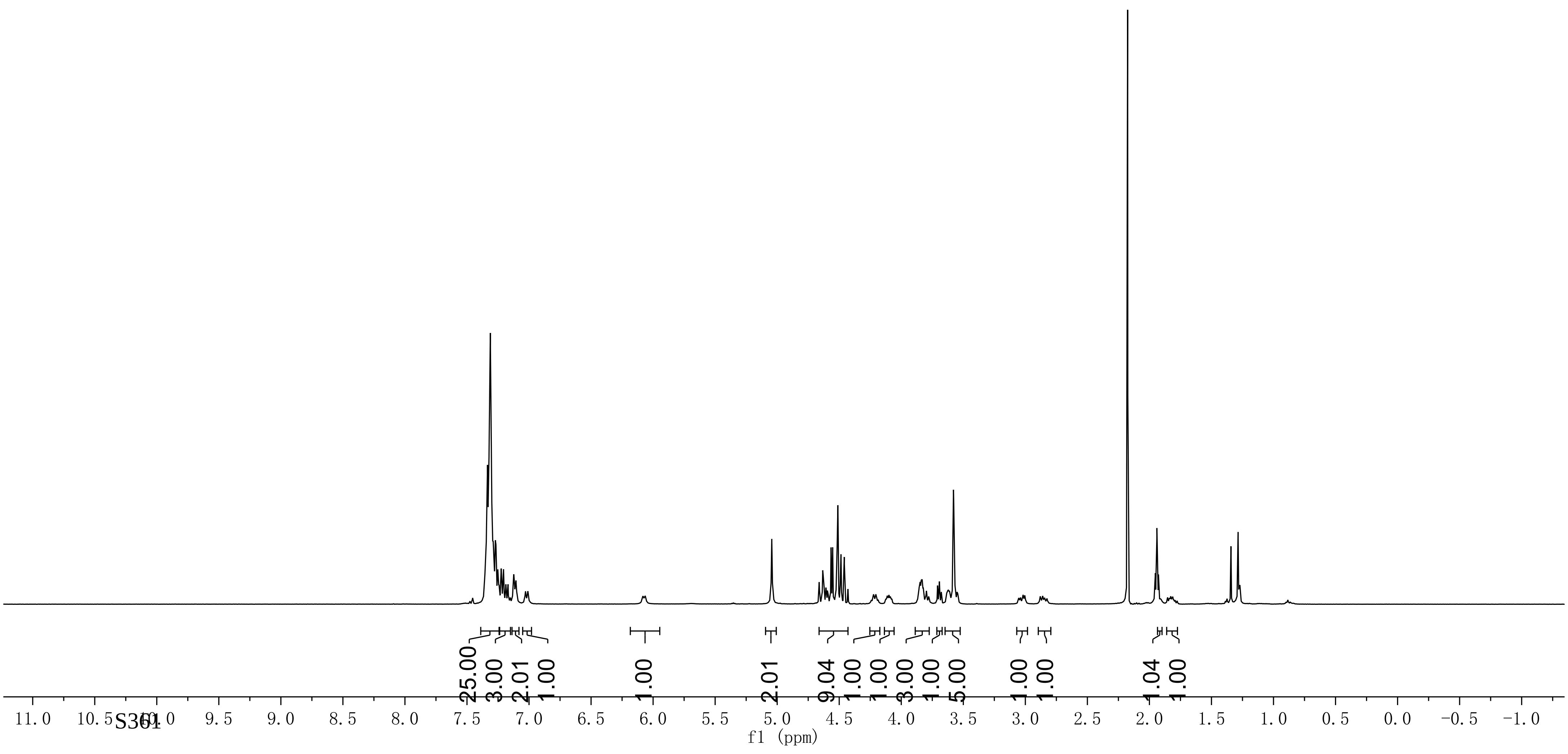


25 (¹H - ¹³C HSQC)
Cbz
H
N
O
OH
BnO
O
BnO
OBn
OBn
25
f2 (ppm)
f1 (ppm)

26 (^{1}H NMR, 400MHz, CD_3CN)

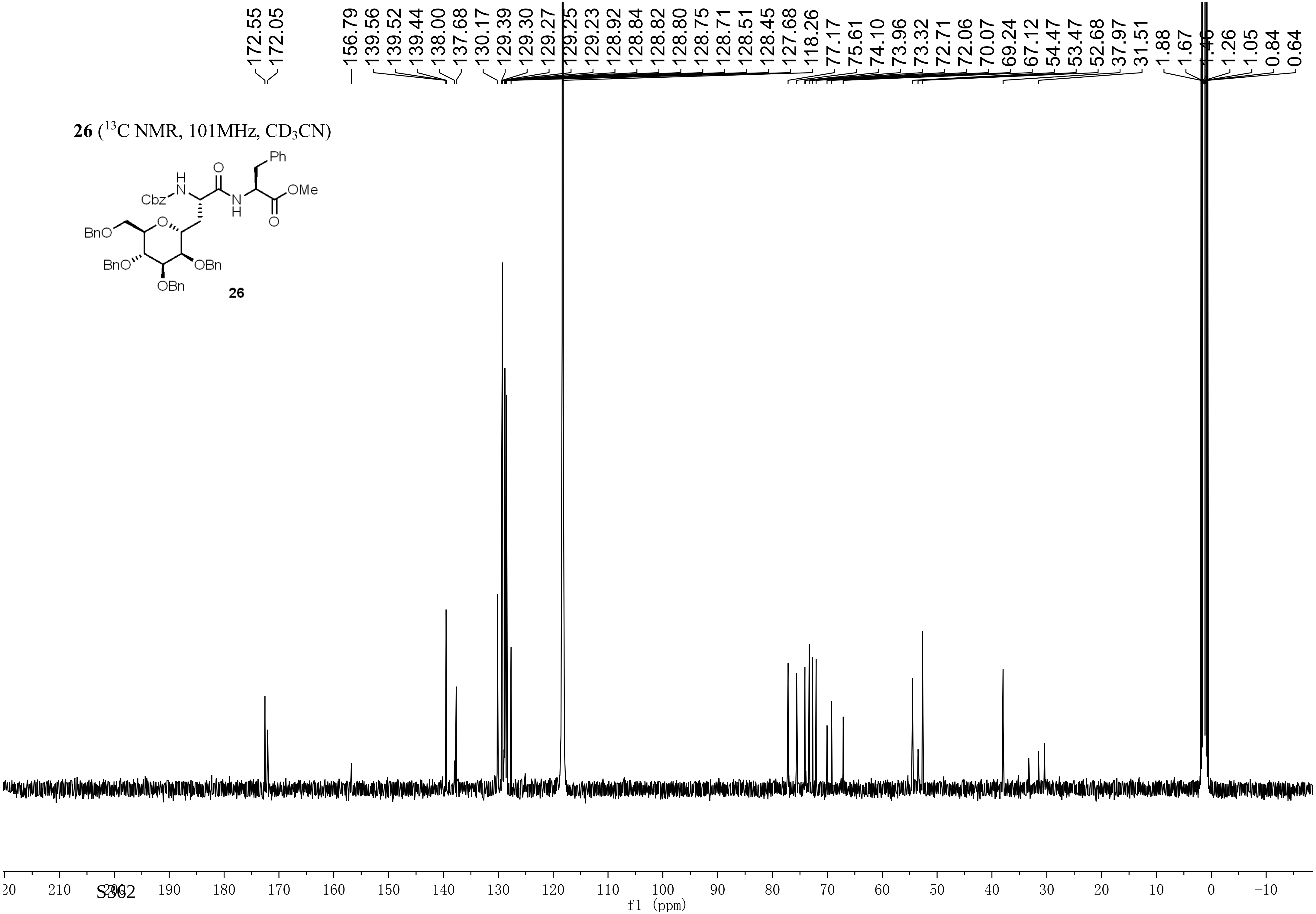


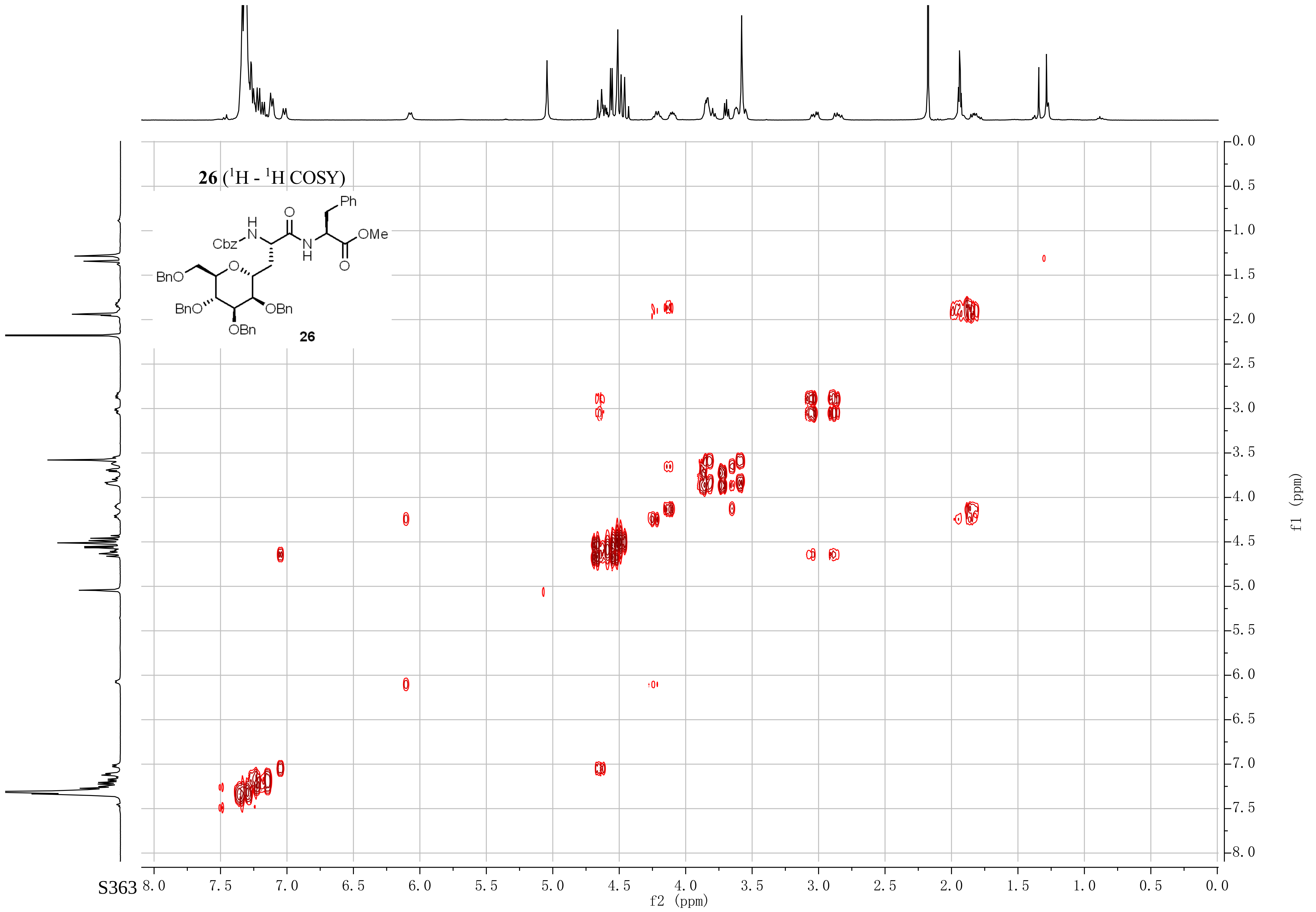
26



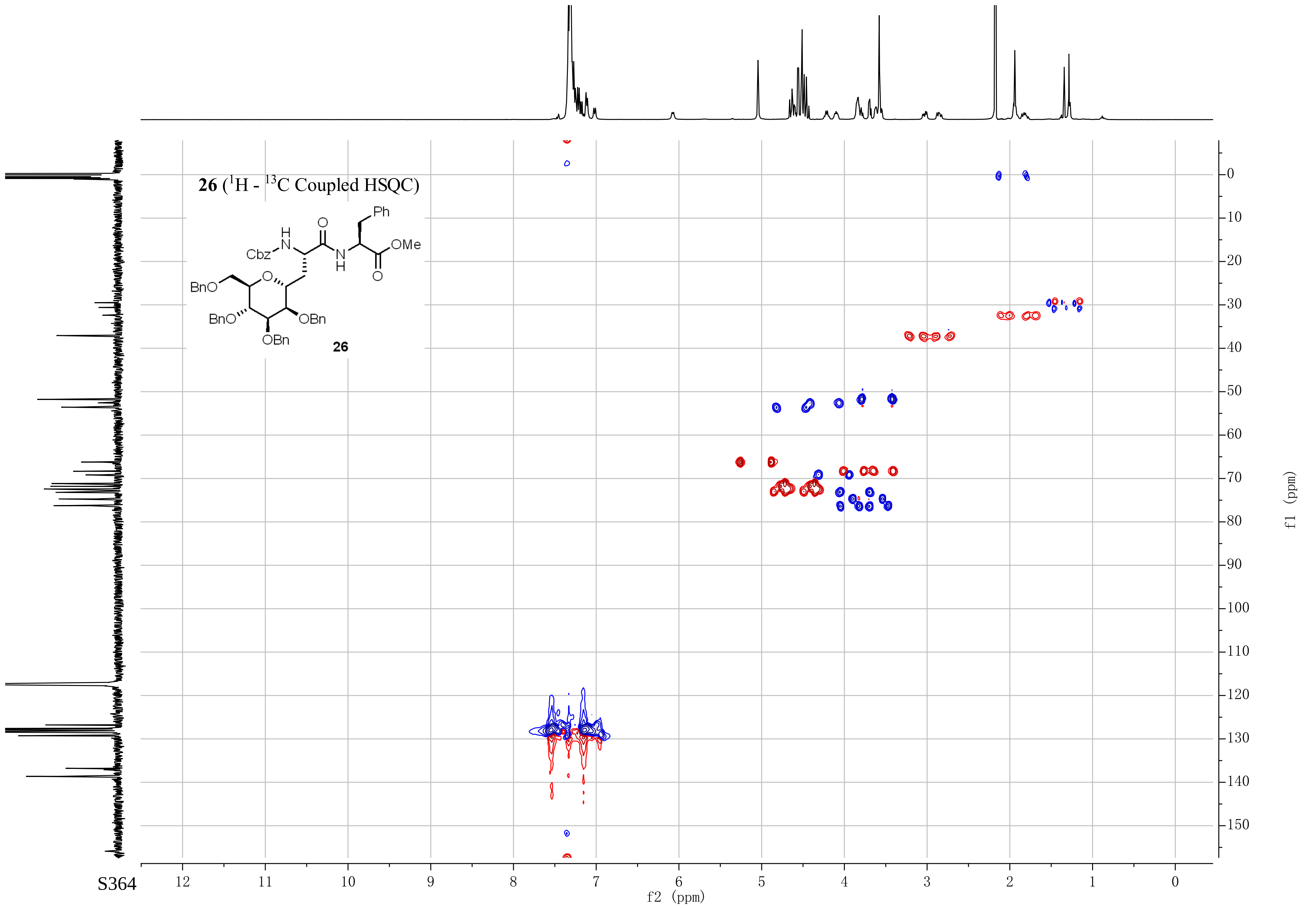
26 (^{13}C NMR, 101MHz, CD_3CN)

26

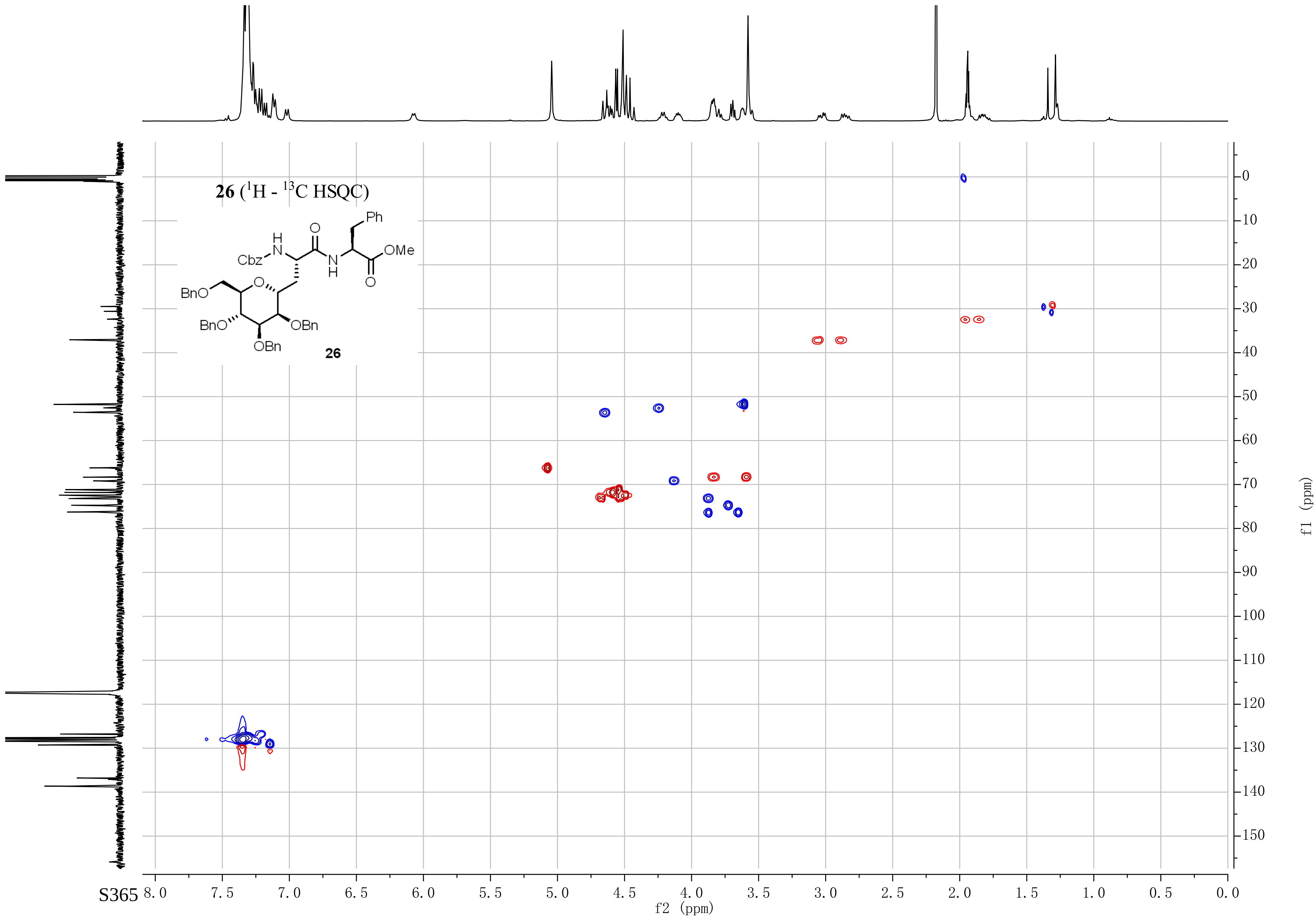




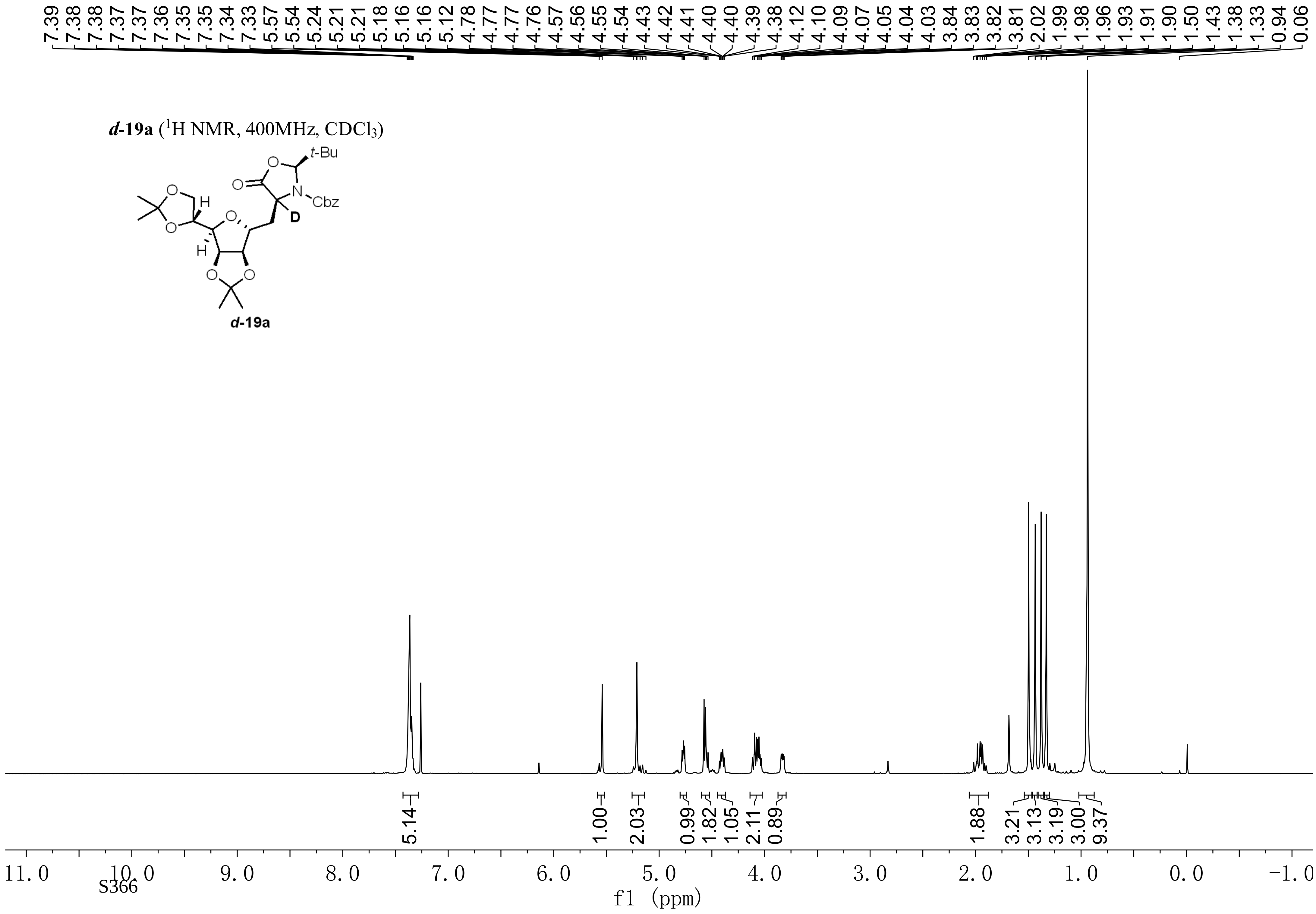
26 (¹H - ¹H COSY)
Ph
H
N
Cbz
O
N
H
OMe
O
BnO
O
BnO
OBn
OBn
26
f2 (ppm)
f1 (ppm)



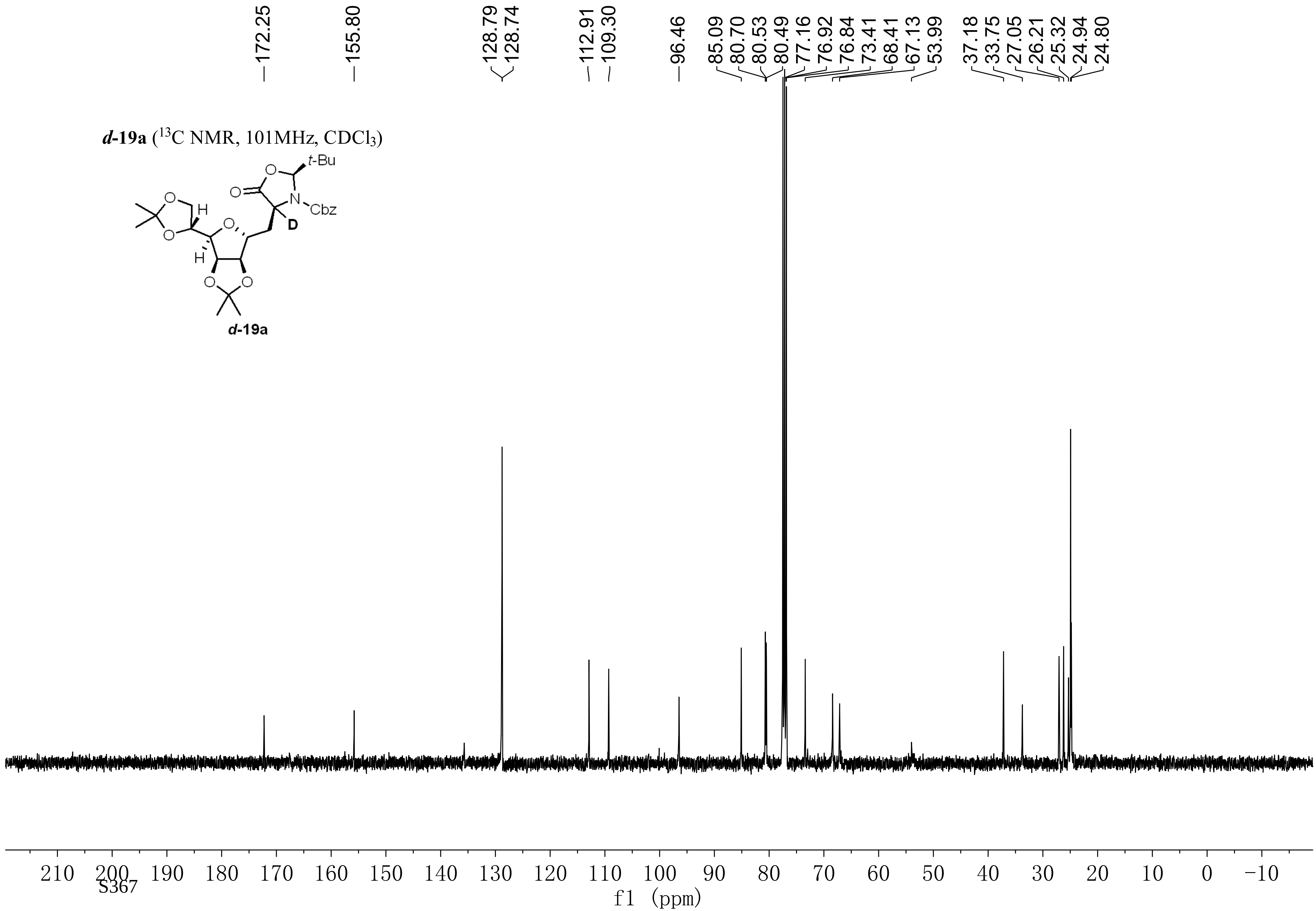
26 ([1]H - [13]C Coupled HSQC)
Ph
O
H
N
Cbz
N
H
OMe
O
BnO
O
BnO
OBn
OBn
26
f2 (ppm)
f1 (ppm)



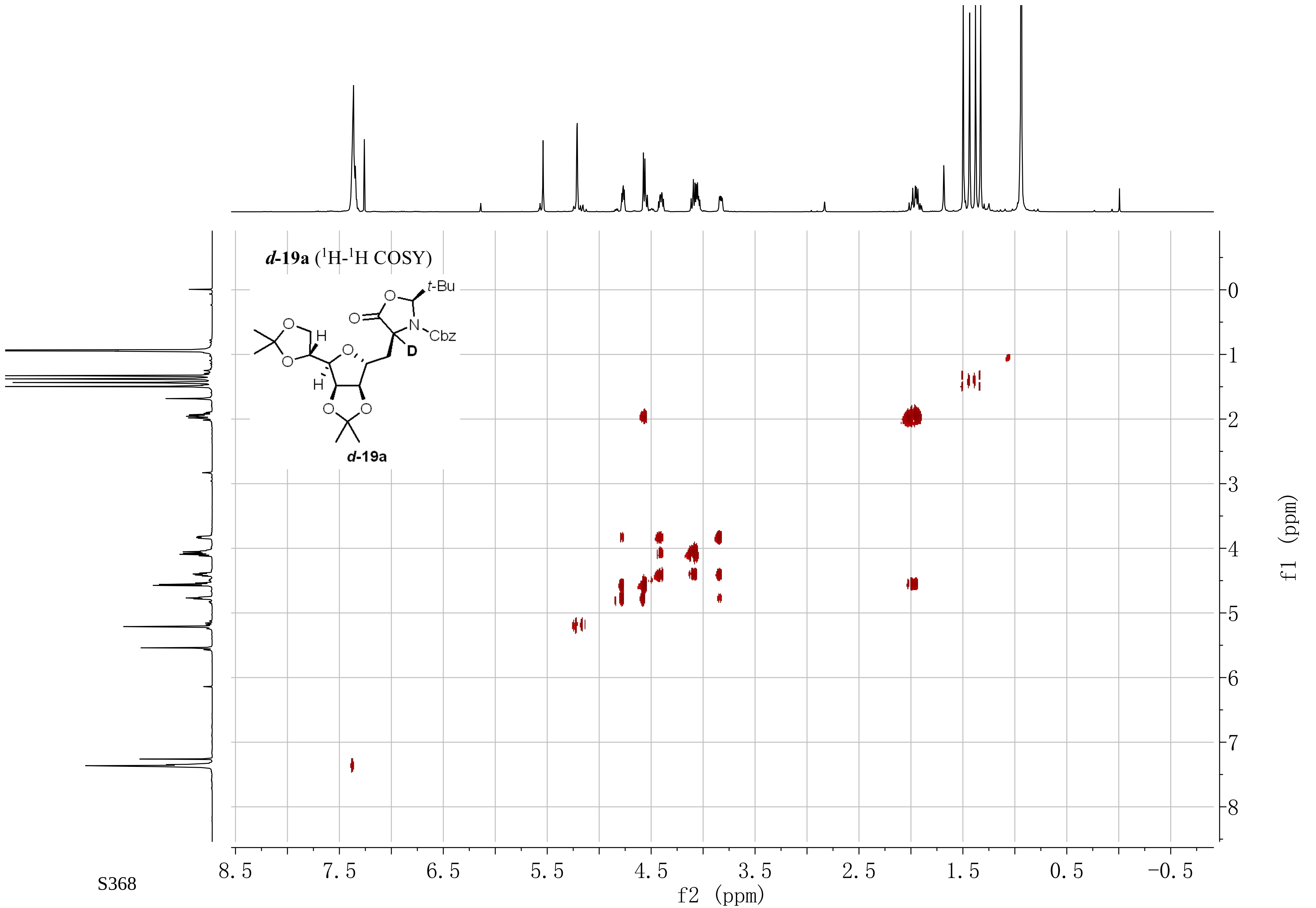
26 (1H - 13C HSQC)
Ph
O
H
N
Cbz
N
H
OMe
O
BnO
O
BnO
OBn
OBn
26
f2 (ppm)
f1 (ppm)



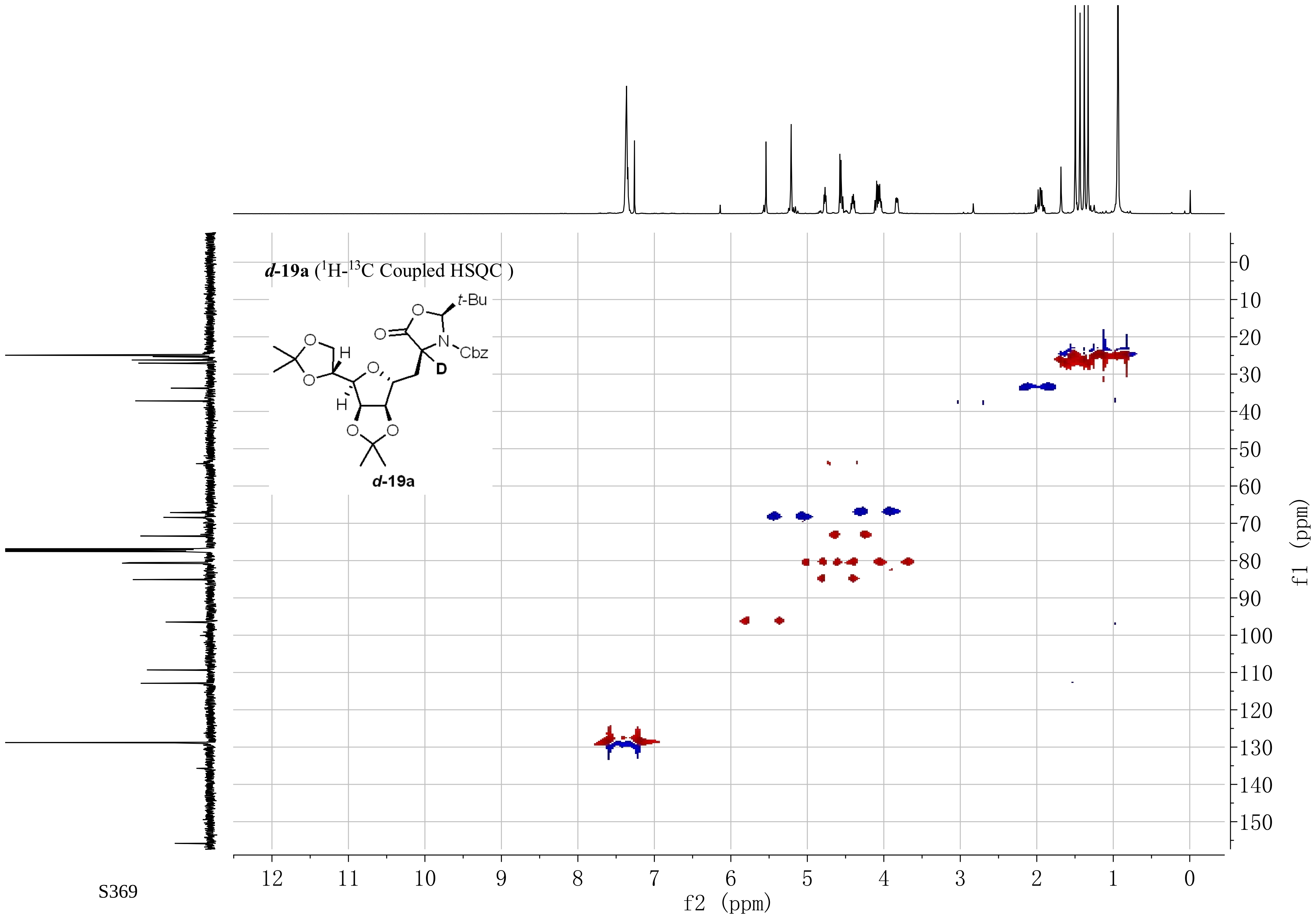
7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.33 5.57 5.54 5.24 5.21 5.21 5.18 5.16 5.16 5.12 4.78 4.77 4.77 4.76 4.57 4.56 4.55 4.54 4.43 4.42 4.41 4.40 4.40 4.39 4.38 4.12 4.10 4.09 4.07 4.05 4.04 4.03 3.84 3.83 3.82 3.81 2.02 1.99 1.98 1.96 1.93 1.91 1.90 1.50 1.43 1.38 1.33 0.94 0.06
d-19a (1H NMR, 400MHz, CDCl3)
t-Bu
O
N
Cbz
D
H
d-19a
5.14
1.00
2.03
0.99
1.82
1.05
2.11
0.89
1.88
3.21
3.13
3.19
3.00
9.37
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)



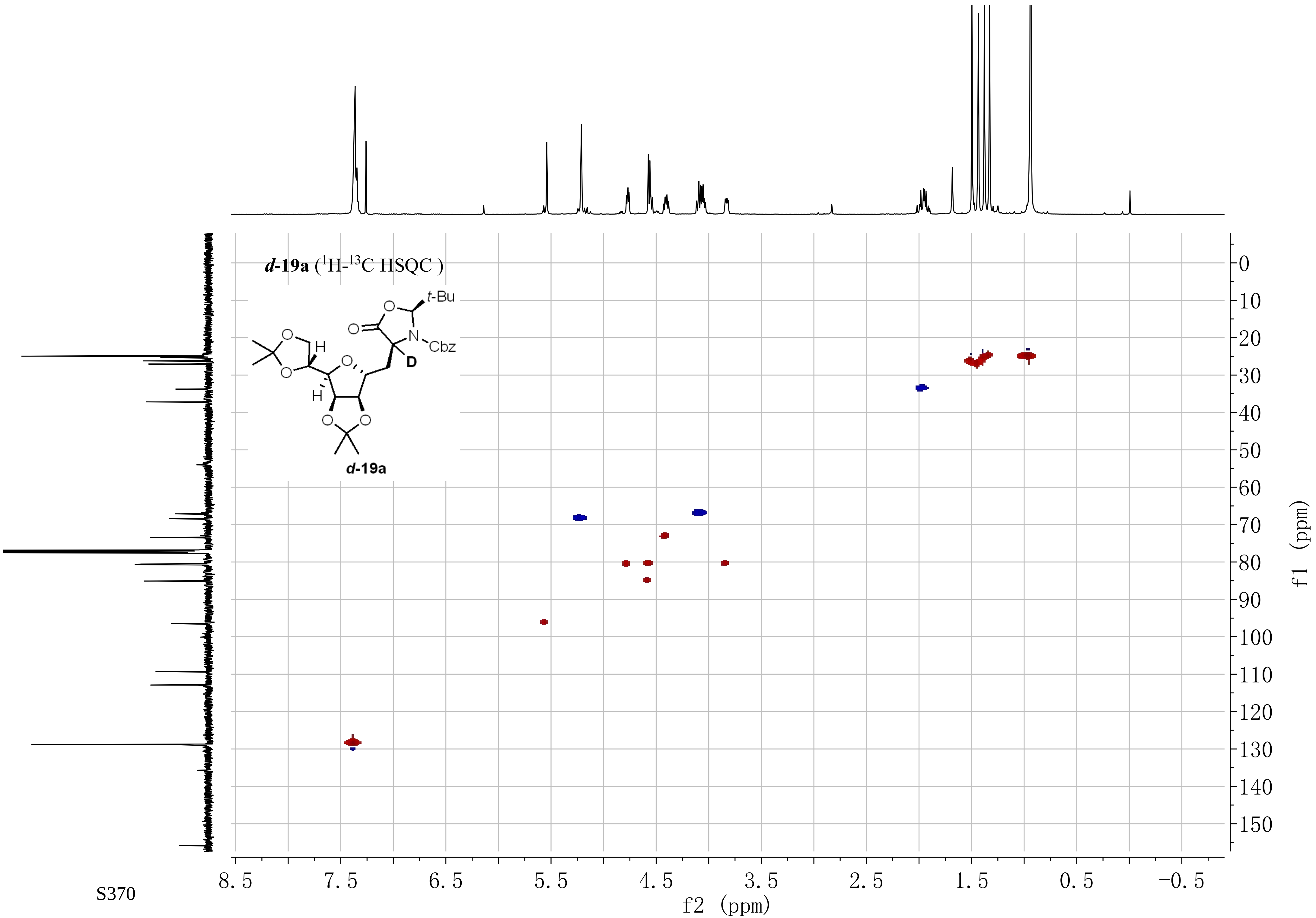
172.25
155.80
128.79
128.74
112.91
109.30
96.46
85.09
80.70
80.53
80.49
77.16
76.92
76.84
73.41
68.41
67.13
53.99
37.18
33.75
27.05
26.21
25.32
24.94
24.80
d-19a (^{13}C NMR, 101MHz, CDCl$_3$)
t-Bu
O
N
Cbz
H
D
H
d-19a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

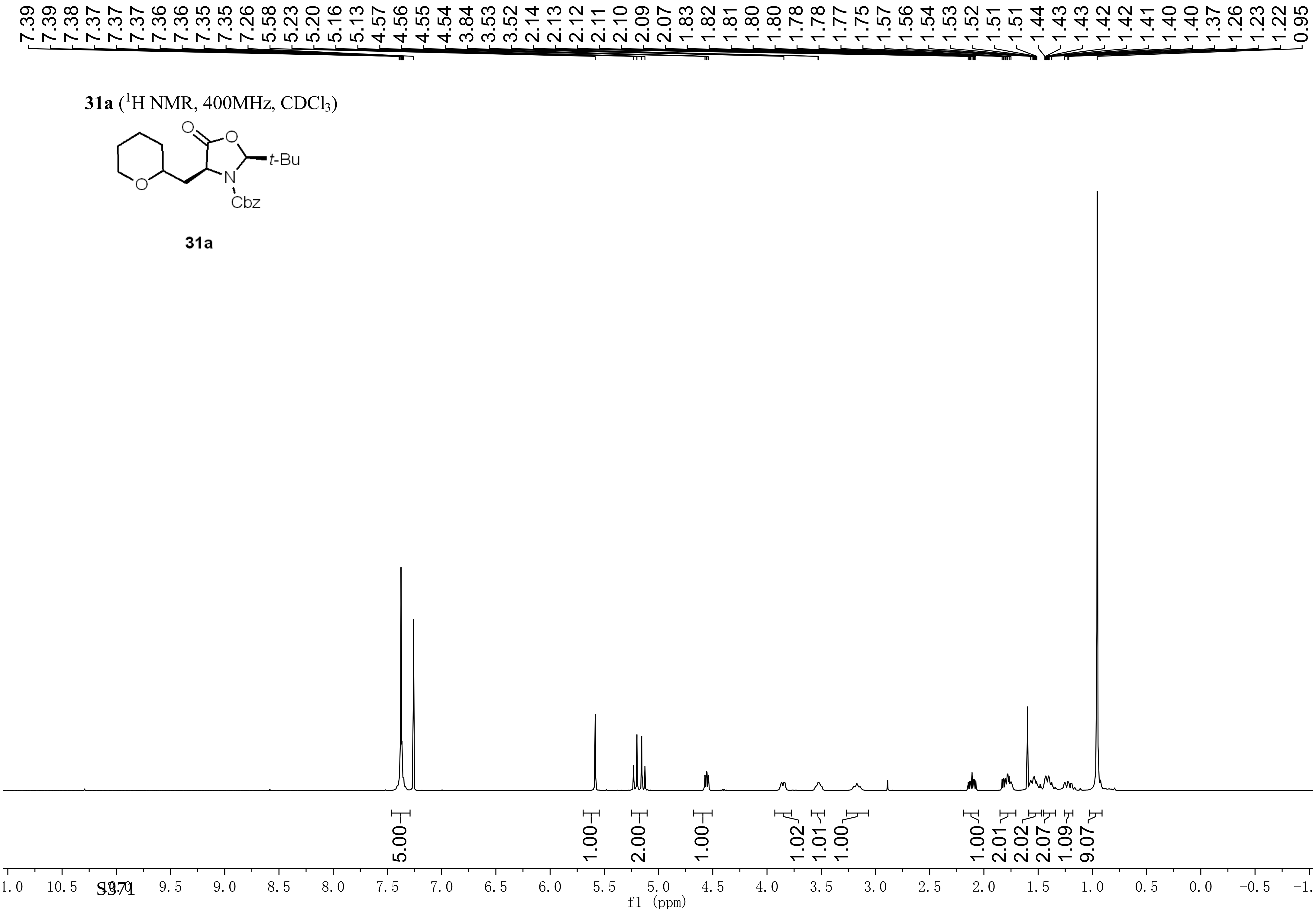


d-19a (¹H-¹H COSY)
t-Bu
Cbz
D
d-19a
f2 (ppm)
f1 (ppm)



***d*-19a** ([1]H-[13]C Coupled HSQC)
t-Bu
O
N
Cbz
D
H
H
O
O
O
O
O
d-19a
f2 (ppm)
f1 (ppm)


d-19a (1H-13C HSQC)
t-Bu
O
O
N
Cbz
D
H
H
d-19a
f2 (ppm)
f1 (ppm)


31a (1H NMR, 400MHz, CDCl3)
O
O
N
t-Bu
Cbz
31a
f1 (ppm)

31a (^{13}C NMR, 101MHz, $CDCl_3$)