Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible Light Induced Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling of Glycosyl Chlorides to Form *C*-Aryl Glycosides

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1. General information

All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under an argon atmosphere. NMR spectra were recorded on Bruker 400 MHz and Bruker 600 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, dt = doublet of triplet, dd = double doublet, ddd = doublet of a double doublet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on Bruker 400 MHz and Bruker 600 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.20 ppm). ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer with complete proton decoupling or proton coupling. High-resolution mass spectrometric data (HRMS) were obtained using Agilent 7200 Q-TOF (APCI, or Electrospray ionization, ESI). Reactions were monitored by thin-layer chromatography (TLC) and compounds were visualized by UV light (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH. Values for α/β, *Z/E* of products were determined by ^1H NMR. The was running in a parallel photoreactor (455 nm, 10W) from Rogertech.

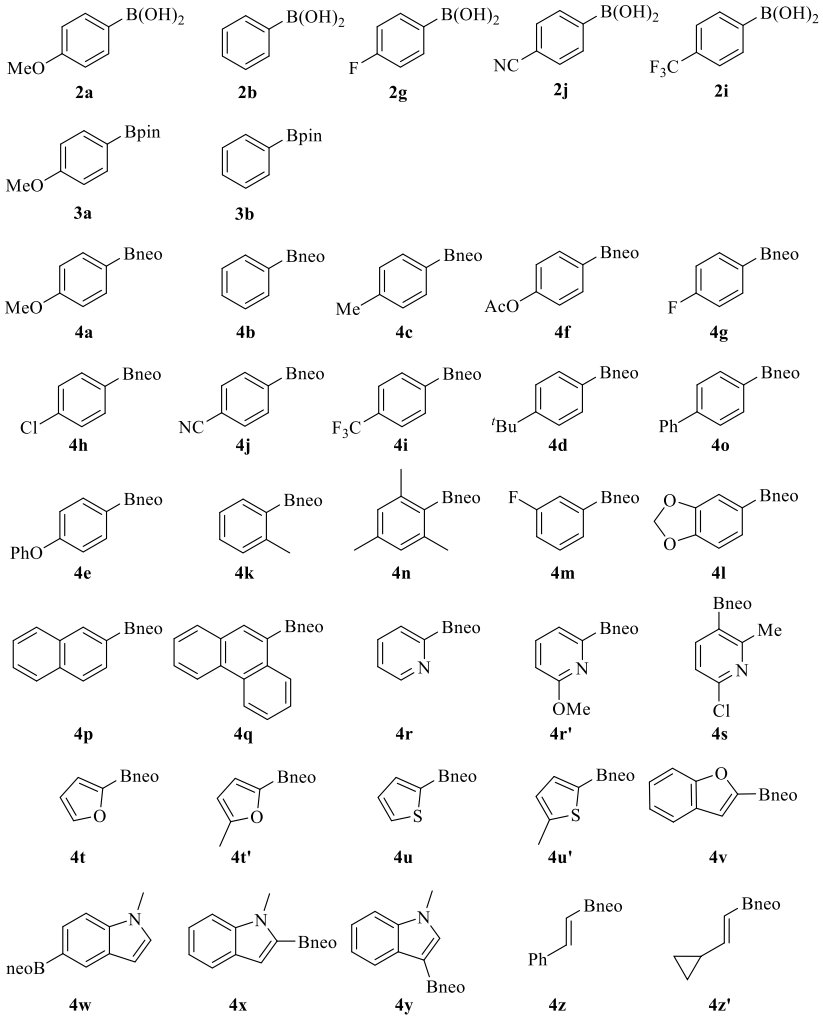
Solvents and regents

Solvents (tetrahydrofuran) were fetched under a positive pressure of dry nitrogen gas by a purification system and further dried by molecular sieves. 1,2-Dimethoxyethane (anhydrous), Trimethyl borate were purchased from Energy-Chemical and used as received.

Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa, or other commercial suppliers and were used as received. $Pd(PPh_3)Cl_2$, $Pd(PPh_3)_4$ were purchased from Energy-Chemical and TCI.

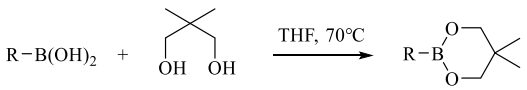
2. the substrates were used in article

Aryl boronic acids (**2a/b/g/j/i**) are commercially available substrates. Aryl boronic acid esters **3a**, **3b**, **4a**, **4b**, **4v** are commercially available substrates. **4c-4z** are known compounds and prepared according to reported methods.[1]

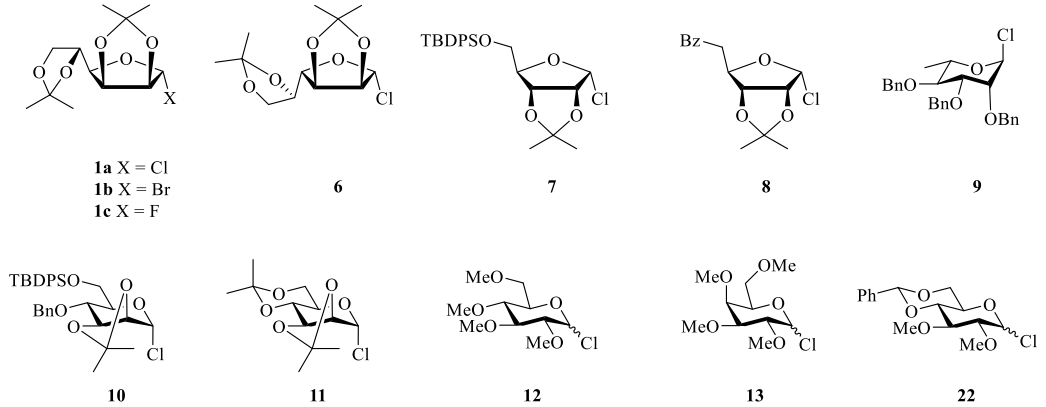


Scheme S1. Substrate scope of aryl boronic acids, aryl boronic acid esters

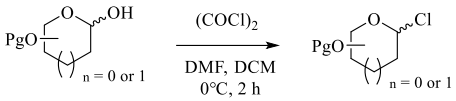
Methods of boroneopentylates: A THF solution of an organoboronic acid and 2,2-dimethylpropane-1,3-diol (neopentyl glycol) (1.2-1.5 equiv) was refluxed for 40 min under a Dean Stark apparatus, the reaction mixture was cooled and concentrated in vacuo. The residue was subjected to flash SiO2 column chromatography to yield the product.



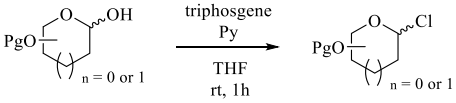
All glycosyl donors (**Scheme S2**) prepared according to reported methods. **The methods for the synthesis of glycosyl chlorides as follow:**



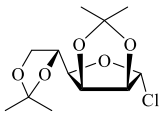
Scheme S2. glycosyl chlorides



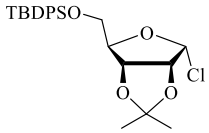
Method 1: $(COCl)_2$ (2.0 equiv), DMF (5.0 equiv) was added to a solution of the relevant hemiacetal (1.0 equiv) in DCM at 0℃. The mixture was stirred at 0℃. After the complete consumption of hemiacetal monitored by TLC analysis, the reaction mixture was diluted with EtOAc and washed with saturated aq. $NaHCO_3$, water and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography to give the glycosyl chloride (glycosyl chlorides are known compounds and the spectra data are consistent with those reported in literature[2]).



Method 2: The relevant hemiacetal (1.0 equiv) was dissolved in dry THF, triphosgene (0.4 equiv) was added, and the mixture was stirred at rt with exclusion of moisture. Pyridine (1.2 equiv) was added in three portions, and the mixture was allowed to stir at rt for 1 h while being monitored by TLC. After the reaction was complete, pyridinium hydrochloride was filtered, the solid was washed with THF, and the filtrate was evaporated in vacuo below 30 ℃. The resulting residue was purified by silica gel flash chromatography to give the glycosyl chloride.

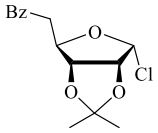


Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.07 (s, 1H), 4.96 (d, *J* = 5.8 Hz, 1H), 4.89 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.47 – 4.39 (m, 1H), 4.21 (dd, *J* = 7.8, 3.6 Hz, 1H), 4.10 (dd, *J* = 8.9, 6.1 Hz, 1H), 4.02 (dd, *J* = 8.9, 4.4 Hz, 1H), 1.47 (s, 6H), 1.38 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 113.3, 109.5, 97.6, 89.2, 82.4, 78.5, 72.3, 66.7, 26.9, 25.8, 25.1, 24.6.

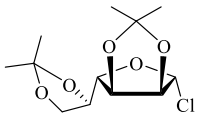


Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 4H), 7.46 – 7.35 (m, 6H), 6.09 (s, 1H), 4.90 (d, *J* = 5.8 Hz, 1H), 4.82 (d, *J* = 5.8 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 1H), 3.91 – 3.79 (m, 2H), 1.47 (s, 3H), 1.33 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.7, 135.6, 133.2,

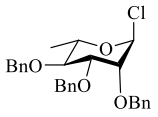
133.0, 129.9, 127.80, 127.77, 113.2, 98.5, 90.1, 89.5, 81.5, 63.3, 26.9, 26.6, 25.3, 19.2.



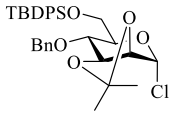
Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.19 (s, 1H), 5.07 (d, *J* = 5.8 Hz, 1H), 4.95 (d, *J* = 5.7 Hz, 1H), 4.67 (t, *J* = 6.8 Hz, 1H), 4.61 (dd, *J* = 11.3, 7.4 Hz, 1H), 4.53 (dd, *J* = 11.3, 6.2 Hz, 1H), 1.50 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.0, 133.3, 129.8, 129.5, 128.4, 113.7, 98.2, 89.5, 87.5, 81.5, 63.9, 26.6, 25.3.



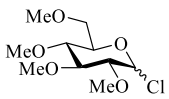
Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.16 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.77 (dd, *J* = 5.8, 3.9 Hz, 1H), 4.45 – 4.37 (m, 1H), 4.26 – 4.20 (m, 2H), 3.80 – 3.73 (m, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 113.6, 110.1, 97.5, 89.2, 84.3, 78.7, 74.6, 66.0, 26.8, 25.9, 25.4, 24.9.



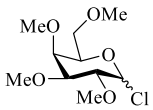
White solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.24 (m, 15H), 6.14 (d, *J* = 3.8 Hz, 1H), 4.99 (d, *J* = 11.4 Hz, 1H), 4.89 (d, *J* = 11.8 Hz, 1H), 4.79 – 4.69 (m, 3H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.20 (dd, *J* = 9.8, 3.8 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.97 (dd, *J* = 9.8, 2.1 Hz, 1H), 3.68 (s, 1H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.6, 138.3, 137.9, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 95.5, 78.7, 77.24, 77.19, 76.2, 75.1, 73.6, 73.0, 70.05, 69.99, 16.4.



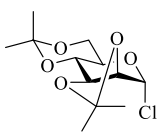
Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 4H), 7.45 – 7.22 (m, 11H), 6.35 (s, 1H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 1H), 4.43 (d, *J* = 5.4 Hz, 1H), 4.05 – 3.98 (m, 2H), 3.98 – 3.88 (m, 2H), 1.56 (s, 3H), 1.40 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.2, 135.9, 135.6, 133.6, 133.1, 129.7, 128.4, 127.8, 127.7, 127.6, 110.5, 91.2, 91.1, 78.6, 77.9, 74.8, 73.5, 72.7, 62.2, 28.1, 26.8, 26.8, 19.4.



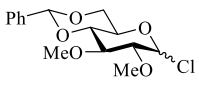
Colorless oil; α isomer: ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.34 (s, 1H), 3.82 (d, *J* = 10.4 Hz, 1H), 3.64 – 3.58 (m, 1H), 3.57 (s, 3H), 3.54 – 3.51 (m, 1H), 3.50 (s, 3H), 3.45 (s, 3H), 3.42 – 3.35 (m, 2H), 3.33 (s, 3H), 3.19 (t, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 93.7, 82.8, 81.6, 78.1, 73.5, 70.5, 60.2, 59.9, 58.3, 57.4.



Colorless oil; α isomer: ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.37 (s, 1H), 4.14 – 4.08 (m, 1H), 3.79 (s, 1H), 3.71 (d, *J* = 10.0 Hz, 1H), 3.59 – 3.53 (m, 2H), 3.50 (s, 3H), 3.48 (s, 3H), 3.44 (s, 3H), 3.43 – 3.40 (m, 1H), 3.32 (s, 3H).



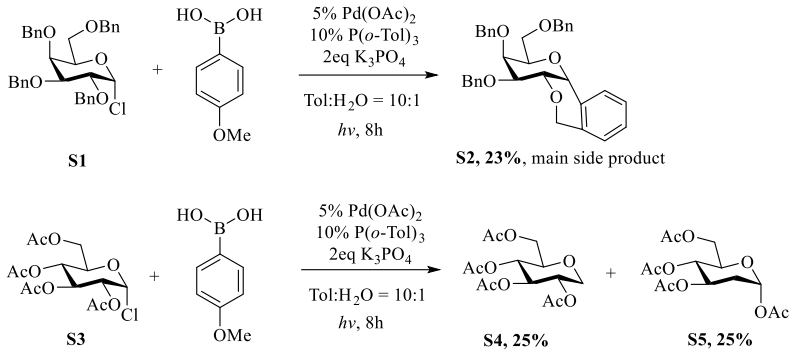
Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.26 (s, 1H), 4.44 (d, *J* = 5.3 Hz, 1H), 4.31 (dd, *J* = 7.8, 5.3 Hz, 1H), 3.95 – 3.87 (m, 2H), 3.87 – 3.83 (m, 1H), 3.82 – 3.76 (m, 1H), 1.55 (s, 3H), 1.52 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 111.7, 101.3, 93.1, 80.5, 75.6, 73.9, 66.4, 62.7, 30.2, 29.3, 27.6, 20.0.



White solid; **α isomer**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.37 (dd, *J* = 5.5, 2.0 Hz, 3H), 6.19 (d, *J* = 3.9 Hz, 1H), 5.55 (s, 1H), 4.32

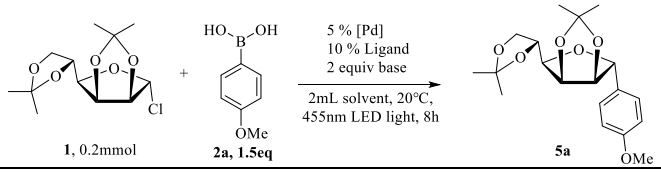
(dd, *J* = 10.3, 4.9 Hz, 1H), 4.16 (td, *J* = 9.9, 4.9 Hz, 1H), 3.78 – 3.70 (m, 2H), 3.65 (s, 3H), 3.60 (t, *J* = 9.5 Hz, 1H), 3.55 (s, 3H), 3.47 (dd, *J* = 9.0, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.0, 129.1, 128.3, 126.1, 101.6, 92.7, 81.6, 81.2, 79.1, 68.3, 65.2, 61.2, 58.9. **β isomer**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.41 – 7.34 (m, 3H), 5.55 (s, 1H), 5.19 (d, *J* = 8.1 Hz, 1H), 4.37 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.78 (t, *J* = 10.3 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.50 (dd, *J* = 5.5, 4.2 Hz, 1H), 3.43 (dd, *J* = 9.2, 8.0 Hz, 1H), 3.28 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.0, 129.1, 128.3, 126.0, 101.3, 90.3, 86.2, 83.4, 80.6, 69.3, 68.4, 61.4, 61.0.

3. Examination of conditions



Scheme S3. The reactions of per-acetal and per-benzyl glycosyl chlorides

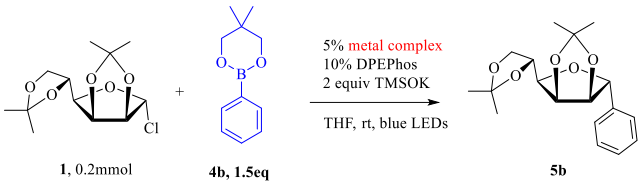
Table S1. Using 4-Methoxyphenylboronic acid



Entry	Cat.	Ligands	Base	Slovent	Yield (%)[a]
1	$Pd(OAc)_2$	DPEPhos	Cs_2CO_3	PhH	32
2	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	CH_3CN	Trace
3	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	Dioxane	N.R
4	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	Acetone	Trace
5	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	DMF	Trace
6	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	MeOH	18
7	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	EA	37
8	$Pd(Ph_3P)_2Cl_2$	DPEPhos	Cs_2CO_3	$PhH:H_2O$ = 2:1	40
9	$Pd(o\text{-}Tol)_2Cl_2$	DPEPhos	Cs_2CO_3	$PhH:H_2O$ = 2:1	Trace
10	$Pd(CH_3CN)_4(BF_4)_2$	DPEPhos	Cs_2CO_3	$PhH:H_2O$ = 2:1	Trace
11	$Pd(acac)_2$	DPEPhos	Cs_2CO_3	$PhH:H_2O$ = 2:1	5
12	$Pd(dppf)_2Cl_2$	DPEPhos	Cs_2CO_3	$PhH:H_2O$ = 2:1	N.D
13	$Pd(Ph_3)_4$	DPEPhos	Cs_2CO_3	$PhH:H_2O$ = 2:1	50
14	$Pd(Ph_3)_4$	DPEPhos	K_2CO_3	$PhH:H_2O$ = 2:1	47
15	$Pd(Ph_3)_4$	DPEPhos	Na_2CO_3	$PhH:H_2O$ = 2:1	54
16	$Pd(Ph_3)_4$	DPEPhos	$NaHCO_3$	$PhH:H_2O$ = 2:1	33
17	$Pd(Ph_3)_4$	DPEPhos	K_3PO_4	$PhH:H_2O$ = 2:1	61
18	$Pd(Ph_3)_4$	DPEPhos	CsF	$PhH:H_2O$ = 2:1	40
19	$Pd(Ph_3)_4$	DPEPhos	CH_3COONa	$PhH:H_2O$ = 2:1	Trace
20	$Pd(Ph_3)_4$	DPEPhos	Quinuclidine	$PhH:H_2O$ = 2:1	Trace
21	$Pd(Ph_3)_4$	DPEPhos	DBU	$PhH:H_2O$ = 2:1	Trace
22	$Pd(Ph_3)_4$	DPEPhos	Et_3N	$PhH:H_2O$ = 2:1	53
23	$Pd(Ph_3)_4$	DPEPhos	K_2CO_3	$PhH:H_2O$ = 2:1	42
24	$Pd(Ph_3)_4$	DPEPhos	Dipea	$PhH:H_2O$ = 2:1	61
25	$Pd(Ph_3)_4$	DPEPhos	Dipea	$PhMe:H_2O$ = 2:1	63
26	$Pd(Ph_3)_4$	DPEPhos	Dipea	$PhMe:H_2O$ = 10:1	64
27	$Pd(Ph_3)_4$	$P(o\text{-}Tol)_3$	Dipea	$PhMe:H_2O$ =10:1	71
28	$Pd(Ph_3)_4$	dppb	Dipea	$PhMe:H_2O$ =10:1	Trace
28	$Pd(Ph_3)_4$	SPhos	Dipea	$PhMe:H_2O$ =10:1	25
30	$Pd(Ph_3)_4$	BiNap	Dipea	$PhMe:H_2O$ =10:1	45
31	$Pd(Ph_3)_4$	XantPhos	Dipea	$PhMe:H_2O$ =10:1	N.D
32	$Pd(Ph_3)_4$	$P(4\text{-}FPh)_3$	Dipea	$PhMe:H_2O$ =10:1	53
33	$Pd(Ph_3P)_2Cl_2$	$P(o\text{-}Tol)_3$	Dipea	$PhMe:H_2O$ = 10:1	86
34	$Pd(Ph_3P)_2Cl_2$	$P(o\text{-}Tol)_3$	^tBuONa	$PhMe:H_2O$ = 10:1	Trace
35	$Pd(Ph_3P)_2Cl_2$	$P(o\text{-}Tol)_3$	K_3PO_4	$PhMe:H_2O$ = 10:1	87
36	**$Pd(Ph_3P)_2Cl_2$**	**$P(o\text{-}Tol)_3$**	**K_3PO_4**	**$PhMe:H_2O$ = 10:1**	**90**[b]

[a] 0.2 mmol, 20℃, isolated yield. [b] 3 mL solvent.

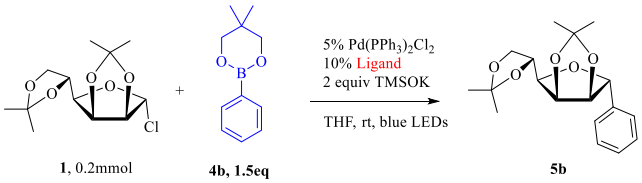
Table S2. Transition metal complex screening



1, 0.2mmol **4b, 1.5eq** **5b**

Entry	Cat.	Yield/%
1	$Pd(OAc)_2$	trace
2	$Pd(Ph_3P)_2Cl_2$	74
3	$PdCl_2$	N.R
4	$Pd(CF_3COO)_2$	trace
5	$Pd(^tBu)_2$	N.R
6	$Pd(Ph_3P)_4$	69
7	$Pd(o\text{-}Tol_3P)_2Cl_2$	37
8	XantPhosPdG$_3$	N.R
9	$Ni(PPh_3)_2Cl_2$	N.R
10	$Cu(acac)_2$	N.R

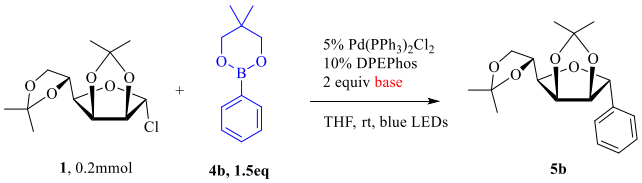
Table S3. Ligands screening



1, 0.2mmol **4b, 1.5eq** **5b**

Entry	Ligand	Yield/%
1	DPEPhos	74
2	P(*o*-Tol)$_3$	71
3	XantPhos	47
4	BiNap	56
5	DPPB	trace
6	SPhos	trace
7	DFFP	trace
8	P(4-FPh)$_3$	59

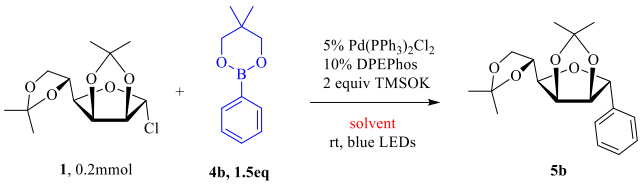
Table S4. Base screening



1, 0.2mmol **4b, 1.5eq** **5b**

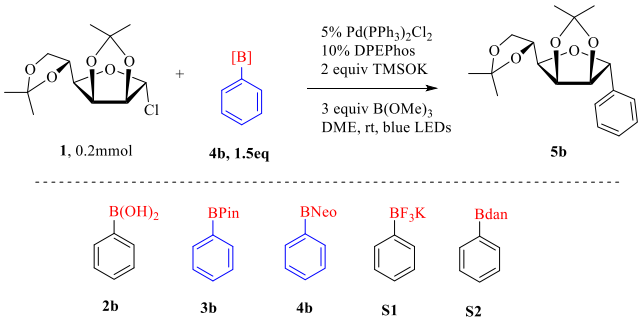
Entry	Base	Yield/%
1	TMSOK	74
2	Cs_2CO_3	49
3	K_3PO_4	trace
4	K_2CO_3	36
5	Na_2CO_3	trace
6	CH_3CO_2Na	trace
7	Dipea	trace
8	^{t}BuLi	57

Table S5. Solvent screening



Entry	Solvent	Yield/%
1	THF	74
2	DME	83
3	Tol	56
4	DMF	trace
5	CH_3CN	trace
6	Dioxane	trace
7	Acetone	trace
8	DMSO	trace

Table S6. Boron species screening



Entry	Boron species	Yield/%
1	**2b**	35
2	**3b**	56
3	**4b**	83
4	**S1**	trace
5	**S2**	n.r

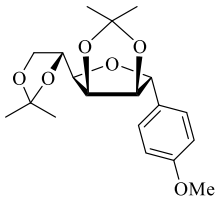
4. General procedure for cross-coupling reaction:

General procedure A: To a 10 mL Schlenk flask equipped with a stir bar, glycosyl chloride (1 equiv), aryl boronic ester (1.5 equiv), $Pd(PPh_3)Cl_2$ (5 mmol%) and DPEPhos (10 mmol%) were added with nitrogen. Then TMSOK (2 equiv, 2.00 M in DME) and trimethyl borate (3 equiv) were added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm,10W) at 20°C until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product.

General procedure B: To a 10 mL Schlenk flask equipped with a stir bar, glycosyl chloride (1 equiv), aryl boronic acid (1.5 equiv), $Pd(PPh_3)Cl_2$ (5 mmol%), P(*o*-Tol)$_3$ (10 mmol%) and K_3PO_4 (2 equiv) were added with nitrogen. Then the solvent toluene:H_2O (10:1, 2 mL) was added to the mixture. The reaction was running in a parallel photoreactor (455 nm,10W) at 20°C until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product.

5. Characterization Data of Products

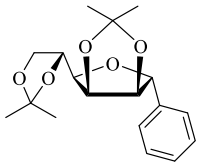
(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-(4-methoxyphenyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5a) [3]:



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (63.5 mg, 91% yield).

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (63.0 mg, 90% yield). $[\alpha]_D^{20}$ = +18.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.15 (s, 1H, H-1), 4.95 (d, *J* = 6.0 Hz, 1H, H-2), 4.76 (dd, *J* = 6.0, 3.8 Hz, 1H, H-3), 4.53 – 4.44 (m, 1H, H-5), 4.18 (d, *J* = 5.4 Hz, 2H, H-6), 3.84 (dd, *J* = 7.7, 3.8 Hz, 1H, H-4), 3.80 (s, 3H), 1.57 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.9, 130.2, 126.8, 114.1, 112.8, 109.2, 87.2 (C-2), 84.6 (C-1), 81.1 (C-3, C-4), 73.5 (C-5), 67.0 (C-6), 55.3, 26.9, 26.2, 25.2, 24.7. HRMS (ESI) calculated for $C_{19}H_{27}O_6$ $(M+H)^+$ *m/z* 351.1802, found 351.1801.

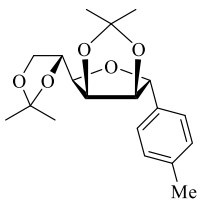
(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-d][1,3]dioxole (5b):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (57.0 mg, 89% yield).

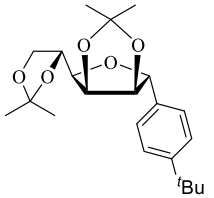
The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (32.2 mg, 50% yield). $[\alpha]_D^{20}$ = +0.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 5H), 5.20 (s, 1H, H-1), 4.98 (d, *J* = 6.0 Hz, 1H, H-1), 4.77 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.56 – 4.44 (m, 1H, H-5), 4.26 – 4.13 (m, 2H, H-6), 3.89 (dd, *J* = 7.6, 3.7 Hz, 1H, H-4), 1.58 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.3, 128.7, 127.5, 125.4, 112.9, 109.3, 87.5 (C-2), 85.0 (C-1), 81.3 (C-4), 81.1 (C-3), 73.5 (C-5), 67.0 (C-6), 26.9, 26.2, 25.2, 24.8. HRMS (ESI) calculated for $C_{18}H_{25}O_5$ $(M+H)^+$ *m/z* 321.1697, found 321.1694.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(p-tolyl)tetrahydrofuro[3,4-d][1,3]dioxole (5c):



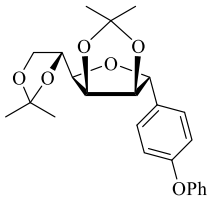
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (64.8 mg, 97% yield). $[\alpha]_D^{20}$ = +17.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.09 (m, 4H), 5.09 (s, 1H, H-1), 4.89 (d, *J* = 6.1 Hz, 1H, H-2), 4.71 – 4.66 (m, 1H, H-3), 4.46 – 4.38 (m, 1H, H-5), 4.11 (d, *J* = 5.5 Hz, 2H, H-6), 3.79 (dd, *J* = 7.6, 3.7 Hz, 1H, H-4), 2.27 (s, 3H), 1.50 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.3, 135.5, 129.5, 125.6, 112.9, 109.3, 87.5 (C-2), 85.0 (C-1), 81.4 (C-4), 81.3 (C-3), 73.7 (C-5), 67.2 (C-6), 27.0, 26.3, 25.4, 24.9, 21.2. HRMS (ESI) calculated for $C_{19}H_{27}O_5$ $(M+H)^+$ *m/z* 335.1853, found 335.1590.

(4R,6R)-4-(4-(tert-butyl)phenyl)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5d):



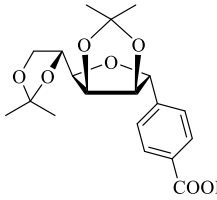
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (72.2 mg, 96% yield). $[\alpha]_D^{20}$ = +10.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.18 (s, 1H, H-1), 4.99 (d, *J* = 6.0 Hz, 1H, H-2), 4.76 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.53 – 4.46 (m, 1H, H-5), 4.24 – 4.16 (m, 2H, H-6), 3.87 (dd, *J* = 7.7, 3.7 Hz, 1H, H-4), 1.58 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.5, 135.3, 125.6, 125.3, 112.8, 109.2, 87.4 (C-2), 84.9 (C-1), 81.3 (C-4), 81.2 (C-3), 73.5 (C-5), 67.1 (C-6), 34.5, 31.3, 26.9, 26.2, 25.2, 24.8. HRMS (ESI) calculated for $C_{22}H_{33}O_5$ $(M+H)^+$ *m/z* 377.2323, found 377.2321.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(4-phenoxyphenyl)tetrahydrofuro[3,4-d][1,3]dioxole (5e):



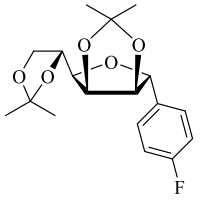
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (70.0 mg, 85% yield). $[\alpha]_D^{20}$ = +7.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.98 (m, 4H), 5.17 (s, 1H, H-1), 4.96 (d, *J* = 6.0 Hz, 1H, H-2), 4.78 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.52 – 4.46 (m, 1H, H-5), 4.18 (d, *J* = 5.5 Hz, 2H, H-6), 3.89 (dd, *J* = 7.5, 3.7 Hz, 1H, H-4), 1.58 (s, 3H), 1.45 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.0, 156.8, 133.0, 129.8, 127.0, 123.5, 119.0, 118.9, 112.9, 109.2, 87.3 (C-2), 84.7 (C-1), 81.3 (C-4), 81.2 (C-3), 73.5 (C-5), 67.0 (C-6), 26.9, 26.2, 25.2, 24.8. HRMS (ESI) calculated for $C_{24}H_{29}O_6$ $(M+H)^+$ *m/z* 413.1959, found 413.1955.

4-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)phenyl acetate (5f):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a white solid (56.0 mg, 74% yield). $[\alpha]_D^{20}$ = +9.3 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 5.14 (s, 1H, H-1), 5.01 (d, *J* = 5.8 Hz, 1H, H-2), 4.84 (dd, *J* = 5.9, 3.6 Hz, 1H. H-3), 4.43 (q, *J* = 6.2 Hz, 1H, H-5), 4.12 (d, *J* = 6.0 Hz, 2H, H-6), 3.95 (dd, *J* = 6.6, 3.6 Hz, 1H, H-4), 3.88 (s, 3H), 1.51 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 167.1, 145.6, 130.6, 126.8, 113.4, 109.4, 88.3 (C-2), 86.0 (C-1), 82.7 (C-4), 82.1 (C-3), 74.4 (C-5), 67.4 (C-6), 52.5, 27.1, 26.8, 25.8, 25.2. HRMS (ESI) calculated for $C_{20}H_{26}O_7Na$ $(M+Na)^+$ *m/z* 401.1571, found 401.1564.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-(4-fluorophenyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5g) [3]:



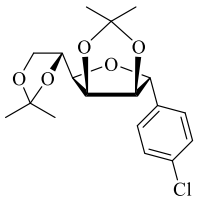
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure

product as a colorless oil (49.4 mg, 73% yield).

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (35.8 mg, 53% yield).

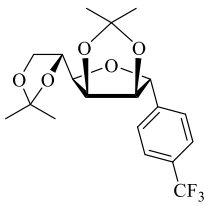
$[\alpha]_D^{20}$ = +3.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 5.16 (s, 1H, H-1), 4.93 (d, *J* = 6.0 Hz, 1H, H-2), 4.79 – 4.75 (m, 1H, H-3), 4.53 – 4.47 (m, 1H, H-5), 4.19 (d, *J* = 5.4 Hz, 2H, H-6), 3.86 (dd, *J* = 7.5, 3.7 Hz, 1H, H-4), 1.58 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1 (*C*F), 134.1, 134.0, 127.2, 127.1, 115.7, 115.5, 113.0, 109.2, 87.4 (C-2), 84.5 (C-1), 81.3 (C-4), 81.1 (C-3), 73.5 (C-5), 66.9 (C-6), 26.9, 26.2, 25.2, 24.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.03. HRMS (ESI) calculated for $C_{18}H_{24}O_5F$ $(M+H)^+$ *m/z* 339.1603, found 339.1594.

(4R,6R)-4-(4-chlorophenyl)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5h):



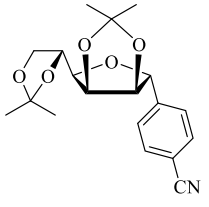
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a white solid (54.5 mg, 77% yield). $[\alpha]_D^{20}$ = +14.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.15 (s, 1H, H-1), 4.91 (d, *J* = 5.9 Hz, 1H, H-2), 4.76 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.53 – 4.45 (m, 1H, H-5), 4.18 (d, *J* = 5.4 Hz, 2H, H-6), 3.85 (dd, *J* = 7.4, 3.7 Hz, 1H, H-4), 1.57 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.0, 133.4, 128.9, 126.9, 113.1, 109.3, 87.4 (C-2), 84.6 (C-1), 81.4 (C-4), 81.1 (C-3), 73.5 (C-5), 66.9 (C-6), 26.9, 26.2, 25.2, 24.8. HRMS (ESI) calculated for $C_{18}H_{24}O_5Cl$ $(M+H)^+$ *m/z* 355.1307, found 355.1303.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(4-(trifluoromethyl)phenyl)tetrahydrofuro[3,4-d][1,3]dioxole (5i):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a white solid (52.7 mg, 68% yield). $[\alpha]_D^{20}$ = +19.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.23 (s, 1H, H-1), 4.94 (d, *J* = 5.9 Hz, 1H, H-2), 4.77 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.54 – 4.47 (m, 1H, H-5), 4.26 – 4.15 (m, 2H, H-6), 3.88 (dd, *J* = 7.4, 3.7 Hz, 1H, H-4), 1.59 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.6, 129.8 (q, *C*F_3), 125.74, 125.70, 125.66, 113.2, 109.3, 87.5 (C-2), 84.7 (C-1), 81.6 (C-24), 81.0 (C-3), 73.4 (C-5), 66.9 (C-6), 26.9, 26.2, 25.1, 24.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.56. HRMS (ESI) calculated for $C_{19}H_{24}O_5F_3$ $(M+H)^+$ *m/z* 389.1571, found 389.1570.

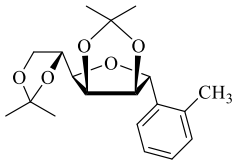
4-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)benzonitrile (5j):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a white solid (20.1 mg, 29% yield). $[\alpha]_D^{20}$ = +42.5 (c

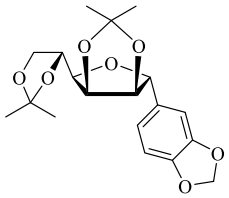
= 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 1H, H-1), 5.02 (d, *J* = 5.6 Hz, 1H, H-2), 4.85 (dd, *J* = 6.0, 3.6 Hz, 1H, H-3), 4.43 (q, *J* = 6.2 Hz, 1H, H-5), 4.12 (d, *J* = 6.1 Hz, 2H, H-6), 3.96 (dd, *J* = 6.6, 3.6 Hz, 1H, H-4), 1.51 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 144.9, 132.4, 126.6, 118.3, 112.5, 111.1, 108.4, 87.2 (C-2), 84.8 (C-1), 81.7 (C-4), 81.1 (C-3), 73.4 (C-5), 66.4 (C-6), 26.1, 25.7, 24.7, 24.1. HRMS (ESI) calculated for $C_{19}H_{23}NO_5Na$ $(M+Na)^+$ *m/z* 368.1468, found 368.1461.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(*o*-tolyl)tetrahydrofuro[3,4-d][1,3]dioxole (5k):



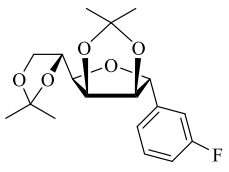
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (62.7 mg, 94% yield). $[\alpha]_D^{20}$ = +13.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 4H), 5.24 (s, 1H, H-1), 4.85 – 4.76 (m, 2H, H-2, H-3), 4.55 – 4.48 (m, 1H, H-5), 4.22 – 4.17 (m, 2H, H-6), 4.06 (dd, *J* = 7.7, 2.8 Hz, 1H, H-4), 2.36 (s, 3H), 1.60 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.1, 135.5, 131.0, 127.5, 125.9, 124.3, 113.0, 109.2, 86.9 (C-2), 84.6 (C-1), 81.9 (C-4), 81.3 (C-3), 73.7 (C-5), 67.0 (C-6), 27.0, 26.4, 25.3, 25.0, 19.5. HRMS (ESI) calculated for $C_{19}H_{27}O_5$ $(M+H)^+$ *m/z* 335.1853, found 335.1848.

5-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)benzo[d][1,3]dioxole (5l):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (61.6 mg, 89% yield). $[\alpha]_D^{20}$ = +2.0 (c = 19.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.82 – 6.74 (m, 3H), 5.96 (s, 2H), 5.10 (s, 1H, H-1), 4.92 (d, *J* = 6.0 Hz, 1H, H-2), 4.77 (dd, *J* = 6.0, 3.8 Hz, 1H, H-3), 4.51 – 4.44 (m, 1H, H-5), 4.17 (d, *J* = 5.4 Hz, 2H, H-6), 3.85 (dd, *J* = 7.6, 3.7 Hz, 1H, H-4), 1.56 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 148.1, 147.0, 133.0, 119.0, 112.1, 108.3, 108.1, 106.3, 101.2, 87.0 (C-2), 84.9 (C-1), 81.2 (C-4), 81.1 (C-3), 73.5 (C-5), 66.4 (C-6), 26.2, 25.7, 24.8, 24.1. HRMS (ESI) calculated for $C_{19}H_{25}O_7$ $(M+H)^+$ *m/z* 365.1595, found 365.1588.

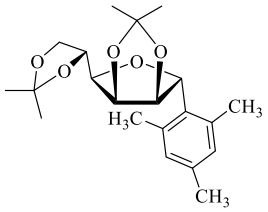
(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-(3-fluorophenyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5m):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (59.0 mg, 87% yield). $[\alpha]_D^{20}$ = +2.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 9.8 Hz, 1H), 7.00 – 6.93 (m, 1H), 5.17 (s, 1H, H-1), 4.94 (d, *J* = 6.0 Hz, 1H, H-2), 4.77 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.53 – 4.47 (m, 1H, H-5), 4.20 (d, *J* = 5.4 Hz, 2H, H-6), 3.87 (dd, *J* = 7.5, 3.7 Hz, 1H, H-4), 1.58 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.3, 161.9, 141.32,

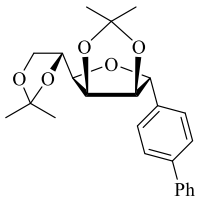
141.25, 130.4, 130.3, 120.98, 120.95, 114.5, 114.3, 113.1, 112.7, 112.4, 109.3, 87.4 (C-2), 84.6 (C-1), 81.5 (C-4), 81.0 (C-3), 73.4 (C-5), 66.9 (C-6), 26.9, 26.2, 25.2, 24.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.06, -112.08, -112.10, -112.12. HRMS (ESI) calculated for $C_{18}H_{24}FO_5$ $(M+H)^+$ *m/z* 339.1603, found 339.1602.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-mesityl-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5n):



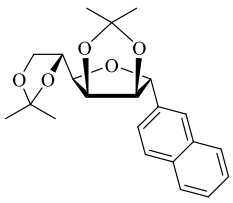
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (11.6 mg, 16% yield). $[\alpha]_D^{20}$ = +104.5 (c = 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 5.32 (d, *J* = 6.2 Hz, 1H, H-1), 4.96 – 4.93 (m, 1H, H-2), 4.85 (t, *J* = 6.0 Hz, 1H, H-3), 4.57 – 4.51 (m, 1H, H-5), 4.31 (dd, *J* = 7.8, 4.6 Hz, 1H, H-4), 4.13 (dd, *J* = 8.7, 6.2 Hz, 1H, H-6a), 4.03 (dd, *J* = 8.7, 5.0 Hz, 1H, H-6b), 2.32 (s, 6H), 2.23 (s, 3H), 1.64 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.1, 136.3, 132.3, 130.1, 114.1, 109.3, 86.3 (C-2), 83.3 (C-1), 81.5 (C-4), 80.6 (C-3), 74.0 (C-5), 66.9 (C-6), 27.6, 27.0, 25.6, 25.4, 20.9, 20.8. HRMS (ESI) calculated for $C_{21}H_{31}O_5$ $(M+H)^+$ *m/z* 363.2166, found 363.2170.

(4R,6R)-4-([1,1'-biphenyl]-4-yl)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5o):



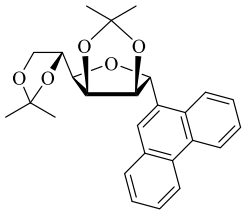
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (76.0 mg, 96% yield). $[\alpha]_D^{20}$ = +27.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 8.0 Hz, 4H), 7.47 – 7.36 (m, 5H), 5.24 (s, 1H, H-1), 5.01 (d, *J* = 6.0 Hz, 1H, H-2), 4.79 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.55 – 4.49 (m, 1H, H-5), 4.26 – 4.18 (m, 2H, H-6), 3.93 (dd, *J* = 7.5, 3.7 Hz, 1H, H-4), 1.59 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.6, 140.5, 137.4, 128.8, 127.4, 127.1, 125.9, 112.9, 109.3, 87.5 (C-2), 84.9 (C-1), 81.4 (C-4), 81.2 (C-3), 73.6 (C-5), 67.1 (C-6), 26.9, 26.2, 25.2, 24.8. HRMS (ESI) calculated for $C_{24}H_{29}O_5$ $(M+H)^+$ *m/z* 397.2010, found 397.2011.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-d][1,3]dioxole (5p):



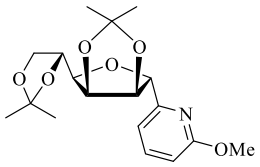
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a white solid (61.0 mg, 82% yield). $[\alpha]_D^{20}$ = +17.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 3H), 7.76 (s, 1H), 7.52 – 7.42 (m, 3H), 5.35 (s, 1H, H-1), 5.09 (d, *J* = 6.0 Hz, 1H, H-2), 4.79 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.58 – 4.51 (m, 1H, H-5), 4.30 – 4.20 (m, 2H, H-6), 3.98 (dd, *J* = 7.5, 3.8 Hz, 1H, H-4), 1.61 (s, 3H), 1.45 (s, 3H), 1.41 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.9, 133.2, 132.7, 128.6, 128.0, 127.7, 126.4, 126.1, 124.1, 123.6, 113.0, 109.3, 87.4 (C-2), 85.2 (C-1), 81.6 (C-4), 81.2 (C-3), 73.6 (C-5), 67.1 (C-6), 26.9, 26.3, 25.2, 24.9. HRMS (ESI) calculated for $C_{22}H_{27}O_5$ $(M+H)^+$ *m/z* 371.1853, found 371.1852.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(phenanthren-9-yl)tetrahydrofuro[3,4-d][1,3]dioxole (5q) [3]:



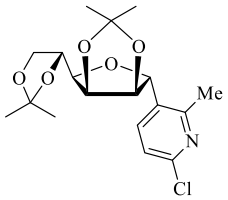
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a faint yellow solid (62.2 mg, 74% yield). $[\alpha]_D^{20}$ = +34.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 – 8.70 (m, 1H), 8.64 (d, *J* = 7.9 Hz, 1H), 8.10 – 8.05 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 6.1 Hz, 3H), 7.66 – 7.57 (m, 2H), 5.78 (s, 1H, H-1), 4.98 (d, *J* = 5.9 Hz, 1H, H-2), 4.79 – 4.74 (m, 1H, H-3), 4.64 – 4.58 (m, 1H, H-5), 4.38 (dd, *J* = 8.8, 4.5 Hz, 1H, H-6a), 4.32 – 4.25 (m, 2H, H-6b, H-4), 1.69 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 132.3, 131.04, 130.99, 130.12, 129.3, 129.0, 127.0, 126.94, 126.93, 126.87, 126.5, 124.2, 123.4, 122.8, 122.5, 113.2, 109.3, 87.2 (C-2), 85.0 (C-1), 82.5 (C-4), 81.1 (C-3), 73.8 (C-5), 67.2 (C-6), 27.0, 26.6, 25.3, 25.2. HRMS (ESI) calculated for $C_{27}H_{29}O_5$ $(M+H)^+$ *m/z* 421.2010, found 421.2007.

2-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-6-methoxypyridine (5r')



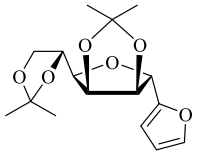
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a colorless oil (66.0 mg, 94% yield). $[\alpha]_D^{20}$ = +39.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 5.14 (s, 1H, H-1), 4.93 (d, *J* = 5.9 Hz, 1H, H-2), 4.80 (dd, *J* = 6.0, 3.7 Hz, 1H, H-3), 4.51 – 4.44 (m, 1H, H-5), 4.19 – 4.11 (m, 2H, H-6), 3.94 (s, 3H), 3.82 (dd, *J* = 7.5, 3.7 Hz, 1H, H-4), 1.57 (s, 3H), 1.43 (s, 3H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.7, 144.2, 136.6, 126.3, 113.0, 111.1, 109.3, 86.7 (C-2), 83.2 (C-1), 81.3 (C-4), 81.1 (C-3), 73.4 (C-5), 66.9 (C-6), 53.5, 26.9, 26.2, 25.2, 24.7. HRMS (ESI) calculated for $C_{18}H_{26}NO_6$ $(M+H)^+$ *m/z* 352.1755, found 352.1754.

6-chloro-3-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-2-methoxypyridine (5s):



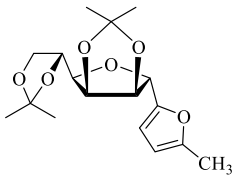
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 13:1) gave the pure product as a colorless oil (31.8 mg, 41% yield). $[\alpha]_D^{20}$ = -6.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 1H, H-1), 4.89 (d, *J* = 1.9 Hz, 2H, H-2, H-3), 4.44 (q, *J* = 6.2 Hz, 1H, H-5), 4.10 (dd, *J* = 9.1, 5.7 Hz, 3H, H-6, H-4), 2.50 (s, 3H), 1.54 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 156.9, 148.6, 135.6, 132.7, 121.2, 112.7, 108.4, 86.5 (C-2), 83.4 (C-1), 82.0 (C-4), 81.3 (C-3), 73.5 (C-5), 66.4 (C-6), 26.1, 26.0, 24.8, 24.4, 21.5. HRMS (ESI) calculated for $C_{18}H_{25}ClNO_5$ $(M+H)^+$ *m/z* 370.1416, found 370.1426.

(4R,6S)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-(furan-2-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5t):



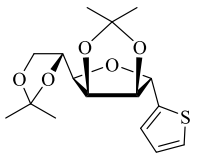
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (14.1 mg, 23% yield). $[\alpha]_D^{20}$ = +24.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 1.8 Hz, 1H), 6.36 – 6.31 (m, 1H), 6.24 (d, *J* = 3.3 Hz, 1H), 5.07 (s, 1H, H-1), 5.01 (d, *J* = 6.0 Hz, 1H, H-2), 4.90 (dd, *J* = 6.0, 3.8 Hz, 1H, H-3), 4.46 – 4.40 (m, 1H, H-5), 4.11 (dd, *J* = 8.7, 6.2 Hz, 1H, H-6a), 4.04 (dd, *J* = 8.7, 4.5 Hz, 1H, H-6b), 3.92 (dd, *J* = 7.8, 3.8 Hz, 1H, H-4), 1.55 (s, 3H), 1.44 (s, 3H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.9, 142.8, 112.8, 110.3, 109.2, 108.0, 84.1 (C-1), 81.5 (C-4), 81.0 (C-3), 79.5 (C-2), 73.4 (C-5), 67.0 (C-6), 26.9, 26.1, 25.2, 24.7. HRMS (ESI) calculated for $C_{16}H_{23}O_6$ $(M+H)^+$ *m/z* 311.1489, found 311.1485.

(4R,6S)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(5-methylfuran-2-yl)tetrahydrofuro[3,4-d][1,3]dioxole (5t'):



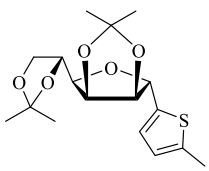
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (21.0 mg, 32% yield). $[\alpha]_D^{20}$ = +35.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.25 (d, *J* = 3.1 Hz, 1H), 5.98 (d, *J* = 2.8 Hz, 1H), 5.02 (d, *J* = 6.0 Hz, 1H, H-2), 4.94 (s, 1H, H-1), 4.90 (dd, *J* = 6.0, 3.6 Hz, 1H, H-3), 4.36 (q, *J* = 6.3 Hz, 1H, H-5), 4.03 (dd, *J* = 8.5, 6.4 Hz, 1H, H-6a), 3.94 – 3.89 (m, 2H, H-6b, H-4), 2.25 (s, 3H), 1.46 (s, 3H), 1.32 (s, 6H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 152.3, 150.4, 112.1, 108.7, 108.2, 106.2, 84.0 (C-1), 81.1 (C-4), 81.0 (C-3), 79.4 (C-2), 73.3 (C-5), 66.3 (C-6), 26.1, 25.5, 24.7, 23.9, 12.6. HRMS (ESI) calculated for $C_{17}H_{25}O_6$ $(M+H)^+$ *m/z* 325.1646, found 325.1645.

(4R,6S)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(thiophen-2-yl)tetrahydrofuro[3,4-d][1,3]dioxole (5u):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (19.0 mg, 29% yield). $[\alpha]_D^{20}$ = +20.9 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 5.2 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.97 – 6.94 (m, 1H), 5.33 (s, 1H, H-1), 5.04 (d, *J* = 5.9 Hz, 1H, H-2), 4.84 (dd, *J* = 6.0, 3.6 Hz, 1H, H-3), 4.50 – 4.42 (m, 1H, H-5), 4.16 (dd, *J* = 8.7, 6.2 Hz, 1H, H-6a), 4.10 (dd, *J* = 8.7, 4.4 Hz, 1H, H-6b), 3.88 (dd, *J* = 7.9, 3.7 Hz, 1H, H-4), 1.56 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 142.6, 127.1, 125.5, 124.8, 112.2, 108.4, 86.4 (C-2), 81.9 (C-1), 81.3 (C-4), 81.0 (C-3), 73.1 (C-5), 66.5 (C-6), 26.1, 25.6, 24.7, 24.0. HRMS (ESI) calculated for $C_{16}H_{23}O_5S$ $(M+H)^+$ *m/z* 327.1260, found 327.1263.

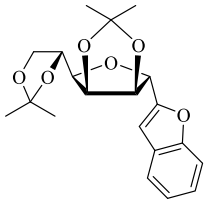
(4R,6S)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(5-methylthiophen-2-yl)tetrahydrofuro[3,4-d][1,3]dioxole (5u'):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (21.0 mg, 31% yield). $[\alpha]_D^{20}$ = +58.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 3.3 Hz, 1H), 6.62 (d, *J* = 3.4 Hz, 1H), 5.25 (s, 1H, H-1), 5.00 (d, *J* = 6.0 Hz, 1H, H-2),

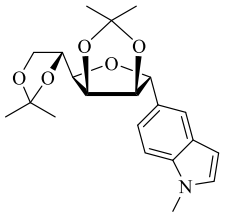
4.82 (dd, *J* = 6.0, 3.6 Hz, 1H, H-3), 4.48 – 4.41 (m, 1H, H-5), 4.14 (dd, *J* = 8.7, 6.2 Hz, 1H, H-6a), 4.08 (dd, *J* = 8.7, 4.5 Hz, 1H, H-6b), 3.87 (dd, *J* = 7.9, 3.6 Hz, 1H, H-4), 2.45 (s, 3H), 1.55 (s, 3H), 1.43 (s, 3H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.2, 139.4, 125.1, 124.5, 112.9, 109.3, 86.4 (C-2), 82.0 (C-1), 81.2 (C-4), 81.0 (C-3), 73.2 (C-5), 67.1 (C-6), 26.9, 26.1, 25.2, 24.8, 15.3. HRMS (ESI) calculated for $C_{17}H_{25}O_5S$ $(M+H)^+$ *m/z* 341.1417, found 341.1411.

2-((4S,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)benzofuran (5v):



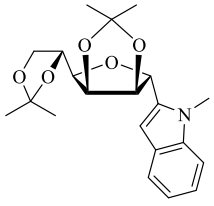
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (23.0 mg, 32% yield). $[\alpha]_D^{20}$ = +69.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.64 (s, 1H), 5.23 (s, 1H, H-1), 5.14 (d, *J* = 6.0 Hz, 1H, H-2), 4.96 – 4.92 (m, 1H, H-3), 4.51 – 4.44 (m, 1H, H-5), 4.17 – 4.09 (m, 2H, H-6), 4.06 (dd, *J* = 7.8, 3.9 Hz, 1H, H-4), 1.58 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.1, 154.3, 127.8, 124.5, 123.0, 121.2, 113.0, 111.4, 109.3, 104.6, 84.2 (C-2), 82.0 (C-1), 81.0 (C-4), 80.2 (C-3), 73.4 (C-5), 66.9 (C-6), 26.9, 26.1, 25.2, 24.7. HRMS (ESI) calculated for $C_{20}H_{25}O_6$ $(M+H)^+$ *m/z* 361.1646, found 361.1644.

5-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-methyl-1H-indole (5w):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a faint yellow oil (45.4 mg, 61% yield). $[\alpha]_D^{20}$ = +34.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.48 (d, *J* = 3.1 Hz, 1H), 5.33 (s, 1H, H-1), 5.10 (d, *J* = 6.0 Hz, 1H, H-2), 4.79 (dd, *J* = 6.0, 3.8 Hz, 1H, H-3), 4.55 – 4.48 (m, 1H, H-5), 4.24 – 4.18 (m, 2H, H-6), 3.96 (dd, *J* = 7.8, 3.8 Hz, 1H, H-4), 3.77 (s, 3H), 1.60 (s, 3H), 1.44 (s, 3H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.1, 129.6, 129.0, 128.4, 119.5, 117.7, 112.7, 109.6, 109.2, 101.1, 87.6 (C-2), 85.5 (C-1), 81.25 (C-4), 81.18 (C-3), 73.6 (C-5), 67.2 (C-6), 26.9, 26.3, 25.3, 24.8. HRMS (ESI) calculated for $C_{21}H_{28}NO_5$ $(M+H)^+$ *m/z* 374.1962, found 374.1962.

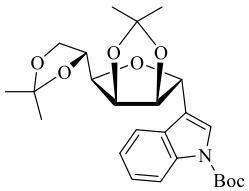
2-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-methyl-1H-indole (5x):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a faint yellow oil (47.0 mg, 63% yield). $[\alpha]_D^{20}$ = +75.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.51 (s, 1H), 5.40 (d, *J* = 6.0 Hz, 1H, H-2), 5.35 (s, 1H, H-1), 5.00 – 4.96 (m, 1H, H-3), 4.39 (q, *J* = 6.2 Hz, 1H, H-5), 4.08 – 4.01 (m, 1H, H-6a), 3.93 (dd, *J* = 8.5, 5.6 Hz, 1H, H-6b), 3.83 (s, 3H), 3.75 – 3.70 (m, 1H, H-4), 1.51 (s, 3H), 1.39 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100

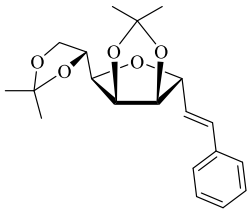
MHz, Acetone-d_6) δ 138.2, 135.6, 127.1, 121.8, 120.4, 119.3, 112.0, 109.3, 108.2, 100.3, 83.8 (C-1), 81.1 (C-4), 80.2 (C-3), 78.5 (C-2), 73.2 (C-5), 66.3 (C-6), 26.1, 25.5, 24.8, 23.9. HRMS (ESI) calculated for $C_{21}H_{28}NO_5$ $(M+H)^+$ *m/z* 374.1962, found 374.1961.

tert-butyl-3-((4R,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1H-indole-1-carboxylate (5y):



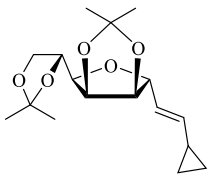
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 14:1) gave the pure product as a colorless oil (52.3 mg, 57% yield).
$[\alpha]_D^{20}$ = +20.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.65 (d, *J* = 1.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 5.31 (s, 1H, H-1), 5.23 (dd, *J* = 6.0, 1.1 Hz, 1H, H-2), 4.91 (dd, *J* = 6.0, 3.6 Hz, 1H, H-3), 4.42 (q, *J* = 6.3 Hz, 1H, H-5), 4.09 (dd, *J* = 8.4, 6.5 Hz, 1H, H-6a), 3.97 (dd, *J* = 8.4, 5.7 Hz, 1H, H-6b), 3.83 (dd, *J* = 6.7, 3.5 Hz, 1H, H-4), 1.68 (s, 9H), 1.52 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 124.6, 122.7, 122.6, 120.2, 118.1, 115.1, 112.1, 108.3, 84.6 (C-2), 81.0 (C-3), 80.9 (C-4), 79.8 (C-1), 73.3 (C-5), 66.5 (C-6), 27.3, 26.1, 25.6, 24.7, 24.1. HRMS (ESI) calculated for $C_{25}H_{34}NO_7(M+H)^+$ *m/z* 460.2330, found 460.2304.

(4R,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((E)-styryl)tetrahydrofuro[3,4-d][1,3]dioxole (5z):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (50.0 mg, 72% yield, α/β = 3.5:1).
α isomer: $[\alpha]_D^{20}$ = +26.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 16.1, 5.2 Hz, 1H), 4.80 (dd, *J* = 6.1, 3.7 Hz, 1H, H-3), 4.77 – 4.73 (m, 2H, H-1, H-2), 4.48 – 4.42 (m, 1H, H-5), 4.18 – 4.11 (m, 2H, H-6), 3.88 (dd, *J* = 7.6, 3.6 Hz, 1H, H-4), 1.54 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.1, 131.6, 128.6, 128.0, 126.5, 125.5, 112.7, 109.2, 85.6 (C-2), 84.3 (C-1), 81.1 (C-4), 80.9 (C-3), 73.5 (C-5), 67.1 (C-1), 26.9, 26.2, 25.2, 24.8. HRMS (ESI) calculated for $C_{20}H_{27}O_5$ $(M+H)^+$ *m/z* 347.1853, found 347.1855.
β isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 16.0, 7.7 Hz, 1H), 4.82 (dd, *J* = 6.0, 3.6 Hz, 1H, H-3), 4.72 (dd, *J* = 6.1, 3.7 Hz, 1H, H-2), 4.49 – 4.43 (m, 1H, H-5), 4.17 – 4.08 (m, 3H, H-1, H-6), 3.58 (dd, *J* = 7.8, 3.7 Hz, 1H, H-4), 1.53 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.4, 134.7, 128.4, 128.0, 126.8, 123.1, 112.6, 109.1, 83.2, 82.8, 81.8, 81.0, 73.2, 67.1, 27.0, 25.8, 25.2, 24.6. HRMS (ESI) calculated for $C_{20}H_{27}O_5$ $(M+H)^+$ *m/z* 347.1853, found 347.1855.

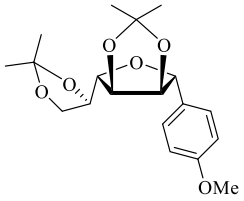
(4R,6R)-4-((E)-2-cyclopropylvinyl)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (5z'):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1)

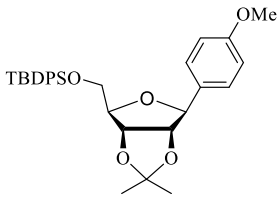
gave the pure product as a colorless oil (38.3 mg, 63% yield). $[\alpha]_D^{20}$ = +135.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.46 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.20 (dd, *J* = 15.7, 8.9 Hz, 1H), 4.76 (s, 1H, H-3), 4.62 (d, *J* = 6.1 Hz, 1H, H-2), 4.52 (d, *J* = 5.7 Hz, 1H, H-1), 4.43 – 4.35 (m, 1H, H-5), 4.14 – 4.02 (m, 2H, H-6), 3.82 – 3.76 (m, 1H, H-4), 1.50 (s, 3H), 1.45 (s, 3H), 1.38 (s, 4H), 1.34 (s, 3H), 0.73 (d, *J* = 8.0 Hz, 2H), 0.39 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.4, 123.2, 112.5, 109.1, 85.5 (C-2), 84.1 (C-1), 80.8 (C-4), 80.7 (C-3), 73.4 (C-5), 67.1 (C-6), 26.9, 26.1, 25.2, 24.7, 13.6, 6.9, 6.8. HRMS (ESI) calculated for $C_{17}H_{27}O_5$ $(M+H)^+$ *m/z* 311.1853, found 311.1851.

(4S,6R)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-(4-methoxyphenyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (14a):



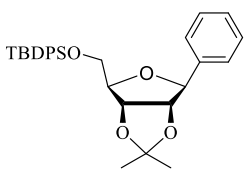
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (65.8 mg, 94% yield, α:β = 5:1). ***α isomer***: $[\alpha]_D^{20}$ = -30.8 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 9.1 Hz, 2H), 6.92 – 6.88 (m, 2H), 5.22 (s, 1H, H-1), 4.91 (d, *J* = 5.9 Hz, 1H, H-2), 4.65 (dd, *J* = 6.1, 4.3 Hz, 1H, H-3), 4.51 – 4.44 (m, 1H, H-5), 4.22 (dd, *J* = 8.5, 6.6 Hz, 1H, H-6a), 3.92 (dd, *J* = 8.3, 4.3 Hz, 1H, H-4), 3.80 (s, 3H), 3.72 – 3.63 (m, 1H, H-6b), 1.55 (s, 3H), 1.47 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.0, 130.3, 127.0, 114.0, 113.2, 109.6, 87.5 (C-2), 84.6 (C-1), 82.8 (C-4), 81.3 (C-3), 75.9 (C-5), 66.1 (C-6), 55.3, 26.9, 26.2, 25.4, 25.0. HRMS (ESI) calculated for $C_{19}H_{27}O_6$ $(M+H)^+$ *m/z* 351.1802, found 351.1802.

tert-butyl(((4R,6S)-6-(4-methoxyphenyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methoxy)diphenylsilane (15a) [4]:



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a colorless oil (75.5 mg, 73% yield, β:α >20:1). $[\alpha]_D^{20}$ = +26.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.80 – 7.72 (m, 4H), 7.52 – 7.40 (m, 6H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.85 (dd, *J* = 6.8, 4.0 Hz, 1H, H-3), 4.78 (d, *J* = 5.5 Hz, 1H, H-1), 4.54 – 4.50 (m, 1H, H-2), 4.15 (q, *J* = 4.1 Hz, 1H, H-4), 3.98 – 3.88 (m, 2H, H-5), 3.79 (s, 3H), 1.56 (s, 3H), 1.32 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 159.4, 135.5, 133.2, 132.3, 129.8, 127.8, 127.2, 114.2, 113.6, 86.9 (C-2), 85.4 (C-1), 84.3 (C-4), 81.7 (C-3), 64.2 (C-5), 54.7, 27.1, 26.3, 26.3, 24.9, 18.9. HRMS (ESI) calculated for $C_{31}H_{38}O_5SiNa$ $(M+Na)^+$ *m/z* 541.2381, found 541.2382.

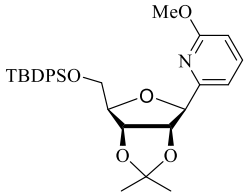
tert-butyl(((4R,6S)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methoxy)diphenylsilane (15b) [3]:



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a colorless oil (69.2 mg, 71% yield, β:α >20:1). $[\alpha]_D^{20}$ = +39.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 4H), 7.37 – 7.26 (m, 9H), 7.21 (dd, *J* = 13.6, 7.3 Hz, 2H), 4.82 (d, *J* = 5.3 Hz, 1H, H-1), 4.73 (dd, *J* = 6.7, 3.9 Hz, 1H, H-3), 4.48 – 4.42 (m, 1H, H-2), 4.12

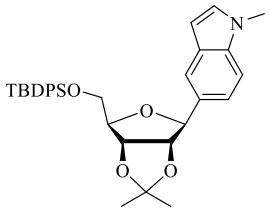
(q, *J* = 3.8 Hz, 1H, H-4), 3.87 (dd, *J* = 11.2, 3.5 Hz, 1H, H-5a), 3.80 (dd, *J* = 11.2, 3.9 Hz, 1H, H-5b), 1.54 (s, 3H), 1.27 (s, 3H), 0.99 (s, 9H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 140.1, 135.7, 133.30, 133.28, 129.8, 129.74, 129.72, 128.4, 127.8, 127.74, 127.70, 125.8, 114.5, 87.1 (C-2), 85.7 (C-1), 84.4 (C-4), 81.6 (C-3), 64.0 (C-5), 27.7, 26.9, 26.8, 25.7, 19.3. HRMS (ESI) calculated for $C_{30}H_{37}O_4Si$ $(M+H)^+$ *m/z* 489.2456, found 489.2463.

2-((4S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-6-methoxypyridine (15r'):



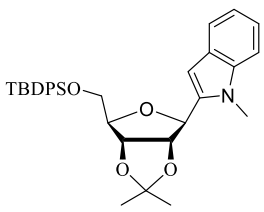
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 35:1) gave the pure product as a colorless oil (60.1 mg, 58% yield, β only). $[\alpha]_D^{20}$ = -2.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 2.3 Hz, 1H), 7.70 – 7.66 (m, 4H), 7.63 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 4H), 6.68 (d, *J* = 8.6 Hz, 1H), 4.84 – 4.79 (m, 2H, H-1, H-3), 4.49 (t, *J* = 6.1 Hz, 1H, H-2), 4.18 (q, *J* = 3.7 Hz, 1H, H-4), 3.94 (s, 3H), 3.94 – 3.89 (m, 1H, H-5a), 3.86 (dd, *J* = 11.3, 3.8 Hz, 1H, H-5b), 1.61 (s, 3H), 1.35 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.9, 144.6, 136.9, 135.7, 135.6, 133.2, 133.1, 129.82, 129.76, 128.2, 127.8, 127.7, 114.7, 110.8, 86.6 (C-2), 84.4 (C-1), 83.6 (C-4), 81.7 (C-3), 63.9 (C-5), 58.5, 53.7, 27.6, 26.9, 25.6, 19.3, 18.5. HRMS (ESI) calculated for $C_{30}H_{38}NO_5Si$ $(M+H)^+$ *m/z* 520.2514, found 520.2514.

5-((4S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-methyl-1H-indole (15w):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a colorless oil (66.0 mg, 61% yield, β only). $[\alpha]_D^{20}$ = -11.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.69 (m, 5H), 7.43 – 7.34 (m, 6H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.24 (s, 1H), 7.02 (d, *J* = 3.1 Hz, 1H), 6.41 (d, *J* = 3.0 Hz, 1H), 5.02 (d, *J* = 5.1 Hz, 1H, H-1), 4.84 (dd, *J* = 6.7, 4.2 Hz, 1H, H-3), 4.61 – 4.56 (m, 1H, H-2), 4.20 (q, *J* = 3.9 Hz, 1H, H-4), 3.98 (dd, *J* = 11.2, 3.6 Hz, 1H, H-5a), 3.91 (dd, *J* = 11.2, 4.0 Hz, 1H, H-5b), 3.77 (s, 3H), 1.64 (s, 3H), 1.35 (s, 3H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.5, 135.7, 133.4, 130.9, 129.72, 129.66, 129.1, 128.4, 127.75, 127.72, 119.8, 118.3, 114.4, 109.2, 101.1, 87.5 (C-2), 86.4 (C-1), 84.3 (C-4), 81.6 (C-3), 64.1 (C-5), 32.9, 27.7, 26.9, 25.7, 19.3. HRMS (ESI) calculated for $C_{33}H_{40}NO_4Si$ $(M+H)^+$ *m/z* 542.2721, found 542.2753.

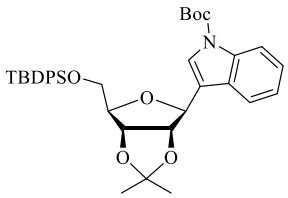
2-((4S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-methyl-1H-indole (15x):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a colorless oil (68.1 mg, 63% yield, β only). $[\alpha]_D^{20}$ = -16.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 4H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.29 (t, *J* = 7.1 Hz, 5H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.45 (s, 1H), 5.13 (d, *J* = 4.6 Hz, 1H, H-1), 4.95 (dd, *J* = 6.6, 4.7 Hz, 1H, H-3), 4.84

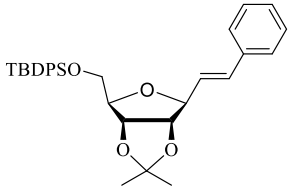
(dd, *J* = 6.6, 3.3 Hz, 1H, H-2), 4.24 (q, *J* = 4.6 Hz, 1H, H-4), 3.77 (s, 3H), 3.73 (d, *J* = 4.8 Hz, 2H (C-5)), 1.61 (s, 3H), 1.40 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2, 137.4, 135.6, 133.21, 133.17, 129.7, 127.8, 127.7, 127.3, 121.8, 120.8, 119.5, 114.4, 109.0, 99.8, 85.0, 84.1 (C-1), 82.0, 79.7, 63.9, 30.5, 27.5, 26.8, 25.5, 19.2. HRMS (ESI) calculated for $C_{33}H_{40}NO_4Si$ $(M+H)^+$ *m/z* 542.2721, found 542.2730.

tert-butyl-3-((4S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1H-indole-1-carboxylate (15y):



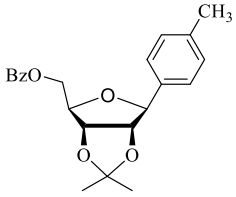
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a colorless oil (69.0 mg, 55% yield, β only). $[\alpha]_D^{20}$ = -2.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.79 – 7.71 (m, 5H), 7.68 (s, 1H), 7.47 – 7.31 (m, 7H), 7.18 (t, *J* = 7.5 Hz, 1H), 5.11 (d, *J* = 5.3 Hz, 1H, H-1), 4.95 (dd, *J* = 6.8, 3.8 Hz, 1H, H-3), 4.83 – 4.79 (m, 1H, H-2), 4.23 (q, *J* = 4.0 Hz, 1H, H-4), 3.96 (dd, *J* = 11.2, 3.8 Hz, 1H, H-5a), 3.91 (dd, *J* = 11.2, 4.3 Hz, 1H, H-5b), 1.64 (s, 9H), 1.61 (s, 3H), 1.36 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 135.5, 133.2, 129.82, 129.77, 127.81, 127.78, 124.5, 122.5, 122.4, 120.4, 119.9, 115.1, 114.4, 85.2 (C-2), 84.6 (C-1), 83.5, 81.9 (C-4), 80.8 (C-3), 64.1 (C-5), 27.4, 27.1, 26.4, 24.9, 19.0. HRMS (ESI) calculated for $C_{37}H_{45}NO_6SiK$ $(M+K)^+$ *m/z* 666.2648, found 666.2560.

tert-butyl(((4R,6S)-2,2-dimethyl-6-((E)-styryl)tetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methoxy)diphenylsilane (15z):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a colorless oil (70.0 mg, 68% yield, β only). $[\alpha]_D^{20}$ = +20.9 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.63 (m, 4H), 7.46 – 7.32 (m, 6H), 7.35 – 7.20 (m, 5H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.30 – 6.19 (m, 1H), 4.79 (dd, *J* = 5.9, 3.1 Hz, 1H, H-3), 4.57 – 4.46 (m, 2H, H-1, H-2), 4.17 (q, *J* = 3.7 Hz, 1H, H-4), 3.89 – 3.78 (m, 2H, H-5), 1.59 (s, 3H), 1.37 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.5, 135.7, 135.65, 135.58, 133.3, 133.2, 132.0, 129.79, 129.75, 128.5, 127.8, 127.7, 127.4, 126.6, 114.1, 85.6 (C-1), 85.4 (C-2), 84.4 (C-4), 82.2 (C-3), 64.3 (C-5), 27.6, 26.9, 25.6, 19.3. HRMS (ESI) calculated for $C_{32}H_{38}O_4SiNa$ $(M+Na)^+$ *m/z* 537.2632, found 537.2635.

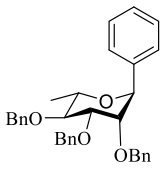
((4R,6S)-2,2-dimethyl-6-(p-tolyl)tetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl benzoate (16c):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 50:1) gave the pure product as a white solid (35.2 mg, 48% yield, β only). $[\alpha]_D^{20}$ = +8.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.96 (d, *J* = 4.7 Hz, 1H, H-1), 4.74 (dd, *J* = 6.7, 4.2 Hz, 1H), 4.63 – 4.58 (m, 2H), 4.52 (dd, *J* = 11.9, 4.6 Hz, 1H), 4.43 (q, *J* = 4.2 Hz, 1H), 2.31 (s, 3H), 1.63 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.3, 137.5, 136.6, 133.1, 129.8, 129.7, 129.2, 128.4, 125.6, 114.9, 87.2, 85.9 (C-1), 82.03, 82.0, 64.6, 27.6, 25.6, 21.1. HRMS (ESI)

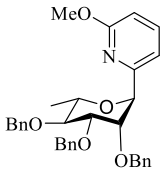
calculated for $C_{22}H_{25}O_5$ $(M+H)^+$ *m/z* 369.1702, found 369.1701.

(2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-2-methyl-6-phenyltetrahydro-2H-pyran (17b):



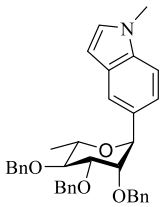
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 30:1) gave the pure product as a colorless oil (64.1 mg, 65% yield, α only). $[\alpha]_D^{20}$ = -1.8 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.43 – 7.25 (m, 20H), 5.05 (d, *J* = 5.0 Hz, 1H, H-1), 4.81 – 4.74 (m, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.66 – 4.60 (m, 2H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.30 (dd, *J* = 5.0, 2.9 Hz, 1H, H-2), 3.81 – 3.76 (m, 1H, H-3), 3.74 – 3.68 (m, 2H, H-4, H-5), 1.35 (d, *J* = 5.8 Hz, 3H, H-6). ^{13}C NMR (100 MHz, Acetone-d_6) δ 139.4, 139.1, 139.02, 138.98, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4, 127.3, 127.2, 126.6, 79.8 (C-4), 77.7 (C-3), 76.7 (C-2), 73.24 (C-1), 73.23, 71.9, 71.7, 70.6 (C-5), 17.2 (C-6). HRMS (ESI) calculated for $C_{33}H_{34}O_4Na$ $(M+Na)^+$ *m/z* 517.2349, found 517.2361.

2-methoxy-6-((2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)pyridine (17r'):



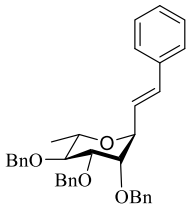
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a colorless oil (66.0 mg, 63% yield, α only). $[\alpha]_D^{20}$ = +12.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.14 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.22 (m, 15H), 6.73 (d, *J* = 8.6 Hz, 1H), 5.01 (d, *J* = 6.3 Hz, 1H, H-1), 4.79 (d, *J* = 11.8 Hz, 1H), 4.75 – 4.70 (m, 2H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.17 – 4.12 (m, 1H, H-2), 3.95 – 3.90 (m, 1H), 3.88 (s, 3H), 3.86 – 3.80 (m, 1H), 3.73 (t, *J* = 5.5 Hz, 1H), 1.38 (d, *J* = 6.7 Hz, 3H, H-6). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.7, 144.2, 144.1, 144.0, 133.45, 133.37, 133.3, 133.0, 132.9, 132.8, 132.7, 132.5, 84.5 (C-4), 81.9, 81.8, 77.9, 77.3, 76.6, 76.1, 75.6, 57.8 (C-5), 22.1 (C-6). HRMS (ESI) calculated for $C_{33}H_{36}NO_5$ $(M+H)^+$ *m/z* 526.2588, found 526.2618.

1-methyl-5-((2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)-1H-indole (17w):



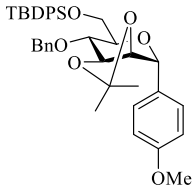
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a colorless oil (63.5 mg, 58% yield, α only). $[\alpha]_D^{20}$ = +29.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.48 (s, 1H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.22 (m, 15H), 7.20 (d, *J* = 3.4 Hz, 1H), 6.40 (d, *J* = 3.1 Hz, 1H), 5.16 (d, *J* = 4.2 Hz, 1H, H-1), 4.84 – 4.76 (m, 2H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.5 Hz, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.46 (t, *J* = 3.6 Hz, 1H, H-2), 3.85 – 3.82 (m, 1H, H-3), 3.81 (s, 3H), 3.74 – 3.66 (m, 2H, H-4, H-5), 1.34 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 140.2, 140.0, 137.1, 130.4, 130.3, 129.5, 129.1, 129.05, 128.97, 128.8, 128.6, 128.4, 128.3, 128.11, 128.08, 120.9, 119.3, 110.1, 101.6, 81.2 (C-4), 79.3 (C-3), 77.7 (C-2), 75.1 (C-1), 74.4, 72.7, 72.6, 71.0 (C-5), 32.9, 18.3 (C-6). HRMS (ESI) calculated for $C_{36}H_{37}NO_4Na$ $(M+Na)^+$ *m/z* 570.2615, found 570.2630.

(2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-2-methyl-6-((E)-styryl)tetrahydro-2H-pyran (17z):



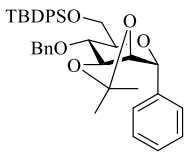
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 30:1) gave the pure product as a colorless oil (62.5 mg, 60% yield, α only, E:Z = 9:1). $[\alpha]_D^{20}$ = +29.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.46 (d, *J* = 7.5 Hz, 4H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.22 (m, 14H), 6.65 (d, *J* = 16.2 Hz, 1H), 6.47 (dd, *J* = 16.2, 5.3 Hz, 1H), 4.89 (d, *J* = 11.3 Hz, 1H), 4.79 – 4.70 (m, 4H, H-1, PhH_2), 4.66 (dd, *J* = 11.5, 4.2 Hz, 2H), 4.08 – 4.02 (m, 1H, H-2), 3.89 (dd, *J* = 8.4, 2.9 Hz, 1H, H-3), 3.85 – 3.74 (m, 1H, H-5), 3.64 (t, *J* = 8.2 Hz, 1H, H-4), 1.29 (d, *J* = 6.2 Hz, 3H, H-6). ^{13}C NMR (100 MHz, Acetone-d_6) δ 139.24, 139.19, 139.0, 136.9, 132.1, 128.5, 128.20, 128.16, 128.1, 127.7, 127.6, 127.4, 127.32, 127.27, 126.5, 80.4 (C-4), 79.2 (C-3), 77.4 (C-2), 74.3, 74.1 (C-1), 71.7, 71.3, 69.9 (C-5), 17.9 (C-6). HRMS (ESI) calculated for $C_{35}H_{37}O_4$ $(M+H)^+$ *m/z* 521.2684, found 521.2691.

(((4R,6R,7R,7aS)-7-(benzyloxy)-4-(4-methoxyphenyl)-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyran-6-yl)methoxy)(tert-butyl)diphenylsilane (18a):



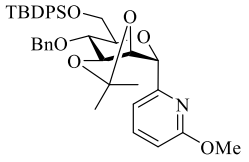
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 40:1) gave the pure product as a colorless oil (93.2 mg, 73% yield, α only). $[\alpha]_D^{20}$ = +35.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 7.2, 2.3 Hz, 4H), 7.41 – 7.32 (m, 4H), 7.31 – 7.20 (m, 9H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.96 (d, *J* = 11.4 Hz, 1H), 4.86 (d, *J* = 7.2 Hz, 1H, H-1), 4.63 (d, *J* = 11.5 Hz, 1H), 4.50 – 4.38 (m, 2H, H-3, H-2), 4.20 (dd, *J* = 9.5, 7.2 Hz, 1H, H-4), 3.91 (d, *J* = 2.9 Hz, 2H, H-6), 3.79 (s, 3H), 3.72 – 3.67 (m, 1H, H-5), 1.57 (s, 3H), 1.38 (s, 3H), 1.05 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.3, 138.4, 135.8, 135.7, 133.4, 133.2, 131.9, 129.7, 129.6, 128.4, 128.2, 127.9, 127.72, 127.66, 127.6, 113.9, 109.4, 79.4 (C-3), 77.9 (C-2), 75.7 (C-4), 75.0 (C-1), 74.6 (C-5), 73.2, 64.1 (C-6), 55.3, 27.7, 26.9, 25.4, 19.3. HRMS (ESI) calculated for $C_{39}H_{46}O_6SiNa$ $(M+Na)^+$ *m/z* 661.2956, found 661.2955.

(((4R,6R,7R,7aS)-7-(benzyloxy)-2,2-dimethyl-4-phenyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyran-6-yl)methoxy)(tert-butyl)diphenylsilane (18b):



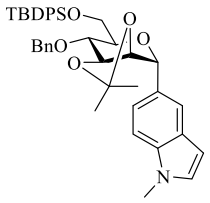
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 40:1) gave the pure product as a colorless oil (86.0 mg, 71% yield, α only). $[\alpha]_D^{20}$ = +21.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 4H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.10 (m, 14H), 4.87 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 6.7 Hz, 1H, H-1), 4.55 (d, *J* = 11.1 Hz, 1H), 4.40 – 4.30 (m, 2H, H-3, H-2), 4.12 (t, *J* = 8.0 Hz, 1H, H-4), 3.86 – 3.80 (m, 2H, H-6), 3.66 – 3.59 (m, 1H, H-5), 1.49 (s, 3H), 1.29 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.8, 138.4, 135.8, 135.7, 133.3, 133.2, 129.7, 129.6, 128.5, 128.4, 128.0, 127.9, 127.84, 127.78, 127.72, 127.69, 127.6, 126.8, 109.5, 79.4 (C-3), 77.9 (C-2), 75.7 (C-4), 75.3 (C-1), 74.8 (C-5), 73.3, 64.1 (C-6), 27.8, 26.9, 25.4, 19.3. HRMS (ESI) calculated for $C_{38}H_{44}O_5SiNa$ $(M+Na)^+$ *m/z* 631.2850, found 631.2853.

2-((4R,6R,7R,7aS)-7-(benzyloxy)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)-6-methoxypyridine (18r'):



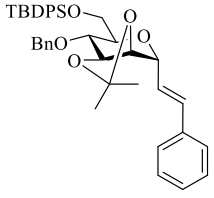
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 20:1) gave the pure product as a colorless oil (79.0 mg, 62% yield, α only). $[\alpha]_D^{20}$ = +8.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.19 (d, *J* = 2.4 Hz, 1H), 7.75 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 4H), 7.42 (q, *J* = 7.5 Hz, 2H), 7.37 – 7.25 (m, 9H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.85 (d, *J* = 8.2 Hz, 1H, H-1), 4.69 (d, *J* = 11.7 Hz, 1H), 4.55 (t, *J* = 7.4 Hz, 1H), 4.47 – 4.41 (m, 1H), 4.27 (dd, *J* = 9.5, 7.4 Hz, 1H), 4.00 – 3.91 (m, 2H), 3.90 (s, 3H), 3.74 (dt, *J* = 9.4, 2.9 Hz, 1H), 1.54 (s, 3H), 1.37 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 163.9, 145.6, 138.7, 137.4, 135.5, 135.5, 133.2, 133.1, 129.8, 129.7, 128.6, 128.2, 127.7, 127.7, 127.6, 127.4, 110.3, 109.3, 79.2, 77.6, 75.5, 74.7, 73.2, 72.6, 64.0, 52.7, 27.0, 26.3, 24.5, 18.9. HRMS (ESI) calculated for $C_{38}H_{46}NO_6Si$ $(M+H)^+$ *m/z* 640.3089, found 640.3127.

5-((4R,6R,7R,7aS)-7-(benzyloxy)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)-1-methyl-1H-indole (18w):



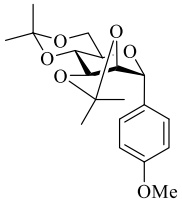
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 20:1) gave the pure product as a colorless oil (79.2 mg, 60% yield, α only). $[\alpha]_D^{20}$ = +22.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.2, 1.7 Hz, 5H), 7.39 – 7.22 (m, 11H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.0 Hz, 1H), 5.07 (d, *J* = 6.9 Hz, 1H, H-1), 4.97 (d, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.58 (t, *J* = 7.0 Hz, 1H, H-2), 4.50 (t, *J* = 7.3 Hz, 1H, H-3), 4.22 (dd, *J* = 9.5, 7.5 Hz, 1H, H-4), 3.92 (d, *J* = 3.0 Hz, 2H, H-6), 3.77 (s, 3H), 3.73 – 3.68 (m, 1H, H-5), 1.59 (s, 3H), 1.39 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.5, 136.5, 135.8, 135.7, 133.5, 133.3, 130.4, 129.6, 129.5, 129.1, 128.4, 128.3, 127.9, 127.70, 127.69, 127.6, 121.0, 119.5, 109.3, 109.2, 101.3, 79.5 (C-3), 78.1 (C-2), 75.99 (C-4), 75.97 (C-1), 74.3 (C-5), 73.2, 64.2 (C-1), 32.9, 27.8, 27.0, 26.9, 25.6, 19.3. HRMS (ESI) calculated for $C_{41}H_{48}NO_5Si$ $(M+H)^+$ *m/z* 662.3297, found 662.3295.

(((4R,6R,7R,7aS)-7-(benzyloxy)-2,2-dimethyl-4-((E)-styryl)tetrahydro-4H-[1,3]dioxolo[4,5-c]pyran-6-yl)methoxy)(tert-butyl)diphenylsilane (18z):



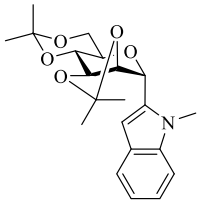
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 40:1) gave the pure product as a white solid (76.5 mg, 63% yield, α only). $[\alpha]_D^{20}$ = +44.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 11.1, 7.1 Hz, 4H), 7.44 – 7.20 (m, 16H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.28 (dd, *J* = 16.1, 5.4 Hz, 1H), 4.94 (d, *J* = 11.4 Hz, 1H), 4.65 – 4.55 (m, 2H, PhH*H*, H-1), 4.40 (t, *J* = 7.2 Hz, 1H, H-2), 4.26 (t, *J* = 6.8 Hz, 1H, H-3), 4.12 – 4.05 (m, 1H, H-4), 3.99 – 3.88 (m, 2H, H-6), 3.74 – 3.68 (m, 1H, H-5), 1.56 (s, 3H), 1.41 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.3, 136.7, 135.8, 135.7, 133.4, 133.3, 132.5, 129.7, 129.6, 128.6, 128.4, 127.9, 127.9, 127.8, 127.74, 127.69, 127.66, 126.9, 126.6, 109.5, 79.0 (C-3), 77.07 (C-2), 75.6 (C-4), 74.2 (C-1), 74.0 (C-5), 73.2, 64.0 (C-6), 27.7, 26.9, 25.6, 19.3. HRMS (ESI) calculated for $C_{40}H_{46}O_5SiNa$ $(M+Na)^+$ *m/z* 657.3007, found 657.3026.

(4R,5aR,9aR,9bR)-4-(4-methoxyphenyl)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-d][1,3]dioxine (19a) [4]:



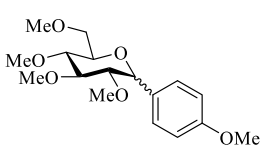
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a white solid (76.5 mg, 63% yield, α only). $[\alpha]_D^{20}$ = +99.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.82 (d, *J* = 6.3 Hz, 1H, H-1), 4.49 (t, *J* = 6.4 Hz, 1H, H-2), 4.33 (t, *J* = 6.9 Hz, 1H, H-3), 4.15 (dd, *J* = 10.8, 7.3 Hz, 1H, H-4), 3.89 (dd, *J* = 10.9, 5.5 Hz, 1H, H-6a), 3.80 (s, 3H), 3.76 – 3.72 (m, 1H, H-6b), 3.54 – 3.45 (m, 1H, H-5), 1.57 (s, 3H), 1.55 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 159.5, 131.5, 128.8, 113.5, 108.8, 98.9, 77.0 (C-2), 76.2 (C-3), 75.2 (C-1), 72.6 (C-4), 64.6 (C-5), 62.7 (C-6), 54.7, 28.6, 27.1, 24.7, 18.5. HRMS (ESI) calculated for $C_{19}H_{27}O_6$ $(M+H)^+$ *m/z* 351.1802, found 351.1804.

1-methyl-2-((4R,5aR,9aR,9bR)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-d][1,3]dioxin-4-yl)-1H-indole (19x):



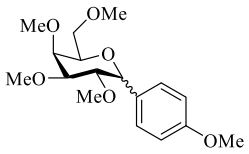
The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 25:1) gave the pure product as a colorless oil (42.4 mg, 57% yield, α only). $[\alpha]_D^{20}$ = +29.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 5.53 (s, 1H, H-2), 4.91 (d, *J* = 5.7 Hz, 1H, H-1), 4.43 – 4.37 (m, 1H, H-3), 3.98 – 3.93 (m, 1H, H-6a), 3.82 (s, 3H), 3.73 (t, *J* = 10.4 Hz, 1H, H-4), 3.64 (dd, *J* = 10.7, 5.5 Hz, 1H, H-6b), 3.18 (td, *J* = 10.2, 5.5 Hz, 1H, H-5), 1.54 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 138.0, 135.2, 127.0, 122.0, 120.5, 119.4, 109.4, 108.4, 102.3, 99.0, 75.3 (C-2), 75.1 (C-3), 73.5 (C-1), 69.8 (C-4), 63.5 (C-5), 61.9 (C-6), 27.6, 25.6, 18.3. HRMS (ESI) calculated for $C_{21}H_{28}NO_5$ $(M+H)^+$ *m/z* 374.1962, found 374.1964.

(2R,3R,4R,5S)-3,4,5-trimethoxy-2-(methoxymethyl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran (20a):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a colorless oil (45.5 mg, 70% yield, α:β = 1:1.6). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H), 7.31 (d, *J* = 8.7 Hz, 3.2H), 6.87 (dd, *J* = 8.8, 2.0 Hz, 5.2H), 5.18 (dd, *J* = 3.1, 1.7 Hz, 1H, **α-anomeric H**), 4.02 (d, *J* = 9.5 Hz, 1.6H, **β-anomeric H**), 3.80 (d, *J* = 0.8 Hz, 7.8H), 3.66 (s, 7.8H), 3.64 (d, *J* = 0.9 Hz, 4.6H), 3.63 – 3.61 (m, 3.2H), 3.58 (s, 5H), 3.56 (s, 1.6H), 3.53 (d, *J* = 6.3 Hz, 1.6H), 3.50 (s, 4.6H), 3.47 (s, 1H), 3.45 (s, 2.6H), 3.41 (s, 1.6H), 3.40 (s, 6.6H), 3.38 (s, 3.2H), 3.32 – 3.21 (m, 5.6H), 3.05 (d, *J* = 8.9 Hz, 1.6H), 3.01 (s, 4.8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.4, 158.8, 131.4, 129.7, 129.4, 128.6, 113.6, 92.8, 88.5, 87.8, 85.9, 83.6, 82.9, 82.7, 81.8, 81.2 (**β-anomeric C**), 80.0, 79.9, 79.8, 79.6, 79.1, 79.0, 78.1, 73.1, 72.9 (**α-anomeric C**), 71.7, 71.6, 71.52, 71.50, 70.3, 67.7, 61.0, 60.8, 60.7, 60.6, 60.5, 60.4, 60.3, 60.2, 60.1, 59.4, 59.24, 59.21, 59.16, 58.8, 58.6, 58.5, 55.22, 55.20. HRMS (ESI) calculated for $C_{17}H_{27}O_6$ $(M+H)^+$ *m/z* 327.1802, found 327.1802.

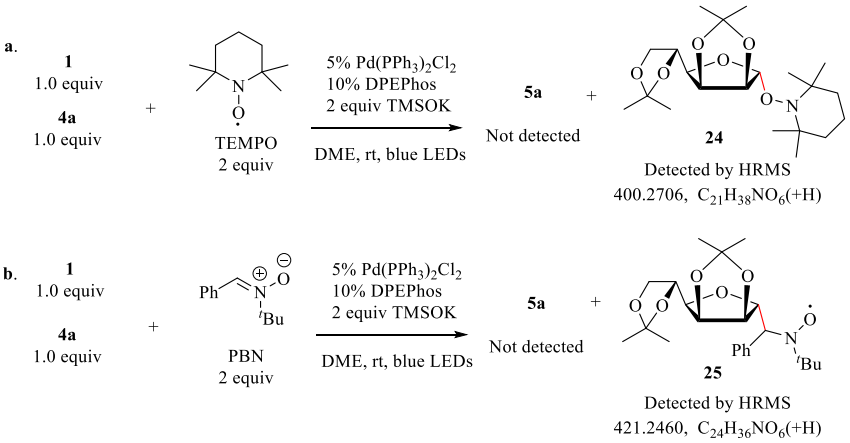
(2R,3S,4R,5S)-3,4,5-trimethoxy-2-(methoxymethyl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran (21a):



The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (PE:EA = 15:1) gave the pure product as a colorless oil (47.0 mg, 71% yield, α:β = 5:1). **α isomer**: $[\alpha]_D^{20}$ = +27.0 (c = 1.00, $CHCl_3$);^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.03 (d, *J* = 2.9 Hz, 1H, H-1), 4.15 – 4.10 (m, 1H, H-5), 3.87 (dd, *J* = 11.0, 8.0 Hz, 1H, H-6a), 3.80 (s, 3H), 3.80 – 3.78 (m, 1H, H-4), 3.72 (dd, *J* = 6.1, 2.9 Hz, 1H, H-3), 3.64 (dd, *J* = 6.0, 3.0 Hz, 1H, H-2), 3.58 – 3.56 (m, 1H, H-6b), 3.55 (s, 3H), 3.51 (s, 3H), 3.36 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 130.3, 128.5, 113.4, 80.1 (C-2), 77.8 (C-3), 75.6 (C-4), 73.4 (C-5), 70.0 (C-1), 68.9 (C-6), 59.2, 59.1, 58.8, 58.7, 55.2. HRMS (ESI) calculated for $C_{17}H_{27}O_6$ $(M+H)^+$ *m/z* 327.1802, found 327.1801.

6. Mechanistic Studies

6.1 Radical trap experiments with TEMPO\PBN and EPR experiment



a. To a 10 mL Schlenk flask equipped with a stir bar, glycosyl chloride **1** (56.0 mg, 0.2 mmol, 1 equiv), aryl boronic ester **4a** (44.0 mg, 0.2mmol, 1.0 equiv), $Pd(PPh_3)Cl_2$ (7.0 mg, 5 mmol%), DPEPhos (11.0 mg, 10 mmol%) and TEMPO (62.5 mg, 0.4 mol, 2.0 equiv) were added with nitrogen. Then TMSOK (2 equiv, 2.00 M in DME) was added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm, 10W) at 20°C. After 30 min, taking a portion of the mixture high-resolution mass spectrometry analysis. Compound **24** was detected instead of compound **5a**. HRMS (ESI) calculated for $C_{21}H_{38}NO_6$ $(M+H)^+$ *m/z* 400.2694, found 400.2706.

b. To a 10 mL Schlenk flask equipped with a stir bar, glycosyl chloride **1** (56.0 mg, 0.2 mmol, 1 equiv), aryl boronic ester **4a** (44.0 mg, 0.2mmol, 1.0 equiv), $Pd(PPh_3)Cl_2$ (7.0 mg, 5 mmol%), DPEPhos (11.0 mg, 10 mmol%) and PBN (70.9 mg, 0.4 mol, 2.0 equiv) were added with nitrogen. Then TMSOK (2 equiv, 2.00 M in DME) was added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm, 10W) at 20°C. After 30 min, taking a portion of the mixture high-resolution mass spectrometry analysis. Compound **25** was detected instead of compound **5a**. HRMS (ESI) calculated for $C_{23}H_{35}NO_6$ $(M+H)^+$ *m/z* 421.2460, found 421.2459.

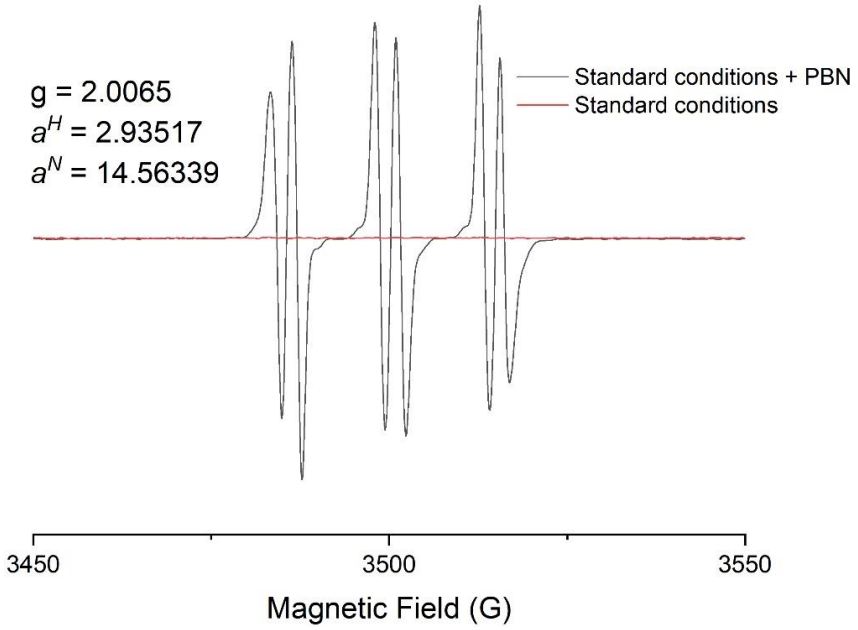
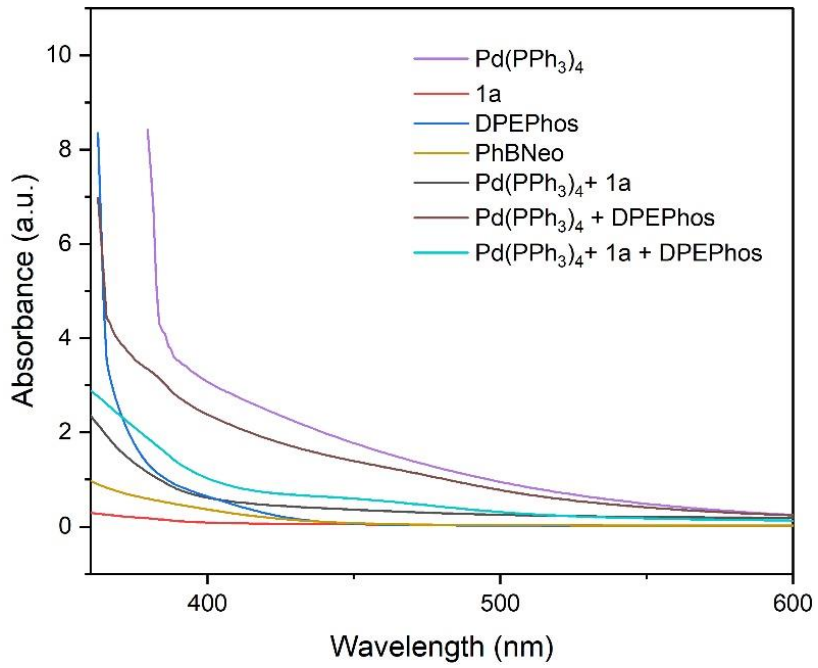


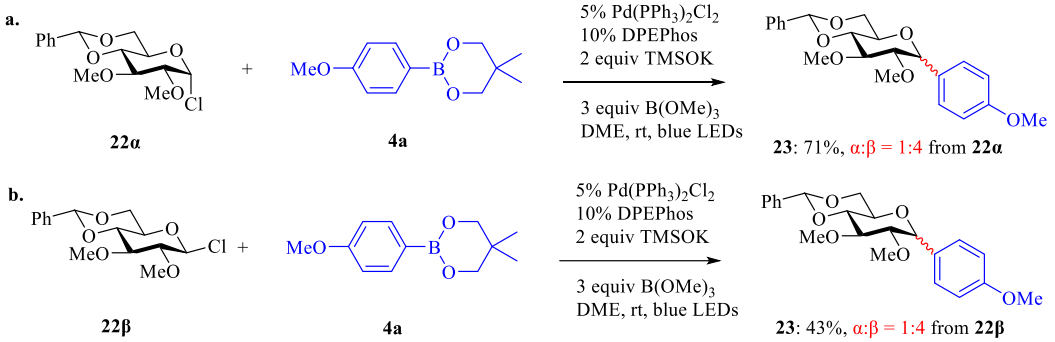
Figure S1. EPR spectra of the reaction mixture: a) PBN (black line); b) without PBN (red line).

6.2 uv-vis experiments

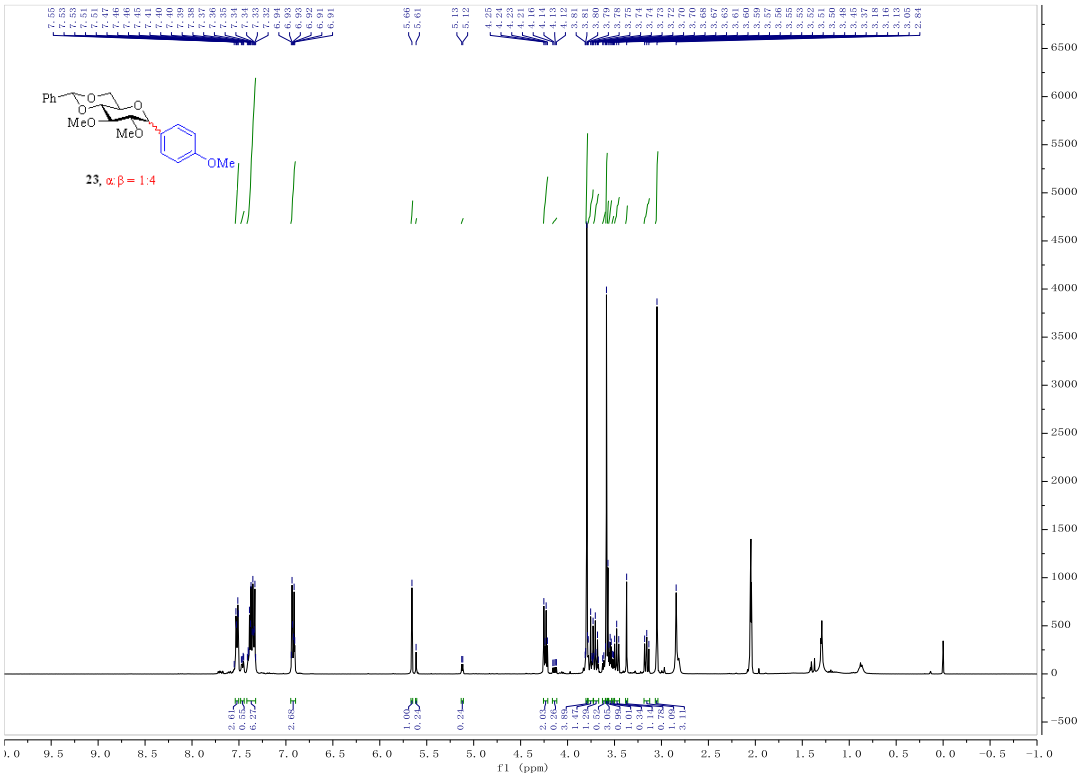
UV-Vis absorption spectrum: the reagents of model reaction and comparison of the mixture of palladium with other components in THF. 1) $Pd(PPh_3)_4$ in THF (0.5 mM). 2) **1** in THF (0.5 mM). 3) DPEphos in THF (0.5 mM). 4) **4b** (PhBNeo) in THF (0.5 mM). 5) $Pd(PPh_3)_4$ and 1 in THF (0.5 mM). 6) $Pd(PPh_3)_4$ and DPEPhos in THF (0.5 mM). 7) $Pd(PPh_3)_4$, DPEPhos and 1 in THF (0.5 mM).



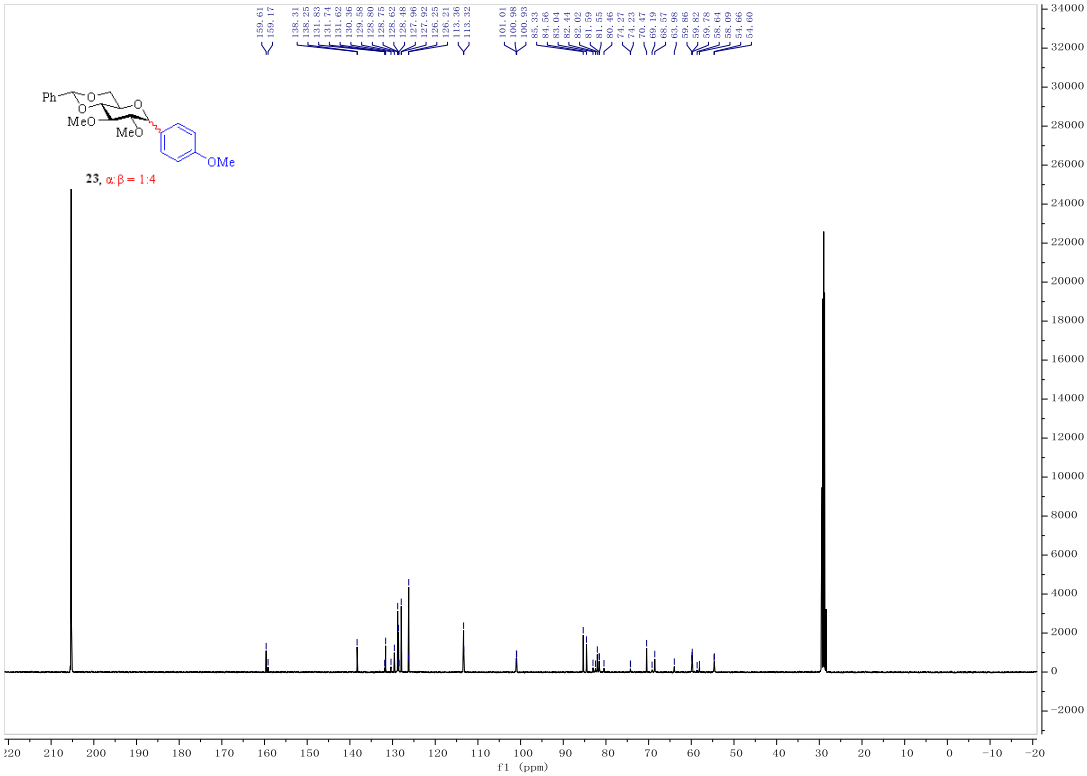
6.3 Experiments about the configuration of glycosyl chlorides



To a 10 mL Schlenk flask equipped with a stir bar, glycosyl chloride **22** (0.2 mmol, 1 equiv), aryl boronic ester **4a** (0.3mmol, 1.5 equiv), $Pd(PPh_3)Cl_2$ (5 mmol%), DPEPhos (10 mmol%) were added with nitrogen. Then TMSOK (2 equiv, 2.00 M in DME) and trimethyl borate (3 equiv) were added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm,10W) at 20°C until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography (PE:EA = 12:1) to give the corresponding product **23** (71%, α:β = 1:4 from **22α**; 41%, α:β = 1:4 from **22β**) as a white solid. **Mixture**: ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.52 (dd, *J* = 7.6, 2.0 Hz, 2.6H), 7.46 (dd, *J* = 6.7, 2.9 Hz, 0.54H), 7.42 – 7.30 (m, 6.27H), 6.92 (dd, *J* = 9.0, 2.6 Hz, 2.57H), 5.66 (s, 1H), 5.61 (s, 0.24H), 5.12 (d, *J* = 4.5 Hz, 0.25H, **α-anomeric H**), 4.24 (d, *J* = 9.8 Hz, 1H, **β-anomeric H**), 4.23 (d, *J* = 10.2 Hz, 1H), 4.14 (dd, *J* = 10.3, 4.9 Hz, 0.26H), 3.80 (s, 3.89H), 3.75 (t, *J* = 10.2 Hz, 1.47H), 3.69 (d, *J* = 9.3 Hz, 1.29H), 3.63 – 3.61 (m, 0.52H), 3.59 (s, 3H), 3.57 (s, 0.99H), 3.56 – 3.53 (m, 1H), 3.52 (d, *J* = 4.9 Hz, 0.34H), 3.48 (t, *J* = 8.8 Hz, 1H), 3.37 (s, 0.74H), 3.19 – 3.12 (m, 1H), 3.05 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 159.6, 159.2, 138.3, 138.2, 131.8, 131.7, 131.6, 130.4, 129.6, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 126.3, 126.2, 113.4, 113.3, 101.01, 100.98, 100.9, 85.3, 84.6, 83.0, 82.4, 82.0, 81.6, 81.5 (**β-anomeric C**), 80.5, 74.3 (**α-anomeric C**), 74.2, 70.5, 69.2, 68.6, 64.0, 59.9, 59.82, 59.78, 58.6, 58.1, 54.7, 54.6. HRMS (ESI) calculated for $C_{22}H_{27}O_6$ $(M+H)^+$ *m/z* 387.1802, found 387.1802.



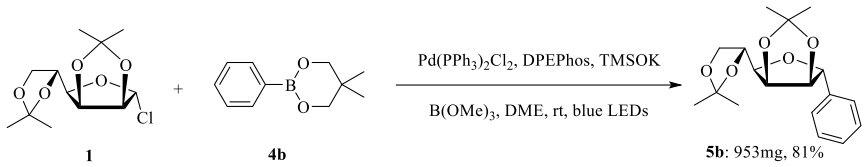
^{1}H NMR spectrum of compound **23** (400 MHz, Acetone-d_6)



^{13}C NMR spectrum of compound **23** (100 MHz, Acetone-d_6)

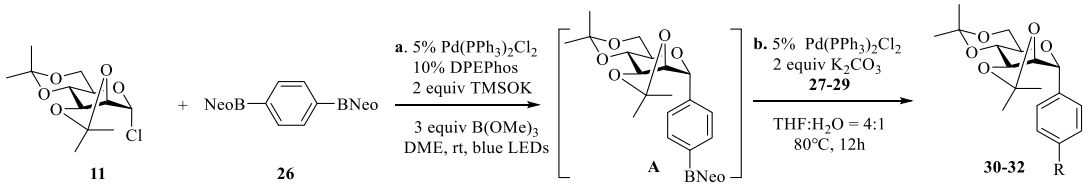
7. Gram-scale and application synthesis

Gram-scale reaction of 5b:



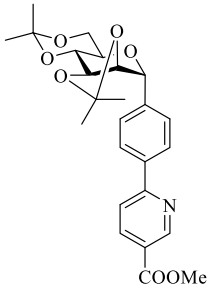
To a 250 mL Schlenk flask equipped with a stir bar, glycosyl chloride **1** (1.00 g, 3.6 mmol, 1 equiv), phenyl boronic ester **4b** (1.03 g, 5.4 mmol, 1.5 equiv), $Pd(PPh_3)Cl_2$ (126 mg, 5 mmol%) and DPEPhos (194 mg, 10 mmol%) were added with nitrogen. Then TMSOK (7.20 mmol, 2 equiv, 2.00 M in DME) and trimethyl borate (1.20 ml, 3 equiv) were added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm, 2×10W) at 20°C until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product **5b** (953 mg, 81% yield, α only).

One-pot synthesis of compounds 30-32



General procedure C: To a 10 mL Schlenk flask equipped with a stir bar, glycosyl chloride **11** (1 equiv), 1,4-Benzenediboronic ester (1.5 equiv), $Pd(PPh_3)Cl_2$ (5 mmol%) and DPEPhos (10 mmol%) were added with nitrogen. Then TMSOK (2 equiv, 2.00 M in DME) and trimethyl borate (3 equiv) were added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm,10W) at 20°C until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, concentrated in vacuo without further purification. The heteroaryl bromide (2 equiv), $Pd(PPh_3)Cl_2$ (5 mmol%) and K_2CO_3 (2 equiv) were added in the residue dissolved in THF: H_2O (4:1) with nitrogen. The reaction was running at 80°C in an oil bath for 12 hours until the starting materials was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product.

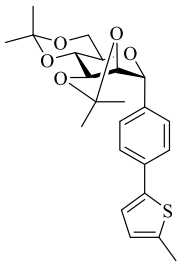
methyl 6-(4-((4R,5aR,9aR,9bR)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-d][1,3]dioxin-4-yl)phenyl)nicotinate (30):



The title compound was prepared from the **General procedure C.** The substrate added in the second step is Methyl 6-bromonicotinate **27** (86.4 mg, 0.4 mmol, 2 equiv). Purification using flash silica gel column chromatography (PE:EA = 9:1) gave the pure product **30** as a colorless oil (41.5 mg, 46% yield with two steps, α only). $[\alpha]_D^{20}$ = +22.1 (c = 1.00, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 9.28 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H),

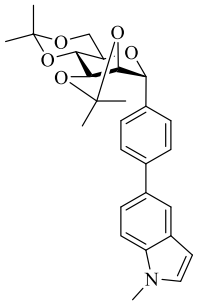
8.08 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 4.90 (d, *J* = 6.8 Hz, 1H, H-1), 4.50 (t, *J* = 6.7 Hz, 1H, H-2), 4.36 (t, *J* = 6.9 Hz, 1H, H-3), 4.24 – 4.18 (m, 1H, H-4), 3.97 (s, 3H), 3.96 – 3.93 (m, 1H, H-6a), 3.79 (t, *J* = 10.5 Hz, 1H, H-6b), 3.60 – 3.52 (m, 1H, H-5), 1.59 (s, 3H), 1.57 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7, 159.2, 149.8, 139.6, 137.0, 128.6, 126.7, 126.6, 126.5, 123.3, 118.9, 108.9, 98.5, 76.2 (C-2), 75.2 (C-3), 74.4 (C-1), 71.5 (C-4), 63.9 (C-5), 61.9 (C-6), 51.4, 51.4, 28.0, 26.6, 24.2, 18.0. HRMS (ESI) calculated for $C_{25}H_{29}NO_7$ $(M+H)^+$ *m/z* 456.2017, found 456.2025.

(4R,5aR,9aR,9bR)-2,2,8,8-tetramethyl-4-(4-(5-methylthiophen-2-yl)phenyl)hexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-d][1,3]dioxine (31):



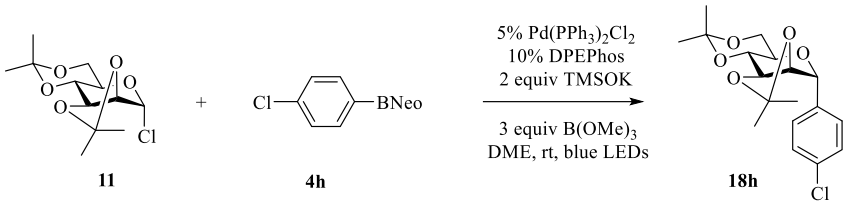
The title compound was prepared from the **General procedure C.** The substrate added in the second step is 2-bromo-5-methylthiophene **28** (70.8 mg, 0.4 mmol, 2 equiv). Purification using flash silica gel column chromatography (PE:EA = 18:1) gave the pure product **31** as a colorless oil (36.5 mg, 44% yield with two steps, α only). $[\alpha]_D^{20}$ = +17.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 3.6 Hz, 1H), 6.79 (d, *J* = 3.5 Hz, 1H), 4.83 (d, *J* = 7.2 Hz, 1H, H-1), 4.54 (t, *J* = 6.9 Hz, 1H, H-2), 4.34 (t, *J* = 6.9 Hz, 1H, H-3), 4.24 (dd, *J* = 10.8, 7.2 Hz, 1H, H-4), 3.84 – 3.72 (m, 2H, H-6), 3.55 – 3.46 (m, 1H, H-5), 2.49 (s, 3H), 1.53 (s, 3H), 1.50 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 141.3, 139.4, 138.6, 134.2, 128.1, 126.5, 124.9, 123.3, 109.1, 98.9, 77.0 (C-2), 76.3 (C-3), 75.2 (C-1), 72.5 (C-4), 65.0 (C-5), 62.7 (C-6), 27.0, 24.6, 18.5, 14.4. HRMS (ESI) calculated for $C_{23}H_{29}O_5S$ $(M+H)^+$ *m/z* 417.1730, found 417.1734.

1-methyl-6-(4-((4R,5aR,9aR,9bR)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-d][1,3]dioxin-4-yl)phenyl)-1H-indole (32):

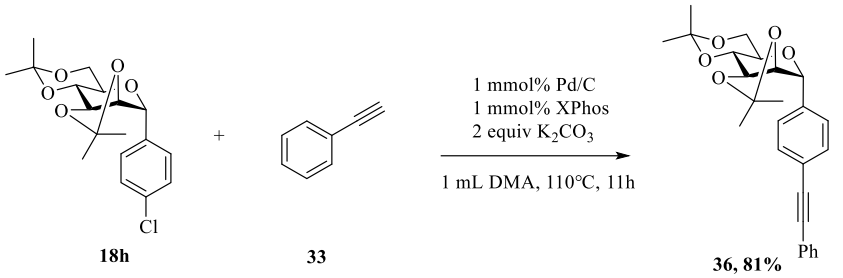


The title compound was prepared from the **General procedure** C. The substrate added in the second step is 2-bromo-5-methylthiophene **29** (84.0 mg, 0.4 mmol, 2 qeuiv). Purification using flash silica gel column chromatography (PE:EA = 18:1) gave the pure product **32** as a colorless oil (35.0 mg, 39% yield with two steps, α only). $[\alpha]_D^{20}$ = +94.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 4H), 7.26 (d, *J* = 3.1 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 4.89 (d, *J* = 6.9 Hz, 1H, H-1), 4.61 (t, *J* = 6.8 Hz, 1H, H-2), 4.36 (t, *J* = 6.9 Hz, 1H, H-3), 4.25 (dd, *J* = 10.7, 7.2 Hz, 1H, H-4), 3.86 (s, 3H), 3.83 – 3.74 (m, 2H, H-6), 3.56 – 3.48 (m, 1H, H-5), 1.54 (s, 3H), 1.51 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 142.2, 137.5, 136.5, 131.9, 129.9, 129.3, 127.9, 126.7, 120.7, 118.8, 109.7, 109.0, 101.0, 98.9, 77.1 (C-2), 76.3 (C-3), 75.4 (C-1), 72.6 (C-4), 64.9 (C-5), 62.7 (C-6), 32.1, 27.1, 24.6, 18.5. HRMS (ESI) calculated for $C_{27}H_{32}NO_5$ $(M+H)^+$ *m/z* 450.2275, found 450.2297.

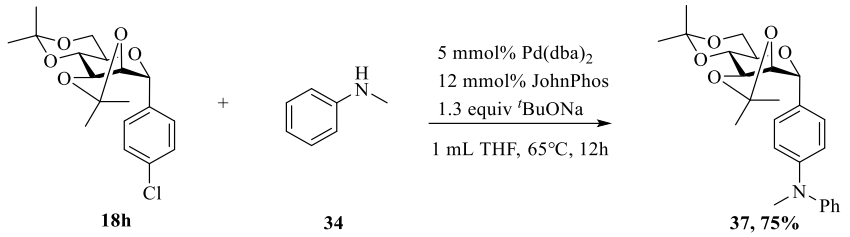
Stepwise synthesis of compounds 33-35



*Gram-scale synthetic compound **19h**:* To a 250 mL Schlenk flask equipped with a stir bar, glycosyl chloride **11** (1.00 g, 3.6 mmol, 1 equiv), phenyl boronic ester **4h** (1.20 g, 5.4 mmol, 1.5 equiv), $Pd(PPh_3)Cl_2$ (126 mg, 5 mmol%) and DPEPhos (194 mg, 10 mmol%) were added with nitrogen. Then TMSOK (7.20 mmol, 2 equiv, 2.00 M in DME) and trimethyl borate (1.20 ml, 3 equiv) were added with syringe under nitrogen respectively. The solvent DME was added to 2 mL to the mixture. The reaction was running in a parallel photoreactor (455 nm, 2×10W) at 20℃ until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product **19h** (917 mg, 72% yield, α only). $[\alpha]_D^{20}$ = +110.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.79 (d, *J* = 7.8 Hz, 1H, H-1), 4.47 (t, *J* = 7.3 Hz, 1H, H-2), 4.34 (t, *J* = 6.9 Hz, 1H, H-3), 4.27 (dd, *J* = 10.8, 7.1 Hz, 1H, H-4), 3.83 (dd, *J* = 10.8, 5.7 Hz, 1H, H-6a), 3.76 (t, *J* = 10.3 Hz, 1H, H-6b), 3.57 – 3.48 (m, 1H, H-5), 1.52 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 140.6, 134.9, 130.9, 130.0, 129.9, 111.0, 100.7, 78.9 (C-2), 78.2 (C-3), 76.5 (C-1), 74.1 (C-4), 66.9 (C-5), 64.5 (C-6), 28.7, 26.2, 20.2. HRMS (ESI) calculated for $C_{18}H_{24}ClO_5$ $(M+H)^+$ *m/z* 355.1307, found 355.1318.

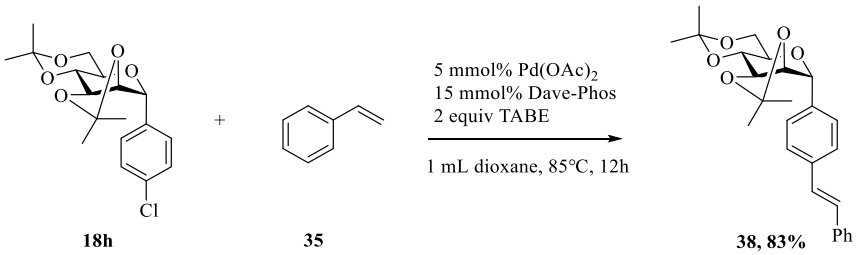


To a 10 mL Schlenk flask equipped with a stir bar, *C*-glycoside **19h** (70.8 mg, 0.2 mmol, 1 equiv), Phenylacetylene **32** (30.6 mg, 0.3mmol, 1.5 equiv), Pd/C (2.0 mg, 1 mmol%), XPhos (1.0 mg, 1 mmol%) and K_2CO_3 (55.3 mg, 0.3 mmol, 2 equiv) were added with nitrogen. The mixture was dissolved in DMA (1 mL). The reaction was running at 110 ℃ in an oil bath for 11 hours until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product **36** (68.0 mg, 81% yield). $[\alpha]_D^{20}$ = +47.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.4 Hz, 4H), 7.39 – 7.32 (m, 5H), 4.84 (d, *J* = 6.8 Hz, 1H, H-1), 4.45 (t, *J* = 6.7 Hz, 1H, H-2), 4.34 (t, *J* = 7.0 Hz, 1H, H-3), 4.18 (dd, *J* = 10.8, 7.2 Hz, 1H, H-4), 3.94 (dd, *J* = 11.0, 5.5 Hz, 1H, H-6a), 3.79 (d, *J* = 10.4 Hz, 1H, H-6b), 3.58 – 3.48 (m, 1H, H-5), 1.58 (s, 3H), 1.56 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.8, 131.8, 131.7, 128.4, 127.2, 126.8, 123.3, 123.2, 109.9, 99.5, 89.8, 89.1, 76.9 (C-2), 76.2 (C-3), 75.5 (C-1), 72.5 (C-4), 64.9 (C-5), 63.0 (C-6), 29.0, 27.6, 25.2, 19.0. HRMS (ESI) calculated for $C_{26}H_{29}O_5$ $(M+H)^+$ *m/z* 421.2010, found 421.2014.



18h **34** **37, 75%**

To a 10 mL Schlenk flask equipped with a stir bar, *C*-glycoside **19h** (70.8 mg, 0.2 mmol, 1 equiv), N-Methylaniline **34** (32.1 mg, 0.3mmol, 1.5 equiv), $Pd(dba)_2$ (9.1 mg, 5 mmol%), JohnPhos (7.1 mg, 12 mmol%) and ^{t}BuONa (29.0 mg, 0.3 mmol, 2 equiv) were added with nitrogen. The mixture was dissolved in THF (1 mL). The reaction was running at 65 °C in an oil bath for 12 hours until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product **37** (63.7 mg, 75% yield). $[\alpha]_D^{20}$ = +3.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.05 – 6.96 (m, 3H), 4.84 (d, *J* = 6.0 Hz, 1H, H-1), 4.52 (t, *J* = 6.3 Hz, 1H, H-2), 4.34 (t, *J* = 6.9 Hz, 1H, H-3), 4.14 (dd, *J* = 10.7, 7.4 Hz, 1H, H-4), 3.89 (dd, *J* = 10.9, 5.4 Hz, 1H, H-6a), 3.76 (t, *J* = 10.6 Hz, 1H, H-6b), 3.54 – 3.46 (m, 1H, H-5), 3.32 (s, 3H), 1.58 (s, 3H), 1.56 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 149.0, 148.9, 131.6, 129.2, 128.5, 121.8, 121.2, 119.1, 108.8, 98.9, 76.9 (C-2), 76.2 (C-3), 75.3 (C-1), 72.7 (C-4), 64.6 (C-5), 62.7 (C-6), 39.6, 28.6, 27.1, 24.7, 18.5. HRMS (ESI) calculated for $C_{25}H_{32}NO_5$ $(M+H)^+$ *m/z* 426.2275, found 426.2286.



18h **35** **38, 83%**

To a 10 mL Schlenk flask equipped with a stir bar, *C*-glycoside **19h** (70.8 mg, 0.2 mmol, 1 equiv), Styrene **35** (31.3 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.0 mg, 5 mmol%), Dave-Phos (9.8 mg, 15 mmol%) and TBAE (100 mg, 0.3 mmol, 2 equiv) were added with nitrogen. The mixture was dissolved in dioxane (1 mL). The reaction was running at 85 °C in an oil bath for 12 hours until the glycosyl chloride was consumed completely monitored by TLC. The reaction mixture was filtered through celite, washed with ethyl acetate and concentrated in vacuo. The rude product was purified by column chromatography to give the corresponding product **38** (70.0 mg, 83% yield). $[\alpha]_D^{20}$ = +73.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.6 Hz, 4H), 7.36 (d, *J* = 8.2 Hz, 4H), 7.29 – 7.23 (m, 1H), 7.10 (s, 2H), 4.86 (d, *J* = 6.4 Hz, 1H, H-1), 4.50 (t, *J* = 6.5 Hz, 1H, H-2), 4.34 (t, *J* = 6.9 Hz, 1H, H-3), 4.17 (dd, *J* = 10.8, 7.3 Hz, 1H, H-4), 3.93 (dd, *J* = 11.0, 5.5 Hz, 1H, H-6a), 3.77 (t, *J* = 10.5 Hz, 1H, H-6b), 3.57 – 3.48 (m, 1H, H-5), 1.59 (s, 3H), 1.56 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.9, 137.5, 137.2, 129.2, 128.7, 128.1, 127.8, 127.6, 126.7, 126.6, 109.8, 99.5, 76.9 (C-2), 76.2 (C-3), 75.6 (C-1), 72.6 (C-4), 64.8 (C-5), 63.0 (C-6), 29.1, 27.7, 25.3, 19.0. HRMS (ESI) calculated for $C_{26}H_{31}O_5$ $(M+H)^+$ *m/z* 423.2166, found 423.2171.

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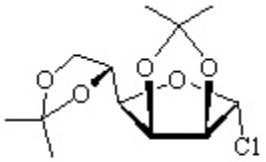
2. (a) Wen, P.; Simmons, C. J.; Ma, Z.-x.; Blaszczyk, S. A.; Balzer, P. G.; Ye, W.; Duan, X.; Wang, H.-Y.; Yin, D.; Stevens, C. M.; Tang, W., Synthesis of glycosyl chlorides and bromides by chelation assisted activation of picolinic esters under mild neutral conditions. *Org. Lett*, **2020,** 22, 1495-1498; (b) Wang, Q.; Sun, Q.; Jiang, Y.; Zhang, H.; Yu, L.; Tian, C.; Chen, G.; Koh, M. J., Iron-catalysed reductive cross-coupling of glycosyl radicals for the stereoselective synthesis of *C*-glycosides. *Nat. Syn*, **2022,** 1, 235-244; (c) Wang, Q.; An, S.; Deng, Z.; Zhu, W.; Huang, Z.; He, G.; Chen, G., Palladium-catalysed C−H glycosylation for synthesis of *C*-aryl glycosides. *Nat. Cat*, **2019,** 2, 793-800.

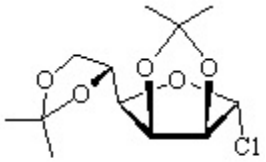
3. Wang, Q.; Lee, B. C.; Song, N.; Koh, M. J., Stereoselective *C*-aryl glycosylation by catalytic cross-coupling of heteroaryl glycosyl sulfones. *Angew. Chem. Int. Ed*, **2023,** 62, e202301081.

4. Li, Y.; Wang, Z.; Li, L.; Tian, X.; Shao, F.; Li, C., Chemoselective and diastereoselective synthesis of *C*-aryl nucleoside analogues by nickel-catalyzed cross-coupling of furanosyl acetates with aryl iodides. *Angew. Chem. Int. Ed*, **2022,** 61, e202110391.



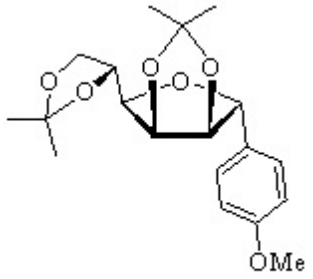
1a

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



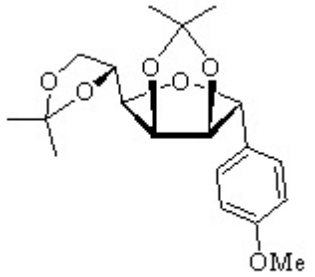
1a

^{13}C NMR (100 MHz, $CDCl_3$)



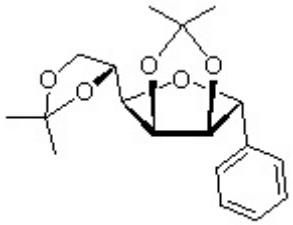
5a

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



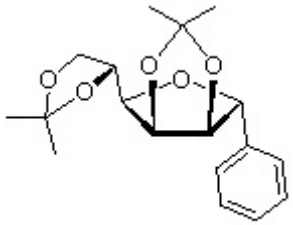
5a

^{13}C NMR (100 MHz, $CDCl_3$)



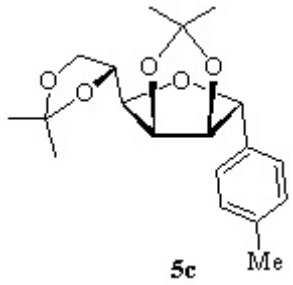
5b

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



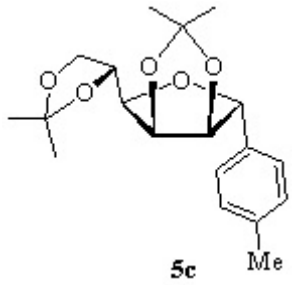
5b

^{13}C NMR (100 MHz, $CDCl_3$)



5c

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



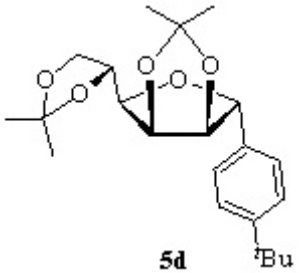
5c

^{13}C NMR (100 MHz, $CDCl_3$)

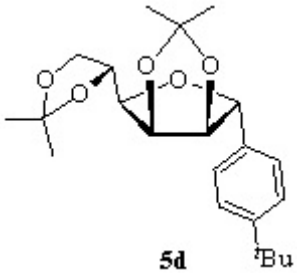
137.32
135.46
129.48
125.59
112.93
109.35
87.55
85.04
81.41
81.27
73.66
67.20
27.04
26.34
25.35
24.93
21.17

f1 (ppm)

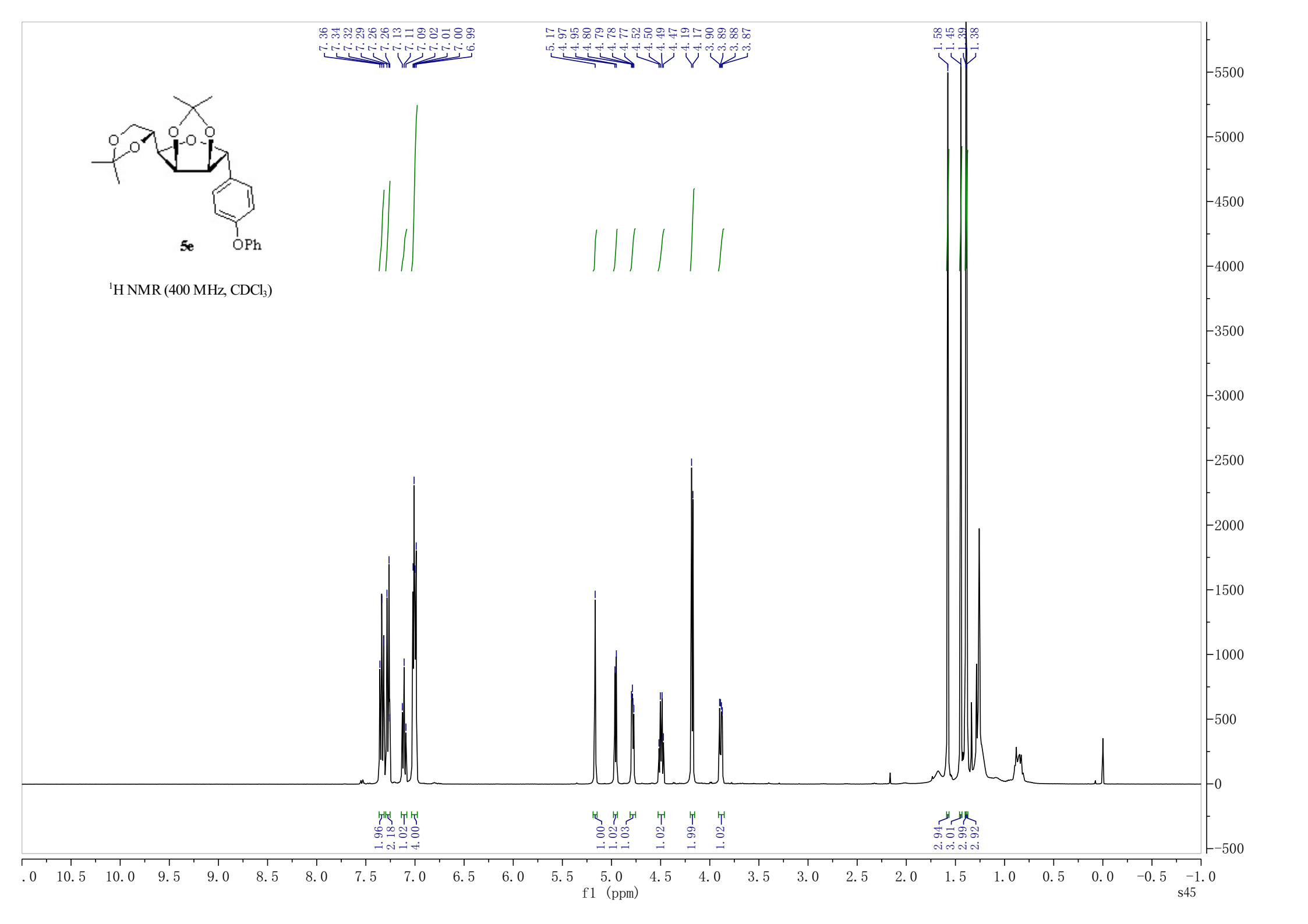
s42

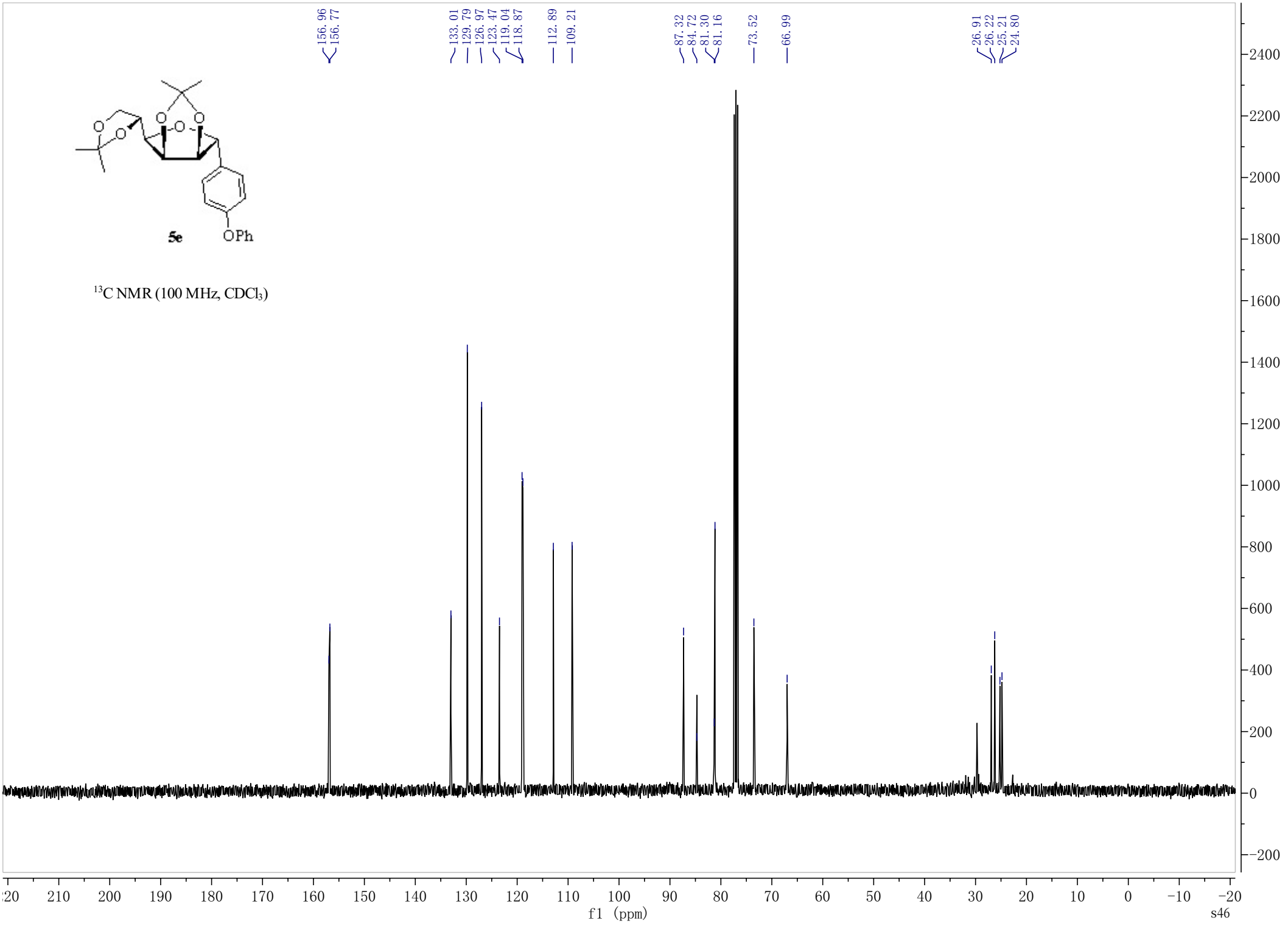


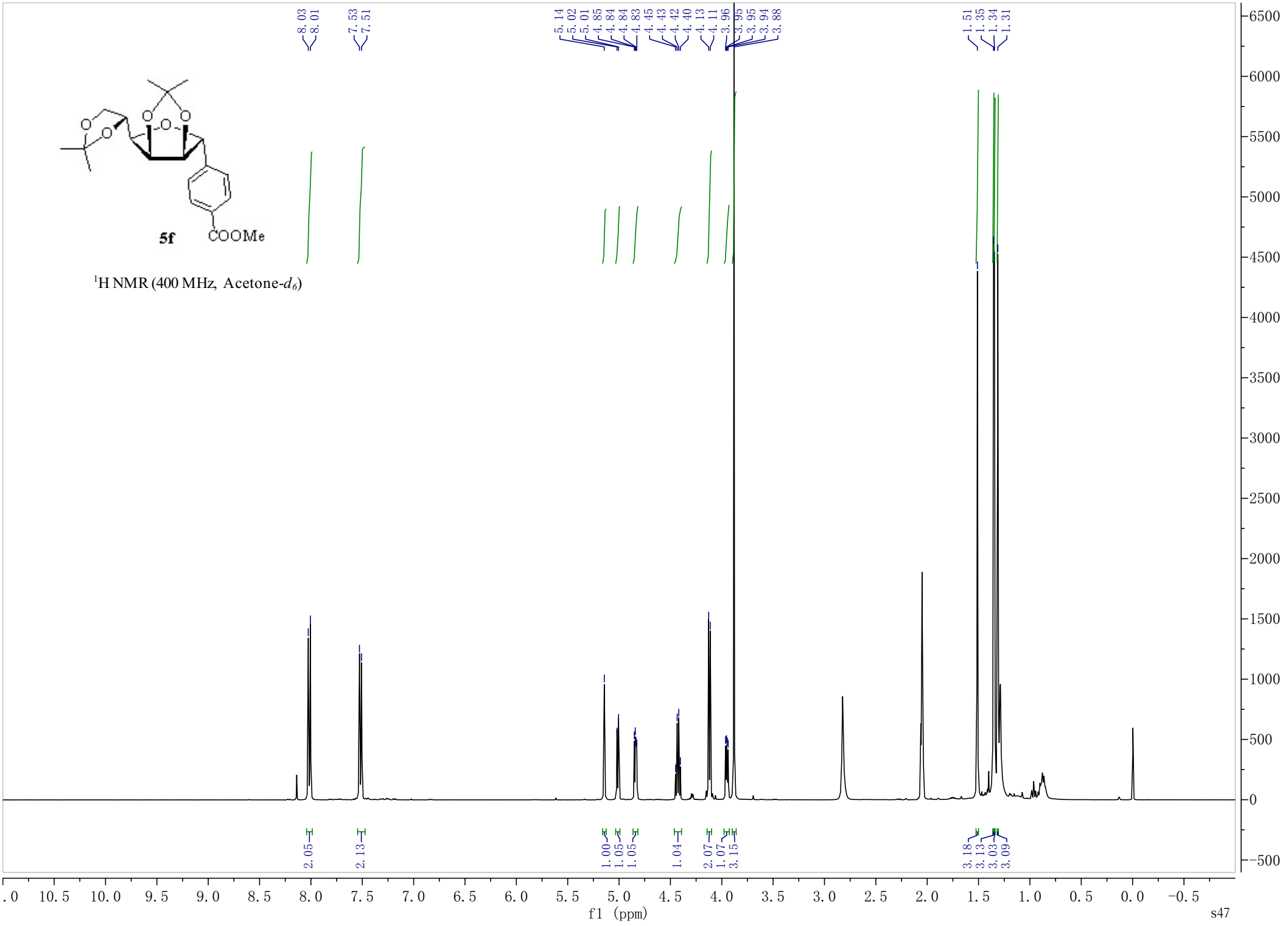
^{1}H NMR (400 MHz, $CDCl_3$)



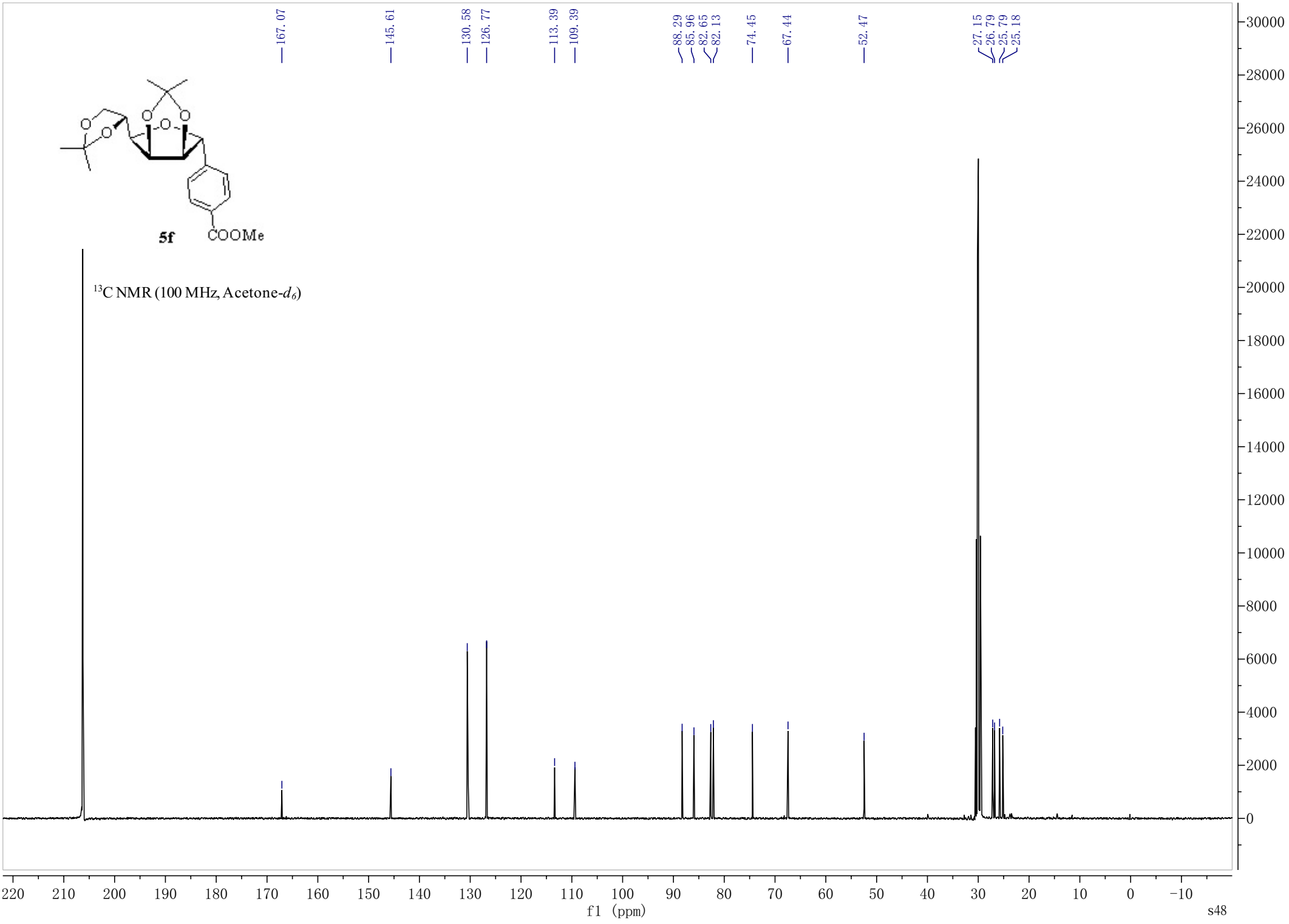
^{13}C NMR (100 MHz, $CDCl_3$)

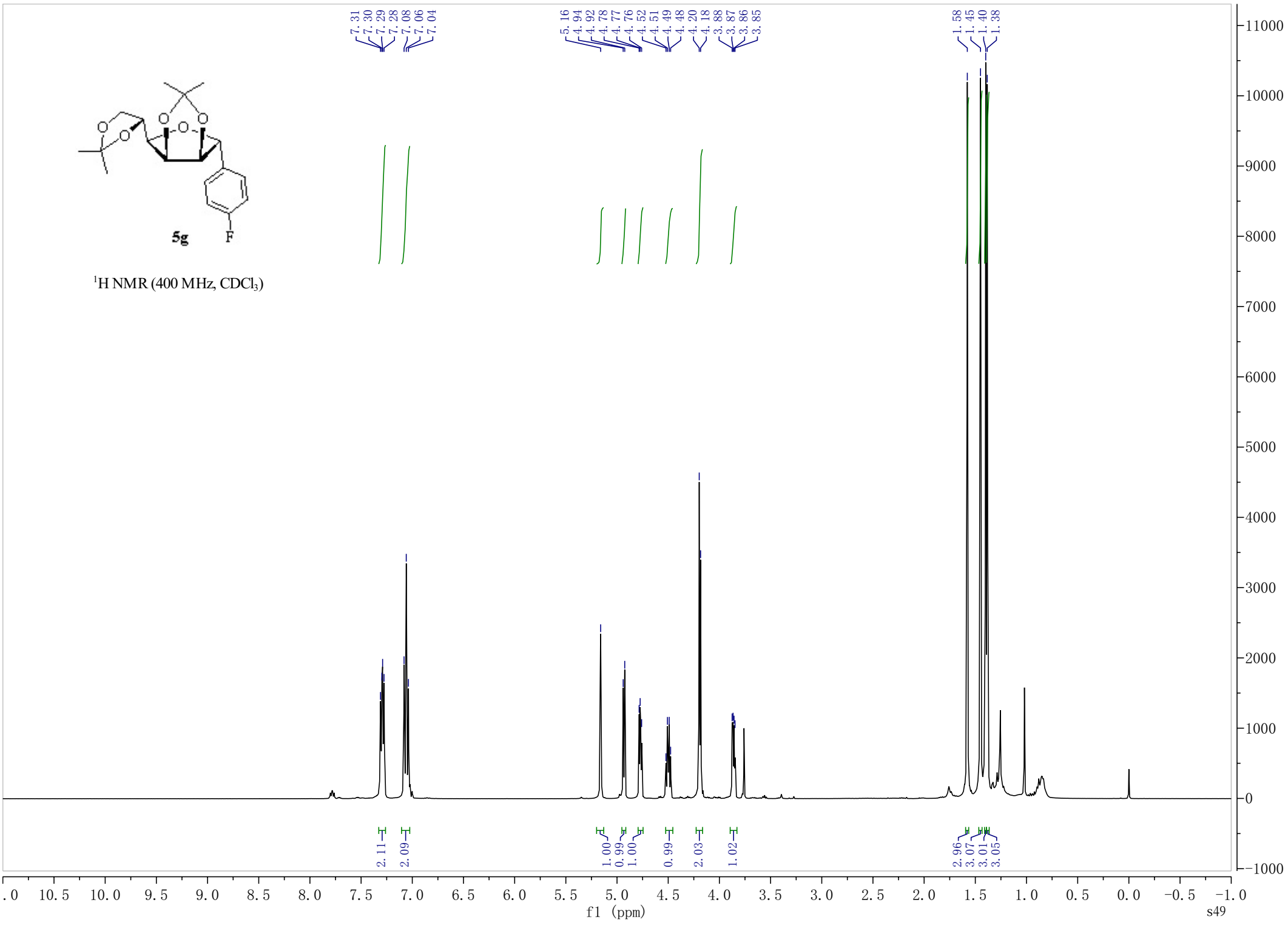

7.36
7.34
7.32
7.29
7.26
7.26
7.13
7.11
7.09
7.02
7.01
7.00
6.99
5.17
4.97
4.95
4.80
4.79
4.78
4.77
4.52
4.50
4.49
4.47
4.19
4.17
3.90
3.89
3.88
3.87
1.58
1.45
1.39
1.38
5e
OPh
1H NMR (400 MHz, CDCl3)
1.96
2.18
1.02
4.00
1.00
1.02
1.03
1.02
1.99
1.02
2.94
3.01
2.99
2.92
f1 (ppm)
s45

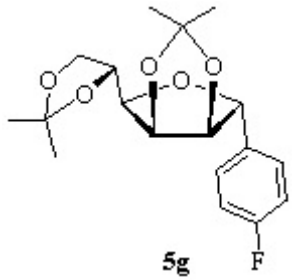

156.96
156.77
133.01
129.79
126.97
123.47
119.04
118.87
112.89
109.21
87.32
84.72
81.30
81.16
73.52
66.99
26.91
26.22
25.21
24.80
5e
OPh
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)
s46



^{1}H NMR (400 MHz, Acetone-d_6)

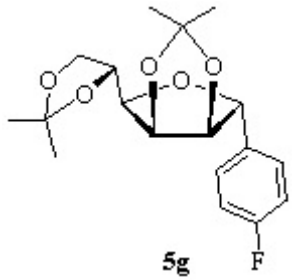

167.07
145.61
130.58
126.77
113.39
109.39
88.29
85.96
82.65
82.13
74.45
67.44
52.47
27.15
26.79
25.79
25.18
5f
COOMe
13C NMR (100 MHz, Acetone-d6)
f1 (ppm)
s48


7.31
7.30
7.29
7.28
7.08
7.06
7.04
5.16
4.94
4.92
4.78
4.77
4.76
4.52
4.51
4.49
4.48
4.20
4.18
3.88
3.87
3.86
3.85
1.58
1.45
1.40
1.38
5g
F
1H NMR (400 MHz, CDCl3)
2.11
2.09
1.00
0.99
1.00
0.99
2.03
1.02
2.96
3.07
3.01
3.05
f1 (ppm)
s49



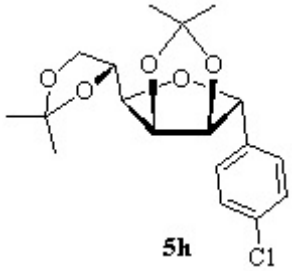
5g

^{13}C NMR (100 MHz, $CDCl_3$)

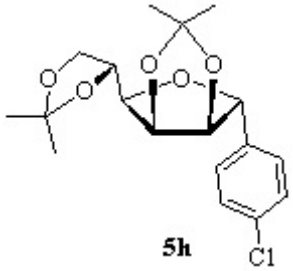


5g

^{1}F NMR (375 MHz, $CDCl_3$)



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

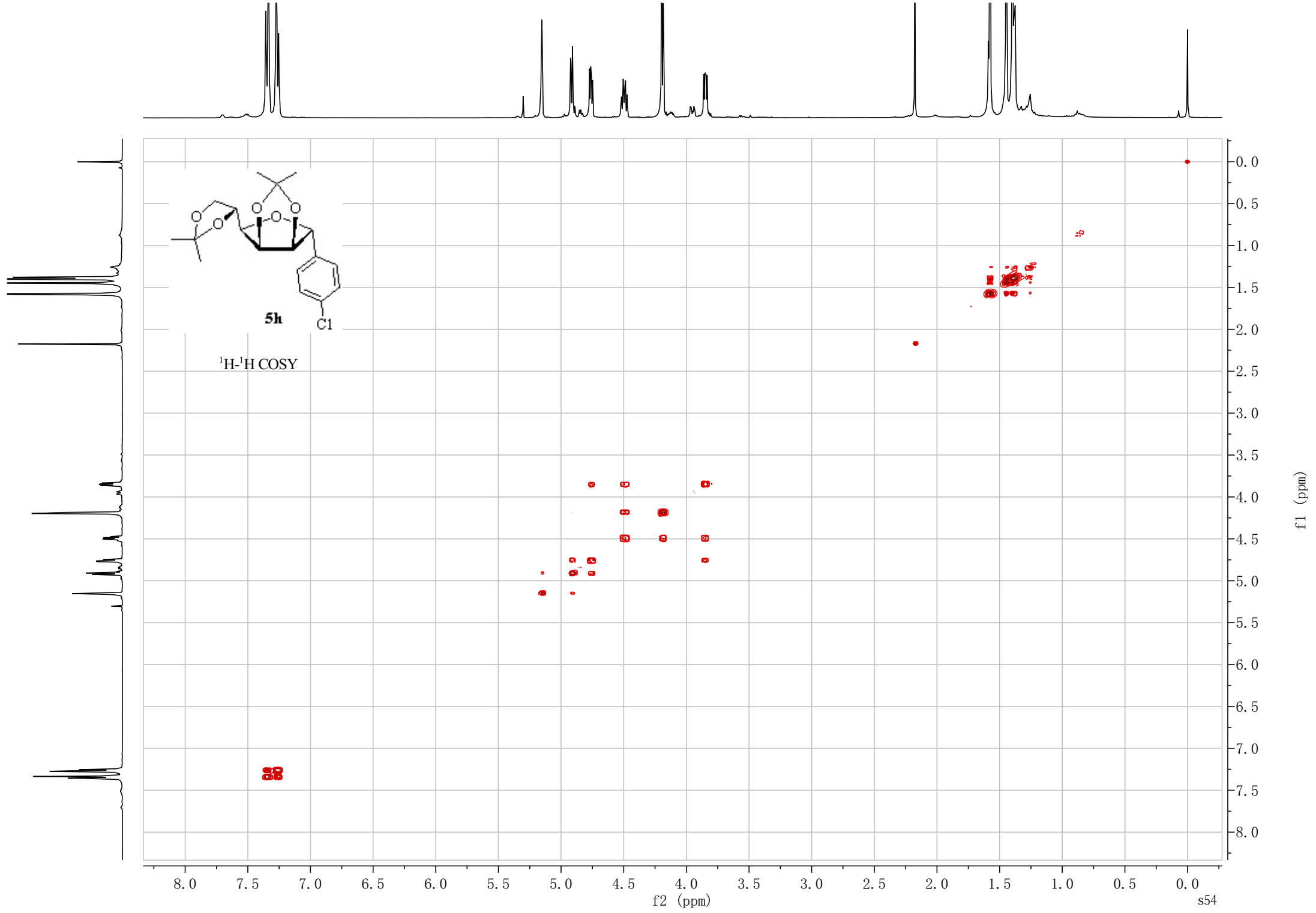


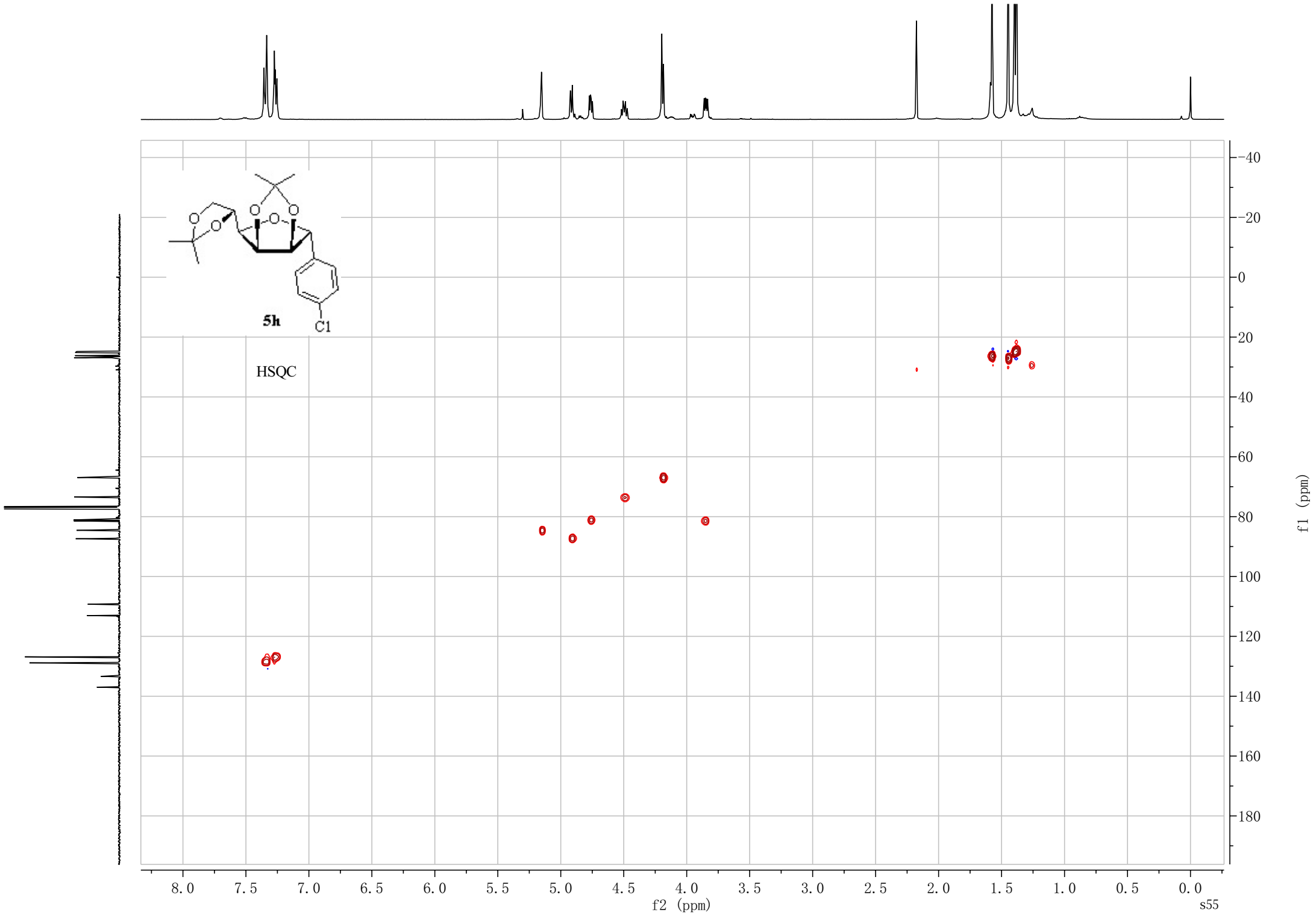
^{13}C NMR (100 MHz, $CDCl_3$)

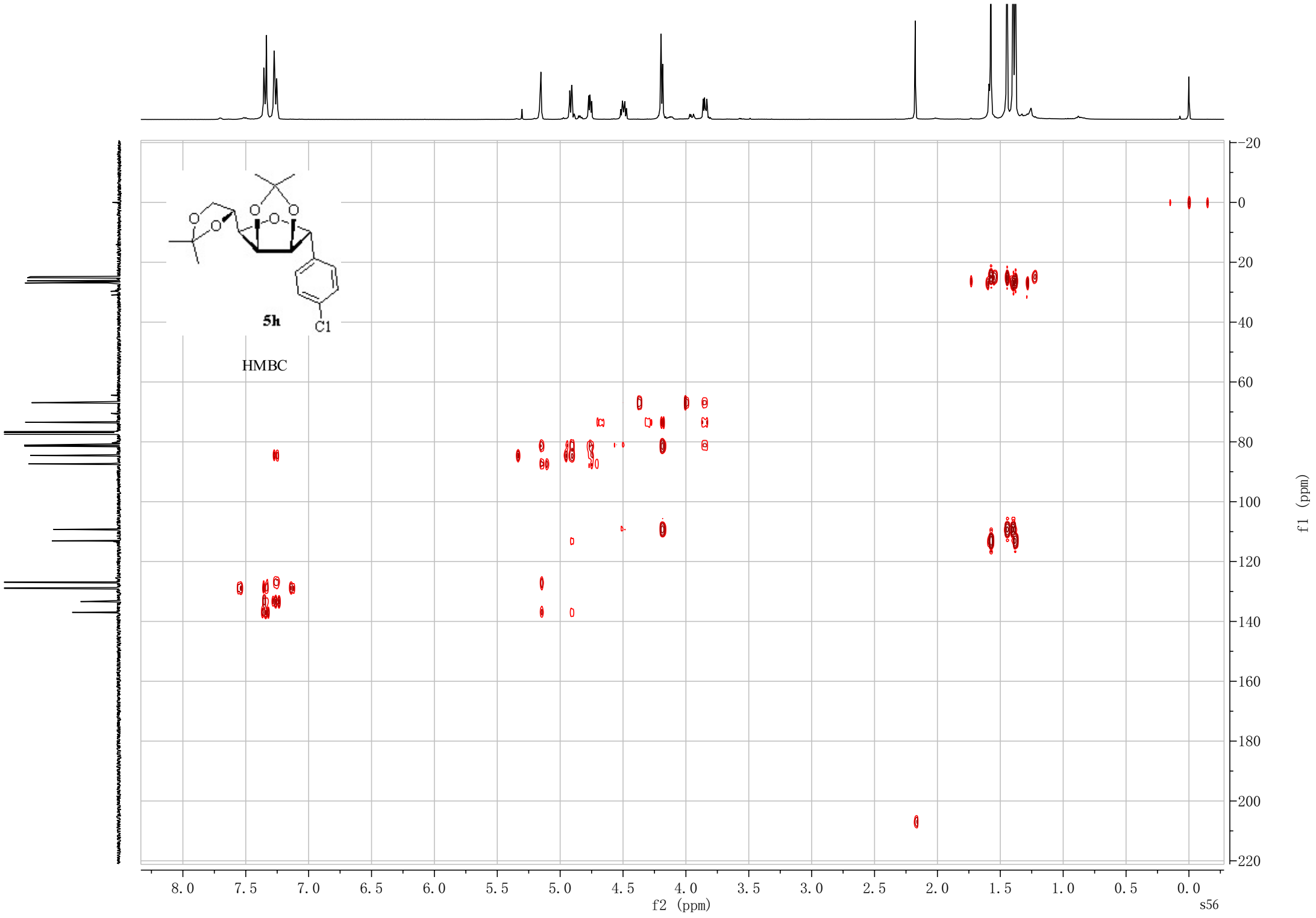
136.97
133.36
128.86
126.86
113.06
109.26
87.39
84.58
81.42
81.08
73.46
66.92
26.91
26.22
25.18
24.80

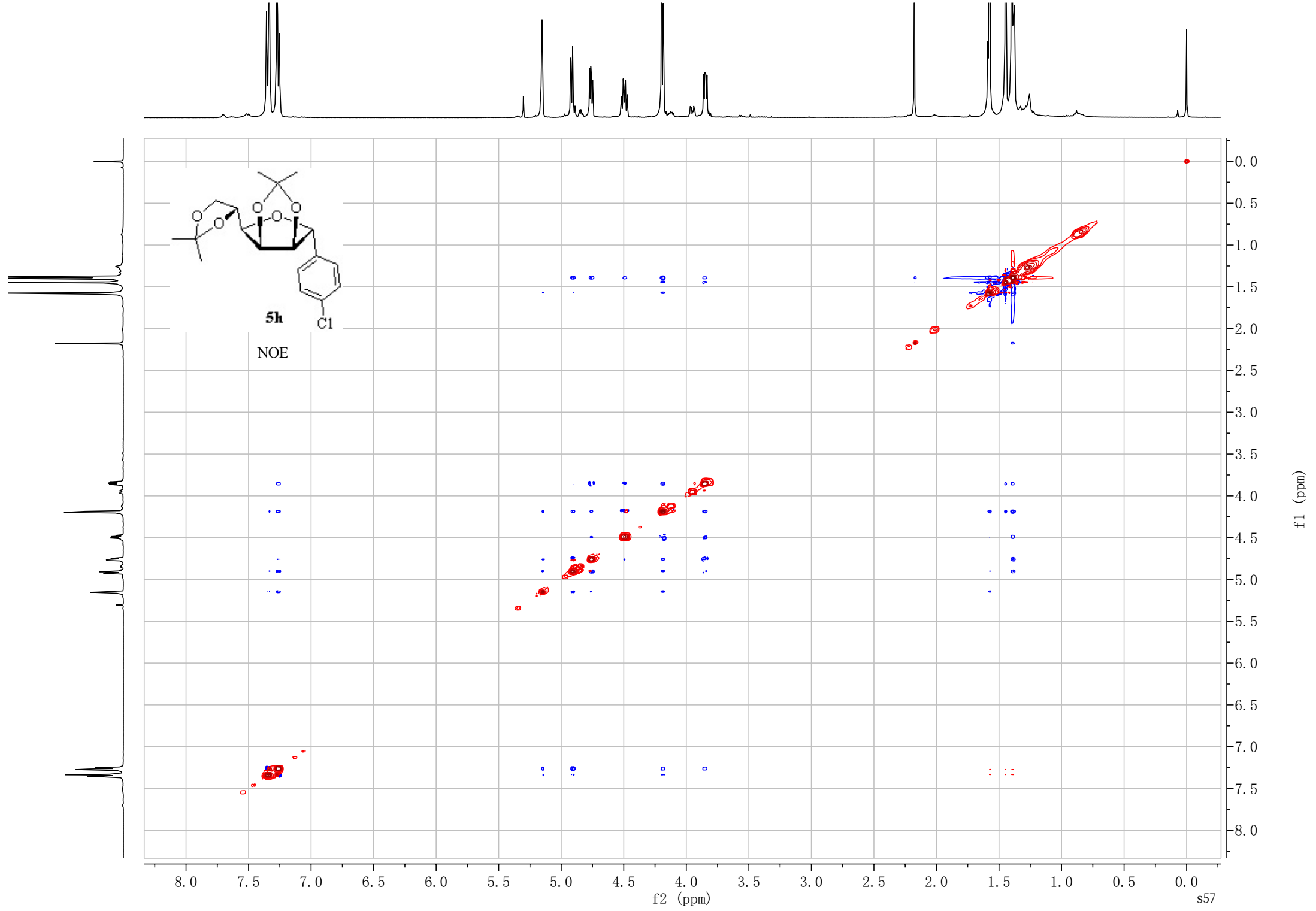
f1 (ppm)

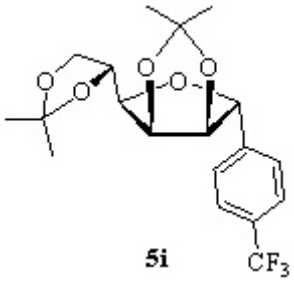
s53


5h
C1
^{1}H-^{1}H COSY
f2 (ppm)
f1 (ppm)
s54

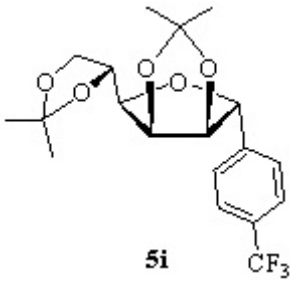

5h
C1
HSQC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-40
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
s55


5h
C1
HMBC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
s56


5h
C1
NOE
f2 (ppm)
f1 (ppm)
s57



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

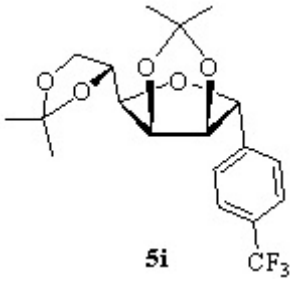


^{13}C NMR (100 MHz, $CDCl_3$)

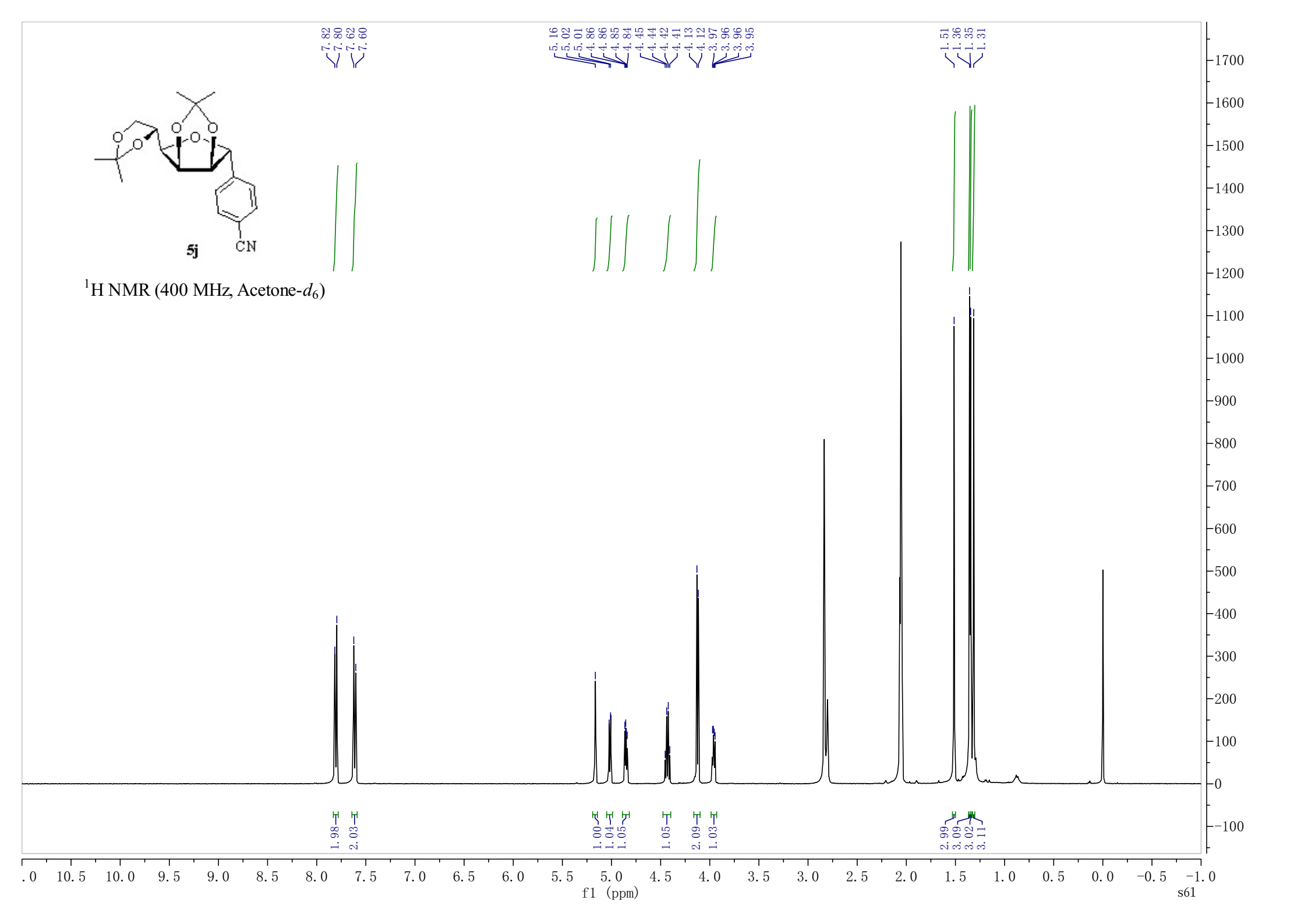
142.63
129.84
125.74
125.70
125.66
113.20
109.30
87.50
84.73
81.58
81.04
73.43
66.89
26.91
26.23
25.15
24.79

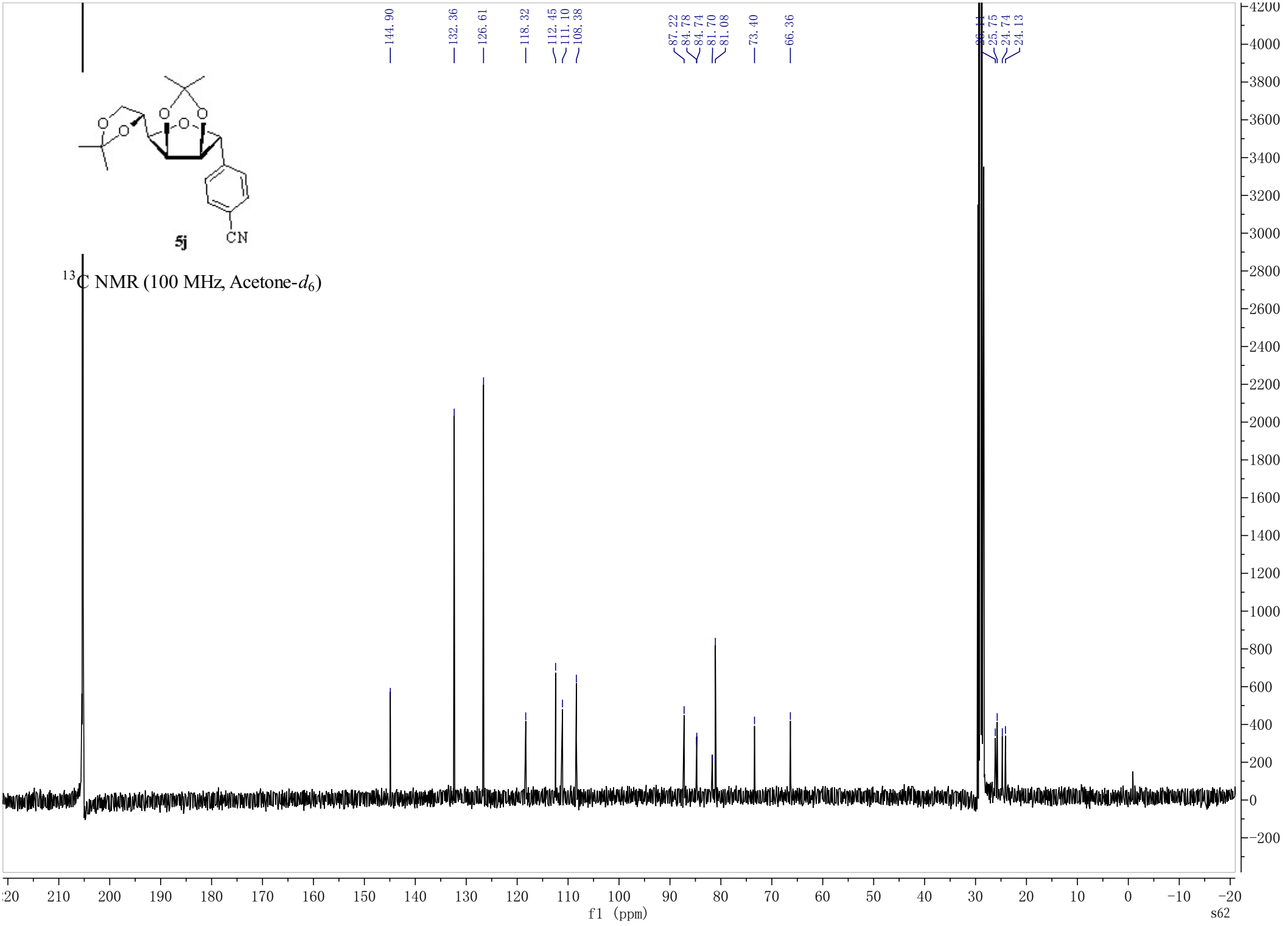
f1 (ppm)

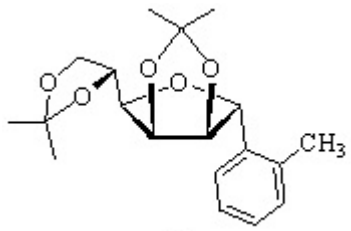
s59



^{19}F NMR (375 MHz, $CDCl_3$)

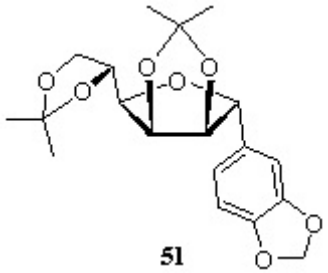

7.82
7.80
7.62
7.60
5.16
5.02
5.01
4.86
4.85
4.84
4.45
4.44
4.42
4.41
4.13
4.12
3.97
3.96
3.96
3.95
1.51
1.36
1.35
1.31
5j
CN
1H NMR (400 MHz, Acetone-d6)
1.98
2.03
1.00
1.04
1.05
1.05
2.09
1.03
2.99
3.09
3.02
3.11
f1 (ppm)
s61


144.90
132.36
126.61
118.32
112.45
111.10
108.38
87.22
84.78
84.74
81.70
81.08
73.40
66.36
26.11
25.75
24.74
24.13
5j
CN
13C NMR (100 MHz, Acetone-d6)
f1 (ppm)
s62



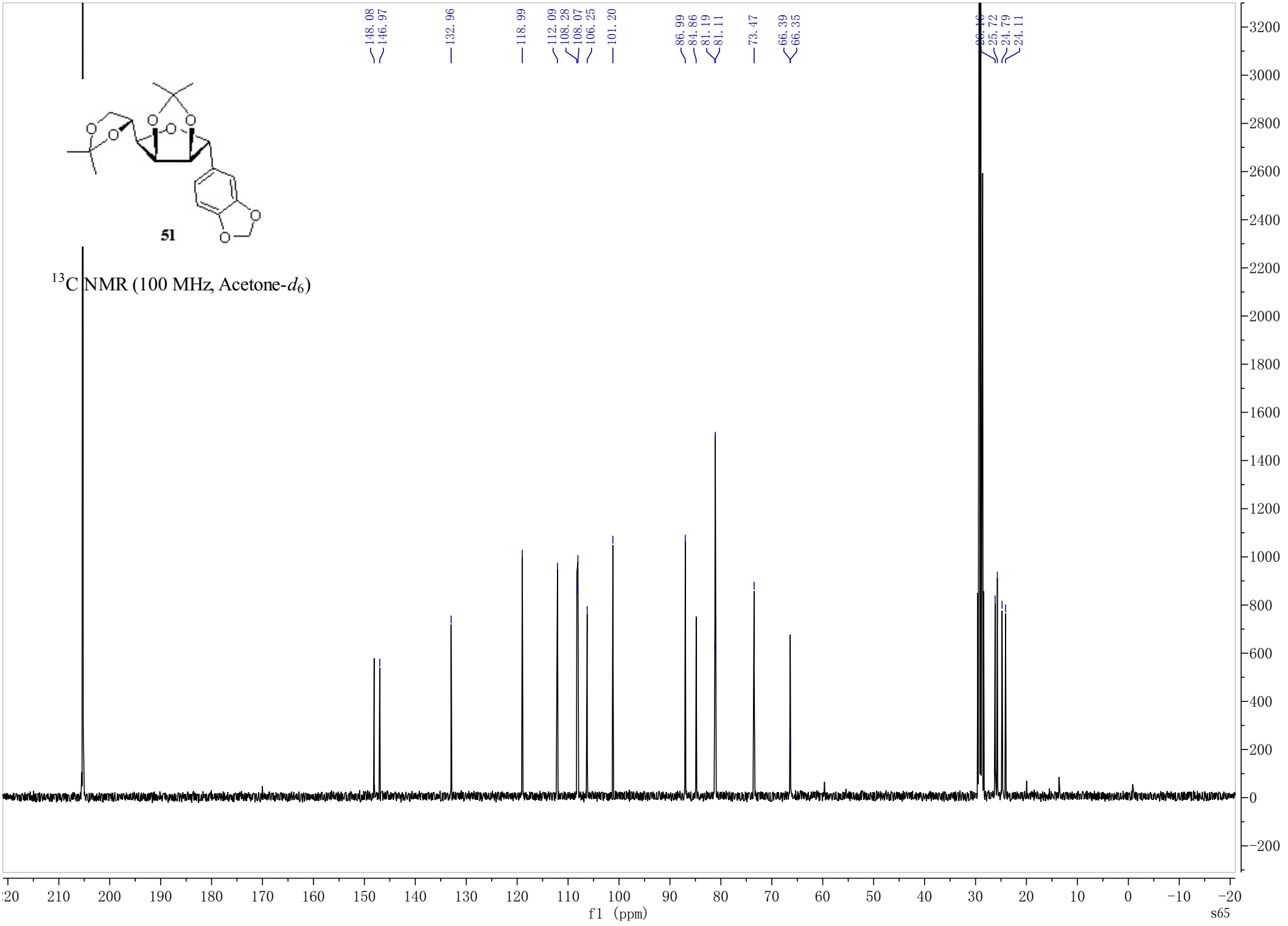
5k

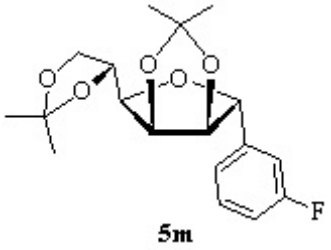
^{1}H NMR (400 MHz, $CDCl_3$)



51

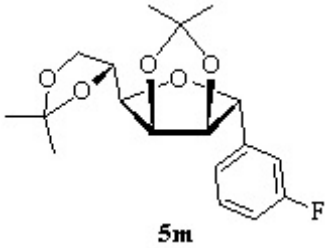
^{1}H NMR (400 MHz, $CDCl_3$)


148.08
146.97
132.96
118.99
112.09
108.28
108.07
106.25
101.20
86.99
84.86
81.19
81.11
73.47
66.39
66.35
26.16
25.72
24.79
24.11
51
^{13}C NMR (100 MHz, Acetone-d_6)
f1 (ppm)
s65



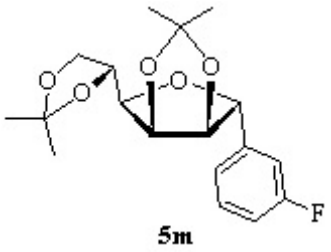
5m

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



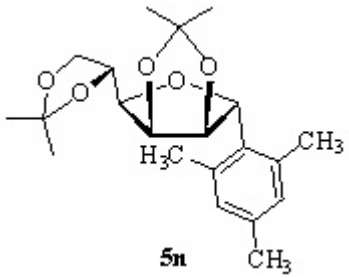
5m

^{13}C NMR (100 MHz, $CDCl_3$)



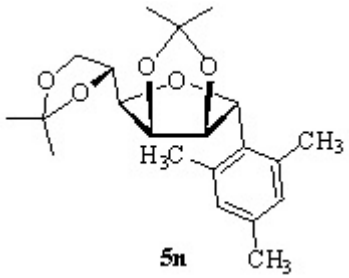
5m

^{19}F NMR (375 MHz, $CDCl_3$)



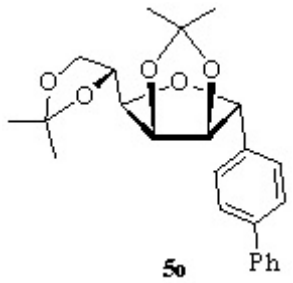
5n

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



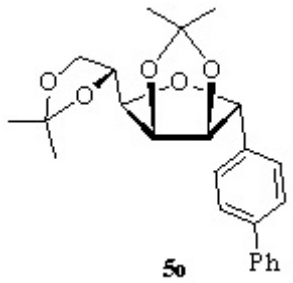
5n

^{13}C NMR (100 MHz, $CDCl_3$)



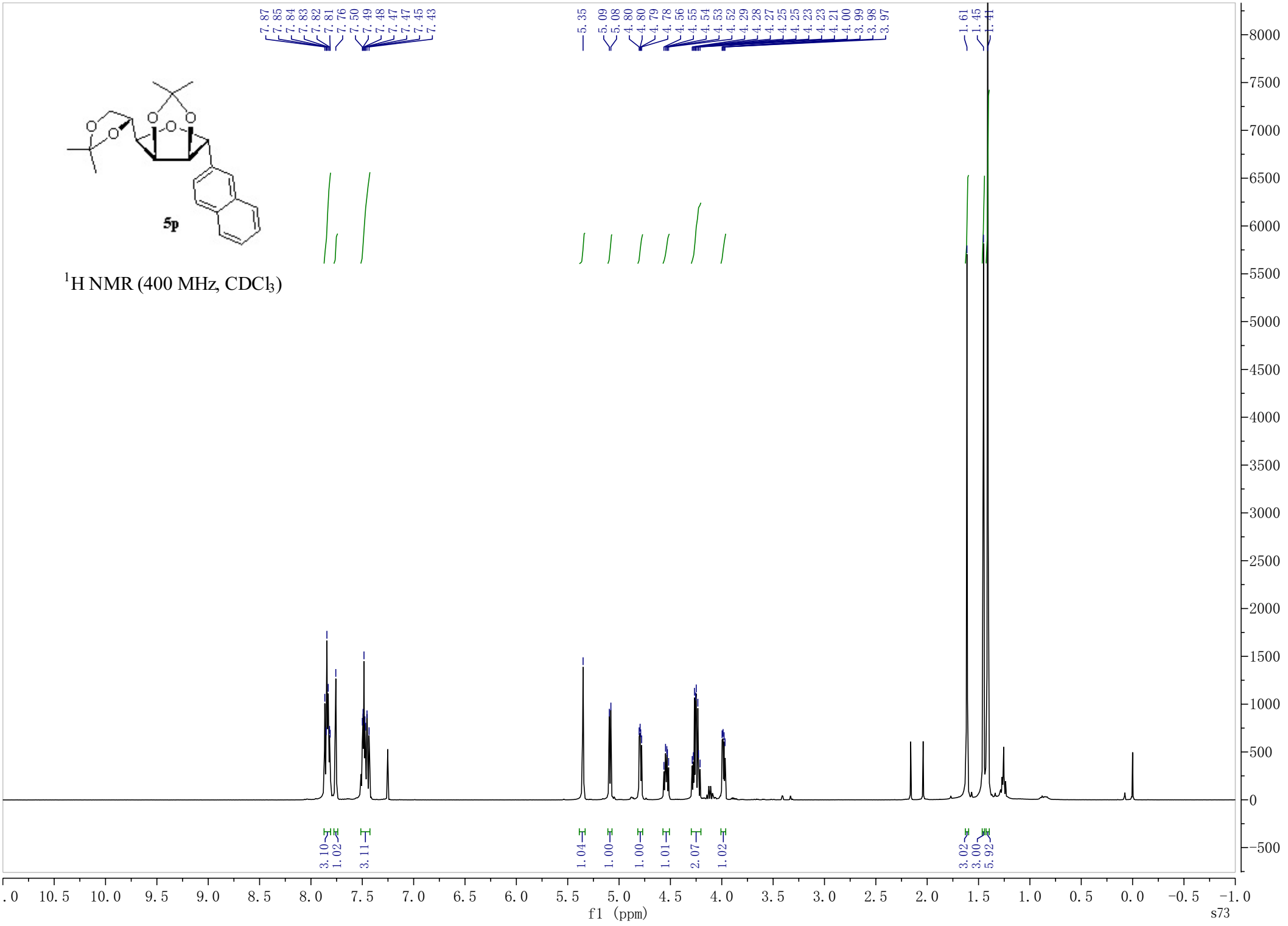
5o

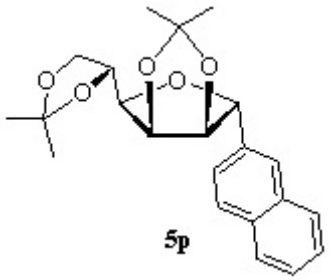
^{1}H NMR (400 MHz, $CDCl_3$)



5o

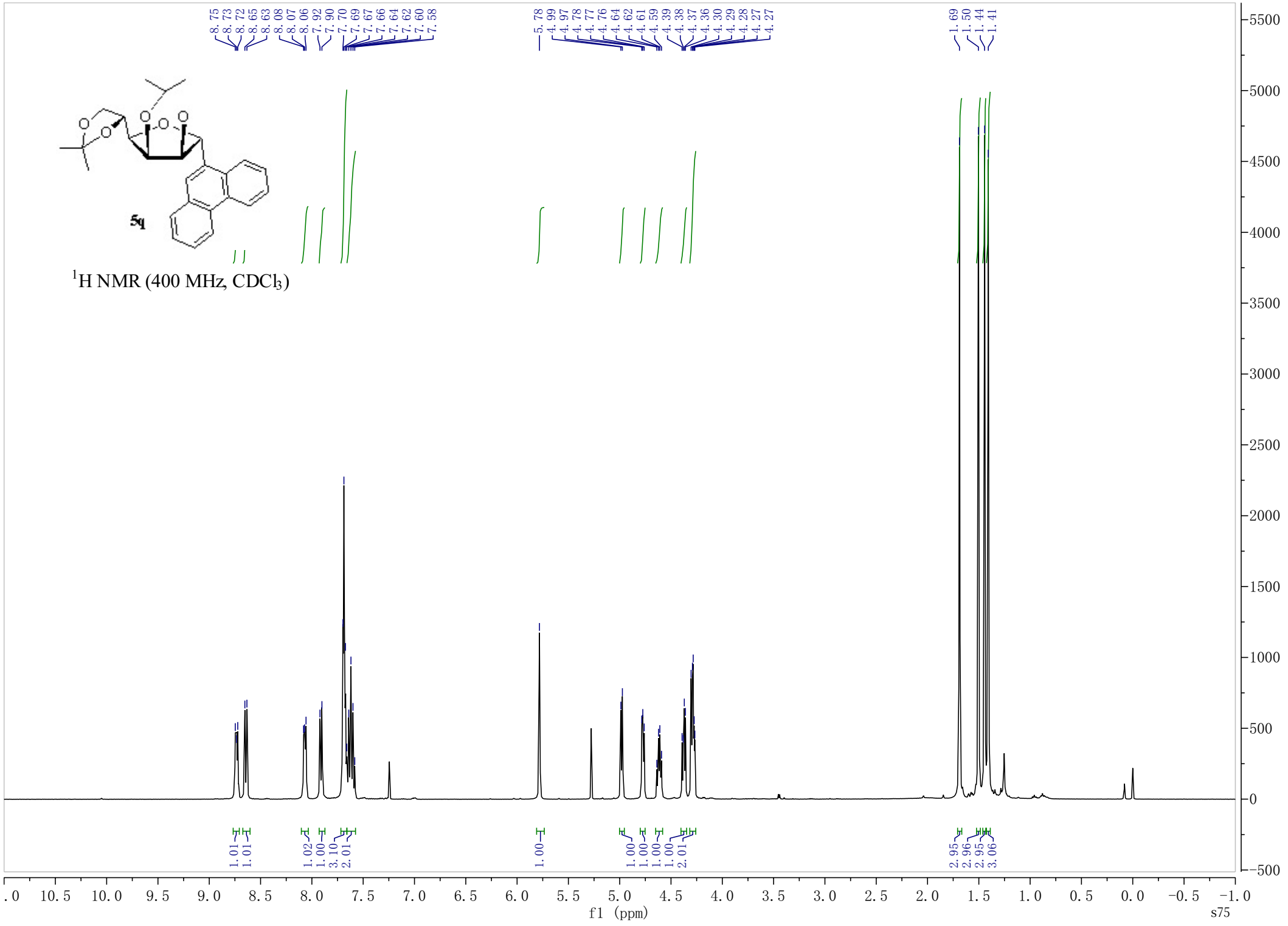
^{13}C NMR (100 MHz, $CDCl_3$)

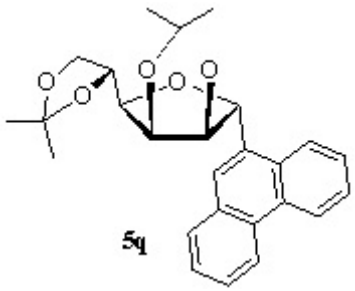

7.87
7.85
7.84
7.83
7.82
7.81
7.76
7.50
7.49
7.48
7.47
7.47
7.45
7.43
5.35
5.09
5.08
4.80
4.80
4.79
4.78
4.56
4.55
4.54
4.53
4.52
4.29
4.28
4.27
4.25
4.25
4.23
4.23
4.21
4.00
3.99
3.98
3.97
1.61
1.45
1.41
5p
[1]H NMR (400 MHz, CDCl3)
3.10
1.02
3.11
1.04
1.00
1.00
1.01
2.07
1.02
3.02
3.00
5.92
f1 (ppm)
s73



5p

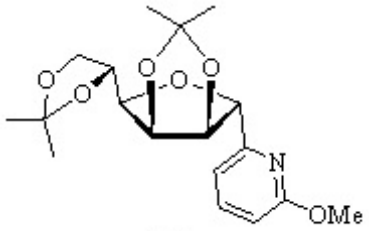
^{13}C NMR (100 MHz, $CDCl_3$)


8.75
8.73
8.72
8.65
8.63
8.08
8.07
8.06
7.92
7.90
7.70
7.69
7.67
7.66
7.64
7.62
7.60
7.58
5.78
4.99
4.97
4.78
4.77
4.76
4.64
4.62
4.61
4.59
4.39
4.38
4.37
4.36
4.30
4.29
4.28
4.27
4.27
1.69
1.50
1.44
1.41
5q
1H NMR (400 MHz, CDCl3)
1.01
1.01
1.02
1.00
3.10
2.01
1.00
1.00
1.00
1.00
2.01
2.95
2.96
2.95
3.06
f1 (ppm)
s75



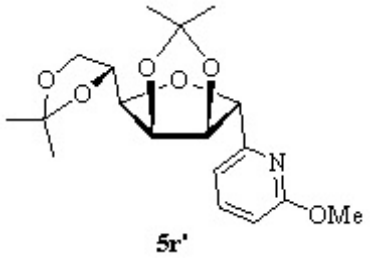
5q

^{13}C NMR (100 MHz, $CDCl_3$)



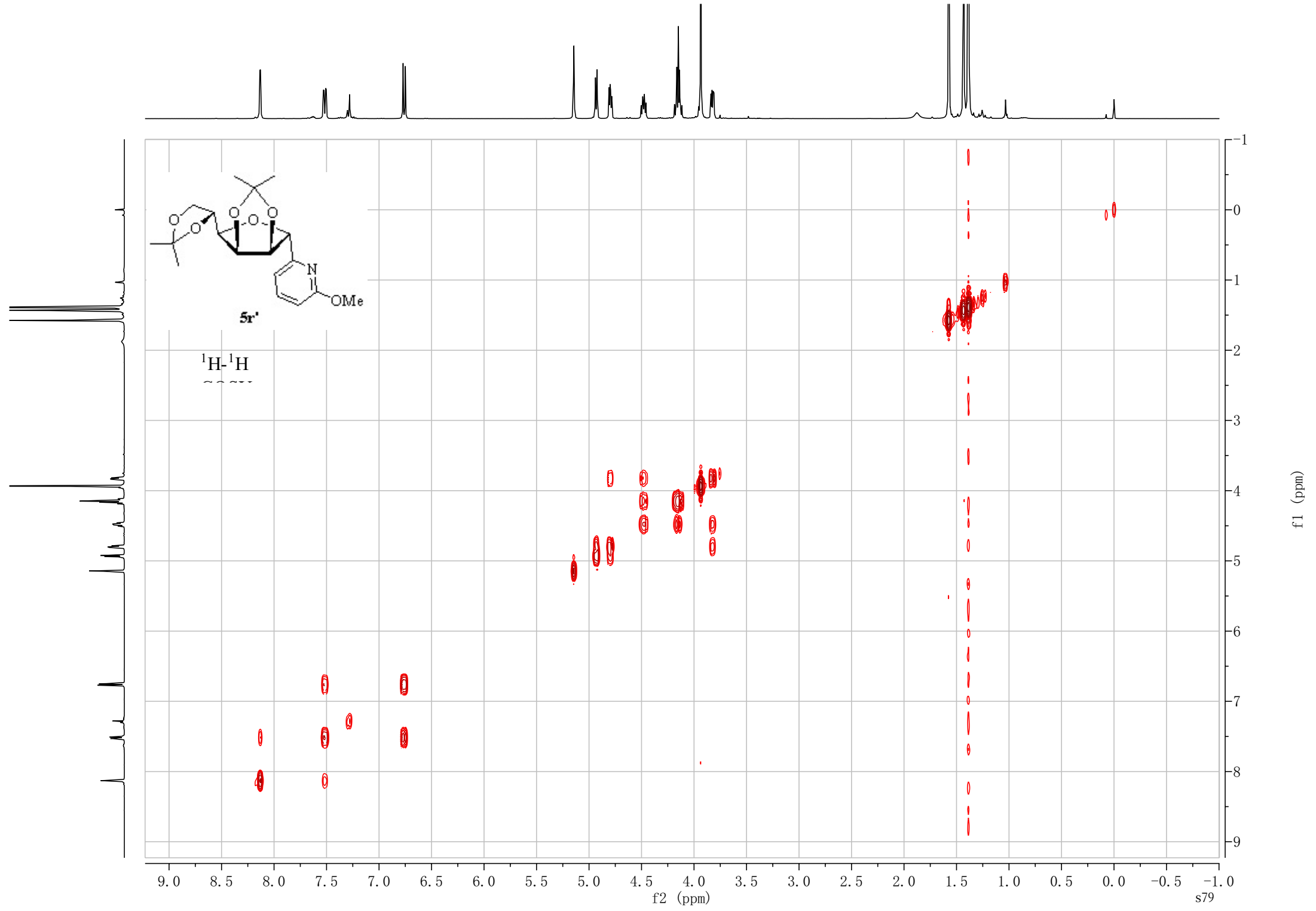
5r'

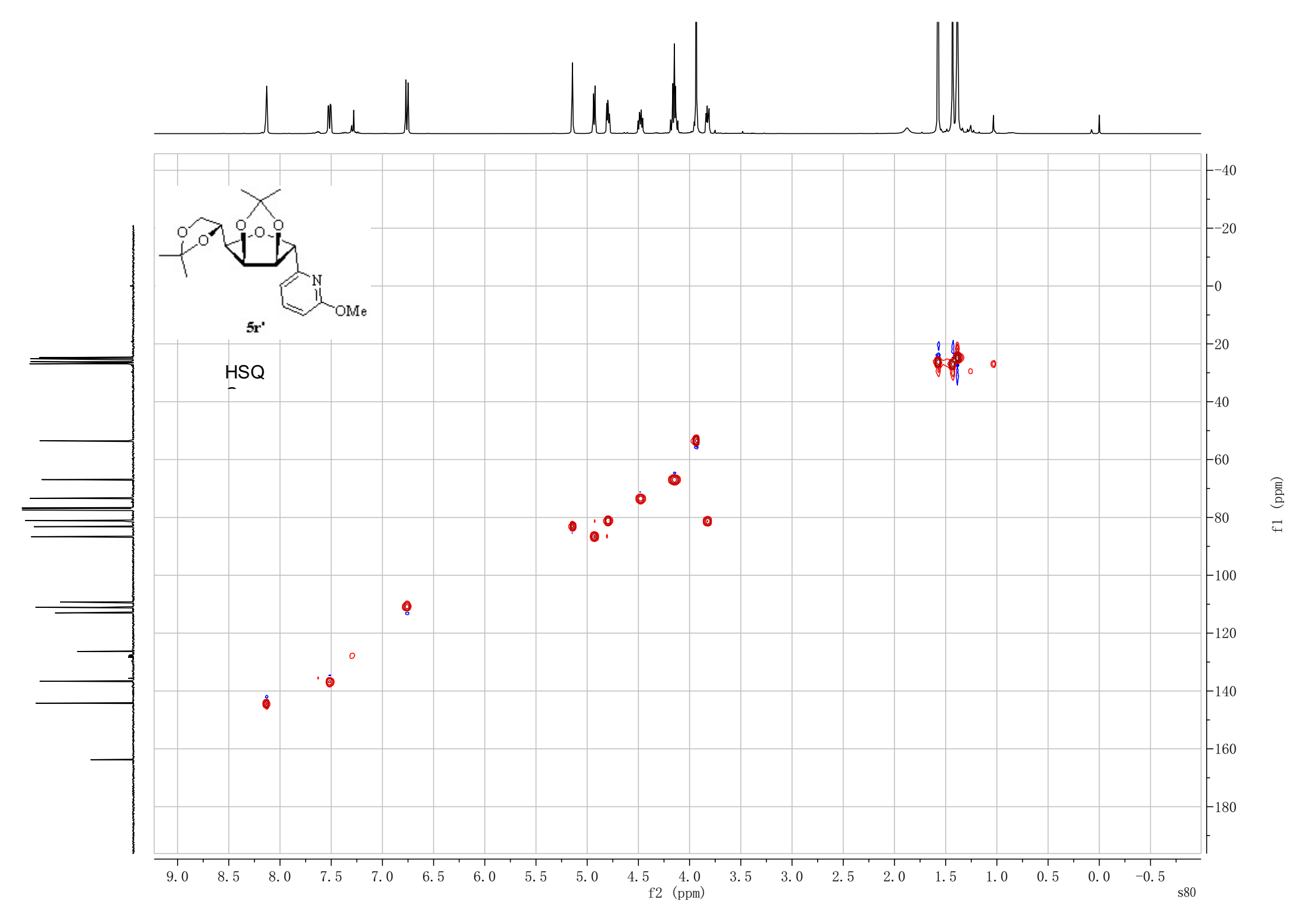
^{1}H NMR (400 MHz, $CDCl_3$)

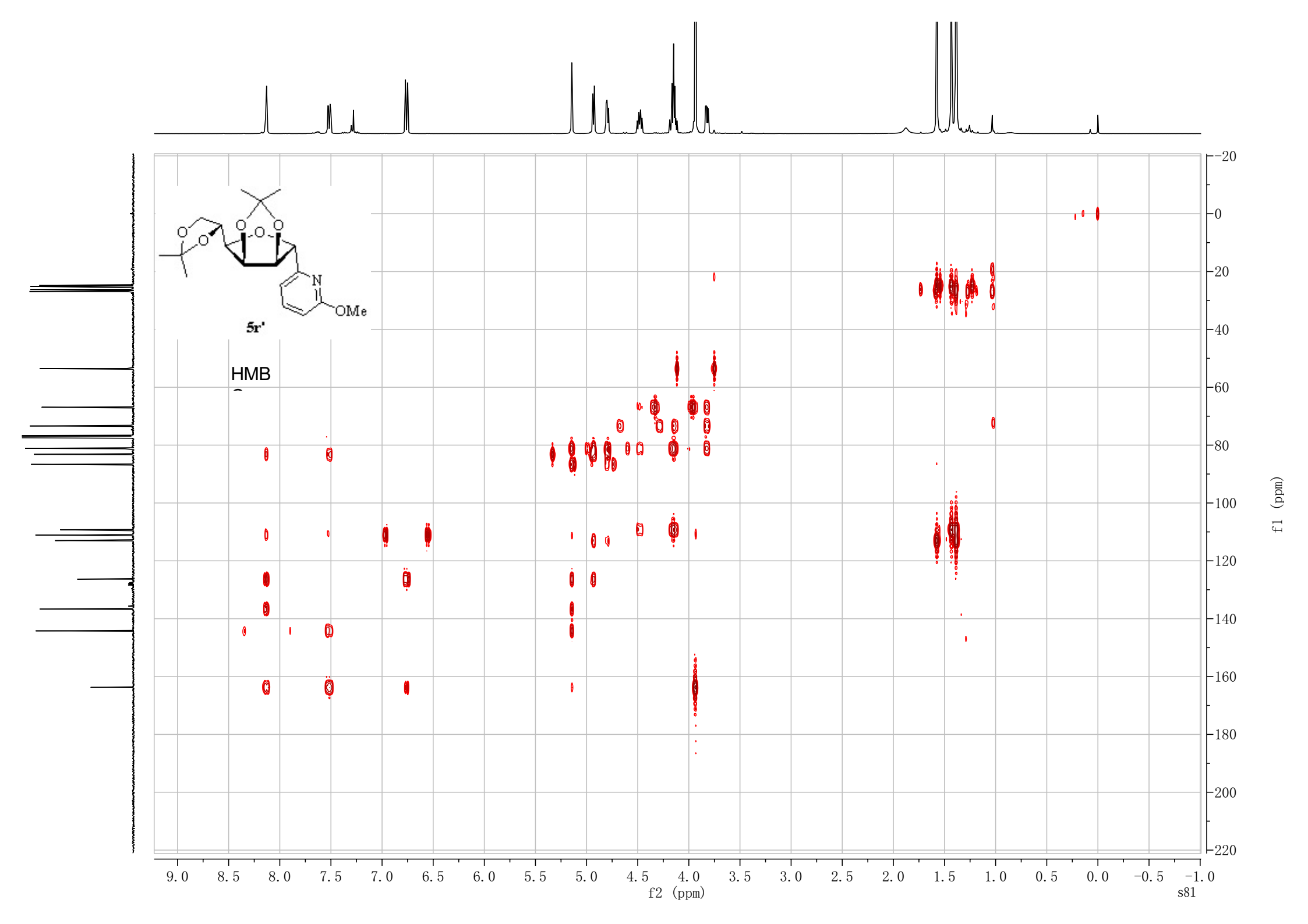


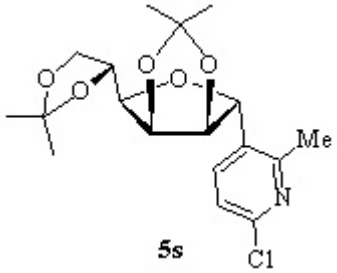
5r'

^{13}C NMR (100 MHz, $CDCl_3$)


OMe
5r'
^{1}H-^{1}H
f2 (ppm)
f1 (ppm)
s79

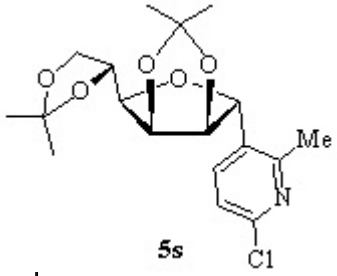

OMe
5r'
HSQ
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-40
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
s80


5r'
HMB
f2 (ppm)
f1 (ppm)
s81



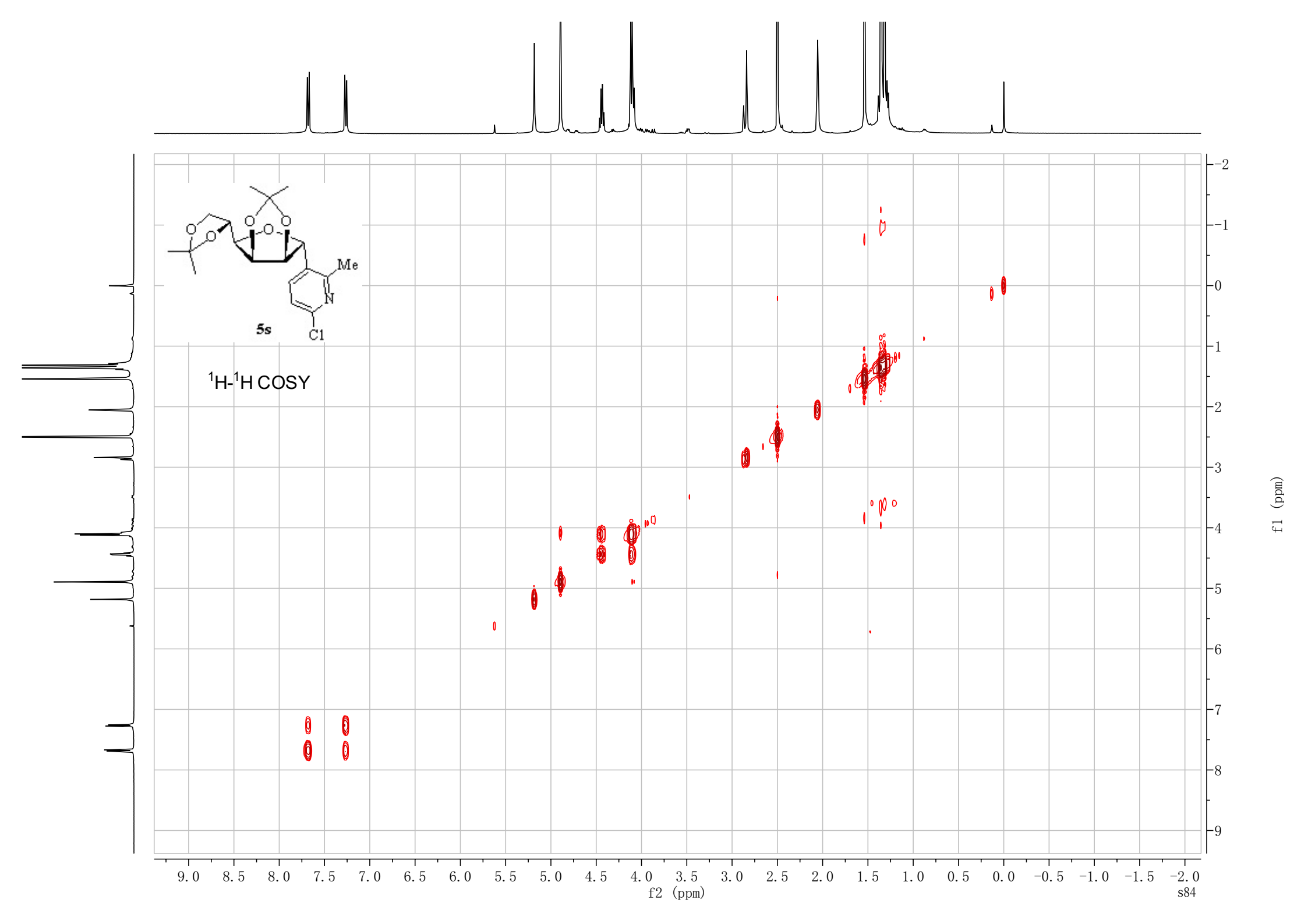
5s

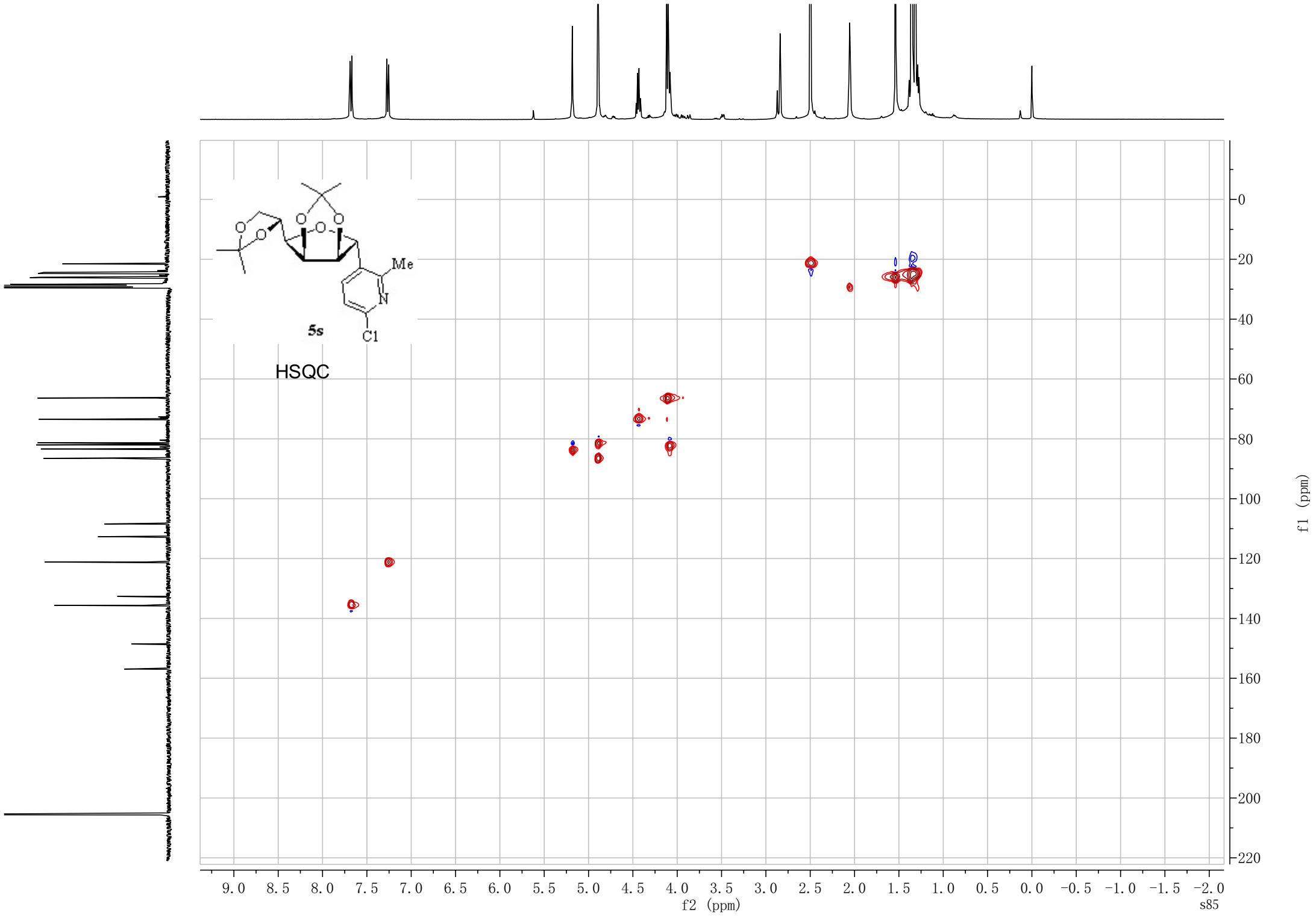
^{1}H NMR (400 MHz, Acetone-d_6)

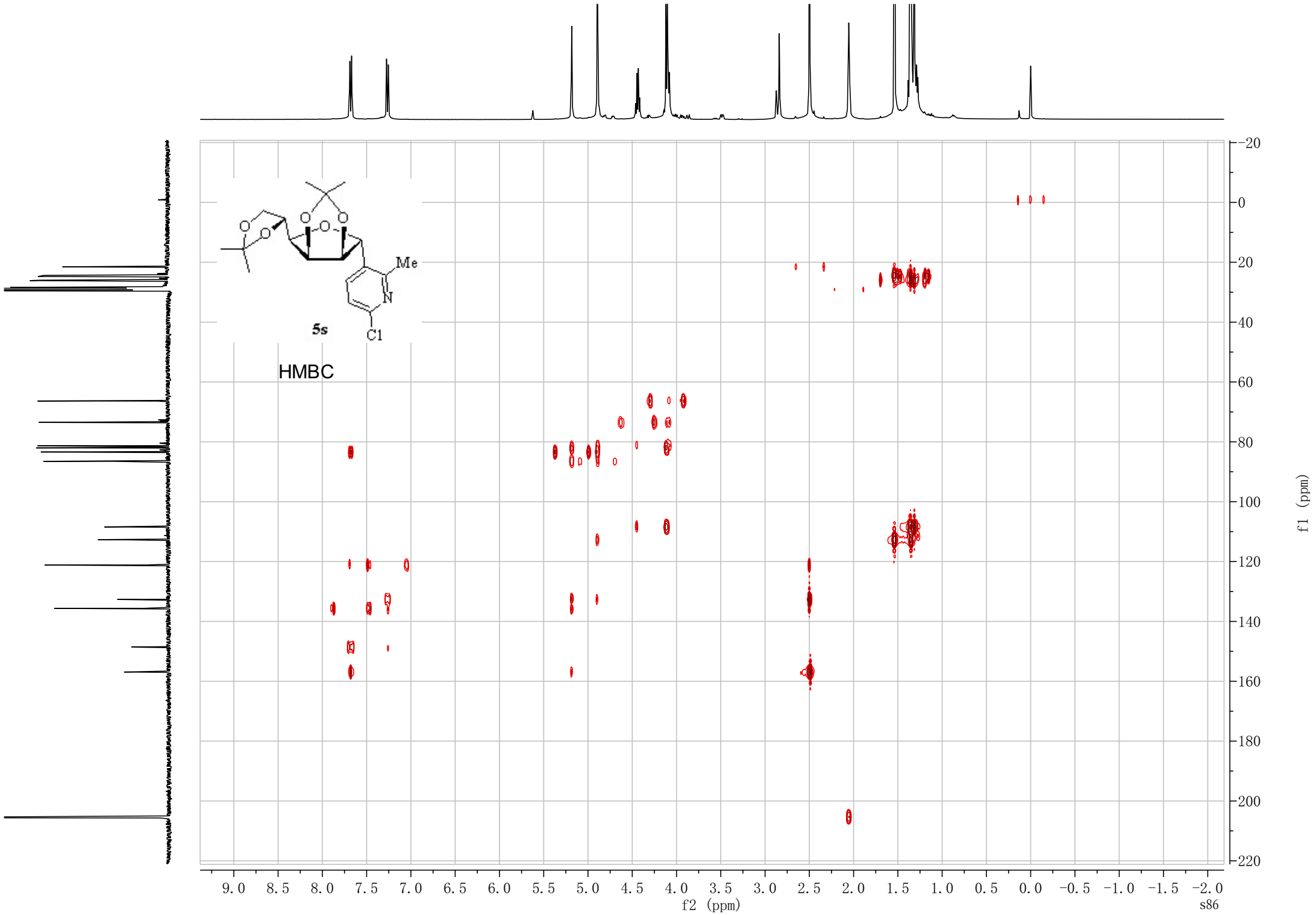


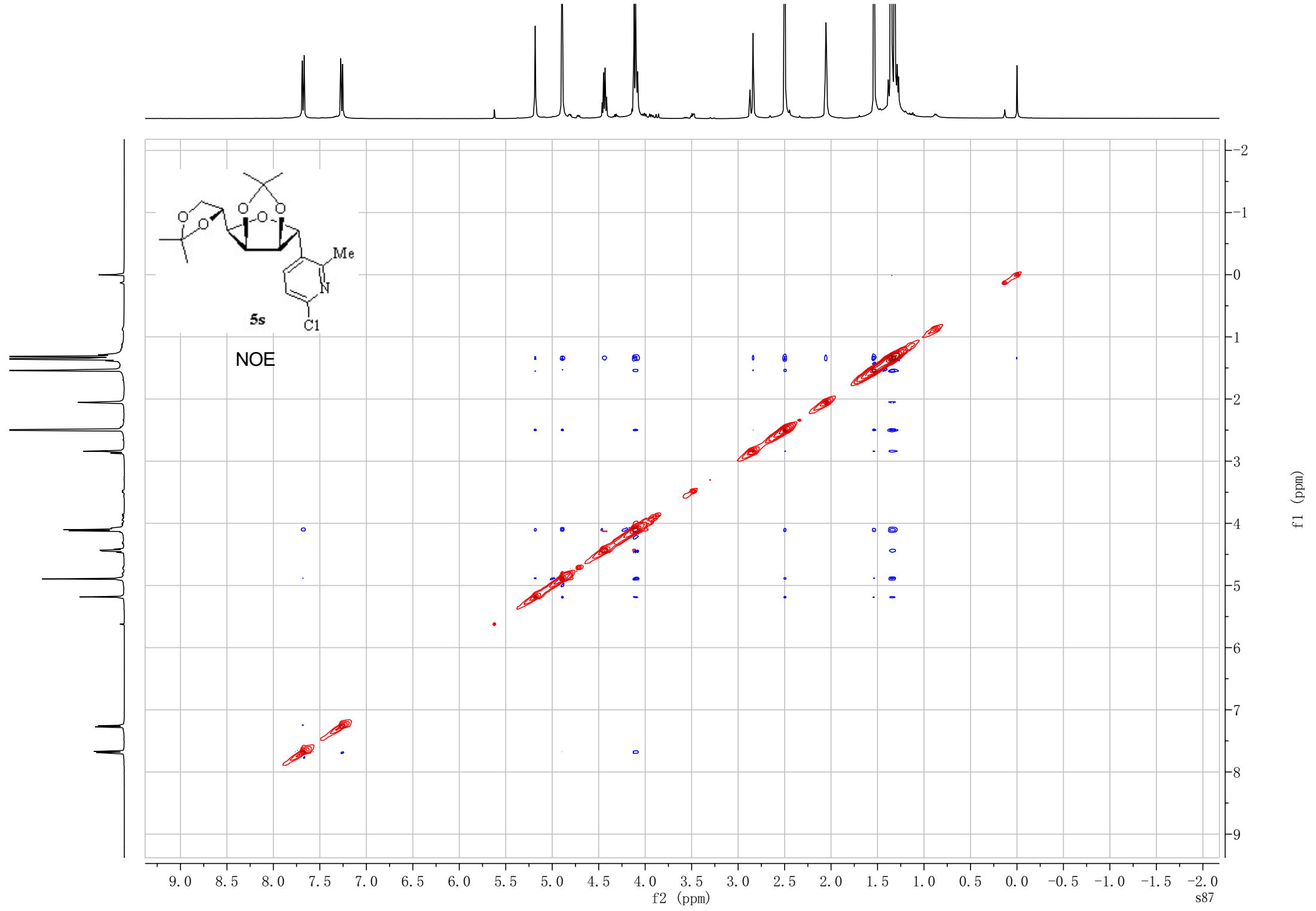
5s

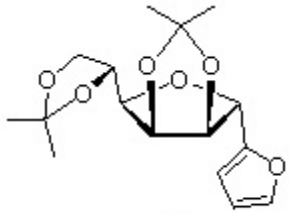
^{13}C NMR (100 MHz, Acetone-d_6)


Me
N
Cl
5s
^{1}H-^{1}H COSY
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 -2.0
f2 (ppm)
s84
f1 (ppm)


Me
N
Cl
5s
HSQC
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 -2.0
f2 (ppm)
s85
0 20 40 60 80 100 120 140 160 180 200 220
f1 (ppm)

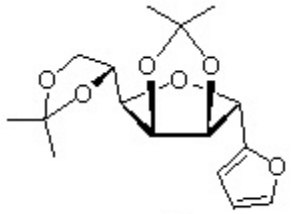

Me
N
Cl
5s
HMBC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f2 (ppm)
-20 0 20 40 60 80 100 120 140 160 180 200 220
f1 (ppm)
s86


Me
N
Cl
5s
NOE
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 -2.0
f2 (ppm)
s87
-2 -1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)



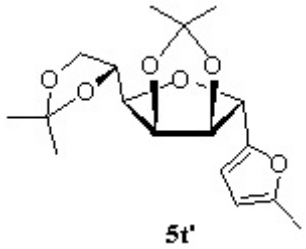
5t

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



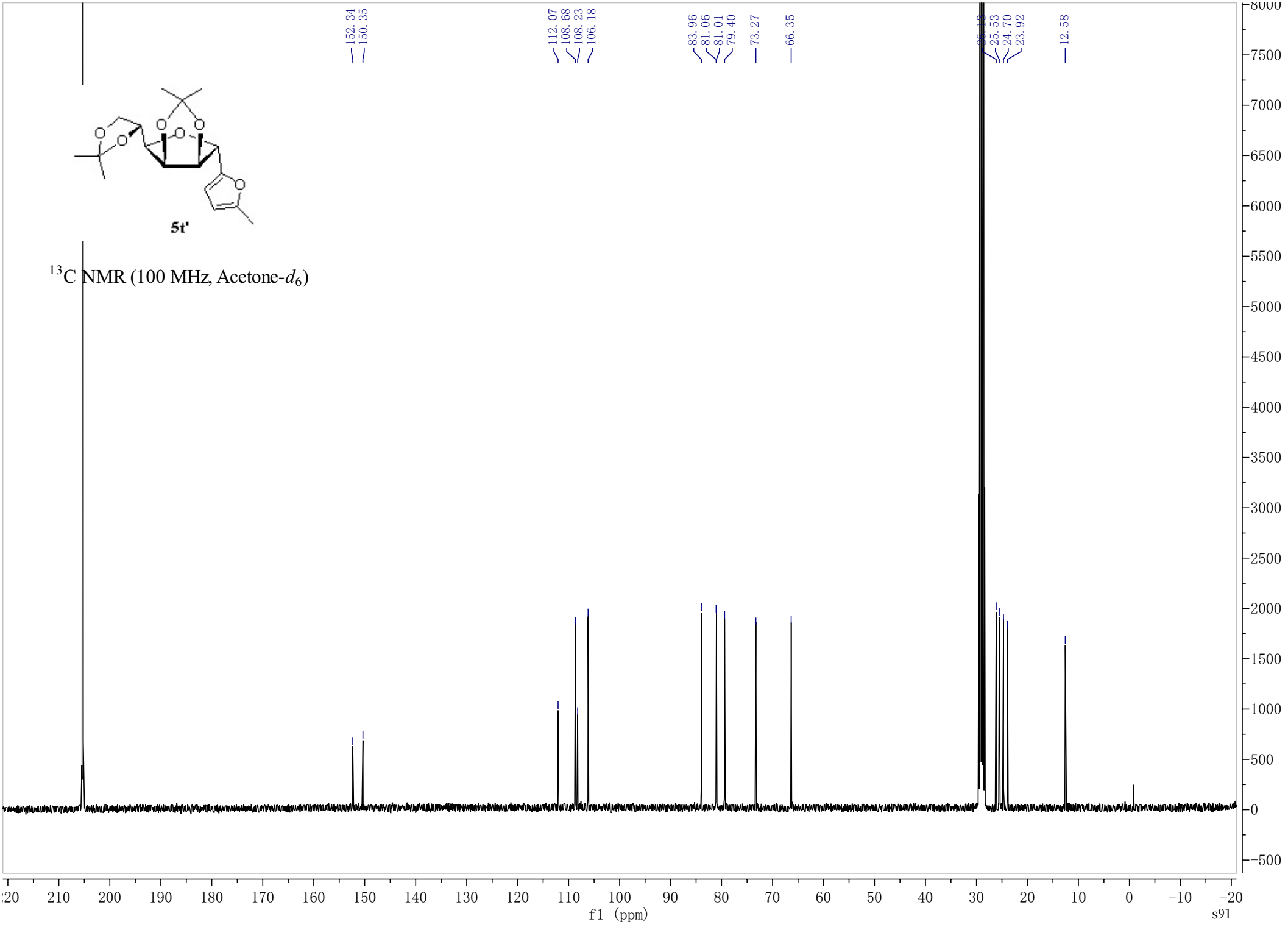
5t

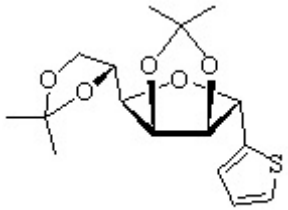
^{13}C NMR (100 MHz, $CDCl_3$)



5t'

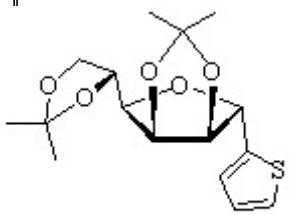
^{1}H NMR (400 MHz, Acetone-d_6)


152.34
150.35
112.07
108.68
108.23
106.18
83.96
81.06
81.01
79.40
73.27
66.35
26.13
25.53
24.70
23.92
12.58
5t'
^{13}C NMR (100 MHz, Acetone-d_6)
f1 (ppm)
s91



5u

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



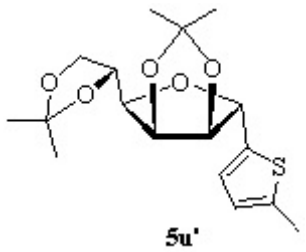
5u

^{13}C NMR (100 MHz, Acetone-d_6)

142.60
127.10
125.51
124.77
112.19
108.41
86.38
81.88
81.30
81.00
73.11
66.50
26.14
25.56
24.71
24.03

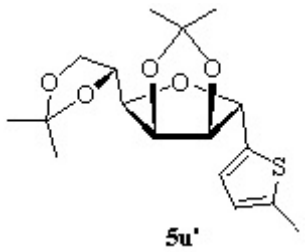
f1 (ppm)

s93



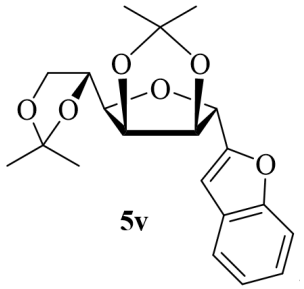
5u'

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



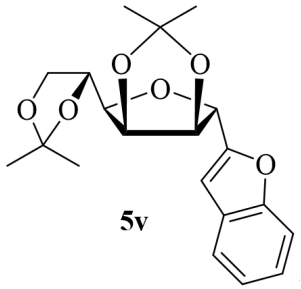
5u'

^{13}C NMR (100 MHz, $CDCl_3$)



5v

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



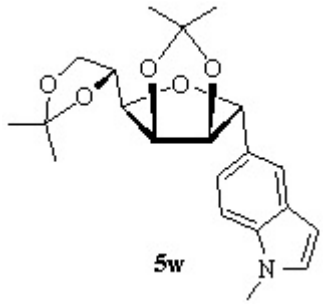
5v

^{13}C NMR (100 MHz, $CDCl_3$)

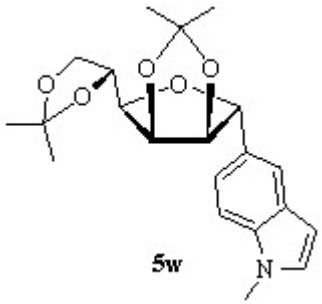
155.12
154.31
127.76
124.54
123.04
121.19
113.02
111.38
109.25
104.55
84.20
82.01
81.04
80.20
80.16
73.36
66.95
26.94
26.13
25.16
24.70

f1 (ppm)

s97



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

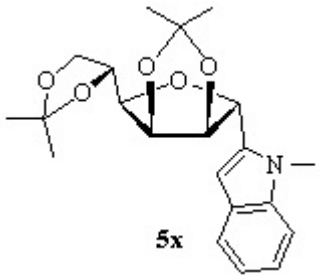


^{13}C NMR (100 MHz, $CDCl_3$)

136.07
129.56
129.04
128.45
119.49
117.72
112.66
109.55
109.23
101.12
87.61
85.50
81.25
81.18
73.63
67.19
26.94
26.25
25.25
24.81

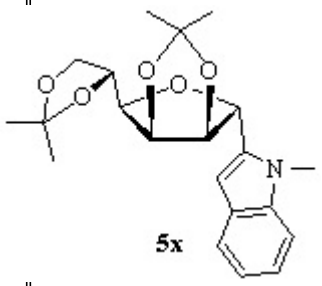
f1 (ppm)

s99



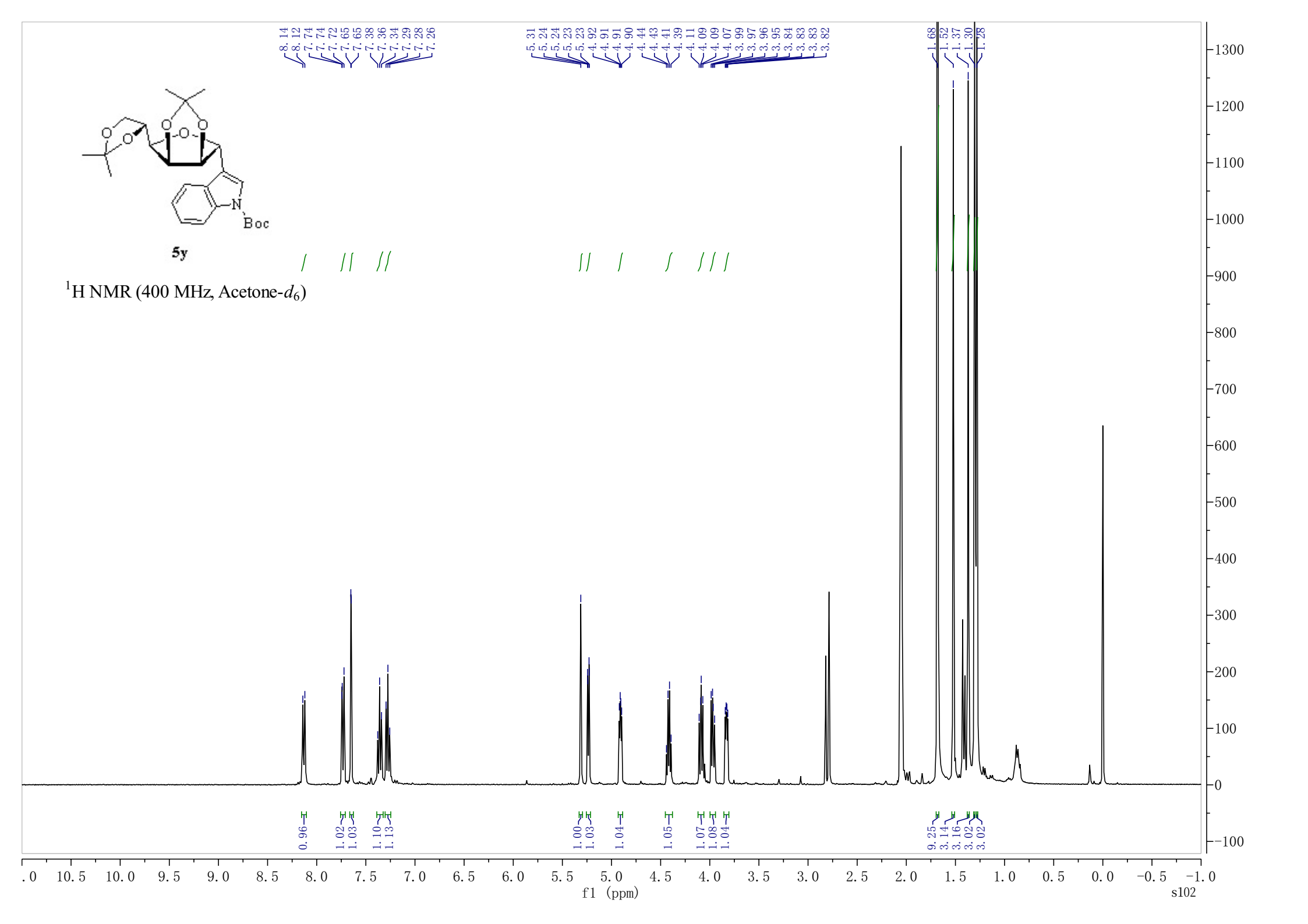
5x

^{1}H NMR (400 MHz, Acetone-d_6)

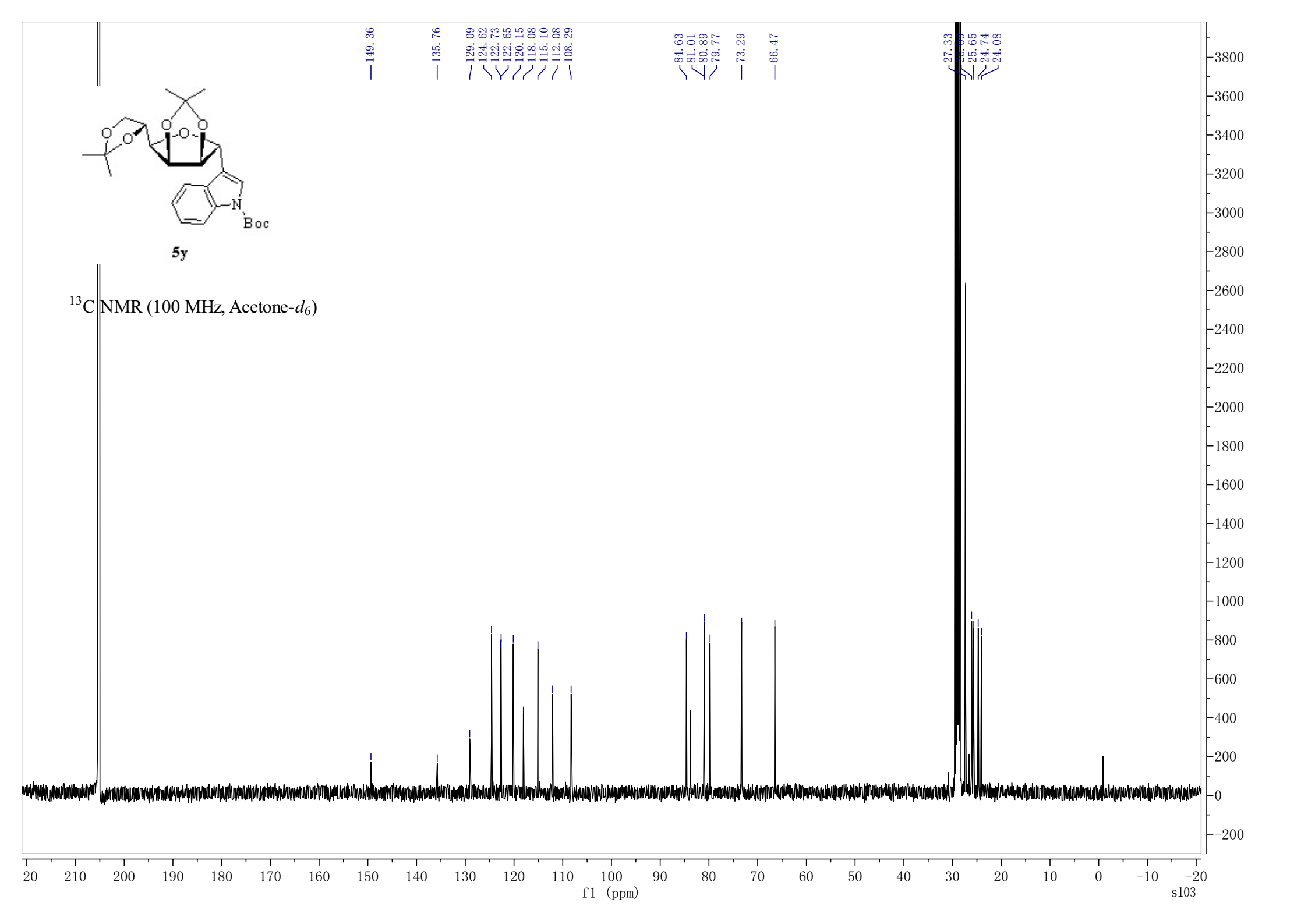


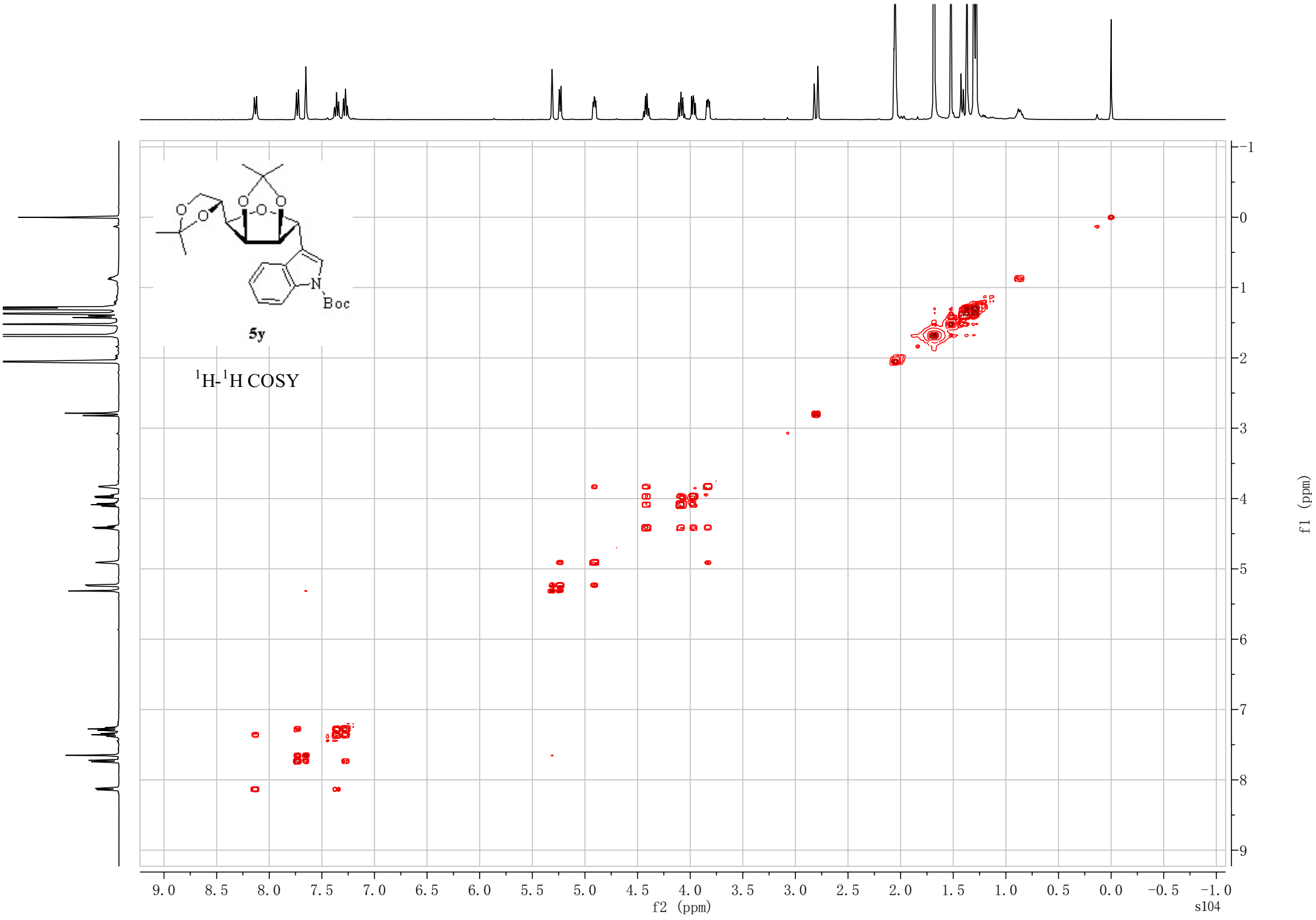
5x

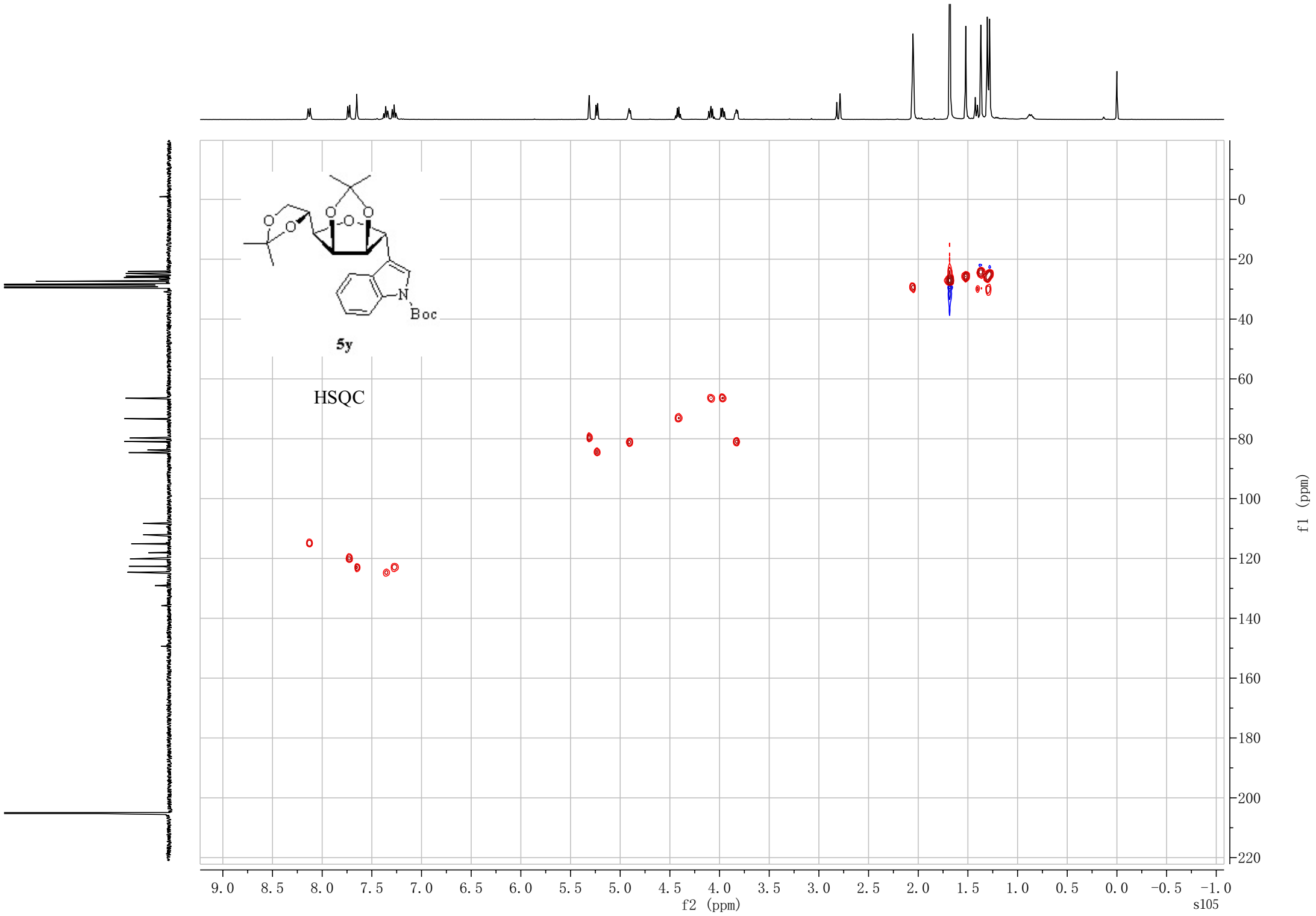
^{13}C NMR (100 MHz, Acetone-d_6)

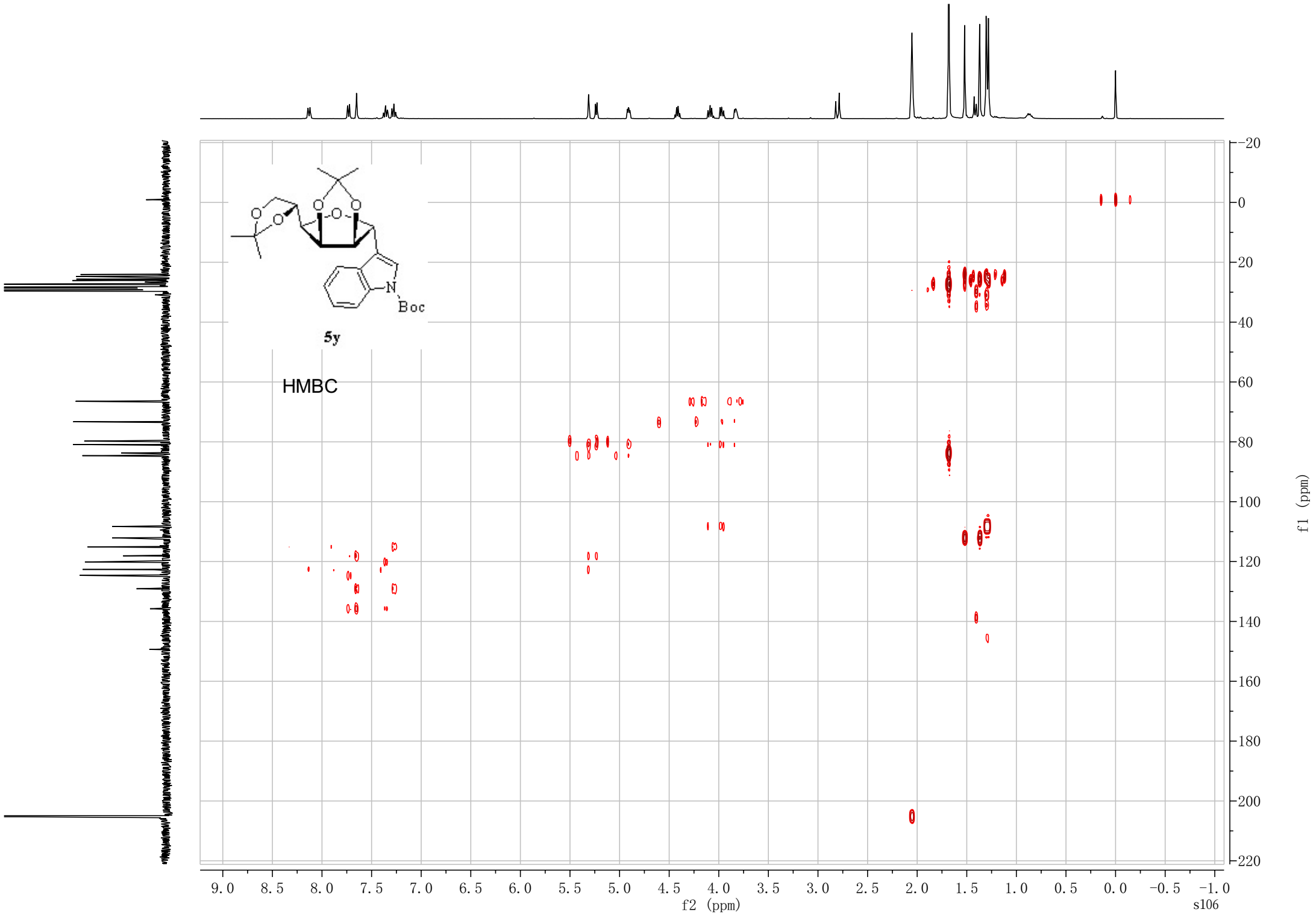


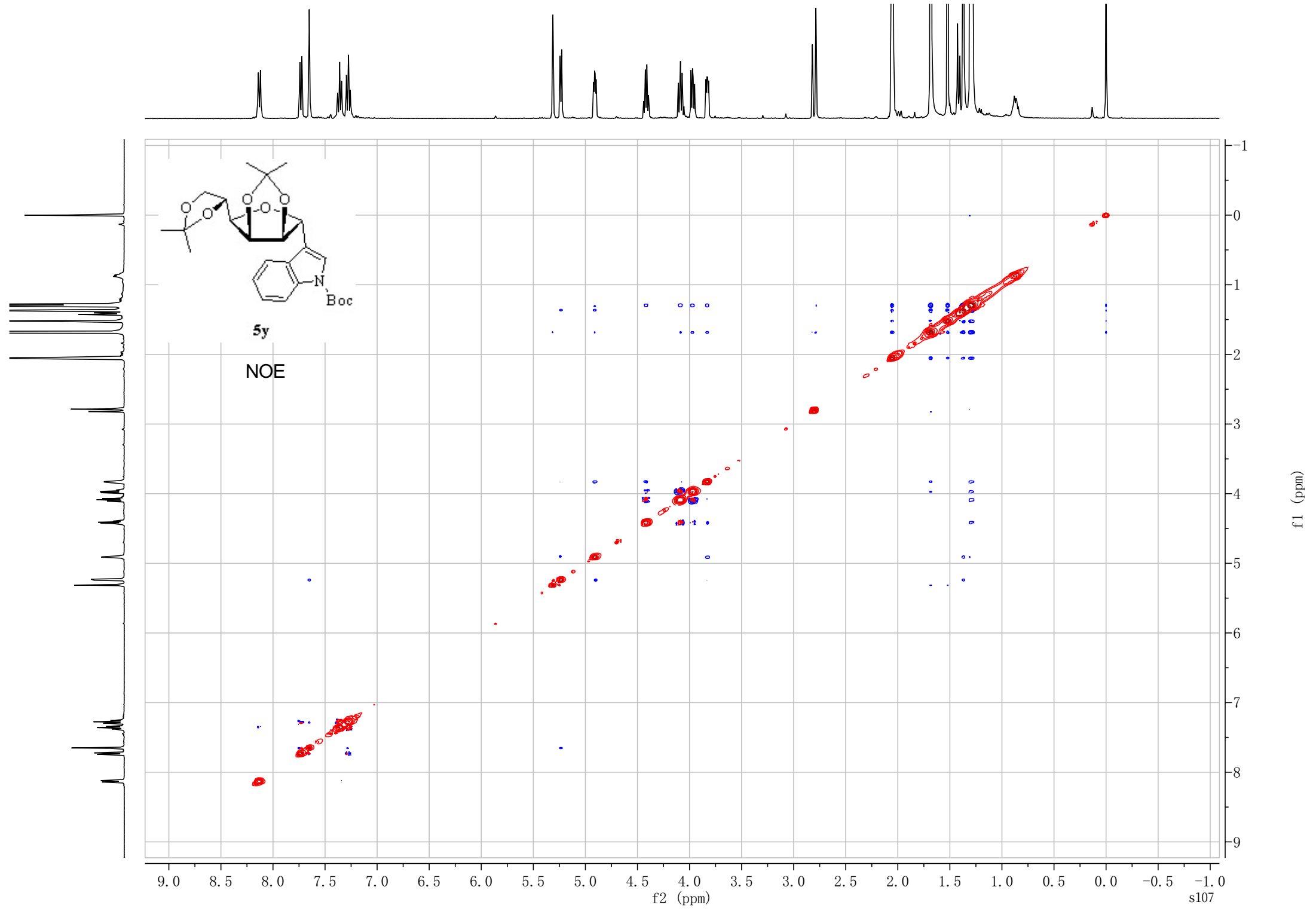
^{1}H NMR (400 MHz, Acetone-d_6)

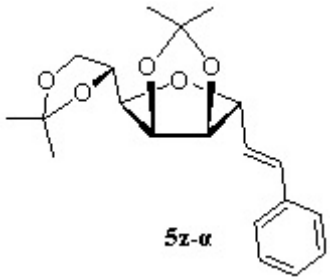

149.36
135.76
129.09
124.62
122.73
122.65
120.15
118.08
115.10
112.08
108.29
84.63
81.01
80.89
79.77
73.29
66.47
27.33
26.69
25.65
24.74
24.08
Boc
5y
13C NMR (100 MHz, Acetone-d6)
f1 (ppm)
s103


Boc
5y
^{1}H-^{1}H COSY
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
s104
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)

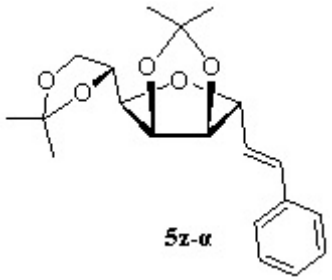

5y
HSQC
Boc
N
f2 (ppm)
f1 (ppm)
s105


Boc
5y
HMBC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-20 0 20 40 60 80 100 120 140 160 180 200 220
f1 (ppm)
s106


Boc
5y
NOE
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9
f1 (ppm)
s107

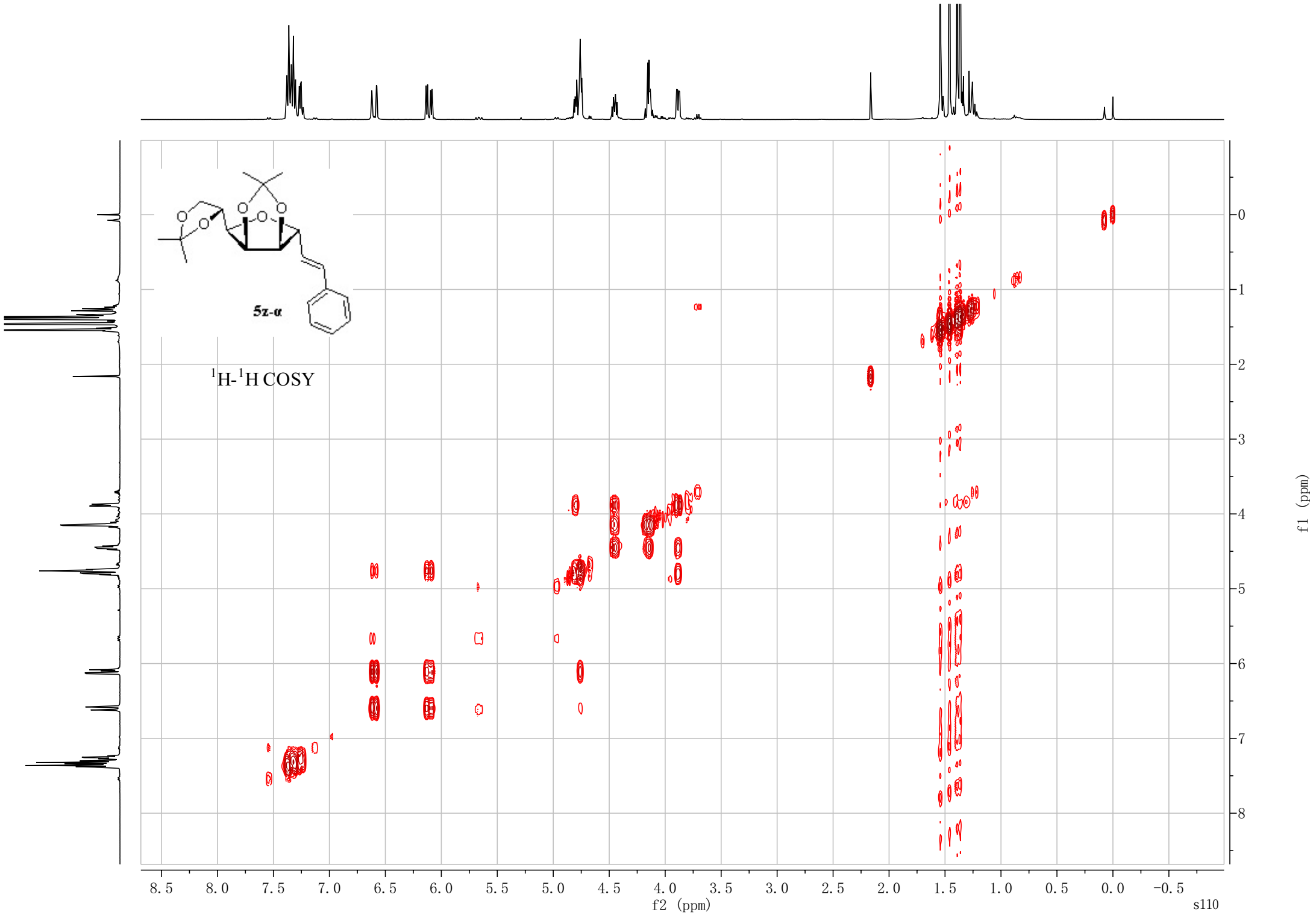


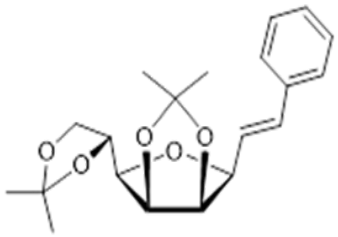
^{1}H NMR (400 MHz, $CDCl_3$)



5z-α

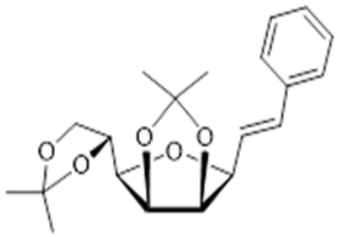
^{13}C NMR (100 MHz, $CDCl_3$)


5z-α
^{1}H-^{1}H COSY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)
s110



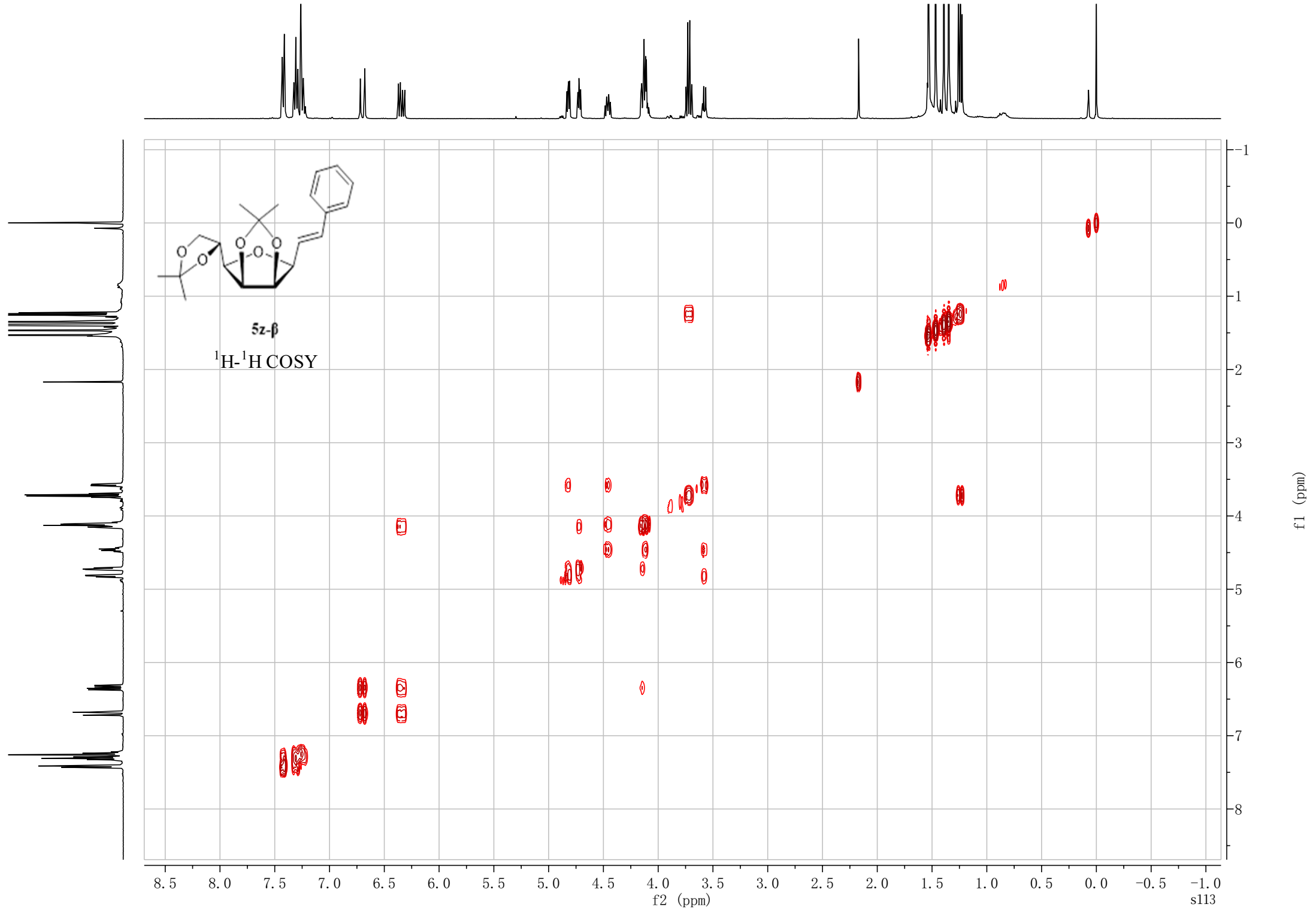
5z-β

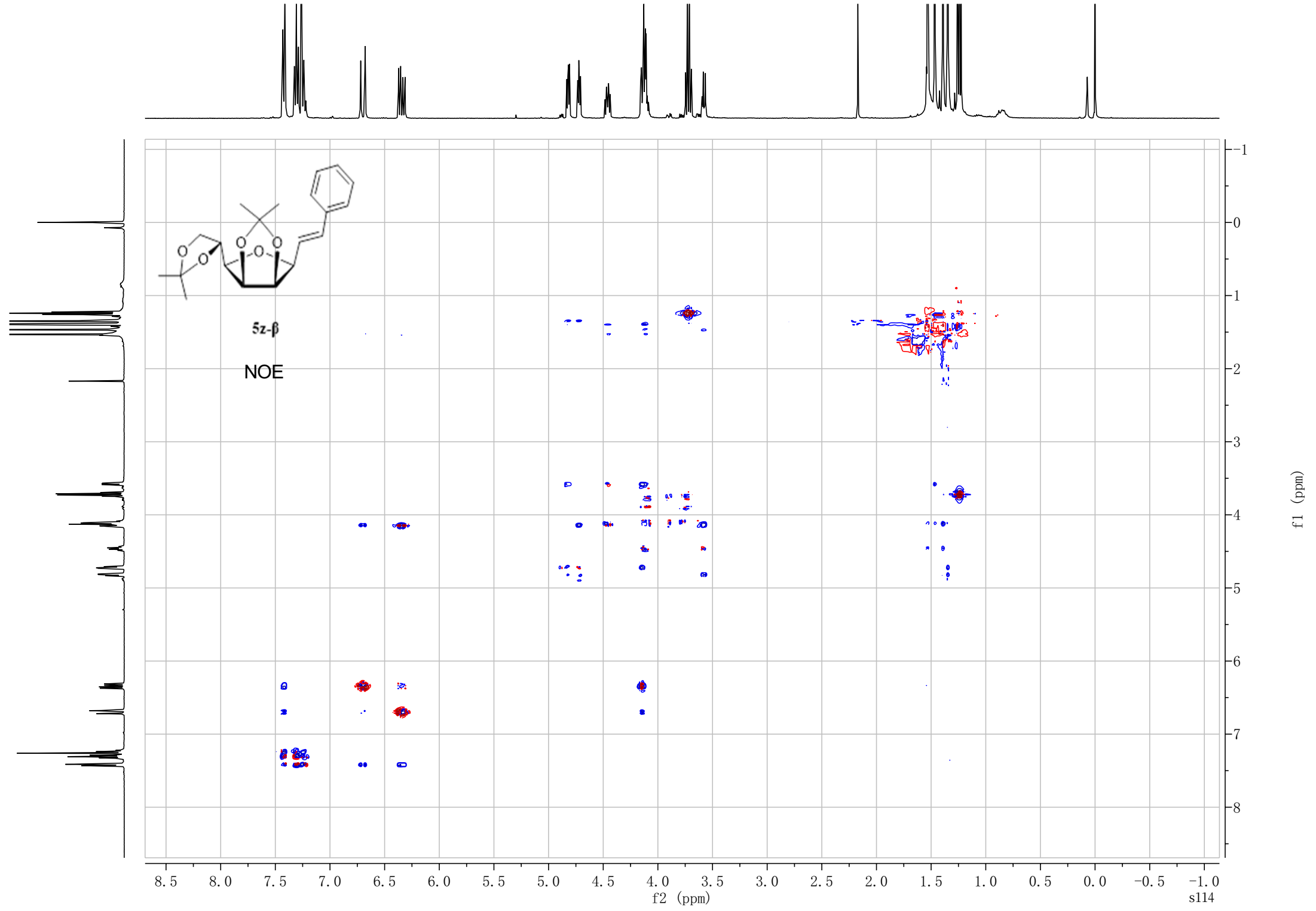
^{1}H NMR (400 MHz, $CDCl_3$)

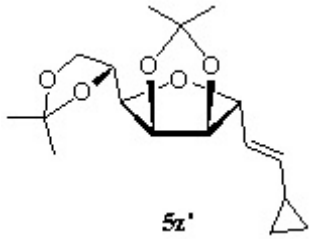


5z-β

^{13}C NMR (100 MHz, $CDCl_3$)

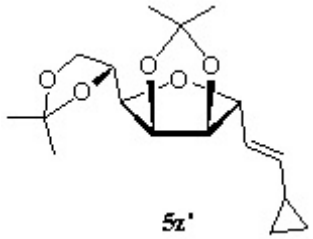

5z-β
^{1}H-^{1}H COSY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s113
f1 (ppm)


5z-β
NOE
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s114
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)



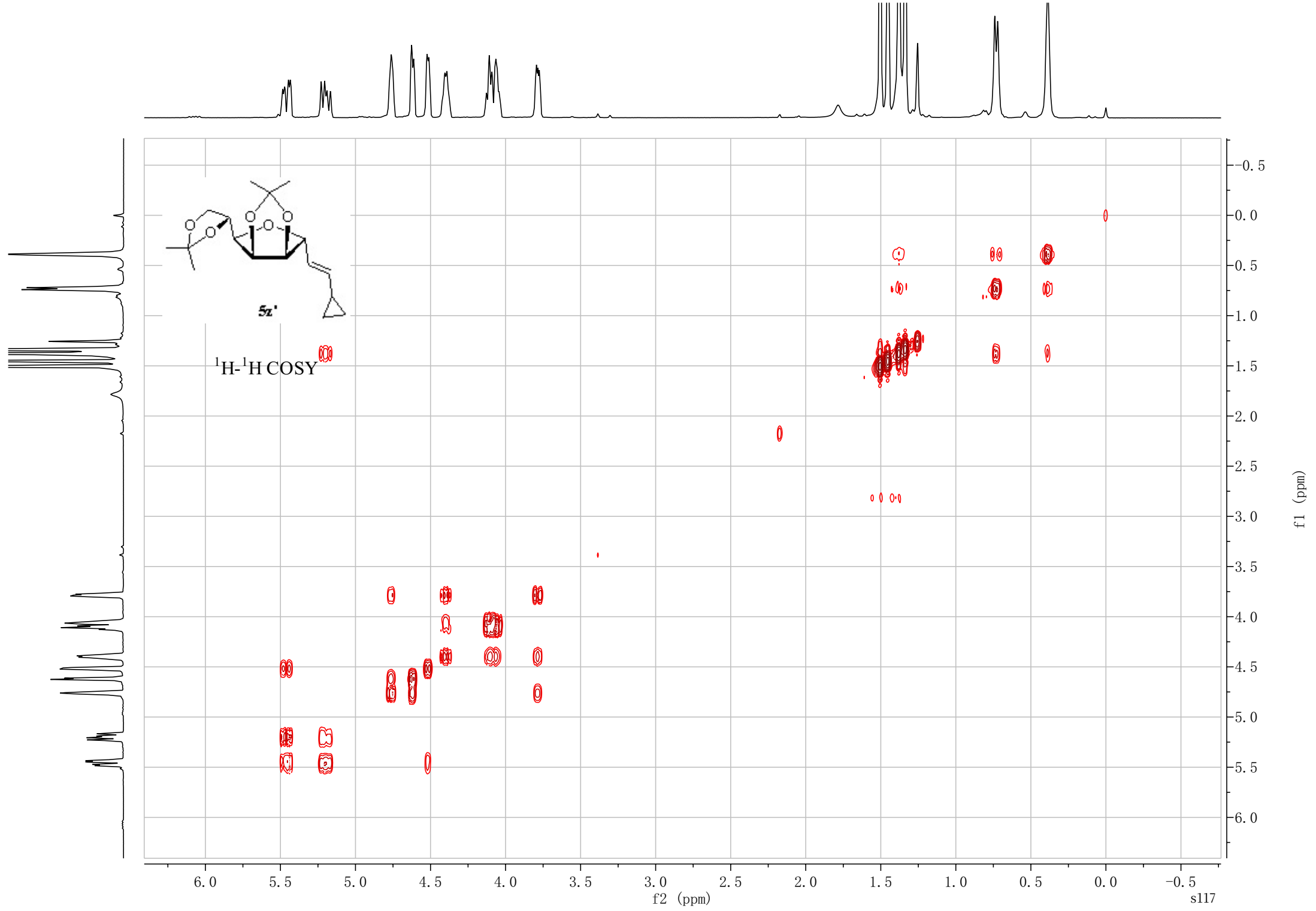
5z'

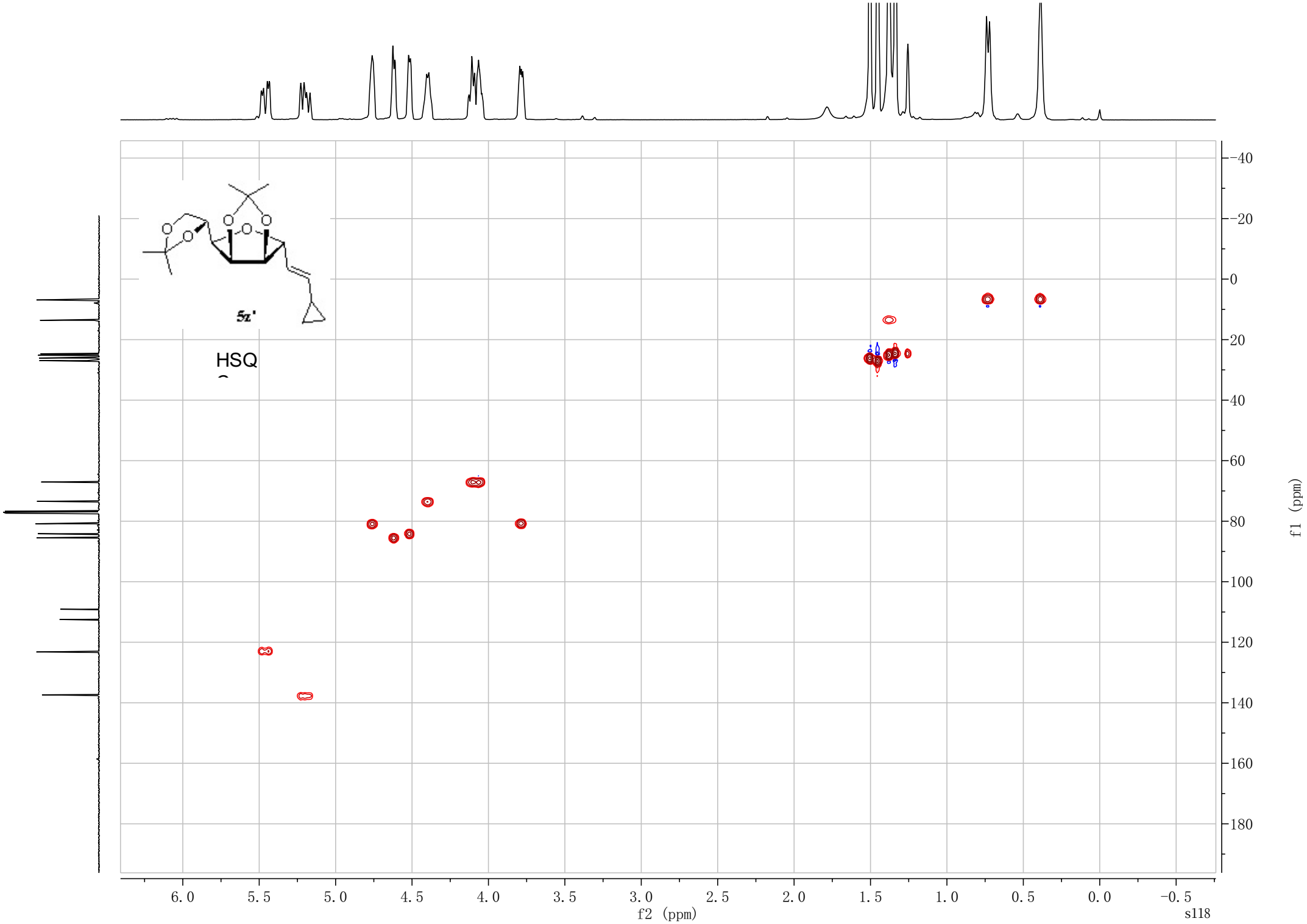
^{1}H NMR (400 MHz, $CDCl_3$)

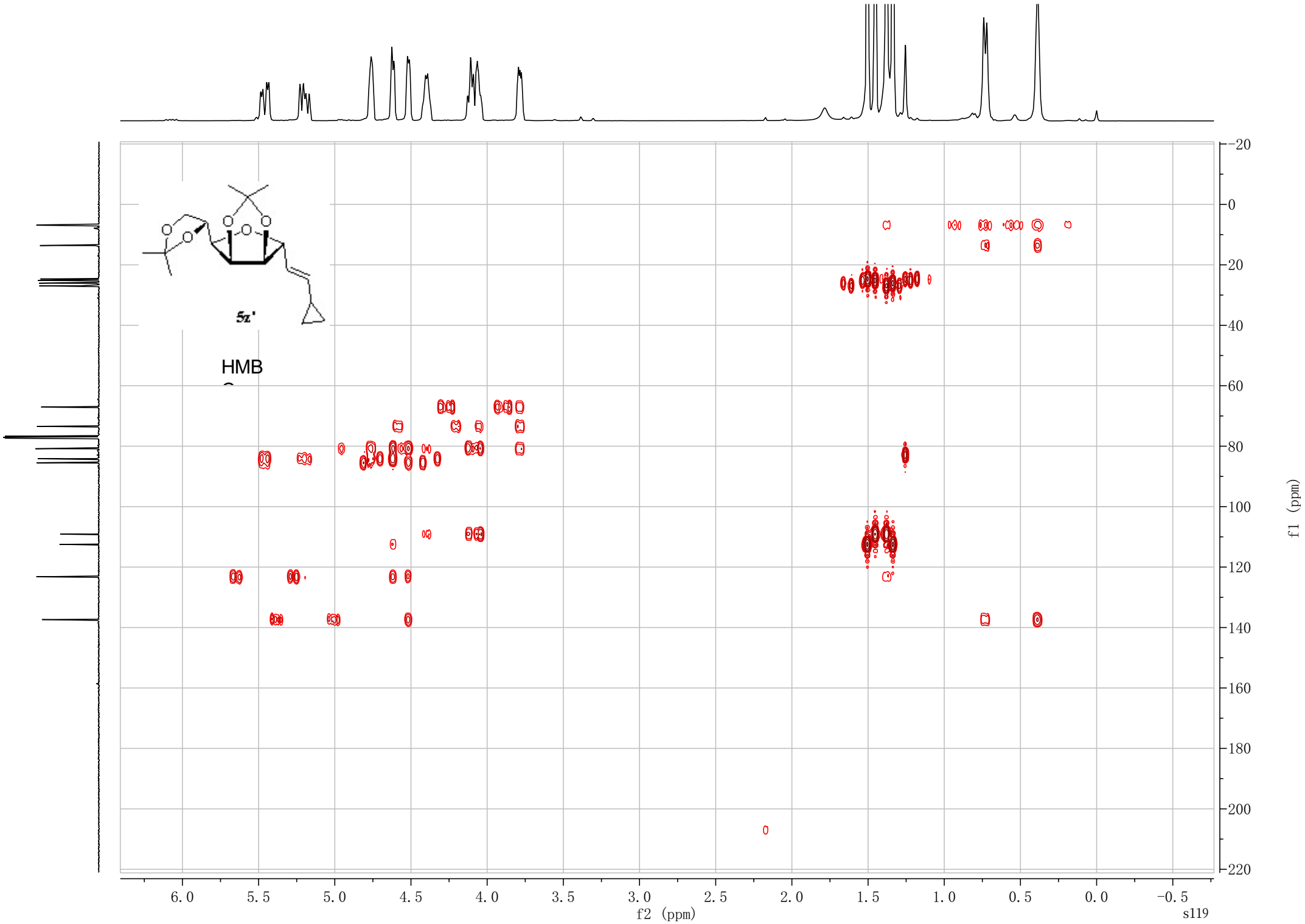


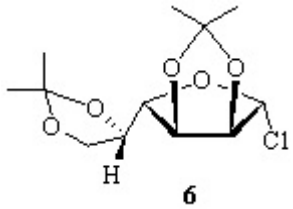
5z'

^{13}C NMR (100 MHz, $CDCl_3$)


5z'
^{1}H-^{1}H COSY
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)
f1 (ppm)
s117

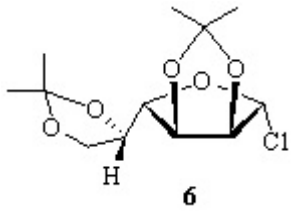

5z'
HSQ
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-40
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
s118


5z'
HMB
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
s119



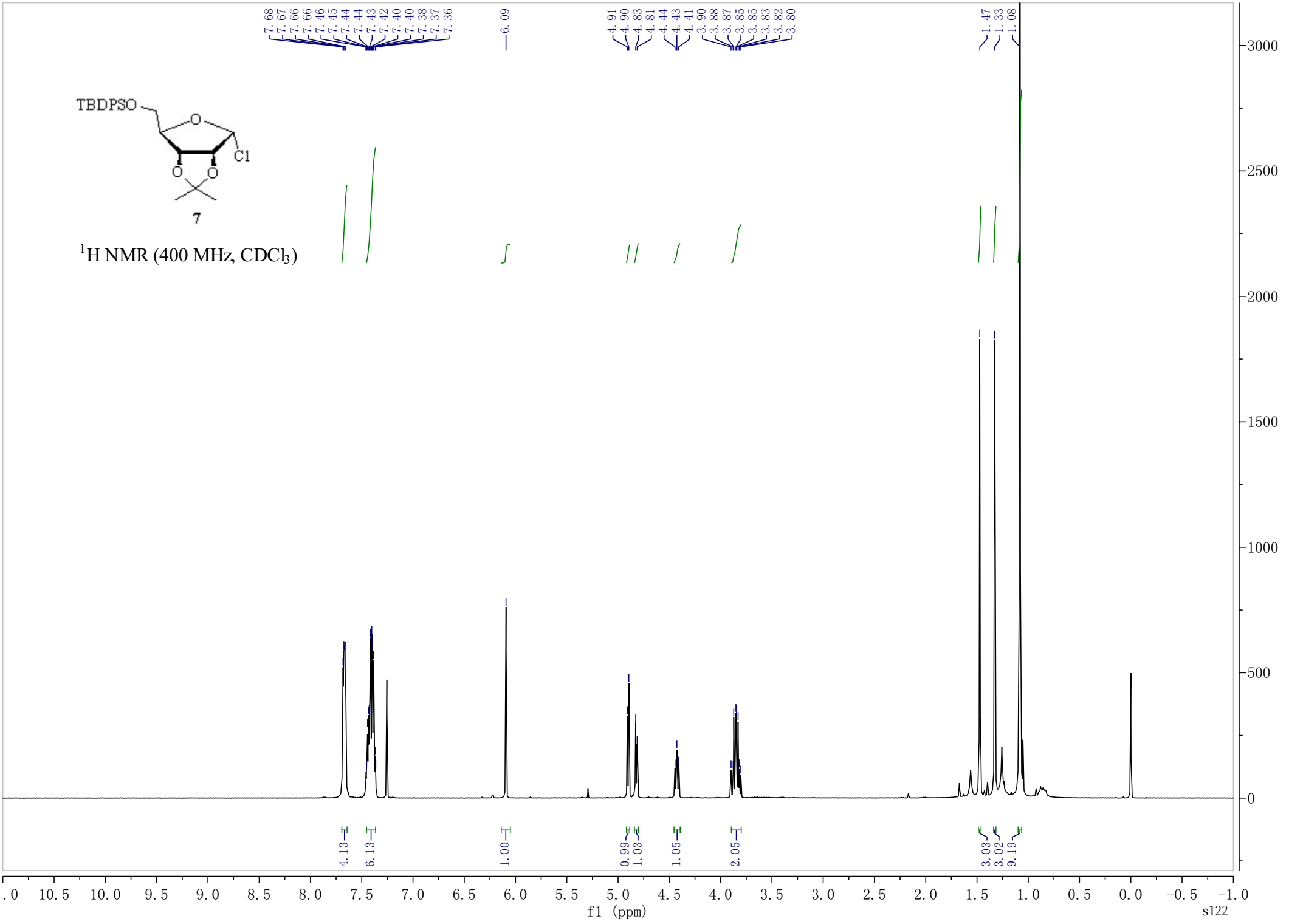
6

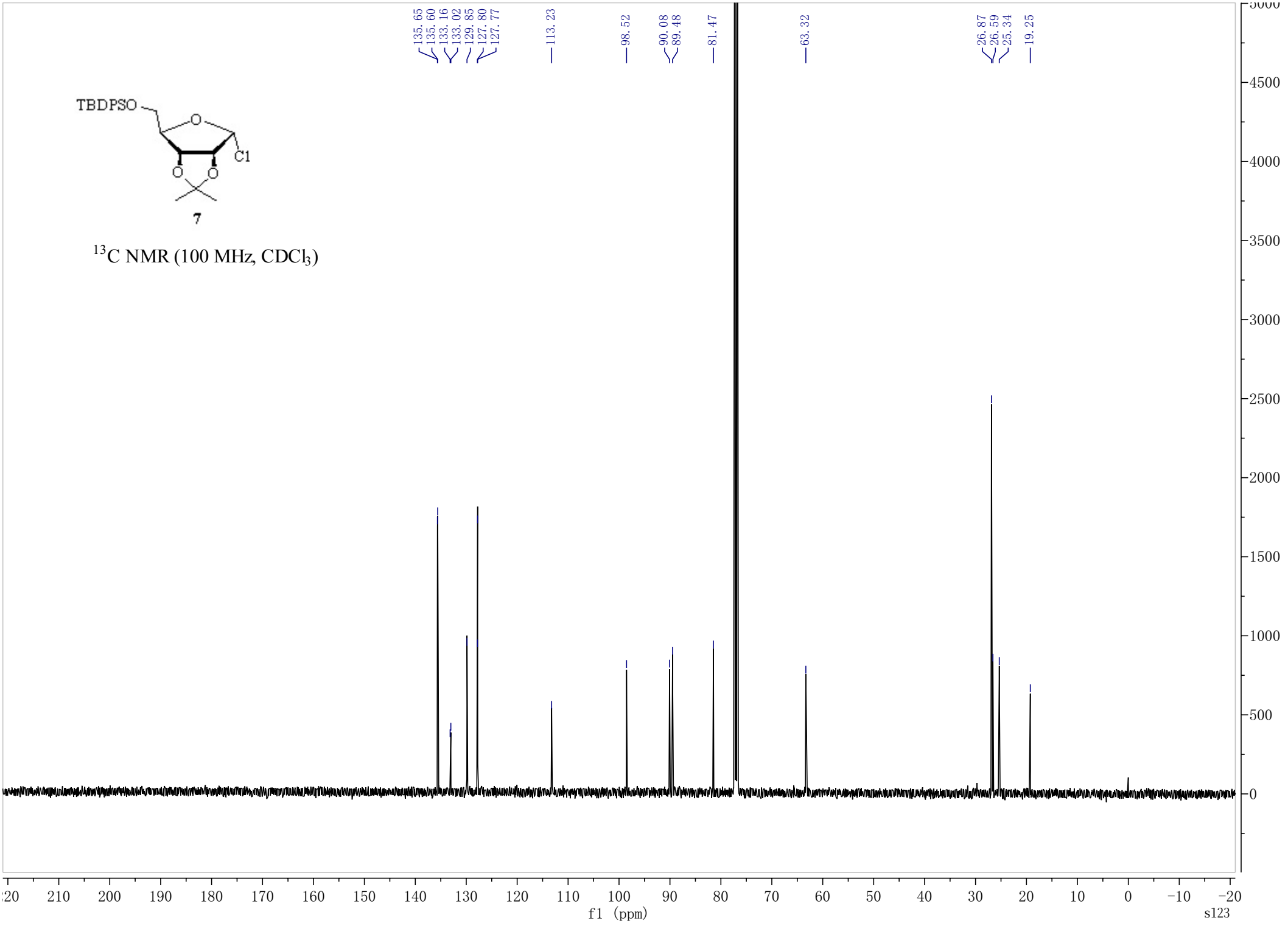
^{1}H NMR (400 MHz, $CDCl_3$)

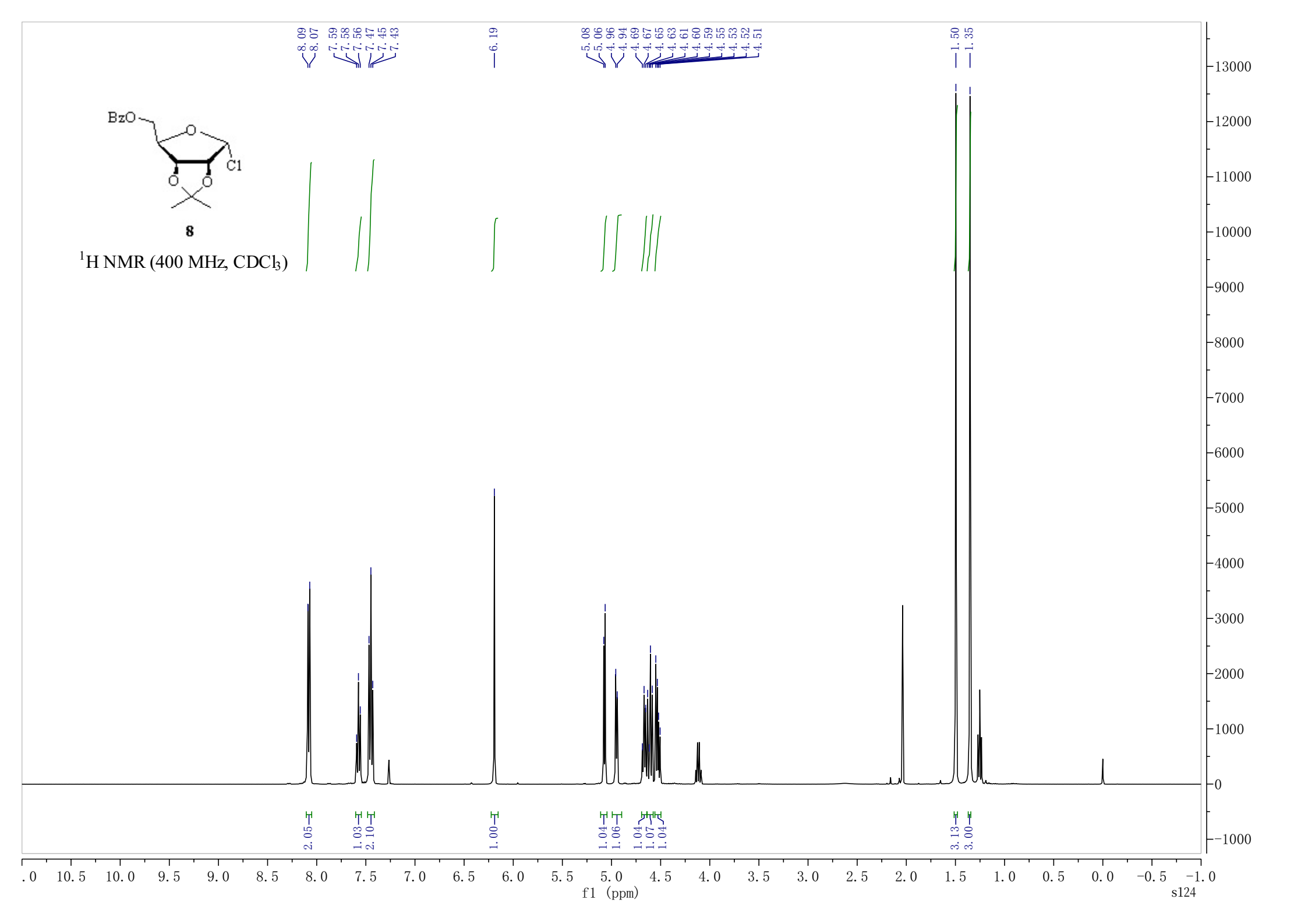


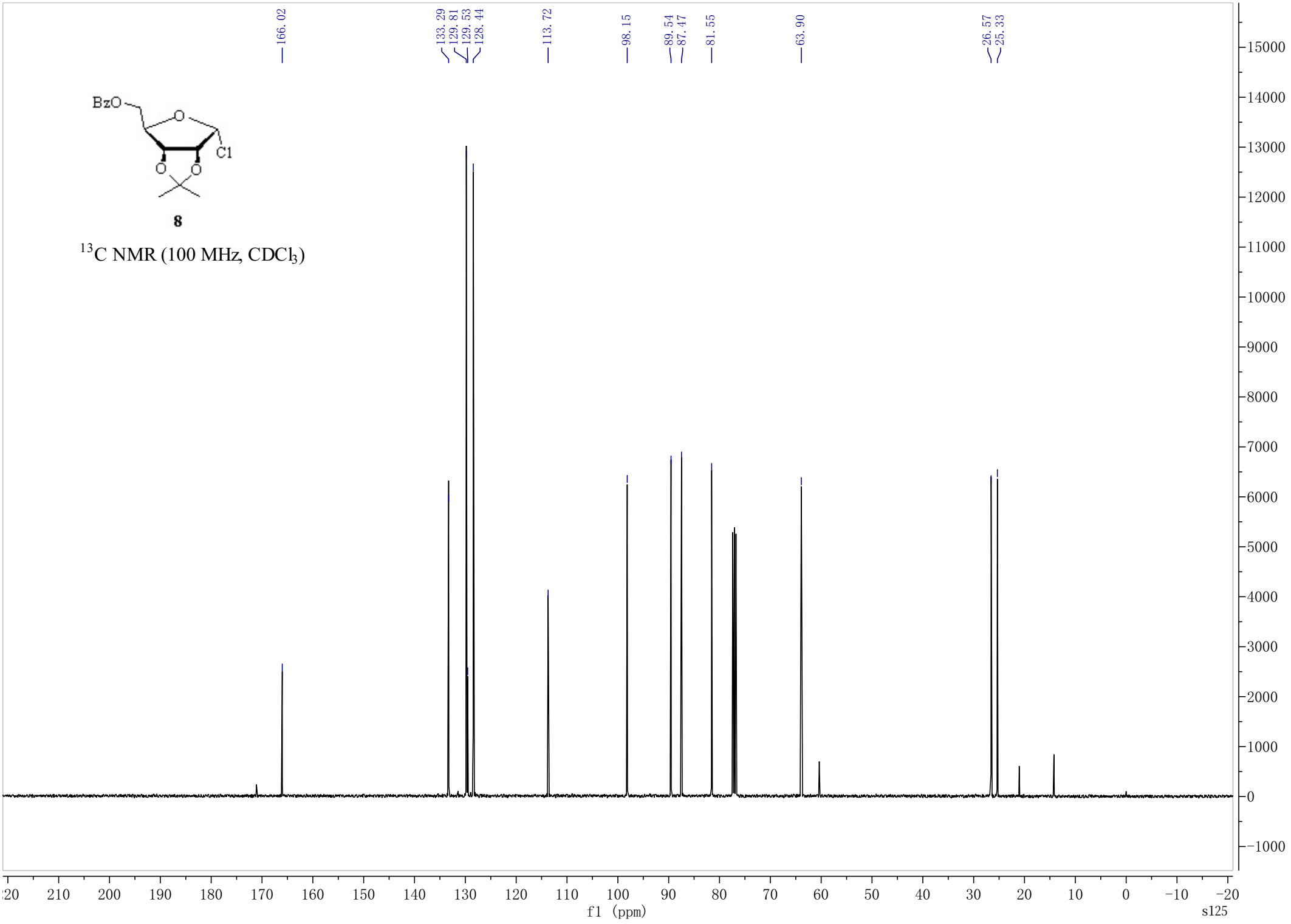
6

^{13}C NMR (100 MHz, $CDCl_3$)


7.68
7.67
7.66
7.66
7.46
7.45
7.44
7.44
7.43
7.42
7.40
7.40
7.38
7.37
7.36
6.09
4.91
4.90
4.83
4.81
4.44
4.43
4.41
3.90
3.88
3.87
3.85
3.85
3.83
3.82
3.80
1.47
1.33
1.08
TBDPSO
O
C1
O
O
7
^{1}H NMR (400 MHz, $CDCl_3$)
4.13
6.13
1.00
0.99
1.03
1.05
2.05
3.03
3.02
9.19
3000
2500
2000
1500
1000
500
0
f1 (ppm)
s122

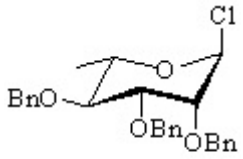

135.65
135.60
133.16
133.02
129.85
127.80
127.77
113.23
98.52
90.08
89.48
81.47
63.32
26.87
26.59
25.34
19.25
TBDPSO
O
C1
O
O
7
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)
s123


8.09
8.07
7.59
7.58
7.56
7.47
7.45
7.43
6.19
5.08
5.06
4.96
4.94
4.69
4.67
4.65
4.63
4.61
4.60
4.59
4.55
4.53
4.52
4.51
1.50
1.35
BzO
O
Cl
O
O
8
1H NMR (400 MHz, CDCl3)
2.05
1.03
2.10
1.00
1.04
1.06
1.04
1.07
1.04
3.13
3.00
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
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)
s124



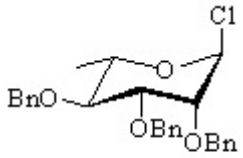
8

^{13}C NMR (100 MHz, $CDCl_3$)



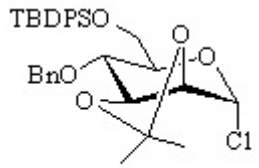
9

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



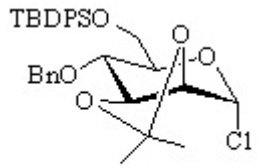
9

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



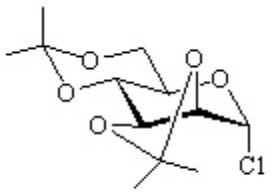
10

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



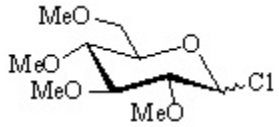
10

^{13}C NMR (100 MHz, $CDCl_3$)



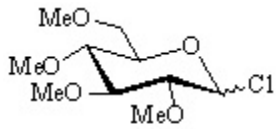
11

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



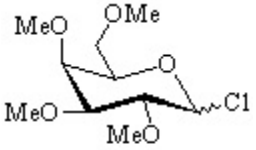
12

^{1}H NMR (400 MHz, Acetone-d_6)



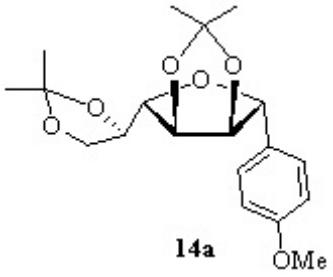
12

^{13}C NMR (100 MHz, Acetone-d_6)

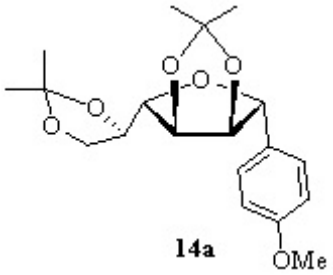


13

^{1}H NMR (400 MHz, Acetone-d_6)



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



^{13}C NMR (100 MHz, $CDCl_3$)

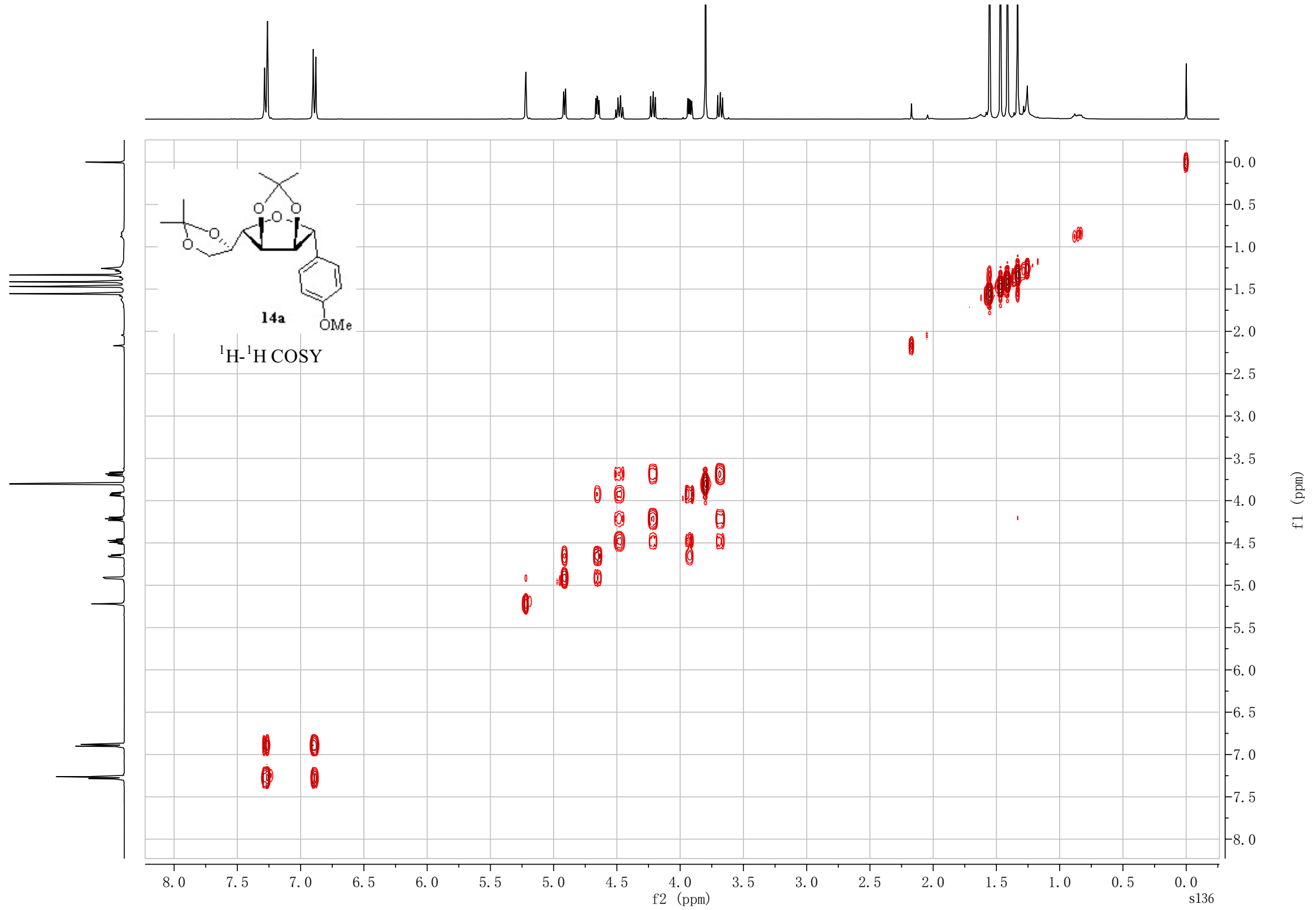
159.00
130.31
126.99
113.96
113.19
109.65
87.48
84.57
82.77
81.27
75.88
66.13
55.31
26.89
26.25
25.38
25.03

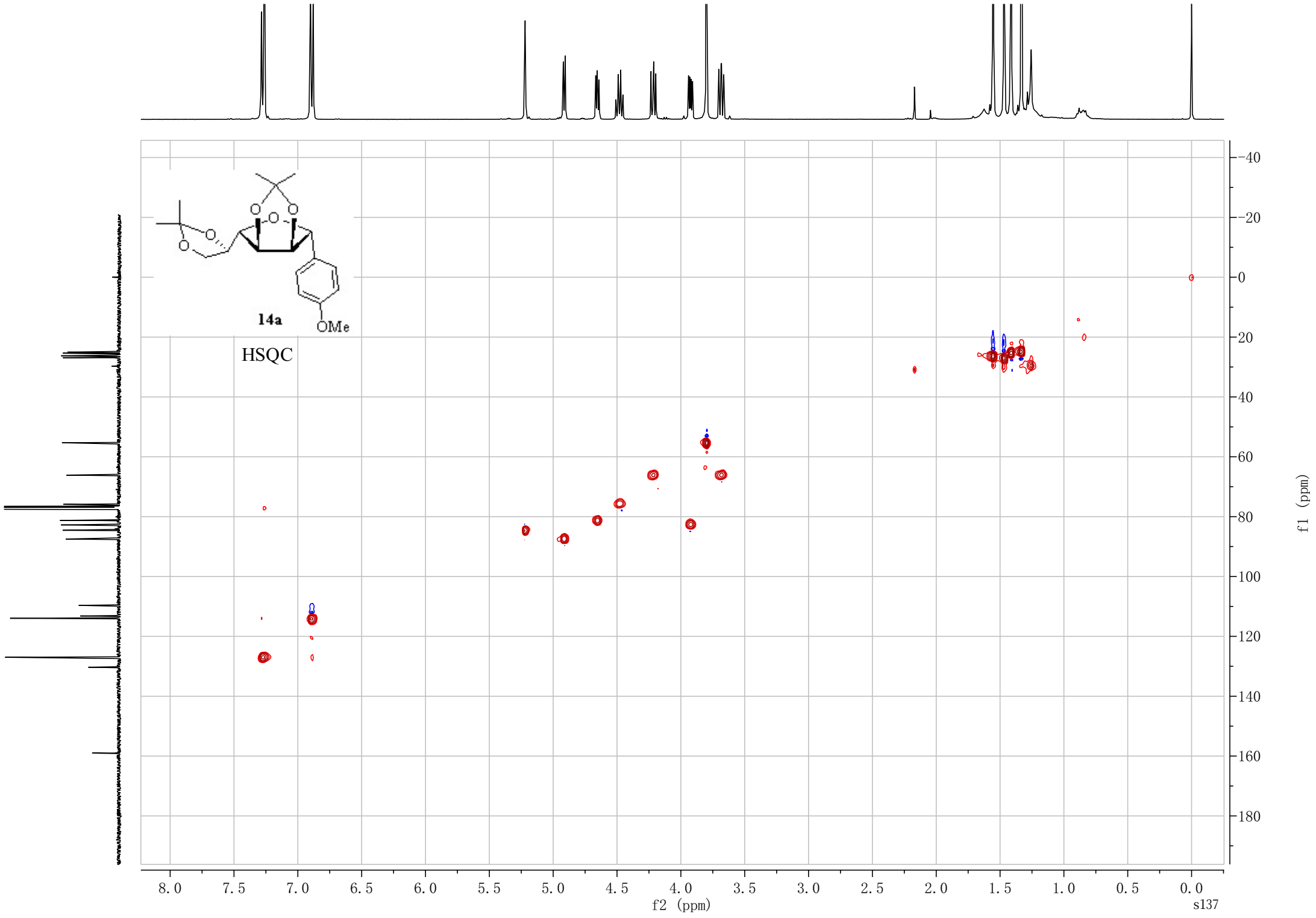
4000
3500
3000
2500
2000
1500
1000
500
0

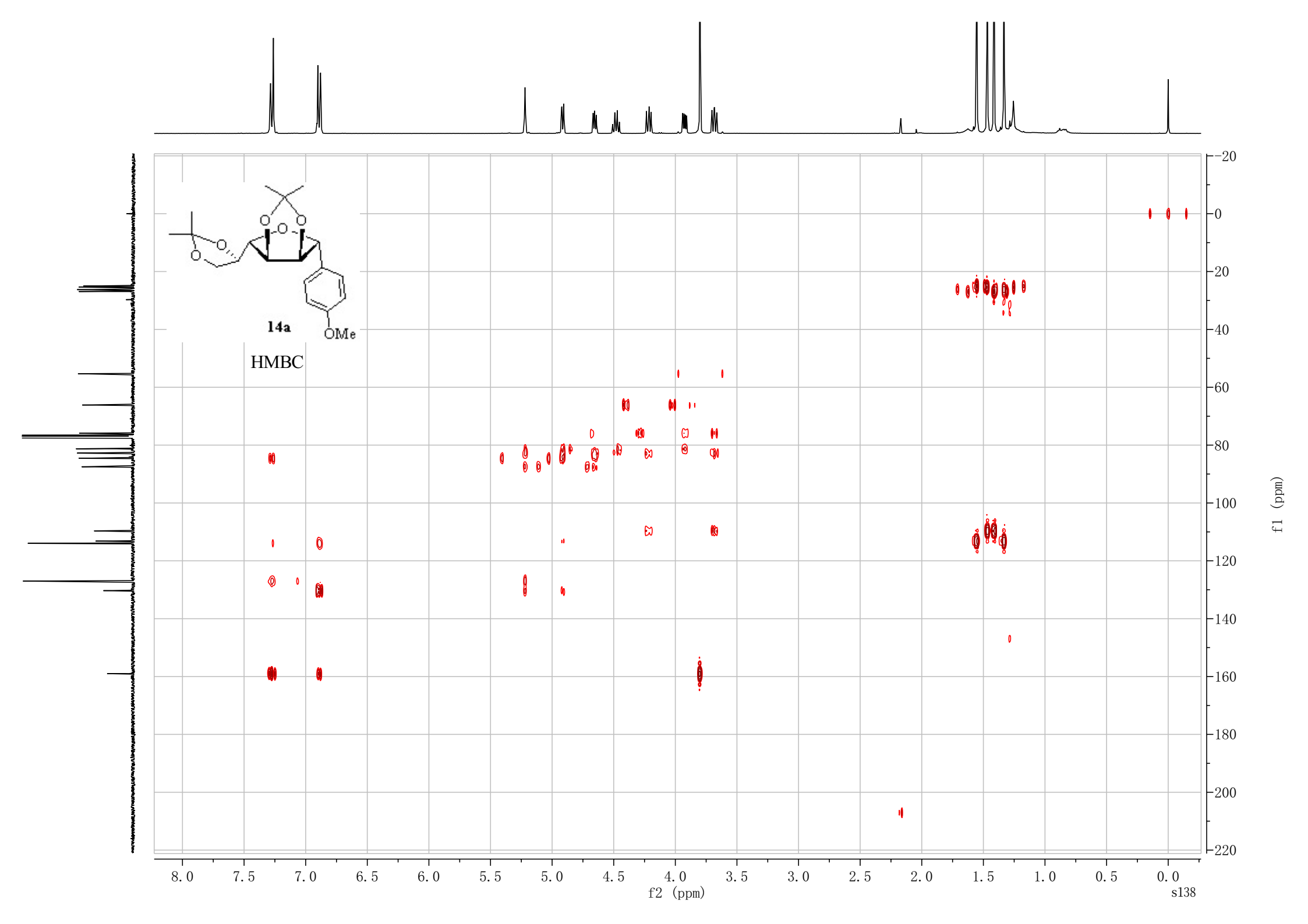
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20

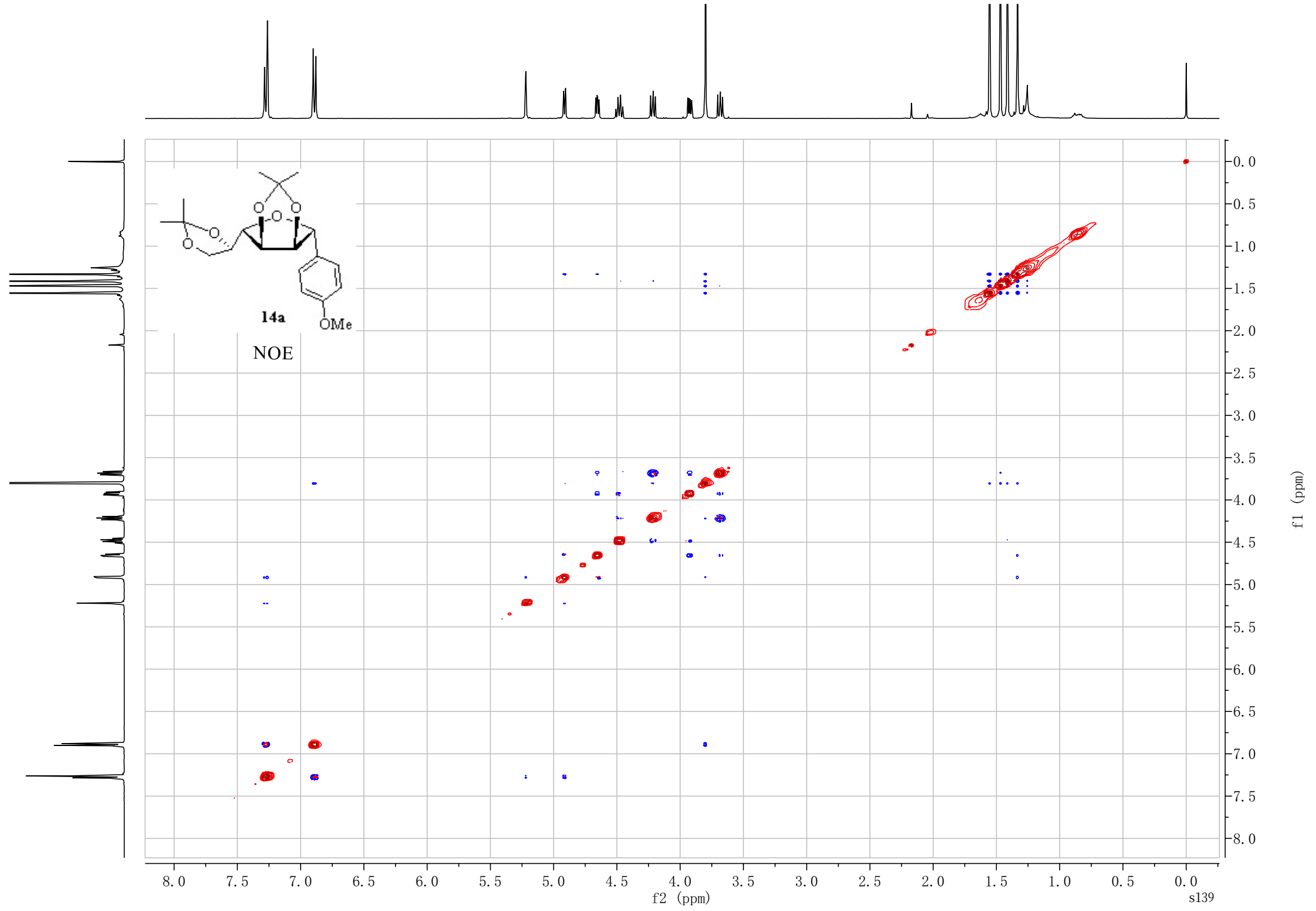
f1 (ppm)

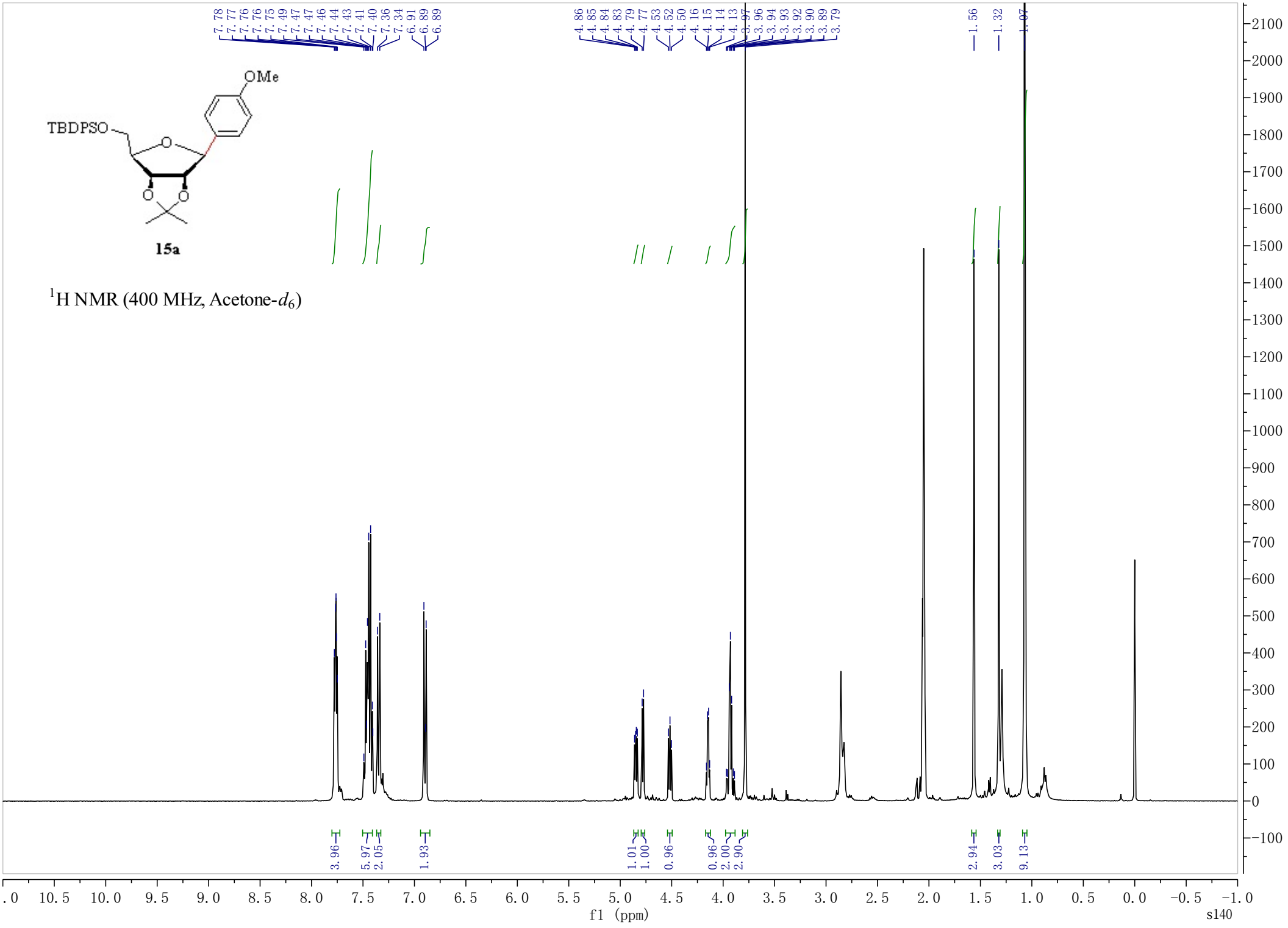
s135

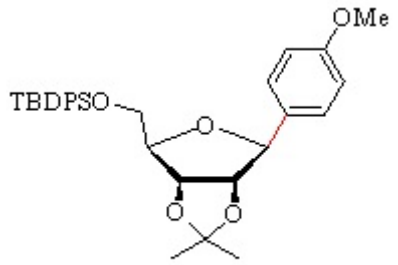

14a
OMe
^{1}H-^{1}H COSY
f2 (ppm)
f1 (ppm)
s136


14a
OMe
HSQC
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)
-40
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
s137


14a
OMe
HMBC
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)
s138
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)

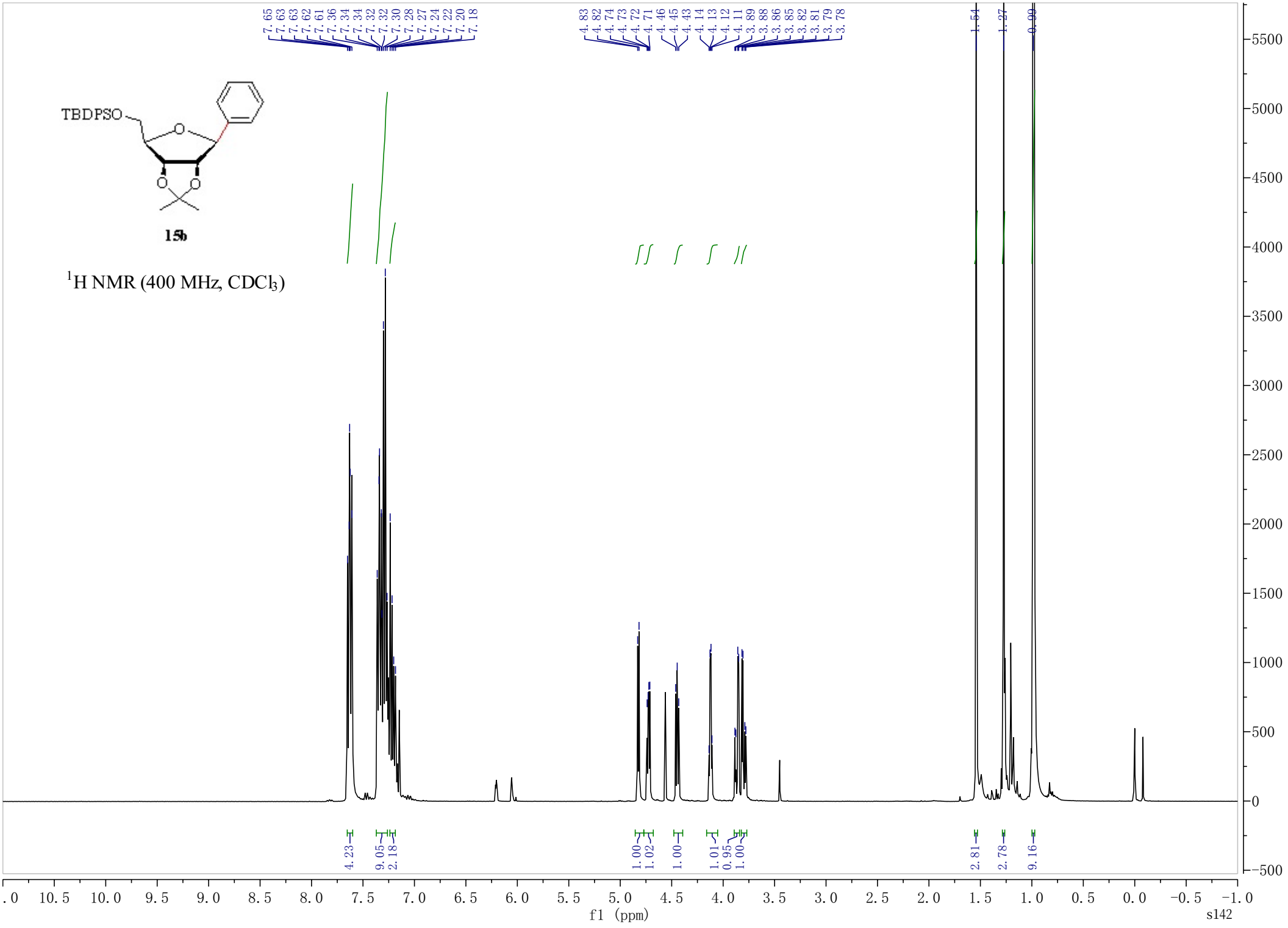

14a
OMe
NOE
f2 (ppm)
f1 (ppm)
s139

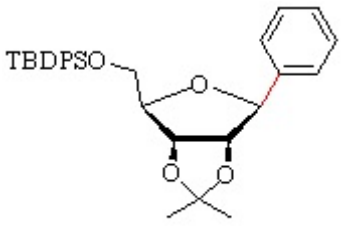

7.78
7.77
7.76
7.76
7.75
7.49
7.47
7.47
7.46
7.44
7.43
7.41
7.40
7.36
7.34
6.91
6.89
6.89
4.86
4.85
4.84
4.83
4.79
4.77
4.53
4.52
4.50
4.16
4.15
4.14
4.13
3.97
3.96
3.94
3.93
3.92
3.90
3.89
3.79
1.56
1.32
1.07
OMe
TBDPSO
O
O
O
O
15a
[1]H NMR (400 MHz, Acetone-d_6)
3.96
5.97
2.05
1.93
1.01
1.00
0.96
0.96
2.00
2.90
2.94
3.03
9.13
f1 (ppm)
s140



15a

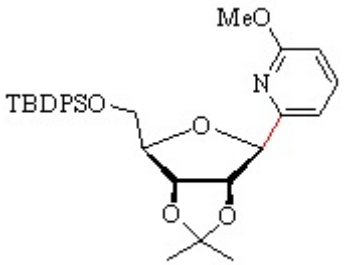
^{13}C NMR (100 MHz, Acetone-d_6)


TBDPSO
15b
^{1}H NMR (400 MHz, CDCl$_3$)
7.65 7.63 7.63 7.62 7.61 7.36 7.34 7.34 7.32 7.32 7.30 7.28 7.27 7.24 7.22 7.20 7.18
4.83 4.82 4.74 4.73 4.72 4.71 4.46 4.45 4.43 4.14 4.13 4.12 4.11 3.89 3.88 3.86 3.85 3.82 3.81 3.79 3.78
1.54 1.27 0.99
4.23 9.05 2.18 1.00 1.02 1.00 1.01 0.95 1.00 2.81 2.78 9.16
f1 (ppm)
s142



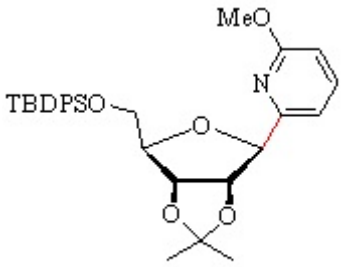
15b

^{13}C NMR (150 MHz, $CDCl_3$)



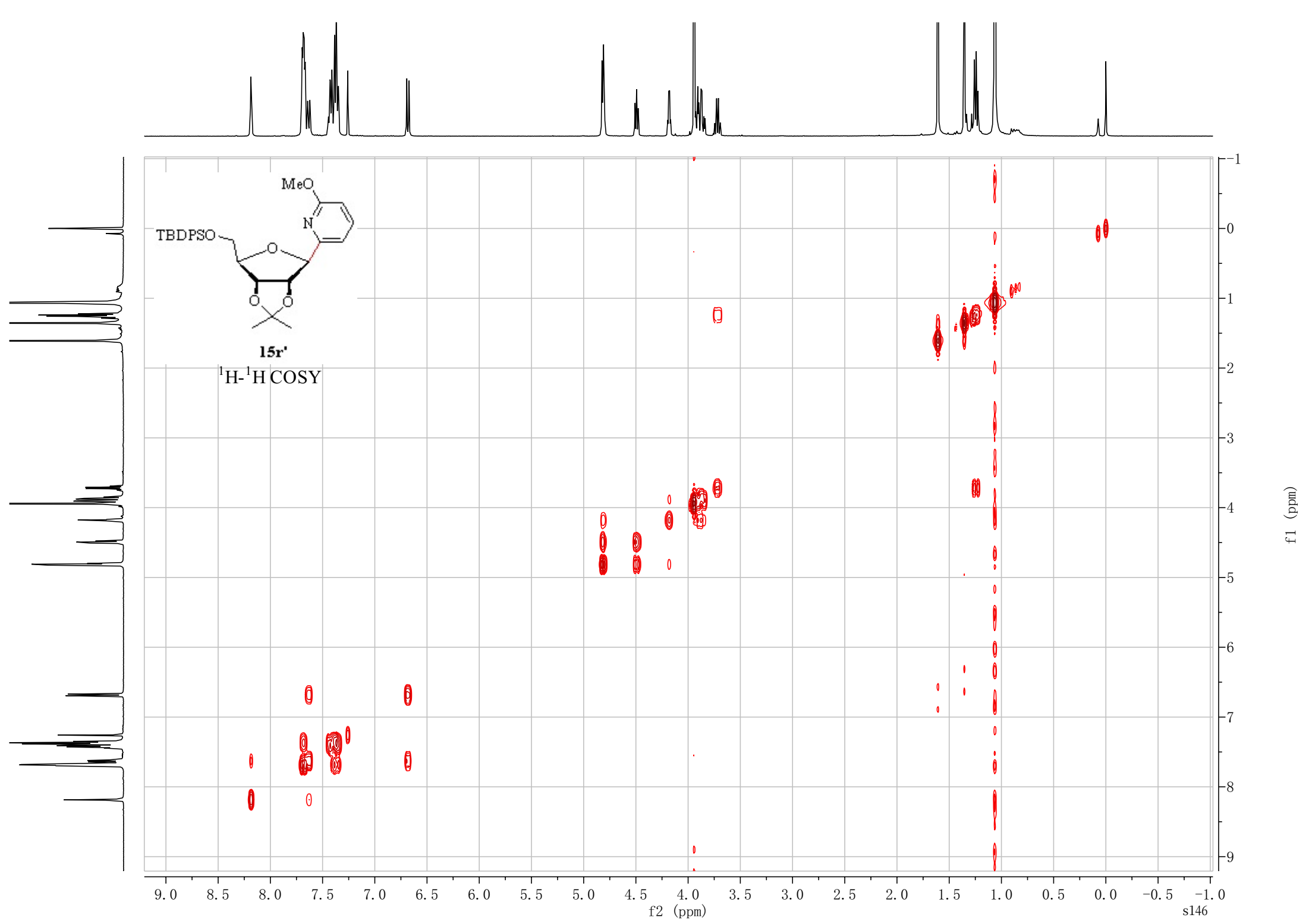
15r'

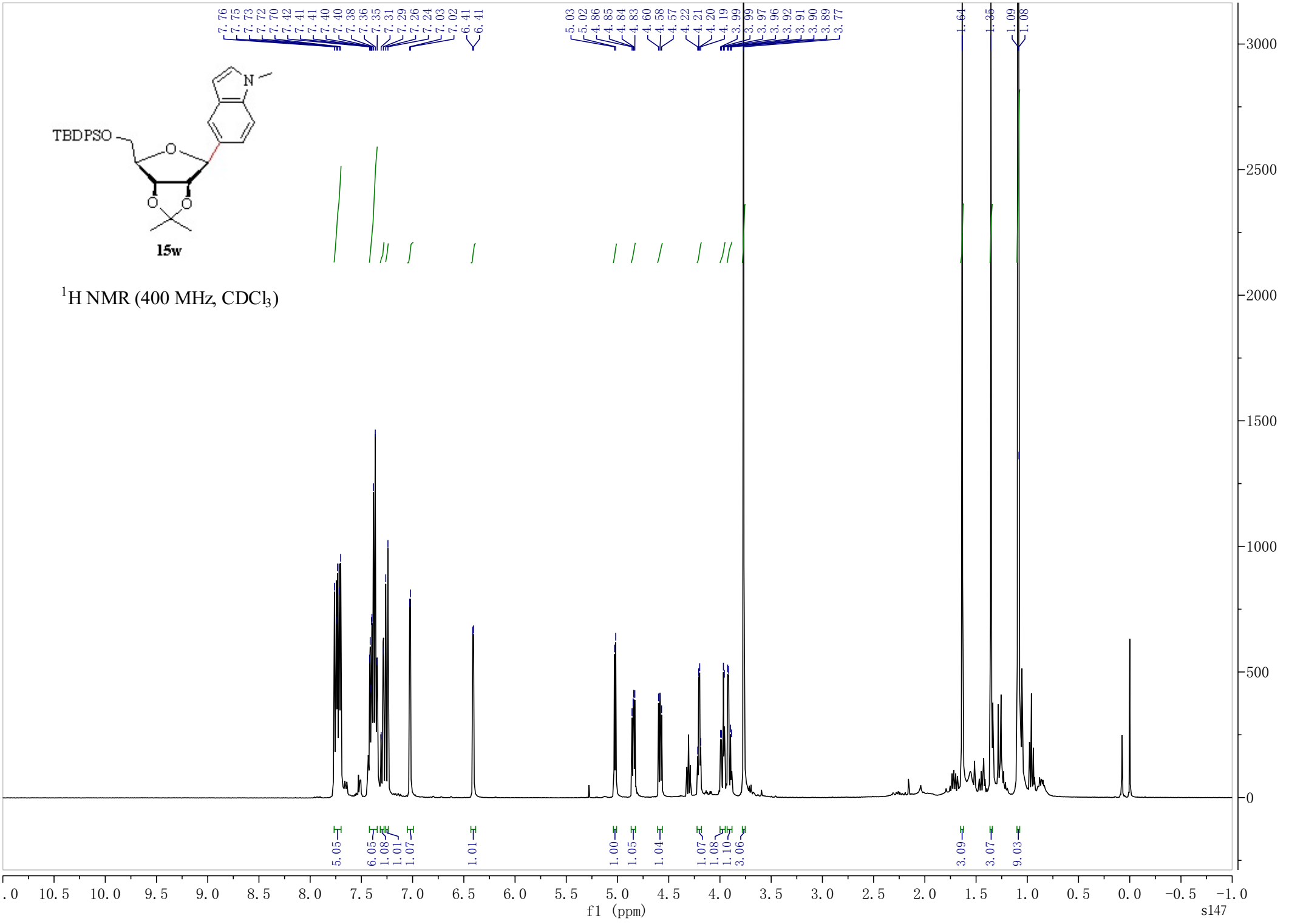
^{1}H NMR (400 MHz, $CDCl_3$)

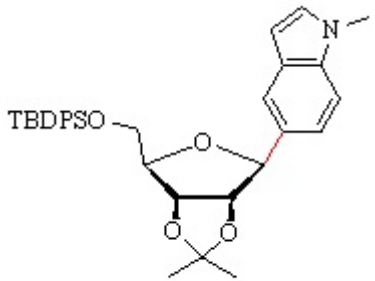


15r'

^{13}C NMR (100 MHz, $CDCl_3$)


MeO
N
TBDPSO
O
O
O
15r'
^{1}H-^{1}H COSY
f2 (ppm)
f1 (ppm)
s146


TBDPSO
O
O
O
N
15w
^{1}H NMR (400 MHz, $CDCl_3$)
7.76 7.75 7.73 7.72 7.70 7.42 7.41 7.41 7.40 7.40 7.38 7.36 7.35 7.31 7.29 7.26 7.24 7.03 7.02 6.41 6.41
5.03 5.02 4.86 4.85 4.84 4.83 4.60 4.58 4.57 4.22 4.21 4.20 4.19 3.99 3.99 3.97 3.96 3.92 3.91 3.90 3.89 3.77
1.64 1.35 1.09 1.08
5.05 6.05 1.08 1.01 1.07 1.01 1.00 1.05 1.04 1.07 1.08 1.10 3.06 3.09 3.07 9.03
3000 2500 2000 1500 1000 500 0
f1 (ppm)
s147



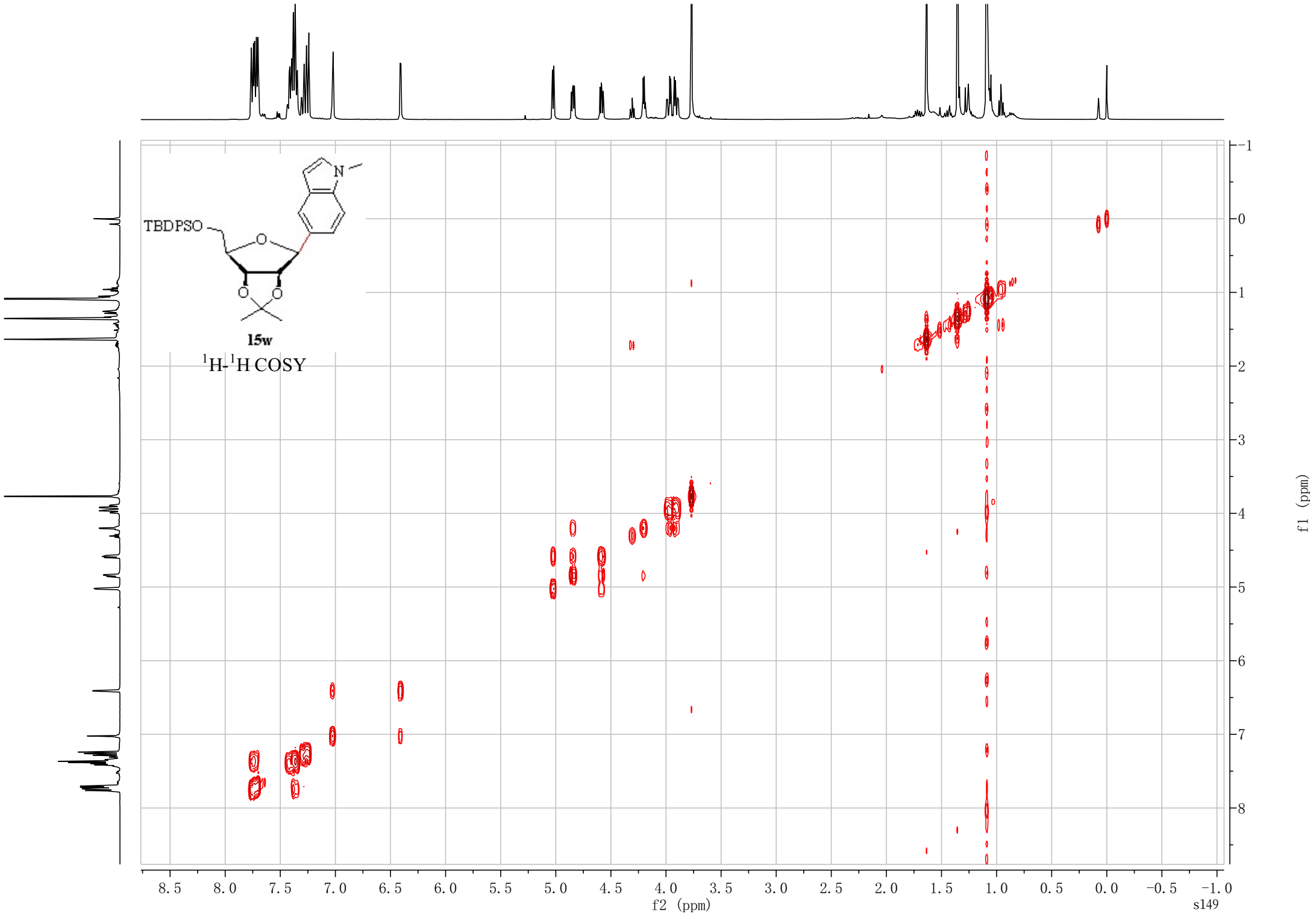
15w

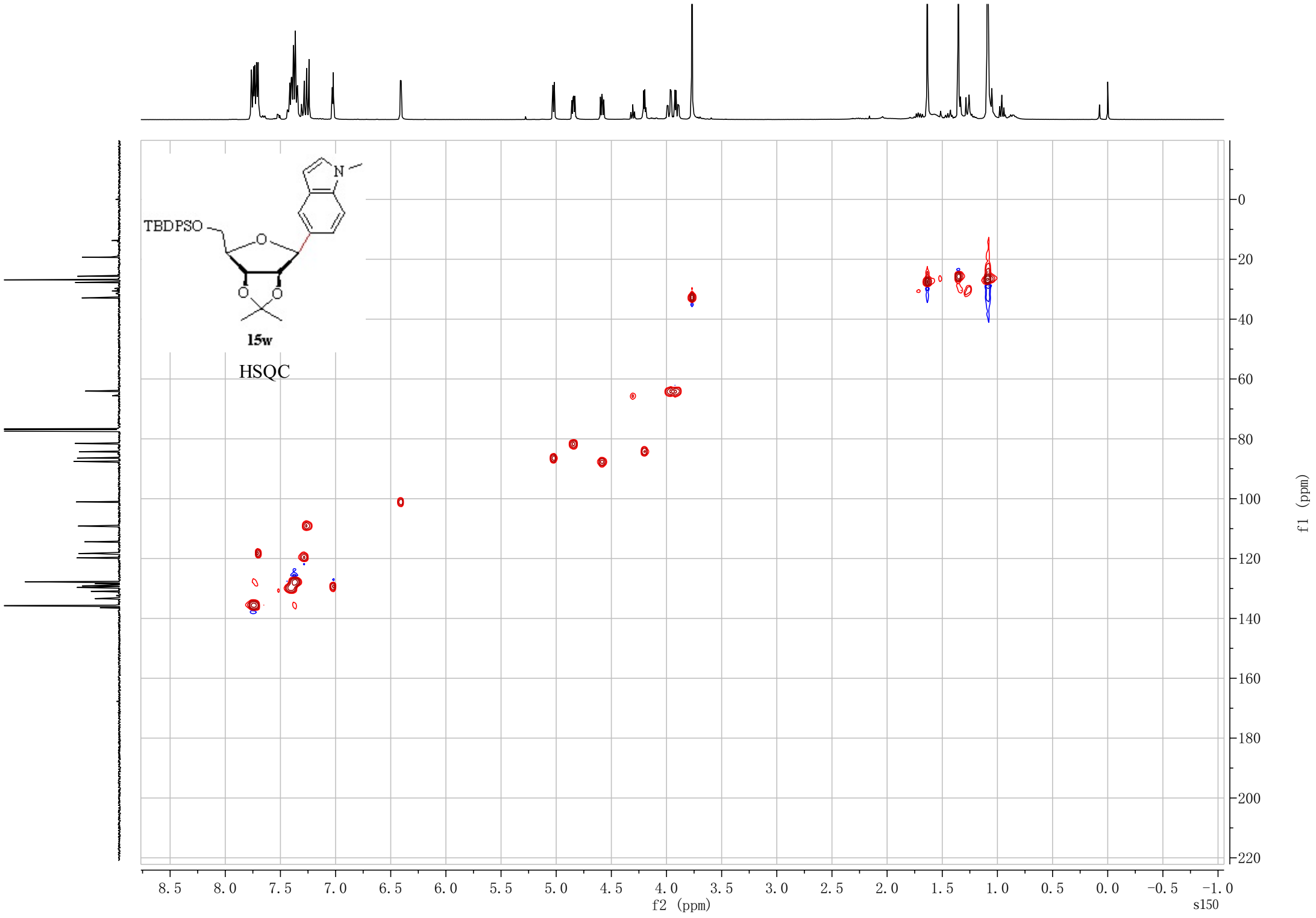
^{13}C NMR (100 MHz, $CDCl_3$)

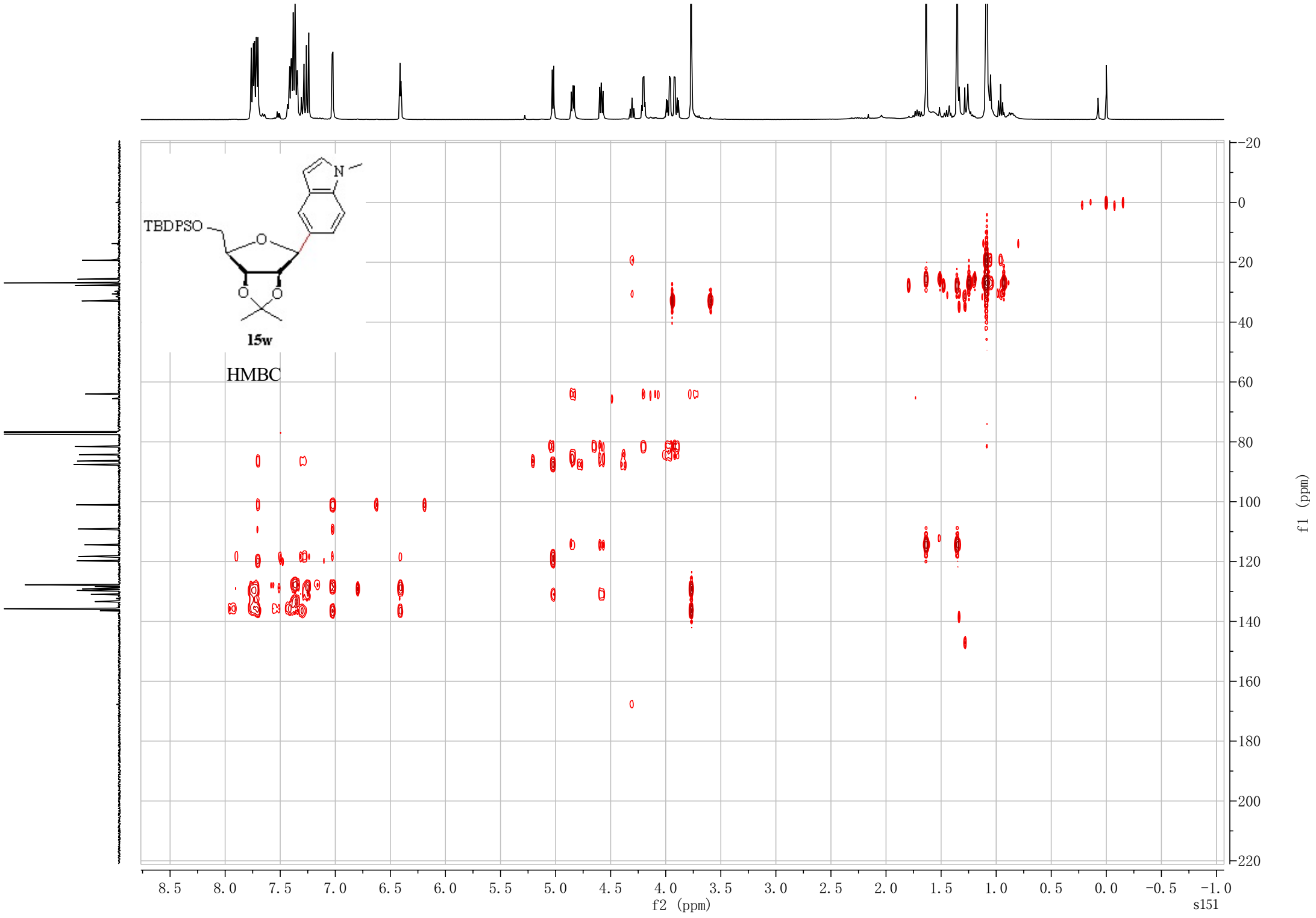
136.47
135.73
133.37
130.95
129.72
129.66
129.13
128.42
127.75
127.72
119.79
118.32
114.39
109.15
101.09
87.54
86.44
84.30
81.56
64.06
32.91
27.73
26.90
25.67
19.33

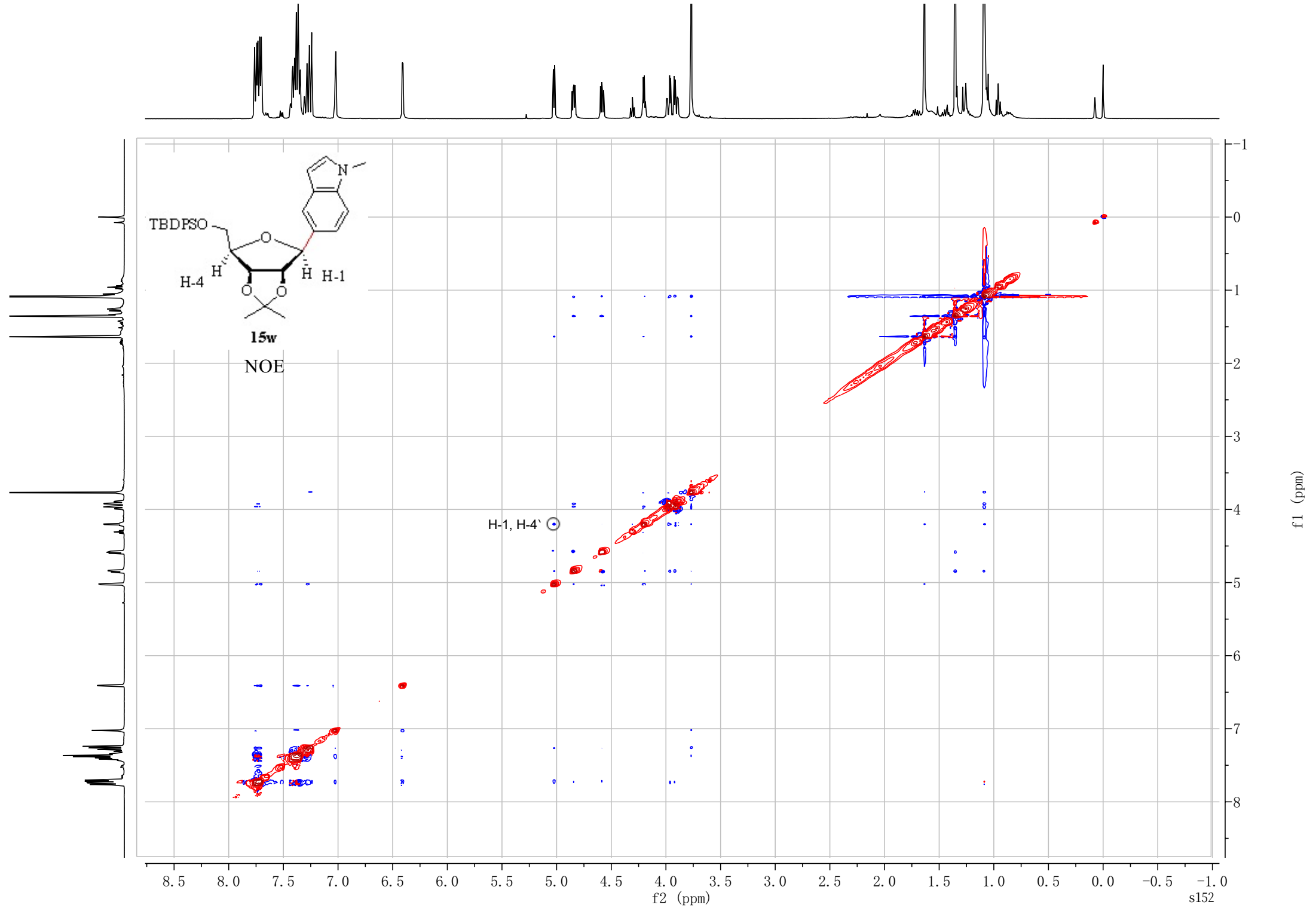
f1 (ppm)

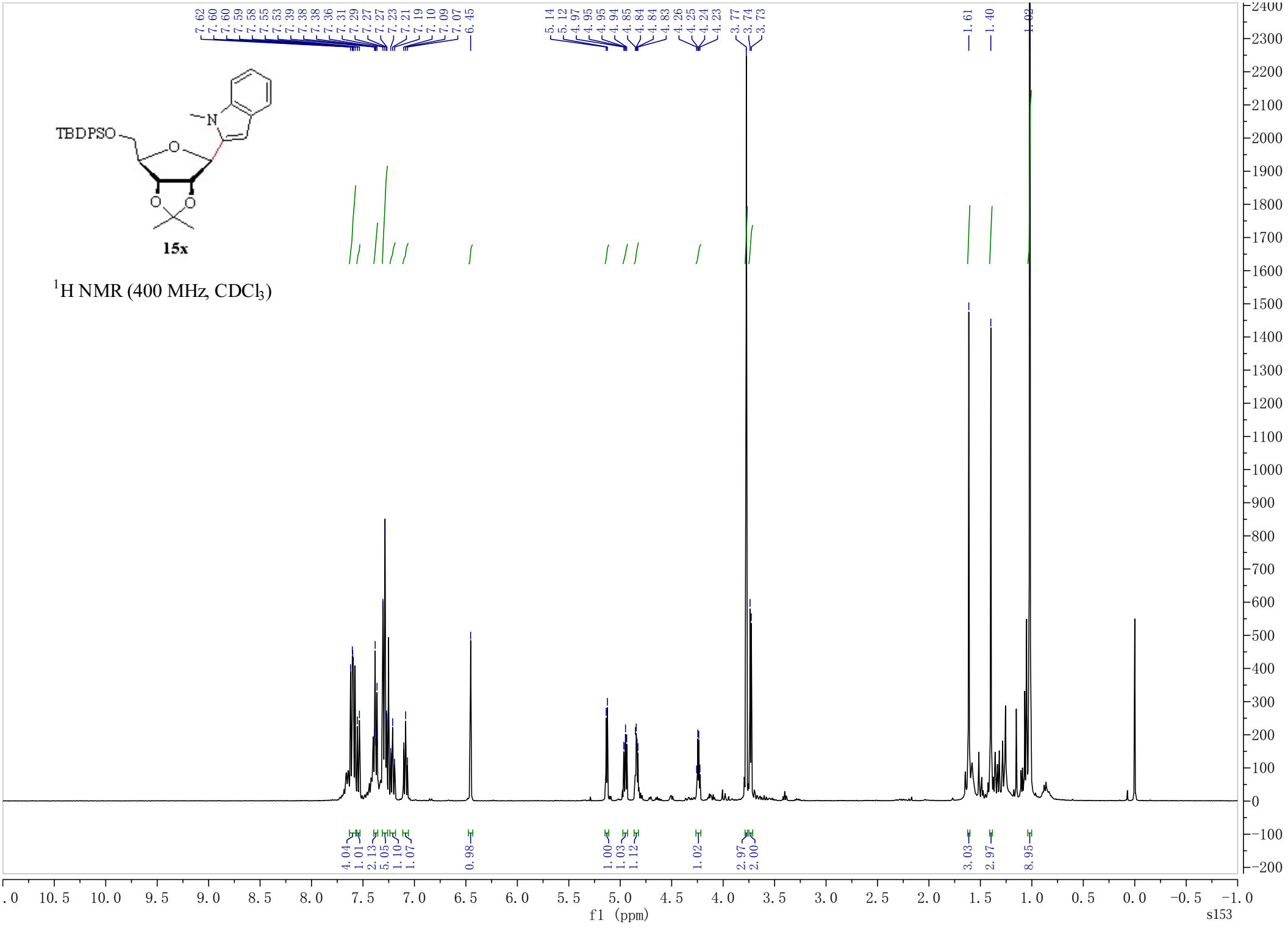
s148

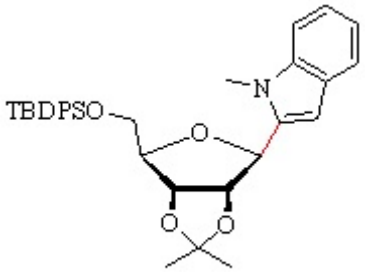

TBDPSO
O
O
O
N
15w
^{1}H-^{1}H COSY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s149
f1 (ppm)
-1
0
1
2
3
4
5
6
7
8


TBDPSO
O
O
O
N
15w
HSQC
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s150


TBDPSO
O
O
O
N
15w
HMBC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s151
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)


TBDPSO
O
H
H-4
H
H-1
O
O
N
15w
NOE
H-1, H-4`
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s152
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)


TBDPSO
O
N
O
O
15x
^{1}H NMR (400 MHz, $CDCl_3$)
7.62 7.60 7.60 7.59 7.58 7.55 7.53 7.39 7.38 7.38 7.36 7.31 7.29 7.27 7.27 7.23 7.21 7.19 7.10 7.09 7.07 6.45
5.14 5.12 4.97 4.95 4.95 4.94 4.85 4.84 4.84 4.83 4.26 4.25 4.24 4.23 3.77 3.74 3.73
1.61 1.40 1.02
4.04 1.01 2.13 5.05 1.10 1.07 0.98 1.00 1.03 1.12 1.02 2.97 2.00 3.03 2.97 8.95
f1 (ppm)
s153



15x

^{13}C NMR (100 MHz, $CDCl_3$)

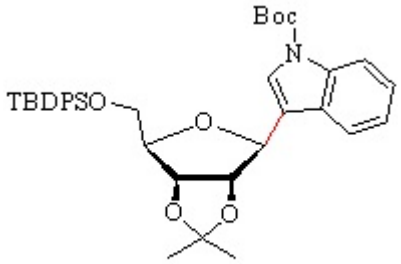
138.23
137.44
135.61
133.21
133.17
129.70
127.67
127.27
121.78
120.82
119.45
114.38
109.03
99.79
84.97
84.12
81.99
79.72
63.85
30.49
27.46
26.82
25.50
19.24

2500
2000
1500
1000
500
0

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20

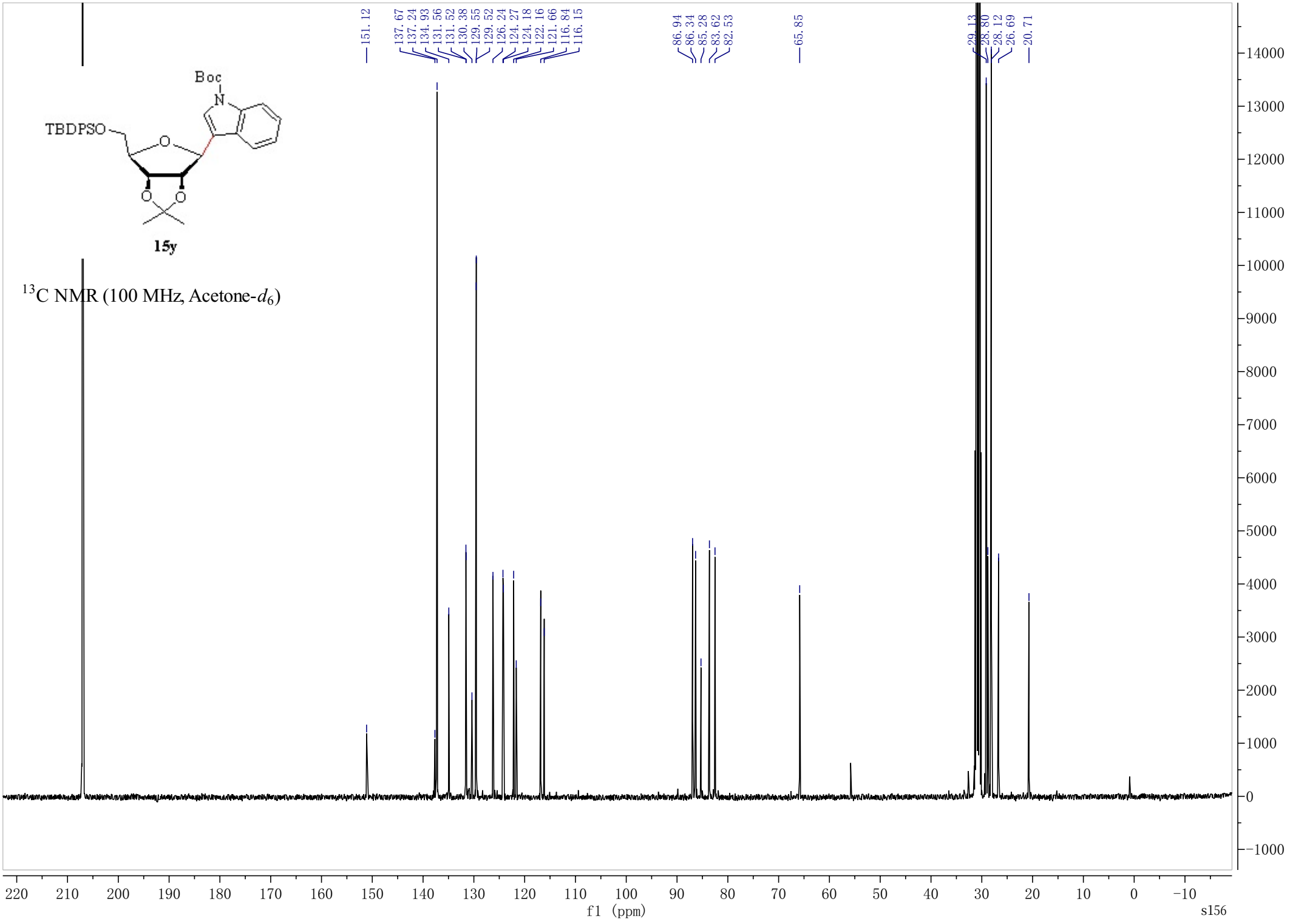
f1 (ppm)

s154



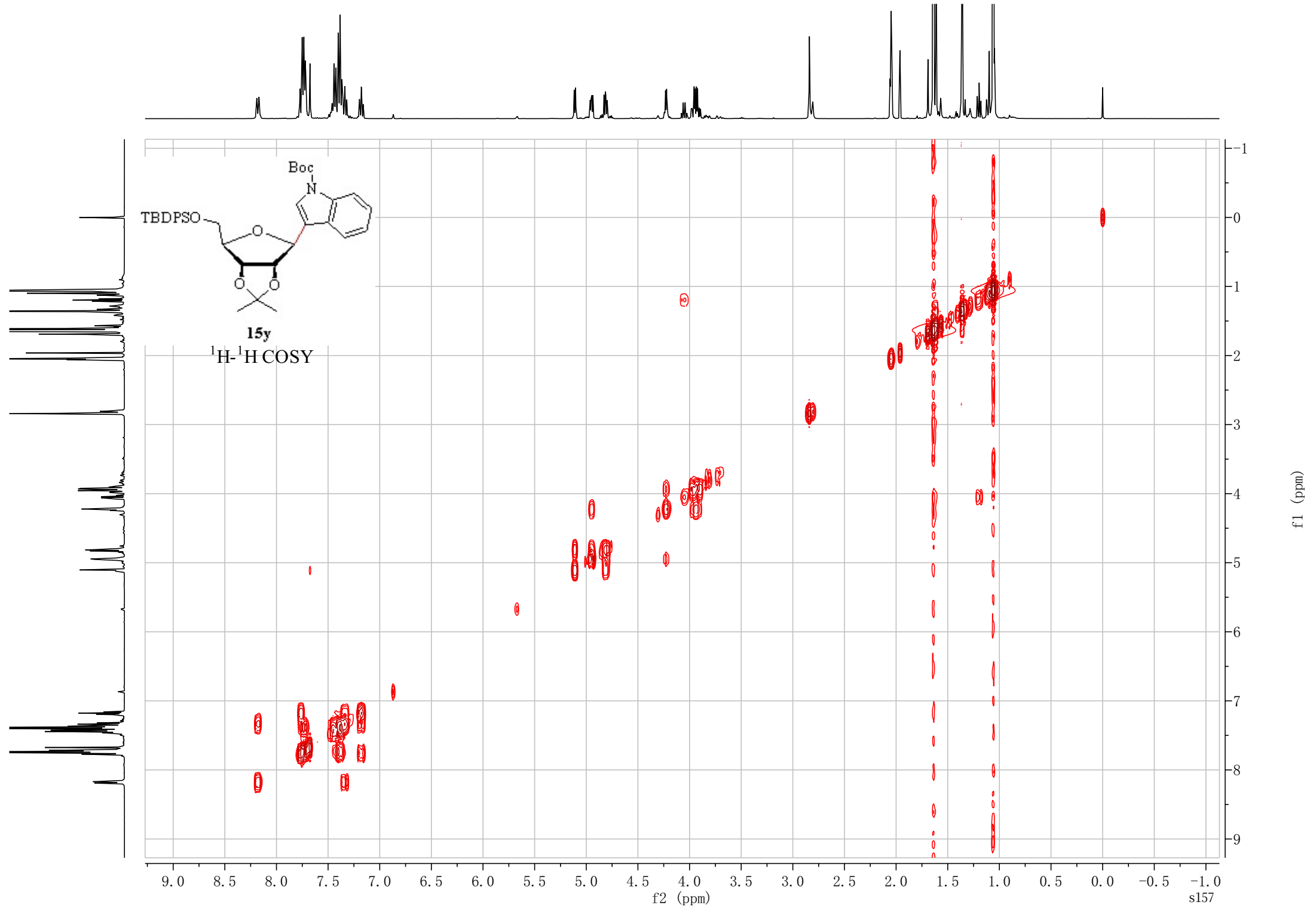
15y

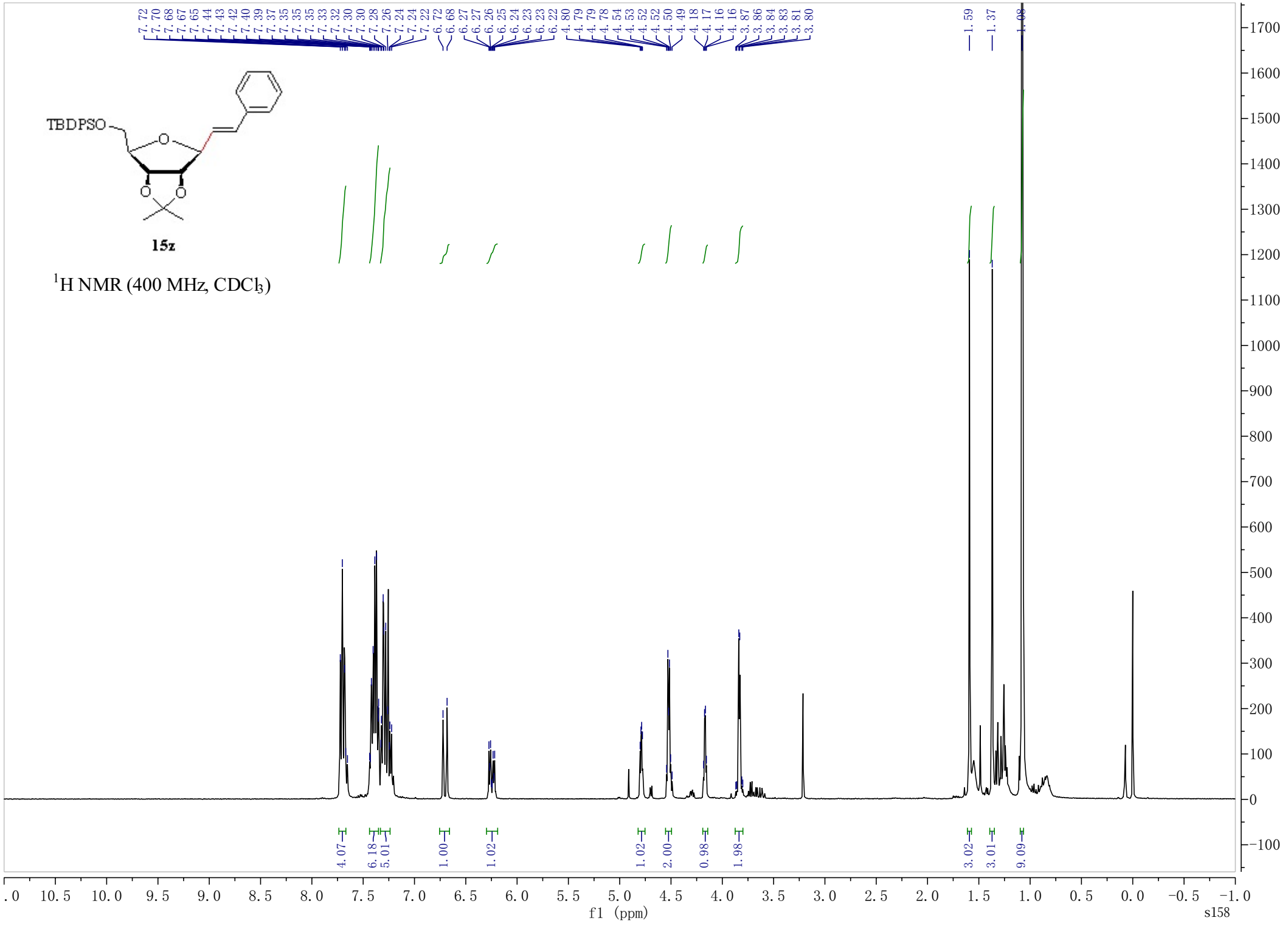
^{1}H NMR (400 MHz, Acetone-d_6)

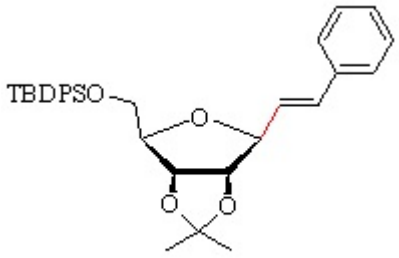


15y

^{13}C NMR (100 MHz, Acetone-d_6)


Boc
N
TBDPSO
O
O
O
15y
^{1}H-^{1}H COSY
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s157
-1
0
1
2
3
4
5
6
7
8
9
f1 (ppm)


7.72 7.70 7.68 7.67 7.65 7.44 7.43 7.42 7.40 7.39 7.37 7.35 7.35 7.35 7.33 7.32 7.30 7.30 7.28 7.26 7.24 7.24 7.22 6.72 6.68 6.27 6.26 6.25 6.24 6.23 6.23 6.22 4.80 4.79 4.79 4.78 4.54 4.53 4.52 4.52 4.50 4.49 4.18 4.17 4.16 4.16 3.87 3.86 3.84 3.83 3.81 3.80 1.59 1.37 1.08
TBDPSO
O
O
O
15z
1H NMR (400 MHz, CDCl3)
4.07 6.18 5.01 1.00 1.02 1.02 2.00 0.98 1.98 3.02 3.01 9.09
f1 (ppm)
s158



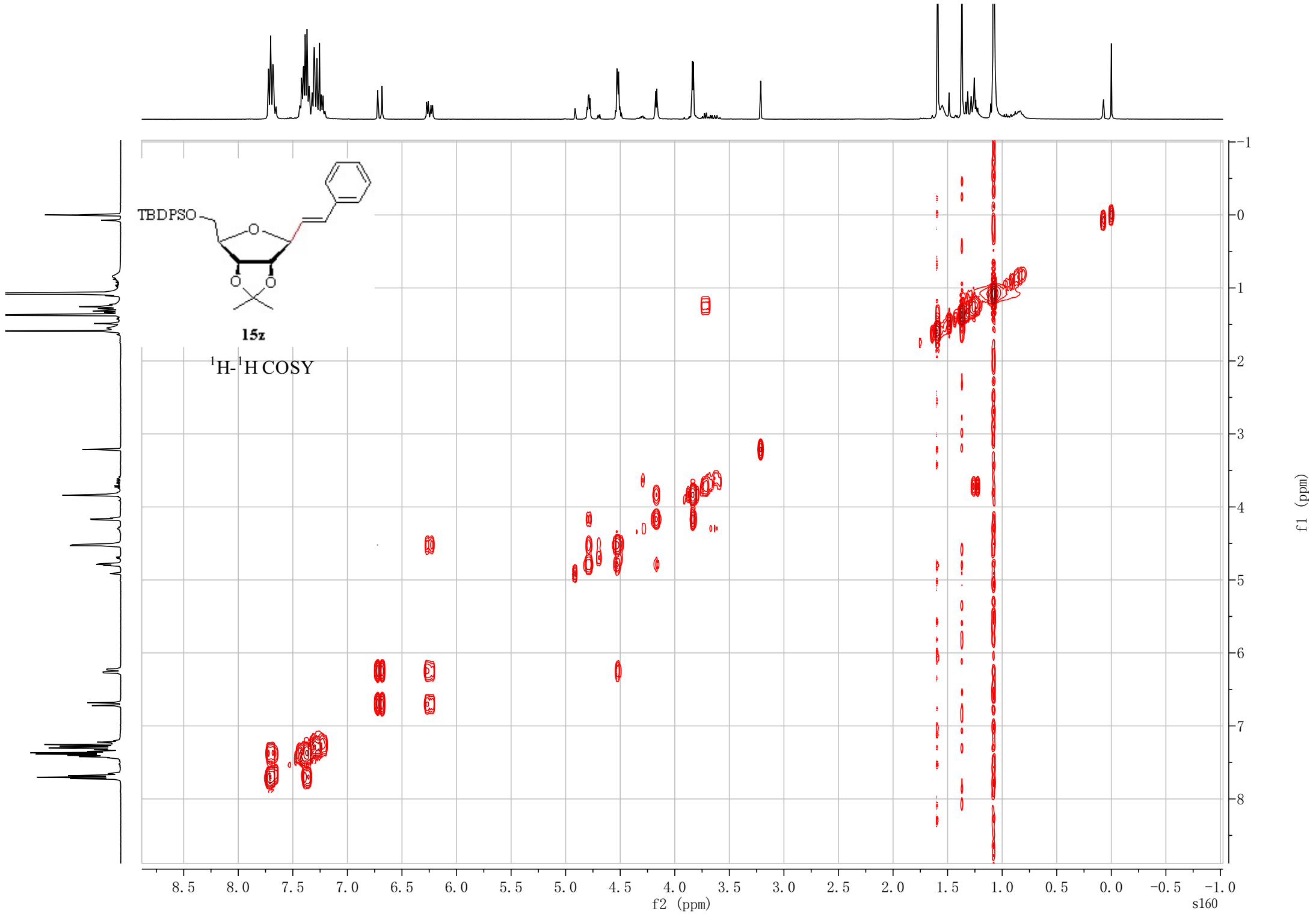
15z

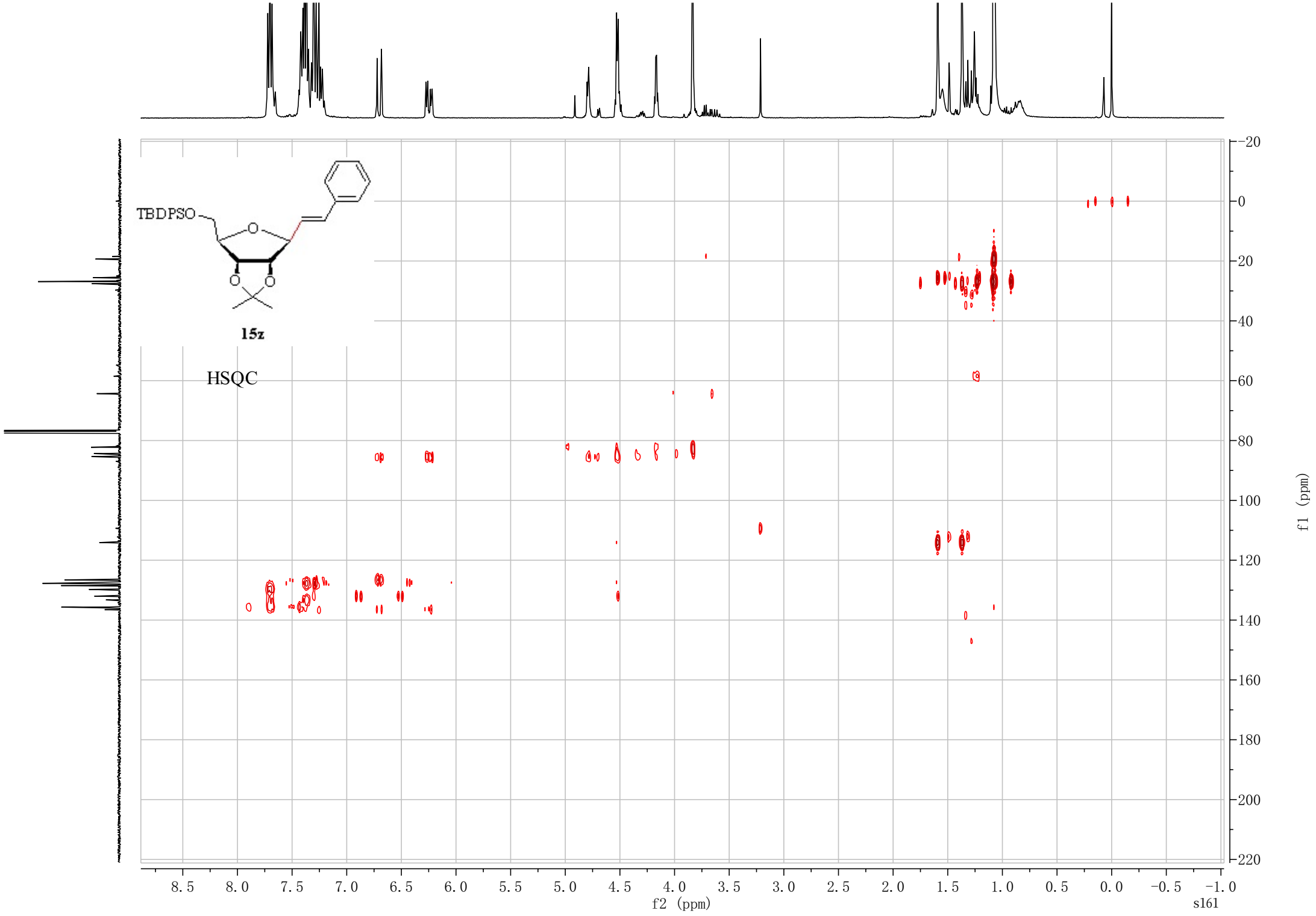
^{13}C NMR (100 MHz, $CDCl_3$)

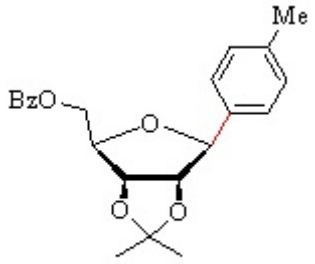
136.54
135.68
135.65
135.58
133.27
133.23
132.01
129.79
129.75
128.50
127.76
127.73
127.44
126.58
114.09
85.56
85.37
84.36
82.24
64.32
27.57
26.88
25.58
19.34

f1 (ppm)

s159

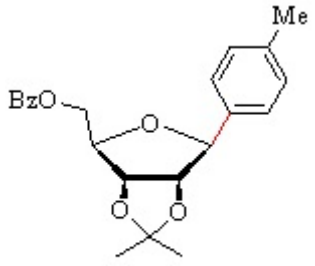

TBDPSO
15z
^{1}H-^{1}H COSY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s160
f1 (ppm)


TBDPSO
15z
HSQC
f2 (ppm)
f1 (ppm)
s161



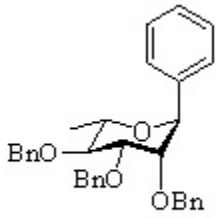
16c

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



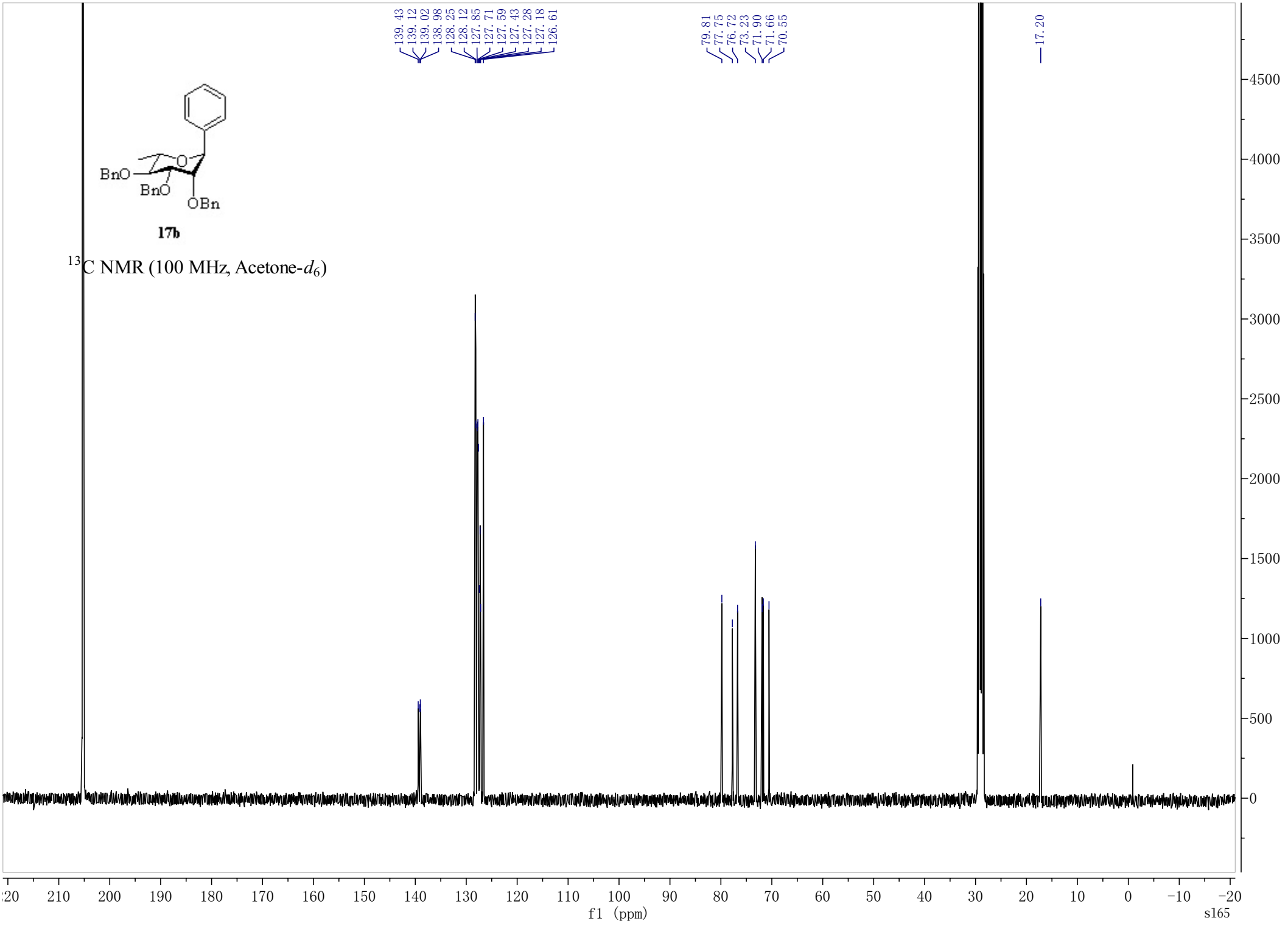
16c

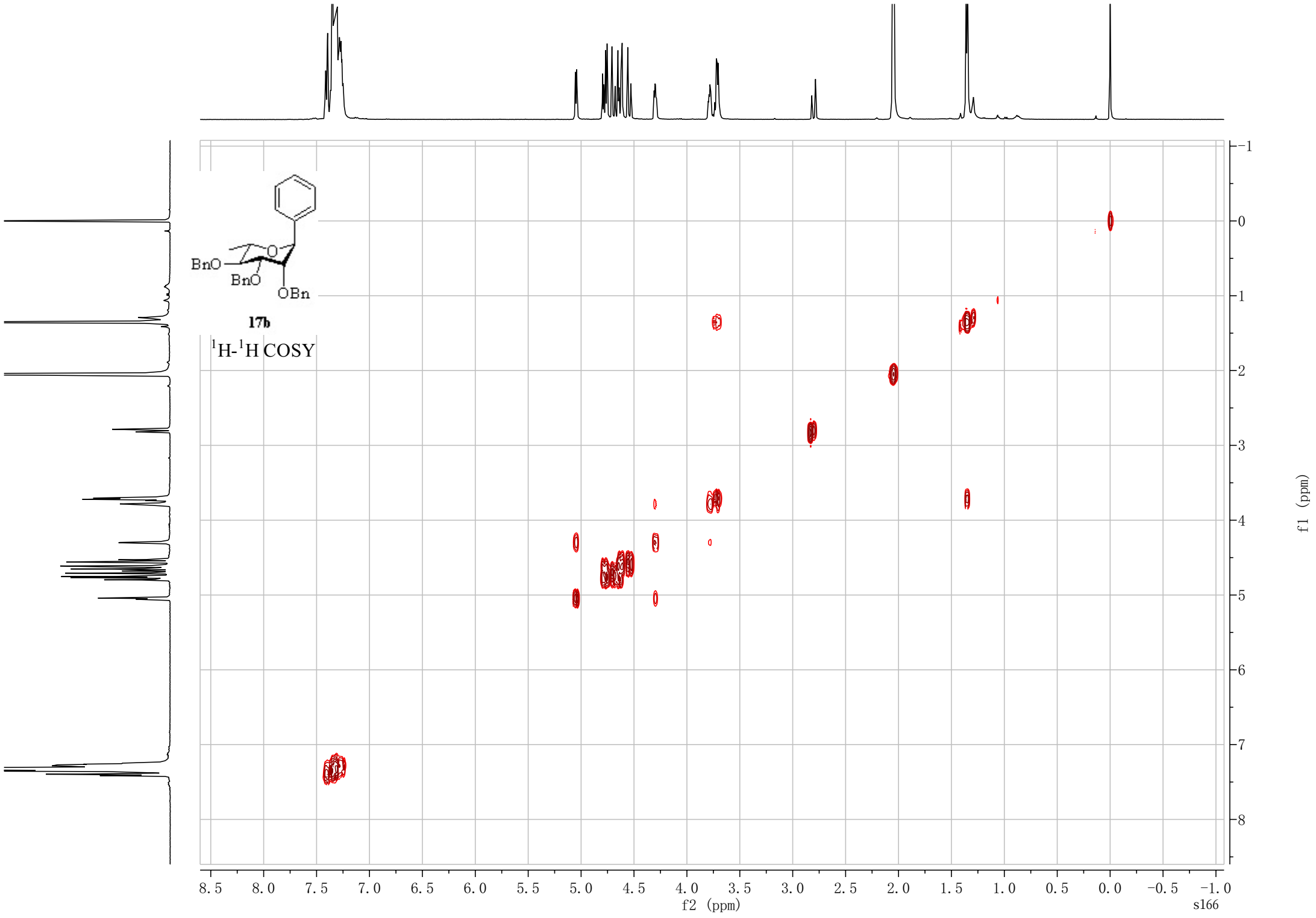
^{13}C NMR (100 MHz, $CDCl_3$)

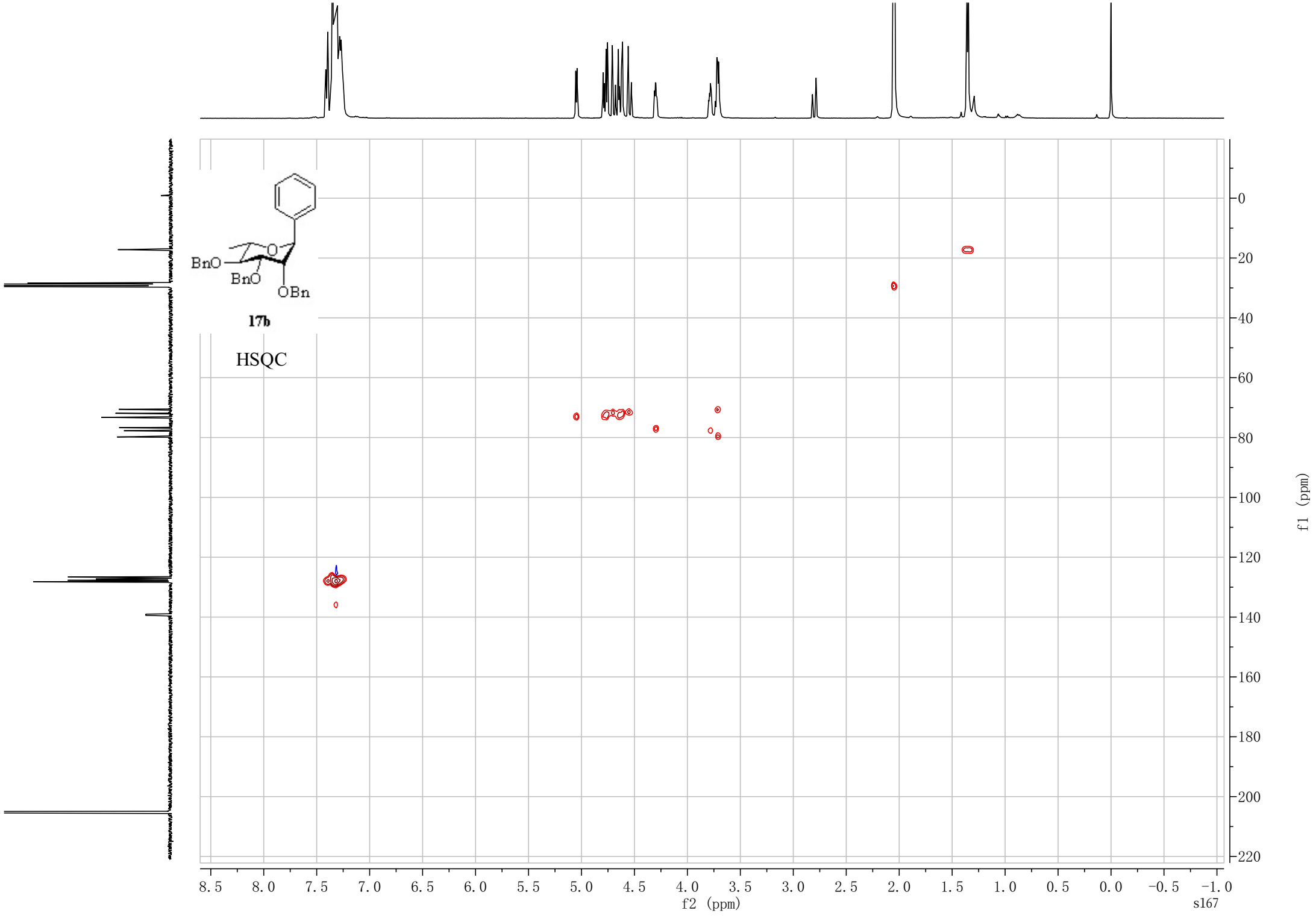


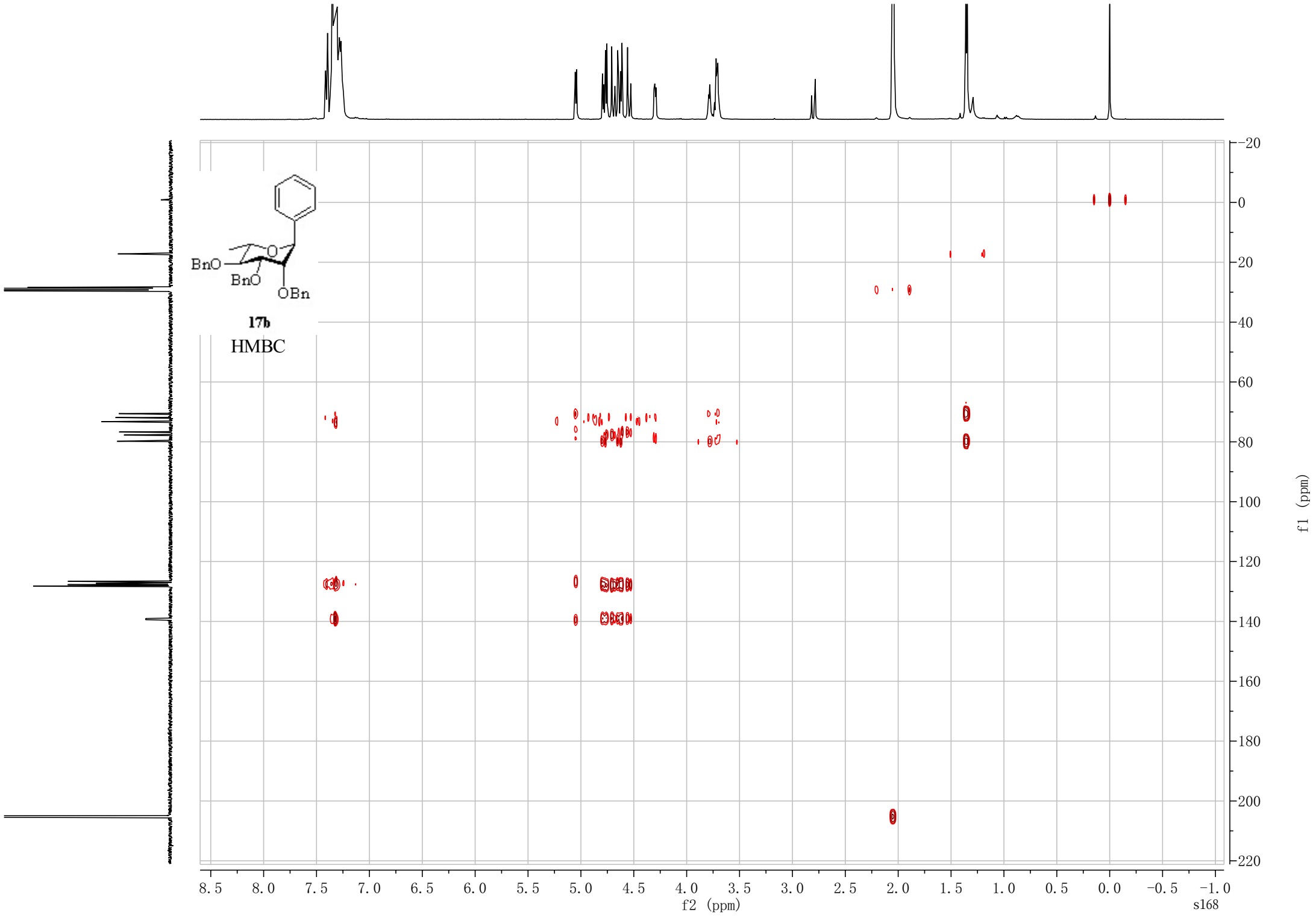
17b

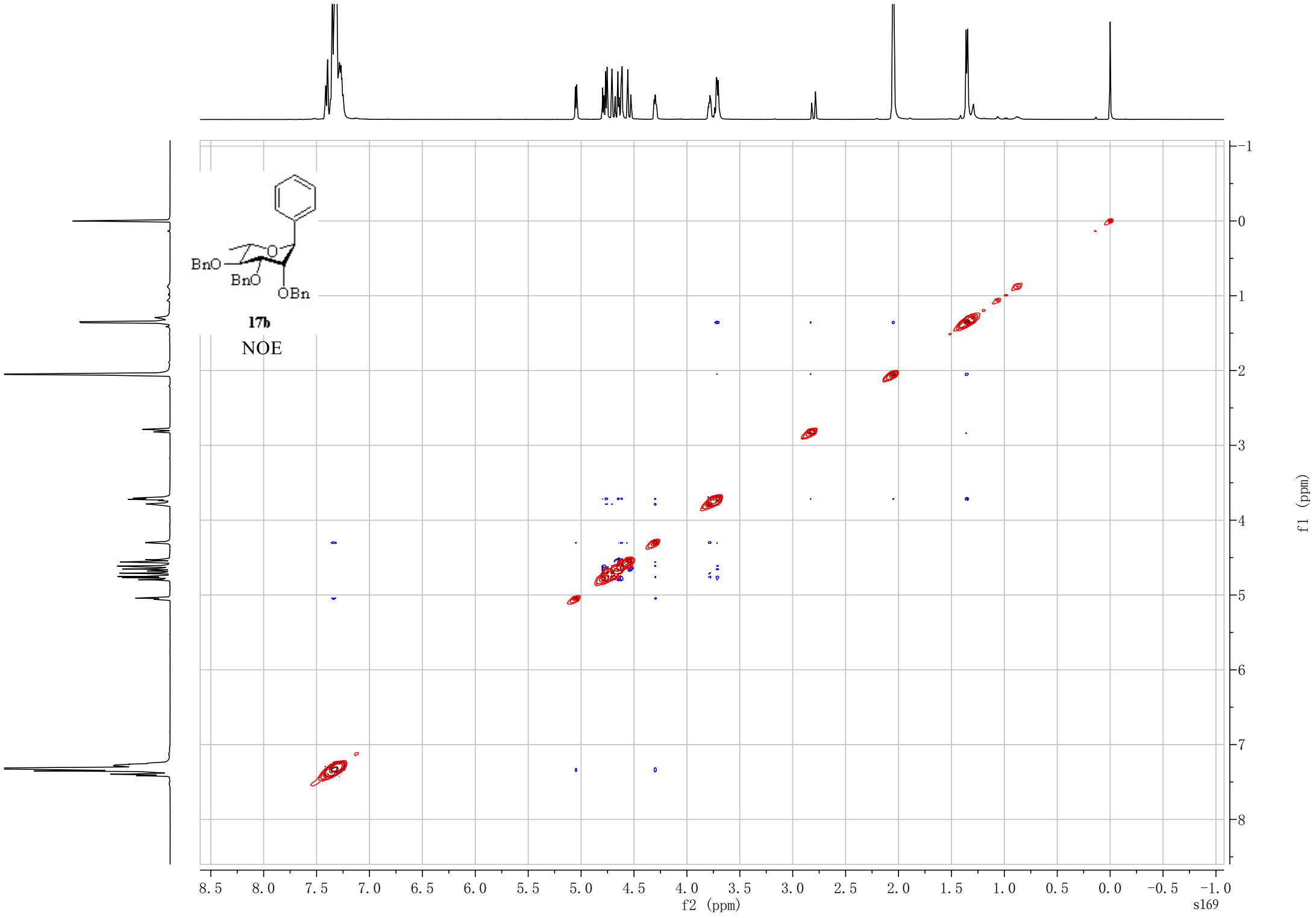
^{1}H NMR (400 MHz, Acetone-d_6)

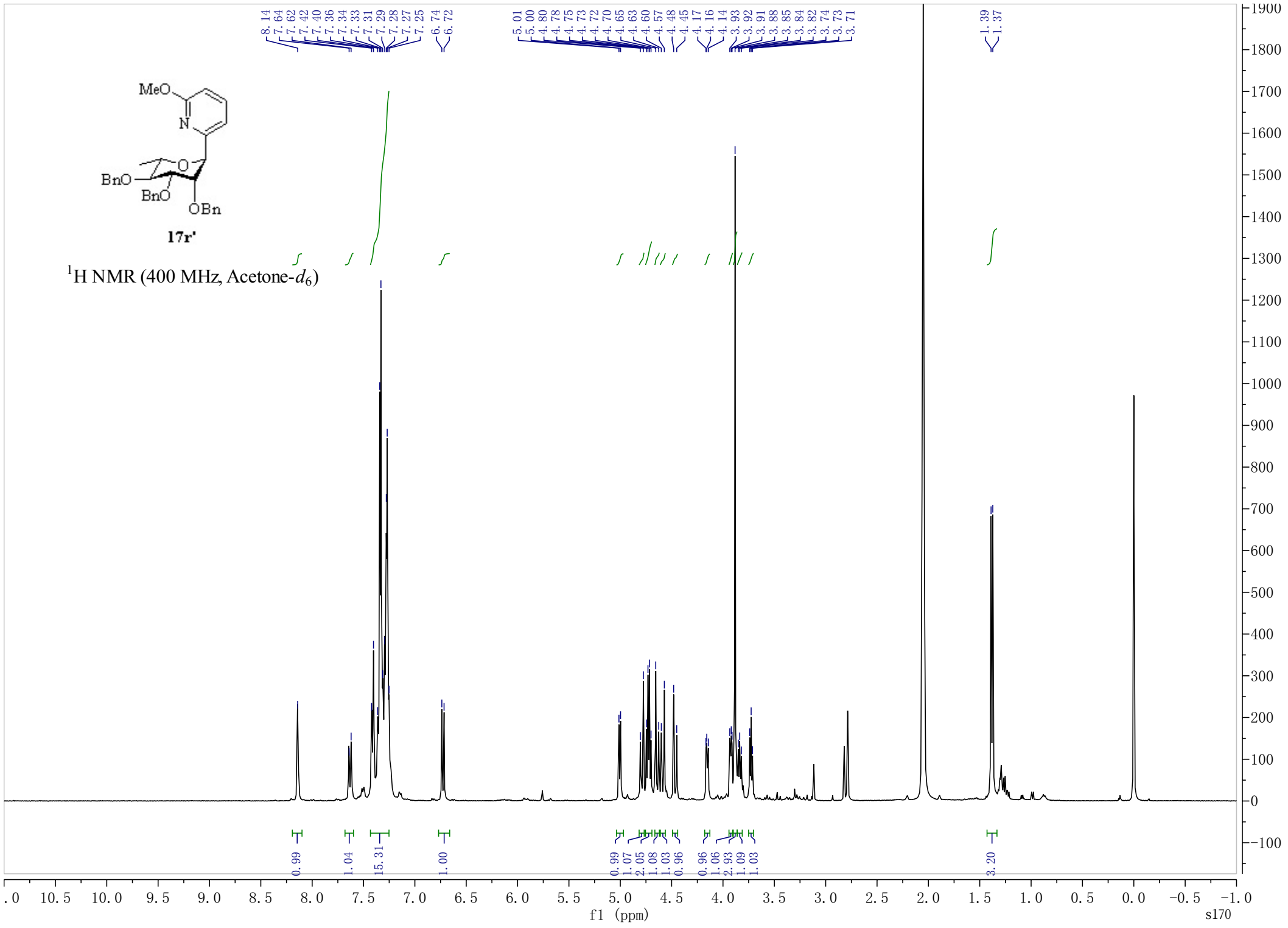

139.43
139.12
139.02
138.98
128.25
128.12
127.85
127.71
127.59
127.43
127.28
127.18
126.61
79.81
77.75
76.72
73.23
71.90
71.66
70.55
17.20
BnO
BnO
OBn
O
17b
13C NMR (100 MHz, Acetone-d6)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
s165

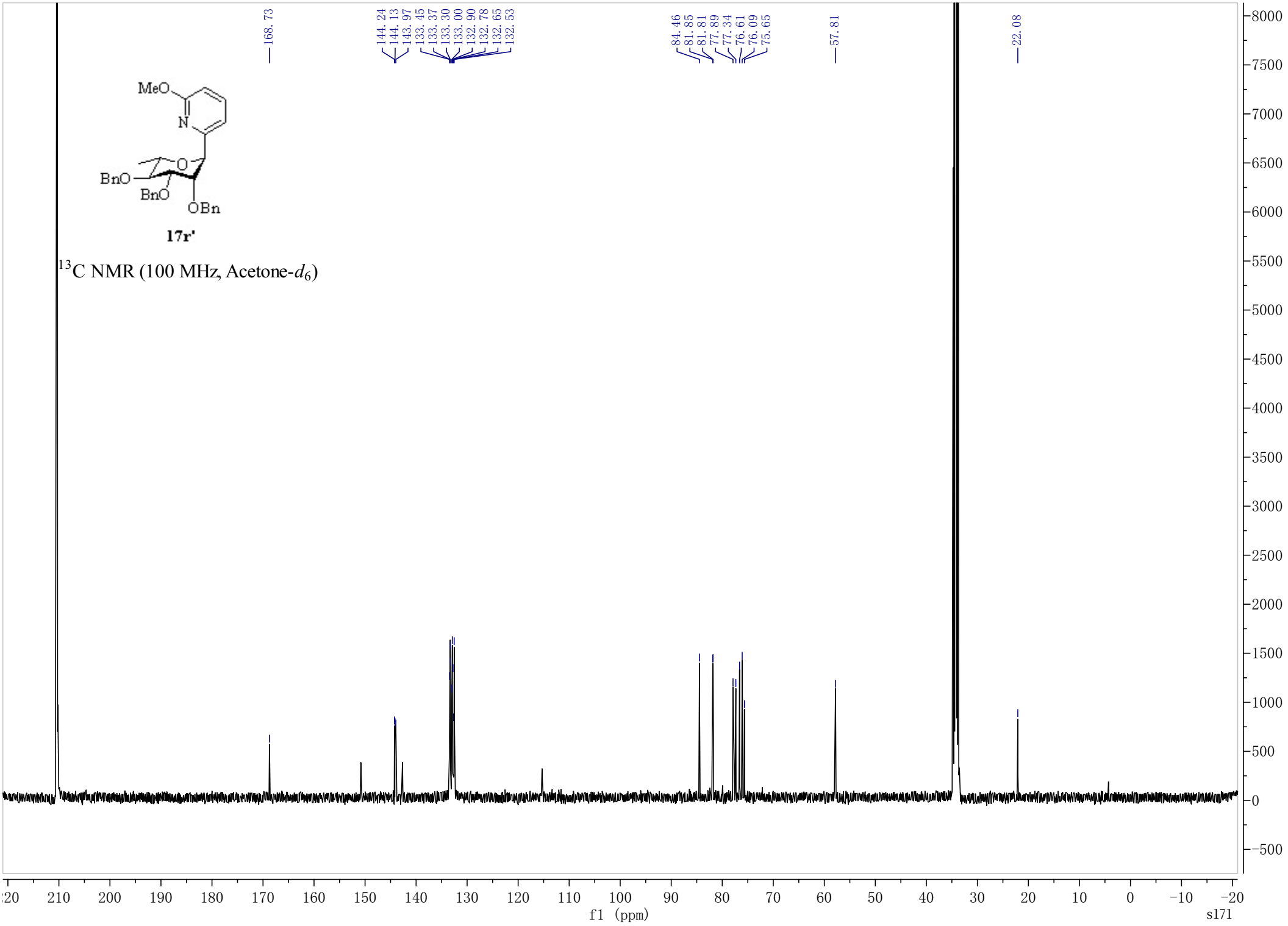

BnO
BnO
OBn
17b
^{1}H-^{1}H COSY
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8
f1 (ppm)
s166

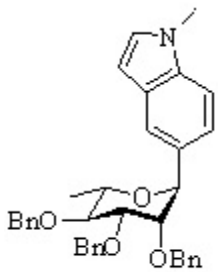

BnO
BnO
OBn
17b
HSQC
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
s167


BnO
BnO
OBn
17b
HMBC
f2 (ppm)
f1 (ppm)
s168


BnO
BnO
OBn
17b
NOE
f2 (ppm)
f1 (ppm)
s169

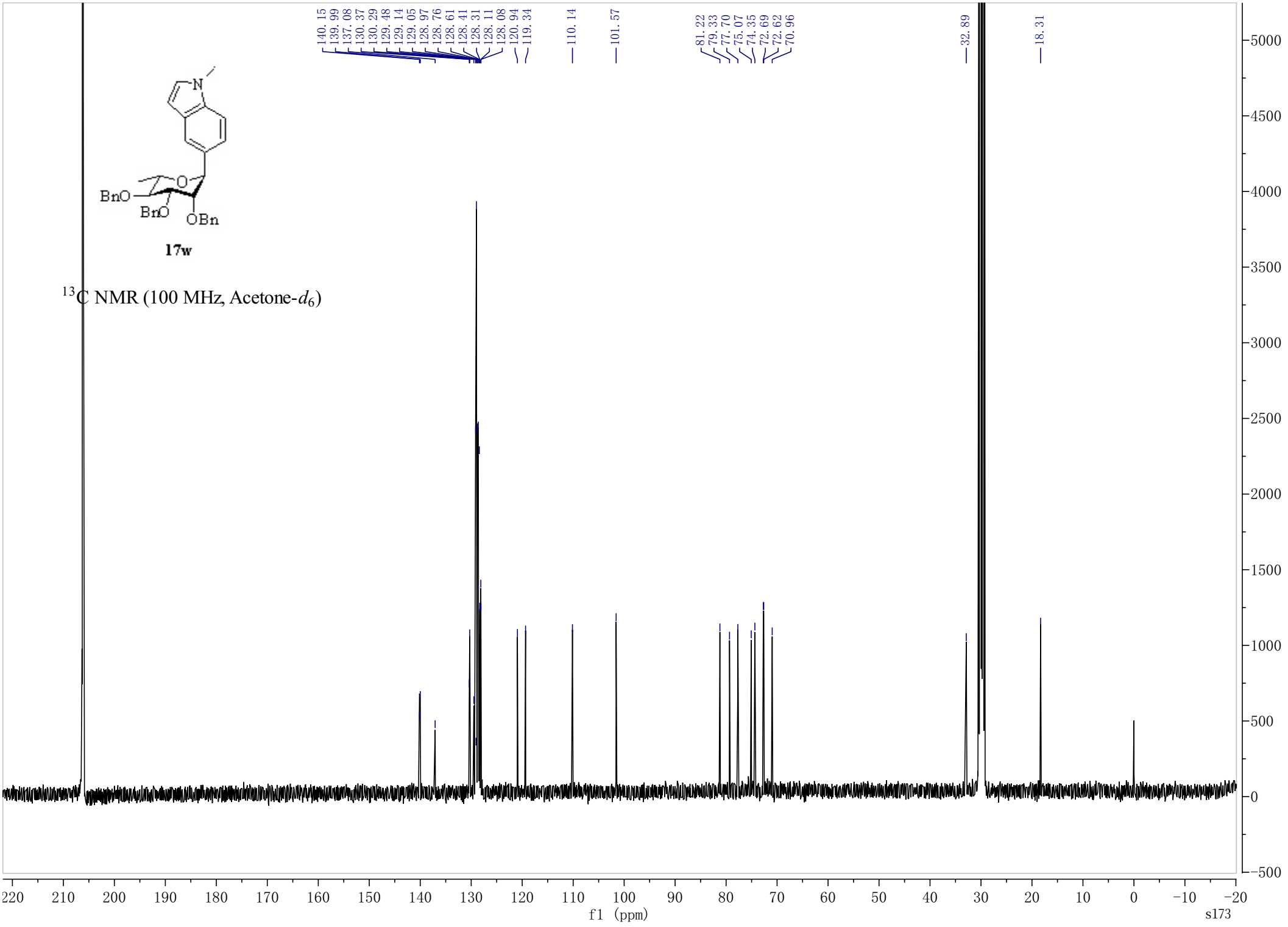

MeO
N
O
BnO
BnO
OBn
17r'
^{1}H NMR (400 MHz, Acetone-d_6)
8.14 7.64 7.62 7.42 7.40 7.36 7.34 7.33 7.31 7.29 7.28 7.27 7.25 6.74 6.72
5.01 5.00 4.80 4.78 4.75 4.73 4.72 4.70 4.65 4.63 4.60 4.57 4.48 4.45 4.17 4.16 4.14 3.93 3.92 3.91 3.88 3.85 3.84 3.82 3.74 3.73 3.71
1.39 1.37
0.99 1.04 15.31 1.00 0.99 1.07 2.05 1.08 1.03 0.96 0.96 1.06 2.93 1.09 1.03 3.20
f1 (ppm)
s170

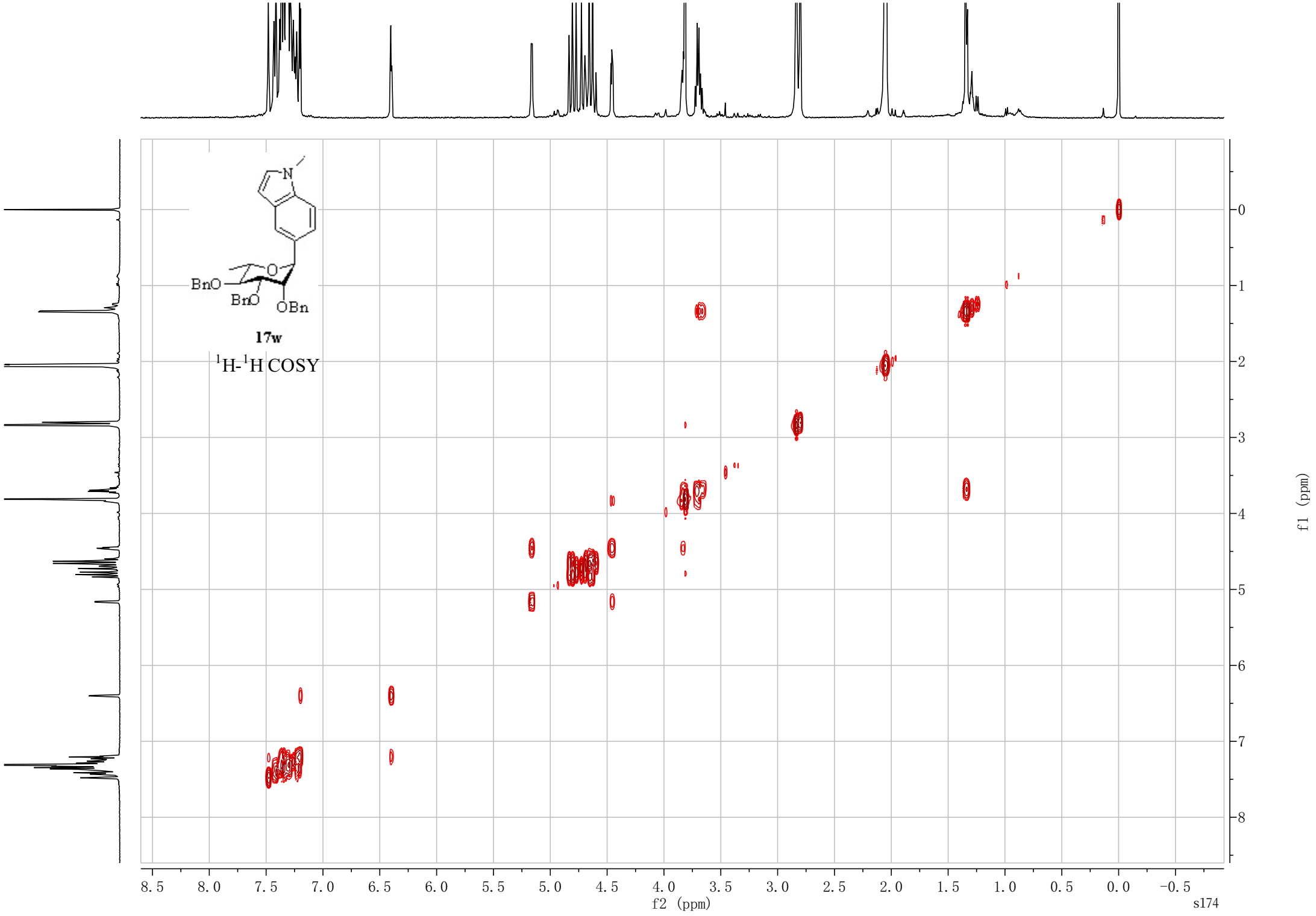

168.73
144.24
144.13
143.97
133.45
133.37
133.30
133.00
132.90
132.78
132.65
132.53
84.46
81.85
81.81
77.89
77.34
76.61
76.09
75.65
57.81
22.08
MeO
N
O
BnO
BnO
OBn
17r'
13C NMR (100 MHz, Acetone-d6)
f1 (ppm)
s171

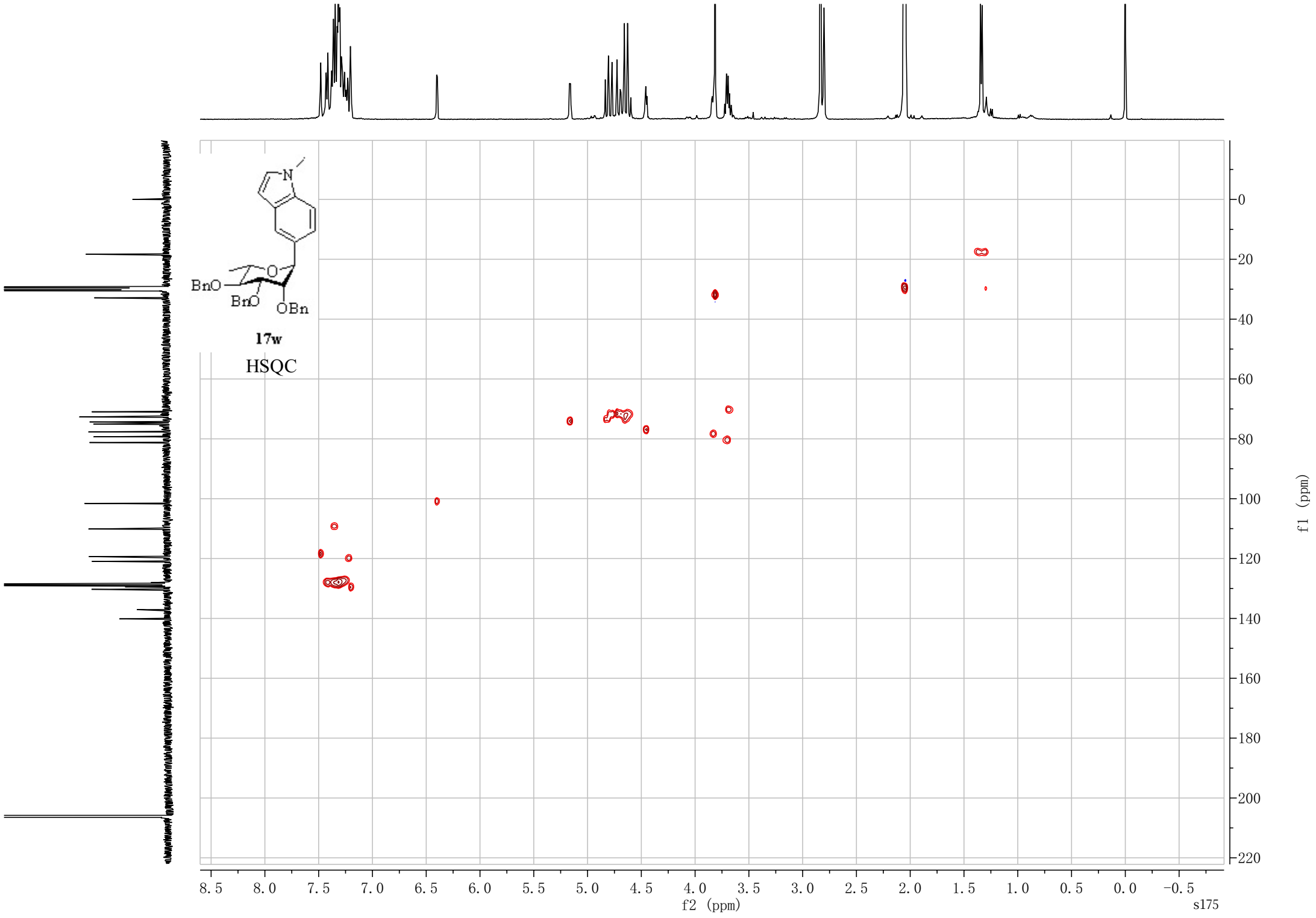


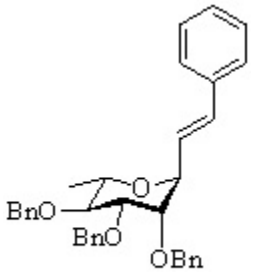
17w

^{1}H NMR (400 MHz, Acetone-d_6)


140.15
139.99
137.08
130.37
130.29
129.48
129.14
129.05
128.97
128.76
128.61
128.41
128.31
128.11
128.08
120.94
119.34
110.14
101.57
81.22
79.33
77.70
75.07
74.35
72.69
72.62
70.96
32.89
18.31
BnO
BnO
OBn
17w
^{13}C NMR (100 MHz, Acetone-d_6)
f1 (ppm)
s173

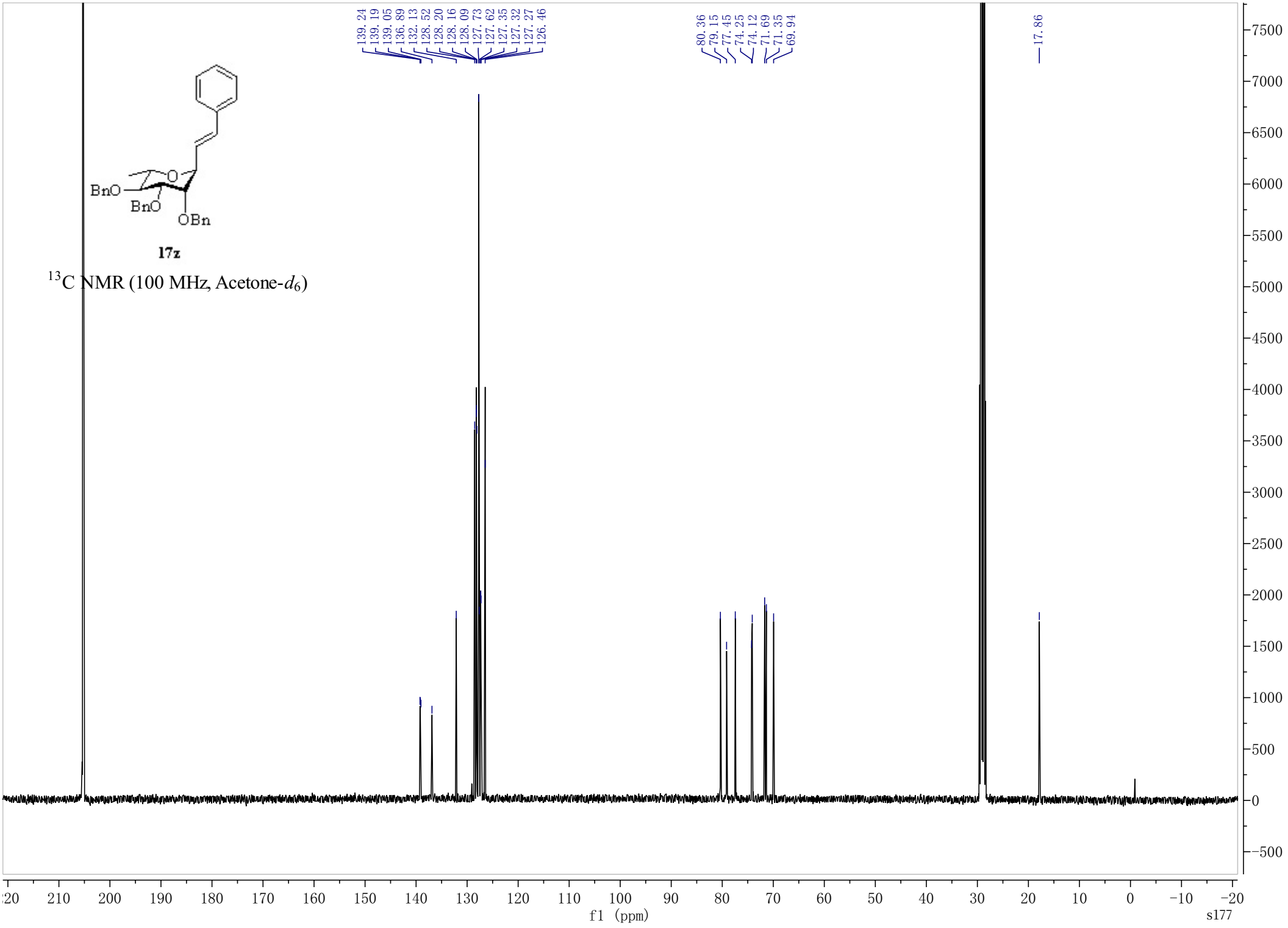

BnO
BnO
OBn
17w
^{1}H-^{1}H COSY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)
s174


BnO
BnO
OBn
17w
HSQC
f2 (ppm)
f1 (ppm)
s175



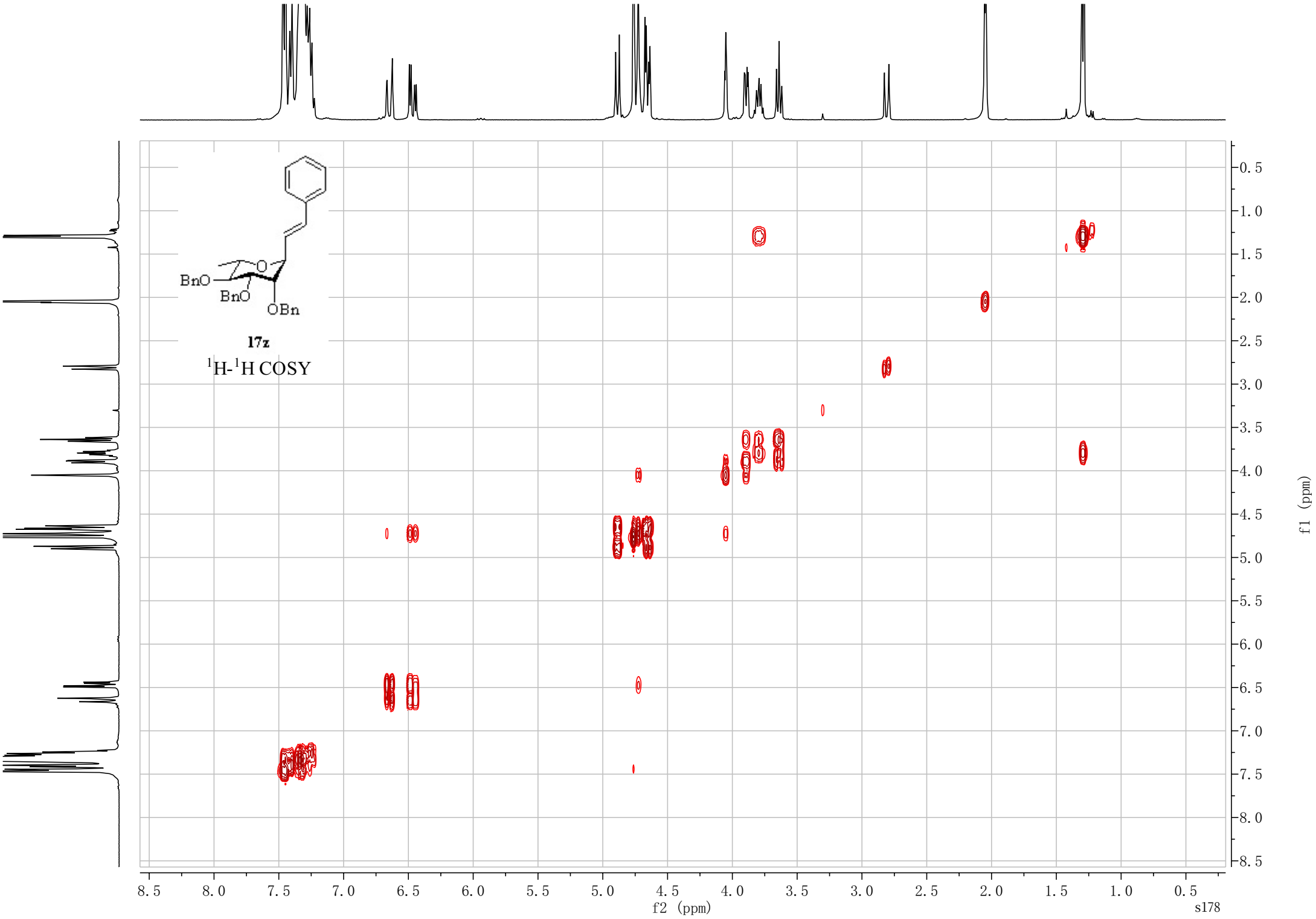
17z

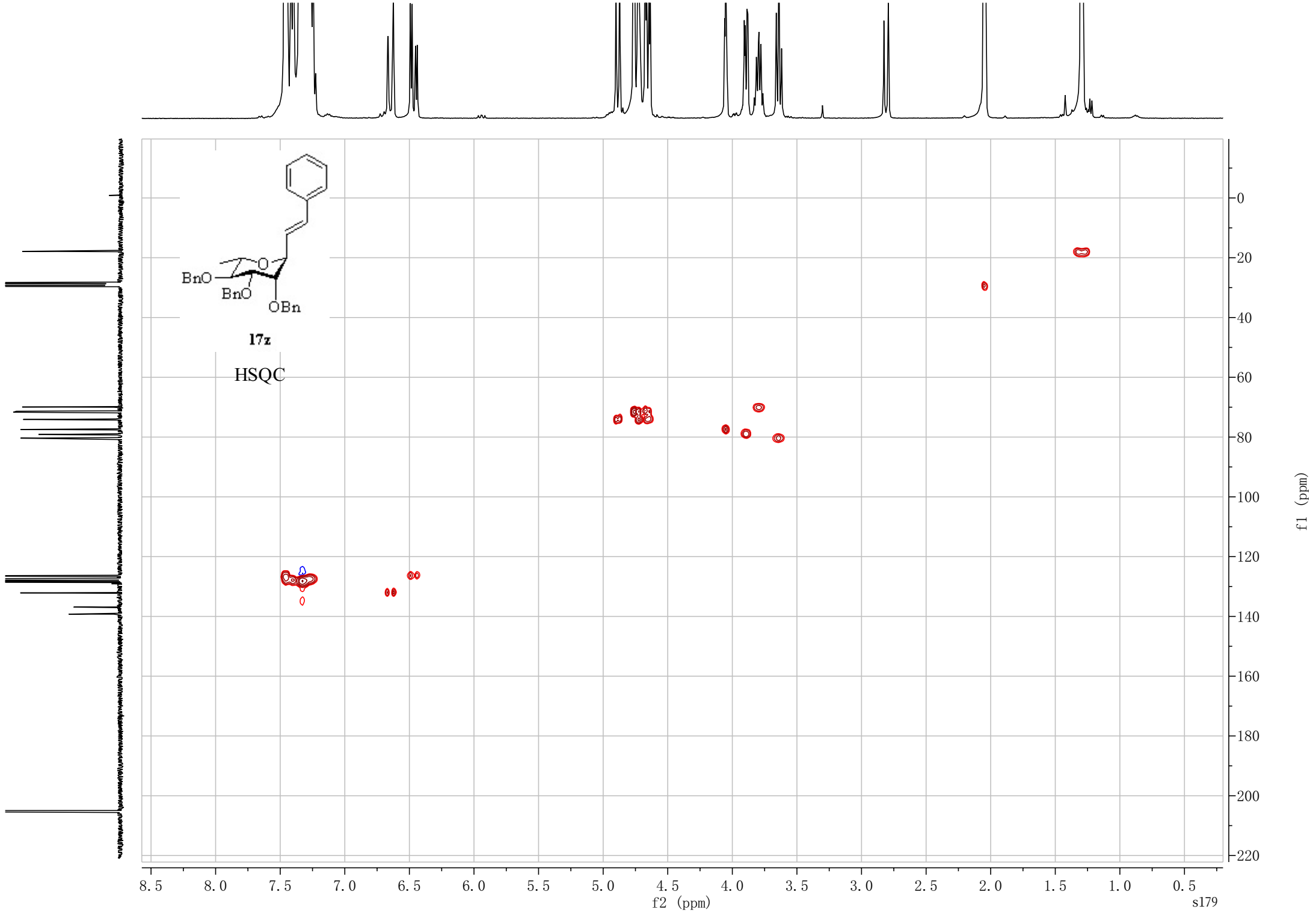
^{1}H NMR (400 MHz, Acetone-d_6)

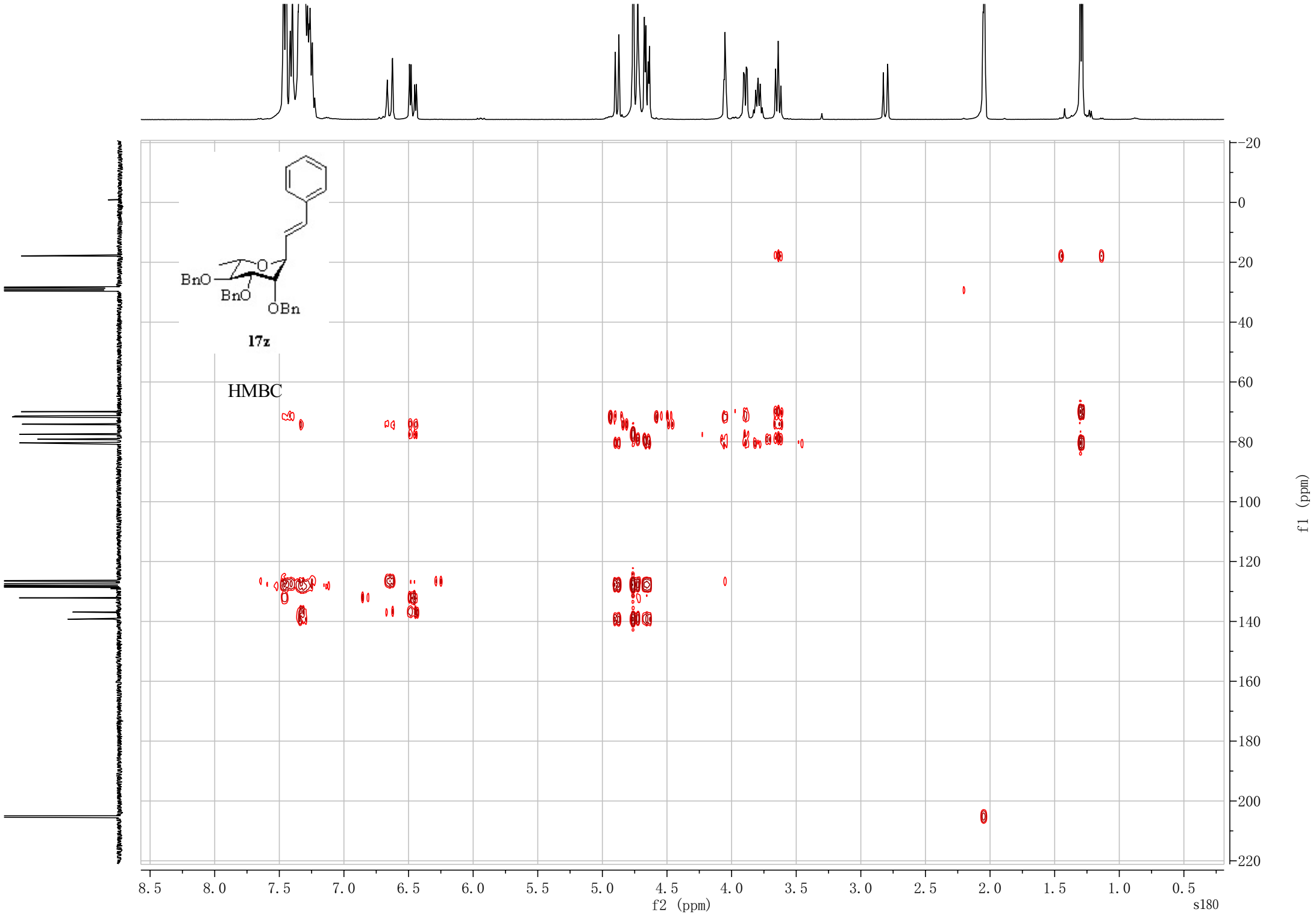


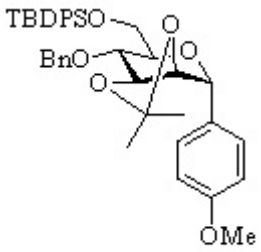
17z

^{13}C NMR (100 MHz, Acetone-d_6)


BnO
BnO
OBn
17z
^{1}H-^{1}H COSY
f2 (ppm)
f1 (ppm)
s178

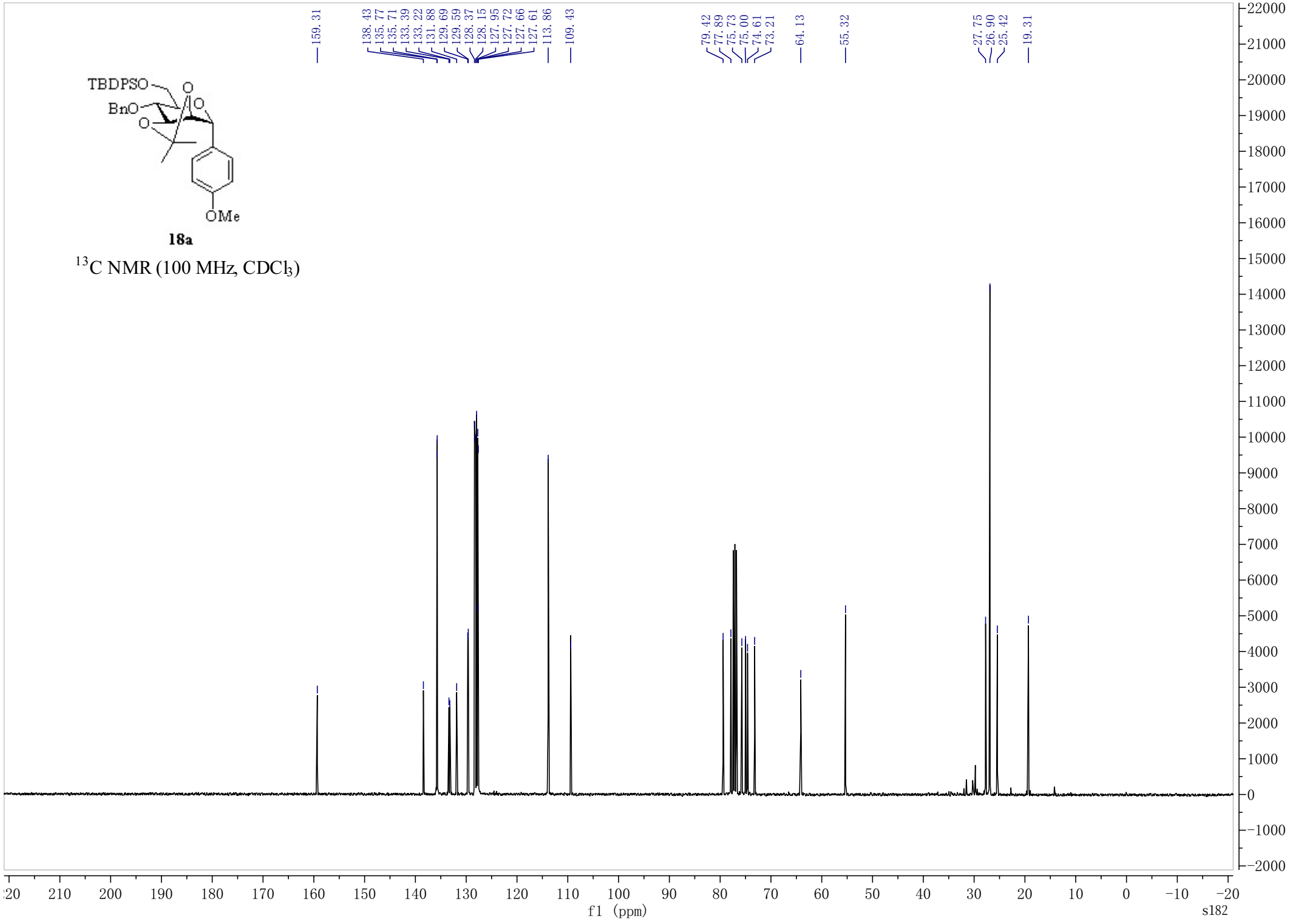

BnO
BnO
OBn
17z
HSQC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
s179

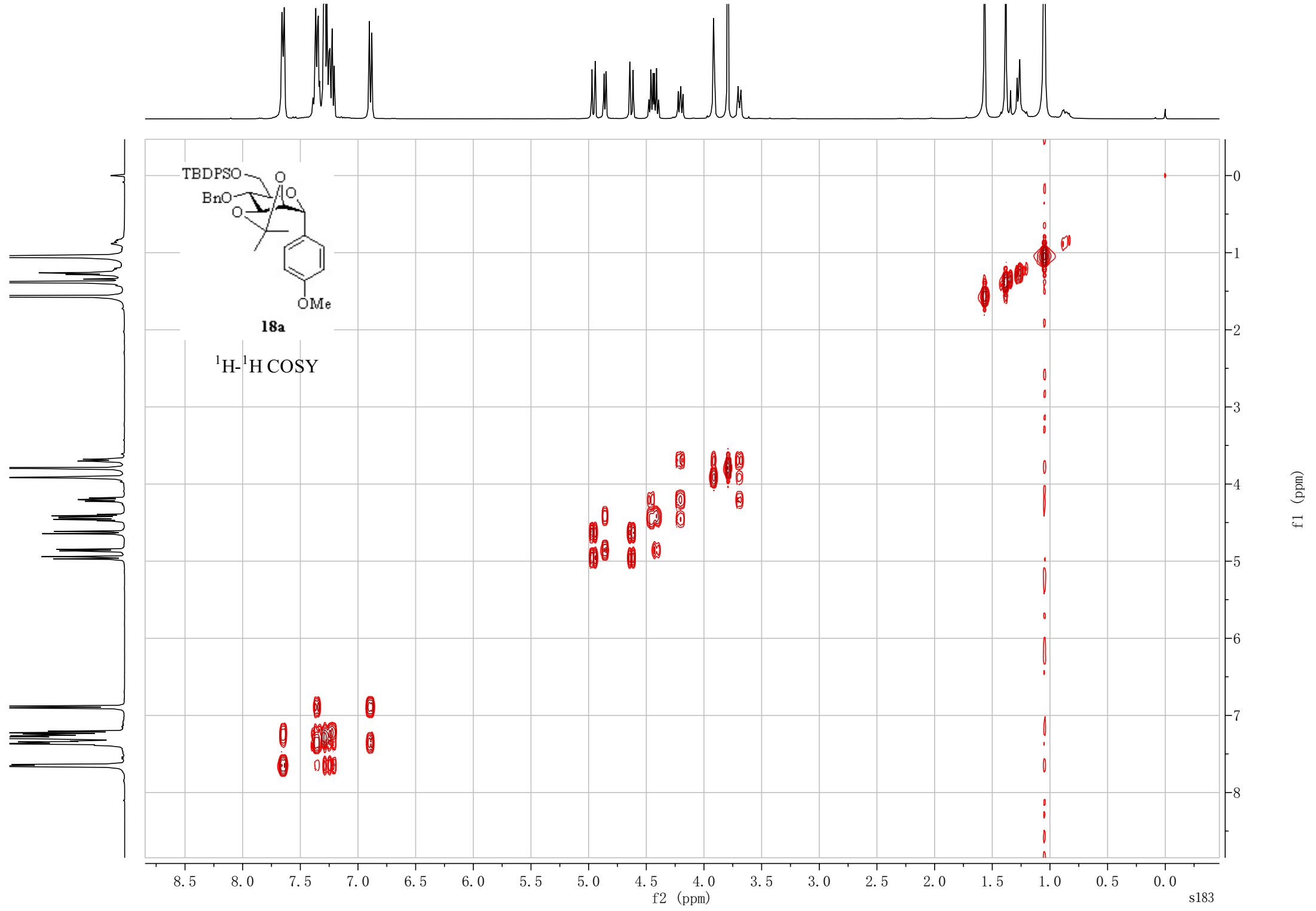

BnO
BnO
OBn
17z
HMBC
f2 (ppm)
f1 (ppm)
s180

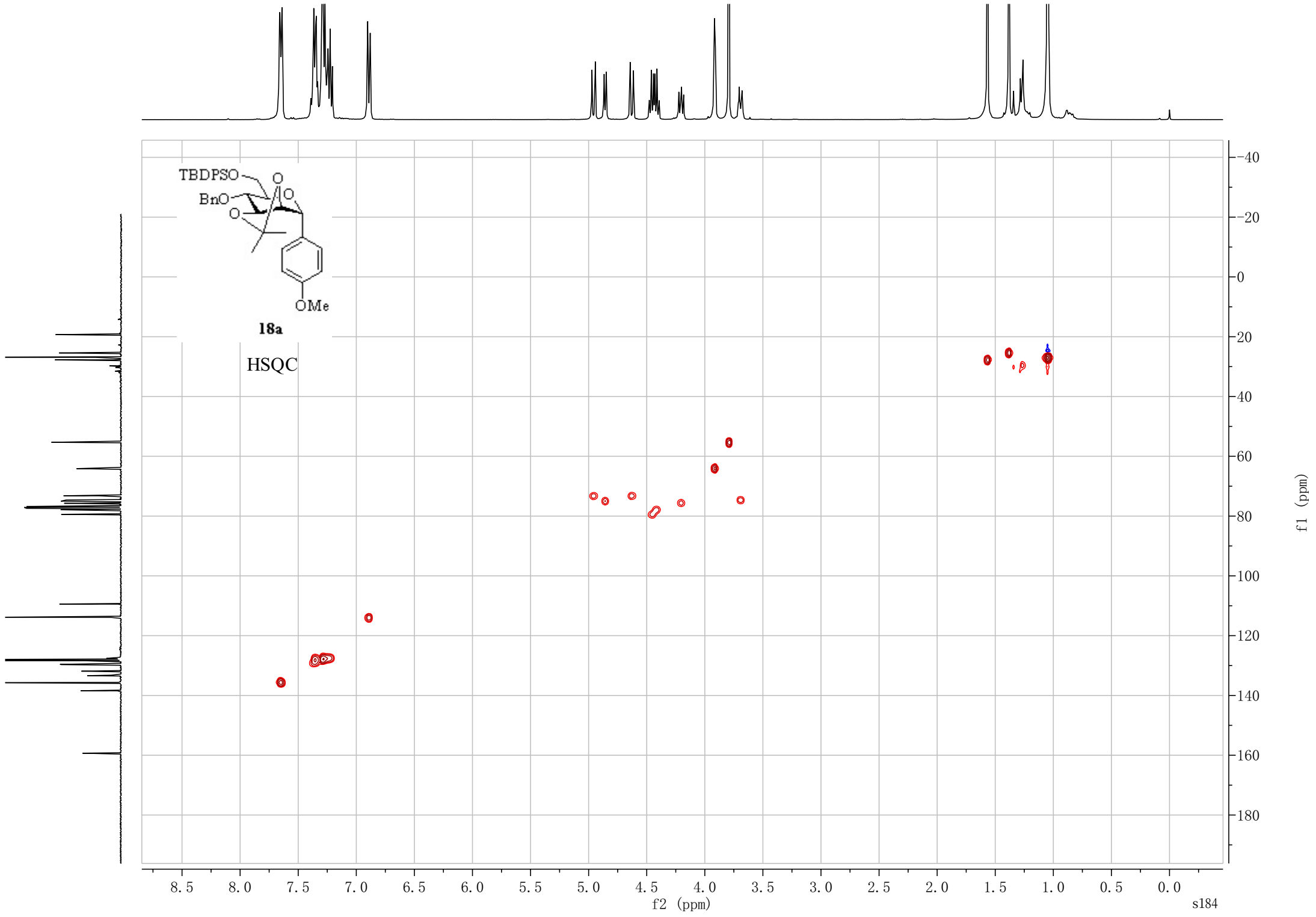


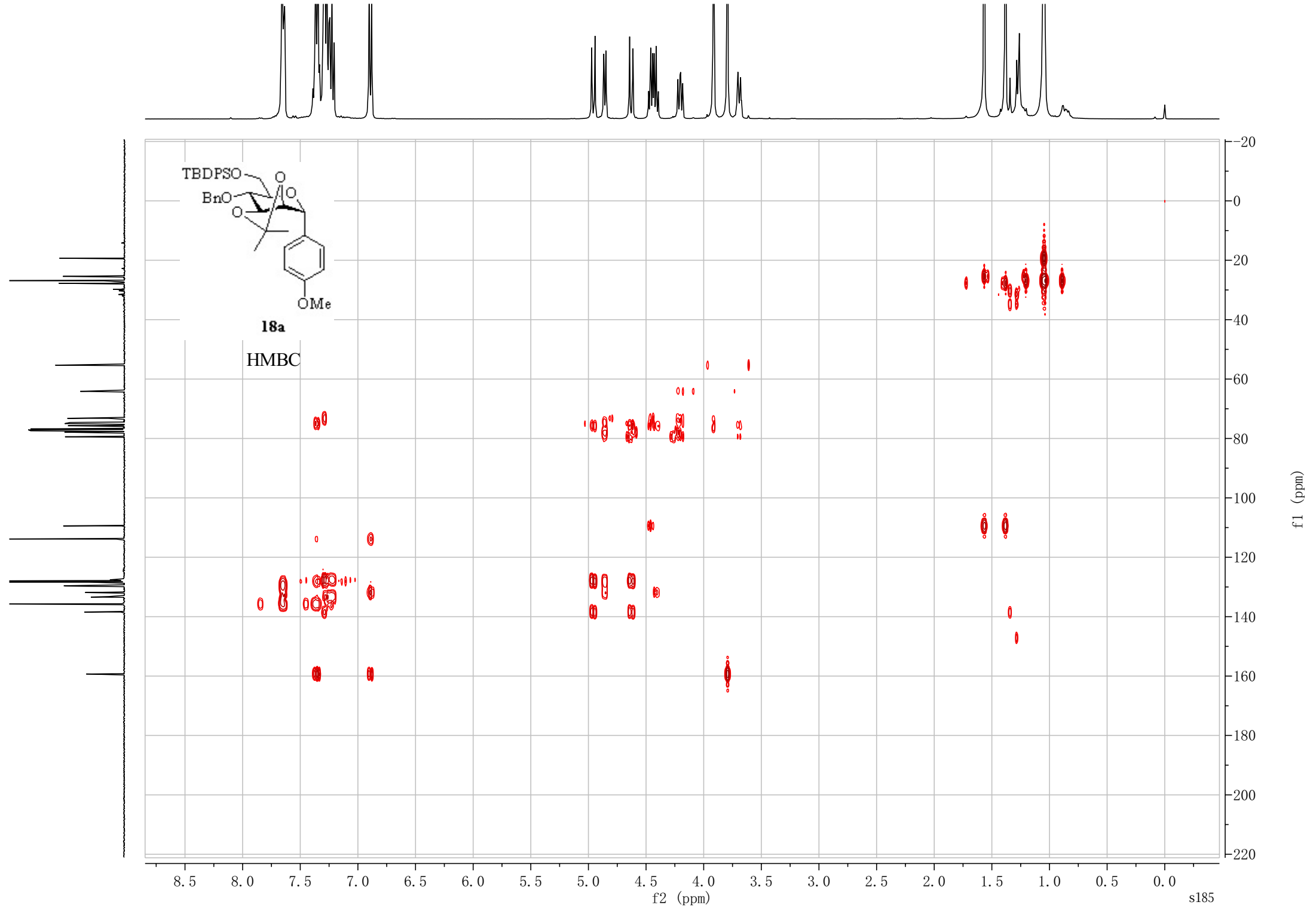
18a

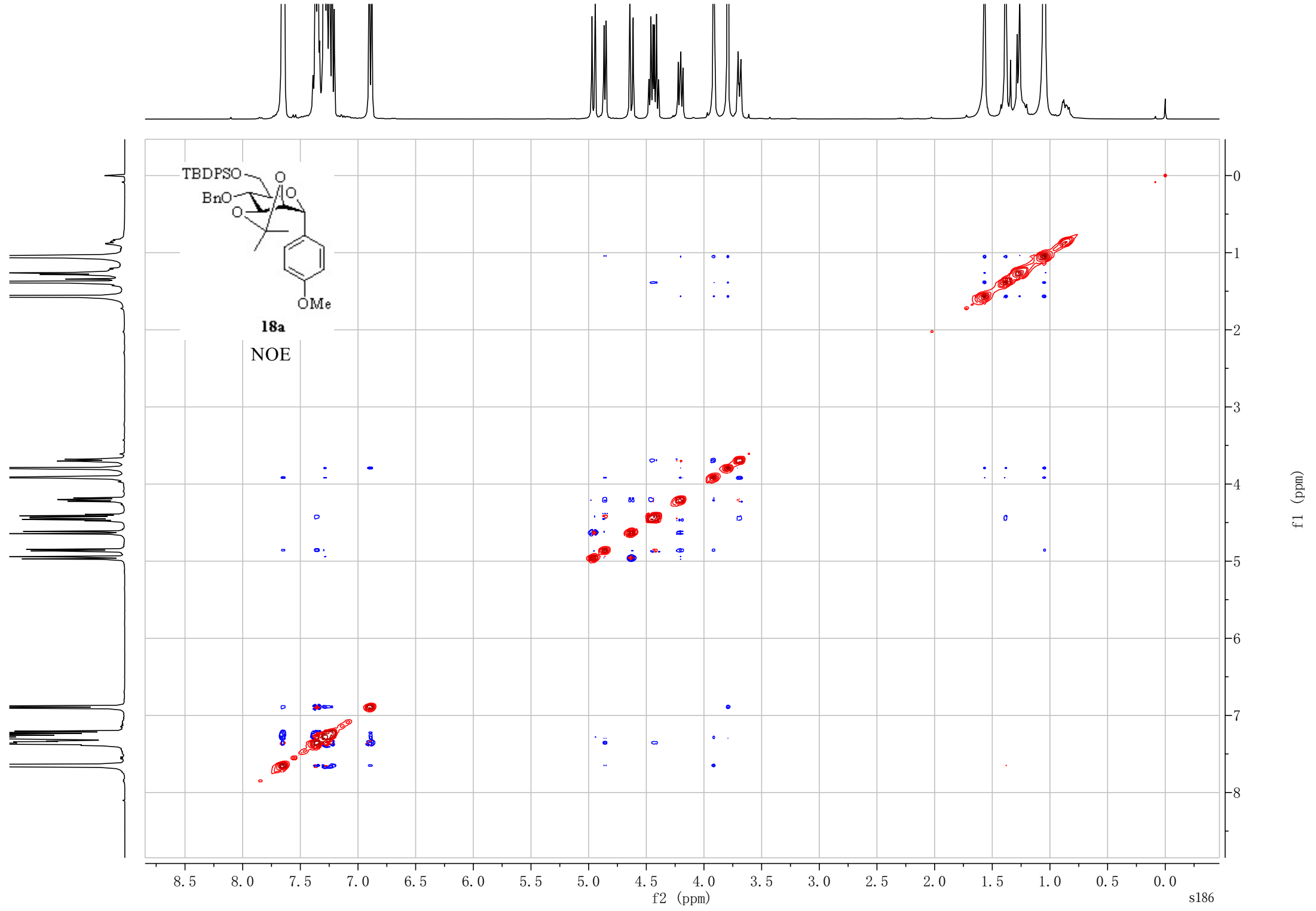
^{1}H NMR (400 MHz, $CDCl_3$)

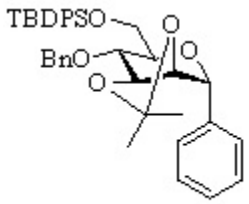

159.31
138.43
135.77
135.71
133.39
133.22
131.88
129.69
129.59
128.37
128.15
127.95
127.72
127.66
127.61
113.86
109.43
79.42
77.89
75.73
75.00
74.61
73.21
64.13
55.32
27.75
26.90
25.42
19.31
TBDPSO
BnO
O
O
O
OMe
18a
13C NMR (100 MHz, CDCl3)
f1 (ppm)
s182


TBDPSO
BnO
O
O
O
OMe
18a
^{1}H-^{1}H COSY
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)
s183


TBDPSO
BnO
O
O
O
OMe
18a
HSQC
f2 (ppm)
f1 (ppm)
s184

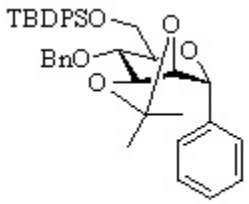

TBDPSO
BnO
O
O
O
OMe
18a
HMBC
f2 (ppm)
f1 (ppm)
s185


TBDPSO
BnO
O
O
O
OMe
18a
NOE
f2 (ppm)
f1 (ppm)
s186



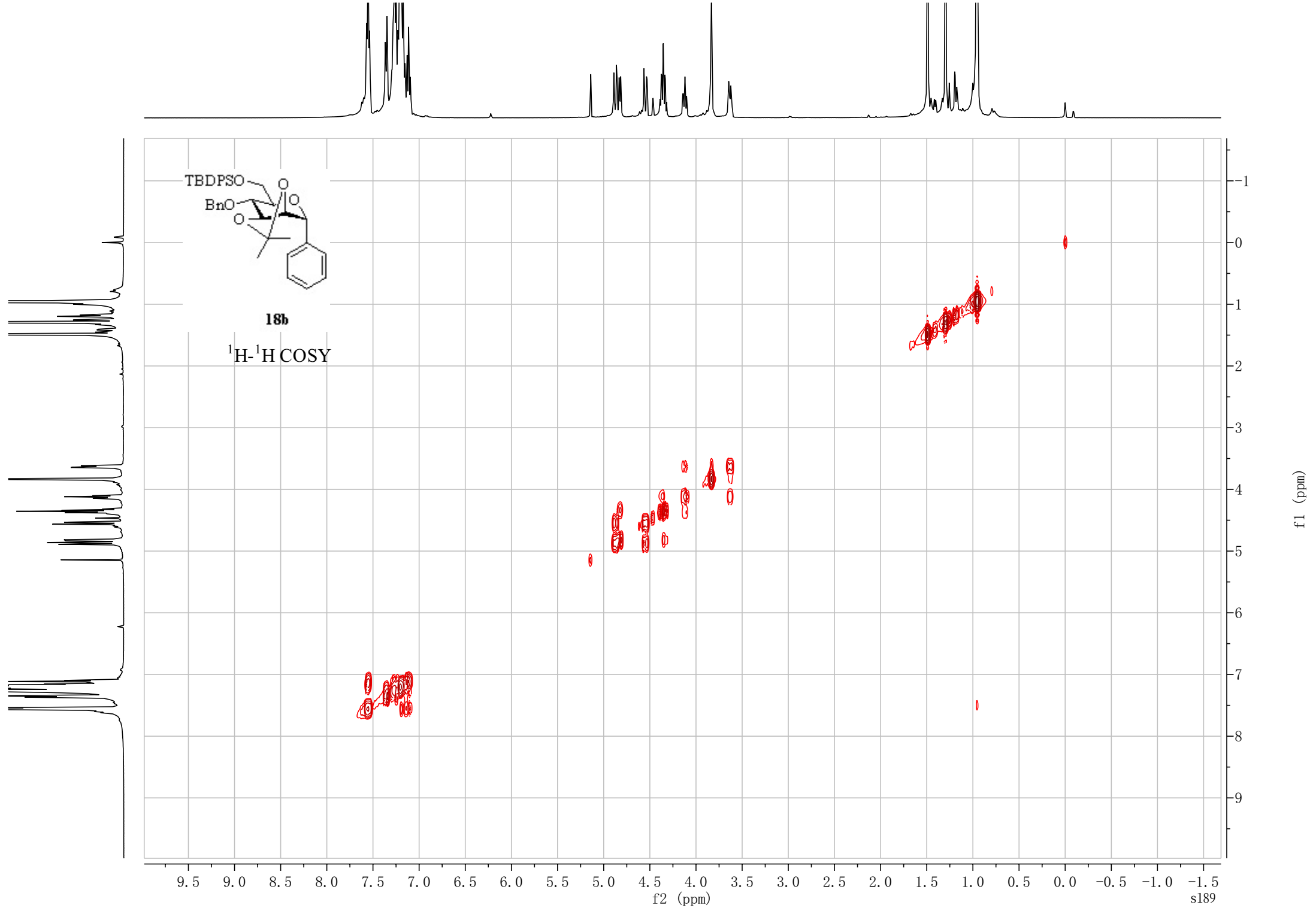
18b

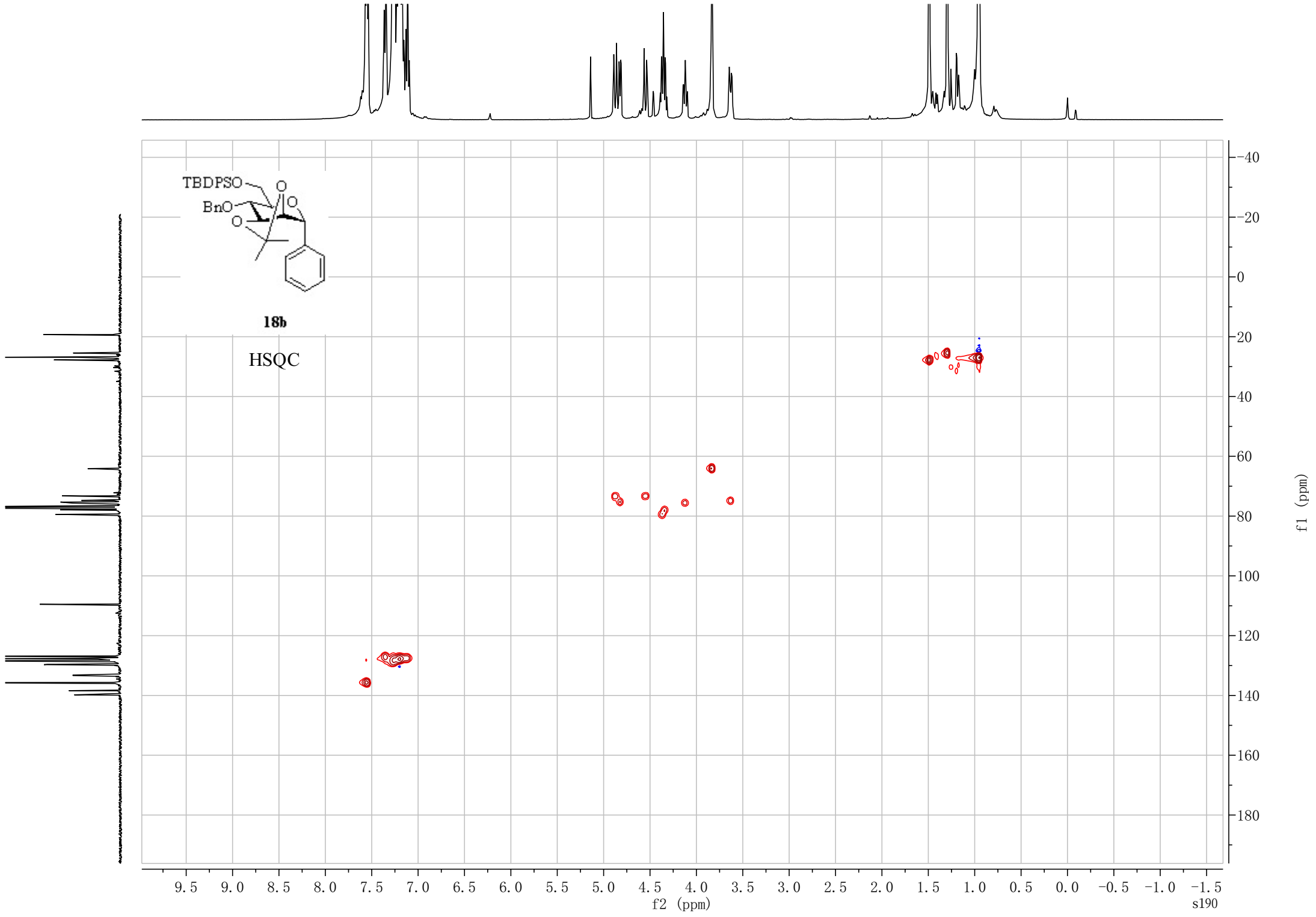
^{1}H NMR (400 MHz, $CDCl_3$)

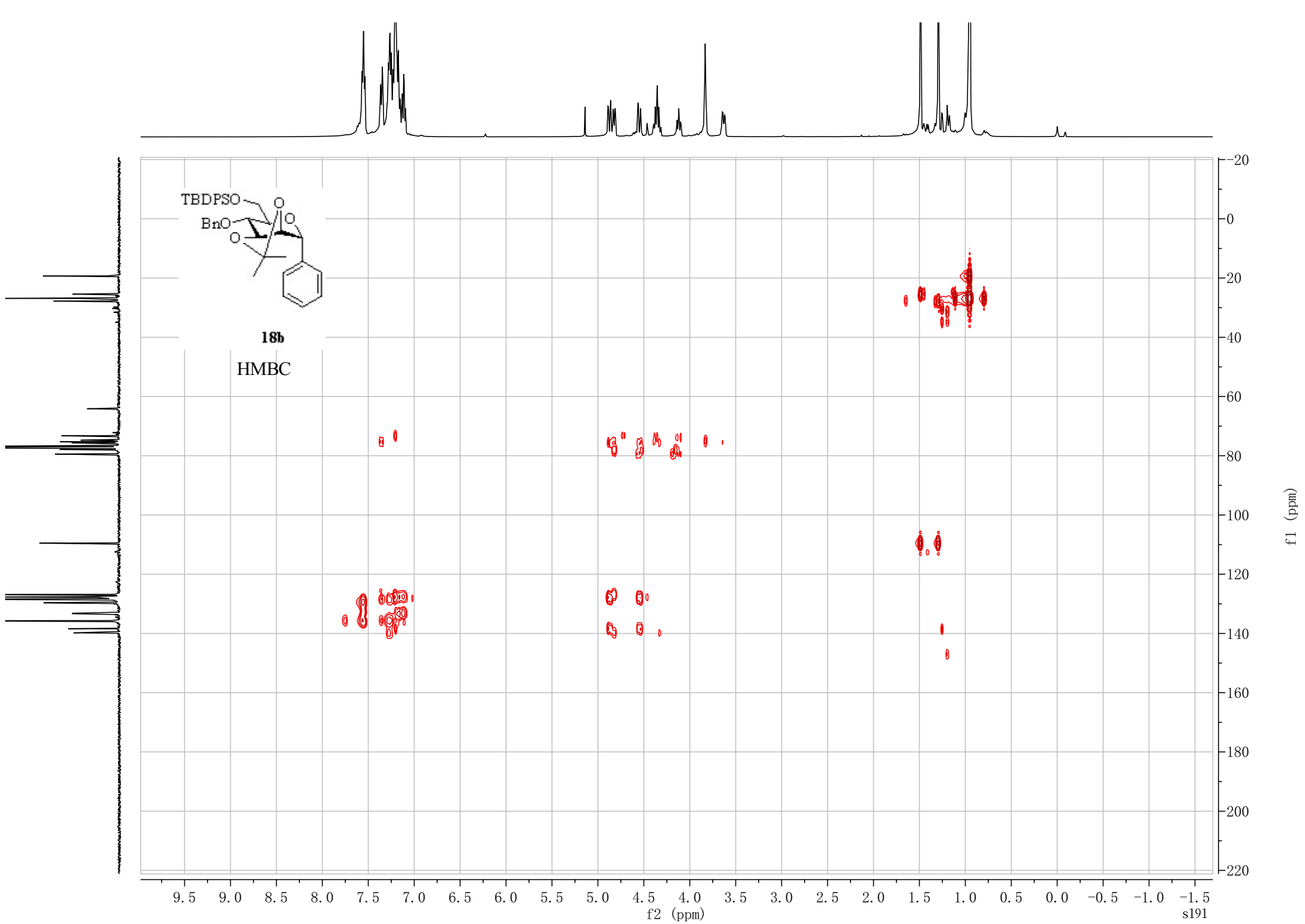


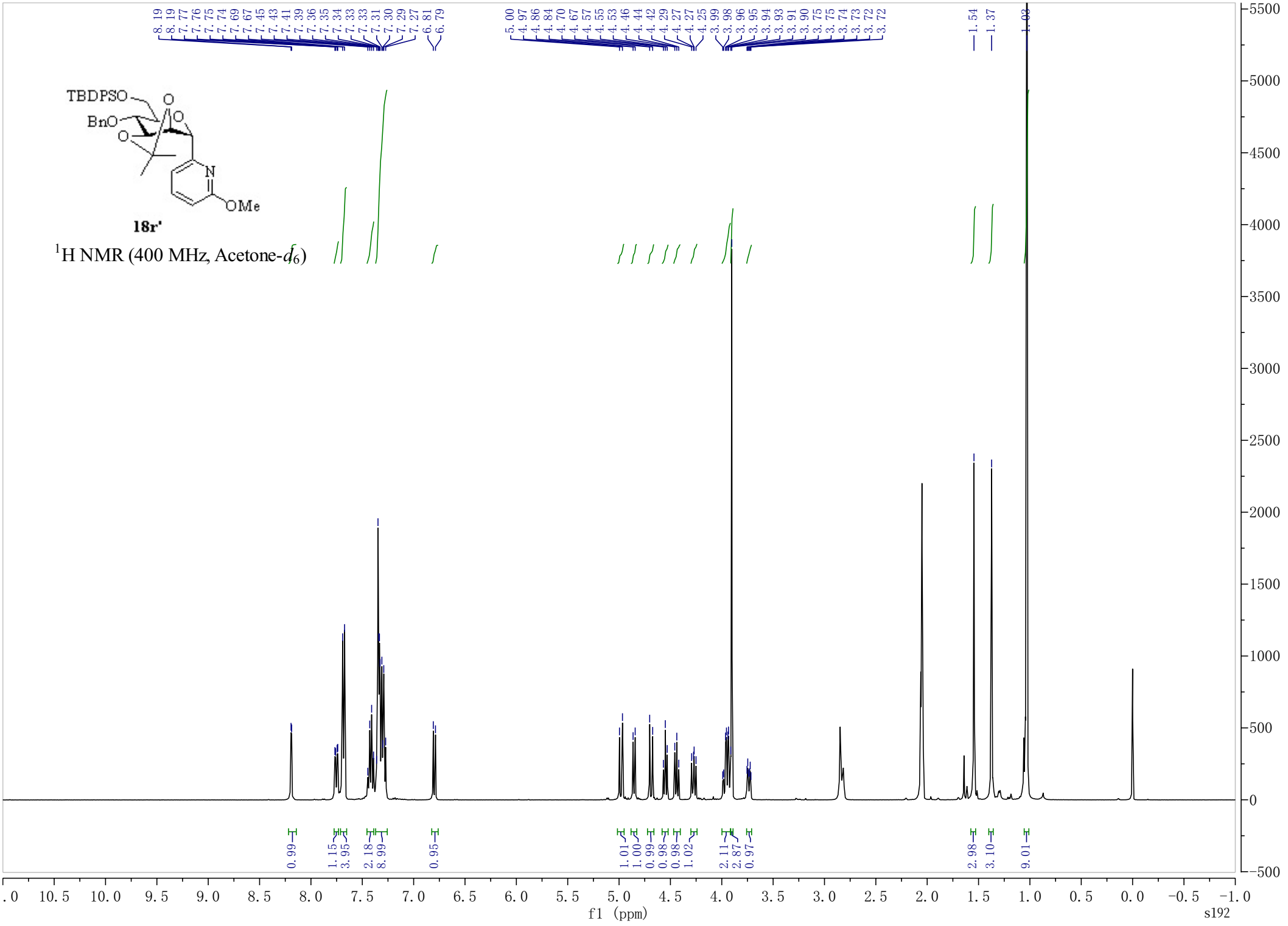
18b

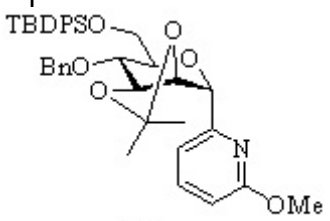
^{13}C NMR (100 MHz, $CDCl_3$)


TBDPSO
BnO
O
O
O
18b
^{1}H-^{1}H COSY
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
f2 (ppm)
f1 (ppm)
s189


TBDPSO
BnO
O
O
O
18b
HSQC
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
f2 (ppm)
-40 -20 0 20 40 60 80 100 120 140 160 180
f1 (ppm)
s190

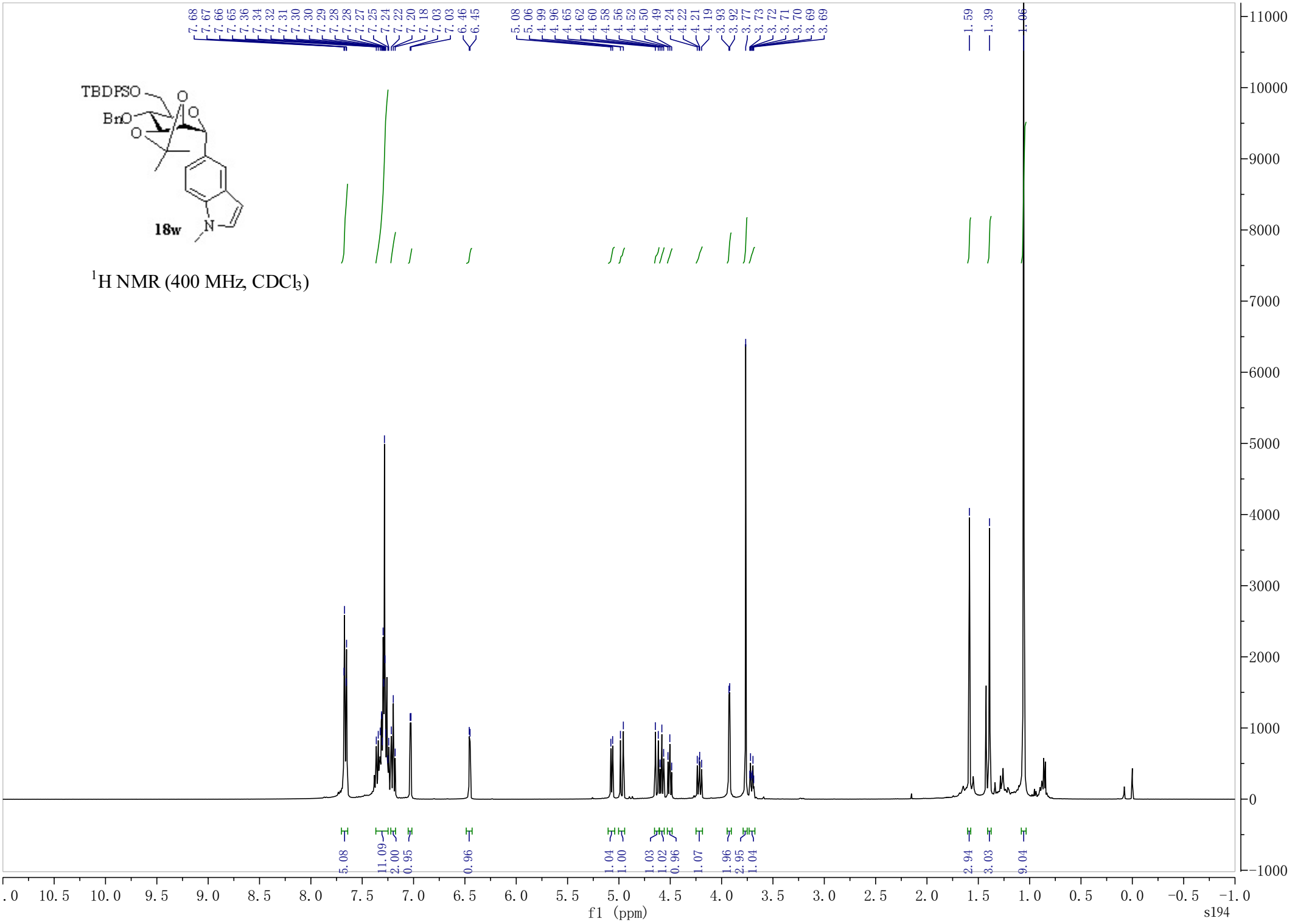

TBDPSO
BnO
O
O
O
18b
HMBC
f2 (ppm)
f1 (ppm)
s191

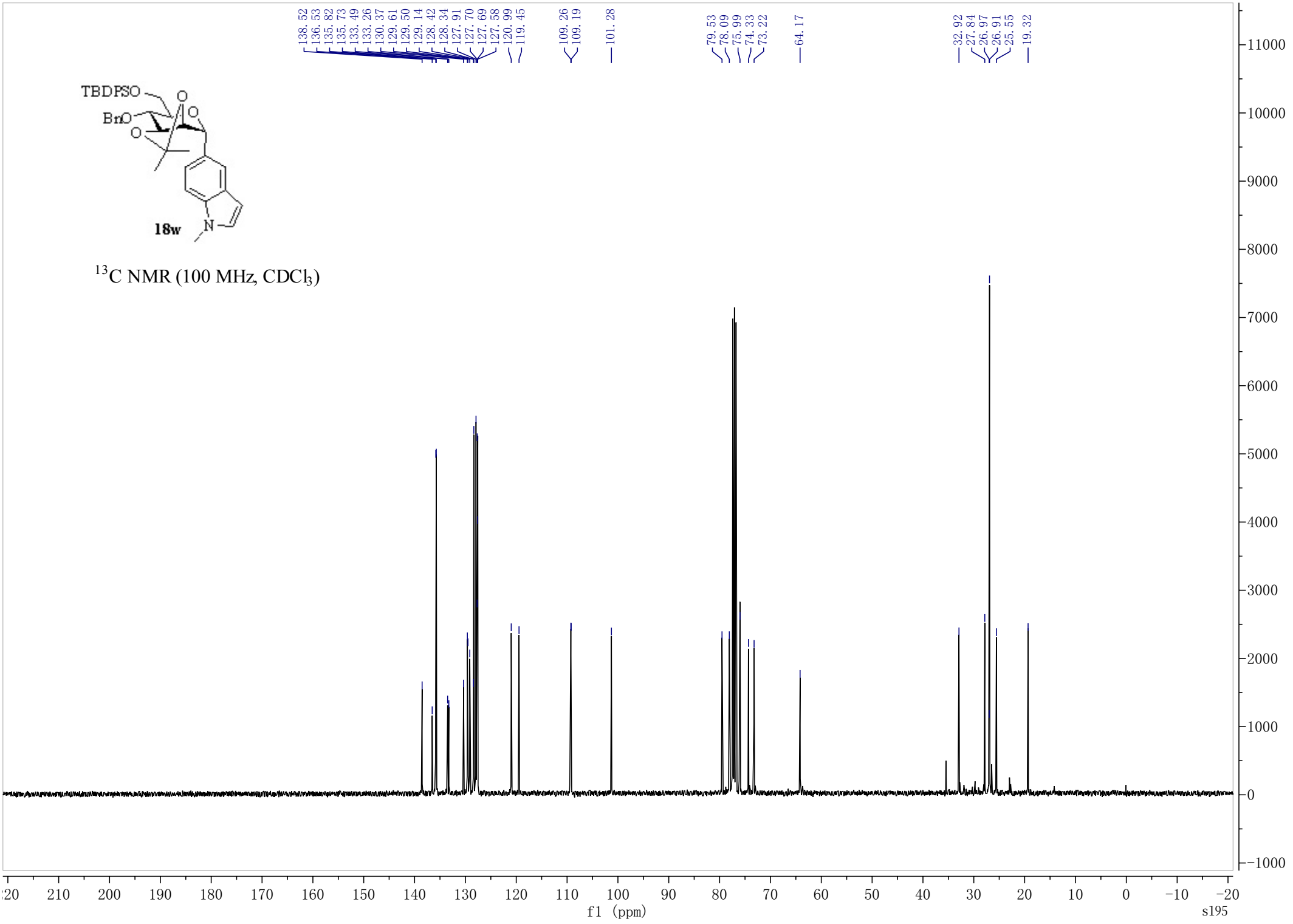

TBDPSO
BnO
O
O
O
N
OMe
18r'
1H NMR (400 MHz, Acetone-d6)
f1 (ppm)
s192

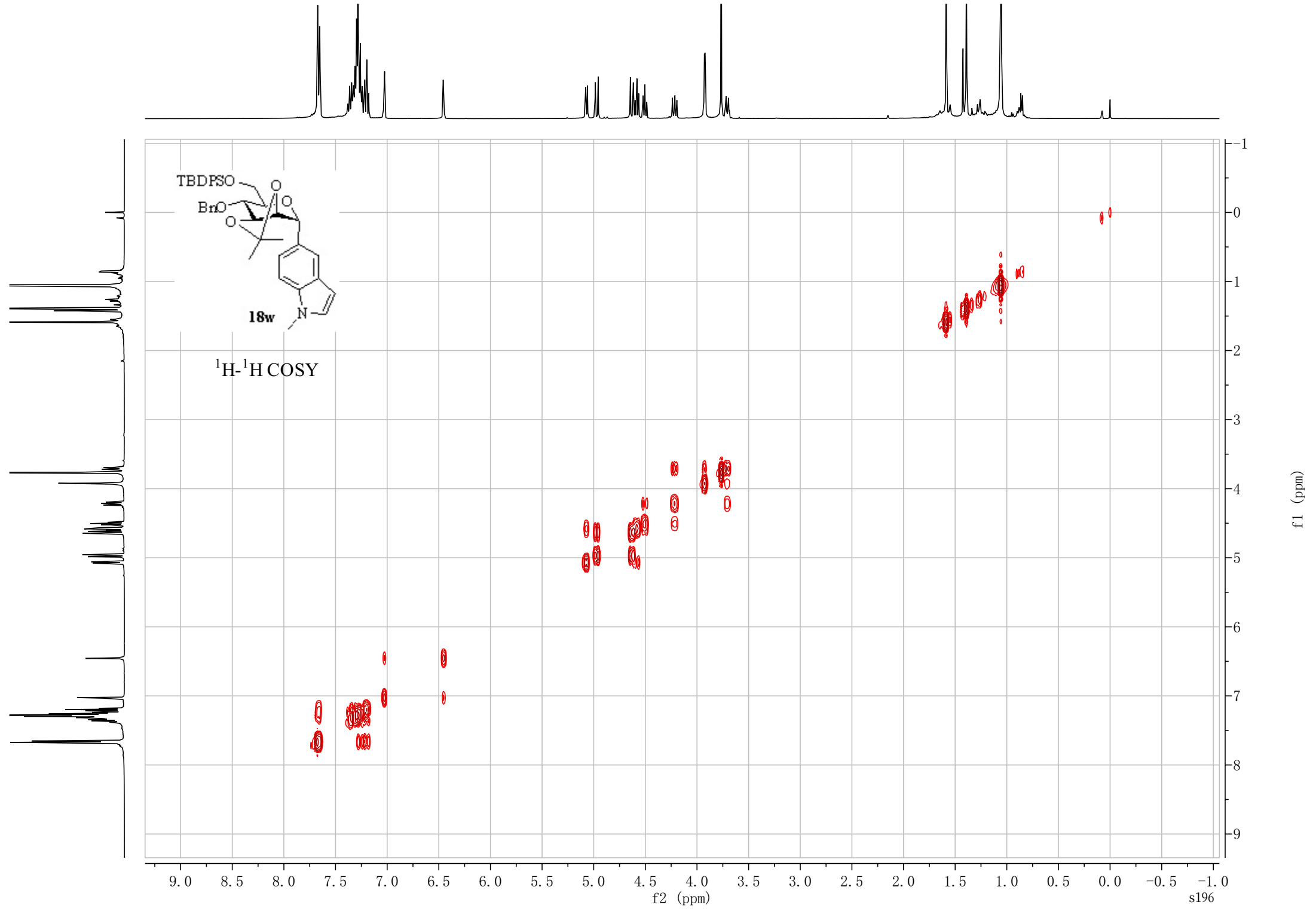


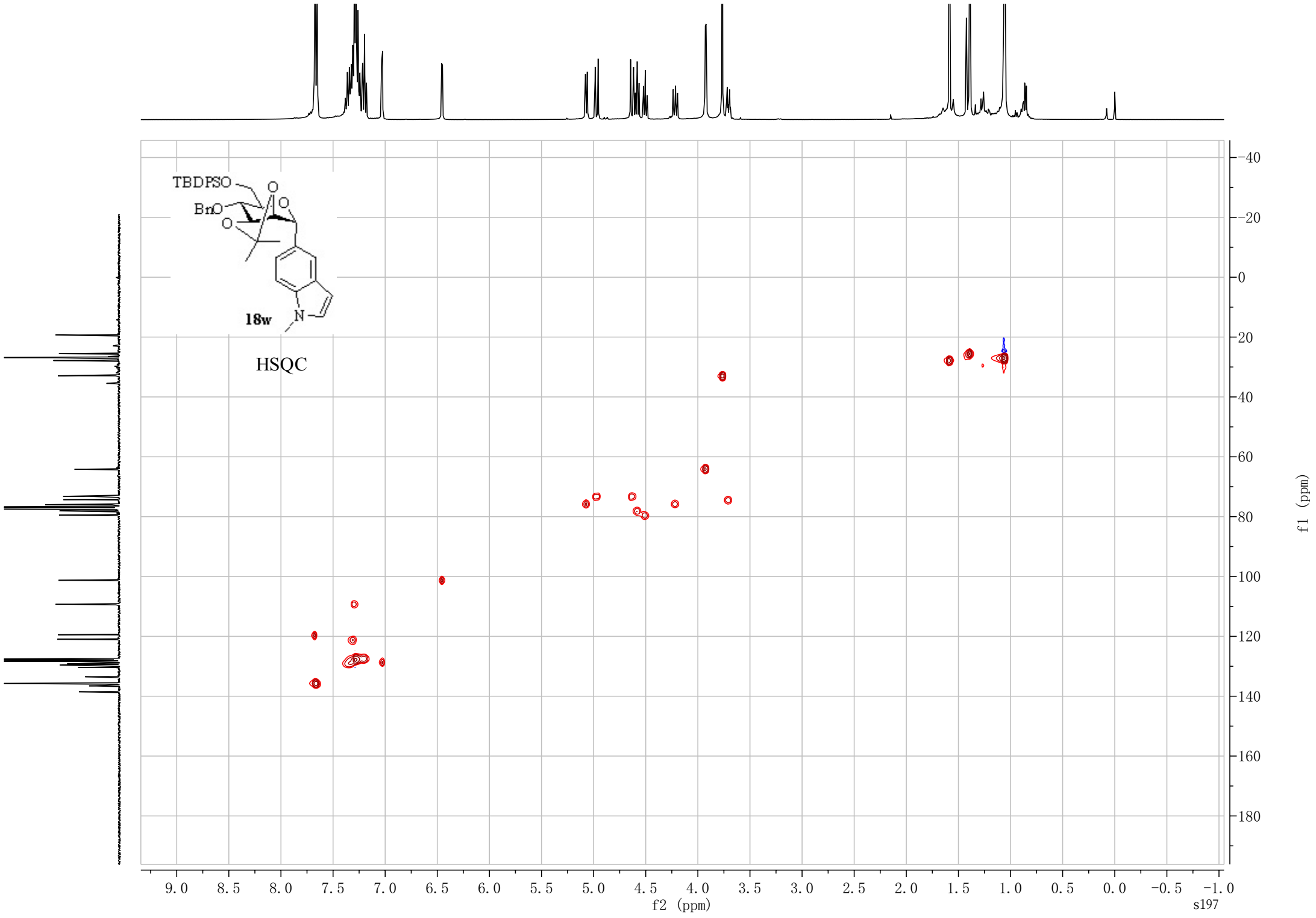
18r'

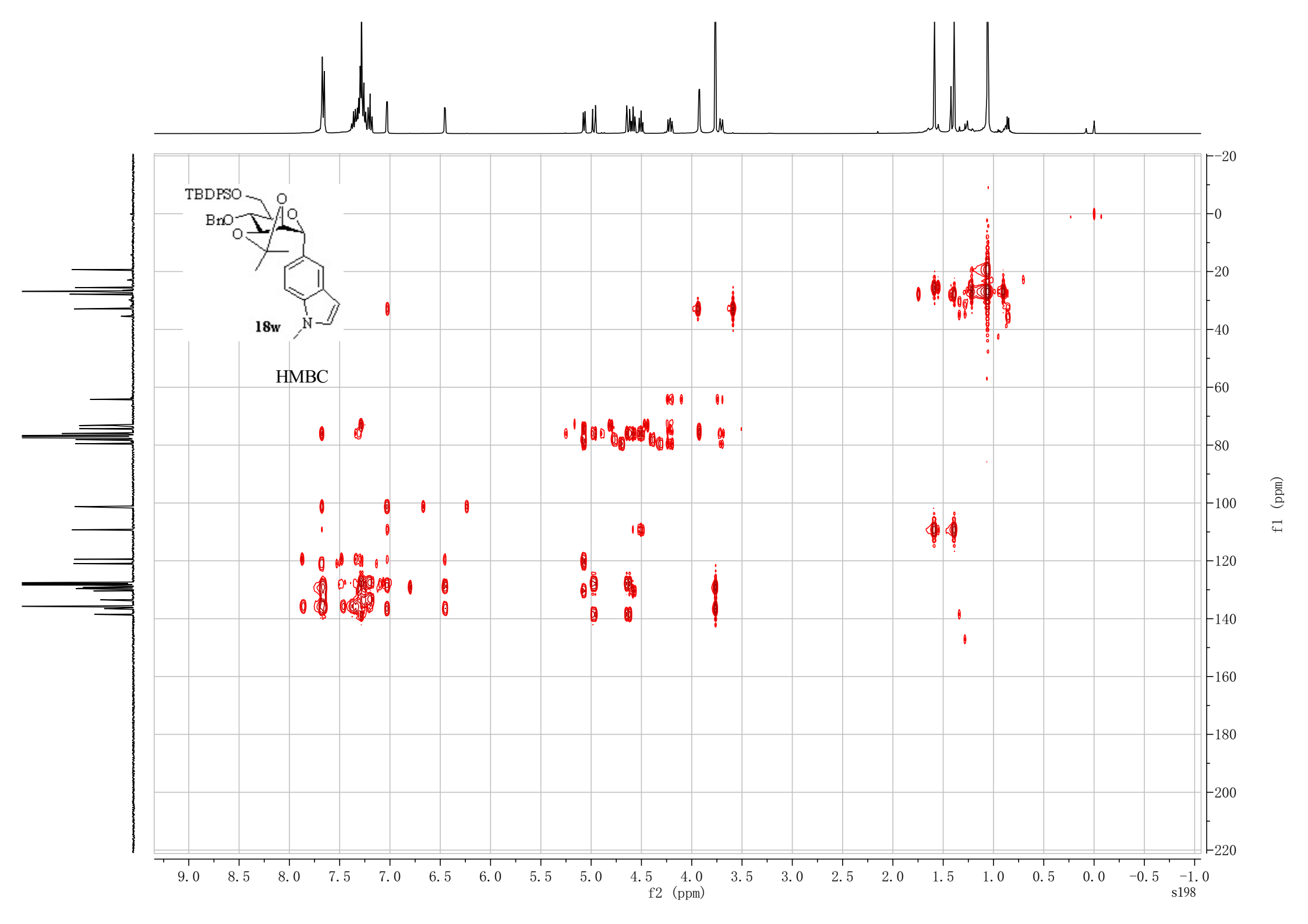
^{13}C NMR (100 MHz, Acetone-d_6)

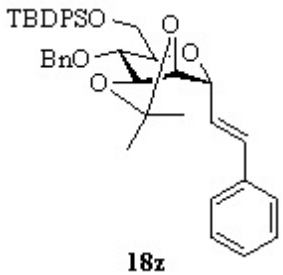

TBDPSO
BnO
O
O
O
N
18w
^{1}H NMR (400 MHz, $CDCl_3$)
7.68 7.67 7.66 7.65 7.36 7.34 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.25 7.24 7.22 7.20 7.18 7.03 7.03 6.46 6.45
5.08 5.06 4.99 4.96 4.65 4.62 4.60 4.58 4.56 4.52 4.50 4.49 4.24 4.22 4.21 4.19 3.93 3.92 3.77 3.73 3.72 3.71 3.70 3.69 3.69
1.59 1.39 1.06
5.08 11.09 2.00 0.95 0.96 1.04 1.00 1.03 1.02 0.96 1.07 1.96 2.95 1.04 2.94 3.03 9.04
f1 (ppm)
s194


138.52
136.53
135.82
135.73
133.49
133.26
130.37
129.61
129.50
129.14
128.42
128.34
127.91
127.70
127.69
127.58
120.99
119.45
109.26
109.19
101.28
79.53
78.09
75.99
74.33
73.22
64.17
32.92
27.84
26.97
26.91
25.55
19.32
TBDPSO
BnO
O
O
O
N
18w
^{13}C NMR (100 MHz, CDCl$_3$)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
s195


TBDPSO
BnO
O
O
O
N
18w
^{1}H-^{1}H COSY
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)
s196

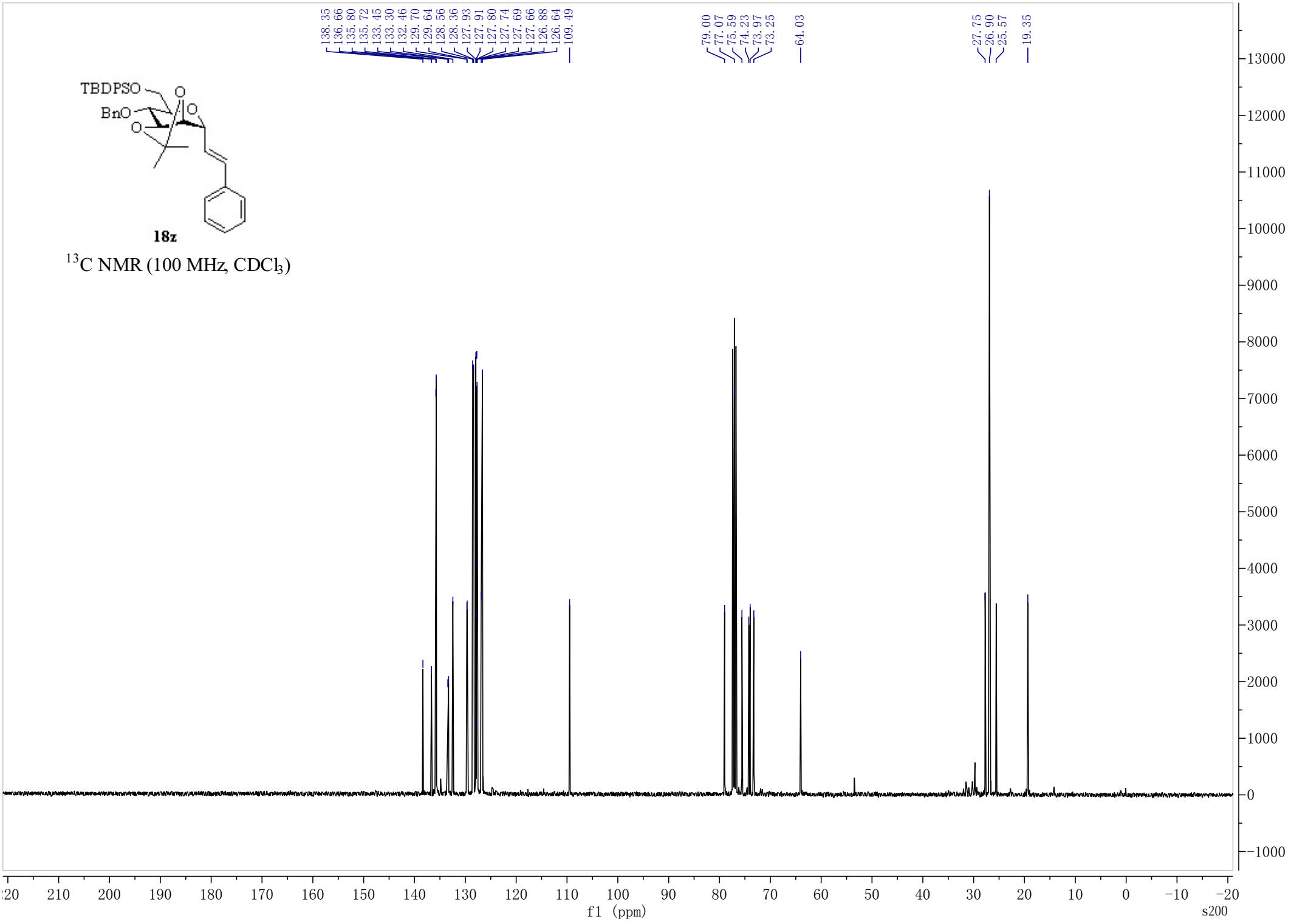

TBDPSO
BnO
O
O
O
N
18w
HSQC
f2 (ppm)
f1 (ppm)
s197

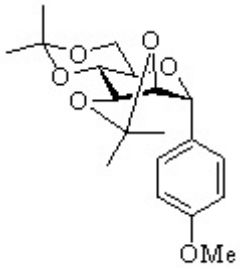

TBDPSO
BnO
O
O
O
N
18w
HMBC
f2 (ppm)
f1 (ppm)
s198



18z

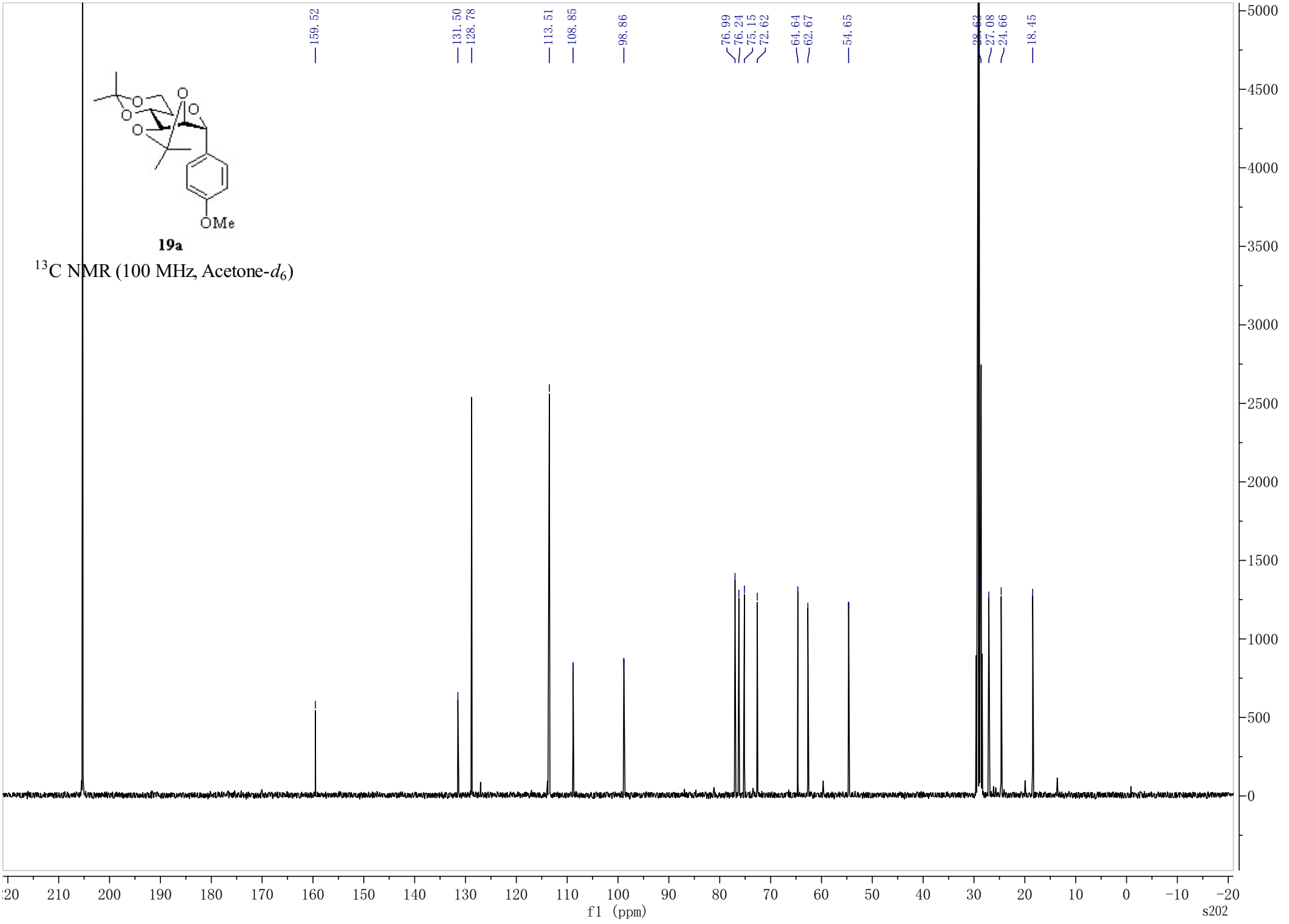
^{1}H NMR (400 MHz, $CDCl_3$)


138.35
136.66
135.80
135.72
133.45
133.30
132.46
129.70
129.64
128.56
128.36
127.93
127.91
127.80
127.74
127.69
127.66
126.88
126.64
109.49
79.00
77.07
75.59
74.23
73.97
73.25
64.03
27.75
26.90
25.57
19.35
TBDPSO
BnO
O
O
O
18z
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)
s200



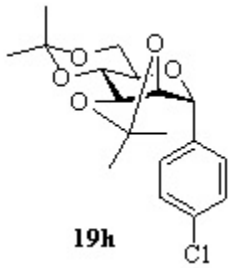
19a

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

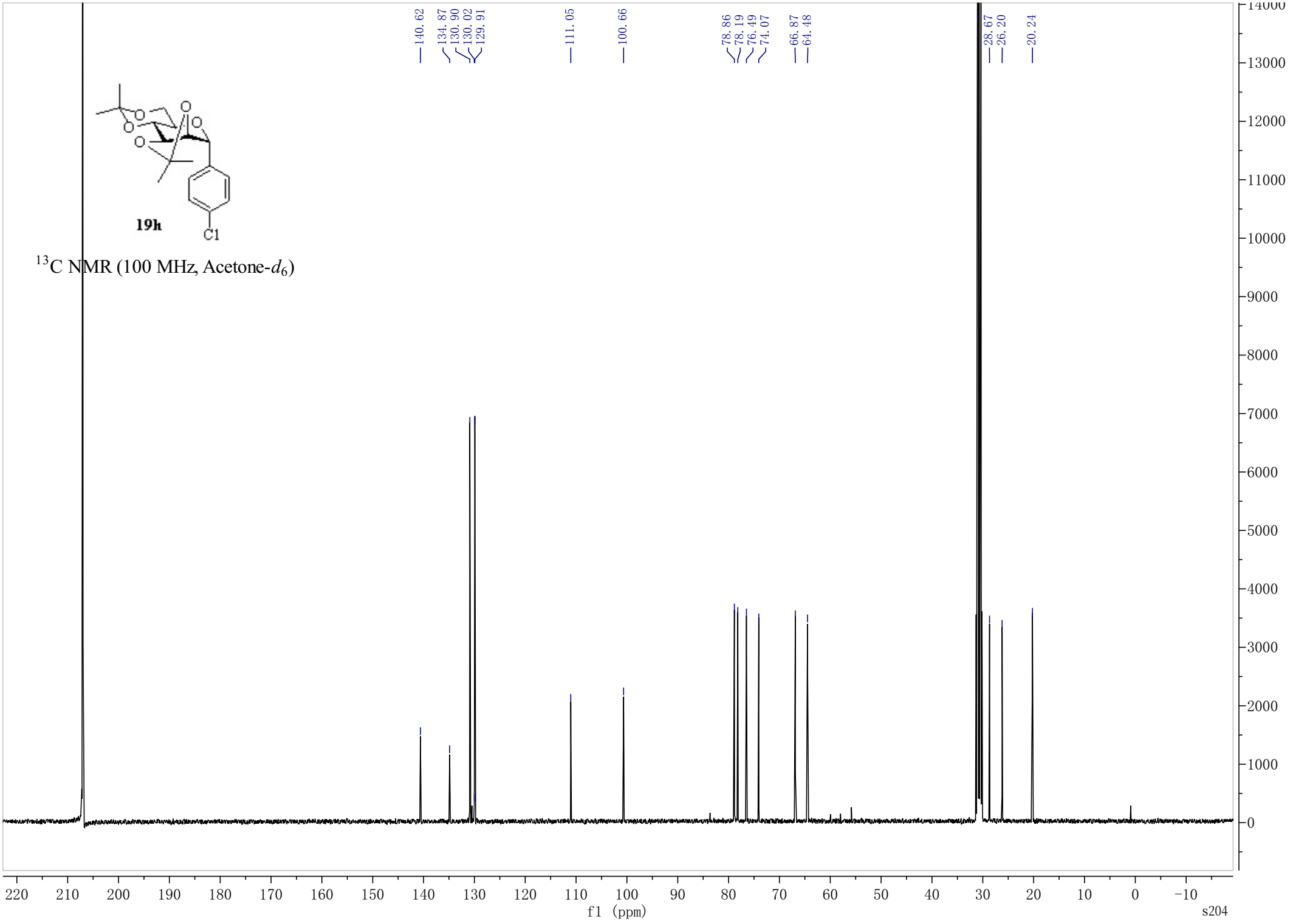


19a

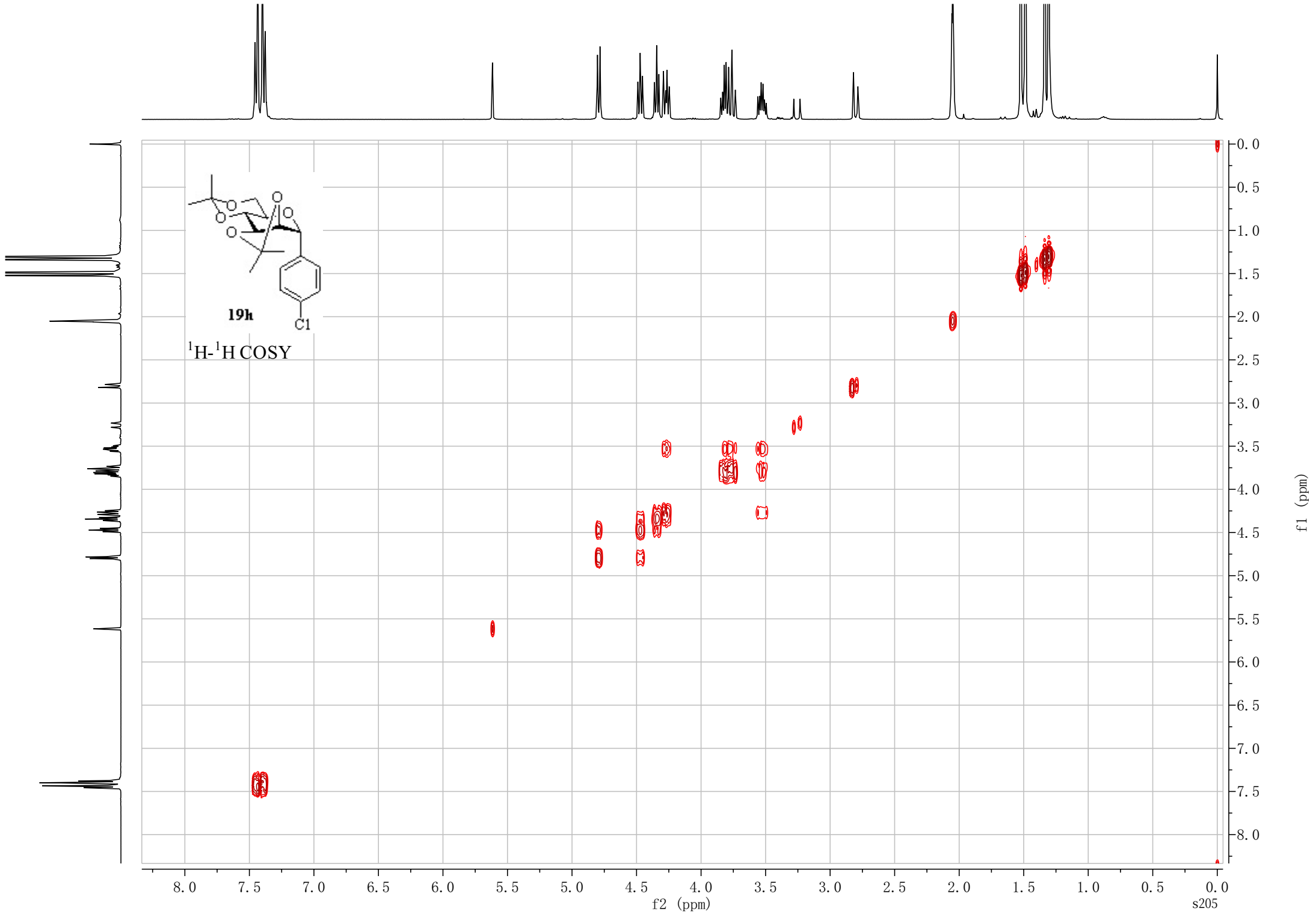
^{13}C NMR (100 MHz, Acetone-d_6)

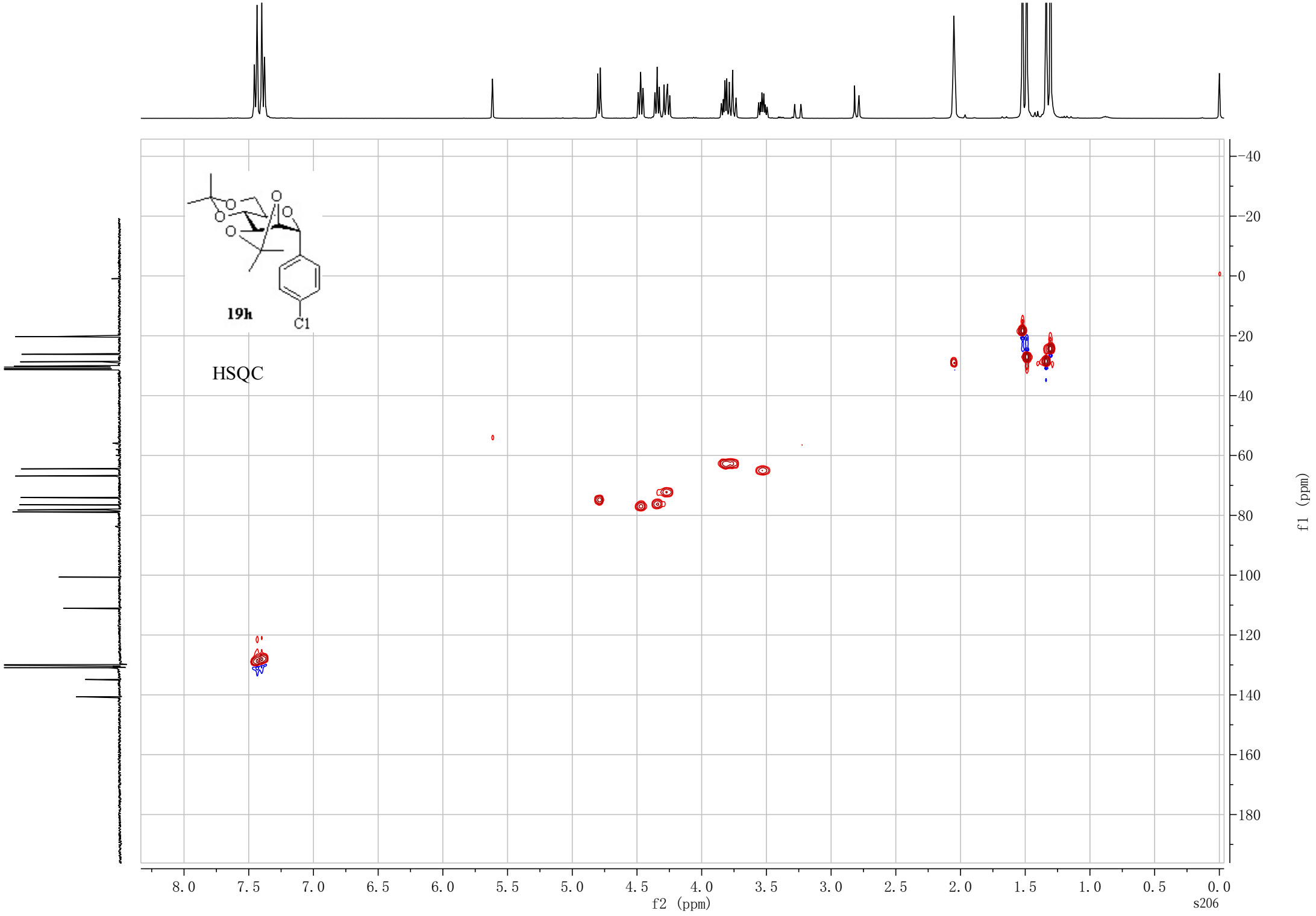


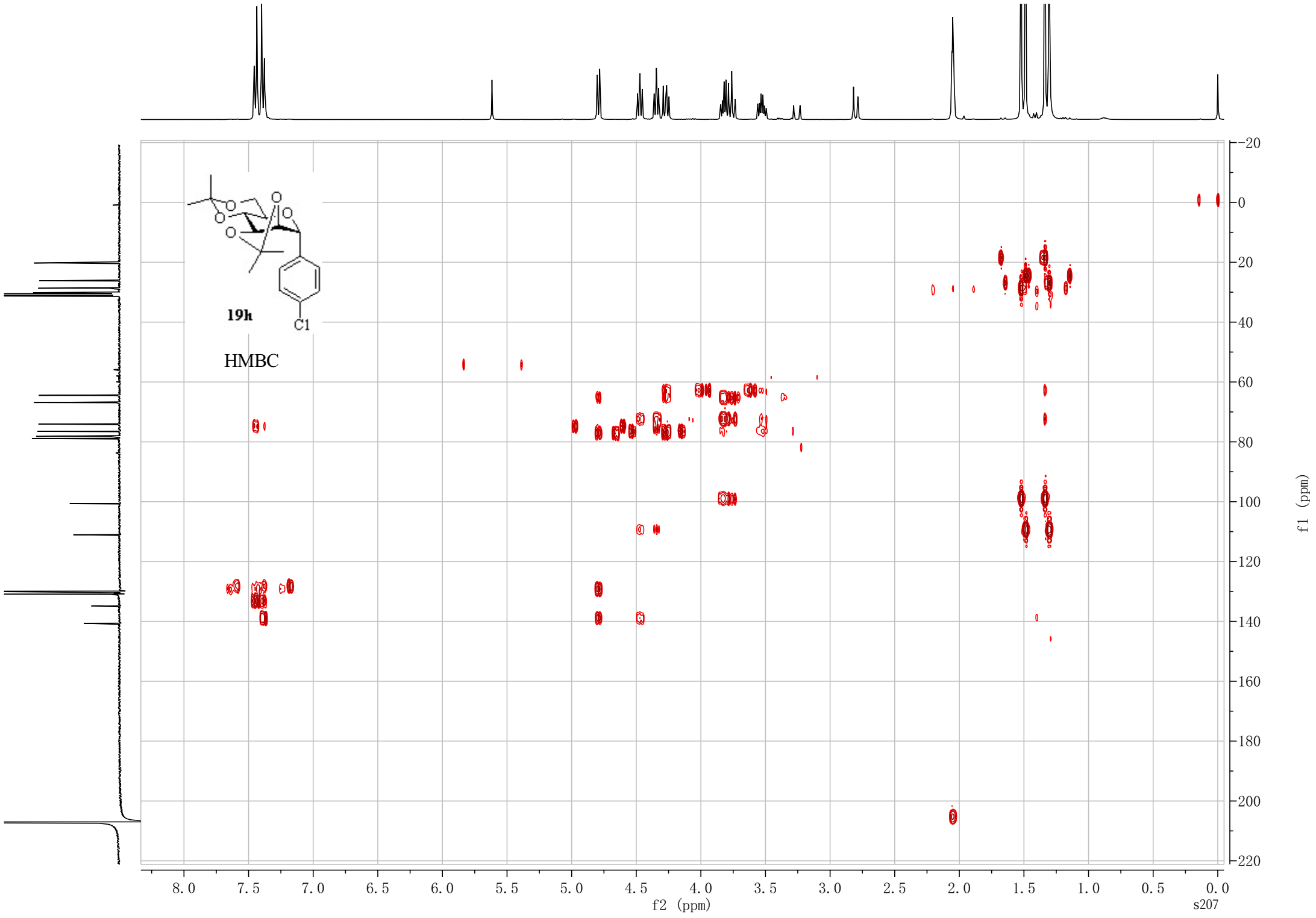
^{1}H NMR (400 MHz, Acetone-d_6)

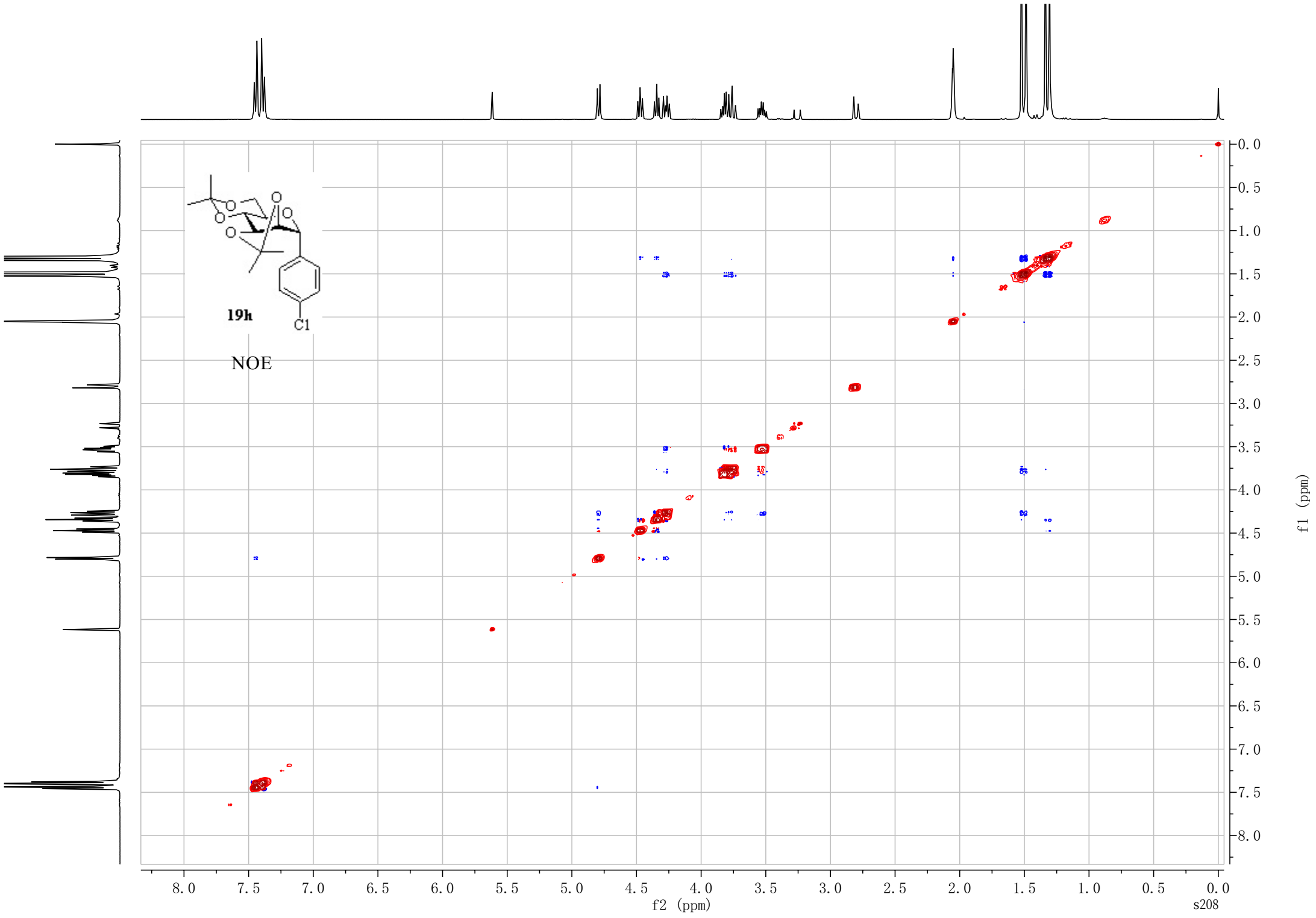


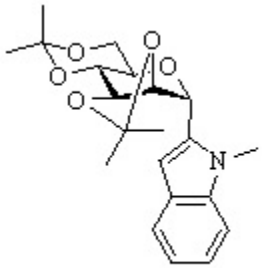
^{13}C NMR (100 MHz, Acetone-d_6)


19h
Cl
^{1}H-^{1}H COSY
f2 (ppm)
f1 (ppm)
s205


19h
Cl
HSQC
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)
s206
-40
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)

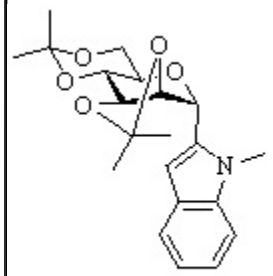

19h
C1
HMBC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
s207
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)


19h
Cl
NOE
f2 (ppm)
f1 (ppm)
s208



19x

^{1}H NMR (400 MHz, Acetone-d_6)



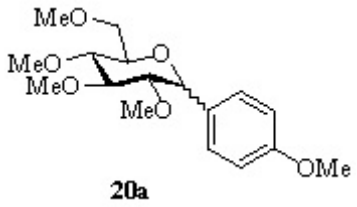
19x

^{13}C NMR (100 MHz, Acetone-d_6)

137.99
135.23
127.00
121.98
120.52
119.40
109.41
108.44
102.29
99.03
75.34
75.13
73.52
69.78
63.46
61.87
27.37
25.59
18.32

f1 (ppm)

s210

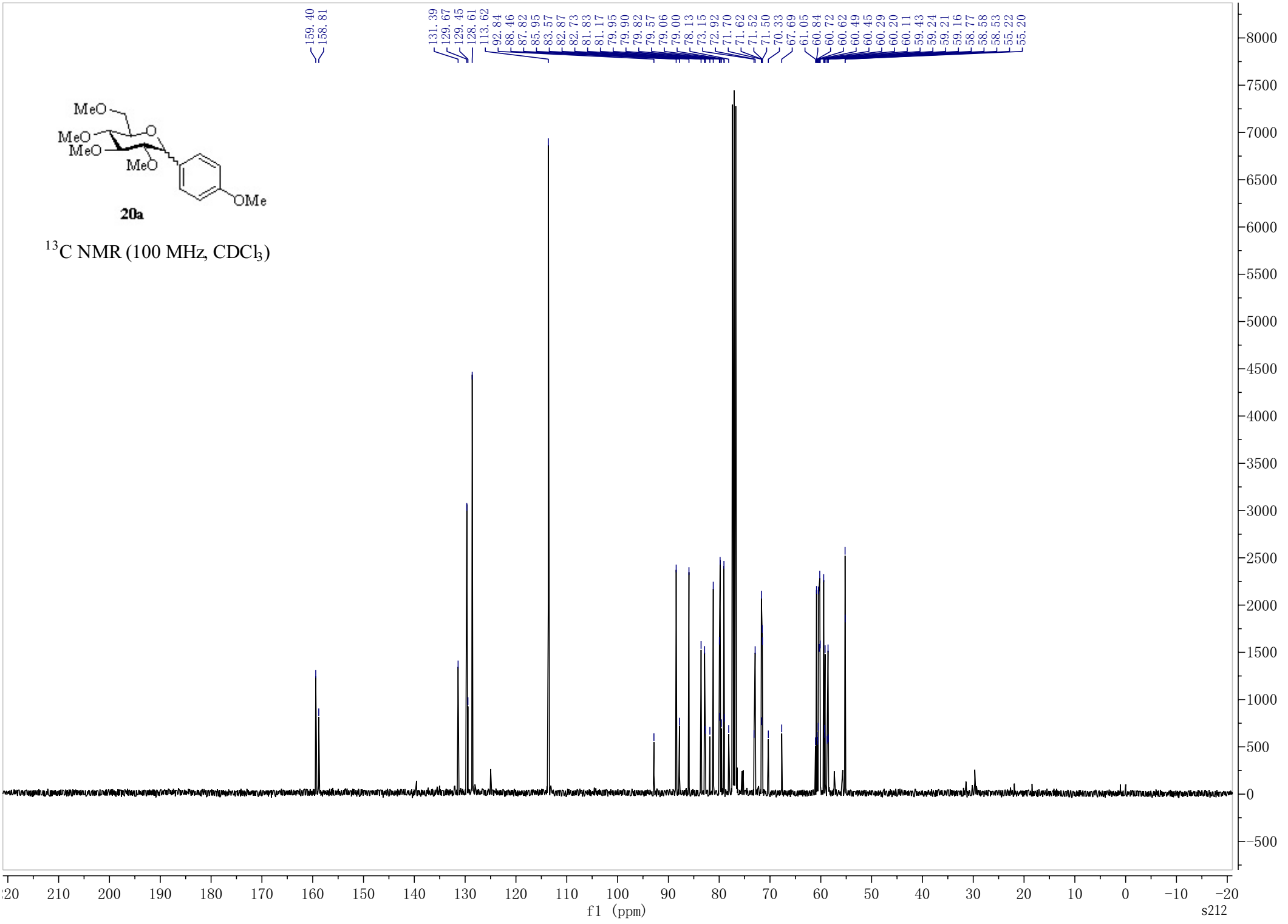


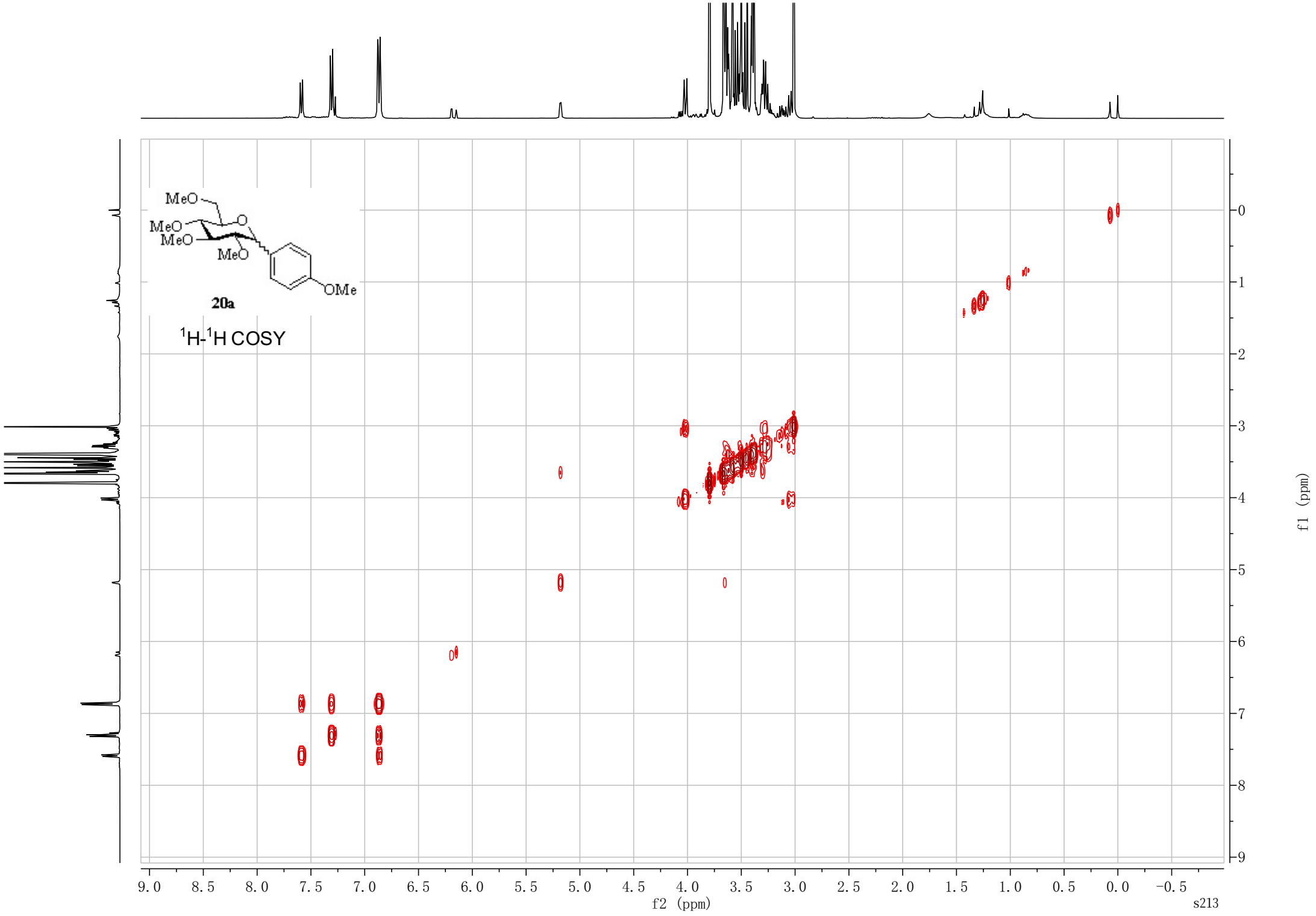
20a

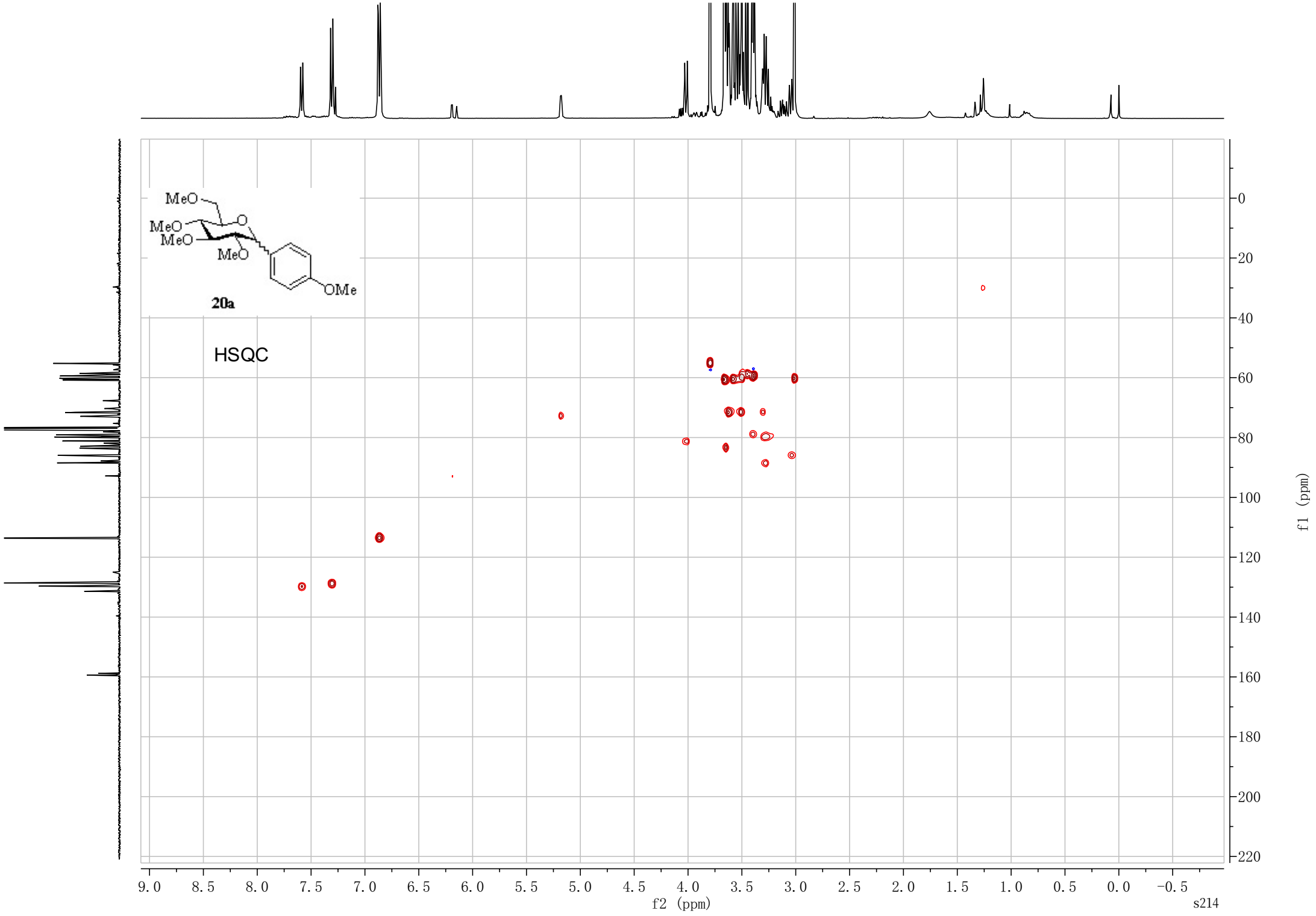
^{1}H NMR (400 MHz, $CDCl_3$)

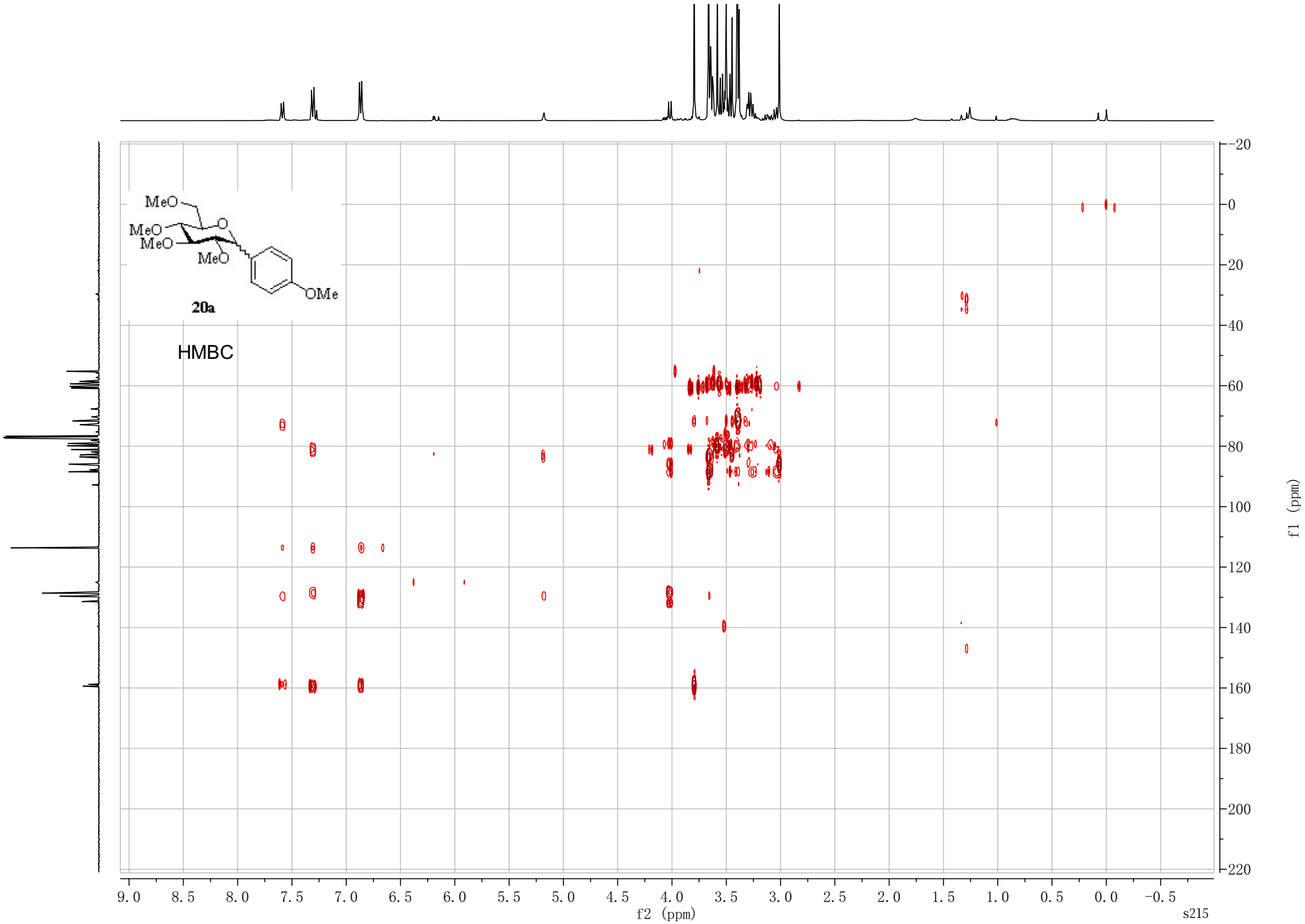
f1 (ppm)

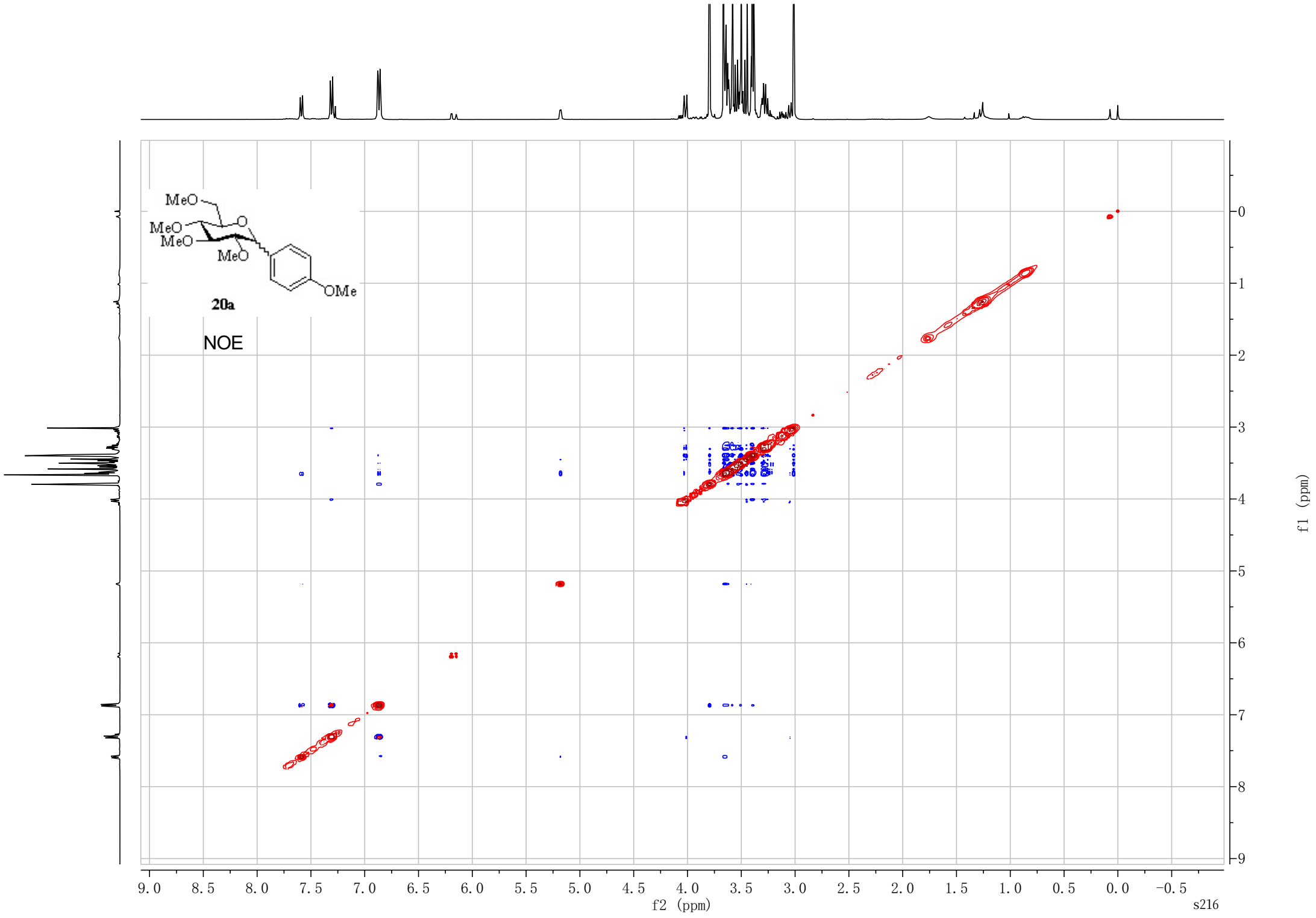
s211

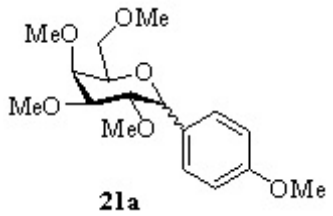

159.40
158.81
131.39
129.67
129.45
128.61
113.62
92.84
88.46
87.82
85.95
83.57
82.87
82.73
81.83
81.17
79.95
79.90
79.82
79.57
79.06
79.00
78.13
73.15
72.92
71.70
71.62
71.52
71.50
70.33
67.69
61.05
60.84
60.72
60.62
60.49
60.45
60.29
60.20
60.11
59.43
59.24
59.21
59.16
58.77
58.58
58.53
55.22
55.20
MeO
MeO
MeO
MeO
O
OMe
20a
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)
s212


MeO
MeO
MeO
MeO
O
OMe
20a
^{1}H-^{1}H COSY
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
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)
s213


MeO
MeO
MeO
MeO
OMe
20a
HSQC
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
s214

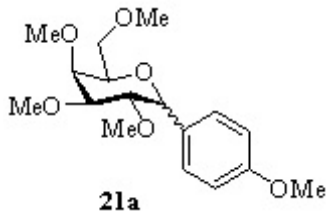

MeO
MeO
MeO
MeO
OMe
20a
HMBC
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
s215


MeO
MeO
MeO
MeO
OMe
20a
NOE
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
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)
s216



21a

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



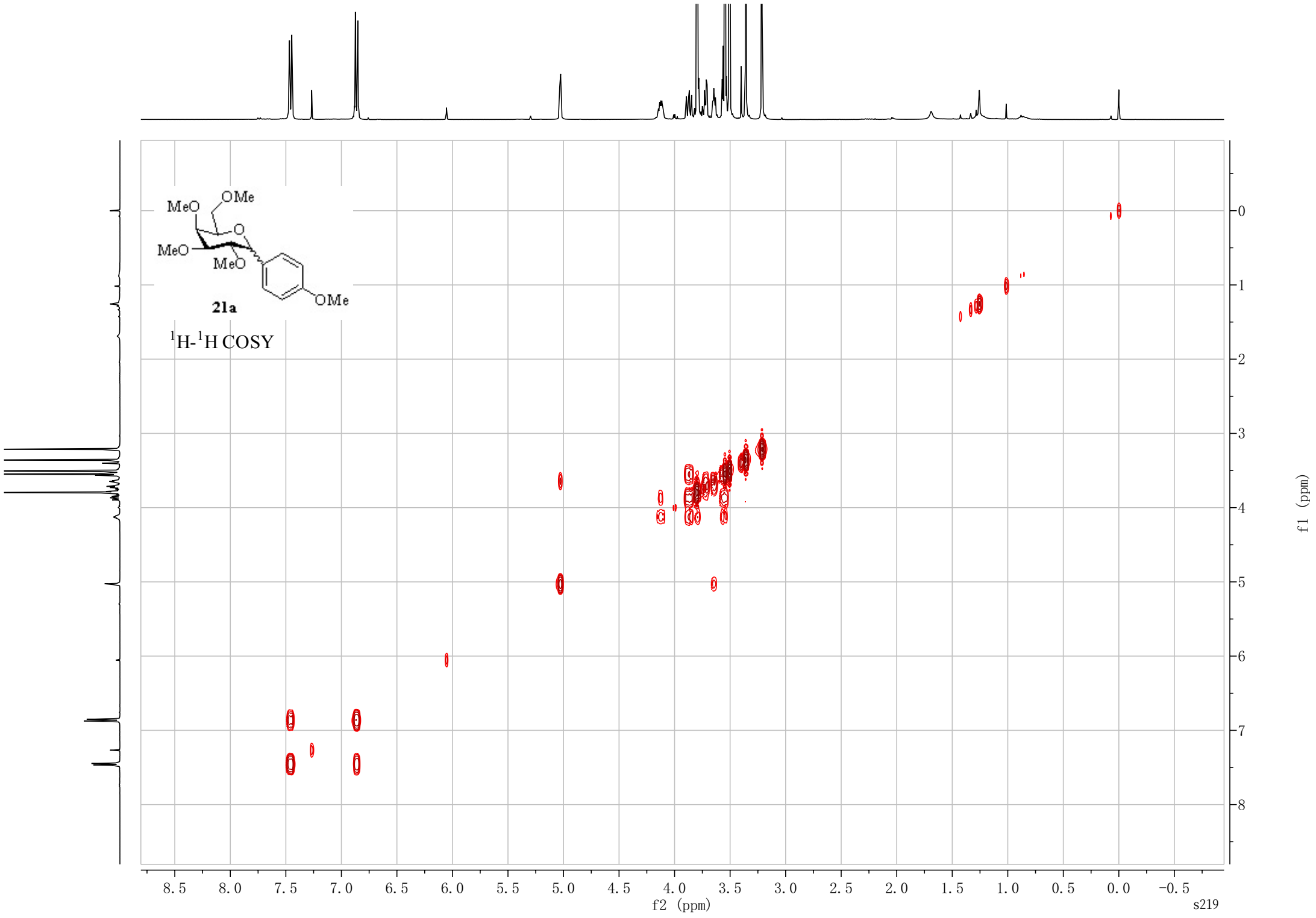
21a

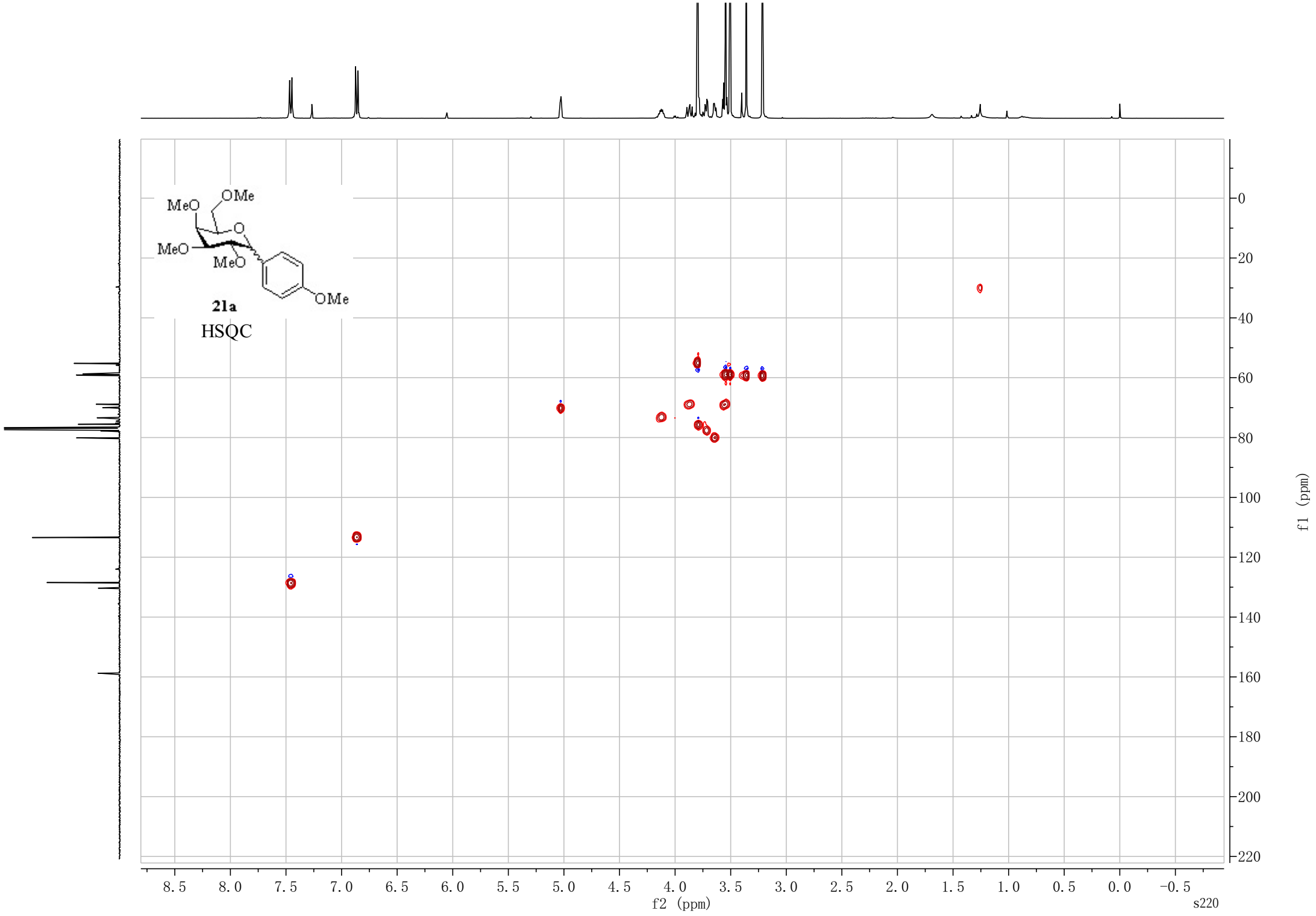
^{13}C NMR (100 MHz, $CDCl_3$)

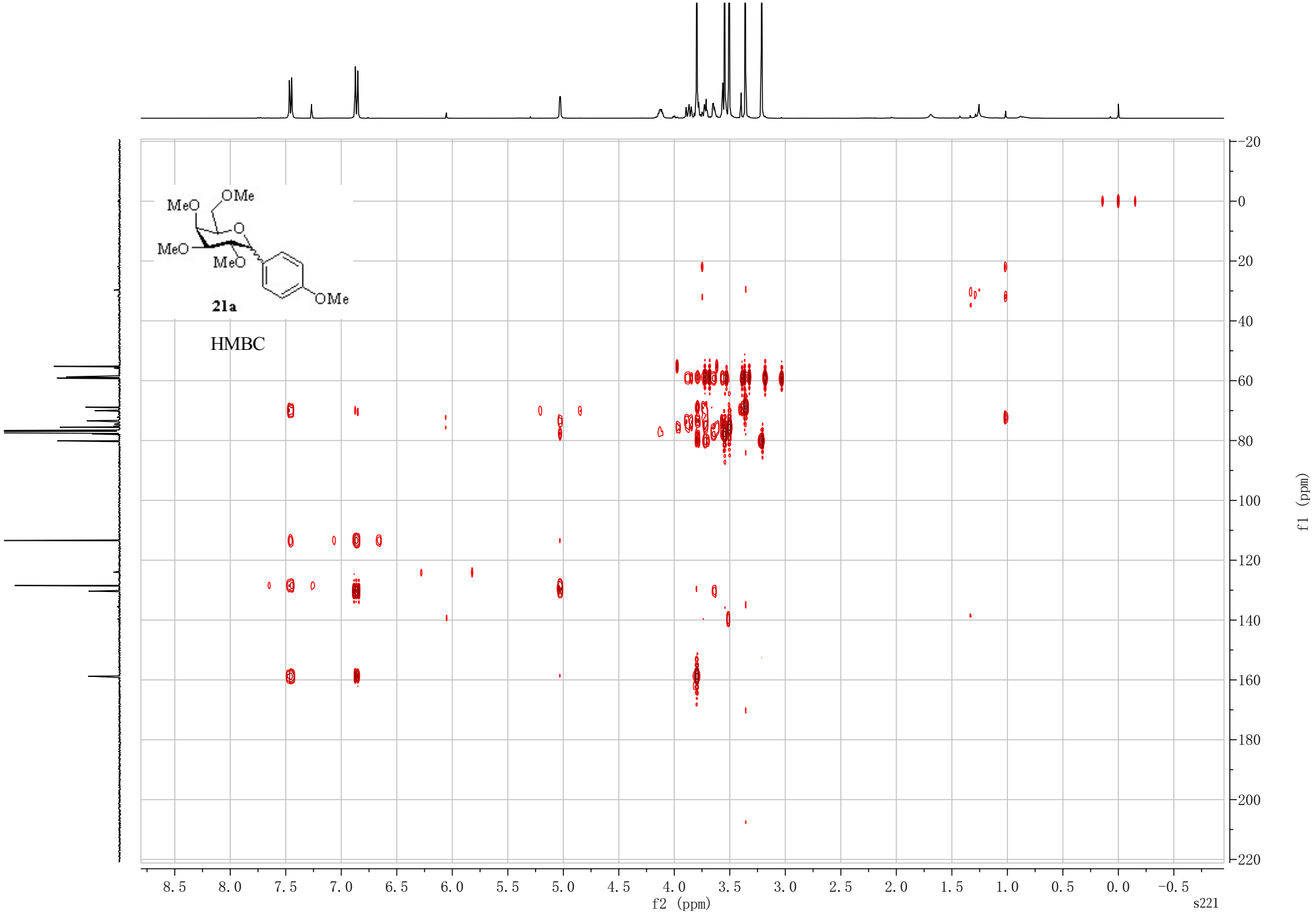
158.75
130.34
128.47
113.42
80.10
77.78
75.57
73.38
70.00
68.89
59.21
59.08
58.79
58.71
55.22

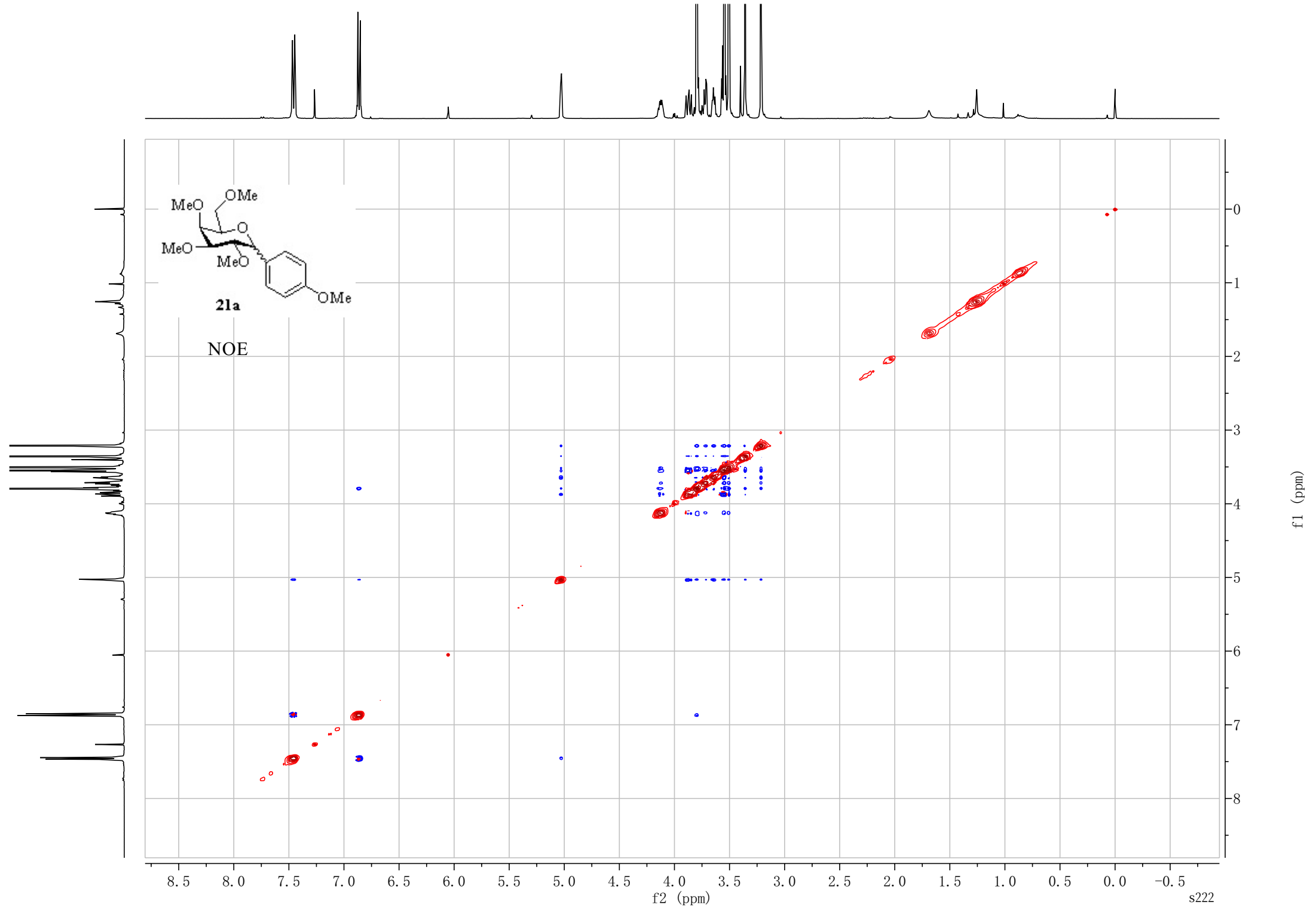
f1 (ppm)

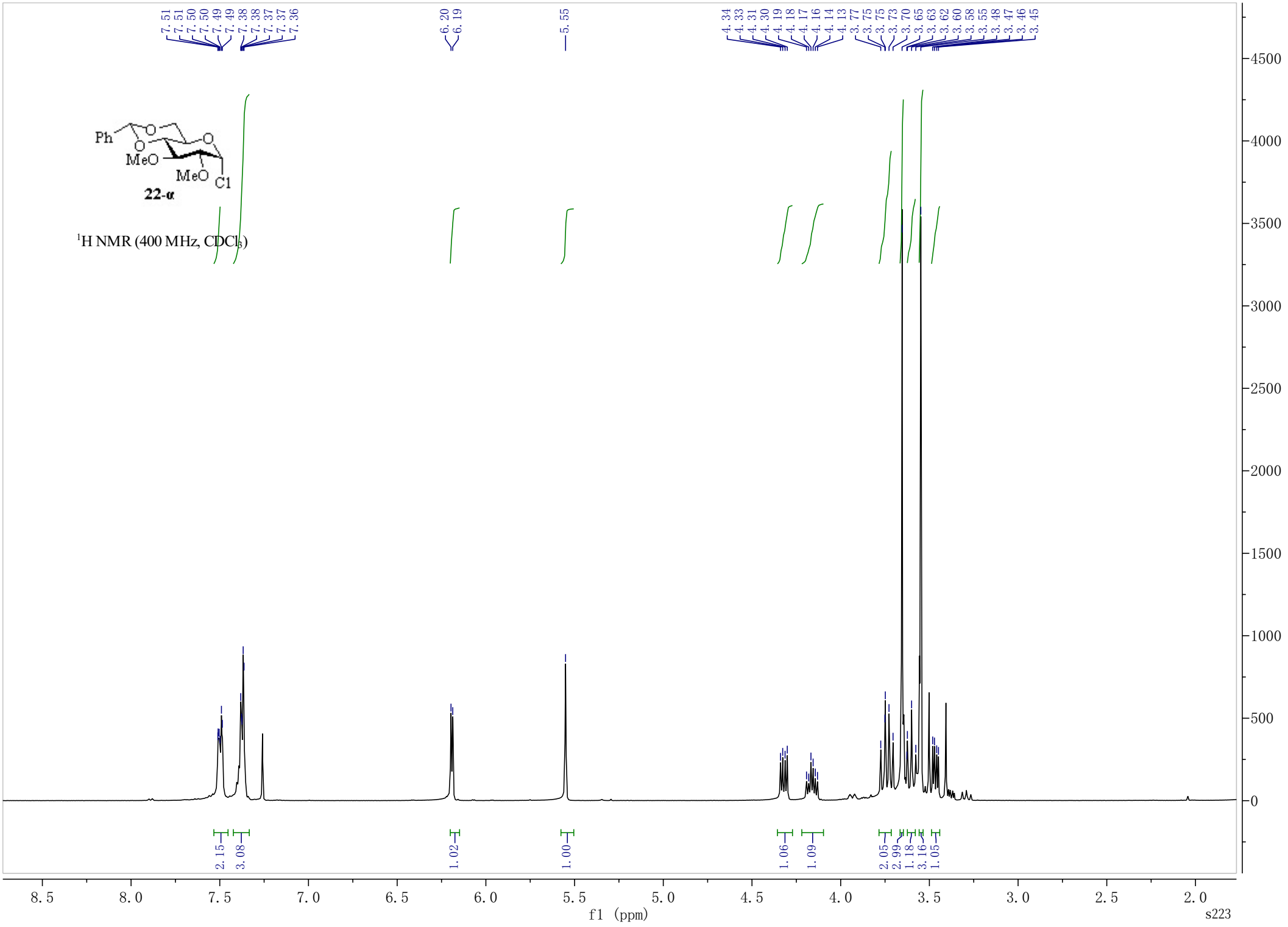
s218

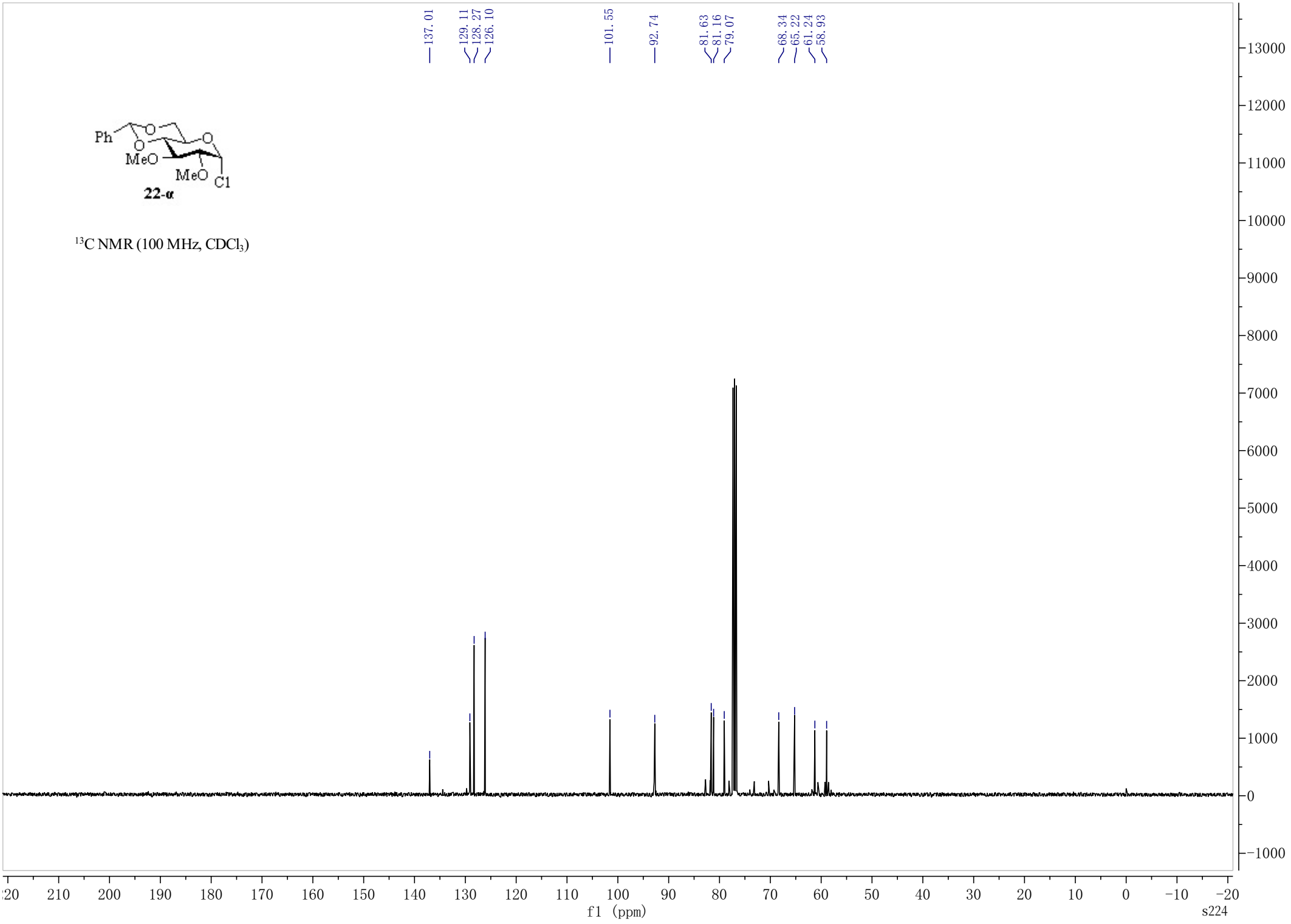

MeO
OMe
O
MeO
MeO
OMe
21a
^{1}H-^{1}H COSY
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)
s219

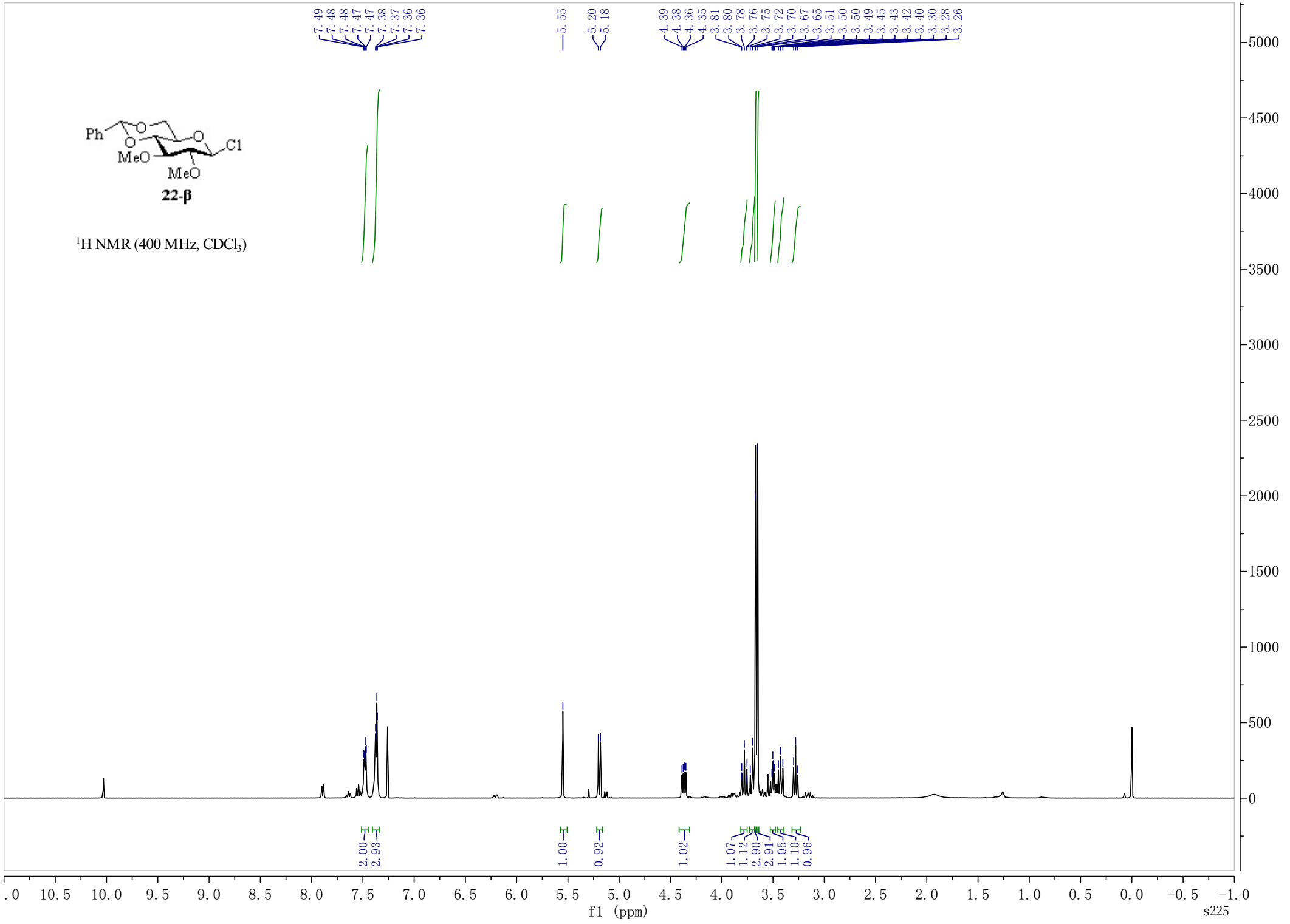

MeO
OMe
O
MeO
MeO
OMe
21a
HSQC
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
s220

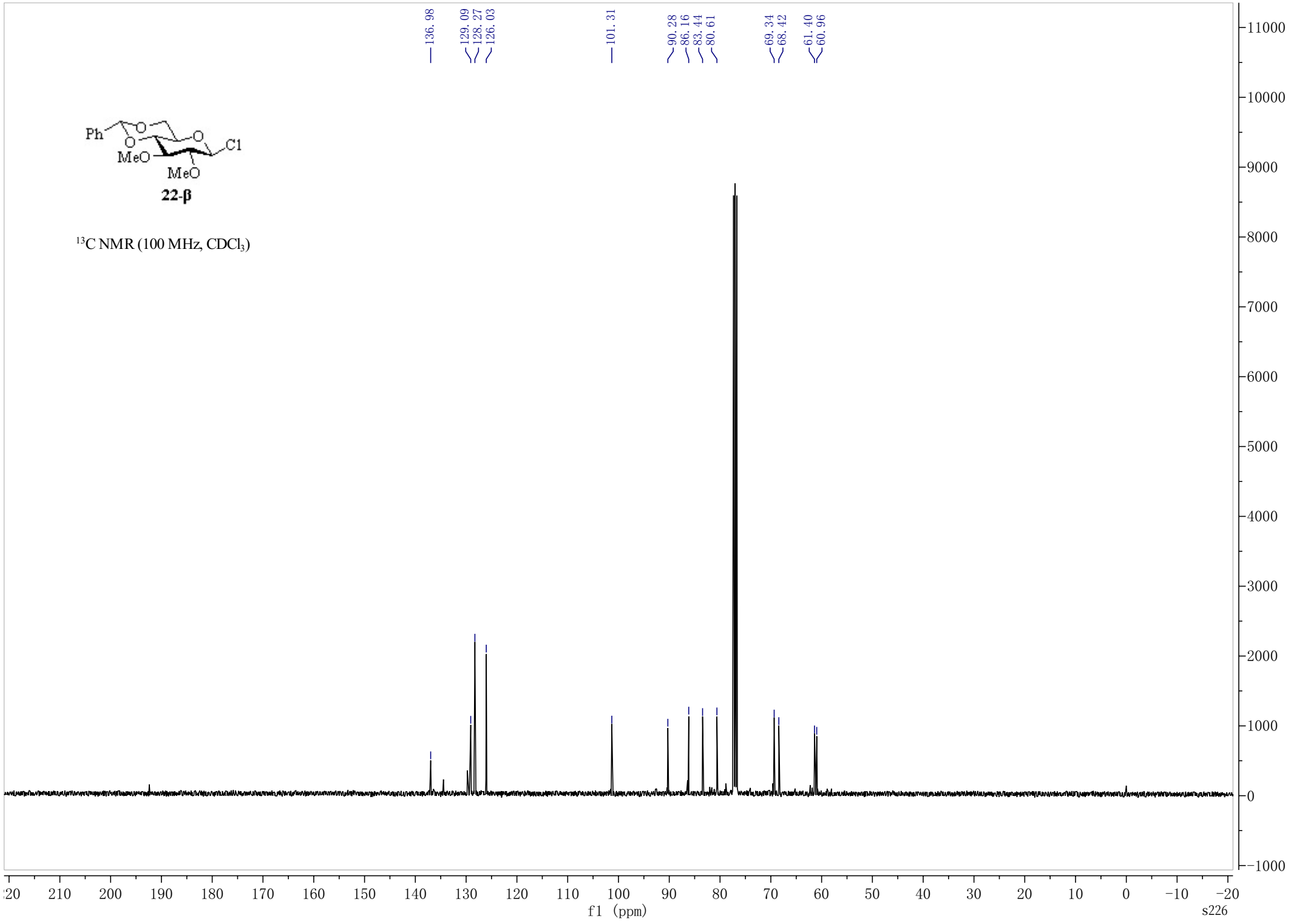

MeO
OMe
MeO
O
MeO
OMe
21a
HMBC
f2 (ppm)
f1 (ppm)
s221

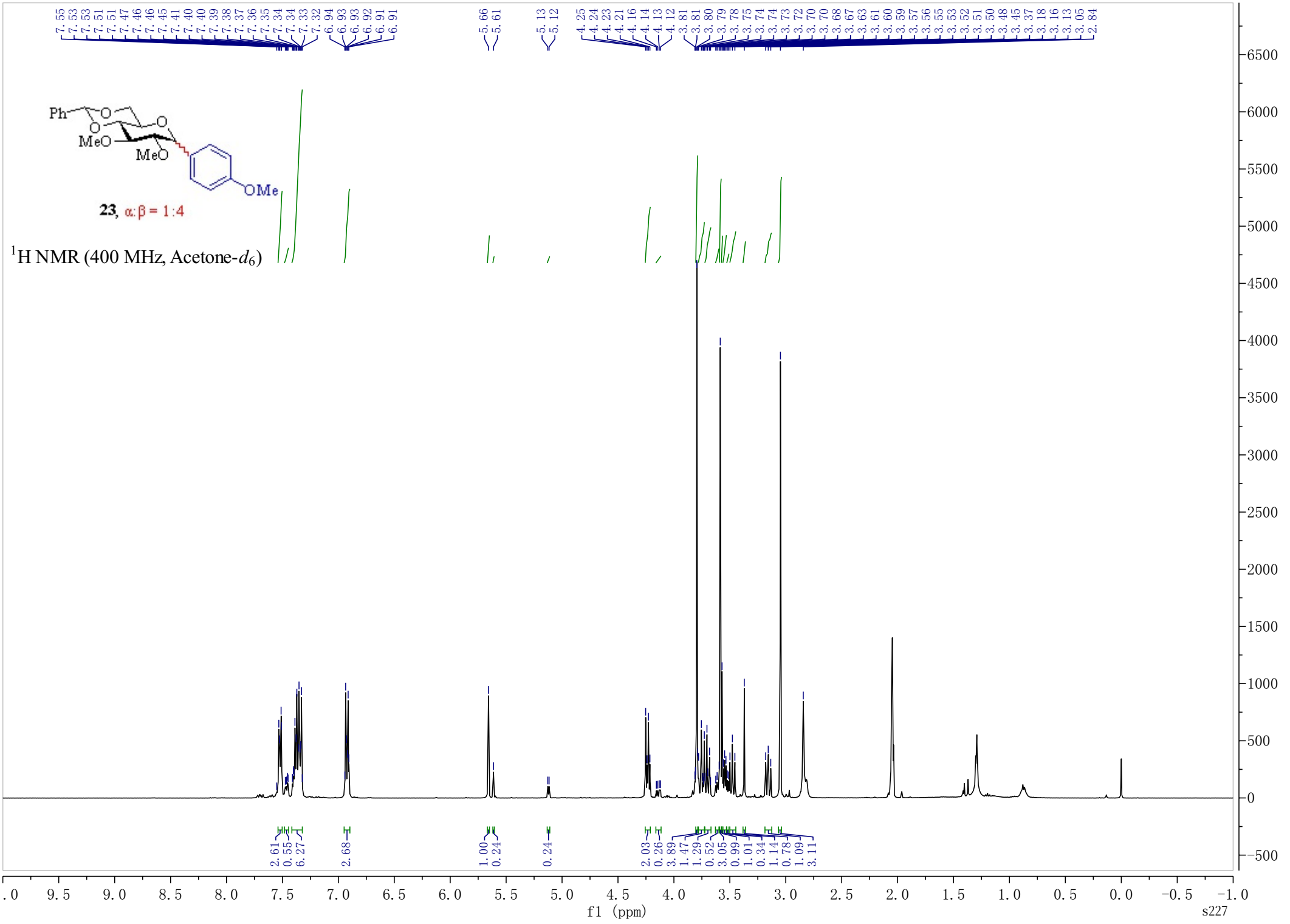

MeO
OMe
O
MeO
MeO
OMe
21a
NOE
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)
s222

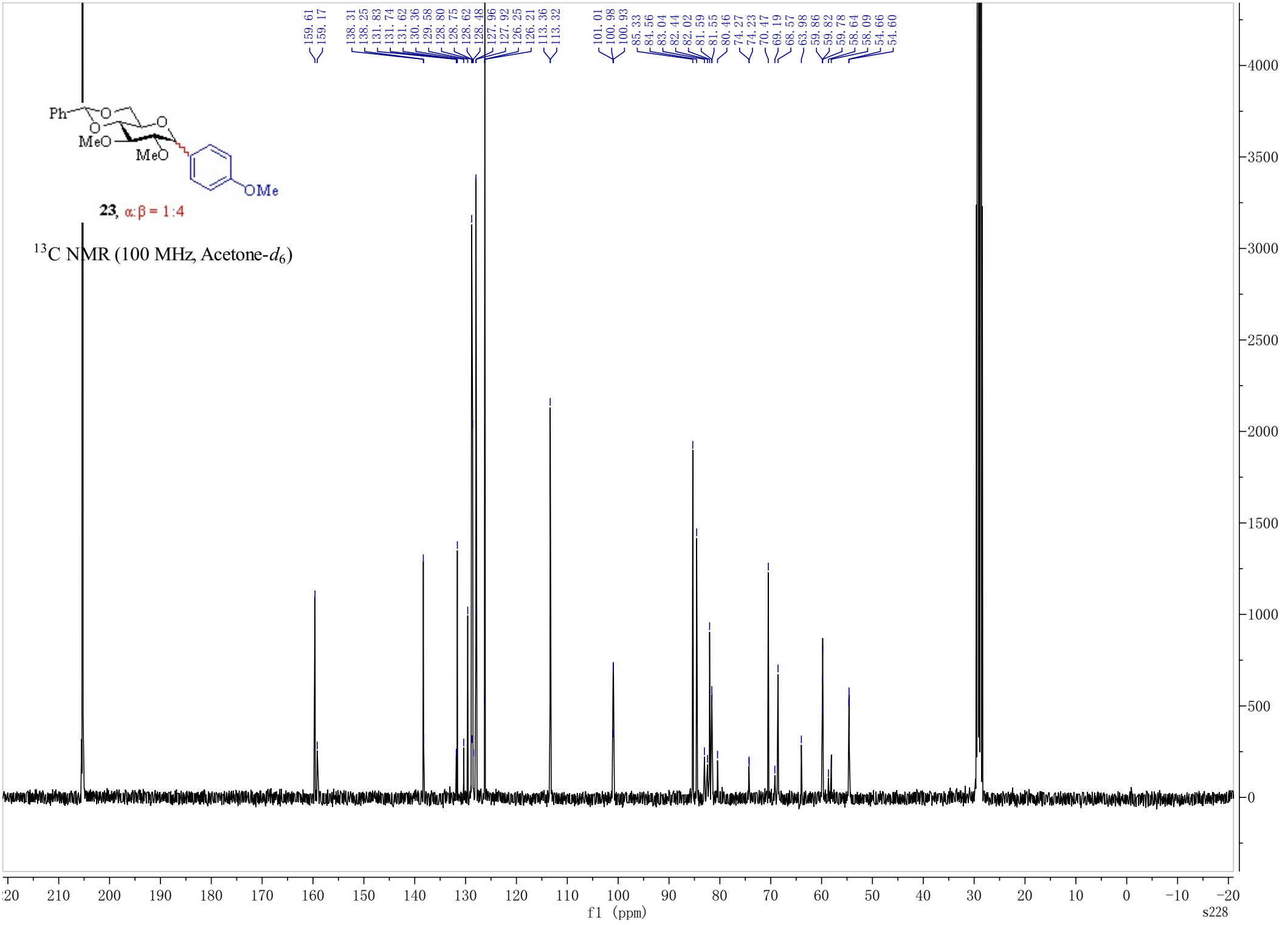

7.51
7.51
7.50
7.50
7.49
7.49
7.38
7.38
7.37
7.37
7.36
6.20
6.19
5.55
4.34
4.33
4.31
4.30
4.19
4.18
4.17
4.16
4.14
4.13
3.77
3.75
3.75
3.73
3.70
3.65
3.63
3.62
3.60
3.58
3.55
3.48
3.47
3.46
3.45
Ph
O
O
O
MeO
MeO
C1
22-α
1H NMR (400 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2.15
3.08
1.02
1.00
1.06
1.09
2.05
2.99
1.18
3.16
1.05
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
f1 (ppm)
s223


137.01
129.11
128.27
126.10
101.55
92.74
81.63
81.16
79.07
68.34
65.22
61.24
58.93
Ph
O
O
O
MeO
MeO
C1
22-α
13C NMR (100 MHz, CDCl3)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
s224


Ph
O
O
O
Cl
MeO
MeO
22-β
^{1}H NMR (400 MHz, $CDCl_3$)
7.49
7.48
7.48
7.47
7.47
7.38
7.37
7.36
7.36
5.55
5.20
5.18
4.39
4.38
4.36
4.35
3.81
3.80
3.78
3.76
3.75
3.72
3.70
3.67
3.65
3.51
3.50
3.50
3.49
3.45
3.43
3.42
3.40
3.30
3.28
3.26
2.00
2.93
1.00
0.92
1.02
1.07
1.12
2.90
2.91
1.05
1.10
0.96
f1 (ppm)
s225

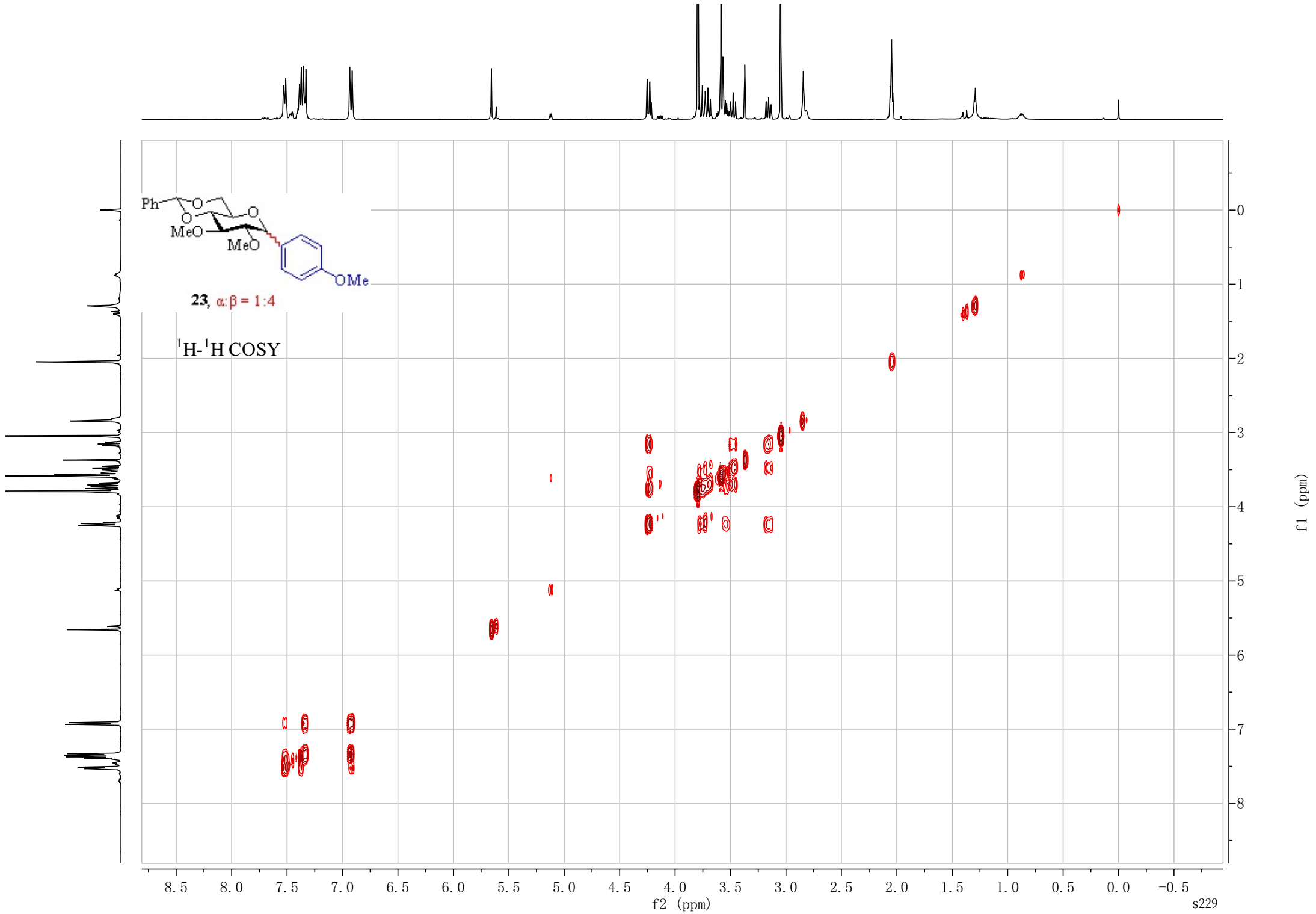

136.98
129.09
128.27
126.03
101.31
90.28
86.16
83.44
80.61
69.34
68.42
61.40
60.96
Ph
O
O
O
Cl
MeO
MeO
22-β
^{13}C NMR (100 MHz, $CDCl_3$)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
s226

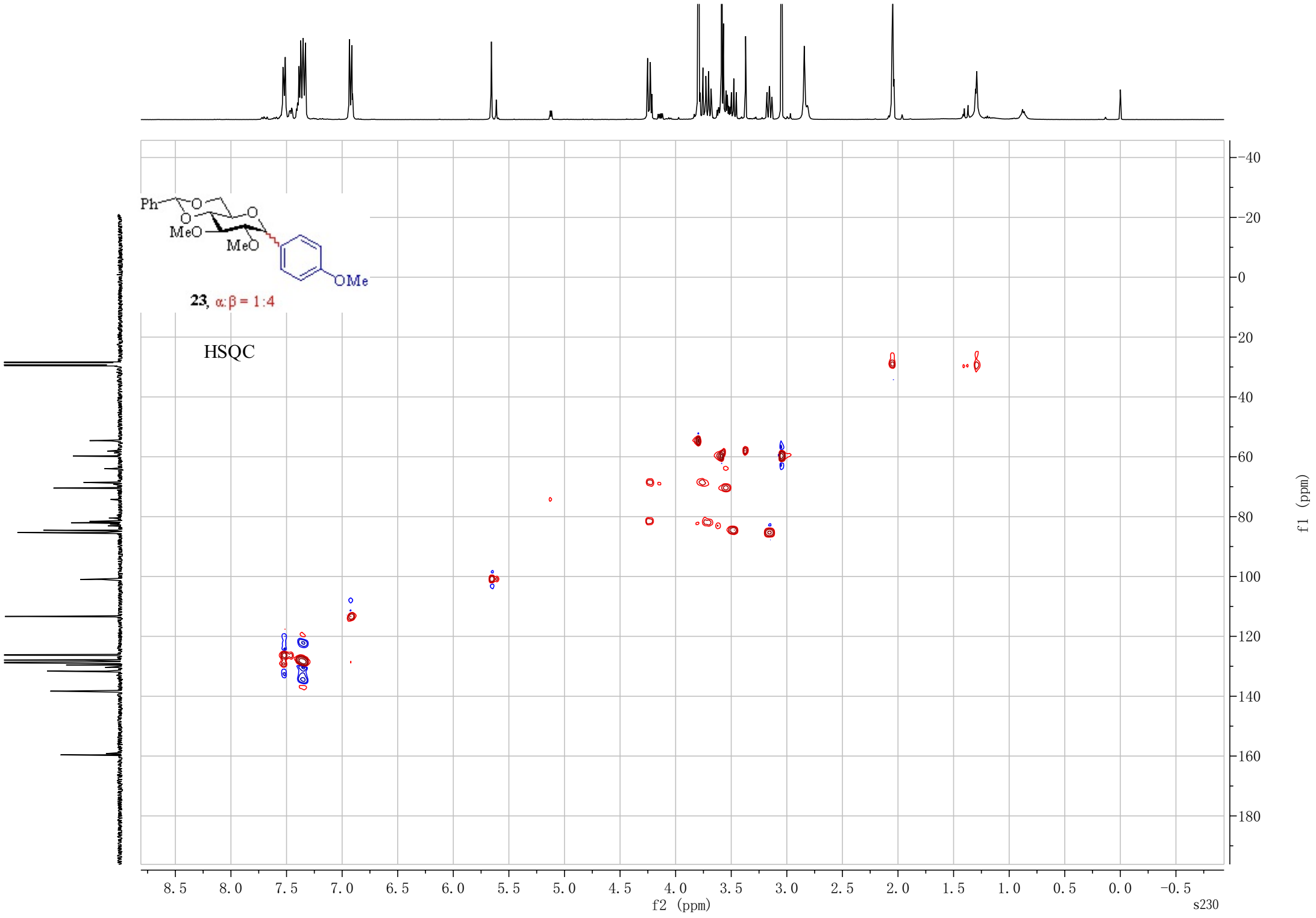

Ph
MeO
MeO
OMe
23, α:β = 1:4
1H NMR (400 MHz, Acetone-d6)
f1 (ppm)
s227

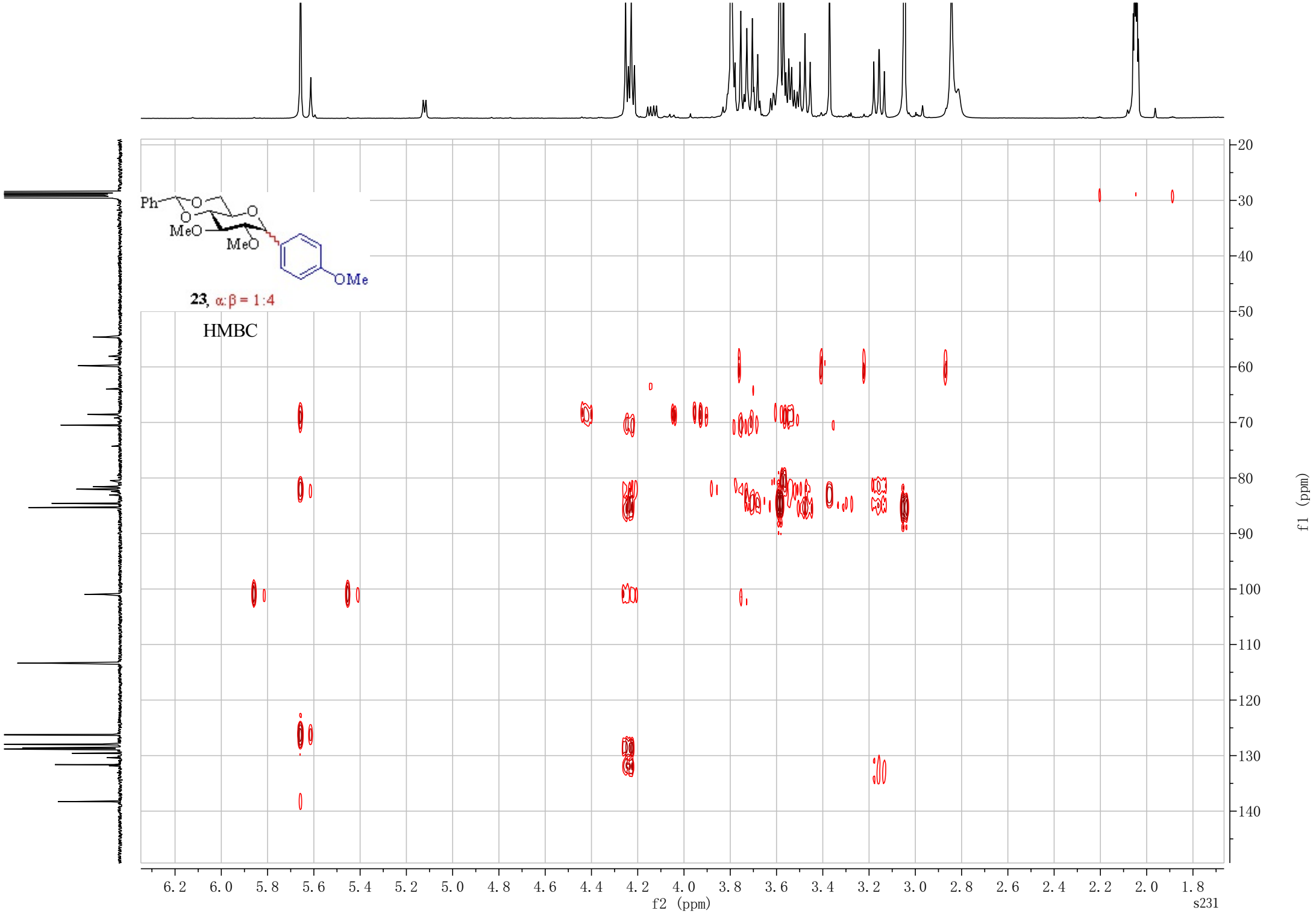


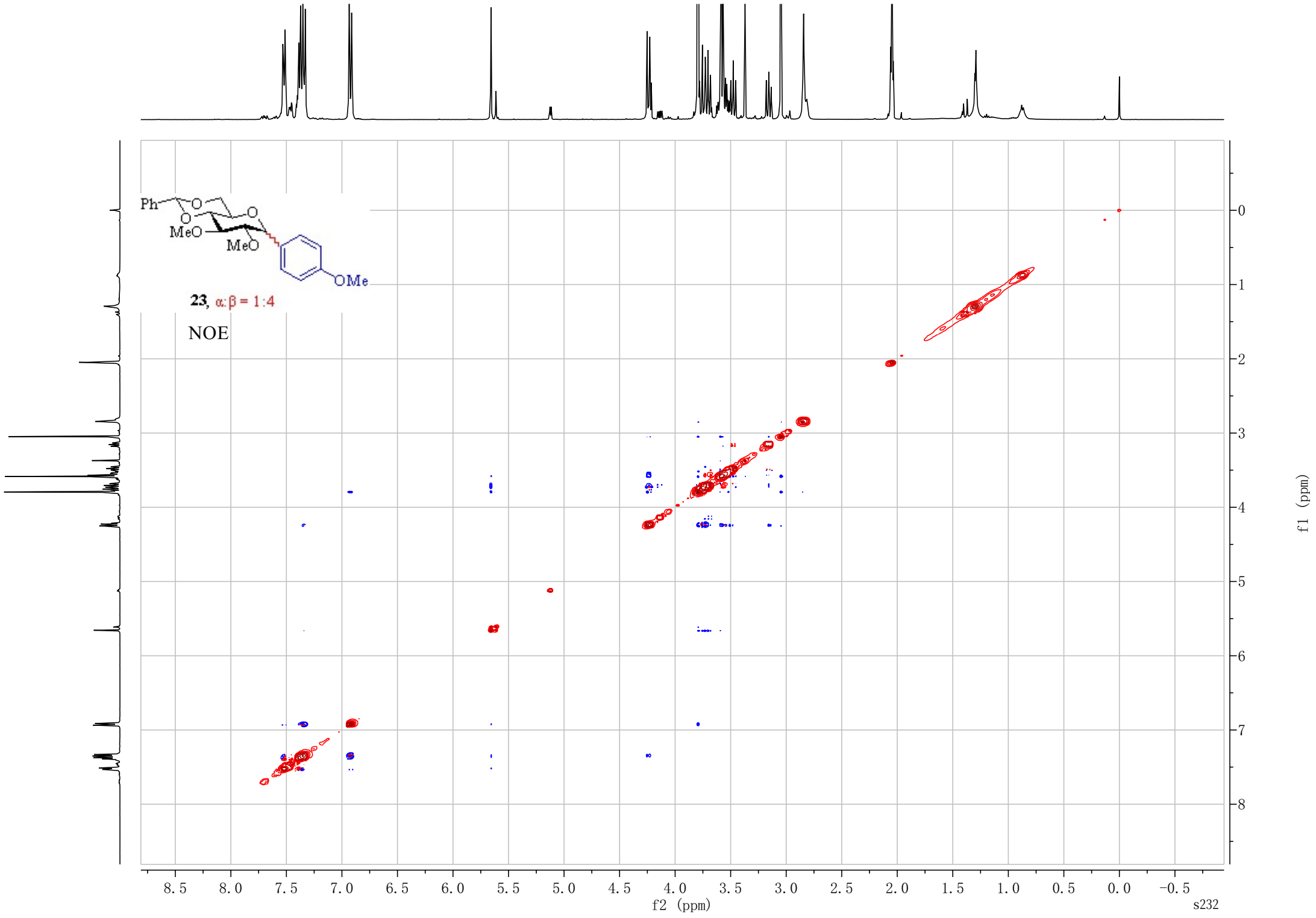
23, α:β = 1:4

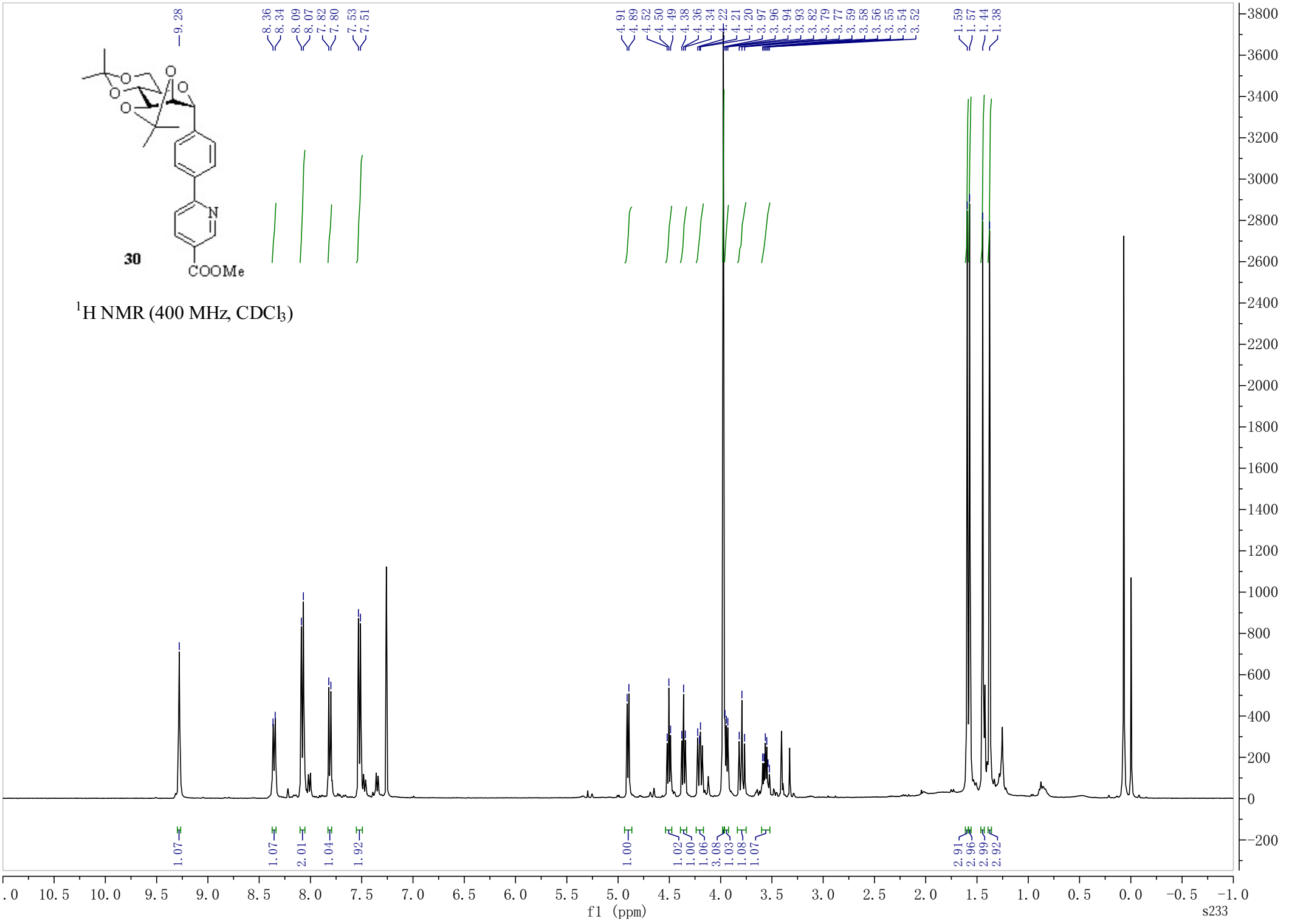
^{13}C NMR (100 MHz, Acetone-d_6)


Ph
MeO
MeO
OMe
23, α:β = 1:4
^{1}H-^{1}H COSY
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)
s229

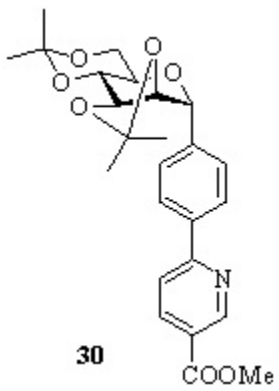

Ph
MeO
MeO
OMe
23, α:β = 1:4
HSQC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-40
-20
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
s230


Ph
MeO
MeO
OMe
23, α:β = 1:4
HMBC
f2 (ppm)
f1 (ppm)
s231


Ph
MeO
MeO
OMe
23, α:β = 1:4
NOE
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)
s232

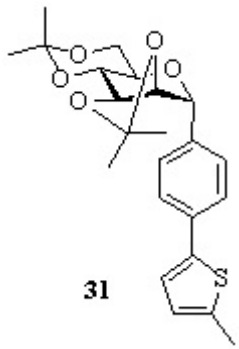


^{1}H NMR (400 MHz, $CDCl_3$)



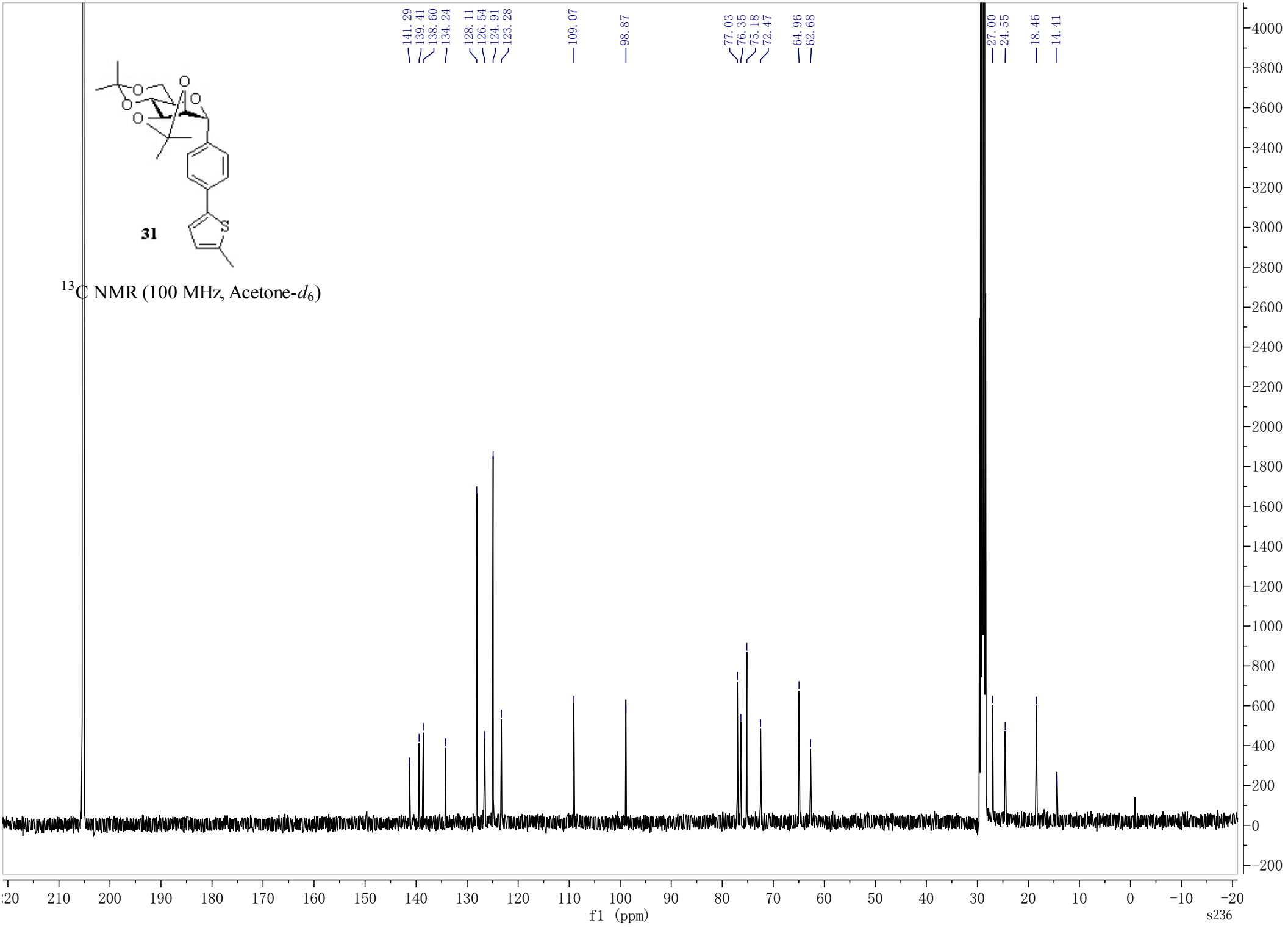
30

^{13}C NMR (100 MHz, $CDCl_3$)

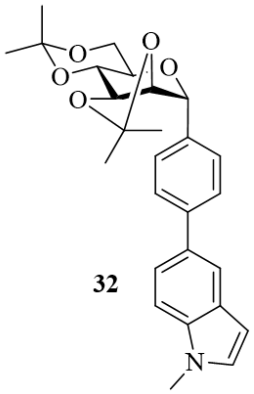


31

^{1}H NMR (400 MHz, Acetone-d_6)

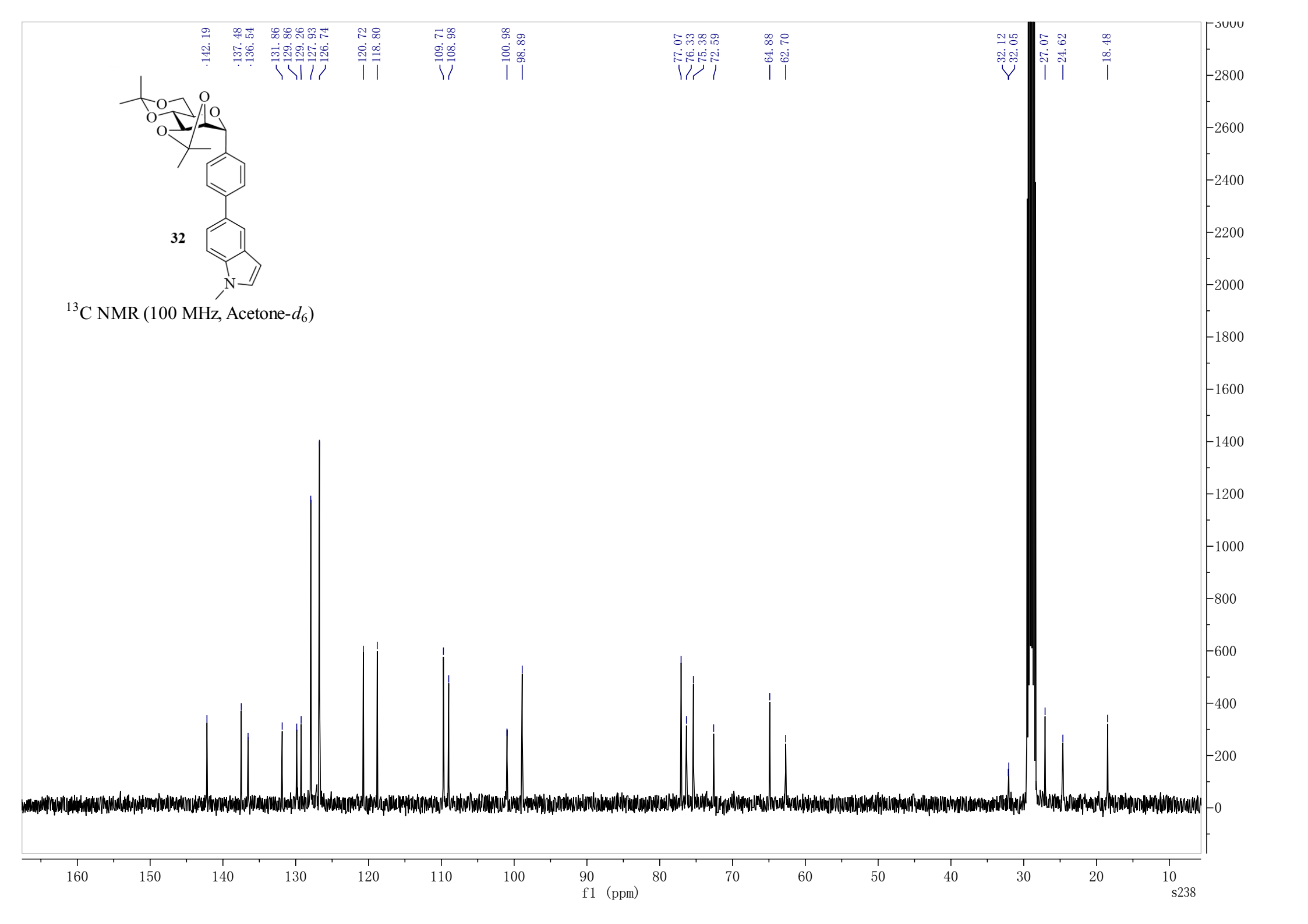


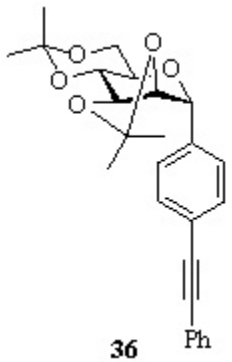
^{13}C NMR (100 MHz, Acetone-d_6)



32

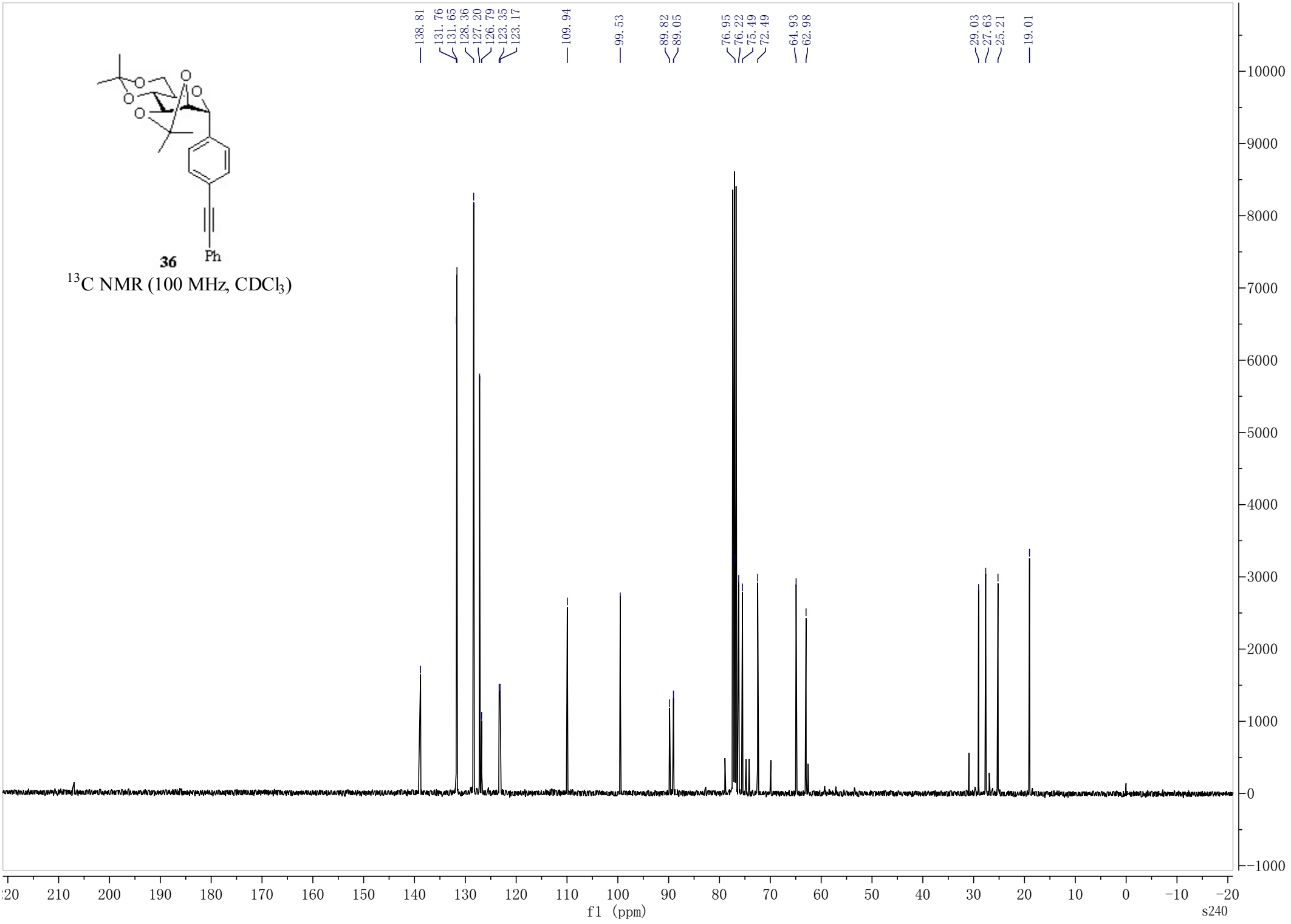
^{1}H NMR (400 MHz, Acetone-d_6)

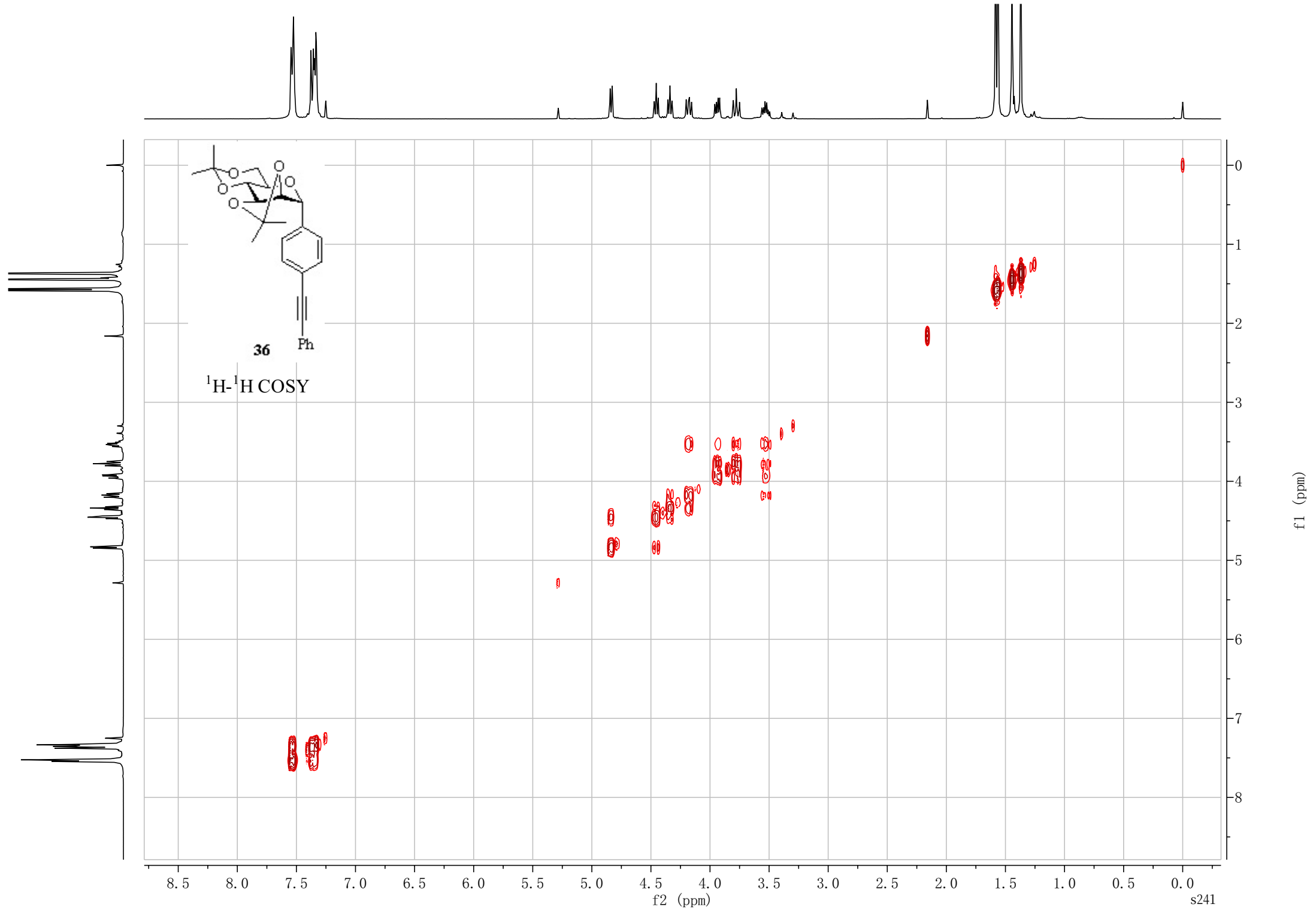

142.19
137.48
136.54
131.86
129.86
129.26
127.93
126.74
120.72
118.80
109.71
108.98
100.98
98.89
77.07
76.33
75.38
72.59
64.88
62.70
32.12
32.05
27.07
24.62
18.48
32
^{13}C NMR (100 MHz, Acetone-d_6)
f1 (ppm)
s238

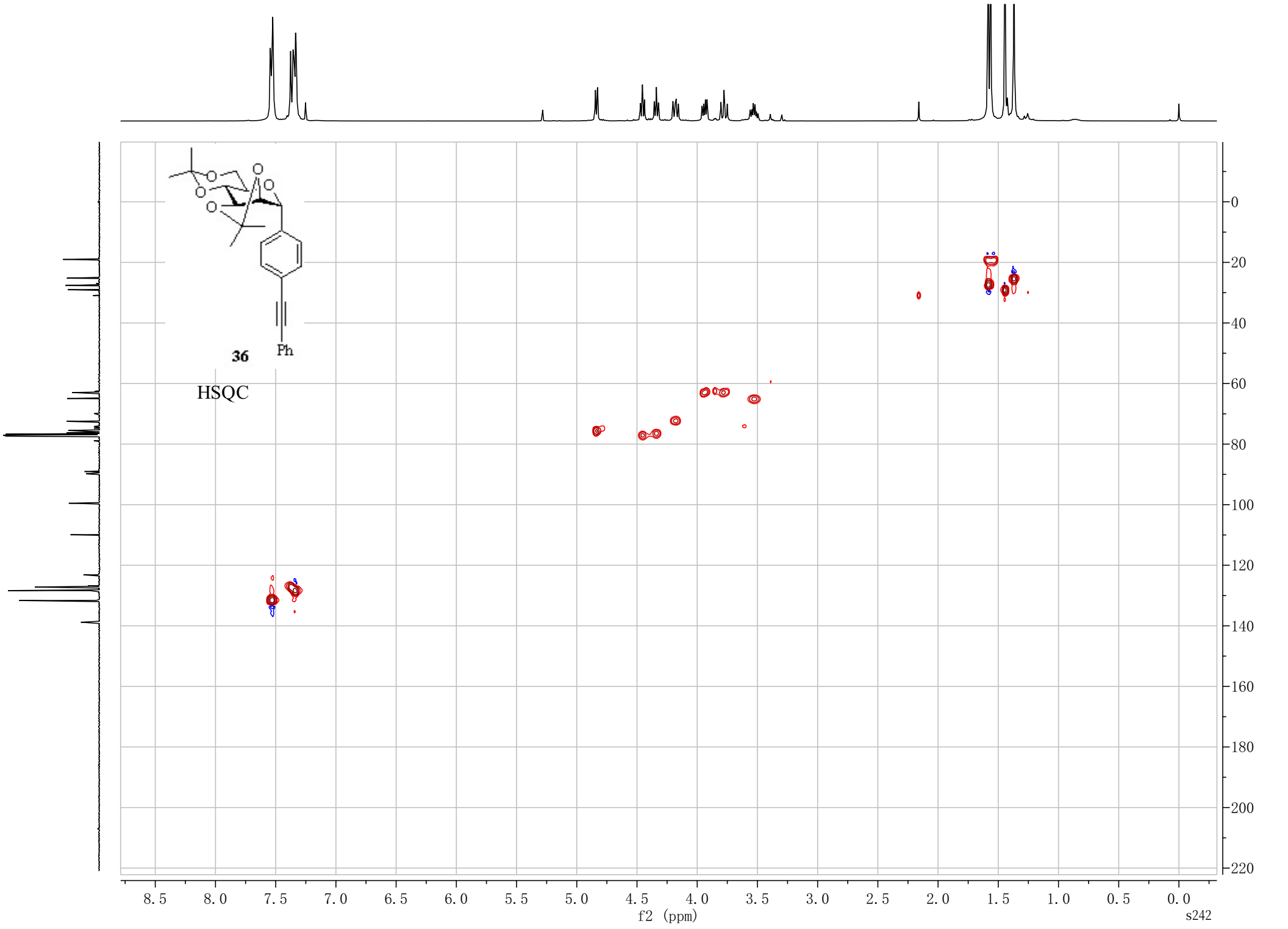


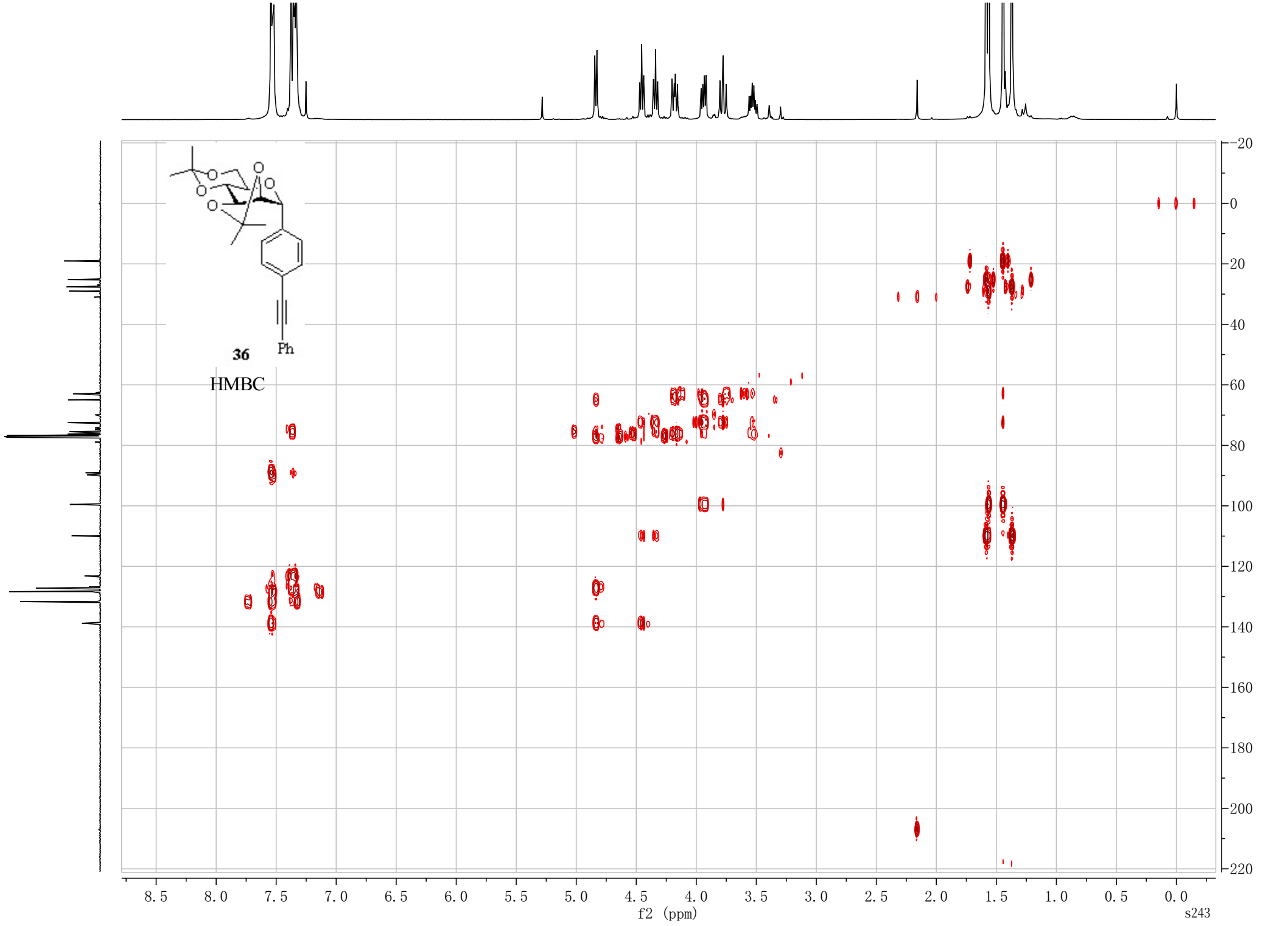
36

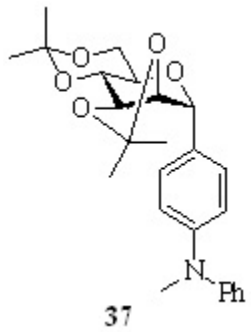
^{1}H NMR (400 MHz, $CDCl_3$)


138.81
131.76
131.65
128.36
127.20
126.79
123.35
123.17
109.94
99.53
89.82
89.05
76.95
76.22
75.49
72.49
64.93
62.98
29.03
27.63
25.21
19.01
Ph
36
13C NMR (100 MHz, CDCl3)
f1 (ppm)
s240


Ph
36
^{1}H-^{1}H COSY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)
s241

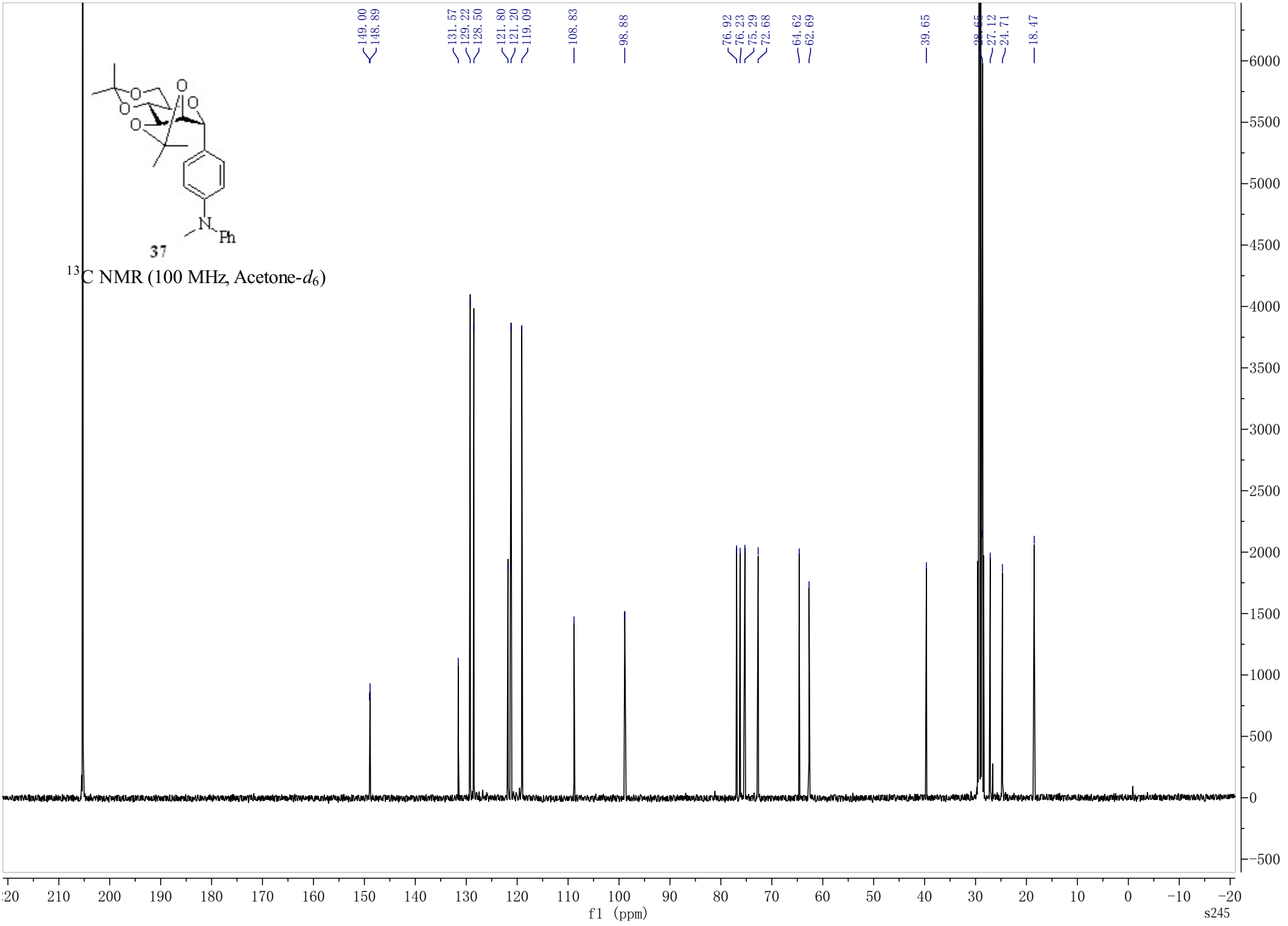

36
Ph
HSQC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
s242

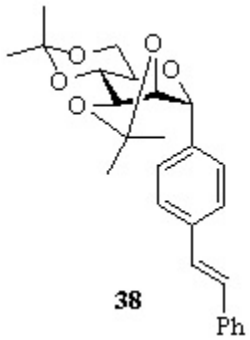

Ph
36
HMBC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
s243



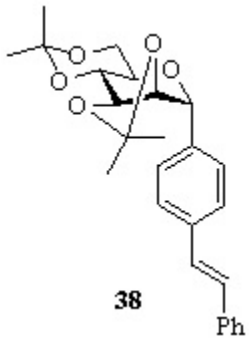
37

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


149.00
148.89
131.57
129.22
128.50
121.80
121.20
119.09
108.83
98.88
76.92
76.23
75.29
72.68
64.62
62.69
39.65
28.65
27.12
24.71
18.47
O
O
O
O
O
N
Ph
37
^{13}C NMR (100 MHz, Acetone-d_6)
f1 (ppm)
s245



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



^{13}C NMR (100 MHz, $CDCl_3$)