Supporting Information

Electrochemical Nickel-Catalyzed Cross-Coupling of Glycosyl Thiols with Preactivated Phenols and Ketones

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General Information

Commercial reagents were used without further purification unless otherwise indicated. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$ (10 g/L) in 10% sulfuric acid (aq.) followed by charring at ~150 °C. Flash column chromatography was performed on silica gel (300-400 mesh). ^1H and ^{13}C spectra were recorded on a Bruker AV 400 in $CDCl_3$. Chemical shifts (δ) are given in ppm relative to tetramethyl silane as internal standard (^1H NMR in $CDCl_3$ or CD_3OD) or the residual signal of the deuterated solvent. Coupling constants (J) are given in Hz. All ^{13}C spectra are proton decoupled. Where applicable COSY, HSQC, NOESY, HMBC experiments were used to further elucidate the structure. Structural assignments were made with additional information from COSY, HSQC, and HMBC experiments.

General Procedure:

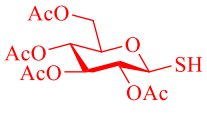
Solution A: A Schlenk tube with stir bar charged with Ni catalyst (0.3 mmol) and dtbbpy (0.3 mmol) were dissolved in 1 mL of DMF under N_2. The solution was stirred for 1 h at 60℃ before usage.

Solution B: A Schlenk tube with stir bar charged with LiBr (1 mmol) were dissolved in 2.5 mL of DMF under N_2. The solution was stirred for 1 h at rt before usage.

In an oven-dried undivided three-necked bottle (5 mL) equipped with a stir bar with thio-sugar (0.3 mmol, 1 eq). The bottle was equipped with Ni electrode (15 mm×15 mm×1 mm) and Mg electrode (15 mm×15 mm×0.3 mm). Aryl halide (0.3 mmol, 1 eq), 1 mL of **Solution A** and 2 mL of **Solution B** was added under nitrogen atmosphere. The reaction mixture was electrolyzed under a constant current of 8 mA for 3 h at rt. After completion of the reaction, aqueous solution was extracted with EA (3 × 15 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: EA / PE = 1:5).

Scheme S1. The substrates structures used in article

Thio-sugars:



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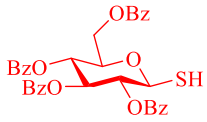

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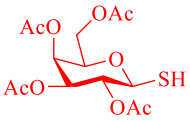

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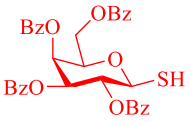

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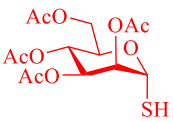

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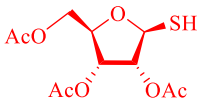

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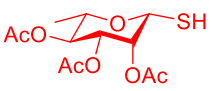

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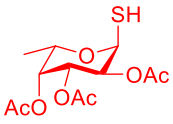

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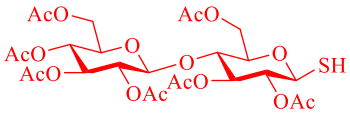

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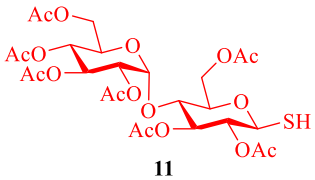

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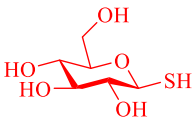

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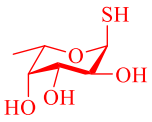

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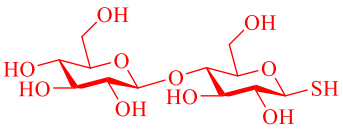

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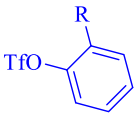
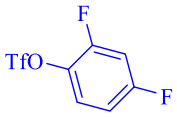
Preactivated Phenols and Ketones:

2a: R = CF_3
2b: R = CN
2c: R = Cl
2d: R = COOMe
2e: R = H
2f: R = OMe
2g: R = OAc
2h: R = Ph



2i: R = CN
2j: R = CHO



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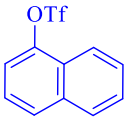

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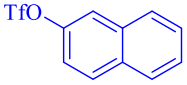

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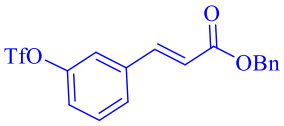
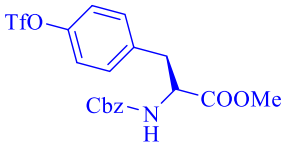


2n



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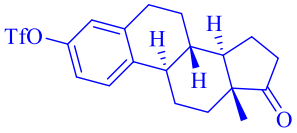

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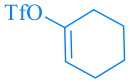
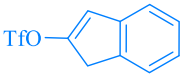


22a



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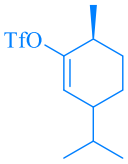

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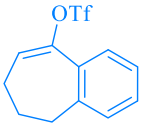

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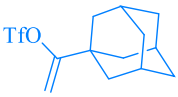

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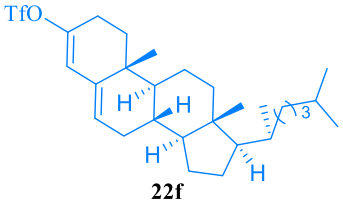

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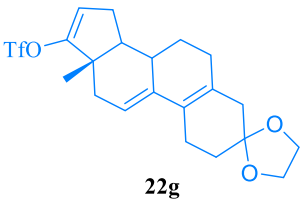
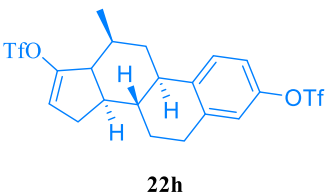
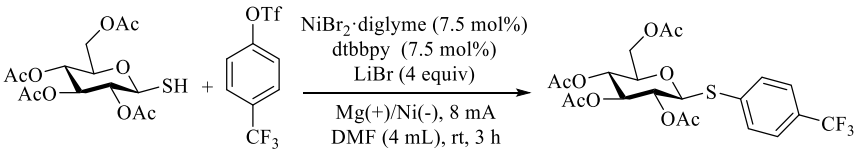


22g



22h

Table S1. Optimization of the Reaction Conditions[a]



1 0.3 mmol **2a** 0.6 mmol **12a**

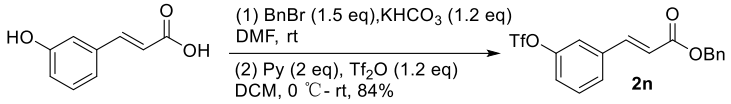
Entry	Cat.	Ligand	Solvent	Current	Time	Electrolyte	Yield(%)[b]
1[c]	$NiBr_2$·diglyme	dtbbpy	DMF	4 mA	6 h	LiBr	53.3
2[c]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	52.6
3[d]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	24
4	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	71
5[e]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	63.1
6[e]	$NiBr_2$·diglyme	dtbbpy	DMF	-	3 h	LiBr	ND
7	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	TBAB	58.5
8	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	KI	65.1
9	$NiBr_2$·dme	dtbbpy	DMF	8 mA	3 h	LiBr	61
10	$Ni(acac)_2$	dtbbpy	DMF	8 mA	3 h	LiBr	41.8
11	$Ni(PPh_3)_2Cl_2$	dtbbpy	DMF	8 mA	3 h	LiBr	7.2
12	$NiBr_2$·diglyme	bpy	DMF	8 mA	3 h	LiBr	10.6
13	$NiBr_2$·diglyme	dtbbpy	DMA	8 mA	3 h	LiBr	62.5
14[f]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	56.4
15[g]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	70.5
16[h]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	60
17[i]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	43.4
18[j]	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	LiBr	NR
19	-	dtbbpy	DMF	8 mA	3 h	LiBr	trace
20	$NiBr_2$·diglyme	dtbbpy	DMF	8 mA	3 h	-	28.8
21	$NiBr_2$·diglyme	dtbbpy	DMF	-	3 h	LiBr	NR
22[k]	$NiBr_2$·diglyme	dtbbpy	DMF	-	3 h	-	Trace

[a] standard condition: **1** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·diglyme (7.5 mol%), dtbbpy (7.5 mol%), LiBr (1.2 mmol), DMF (4 mL) in an undivided cell with a Ni as electrode and Mg sheet as anode, 8 mA, rt, 3h. [b] Isolated yield. [c] **3-1a** (0.3 mmol), **3-2a** (0.3 mmol). [d] **3-1a** (0.6 mmol), **3-2a** (0.3 mmol). [e] NEt_3 (1.2 equiv). [f] [Ni] (5 mol%), ligand (5 mol%). [g] [Ni] (10 mol%), ligand (10 mol%). [h] [Ni] (20 mol%), ligand (20 mol%). [i] Zn anode. [j] C cathode. [k] Zn (2 eq).

Experimental Procedures and Characterization Data of Products

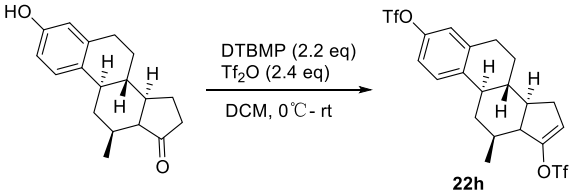
The synthesis procedure and data for the known compounds **1, 3-11, 30-32** to see references 1.[1] The synthesis procedure and data for the known compounds **2a-2m** and **2o-p** to see references 2.[2] And the synthesis procedure and data for the known compounds **22a-22h** to see references 3.[3]

benzyl (E)-3-(3-(((trifluoromethyl)sulfonyl)oxy)phenyl)acrylate 2n



p-Hydroxy cinnamic acid (164.2 mg, 1 mmol) was dissolved in 5.0 mL DMF, and $KHCO_3$ (120 mg, 1.2 mmol) was added slowly. The resultant mixture was stirred for several minutes at room temperature. Then, benzyl bromide (0.2 mL, 1.5 mmol) was added and stirred for 8 h at room temperature. Upon completion, the reaction mixture was added to water and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated, then to dissolve in DCM (2 mL) and Pyridine (0.13 mL, 2 equiv) was added. The mixture was cooled to 0 ℃ Trifluoromethanesulfonic anhydride (0.16 mL, 1.2 equiv) was added dropwise and stirred for 1.5 h at room temperature. Thereafter, H_2O (5 mL) was added, the organic layer was separated, washed with brine, and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure and the residue was directly subjected to purification by flash column chromatography to give **2n**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 5.26 (s, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 149.9, 142.6, 137.1, 135.7, 130.8, 128.7, 128.5, 128.4, 127.9, 122.6, 120.6, 120.4, 118.72 (CF_3), 66.74. ^{19}F NMR (565 MHz, $CDCl_3$) δ -72.75. HRMS (ESI-TOF) Calculated for $C_{17}H_{14}F_3O_5S$ $[M+H]^+$ 387.0509, found 387.0510.

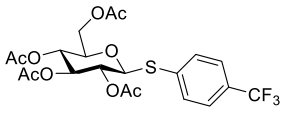
(8R,9R,12S,14R)-12-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthrene-3,16-diyl bis(trifluoromethanesulfonate) 22h



Estrone (1.0 g, 3.7 mmol) was dissolved in 14.8 mL DCM, and 2,6-Di-tert-butyl-4-methylpyridine (1.6 g, 8.1 mmol) was added slowly. The mixture was cooled to 0 ℃ Trifluoromethanesulfonic anhydride (1.5 mL, 8.9 mmol) was added dropwise and stirred for 3 h at room temperature. Thereafter, H_2O (20 mL) was added, the organic layer was separated, washed with brine, and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure and the residue was directly subjected to purification by flash column chromatography to give **22h**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 1H), 7.08 – 6.93 (m, 2H), 5.68 – 5.58 (m, 1H), 2.94 (dd, *J* = 8.9, 4.2 Hz, 2H), 2.44 – 2.30 (m, 3H), 2.17 – 2.07 (m, 1H), 2.00 – 1.88 (m, 2H), 1.84 – 1.75 (m, 1H), 1.72 – 1.56 (m, 3H), 1.53 – 1.43 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 147.6, 140.4, 139.2, 128.4, 127.8, 126.8, 121.3, 118.8 (CF_3), 118.6 (CF_3), 118.3, 53.5, 45.0, 44.3, 36.1, 32.7, 29.2, 28.4, 26.3, 25.6, 15.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.03, -73.60. HRMS (ESI-TOF) Calculated for $C_{20}H_{20}F_6O_6S_2Na$ $[M+Na]^+$ 557.0498, found 557.0455.

4-(trifluoromethyl)phenyl-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12a

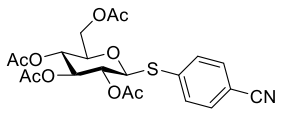
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12a** (108.3 mg, 71% yield, β only, PE:EA = 3:1, R*f* = 0.25) was obtained as white solid.



$[\alpha]_D^{25}$ 24.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.50 (m, 4H), 5.27 (t, *J* = 10.0 Hz, 1H, H-3), 5.18 – 4.92 (m, 2H, H-4, H-2), 4.81 (d, *J* = 10.0 Hz, 1H, H-1), 4.32 – 4.16 (m, 2H, H-6), 3.87 – 3.71 (m, 1H, H-5), 2.09 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.1, 169.3, 169.2, 136.9, 132.2, 130.5, 130.2, 130.0, 129.6, 125.7, 125.7, 125.7, 125.6, 123.9 (CF_3), 84.8 (C-1), 75.9 (C-5), 73.7 (C-3), 69.7 (C-2), 68.1 (C-4), 62.0 (C-6), 20.6, 20.5. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}F_3O_9S$ $[M+H]^+$ 509.1093, found 509.1087.

4-cyanobphenyl-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12b

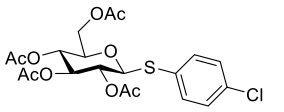
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2b** (95 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12b** (77.9 mg, 56% yield, β only, PE:EA = 3:1, R*f* = 0.25) was obtained as white solid.



$[\alpha]_D^{25}$ 37.8 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.49 (m, 4H), 5.27 (t, *J* = 10.0 Hz, 1H, H-3), 5.07 (t, *J* = 10.0 Hz, 1H, H-4), 5.03 (t, *J* = 8.0 Hz, 1H, H-2), 4.85 (d, *J* = 8.0 Hz, 1H, H-1), 4.29 – 4.16 (m, 2H, H-6), 3.88 – 3.72 (m, 1H, H-5), 2.10 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.0, 169.4, 169.2, 139.2, 132.3, 131.4, 118.3, 111.3, 84.4 (C-1), 76.0 (C-5), 73.6 (C-3), 69.6 (C-2), 68.0 (C-4), 62.1 (C-6), 20.7, 20.7, 20.5. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}NO_9S$ $[M+H]^+$ 466.1172, found 466.1159.

4-chlorophenyl-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12c

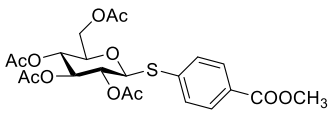
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2c** (98 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12c** (90.8 mg, 64% yield, β only, PE:EA = 3:1, R*f* =0.25) was obtained as white foam.



$[\alpha]_D^{25}$ +1.2 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 2H), 7.33 – 7.25 (m, 2H), 5.22 (t, *J* = 8 Hz, 1H, H-3), 5.02 (t, *J* = 10.0 Hz, 1H, H-4), 4.93 (t, *J* = 10.0 Hz, 1H, H-2), 4.65 (d, *J* = 12.0 Hz, 1H, H-1), 4.25 – 4.15 (m, 2H, H-6), 3.76 – 3.67 (m, 1H, H-5), 2.09 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.2, 135.0, 129.5, 129.1, 85.2 (C-1), 75.9 (C-5), 73.9 (C-3), 69.8 (C-2), 68.1 (C-4), 62.0 (C-6), 20.74, 20.72, 20.6. HRMS (ESI-TOF) Calculated for $C_{20}H_{23}ClO_9SNa$ $[M+Na]^+$ 497.0649, found 497.0645.

4-methylbenzoate-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12d

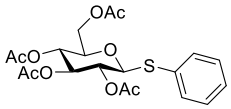
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2d** (113 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12d** (101.3 mg, 68% yield, β only, PE:EA = 3:1, R*f* =0.2) was obtained as white solid.



$[\alpha]_D^{25}$ 21.4 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 5.28 (t, *J* = 10.0 Hz, 1H, H-3), 5.08 (t, *J* = 6.0 Hz, 1H, H-4), 5.04 (t, *J* = 6.0 Hz, 1H, H-2), 4.86 (d, *J* = 12.0 Hz, 1H, H-1), 4.25 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.19 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.92 (s, 3H), 3.87 – 3.78 (m, 1H, H-5), 2.10 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.3, 169.2, 166.4, 138.7, 130.8, 129.9, 129.3, 84.8 (C-1), 75.9 (C-5), 73.7 (C-3), 69.7 (C-2), 68.1 (C-4), 62.1 (C-6), 52.2, 20.7, 20.6, 20.5. HRMS (ESI-TOF) Calculated for $C_{22}H_{27}O_{11}S$ $[M+H]^+$ 499.1274, found 499.1256.

Phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12e

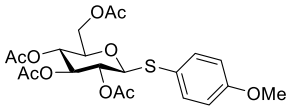
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2e** (97 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12e** (73.7 mg, 56% yield, β only, PE:EA =3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 36.0(c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.40 – 7.16 (m, 3H), 5.24 (t, *J* = 10.0 Hz, 1H, H-3), 5.04 (t, *J* = 10.0 Hz, 1H, H-4), 4.97 (t, *J* = 10.0 Hz, 1H, H-2), 4.73 (d, *J* = 8.0 Hz, 1H, H-1), 4.27 – 4.15 (m, 2H, H-6), 3.78 – 3.68 (m, 1H, H-5), 2.08 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.3, 169.2, 133.0, 131.6, 128.9, 128.4, 85.6 (C-1), 75.7 (C-5), 73.9 (C-3), 69.9 (C-2), 68.2 (C-4), 62.1 (C-6), 20.69, 20.68, 20.54, 20.53. HRMS (ESI-TOF) Calculated for $C_{20}H_{24}O_9SNa$ $[M+Na]^+$ 463.1039, found 463.1018.

4-methoxyphenyl-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12f

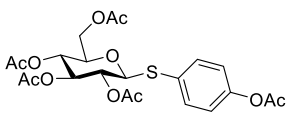
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2f** (109 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12e** (28.2 mg, 20% yield, β only, PE:EA =3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 23.0 (c = 0.50, $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 4.0 Hz, 2H), 6.98 – 6.63 (m, 2H), 5.20 (t, *J* = 6.0 Hz, 1H), 5.00 (t, *J* = 6.0 Hz, 1H), 4.89 (t, *J* = 8.0 Hz, 1H), 4.56 (d, *J* = 8.0 Hz, 1H), 4.31 – 4.08 (m, 2H), 3.82 (s, 3H), 3.73 – 3.58 (m, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.01 (s,3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 160.5, 136.6, 120.8, 114.4, 85.7, 75.7, 74.1, 69.9, 68.2, 62.1, 55.3, 20.81, 20.8, 20.6, 20.6. HRMS (ESI-TOF) Calculated for $C_{21}H_{27}O_{10}S$ $[M+H]^+$ 471.1320, found 471.1320.

4-Acetoxyphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12g

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2g** (106 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12g** (31.3 mg, 21% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.

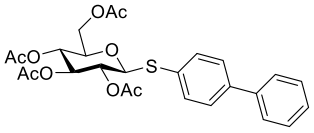


$[\alpha]_D^{25}$ 32.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.22 (t, *J* = 8.0 Hz, 1H, H-3), 5.04 (t, *J* = 10.0 Hz, 1H, H-4), 4.97 (t, *J* = 10.0 Hz, 1H, H-2), 4.67 (d, *J* = 8.0 Hz, 1H, H-1), 4.25 – 4.14 (m, 2H, H-6), 3.75 – 3.68 (m, 1H, H-5), 2.31 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 169.2, 151.1,

134.8, 128.6, 122.2, 85.8 (C-1), 75.8 (C-5), 73.9 (C-3), 70.0 (C-2), 68.2 (C-4), 62.1 (C-6), 21.1, 20.77, 20.75, 20.60, 20.58. HRMS (ESI-TOF) Calculated for $C_{22}H_{27}O_{11}S$ $[M+H]^+$ 499.1274, found 499.1266.

1,1'-biphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12h

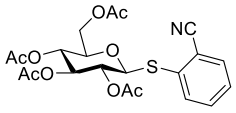
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2h** (129 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12h** (91.1 mg, 59% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 12.7 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 6H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 6.0 Hz, 1H), 5.25 (t, *J* = 8.0 Hz, 1H, H-3), 5.11 – 4.97 (m, 2H, H-4, H-2), 4.74 (d, *J* = 8.0 Hz, 1H, H-1), 4.32 – 4.15 (m, 2H, H-6), 3.80 – 3.71 (m, 1H, H-5), 2.11 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 141.4, 140.1, 133.6, 130.4, 128.9, 127.7, 127.6, 127.1, 85.7 (C-1), 75.8 (C-5), 74.0 (C-3), 70.0 (C-2), 68.2 (C-4), 62.1 (C-6), 20.79, 20.78, 20.62, 20.60. HRMS (ESI-TOF) Calculated for $C_{26}H_{28}O_9SNa$ $[M+Na]^+$ 539.1352, found 539.1346.

2-cyanophenyl-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12i

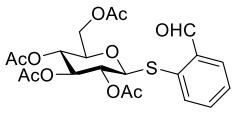
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2i** (129 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12i** (94.5 mg, 68% yield, β only, PE:EA = 3:1, R*f* = 0.25) was obtained as white solid.



$[\alpha]_D^{25}$ -7.8 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.71 (m, 1H), 7.63 – 7.55 (m, 1H), 7.49 (m, 1H), 5.25 (t, *J* = 10.0 Hz, 1H, H-3), 5.05 (t, *J* = 10.0 Hz, 1H, H-4), 4.94 (t, *J* = 8.0 Hz, 1H, H-2), 4.78 (d, *J* = 12.0 Hz, 1H, H-1), 4.26 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.17 (dd, J_1 = 12.0, J_1 = 4.0 Hz, 1H, H-6b), 3.83 – 3.74 (m, 1H), 2.14 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.5, 169.4, 135.2, 134.8, 133.7, 132.9, 129.2, 117.9, 116.9, 85.0 (C-1), 76.0 (C-5), 73.7 (C-3), 69.4 (C-2), 68.0 (C-4), 62.0 (C-6), 20.72, 20.69, 20.53. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}NO_9S$ $[M+H]^+$ 466.1172, found 466.1159.

2-formylphenyl-2,3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside 12j

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2j** (101 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12j** (96.6 mg, 69% yield, β only, PE:EA = 3:1, R*f* = 0.2) was obtained as white solid.

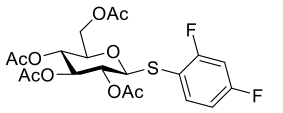


$[\alpha]_D^{25}$ -12.6 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.95 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 5.22 (t, *J* = 10.0 Hz, 1H, H-3), 5.09 – 4.87 (m, 2H, H-4, H-2), 4.72 (d, *J* = 12.0 Hz, 1H, H-1), 4.22 – 4.04 (m, 2H, H-6), 3.77 – 3.66 (m, 1H, H-5), 2.12 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 170.5, 170.1, 169.3, 169.2, 137.8, 135.7, 134.2, 134.0, 129.44, 129.39, 84.6 (C-1), 75.8 (C-5), 73.8 (C-3), 69.9 (C-2), 68.0 (C-4), 62.0 (C-6), 20.7, 20.62, 20.54, 20.52. HRMS (ESI-TOF) Calculated for $C_{21}H_{25}O_{10}S$ $[M+H]^+$ 469.1168, found 469.1150.

2,4-Difluorphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12k

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg,

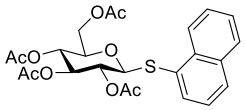
0.3mmol), aryl triflates **2k** (96 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12k** (101.1 mg, 71% yield, β only, PE:EA = 3:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ -11.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 1H), 6.94 – 6.81 (m, 2H), 5.21 (t, *J* = 10.0 Hz, 1H, H-3), 5.04 (t, *J* = 10.0 Hz, 1H, H-4), 4.88 (t, *J* = 10.0 Hz, 1H, H-2), 4.63 (d, *J* = 10.0 Hz, 1H, H-1).4.22 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.14 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.73 – 3.65 (m, 1H, H-5), 2.11 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170. 6, 170.2, 169.4, 164.7 (CF), 162.2 (CF), 138.2, 138.1, 113.09, 113.05, 112.91, 112.87, 112.2, 112.1, 112.0, 111.9, 104.9, 104.7, 104.4, 84.9 (C-1), 75.9 (C-5), 73.8 (C-3), 69.2 (C-2), 68.0 (C-4), 62.0 (C-6), 20.7, 20.7, 20.61, 20.60. HRMS (ESI-TOF) Calculated for $C_{20}H_{23}F_2O_9S$ $[M+H]^+$ 499.0850, found 499.0839.

1-Naphthoic -2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12l

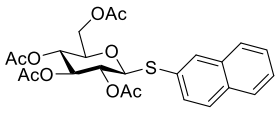
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2l** (118 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12l** (99.7 mg, 68% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ -25.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.86 (m, 2H), 7.82 (d, *J* = 4.0 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 1H), 5.19 (t, *J* = 10.0 Hz, 1H, H-3), 5.09 – 5.05 (m, 2H, H-4, H-2), 4.72 (d, *J* = 12.0 Hz, 1H, H-1), 4.19 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-6a), 4.08 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.64 – 3.56 (m, 1H, H-5), 2.12 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 169.4, 169.3, 134.3, 134.1, 133.5, 129.9, 129.2, 128.5, 126.8, 126.4, 125.8, 125.5, 86.6 (C-1), 75.7 (C-5), 74.0 (C-3), 70.4 (C-2), 68.2 (C-4), 62.2 (C-6), 20.8, 20.7, 20.58, 20.55. HRMS (ESI-TOF) Calculated for $C_{24}H_{27}O_9S$ $[M+H]^+$ 491.1376, found 491.1380.

2-Naphthoic-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12m

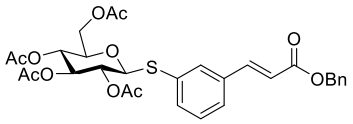
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2m** (111 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12m** (117.3 mg, 80% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 2.4 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.85 – 7.75 (m, 3H), 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 5.24 (t, *J* = 10.0 Hz, 1H, H-3), 5.03 (dd, J_1 = 10.0, J_2 = 8.0 Hz, 2H, H-4, H-2), 4.79 (d, *J* = 8.0 Hz, 1H, H-1), 4.24 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-6a), 4.18 (m, 1H, H-6b), 3.77 – 3.68 (m, 1H, H-5), 2.11 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 133.5, 132.9, 132.7, 130.2, 128.8, 128.5, 127.7, 126.8, 126.7, 85.8 (C-1), 75.9 (C-5), 75.8 (C-5), 74.0 (C-3), 70.1 (C-2), 68.2 (C-4), 62.2 (C-6), 20.80, 20.77, 20.71, 20.69, 20.58, 20.56. HRMS (ESI-TOF) Calculated for $C_{24}H_{30}O_9SN$ $[M+NH_4^+]^+$ 508.1641, found 508.1685.

benzyl cinnamate-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12n

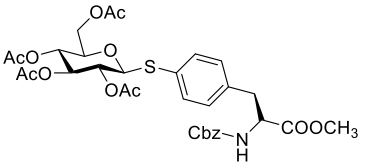
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2n** (231 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12n** (96.9 mg, 54% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as colorless oil.



$[\alpha]_D^{25}$ 26.4 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 2H), 7.53 – 7.46 (m, 2H), 7.43 – 7.38 (m, 3H), 7.37 – 7.31 (m, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.30 – 5.19 (m, 3H, H-3), 5.02 (t, *J* = 8.0 Hz, 1H, H-4), 4.96 (t, *J* = 10.0 Hz, 1H, H-2), 4.71 (d, *J* = 12.0 Hz, 1H, H-1), 4.24 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.17 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.78 – 3.72 (m, 1H, H-5), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.2, 166.5, 144.1, 135.9, 135.2, 134.8, 132.7, 132.4, 129.4, 128.6, 128.3, 128.0, 119.0, 85.3 (C-1), 75.9 (C-5), 73.9 (C-3), 69.8 (C-2), 68.1 (C-4), 66.5, 62.1 (C-6), 20.74, 20.65, 20.6. HRMS (ESI-TOF) Calculated for $C_{30}H_{33}O_{11}S$ $[M+H]^+$ 601.1738, found 601.1737.

((4-((R)-2-(((benzyloxy)carbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12o

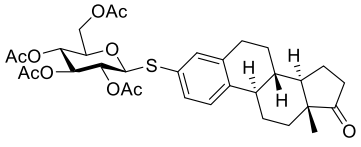
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2o** (276 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12o** (60.6 mg, 30% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.



$[\alpha]_D^{25}$ 30.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 7H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.28 (d, *J* = 8.0 Hz, 1H), 5.22 (t, *J* = 10.0 Hz, 1H, H-3), 5.12 – 5.00 (m, 3H, H-4), 4.95 (t, *J* = 10.0 Hz, 1H, H-2), 4.72 – 4.63 (m, 2H, H-1), 4.28 – 4.10 (m, 2H, H-6a, H-6b), 3.73 (s, 3H), 3.18 – 3.03 (m, 2H, H-5), 2.07 (s, 6H), 2.02 (s, 3H), 1.98 (s, 3H), 1.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 170.6, 170.2, 169.4, 169.3, 155.6, 136.3, 136.2, 133.2, 130.5, 129.9, 128.6, 128.3, 128.1, 85.7 (C-1), 75.8 (C-5), 74.0 (C-3), 69.9 (C-2), 68.2 (C-4), 67.0, 62.1 (C-6), 54.7, 52.4, 37.7, 20.7, 20.6. HRMS (ESI-TOF) Calculated for $C_{32}H_{41}N_2O_{13}S$ $[M+NH_4]^+$ 675.2224, found 675.2238.

(((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 12p

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **2p** (276 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **12p** (92.2 mg, 50% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.

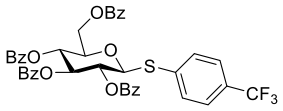


$[\alpha]_D^{25}$ 63.8 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.21 (t, *J* = 10.0 Hz, 1H, H-3), 5.04 (t, *J* = 10.0 Hz, 1H, H-4), 4.93 (t, *J* = 10.0 Hz, 1H, H-2), 4.66 (d, *J* = 8.0 Hz, 1H, H-1), 4.24 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.18 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.77 – 3.69 (m, 1H, H-5), 2.95 – 2.86 (m, 2H), 2.52 (dd, J_1 = 16.0, J_2 = 8.0 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.36 – 2.24 (m, 1H), 2.17 (m, 1H), 2.11 – 1.95 (m, 16H), 1.68 – 1.40 (m, 5H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.2, 140.5, 137.38, 134.3, 131.1, 127.9, 126.0, 85.7 (C-1), 75.7 (C-5), 74.1 (C-3), 69.9 (C-2), 68.2 (C-4), 62.1 (C-6), 50.5, 47.9, 44.3, 37.9, 35.8, 31.6, 29.3, 26.3, 25.6, 21.6, 20.80, 20.77, 20.6, 13.9, 13.8. HRMS (ESI-TOF) Calculated for $C_{32}H_{41}O_{10}S$ $[M+H]^+$ 617.2420, found 617.2408.

4-(trifluoromethyl)phenyl-2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside 13a

The reaction was carried out according to the general procedure, using glycosyl thiols **3** (183 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF

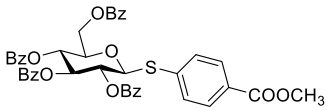
(1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **13a** (161.2 mg, 71% yield, β only, PE:EA = 4:1, R*f* = 0.3) was obtained as white foam.



$[\alpha]_D^{25}$ 44.1 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.99 – 7.89 (m, 4H), 7.84 – 7.77 (m, 2H), 7.61 (t, *J* = 6.0 Hz, 1H), 7.58 – 7.34 (m, 11H), 7.32 – 7.23 (m, 4H), 5.97 (t, *J* = 10.0 Hz, 1H, H-3), 5.63 (t, *J* = 10.0 Hz, 1H, H-4), 5.54 (t, *J* = 10.0 Hz, 1H, H-2), 5.13 (d, *J* = 8.0 Hz, 1H, H-1), 4.73 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.51 (dd, *J* = 12.0, 4.0 Hz, 1H, H-6b), 4.31 – 4.23 (m, 1H, H-5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 165.2, 165.1, 137.1, 133.6, 133.54, 133.49, 133.4, 132.0, 130.1, 129.9, 129.8, 129.5, 128.9, 128.7, 128.60, 128.56, 128.5, 128.4, 125.71, 125.67, 123.9 (CF_3), 85.4 (C-1), 76.6 (C-5), 74.0 (C-3), 70.4 (C-2), 69.3 (C-4), 63.1 (C-6). HRMS (ESI-TOF) Calculated for $C_{41}H_{31}F_3O_9SNa$ $[M+Na]^+$ 779.1539, found 779.1533.

4-(methoxycarbonyl)phenyl-2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside 13d

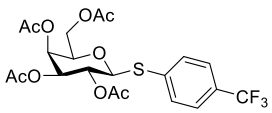
The reaction was carried out according to the general procedure, using glycosyl thiols **3** (183 mg, 0.3mmol), aryl triflates **2d** (113 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **13d** (138.9 mg, 62% yield, β only, PE:EA = 3:1, R*f* = 0.25) was obtained as white foam.



$[\alpha]_D^{25}$ 47.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 4.0 Hz, 2H), 7.94 (m, 4H), 7.80 (t, *J* = 6.0 Hz, 4H), 7.61 (t, *J* = 6.0 Hz, 1H), 7.57 – 7.33 (m, 11H), 7.28 (m, 2H), 5.97 (t, *J* = 10.0 Hz, 1H, H-3), 5.64 (t, *J* = 10.0 Hz, 1H, H-4), 5.57 (t, *J* = 8.0 Hz, 1H, H-2), 5.19 (d, *J* = 10.0 Hz, 1H, H-1), 4.70 (d, *J* = 12.0 Hz, 1H, H-6a), 4.50 (m, 1H, H-6b), 4.34 – 4.23 (m, 1H, H-5), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 165.8, 165.2, 165.1, 138.8, 133.6, 133.5, 133.4, 130.9, 130.0, 129.92, 129.90, 129.79, 129.76, 129.5, 129.3, 128.9, 128.64, 128.60, 128.55, 128.50, 128.48, 128.3, 85.3 (C-1), 76.6 (C-5), 74.0 (C-3), 70.4 (C-2), 69.3 (C-4), 63.2 (C-6), 52.2. HRMS (ESI-TOF) Calculated for $C_{30}H_{33}O_{11}S$ $[M+H]^+$ 601.1738, found 601.1737.

4-(trifluoromethyl)phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside 14a

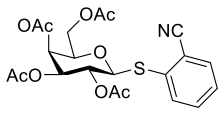
The reaction was carried out according to the general procedure, using glycosyl thiols **4** (109.3 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **14a** (93 mg, 61% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 15.4 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 12.0 Hz, 2H), 5.44 (d, *J* = 2.7 Hz, 1H, H-4), 5.25 (t, *J* = 10.0 Hz, 1H, H-2), 5.08 (dd, J_1 = 8.0, J_2 = 4.0 Hz, 1H, H-3), 4.79 (d, *J* = 12.0 Hz, 1H, H-1), 4.20 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.12 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.99 (t, *J* = 6.0 Hz, 1H, H-5), 2.12 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 170.0, 169.4, 137.6, 130.1, 129.8, 129.5, 125.64, 125.61, 125.57, 123.9 (CF_3), 85.5 (C-1), 74.6 (C-5), 71.9 (C-3), 67.1 (C-4), 67.0 (C-2), 61.6 (C-5), 20.8, 20.63, 20.55, 20.5. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}F_3O_9S$ $[M+H]^+$ 509.1093, found 509.1089.

2-cyanophenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside 14i

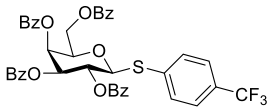
The reaction was carried out according to the general procedure, using glycosyl thiols **4** (109.3 mg, 0.3mmol), aryl triflates **2i** (129 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **14i** (85.2 mg, 61% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 17.8 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 5.44 (d, *J* = 4.0 Hz, 1H, H-4), 5.22 (t, *J* =10.0 Hz, 1H, H-2), 5.07 (dd, J_1 = 8.0, J_2 = 4.0 Hz, 1H, H-3), 4.77 (d, *J* = 12.0 Hz, 1H, H-1), 4.20 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-6a), 4.12 (dd, *J* = 12.0, 8.0 Hz, 1H, H-6b), 3.97 (t, *J* = 8.0 Hz, 1H, H-5), 2.16 (s, 3H), 2.13 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.01, 169.95, 169.7, 135.7, 134.7, 133.7, 132.7, 129.0, 117.5, 116.9, 86.0 (C-1), 74.7 (C-5), 71.8 (C-3), 67.1 (C-4), 66.6 (C-2), 61.5 (C-5), 20.8, 20.7, 20.6, 20.5. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}NO_9S$ $[M+H]^+$ 466.1172, found 466.1157.

4-(trifluoromethyl)phenyl-2,3,4,6-tetra- O-benzoyl-1-thio-β-D-galactopyranoside 15a

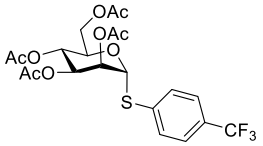
The reaction was carried out according to the general procedure, using glycosyl thiols **5** (183 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **15a** (156.6 mg, 69% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.



$[\alpha]_D^{25}$ 83.1(c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 4.0 Hz, 4H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.58 (m, 4H), 7.56 – 7.37 (m, 10H), 7.27 – 7.20 (m, 2H), 6.04 (s, 1H, H-4), 5.81 (t, *J* = 8.0 Hz, 1H, H-3), 5.66 (d, *J* = 8.0 Hz, 1H, H-2), 5.12 (d, *J* = 8.0 Hz, 1H, H-1), 4.71 – 4.61 (m, 1H, H-6a), 4.57 – 4.41 (m, 2H, H-6b, H-5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.5, 165.2, 136.9, 133.8, 133.6, 133.5, 133.4, 132.5, 129.9, 129.9, 129.80, 129.78, 129.4, 129.0, 128.8, 128.7, 128.60, 128.56, 128.5, 128.4, 125.7, 124.1 (CF_3), 85.4 (C-1), 75.5 (C-5), 72.7 (C-2), 68.3 (C-4), 67.8 (C-3), 62.7 (C-6). HRMS (ESI-TOF) Calculated for $C_{21}H_{24}NO_9S$ $[M+H]^+$ 466.1172, found 466.1159.

4-(trifluoromethyl)phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside 16a

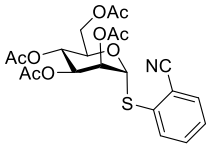
The reaction was carried out according to the general procedure, using glycosyl thiols **6** (109.3 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **16a** (65.6 mg, 43% yield, α only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.



$[\alpha]_D^{25}$ 44.4 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.51 (m, 4H), 5.61 (d, *J* = 1.1 Hz, 1H, H-1), 5.49 (dd, J_1 = 3.0, J_2 = 1.6 Hz, 1H, H-2), 5.40 – 5.27 (m, 2H, H-4, H-3), 4.51 – 4.42 (m, 1H, H-5), 4.30 (dd, J_1 = 12.0, J_2 = 6.0 Hz, 1H, H-6a), 4.11 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 2.18 (s, 3H), 2.08 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 169.8, 169.7, 137.9, 130.7, 129.9, 129.6, 126.0, 125.93, 125.89, 123.8 (CF_3), 84.8 (C-1), 84.7, 70.7 (C-2), 69.9 (C-5), 69.3 (C-3), 66.2 (C-4), 62.3 (C-6), 20.9, 20.8, 20.7, 20.62, 20.60. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}F_3O_9S$ $[M+H]^+$ 509.1093, found 509.1094.

2-cyanophenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside 16i

The reaction was carried out according to the general procedure, using glycosyl thiols **6** (109.3 mg, 0.3mmol), aryl triflates **2i** (129 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **16i** (64.2 mg, 46% yield, α only, PE:EA = 3:1, R*f* = 0.3) was obtained as white solid.

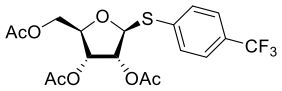


$[\alpha]_D^{25}$ 35.4 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, J_1 = 8.0, J_2 = 1.2 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.48 – 7.41 (m, 1H), 5.58 – 5.53 (m, 2H, H-1, H-2), 5.38 (t, *J* = 10.0 Hz, 1H, H-4), 5.31 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-3), 4.63 – 4.53 (m, 1H, H-5), 4.34 (dd, J_1 = 12.0, J_2 = 4.0 Hz,

1H, H-6a), 4.12 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 2.17 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.8, 169.7, 136.7, 133.9, 133.8, 133.4, 128.8, 117.2, 117.0, 86.3 (C-1), 70.7 (C-2), 70.3 (C-5), 69.2 (C-3), 65.9 (C-4), 62.1 (C-6), 20.8, 20.68, 20.66, 20.6. HRMS (ESI-TOF) Calculated for $C_{21}H_{24}NO_9S$ $[M+H]^+$ 466.1167, found 466.1168.

4-(trifluoromethyl)phenyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-ribofuranoside 17a

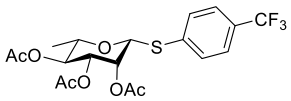
The reaction was carried out according to the general procedure, using glycosyl thiols **7** (87.7 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **17a** (66.8 mg, 51% yield, α only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.



$[\alpha]_D^{25}$ 0.9 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 4H), 5.50 (t, J = 4.0 Hz, 1H, H-3), 5.28 (d, J = 8.0 Hz, 1H, H-1), 5.14 – 5.05 (m, 2H, H-4, H-2), 4.18 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-5a), 3.84 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-5b), 2.12 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.73, 169.70, 169.3, 137.7, 131.1, 130.2, 130.1, 129.8, 129.5, 129.2, 125.92, 125.88, 125.84, 125.80, 123.9 (CF_3), 83.5 (C-1), 68.2 (C-2), 67.1 (C-3), 66.33, 66.29 (C-4), 63.4 (C-5), 20.73, 20.70, 20.66. HRMS (ESI-TOF) Calculated for $C_{18}H_{20}F_3O_7S$ $[M+H]^+$ 437.0882, found 437.0880.

4-(trifluoromethyl)phenyl-2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside 18a

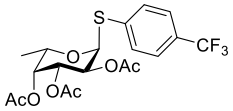
The reaction was carried out according to the general procedure, using glycosyl thiols **8** (92 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **18a** (56.7 mg, 42% yield, β only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.



$[\alpha]_D^{25}$ -12.1 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.58 (m, 4H), 5.54 (s, 1H, H-1), 5.49 (dd, J_1 = 3.1, J_1 = 1.5 Hz, 1H, H-2), 5.26 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-3), 5.17 (t, J = 10.0 Hz, 1H, H-4), 4.37 – 4.26 (m, 1H, H-5), 2.17 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.26 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.9, 138.7, 130.3, 129.9, 129.6, 129.3, 128.9, 125.99, 125.96, 125.92, 125.88, 123.9 (CF_3), 84.8 (C-1), 71.1 (C-2), 70.9 (C-4), 69.3 (C-3), 68.1 (C-5), 20.9, 20.8, 20.7, 17.3. HRMS (ESI-TOF) Calculated for $C_{19}H_{22}F_3O_7S$ $[M+H]^+$ 451.1038, found 451.1040.

4-(trifluoromethyl)phenyl-2,3,4-tri-*O*-acetyl-1-thio-α-L-fucosepyranoside 19a

The reaction was carried out according to the general procedure, using glycosyl thiols **9** (92 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **19a** (81.1 mg, 60% yield, α only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.

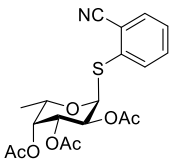


$[\alpha]_D^{25}$ 40.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), δ 7.56 (d, J = 8.0 Hz, 2H),5.29 (d, J = 3.1 Hz, 1H, H-4), 5.24 (t, J = 10.0 Hz, 1H, H-3), 5.08 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-2), 4.78 (d, J = 12.0 Hz, 1H, H-1), 3.93 – 3.86 (m, 1H, H-5), 2.15 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.26 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.5, 137.9, 131.4, 130.1, 129.8, 129.5, 129.1, 125.7, 125.62, 125.58, 125.55, 124.0 (CF_3), 85.2 (C-1), 73.3 (C-5), 72.3 (C-3), 70.2 (C-4), 67.0 (C-2), 20.8, 20.6, 16.4. HRMS (ESI-TOF) Calculated for $C_{19}H_{22}F_3O_7S$ $[M+H]^+$ 451.1038, found 451.1034.

2-cyanophenyl-2,3,4-tri-*O*-acetyl-1-thio-α-L-fucosepyranoside 19i

The reaction was carried out according to the general procedure, using glycosyl thiols **9** (92 mg,

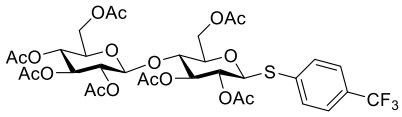
0.3mmol), aryl triflates **2i** (129 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **19i** (80.7 mg, 66% yield, α only, PE:EA = 3:1, R*f* = 0.3) was obtained as white foam.



$[\alpha]_D^{25}$ 33.7 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.49 – 7.39 (m, 1H), 5.28 (d, *J* = 2.7 Hz, 1H, H-4), 5.20 (t, *J* = 10.0 Hz, 1H, H-3), 5.07 (dd, J_1 = 10.0, J_2 = 4.0 Hz, 1H, H-2), 4.74 (d, *J* = 8.0 Hz, 1H, H-1), 3.90 – 3.74 (m, 1H, H-5), 2.15 (s, 3H), 2.14 (s, 3H), 1.97 (s, 3H), 1.25 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 170.0, 169.7, 136.3, 134.4, 133.7, 132.7, 128.7, 117.2, 117.0, 85.8 (C-1), 73.5 (C-5), 72.3 (C-3), 70.2 (C-4), 66.7 (C-2), 20.8, 20.63, 20.58, 16.4. HRMS (ESI-TOF) Calculated for $C_{19}H_{22}NO_7S$ $[M+H]^+$ 408.1117, found 408.1108.

4-(trifluoromethyl)pheny-2,3,6,2',3',4',6'-hepta-*O*-benzoyl-1-thio-β-cellobioside 20a

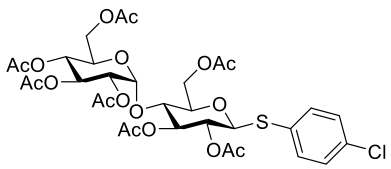
The reaction was carried out according to the general procedure, using glycosyl thiols **9** (195.7 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **20a** (162.5 mg, 68% yield, β only, PE:EA = 3:1, R*f* = 0.25) was obtained as white foam.



$[\alpha]_D^{25}$ -23.5(c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.49 (m, 4H), 5.22 (t, *J* = 10.0 Hz, 1H), 5.15 (t, *J* = 10.0 Hz, 1H), 5.07 (t, *J* = 8.0 Hz, 1H), 4.98 – 4.88 (m, 2H), 4.73 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.38 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H), 4.10 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H), 4.06 – 4.00 (m, 1H), 3.74 (t, *J* = 10.0 Hz, 1H), 3.70 – 3.61 (m, 2H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 170.1, 169.7, 169.52, 169.3, 169.0, 136.8, 132.3, 130.3, 130.0, 125.7, 125.6, 123.9 (CF_3), 100.8, 84.6, 76.2, 73.4, 72.9, 72.02, 71.59, 70.0, 67.7, 61.9, 61.5, 20.8, 20.72, 20.6, 20.54, 20.50. HRMS (ESI-TOF) Calculated for $C_{33}H_{40}F_3O_{17}S$ $[M+H]^+$ 797.1938, found 797.1931.

4-chlorophenyl-2,3,6,2',3',4',6'-hepta-*O*-benzoyl-1-thio-β-maltobioside 21c

The reaction was carried out according to the general procedure, using glycosyl thiols **9** (195.7 mg, 0.3mmol), aryl triflates **2c** (98 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **21c** (162.5 mg, 68% yield, β only, PE:EA = 3:1, R*f* = 0.25) was obtained as colorless oil.

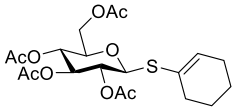


$[\alpha]_D^{25}$ 74.2 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.27 – 7.22 (m, 1H), 5.43 – 5.25 (m, 3H), 5.10 – 5.00 (m, 1H), 4.89 – 4.82 (m, 1H), 4.82 – 4.65 (m, 2H), 4.62 – 4.53 (m, 1H), 4.29 – 4.17 (m, 2H), 4.10 – 4.02 (m, 1H), 4.00 – 3.89 (m, 2H), 3.79 – 3.69 (m, 1H), 2.13 (d, *J* = 4.0 Hz, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 – 2.02 (m, 6H), 2.01 – 1.98 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.3, 170.1, 170.0, 169.6, 169.4, 135.3, 135.1, 132.1, 129.1, 121.8, 95.60, 95.56, 84.5, 84.4, 76.3, 76.2, 72.3, 70.6, 70.0, 69.3, 69.0, 68.5, 68.0, 62.6, 61.5, 20.90, 20.85, 20.8, 20.73, 20.69, 20.62, 20.60, 20.58. HRMS (ESI-TOF) Calculated for $C_{32}H_{39}ClO_{17}SK$ $[M+K]^+$ 801.1234, found 801.1210.

6-cyclohex-1-en-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23a

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg,

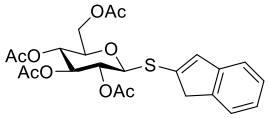
0.3mmol), aryl triflates **22a** (105 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23a** (88 mg, 66% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 18.6 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 – 5.95 (m, 1H), 5.23 (t, *J* = 8.0 Hz, 1H, H-3), 5.07 (t, *J* = 10.0 Hz, 1H, H-4), 5.02 (t, *J* =10.0 Hz, 1H, H-2), 4.65 (d, *J* = 12.0 Hz, 1H, H-1), 4.22 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-6a), 4.15 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.80 – 3.55 (m, 1H, H-5), 2.26 – 2.09 (m, 4H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.74 – 1.64 (m, 2H), 1.63 – 1.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 132.0, 129.4, 84.2 (C-1), 75.8 (C-5), 74.1 (C-3), 69.9 (C-2), 68.3 (C-4), 62.3 (C-6), 31.4, 26.7, 23.4, 21.5, 20.8, 20.7, 20.62, 20.59. HRMS (ESI-TOF) Calculated for $C_{20}H_{28}O_9SNa$ $[M+Na]^+$ 467.1346, found 467.1342.

(1H-inden-2-yl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23b

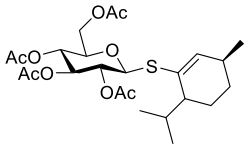
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22b** (113.2 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23b** (81.8 mg, 57% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 148.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 6.0 Hz, 1H), 6.90 (s, 1H), 5.27 (t, *J* = 8.0 Hz, 1H, H-3), 5.15 – 5.04 (m, 2H, H-2, H-4), 4.78 (d, *J* = 12.0 Hz, 1H, H-1), 4.25 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-6a), 4.19 (dd, J_1 = 12.3, J_2 = 2.4 Hz, 1H, H-6b), 3.80 (m, *J* = 10.0, 1H, H-5), 3.66 – 3.47 (m, 2H), 2.08 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 169.4, 169.3, 144.1, 143.4, 136.9, 133.5, 126.7, 124.9, 123.3, 120.4, 84.1 (C-1), 75.9 (C-5), 73.8 (C-3), 69.9 (C-2), 68.2 (C-4), 62.2 (C-6), 43.7, 20.7, 20.6. HRMS (ESI-TOF) Calculated for $C_{20}H_{28}O_9S$ $[M+Na]^+$ 467.1346, found 467.1342.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((3S)-6-isopropyl-3-methylcyclohex-1-en-1-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 23c

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22c** (98 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23c** (123.1 mg, 82% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.

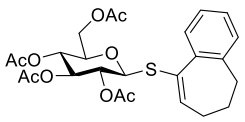


$[\alpha]_D^{25}$ 58.6 (c = 0.50, $CHCl_3$); 1H NMR (400 MHz, CDCl3) δ 5.98 (d, J = 1.3 Hz, 1H), 5.23 (t, *J* = 10.0 Hz, 1H), 5.13 – 4.89 (m, 2H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.23 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H), 4.12 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H), 3.78 – 3.64 (m, 1H), 2.45 – 2.27 (m, 1H), 2.26 – 2.11 (m, 2H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.86 – 1.77 (m, 1H), 1.77 – 1.68 (m, 1H), 1.43 – 1.30 (m, 1H), 1.18 – 1.04 (m, 1H), 1.00 (d, J = 7.0 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 0.70 (d, J = 6.8 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 170.5, 170.2, 169.4, 169.1, 141.2, 134.4, 85.5, 75.8, 74.2, 69.7, 68.3, 62.4, 45.1, 32.6, 30.6, 28.2, 22.2, 21.7, 20.70, 20.67, 20.57, 20.55, 20.5, 15.6. HRMS (ESI-TOF) Calculated for $C_{24}H_{37}O_9S$ $[M+H]^+$ 501.2153, found 501.2153.

(6,7-dihydro-5H-benzo[7]annulen-9-yl) -2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23d

The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22d** (125.2 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF

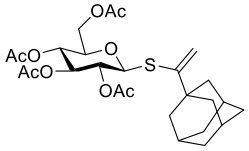
(1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23d** (88.1 mg, 58% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 99.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.20 (m, 2H), 6.63 (t, *J* = 8.0 Hz, 1H), 5.18 – 4.92 (m, 3H, H-3, H-2, H-4), 4.36 (d, *J* = 8.0 Hz, 1H, H-1), 4.11 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.00 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.44 – 3.28 (m, 1H, H-5), 2.73 – 2.54 (m, 2H), 2.22 – 2.13 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 – 1.90 (m, 1H), 1.87 – 1.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.3, 142.0, 137.6, 135.9, 132.1, 128.9, 128.1, 127.9, 126.3, 84.1 (C-1), 75.7 (C-5), 73.9 (C-3), 70.1 (C-2), 68.3 (C-4), 62.2 (C-6), 35.5, 32.1, 25.8, 20.74, 20.72, 20.6, 20.5. HRMS (ESI-TOF) Calculated for $C_{25}H_{31}O_9S$ $[M+H]^+$ 507.1684, found 507.1683.

1-((3S,5S,7S)-adamantan-1-yl)vinyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23e

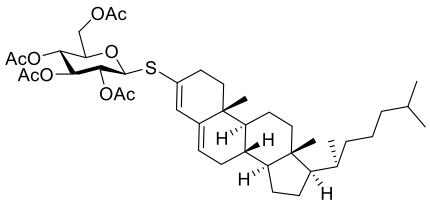
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22e** (132.9 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23e** (70.8 mg, 45% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 102.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.29 – 5.19 (m, 3H, H-3), 5.09 (t, *J* = 8.0 Hz, 2H, H-4, H-2), 4.62 (d, *J* = 12.0 Hz, 1H, H-1), 4.26 – 4.18 (m, 1H, H-6a), 4.14 (d, *J* = 12.3 Hz, 1H, H-6b), 3.77 – 3.69 (m, 1H, H-5), 2.11 – 2.06 (m, 6H), 2.05 – 1.98 (m, 9H), 1.84 – 1.69 (m, 7H), 1.67 – 1.56 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 169.4, 155.5, 110.9, 87.0 (C-1), 75.7 (C-5), 74.0 (C-3), 70.0 (C-2), 68.4 (C-4), 62.4 (C-6), 41.1, 39.8, 38.3, 36.6, 36.6, 28.5, 28.0, 20.8, 20.7, 20.6. HRMS (ESI-TOF) Calculated for $C_{26}H_{36}O_9SNa$ $[M+Na]^+$ 547.1972, found 547.1935.

((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23f

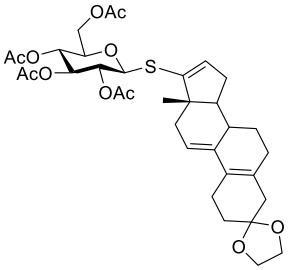
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22f** (310 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23f** (146.9 mg, 67% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 126.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.16 (d, *J* = 1.6 Hz, 1H), 5.46 – 5.39 (m, 1H), 5.24 (t, *J* = 10.0 Hz, 1H, H-3), 5.09 – 5.04 (m, 1H, H-4), 5.04 – 4.99 (m, 1H, H-2), 4.71 (d, *J* = 8.0 Hz, 1H, H-1), 4.22 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.14 (dd, J_1 = 12.0, J_2 = 2.2 Hz, 1H, H-6b), 3.80 – 3.72 (m, 1H, H-5), 2.41 (t, *J* = 10.0 Hz, 1H), 2.29 – 2.13 (m, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (d, *J* = 12.0 Hz, 6H), 1.85 – 1.81 (m, 2H), 1.74 – 1.47 (m, 5H), 1.46 – 1.31 (m, 4H), 1.30 – 1.20 (m, 3H), 1.19 – 0.97 (m, 9H), 0.96 – 0.90 (m, 6H), 0.87 (dd, J_1 = 8.0, J_2 = 4.0 Hz, 6H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.2, 141.2, 131.86, 127.3, 125.3, 84.0 (C-1), 75.8 (C-5), 74.0 (C-3), 70.0 (C-2), 68.3 (C-4), 62.4 (C-6), 56.8, 56.1, 48.0, 42.4, 39.7, 39.5, 36.2, 35.8, 34.52, 34.50, 31.8, 31.7, 29.0, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.1, 20.7, 20.59, 20.57, 19.0, 18.7, 12.0. HRMS (ESI-TOF) Calculated for $C_{41}H_{63}O_9S$ $[M+H]^+$ 731.4188, found 731.4183.

((13S)-13-methyl-1,2,4,6,7,8,12,13,14,15-decahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-yl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23g

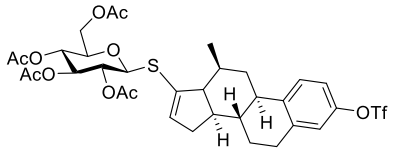
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22g** (267 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23g** (166.5 mg, 84% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 10.6 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (d, *J* = 1.1 Hz, 1H), 5.54 (s, 1H), 5.25 (t, *J* = 10.0 Hz, 1H, H-3), 5.13 (t, 1H, *J* = 6.0 Hz,H-2), 5.09 (t, *J* = 6.0 Hz, 1H, H-4), 4.72 (d, *J* = 8.0 Hz, 1H, H-1), 4.24 (dd, J_1 = 12.3, J_2 = 5.4 Hz, 1H, H-6a), 4.14 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6b), 3.99 (s, 4H), 3.85 – 3.69 (m, 1H, H-5), 2.56 – 2.46 (m, 1H), 2.39 – 2.26 (m, 3H), 2.26 – 2.16 (m, 3H), 2.15 – 2.09 (m, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 6H), 1.99 – 1.72 (m, 5H), 1.71 – 1.61 (m, 1H), 1.34 – 1.22 (m, 1H), 0.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 169.4, 169.3, 143.9, 137.7, 130.3, 127.9, 126.2, 117.3, 108.0, 84.1(C-1), 75.8 (C-5), 74.0 (C-3), 69.6 (C-2), 68.2 (C-4), 64.4, 64.3, 62.2 (C-6), 52.2, 47.3, 41.3, 37.0, 36.4, 32.5, 31.3, 30.9, 27.6, 24.6, 20.7, 20.59, 20.56, 16.4. HRMS (ESI-TOF) Calculated for $C_{34}H_{45}O_{11}S$ $[M+H]^+$ 661.2677, found 661.2675.

((8R,9R,12S,14R)-12-methyl-3-(((trifluoromethyl)sulfonyl)oxy)-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-17-yl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside 23h

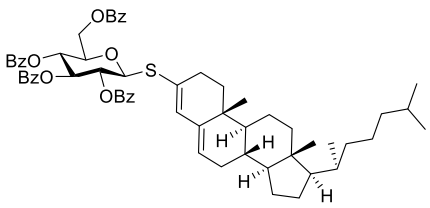
The reaction was carried out according to the general procedure, using glycosyl thiols **1** (109.3 mg, 0.3mmol), aryl triflates **22h** (320.7 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **23h** (172.9 mg, 77% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 69.0 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 12.0 Hz, 1H), 7.02 (dd, J_1 = 8.0, J_2 = 4.0 Hz 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 5.81 – 5.64 (m, 1H), 5.26 (t, *J* = 10.0 Hz, 1H, H-3), 5.16 (t, *J* = 8.0 Hz, 1H, H-2), 5.11 (t, *J* = 8.0 Hz, 1H, H-4), 4.72 (d, *J* = 8.0 Hz, 1H, H-1), 4.26 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.14 (dd, J_1 = 12.0, J_2 = 2.1 Hz, 1H, H-6b), 3.79 – 3.67 (m, 1H, H-5), 2.99 – 2.88 (m, 2H), 2.39 – 2.25 (m, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 – 1.88 (m, 2H), 1.71 – 1.59 (m, 3H), 1.59 – 1.39 (m, 3H), 0.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.3, 169.5, 169.3, 147.5, 145.3, 140.8, 139.4, 127.6, 126.9, 121.2, 118.7 (CF_3), 118.2, 84.1 (C-1), 76.0 (C-5), 74.1 (C-3), 69.6 (C-4), 68.2 (C-2), 62.2 (C-6), 55.5, 48.8, 44.3, 36.8, 34.4, 31.8, 29.4, 27.1, 26.1, 20.8, 20.7, 20.6, 16.1. HRMS (ESI-TOF) Calculated for $C_{33}H_{40}F_3O_{12}S_2$ $[M+H]^+$ 749.1908, found 749.1904.

((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside 24f

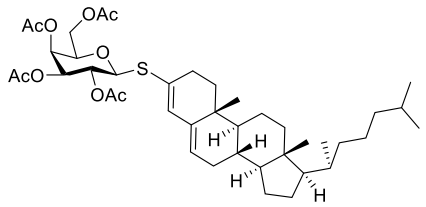
The reaction was carried out according to the general procedure, using glycosyl thiols **3** (183 mg, 0.3mmol), aryl triflates **22f** (310 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **24f** (196.8 mg, 67% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 33.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz,2H), 7.52 – 7.40 (m, 3H), 7.38 – 7.29 (m, 6H), 7.23 – 7.17 (m, 3H), 6.05 (s, 1H), 5.86 (t, *J* = 10.0 Hz, 1H, H-3), 5.55 (t, *J* = 10.0 Hz, 1H, H-4), 5.47 (t, *J* = 10.0 Hz, 1H, H-2), 5.18 (s, 1H), 4.96 (d, *J* = 8.0 Hz, 1H, H-1), 4.58 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-6a), 4.41 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H, H-6b), 4.21 – 4.11 (m, 1H, H-5), 2.35 – 2.22 (m, 1H), 2.20– 2.12 (m, 1H), 2.06 – 1.91 (m, 2H), 1.82 – 1.71 (m, 1H), 1.53 – 1.41 (m, 6H), 1.37 – 1.23 (m, 5H), 1.23 – 1.17 (m, 2H), 1.11 – 1.01 (m, 5H), 0.97 – 0.91 (m, 2H), 0.89 – 0.74 (m, 13H), 0.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.8, 164.2, 164.1, 140.1, 132.5, 132.3, 132.2, 132.1, 131.1, 128.89, 128.85, 128.8, 128.7, 128.6, 128.2, 127.8, 127.7, 127.42, 127.35, 127.3, 126.5, 124.3, 83.9 (C-1), 75.3 (C-5), 73.2 (C-3), 69.6 (C-2), 68.6 (C-4), 62.5 (C-6), 55.8, 55.1, 46.9, 41.4, 38.7, 38.5, 35.2, 34.8, 33.4, 30.8, 30.7, 28.1, 27.2, 27.0, 23.1, 22.8, 21.8, 21.6, 20.0, 17.8, 17.7, 10.9. HRMS (ESI-TOF) Calculated for $C_{61}H_{71}O_9S$ $[M+H]^+$ 979.4814, found 979.4811.

((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside 25f

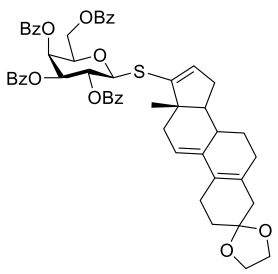
The reaction was carried out according to the general procedure, using glycosyl thiols **3** (183 mg, 0.3mmol), aryl triflates **22f** (310 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **25f** (153.51 mg, 70% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ -12.1 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.19 (d, *J* = 4.0 Hz, 1H), 5.44 (d, *J* = 4.0 Hz, 2H, H-4), 5.25 (t, *J* = 10.0 Hz, 1H, H-3), 5.06 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-2), 4.69 (d, *J* = 10.0 Hz, 1H, H-1), 4.23 – 4.08 (m, 2H, H-6), 3.96 (t, *J* = 6.0 Hz, 1H, H-5), 2.44 (t, *J* = 12.0 Hz, 1H), 2.29 – 2.13 (m, 5H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 – 1.96 (m, 4H), 1.88 – 1.81 (m, 2H), 1.74 – 1.50 (m, 5H), 1.44 – 1.32 (m, 3H), 1.30 – 1.21 (m, 3H), 1.19 – 1.05 (m, 7H), 1.01 – 0.95 (m, 5H), 0.92 (d, *J* = 8.0 Hz, 3H), 0.87 (dd, J_1 = 8.0, J_2 = 4.0 Hz, 6H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 170.1, 169.4, 141.2, 132.4, 127.1, 125.4, 84.5 (C-1), 74.5 (C-5), 72.0 (C-2), 67.4 (C-4), 67.2 (C-3), 61.9 (C-6), 56.8, 56.1, 48.0, 42.4, 39.7, 39.5, 36.2, 35.8, 34.6, 34.5, 31.8, 31.7, 29.2, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.1, 20.9, 20.71, 20.69, 20.6, 19.0, 18.7, 12.0. HRMS (ESI-TOF) Calculated for $C_{41}H_{63}O_9S$ $[M+H]^+$ 731.4188, found 731.4191.

((13S)-13-methyl-1,2,4,6,7,8,12,13,14,15-decahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-yl)-2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D- galactopyranoside 26g

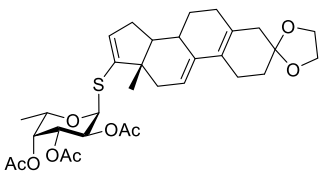
The reaction was carried out according to the general procedure, using glycosyl thiols **9** (183 mg, 0.3mmol), aryl triflates **22g** (267 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **26g** (166.3 mg, 92% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam. $[\alpha]_D^{25}$ 167.0 (c = 0.50, $CHCl_3$);^1H NMR (600 MHz, CDCl3) δ 8.10 – 8.06 (m, 2H), 8.05 – 7.99 (m, 2H), 7.98 – 7.92 (m, 2H), 7.83 – 7.76 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.45 – 7.35 (m, 5H), 7.26 – 7.24 (m, 1H), 6.04 (d, *J* = 3.4 Hz, 1H), 6.01 – 5.87 (m, 2H), 5.64 (dd, J_1 = 10.0, J_2 = 3.4 Hz, 1H), 5.47 (d, *J* = 5.3 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 4.70 – 4.57 (m, 1H),



4.46 (dd, J_1 = 11.5, J_2 = 5.6 Hz, 1H), 4.39 (t, J = 6.4 Hz, 1H), 3.98 (d, J = 2.5 Hz, 4H), 2.47 (d, J = 16.7 Hz, 1H), 2.29 (s, 3H), 2.24 – 2.15 (m, 3H), 2.14 – 2.08 (m, 2H), 2.08 – 1.90 (m, 2H), 1.88 – 1.71 (m, 3H), 1.68 – 1.61 (m, 1H), 1.35 – 1.16 (m, 1H), 0.77 (s, 3H).^{13}C NMR (150 MHz, CDCl3) δ 167.5, 167.03, 166.99, 166.8, 145.3, 139.0, 135.1, 134.8, 134.7, 131.6, 131.5, 131.3, 130.9, 130.7, 130.4, 130.2, 130.1, 129.90, 129.86, 129.8, 129.6, 127.8, 119.0, 109.5, 86.2, 76.8, 74.4, 70.0, 69.1, 65.9, 65.8, 64.1, 53.6, 48.9, 42.8, 38.6, 37.9, 33.9, 32.7, 32.4, 29.1, 26.1, 18.1. HRMS (ESI-TOF) Calculated for $C_{54}H_{52}O_{11}SNa$ $[M+Na]^+$ 931.3122, found 931.3121.

((13S)-13-methyl-1,2,4,6,7,8,12,13,14,15-decahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-yl) -2,3,4-tri-*O*-acetyl-1-thio-α-L-fucosepyranoside 27g

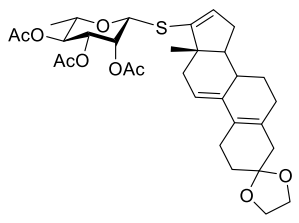
The reaction was carried out according to the general procedure, using glycosyl thiols **9** (92 mg, 0.3mmol), aryl triflates **22g** (267 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **27g** (166.3 mg, 92% yield, α only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 133.2 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 – 5.68 (m, 1H), 5.54 (d, J = 4.0 Hz, 1H), 5.36 – 5.27 (m, 2H, H-2, H-4), 5.07 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-3), 4.70 (d, J = 12.0 Hz, 1H, H-1), 3.99 (s, 4H), 3.91 – 3.83 (m, 1H, H-5), 2.53 (d, J = 12.0 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.30 – 2.15 (m, 8H), 2.13 – 2.03 (m, 5H), 2.02 – 1.90 (m, 5H), 1.89 – 1.64 (m, 4H), 1.36 – 1.30 (m, 1H), 1.26 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 3H), 0.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.6, 145.2, 137.6, 130.2, 126.3, 124.9, 117.4, 108.1, 85.1 (C-1), 73.2(C-5), 72.3(C-3), 70.3(C-4), 67.1(C-2), 64.5, 64.3, 52.1, 47.3, 41.3, 36.6, 36.4, 32.4, 31.3, 31.0, 27.6, 24.6, 20.8, 20.7, 20.6, 16.5, 16.4. HRMS (ESI-TOF) Calculated for $C_{32}H_{43}O_9S$ $[M+H]^+$ 603.2623, found 603.2616.

((13S)-13-methyl-1,2,4,6,7,8,12,13,14,15-decahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-yl)-2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside 28g

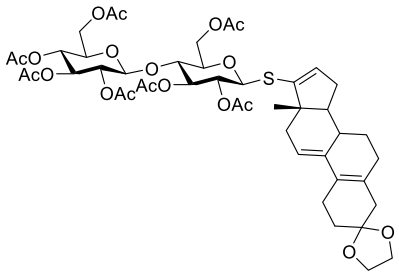
The reaction was carried out according to the general procedure, using glycosyl thiols **8** (92 mg, 0.3mmol), aryl triflates **22g** (267 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **28g** (139.2 mg, 77% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 22.4 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (d, J = 1.1 Hz, 1H), 5.56 (s, 1H), 5.44 (d, J = 1.1 Hz, 1H, H-1), 5.41 (dd, J_1 = 3.3, J_1 = 1.5 Hz, 1H, H-2), 5.28 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H, H-3), 5.10 (t, J = 10.0 Hz, 1H, H-4), 4.24 – 4.12 (m, 1H, H-5), 3.99 (s, 4H), 2.53 (d, J = 16.0 Hz, 1H), 2.36 – 2.25 (m, 4H), 2.24 – 2.18 (m, 2H), 2.19 – 2.12 (m, 5H), 2.06 (s, 3H), 2.02 – 1.91 (m, 5H), 1.88 – 1.76 (m, 3H), 1.71 – 1.60 (m, 1H), 1.29 – 1.17 (m, 4H), 0.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.03, 170.00, 169.9, 143.9, 137.7, 130.2, 126.5, 126.3, 117.5, 108.1, 82.4 (C-1), 71.4 (C-2), 71.3 (C-4), 69.4 (C-3), 67.7 (C-5), 64.5, 64.3, 52.1, 47.5, 41.3, 37.1, 36.4, 32.5, 31.3, 31.0, 27.6, 24.6, 21.0, 20.8, 20.7, 17.5, 16.5. HRMS (ESI-TOF) Calculated for $C_{32}H_{43}O_9S$ $[M+H]^+$ 603.2623, found 603.2632.

((13S)-13-methyl-1,2,4,6,7,8,12,13,14,15-decahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-yl)-2,3,6,2',3',4',6'-hepta-*O*-benzoyl-1-thio-β-cellobioside 29g

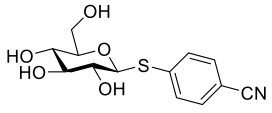
The reaction was carried out according to the general procedure, using glycosyl thiols **9** (195.7 mg, 0.3mmol), aryl triflates **22g** (267 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **29g** (259.1 mg, 91% yield, β only, PE:EA = 5:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 38.0(c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 1H), 5.54 (s, 1H), 5.21 (t, *J* = 10.0 Hz, 1H), 5.14 (t, *J* = 10.0 Hz, 1H), 5.10 – 5.05 (m, 1H), 5.02 (t, *J* = 8.0 Hz, 1H), 4.95 – 4.90 (m, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.53 – 4.45 (m, 2H), 4.38 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H), 4.10 (dd, J_1 = 12.0, J_2 = 8.0 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.99 (s, 4H), 3.77 (t, *J* = 10.0 Hz, 1H), 3.70 – 3.60 (m, 2H), 2.57 – 2.47 (m, 1H), 2.36 – 2.27 (m, 3H), 2.25 – 2.14 (m, 4H), 2.12 – 2.07 (m, 7H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.92 (s, 1H), 1.89 – 1.75 (m, 4H), 1.70 – 1.60 (m, 1H), 1.29 – 1.24 (m, 1H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.2, 169.8, 169.6, 169.3, 169.1, 144.2, 137.7, 130.3, 127.8, 126.3, 117.4, 108.0, 100.8, 84.2, 76.6, 73.7, 72.9, 72.0, 71.6, 70.0, 67.7, 64.5, 64.3, 62.4, 61.5, 52.3, 47.3, 41.3, 37.1, 36.4, 32.5, 31.3, 30.9, 27.6, 24.6, 20.8, 20.7, 20.6, 20.5, 16.5. HRMS (ESI-TOF) Calculated for $C_{46}H_{60}O_{19}SNa$ $[M+Na]^+$ 971.3342, found 971.3336.

4-(((2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)thio)benzonitrile 33

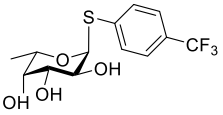
The reaction was carried out according to the general procedure, using glycosyl thiols **30** (58.8 mg, 0.3mmol), aryl triflates **2b** (95 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **33** (60.6 mg, 68% yield, β only, DCM:MeOH = 10:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ -2.0(c = 0.50, MeOH); ^{1}H NMR (400 MHz, D_2O) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 4.93 (d, *J* = 8.0 Hz, 1H), 3.85 (dd, J_1 = 12.0, J_2 = 4.0 Hz, 1H), 3.66 (dd, J_1 = 16.0, J_2 = 8.0 Hz, 1H), 3.56 – 3.46 (m, 2H), 3.43 – 3.31 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 140.6, 132.8, 129.4, 119.4, 109.1, 85.8, 79.9, 77.2, 71.7, 69.3, 60.7. HRMS (ESI-TOF) Calculated for $C_{13}H_{15}NO_5S$ $[M+NH_4]^+$ 315.1015, found 315.1011. HRMS (ESI-TOF) Calculated for $C_{13}H_{19}N_2O_5S$ $[M+NH_4]^+$ 315.1015, found 315.1011.

4-(((2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)thio)benzonitrile 34

The reaction was carried out according to the general procedure, using glycosyl thiols **31** (54.0 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **34** (66 mg, 68% yield, α only, DCM:MeOH = 10:1, R*f* = 0.4) was obtained as foam.

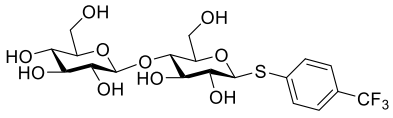


$[\alpha]_D^{25}$ -35.2(c = 0.50, MeOH); ^{1}H NMR (600 MHz, MeOD) δ 7.64 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 4.71 (d, J = 4.0 Hz, 1H), 3.87 – 3.71 (m, 1H), 3.69 (d, J = 3.3, 1.0 Hz, 1H), 3.62 (t, J = 6.0 Hz, 1H), 3.54 – 3.50 (m, 1H), 1.28 (d, J = 4.0 Hz, 3H). ^{13}C NMR (150 MHz, MeOD) δ 142.3, 130.84, 130.82, 129.4, 129.2, 128.4, 126.62, 126.59, 126.57, 126.5, 125.8 (CF_3), 88.6, 76.5, 76.2, 73.1, 70.6, 17.1. HRMS (ESI-TOF) Calculated for $C_{13}H_{15}F_3O_4SNa$ $[M+Na]^+$ 347.0535, found 347.0534.

(2S,3R,4S,5S,6R)-2-(((2R,3S,4R,5R,6S)-4,5-dihydroxy-2-(hydroxymethyl)-6-((4-

(trifluoromethyl)phenyl)thio)tetrahydro-2H-pyran-3-yl)oxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol 35

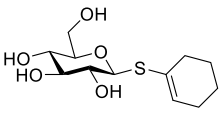
The reaction was carried out according to the general procedure, using glycosyl thiols **32** (107 mg, 0.3mmol), aryl triflates **2a** (110 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **35** (82.9 mg, 55% yield, β only, DCM:MeOH = 3:1, R*f* = 0.4) was obtained as colorless oil.



$[\alpha]_D^{25}$ 68.8(c = 0.50, MeOH); ^{1}H NMR (400 MHz, D_2O) δ 7.64 – 7.56 (m, 4H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 3.95 – 3.81 (m, 2H), 3.79 – 3.71 (m, 1H), 3.70 – 3.58 (m, 4H), 3.47 – 3.30 (m, 4H), 3.29 – 3.20 (m, 1H). ^{13}C NMR (100 MHz, D_2O) δ 137.8, 130.3, 128.9, 128.5, 126.0, 125.9, 124.1 (CF_3), 102.5, 102.5, 100.0, 86.3, 78.7, 78.2, 76.0, 75.7, 75.5, 73.2, 71.5, 69.5, 60.6, 60.1. HRMS (ESI-TOF) Calculated for $C_{19}H_{26}F_3O_{10}S$ $[M+H]^+$ 503.1194, found 503.1195.

(2S,3R,4S,5S,6R)-2-(cyclohex-1-en-1-ylthio)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol 36

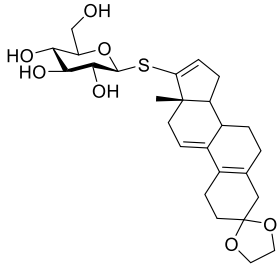
The reaction was carried out according to the general procedure, using glycosyl thiols **30** (58.8 mg, 0.3mmol), aryl triflates **22a** (105 μL, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **36** (56.3 mg, 68% yield, β only, DCM:MeOH = 10:1, R*f* = 0.4) was obtained as colorless oil.



$[\alpha]_D^{25}$ -25.6(c = 0.50, MeOH); ^{1}H NMR (400 MHz, MeOD) δ 6.03 – 5.93 (m, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 3.85 (d, *J* = 12.0 Hz, 1H), 3.74 – 3.62 (m, 1H), 3.33 – 3.16 (m, 4H), 2.94 – 2.77 (m, 1H), 2.33 – 2.20 (m, 1H), 2.11 (s, 2H), 1.70 (s, 2H), 1.60 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, MeOD) δ 130.4, 128.9, 85.8, 80.5, 78.2, 72.5, 70.0, 61.5, 30.7, 26.1, 23.2, 21.4. HRMS (ESI-TOF) Calculated for $C_{26}H_{36}O_7SNa$ $[M+Na]^+$ 299.0929, found 299.0963.

(2R,3S,4S,5R,6S)-2-(hydroxymethyl)-6-(((13S)-13-methyl-1,2,4,6,7,8,12,13,14,15-decahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-yl)thio)tetrahydro-2H-pyran-3,4,5-triol 37

The reaction was carried out according to the general procedure, using glycosyl thiols **30** (58.8 mg, 0.3mmol), aryl triflates **22g** (267 mg, 0.6 mmol), **Solution A** (1 mL), **Solution B** (2 mL) and DMF (1 mL) in 5 mL undivided three-necked bottle. The product was purified by silica chromatography. Compound **37** (91.6 mg, 62% yield, β only, DCM:MeOH = 10:1, R*f* = 0.4) was obtained as white foam.



$[\alpha]_D^{25}$ 7.0(c = 0.50, MeOH); ^{1}H NMR (400 MHz, MeOD) δ 5.67 (s, 1H), 5.55 (s, 1H), 4.61 (d, J = 12.0 Hz, 1H), 3.95 (s, 4H), 3.85 (d, J = 12.0 Hz, 1H), 3.71 – 3.57 (m, 1H), 3.42 – 3.26 (m, 4H), 2.52 – 2.45 (m, 1H), 2.36 – 2.27 (m, 1H), 2.26 – 1.59 (m, 13H), 1.34 – 1.18 (m, 1H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, MeOD) δ 145.2, 138.0, 130.0, 126.0, 123.5, 116.9, 107.9, 85.7, 80.6, 78.4, 72.6, 70.0, 63.9, 63.9, 61.3, 52.4, 40.8, 37.1, 36.6, 32.0, 30.9, 30.7, 27.5, 24.3, 15.6. HRMS (ESI-TOF) Calculated for $C_{26}H_{40}O_7SN$ $[M+NH_4]^+$ 510.2520, found 510.2498.

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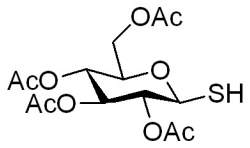
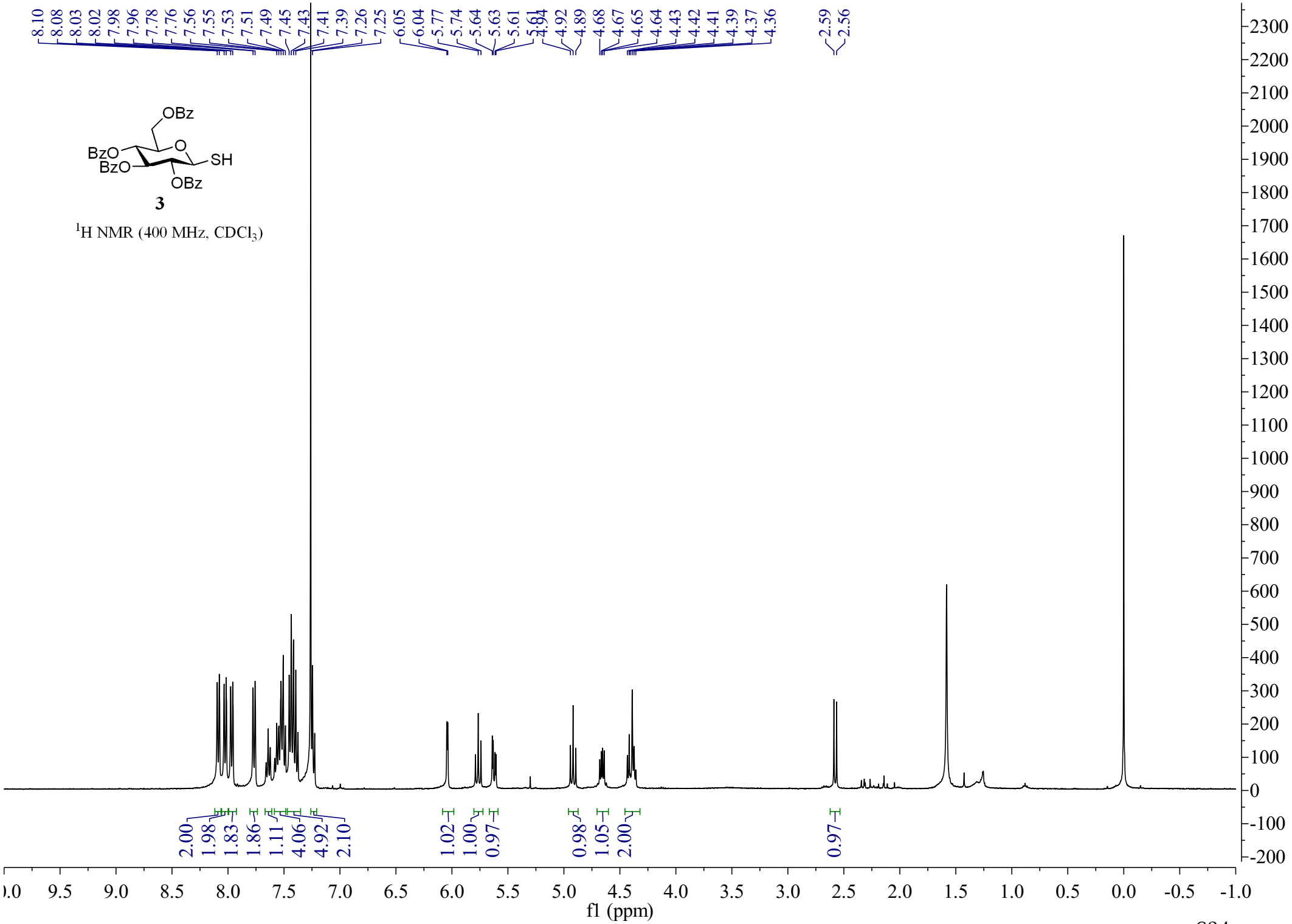


1

^{1}H NMR (400 MHz, $CDCl_3$)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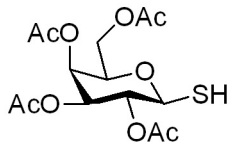
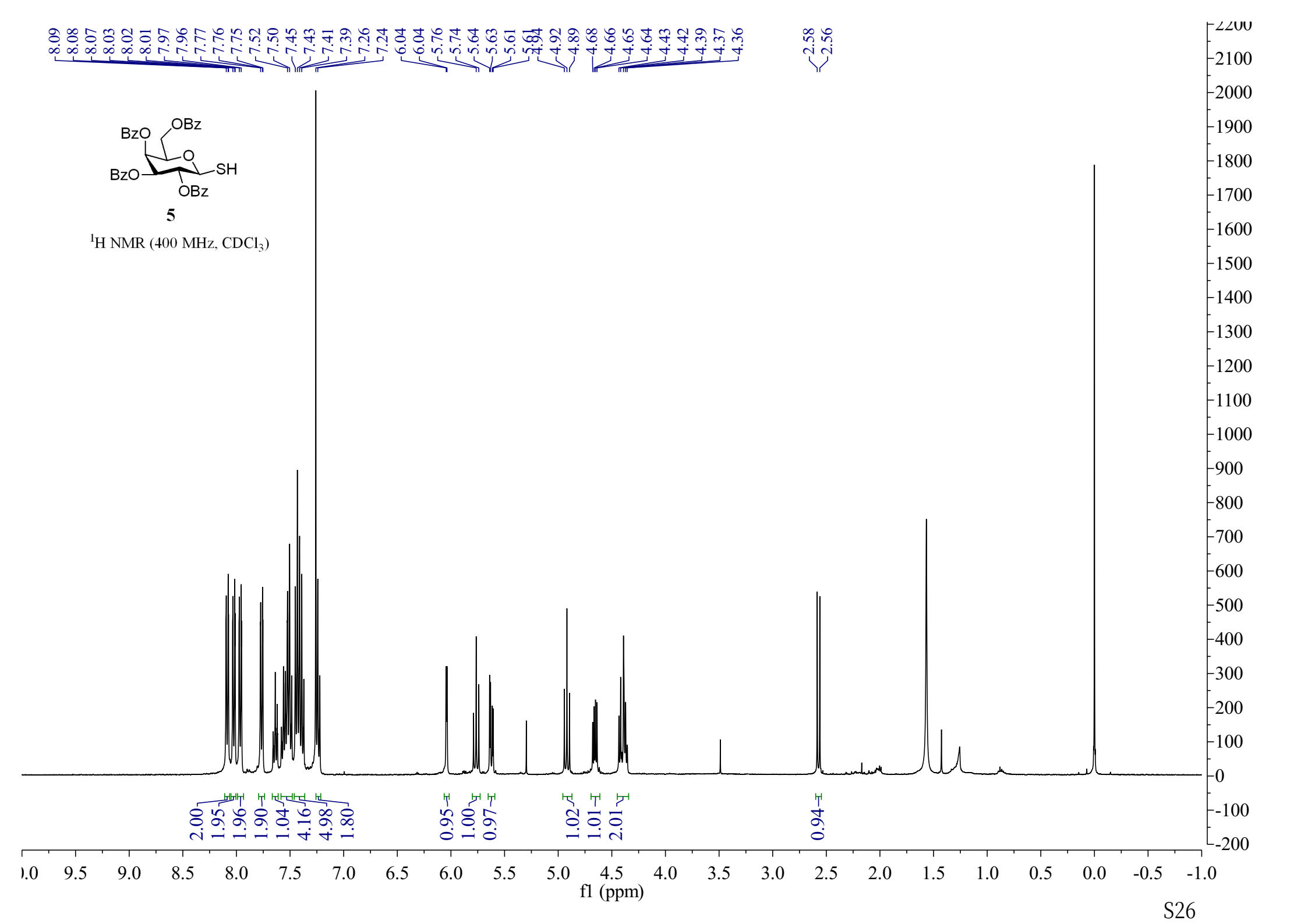
8.08
8.03
8.02
7.98
7.96
7.78
7.76
7.56
7.55
7.53
7.51
7.49
7.45
7.43
7.41
7.39
7.26
7.25
6.05
6.04
5.77
5.74
5.64
5.63
5.61
4.92
4.89
4.68
4.67
4.65
4.64
4.43
4.42
4.41
4.39
4.37
4.36
2.59
2.56
OBz
BzO
BzO
O
SH
OBz
3
1H NMR (400 MHz, CDCl3)
2.00
1.98
1.83
1.86
1.11
4.06
4.92
2.10
1.02
1.00
0.97
0.98
1.05
2.00
0.97
fl (ppm)



4

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


8.09
8.08
8.07
8.03
8.02
8.01
7.97
7.96
7.77
7.76
7.75
7.52
7.50
7.45
7.43
7.41
7.39
7.26
7.24
6.04
6.04
5.76
5.74
5.64
5.63
5.61
4.92
4.89
4.68
4.66
4.65
4.64
4.43
4.42
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4.37
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2.58
2.56
BzO
OBz
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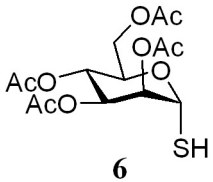
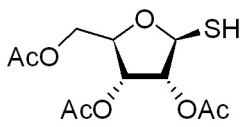
SH
BzO
OBz
5
1H NMR (400 MHz, CDCl3)
2.00
1.95
1.96
1.90
1.04
4.16
4.98
1.80
0.95
1.00
0.97
1.02
1.01
2.01
0.94
f1 (ppm)



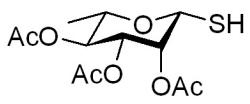
6

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



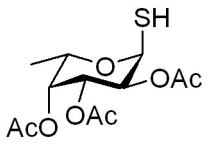
7

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



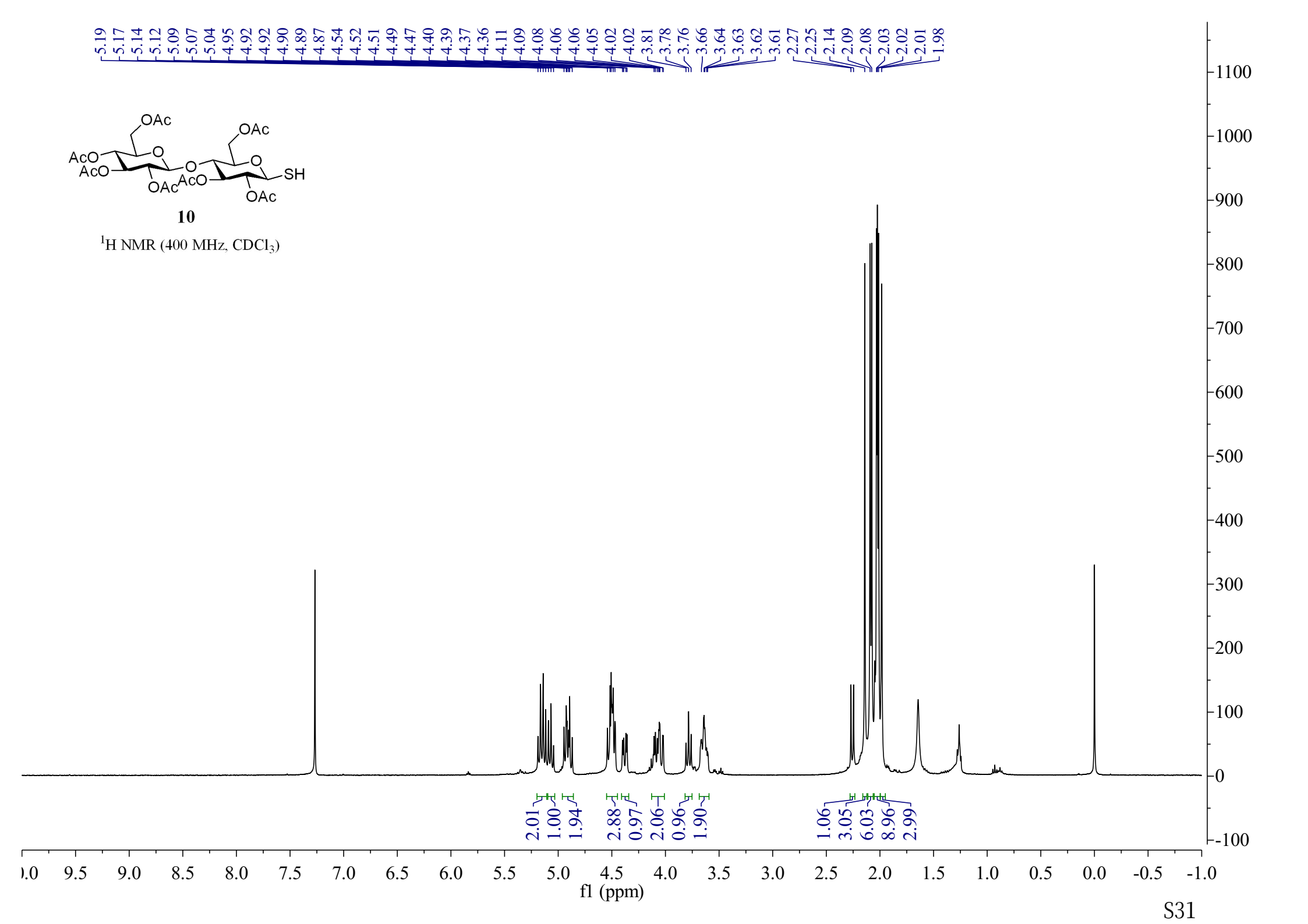
8

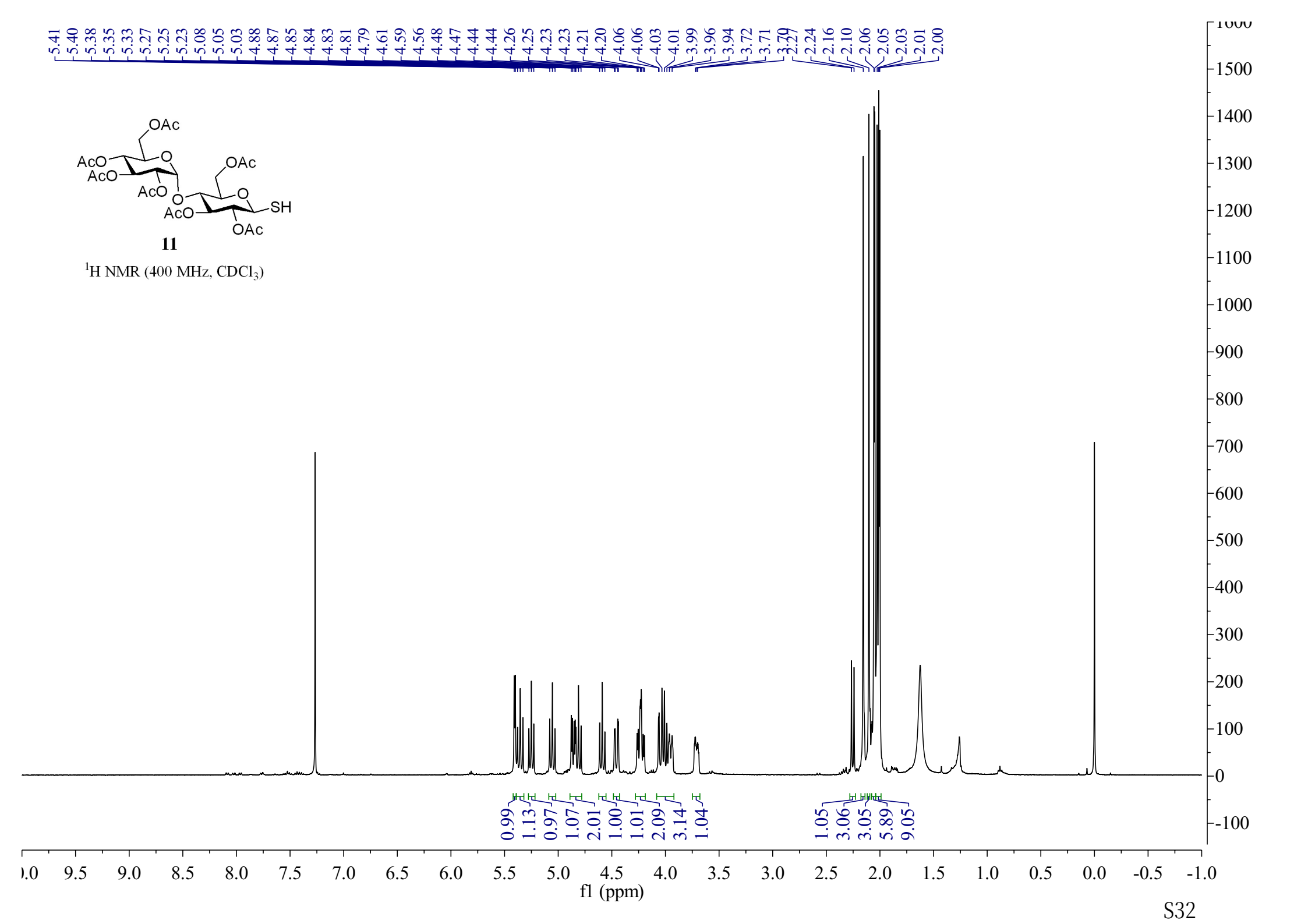
^{1}H NMR (400 MHz, $CDCl_3$)

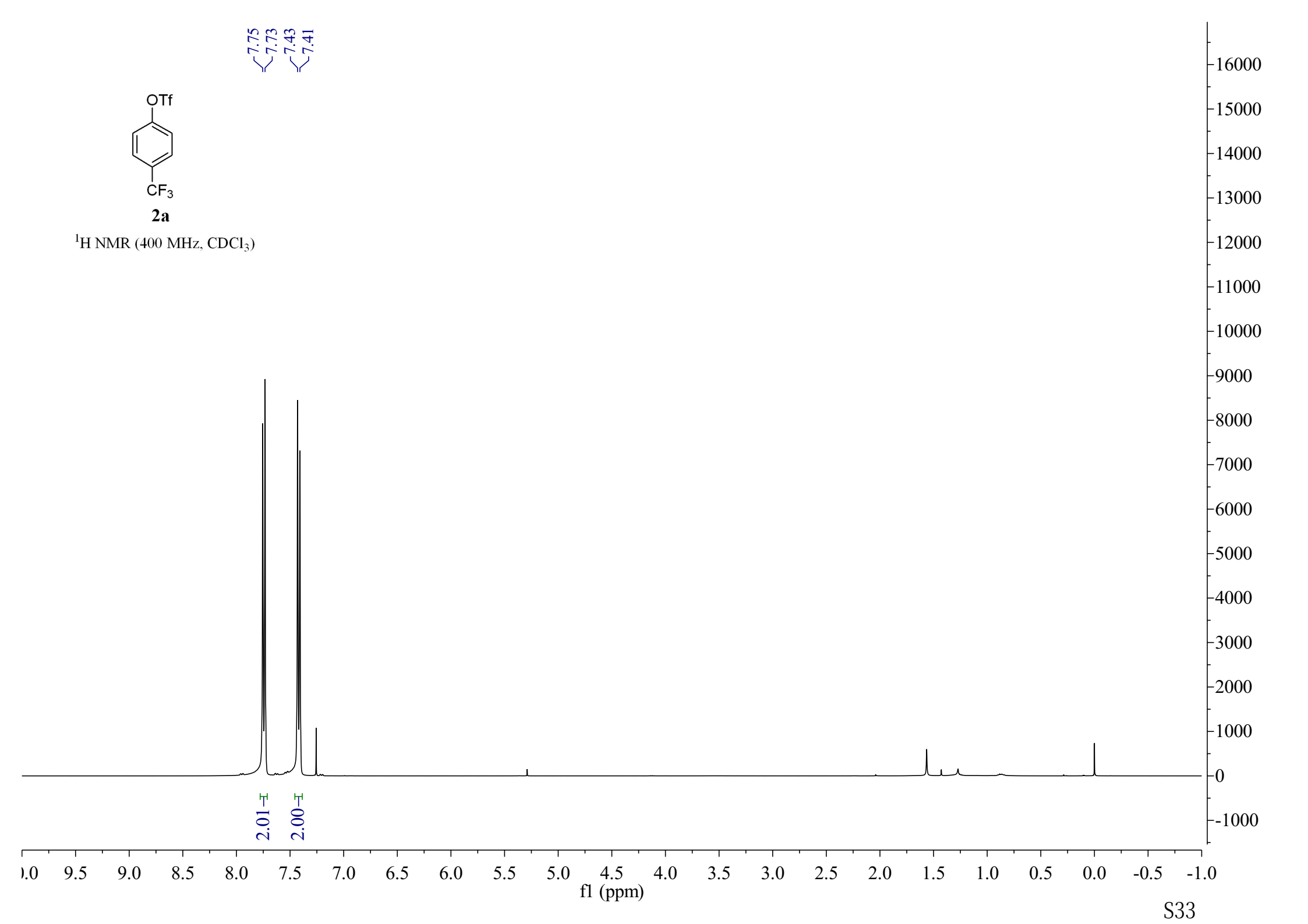


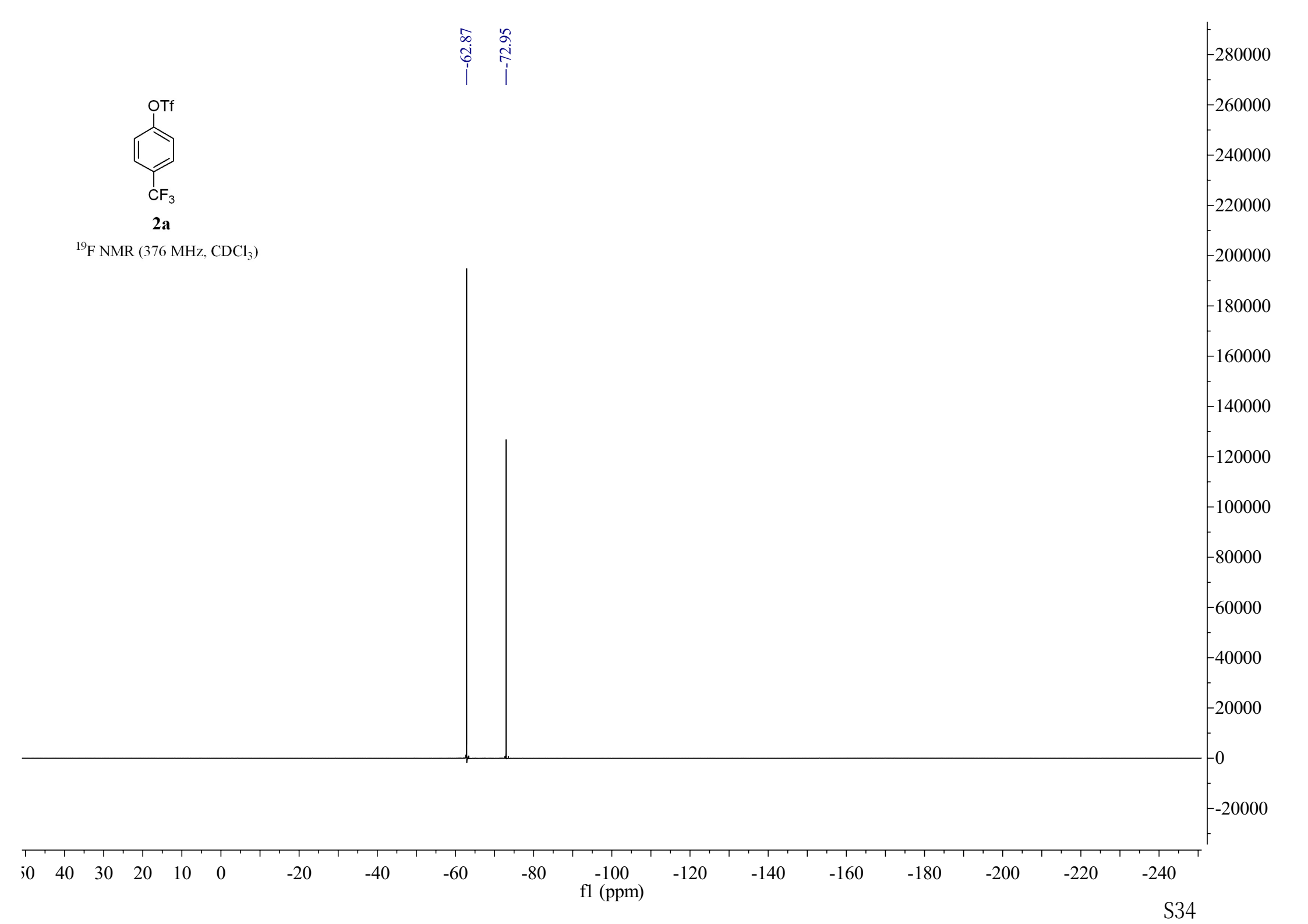
9

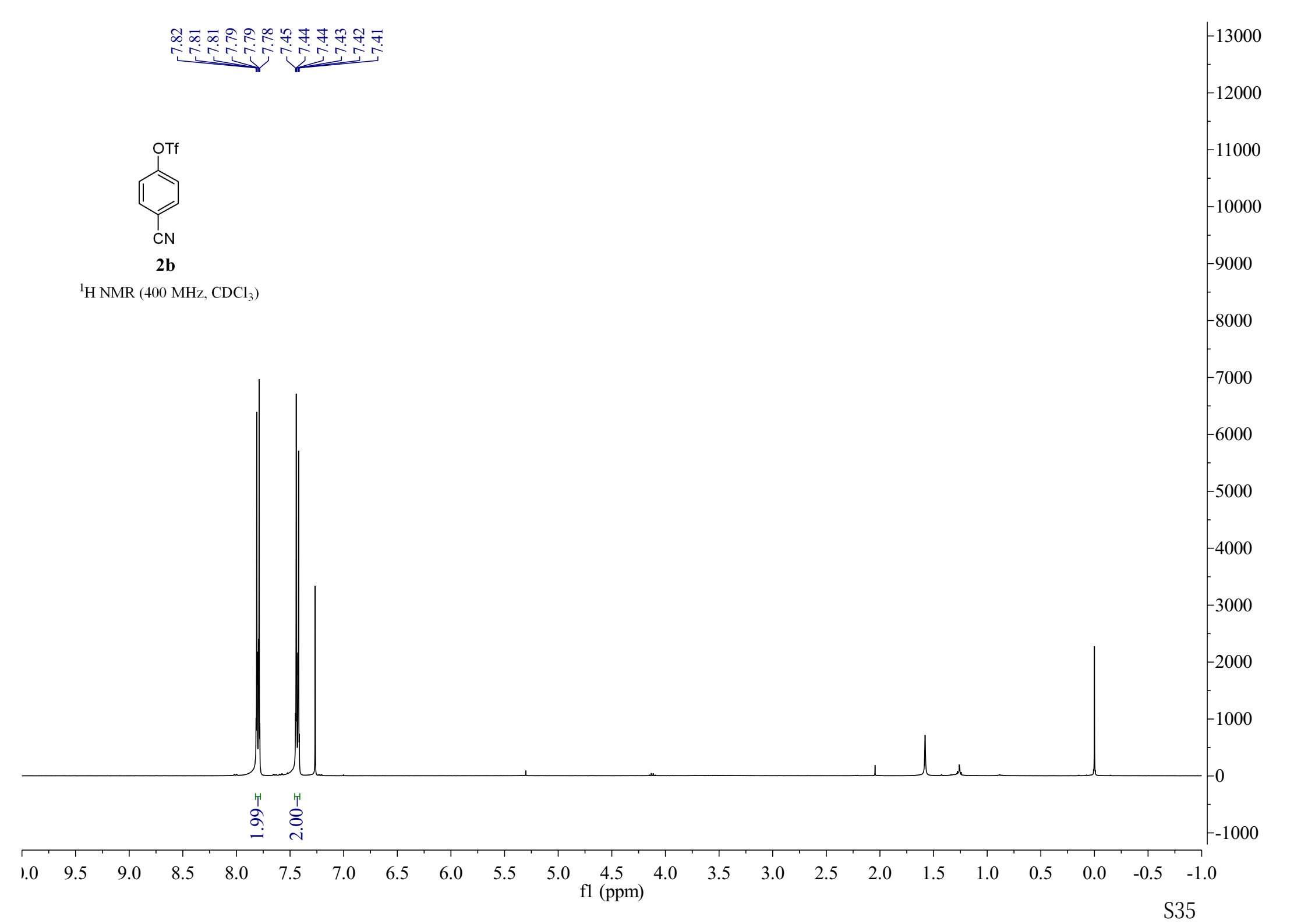
^{1}H NMR (400 MHz, $CDCl_3$)

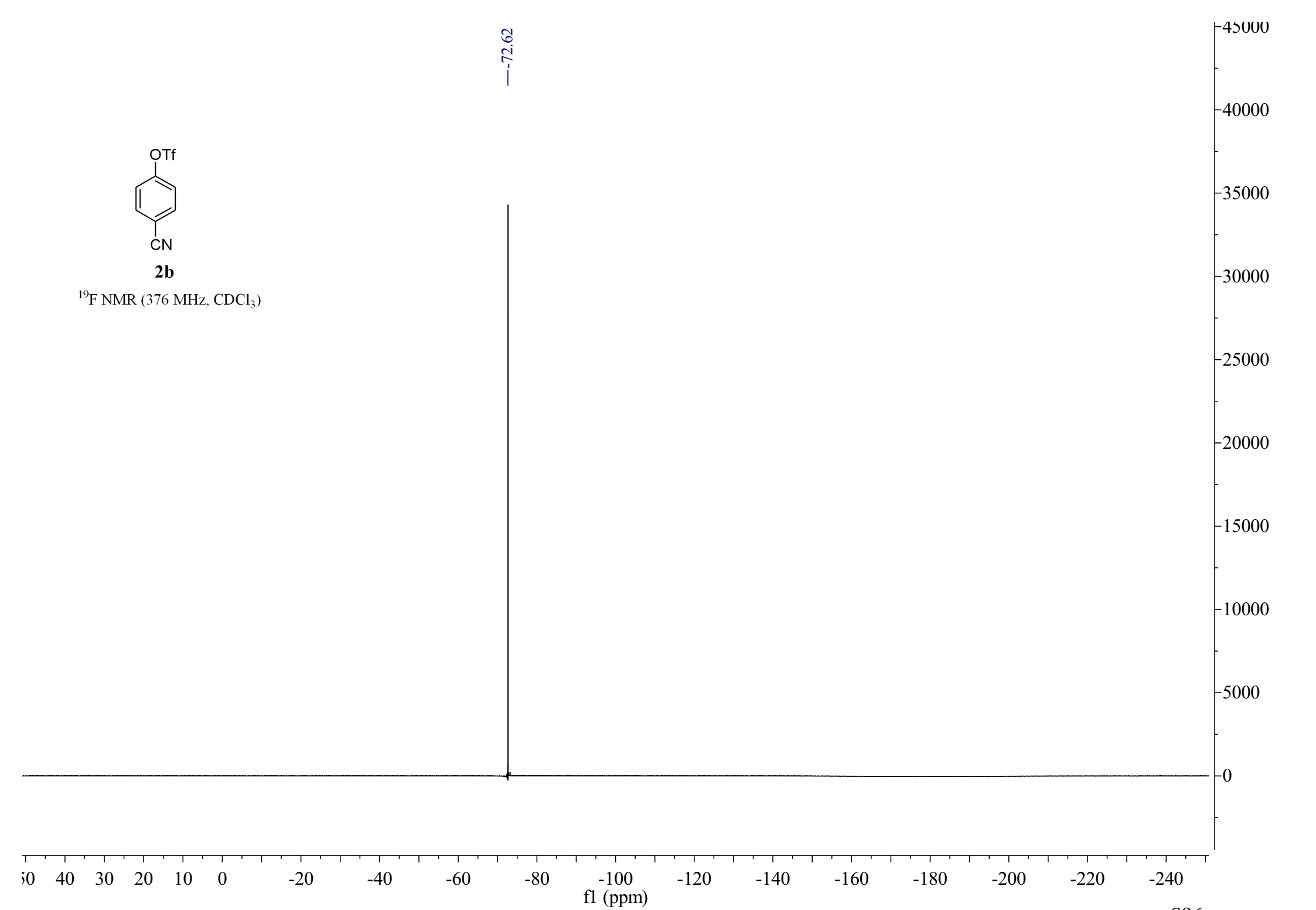

5.19 5.17 5.14 5.12 5.09 5.07 5.04 4.95 4.92 4.92 4.90 4.89 4.87 4.54 4.52 4.51 4.49 4.47 4.40 4.39 4.37 4.36 4.11 4.09 4.08 4.06 4.06 4.05 4.02 4.02 3.81 3.78 3.76 3.66 3.64 3.63 3.62 3.61 2.27 2.25 2.14 2.09 2.08 2.03 2.02 2.01 1.98
OAc
AcO
AcO
O
O
OAc
AcO
OAc
O
SH
OAc
10
1H NMR (400 MHz, CDCl3)
2.01 1.00 1.94 2.88 0.97 2.06 0.96 1.90 1.06 3.05 6.03 8.96 2.99
f1 (ppm)

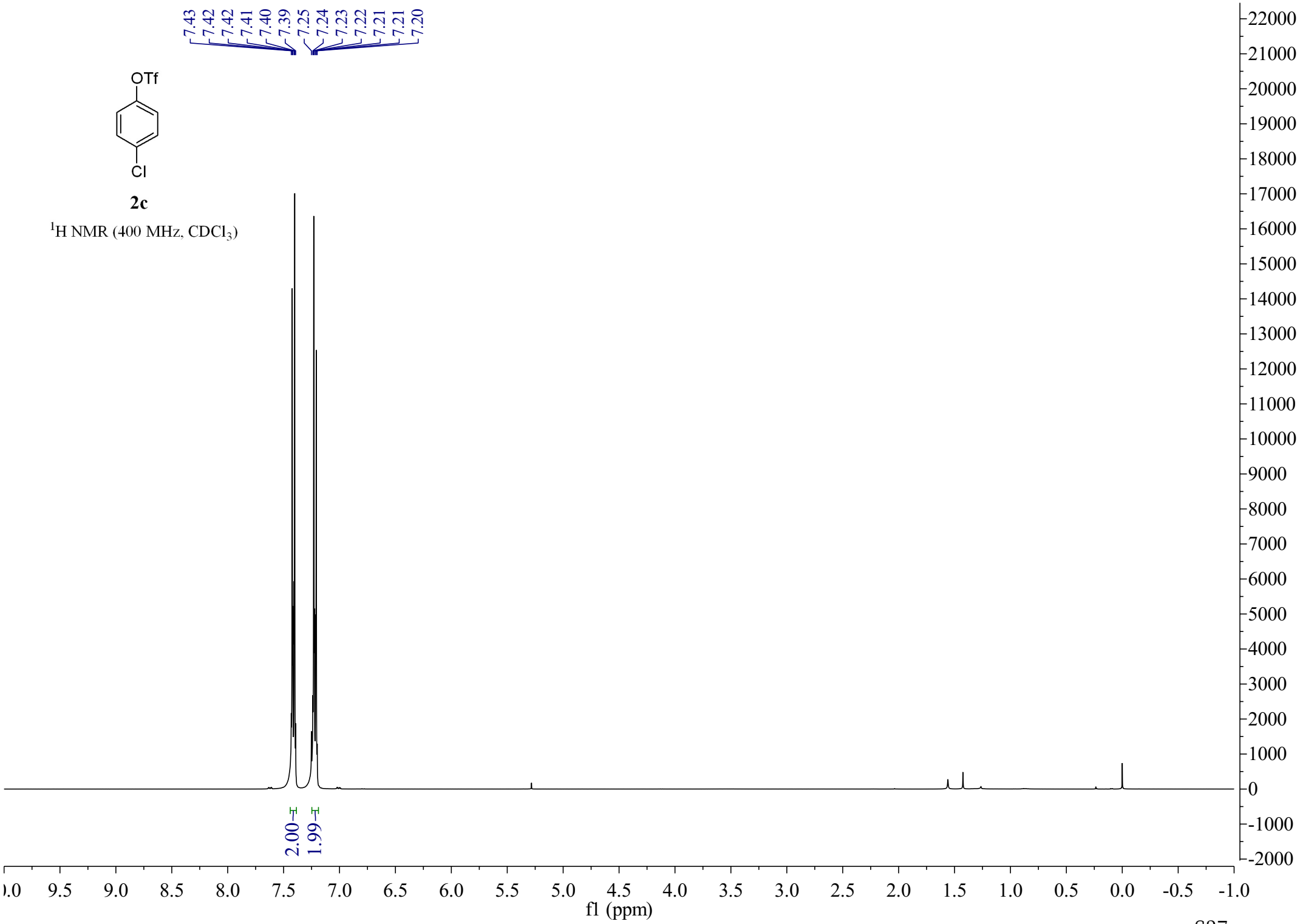

5.41 5.40 5.38 5.35 5.33 5.27 5.25 5.23 5.08 5.05 5.03 4.88 4.87 4.85 4.84 4.83 4.81 4.79 4.61 4.59 4.56 4.48 4.47 4.44 4.44 4.26 4.25 4.23 4.23 4.21 4.20 4.06 4.06 4.03 4.01 3.99 3.96 3.94 3.72 3.71 3.70 2.27 2.24 2.16 2.10 2.06 2.05 2.03 2.01 2.00
OAc
AcO
AcO
O
AcO
O
OAc
O
SH
OAc
11
1H NMR (400 MHz, CDCl3)
0.99 1.13 0.97 1.07 2.01 1.00 1.01 2.09 3.14 1.04
1.05 3.06 3.05 5.89 9.05
f1 (ppm)

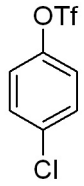

7.75
7.73
7.43
7.41
OTf
CF3
2a
1H NMR (400 MHz, CDCl3)
2.01
2.00
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


-62.87
-72.95
OTf
CF3
2a
19F NMR (376 MHz, CDCl3)
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


7.82
7.81
7.81
7.79
7.79
7.78
7.45
7.44
7.44
7.43
7.42
7.41
OTf
CN
2b
1H NMR (400 MHz, CDCl3)
1.99
2.00
fl (ppm)

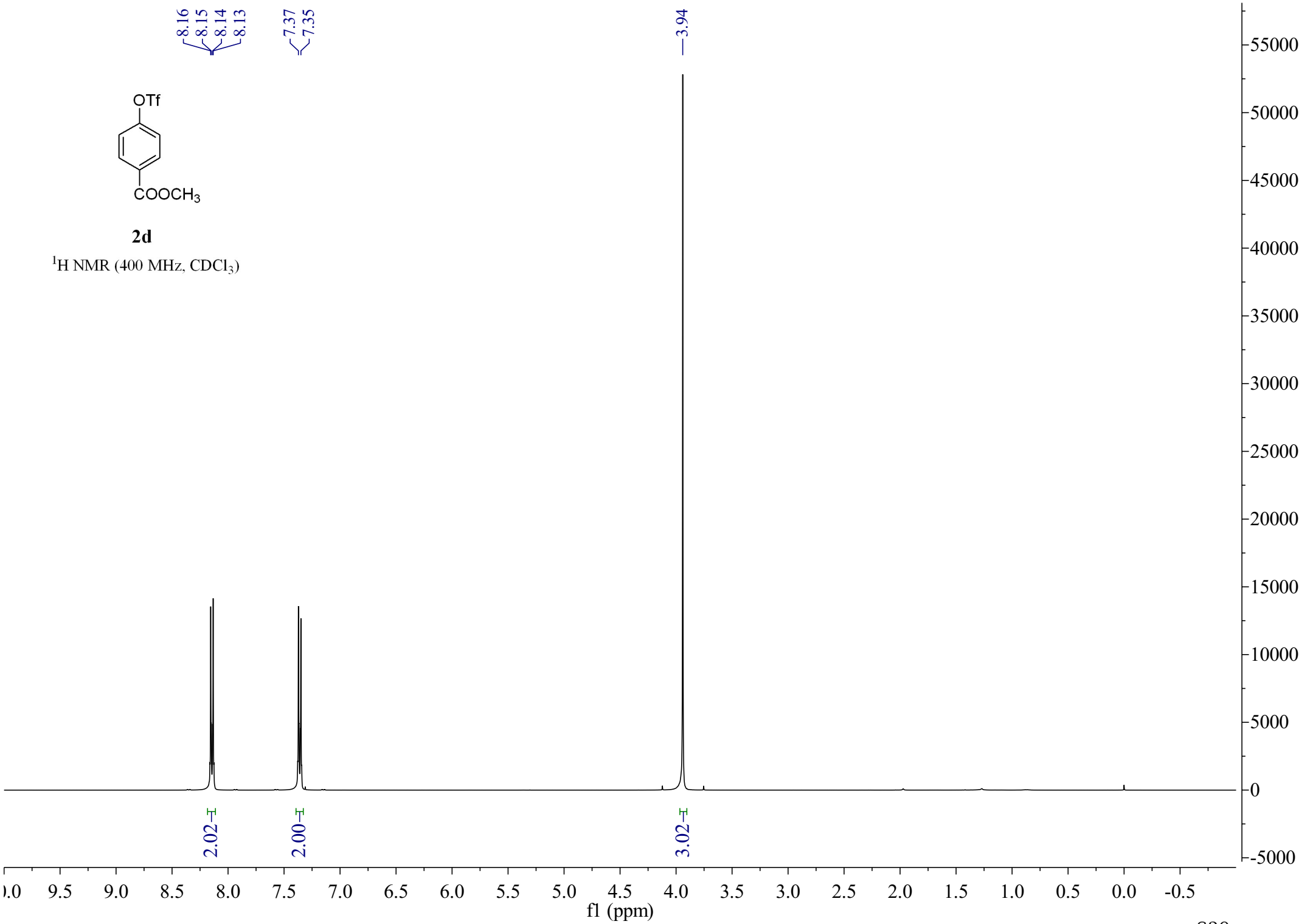

-72.62
OTf
CN
2b
^{19}F NMR (376 MHz, $CDCl_3$)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

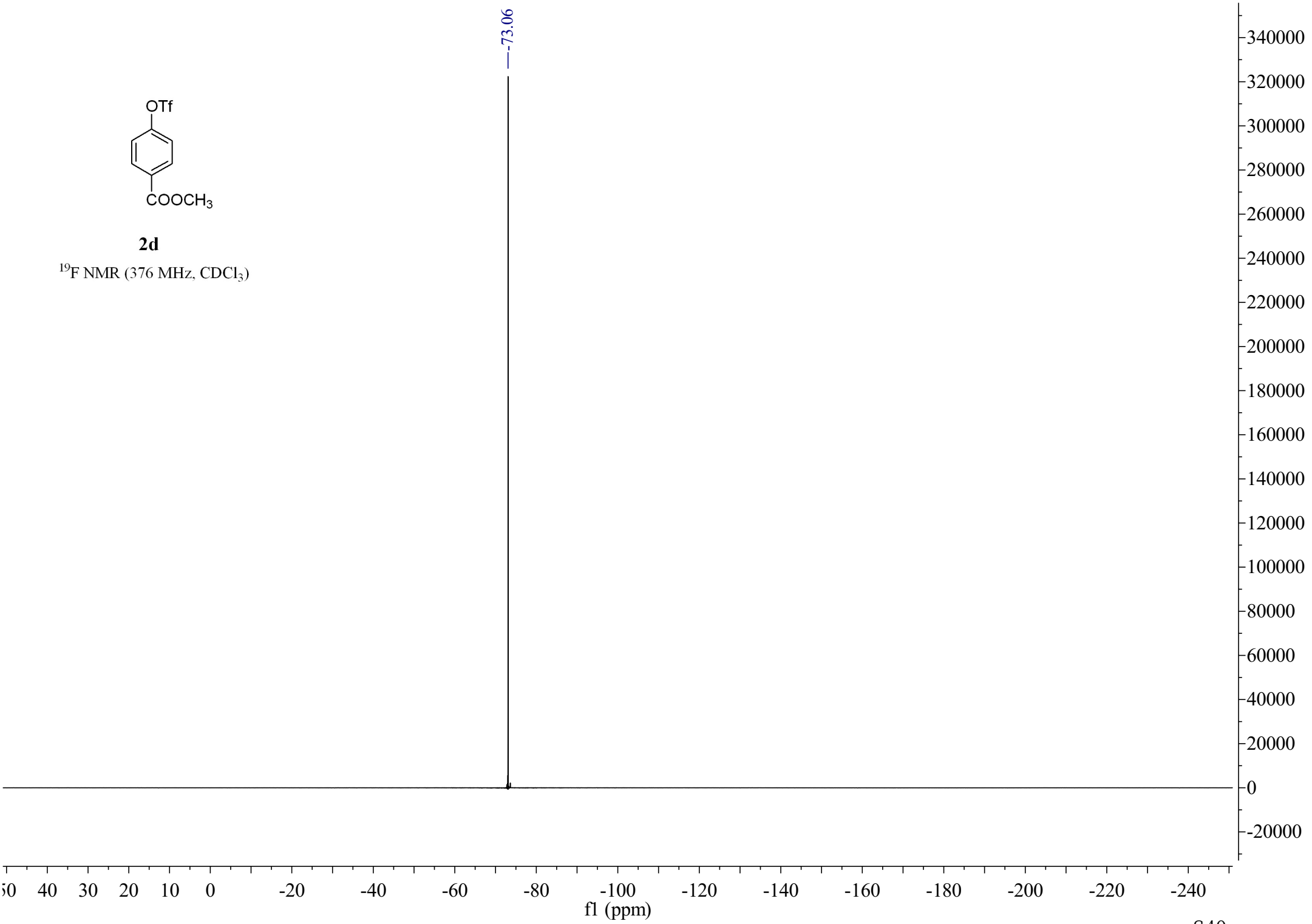

7.43
7.42
7.42
7.41
7.40
7.39
7.25
7.24
7.23
7.22
7.21
7.21
7.20
OTf
Cl
2c
1H NMR (400 MHz, CDCl3)
2.00
1.99
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

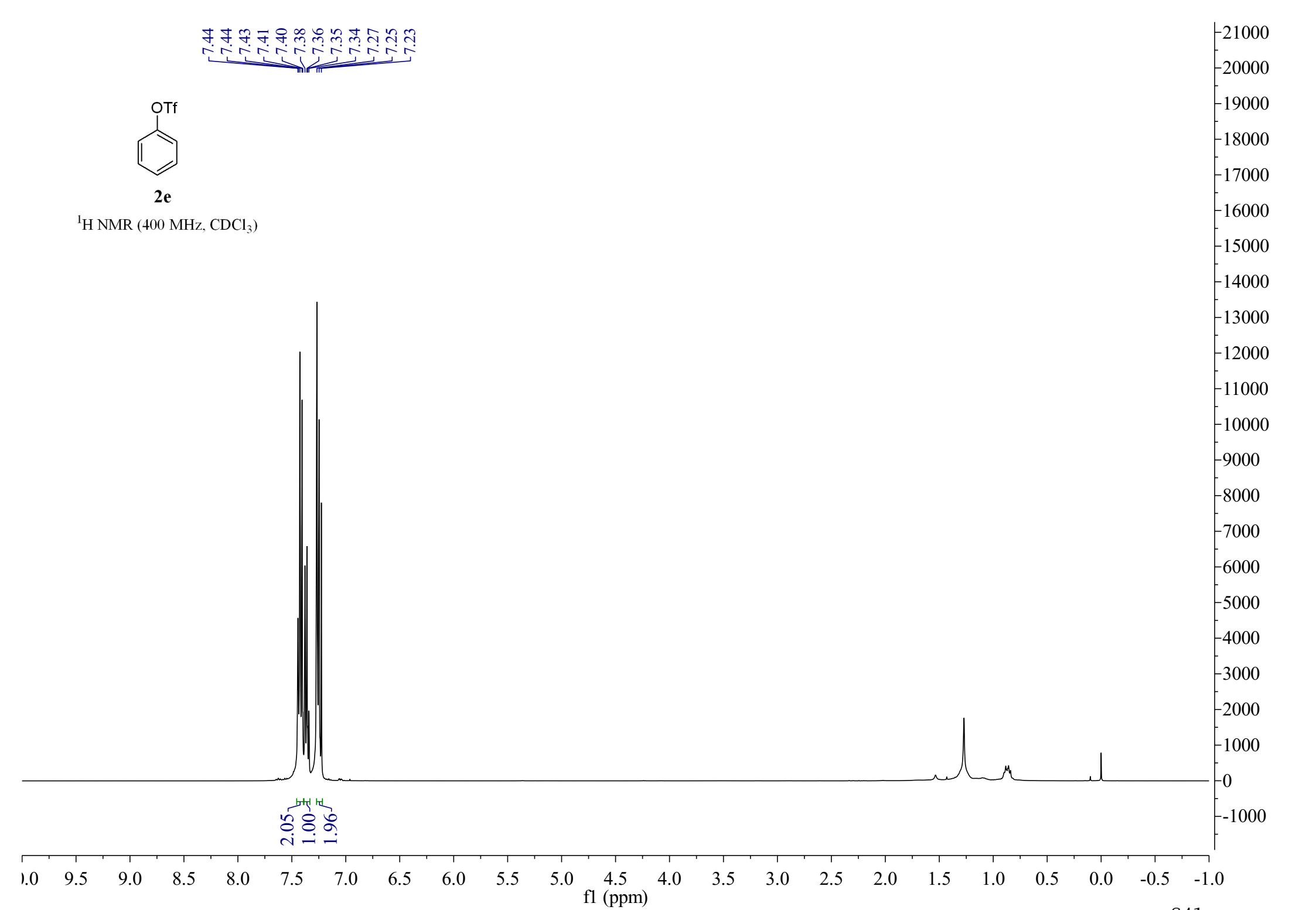


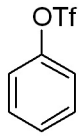
2c

^{19}F NMR (376 MHz, $CDCl_3$)


8.16
8.15
8.14
8.13
7.37
7.35
3.94
OTf
COOCH3
2d
1H NMR (400 MHz, CDCl3)
2.02
2.00
3.02
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
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
f1 (ppm)

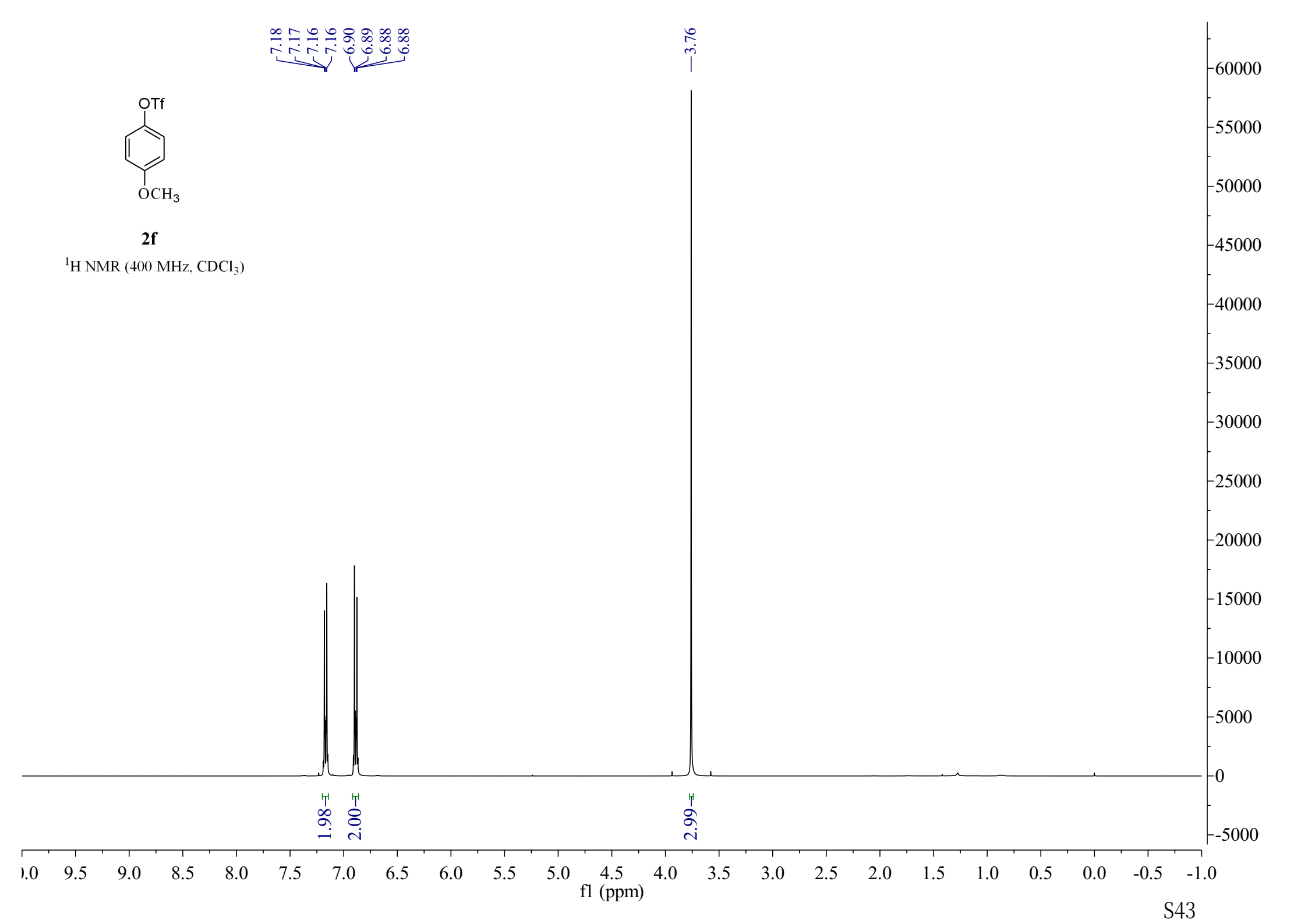

OTf
COOCH3
2d
19F NMR (376 MHz, CDCl3)
-73.06
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

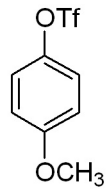

7.44
7.44
7.43
7.41
7.40
7.38
7.36
7.35
7.34
7.27
7.25
7.23
OTf
2e
1H NMR (400 MHz, CDCl3)
2.05
1.00
1.96
f1 (ppm)



2e

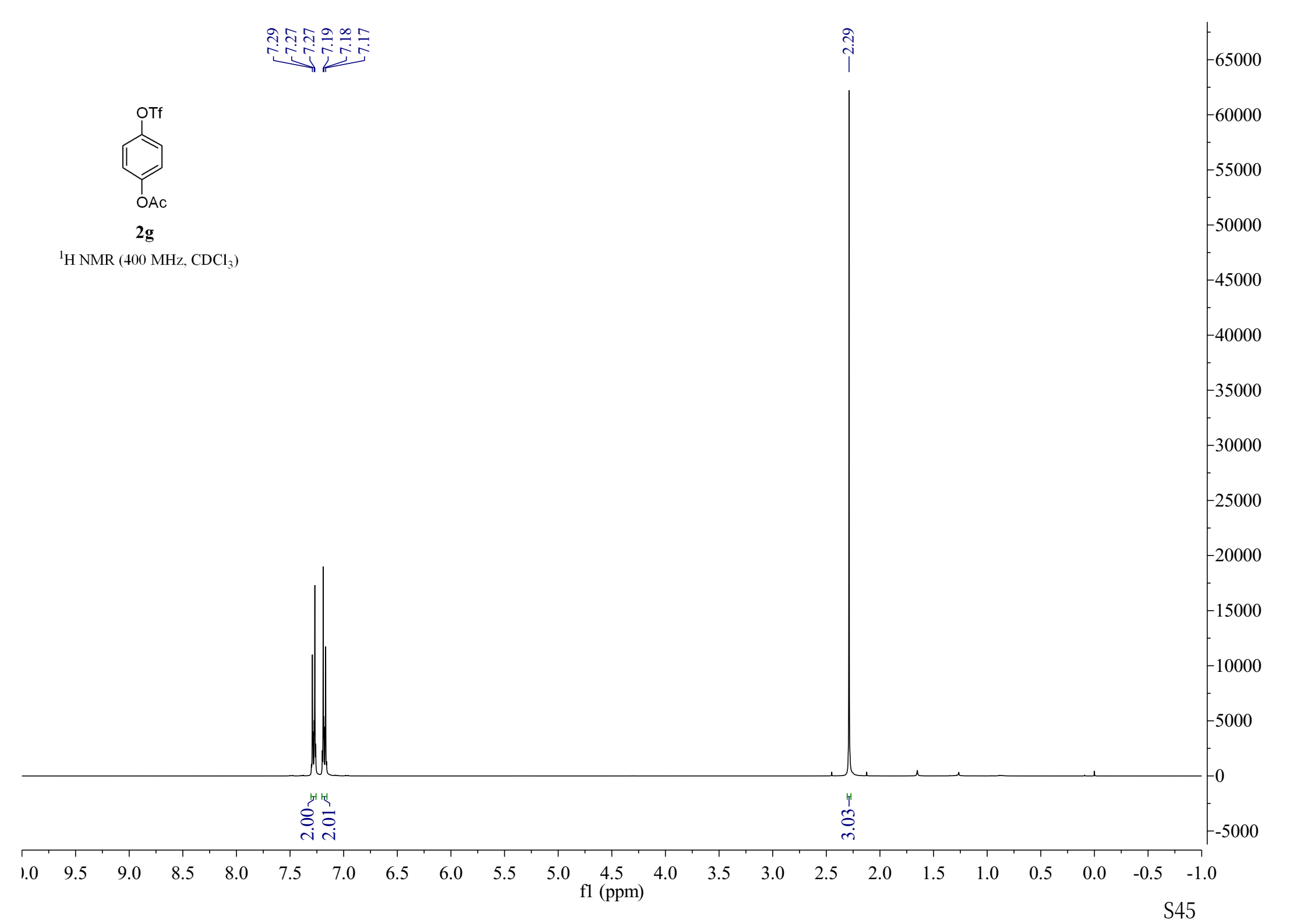
^{19}F NMR (376 MHz, $CDCl_3$)

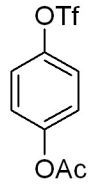

OTf
OCH3
2f
1H NMR (400 MHz, CDCl3)
7.18
7.17
7.16
7.16
6.90
6.89
6.88
6.88
3.76
1.98
2.00
2.99
f1 (ppm)



2f

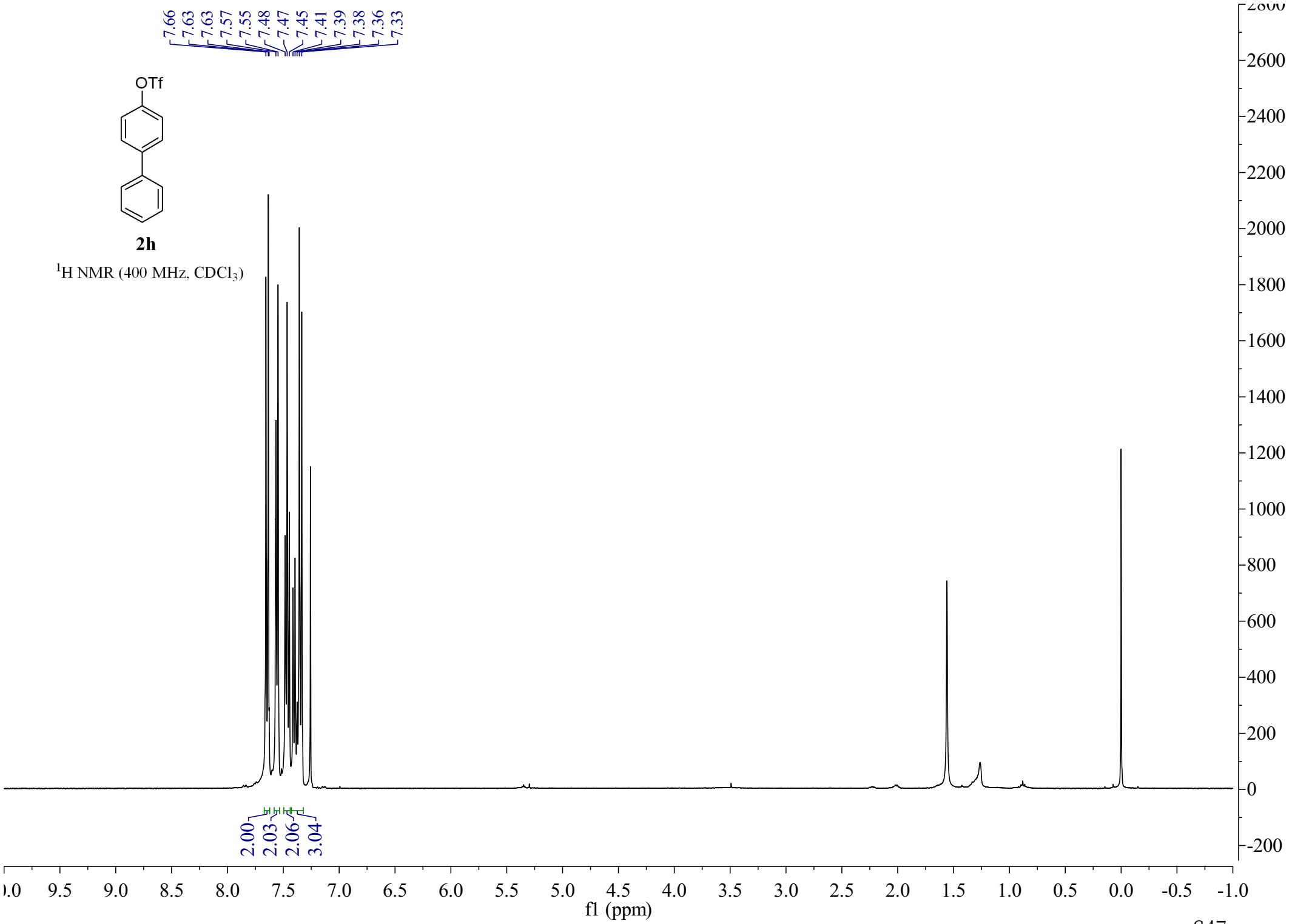
^{19}F NMR (376 MHz, $CDCl_3$)

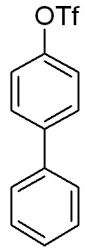

OTf
OAc
2g
^{1}H NMR (400 MHz, $CDCl_3$)
7.29
7.27
7.27
7.19
7.18
7.17
2.29
2.00
2.01
3.03
fl (ppm)



2g

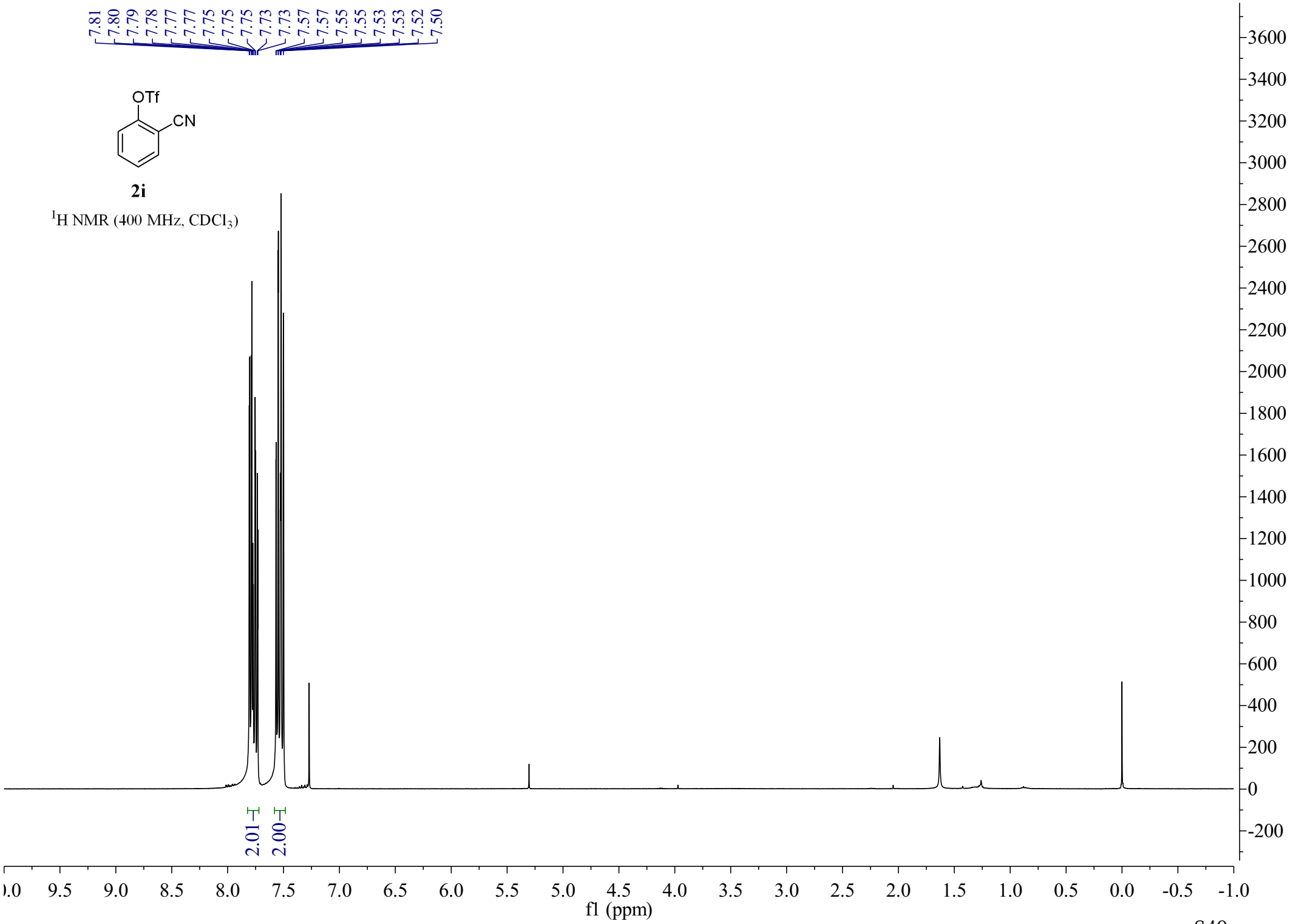
^{19}F NMR (376 MHz, $CDCl_3$)

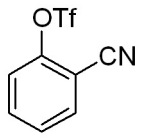

7.66
7.63
7.63
7.57
7.55
7.48
7.47
7.45
7.41
7.39
7.38
7.36
7.33
OTf
2h
1H NMR (400 MHz, CDCl3)
2.00
2.03
2.06
3.04
fl (ppm)



2h

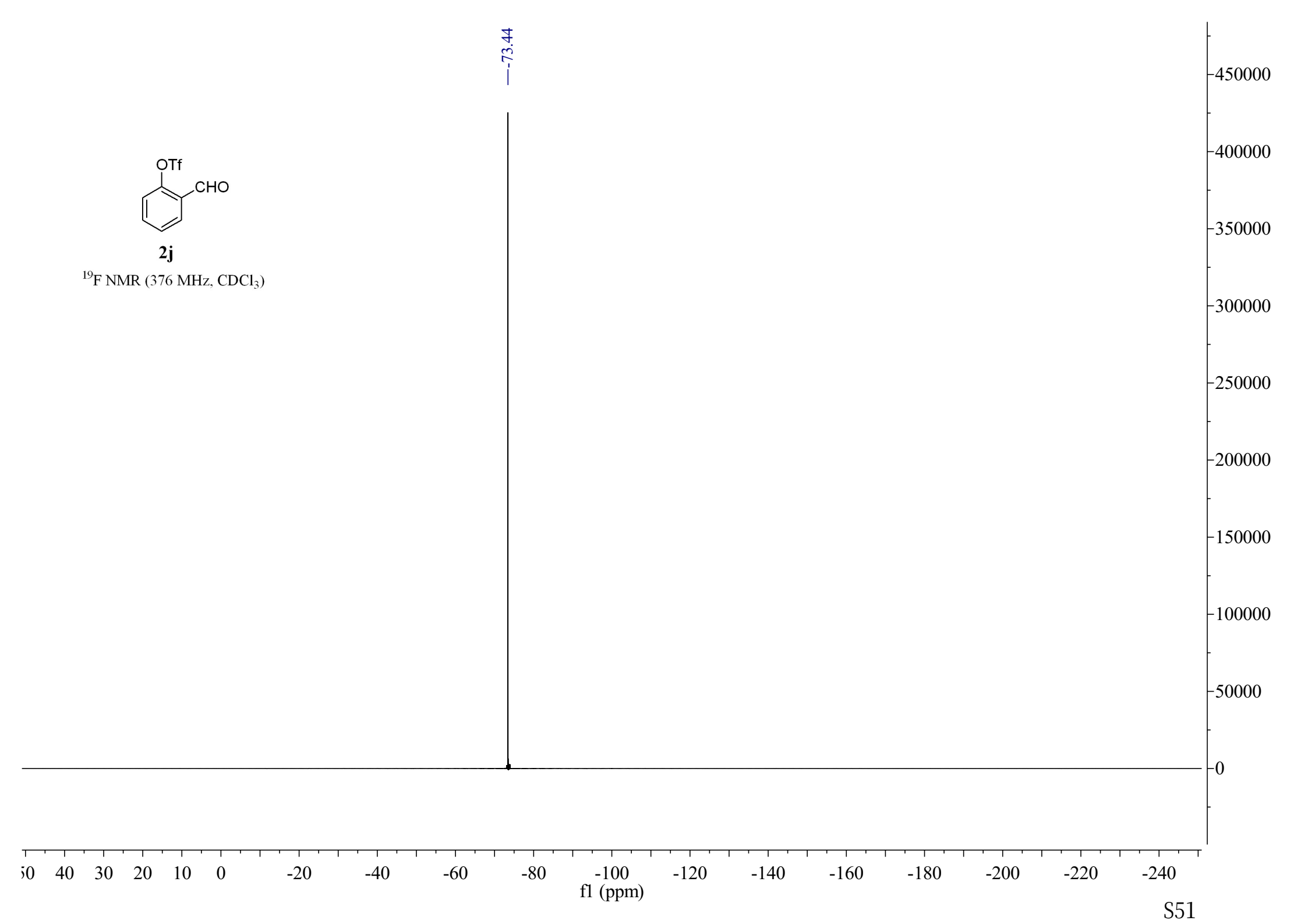
^{19}F NMR (376 MHz, $CDCl_3$)

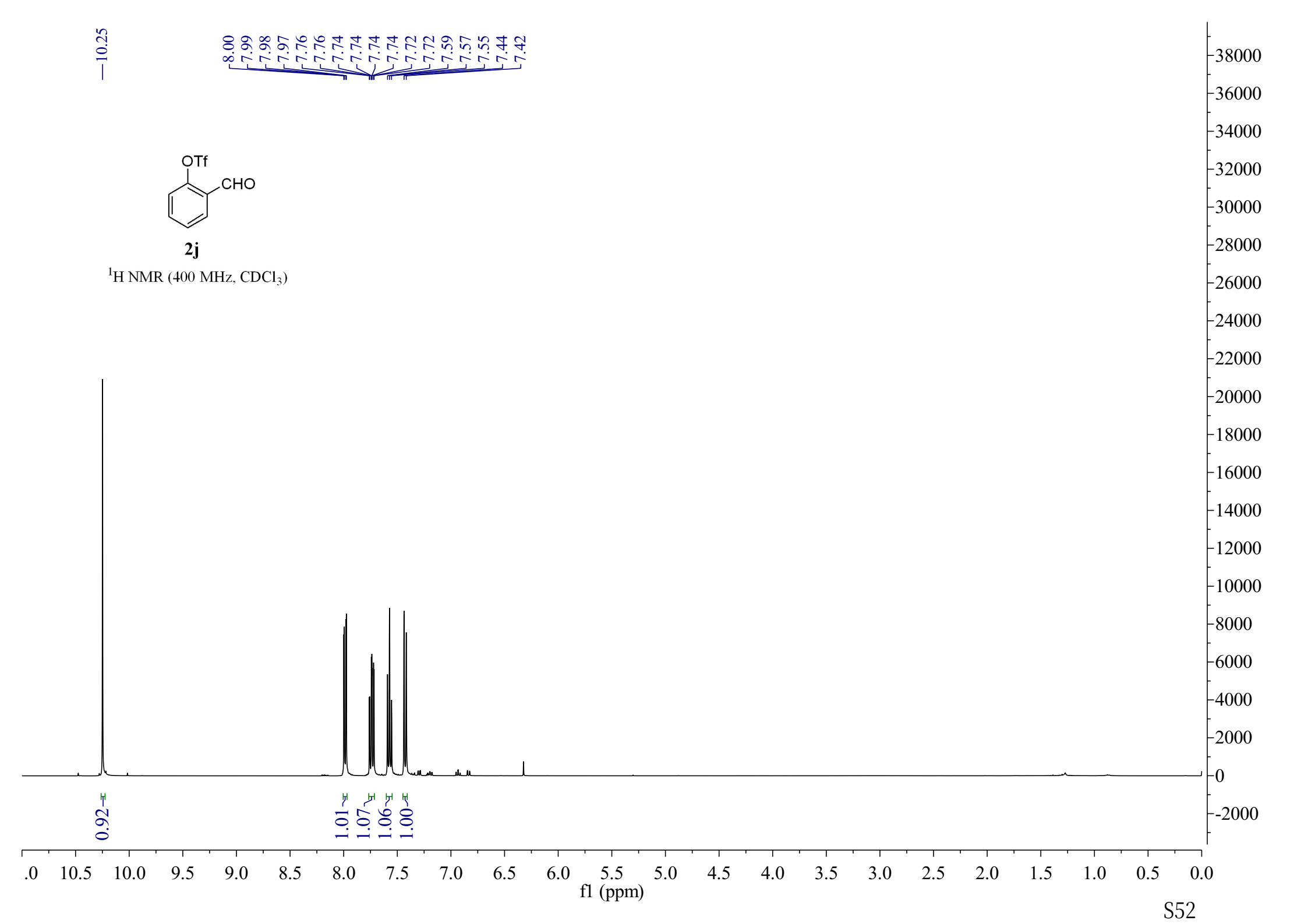

7.81
7.80
7.79
7.78
7.77
7.77
7.75
7.75
7.75
7.73
7.73
7.57
7.57
7.55
7.55
7.53
7.53
7.52
7.50
OTf
CN
2i
1H NMR (400 MHz, CDCl3)
2.01
2.00
fl (ppm)

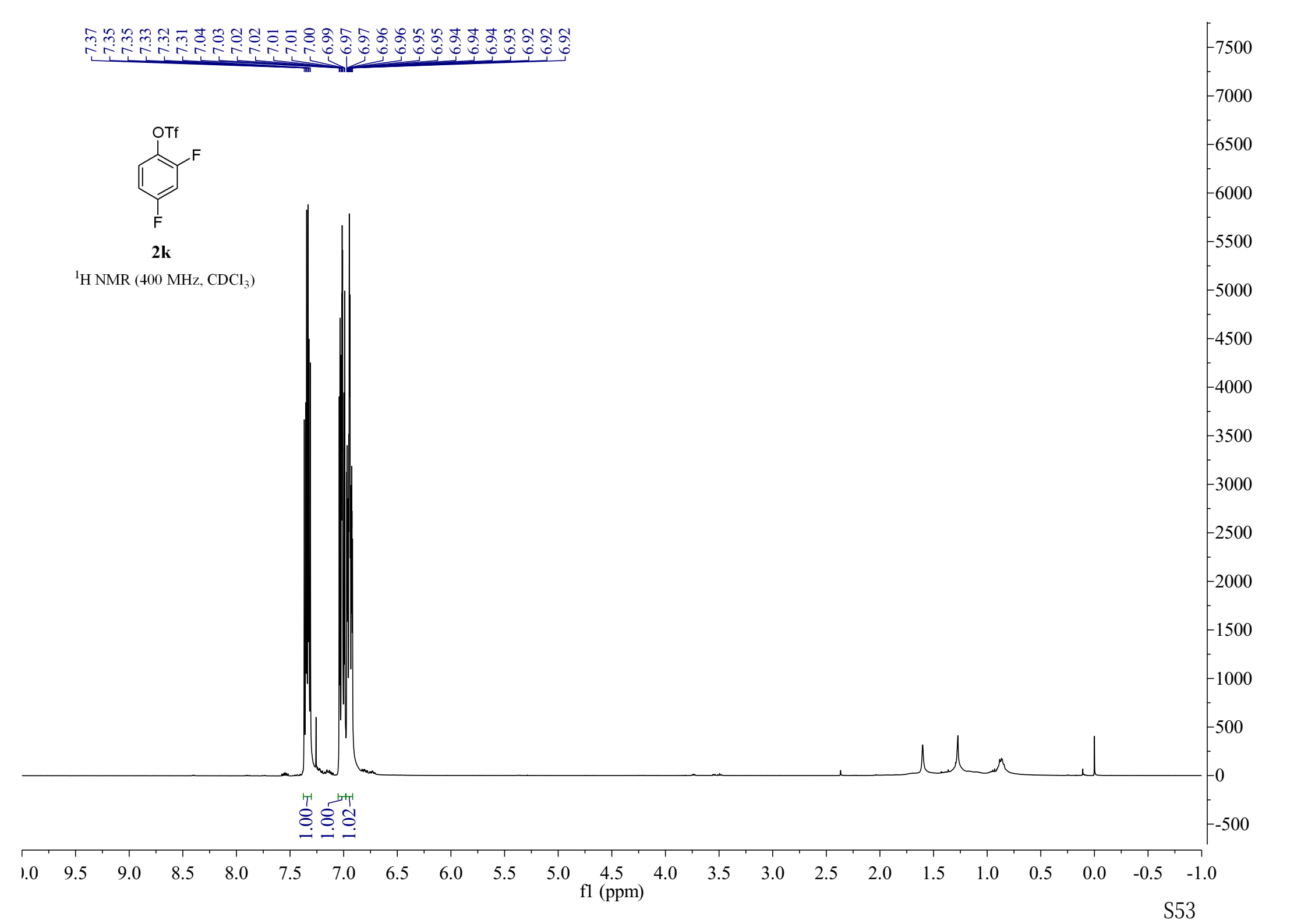


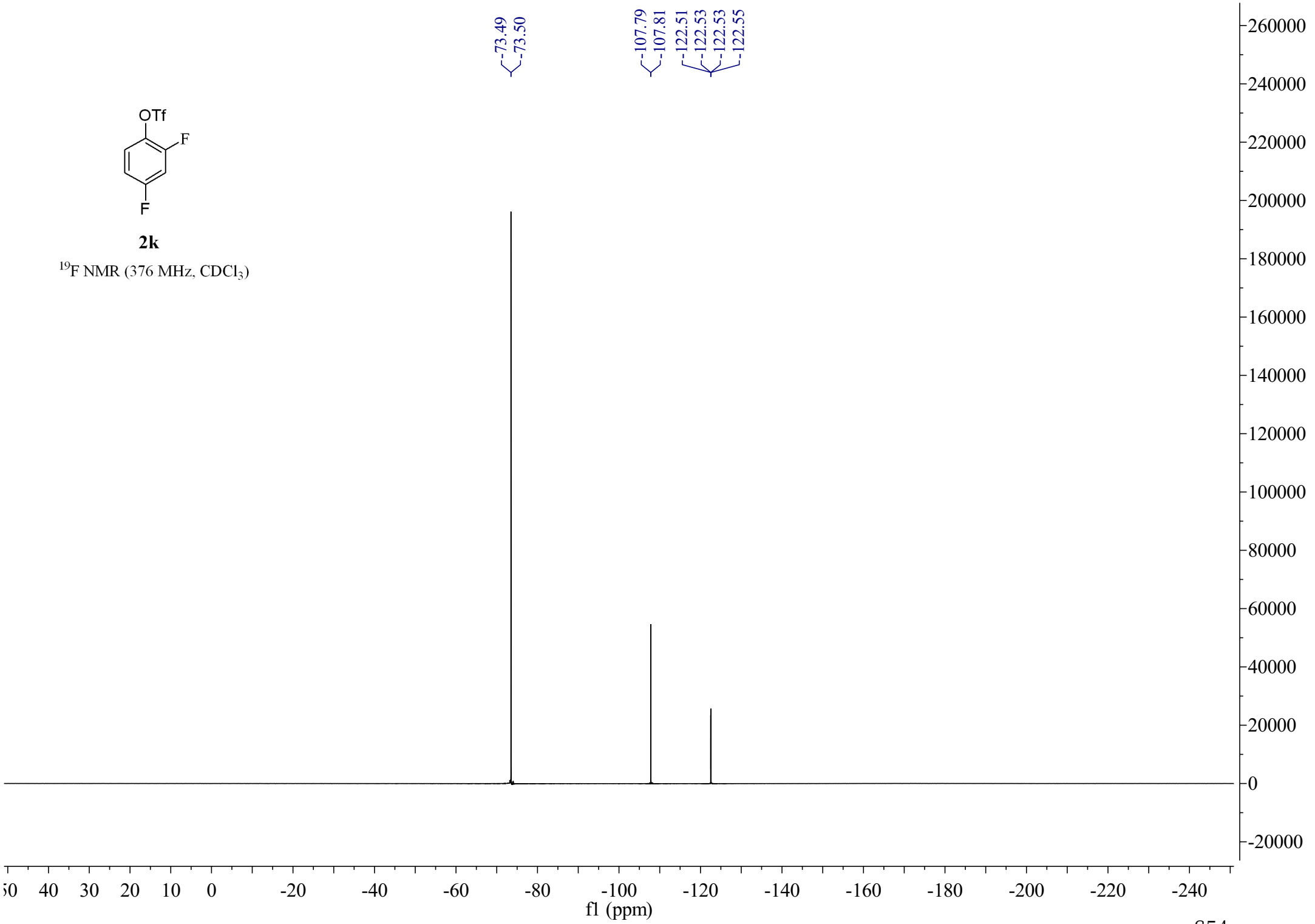
2i

^{19}F NMR (376 MHz, $CDCl_3$)


OTf
CHO
2j
^{19}F NMR (376 MHz, $CDCl_3$)
-73.44
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

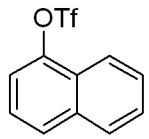

10.25
8.00
7.99
7.98
7.97
7.76
7.76
7.74
7.74
7.74
7.74
7.72
7.72
7.59
7.57
7.55
7.44
7.42
OTf
CHO
2j
1H NMR (400 MHz, CDCl3)
0.92
1.01
1.07
1.06
1.00
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.37
7.35
7.35
7.33
7.32
7.31
7.04
7.03
7.02
7.02
7.01
7.01
7.00
6.99
6.97
6.97
6.96
6.96
6.95
6.95
6.94
6.94
6.94
6.93
6.92
6.92
6.92
OTf
F
F
2k
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.02
fl (ppm)



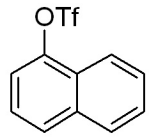
2k

^{19}F NMR (376 MHz, $CDCl_3$)



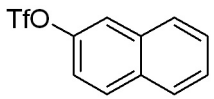
2l

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



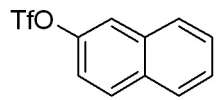
2l

^{19}F NMR (376 MHz, $CDCl_3$)



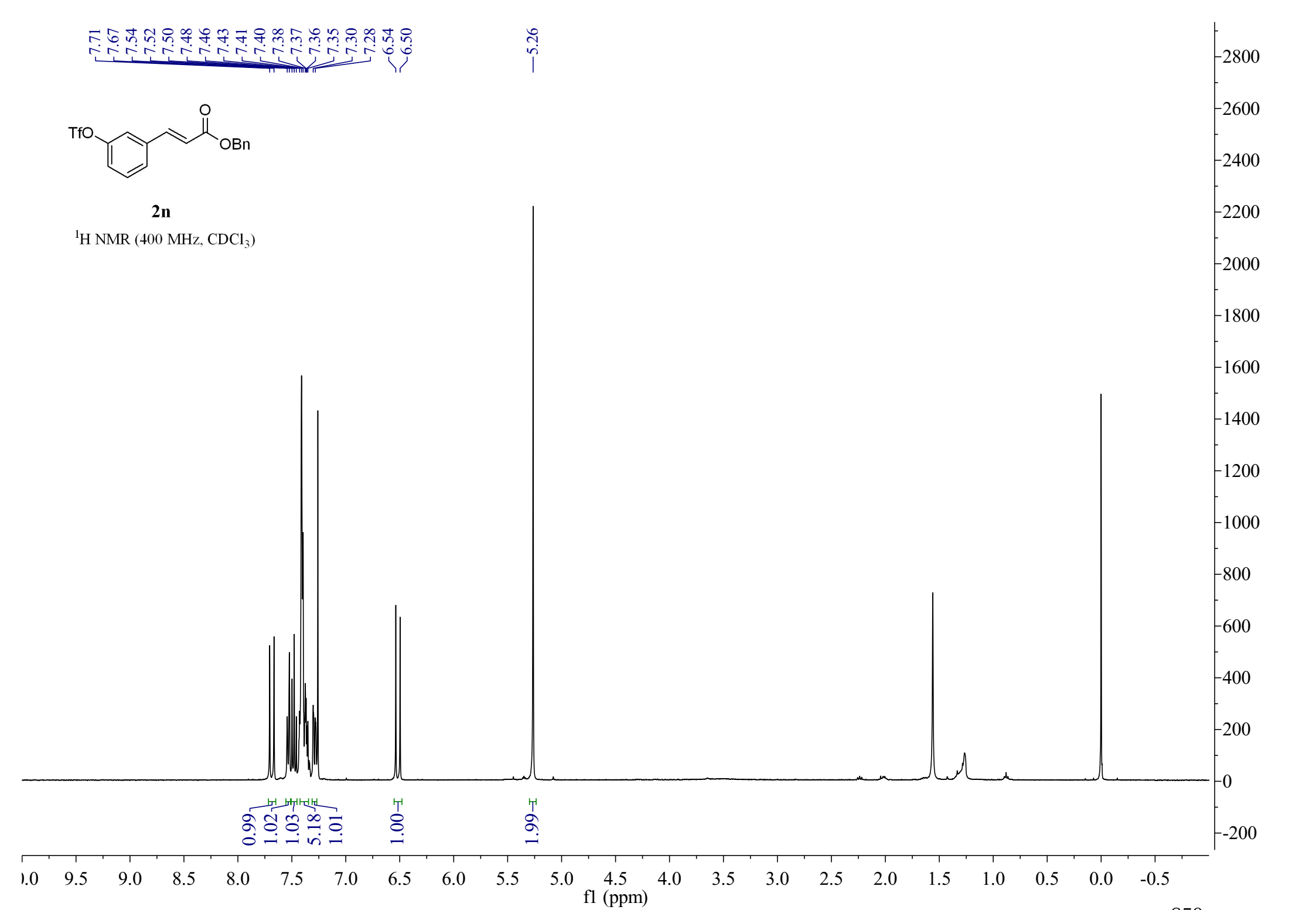
2m

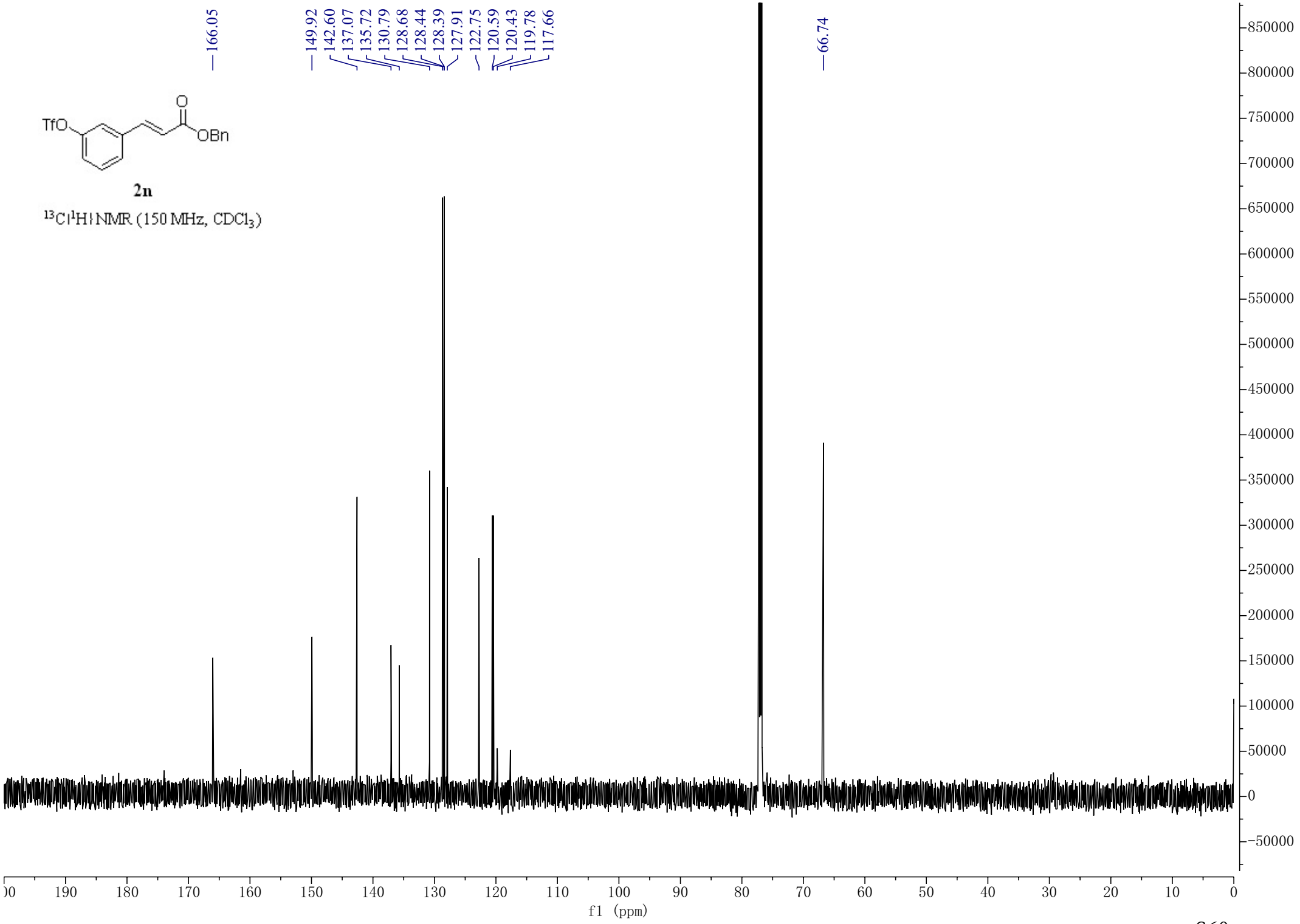
^{1}H NMR (400 MHz, $CDCl_3$)

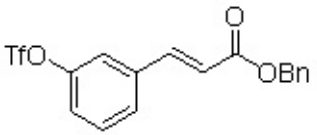


2m

^{19}F NMR (376 MHz, $CDCl_3$)

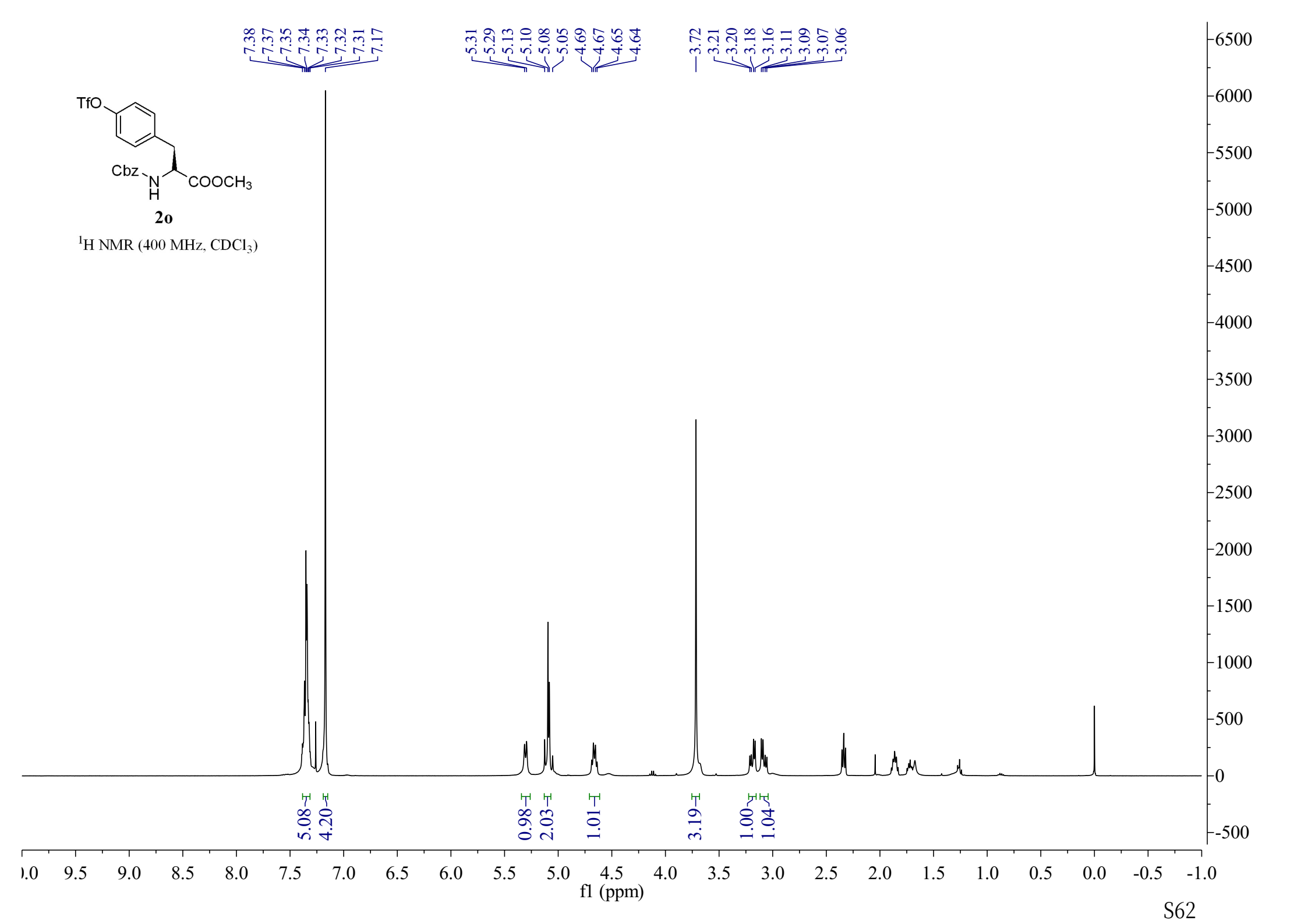

7.71
7.67
7.54
7.52
7.50
7.48
7.46
7.43
7.41
7.40
7.38
7.37
7.36
7.35
7.30
7.28
6.54
6.50
5.26
TfO
O
OBn
2n
1H NMR (400 MHz, CDCl3)
0.99
1.02
1.03
5.18
1.01
1.00
1.99
fl (ppm)

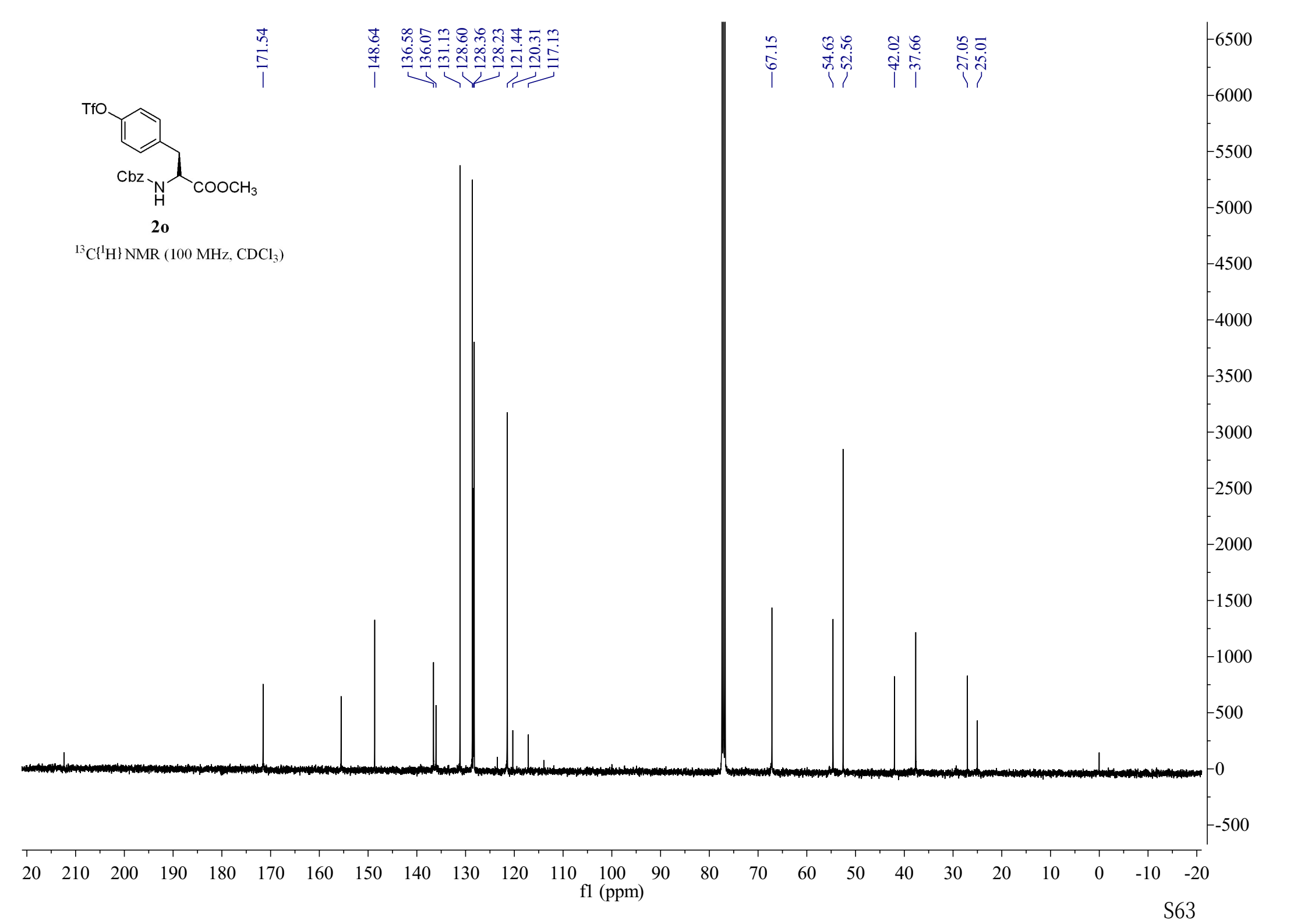

166.05
149.92
142.60
137.07
135.72
130.79
128.68
128.44
128.39
127.91
122.75
120.59
120.43
119.78
117.66
66.74
TfO
O
OBn
2n
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)
f1 (ppm)



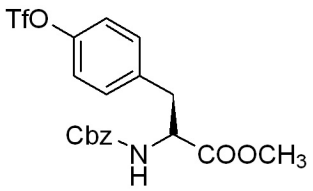
2n

^{19}F NMR (565 MHz, $CDCl_3$)


7.38
7.37
7.35
7.34
7.33
7.32
7.31
7.17
5.31
5.29
5.13
5.10
5.08
5.05
4.69
4.67
4.65
4.64
3.72
3.21
3.20
3.18
3.16
3.11
3.09
3.07
3.06
TfO
Cbz
N
H
COOCH3
2o
1H NMR (400 MHz, CDCl3)
5.08
4.20
0.98
2.03
1.01
3.19
1.00
1.04
f1 (ppm)

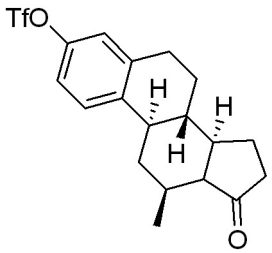

171.54
148.64
136.58
136.07
131.13
128.60
128.36
128.23
121.44
120.31
117.13
67.15
54.63
52.56
42.02
37.66
27.05
25.01
TfO
Cbz
N
H
COOCH3
2o
13C{1H} NMR (100 MHz, CDCl3)
fl (ppm)

LFX10052
LFX10052



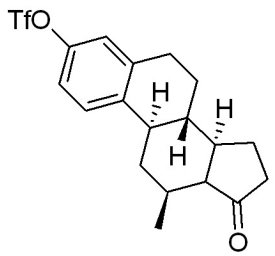
2o

^{19}F NMR (376 MHz, $CDCl_3$)



2p

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

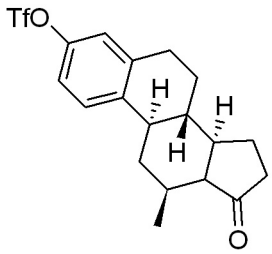


2p

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

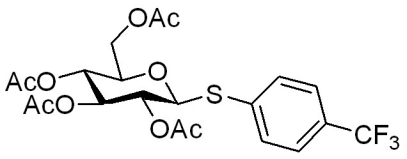
147.59
140.28
139.31
127.23
121.28
120.34
118.34
50.36
47.89
44.10
37.74
35.84
31.47
29.42
26.11
25.69
21.59
13.82

f1 (ppm)



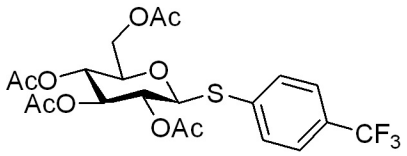
2p

^{19}F NMR (376 MHz, $CDCl_3$)



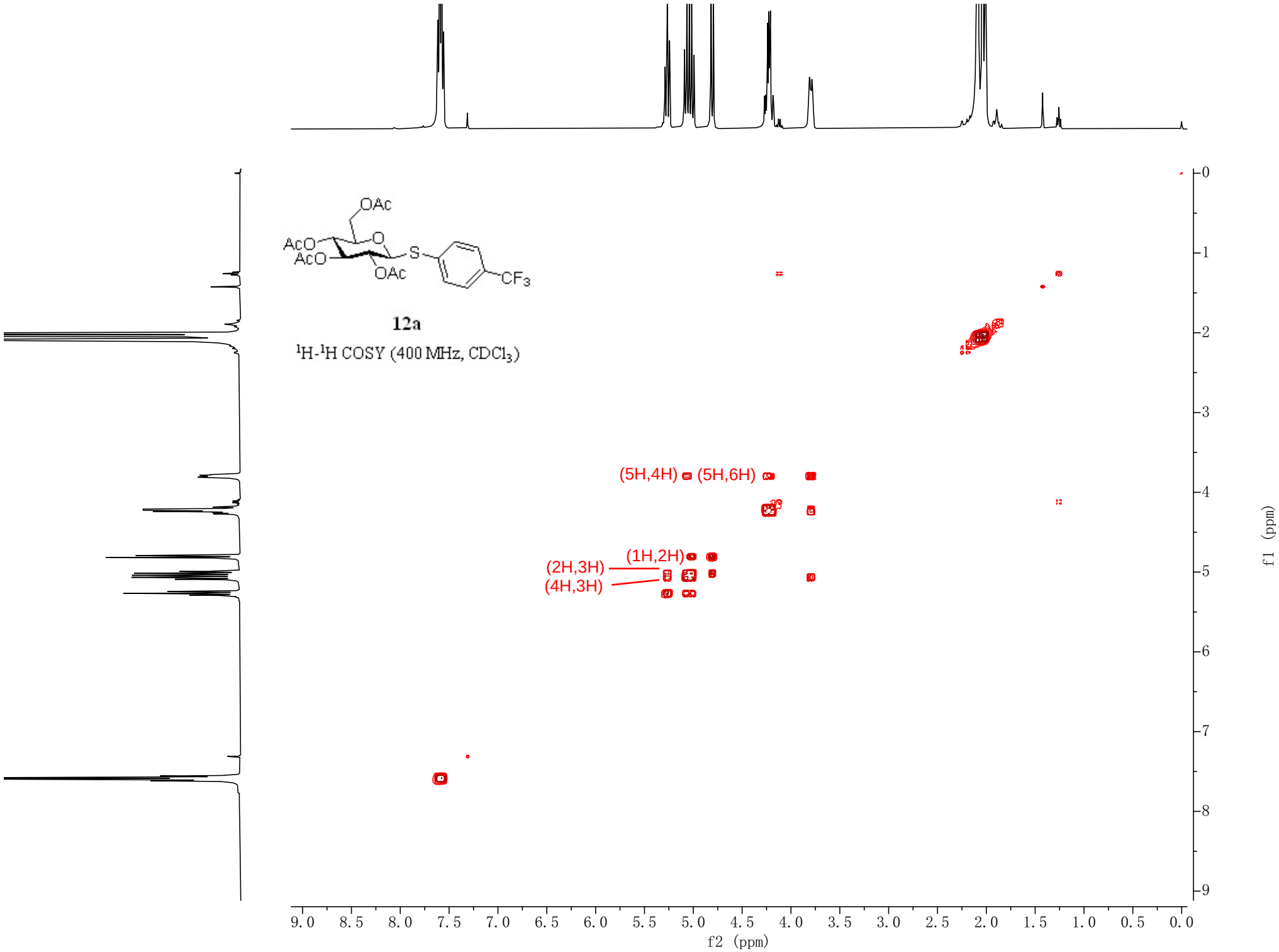
12a

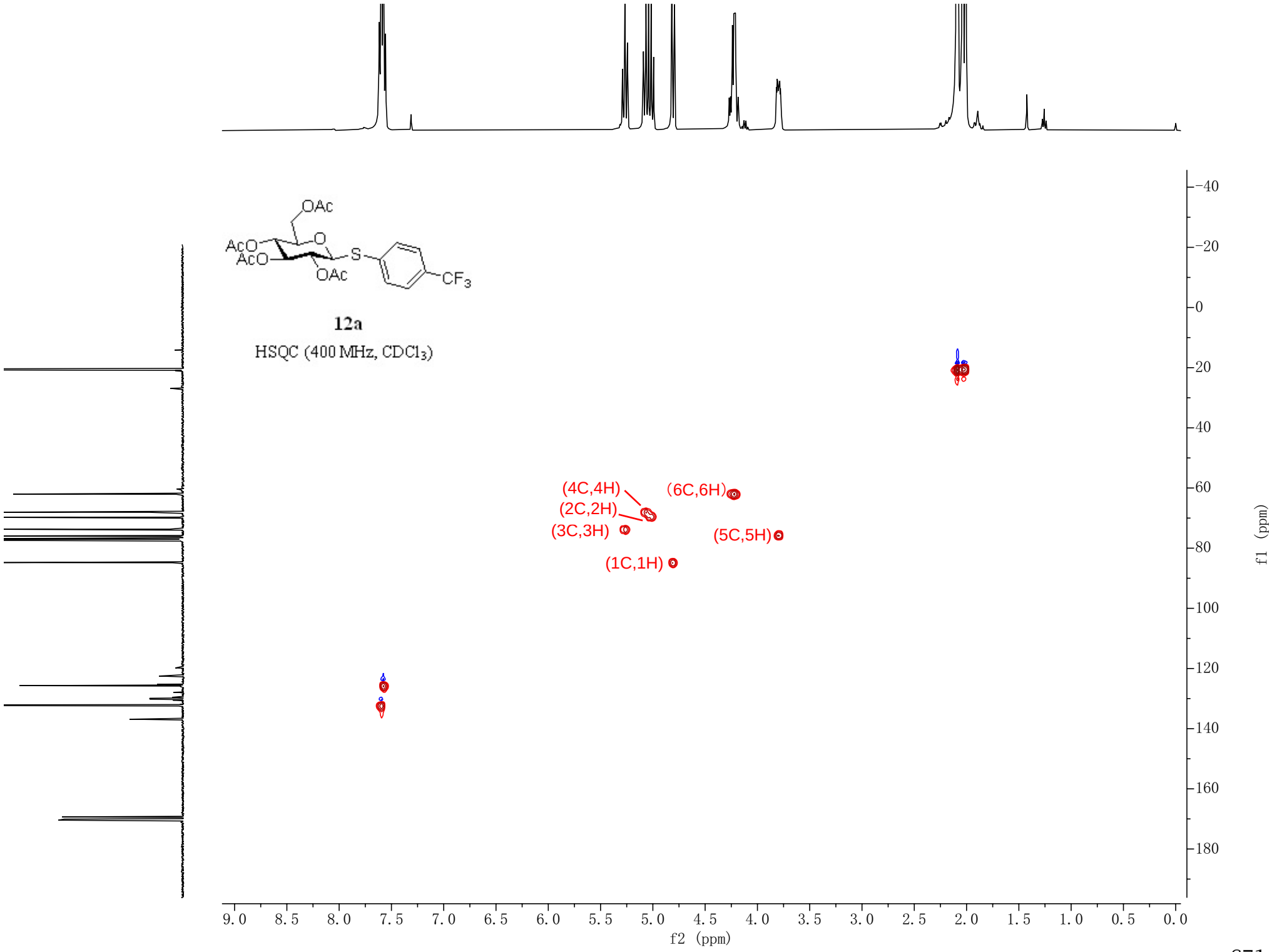
^{1}H NMR (400 MHz, $CDCl_3$)

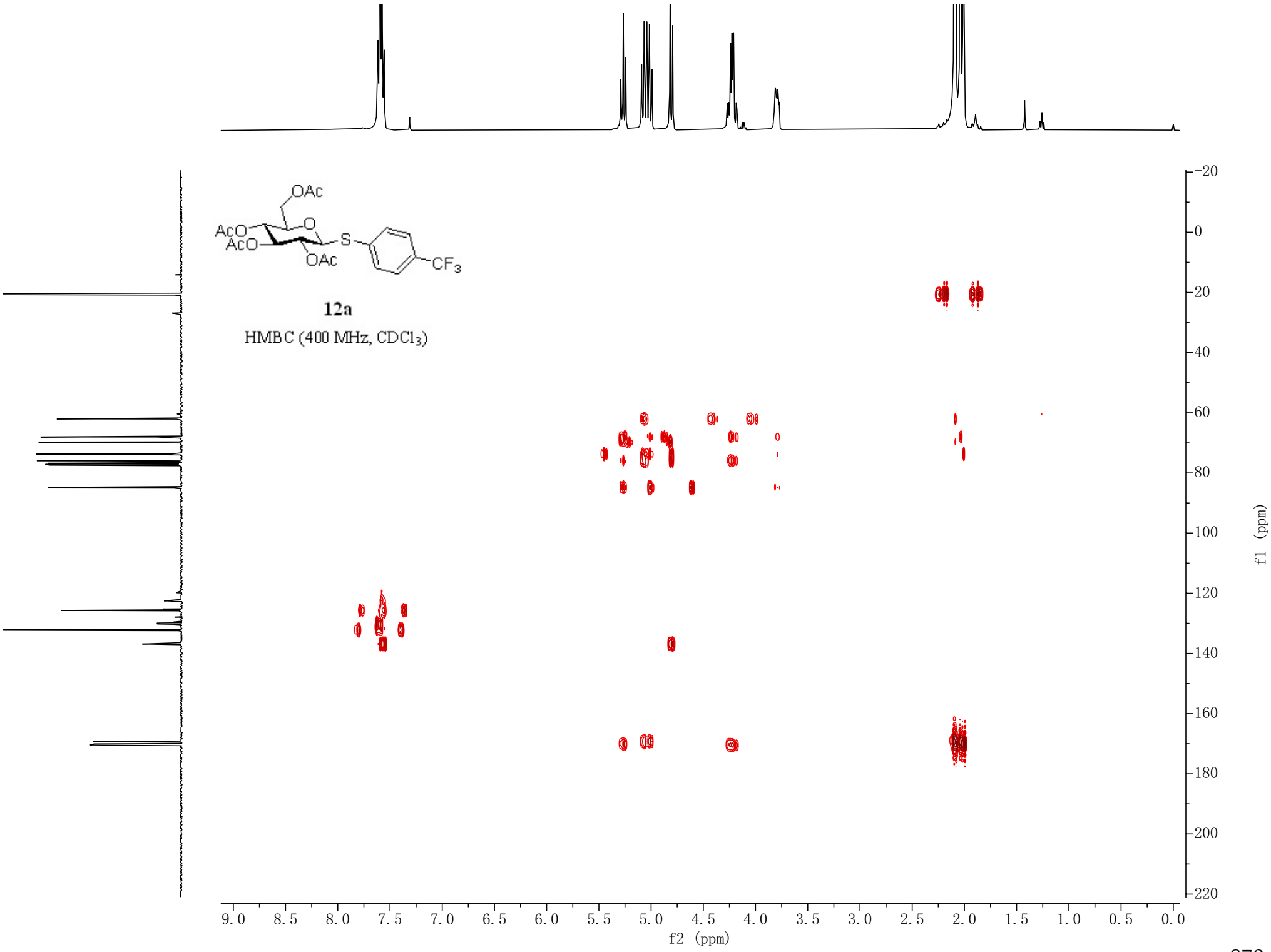


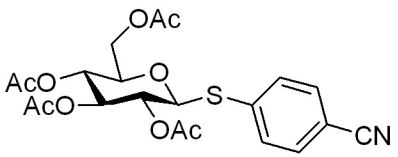
12a

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)


OAc
AcO
AcO
O
S
OAc
CF3
12a
1H-1H COSY (400 MHz, CDCl3)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)

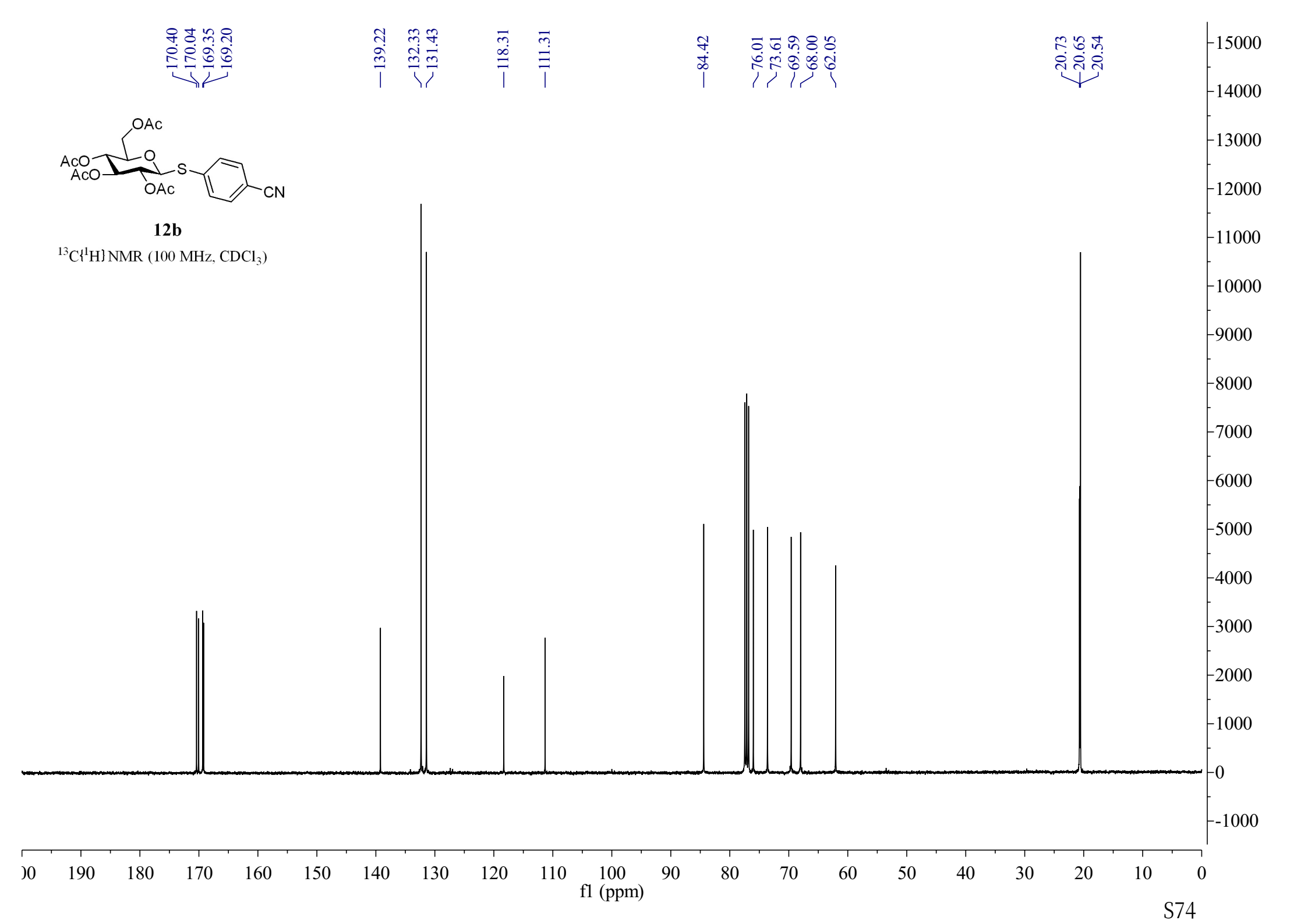

OAc
AcO
AcO
O
S
OAc
CF3
12a
HSQC (400 MHz, CDCl3)
(4C,4H)
(2C,2H)
(3C,3H)
(6C,6H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)

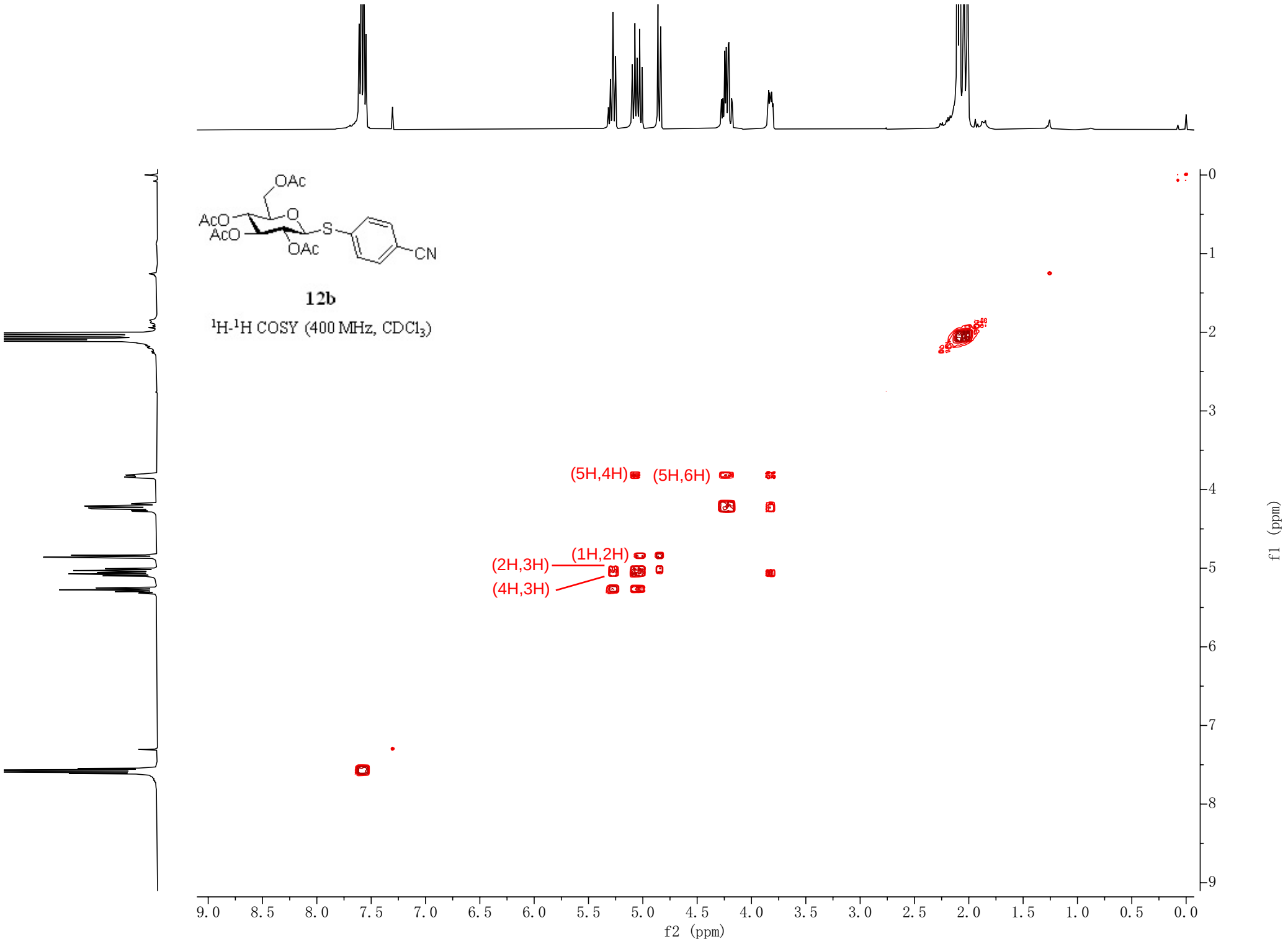

OAc
AcO
AcO
O
S
OAc
CF3
12a
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

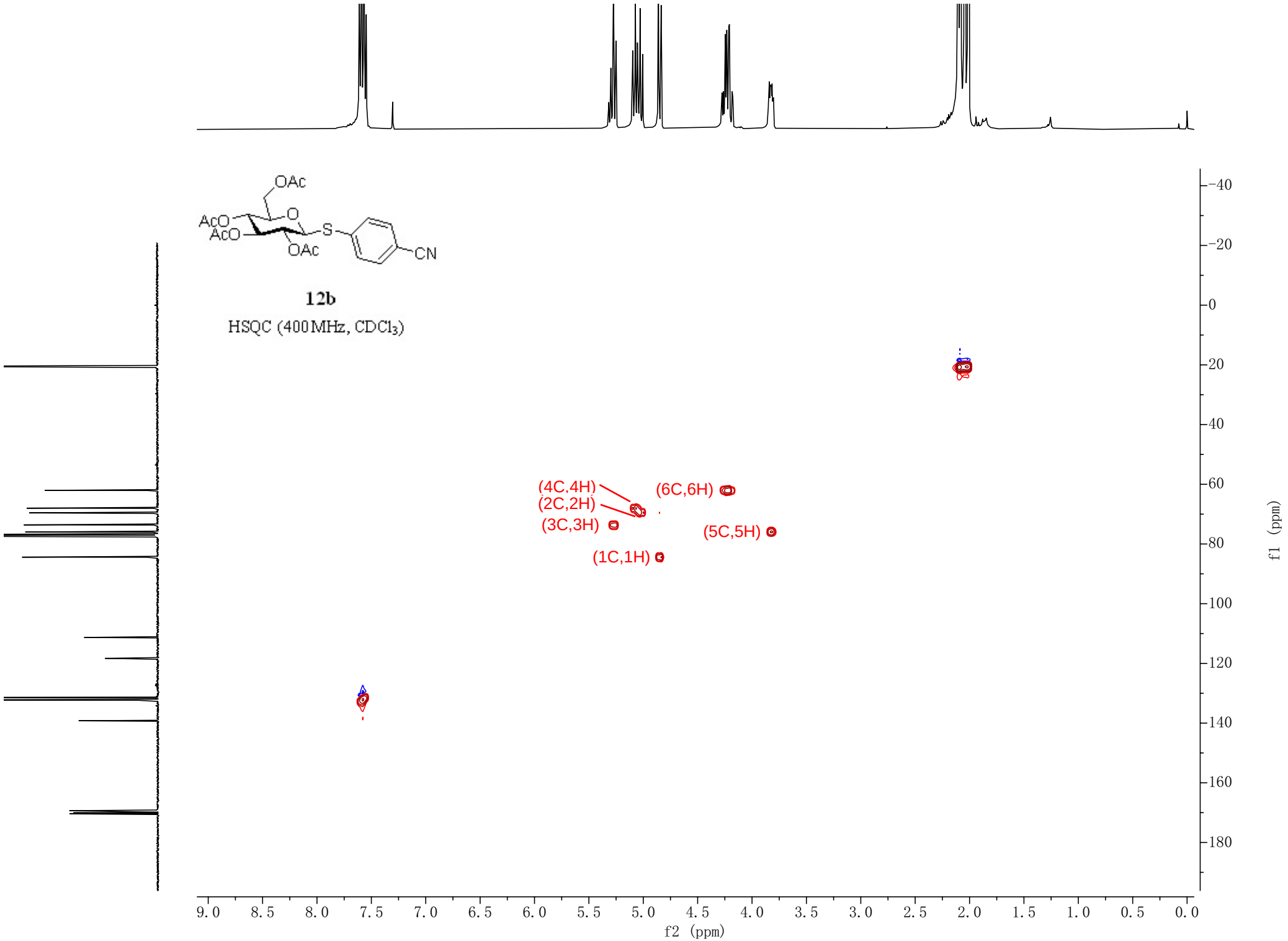


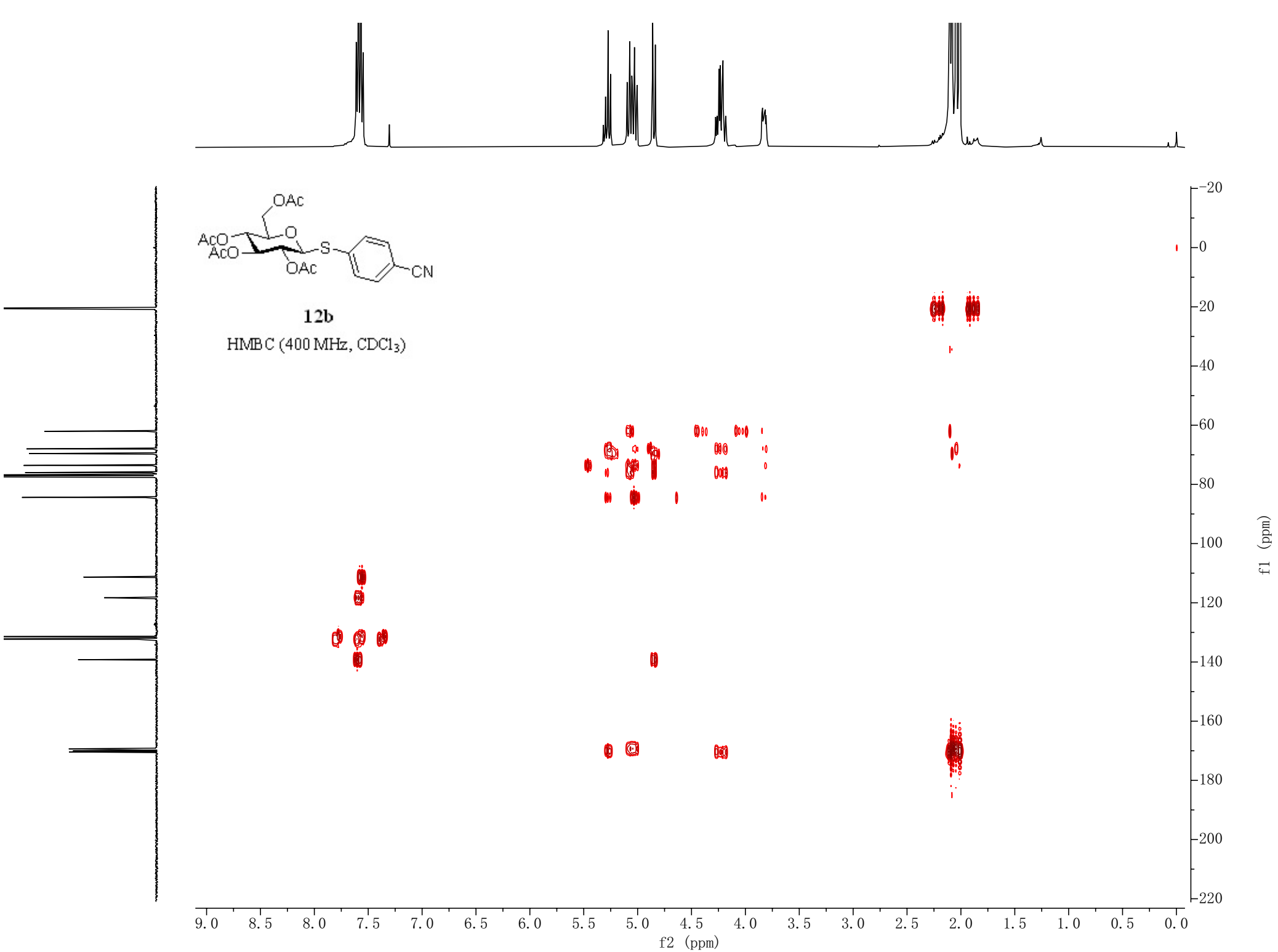
12b

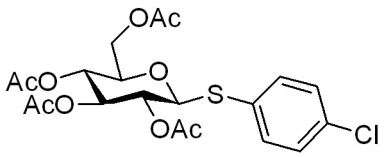
^{1}H NMR (400 MHz, $CDCl_3$)


170.40
170.04
169.35
169.20
139.22
132.33
131.43
118.31
111.31
84.42
76.01
73.61
69.59
68.00
62.05
20.73
20.65
20.54
OAc
AcO
AcO
OAc
O
S
CN
12b
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)
fl (ppm)


OAc
AcO
AcO
O
S
OAc
CN
12b
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f2 (ppm)
f1 (ppm)

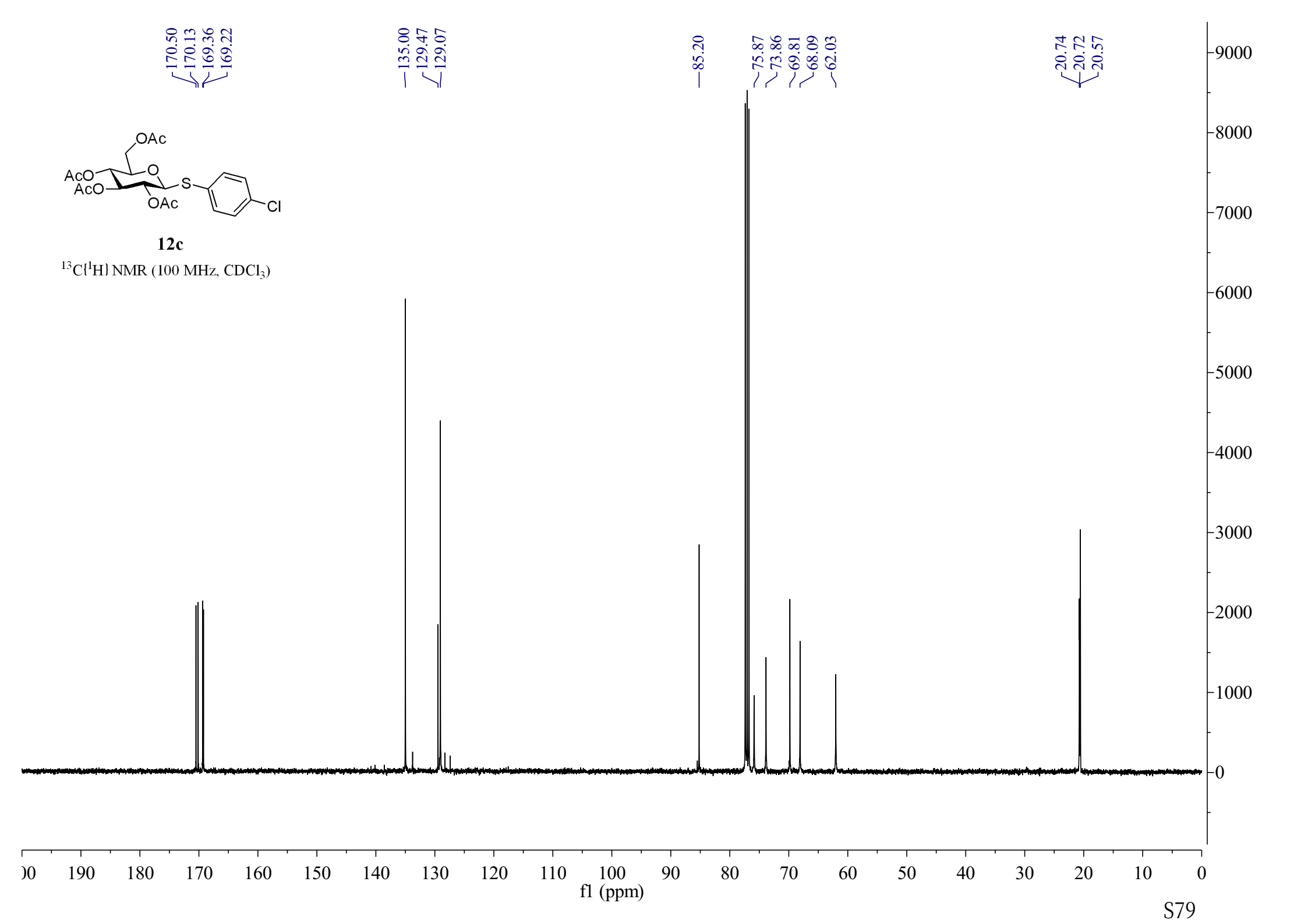

OAc
AcO
AcO
O
S
OAc
CN
12b
HSQC (400MHz, CDCl3)
(4C,4H)
(2C,2H)
(3C,3H)
(6C,6H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)

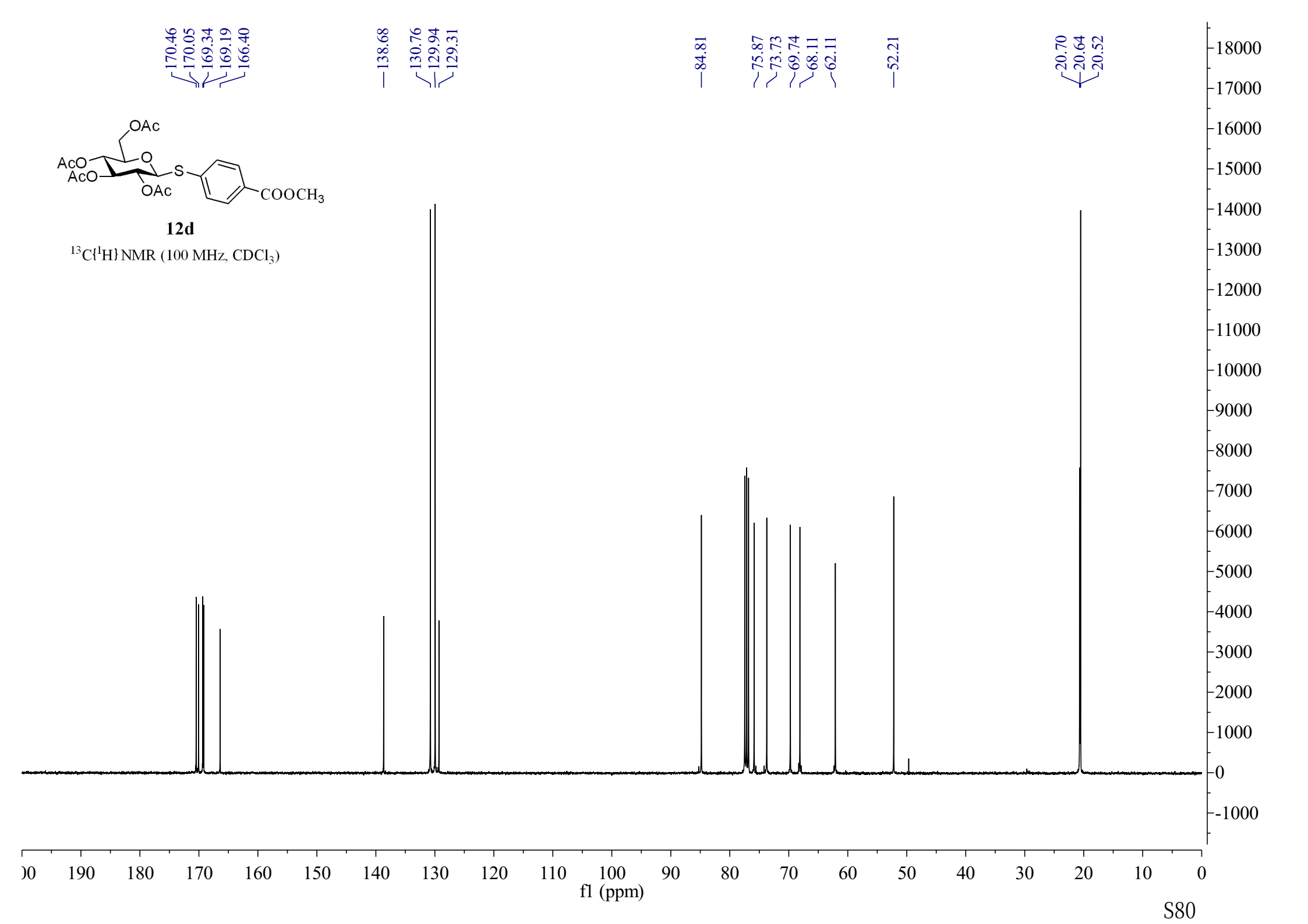

OAc
AcO
AcO
O
S
OAc
CN
12b
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

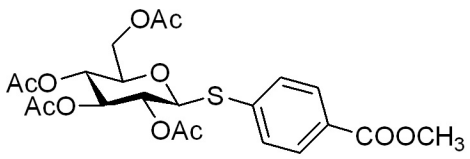


12c

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

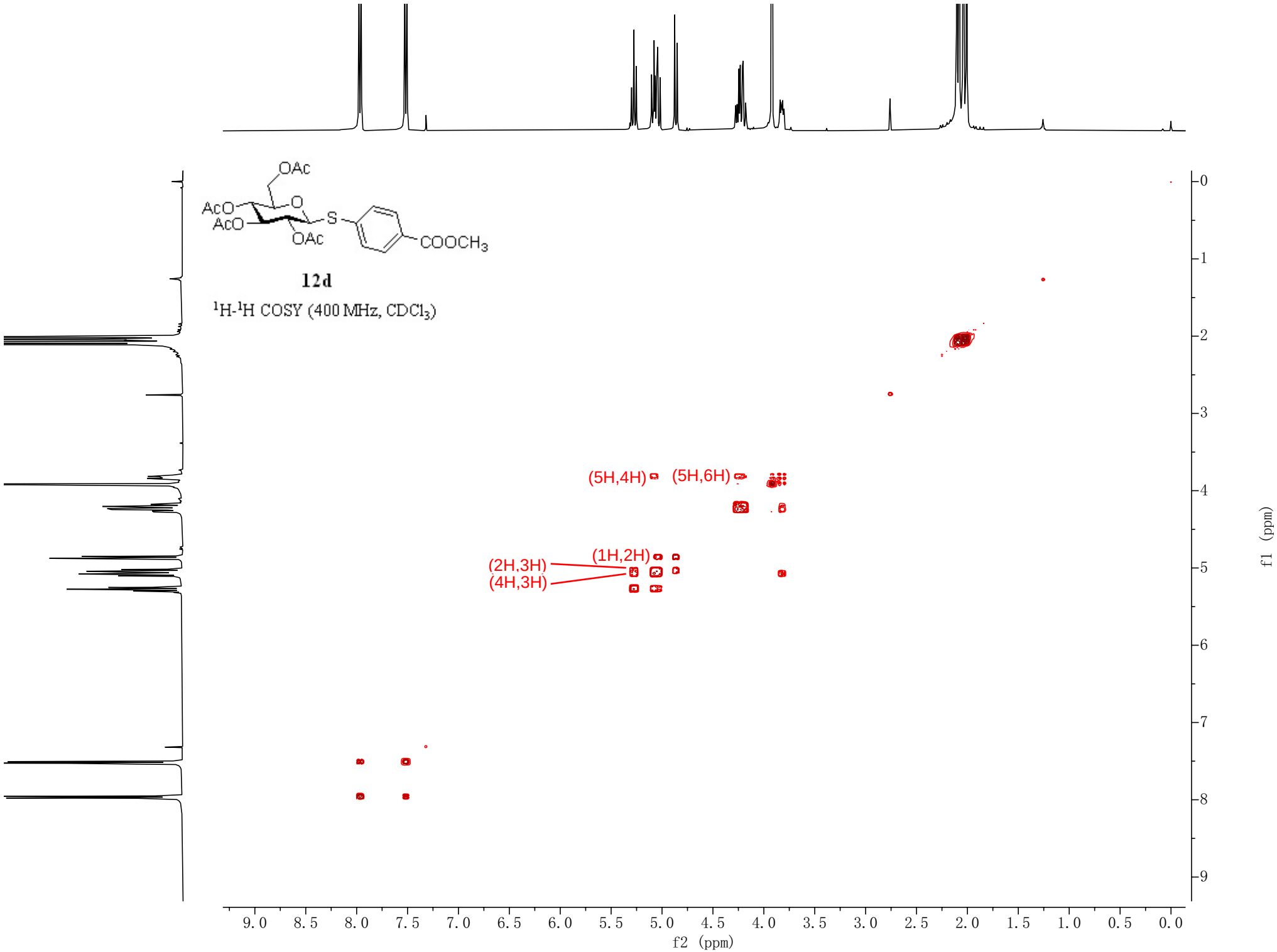

170.50
170.13
169.36
169.22
135.00
129.47
129.07
85.20
75.87
73.86
69.81
68.09
62.03
20.74
20.72
20.57
OAc
AcO
AcO
OAc
O
S
Cl
12c
13C{1H} NMR (100 MHz, CDCl3)
fl (ppm)

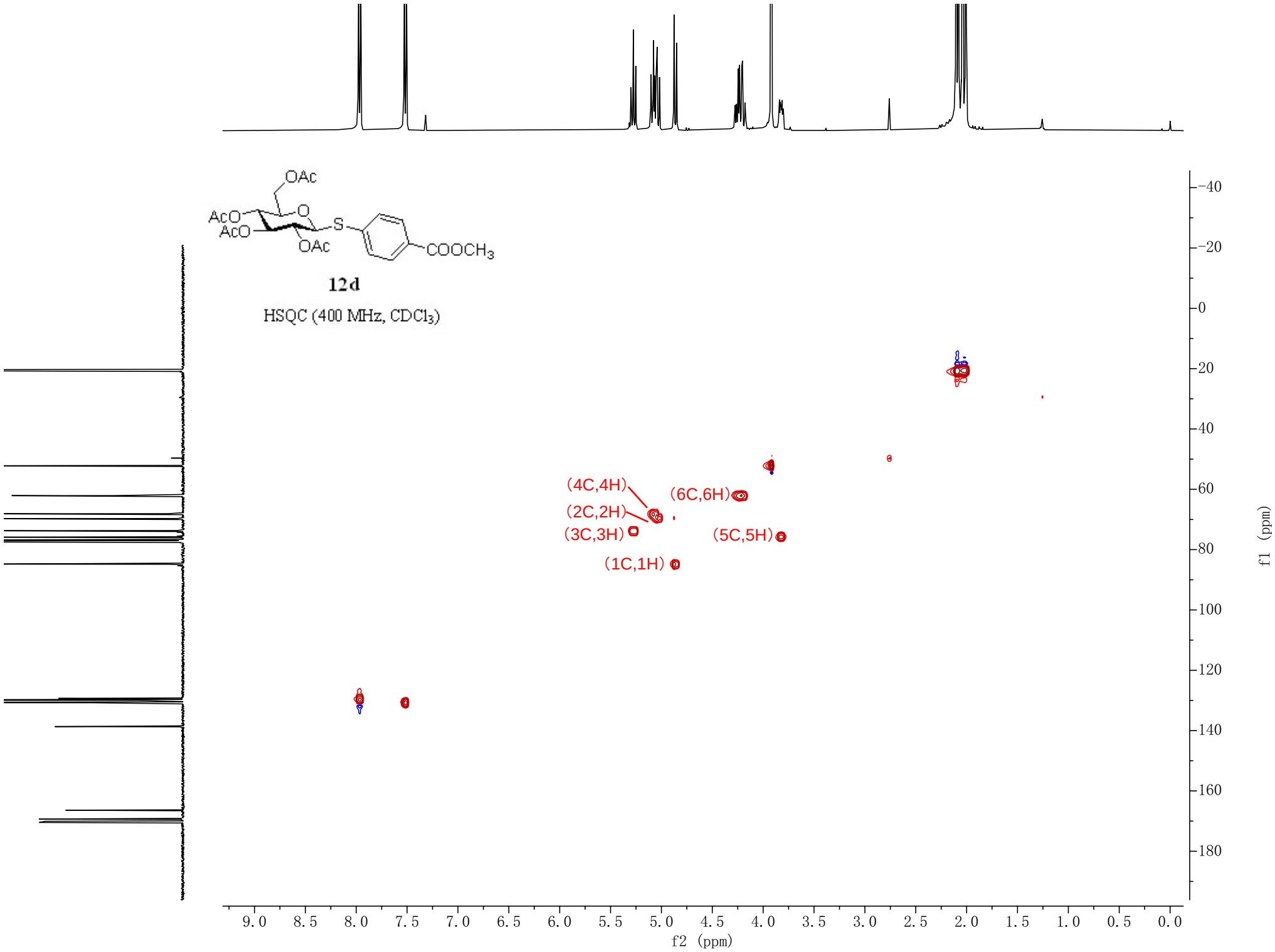

170.46
170.05
169.34
169.19
166.40
138.68
130.76
129.94
129.31
84.81
75.87
73.73
69.74
68.11
62.11
52.21
20.70
20.64
20.52
OAc
AcO
AcO
OAc
O
S
COOCH3
12d
13C{1H} NMR (100 MHz, CDCl3)
fl (ppm)

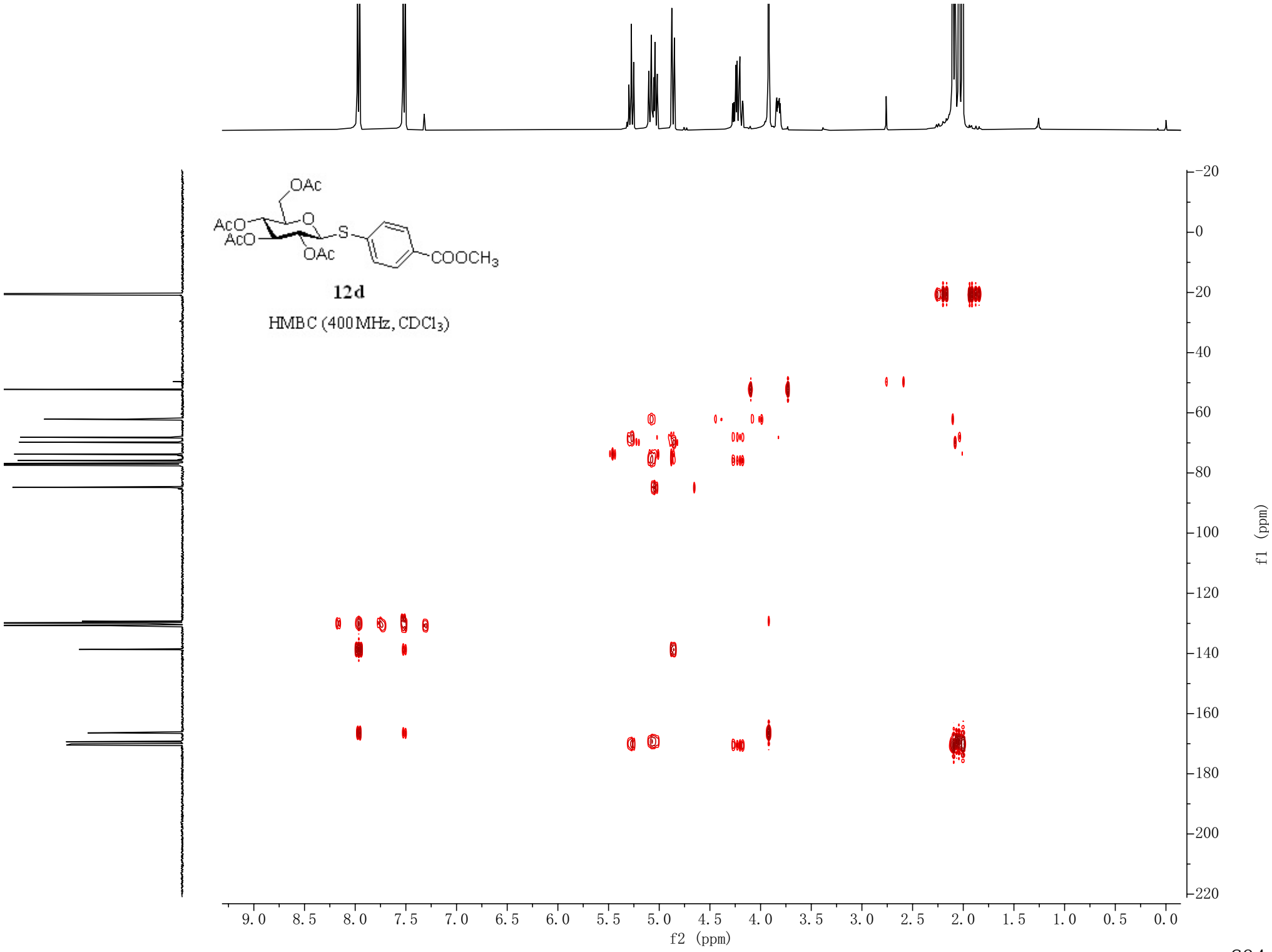


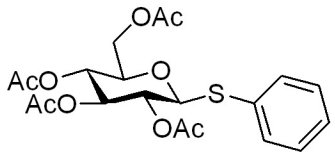
12d

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


OAc
AcO
AcO
O
S
OAc
COOCH3
12d
1H-1H COSY (400 MHz, CDCl3)
(5H,4H)
(5H,6H)
(1H,2H)
(2H.3H)
(4H,3H)
f1 (ppm)
f2 (ppm)

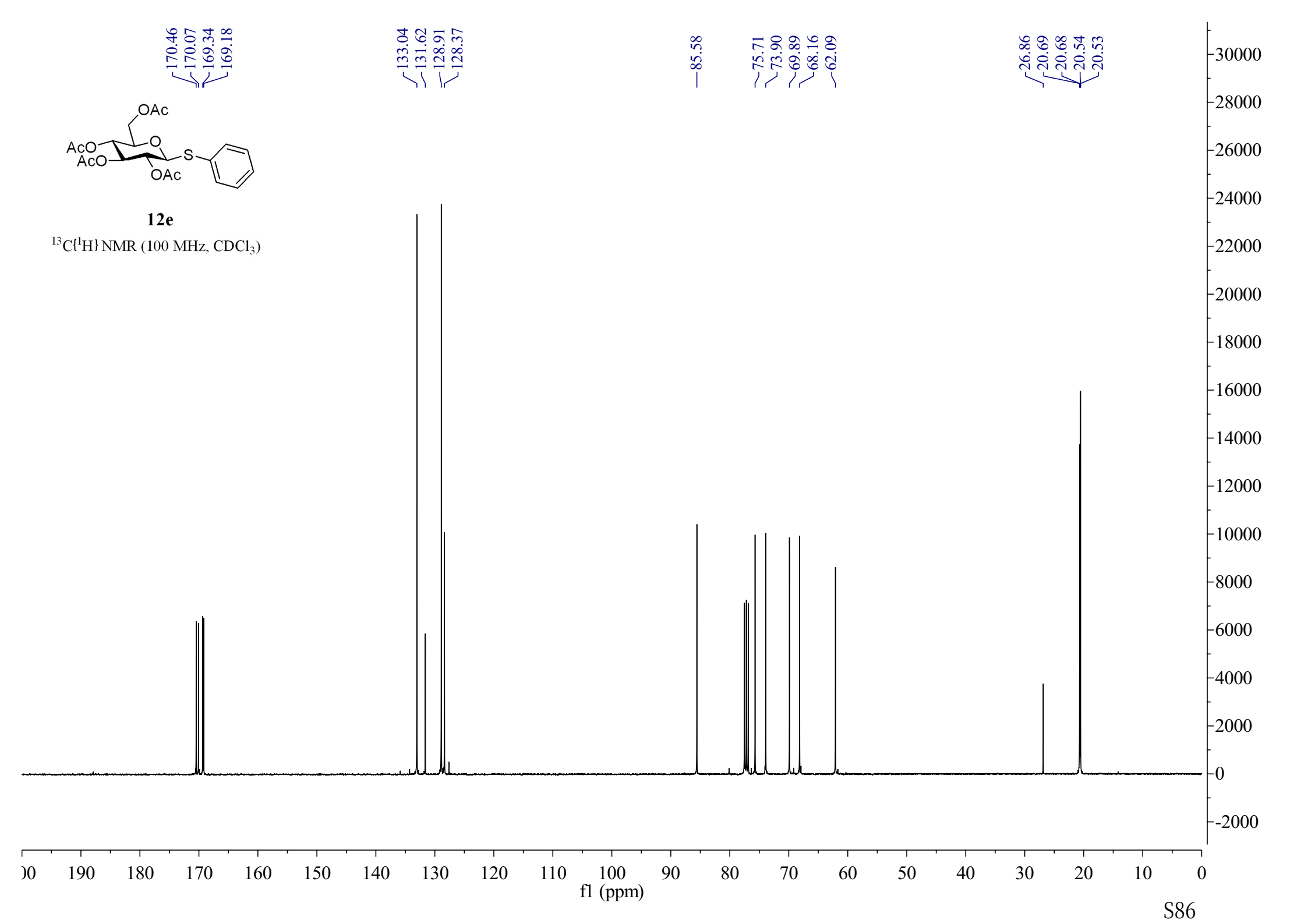

OAc
AcO
AcO
O
S
OAc
COOCH3
12d
HSQC (400 MHz, CDCl3)
(4C,4H)
(6C,6H)
(2C,2H)
(3C,3H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)

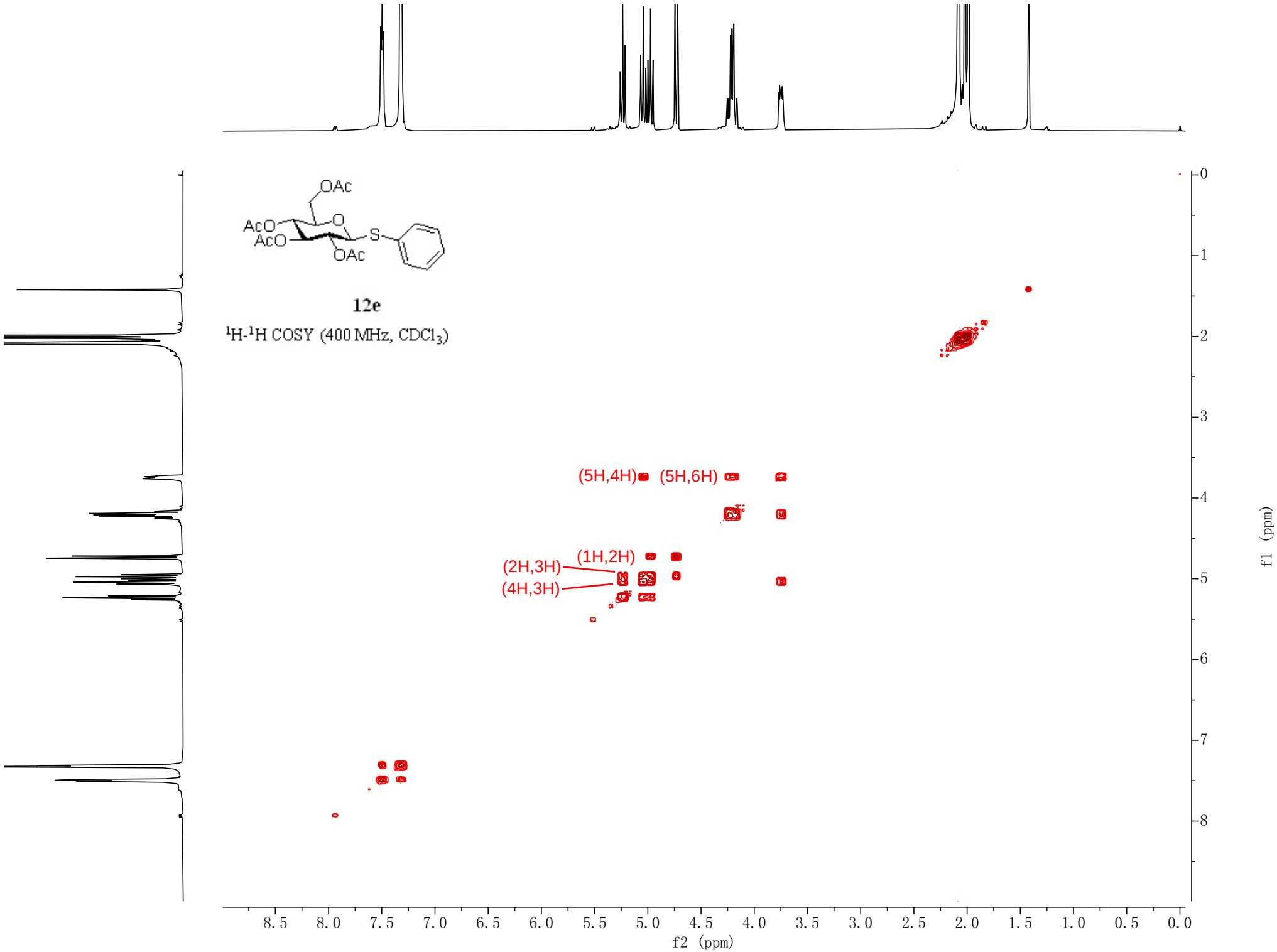

OAc
AcO
AcO
O
S
OAc
COOCH3
12d
HMBC (400MHz, CDCl3)
f2 (ppm)
f1 (ppm)

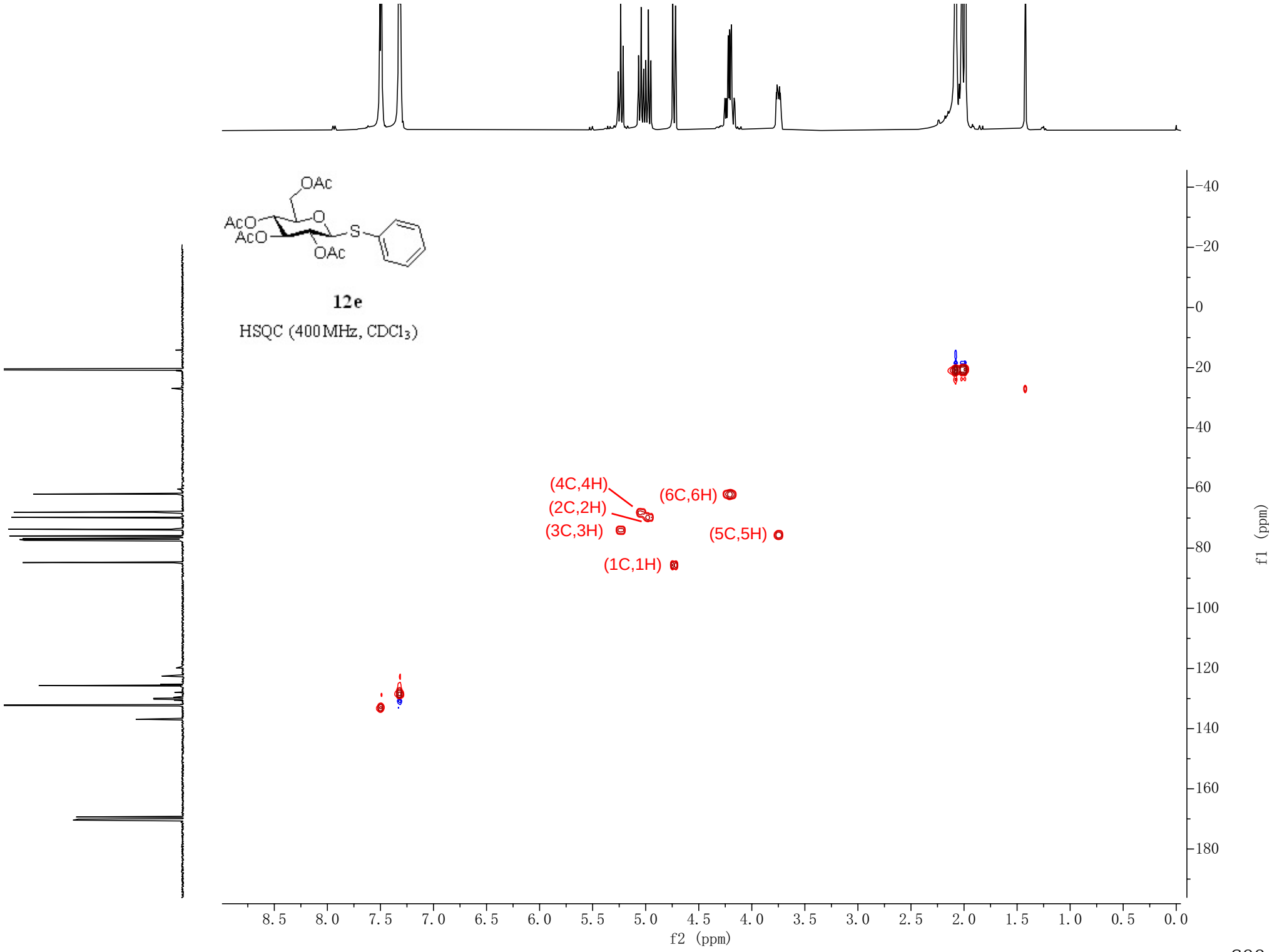


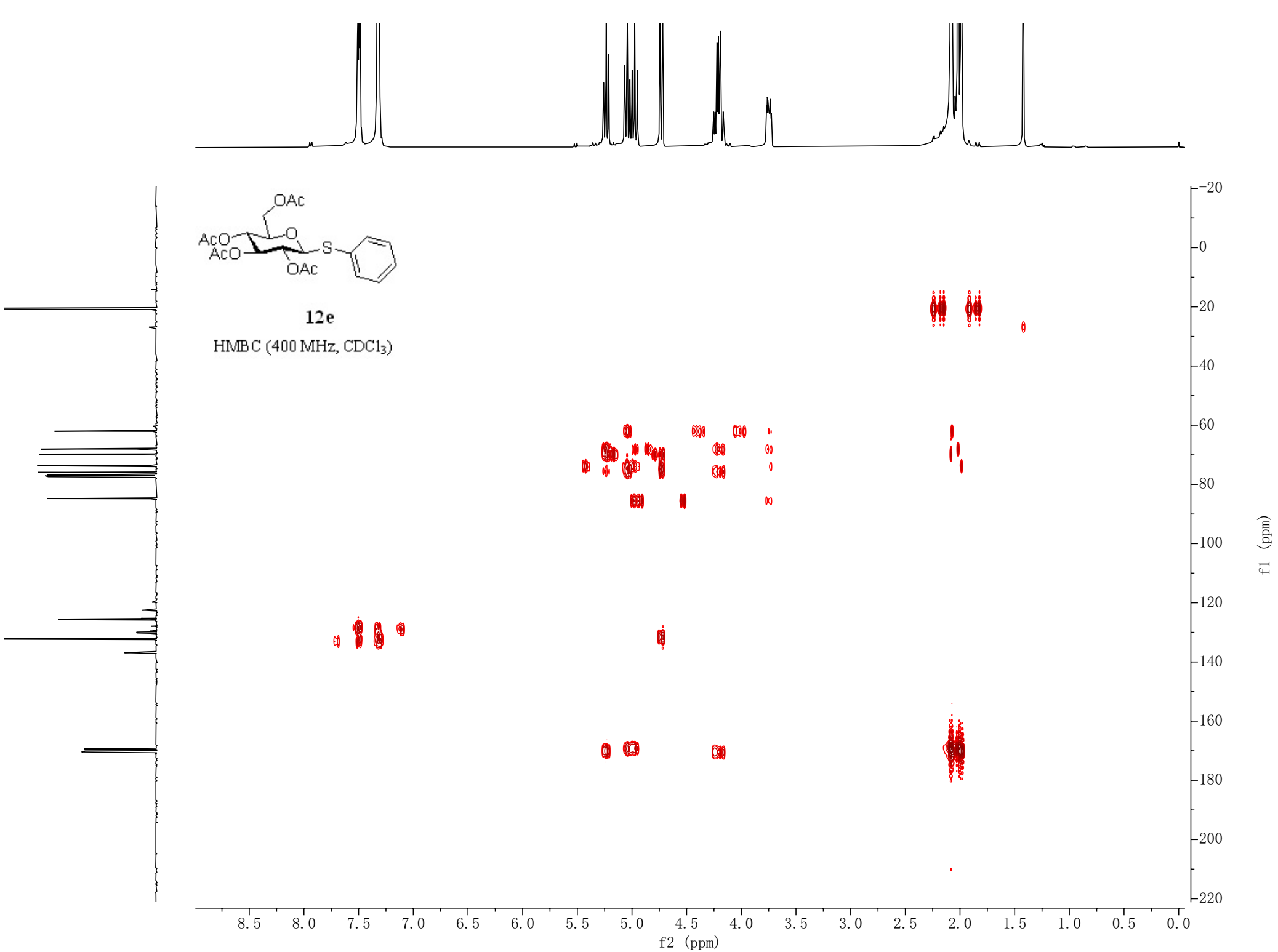
12e

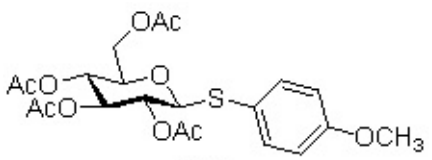
^{1}H NMR (400 MHz, $CDCl_3$)


170.46
170.07
169.34
169.18
133.04
131.62
128.91
128.37
85.58
75.71
73.90
69.89
68.16
62.09
26.86
20.69
20.68
20.54
20.53
OAc
AcO
AcO
O
S
OAc
12e
13C{1H} NMR (100 MHz, CDCl3)
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
12e
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f2 (ppm)
f1 (ppm)

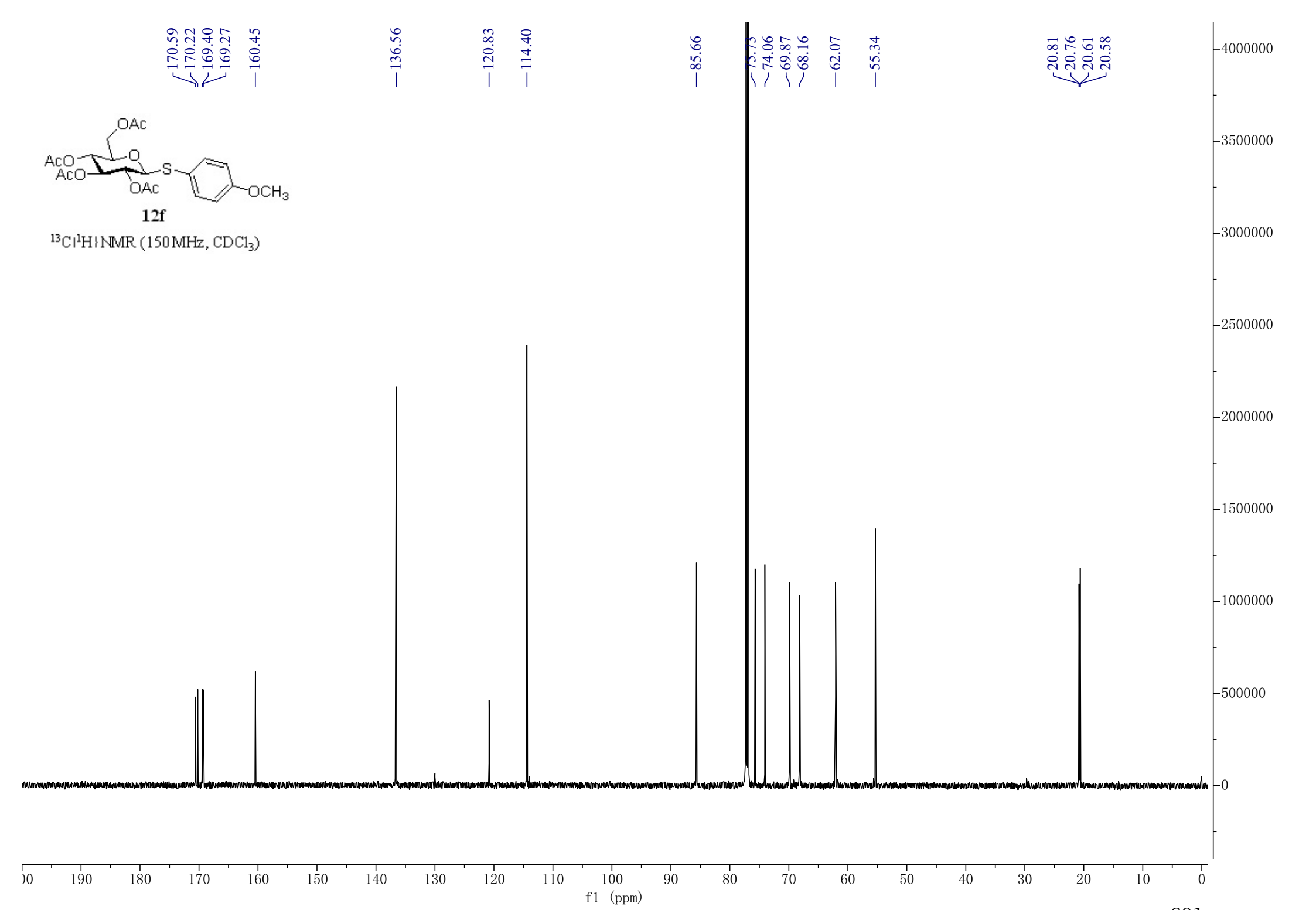

OAc
AcO
AcO
O
S
OAc
12e
HSQC (400 MHz, CDCl3)
(4C,4H)
(2C,2H)
(3C,3H)
(6C,6H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)

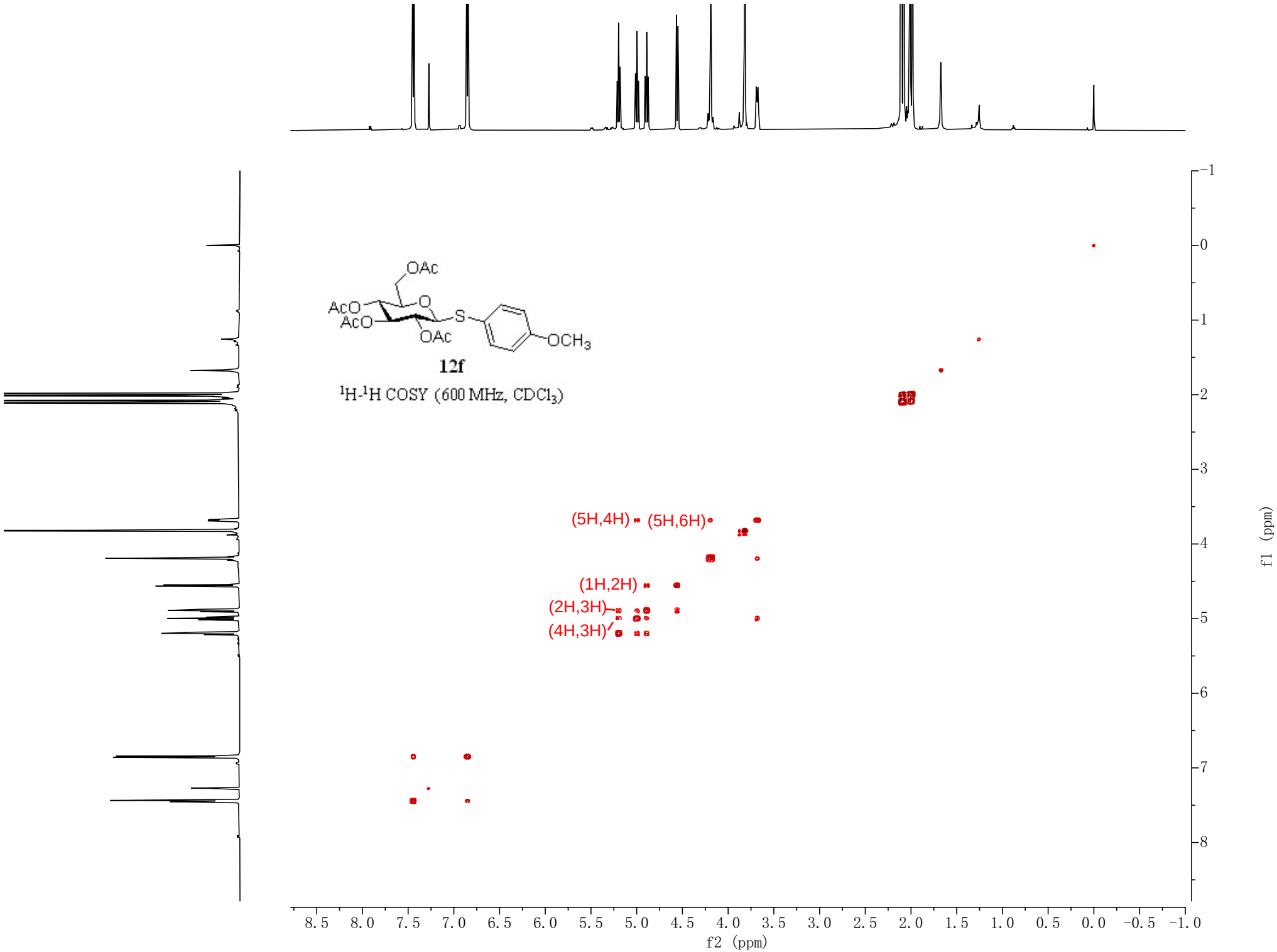

OAc
AcO
AcO
O
S
OAc
12e
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

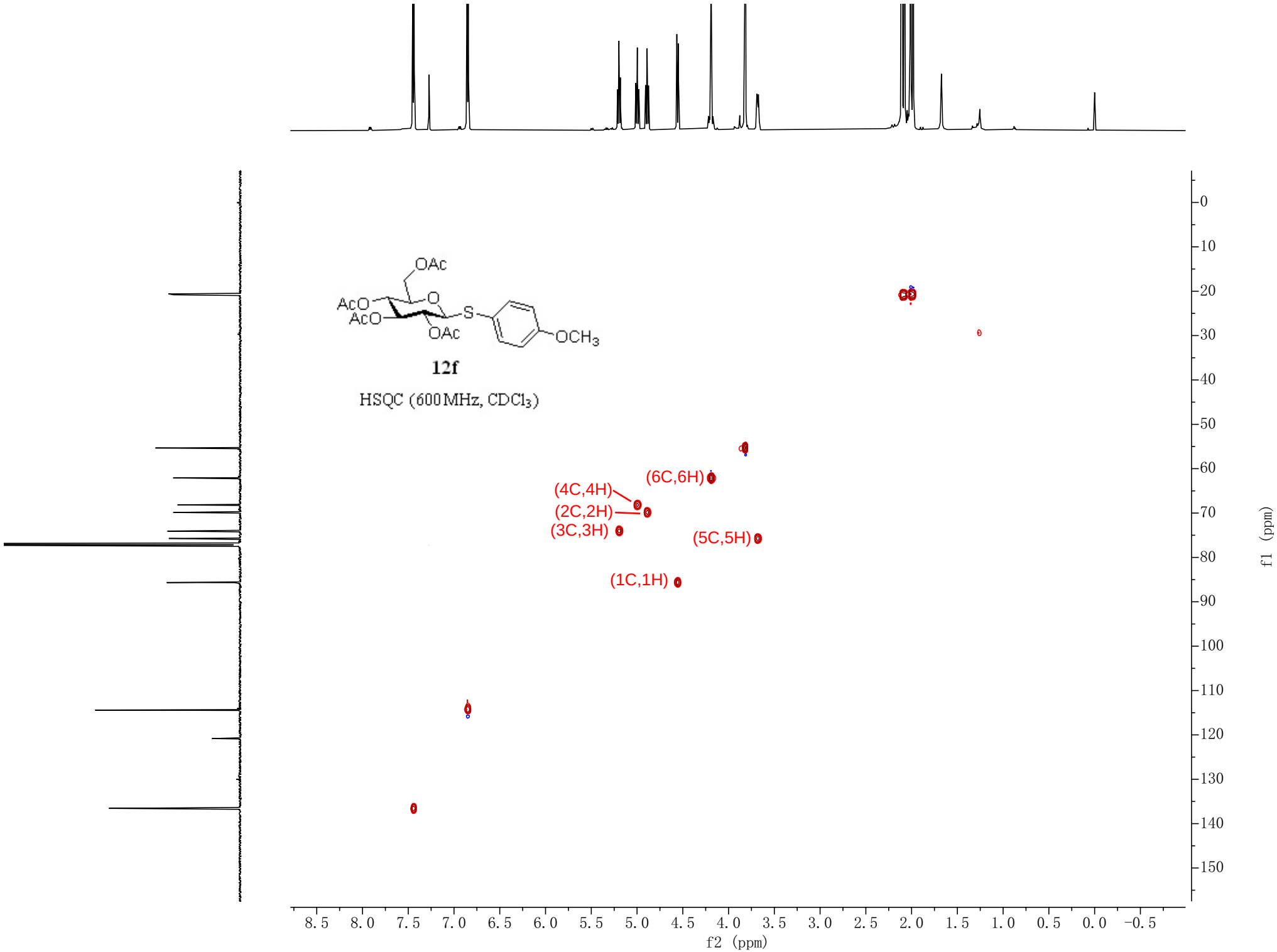


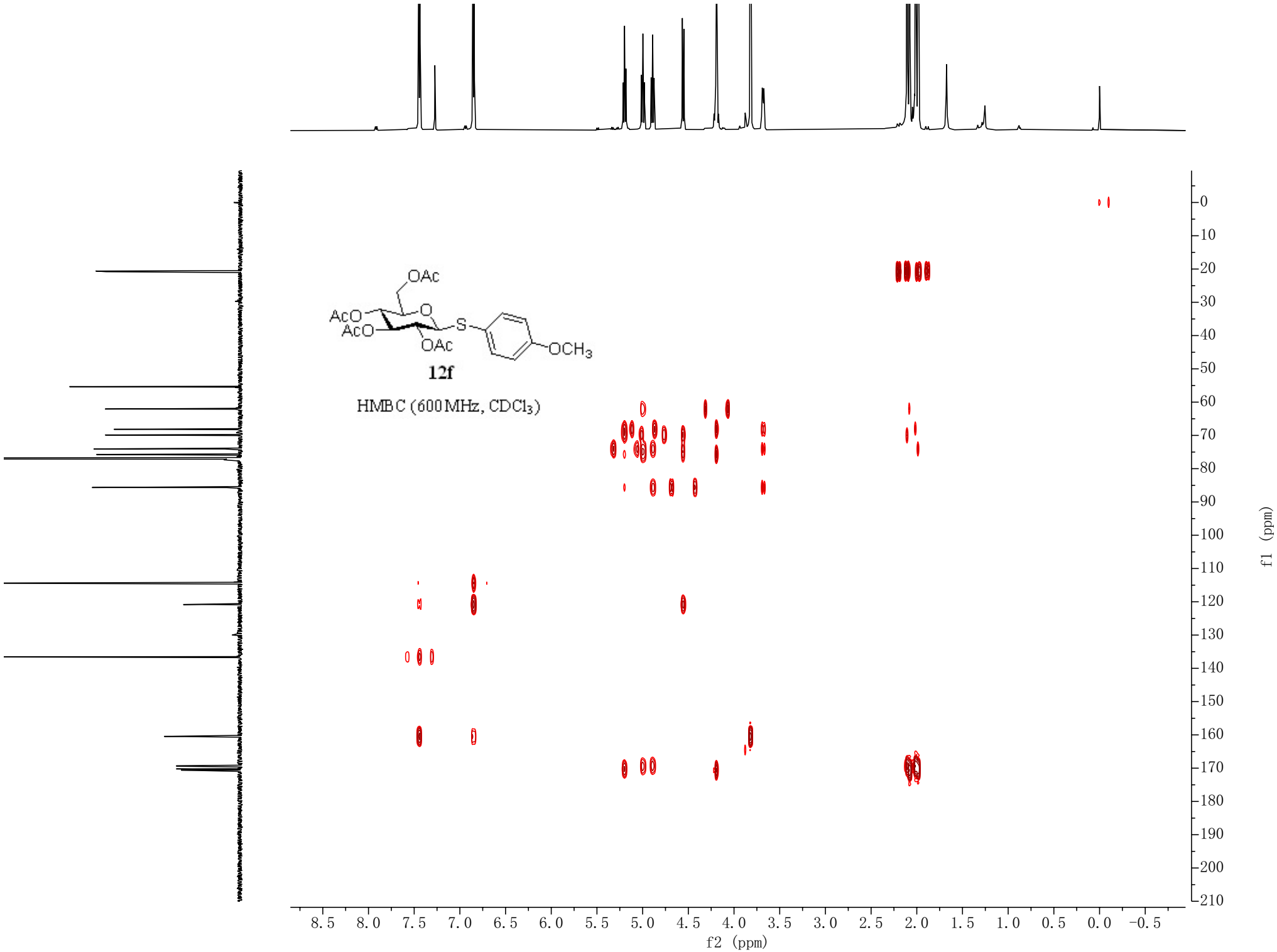
12f

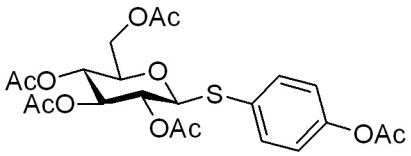
^{1}H NMR (600 MHz, $CDCl_3$)


170.59
170.22
169.40
169.27
160.45
136.56
120.83
114.40
85.66
75.73
74.06
69.87
68.16
62.07
55.34
20.81
20.76
20.61
20.58
OAc
AcO
AcO
O
S
OAc
OCH3
12f
13C{1H} NMR (150 MHz, CDCl3)
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
OCH3
12f
1H-1H COSY (600 MHz, CDCl3)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)

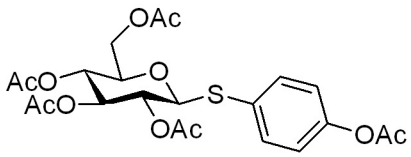

OAc
AcO
AcO
O
S
OAc
OCH3
12f
HSQC (600MHz, CDCl3)
(6C,6H)
(4C,4H)
(2C,2H)
(3C,3H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
OCH3
12f
HMBC (600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



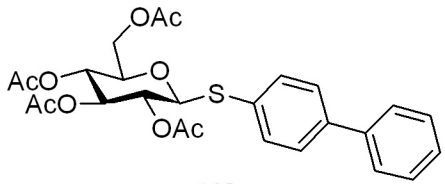
12g

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



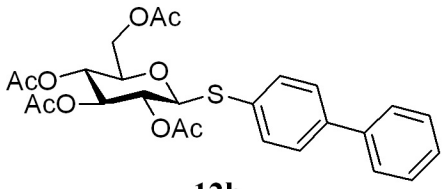
12g

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



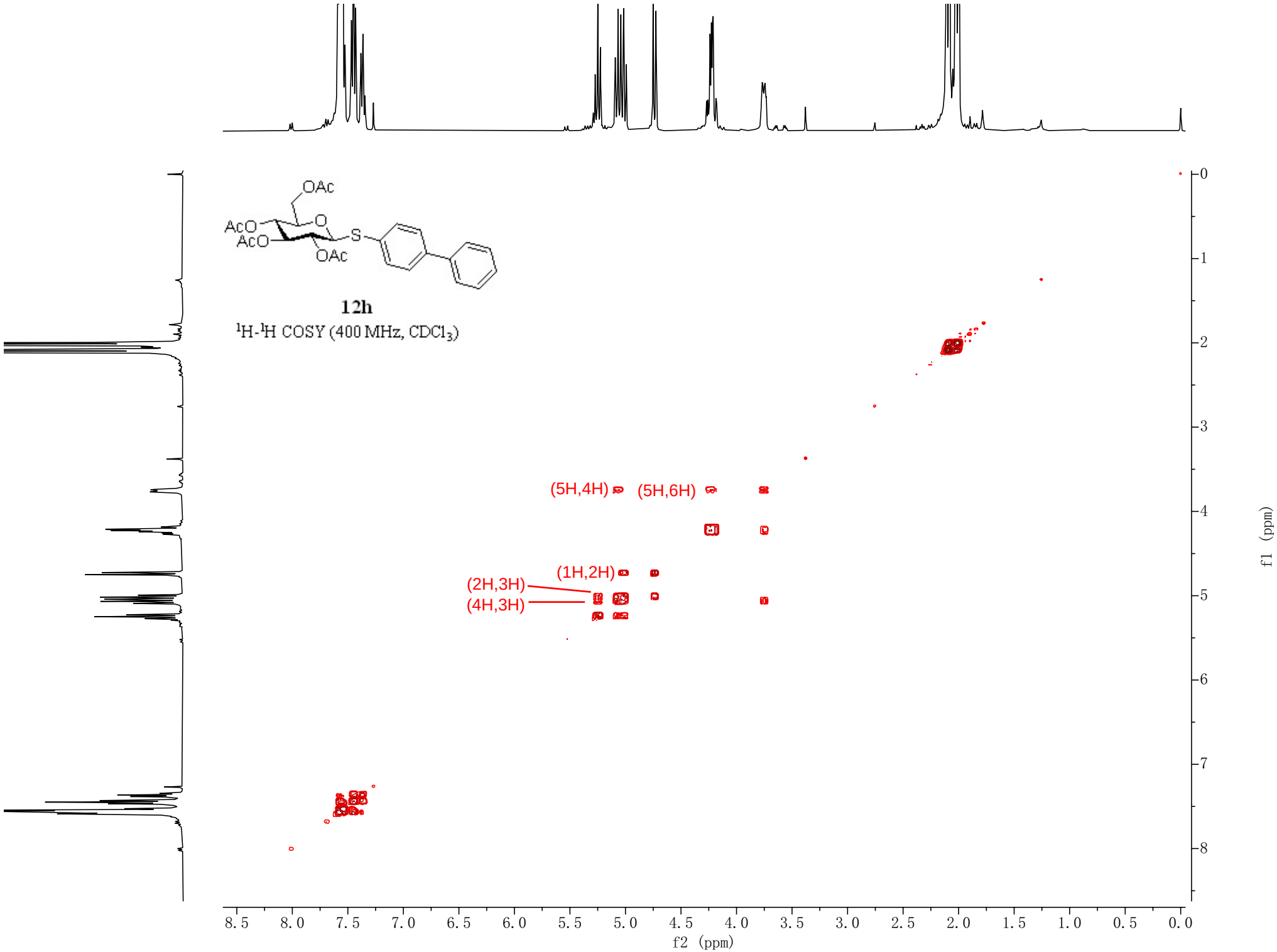
12h

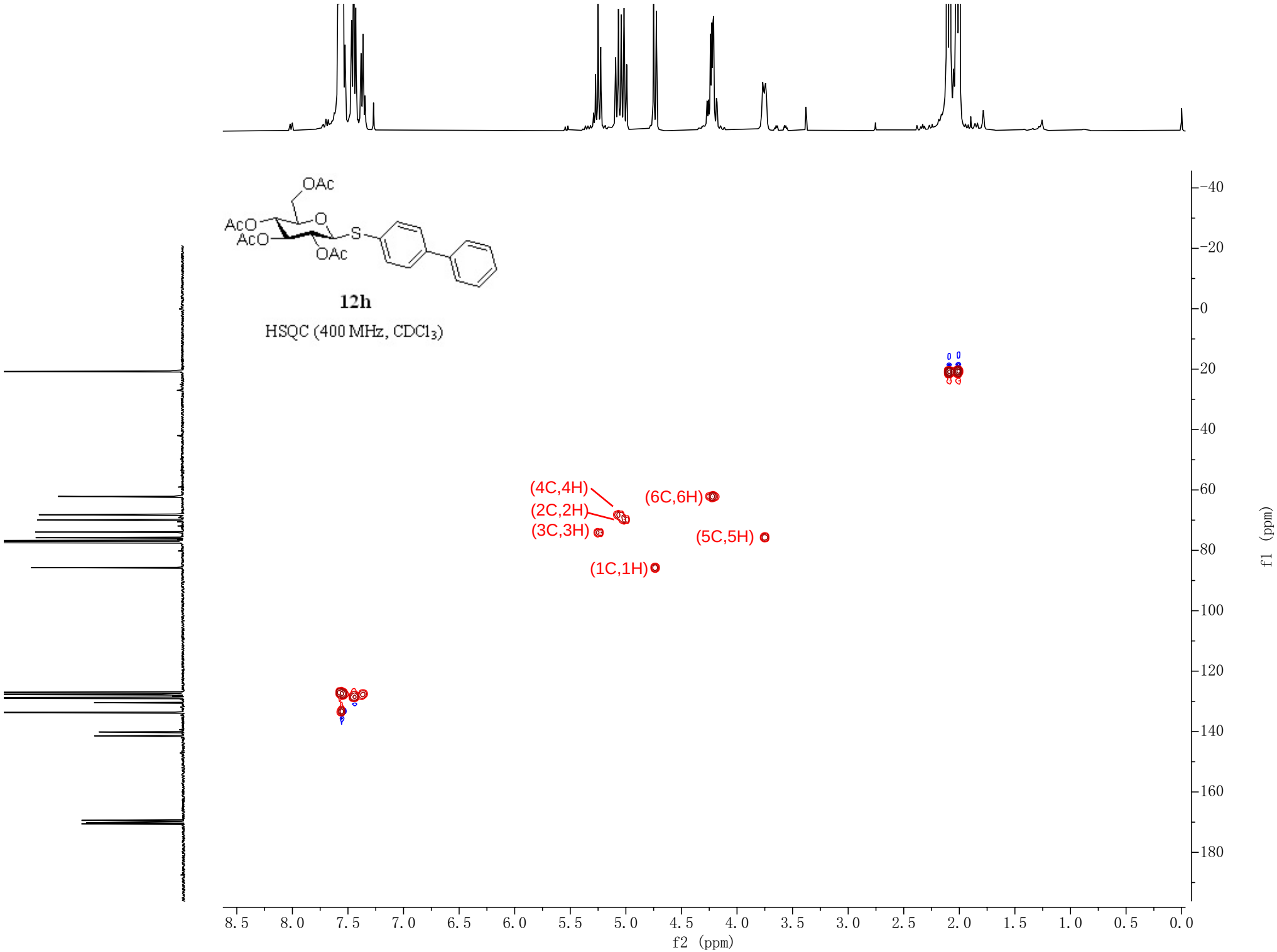
^{1}H NMR (400 MHz, $CDCl_3$)

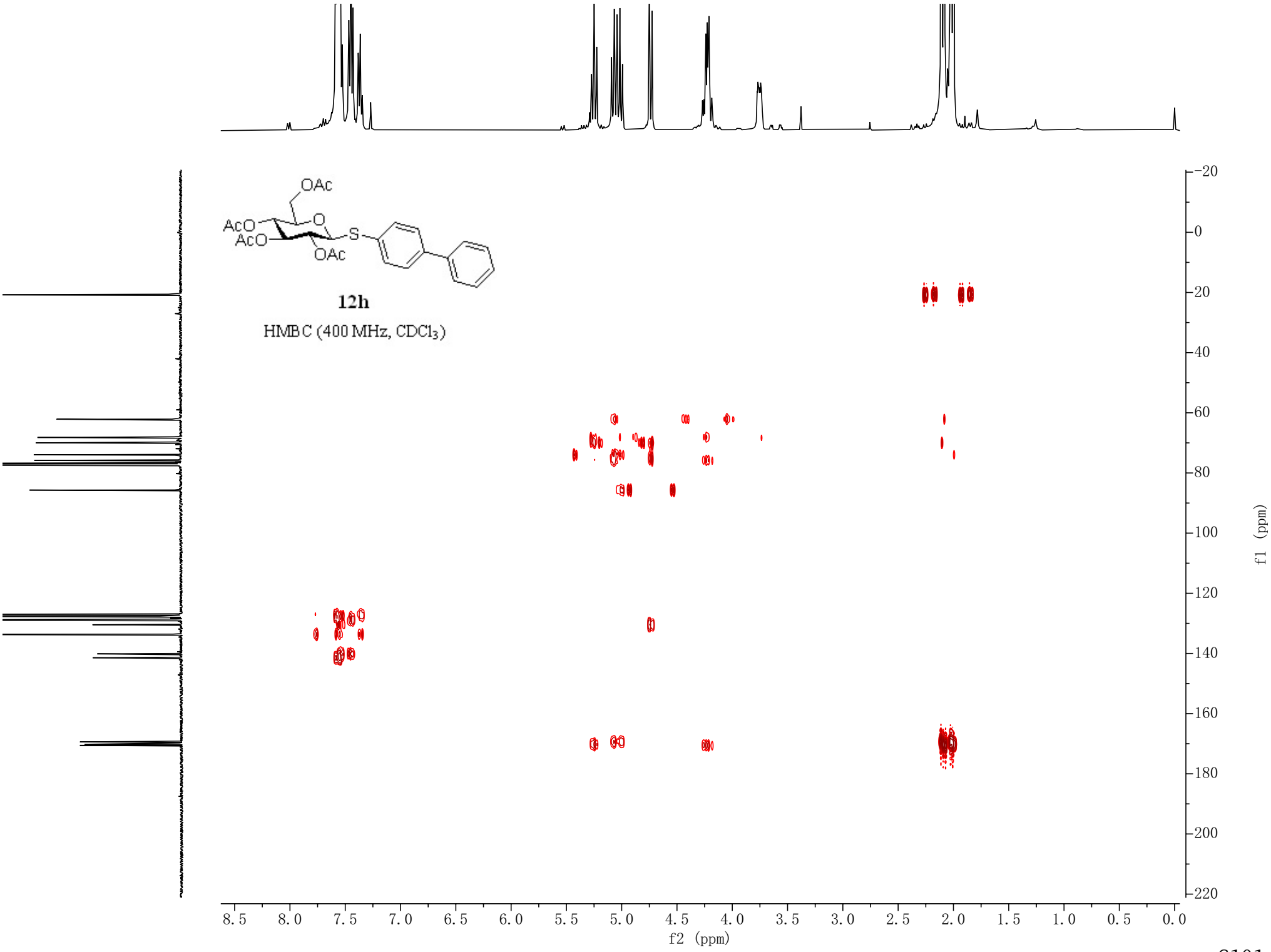


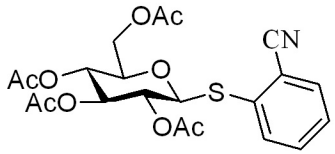
12h

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)


OAc
AcO
AcO
O
S
OAc
12h
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8

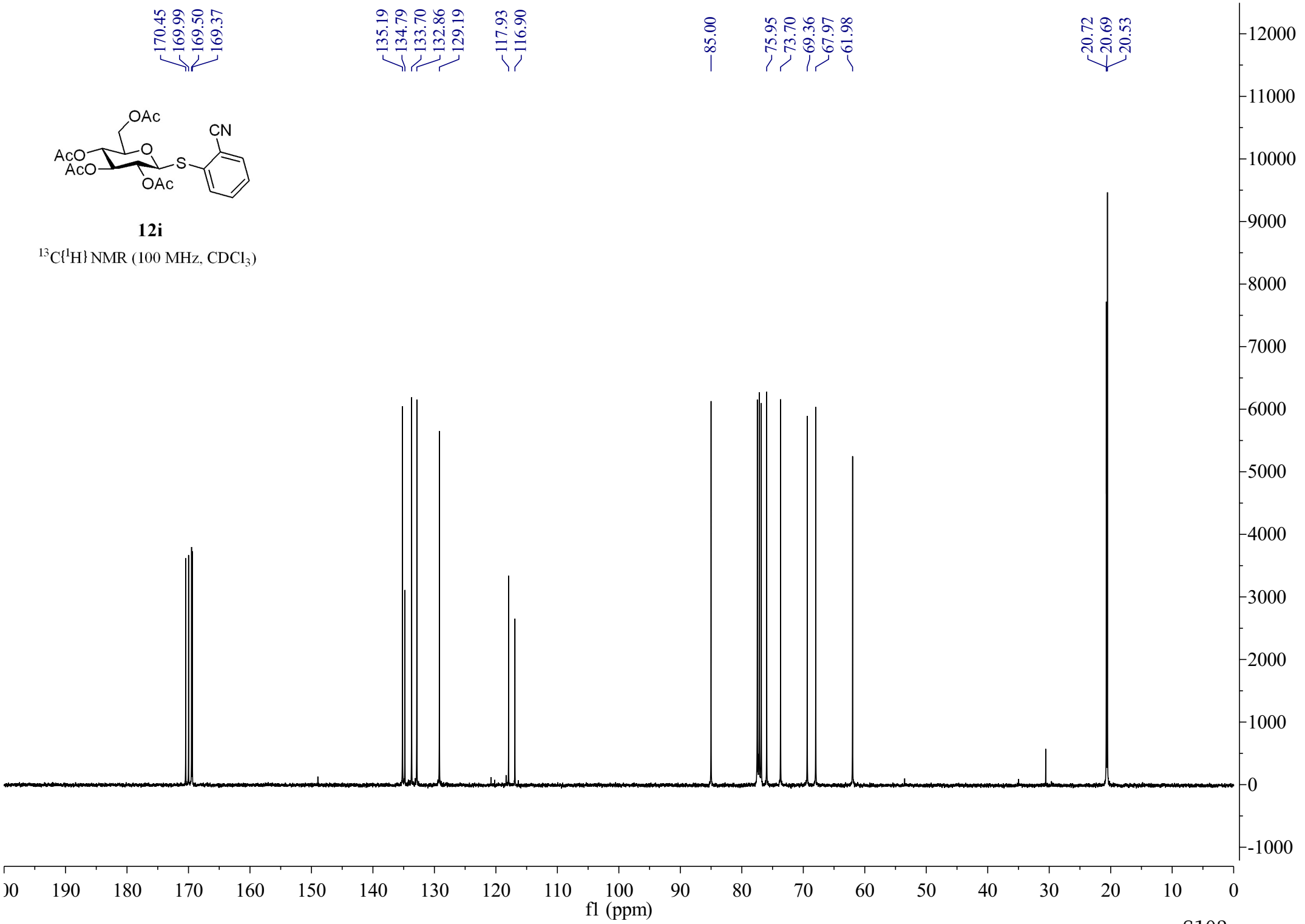

OAc
AcO
AcO
O
S
OAc
12h
HSQC (400 MHz, CDCl3)
(4C,4H)
(2C,2H)
(3C,3H)
(6C,6H)
(5C,5H)
(1C,1H)
f1 (ppm)
f2 (ppm)

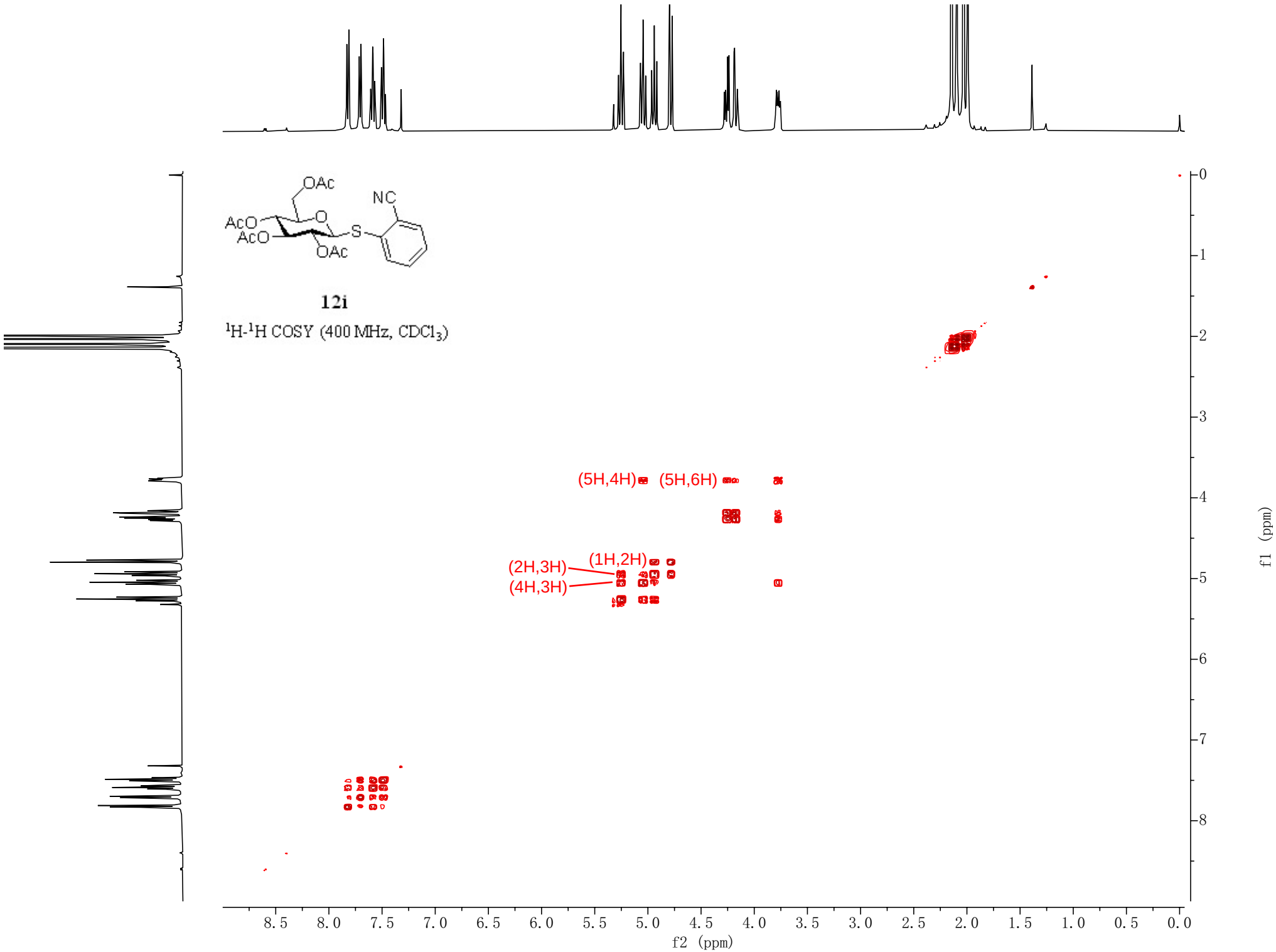

OAc
AcO
AcO
O
S
OAc
12h
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

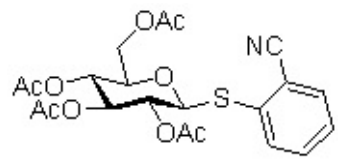


12i

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


170.45
169.99
169.50
169.37
135.19
134.79
133.70
132.86
129.19
117.93
116.90
85.00
75.95
73.70
69.36
67.97
61.98
20.72
20.69
20.53
OAc
AcO
AcO
O
S
OAc
CN
12i
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
NC
AcO
AcO
O
S
OAc
12i
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8



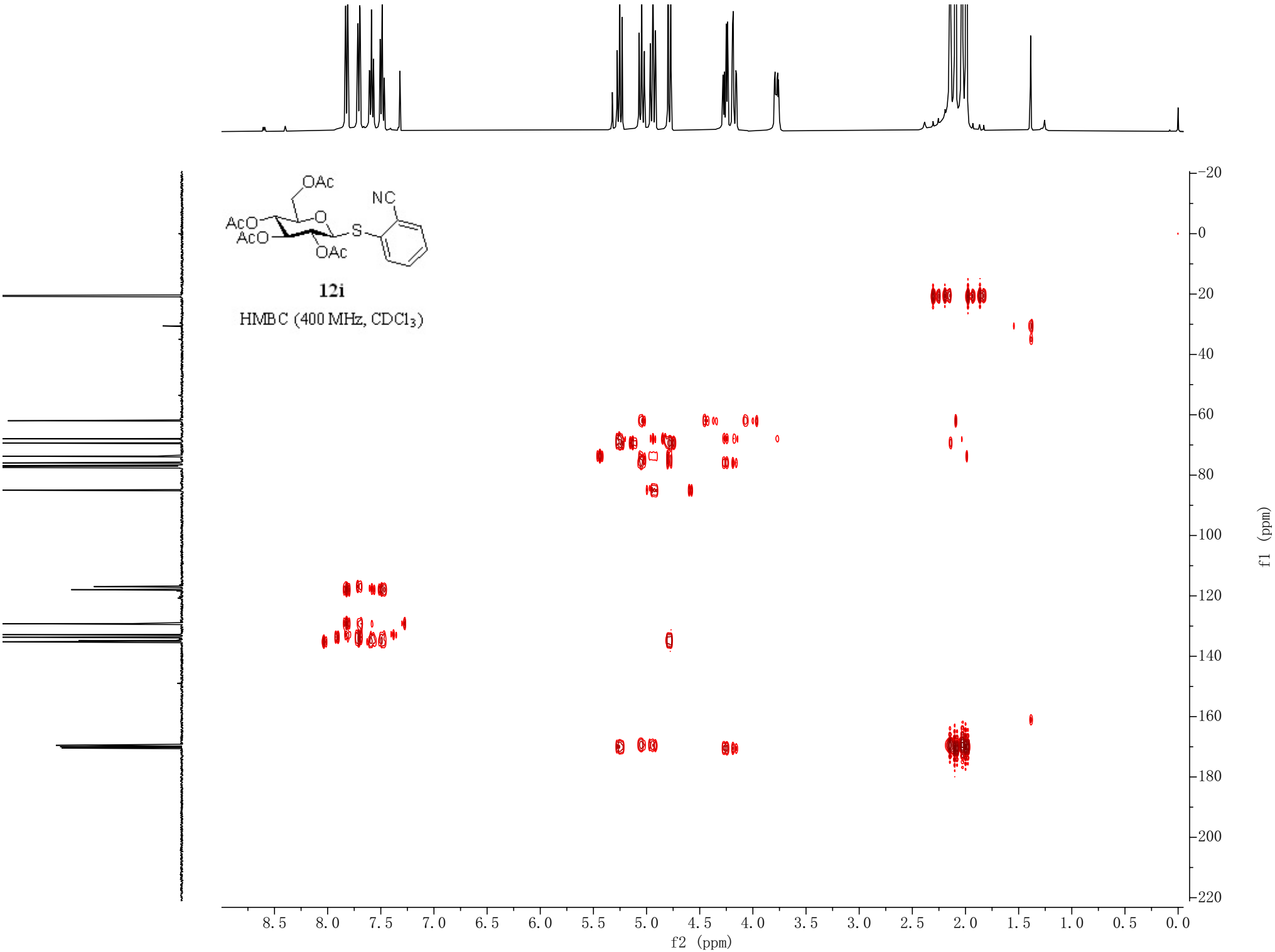
12i

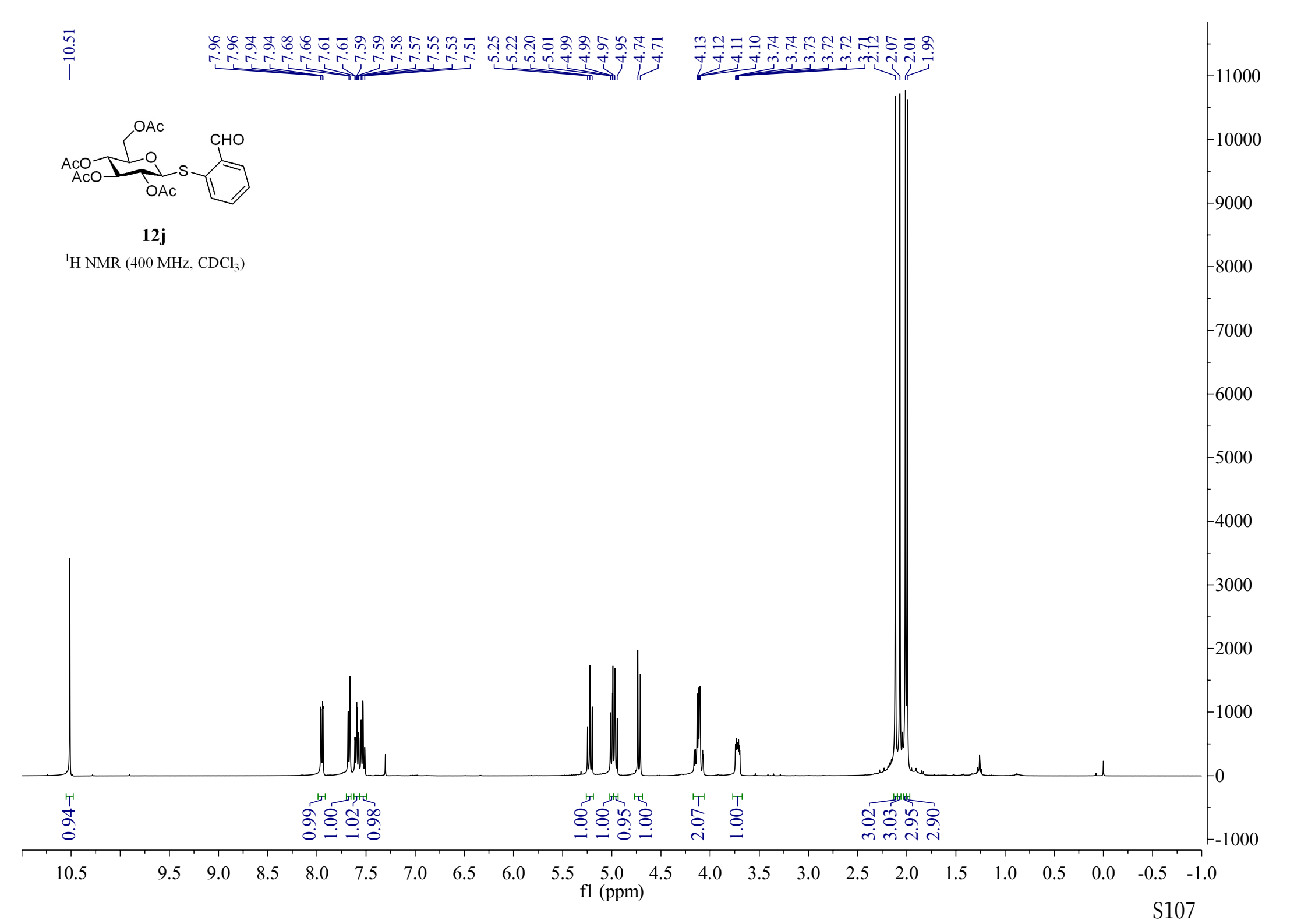
HSQC (400 MHz, $CDCl_3$)

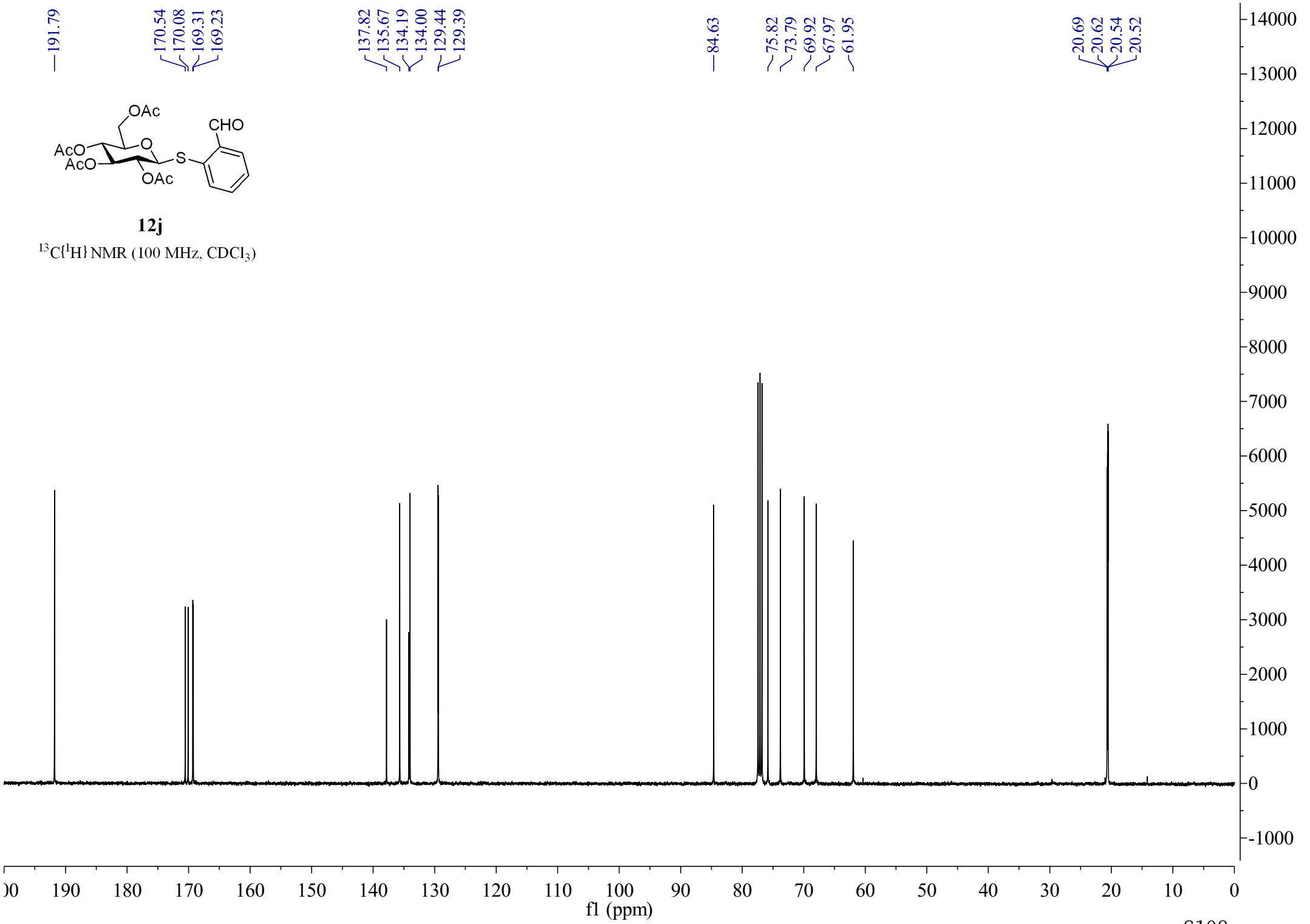
(4C,4H)
(2C,2H)
(3C,3H)
(6C,6H)
(5C,5H)
(1C,1H)

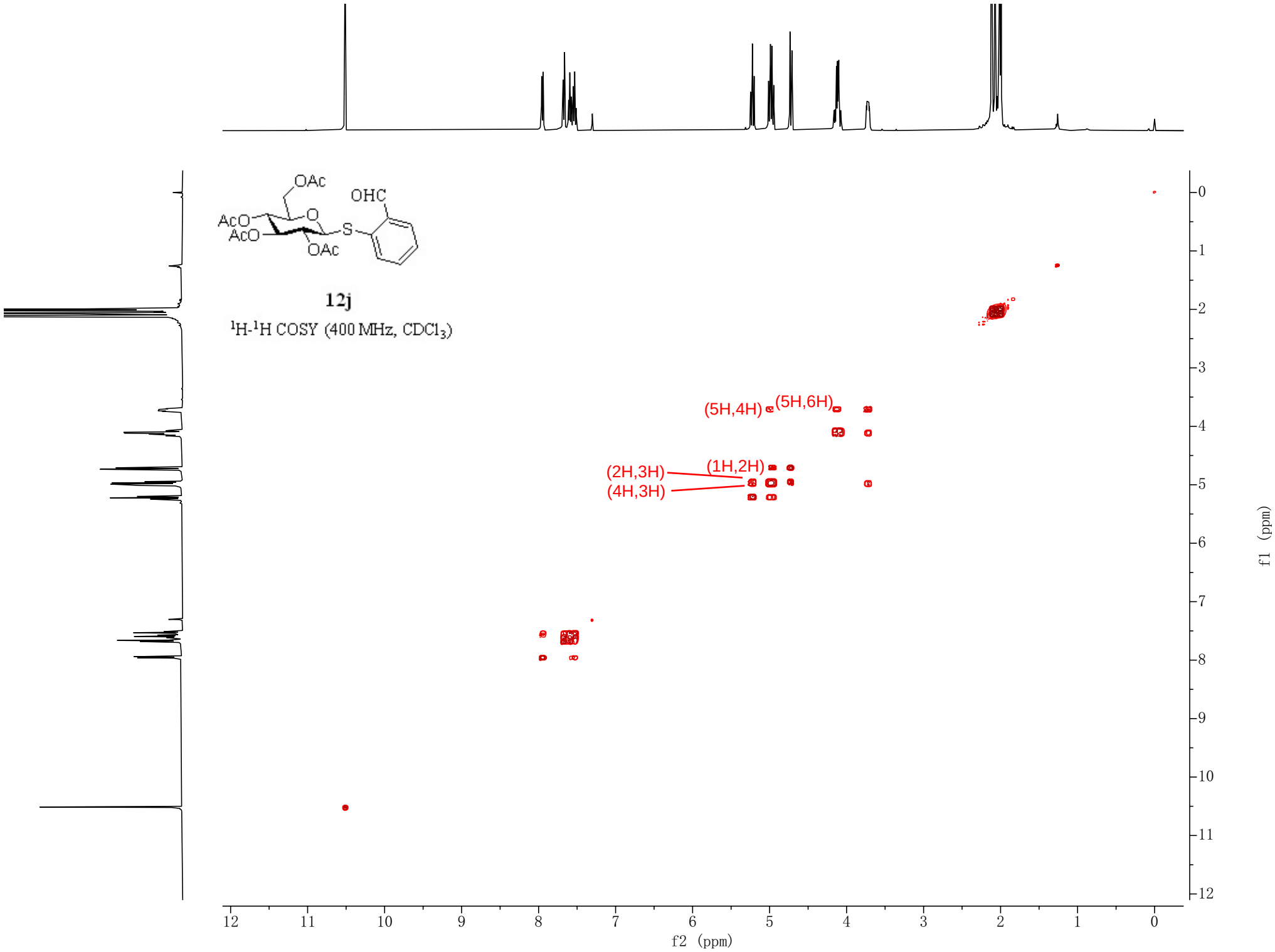
f2 (ppm)

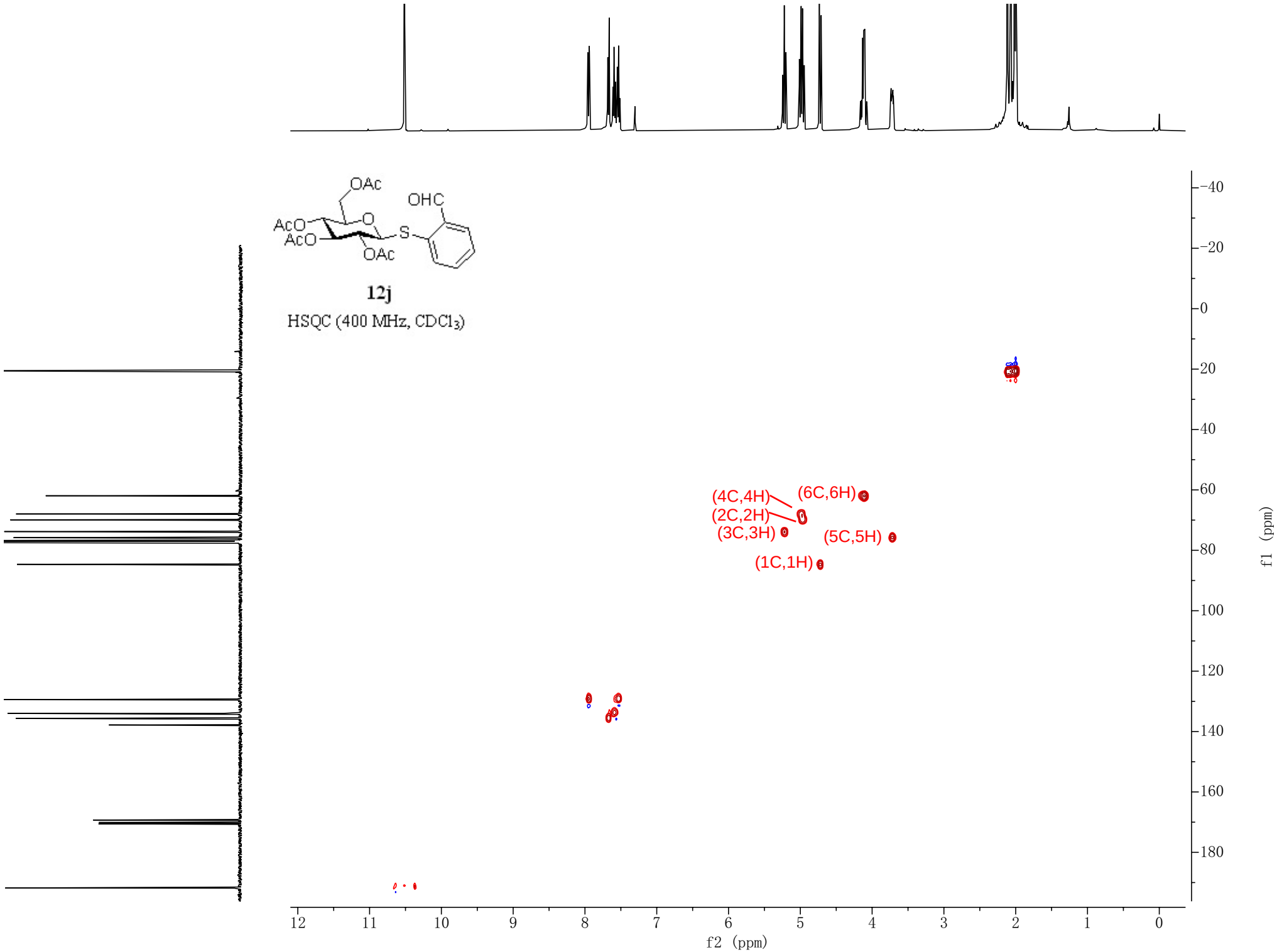
f1 (ppm)

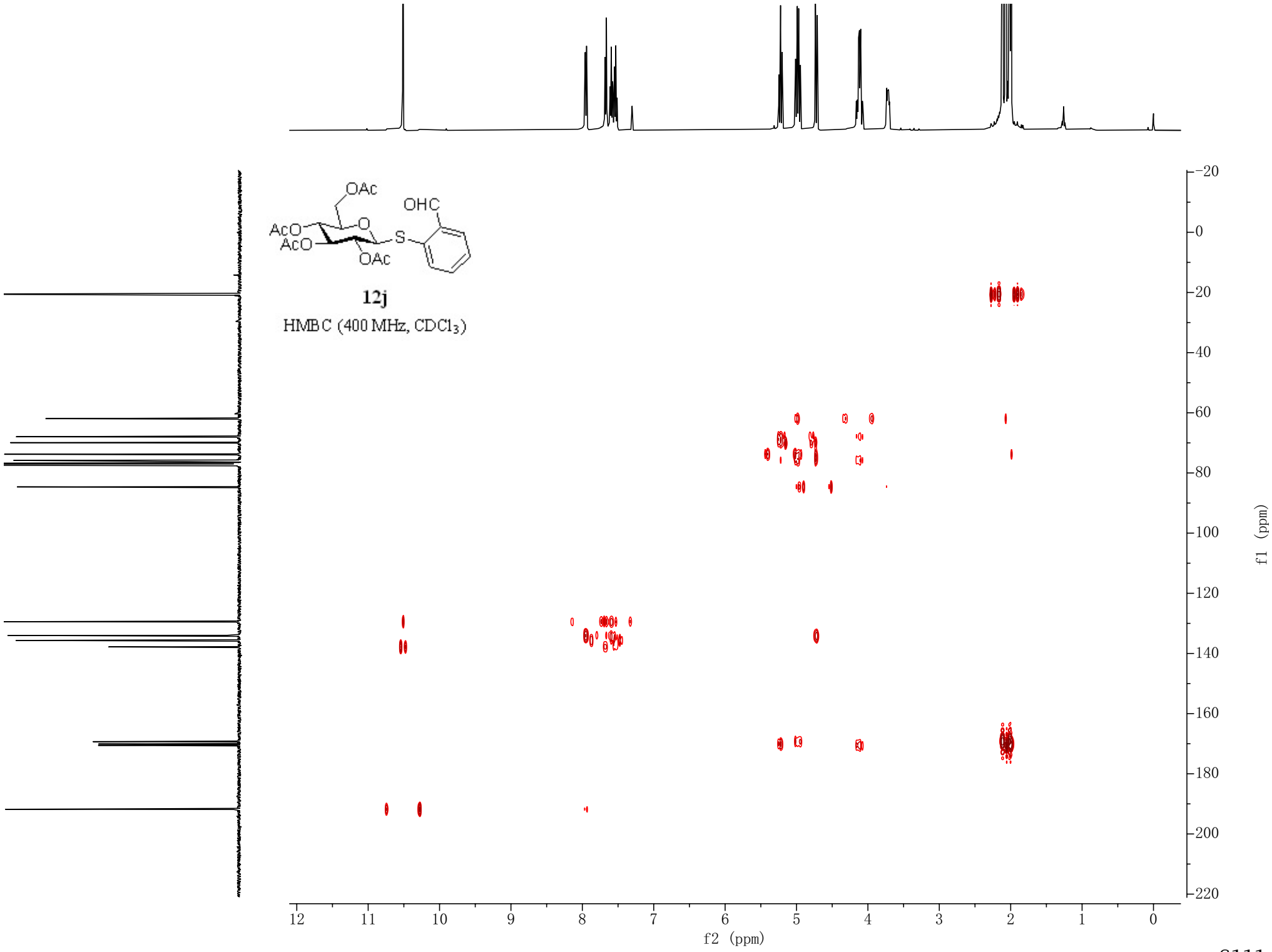

OAc
NC
AcO
O
AcO
S
OAc
12i
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

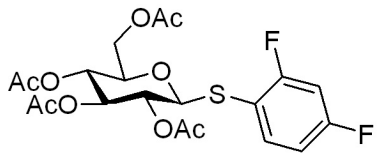

10.51
7.96
7.96
7.94
7.94
7.68
7.66
7.61
7.61
7.59
7.59
7.58
7.57
7.55
7.53
7.51
5.25
5.22
5.20
5.01
4.99
4.99
4.97
4.95
4.74
4.71
4.13
4.12
4.11
4.10
3.74
3.74
3.73
3.72
3.72
3.71
2.12
2.07
2.01
1.99
OAc
CHO
AcO
AcO
O
S
OAc
12j
1H NMR (400 MHz, CDCl3)
0.94
0.99
1.00
1.02
0.98
1.00
1.00
0.95
1.00
2.07
1.00
3.02
3.03
2.95
2.90
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
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)


191.79
170.54
170.08
169.31
169.23
137.82
135.67
134.19
134.00
129.44
129.39
84.63
75.82
73.79
69.92
67.97
61.95
20.69
20.62
20.54
20.52
OAc
CHO
AcO
AcO
O
S
OAc
12j
13C{1H} NMR (100 MHz, CDCl3)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
OHC
AcO
AcO
O
S
OAc
12j
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)

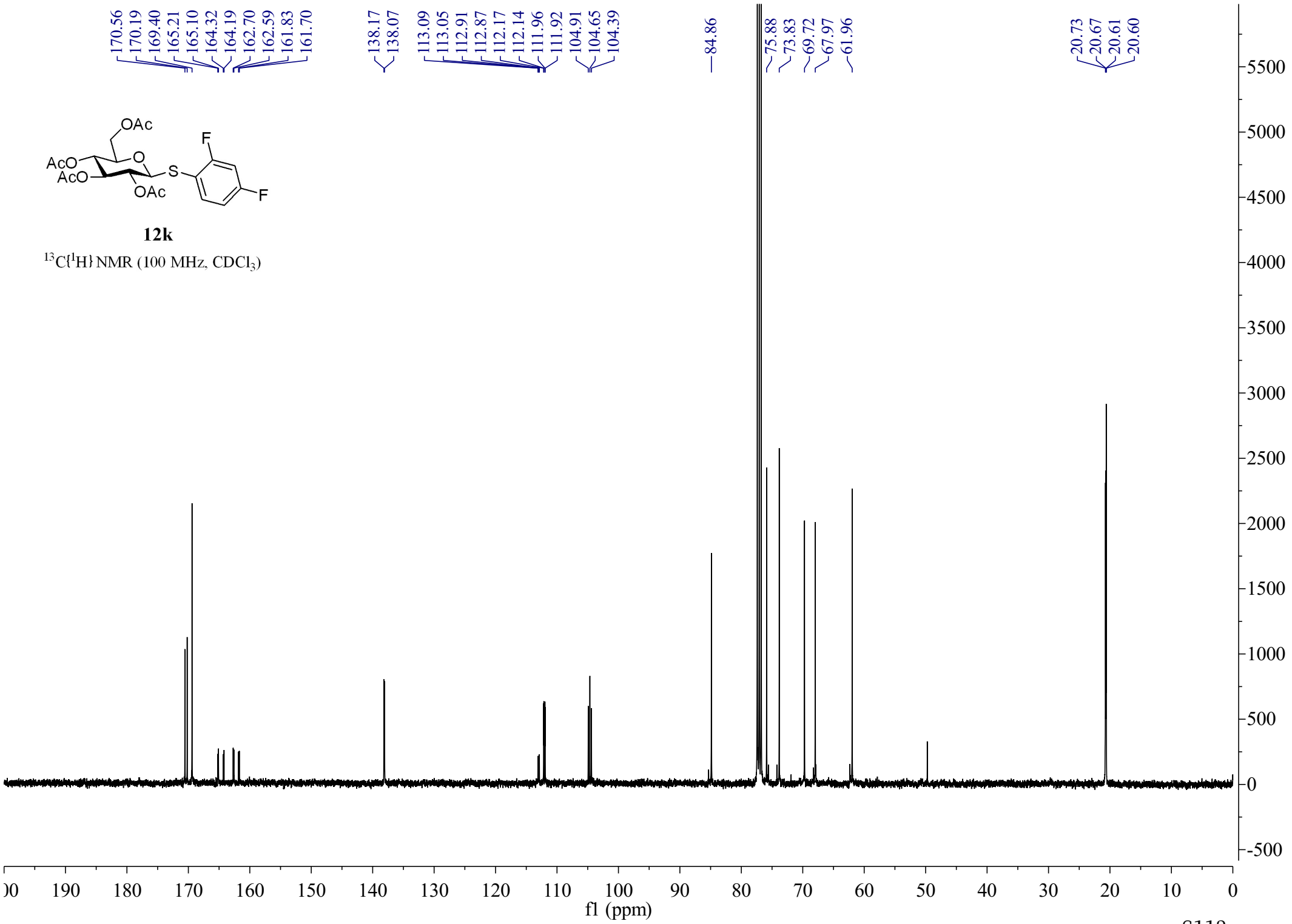

OAc
OHC
AcO
AcO
O
S
OAc
12j
HSQC (400 MHz, CDCl3)
(4C,4H)
(6C,6H)
(2C,2H)
(3C,3H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)


OAc
OHC
AcO
AcO
O
S
OAc
12j
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



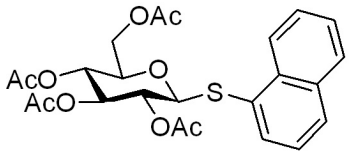
12k

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



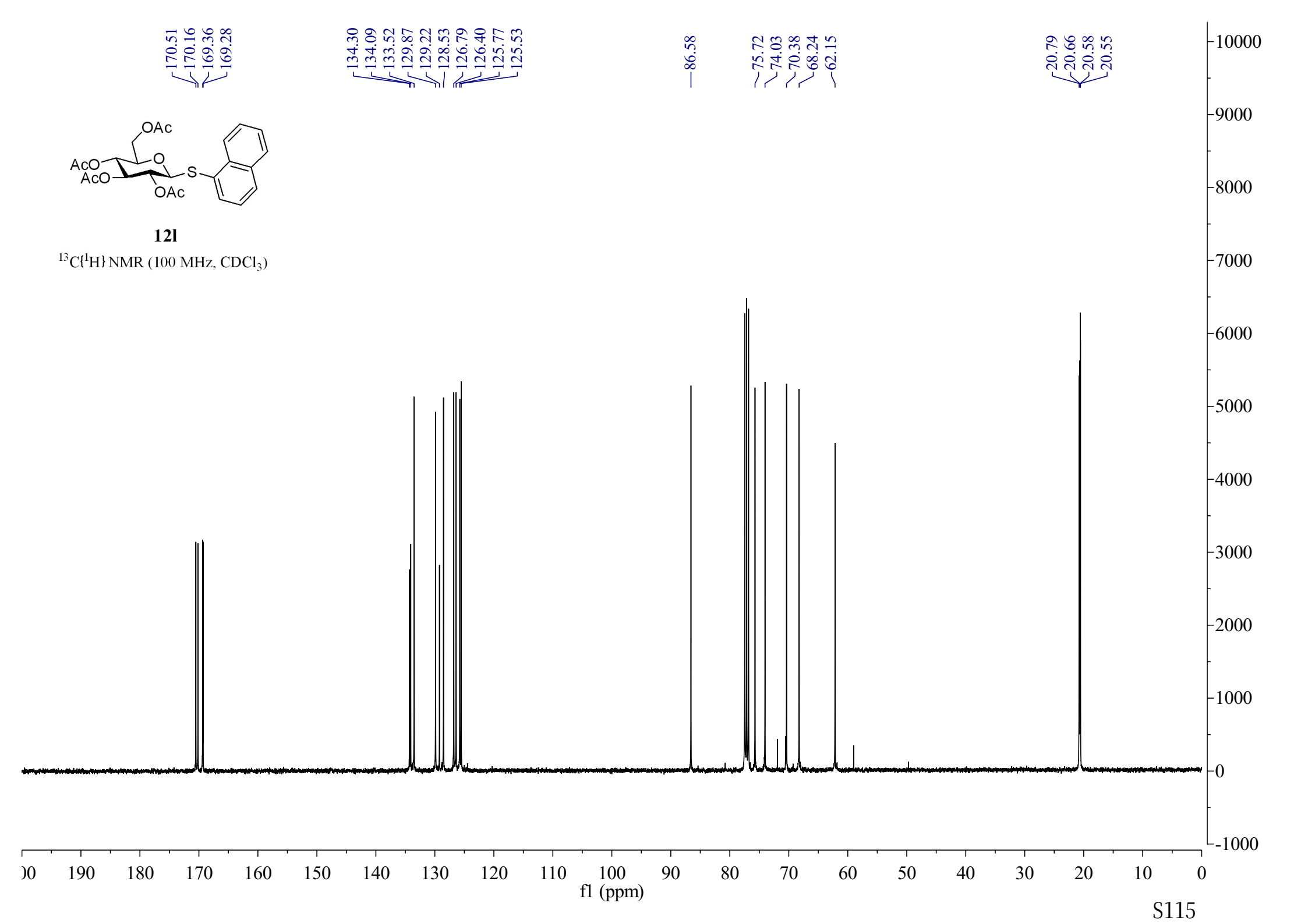
12k

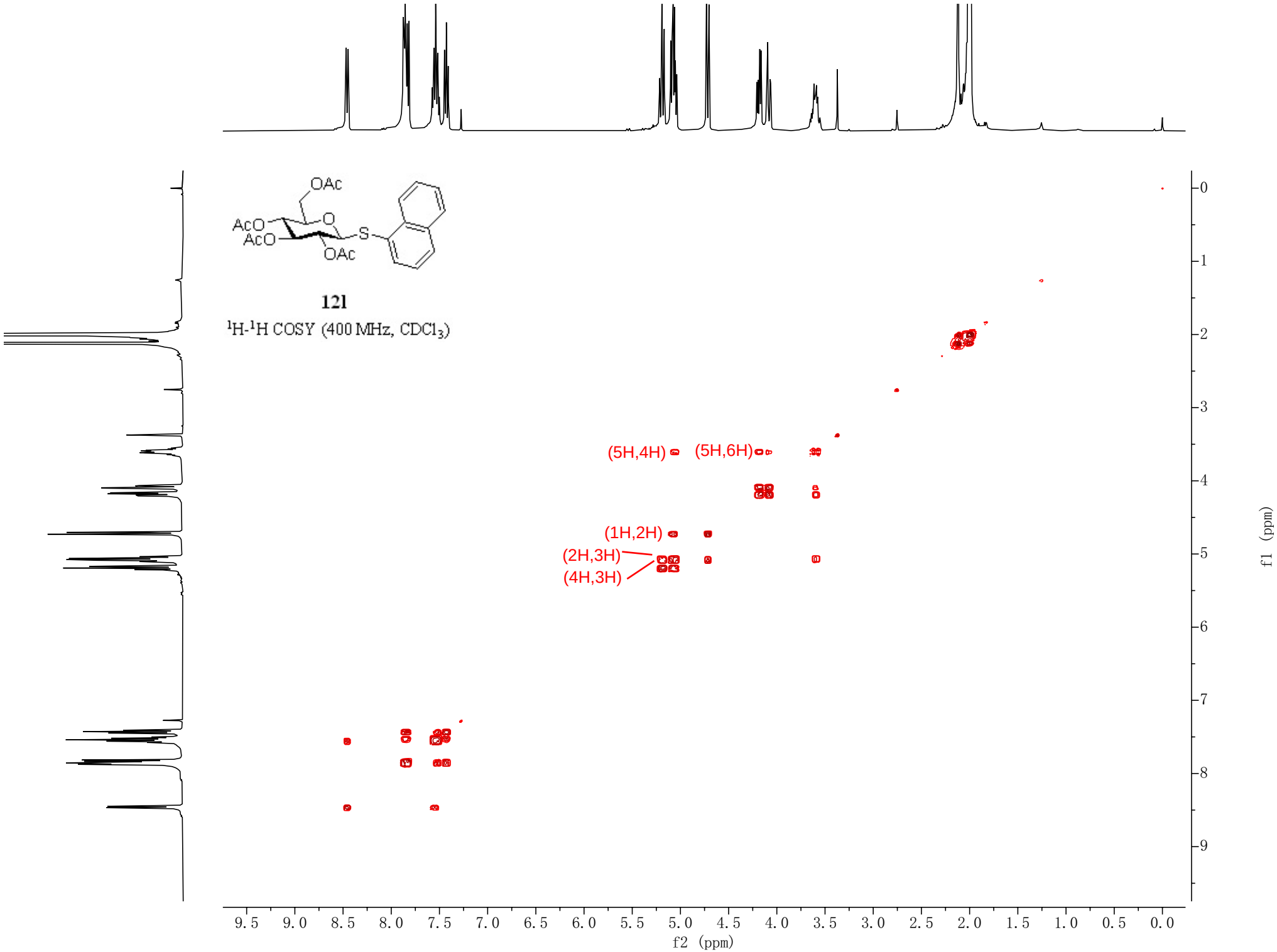
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

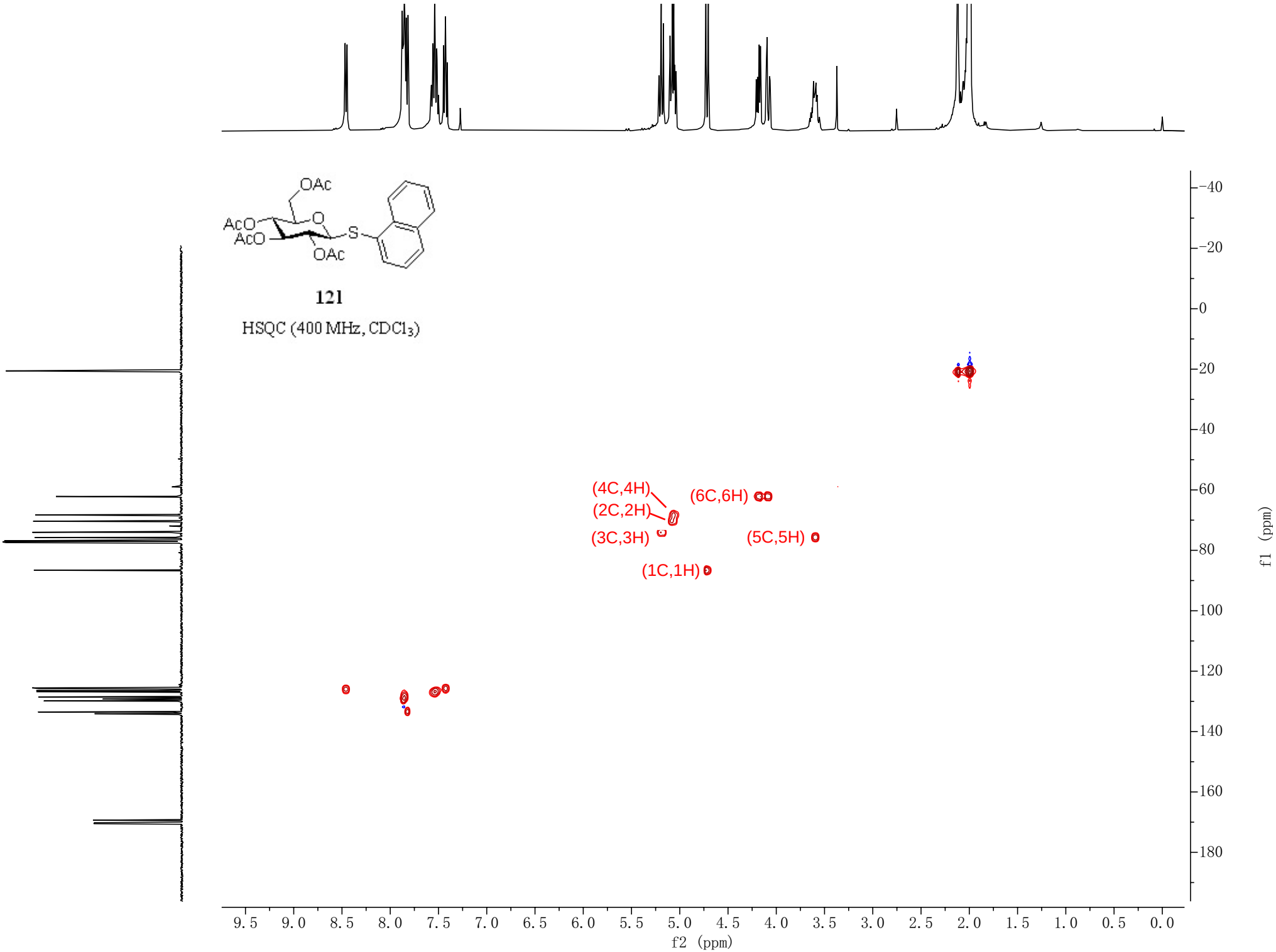


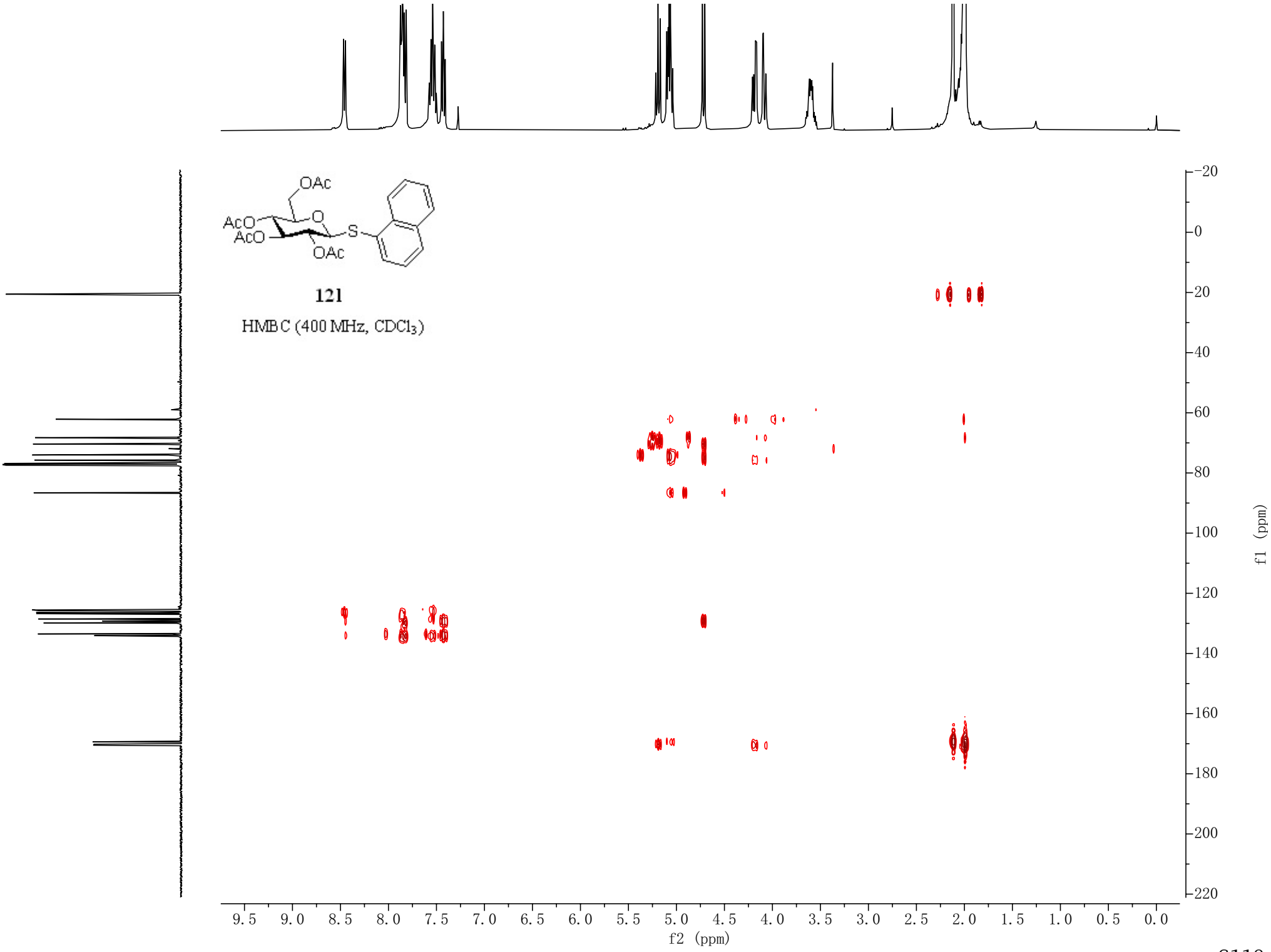
12l

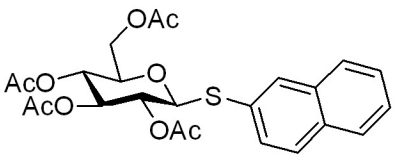
^{1}H NMR (400 MHz, $CDCl_3$)


170.51
170.16
169.36
169.28
134.30
134.09
133.52
129.87
129.22
128.53
126.79
126.40
125.77
125.53
86.58
75.72
74.03
70.38
68.24
62.15
20.79
20.66
20.58
20.55
OAc
AcO
AcO
O
S
OAc
12l
13C{1H} NMR (100 MHz, CDCl3)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
121
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)

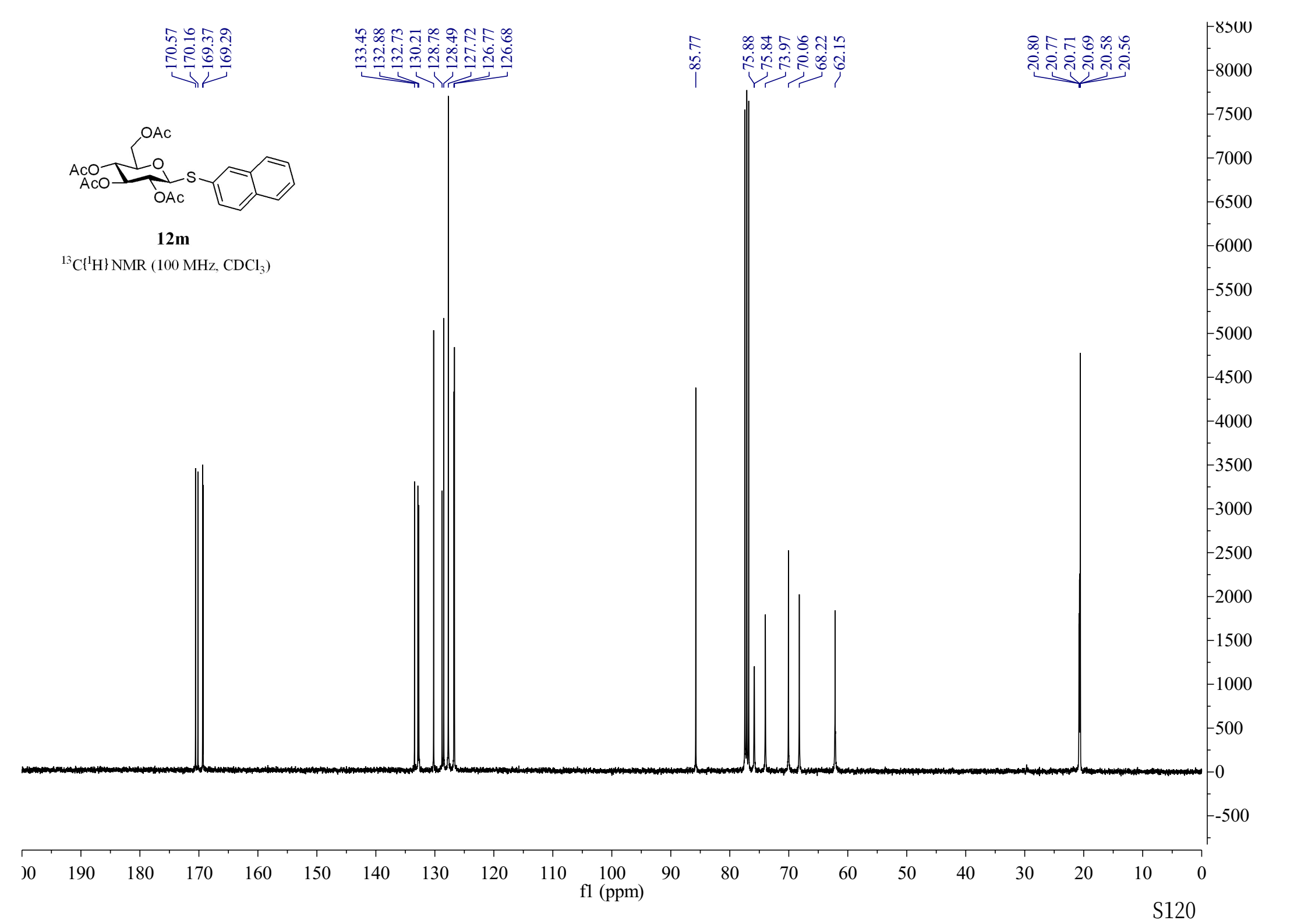

OAc
AcO
AcO
O
S
OAc
121
HSQC (400 MHz, CDCl3)
(4C,4H)
(2C,2H)
(3C,3H)
(6C,6H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)

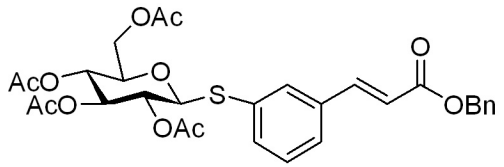

OAc
AcO
AcO
O
S
OAc
121
HMBC (400 MHz, CDCl3)
-20
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)



12m

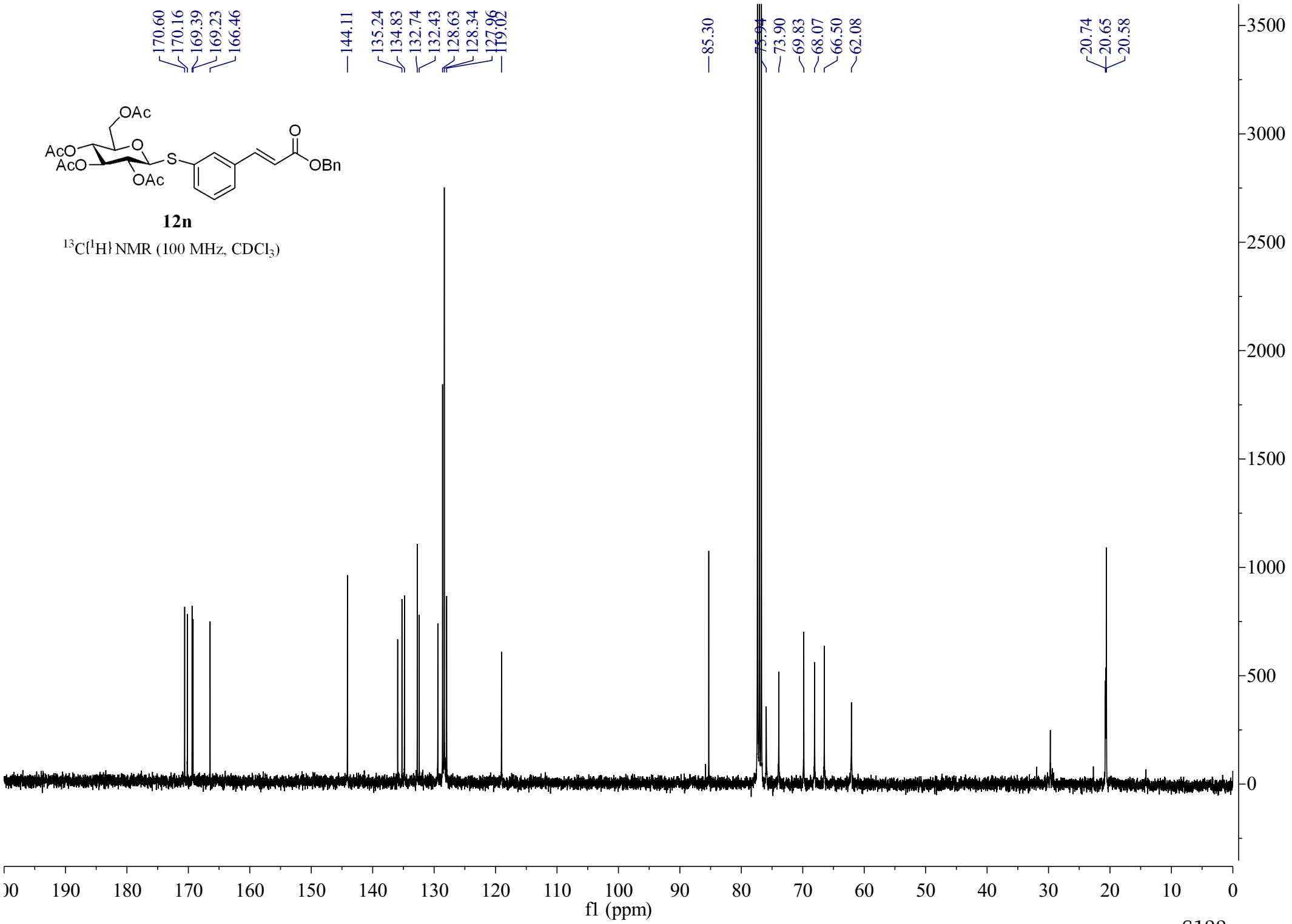
^{1}H NMR (400 MHz, $CDCl_3$)

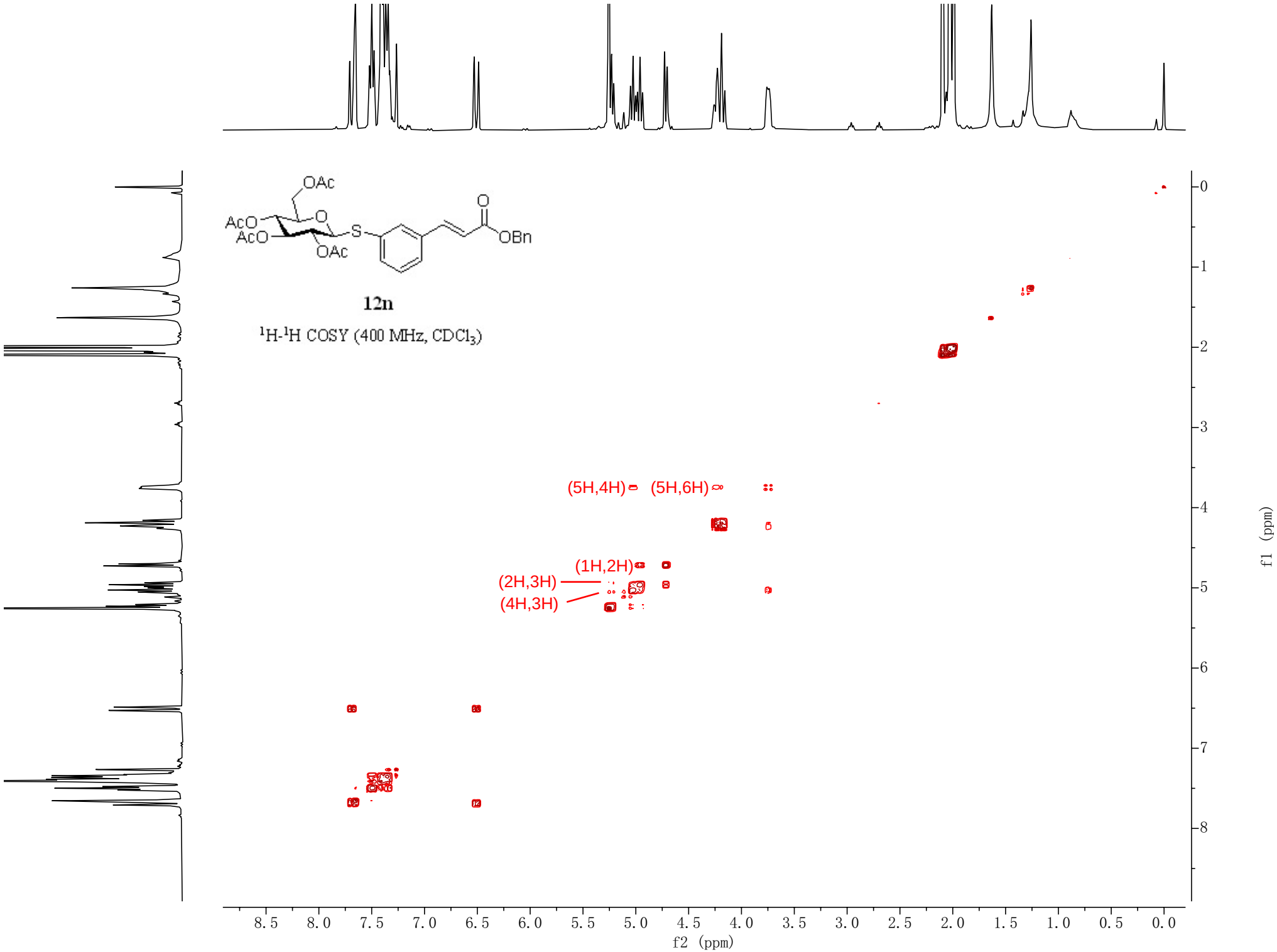

170.57
170.16
169.37
169.29
133.45
132.88
132.73
130.21
128.78
128.49
127.72
126.77
126.68
85.77
75.88
75.84
73.97
70.06
68.22
62.15
20.80
20.77
20.71
20.69
20.58
20.56
OAc
AcO
AcO
O
S
OAc
12m
13C{1H} NMR (100 MHz, CDCl3)
fl (ppm)

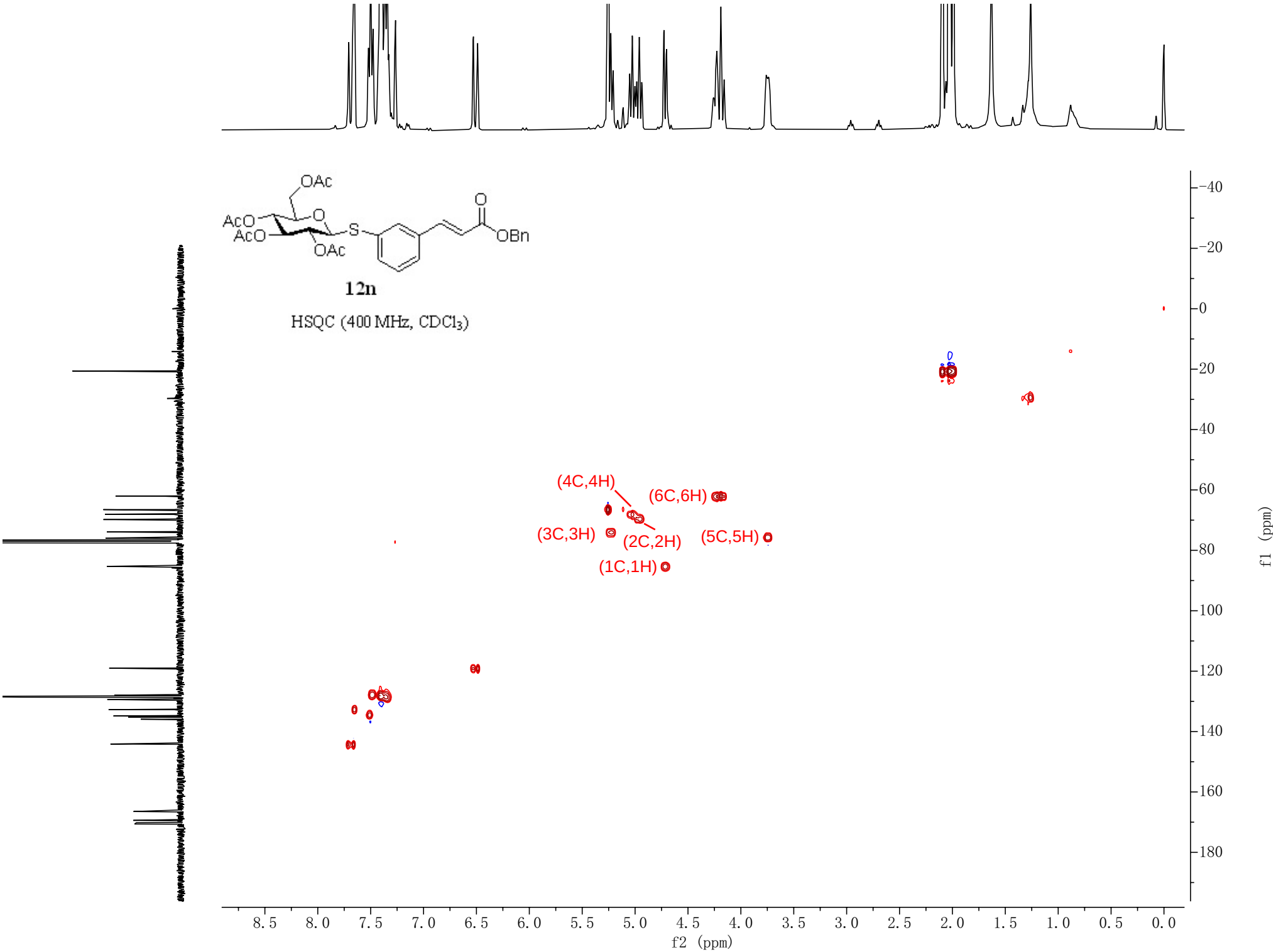


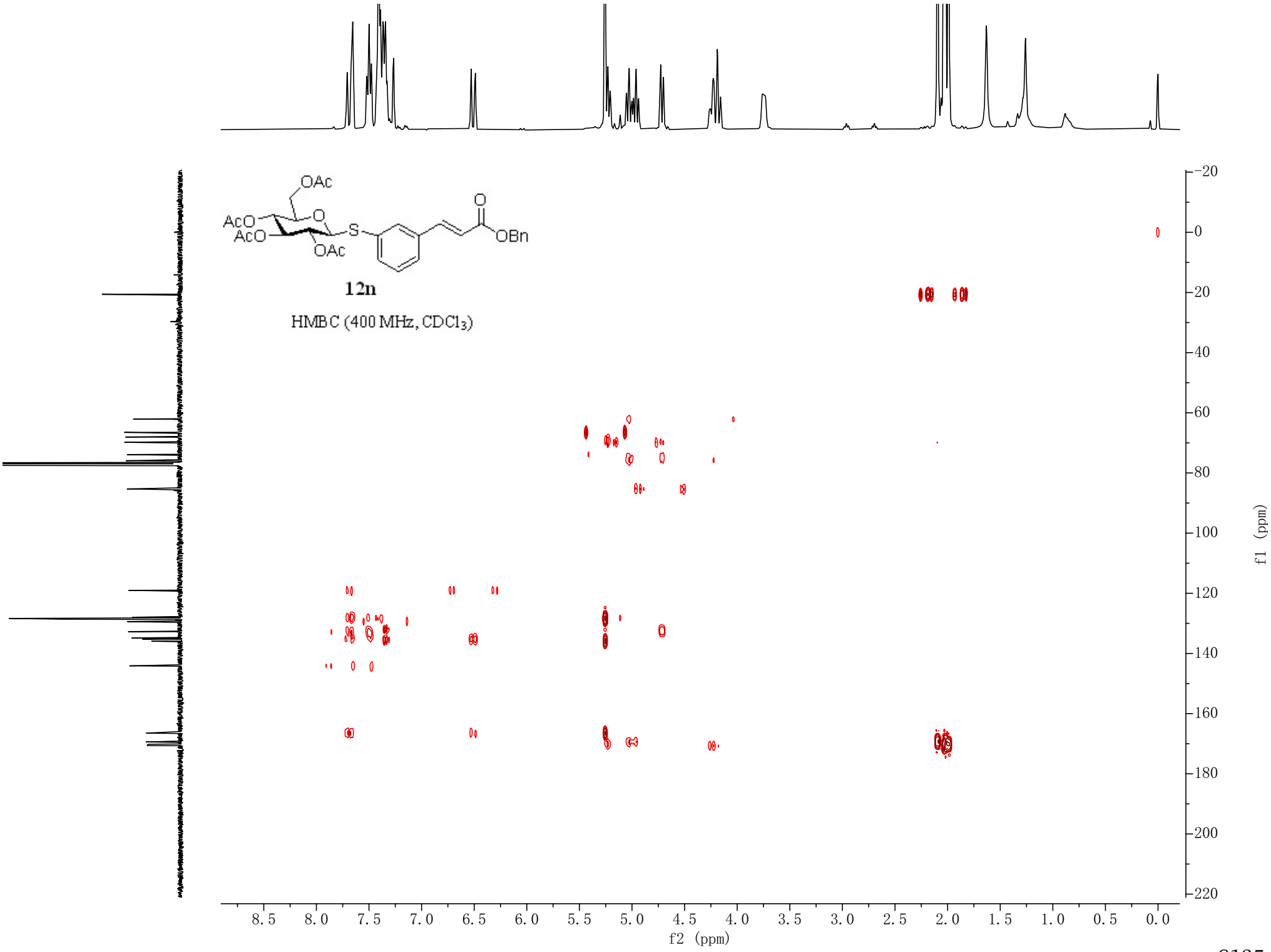
12n

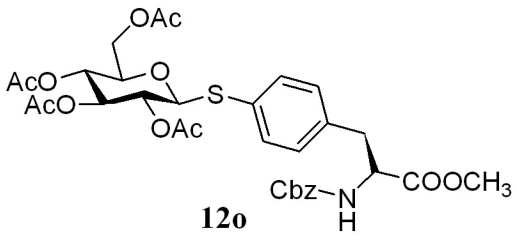
^{1}H NMR (400 MHz, $CDCl_3$)


170.60
170.16
169.39
169.23
166.46
144.11
135.24
134.83
132.74
132.43
128.63
128.34
127.96
119.02
85.30
75.94
73.90
69.83
68.07
66.50
62.08
20.74
20.65
20.58
OAc
AcO
AcO
OAc
O
S
O
OBn
12n
13C{1H} NMR (100 MHz, CDCl3)
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
O
OBn
12n
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8

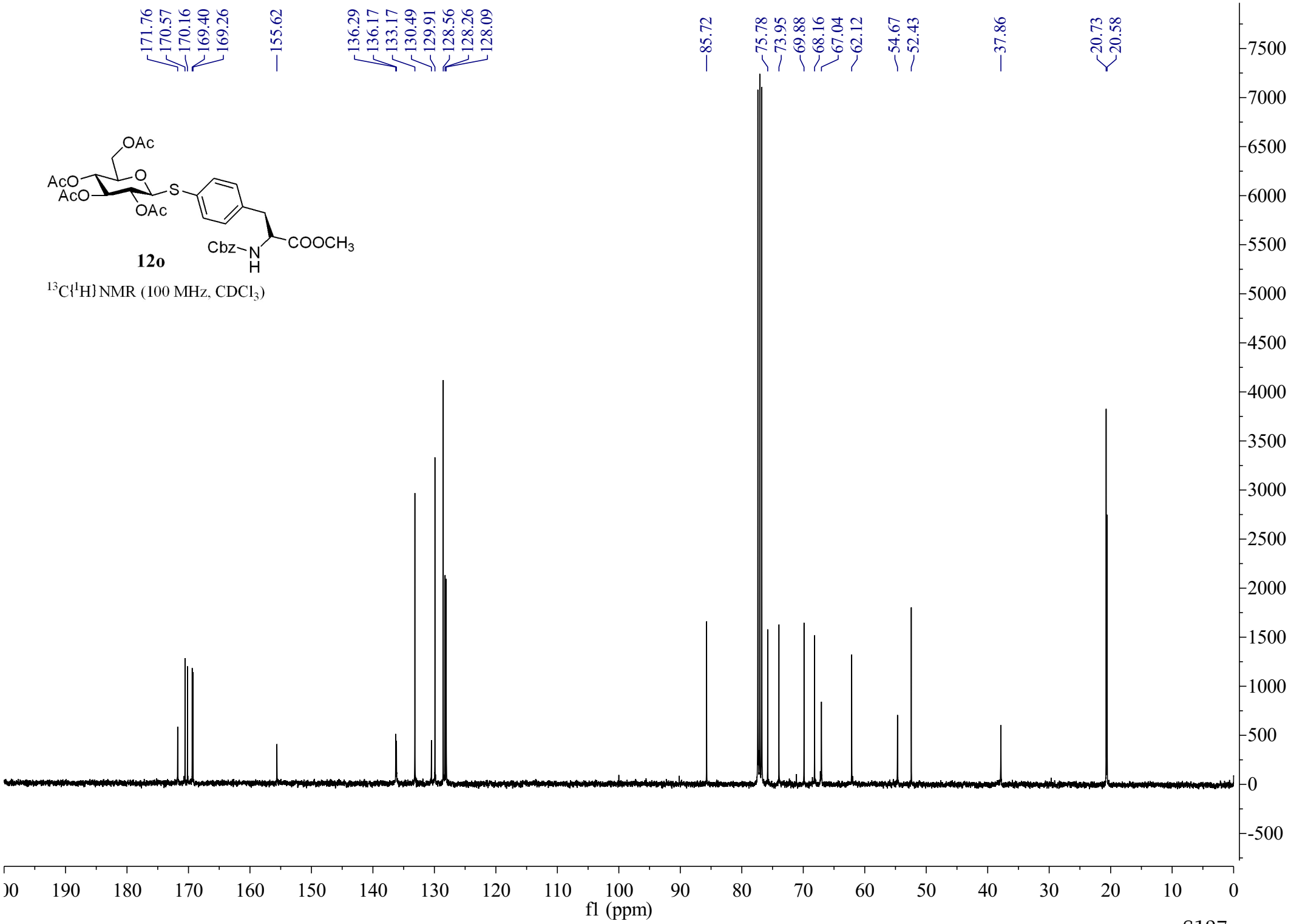

OAc
AcO
AcO
O
S
OAc
O
OBn
12n
HSQC (400 MHz, CDCl3)
(4C,4H)
(6C,6H)
(3C,3H)
(2C,2H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)

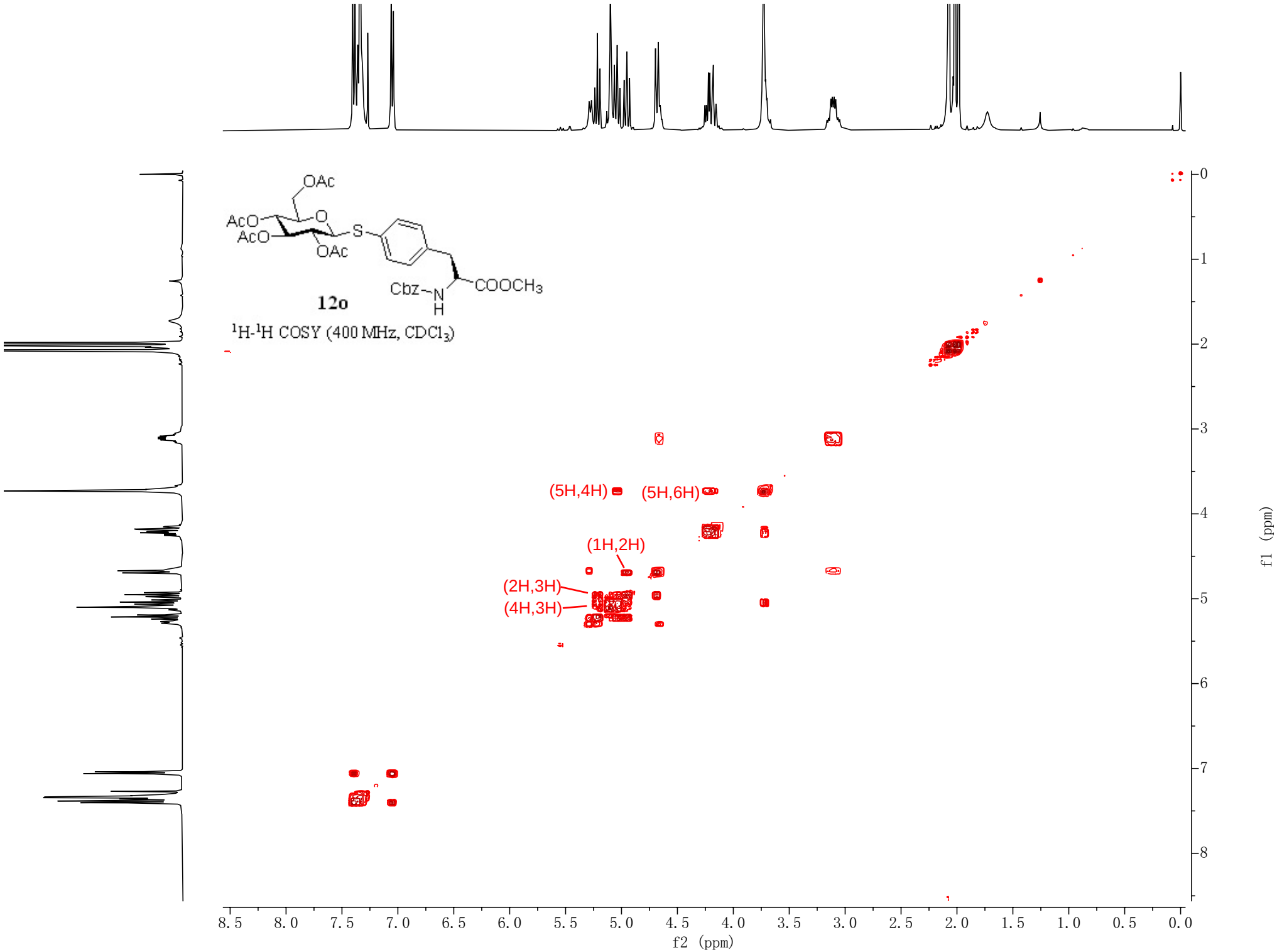

OAc
AcO
AcO
O
S
OAc
O
OBn
12n
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

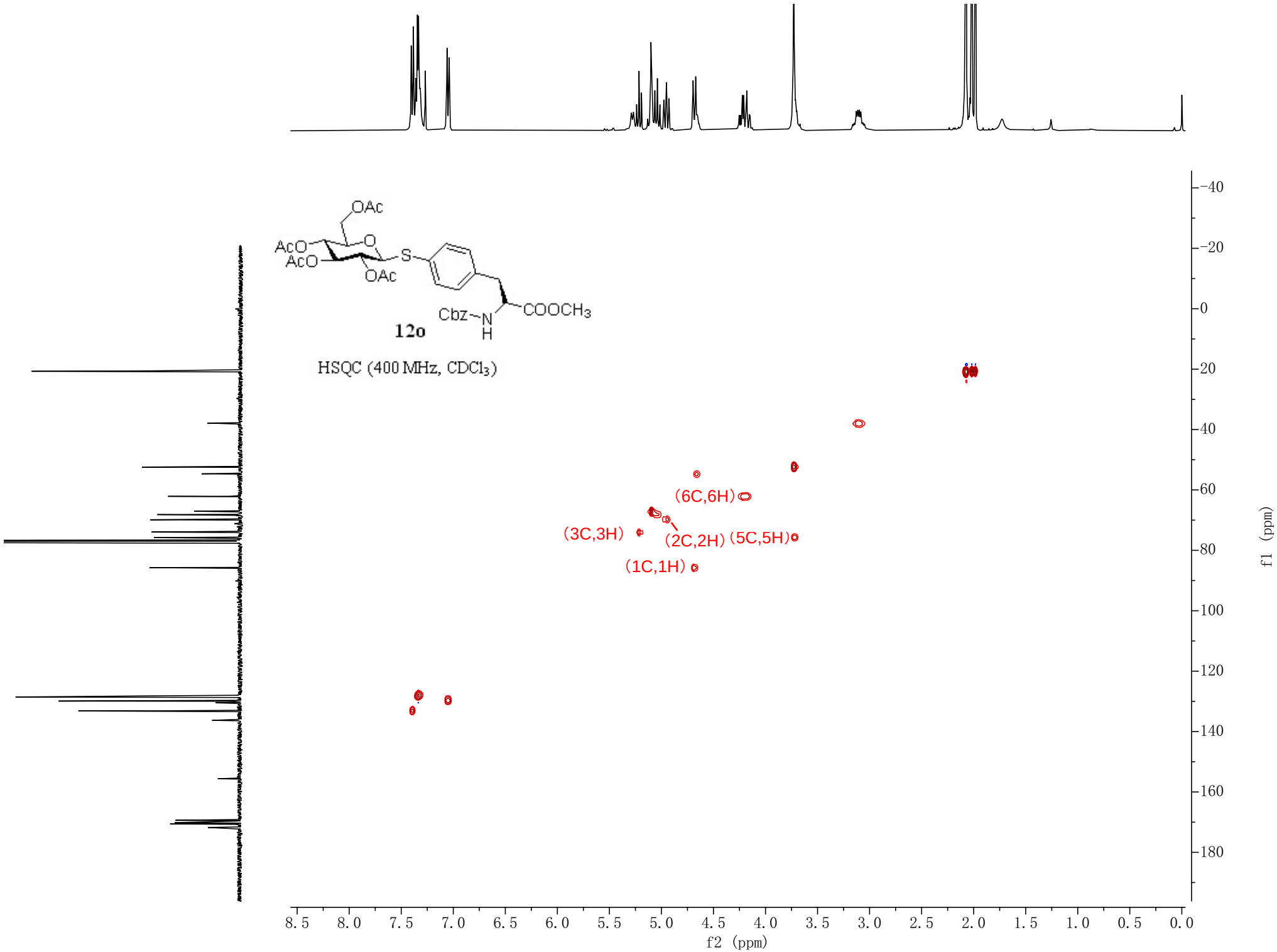


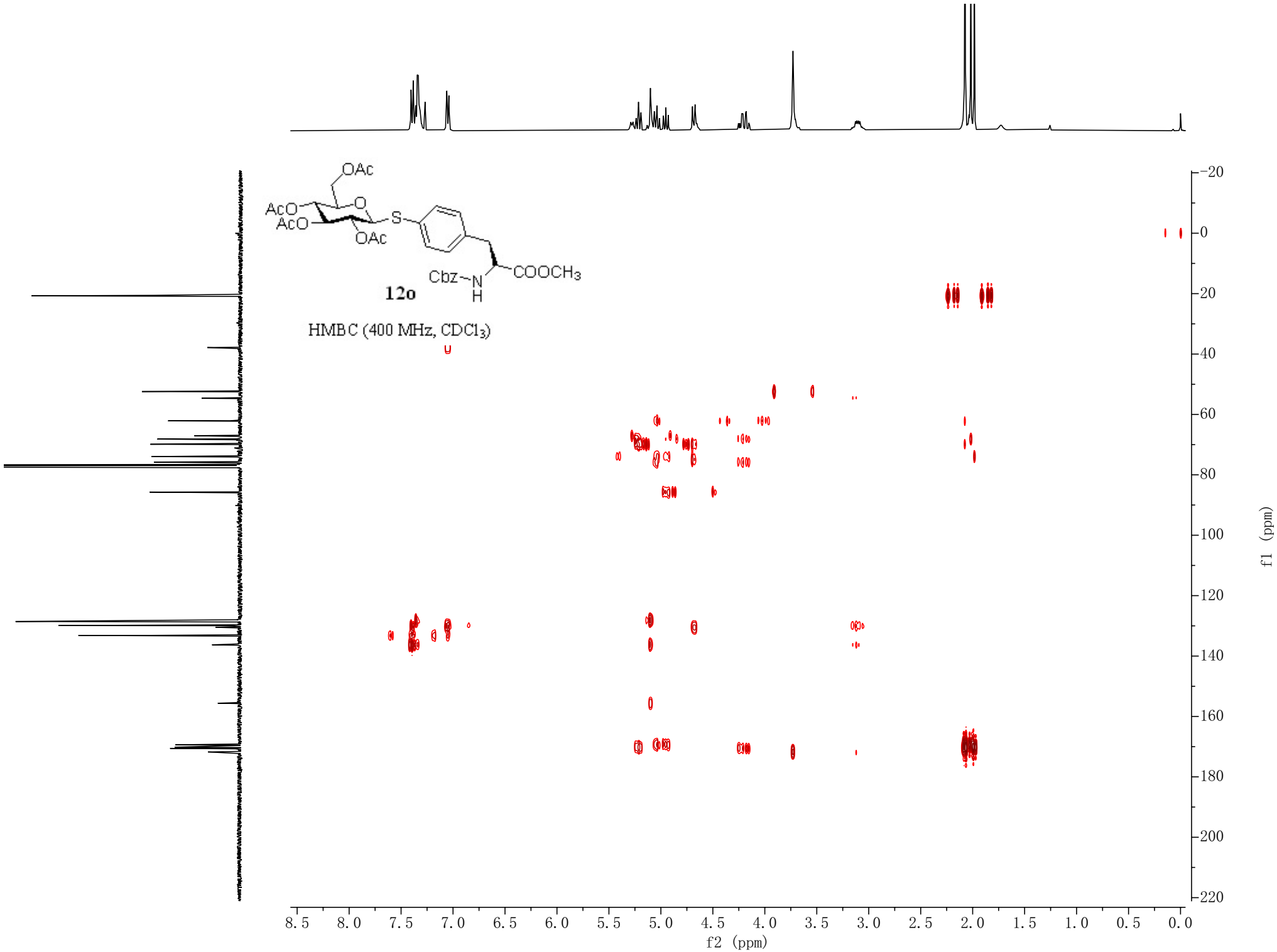
12o

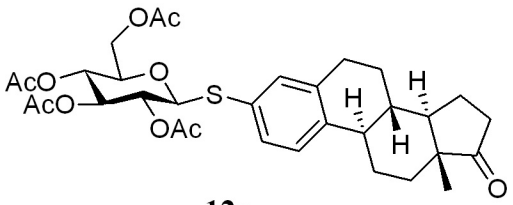
^{1}H NMR (400 MHz, $CDCl_3$)


171.76
170.57
170.16
169.40
169.26
155.62
136.29
136.17
133.17
130.49
129.91
128.56
128.26
128.09
85.72
75.78
73.95
69.88
68.16
67.04
62.12
54.67
52.43
37.86
20.73
20.58
OAc
AcO
AcO
OAc
O
S
Cbz
N
H
COOCH3
12o
13C{1H} NMR (100 MHz, CDCl3)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
Cbz
N
H
COOCH3
12o
1H-1H COSY (400 MHz, CDCl3)
(5H,4H)
(5H,6H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8

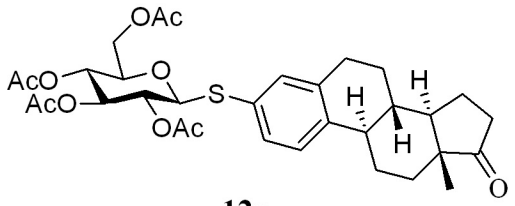

OAc
AcO
AcO
OAc
O
S
Cbz
N
H
COOCH3
12o
HSQC (400 MHz, CDCl3)
(6C,6H)
(3C,3H)
(2C,2H)
(5C,5H)
(1C,1H)
f2 (ppm)
f1 (ppm)


OAc
AcO
AcO
O
S
OAc
Cbz
N
H
COOCH3
12o
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



12p

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



12p

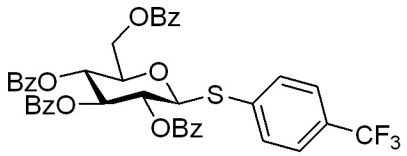
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

170.57
170.19
169.44
169.24
140.54
137.38
134.26
131.08
127.93
125.96
85.71
75.73
74.08
69.90
68.15
62.14
50.49
47.93
44.29
37.91
31.55
29.25
26.33
21.58
20.80
20.77
20.60
13.88
13.83

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

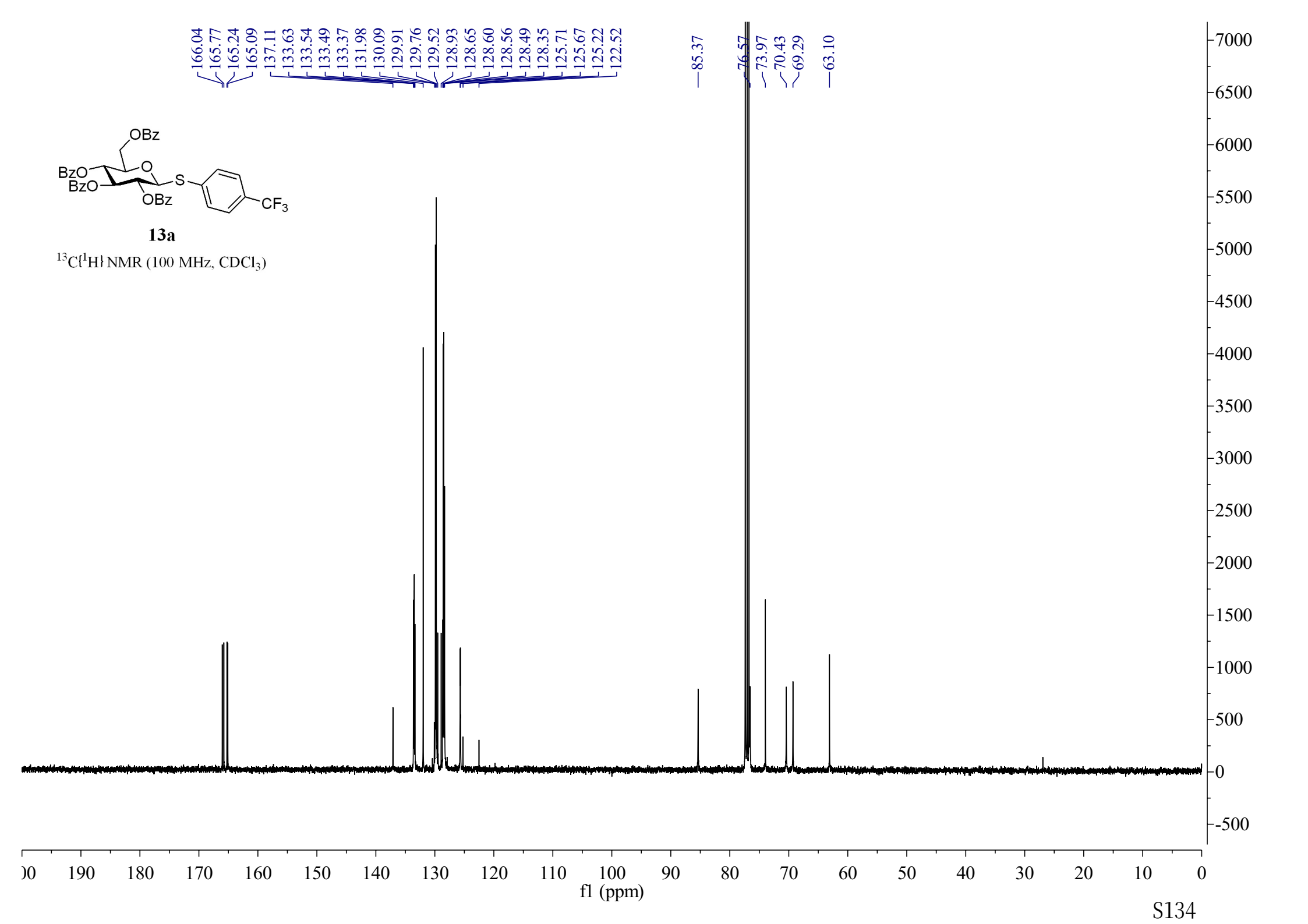
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

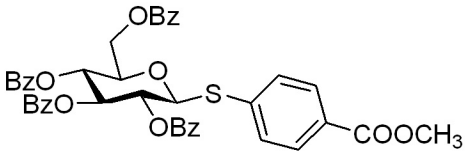
f1 (ppm)



13a

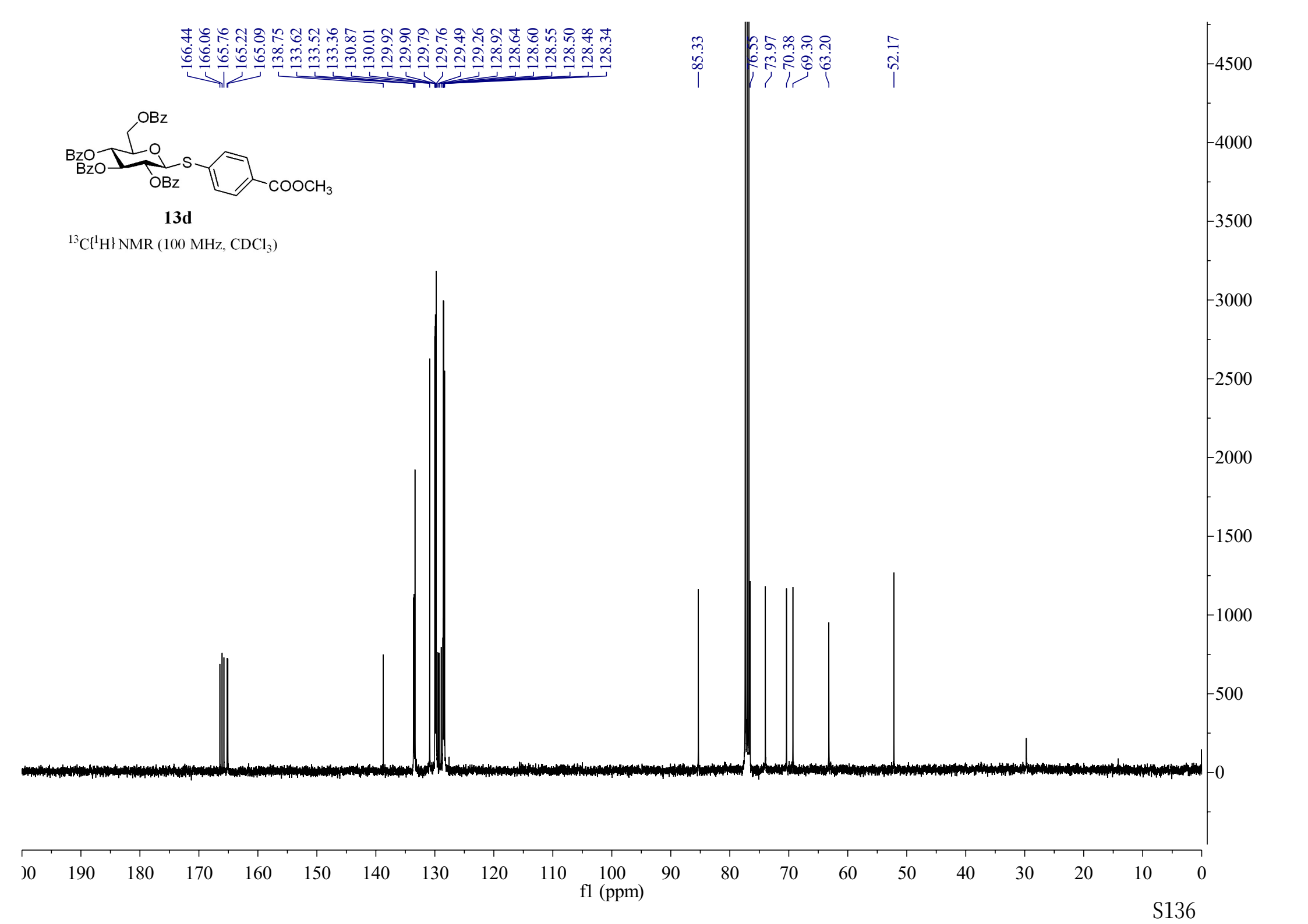
^{1}H NMR (400 MHz, $CDCl_3$)

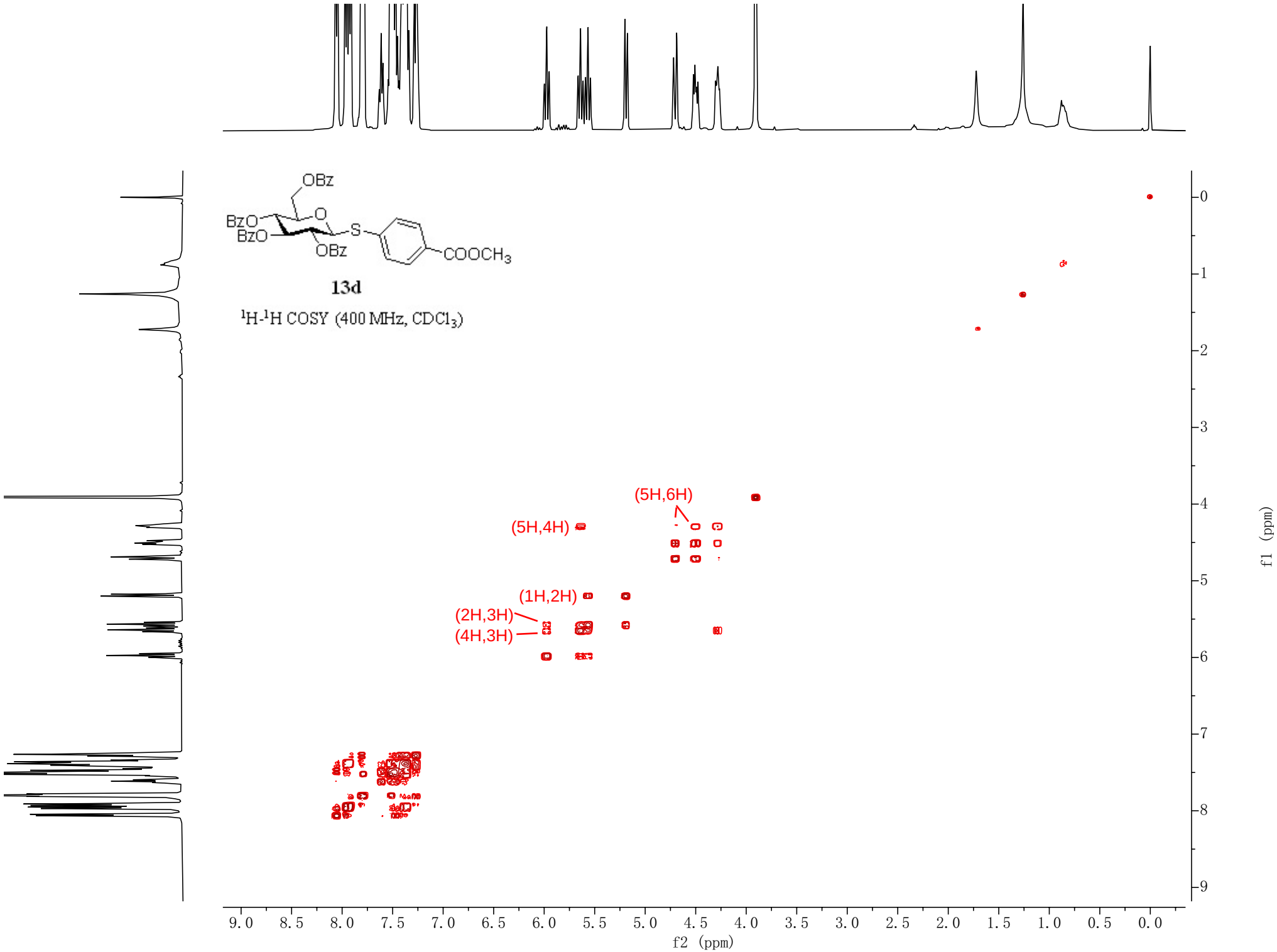

166.04
165.77
165.24
165.09
137.11
133.63
133.54
133.49
133.37
131.98
130.09
129.91
129.76
129.52
128.93
128.65
128.60
128.56
128.49
128.35
125.71
125.67
125.22
122.52
85.37
76.57
73.97
70.43
69.29
63.10
OBz
BzO
BzO
OBz
O
S
CF3
13a
13C{1H} NMR (100 MHz, CDCl3)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

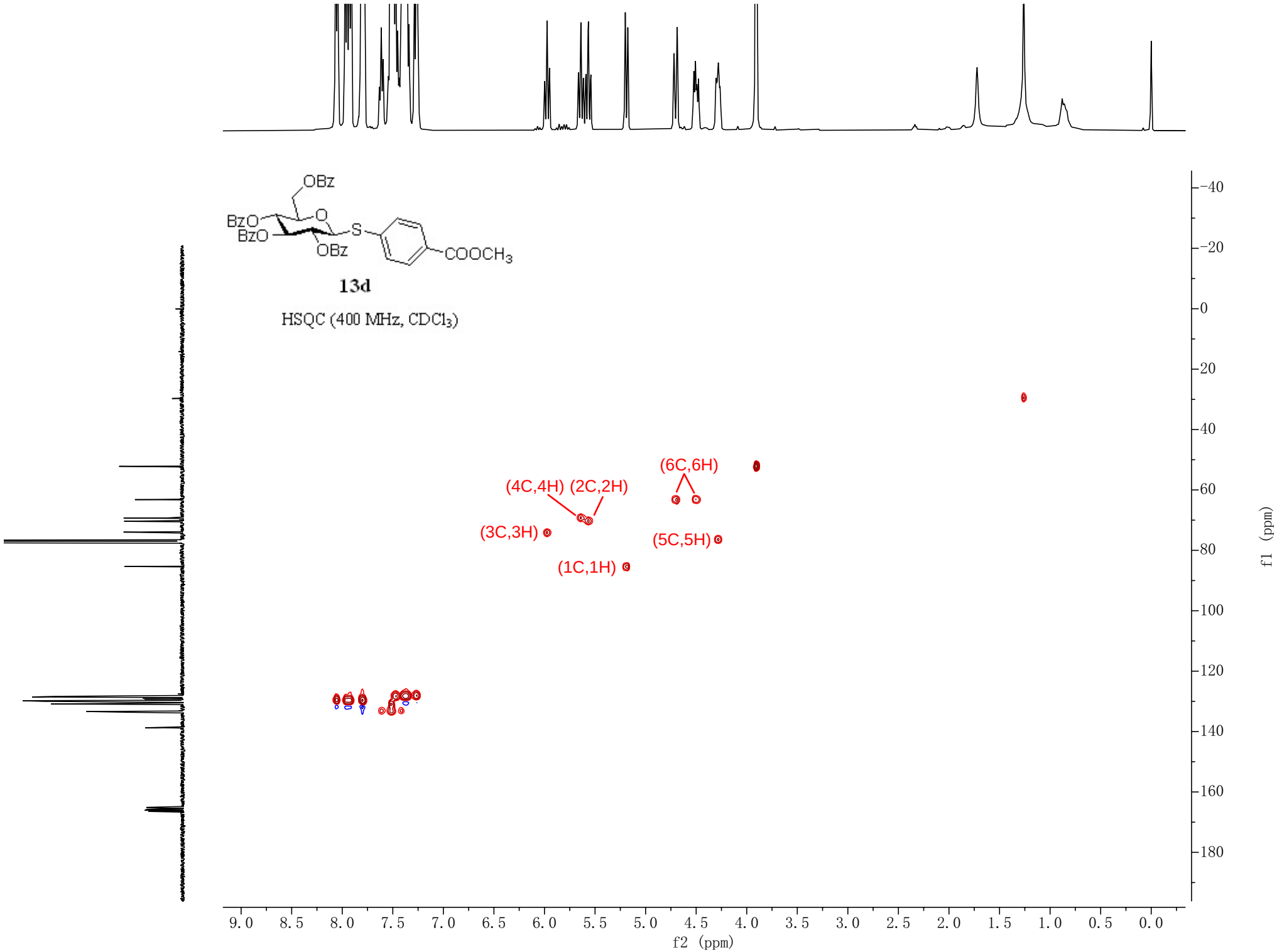


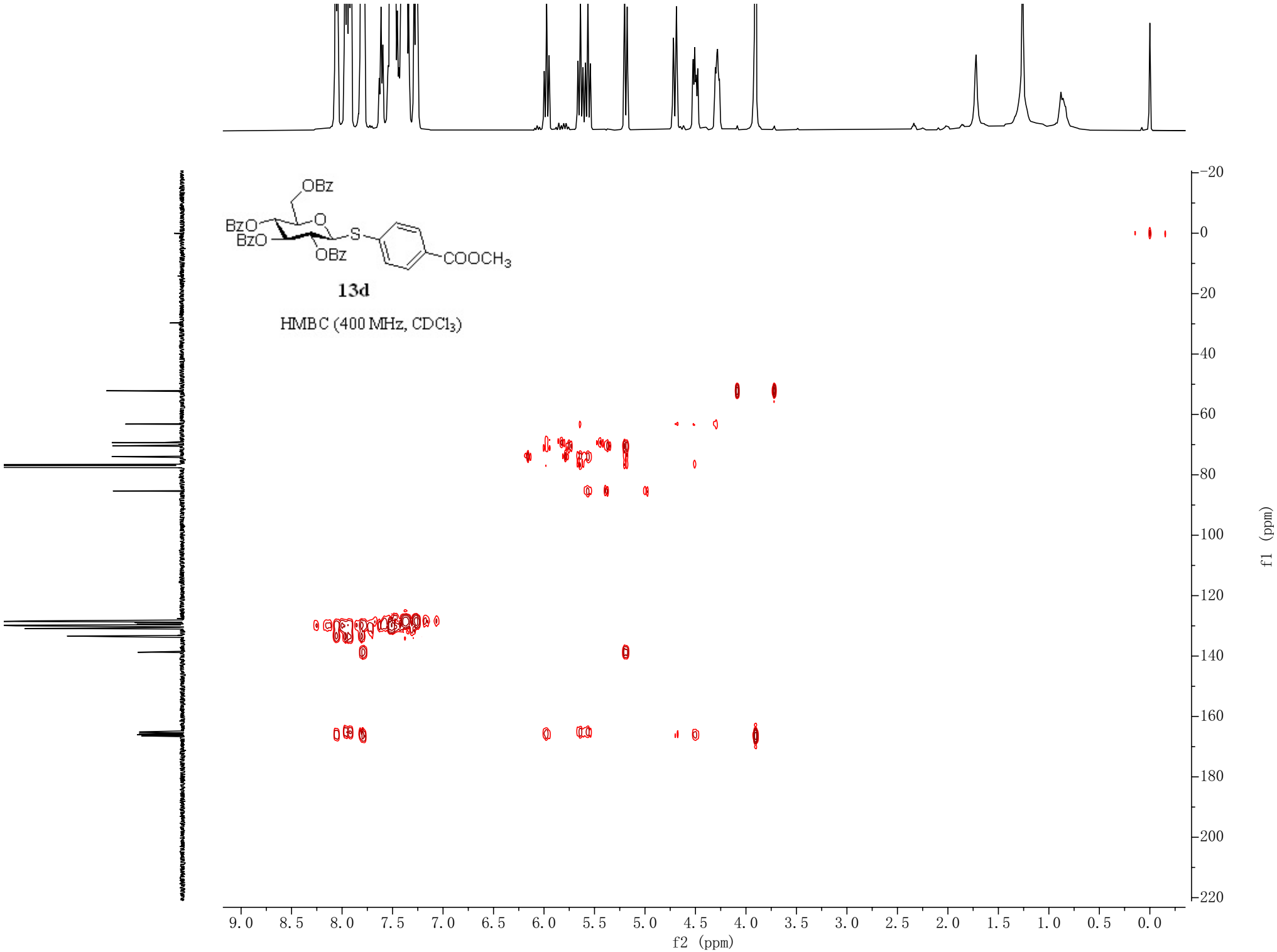
13d

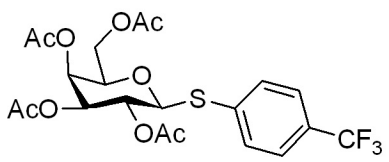
^{1}H NMR (400 MHz, $CDCl_3$)


166.44
166.06
165.76
165.22
165.09
138.75
133.62
133.52
133.36
130.87
130.01
129.92
129.90
129.79
129.76
129.49
129.26
128.92
128.64
128.60
128.55
128.50
128.48
128.34
85.33
76.55
73.97
70.38
69.30
63.20
52.17
OBz
BzO
BzO
OBz
O
S
COOCH3
13d
13C{1H} NMR (100 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OBz
BzO
BzO
O
S
OBz
COOCH3
13d
1H-1H COSY (400 MHz, CDCl3)
(5H,6H)
(5H,4H)
(1H,2H)
(2H,3H)
(4H,3H)
f1 (ppm)
f2 (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 1 2 3 4 5 6 7 8 9

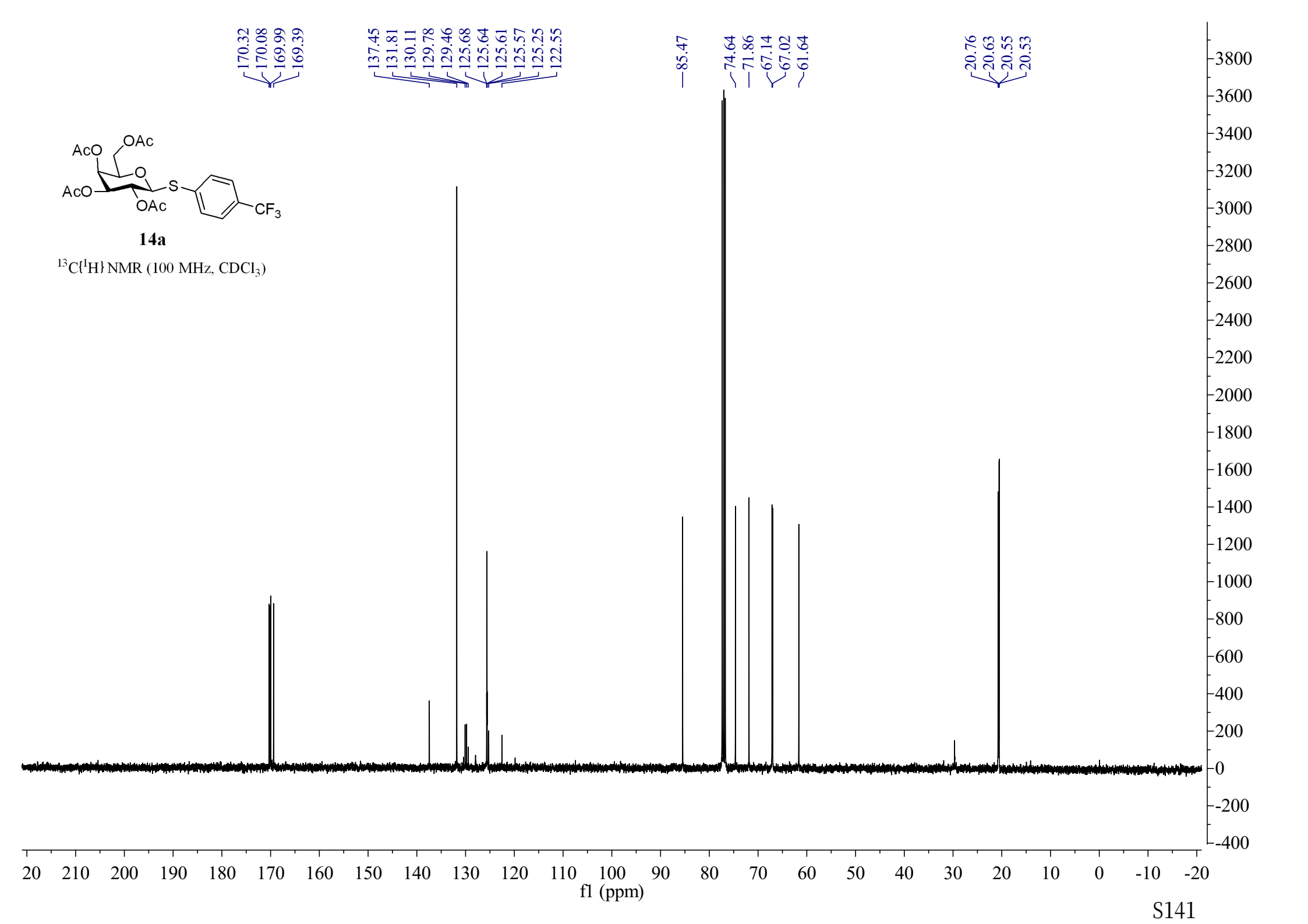

OBz
BzO
BzO
O
S
OBz
COOCH3
13d
HSQC (400 MHz, CDCl3)
(6C,6H)
(4C,4H) (2C,2H)
(3C,3H)
(5C,5H)
(1C,1H)
f1 (ppm)
f2 (ppm)


OBz
BzO
BzO
O
S
OBz
COOCH3
13d
HMBC (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



14a

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


170.32
170.08
169.99
169.39
137.45
131.81
130.11
129.78
129.46
125.68
125.64
125.61
125.57
125.25
122.55
85.47
74.64
71.86
67.14
67.02
61.64
20.76
20.63
20.55
20.53
AcO
OAc
AcO
OAc
O
S
CF3
14a
13C{1H} NMR (100 MHz, CDCl3)
fl (ppm)