Electronic Supplementary Material (ESI) for Green Chemistry.

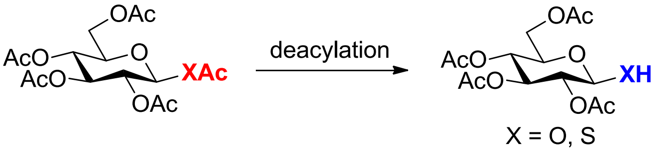
Table of Contents

1. General comments

All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized by warming 10% H_2SO_4 (10% H_2SO_4 in ethanol) sprayed plates on a hot plate. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China). 1,4-Dithiothreitol (DTT), paclitaxel (taxol) and dihydroartemisinin were purchased from Adamas and used without purified. NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz), and the ^{1}H and ^{13}C NMR chemical shifts were referenced to the solvent or solvent impurity peaks for $CDCl_3$ at δ_H 7.24 and δ_C 77.23, for DMF-d_7 at δ_H 8.02 and δ_C 163.15. Optical rotations were measured on a Perkin-Elmer 341LC polarimeter using a quartz cell with 3 mL capacity and a 1 dm path length. Concentrations (*c*) are given in g/100 ml. High resolution mass spectra were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI). Commercially available grades of organic solvents of adequate purity were used in all reactions.

2. Additional information of *S*-deacetylation reaction conditions optimization

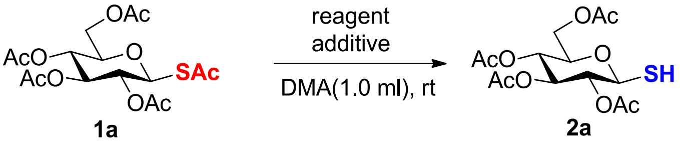
Table S1. Comparison among O- and *S*-deacylation reaction conditions[a]



Entry	Conditions	Ref.	X = O		X = S	
			t (h)	Yield (%)	t (h)	Yield (%)
1	Imidazole (1.0 eq.), CH_3OH, 40 ℃	1	26	71	1	46[b]
2	Ammonium acetate (2.0 eq.), DMF, rt	2	16	91	1	30[c]
3	$BnNH_2$ (1.5 eq.), THF, rt	3	16	90	1.5	89
4	DTT (1.5 eq), $NaHCO_3$ (0.1 eq), DMA, rt	This work	24	trace	1	98
5	L-Cysteine methyl ester hydrochloride (1.2 eq), TEA (1.0 eq), DMA, rt	This work	24	trace	1	94

[a]All reactions were conducted in 0.2 mmol scale. All yields were gained after purification by coloumn chromatography. [b]11% of the starting material was recovered; most of the starting material degraded. [c]Most of the starting material degraded.

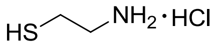
Table S2. Screening of reagents appropriate for the reaction[a]



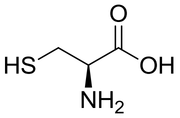
1a **2a**

Entry	Reagent(eq.)	Additive(eq.)	Time(h)	Yield[b]
1	**I** (1.2)	-	24	65% (30%)
2	**I** (1.2)	$NaHCO_3$ (0.1)	24	72% (15%)
3	**I** (1.2)	$NaHCO_3$ (1.0)	1	92%
4	**I** (1.2)	TEA (1.0)	1	93%
5	**II** (1.2)	-	12	52%[c]
6	**II** (1.2)	$NaHCO_3$ (0.1)	5	35%[c]
7	**III** (1.2)	-	24	80% (12%)

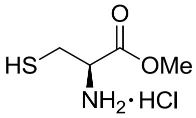
8	**III** (1.2)	$NaHCO_3$ (1.2)	1	95%
9	**III** (1.2)	$NaHCO_3$ (1.0)	1	94%
10	**III** (1.2)	$NaHCO_3$ (0.6)	5	88% (7%)
11	**III** (1.2)	TEA (1.0)	1	94%
12	**IV** (1.5)	-	24	20%^{c}
13	**IV** (1.5)	$NaHCO_3$ (0.1)	5	30%^{c}
14	**V** (1.2)	$NaHCO_3$ (0.1)	1	90%
15	**V** (1.5)	$NaHCO_3$ (0.1)	1	98%
16	**V** (1.5)	TEA (0.1)	1	98%
17	**V** (0.6)	$NaHCO_3$ (0.1)	24	75% (17%)
18	**V** (0.6)	$NaHCO_3$ (0.6)	24	74% (20%)
19	**V** (1.5)	-	24	65% (28%)
20	**VI** (1.5)	-	>24	No Reaction
21	**VI** (1.5)	$NaHCO_3$ (0.1)	48	-^{d}
22	**VII** (1.5)	-	24	30% (56%)
23	**VII** (1.5)	$NaHCO_3$ (0.1)	2	48% (40%)
24	**VIII** (1.5)	-	24	55% (36%)
25	**VIII** (1.5)	$NaHCO_3$ (0.1)	2	92%



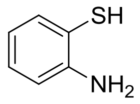
I



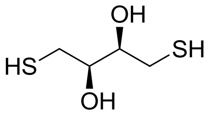
II



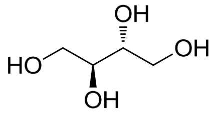
III



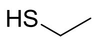
IV



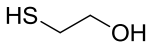
V



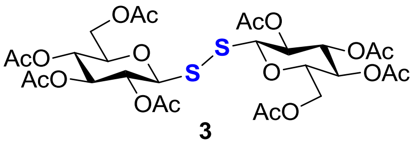
VI



VII



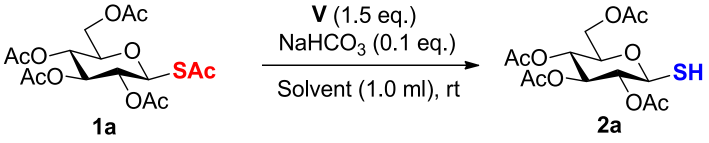
VIII



3

[a]The reactions were conducted in 0.2 mmol scale. Procedure: To a solution of **1a** and reagents (**I~VIII**) in DMA was added additive or nothing, and the mixture was stirred at room temperature for appropriate time. The reaction mixture was diluted with water and extracted with tolune. The combined organic layers were washed with water, brine, dried over Na_2SO_4, concentrated, and purified by flash chromatography. [b]Isolated yield, yield in parentheses was of recovered starting material. [c]Most of the starting material degraded. [d]76% of the starting material was recovered and yield 16% of disulfide bond linked glycoside (**3**)[4]: Colorless oil; R_f = 0.4 (petroleum-EtOAc 2:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (1H, dd, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 5.17 (1H, dd, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.07 (1H, dd, $J_{1,2} = J_{2,3} = 9.6$ Hz, H-2), 4.63 (1H, d, $J_{1,2} = 9.6$ Hz, H-1), 4.31 (1H, dd, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 4.4$ Hz, H-6a), 4.20 (1H, dd, $J_{6a,6b} = 12.4$ Hz, $J_{5,6b} = 2.0$ Hz, H-6b), 3.77 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6a} = 4.4$ Hz, $J_{5,6b} = 2.0$ Hz, H-5),2.11, 2.08, 2.00, 1.98 (12H, 4 × s, $COCH_3$).

Table S3. Screening of solvents appropriate for the reaction[a]

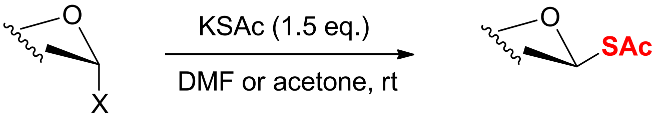


Entry	Solvent	Time(h)	Yield[b]
1	CH_3OH	2	90%
2	CH3CN	4	92%
3	$CHCl_3$	20	96%
4	CH_2Cl_2	20	96%
5	Toluene	20	95%
6	THF	72	trace
7	DMF	1	96%
8	DMA	1	98%

[a] All reactions were conducted in 0.2 mmol scale. Procedure: To a solution of **1a** and **V** was added 0.1 eq. $NaHCO_3$, and the mixture was stirred at room temperature for appropriate time. Then the reaction mixture was diluted with water and extracted with tolune. The combined organic layers were washed with water, brine, dried over Na_2SO_4, concentrated, and purified by flash chromatography. [b] Isolated yield.

3. Synthesis of thiolacetate derivatives

General procedure A.

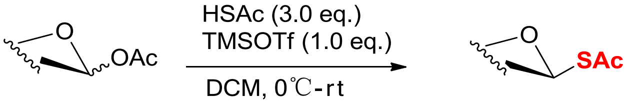


X = Br, Cl

(**1a-1c**, **1e-1i**, **1k-1m**, **1p**, **1r**, **1s**, **4**)

To asolution of the glycosyl halide (1.0 eq.) in acetone or DMF (0.3 M) was added potassium thioacetate (1.5 eq.). The mixture was stirred at room temperature until TLC indicated complete consumption of the starting material, then poured into water, and extracted with EtOAc. The organic layer was washed with water, brine, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography.

General procedure B.

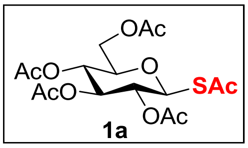


(**1d**, **1j**, **1n**, **1o**, **1q**)

Per-*O*-acetyl/benzyl glycoside (1.0 eq.) was coevaporated in toluene and dissolved in anhydrous CH_2Cl_2 (0.1 M), to which HSAc (3.0 eq.) was added, and cooled to 0 ℃. After addition of TMSOTf (1.0 eq.), the reaction was allowed to proceed at 0 ℃

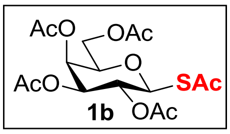
(compounds **1j**, **1n**, **1o**) or room temperature (compounds **1d** and **1q**) until TLC indicated complete consumption of the starting material, then poured into aqueous $NaHCO_3$, and extracted with EtOAc. The organic layer was washed successively with water and brine, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography.

2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-glucopyranose (1a)[5]:



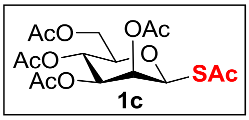
Prepared from 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide (3.0 g, 7.29 mmol) in acetone according to procedure A (8 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1a** (2.60 g, 88% yield) as white solid: R_f = 0.58 (petroleum-EtOAc 2:1). ^1H NMR (400 MHz, $CDCl_3$): δ 5.27 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 5.24 (1H, d, $J_{1,2}$ = 10.0 Hz, H-1), 5.13 – 5.06 (2H, m, H-2, H-4), 4.23 (1H, dd, $J_{6a,6b}$ = 12.8 Hz, $J_{5,6a}$ = 4.8 Hz, H-6a), 4.07 (1H, dd, $J_{6a,6b}$ = 12.8 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.81 (1H, ddd, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.36 (3H, s, $SCOCH_3$), 2.05, 2.01, 2.00, 1.98 (12H, 4 × s, $COCH_3$).

2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-galactopyranose (1b)[6]:



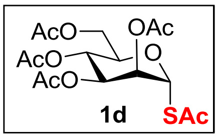
Prepared from 2,3,4,6-tetra-*O*-acetyl-*α*-D-galactopyranosyl bromide (2.5 g, 6.08 mmol) in acetone according to procedure A (6 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1b** (2.20 g, 90% yield) as white solid: R_f = 0.56 (petroleum-EtOAc 2:1). ^1H NMR (400 MHz, $CDCl_3$): δ 5.43 (1H, dd, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.31 (1H, dd, $J_{1,2}$ = 10.0 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.23 (1H, d, $J_{1,2}$ = 10.0 Hz, H-1), 5.09 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.2 Hz, H-3), 4.02–4.13 (3H, m, H-5, H-6a, H-6b), 2.37 (3H, s, $SCOCH_3$), 2.13, 2.02, 2.01, 1.96 (12H, 4 × s, $COCH_3$).

2,3,4,6-tetra-O-acetyl-1-S-acetyl-1-thio-β-D-mannopyranose (1c)[7]:



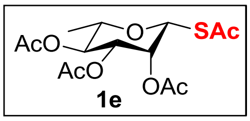
Prepared from 2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranosyl bromide (3.0 g, 7.29 mmol) in DMF according to procedure A (2 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1c** (1.68 g, 57% yield) as white solid: R_f = 0.58 (petroleum-EtOAc 2:1). ^1H NMR (400 MHz, $CDCl_3$): δ 5.47 (1H, d, $J_{1,2}$ = 1.2 Hz, H-1), 5.46 (1H, dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 1.2 Hz, H-2), 5.24 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.13 (1H, dd, $J_{3,4}$ = 10.0 Hz, $J_{2,3}$ =3.2 Hz, H-3), 4.24 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 5.6 Hz, H-6a), 4.10 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.80 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.6 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.35 (3H, s, $SCOCH_3$), 2.17, 2.06, 2.03, 1.96 (12H, 4 × s, $COCH_3$).

2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-*α*-D-mannopyranose (1d)[8]:



Prepared from per-*O*-acetylatedmannopyranose (500 mg, 1.28 mmol) in anhydrous CH_2Cl_2 according to procedure B (54 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1d** (410 mg, 79% yield) as white solid: R_f = 0.59 (petroleum-EtOAc 2:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (1H, d, $J_{1,2}$ = 1.6 Hz, H-1), 5.33 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.31 (1H, dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 1.6 Hz, H-2), 5.08 (1H, dd, $J_{3,4}$ = 10.0 Hz, $J_{2,3}$ = 3.2 Hz, H-3), 4.26 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.8 Hz, H-6a), 4.05 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.91 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.41 (3H, s, SCOCH_3), 2.16, 2.06, 2.02, 1.97 (12H, 4 × s, COCH_3).

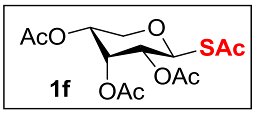
2,3,4-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-L-rhamnopyranose (1e)[9]:



1e

Prepared from 2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranosyl bromide (1.5 g, 4.24 mmol) in DMF according to procedure A (7 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1e** (768 mg, 52% yield) as white solid: R_f = 0.56 (petroleum-EtOAc 2:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (1H, d, $J_{1,2}$ = 1.6 Hz, H-1), 5.30 (1H, dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 1.6 Hz, H-2), 5.09 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 5.03 (1H, dd, $J_{3,4}$ = 9.2 Hz, $J_{2,3}$ = 3.2 Hz, H-3), 3.77 (1H, dq, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 6.0 Hz, H-5), 2.39 (3H, s, SCOCH_3), 2.15, 2.03, 1.97 (9H, 3 × s, COCH_3), 1.21 (3H, d, $J_{5,6}$ = 6.0 Hz, CH_3-6).

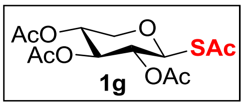
2,3,4-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-ribopyranose (1f)[10]:



1f

Prepared from 2,3,4-tri-*O*-acetyl-*α*-D-ribopyranosyl bromide (227 mg, 0.68 mmol) in acetone according to procedure A (3 h) and purified by flash column chromatography (petroleum-EtOAc 6:1) to give **1f** (180 mg, 80% yield) as white solid: R_f = 0.40 (petroleum-EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (1H, d, $J_{1,2}$ = 8.0 Hz, H-1), 5.47 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 3.2 Hz, H-3), 5.06 (1H, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 5.04 (1H, ddd, $J_{4,5a}$ = 8.0 Hz, $J_{4,5e}$ = 4.4 Hz, $J_{3,4}$ = 3.2 Hz, H-4), 3.93 (1H, dd, $J_{5a,5e}$ = 11.6 Hz, $J_{4,5e}$ = 4.4 Hz, H-5e), 3.85 (1H, dd, $J_{5a,5e}$ = 11.6 Hz, $J_{4,5a}$ = 8.0 Hz, H-5a), 2.38 (3H, s, SCOCH_3), 2.12, 2.04, 2.04 (9H, 3 × s, COCH_3).

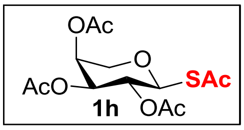
2,3,4-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-xylopyranose (1g)[10]:



1g

Prepared from 2,3,4-tri-*O*-acetyl-*α*-D-xylopyranosyl bromide (1.00 g, 2.96 mmol) in acetone according to procedure A (1 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1g** (813 mg, 82% yield) as white solid: R_f = 0.42 (petroleum-EtOAc 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (1H, d, $J_{1,2}$ = 8.4 Hz, H-1), 5.16 (1H, dd, $J_{3,4}$ = $J_{2,3}$ = 8.0 Hz, H-3), 4.98 (1H, dd, $J_{1,2}$ = 8.4 Hz, $J_{2,3}$ = 8.0 Hz, H-2), 4.89 (1H, ddd, $J_{4,5a}$ = 8.4 Hz, $J_{3,4}$ = 8.0 Hz, $J_{4,5e}$ = 4.8 Hz, H-4), 4.11 (1H, dd, $J_{5a,5e}$ = 12.0 Hz, $J_{4,5e}$ = 4.8 Hz, H-5e), 3.51 (1H, dd, $J_{5a,5e}$ = 12.0 Hz, $J_{4,5a}$ = 8.4 Hz, H-5a), 2.35 (3H, s, SCOCH_3), 2.03, 2.03, 2.02 (9H, 3 × s, COCH_3).

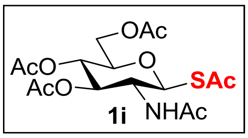
2,3,4-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*α*-L-arabinopyranose (1h)[10]:



1h

Prepared from 2,3,4-tri-*O*-acetyl-*β*-L-arabinopyranosyl bromide (600 mg, 1.78 mmol) in acetone according to procedure A (2 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1h** (500 mg, 84% yield) as white solid: R_f = 0.44 (petroleum-EtOAc 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (1H, d, $J_{1,2}$ = 7.2 Hz, H-1), 5.28 (1H, ddd, $J_{4,5a}$ = 4.8 Hz, $J_{3,4}$ = 3.2 Hz, $J_{4,5e}$ = 2.4 Hz, H-4), 5.21 (1H, dd, $J_{2,3}$ = 8.0 Hz, $J_{1,2}$ = 7.2 Hz, H-2), 5.12 (1H, dd, $J_{2,3}$ = 8.0 Hz, $J_{3,4}$ = 3.2 Hz, H-3), 3.97 (1H, dd, $J_{5a,5e}$= 12.8 Hz, $J_{4,5a}$ = 4.8 Hz, H-5a), 3.75 (1H, dd, $J_{5a,5e}$= 12.8 Hz, $J_{4,5e}$ = 2.4 Hz, H-5e), 2.36 (3H, s, $SCOCH_3$), 2.08, 2.04, 2.04 (9H, 3 × s, $COCH_3$).

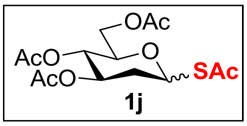
3,4,6-Tri-*O*-acetyl-*N*-acetyl-*S*-acetyl-1-thio-β-D-glucosamine (1i)[11]:



1i

Prepared from 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranosyl chloride (155 mg, 0.42 mmol) in DMF according to procedure A (5 h) and purified by flash column chromatography (petroleum-EtOAc 1:1) to give **2i** (106 mg, 62% yield) as white solid: R_f = 0.50 (petroleum-EtOAc 1:5).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 (1H, d, $J_{NH,2}$ = 10.0 Hz, NH), 5.13 (1H, d, $J_{1,2}$ = 10.8 Hz, H-1), 5.11 – 5.06 (2H, m, H-3, H-4), 4.35 (1H, m, H-2),4.21 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.4 Hz, H-6a), 4.06 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.76(1H, ddd, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 2.35 (3H, s, $SCOCH_3$), 2.06, 2.02, 2.02, 1.90 (12H, 4 × s, $COCH_3$)

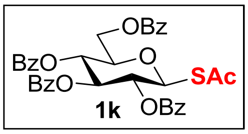
3,4,6-Tri-*O*-acetyl-2-deoxy-1-*S*-acetyl-1-thio-α/β-D-arabino-hexopyranose (1j)[12]:



1j

Prepared from per-*O*-acetylated-D-glucopyranose (121 mg, 0.37 mmol) in anhydrous CH_2Cl_2 according to procedure B (3 h) and purified by flash column chromatography (petroleum-EtOAc 7:1) to give **1j** (96 mg, 76% yield) as white solid: R_f = 0.60 (petroleum-EtOAc 5:1). Analysis by ^{1}H NMR indicated an anomeric mixture of 1-thiols (α/β, 1.4:1). α: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (1H, m, H-1), 5.06 – 4.98 (2H, m, H-3, H-4), 4.30 (1H, m, H-6a), 4.05 – 3.97 (1H, m, H-6b), 3.92 (1H, m, H-5), 2.37 (3H, s, $SCOCH_3$), 2.25 – 2.27 (1H, m, H-2eq), 2.05, 2.02, 2.00 (9H, 3 × s, $COCH_3$), 1.98 – 1.88 (1H, m, H-2ax). β: ^{1}H NMR (400 MHz, $CDCl_3$) δ5.28 (1H, m, H-1), 5.06 – 4.98 (2H, m, H-3, H-4), 4.24 (1H, m, H-6a), 4.05 – 3.97 (1H, m, H-6b), 3.73 (1H, m, H-5), 2.34 (3H, s, $SCOCH_3$), 2.25 – 2.27 (1H, m, H-2eq), 2.05, 2.02, 2.00 (9H, 3 × s, $COCH_3$), 1.88 – 1.98 (1H, m, H-2ax)

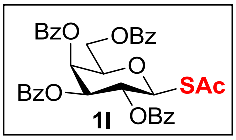
2,3,4,6-tetra-*O*-benzoyl-1-*S*-acetyl-1-thio-β-D-glucopyranose (1k)[13]:



1k

Prepared from 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (479 mg, 0.74 mmol) in DMF according to procedure A (5 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1k** (423 mg, 90% yield) as white solid: R_f = 0.52 (petroleum-EtOAc 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.24 (20H, m, Ar-H), 5.96 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.71 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 5.64 (1H, dd, $J_{1,2}$ =$J_{2,3}$ = 9.6 Hz, H-2), 5.61 (1H,d,$J_{1,2}$ = 9.6 Hz, H-1),4.59(1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.8 Hz, H-6a), 4.44 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.29 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6b}$ = 4.8 Hz,$J_{5,6a}$ = 2.8 Hz, H-5), 2.30 (3H, s, SCOCH_3).

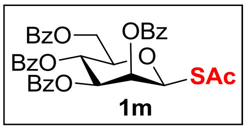
2,3,4,6-tetra-*O*-benzoyl-1-*S*-acetyl-1-thio-*β*-D-galactopyranose (1l)[14]:



1l

Prepared from 2,3,4,6-tetra-*O*-benzoyl-*α*-D-galactopyranosyl bromide (184 mg, 0.29 mmol) in DMF according to procedure A (2 h) and purified by flash column chromatography (petroleum-EtOAc 6:1) to give **1l** (135 mg, 72% yield) as white solid: R_f = 0.32 (petroleum-EtOAc 4:1).^{1}H NMR (400 MHz, CDCl$_3$) δ8.06-7.20 (20H, m, Ar-H), 6.04 (1H, dd, $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.89 (1H, dd, $J_{1,2}$ =$J_{2,3}$ = 10.4 Hz, H-2), 5.70 (1H, dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 5.61 (1H, d, $J_{1,2}$ = 10.4 Hz, H-1), 4.60 (1H, dd, $J_{6a,6b}$ = 11.2 Hz, $J_{5,6a}$ = 6.4 Hz, H-6a), 4.47 (1H, ddd, $J_{5,6a}$ = $J_{5,6b}$ = 6.4 Hz, $J_{4,5}$ = 0.8 Hz, H-5), 4.35 (1H, dd, $J_{6a,6b}$ = 11.2 Hz, $J_{5,6b}$ = 6.4 Hz, H-6b), 2.32 (3H, s, SCOCH_3).

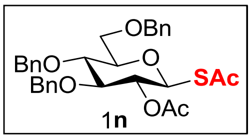
2,3,4,6-tetra-*O*-benzoyl-1-*S*-acetyl-1-thio-*β*-D-mannopyranose (1m):



1m

Prepared from 2,3,4,6-tetra-*O*-benzoyl-*α*-D-mannopyranosyl bromide (232 mg, 0.36 mmol) in DMF according to procedure A (3 h) and purified by flash column chromatography (petroleum-EtOAc 6:1) to give **1m** (133 mg, 56% yield) as white solid: R_f = 0.30 (petroleum-EtOAc 3:1). $[\alpha]_D^{20}$ — 56.6 (*c*, 1.9 in CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ8.10-7.24 (20H, m, Ar-H), 6.05 (1H, dd, $J_{3,4}$ = $J_{4,5}$= 10.0 Hz, H-4), 5.99 (1H, dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 0.8 Hz, H-2), 5.83 (1H, d, $J_{1,2}$ = 0.8 Hz, H-1), 5.72 (1H, dd, $J_{3,4}$ = 10.0 Hz, $J_{2,3}$ = 3.2 Hz, H-3), 4.68 (1H, dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 2.4 Hz, H-6a), 4.48 (1H, dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.30 (1H, ddd, $J_{4,5}$= 10.0 Hz,$J_{5,6b}$ = 4.0 Hz,$J_{5,6a}$ = 2.4 Hz, H-5), 2.35 (3H, s, SCOCH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ191.9(S*C*OCH$_3$), 166.3, 165.7, 165.4, 165.3(4 ×Ph*C*O), 133.8, 133.7, 133.5, 133.3, 130.2, 130.2, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 129.2, 129.0, 128.9, 128.8, 128.8, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5 (24 ×C-Ar), 79.9(C-1), 77.1(C-5), 72. 9(C-3), 71.7 (C-2), 66.3 (C-4), 63.0(C-6), 30.9 (SCO*C*H$_3$). HRMS calc. for $C_{36}H_{30}NaO_{10}S$ $[M+Na]^+$: 677.1452, found: 677.1426.

1,2-di-*S*,*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranose (1n)[15]:

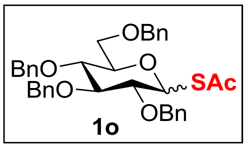


1n

Prepared from 1,2-di-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (233 mg, 0.44 mmol) in anhydrous CH$_2$Cl$_2$ according to procedure B (3 h) and purified by flash column chromatography (DCM) to give **1n** (196 mg, 82% yield) as white solid: R_f = 0.52 (DCM-EtOAc 200:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ7.31 – 7.10 (15H, m, Ar-H), 5.12 (1H, d, $J_{1,2}$ = 10.4 Hz, H-1), 5.07 (1H, dd, $J_{1,2}$ = 10.4 Hz, $J_{2,3}$ = 8.4 Hz, H-2), 4.81 – 4.44 (6H, m, 3 × CH$_2$Ph), 3.79 – 3.68 (4H, m, H-3, H-4, H-6a, H-6b), 3.58 (1H, m, H-5), 2.34 (3H, s, SCOCH_3), 1.90 (3H, s, COCH_3); ^{13}C NMR (100 MHz, CDCl$_3$) δ193.2 (S*C*OCH$_3$), 169.8 (*C*OCH$_3$), 138.3, 138.1, 138.1, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6,128.1,128.1,128.1,128.1,128.0,128.0, 127.9, 127.9, 127.9 (18 × C-Ar), 84.5

(C-1), 80.5 (C-2), 79.9 (C-5), 77.6 (C-3), 75.5, 75.2, 73.6 (3 × Ph*C*H), 71.2 (C-4), 68.5 (C-6).

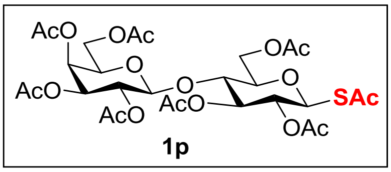
2,3,4,6-tetra-*O*-benzyl-1-*S*-acetyl-1-thio-*β*-D-glucopyranose (1o)[16]:



1o

Prepared from 1-O-acetyl-2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (400 mg, 0.69 mmol) in anhydrous CH_2Cl_2 according to procedure B (1 h) and purified by flash column chromatography (petroleum-EtOAc 10:1) to give **1o** (328 mg, 80% yield) as colorless oil: R_f = 0.42 (petroleum-EtOAc 5:1). Analysis by ^{1}H NMR indicated an anomeric mixture of 1-thioacetyl glycosides (*α*/*β*, 10:1). *α*: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.27 – 7.05 (20H, m, Ar-H), 6.19 (1H, d, $J_{1,2}$ = 5.2 Hz, H-1), 4.91 – 4.38 (8H, m, 4 × CH_2Ph), 3.85 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 5.2 Hz, H-2), 3.70 – 3.47 (5H, m, H-3, H-4, H-5, H-6a, H-6b), 2.36 (3H, s, SCOCH_3). *β*: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.27 – 7.05 (20H, m, Ar-H), 5.10 (1H, d, $J_{1,2}$ = 10.4 Hz, H-1), 4.82 – 4.38 (8H, m, 4 × CH_2Ph), 3.70 – 3.47 (6H, m, H-2, H-3, H-4, H-5, H-6a, H-6b), 2.31 (3H, s, SCOCH_3).

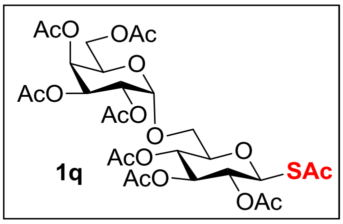
2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl(1→4)-2,3,6-tri-*O*-acetyl-l-*S*-acetyl-1-thio-*β*-D-glucopyranose (1p)[17]:



1p

Prepared from 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl(1⟶4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (260 mg, 0.37 mmol) in DMF according to procedure A (4 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **1p** (208 mg, 81% yield) as white solid: R_f= 0.29 (petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (1H, dd, $J_{3',4'}$= 3.4 Hz, $J_{4',5'}$= 0.8 Hz, H-4'), 5.23 (1H, dd, $J_{3,4}$ = 10.4 Hz, $J_{2,3}$ = 9.2 Hz, H-3), 5.19 (1H, d, $J_{1,2}$ = 10.4 Hz, H-1), 5.09 (1H, dd, $J_{2',3'}$= 10.4 Hz, $J_{1',2'}$ = 8.0 Hz, H-2'), 5.02 (1H, dd, $J_{1,2}$ = 10.4 Hz, $J_{2,3}$ = 9.2 Hz, H-2), 4.92 (1H, dd, $J_{2',3'}$= 10.4 Hz, $J_{3',4'}$= 3.4 Hz, H-3'), 4.44 (1H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.43 (1H, dd, $J_{6'a,6'b}$ = 12.4, $J_{5',6'a}$ =1.6 Hz, H-6'a), 4.12 – 4.03 (3H, m, H-6a, H-6b, H-6'b), 3.84 (1H, m, H-5'), 3.79 (1H, dd, $J_{3,4}$ = $J_{4,5}$= 10.4 Hz, H-4), 3.72 (1H, ddd, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 2.35 (3H, s, SCOCH_3), 2.13, 2.09, 2.05, 2.02, 2.02, 2.00, 1.94 (21H, 7 × s, COCH_3).

2,3,4,6-Tetra-*O*-acetyl-*α*-D-galactopyranosyl(1→6)-2,3,4-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-glucopyranoside (1q)[17]:

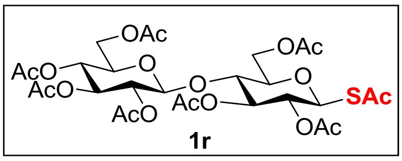


1q

Prepared from per-O-acetylated melibiose (84 mg, 0.12 mmol) in anhydrous CH_2Cl_2 according to procedure B (34 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **1q** (54 mg, 67% yield) as white solid: R_f = 0.42 (petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (1H, dd, $J_{3',4'}$ =3.2 Hz, $J_{4',5'}$ = 0.8 Hz, H-4'), 5.30 (1H, dd, $J_{2',3'}$ = 10.8 Hz, $J_{3',4'}$ = 3.2 Hz, H-3'), 5.25 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.20 (1H, d, $J_{1,2}$ = 10.8 Hz, H-1), 5.14 – 5.11 (1H, m, H-2'), 5.08

(1H, d, $J_{1',2'}$ = 3.6 Hz, H-1'), 5.08 – 5.01 (2H, m, H-2, H-4), 4.16 (1H, m, H-5'), 4.08 – 3.98 (2H, m, H-6'a, H-6'b), 3.78 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 3.67 (1H, dd, $J_{6a,6b}$ = 11.6 Hz, $J_{5,6a}$ = 4.8 Hz, H-6a),3.58 (1H, dd, $J_{6a,6b}$ = 11.6 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 2.37 (3H, s, $SCOCH_3$), 2.12, 2.11, 2.03, 2.03, 2.00, 1.98, 1.96(21H, 7 × s, $COCH_3$).

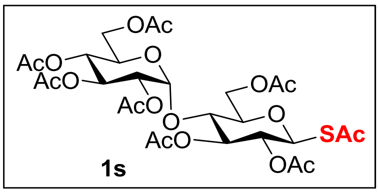
2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl(1→4)-2,3,6-tri-*O*-acetyl-l-*S*-acetyl-1-thio-*β*-D-glucopyranose (1r)[17]:



1r

Prepared from 2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl(1→4)-2,3,6-tri-O-acetyl-*α*-D-glucopyranosyl bromide (584 mg, 0.85 mmol) in DMF according to procedure A (3 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **1r** (450 mg, 76% yield) as white solid: R_f = 0.43 (petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 8.8 Hz, H-3), 5.17 (1H, d, $J_{1,2}$ = 10.0 Hz, H-1), 5.11 (1H,dd, $J_{2,3}$ = $J_{3,4}$ = 8.8 Hz, H-3'), 5.05 – 5.00 (2H,m, H-4, H-4'), 4.89 (1H, dd, $J_{2',3'}$= 8.8 Hz, $J_{1',2'}$ = 7.6 Hz, H-2'), 4.47 (1H, d, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.45 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 1.6 Hz, H-6a), 4.33 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.4 Hz, H-6b), 4.07 (1H, dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 4.4 Hz, H-6'a), 4.01 (1H, dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 2.0 Hz, H-6'b), 3.77 (1H, dd, $J_{1,2}$ = 10.0 Hz, $J_{2,3}$ = 8.8 Hz, H-2), 3.71 (1H, ddd, $J_{4,5}$ = 9.2 Hz, $J_{5,6b}$ = 4.4 Hz, $J_{5,6a}$ = 1.6 Hz, H-5), 3.62 (1H, ddd, $J_{4',5'}$= 9.6 Hz, $J_{5',6'a}$ = 4.4 Hz, $J_{5',6'b}$ = 2.0 Hz, H-5'), 2.34 (3H, s, $SCOCH_3$), 2.09, 2.06, 2.01, 1.99, 1.99, 1.98, 1.95(21H, 7 × s, $COCH_3$).

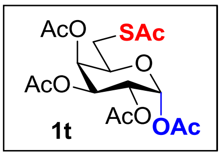
2,3,4,6-Tetra-*O*-acetyl-*α*-D-glucopyranosyl(1→4)-2,3,6-tri-*O*-acetyl-l-*S*-acetyl-1-thio-*β*-D-glucopyranose (1s)[17]:



1s

Prepared from 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl(1→4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (601 mg, 0.88 mmol) in DMF according to procedure A (4 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **1s** (200 mg, 33% yield) as white solid: R_f = 0.48 (petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (1H, d, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.33 (1H, dd, $J_{2',3'}$= 10.4 Hz, $J_{3',4'}$= 9.6 Hz, H-3'), 5.30 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 5.26 (1H, d, $J_{1,2}$ = 10.4 Hz, H-1), 5.03 (1H, dd, $J_{3',4'}$= $J_{4',5'}$= 9.6 Hz, H-4'), 4.95 (1H, dd, $J_{1,2}$ = 10.4 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.83 (1H, dd, $J_{2',3'}$= 10.4 Hz, $J_{1',2'}$ = 4.0 Hz, H-2'), 4.42 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.0 Hz, H-6a), 4.21 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.18 (1H, dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 4.0 Hz, H-6a'), 4.00 (1H, dd, $J_{6'a,6'b}$ = 12.4, $J_{5',6'a}$ =1.6 Hz, H-6'b), 3.99 (1H, dd, $J_{3,4}$ = $J_{4,5}$= 9.2 Hz, H-4), 3.91 (1H, ddd, $J_{4',5'}$= 9.6 Hz, $J_{5',6'a}$ = 4.0 Hz, $J_{5',6'b}$ = 1.6 Hz, H-5'), 3.80 (1H, ddd, $J_{4,5}$ = 9.2 Hz, $J_{5,6b}$ = 4.0 Hz, $J_{5,6a}$ = 2.0 Hz, H-5), 2.35 (3H, s, $SCOCH_3$), 2.10, 2.07, 2.03, 2.00, 1.98, 1.97, 1.97 (21H, 7 × s, $COCH_3$).

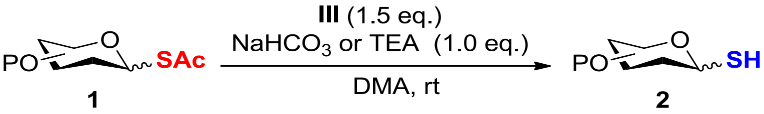
1,2,3,4-Tetra-*O*-acetyl-6-*S*-acetyl-6-thio-*α*-D-galactopyranose (1t)[18]:


1t

1:2,3:4-di-*O*-isopropylidene-6-*S*-acetyl-6-thio-*α*-D-galactopyranose (318 mg, 1 mmol) was dissolved in Ac_2O (18 ml) and HOAc (18 ml glacial) at 0 ℃. Concentrated H_2SO_4 (370 ul) was added dropwise while stirring for 30 min at 0 ℃. The reaction proceeded for 20 h during which time it was allowed to warm to rt. The reaction was poured over ice-water and extracted with CH_2Cl_2. The organic layer was washed successively with ice-cold water and satd. aq. $NaHCO_3$, dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1t** (252 mg, 62% yield) as white solid: R_f = 0.62 (petroleum-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 5.49 (1H, m, H-4), 5.29 (2H, m, H-2, H-3), 4.11 (1H, m, H-5), 3.05 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6b}$ = 7.6 Hz, H-6a), 2.95 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6b}$ = 6.8 Hz, H-6b), 2.31 (3H, s, SCOCH_3), 2.16, 2.13, 1.99, 1.98 (12H, 4 × s, COCH_3).

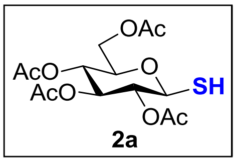
4. Synthesis of glycosyl thiols

General procedure C.



To a 0.15 M solution of thiolacetate derivative (0.2 mmol, 1.0 eq.) and **III** (0.24 mmol, 1.2 eq.) in DMA was added $NaHCO_3$ or TEA (0.2 mmol, 1.0 eq.), and the mixture was stirred at room temperature until complete consumption of the starting material. The reaction mixture was poured into water and extracted with tolune three times. The combined organic layers were washed with water, brine and concentrated to furnish the crude product, which was purified over silica gel chromatography.

2,3,4,6-Tetra-*O*-acetyl-1-thio-*β*-D-glucopyranose (2a)[4]:


2a

Prepared from **1a** (82 mg, 0.2 mmol) according to procedure C (1 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2a** (69 mg, 95% yield) as white solid: R_f = 0.48(petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) 5.17 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.08 (1H, dd, $J_{3,4}$ = $J_{4,5}$ =9.6 Hz, H-4), 4.95 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 9.6 Hz, H-2), 4.53 (1H, dd, $J_{1,2}$ = $J_{1,SH}$ = 9.6 Hz, H-1), 4.23 (1H, dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.8 Hz, H-6a), 4.11 (1H, dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.70 (1H, ddd, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.29 (1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.08, 2.06, 2.00, 1.99 (12H, 4 × s, COCH_3).

In fact, the simple extraction of the water quenched reaction mixture with toluene without further purification produced the desired product with satisfactory purity (Figure S1):

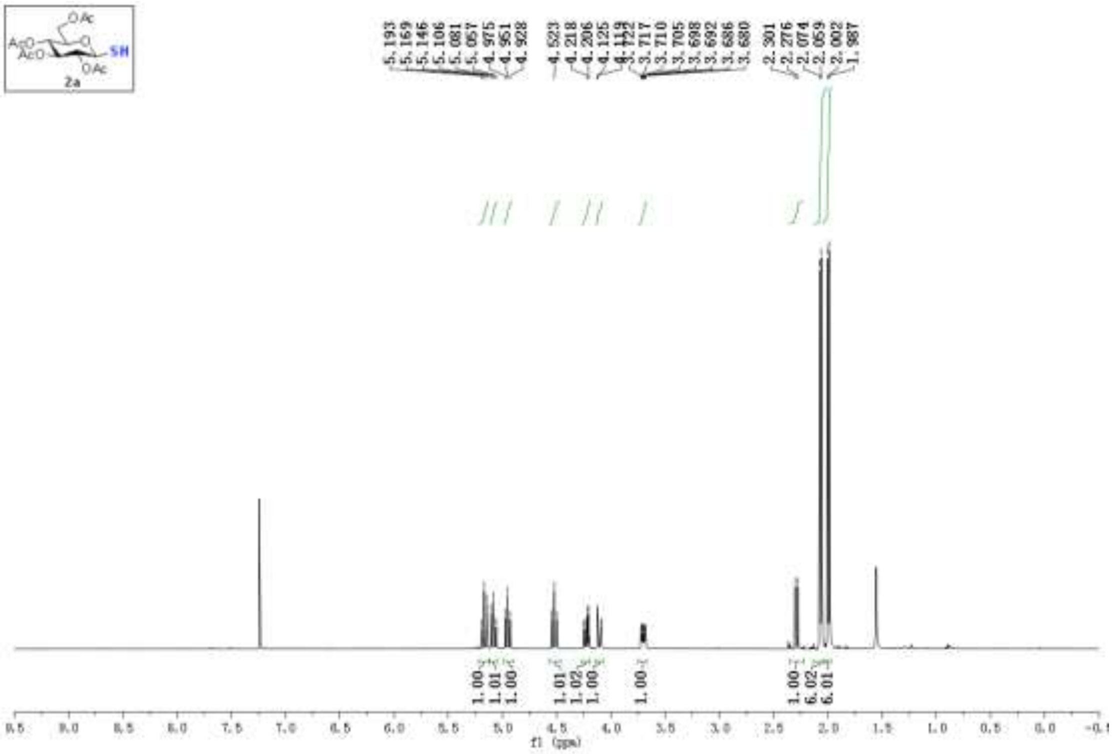
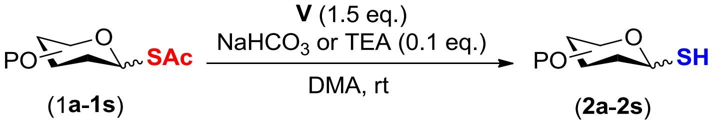


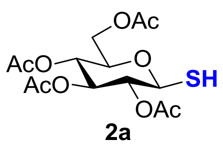
Figure S1. ^{1}H NMR spectrum of crude **2a** prepared with **III** in $CDCl_3$ (>95% purity)

General procedure D.



To a 0.15 M solution of thiolacetate derivative (0.2 mmol, 1.0 eq.) and **V** (0.3 mmol, 1.5 eq.) in DMA was added $NaHCO_3$ or TEA (0.02 mmol, 0.1 eq.), and the mixture was stirred at room temperature for an appropriate time until complete consumption of the starting material. The reaction mixture was poured into water and extracted with tolune three times. The combined organic layers were washed with water, brine and concentrated to furnish the crude product, which was further purified over silica gel chromatography.

2,3,4,6-Tetra-*O*-acetyl-1-thio-*β*-D-glucopyranose (2a)[4]:



2a

Prepared from **1a** (82 mg, 0.2 mmol) according to the general procedure D (1 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **1b** (72 mg, 98% yield) as white solid.

In fact, the simple extraction of the water quenched reaction mixture with toluene without further purification produced **1b** with satisfactory purity (Figure S2).

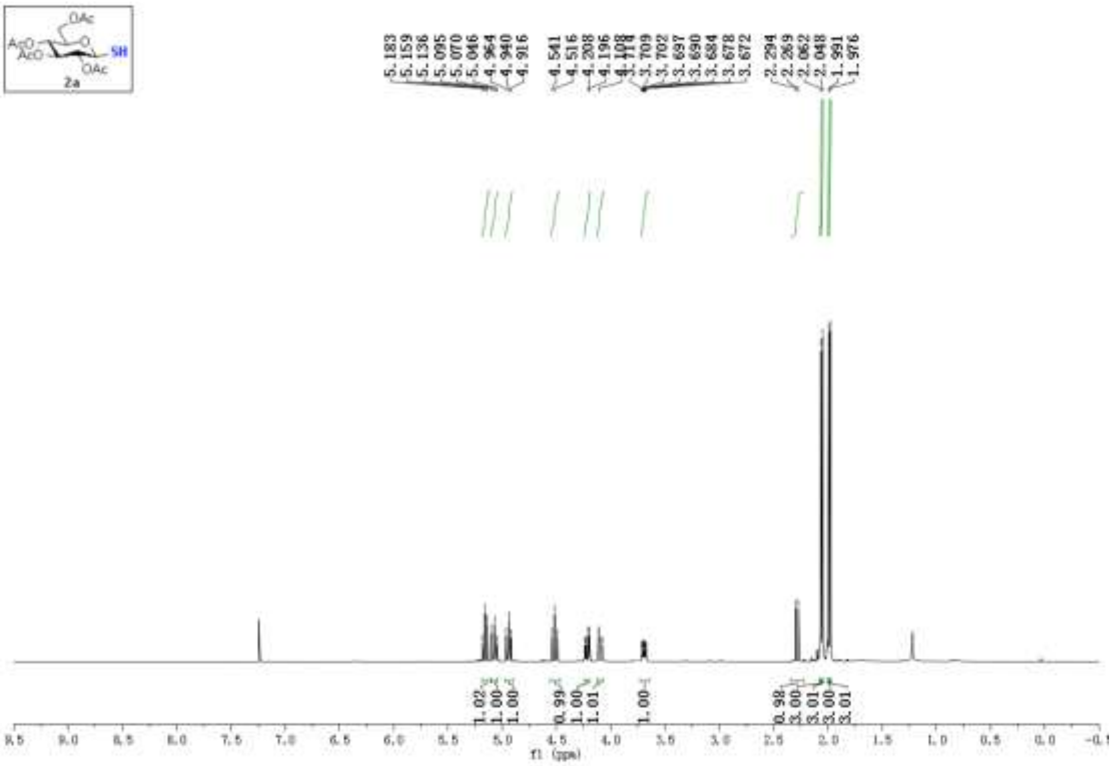
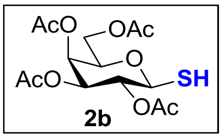


Figure S2. ^{1}H NMR spectrum of crude **2a** prepared with **V** in $CDCl_3$ (>95% purity)

2,3,4,6-Tetra-*O*-acetyl-1-thio-*β*-D-galactopyranose (2b)[4]**:**



Prepared from **1b** (82 mg, 0.2 mmol) according to the general procedure D (1 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2b** (71 mg, 97% yield) as colorless oil: R_f = 0.S50 (petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (1H, dd, $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.13 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, H-2), 4.96 (1H, dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6 Hz, H-3), 4.48 (1H, dd, $J_{1,2}$ = $J_{1,SH}$ = 10.0 Hz, H-1), 4.08 – 4.06 (2H, m, H-6a, H-6b), 3.90 (1H, ddd, $J_{5,6a}$ = $J_{5,6b}$ =6.8 Hz, $J_{4,5}$ = 0.8 Hz, H-5), 2.32 (1H, d, $J_{1,SH}$ = 10.0 Hz, SH), 2.11, 2.04, 2.00, 1.93 (12H, 4 × s, $COCH_3$).

Gram-scale synthesis of 2b:

To a solution of **1b** (4.92 mmol, 1.0 eq.) and **V** (7.38 mmol, 1.5 eq.) in DMA was added 0.1 eq $NaHCO_3$, and the mixture was stirred at room temperature for 1h. The reaction mixture was poured into water and extracted with tolune three times. The combined organic layers were washed with water, brine and concentrated to furnish the crude product **2b** (1.68 g, 94%). Without further purification, the perfect purity was confirmed by NMR analysis (Figure S3):

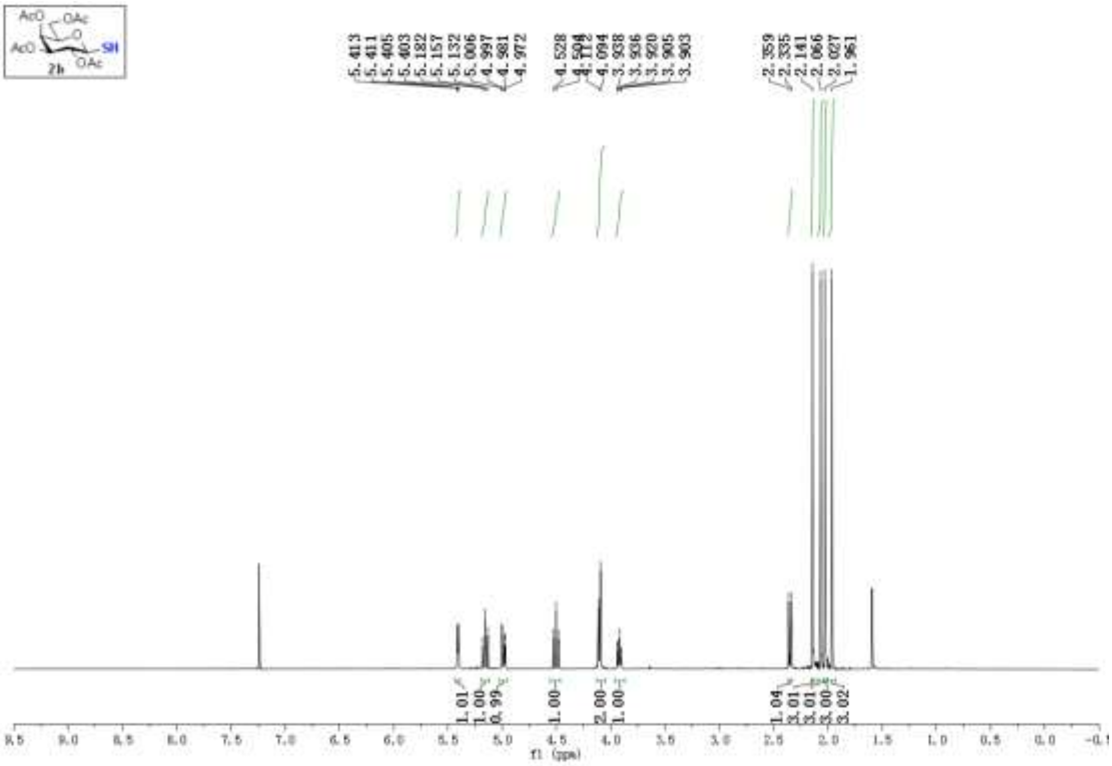
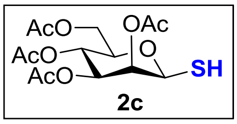


Figure S3. ^{1}H NMR spectrum of crude **2b** prepared with **V** at gram-scale in $CDCl_3$ (>95% purity)

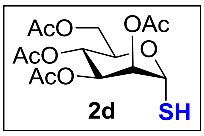
2,3,4,6-Tetra-*O*-acetyl-1-thio-*β*-D-mannopyranose (2c)[19]:



2c

Prepared from **1c** (82 mg, 0.2 mmol) according to the general procedure D (1.5 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2c** (64 mg, 88% yield) as white solid: R_f = 0.48(petroleum-EtOAc 1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ5.42 (1H, dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 0.8 Hz, H-2), 5.21 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.06 (1H, dd, $J_{3,4}$ = 10.0 Hz, $J_{2,3}$ = 3.2 Hz, H-3), 4.87 (1H, dd, $J_{1,SH}$ = 9.6 Hz, $J_{1,2}$ = 0.8 Hz, H-1), 4.22 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 5.6 Hz, H-6a), 4.11 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.69 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.6 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.52 (1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.22, 2.08, 2.02, 1.96 (12H, 4 × s, $COCH_3$).

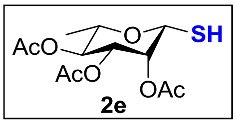
2,3,4,6-Tetra-*O*-acetyl-1-thio-*α*-D-mannopyranose (2d)[19]:



2d

Prepared from **1d** (82 mg, 0.2 mmol) according to the general procedure D (2 h) and purified by flash column chromatography (petroleum-EtOAc 4:1) to give **2d** (49 mg, 67% yield) as white solid: R_f = 0.3 (petroleum-EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (1H, d, J = 6.4 Hz, H-1), 5.36 – 5.23 (3H, m, H-2, H-3, H-4), 4.34 (1H, m, H-5), 4.29 (1H, dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 4.8 Hz, H-6a), 4.10 (1H, dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 2.0 Hz, H-6b), 2.25 (1H, d, J = 6.9 Hz, SH), 2.15 (3H, s, $COCH_3$), 2.09 (3H, s, $COCH_3$), 2.04 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$).

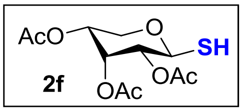
2,3,4-Tri-*O*-acetyl-1-thio-*β*-L-rhamnopyranose (2e)[20]:



2e

Prepared from **1e** (70 mg, 0.2 mmol) according to the general procedure D (1 h) and purified by flash column chromatography (petroleum-EtOAc 7:1) to give **2e** (55 mg, 89% yield) as white solid: R_f = 0.5 (petroleum-EtOAc 1.5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (1H, dd, $J_{2,3}$ = 2.8 Hz, $J_{1,2}$ = 1.2 Hz, H-2), 5.03 – 5.00 (2H, m, H-3, H-4), 4.83 (1H, dd, $J_{1,SH}$ = 9.6 Hz, $J_{1,2}$ = 1.2 Hz, H-1), 3.58 – 3.52 (1H, m, H-5), 2.47 (1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.21, 2.03, 1.96 (9H, 3 × s, $COCH_3$), 1.25 (3H, d, $J_{5,6}$ = 6.4 Hz, CH_3).

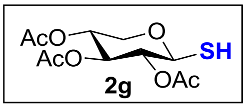
2,3,4-Tri-*O*-acetyl-1-thio-*β*-D-ribopyranose (2f)[21]:



2f

Prepared from **1f** (67 mg, 0.2 mmol) according to the general procedure D (1.5 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2f** (43 mg, 73% yield) as colorless syrup: R_f = 0.3 (petroleum-EtOAc 2:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (1H, dd, $J_{2,3}$ =$J_{3,4}$ = 2.8 Hz, H-3), 5.06 (1H, ddd, $J_{4,5a}$ = 8.8 Hz,$J_{4,5e}$ = 4.4 Hz,$J_{3,4}$ = 2.8 Hz,H-4), 4.96 (1H, dd, $J_{1,SH}$ = $J_{1,2}$ = 8.0 Hz, H-1), 4.90 (1H, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 2.8 Hz,H-2), 4.04 (1H, dd, $J_{5a,5e}$= 11.6 Hz, $J_{4,5e}$ = 4.4 Hz, H-5e), 3.75 (1H, dd, $J_{5a,5e}$= 11.6 Hz, $J_{4,5a}$ = 8.8 Hz, H-5a), 2.13 (1H, d, $J_{1,SH}$ = 8.8 Hz, SH), 2.11, 2.07, 2.02(9H, 3 × s, $COCH_3$).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.8, 169.7 (3 ×$COCH_3$), 76.5(C-1), 71.5(C-3), 67.6(C-2), 66.6 (C-4), 64.2 (C-5), 21.0, 20.9, 20.9(3 ×$COCH_3$).

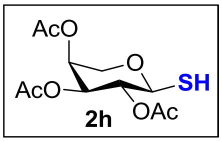
2,3,4-Tri-*O*-acetyl-1-thio-*β*-D-xylopyranose (2g)[21]:



2g

Prepared from **1g** (67 mg, 0.2 mmol) according to the general procedure D (1 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2g** (56 mg, 96% yield) as colorless syrup: R_f= 0.3 (petroleum-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (1H, dd, $J_{2,3}$ = $J_{3,4}$= 8.8 Hz, H-3), 4.96 (1H, ddd, $J_{4,5a}$ = 9.6 Hz, $J_{3,4}$ = 8.8 Hz, $J_{4,5e}$ = 5.2 Hz, H-4), 4.89 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 8.8 Hz, H-2), 4.54 (1H, dd, $J_{1,SH}$ = 10.0 Hz, $J_{1,2}$ = 8.8 Hz, H-1) 4.18 (1H, dd, $J_{5a,5e}$= 11.6 Hz, $J_{4,5e}$ = 5.2 Hz, H-5e), 3.36 (1H, dd, $J_{5a,5e}$= 11.6 Hz, $J_{4,5a}$ = 9.6 Hz, H-5a), 2.26 (1H, d, $J_{1,SH}$ = 10.0 Hz, SH), 2.06, 2.02, 2.02 (9H, 3 × s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.0, 169.9 (3 ×$COCH_3$), 79.2 (C-1), 73.5(C-3), 72.6(C-2), 68.8(C-4), 66.5 (C-5), 21.0, 20.9, 20.9 (3 ×$COCH_3$).

2,3,4-Tri-*O*-acetyl-1-thio-*α*-L-arabinopyranose (2h)[22]:

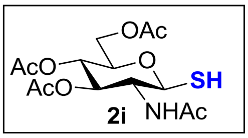


2h

Prepared from **1h** (67 mg, 0.2 mmol) according to the general procedure D(1 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2h** (54 mg, 92% yield) as white crystalline product: R_f = 0.3 (petroleum-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (1H, ddd, $J_{3,4}$ = 3.6 Hz, $J_{4,5a}$ = 2.8 Hz,$J_{4,5e}$ = 1.6 Hz, H-4), 5.17 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 9.2 Hz, H-2), 5.02 (1H, dd, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 4.53 (1H, dd, $J_{1,SH}$ = 9.6 Hz, $J_{1,2}$ = 9.2 Hz, H-1), 4.06 (1H, dd, $J_{5a,5e}$= 13.2 Hz, $J_{4,5a}$ = 2.8 Hz, H-5a), 3.67 (1H, dd, $J_{5a,5e}$= 13.2 Hz, $J_{4,5e}$ = 1.6 Hz, H-5e), 2.35 (1H, d, $J_{1,SH}$ =

9.6 Hz, SH), 2.13, 2.08, 2.01 (9H, 3 × s, COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 170.0(3 ×COCH$_3$), 79.3(C-1), 71.5(C-3), 71.0(C-2), 68.1 (C-4), 67.3(C-5), 21.1, 21.1, 20.9 (3 ×COCH$_3$).

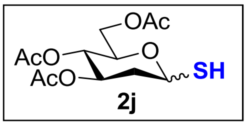
3,4,6-Tri-*O*-acetyl-1-thio-2-acetamido-2-deoxy-*β*-D-glucopyranose (2i)[4]:



2i

Prepared from **1i**(82 mg, 0.2 mmol) according to the general procedure D(2 h) and purified by flash column chromatography (petroleum-EtOAc 1:1) to give **2i** (66 mg, 90% yield) as white solid: R_f = 0.6(DCM-MeOH 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (1H, d, $J_{2,NH}$ = 9.6 Hz, NH), 5.11 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-4), 5.05 (1H, dd, $J_{3,4}$ = $J_{4,5}$ =9.6 Hz, H-3), 4.55 (1H, dd, $J_{1,2}$ = 9.6 Hz, $J_{1,SH}$ = 9.2 Hz, H-1), 4.22 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.8 Hz, H-6a), 4.10 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.4 Hz, H-6b), 4.07 (1H, ddd, $J_{1,2}$ = $J_{2,3}$ =$J_{2,NH}$ =9.6 Hz, H-2), 3.66 (1H, ddd, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.55 (1H, d, $J_{1,SH}$ = 9.2 Hz, SH), 2.08, 2.02, 2.01, 1.96 (12H, 4 ×s, COCH_3).

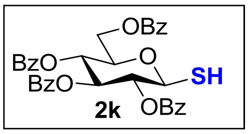
3,4,6-Tri-*O*-acetyl-2-deoxy-1-thio-*α*/*β*-D-arabino-hexopyranose (2j)[23]:



2j

Prepared from **1j** (70 mg, 0.2 mmol) according to the general procedure D(2 h) and purified by flash column chromatography (petroleum-EtOAc 1:1) to give **2j** (47 mg, 77% yield) as colorless syrup: R_f = 0.42 (petroleum-EtOAc 1:1). Analysis by ^{1}H NMR indicated an anomeric mixture of 1-thiols(α/β, 1.4:1). *α*: ^{1}H NMR (400 MHz, $CDCl_3$) δ5.75 (1H, ddd, $J_{1,SH}$ = 6.0 Hz, $J_{1,2ax}$ = 5.6 Hz, $J_{1,2eq}$ = 1.0 Hz, H-1), 5.24 (1H, ddd, $J_{2ax,3}$= 11.2 Hz, $J_{3,4}$ = 9.2 Hz,$J_{2eq,3}$ = 4.8 Hz, H-3), 4.98 (1H, dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.2 Hz, H-4), 4.38 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 4.32 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.4 Hz, H-6a), 4.06 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.0 Hz, H-6b), 2.26 (1H, ddd, $J_{2eq,2ax}$= 13.6 Hz, $J_{2eq,3}$ = 4.8 Hz, $J_{1,2eq}$ = 1.0Hz, H-2eq), 2.17 (1H, ddd, $J_{2eq,2ax}$= 13.6 Hz, $J_{2ax,3}$ = 11.2 Hz, $J_{1,2ax}$ = 5.6 Hz, H-2ax), 2.16 (1H, d, $J_{1,SH}$ = 6.0 Hz, SH), 2.06, 2.03, 1.99 (9H, 3 × s, COCH_3). *β*: ^{1}H NMR (400 MHz, $CDCl_3$) 4.98 (1H, ddd, $J_{2ax,3}$= 12.0 Hz, $J_{3,4}$ = 9.6 Hz,$J_{2eq,3}$ = 4.0 Hz, H-3), 4.96 (1H, dd, $J_{4,5}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 4.71 (1H, ddd, $J_{1,2ax}$ = 11.2 Hz, $J_{1,SH}$ = 8.8 Hz, $J_{1,2eq}$ = 2.0 Hz, H-1), 4.22 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 5.2 Hz, H-6a), 4.03 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.62 (1H, ddd, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 2.50 (1H, ddd, $J_{2eq,2ax}$= 12.8 Hz, $J_{2eq,3}$ = 4.0 Hz, $J_{1,2eq}$ = 2.0Hz, H-2eq), 2.47 (1H, d, $J_{1,SH}$ = 8.8 Hz, SH), 1.84 (1H, ddd, $J_{2eq,2ax}$= 12.8 Hz, $J_{2ax,3}$ = 12.0 Hz, $J_{1,2ax}$ = 11.2 Hz, H-2ax), 2.06, 2.01, 2.00(9H, 3 ×s, COCH_3).

2,3,4,6-Tetra-*O*-benzoyl-1-thio-*β*-D-glucopyranose (2k)[24]:

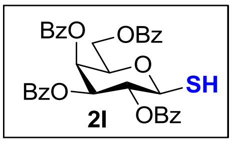


2k

Prepared from **1k** (131 mg, 0.2 mmol) according to the general procedure D(3 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2k** (119 mg, 97% yield) as colorless oil: R_f = 0.48 (petroleum-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.25 (20H, m, Ar-H), 5.88 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.71 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 5.50 (1H, dd, $J_{1,2}$ =$J_{2,3}$ = 9.6 Hz, H-2), 4.90

(1H, dd, $J_{1,2}$ = $J_{1,\mathrm{SH}}$ = 9.6 Hz, H-1), 4.43 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.8 Hz, H-6a), 4.22 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.17 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6b}$ = 4.8 Hz, $J_{5,6a}$ = 2.8 Hz, H-5), 2.47 (1H, d, $J_{1,\mathrm{SH}}$ = 9.6 Hz, SH).

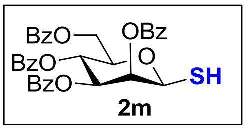
2,3,4,6-Tetra-*O*-benzoyl-1-thio-*β*-D-galactopyranose (2l)[25]:



2l

Prepared from **1l** (131 mg, 0.2 mmol) according to the general procedure D(3 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2l** (114 mg, 93% yield) as white solid: R_f = 0.45 (petroleum-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.22 (20H, m, Ar-H), 6.02 (1H, dd, $J_{3,4}$ = 2.7 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.75 (1H, dd, $J_{1,2}$ =$J_{2,3}$ = 9.6 Hz, H-2), 5.61 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 2.7 Hz, H-3), 4.90 (1H, dd, $J_{1,2}$ = $J_{1,\mathrm{SH}}$ = 9.6 Hz, H-1), 4.64 (1H, dd, $J_{6a,6b}$ = 10.4 Hz, $J_{5,6b}$ = 5.6 Hz, H-6a), 4.42-4.34 (2H, m, H-6b, H-5), 2.56 (1H, d, $J_{1,\mathrm{SH}}$ = 9.6 Hz, SH).

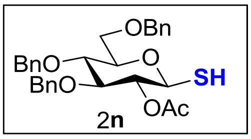
2,3,4,6-Tetra-*O*-benzoyl-1-thio-*β*-D-mannopyranose (2m):



2m

Prepared from **1m** (131 mg, 0.2 mmol) according to the general procedure D(5 h) and purified by flash column chromatography (petroleum-EtOAc 8:1) to give **2m** (104 mg, 85% yield) as colorless syrup: R_f = 0.32 (petroleum-EtOAc 1:1). $[\alpha]_D^{20}$ − 102 (c, 0.8 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-7.22 (20H, m, Ar-H), 6.01(1H, dd, $J_{3,4}$ = $J_{4,5}$= 10.0 Hz, H-4),5.93(1H, dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 0.8 Hz, H-2),5.63 (1H, dd, $J_{3,4}$ = 10.0 Hz, $J_{2,3}$ = 3.2 Hz, H-3), 5.17 (1H, dd, $J_{1,\mathrm{SH}}$ = 10.0 Hz, $J_{1,2}$ = 0.8 Hz, H-1), 4.70 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.8 Hz, H-6a), 4.47 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.4 Hz, H-6b),4.17 (1H, ddd, $J_{4,5}$= 10.0 Hz,$J_{5,6b}$ = 4.4 Hz,$J_{5,6a}$ = 2.8 Hz, H-5), 2.63 (1H, d, $J_{1,\mathrm{SH}}$ = 10.0 Hz, SH). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.3, 165.8, 165.5, 165.5 (4 × O*C*OPh), 133.9, 133.7, 133.5, 133.3, 130.2, 130.2,130.0,130.0,130.0,130.0,130.0,130.0,130.0,130.0,129.1, 129.0, 128.9, 128.9,128.7, 128.7, 128.6,128.6, 128.5,128.5 (24 × C-Ar), 77.1 (C-1), 77.1(C-5), 73.2 (C-3), 72.7 (C-2), 66.3 (C-4), 63.2 (C-6). HRMS calc. for $C_{34}H_{28}NaO_9S$ $[M+Na]^+$: 635.1346, found: 635.1335.

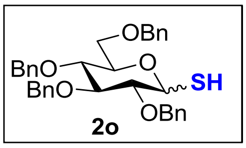
3,4,6-Tri-*O*-benzyl-2-*O*-acetyl-1-thio-*β*-D-glucopyranose (2n)[26]:



2n

Prepared from **1n** (110 mg, 0.2 mmol) according to the general procedure D(2 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2n** (99 mg, 97% yield) as colorless oil: R_f = 0.5 (petroleum-EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.32 – 7.10 (15H, m, Ar-H), 4.94 (1H, dd, $J_{1,2}$ = $J_{1,\mathrm{SH}}$ = 10.0 Hz, H-1), 4.81 – 4.50 (6H, m, 3 × CH_2Ph), 4.39 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, H-2), 3.75 – 3.66 (4H, m, H-3, H-4, H-6a, H-6b), 3.48 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 2.25 (1H, d, $J_{1,\mathrm{SH}}$ = 10.0 Hz, SH), 1.97 (3H, s, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ170.1 ($COCH_3$), 138.3, 138.1, 138.0, 128.7, 128.7, 128.7, 128.7, 128.6, 128.6,128.2,128.2,128.1,128.1,128.1,128.0, 128.0, 128.0, 127.9 (18 ×C-Ar), 84.3 (C-1), 80.0 (C-2), 79.1 (C-5), 77.9 (C-3), 75.8 (C-4), 75.5, 75.3, 73.8 (3 ×Ph*C*H), 68.8 (C-6).

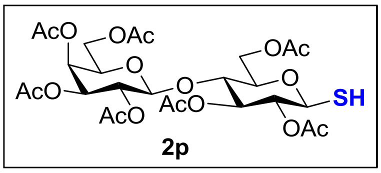
2,3,4,6-Tetra-*O*-benzyl-1-thio-*α*/*β*-D-glucopyranose (2o)[27]:



2o

Prepared from **1o** (120 mg, 0.2 mmol) according to the general procedure D(2 h) and purified by flash column chromatography (petroleum-EtOAc 12:1) to give **2o** (105 mg, 94% yield) as colorless oil: R_f= 0.58 (petroleum-EtOAc 3:1). Analysis by 1H NMR indicated an anomeric mixture of 1-thiols (*α*/*β*, 6:1). R_f = 0.6 (petroleum-EtOAc 3:1); eluant, petroleum-EtOAc (12:1).*α*: ^{1}H NMR (400 MHz, CDCl$_3$) δ7.37 – 7.11 (20H, m, Ar-H), 5.74 (1H, dd, $J_{1,2}$ = 5.2 Hz, $J_{1,SH}$ = 4.8 Hz, H-1), 4.94 – 4.45 (8H, m, 4 × CH$_2$Ph), 4.19 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 3.2 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 3.87 – 3.60 (5H, m, H-2, H-3, H-4, H-6a, H-6b), 1.88 (d, $J_{1,SH}$ = 4.8 Hz, SH). *β*: ^{1}H NMR (400 MHz, CDCl$_3$) δ7.37 – 7.11 (20H, m, Ar-H), 4.94 – 4.45 (9H, m, 4 × CH$_2$Ph, H-1), 3.87 – 3.60 (4H, m, H-3, H-4, H-6a, H-6b), 3.49 – 3.50 (1H, m, H-5), 3.38 – 3.34 (1H, m, H-2), 2.30 (d, $J_{1,SH}$ = 8.08 Hz, SH).

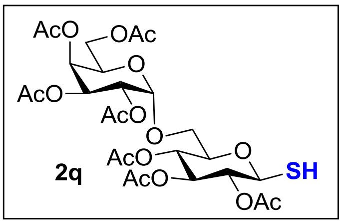
2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-*β*-D -glucopyranose (2p)[28]:



2p

Prepared from **1p** (139 mg, 0.2 mmol) according to the general procedure D(1 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **2p** (117 mg, 89% yield) as white crystalline product: R_f = 0.5 (petroleum-EtOAc 1:2). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.32 (1H, dd, $J_{3',4'}$= 3.0 Hz, $J_{4',5'}$= 0.8 Hz, H-4'), 5.15 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.07 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 8.0 Hz, H-2), 4.92 (1H, dd, $J_{2',3'}$= 9.6 Hz, $J_{3',4'}$= 3.0 Hz, H-3'), 4.85 (1H, dd, $J_{2',3'}$=9.6 Hz, $J_{1',2'}$ = 8.0 Hz, H-2'), 4.50 (1H, dd, $J_{1,SH}$ = 9.6 Hz, $J_{1,2}$ = 8.0 Hz, H-1), 4.45 (1H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.43 (1H, dd, $J_{6a',6'b}$ = 12.0 Hz, $J_{5',6'a}$ = 2.0 Hz, H-6'a), 4.12 – 4.03 (3H, m, H-6a, H-6b, H-6'b), 3.84 (1H, m, H-5'), 3.78 (1H, dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 3.60 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 2.21 (1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.12, 2.10, 2.05, 2.04, 2.02, 2.01, 1.93 (21H, 7 × s, COCH_3).

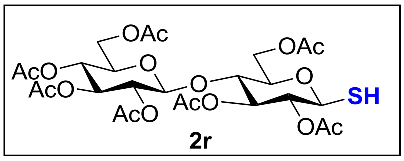
2,3,4-Tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-*α*-D-galactopyranosyl)-1-thio-*β*-D -glucopyranose (2q)[28]:



2q

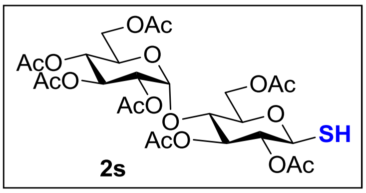
Prepared from **1q** (139 mg, 0.2 mmol) according to the general procedure D (1.5 h) and purified by flash column chromatography (petroleum-EtOAc 2.5:1) to give **2q** (117 mg, 89% yield) as white solid: R_f = 0.40 (petroleum-EtOAc 1:2). ^{1}H NMR (400 MHz, CDCl$_3$) δ5.44 (1H, dd, $J_{3',4'}$ =3.6 Hz, $J_{4',5'}$ = 0.8 Hz, H-4'), 5.34 (1H, dd, $J_{2',3'}$ = 10.8 Hz, $J_{3',4'}$ = 3.6 Hz, H-3'), 5.20 (1H, d, $J_{1',2'}$ = 3.6 Hz, H-1'), 5.17 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.07 (1H, dd, $J_{4,5}$ = $J_{3,4}$ = 9.6 Hz, H-4), 5.07 (1H, dd, $J_{2',3'}$ = 10.8 Hz, $J_{1',2'}$ = 3.6 Hz, H-2'), 4.89 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 9.6 Hz, H-2), 4.49 (1H, dd, $J_{1,SH}$ = $J_{1,2}$ = 9.6 Hz, H-1), 4.25 (1H, m, H-5'), 4.15 – 3.99 (2H, m, H-6'a, H-6'b), 3.71 – 3.60 (3H,m, H-5, H-6a, H-6b), 2.26 (1H, d, $J_{1,SH}$ = 10.0 Hz, SH), 2.13, 2.12, 2.06, 2.02, 2.02,1.99, 1.98 (21H, 7 × s, COCH_3).

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl(1→4)-2,3,6-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-glucopyranose (2r)[29]:


2r

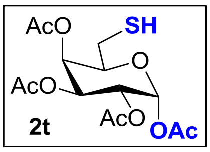
Prepared from **1r** (139 mg, 0.2 mmol) according to the general procedure D(1 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **2r** (127 mg, 97% yield) as white crystalline product: R_f= 0.35 (petroleum-EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.12 (1H, dd, $J_{2',3'}$= $J_{3',4'}$= 9.6 Hz, H-3'), 5.04 (1H, dd, $J_{3',4'}$= $J_{4',5'}$= 9.6 Hz, H-4'), 4.89 (1H, dd, $J_{2',3'}$= 9.6 Hz, $J_{1',2'}$ = 8.0 Hz, H-2'), 4.85 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 9.6 Hz, H-2), 4.50 (1H, dd, $J_{1,SH}$ = $J_{1,2}$ = 9.6 Hz, H-1), 4.47 (1H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.45 (1H, dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 0.8 Hz, H-6a), 4.35 (1H, dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 4.4 Hz, H-6a'), 4.06 (1H, dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 5.0 Hz, H-6b), 4.02 (1H, dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5,6'b}$ = 1.6 Hz, H-6'b), 3.76 (1H, dd, $J_{4,5}$= $J_{3,4}$= 9.6 Hz, H-4), 3.63 (1H, ddd, $J_{4',5'}$= 9.6 Hz, $J_{5',6a'}$ = 4.4 Hz, $J_{5',6b'}$ = 1.6 Hz, H-5'), 3.60 (1H, ddd, $J_{4,5}$= 9.6 Hz, $J_{5,6b}$ = 5.0 Hz, $J_{5,6a}$ = 0.8 Hz, H-5), 2.23 (1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.11, 2.07, 2.05, 2.00, 2.00, 1.99, 1.96(21H, 7 × s, COCH_3).

2,3,4,6-Tetra-*O*-acetyl-*α*-D-glucopyranosyl(1→4)-2,3,6-tri-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-glucopyranose (2s)[28]:


2s

Prepared from **1s** (139 mg, 0.2 mmol) according to the general procedure D (1 h) and purified by flash column chromatography (petroleum-EtOAc 2:1) to give **2s** (124 mg, 95% yield) as white crystalline product: R_f= 0.35 (petroleum-EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (1H, d, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.33 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 5.23 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 9.6 Hz, H-2), 5.03 (1H, dd, $J_{2',3'}$= 10.4 Hz, $J_{3',4'}$= 9.6 Hz, H-3'), 4.84 (1H, dd, $J_{2',3'}$= 10.4 Hz, $J_{1',2'}$ = 4.0 Hz, H-2'), 4.79 (1H, dd, $J_{3',4'}$= $J_{4',5'}$= 9.6 Hz, H-4'), 4.56 (1H, dd, $J_{1,SH}$ = $J_{1,2}$ = 9.6 Hz, H-1), 4.43 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.4 Hz, H-6a), 4.22 (1H, dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.19 (1H, dd, $J_{6'a,6'b}$ = 12.0 Hz, $J_{5',6'a}$ = 4.4 Hz, H-6a'), 4.02 (1H, dd, $J_{6'a,6'b}$ = 12.0 Hz, $J_{5,6'b}$ = 2.0 Hz, H-6'b), 3.97 (1H, dd, $J_{4,5}$= $J_{3,4}$= 9.2 Hz, H-4), 3.92 (1H, ddd, $J_{4,5}$= 9.2 Hz, $J_{5,6b}$ = 4.0 Hz, $J_{5,6a}$ = 2.4 Hz, H-5), 3.68 (1H, ddd, $J_{4',5'}$= 9.6 Hz, $J_{5',6a'}$ = 4.4 Hz, $J_{5',6b'}$ = 2.0 Hz, H-5'), 2.23 (1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.13, 2.08, 2.03, 2.02, 2.00, 1.99, 1.98 (21H, 7 × s, COCH_3).

1,2,3,4-Tetra-*O*-acetyl-6-thio-*α*-D-galactopyranose (2t):


2t

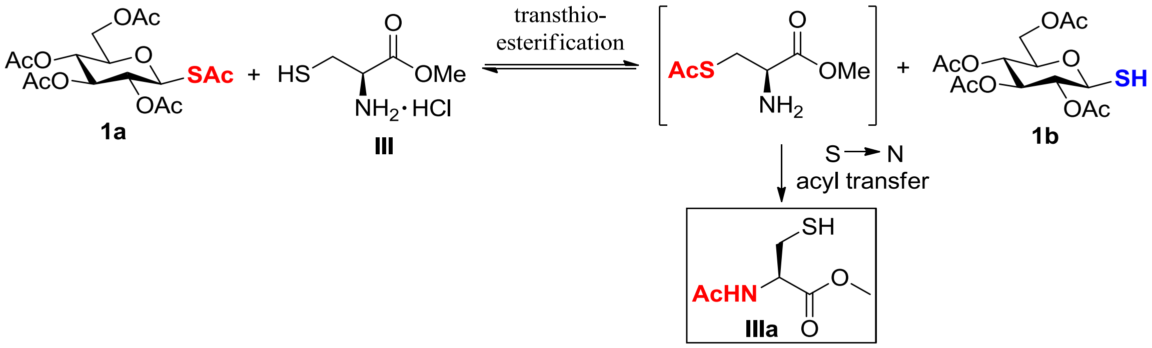
Prepared from **1t** (82 mg, 0.2 mmol) according to the general procedure D (24 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **2t** (69 mg, 95% yield) as white solid: R_f = 0.54 (petroleum-EtOAc 1:1). $[\alpha]_D^{20}$ + 108 (*c*, 0.1 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (1H, d, $J_{1,2}$ = 3.2 Hz, H-1), 5.62 (1H, dd, $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 1.2 Hz, H-4), 5.34 (1H, dd, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 2.8 Hz, H-3), 5.29 (1H, dd, $J_{2,3}$ = 10.8 Hz, $J_{1,2}$ = 3.2 Hz, H-2), 4.09 (1H, m, H-5), 2.66 (1H, ddd, $J_{6a,6b}$ =

14.0 Hz, $J_{6a,SH}$ = 8.0 Hz, $J_{5,6a}$ = 6.8 Hz, H-6a), 2.45 (1H, ddd, $J_{6a,6b}$ = 14.0 Hz, $J_{SH,6b}$ = 10.0 Hz, $J_{5,6b}$ = 7.2 Hz, H-6b), 2.15, 2.14, 2.00, 1.99 (12H, 4 × s, $COCH_3$), 1.55 (1H, dd, $J_{6b,SH}$ = 10.0 Hz, $J_{6a,SH}$ = 8.0 Hz, SH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 169.2 (4 ×$COCH_3$), 89.9 (C-1), 73.4 (C-5), 68.3 (C-3), 67.9 (C-4), 66.7 (C-2), 24.2 (C-6), 21.1, 20.9, 20.8, 20.8 (4 × $COCH_3$). HRMS calc. for $C_{14}H_{20}NaO_9S$ $[M+Na]^+$: 387.0720, found: 387.0707.

5. Mechanism studies

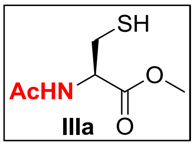
1) Deacylation mediated by cysteine methyl ester hydrochloride (NCL)

The reaction mediated by cysteine methyl ester hydrochloride (**III**) should involve NCL (Scheme S1). Indeed, we isolated the *N*-acetyl-L-cysteine-methyl ester **IIIa**, in which the acetyl group is located on the nitrogen atom due to the transthioesterification and *S* to *N* acyl transfer sequence.



Scheme S1. NCL inspired *S*-deacylation

N-acetyl-L-cysteine-methyl ester (IIIa)[30]:

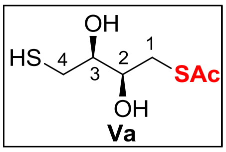


White crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ6.33 (1H, br s, NH), 4.87 (1H, dt, *J* = 7.6, 4.0 Hz, α-H), 3.78 (3H, s, CO_2CH_3), 2.99 (2H, m, CH_2), 2.05 (3H, s, $COCH_3$), 1.31 (1H, t, *J* = 9.2 Hz, SH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.1, 53.7, 53.0, 27.1, 23.3.

2) Deacylation mediated by DTT

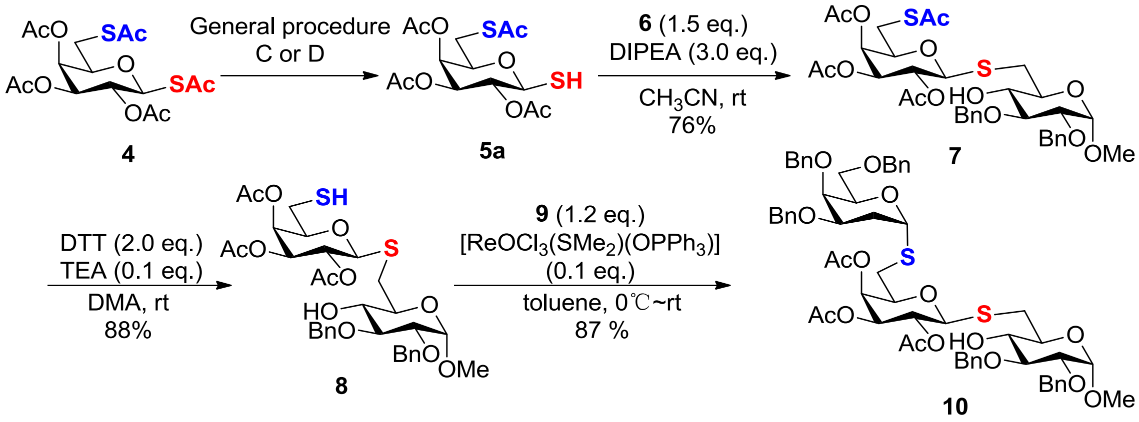
The reaction mediated by DTT (**V**) should pass through transthioesterfication pathway, thus the anomeric *S*-acetyl group is transferred to the *S* atom of DTT but without occurrence of the further *S* to *O* shift. Indeed, this *S*-acylated DTT **Va** was isolated.

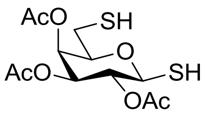
***S*-acetyl-DTT (Va):**



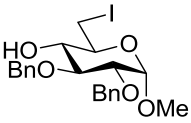
White solid. $[\alpha]_D^{20}$ — 3 (*c*, 0.1 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (1H, m, H-2), 3.55 (1H, m, H-3), 3.13 (1H, dd, $J_{1a,1b}$ = 14.0 Hz, $J_{1b,2}$ = 5.6 Hz, H-1b), 3.01 (1H, dd, $J_{1a,1b}$ = 14.0 Hz, $J_{1a,2}$ = 7.2 Hz, H-1b), 2.71 (2H, m, H-4), 2.36 (3H, s, $SCOCH_3$), 1.50 (1H, t, *J* = 9.2 Hz, SH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3 ($SCOCH_3$), 73.4 (C-2), 72.1 (C-3), 33.0 (C-1), 30.8 ($SCOCH_3$), 28.5 (C-4). HRMS calc. for $C_6H_{12}NaO_3S_2$ $[M+Na]^+$: 219.0120, found: 219.0109.

6. Synthesis of thiolinked trisaccharide

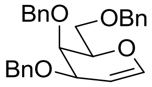




5b

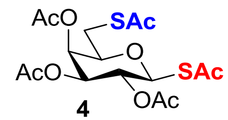


6



9

1,6-Dideoxy-1,6-diacetylthio-2,3,4-tri-*O*-acetyl-*β*-D-galactopyranose (4):

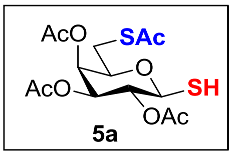


Prepared from 2,3,4-tri-O-acetyl-6-*S*-acetyl-6-thio-*α*-D-galactopyranosyl bromide (1.95 g, 4.79 mmol) in acetone according to procedure A (0.5 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **4** (1.62 g, 80% yield) as white solid: R_f = 0.50 (petroleum-EtOAc 2:1). $[\alpha]_D^{20}$ + 55 (*c*, 0.3 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$):δ 5.44 (1H, dd, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.26 (1H, dd, $J_{1,2}$ = 10.4 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.18 (1H, d, $J_{1,2}$ = 10.4 Hz, H-1), 5.04 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.2 Hz, H-3), 3.81 (1H, ddd, $J_{5,6a}$ = 7.2 Hz, $J_{5,6b}$ = 6.8 Hz, $J_{4,5}$ = 0.8 Hz,H-5), 3.10 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6a}$ = 7.2 Hz, H-6a), 2.93 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6b}$ = 6.8 Hz, H-6b), 2.37, 2.30 (6H, 2 × s, $\mathrm{SCOC}H_3$), 2.14, 1.99, 1.95 (9H, 3 × s, $\mathrm{COC}H_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ194.5, 192.3 (2 × $\mathrm{S}C\mathrm{OCH_3}$), 170.5, 170.1, 169.8 (3 ×$C\mathrm{OCH_3}$), 80.7 (C-1), 76.7 (C-5), 72.3 (C-3), 68.1 (C-4), 66.5 (C-2), 31.1, 30.6 (2 × $\mathrm{SCO}CH_3$), 28.6 (C-6), 20.9, 20.9, 20.8 (3 × $\mathrm{CO}CH_3$). HRMS calc. for $C_{16}H_{22}NaO_9S_2$ $[M+Na]^+$: 445.0597, found: 445.0586.

2,3,4-tri-*O*-acetyl-6-deoxy-6-acetylthio-1-thio-*β*-D-galactopyranose (5a):

Method A: Prepared from **4** (300 mg, 0.71 mmol) according to procedure C (0.5 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **5a** (248 mg, 92% yield).

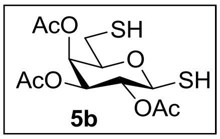
Method B: Prepared from **4** (300 mg, 0.71 mmol) according to procedure C (0.5 h) and purified by flash column chromatography (petroleum-EtOAc 5:1) to give **5a** (172 mg, 64% yield) and **5b** (76 mg, 28% yield).



5a

Colorless oil: R_f = 0.64 (petroleum-EtOAc 2:1). $[\alpha]_D^{20}$ + 44 (*c*, 0.8 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$):δ 5.43 (1H, dd, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.12 (1H, dd, $J_{1,2}$ = 10.0 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.95 (1H, dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.2 Hz, H-3), 4.47 (1H, d, $J_{1,2}$ = 10.0 Hz, $J_{1,SH}$ = 9.6 Hz, H-1), 3.69 (1H, ddd, $J_{5,6a}$ = 7.2 Hz, $J_{5,6b}$ = 6.8 Hz, $J_{4,5}$ = 0.8 Hz,H-5), 3.07-2.98 (2H, m, H-6a, H-6b), 2.33(1H, d, $J_{1,SH}$ = 9.6 Hz, SH), 2.31 (3H, s, $SCOCH_3$), 2.15, 2.05, 1.95 (9H, 3 × s, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ194.8 ($SCOCH_3$), 170.5, 170.2, 170.1 (3 ×$COCH_3$), 79.3 (C-1), 76.6 (C-5), 72.0 (C-3), 71.0 (C-4), 68.2 (C-2), 30.7 ($SCOCH_3$), 28.7 (C-6), 21.1, 20.9, 20.8 (3 × $COCH_3$). HRMS calc. for $C_{14}H_{20}NaO_8S_2$ $[M+Na]^+$: 403.0492, found: 403.0481.

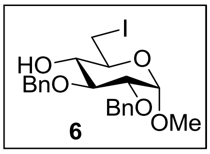
2,3,4-tri-*O*-acetyl-1,6-dithio-*β*-D-galactopyranose (5b):



5b

Colorless oil, R_f = 0.50 (petroleum-EtOAc 2:1). $[\alpha]_D^{20}$ + 72 (*c*, 0.1 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 5.55 (1H, dd, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 0.8 Hz, H-4), 5.14 (1H, dd, $J_{1,2}$ =$J_{2,3}$ = 10.0 Hz, H-2), 5.00 (1H, dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.2 Hz, H-3), 4.51 (1H, d, $J_{1,2}$ = 10.0 Hz, $J_{1,SH'}$ = 9.6 Hz, H-1), 3.69 (1H, ddd, $J_{5,6b}$ = 7.2 Hz, $J_{5,6a}$ = 6.8 Hz, $J_{4,5}$ = 0.8 Hz,H-5), 2.71 (1H, ddd, $J_{6a,6b}$ = 14.0 Hz, $J_{6a,SH}$ = 8.0 Hz, $J_{5,6a}$ = 6.8 Hz, ,H-6a), 2.48 (1H, ddd, $J_{6a,6b}$ = 14.0 Hz, $J_{6b,SH}$ = 10.0 Hz, $J_{5,6b}$ = 7.2 Hz,H-6b), 2.33(1H, d, $J_{1,SH'}$ = 9.6 Hz, SH'), 2.15, 2.06, 1.97 (9H, 3 × s, $COCH_3$), 1.60 (1H, dd, $J_{6b,SH}$ = 10.0 Hz, $J_{6a,SH}$ = 8.0 Hz, SH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 170.1 (3 ×$COCH_3$), 79.8 (C-1), 79.3 (C-5), 72.0 (C-3), 71.2 (C-4), 68.1 (C-2), 24.4 (C-6), 21.1, 20.9, 20.8 (3 ×$COCH_3$). HRMS calc. for $C_{12}H_{18}NaO_7S_2$ $[M+Na]^+$: 361.0386, found: 361.0381.

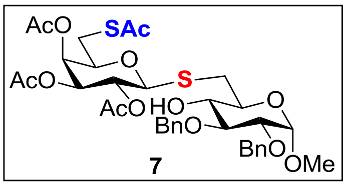
Methyl-2,3-di-O-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (6)[31]:



6

To a solution of methyl 2,3-di-*O*-benzyl-*α*-D-glucopyranoside (1.32 g, 3.54 mmol) in toluene (36 ml), I_2(1.35 g, 5.31 mmol), triphenylphosphine (1.30 g, 4.96 mmol), and imidazole (723 mg, 10.62 mmol) were added. The reaction washeated to 50°C and stired for 1 h, then cooled to rt. Ten percent $Na_2S_2O_3$ (20 mL) was added to the residue, which was thenextracted with EtOAc. The organic layers were combined, dried with Na_2SO_4, decanted andevaporated to dryness. The crude product was chromatographed through silicagel using petroleum-EtOAc at a 8:1 ratio followed by a 5:1 ratio toafford **6** (1.47g，86% yield) as white solid: R_f= 0.38 (petroleum-EtOAc 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ7.34 – 7.28 (10H, m, Ar-H)，5.01 – 4.62 (4H, m, $PhCH$), 4.62 (1H, d, $J_{1,2}$ = 4.0 Hz, H-1), 3.76 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 3.50 (1H, dd, $J_{6a,6b}$ = 9.6 Hz, $J_{5,6a}$ = 2.8 Hz, H-6a), 3.49 (1H, dd, $J_{2,3}$ =9.2 Hz, $J_{1,2}$ =4.0 Hz,H-2),3.41 (3H, s, OCH_3),3.39 (1H, m, H-6b),3.30 – 3.21 (2H, m, H-4, H-5), 2.14 (1H, d, $J_{4,OH}$ = 2.4 Hz, OH).

Synthesis of *S*-linked disaccharide 7:



7

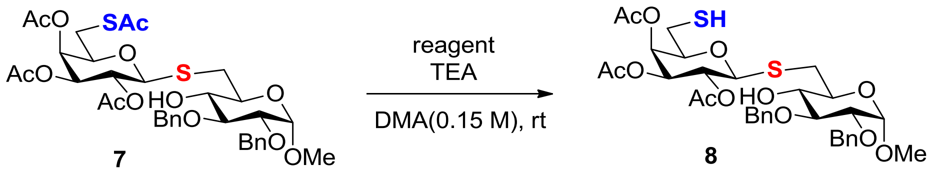
A solution of **5a** (208 mg, 0.56 mmol) and **6** (396 mg, 0.84 mmol) in CH_3CN (5.6 ml, 0.1 M) was treated with DIPEA (284 ul, 212 mg, 1.68 mmol) and stirred at rt for

5 h. The reaction mixture was concentrated. The crude material was extracted with EtOAc. The organic layer was washed with water, brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography (petroleum-EtOAc 3:1) to give **7** (304 mg, 76% yield) as colorless oil: R_f = 0.52 (petroleum-EtOAc 2:1). $[\alpha]_D^{20}$ + 28 (*c*, 0.2 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ7.36 – 7.27 (10H, m, Ar-H)，5.40 (1H, dd, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$ = 0.8 Hz, H-4'), 5.15 (1H, dd, $J_{1',2'}$ =$J_{2',3'}$ = 10.0 Hz, H-2'), 4.98 (1H, d, $J_{1',2'}$ = 10.0 Hz, H-1'), 4.97 (1H, dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.2 Hz, H-3'), 4.76 – 4.56 (4H, m, PhC*H*), 4.58 (1H, d, $J_{1,2}$ = 4.0 Hz, H-1), 3.77 – 3.72 (2H, m, H-3, H-5), 3.67 (1H, m, H-5'), 3.50 – 3.42 (2H, m, H-2, H-4), 3.37 (3H, s, OC*H*3), 3.07 – 2.96 (3H, m, H-6a, H-6'a, H-6'b), 2.87 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6b}$ = 7.2 Hz,H-6b), 2.42 (1H, m, OH), 2.28 (3H, s, SCOC*H*3), 2.13, 2.00, 1.95 (9H, 3 × s, COC*H*3);^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9 (S*C*OCH3), 170.5, 170.3, 169.7 (3 ×*C*OCH3), 139.0, 138.2, 128.8, 128.8, 128.7, 128.7, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1 (12 × Ar-C), 98.2 (C-1), 84.2 (C-1'), 81.3 (C-3), 79.9 (C-2), 76.1 (C-5'), 75.6, 73.3 (2 × Ph*C*H), 72.6 (C-3'), 72.3 (C-4), 71.4 (C-5), 68.3 (C-4'), 67.5 (C-2'), 55.4 (O*C*H3), 31.3 (C-6), 30.7 (SCO*C*H3), 28.8 (C-6'), 21.0, 20.9, 20.8 (3 × CO*C*H3). HRMS calc. for $C_{35}H_{44}NaO_{13}S_2$ $[M+Na]^+$: 759.2116, found: 759.2091.

Synthesis of *S*-linked disaccharide (8):

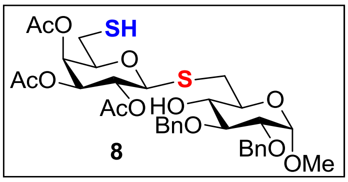
The selective *S*-deacylation of *C*-6 SAc group of **7** according to procedure C afforded **8** in 56% yield. In this case, the NCL strategy is less efficient. When following procedure D, the yield increased to 82%. Furthermore, increasing the amount of **III** to 2.0 eq. led to 88% yield (Table S4).

Table S4. Optimization of reaction conditions for selective deacylation at anomeric SAc group of 7[a]



Entry	Reagent (eq.)	TEA (eq.)	Time (h)	Yield(%)[b]
1	**III** (1.2)	1.0	5	56
2	**IV** (1.5)	0.1	8	82
3	**IV** (2.0)	0.1	6	88

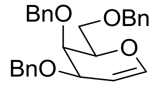
[a]The reactions were conducted in 0.1 mmol scale. Procedure: To a solution of **7** and reagent was added TEA, and the mixture was stirred at room temperature for appropriate time. Then the reaction mixture was diluted with water and extracted with tolune. The combined organic layers were washed with water, brine, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography (petroleum-EtOAc 3:1) to give **8**. [b]Isolated yield.



White solid: R_f = 0.48 (petroleum-EtOAc 2:1). $[\alpha]_D^{20}$ + 6 (*c*, 0.5 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 –

7.34 (10H, m, Ar-H), 5.50 (1H, dd, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$ = 0.8 Hz, H-4'), 5.17 (1H, dd, $J_{1',2'}$ = $J_{2',3'}$ = 10.0 Hz, H-2'), 5.01 (1H, dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.2 Hz, H-3'), 4.98 (1H, d, $J_{1',2'}$ = 10.0 Hz, H-1'), 4.76 – 4.61 (4H, m, PhC*H*), 4.57 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 3.76 (1H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6b}$ = 7.2 Hz, $J_{5,6a}$ = 2.8 Hz, H-5), 3.73 (1H, dd, $J_{1,2}$ = $J_{2,3}$ = 9.2 Hz, H-3), 3.66 (1H, ddd, $J_{5',6'a}$ = 8.0 Hz, $J_{5',6'b}$ = 6.8 Hz, $J_{4',5'}$ = 0.8 Hz, H-5'), 3.48 (1H, dd, $J_{2,3}$ = 9.2 Hz, $J_{1,2}$ = 3.6 Hz, H-2), 3.43 (1H, dd, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 3.38 (3H, s, OCH_3), 3.04 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6a}$ = 2.8 Hz, H-6a), 3.02 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6b}$ = 7.2 Hz, H-6b), 2.71 (1H, ddd, $J_{6'a,6'b}$ = 14.8 Hz, $J_{5',6'a}$ = $J_{6'a,SH}$ = 8.0 Hz, H-6'a),2.45 (1H, ddd, $J_{6'a,6'b}$ = 14.8 Hz, $J_{6'b,SH}$= 9.6 Hz, $J_{5',6'b}$ = 6.8 Hz, H-6'b),2.37 (1H, m, OH), 2.13, 2.00, 1.96 (9H, 3 × s, COCH_3), 1.64 (1H, dd, $J_{6'b,SH}$ = 9.6 Hz, $J_{6'a,SH}$ = 8.0 Hz, SH);^{13}C NMR (100 MHz, $CDCl_3$) δ170.6, 170.2, 169.7 (3 × *C*OCH$_3$), 138.9, 138.2, 128.8, 128.8, 128.7, 128.7, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1 (12 × Ar-C), 98.2 (C-1), 84.2 (C-1'), 81.2 (C-3), 79.9 (C-2), 79.2 (C-5'), 75.6, 73.3 (2 × Ph*C*H), 72.6 (C-3'), 72.3 (C-4), 71.5 (C-5), 68.3 (C-4'), 67.7 (C-2'), 55.4 (O*C*H$_3$), 31.4 (C-6), 24.6 (C-6'), 21.0, 20.9, 20.8 (3 × CO*C*H$_3$). HRMS calc. for $C_{33}H_{42}NaO_{12}S_2$ [M+Na]$^+$: 717.2010, found: 717.2012.

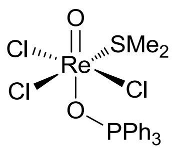
3,4,6-Tri-O-benzyl-D-galactal (9)[32]:



9

A solution of 3,4,6-tri-*O*-acetyl-*D*-galactal (1.27 g, 4.67 mmol) in MeOH (4 ml, 1 M) was treatedwith K_2CO_3 (645 mg, 0.47 mmol) and stirred at rt for 3 h. The reaction mixture was concentrated. The crude material was dissolved in DMF (24 ml,0.2 M) and cooled to 0 ℃ under an atmosphere of Ar. NaH [60% in oil (w/w), 840mg, 21 mmol] wasadded portionwise and stirred over a period of 10 min before benzylbromide (2.5 ml, 21 mmol) was added. Thereaction mixture was warmed to rtand stirred for 10 h. The reaction was quenched by the addition of MeOH(20 ml), stirred for 10 min and evaporated to dryness. The residue was extracted with EtOAc. The organic layer was washed with water, brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography (petroleum-EtOAc 15:1) to give **9** (1.58g, 81% yield over two steps) as white solid: R_f= 0.52 (petroleum-EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.33 – 7.24 (15H, m, Ar-H), 6.34 (1H, dd, $J_{1,2}$ = 6.4 Hz, $J_{1,3}$ = 1.2 Hz, H-1), 4.86 (1H, m, PhC*H*), 4.83 (1H, m, H-2), 4.65 – 4.39 (5H, m, PhC*H*), 4.19 – 4.14 (2H, m, H-3, H-5), 3.92 (1H, m, H-4), 3.75 (1H, dd, $J_{6a,6b}$ = 10.0 Hz, $J_{5,6a}$ = 7.2 Hz, H-6a), 3.02 (1H, dd, $J_{6a,6b}$ = 10.0 Hz, $J_{5,6b}$ = 5.2 Hz, H-6b).

Preparation of $[ReOCl_3(SMe_2)(OPPh_3)]$[33]:

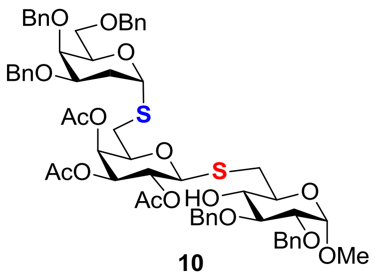


$[ReOCl_3(SMe_2)(OPPh_3)]$

To 5.0 g (5.98 mmol) of $[ReOCl_3(Ph_3P)_2]$ suspended in benzene (150 mL) was added 5 mL (0.08 mol) of DMSO and 25.0 mL of concentrated HCl. The resulting suspension lightened within minutes of addition to afford asea-foam green precipitate suspended in a pale red solution. The reaction mixture was maintained at rt for 4 d at which point the green solid was isolated by filtration and washed with MeOH (3 × 40 mL) and Et_2O (3 × 40 mL). The crude solid was suspended in CH_2Cl_2 (250 mL) and heated at

50°C for about 5 min. The solution was filtered to isolate the desired complex (2.13 g, 55% yield) as a pale green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.42 (15H, m, Ar-H), 2.71 (6H, s, SCH_3).

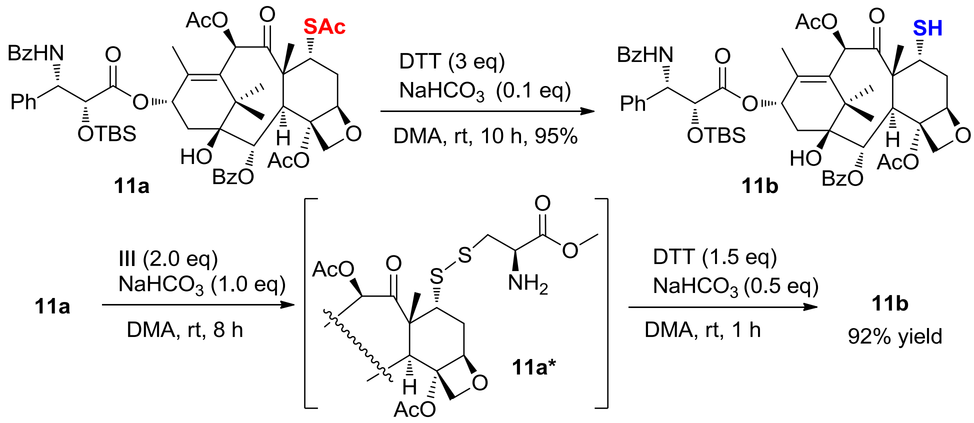
Synthesis of *S*-linked trisaccharide (10):



10

Following the procedure reported[33], to a 0.4 M solution of **8** (46.78 mg, 0.07 mmol) in toluene was added **9** (33.6 mg, 0.08 mmol). The resulting colorless mixture was cooled to 0 °C and 10 mol % of $[ReOCl_3(SMe_2)(OPPh_3)]$ was added. The reaction mixture was slowly warmed to rt, and monitored by TLC until complete. After 3 h crude mixture was purified by flash column chromatography (petroleum-EtOAc 3:1) to afford **10** (70 mg, 87% yield) as a colorless oil: R_f = 0.68 (petroleum-EtOAc 2:1). $[\alpha]_D^{20}$ + 30 (c, 0.7 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.44 – 7.24 (25H, m, Ar-H), 5.55 (1H, dd, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$ = 0.8 Hz, H-4'),5.42(1H, dd, $J_{1'',2''ax}$ = 5.6 Hz, $J_{1'',2''eq}$= 0.8 Hz,H-1"), 5.11 (1H, dd, $J_{1',2'}$ =$J_{2',3'}$ = 10.0 Hz, H-2'), 5.04 (1H, dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.2 Hz, H-3'), 4.97 – 4.62 (5H, m, PhCH), 4.56 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.55 – 4.42 (5H, m, PhCH), 4.23 (1H, d, $J_{1',2'}$ = 10.0 Hz, H-1'), 4.12 (1H, m, H-5"),4.01 (1H, m, H-5'), 3.79 – 3.70 (4H, m, H-3, H-5, H-3", H-4"), 3.59 (1H, dd, $J_{6''a,6''b}$ = 9.6 Hz, $J_{5'',6''a}$ = 7.6 Hz, H-6"a), 3.48 (1H, dd, $J_{3,4}$ =$J_{4,5}$ = 10.0 Hz, H-4), 3.46 (1H, dd, $J_{2,3}$ = 9.2 Hz, $J_{1,2}$ = 3.6 Hz, H-2), 3.76 (1H, dd, $J_{6''a,6''b}$ = 9.6 Hz, $J_{5'',6''b}$ = 4.4 Hz, H-6"b), 3.35 (3H, s, OCH_3), 3.00 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6a}$ = 2.4 Hz, H-6a), 2.83 (1H, dd, $J_{6a,6b}$ = 14.0 Hz, $J_{5,6b}$ = 6.8 Hz, H-6b), 2.79 (1H, dd, $J_{6'a,6'b}$ = 14.4 Hz, $J_{5',6'a}$ =5.6 Hz, H-6'a), 2.65 (1H, dd, $J_{6'a,6'b}$ = 14.4 Hz, $J_{5',6'b}$ = 9.2 Hz, H-6'b),2.48 (1H, ddd, $J_{2''ax,2''eq}$ = 13.6 Hz,$J_{2''ax,3''}$ = 11.6 Hz, $J_{1'',2''ax}$ = 5.6 Hz, H-2"ax), 2.09, 1.99 (6H, 2 × s, COCH_3), 1.96 (1H, ddd, $J_{2''ax,2''eq}$ = 13.6 Hz,$J_{2''eq,3''}$ = 4.0 Hz, $J_{1'',2''ax}$ = 0.8 Hz, H-2"eq), 1.95 (3H, s, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ170.4, 170.2, 169.8 (3 ×$COCH_3$), 139.1, 138.6, 138.3, 138.3, 138.1, 128.7, 128.7, 128.7, 128.7, 128.7, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.8, 127.5, 127.5 (30 × Ar-C), 98.2 (C-1), 83.5 (C-1"), 83.2 (C-1'), 81.3(C-3), 79.9 (C-2),76.3 (C-5'),75.6 (PhCH), 75.5 (C-3"), 74.4, 73.6, 73.4 (3 ×PhCH), 73.4 (C-4"), 72.5 (C-4), 72.3 (C-3'), 71.0 (C-5),71.0 (C-5"), 70.8 (C-6"), 70.7 (PhCH), 68.4 (C-4'), 67.5 (C-2'),55.4 (OCH_3), 31.9 (C-6'), 31.6 (C-2"), 30.8 (C-6), 21.0, 20.9, 20.8 (3 × COCH_3). HRMS calc. for $C_{60}H_{70}NaO_{16}S_2$ $[M+Na]^+$: 1133.3997, found: 1133.4004.

7. Synthesis of thiol containing drug anologues



2'-O-(*t*-Butyldimethylsilyl)-7-deoxy-7*α*-thioacetoxy paclitaxel (11a)[34]:

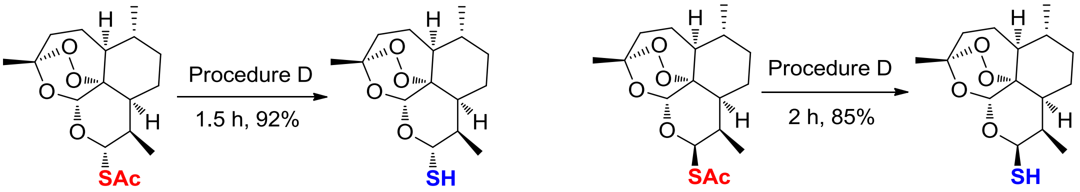
Potassium thioacetate (104 mg, 0.90 mmol) was added to a stirred solution of 2'-*O*-(*t*-butyldimethylsilyl)-7*β*-*O*-trifluoromethanesulfonylpaclitaxel[35,36] (100 mg, 0.09 mmol) in 0.9 ml of absolute EtOH at room temperature under a dry argon atmosphere. After stirring for 45 h in the dark, the reaction was diluted with EtOAc and extracted with water, the organic phase was separated and washed with brine and dried (Na_2SO_4). Removal of the solvents was followed by chromatography on a silica gel column (petroleum-EtOAc 3.5:1) to give **11a** (78 mg, 84% yield) as white solid: *Rf* = 0.50 (petroleum-EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ -0.32 (3H, s), -0.05 (3H, s), 0.78 (9H, s), 1.12 (3H, s, H-17), 1.17 (3H, s, H-16), 1.93 (3H, s, H-19), 2.02-2.66 (4H, m, H-6, H-14), 2.04 (3H, s, H-18), 2.12 (3H, s, OAc), 2.43 (3H, s, OAc), 2.62 (3H, s, SAc), 3.89 (1H, d, *J* = 6.8 Hz, H-3), 4.00 (1H, dd, *J* = 8.8, 2.4 Hz, H-5), 4.28 (1H, d, *J* = 8.8 Hz, H-20), 4.63 (1H, d, *J* = 8.8 Hz, H-20), 4.68 (1H, d, *J* = 2.0 Hz, H-2ʹ), 4.85 (1H, dd, *J* = 8.8, 7.2 Hz), 5.69 (1H, d, *J* = 7.2 Hz, H-2), 5.80 (1H, dd, *J* = 8.8, 2.0 Hz, H-3ʹ), 6.28 (1H, t, *J* = 8.8 Hz, H-13), 6.88 (1H, s, H-10), 7.06 (1H, d, *J* = 9.2 Hz, NH), 7.28-8.16 (15H, m, Ar-H). HRMS calc. for $C_{55}H_{67}NNaO_{14}SSi$ $[M+Na]^+$: 1048.3944, found: 1048.3989.

2'-O-(*t*-Butyldimethylsilyl)-7-deoxy-7*α*-thiopaclitaxel (11b):

To a 0.15 M solution of **5** (11 mg, 0.01 mmol, 1.0 eq) and DTT (4.6 mg, 0.03 mmol, 3 eq) in DMA was added 1% $NaHCO_3$, and the mixture was stirred at room temperature overnight. The reaction mixture was poured into water and extracted with tolune three times. The combined organic layers were washed with water, brine and concentrated to furnish **5** (9.4 mg, 95% yield) as white solid: *Rf* = 0.52 (tolune-EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ -0.33 (3H, s), -0.06 (3H, s), 0.77 (9H, s), 1.16 (3H, s, H-17), 1.18 (3H, s, H-16), 1.84 (3H, s, H-19), 2.07-2.66 (4H, m, H-6, H-14), 1.97 (3H, s, H-18), 2.18 (3H, s, OAc), 2.63 (3H, s, OAc), 2.93 (1H, m), 3.70 (1H, d, *J* = 13.2 Hz, H-3), 4.06 (1H, d, *J* = 6.8 Hz), 4.26 (1H, d, *J* = 8.8 Hz), 4.67 (2H, m), 4.95 (1H, m), 5.71 (1H, d, *J* = 7.2 Hz), 5.78 (1H, d, *J* = 8.4 Hz), 6.28 (1H, m), 7.07 (1H, d, *J* = 9.2 Hz), 7.30-8.16 (15H, m). HRMS calc. for $C_{53}H_{65}NNaO_{13}SSi$ $[M+Na]^+$: 1006.3838, found: 1006.3842. The analysis data were consistant with those reported[34].

However, when the NCL strategy mediated by **III** was adopted, the disulfide bond linked compound **11a***was easily formed (identified by HRMS, calc. for

$C_{57}H_{73}N_2O_{15}S_2Si$ [M+H]$^+$: 1117.4216, found: 1117.4230.), which was further treated with DTT to afforded **11b** in 92% yield.



12a 12b 13a 13b

10-Thioacetoxydihydroartemisinin (12a and 13a)[37]**:**

Thioacetic acid (108 mg, 1.42 mmol) and BF_3Et_2O (201 mg, 1.42 mmol) were added to a stirred solution of dihydroartemisinin (400 mg, 1.42 mmol) in dry CH_2Cl_2 (20 ml) at room temperature. The solution was stirred for 10 min, after which it was diluted with CH_2Cl_2, washed with satd. aq. $NaHCO_3$ and brine. The organic layer was separated, dried with $NaSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash chromatography (petroleum-EtOAc 30:1) to give 117 mg (24%) of **12a** (α-isomer) and 287 mg (59%) of **13a** (β-isomer).

For **12a**: white solid: *Rf* = 0.50 (petroleum-EtOAc 5:1). $[\alpha]_D^{20}$ − 29 (*c*, 1.1 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 5.35 (1H, s, H-12), 5.33 (1H, d, J = 11.6 Hz, H-10), 2.62 (1H, m, H-9), 2.33 (3H, s, $SCOCH_3$), 2.29-2.37 (1H, m, H-4α), 1.38 (3H, s, H-14), 0.94 (3H, d, J = 6.4 Hz, H-16), 0.85 (1H, d, J = 7.2 Hz, H-15). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 104.6, 92.7, 80.6, 79.2, 52.1, 46.3, 37.5, 36.4, 34.2, 31.9, 31.1, 26.2, 24.8, 21.3, 20.4, 14.8. HRMS calc. for $C_{17}H_{26}NaO_5S$ [M+Na]$^+$: 365.1393, found: 365.1405.

For **13a**: white solid: *Rf* = 0.54 (petroleum-EtOAc 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 6.09 (1H, d, J = 5.2 Hz, H-10), 5.29 (1H, s, H-12), 3.14 (1H, m, H-9), 2.34 (3H, s, $SCOCH_3$), 2.29-2.37 (1H, m, H-4α), 1.39 (3H, s, H-14), 0.93 (3H, d, J = 6.4 Hz, H-16), 0.85 (1H, d, J = 7.2 Hz, H-15). HRMS calc. for $C_{17}H_{26}NaO_5S$ [M+Na]$^+$: 365.1393, found: 365.1396. The analysis data were consistant with those reported[37].

10α-Mercaptodihydroartemisinin (12b):

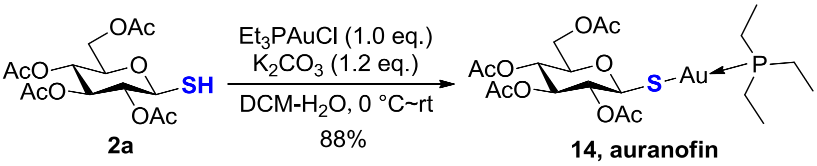
Prepared from **12a** (65 mg, 0.19 mmol) according to procedure D (1.5 h) and purified by flash column chromatography ($CHCl_3$-EtOAc 300:1) to give **12b** (52 mg, 92% yield) as white solid: *Rf* = 0.45 (petroleum-EtOAc 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 5.27 (1H, s, H-12), 4.64 (1H, dd, J = 10.4, 8.8 Hz, H-10), 2.45 (1H, m, H-9), 2.31-2.39 (1H, m, H-4α), 2.19 (1H, d, J = 8.8 Hz, SH), 1.41 (3H, s, H-14), 0.94 (3H, d, J = 7.2 Hz, H-16), 0.93 (1H, d, J = 6.4 Hz, H-15). HRMS calc. for $C_{15}H_{24}NaO_4S$ [M+Na]$^+$: 323.1288, found: 323.1305. The analysis data were consistant with those reported[37].

10β-Mercaptodihydroartemisinin (13b):

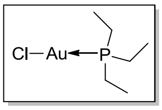
Prepared from **13a** (69 mg, 0.2 mmol) according to procedure D (2 h) and purified by flash column chromatography ($CHCl_3$-EtOAc 300:1) to give **13b** (51 mg, 85% yield) as white solid: *Rf* = 0.58 (petroleum-EtOAc 5:1). $[\alpha]_D^{20}$ + 184 (*c*, 0.3 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 5.70 (1H, s, H-12), 5.69 (1H, t, J = 5.2 Hz, H-10), 2.99

(1H, m, H-9), 2.31-2.39 (1H, m, H-4*α*), 2.02 (1H, d, *J* = 6.4 Hz, SH), 1.40 (3H, s, H-14), 0.94 (3H, d, *J* = 6.4 Hz, H-15), 0.93 (1H, d, *J* = 7.6 Hz, H-16). ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.5, 88.0, 81.1, 80.5, 52.9, 45.4, 37.5, 36.5, 34.7, 31.9, 26.3, 24.8, 24.4, 20.5, 15.2. HRMS calc. for $C_{15}H_{24}NaO_4S$ $[M+Na]^+$: 323.1288, found: 323.1301.

8. Synthesis of auranofin

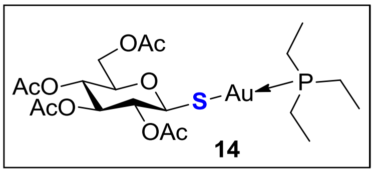


Preparation of $[Et_3PAuCl]$[38,39]:



A solution of 10.0 g (0.08 mole) of thiodiglycol in 5 ml of ethanol is mixed with a solution of 15.76 g (0.04 mole) of gold acid chloride trihydrate in 75 ml of distilled water. When the bright orange-yellow solution is almost colorless, it is cooled to 0-5 °C, and an equally cold solution of 5.0 g (0.0425 mole) of triethylphosphine in 2.5 ml of ethanol is added dropwise to the stirred solution. After the addition is complete the cooled mixture is stirred for 1/2 hour. Solid that separates is removed and the filtrate is concentrated to about 30ml to yield a second crop ond crop. The combined solid is washed with aqueous ethanol (2:1) and recrystallized from ethanol by adding water to the cloud point. The product is obtained as white needles. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (6H, dq, *J* = 8.0, 7.6 Hz, CH_2CH_3), 1.16 (9H, dt, *J* = 18.8, 7.6 Hz, CH_2CH_3).

Auranofin (14)[40]:



2a (400 mg, 1.10 mmol) and triethylphosphinegold chloride (385 mg, 1.10 mmol) were dissolved in 2 ml DCM and cooled to 0–5 °C. To the stirred solution was added dropwise an equally cold solution of K_2CO_3 (182 mg, 1.32 mmol) in 1.3 ml distilled water. After the addition was complete, the mixture was stirred at room temperature for 1 hour. Then the DCM layer was separated. The aqueous layer was extracted three times with DCM. The combined organic layers were dried (Na_2SO_4) and filtered. After removal of solvent, the crude product was recrystallized from methanol-water (2:5) to give auranofin as white solid (655 mg, yield 88%). R_f = 0.45 (petroleum-EtOAc 1:1). $[\alpha]_D^{20}$ = −52 °(*c* = 1, CH_3OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12-5.03 (3H, m, H-1, H-3, H-4), 4.93 (1H, m, H-2), 4.18 (1H, dd, *J* = 12.0, 4.8 Hz, H-6a), 4.04 (1H, dd, *J* = 12.0, 2.4 Hz, H-6b), 3.67 (1H, m, H-6), 2.03, 2.01, 1.96. 1.94 (12H, 4×s, $COCH_3$), 1.80 (6H, dq, *J* = 9.6, 7.6 Hz, CH_2CH_3), 1.16 (9H, dt, *J* = 18.4, 7.6 Hz, CH_2CH_3).

9. References

1. R. Halasya, *Indian Pat. Appl.*, 2005CH01609.

2. S. Chittaboina, B. Hodges, Q. Wang, *Lett. Org. Chem.* 2006, **3**, 35.

3. M. M. Sim, H. Kondo, C.-H. Wong, *J. Am. Chem. Soc*. 1993, **115**, 2260.

4. N. Floyd, B. Vijayakrishana, J. R. Koeppe, B. G. Davis, *Angew. Chem. Int. Ed.* 2009, **48**, 7798.

5. K. Czifrák, L. Somsák, *Carbohydr. Res.* 2009, **344**, 269.

6. S. Martín-Santamaría, S. André, E. Buzamet, R. Caraballo, G. Fernández-Cureses, M. Morando, J. P. Ribeiro, K. Ramírez-Gualito, B. de Pascual-Teresa, F. J. Cañada, M. Menéndez, O. Ramström, J. Jiménez-Barbero, D. Solís, H.-J. Gabius, *Org. Biomol. Chem.* 2011, **9**, 5445.

7. H. N. Yu, C.-C. Ling, D. R. Bundle, *J. Chem. Soc.*, *Perkin Trans. 1*, 2001, 832.

8. Z. C. Pei, R. Larsson, T. Aastrup, H. Anderson, J.-M. Lehn, O. Ramström, *Biosens. Bioelectron.* 2006, **22**, 42.

9. C. E. Jakobsche, C. G. Parker, R. N. Tao, M. D. Kolesnikova, E. F. Douglass, Jr., D. A. Spiegel. *ACS Chem. Biol.* 2013, **8**, 2404.

10. C. V. Holland, D. Horton, M. J. Miller, N. S., Bhacca, *J. Org. Chem.* 1967, **32**, 3077.

11. J. M. Chalker, L. Lercher, N. R. Rose, C. J. Schofield, B. G. Davis, *Angew. Chem. Int. Ed.* 2012, **51**, 1835.

12. W. Priebe, G. Grynkiewicz, N. Neamati, *Tetrahedron Lett.* 1991, **32**, 2097.

13. M. Li, B. Yu, *Org. Lett.*, 2006, **8**, 2679.

14. W. Pilgrim, P. V. Murphy, *J. Org. Chem.* 2010, **75**, 6747.

15. R. T. Dere, A. Kumar, V. Kumar, X. M. Zhu, R. R. Schmidt, *J. Org. Chem.* 2011, **76**, 7539.

16. Z. J. Li, P. L. Liu, Z. J., Li, D. X. Qiu, M. S. Cai, *Synth. Commun.* 1990, **20**, 2169.

17. K.-T. Huang, K. Gorska, S. Alvarez, S. Barluenga, N. Winssinger, *ChemBioChem* 2011, **12**, 56.

18. J. Elhalabi, K. G. Rice, *Carbohydr. Res.* 2002, **337**, 1935.

19. M. B. Haque, B. P. Roberts, D. A. Tocher, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2881.

20. E. J. Grayson, G. J. L. Bernardes, J. M. Chalker, O. Boutureira, J. R. Koeppe, and B. G. Davis, *Angew. Chem. Int. Ed.* 2011, **50**, 4127.

21. M. Z. Gao, Y. W. Chen, S. D. Tan, J. H. Reibenspies, R. A. Zingaro, *Heteroat. Chem.* 2008, **19**, 199.

22. D. Ljevakovic, J. Horvat, K. Branimir, T. Srdanka, *J. Carbohydr. Chem.* 1983, **2**, 263.

23. H. Streicher, L. Latxague, T. Wiemann, P. Rollin, J. Thiem, *Carbohydr. Res.* 1995, **278**, 257.

24. Y. D. Cai, B. P. Roberts, D. A. Tocher, *J. Chem. Soc.*, *Perkin Trans. 1*, 2002, 1376.

25. W. Pilgrim, P. V. Murphy, *J. Org. Chem.* 2010, **75**, 6747.

26. W. B. Turnbull, M. A. Fascione, S. A. Stalford, *Sci. Synth.* 2007, **29**, 923.

27. B. D. Johnston, B. M. Pinto, *J. Org. Chem.* 2000**,** **65**, 4607.

28. M. Jana, A. K. Misra, *J. Org. Chem.* 2013, **78**, 2680.

29. S. Noguchi, S. Takemoto, S.-I. Kidokoro, K. Yamamoto, M. Hashimoto, *Bioorg. Med. Chem.* 2011, **19**, 3812.

30. G. J. L. Bernardes, E. J. Grayson, S. Thompson, J. M. Chalker, J. C. Errey, F. E. Oualid, T. D. W. Claridge, B. G. Davis, *Angew. Chem. Int. Ed.* 2008, **47**, 2244.

31. E. M. Sletten, L. J. Liotta, *J. Org. Chem.* 2006, **71**, 1335.

32. E. Durantie, C. Bucher, R. Gilmour, *Chem. Eur. J.* 2012, **18**, 8208.

33. B. D. Sherry, R. N. Loy, F. D. Toste, *J. Am. Chem. Soc.* 2004, **126**, 4510.

34. H. Mastalerz, G. Zhang, J. Kadow, C. Fairchild, B. Long, D. M. Vyas, *Org. Lett.* 2001, **3**, 1613.

35. J. D. Gibson, B. P. Khanal, E. R. Zubarev, *J. Am. Chem. Soc*. 2007, **129**, 11653.

36. X. Liang, D. G. I. Kingston, C. M. Lin, E. Hamel, *Tetrahedron Lett.* 1995, **36**, 2901.

37. S. Oh, I. H. Jeong, C. M. Ahn, W.-S. Shin, S. Lee, *Bioorg. Med. Chem. Lett.* 2004, **12**, 3783.

38. B. M. Sutton, E. McGusty, D. T. Walz, M. J. DiMartino, *J. Med. Chem.* 1972, **15**, 1095.

39. A. F. A. Peacock, G. A. Bullen, L. A. Gethings, J. P. Williams, F. H. Kriel, J. Coates, *J. Inorg. Biochem.* 2012, **117**, 298.

40. P. S. Pregosin, E. D. Becker, *Helv. Chim. Acta* 1983, **66**, 1436.

41. NMR spectra

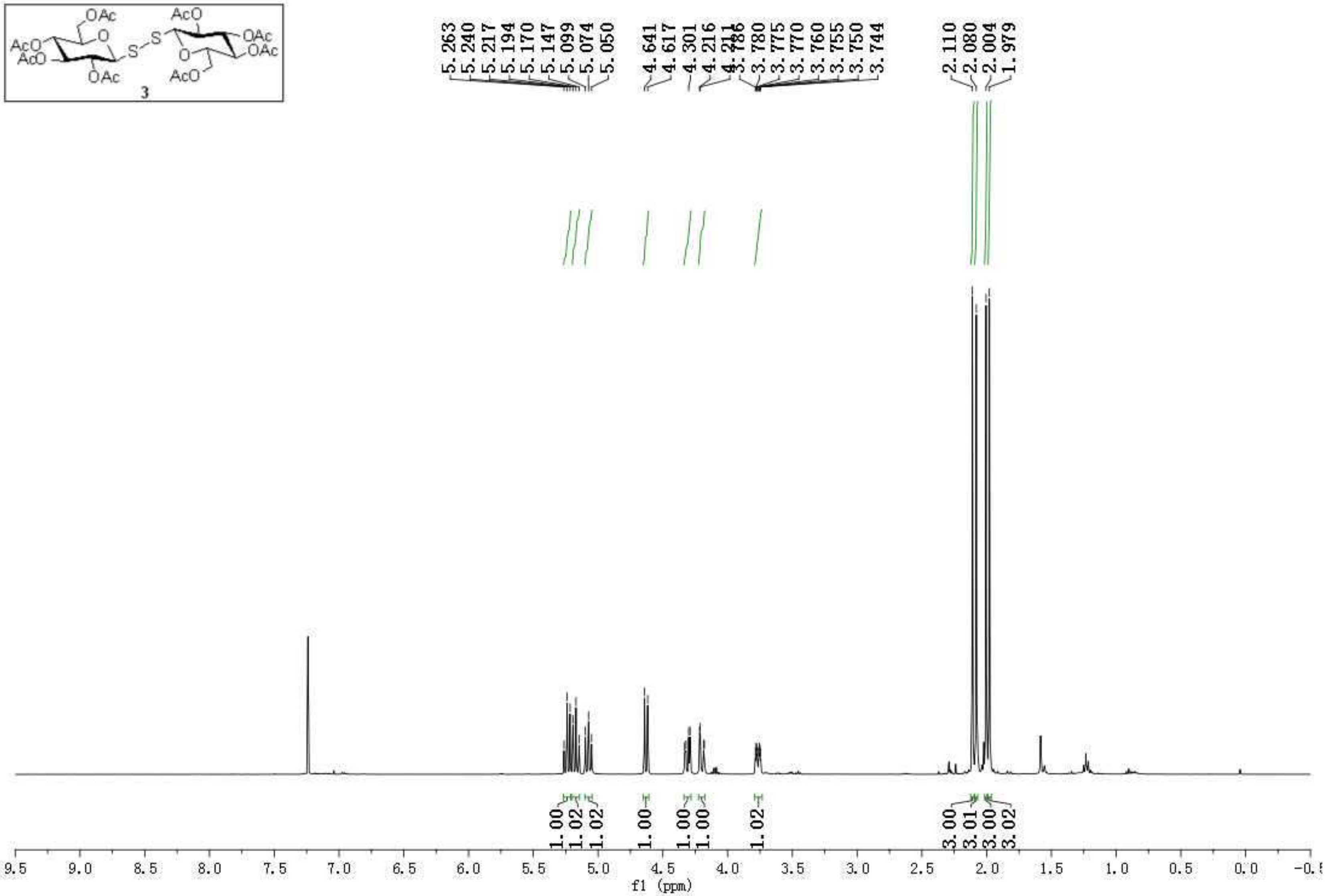


Figure S5. ^{1}H NMR spectrum of **3** in $CDCl_3$

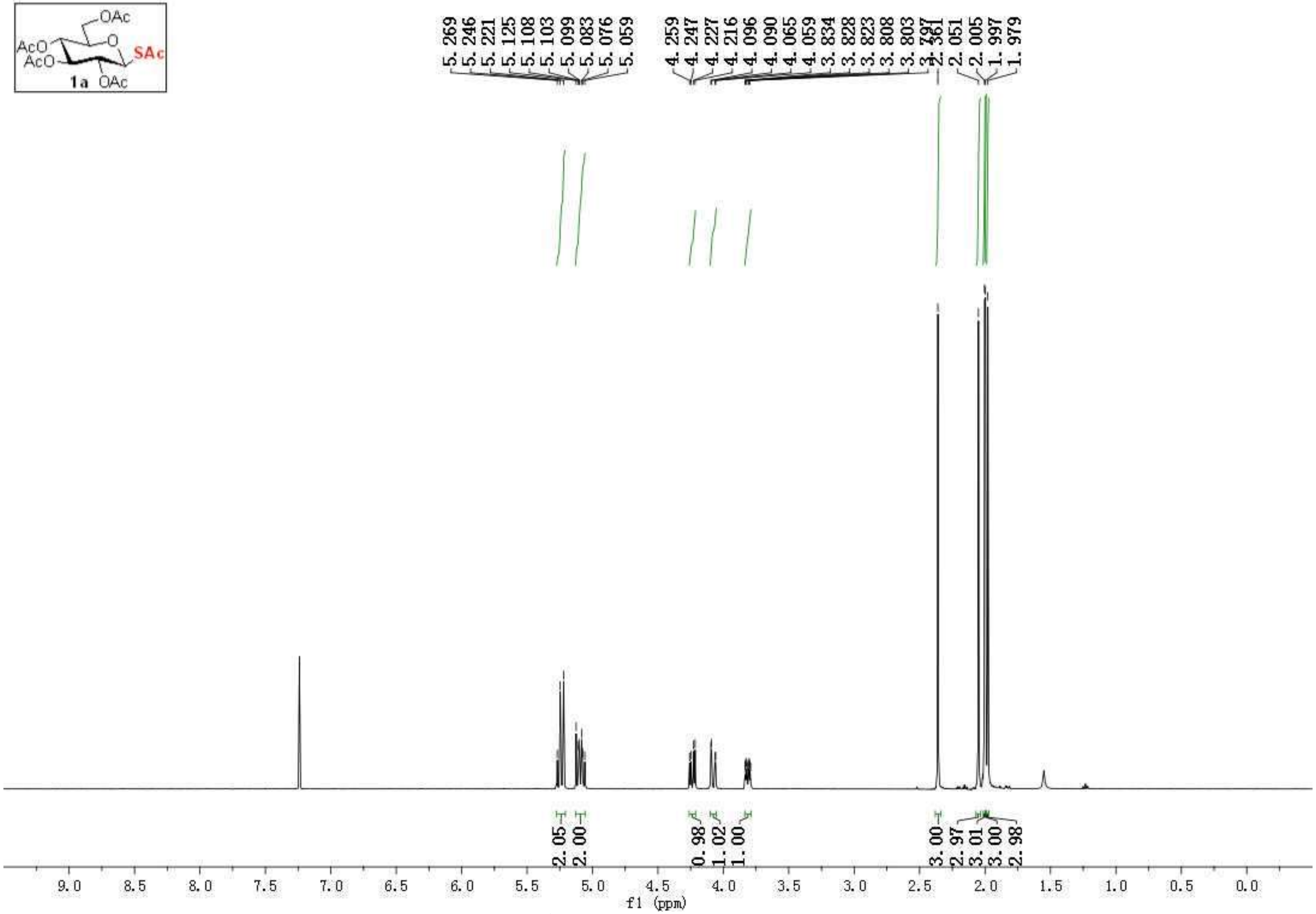


Figure S6. ^{1}H NMR spectrum of **1a** in CDCl$_3$

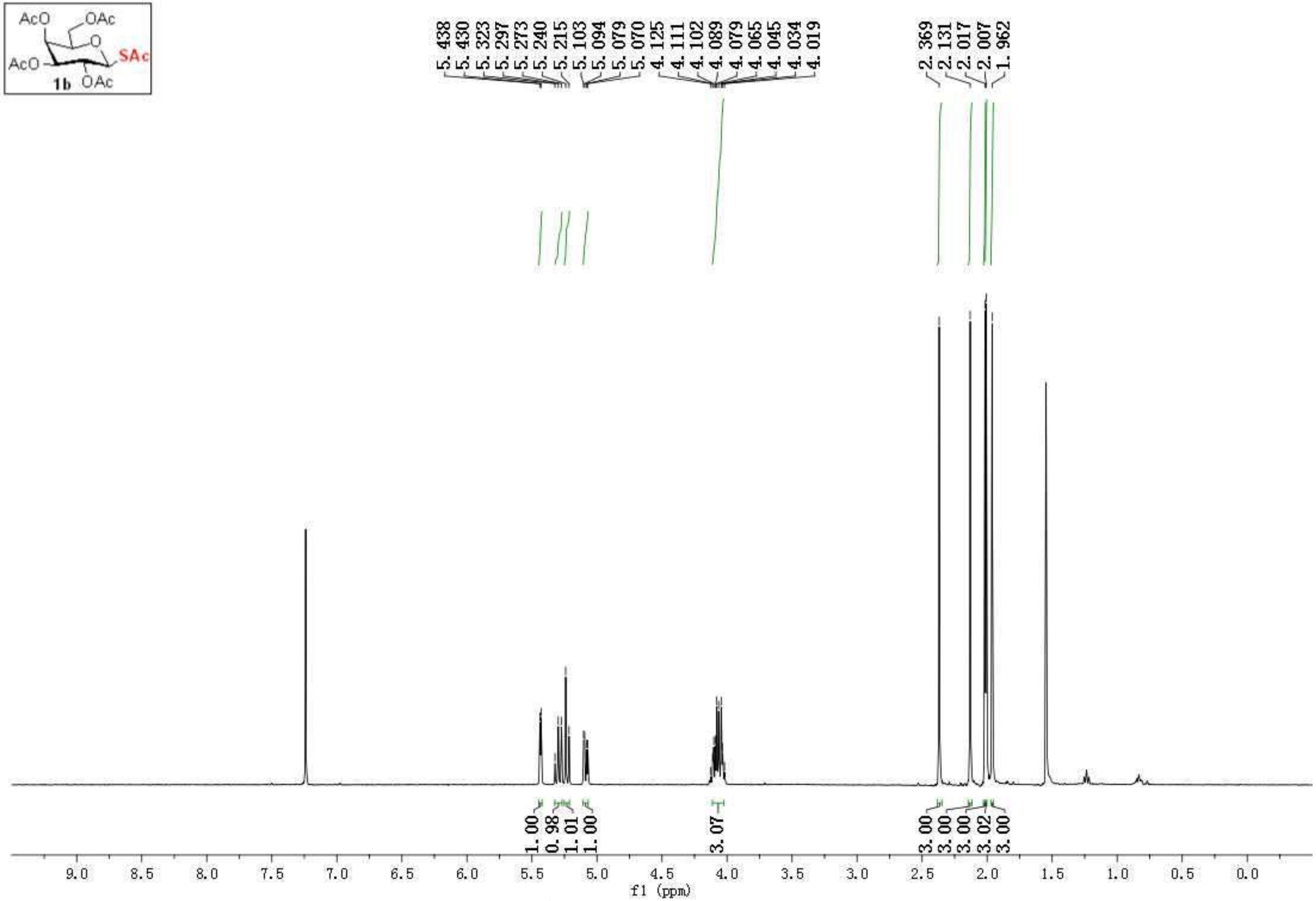


Figure S7. ^{1}H NMR spectrum of **1b** in $CDCl_3$

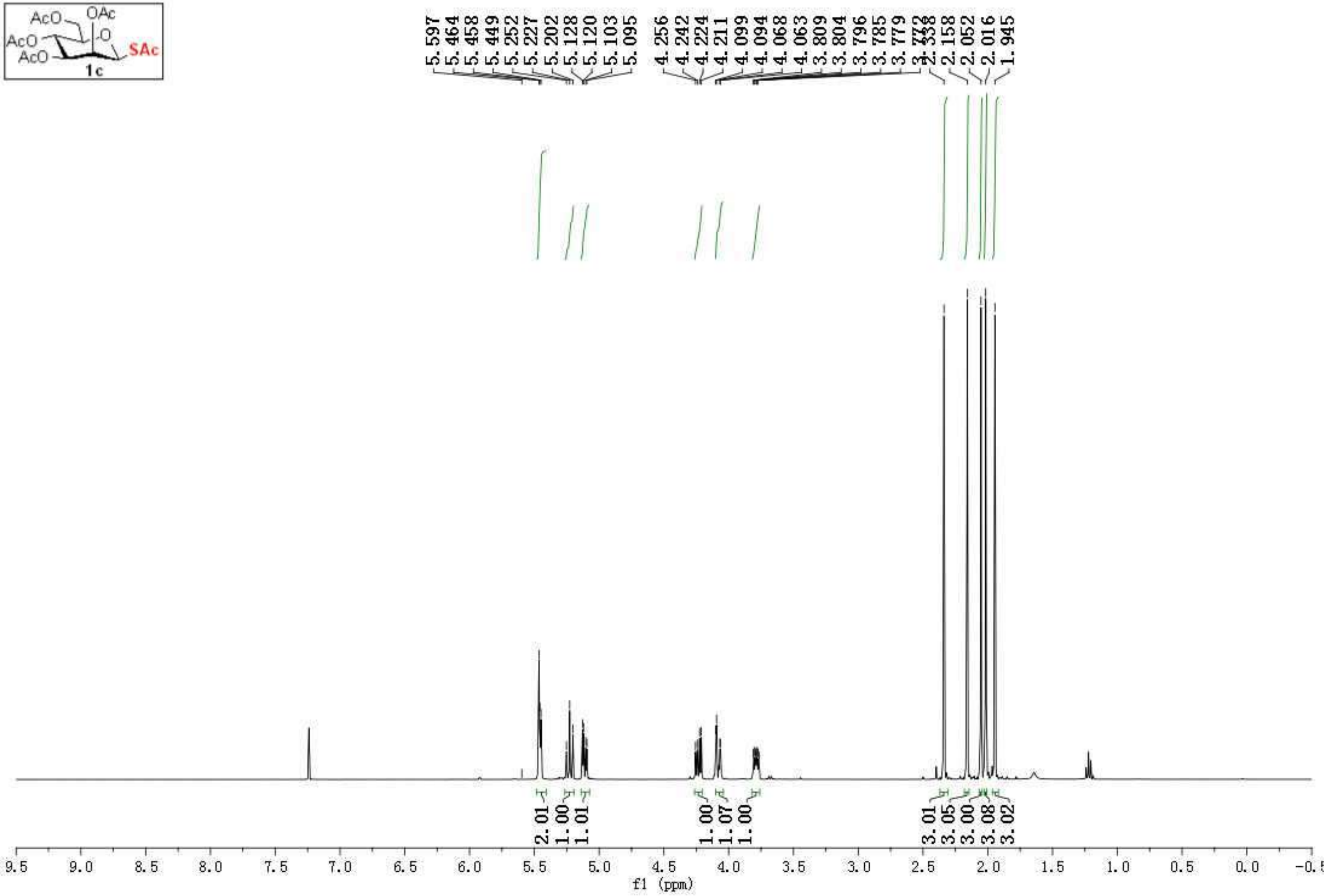


Figure S8. ^{1}H NMR spectrum of **1c** in CDCl$_3$

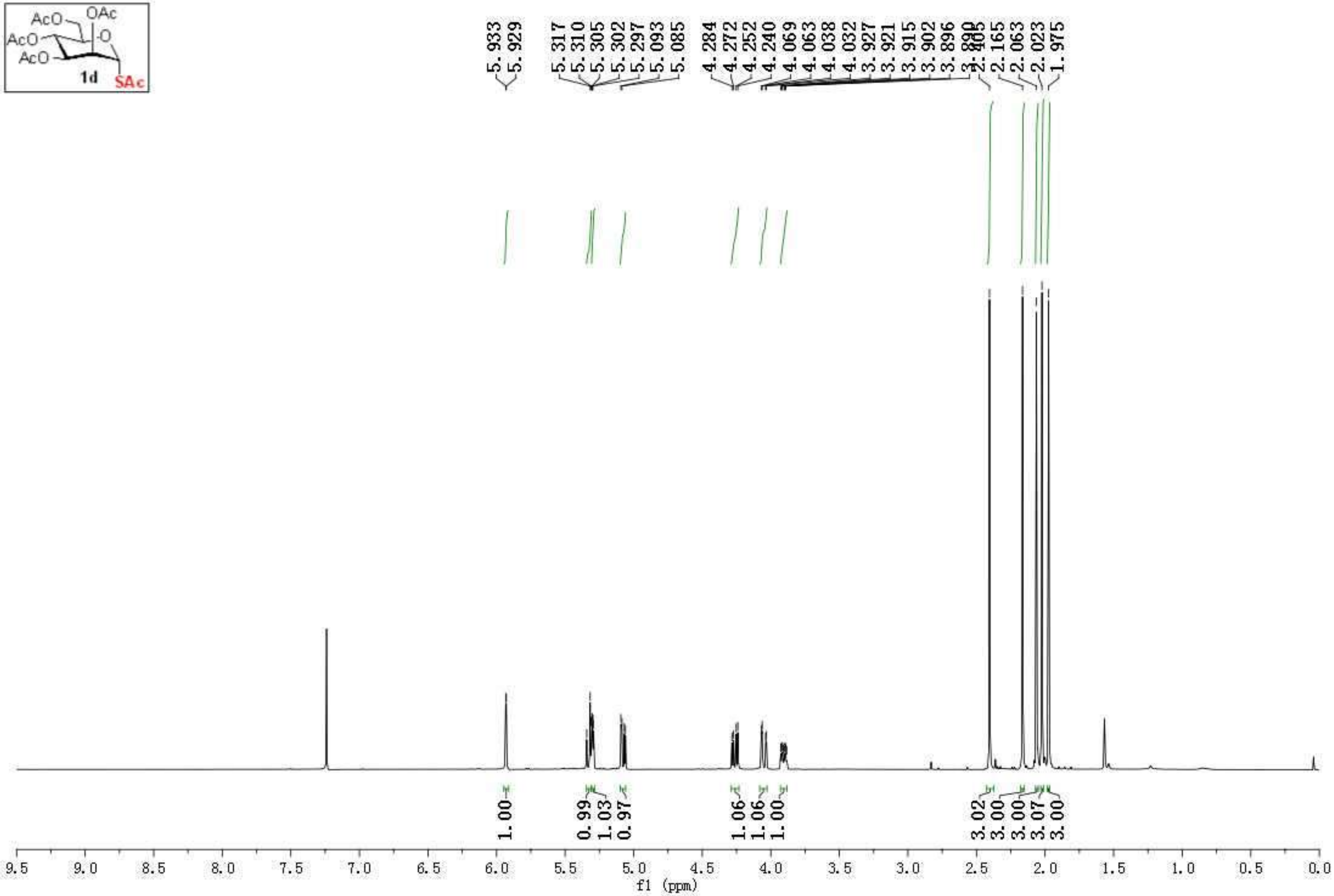


Figure S9. ^{1}H NMR spectrum of **1d** in $CDCl_3$

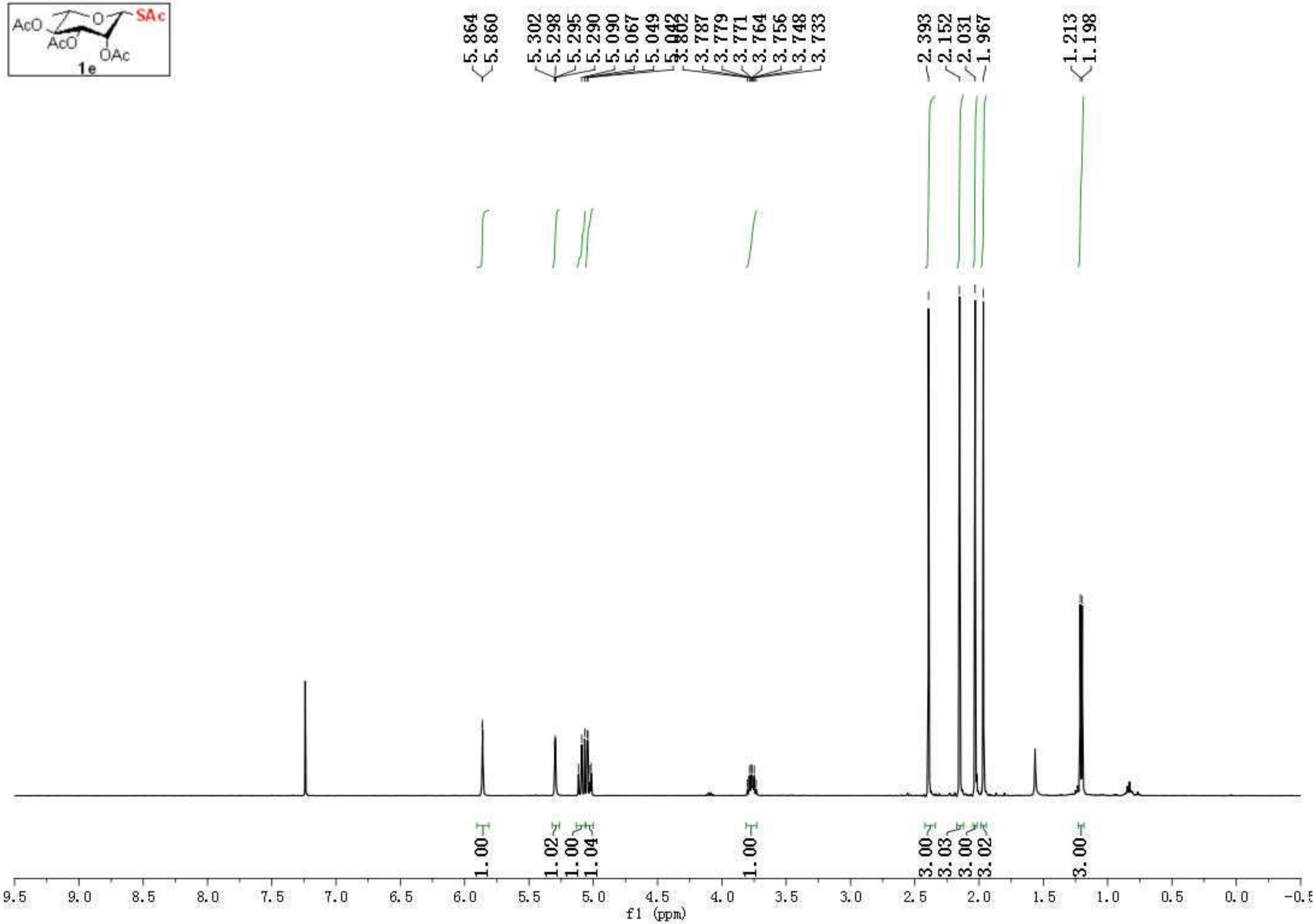


Figure S10. ^{1}H NMR spectrum of **1e** in $CDCl_3$

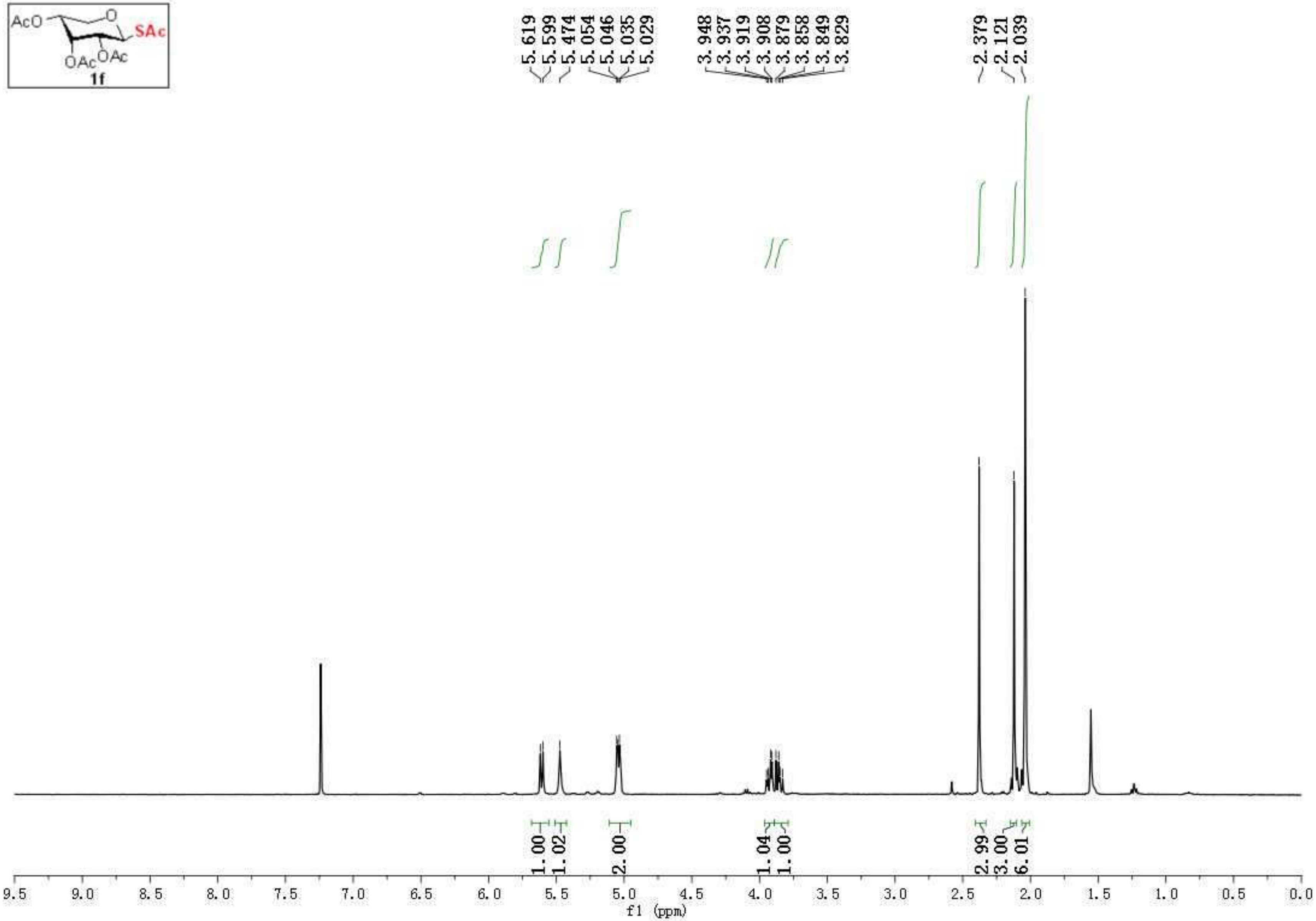


Figure S11. ^{1}H NMR spectrum of **1f** in $CDCl_3$

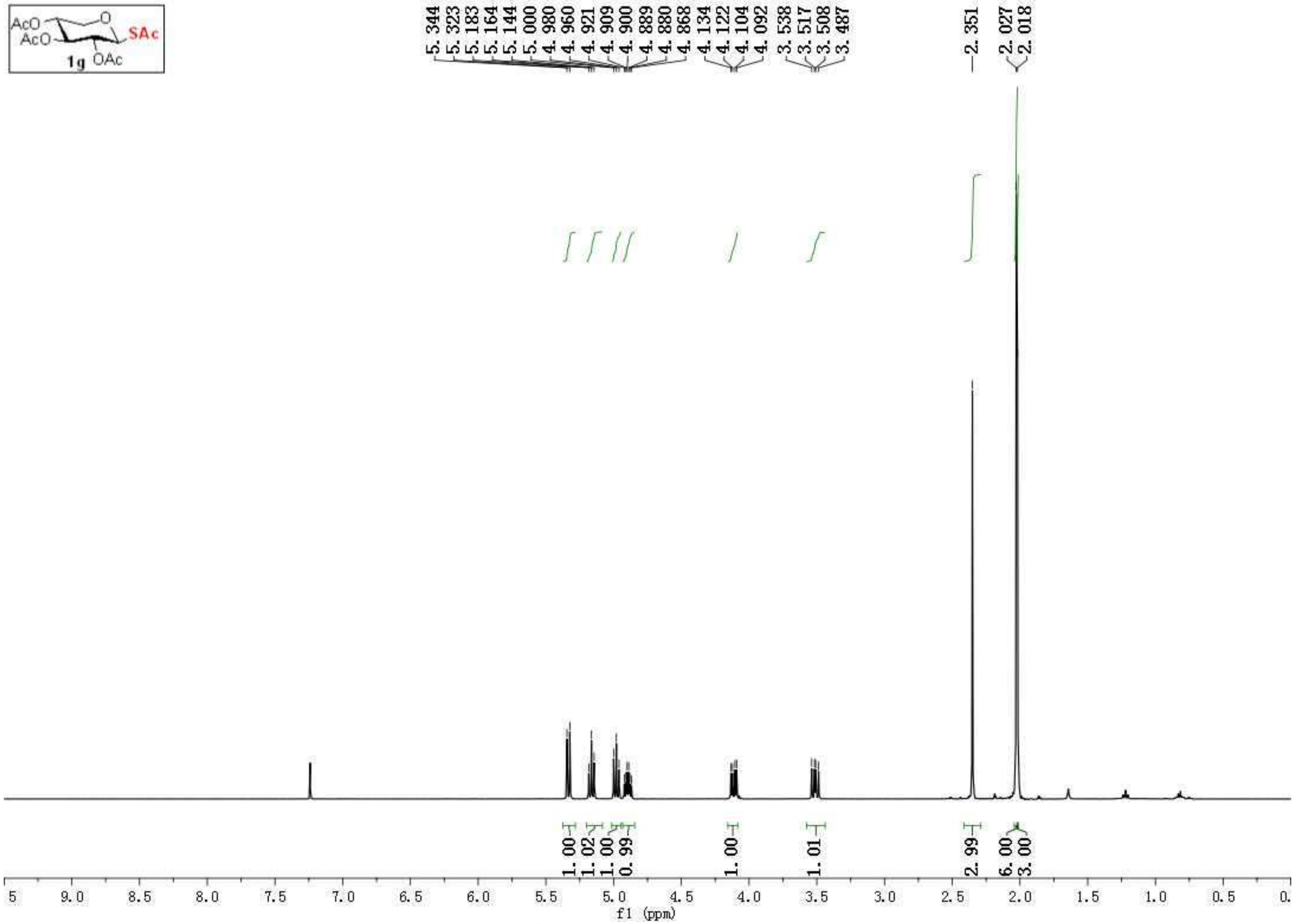


Figure S12. ^{1}H NMR spectrum of **1g** in $CDCl_3$

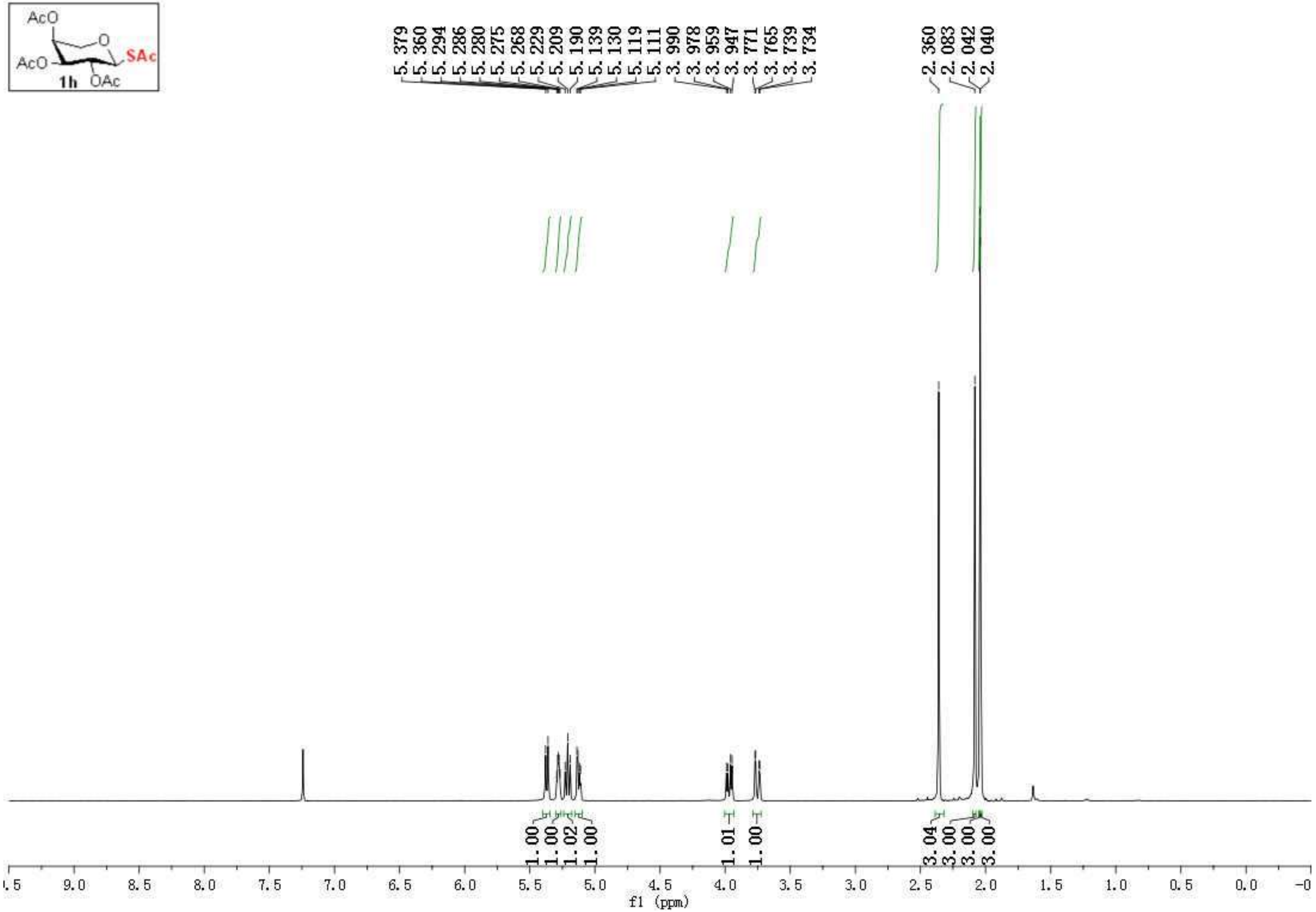


Figure S13. ^{1}H NMR spectrum of **1h** in $CDCl_3$

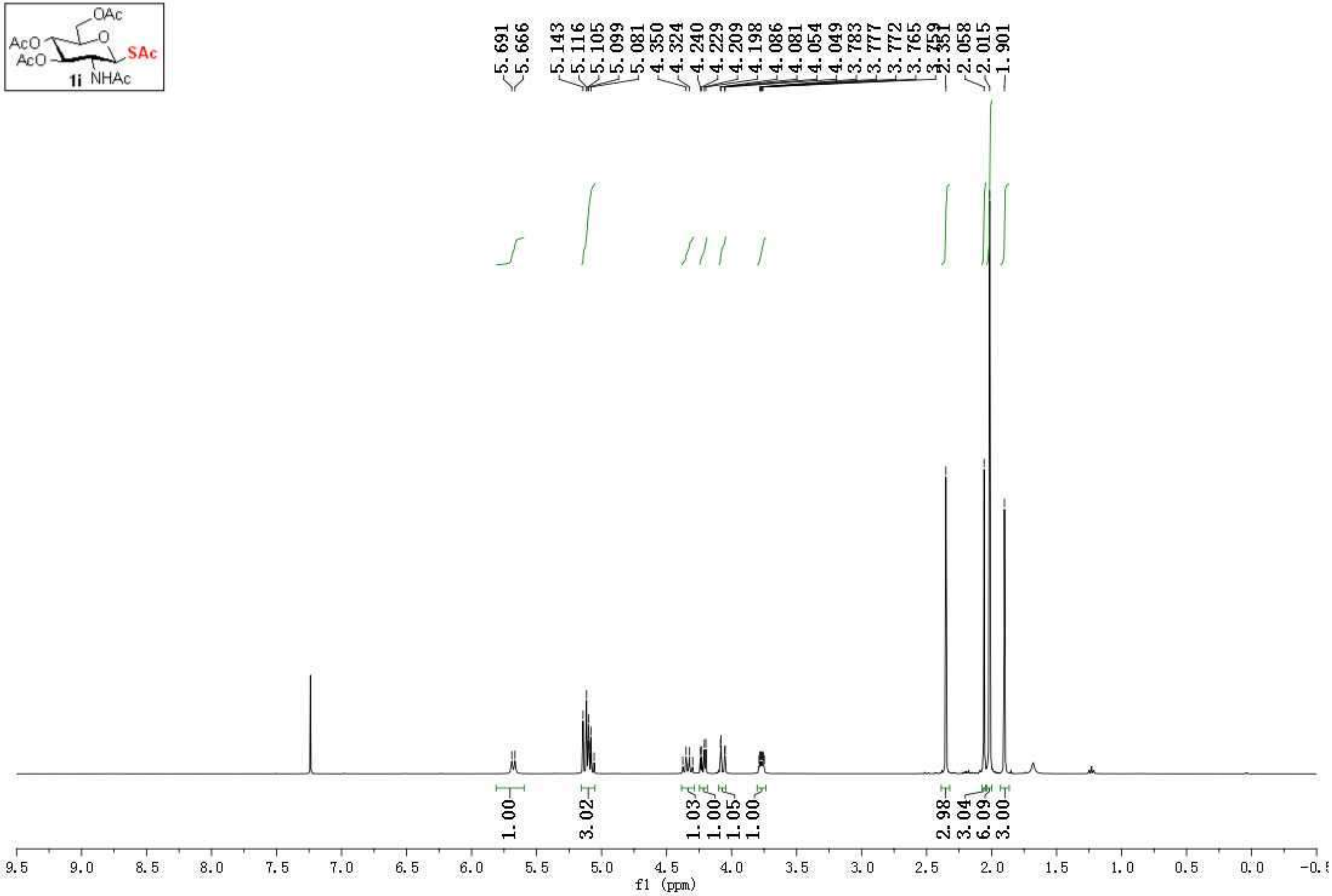


Figure S14. ^{1}H NMR spectrum of **1i** in $CDCl_3$

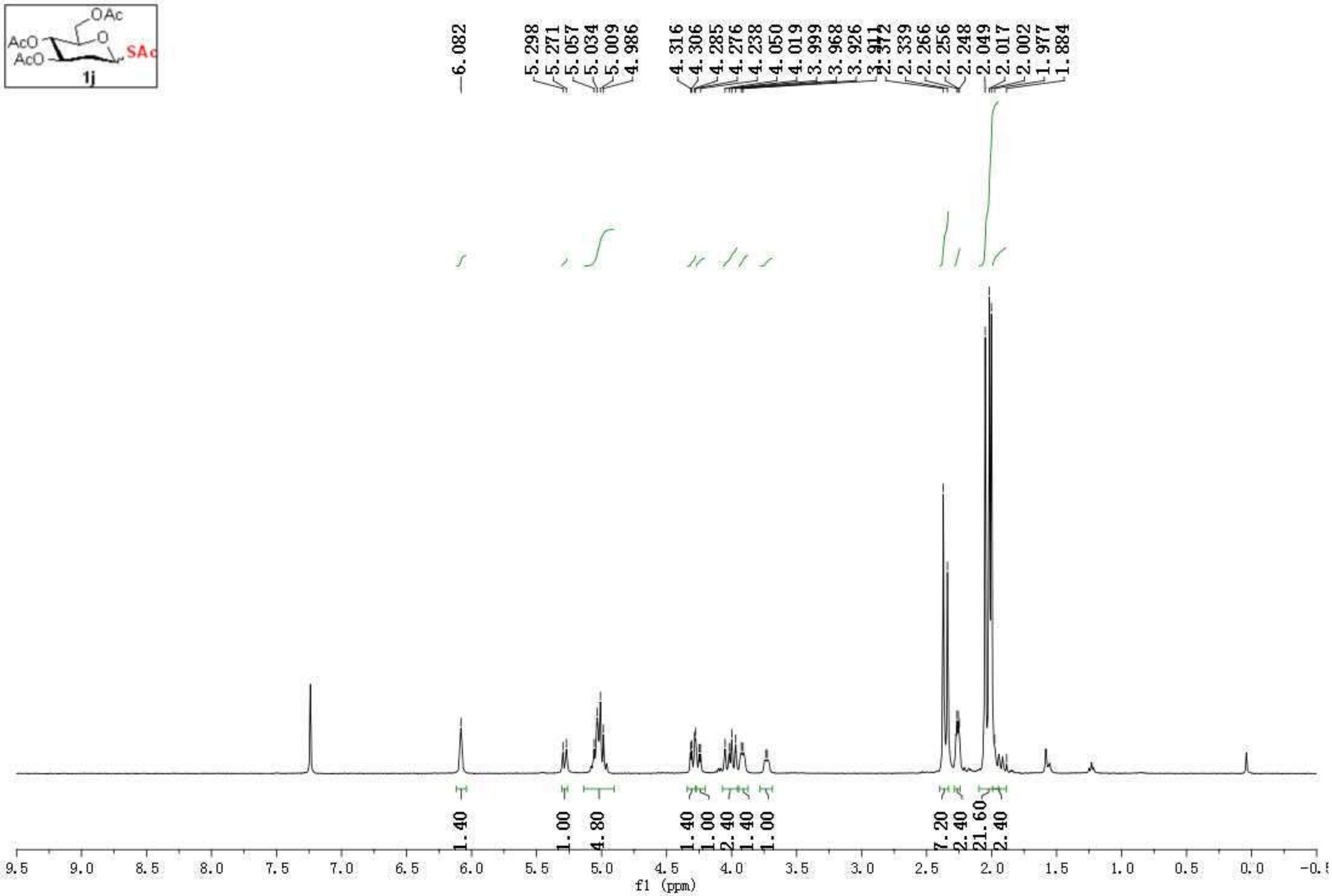


Figure S15. ^{1}H NMR spectrum of **1j** in $CDCl_3$

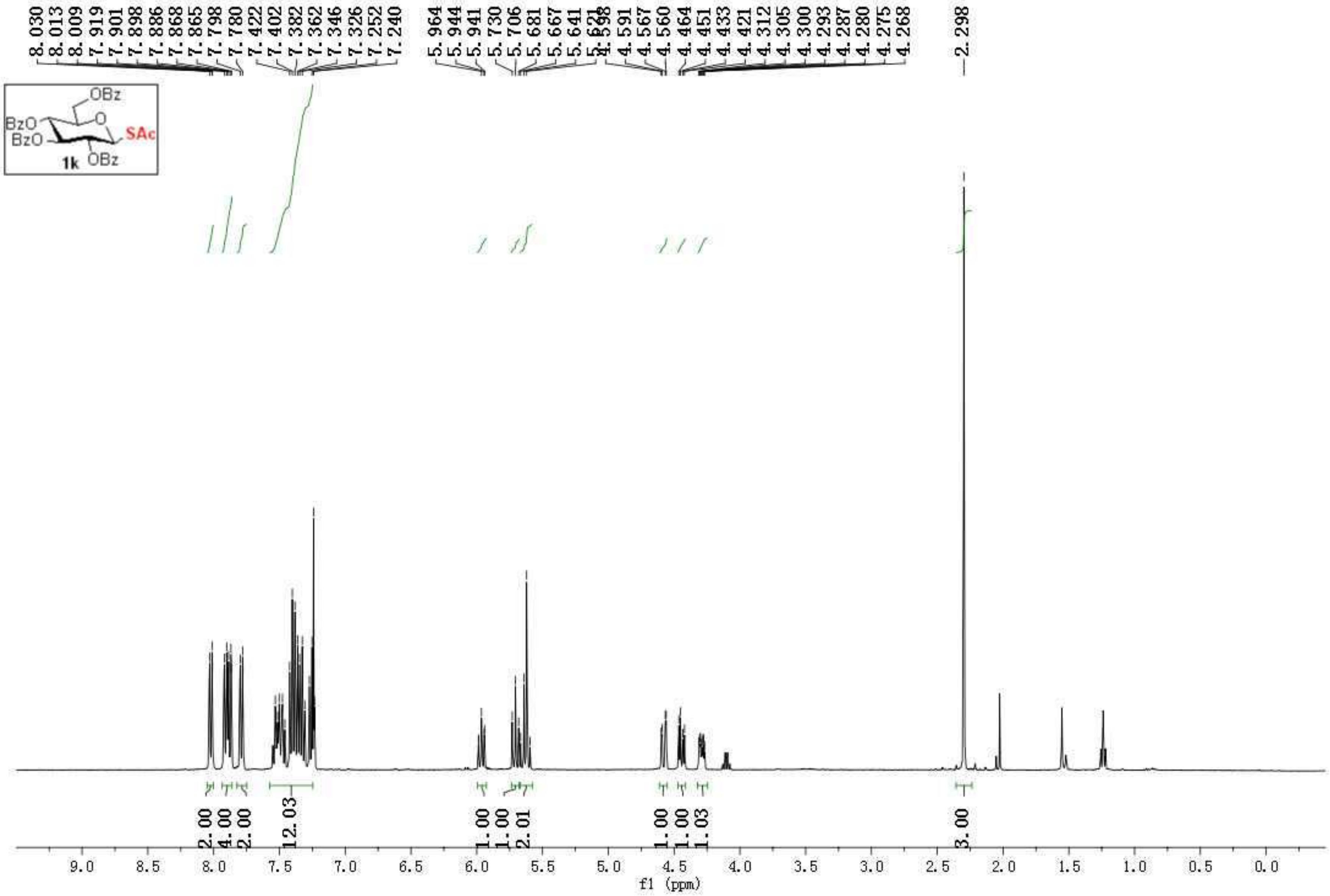


Figure S16. ^{1}H NMR spectrum of **1k** in $CDCl_3$

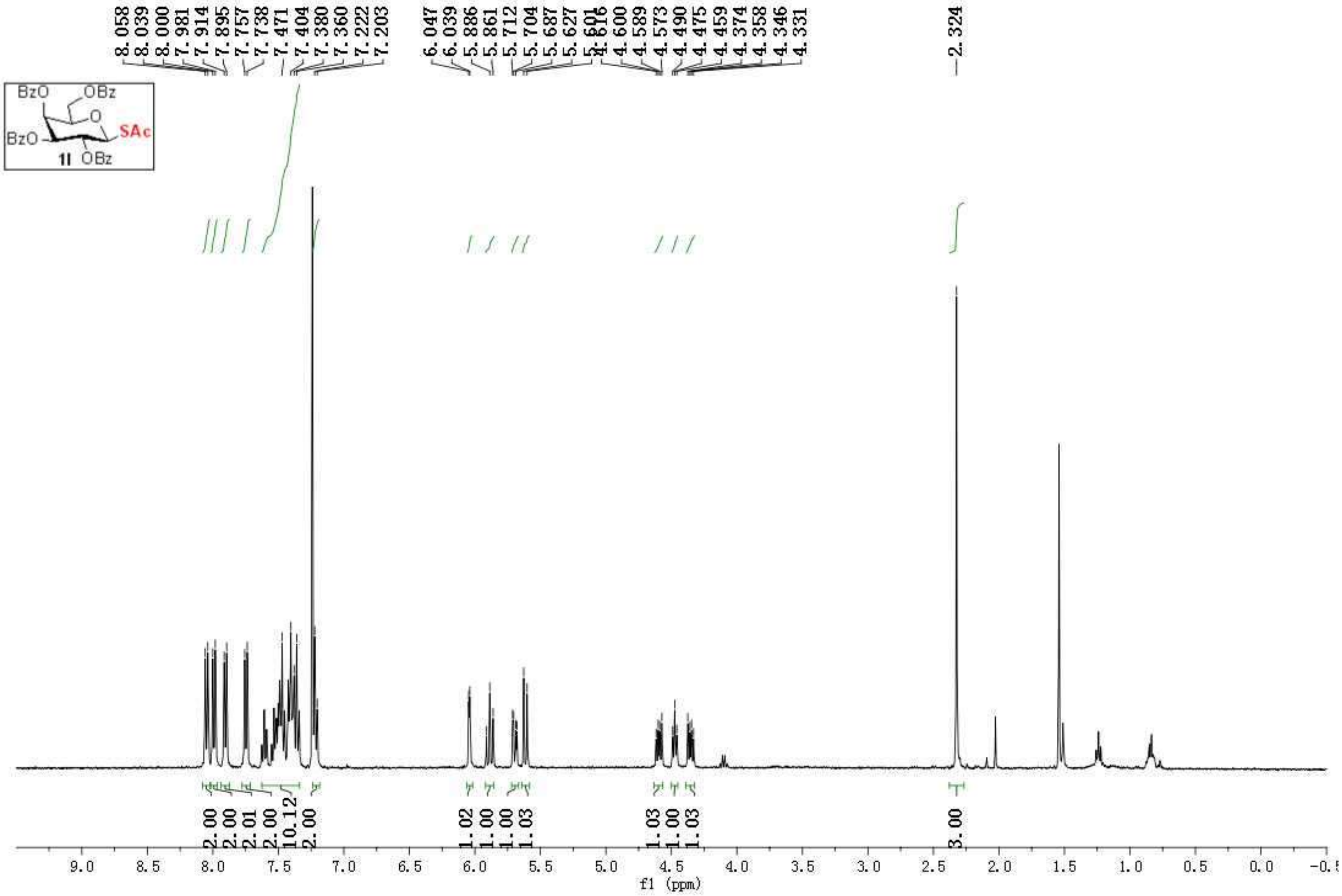


Figure S17. ^{1}H NMR spectrum of **1l** in $CDCl_3$

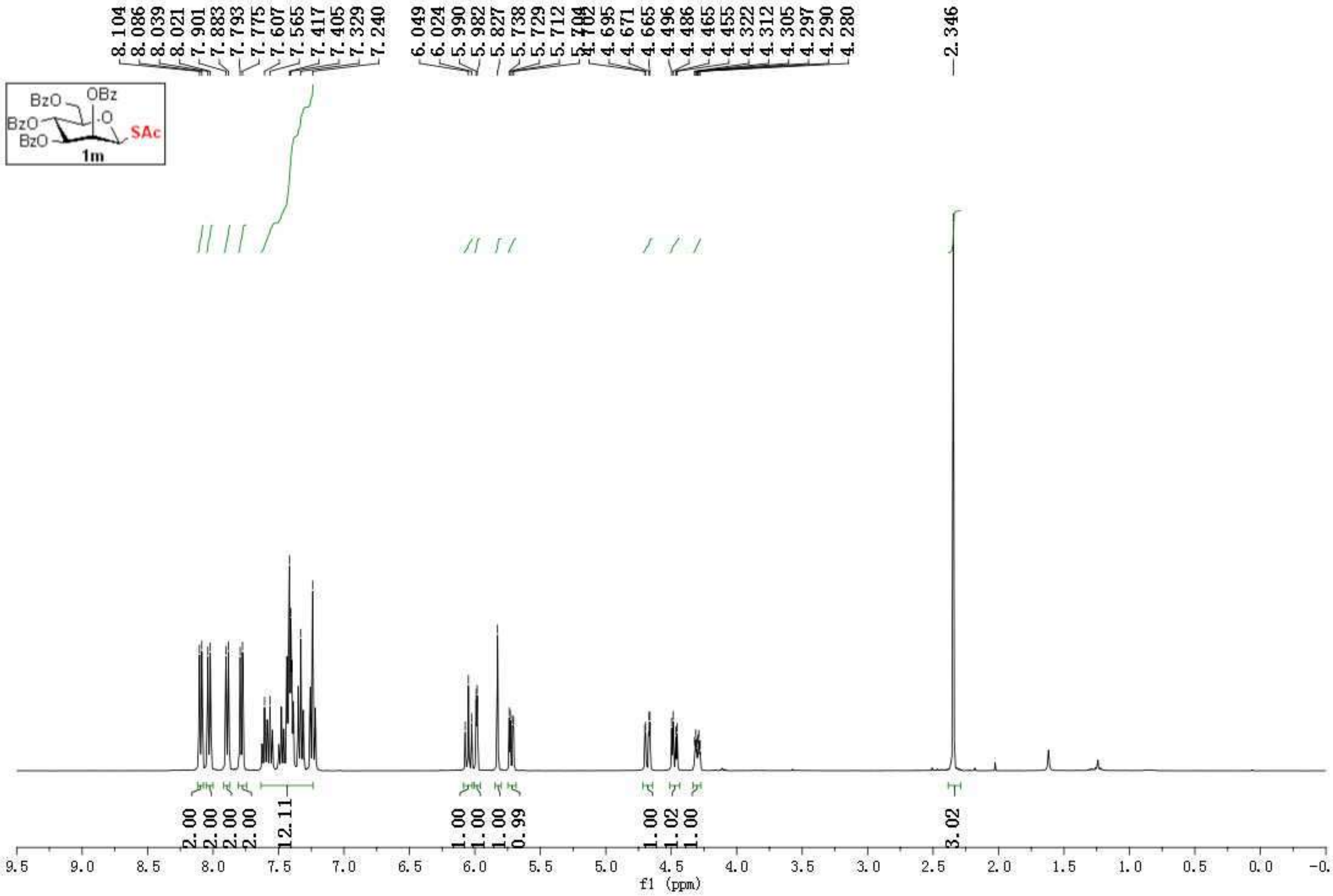


Figure S18. ^{1}H NMR spectrum of **1m** in CDCl$_3$

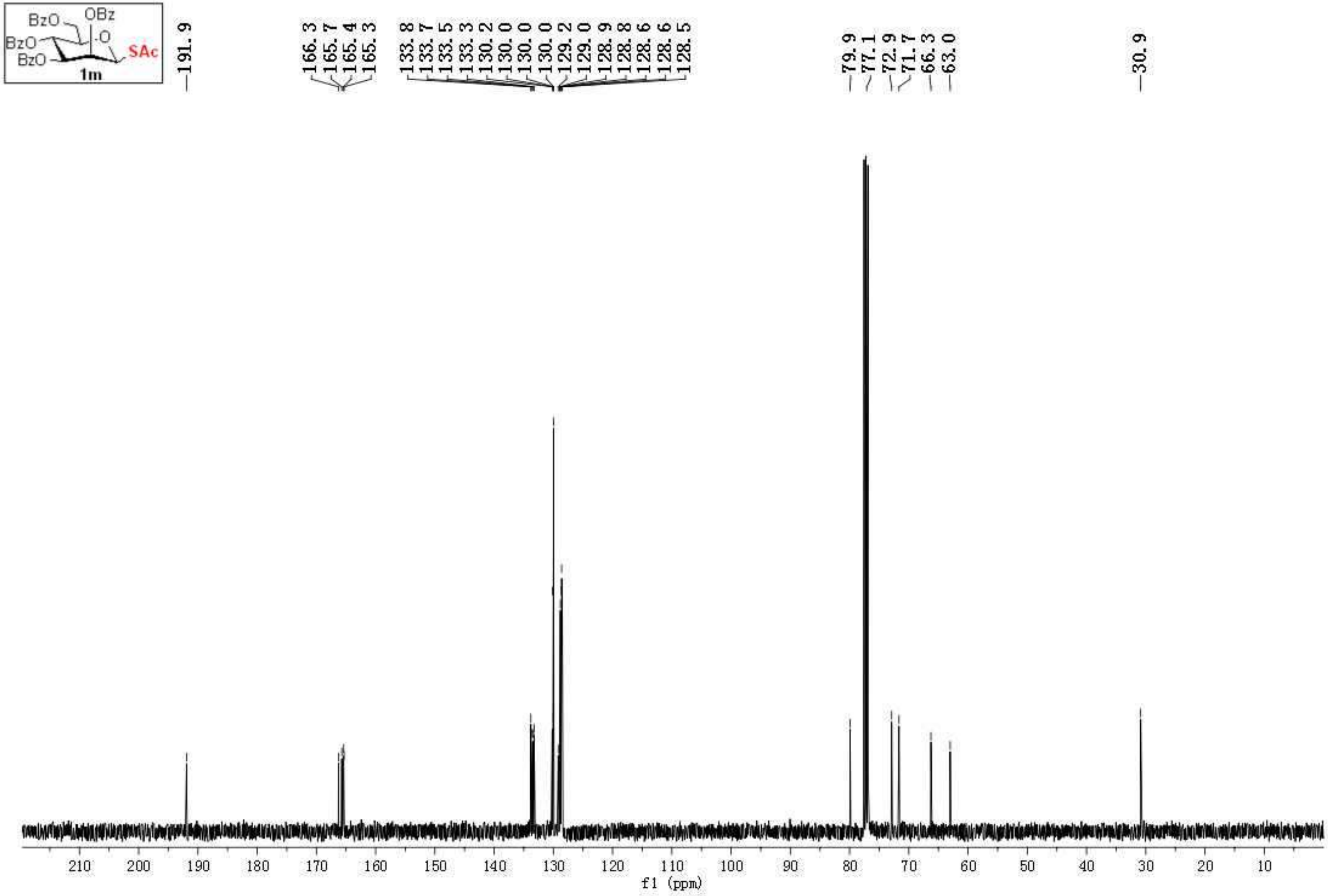


Figure S19. ^{13}C NMR spectrum (100 MHz) of **1m** in $CDCl_3$

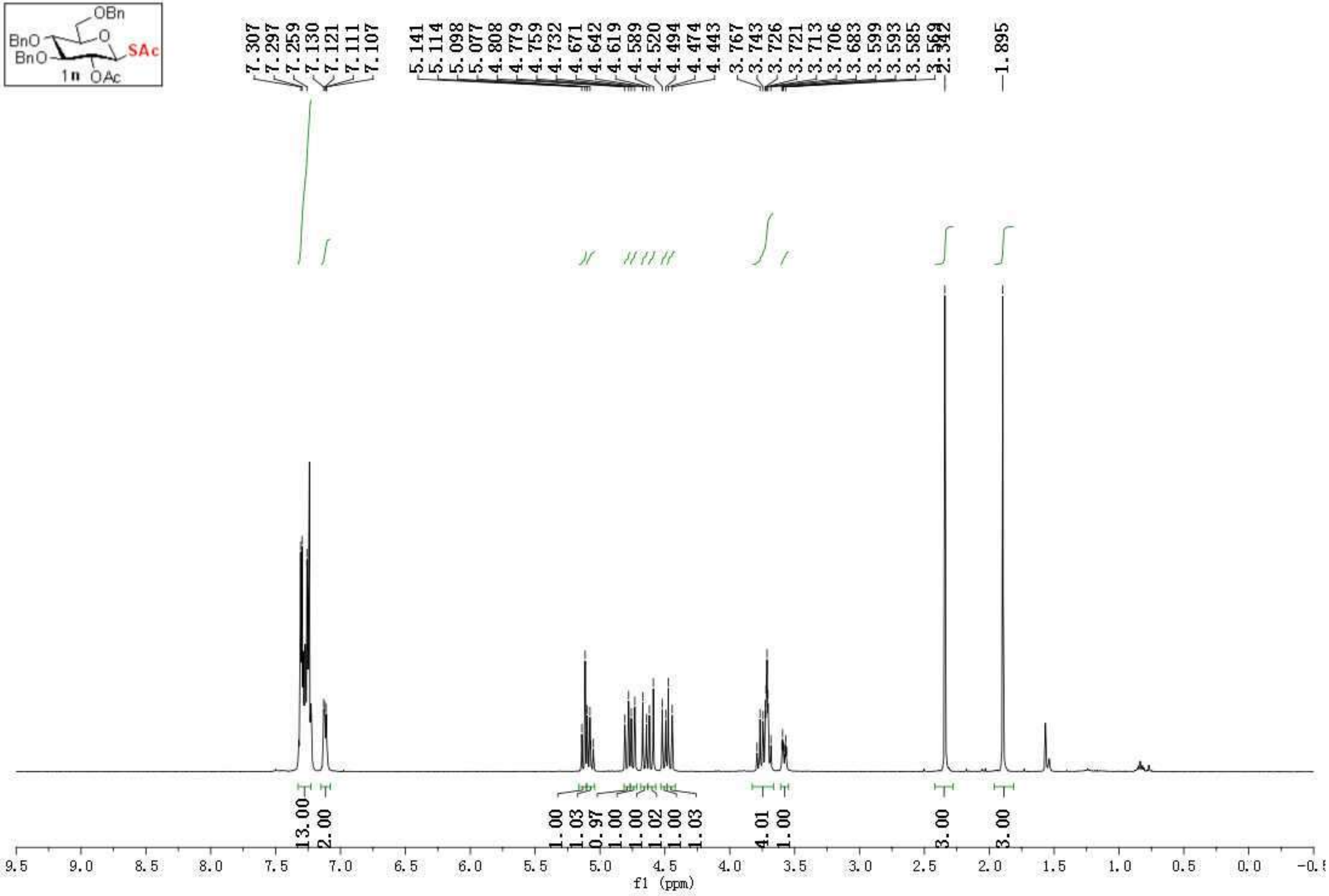


Figure S20. ^{1}H NMR spectrum of **1n** in $CDCl_3$

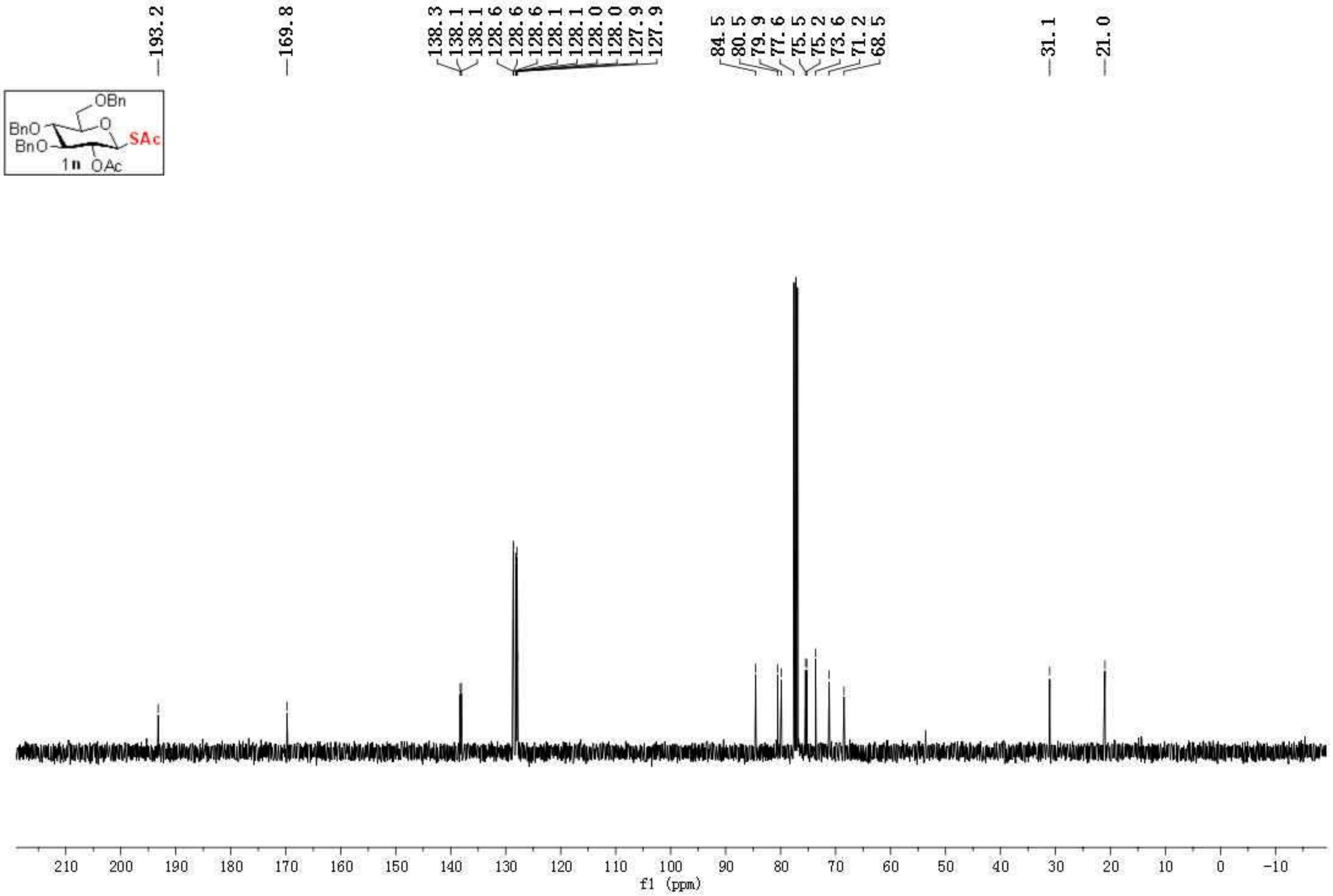


Figure S21. ^{13}C NMR spectrum (100 MHz) of **1n** in $CDCl_3$

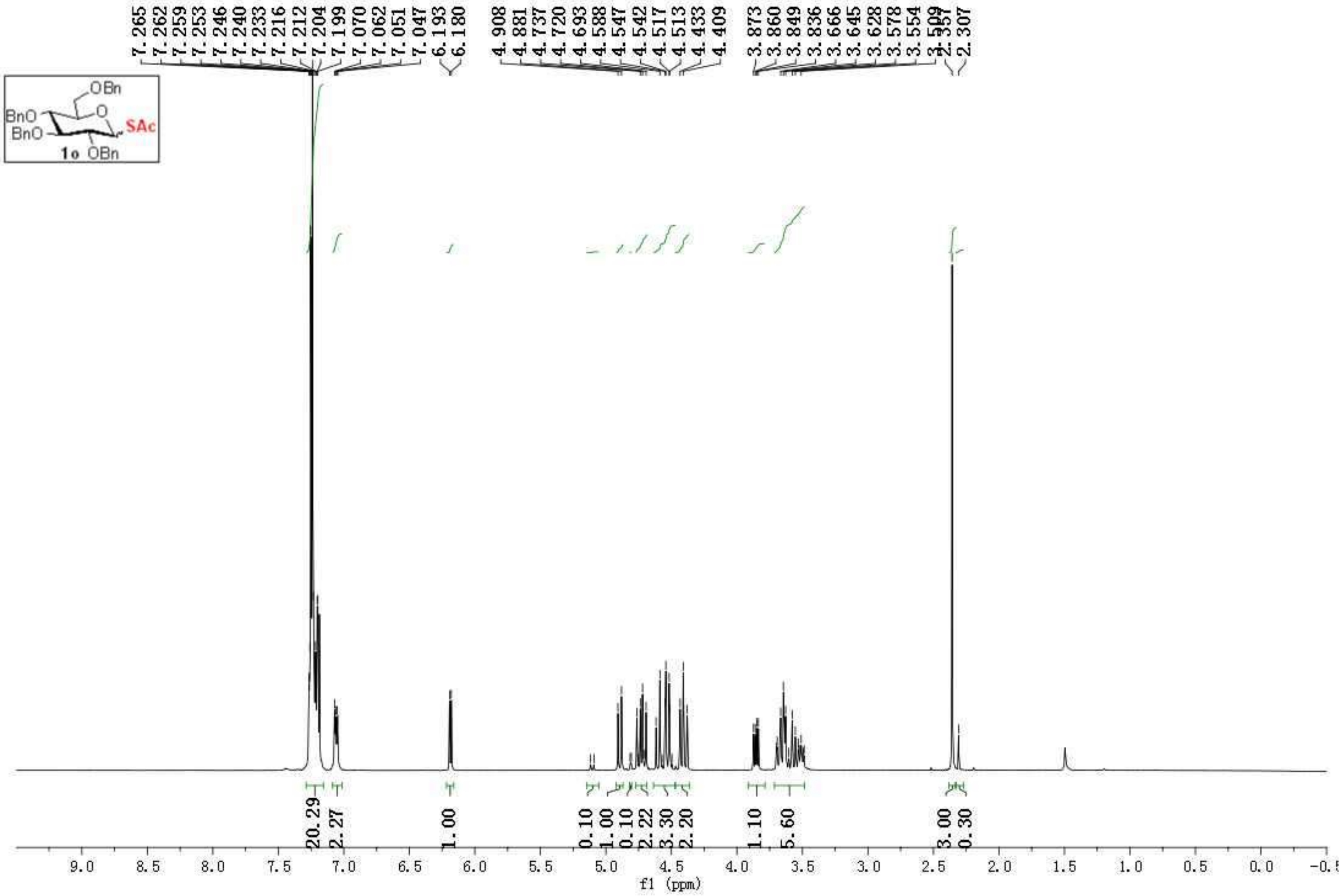


Figure S22. ^{1}H NMR spectrum of **1o** in CDCl$_3$

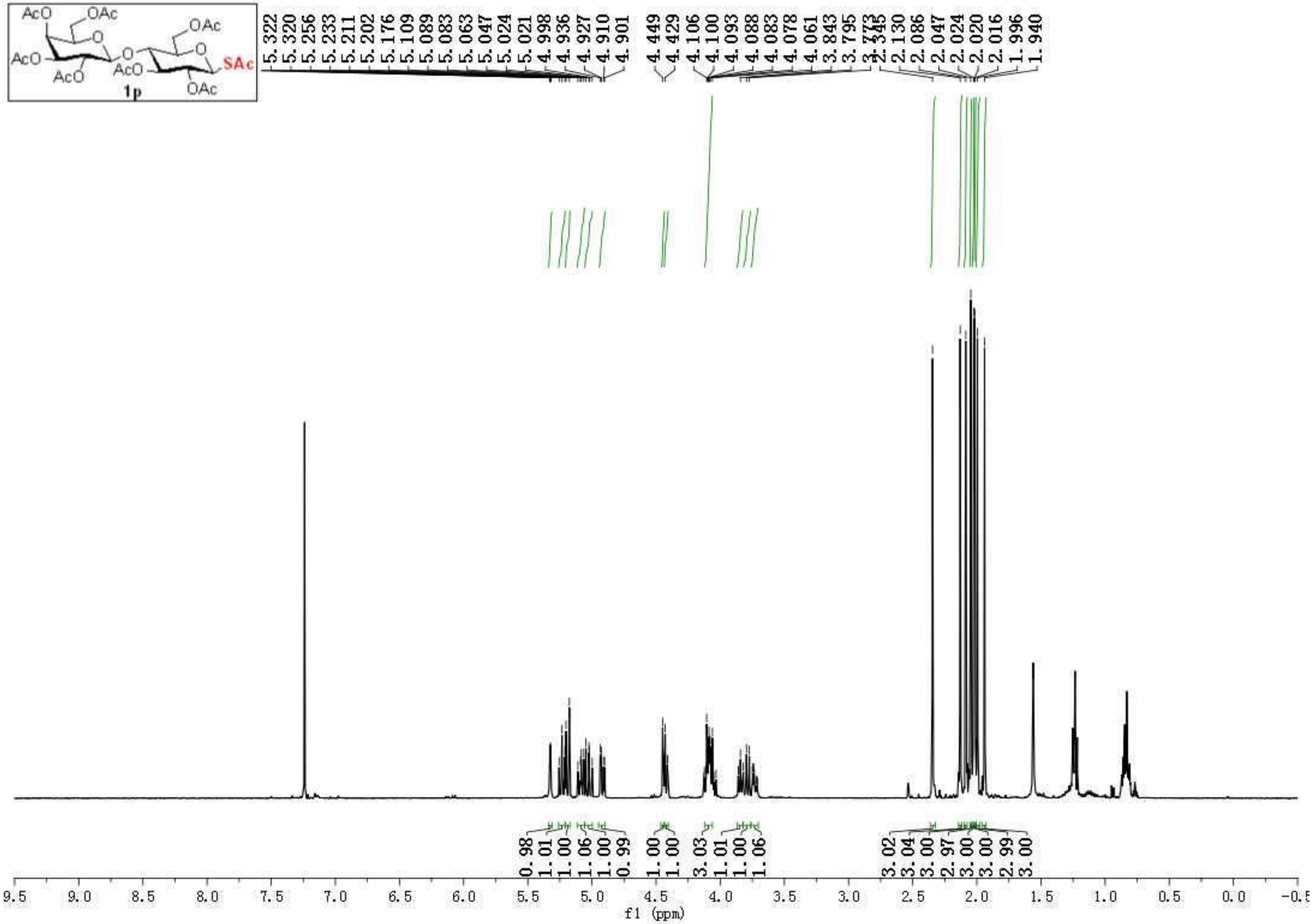


Figure S23. ^{1}H NMR spectrum of **1p** in $CDCl_3$

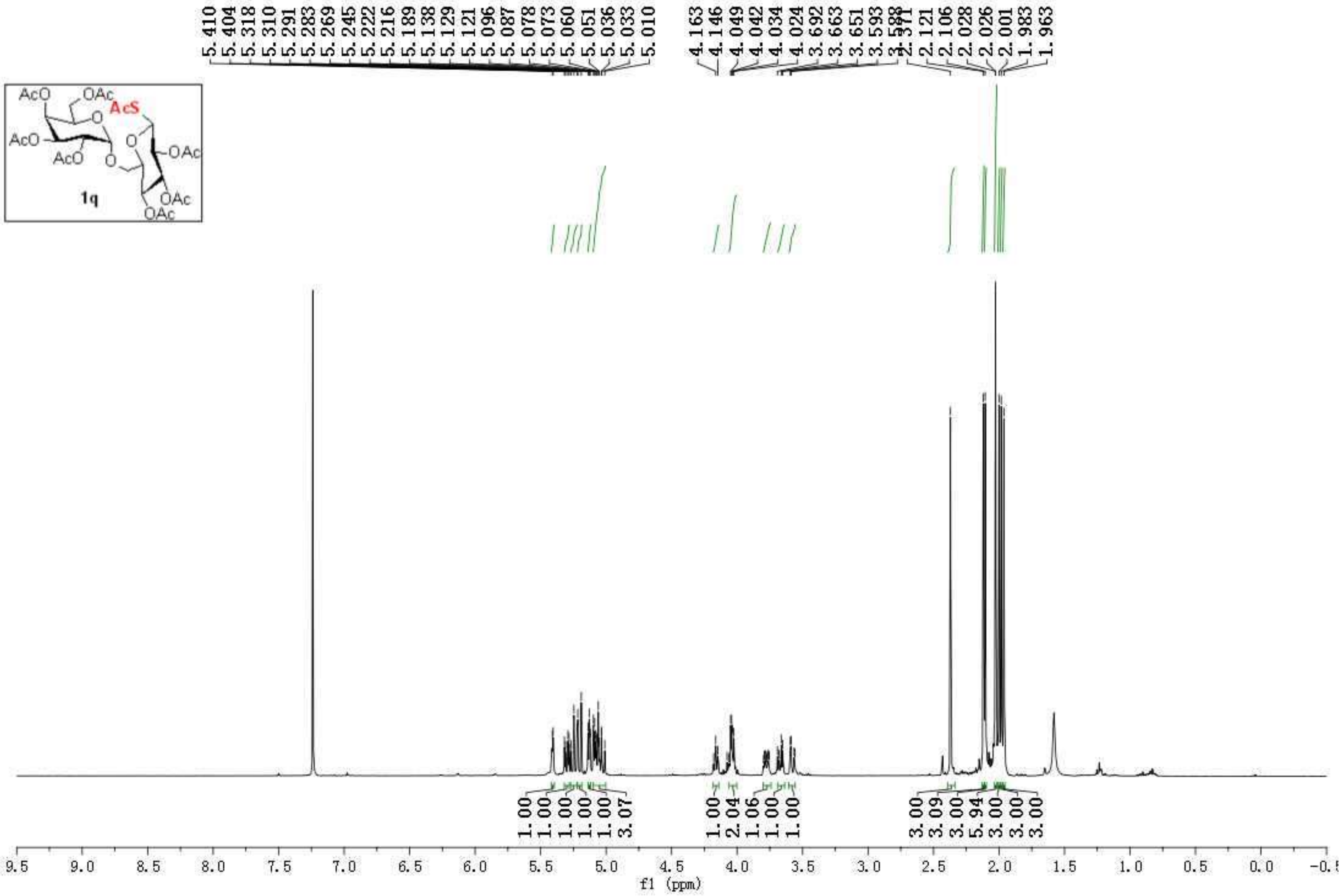


Figure S24. ^{1}H NMR spectrum of **1q** in $CDCl_3$

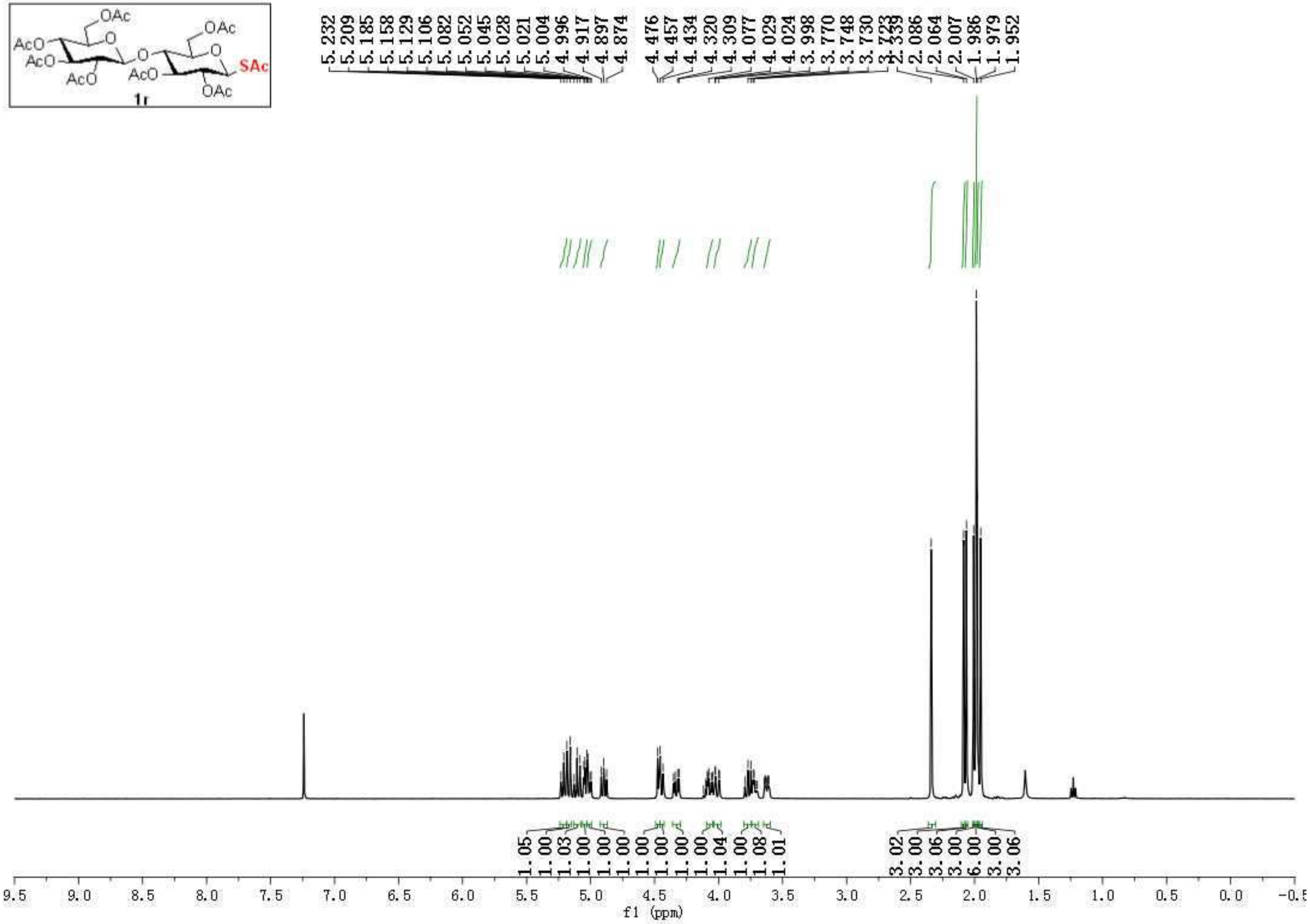


Figure S25. ^{1}H NMR spectrum of **1r** in $CDCl_3$

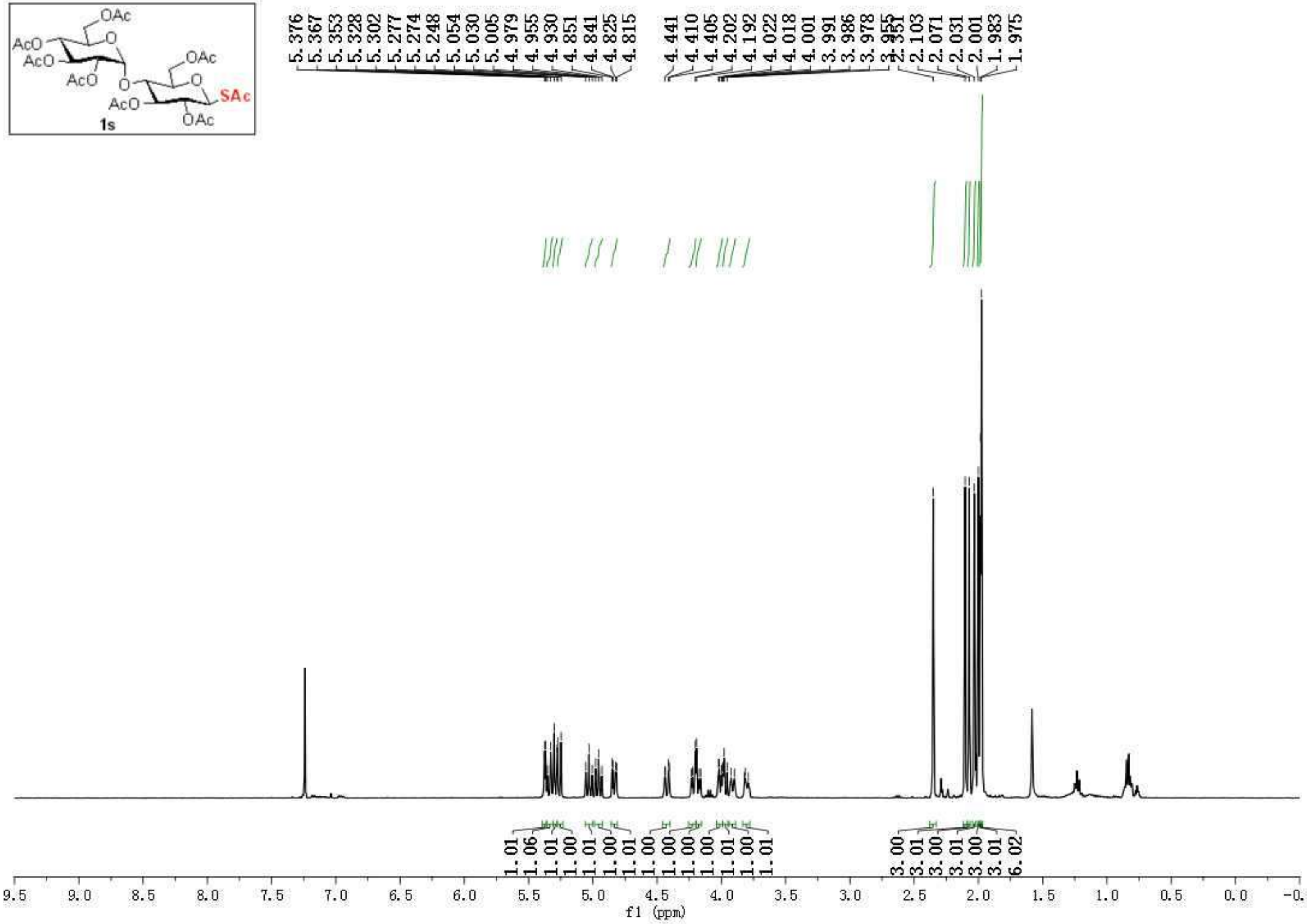


Figure S26. ^{1}H NMR spectrum of **1s** in $CDCl_3$

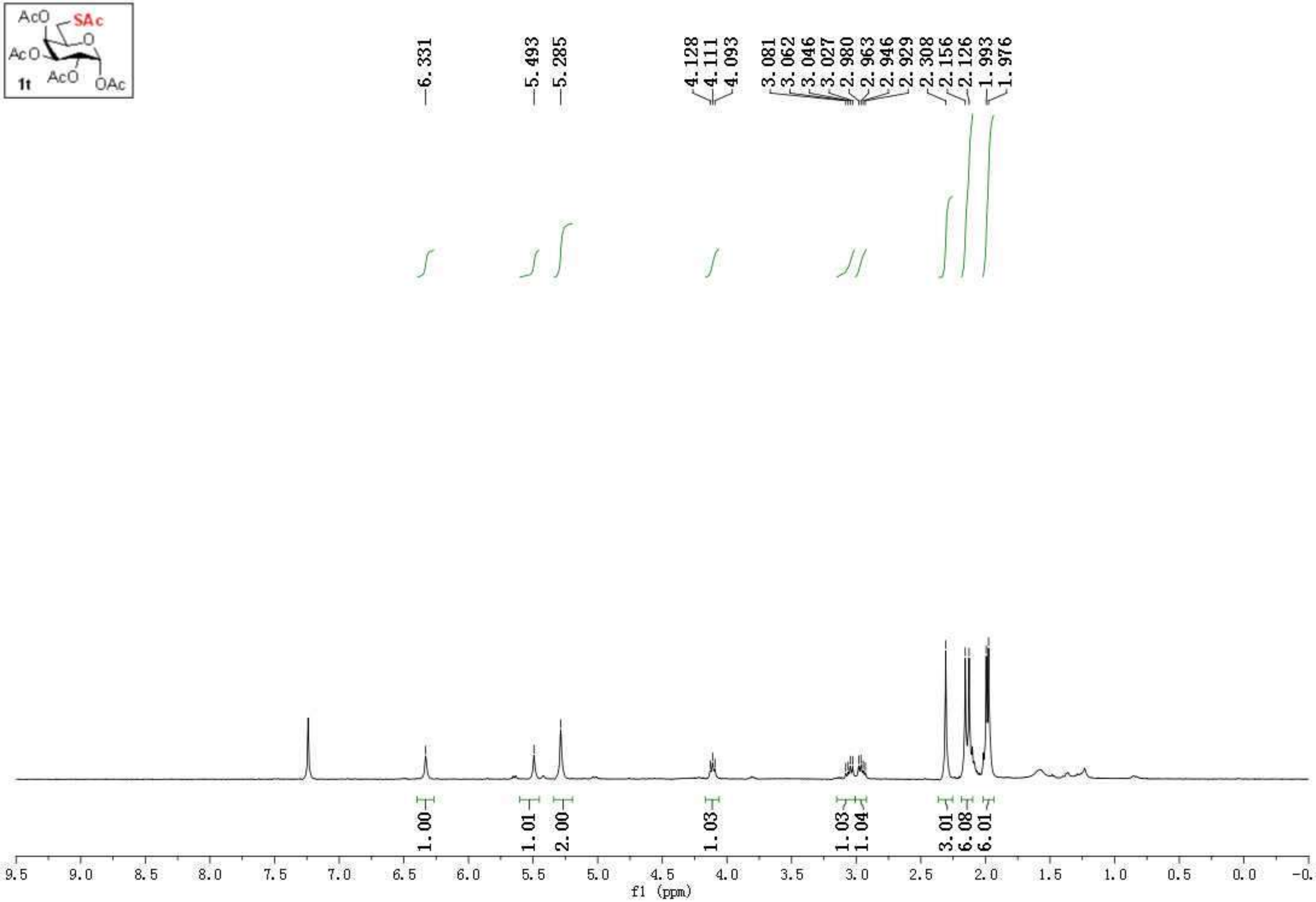


Figure S27. ^{1}H NMR spectrum of **1t** in $CDCl_3$

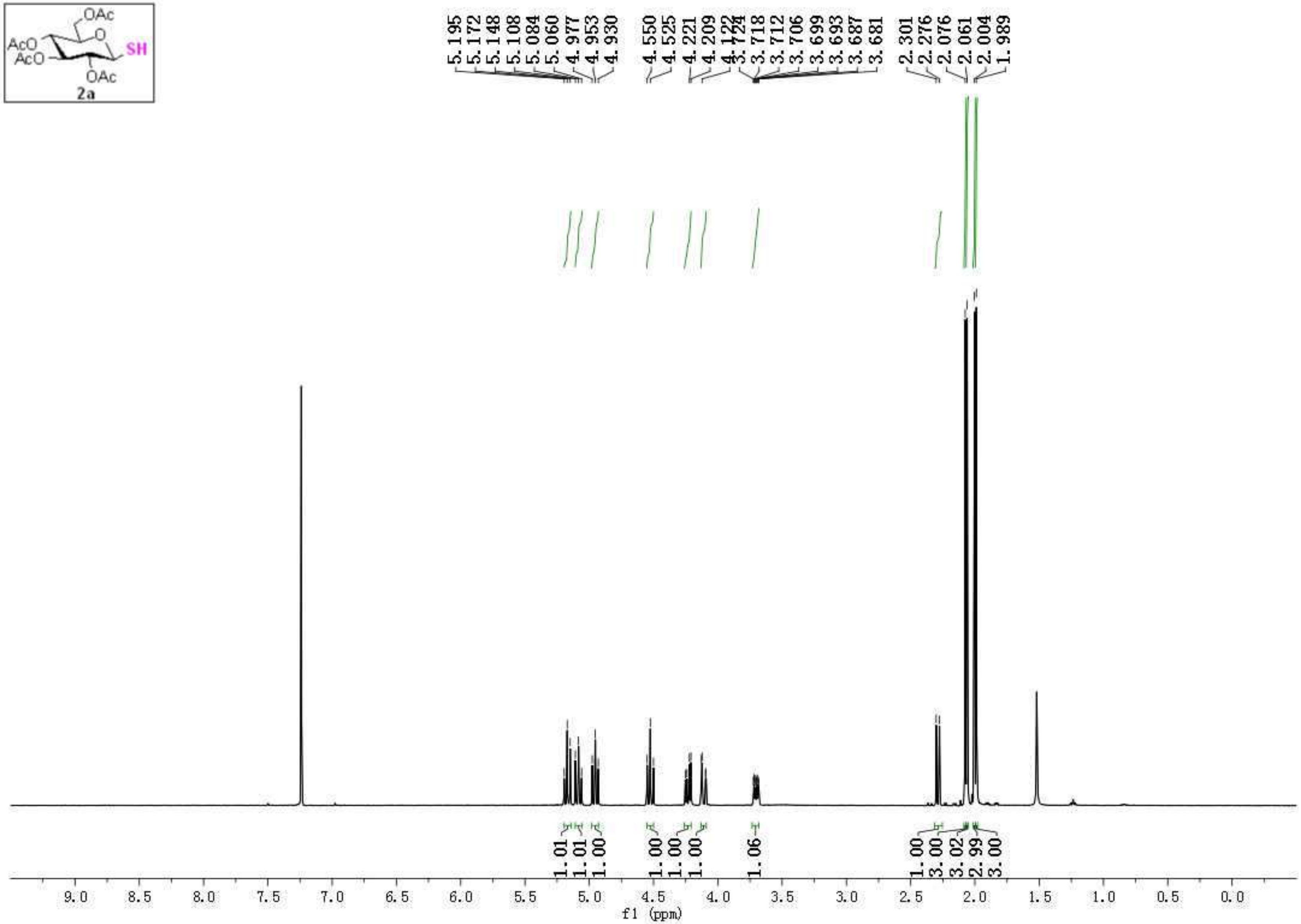


Figure S28. ^{1}H NMR spectrum of **2a** in $CDCl_3$

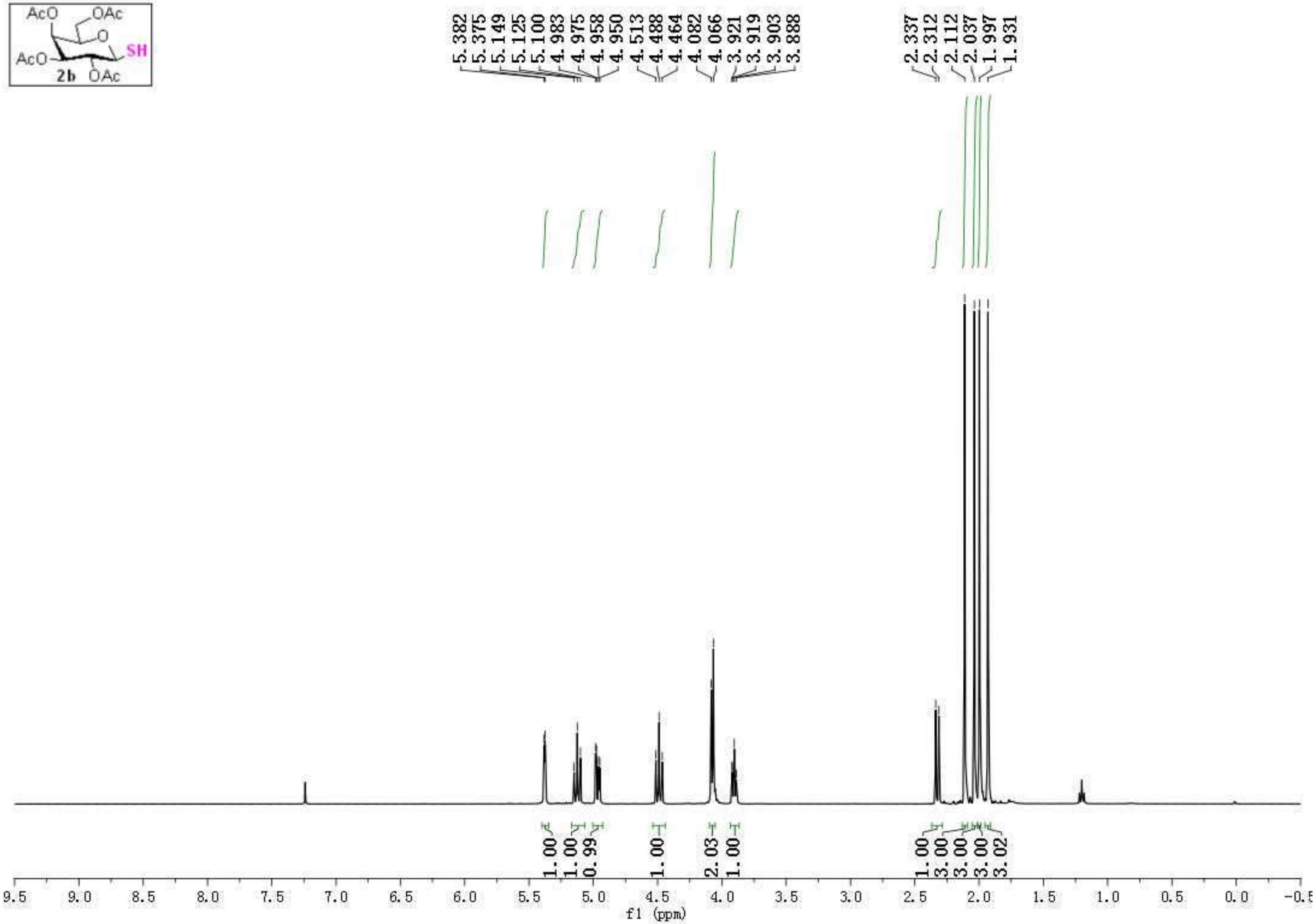


Figure S29. ^{1}H NMR spectrum of **2b** in $CDCl_3$

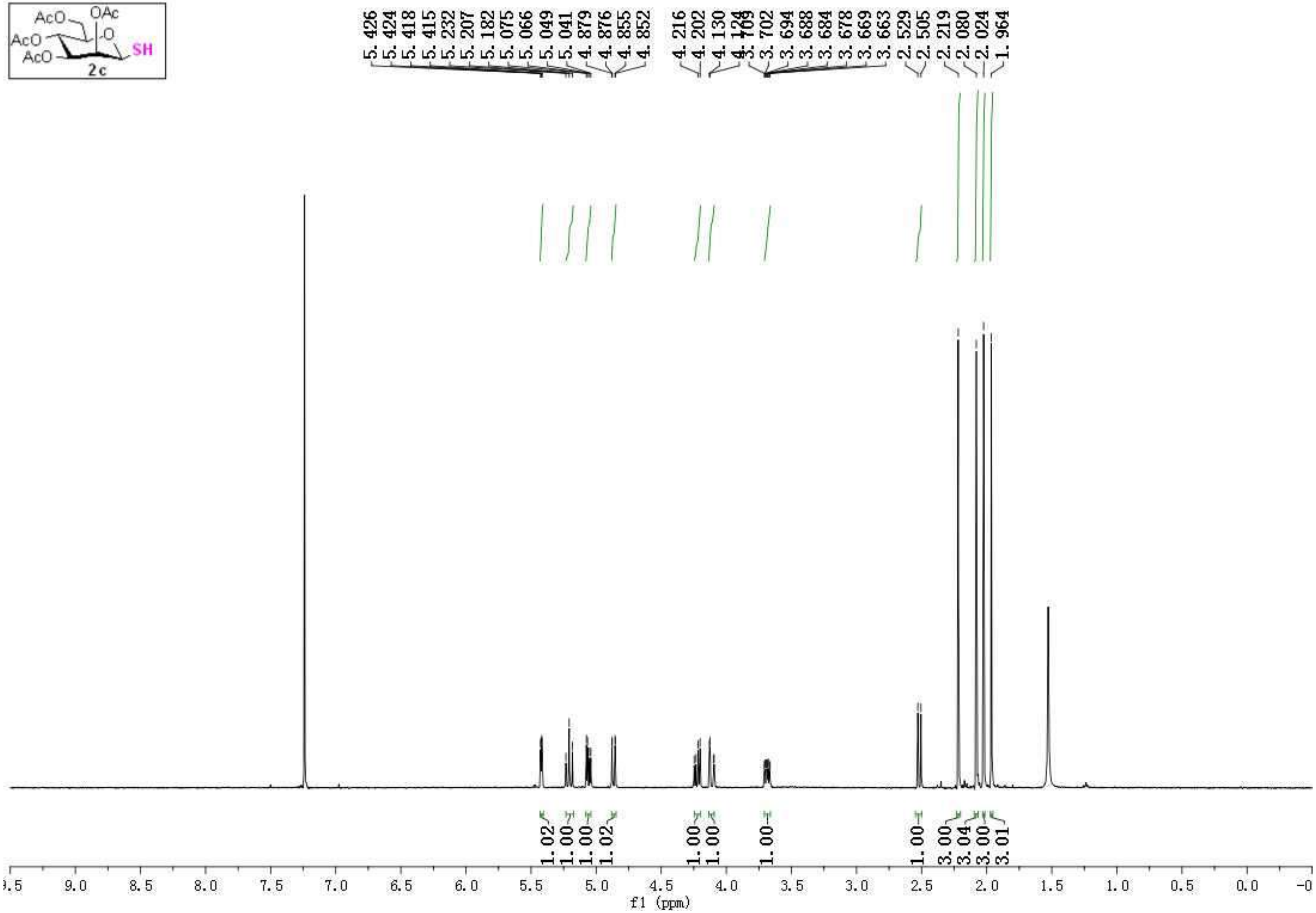


Figure S30. ^{1}H NMR spectrum of **2c** in $CDCl_3$

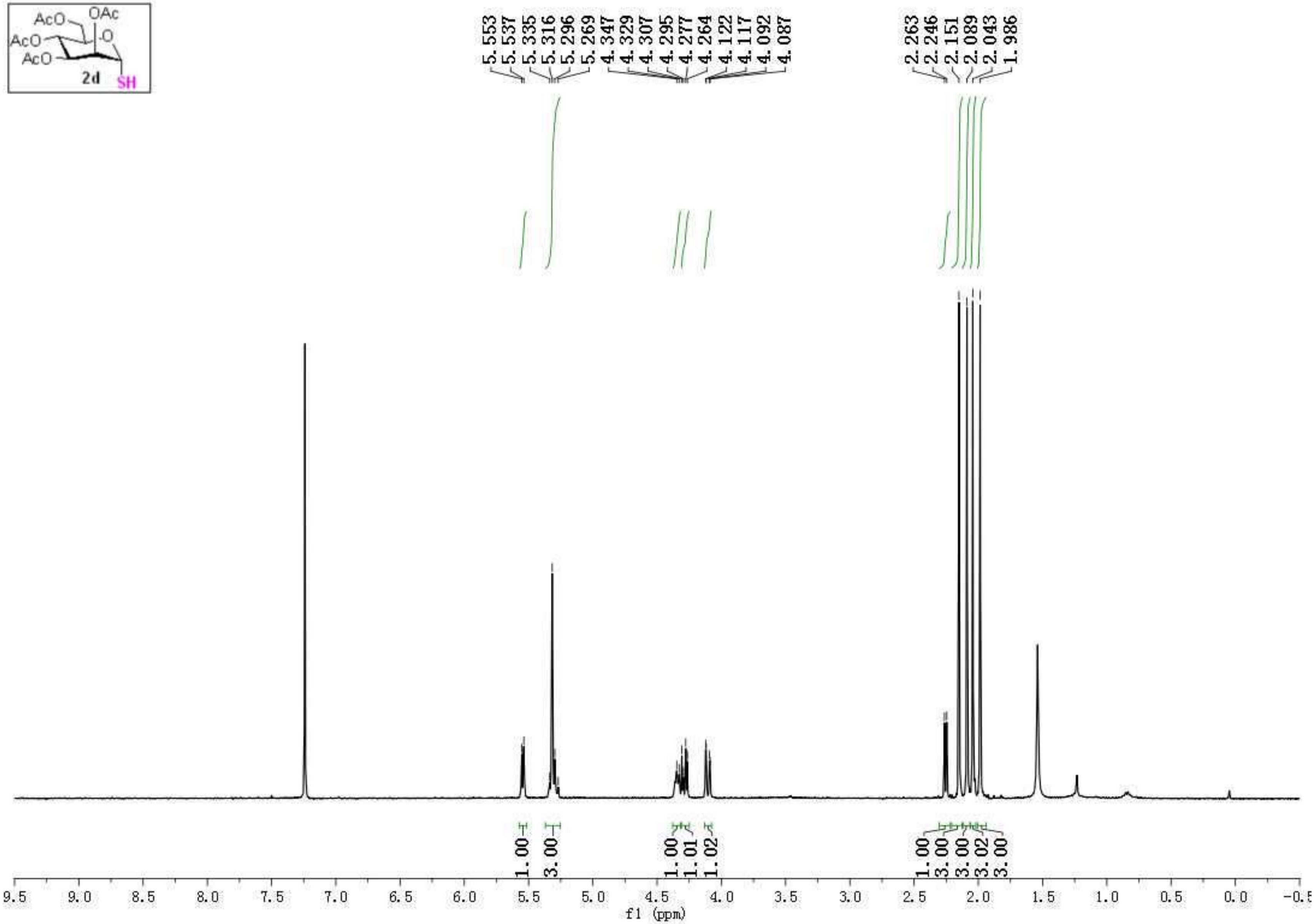


Figure S31. ^{1}H NMR spectrum of **2d** in $CDCl_3$

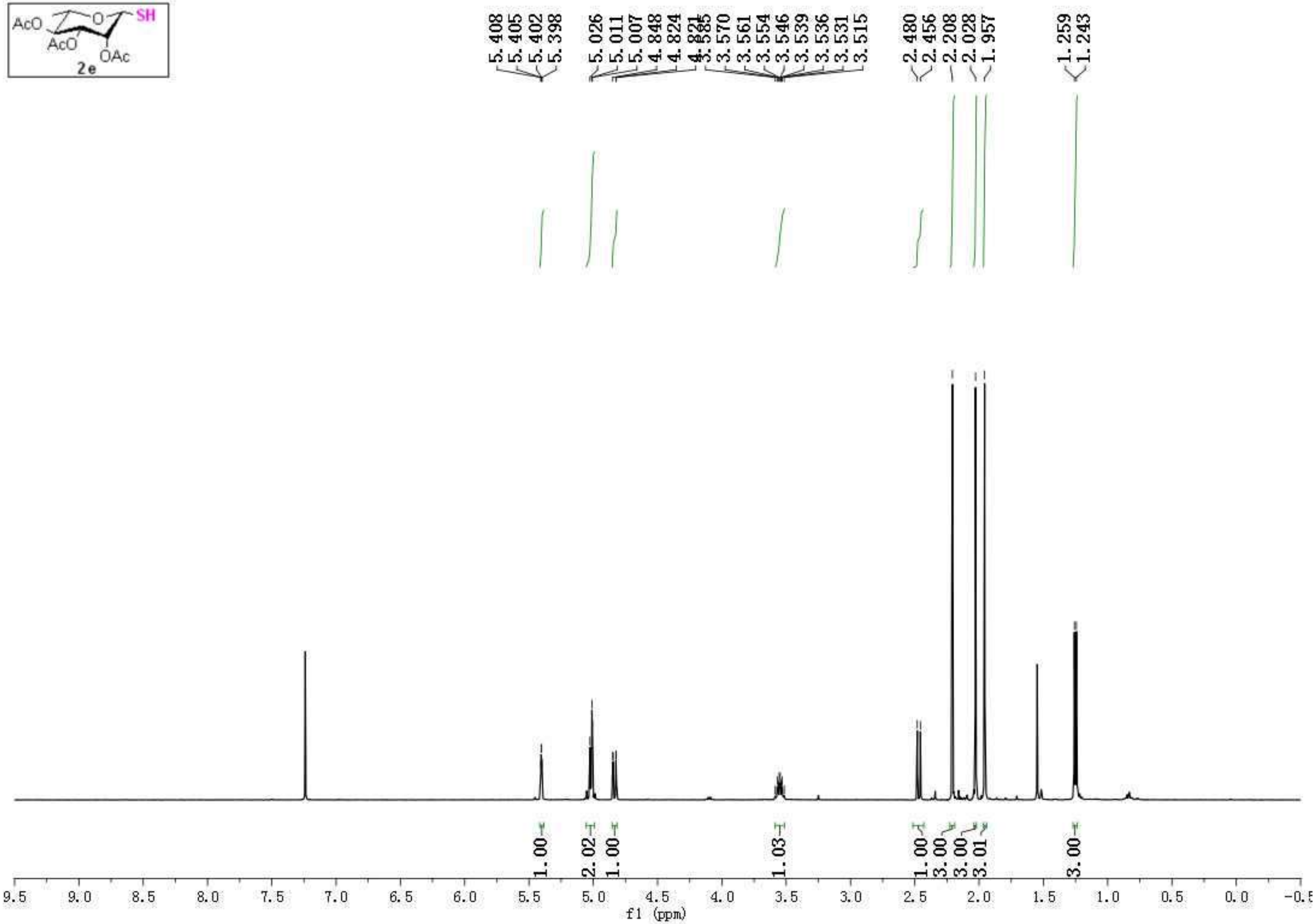


Figure S32. ^{1}H NMR spectrum of **2e** in $CDCl_3$

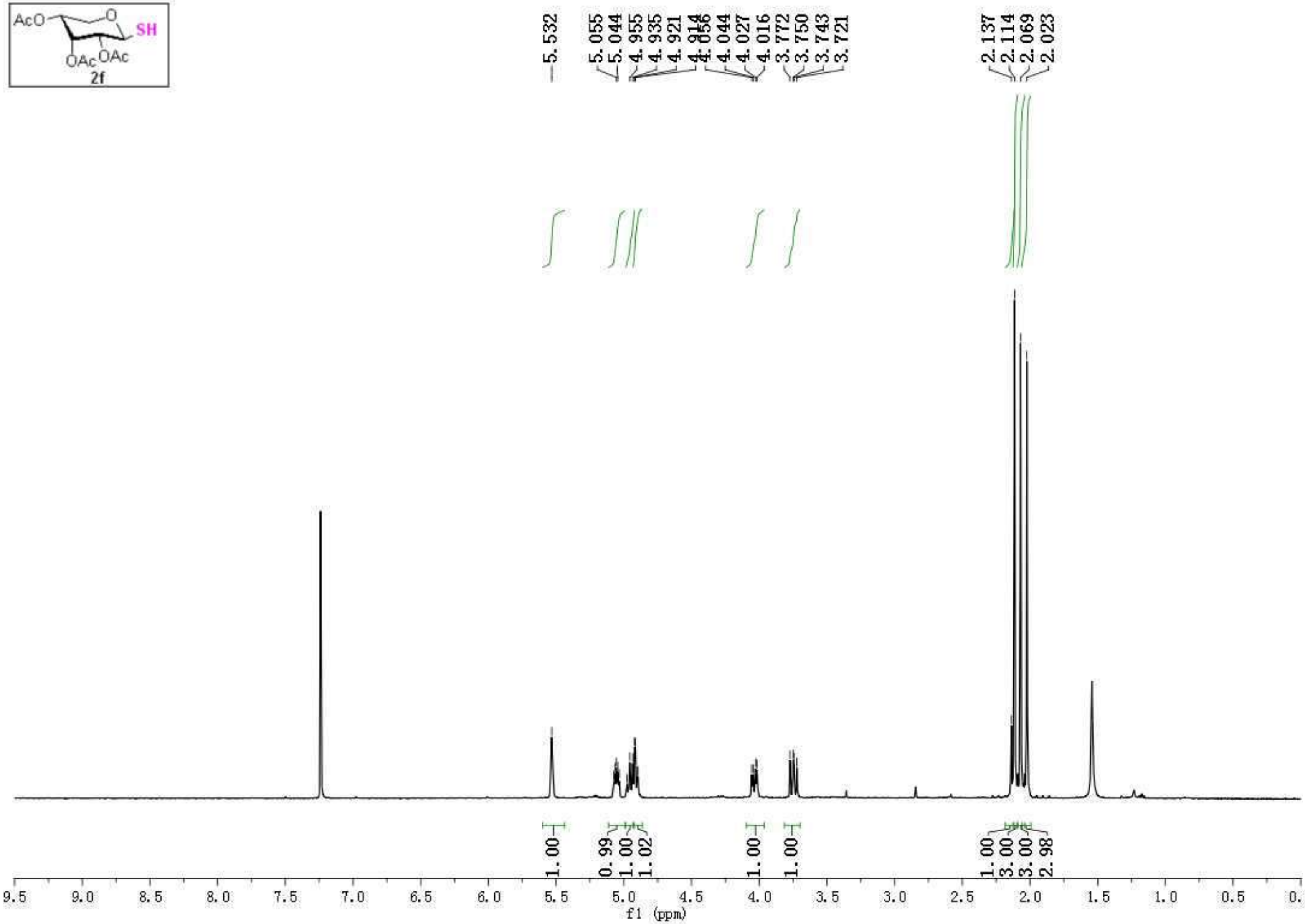


Figure S33. ^{1}H NMR spectrum of **2f** in $CDCl_3$

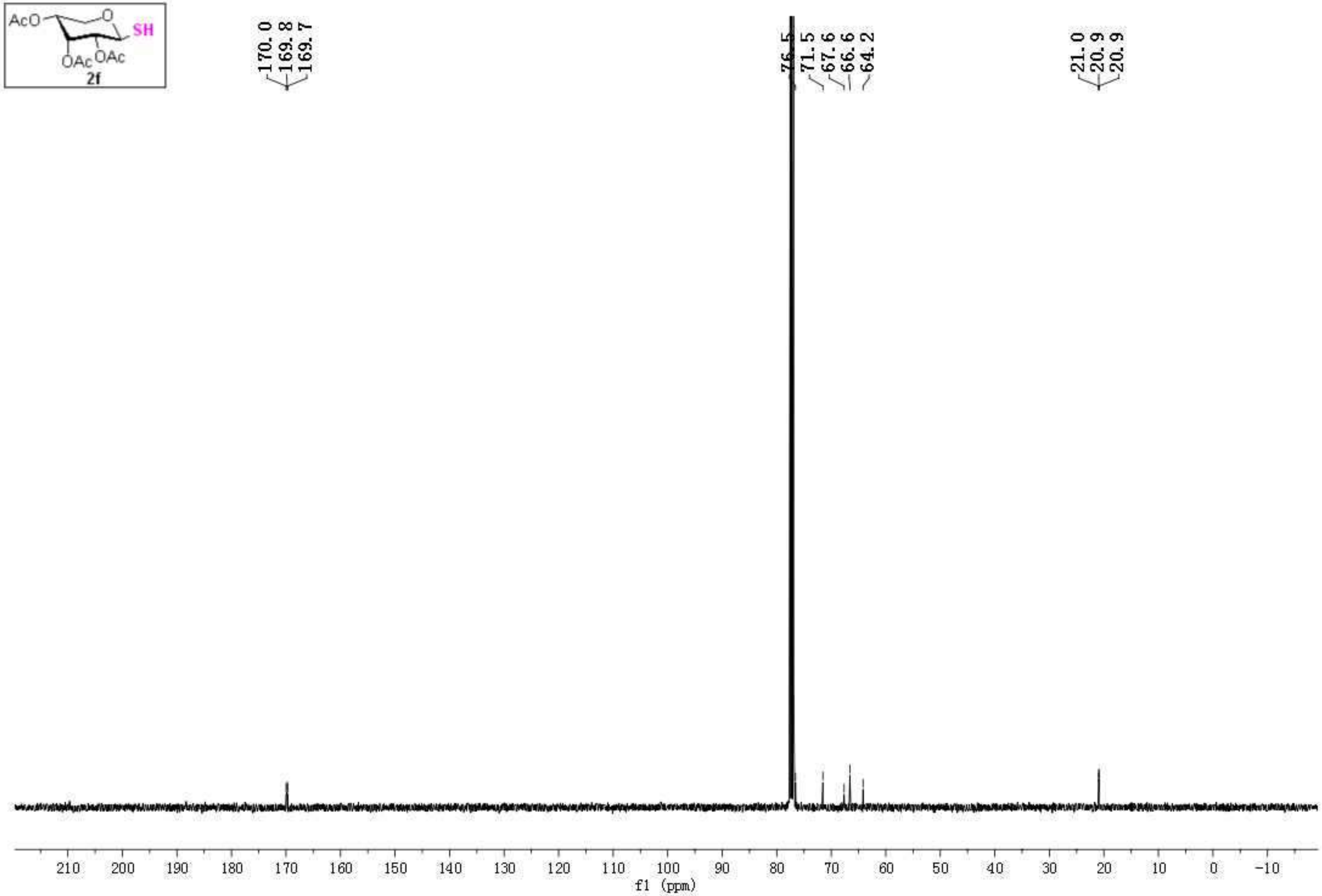


Figure S34. ^{13}C NMR spectrum (100 MHz) of **2f** in $CDCl_3$

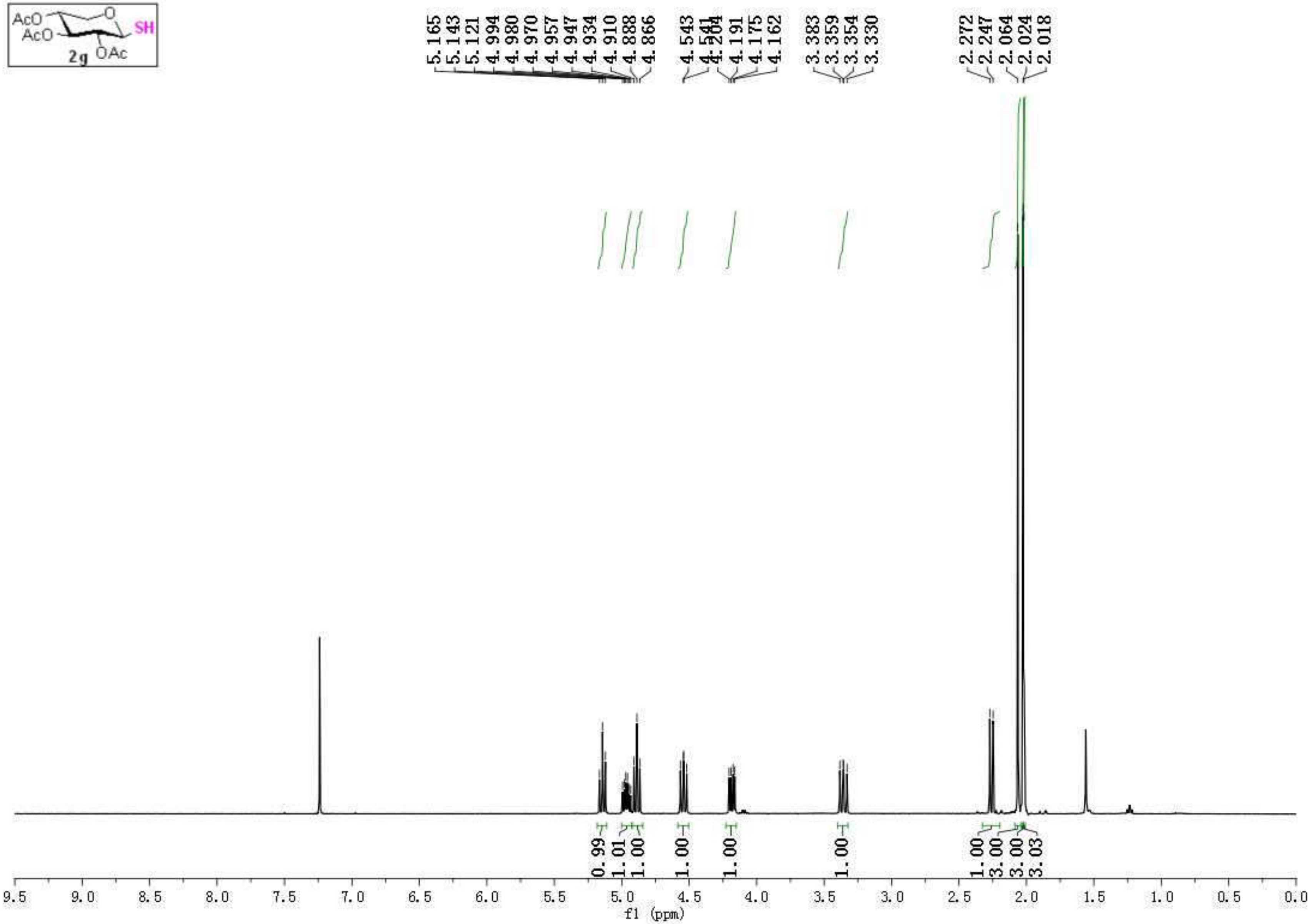


Figure S35. ^{1}H NMR spectrum of **2g** in CDCl$_3$

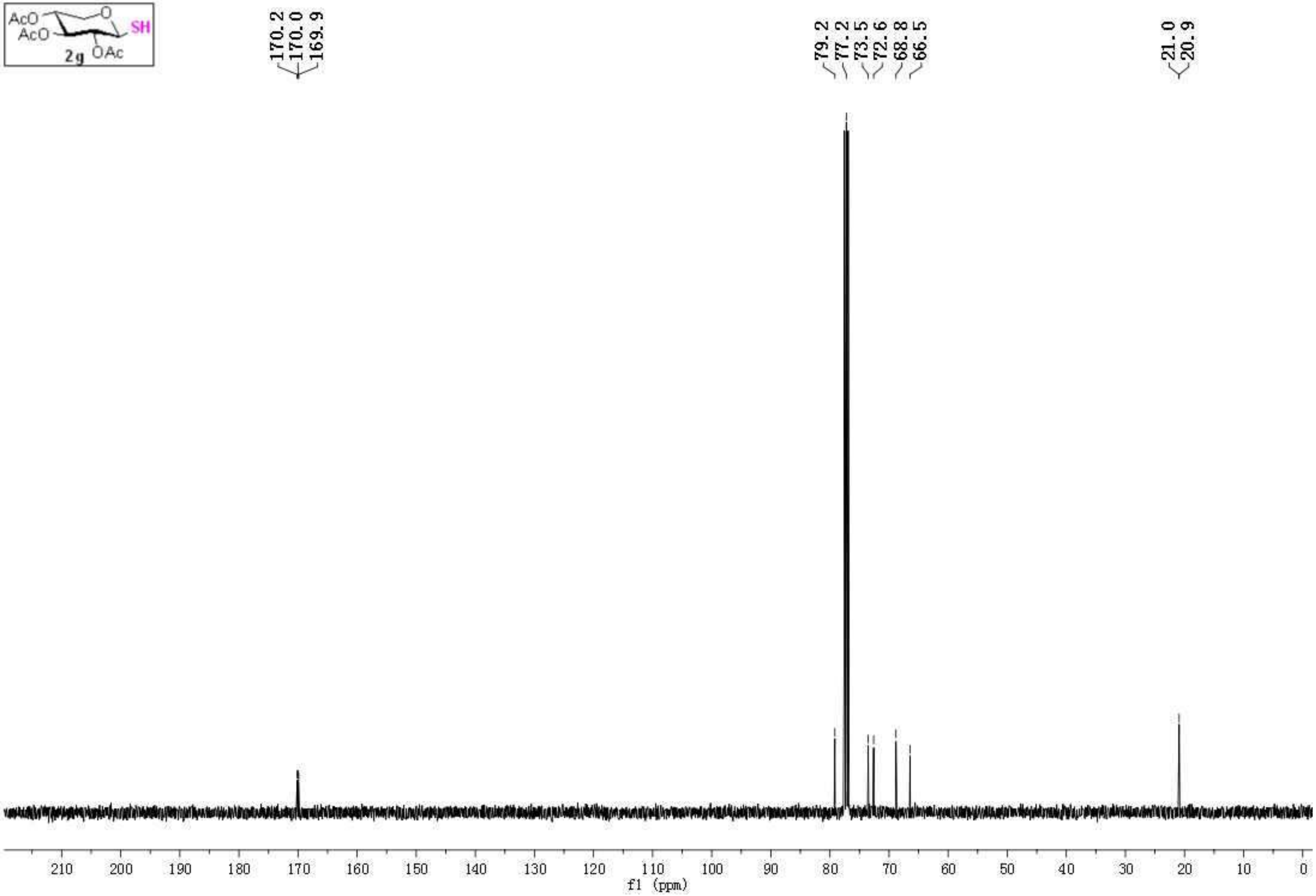


Figure S36. ^{13}C NMR spectrum (100 MHz) of **2g** in $CDCl_3$

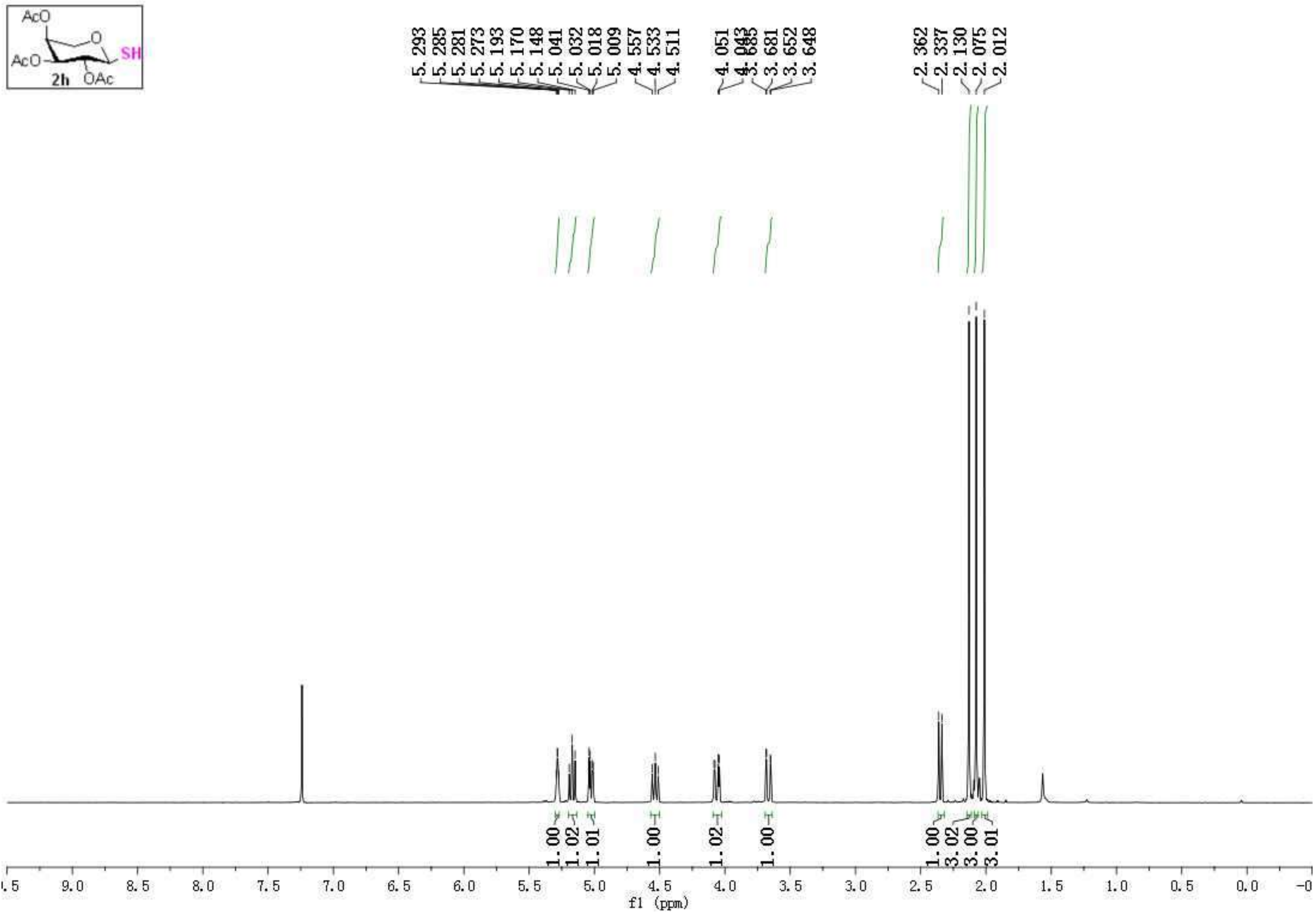


Figure S37. ^{1}H NMR spectrum of **2h** in $CDCl_3$

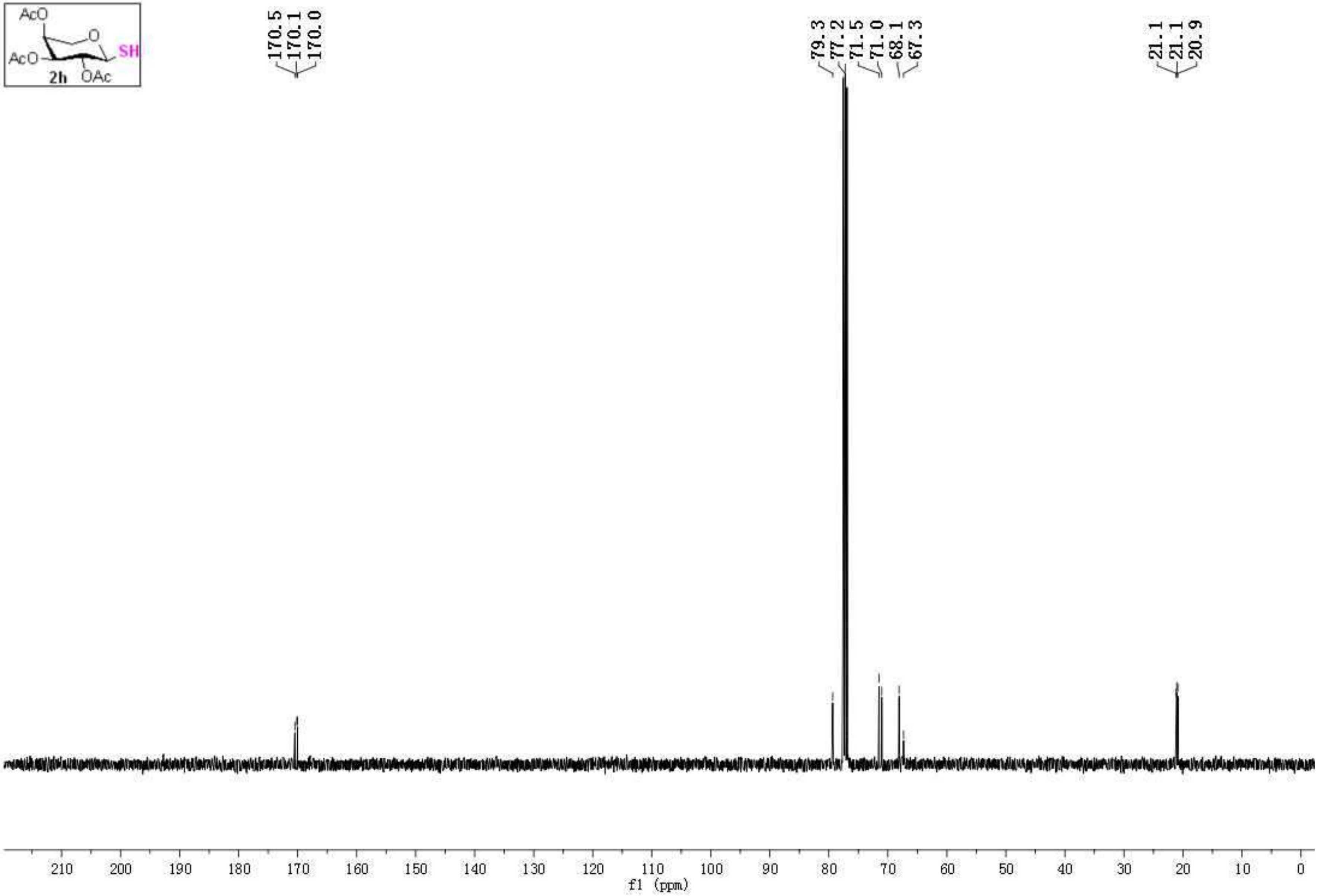


Figure S38. ^{13}C NMR spectrum (100 MHz) of **2h** in $CDCl_3$

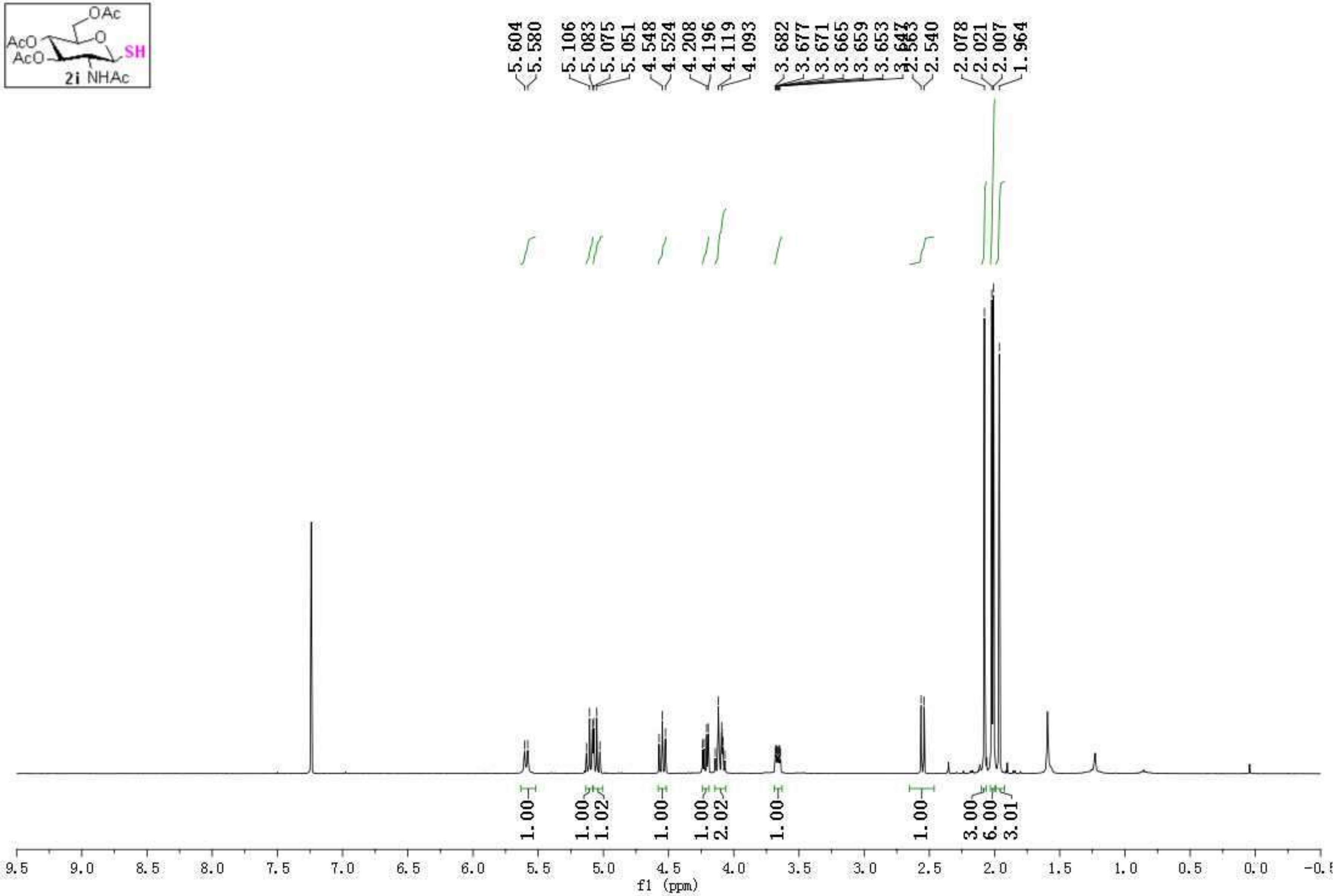


Figure S39. ^{1}H NMR spectrum of **2i** in $CDCl_3$

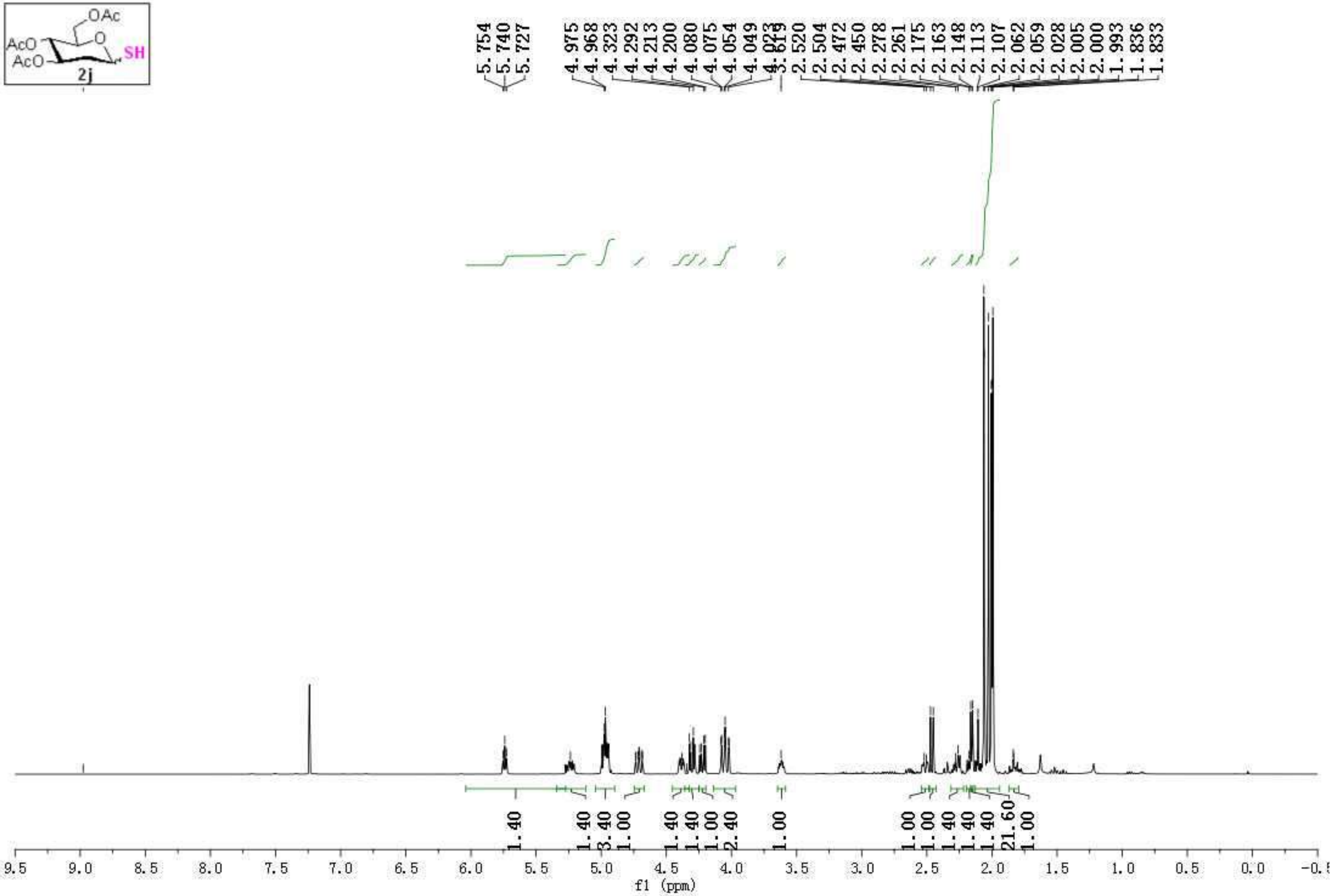


Figure S40. ^{1}H NMR spectrum of **2j** in $CDCl_3$

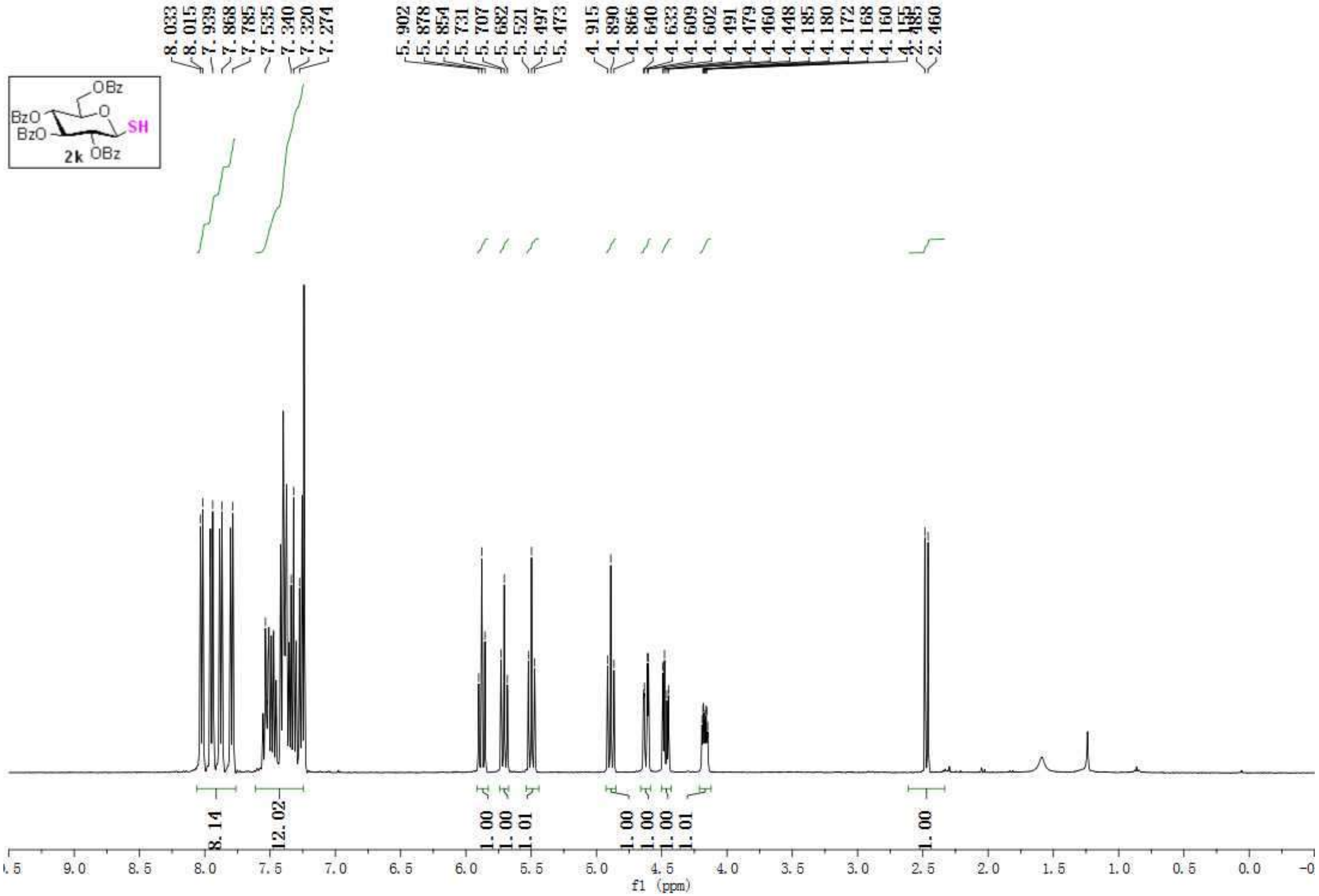


Figure S41. ^{1}H NMR spectrum of **2k** in CDCl$_3$

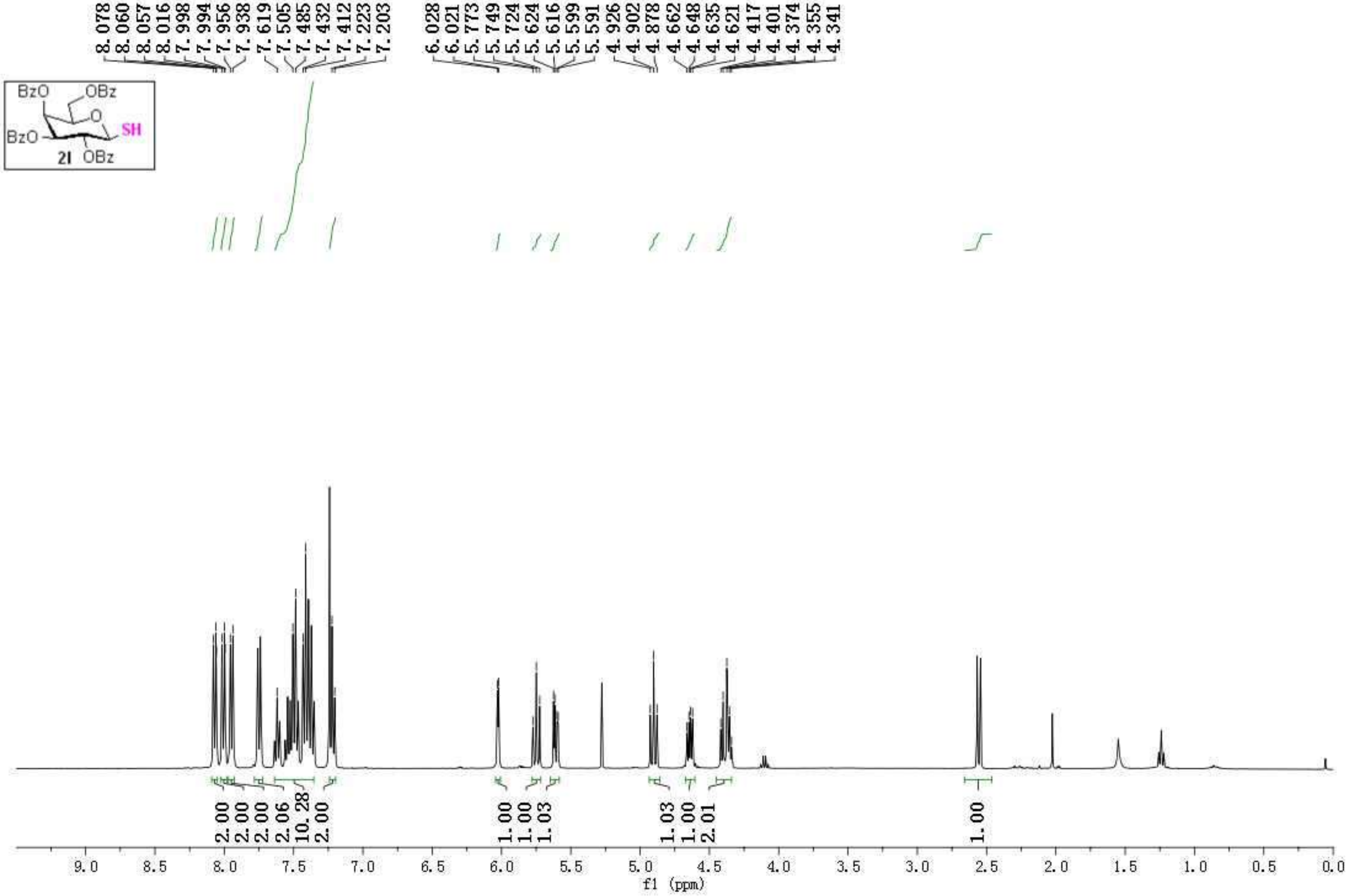


Figure S42. ^{1}H NMR spectrum of **2l** in $CDCl_3$

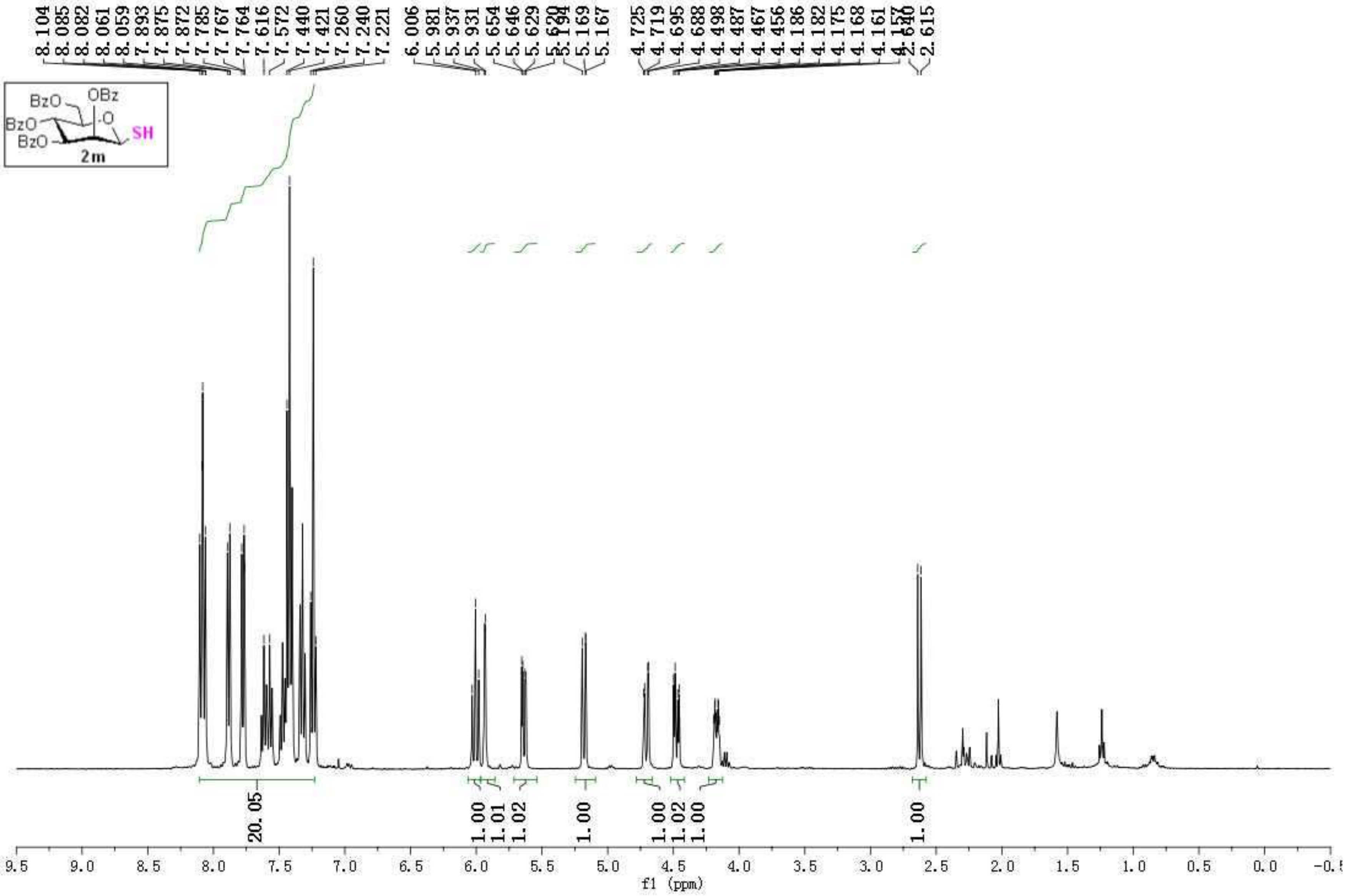


Figure S43. ^{1}H NMR spectrum of **2m** in $CDCl_3$

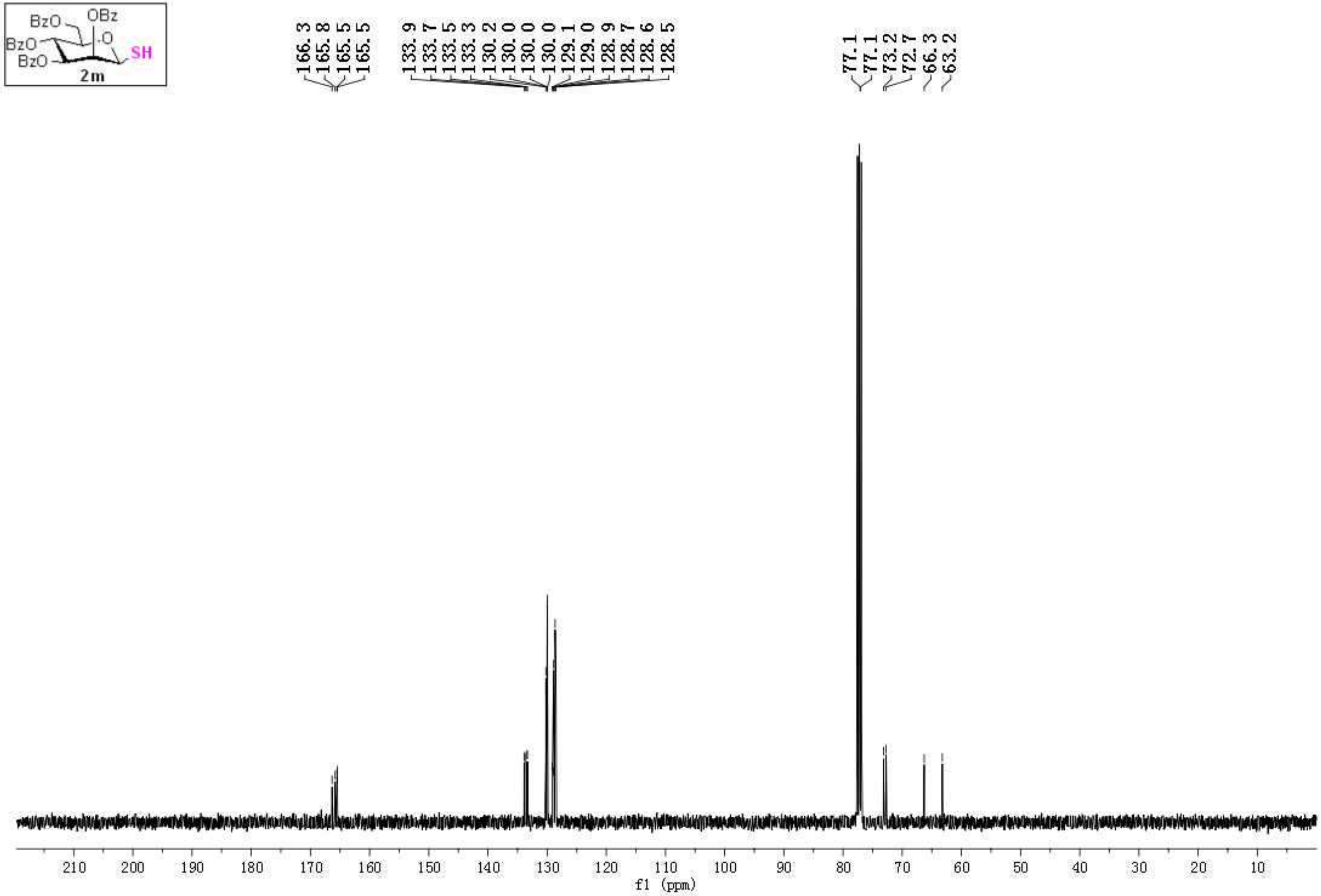


Figure S44. ^{13}C NMR spectrum (100 MHz) of **2m** in CDCl$_3$

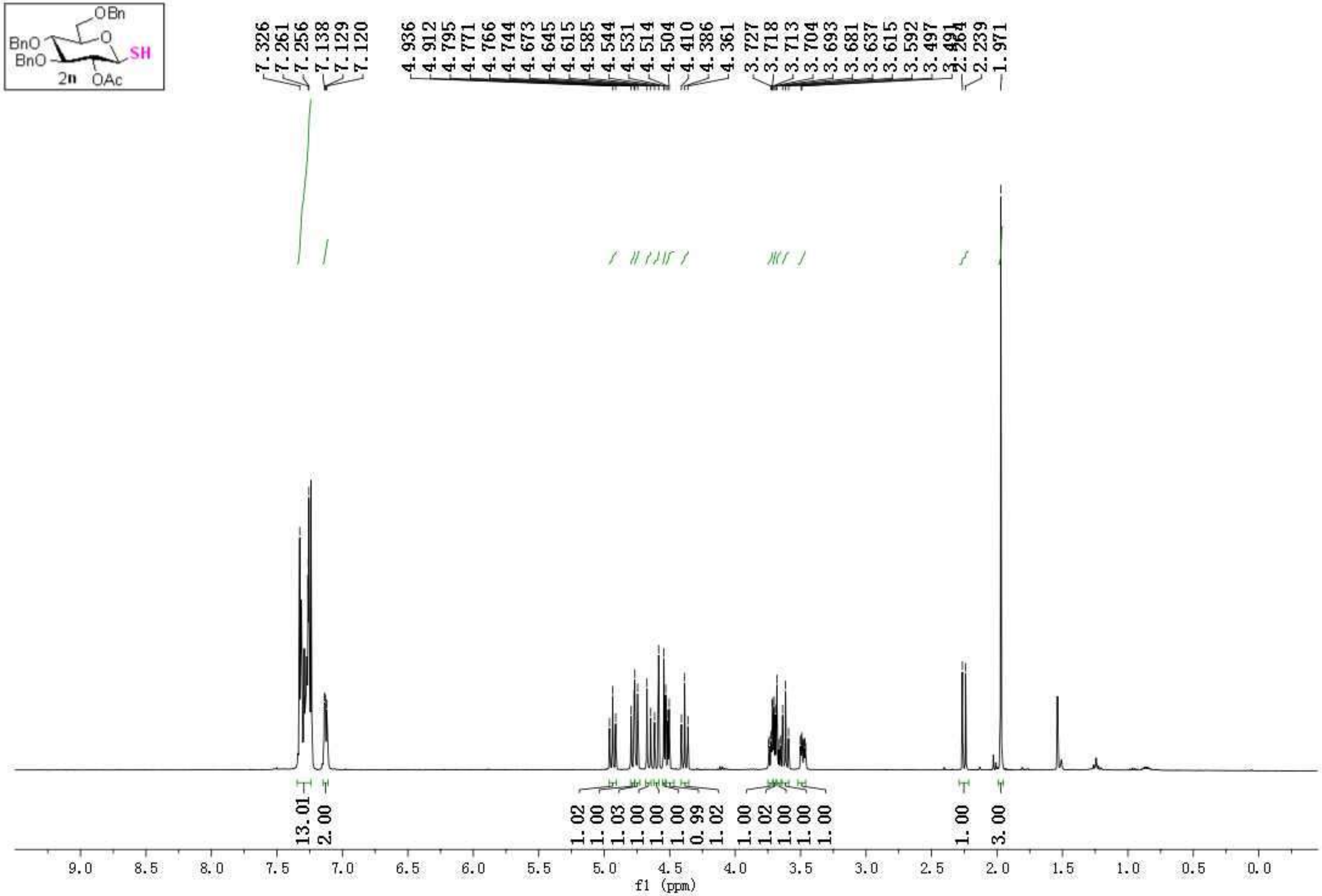


Figure S45. ^{1}H NMR spectrum of **2n** in $CDCl_3$

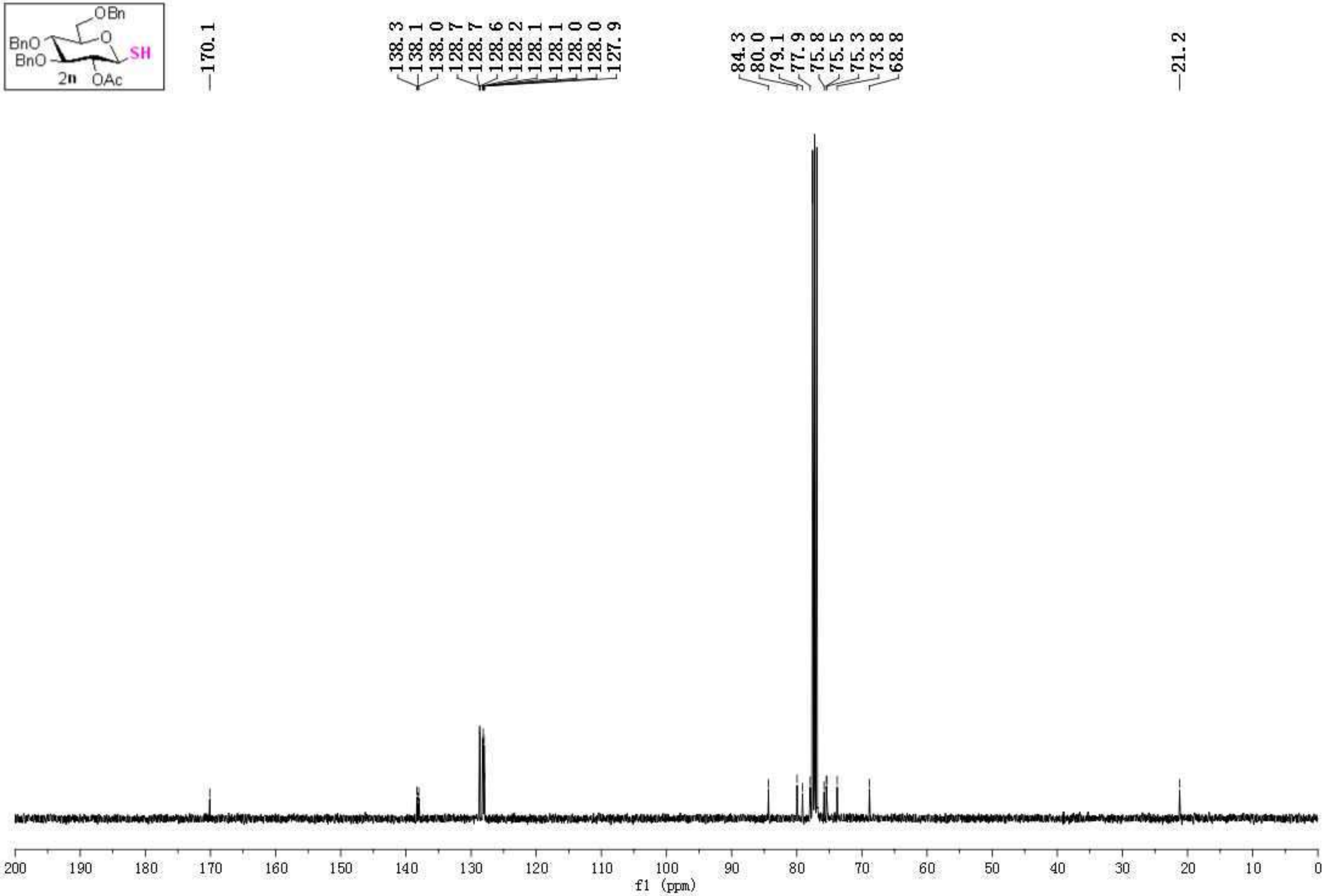


Figure S46. ^{13}C NMR spectrum (100 MHz) of **2n** in $CDCl_3$

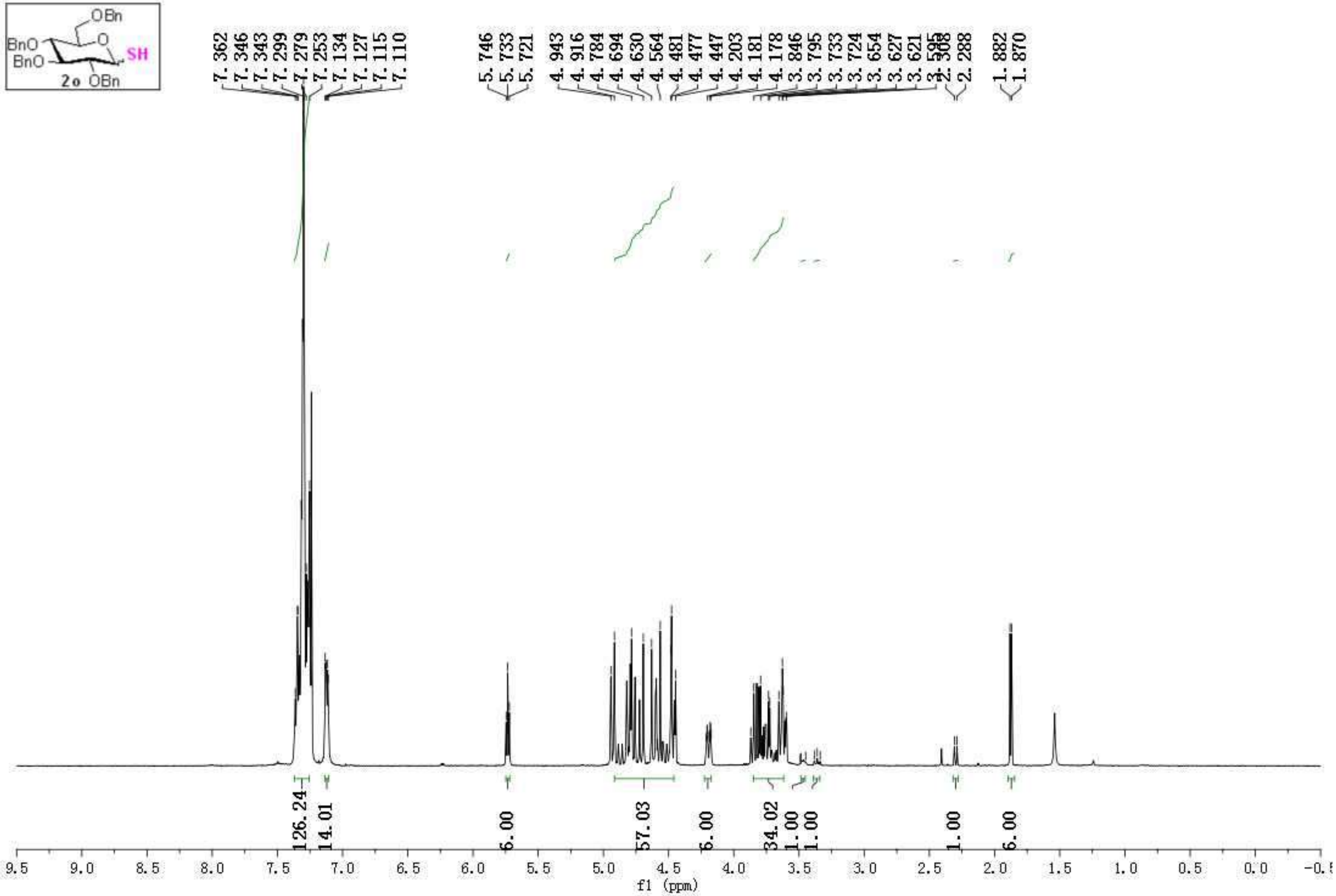


Figure S47. ^{1}H NMR spectrum of **2o** in $CDCl_3$

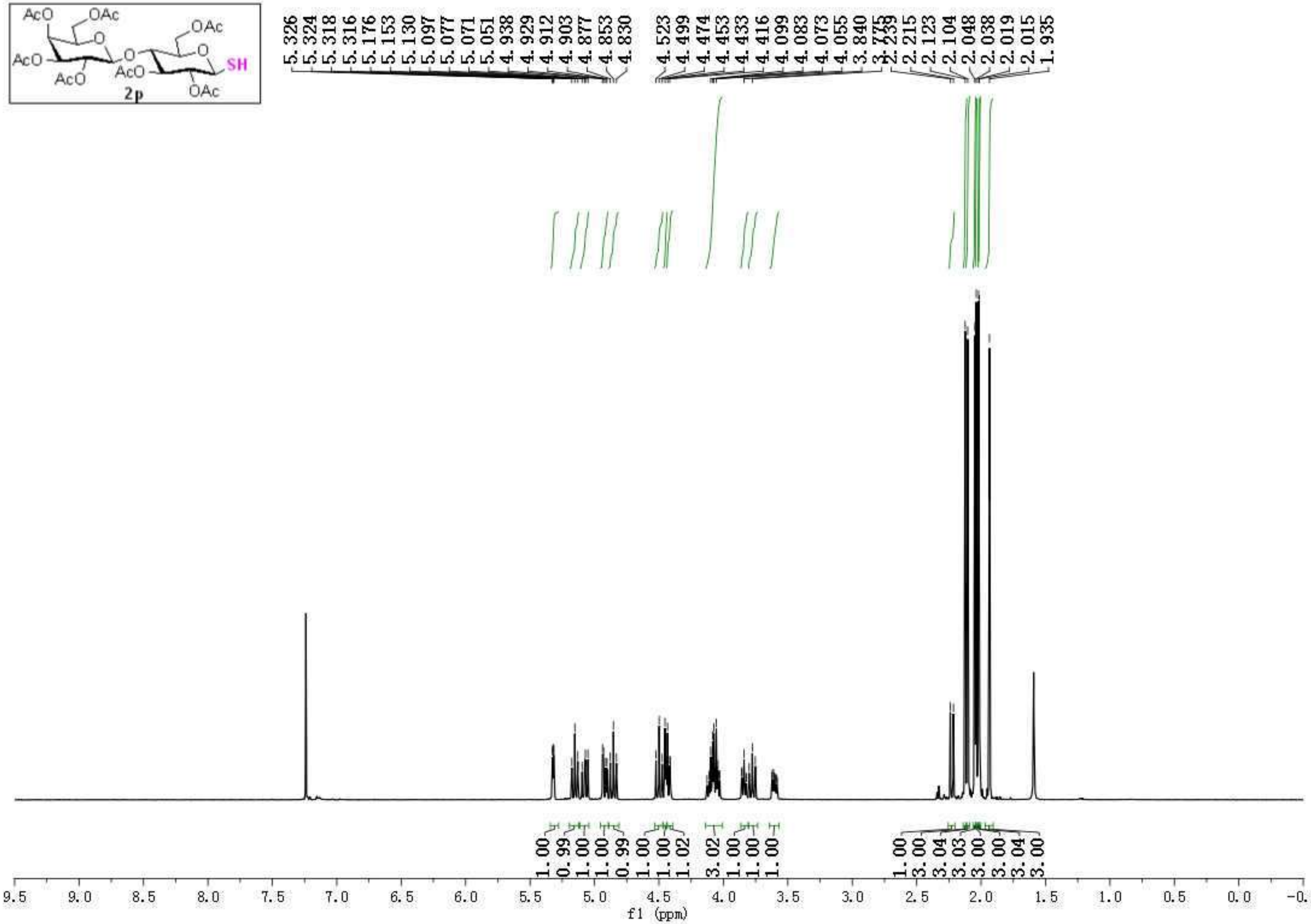


Figure S48. ^{1}H NMR spectrum of **2p** in $CDCl_3$

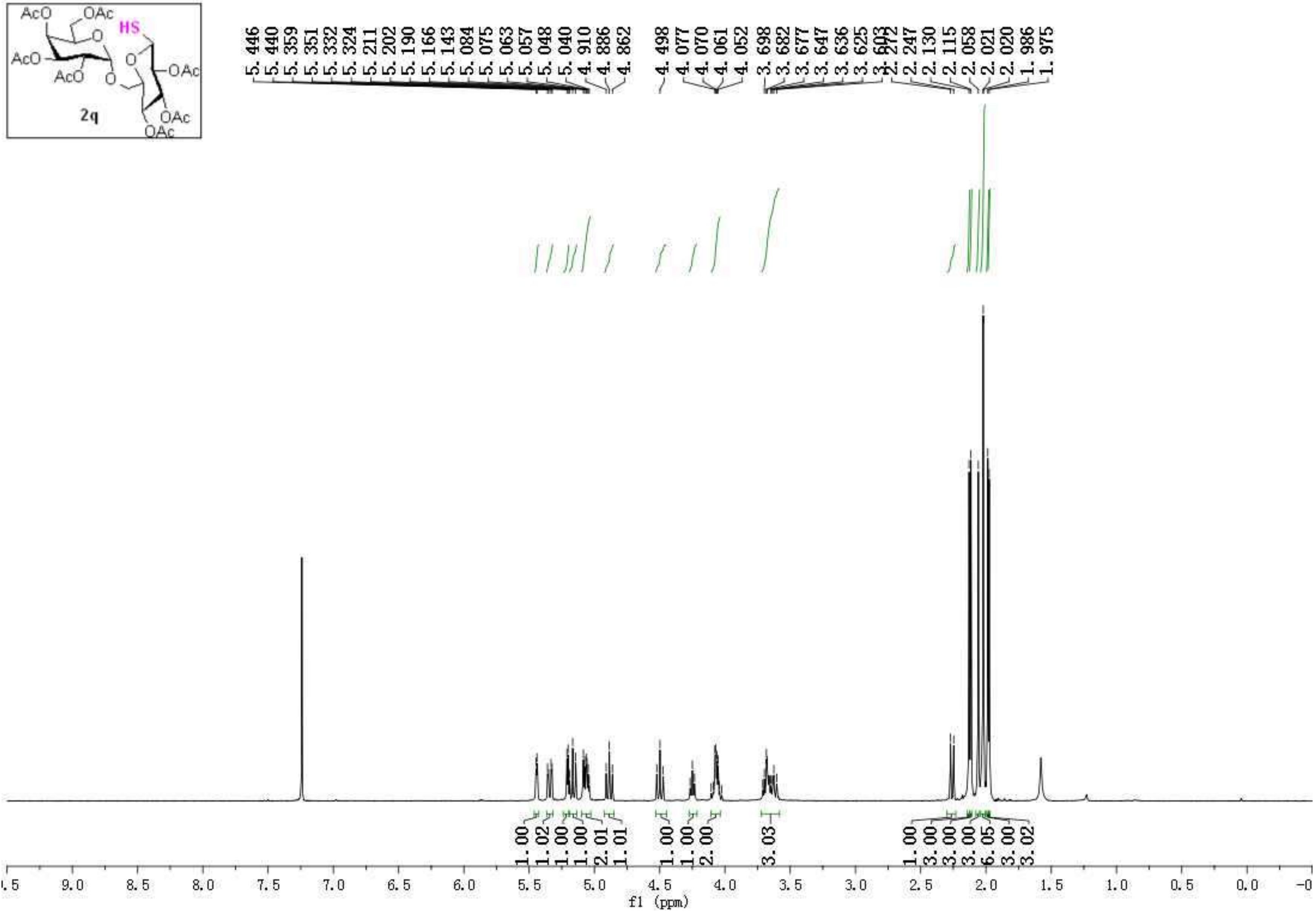


Figure S49. ^{1}H NMR spectrum of **2q** in $CDCl_3$

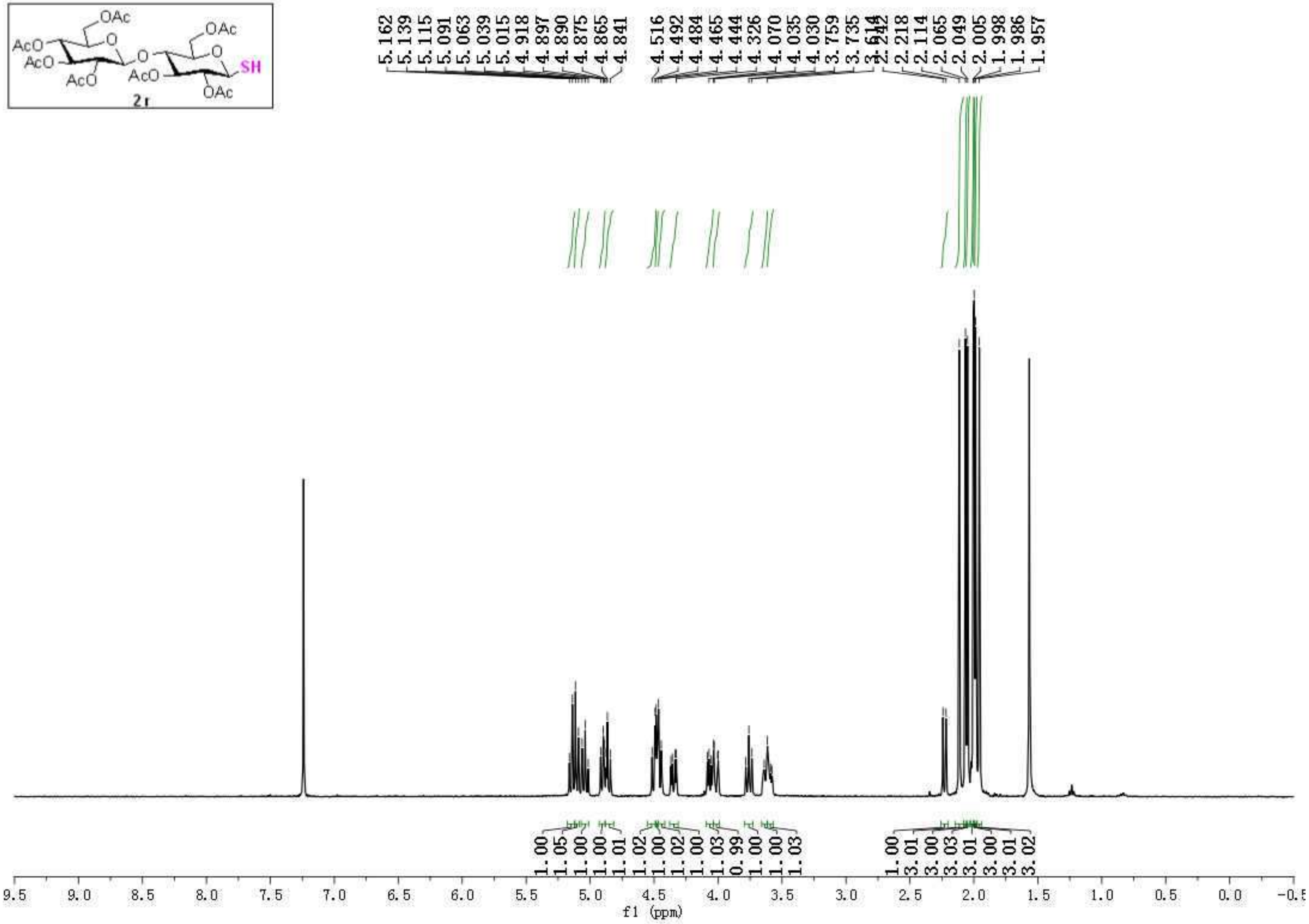


Figure S50. ^{1}H NMR spectrum of **2r** in $CDCl_3$

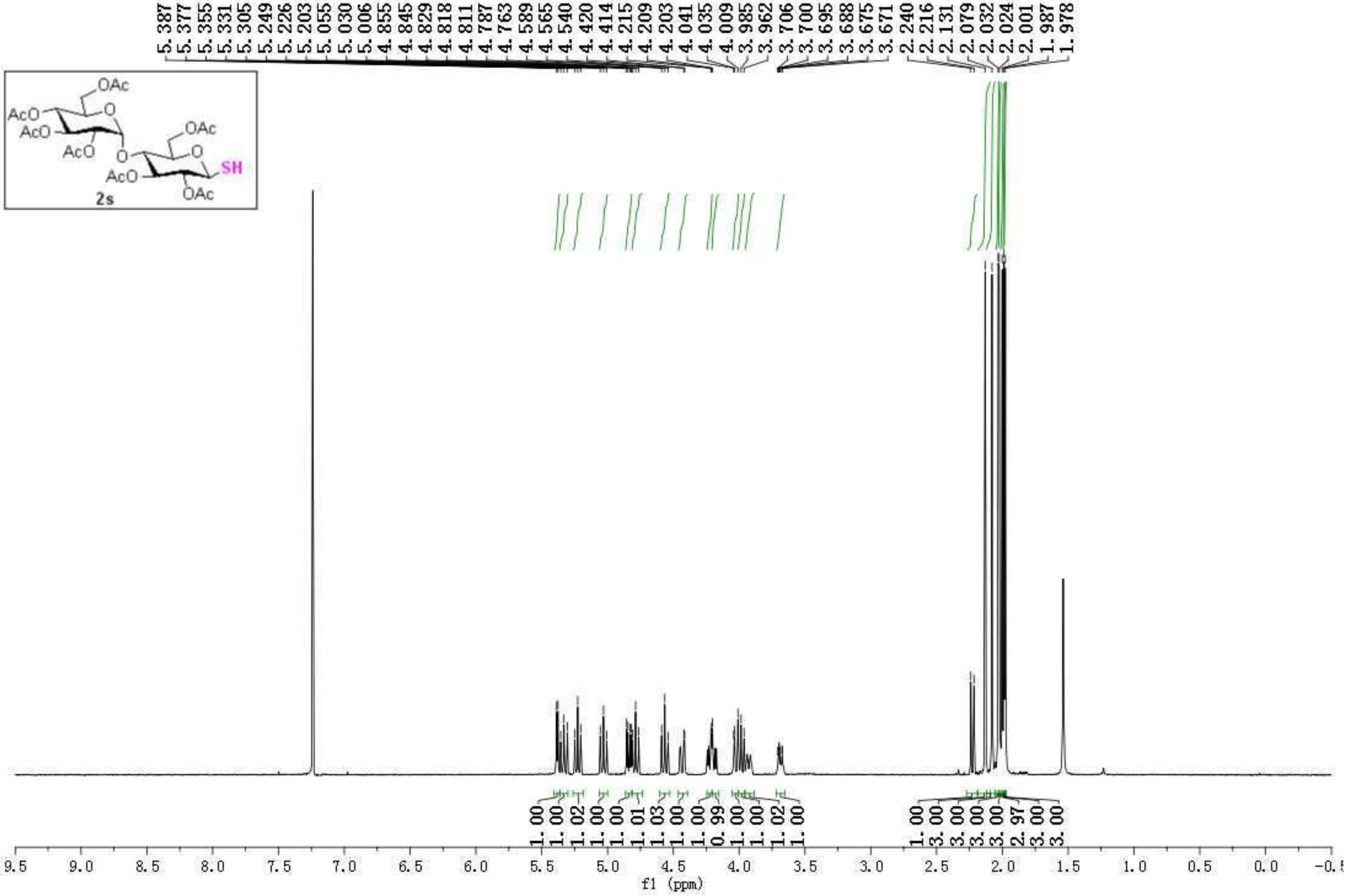


Figure S51. ^{1}H NMR spectrum of **2s** in $CDCl_3$

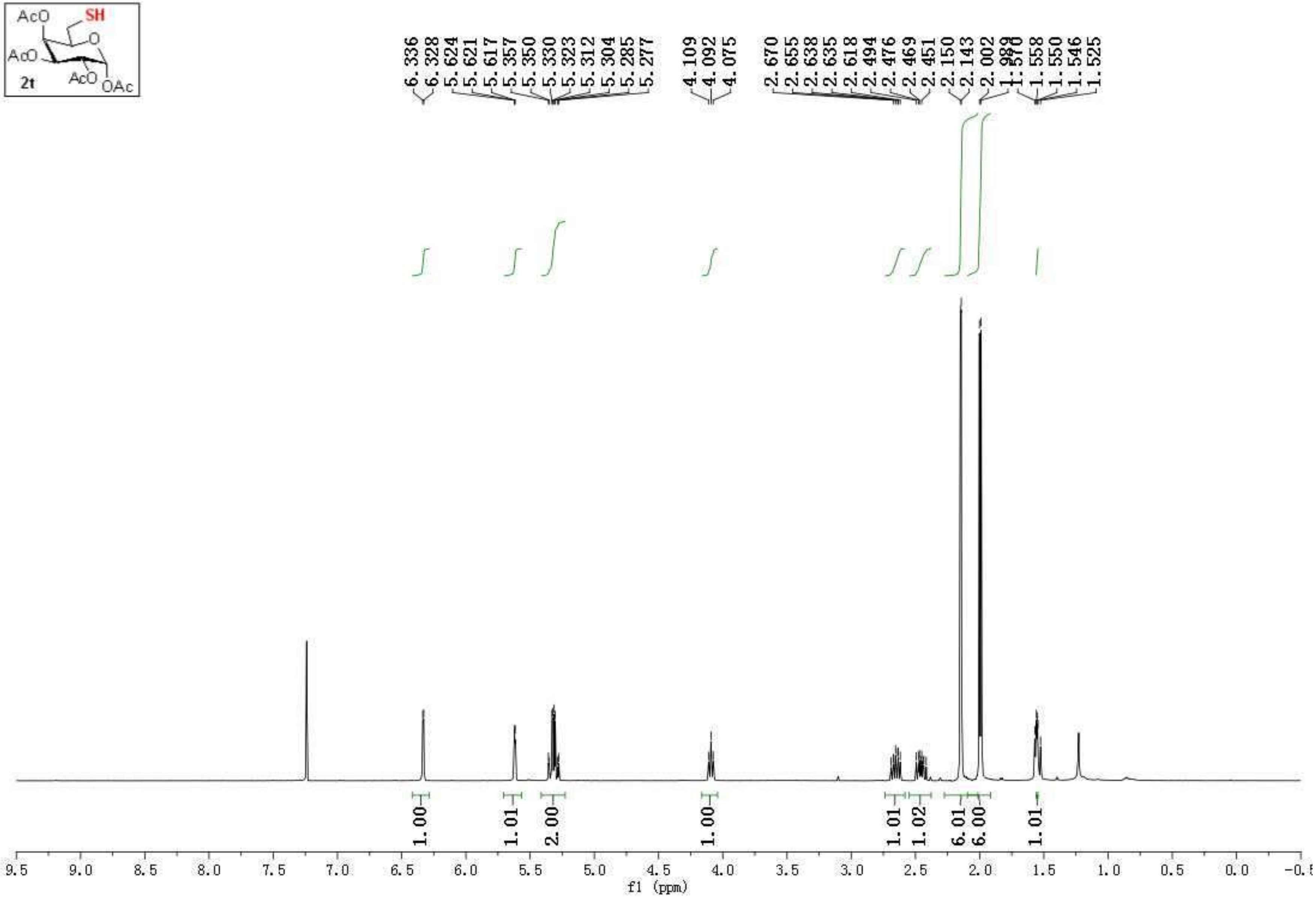


Figure S52. ^{1}H NMR spectrum of **2t** in $CDCl_3$

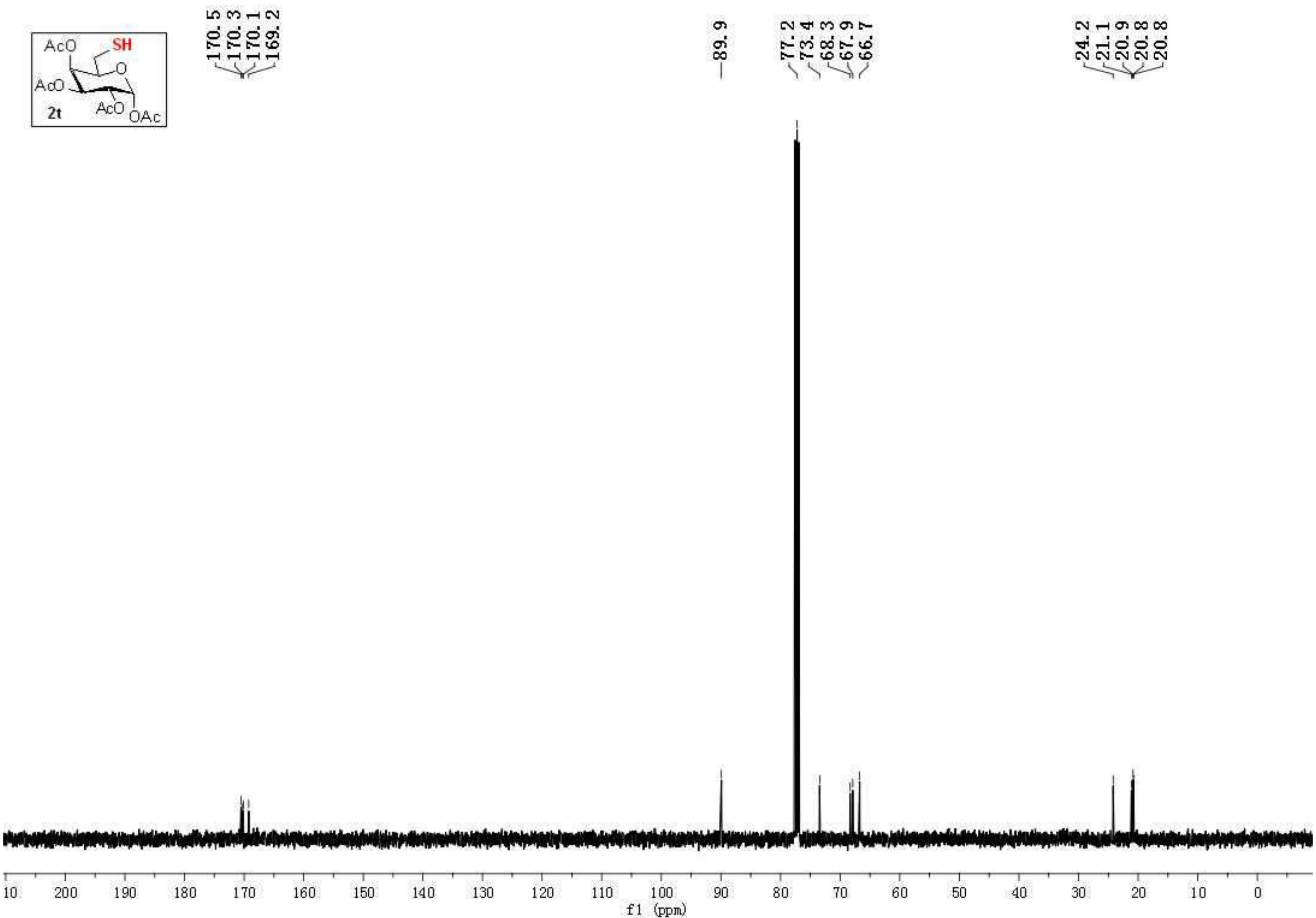


Figure S53. ^{13}C NMR spectrum of **2t** in $CDCl_3$

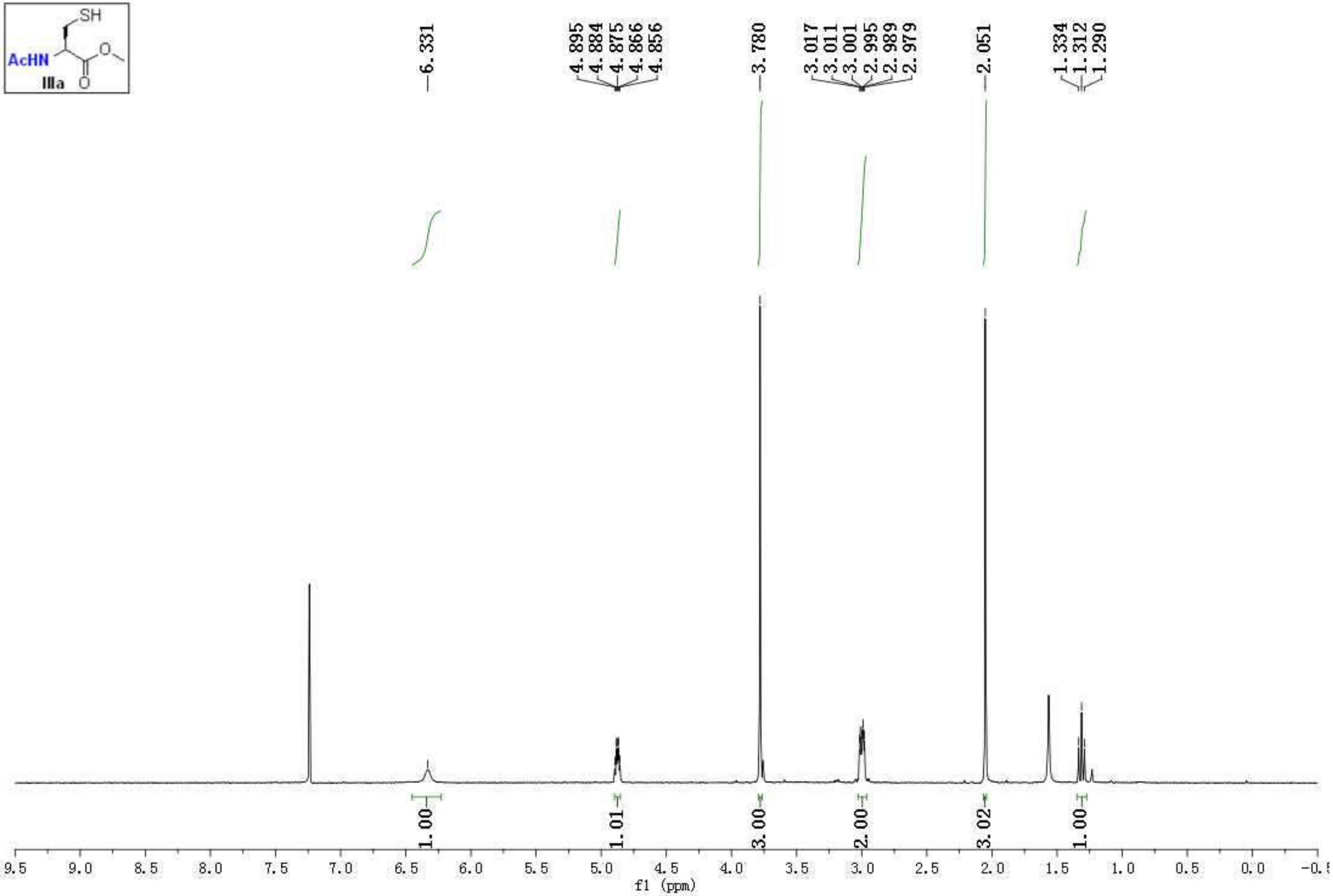


Figure S54. ^{1}H NMR spectrum of **IIIa** in $CDCl_3$

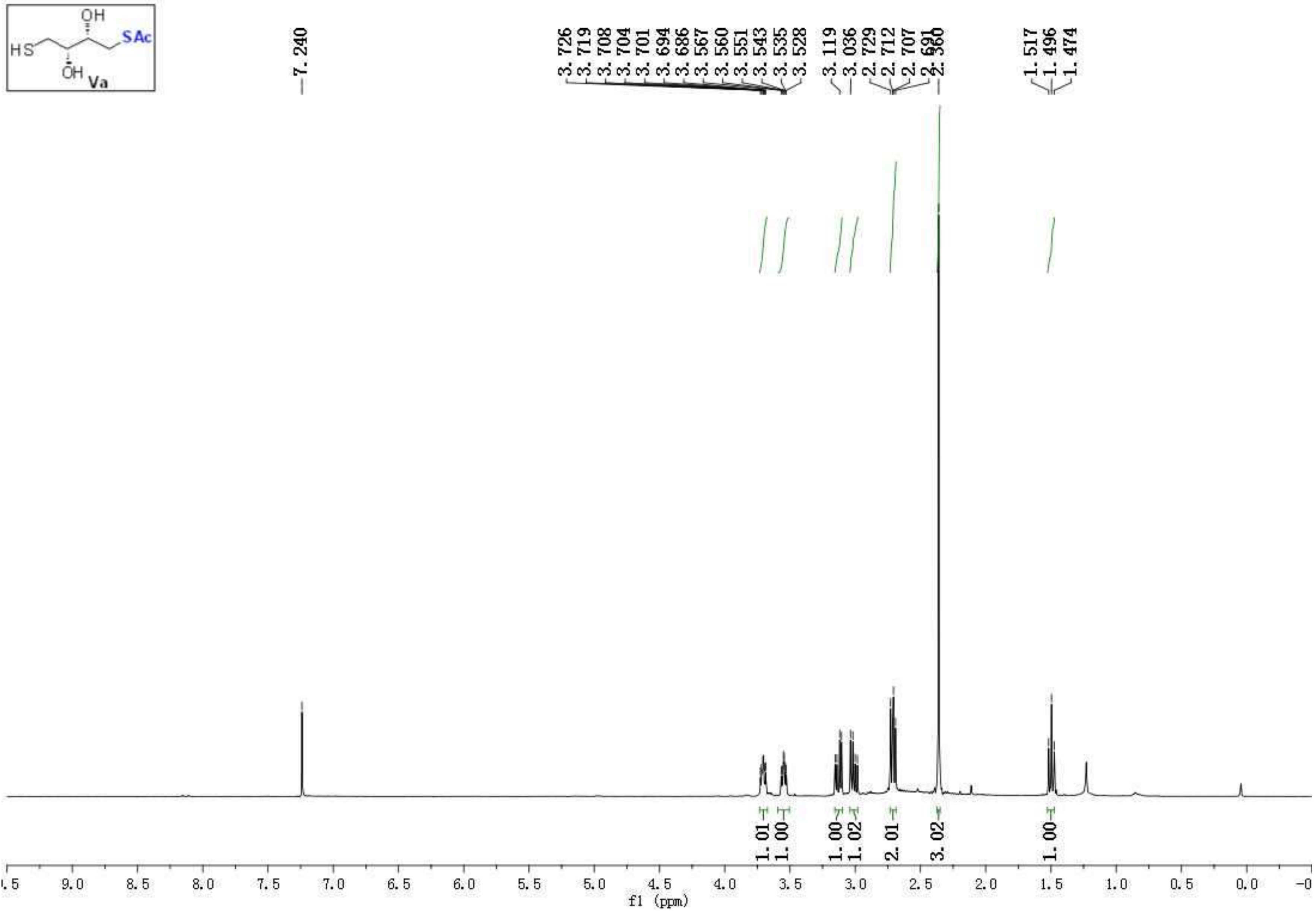


Figure S55. ^{1}H NMR spectrum of **Va** in $CDCl_3$

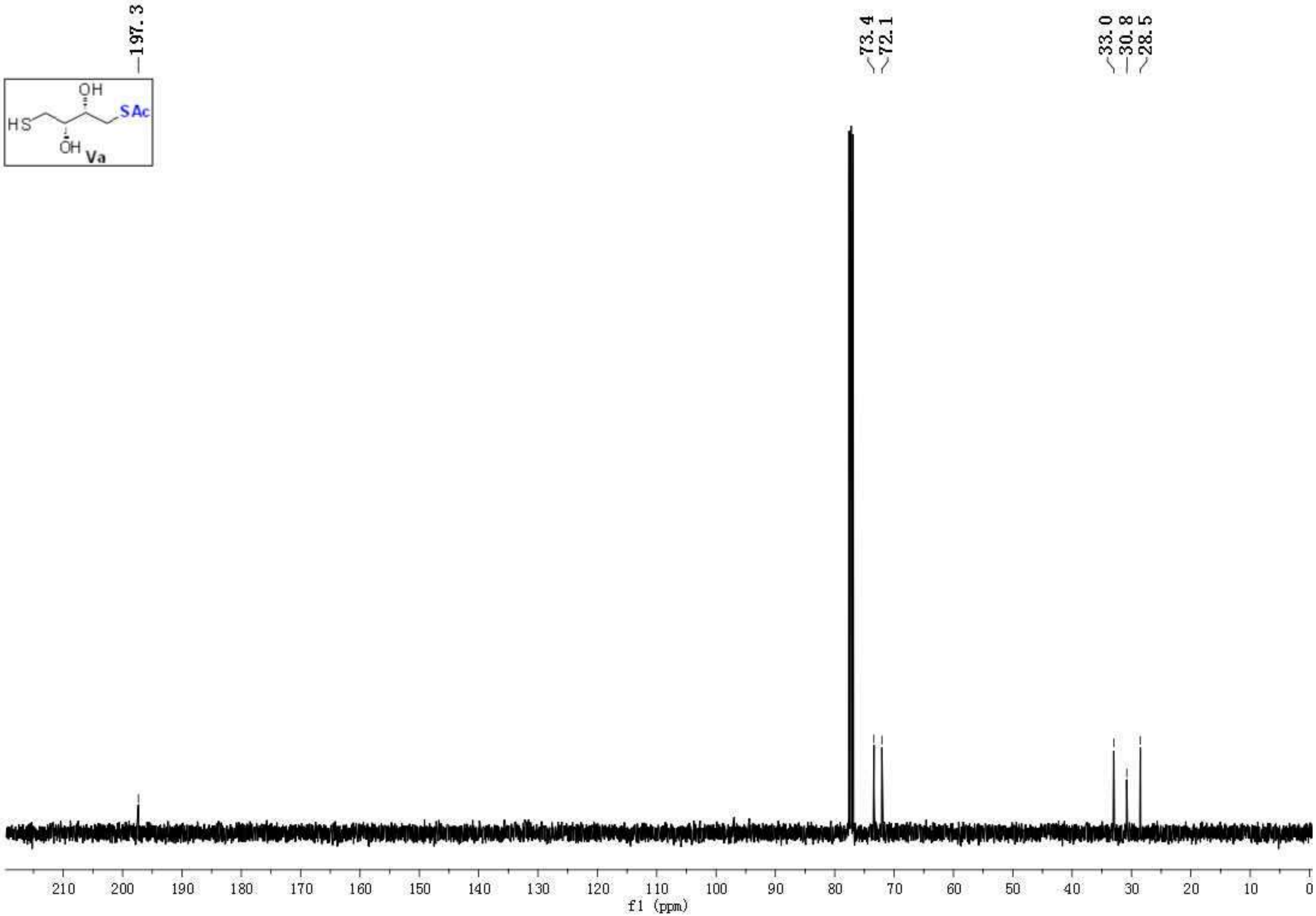


Figure S56. ^{13}C NMR spectrum of **Va** in CDCl$_3$\

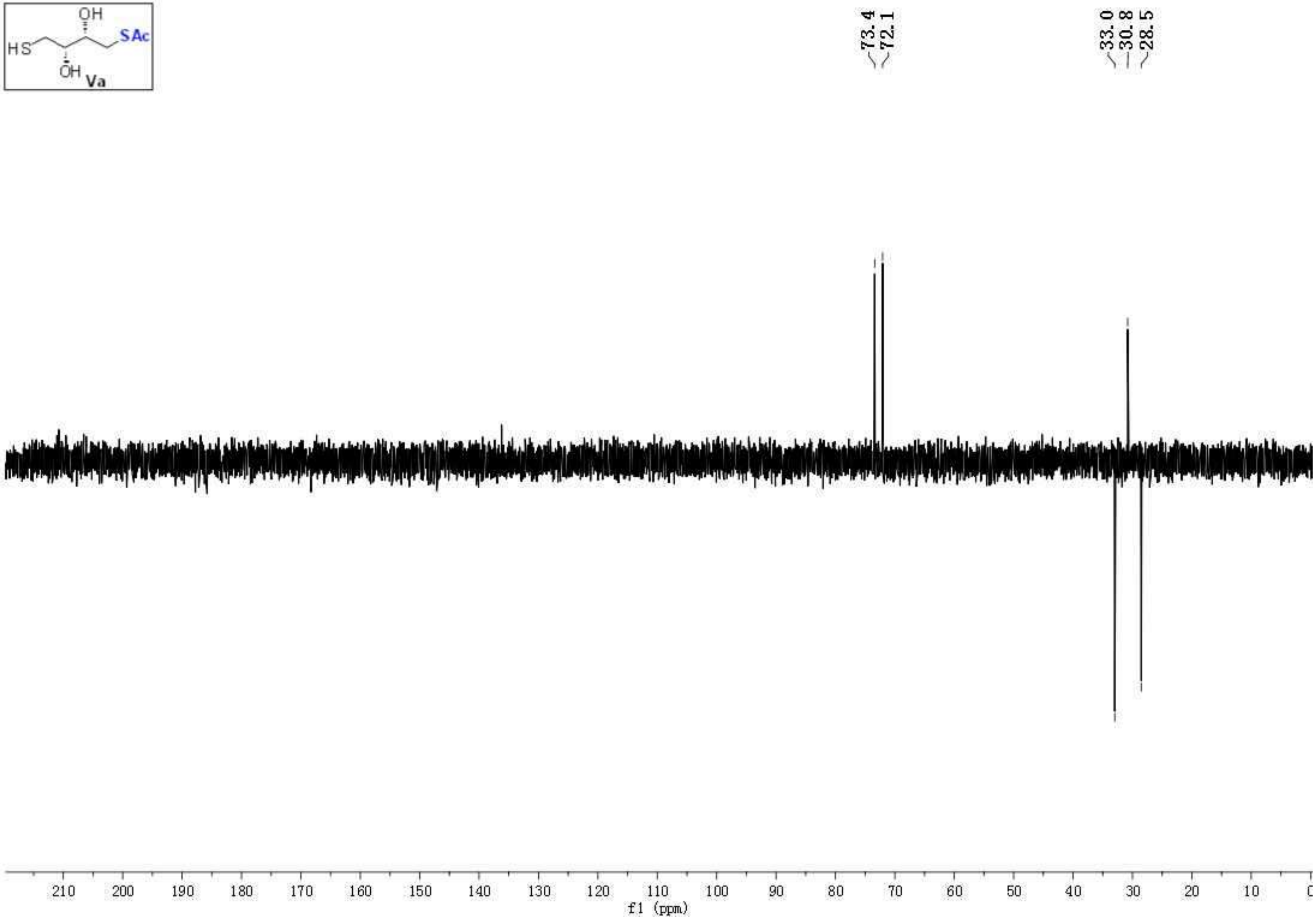


Figure S57. DEPT 135 spectrum of **Va** in $CDCl_3$\

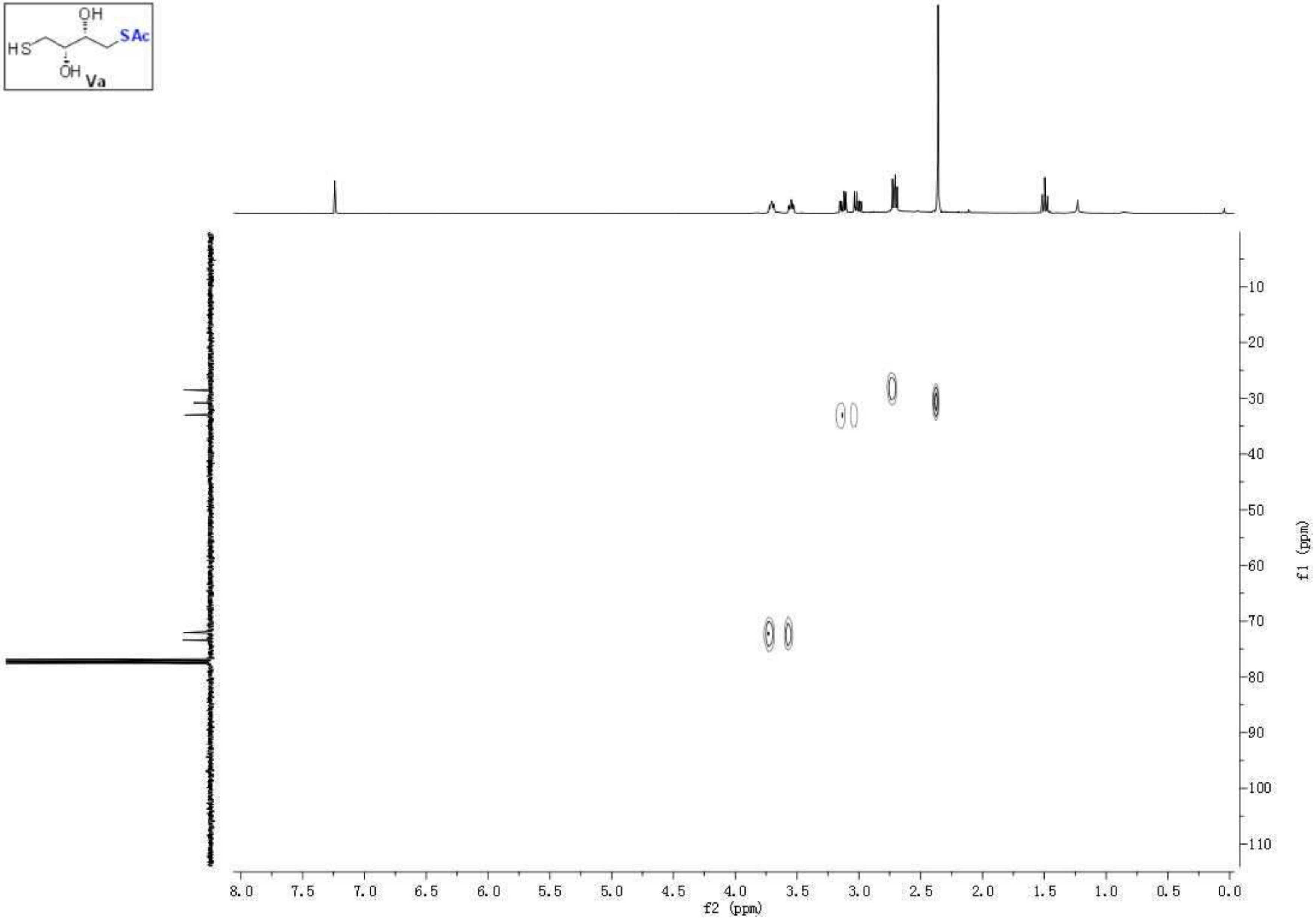


Figure S58. HSQC spectrum of **Va** in $CDCl_3$\

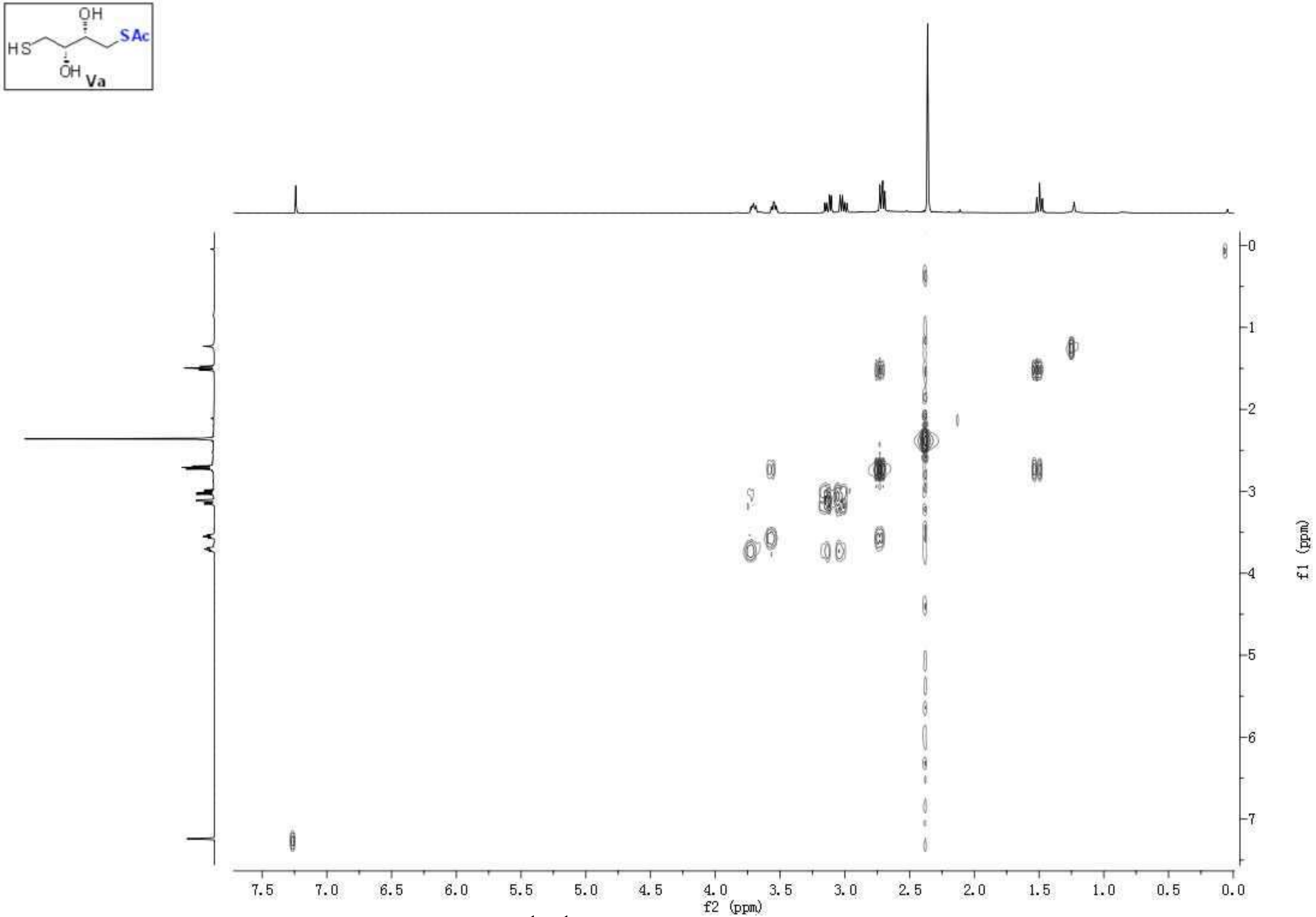


Figure S59. ^{1}H-^{1}H COSY spectrum of **Va** in $CDCl_3$

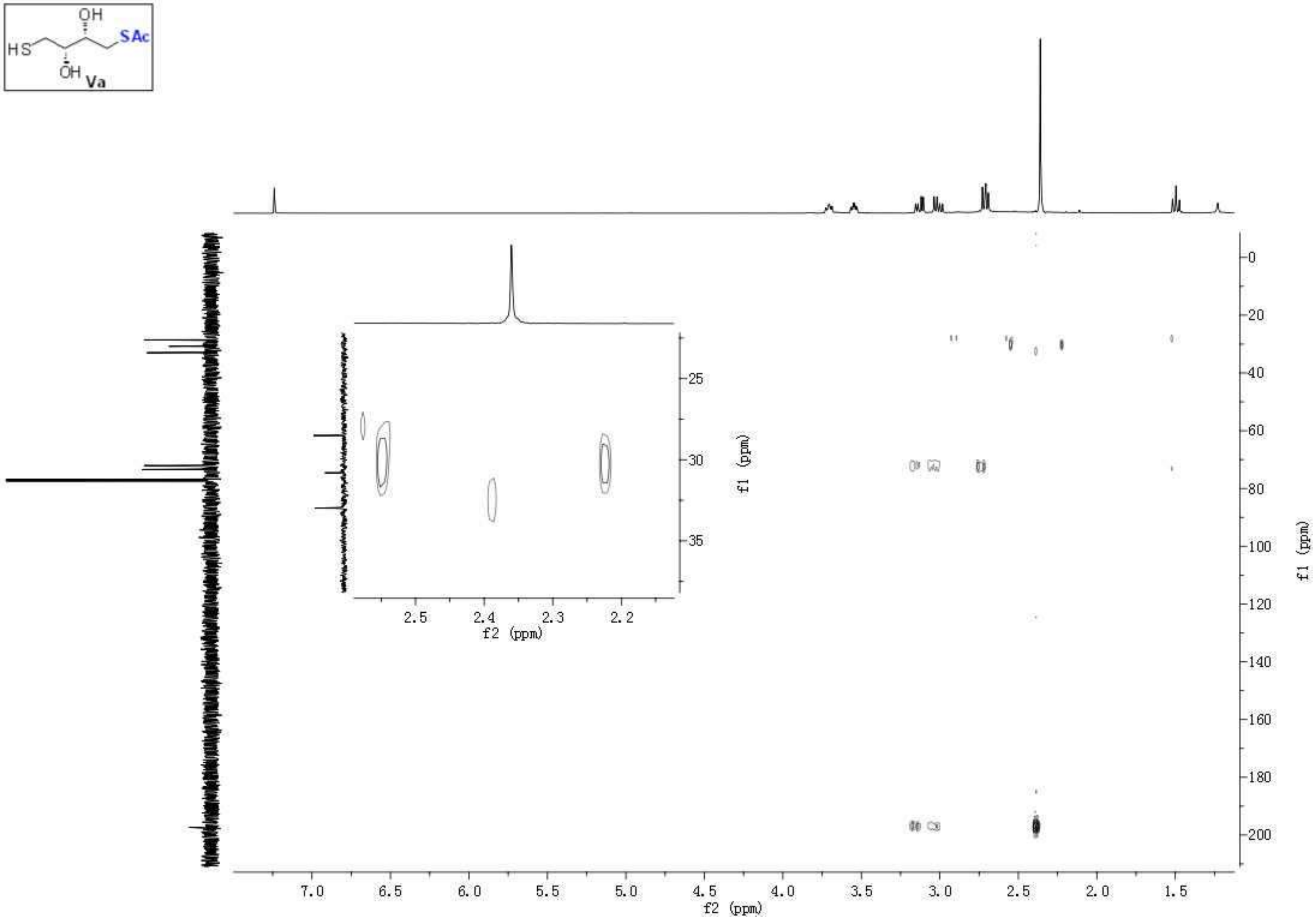


Figure S60. HMBC spectrum of **Va** in $CDCl_3$

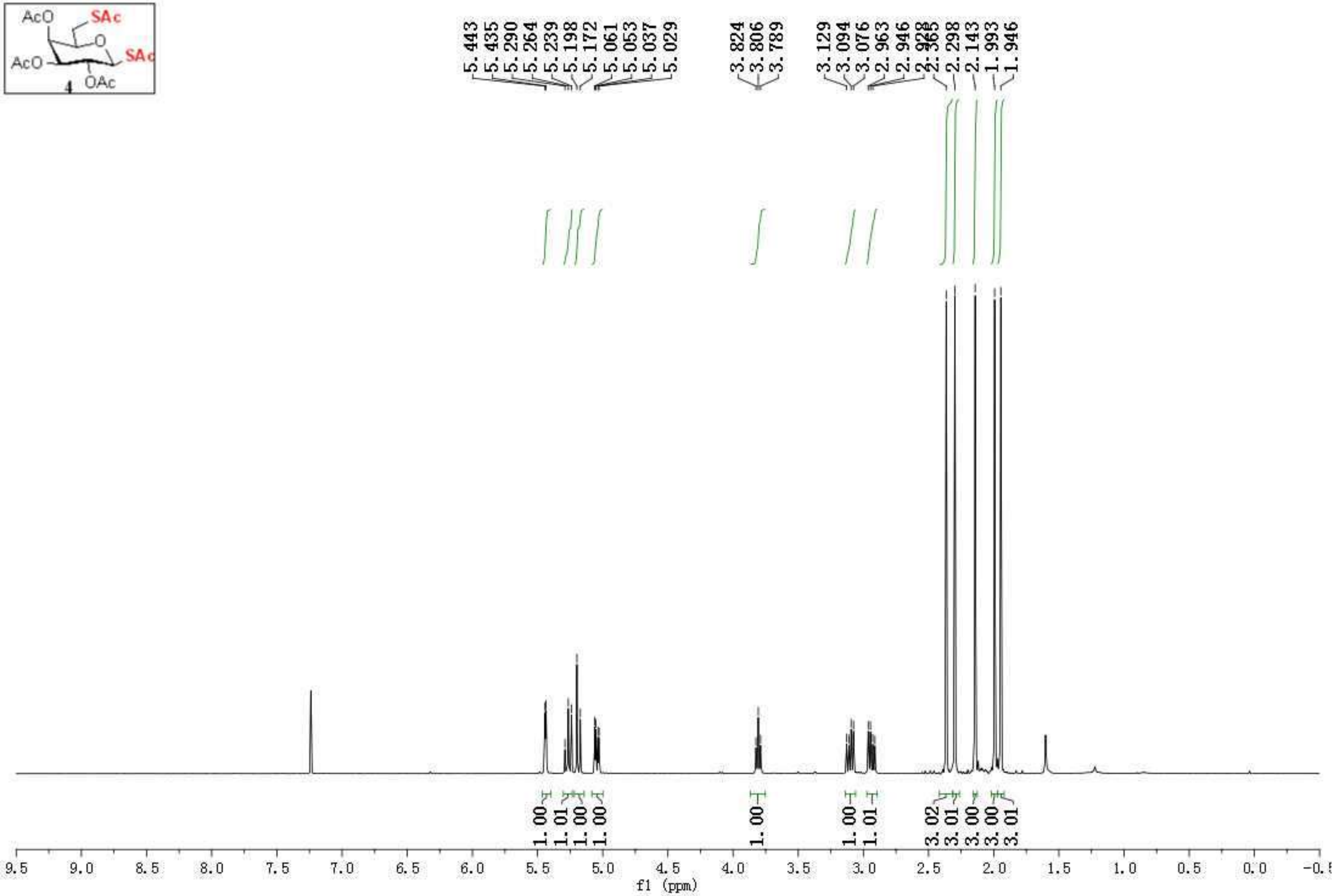


Figure S61. ^{1}H NMR spectrum of **4** in $CDCl_3$

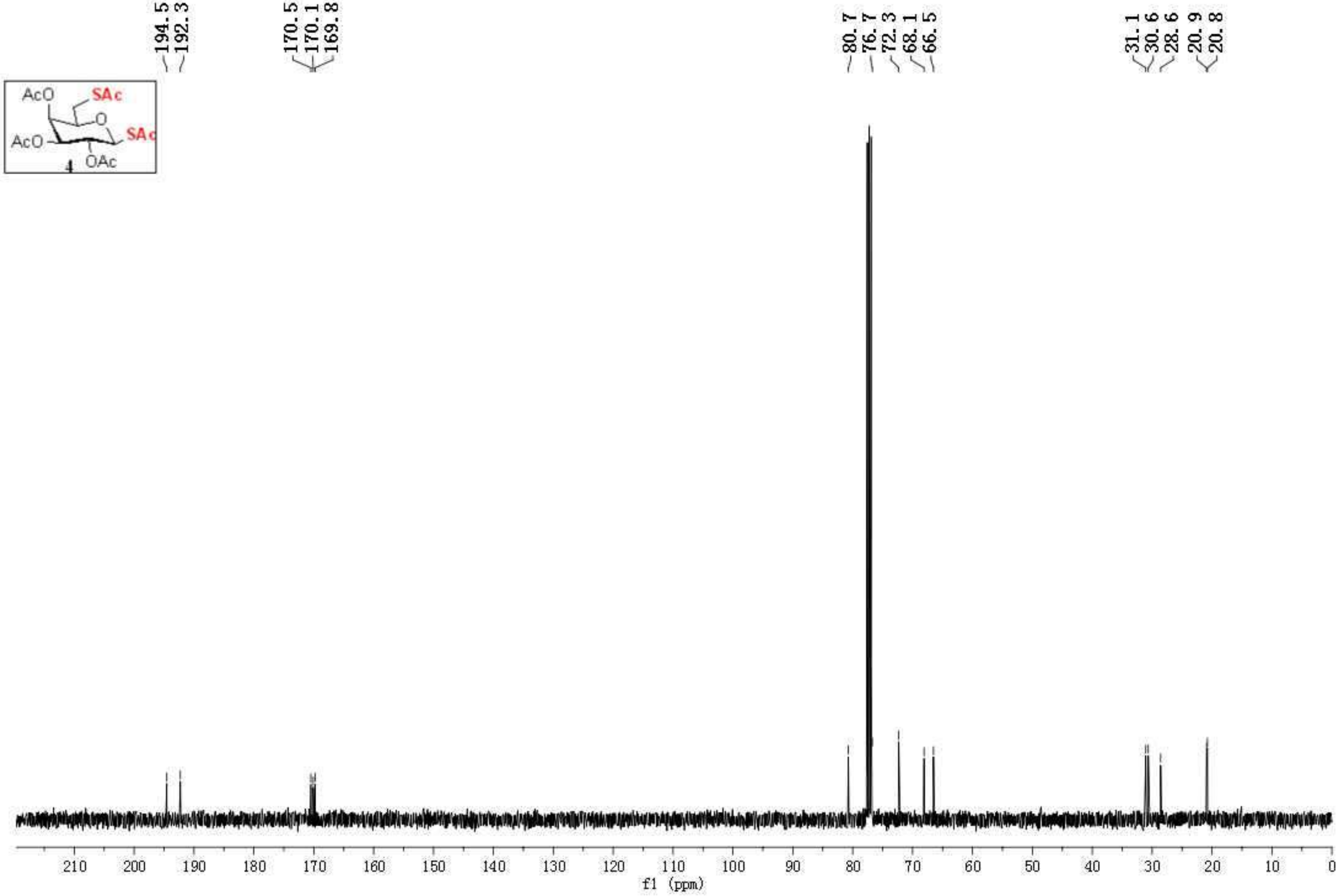


Figure S62. ^{13}C NMR spectrum (100 MHz) of **4** in $CDCl_3$

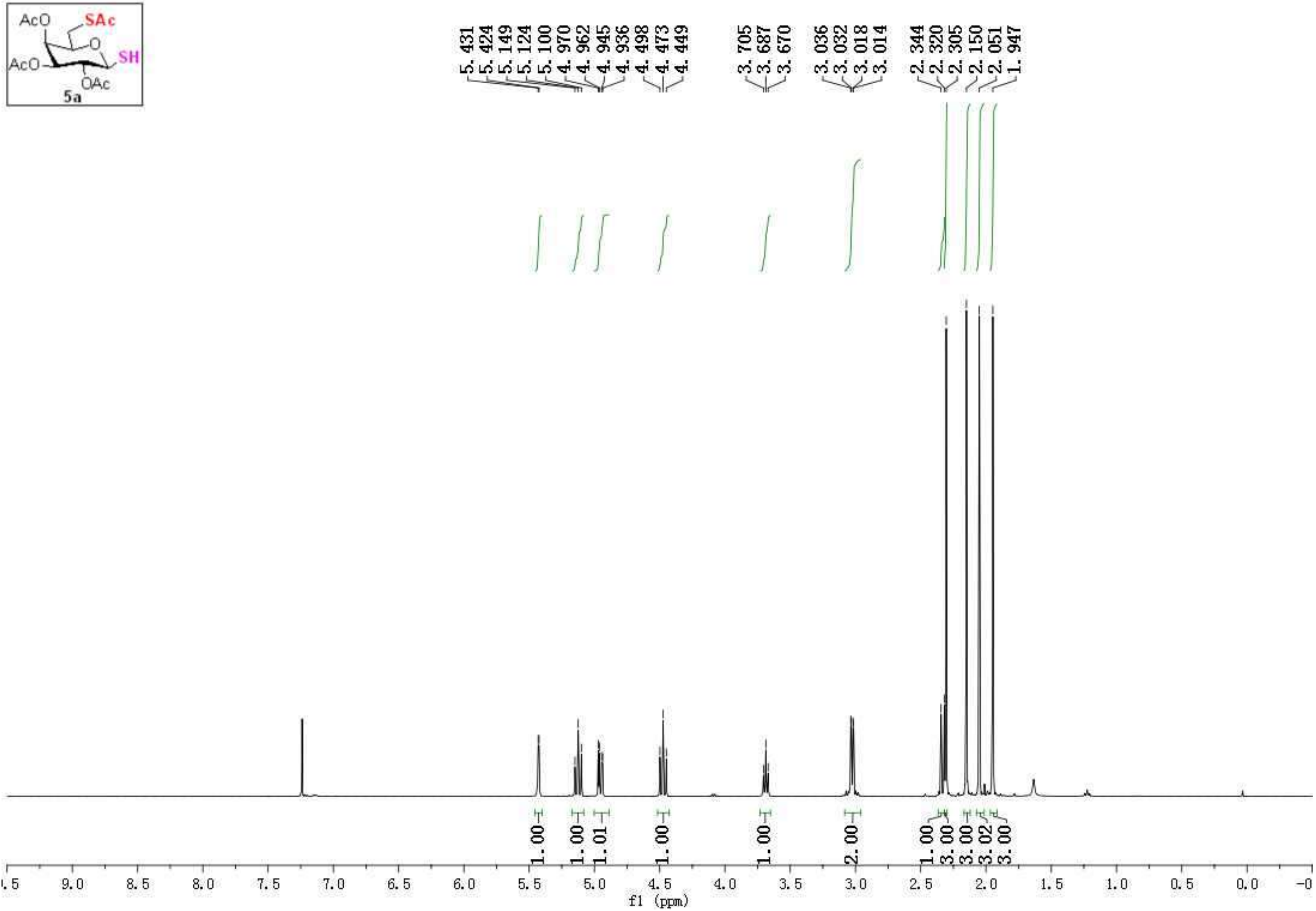


Figure S63. ^{1}H NMR spectrum of **5a** in $CDCl_3$

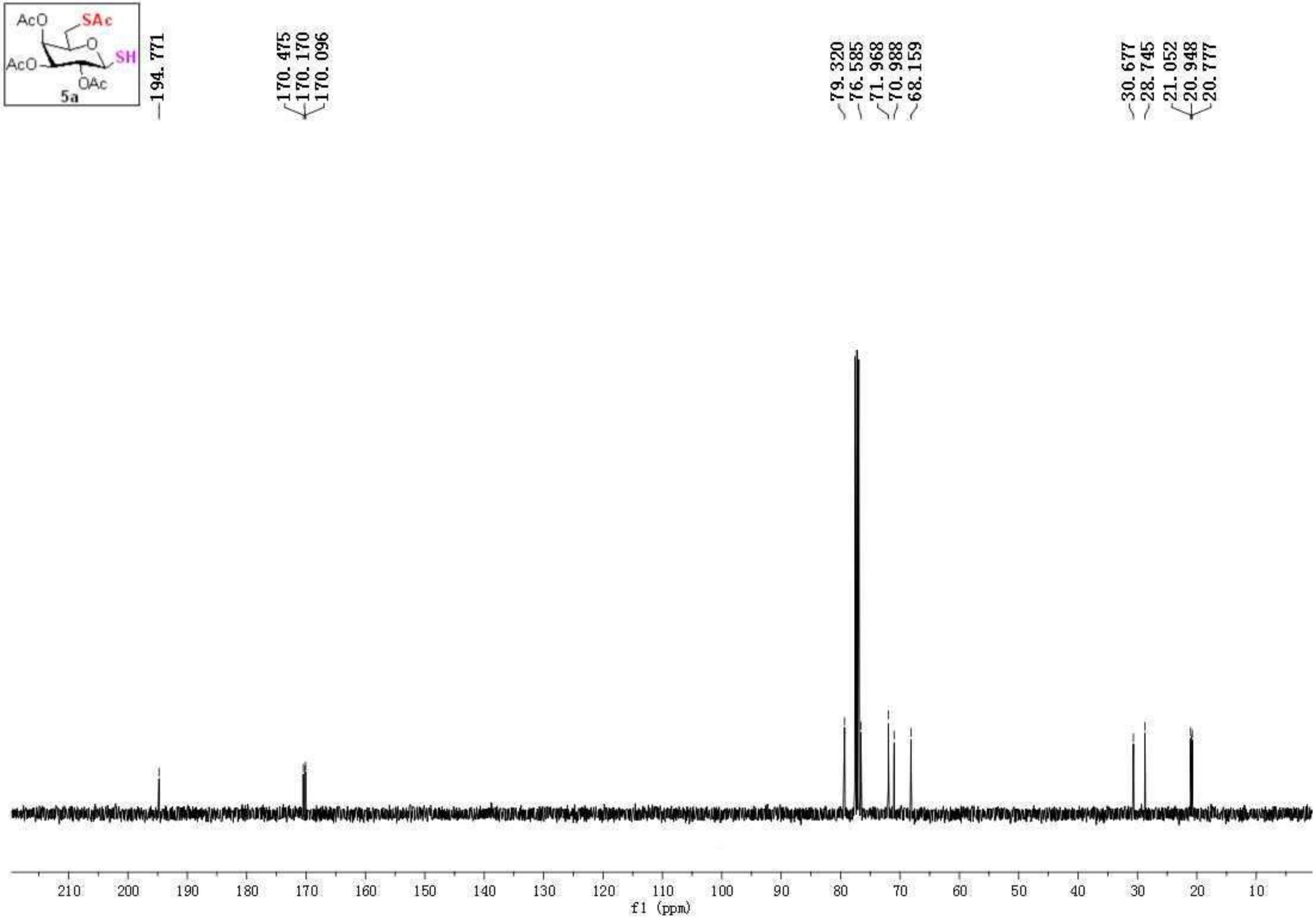
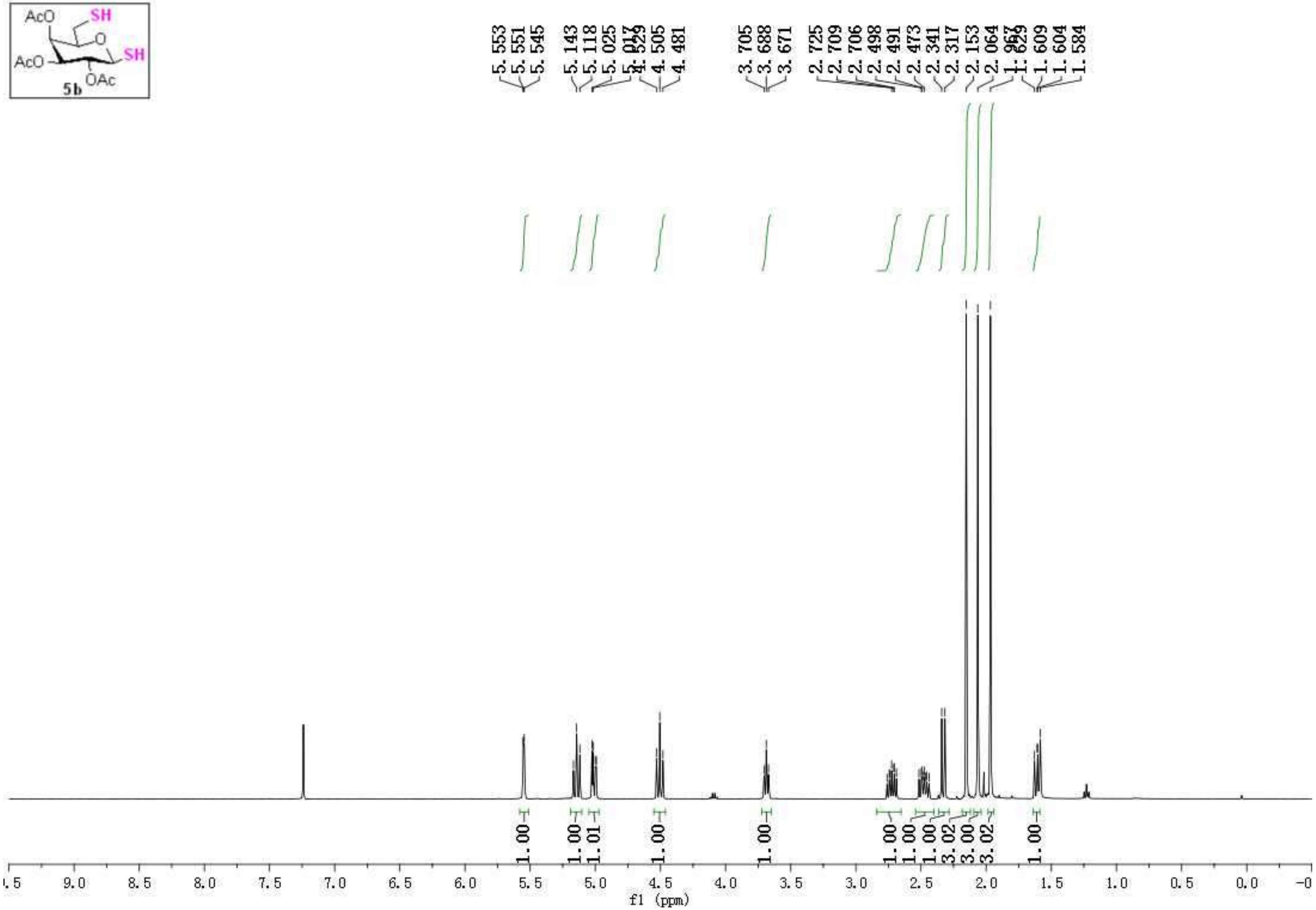


Figure S64. ^{13}C NMR spectrum (100 MHz) of **5a** in CDCl$_3$



5b

Figure S65. ^{1}H NMR spectrum of **5b** in $CDCl_3$

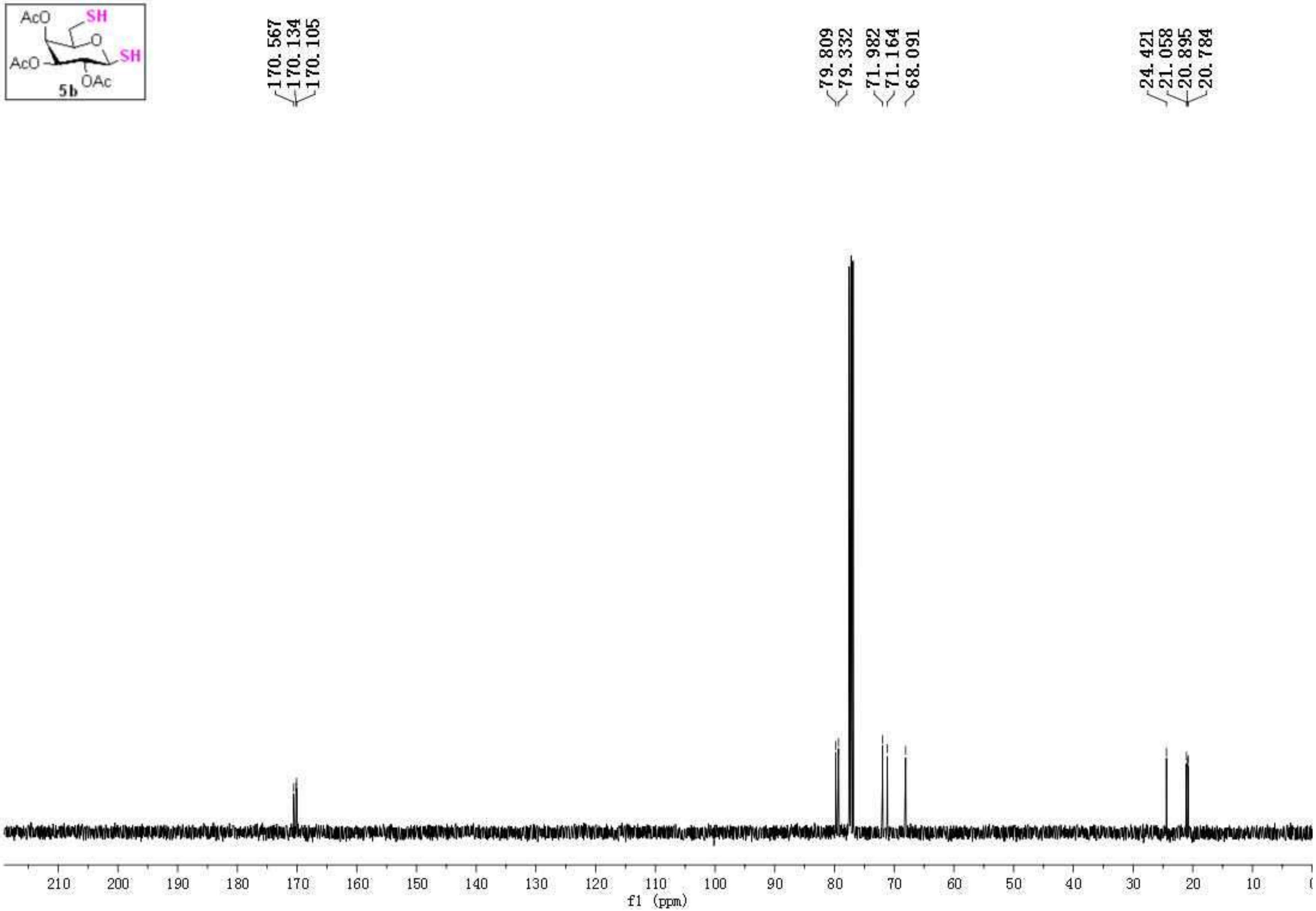


Figure S66. ^{13}C NMR spectrum (100 MHz) of **5b** in $CDCl_3$

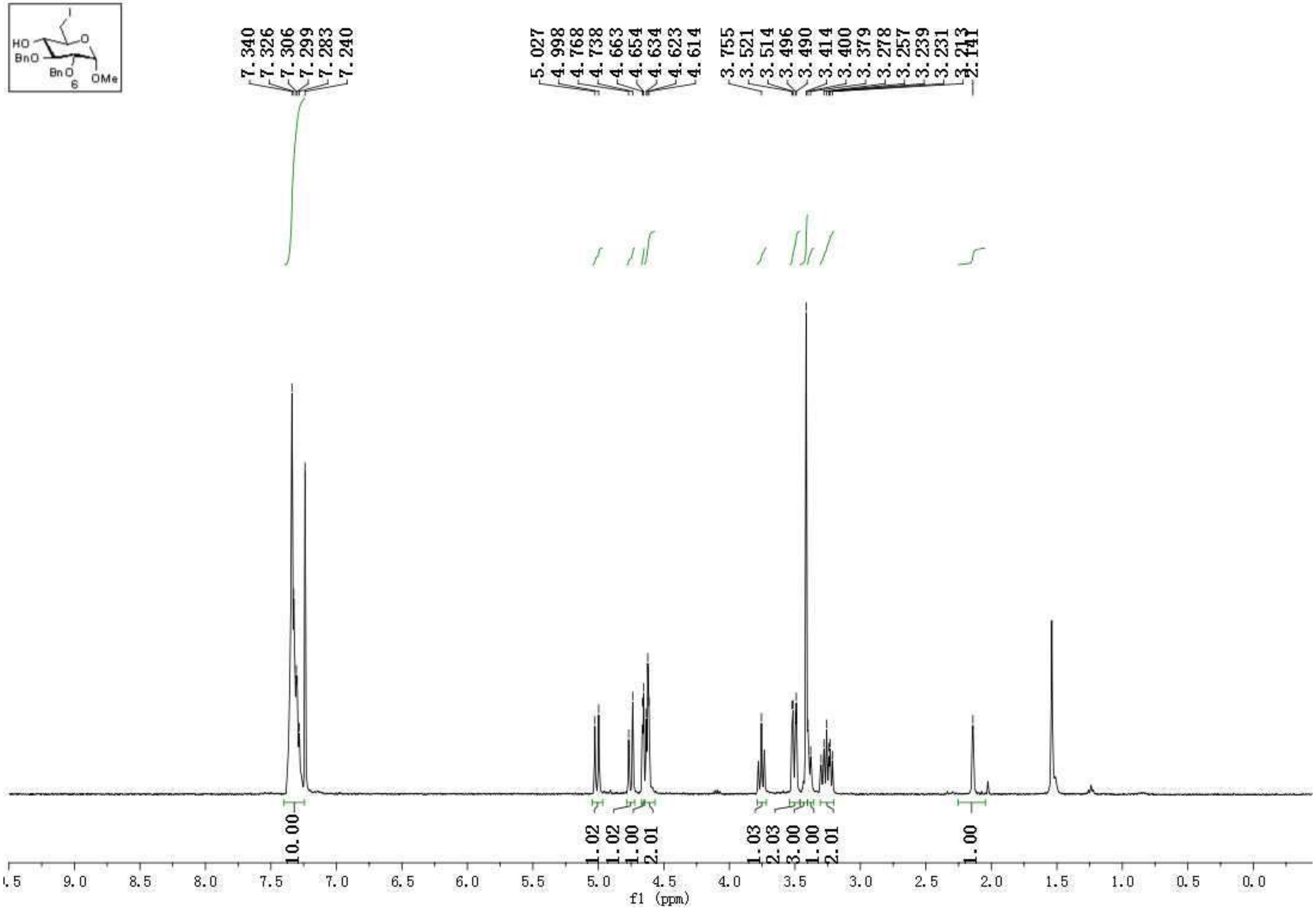


Figure S67. ^{1}H NMR spectrum of **6** in $CDCl_3$

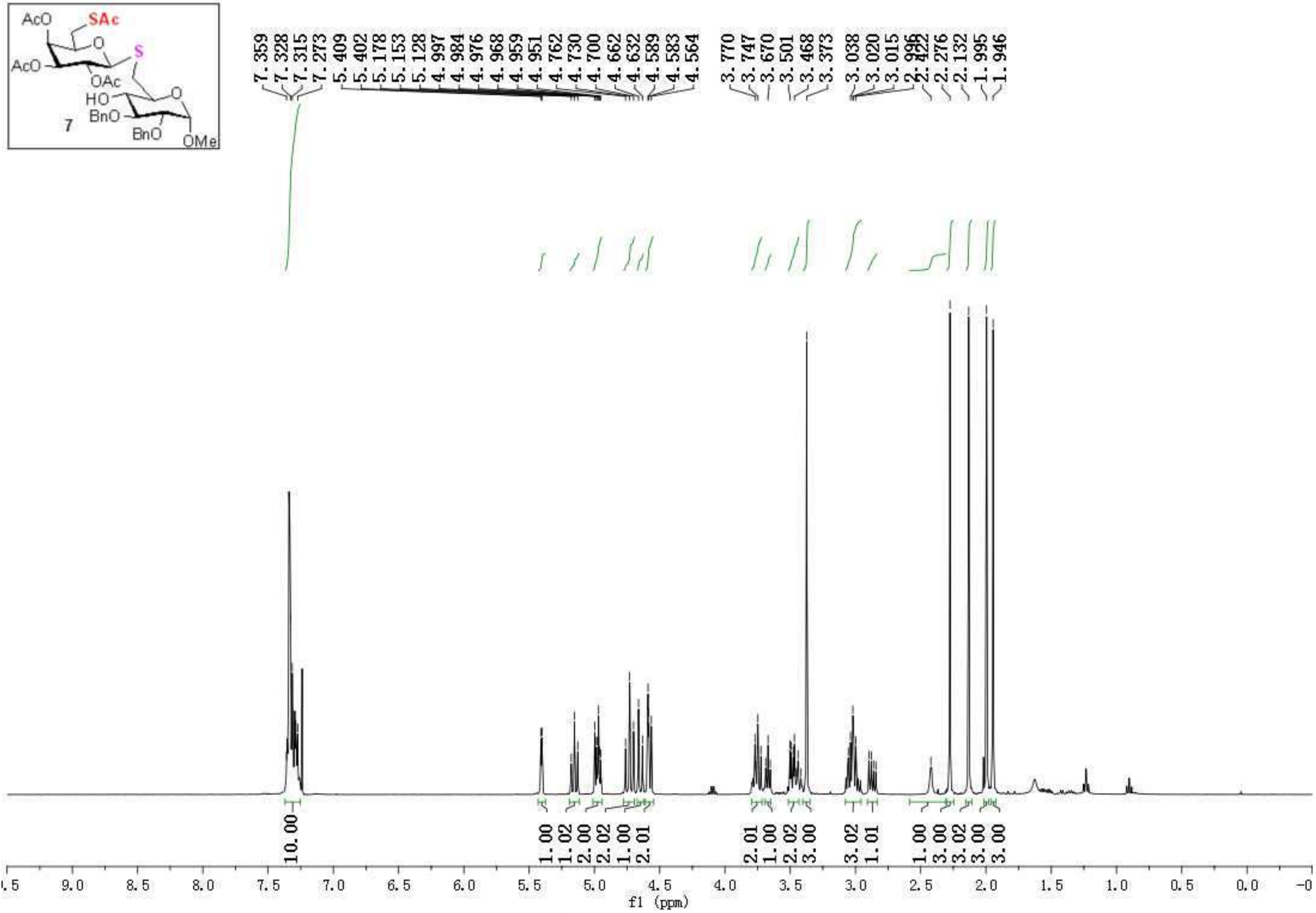


Figure S68. ^{1}H NMR spectrum of **7** in $CDCl_3$

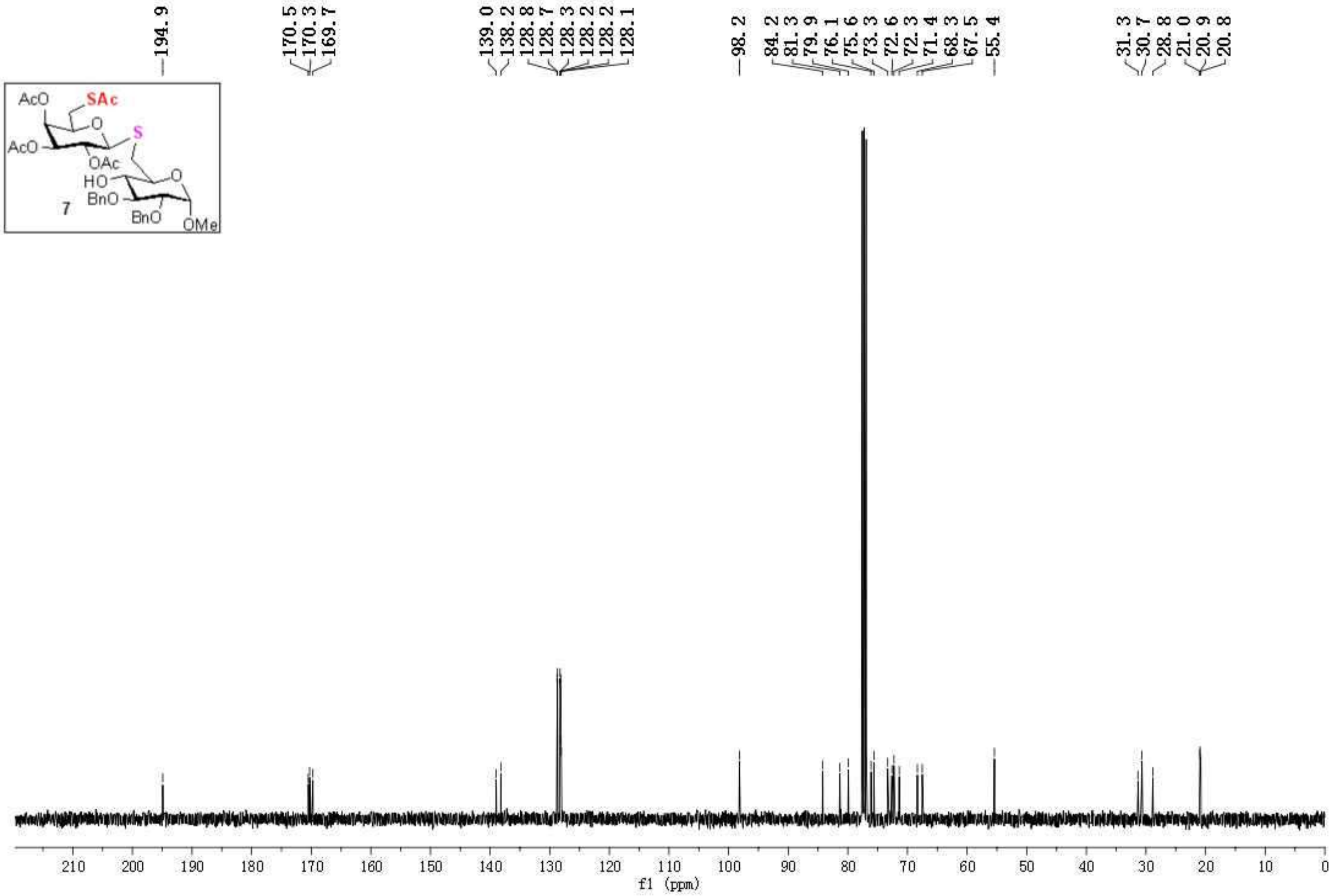


Figure S69. ^{13}C NMR spectrum (100 MHz) of **7** in CDCl$_3$

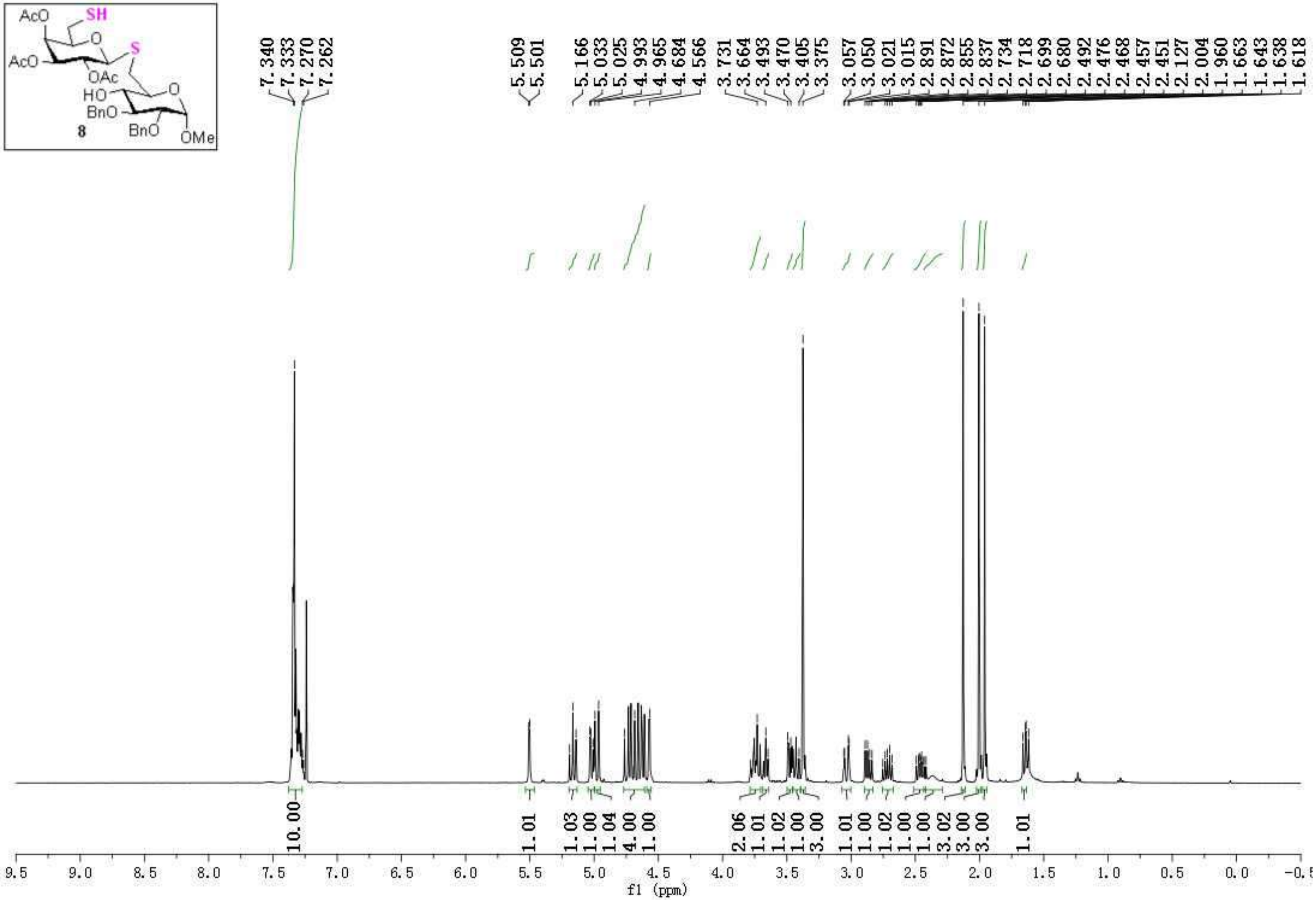


Figure S70. ^{1}H NMR spectrum of **8** in $CDCl_3$

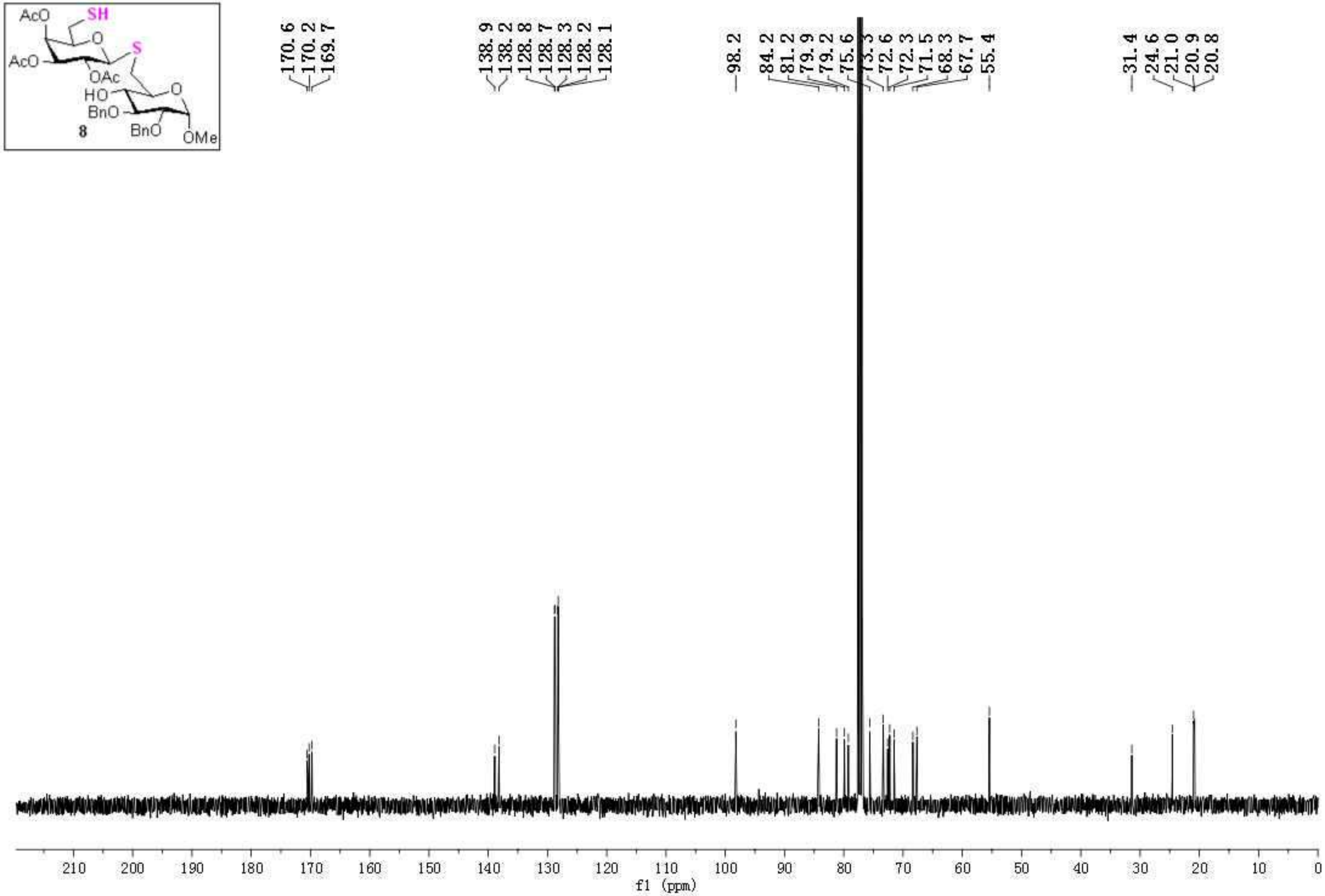


Figure S71. ^{13}C NMR spectrum (100 MHz) of **8** in $CDCl_3$

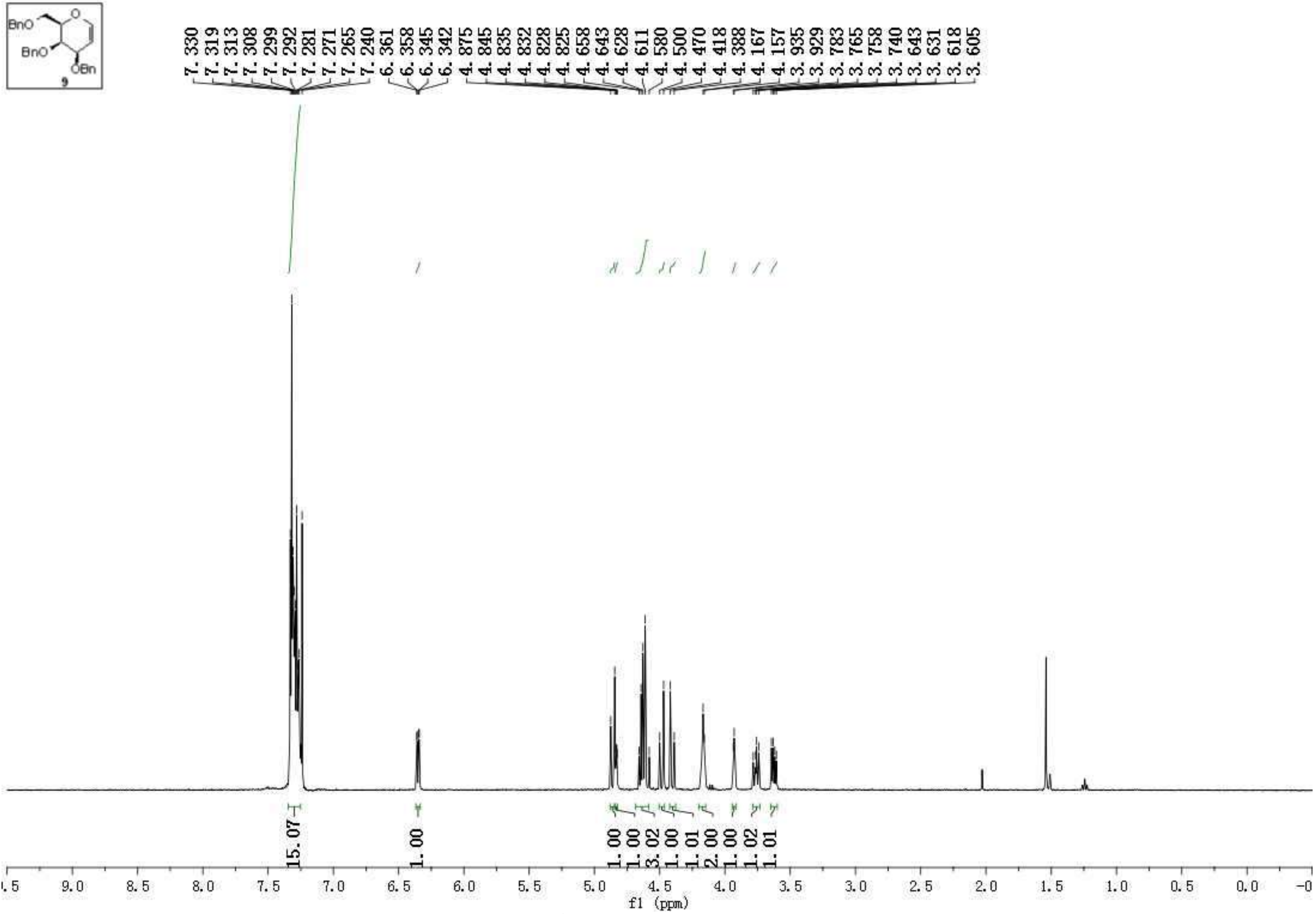


Figure S72. ^{1}H NMR spectrum of **9** in CDCl$_3$

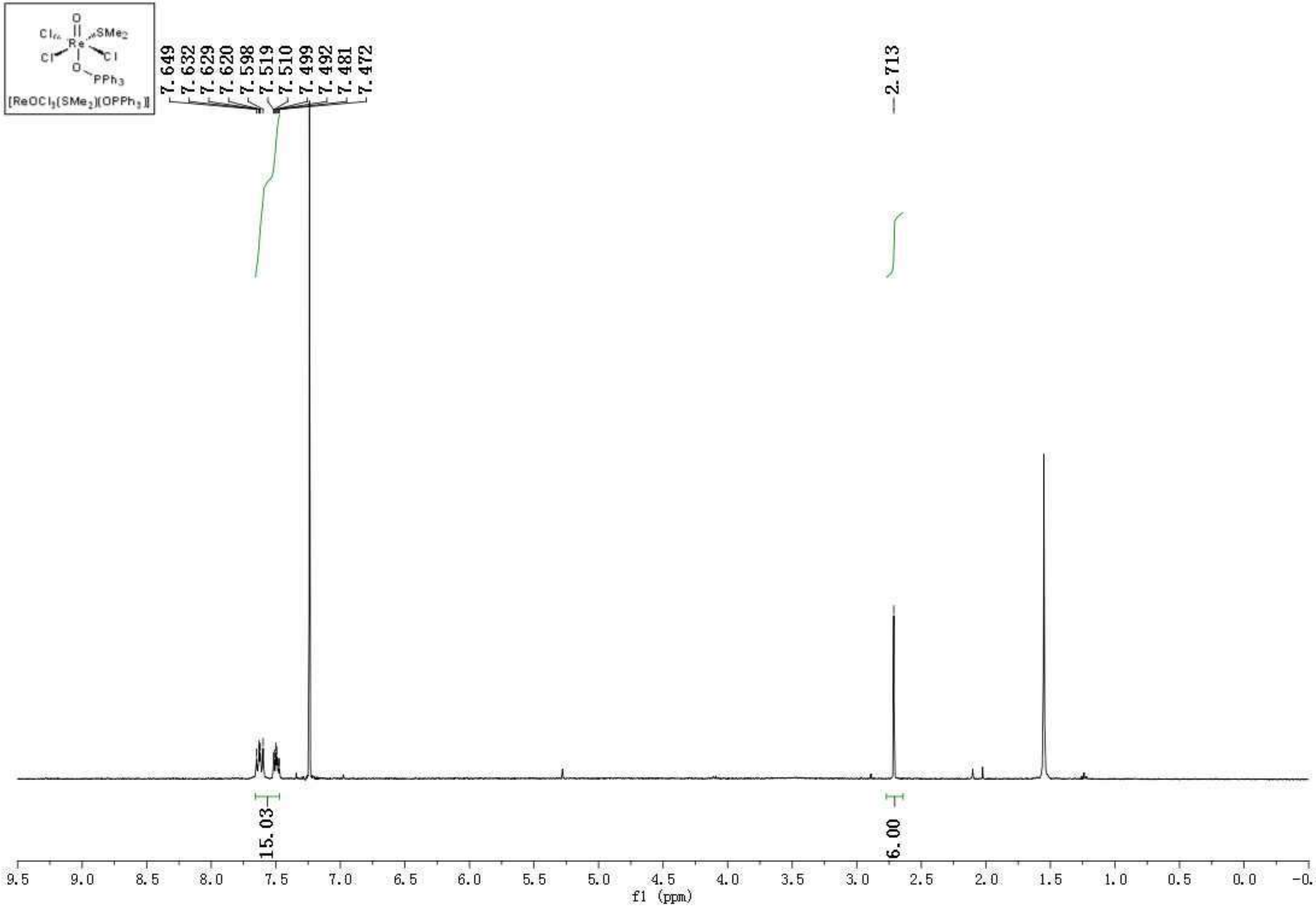


Figure S73. ^{1}H NMR spectrum of **$[ReOCl_3(SMe_2)(OPPh_3)]$** in $CDCl_3$

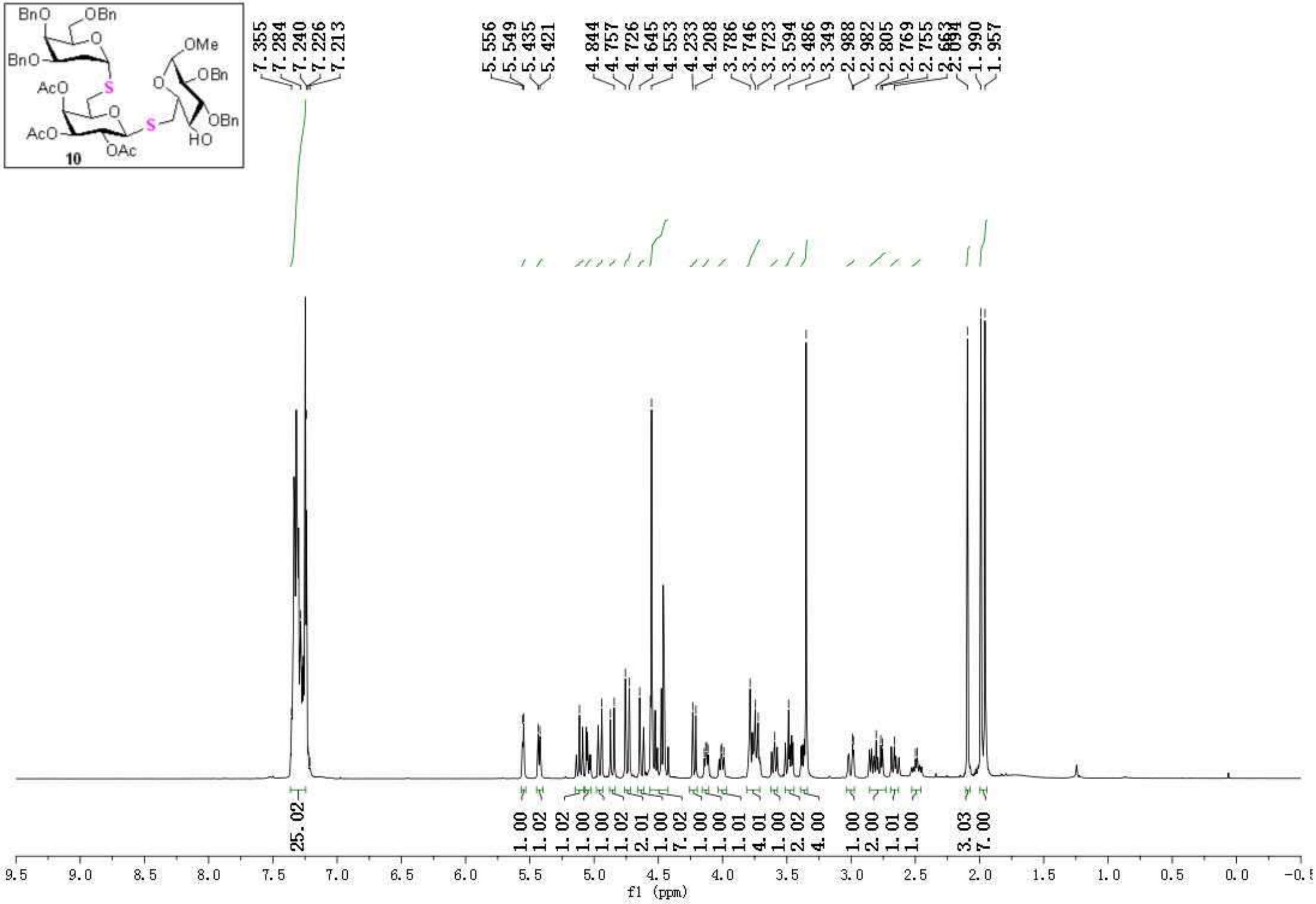


Figure S74. ^{1}H NMR spectrum of **10** in $CDCl_3$

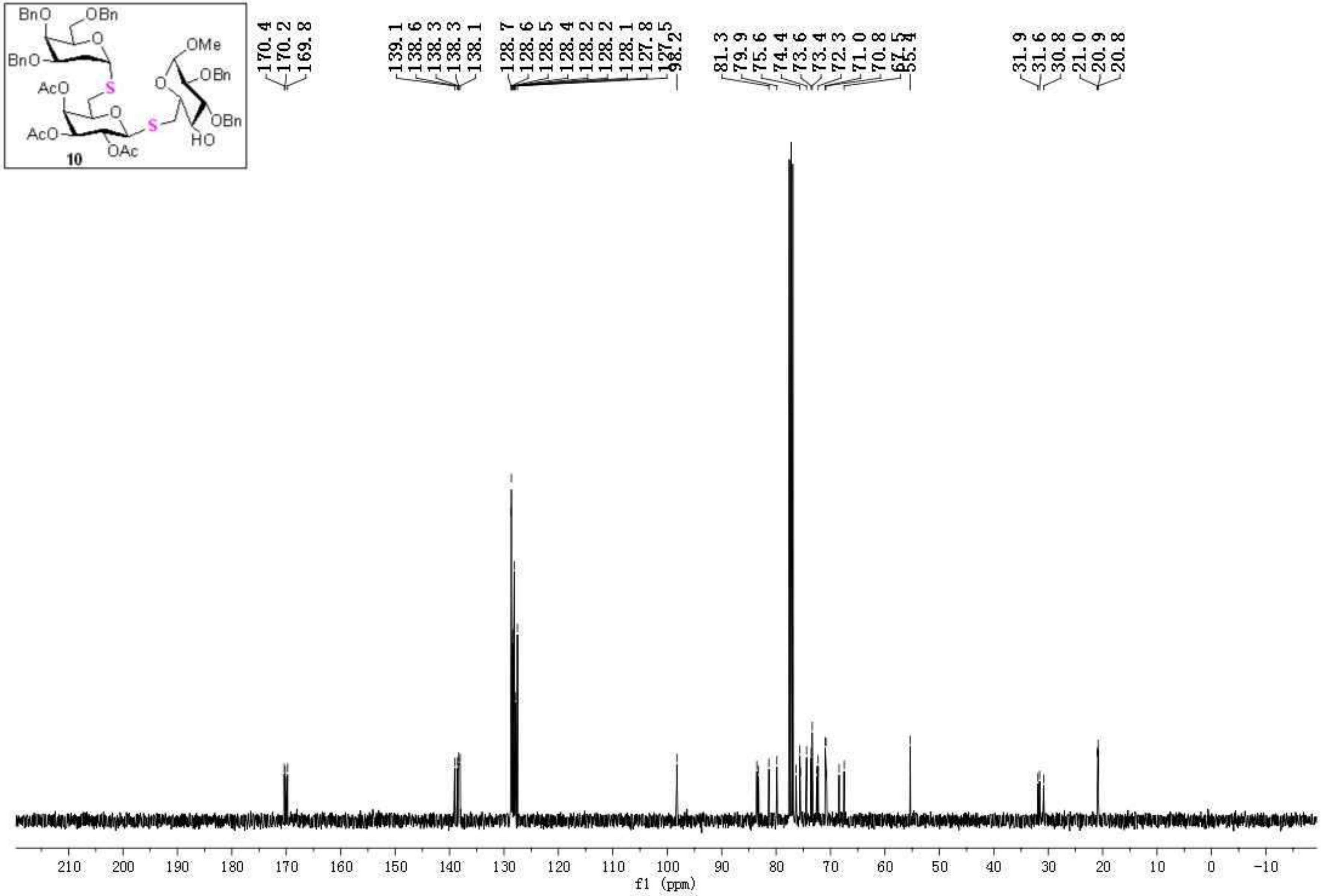


Figure S75. ^{13}C NMR spectrum (100 MHz) of **10** in CDCl$_3$

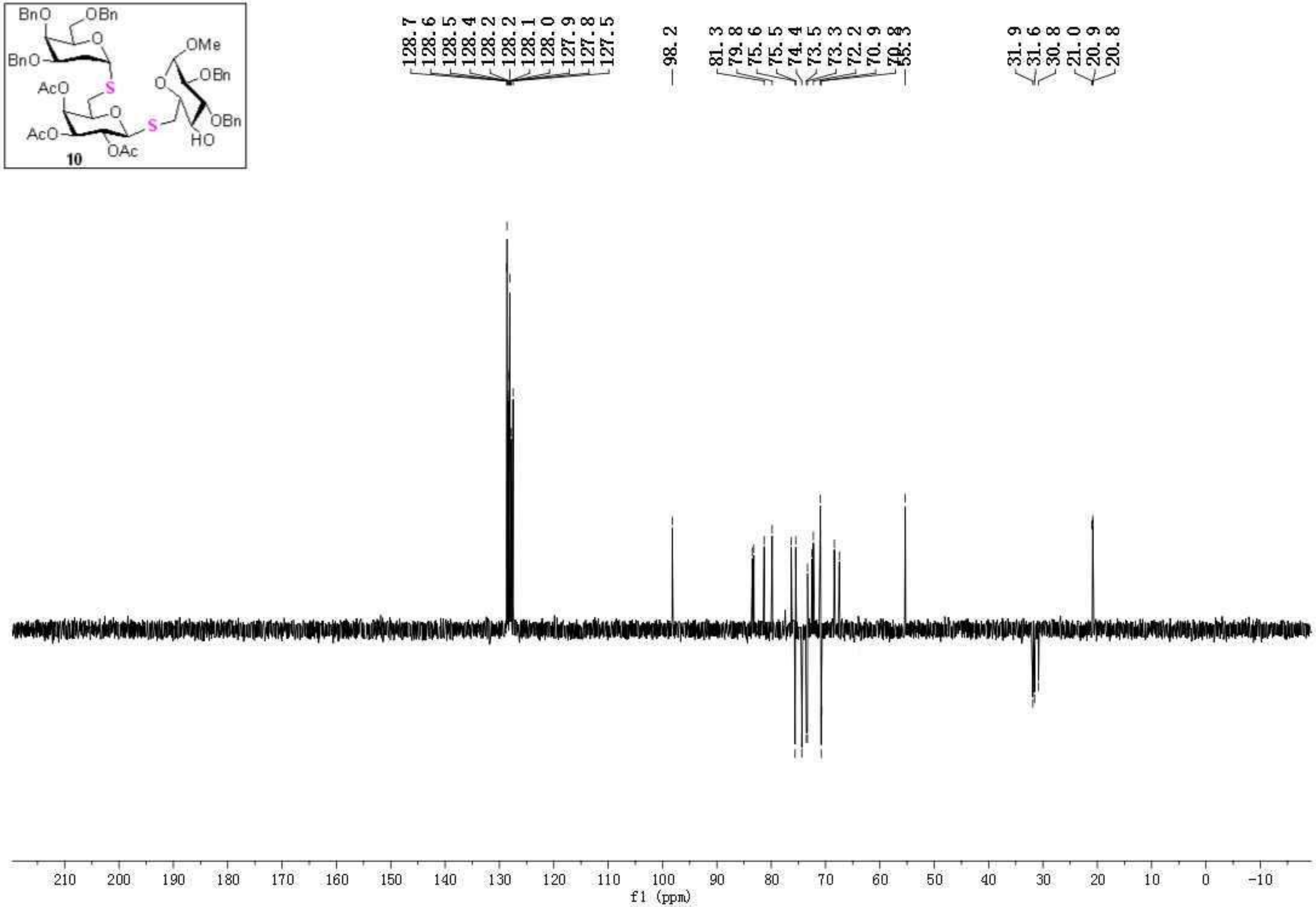


Figure S76. DEPT 135 spectrum of **10** in $CDCl_3$

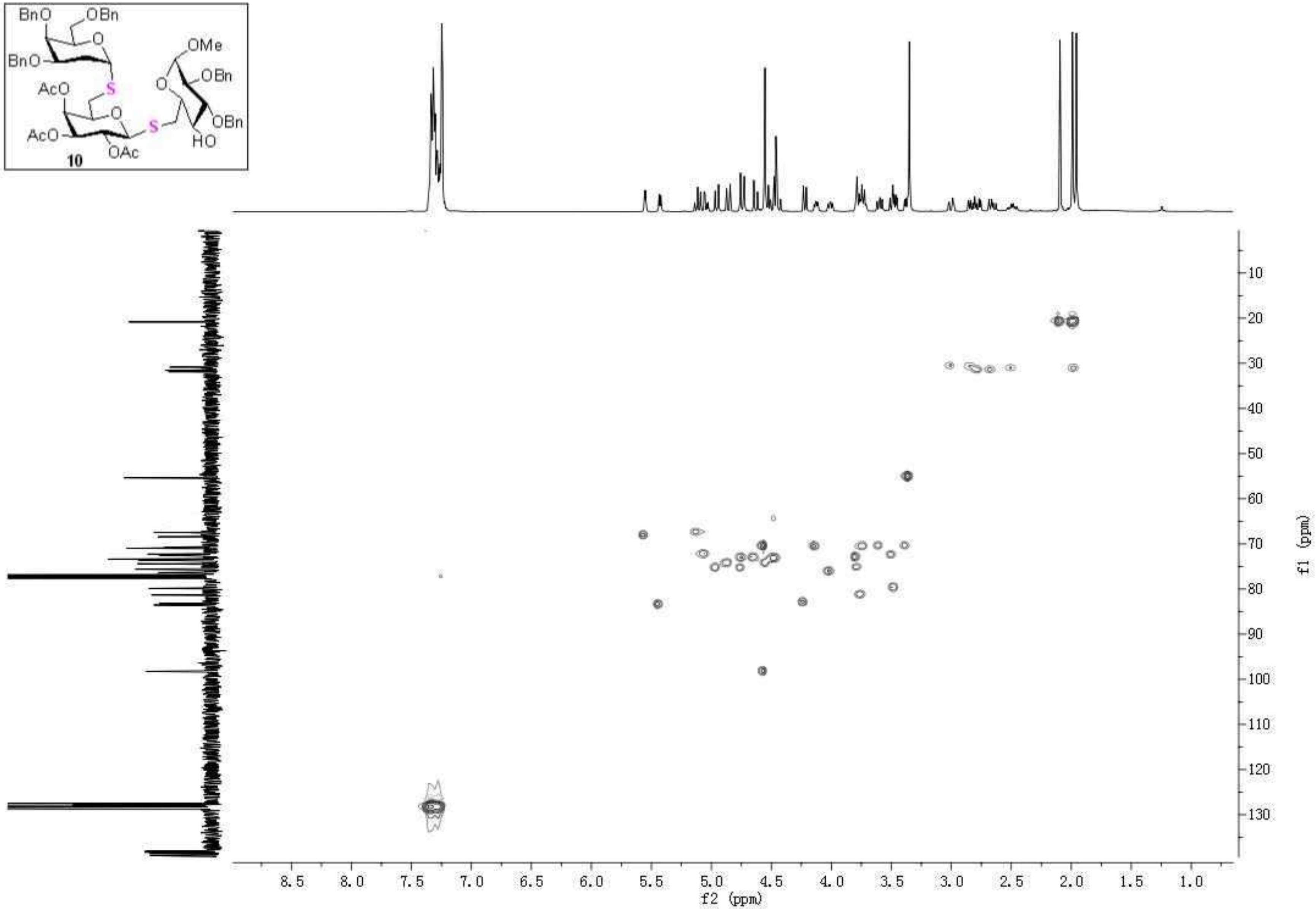


Figure S77. HSQC spectrum of **10** in $CDCl_3$

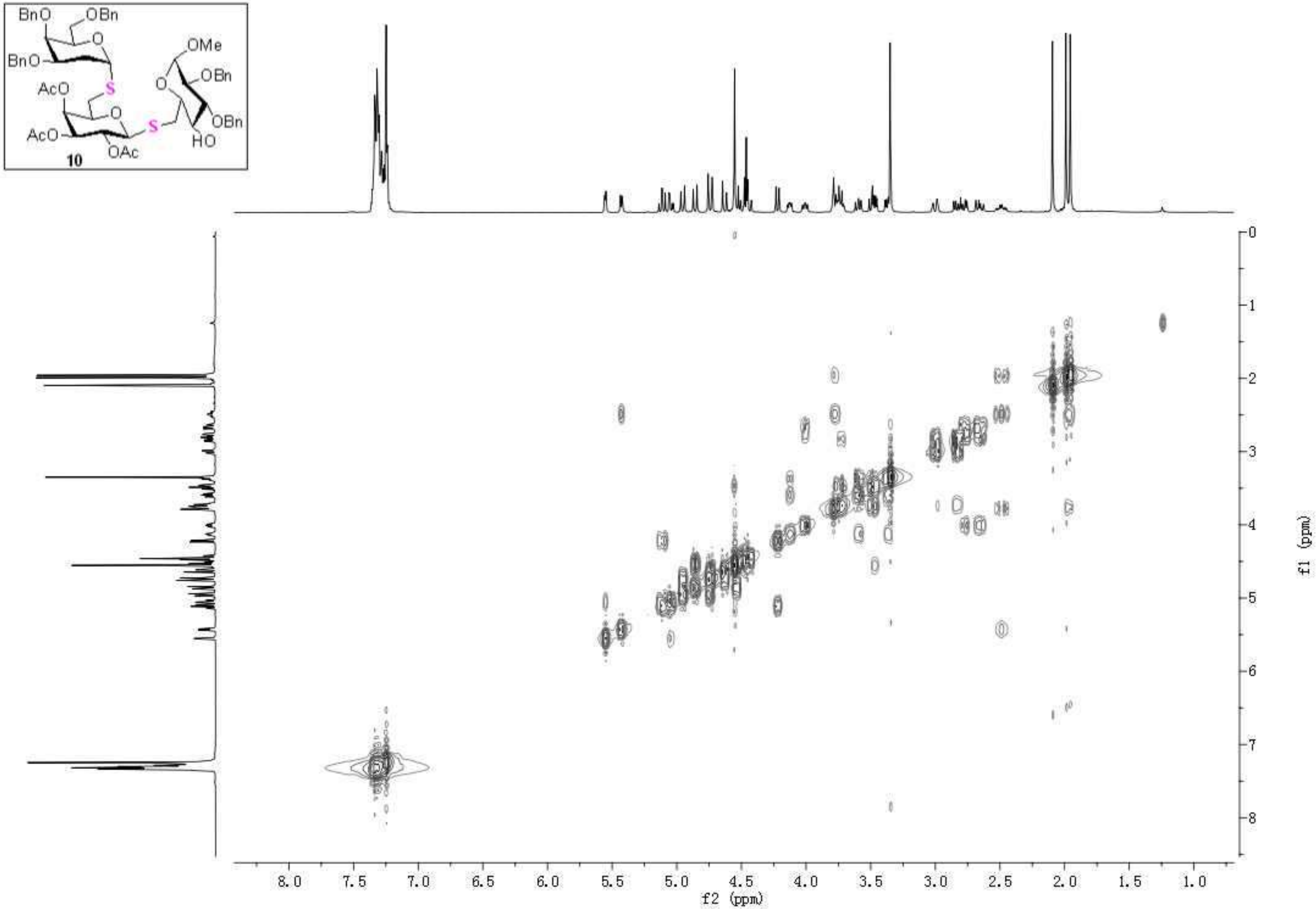


Figure S78. ^{1}H-^{1}H COSY spectrum of **10** in CDCl$_3$

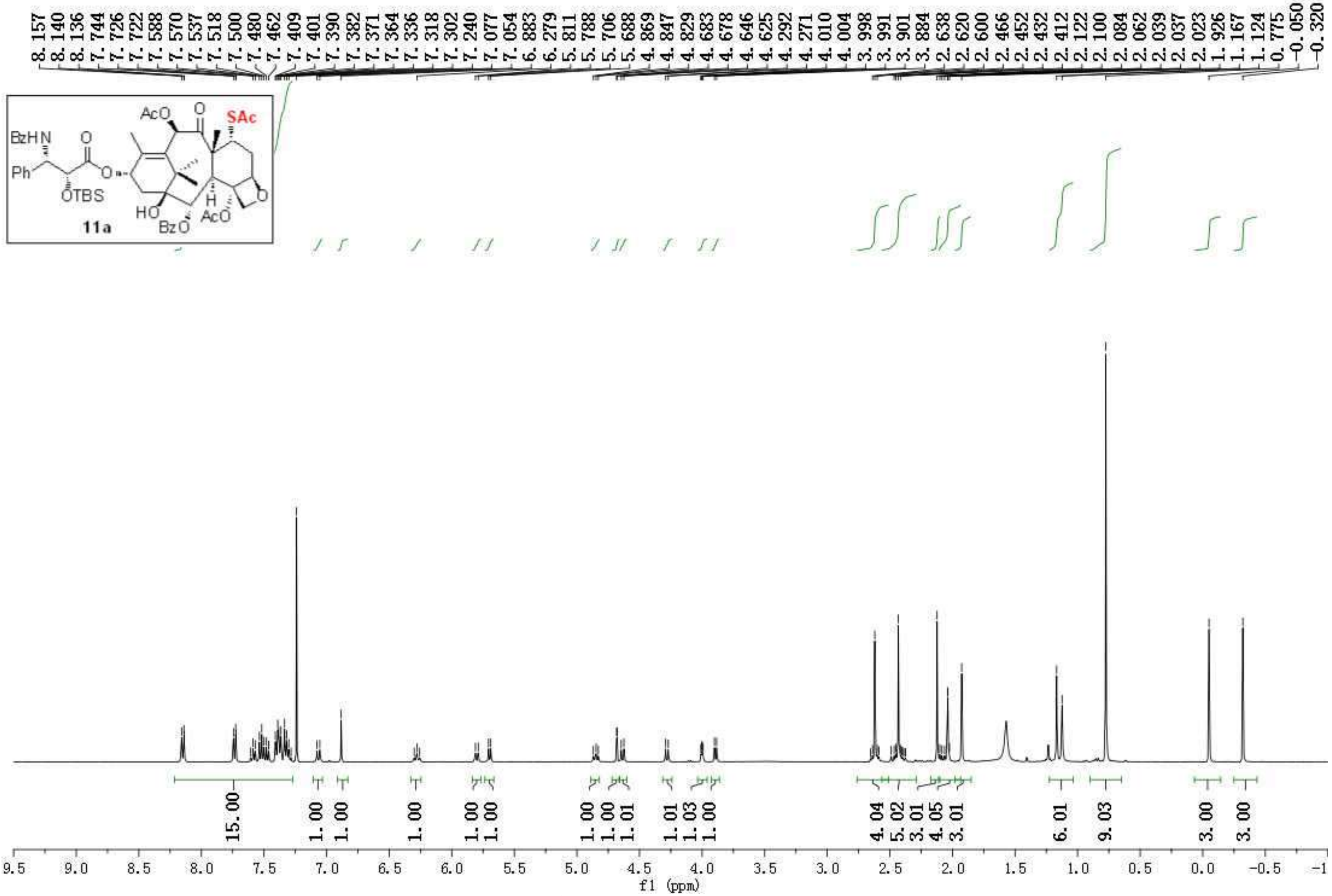


Figure S79. ^{1}H NMR spectrum of **11a** in CDCl$_3$

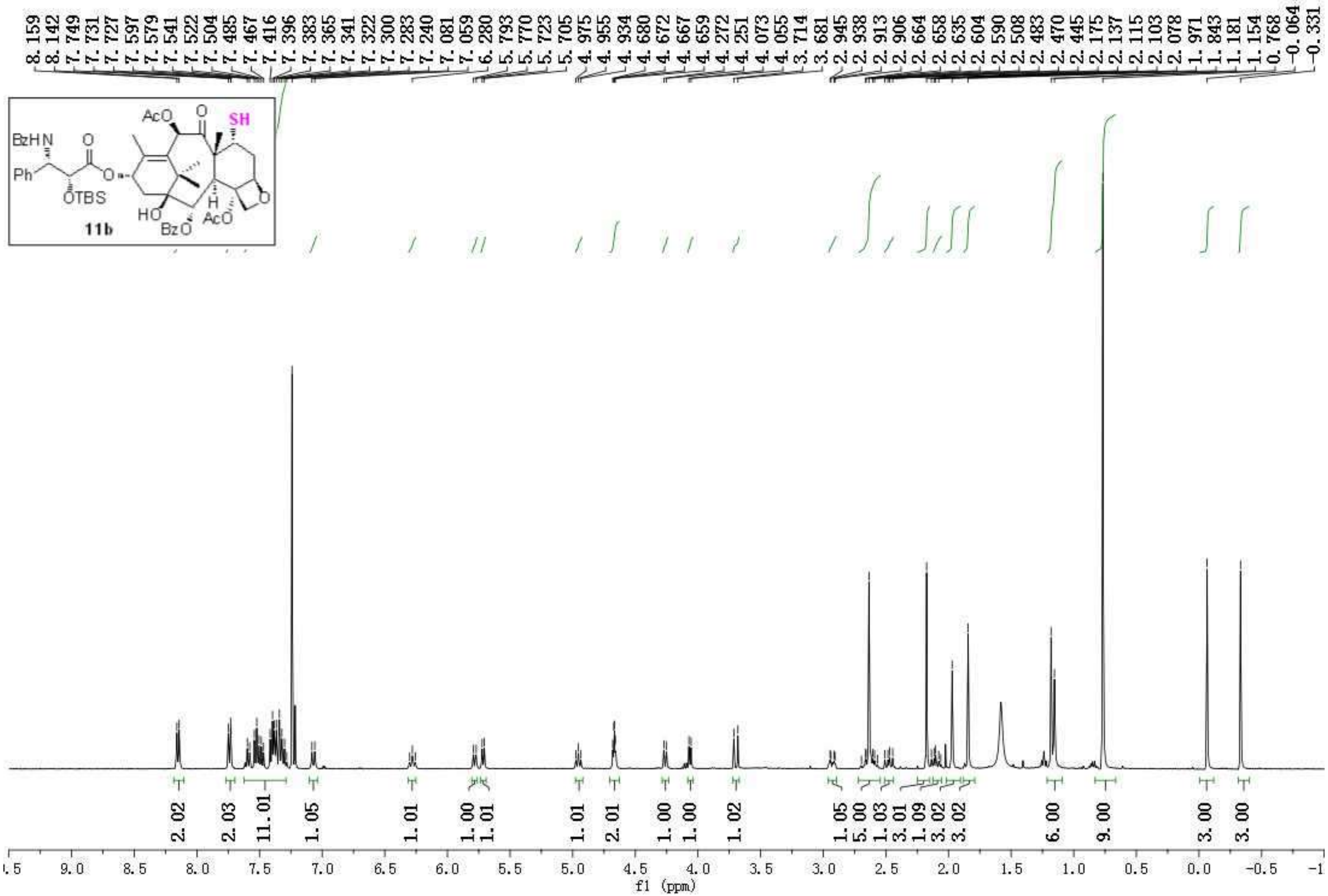


Figure S80. ^{1}H NMR spectrum of **11b** in $CDCl_3$

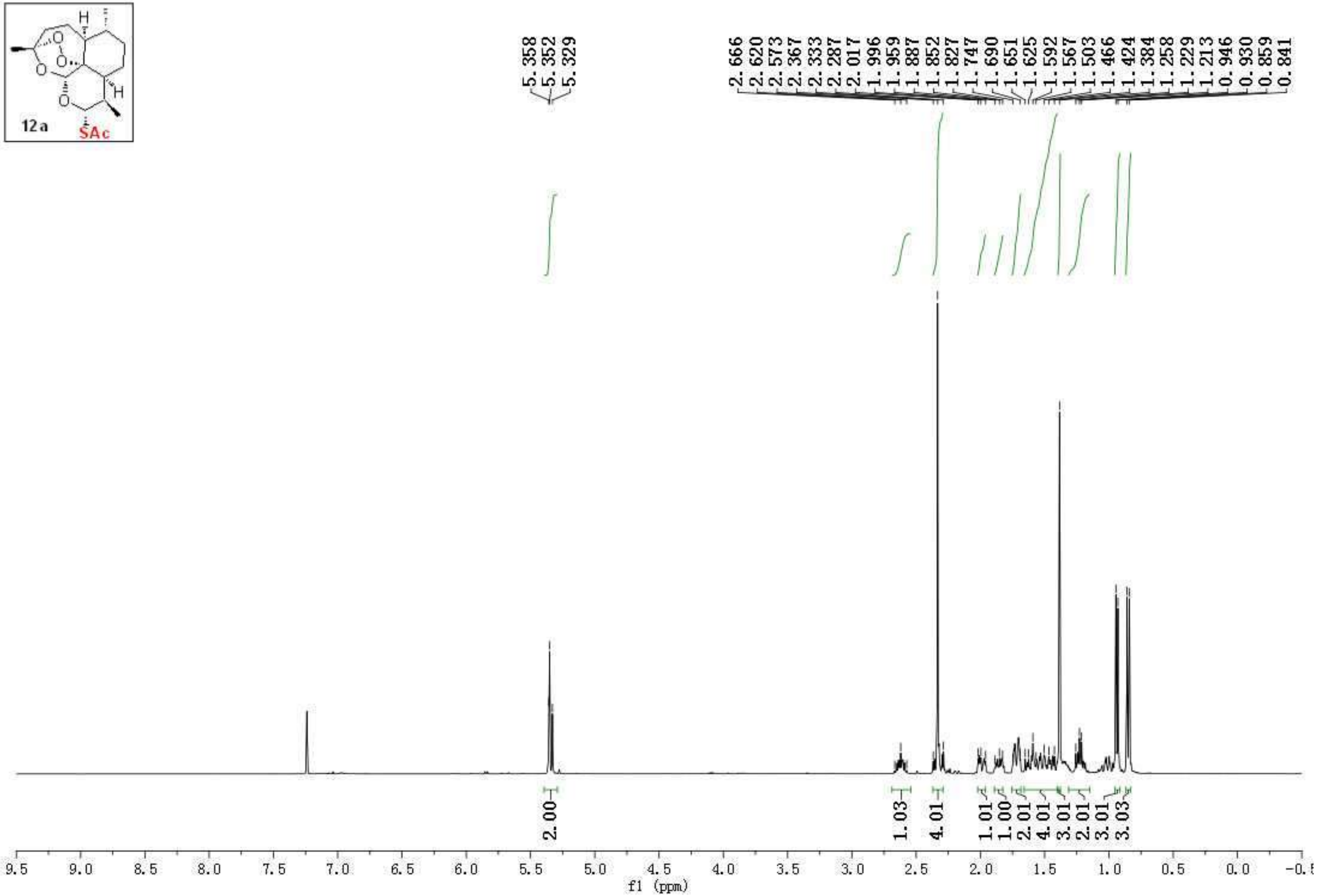


Figure S81. ^{1}H NMR spectrum of **12a** in $CDCl_3$

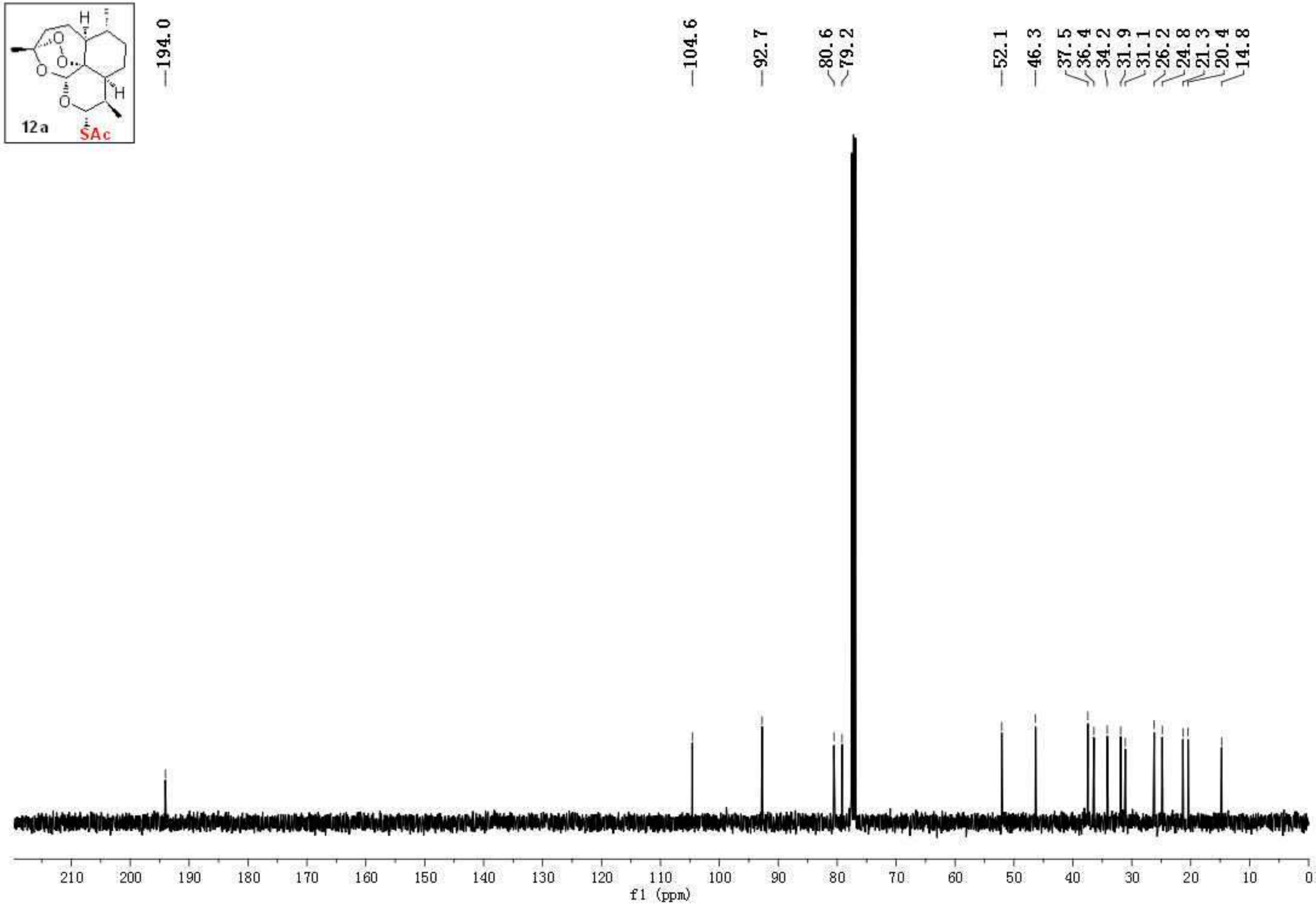


Figure S82. ^{13}C NMR spectrum of **12a** in $CDCl_3$

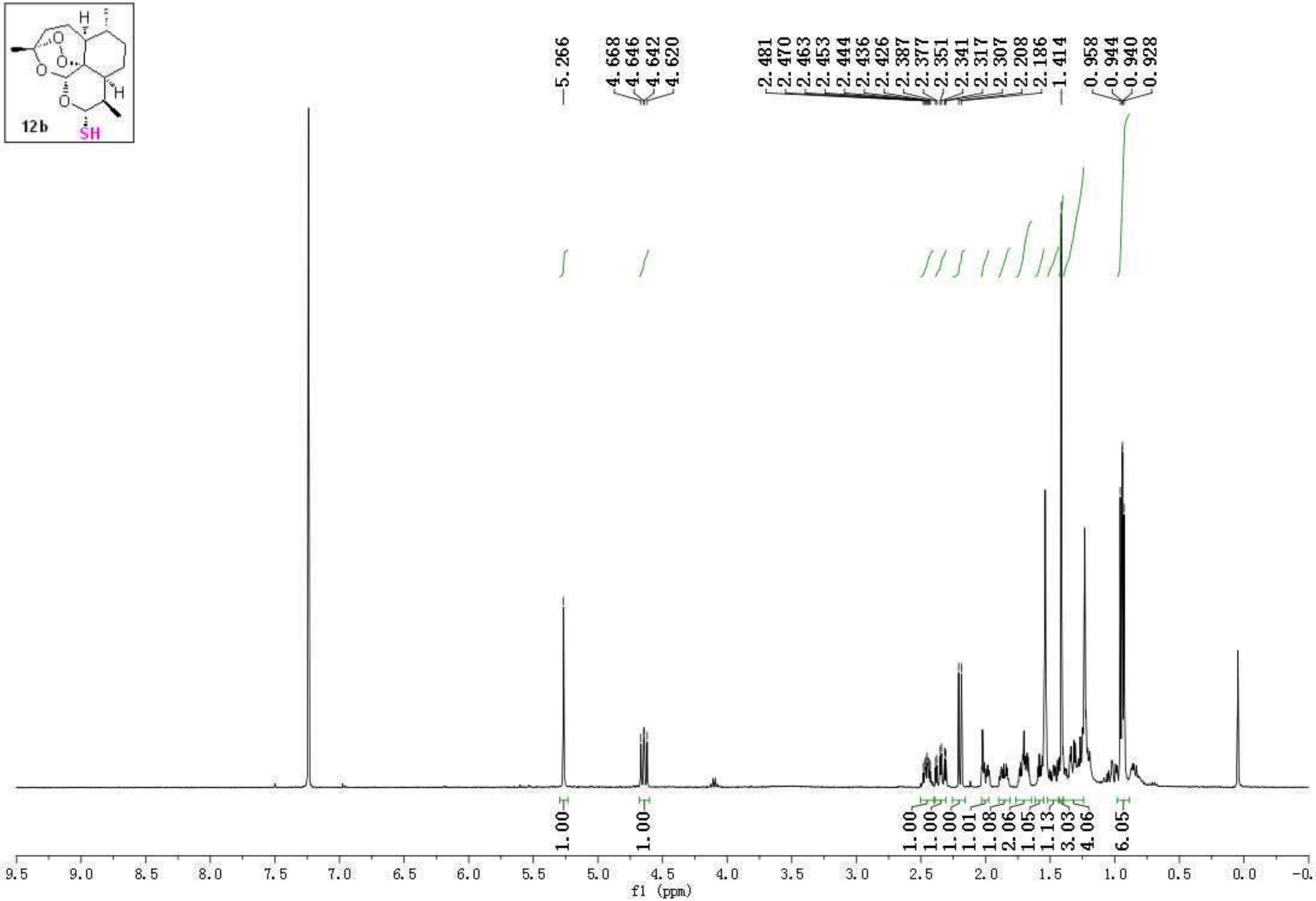


Figure S83. ^{1}H NMR spectrum of **12b** in $CDCl_3$

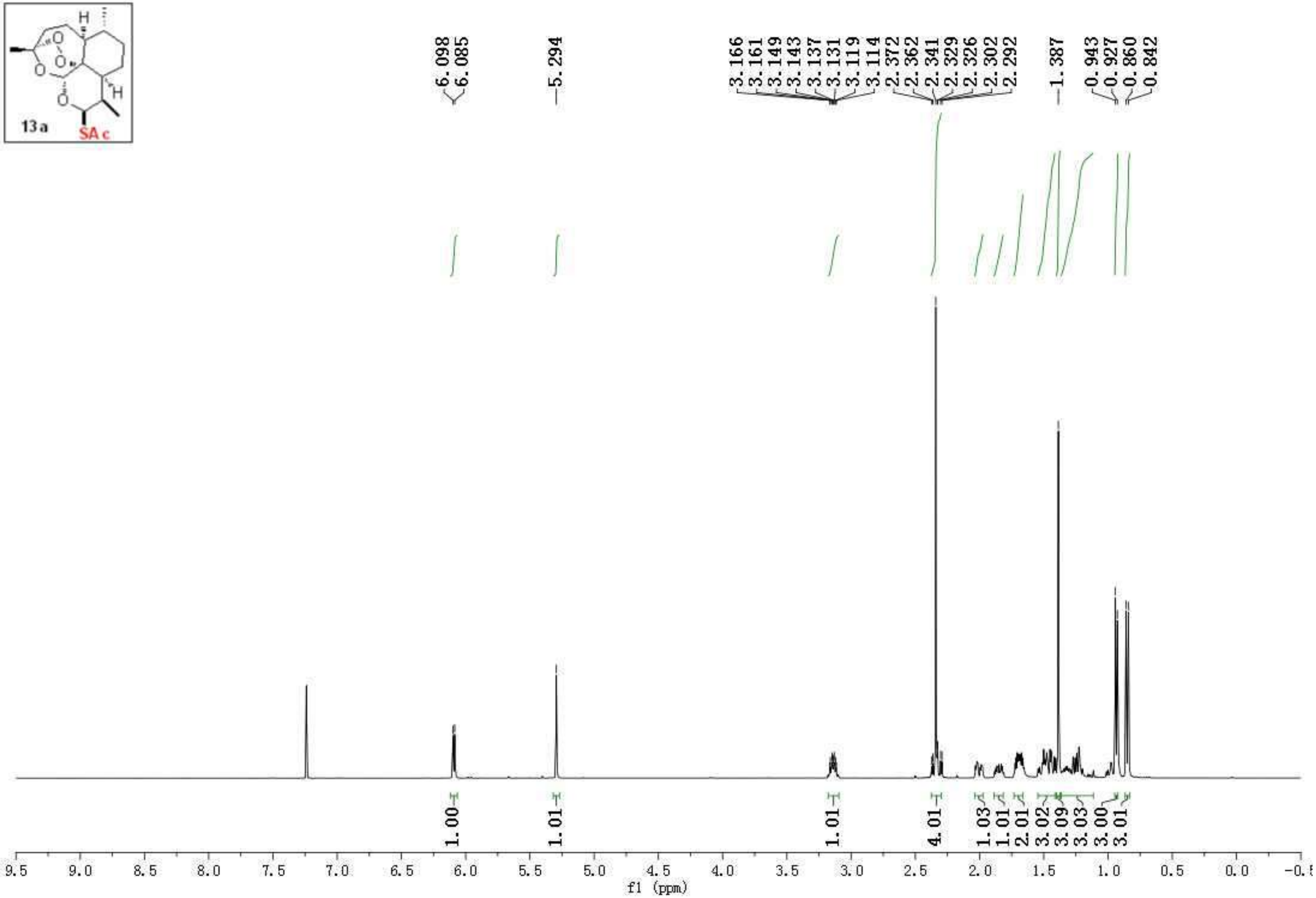


Figure S84. ^{1}H NMR spectrum of **13a** in $CDCl_3$

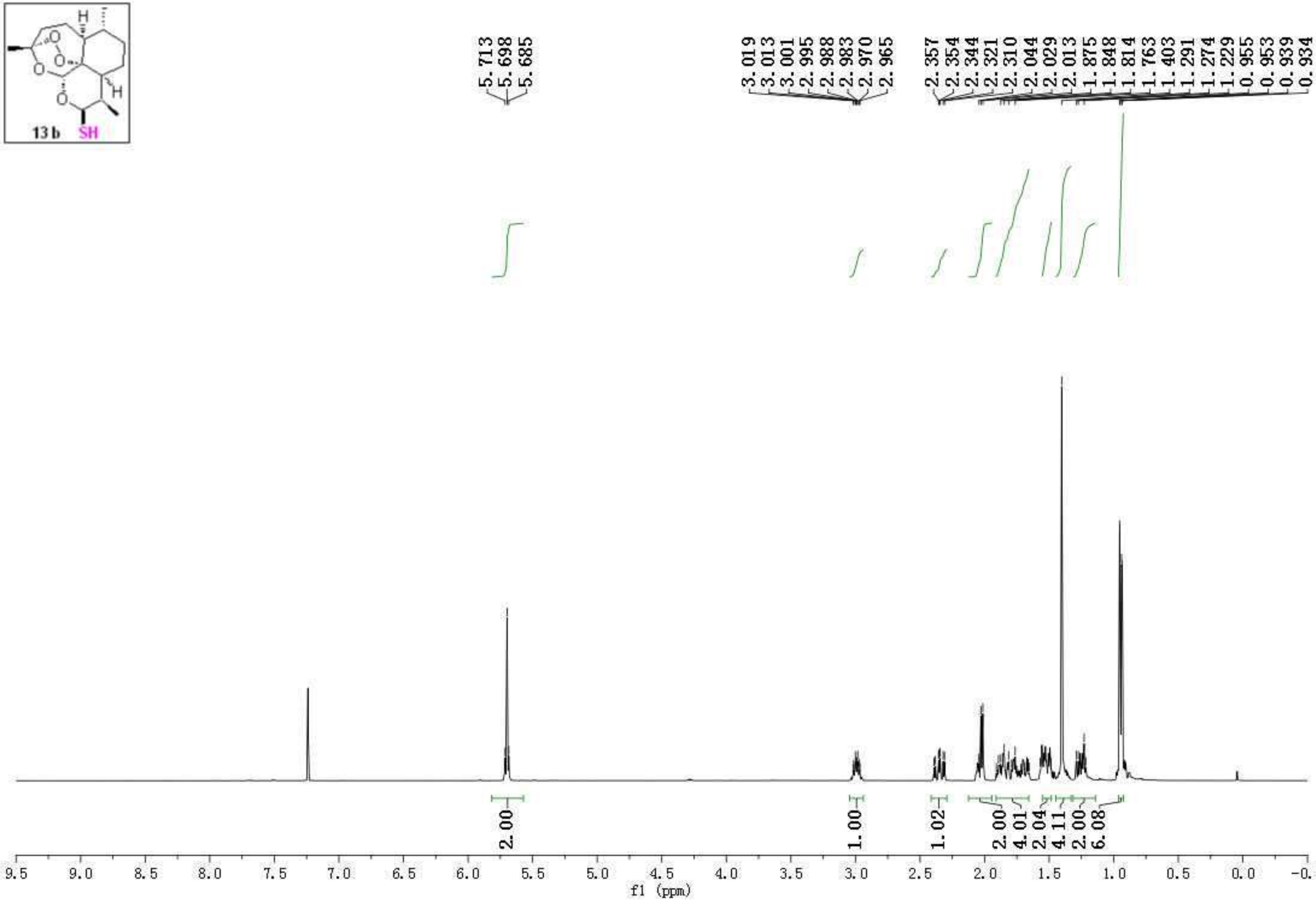


Figure S85. ^{1}H NMR spectrum of **13b** in $CDCl_3$

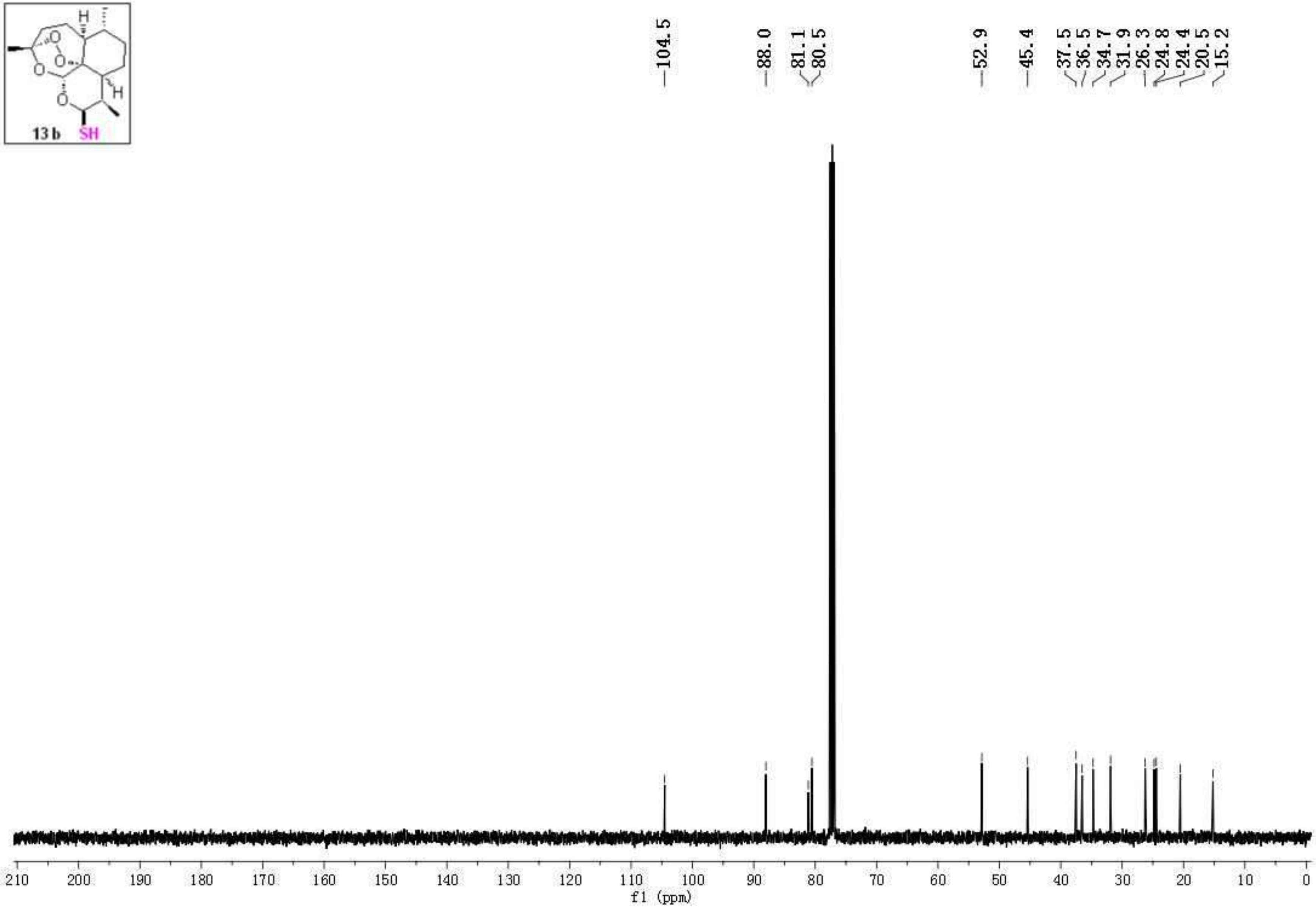


Figure S86. ^{13}C NMR spectrum of **13b** in $CDCl_3$

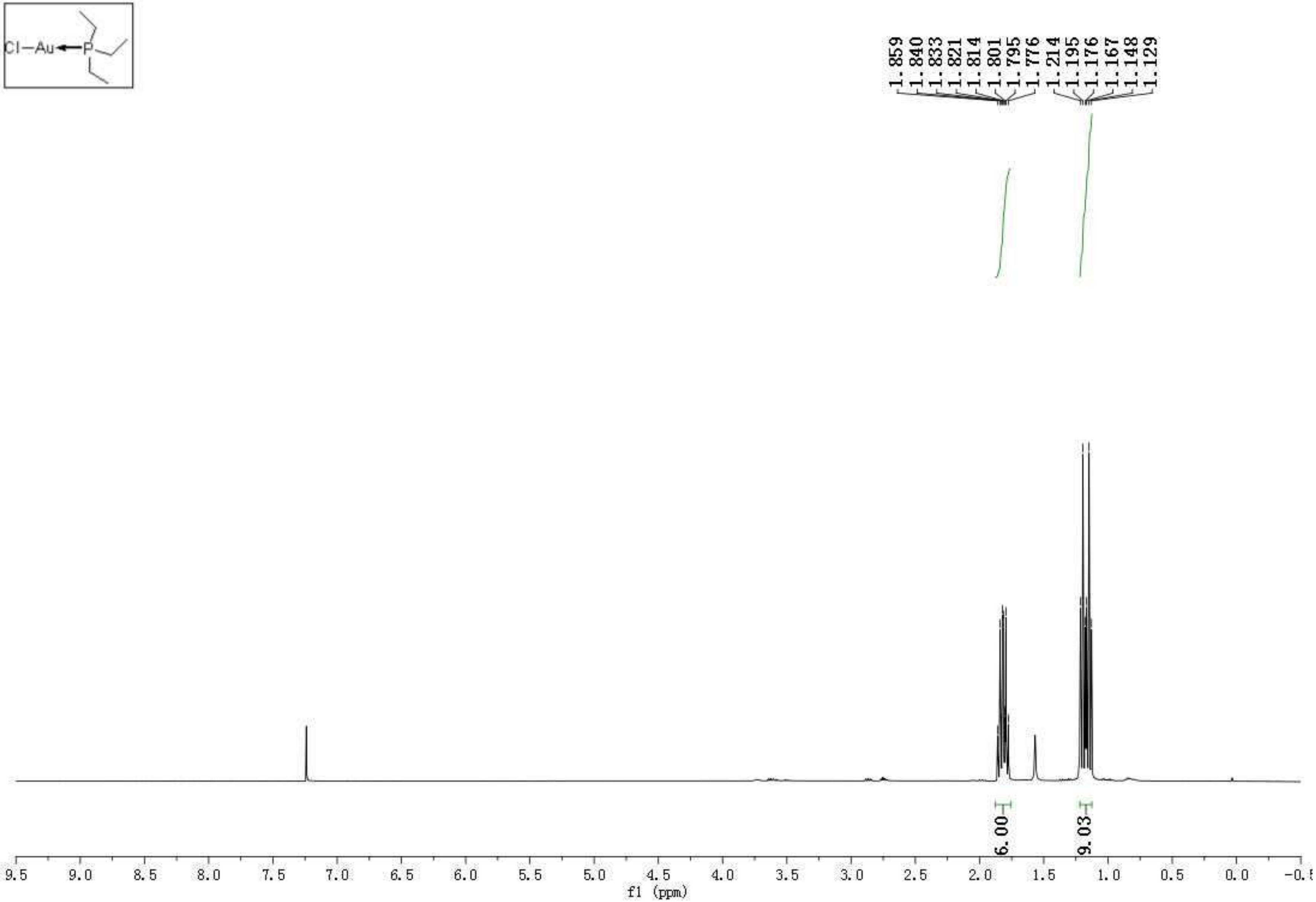


Figure S87. ^{1}H NMR spectrum of **[Et$_3$PAuCl]** in CDCl$_3$

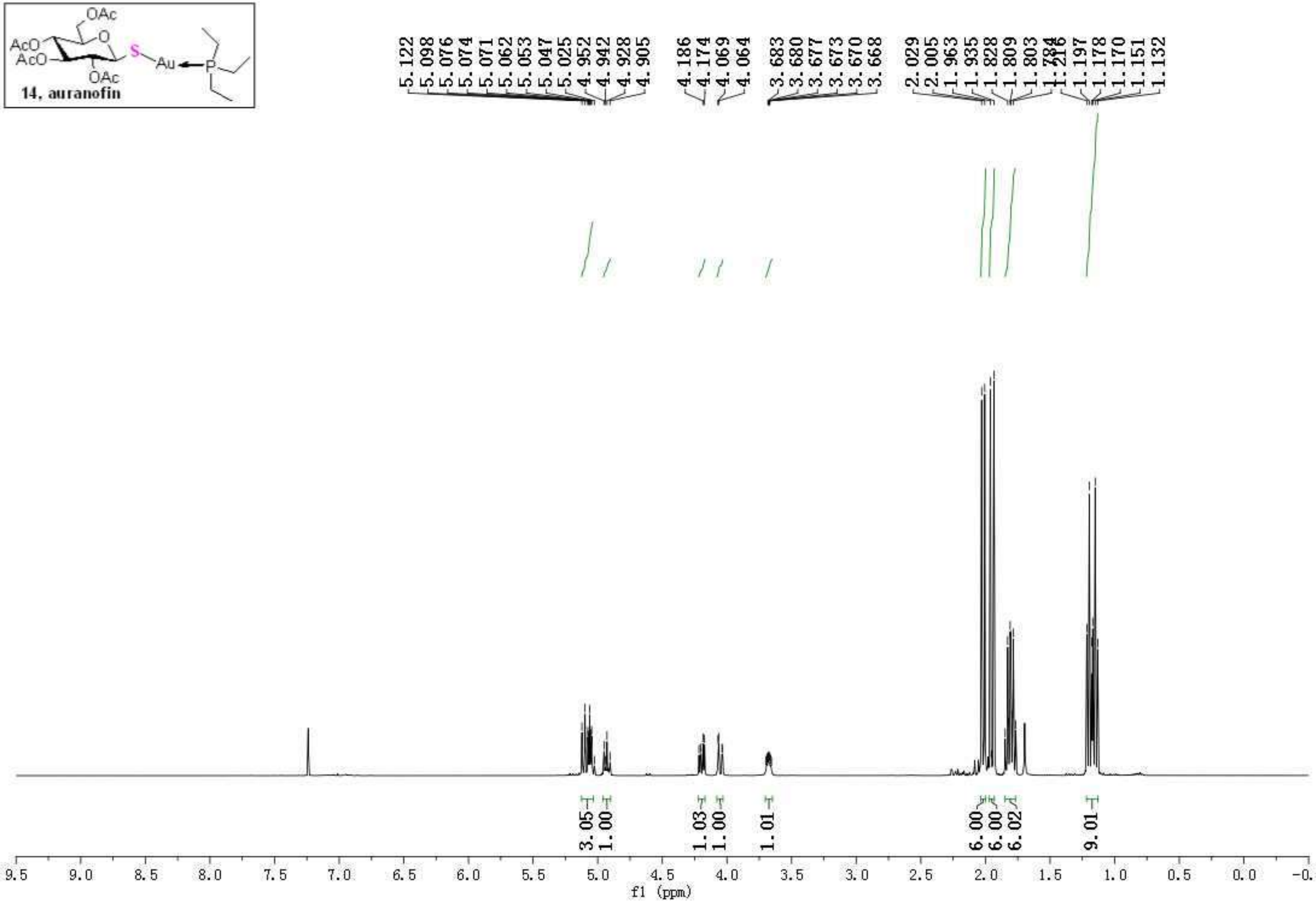


Figure S88. ^{1}H NMR spectrum of **14 (Auranofin)** in $CDCl_3$