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). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz), and the ^1H 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 CD_3OD at δ_H 3.31 and δ_C 49.15. Optical rotations were measured at 20 ℃ with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 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).

2. Materials

Prior to running the glycosylation reactions, all reagents except activators and those with low boiling point (<180 ℃) were dried by repeated azeotropic removal of water using toluene and a rotary evaporator at 27 ℃. Solvents for reactions were dried on an Innovative Technologies Pure Solv400 solvent purifier. Molecular sieves (4Å, powder < 50 μm) for reactions were flame dried immediately before use. Trifluoromethanesulfonic anhydride (Tf_2O) was purchased from Acros. Urea hydrogen peroxide adduct (UHP), cyanuric chloride (CC), PIFA [bis(trifluoroacetoxy)iodobenzene] and all other chemicals were purchased from Adamas and used without further purification. Compouds **S3a-S3d** and **S3f** were commercial available. Compounds **S1a**[1], **S1b**[2], **S2a**[3], **S2b**[4], **S2c**[5], **S2d**[6], **8**[5], **S2e**[7], **S2f**[8] and **S3e**[9] were synthesized following literature procedures.

3. General Procedure

Procedure A for Preparing Thioesters 5a-5g: A suspension of **S1a** (5.0 mmol, 1.0 equiv) and alcohol **S2** or **8** (7.5 mmol, 1.5 equiv) containing activated 4 Å molecular sieves (100 wt%) in dry DCM (25.0 mL) was stirred at – 40 ℃ for 15 min, then TMSOTf (0.36 mL, 2.0 mmol, 0.4 equiv) was added. The reaction mixture was stirred at –40 ℃ for 1 h, and quenched by addition of 0.3 mL Et_3N. The suspension was diluted with EtOAc, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel column chromatography.

Procedure B for Oxidizing Thioether to Sulfoxide: To a solution of thioether **5** (1.0 mmol, 1.0 equiv) and urea hydrogen peroxide adduct (UHP, 1.2 mmol, 1.2 equiv) in dry CH_3CN (10 mL) was added cyanuric chloride (CC, 1.2 mmol, 1.2 equiv). The resulting solution was stirred at room temperature and white solids precipitated gradually. After 3 h, the suspension was filtered through Celite. The filtrate was diluted with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The organic layer was separated, washed with brine, dried (Na_2SO_4), concentrated, and purified by flash column chromatography.

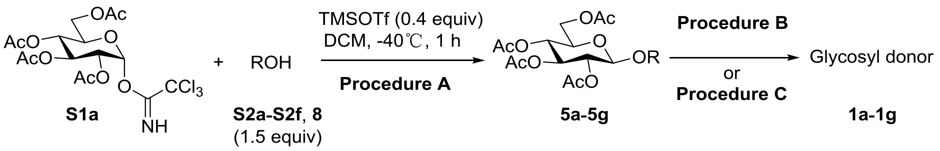
Procedure C for Oxidizing Thioether to Sulfoxide: To a solution of thioether **5** (1.0 mmol, 1.0 equiv) in 10 mL wet CH_3CN (containing ca 5% water) was added PIFA [bis(trifluoroacetoxy)iodobenzene] (PIFA, 1.2 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 10 min, then diluted with water, extracted with EtOAc. The organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel column chromatography.

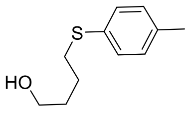
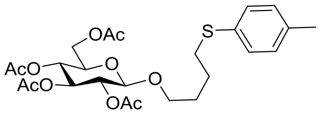
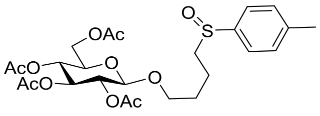
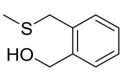
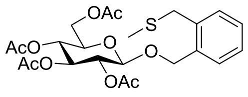
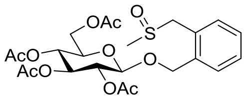
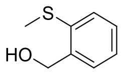
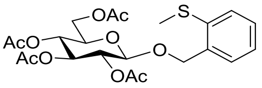
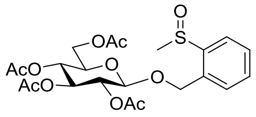
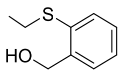
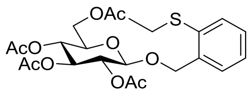
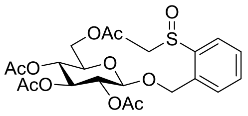
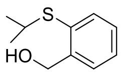
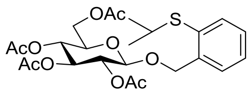
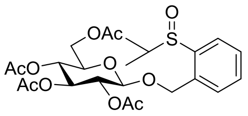
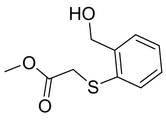
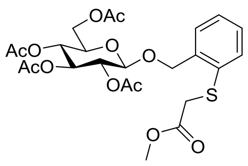
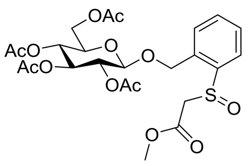
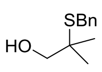
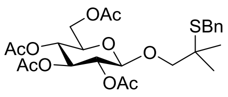
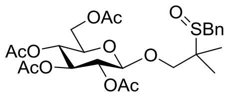
Procedure D for Preparing Thioesters 5h-5m: To a mixture of **S1b** (3.0 mmol, 1.0 equiv), EDCI (3.6 mmol, 1.2 equiv) and DMAP (0.6 mmol, 0.2 equiv) in dry DCM (6 mL) was added **S3** (3.6 mmol, 1.2 equiv). The mixture was stirred at room temperature for 5 h, and then diluted with EtOAc, washed with water, dried (Na_2SO_4), concentrated and purified by silica gel column chromatography.

Procedure E for Glycosylation: A solution of glycosyl donor (0.1 mmol, 1.0 equiv), acceptor (0.2 mmol, 2.0 equiv) and 4 Å MS (100 wt%) in 2.0 mL solvent was stirred at 0 ℃ for 15 min, then activator (0.12 mmol, 1.2 equiv) was added. The reaction mixture was stirred at 0 ℃ for 1 h and then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel column chromatography.

Procedure F for Glycosylation: A solution of glycosyl donor (0.12 mmol, 1.2 equiv), acceptor (0.1 mmol, 1.0 equiv) and 4 Å MS (100 wt%) in 2.0 mL solvent was stirred at 0 ℃ for 15 min, then activator (0.12 mmol, 1.2 equiv) was added. The reaction mixture was stirred at 0 ℃ for 1 h and then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel column chromatography.

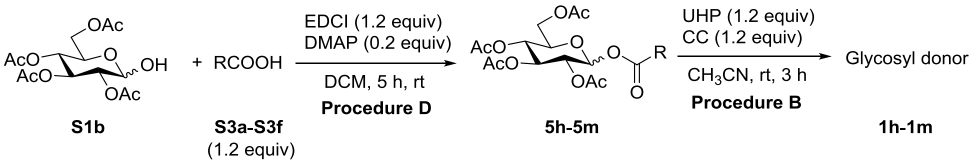
4. **Table S1.** Preparation of Glycosyl Donors **1a-1g**

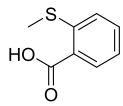
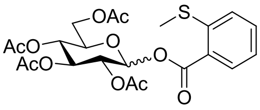
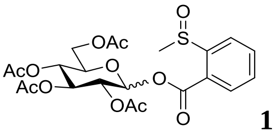
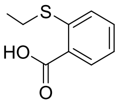
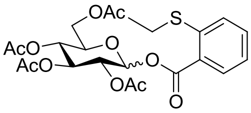
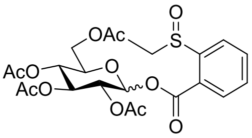
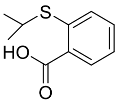
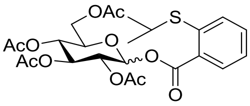
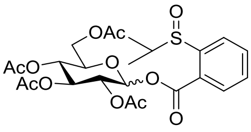
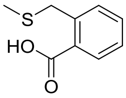
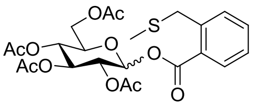
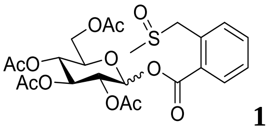
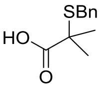
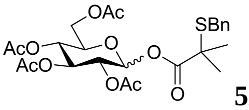
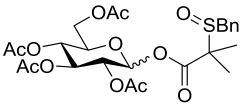
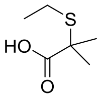
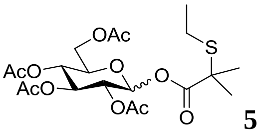
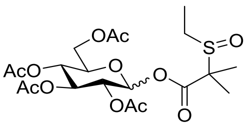


Entry	ROH	Thioester	Yield[a]	Glycosyl donor	Yield
1	 **S2a**	 **5a**	91%	 **1a**	90%[b] (94%)[c]
2	 **S2b**	 **5b**	62%	 **1b**	40%[b] (85%)[c]
3	 **S2c**	 **5c**	62%	 **1c**	80%[b] (95%)[c]
4	 **S2d**	 **5d**	65%	 **1d**	78%[b] (92%)[c]
5	 **8**	 **5e**	83%	 **1e**	82%[b] (90%)[c]
6	 **S2e**	 **5f**	50%	 **1f**	54%[b] (55%)[c]
7	 **S2f**	 **5g**	55%	 **1g**	62%[b] (78%)[c]

[a] Isolated yield, the experiments were conducted according to **Procedure A**. [b] Isolated yield, the experiments were conducted according to **Procedure B**. [c] Isolated yield, the experiments were conducted according to **Procedure C**.

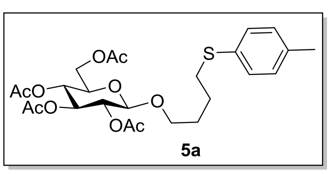
5. **Table S2.** Preparation of Glycosyl Donors **1h-1m**



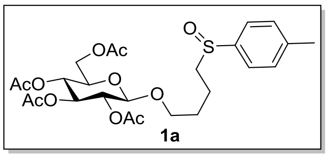
Entry	RCOOH	Ester	Yield^a	Glycosyl donor	Yield^b
1	 **S3a**	 **5h**	87%	 **1h**	96%
2	 **S3b**	 **5i**	97%	 **1i**	96%
3	 **S3c**	 **5j**	95%	 **1j**	89%
4	 **S3d**	 **5k**	95%	 **1k**	73%
5	 **S3e**	 **5l**	93%	 **1l**	75%
6	 **S3f**	 **5m**	85%	 **1m**	70%

^{a}Isolated yield, the experiments were conducted according to **Procedure D**. ^{b}Isolated yield, the experiments were conducted according to **Procedure B**.

Analytical Data.

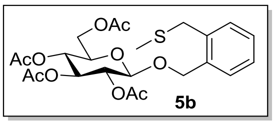

5a

Colorless oil. R_f = 0.65 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ –19.4 (*c*, 0.47 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (2H, d, *J* = 8.0 Hz, Ar-H), 7.07 (2H, d, *J* = 8.0 Hz, Ar-H), 5.17 (1H, t, *J* = 9.6 Hz, H-3), 5.05 (1H, t, *J* = 9.6 Hz, H-4), 4.94 (1H, dd, *J* = 9.6, 8.0 Hz, H-2), 4.44 (1H, d, *J* = 8.0 Hz, H-1), 4.22 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.10 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 3.85 (1H, m), 3.65 (1H, ddd, *J* = 9.6, 4.8, 2.4 Hz, H-5), 3.45 (1H, m), 2.86-2.83 (2H, m), 2.29 (3H, s, CH_3), 2.05, 2.00, 1.99, 1.98 (12H, 4 × s, COCH_3), 1.69-1.62 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.6, 169.5, 136.3, 132.9, 130.2, 130.2, 129.9, 129.9, 100.9, 77.2, 73.1, 72.0, 71.5, 69.6, 68.7, 62.2, 34.2, 28.6, 25.8, 21.2, 20.9, 20.8, 20.8. HRMS calc. for $C_{25}H_{34}NaO_{10}S$ $[M+Na]^+$: 549.1765, found: 549.1790.



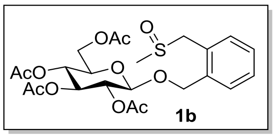
1a

White solid. R_f = 0.30 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (*R* and *S*). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (2H, m, Ar-H), 7.30 (2H, d, *J* = 8.0 Hz, Ar-H), 5.16 (1H, t, *J* = 9.6 Hz, H-3), 5.05 (1H, t, *J* = 9.6 Hz, H-4), 4.92 (1H, dd, *J* = 9.6, 8.0 Hz, H-2), 4.45 (1H, d, *J* = 7.6 Hz, H-1), 4.22 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.09 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 3.83 (1H, m), 3.65 (1H, ddd, *J* = 9.6, 4.8, 2.4 Hz, H-5), 3.47 (1H, m), 2.76 (2H, m), 2.40 (3H, s, CH_3), 2.06, 2.03, 2.00, 1.98 (12H, 4 × s, $COCH_3$), 1.79-1.69 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.6, 169.5, 141.7, 141.7, 130.2, 130.2, 124.3, 124.3, 100.9, 77.2, 73.0, 72.0, 71.5, 69.4, 68.6, 62.2, 57.1, 28.6, 21.6, 20.9, 20.8, 19.4, 19.1. HRMS calc. for $C_{25}H_{34}NaO_{11}S$ $[M+Na]^+$: 565.1714, found: 565.1720.



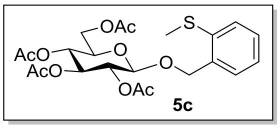
5b

Colorless oil. R_f = 0.55 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ –22 (*c*, 0.05 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (4H, m, Ar-H), 5.18 (1H, t, *J* = 9.2 Hz, H-3), 5.11 (1H, t, *J* = 9.2 Hz, H-4), 5.07 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 5.05 (1H, d, *J* = 12.0 Hz), 4.79 (1H, d, *J* = 12.0 Hz), 4.55 (1H, d, *J* = 8.0 Hz, H-1), 4.29 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.18 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 3.78 (1H, d, *J* = 13.2 Hz), 3.69 (1H, m, H-5), 3.67 (1H, d, *J* = 13.2 Hz), 2.12 (3H, s, CH_3), 2.03, 2.01, 2.01, 2.00 (12H, 4 × s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.6, 169.5, 136.5, 134.9, 130.5, 129.8, 128.3, 127.5, 99.3, 73.1, 72.0, 71.5, 68.6, 68.5, 62.1, 35.3, 21.0, 20.8, 20.8, 20.8, 15.4. HRMS calc. for $C_{23}H_{30}NaO_{10}S$ $[M+Na]^+$: 521.1452, found: 521.1457.



1b

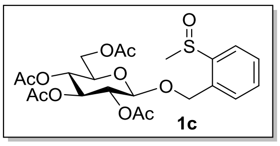
White solid. R_f = 0.35 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (*R* and *S* 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (8H, m, Ar-H), 5.18-4.97 (8H, m, H-2, H-3, H-4, CH_2Ph), 4.67 (2H, m, CH_2Ph), 4.57 (1H, d, *J* = 8.0 Hz, H-1), 4.56 (1H, d, *J* = 8.0 Hz, H-1), 4.29-4.15 (6H, m, H-6a, H-6b, CH_2Ph), 4.00 (2H, m, CH_2Ph), 3.67 (2H, m, H-5), 2.52 (3H, s, CH_3), 2.50 (3H, s, CH_3), 2.09, 2.09, 2.00, 2.00, 1.97, 1.97, 1.97, 1.97 (24H, 4 × s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.7, 170.3, 170.3, 169.4, 169.4, 169.3, 169.3, 135.8, 135.7, 131.8, 131.4, 130.3, 130.2, 129.7, 129.4, 129.0, 129.0, 128.7, 128.7, 99.6, 99.5, 72.9, 72.8, 72.0, 72.0, 71.3, 71.2, 69.3, 69.2, 68.3, 68.3, 61.9, 61.8, 57.3, 57.3, 38.1, 38.1, 20.8, 20.8, 20.7, 20.7, 20.6, 20.6, 20.6, 20.6. HRMS calc. for $C_{23}H_{30}NaO_{11}S$ $[M+Na]^+$: 537.1401, found: 537.1397.



5c

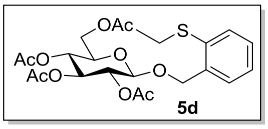
Colorless oil. R_f = 0.60 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ –32.8 (*c*, 0.54 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.29-7.10 (4H, m, Ar-H), 5.15 (1H, t, J = 9.2 Hz, H-3), 5.07 (1H, t, J = 9.2 Hz, H-4), 5.03 (1H, dd, J = 9.2, 8.0 Hz, H-2), 4.89 (1H, d, J = 12.4 Hz), 4.71 (1H, d, J = 12.4 Hz), 4.52 (1H, d, J = 8.0 Hz, H-1), 4.25 (1H, dd, J = 12.4, 4.8 Hz, H-6a), 4.13 (1H, dd, J = 12.4, 2.4 Hz, H-6b), 3.66 (1H, m, H-5), 2.43 (3H, s, CH_3), 2.07, 1.98, 1.97, 1.96 (12H, 4 × s, COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.6, 169.6, 137.9, 134.8, 128.9, 128.9, 126.4, 125.3, 99.5, 73.0, 72.0, 71.4, 68.8, 68.7, 62.1, 20.9, 20.9, 20.8, 20.8, 16.2. HRMS calc. for $C_{22}H_{28}NaO_{10}S$ $[M+Na]^+$: 507.1295, found: 507.1318.



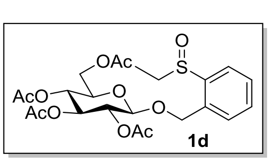
1c

White solid. R_f = 0.36 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (R and S 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.33 (8H, m, Ar-H), 5.18 (1H, t, J = 9.2 Hz, H-3), 5.16 (1H, t, J = 9.2 Hz, H-3), 5.10-5.03 (2H, m, H-4), 5.02-4.98 (2H, m, H-2), 4.97 (1H, d, J = 12.0 Hz), 4.83 (1H, d, J = 12.0 Hz), 4.80 (1H, d, J = 11.6 Hz), 4.66 (1H, d, J = 8.0 Hz, H-1), 4.59 (1H, d, J = 11.6 Hz), 4.55 (1H, d, J = 8.0 Hz, H-1), 4.27 (1H, dd, J = 12.4, 4.8 Hz, H-6a), 4.22 (1H, dd, J = 12.4, 4.8 Hz, H-6a), 4.17 (1H, dd, J = 12.4, 2.4 Hz, H-6b), 4.08 (1H, dd, J = 12.4, 2.4 Hz, H-6b), 3.73-3.66 (2H, m, H-5), 2.71, 2.68 (6H, 2 × s, CH_3), 2.09, 2.05, 2.05, 2.00, 1.99, 1.97, 1.96, 1.92 (24H, 8 × s, COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 171.0, 170.5, 170.5, 169.8, 169.7, 169.6, 169.6, 148.8, 148.8, 133.4, 133.0, 131.4, 131.3, 130.3, 130.3, 129.9, 129.9, 123.7, 123.6, 100.0, 96.6, 72.9, 72.8, 72.0, 71.9, 71.3, 71.2, 68.6, 68.3, 68.2, 67.3, 61.9, 61.8, 43.6, 43.6, 20.7, 20.7, 20.5, 20.5, 20.5, 20.5, 20.5, 20.5. HRMS calc. for $C_{22}H_{28}NaO_{11}S$ $[M+Na]^+$: 523.1245, found: 523.1266.



5d

Colorless oil. R_f = 0.58 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ –35.7 (c, 0.54 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (4H, m, Ar-H), 5.15 (1H, t, J = 9.2 Hz, H-3), 5.08 (1H, t, J = 9.6 Hz, H-4), 5.04 (1H, dd, J = 9.2, 8.0 Hz, H-2), 4.90 (1H, d, J = 12.4 Hz), 4.75 (1H, d, J = 12.4 Hz), 4.52 (1H, d, J = 8.0 Hz, H-1), 4.26 (1H, dd, J = 12.0, 4.8 Hz, H-6a), 4.13 (1H, dd, J = 12.0, 2.4 Hz, H-6b), 3.66 (1H, m, H-5), 2.88 (2H, q, J = 7.6 Hz), 2.07, 1.98, 1.98, 1.96 (12H, 4 × s, COCH_3), 1.26 (3H, t, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.6, 169.5, 136.3, 136.0, 129.0, 128.9, 128.6, 126.0, 99.6, 73.0, 71.9, 71.3, 69.0, 68.6, 62.1, 27.9, 20.9, 20.9, 20.8, 20.8, 14.4. HRMS calc. for $C_{23}H_{30}NaO_{10}S$ $[M+Na]^+$: 521.1452, found: 521.1467.

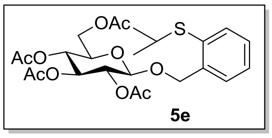


1d

White solid. R_f = 0.34 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (R and S 2:1).

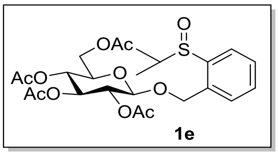
Minor ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.35 (4H, m, Ar-H), 5.20-4.58 (5H, m, H-2, H-3, H-4, -CH_2Ph), 4.63 (1H, d, J = 8.0 Hz, H-1), 4.20 (1H, dd, J = 12.4, 4.4 Hz, H-6a), 4.07 (1H, dd, J = 12.4, 2.0 Hz, H-6b), 3.69 (1H, m, H-5), 2.93 (1H, m), 2.70 (1H, m), 2.05, 2.03, 1.99, 1.97 (12H, 4 × s, COCH_3), 1.20 (3H, t, J = 7.2 Hz). Minor ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.4, 169.6, 169.5, 133.9, 131.1, 131.1, 130.1, 129.6, 125.1, 100.1, 73.0, 72.2, 71.4, 68.4,

67.9, 62.0, 50.5, 20.9, 20.9, 20.8, 20.8, 6.4.
Major ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96-7.35 (4H, m, Ar-H), 5.20-4.58 (5H, m, H-2, H-3, H-4, -CH_2Ph), 4.55 (1H, d, J = 8.0 Hz, H-1), 4.28 (1H, dd, J = 12.4, 4.4 Hz, H-6a), 4.16 (1H, dd, J = 12.4, 2.0 Hz, H-6b), 3.68 (1H, m, H-5), 2.92 (1H, m), 2.71 (1H, m), 2.09, 2.00, 1.96, 1.93 (12H, 4 × s, COCH_3), 1.25 (3H, t, J = 7.2 Hz). Major ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.8, 170.4, 169.6, 169.4, 134.4, 131.1, 129.9, 129.8, 129.8, 124.8, 99.7, 72.9, 72.2, 71.3, 68.4, 67.0, 62.0, 50.5, 21.0, 20.8, 20.8, 20.8, 6.8. HRMS calc. for $C_{23}H_{30}NaO_{11}S$ [M+Na]$^+$: 537.1401, found: 537.1427.



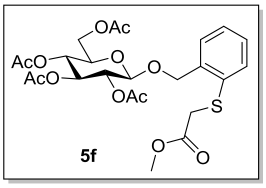
5e

White solid. R_f = 0.58 (Toluene-EtOAc 4:1). $[\alpha]_D^{20}$ –11.6 (c, 0.64 in CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.32 (2H, m, Ar-H), 7.26-7.16 (2H, m, Ar-H), 5.16 (1H, dd, J = 9.6, 9.2 Hz, H-4), 5.10-5.01 (2H, m, H-2, H-3), 4.94 (1H, d, J = 12.8 Hz), 4.81 (1H, d, J = 12.8 Hz), 4.54 (1H, d, J = 8.0 Hz, H-1), 4.26 (1H, dd, J = 12.4, 4.8 Hz, H-6a), 4.13 (1H, dd, J = 12.4, 2.4 Hz, H-6b), 3.67 (1H, ddd, J = 9.6, 4.8, 2.4 Hz, H-5), 3.32 (1H, m), 2.07, 1.99, 1.98, 1.97 (12H, 4 × s, COCH_3), 1.24, 1.23 (6H, 2 × s, CH_3). HRMS calc. for $C_{24}H_{32}NaO_{10}S$ [M+Na]$^+$: 535.1608, found: 535.1616. Analytical data were essentially the same as those reported in the literature.[10]



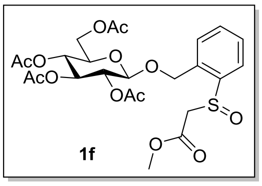
1e

White solid. R_f = 0.48 (petroleum ether-EtOAc 1:3). A sulfoxide mixture (R and S 1:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82-7.77 (2H, m, Ar-H), 7.47-7.32 (6H, m, Ar-H), 5.14-4.85 (8H, m, H-2, H-3, H-4, -CH_2Ph), 4.72 (1H, d, J = 12.4 Hz), 4.63 (1H, d, J = 12.0 Hz), 4.57 (1H, d, J = 8.0 Hz, H-1), 4.51 (1H, d, J = 8.0 Hz, H-1), 4.21(1H, dd, J = 12.0, 4.8 Hz, H-6a), 4.16 (1H, dd, J = 12.4, 4.8 Hz, H-6a), 4.09 (1H, dd, J = 12.4, 2.0 Hz, H-6b), 4.01 (1H, dd, J = 12.4, 2.0 Hz, H-6b), 3.69-3.61 (2H, m, H-5), 2.88-2.80 (2H, m), 2.03, 2.00, 1.97, 1.94, 1.94, 1.92, 1.91, 1.90 (24H, 8 × s, COCH_3), 1.23 (3H, d, J = 6.8 Hz, CH_3), 1.18 (3H, d, J = 6.8 Hz, CH_3), 1.05 (3H, d, J = 6.8 Hz, CH_3), 1.02 (3H, d, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.6, 170.6, 170.2, 170.2, 169.5, 169.4, 169.3, 169.3, 141.8, 141.3, 134.7, 134.1, 131.0, 131.0, 129.7, 129.5, 129.2, 129.0, 125.5, 125.3, 99.9, 99.6, 72.8, 72.8, 72.0, 72.0, 71.2, 71.2, 68.3, 68.3, 67.1, 66.4, 61.9, 61.9, 53.9, 53.7, 20.8, 20.8, 20.7, 20.6, 20.6, 20.6, 20.6, 20.6, 17.3, 17.2, 13.3, 12.8. HRMS calc. for $C_{24}H_{32}NaO_{11}S$ [M+Na]$^+$: 551.1558, found: 551.1563.

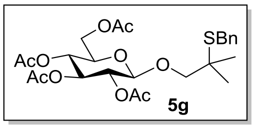


5f

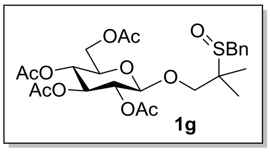
White solid. R_f = 0.30 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ –31.4 (c, 0.51 in CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.19 (4H, m, Ar-H), 5.15 (1H, t, J = 9.6 Hz, H-3), 5.07 (1H, t, J = 9.6 Hz, H-4), 5.02 (1H, dd, J = 9.6, 8.0 Hz, H-2), 4.94 (1H, d, J = 12.4 Hz), 4.79 (1H, d, J = 12.4 Hz), 4.54 (1H, d, J = 8.0 Hz, H-1), 4.25 (1H, dd, J = 12.0, 4.8 Hz, H-6a), 4.13 (1H, dd, J = 12.0, 2.4 Hz, H-6b), 3.70-3.65 (1H, m, H-5), 3.64 (3H, s, OCH_3), 3.59 (2H, s), 2.06, 1.98, 1.98, 1.96 (12H, 4 × s, COCH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.8, 170.4, 170.0, 169.6, 169.5, 137.4, 134.4, 131.0, 129.3, 129.1, 127.5, 99.6, 73.0, 72.0, 71.4, 69.2, 68.6, 62.1, 52.7, 36.9, 20.9, 20.8, 20.7, 20.7. HRMS calc. for $C_{24}H_{30}NaO_{12}S$ $[M+Na]^+$: 565.1350, found: 565.1351.



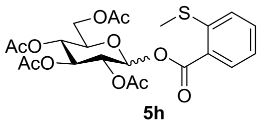
White solid. R_f = 0.45 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (*R* and *S* 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.01 (2H, m, Ar-H), 7.60-7.35 (6H, m, Ar-H), 5.21-4.97 (7H, m, H-2, H-3, H-4, -C*H*$_2$Ph), 4.90 (1H, d, *J* = 11.6 Hz), 4.84 (1H, d, *J* = 12.0 Hz), 4.66 (1H, d, *J* = 8.0 Hz, H-1), 4.61 (1H, d, *J* = 11.6 Hz), 4.59 (1H, d, *J* = 8.0 Hz, H-1), 4.25 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.20 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 4.18 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.06 (1H, dd, *J* = 12.4, 2.0 Hz, H-6b), 3.92 (1H, d, *J* = 14.0 Hz), 3.89 (1H, d, *J* = 14.0 Hz), 3.76 (3H, s, OC*H*$_3$), 3.74 (3H, s, OC*H*$_3$), 3.76-3.65 (2H, m, H-5), 3.68 (1H, d, *J* = 14.0 Hz), 3.66 (1H, d, *J* = 14.0 Hz), 2.11, 2.06, 2.02, 2.01, 2.00, 1.97, 1.97, 1.95 (24H, 8 × s, COC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.3, 169.5, 169.5, 169.5, 169.4, 165.8, 165.7, 143.2, 142.8, 134.1, 133.5, 131.7, 131.6, 130.1, 130.0, 130.0, 129.9, 124.7, 124.7, 100.1, 99.6, 72.9, 72.8, 72.1, 72.1, 71.2, 71.2, 68.5, 68.3, 67.9, 67.2, 62.0, 61.9, 61.4, 61.1, 52.9, 52.9, 20.8, 20.8, 20.7, 20.7, 20.7, 20.7, 20.7, 20.7. HRMS calc. for $C_{24}H_{30}NaO_{13}S$ $[M+Na]^+$: 581.1299, found: 581.1304.



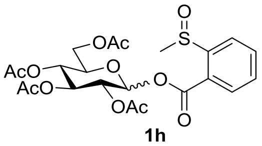
Colorless oil. R_f = 0.40 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +17.9 (*c*, 1.36 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (5H, m, Ar-H), 5.18 (1H, t, *J* = 9.6 Hz, H-3), 5.07 (1H, t, *J* = 9.2 Hz, H-4), 5.00 (1H, dd, *J* = 9.6, 8.0 Hz, H-2), 4.39 (1H, d, *J* = 8.0 Hz, H-1), 4.25 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.12 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 3.82 (1H, d, *J* = 9.6 Hz), 3.75 (2H, br s), 3.65-3.61 (1H, m, H-5), 3.32 (1H, d, *J* = 9.6 Hz), 2.07, 2.01, 2.00, 1.99 (12H, 4 × s, COC*H*$_3$), 1.29 (3H, s, C*H*$_3$), 1.25 (3H, s, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.6, 169.5, 138.6, 129.3, 129.2, 128.8, 128.7, 127.1, 101.4, 78.4, 72.9, 72.0, 71.4, 68.7, 62.1, 45.7, 33.4, 25.6, 25.7, 21.0, 20.9, 20.8, 20.8. HRMS calc. for $C_{25}H_{34}NaO_{10}S$ $[M+Na]^+$: 549.1765, found: 549.1765.



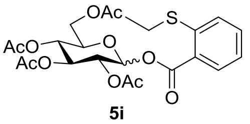
White solid. R_f = 0.32 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (*R* and *S* 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.39-7.35 (10H, m, Ar-H), 5.30 (1H, t, *J* = 9.6 Hz, H-3), 5.27 (1H, t, *J* = 9.2 Hz, H-3), 5.05 (1H, t, *J* = 9.6 Hz, H-4), 5.04 (1H, t, *J* = 9.6 Hz, H-4), 4.96 (1H, dd, *J* = 9.6, 8.0 Hz, H-2), 4.93 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 4.75 (1H, d, *J* = 8.0 Hz, H-1), 4.69 (1H, d, *J* = 8.0 Hz, H-1), 4.32 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.30 (1H, dd, *J* = 12.4, 2.4 Hz, H-6a), 4.19-4.13 (2H, m, H-6b), 4.13-4.00 (2H, m, C*H*$_2$Ph), 3.93-3.87 (2H, m, H-5), 3.81-3.69 (2H, m, C*H*$_2$Ph), 2.05, 2.03, 2.01, 2.00, 1.97, 1.97, 1.96, 1.91 (24H, 8 × s, COC*H*$_3$), 1.34, 1.33, 1.32, 1.32 (12H, 4 × s, C*H*$_3$). ^{13}C NMR (100 MHz, CD_3OD) δ 172.4, 172.4, 171.7, 171.7, 171.4, 171.4, 171.3, 171.2, 133.6, 133.5, 131.6, 131.6, 131.6, 131.6, 130.1, 130.1, 130.0, 130.0, 129.4, 129.4, 102.2, 101.7, 74.1, 74.0, 73.6, 73.2, 73.1, 72.8, 72.8, 72.8, 69.9, 69.9, 69.9, 63.1, 63.1, 59.2, 58.9, 54.3, 53.0, 20.8, 20.8, 20.8, 20.8, 20.7, 20.7, 20.7, 20.7, 19.2, 18.7, 18.3, 17.7. HRMS calc. for $C_{25}H_{34}NaO_{11}S$ $[M+Na]^+$: 565.1714, found: 565.1735.


5h

White solid. R_f = 0.50 (petroleum ether-EtOAc 2:1). An anomeric mixture (α/β, 1:1). β isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (1H, dd, *J* = 8.0, 1.2 Hz, Ar-H), 7.50 (1H, m, Ar-H), 7.25 (1H, m, Ar-H), 7.16 (1H, m, Ar-H), 5.91 (1H, *J* = 8.0 Hz, H-1), 5.35-5.28 (2H, m, H-2, H-3), 5.16 (1H, t, *J* = 9.2 Hz, H-4), 4.32 (1H, dd, *J* = 12.8, 4.4 Hz, H-6a), 4.09 (1H, dd, *J* = 12.8, 2.0 Hz, H-6b), 3.90 (1H, ddd, *J* = 9.2, 4.4, 2.0 Hz, H-5), 2.45 (3H, s, CH_3), 2.05, 2.02, 2.02, 1.97 (12H, 4 × s, $COCH_3$). HRMS calc. for $C_{22}H_{26}NaO_{11}S$ $[M+Na]^+$: 521.1088, found: 521.1106.


1h

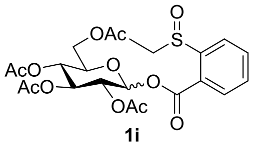
White solid. R_f = 0.30 (petroleum ether-EtOAc 1:1). An anomeric and sulfoxide mixture (α/β, R/S). Partial ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (1H, dd, *J* = 7.6 Hz, Ar-H), 8.09 (1H, d, *J* = 8.0 Hz, Ar-H), 7.86 (1H, t, *J* = 7.2 Hz, Ar-H), 7.58 (1H, t, *J* = 7.6 Hz, Ar-H), 5.84 (1H, m, H-1), 5.34-5.28 (2H, m, H-3, H-4), 5.18 (1H, m, H-2), 4.30 (1H, dd, *J* = 12.4, 4.4 Hz, H-6a), 4.12 (1H, dd, *J* = 12.4, 2.0 Hz, H-6b), 3.90 (1H, m, H-5), 2.81 (3H, s, CH_3), 2.05, 2.03, 2.02, 1.97 (12H, 4 × s, $COCH_3$). HRMS calc. for $C_{22}H_{26}NaO_{12}S$ $[M+Na]^+$: 537.1037, found: 537.1055.


5i

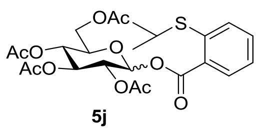
White solid. R_f = 0.54 (petroleum ether-EtOAc 2:1). An anomeric mixture (α/β, 1:5).

α isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.11 (4H, m, Ar-H), 6.58 (1H, d, *J* = 3.6 Hz, H-1), 5.65 (1H, dd, *J* = 10.0, 9.6 Hz, H-3), 5.34-5.13 (2H, m, H-2, H-4), 4.27 (1H, dd, *J* = 12.4, 4.4 Hz, H-6a), 4.26 (1H, m, H-5), 4.07 (1H, dd, *J* = 12.4, 2.0 Hz, H-6b), 2.95 (2H, m), 2.07, 2.01, 2.01, 1.99 (12H, 4 × s, $COCH_3$), 1.39 (3H, t, *J* = 7.2 Hz).

β isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.11 (4H, m, Ar-H), 5.90 (1H, d, *J* = 8.0 Hz, H-1), 5.34-5.13 (3H, m, H-2, H-3, H-4), 4.30 (1H, dd, *J* = 12.4, 4.4 Hz, H-6a), 4.08 (1H, dd, *J* = 12.4, 2.0 Hz, H-6b), 3.87 (1H, m, H-5), 2.95 (2H, m), 2.05, 2.01, 2.01, 1.97 (12H, 4 × s, $COCH_3$), 1.37 (3H, t, *J* = 7.2 Hz). HRMS calc. for $C_{23}H_{28}NaO_{11}S$ $[M+Na]^+$: 535.1245, found: 535.1283.


1i

White solid. R_f = 0.28 (petroleum ether-EtOAc 1:1). An anomeric and sulfoxide mixture (α/β, R/S). Partial ^1H NMR (400 MHz, CD_3OD) δ 8.20-7.70 (4H, m, Ar-H), 6.11 (1H, d, *J* = 8.0 Hz, H-1), 5.92 (1H, d, *J* = 9.6 Hz, H-3), 5.34 (1H, dd, *J* = 9.6, 8.0 Hz, H-2), 5.23 (1H, t, *J* = 9.6 Hz, H-4), 4.40-4.15 (3H, m, H-5, H-6), 3.25 (1H, m), 2.78 (1H, m), 2.07, 2.05, 2.05, 2.04 (12H, 4 × s, $COCH_3$), 1.27 (3H, m). HRMS calc. for $C_{23}H_{28}NaO_{12}S$ $[M+Na]^+$: 551.1194, found: 551.1173.

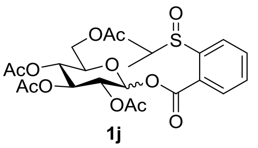


5j

Colorless oil. R_f = 0.40 (petroleum ether-EtOAc 2:1). An anomeric mixture (α/β, 1:2).

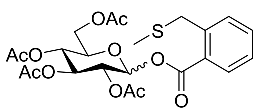
α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90 (1H, d, *J* = 8.0 Hz, Ar-H), 7.43 (1H, m, Ar-H), 7.40 (1H, m, Ar-H), 7.18 (1H, m, Ar-H), 6.54 (1H, d, *J* = 3.6 Hz, H-1), 5.63 (1H, d, *J* = 9.6 Hz, H-3), 5.17-5.11 (3H, m, H-2, H-4), 4.30-4.23 (2H, m, H-6a, H-6b), 4.04 (1H, m, H-5), 3.53 (1H, m), 2.03, 1.99, 1.98, 1.96 (12H, 4 × s, $COCH_3$), 1.33 (3H, d, *J* = 6.4 Hz, CH_3), 1.31 (3H, d, *J* = 6.4 Hz, CH_3).

β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.92 (1H, d, *J* = 8.0 Hz, Ar-H), 7.40 (1H, m, Ar-H), 7.34 (1H, m, Ar-H), 7.11 (1H, m, Ar-H), 5.88 (1H, d, *J* = 8.0 Hz, H-1), 5.30-5.25 (3H, m, H-2, H-3, H-4), 4.30-4.23 (1H, m, H-6a), 4.08-4.04 (1H, m, H-6b), 3.85 (1H, m, H-5), 3.54 (1H, m), 2.01, 1.99, 1.98, 1.94 (12H, 4 × s, $COCH_3$), 1.34 (3H, d, *J* = 6.4 Hz, CH_3), 1.32 (3H, d, *J* = 6.4 Hz, CH_3). HRMS calc. for $C_{24}H_{30}NaO_{11}S$ $[M+Na]^+$: 549.1401, found: 549.1403.



1j

White solid. R_f = 0.30 (petroleum ether-EtOAc 1:1). An anomeric and sulfoxide mixture (α/β, R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.14-7.53 (4H, m, Ar-H), 5.86 (1H, d, *J* = 8.0 Hz, H-1), 5.32-5.14 (3H, m, H-2, H-3, H-4), 4.32 (1H, dd, *J* = 12.4, 4.4 Hz, H-6a), 4.13 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 3.91 (1H, m, H-5), 3.08 (1H, m), 2.04, 2.03, 2.01, 1.96 (12H, 4 × s, $COCH_3$), 1.50 (3H, d, *J* = 6.8 Hz, CH_3), 0.88 (3H, d, *J* = 6.8 Hz, CH_3). HRMS calc. for $C_{24}H_{30}NaO_{12}S$ $[M+Na]^+$: 565.1350, found: 565.1368.

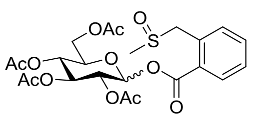


5k

Colorless oil. R_f = 0.62 (petroleum ether-EtOAc 2:1). An anomeric mixture (α/β, 1:1).

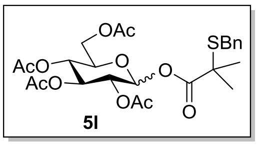
α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90 (1H, m, Ar-H), 7.48 (1H, m, Ar-H), 7.38-7.30 (2H, m, Ar-H), 6.52 (1H, d, *J* = 3.6 Hz, H-1), 5.56 (1H, t, *J* = 9.6 Hz, H-3), 5.31-5.14 (2H, m, H-2, H-4), 4.28 (1H, dd, *J* = 12.8, 4.4 Hz, H-6a), 4.19 (1H, m, H-5), 4.14-3.95 (3H, m, H-6b, CH_2), 2.05, 2.02, 2.00, 1.99 (12H, 4 × s, $COCH_3$), 1.96 (3H, s, CH_3).

β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (1 H, m, Ar-H), 7.49 (1H, m, Ar-H), 7.38-7.28 (2H, m, Ar-H), 5.90 (1H, d, *J* = 8.0 Hz, H-1), 5.31-5.14 (3H, m, H-2, H-3, H-4), 4.27 (1H, dd, *J* = 12.8, 4.4 Hz, H-6a), 4.14-3.95 (3H, m, H-6b, CH_2), 3.90 (1H, m, H-5), 2.06, 2.02, 2.00, 1.99 (12H, 4 × s, $COCH_3$), 1.97 (3H, s, CH_3). HRMS calc. for $C_{23}H_{28}NaO_{11}S$ $[M+Na]^+$: 535.1245, found: 535.1269.



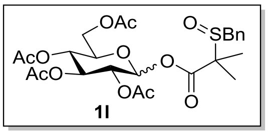
1k

White solid. R_f = 0.33 (petroleum ether-EtOAc 1:4). An anomeric and sulfoxide mixture (α/β, R/S). Partial ^{1}H NMR (400 MHz, CD_3OD) *δ* 8.07-7.48 (8H, m, Ar-H), 6.10 (1H, d, *J* = 8.4 Hz, H-1), 6.08 (1H, d, *J* = 8.4 Hz, H-1), 5.48 (1H, t, *J* = 9.6 Hz, H-3), 5.47 (1H, t, *J* = 9.6 Hz, H-3), 5.27 (1H, dd, *J* = 9.6, 8.4 Hz, H-2), 5.26 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 5.21 (1H, t, *J* = 9.6 Hz, H-4), 5.18 (1H, t, *J* = 9.6 Hz, H-4), 4.40-4.11 (10H, m, H-5, H-6a, H-6b, CH_2), 2.64 (3H, s, CH_3), 2.62 (3H, s, CH_3), 2.04, 2.04, 2.04, 2.04, 2.04, 2.04, 2.02, 2.00 (24H, 4 × s, COCH_3). HRMS calc. for $C_{23}H_{28}NaO_{12}S$ [M+Na]$^+$: 551.1194, found: 551.1190.



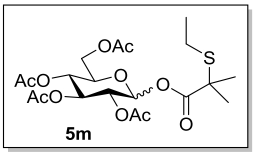
5l

Colorless oil. R_f = 0.65 (petroleum ether-EtOAc 2:1). An anomeric mixture (α/β). β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (5H, m, Ar-H), 5.65 (1H, d, J = 8.0 Hz, H-1), 5.28 (1H, t, J = 9.6 Hz, H-3), 5.22 (1H, dd, J = 9.6, 8.0 Hz, H-2), 5.13 (1H, t, J = 9.6 Hz, H-4), 4.29 (1H, dd, J = 12.8, 4.8 Hz, H-6a), 4.12 (1H, dd, J = 12.8, 2.4 Hz, H-6b), 3.87 (1H, ddd, J = 9.6, 4.8, 2.4 Hz, H-5), 3.79 (1H, d, J = 12.0 Hz), 3.76 (1H, d, J = 12.0 Hz), 2.04, 2.02, 2.00, 1.93 (12H, 4 × s, COCH_3), 1.51 (3H, s, CH_3), 1.49 (3H, s, CH_3). HRMS calc. for $C_{25}H_{32}NaO_{11}S$ [M+Na]$^+$: 563.1569, found: 563.1558.



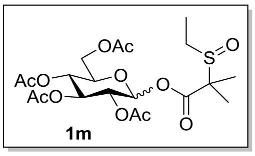
1l

White solid. R_f = 0.43 (petroleum ether-EtOAc 1:1). An anomeric and sulfoxide mixture (α/β, R/S), Mainly β isomers. Major ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (5H, m, Ar-H), 5.71 (1H, d, J = 7.6 Hz, H-1), 5.30-5.10 (3H, m, H-2, H-3, H-4), 4.26 (1H, dd, J = 9.6, 4.8 Hz, H-6a), 4.11 (1H, dd, J = 9.6, 2.0 Hz, H-6b), 3.89 (1H, d, J = 12.8 Hz), 3.67 (1H, d, J = 12.8 Hz), 3.87 (1H, m, H-5), 2.01, 1.99, 1.98, 1.95 (12H, 4 × s, COCH_3), 1.56 (3H, s, CH_3), 1.55 (3H, s, CH_3). Minor ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (5H, m, Ar-H), 5.77 (1H, d, J = 8.0 Hz, H-1), 5.30-5.10 (3H, m, H-2, H-3, H-4), 4.28 (1H, dd, J = 9.6, 4.8 Hz, H-6a), 4.09 (1H, dd, J = 9.6, 2.0 Hz, H-6b), 3.82 (1H, d, J = 12.8 Hz), 3.61 (1H, d, J = 12.8 Hz), 3.86 (1H, m, H-5), 2.01, 2.00, 1.98, 1.98 (12H, 4 × s, COCH_3), 1.55 (3H, s, CH_3), 1.53 (3H, s, CH_3). HRMS calc. for $C_{25}H_{32}NaO_{12}S$ [M+Na]$^+$: 579.1507, found: 579.1501.



5m

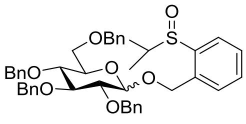
Colorless oil. R_f = 0.50 (petroleum ether-EtOAc 2:1). An anomeric mixture (α/β). β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (1H, d, J = 8.0 Hz, H-1), 5.25 (1H, t, J = 9.2 Hz, H-3), 5.19 (1H, dd, J = 9.2, 8.0 Hz, H-2), 5.12 (1H, t, J = 9.2 Hz, H-4), 4.26 (1H, dd, J = 12.4, 4.4 Hz, H-6a), 4.09 (1H, dd, J = 12.4, 2.4 Hz, H-6b), 3.82 (1H, ddd, J = 9.2, 4.4, 2.4 Hz, H-5), 2.59-2.53 (2H, m), 2.06, 2.02, 2.01, 2.00 (12H, 4 × s, COCH_3), 1.47 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.16 (3H, t, J = 7.2 Hz). HRMS calc. for $C_{20}H_{30}NaO_{11}S$ [M+Na]$^+$: 501.1401, found: 501.1424.



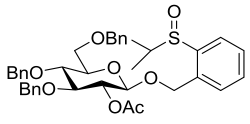
1m

White solid. R_f = 0.44 (petroleum ether-EtOAc 1:2). An anomeric and sulfoxide mixture (α/β, R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (1H, d, J = 8.0 Hz, H-1), 5.23 (1H, t, J = 9.2 Hz, H-3), 5.16 (1H, dd, J = 9.2, 8.0 Hz, H-2), 5.10 (1H, t, J = 9.2 Hz, H-4), 4.24 (1H, dd, J = 12.4, 4.4 Hz, H-6a), 4.09 (1H, dd, J = 12.4, 2.0 Hz, H-6b), 3.81 (1H, ddd, J = 9.2, 4.4, 2.0 Hz, H-5), 2.58-2.47 (2H, m), 2.06, 2.02, 2.01, 2.00 (12H, 4 × s, COCH_3), 1.53 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.35 (3H, t, J = 7.6 Hz). HRMS calc. for $C_{20}H_{30}NaO_{12}S$ [M+Na]$^+$: 517.1350, found: 517.1363.

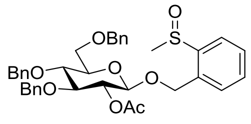
6. Preparation of Glycosyl Donors 1n-1w



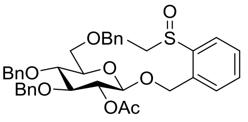
1n



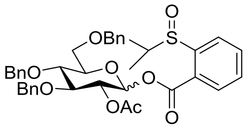
1o



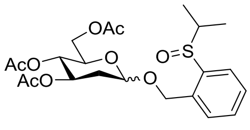
1p



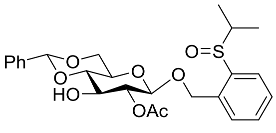
1q



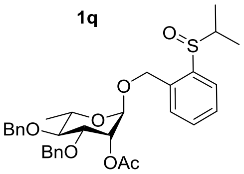
1r



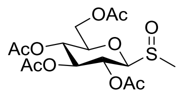
1s



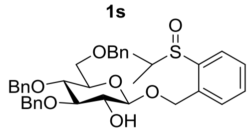
1t



1u



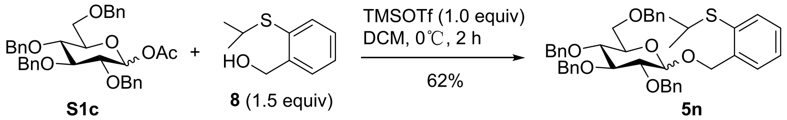
1v



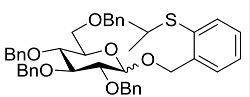
1w

Compounds **1p-1r**, **5o** and **5t-5w** were synthesized following literature procedures.[10]

Preparation of 5n.



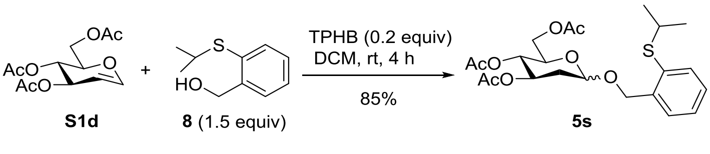
A suspension of **S1c**[11] (710 mg, 1.22 mmol) and **8** (111 mg, 2.44 mmol) containing activated 4 Å molecular sieves (100 wt%) in dry DCM (2.5 mL) was stirred at 0 ℃ for 5 min, then TMSOTf (0.22 mL, 1.22 mmol) was added. The reaction mixture was stirred at 0 ℃ for another 2 h and quenched by addition of 0.2 mL Et_3N. The suspension was diluted with EtOAc, filtered through Celite, concentrated, and purified by flash column chromatography (petroleum ether-EtOAc 10:1) to give **5n** (530 mg, 62% yield).



5n

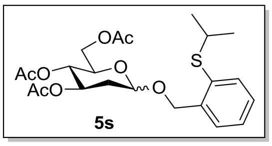
Colorless oil. R_f = 0.72 (petroleum ether-EtOAc 10:1). An anomeric mixture (α/β). *β* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51-7.10 (24H, m, Ar-H), 5.05 (1H, d, *J* = 12.8 Hz), 4.94 (1H, d, *J* = 10.8 Hz), 4.87 (1H, d, *J* = 10.8 Hz), 4.86 (1H, d, *J* = 12.8 Hz), 4.77 (1H, d, *J* = 10.8 Hz), 4.72 (1H, d, *J* = 10.8 Hz), 4.66 (1H, d, *J* = 10.8 Hz), 4.60 (1H, d, *J* = 12.0 Hz), 4.52 (1H, d, *J* = 12.0 Hz), 4.49 (1H, d, *J* = 10.8 Hz), 4.48 (1H, d, *J* = 7.6 Hz, H-1), 3.72 (1H, dd, *J* = 10.8, 2.0 Hz, H-6a), 3.66 (1H, dd, *J* = 10.8, 4.4 Hz, H-6b), 3.63-3.48 (3H, m, H-2, H-3, H-4), 3.43 (1H, m, H-5), 3.30 (1H, m), 1.20 (3H, d, *J* = 6.4 Hz, C*H$_3$*), 1.19 (3H, d, *J* = 6.4 Hz, C*H$_3$*). HRMS calc. for $C_{44}H_{48}NaO_6S$ $[M+Na]^+$: 727.3064, found: 727.3064.

Preparation of 5s.



Compound **1s** was synthesized according to the procedure reported in literature.[12]

To a solution of **S1d** (2.01 g, 7.38 mmol) and **8** (1.98 g, 10.87 mmol) in dry DCM (14.7 mL) was added triphenylphosphine hydrobromide (TPHB, 505 mg, 1.47 mmol), and the resulting solution was stirred at room temperature for 4 h. The reaction mixture was diluted with EtOAc and washed successively with aqueous $NaHCO_3$, water, brine and dried (Na_2SO_4). The organic layer was concentrated, and purified by flash column chromatography (petroleum ether-EtOAc 7:1) to give **5s** (2.86 g, 85% yield).

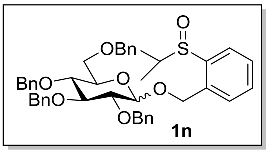


5s

Pale yellow oil. R_f = 0.20 (petroleum ether-acetone 8:1). An anomeric mixture (α/β). α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (2H, m, Ar-H), 7.27–7.22 (2H, m, Ar-H), 5.35 (1H, ddd, J = 12.0, 11.6, 5.2 Hz, H-3), 5.09 (1H, dd, J = 3.6, 0.8 Hz, H-1), 5.00 (1H, dd, J = 12.0, 10.0 Hz, H-4), 4.82 (1H, d, J = 12.4 Hz), 4.59 (1H, d, J = 12.4 Hz), 4.30 (1H, dd, J = 12.0, 4.4 Hz, H-6a), 4.07 (1H, ddd, J = 10.0, 4.4, 2.4 Hz, H-5), 4.02 (1H, dd, J = 12.0, 2.4 Hz, H-6b), 3.35 (1H, m), 2.29 (1H, ddd, J = 12.8, 5.2, 0.8 Hz, H-2eq), 2.09, 2.01, 1.99 (9H, 3 × s, COCH_3), 1.85 (1H, ddd, J = 12.8, 11.6, 3.6 Hz, H-2ax), 1.26 (3H, d, J = 6.8 Hz, CH_3), 1.25 (3H, d, J = 6.8 Hz, CH_3). HRMS calc. for $C_{22}H_{30}NaO_8S$ $[M+Na]^+$: 477.1554, found: 477.1581.

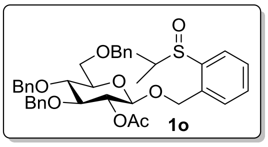
Preparation of sulfoxides 1n-1o and 1s-1t.

The sulfoxides were synthesized from corresponding thioethers according to procedure C.



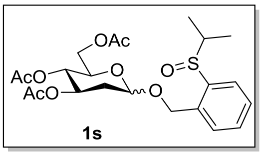
1n

87% yield. Colorless oil. R_f = 0.42 (petroleum ether-EtOAc 2:1). An anomeric and sulfoxide mixture (α/β, R/S). Minor ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.15 (24H, m, Ar-H), 5.0-4.47 (11H, m, CH_2Ph, H-1), 3.78-3.41 (7H, m, H-2, H-3, H-4, H-5, H-6a, H-6b), 3.00-2.86 (1H, m, CH(CH_3)$_2$), 1.20 (3H, d, J = 7.2 Hz, CH_3), 1.01 (3H, d, J = 7.2 Hz, CH_3). Major ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.15 (24H, m, Ar-H), 5.0-4.47 (11H, m, CH_2Ph, H-1), 3.78-3.41 (7H, m, H-2, H-3, H-4, H-5, H-6a, H-6b), 3.00-2.86 (1H, m, CH(CH_3)$_2$), 1.25 (3H, d, J = 7.2 Hz, CH_3), 1.03 (3H, d, J = 6.4 Hz, CH_3). HRMS calc. for $C_{44}H_{48}NaO_7S$ $[M+Na]^+$: 743.3013, found: 743.3020.



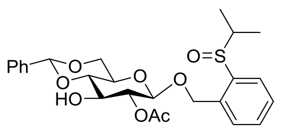
1o

92% yield. Colorless syrup. R_f= 0.50 (petroleum ether-EtOAc 1:1). A sulfoxide mixture (R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.11 (19H, m, Ar-H), 4.95 (1H, dd, J = 9.2, 8.0 Hz, H-2), 4.90 (1H, d, J = 11.6 Hz), 4.75 (1H, d, J = 10.8 Hz), 4.74 (1H, d, J = 11.6 Hz), 4.60 (3H, d, J = 12.0 Hz), 4.53 (1H, d, J = 10.8 Hz), 4.52 (1H, d, J = 12.0 Hz), 4.40 (1H, d, J = 8.0 Hz, H-1), 3.75 (1H, dd, J = 10.8, 1.6 Hz, H-6a), 3.71 (1H, dd, J = 10.8, 4.4 Hz, H-6b), 3.70 (1H, dd, J = 9.2, 9.2 Hz, H-4), 3.61 (1H, dd, J = 9.2, 9.2 Hz, H-3), 3.47 (1H, ddd, J = 9.2, 4.4, 1.6 Hz, H-5), 2.90 (1H, m, CH(CH_3)$_2$), 1.83 (3H, s, COCH_3), 1.24 (3H, d, J = 7.2 Hz, CH_3), 1.03 (3H, d, J = 6.8 Hz, CH_3). Analytical data were essentially the same as those reported in the literature.[10]



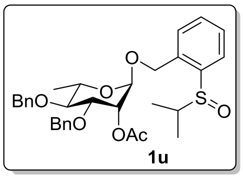
1s

86% yield. Pale yellow oil. R_f = 0.30 (petroleum ether-EtOAc 1:1). An anomeric and sulfoxide mixture (α/β, R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.38 (8H, m, Ar-H), 5.26 (1H, ddd, J = 12.0, 11.6, 5.2 Hz, H-3), 5.18 (1H, ddd, J = 12.0, 11.6, 5.2 Hz, H-3), 5.09 (1H, dd, J = 3.6, 0.8 Hz, H-1), 5.04–4.97 (3H, m, H-1, H-4, H-4), 4.77 (1H, d, J = 12.4 Hz), 4.59 (1H, d, J = 11.6 Hz), 4.56 (1H, d, J = 11.6 Hz), 4.52 (1H, d, J = 12.4 Hz), 4.33 (1H, dd, J = 12.0, 4.4 Hz, H-6a), 4.25 (1H, dd, J = 12.0, 4.4 Hz, H-6a), 4.07 (1H, dd, J = 12.0, 2.4 Hz, H-6b), 4.04 (1H, dd, J = 12.0, 2.4 Hz, H-6b), 4.02 (1H, ddd, J = 10.0, 4.4, 2.4 Hz, H-5), 3.89 (1H, ddd, J = 10.0, 4.4, 2.4 Hz, H-5), 3.01–2.91 (2H, m), 2.26 (1H, ddd, J = 12.8, 5.2, 0.8 Hz, H-2eq), 2.19 (1H, ddd, J = 12.8, 5.2, 0.8 Hz, H-2eq), 2.10, 2.08, 2.03, 1.99, 1.99, 1.98 (18H, 6 × s, $COCH_3$), 1.87 (1H, ddd, J = 12.8, 11.6, 3.6 Hz, H-2ax), 1.81 (1H, ddd, J = 12.8, 11.6, 3.6 Hz, H-2ax), 1.32 (3H, d, J = 6.8 Hz, CH_3), 1.31 (3H, d, J = 6.8 Hz, CH_3), 1.15 (3H, d, J = 6.8 Hz, CH_3), 1.14 (3H, d, J = 6.8 Hz, CH_3). HRMS calc. for $C_{22}H_{30}NaO_9S$ $[M+Na]^+$: 493.1503, found: 493.1509.



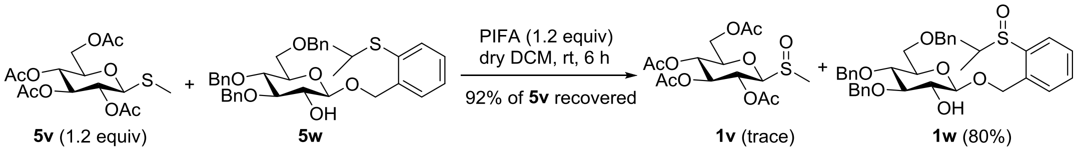
1t

94% yield. White solid. R_f = 0.50 (petroleum ether-EtOAc 1:3). A sulfoxide mixture (R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.35 (9H, m, Ar-H), 5.54 (1H, br s, $PhCHO_2$), 4.94 (1H, dd, J = 9.2, 8.0 Hz, H-2), 4.92 (1H, d, J = 12.4 Hz), 4.67 (1H, d, J = 12.4 Hz), 4.59 (1H, d, J = 8.0 Hz, H-1), 4.40 (1H, dd, J = 10.8, 4.8 Hz, H-6a), 3.87 (1H, dd, J = 9.2 Hz, H-3), 3.80 (1H, dd, J = 10.8, 10.8 Hz, H-6b), 3.59 (1H, dd, J = 9.6, 9.2 Hz, H-4), 3.46 (1H, m, H-5), 2.91 (1H, m), 2.04 (3H, s, $COCH_3$), 1.28 (3H, d, J = 6.8 Hz, CH_3), 1.10 (3H, d, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.5, 137.0, 134.7, 131.2, 129.6, 129.5, 129.2, 128.6, 128.6, 126.5, 126.5, 125.4, 102.2, 100.7, 81.0, 74.0, 72.4, 68.7, 66.9, 66.5, 54.1, 21.1, 17.4, 13.1. HRMS calc. for $C_{25}H_{31}O_8S$ $[M+H]^+$: 491.1734, found: 491.1758.

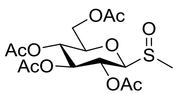


1u

96% yield. Colorless oil. R_f = 0.6 (petroleum ether-EtOAc 1:1). A sulfoxide mixture (R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.25 (14H, m, Ar-H), 5.30 (1H, dd, J = 3.2, 2.0 Hz, H-2), 4.92 (1H, d, J = 10.8 Hz), 4.75 (1H, d, J = 2.0 Hz, H-1), 4.74 (1H, d, J = 11.6 Hz), 4.68 (1H, d, J = 11.2 Hz), 4.61 (1H, d, J = 10.8 Hz), 4.55 (1H, d, J = 11.2 Hz), 4.50 (1H, d, J = 11.6 Hz), 3.88 (1H, dd, J = 9.2, 3.2 Hz, H-3), 3.78 (1H, m, H-5), 3.45 (1H, t, J = 9.2 Hz, H-4), 2.81 (1H, m, $CH(CH_3)_2$), 2.13 (3H, s, $COCH_3$), 1.35 (3H, d, J = 6.4 Hz, CH_3), 1.23 (3H, d, J = 7.2 Hz, CH_3), 1.10 (3H, d, J = 6.8 Hz, CH_3). Analytical data were essentially the same as those reported in the literature.[10]

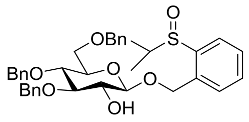


To a solution of **5v** (453 mg, 1.2 mmol) and PIFA (516 mg, 1.2 mmol) in dry DCM (12 mL) in the presence of 4 Å MS (100 wt%) was stirred for 15 min at 0 °C. After addition of **5w** (614 mg, 1.0 mmol) in 2 mL DCM, the solution was stirred at room temperature for 6 h. Then 2 mL water was added and the reaction was stirred for 10 min, extracted with EtOAc/water. The organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel flash column chromatography to give **lv** (14.2 mg, 3% yield) and **1w** (504 mg, 80% yield), with 383 mg of **5v** recovered (92% recovery).



1v

White solid. R_f = 0.24 (petroleum ether-EtOAc 1:3). A sulfoxide mixture (R/S). Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (1H, t, *J* = 9.2 Hz, H-3), 5.10 (1H, dd, *J* = 10.0, 9.2 Hz, H-4), 5.05 (1H, t, *J* = 9.6 Hz, H-2), 4.36 (1H, d, *J* = 10.4 Hz, H-1), 4.31 (1H, dd, *J* = 12.8, 4.4 Hz, H-6a), 4.19 (1H, dd, *J* = 12.8, 1.6 Hz, H-6b), 3.82 (1H, dd, *J* = 9.6, 4.4, 1.6 Hz, H-5), 2.67 (3H, s, CH_3), 2.07, 2.05, 2.02, 2.00 (12H, 4 × s, $COCH_3$). HRMS calc. for $C_{15}H_{22}NaO_{10}S$ $[M+Na]^+$: 417.0826, found: 417.0868. Analytical data were essentially the same as those reported in the literature.[13]



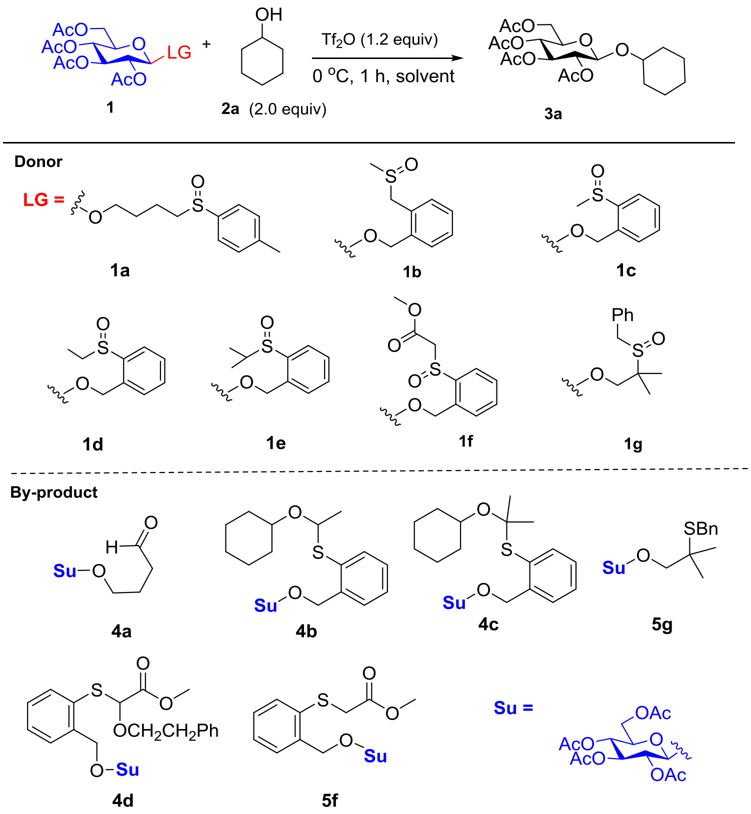
1w

White solid. R_f = 0.73 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (R/S).

Minor ^{1}H NMR (400 MHz, CD_3OD) δ 7.84-7.82 (1H, m, Ar-H), 7.61-7.51 (3H, m, Ar-H), 7.37-7.22 (13H, m, Ar-H), 7.17-7.13 (2H, m, Ar-H), 5.02 (1H, d, *J* = 11.2 Hz), 4.97 (1H, d, *J* = 11.2 Hz), 4.76 (1H, d, *J* = 11.2 Hz), 4.74 (1H, d, *J* = 11.2 Hz), 4.73 (1H, d, *J* = 12.0 Hz), 4.61-4.37 (3H, m, CH_2Ph), 4.46 (1H, d, *J* = 8.0 Hz, H-1), 3.65-3.40 (6H, m, H-2, H-3, H-4, H-5, H-6a, H-6b), 3.29-3.19 (1H, m, $CH(CH_3)_2$), 1.30 (3H, d, *J* = 6.8 Hz, CH_3), 1.04 (3H, d, *J* = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, CD_3OD) δ 141.6, 140.3, 139.8, 139.6, 137.4, 132.5, 131.6, 130.0, 129.6, 129.6, 129.5, 129.4, 129.2, 129.1, 129.1, 129.1, 129.1, 128.9, 128.9, 128.8, 128.8, 128.7, 128.7, 126.2, 104.4, 86.7, 79.6, 79.0, 76.5, 76.2, 76.0, 75.7, 70.2, 68.8, 54.5, 18.0, 13.0.

Major ^{1}H NMR (400 MHz, CD_3OD) δ 7.84-7.82 (1H, m, Ar-H), 7.61-7.51 (3H, m, Ar-H), 7.37-7.22 (13H, m, Ar-H), 7.17-7.13 (2H, m, Ar-H), 5.03 (1H, d, *J* = 11.2 Hz), 4.96 (1H, d, *J* = 11.2 Hz), 4.78 (1H, d, *J* = 11.2 Hz), 4.75 (1H, d, *J* = 11.2 Hz), 4.70 (1H, d, *J* = 12.0 Hz), 4.61-4.37 (3H, m, CH_2Ph), 4.37 (1H, d, *J* = 8.0 Hz, H-1), 3.77 (1H, dd, *J* = 10.8, 2.0 Hz, H-6a), 3.70 (1H, dd, *J* = 10.8, 4.4 Hz, H-6b), 3.65-3.40 (4H, m, H-2, H-3, H-4, H-5), 3.29-3.19 (1H, m, $CH(CH_3)_2$), 1.33 (3H, d, *J* = 6.8 Hz, CH_3), 1.03 (3H, d, *J* = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, CD_3OD) δ 142.1, 140.3, 139.8, 139.6, 136.6, 132.5, 132.2, 130.2, 129.6, 129.6, 129.5, 129.4, 129.2, 129.1, 129.1, 129.1, 129.1, 128.9, 128.9, 128.8, 128.8, 128.7, 128.7, 126.2, 103.4, 86.6, 79.0, 76.5, 76.2, 76.0, 75.9, 74.6, 70.3, 67.9, 54.7, 18.0, 12.6. HRMS calc. for $C_{37}H_{42}NaO_7S$ $[M+Na]^+$: 653.2543, found: 653.2507.

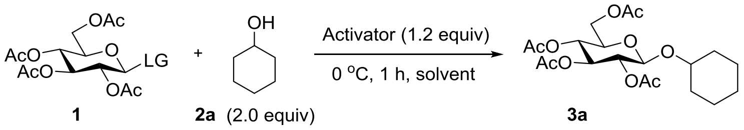
7. **Table S3.** Glycosylation of Acceptor **2a** with Donors **1a-1g** by Procedure E



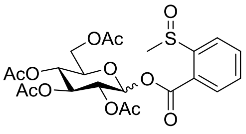
Entry	Donor	Solvent	Activator	Yield[a] (Recovery of **1**)	By-product, Yield[a]
1	**1a**	DCM	TFAA	0% (98%)	-
2	**1a**	DCE	TFAA	0% (98%)	-
3	**1a**	DMA	TFAA	0% (97%)	-
4	**1a**	DMA	Tf$_2$O	0% (-)[b]	**4a**, 30%
5	**1a**	DCM	Tf$_2$O	0% (98%)	-
6	**1b**	PhMe	Tf$_2$O	15% (-)[b]	-
7	**1b**	DCM	Tf$_2$O	trace (-)[b]	-
8	**1c**	DCM	TFAA	0% (98%)	-
9	**1c**	DCM	Tf$_2$O	0% (45%)[b]	-
10	**1d**	DCM	Tf$_2$O	0%	**4b**, 95%
11	**1e**	DCM	Tf$_2$O	0%	**4c**, 93%
12	**1e**	CH$_3$CN	Tf$_2$O	0%	**4c**, 95%
13	**1e**	PhMe	Tf$_2$O	0%	**4c**, 94%
14[c]	**1f**	DCM	Tf$_2$O	0% (10%)	**4d**, 50%; **5f**, 30%
15[c]	**1f**	DCM	TFAA	0% (93%)	-
16[c]	**1f**	CH$_3$CN	Tf$_2$O	0% (-)[b]	**4d**, 54%
17[c]	**1f**	PhMe	Tf$_2$O	0%	**4d**, 93%
18	**1g**	PhMe	Tf$_2$O	0%	**5g**, 65%

[a] Isolated yield. [b] Most of the glycosyl donor degraded. [c] PhCH$_2$CH$_2$OH was used as acceptor. TFAA = trifluoroacetic anhydride.

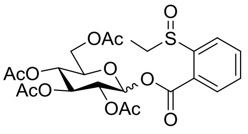
8. **Table S4.** Glycosylation of Acceptor **2a** with Donors **1h-1m** by Procedure E



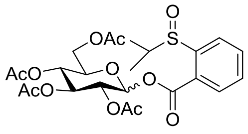
Donor



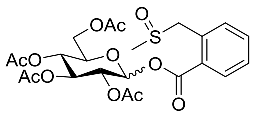
1h



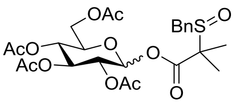
1i



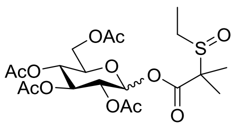
1j



1k



1l

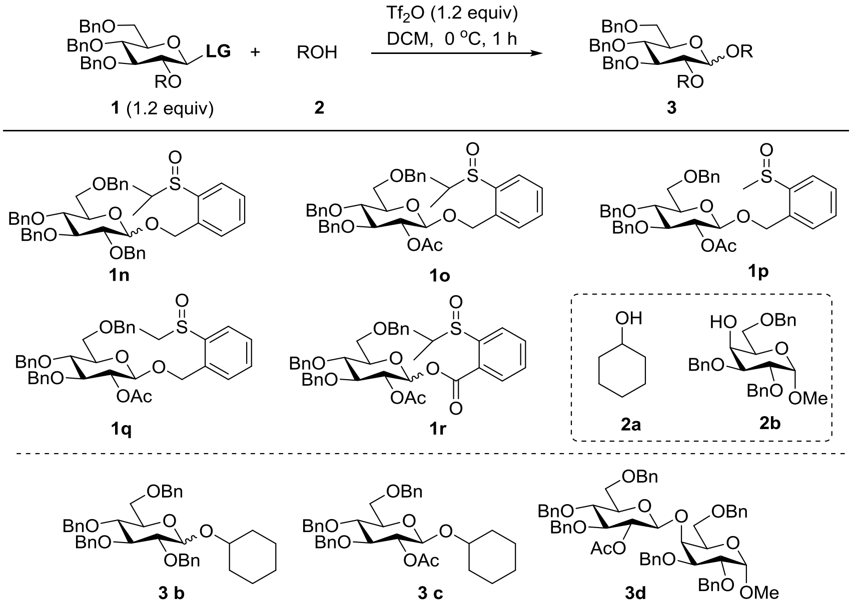


1m

Entry	Donor	Solvent	Activator	Yield (α/β)[a]	Recovery of **1**
1	**1h**	DCM	TFAA	0%	90%
2	**1h**	CH_3CN	TFAA	0%	96%
3	**1h**	DCM	Tf_2O	15% (*β* only)	-[b]
4	**1i**	DCM	TFAA	0%	94%
5	**1i**	CH_3CN	TFAA	0%	95%
6	**1i**	DCM	Tf_2O	15% (1:2)	-[b]
7	**1j**	CH_3CN	TFAA	0%	96%
8	**1j**	CH_3CN	Tf_2O	40% (1:1)	-[b]
9	**1j**	DCM	Tf_2O	20% (1:1)	-[b]
10	**1k**	CH_3CN	Tf_2O	0%	-[b]
11	**1k**	DCM	Tf_2O	trace	-[b]
12	**1k**	PhMe	Tf_2O	32% (*β* only)	-[b]
13	**1l**	DCM	Tf_2O	0%	-[b]
14	**1l**	PhMe	Tf_2O	30% (*β* only)	-[b]
15	**1m**	DCM	TFAA	0%	98%
16	**1m**	DCM	Tf_2O	18% (1:1)	-[b]
17	**1m**	PhMe	Tf_2O	23% (1:2)	-[b]

[a] Isolated yield. [b] Most of the glycosyl donor degraded.

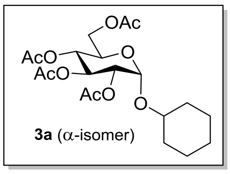
9. **Table S5.** Glycosylation of Acceptors **2a**, **2b** with Donors **1n-1r** by Procedure F



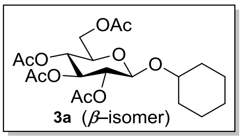
Entry	Donor	Acceptor	Solvent	Yield (α/β)[a]
1	**1n**	**2a**	DCM	**3b**, 78% (1:1)
2	**1n**	**2a**	Et_2O	**3b**, 82% (5:1)
3	**1n**	**2a**	CH_3CN	**3b**, 84% (1:5)
4	**1o**	**2a**	DCM	**3c**, 87%, β only
5	**1o**	**2b**	DCM	**3d**, 95%, β only
6	**1p**	**2b**	DCM	**3d** ,79%, β only[b]
7	**1q**	**2b**	DCM	**3d** , 82%, β only[c]
8	**1r**	**2b**	DCM	**3d** ,68%, β only[d]

[a]Isolated yield. [b]13% of **2b** recovered. [c]11% of **2b** recovered. [d]21% of **2b** recovered.

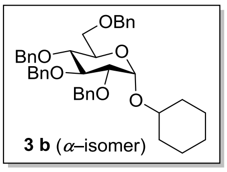
Analytical Data.


3a (α-isomer)

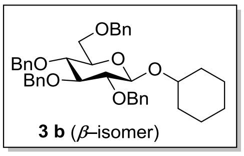
White solid. R_f = 0.64 (petroleum ether-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 5.46 (1H, t, J = 9.6 Hz, H-3), 4.20 (1H, d, J = 3.6 Hz, H-1), 5.01 (1H, t, J = 9.6 Hz, H-4), 4.76 (1H, dd, J = 9.6, 3.6 Hz, H-2), 4.20-4.03 (3H, m, H-5, H-6a, H-6b), 3.52 (1H, m, CH), 2.06, 2.03, 2.01, 1.99 (12H, 4 × s, $COCH_3$), 1.84-1.19 (10H, m, CH_2). Analytical data were essentially the same as reported previously.[14]


3a (*β*–isomer)

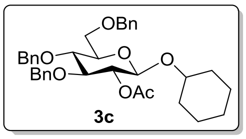
White solid. R_f = 0.62 (petroleum ether-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 5.18 (1H, t, J = 9.6 Hz, H-3), 5.06 (1H, t, J = 9.6 Hz, H-4), 4.94 (1H, dd, J = 9.6, 8.0 Hz, H-2), 4.56 (1H, d, J = 8.0 Hz, H-1), 4.24 (1H, dd, J = 12.4, 4.8 Hz, H-6a), 4.09 (1H, dd, J = 12.4, 2.4 Hz, H-6b), 3.65 (1H, m, H-5), 3.60 (1H, m), 2.06, 2.02, 2.00, 1.98 (12H, 4 × s, $COCH_3$), 1.82-1.23 (10H, m). Analytical data were essentially the same as reported previously.[15]


3 b (α–isomer)

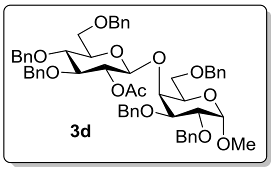
Colorless syrup. R_f = 0.64 (Hexane-EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.10 (20H, m, Ar-H), 4.98 (1H, d, *J* = 10.8 Hz), 4.94 (1H, d, *J* = 3.6 Hz, H-1), 4.81 (1H, d, *J* = 10.4 Hz), 4.80 (1H, d, *J* = 10.8 Hz), 4.73 (1H, d, *J* = 12.0 Hz), 4.64 (1H, d, *J* = 12.0 Hz), 4.60 (1H, d, *J* = 12.4 Hz), 4.45 (1H, d, *J* = 12.0 Hz), 4.44 (1H, d, *J* = 10.8 Hz), 3.99 (1H, dd, *J* = 9.2 Hz, H-3), 3.86 (1H, m, H-5), 3.72 (1H, dd, *J* = 10.4, 3.6 Hz, H-2), 3.64-3.52 (3H, m, H-6a, H-6b, H-4), 3.53 (1H, m), 1.90-1.14 (10H, m).


3 b (β–isomer)

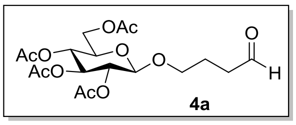
White solid. R_f = 0.68 (Hexane-EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (20H, m, Ar-H), 4.98 (1H, d, *J* = 10.8 Hz), 4.91 (1H, d, *J* = 11.2 Hz), 4.80 (1H, d, *J* = 10.8 Hz), 4.76 (1H, d, *J* = 10.8 Hz), 4.69 (1H, d, *J* = 11.2 Hz), 4.60 (1H, d, *J* = 12.4 Hz), 4.55 (1H, d, *J* = 11.6 Hz), 4.52 (1H, d, *J* = 11.6 Hz), 4.49 (1H, d, *J* = 8.0 Hz, H-1), 3.73 (1H, dd, *J* = 10.8, 2.0 Hz, H-6a), 3.70 (1H, m), 3.63 (1H, dd, *J* = 10.8, 4.8 Hz, H-6b), 3.62 (1H, dd, *J* = 9.2, 8.8 Hz, H-3), 3.53 (1H, dd, *J* = 9.6, 8.8 Hz, H-4), 3.44 (1H, m, H-5), 3.43 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 1.99-1.21 (10H, m). Analytical data were essentially the same as reported previously.[16]


3c

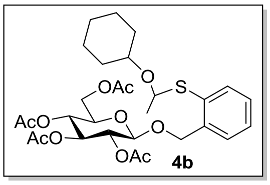
White solid. R_f = 0.42 (petroleum ether-EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.16 (15H, m, Ar-H), 4.95 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 4.77 (1H, d, *J* = 11.2 Hz), 4.76 (1H, d, *J* = 11.6 Hz), 4.65 (1H, d, *J* = 11.6 Hz), 4.60 (1H, d, *J* = 12.4 Hz), 4.55 (1H, d, *J* = 12.4 Hz), 4.54 (1H, d, *J* = 11.2 Hz), 4.40 (1H, d, *J* = 8.0 Hz, H-1), 3.73 (1H, dd, *J* = 10.8, 2.0 Hz, H-6a), 3.65 (1H, dd, *J* = 10.8, 5.2 Hz, H-6b), 3.63 (1H, t, *J* = 9.2 Hz, H-3), 3.62 (1H, t, *J* = 9.2 Hz, H-4), 3.58 (1H, m), 3.45 (1H, ddd, *J* = 9.2, 5.2, 2.0 Hz, H-5), 1.94 (3H, s, $COCH_3$), 1.90-1.64 (4H, m), 1.48-1.17 (6H, m). Analytical data were essentially the same as reported previously.[17]


3d

White solid. R_f = 0.52 (petroleum ether-EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.09 (30H, m, Ar-H), 4.92 (1H, t, *J* = 8.4 Hz), 4.73 (1H, d, *J* = 12.0 Hz), 4.70 (2H, d, *J* = 11.2 Hz), 4.67 (1H, d, *J* = 12.0 Hz), 4.51 (1H, d, *J* = 12.0 Hz), 4.48 (1H, d, *J* = 12.0 Hz), 4.62-4.58 (2H, m), 4.57 (1H, d, *J* = 4.0 Hz, H-1), 4.56 (1H, d, *J* = 8.0 Hz, H-1'), 4.43 (1H, d, *J* = 12.0 Hz), 4.40 (2H, d, *J* = 12.0 Hz), 4.32 (1H, d, *J* = 12.0 Hz), 3.96 (1H, m), 3.83-3.80 (1H, m), 3.77 (1H, dd, *J* = 10.0, 2.8 Hz), 3.74-3.69 (2H, m), 3.65-3.52 (5H, m), 3.33-3.28 (1H, m), 3.27 (s, 3H, OCH_3), 1.66 (3H, s, $COCH_3$). Analytical data were essentially the same as those reported previously.[10]

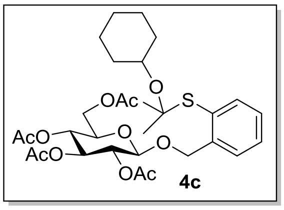

4a

White solid. R_f = 0.28 (petroleum ether-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (1H, s, C*H*O), 5.17 (1H, d, *J* = 9.6 Hz, H-3), 5.05 (1H, t, *J* = 9.6 Hz, H-4), 4.95 (1H, dd, *J* = 9.6, 8.0 Hz, H-2), 4.45 (1H, d, *J* = 8.0 Hz, H-1), 4.22 (1H, dd, *J* = 12.4, 4.8 Hz, H-6a), 4.10 (1H, dd, *J* = 12.4, 2.4 Hz, H-6b), 3.85 (1H, m), 3.65 (1H, m, H-5), 3.51 (1H, m), 2.51-2.47 (2H, m), 2.06, 2.03, 2.00, 1.98 (12H, 4 × s, COC*H*$_3$), 1.94-1.84 (2H, m). Analytical data were essentially the same as reported previously.[18]



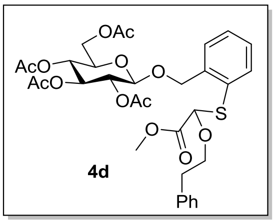
4b

White solid. R_f = 0.52 (DCM-MeOH 15:1). A mixture of R/S isomers. Major ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.43 (4H, m, Ar-H), 5.27-4.93 (5H, m, H-2, H-3, H-4, -C*H*$_2$Ph), 4.69 (1H, d, *J* = 8.0 Hz, H-1), 4.37-4.09 (2H, m, H-6), 3.80 (1H, m, H-5), 3.73 (1H, m), 2.13, 2.07, 2.05, 2.00 (12H, 4 × s, COC*H*$_3$), 1.96-1.13 (13H, CH_2, CH_3). HRMS calc. for $C_{29}H_{41}O_{11}S$ $[M+H]^+$: 597.2364, found: 597.2358.



4c

White solid. R_f = 0.48 (DCM-MeOH 20:1). A mixture of R/S isomers. Major ^{1}H NMR (400 MHz, CD_3OD) δ 8.10-7.69 (4H, m, Ar-H), 5.37-4.90 (6H, m, H-1, H-2, H-3, H-4, -C*H*$_2$Ph), 4.63 (1H, m), 4.40 (1H, dd, *J* = 12.8, 4.8 Hz, H-6a), 4.16 (1H, m, H-6b), 4.03 (1H, m, H-5), 2.05, 2.03, 2.00, 1.98 (12H, 4 × s, COC*H*$_3$), 1.98-1.30 (10H, m), 1.53 (3H, s, CH_3), 1.52 (3H, s, CH_3). Minor ^{1}H NMR (400 MHz, CD_3OD) δ 8.10-7.69 (4H, m, Ar-H), 5.37-4.90 (6H, m, H-1, H-2, H-3, H-4, -C*H*$_2$Ph), 4.63 (1H, m), 4.30 (1H, dd, *J* = 12.8, 4.8 Hz, H-6a), 4.04 (1H, m, H-6b), 3.96 (1H, m, H-5), 2.04, 2.02, 2.02, 1.98 (12H, 4 × s, COC*H*$_3$), 1.98-1.30 (10H, m), 1.62 (3H, s, CH_3), 1.60 (3H, s, CH_3). HRMS calc. for $C_{30}H_{43}O_{11}S$ $[M+H]^+$: 611.2521, found: 611.2445.



4d

White solid. R_f = 0.25 (petroleum ether-EtOAc 2:1). A mixture of R/S isomers. Partial ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.18 (18H, m, Ar-H), 5.17-5.00 (8H, m, H-3, H-4, H-2, C*H*), 4.96 (1H, d, *J* = 12.8 Hz), 4.95 (1H, d, *J* = 12.4 Hz), 4.80 (1H, d, *J* = 12.8 Hz), 4.79 (1H, d, *J* = 12.4 Hz), 4.55 (1H, d, *J* = 7.6 Hz, H-1), 4.47 (1H, d, *J* = 8.0 Hz, H-1), 4.28-4.00 (4H, m) 3.77-3.62 (4H, m), 3.60 (3H, s, OC*H*$_3$), 3.59 (3H, s, OC*H*$_3$), 2.94 (4H, t, *J* = 7.2 Hz), 2.07, 2.07, 2.00, 2.00, 1.99, 1.98, 1.98, 1.97 (24H, 8 × s, COC*H*$_3$). HRMS calc. for $C_{32}H_{38}NaO_{13}S$ $[M+Na]^+$: 685.1925, found: 685.1925.

NMR Spectra

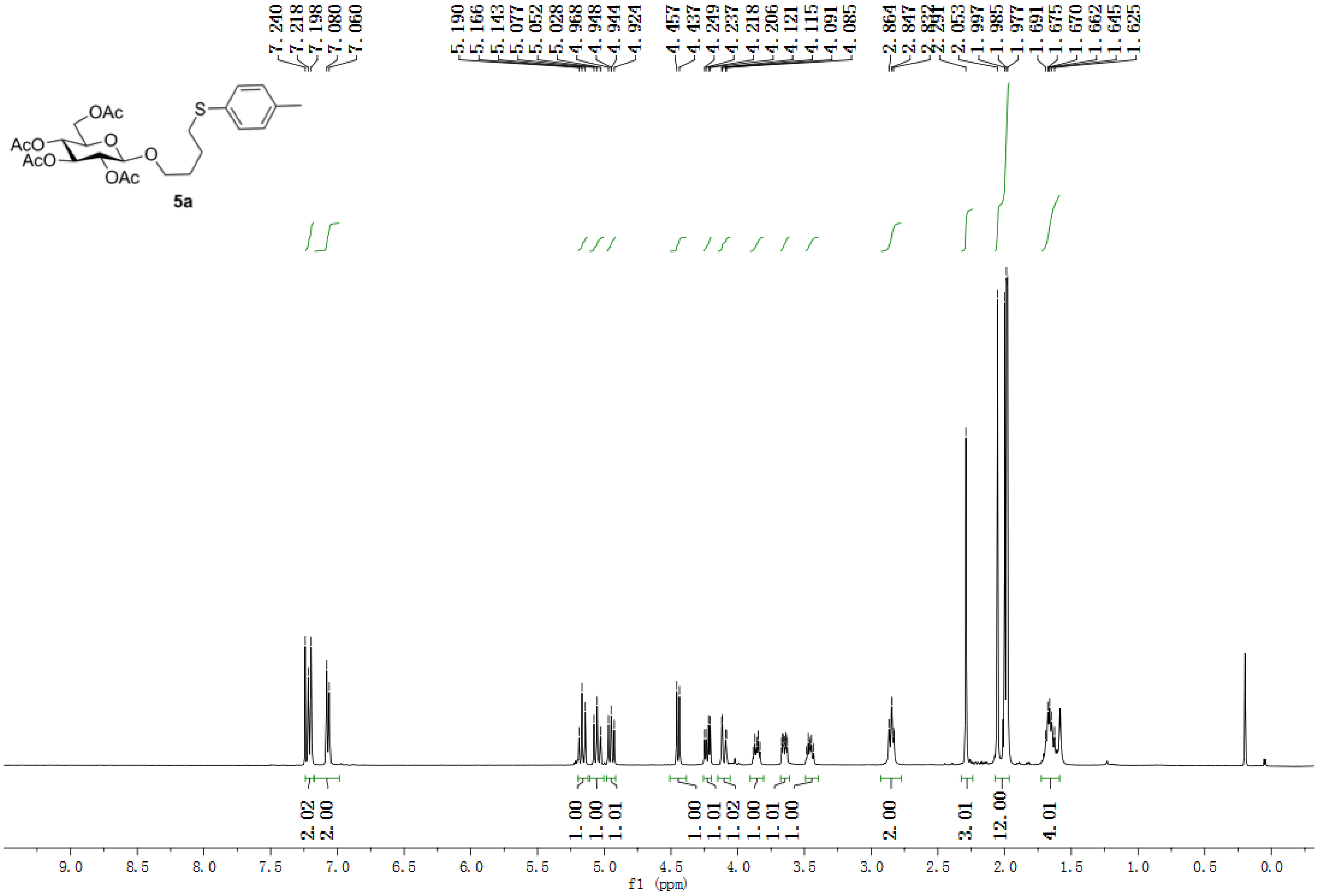


Figure S1. ^{1}H NMR spectrum of **5a** in $CDCl_3$

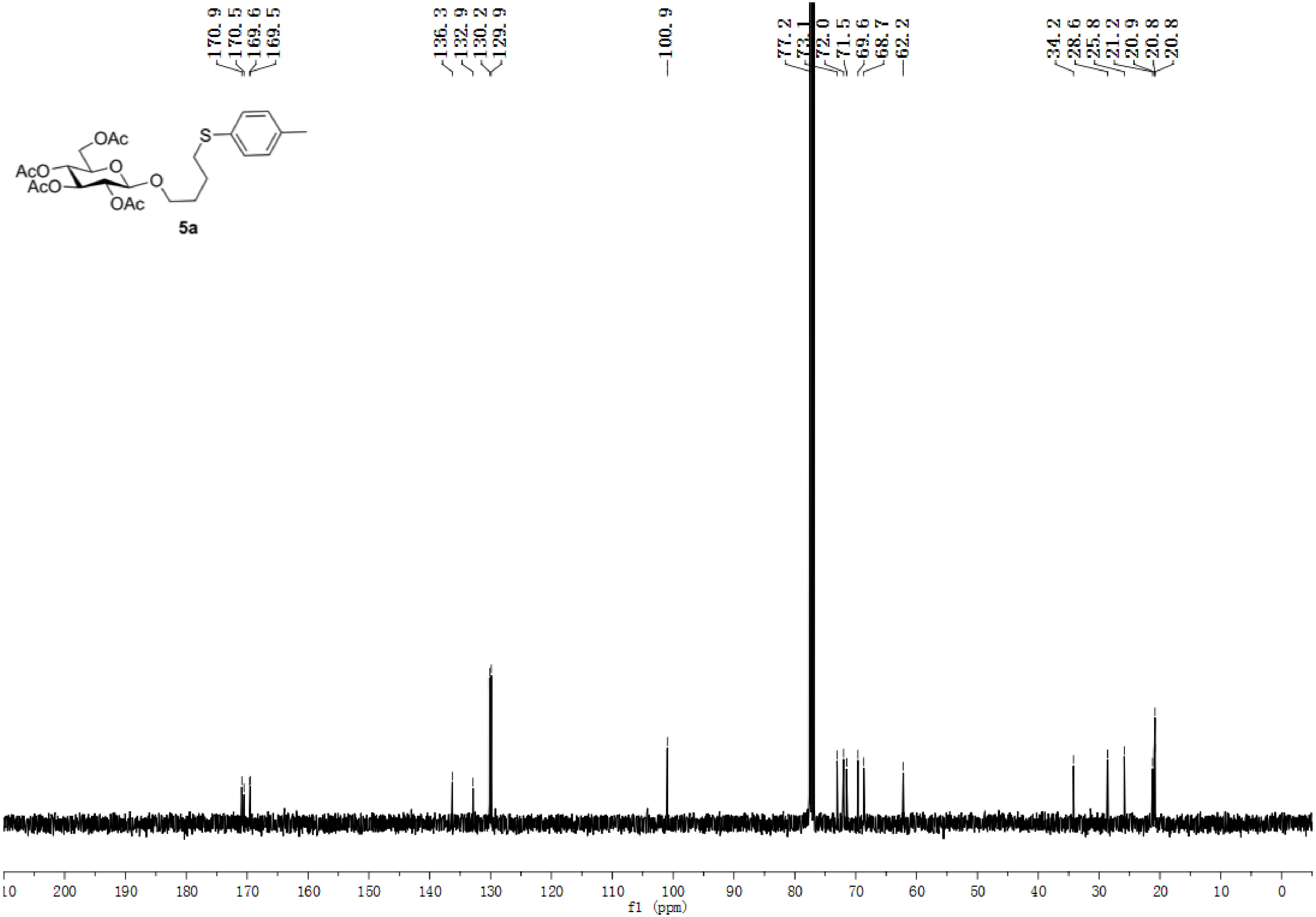


Figure S2. ^{13}C NMR spectrum of **5a** in $CDCl_3$

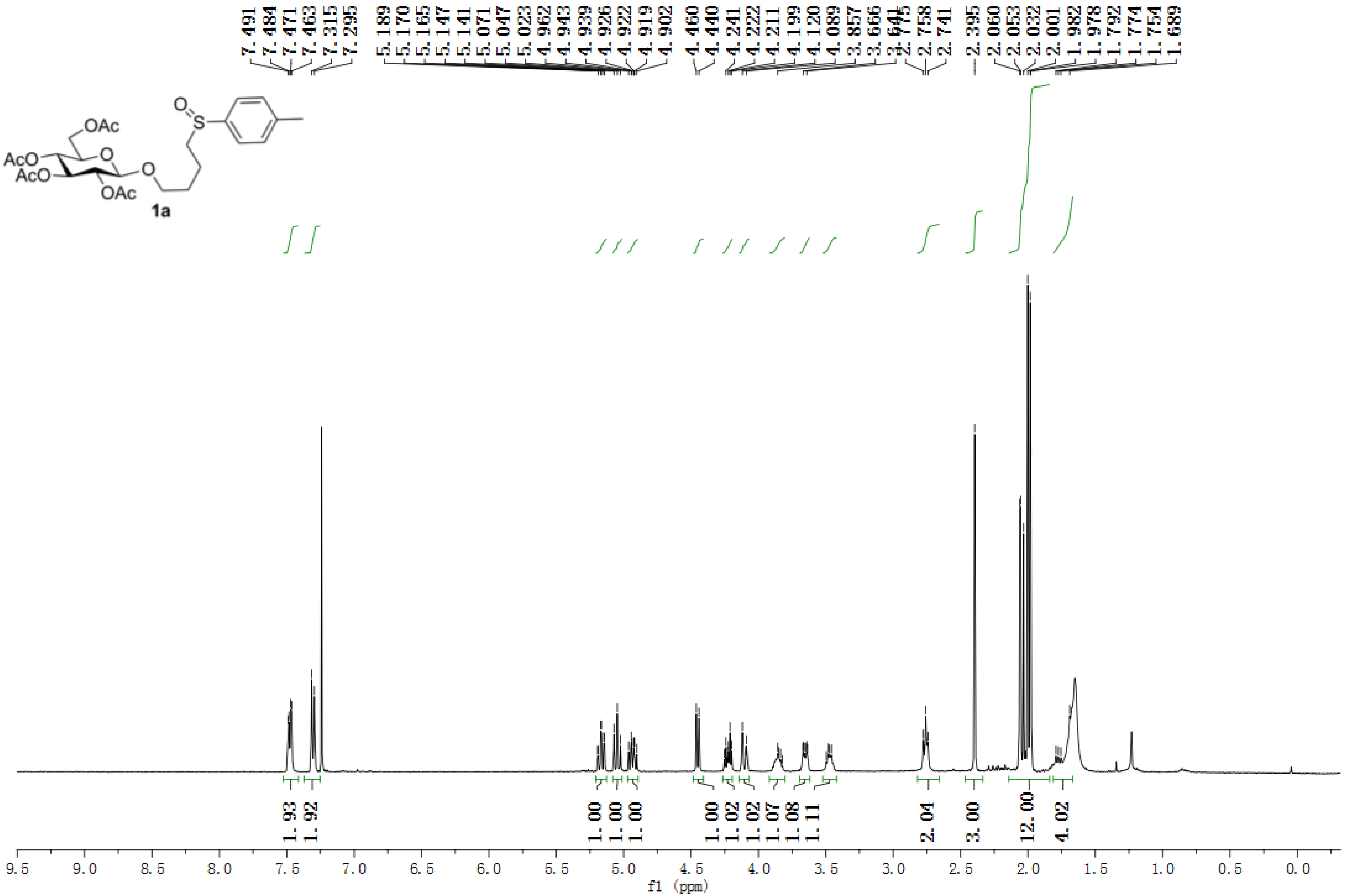


Figure S3. ^{1}H NMR spectrum of **1a** in $CDCl_3$

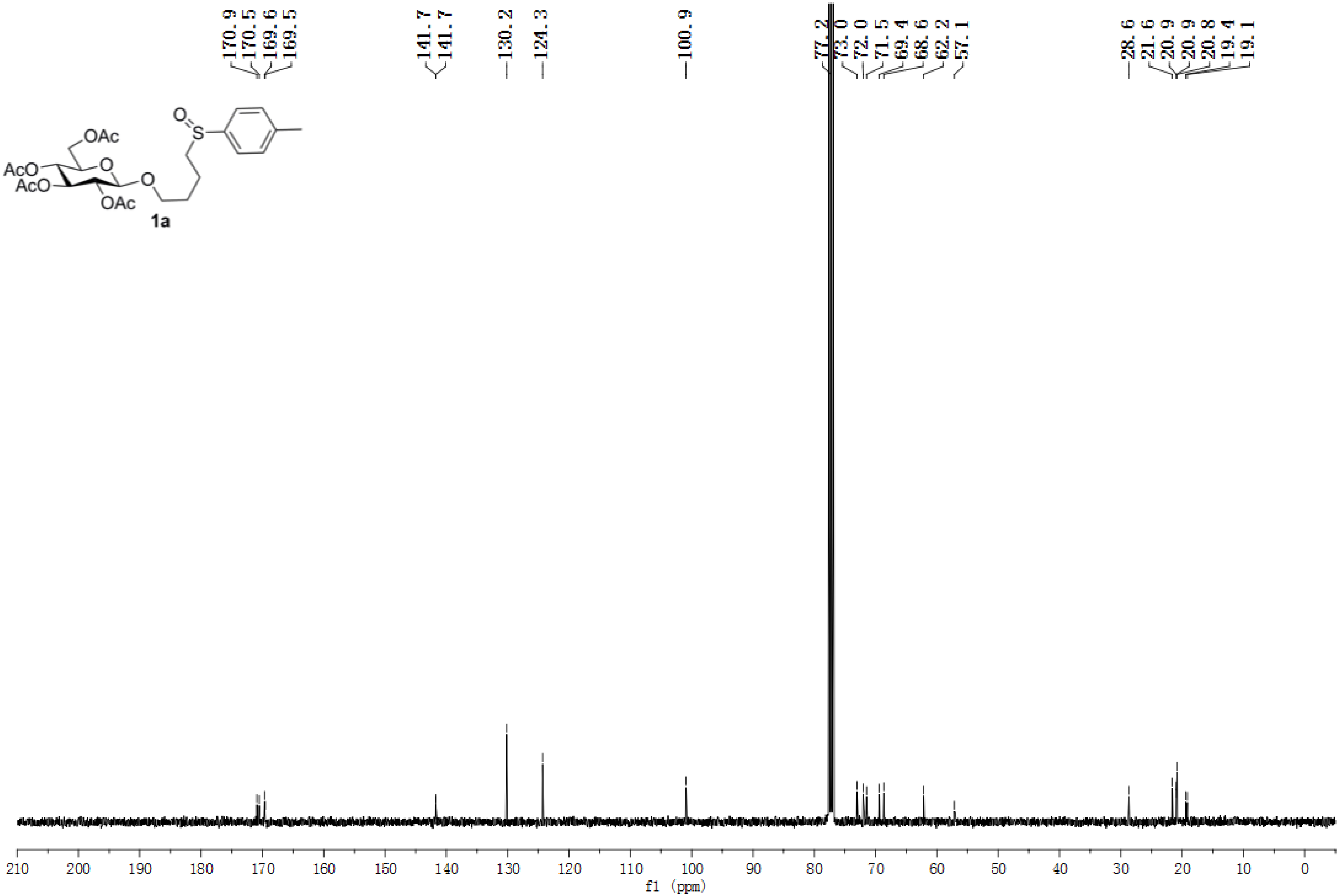


Figure S4. ^{13}C NMR spectrum of **1a** in $CDCl_3$

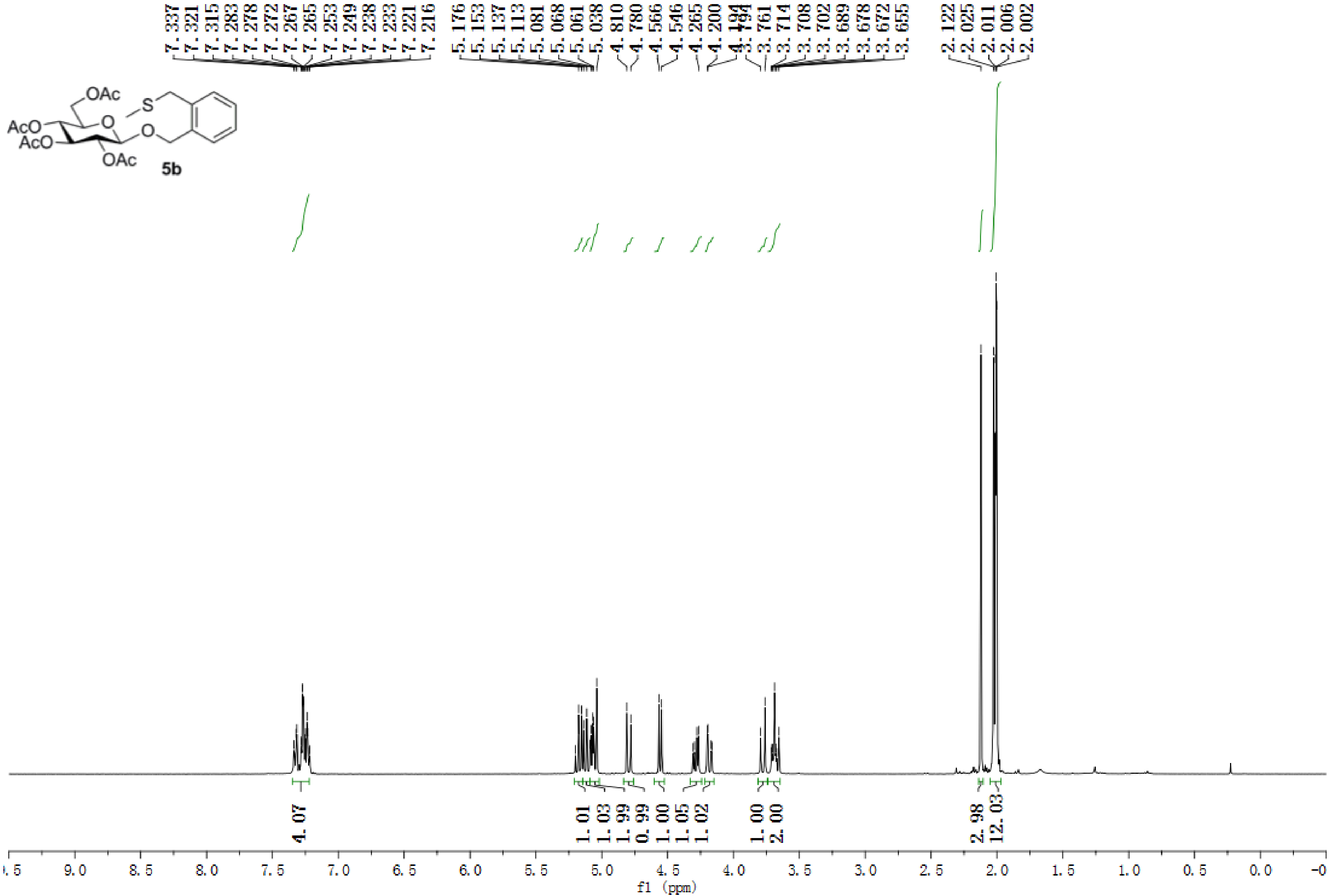


Figure S5. ^{1}H NMR spectrum of **5b** in $CDCl_3$

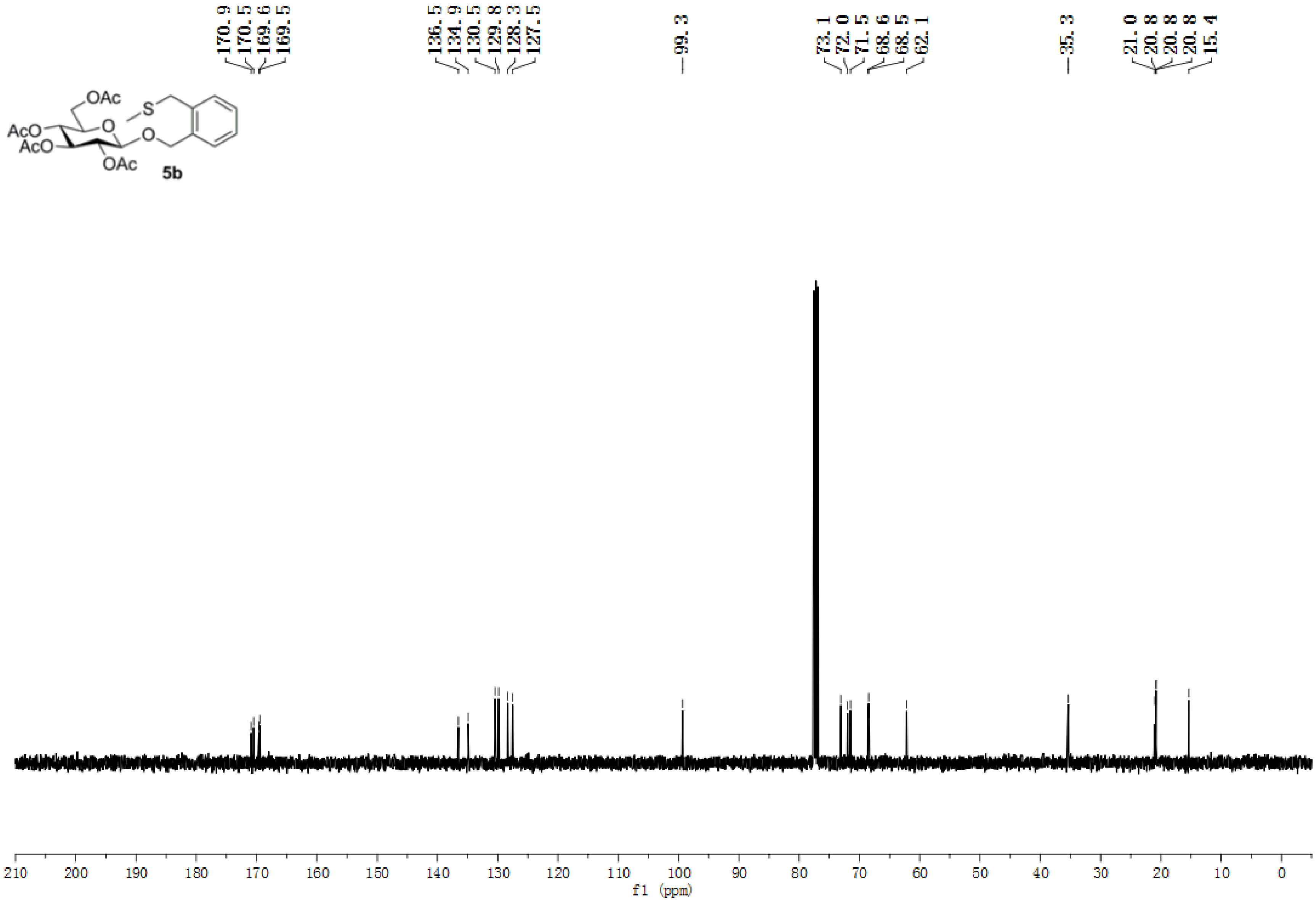


Figure S6. ^{13}C NMR spectrum of **5b** in $CDCl_3$

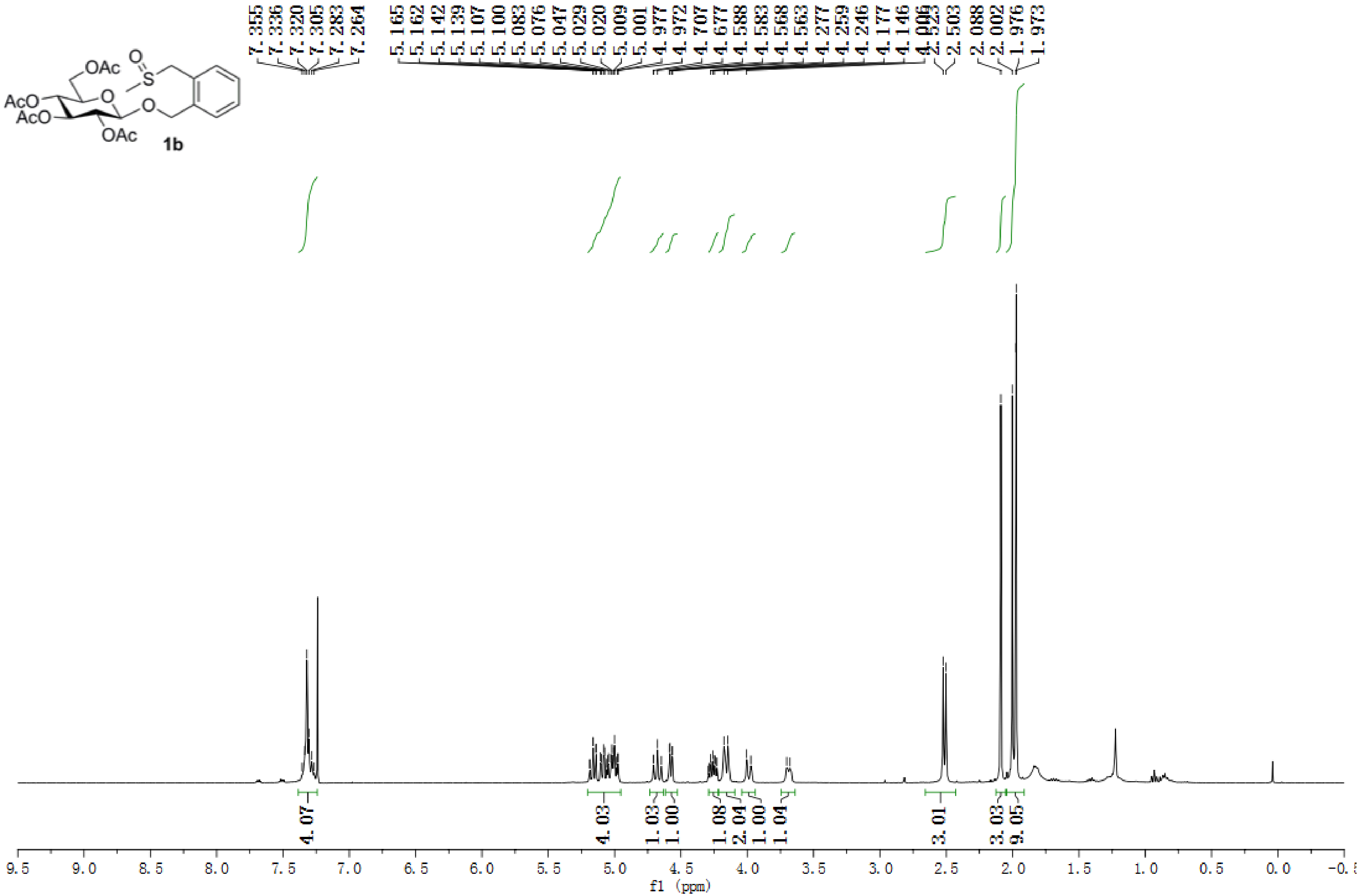


Figure S7. ^{1}H NMR spectrum of **1b** in $CDCl_3$

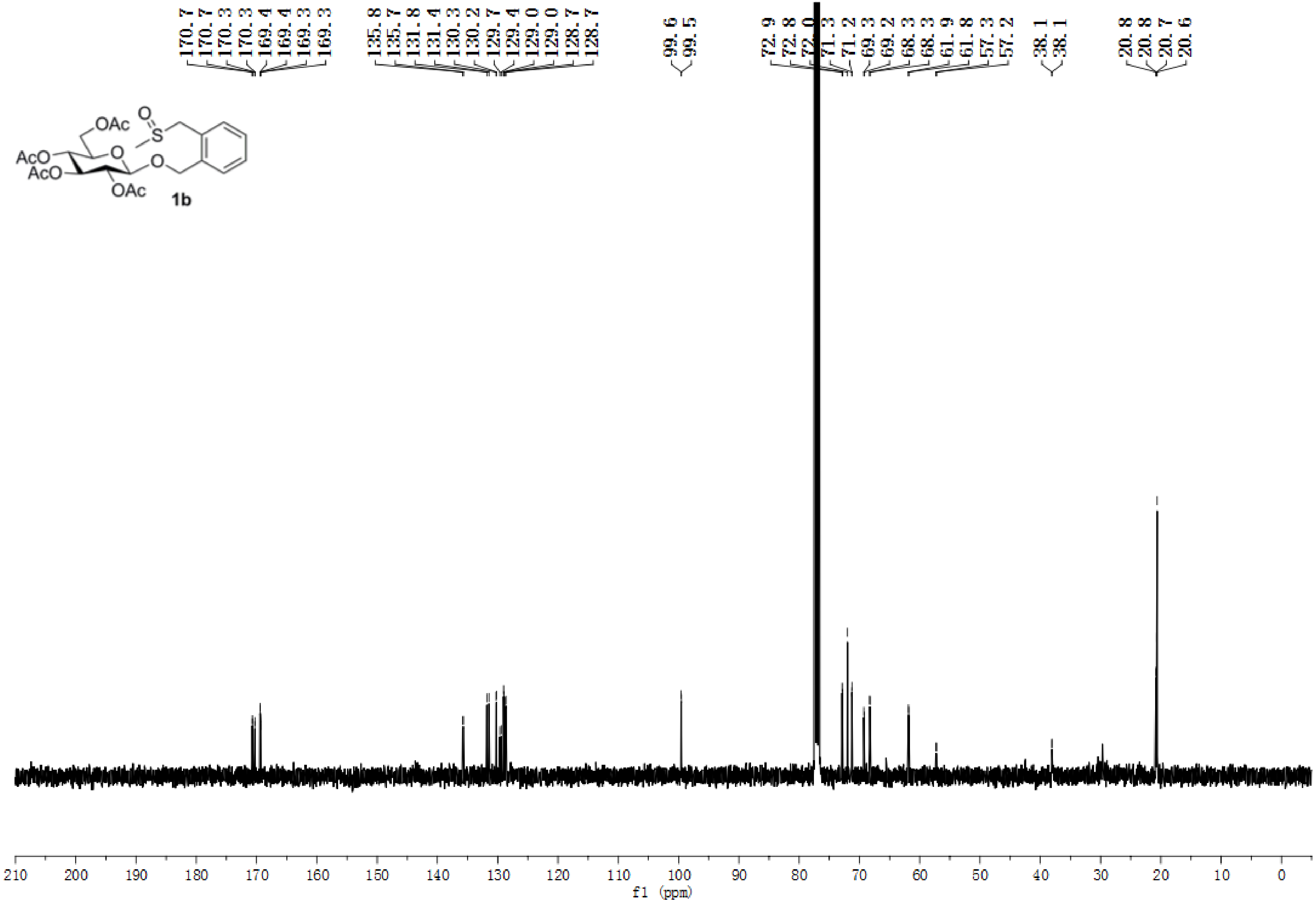


Figure S8. ^{13}C NMR spectrum of **1b** in $CDCl_3$

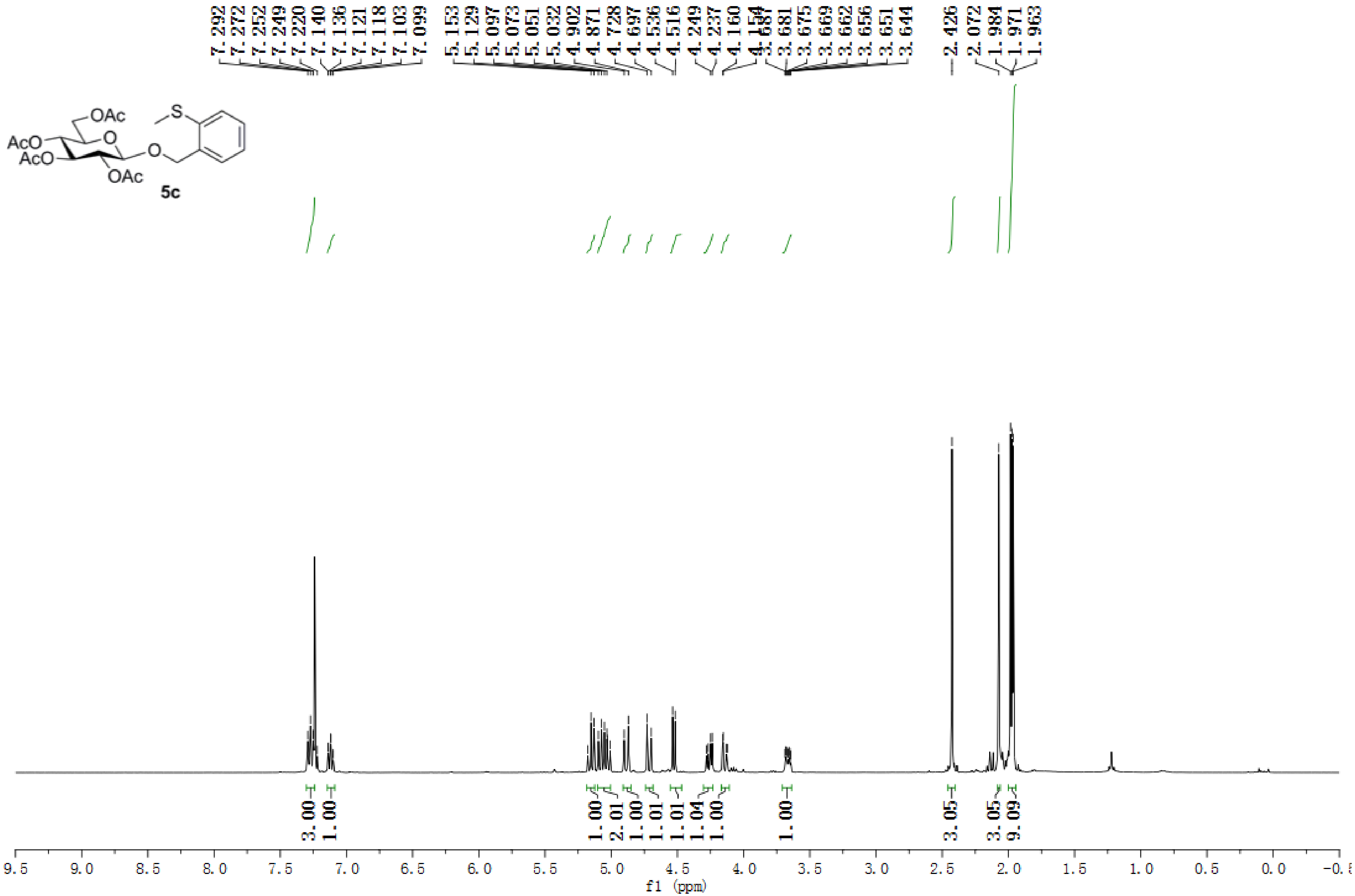


Figure S9. ^{1}H NMR spectrum of **5c** in $CDCl_3$

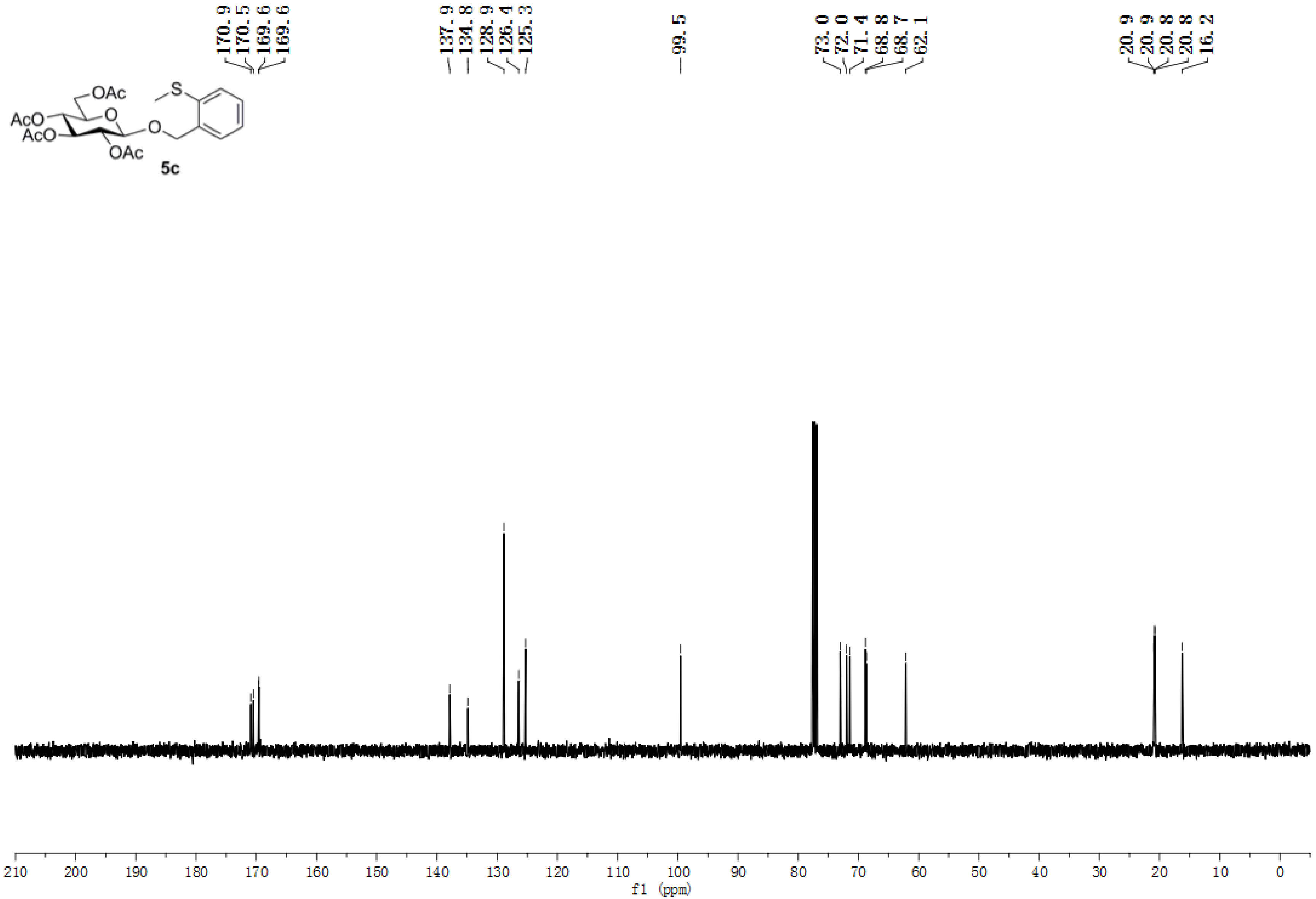


Figure S10. ^{13}C NMR spectrum of **5c** in $CDCl_3$

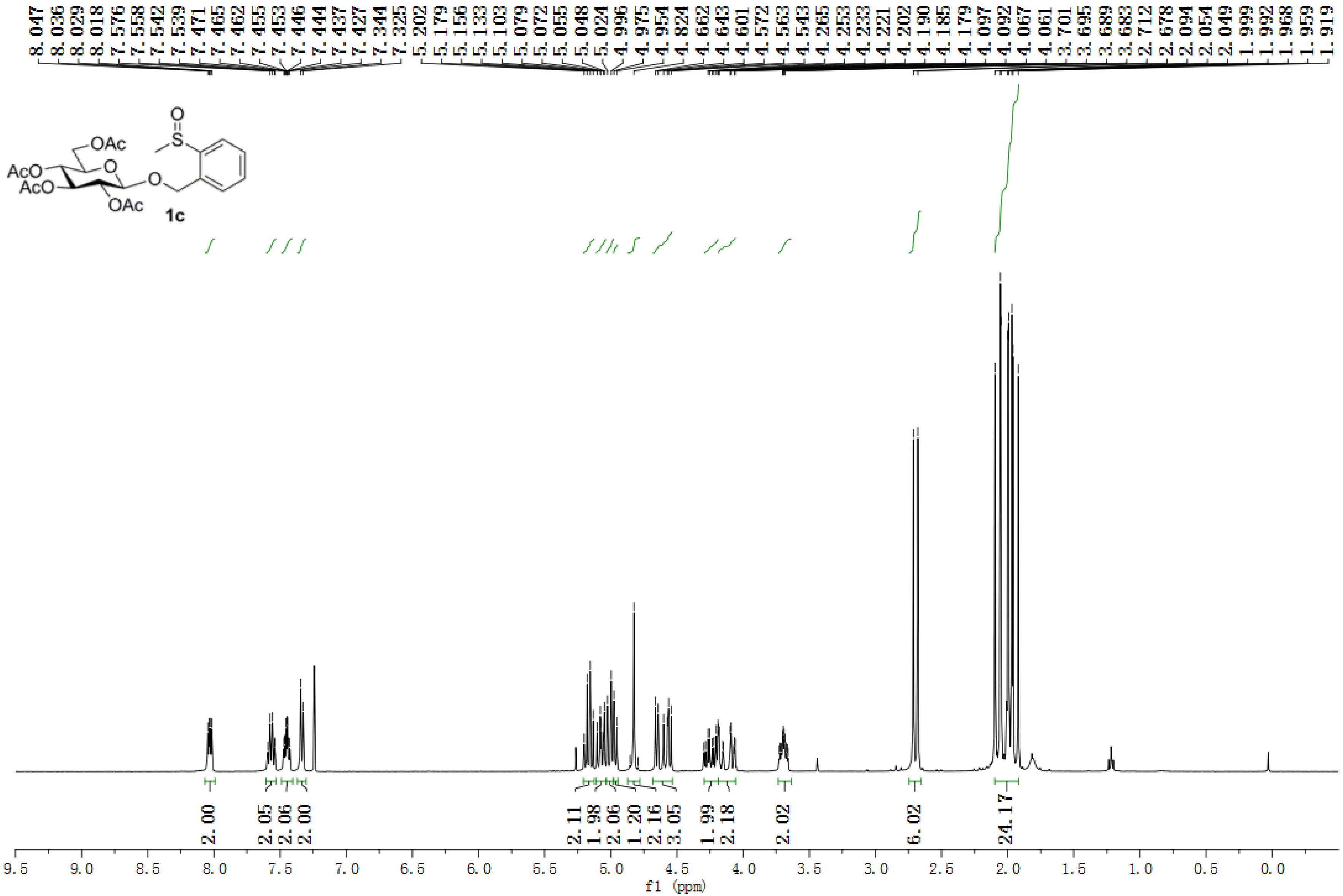


Figure S11. ^{1}H NMR spectrum of **1c** in $CDCl_3$

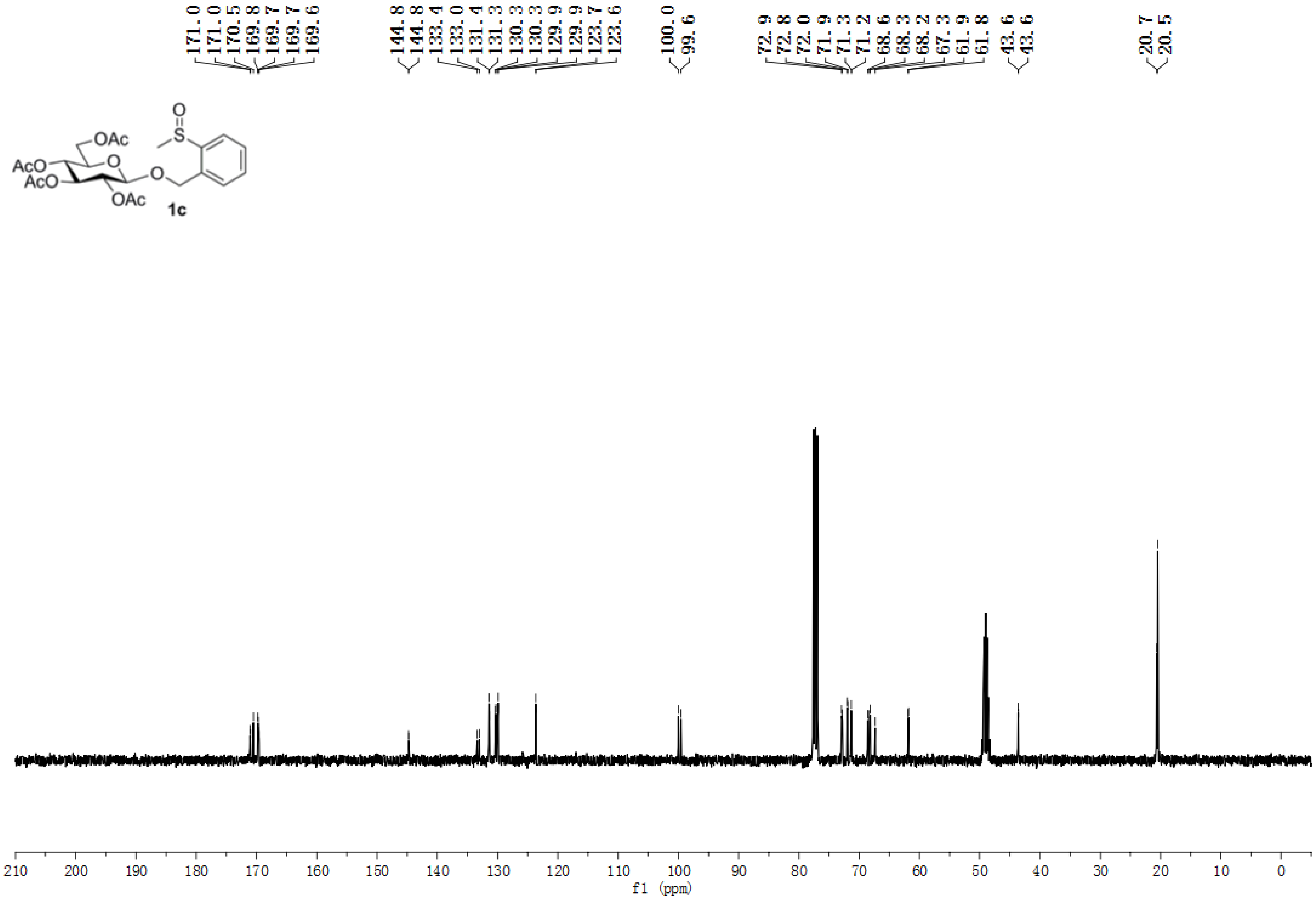


Figure S12. ^{13}C NMR spectrum of **1c** in $CDCl_3$

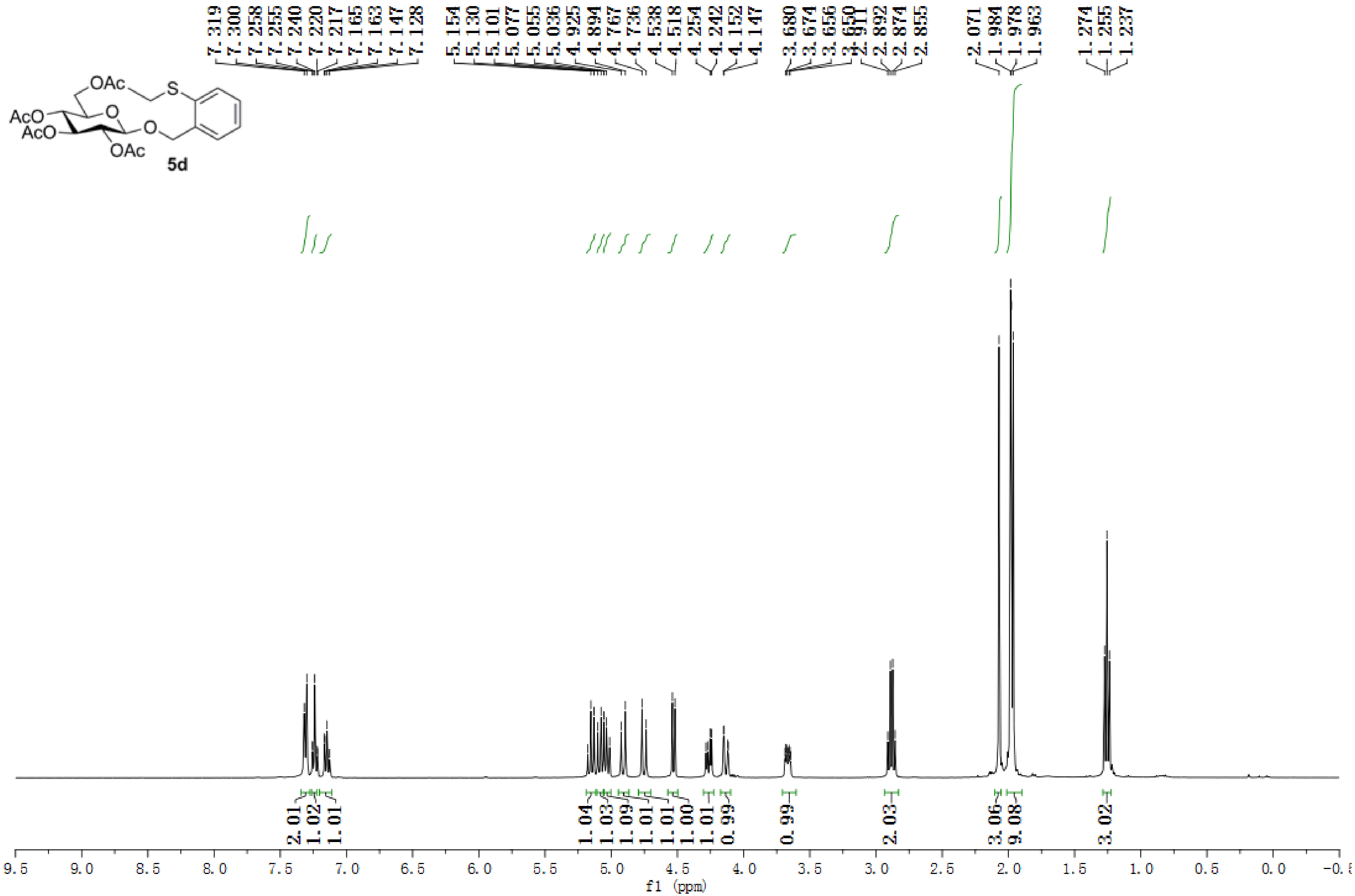


Figure S13. ^{1}H NMR spectrum of **5d** in $CDCl_3$

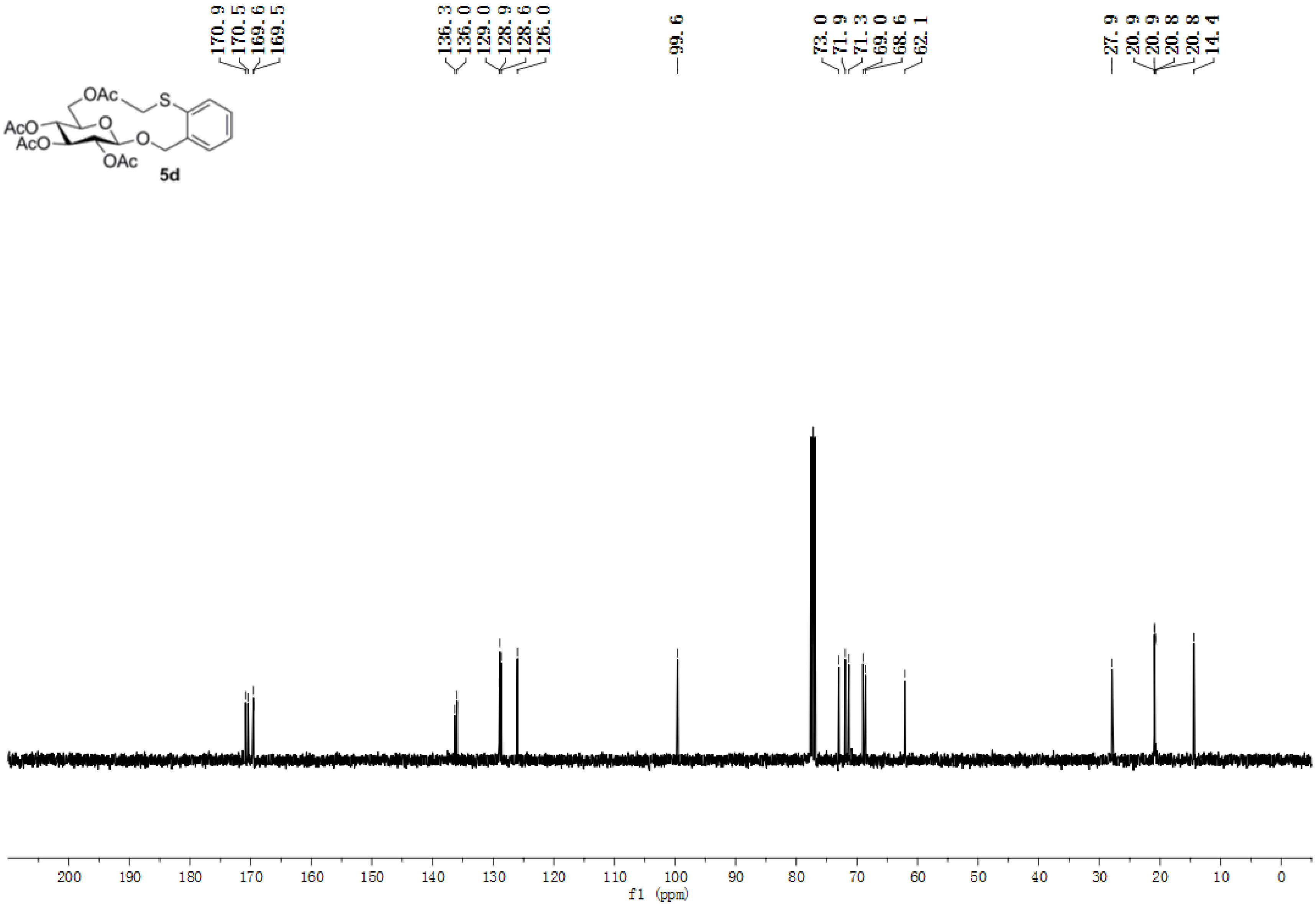


Figure S14. ^{13}C NMR spectrum of **5d** in $CDCl_3$

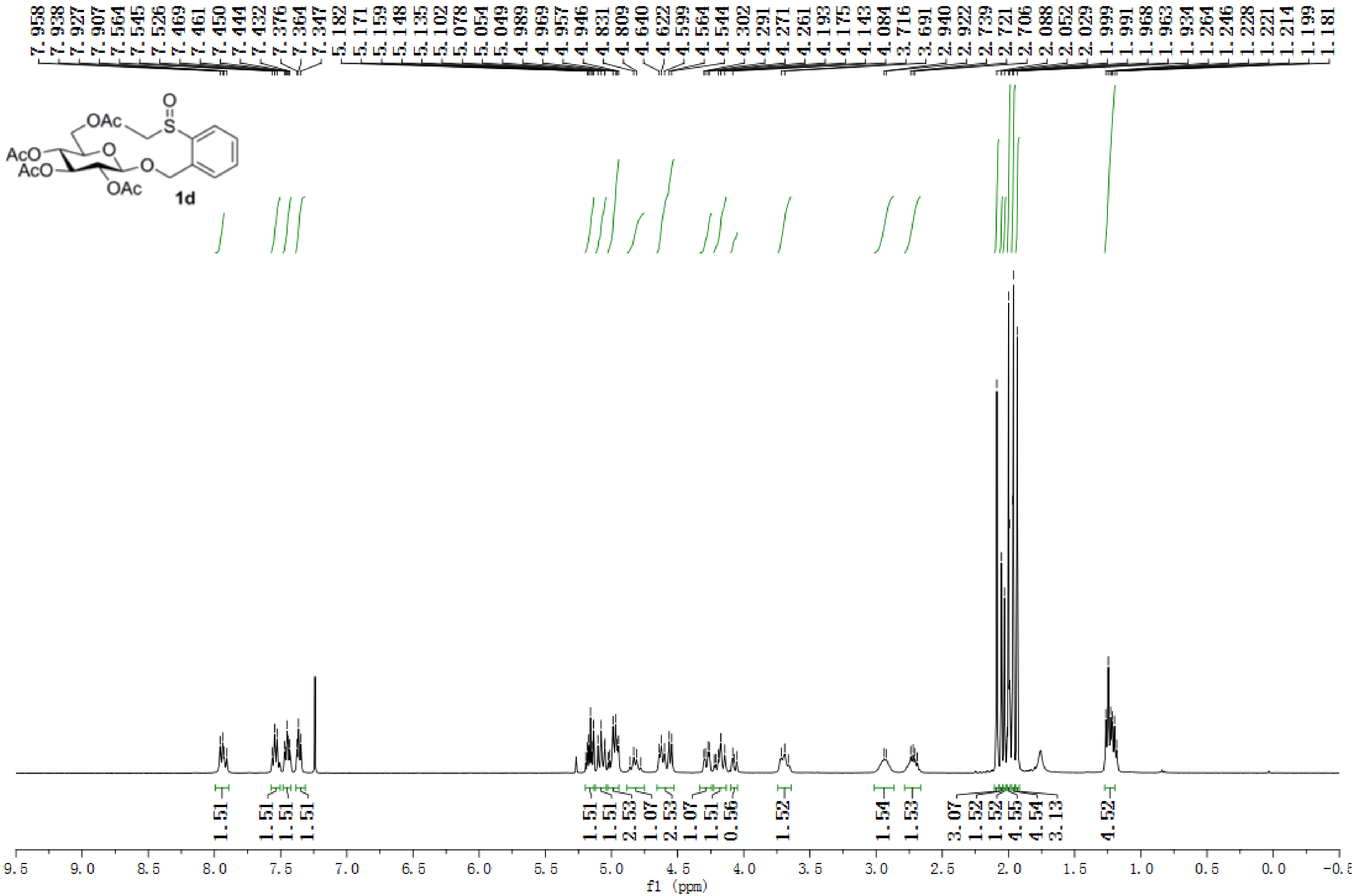


Figure S15. ^{1}H NMR spectrum of **1d** in $CDCl_3$

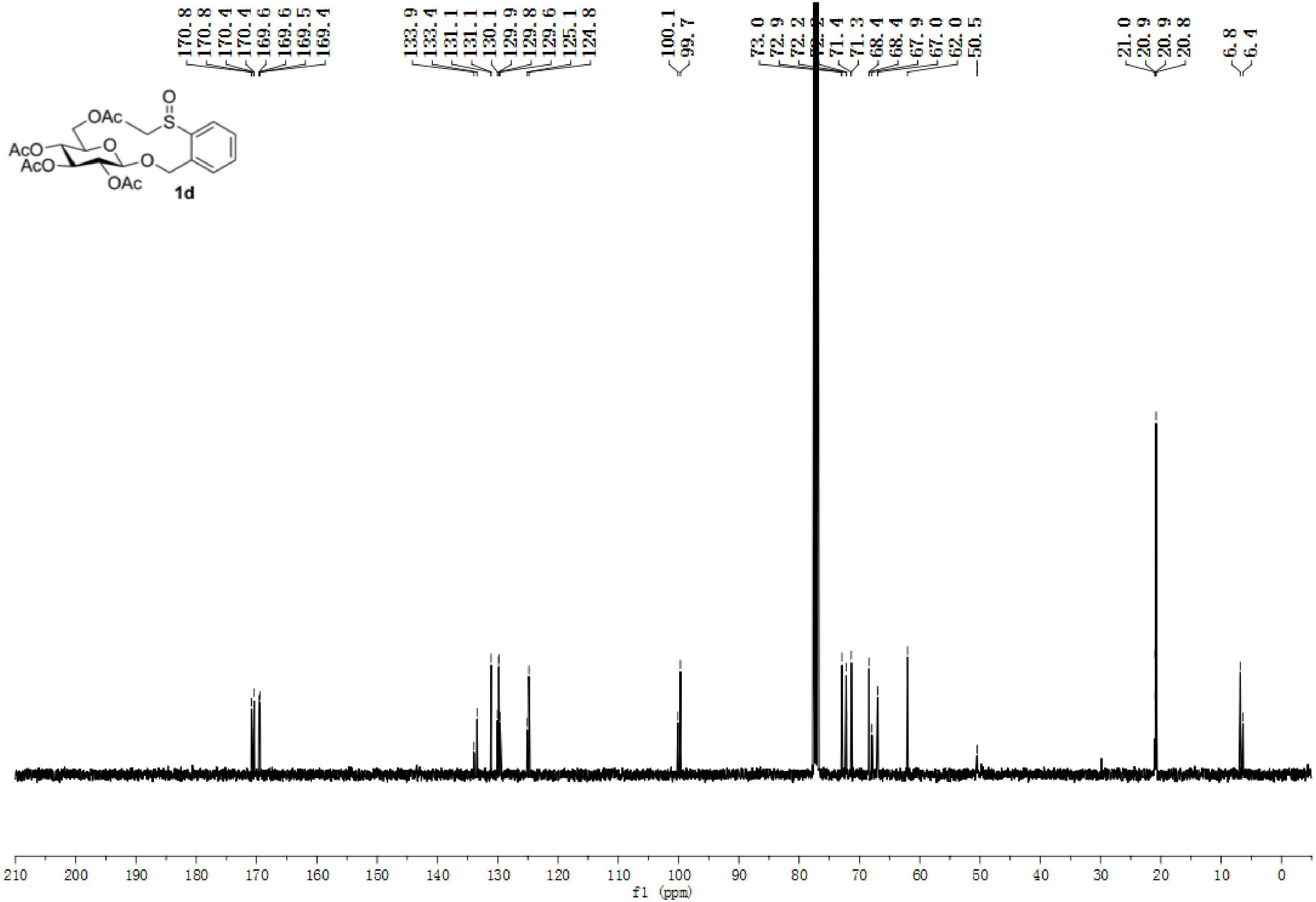


Figure S16. ^{13}C NMR spectrum of **1d** in $CDCl_3$

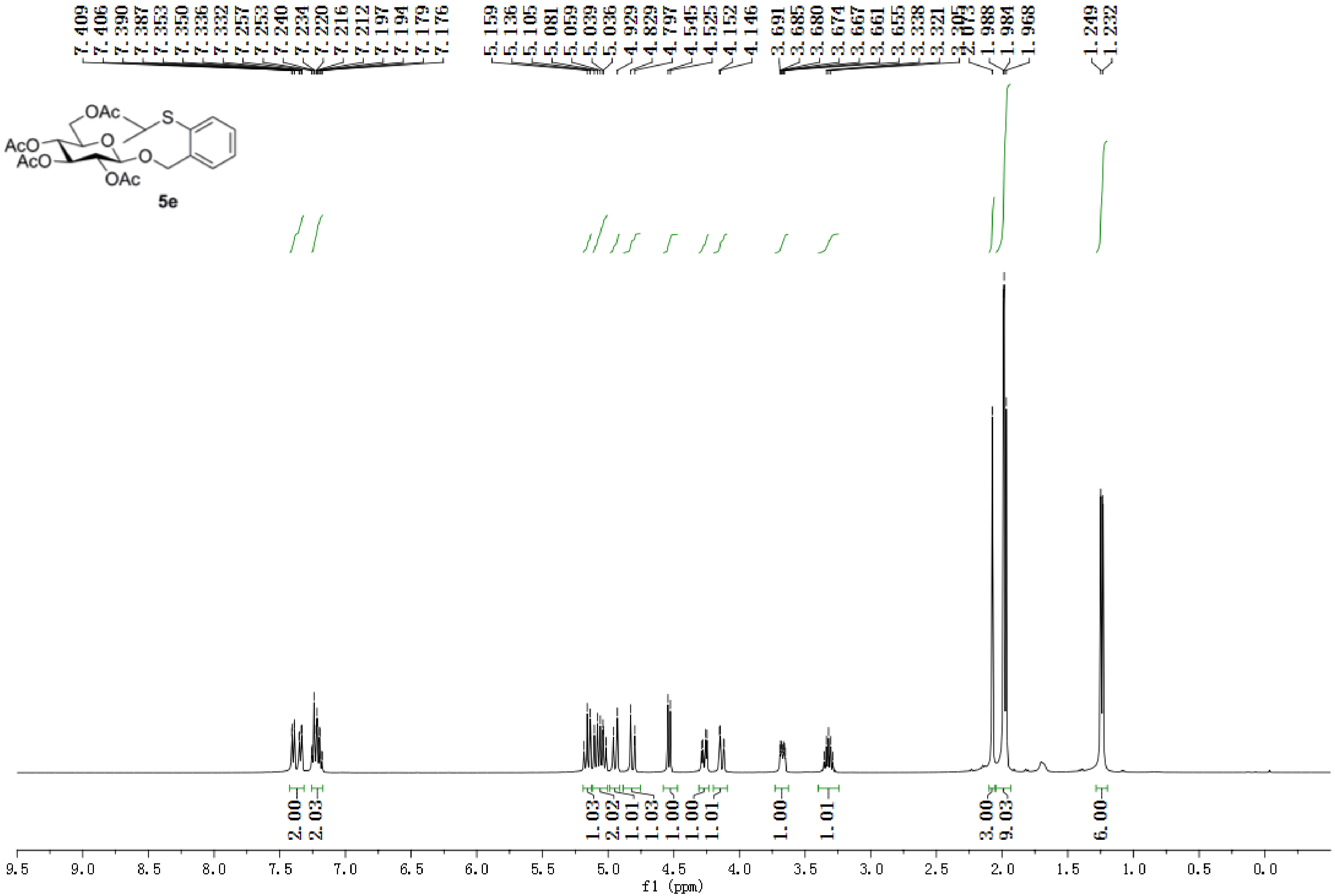


Figure S17. ^{1}H NMR spectrum of **5e** in $CDCl_3$

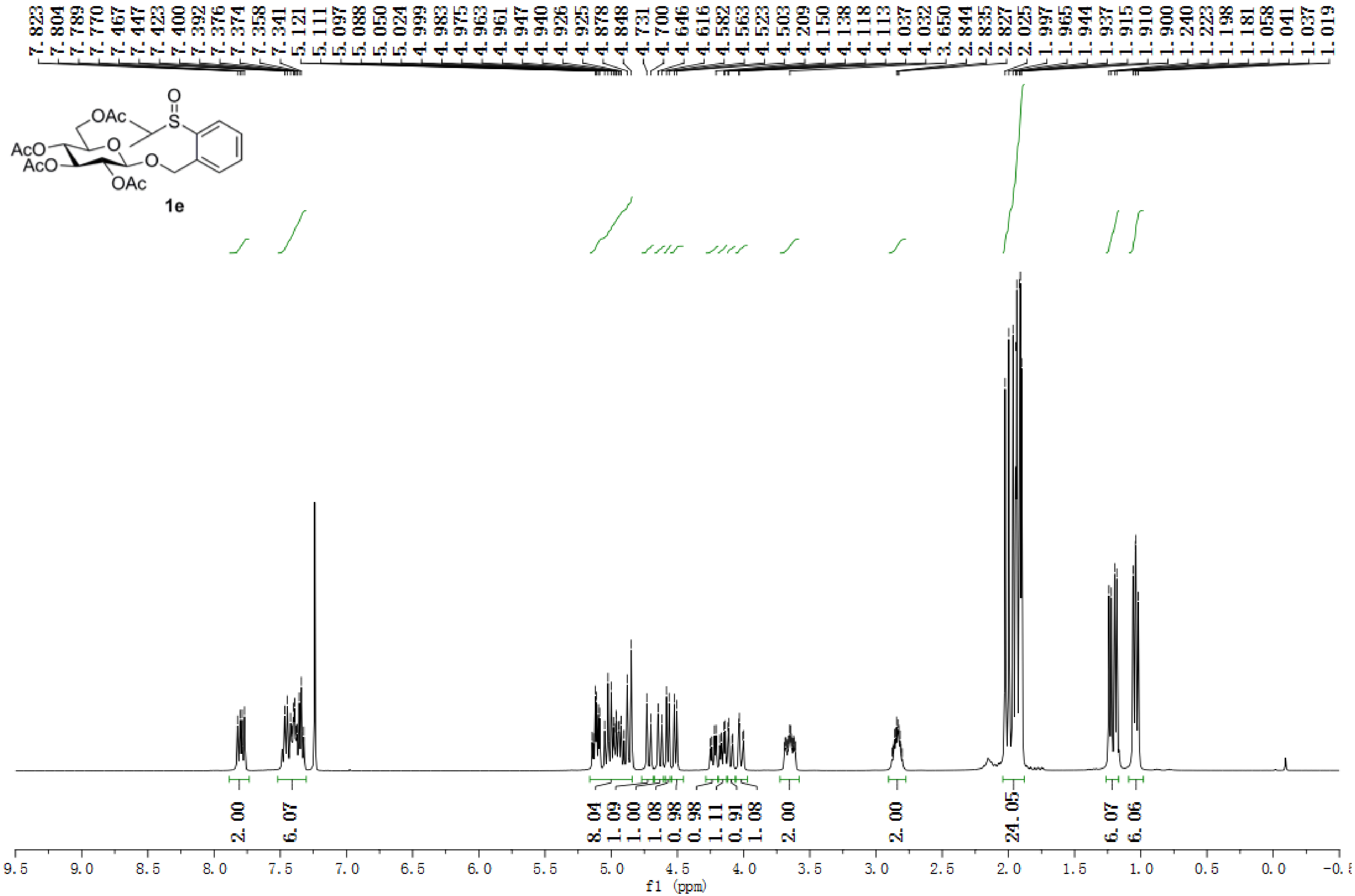


Figure S18. ^{1}H NMR spectrum of **1e** in CDCl$_3$

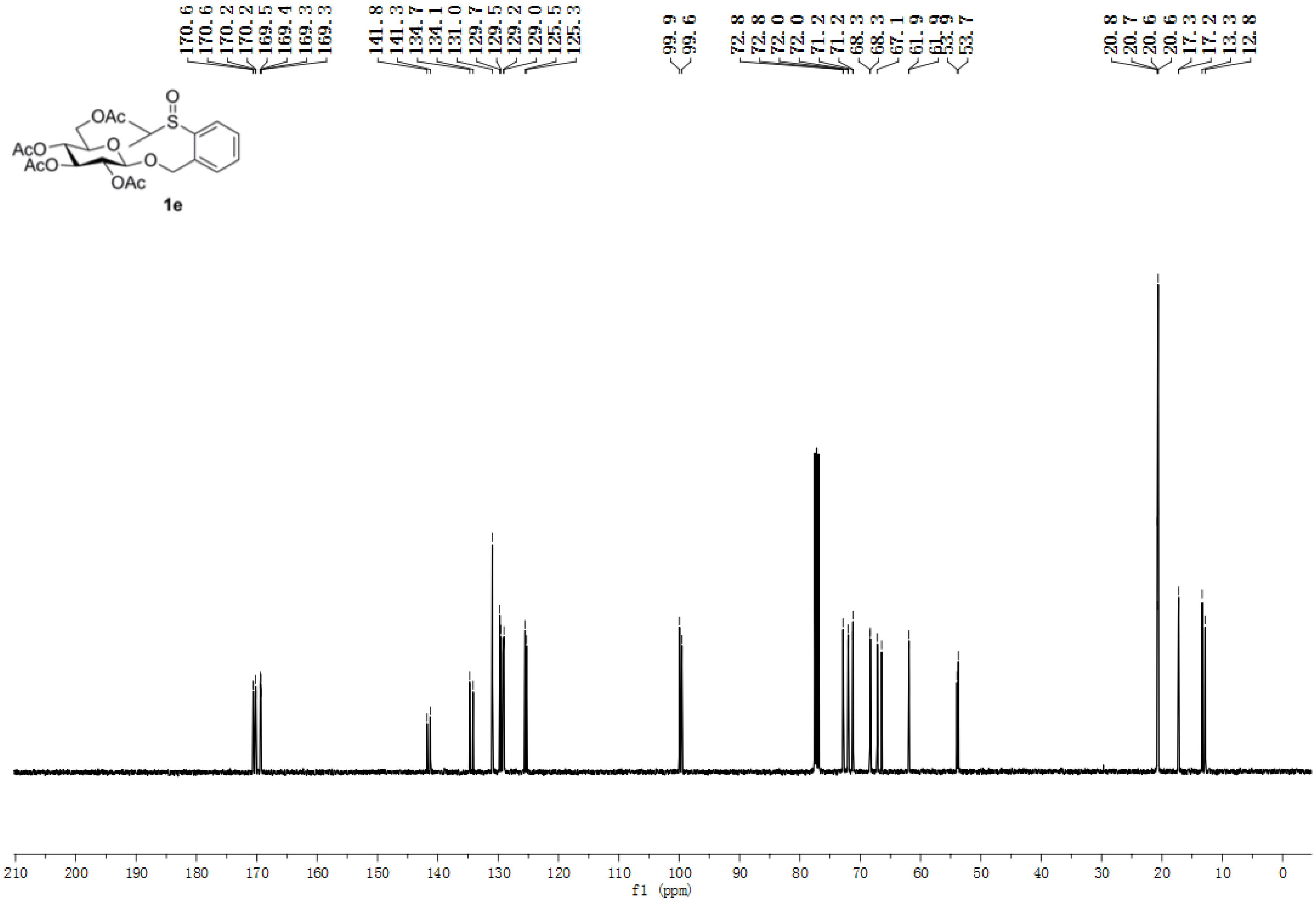


Figure S19. ^{13}C NMR spectrum of **1e** in $CDCl_3$

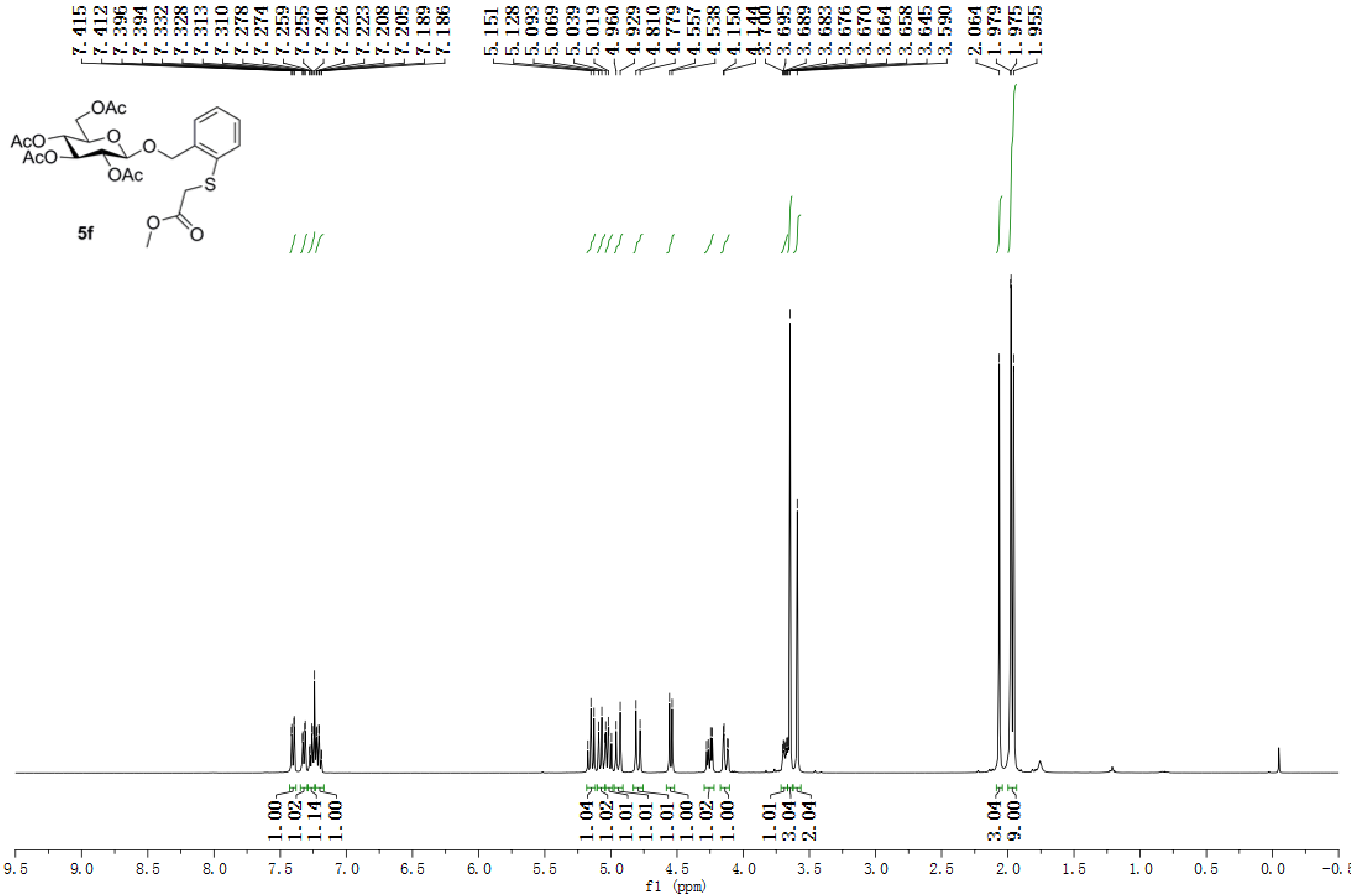


Figure S20. ^{1}H NMR spectrum of **5f** in $CDCl_3$

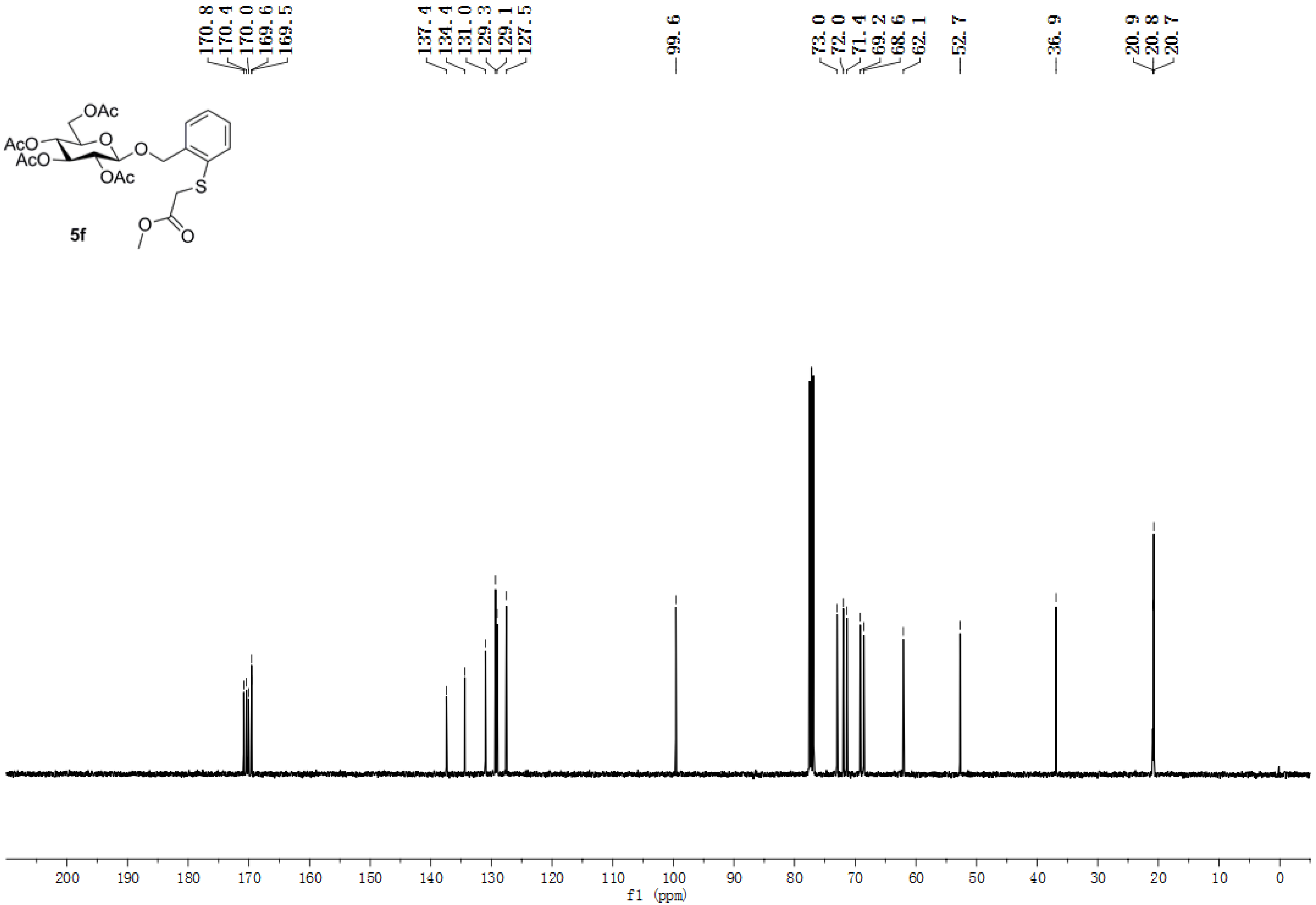


Figure S21. ^{13}C NMR spectrum of **5f** in $CDCl_3$

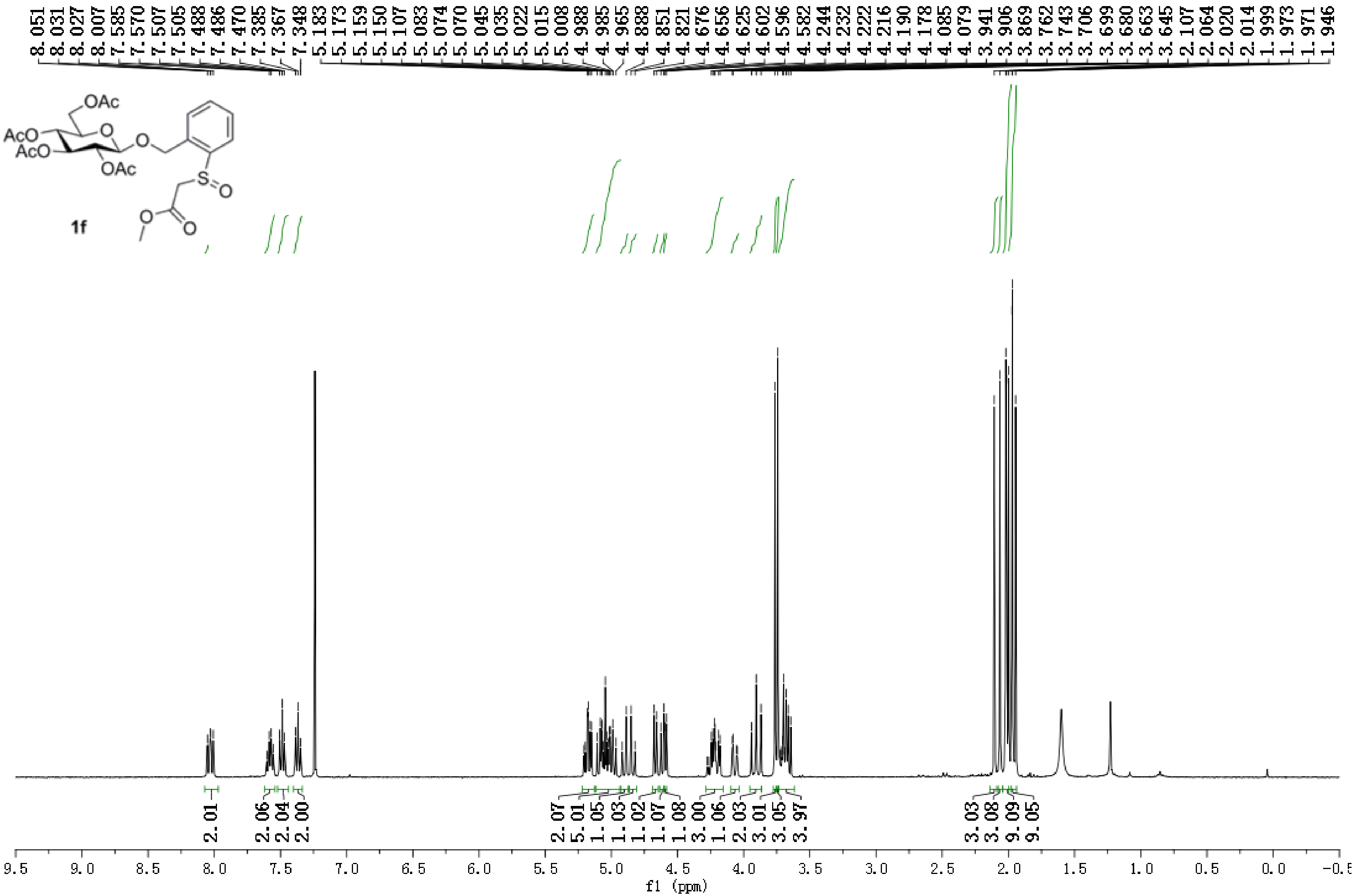


Figure S22. ^{1}H NMR spectrum of **1f** in $CDCl_3$

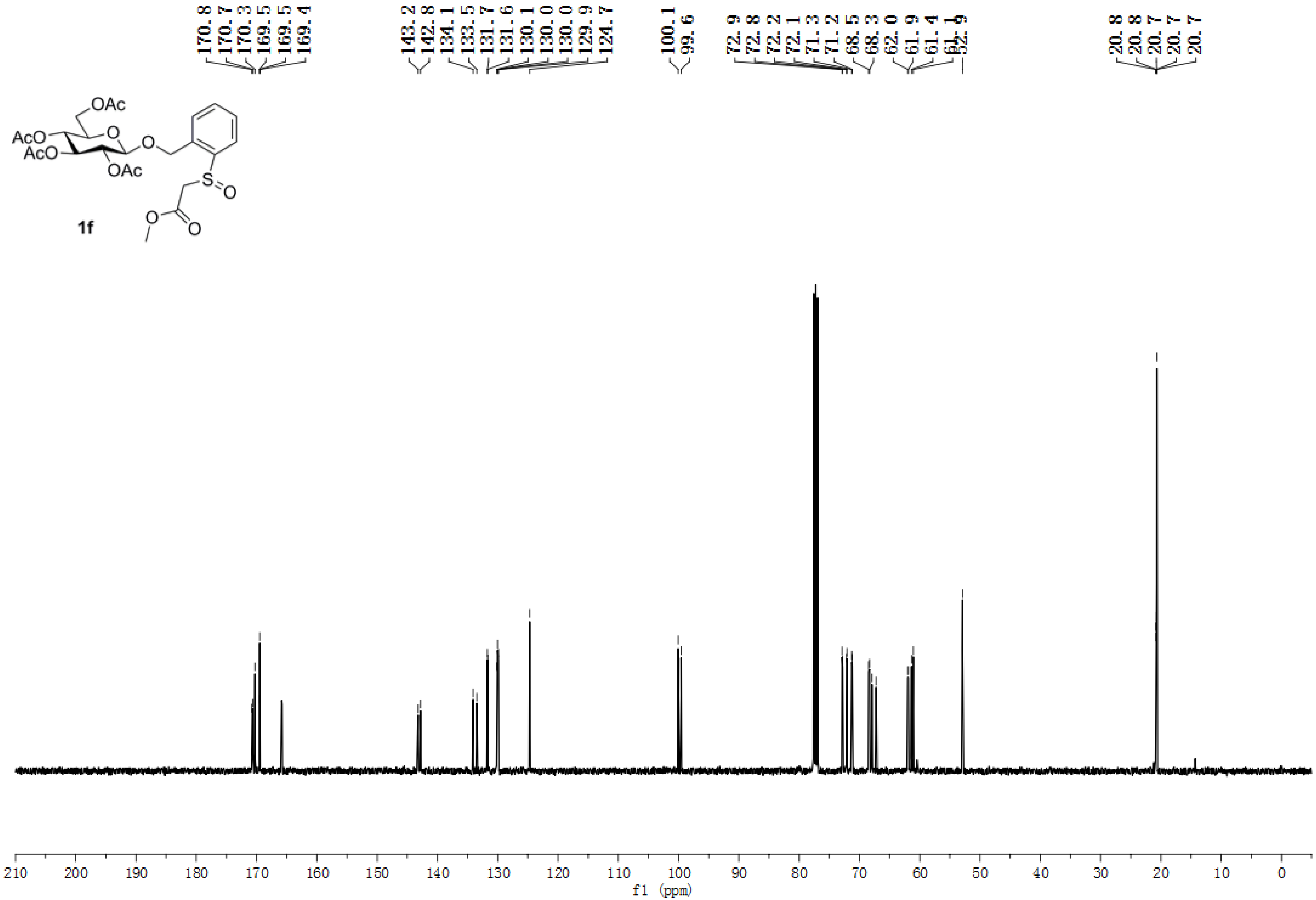


Figure S23. ^{13}C NMR spectrum of **1f** in CDCl$_3$

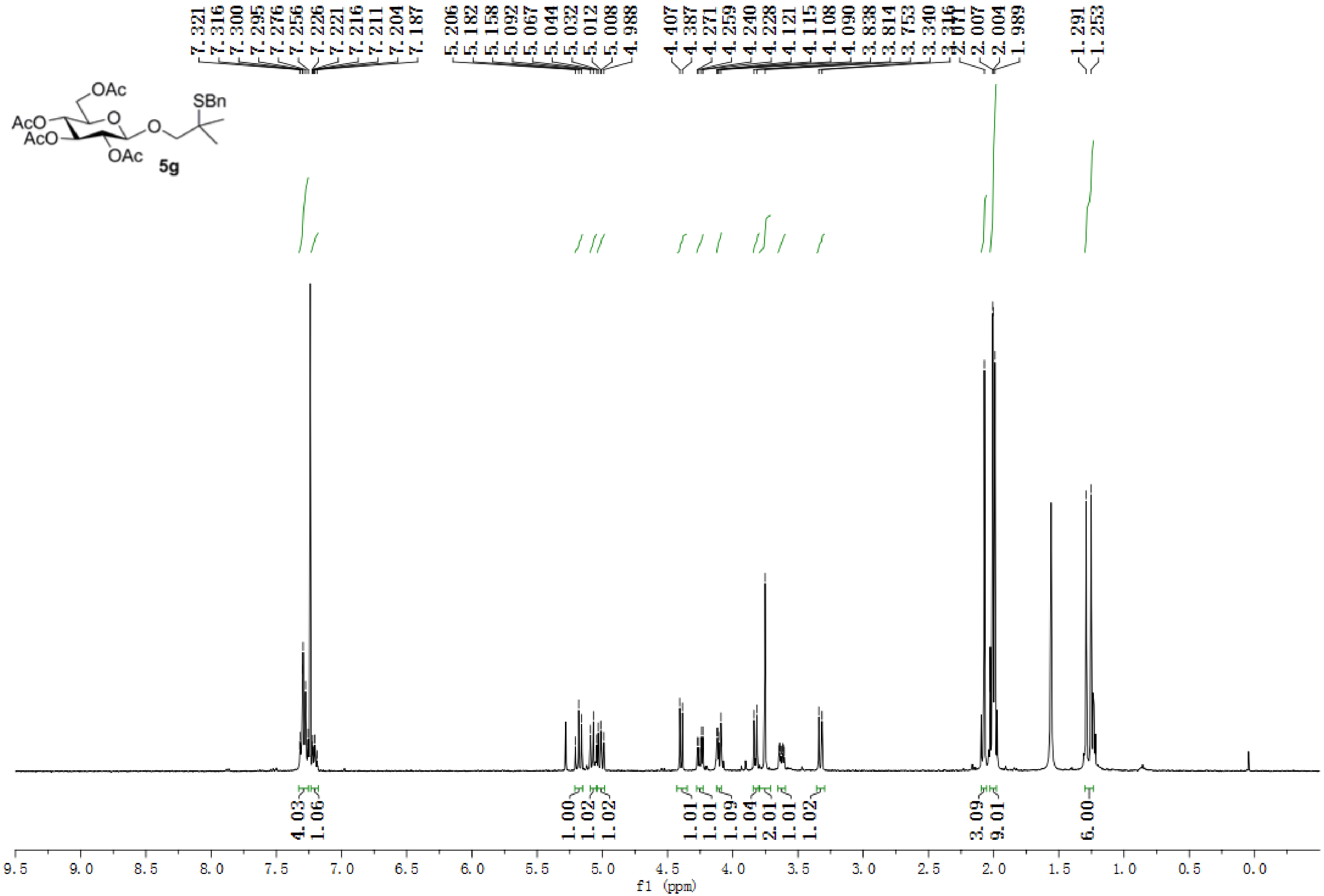


Figure S24. ^{1}H NMR spectrum of **5g** in $CDCl_3$

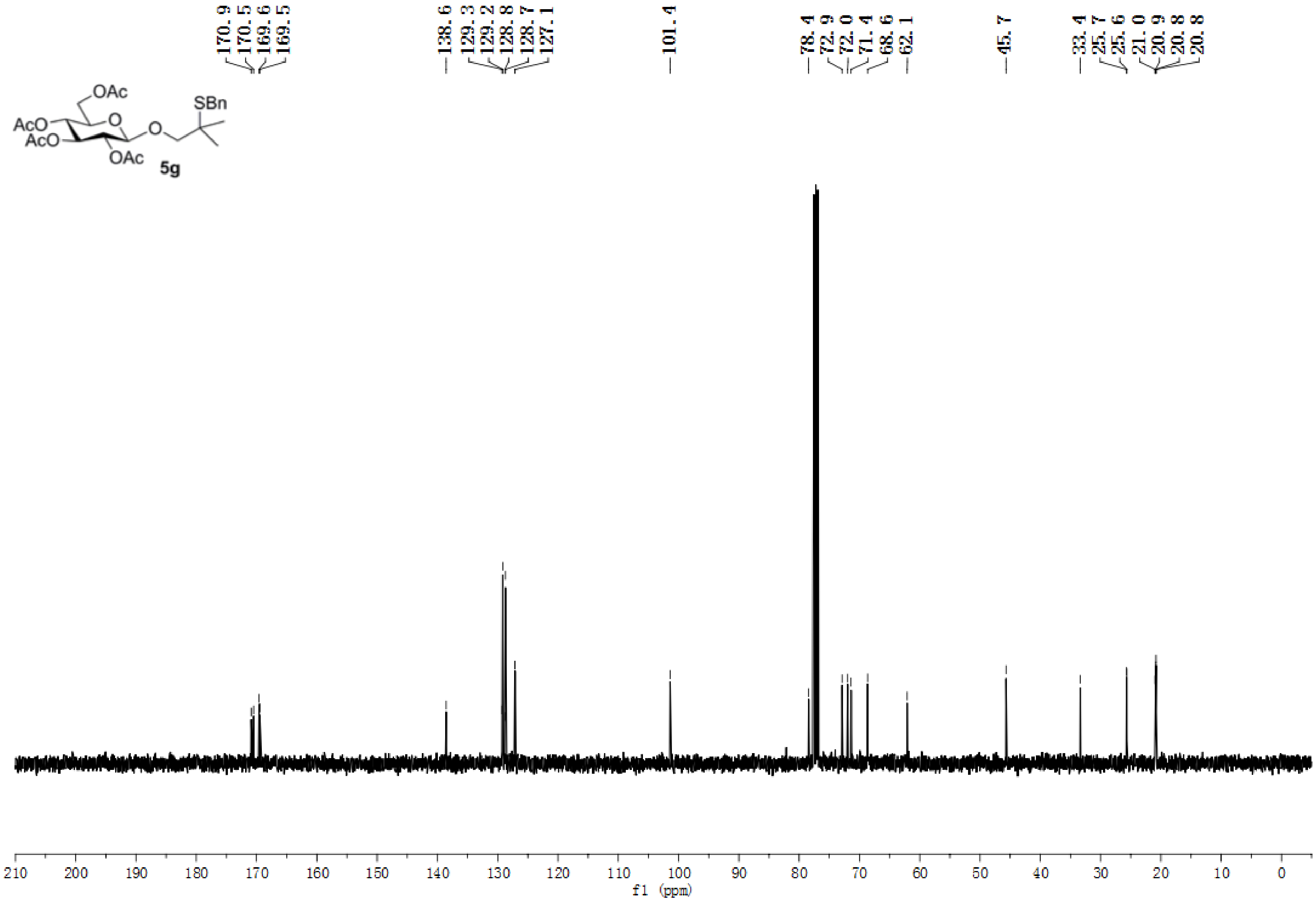


Figure S25. ^{13}C NMR spectrum of **5g** in $CDCl_3$

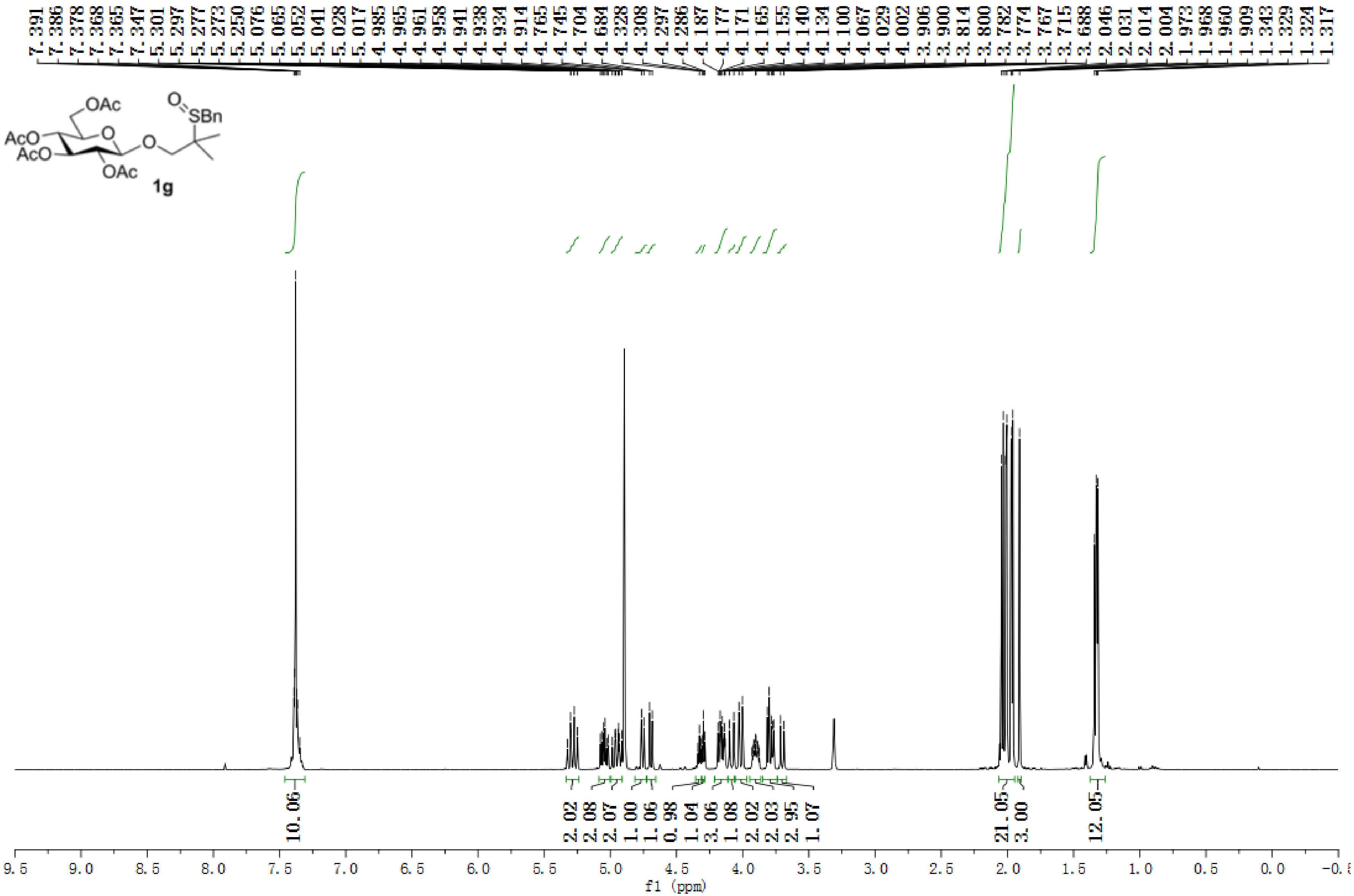


Figure S26. ^{1}H NMR spectrum of **1g** in CD_3OD

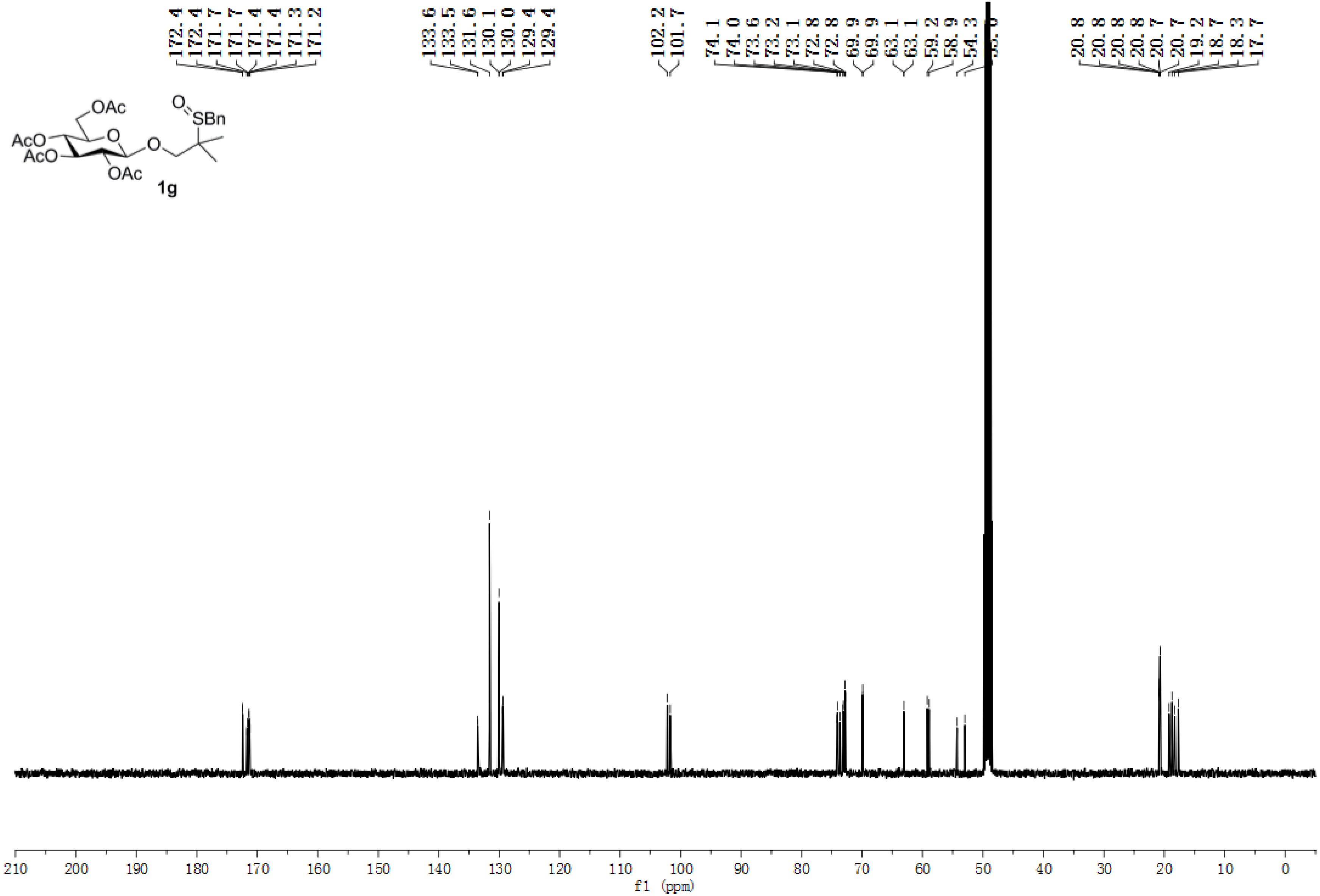


Figure S27. ^{13}C NMR spectrum of **1g** in CD_3OD

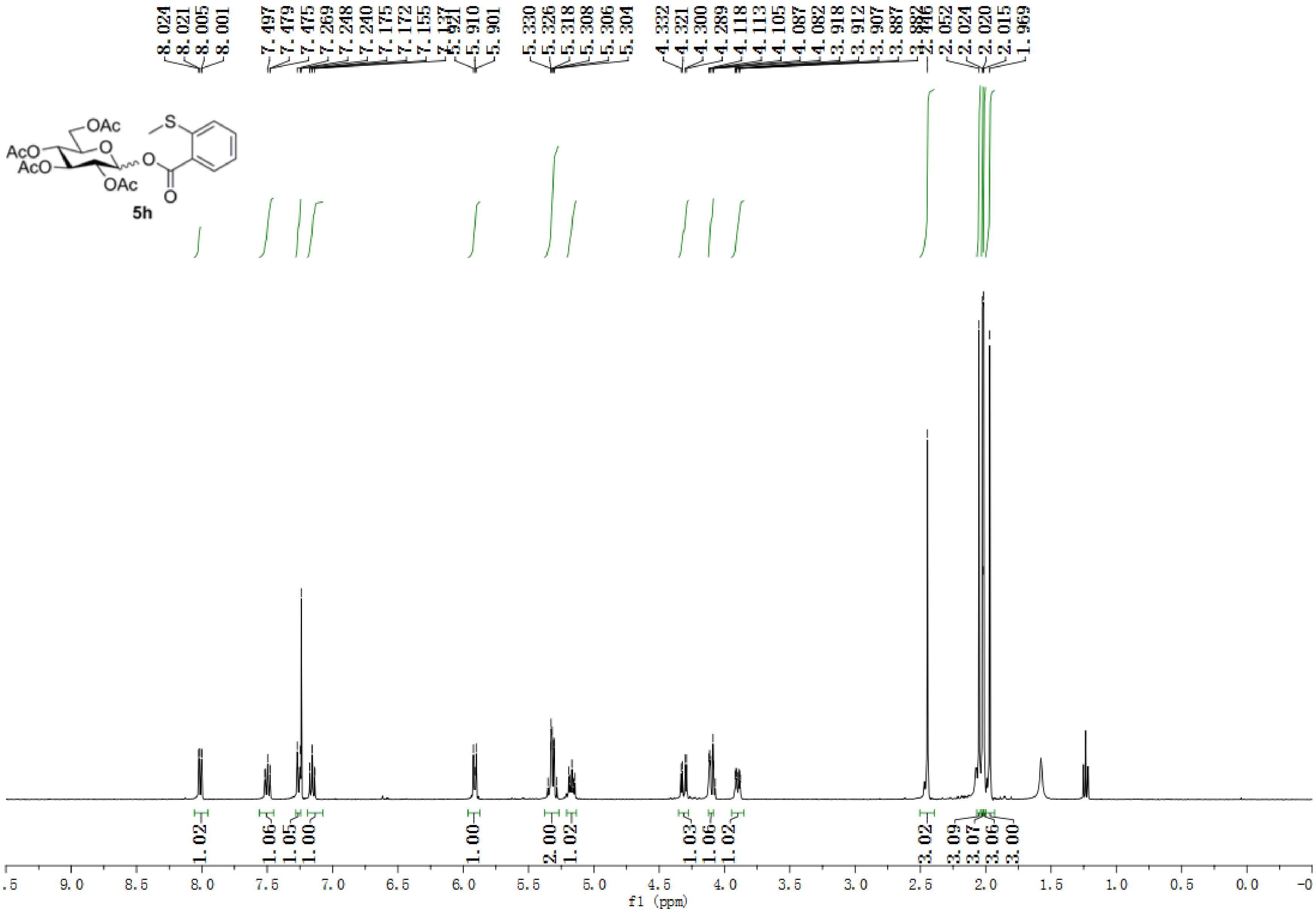


Figure S28. ^{1}H NMR spectrum of **5h** in $CDCl_3$

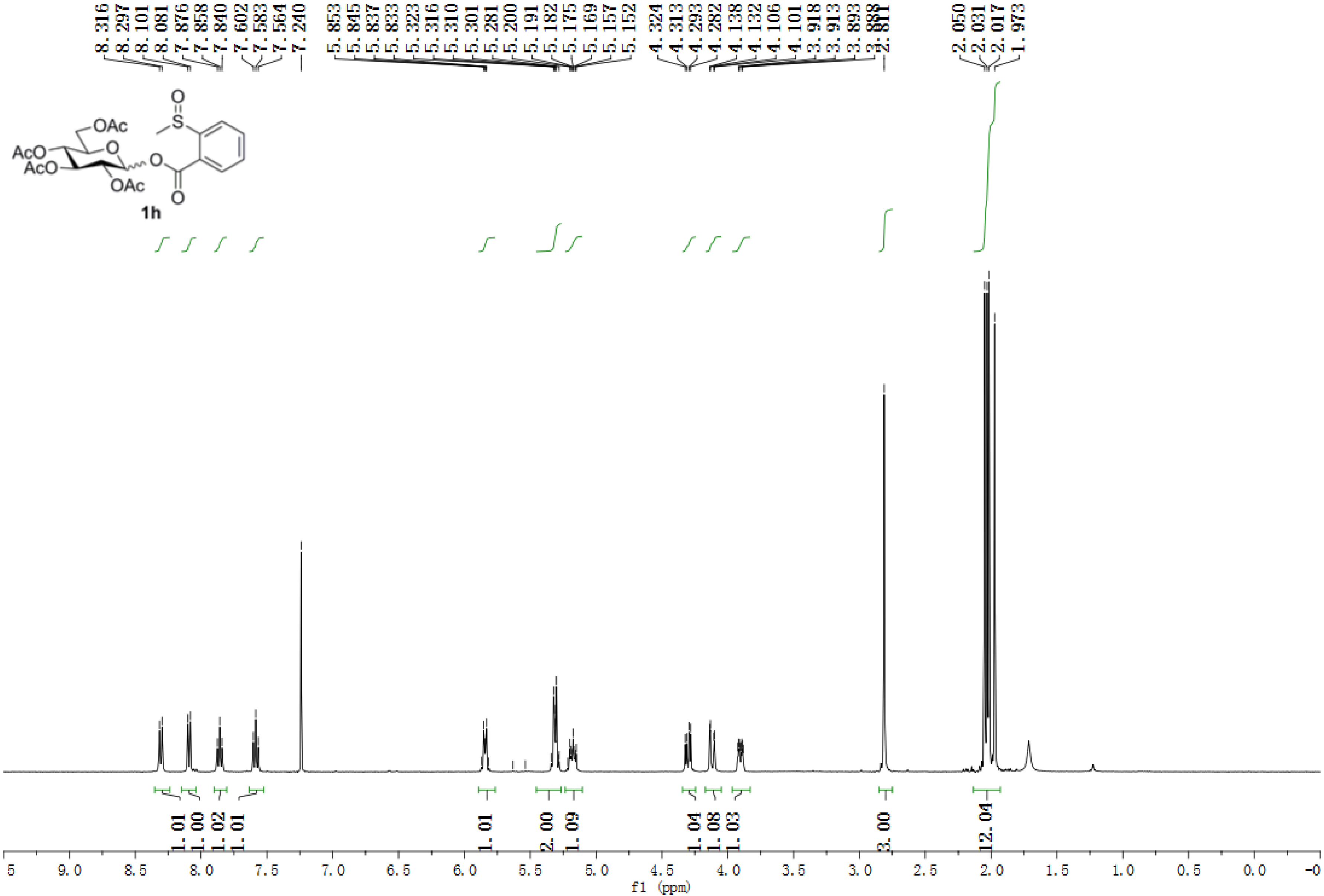


Figure S29. ^{1}H NMR spectrum of **1h** in $CDCl_3$

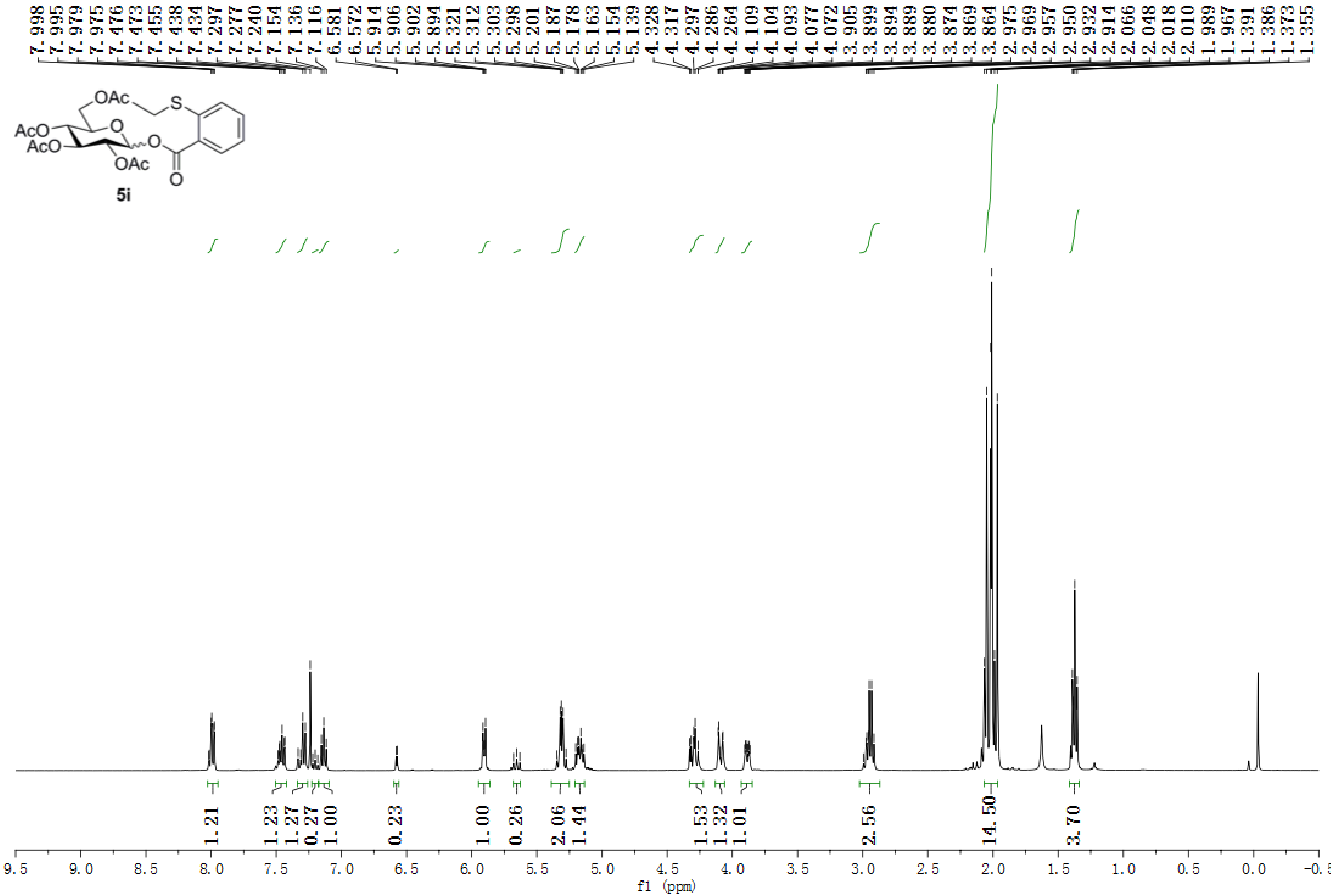


Figure S30. ^{1}H NMR spectrum of **5i** in $CDCl_3$

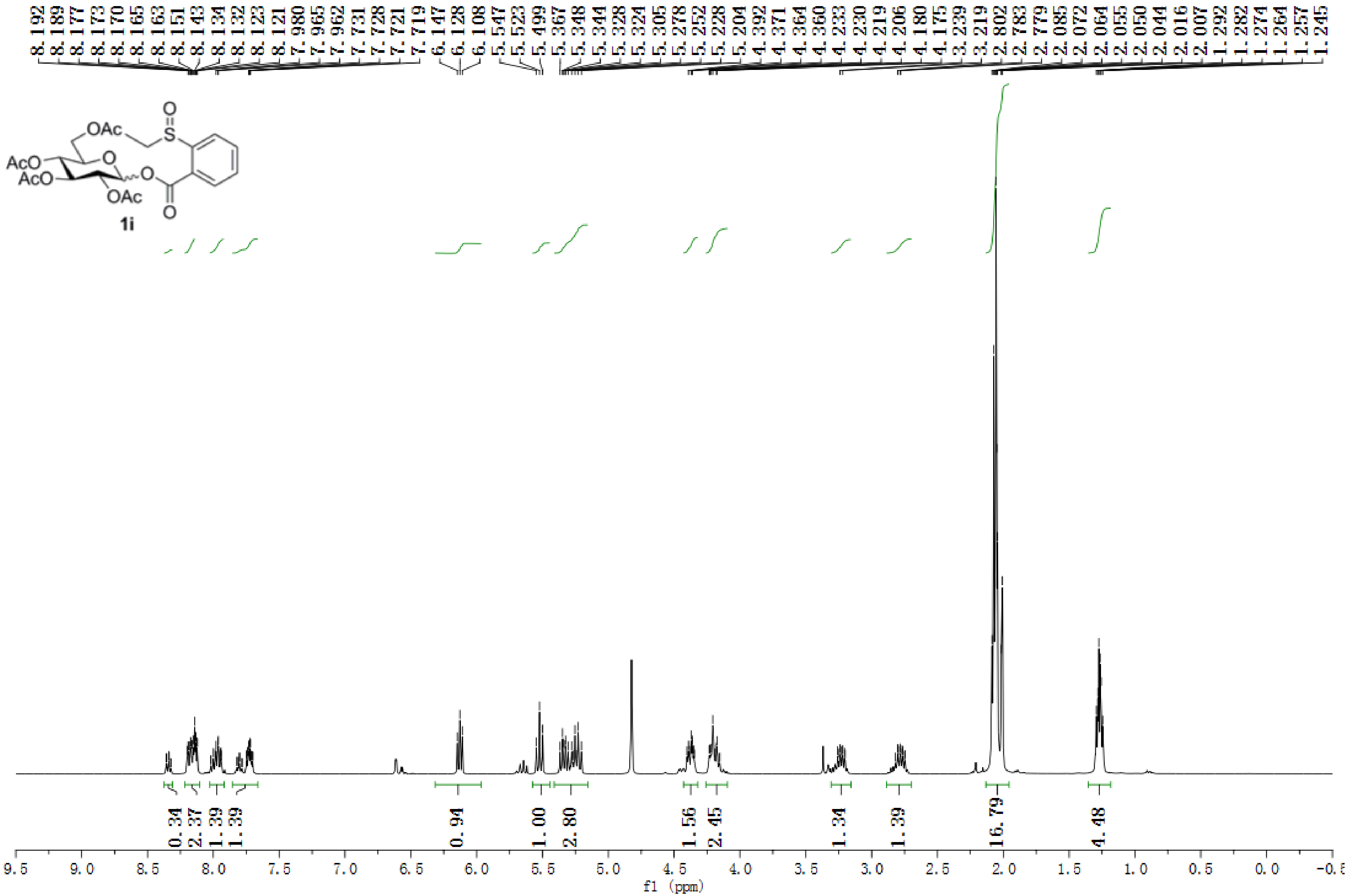


Figure S31. ^{1}H NMR spectrum of **1i** in CD_3OD

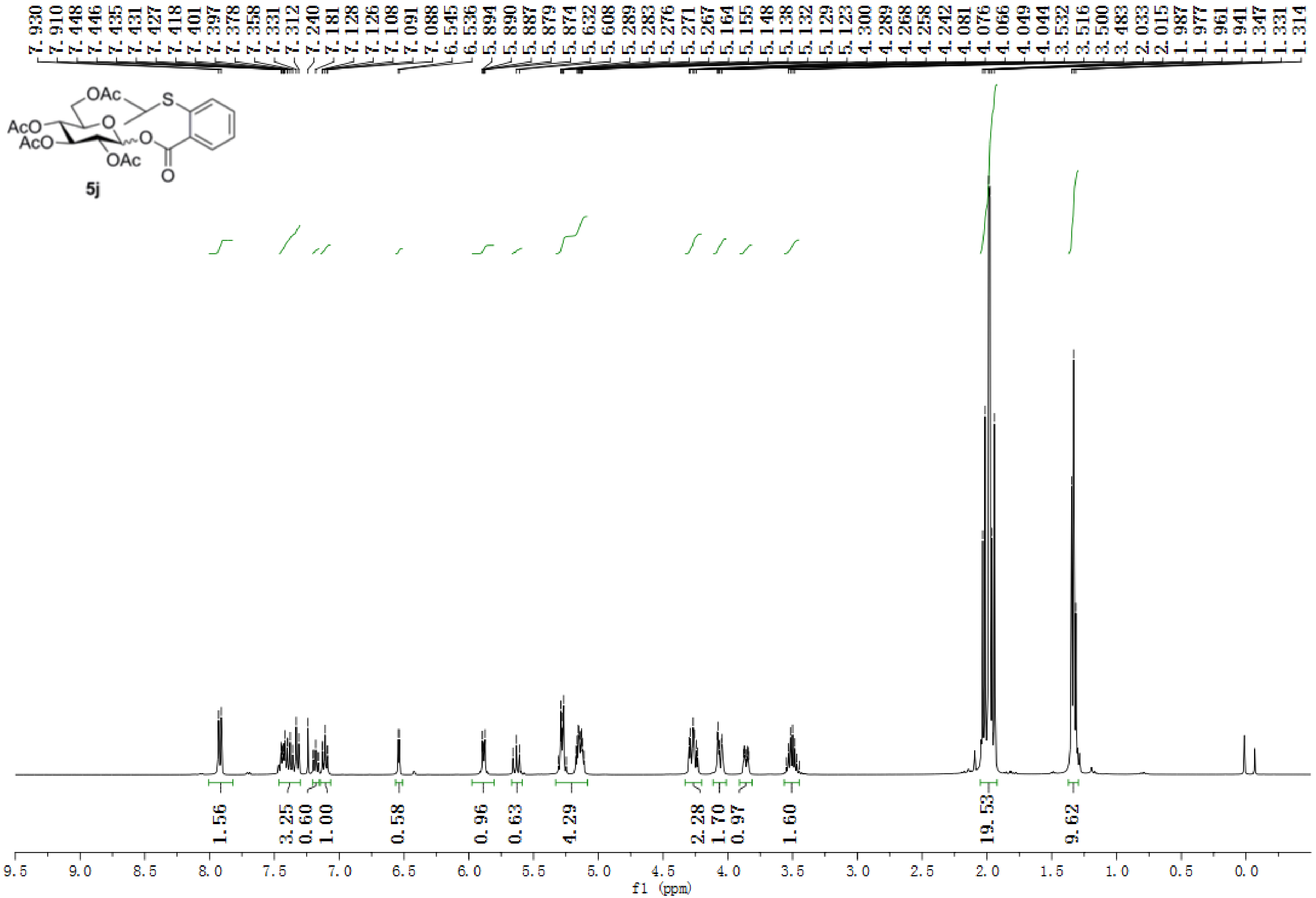


Figure S32. ^{1}H NMR spectrum of **5j** in $CDCl_3$

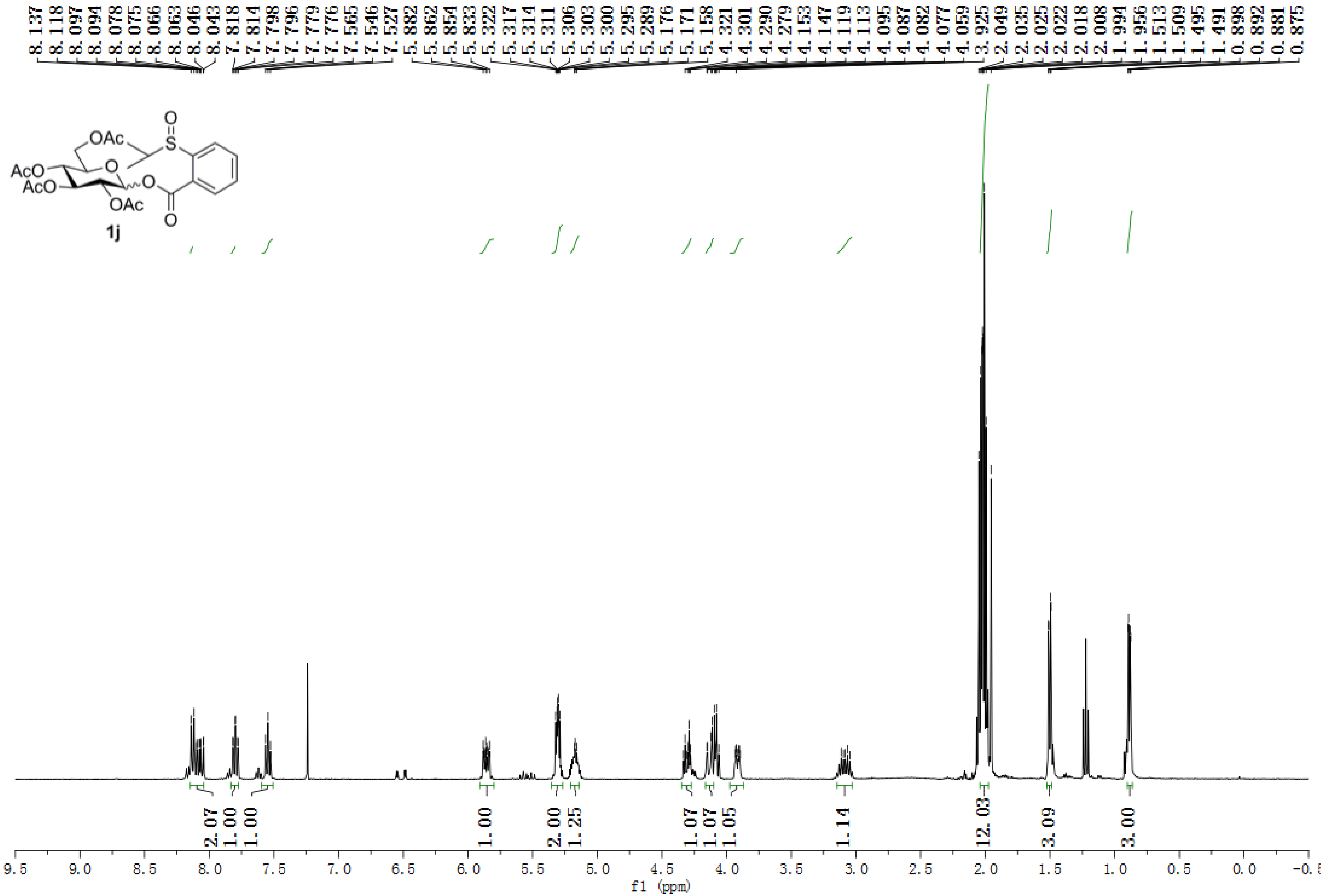


Figure S33. ^{1}H NMR spectrum of **1j** in $CDCl_3$

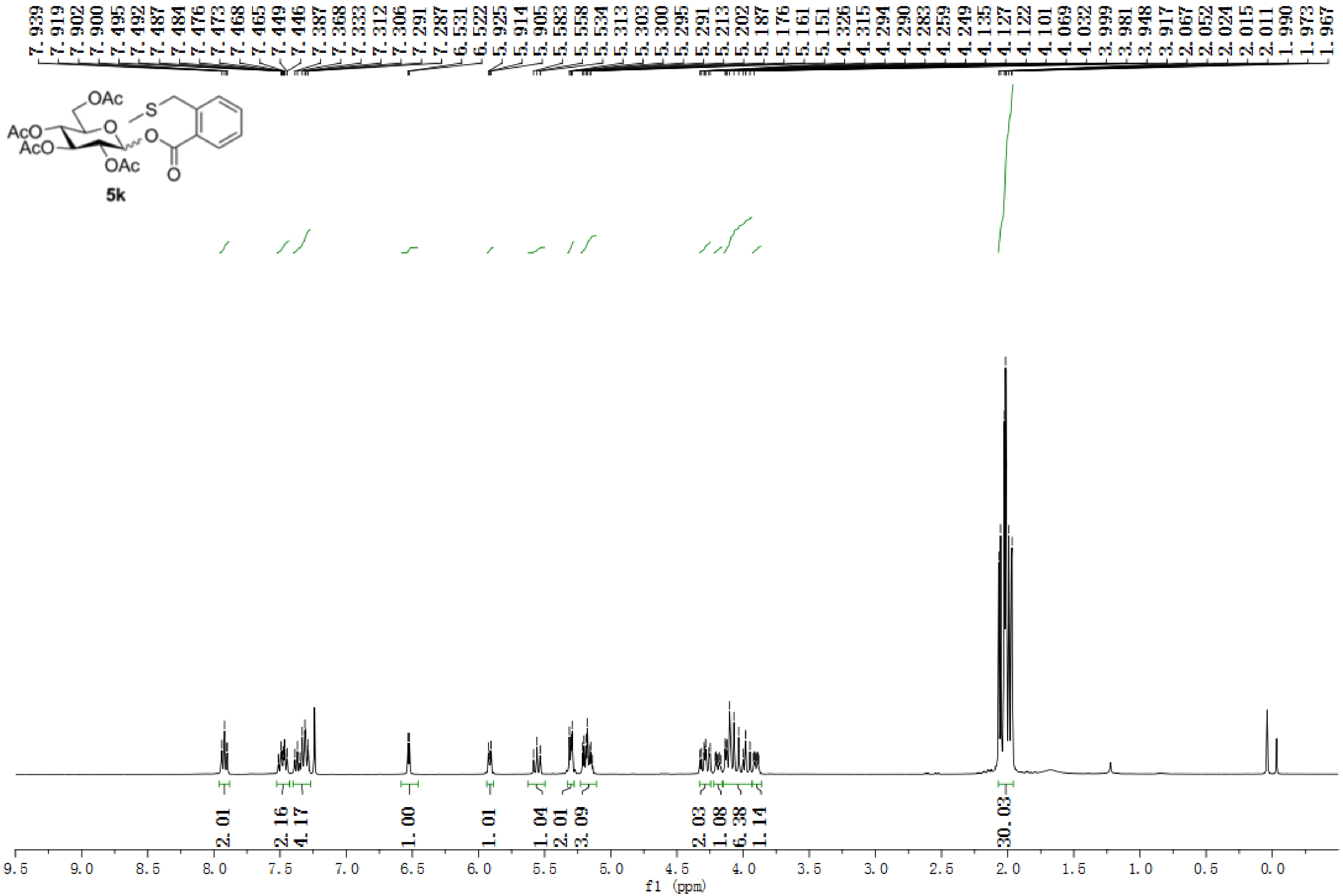


Figure S34. ^{1}H NMR spectrum of **5k** in $CDCl_3$

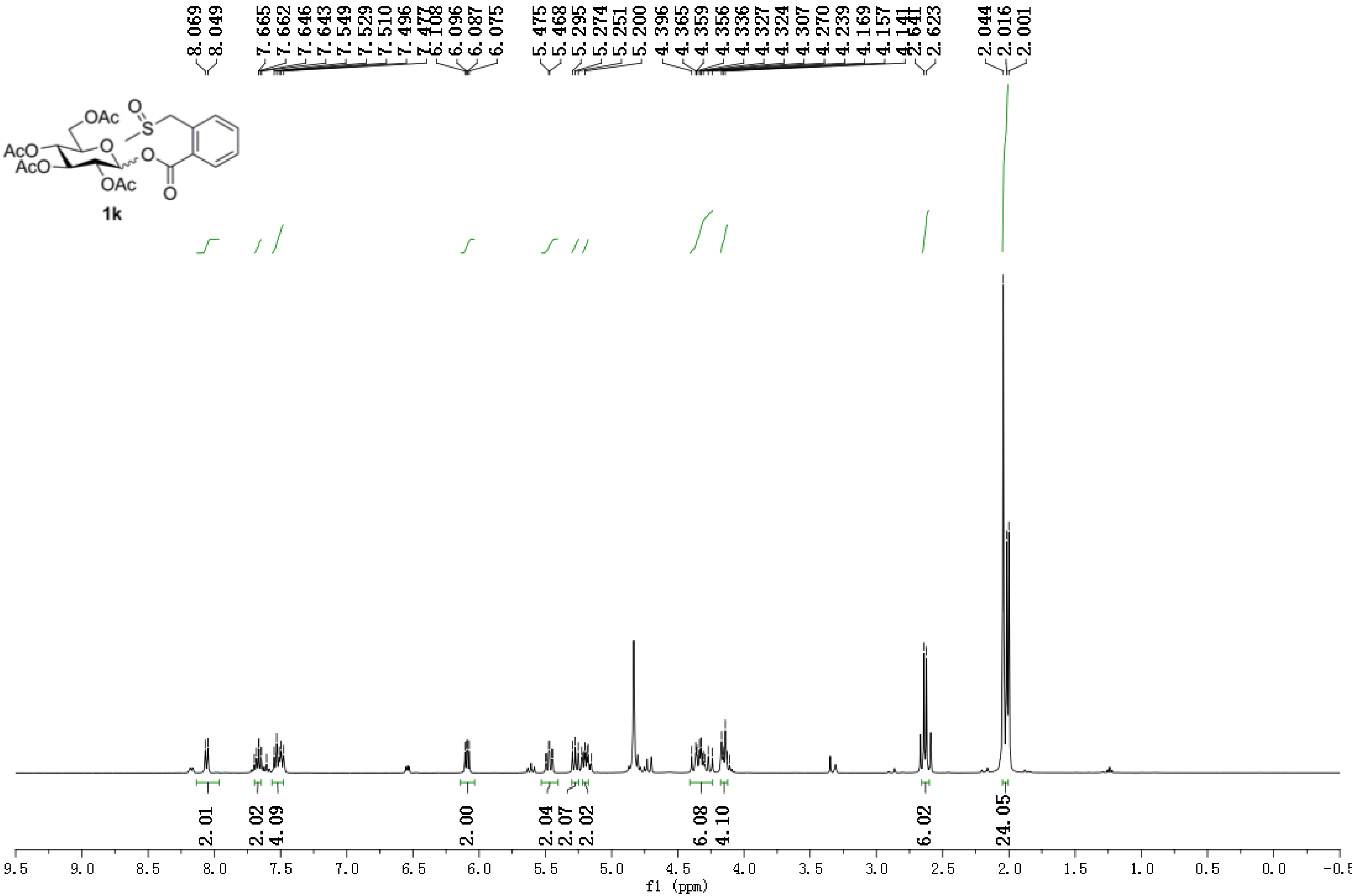


Figure S35. ^{1}H NMR spectrum of **1k** in CD_3OD

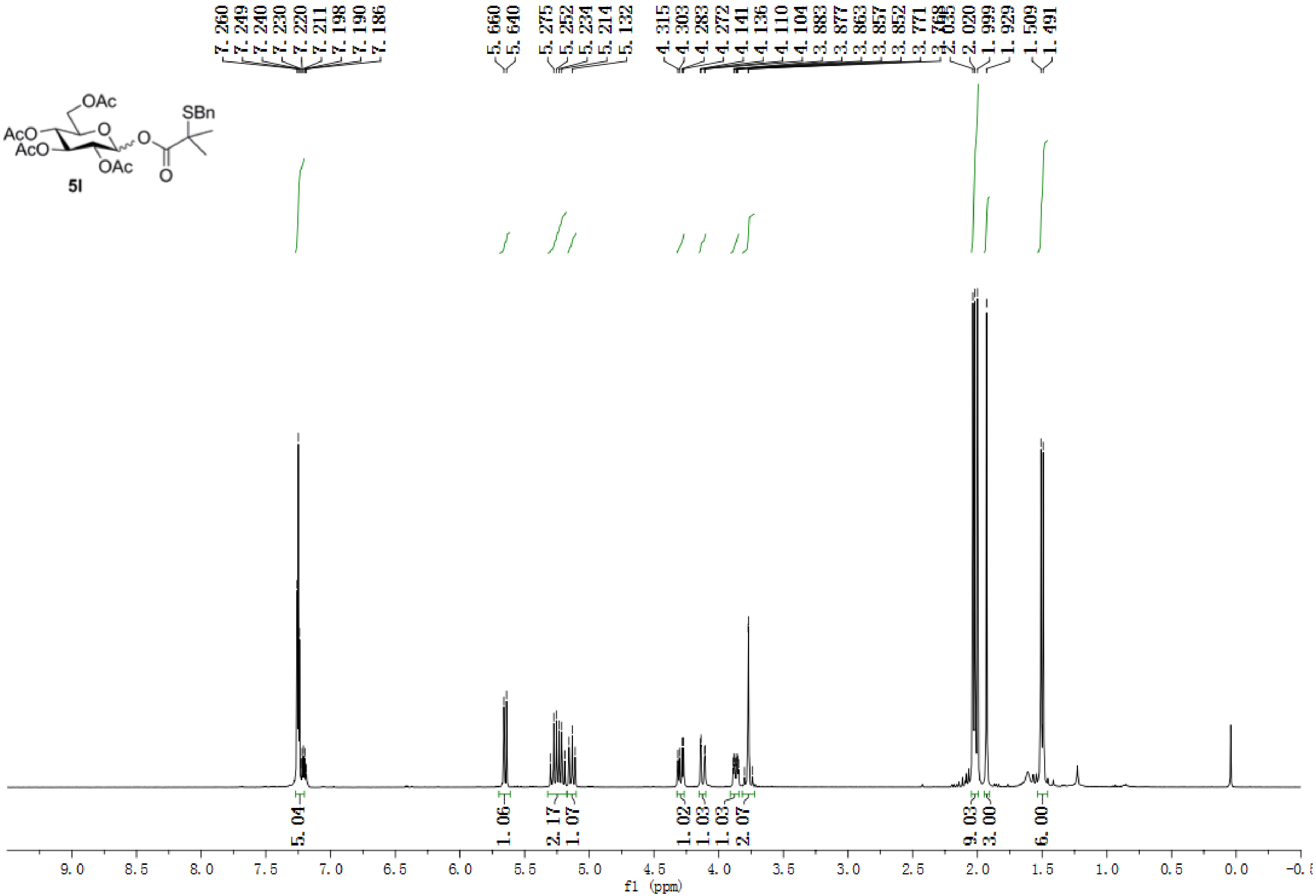


Figure S36. ^{1}H NMR spectrum of **5l** in $CDCl_3$

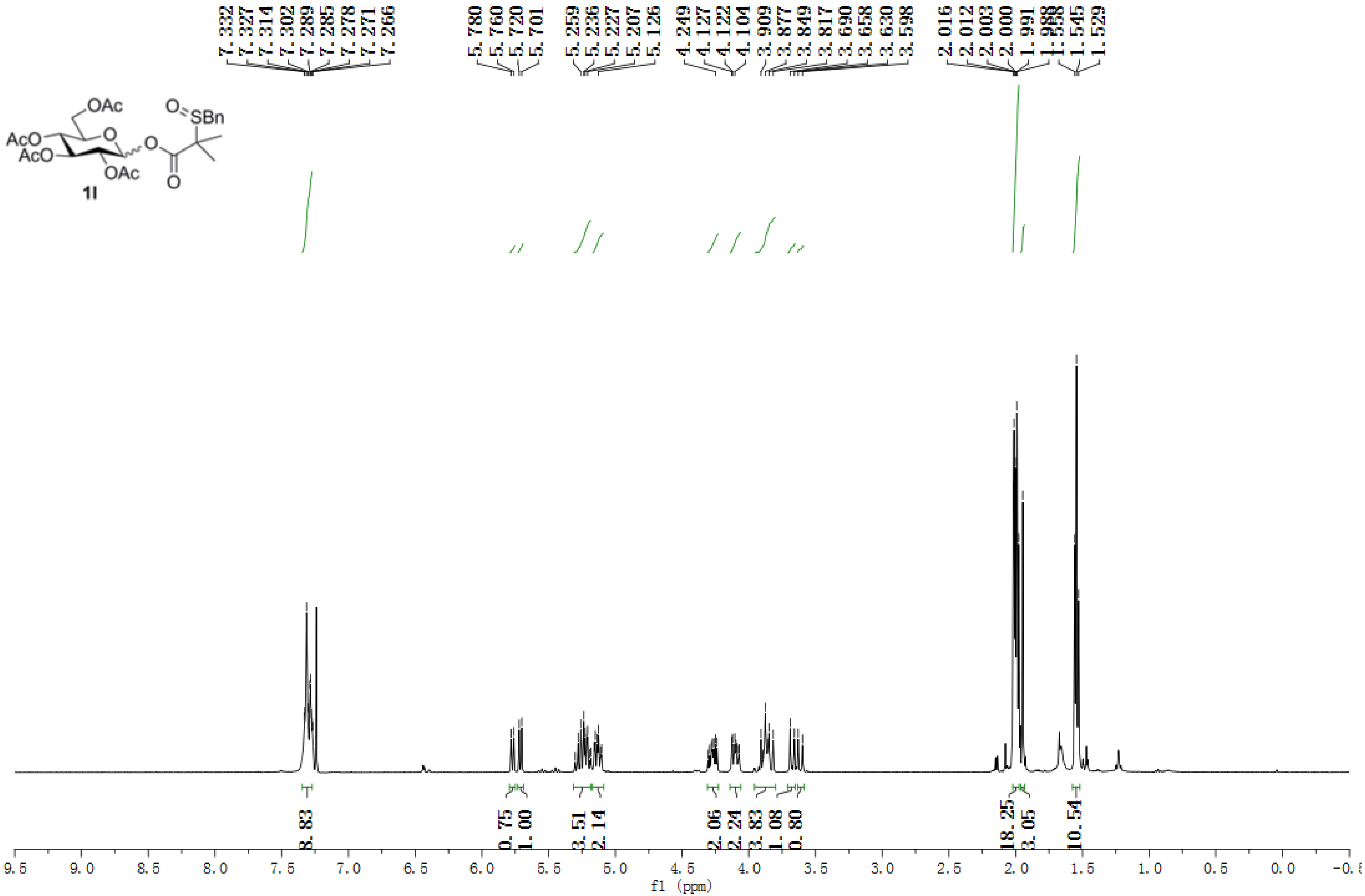


Figure S37. ^{1}H NMR spectrum of **1l** in $CDCl_3$

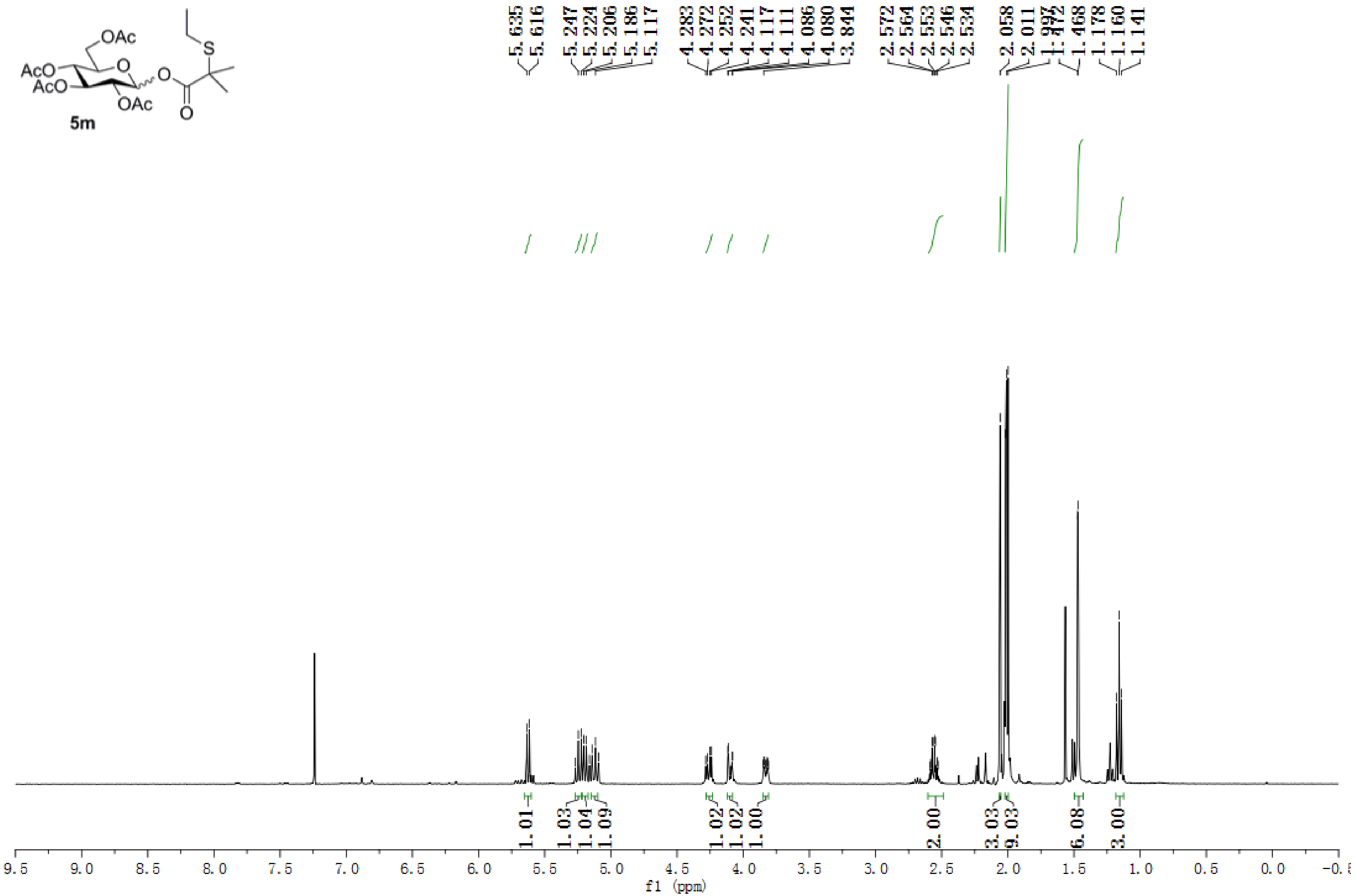


Figure S38. ^{1}H NMR spectrum of **5m** in $CDCl_3$

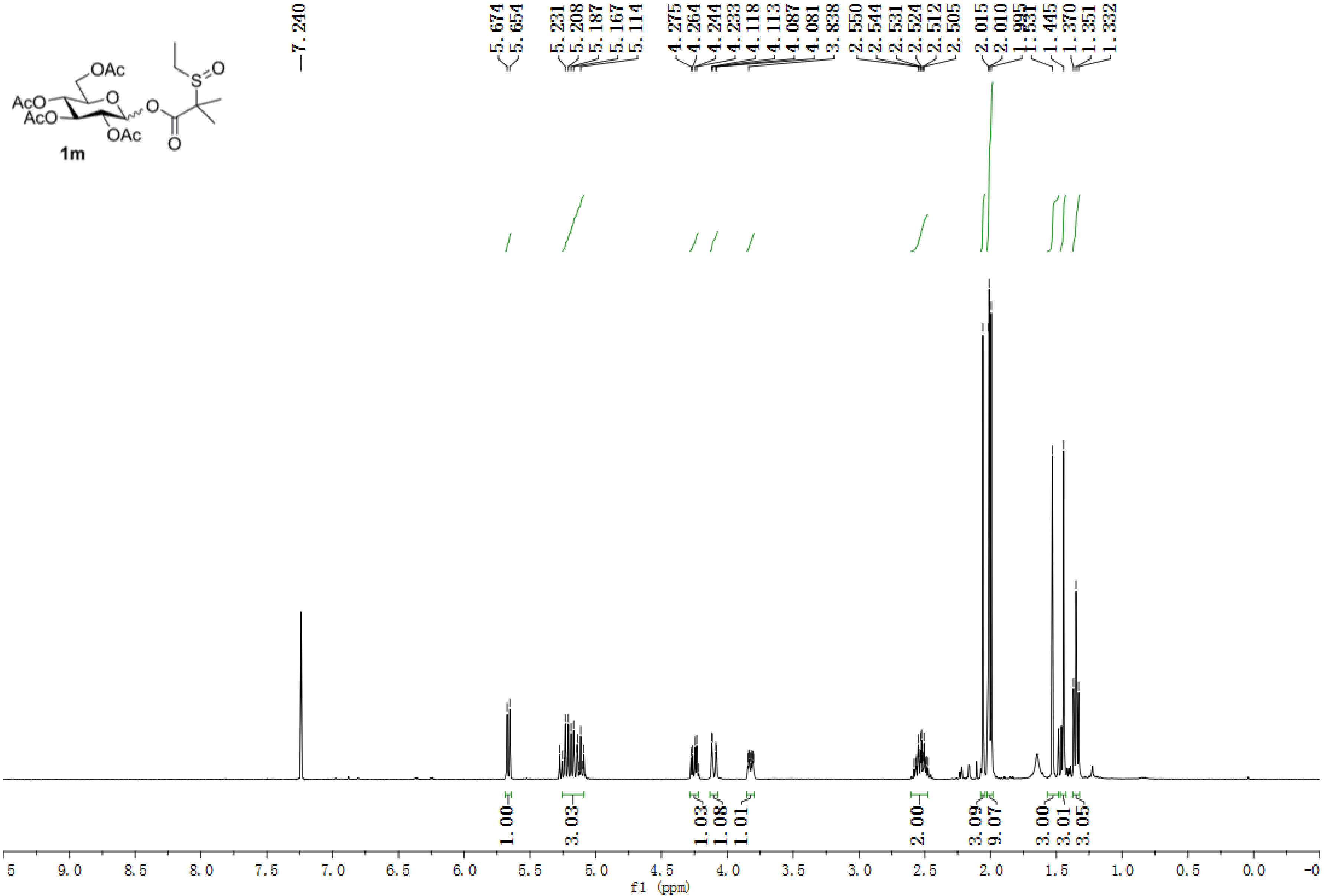


Figure S39. ^{1}H NMR spectrum of **1m** in $CDCl_3$

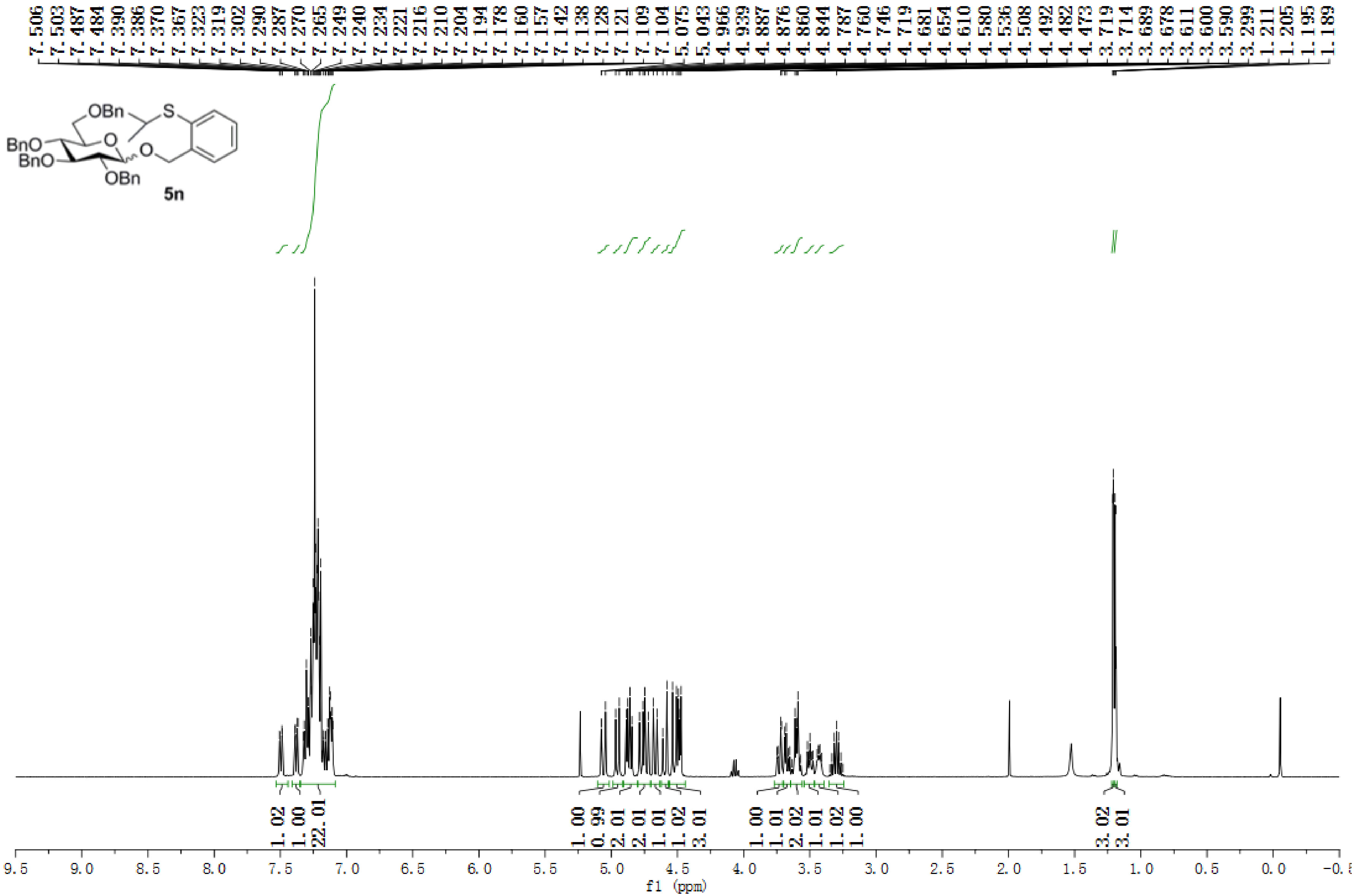


Figure S40. ^{1}H NMR spectrum of **5n** in $CDCl_3$

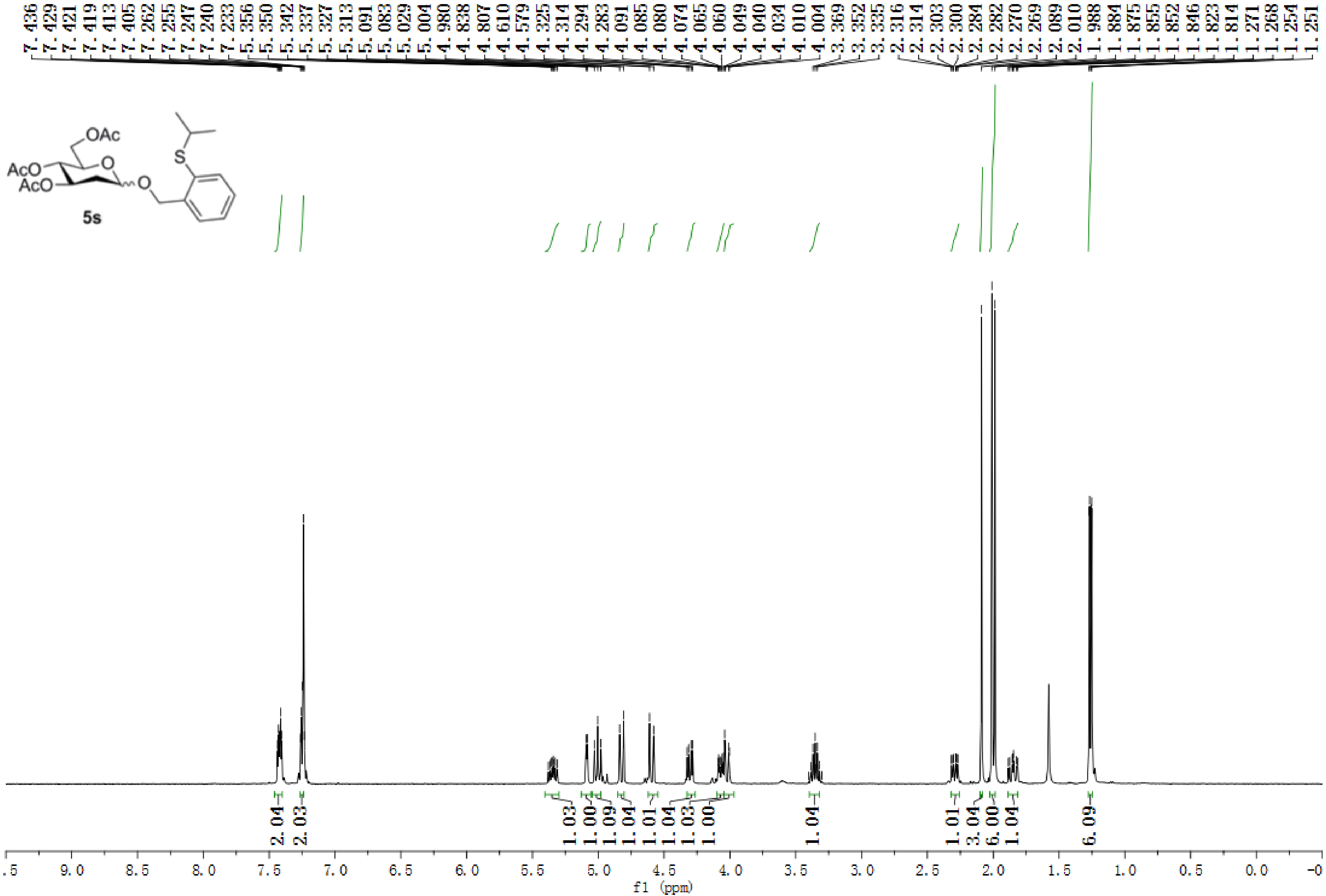


Figure S41. ^{1}H NMR spectrum of **5s** in $CDCl_3$

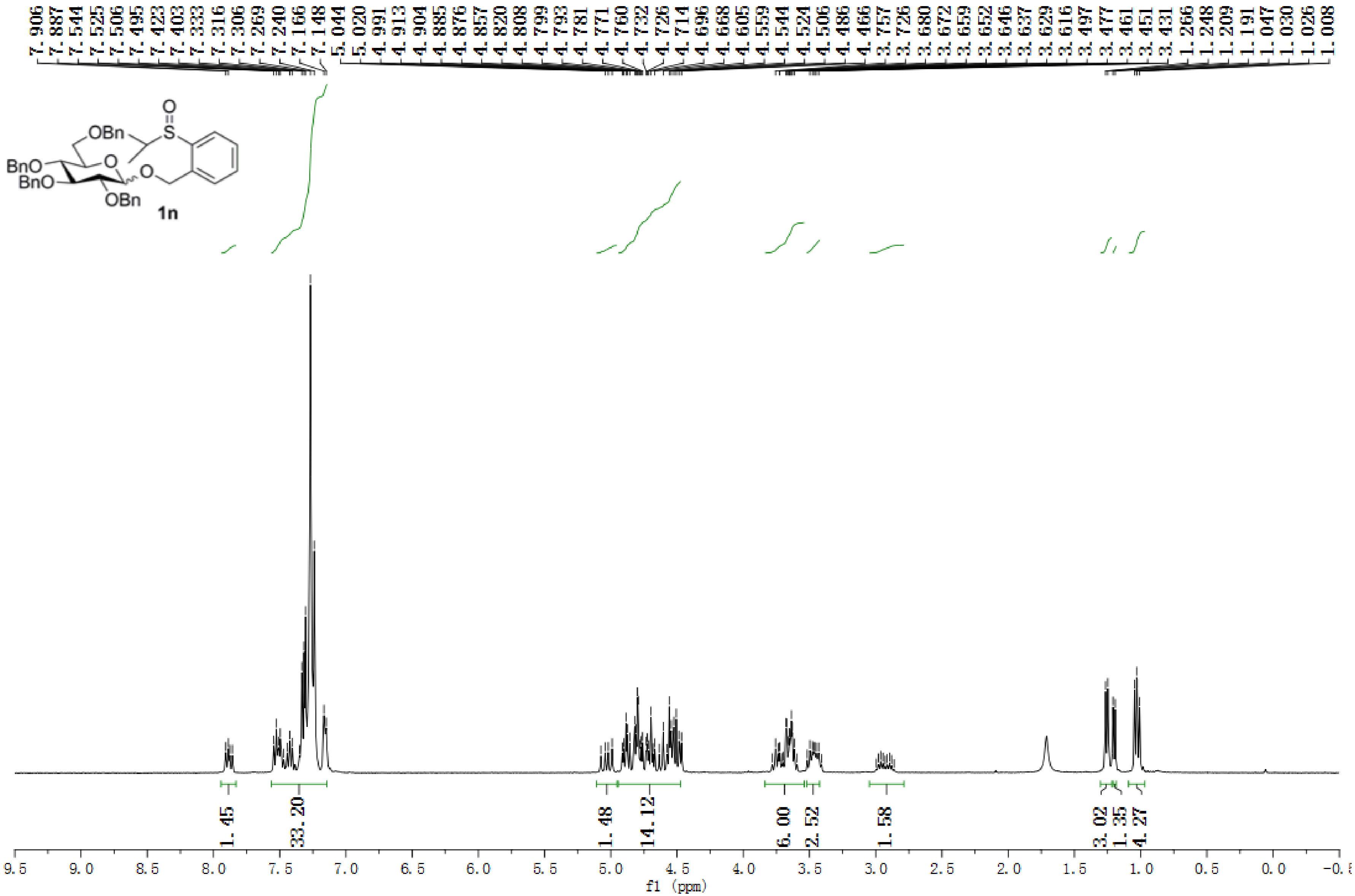


Figure S42. ^{1}H NMR spectrum of **1n** in $CDCl_3$

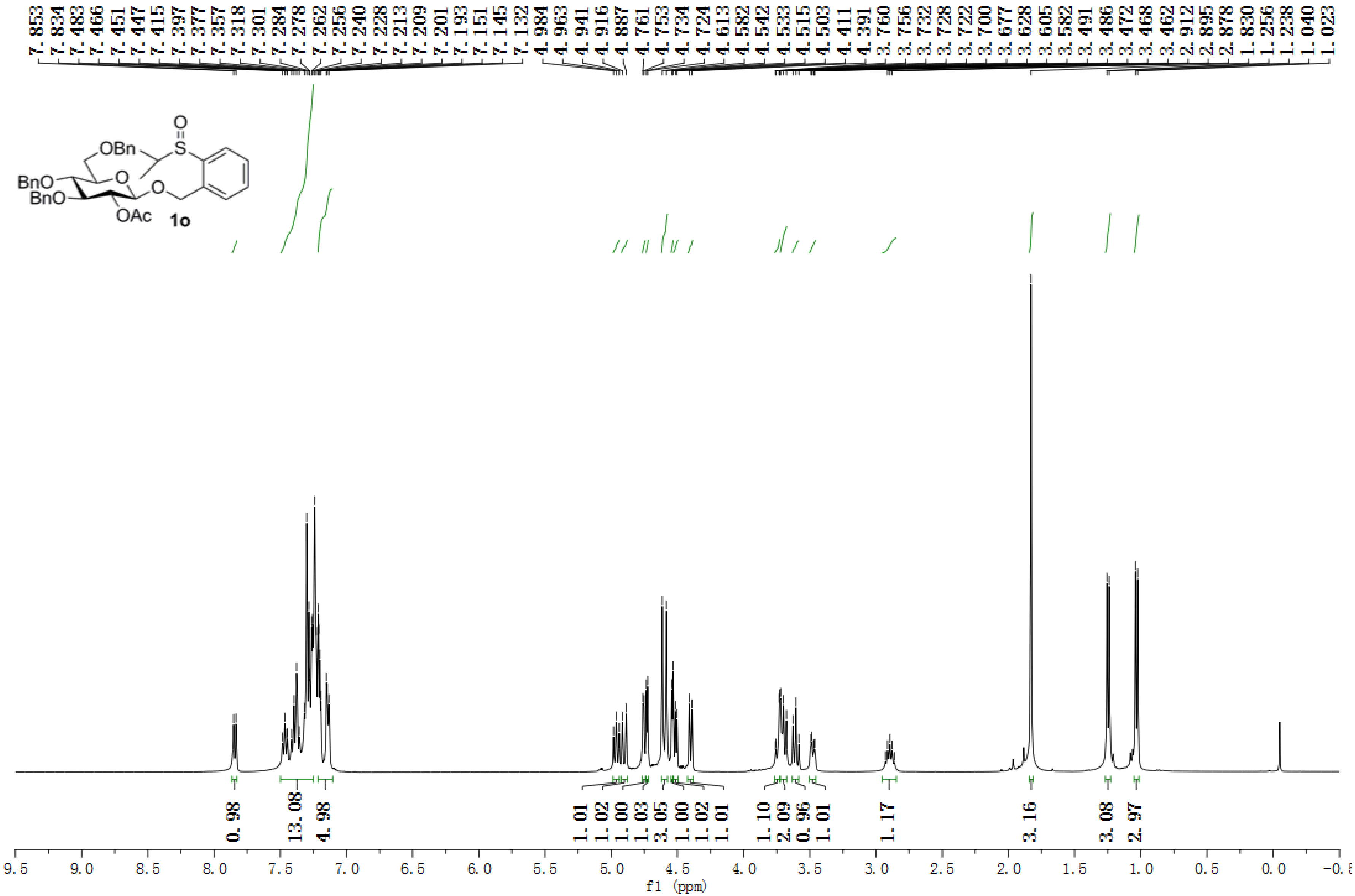


Figure S43. ^{1}H NMR spectrum of **1o** in CDCl$_3$

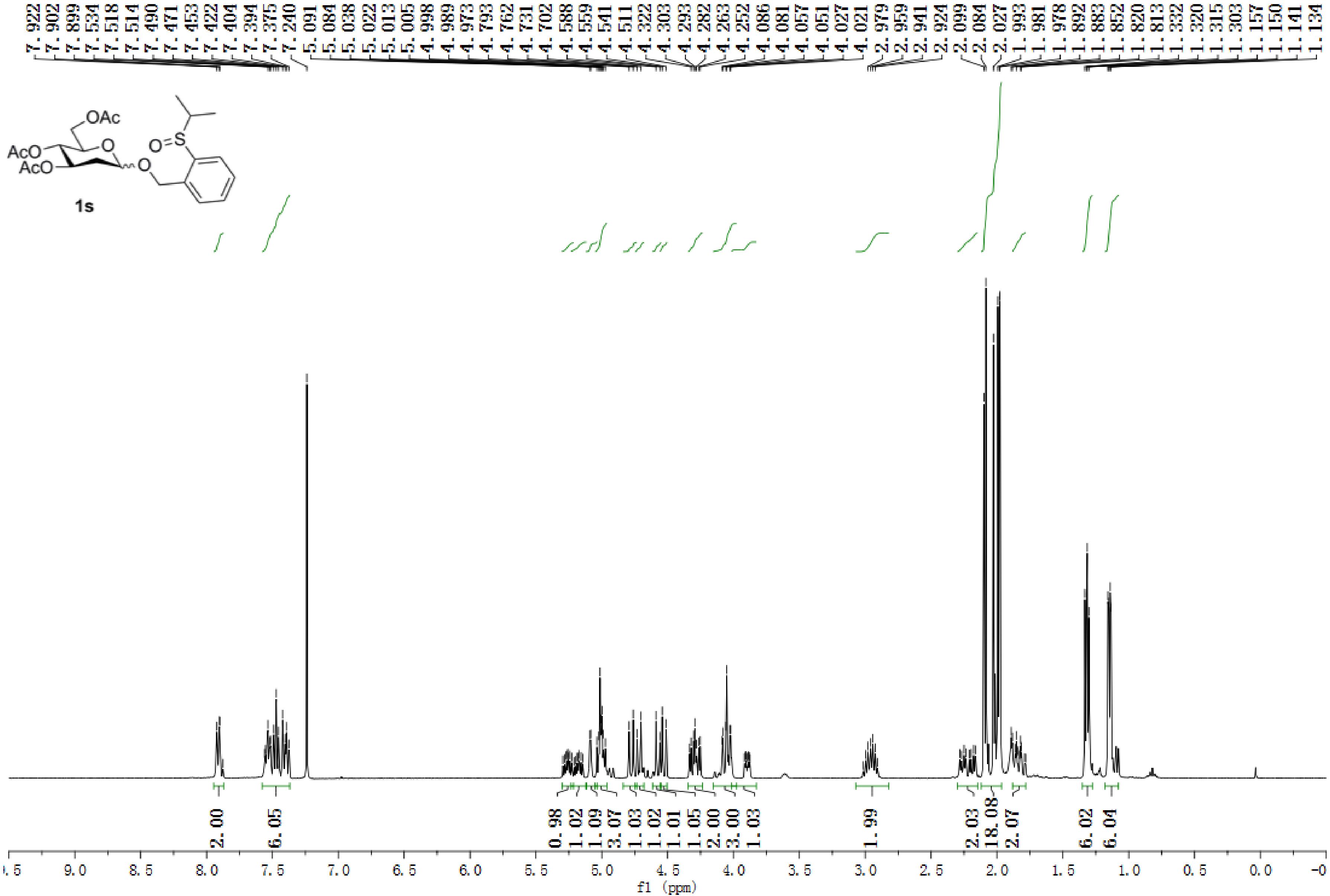


Figure S44. ^{1}H NMR spectrum of **1s** in $CDCl_3$

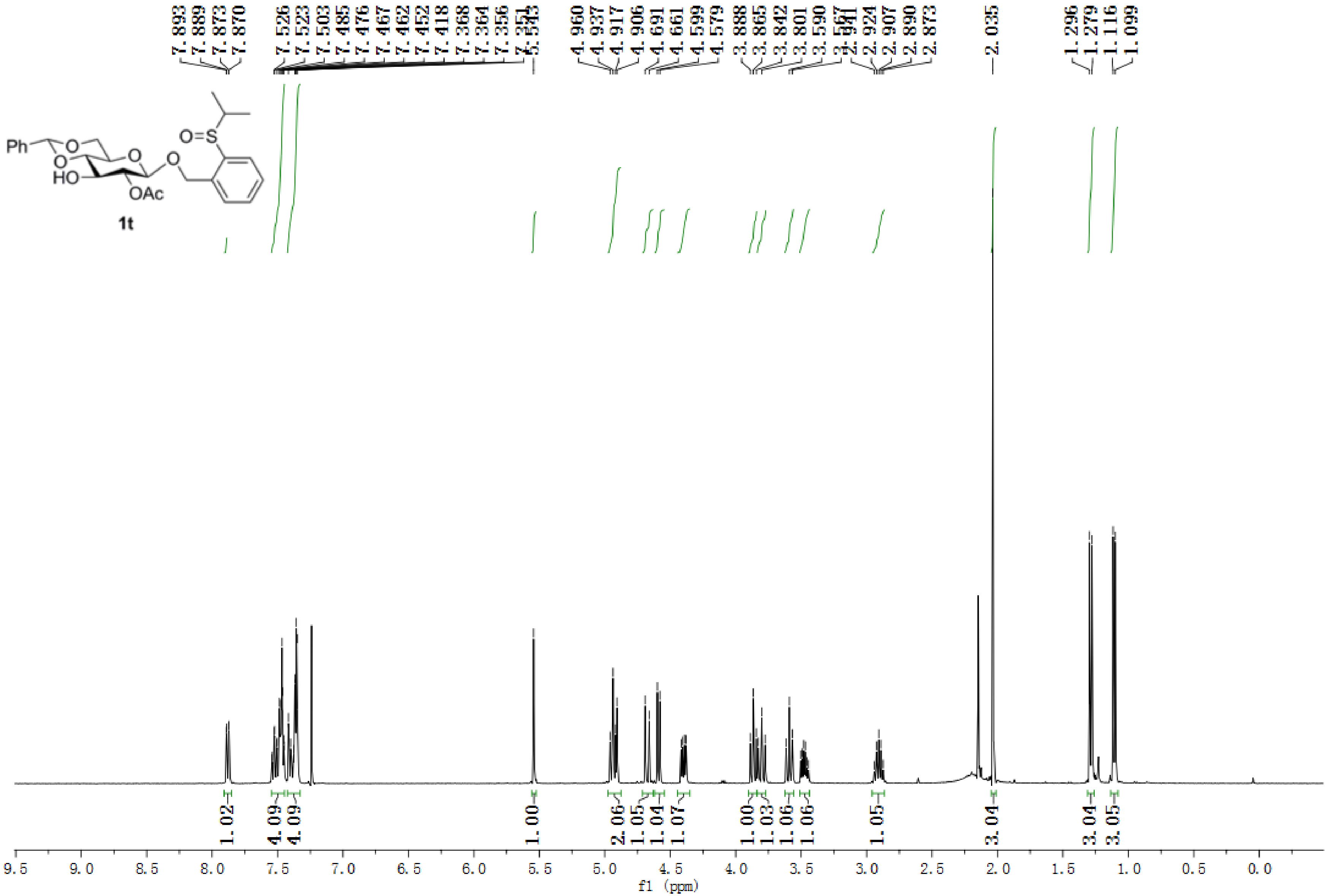


Figure S45. ^{1}H NMR spectrum of **1t** in $CDCl_3$

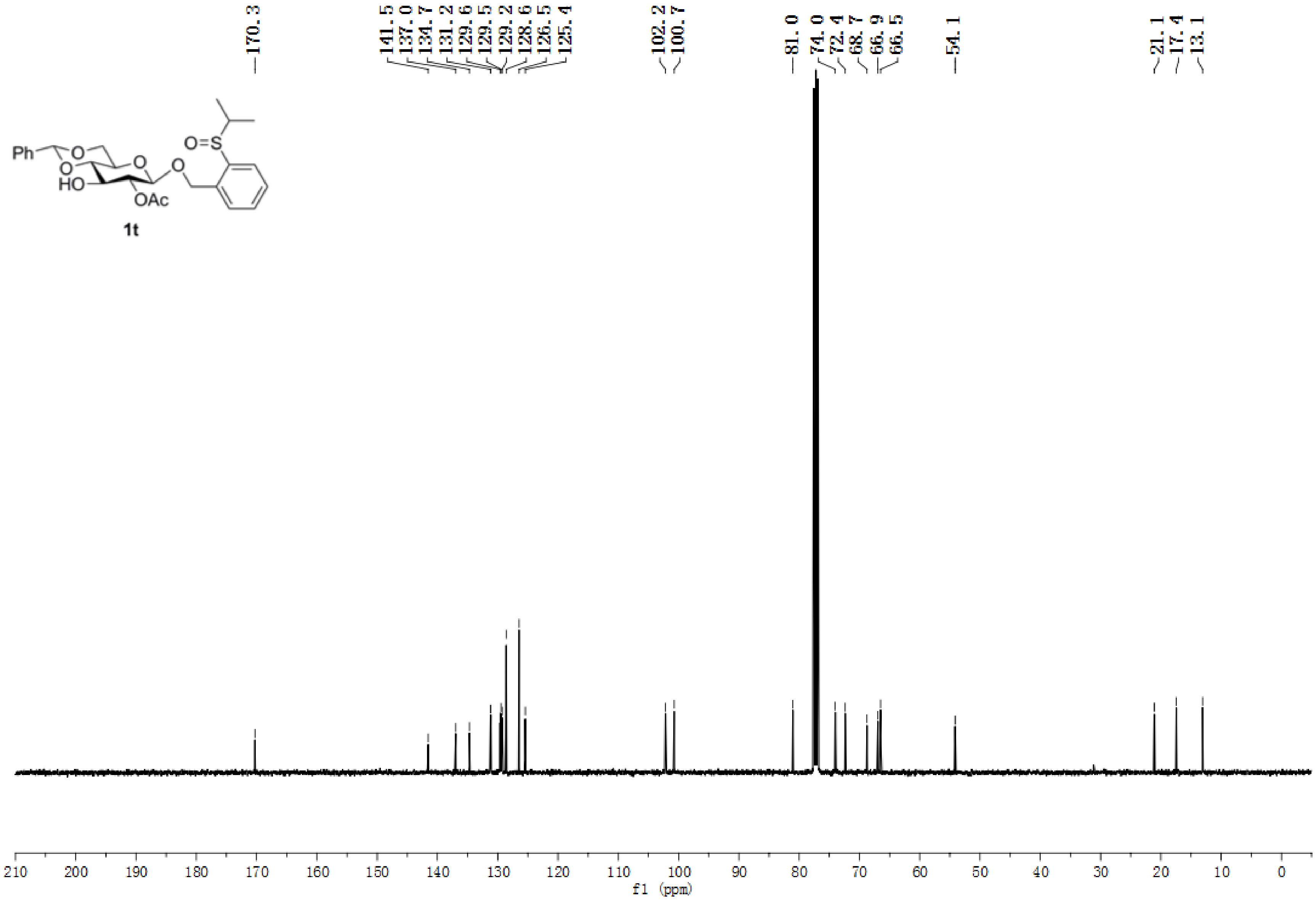


Figure S46. ^{13}C NMR spectrum of **1t** in $CDCl_3$

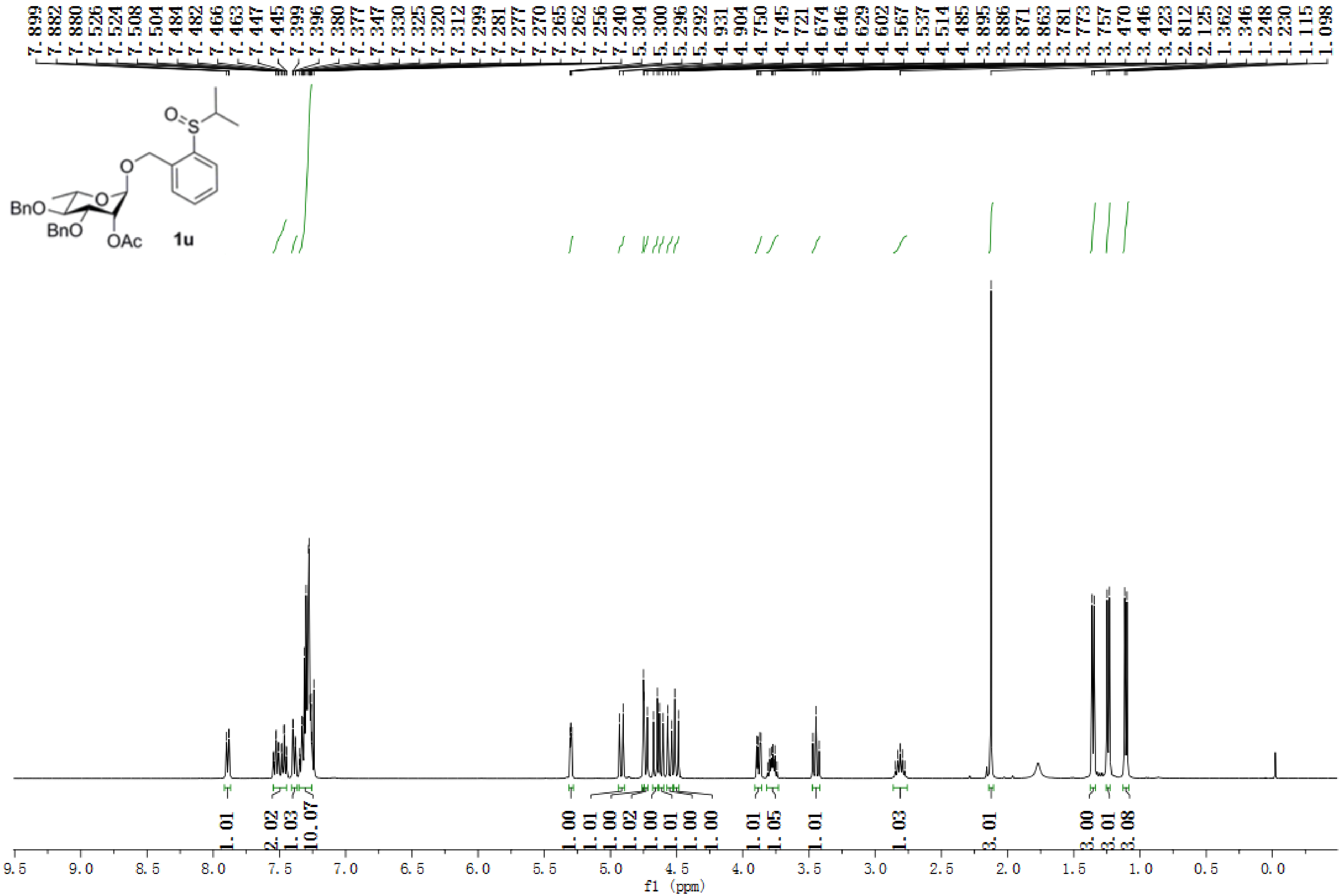


Figure S47. ^{1}H NMR spectrum of **1u** in $CDCl_3$

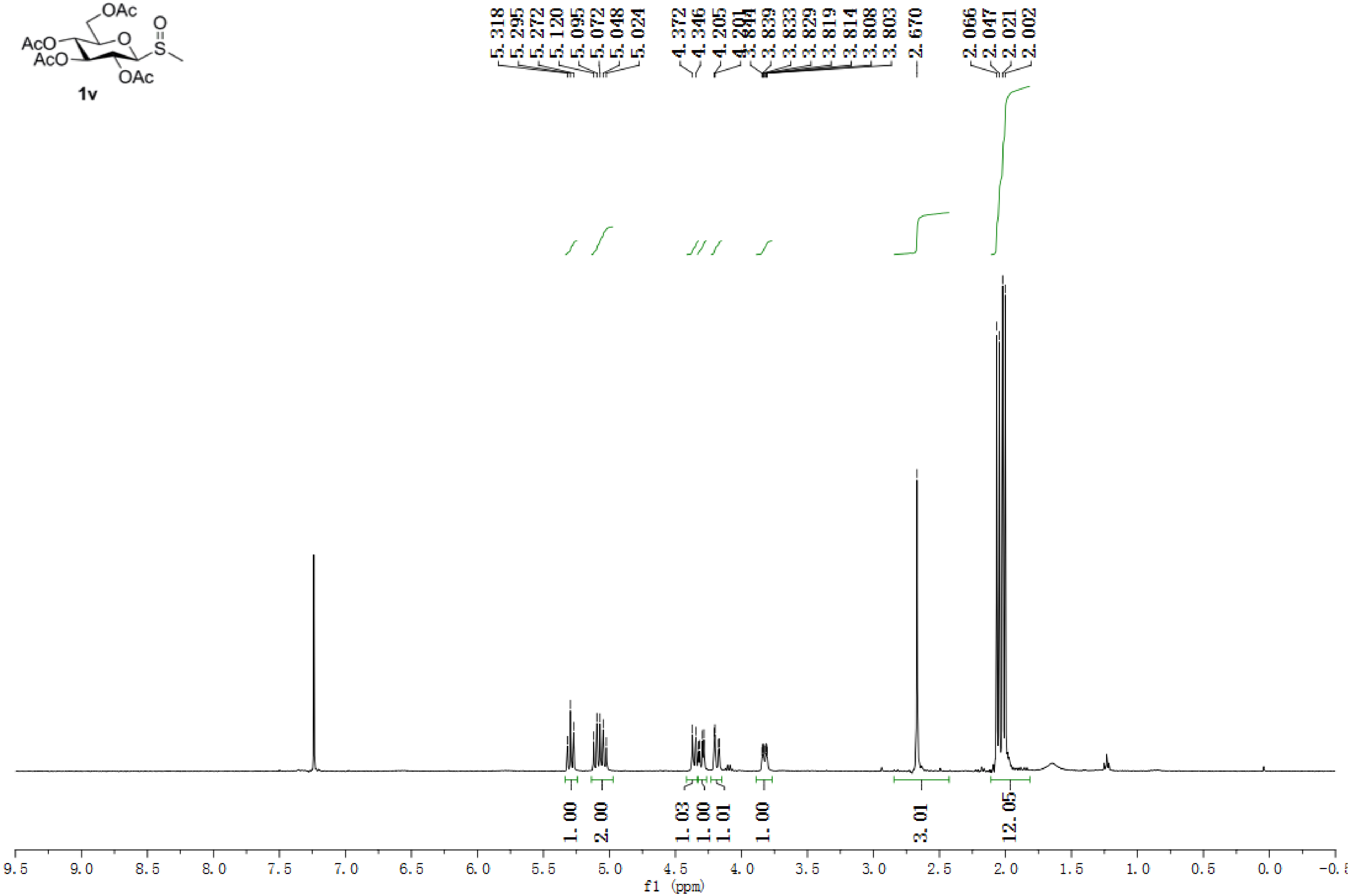


Figure S48. ^{1}H NMR spectrum of **1v** in $CDCl_3$

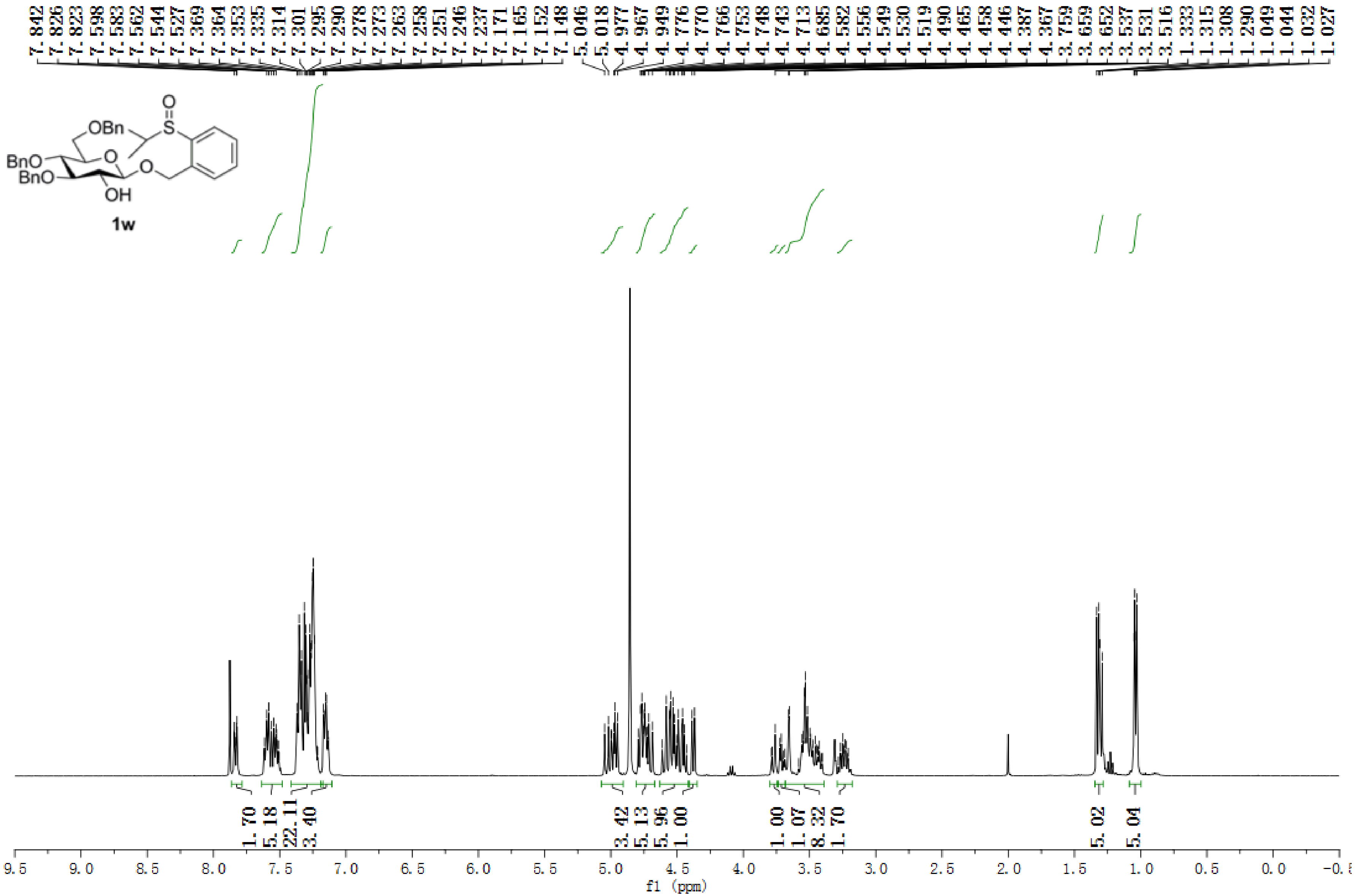


Figure S49. ^{1}H NMR spectrum of **1w** in CD_3OD

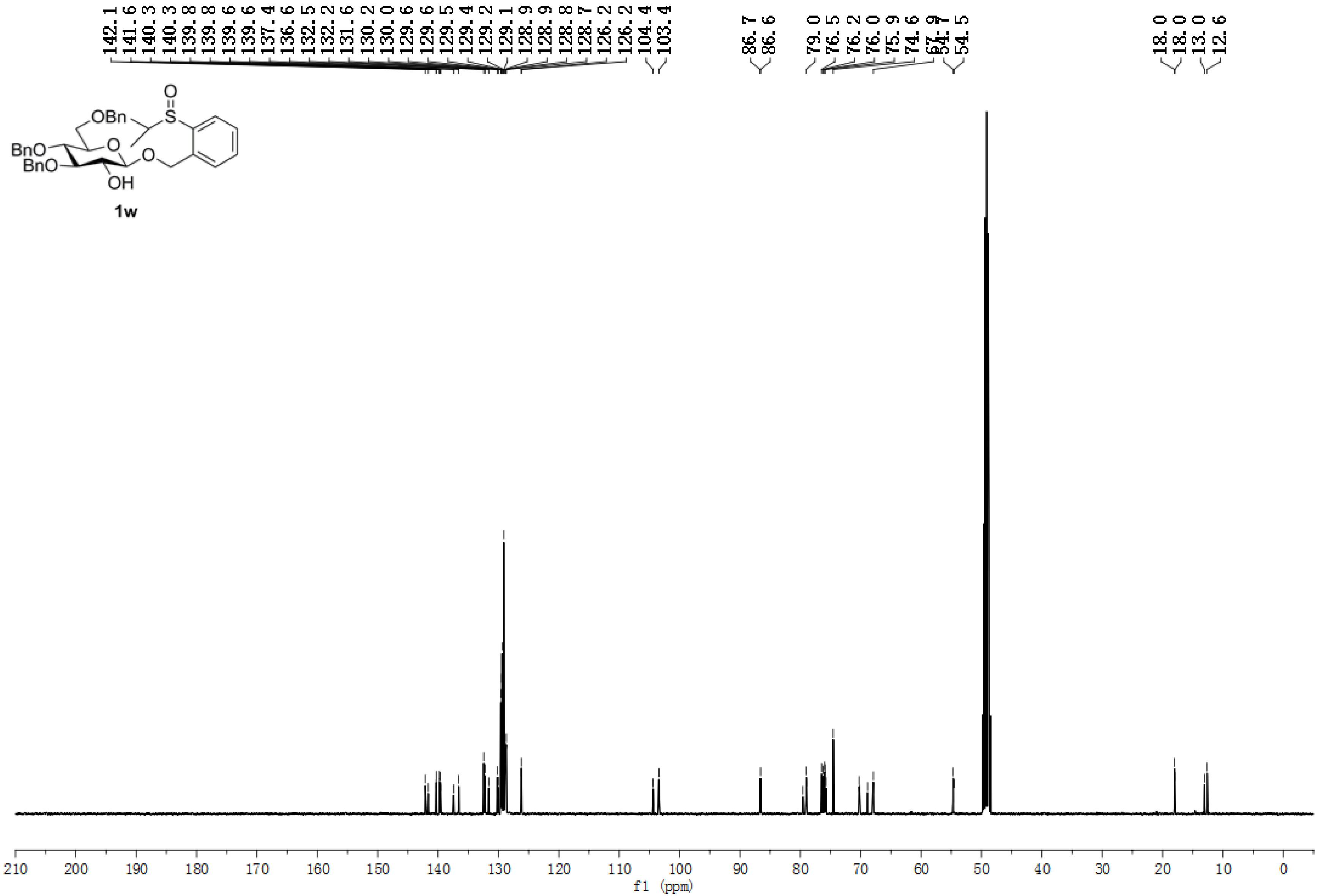


Figure S50. ^{13}C NMR spectrum of **1w** in CD_3OD

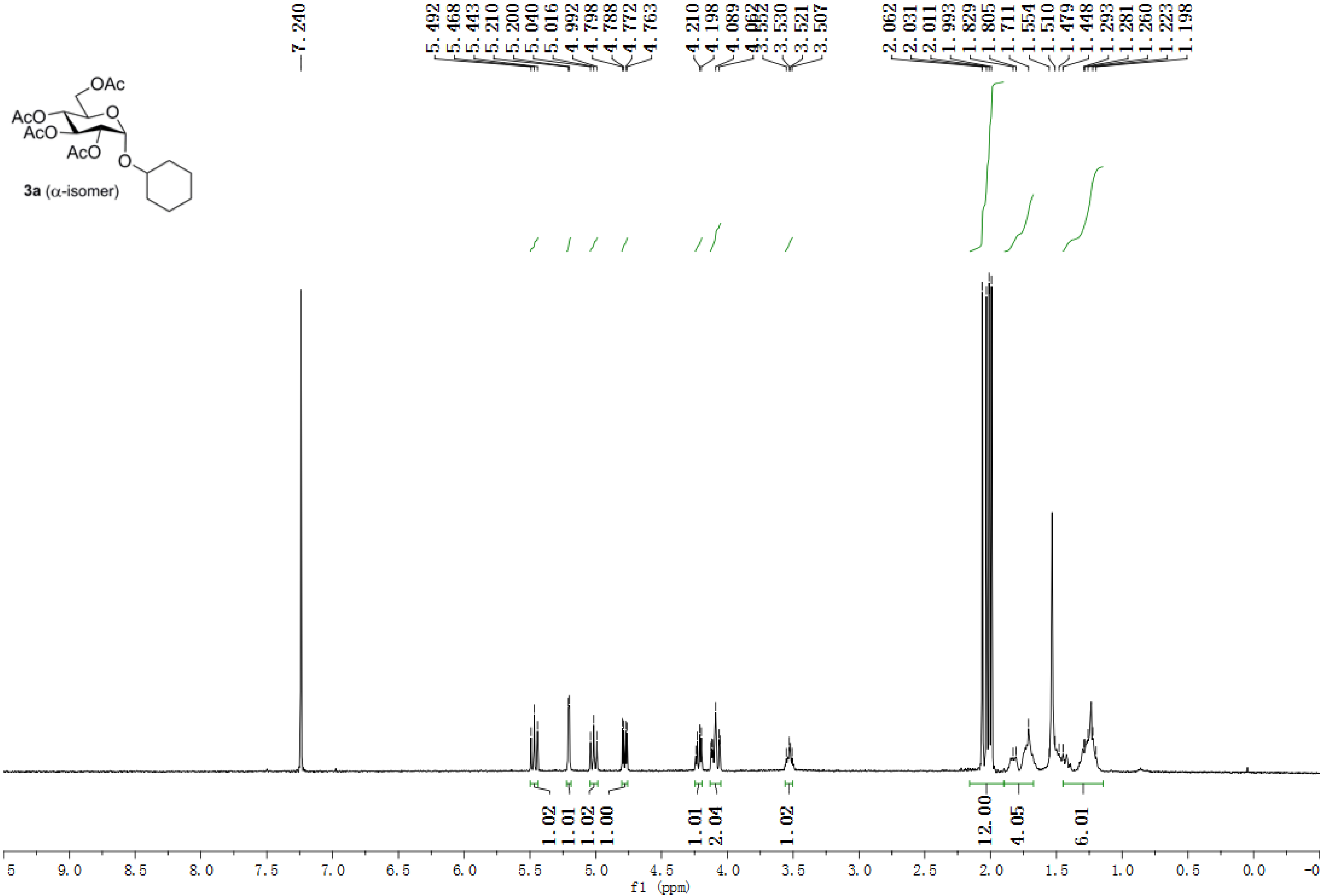


Figure S51. ^{1}H NMR spectrum of **3a** (α-isomer) in $CDCl_3$

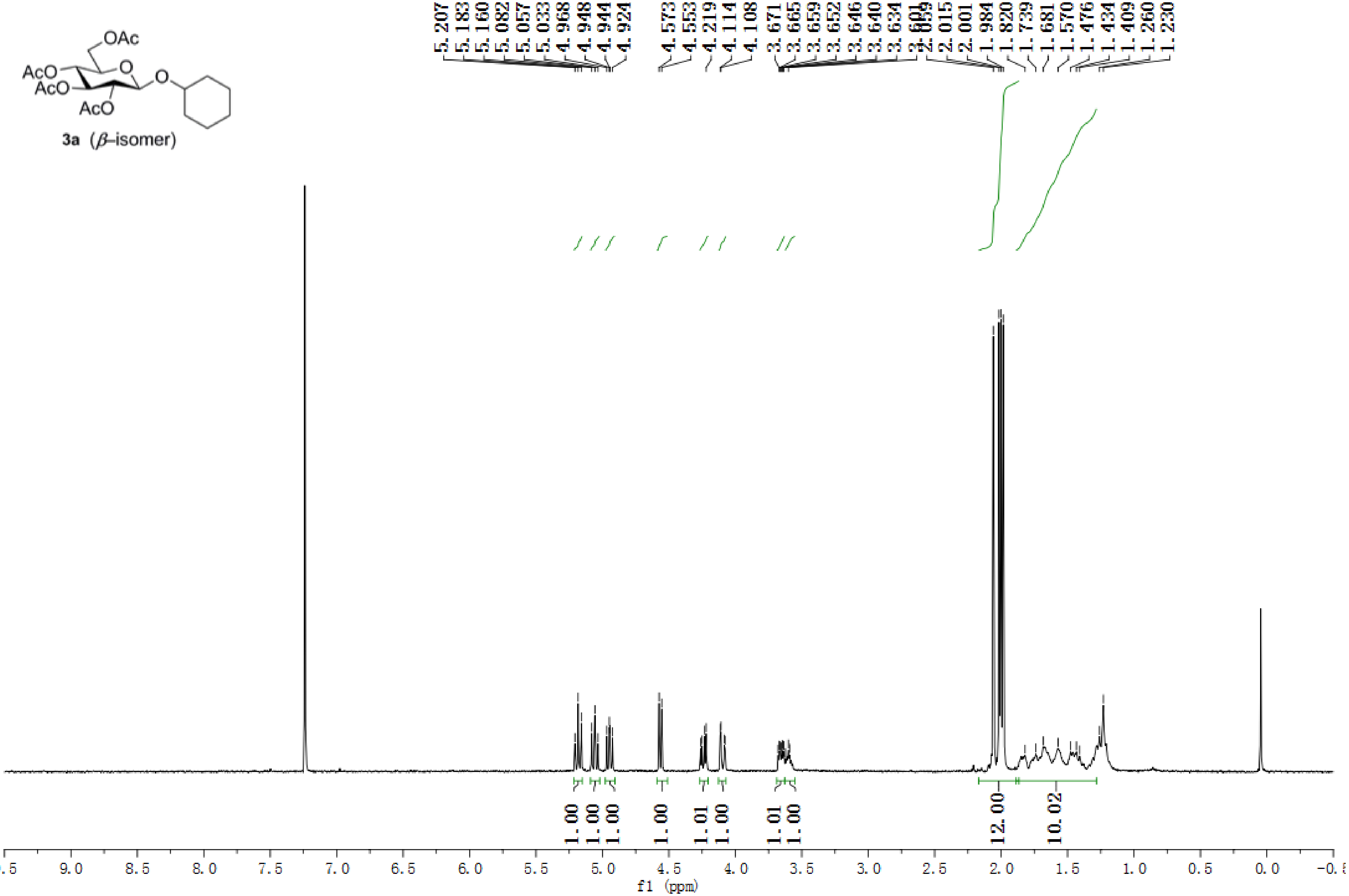


Figure S52. ^{1}H NMR spectrum of **3a** (β-isomer) in $CDCl_3$

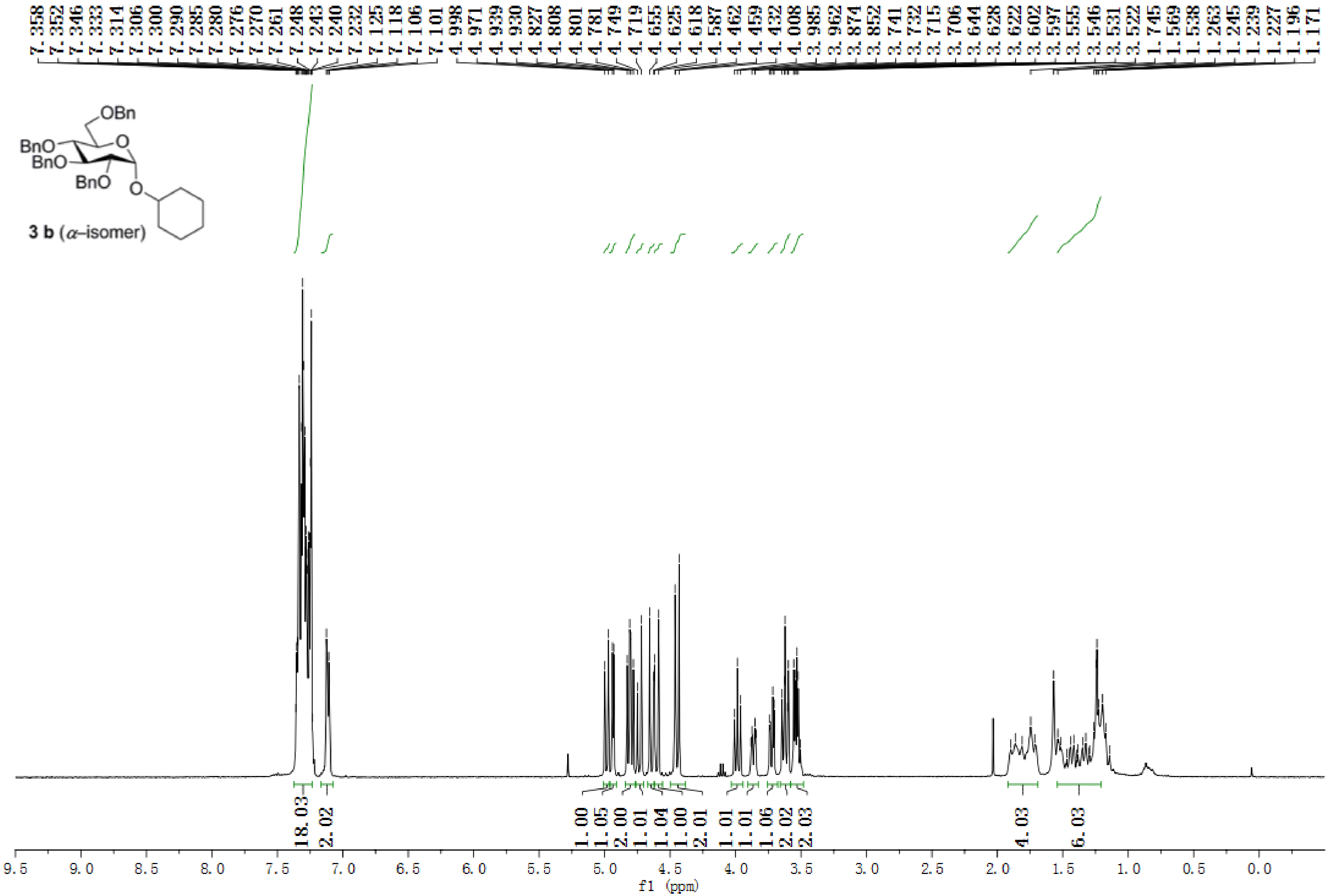


Figure S53. ^{1}H NMR spectrum of **3b** (α-isomer) in $CDCl_3$

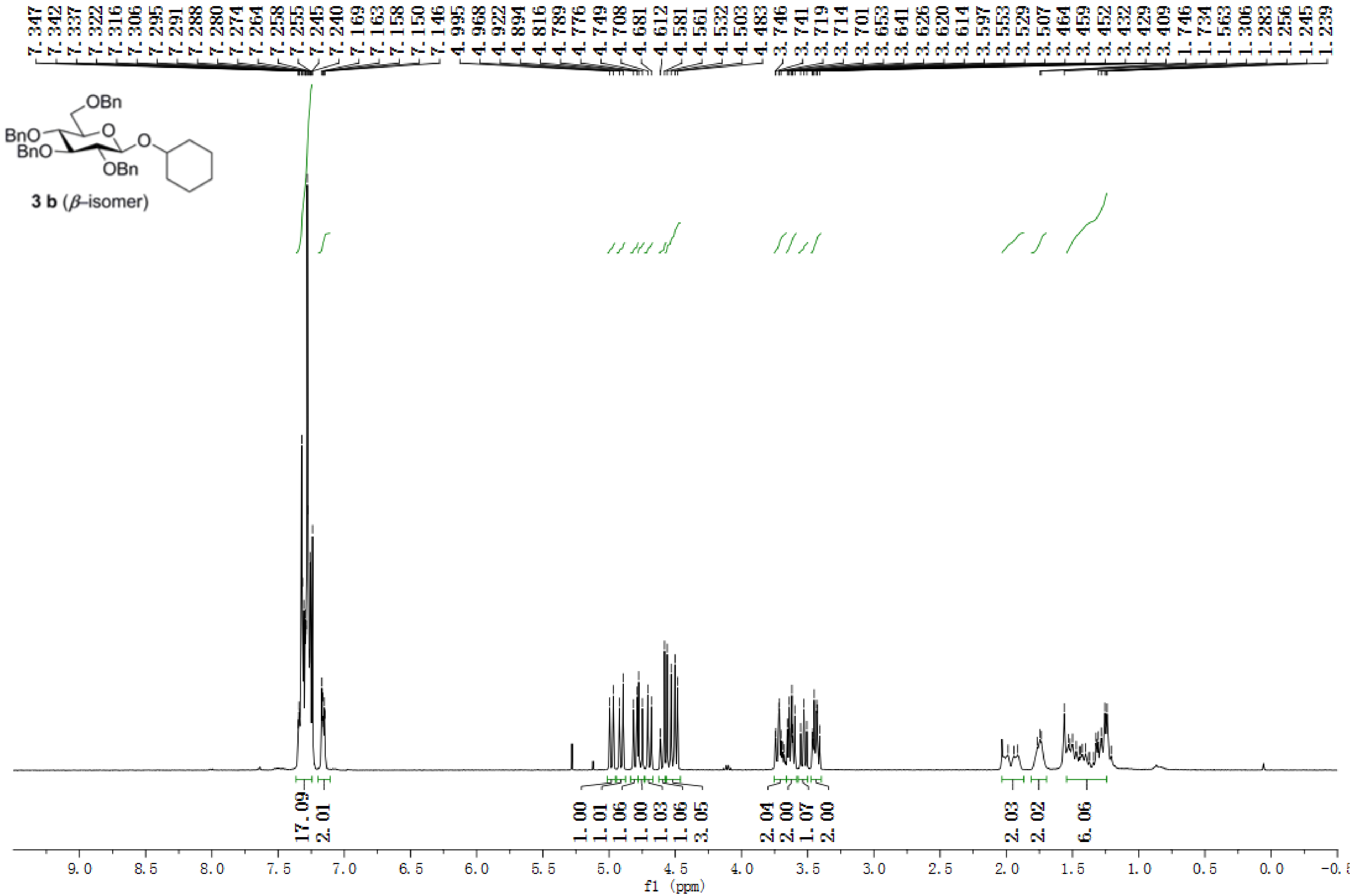


Figure S54. ^{1}H NMR spectrum of **3b** (β-isomer) in $CDCl_3$

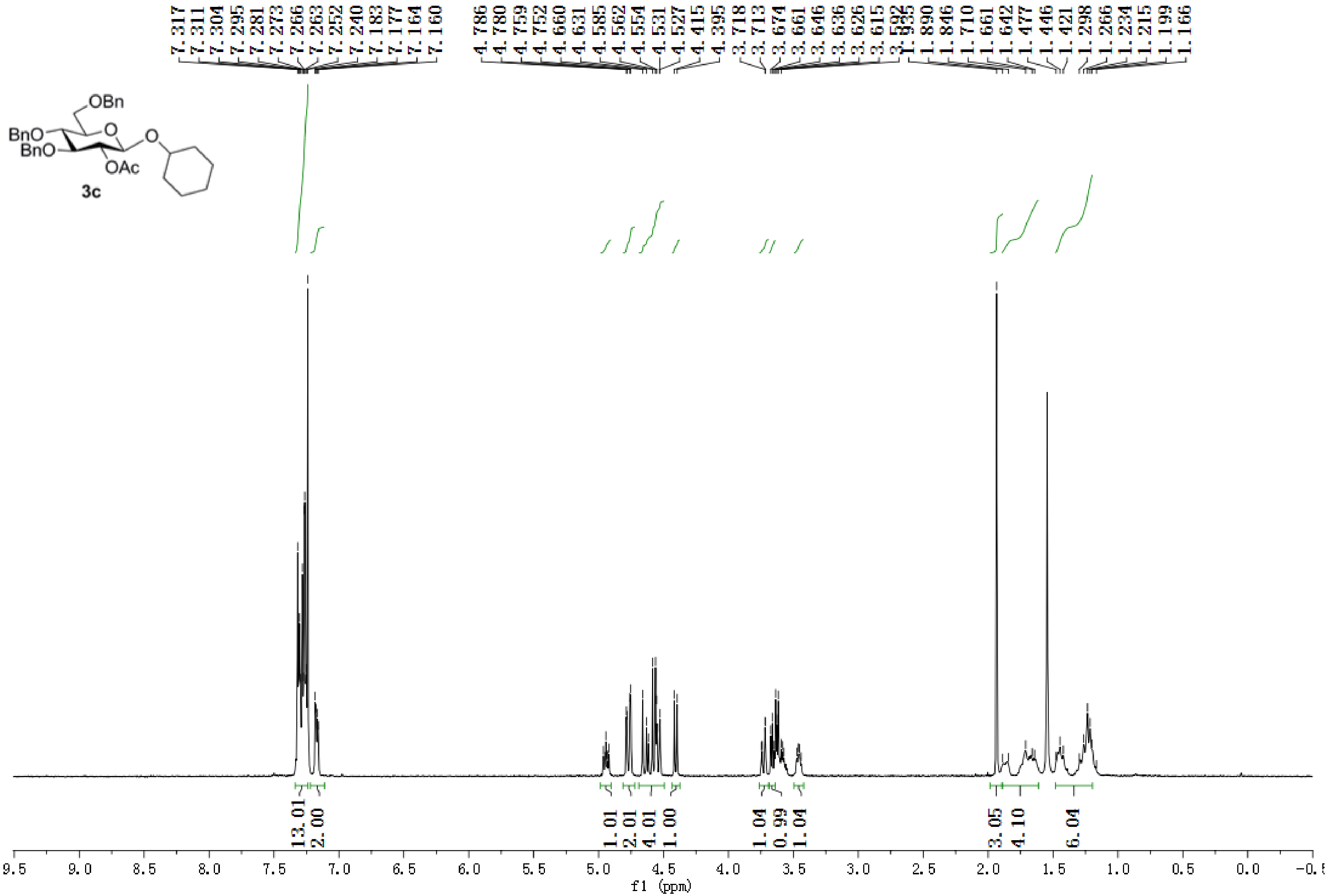


Figure S55. ^{1}H NMR spectrum of **3c** in $CDCl_3$

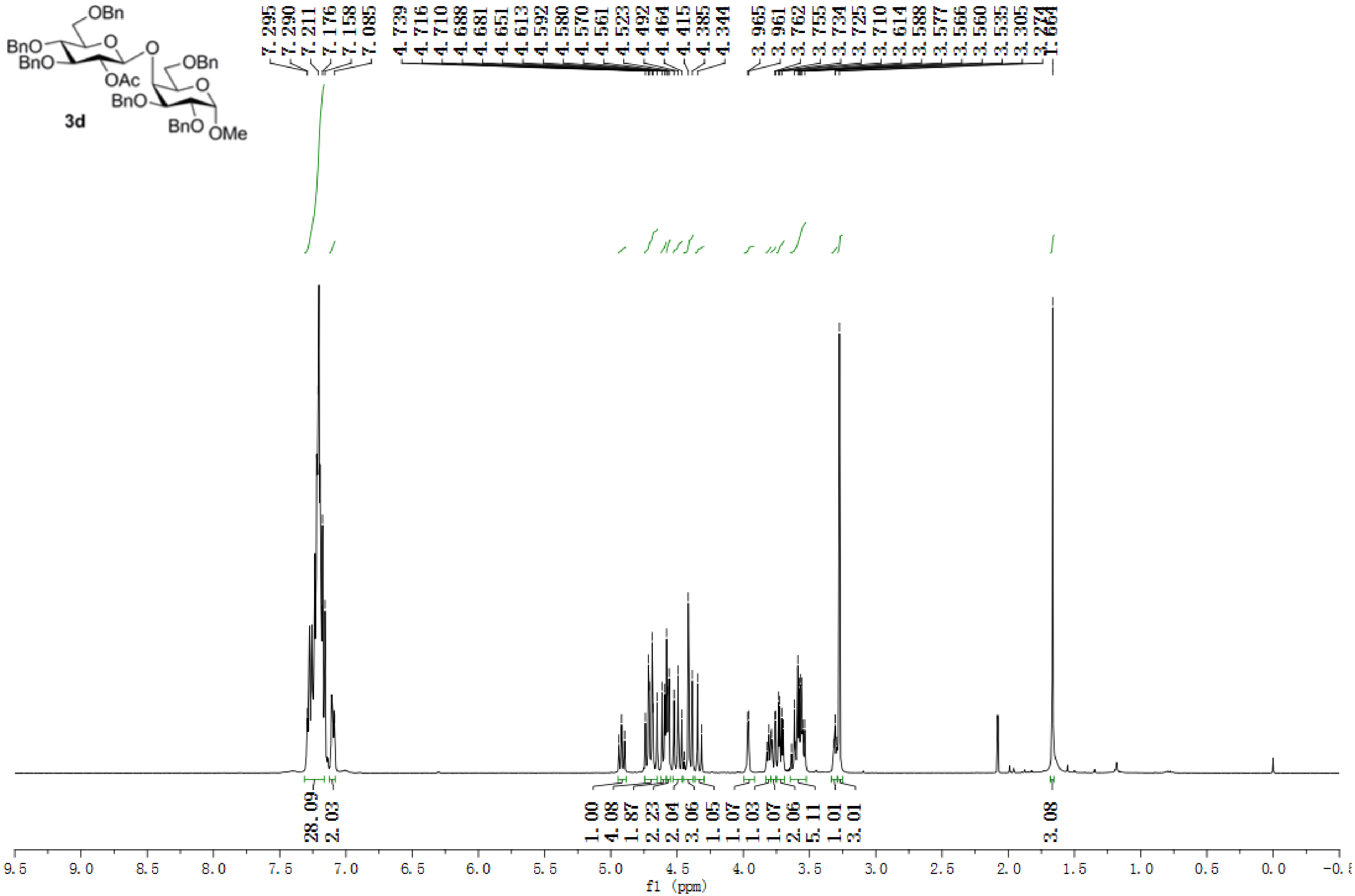


Figure S56. ^{1}H NMR spectrum of **3d** in $CDCl_3$

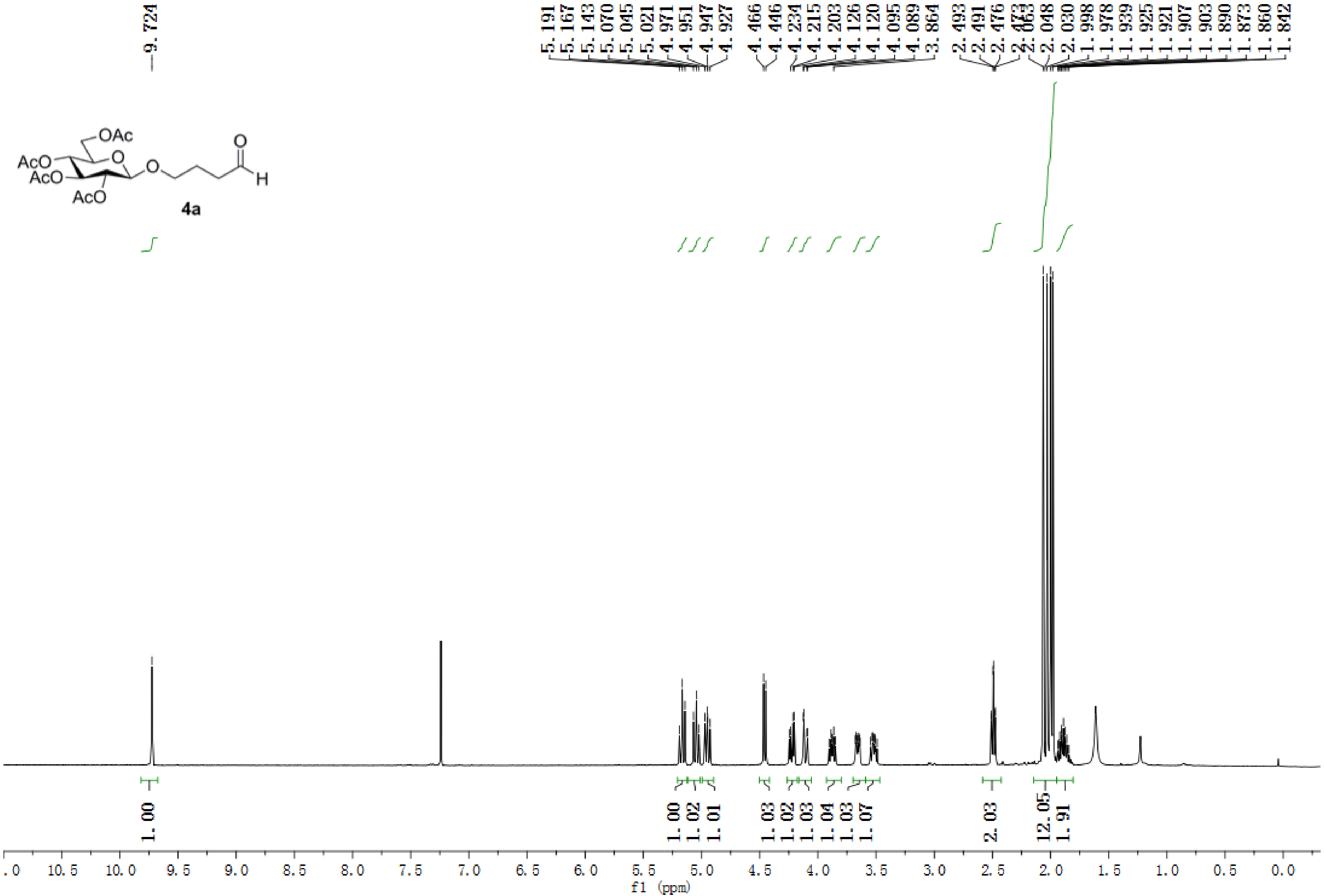


Figure S57. ^{1}H NMR spectrum of **4a** in $CDCl_3$

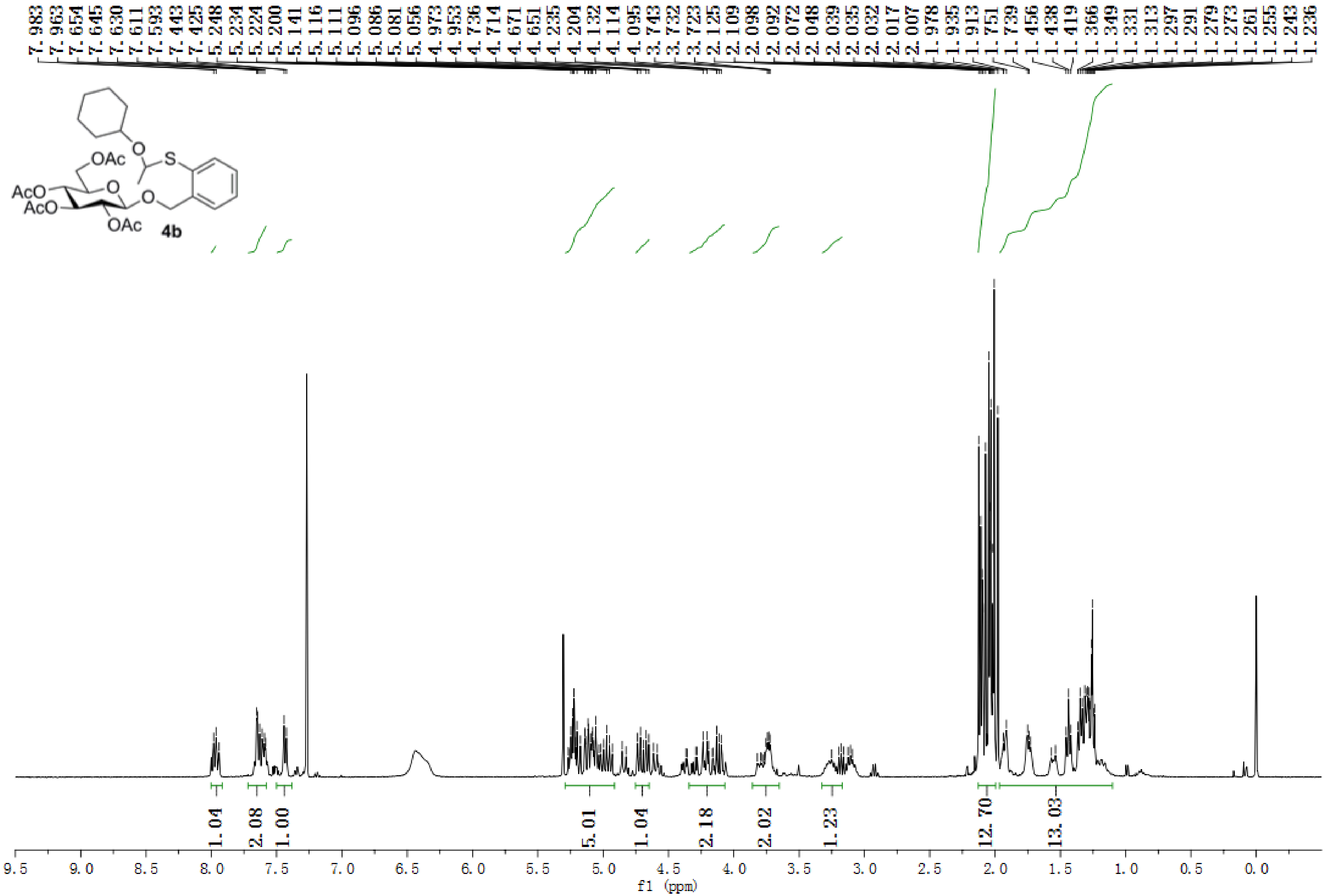


Figure S58. ^{1}H NMR spectrum of **4b** in $CDCl_3$

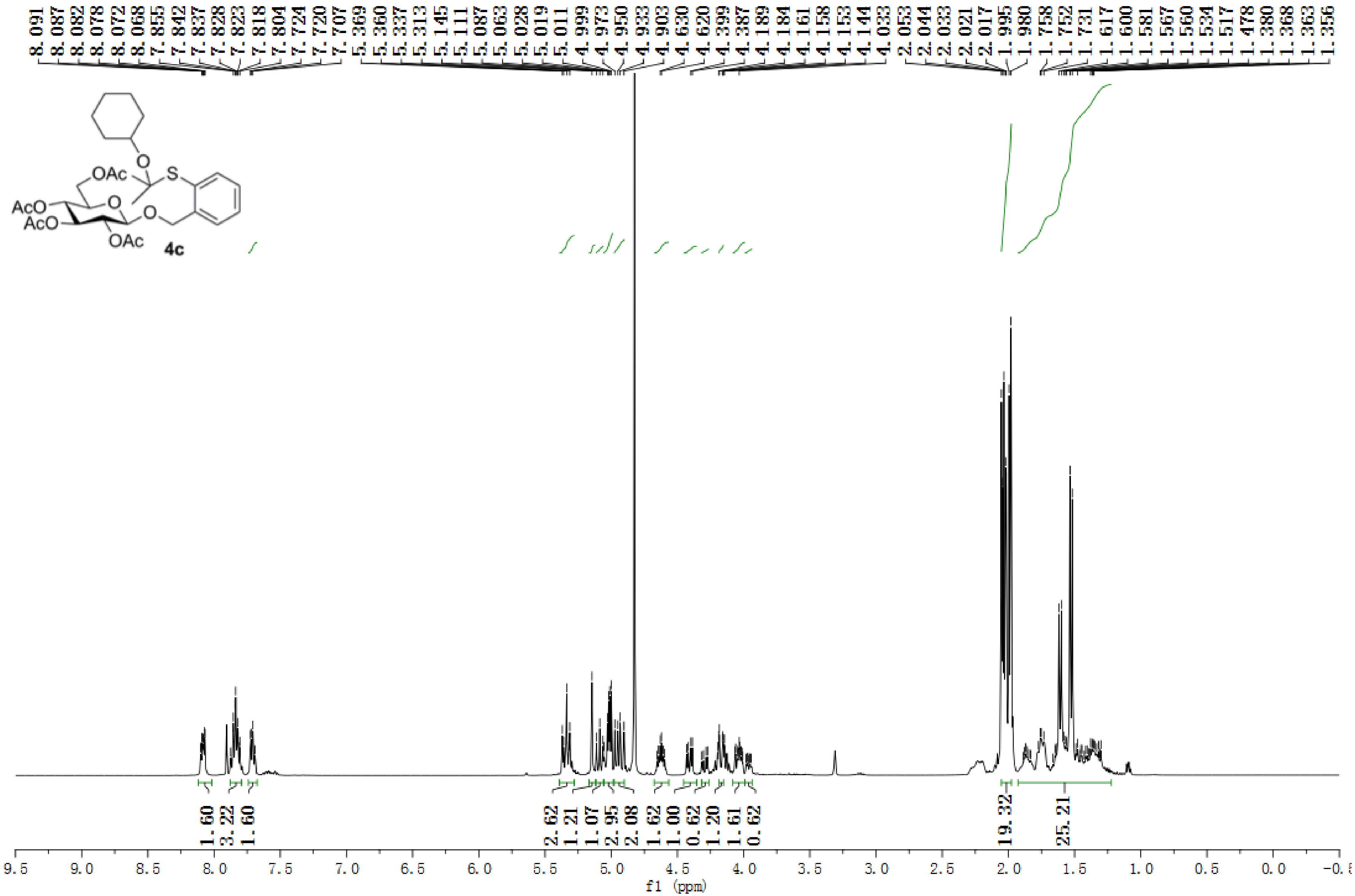


Figure S59. ^{1}H NMR spectrum of **4c** in CD_3OD

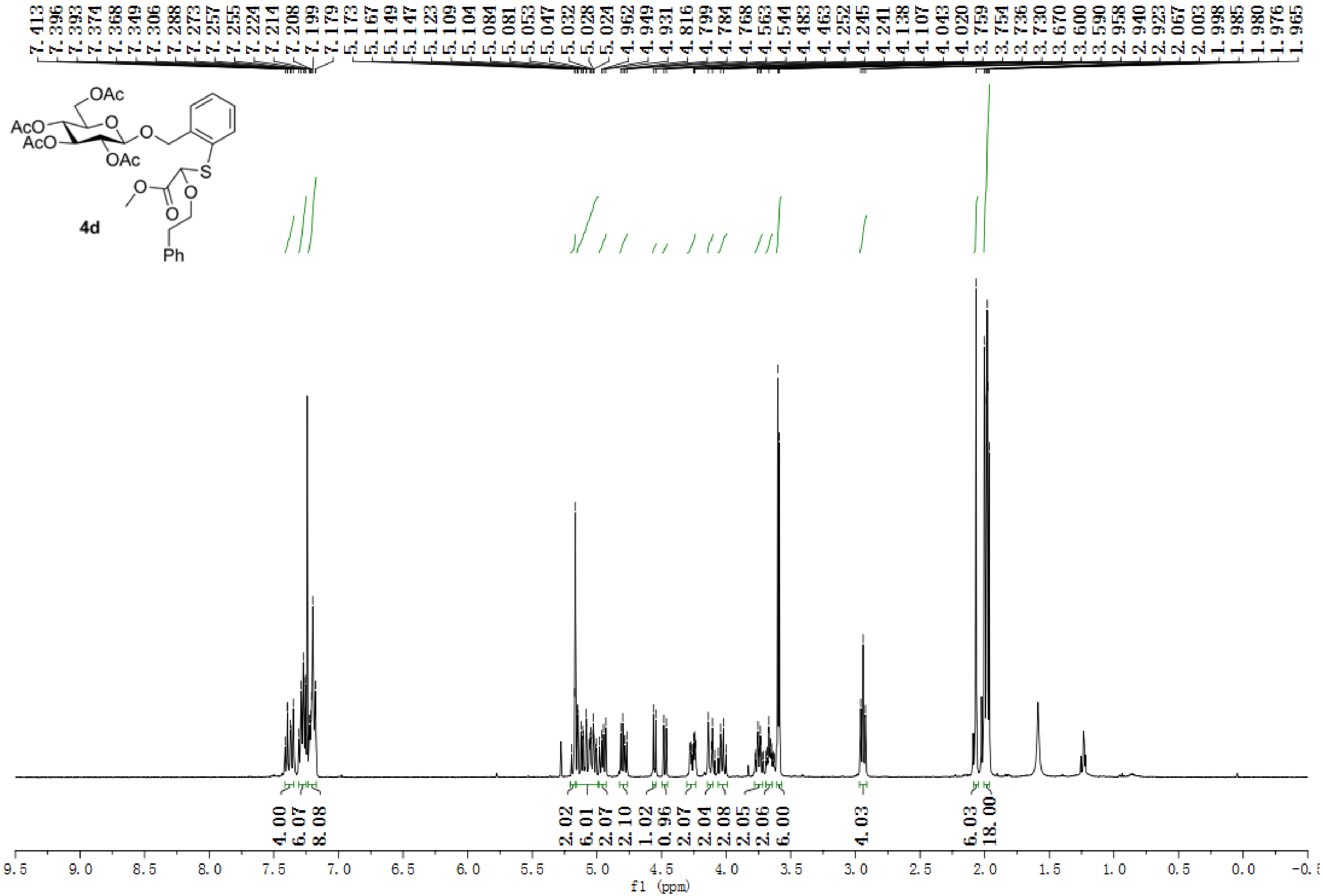


Figure S60. ^{1}H NMR spectrum of **4d** in $CDCl_3$

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