Boron-Promoted Umpolung Reaction of Sulfonyl Chlorides for the Stereospecific Synthesis of Thioglycosides via Reductive Deoxygenation Coupling Reactions

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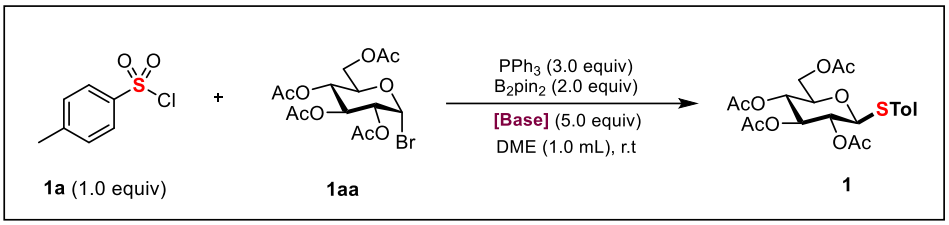
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) or 600MR DD2 (600 MHz) spectrometer at ambient temperature. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet. NMR yield was determined by ^{1}H NMR using mesitylene as an internal standard before working up the reaction. High resolution mass spectra (HRMS) were acquired on a 7 Tesla SolariX FT-ICR MS (Bruker Daltonics, Bremen, Germany) with an ESI source or GCT Premier (waters, United States) with an EI source. All deuterated solvents were purchased from Cambridge Isotope Laboratories. All air and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen.

Materials: All reagents from commercial sources were used as received, unless otherwise specified. B_2pin_2 was purchased from Adamas. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide was purchased from Bide Pharmatech. Tosyl chloride was purchased from Energy Chem. All solvents were refluxed with sodium/benzophenone or calcium hydride and distilled before use.

Optimization of the Reaction for the Synthesis of Thioglycosides (Table S1-S6):

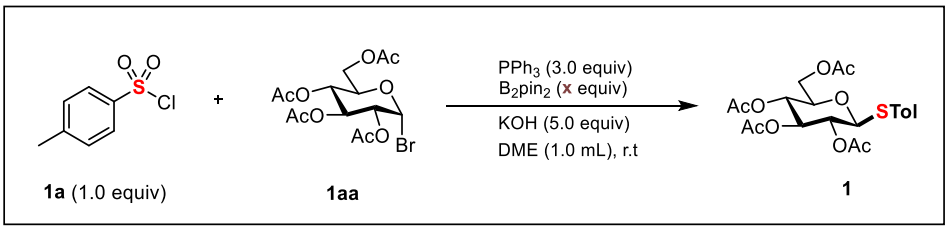
Table S1. Screening of Bases.[a]



Entry	Solvent	[Base]	Yield[b]
1	DME	**KOH**	**52%**
2	DME	NaOH	50%
3	DME	LiOH	17%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.5 equiv), PPh_3 (3.0 equiv), B_2pin_2 (2.0 equiv), base (5.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

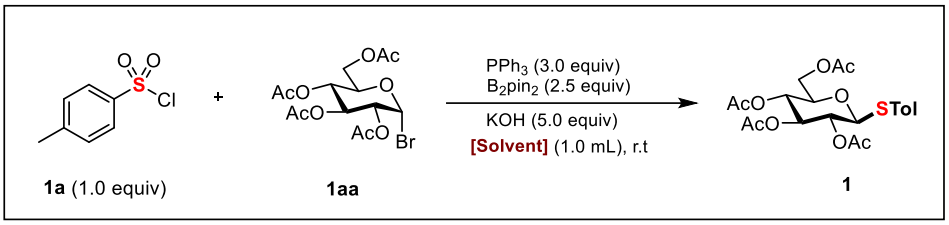
Table S2. Screening the Loading of B_2pin_2. [a]



Entry	Solvent	x	Yield[b]
1	DME	1.5	28%
2	DME	2.0	52%
3	DME	**2.5**	**61%**

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.5 equiv), PPh_3 (3.0 equiv), B_2pin_2, KOH (5.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

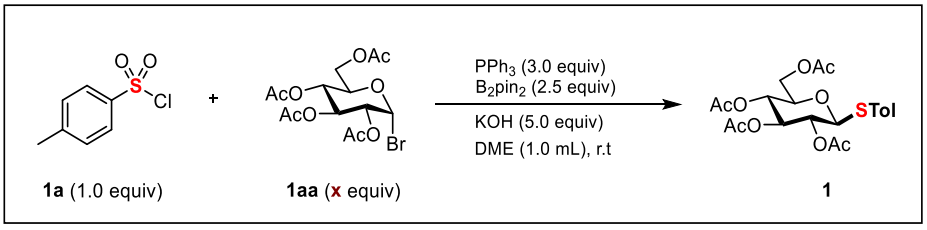
Table S3. Screening of Solvent. [a]



Entry	Solvent	[Base]	Yield[b]
1	**DME**	KOH	**61%**
2	MTBE	KOH	12%
3	Diethyl ether	KOH	4%
4	CPME	KOH	**25%**
5	Isopropyl ether	KOH	51%
6	DMSO	KOH	13%
7	1,2-Diethoxyethane	KOH	56%
8	THF	KOH	trace
9	$PhCF_3$	KOH	trace
10	NMP	KOH	trace
11	DMF	KOH	trace

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.5 equiv), PPh_3 (3.0 equiv), B_2pin_2 (2.5 equiv), KOH (5.0 equiv), solvent (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

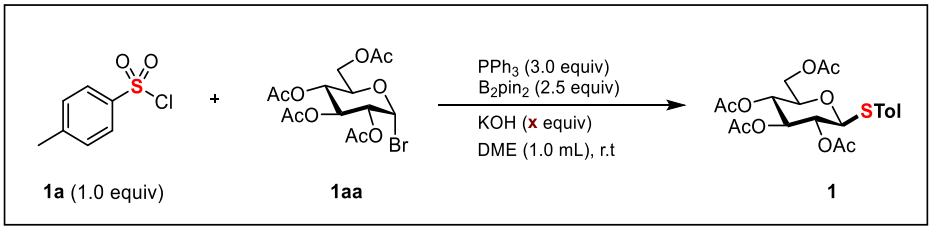
Table S4. Screening the loading of 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide (1aa). [a]



Entry	Solvent	**1aa** (x equiv)	Yield[b]
1	DME	1.0	64%
2	DME	1.1	70%
3	DME	**1.2**	**84%**
4	DME	1.3	80%
5	DME	1.4	62%
6	DME	1.5	61%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa**, PPh_3 (3.0 equiv), B_2pin_2 (2.5 equiv), KOH (5.0 equiv), solvent (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

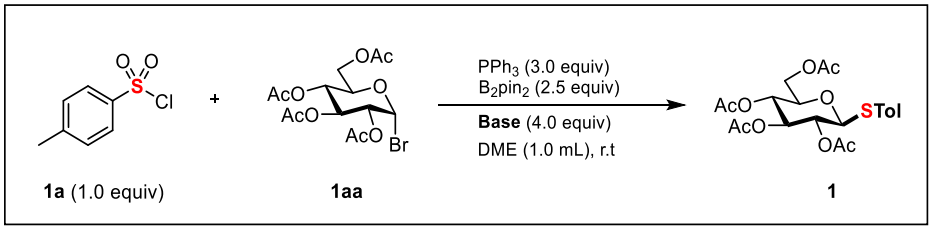
Table S5. Screening the loading of KOH. [a]



Entry	Solvent	KOH (x equiv)	Yield[b]
1	DME	3.0	47%
2	DME	3.5	87%
3	DME	**4.0**	**95% (90%)**
4	DME	4.5	81%
5	DME	5.0	84%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.2 equiv), PPh_3 (3.0 equiv), B_2pin_2 (2.5 equiv), KOH, DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

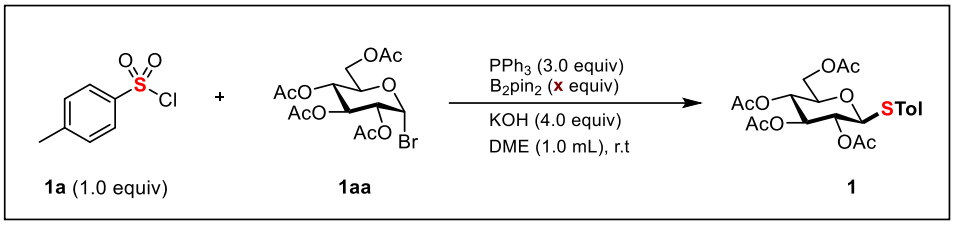
Table S6. Screening other bases. [a]



Entry	Solvent	Base	Yield[b]
1	DME	K_2CO_3	13%
2	DME	Na_2CO_3	15%
3	DME	Cs_2CO_3	77%
4	DME	NaOAc	NR
5	DME	Na_3PO_4	NR
6	DME	K_3PO_4	33%

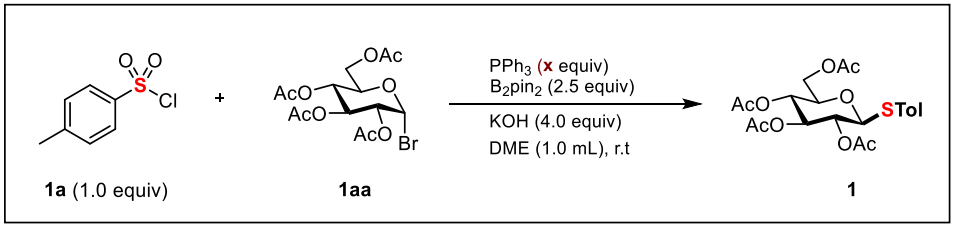
[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.2 equiv), PPh_3 (3.0 equiv), B_2pin_2 (2.5 equiv), Base (4.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

Control Experiments



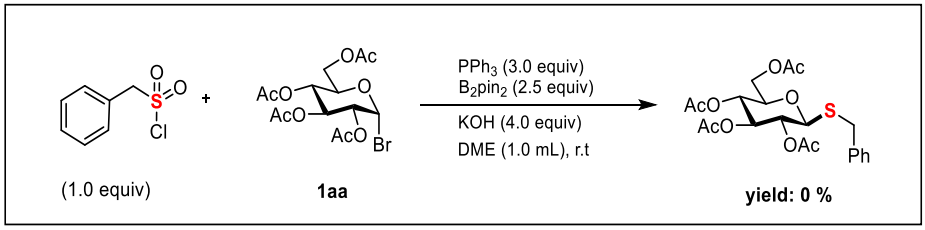
Entry	Solvent	B_2pin_2 (x equiv)	Yield[b]
1	DME	**2.5**	**95% (90%)**
2	DME	1.0	36%
3	DME	0.5	10%
4	DME	0	7%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.2 equiv), PPh_3 (3.0 equiv), B_2pin_2, KOH (4.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.



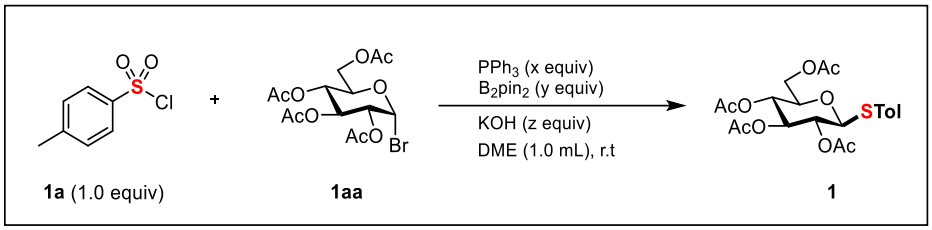
Entry	PPh_3 (x equiv)	Yield[b]
1	**3.0**	**95% (90%)**
2	2.0	14%
3	1.0	7%
4	0.5	1%
5	0	0%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.2 equiv), PPh_3, B_2pin_2(2.5 equiv), KOH (4.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.



[a]Reaction conditions (unless otherwise specified): **Benzylsulfonyl chloride** (0.2 mmol, 1.0 equiv),

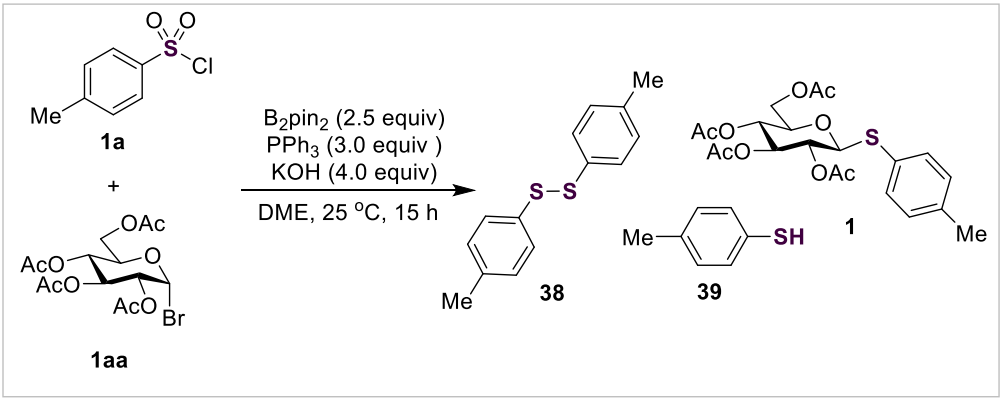
1aa (1.2 equiv), PPh_3 (3.0 equiv), B_2pin_2 (2.5 equiv), KOH (4.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.



Entry	x	y	z	Yield[b]
1	1.5	1.25	2.0	trace
2	0.75	0.625	1.0	trace

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa** (1.2 equiv), PPh_3, B_2pin_2, KOH, DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

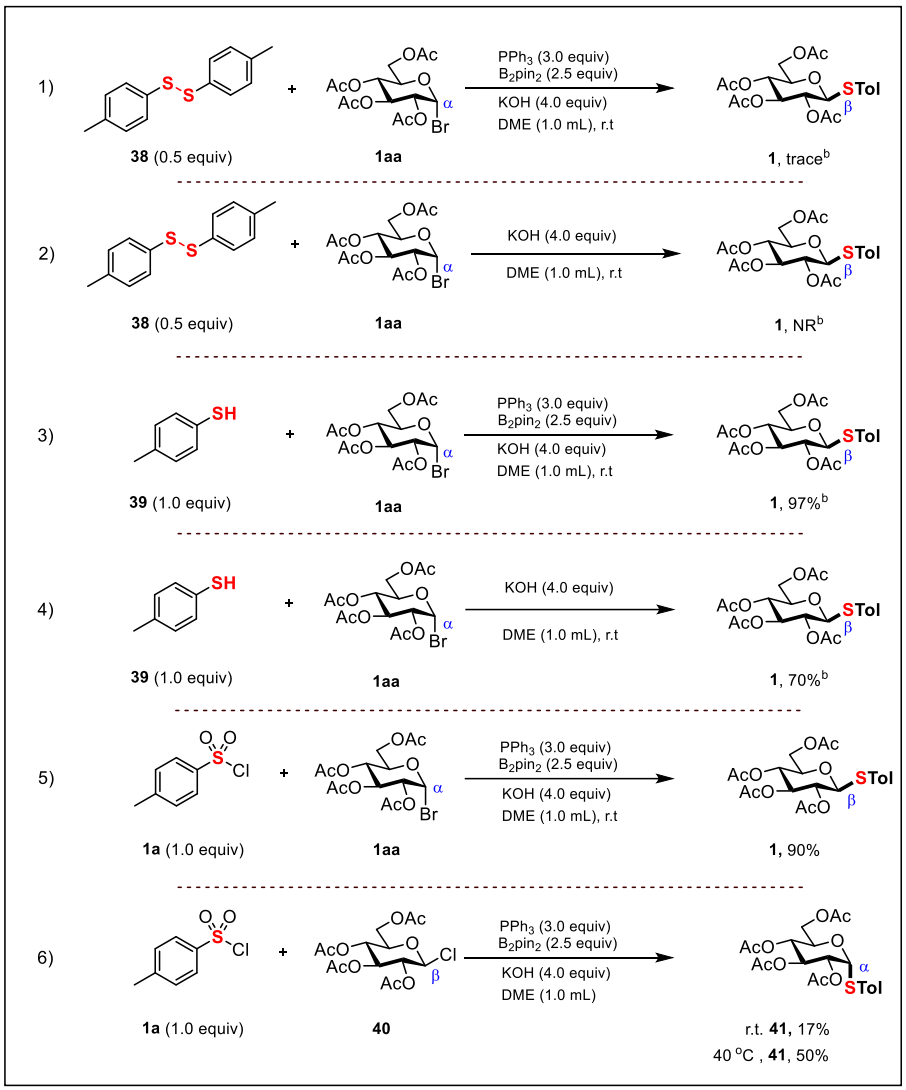
Mechanistic Studies



Entry	x	Yield[b]
1	1.2	**1**, 95% (90%)
2	0.5	**1**, 42% + **38**, 50%
3	0.3	**1**, 30% + **39**, 2% + **38**, 53%
4	0.1	**1**, 10% + **39**, 15% + **38**, 30%
5	0	**38**, 64%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **1aa**, PPh_3(3.0 equiv), B_2pin_2(2.5 equiv), KOH (4.0 equiv), DME (1.0 mL), room temperature, 15 h, under nitrogen atmosphere. [b]Determined by ^1H NMR using mesitylene as an internal standard.

Conclusion: The possible intermediates, *p*-tolyl disulfide **38** and *p*-thiocresol **39** were found in this transformation.



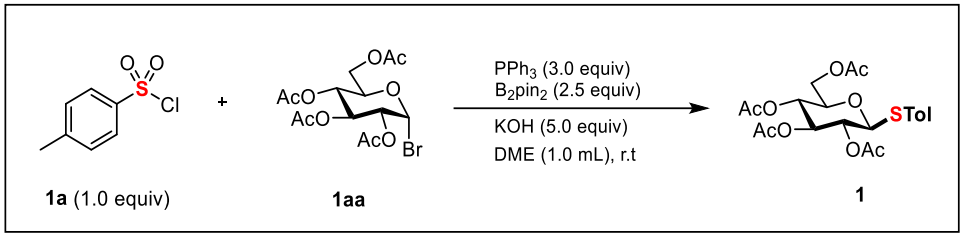
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(p-tolylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (41).

Known compound.[1] The product (15.5 mg, 17% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 (d, *J*= 8.4 Hz, 2 H), 7.09 (d, *J*= 7.8 Hz, 2 H), 5.81 (d, *J*= 6.0 Hz, 1 H), 5.41 (d, *J*= 10.2 Hz, 1 H), 5.08-5.03 (m, 2 H), 4.58-4.55 (m, 1 H), 4.25 (dd, *J*= 5.4, 12.6 Hz, 1 H), 4.01 (dd, *J*= 2.4, 12.6 Hz, 1 H), 2.30 (s, 3 H), 2.09(s, 3 H), 2.06(s, 3 H), 2.03(s, 3 H), 2.00(s, 3 H).

Conclusion: *p*-Tolyl disulfide **38** could not undergo this transformation, while *p*-thiocresol **39** could react well in this borane-promoted system, which suggested that *p*-thiocresol **39** may be the intermediate. Complete stereoinversion of the glycosyl donors

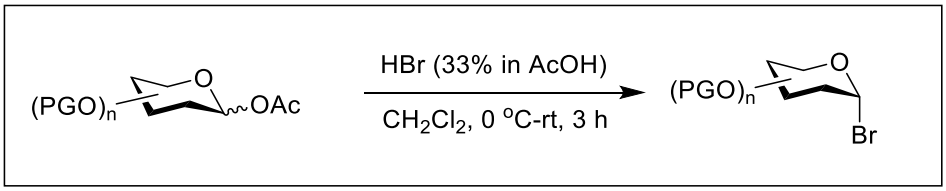
suggests that an S_N2 substitution process might be involved in this transformation.

Gram-scale Experimental Procedures.



To a 100 mL of round bottom flask equipped with a magnetic stir bar, PPh_3 (1.57 g, 6.0 mmol), B_2pin_2 (1.27 g, 5 mmol), **1a** (0.381 g, 2 mmol), **1aa** (0.986 g, 2.4 mmol) were added in a round bottom flask, followed by KOH (0.448 g, 8 mmol), then fresh distilled DME (10 mL) was added. The reaction mixture was stirred at room temperature for 30 h. The reaction solution was quenched with water, extracted with ethyl acetate (20 mL×3), and the organic layer was separated. The organic phase was dried over Na_2SO_4 and concentrated in vacuum. The concentrate was separated and purified by silica gel flash chromatography (PE/EA = 5/1~3/1) to obtain the corresponding product 1 (1.13 g, 78%).

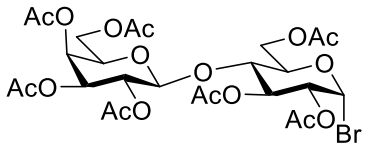
General Procedure (for the synthesis of 1-bromoglycosides):



To a solution of the C-1 acetyl protected sugar (1.0 equiv) in anhydrous DCM (0.5 M) was added HBr (33% Wt in AcOH, 2.0 equiv) at 0 °C. After addition, the reaction mixture was warmed to room temperature and stirred for 3 h, then the reaction mixture was poured onto an ice/water mixture. The organic phase was collected, and the aqueous phase was extracted with DCM twice. The combined organic layers were washed with satd. $NaHCO_3$, brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford the desired compound.

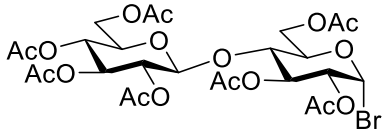
Experimental Procedures and Characterization Data.

2,3,6,2',3',4',6'-Hepta-O-acetyl-α-D-lactosyl bromide (30aa).



The reaction used peracetylated lactose (1.0 g, 1.47 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 2.5/1) to afford the title compound (906 mg, 88%) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.52 (d, *J* = 4.1 Hz, 1 H, H-1), 5.54 (t, *J* = 9.6 Hz, 1 H), 5.35 (d, *J* = 3.4 Hz, 1 H), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1 H), 4.95 (dd, *J* = 10.4, 3.5 Hz, 1 H), 4.75 (dd, *J* = 10.0, 4.0 Hz, 1 H), 4.50 (t, *J* = 9.0 Hz, 2 H), 4.23 – 4.12 (m, 3 H), 4.07 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.91 – 3.80 (m, 2 H), 2.15 (s, 3 H), 2.12 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.05 (s, 3 H), 1.96 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.3, 170.1, 170.1, 170.0 169.9, 169.2, 168.9, 100.8, 86.4, 74.9, 73.0, 71.0, 70.8, 70.8, 69.6, 69.0, 66.6, 61.0, 60.9, 20.8, 20.8, 20.6, 20.6, 20.5. The NMR spectroscopic data is identical to those in the previous report. [2]

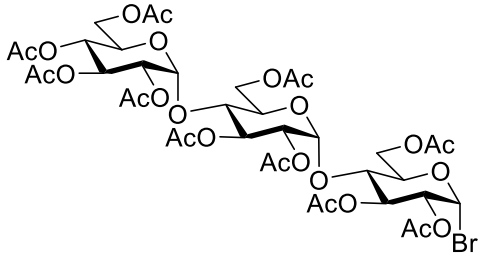
2,3,6,2',3',4',6'-Hepta-O-acetyl-α-D-cellobiosyl bromide (31aa).



The reaction used peracetylated cellobiose (1.5 g, 2.21 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound (1.31 g, 85%) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.48 (d, *J* = 4.0 Hz, 1 H, H-1), 5.47 (t, *J* = 9.7 Hz, 1 H), 5.10 (t, *J* = 9.4 Hz, 1 H), 5.02 (t, *J* = 9.7 Hz, 1 H), 4.88 (t, *J* = 8.6 Hz, 1 H), 4.71 (dd, *J* = 10.0, 4.1 Hz, 1 H), 4.50 (d, *J* = 7.9 Hz, 1 H), 4.47 (d, *J* = 11.6 Hz, 1 H), 4.31 (dd, *J* = 12.5, 4.5 Hz, 1 H), 4.18 – 4.09 (m, 2 H), 4.00 (dd, *J* = 12.4, 2.3 Hz, 1 H), 3.80 (t, *J* = 9.6 Hz, 1 H), 3.63 (ddd, *J* = 10.1, 4.5, 2.3 Hz, 1 H), 2.08 (s, 3 H), 2.03 (s, 6 H), 1.99 (d, *J* = 2.7 Hz, 6 H), 1.96 (s, 3 H), 1.93 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.3,

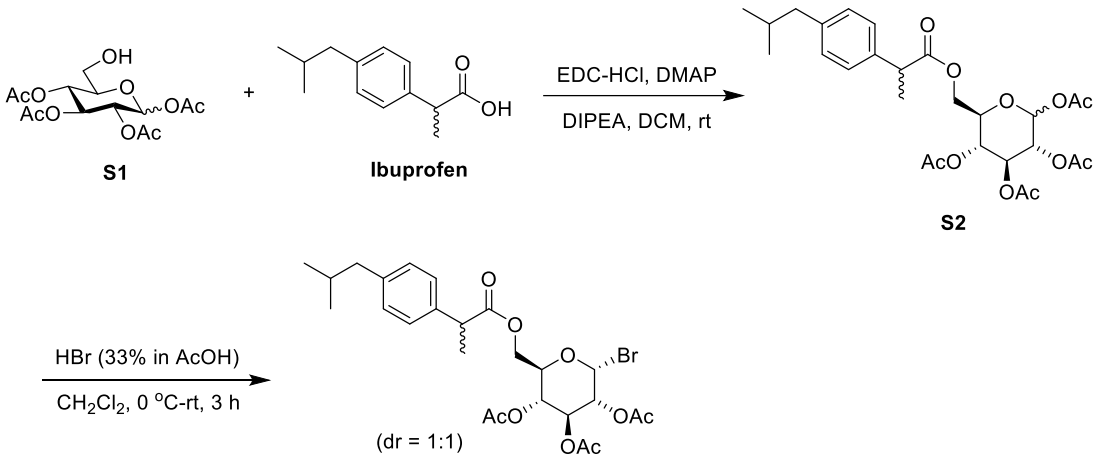
170.1, 169.9, 169.8, 169.2, 169.1, 168.8, 100.4, 86.4, 75.1, 72.9, 72.8, 71.9, 71.4, 70.6, 69.3, 67.6, 61.5, 60.8, 20.6, 20.5, 20.5, 20.4, 20.4. The NMR spectroscopic data is identical to those in the previous report. [3]

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-Glucopyranosyl Bromide (33aa).



The reaction used peracetylated maltotriose (1.0 g, 1.03 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 2/1) to afford the title compound (940 mg, 92%) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.48 (d, *J* = 4.0 Hz, 1 H, H-1), 5.58 (t, *J* = 9.4 Hz, 1 H), 5.41 – 5.36 (m, 2H), 5.33 (t, *J* = 10.0 Hz, 1 H), 5.26 (d, *J* = 4.1 Hz, 1 H), 5.05 (t, *J* = 9.9 Hz, 1 H), 4.83 (dd, *J* = 10.5, 4.0 Hz, 1 H), 4.72 (dd, *J* = 10.4, 4.1 Hz, 1 H), 4.69 (dd, *J* = 9.8, 4.0 Hz, 1 H), 4.54 – 4.45 (m, 2 H), 4.33 – 4.20 (m, 3 H), 4.14 (dd, *J* = 12.3, 2.4 Hz, 1 H), 4.06 – 3.99 (m, 2 H), 3.95 – 3.86 (m, 3 H), 2.16 (s, 3 H), 2.13 (s, 3 H), 2.07 (s, 3 H), 2.04 (s, 6 H), 2.03 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.99 (s, 3 H), 1.97 (s, 3 H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.7, 170.6, 170.5, 170.3, 169.8, 169.8, 169.6, 169.4, 95.9, 95.5, 85.9, 72.5, 72.2, 72.2, 71.6, 71.0, 70.4, 70.0, 69.3, 69.1, 68.4, 67.9, 62.8, 61.9, 61.3, 20.8, 20.8, 20.7, 20.6, 20.5, 20.5. The NMR spectroscopic data is identical to those in the previous report.[4]

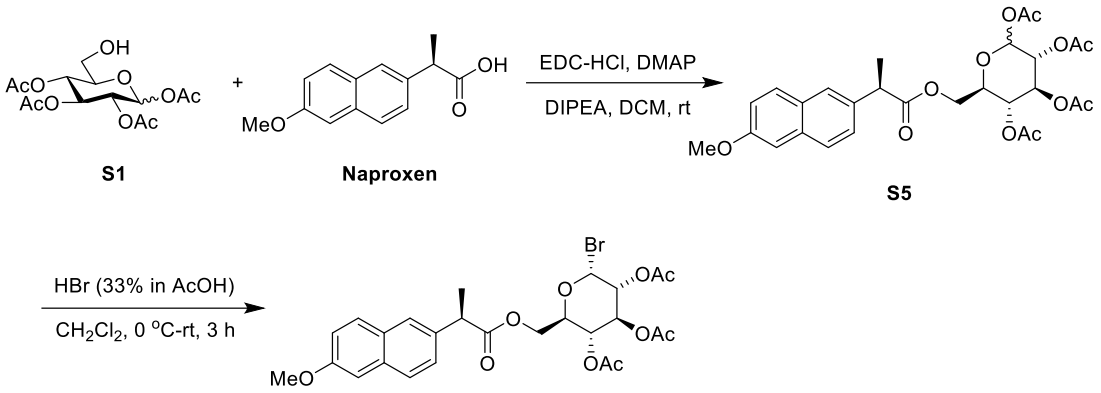
2,3,4-Tri-O-acetyl-6-O-[2-(4-isobutylphenyl) propanoyl]-α-D-glucopyranosyl bromide (34aa).



To a solution of compound **S1**[5] (294 mg, 0.80 mmol) in dry DCM (6 mL) were added ibuprofen (198 mg, 0.96 mmol), DMAP (19.5 mg, 0.16 mmol), EDC·HCl (276 mg, 1.44 mmol) and DIPEA (0.25 mL, 1.44 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with sat. $NaHCO_3$ and brine, respectively. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 3/1), to give **S2** (378 mg, 88% yield) as a colorless oil (mixture of α and β anomers).

34aa was synthesized using **S2** (300 mg, 0.558 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound (233 mg, 75%) as a colorless syrup (dr = 1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.0, 4.1 Hz, 4 H), 7.10 (dd, *J* = 8.1, 2.5 Hz, 4 H), 6.55 (d, *J* = 4.0 Hz, 1 H, H-1), 6.52 (d, *J* = 4.0 Hz, 1 H, H-1), 5.50 (td, *J* = 9.7, 2.7 Hz, 2 H), 5.06 – 4.97 (m, 2 H), 4.71 (dd, *J* = 10.1, 4.0 Hz, 1 H), 4.67 (dd, *J* = 10.0, 4.0 Hz, 1 H), 4.28 – 4.16 (m, 6 H), 3.73 (qd, *J* = 7.2, 2.0 Hz, 2 H), 2.44 (d, *J* = 7.2 Hz, 4 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 6 H), 1.99 (s, 3 H), 1.84 (hept, *J* = 6.7 Hz, 2 H), 1.51 (d, *J* = 7.2 Hz, 3 H), 1.49 (d, *J* = 7.1 Hz, 3 H), 0.89 (d, *J* = 6.6 Hz, 12 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.1, 174.1, 169.8, 169.8, 169.7, 169.7, 169.3, 169.2, 140.6, 140.6, 137.2, 137.0, 129.3, 129.3, 127.3, 127.2, 86.5, 86.4, 72.3, 72.2, 70.5, 70.1, 70.1, 67.4, 67.1, 61.2, 60.8, 45.0, 44.8, 30.1, 30.1, 22.4, 20.6, 20.6, 20.5, 20.4, 18.3, 18.1. The NMR spectroscopic data is identical to those in the previous report.[5]

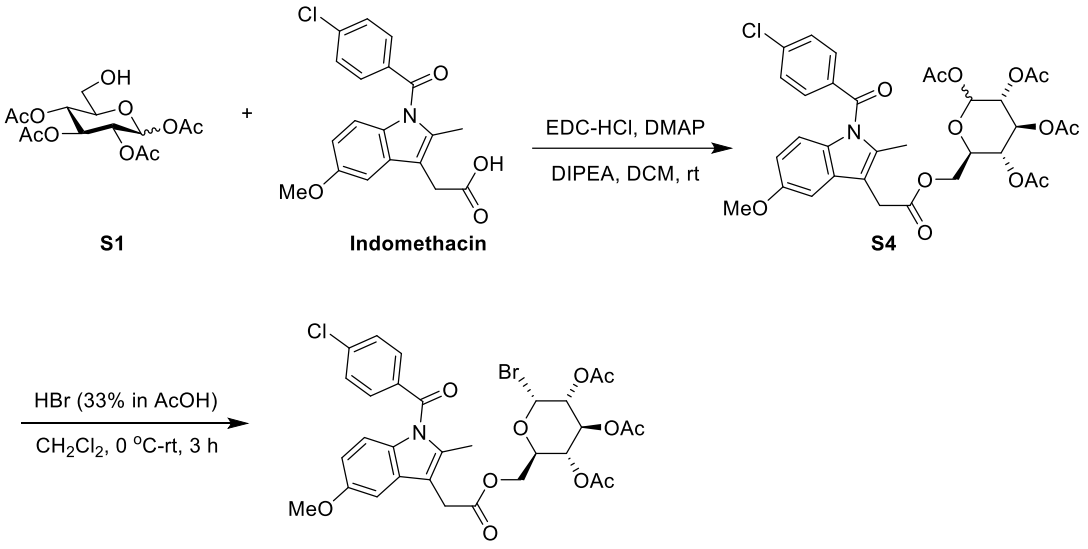
2,3,4-Tri-O-acetyl-6-O-[(R)-2-(6-methoxynaphthalen-2-yl) propanoyl]-α-D-glucopyranosyl bromide (35aa).



To a solution of compound **S1** (294 mg, 0.80 mmol) in dry DCM (6 mL) were added ibuprofen (221 mg, 0.96 mmol), DMAP (19.5 mg, 0.16 mmol), EDC·HCl (276 mg, 1.44 mmol) and DIPEA (0.25 mL, 1.44 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with sat. $NaHCO_3$ and brine, respectively. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 3/1), to give **S5** (430 mg, 96% yield) as a colorless oil (mixture of α and β anomers).

35aa was synthesized using **S5** (420 mg, 0.61 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound (266 mg, 75%) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 – 7.64 (m, 3 H), 7.41 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.18 – 7.07 (m, 2 H), 6.52 (d, *J* = 4.0 Hz, 1 H, H-1), 5.46 (t, *J* = 9.7 Hz, 1 H), 4.94 (t, *J* = 9.7 Hz, 1 H), 4.59 (dd, *J* = 10.0, 4.1 Hz, 1 H), 4.31 – 4.15 (m, 3 H), 3.91 (d, *J* = 7.2 Hz, 1 H), 3.89 (s, 3 H), 2.07 (s, 3 H), 1.99 (s, 3 H), 1.96 (s, 3 H), 1.61 (d, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.9, 169.8, 169.6, 169.2, 157.5, 134.9, 133.7, 129.3, 128.8, 127.1, 126.4, 126.0, 118.8, 105.5, 86.4, 72.2, 70.5, 70.0, 67.3, 61.1, 55.2, 45.2, 20.5, 20.4, 17.9. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{26}H_{29}BrO_{10}Na$ 603.0842; Found 603.0835.

2,3,4-Tri-O-acetyl-6-O-[(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)carbonyl]-α-D-glucopyranosyl bromide (36aa).

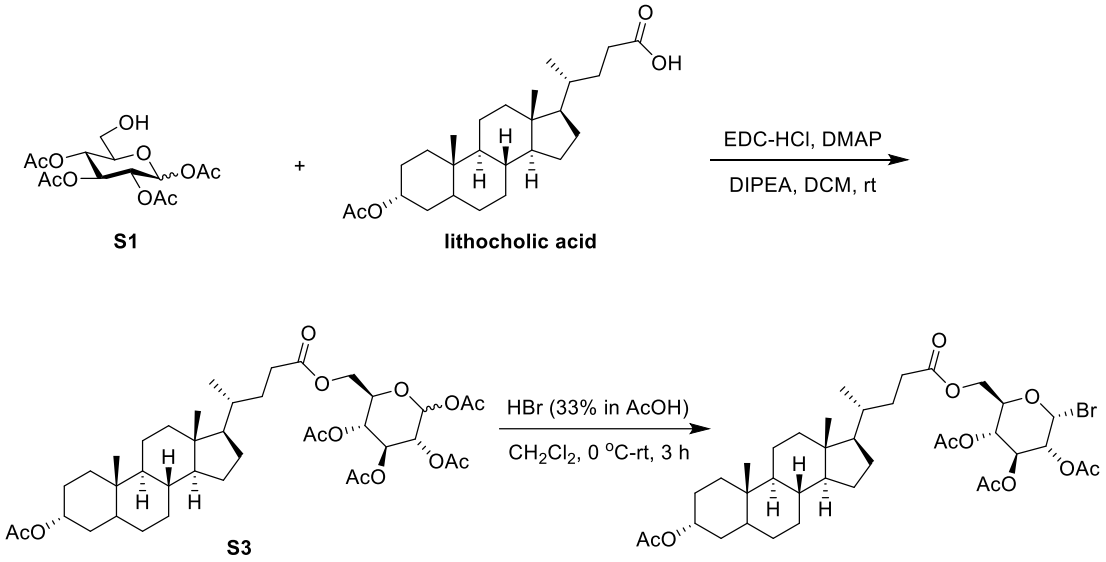


To a solution of compound **S1** (294 mg, 0.80 mmol) in dry DCM (6 mL) were added indomethacin (286 mg, 0.96 mmol), DMAP (19.5 mg, 0.16 mmol), EDC·HCl (276 mg, 1.44 mmol) and DIPEA (0.25 mL, 1.44 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with sat. $NaHCO_3$ and brine, respectively. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 3/1), to give **S4** (517 mg, 94% yield) as a colorless oil (mixture of α and β anomers).

36aa was synthesized using **S4** (500 mg, 0.727 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound (267 mg, 52%) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.4, 1.3 Hz, 2 H), 7.51 – 7.41 (m, 2 H), 6.99 (d, *J* = 2.6 Hz, 1 H), 6.89 (d, *J* = 9.0 Hz, 1 H), 6.67 (dt, *J* = 8.9, 1.6 Hz, 1 H), 6.54 (d, *J* = 4.0 Hz, 1 H, H-1), 5.49 (t, *J* = 9.7 Hz, 1 H), 5.02 (t, *J* = 9.8 Hz, 1 H), 4.60 (ddd, *J* = 10.0, 4.1, 1.2 Hz, 1 H), 4.32 (dd, *J* = 12.6, 4.2 Hz, 1 H), 4.25 (dd, *J* = 10.5, 4.1 Hz, 1 H), 4.19 (dd, *J* = 12.6, 1.8 Hz, 1 H), 3.85 (d, *J* = 1.2 Hz, 3 H), 3.71 (s, 2 H), 2.37 (s, 3 H), 2.09 (s, 3 H), 2.02 (s, 6 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.3, 169.8, 169.6, 169.3, 168.3, 156.0, 139.2, 136.2, 134.0, 131.2, 130.8, 130.5, 129.1, 115.0, 112.0, 111.6, 101.4, 86.5,

72.1, 70.6, 70.1, 67.0, 61.2, 55.7, 30.0, 25.0, 24.8, 20.6, 20.6, 20.5, 13.3. The NMR spectroscopic data is identical to those in the previous report.[5]

2,3,4-Tri-O-acetyl-6-O-[(4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl]-α-D-glucopyranosyl bromide (37aa).

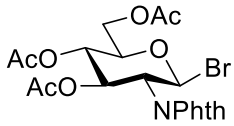


To a solution of compound **S1** (294 mg, 0.80 mmol) in dry DCM (6 mL) were added 3-O-acetyl lithocholic acid (402 mg, 0.96 mmol), DMAP (19.5 mg, 0.16 mmol), EDC·HCl (276 mg, 1.44 mmol) and DIPEA (0.25 mL, 1.44 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with sat. $NaHCO_3$ and brine, respectively. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 3/1), to give **S2** (551 mg, 92% yield) as a colorless oil (mixture of α and β anomers).

37aa was synthesized using **S3** (500 mg, 0.667 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound (275 mg, 67%) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.60 (d, *J* = 4.0 Hz, 1 H, H-1), 5.55 (t, *J* = 9.7 Hz, 1 H), 5.14 (t, *J* = 9.5 Hz, 1 H), 4.83 (dd, *J* = 10.0, 4.1 Hz, 1 H), 4.71 (ddt, *J* = 16.2, 11.1, 4.7 Hz, 1 H), 4.33 – 4.26 (m, 2 H), 4.17 – 4.12 (m, 1 H), 2.38 (ddd, *J* = 15.7, 10.3, 5.3 Hz, 1 H), 2.26 (ddd, *J* = 16.0, 9.8, 6.5 Hz, 1 H), 2.10 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.98

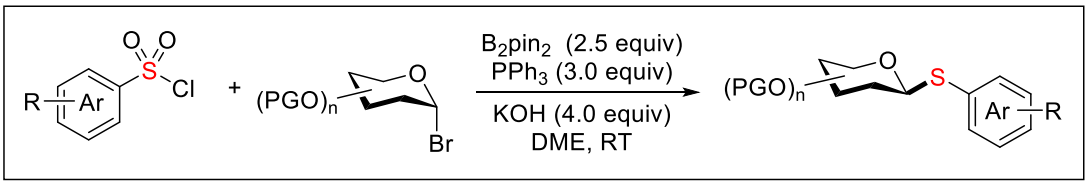
– 1.94 (m, 1 H), 1.89 – 1.74 (m, 6 H), 1.70 – 1.50 (m, 6 H), 1.47 – 1.35 (m, 9 H), 1.34 – 1.26 (m, 3 H), 1.17 – 1.00 (m, 7 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.8, 170.7, 169.8, 169.8, 169.4, 86.6, 83.5, 74.4, 72.2, 70.6, 70.2, 67.2, 60.8, 56.5, 55.9, 42.7, 41.9, 40.4, 40.1, 35.8, 35.3, 35.0, 34.6, 32.2, 30.9, 30.7, 28.1, 27.0, 26.6, 26.3, 24.2, 23.3, 21.5, 20.8, 20.6, 20.6, 20.5, 18.2, 12.0. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{38}H_{57}BrO_{11}Na$ 791.2982; Found 791.2975.

2-N-phthalimido-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucopyranosyl bromide (40aa)



The reaction used 2-N-phthalimido-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucopyranosyl acetate (500 mg, 1.05 mmol) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel (PE/EA = 2/1) to afford the title compound (471 mg, 90%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2 H), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2 H), 6.41 (d, *J* = 9.6 Hz, 1 H, H-1), 5.76 (t, *J* = 9.3 Hz, 1 H), 5.26 (t, *J* = 9.3 Hz, 1 H), 4.63 (t, *J* = 9.7 Hz, 1 H), 4.32 (dd, *J* = 12.6, 4.6 Hz, 1 H), 4.19 (dd, *J* = 12.5, 1.7 Hz, 1 H), 4.04 – 3.85 (m, 1 H), 2.13 (s, 3 H), 2.04 (s, 3 H), 1.87 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 169.9, 169.3, 134.6, 131.2, 123.89, 77.3, 76.9, 70.6, 68.1, 61.7, 58.1, 20.7, 20.6, 20.4. The NMR spectroscopic data is identical to those in the previous report.[6]

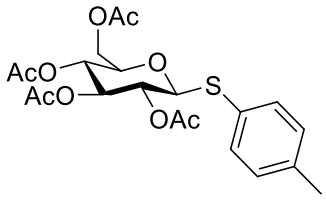
General Procedure (for the synthesis of thioglycosides):



To a 25 mL of Schlenk tube charged with a magnetic stir bar, were added PPh_3 (157 mg, 0.6 mmol), B_2pin_2 (127 mg, 0.5 mmol) and sulfonyl chloride (0.2 mmol), glycosyl bromide (0.24 mmol) were added in, followed by the addition of KOH (44.8

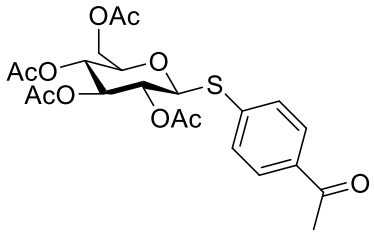
mg, 0.8 mmol), then fresh distilled DME (1.0 mL) was added. The reaction mixture was stirred at room temperature for 15 h. The reaction solution was quenched with water, extracted with ethyl acetate (10 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (PE/EtOAc) to provide the corresponding product.

Experimental Procedures and Characterization Data.



4-Methylphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (1).

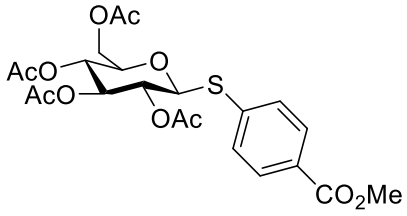
Known compound.[7] The product (81.8 mg, 90% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 7.6 Hz, 2 H), 5.20 (t, *J* = 9.6 Hz, 1 H), 5.02 (t, *J* =10.0 Hz, 1 H), 4.93 (t, *J* = 10.0 Hz, 1 H), 4.63 (d, *J* = 10.0 Hz, 1 H, H-1), 4.23-4.15 (m, 2 H), 3.72-3.67 (m, 1 H), 2.35 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.01 (s, 3 H), 1.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 138.8, 133.8, 129.7, 127.5, 85.8, 75.7, 74.0, 69.9, 68.1, 62.1, 24.8, 21.2, 20.8, 20.7, 20.6.



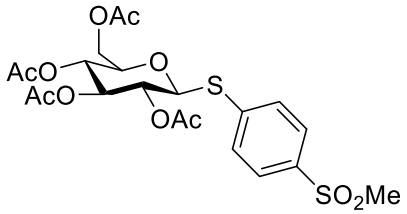
4-Acetylphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (2).

Known compound.[8] The product (52.1 mg, 54% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 5.23 (t, *J* = 9.2 Hz, 1 H), 5.07-4.98 (m,

2 H), 4.81 (d, *J* = 10.4 Hz, 1 H, H-1), 4.25-4.14 (m, 2 H), 3.80-3.75 (m, 1 H), 2.57 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.2, 170.5, 170.1, 169.4, 169.2, 138.8, 136.1, 132.0, 131.0, 128.7, 128.4, 84.7, 75.9, 73.7, 69.7, 68.1, 62.1, 26.6, 20.7, 20.7, 20.5.



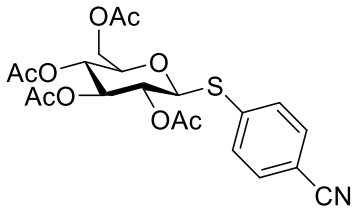
4-(Methoxycarbonyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (3). Known compound.[7] The product (53.4 mg, 54% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 5.24 (t, *J* = 9.6 Hz, 1 H), 5.07-4.99 (m, 2 H), 4.81 (d, *J* = 10.0 Hz, 1 H, H-1), 4.24-4.14 (m, 2 H), 3.89 (s, 3 H), 3.80-3.75 (m, 1 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.3, 169.2, 166.4, 138.6, 130.8, 130.0, 129.3, 84.9, 75.9, 73.7, 69.7, 68.1, 62.1, 52.2, 20.7, 20.7, 20.5.



4-(Methylsulfonyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (4).

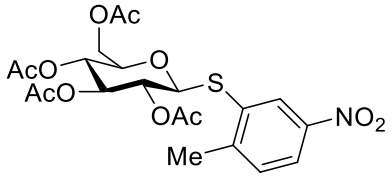
The product (69.5 mg, 67% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 5.25 (t, *J* = 9.2 Hz, 1 H), 5.08-4.99 (m, 2 H), 4.83 (d, *J* = 10.4 Hz, 1 H, H-1), 4.26-4.16 (m, 2 H), 3.82-3.78 (m, 1 H), 3.05 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.02 (s, 3 H), 1.99 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4,

170.0, 169.4, 169.2, 140.2, 139.6, 131.5, 127.8, 84.5, 76.0, 73.6, 69.6, 68.0, 62.0, 44.5, 20.8, 20.7, 20.5, 14.2. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{21}H_{26}NaO_{11}S_2$ 541.0809; Found 541.0806.



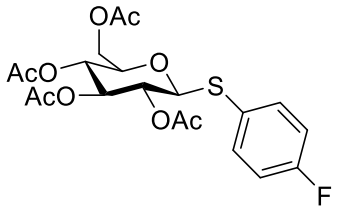
4-Cyanophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (5).

Known compound.[7] The product (63.3 mg, 68% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.52 (m, 4 H), 5.25 (t, *J* = 9.2 Hz, 1 H), 5.08-4.98 (m, 2 H), 4.81 (d, *J* = 10.4 Hz, 1 H, H-1), 4.25-4.15 (m, 2 H), 3.81-3.76 (m, 1 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.03 (s, 3 H), 1.99 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 170.1, 169.3, 169.2, 139.2, 132.3, 131.5, 118.3, 111.4, 84.5, 76.0, 73.6, 69.6, 68.0, 62.0, 20.7, 20.7, 20.5.



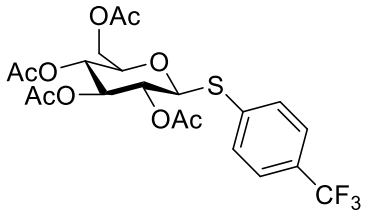
2-Methyl-5-nitrophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (6).

The product (69.9 mg, 70% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.4 Hz, 1 H), 8.02 (dd, *J* = 2.4, 8.4 Hz, 1 H), 7.34 (d, *J* = 8.4 Hz, 1 H), 5.26 (t, *J* = 9.2 Hz, 1 H), 5.10-5.05 (m, 2 H), 4.83 (d, *J* = 10.0 Hz, 1 H, H-1), 4.25-4.15 (m, 2 H), 3.85-3.80 (m, 1 H), 2.42 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 1.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.0, 169.3, 169.2, 146.6, 146.6, 134.6, 130.8, 125.4, 122.4, 85.0, 76.1, 73.7, 69.7, 67.9, 62.1, 21.0, 20.6, 20.6, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}NNaO_{11}S$ 522.1041; Found 522.1036.

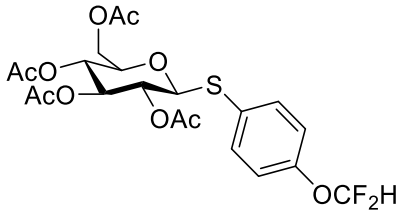


4-Fluorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (7).

Known compound.[9] The product **1** (50.4 mg, 55% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2 H), 7.00 (t, *J* = 8.8 Hz, 2 H), 5.19 (t, *J* = 9.2 Hz, 1 H), 4.98 (t, *J* = 10.0 Hz, 1 H), 4.88 (t, *J* = 9.6 Hz, 1 H), 4.58 (d, *J* = 10.0 Hz, 1 H, H-1), 4.18-4.17 (m, 2 H), 3.70-3.66 (m, 1 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.2, 169.4, 169.2, 163.3 (d, *J* = 248.2 Hz), 136.5 (d, *J* = 8.4 Hz), 125.7 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 21.7 Hz), 85.3, 75.8, 73.9, 69.8, 68.0, 62.0, 60.9, 20.7, 20.6.

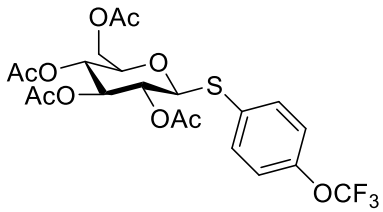


4-(Trifluoromethyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (8). Known compound.[8] The product (70.2 mg, 71% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 4 H), 5.23 (t, *J* = 9.2 Hz, 1 H), 5.06-4.96 (m, 2 H), 4.76 (d, *J* = 10.0 Hz, 1 H, H-1), 4.24-4.15 (m, 2 H), 3.77-3.73 (m, 1 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.01 (s, 3 H), 1.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.3, 169.2, 136.8, 132.2, 130.1 (d, *J* = 32.6 Hz), 125.7 (q, *J* = 3.1 Hz), 123.9 (d, *J* = 270.6 Hz), 84.9, 75.9, 73.7, 69.7, 68.0, 62.0, 20.7, 20.5.



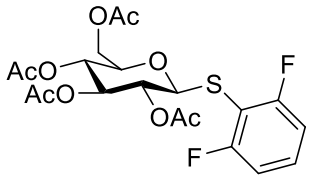
4-Difluoromethoxyphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (9).

The product (57.7 mg, 74% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 6.52 (t, *J* = 73.2 Hz, 1 H), 5.19 (t, *J* = 9.6 Hz, 1 H), 4.98 (t, *J* = 9.6 Hz, 1 H), 4.89 (t, *J* = 9.6 Hz, 1 H), 4.61 (d, *J* = 10.0 Hz, 1 H, H-1), 4.18-4.16 (m, 2 H), 3.71-3.67 (m, 1 H), 2.07 (s, 3 H), 2.04 (s, 3 H), 1.99 (s, 3 H), 1.96 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.2, 151.6, 135.8, 127.4, 119.7, 115.6 (t, *J* = 259.0 Hz), 85.2, 85.2, 75.8, 73.6, 69.8, 68.0, 62.0, 20.7, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}F_2NaO_{10}S$ 529.0951; Found 529.0943.



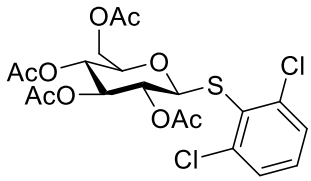
4-Trifluoromethoxyphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (10).

The product (80.8 mg, 77% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 5.21 (t, *J* = 9.6 Hz, 1 H), 5.00 (t, *J* = 9.6 Hz, 1 H), 4.94 (t, *J* = 10.0 Hz, 1 H), 4.65 (d, *J* = 10.0 Hz, 1 H, H-1), 4.19-4.18 (m, 2 H), 3.73-3.69 (m, 1 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.2, 149.5 (d, *J* = 2.0 Hz), 135.2, 129.6, 121.6, 120.3 (q, *J* = 256.6 Hz), 85.1, 75.9, 73.8, 69.8, 68.1, 62.0, 20.7, 20.6, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{21}H_{23}F_3NaO_{10}S$ 547.0856; Found 547.0851.



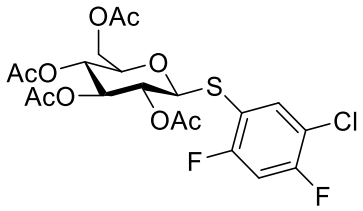
2,4-Difluorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (11).

The product **1** (74.3 mg, 78% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 1 H), 6.96-6.92 (m, 2 H), 5.17 (t, *J* = 9.2 Hz, 1 H), 5.03 (t, *J* = 9.6 Hz, 1 H), 4.96 (t, *J* = 9.6 Hz, 1 H), 4.67 (d, *J* = 10.0 Hz, 1 H, H-1), 4.17 (dd, *J* = 5.2, 12.4 Hz, 1 H), 4.05 (dd, *J* = 2.4, 12 Hz, 1 H), 3.64-3.59 (m, 1 H), 2.07 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 163.5 (dd, *J* = 4.1, 249.0 Hz), 131.7 (t, *J* = 10.2 Hz), 111.9, 111.8 (d, *J* = 25.3 Hz), 107.2 (t, *J* = 22.1 Hz), 85.4, 75.8, 73.8, 70.6, 68.0, 61.9, 20.6, 20.6. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}F_2NaO_9S$ 499.0845; Found 499.0844.

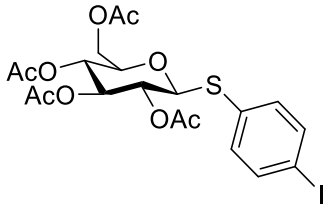


2,6-Dichlorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (12).

错误!未找到引用源。 The product (84.6 mg, 83% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2 H), 7.23 (dd, *J* = 7.6 Hz, 7.6 Hz, 1 H), 5.23-5.06 (m, 3 H), 4.72 (d, *J* = 9.6 Hz, 1 H, H-1), 4.19 (dd, *J* = 5.6, 12.4 Hz, 1 H), 4.02 (d, *J* = 12.0 Hz, 1 H), 3.60-3.55 (m, 1 H), 2.08 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.99 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.5, 169.4, 141.6, 130.8, 130.2, 128.8, 86.7, 75.8, 73.8, 70.8, 68.3, 62.1, 20.8, 20.6. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}Cl_2NaO_9S$ 531.0254; Found 531.0251.

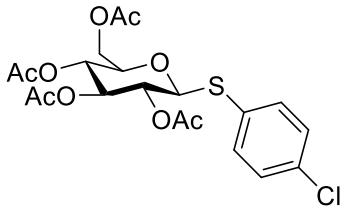


2,4-Difluoro-5-chlorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (13). The product (76.6 mg, 75% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 7.6 Hz, 1 H), 6.96 (t, *J* = 8.4 Hz, 1 H), 5.20 (t, *J* = 9.2 Hz, 1 H), 5.02 (t, *J* = 10.0 Hz, 1 H), 4.86 (t, *J* = 9.6 Hz, 1 H), 4.63 (d, *J* = 10.0 Hz, 1 H, H-1), 4.23-4.12 (m, 2 H), 3.73-3.68 (m, 1 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.3, 161.1 (dd, *J* = 249 Hz, 4 Hz), 158.8 (dd, *J* = 253 Hz, 4.8 Hz), 137.1, 115.8 (dd, *J* = 246 Hz, 4 Hz), 115.6 (dd, *J* = 229 Hz, 4 Hz), 105.6 (dd, *J* = 28 Hz, 2 Hz), 84.6, 76.0, 73.7, 69.5, 67.8, 61.7, 20.7, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{20}H_{21}ClF_2NaO_9S$ 533.0455; Found 533.0458.



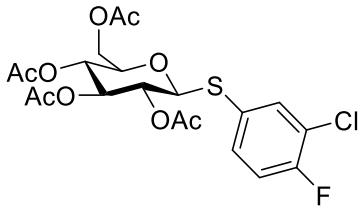
4-Iodophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (14).

The product (71.4 mg, 63% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 5.20 (t, *J* = 9.6 Hz, 1 H), 5.01 (t, *J* = 10.0 Hz, 1 H), 4.93 (t, *J* = 10.0 Hz, 1 H), 4.65 (d, *J* = 10.0 Hz, 1 H, H-1), 4.22-4.14 (m, 2 H), 3.72-3.68 (m, 1 H), 2.07 (s, 6 H), 2.01 (s, 3 H), 1.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.2, 138.0, 135.1, 131.1, 94.6, 85.1, 75.9, 73.8, 69.8, 68.1, 62.0, 20.7, 20.6. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{20}H_{23}INaO_9S$ 589.0000; Found 588.9996.



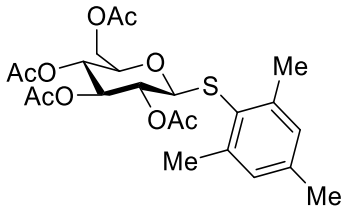
4-Chlorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (15).

Known compound.[7]错误!未找到引用源。 The product (69.3 mg, 73% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2 H), 7.29-7.25 (m, 2 H),5.22-5.17 (m, 1 H), 5.02-4.97 (m, 1 H), 4.94-4.88 (m, 1 H), 4.63 (dd, *J* = 2.4, 10.0 Hz, 1 H, H-1), 4.22-4.14 (m, 2 H), 3.72-3.68 (m, 1 H), 2.07 (s, 6 H), 2.00 (m, 3 H), 1.97 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.2, 135.0, 129.4, 129.1, 85.2, 75.8, 73.8, 69.8, 68.0, 62.0, 20.7, 20.6.



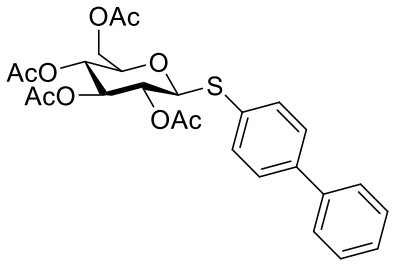
3-Chloro-4-fluorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (16).

The product (72.9 mg, 74% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 2.0, 6.8 Hz, 1 H), 7.38-7.35 (m, 1 H), 7.09 (t, *J* = 8.8 Hz, 1 H), 5.21 (t, *J* = 9.2 Hz, 1 H), 5.00 (t, *J* = 10.0 Hz, 1 H), 4.89 (t, *J* = 9.6 Hz, 1 H), 4.61 (d, *J* = 10.0 Hz, 1 H, H-1), 4.23-4.15 (m, 2 H), 3.74-3.70 (m, 1 H), 2.09 (s, 6 H), 2.01 (s, 3 H), 1.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.3, 169.2, 158.6 (d, *J* = 250.5 Hz), 136.1, 134.2 (d, *J* = 7.4 Hz), 127.1 (d, *J* = 4.0 Hz), 121.4 (d, *J* = 18.2 Hz), 116.9 (d, *J* = 21.4 Hz), 85.1, 75.9, 73.8, 69.7, 67.9, 62.0, 20.7, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}ClFNaO_9S$ 515.0549; Found 515.0547.



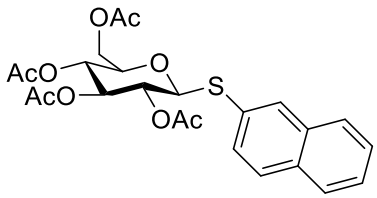
2,4,6-Trimethylphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (17).

The product (55.0 mg, 57% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (s, 2 H), 5.18-5.02 (m, 3 H), 4.37 (d, *J* = 10.0 Hz, 1 H, H-1), 4.14 (dd, *J* = 6.0, 12.4 Hz, 1 H), 4.03 (dd, *J* = 2.8, 12.4 Hz, 1 H), 3.51-3.47 (m, 1 H), 2.47 (s, 6 H), 2.26 (s, 3 H), 2.11 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H), 1.99 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.3, 169.4, 143.9, 139.5, 129.2, 127.5, 88.7, 75.3, 74.0, 70.6, 68.4, 62.3, 22.2, 21.0, 20.7, 20.6. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{23}H_{30}NaO_9S$ 505.1503; Found 505.1500.



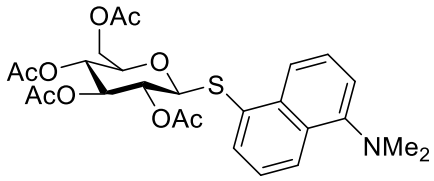
4-(Phenyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (18).[错误!未找到引用源。]

The product (87.8 mg, 85% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 5 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 5.23 (t, *J* = 9.2 Hz, 1 H), 5.08-4.98 (m, 2 H), 4.72 (d, *J* = 10.0 Hz, 1 H, H-1), 4.26-4.17 (m, 2 H), 3.76-3.72 (m, 1 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.01 (s, 3 H), 1.99 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169. 3, 141.4, 140.1, 133.6, 130.4, 128.9, 127.7, 127.6, 127.0, 85.7, 75.8, 73.9, 69.9, 68.2, 62.1, 20.8, 20.6, 20.6. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{26}H_{28}NaO_9S$ 539.1346; Found 539.1372.



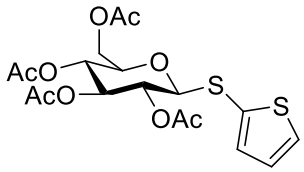
2-Naphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (19).

Known compound.[10] The product (41.2 mg, 42% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1 H), 7.83-7.76 (m, 3 H), 7.56-7.47 (m, 3 H), 5.23 (t, *J* = 9.6 Hz, 1 H), 5.02 (dd, *J* = 9.6, 19.2 Hz, 2 H), 4.78 (d, *J* = 10.0 Hz, 1 H, H-1), 4.25-4.16 (m, 2 H), 3.75-3.70 (m, 1 H), 2.10 (s, 3 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3, 133.4, 132.9, 132.7, 130.2, 128.7, 128.5, 127.7, 126.8, 126.7, 85.8, 75.8, 73.9, 70.0, 68.2, 62.1, 20.8, 20.7, 20.6.



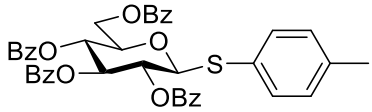
5-(Dimethylamino)-1-naphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (20).

The product (57.0 mg, 55% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 1 H), 8.13 (d, *J* = 8.8 Hz, 1 H), 7.79 (d, *J* = 7.2 Hz, 1 H), 7.47-7.38 (m, 1 H), 7.11 (d, *J* = 7.6 Hz, 1 H), 5.18 (t, *J* = 9.2 Hz, 1 H), 5.10-5.04 (m, 2 H), 4.69 (d, *J* = 10.0 Hz, 1 H, H-1), 4.19 (dd, *J* = 5.6 Hz, 12.4Hz, 1 H), 4.08 (dd, *J* = 2.0, 12.0Hz, 1 H), 3.62-3.58 (m, 1 H), 2.87 (s, 6 H), 2.11 (s, 3 H), 2.02 (s, 3 H), 1.98 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 151.5, 135.5, 133.3, 129.6, 129.5, 126.6, 126.0, 124.6, 120.4, 114.6, 86.8, 75.7, 74.0, 70.4, 68.2, 62.2, 45.4, 20.8, 20.7, 20.6, 20.6. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{26}H_{31}NNaO_9S$ 556.1612; Found 556.1606.



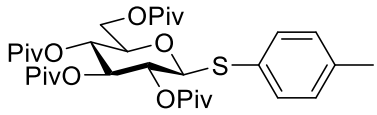
2-Thiophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (21).

Known compound.[8]错误!未找到引用源。 The product (51.8 mg, 58% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 5.2 Hz, 1 H), 7.20 (d, *J* = 2.8 Hz, 1 H), 7.01 (t, *J* = 4.4 Hz, 1 H), 5.19 (t, *J* = 9.2 Hz, 1 H), 4.99 (t, *J* = 10.0 Hz, 1 H), 4.91 (t, *J* = 9.6 Hz, 1 H), 4.49 (d, *J* = 10.0 Hz, 1 H, H-1), 4.23-4.15 (m, 2 H), 3.71-3.67 (m, 1 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.2, 136.6, 131.6, 127.5, 127.1, 85.4, 75.9, 73.9, 69.6, 68.0, 62.0, 20.7, 20.5.



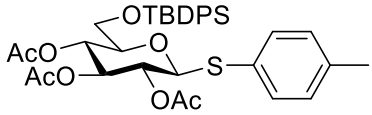
4-Methylphenyl 2,3,4,6-tetra-O-benzoyl-β-D-thioglucopyranoside (22).

Known compound.[11] The product (119.4 mg, 85% yield) as a white solid was purified with silica gel chromatography (PE/EA = 6/1~4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.3, 1.4 Hz, 2 H), 8.01-7.94 (m, 2 H), 7.94-7.86 (m, 2 H), 7.84-7.77 (m, 2 H), 7.61-7.35 (m, 10 H), 7.32 (t, *J* = 7.7 Hz, 2 H), 7.24 (t, *J* = 7.7 Hz, 2 H), 6.93 (d, *J* = 7.9 Hz, 2 H), 5.93 (t, *J* = 9.5 Hz, 1 H), 5.62 (t, *J* = 9.8 Hz, 1 H), 5.48 (t, *J* = 9.7 Hz, 1 H), 5.01 (d, *J* = 10.0 Hz, 1 H, H-1), 4.70 (dd, *J* = 12.2, 2.7 Hz, 1 H), 4.49 (dd, *J* = 12.2, 5.6 Hz, 1 H), 4.20 (ddd, *J* = 10.0, 5.7, 2.8 Hz, 1 H), 2.26 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.7, 165.1, 165.0, 138.6, 133.8, 133.4, 133.3, 133.2, 133.1, 130.1, 129.8, 129.8, 129.7, 129.6, 129.1, 128.7, 128.6, 128.3, 128.2, 127.4, 86.1, 76.2, 74.2, 70.4, 69.3, 63.0, 21.1. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{41}H_{34}O_9SNa$ 725.1821; Found 725.1827.



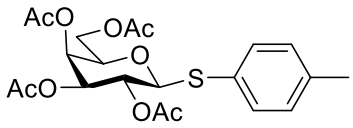
4-Methylphenyl 2,3,4,6-tetra-O-pivaloyl-β-D-thioglucopyranoside (23).

The product (73.5 mg, 59% yield) as a white solid was purified with silica gel chromatography (PE/EA = 8/1~5/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2 H), 7.09 (d, *J* = 7.8 Hz, 2 H), 5.32 (t, *J* = 9.4 Hz, 1 H), 5.06 (t, *J* = 9.8 Hz, 1 H), 4.99 (t, *J* = 9.7 Hz, 1 H), 4.65 (d, *J* = 10.1 Hz, 1 H, H-1), 4.23 (dd, *J* = 12.3, 1.8 Hz, 1 H), 4.04 (dd, *J* = 12.3, 5.8 Hz, 1 H), 3.73 (ddd, *J* = 10.1, 5.8, 1.8 Hz, 1 H), 2.33 (s, 3 H), 1.20 (s, 18 H), 1.13 (s, 9 H), 1.09 (s, 9 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.0, 177.1, 176.4, 176.3, 138.5, 133.3, 129.7, 128.3, 86.6, 76.3, 73.3, 69.5, 67.6, 62.2, 38.8, 38.7, 38.7, 27.1, 27.1, 27.0, 21.2. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{33}H_{50}O_9SNa$ 645.3073; Found 645.3068.



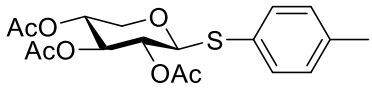
4-Methylphenyl 2,3,4-tri-O-acetyl-6-*tert*-butyldiphenylsilyl β-D-thioglucopyranoside (24).

Known compound.[12] The product (98.9 mg, 76% yield) as a white solid was purified with silica gel chromatography (PE/EA = 6/1~4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 17.1, 8.4 Hz, 4 H), 7.54 – 7.31 (m, 8 H), 7.06 (d, *J* = 7.7 Hz, 2 H), 5.26 – 5.07 (m, 2 H), 4.97 (t, *J* = 9.5 Hz, 1 H), 4.66 (d, *J* = 10.0 Hz, 1 H, H-1), 3.85 – 3.67 (m, 2 H), 3.58 (dq, *J* = 7.2, 2.4 Hz, 1 H), 2.32 (s, 3H), 2.10 (s, 3 H), 1.99 (s, 3 H), 1.88 (s, 3 H), 1.07 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 169.2, 169.1, 138.4, 135.6, 135.6, 133.5, 132.9, 129.7, 127.8, 127.7, 85.7, 78.7, 74.5, 69.9, 68.1, 62.4, 26.6, 21.1, 20.7, 20.6, 20.4, 19.1. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{35}H_{42}O_8SSiNa$ 673.2267; Found 673.2262.



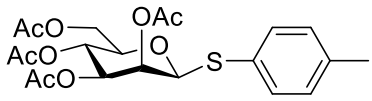
4-Methylphenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (25).

Known compound.[13] The product (71.8 mg, 79% yield) as a white solid was purified with silica gel chromatography (PE/EA = 4/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 2 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 5.38 (d, *J* = 3.3 Hz, 1 H), 5.19 (t, *J* = 10.0 Hz, 1 H), 5.02 (dd, *J* = 9.9, 3.3 Hz, 1 H), 4.63 (d, *J* = 10.0 Hz, 1 H, H-1), 4.20 – 4.04 (m, 2 H), 3.89 (t, *J* = 6.6 Hz, 1 H), 2.32 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.95 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.3, 170.1, 170.0, 169.3, 138.4, 133.1, 129.5, 128.5, 86.8, 74.3, 71.9, 67.2, 67.1, 61.5, 21.1, 20.8, 20.6, 20.5, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{21}H_{26}O_9SNa$ 477.1195; Found 477.1198.



4-Methylphenyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside (26).

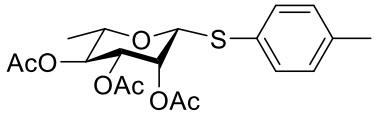
Known compound.[14] The product (61.9 mg, 81% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2 H), 7.10 (d, *J* = 7.9 Hz, 2 H), 5.15 (t, *J* = 8.3 Hz, 1 H), 4.88 (tt, *J* = 8.8, 2.9 Hz, 2 H), 4.69 (d, *J* = 8.5 Hz, 1 H, H-1), 4.22 (dd, *J* = 11.8, 5.0 Hz, 1 H), 3.37 (dd, *J* = 11.7, 8.9 Hz, 1 H), 2.31 (s, 3 H), 2.07 (s, 3 H), 2.01 (d, *J* = 2.5 Hz, 6 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.5, 172.4, 171.9, 141.2, 136.1, 132.4, 130.7, 89.0, 74.9, 72.5, 71.1, 68.0, 23.8, 23.4, 23.3. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{18}H_{22}O_7SNa$ 405.0984; Found 405.0993.



4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-mannopyranoside (27).

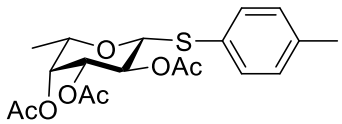
Known compound.[15] The product (62.7 mg, 69% yield) as a white solid was purified

with silica gel chromatography (PE/EA = 4/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.6 Hz, 2 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 5.64 (d, *J* = 3.5 Hz, 1 H), 5.26 (t, *J* = 10.1 Hz, 1 H), 5.03 (dd, *J* = 10.1, 3.6 Hz, 1 H), 4.83 (s, 1 H, H-1), 4.27 (dd, *J* = 12.2, 6.5 Hz, 1 H), 4.14 (dt, *J* = 12.0, 2.1 Hz, 1 H), 3.65 (ddd, *J* = 9.3, 6.4, 2.4 Hz, 1 H), 2.32 (s, 3 H), 2.19 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.97 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.5, 170.1, 170.0, 169.6, 138.4, 132.6, 129.8, 129.4, 86.0, 76.4, 71.8, 70.6, 65.8, 62.8, 21.1, 20.7, 20.6, 20.5, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{21}H_{26}O_9SNa$ 477.1195; Found 477.1191.



4-Methylphenyl 2,3,4-tri-O-acetyl-β-L-rhamnopyranoside (28).

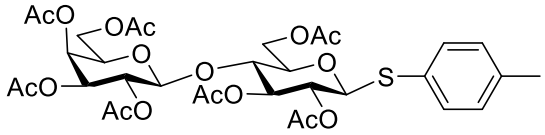
Known compound.[16] The product (57.1 mg, 72% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 2 H), 7.08 (d, *J* = 7.8 Hz, 2 H), 5.66 – 5.54 (m, 1 H), 5.07 (t, *J* = 9.8 Hz, 1 H), 4.96 (dd, *J* = 10.2, 3.5 Hz, 1 H), 4.80 (d, *J* = 1.3 Hz, 1 H, H-1), 3.48 (dq, *J* = 9.4, 6.1 Hz, 1 H), 2.29 (s, 3 H), 2.16 (s, 3 H), 2.00 (s, 3 H), 1.94 (s, 3 H), 1.26 (d, *J* = 6.3 Hz, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.1, 169.9, 169.6, 138.2, 132.5, 129.7, 129.4, 85.5, 74.7, 71.7 70.8, 70.1, 20.9, 20.6, 20.4, 20.4, 17.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{19}H_{24}O_7SNa$ 419.1140; Found 419.1141.



4-Methylphenyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (29).

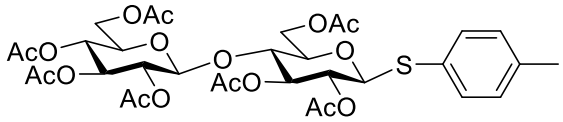
Known compound.[16] The product (60.3 mg, 76% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 7.9 Hz, 2 H), 5.22 (d, *J* = 3.4 Hz, 1 H), 5.17 (t, *J* = 9.9 Hz, 1 H), 5.02 (dd, *J* = 9.9, 3.3 Hz, 1 H), 4.62 (d, *J* = 9.9 Hz, 1 H, H-1), 3.78 (q, *J* = 6.4 Hz, 1 H), 2.31 (s, 3 H), 2.11 (s, 3 H), 2.06 (s, 3 H), 1.94 (s, 3 H), 1.20 (d, *J* = 6.4 Hz, 3

H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.5, 170.0, 169.4, 138.1, 132.8, 129.5, 128.9, 86.7, 73.0, 72.4, 70.3, 67.3, 21.0, 20.8, 20.5, 20.5, 16.3. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{19}H_{24}O_7SNa$ 419.1140; Found 419.1138.



4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (30).

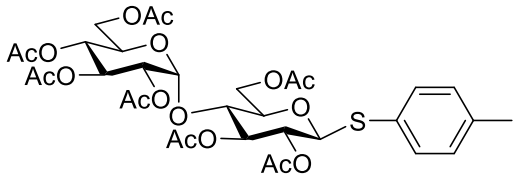
Known compound.[13] The product (105.4 mg, 71% yield) as a white solid was purified with silica gel chromatography (PE/EA = 3/1~1/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 2 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 5.30 (d, *J* = 3.5 Hz, 1 H), 5.16 (t, *J* = 9.2 Hz, 1 H), 5.05 (dd, *J* = 10.4, 7.9 Hz, 1 H), 4.92 (dd, *J* = 10.4, 3.5 Hz, 1 H), 4.82 (t, *J* = 9.7 Hz, 1 H), 4.57 (d, *J* = 10.0 Hz, 1 H, H-1), 4.49 (dd, *J* = 12.0, 2.1 Hz, 1 H), 4.44 (d, *J* = 7.9 Hz, 1 H, H-1), 4.11 – 4.00 (m, 3 H), 3.83 (t, *J* = 6.8 Hz, 1 H), 3.70 (t, *J* = 9.5 Hz, 1 H), 3.58 (ddd, *J* = 10.1, 5.6, 2.1 Hz, 1 H), 2.30 (s, 3 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.02 – 1.96 (m, 9 H), 1.92 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.2, 170.1, 170.0, 169.9, 169.6, 169.4, 168.9, 138.5, 133.6, 129.5, 127.6, 100.9, 85.5, 76.5, 76.0, 73.8, 70.8, 70.5, 70.1, 69.0, 66.5, 62.0, 60.7, 21.0, 20.7, 20.7, 20.6, 20.5, 20.5, 20.4. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{33}H_{42}O_{17}SNa$ 765.2040; Found 765.2025.



4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (31).

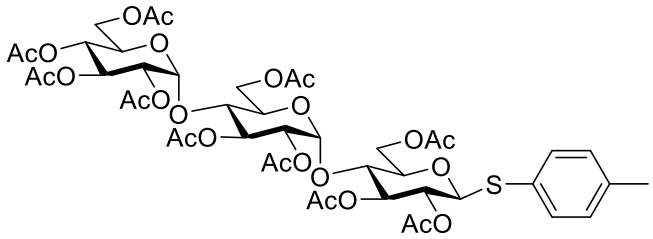
The product (99.6 mg, 67% yield) as a white solid was purified with silica gel chromatography (PE/EA = 3/1~1/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2 H), 7.09 (d, *J* = 7.7 Hz, 2 H), 5.20 – 5.08 (m, 2 H), 5.04 (t, *J* = 9.7 Hz, 1 H), 4.93 –

4.81 (m, 2 H), 4.60 – 4.51 (m, 2 H), 4.47 (d, *J* = 8.0 Hz, 1 H, H-1), 4.35 (dd, *J* = 12.4, 4.3 Hz, 1 H), 4.07 (dd, *J* = 12.1, 5.6 Hz, 1 H), 4.01 (dd, *J* = 12.4, 2.3 Hz, 1 H), 3.69 (t, *J* = 9.6 Hz, 1 H), 3.66 – 3.55 (m, 2 H), 2.32 (s, 3 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.99 (d, *J* = 1.7 Hz, 6 H), 1.96 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.4, 170.2, 169.7, 169.5, 169.2, 169.0, 138.6, 133.7, 129.6, 127.7, 100.7, 85.6, 76.7, 76.3, 73.6, 72.9, 71.9, 71.5, 70.1, 67.7, 61.9, 61.5, 21.1, 20.8, 20.7, 20.6, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{33}H_{42}O_{17}SNa$ 765.2040; Found 765.2029.



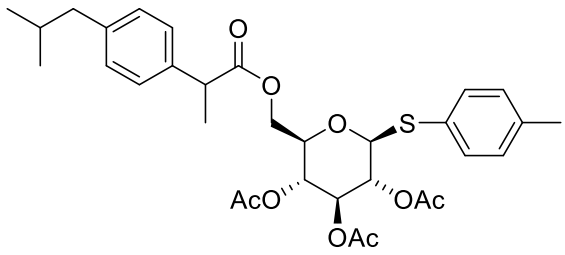
4-Methylphenyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (32).

The product (93.7 mg, 63% yield) as a white solid was purified with silica gel chromatography (PE/EA = 3/1~1/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 2 H), 7.04 (d, *J* = 7.8 Hz, 2 H), 5.31 (d, *J* = 4.1 Hz, 1 H), 5.27 (t, *J* = 10.1 Hz, 1 H), 5.20 (t, *J* = 9.0 Hz, 1 H), 4.97 (t, *J* = 9.9 Hz, 1 H), 4.77 (dd, *J* = 10.6, 4.0 Hz, 1 H), 4.68 (t, *J* = 9.6 Hz, 1 H), 4.59 (d, *J* = 10.0 Hz, 1 H, H-1), 4.47 (dd, *J* = 12.1, 2.6 Hz, 1 H), 4.15 (ddd, *J* = 17.2, 12.2, 4.3 Hz, 2 H), 3.98 (dd, *J* = 12.5, 2.3 Hz, 1 H), 3.90 – 3.80 (m, 2 H), 3.62 (ddd, *J* = 9.7, 4.7, 2.6 Hz, 1 H), 2.27 (s, 3 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.99 (s, 3 H), 1.96 (s, 3 H), 1.95 (s, 3 H), 1.92 (s, 3 H), 1.91 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 169.8, 169.5, 169.3, 138.7, 134.0, 129.6, 127.1, 95.5, 85.0, 76.5, 76.0, 72.3, 70.6, 69.9, 69.2, 68.4, 68.0, 62.7, 61.4, 21.1, 20.8, 20.7, 20.7, 20.6, 20.5, 20.5, 20.5. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{33}H_{42}O_{17}SNa$ 765.2040; Found 765.2031.



4-Methylphenyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-2,3,6-tri-O-acetyl-β-D-glucopyranoside (33).

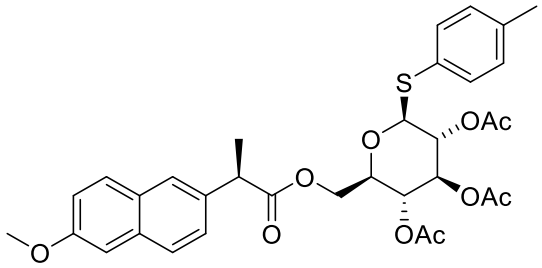
The product (107.2 mg, 52% yield) as a white solid was purified with silica gel chromatography (PE/EA = 3/1~1/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 2 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 5.37 – 5.27 (m, 3 H), 5.22 (t, *J* = 9.0 Hz, 1 H), 5.19 (d, *J* = 4.1 Hz, 1 H), 5.01 (t, *J* = 9.8 Hz, 1 H), 4.80 (dd, *J* = 10.6, 4.0 Hz, 1 H), 4.72 – 4.64 (m, 2 H), 4.60 (d, *J* = 10.0 Hz, 1 H, H-1), 4.49 (dd, *J* = 12.2, 2.8 Hz, 1 H), 4.41 (dd, *J* = 12.3, 2.3 Hz, 1 H), 4.26 – 4.17 (m, 2 H), 4.12 (dd, *J* = 12.3, 3.4 Hz, 1 H), 4.00 (dd, *J* = 12.5, 2.4 Hz, 1 H), 3.93 – 3.80 (m, 4 H), 3.67 (dt, *J* = 9.7, 3.5 Hz, 1 H), 2.30 (s, 3 H), 2.10 (s, 3 H), 2.10 (s, 3 H), 2.04 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 3 H), 1.95 (d, *J* = 4.9 Hz, 9 H), 1.91 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.4, 170.4, 170.4, 170.2, 169.9, 169.7, 169.5, 169.4, 169.3, 138.7, 134.1, 129.5, 126.9, 95.6, 95.5, 84.7, 76.3, 75.9, 73.3, 72.4, 71.6, 70.5, 70.3, 69.9, 69.2, 68.8, 68.4, 67.8, 62.8, 62.2, 61.3, 21.0, 20.7, 20.7, 20.6, 20.6, 20.5, 20.4, 20.4. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{45}H_{58}O_{25}SNa$ 1053.2886; Found 1053.2880.



4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[2-(4-isobutylphenyl) propanoyl]-β-D-thioglucopyranoside (34).

The product (78.1 mg, 65% yield) as a white solid (dr = 1: 0.8) was purified with silica gel chromatography (PE/EA = 5/1~3/1). **Major isomer: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 7.15 – 7.05 (m, 4 H), 5.17 (t, *J* =

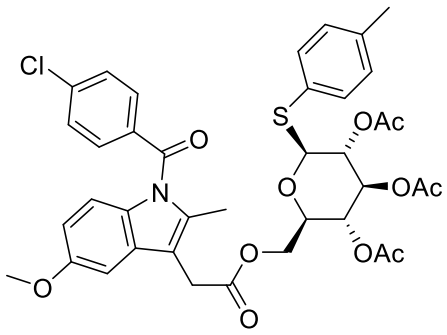
9.4 Hz, 1 H), 4.94 (t, *J* = 9.8 Hz, 1 H), 4.88 (t, *J* = 9.7 Hz, 1 H), 4.59 (d, *J* = 10.0 Hz, 1 H, H-1), 4.32 – 4.03 (m, 2 H), 3.72 (q, *J* = 7.2 Hz, 1 H), 3.67-3.62 (m, 1H), 2.44 (d, *J* = 7.2 Hz, 2 H), 2.35 (s, 3 H), 2.08 (s, 3 H), 1.97 (s, 6 H), 1.84 (m, 1 H), 1.50 (d, *J* = 6.8 Hz, 3 H), 0.89 (d, *J* = 6.8 Hz, 6 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.2, 170.1, 169.2, 169.1, 140.6, 138.7, 137.3, 133.9, 129.6, 129.3, 127.3, 127.2, 85.6, 75.9, 74.0, 69.8, 68.1, 62.2, 45.0, 30.1, 22.3, 21.1, 20.7, 20.5, 20.5, 18.4. **Minor isomer: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 7.12 – 7.05 (m, 4H), 5.18 (t, *J* = 9.5 Hz, 1 H), 4.94 (t, *J* = 9.8 Hz, 1 H), 4.89 (t, *J* = 9.6 Hz, 1 H), 4.60 (d, *J* = 10.0 Hz, 1 H, H-1), 4.32 – 4.03 (m, 2 H), 3.72 (q, *J* = 7.2 Hz, 1 H), 3.67-3.62 (m, 1 H), 2.43 (d, *J* = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.09 (s, 3 H), 1.97 (s, 6 H), 1.84 (m, 1 H), 1.51 (d, *J* = 6.6 Hz, 3 H), 0.88 (d, *J* = 6.8 Hz, 6 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.1, 170.1, 169.2, 169.1, 140.6, 138.8, 137.1, 134.0, 129.6, 129.3, 127.3, 127.1, 85.6, 75.8, 74.0, 69.8, 68.4, 62.6, 44.9, 30.1, 22.3, 21.1, 20.7, 20.5, 20.4, 18.2. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{32}H_{40}O_9SNa$ 623.2291; Found 623.2289.



4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[(R)-2-(6-methoxynaphthalen-2-yl) propanoyl]-β-D-thioglucopyranoside (35).

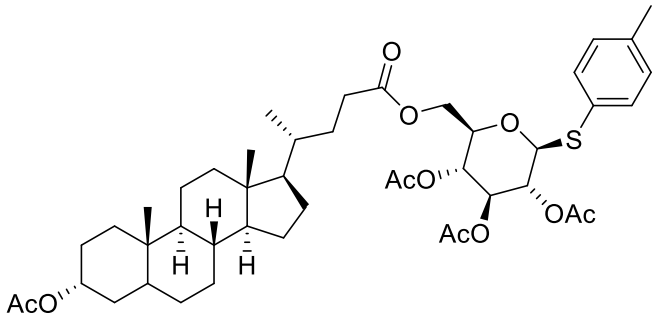
The product (87.4 mg, 70% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 3H), 7.44 – 7.33 (m, 3 H), 7.16 – 7.05 (m, 4 H), 5.17 (t, *J* = 9.3 Hz, 1 H), 4.90 (dt, *J* = 16.6, 9.8 Hz, 2 H), 4.60 (d, *J* = 10.1 Hz, 1 H, H-1), 4.29 (dd, *J* = 12.3, 2.3 Hz, 1 H), 4.11 (dd, *J* = 12.2, 5.5 Hz, 1 H), 3.90 (s, 3 H), 3.88 (d, *J* = 7.2 Hz, 1 H), 3.68 (ddd, *J* = 10.2, 5.5, 2.3 Hz, 1 H), 2.33 (s, 3 H), 2.09 (s, 3 H), 1.96 (s, 3 H), 1.92 (s, 3 H), 1.60 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.1, 170.1, 169.2, 169.1, 157.6, 138.8, 135.1, 133.9, 133.7, 129.6, 129.3, 128.9, 127.3, 127.1, 126.2, 126.0, 118.9, 105.5,

85.7, 75.8, 74.0, 69.8, 68.3, 62.6, 55.2, 45.3, 21.1, 20.7, 20.5, 20.4, 18.2. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{33}H_{36}O_{10}SNa$ 647.1927; Found 647.1925.



4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)carbonyl]- β-D-thioglucopyranoside (36).

The product (93.3 mg, 62% yield) as a white solid was purified with silica gel chromatography (PE/EA = 5/1~3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2 H), 7.49 – 7.42 (m, 2 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 6.98 (d, *J* = 2.5 Hz, 1 H), 6.90 (d, *J* = 9.0 Hz, 1 H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1 H), 5.20 (t, *J* = 9.4 Hz, 1 H), 5.01 (t, *J* = 9.8 Hz, 1 H), 4.88 (t, *J* = 9.6 Hz, 1 H), 4.63 (d, *J* = 10.0 Hz, 1 H, H-1), 4.32 – 4.16 (m, 2 H), 3.83 (s, 3 H), 3.71 (s, 2 H), 3.70 – 3.67 (m, 1 H), 2.37 (s, 3 H), 2.33 (s, 3 H), 2.09 (s, 3 H), 1.98 (d, *J* = 4.1 Hz, 6 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.4, 170.1, 169.3, 169.2, 168.3, 156.1, 139.2, 138.8, 136.1, 134.0, 133.7, 131.2, 130.8, 130.6, 129.7, 129.1, 127.6, 115.0, 112.1, 111.7, 101.3, 86.0, 75.8, 74.0, 70.0, 68.0, 62.4, 55.7, 29.9, 21.2, 20.7, 20.6, 20.5, 13.3. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{38}H_{38}ClNO_{11}SNa$ 774.1752; Found 774.1769.

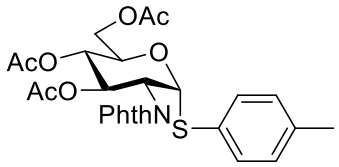


4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[(4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-

acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl]-β-D-thioglucopyranoside (37).

The product (87.8 mg, 54% yield) as a white solid was purified with silica gel chromatography (PE/EA = 8/1~5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2 H), 7.11 (d, *J* = 8.2 Hz, 2 H), 5.19 (t, *J* = 9.4 Hz, 1 H), 5.01 (t, *J* = 9.8 Hz, 1 H), 4.92 (t, *J* = 9.6 Hz, 1 H), 4.71 (dt, *J* = 11.4, 6.4 Hz, 1 H), 4.62 (d, *J* = 10.0 Hz, 1 H), 4.18 (d, *J* = 3.7 Hz, 2 H), 3.69 (dt, *J* = 10.4, 3.7 Hz, 1 H), 2.43 – 2.36 (m, 1 H), 2.34 (s, 3 H), 2.28 – 2.19 (m, 1 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H), 1.89 – 1.75 (m, 7 H), 1.67 (d, *J* = 10.7 Hz, 2 H), 1.61 – 1.49 (m, 3 H), 1.47 – 1.21 (m, 18 H), 1.19 – 0.99 (m, 8 H), 0.91 (s, 6 H), 0.64 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.8, 170.6, 170.2, 169.3, 169.2, 138.7, 133.7, 129.6, 127.6, 85.8, 75.8, 74.4, 74.0, 69.9, 68.2, 62.0, 56.5, 55.9, 42.7, 41.8, 40.4, 40.1, 35.7, 35.3, 35.0, 34.5, 32.2, 30.9, 30.7, 28.1, 27.0, 26.6, 26.3, 24.1, 23.3, 21.4, 21.2, 20.8, 20.7, 20.5, 20.5, 18.2, 12.0. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{45}H_{64}O_{11}SNa$ 835.4067; Found 835.4071.

***p*-Tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-α-D-glucopyranoside (40)**



The product (74.7 mg, 69% yield) as a white solid was purified with silica gel chromatography (PE/EA = 4/1~2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2 H), 7.76 (dd, *J* = 5.6, 3.0 Hz, 2 H), 7.25 (d, *J* = 7.9 Hz, 2 H), 7.05 (d, *J* = 7.9 Hz, 2 H), 6.53 (dd, *J* = 11.9, 8.9 Hz, 1 H), 5.67 (d, *J* = 5.6 Hz, 1 H, H-1), 5.13 – 5.02 (m, 1 H), 4.87 (dd, *J* = 11.9, 5.5 Hz, 1 H), 4.76 (ddd, *J* = 10.3, 4.7, 2.0 Hz, 1 H), 4.40 (dd, *J* = 12.3, 4.8 Hz, 1 H), 4.09 (dd, *J* = 12.4, 2.1 Hz, 1 H), 2.28 (s, 3 H), 2.08 (s, 3 H), 2.08 (s, 3 H), 1.88 (s, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 170.1, 169.3, 138.0, 134.4, 132.0, 129.8, 129.4, 123.8, 87.1, 70.3, 68.4, 67.6, 62.1, 53.8, 21.0, 20.7, 20.7. **HRMS** (ESI/FT-ICR) m/z: $[M+Na]^+$ calcd for $C_{27}H_{27}NO_9SNa$ 564.1304; Found: 564.1306.

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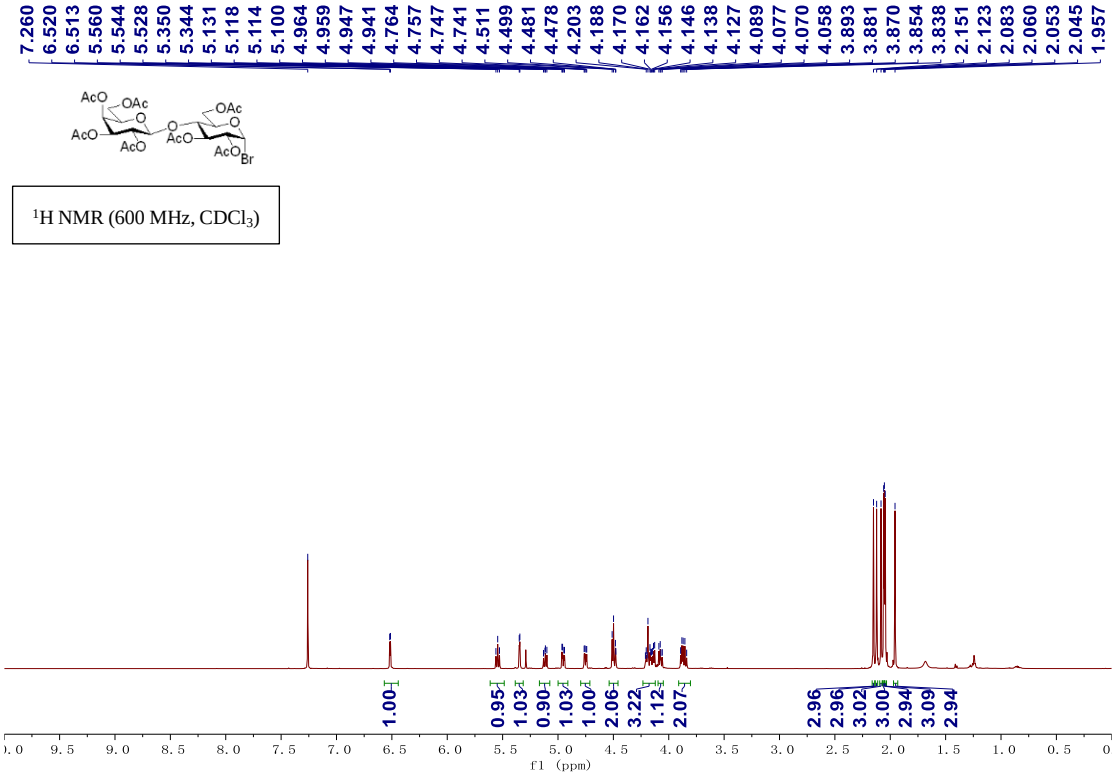
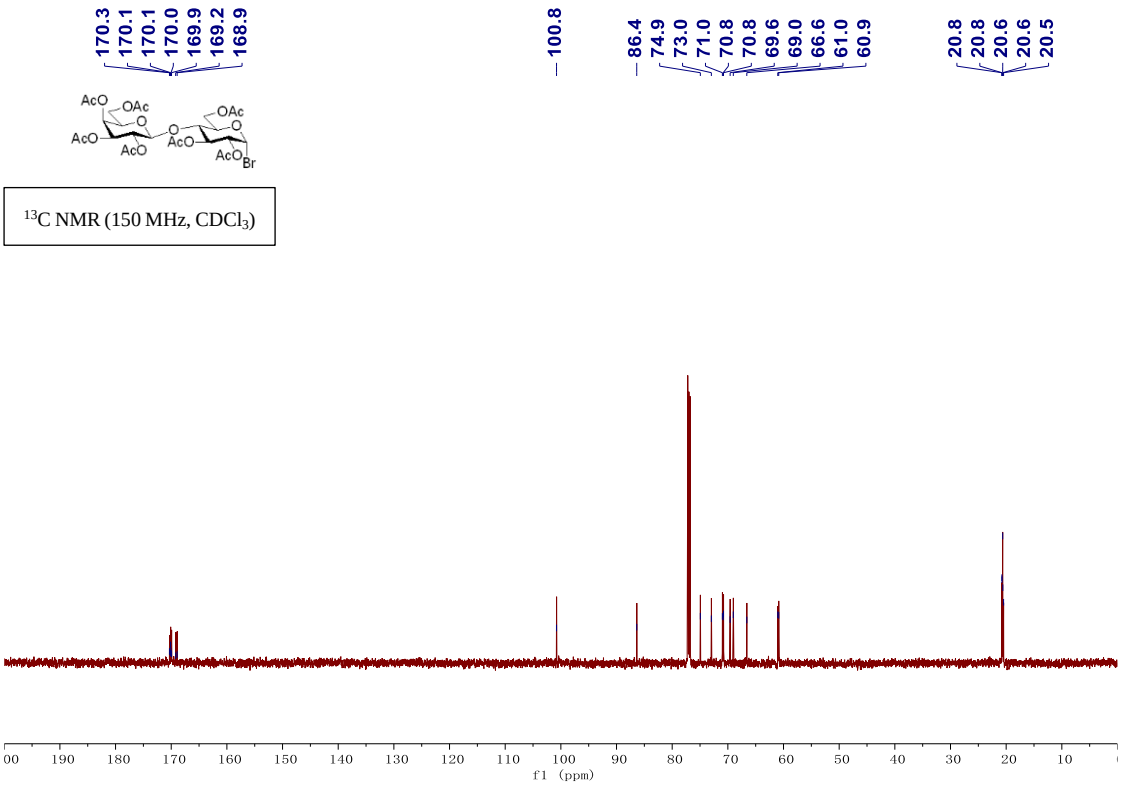
Spectra of Glycosyl bromides and Thioglycosides

2,3,6,2',3',4',6'-Hepta-O-acetyl-α-D-lactosyl bromide (30aa).

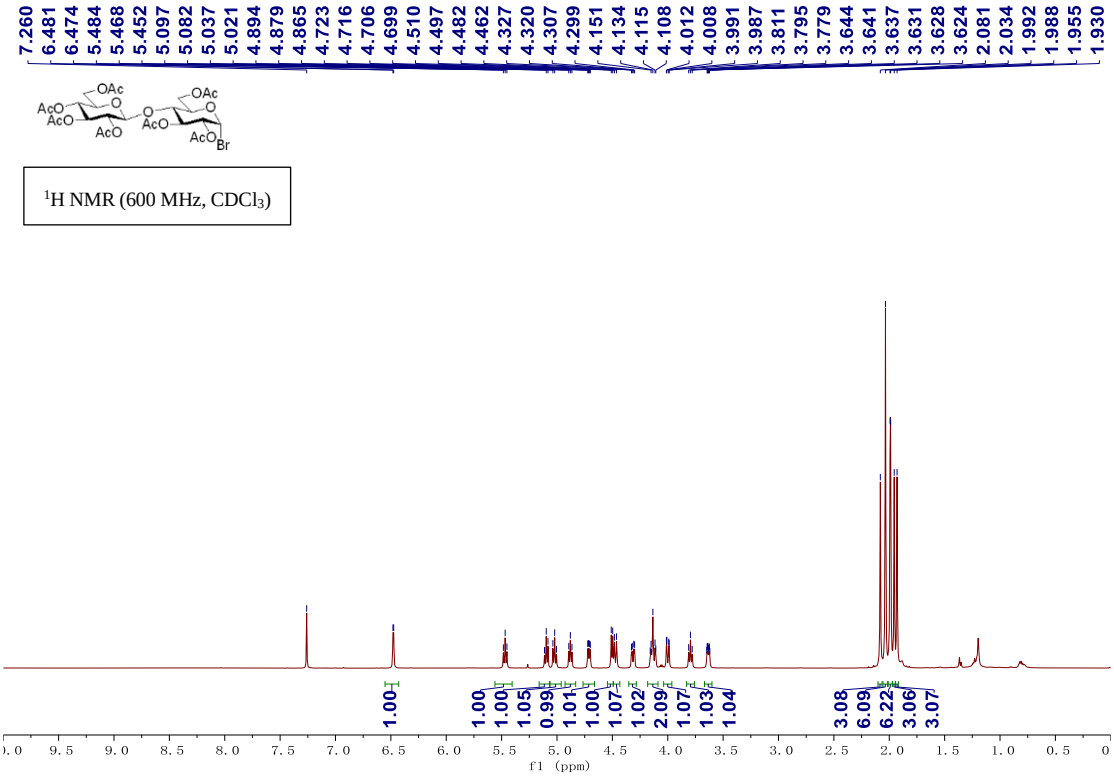


^{1}H NMR (600 MHz, $CDCl_3$)

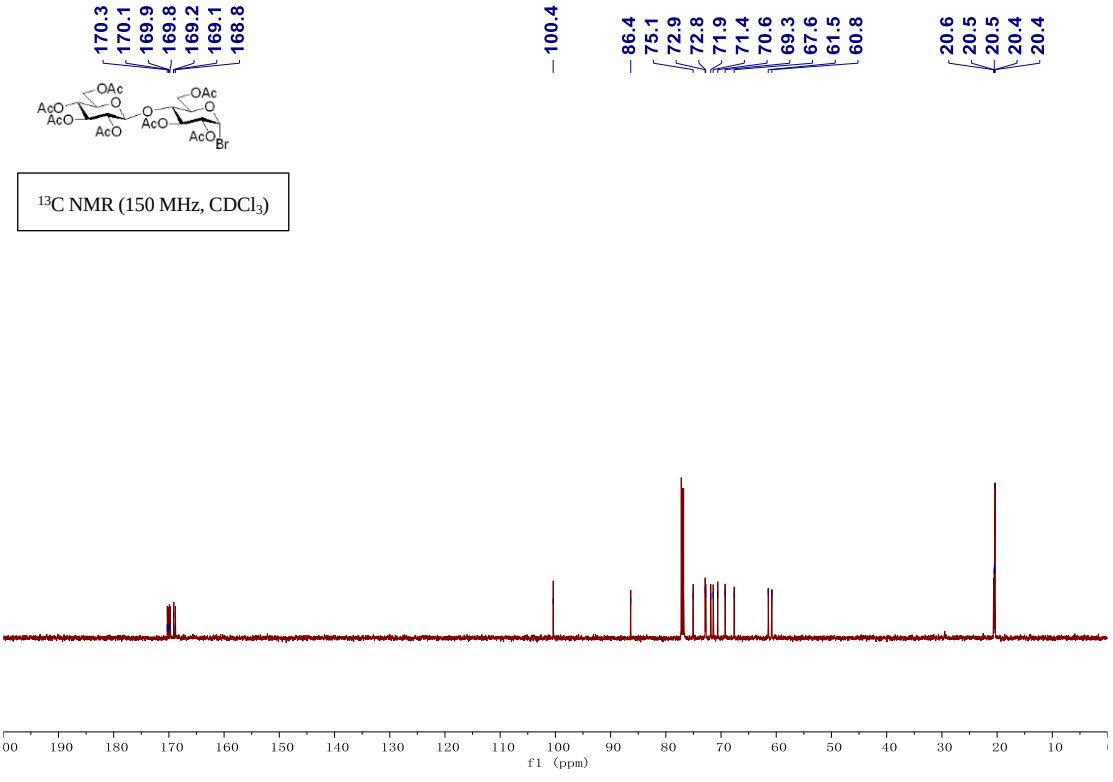


^{13}C NMR (150 MHz, $CDCl_3$)

2,3,6,2',3',4',6'-Hepta-O-acetyl-α-D-cellobiosyl bromide (31aa).

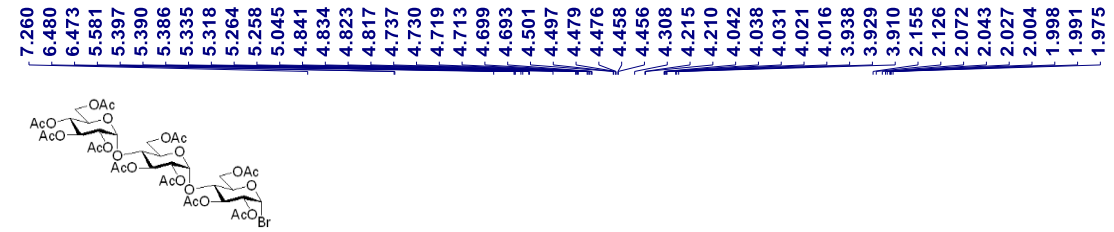


^{1}H NMR (600 MHz, $CDCl_3$)

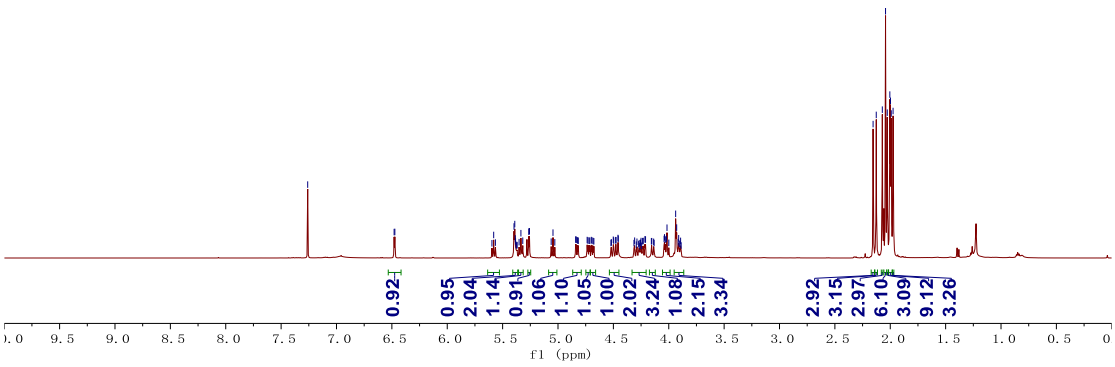


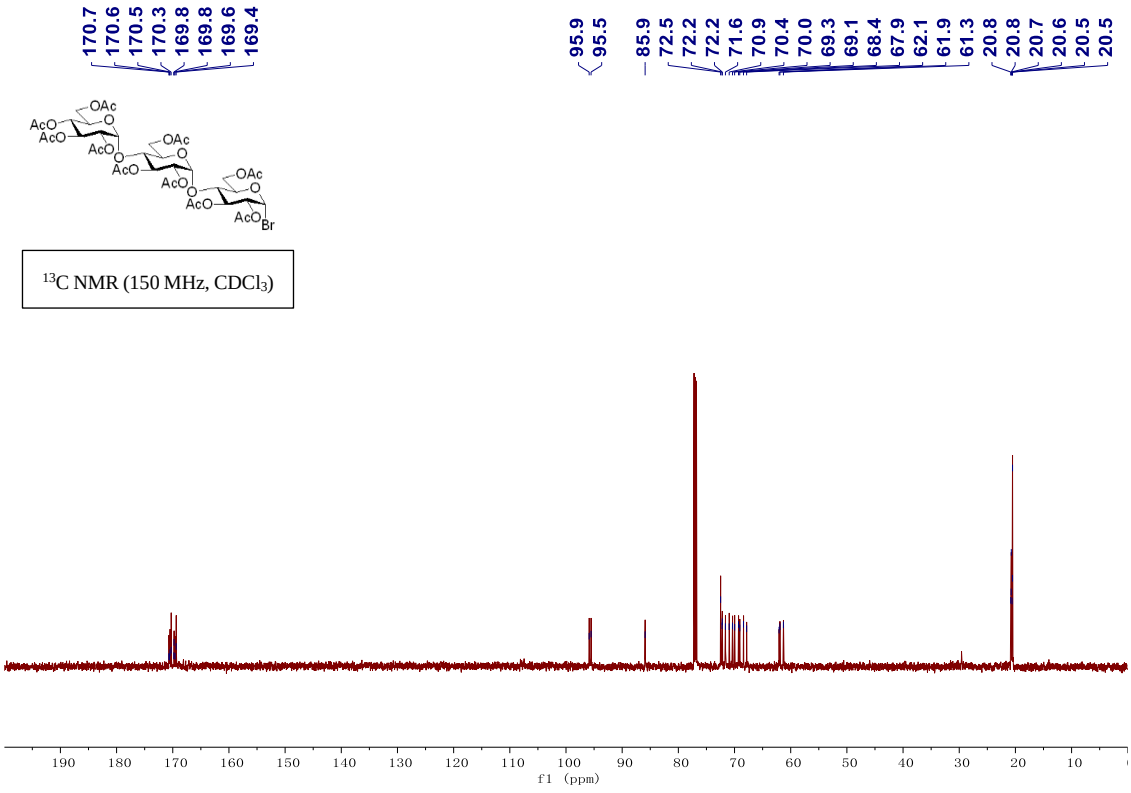
^{13}C NMR (150 MHz, $CDCl_3$)

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-Glucopyranosyl Bromide (33aa).



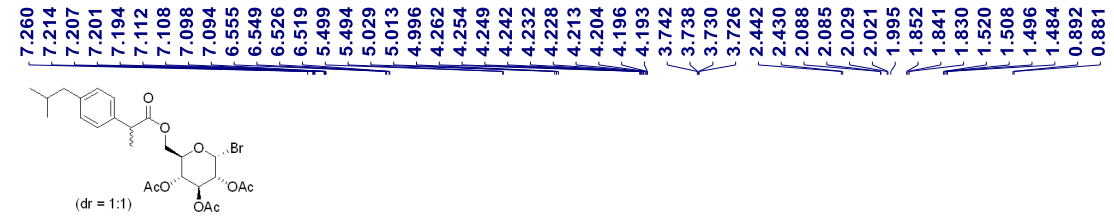
^{1}H NMR (600 MHz, $CDCl_3$)



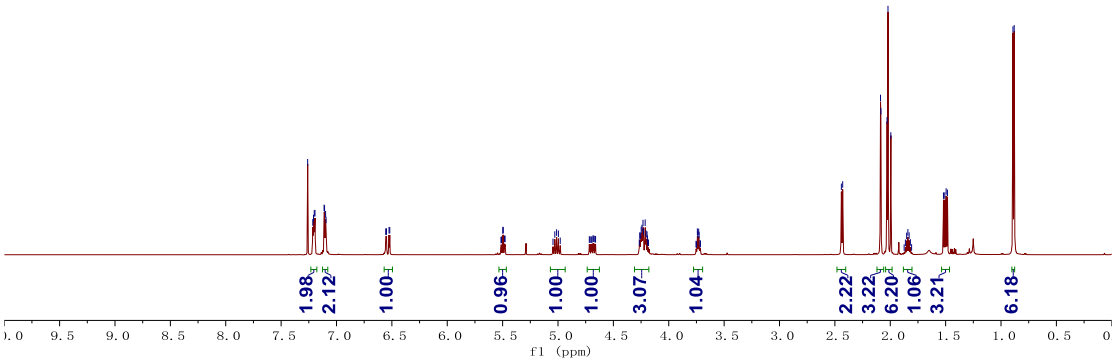


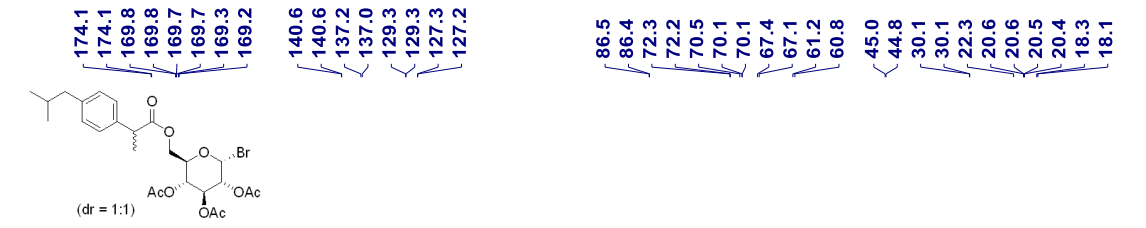
^{13}C NMR (150 MHz, $CDCl_3$)

2,3,4-Tri-O-acetyl-6-O-[2-(4-isobutylphenyl) propanoyl]-α-D-glucopyranosyl bromide (34aa).

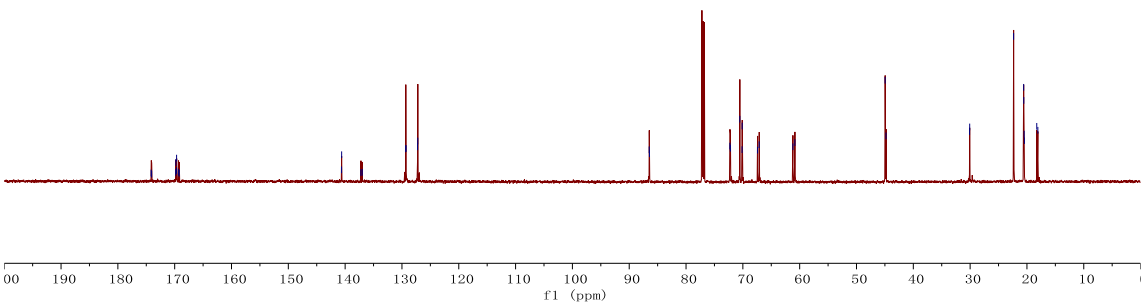


^{1}H NMR (600 MHz, $CDCl_3$)

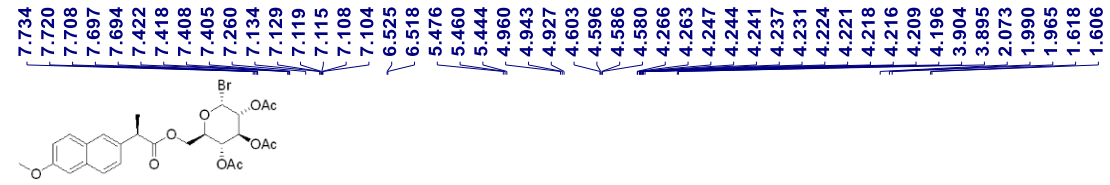




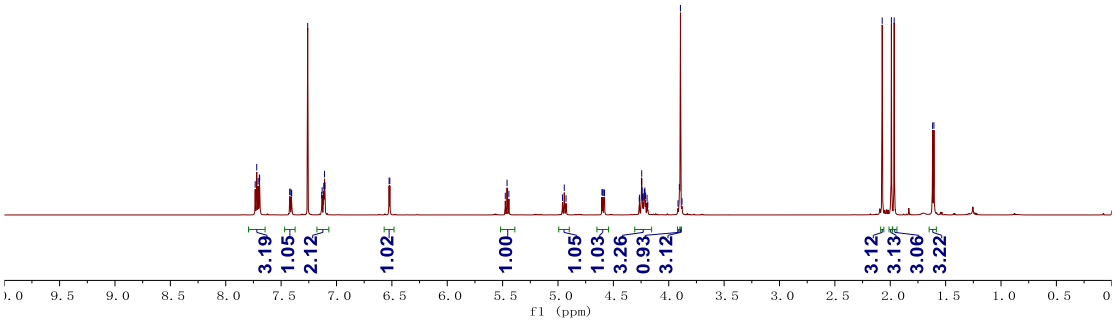
^{13}C NMR (150 MHz, $CDCl_3$)

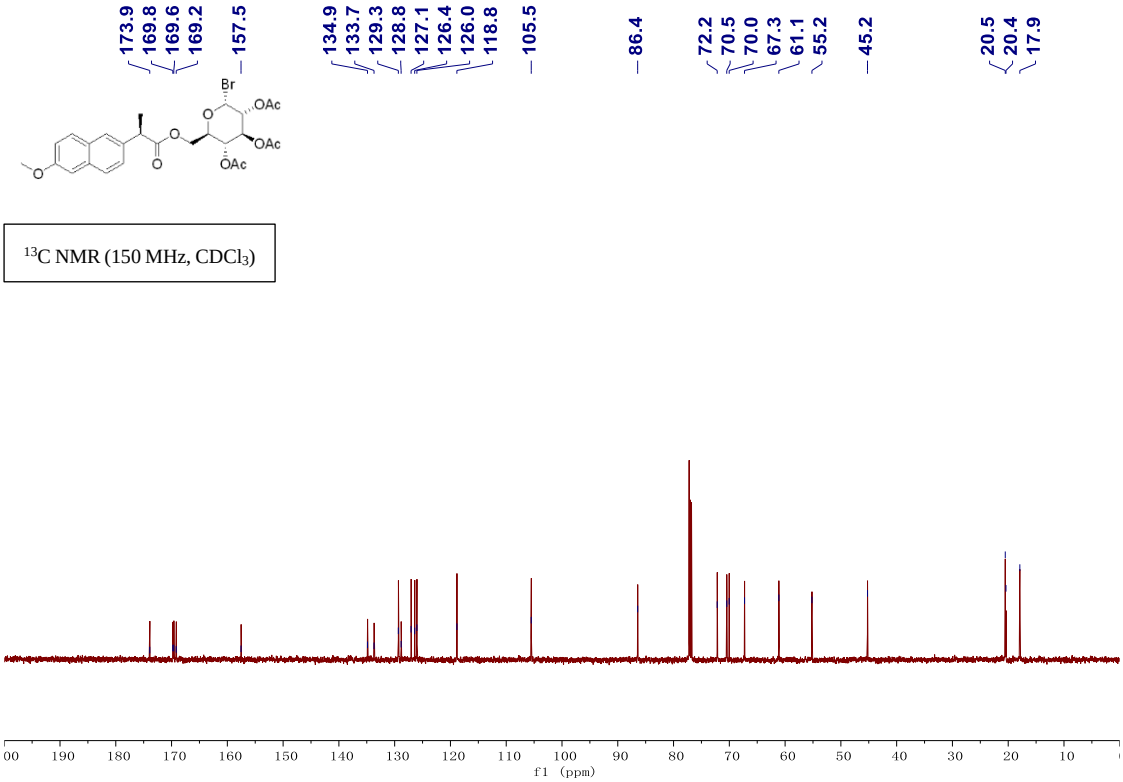


2,3,4-Tri-O-acetyl-6-O-[(R)-2-(6-methoxynaphthalen-2-yl) propanoyl]-α-D-glucopyranosyl bromide (35aa).



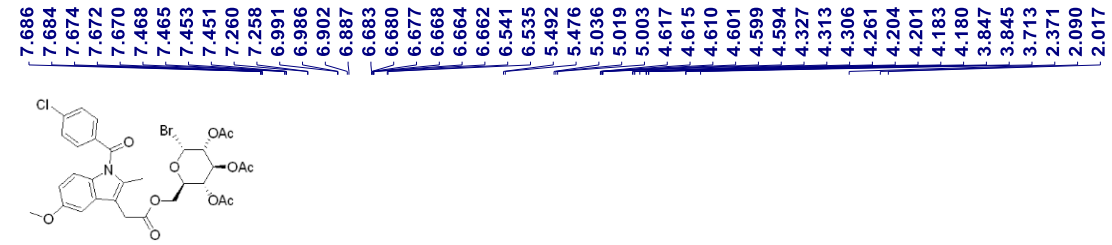
^{1}H NMR (600 MHz, $CDCl_3$)



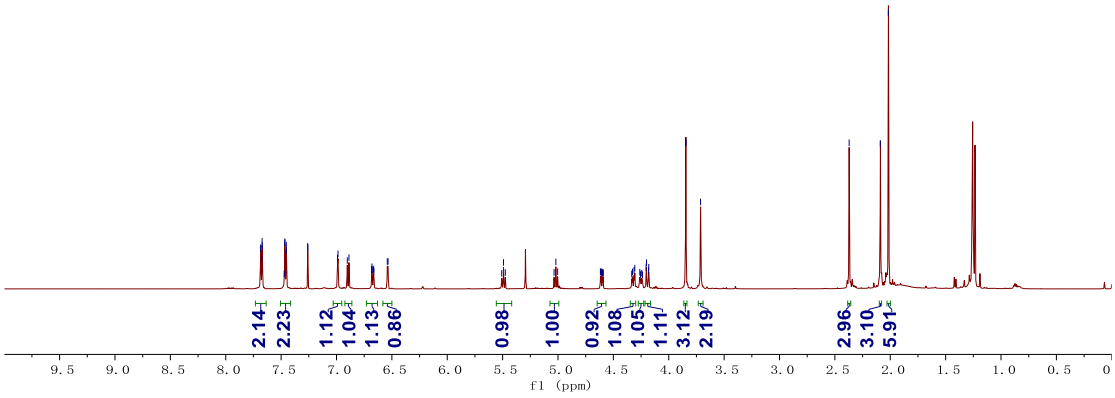


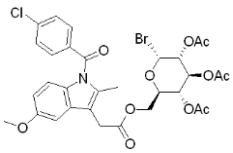
^{13}C NMR (150 MHz, $CDCl_3$)

2,3,4-Tri-O-acetyl-6-O-[(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)carbonyl]-α-D-glucopyranosyl bromide (36aa).

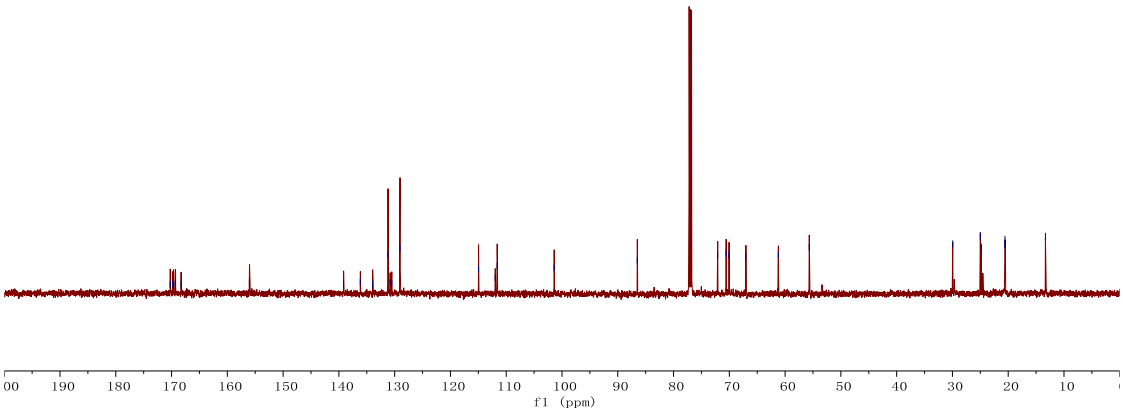


^{1}H NMR (600 MHz, $CDCl_3$)

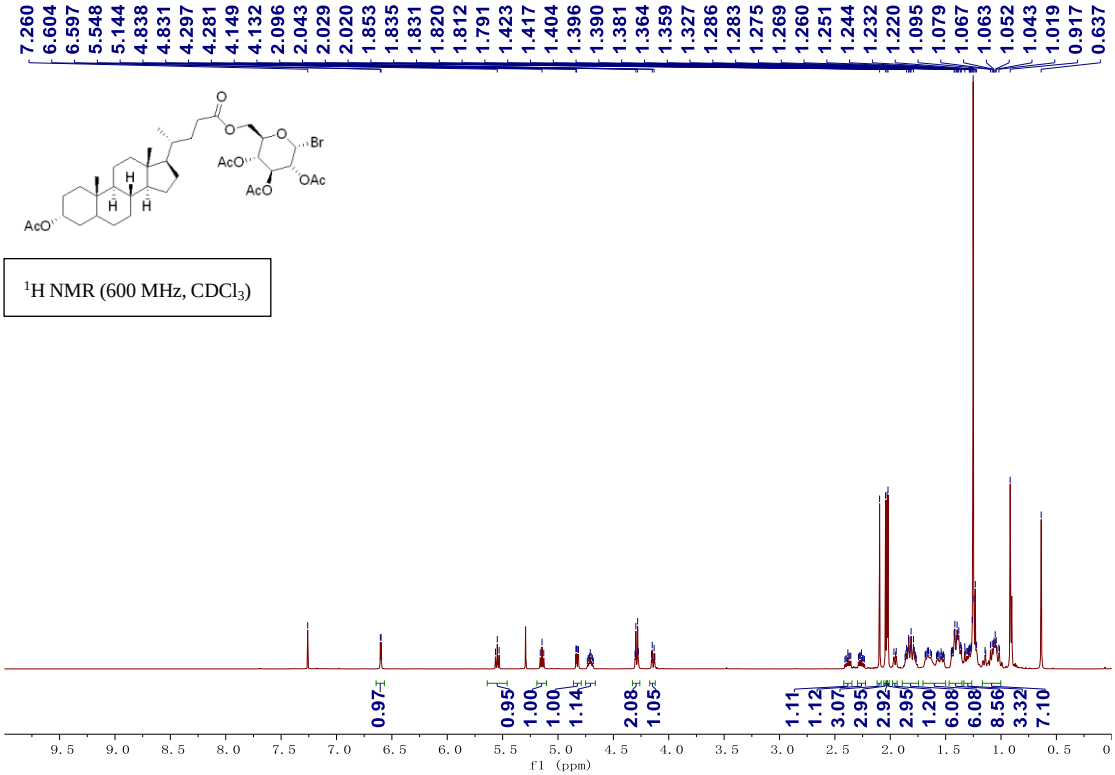




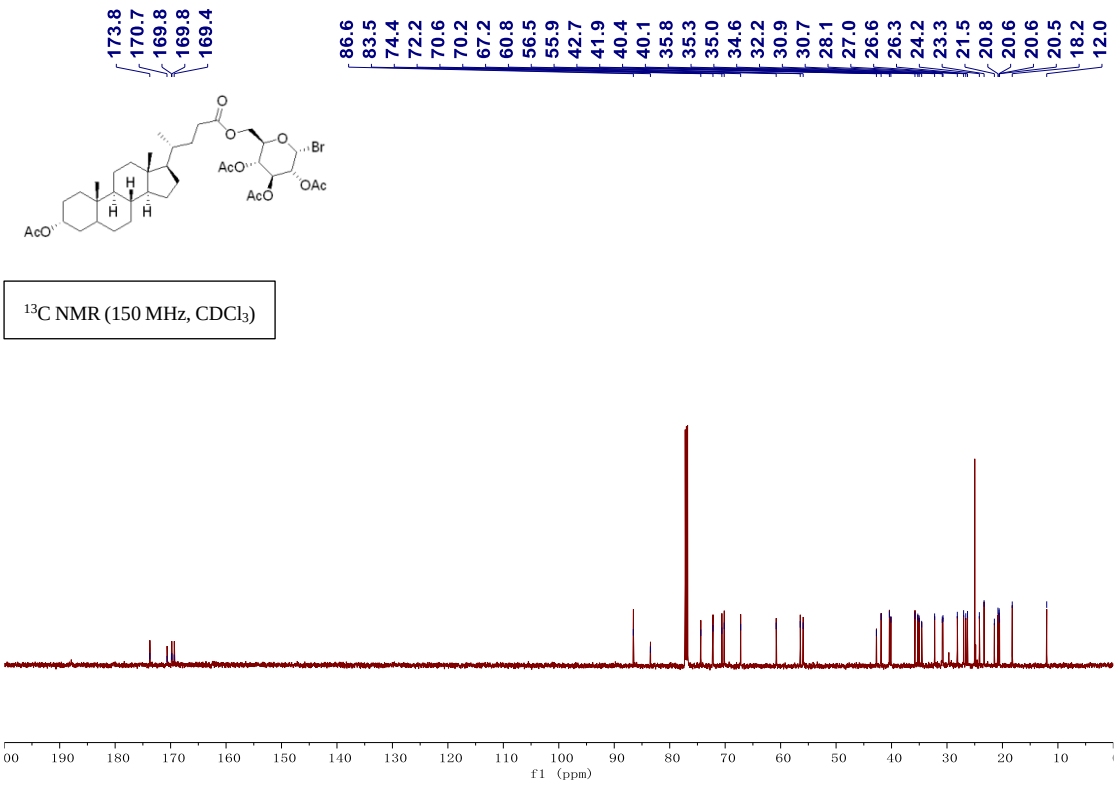
^{13}C NMR (150 MHz, $CDCl_3$)



2,3,4-Tri-O-acetyl-6-O-[(4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl]-α-D-glucopyranosyl bromide (37aa).

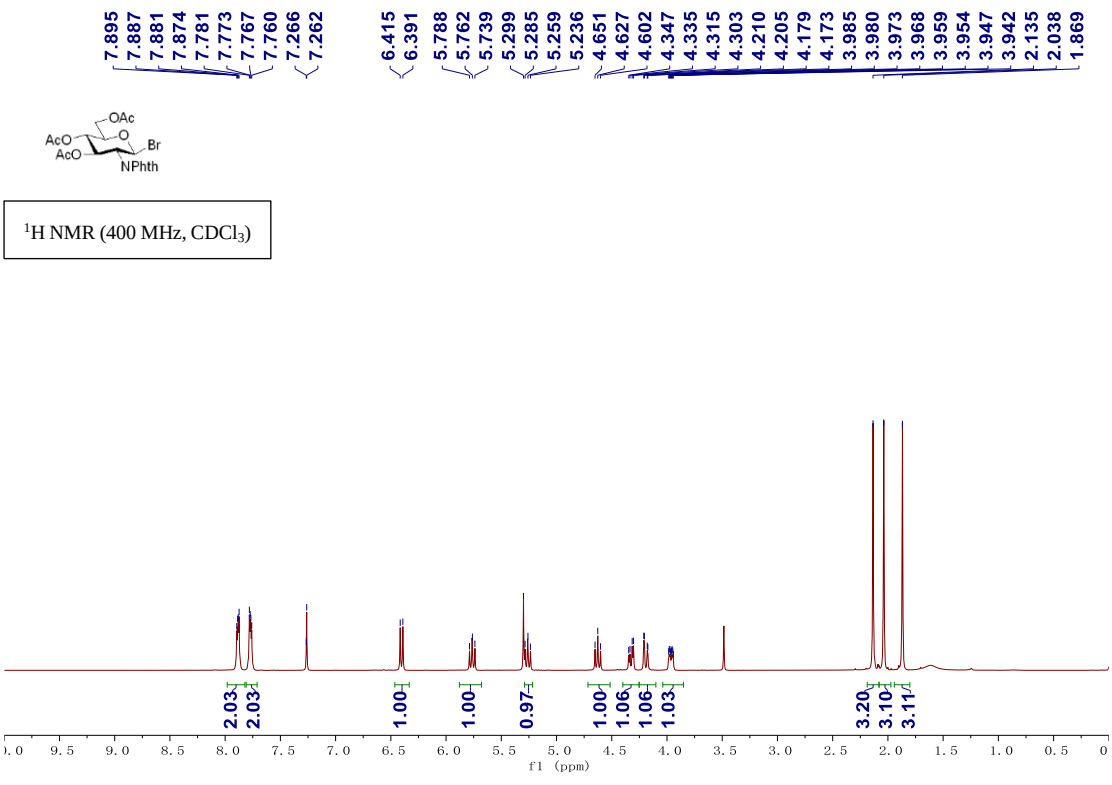


^{1}H NMR (600 MHz, $CDCl_3$)

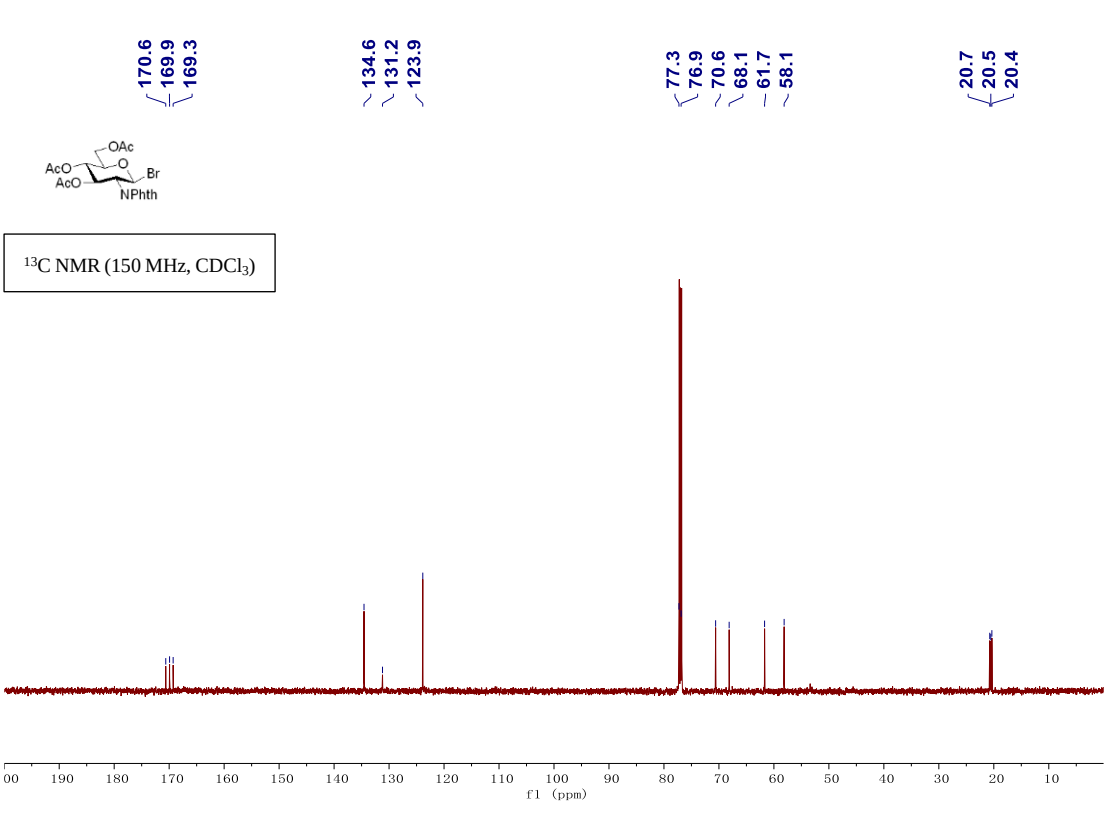


^{13}C NMR (150 MHz, $CDCl_3$)

2-*N*-phthalimido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl bromide (40aa)

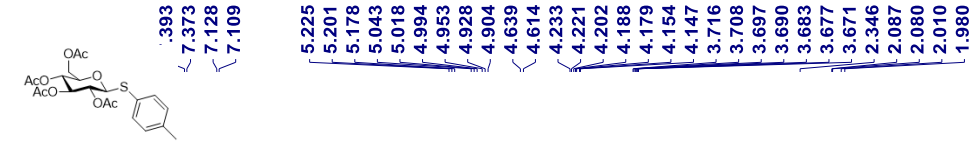


^{1}H NMR (400 MHz, $CDCl_3$)

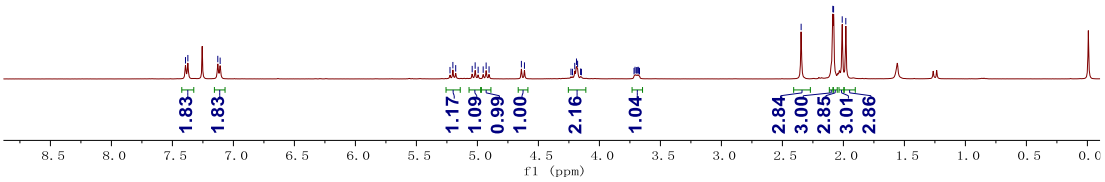


^{13}C NMR (150 MHz, $CDCl_3$)

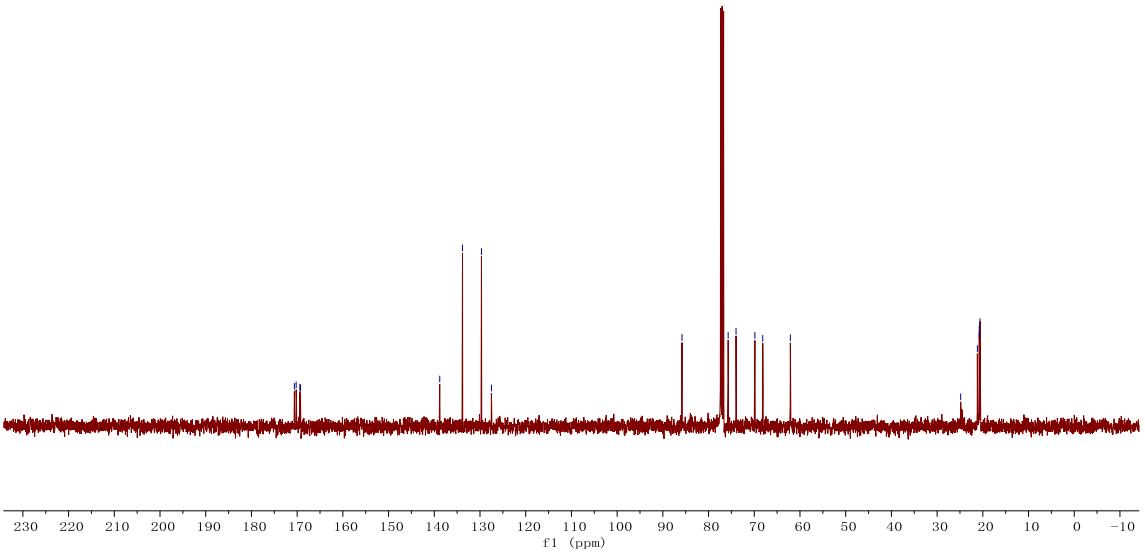
4-Methylphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (1).



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



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



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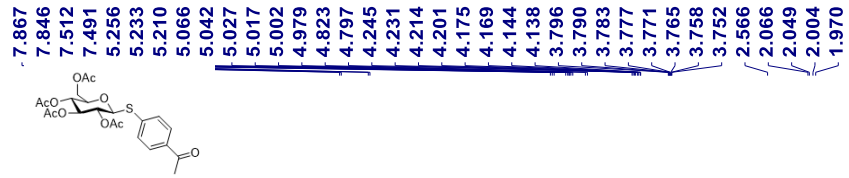
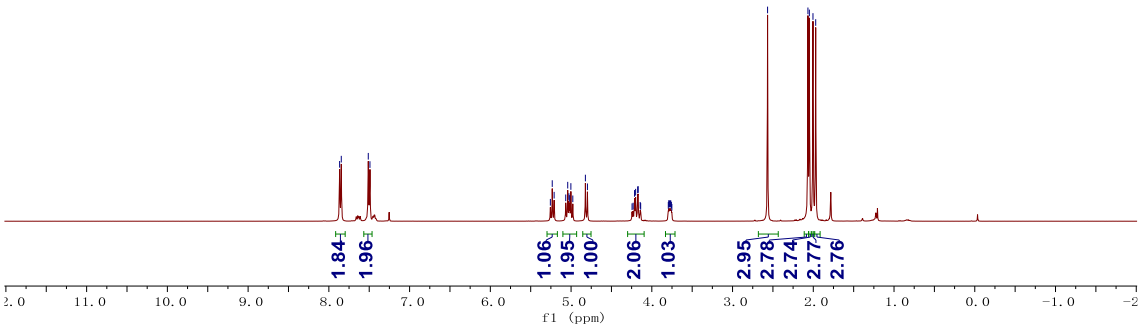
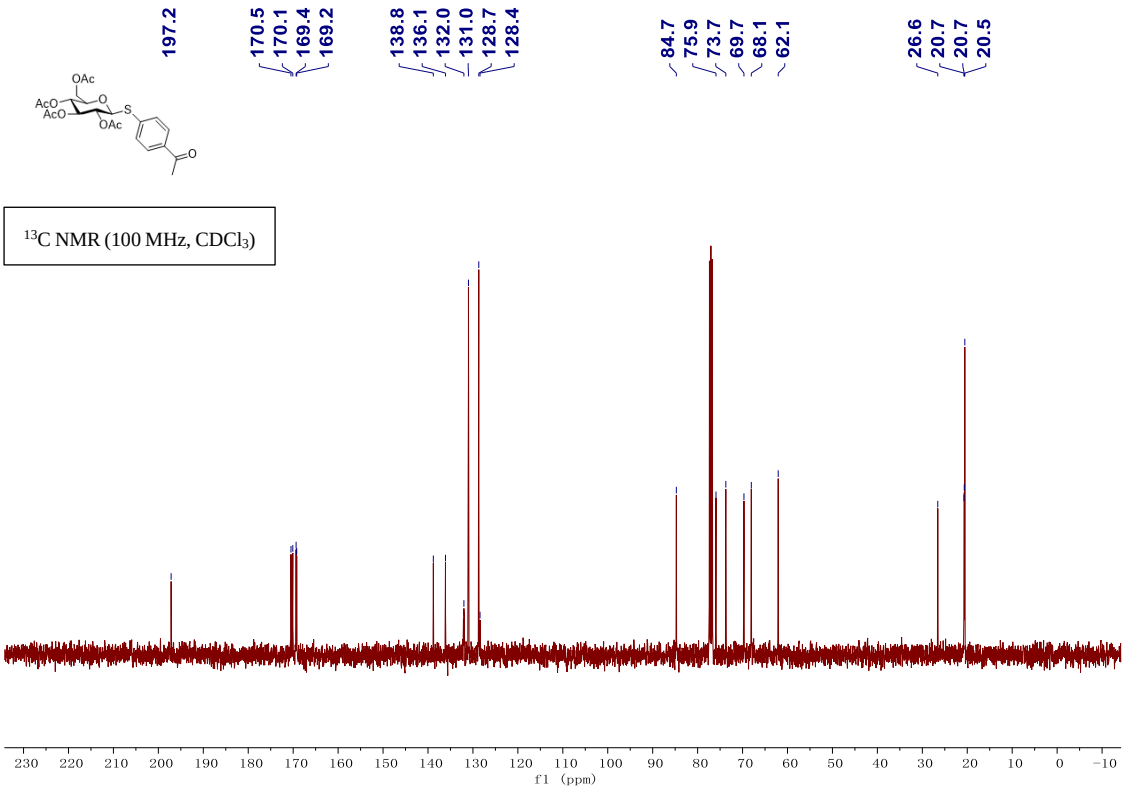
4-Acetylphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (2).



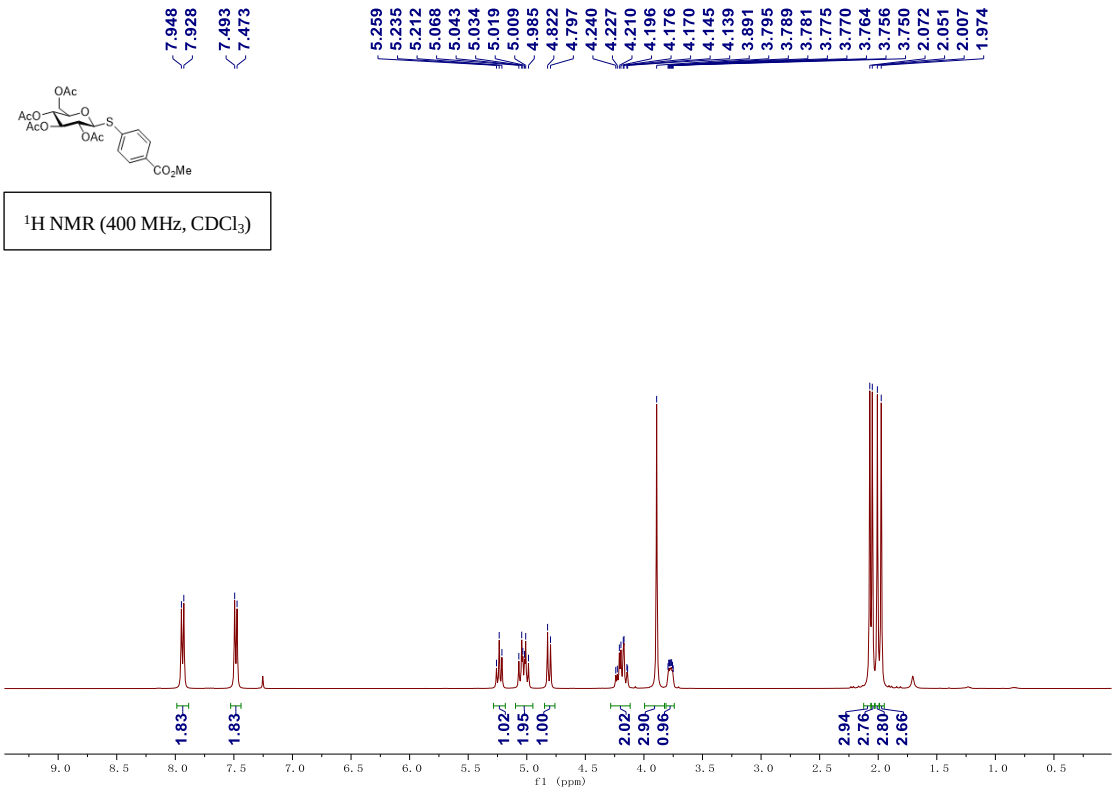
^{1}H NMR (400 MHz, $CDCl_3$)



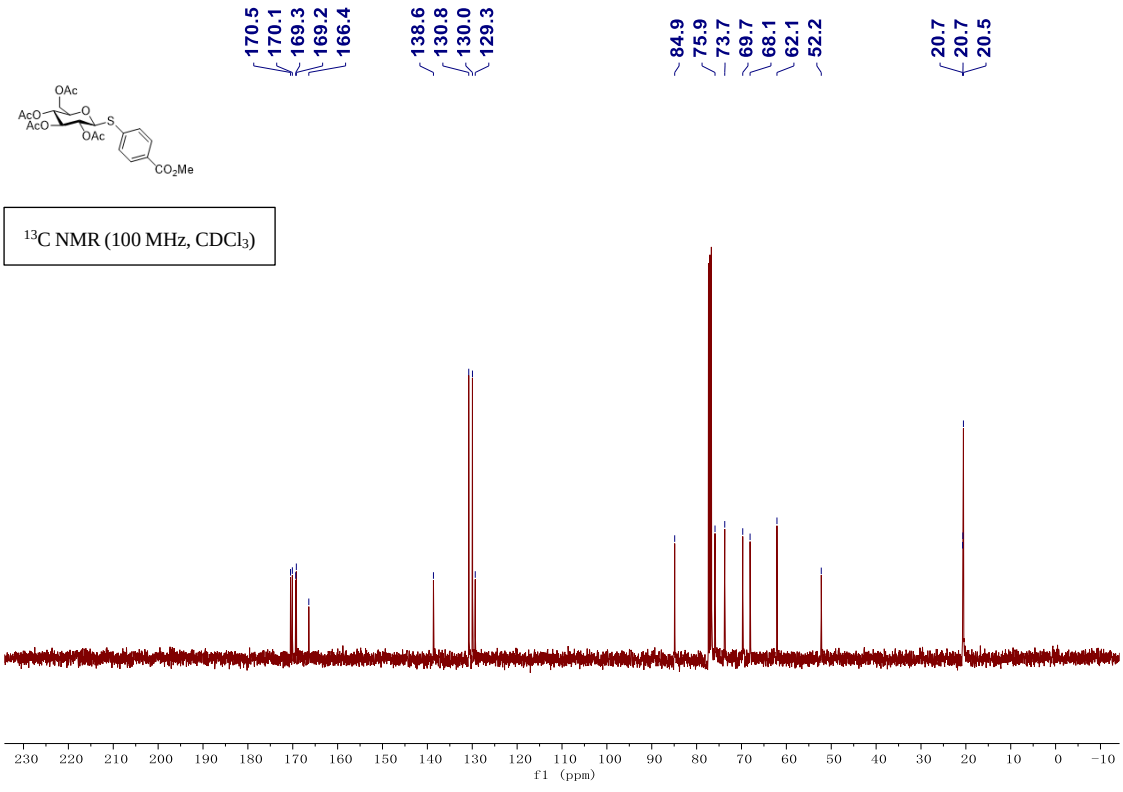


^{13}C NMR (100 MHz, $CDCl_3$)

4-(Methoxycarbonyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (3).

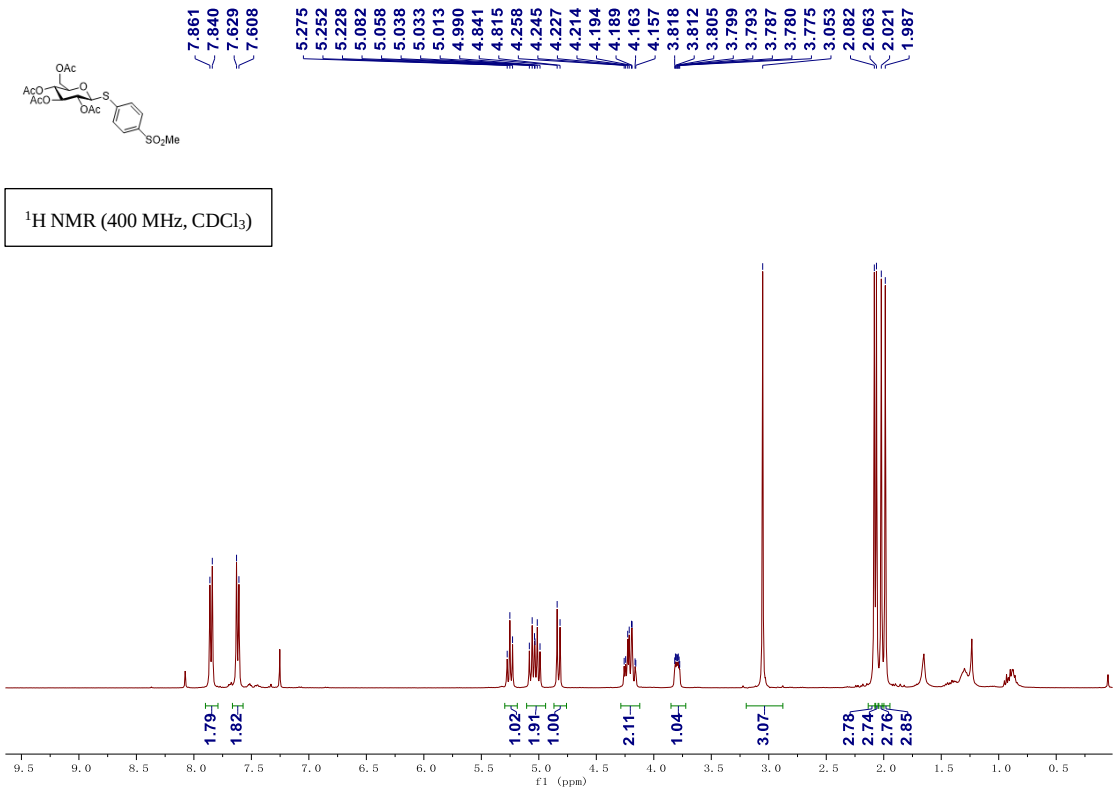


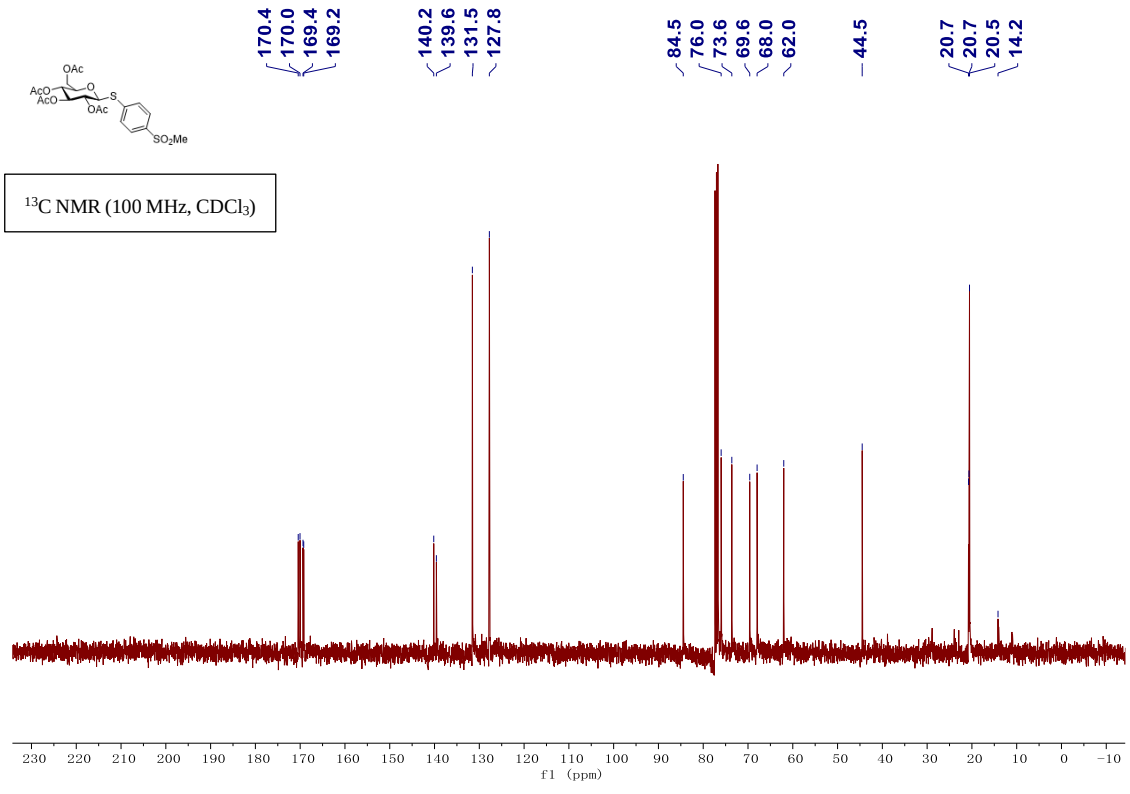
^{1}H NMR (400 MHz, $CDCl_3$)



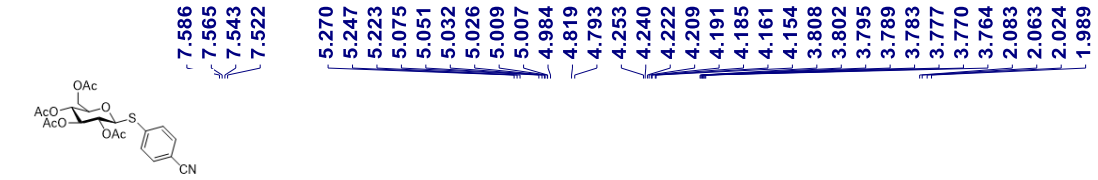
^{13}C NMR (100 MHz, $CDCl_3$)

4-(Methylsulfonyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (4).

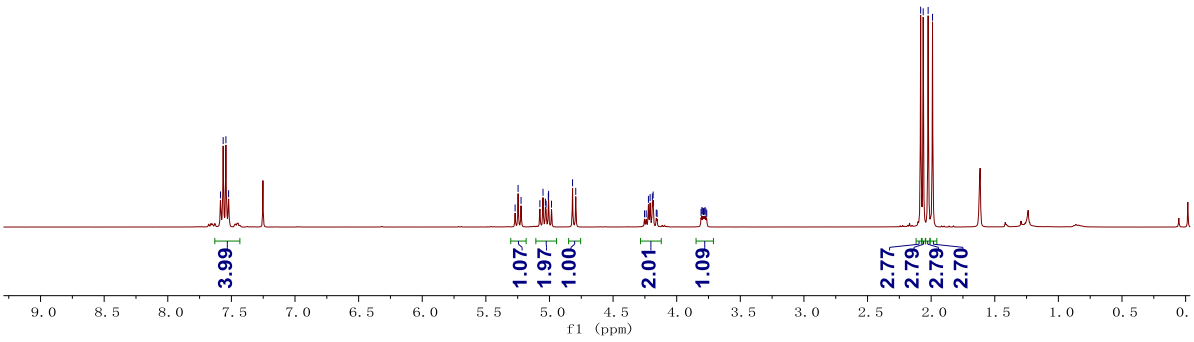


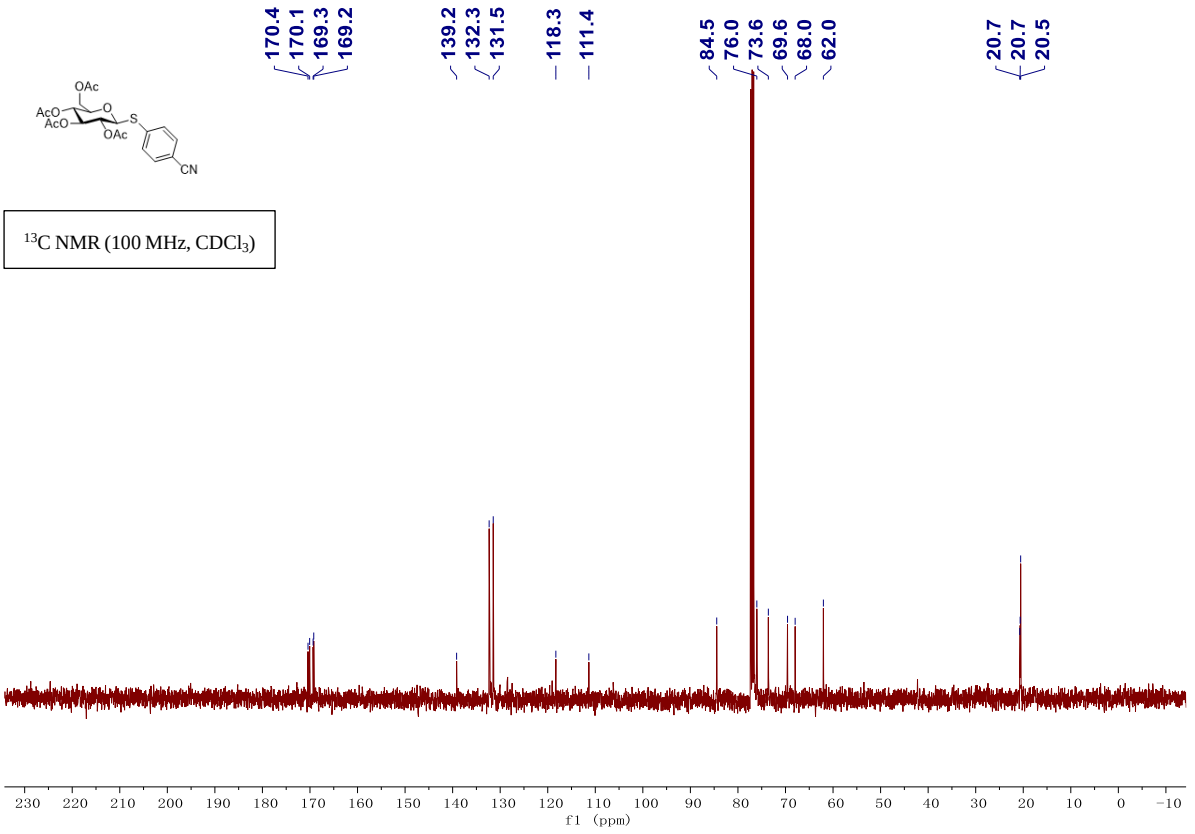


4-Cyanophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (5).



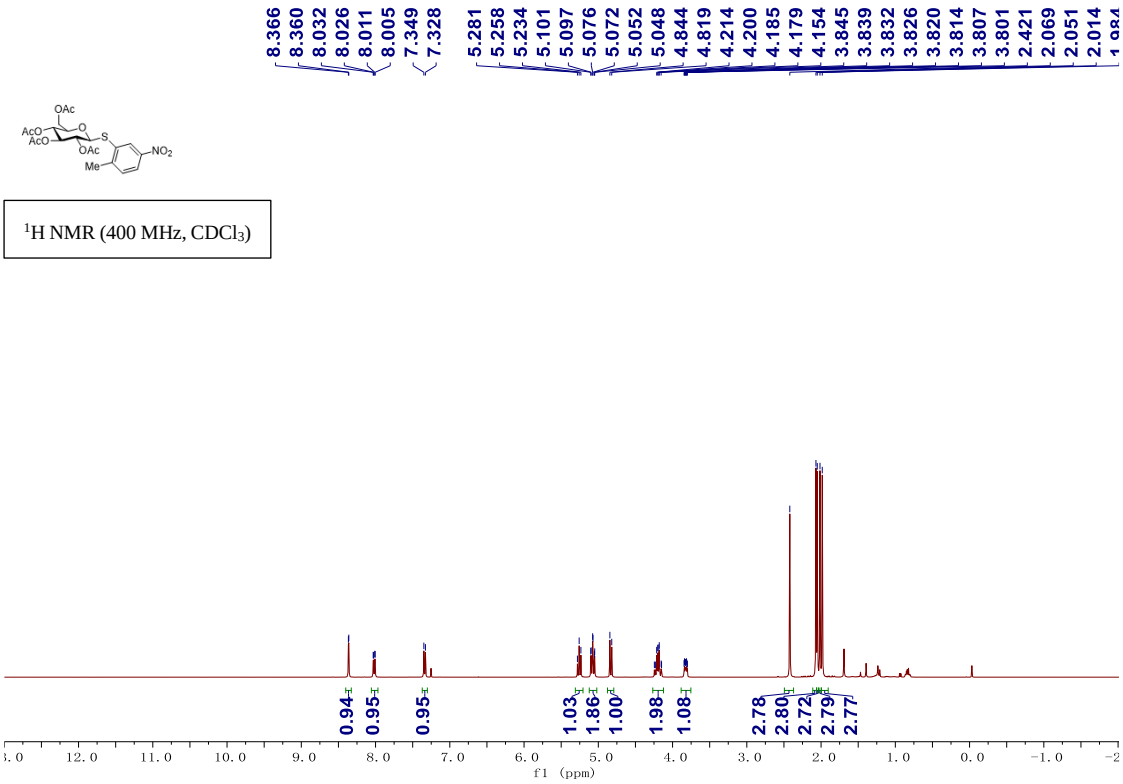
^{1}H NMR (400 MHz, $CDCl_3$)



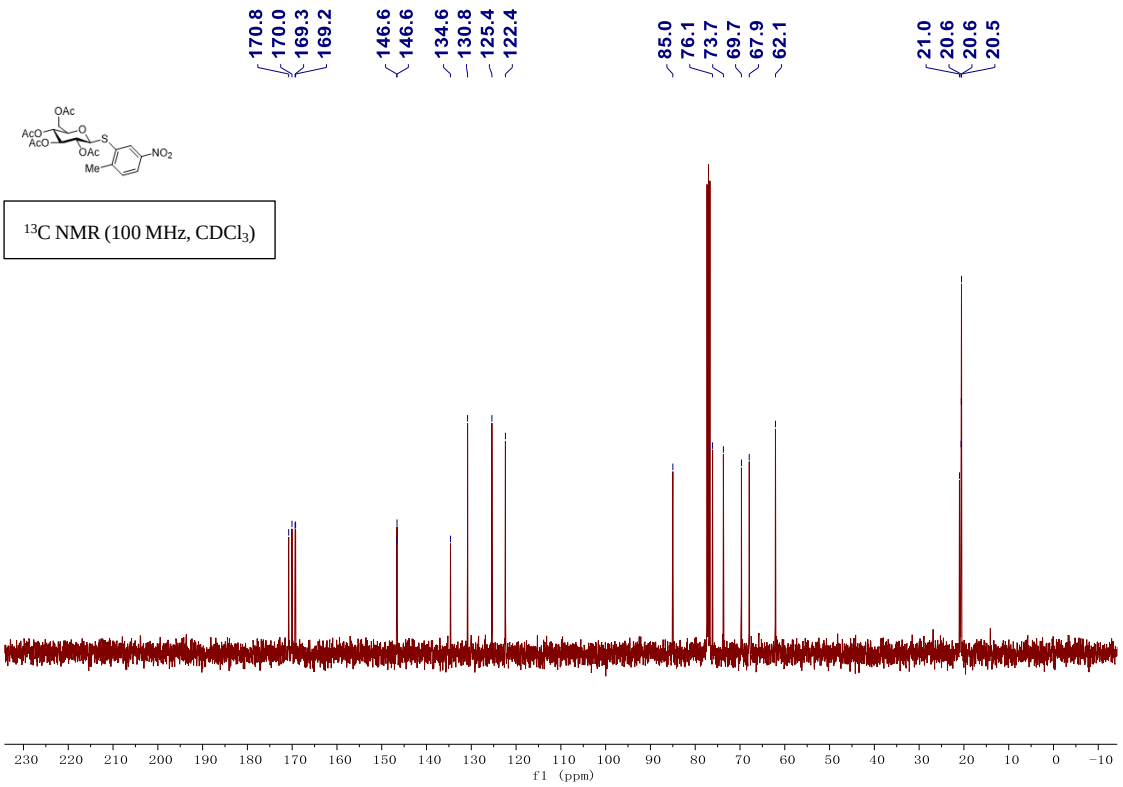


^{13}C NMR (100 MHz, $CDCl_3$)

2-Methyl-5-nitrophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (6).

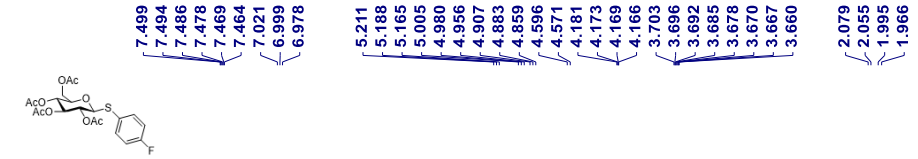


^{1}H NMR (400 MHz, $CDCl_3$)

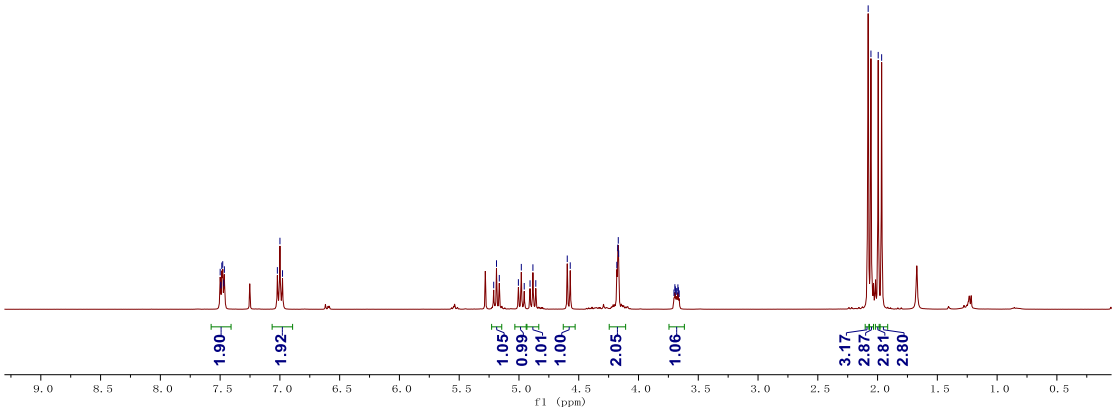


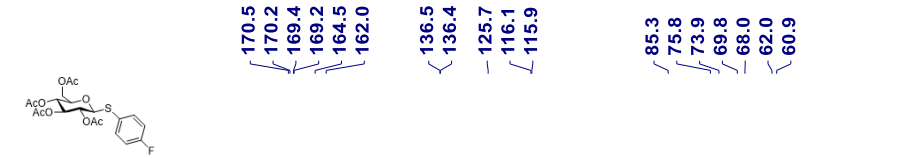
^{13}C NMR (100 MHz, $CDCl_3$)

4-Fluorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (7).

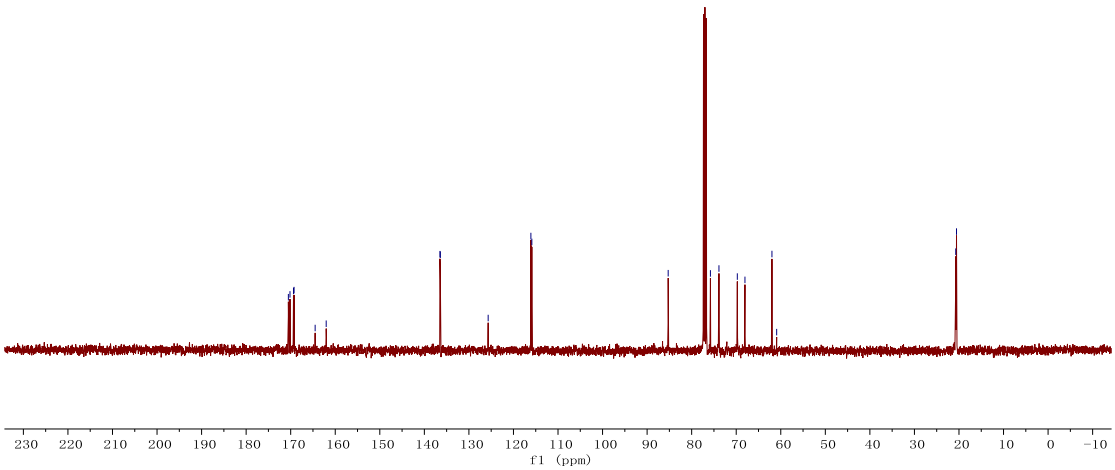


^{1}H NMR (400 MHz, $CDCl_3$)

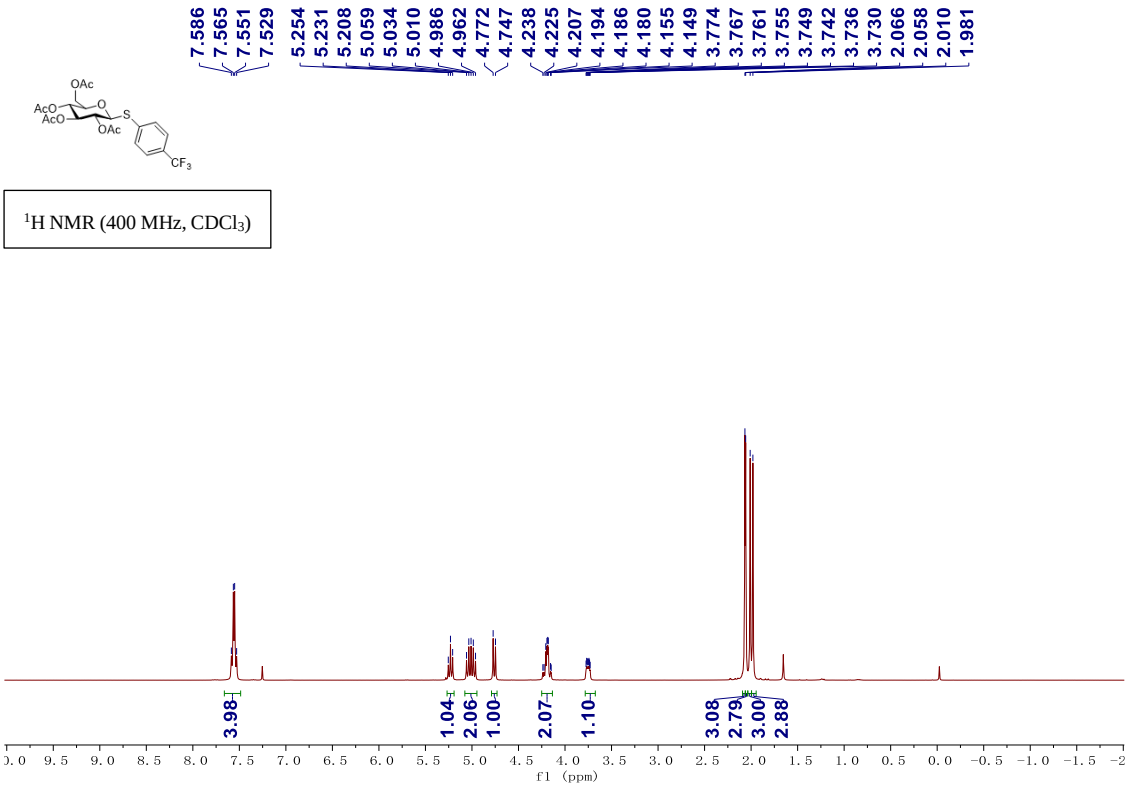




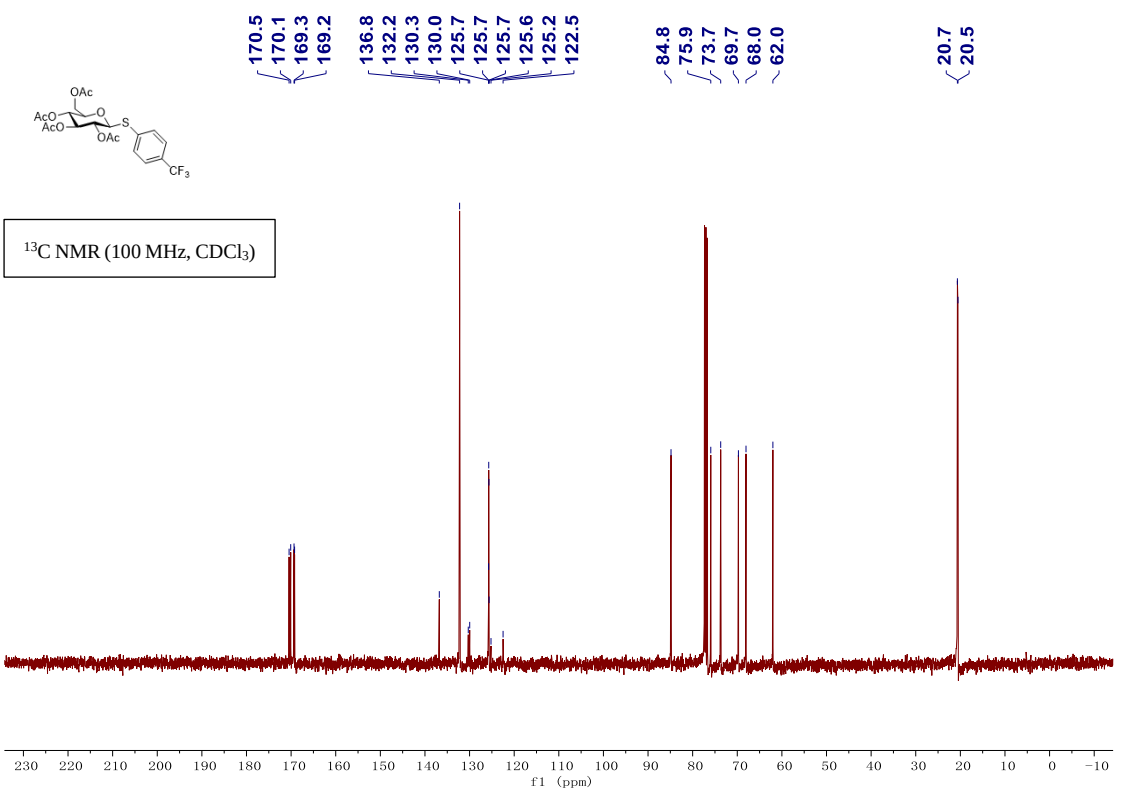
^{13}C NMR (100 MHz, $CDCl_3$)



4-(Trifluoromethyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (8).

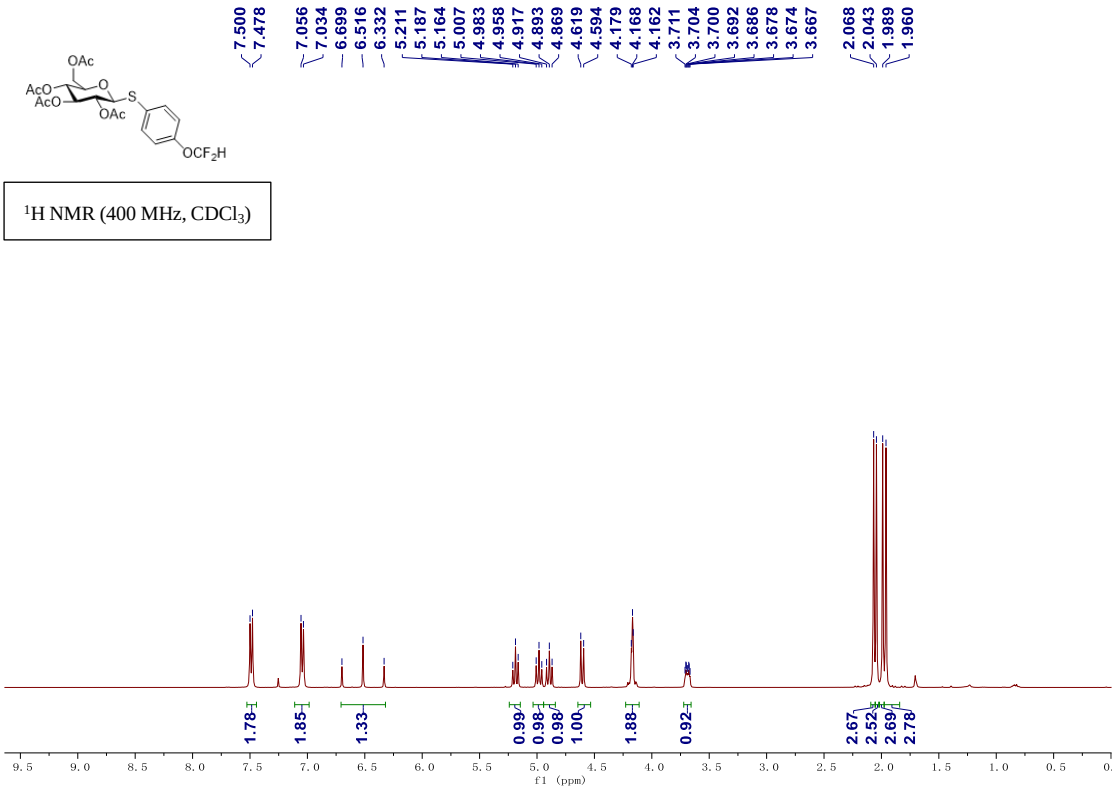


^{1}H NMR (400 MHz, $CDCl_3$)

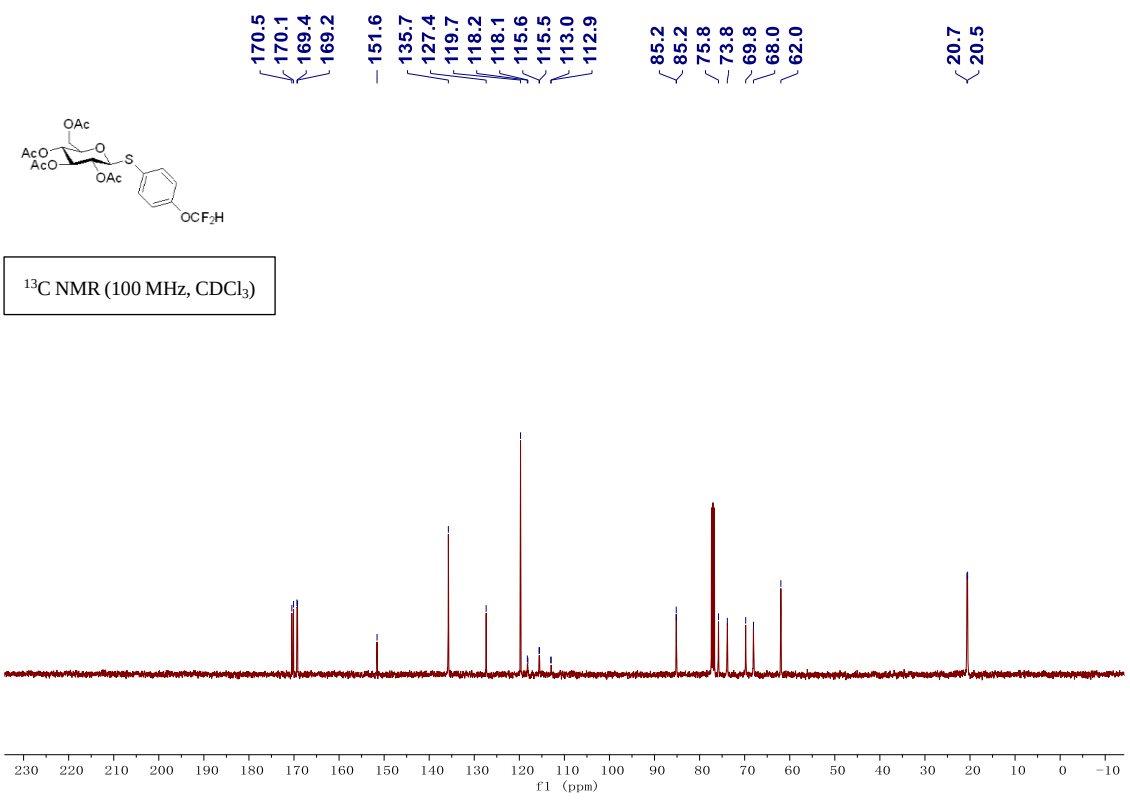


^{13}C NMR (100 MHz, $CDCl_3$)

4-Difluoromethoxyphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (9).

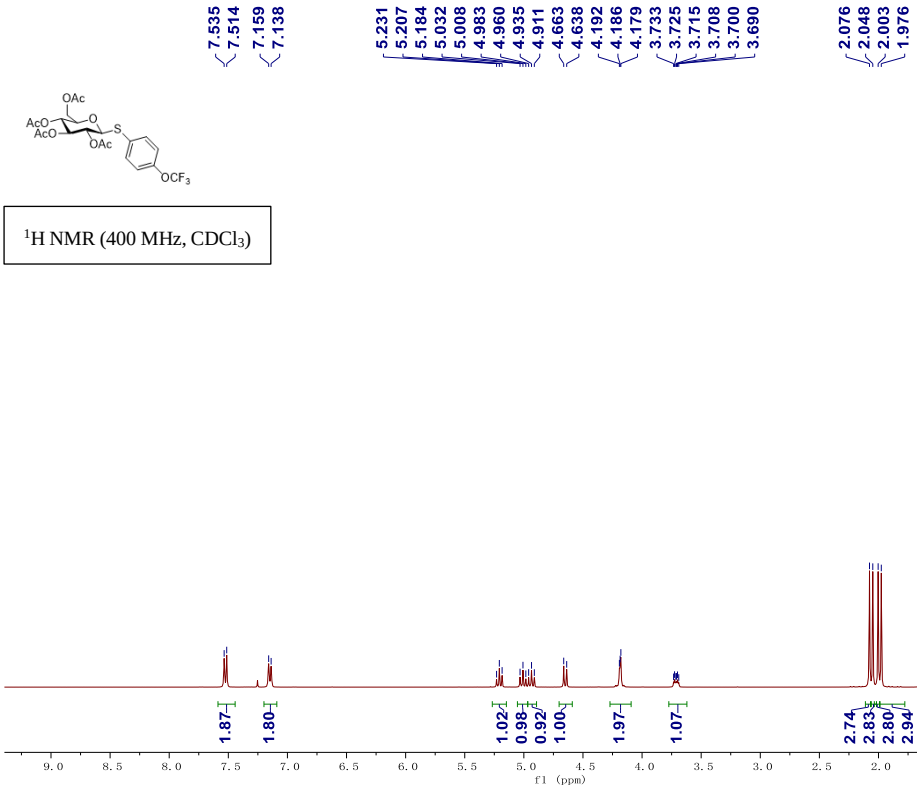


^{1}H NMR (400 MHz, $CDCl_3$)

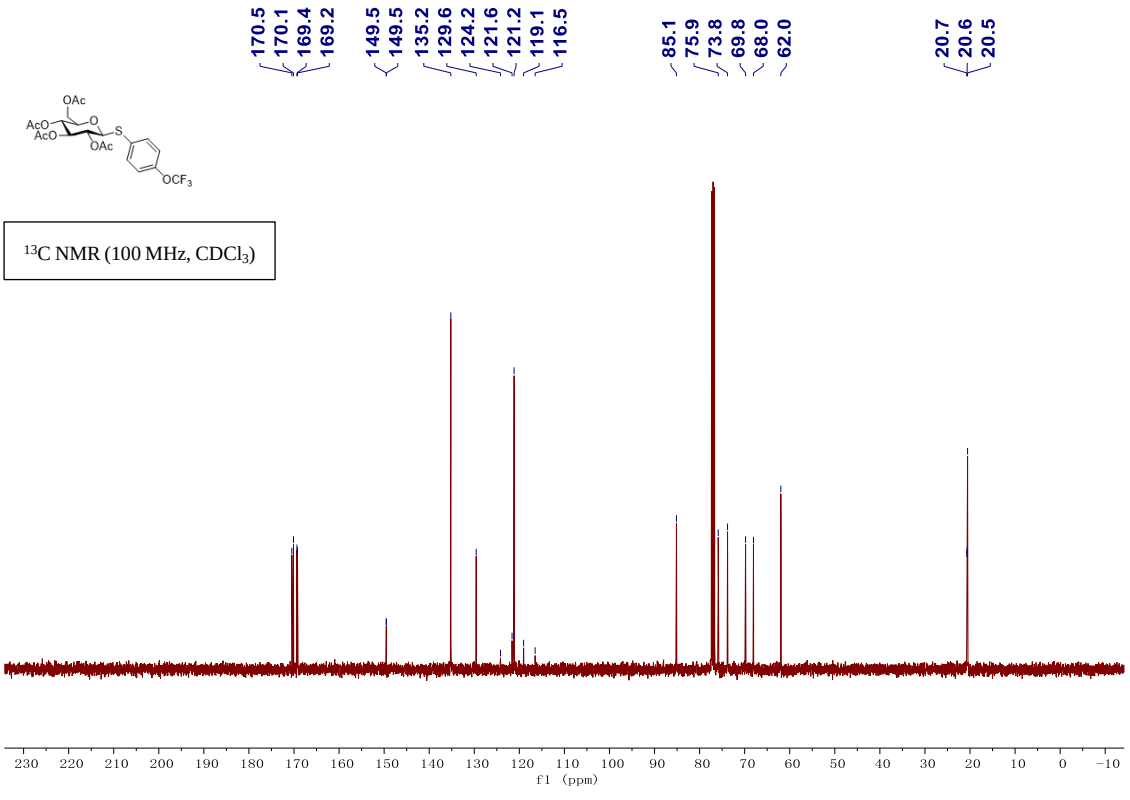


^{13}C NMR (100 MHz, $CDCl_3$)

4-Trifluoromethoxyphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (10).

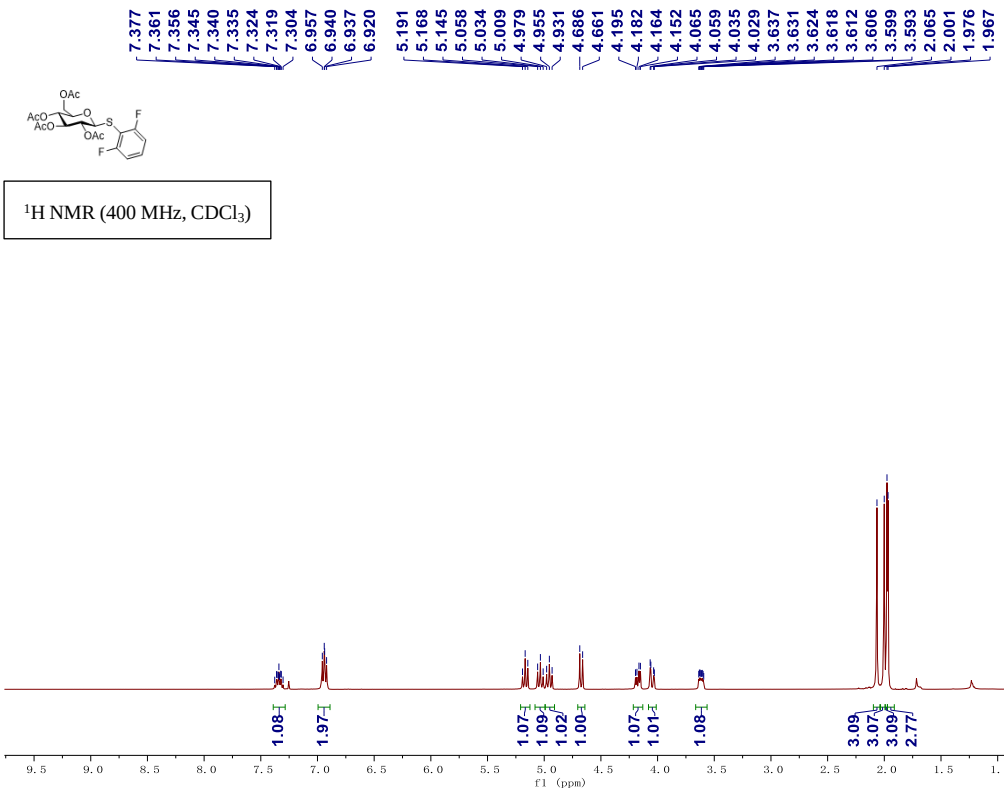


^{1}H NMR (400 MHz, $CDCl_3$)

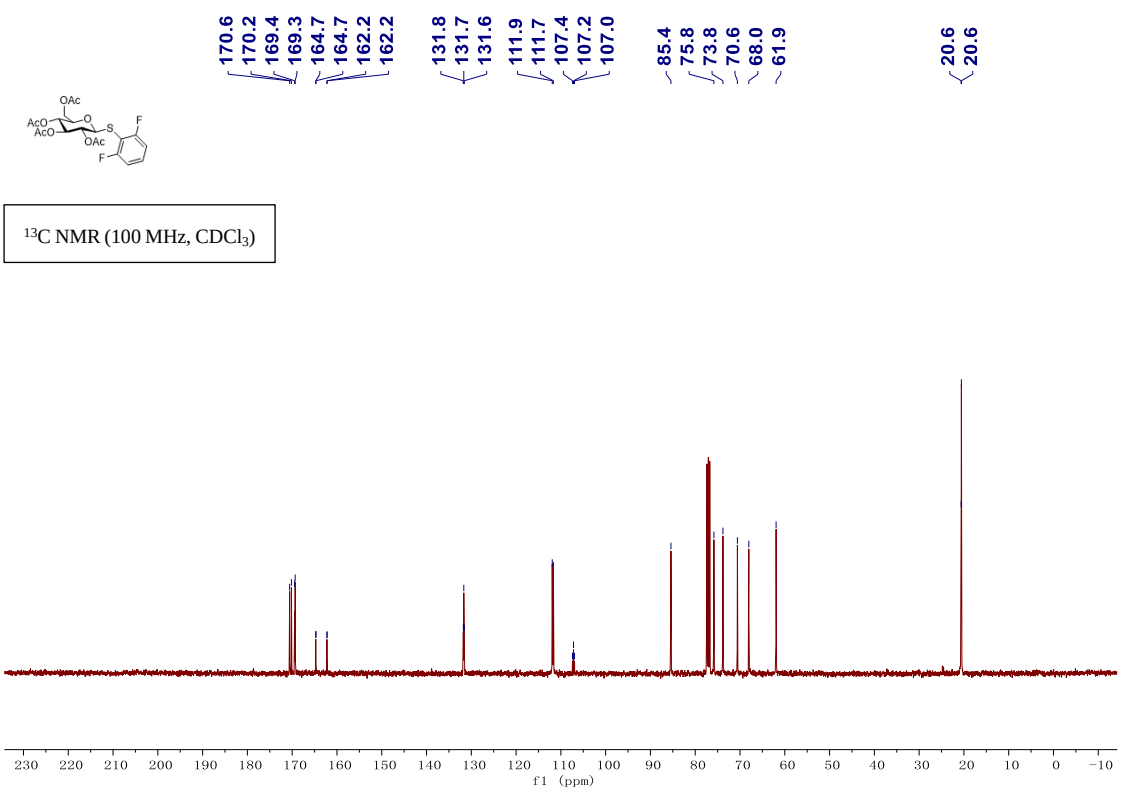


^{13}C NMR (100 MHz, $CDCl_3$)

2,4-Difluorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (11).

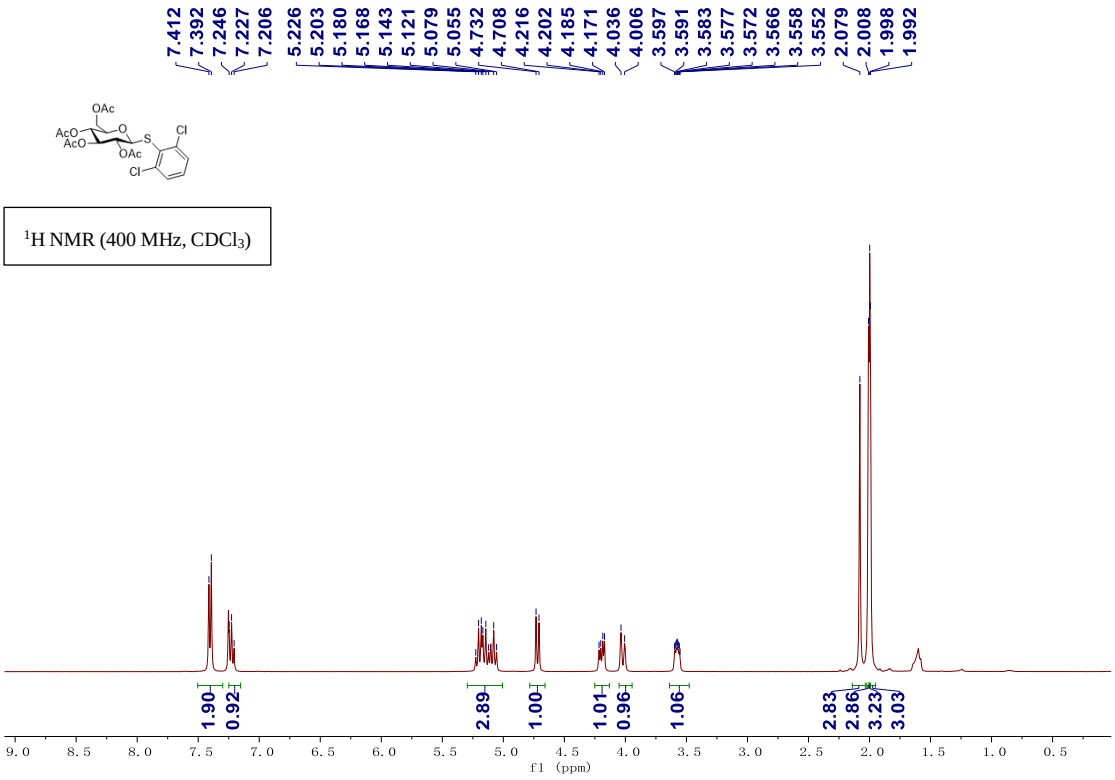


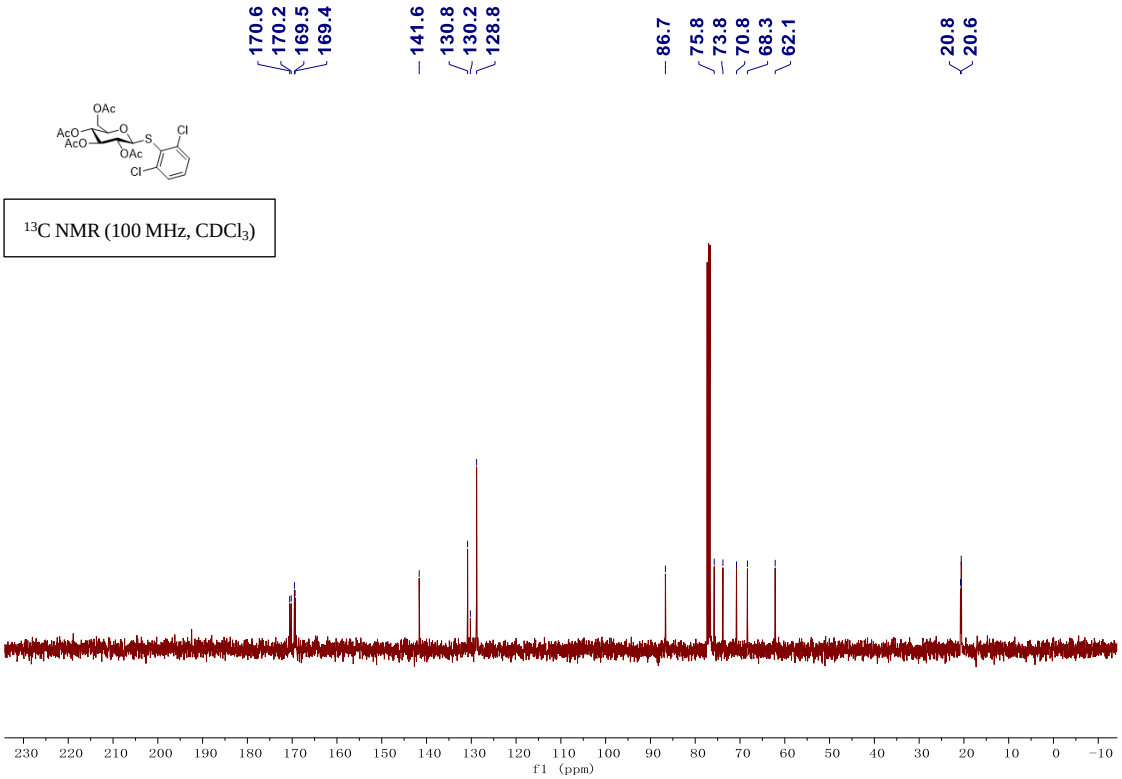
^{1}H NMR (400 MHz, $CDCl_3$)



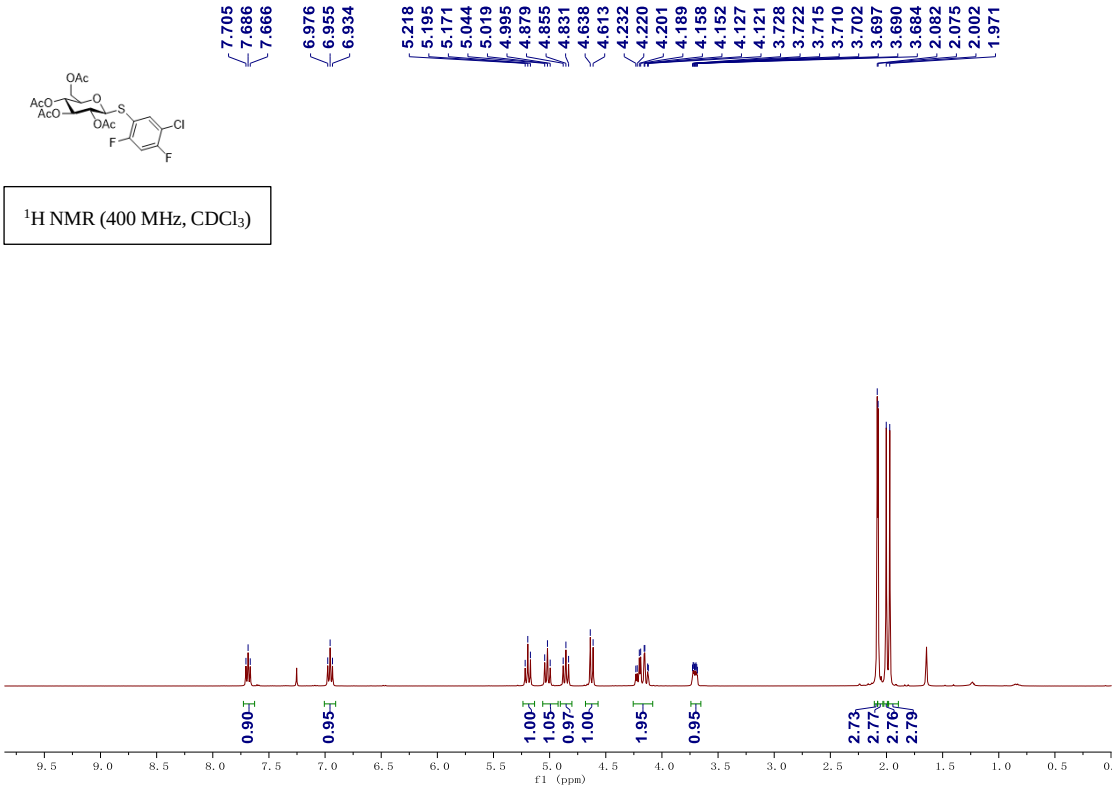
^{13}C NMR (100 MHz, $CDCl_3$)

2,6-Dichlorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (12).

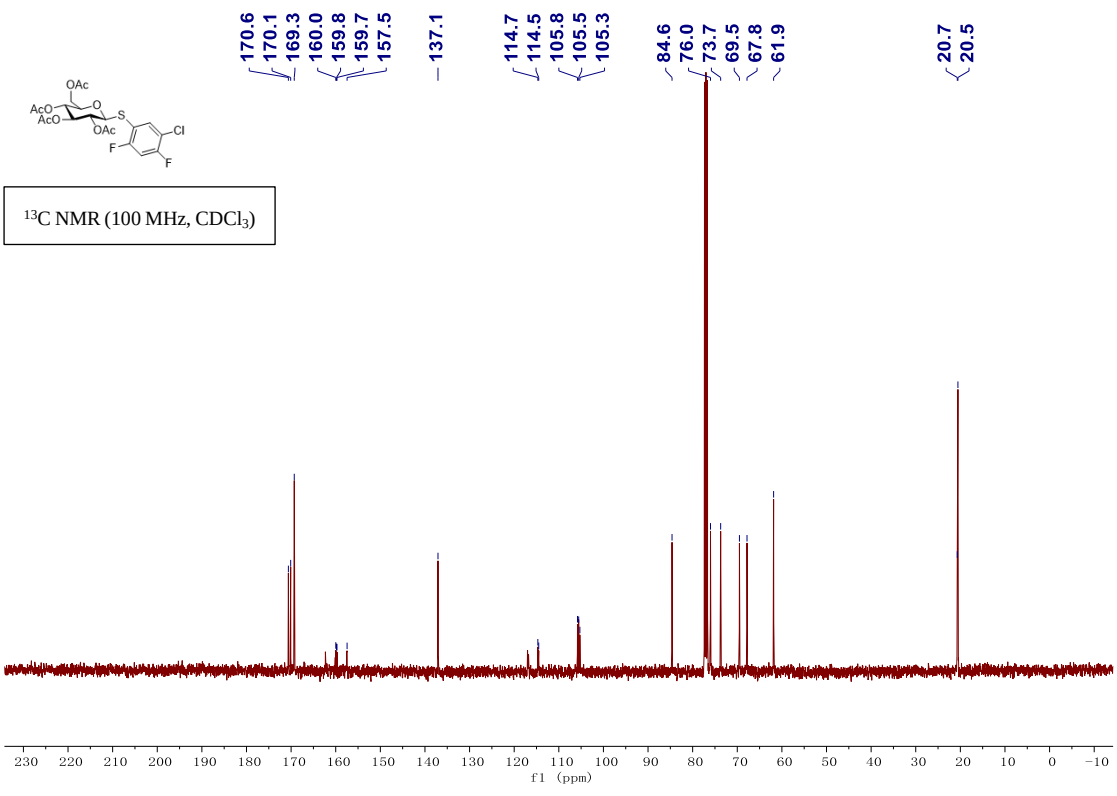




2,4-Difluoro-5-chlorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (13).

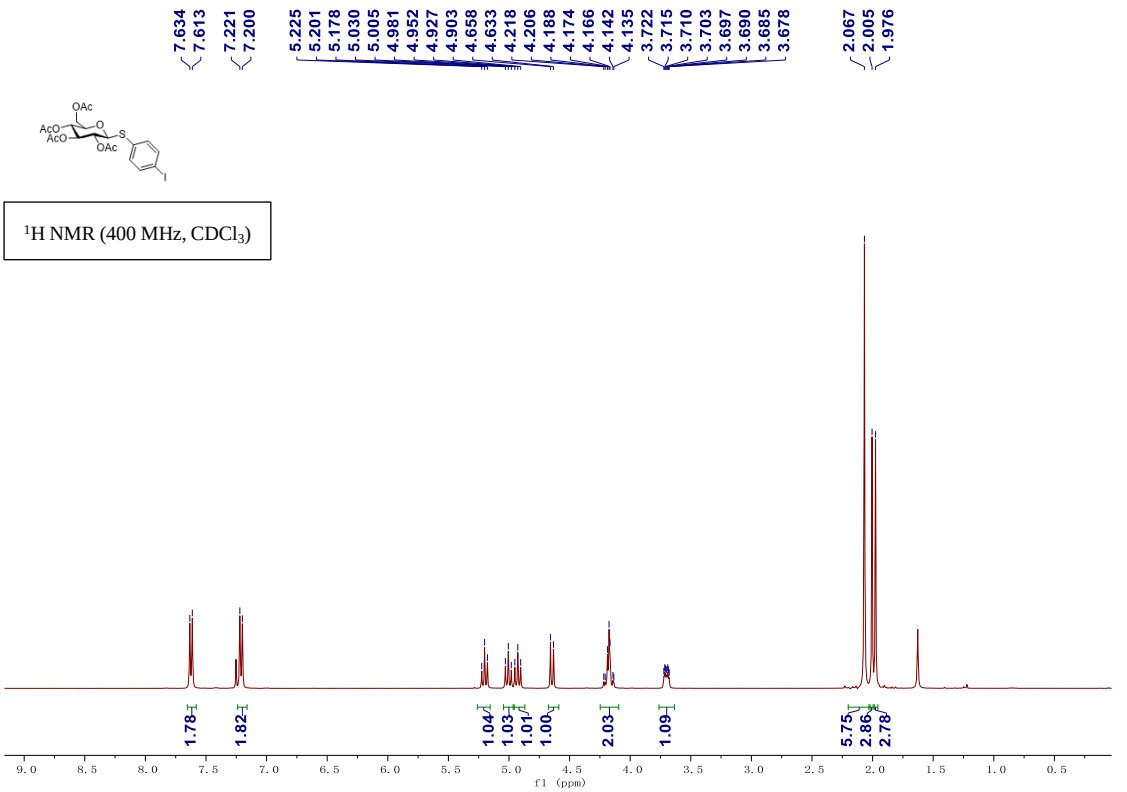


^{1}H NMR (400 MHz, $CDCl_3$)

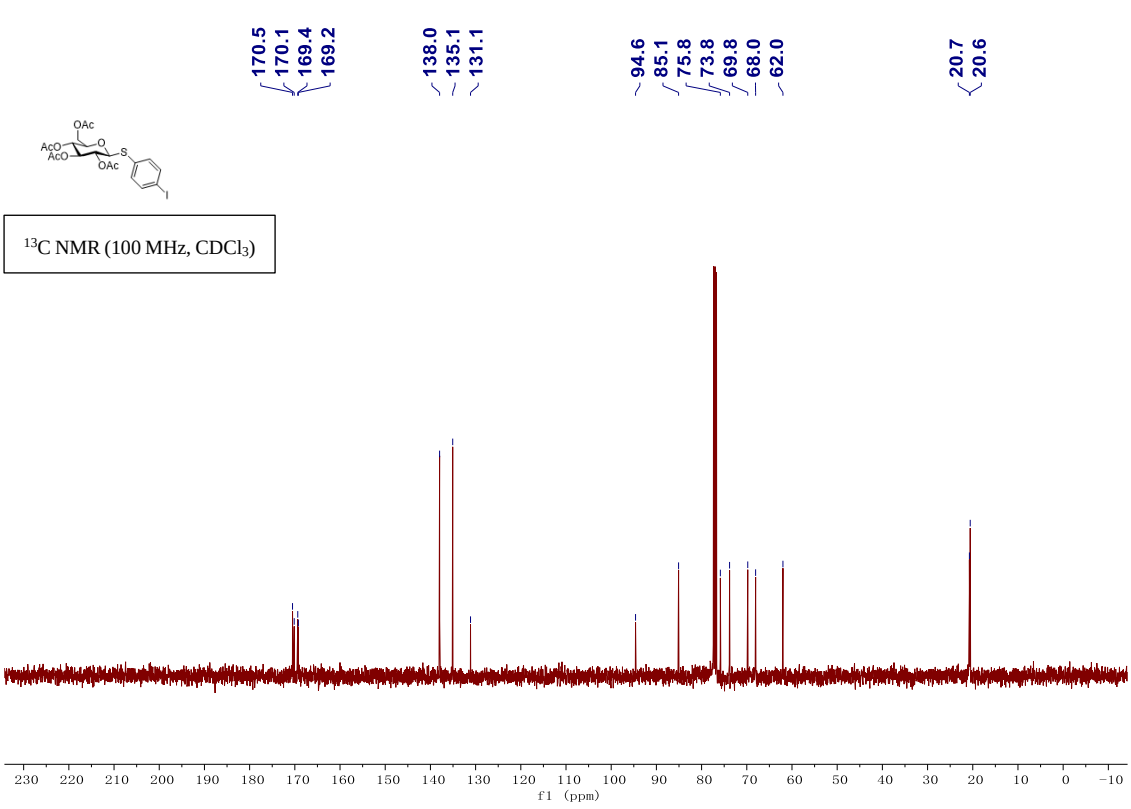


^{13}C NMR (100 MHz, $CDCl_3$)

4-Iodophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (14).

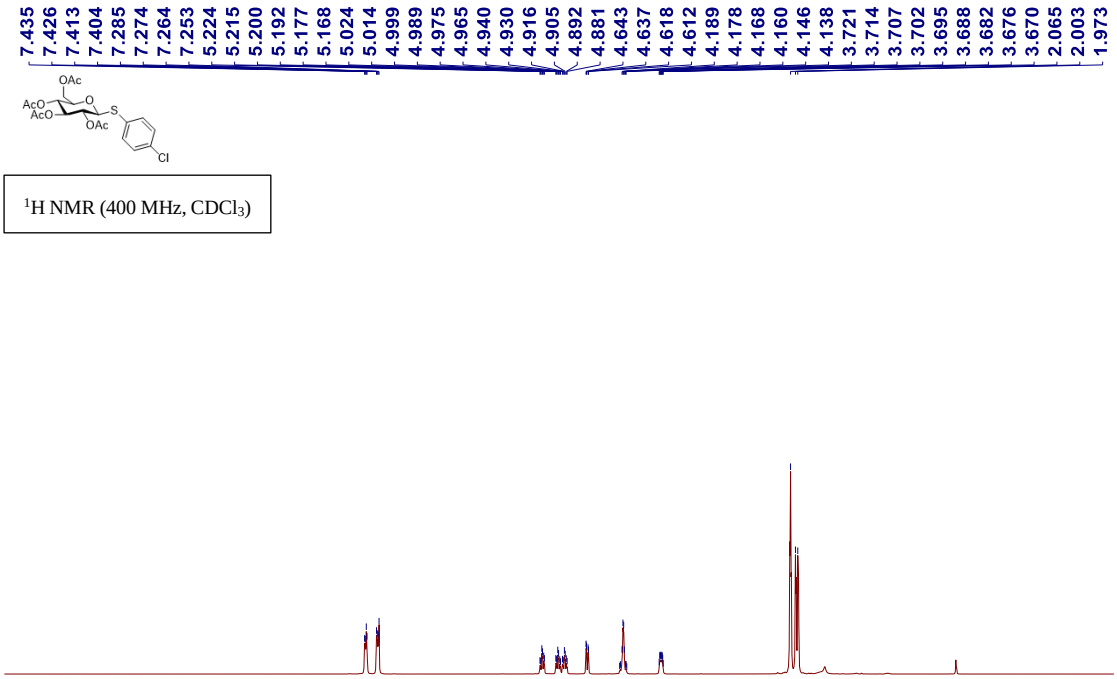


^{1}H NMR (400 MHz, $CDCl_3$)

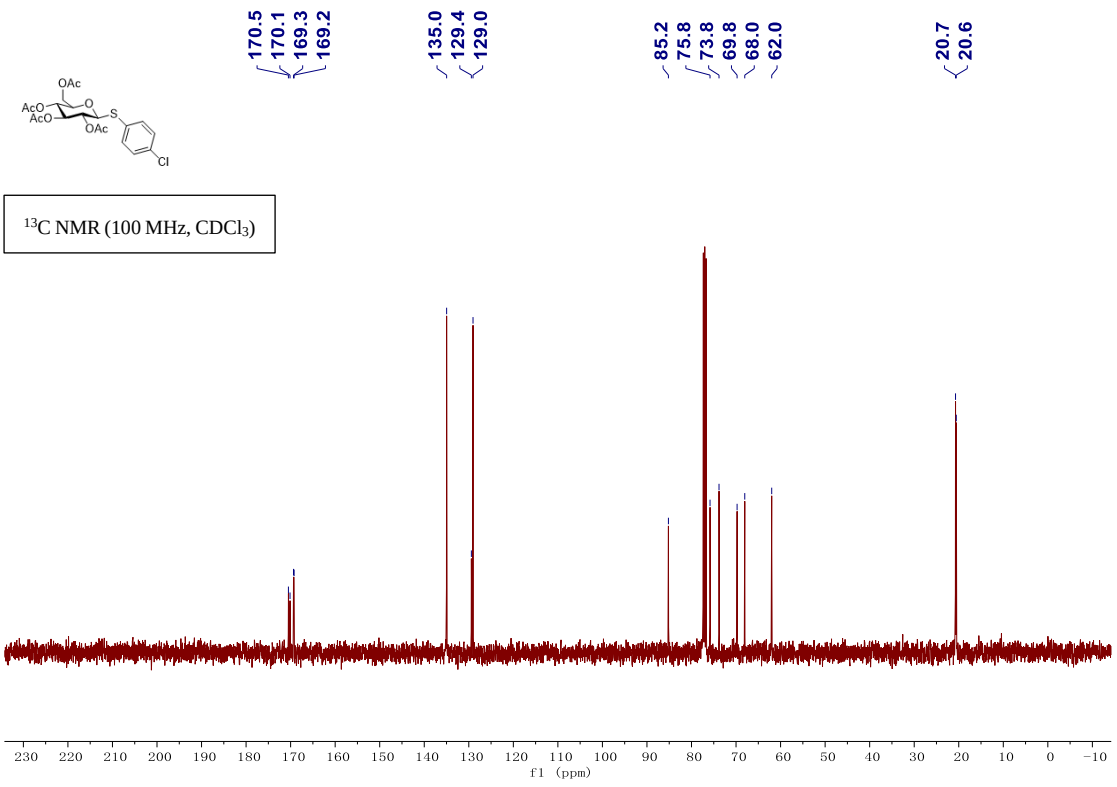


^{13}C NMR (100 MHz, $CDCl_3$)

4-Chlorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (15).

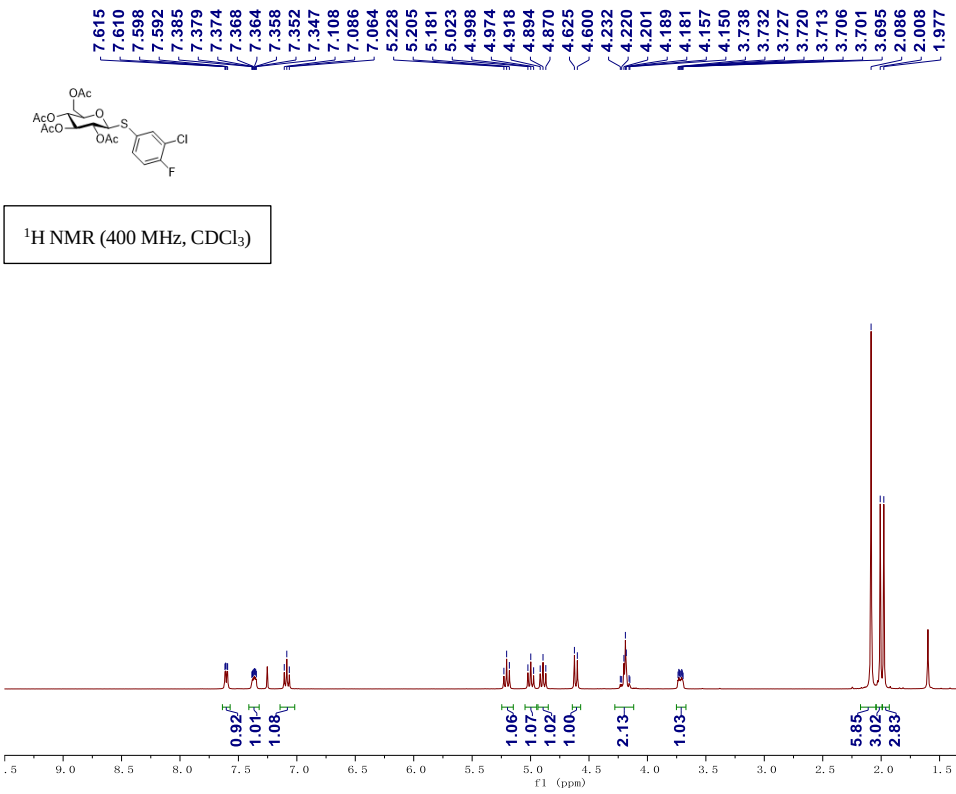


^{1}H NMR (400 MHz, $CDCl_3$)

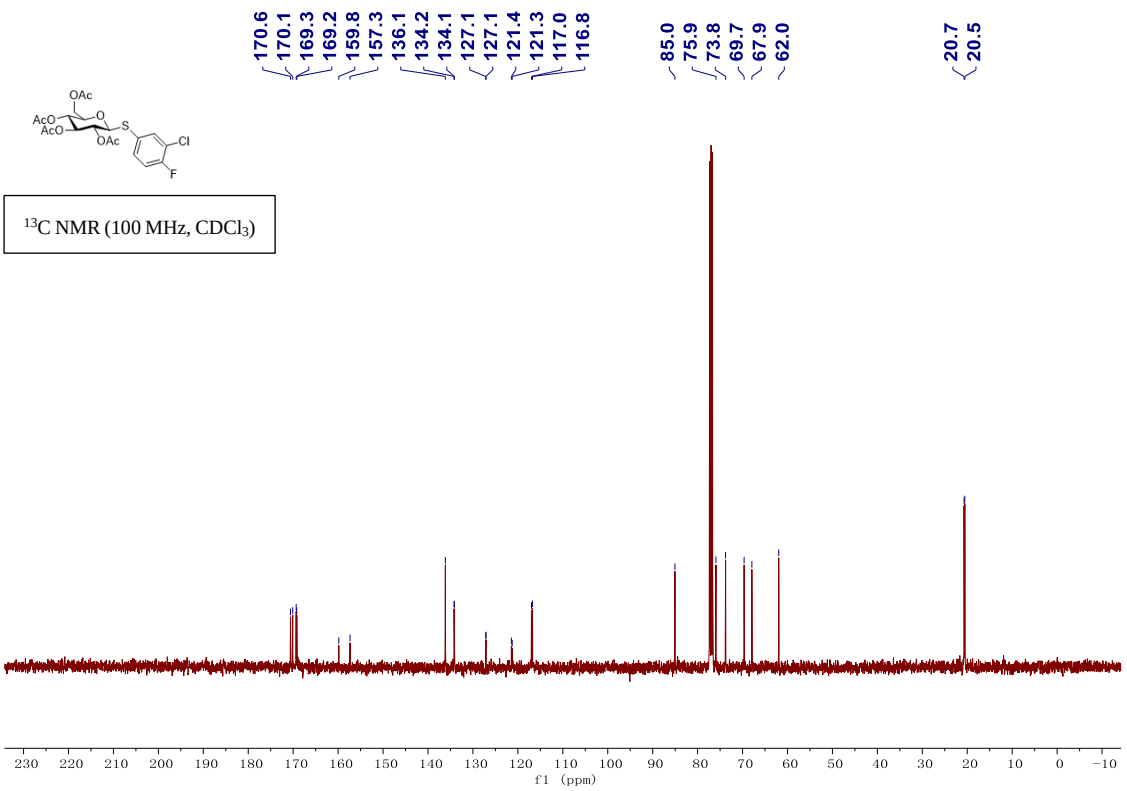


^{13}C NMR (100 MHz, $CDCl_3$)

3-Chloro-4-fluorophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (16).

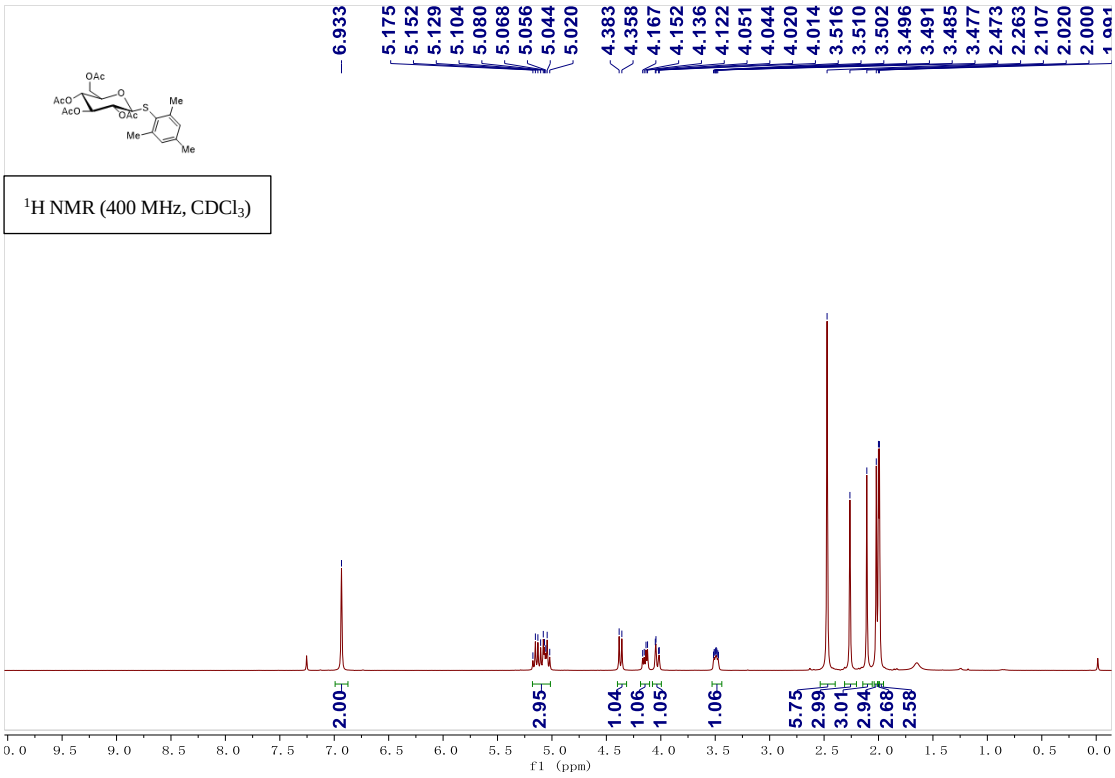


^{1}H NMR (400 MHz, $CDCl_3$)

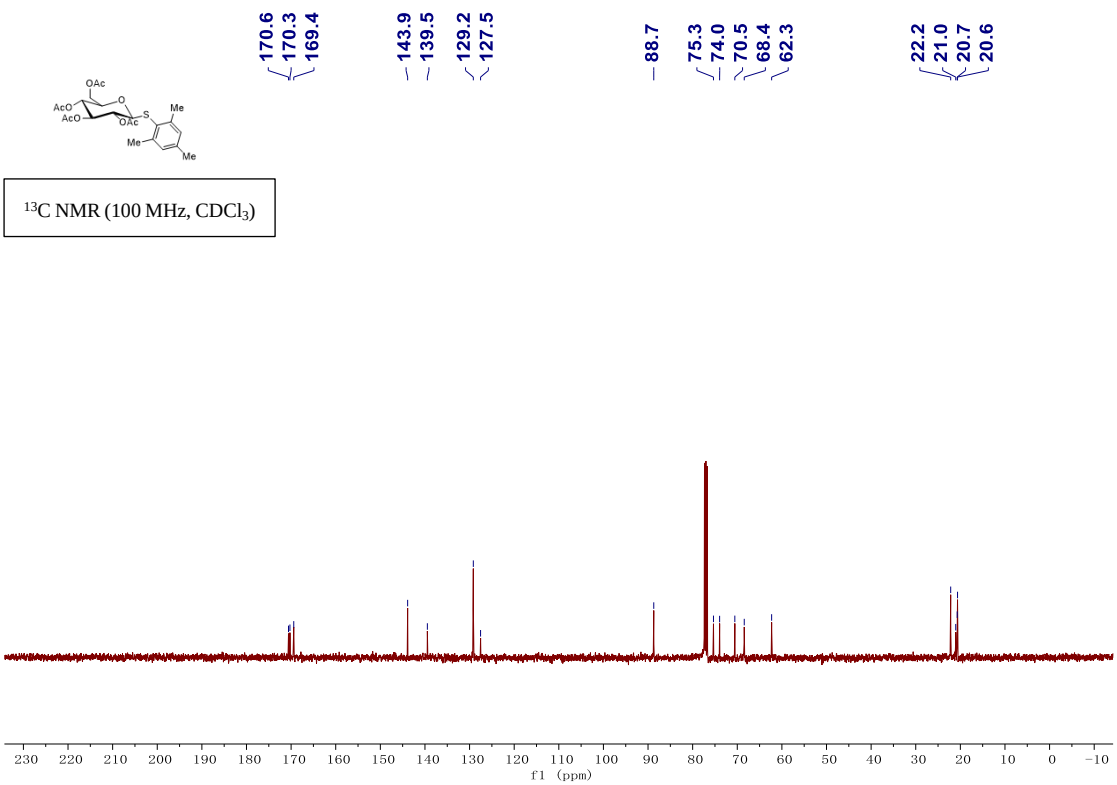


^{13}C NMR (100 MHz, $CDCl_3$)

2,4,6-Trimethylphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (17).

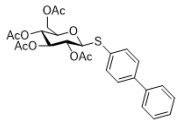


^{1}H NMR (400 MHz, $CDCl_3$)

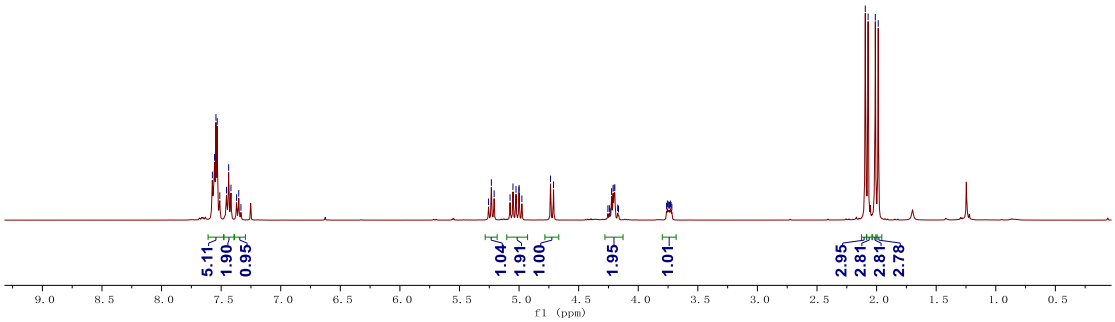


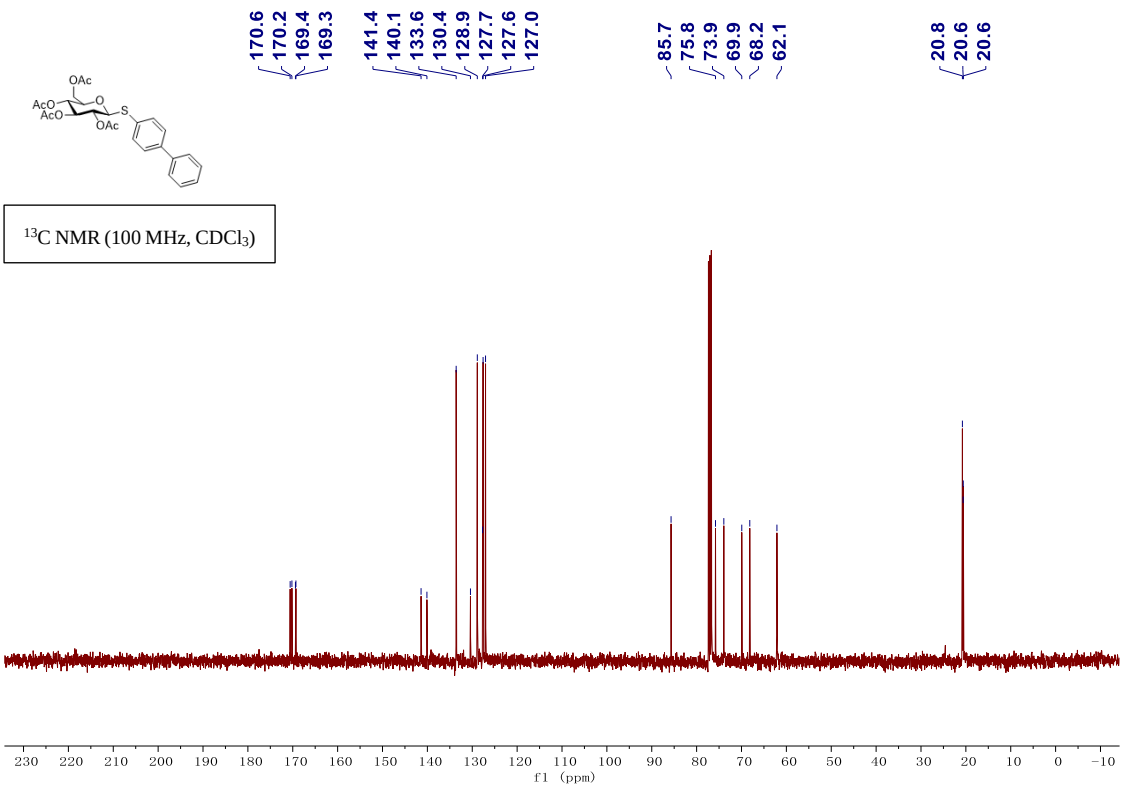
^{13}C NMR (100 MHz, $CDCl_3$)

4-(Phenyl)phenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (18).



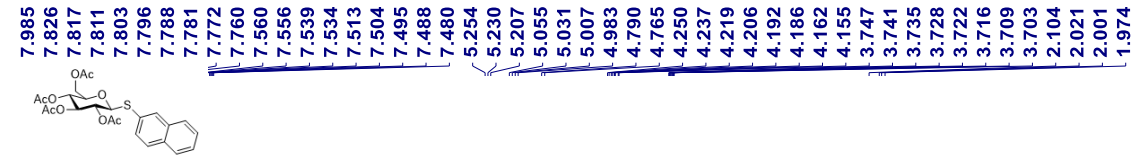
^{1}H NMR (400 MHz, $CDCl_3$)



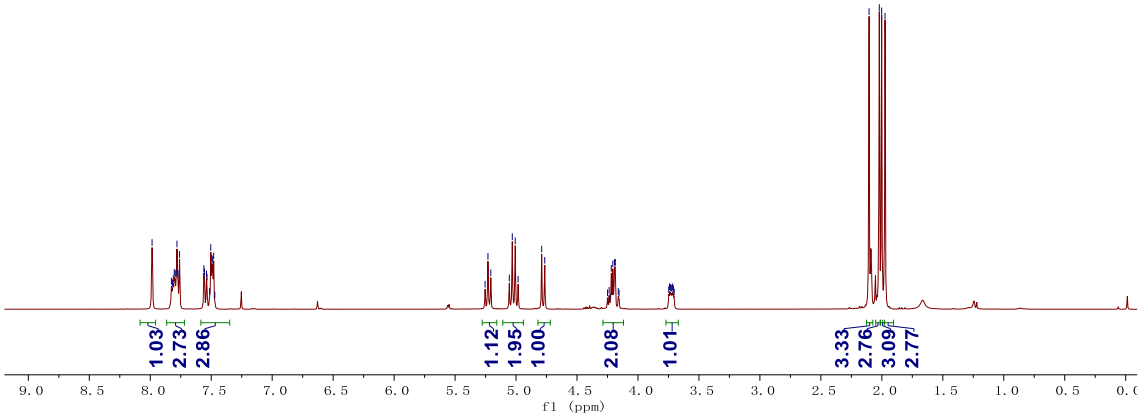


^{13}C NMR (100 MHz, $CDCl_3$)

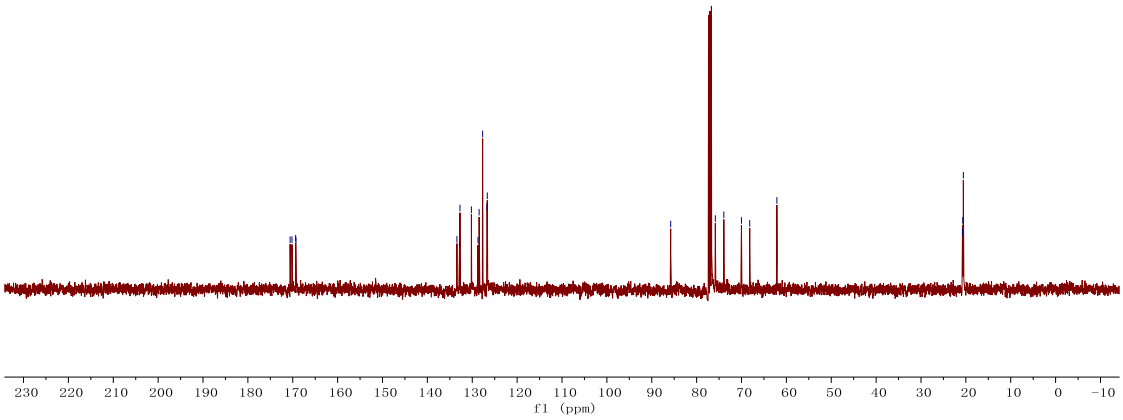
2-Naphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (19).



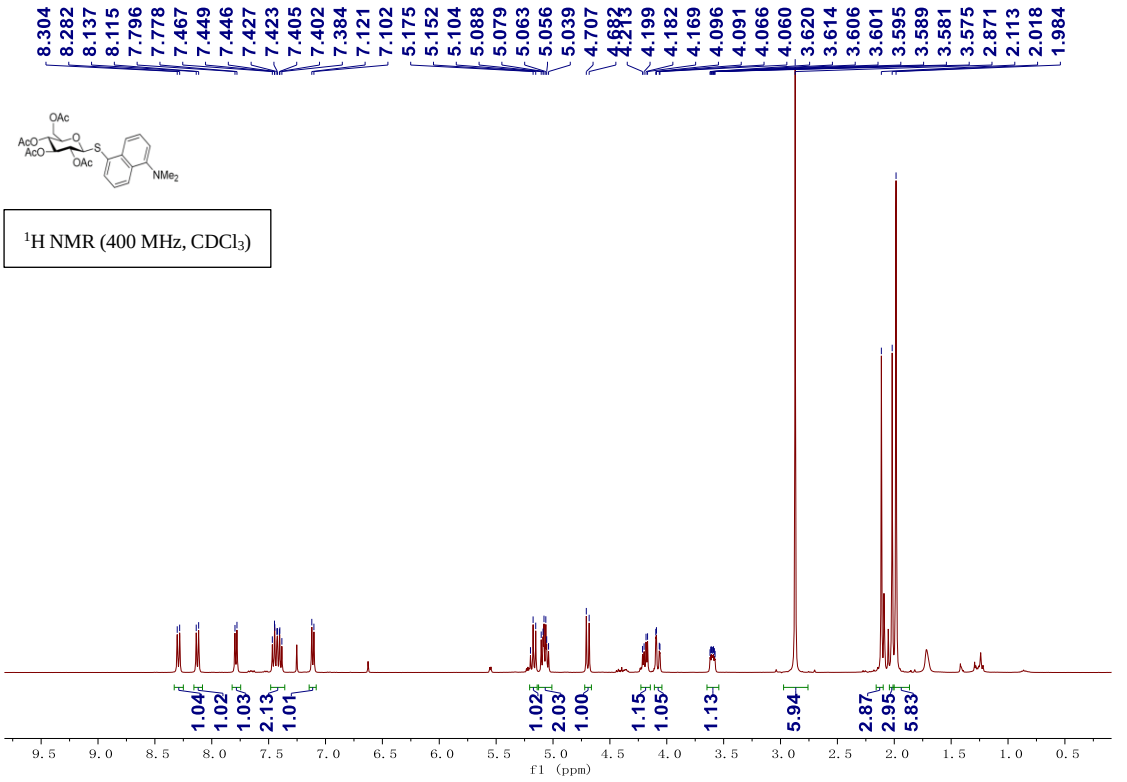
^{1}H NMR (400 MHz, $CDCl_3$)



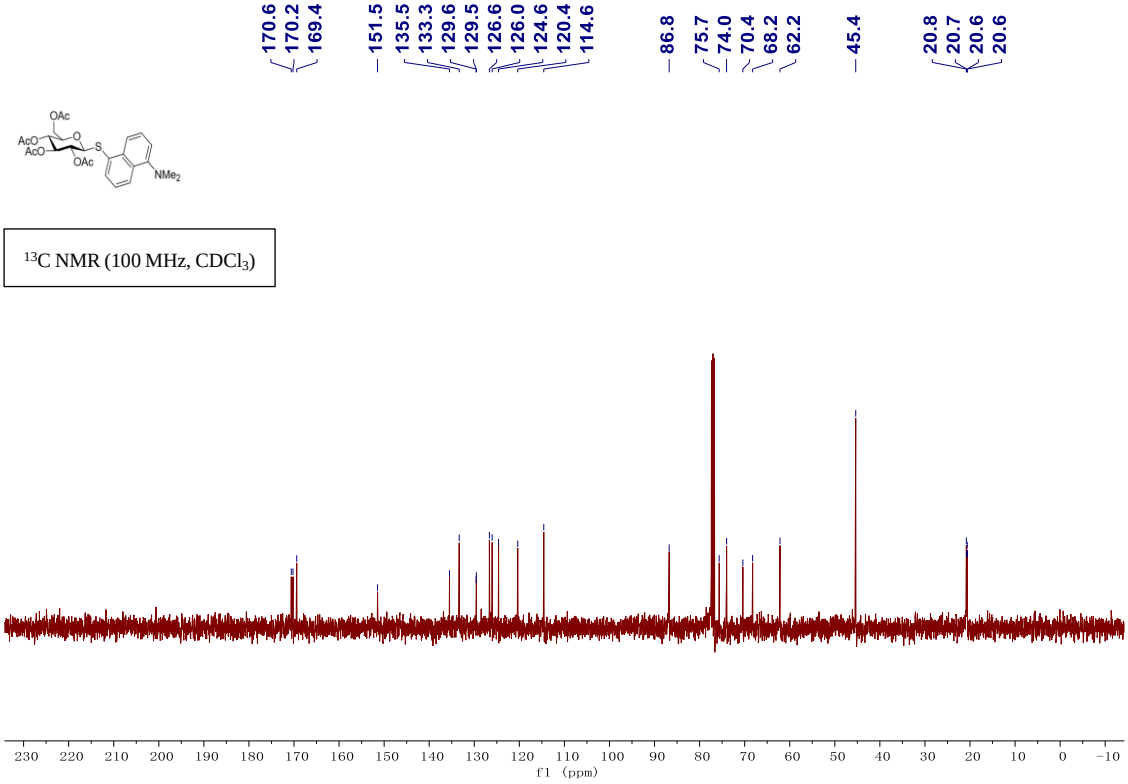
^{13}C NMR (100 MHz, $CDCl_3$)



5-(Dimethylamino)-1-naphenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (20).[错误!未找到引用源。]

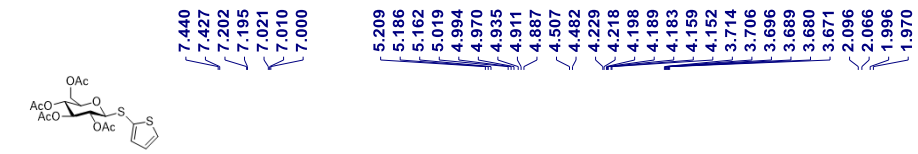


^{1}H NMR (400 MHz, $CDCl_3$)

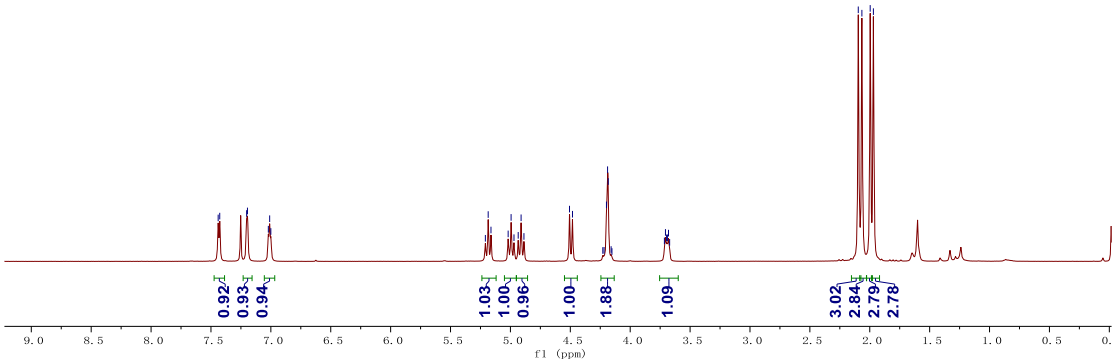


^{13}C NMR (100 MHz, $CDCl_3$)

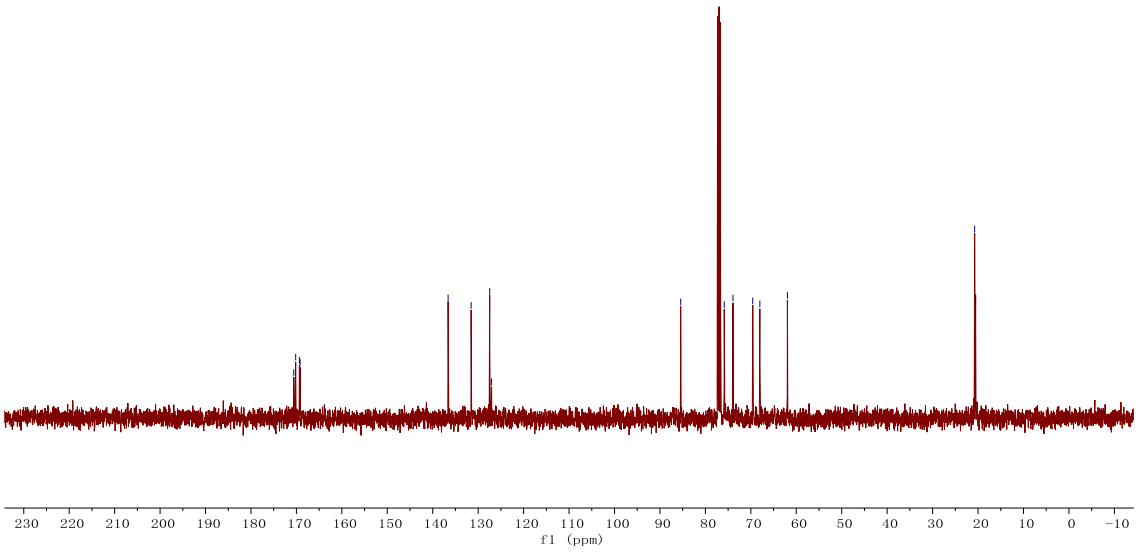
2-Thiophenyl 2,3,4,6-Tetra-O-acetyl-β-D-thioglucopyranoside (21).



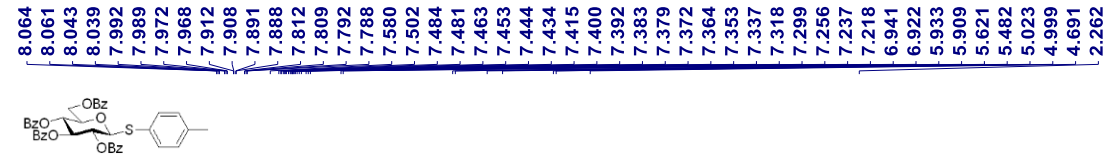
^{1}H NMR (400 MHz, $CDCl_3$)



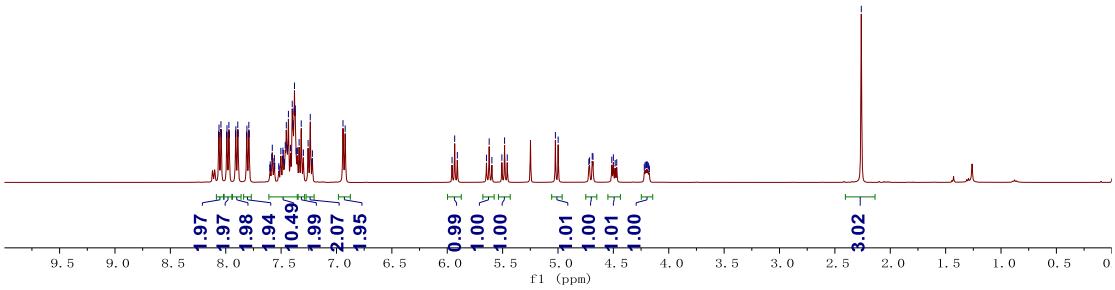
^{13}C NMR (100 MHz, $CDCl_3$)

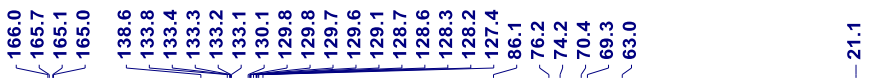


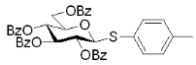
4-Methylphenyl 2,3,4,6-tetra-O-benzoyl-β-D-thioglucopyranoside (22).



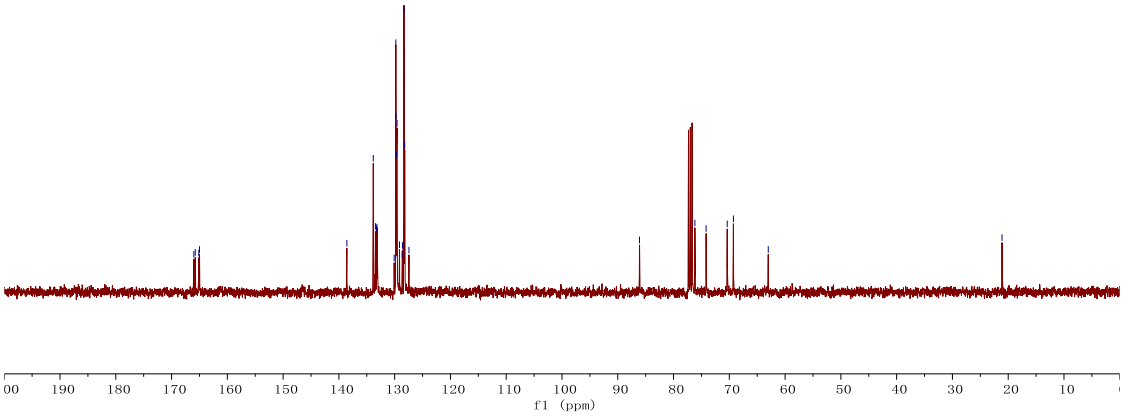
^{1}H NMR (400 MHz, $CDCl_3$)



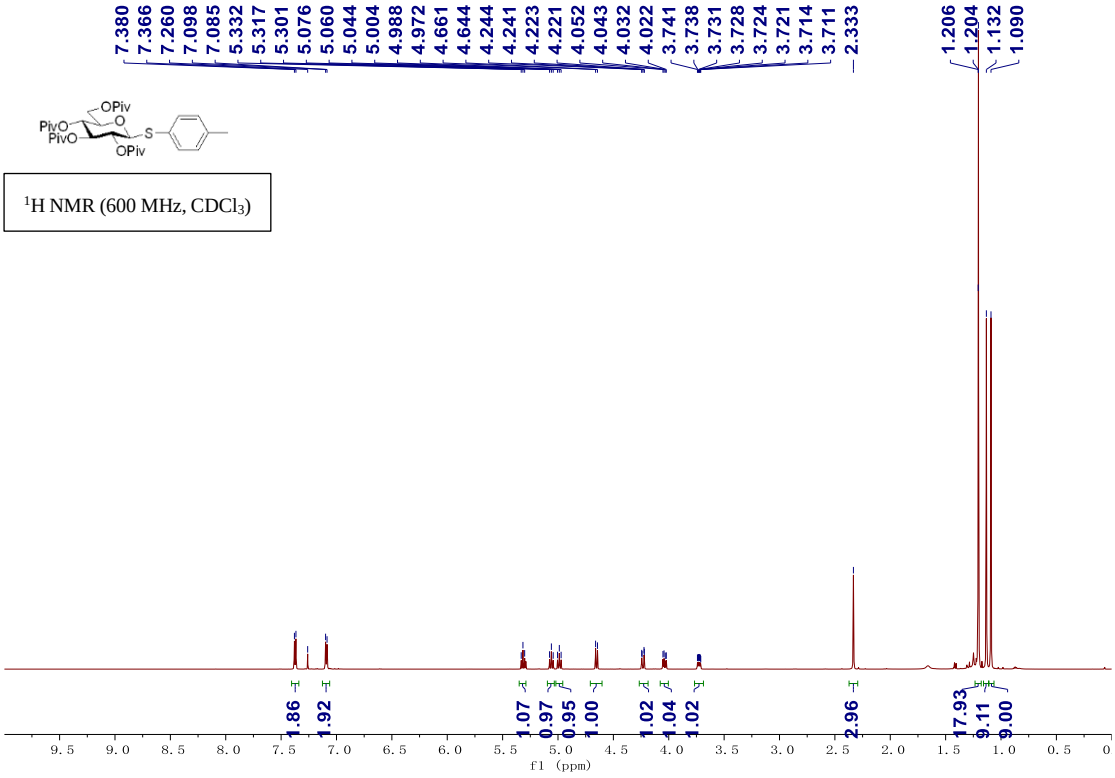




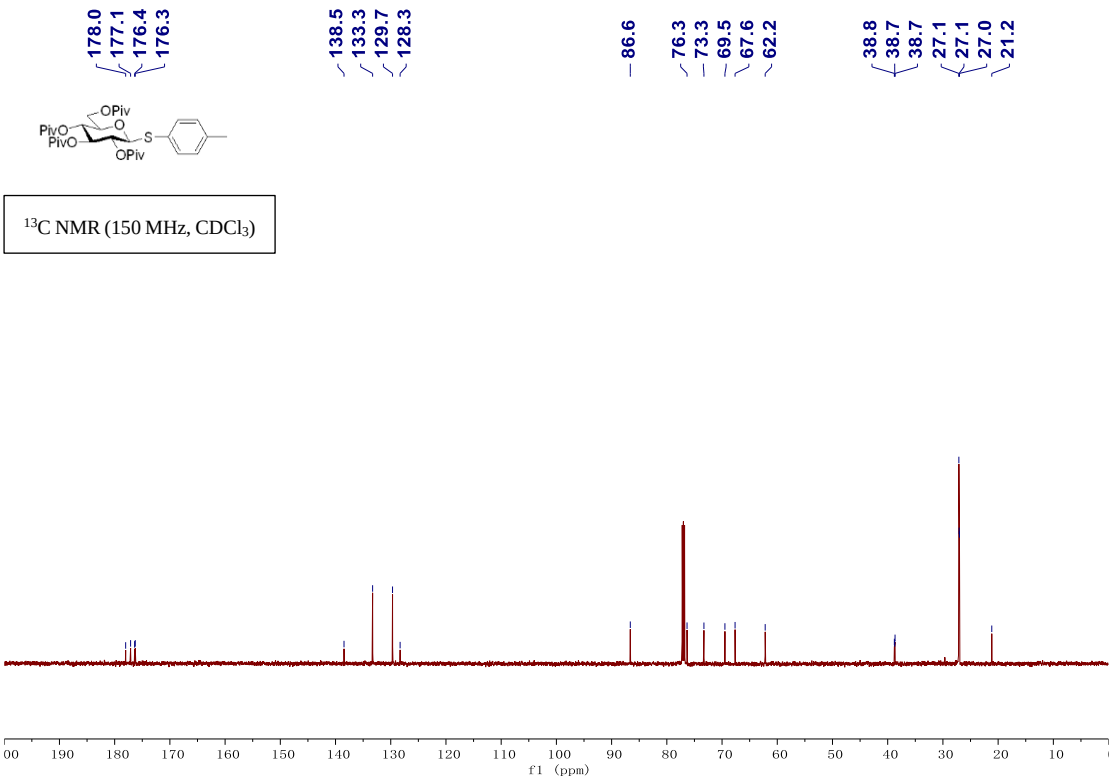
^{13}C NMR (100 MHz, $CDCl_3$)



4-Methylphenyl 2,3,4,6-tetra-O-pivaloyl-β-D-thioglucopyranoside (23).

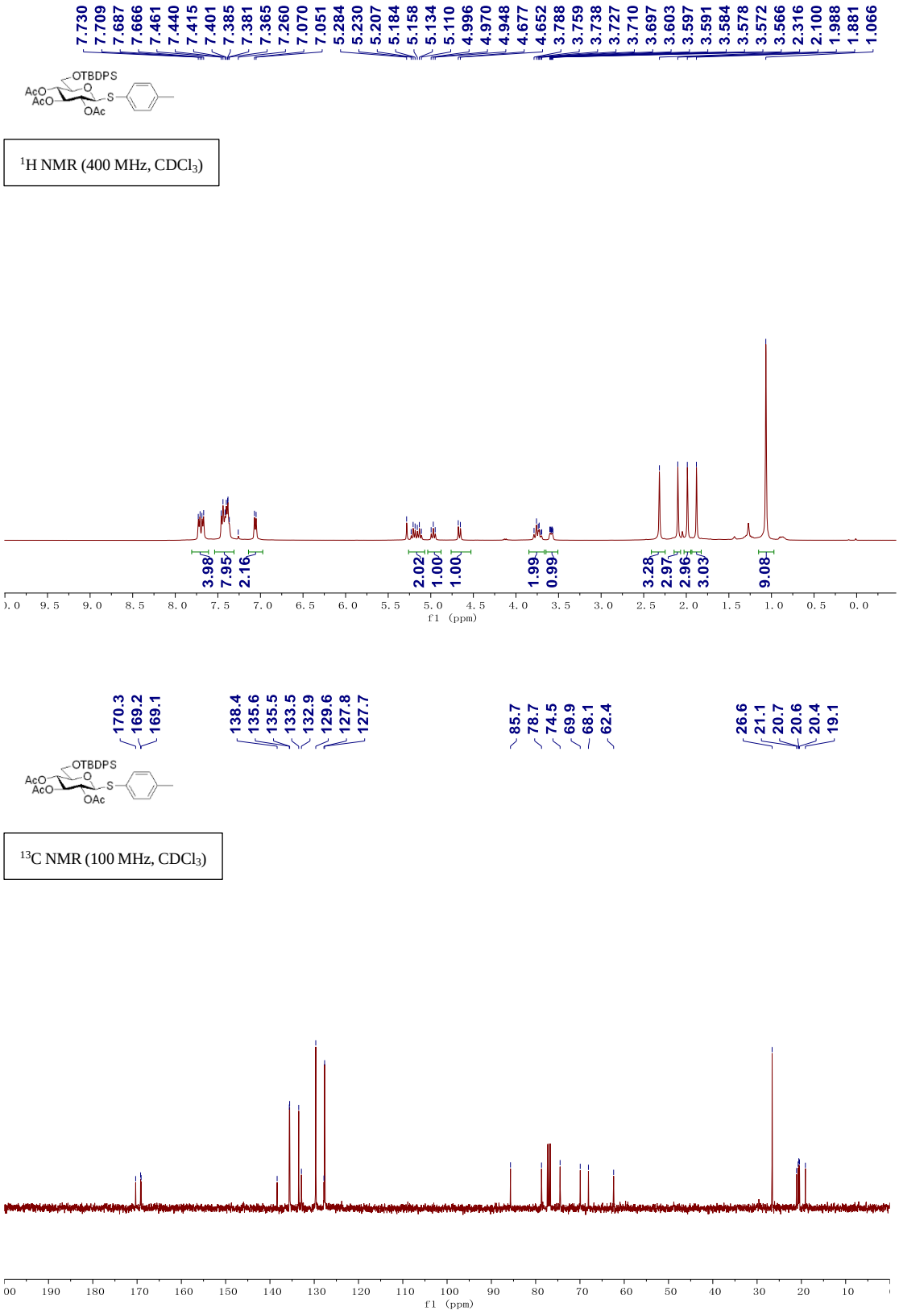


^{1}H NMR (600 MHz, $CDCl_3$)



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

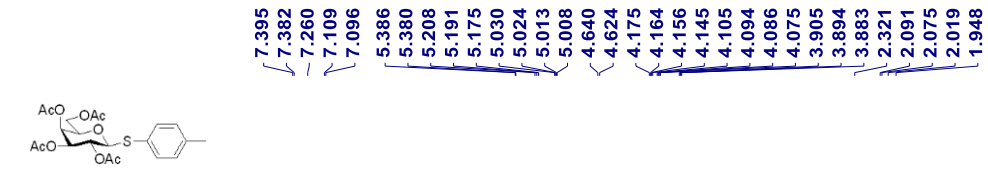
4-Methylphenyl 2,3,4-tri-O-acetyl-6-*tert*-butyldiphenylsilyl β-D-thioglucopyranoside (24).



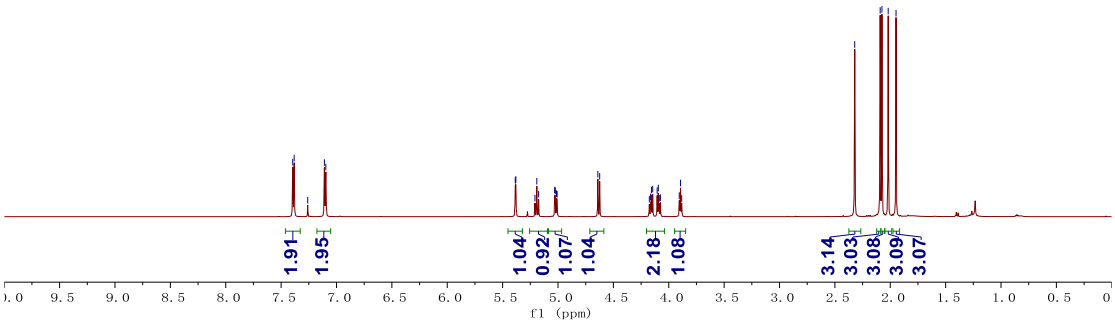
^{1}H NMR (400 MHz, $CDCl_3$)

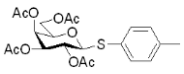
^{13}C NMR (100 MHz, $CDCl_3$)

4-Methylphenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (25).

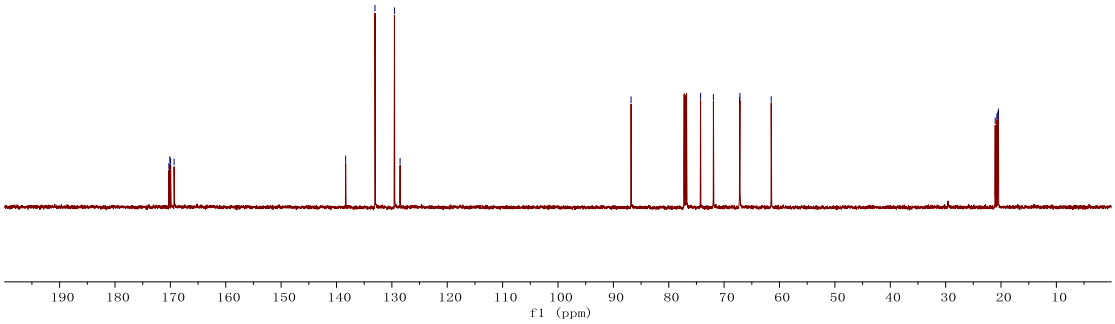


^{1}H NMR (600 MHz, $CDCl_3$)



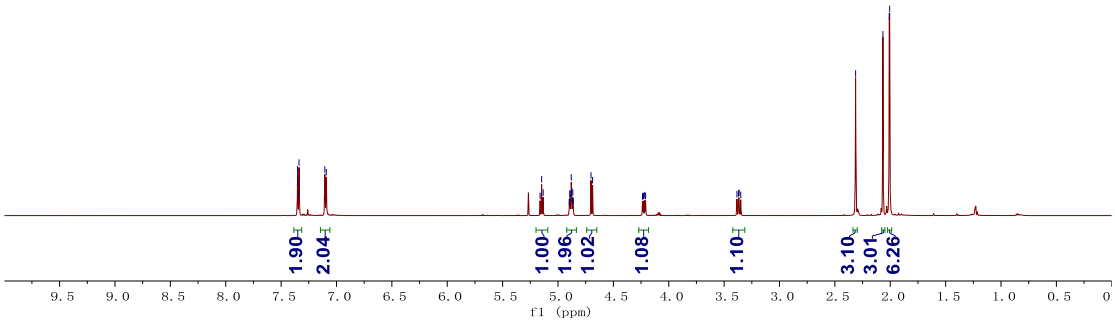


^{13}C NMR (150 MHz, $CDCl_3$)

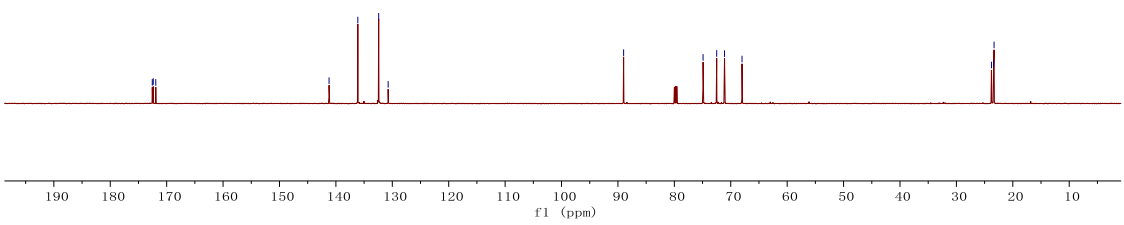


4-Methylphenyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside (26).

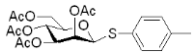
^{1}H NMR (600 MHz, $CDCl_3$)



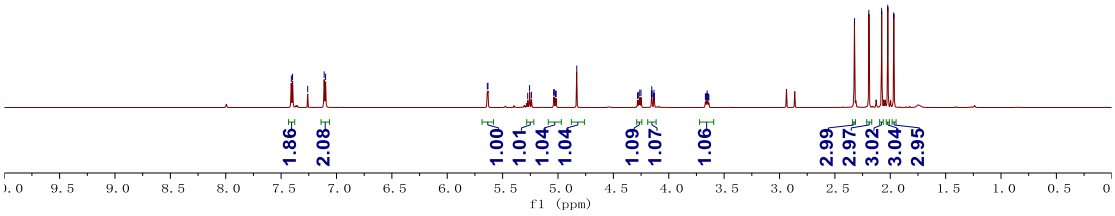
^{13}C NMR (150 MHz, $CDCl_3$)

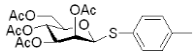


4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-mannopyranoside (27).

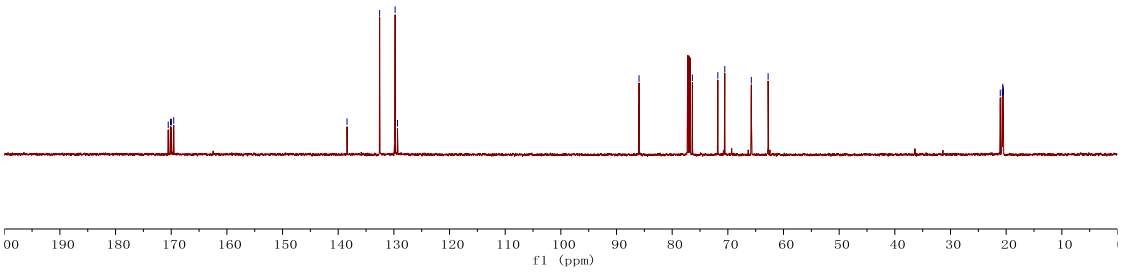


^{1}H NMR (600 MHz, $CDCl_3$)

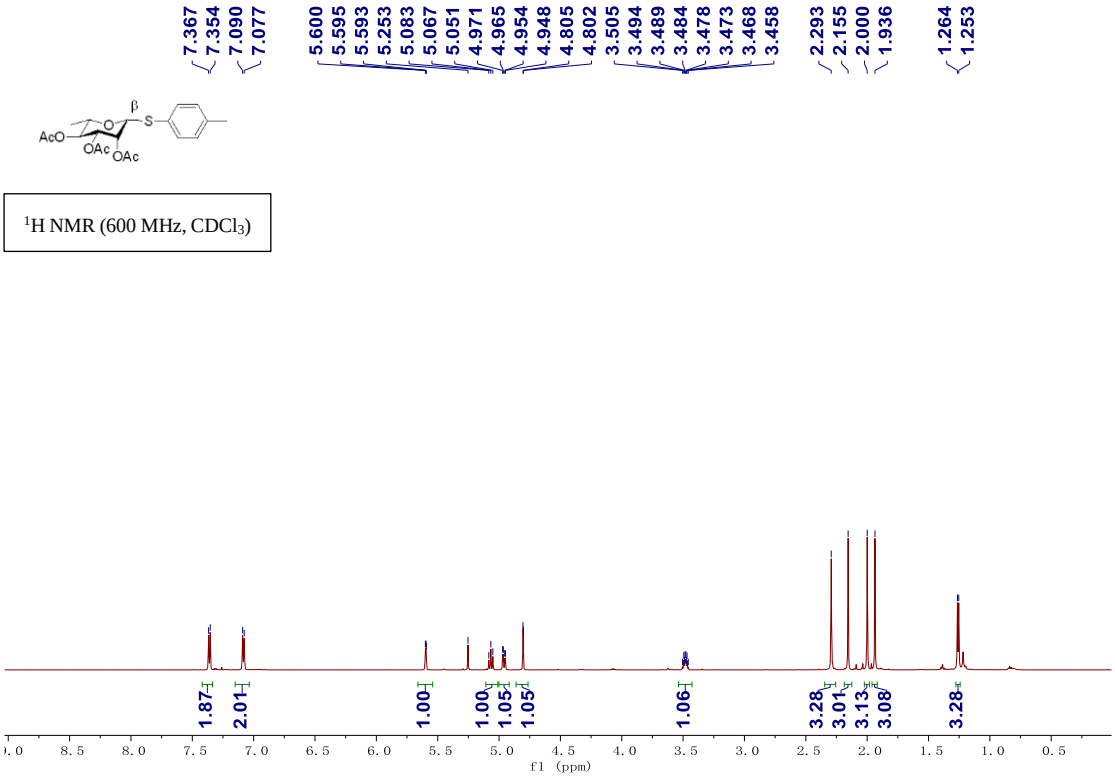




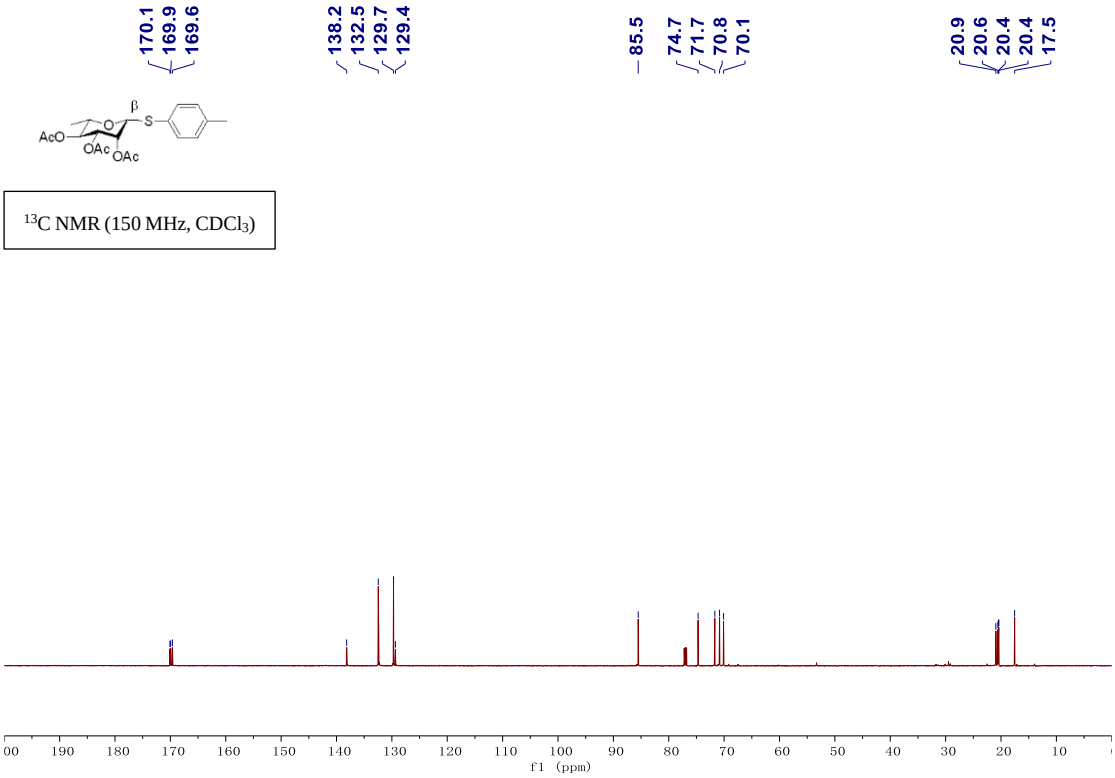
^{13}C NMR (150 MHz, $CDCl_3$)



4-Methylphenyl 2,3,4-tri-O-acetyl-β-L-rhamnopyranoside (28).

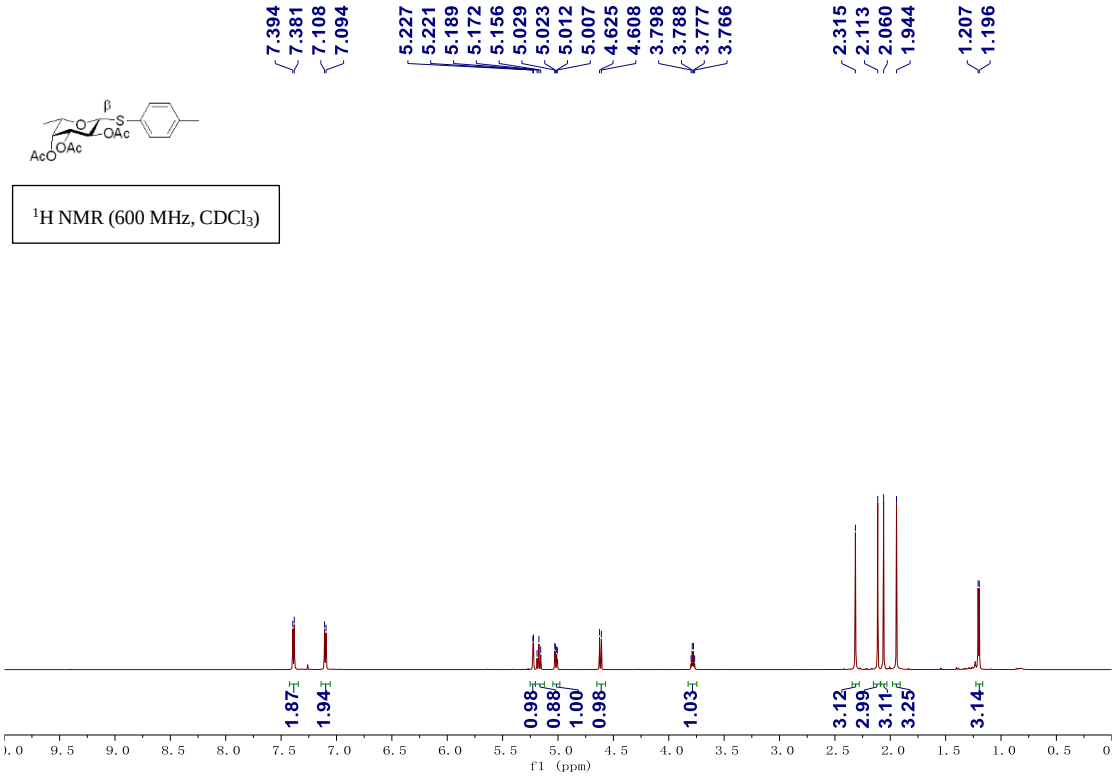


^{1}H NMR (600 MHz, $CDCl_3$)

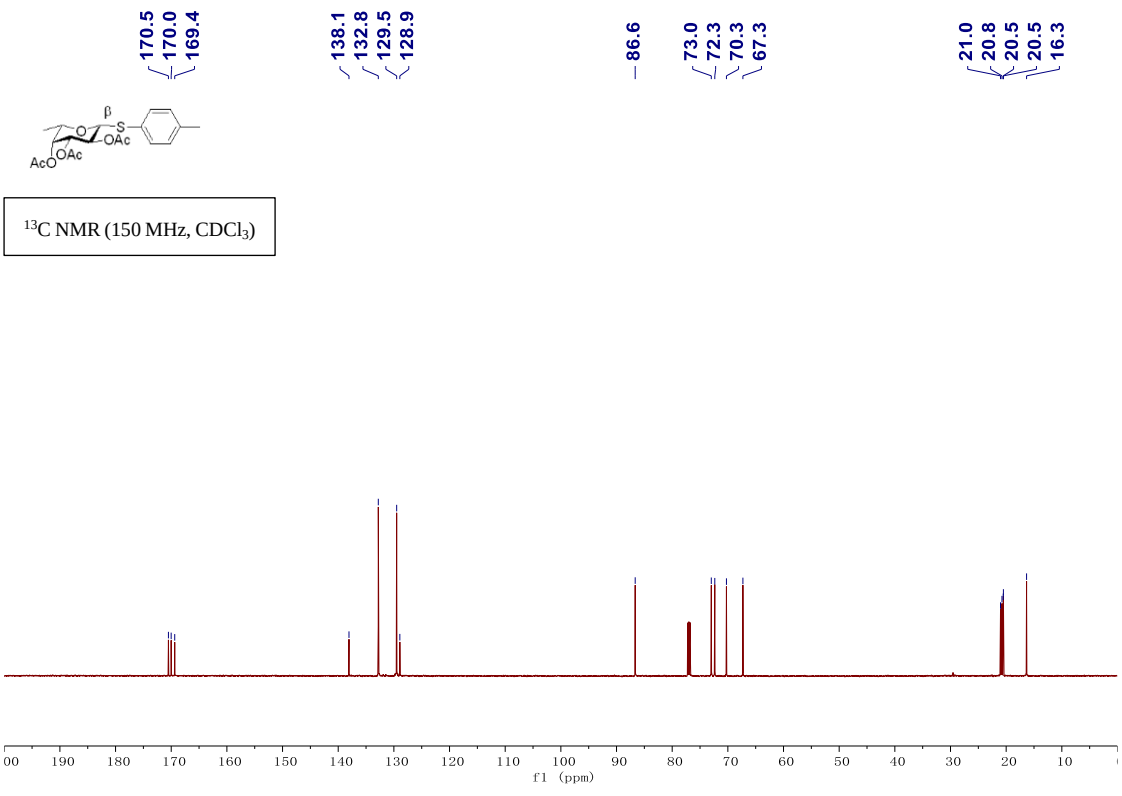


^{13}C NMR (150 MHz, $CDCl_3$)

4-Methylphenyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (29).

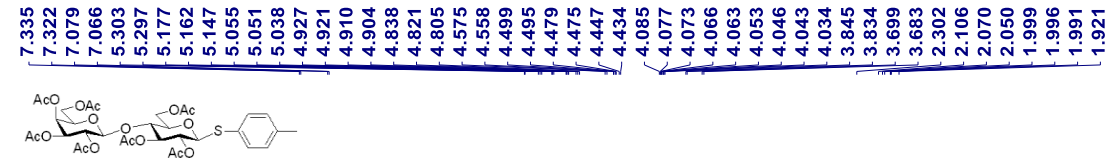


^{1}H NMR (600 MHz, $CDCl_3$)

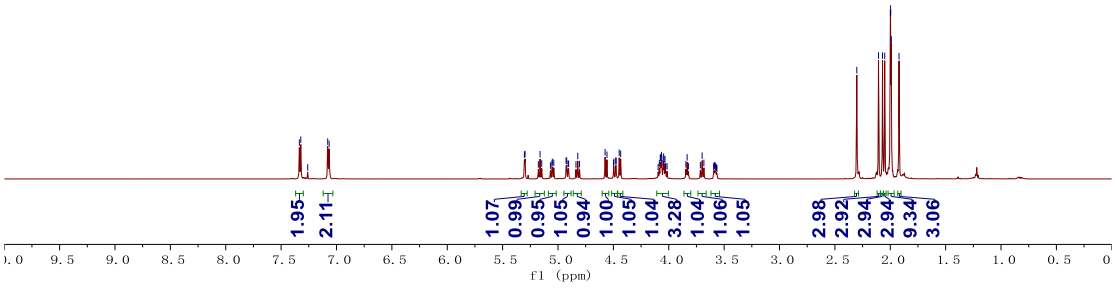


^{13}C NMR (150 MHz, $CDCl_3$)

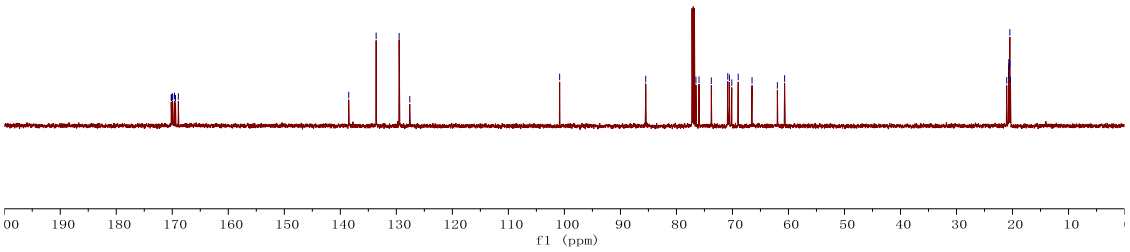
4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (30).



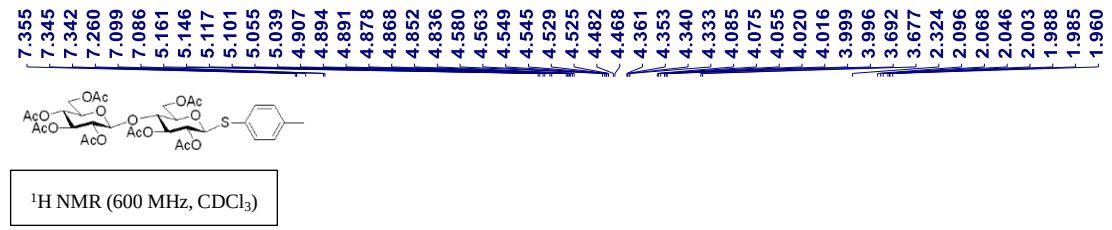
^{1}H NMR (600 MHz, $CDCl_3$)



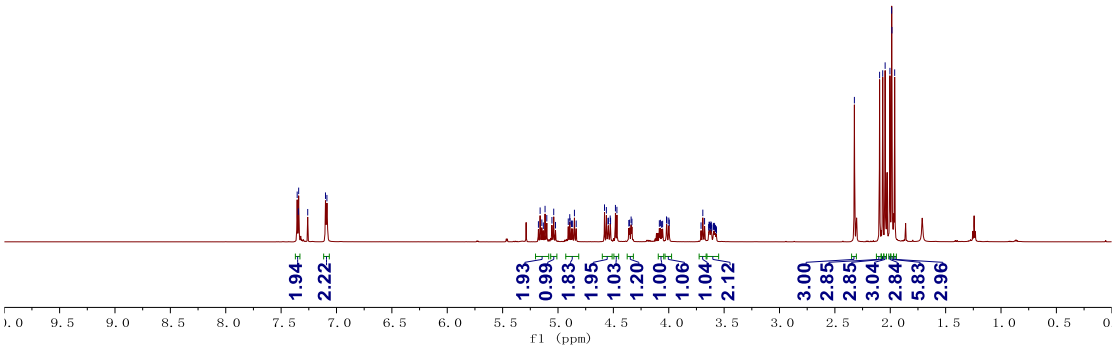
^{13}C NMR (150 MHz, $CDCl_3$)

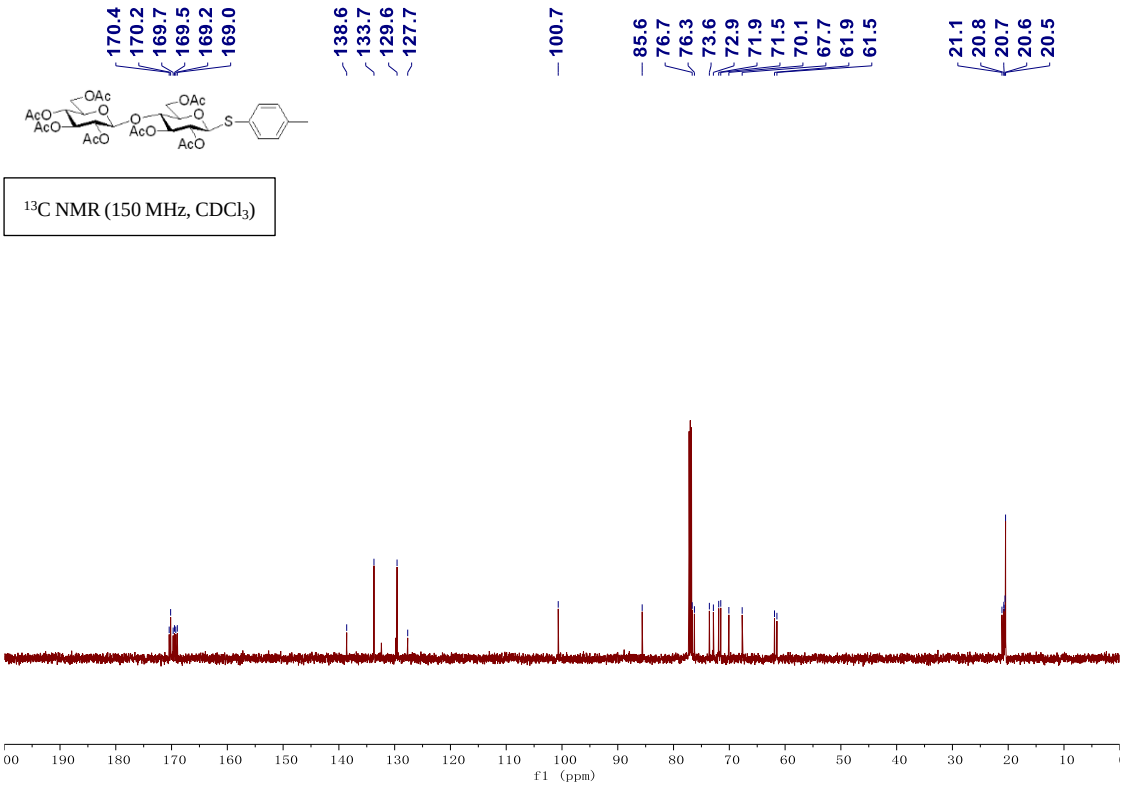


4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (31).



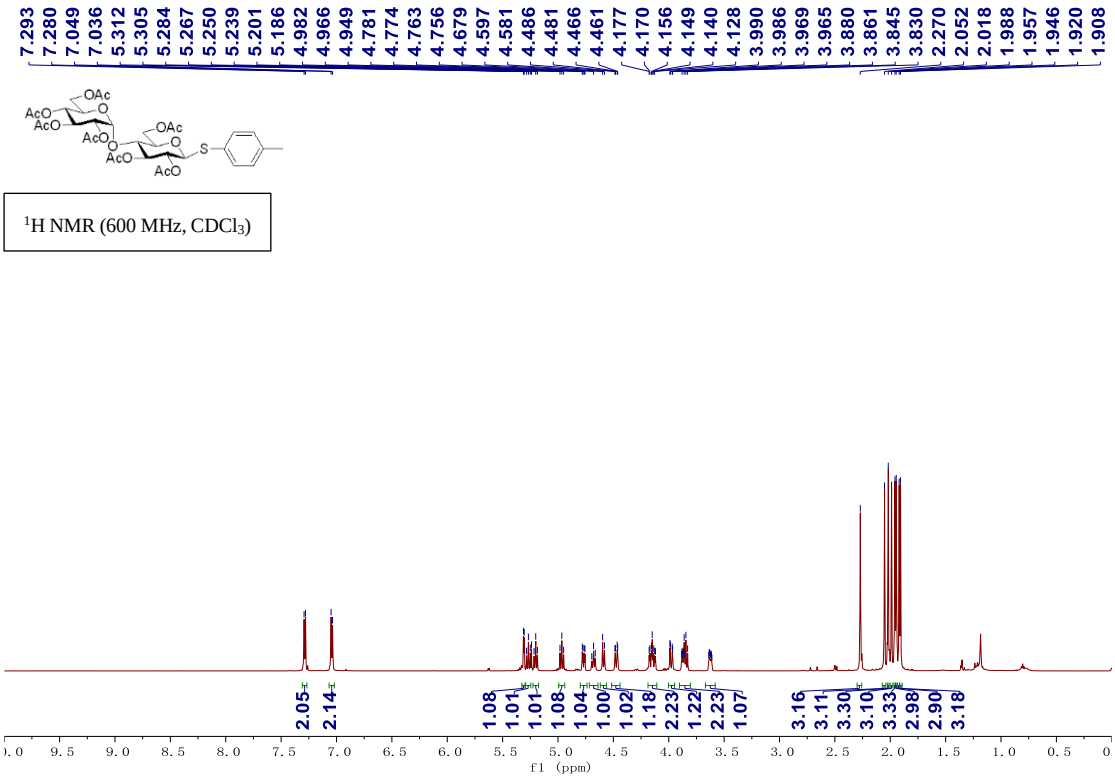
^{1}H NMR (600 MHz, $CDCl_3$)



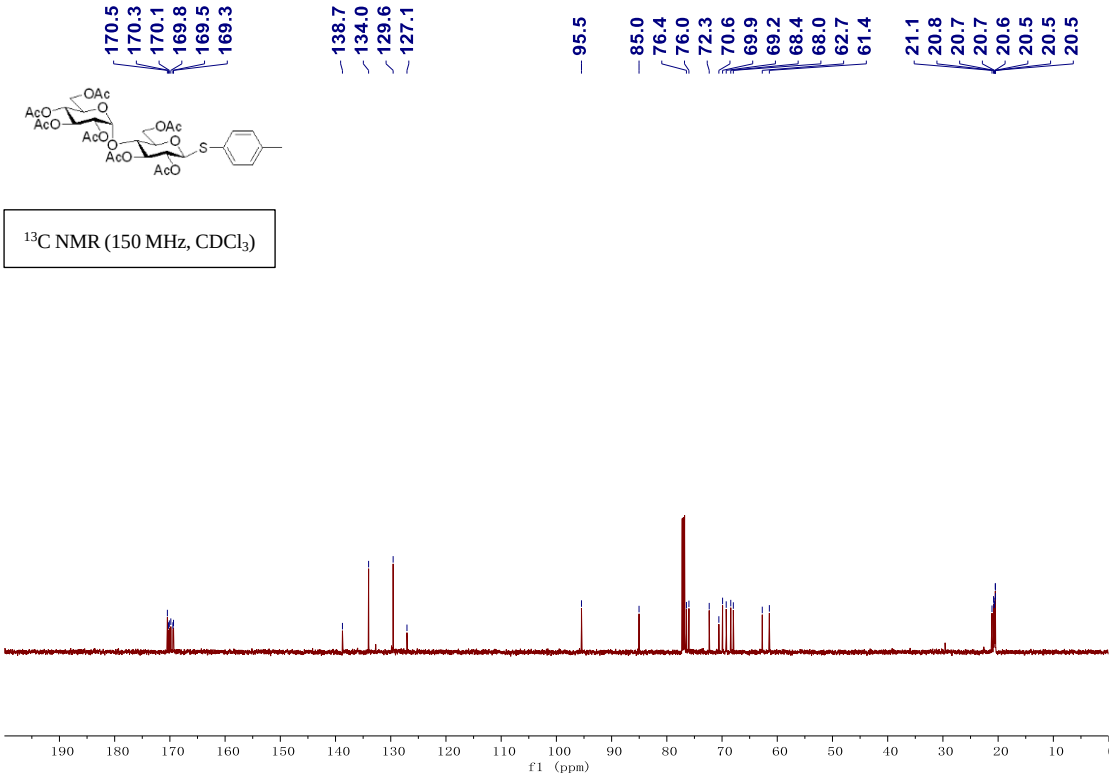


^{13}C NMR (150 MHz, $CDCl_3$)

4-Methylphenyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (32).

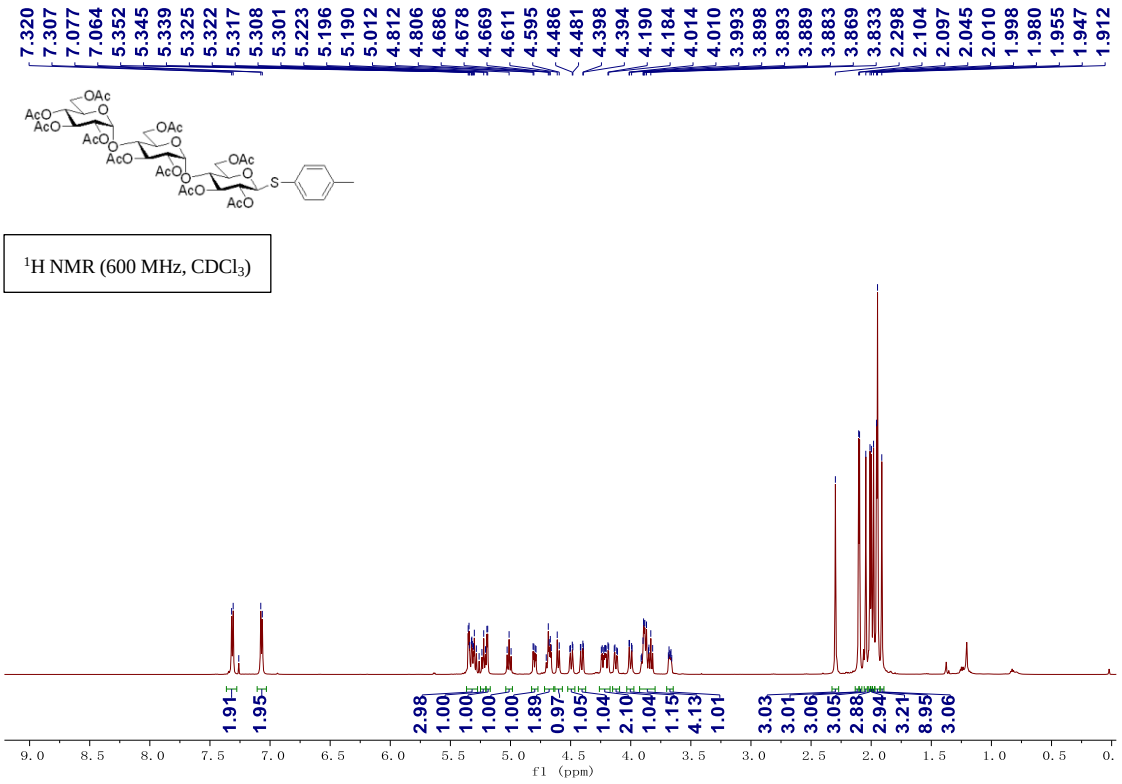


^{1}H NMR (600 MHz, $CDCl_3$)

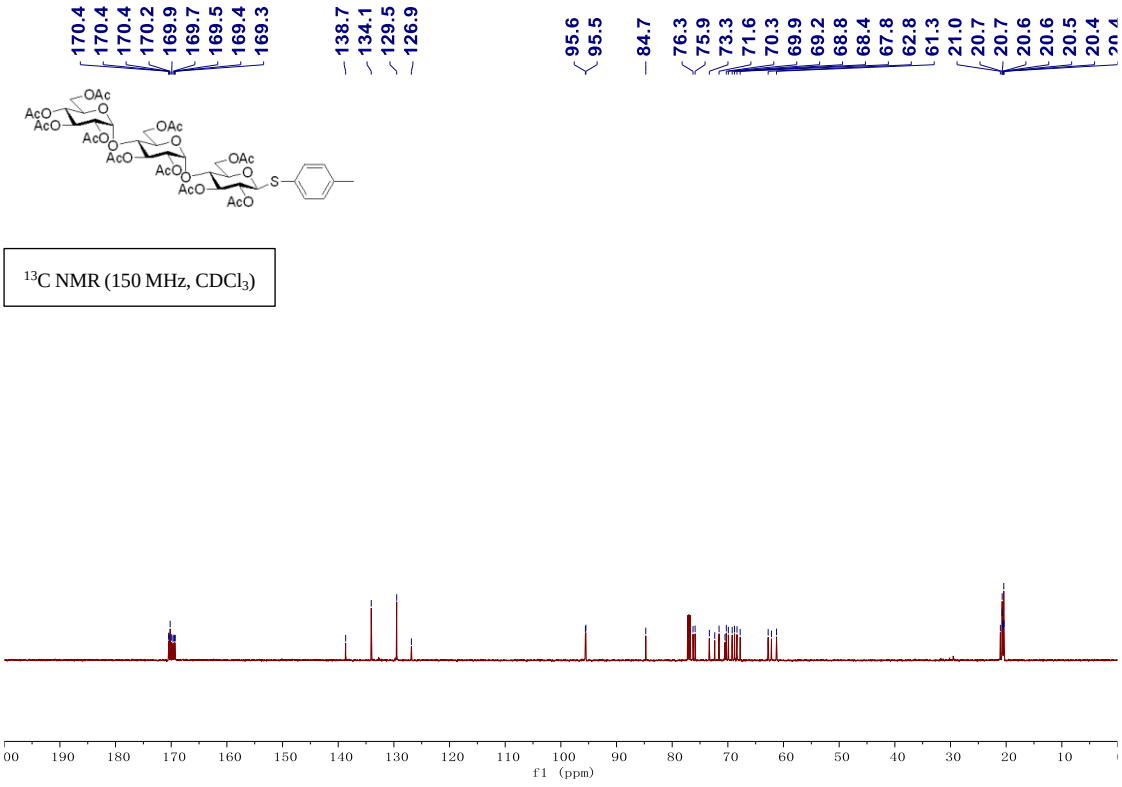


^{13}C NMR (150 MHz, $CDCl_3$)

4-Methylphenyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-2,3,6-tri-O-acetyl-β-D-glucopyranoside (33).

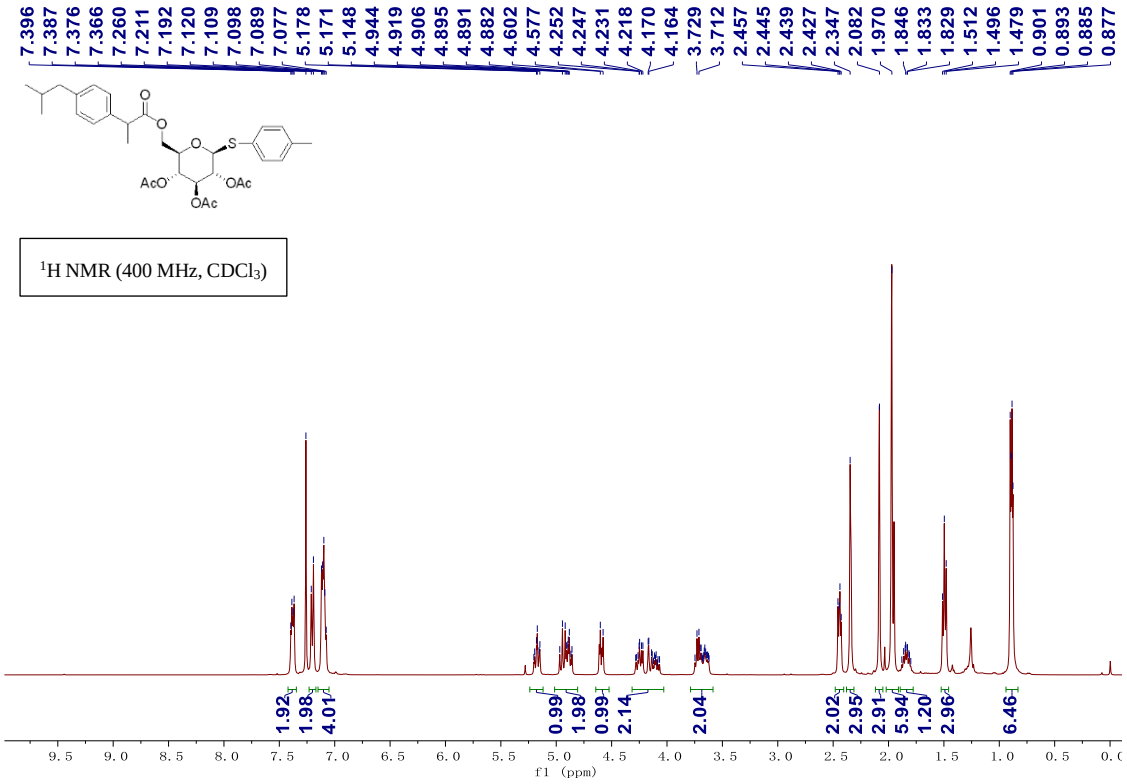


^{1}H NMR (600 MHz, $CDCl_3$)

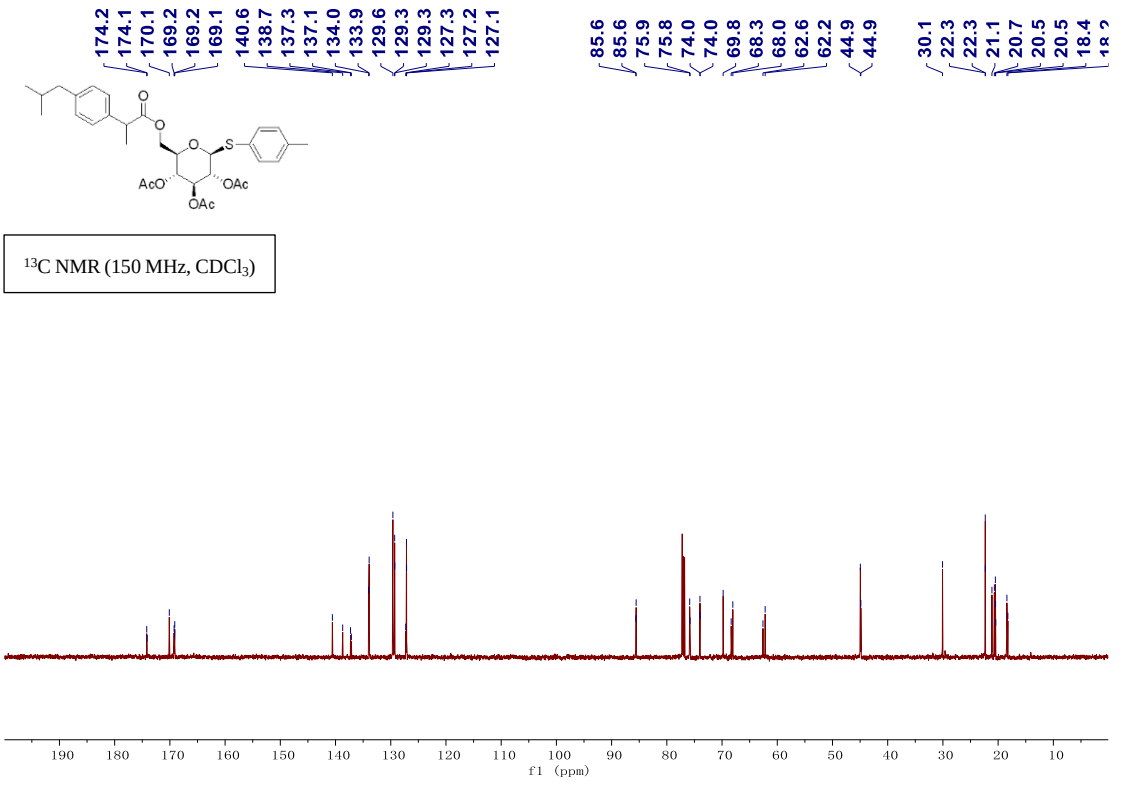


^{13}C NMR (150 MHz, $CDCl_3$)

4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[2-(4-isobutylphenyl) propanoyl]-β-D-thioglucopyranoside (34).

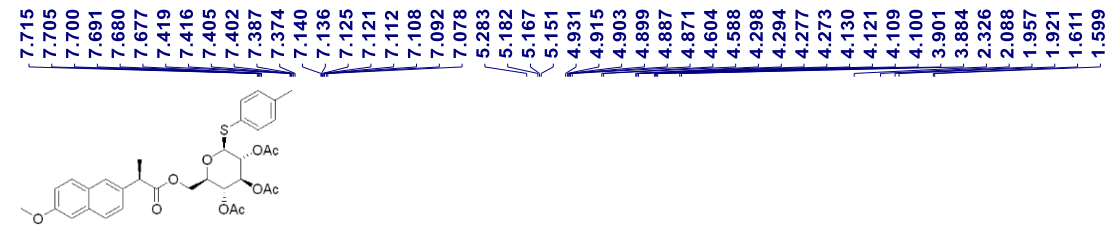


^{1}H NMR (400 MHz, $CDCl_3$)

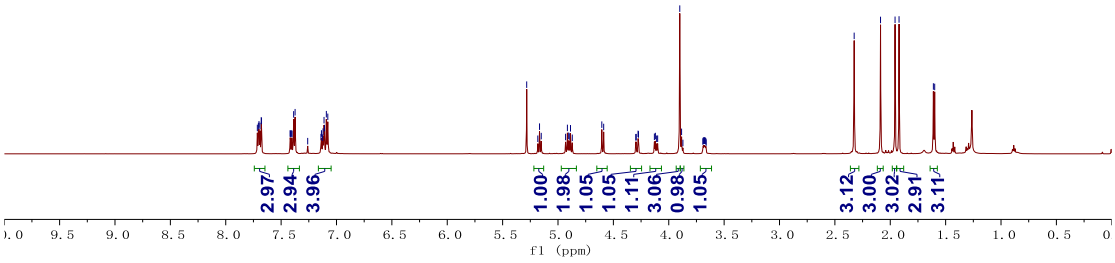


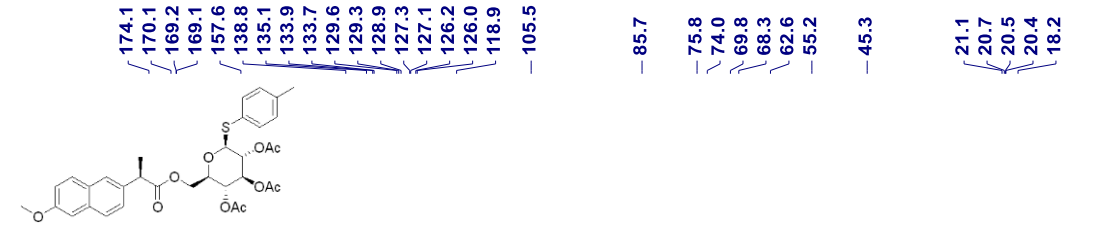
^{13}C NMR (150 MHz, $CDCl_3$)

4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[(R)-2-(6-methoxynaphthalen-2-yl) propanoyl]-β-D-thioglucopyranoside (35).

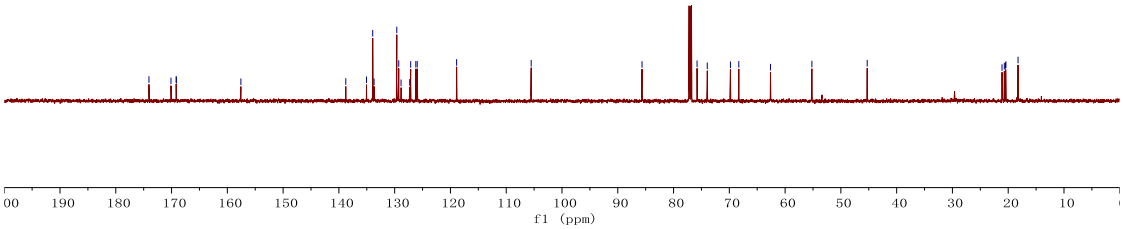


^{1}H NMR (600 MHz, $CDCl_3$)

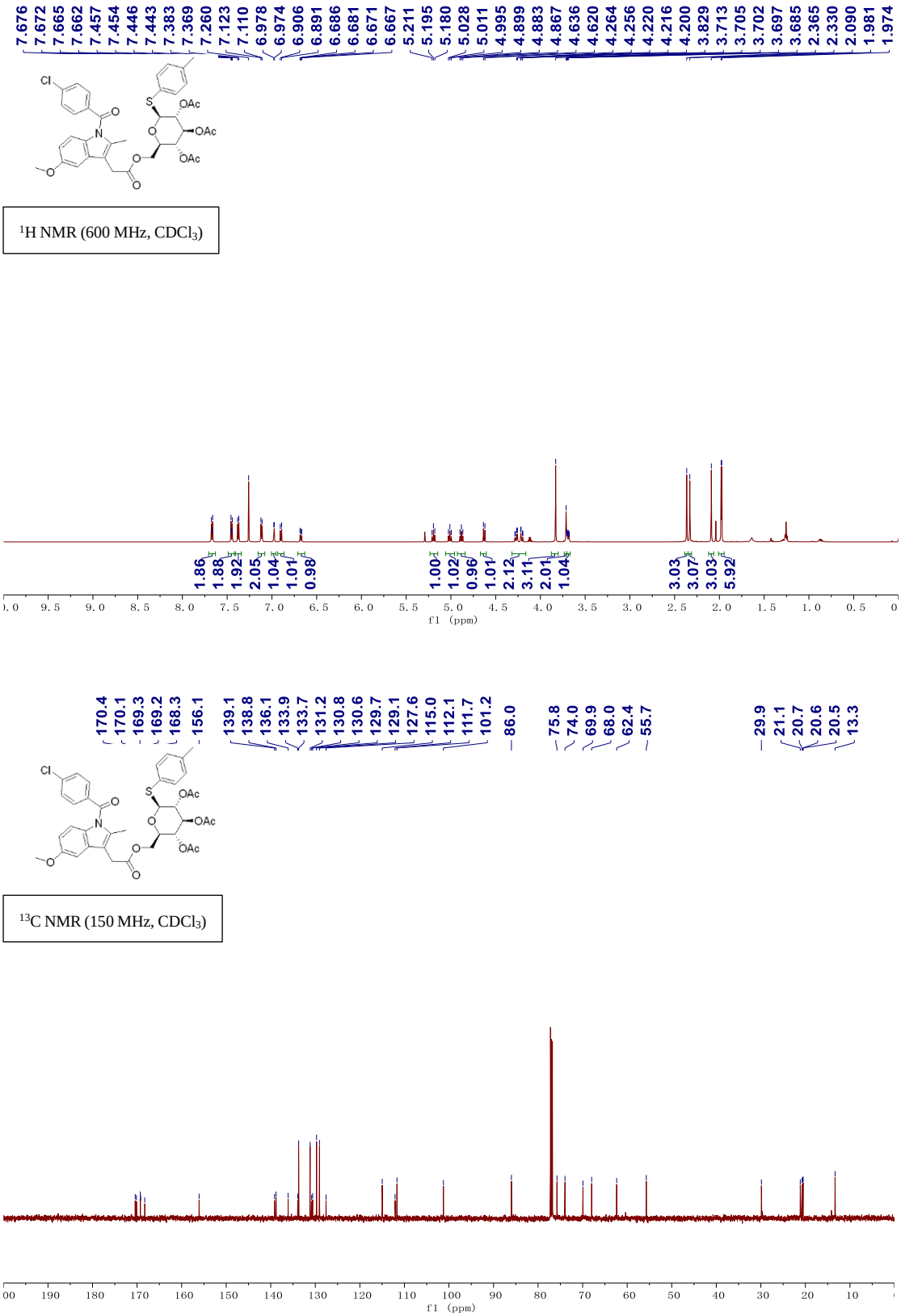




^{13}C NMR (150 MHz, $CDCl_3$)



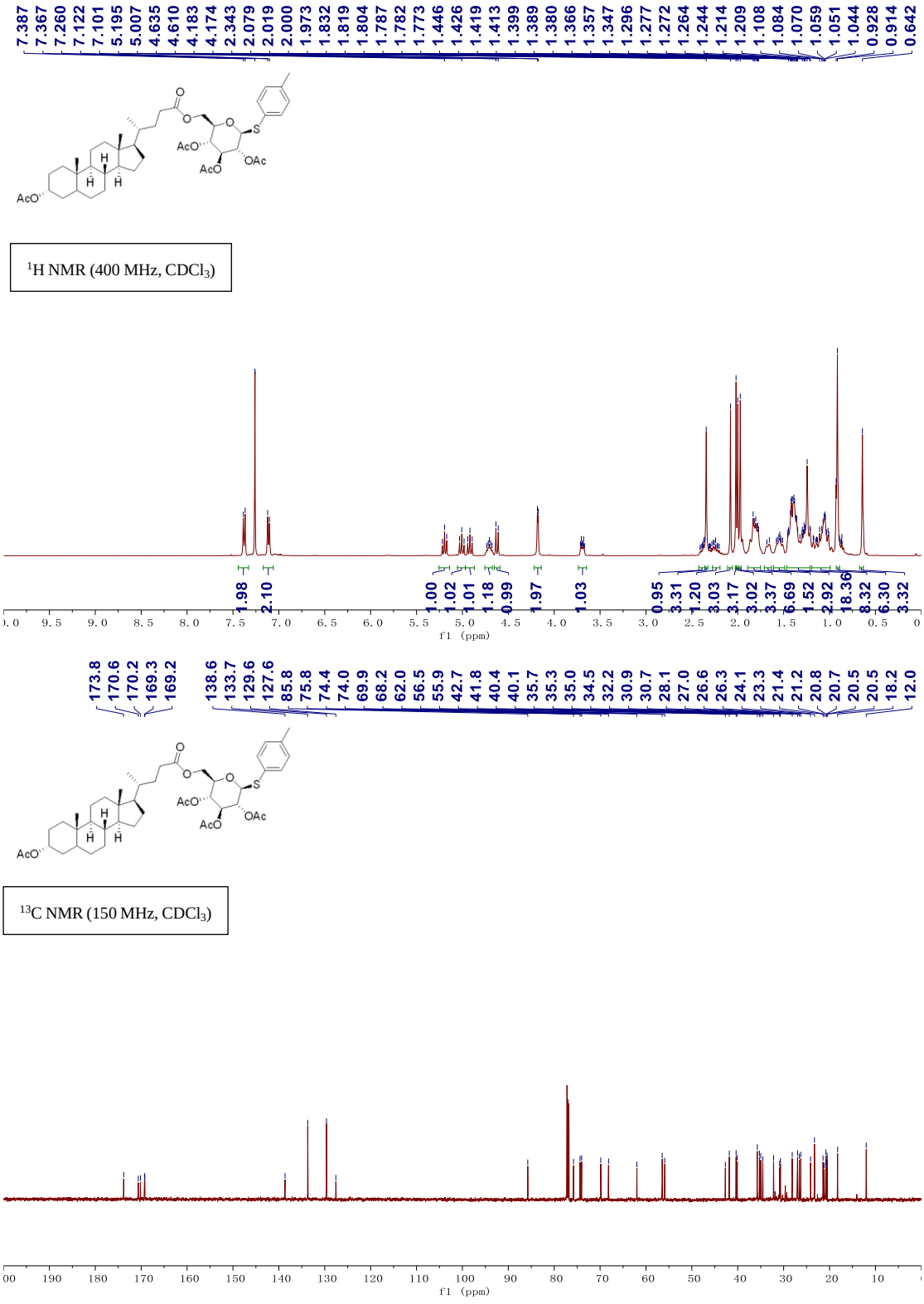
4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)carbonyl]- β-D-thioglucopyranoside (36).



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

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

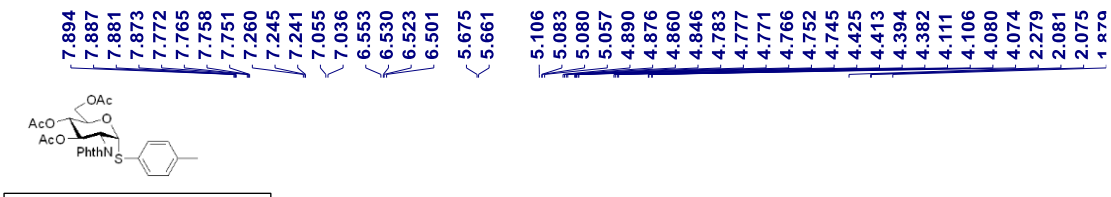
4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-[(4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl]-β-D-thioglucopyranoside (37).



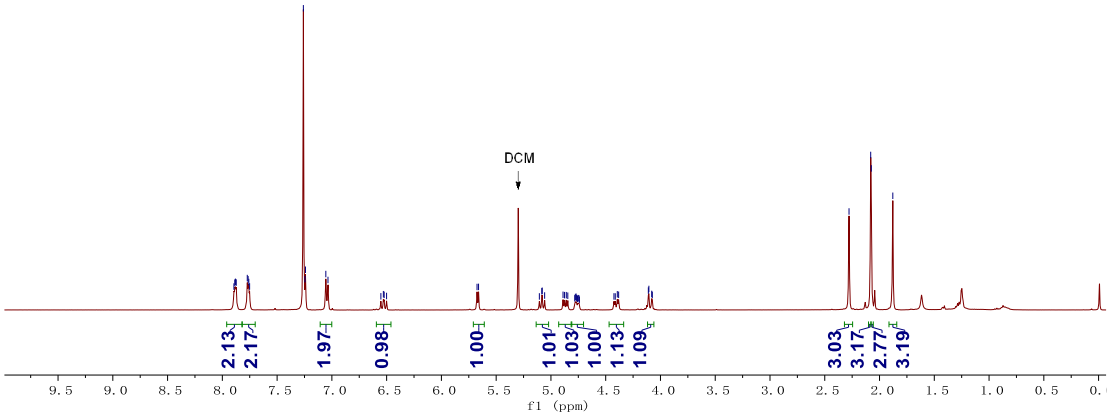
^{1}H NMR (400 MHz, $CDCl_3$)

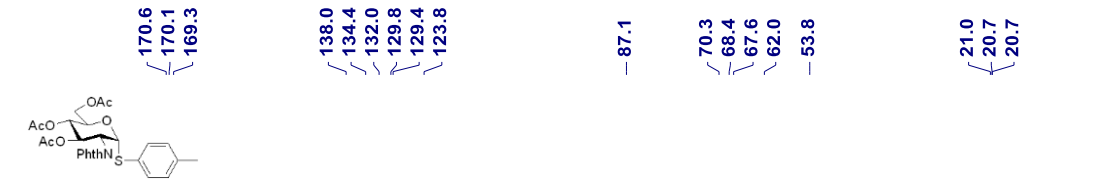
^{13}C NMR (150 MHz, $CDCl_3$)

p-Tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-α-D-glucopyranoside (40)



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





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