Electronic Supplementary Material (ESI) for RSC Advances.

Transition-Metal-Free Synthesis of Aryl 1-Thioglycosides with Arynes at room temperature

Supporting Information

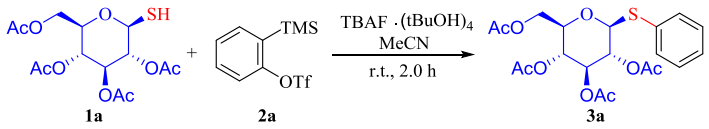
Contents

1. General information

All reactions were carried out in dried Schlenk tubes with PTFE Thread and all solvents used in reaction were dried over activated 4Å molecular sieves. Commercial reagents were used without further purification unless otherwise stated. Reactions were monitored by analytical thin-layer chromatography (TLC) on the pre-coated silica gel G plates. Spots were detected under UV Light (254 nm) and charring with a solution of CeO_8S_2 (1.00 g, 3.00 mmol) and $H_8MoN_2O_4$ (25.00 g, 127.55 mmol) in sulfuric acid (10%, 500 mL). Purification of reaction products were carried out by flash chromatography on silica gel (200-300 mesh). Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DPX-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{19}F at 376 MHz) spectrometer and ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts were expressed in δ (ppm) units and coupling constants (J) were expressed in Hz. The following standard abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and br = broad. High resolution mass spectra were performed on a Waters SYNAPT G2-Si mass spectrometer. Single crystal structure was determined by Rigaku R-AXISRAPID IP X-ray single crystal diffractometer. Specific optical rotations $[\alpha]_D$ were measured by Optical Activity AA-10R polarimeter.

2. General procedure

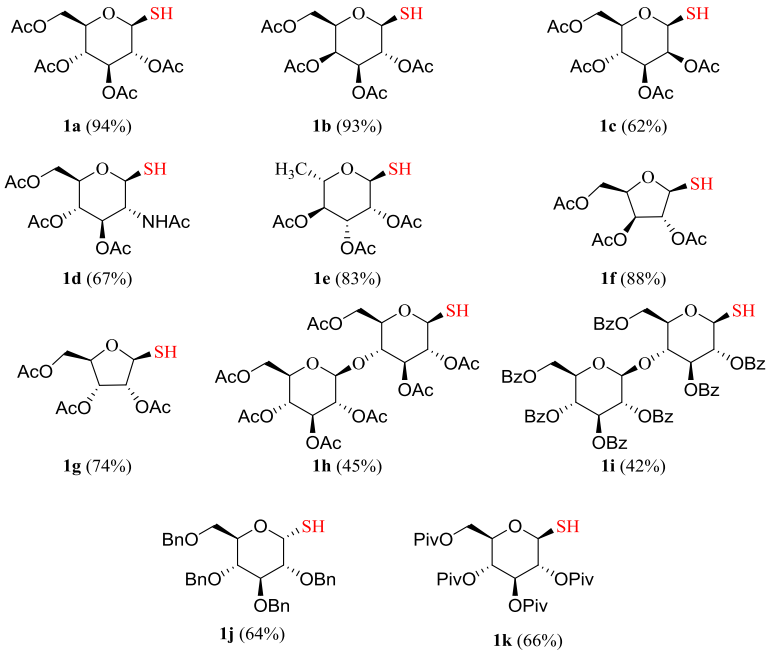
2.1 General procedure for synthesis of thioglycosides:



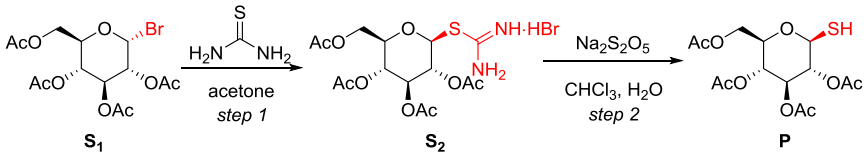
The glycosyl thiol **1** (50 mg, 0.14 mmol, 1.0 equiv), aryne precursor **2** (45 mg, 0.150 mmol, 1.1 equiv) and tetrabutylammonium fluoride tetra-tert-butanol complex (153 mg, 0.274 mmol, 2.0 equiv) were sequentially added in a clean and dry Schlenk tube, and the tube was then evacuated and backfilled with nitrogen (this sequence was repeated three times). Under nitrogen atmosphere, MeCN (1.5 mL) was added to the mixture system, then the mixture was stirred at room temperature for 2.0 hours. Saturated NaCl solution was added to dilute the system and extracted with EtOAc (3 × 2 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuo. Finally, the crude product was purified via flash column chromatography on silica gel to give the desired product (53 mg, 86%).

2.2 General procedure for synthesis of glycosyl thiols 1:

The glycosyl thiols were prepared as shown as follows:



Take glucose thiol **1a**[1] as an example(other glucose thiols were prepared via the references[2-5]), the preparation method of glycosyl thiols as depicted as follows:

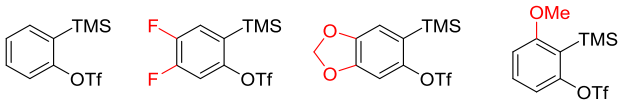


Step 1: bromide $\mathbf{S_1}$(1.0 g, 2.44 mmol, 1.0 equiv) and thiourea (0.3 g, 3.66 mmol, 1.5 equiv) were dissolved in dry acetone (35 mL) under N_2 atmosphere. The solution was heated to reflux, and a white precipitate formed after 2 hours. The precipitate was filtered off, and the filtrate was heated to reflux again. This process was repeated until formation of precipitate no longer occurred. The combined precipitates were recrystallized from isopropanol, and the final product $\mathbf{S_2}$ was obtained as white crystals.

Step 2: Sodium metabisulfite (0.78 g, 4.94 mmol, 4.8 equiv) was added to a solution of $\mathbf{S_2}$ (0.5 g, 1.03 mmol, 1 equiv) dissolved in H_2O (5 mL) and chloroform (10 mL) under N_2 atmosphere, and then the mixture was heated to reflux for 6 h. The TLC indicated the start material has reacted completely, the system cooled to room temperature and diluted with H_2O, extracted with DCM for three times, combined the organic phase and dried over Na_2SO_4, filtered, and evaporated in vacuo. Finally, the crude material was purified via flash column chromatography on silica gel to give the desired product.

2.3 General procedure for synthesis of aryne precursors 2:

As shown below picture, there are some aryne precursors we have prepared.

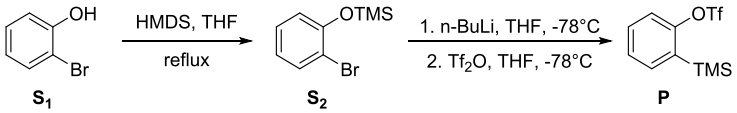


2a **2b** **2c** **2d**

2e **2f** **2g**

Take the benzyne precursor **2a** as example[6], HMDS (3.6 mL, 17.4 mmol, 2.0 equiv) was added into the solution of the S_1(1.5 g , 8.7 mmol, 1.0 equiv) dissolved in anhydrous THF under N_2 atmosphere, and the mixture was heated to reflux for 2 h. After cooling to room temperature, the crude product **S_2** was attained by removing the solvent *in vacuo* and used for the next step without further purification.

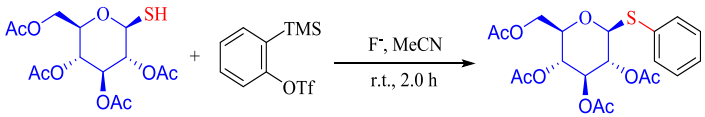
The **S_2** was dissolved in anhydrous THF under N_2 atmosphere and cooled to -78 ℃, then *n*-BuLi (6.0 mL, 9.6 mmol, 1.1 equiv, 1.6 mol/L in hexane) was added dropwise to the mixture and stirred at the same temperature for 40 min. And then, the Tf_2O (1.8 mL, 10.4 mmol, 1.2 equiv) was added dropwise into the mixture at -78 ℃ and stirred at -78 ℃ for another 40 min. The reaction mixture was quenched with cold sat. $NaHCO_3$ solution at -78 ℃ and warmed to room temperature. The mixture was extracted with EtOAc for three times, combined the organic phase and dried over Na_2SO_4, filtered, and evaporated in vacuo. Finally, the crude material was purified via flash column chromatography on silica gel to give the desired product.



S_1 **S_2** **P**

3. Optimization of the reaction conditions

Table S1. Effect of F^- sources

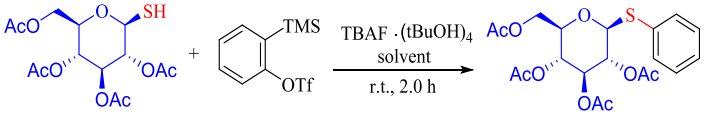


1a **2a** **3a**

Entry	F^- source	**3a**, Yield (%) [a]
1	CsF	70
2	AgF	51
3	KF	42
4	ZnF_2	35
5	TBAF $3H_2O$	63
6	TBAF(THF)	67
7[b]	TBAF(*t*BuOH)$_4$	86
8[c]	TBAF(*t*BuOH)$_4$	83

[a] Reaction condition (unless otherwise noted): **1a** (0.1 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), F^- source (0.2 mmol, 2.0 equiv), dry acetonitrile (1.5 mL), r.t., 2 h; [b]**1a** (0.1 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), TBAF (^{t}BuOH)$_4$ (0.2 mmol, 2.0 equiv), dry acetonitrile (1.5 mL), r.t., 2 h; [c]**1a** (0.1 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), TBAF (*t*BuOH)$_4$ (0.3 mmol, 3.0 equiv), dry acetonitrile (1.5 mL), r.t., 2 h.

Table S2. The Influence of Solvent

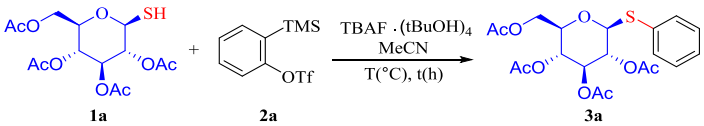


1a **2a** **3a**

Entry	Solvent	**3a,** Yield (%)
1	1,4-dioxane	54
2	DCM	78
3	Acetone	46
4	THF	40
5	Toluene	33
6	Acetonitrile	86
7	Methanol	37
8	DMF	30
9	DMSO	26

Reaction condition (unless otherwise noted): **1a** (0.1 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), TBAF (*t*BuOH)$_4$ (0.2 mmol, 2.0 equiv), dry solvent (1.5 mL), r.t., 2 h.

Table S3. Effect of Times and Temperatures



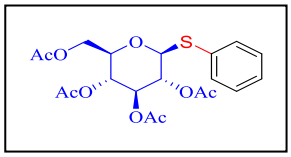
1a **2a** **3a**

Entry	Time(h)	Temperature (℃)	**3a**, Yield (%)
1	0.5	25	70
2	1.0	25	82
3	2.0	25	86
4	3.0	25	83
5	4.0	25	82
6	2.0	40	85
7	2.0	50	72
8	2.0	60	60

Reaction condition (unless otherwise noted): **1a** (0.1 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), TBAF (tBuOH)$_4$ (0.2 mmol, 2.0 equiv), dry acetonitrile (1.5 mL), r.t., 2 h.

4. Characterization of compounds

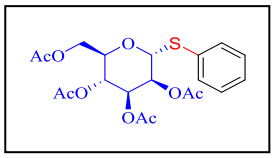
Phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3a)[1]



Purified by flash column chromatography R_f =0.35 (petroleum ether/AcOEt =2:1), white solid (38.2 mg, 86% yield); $[\alpha]_D^{25}$ = -100.5 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.32 – 7.31 (m, 3H), 5.22 (t, *J* = 9.4 Hz, 1H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.97 (dd, *J* = 10.1, 9.2 Hz, 1H), 4.70 (d, *J* = 10.0 Hz, 1H), 4.26 – 4.14 (m, 2H), 3.72 (ddd, *J* = 10.1, 5.0, 2.6 Hz, 1H), 2.08 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H);

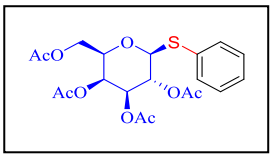
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5, 169.4, 133.2, 131.8, 129.1, 128.6, 85.9, 75.9, 74.1, 70.0, 68.3, 62.3, 20.9, 20.8, 20.7, 20.7.

Phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (3b)[7]



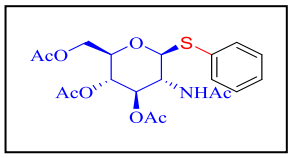
Purified by flash column chromatography R_f =0.37 (petroleum ether/AcOEt = 2:1), white solid (35.0 mg, 80% yield); $[\alpha]_D^{25}$ = 78.2 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.36 – 7.28 (m, 3H), 5.53–5.47 (m, 2H), 5.37 – 5.28 (m, 2H), 4.57 – 4.52 (m, 1H), 4.30 (dd, *J* = 12.3, 5.9 Hz, 1H), 4.10 (dd, *J* = 12.3, 2.4 Hz, 1H), 2.15 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.1, 169.9, 169.8, 132.7, 132.1, 129.3, 128.2, 85.8, 70.9, 69.6, 69.5, 66.4, 62.5, 21.0, 21.0, 20.8, 20.8.

Phenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (3c)[7]



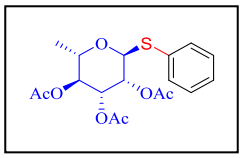
Purified by flash column chromatography R_f =0.33 (petroleum ether/AcOEt = 2:1), white solid (37.4 mg, 85% yield); $[\alpha]_D^{25}$ = -83.2 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.33-7.29 (m, *J* = 2.7 Hz, 3H), 5.41 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.24 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.04 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 4.19 (dd, *J* = 11.3, 7.0 Hz, 1H), 4.11 (dd, *J* = 11.4, 6.1 Hz, 1H), 3.98 – 3.90 (m, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.2, 169.6, 132.6, 132.6, 129.0, 128.3, 86.7, 74.5, 72.1, 67.3, 67.3, 61.7, 21.0, 20.8, 20.8, 20.7.

Phenyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-glucopyranoside (3d)[8]



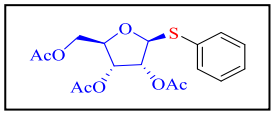
Purified by flash column chromatography R_f =0.30 (petroleum ether/AcOEt = 1:2), white solid (32.9 mg, 75% yield), m.p. = 188-191 ℃; $[\alpha]_D^{25}$ = -21.0 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.33 – 7.27 (m, 3H), 5.74 (d, *J* = 9.2 Hz, 1H), 5.22 (t, *J* = 9.8 Hz, 1H), 5.05 (t, *J* = 9.7 Hz, 1H), 4.85 (d, *J* = 10.4 Hz, 1H), 4.21 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.6 Hz, 1H), 4.03 (q, *J* = 9.6 Hz, 1H), 3.72 (ddd, *J* = 10.1, 5.3, 2.6 Hz, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.8, 170.2, 169.5, 132.6, 132.5, 129.0, 128.2, 86.7, 75.8, 73.8, 68.5, 62.5, 53.4, 23.4, 20.9, 20.8, 20.7.

Phenyl-2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (3e)[9]



Purified by flash column chromatography R_f =0.45 (petroleum ether/AcOEt = 2:1), white solid (29.3 mg, 77% yield); $[\alpha]_D^{25}$ = -82.7 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.35 – 7.26 (m, 3H), 5.49 (dd, *J* = 3.4, 1.6 Hz, 1H), 5.40 (d, *J* = 1.6 Hz, 1H), 5.28 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.14 (t, *J* = 9.8 Hz, 1H), 4.40 – 4.32 (m, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.24 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 170.1, 170.0, 133.3, 131.9, 129.3, 127.9, 85.8, 71.4, 71.2, 69.5, 67.8, 21.0, 20.9, 20.8, 17.4.

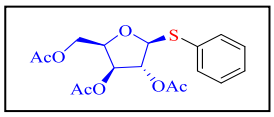
Phenyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-ribofuranoside (3f)[10]



Purified by flash column chromatography R_f =0.40 (petroleum ether/AcOEt = 3:1), white solid (30.2 mg, 82% yield); $[\alpha]_D^{25}$ = 12.8 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.47(m, 2H),

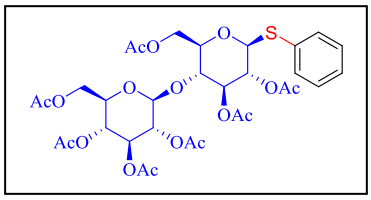
7.46-7.31 (m, 3H), 5.49 (t, *J* = 3.2 Hz, 1H), 5.17 (d, *J* = 6.9 Hz, 1H), 5.07 (dt, *J* = 7.3, 3.6 Hz, 1H), 5.00 (dd, *J* = 6.9, 3.2 Hz, 1H), 4.18 (dd, *J* = 11.8, 4.0 Hz, 1H), 3.80 (dd, *J* = 11.8, 7.4 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 169.8, 169.5, 132.6, 132.1, 129.2, 128.2, 84.1, 68.4, 67.3, 66.6, 63.5, 20.9, 20.9, 20.8.

Phenyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside (3g)



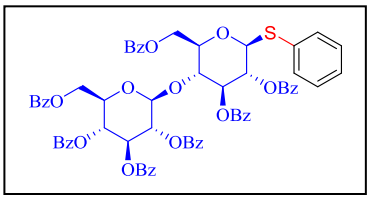
Purified by flash column chromatography R_f =0.39 (petroleum ether/AcOEt = 3:1), white solid (29.8 mg, 81% yield), m.p. = 68-69 ℃; $[\alpha]_D^{25}$ = -55.4 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H, ArH), 7.40 – 7.28 (m, 3H, ArH), 5.18 (t, *J* = 8.2 Hz, 1H), 5.06 – 4.87 (m, 2H), 4.80 (d, *J* = 8.4 Hz, 1H), 4.28 (dd, *J* = 11.8, 4.9 Hz, 1H), 3.42 (dd, *J* = 11.8, 8.7 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 169.8, 169.3, 132.7, 132.2, 129.1, 128.3, 86.2, 71.9, 69.8, 68.4, 65.2, 20.8, 20.8, 20.7; **HRMS (ESI)** m/z calcd for $C_{17}H_{20}O_7SNa^+$ $(M+Na)^+$ 391.0822, found 391.0822.

Phenyl-2,3,6,2',3',4',6'-hepta-*O*-acetyl-1-thio-β-cellobioside (3h)[11]



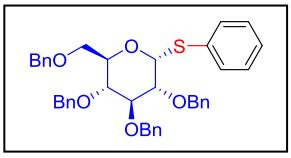
Purified by flash column chromatography R_f =0.29 (petroleum ether/AcOEt = 2:1), white solid (56.8 mg, 78% yield), m.p. = 235-237 ℃ ; $[\alpha]_D^{25}$ = -16.5 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.31 -7.27 (m, 3H), 5.18 (t, *J* = 9.2 Hz, 1H), 5.13 (t, *J* = 9.3 Hz, 1H), 5.05 (t, *J* = 9.6 Hz, 1H), 4.94 – 4.87 (m, 2H), 4.65 (d, *J* = 10.1 Hz, 1H), 4.55 (dd, *J* = 11.9, 2.0 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.36 (dd, *J* = 12.5, 4.3 Hz, 1H), 4.08 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.01 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.71 (t, *J* = 9.5 Hz, 1H), 3.66 – 3.59 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 2.00 (s, 6H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.4, 169.9, 169.7, 169.4, 169.2, 133.2, 131.9, 129.0, 128.4, 100.9, 85.6, 76.5, 73.7, 73.0, 72.1, 71.7, 70.3, 67.8, 62.1, 61.6, 21.0, 20.9, 20.8, 20.7, 20.7.

Phenyl-2,3,6,2',3',4',6'-hepta-*O*-benzoyl-1-thio-β-cellobioside (3i)[12]



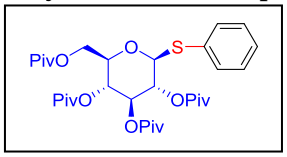
Purified by flash column chromatography R_f =0.45 (petroleum ether/AcOEt = 3:1), white solid (86.0 mg, 74% yield), m.p. = 173- 175 ℃; $[\alpha]_D^{25}$ = 21.3 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.92 (m, 10H), 7.83 – 7.71 (m, 4H), 7.63 – 7.48 (m, 3H), 7.47 – 7.30 (m, 13H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.21 (dd, *J* = 14.6, 6.9 Hz, 6H), 7.09 (t, *J* = 7.6 Hz, 2H), 5.83-5.73 (m, 2H), 5.51 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.38 (td, *J* = 9.7, 3.1 Hz, 2H), 4.93 (d, *J* = 7.9 Hz, 2H), 4.89 (d, *J* = 10.0 Hz, 1H), 4.66 (dd, *J* = 12.1, 1.9 Hz, 1H), 4.47 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.16 (t, *J* = 9.5 Hz, 1H), 4.03 (dd, *J* = 11.9, 3.0 Hz, 1H), 3.92 – 3.80 (m, 1H), 3.75 (dd, *J* = 11.9, 5.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 165.8, 165.7, 165.5, 165.3, 165.1, 164.8, 133.5, 133.5, 133.4, 133.4, 133.3, 133.3, 133.2, 133.0, 131.8, 130.0, 129.9, 129.8, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 101.1, 85.9, 77.4, 76.6, 74.1, 72.9, 72.5, 72.0, 70.6, 69.5, 62.7, 62.6. **HRMS (ESI)** m/z calcd for $C_{67}H_{54}O_{17}SNa^+$ $(M+Na)^+$ 1185.2974, found 1185.2972.

Phenyl-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3j)[13]



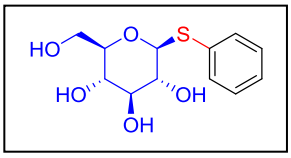
Purified by flash column chromatography R_f =0.40 (petroleum ether/AcOEt = 6:1), white solid (24.2 mg, 78% yield), m.p. = 70-72 ℃; $[\alpha]_D^{25}$ = 124 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.38-7.16 (m, 21H), 7.11 (dd, *J* = 7.4, 2.2 Hz, 2H), 5.62-5.59 (m, 1H), 4.97 (d, *J* = 10.7 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.29 (ddd, *J* = 10.1, 3.8, 2.0 Hz, 1H), 3.86 (dd, *J* = 5.6, 1.9 Hz, 2H), 3.73 (dd, *J* = 10.7, 3.8 Hz, 1H), 3.69-3.61 (m, 1H), 3.57 (dd, *J* = 10.7, 2.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 138.3, 138.0, 137.8, 134.6, 131.6, 129.0, 128.6, 128.5, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.2, 87.1, 82.7, 79.8, 77.5, 75.9, 75.3, 73.5, 72.7, 71.2, 68.6.

Phenyl-2,3,4,6-tetra-*O*-pivaloyl-1-thio-β-D-glucopyranoside (3k)[14]



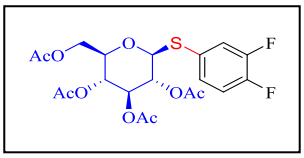
Purified by flash column chromatography R_f =0.30 (petroleum ether/AcOEt = 10:1), white solid (43.0 mg, 71% yield), m.p. = 130-131 ℃; $[\alpha]_D^{25}$ = -5.6 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.33-7.25 (m, 3H), 5.33 (t, J = 9.4 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 5.02 (t, *J* = 9.7 Hz, 1H), 4.73 (d, *J* = 10.1 Hz, 1H), 4.24 (dd, *J* = 12.3, 1.8 Hz, 1H), 4.04 (dd, *J* = 12.3, 5.9 Hz, 1H), 3.76 (ddd, *J* = 10.1, 5.9, 1.8 Hz, 1H), 1.21 (s, 9H), 1.20 (s, 9H), 1.13 (s, 9H), 1.09 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 177.3, 176.6, 176.5, 132.7, 132.5, 129.1, 128.4, 86.7, 76.5, 73.3, 69.5, 67.7, 62.4, 39.0, 38.9, 38.8, 27.3, 27.2, 27.1.

Phenyl-1-thio-α-D-glucopyranoside (3l)[15]



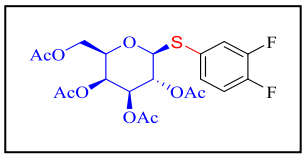
Purified by flash column chromatography R_f =0.30 (DCM/CH_3OH = 10:1), white solid (16.0 mg, 30% yield), m.p. = 132-133 ℃; $[\alpha]_D^{21}$ = -70.5 (*c*= 0.8, H_2O); **^{1}H NMR** (400 MHz, MeOD) δ 7.62-7.55 (m, 2H), 7.39-7.20 (m, 3H), 4.62 (d, *J* = 9.8 Hz, 1H), 3.89 (dd, *J* = 12.1, 1.9 Hz, 1H), 3.69 (dd, *J* = 12.0, 5.3 Hz, 1H), 3.41 (t, *J* = 8.5 Hz, 1H), 3.34-3.32 (m, 2H), 3.24 (dd, *J* = 9.8, 8.7 Hz, 1H). **^{13}C NMR** (100 MHz, MeOD) δ 135.3, 132.6, 129.9, 128.3, 89.4, 82.0, 79.7, 73.7, 71.3, 62.8.

3,4-Difluorphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4a)



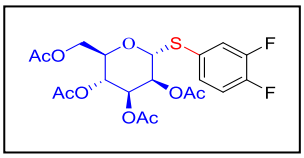
Purified by flash column chromatography R_f =0.30 (petroleum ether/AcOEt = 3:1), white solid (39.1 mg, 2% yield), m.p. = 87-88 ℃**;** $[\alpha]_D^{25}$ = -20.7 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (ddd, *J* = 10.2, 7.5, 2.2 Hz, 1H), 7.24 - 7.19 (m, 1H), 7.10 (dt, *J* = 10.0, 8.3 Hz, 1H), 5.21 (t, *J* = 9.4 Hz, 1H), 5.00 (t, *J* = 9.8 Hz, 1H), 4.90 (t, *J* = 9.6 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 4.19 (d, *J* = 3.8 Hz, 2H), 3.73 (dt, *J* = 10.1, 3.8 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.81 (dt, *J* = 19.7, 9.3 Hz), -136.61(m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.81 (d, *J* = 20.9 Hz), -136.61 (d, *J* = 21.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.3, 169.2, 150.9 (dd, *J* = 251.0, 12.3 Hz), 149.9 (dd, *J* = 251.1, 12.5 Hz), 130.3 (dd, *J* = 6.4, 3.6 Hz), 127.1 (dd, *J* = 6.2, 4.2 Hz), 122.9 (d, *J* = 18.2 Hz), 117.5 (d, *J* = 17.6 Hz), 85.1, 75.9, 73.8, 69.6, 68.0, 62.0, 20.7, 20.6, 20.5; **HRMS (ESI)** m/z calcd for $C_{20}H_{22}F_2O_9SNa^+$ $(M+Na)^+$ 499.0845, found 499.0843.

3,4-Difluorphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (4b)



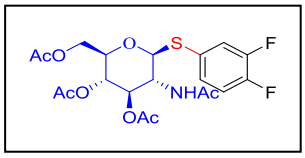
Purified by flash column chromatography R_f =0.28 (petroleum ether/AcOEt = 3:1), colorless oil (37.1 mg, 78% yield); $[\alpha]_D^{25} = 6.8$ (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (ddd, *J* = 10.2, 7.5, 2.2 Hz, 1H), 7.24-7.19 (m, 1H), 7.11 (dt, *J* = 10.0, 8.4 Hz, 1H), 5.41 (dd, *J* = 3.3, 1.1 Hz, 1H), 5.18 (dd, *J* = 9.9 Hz, 1H), 5.03 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.64 (d, *J* = 9.9 Hz, 1H), 4.20-4.09 (m, 2H), 3.95 (td, *J* = 5.8, 2.9 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 1.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 169.1, 168.9, 168.3, 149.6 (dd, *J* = 250.8, 12.5 Hz), 148.9 (dd, *J* = 250.9, 13.0 Hz), 128.5 (dd, *J* = 6.2, 3.7 Hz), 127.1 (dd, *J* = 6.1, 4.2 Hz), 121.1 (d, *J* = 18.3 Hz), 116.4 (d, *J* = 17.7 Hz), 84.9, 73.6, 70.8, 66.2, 65.9, 60.8, 19.8, 19.6, 19.5, 19.5; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.92 (dt, *J* = 19.8, 9.3 Hz), -137.16 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.92 (d, *J* = 21.0 Hz), -137.17 (d, *J* = 20.9 Hz). **HRMS (ESI)** m/z calcd for $C_{20}H_{22}F_2O_9SNa^+$ $(M+Na)^+$ 499.0845, found 499.0840.

3,4-Difluorphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (4c)



Purified by flash column chromatography R_f =0.33 (petroleum ether/AcOEt = 3:1), white solid (35.7 mg, 75% yield), m.p. = 77-78 ℃; $[\alpha]_D^{25} = 95.6$ (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.39 (ddd, *J* = 9.9, 7.3, 2.2 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.12 (dd, *J* = 10.1, 8.4 Hz, 1H), 5.46 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.41 (d, *J* = 1.5 Hz, 1H), 5.35 – 5.28 (m, 1H), 5.25 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.51 (ddd, *J* = 9.4, 6.6, 2.2 Hz, 1H), 4.28 (dd, *J* = 12.2, 6.6 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.3 Hz, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 169.9, 169.9, 169.8, 150.7 (dd, *J* = 251.0, 12.6 Hz), 150.3 (dd, *J* = 251.7, 13.1 Hz), 129.0 (dd, *J* = 6.3, 3.7 Hz), 128.8 (dd, *J* = 6.2, 4.1 Hz), 121.72(d, *J* = 18.3 Hz), 118.0 (d, *J* = 17.7 Hz), 85.9, 70.7, 69.8, 69.3, 66.4, 62.7, 20.9, 20.8, 20.7; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.45 (dt, *J* = 19.7, 9.3 Hz), -137.00 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.45 (d, *J* = 20.9 Hz), -137.00 (d, *J* = 21.2 Hz). **HRMS (ESI)** m/z calcd for $C_{20}H_{22}F_2O_9SNa^+$ $(M+Na)^+$ 499.0845, found 499.0840.

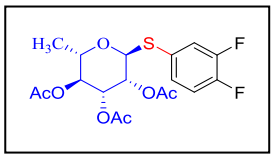
3,4-Difluorphenyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-glucopyranoside (4d)



Purified by flash column chromatography R_f =0.28 (petroleum ether/AcOEt = 1:2), white solid (33.6 mg, 71% yield), m.p. = 232-234 ℃; $[\alpha]_D^{25} = -24.5$ (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (ddd, *J* = 10.0, 7.4, 2.1 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.09 (dt, *J* = 10.1, 8.4 Hz, 1H), 5.76 (d, *J* = 9.1 Hz, 1H), 5.19 (t, *J* = 9.8 Hz, 1H), 5.02 (t, *J* = 9.7 Hz, 1H), 4.77 (d, *J* = 10.4 Hz, 1H), 4.21 – 4.13 (m, 2H), 4.00 (q, *J* = 9.8 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.08 (s, 3H), 2.02 (s, 6H),

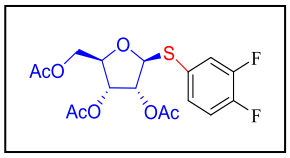
1.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 170.6, 170.1, 169.3, 150.6 (dd, *J* = 251.0, 12.6 Hz), 149.9 (dd, *J* = 250.9, 12.8 Hz), 129.6 (dd, *J* = 6.3, 3.6 Hz), 128.2 (dd, *J* = 6.3, 4.2 Hz), 122.1 (d, *J* = 18.2 Hz), 117.5 (d, *J* = 17.5 Hz), 86.4, 75.9, 73.5, 68.2, 62.3, 53.2, 23.3, 20.6, 20.6, 20.5; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.93 (dt, *J* = 19.9, 9.3 Hz), -137.28 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.93 (d, *J* = 21.4 Hz), -137.29 (d, *J* = 21.0 Hz). **HRMS (ESI)** m/z calcd for $C_{20}H_{23}F_2NO_8SNa^+$ $(M+Na)^+$ 498.1005, found 498.1006.

3,4-Difluorphenyl-2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (4e)



Purified by flash column chromatography R_f =0.47 (petroleum ether/AcOEt = 3:1), white solid (31.8 mg, 76% yield), m.p. = 105-110 ℃; $[\alpha]_D^{25}$ = -116.0 (*c*=1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (ddd, *J* = 10.0, 7.3, 2.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.11 (dt, *J* = 10.0, 8.3 Hz, 1H), 5.45 (dd, *J* = 3.3, 1.7 Hz, 1H), 5.35 (d, *J* = 1.6 Hz, 1H), 5.21 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.14 (t, *J* = 9.8 Hz, 1H), 4.34 – 4.26 (m, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.25 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 170.0, 170.4, 150.5 (dd, *J* = 250.5, 12.6 Hz), 150.3 (dd, *J* = 251.8, 13.1 Hz).129.4 (dd, *J* = 6.1, 4.1 Hz), 128.6 (dd, *J* = 6.3, 3.7 Hz), 121.2 (d, *J* = 18.2 Hz), 118.0 (d, *J* = 17.7 Hz), 86.0, 71.1, 71.0, 69.4, 68.1, 21.0, 20.9, 20.8, 17.4; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.57 (dt, *J* = 20.9, 9.2 Hz), -137.48 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.57 (d, *J* = 20.9 Hz), -137.50 (d, *J* = 21.0 Hz). **HRMS (ESI)** m/z calcd for $C_{18}H_{20}F_2O_7SNa^+$ $(M+Na)^+$ 441.0790, found 441.0795.

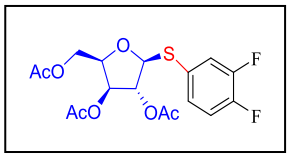
3,4-Difluorphenyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-ribofuranoside (4f).



Purified by flash column chromatography R_f =0.33 (petroleum ether/AcOEt = 3:1), colorless oil (29.0 mg, 71% yield); $[\alpha]_D^{25}$ = -38.5 (*c*= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 10.0, 7.3, 2.2 Hz, 1H), 7.23 -7.17 (m, 1H), 7.11 (dt, *J* = 10.3, 8.3 Hz, 1H), 5.47 (t, *J* = 3.1 Hz, 1H), 5.08 – 5.02 (m, 2H), 4.95 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.12 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.78 (dd, *J* = 11.7, 7.9 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 169.6, 169.3, 150.6 (dd, *J* = 250.8, 12.5 Hz), 150.0 (dd, *J* = 251.6, 13.0 Hz), 129.5 (dd, *J* = 5.7, 3.6 Hz), 127.8 (dd, *J* = 6.0, 4.2 Hz), 122.1 (d, *J* = 18.1 Hz), 117.8 (d, *J* = 17.7 Hz), 83.9, 68.0, 67.2, 66.3, 63.5, 20.8, 20.7; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.74 (dt, *J* = 19.9, 9.2 Hz), -137.11 (m);

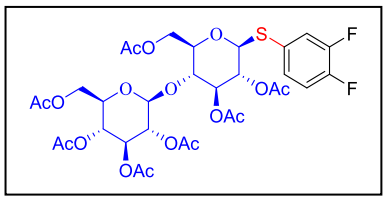
^{19}F NMR (376 MHz, $CDCl_3$) δ -135.74 (d, J = 21.3 Hz), -137.10 (d, J = 21.2 Hz). **HRMS (ESI)** m/z calcd for $C_{17}H_{18}F_2O_7SNa^+$ $(M+Na)^+$ 427.0634, found 427.0635.

3,4-Difluorophenyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside (4g)



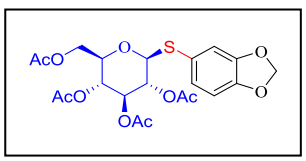
Purified by flash column chromatography R_f =0.38 (petroleum ether/AcOEt = 3:1), white solid (29.9 mg, 74% yield), m.p. = 75-76 ℃; $[\alpha]_D^{25}$ = -56.9 (c= 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (ddd, J = 10.0, 7.4, 2.2 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.11 (dt, J = 10.1, 8.3 Hz, 1H), 5.17 (t, J = 8.1 Hz, 1H), 4.94 – 4.85 (m, 2H), 4.73 (d, J = 8.2 Hz, 1H), 4.27 (dd, J = 11.8, 4.9 Hz, 1H), 3.43 (dd, J = 11.8, 8.6 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 169.9, 169.5, 150.9 (dd, J = 250.9, 12.5 Hz), 150.1 (dd, J = 251.7, 12.9 Hz), 130.1 (dd, J = 5.9, 3.8 Hz), 128.0 – 127.7 (m), 122.6 (d, J = 18.0 Hz), 117.8 (d, J = 17.6 Hz), 85.9, 71.8, 69.7, 68.3, 65.3, 20.9, 20.9, 20.8; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.81 (dt, J = 21.3, 9.2 Hz), -136.89 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.81 (d, J = 21.5 Hz), -136.90 (d, J = 21.4 Hz). **HRMS (ESI)** m/z calcd for $C_{17}H_{18}F_2O_7SNa^+$ $(M+Na)^+$ 427.0634, found 427.0633.

3,4-Difluorophenyl-2,3,6,2',3',4',6'-hepta-*O*-acetyl-1-thio-β-cellobioside (4h)



Purified by flash column chromatography R_f =0.49 (petroleum ether/AcOEt = 1:1), white solid (55.8 mg, 73% yield), m.p. = 185-189 ℃ ; $[\alpha]_D^{25}$ = -28.0 (c = 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (ddd, J = 10.1, 7.5, 2.2 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.09 (dt, J = 9.9, 8.2 Hz, 1H), 5.20-5.11 (m, 2H), 5.05 (t, J = 9.6 Hz, 1H), 4.90 (dd, J = 9.3, 7.9 Hz, 1H), 4.82 (t, J = 9.6 Hz, 1H), 4.58 (d, J = 10.1 Hz, 2H), 4.48 (d, J = 7.9 Hz, 1H), 4.36 (dd, J = 12.5, 4.2 Hz, 1H), 4.08 (dd, J = 12.0, 5.3 Hz, 1H), 4.01 (dd, J = 12.5, 2.3 Hz, 1H), 3.73 – 3.58 (m, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 6H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.4, 170.3, 169.8, 169.6, 169.4, 169.1, 150.9 (dd, J = 251.1, 12.4 Hz), 150.0 (dd, J = 250.8, 12.7 Hz), 130.6–130.3 (m), 127.33 (dd, J = 6.3, 4.2 Hz), 122.98 (d, J = 17.9 Hz), 117.6 (d, J = 17.6 Hz), 100.9, 85.0, 77.0, 76.3, 73.6, 73.0, 72.1, 71.7, 70.0, 67.8, 61.9, 61.6, 20.9, 20.8, 20.7, 20.7, 20.6, 20.6, 20.6; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -135.83 (dt, J = 19.6, 9.4 Hz), -136.71 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.83 (d, J = 20.9 Hz), -136.71 (d, J = 21.2 Hz). **HRMS (ESI)** m/z calcd for $C_{32}H_{38}F_2O_{17}SNa^+$ $(M+Na)^+$ 787.1690, found 787.1688.

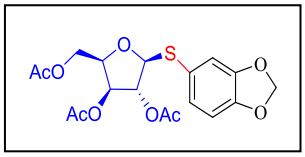
6-Benzo[d][1,3]dioxolyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4i)



Purified by flash column chromatography R_f =0.24 (petroleum ether/AcOEt = 3:1), white solid (40.2 mg, 83% yield), m.p. = 90-91 ℃; $[\alpha]_D^{25}$ = -25.6 (c= 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (d, J = 1.7 Hz, 1H), 6.97 (dd, J = 8.1, 1.8 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 5.98 (s, 2H), 5.19 (t, J = 9.4 Hz, 1H), 5.00 (t,

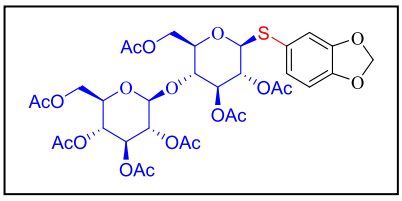
J = 9.8 Hz, 1H), 4.89 (t, *J* = 9.6 Hz, 1H), 4.57 (d, *J* = 10.0 Hz, 1H), 4.19 (d, *J* = 3.7 Hz, 2H), 3.69 (dt, *J* = 10.1, 3.7 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.2, 169.4, 169.2, 148.6, 147.8, 128.8, 122.5, 114.7, 108.5, 101.5, 85.8, 75.7, 74.0, 69.7, 68.1, 62.1, 20.8, 20.7, 20.6, 20.6; **HRMS (ESI)** m/z calcd for $C_{21}H_{24}O_{11}SNa^+$ $(M+Na)^+$ 507.0932, found 507.0933.

6-Benzo[d][1,3]dioxolyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside (4j)



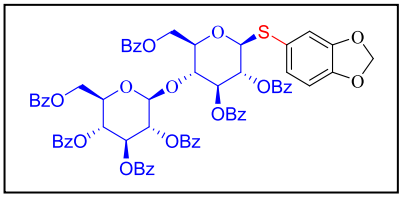
Purified by flash column chromatography R_f =0.34 (petroleum ether/AcOEt = 3:1), brown oil (34.6 mg, 84% yield), m.p. = 121-124 ℃; $[\alpha]_D^{25}$ = -68.5(*c*= 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 – 6.95 (m, 2H), 6.74 (dd, *J* = 5.9, 2.5 Hz, 1H), 5.98 (s, 2H), 5.16 (t, *J* = 8.5 Hz, 1H), 4.93 – 4.82 (m, 2H), 4.62 (d, *J* = 8.7 Hz, 1H), 4.23 (dd, *J* = 11.6, 5.1 Hz, 1H), 3.37 (dd, *J* = 11.7, 9.2 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 169.8, 169.3, 148.6, 147.9, 128.6, 122.9, 114.6, 108.6, 101.5, 86.5, 72.4, 69.7, 68.5, 65.5, 20.8, 20.7, 20.7; **HRMS (ESI)** m/z calcd for $C_{18}H_{20}O_9SNa^+$ $(M+Na)^+$ 435.0720, found 435.0721.

6-Benzo[d][1,3]dioxolyl-2,3,6,2',3',4',6'-hepta-*O*-acetyl-1-thio-β-cellobioside (4k)



Purified by flash column chromatography R_f =0.41 (petroleum ether/AcOEt = 1:1), white solid (58.6 mg, 76% yield), m.p. = 208-209 ℃; $[\alpha]_D^{25}$ = -24.5 (*c*= 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 1.8 Hz, 1H), 6.95 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 5.14 (dt, *J* = 14.9, 9.3 Hz, 2H), 5.05 (t, *J* = 9.6 Hz, 1H), 4.90 (dd, *J* = 9.2, 7.9 Hz, 1H), 4.82 (t, *J* = 9.7 Hz, 1H), 4.58 (dd, *J* = 11.9, 2.0 Hz, 1H), 4.50 (dd, *J* = 13.5, 9.0 Hz, 2H), 4.37 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.07 (dd, *J* = 11.9, 5.3 Hz, 1H), 4.01 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.69 (t, *J* = 9.5 Hz, 1H), 3.65 – 3.56 (m, 2H), 2.12 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.4, 170.4, 169.9, 169.6, 169.4, 169.1, 148.6, 147.9, 128.8, 122.8, 114.8, 108.6, 101.6, 100.9, 85.8, 76.4, 73.8, 73.0, 72.1, 71.7, 70.0, 67.8, 61.9, 61.6, 20.9, 20.8(3C) , 20.7(3C), 20.6; **HRMS (ESI)** m/z calcd for $C_{33}H_{40}O_{19}SNa^+$ $(M+Na)^+$ 795.1777, found 795.1774.

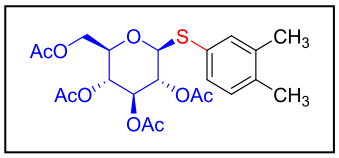
6-Benzo[d][1,3]dioxolyl-2,3,6,2',3',4',6'-hepta-O-benzoyl-1-thio-β-cellobioside (4l)



Purified by flash column chromatography R_f =0.32 (petroleum ether/AcOEt = 3:1), white solid (86.9 mg, 72% yield), m.p. = 216-217 ℃; $[\alpha]_D^{25}$ = 21.5 (*c*= 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.97 – 7.89 (m, 10H), 7.80 – 7.70 (m, 4H), 7.59 – 7.48 (m, 3H), 7.46 – 7.32 (m, 10H), 7.28 (dd, *J* = 7.9, 3.1 Hz, 3H), 7.26 – 7.16 (m, 5H), 7.00 – 6.89 (m, 2H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.86 (d, *J* = 1.5 Hz, 1H), 5.80 (d, *J* = 1.5 Hz, 1H), 5.76 (dt, *J* = 14.2, 9.6 Hz, 2H), 5.50 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.35 (dt, *J* = 13.6, 9.7 Hz, 2H), 4.91 (d, *J* = 7.9 Hz, 1H), 4.75 (d, *J* = 9.9 Hz, 1H), 4.65 (dd, *J* = 12.1, 1.9 Hz, 1H), 4.46 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.14 (t, *J* = 9.5 Hz, 1H), 4.03 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.86 – 3.78 (m, 2H), 3.73 (dd, *J* =

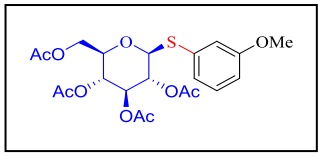
11.9, 5.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 1658, 165.7, 165.5, 165.1, 164.8, 147.8, 133.5, 133.4, 133.3, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 122.7, 114.9, 108.6, 101.4, 101.0, 86.0, 77.4, 76.5, 74.1, 72.9, 72.5, 72.0, 70.5, 69.6, 62.7, 62.6. **HRMS (ESI)** m/z calcd for $C_{68}H_{54}O_{19}S_{Na+}$ $(M+Na)^+$ 1229.2872, found 1229.2878.

3,4-Dimethyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4m)



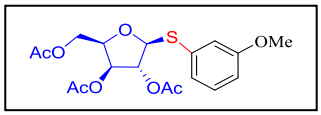
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 2.2 Hz, 1H), 7.16 (dd, J = 7.8, 2.0 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 5.14 (t, J = 9.4 Hz, 1H), 4.97 (t, J = 9.8 Hz, 1H), 4.87 (t, J = 9.7 Hz, 1H), 4.57 (d, J = 10.1 Hz, 1H), 4.16 (dd, J = 12.3, 5.0 Hz, 1H), 4.10 (dd, J = 12.3, 2.4 Hz, 1H), 3.66-3.61 (m, J = 10.1, 5.0, 2.4 Hz, 1H), 2.18 (s, 6H), 2.03 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.4, 169.6, 169.4, 137.6, 137.5, 135.0, 131.3, 130.3, 127.9, 86.2, 75.8, 74.1, 70.0, 68.2, 62.2, 20.9, 20.9, 20.8, 20.7, 19.9, 19.7.

3-Methoxyphenyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4n)[16]



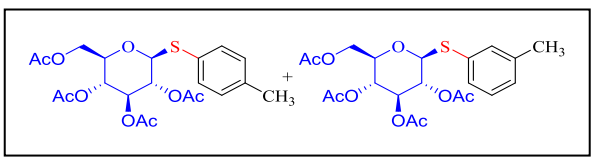
Purified by flash column chromatography R_f =0.23 (petroleum ether/AcOEt = 3:1), white solid (37.6 mg, 80% yield); $[\alpha]_D^{25}$ = -10.0 (c= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, J = 8.2 Hz, 1H), 7.05 (dd, J = 7.1, 1.4 Hz, 2H), 6.88 – 6.83 (m, 1H), 5.23 (t, J = 9.3 Hz, 1H), 5.05 (t, J = 9.8 Hz, 1H), 4.99 (dd, J = 10.1, 9.2 Hz, 1H), 4.73 (d, J = 10.1 Hz, 1H), 4.26 – 4.15 (m, 2H), 3.80 (s, 3H), 3.74 (ddd, J = 10.1, 5.1, 2.6 Hz, 1H), 2.08 (s, 6H), 2.02 (s, 3H), 1.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.3, 169.5, 169.4, 159.8, 133.0, 129.8, 125.1, 118.4, 114.1, 85.8, 75.9, 74.1, 70.1, 68.3, 62.3, 55.4, 20.9, 20.8, 20.7, 20.7.

3-Methoxyphenyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside (4o)



Purified by flash column chromatography R_f =0.35 (petroleum ether/AcOEt = 3:1), white solid (31.0 mg, 78% yield); $[\alpha]_D^{25}$ = -31.5 (c= 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.9 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.84 (ddd, J = 8.2, 2.5, 0.9 Hz, 1H), 5.17 (t, J = 8.1 Hz, 1H), 4.99 – 4.89 (m, 2H), 4.84 (d, J = 8.2 Hz, 1H), 4.28 (dd, J = 11.8, 4.9 Hz, 1H), 3.80 (s, 3H), 3.43 (dd, J = 11.8, 8.6 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 169.9, 169.4, 159.9, 133.6, 129.9, 124.7, 117.8, 114.2, 86.3, 72.1, 69.9, 68.5, 65.3, 55.5, 20.9, 20.8, 20.8; **HRMS (ESI)** m/z calcd for $C_{18}H_{22}O_8SNa^+$ $(M+Na)^+$ 421.0928, found 421.0927.

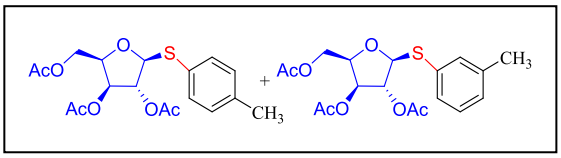
***m*-Tolyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside(4p)[17]/*p*-tolyl-2,3,4,6-tetra-*O*-acetyl -1-thio-β-D-glucopyranoside (4p')[18]**



Purified by flash column chromatography R_f =0.40 (petroleum ether/AcOEt = 3:1),

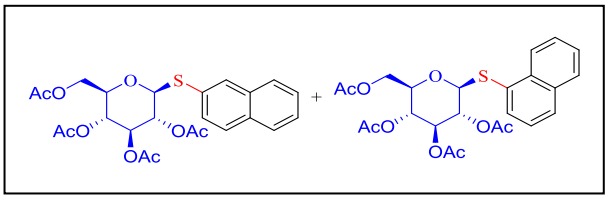
white solid (37.2 mg, 82% yield, 1.0:1.2), m.p. = 86-87 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.19 (td, *J* = 7.4, 1.2 Hz, 1H), 7.12 (dd, *J* = 7.7, 3.6 Hz, 3H), 5.21 (td, *J* = 9.4, 6.7 Hz, 2H), 5.07 – 5.01 (m, 2H), 4.98 (d, *J* = 9.8 Hz, 1H), 4.95 – 4.88 (m, 1H), 4.70 (d, *J* = 10.1 Hz, 1H), 4.62 (d, *J* = 10.1 Hz, 1H), 4.27 – 4.13 (m, 4H), 3.75 -3.66 (m, 2H), 2.34 (s, 3H), 2.34 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.7, 170.3, 170.3, 169.5, 169.5,169.4, 169.4, 138.9, 138.8, 133.9, 133.7, 131.5, 130.1, 129.8, 129.3, 128.9, 127.6, 86.0, 85.9, 75.9, 75.8, 74.1, 74.1, 70.0, 69.9, 68.3, 68.3, 62.3, 62.2, 21.5, 21.3, 20.9, 20.8, 20.8, 20.8, 20.7, 20.7, 20.7, 20.7.

_m_-Tolyl-2,3,5-tri-_O_-acetyl-1-thio-β-D-xylofuranoside(4q)/_p_-tolyl-2,3,5-tri-_O_-acetyl-1-thio-β-D-xylofuranoside (4q')



Purified by flash column chromatography R_f =0.50 (petroleum ether/AcOEt = 3:1), white solid (34.4 mg, 90% yield 1.0:1.2), m.p. = 84-85 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.29 – 7.25 (m, 2H), 7.20 (td, *J* = 7.5, 0.9 Hz, 1H), 7.14 – 7.08 (m, 3H), 5.17 (td, *J* = 8.2, 3.0 Hz, 2H), 4.98 – 4.84 (m, 4H), 4.81 (d, *J* = 8.3 Hz, 1H), 4.71 (d, *J* = 8.5 Hz, 1H), 4.26 (td, *J* = 12.1, 5.0 Hz, 2H), 3.40 (ddd, *J* = 15.6, 11.7, 8.8 Hz, 2H), 2.33 (s, 3H), 2.33 (s, 3H), 2.09 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 170.0, 169.9, 169.9, 169.4, 169.4, 139.0, 138.7, 133.6, 133.3, 132.1, 129.9, 129.7, 129.2, 129.0, 128.1, 86.5, 86.4, 72.4, 72.0, 69.9, 69.9, 68.6, 68.5, 65.5, 65.2, 20.9 (2C), 20.8(6C); **HRMS (ESI)** m/z calcd for $C_{18}H_{22}O_7SNa^+$ $(M+Na)^+$ 405.0978, found 405.0979.

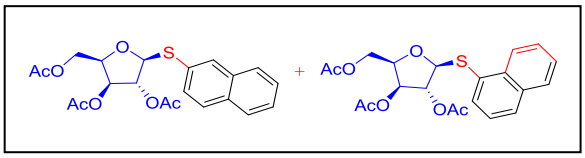
2-Naphthyl-2,3,4,6-tetra-_O_-acetyl-1-thio-β-D-glucopyranoside(4r)/1-Naphthyl 2,3,4,6-tetra-_O_-acetyl-1-thio-β-D- glucopyranoside (4r')[1]



Purified by flash column chromatography R_f =0.38 (petroleum ether/AcOEt = 3:1), white solid (42.6 mg, 87% yield, 1.3:1.0); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.40 (m, 1H), 7.99 (d, *J* = 1.8 Hz, 1H), 7.91 – 7.73 (m, 6H), 7.59 – 7.47 (m, 5H), 7.43 (dd, *J* = 8.2, 7.2 Hz, 1H), 5.24 (t, *J* = 9.4 Hz, 1H), 5.19 (t, *J* = 9.3 Hz, 1H), 5.11 – 4.97 (m, 4H), 4.79 (d, *J* = 10.1 Hz, 1H), 4.71 (d, *J* = 10.1 Hz, 1H), 4.34 – 4.13 (m, 3H), 4.08 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.74 (ddd, *J* = 10.1, 5.0, 2.5 Hz, 1H), 3.60 (ddd, *J* = 10.1, 5.3, 2.4 Hz, 1H), 2.12 (s, 3H), 2.12 (s, 3H), 2.03 (s, 3H), 2.01 (s, 6H), 1.99 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.6, 170.3, 170.2, 169.5, 169.5, 169.4, 169.4, 134.4, 134.2, 133.6, 133.5, 133.0, 132.9, 130.3, 130.0, 129.3, 128.8, 128.6, 128.6, 127.8, 126.9, 126.8, 126.7, 126.5, 125.9,

125.6, 86.7, 85.9, 75.9, 75.8, 74.1, 74.1, 70.5, 70.1, 68.3, 68.3, 62.2, 62.2, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.6, 20.6.

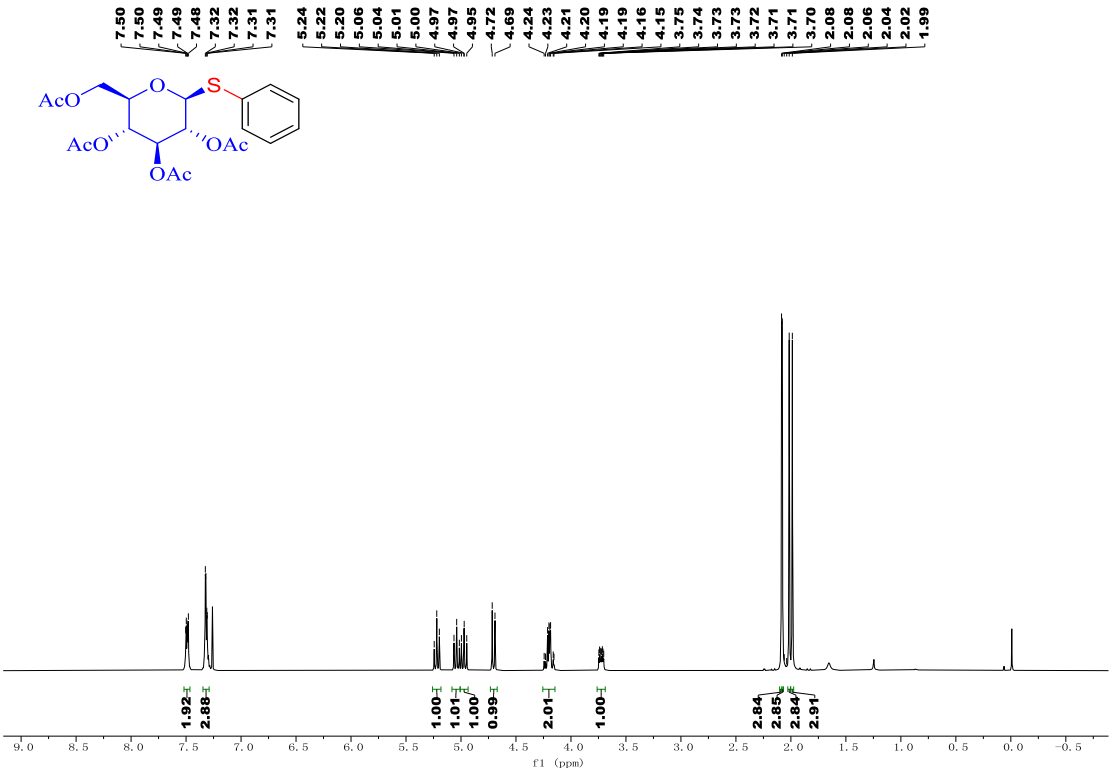
2-Naphthyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside(4s)/1-Naphthyl-2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside (4s')



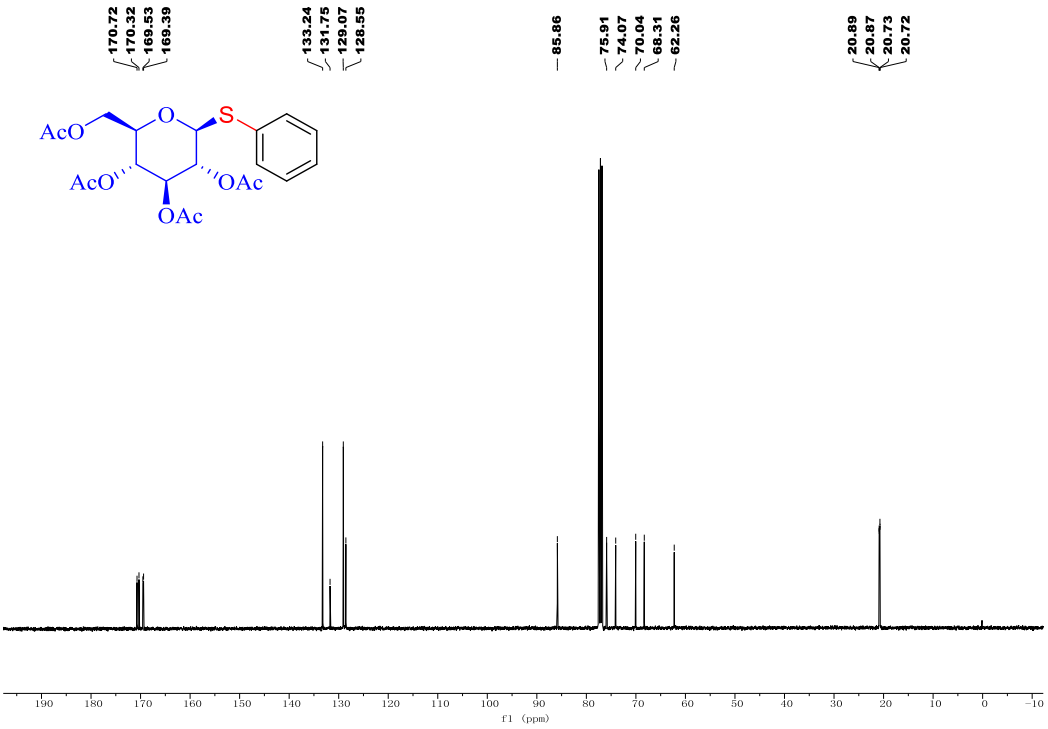
Purified by flash column chromatography R_f =0.55 (petroleum ether/AcOEt = 3:1), white solid (36.8 mg, 88% yield, 1.2:1.0), m. p. = 91-96 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.98 (d, *J* = 1.7 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.84 – 7.76 (m, 4H), 7.60 – 7.47 (m, 5H), 7.44 (dd, *J* = 8.2, 7.2 Hz, 1H), 5.19 (dt, *J* = 12.7, 8.1 Hz, 2H), 5.06 (t, *J* = 8.3 Hz, 1H), 5.02 – 4.88 (m, 4H), 4.82 (d, *J* = 8.4 Hz, 1H), 4.29 (ddd, *J* = 22.6, 11.8, 4.9 Hz, 2H), 3.45 (dd, *J* = 11.8, 8.6 Hz, 1H), 3.33 (dd, *J* = 11.8, 8.8 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 170.0, 169.9, 169.9, 169.5, 169.5, 134.2, 134.1, 133.6, 133.3, 132.9, 132.2, 129.9, 129.8, 129.7, 129.6, 128.7, 128.7, 127.8, 127.8, 127.0, 126.8, 126.7, 126.5, 125.7, 125.6, 87.1, 86.4, 72.2, 72.0, 70.4, 70.0, 68.6, 68.5, 65.4, 65.3, 21.0, 21.0, 20.9, 20.9, 20.8, 20.8; **HRMS (ESI)** m/z calcd for $C_{21}H_{22}O_7SNa^+$ $(M+Na)^+$ 441.0978, found 441.0979.

5. ^{1}H and ^{13}C NMR spectra

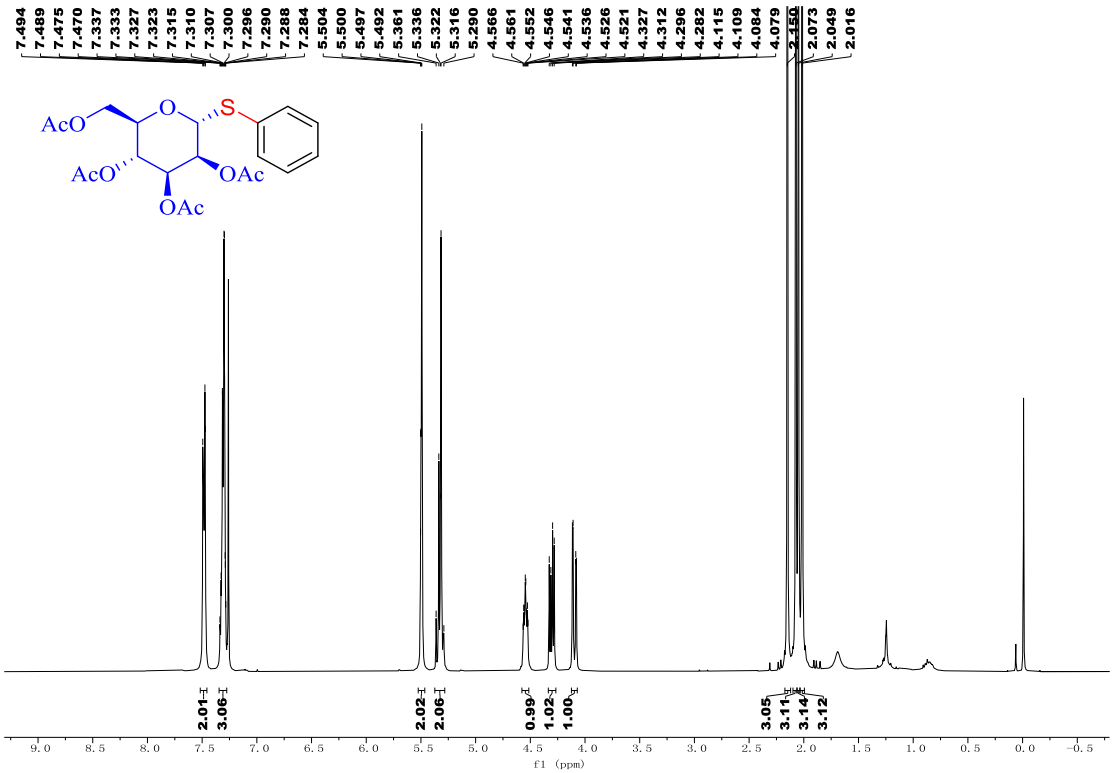
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



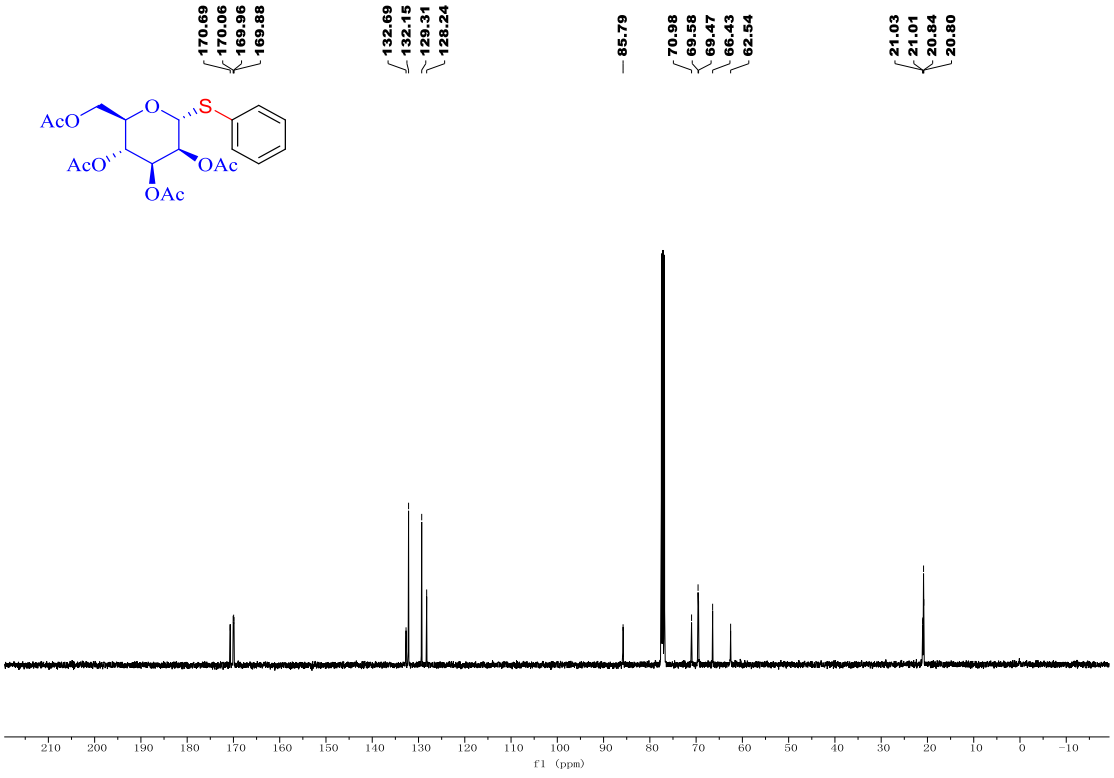
^{13}C NMR (100 MHz, $CDCl_3$) of **3a**



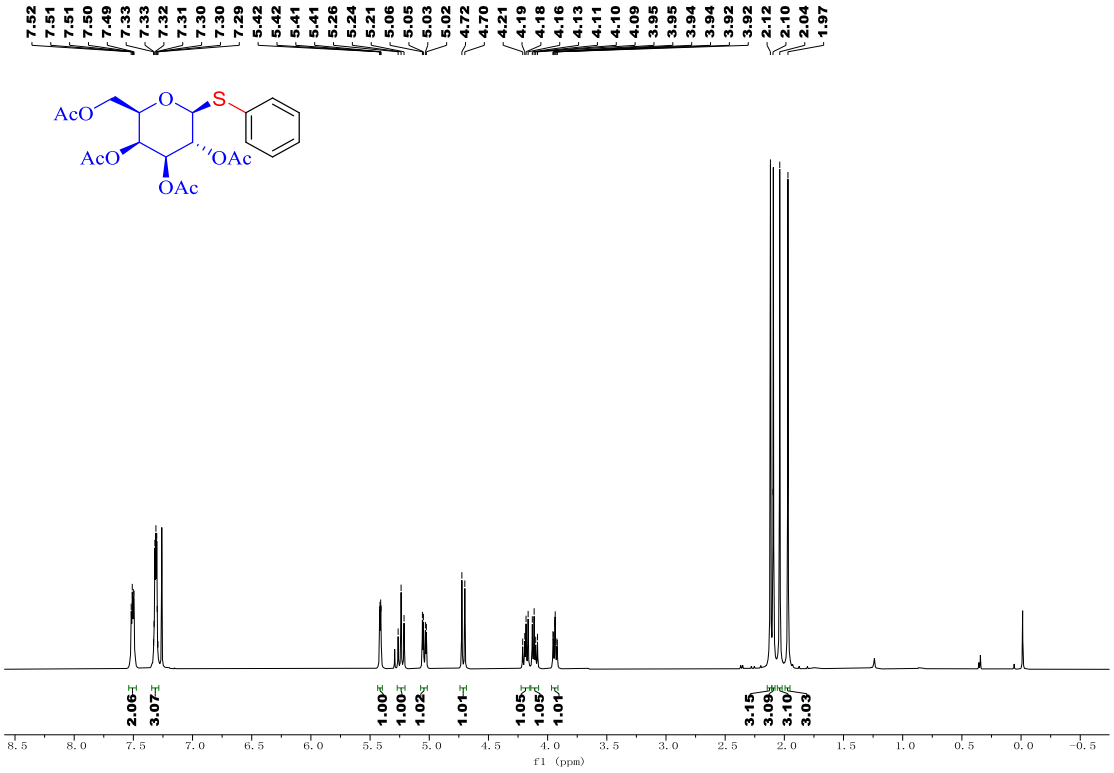
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



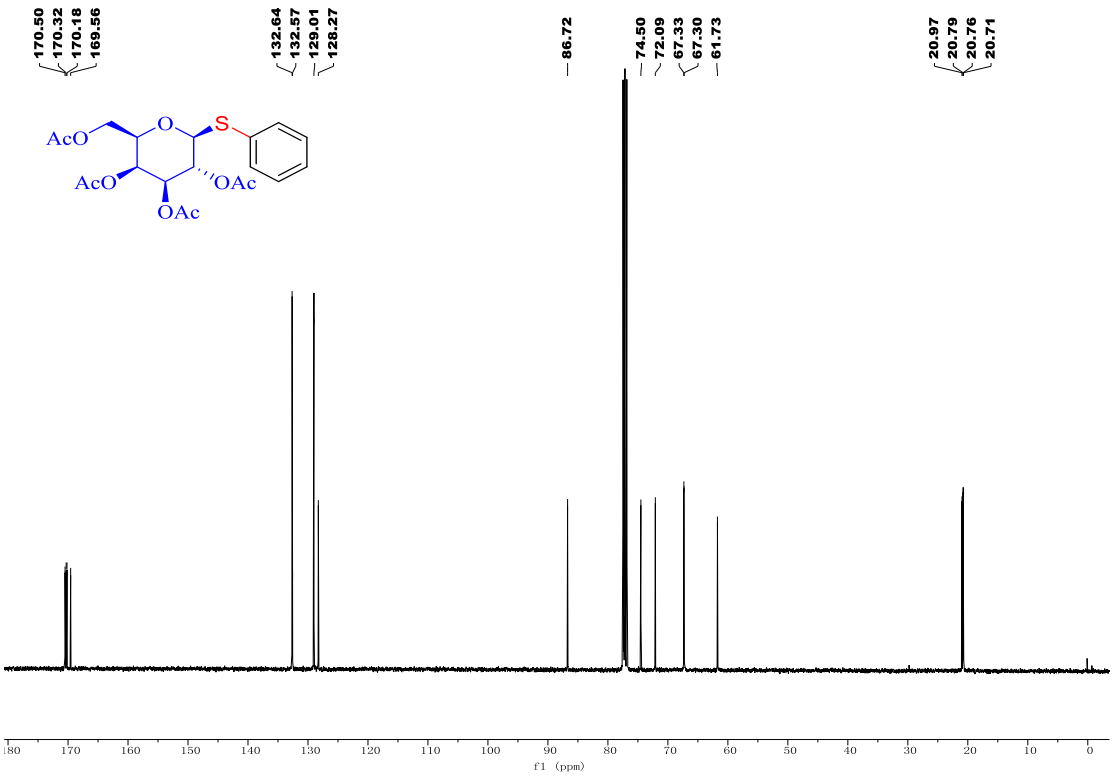
^{13}C NMR (100 MHz, $CDCl_3$) of **3b**



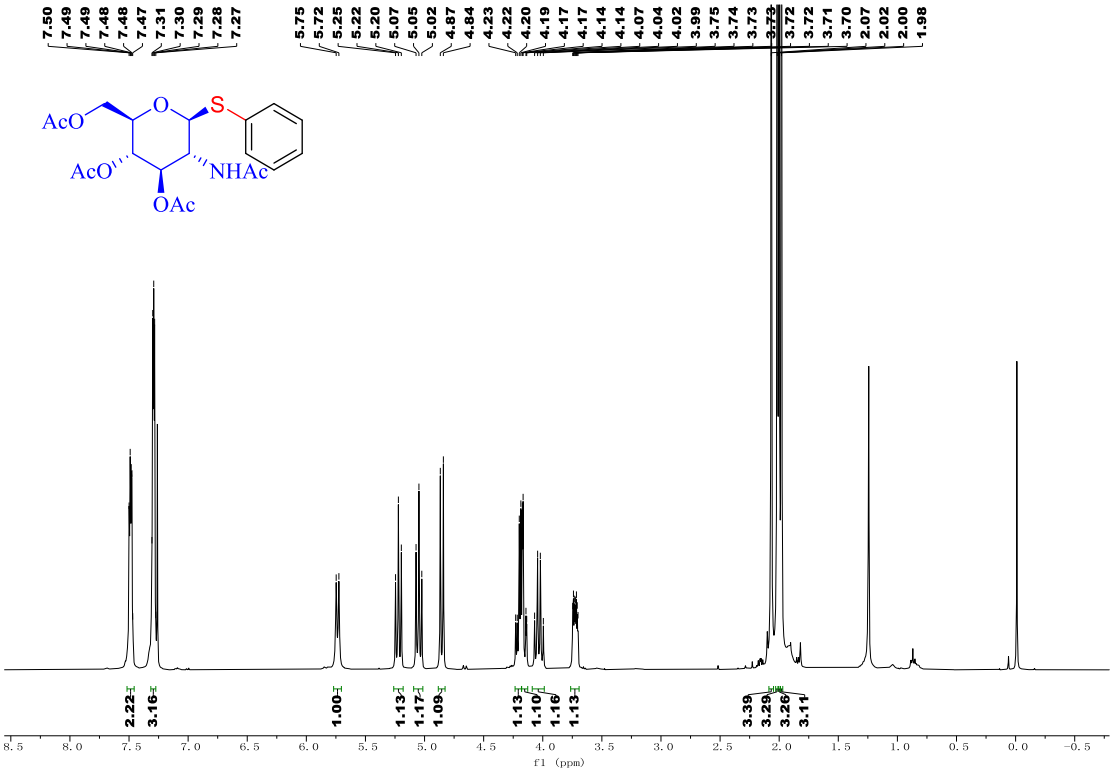
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



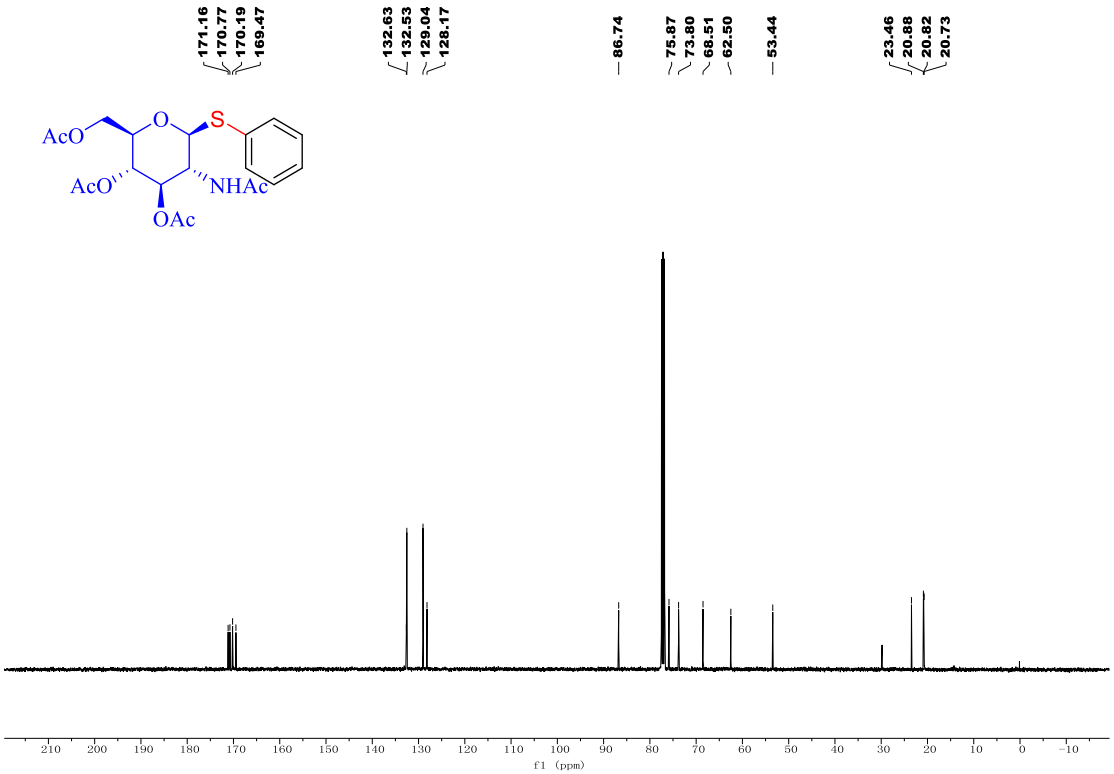
^{13}C NMR (100 MHz, $CDCl_3$) of **3c**



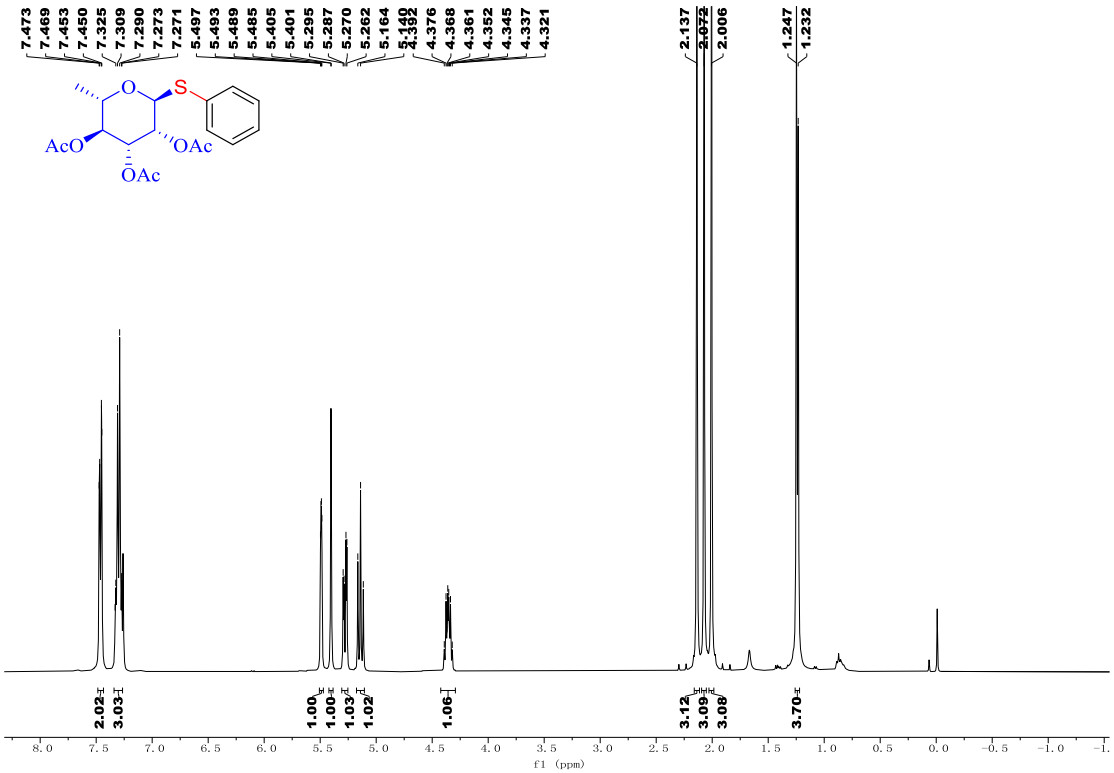
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



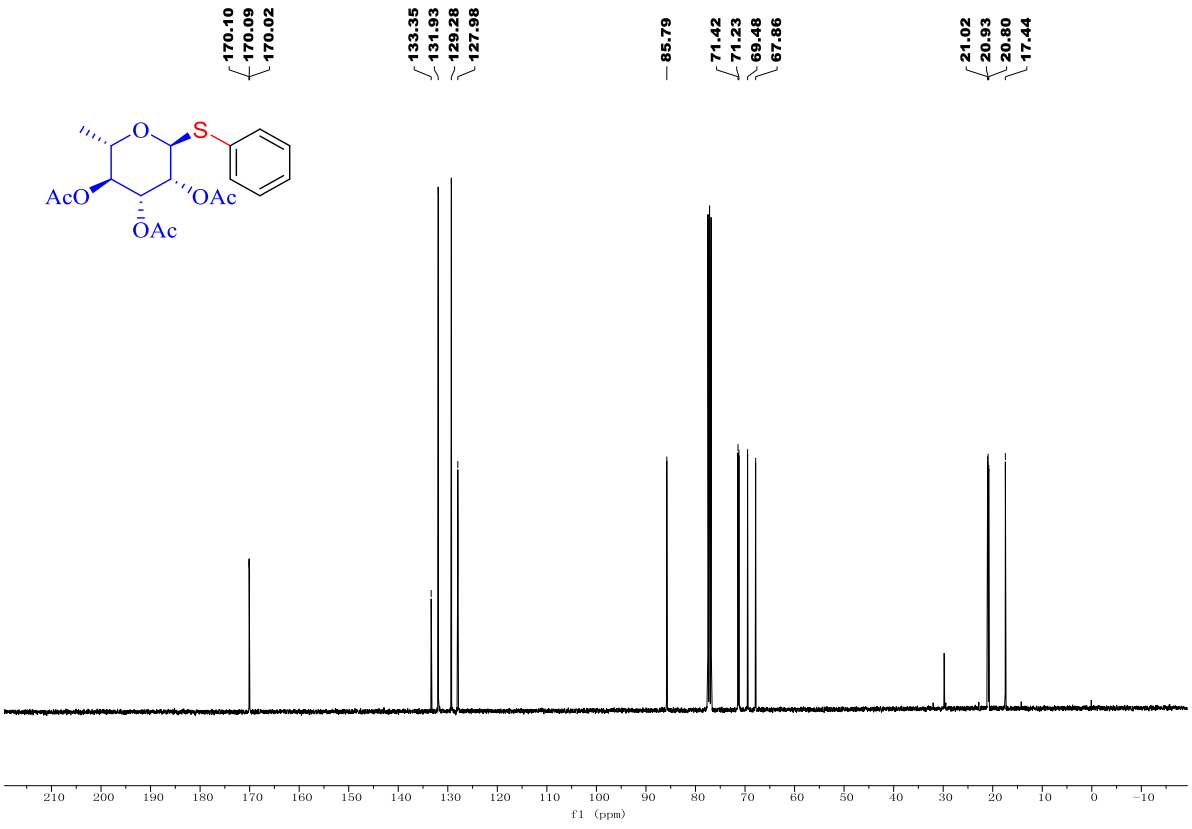
^{13}C NMR (100 MHz, $CDCl_3$) of **3d**



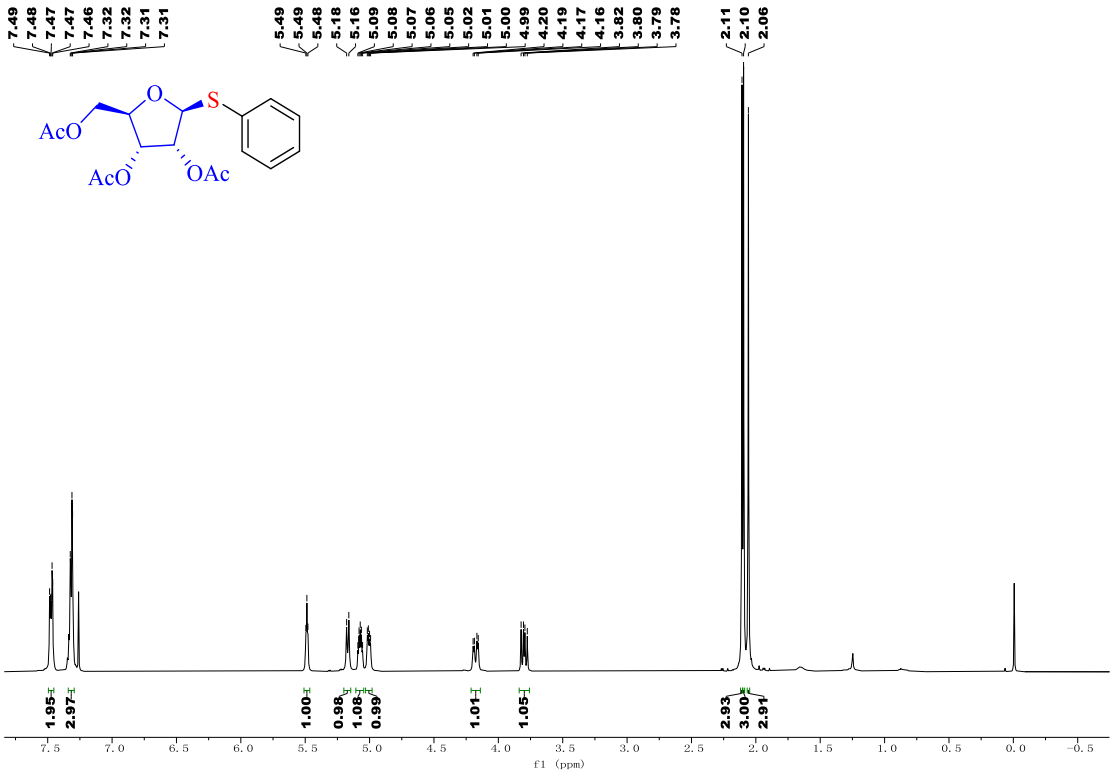
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



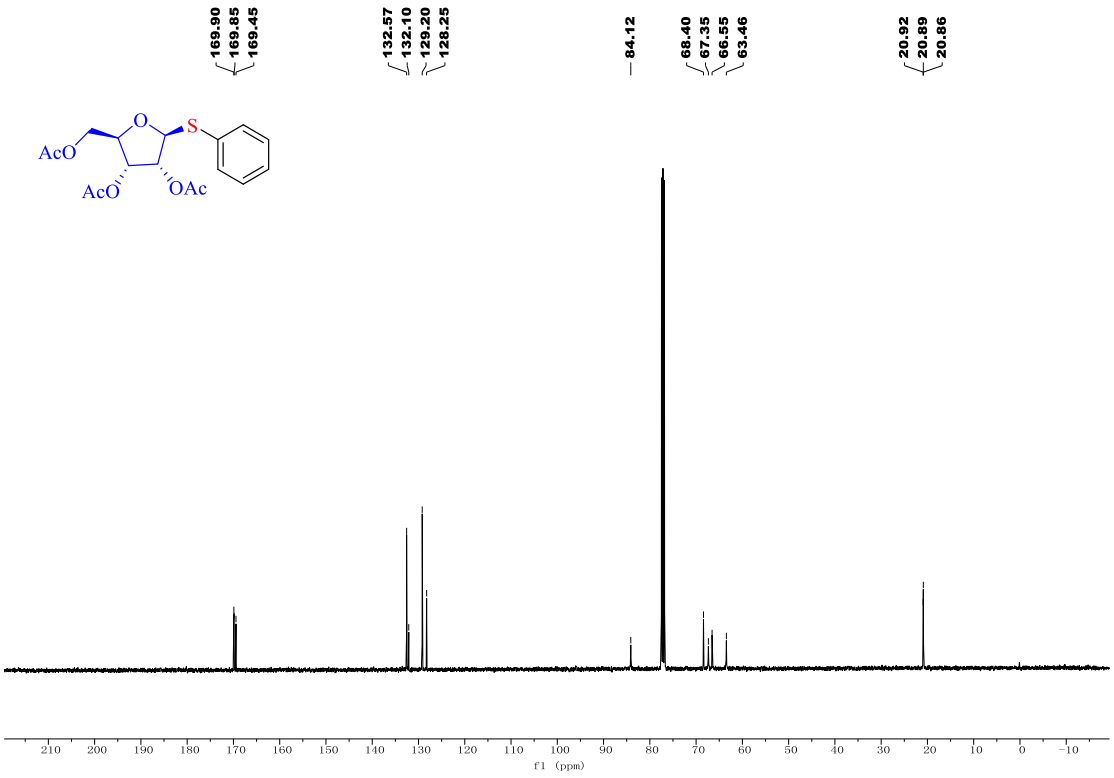
^{13}C NMR (100 MHz, $CDCl_3$) of **3e**



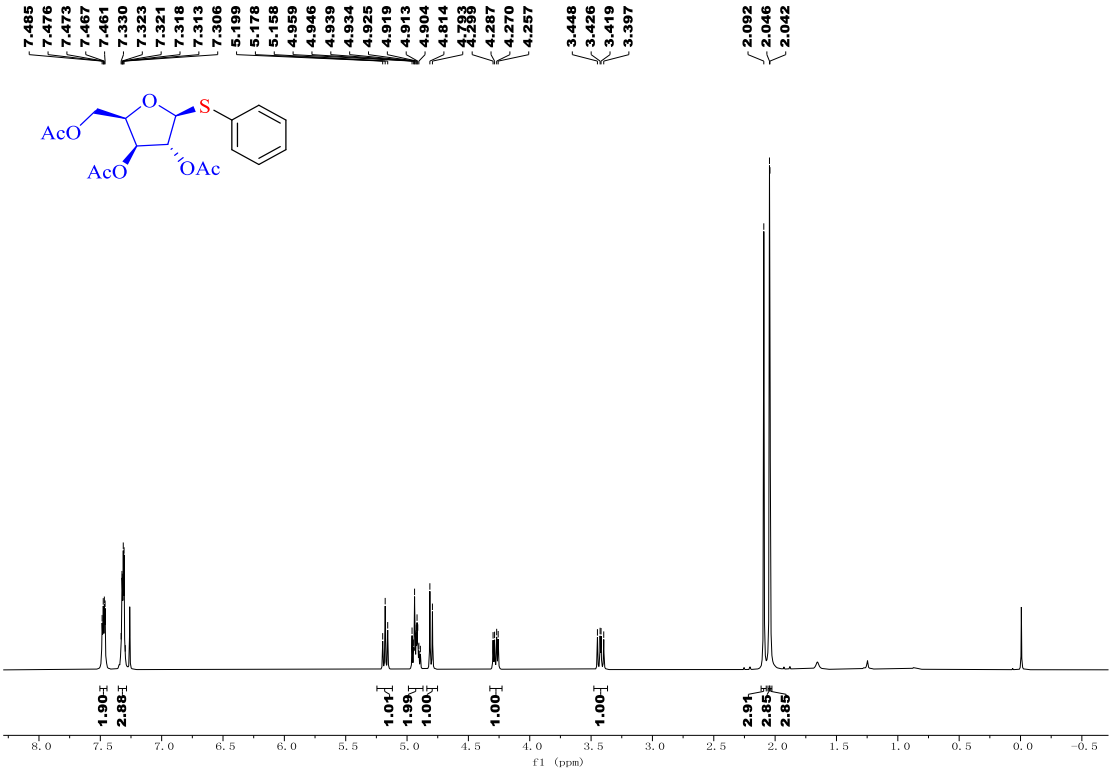
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



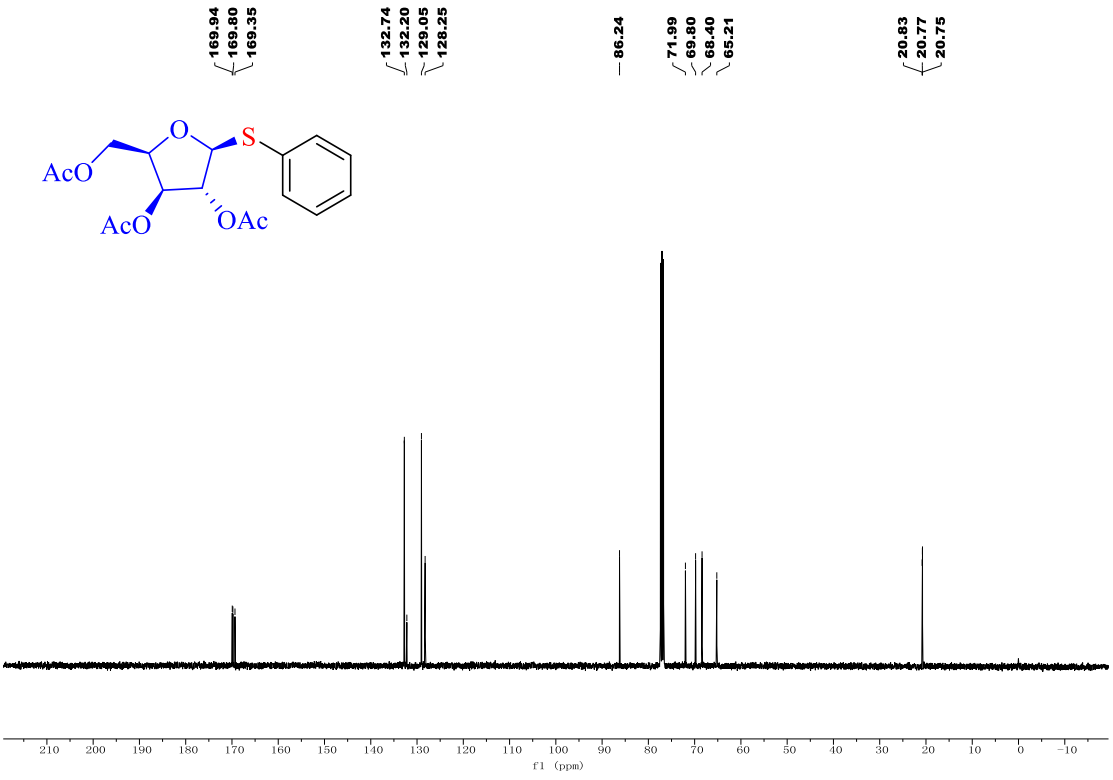
^{13}C NMR (100 MHz, $CDCl_3$) of **3f**



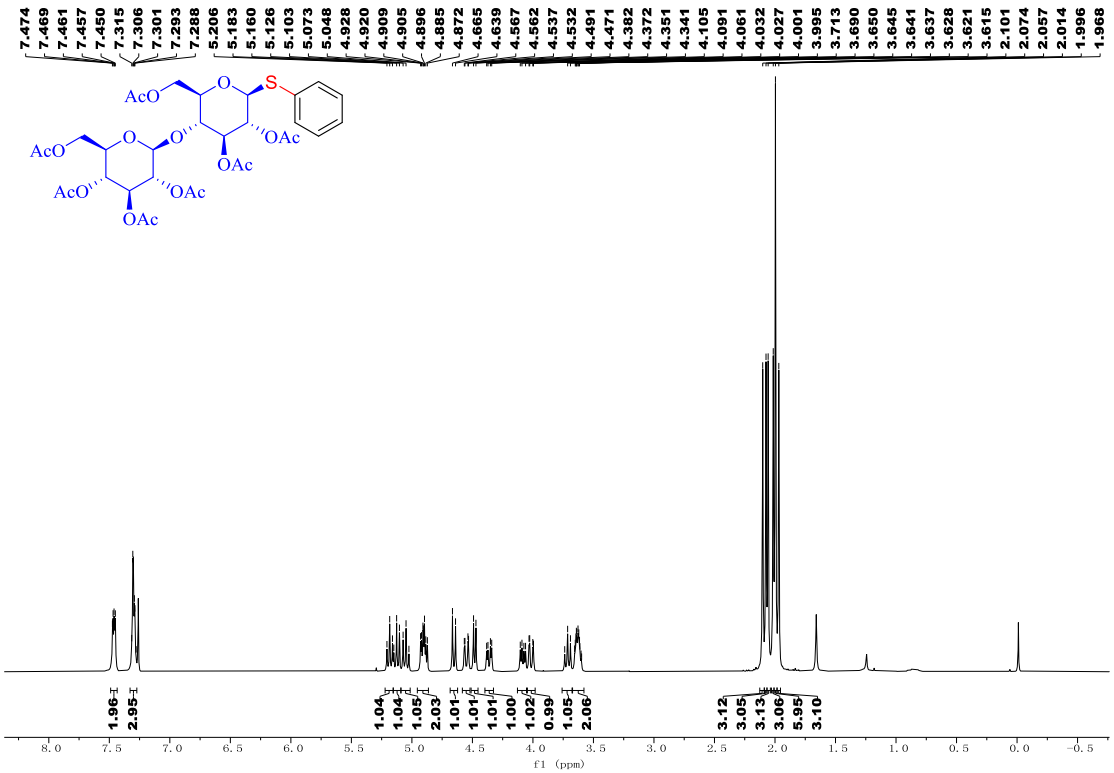
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



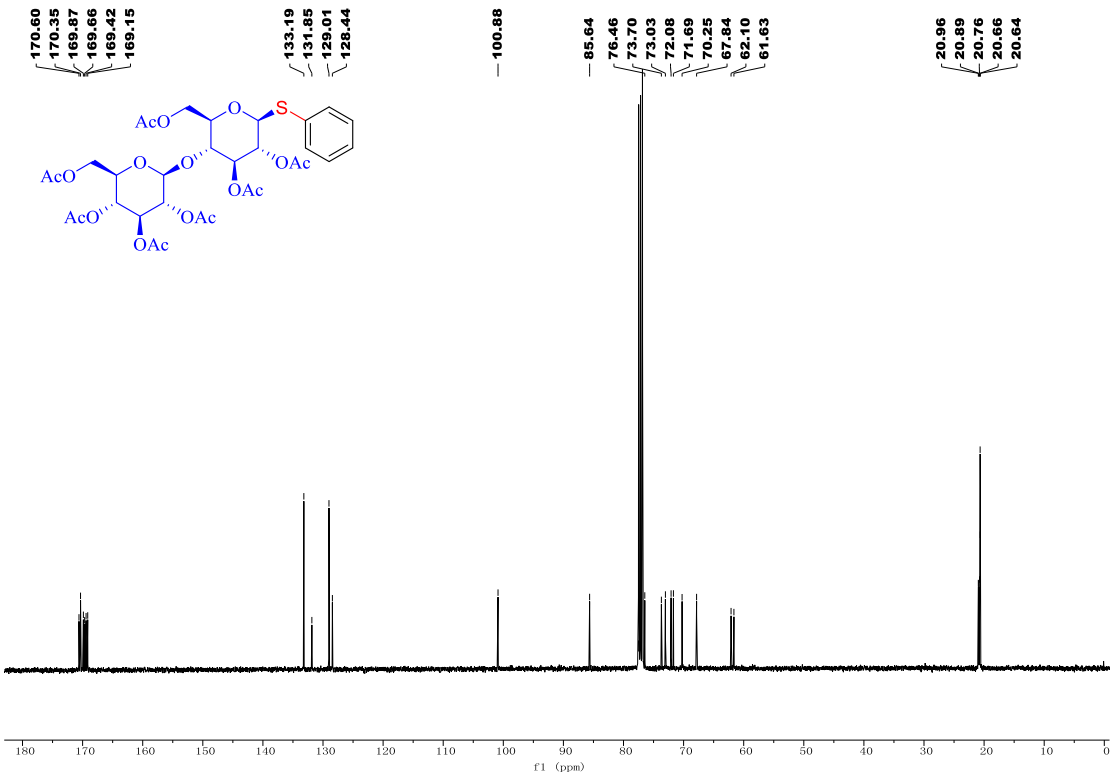
^{13}C NMR (100 MHz, $CDCl_3$) of **3g**



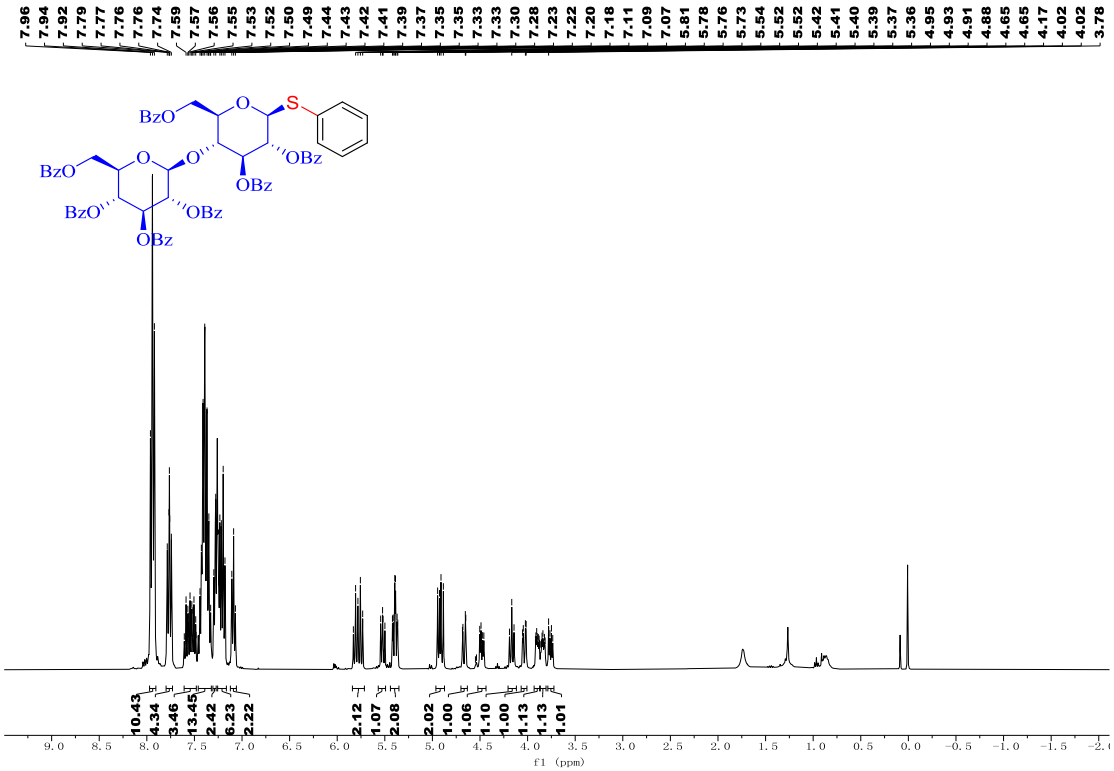
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



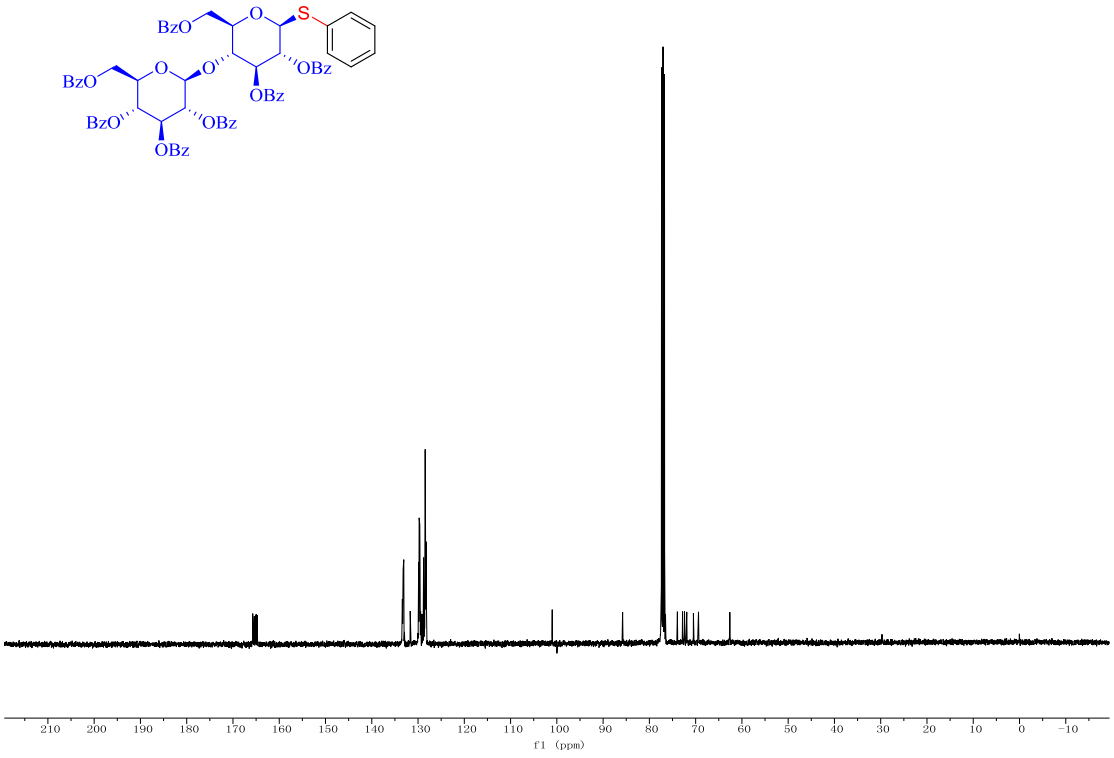
^{13}C NMR (100 MHz, $CDCl_3$) of **3h**



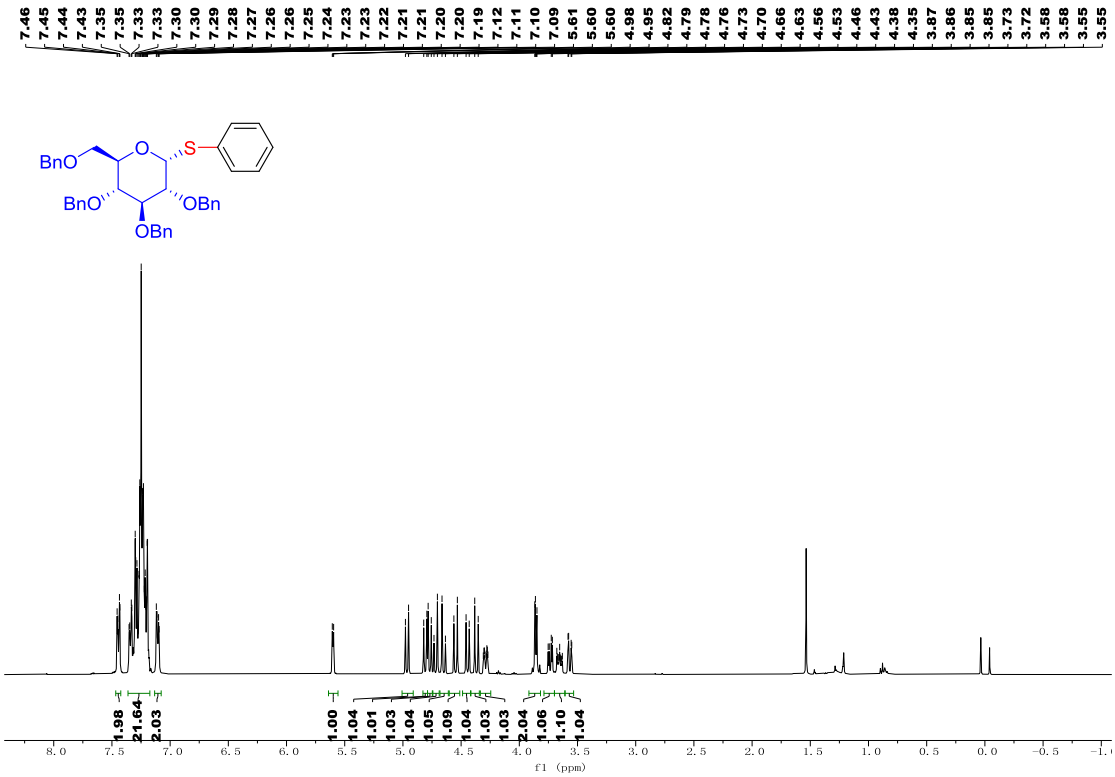
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



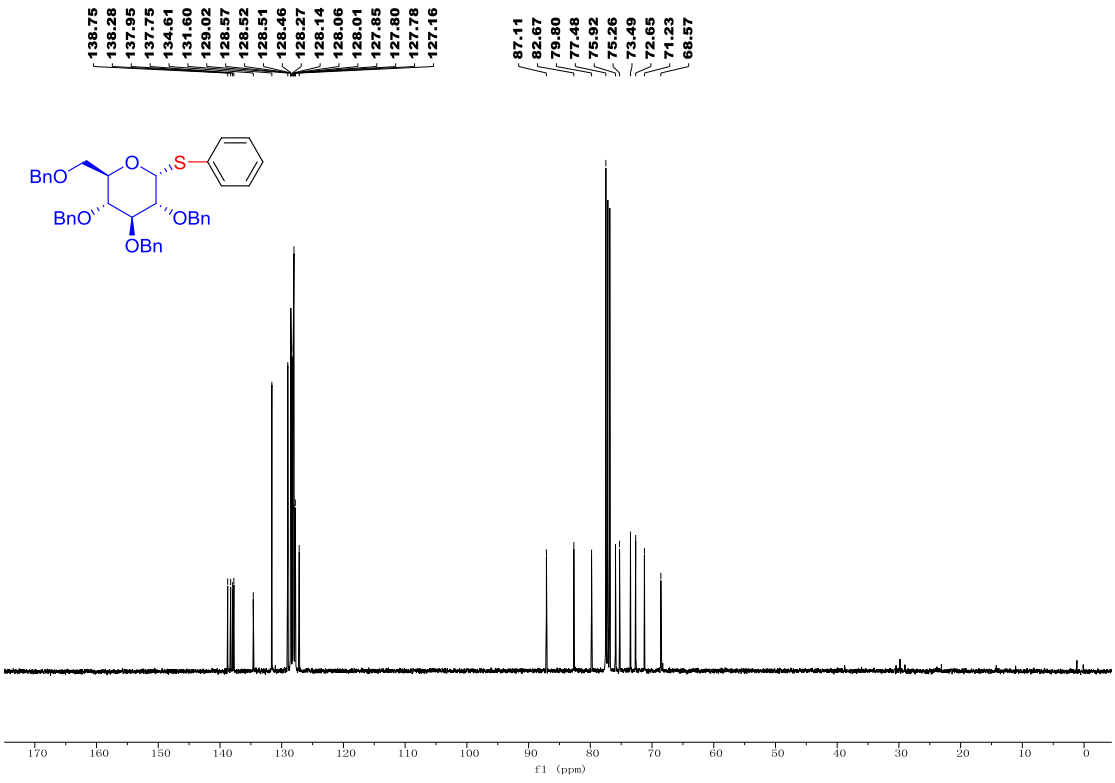
^{13}C NMR (100 MHz, $CDCl_3$) of **3i**



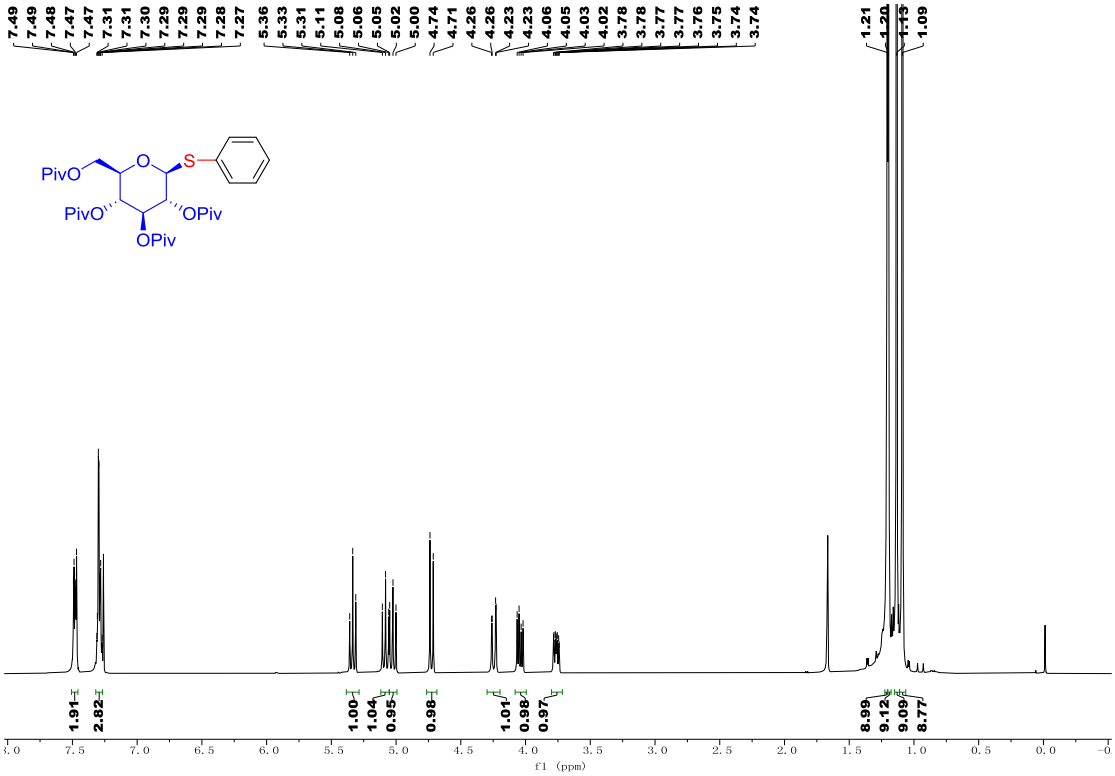
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



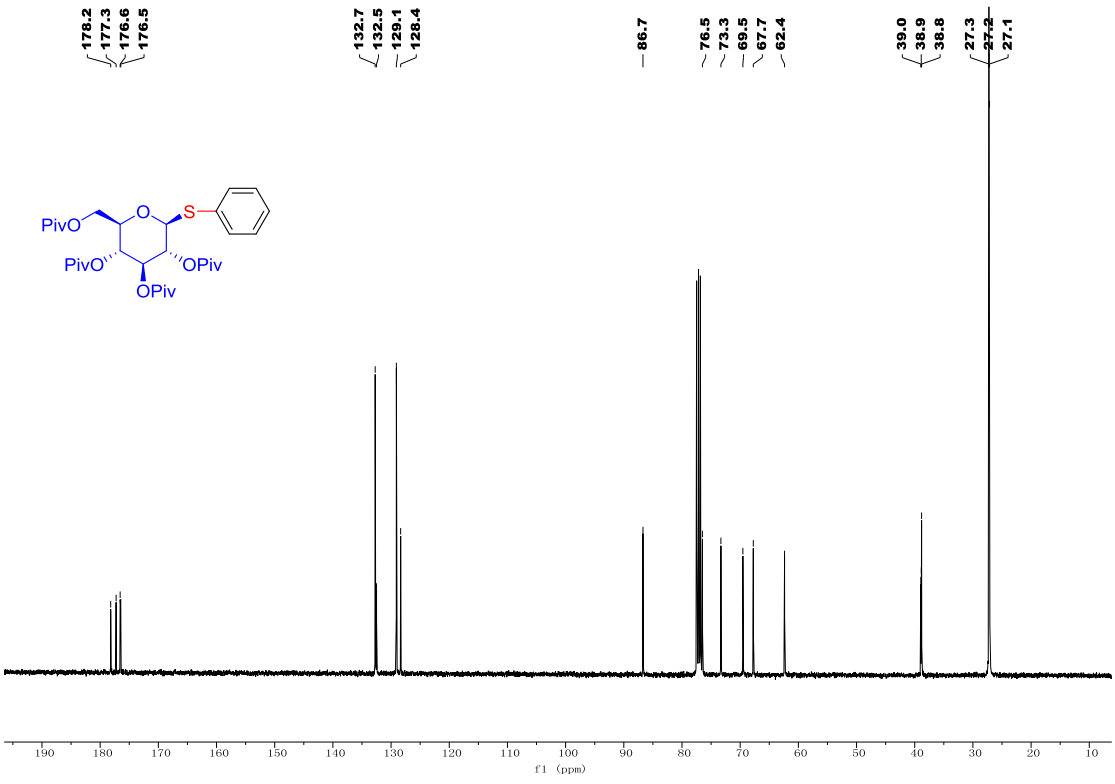
^{13}C NMR (100 MHz, $CDCl_3$) of **3j**



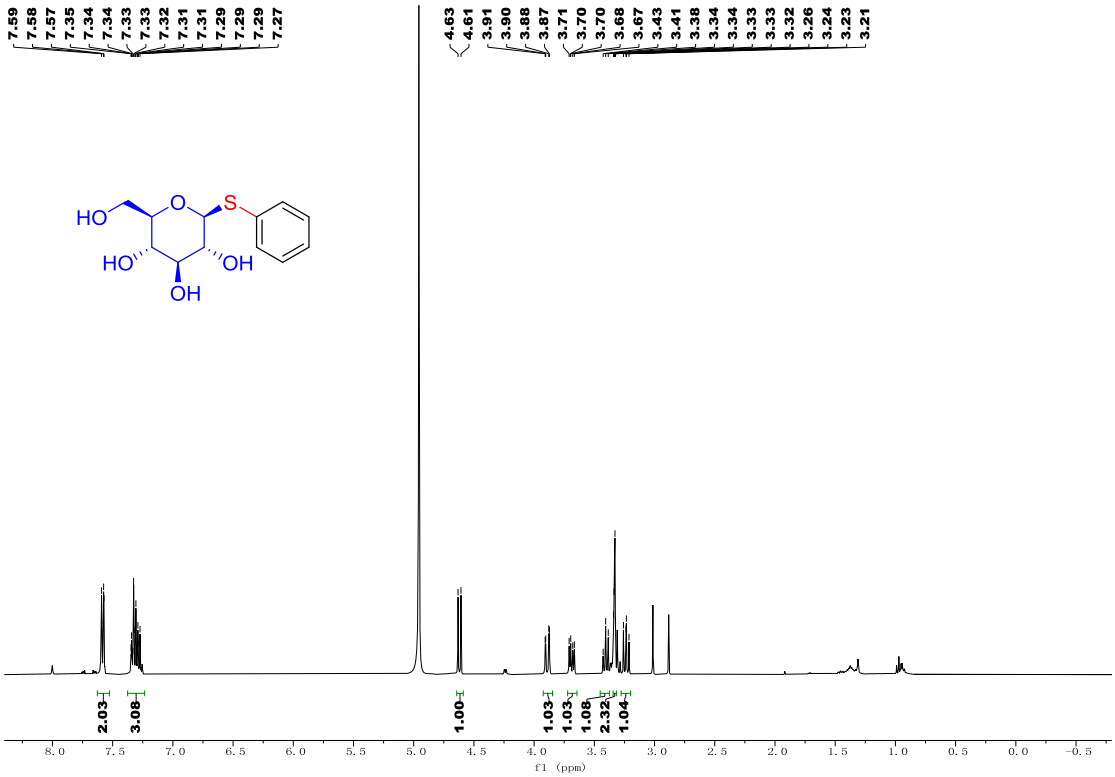
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



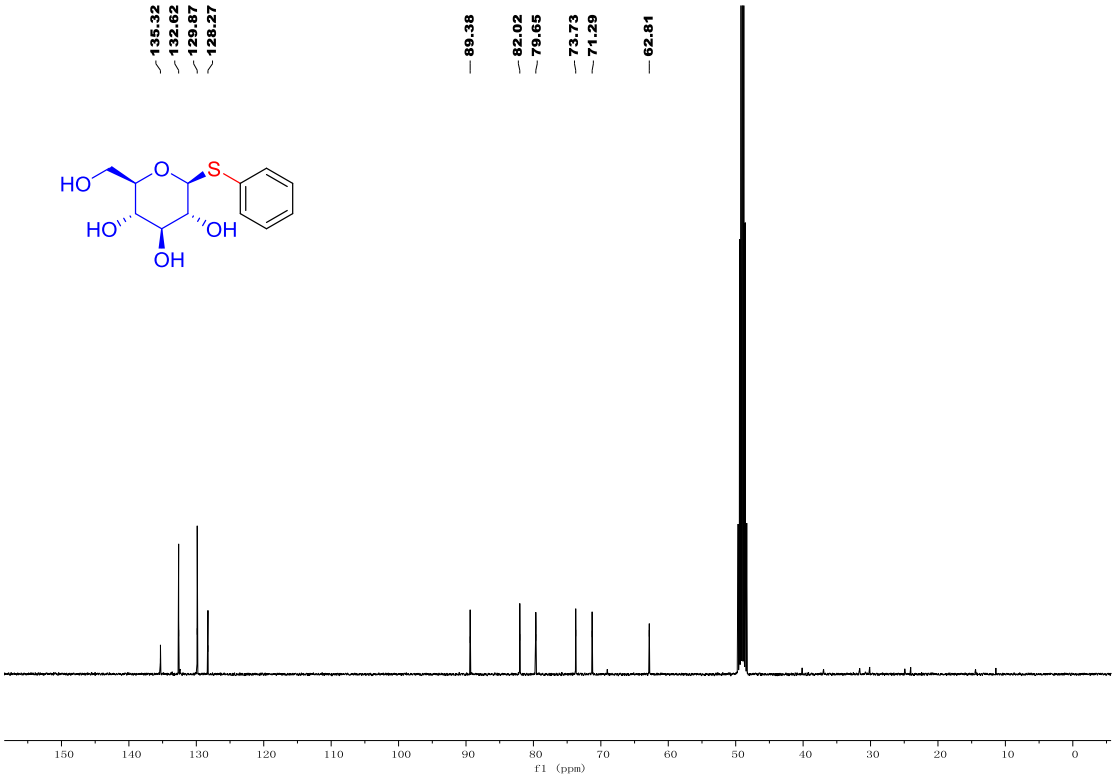
^{13}C NMR (100 MHz, $CDCl_3$) of **3k**



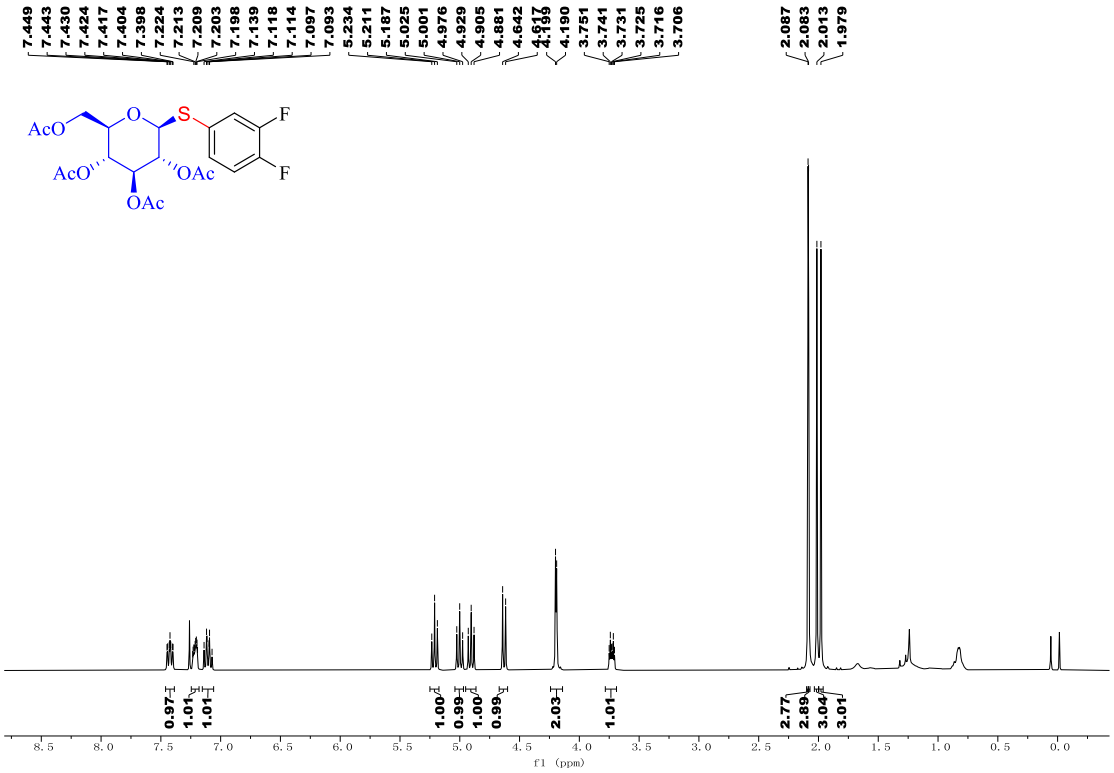
^{1}H NMR (400 MHz, MeOD) of **3l**



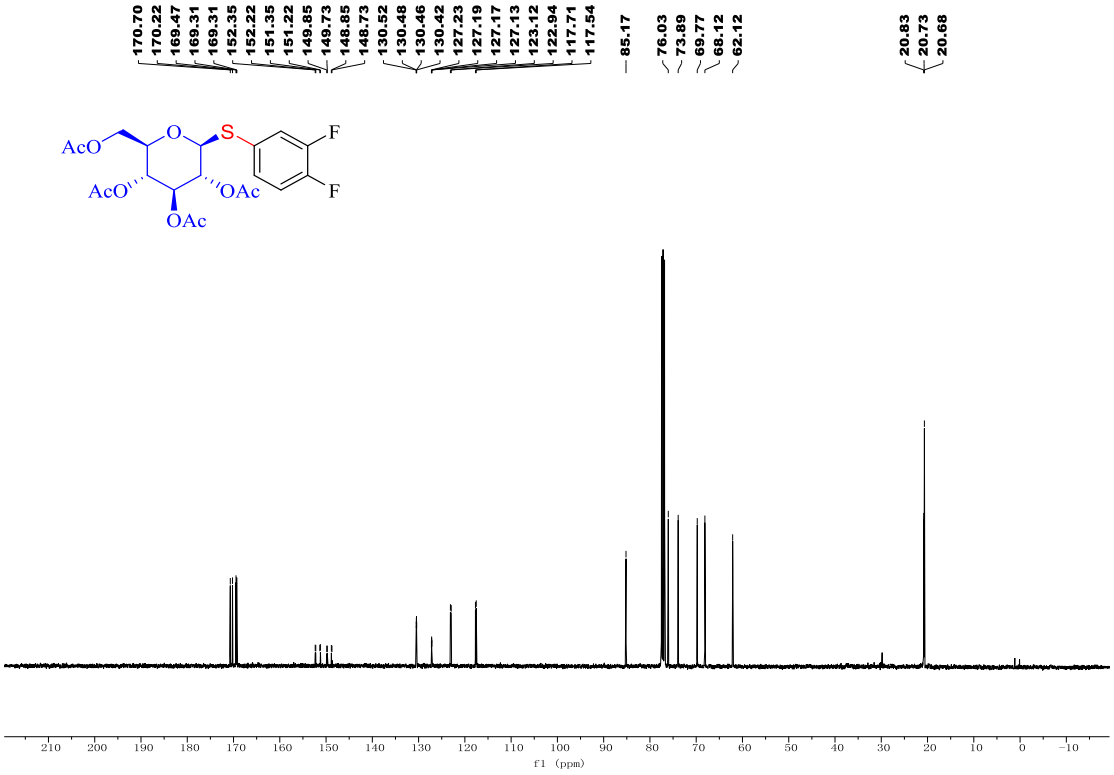
^{13}C NMR (100 MHz, MeOD) of **3l**



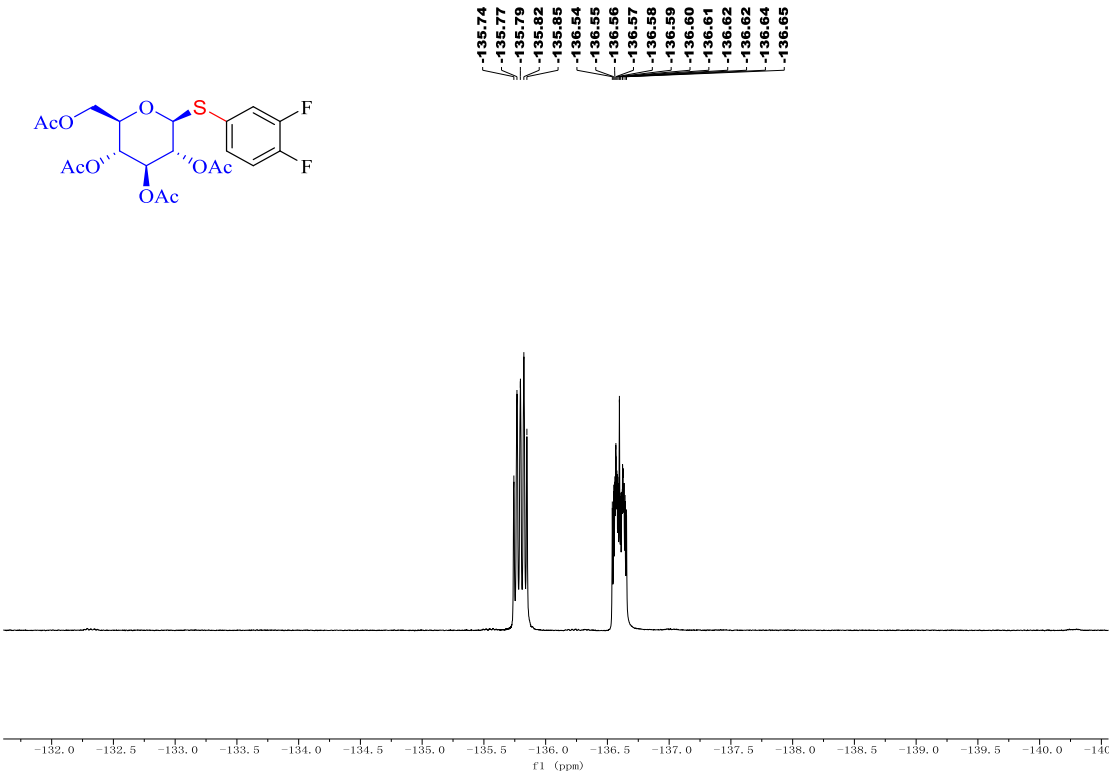
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



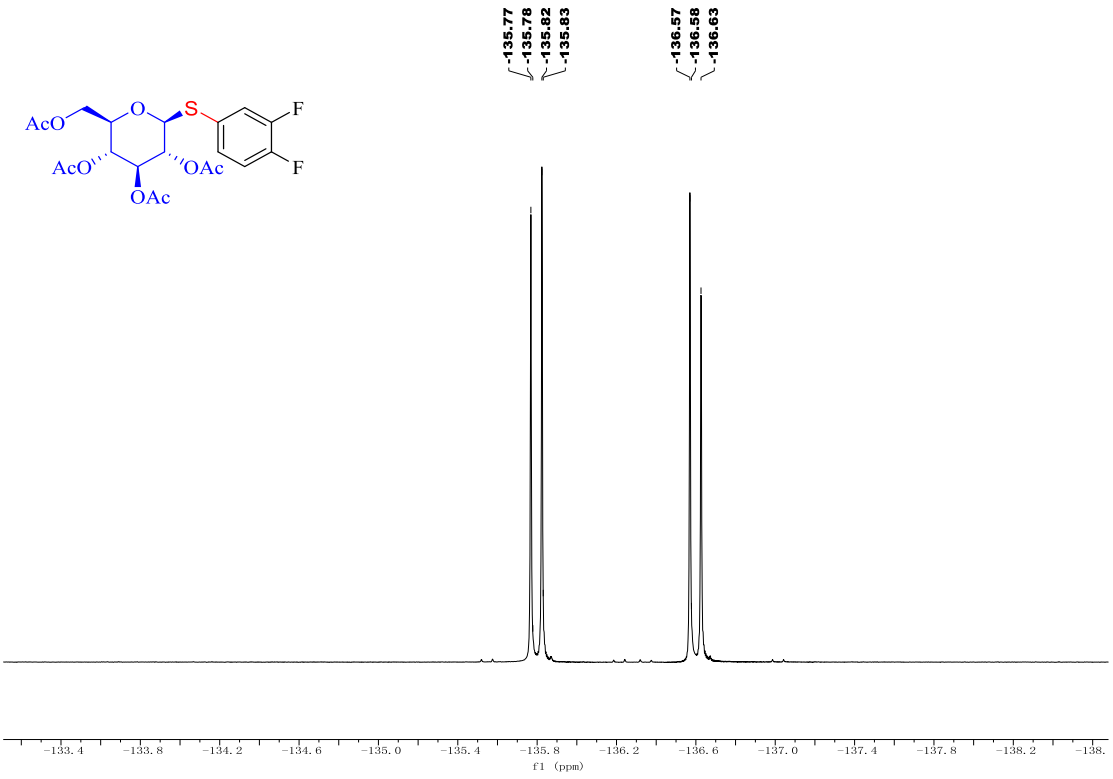
^{13}C NMR (100 MHz, $CDCl_3$) of **4a**



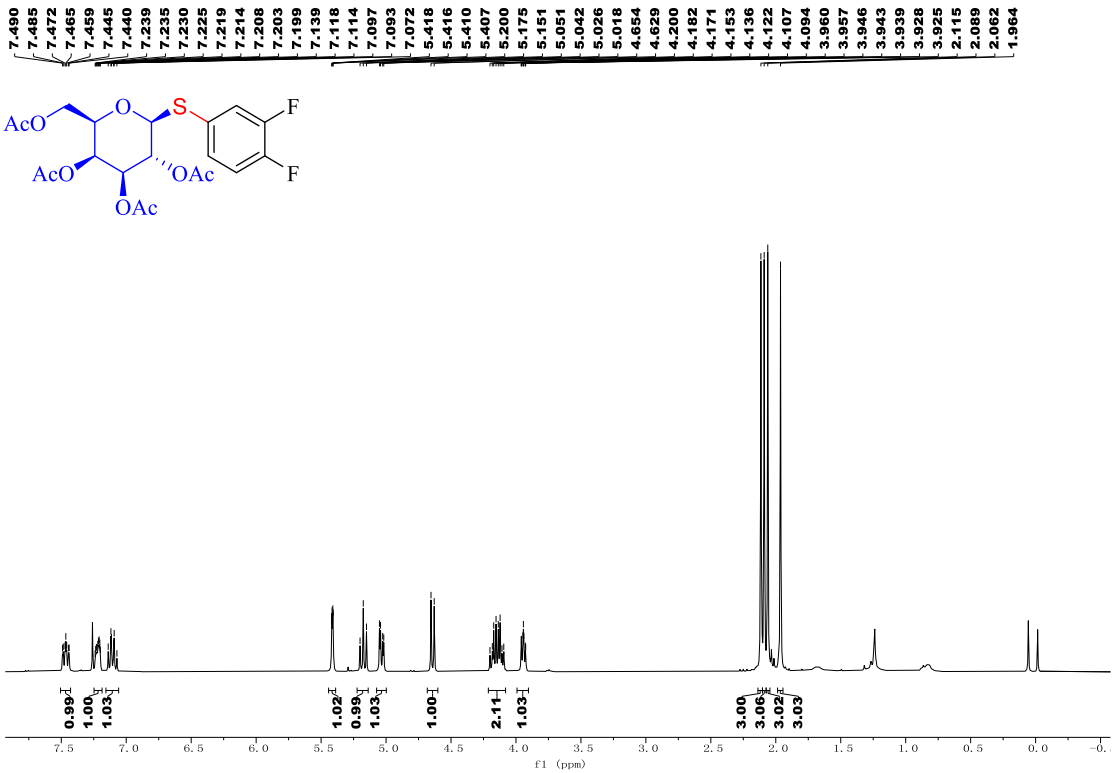
^{19}F {^{1}H} NMR (367 MHz, $CDCl_3$) of **4a**



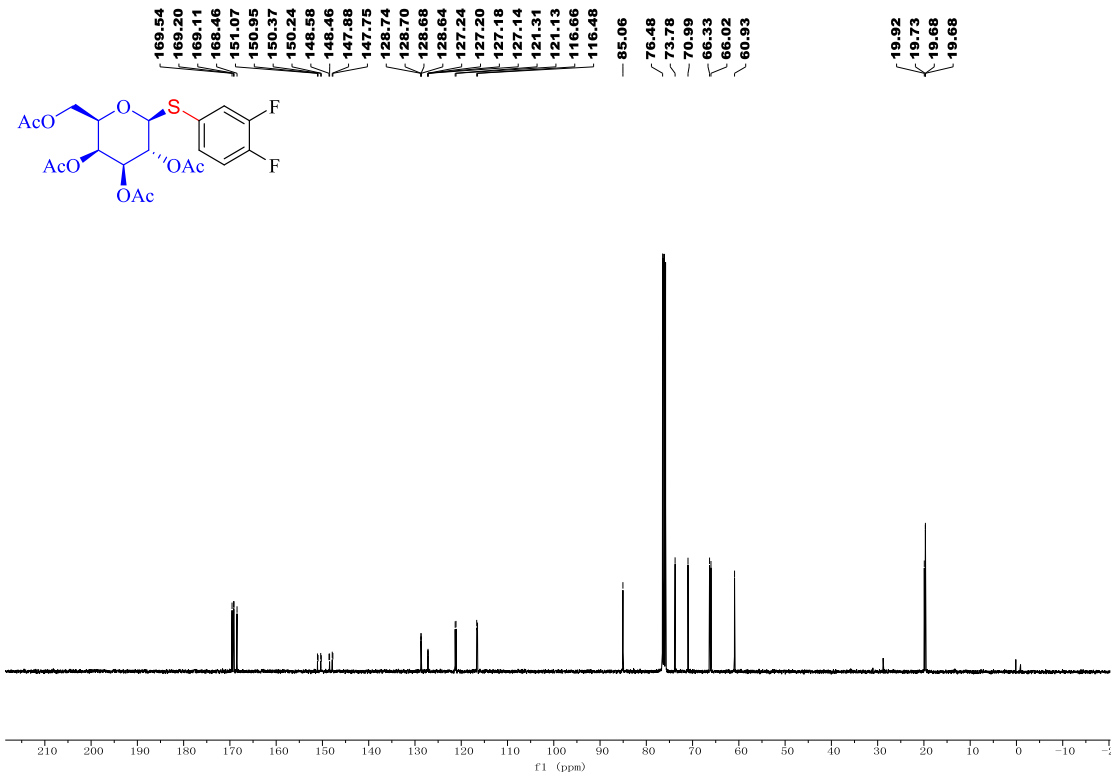
^{19}F NMR (367 MHz, $CDCl_3$) of **4a**



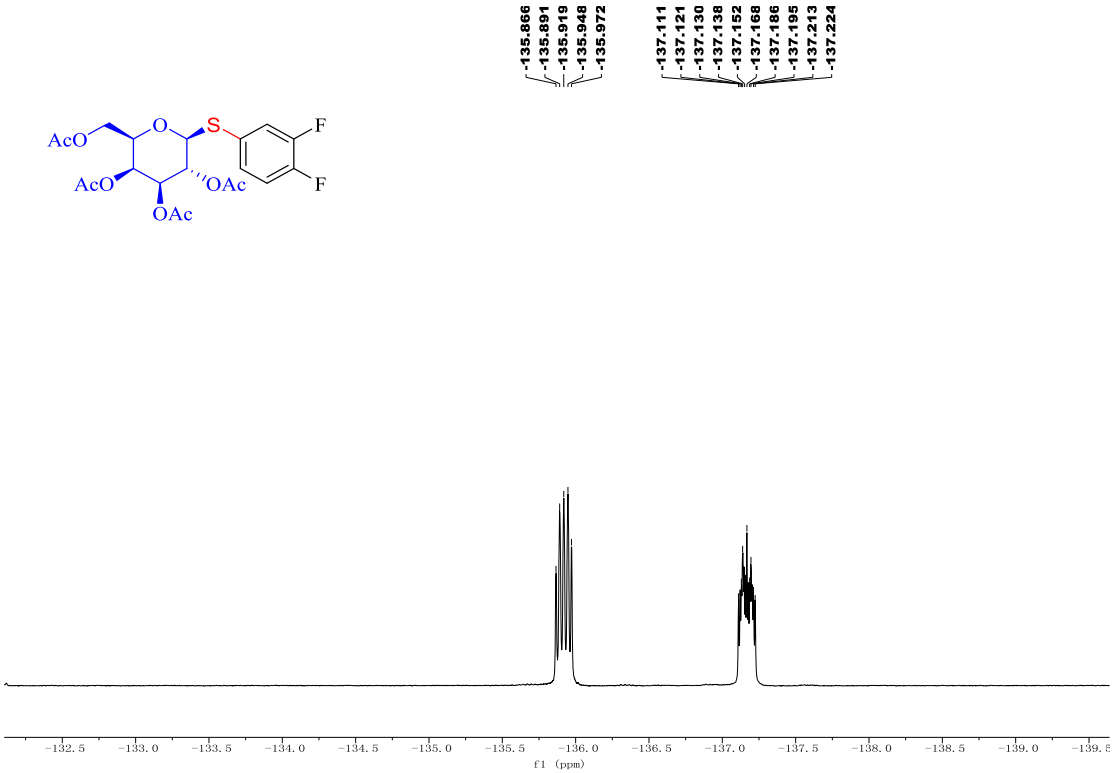
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



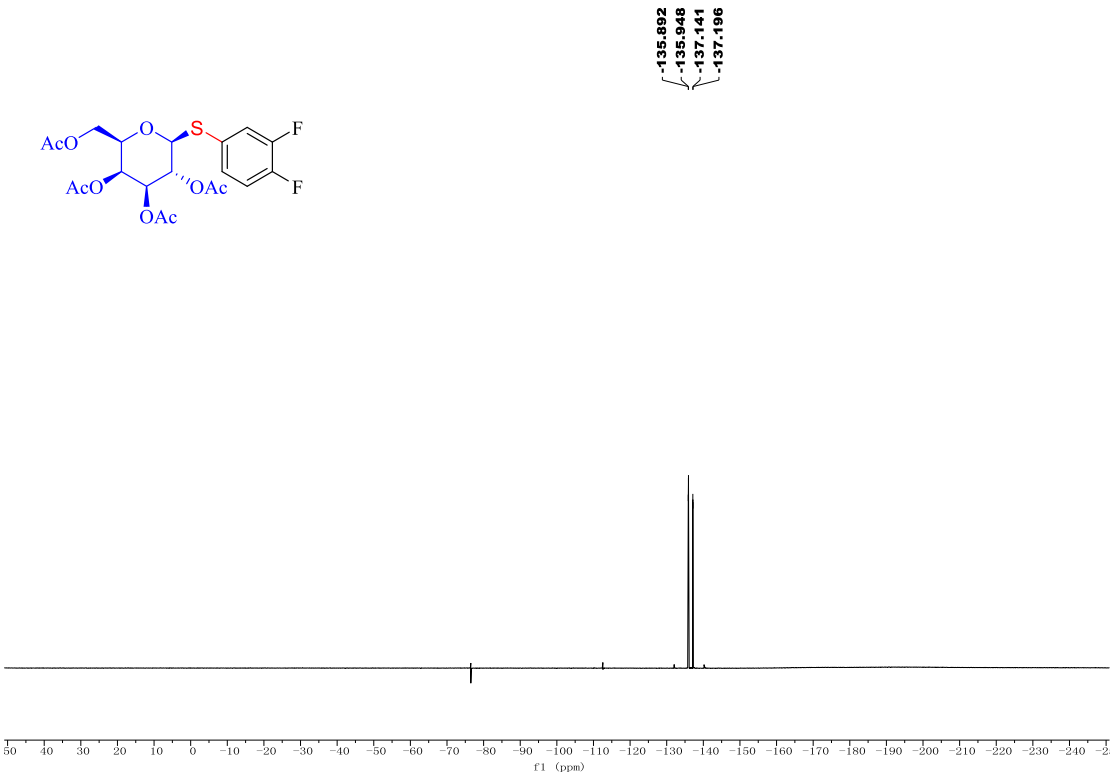
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



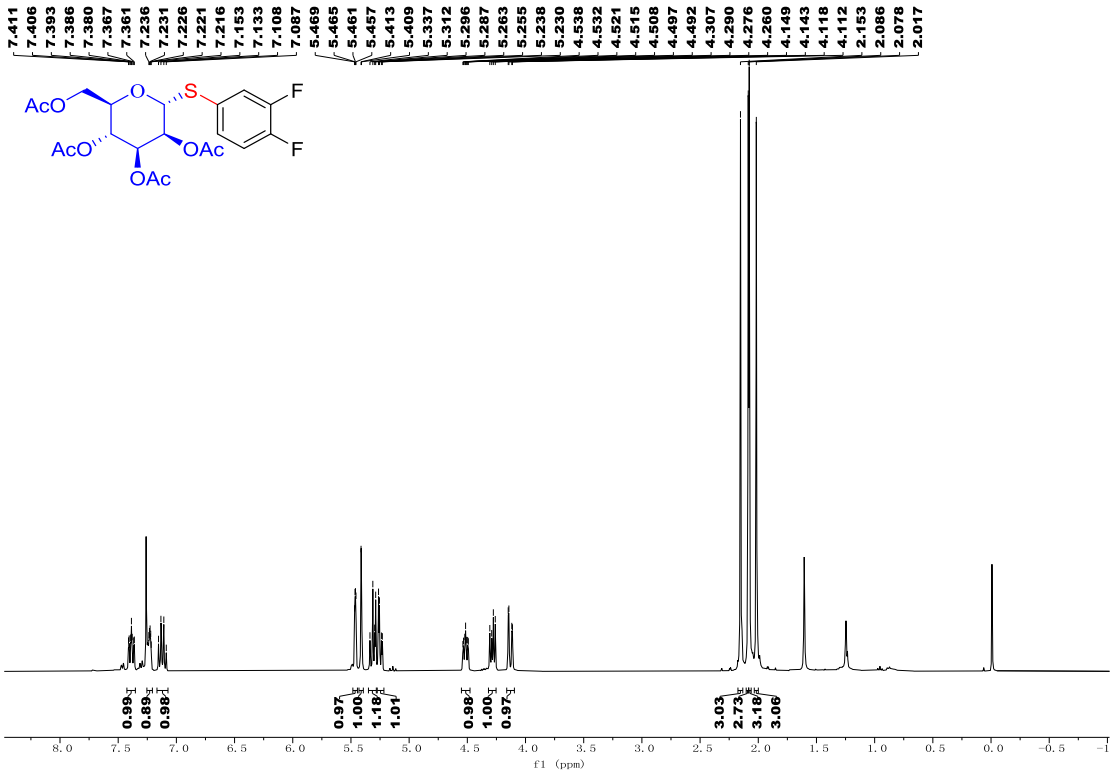
^{19}F {^{1}H} NMR (367 MHz, $CDCl_3$) of **4b**



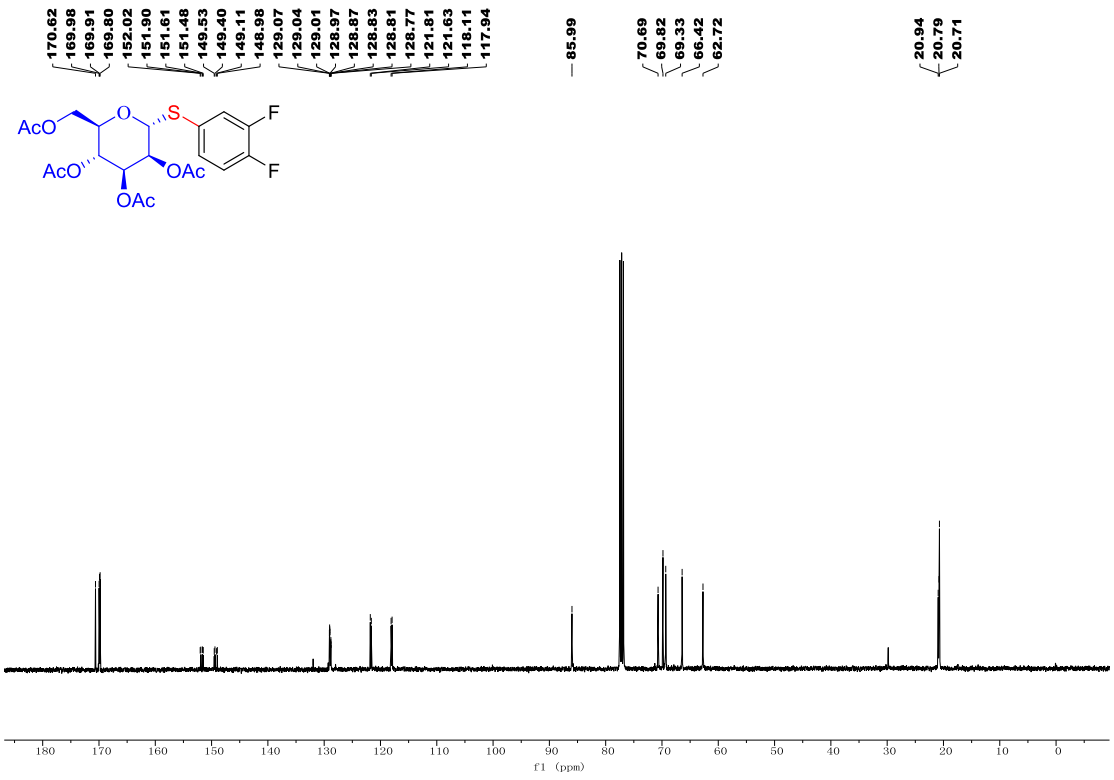
^{19}F NMR (367 MHz, $CDCl_3$) of **4b**



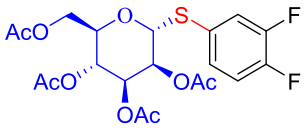
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**

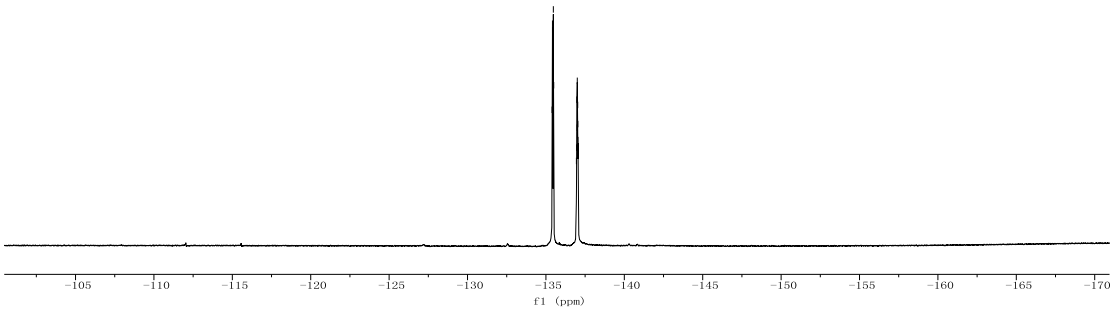


^{13}C NMR (100 MHz, $CDCl_3$) of **4c**

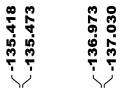


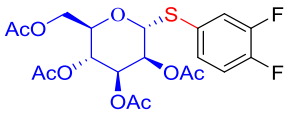
^{19}F {^{1}H} NMR (367 MHz, $CDCl_3$) of **4c**

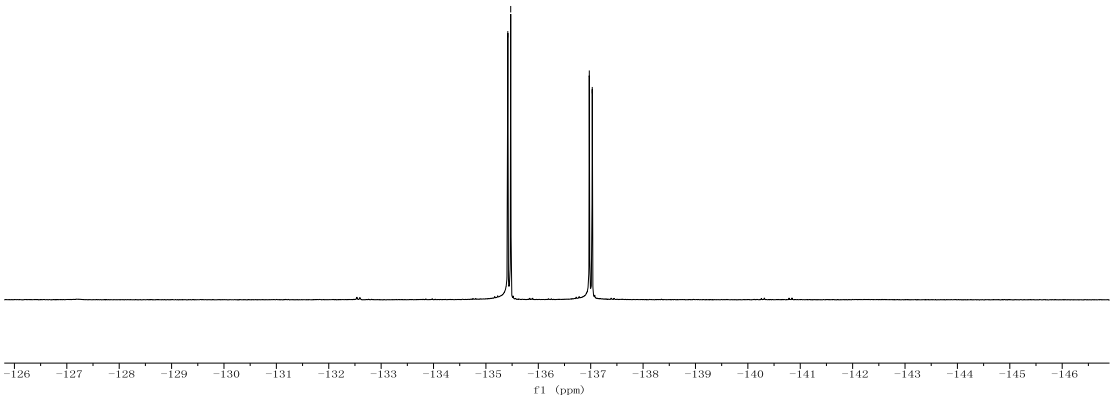




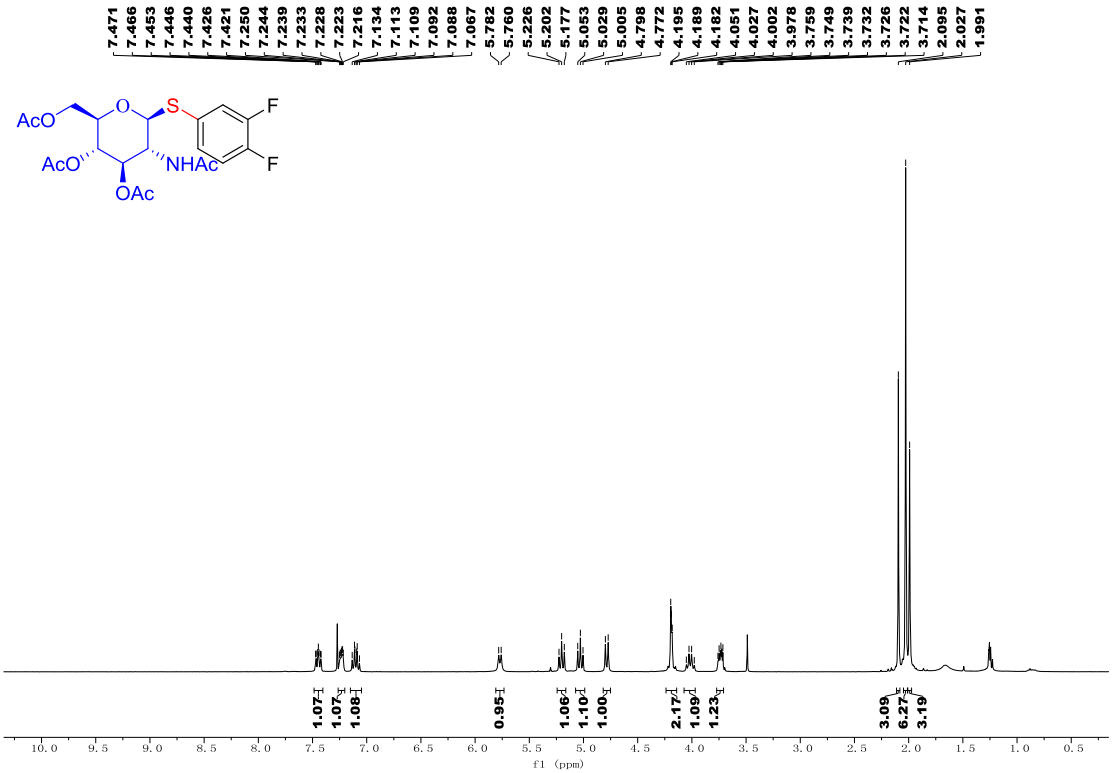
^{19}F NMR (367 MHz, $CDCl_3$) of **4c**



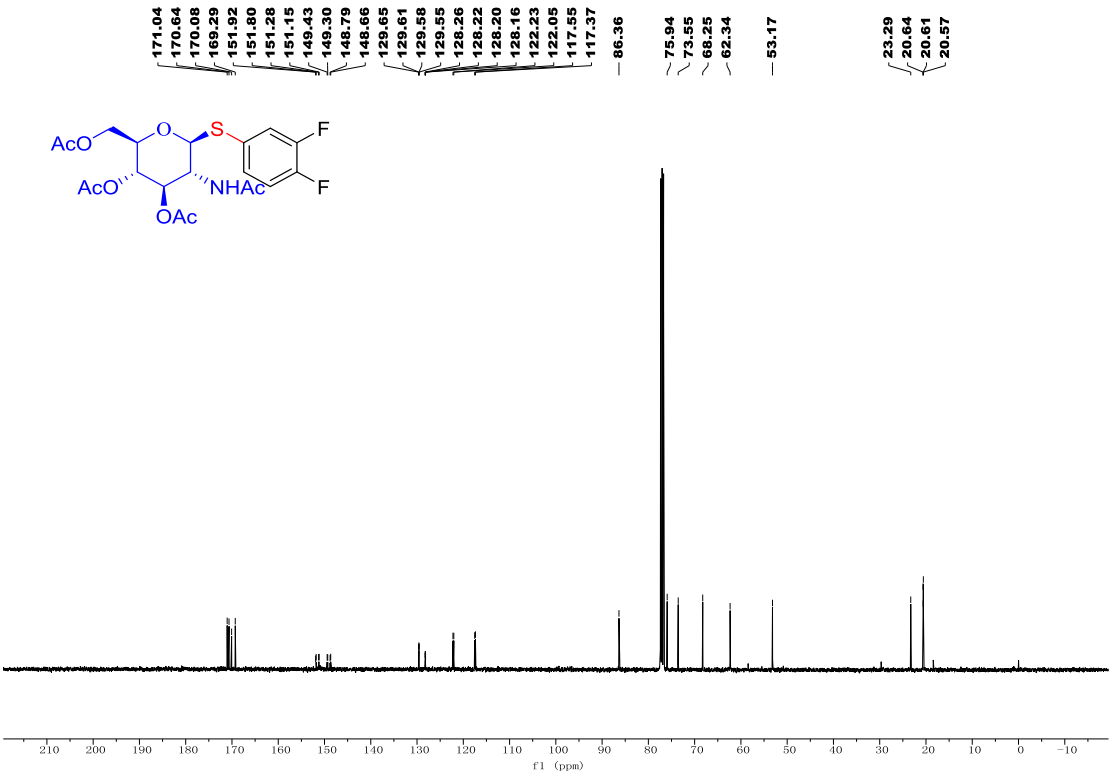




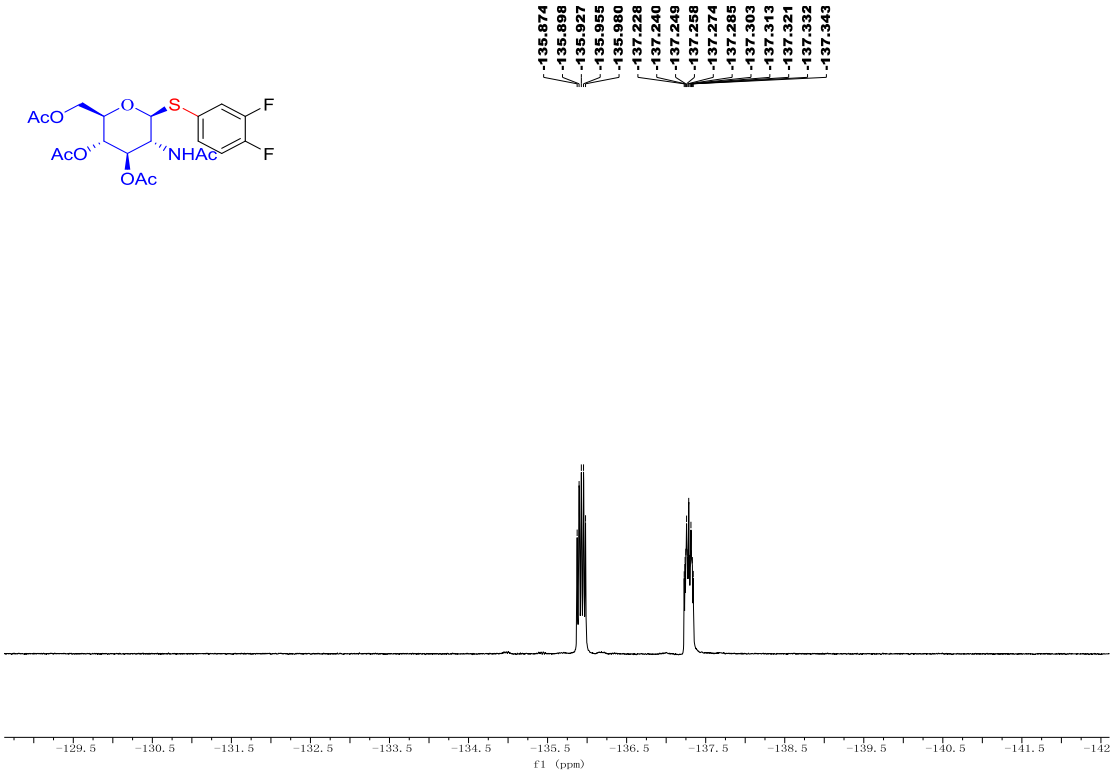
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



^{13}C NMR (100 MHz, $CDCl_3$) of **4d**

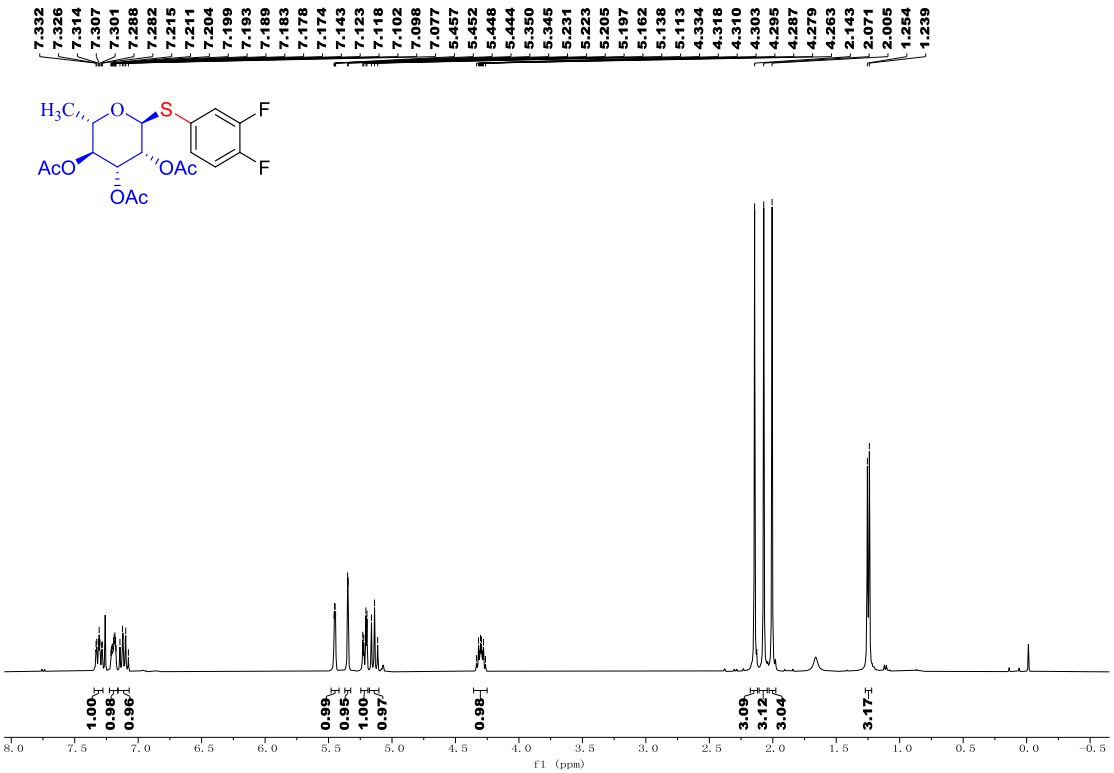


^{19}F {^{1}H} NMR (367 MHz, $CDCl_3$) of **4d**

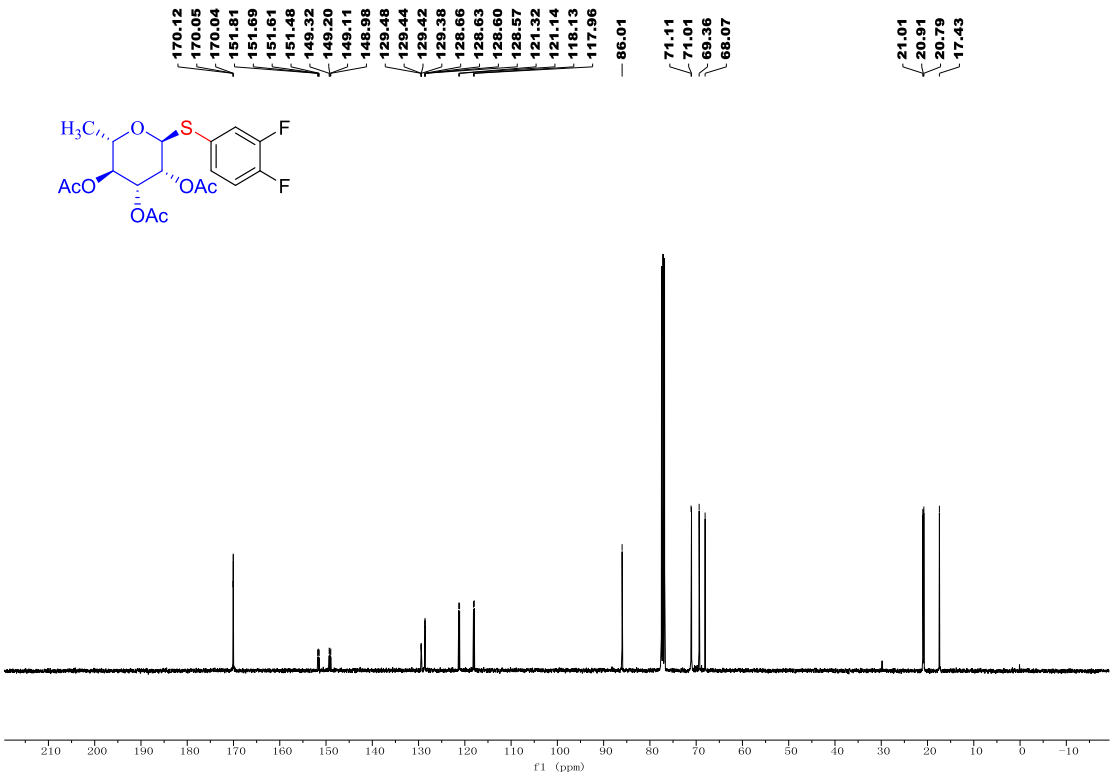


^{19}F NMR (367 MHz, $CDCl_3$) of **4d**

^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



^{13}C NMR (100 MHz, $CDCl_3$) of **4e**



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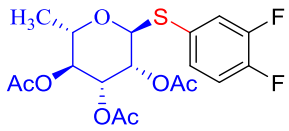

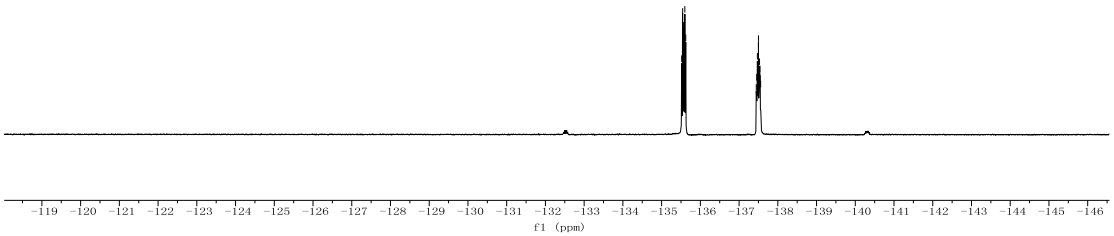

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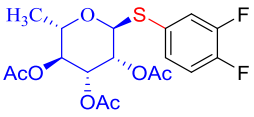

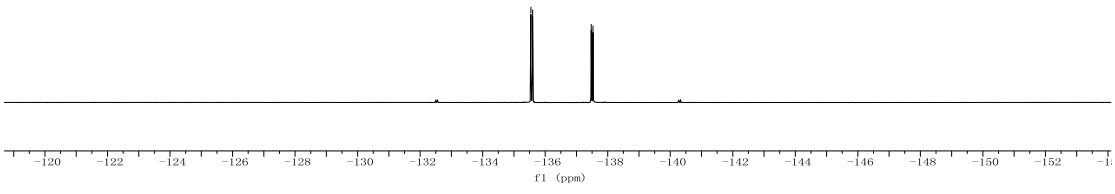

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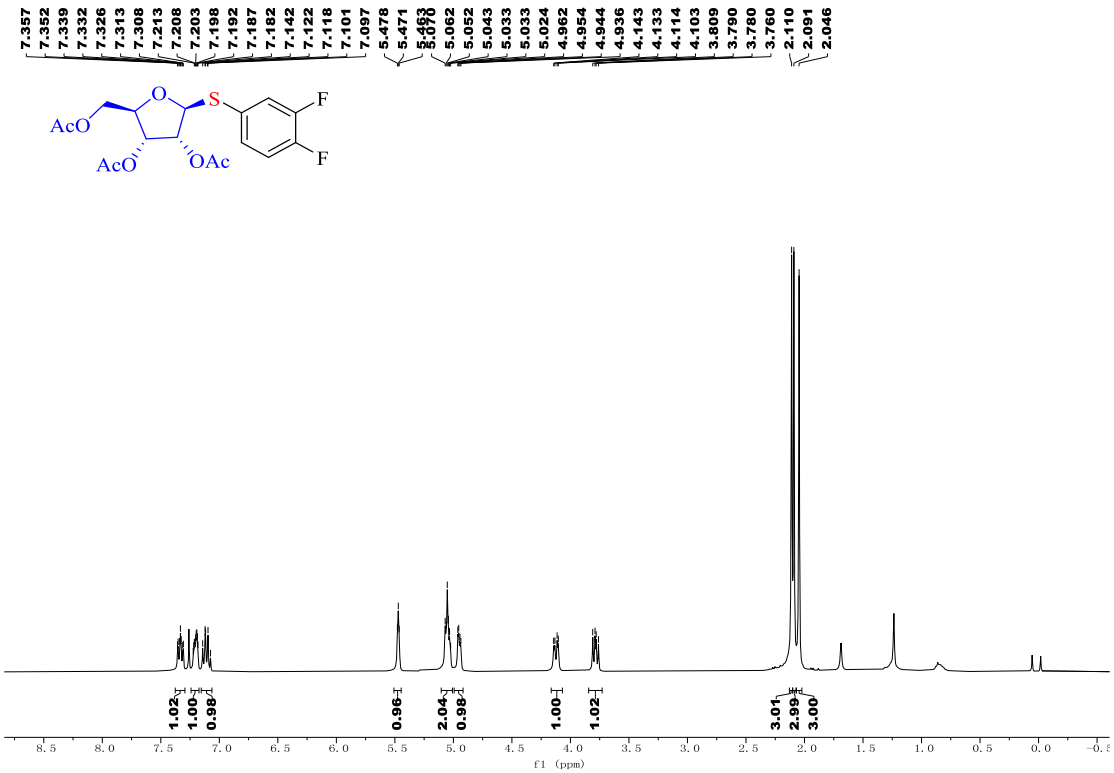
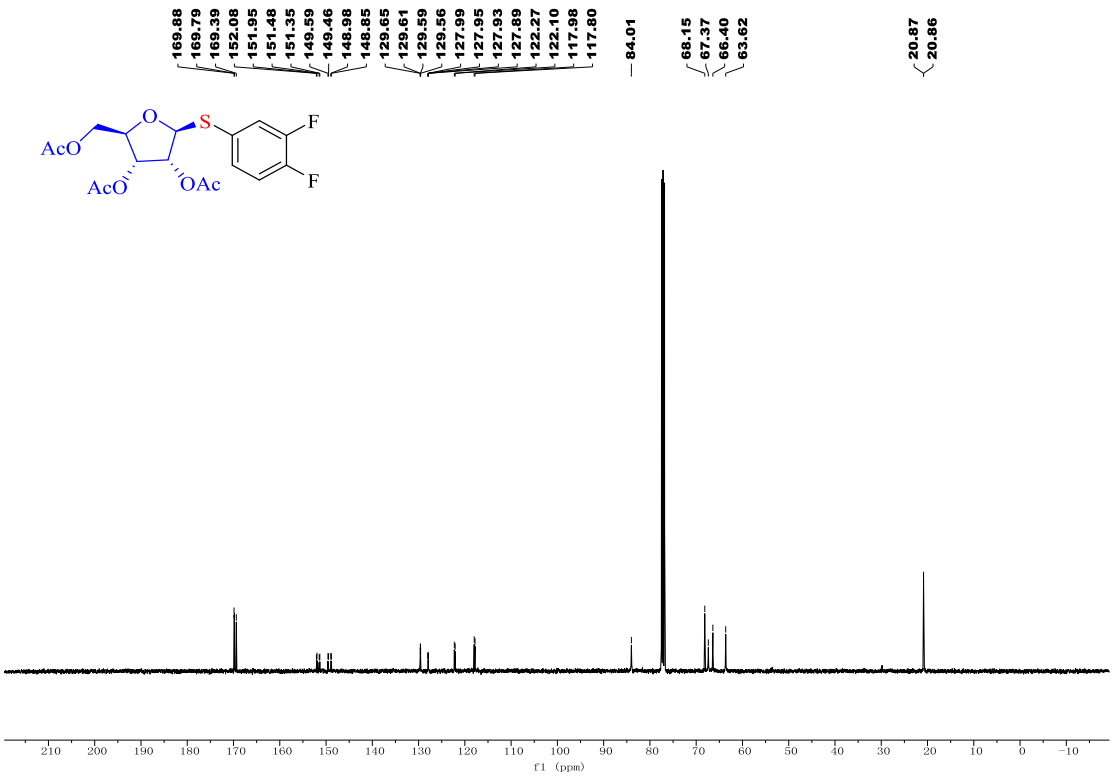
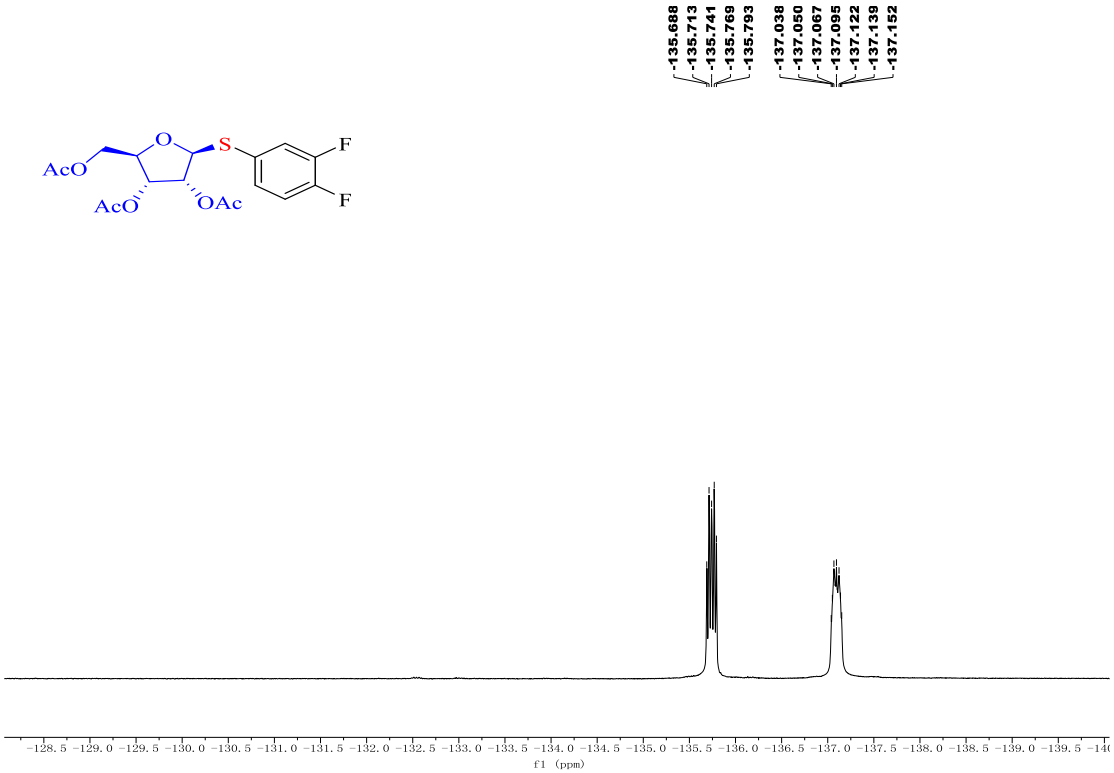


^{13}C NMR (100 MHz, $CDCl_3$) of **4f**



^{19}F {^{1}H} NMR (367 MHz, $CDCl_3$) of **4f**



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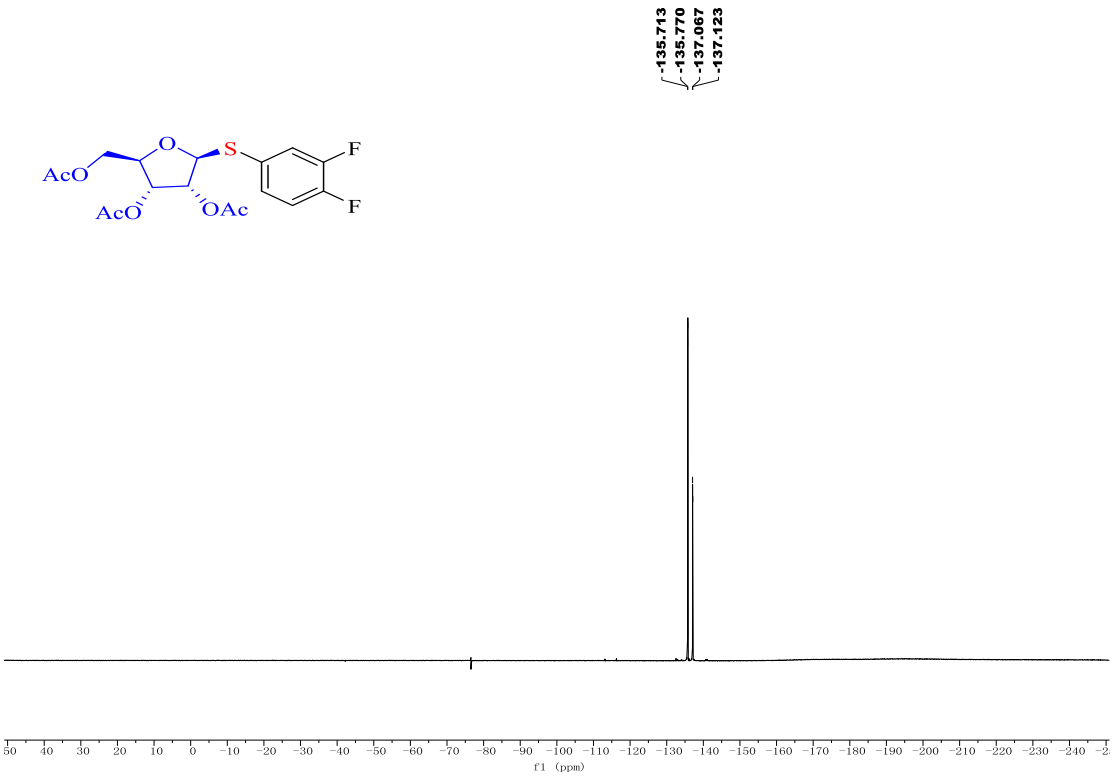

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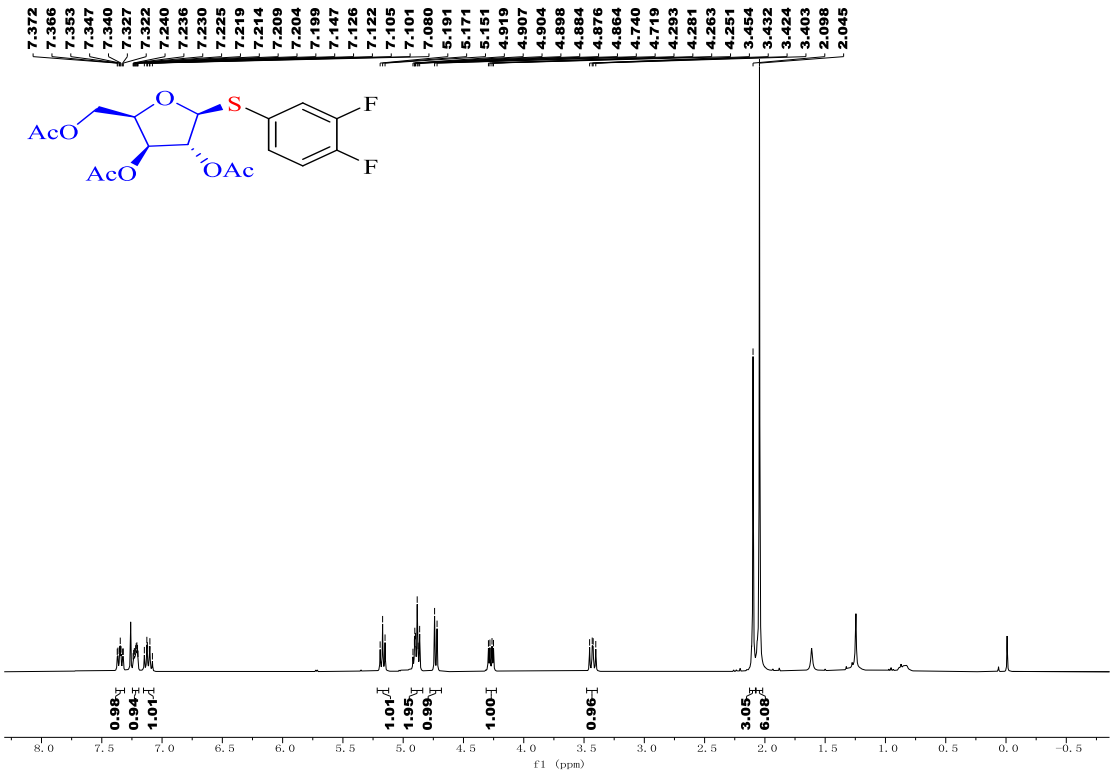

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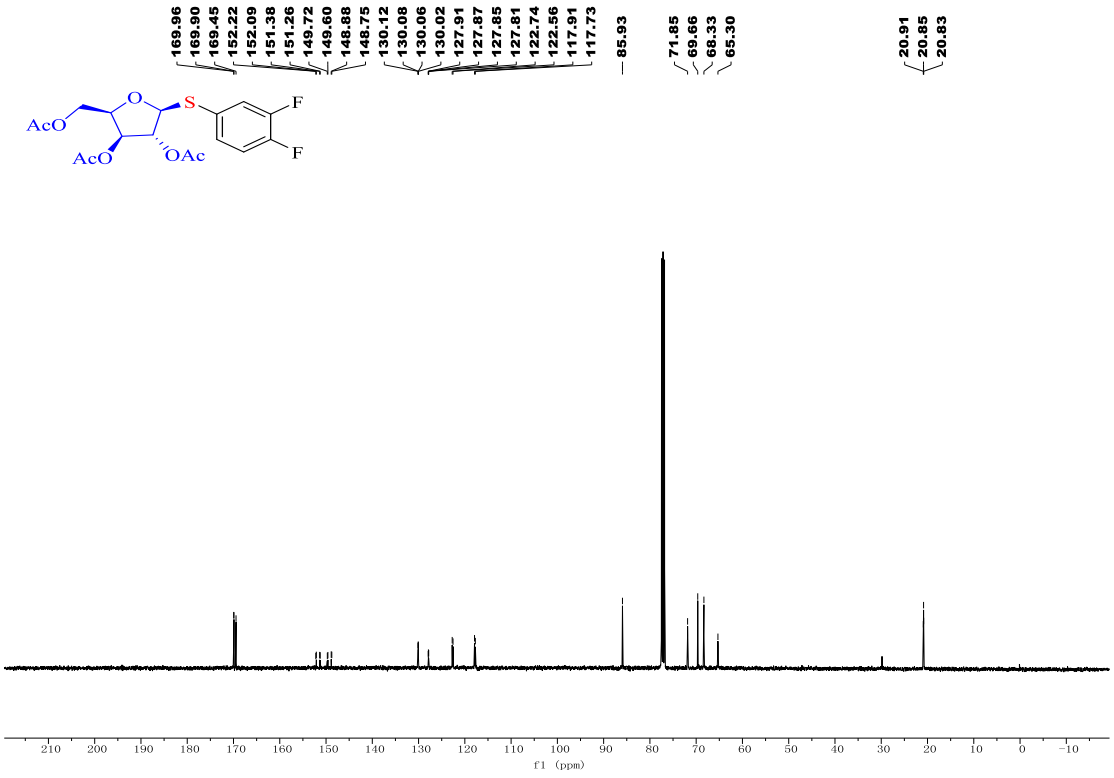

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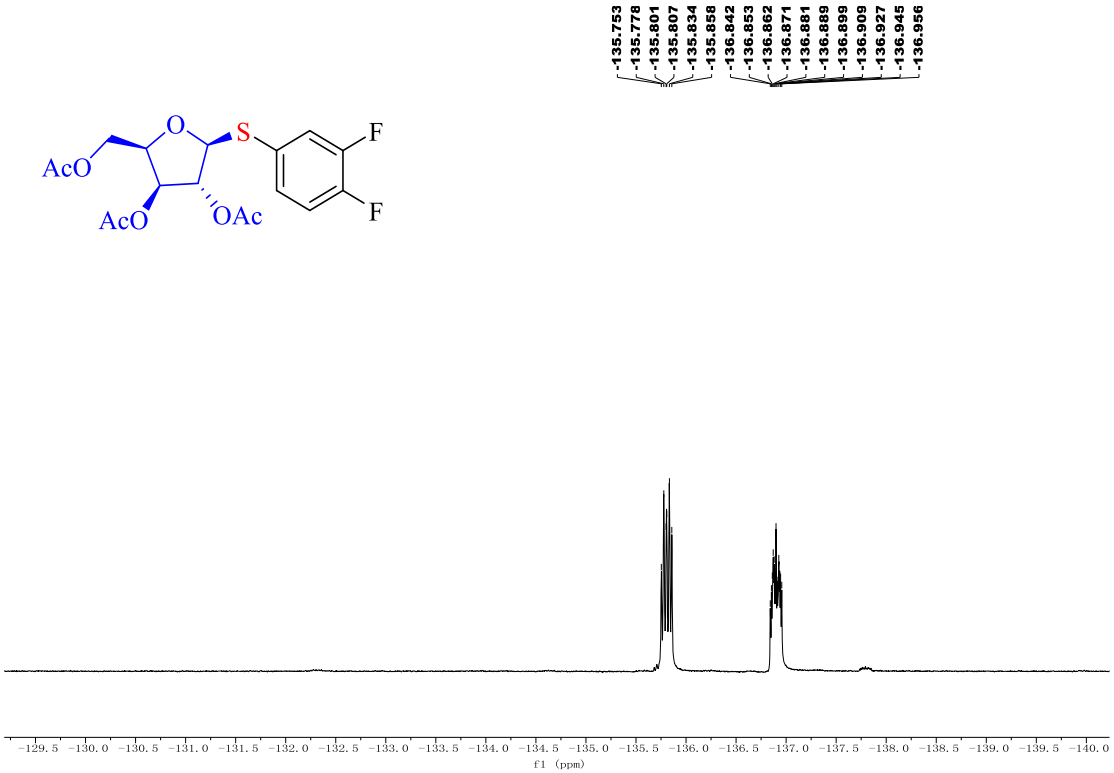

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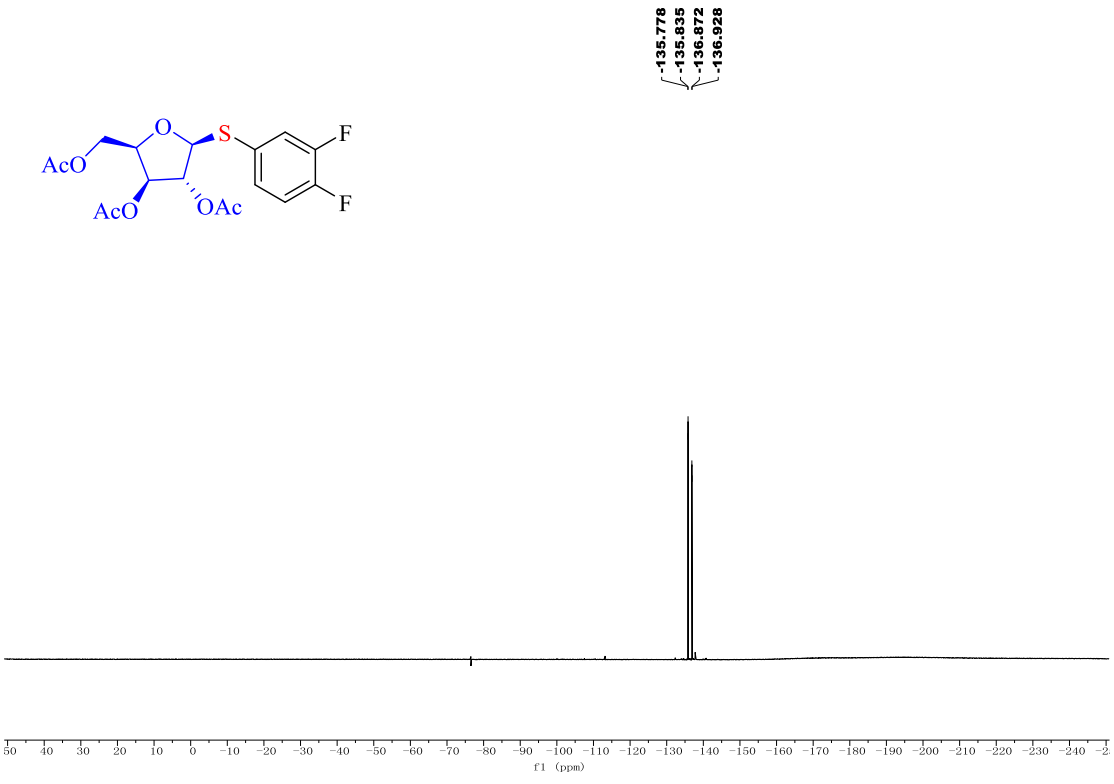
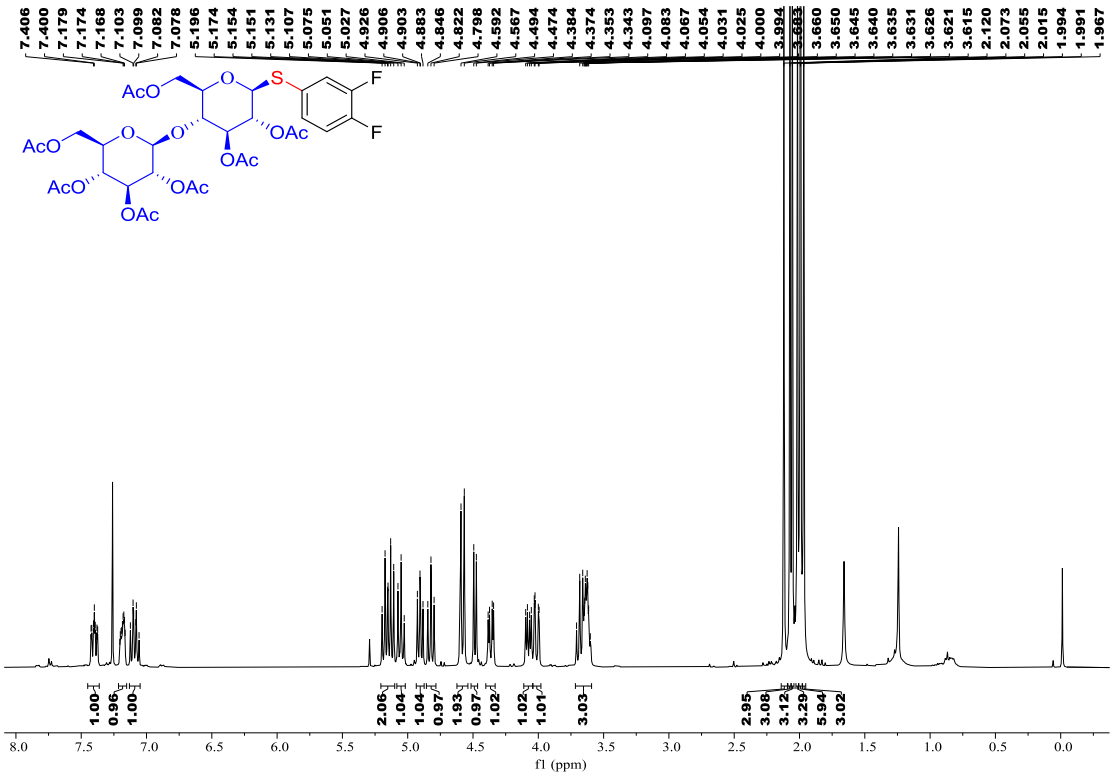
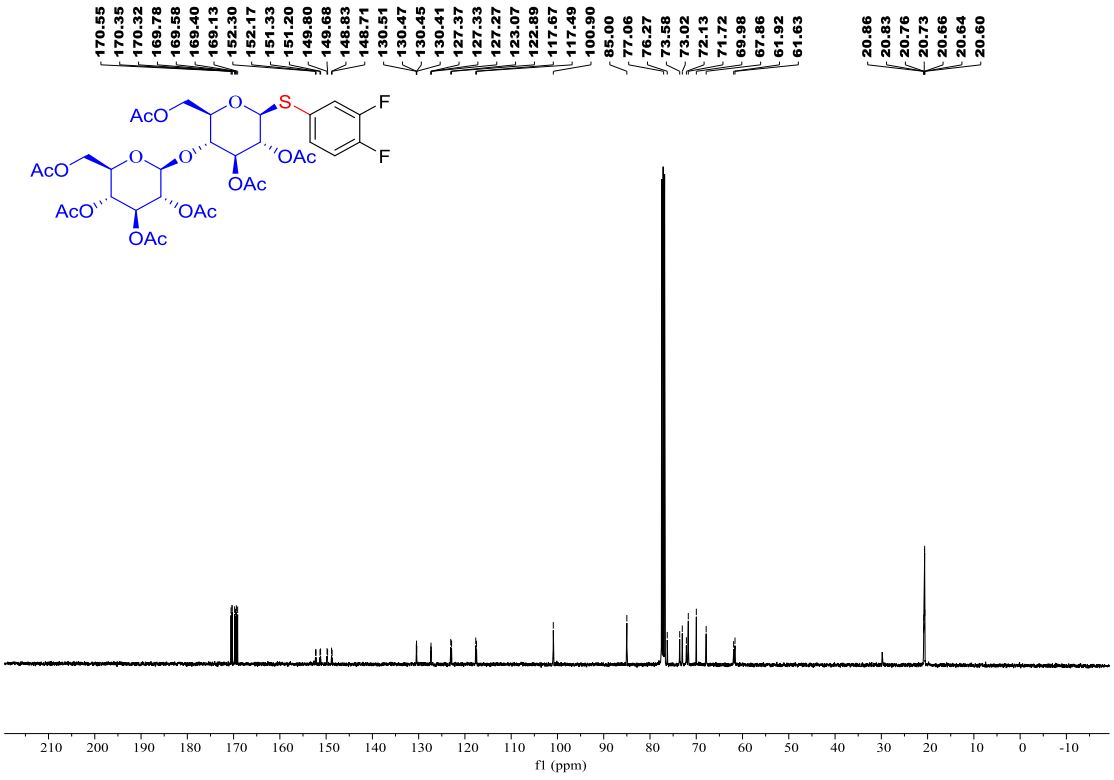


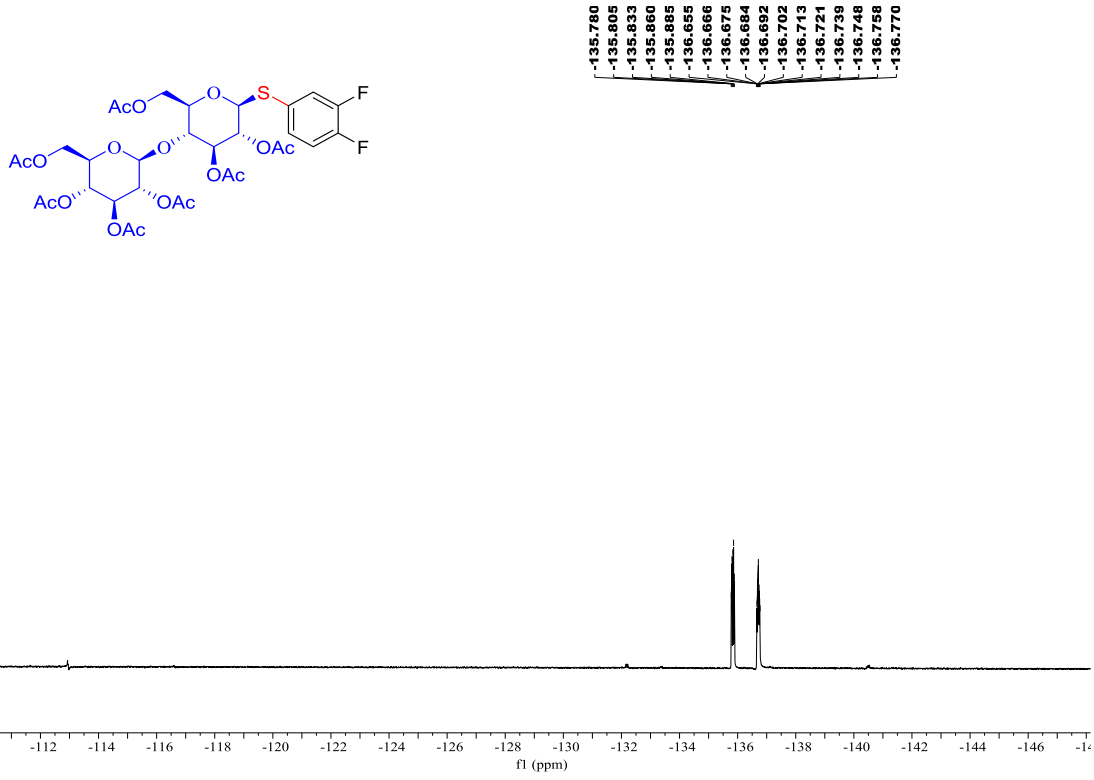
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



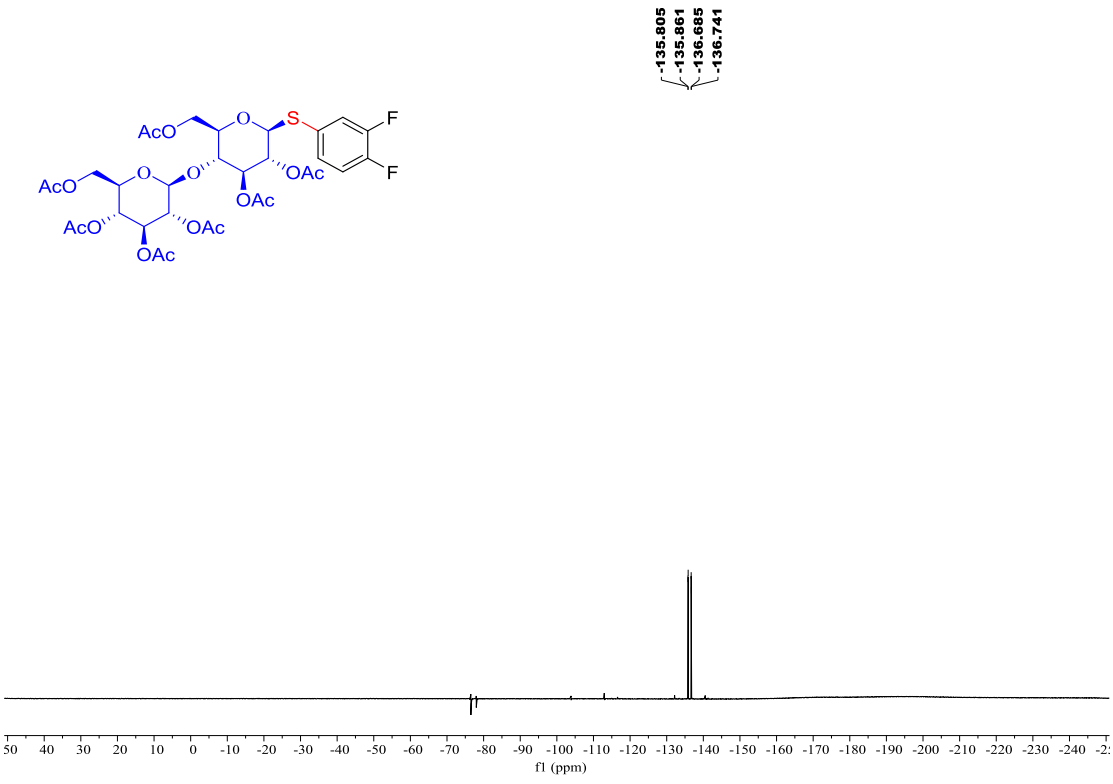
^{13}C NMR (100 MHz, $CDCl_3$) of **4h**



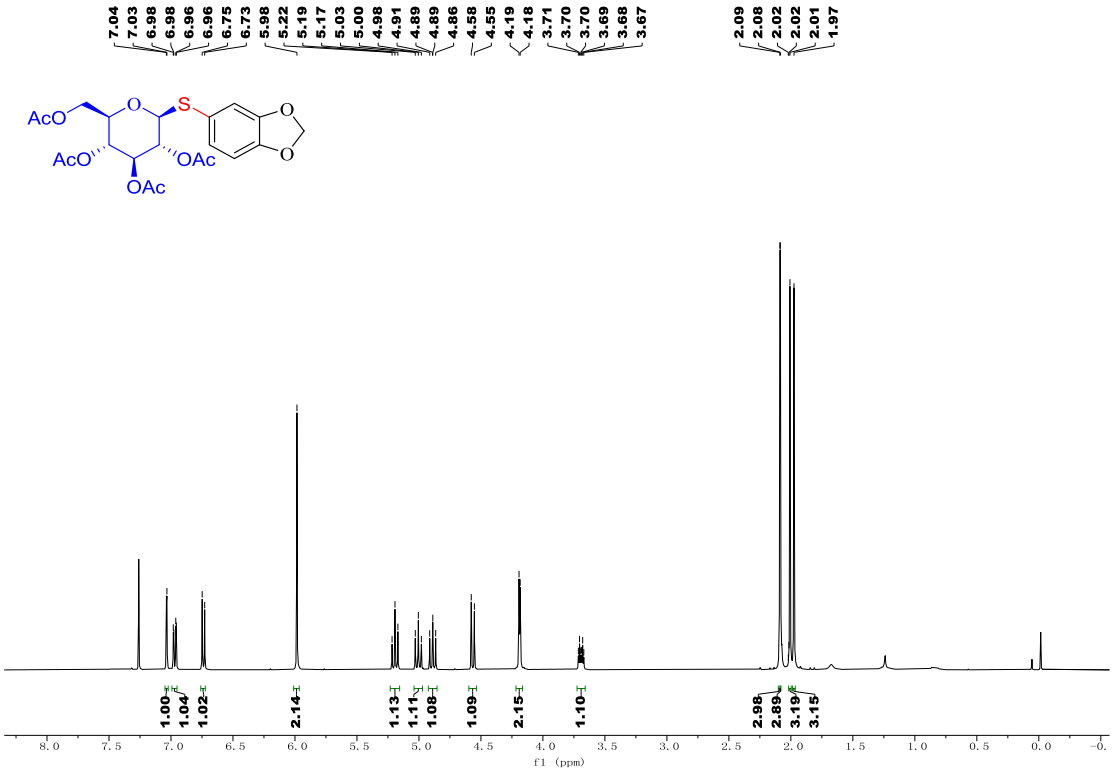
^{19}F {^{1}H} NMR (367 MHz, $CDCl_3$) of **4h**



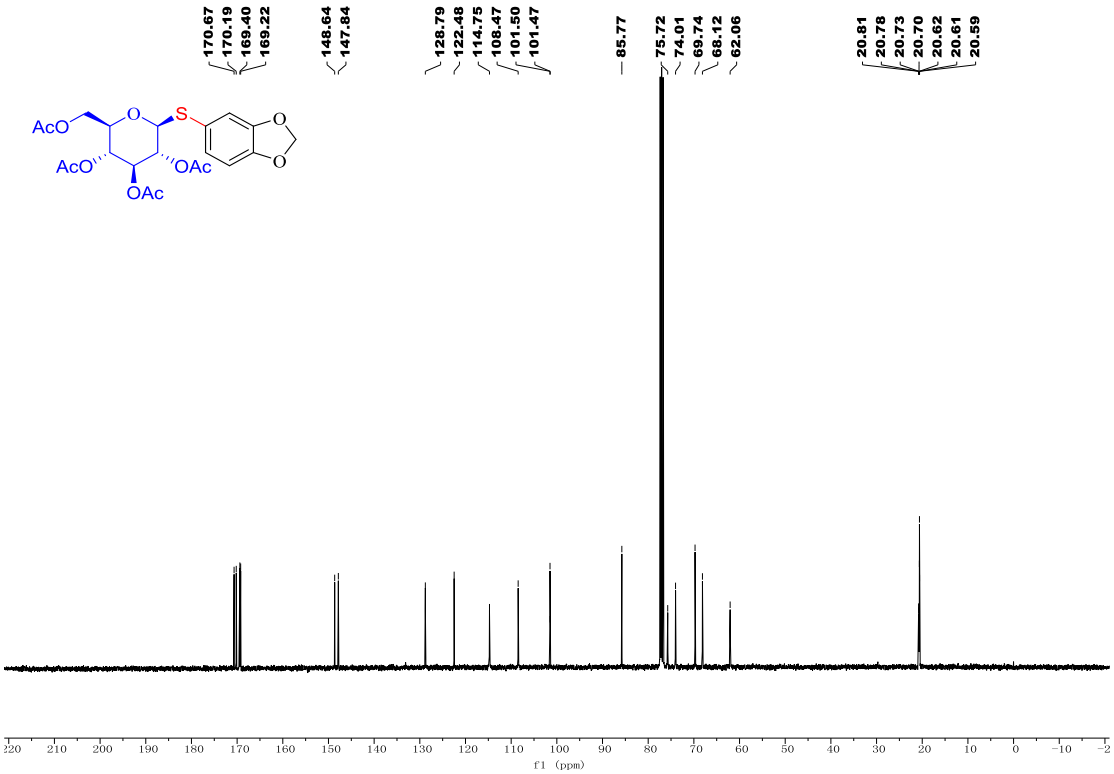
^{19}F NMR (367 MHz, $CDCl_3$) of **4h**



^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



^{13}C NMR (100 MHz, $CDCl_3$) of **4i**



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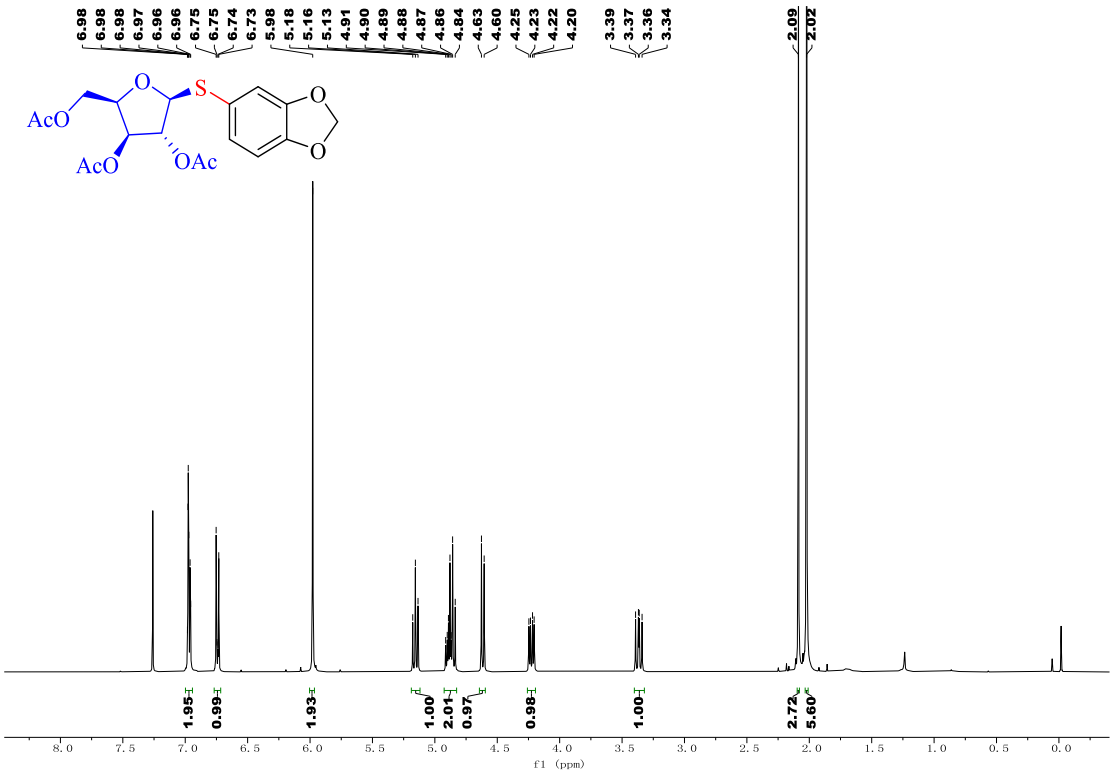

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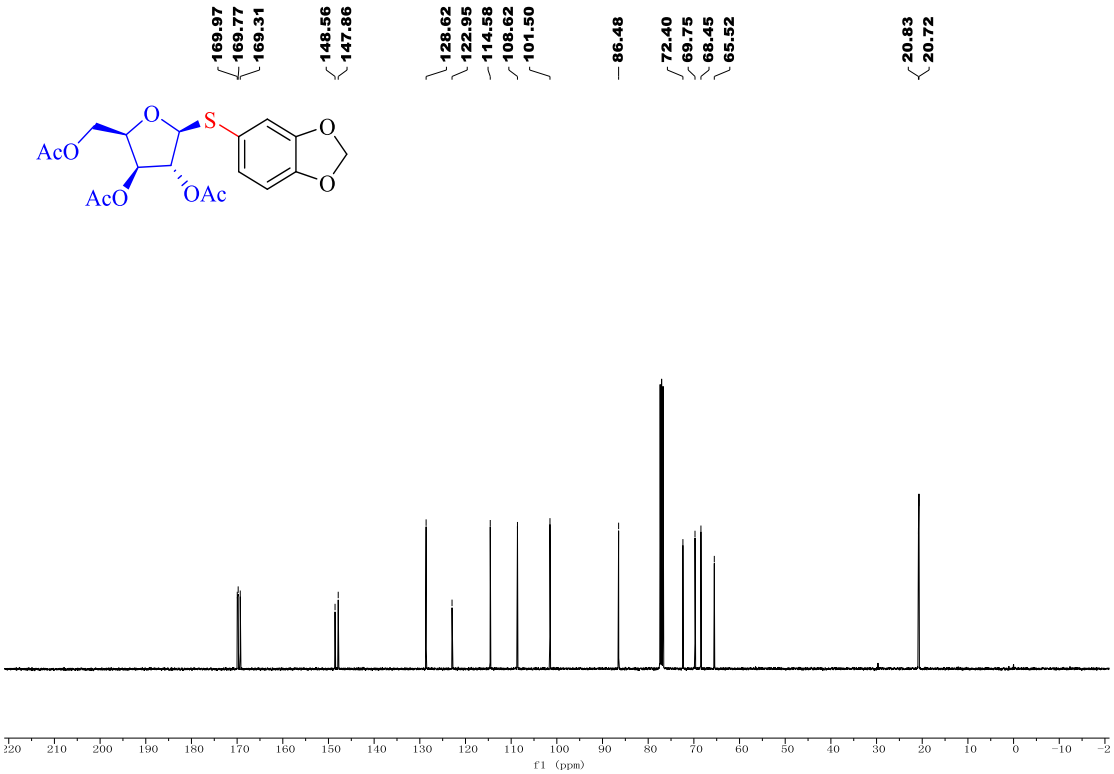

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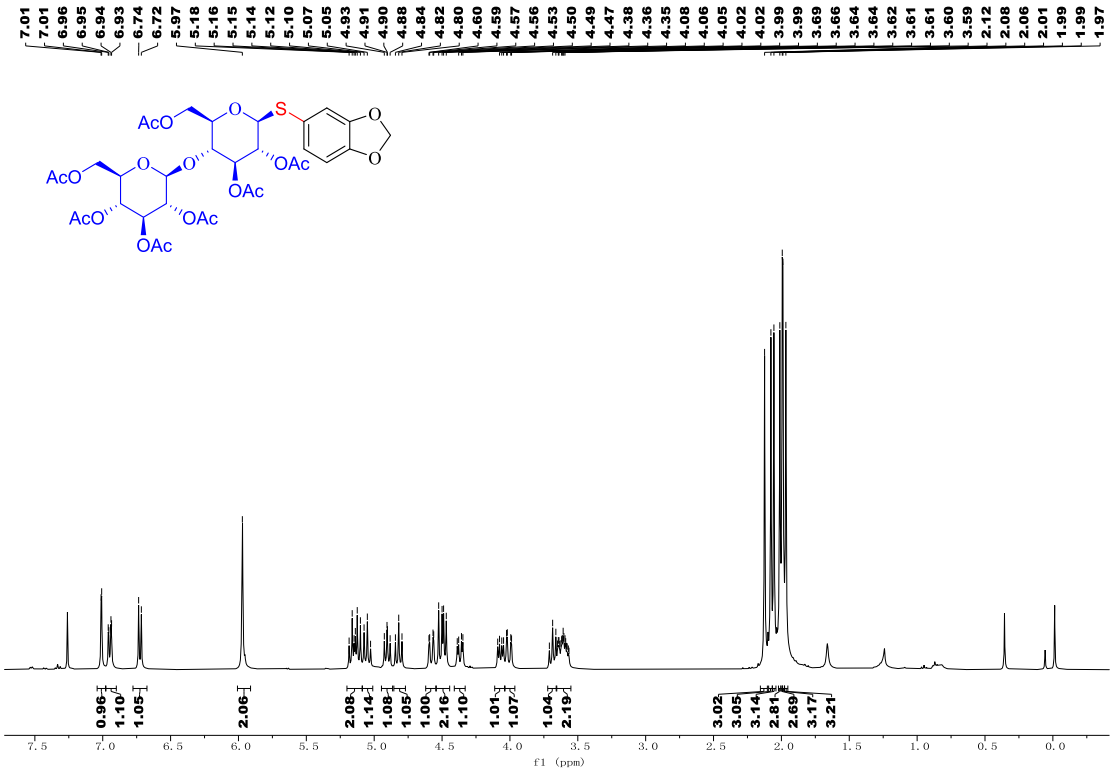
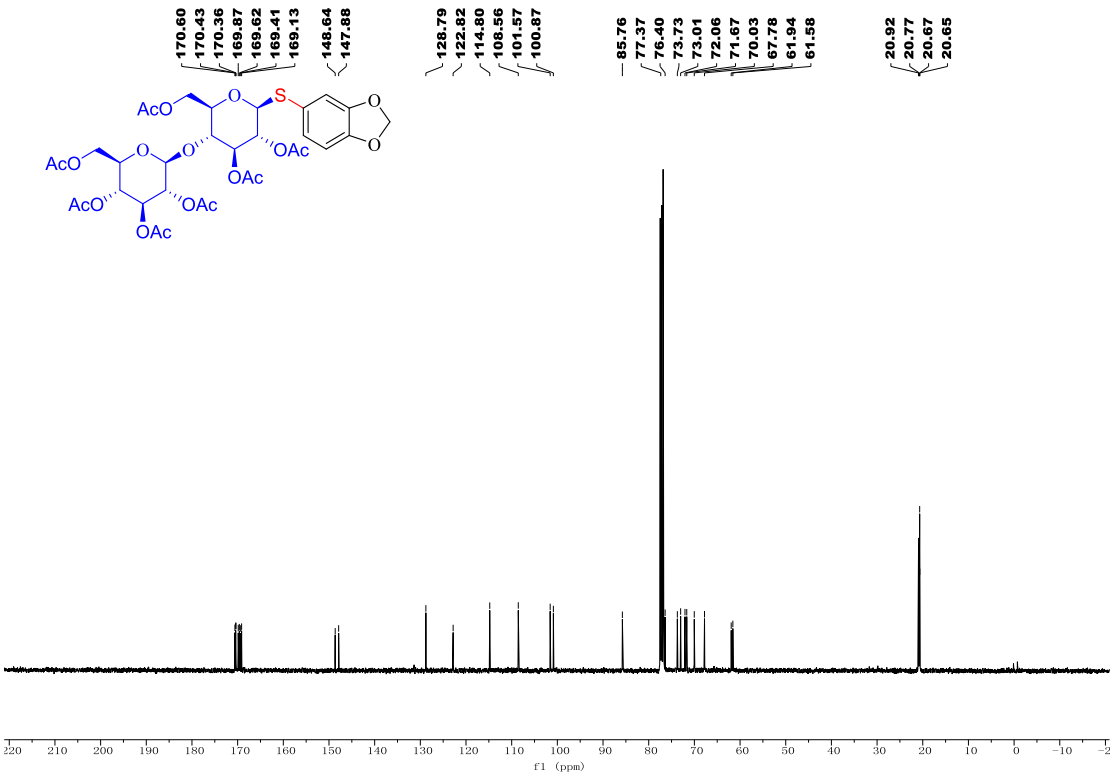
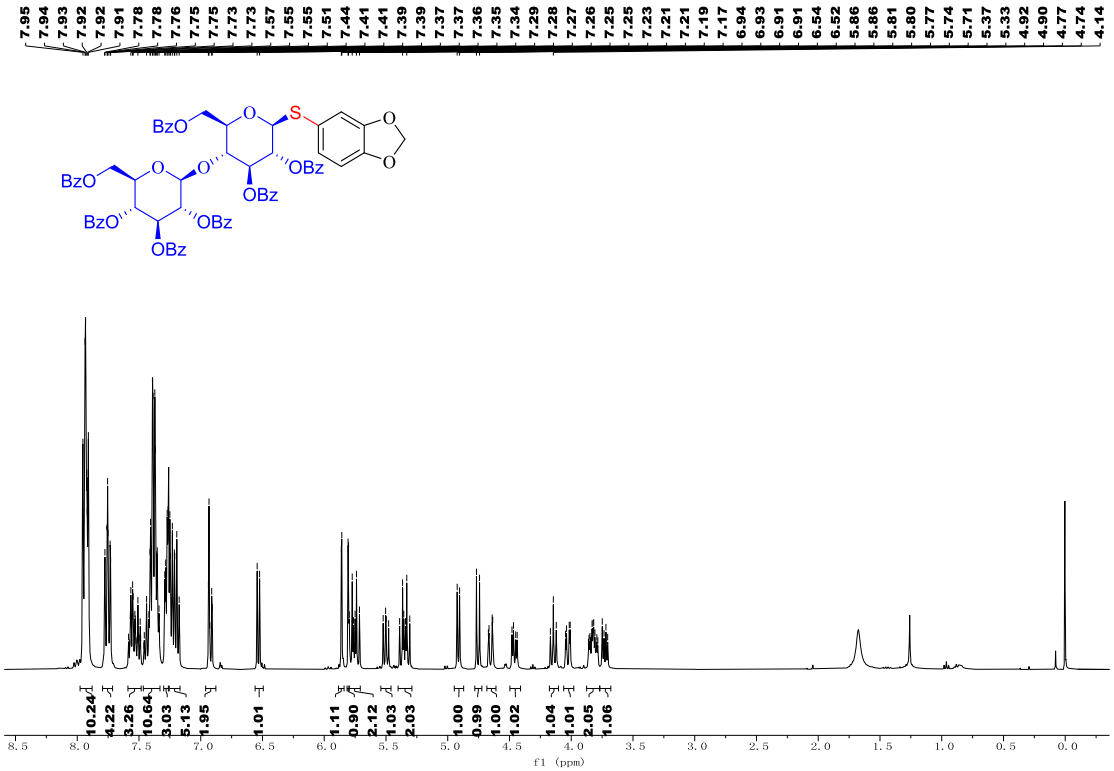


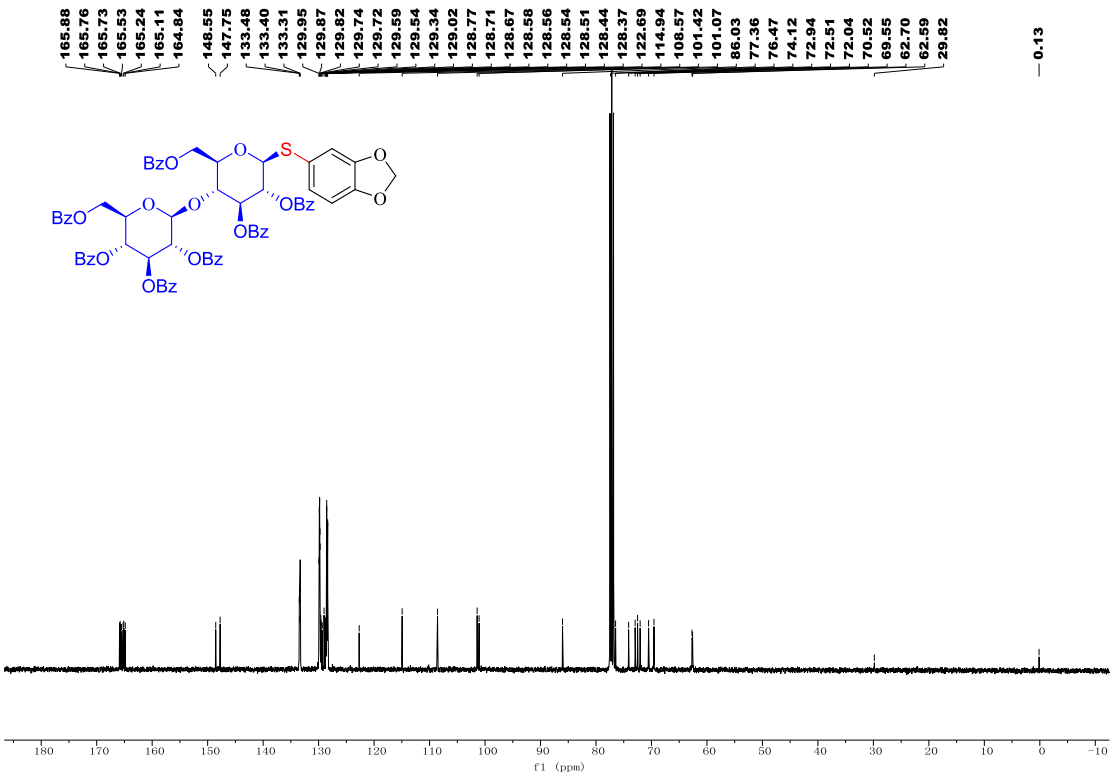
^{13}C NMR (100 MHz, $CDCl_3$) of **4k**



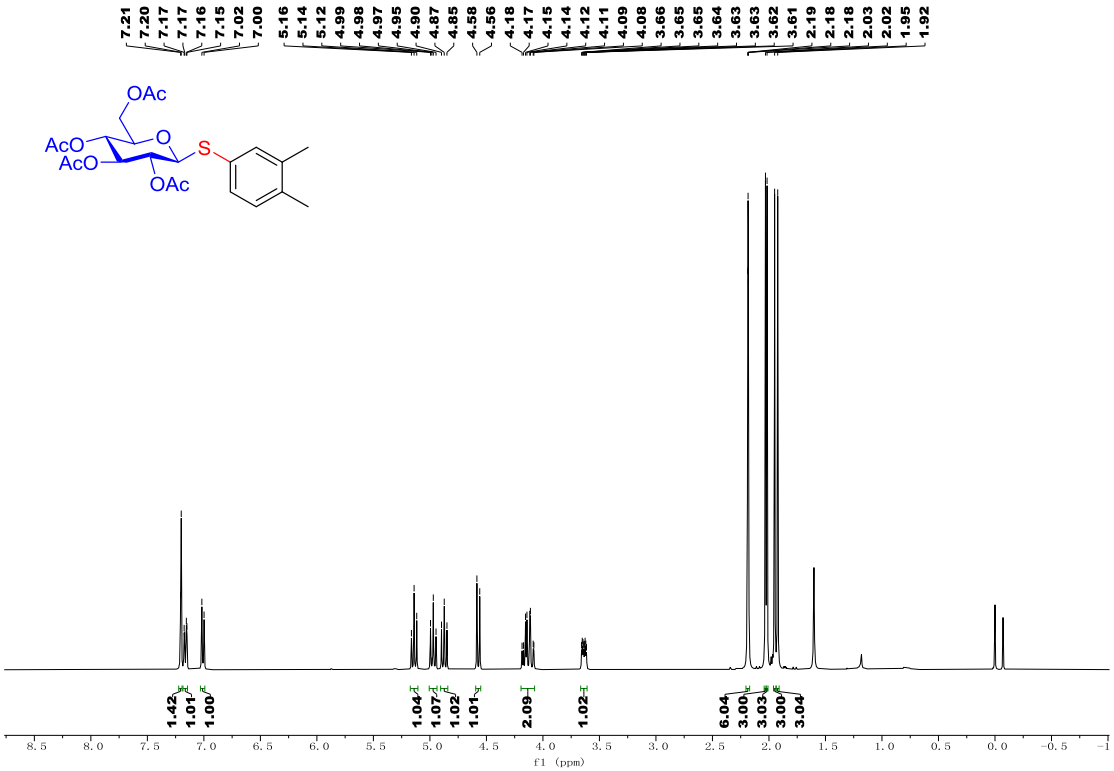
^{1}H NMR (400 MHz, $CDCl_3$) of **4l**



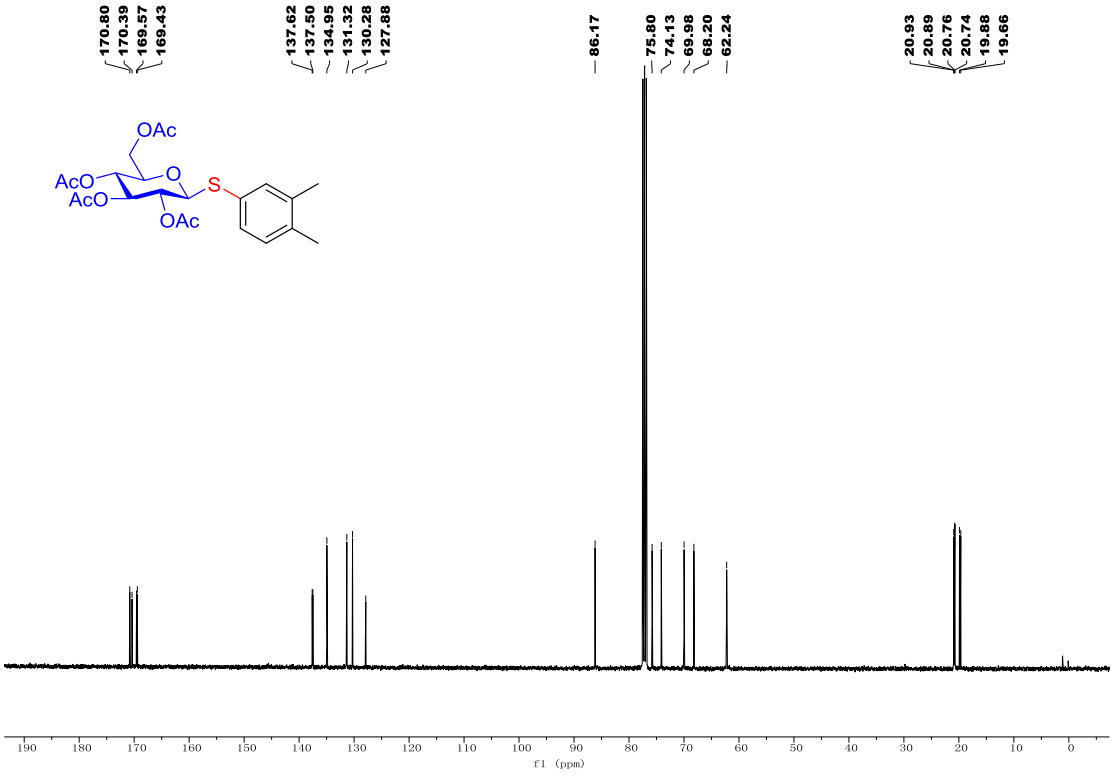
^{13}C NMR (100 MHz, $CDCl_3$) of **4l**



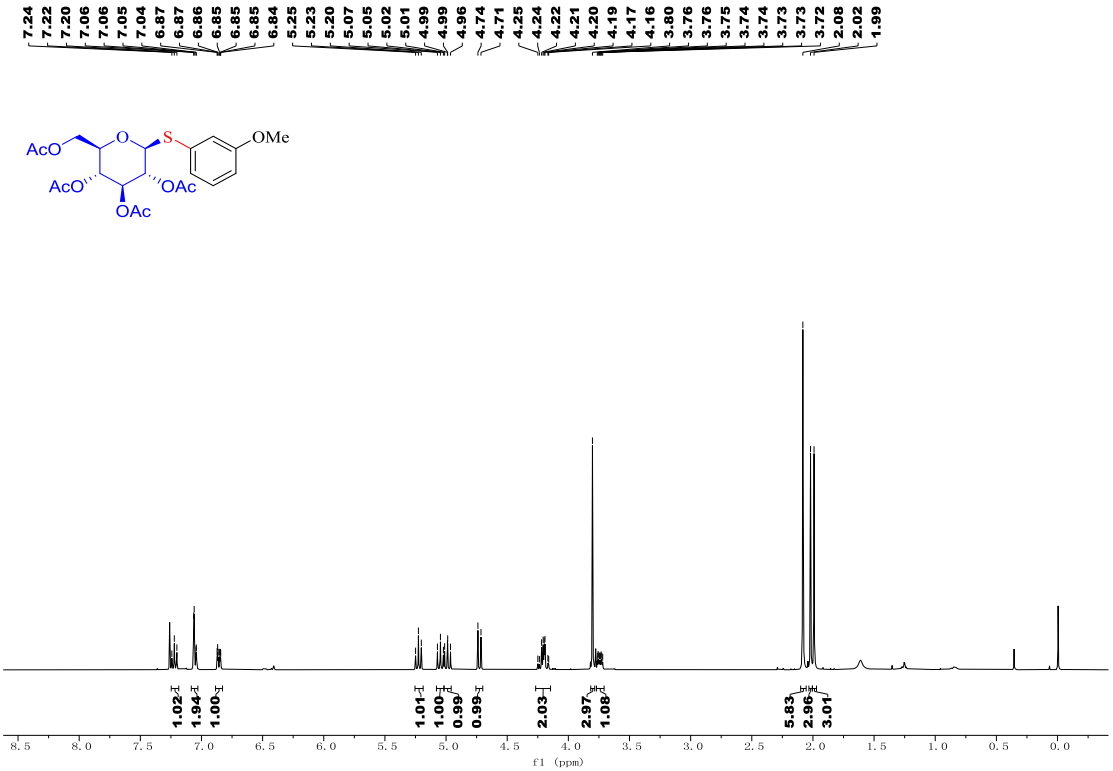
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



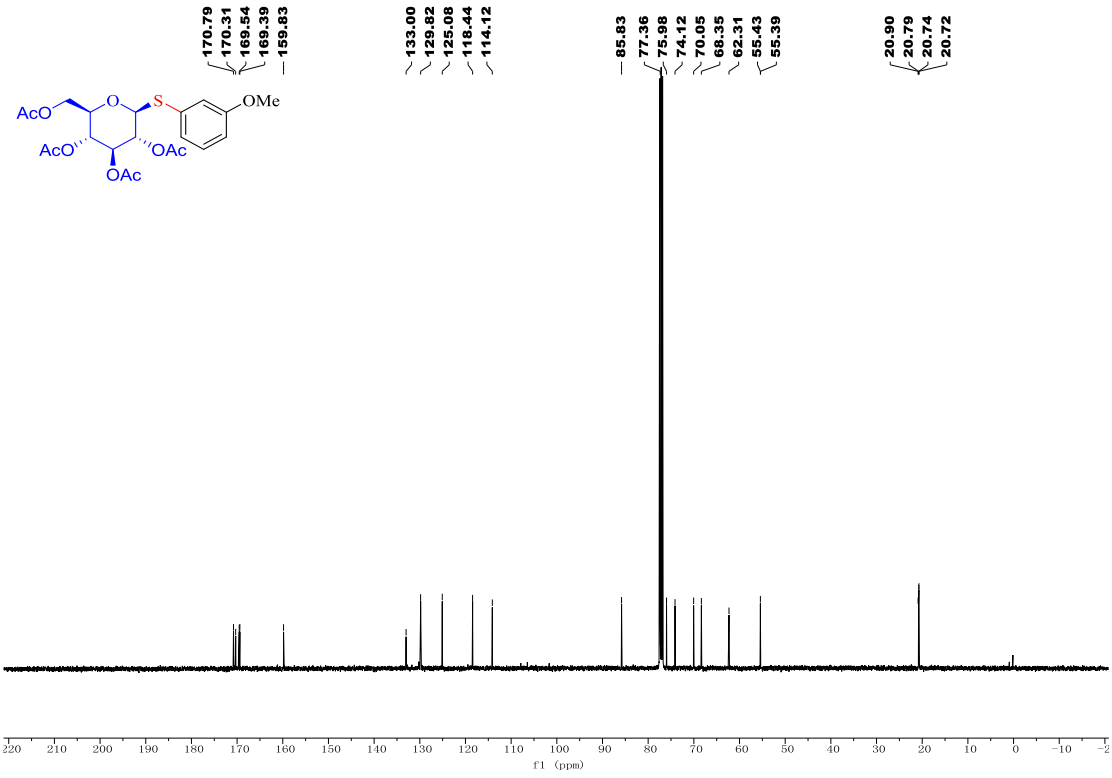
^{13}C NMR (100 MHz, $CDCl_3$) of **4m**



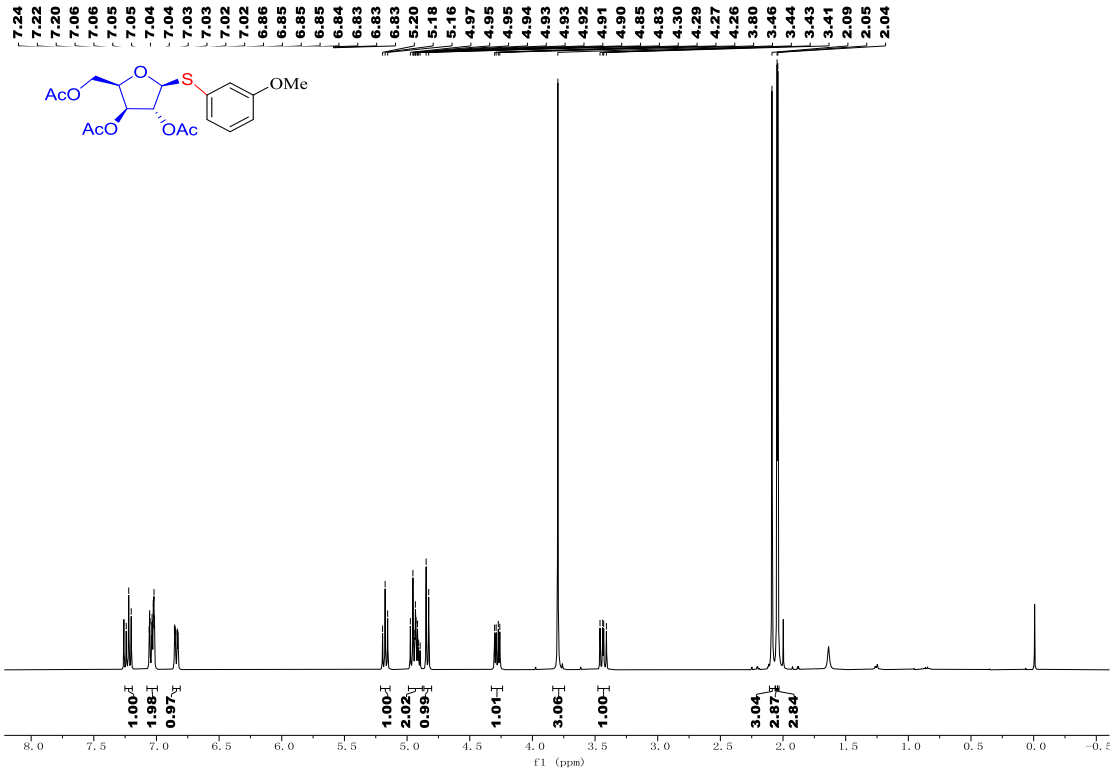
^{1}H NMR (400 MHz, $CDCl_3$) of **4n**



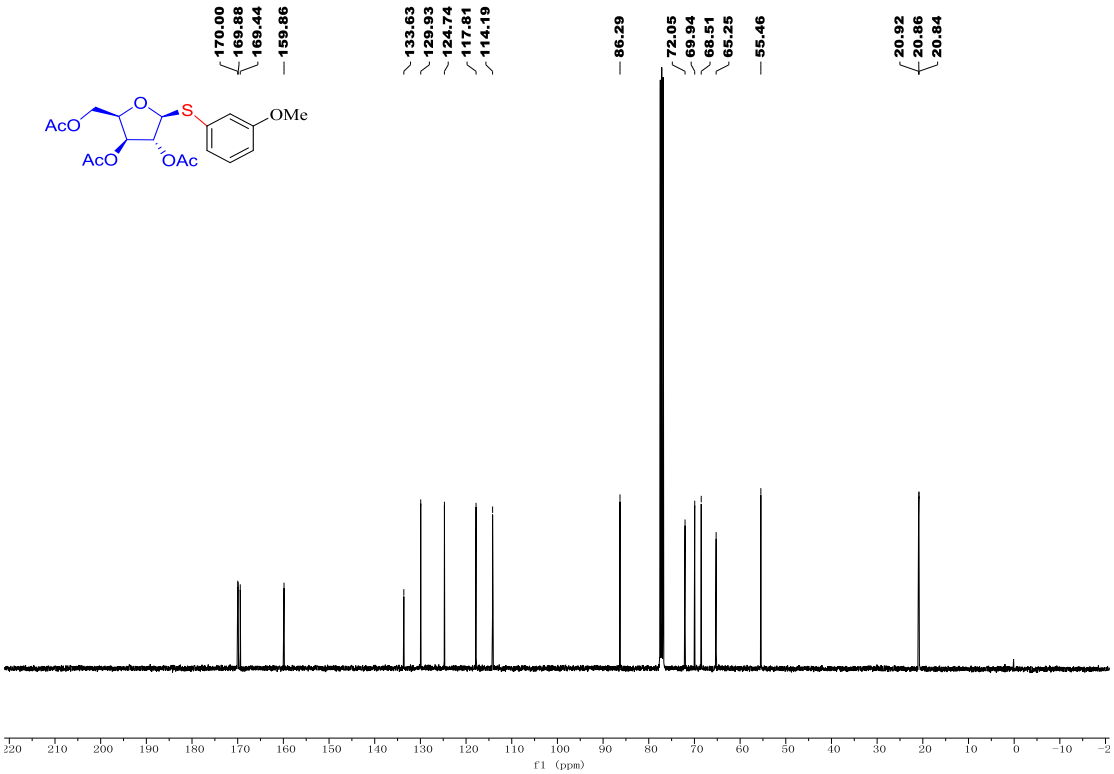
^{13}C NMR (100 MHz, $CDCl_3$) of **4n**



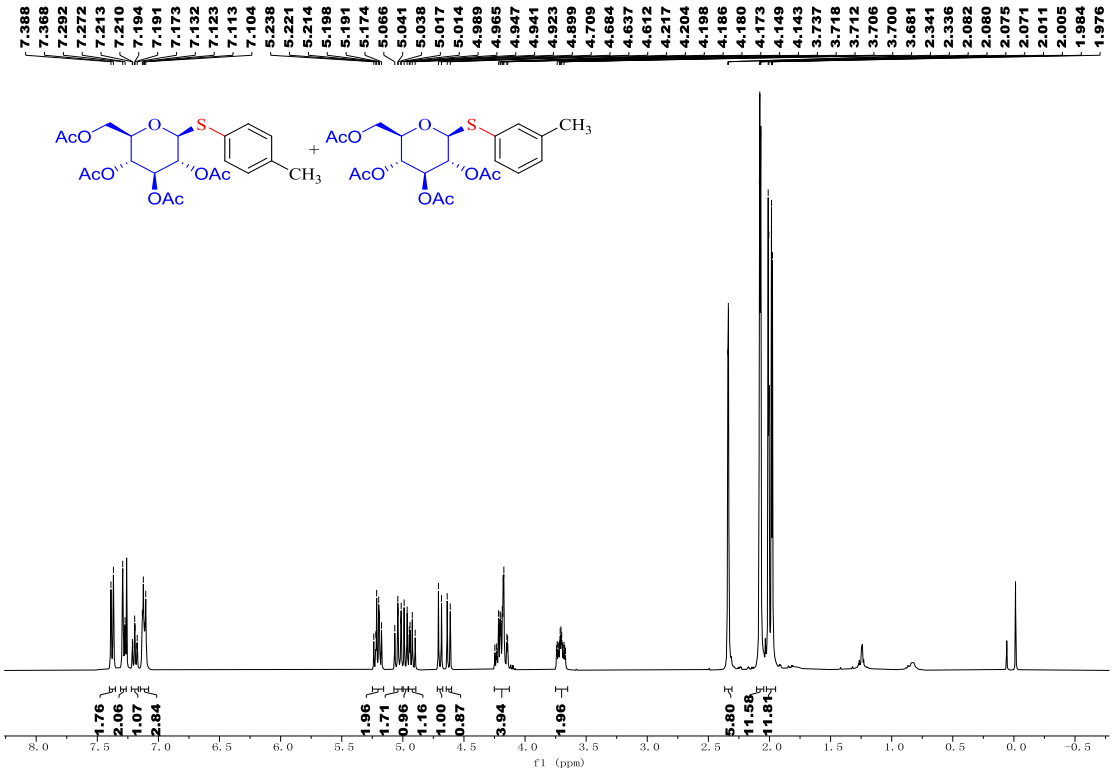
^{1}H NMR (400 MHz, $CDCl_3$) of **4o**



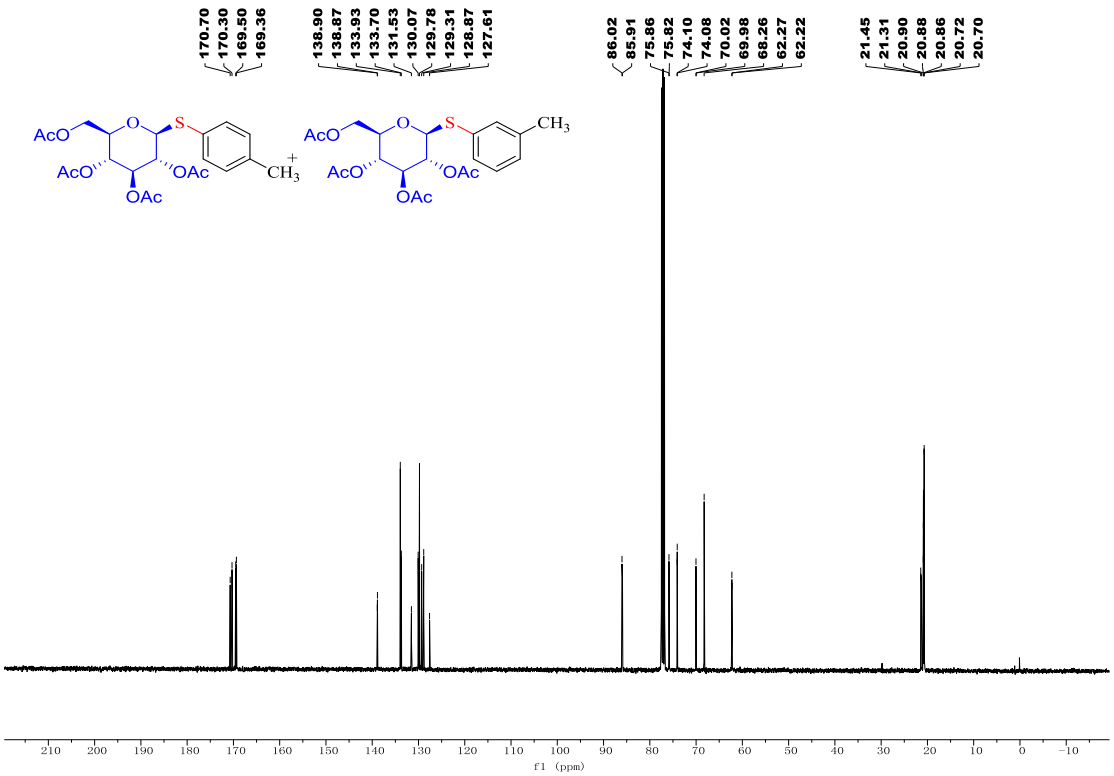
^{13}C NMR (100 MHz, $CDCl_3$) of **4o**



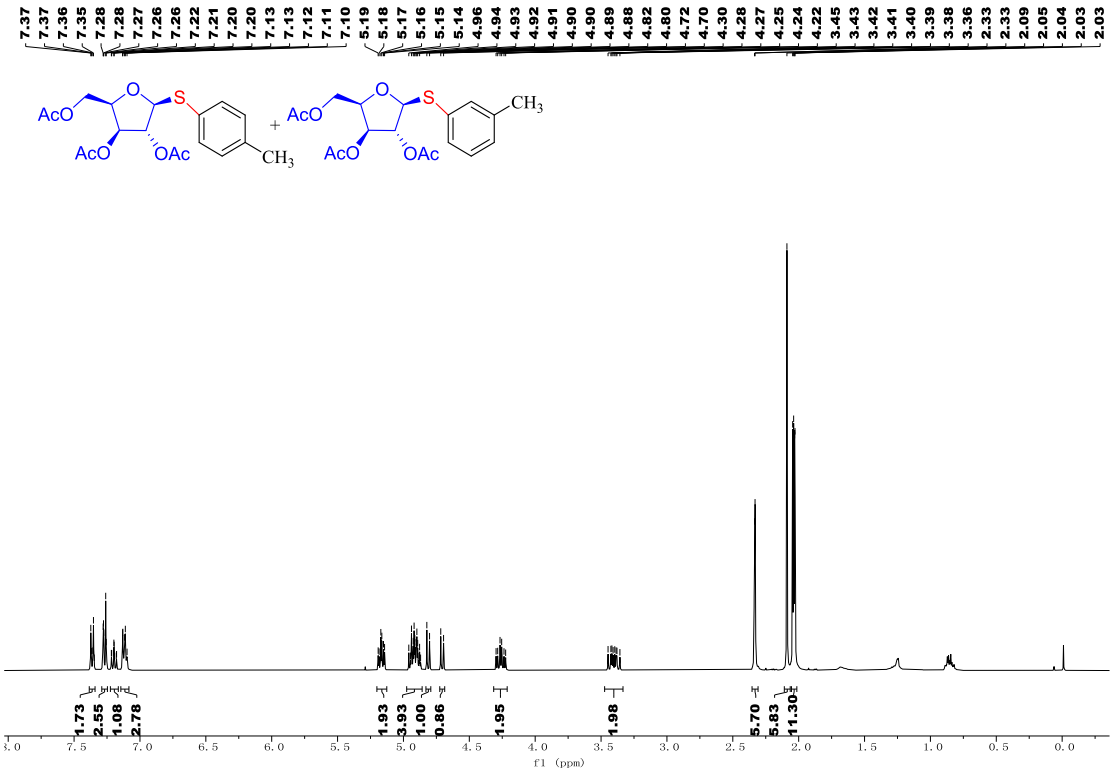
^{1}H NMR (400 MHz, $CDCl_3$) of **4p+4p'**



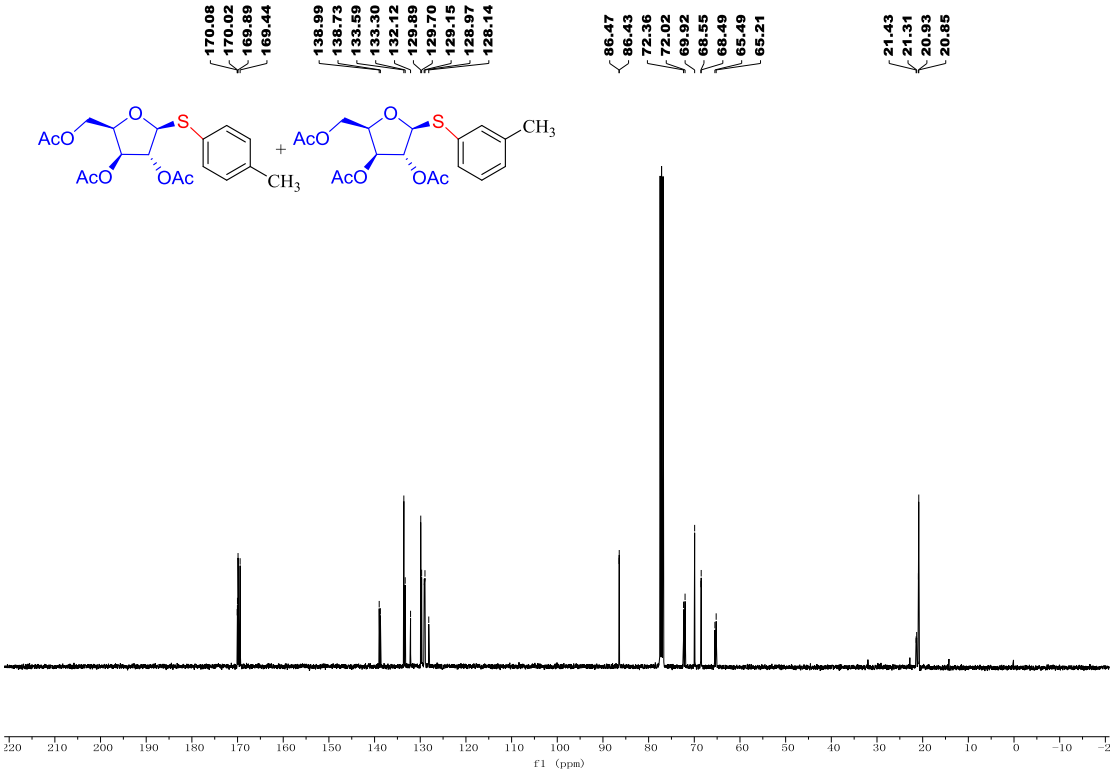
^{13}C NMR (100 MHz, $CDCl_3$) of **4p+4p'**



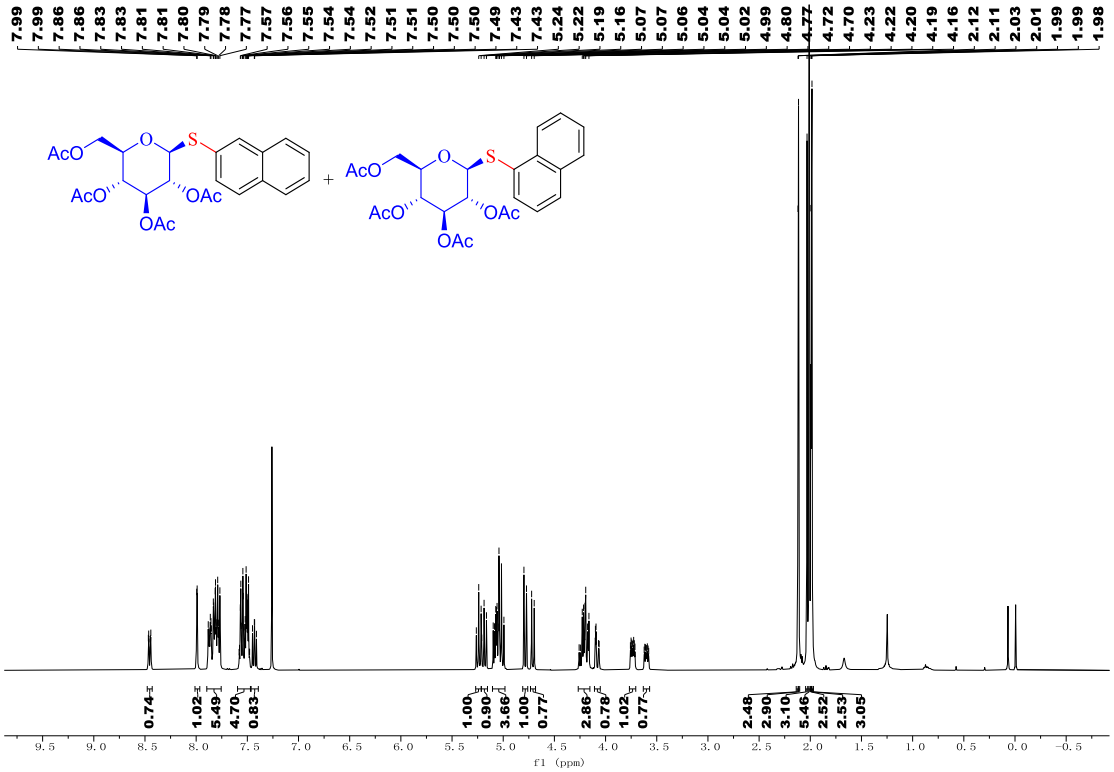
^{1}H NMR (400 MHz, $CDCl_3$) of **4q+4q'**



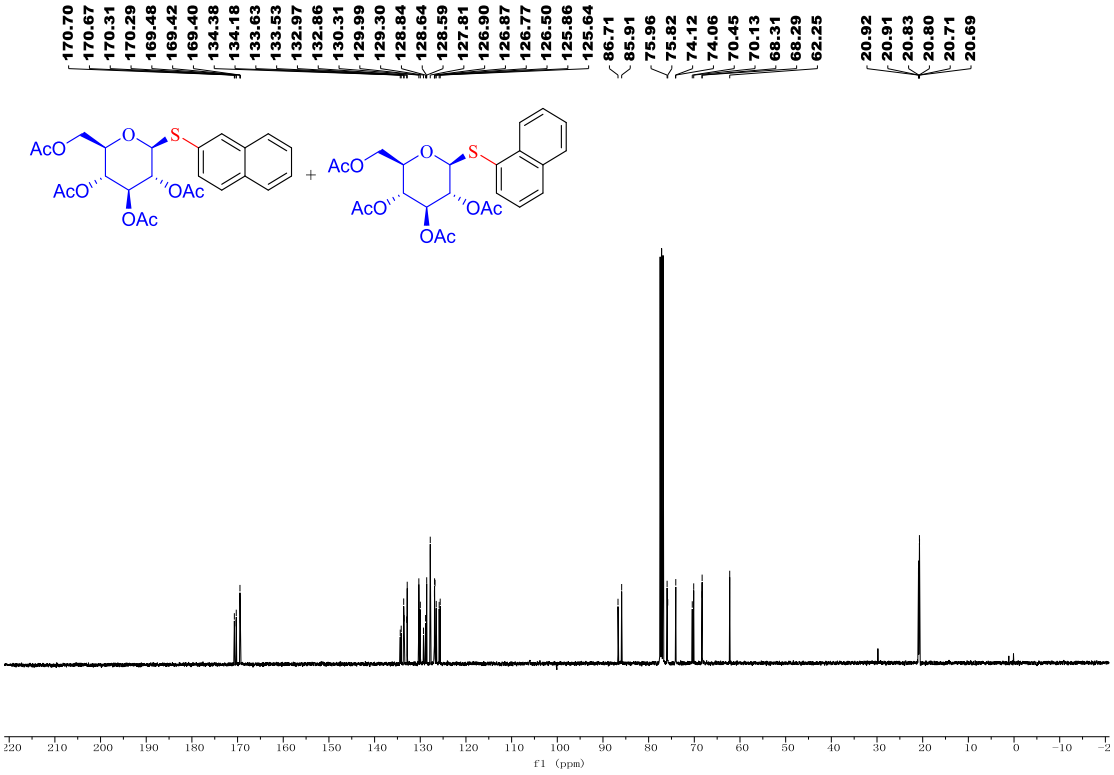
^{13}C NMR (100 MHz, $CDCl_3$) of **4q+4q'**



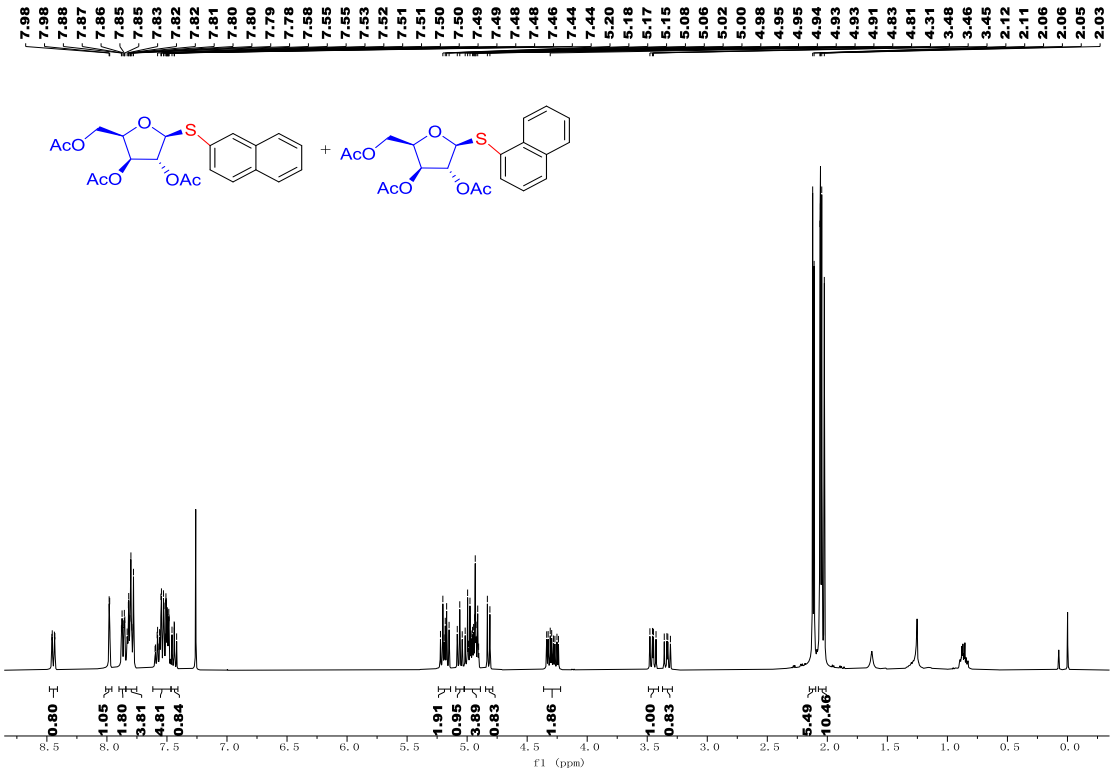
^{1}H NMR (400 MHz, $CDCl_3$) of **4r+4r'**



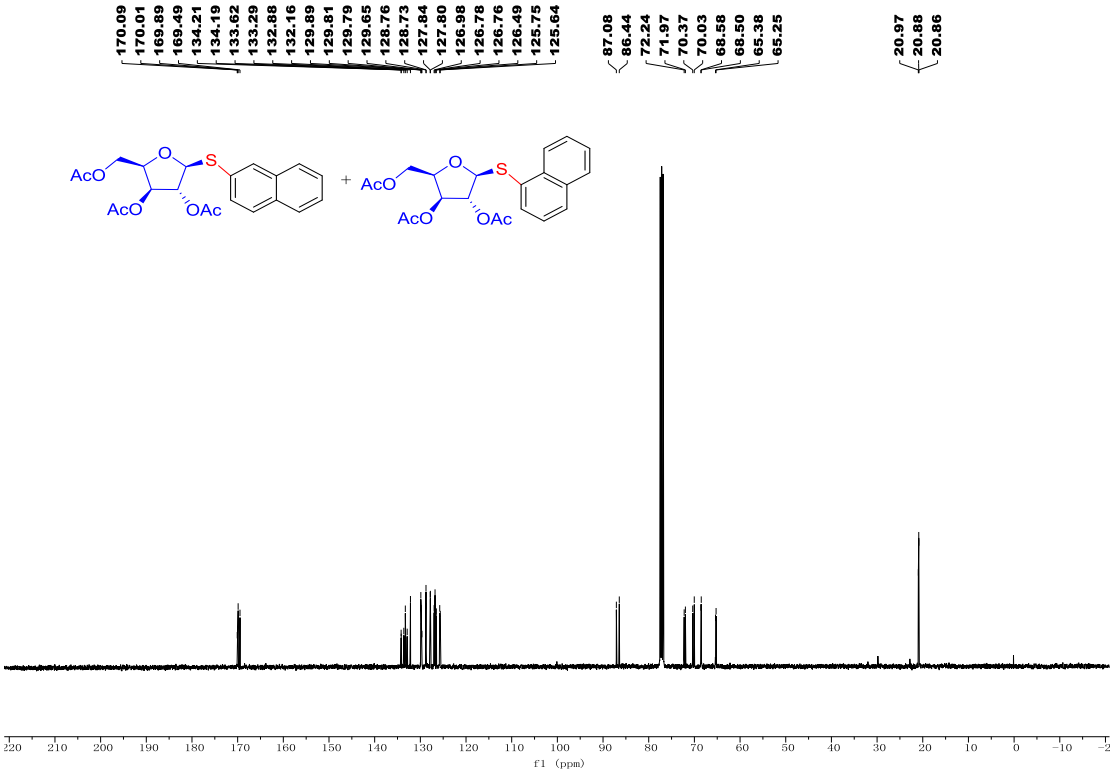
^{13}C NMR (100 MHz, $CDCl_3$) of **4r+4r'**



^{1}H NMR (400 MHz, $CDCl_3$) of **4s+4s'**



^{13}C NMR (100 MHz, $CDCl_3$) of **4s+4s'**



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