Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

# Electrochemical Nickel-Catalyzed Migita Cross-Coupling of Thiosugars with Aryl, alkenyl and alkynyl Bromides

**Table of Contents**

## 1. General information

Solvents and reagents are obtained from commercial suppliers and were used without further purification. Analytical TLC was performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by UV light or by staining upon heating with vanilin solution (15 g of vanilin in 250 mL ethanol and 2.5 mL of concentrated sulfuric acid). For silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230-400 mesh) and p.a. grade solvents unless otherwise noted. The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded in either $CDCl_3$ or MeOD-d4 on Bruker Avance 300 spectrometers. The chemical shifts of $^{1}H$ and $^{13}C$ are reported in ppm relative to the solvent residual peaks. IR spectra were measured on a Bruker Vector 22 spectrophotometer.

Merck silica gel 60 (0.015–0.040 mm) was used for column chromatography. Melting points were recorded on a Büchi B-450 apparatus and are uncorrected. High resolution mass spectra (HR-MS) were recorded on a MicroMass LCT Premier Spectrometer spectrometer. Optical rotations were obtained with a PolAAr 32 polarimeter. Thiosugars were synthesized as according the following protocols.[1, 2]

ElectraSyn 2.0 Package used is from IKA.

### Electrode materials and dimensions

The Mg electrodes were purchased from commercial Mg block (purchased from IKA) and Ni foam electrodes were furnished from Nickel Foam (purchased from IKA).

## 2. General Procedures

**The preparation of Solution A:** A screwed-capped tube with stir bar charged with Ni catalyst (6 mmol) and dtbbpy (6 mmol) were dissolved in 20 mL of DMF under Ar. The solution was stirred for 1 h at 60 $^{o}$C before usage.

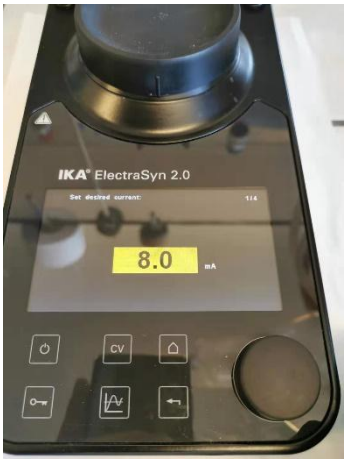
**The preparation of Solution B:** A screwed-capped tube with a stir bar charged with LiBr (8 mmol) was flame-dried under vacuum until the disappearance of water deposit on the walls. The tube was backfilled with an argon balloon and 20 mL of DMF. The solution was stirring for 1 h under room temperature before usage.

An ElectraSyn vial (5 mL) with a stir bar was charged with thiosugar (0.3 mmol, 1 eq), aryl halide (if solid) (0.3 mmol, 1eq). The ElectraSyn vial cap equipped with sacrificial anode (Mg) and cathode (Ni foam) were inserted into the mixture. The vial was then evacuated and backfilled with an argon balloon. And then, aryl halide (if liquid) (0.3 mmol, 1 eq), 1 mL of **Solution A** and 2 mL of **Solution B** was added. The reaction mixture was electrolyzed under a constant current of 8 mA for 3 h at rt. The mixture was dissolved in water and DCM. The layers were separated and the aqueous solution was extracted with further DCM (3×50 mL). The combined organic layers were dried with MgSO4 and the solvent was removed under reduced pressure. Purification was performed with flash chromatography on silica gel.

### 3. Graphical guide for electrochemical C-S thiolation

**Step to step:**






**Left.** Chose “New Experiments”. **Middle.** Chose “Constant Current”. **Right.** Select “8.0 mA”.




**Left. “**Reference electrodes:” chose “No”. **Middle.** Chose “Time”. **Right.** Select “3 hours”.

**Left.** Chose “0.30”. **Middle.** “Polarity” Chose “No”. **Right.** Chose “Start”.



**Left.** Electrode, Mg and Ni form. **Middle.** The mixture before reaction. **Right.** The mixture after reaction.

**Proposed mechanism:**

Based on the previous literature report on the Nickel-catalyzed thiolation of aryl halides and heteroaryl halides through electrochemistry,[3] we could assume that catalytic cycle may be initiated by cathodic reduction of Ni(II) to Ni(0) (Scheme 1). In another hand, glycosyl sulfhydryl group generates a glycosyl thiolate from a cathodic reduction. This later reacts with the complex (**I**) which arises from Ni(0) oxidative addition (OA) with the aryl bromide, to led to a complex (**II**). Reductive elimination (RE) delivers the S-arylated sugar. In a possible alternative of the catalytic cycle, the addition of a formed thiyl radical to the complex (**I**) to generate a Ni(III) complex may be envisioned.[3]

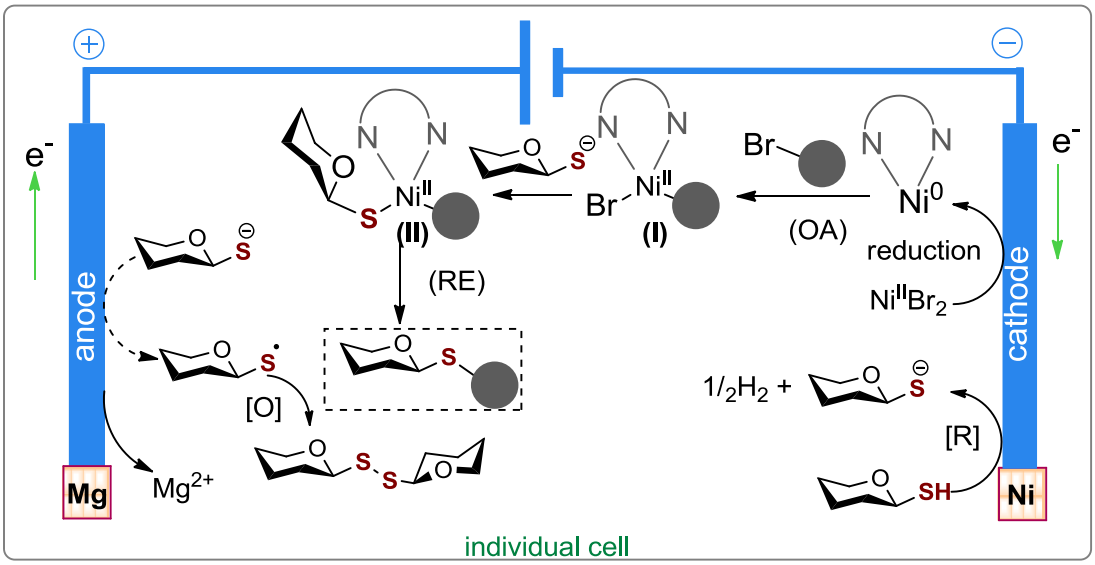



**Figure S1**. Proposed mechanism

**Cyclic voltammetry**

Cyclic voltammetry were performed with AUTOLAB potentiostat/galvanostat PGSTAT302N. A glassy carbon disc (diameter 3 mm) working electrode, a platinum wire counter electrode and a saturated (KCl 3M) calomel electrode (SCE) as reference electrode (Ag wire) were used at a scan rate of 200 mV/s. The experiments were conducted in a 10 mL vial without stirring in DMF (4.5 mL).

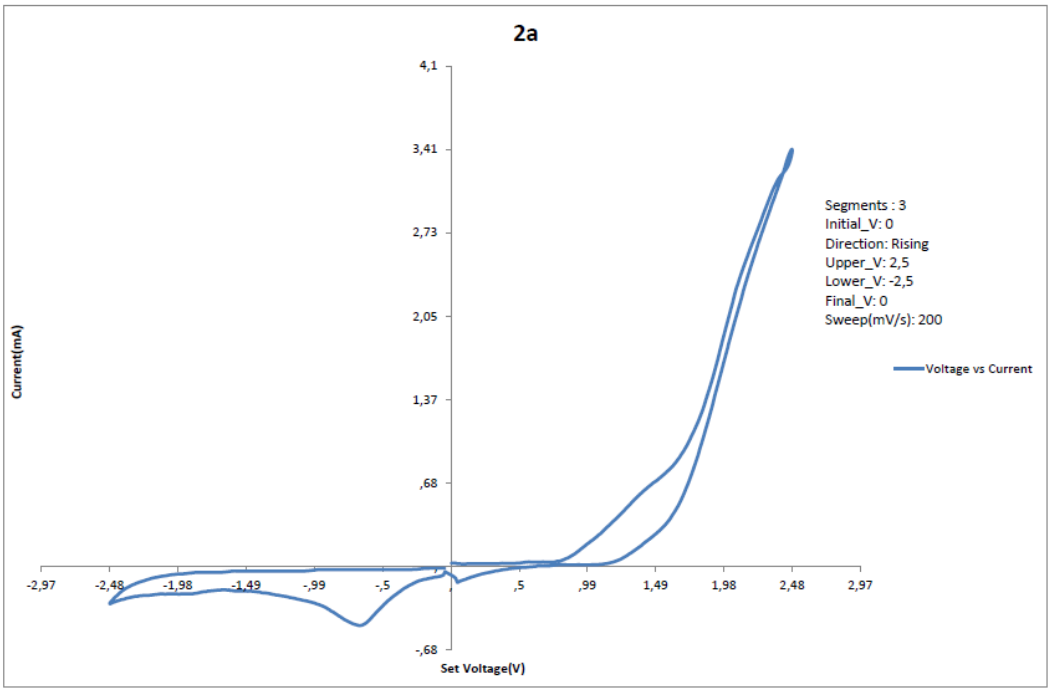



**Figure S2**: Cyclic voltammetry of **2a** (0.45 mmol) in DMF at the [-2.5 to 2.5 V] range vs SCE

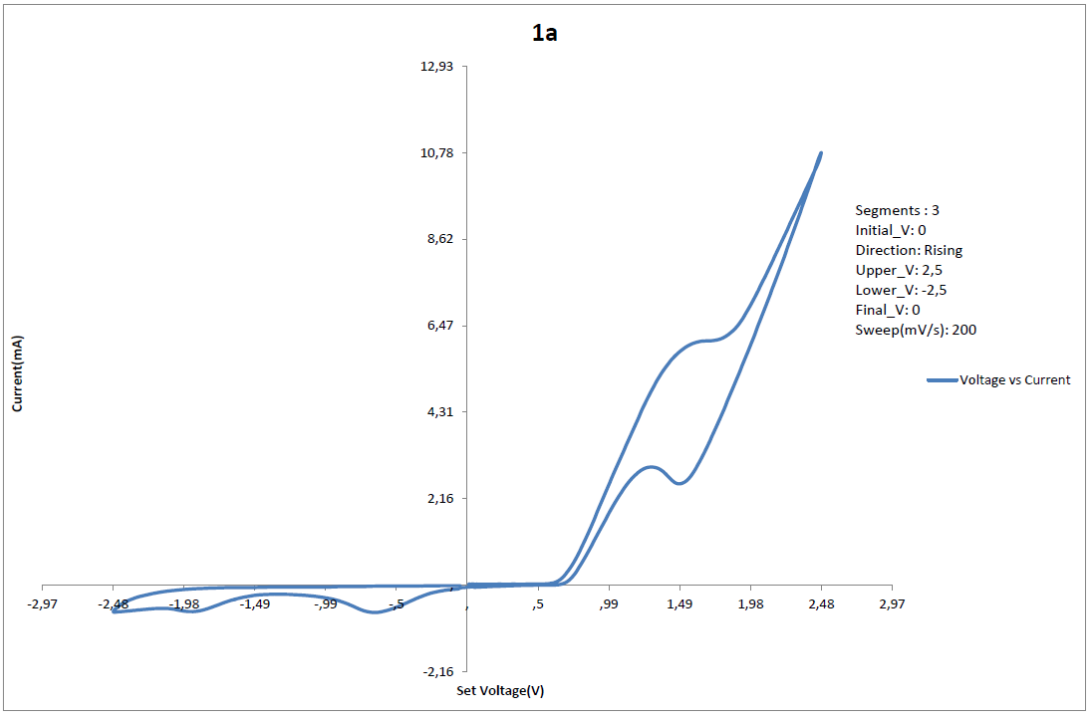



**Figure S3**: Cyclic voltammetry of **1a** (0.45 mmol) in DMF at the [-2.5 to 2.5 V] range vs SCE

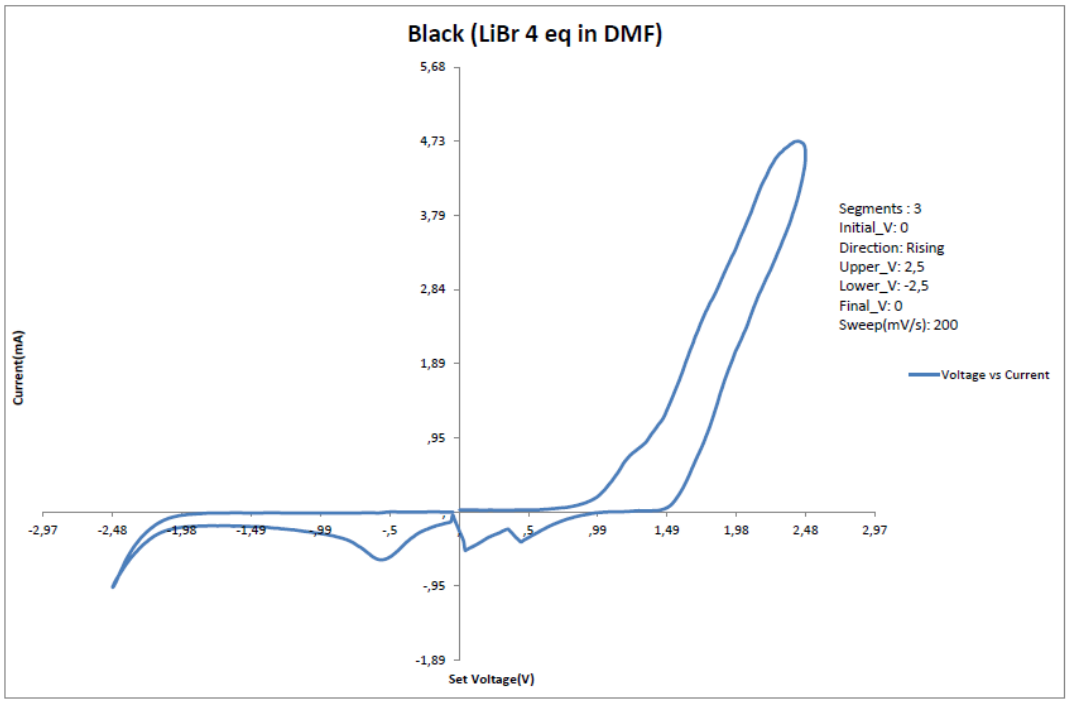



**Figure S3**: Cyclic voltammetry of **LiBr** (1.8 mmol) in DMF at the [-2.5 to 2.5 V] range vs SCE

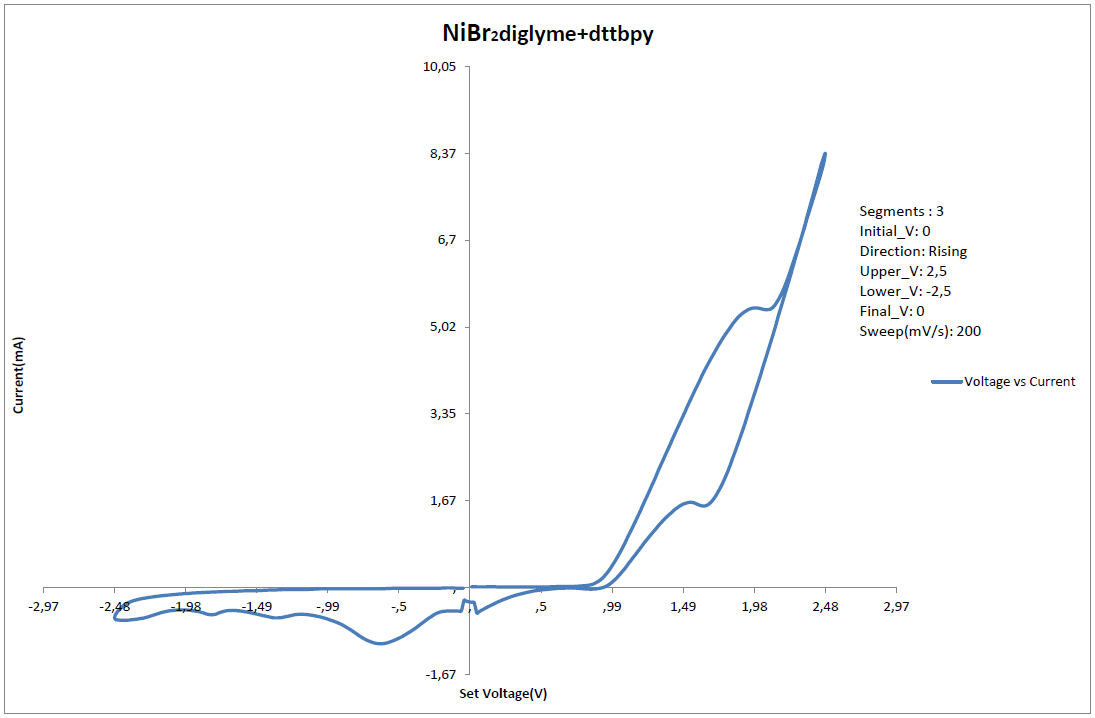



**Figure S4**: Cyclic voltammetry of **NiBr.diglyme** (0.045 mmol) + **dttbpy** (0.045 mmol) in DMF at the [-2.5 to 2.5 V] range vs SCE

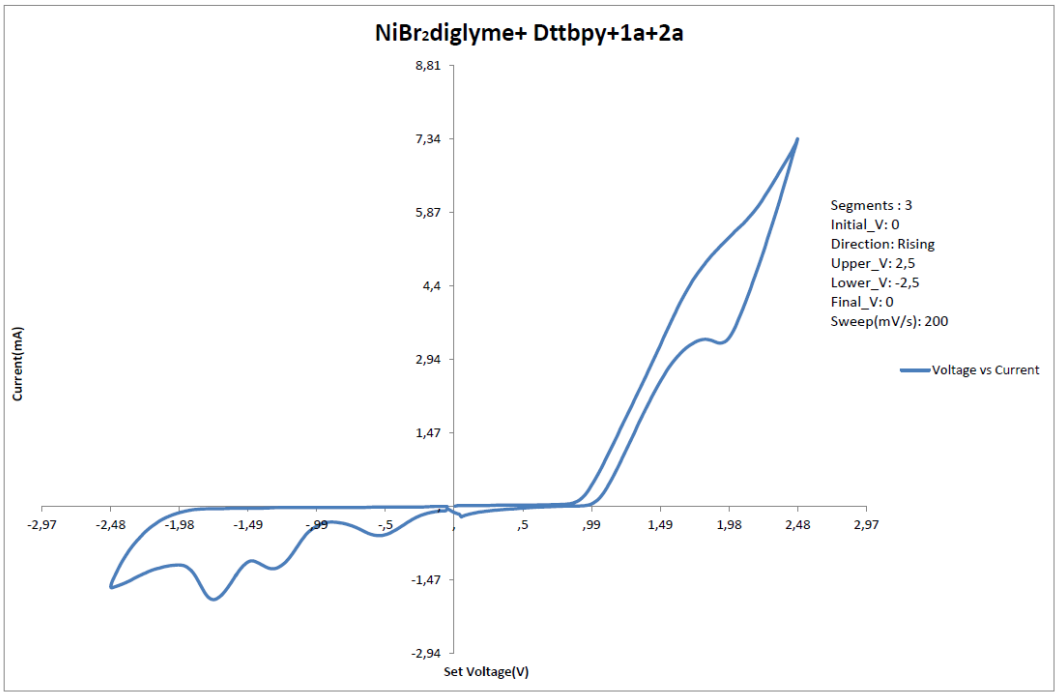
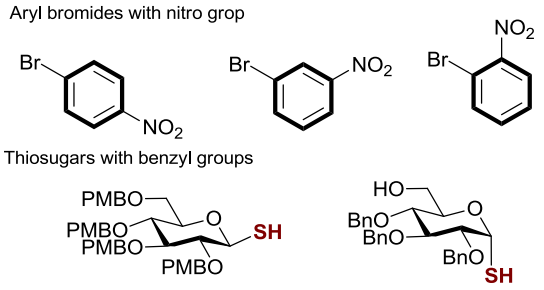



**Figure S5**: Cyclic voltammetry of **1a** (0.45 mmol) + **2a** (0.45 mmol) + NiBr.diglyme + Dttbpy + LiBr in DMF at the [-2.5 to 2.5 V] range vs SCE

**Unsuccessful substrates:**



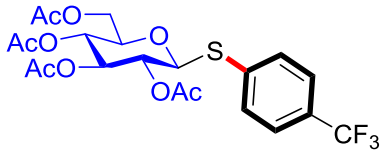

Conclusion:

- The nitro group is not compatible with this procedure.
- Oxidative sensitive groups such as PMB or Bn are not tolerated in this protocol (see SI, Figure S7). Only disulfide dimer was formed during the reaction.

**Figure S7.**

## 3. Experimental data

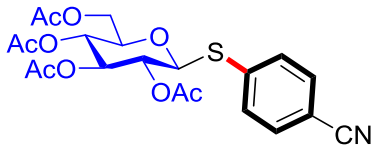
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-(trifluoromethyl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3a** [4]




Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid, $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.53-7.60 (m,

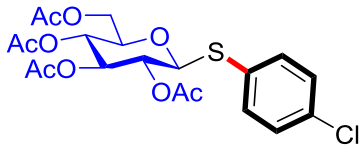
4H), 5.23 (t, *J* = 12.0 Hz, 1H), 5.01 (td, *J* = 9.0, 12.0 Hz, 2H), 4.77 (d, *J* = 9.0 Hz, 1H), 4.14-4.25 (m, 2H), 3.72-3.78 (m, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). HRMS (ESI): m/z calc. for $C_{21}H_{23}F_3NaO_9S$ $[M+Na]^+$ 531.0907; found 531.0897.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-cyanophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3b** [4]



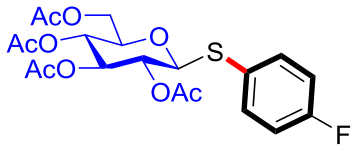

Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, $^1$H NMR (300 MHz, $CDCl_3$) δ 7.51-7.58 (m, 4H), 5.24 (t, *J* = 9.0 Hz, 1H), 5.01 (td, *J* = 12.0, 9.0 Hz, 2H), 4.81 (d, *J* = 9.0 Hz, 1H), 4.13-4.25 (m, 2H), 3.75-3.81 (m, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H). HRMS (ESI): m/z calc. for $C_{21}H_{23}NNaO_9S$ $[M+Na]^+$ 488.0986; found 488.0993.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-chlorophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3c** [4]



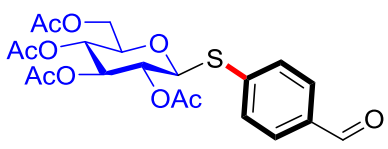

Rf = 0.2 (EtOAc /cyclohexane: 3/7); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 5.20 (t, *J* = 9.0 Hz, 1H), 4.96 (td, *J* = 24.0, 12.0 Hz, 2H), 4.64 (d, *J* = 9.0 Hz, 1H), 4.13-4.23 (m, 2H), 3.67-3.73 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H); HRMS (ESI): m/z calc. for $C_{20}H_{23}ClNaO_9S$ $[M+Na]^+$ 497.0644; found 497.0652.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-fluorophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3d** [4]




Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.46-7.51 (m, 2H), 6.97-7.03 (m, 2H), 5.19 (t, *J* = 9.0 Hz, 1H), 4.94 (td, *J* = 9.0, 30.0 Hz, 2H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.13-4.23 (m, 2H), 3.65-3.71 (m, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H). HRMS (ESI): m/z calc. for $C_{20}H_{23}FNaO_9S$ $[M+Na]^+$ 481.0939; found 481.0937.

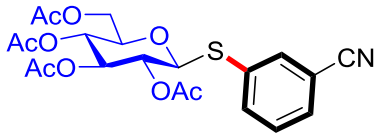
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-formylphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3e**




Rf = 0.3 (EtOAc /cyclohexane: 1/1); colorless oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H),

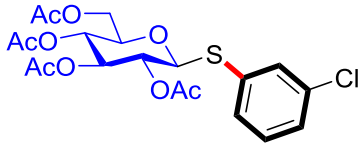
7.80 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 5.26 (t, *J* = 9.0 Hz, 1H), 5.05 (td, *J* = 6.0, 9.0 Hz, 2H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.15-4.27 (m, 2H), 3.78-3.83 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.2 (CH), 170.4 (C), 170.0 (C), 169.3 (C), 169.2 (C), 140.9 (C), 135.3 (C), 130.9 (2CH), 129.9 (2CH), 84.6 (CH), 76.0 (CH), 73.7 (CH), 69.7 (CH), 68.1 (CH), 62.1 ($CH_2$), 20.7 ($CH_3$), 20.6 ($CH_3$), 20.5 ($2CH_3$); IR (neat): 2360, 1755, 1700, 1593, 1564, 1368, 1248, 1173, 1089, 1037, 915, 837, 711 cm$^{-1}$; HRMS (ESI): m/z calc. for $C_{21}H_{24}NaO_{10}S$ $[M+Na]^+$ 491.0988; found 491.0991.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3-cyanophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3f**



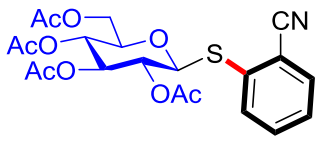

Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 133.2-133.6 °C; $[\alpha]_D^{18}$ = – 29.0 (c, 0.31, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.43 (t, *J* = 9.0 Hz, 1H), 5.24 (t, *J* = 9.0 Hz, 1H), 4.98 (td, *J* = 9.0 Hz, 21.0 Hz, 2H), 4.72 (d, *J* = 9.0 Hz, 1H), 4.16-4.27 (m, 2H), 3.74-3.80 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.6 (C), 170.0 (C), 169.3 (C), 169.1 (C), 137.1 (CH), 135.9 (CH), 133.7 (C), 131.8 (CH), 129.5 (CH), 118.0 (C), 113.4 (C), 84.8 (CH), 76.1 (CH), 73.7 (CH), 69.7 (CH), 68.0 (CH), 62.0 ($CH_2$), 20.7 ($2CH_3$), 20.5 ($2CH_3$); IR (neat): 2988, 2901, 2361, 1754, 1248, 1086, 915, 798 cm$^{-1}$; HRMS (ESI): m/z calc. for $C_{21}H_{23}NNaO_9S$ $[M+Na]^+$ 488.0986; found 488.0993.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3-chlorophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3g [4]**




Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.53 (m, 1H), 7.23-7.38 (m, 3H), 5.25 (t, *J* = 9.0 Hz, 1H), 5.02 (td, *J* = 21.0, 12.0 Hz, 2H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.17-4.28 (m, 2H), 3.74-3.81 (m, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). HRMS (ESI): m/z calc. for $C_{20}H_{23}ClNaO_9S$ $[M+Na]^+$ 497.0644; found 497.0651.

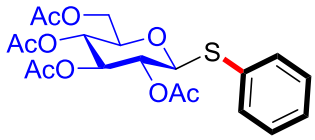
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((2-cyanophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3h**




Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 69.1-70.8 °C; $[\alpha]_D^{18}$ = – 27.9 (c, 0.43,

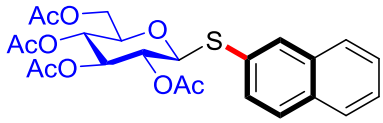
$CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.55 (t, *J* = 6.0 Hz, 1H), 7.45 (t, *J* = 9.0 Hz, 1H), 5.22 (t, *J* = 9.0 Hz, 1H), 4.96 (td, *J* = 9.0 Hz, 30.0 Hz, 2H), 4.75 (d, *J* = 9.0 Hz, 1H), 4.12-4.26 (m, 2H), 3.70-3.76 (m, 2H), 2.12 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 170.4 (C), 170.0 (C), 169.5 (C), 169.3 (C), 135.3 (CH), 134.8 (C), 133.7 (CH), 132.8 (CH), 129.2 (CH), 118.1 (C), 116.9 (C), 85.1 (CH), 76.1 (CH), 73.8 (CH), 69.4 (CH), 68.1 (CH), 62.0 ($CH_2$), 20.7 ($2CH_3$), 20.5 ($2CH_3$); IR (neat): 2360, 2228, 1755, 1469, 1435, 1367, 1248, 1213, 1090, 1062, 1036, 914, 824, 765 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{21}H_{23}NNaO_9S$ $[M+Na]^+$ 488.0986; found 488.0990.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(phenylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3i** [5]



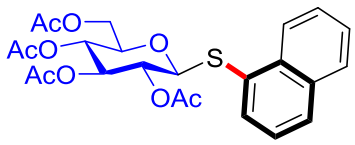

Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.47-7.50 (m, 2H), 7.28-7.31 (m, 3H), 5.21 (t, *J* = 9.0 Hz, 1H), 4.99 (td, *J* = 9.0 Hz, 18.0 Hz, 2H), 4.69 (d, *J* = 9.0 Hz, 1H), 4.13-4.24 (m, 2H), 4.69 (d, *J* = 9.0 Hz, 1H), 4.13-4.24 (m, 2H), 3.68-3.75 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H). HRMS (ESI): m/z calc. for $C_{20}H_{24}NaO_9S$ $[M+Na]^+$ 463.1039; found 463.1038.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(naphthalen-2-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3j**




Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 112.4-113.1 °C; $[\alpha]_D^{18}$ = – 16.0 (c, 0.38, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.75-7.82 (m, 3H), 7.47-7.56 (m, 3H), 5.23 (t, *J* = 9.0 Hz, 1H), 5.02 (td, *J* = 6.0, 9.0 Hz, 2H), 4.78 (d, *J* = 9.0 Hz, 1H), 4.14-4.26 (m, 2H), 3.69-3.74 (m, 1H), 2.10 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 170.5 (C), 170.1 (C), 169.3 (C), 169.2 (C), 133.5 (C), 132.9 (C), 132.7 (CH), 130.2 (CH), 128.8 (C), 128.5 (CH), 127.7 (2CH), 126.7 (2CH), 85.7 (CH), 75.9 (CH), 74.0 (CH), 70.1 (CH), 68.2 (CH), 62.1 ($CH_2$), 20.8 ($CH_3$), 20.7 ($CH_3$), 20.5 ($2CH_3$); IR (neat): 1755, 1367, 1249, 1215, 1091, 1062, 1037, 915, 861, 818, 749 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{24}H_{26}NaO_9S$ $[M+Na]^+$ 513.1195; found 513.1193.

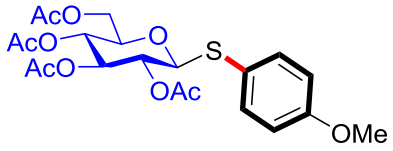
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(naphthalen-1-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3k** [4]




Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.0

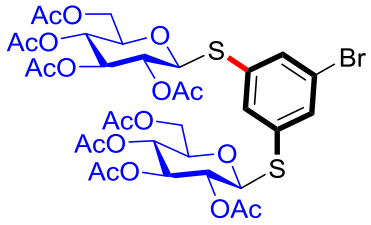
Hz, 1H), 7.81-7.88 (m, 3H), 7.40-7.58 (m, 3H), 5.19 (t, *J* = 9.0 Hz, 1H), 5.02-5.10 (m, 2H), 4.71 (d, *J* = 9.0 Hz, 1H), 4.06-4.21 (m, 2H), 3.57-3.63 (m, H), 2.11 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H). HRMS (ESI): m/z calc. for $C_{24}H_{26}NaO_9S$ $[M+Na]^+$ 513.1190; found 513.1195.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-methoxyphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3l[4]**



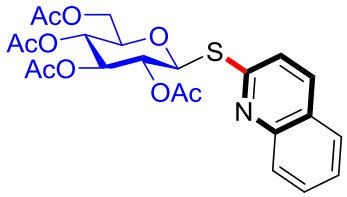

Rf = 0.2 (EtOAc /cyclohexane: 7/3); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.18 (t, *J* = 9.0 Hz, 1H), 4.93 (td, *J* = 12.0, 30.0 Hz, 2H), 4.54 (d, *J* = 9.0 Hz, 1H), 4.14-4.24 (m, 2H), 3.80 (s, 3H), 3.63-3.69 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H); HRMS (ESI): m/z calc. for $C_{21}H_{26}NaO_{10}S$ $[M+Na]^+$ 493.1139; found 493.1148.

**2-(acetoxymethyl)-6-((3-bromo-5-(((2S,3R,4S,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)thio)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3m**




Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 151.1-151.3 °C; $[\alpha]_D^{18}$ = – 26.9 (c, 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.44 (s, 1H), 5.23 (t, *J* = 9.0 Hz, 2H), 4.97 (td, *J* = 9.0, 27.0 Hz, 4H), 4.75 (d, *J* = 9.0 Hz, 2H), 4.13-4.26 (m, 4H), 3.75-3.80 (m, 2H), 2.10 (s, 6H), 2.07 (s, 6H),, 2.00 (s, 6H), 1.97 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.6 (2C), 170.0 (2C), 169.3 (2C), 169.1 (2C), 135.2 (CH), 135.0 (2CH), 134.3 (2C), 122.5 (C), 85.1 (2CH), 76.0 (2CH), 73.8 (2CH), 69.8 (2CH), 68.0 (2CH), 62.0 ($2CH_2$), 20.8 ($2CH_3$), 20.6 ($2CH_3$), 20.5 ($4CH_3$); IR (neat): 2359, 1755, 1740, 1367, 1089, 980, 827, 758 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{34}H_{41}BrNaO_{18}S_2$ $[M+Na]^+$ 903.0815; found 903.0821.

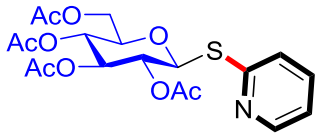
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(quinolin-2-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3n**




Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 155.9-156.4 °C; $[\alpha]_D^{18}$ = + 2.6(c, 0.38, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.91-7.96 (m, 2H), 7.63-7.75 (m, 2H), 7.46 (t, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.13 (d, *J* = 9.0 Hz, 1H), 5.43 (t, *J* = 9.0 Hz, 1H), 5.28 (t, *J* = 9.0 Hz, 1H), 5.17 (t, *J* = 9.0 Hz, 1H), 4.25 (dd, *J* = 3.0, 12.0 Hz, 1H), 4.04-4.14 (m, 1H), 3.98-4.01 (m,

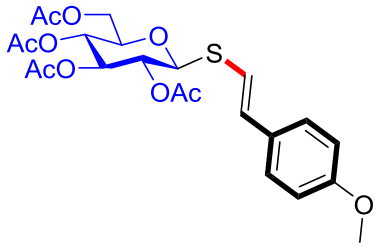
1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.6 (C), 170.2 (C), 169.5 (2C), 155.3 (C), 148.1 (C), 136.2 (CH),129.9 (CH), 128.3 (CH), 127.7 (CH), 126.5 (C), 125.9 (CH), 121.0 (CH), 81.1 (CH), 76.1 (CH), 74.3 (CH), 69.4 (CH), 68.6 (CH), 62.1 ($CH_2$), 20.6 ($4CH_3$). IR (neat): 2360, 1755, 1296, 1090, 1062, 825, 772 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{23}H_{25}NNaO_9S$ $[M+Na]^+$ 514.1148; found 514.1151.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(pyridin-2-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3o [6]**



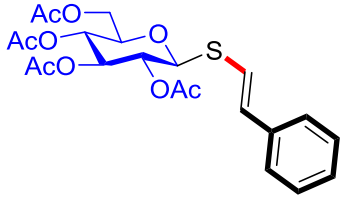

Rf = 0.2 (EtOAc /cyclohexane: 1/1); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.38 (m, 1H), 7.45-7.51 (m, 1H), 7.14-7.17 (m, 1H), 6.99-7.03 (m, 1H), 5.77 (d, *J* = 12.0 Hz, 1H), 5.30 (t, *J* = 9.0 Hz, 1H), 5.12 (td, *J* = 12.0 Hz, 21.0 Hz, 2H), 4.20 (dd, *J* = 3.0, 12.0 Hz, 1H), 4.01-4.06 (m, 1H), 3.80-3.86 (m, 1H), 1.97 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H). HRMS (ESI): m/z calc. for $C_{19}H_{23}NNaO_9S$ $[M+Na]^+$ 464.0991; found 464.0996.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((E)-4-methoxystyryl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3p [4]**




Rf = 0.3 (EtOAc /cyclohexane: 1/1); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 15.0 Hz, 1H), 6.59 (d, *J* = 15.0 Hz, 1H), 5.27 (t, *J* = 9.0 Hz, 1H), 5.08-5.16 (m, 2H), 4.62 (d, *J* = 9.0Hz, 1H), 4.16-4.31 (m, 2H), 3.83 (s, 3H), 3.76-3.80 (m, 1H), 2.09 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); HRMS (ESI): m/z calc. for $C_{23}H_{28}NaO_{10}S$ $[M+Na]^+$ 519.1295; found 519.1307.

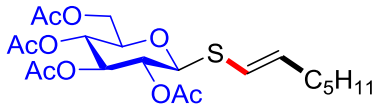
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((E)-styryl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3q**




Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 114.3-115.5 °C; $[\alpha]_D^{18}$ = – 42.3 (c, 0.36, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.27-7.28 (m, 2H), 7.15-7.23 (m, 2H), 6.70 (s, 2H), 5.21 (t, *J* = 9.0 Hz, 1H), 5.02-5.11 (m, 2H), 4.61 (d, *J* = 9.0 Hz, 1H), 4.09-4.24 (m, 2H), 3.70-3.76 (m, 1H), 2.01 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.5 (C),

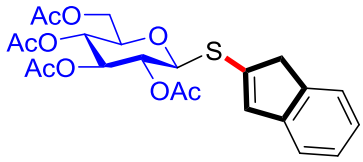
170.1 (C), 169.3 (C), 169.2 (C), 136.3 (C), 134.8 (CH), 128.7 (2CH), 128.0 (CH), 126.2 (2CH), 118.3 (CH), 83.6 (CH), 76.1 (CH), 73.8 (CH), 69.9 (CH), 68.2 (CH), 62.1 ($CH_2$), 20.6 ($2CH_3$),20.5 ($2CH_3$). IR (neat): 2360, 1755, 1433, 1248, 1091, 1062, 915, 773 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{22}H_{26}NaO_9S$ $[M+Na]^+$ 489.1195; found 489.1198.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((E)-hept-1-en-1-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3r**



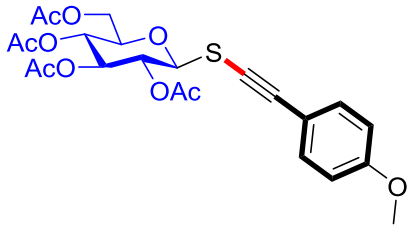

Mixture of *E* and *Z*. Rf = 0.3 (EtOAc /cyclohexane: 1/1); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 5.74-6.06 (m, 2H), 5.21 (t, *J* = 9.0 Hz, 1H), 5.01-5.12 (m, 2H), 4.54 (d, *J* = 12.0 Hz, 0.4H), 4.48 (d, *J* = 12.0 Hz, 0.6H), 4.10-4.24 (m, 2H), 3.70-3.75 (m, 1H), 2.10-2.14 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.27-1.44 (m, 6H), 0.85-0.91 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.6 (C), 170.2 (C), 169.4 (C), 169.1 (C), 140.2 (CH), 134.7 (CH), 118.0 (CH), 116.2 (CH), 83.8 (CH), 83.5 (CH), 76.1 (CH), 76.0 (CH), 74.0 (CH), 73.9 (CH), 70.1 (CH), 69.8 (CH), 68.3 (CH), 62.1 ($CH_2$), 33.2 ($CH_2$), 31.4 ($CH_2$), 31.3 ($CH_2$), 29.2 ($CH_2$), 28.5 ($CH_2$), 28.4 ($CH_2$), 22.4 ($CH_2$), 20.7 ($CH_3$), 20.6 ($3CH_3$), 14.0 ($CH_3$). IR (neat): 2959, 2930, 2856, 1757, 1433, 1367, 1248, 1214, 1092, 1036, 915 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{21}H_{32}NaO_9S$ $[M+Na]^+$ 483.1665; found 483.1656.

**(2S,3R,4S,5R,6R)-2-((1H-inden-2-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3s**



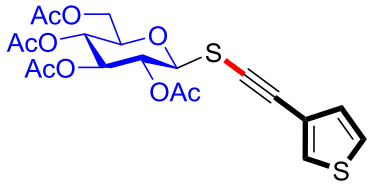

Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 92.0-93.6 °C; $[\alpha]_D^{18}$ = – 46.9 (c, 0.40, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.0 Hz, 1H), 7.24-7.33 (m, 2H), 7.15-7.20 (m, H), 6.92 (s, 1H), 5.28 (t, *J* = 9.0 Hz, 1H), 5.10 (td, *J* = 6.0, 9.0 Hz, 2H), 4.79 (d, *J* = 9.0 Hz, 1H), 4.18-4.29 (m, 2H), 3.78-3.84 (m, 1H), 3.49-3.66 (m, 2H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.5 (C), 170.1 (C), 169.3 (C), 169.2 (C), 144.1 (C), 143.4 (C), 136.8 (C), 133.7 (CH), 126.7 (CH), 124.9 (CH), 123.2 (CH), 120.4 (CH), 84.2 (CH), 76.0 (CH), 73.8 (CH), 70.0 (CH), 68.3 (CH), 62.2 ($CH_2$), 43.7 ($CH_2$), 20.7 ($2CH_3$), 20.5 ($2CH_3$); IR (neat): 2360, 1755, 1457, 1367, 1248, 1090, 925, 754 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{23}H_{26}NaO_9S$ $[M+Na]^+$ 501.1195; found 501.1189.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((4-methoxyphenyl)ethynyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3t**



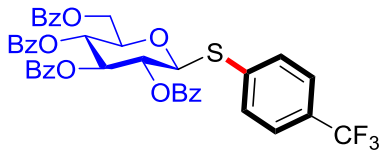

Rf = 0.3 (EtOAc /cyclohexane: 3/7); White solid, m. p.: 78.7-79.8 °C; $[\alpha]_D^{18}$ = – 41.7 (c, 0.24, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.33-7.46 (m, 2H), 6.83-6.89 (m, 2H), 5.21-5.34 (m, 2H), 5.12 (t, *J* = 9.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.13-4.29 (m, 2H), 3.81 (s, 3H), 3.75-3.81 (m, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.6 (C), 170.2 (C), 169.3 (C), 169.0 (C), 160.3 (C), 134.1 (2CH), 114.7 (C), 114.0 (2CH), 97.1 (C), 84.6 (CH), 80.6 (C), 76.5 (CH), 74.0 (CH), 69.8 (CH), 68.0 (CH), 62.0 ($CH_2$), 55.3 ($CH_3$), 20.7 ($CH_3$),20.6 ($CH_3$), 20.5 ($2CH_3$). IR (neat): 2360, 1756, 1605, 1509, 1442, 1367, 1292, 1251, 1214, 1174, 1091, 1061, 1033, 913, 836, 775 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{23}H_{26}NaO_{10}S$ $[M+Na]^+$ 517.1144; found 517.1139.

**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((thiophen-3-ylethynyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 3u** [4]



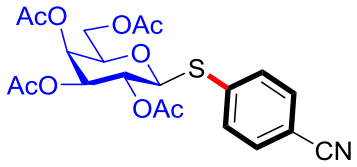

Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.58-7.59 (m, 1H), 7.27-7.29 (m, 1H), 7.17-7.19 (m, 1H), 5.24-5.35 (m, 2H), 5.14 (t, *J* = 9.0 Hz, 1H), 4.62 (d, *J* = 6.0 Hz, 1H), 4.17-4.30 (m, 2H), 3.77 -3.82 (m, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H). HRMS (ESI): m/z calc. for $C_{20}H_{22}NaO_9S_2$ $[M+Na]^+$ 493.0597; found 493.0615.

**(2R,3R,4S,5R,6S)-2-((benzoyloxy)methyl)-6-((4-(trifluoromethyl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate 4a** [4]



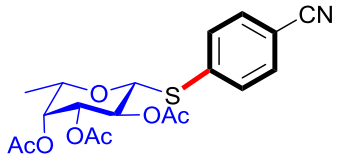

Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.95-8.01 (m, 4H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.26-7.67 (m, 16H), 6.01 (t, *J* = 9.0 Hz, 1H), 5.62 (td, *J* = 12.0, 27.0 Hz, 2H), 5.17 (d, *J* = 9.0 Hz, 1H), 4.74-4.79 (m, 1H), 4.52-4.58 (m, 1H), 4.28-4.34 (m, 1H). HRMS (ESI): m/z calc. for $C_{41}H_{31}F_3NaO_9S$ $[M+Na]^+$ 779.1533; found 779.1543.

**(2R,3S,4S,5R,6S)-2-(acetoxymethyl)-6-((4-cyanophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate 4b** [4]



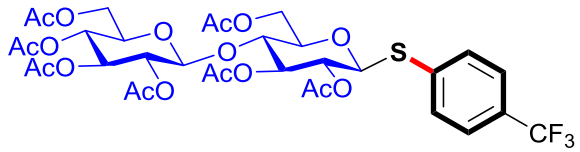

Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.55-7.57 (m, 4H), 5.43 (d, *J* = 3.0 Hz, 1H), 5.24 (t, *J* = 9.0 Hz, 1H), 5.07 (dd, *J* = 3.0, 9.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.08-4.21 (m, 2H), 3.98-4.02 (m, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H). HRMS (ESI): m/z calc. for $C_{21}H_{23}NNaO_9S$ $[M+Na]^+$ 488.0986; found 488.0988.

**(2S,3R,4S,5S,6R)-2-((4-cyanophenyl)thio)-6-methyltetrahydro-2H-pyran-3,4,5-triyl triacetate 4c** [4]




Rf = 0.2 (EtOAc /cyclohexane: 3/7); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.52-7.61 (m, 4H), 5.29 (d, *J* = 3.0 Hz, 1H), 5.24 (t, *J* = 9.0 Hz, 1H), 5.08 (dd, *J* = 3.0, 9.0 Hz, 1H), 4.79 (d, *J* = 9.0 Hz, 1H), 3.90 (q, *J* = 6.0 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.25 (d, *J* = 9.0 Hz, 3H). HRMS (ESI): m/z calc. for $C_{19}H_{21}NNaO_7S$ $[M+Na]^+$ 430.0931; found 430.0933.

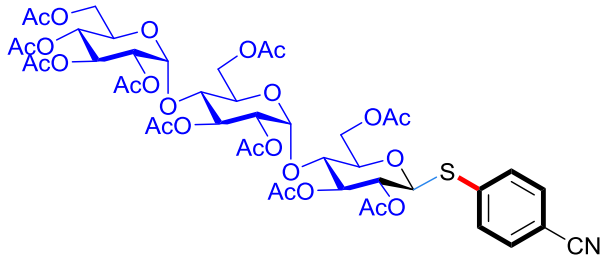
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-((4-(trifluoromethyl)phenyl)thio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate 4d** [4]




Rf = 0.2 (EtOAc /cyclohexane: 1/1); White solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.50-7.56 (m, 4H),5.00-5.22 (m, 3H), 4.86-4.93 (m, 2H), 4.72 (d, *J* = 9.0 Hz, 1H), 4.47-4.56 (m, 2H), 4.33 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.99-4.11 (m, 2H), 3.62-3.75 (m, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H). HRMS (ESI): m/z calc. for $C_{33}H_{39}F_3NaO_{17}S$ $[M+Na]^+$ 819.1752; found 819.1774.

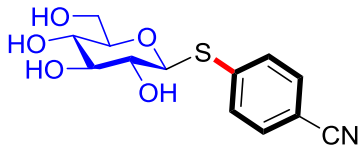
**(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6**

**-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-((4-cyanophenyl)thio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate 4e**



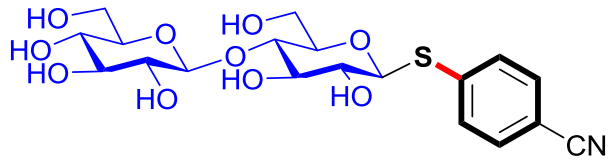

Rf = 0.3 (EtOAc /cyclohexane: 1/1); White solid, m. p.: 128.1-130.6 °C; $[\alpha]_D^{18}$ = – 77.6 (c, 0.34, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.46-7.54 (m, 4H), 5.18-5.34 (m, 5H), 4.99 (t, *J* = 9.0 Hz, 1H), 4.76-4.81 (m, 3H), 4.64-4.69 (m, 1H), 4.38-4.48 (m, 2H), 4.19-4.28 (m, 4H), 3.77-3.97 (m, 4H), 3.74-3.77 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.5 (2C), 170.4 (C), 170.2 (C), 170.1 (C), 169.8 (2C), 169.6 (C), 169.4 (C), 169.3 (C), 138.9 (C), 132.3 (C), 131.7 (2CH), 118.2 (C), 111.4 (C), 95.8 (CH), 95.6 (CH), 83.8 (CH), 76.3 (CH), 75.9 (CH), 73.6 (CH), 72.6 (CH), 71.6 (CH), 70.4 (2CH), 70.0 (CH), 69.3 (CH), 69.1 (CH), 68.5 (CH), 67.9 (CH), 62.9 ($CH_2$), 62.3 ($CH_2$), 61.4 ($CH_2$), 20.8 ($3CH_3$), 20.7 ($2CH_3$), 20.5 ($5CH_3$). IR (neat):2230, 1756, 1747, 1432, 1368, 1239, 1222, 1031, 900, 753 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{45}H_{55}NNaO_{25}S$ $[M+Na]^+$ 1064.2682; found 1064.2688.

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




Rf = 0.3 (EtOAc /MeOH: 9/1); colorless oil $^1$H NMR (300 MHz, MeOD-$d_4$) δ 7.63-7.64 (m, 4H), 4.83 (d, *J* = 9.0 Hz, 1H),3.89-3.94 (m, 1H), 3.61-3.72 (m, 1H), 3.30-3.47 (m, 4H); $^{13}$C NMR (75 MHz, MeOD-$d_4$) δ 144.0 (C), 133.6 (C), 130.6 (2CH), 119.7 (C), 110.5 (C), 87.8 (CH), 82.2 (CH), 79.7 (CH), 73.8 (CH), 71.3 (CH), 62.8 ($CH_2$). IR (neat): 3300, 1754, 1635, 1284, 1102 $cm^{-1}$; HRMS (ESI): m/z calc. for $C_{13}H_{15}NNaO_5S$ $[M+Na]^+$ 320.0569; found 320.0573.

**4-(((2S,3R,4R,5S,6R)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2H-pyran-2-yl)thio)benzonitrile 5b**

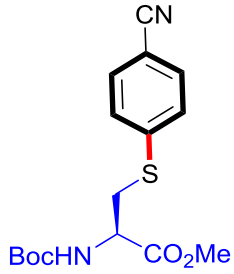



5b

Rf = 0.3 (EtOAc /MeOH: 5/1); White solid, m. p.: 228.5-231.8 °C; $[\alpha]_D^{18}$ = – 74.7 (c, 0.73, MeOH);$^1$H NMR (300 MHz, MeOD-$d_4$) δ 7.59-7.60 (m, 4H), 4.82 (d, *J* = 9.0 Hz, 1H), 4.40 (d, *J* =

6.0 Hz, 1H), 3.83-3.92 (m, 3H), 3.51-3.66 (m, 4H), 3.33-3.38 (m, 2H), 3.18-3.27 (m, 3H); $^{13}$C NMR (75 MHz, MeOD-$d_4$) δ 143.7 (C), 133.4 (2CH), 130.8 (2CH), 119.7 (C), 110.6 (C), 104.5 (CH), 87.5 (CH), 80.6 (CH), 80.1 (CH), 78.1 (CH), 78.0 (CH), 77.9 (CH), 74.9 (CH), 73.6 (CH), 71.4 (CH), 62.5 ($CH_2$), 61.9 ($CH_2$). IR (neat): 3186, 2970, 2406, 1406, 1228, 1025, 926, 740 cm$^{-1}$; HRMS (ESI): m/z calc. for $C_{19}H_{25}NNaO_{10}S$ $[M+Na]^+$ 482.1097; found 482.1088.

**Methyl N-(tert-butoxycarbonyl)-S-(4-cyanophenyl)-L-cysteinate 5c**




Rf = 0.3 (EtOAc /cyclohexane: 1/1); colorless oil; $[\alpha]_D^{18}$ = +32.0 (c, 1.00, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.51-7.54 (m, 2H), 7.26-7.38 (m, 2H), 5.30-5.32 (m, 1H), 4.59-4.62 (m, 1H), 3.67 (s, 3H), 3.51 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.39 (dd, *J* = 3.0, 12.0 Hz, 1H), 1.41 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.6 (C), 154.9 (C), 142.9 (C), 132.3 ($2CH_2$), 128.4 ($2CH_2$), 118.5 (C), 109.4 (C), 53.3 (CH), 52.7 ($CH_3$), 41.2 (C), 35.2 ($CH_3$), 28.2 ($2CH_3$). IR (neat): 2360, 2227, 1748, 1714, 1594, 1487, 1437, 1368, 1255, 1216, 1164, 1088, 1052, 1014, 823, 624 cm$^{-1}$; HRMS (ESI): m/z calc. for $C_{16}H_{20}N_2NaO_4S$ $[M+Na]^+$ 359.1041; found 359.1035.

**4. References**


(1) N. Floyd, B. Vijayakrishnan, J. R. Koeppe, B. G. Davis, *Angew. Chem., Int. Ed.*, **2009**, *48*, 7798-7802.

(2) D.P. Gamblin, P. Garnier, S. van Kasteren, N. J. Oldham, A. J. Fairbanks, B. G. Davis, *Angew. Chem., Int. Ed.*, **2004**, *43*, 828-833.

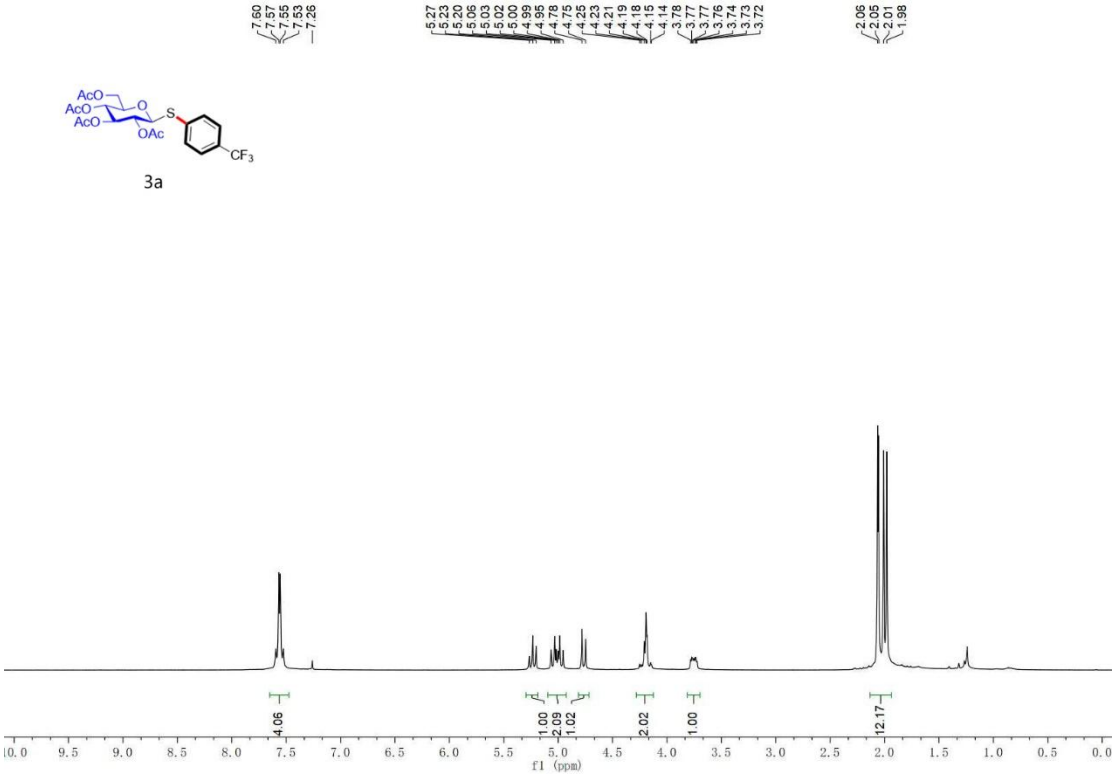
(3) D. Liu, H. Ma, P. Fang, T. Mei, *Angew. Chem. Int. Ed.* **2019**, *58*, 5033- 5037.

(4) M. Zhu, G. Dagousset, M. Alami, E. Magnier, S. Messaoudi, *Org. Lett.*, **2019**, *21*, 5132- 5137.

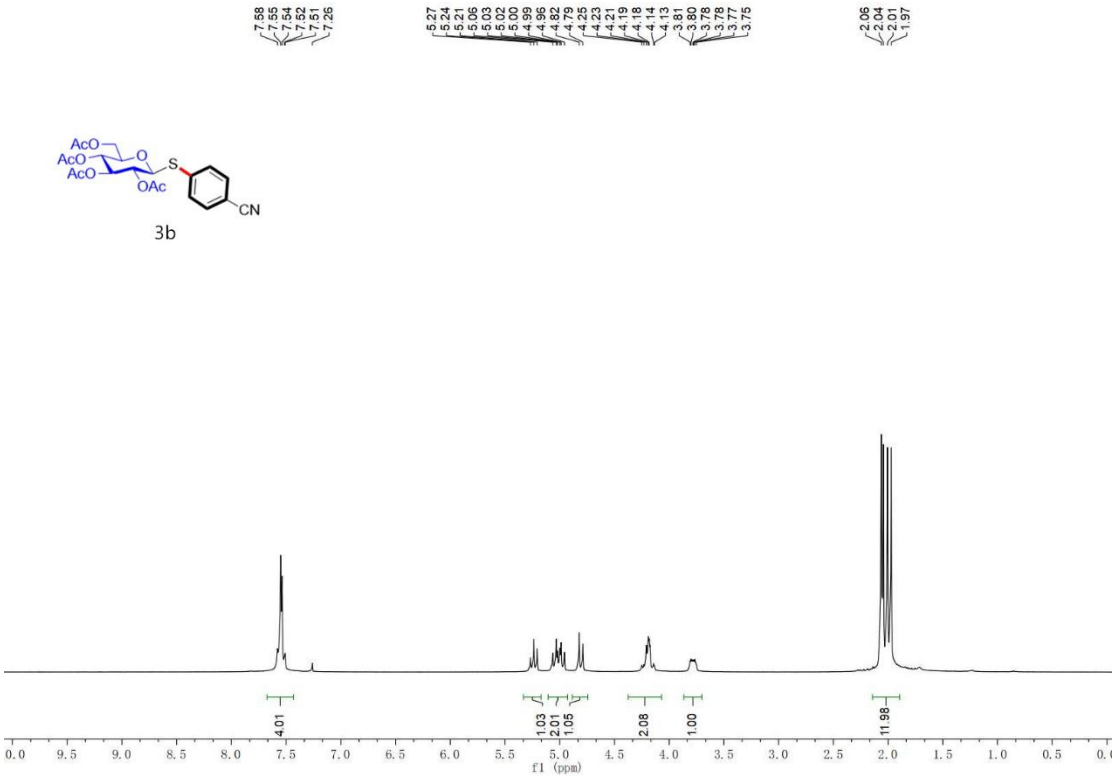
(5) H. G. Thomas, J. Mieusset. *Tetrahedron*, **2008**, *64*, 5124-5131.

(6) A. I. Khodair ,N. Al-Masoudi, J. Gesson, *Nucleos. Nucleot. Nucl*., **2003**, *21*, 2061-2076.

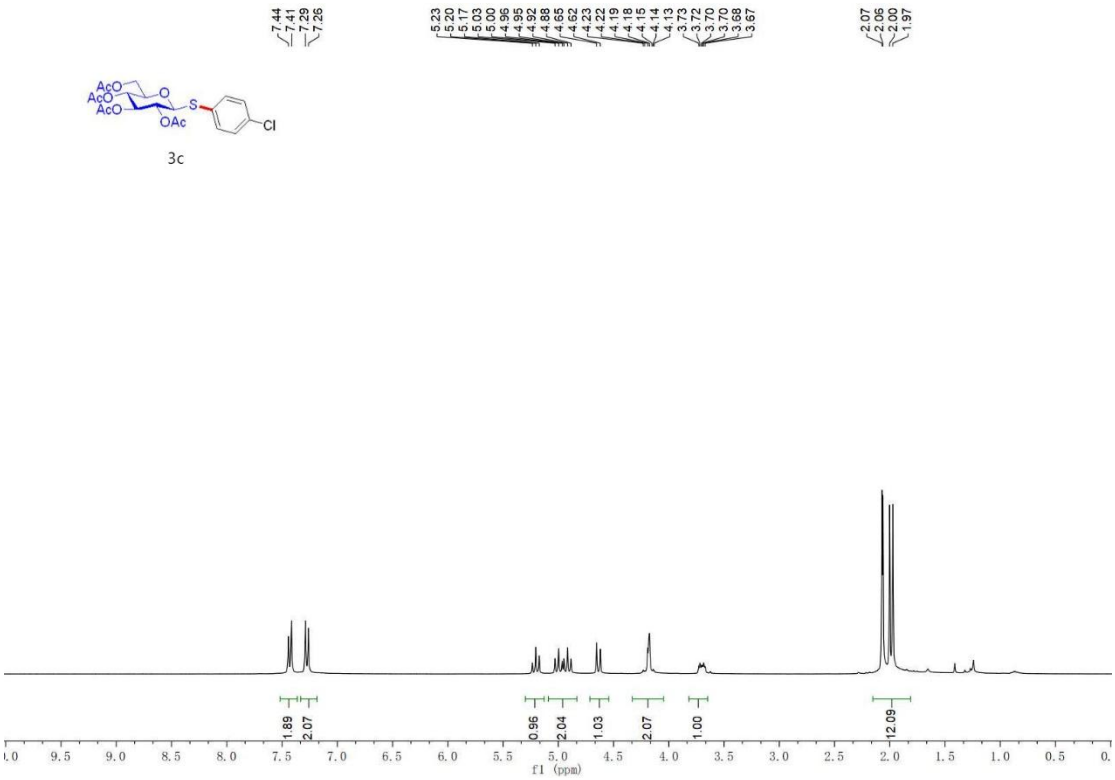
Spectra of compounds **3a-u**, **4a-e**, **5a-c**



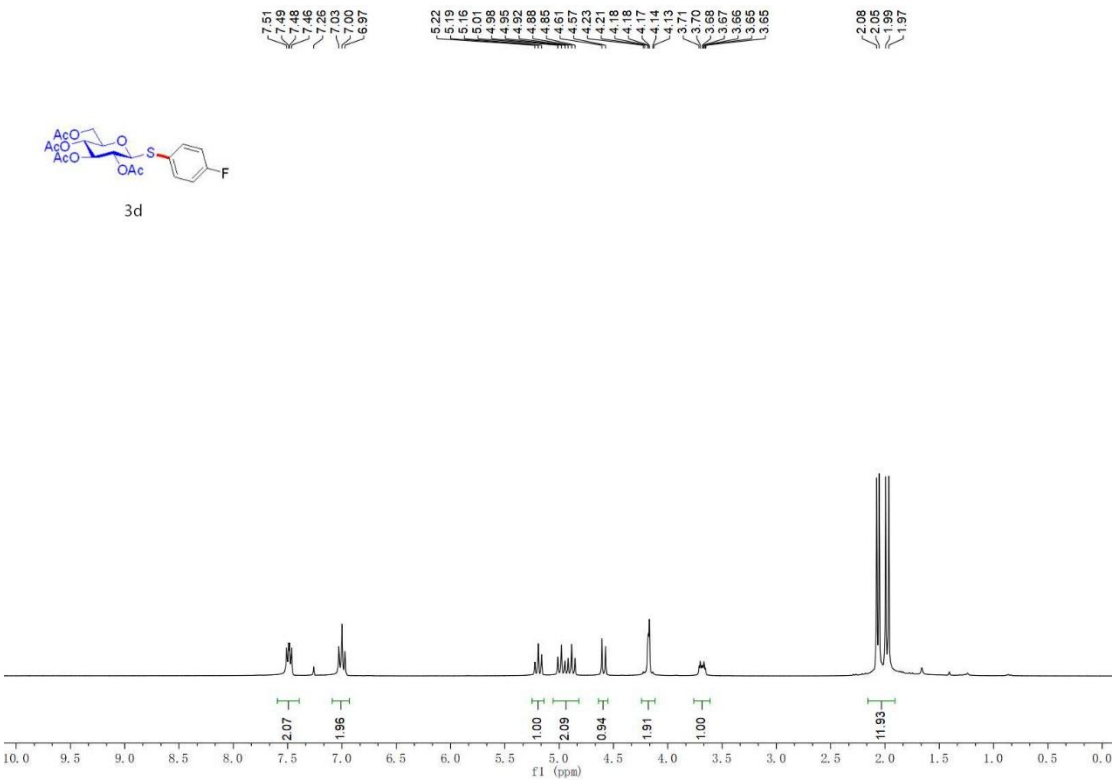

$^1$H NMR spectrum of **3a** (300 MHz, $CDCl_3$)



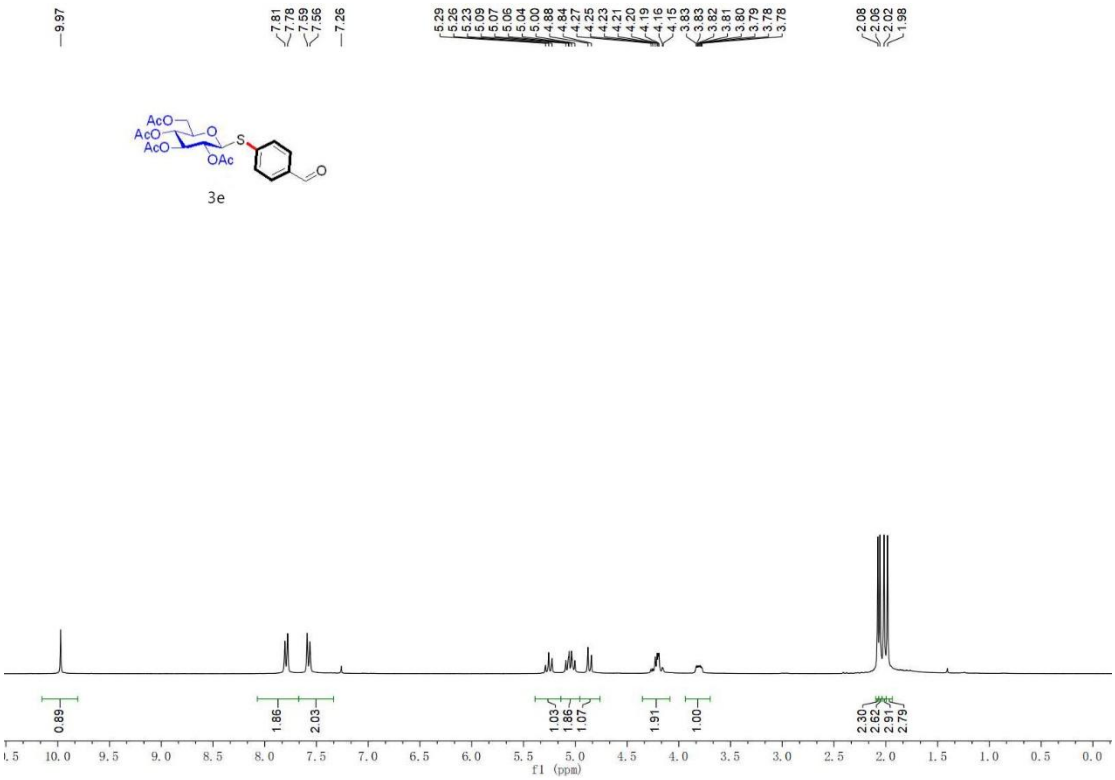

$^1$H NMR spectrum of **3b** (300 MHz, $CDCl_3$)



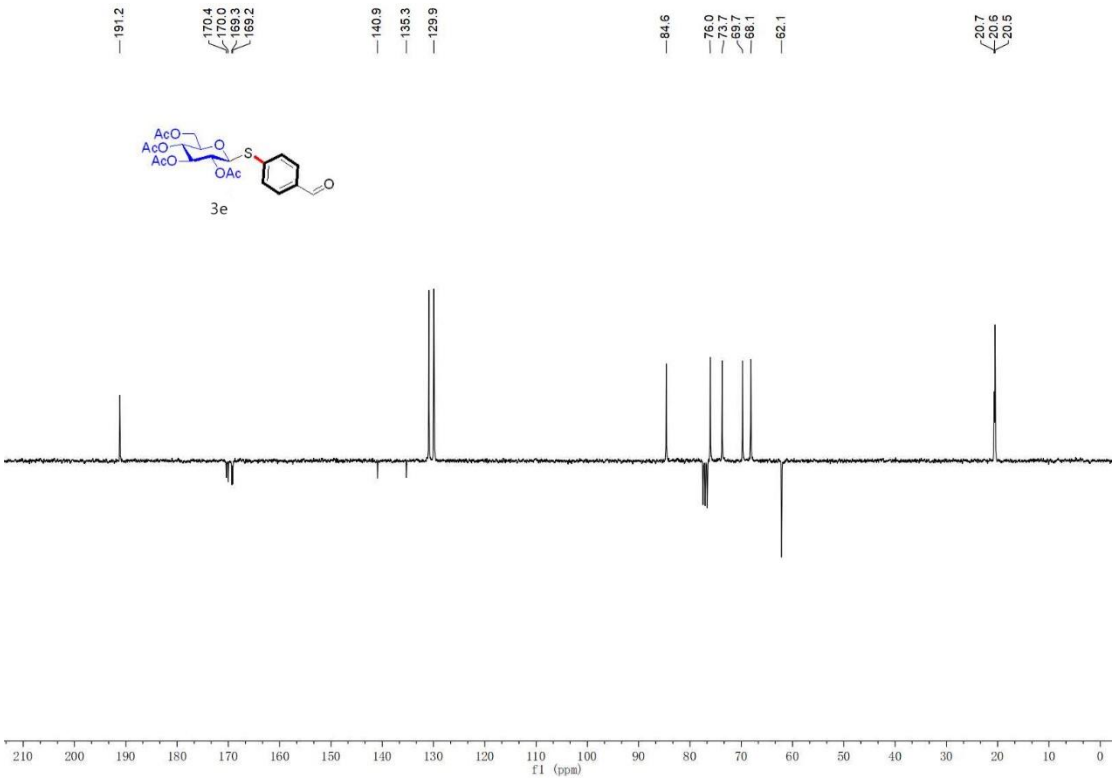

$^1$H NMR spectrum of **3c** (300 MHz, $CDCl_3$)



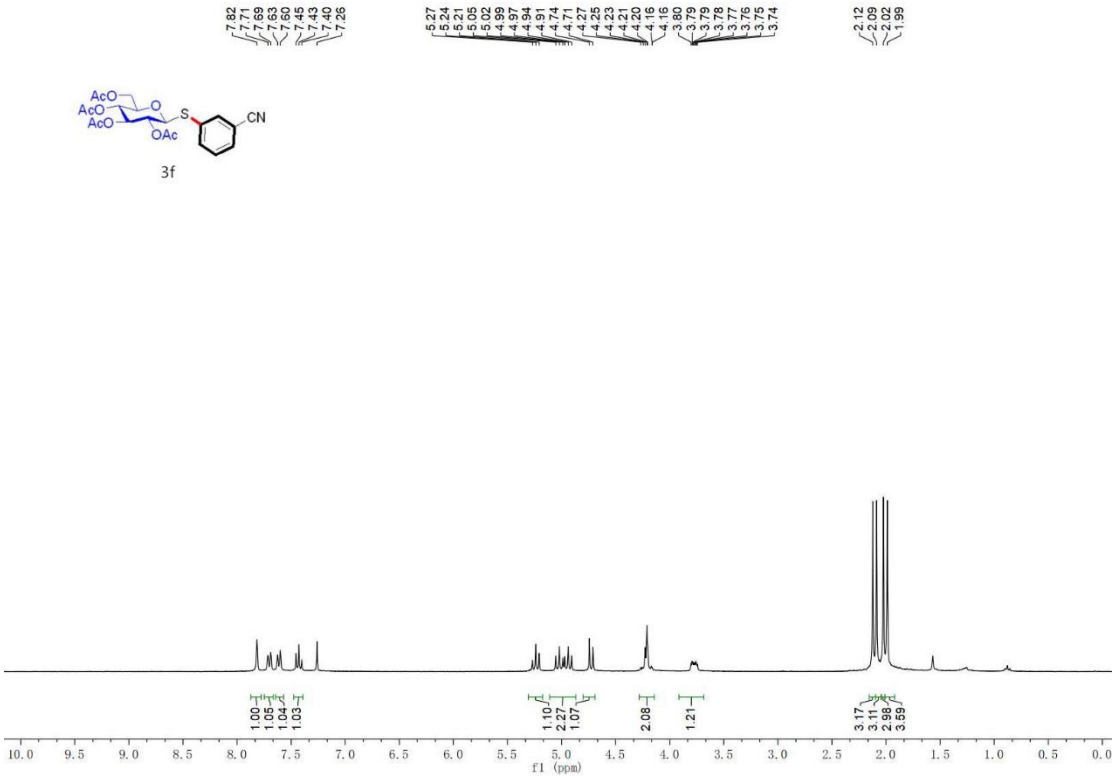

$^1$H NMR spectrum of **3d** (300 MHz, $CDCl_3$)



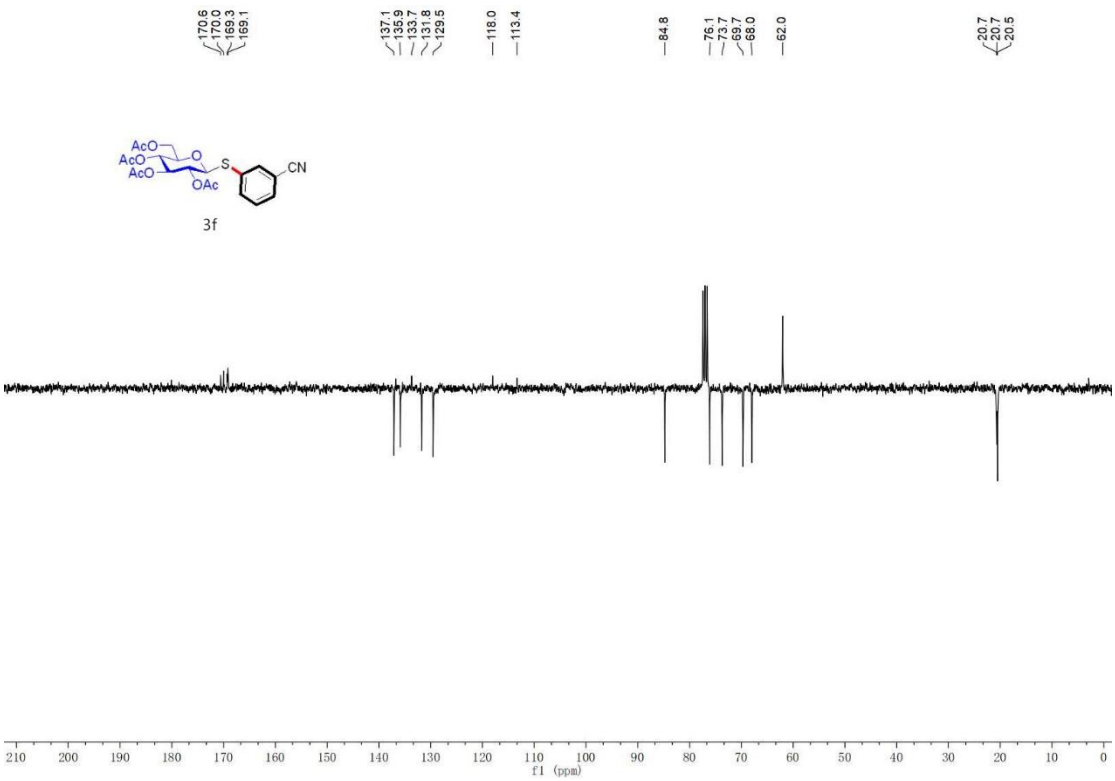

$^{1}$H NMR spectrum of **3e** (300 MHz, $CDCl_3$)



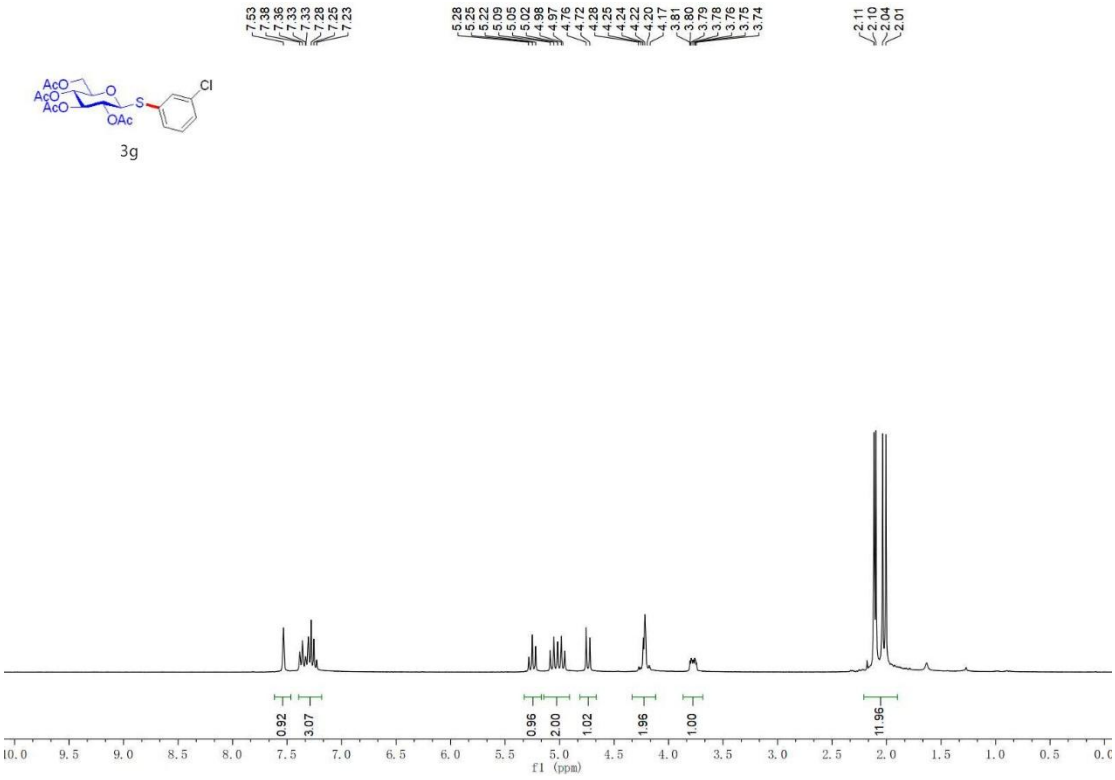

$^{13}$C NMR spectrum of **3e** (75 MHz, $CDCl_3$)



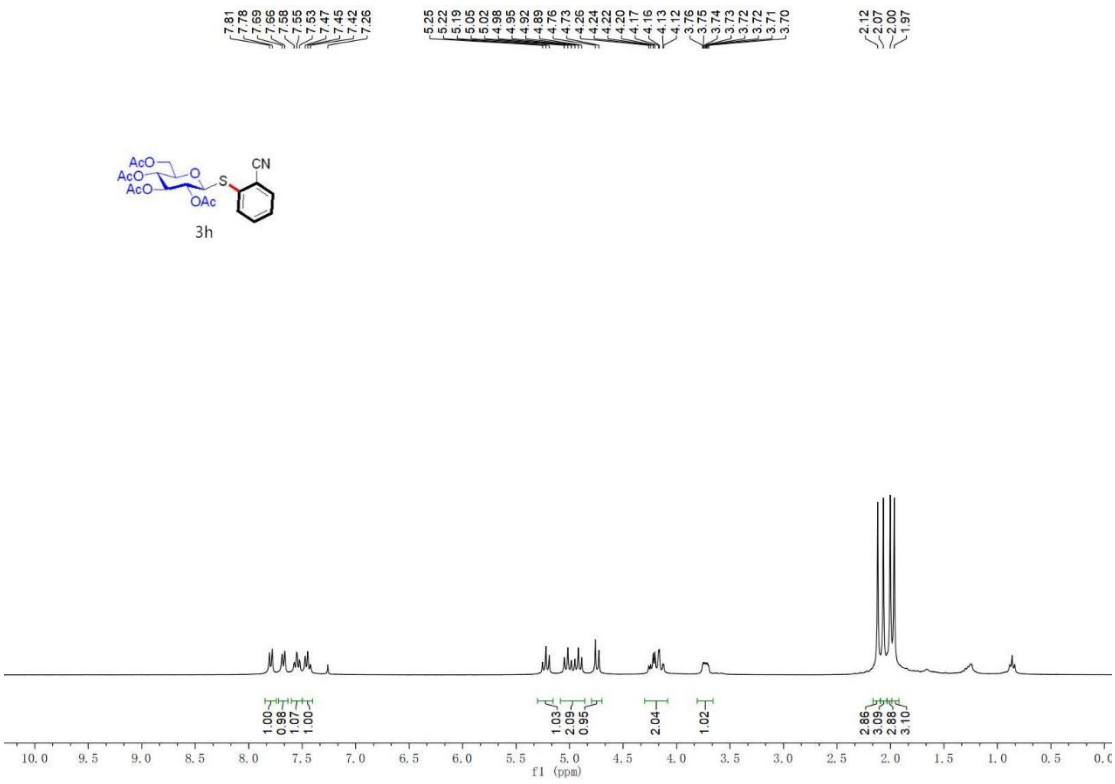

$^{1}$H NMR spectrum of **3f** (300 MHz, $CDCl_3$)



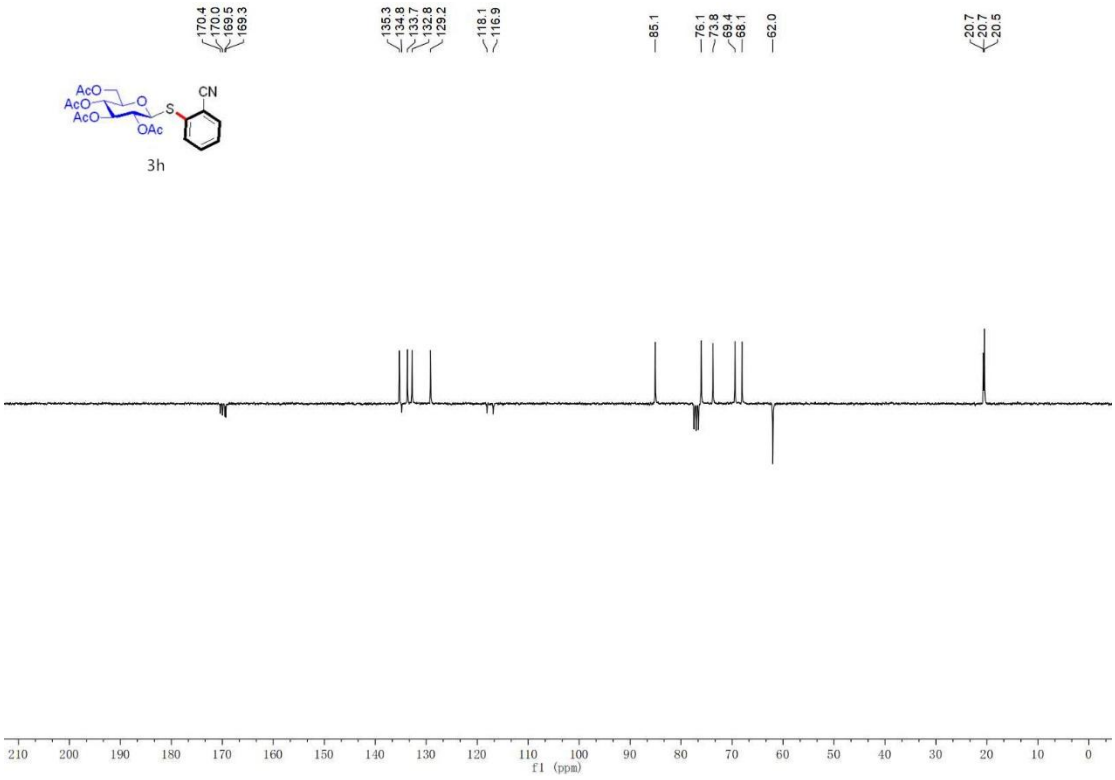

$^{13}$C NMR spectrum of **3f** (75 MHz, $CDCl_3$)



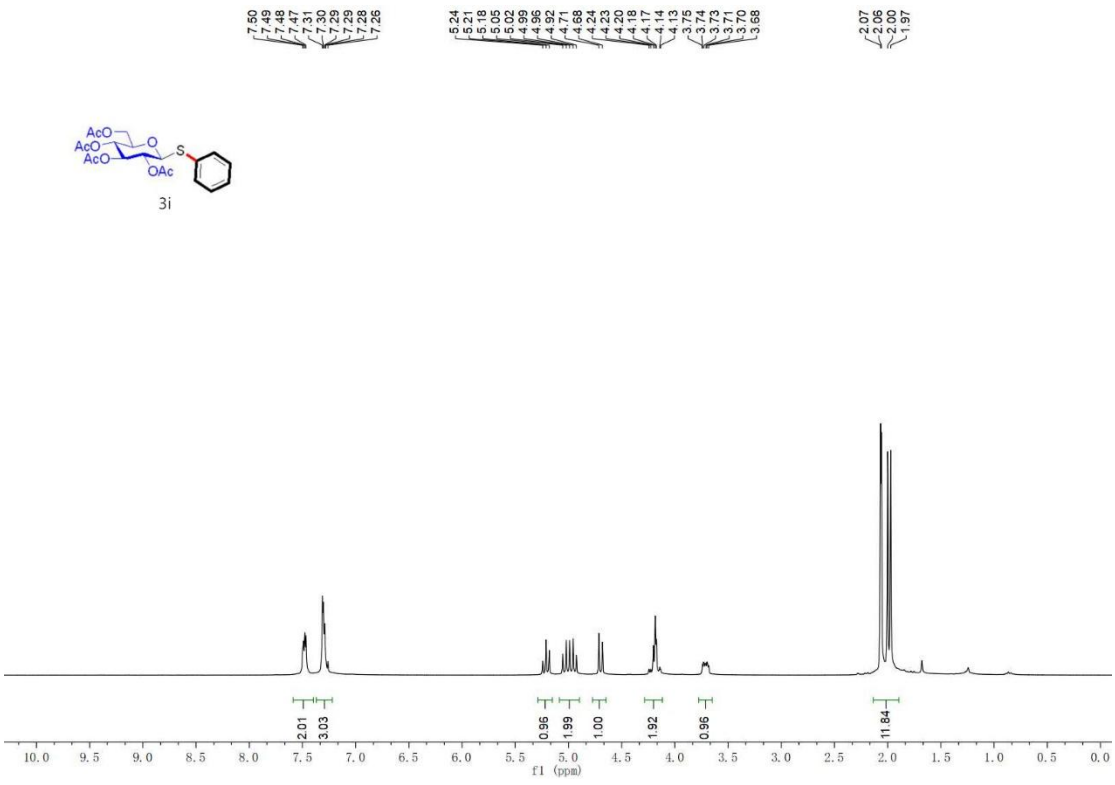

$^1$H NMR spectrum of **3g** (300 MHz, $CDCl_3$)



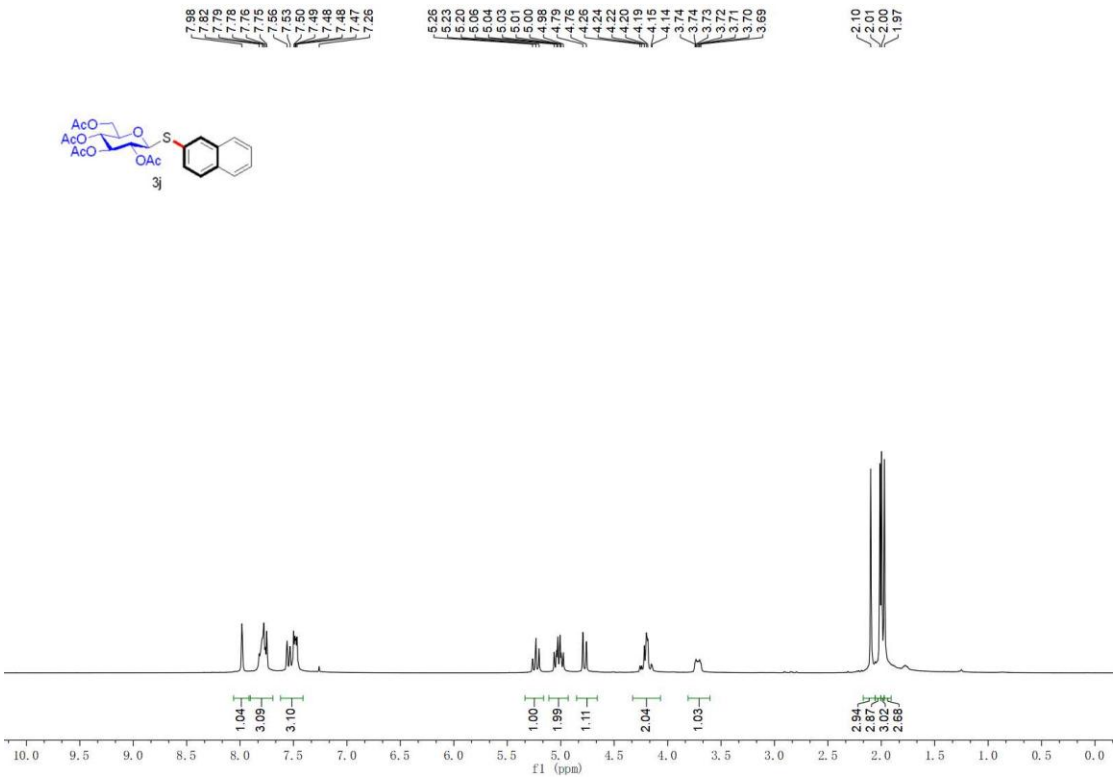

$^1$H NMR spectrum of **3h** (300 MHz, $CDCl_3$)



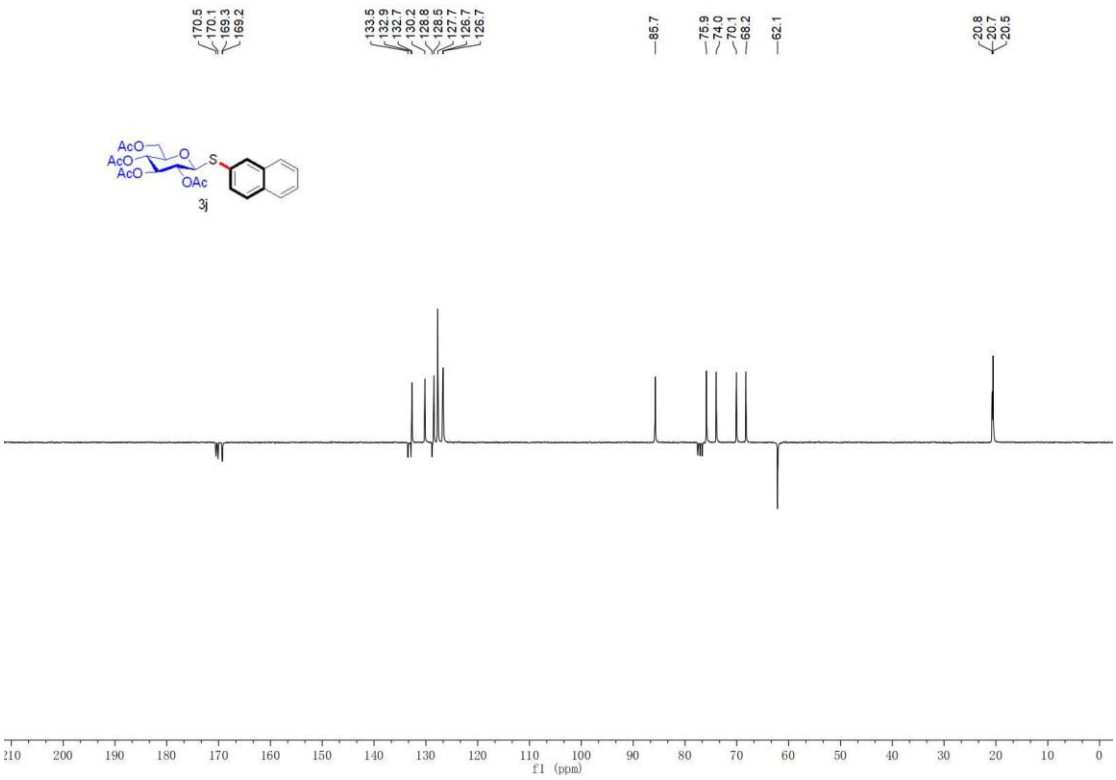

$^{13}$C NMR spectrum of **3h** (75 MHz, $CDCl_3$)



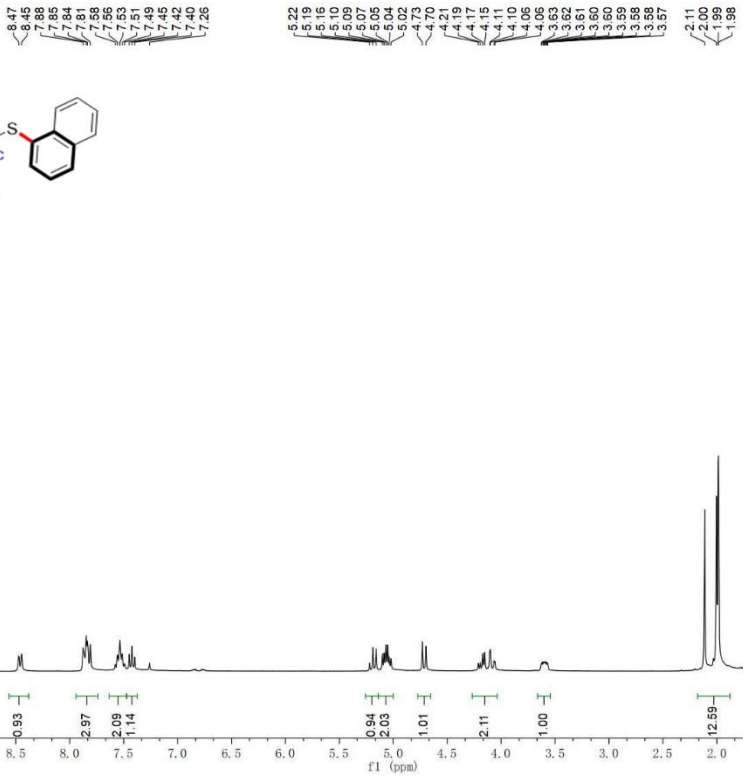

$^{1}$H NMR spectrum of **3i** (300 MHz, $CDCl_3$)



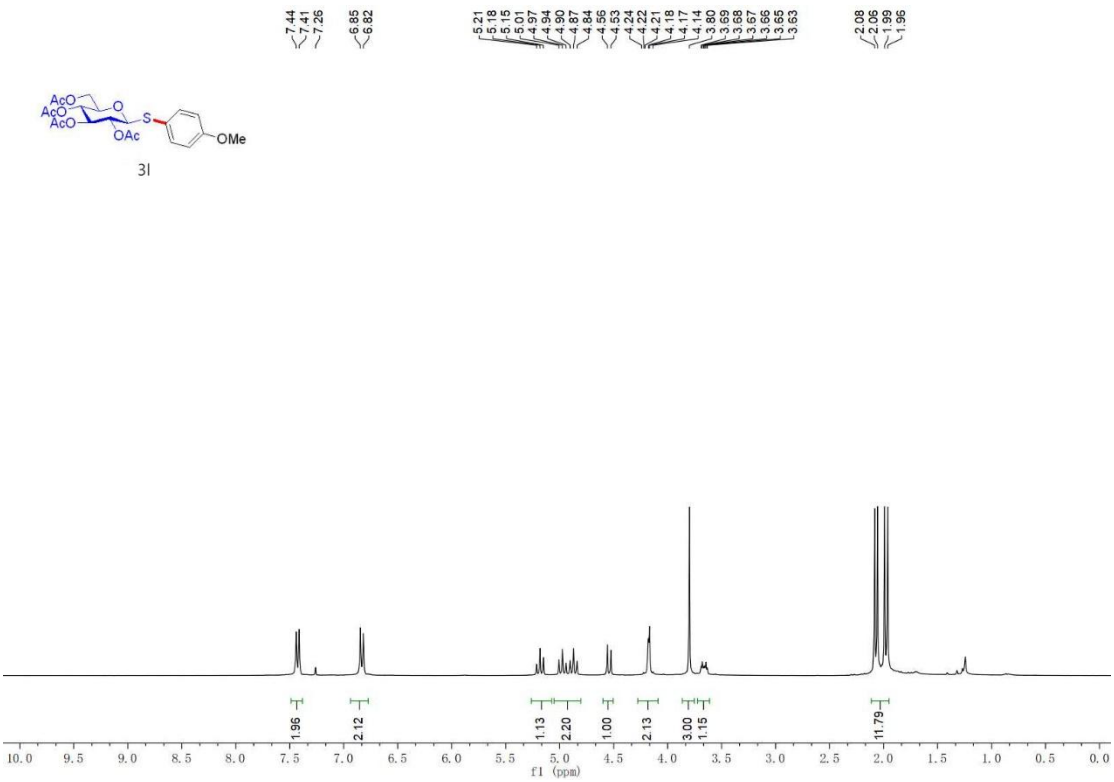

$^{1}$H NMR spectrum of **3j** (300 MHz, $CDCl_3$)



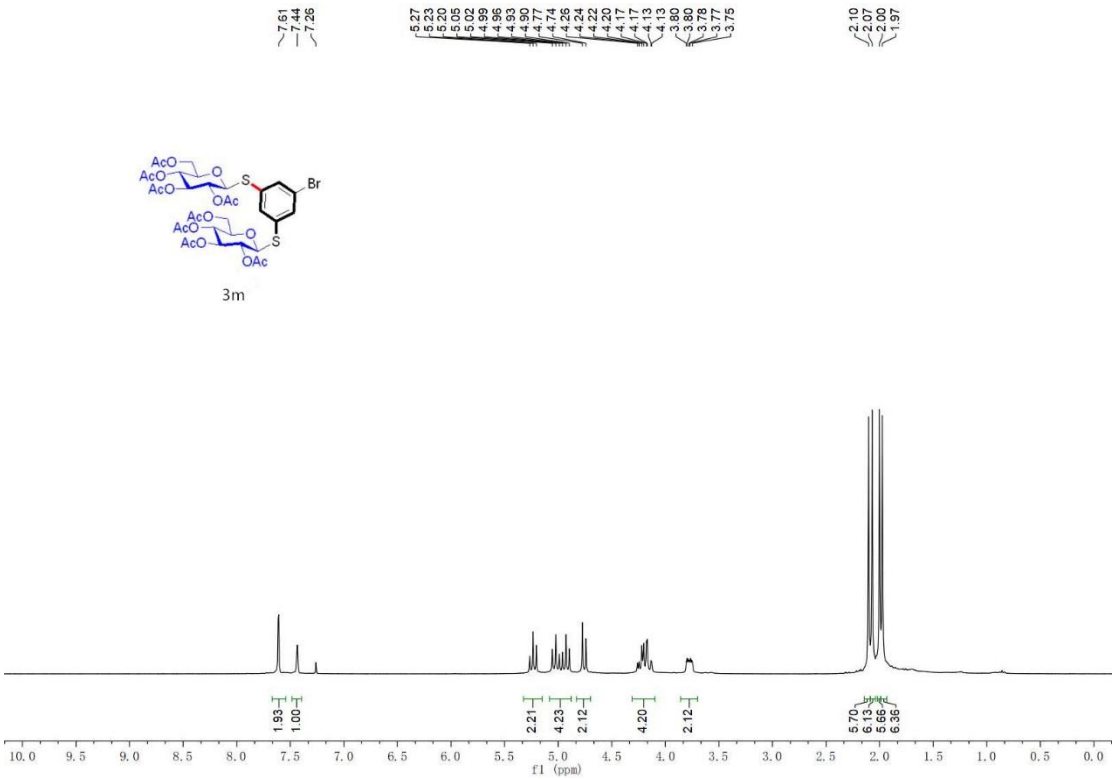

$^{13}$C NMR spectrum of **3j** (75 MHz, $CDCl_3$)



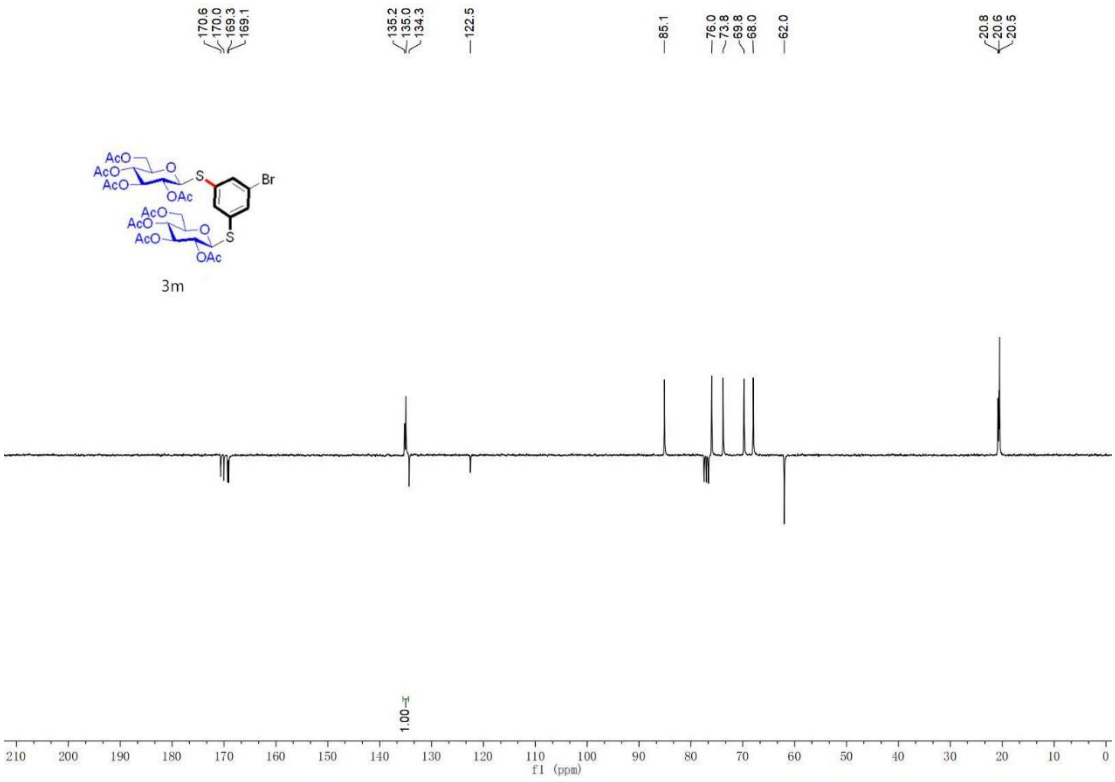

$^1$H NMR spectrum of **3k** (300 MHz, $CDCl_3$)



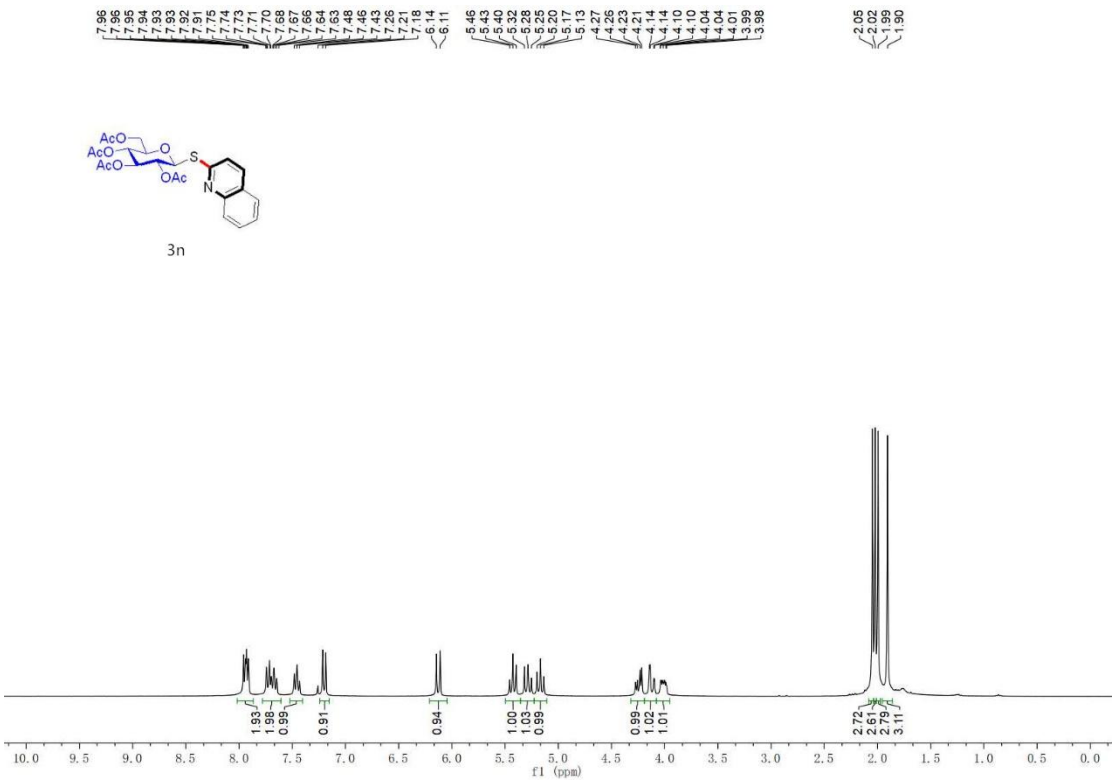

$^1$H NMR spectrum of **3l** (300 MHz, $CDCl_3$)



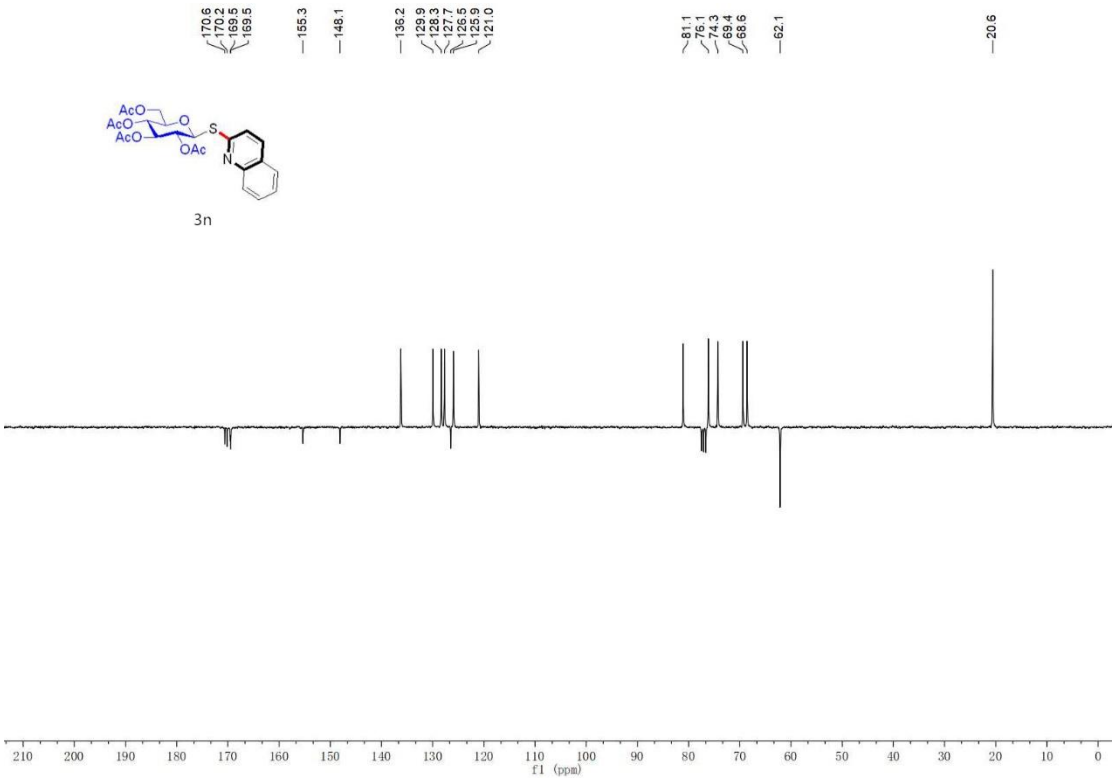

$^{1}$H NMR spectrum of **3m** (300 MHz, $CDCl_3$)



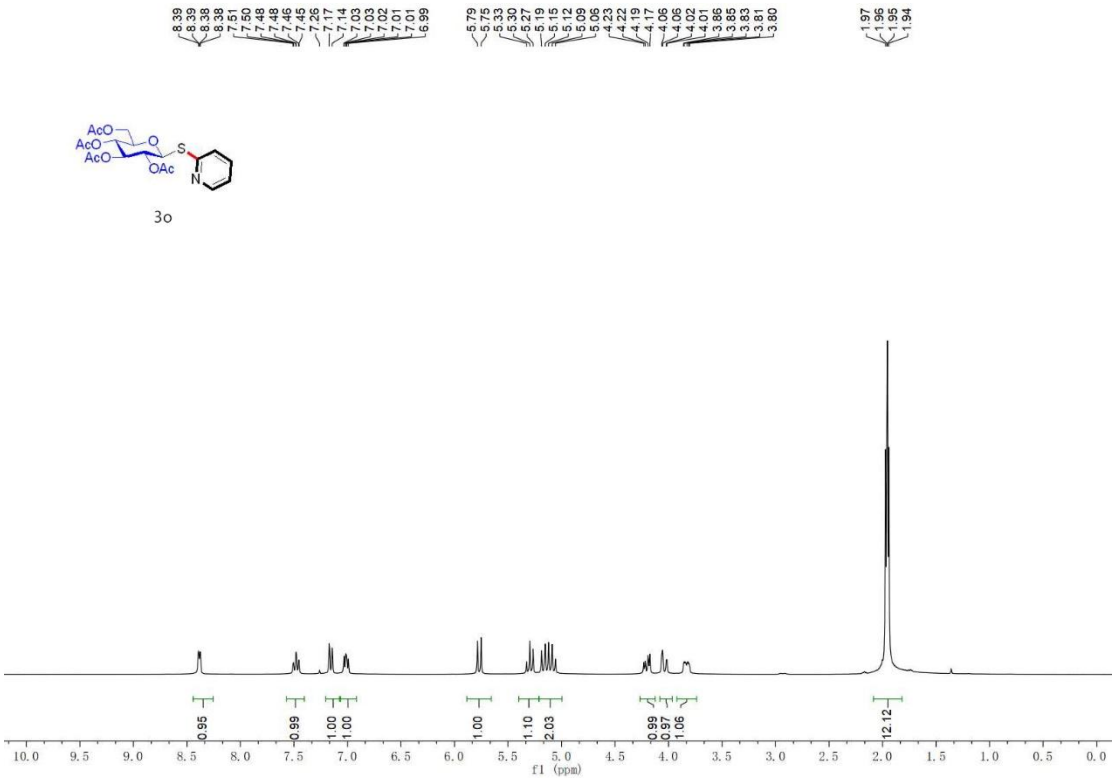

$^{13}$C NMR spectrum of **3m** (75 MHz, $CDCl_3$)



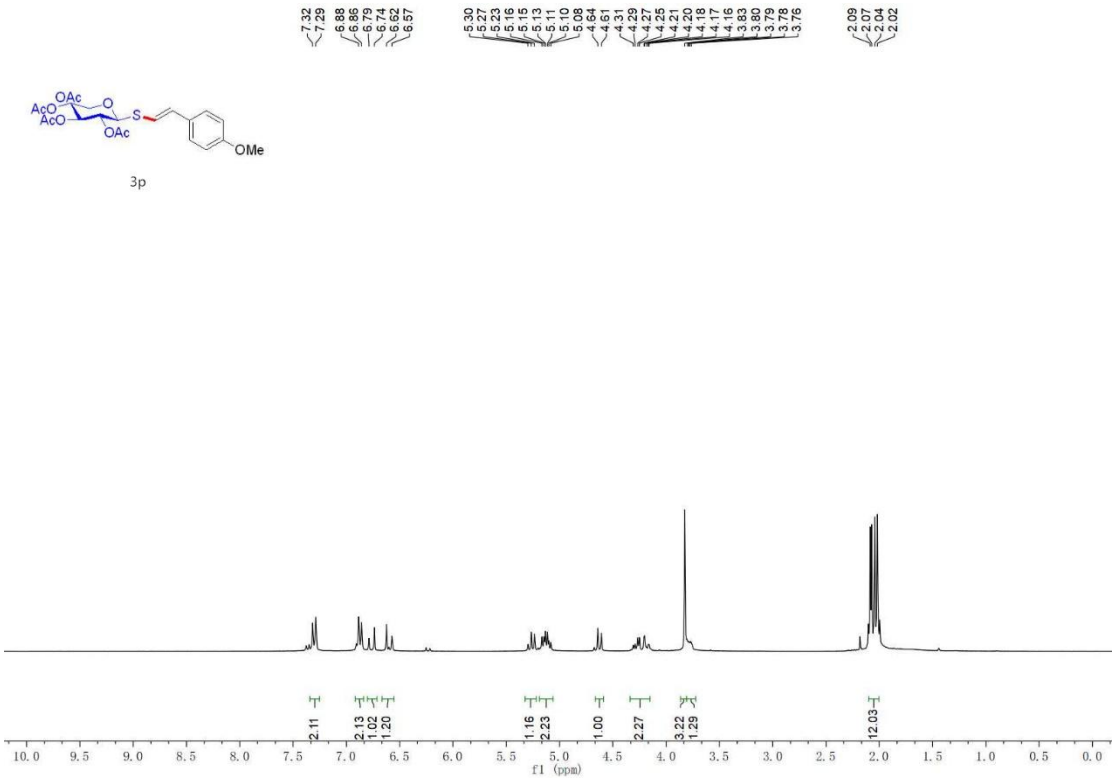

$^{1}$H NMR spectrum of **3n** (300 MHz, $CDCl_3$)



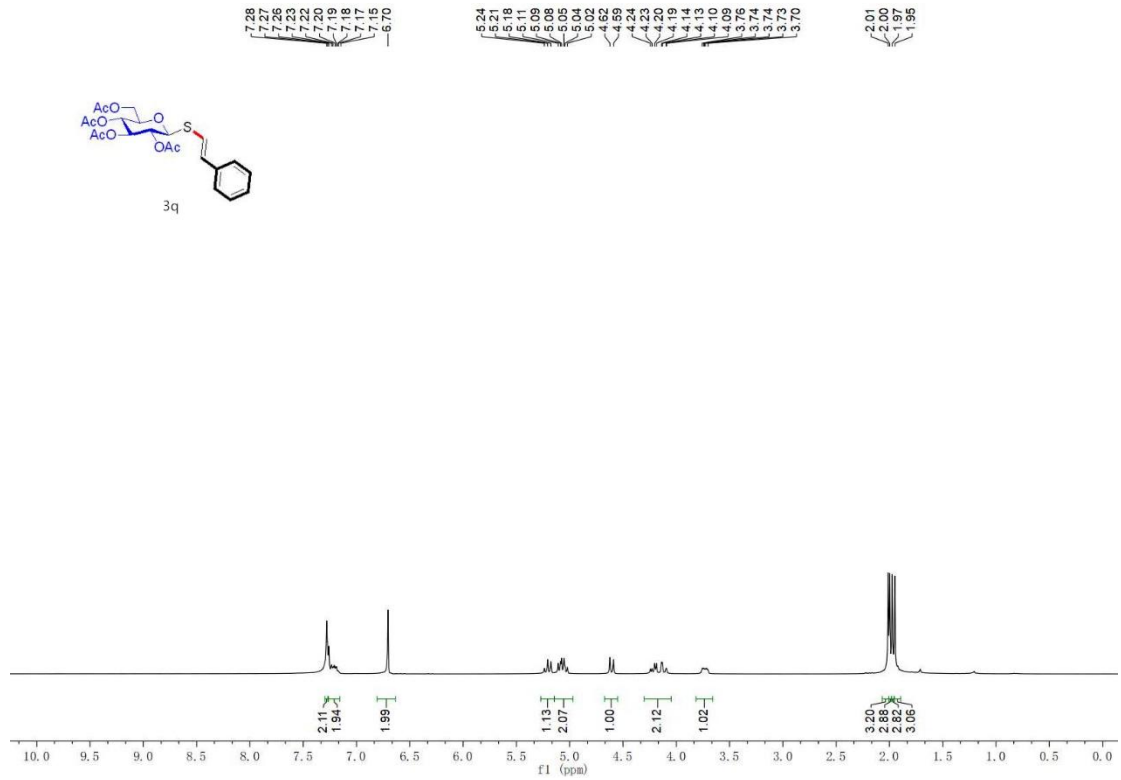

$^{13}$C NMR spectrum of **3n** (75 MHz, $CDCl_3$)



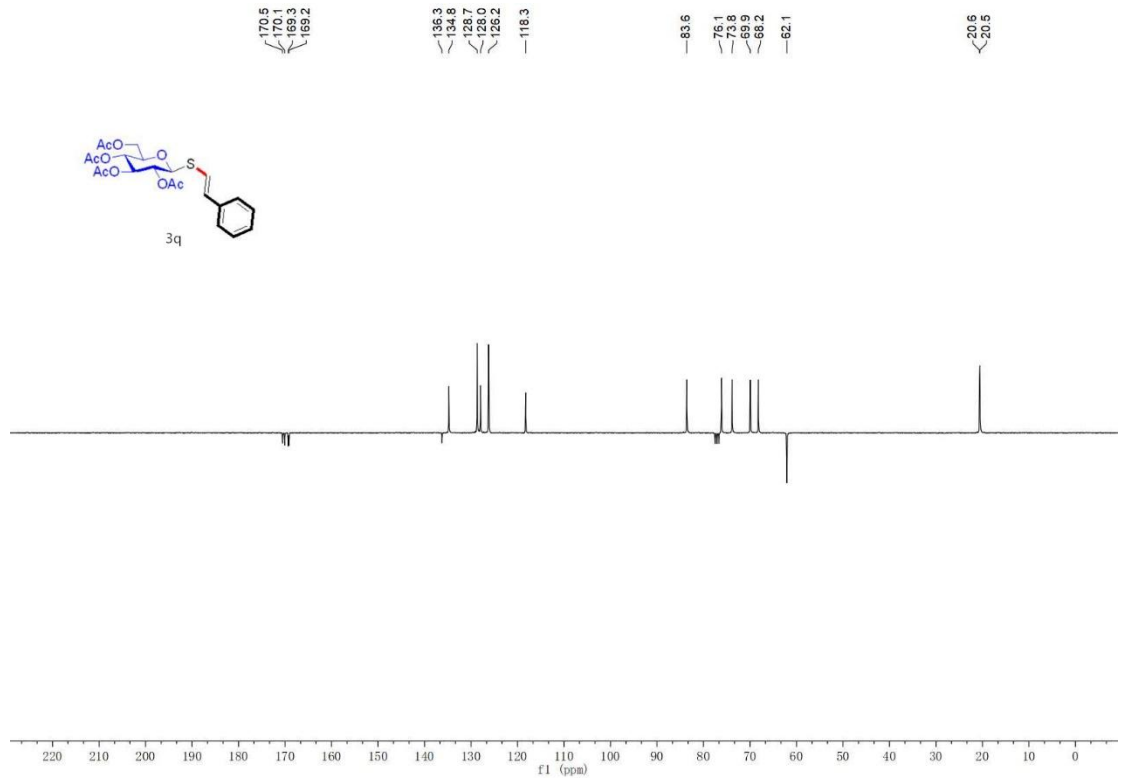

$^1$H NMR spectrum of **3o** (300 MHz, $CDCl_3$)




$^1$H NMR spectrum of **3p** (300 MHz, $CDCl_3$)




$^{1}$H NMR spectrum of **3q** (300 MHz, $CDCl_3$)

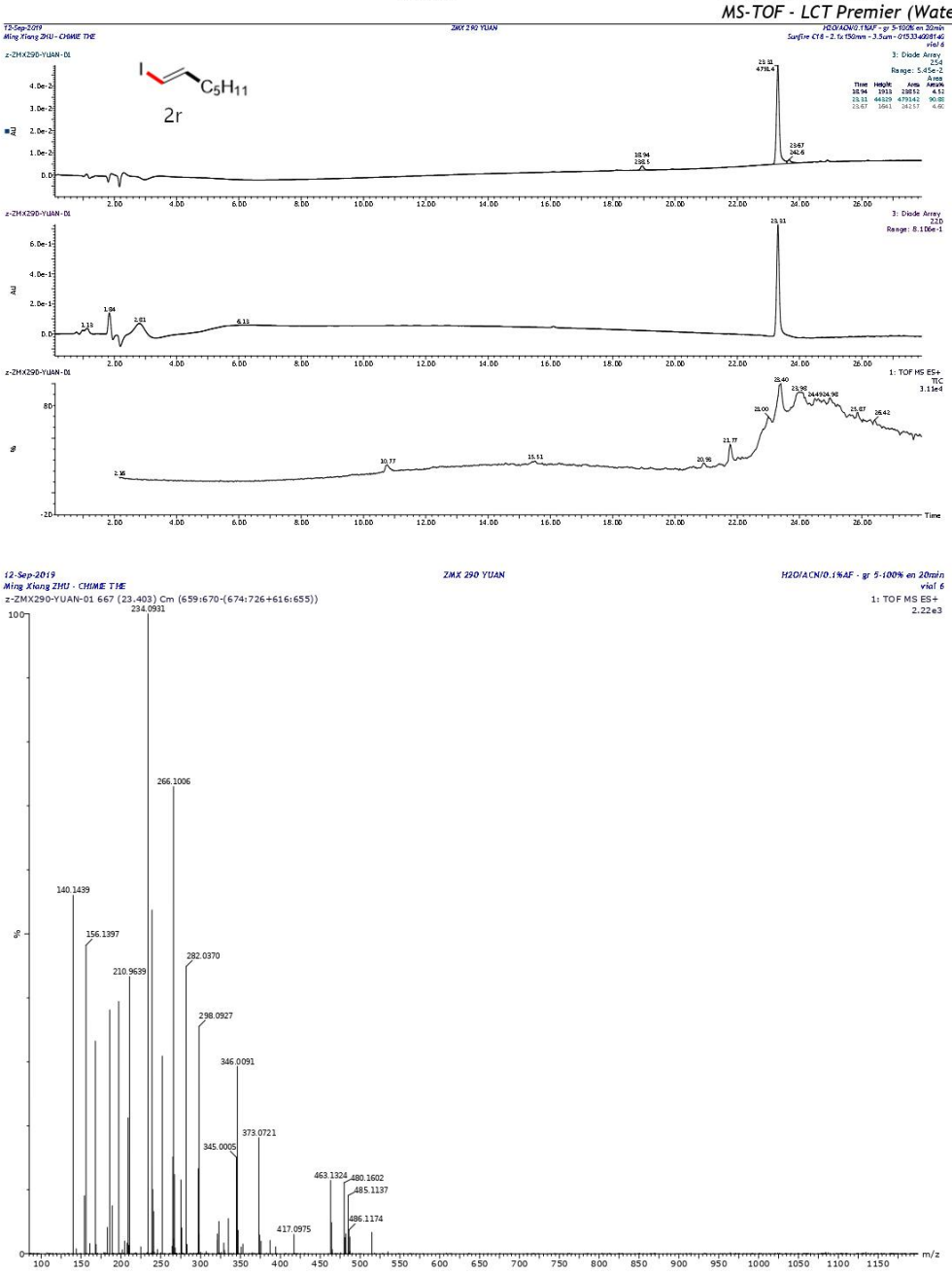



$^{13}$C NMR spectrum of **3q** (75 MHz, $CDCl_3$)

ZMX290-290YUAN.doc

**LC-MS**

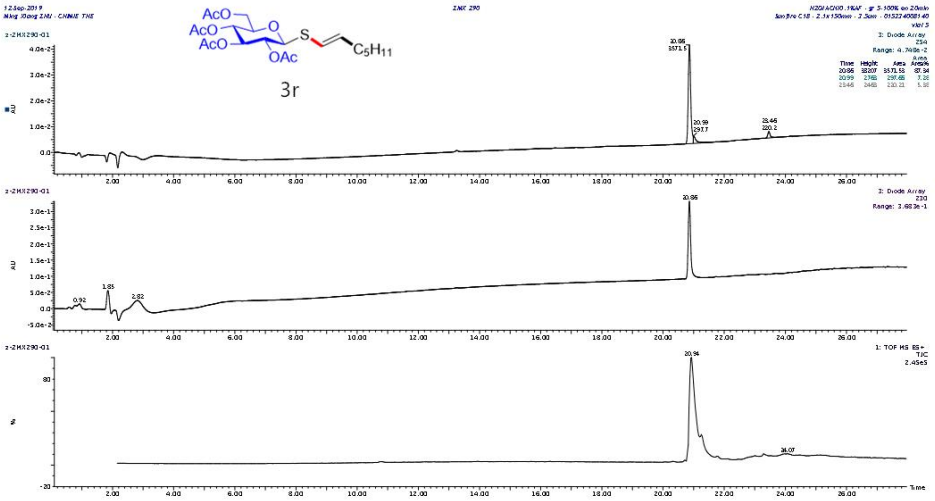
HPLC Alliance 2695
MS-TOF - LCT Premier (Waters)

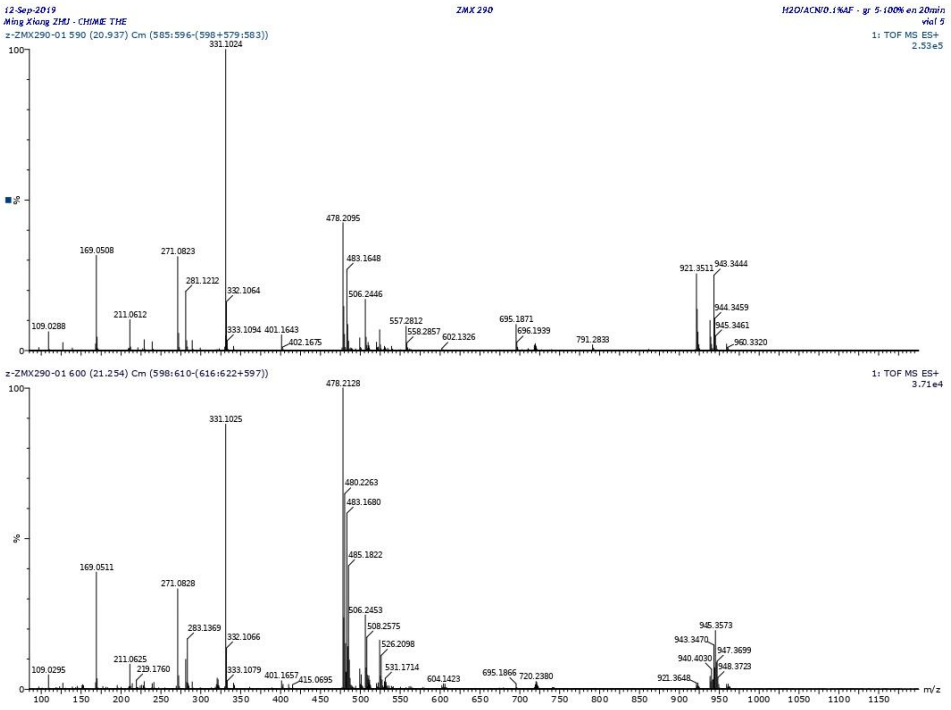



2

LC-MS of **2r**

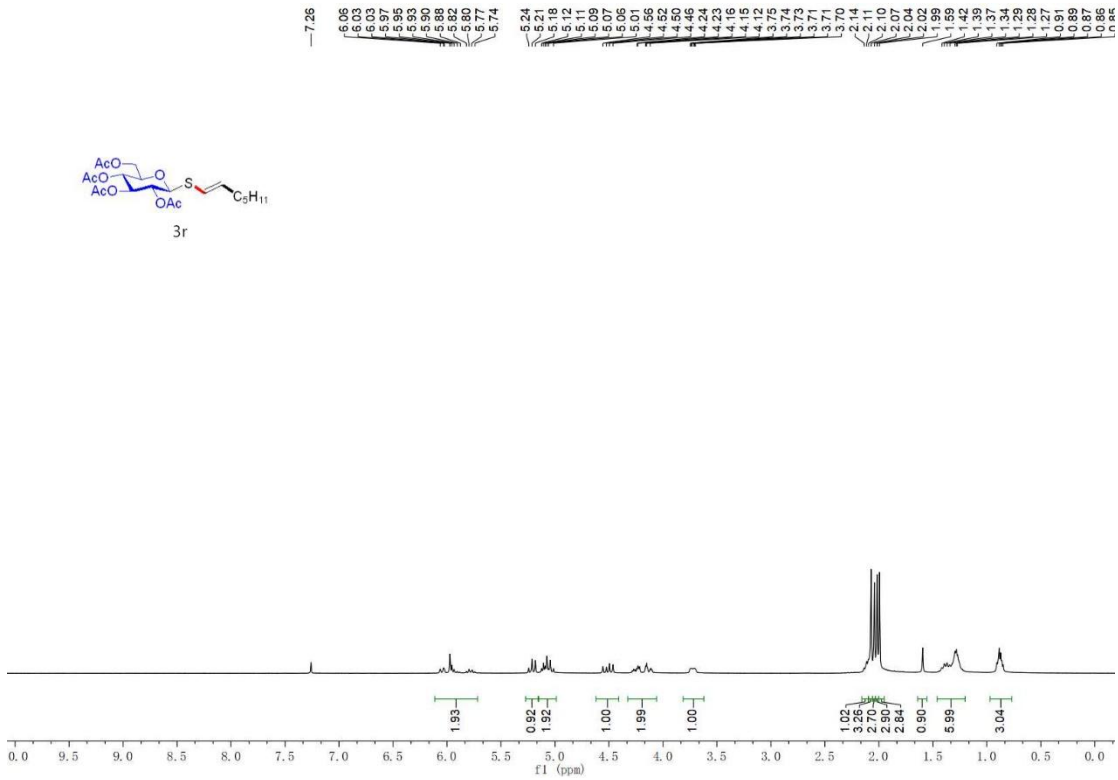
**ZMX 290- 290 YUAN**



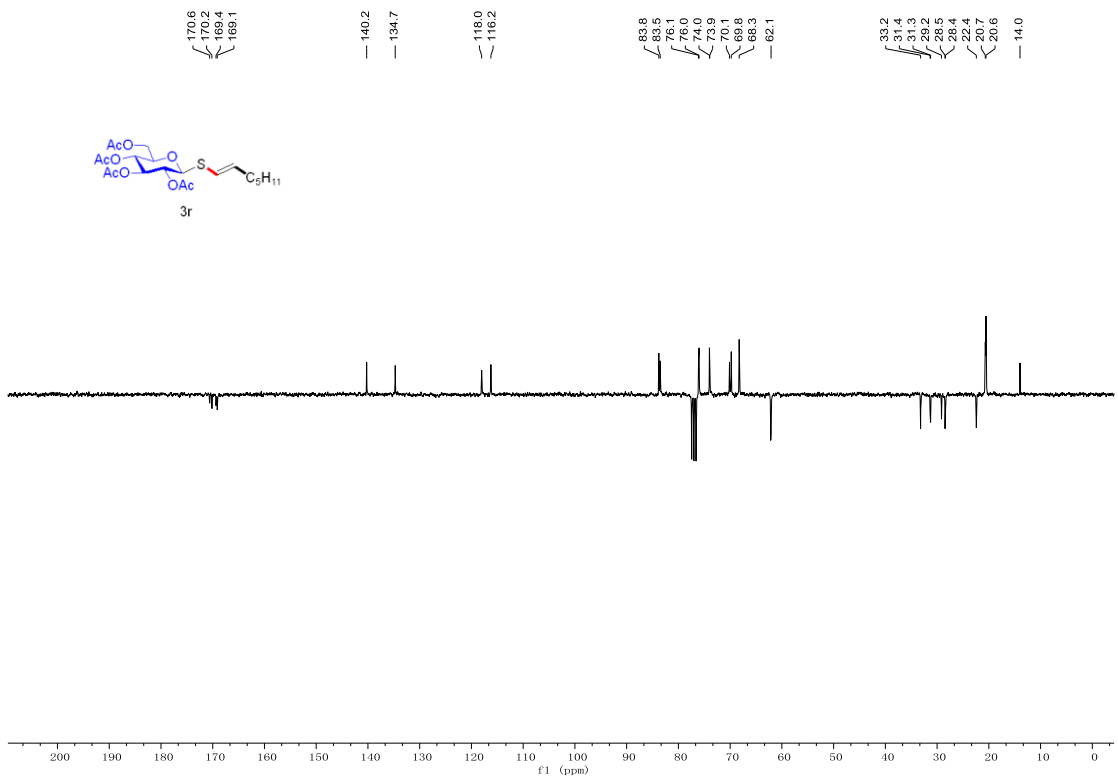




1

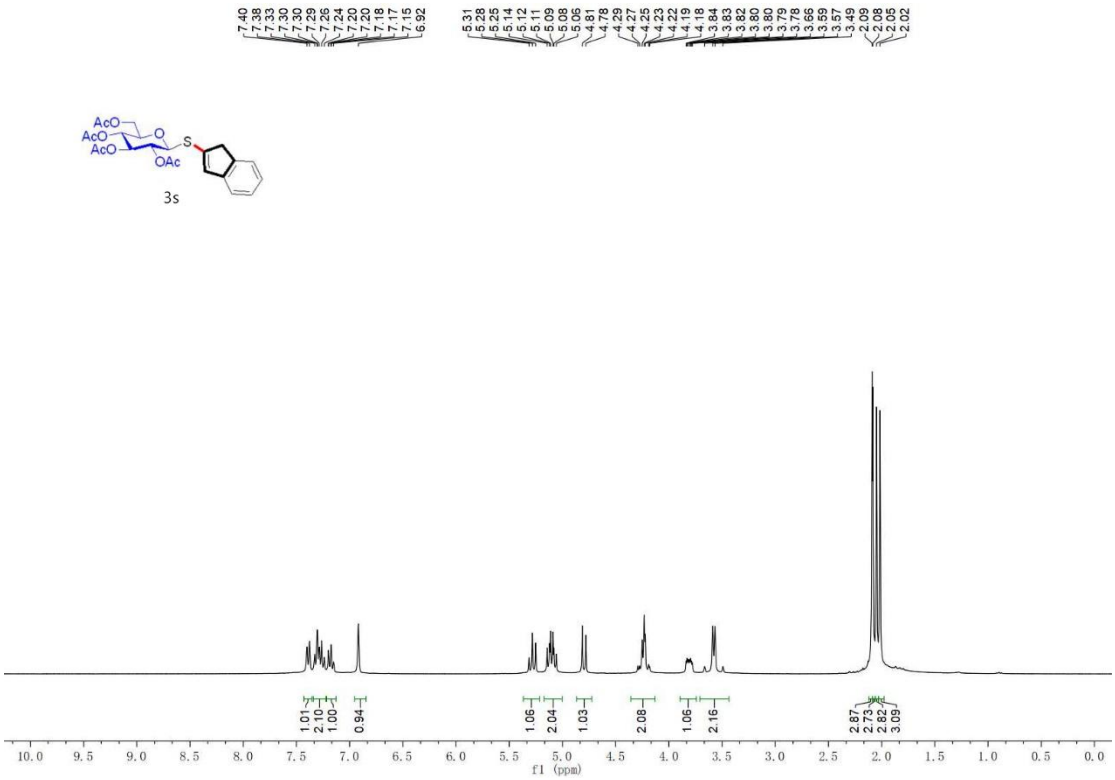
LC-MS of **3r**



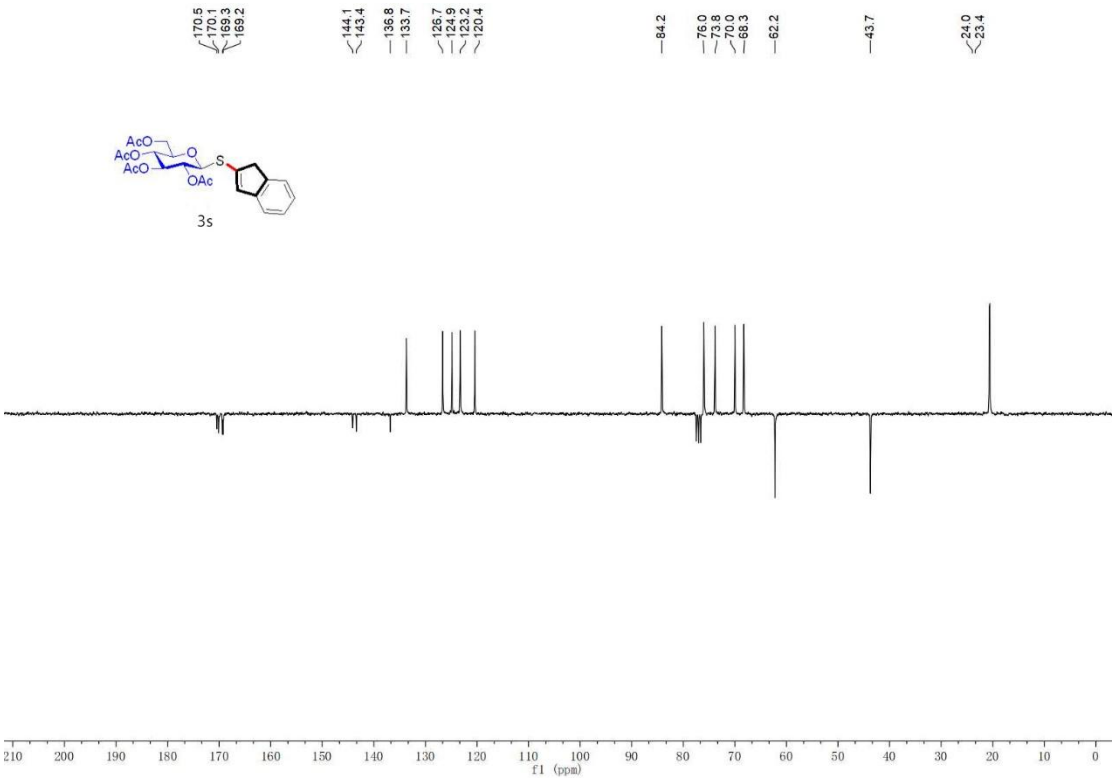

$^{1}$H NMR spectrum of **3r** (300 MHz, $CDCl_3$)



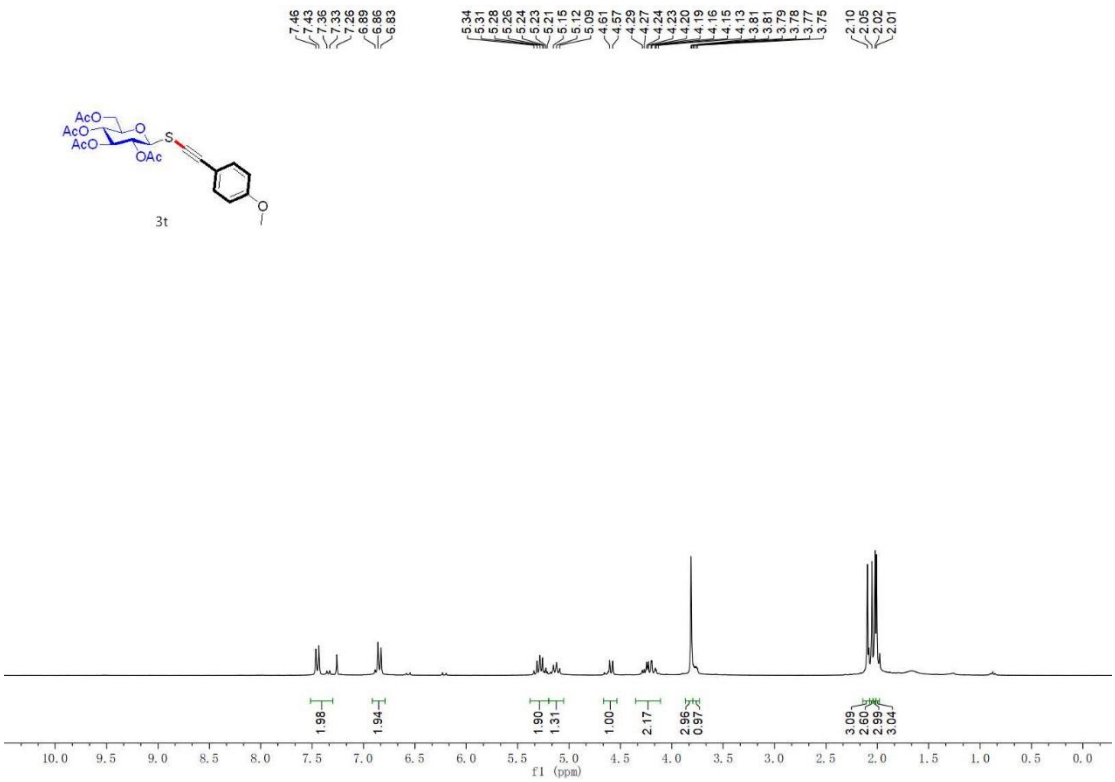

$^{13}$C NMR spectrum of **3r** (75 MHz, $CDCl_3$)



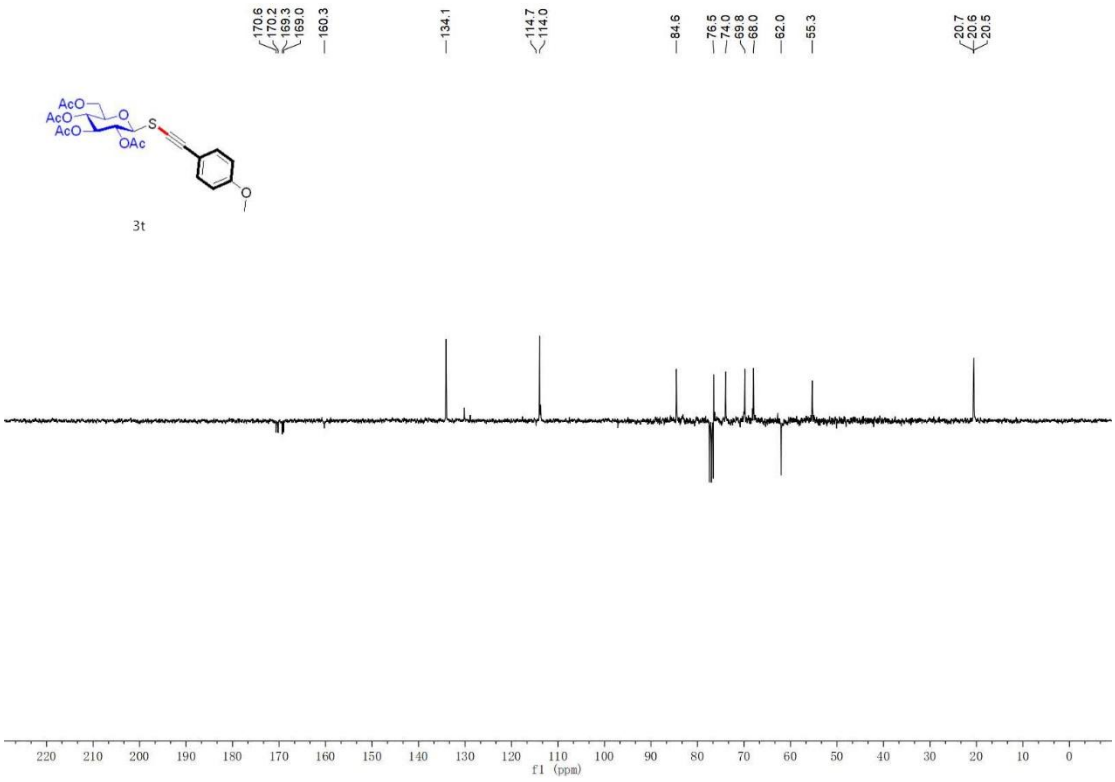

$^{1}$H NMR spectrum of **3s** (300 MHz, $CDCl_3$)



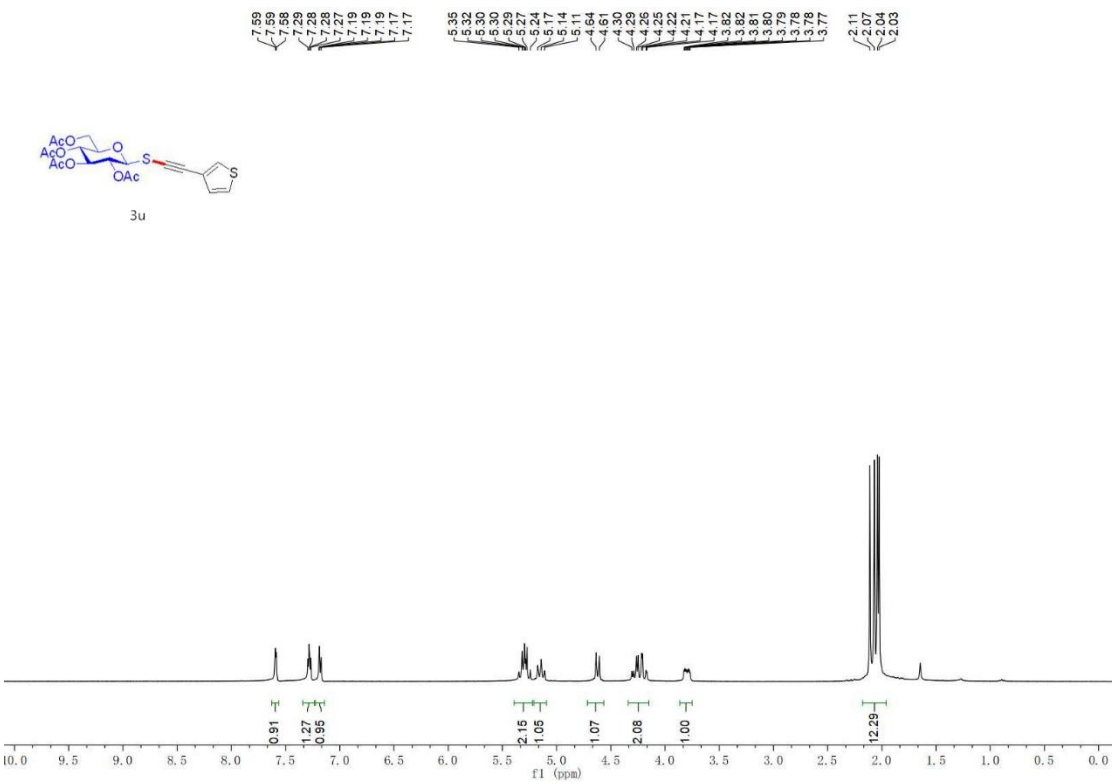

$^{13}$C NMR spectrum of **3s** (75 MHz, $CDCl_3$)



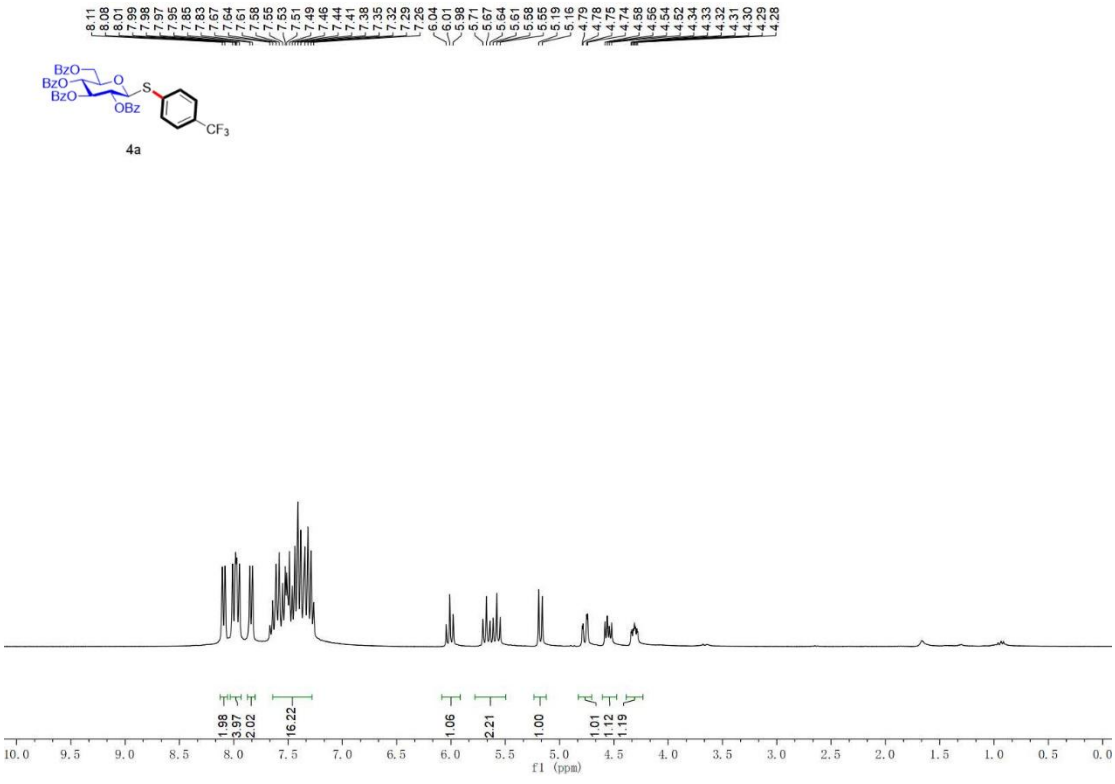

$^{1}$H NMR spectrum of **3t** (300 MHz, $CDCl_3$)



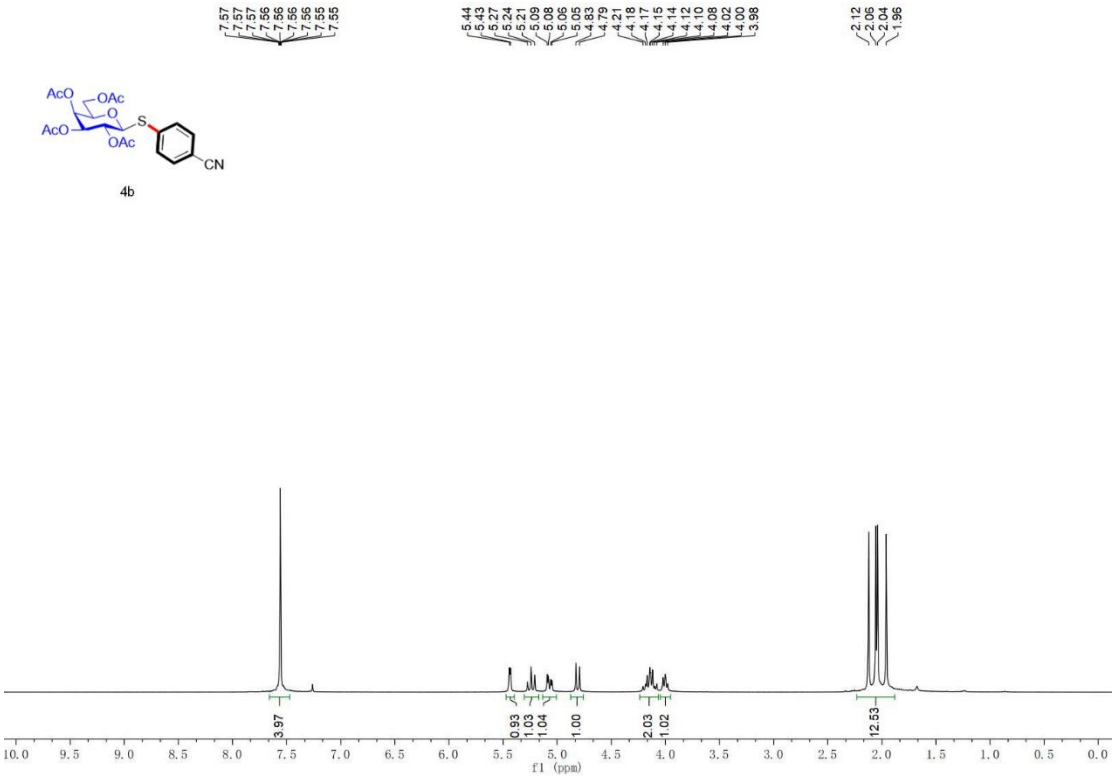

$^{13}$C NMR spectrum of **3t** (75 MHz, $CDCl_3$)



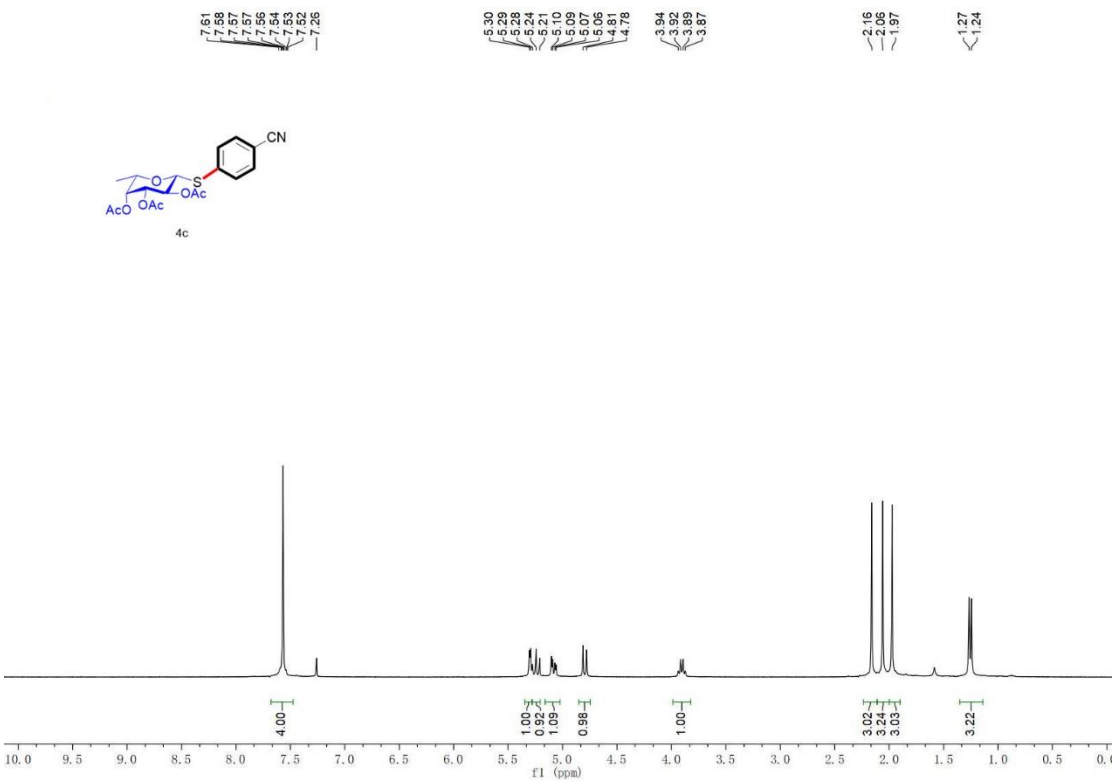

$^1$H NMR spectrum of **3u** (300 MHz, $CDCl_3$)



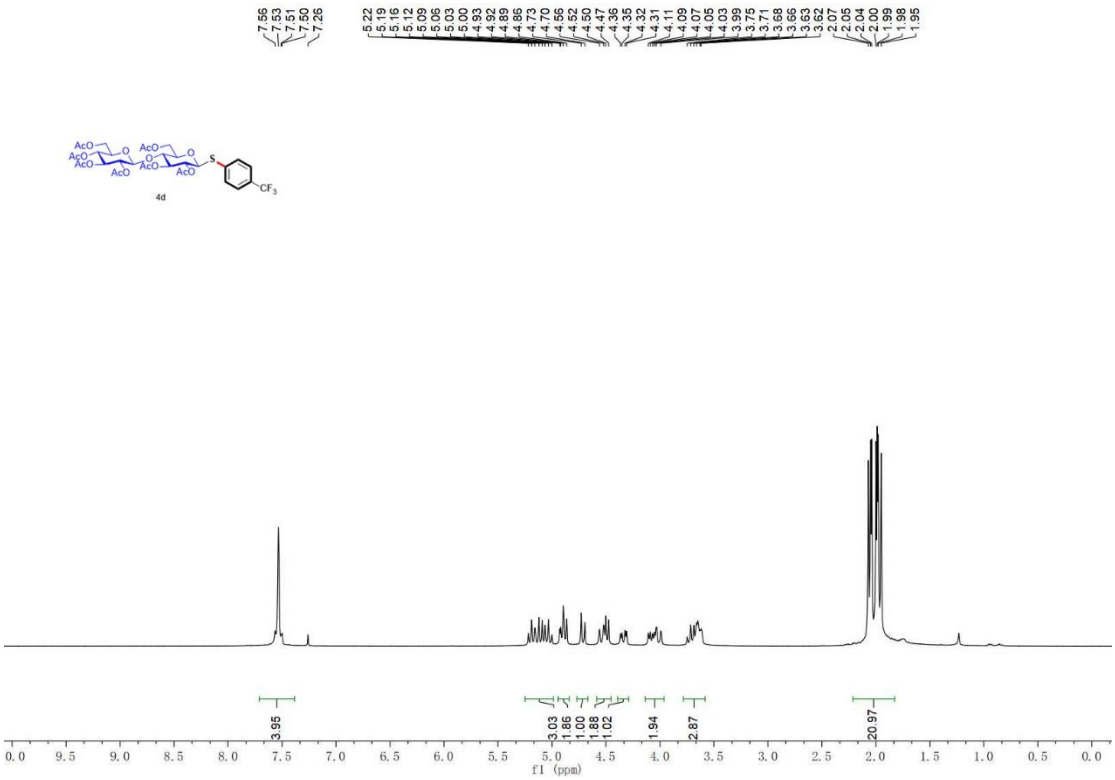

$^1$H NMR spectrum of **4a** (300 MHz, $CDCl_3$)



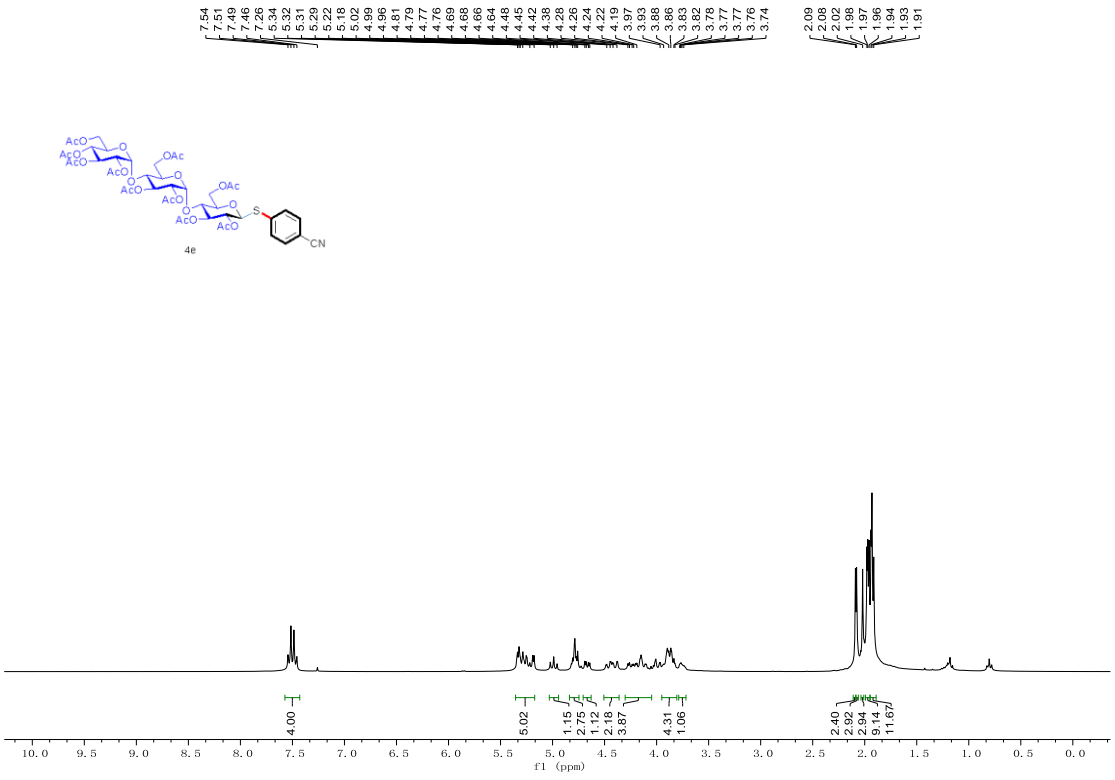

$^1$H NMR spectrum of **4b** (300 MHz, $CDCl_3$)



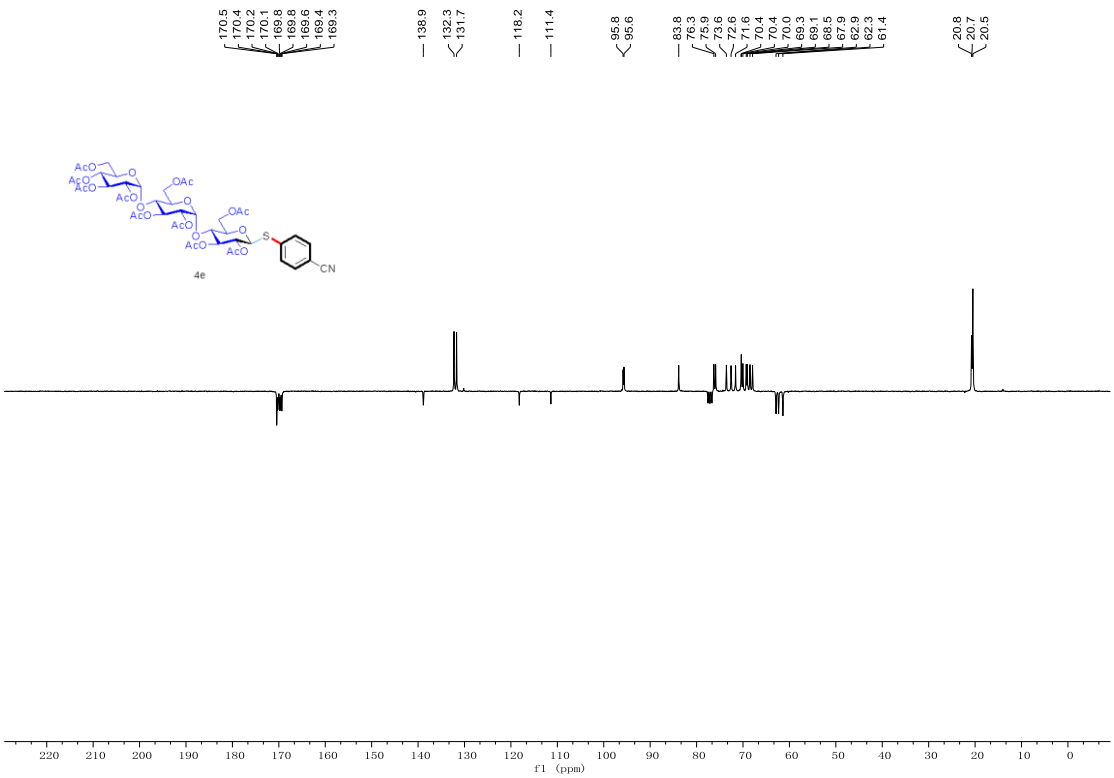

$^1$H NMR spectrum of **4c** (300 MHz, $CDCl_3$)



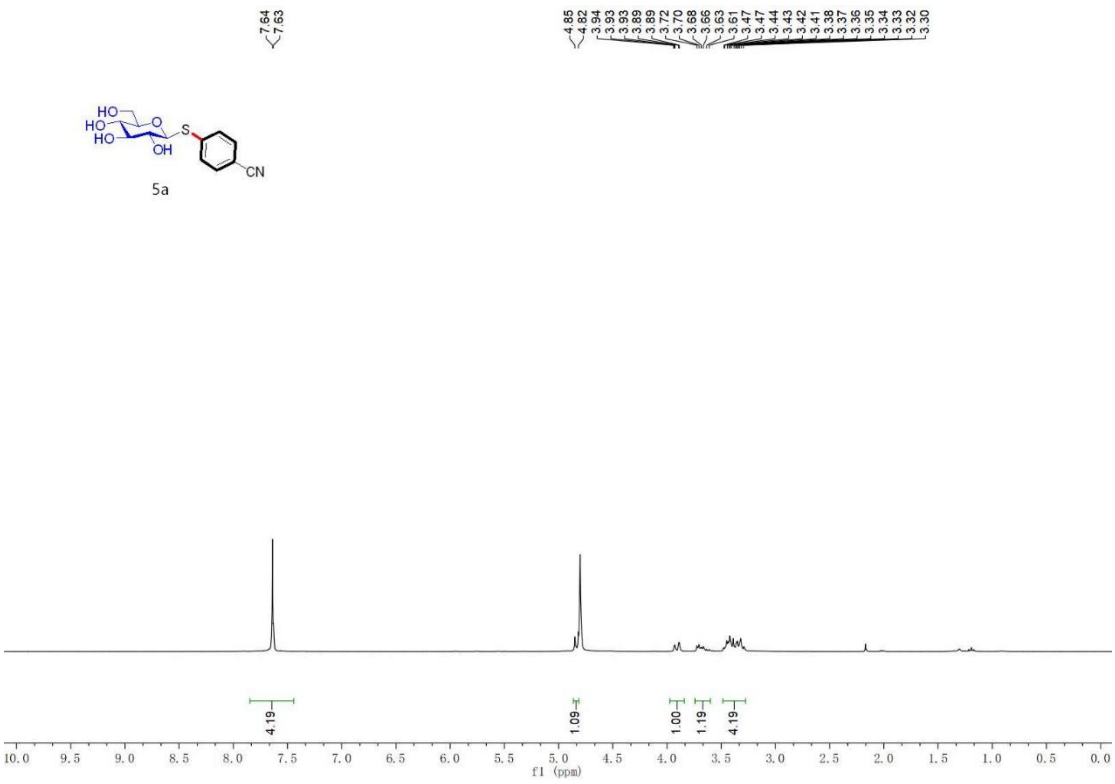
$^1$H NMR spectrum of **4d** (300 MHz, $CDCl_3$)



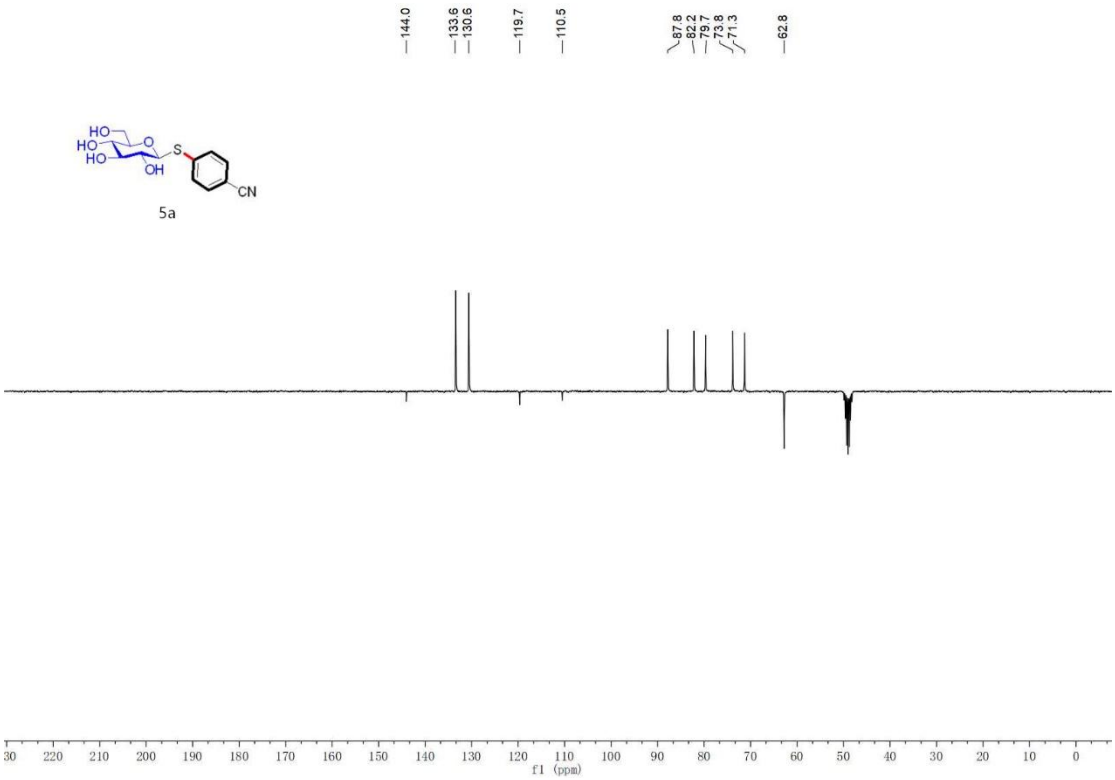
$^1$H NMR spectrum of **4e** (300 MHz, $CDCl_3$)



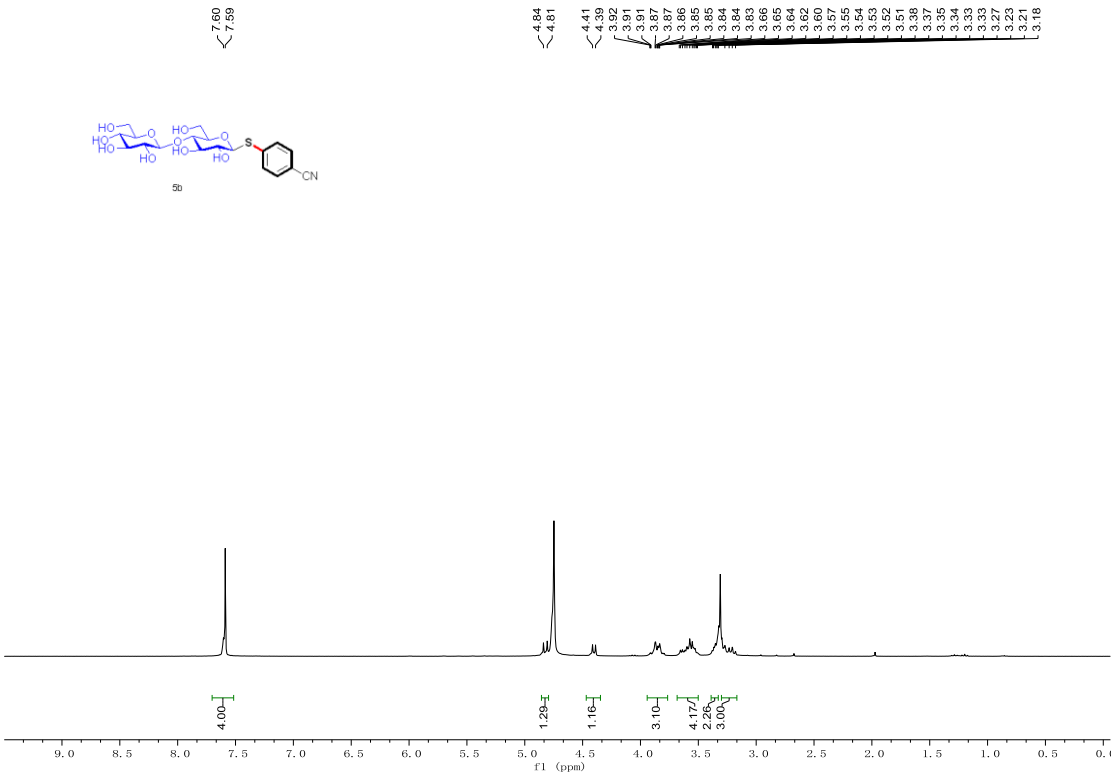

$^{13}$C NMR spectrum of **4e** (75 MHz, $CDCl_3$)



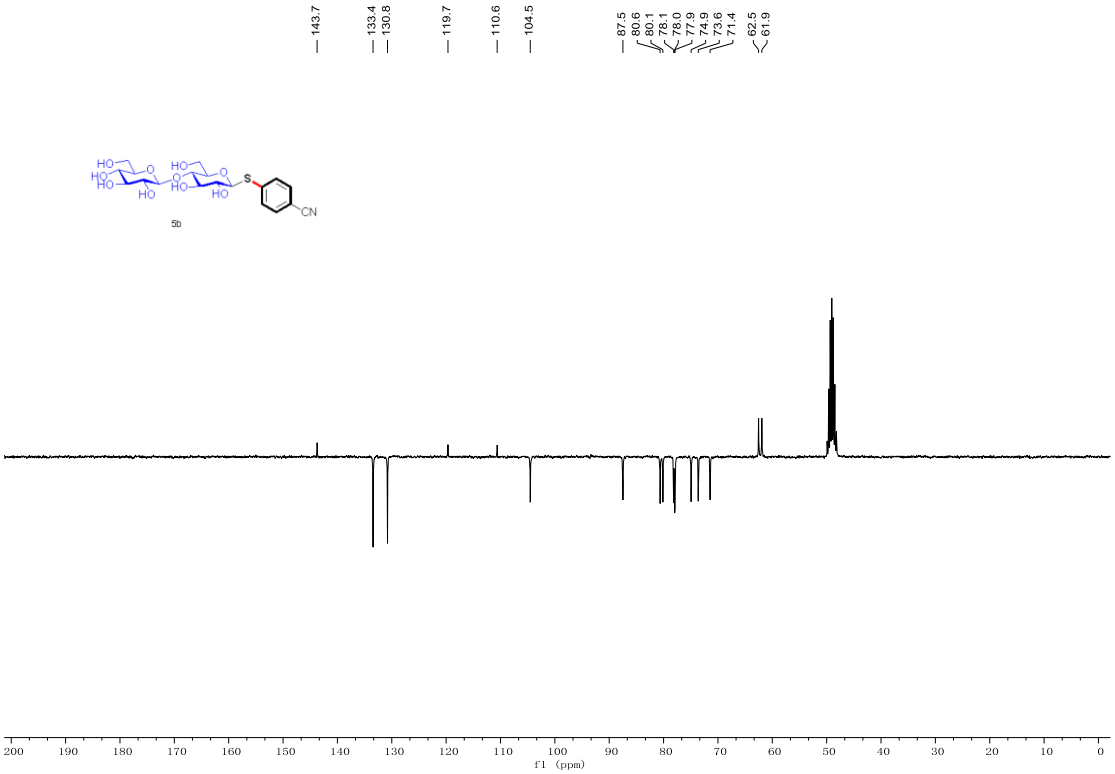

$^{1}$H NMR spectrum of **5a** (300 MHz, MeOD-$d_4$)



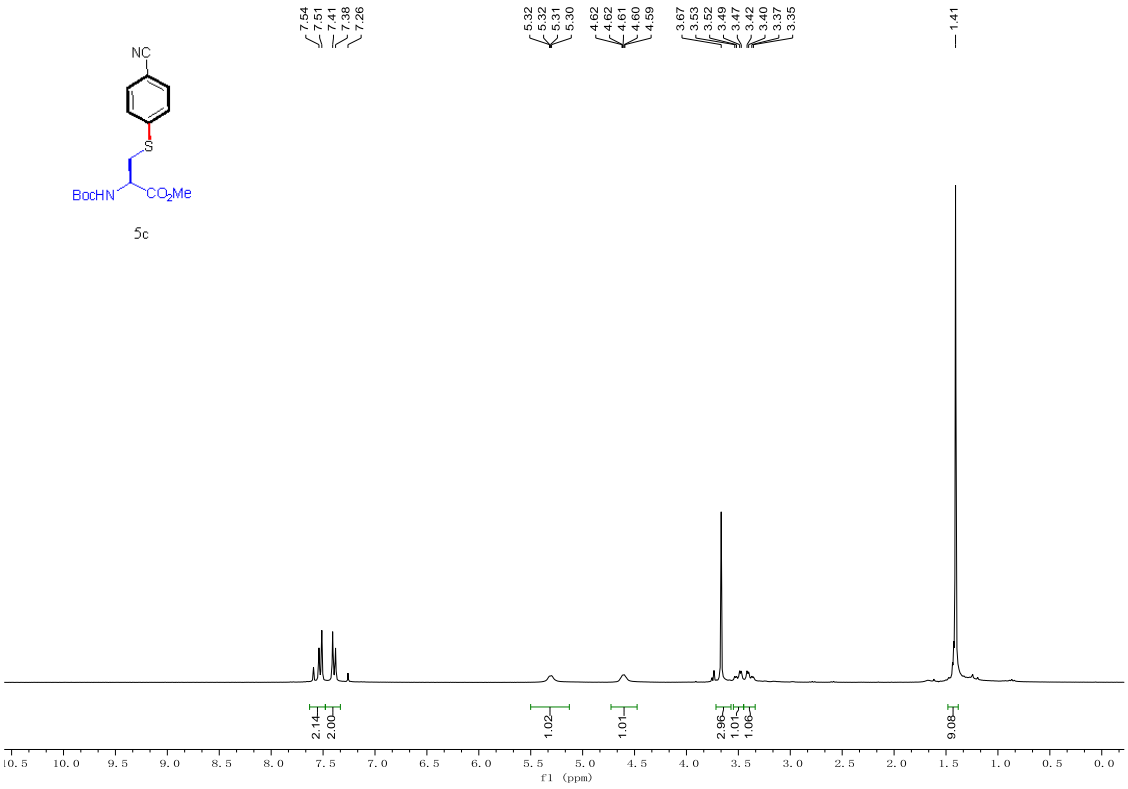

$^{13}$C NMR spectrum of **5a** (75 MHz, MeOD-$d_4$)



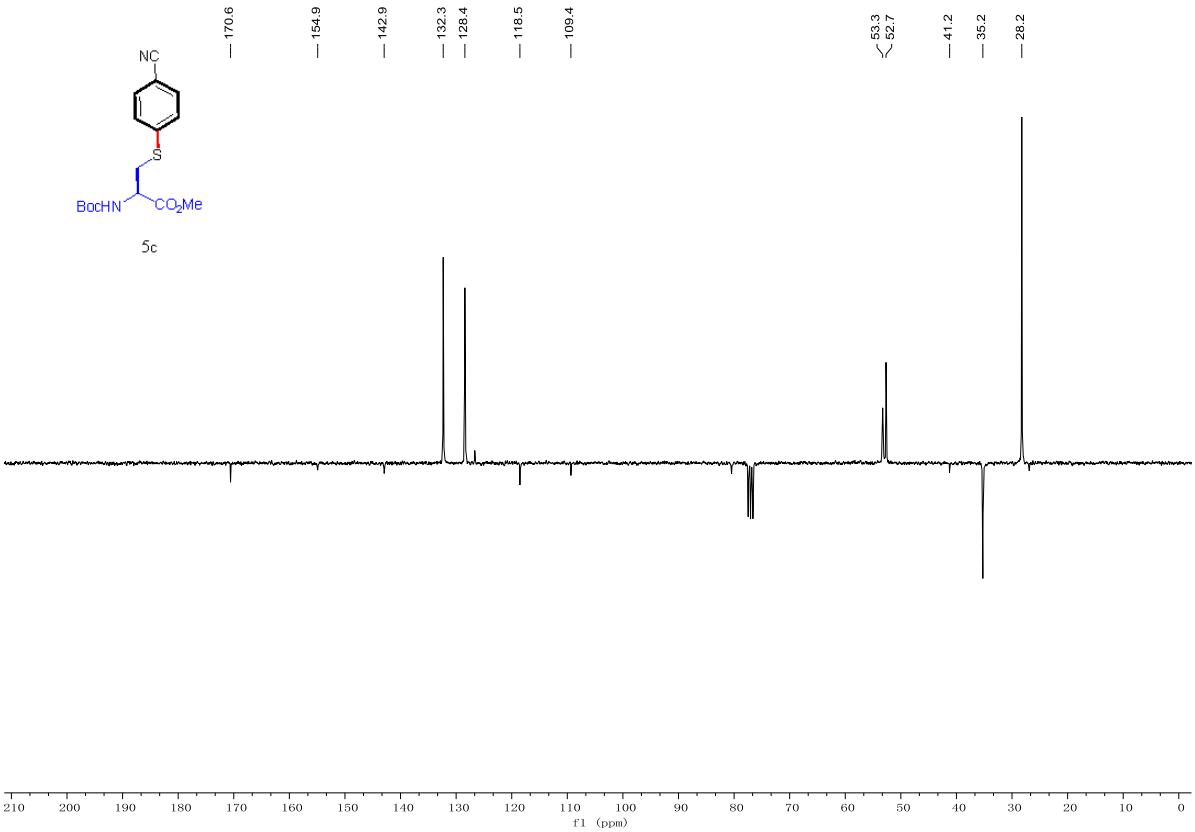

$^{1}$H NMR spectrum of **5b** (300 MHz, MeOD-$d_4$)




$^{13}$C NMR spectrum of **5b** (75 MHz, MeOD-$d_4$)




$^{1}$H NMR spectrum of **5c** (300 MHz, $CDCl_3$)




$^{13}$C NMR spectrum of **5c** (75 MHz, $CDCl_3$)