Supporting Information for:

Electrochemically dehydrogenative C(sp^2)–H/S–H cross-coupling: effective synthesis of *ortho*-aminophenyl thioglycoside derivatives

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Contents

1. General information

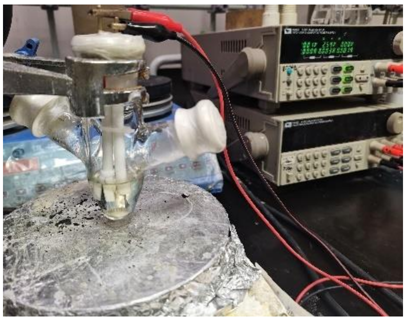
Solvents and reagents were reagent grade and used without purification unless otherwise noted. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Anhydrous solvent were bought from Aladdin Chemicals, Shanghai, China. Compound spots were visualized either by UV light (254 nm) or by heating with a solution with 5% H_2SO_4 in ethanol. Column chromatography was performed using silica gel (200-300 mesh).

Structural assignments were made with additional information from COSY, HSQC, HMBC, and NOESY experiments. ^{1}H, ^{19}F, ^{13}C, and COSY NMR data reported in ppm (δ) were recorded on a 500 MHz NMR JEOL with tetramethylsilane (TMS) as an internal standard and $CDCl_3$ as solvent unless otherwise stated. Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad.

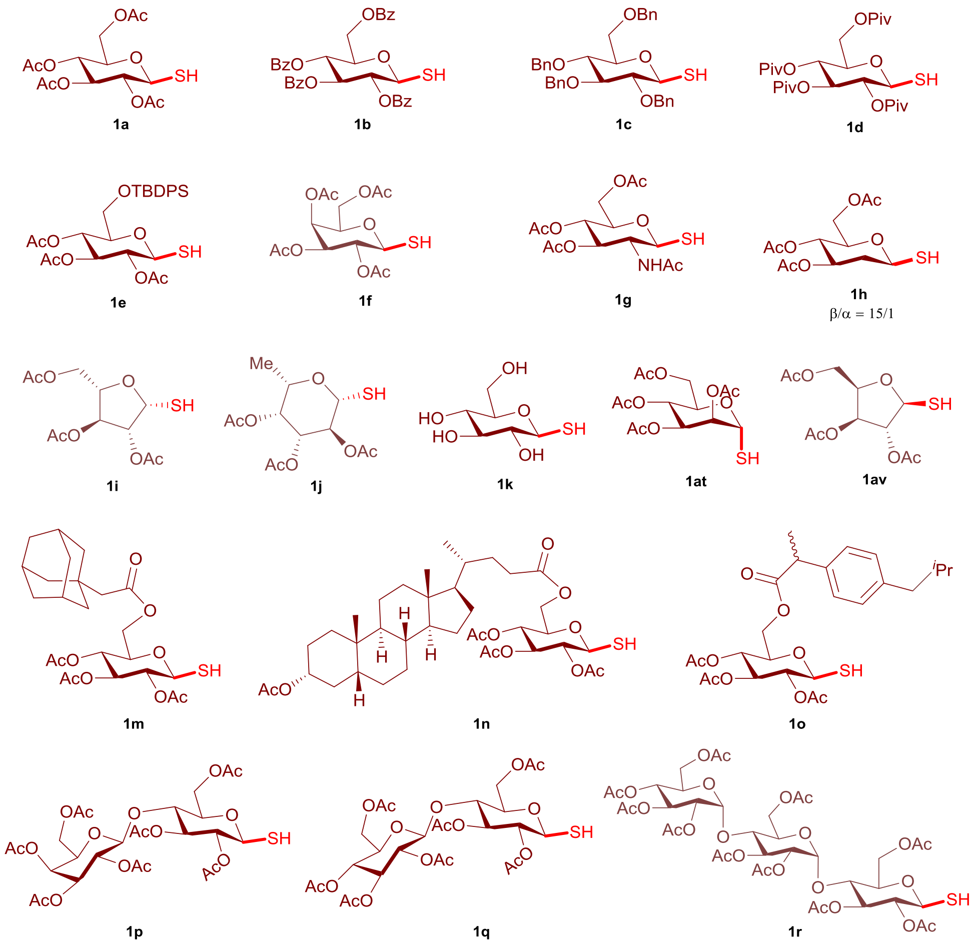
High resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument using EI (70 eV) or an AB Sciex Triple TOF5600 Plus LC/MS using ESI.

Cyclic voltammetry (CV) were taken on a CS2350M electrochemical workstation (Wuhan Corrtest Instrument Co., Ltd) in CH_3CN (EnergySeal, 99.9%, with molecular sieves, water⩽50 ppm (by K.F.)) at room temperature, and the CV experiments were carried out in a three-electrode cell configuration with a glassy carbon (GC) working electrode (3 mm diameter) and a platinum wire counter electrode. The potentials were measured versus an Ag/AgCl reference electrode.

The ElectraSyn Set-up

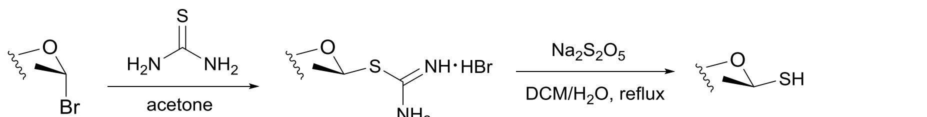


2. Numberings and structures of 1-thiosugars



3. General procedures for 1-thiosugars

3.1 General procedure Ⅰ.

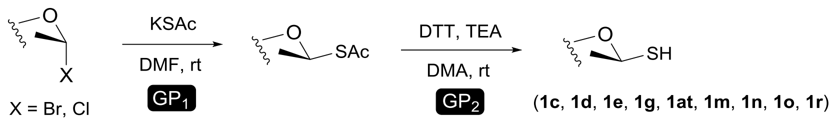


(**1a**, **1b**, **1f**, **1i**, **1j**, **1av**, **1p**, **1q**)

1-Bromosugar (1.0 equiv) and thiourea (1.5 equiv) were dissolved in dry acetone (0.1 M). The solution was heated at reflux for Ca. 4 h until 1-bromosugar was fully consumed as indicated by TLC analysis. The resulting mixture was concentrated in vacuo. $Na_2S_2O_5$ (3.0 equiv) and DCM/H_2O (v/v, 2/1) were added to the resulting mixture, which was then heated at 50 ℃ for ca. 3 h and then diluted by addition of DCM. The organic phase was separated and washed by brine, dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by silica gel chromatography (petroleum-

EtOAc) afforded the desired 1-thiosugar.[1]

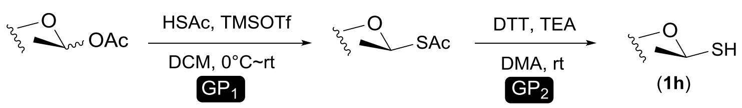
3.2 General procedure Ⅱ.



GP$_1$: Synthesis of thiolacetate derivative. To asolution of the glycosyl halide (1.0 equiv) in dry DMF (0.3 M) was added potassium thioacetate (1.5 equiv). The mixture was stirred at room temperature until TLC indicated complete consumption of the starting material, then poured into water, and extracted with EtOAc. The organic layer was washed with water, brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel chromatography (petroleum-EtOAc) afforded the desired thiolacetate derivative.

GP$_2$: Synthesis of 1-thiosugar. To a 0.15 M solution of thiolacetate derivative (1.0 equiv) and DTT (Dithiothreitol, 1.5 equiv) in DMA was added TEA (0.1 equiv), and the mixture was stirred at room temperature for an appropriate time until complete consumption of the starting material. The reaction mixture was poured into water and extracted with EtOAc. The combined organic layers were washed with water, brine and concentrated to furnish the crude product, which was further purified over silica gel chromatography.[2]

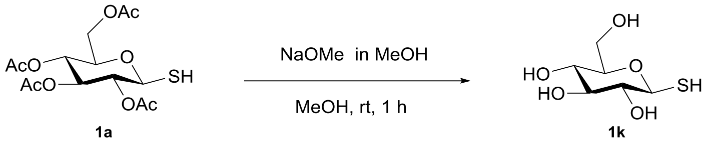
3.3 General procedure Ⅲ.



GP$_1$: Synthesis of thiolacetate derivative. Per-*O*-acetyl glycoside (1.0 equiv) was dissolved in anhydrous DCM (0.1 M), to which HSAc (3.0 equiv) was added, and cooled to 0 ℃. After addition of TMSOTf (1.0 equiv), the reaction was allowed to proceed at 0 ℃ until TLC indicated complete consumption of the starting material, then poured into aqueous $NaHCO_3$, and extracted with EtOAc. The organic layer was washed successively with water and brine, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography.

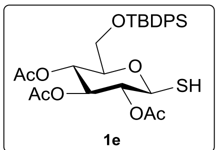
GP2: Synthesis of 1-thiosugar. Prepared from thiolacetate derivative according to **GP2** in General procedure Ⅱ.[2]

3.4 The synthesis of 1k.

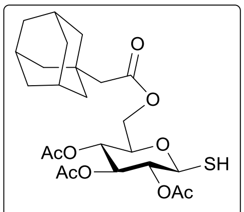


To a round flask, NaOMe in MeOH (60 μL, 0.5 equiv, 5.0 M) was added to a solution of **1a** (0.11 g, 0.3 mmol) in MeOH (3 mL). The solution was stirred at room temperature. When the reaction was completed, the pH of solvent was adjusted to ~7 with Amberlite IR-120 and then filtration and remove the solvent under vacuo to gain the pale-yellow oil. These oils bypass purification and proceed straight to the next step reaction.

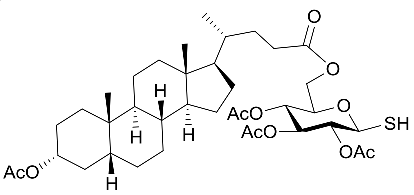
3.5 Characterization of new substrates



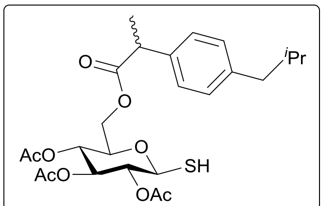
R_f = 0.3, Petroleum Ether/Ethyl Acetate = 10:1 (v/v). Colorless oil; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.72 – 7.70 (m, 2H), 7.67 – 7.65 (m, 2H), 7.45 – 7.36 (m, 6H), 5.21 – 5.13 (m, 2H), 4.94 (t, *J* = 9.4 Hz, 1H), 4.46 (t, *J* = 9.8 Hz, 1H), 3.76 (dd, *J* = 11.8, 2.1 Hz, 1H), 3.70 (dd, *J* = 11.8, 4.6 Hz, 1H), 3.57 – 3.53 (m, 1H), 2.16 (d, *J* = 9.8 Hz, 1H), 2.07 (s, 3H), 2.00 (s, 5H), 1.92 (s, 3H), 1.05 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.5, 169.8, 169.4, 136.0, 135.8, 133.3, 133.2, 129.9, 127.8, 79.1, 78.5, 74.1, 73.9, 68.4, 62.8, 26.8, 20.9, 20.8, 20.7, 19.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{28}H_{37}O_8SSi^+$ 561.1973; Found 561.1949.


1m

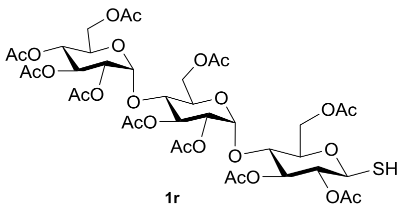
R_f = 0.3, Petroleum Ether/Ethyl Acetate = 2:1 (v/v). Colorless oil; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.22 – 5.13 (m, 2H), 4.94 (t, *J* = 9.5 Hz, 1H), 4.54 (t, *J* = 9.8 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.69 (ddd, *J* = 9.8, 4.8, 2.3 Hz, 1H), 2.30 (d, *J* = 9.9 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (d, *J* = 2.0 Hz, 2H), 1.99 (s, 3H), 1.94 – 1.93 (m, 3H), 1.69 – 1.66 (m, 4H), 1.60 – 1.58 (m, 3H), 1.53 (s, 5H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.1, 169.8, 78.7, 76.7, 74.1, 73.6, 67.5, 62.3, 48.4, 42.3, 36.7, 32.8, 28.6, 20.9, 20.8. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{24}H_{35}O_9S^+$ 499.1996; Found 499.1984.


1n

R_f = 0.2, Petroleum Ether/Ethyl Acetate = 2:1 (v/v). Colorless oil; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.18 (t, *J* = 9.4 Hz, 1H), 5.11 (t, *J* = 9.7 Hz, 1H), 4.96 (t, *J* = 9.5 Hz, 1H), 4.73 – 4.67 (m, 1H), 4.53 (t, *J* = 9.9 Hz, 1H), 4.22 – 4.18 (m, 1H), 4.12 – 4.10 (m, 1H), 3.71 (ddd, *J* = 9.7, 4.8, 2.2 Hz, 1H), 2.30 (d, *J* = 10.0 Hz, 1H), 2.27 – 2.23 (m, 1H), 2.19 – 2.14 (m, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.95 – 1.92 (m, 1H), 1.85 – 1.77 (m, 5H), 1.66 – 1.65 (m, 1H), 1.56 – 1.51 (m, 2H), 1.44 – 1.35 (m, 8H), 1.29 – 1.21 (m, 4H), 1.07 – 1.04 (m, 5H), 0.90 (s, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.62 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.9, 170.8, 170.7, 170.2, 169.8, 78.8, 76.5, 74.5, 73.7, 73.6, 67.9, 62.1, 56.5, 56.0, 42.8, 42.0, 40.5, 40.2, 35.9, 35.5, 35.1, 34.7, 32.3, 31.1, 30.9, 28.2, 27.1, 26.7, 26.4, 24.3, 23.4, 21.6, 20.9, 20.7, 18.3, 12.1. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{59}O_{11}S^+$ 723.3773; Found 723.3775.


1o (dr = 1.4:1)

R_f = 0.3, Petroleum Ether/Ethyl Acetate = 2:1 (v/v). Colorless oil; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.14 – 7.05 (m, 7H), 5.17 (t, *J* = 9.3 Hz, 1H), 5.13 – 5.09 (m, 2H), 4.92 (t, *J* = 9.5 Hz, 1H), 4.86 (t, *J* = 9.3 Hz, 0.6H), 4.50 (q, *J* = 9.7 Hz, 1.7H), 4.17 (dd, *J* = 12.5, 4.8 Hz, 0.7H), 4.05 (dd, *J* = 12.5, 2.2 Hz, 0.7H), 3.90 (dd, J = 12.4, 2.0 Hz, 1H), 3.75 (dd, J = 12.5, 4.9 Hz, 1H), 3.69 – 3.58 (m, 3.4H), 2.41 (d, J = 7.1 Hz, 4H), 2.27 (dd, J = 9.9, 3.4 Hz, 1.7H), 2.08 (s, 2H), 2.05 (s, 3H), 2.01 (s, 5H), 1.86 (s, 3H), 1.84 – 1.79 (m, 1.7H), 1.45 – 1.42 (m, 5H), 0.88 – 0.86 (m, 11H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.4, 173.0, 170.7, 170.4, 170.2, 169.8, 169.7, 141.1, 141.0, 136.8, 136.7, 129.6, 127.2, 127.1, 78.7, 76.6, 76.3, 73.9, 73.8, 73.5, 72.9, 68.0, 67.8, 62.0, 45.1, 45.0, 44.8, 30.2, 22.4, 20.9, 20.8, 20.6, 20.1, 18.1, 18.0. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{35}O_9S^+$ 511.1996; Found 511.1983.

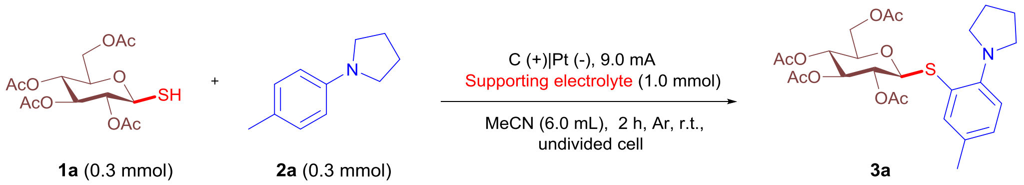


1r

R_f = 0.2, Petroleum Ether/Ethyl Acetate = 1:2 (v/v). Colorless oil; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.38 – 5.34 (m, 2H), 5.32 – 5.21 (m, 3H), 5.04 (t, J = 9.9 Hz, 1H), 4.82 (dd, J = 10.6, 3.9 Hz, 1H), 4.77 (t, J = 9.3 Hz, 1H), 4.71 (dd, J = 10.5, 4.0 Hz, 1H), 4.57 (t, J = 9.6 Hz, 1H), 4.42 (t, J = 12.2 Hz, 2H), 4.29 – 4.21 (m, 2H), 4.14 (d, J = 12.2 Hz, 1H), 4.02 (d, J = 12.5 Hz, 1H), 3.97 – 3.90 (m, 4H), 3.73 – 3.71 (m, 1H), 2.23 (d, J = 9.6 Hz, 1H), 2.16 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.02 (s, 6H), 2.01 (s, 3H), 1.99 (s, 3H), 1.97 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.7, 170.5, 170.1, 170.0, 169.9, 169.8, 169.6, 95.9, 95.7, 78.2, 76.5, 76.0, 74.4, 73.8, 72.6, 71.7, 70.5, 70.2, 69.4, 69.1, 68.6, 67.9, 63.2, 62.3, 61.4, 21.0, 20.9, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{53}O_{25}S^+$ 941.2591; Found 941.2588.

4. Optimization of reaction conditions

Table S1. Supporting electrolytes screening

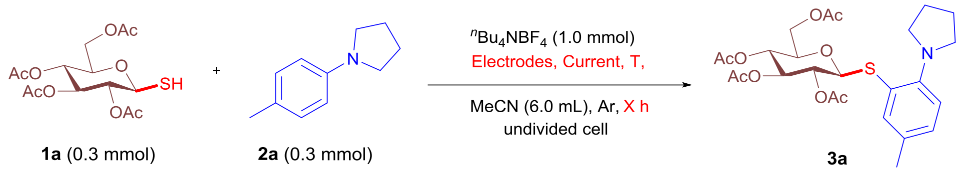


Entry	Supporting electrolyte	Yield (%)[a]
1	$^nBu_4NBF_4$	30
2	$^nBu_4OAc$	Trace
3	$^nBu_4NPF_6$	20
4	$^nBu_4NClO_4$	32[b]

5	TBAB	20
6	LiBr	18
7	$NaBF_4$	31[b]
8	$Mg(ClO_4)_2$	trace

[a] Isolated yields. [b] The electrolyte is adsorbed to the electrode, which greatly reduces the effciency of the reaction, although the yield is similar to entry 1.

Table S2. Electrode material screening

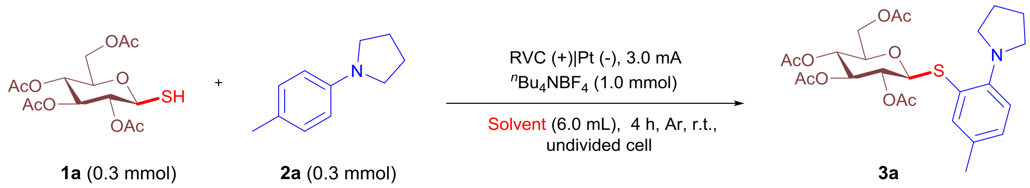


1a (0.3 mmol) **2a** (0.3 mmol) **3a**

Entry	Electrode	Current (mA)	Time (h)	T(℃)	Yield (%)[a]
1	C (+)|Pt (-)	9	2	r.t.	30
2	C (+)|C (-)	9	2	r.t.	7
3	GC (+)|CF (-)	9	2	r.t.	trace
4	Pt (+)|Pt (-)	9	2	r.t.	15
5	RVC (+)|Pt (-)	9	2	r.t.	28
6	C (+)|Pt (-)	3	4	60	60
7	Pt (+)|C (-)	3	4	60	15
8	**RVC (+)|Pt (-)**	**3**	**4**	**r.t.**	**70**
9	RVC (+)|Pt (-) **2a** (2.0 equiv)	3	4	r.t.	68

[a] Isolated yields.

Table S3. The solvent screening

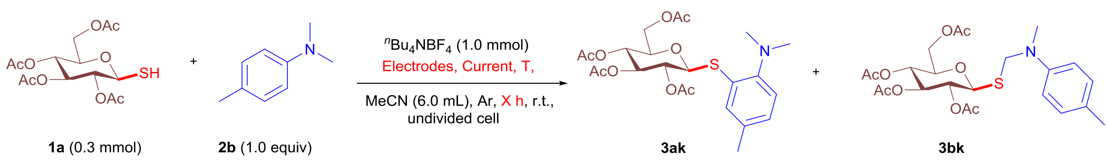


1a (0.3 mmol) **2a** (0.3 mmol) **3a**

Entry	Supporting electrolyte	Yield (%)[a]
1	**MeCN**	**70**
2	DMF	trace
3	MeOH	20
4	DMSO	18

[a] Isolated yields.

Table S4. Electrode material screening

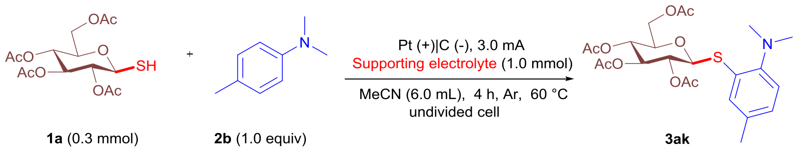


1a (0.3 mmol) **2b** (1.0 equiv) **3ak** **3bk**

Entry	Electrode	Current (mA)	Time (h)	T(℃)	Yield (%)[a]	
					3ak	**3bk**
1	RVC (+)|Pt (-)	3	4	r.t.	18	18
2	Pt (+)|Pt (-)	3	4	r.t.	30	15
3	Pt (+)|C (-)	3	5	r.t.	36	0
4	**Pt (+)|C (-)**	**3**	**4**	**60**	**65**	**0**
5	Pt (+)|RVC (-)	3	4	60	15	15
6	Pt (+)|C (-)	3	4	70	58	0

[a]Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard.

Table S5. Supporting electrolytes screening



1a (0.3 mmol) **2b** (1.0 equiv) **3ak**

Entry	Supporting electrolyte	Yield (%)[a]
1	**^{n}Bu$_4$NBF$_4$**	**65**
2	$NaBF_4$	20
3	$Mg(ClO_4)_2$	15
4	^{n}Bu$_4$NClO$_4$	trace
5	TBAB	25
6	LiBr	30

[a]Isolated yields.

5. General procedure for the synthesis of thioglycosides

General procedure A: An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars (0.3 mmol, 1.0 equiv), aniline derivatives (0.3 mmol, 1.0 equiv), ^{n}Bu$_4$NBF$_4$ (1.0 mmol), and dry MeCN (6.0 mL). The bottle was equipped with reticulated vitreous carbon (RVC) (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at room temperature for 4 h. In the reaction process, the generation of bubbles can be observed at the cathode. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired product.

General procedure B: An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars (0.3 mmol, 1.0 equiv), aniline derivatives (0.3 mmol, 1.0 equiv), ^{n}Bu$_4$NBF$_4$ (1.0 mmol), and dry MeCN (6.0

mL). The bottle was equipped with platinum plate (15 × 15 × 0.1 cm^3) as the anode, graphite plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at 60 ℃ for 4 h. In the reaction process, the generation of bubbles can be observed at the cathode. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired product.

General procedure C: An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars (0.3 mmol, 1.0 equiv), aniline derivatives (0.3 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (1.0 mmol), and dry MeCN (6.0 mL). The bottle was equipped with graphite plate (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 9.0 mA at room temperature for 2 h. In the reaction process, the generation of bubbles can be observed at the cathode. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired product.

6. Cyclic voltammetry studies

All cyclic voltammograms were performed in a three-electrode cell at room temperature. A glassy carbon disk electrode (diameter is 3.0 mm, PTFE shroud) was used as a working electrode. A platinum wire was used as a counter electrode. Ag/AgCl electrode submerged in 3.5 M KCl solution was used as a reference electrode. 30 mL of MeCN containing 0.1 M $^{n}Bu_4NBF_4$ were poured into the electrochemical cell in all experiments. The CV of all substrates were measured at the concentration of 0.01 M. The scan rate was 0.10 V/s, ranging from -3.0 V to 3.0 V.

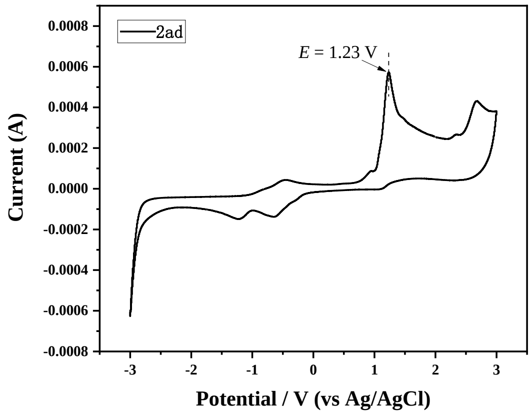


Figure S1. Cyclic voltammogram of **2ad** (0.01 M) in an electrolyte of $^{n}Bu_4NBF_4$ (0.1 M) in CH_3CN. *E* = 1.23 V.

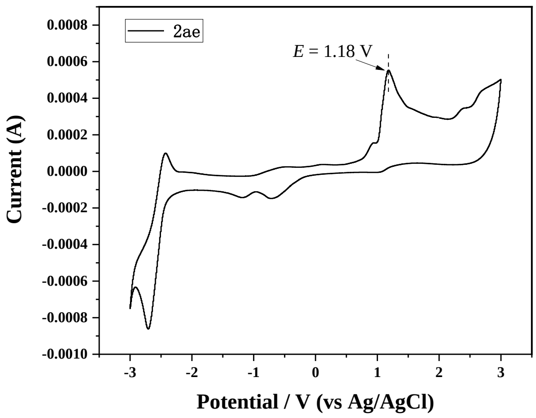


Figure S2. Cyclic voltammogram of **2ae** (0.01 M) in an electrolyte of $^{n}Bu_4NBF_4$ (0.1 M) in CH_3CN. *E* = 1.18 V.

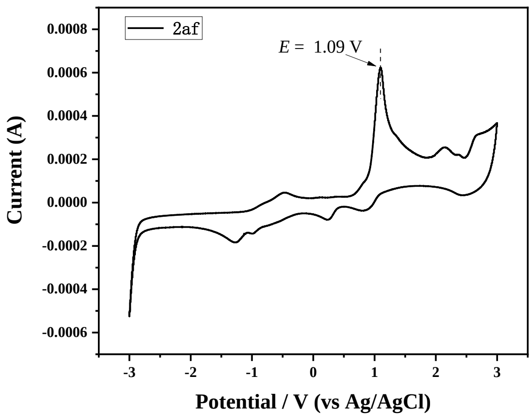


Figure S3. Cyclic voltammogram of **2af** (0.01 M) in an electrolyte of $^{n}Bu_4NBF_4$ (0.1 M) in CH_3CN. *E*

= 1.09 V.

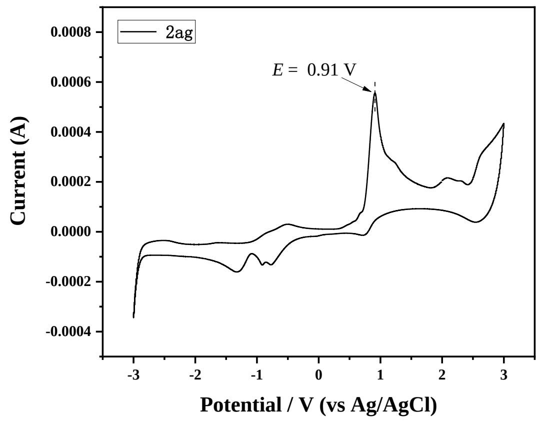


Figure S4. Cyclic voltammogram of **2ag** (0.01 M) in an electrolyte of $^{n}Bu_4NBF_4$ (0.1 M) in CH_3CN. E = 0.91 V.

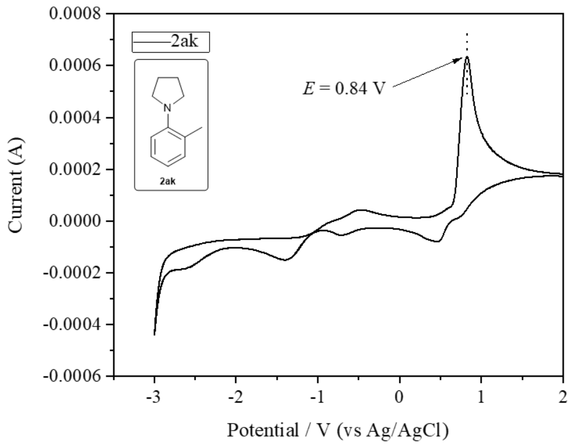


Figure S5. Cyclic voltammogram of **2ak** (0.01 M) in an electrolyte of $^{n}Bu_4NBF_4$ (0.1 M) in CH_3CN. E = 0.84 V.

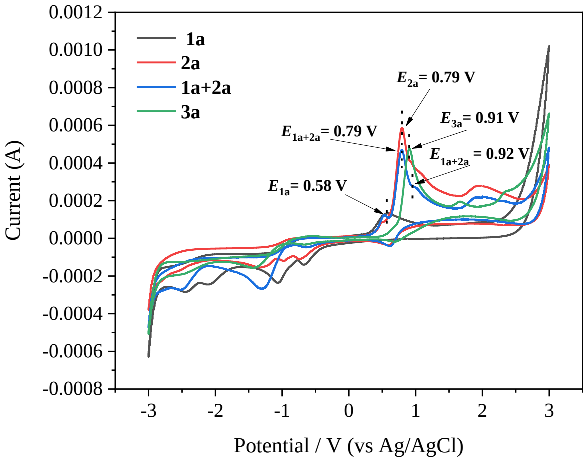
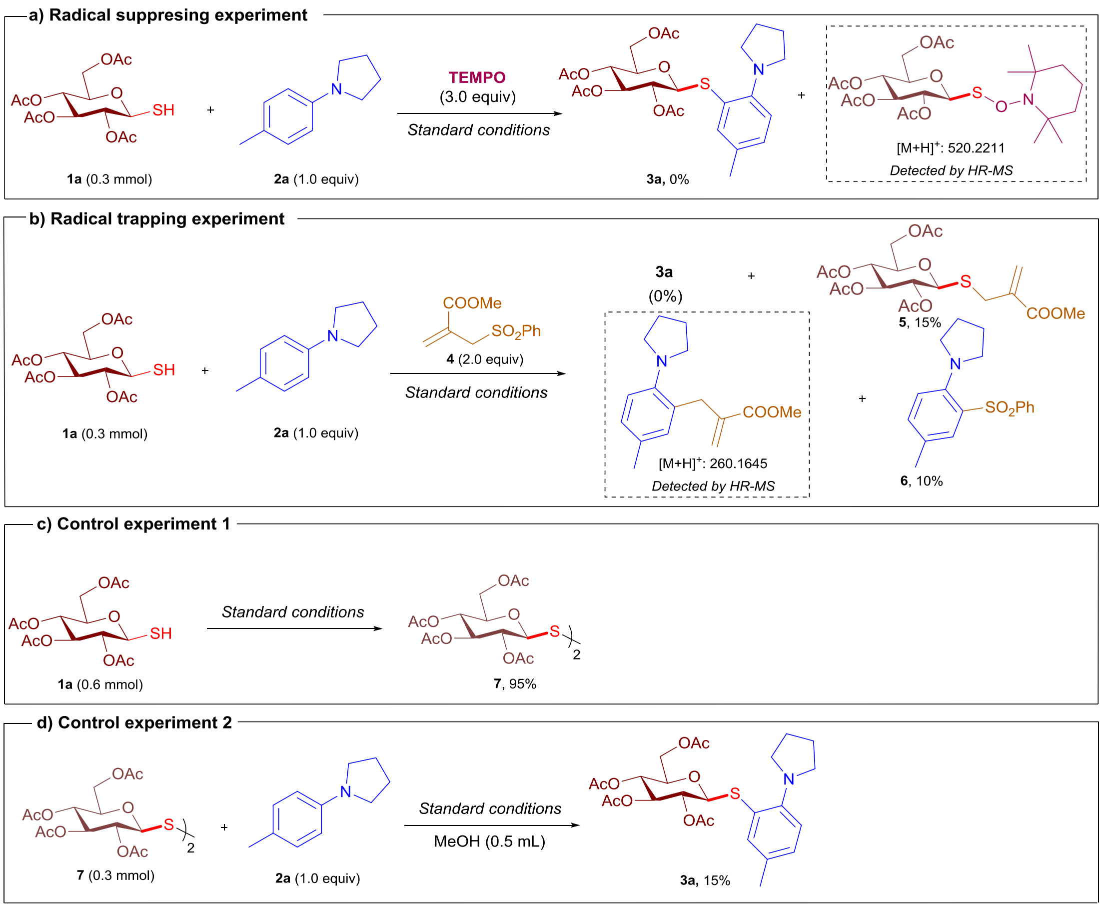


Figure S6. Cyclic voltammograms of reactions.

7. Control experiments



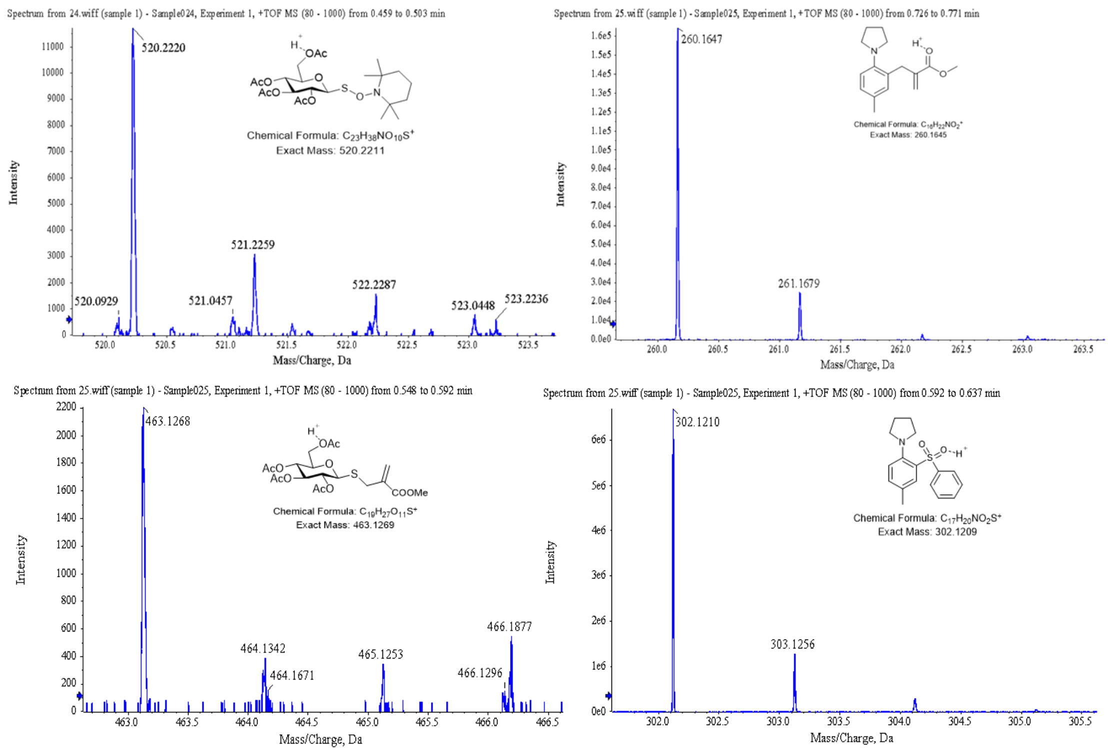
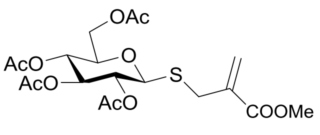


Figure S6. HRMS of radical trapping experiments.

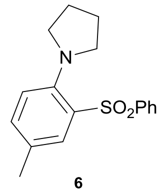
(a) With TEMPO: An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars **1a** (110 mg, 0.3 mmol), aniline derivatives **2a** (49 mg, 0.3 mmol), TEMPO (141 mg, 0.9 mmol), $^{n}Bu_4NBF_4$ (330 mg, 1 mmol), and dry MeCN (6.0 mL). The bottle was equipped with reticulated vitreous carbon (RVC) (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at room temperature for 4 h. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel failed to obtain **3a**.

(b) With **4**: An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars **1a** (110 mg, 0.3 mmol), aniline derivatives **2a** (49 mg, 0.3 mmol), **4** (144 mg, 0.6 mmol), $^{n}Bu_4NBF_4$ (330 mg, 1 mmol), and dry MeCN (6.0 mL). The bottle was equipped with reticulated vitreous carbon (RVC) (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at room temperature for 4 h. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel to afford **5** (21 mg, 15%) and **6** (9 mg, 10%), respectively, and impeded the generation of **3a.**



5

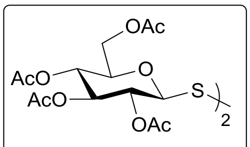
R_f = 0.4, Petroleum Ether/Ethyl Acetate = 2:1 (v/v). Yellow oil; **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.24 (s, 1H), 5.70 (s, 1H), 5.19 (t, *J* = 9.3 Hz, 1H), 5.03 (dt, *J* = 19.2, 9.7 Hz, 2H), 4.48 (d, *J* = 10.1 Hz, 1H), 4.21 (dd, *J* = 12.4, 5.1 Hz, 1H), 4.10 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.76 (s, 3H), 3.64 (ddd, *J* = 10.0, 5.1, 2.3 Hz, 1H), 3.60 – 3.49 (m, 2H), 2.06 (s, 3H), 2.00 (s, 6H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.3, 169.5, 166.3, 136.6, 127.2, 82.7, 75.8, 73.9, 69.9, 68.3, 62.2, 52.3, 30.9, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{27}O_{11}S^+$ 463.1269; Found 463.1268.



6

R_f = 0.5, Petroleum Ether/Ethyl Acetate = 15:1 (v/v). Yellow oil; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 2.2 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.34 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 2.76 – 2.73 (m, 4H), 2.41 (s, 3H), 1.76 – 1.73 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.4, 142.7, 137.6, 135.6, 134.5, 132.3, 130.1, 128.2, 127.8, 124.6, 54.2, 24.8, 21.0. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_2S^+$ 302.1209; Found 302.1210.

(c) An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars **1a** (220 mg, 0.6 mmol), ^{n}Bu$_4$NBF$_4$ (330 mg, 1 mmol), and dry MeCN (6.0 mL). The bottle was equipped with reticulated vitreous carbon (RVC) (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at room temperature for 4 h. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel to afford disulfide **7** (414 mg, 95%).

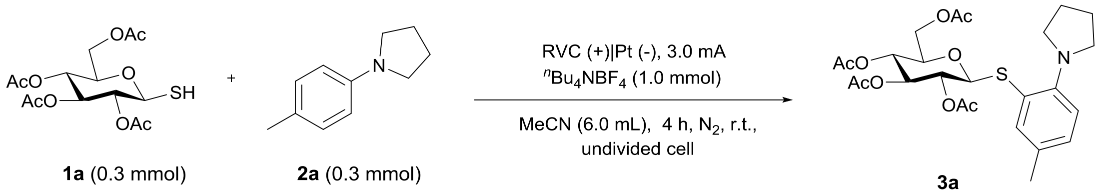


7

R_f = 0.3, Petroleum Ether/Ethyl Acetate = 1:1 (v/v). Yellow oil; **^{1}H NMR** (500 MHz, Chloroform-d) δ 5.25 (t, *J* = 9.3 Hz, 2H), 5.18 (t, *J* = 9.5 Hz, 2H), 5.08 (t, *J* = 9.7 Hz, 2H), 4.64 (d, *J* = 9.7 Hz, 2H), 4.32 (dd, *J* = 12.5, 4.3 Hz, 2H), 4.20 (d, *J* = 10.3 Hz, 2H), 3.79 – 3.76 (m, 2H), 2.12 (s, 6H), 2.09 (s, 7H), 2.01 (s, 6H), 1.99 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.2, 169.4, 169.3, 87.2, 76.2, 73.9, 69.7, 67.8, 61.6, 20.9, 20.7, 20.6. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{28}H_{39}O_{18}S_2^+$ 727.1572; Found 727.1588. The ^{1}H NMR and ^{13}C NMR spectroscopic data of **7** are in accordance with those reported previously.[3]

(d) An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with disulfide **7** (218 mg, 0.3 mmol), aniline derivatives **2a** (49 mg, 0.3 mmol), ^{n}Bu$_4$NBF$_4$ (330 mg, 1.0 mmol), and dry MeCN (6.0 mL). The bottle was equipped with reticulated vitreous carbon (RVC) (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with argon. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at room temperature for 4 h. After completion, the solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel to afford **3a** (24 mg, 15%).

8. GC detection test of H_2



1a (0.3 mmol) **2a** (0.3 mmol) **3a**

An oven-dried 15 mL undivided three-necked bottle fitted with a magnetic stir-bar was charged with 1-thiosugars **1a** (0.11 g, 0.3 mmol), aniline derivatives **2a** (0.048 g, 0.3 mmol), ^{n}Bu$_4$NBF$_4$ (0.33 g, 1.0 mmol), and dry MeCN (6.0 mL). The bottle was equipped with reticulated vitreous carbon (RVC) (15 × 15 × 0.1 cm^3) as the anode, platinum plate (15 × 15 × 0.1 cm^3) as the cathode, and then charged with nitrogen. The reaction mixture was stirred and electrolyzed under a constant current of 3.0 mA at room temperature for 4 h. After reaction was accomplished, gas chromatography (nitrogen was used as a carrier gas) was applied to detect the existence of H_2.

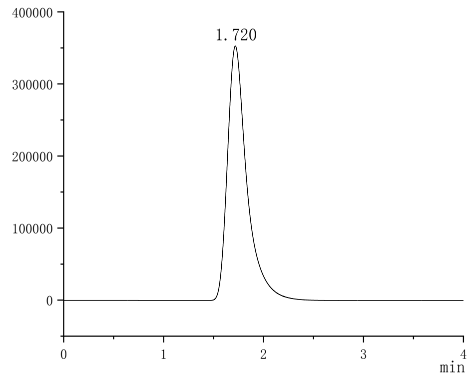


Figure S7. GC of H_2 standard sample

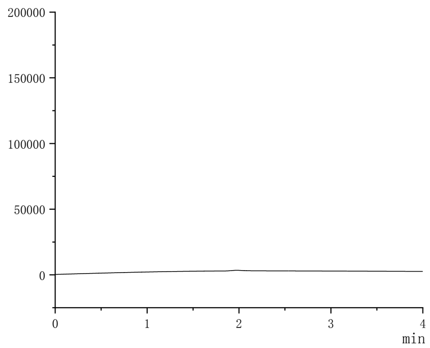


Figure S8. GC of the atmosphere (before electrolysis)

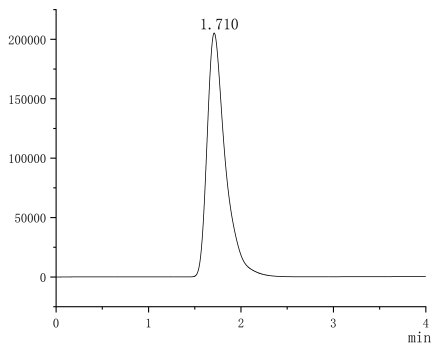
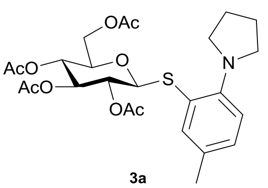


Figure S9. GC of the atmosphere (after electrolysis)

9. Characterization data

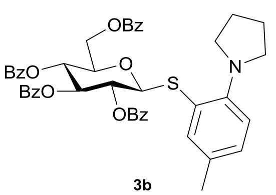
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3a)



3a

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3a** was isolated in 70% (109.9 mg) yield as colorless oil following the general procedure **A**. $[\alpha]_D^{20}$ -0.014 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 10.4 Hz, 1H), 5.18 (t, *J* = 9.3 Hz, 1H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.96 (t, *J* = 9.6 Hz, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.23 – 4.19 (m, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.68 – 3.66 (m, 1H), 3.26 (s, 4H), 2.25 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.88 (s, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.6, 169.3, 148.9, 136.0, 129.8, 129.5, 121.1, 116.6, 85.7, 75.8, 74.3, 70.30, 68.4, 62.5, 51.8, 25.3, 20.8, 20.7, 20.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{34}NO_9S^+$ 524.1949; Found 524.1954. **IR** (film) ν 3446, 2955, 2811, 1746, 1597, 1388, 1222, 1038 cm^{-1}.

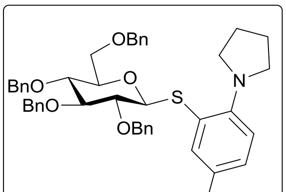
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((benzoyloxy)methyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3b)



3b

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 6:1 (v/v)). Compound **3b** was isolated in 73% (168.9 mg) yield as colorless oil following the general procedure **A**. $[\alpha]_D^{20}$ -0.025 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.41 – 7.37 (m, 5H), 7.35 – 7.33 (m, 3H), 7.28 – 7.26 (m, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.87 (t, *J* = 9.5 Hz, 1H), 5.64 (t, *J* = 9.8 Hz, 1H), 5.49 (t, *J* = 9.7 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.46 (dd, *J* = 12.7, 5.6 Hz, 1H), 4.15 – 4.11 (m, 1H), 3.12 (s, 4H), 2.03 (s, 3H), 1.54 – 1.48 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.3, 165.9, 165.3, 164.9, 149.2, 137.2, 133.5, 133.3, 133.2, 130.1, 129.9, 129.9, 129.8, 129.7, 129.4, 129.0, 128.8, 128.5, 128.4, 119.7, 116.2, 86.5, 76.3, 74.5, 70.8, 69.6, 63.6, 51.7, 25.1, 20.1. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{45}H_{42}NO_9S^+$ 772.2575; Found 772.2590. **IR** (film) ν 3319, 2804, 2730, 1733, 1588, 1395, 1356, 1273, 1099, 719 cm^{-1}.

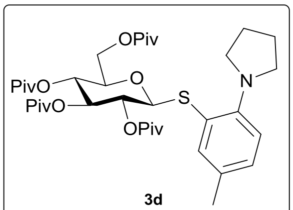
1-(4-methyl-2-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)thio)phenyl)pyrrolidine (3c)



3c

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 8:1 (v/v)). Compound **3c** was isolated in 50% (107.3 mg) yield as colorless oil following the general procedure **A**. $[\alpha]_D^{20}$ -0.003 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 2.1 Hz, 1H), 7.42 (d, *J* = 6.3 Hz, 2H), 7.35 – 7.21 (m, 16H), 7.22 (dd, *J* = 7.5, 1.9 Hz, 2H), 6.96 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.97 – 4.92 (m, 2H), 4.86 (dd, *J* = 10.9, 1.9 Hz, 2H), 4.74 (d, *J* = 10.2 Hz, 1H), 4.69 (d, *J* = 9.9 Hz, 1H), 4.61 (d, *J* = 10.6 Hz, 2H), 4.55 (d, *J* = 12.1 Hz, 1H), 3.79 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.74 – 3.71 (m, 2H), 3.65 (t, *J* = 9.4 Hz, 1H), 3.55 – 3.50 (m, 2H), 3.34 – 3.24 (m, 4H), 2.16 (s, 3H), 1.85 – 1.83 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.2, 138.6, 138.4, 138.2, 134.6, 130.1, 128.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 124.1, 116.5, 87.3, 87.0, 81.2, 79.2, 78.0, 76.0, 75.4, 75.1, 73.6, 69.1, 51.9, 25.1, 20.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{45}H_{50}NO_5S^+$ 716.3404; Found 716.3420.

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)-6-((pivaloyloxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (3d)

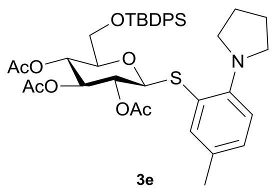


3d

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 10:1 (v/v)). Compound **3d** was isolated in 63% (130.7 mg) yield as white solid following the general procedure **A**; *m.p.*: 71.9 – 72.8 ℃; $[\alpha]_D^{20}$ -0.016 (*c*

1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 6.95 (d, *J* = 10.4 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 5.33 (t, *J* = 9.3 Hz, 1H), 5.17 – 5.10 (m, 2H), 4.84 (d, *J* = 10.3 Hz, 1H), 4.18 (d, *J* = 12.3 Hz, 1H), 4.03 (dd, *J* = 12.3, 5.4 Hz, 1H), 3.71 (dd, *J* = 11.0, 6.3 Hz, 1H), 3.36 – 3.32 (m, 2H), 3.12 – 3.08 (m, 2H), 2.24 (s, 3H), 1.92 – 1.84 (m, 4H), 1.87 – 1.80 (m, 2H), 1.17 (s, 9H), 1.16 (s, 9H), 1.14 (s, 9H), 1.11 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.3, 177.3, 176.6, 176.5, 148.4, 133.8, 130.0, 129.2, 123.1, 116.7, 86.7, 73.6, 70.1, 68.0, 62.3, 51.8, 38.9, 38.8, 27.3, 27.2, 25.2, 20.6. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{37}H_{58}NO_9S^+$ 692.3827; Found 692.3845. **IR** (film) ν 2968, 2868, 1736, 1485, 1279, 1150, 1041, 799, 764 cm^{-1}.

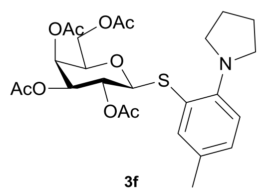
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(((tert-butyldiphenylsilyl)oxy)methyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3e)



3e

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 8:1 (v/v)). Compound **3e** was isolated in 71% (153.2 mg) yield as yellow solid following the general procedure **A**; *m.p.*: 68.2 – 70.0 ℃; $[\alpha]_D^{20}$ -0.008 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.42 – 7.35 (m, 6H), 7.33 (s, 1H), 6.98 (d, *J* = 10.5 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.22 – 5.16 (m, 2H), 5.03 (t, *J* = 9.5 Hz, 1H), 4.78 (d, *J* = 10.1 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.54 – 3.52 (m, 1H), 3.34 – 3.25 (m, 4H), 2.13 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.89 – 1.86 (m, 7H), 1.04 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.6, 169.4, 169.3, 148.8, 136.0, 135.8, 135.7, 133.2, 133.1, 129.8, 129.7, 127.8, 121.6, 116.6, 85.6, 78.7, 74.8, 70.7, 68.5, 62.8, 51.7, 26.8, 25.2, 20.8, 20.7, 20.4, 19.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{39}H_{50}NO_8SSi^+$ 720.3021; Found 720.3027. **IR** (film) ν 3342, 2813, 2730, 1752, 1584, 1395, 1347, 1247, 1215, 1115, 710, 609 cm^{-1}.

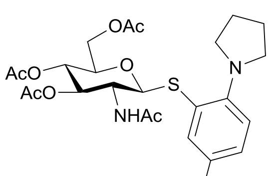
(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3f)



3f

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3f** was isolated in 66% (103.6 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.009 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.40 (d, *J* = 3.4 Hz, 1H), 5.23 (t, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 10.0, 3.4 Hz, 1H), 4.73 (d, *J* = 10.1 Hz, 1H), 4.16 – 4.09 (m, 2H), 3.89 (t, *J* = 7.1 Hz, 1H), 3.32 – 3.28 (m, 2H), 3.24 – 3.20 (m, 2H), 2.25 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.92 – 1.86 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.5, 170.4, 170.3, 169.5, 148.6, 135.6, 129.6, 121.9, 116.7, 86.3, 74.4, 72.2, 67.6, 67.5, 61.9, 51.7, 25.2, 20.9, 20.8, 20.7, 20.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{34}NO_9S^+$ 524.1949; Found 524.1944. **IR** (film) ν 3348, 2827, 2733, 1745, 1598, 1385, 1244, 1044, 609 cm^{-1}.

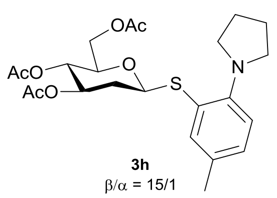
(2*R*,3*S*,4*R*,5*R*,6*S*)-5-acetamido-2-(acetoxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4-diyl diacetate (3g)



3g

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 1:2 (v/v)). Compound **3g** was isolated in 68% (106.5 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.013 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 9.2 Hz, 1H), 5.96 (d, *J* = 8.4 Hz, 1H), 5.37 (t, *J* = 9.5 Hz, 1H), 4.95 (t, *J* = 9.4 Hz, 1H), 4.84 (d, *J* = 9.5 Hz, 1H), 4.21 – 4.18 (m, 1H), 4.11 (d, *J* = 12.2 Hz, 1H), 3.71 – 3.65 (m, 2H), 3.32 – 3.31 (m, 2H), 3.23 – 3.21 (m, 2H), 2.24 (s, 3H), 2.05 (s, 3H), 1.98 (s, 6H), 1.92 (s, 3H), 1.90 (s, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.5, 169.6, 137.0, 130.1, 121.7, 116.8, 85.6, 75.7, 73.6, 68.7, 62.6, 54.0, 52.4, 25.1, 23.4, 20.8, 20.7, 20.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{35}N_2O_8S^+$ 523.2109; Found 523.2109. **IR** (film) ν 3319, 2817, 2717, 1749, 1601, 1379, 1350, 1234, 1037, 600 cm^{-1}.

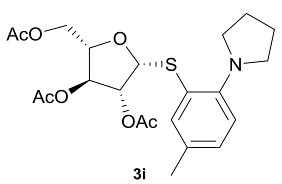
(2*R*,3*S*,4*R*,6*S*)-2-(acetoxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4-diyl diacetate (3h)



3h
β/α = 15/1

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3h** was isolated in 65% (90.7 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.021 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 6.98 (d, *J* = 6.1 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.05 – 4.95 (m, 2H), 4.80 (dd, *J* = 11.9, 1.9 Hz, 1H), 4.23 (dd, *J* = 12.2, 5.7 Hz, 1H), 4.12 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.69 – 3.66 (m, 1H), 3.34 – 3.30 (m, 2H), 3.14 – 3.11 (m, 2H), 2.48 – 2.44 (m, 1H), 2.26 (s, 3H), 2.08 (s, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.92 – 1.88 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.4, 170.0, 147.9, 145.8, 133.5, 129.0, 124.1, 116.9, 81.9, 76.0, 72.0, 69.1, 63.0, 52.0, 36.4, 25.1, 21.0, 20.9, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{32}NO_7S^+$ 466.1894; Found 466.1895. **IR** (film) ν 3303, 2820, 2727, 1762, 1607, 1379, 1347, 1237, 1211, 1037, 777, 600 cm^{-1}.

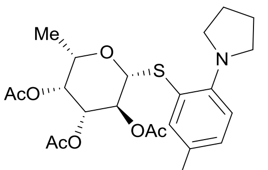
(2*S*,3*S*,4*R*,5*R*)-2-(acetoxymethyl)-5-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydrofuran-3,4-diyl diacetate (3i)



3i

Purified by flash column chromatography R_f = 0.4 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3i** was isolated in 66% (89.3 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.011 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.27 – 5.23 (m, 2H), 5.09 (d, *J* = 5.5 Hz, 1H), 4.93 (d, *J* = 7.7 Hz, 1H), 4.16 – 4.13 (m, 1H), 3.62 (d, *J* = 12.6 Hz, 1H), 3.37 – 3.36 (m, 2H), 3.18 (s, 2H), 2.25 (s, 3H), 2.13 (s, 3H), 2.07 (s, 6H), 1.91 – 1.89 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.4, 170.1, 169.4, 148.5, 135.5, 129.9, 129.5, 116.8, 85.3, 70.6, 68.9, 67.6, 51.5, 25.1, 21.0, 20.8, 20.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{30}NO_7S^+$ 466.1894; Found 466.1895.

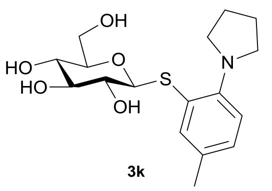
(2*S*,3*R*,4*R*,5*S*,6*R*)-2-methyl-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3j)



3j

Purified by flash column chromatography R_f = 0.2 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3j** was isolated in 75% (104.7 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.012 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 2.2 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 5.24 (dd, *J* = 3.4, 1.2 Hz, 1H), 5.20 (t, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 9.9, 3.4 Hz, 1H), 4.70 (d, *J* = 10.1 Hz, 1H), 3.80 – 3.75 (m, 1H), 3.30 – 3.22 (m, 4H), 2.24 (s, 3H), 2.17 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.89 – 1.86 (m, 4H), 1.21 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.3, 169.5, 148.6, 135.5, 129.6, 129.5, 122.3, 116.6, 86.0, 73.1, 72.7, 70.5, 67.8, 51.7, 25.2, 20.9, 20.8, 20.4, 16.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{32}NO_7S^+$ 466.1894; Found 466.1893.

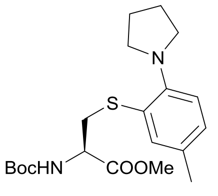
(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(hydroxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triol (3k)



3k

Purified by flash column chromatography R_f = 0.5 (dichloromethane/methyl alcohol = 10:1 (v/v)). Compound **3k** was isolated in 45% (47.9 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ +0.001 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 4.27 (d, *J* = 9.3 Hz, 1H), 3.82 (d, *J* = 10.1 Hz, 1H), 3.66 (dd, *J* = 12.0, 5.1 Hz, 1H), 3.53 – 3.49 (m, 2H), 3.44 (t, *J* = 9.0 Hz, 1H), 3.35 – 3.32 (m, 1H), 3.17 (t, *J* = 9.3 Hz, 1H), 2.91 – 2.86 (m, 2H), 2.64 (t, *J* = 9.2 Hz, 1H), 2.24 (s, 3H), 2.00 – 1.93 (m, 2H), 1.90 – 1.83 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.8, 140.5, 133.3, 131.7, 121.7, 118.2, 87.5, 80.0, 71.7, 70.1, 62.4, 52.9, 24.0, 20.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}NO_5S^+$ 356.1526; Found 356.1523.

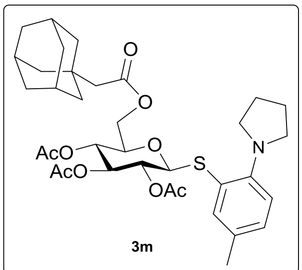
Methyl *N*-(tert-butoxycarbonyl)-*S*-(5-methyl-2-(pyrrolidin-1-yl)phenyl)-*L*-cysteinate (3l)



3l

Purified by flash column chromatography R_f = 0.2 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3l** was isolated in 75% (88.7 mg) yield as yellow oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.015 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.02 (d, *J* = 10.5 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 8.9 Hz, 1H), 4.52 – 4.49 (m, 1H), 3.57 (s, 3H), 3.47 (dd, *J* = 14.1, 3.9 Hz, 1H), 3.44 – 3.40 (m, 2H), 3.22 – 3.18 (m, 2H), 2.95 (dd, *J* = 14.1, 4.5 Hz, 1H), 2.24 (s, 3H), 2.02 – 1.93 (m, 4H), 1.39 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.5, 155.8, 150.2, 138.0, 131.2, 130.1, 124.8, 117.4, 79.7, 53.6, 52.3, 52.2, 39.0, 28.4, 24.9, 20.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{31}N_2O_4S^+$ 395.1999; Found 395.1996. **IR** (film) ν 3328, 2813, 1594, 1401, 1343, 770 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((2-((3*R*,5*R*,7*R*)-adamantan-1-yl)acetoxy)methyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3m)

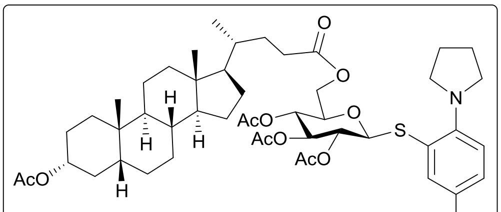


3m

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 4:1 (v/v)). Compound **3m** was isolated in 68% (134.1 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.014 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 5.20 (t, *J* = 9.3 Hz, 1H), 5.10 (t, *J* = 9.8 Hz, 1H), 4.93 (t, *J* = 9.6 Hz, 1H), 4.72 (d, *J* = 10.2 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.66 – 3.63 (m, 1H), 3.28 – 3.25 (m, 4H), 2.24 (s, 3H), 2.06 (s, 3H), 2.03 (s, 2H), 2.01 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H), 1.90 – 1.87 (m, 4H), 1.69 – 1.66 (m, 4H), 1.60 – 1.58 (m, 3H), 1.53 (s, 5H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.3, 170.2, 169.4, 148.9, 136.1, 129.8, 129.5, 121.0, 116.6, 85.6, 76.0, 74.2, 70.7, 67.7, 62.7, 51.8, 48.4, 42.3, 36.7, 32.8, 28.6, 25.3, 20.9, 20.8, 20.5. **HRMS (ESI)** m/z: [M +

H]$^+$ Calcd for $C_{35}H_{48}NO_9S^+$ 658.3044; Found 658.3045. **IR** (film) ν 3325, 2813, 1749, 1588, 1401, 1356, 1230, 1134, 1041, 758 cm^{-1}.

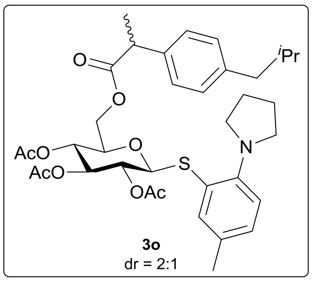
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoyl)oxy)methyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3n)



3n

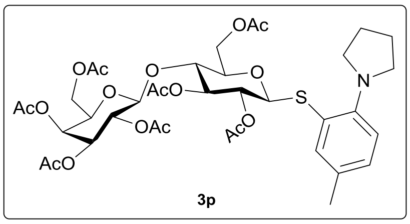
Purified by flash column chromatography R$_f$ = 0.3 (petroleum ether/AcOEt = 4:1 (v/v)). Compound **3m** was isolated in 68% (179.8 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ +0.005 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.01 (d, *J* = 10.5 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 5.19 (t, *J* = 9.4 Hz, 1H), 5.06 (t, *J* = 9.7 Hz, 1H), 4.96 (t, *J* = 9.7 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 2H), 4.18 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.11 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.69 – 3.65 (m, 1H), 3.28 – 3.25 (m, 4H), 2.30 – 2.27 (m, 1H), 2.25 (s, 3H), 2.19 – 2.12 (m, 1H), 2.06 (s, 3H), 2.02 (s, 6H), 1.97 (s, 3H), 1.90 – 1.87 (m, 4H), 1.83 – 1.78 (m, 4H), 1.69 – 1.66 (m, 2H), 1.57 – 1.52 (m, 2H), 1.45 – 1.36 (m, 9H), 1.25 – 1.22 (m, 5H), 1.06 – 1.04 (m, 3H), 0.91 (s, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.62 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.9, 170.8, 170.4, 169.3, 148.9, 136.0, 129.8, 129.5, 121.1, 116.6, 85.7, 75.9, 74.5, 74.3, 70.4, 68.1, 62.5, 56.6, 56.0, 51.8, 42.9, 42.0, 40.5, 40.2, 35.9, 35.5, 35.1, 34.7, 32.4, 31.1, 31.0, 28.2, 27.1, 26.7, 26.4, 25.3, 24.3, 23.5, 21.6, 20.9, 20.8, 20.5, 18.3, 12.1. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{49}H_{72}NO_{11}S^+$ 882.4821; Found 882.4829. **IR** (film) ν 3313, 2820, 1601, 1395, 1350, 1234, 770 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3o)



Purified by flash column chromatography R_f = 0.5 (petroleum ether/AcOEt = 4:1 (v/v)). Compound **3o** was isolated in 60% (120.5 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.011 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.16 – 7.12 (m, 2H), 7.10 (s, 1H), 7.07 (s, 2H), 7.05 (s, 1H), 7.01 – 6.98 (m, 2H), 6.78 – 6.75 (m, 1.5H), 5.17 (t, *J* = 9.4 Hz, 1H), 5.06 (t, *J* = 9.7 Hz, 1H), 4.94 (t, *J* = 9.7 Hz, 1H), 4.87 (t, *J* = 9.9 Hz, 1H), 4.72 – 4.67 (m, 1.5H), 4.18 – 4.14 (m, 0.5H), 4.07 – 4.03 (m, 0.5H), 3.87 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.80 (dd, *J* = 12.3, 5.4 Hz, 1H), 3.65 – 3.60 (m, 2H), 3.58 – 3.55 (m, 1H), 3.25 (s, 6.5H), 2.43 – 2.41 (m, 3.5H), 2.24 – 2.23 (m, 5H), 2.06 (s, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.97 (s, 1H), 1.89 – 1.86 (m, 6H), 1.85 (s, 3H), 1.83 – 1.79 (m, 1H), 1.43 – 1.42 (m, 3.5H), 0.88 – 0.86 (m, 10H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.5, 173.1, 170.7, 170.4, 169.3, 148.9, 141.1, 136.9, 136.1, 135.9, 129.9, 129.8, 129.6, 129.5, 127.3, 127.2, 127.1, 121.1, 116.6, 85.7, 85.6, 76.0, 75.7, 74.2, 73.6, 70.6, 70.5, 68.2, 68.0, 62.4, 62.3, 51.8, 45.2, 45.1, 44.9, 30.3, 25.3, 22.4, 20.9, 20.8, 20.7, 20.6, 20.5, 20.2, 18.1, 18.0. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{36}H_{48}NO_9S^+$ 670.3044; Found 670.3041. **IR** (film) ν 3309, 2817, 1749, 1601, 1398, 1350, 761 cm^{-1}.

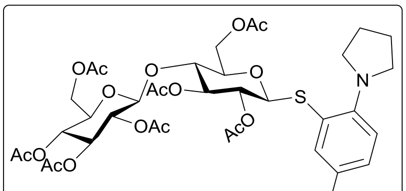
(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3p)



Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 1:1 (v/v)). Compound **3p** was isolated in 55% (133.9 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.011 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 2.2 Hz, 1H), 6.98 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.32 (dd, *J* = 3.5, 1.2 Hz, 1H), 5.16 (t, *J* = 9.1 Hz, 1H), 5.08 (dd, *J* = 10.4, 7.8 Hz, 1H), 4.94 – 4.88 (m, 2H), 4.68 (d, *J* =

10.2 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.42 (dd, *J* = 11.9, 2.0 Hz, 1H), 4.11 – 4.05 (m, 3H), 3.86 (t, *J* = 6.8 Hz, 1H), 3.74 (t, *J* = 9.5 Hz, 1H), 3.60 – 3.56 (m, 1H), 3.28 – 3.22 (m, 4H), 2.23 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.02 – 2.01 (m, 9H), 1.94 (s, 3H), 1.89 – 1.86 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.5, 170.3, 170.2, 169.9, 169.6, 169.2, 148.8, 135.9, 129.7, 129.4, 121.2, 116.6, 101.2, 85.4, 76.6, 76.5, 74.1, 71.1, 70.7, 69.1, 66.7, 62.5, 60.9, 51.7, 25.2, 20.9, 20.8, 20.7, 20.6, 20.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{37}H_{50}NO_{17}S^+$ 812.2794; Found 812.2781. **IR** (film) ν 3345, 2811, 2730, 1755, 1601, 1372, 1230, 1041, 609 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((5-methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3q)

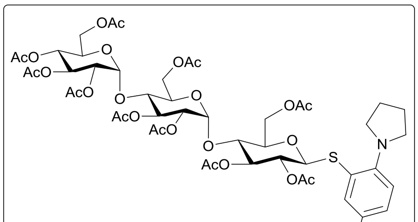


3q

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 1:1 (v/v)). Compound **3q** was isolated in 59% (143.6 mg) yield as colorless oil following the general procedure **A**; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 6.97 (d, *J* = 10.4 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.16 – 5.09 (m, 2H), 5.03 (t, *J* = 9.7 Hz, 1H), 4.92 – 4.87 (m, 2H), 4.67 (d, *J* = 10.2 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 2H), 4.44 (d, *J* = 11.9 Hz, 2H), 4.35 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.06 (dd, *J* = 11.9, 5.8 Hz, 1H), 4.01 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.71 (t, *J* = 9.6 Hz, 1H), 3.65 – 3.62 (m, 1H), 3.58 – 3.55 (m, 1H), 3.28 – 3.21 (m, 4H), 2.23 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.00 (s, 6H), 1.99 (s, 6H), 1.95 (s, 3H), 1.88 – 1.85 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.6, 170.4, 170.3, 169.9, 169.5, 169.4, 169.2, 148.7, 135.9, 129.7, 129.4, 121.2, 116.6, 100.9, 85.4, 76.6, 73.9, 73.0, 72.0, 71.6, 70.6, 67.8, 62.4, 61.6, 51.7, 25.2, 20.9, 20.7, 20.6, 20.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{37}H_{50}NO_{17}S^+$ 812.2794; Found 812.2776.

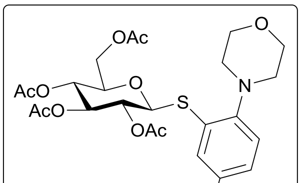
(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((5-

methyl-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3r)


3r

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 1:3 (v/v)). Compound **3r** was isolated in 65% (214.4 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ +0.030 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 2.1 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 5.37 (d, *J* = 3.8 Hz, 1H), 5.36 – 5.28 (m, 2H), 5.24 – 5.21 (m, 2H), 5.04 (t, *J* = 9.9 Hz, 1H), 4.83 (dd, *J* = 10.5, 4.1 Hz, 1H), 4.78 (d, *J* = 8.7 Hz, 1H), 4.75 – 4.72 (m, 1H), 4.72 – 4.70 (m, 1H), 4.44 – 4.40 (m, 2H), 4.27 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.23 (dd, *J* = 12.5, 3.6 Hz, 1H), 4.16 (dd, *J* = 12.3, 3.7 Hz, 1H), 4.03 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.97 – 3.94 (m, 1H), 3.92 – 3.89 (m, 3H), 3.70 – 3.67 (m, 1H), 3.29 – 3.21 (m, 4H), 2.24 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 (d, *J* = 1.2 Hz, 6H), 1.94 (s, 3H), 1.89 – 1.86 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.6, 170.5, 170.3, 169.9, 169.8, 169.6, 148.9, 135.9, 129.8, 129.5, 120.9, 116.6, 95.9, 95.7, 85.0, 76.7, 75.9, 73.9, 72.6, 71.8, 71.1, 70.5, 70.1, 69.4, 69.0, 68.6, 67.9, 63.4, 62.4, 61.4, 51.7, 25.2, 21.0, 20.9, 20.8, 20.7, 20.6, 20.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{49}H_{66}NO_{25}S^+$ 1100.3639; Found 1100.3638. **IR** (film) ν 3351, 2804, 1745, 1591, 1398, 1356, 1227, 1035, 774 cm^{-1}.

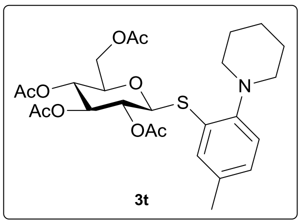
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-methyl-2-morpholinophenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3s)


3s

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3s** was isolated in 40% (153.2 mg) yield as yellow solid following the general procedure **A**; *m.p.*: 100.0 – 101.5 ℃; $[\alpha]_D^{20}$ -0.013 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.20 (s, 1H), 7.04 (d, *J* =

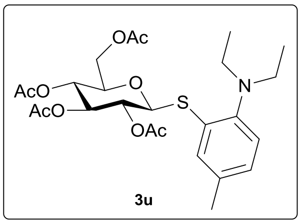
8.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 5.26 (t, *J* = 9.3 Hz, 1H), 5.16 – 5.08 (m, 2H), 4.97 (d, *J* = 10.2 Hz, 1H), 4.23 (dd, *J* = 12.3, 5.9 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.84 – 3.80 (m, 5H), 2.94 – 2.92 (m, 4H), 2.30 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.6, 169.3, 148.8, 134.4, 130.5, 130.0, 128.6, 120.1, 84.3, 76.0, 74.1, 70.4, 68.5, 67.4, 62.7, 52.5, 21.2, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{34}NO_{10}S^+$ 540.1898; Found 540.1898. **IR** (film) ν 2866, 1736, 1379, 1221, 1041 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-methyl-2-(piperidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3t)



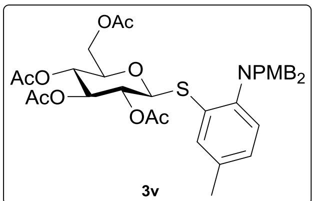
Purified by flash column chromatography R*f* = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3t** was isolated in 35% (56.4 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.020 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.18 (s, 1H), 7.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.27 (t, *J* = 9.3 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 4.24 (dd, *J* = 12.3, 5.9 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.85 – 3.81 (m, 1H), 2.86 – 2.82 (m, 4H), 2.29 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 – 2.01 (m, 6H), 1.68 – 1.65 (m, 4H), 1.54 – 1.53 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.6, 169.4, 150.3, 133.6, 130.5, 129.9, 128.3, 120.1, 84.3, 75.9, 74.2, 70.3, 68.7, 62.7, 53.8, 26.5, 24.3, 21.2, 20.9, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{26}H_{36}NO_9S^+$ 538.2105; Found 538.2116. **IR** (film) ν 2929, 2856, 1739, 1376, 1225, 1035, 912 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(diethylamino)-5-methylphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3u)



Purified by flash column chromatography R*f* = 0.2 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3u** was isolated in 50% (78.8 mg) yield as white solid following the general procedure **A**; *m.p.*: 89.7 – 92.8 ℃; $[\alpha]_D^{20}$ -0.015 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.14 (s, 1H), 6.97 (s, 2H), 5.28 (t, *J* = 8.9 Hz, 1H), 5.15 (t, *J* = 9.3 Hz, 1H), 5.10 (t, *J* = 10.6 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 4.23 (dd, *J* = 12.5, 5.7 Hz, 1H), 4.16 – 4.13 (m, 1H), 3.86 – 3.83 (m, 1H), 2.96 – 2.92 (m, 4H), 2.31 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 6H), 0.95 – 0.93 (m, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.6, 169.4, 146.5, 134.5, 134.2, 128.5, 127.5, 123.1, 84.4, 75.8, 74.2, 70.2, 68.6, 62.8, 48.1, 21.3, 20.9, 20.8, 20.7, 12.6. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{36}NO_9S^+$ 526.2105; Found 526.2110. **IR** (film) ν 3342, 2813, 2720, 1588, 1401, 1353, 774, 626 cm^{-1}.

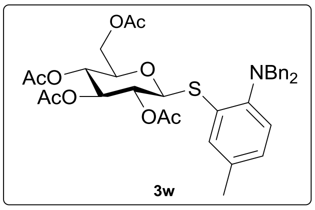
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((2-(bis(4-methoxybenzyl)amino)-5-methylphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3v)



3v

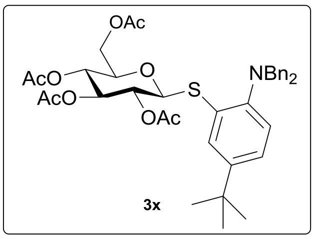
Purified by flash column chromatography R$_f$ = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3v** was isolated in 67% (142.6 mg) yield as yellow oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.024 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.21 – 7.17 (m, 5H), 6.89 – 6.86 (m, 1H), 6.83 – 6.79 (m, 5H), 5.30 (t, *J* = 9.3 Hz, 1H), 5.25 (t, *J* = 10.0 Hz, 1H), 5.14 (t, *J* = 9.7 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 4.24 (dd, *J* = 12.3, 5.9 Hz, 1H), 4.17 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.99 (d, *J* = 14.1 Hz, 2H), 3.91 (d, *J* = 14.1 Hz, 2H), 3.85 – 3.81 (m, 1H), 3.77 (s, 6H), 2.28 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.89 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.6, 169.5, 158.7, 146.6, 134.6, 132.6, 130.4, 130.1, 129.0, 127.6, 123.4, 113.6, 85.2, 75.8, 74.2, 70.1, 68.6, 62.8, 56.2, 55.3, 29.8, 21.3, 20.9, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{37}H_{44}NO_{11}S^+$ 710.2630; Found 710.2628. **IR** (film) ν 3454, 1755, 1588, 1366, 1230, 1035 cm^{-1}.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((2-(dibenzylamino)-5-methylphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3w)



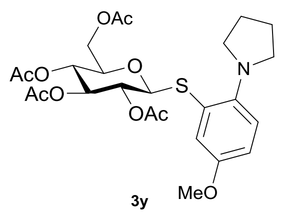
Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 4:1 (v/v)). Compound **3w** was isolated in 62% (120.8 mg) yield as yellow oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.015 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.18 (m, 11H), 6.89 – 6.85 (m, 2H), 5.33 – 5.26 (m, 2H), 5.14 (t, *J* = 9.5 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.25 (dd, *J* = 11.4, 7.0 Hz, 1H), 4.18 (d, *J* = 12.3 Hz, 1H), 4.09 (d, *J* = 14.3 Hz, 2H), 4.00 (d, *J* = 14.3 Hz, 2H), 3.87 – 3.84 (m, 1H), 2.27 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.3, 169.5, 169.4, 146.4, 138.2, 134.6, 132.5, 129.0, 128.8, 128.2, 127.6, 127.1, 123.0, 85.1, 75.8, 74.1, 70.0, 68.5, 62.7, 57.0, 21.3, 20.8, 20.7, 20.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{35}H_{40}NO_9S^+$ 650.2418; Found 650.2416. **IR** (film) ν 3328, 2813, 2714, 1749, 1584, 1398, 1347, 764, 693, 619 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-(tert-butyl)-2-(dibenzylamino)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3x)



Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 4:1 (v/v)). Compound **3x** was isolated in 67% (138.9 mg) yield as yellow oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.020 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.27 – 7.25 (m, 8H), 7.20 – 7.19 (m, 2H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 10.3 Hz, 1H), 5.31 – 5.24 (m, 2H), 5.19 (t, *J* = 9.4 Hz, 1H), 4.93 (d, *J* = 9.4 Hz, 1H), 4.31 (dd, *J* = 12.6, 5.9 Hz, 1H), 4.15 (d, *J* = 12.5 Hz, 1H), 4.08 (d, *J* = 14.4 Hz, 2H), 3.99 (d, *J* = 14.4 Hz, 2H), 3.81 (d, *J* = 7.1 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.82 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.1, 170.5, 169.6, 169.5, 148.0, 146.7, 138.4, 131.9, 128.9, 128.4, 127.2, 125.6, 124.2, 122.7, 85.8, 76.0, 74.3, 70.0, 68.4, 62.6, 57.0, 34.7, 31.6, 21.1, 20.9, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{46}NO_9S^+$ 692.2888; Found 692.2884. **IR** (film) ν 1755, 1591, 1369, 1215, 1031 cm^{-1}.

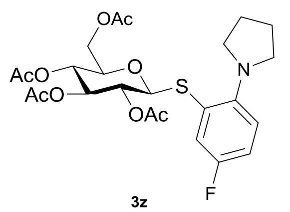
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-methoxy-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3y)



3y

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3y** was isolated in 60% (97.1 mg) yield as colorless oil following the general procedure **A**; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 2.9 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.75 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.20 (t, *J* = 9.3 Hz, 1H), 5.08 – 5.00 (m, 2H), 4.80 (d, *J* = 10.2 Hz, 1H), 4.21 (dd, *J* = 12.2, 5.7 Hz, 1H), 4.13 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.76 – 3.71 (s, 4H), 3.14 – 3.12 (m, 4H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.87 (s, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.3, 169.5, 169.3, 154.4, 144.4, 126.0, 118.7, 118.4, 113.5, 85.0, 75.9, 74.2, 70.1, 68.4, 62.4, 55.6, 52.1, 24.9, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{34}NO_{10}S^+$ 540.1898; Found 540.1895.

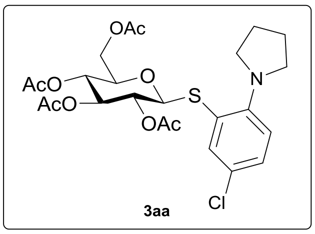
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-fluoro-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3z)



3z

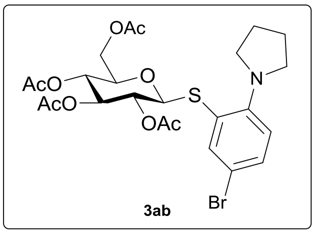
Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3z** was isolated in 67% (106.0 mg) yield as white solid following the general procedure **A**; *m.p.*: 131.2 – 132.6 ℃; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 6.91 – 6.84 (m, 2H), 5.21 (t, *J* = 9.0 Hz, 1H), 5.06 – 4.99 (m, 2H), 4.73 (d, *J* = 10.3 Hz, 1H), 4.18 (s, 2H), 3.77 – 3.74 (m, 1H), 3.18 (s, 4H), 2.10 (s, 3H), 2.03 (s, 6H), 1.99 (s, 3H), 1.89 (s, 4H). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -122.63. **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.0, 170.4, 169.6, 169.3, 157.3 (d, *J* = 239.4 Hz), 146.9, 125.5, 119.3 (d, *J* = 23.9 Hz), 118.0 (d, *J* = 7.6 Hz), 115.0 (d, *J* = 22.7 Hz), 85.2, 76.9, 74.2, 70.0, 68.5, 62.5, 52.1, 25.1, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{24}H_{31}FNO_9S^+$ 528.1698; Found 528.1698.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-chloro-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3aa)



Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3aa** was isolated in 67% (109.2 mg) yield as white solid following the general procedure **A**; *m.p.*: 122.3 – 125.5 ℃; $[\alpha]_D^{20}$ -0.046 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 1H), 5.17 (t, *J* = 9.3 Hz, 1H), 5.01 (t, *J* = 9.4 Hz, 1H), 4.92 (t, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 4.19 – 4.11 (m, 2H), 3.70 – 3.68 (m, 1H), 3.27 (s, 4H), 2.08 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.88 (s, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.3, 169.5, 169.2, 149.6, 134.6, 128.9, 123.9, 121.5, 117.1, 85.7, 74.1, 70.0, 68.3, 62.4, 51.9, 25.5, 20.8, 20.7, 20.6. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{24}H_{31}ClNO_9S^+$ 544.1403; Found 544.1401. **IR** (film) ν 3374, 2813, 1739, 1601, 1391, 1350 cm^{-1}.

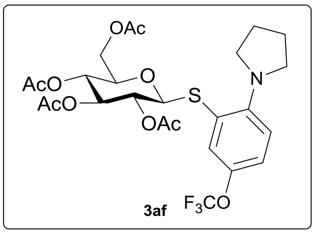
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-bromo-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ab)



Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3ab** was isolated in 65% (114.5 mg) yield as white solid following the general procedure **A**; *m.p.*: 113.4 – 116.8 ℃; $[\alpha]_D^{20}$ -0.017 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.27 (d, *J* = 6.1 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 5.19 (t, *J* = 9.4 Hz, 1H), 5.04 (t, *J* = 9.7 Hz, 1H), 4.94 (t, *J* = 8.6 Hz, 1H), 4.64 (d, *J* = 10.1 Hz, 1H), 4.21 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.14 (d, *J* = 14.6 Hz, 1H), 3.72 – 3.69 (m, 1H), 3.31 – 3.32 (m, 4H), 2.12 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.91 (s, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.3, 169.5, 169.2, 150.1, 137.8, 131.8, 121.4, 117.4, 110.8, 85.9, 75.9, 74.1, 70.1, 68.2, 62.4, 51.8, 25.5, 20.9, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for

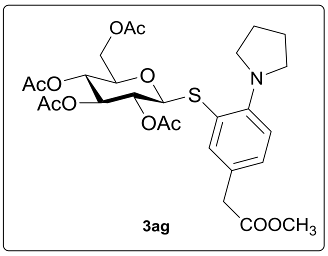
$C_{24}H_{31}BrNO_9S^+$ 588.0897; Found 588.0917. **IR** (film) ν 3328, 2817, 2720, 1755, 1610, 1388, 1350, 1237, 1208, 1041, 777, 604 cm^{-1}.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(pyrrolidin-1-yl)-5-(trifluoromethoxy)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3af)



Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3af** was isolated in 33% (58.7 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.019 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 2.8 Hz, 1H), 7.05 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.79 (d, *J* = 9.1 Hz, 1H), 5.19 (t, *J* = 9.3 Hz, 1H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.94 (t, *J* = 9.6 Hz, 1H), 4.63 (d, *J* = 10.1 Hz, 1H), 4.21 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.13 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.71 – 3.67 (m, 1H), 3.32 – 3.29 (m, 4H), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.92 – 1.89 (m, 4H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -58.14. **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.4, 169.5, 169.2, 149.8, 141.5, 127.7, 121.9, 121.4, 116.3, 86.1, 74.1, 69.9, 68.2, 62.3, 52.0, 25.6, 20.7, 20.6. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{25}H_{31}F_3NO_{10}S^+$ 594.1615; Found 594.1615. **IR** (film) ν 3351, 2817, 2727, 1742, 1601, 1388, 1350, 1237, 1035, 609 cm^{-1}.

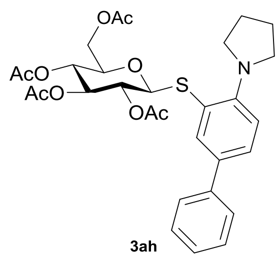
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((5-(2-methoxy-2-oxoethyl)-2-(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3ag)



Purified by flash column chromatography R_f = 0.2 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3ag** was isolated in 32% (55.8 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.030 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.16 (t, *J* = 9.4 Hz, 1H), 5.06 (t, *J* = 9.8 Hz, 1H), 4.92 (t, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 10.2 Hz, 1H), 4.23 (dd,

J = 12.3, 4.9 Hz, 1H), 4.12 (dd, J = 12.3, 2.3 Hz, 1H), 3.67 (s, 3H), 3.66 – 3.63 (m, 1H), 3.50 (s, 2H), 3.32 – 3.29 (m, 4H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.89 – 1.86 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.4, 170.8, 170.4, 169.5, 169.3, 150.3, 136.9, 130.1, 124.8, 119.8, 116.1, 86.3, 75.8, 74.3, 70.1, 68.2, 62.3, 52.2, 51.8, 40.1, 25.5, 20.9, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_{11}S^+$ 582.2004; Found 582.2003. **IR** (film) ν 3348, 2827, 2724, 1745, 1601, 1391, 1353, 1230, 1044, 774, 604 cm^{-1}.

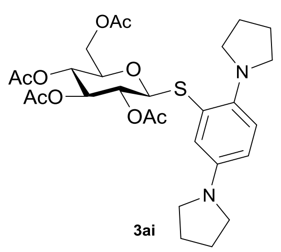
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((4-(pyrrolidin-1-yl)-[1,1'-biphenyl]-3-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ah)



3ah

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 4:1 (v/v)). Compound **3ah** was isolated in 65% (114.1 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.014 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.55 (d, J = 7.7 Hz, 2H), 7.46 (d, J = 8.5 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.26 (s, 1H), 6.90 (d, J = 9.4 Hz, 1H), 5.19 (t, J = 10.1 Hz, 1H), 5.04 (t, J = 9.2 Hz, 1H), 4.98 (t, J = 10.4 Hz, 1H), 4.70 (d, J = 10.1 Hz, 1H), 4.19 (dd, J = 12.5, 5.4 Hz, 1H), 4.09 (d, J = 12.2 Hz, 1H), 3.68 – 3.65 (m, 1H), 3.41 (s, 4H), 2.04 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.93 (s, 4H), 1.78 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.4, 169.5, 169.3, 150.6, 140.3, 135.2, 132.1, 128.9, 128.0, 126.7, 126.4, 119.3, 116.3, 86.2, 75.9, 74.3, 70.3, 68.3, 62.4, 51.9, 25.6, 20.8, 20.7, 20.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{30}H_{36}NO_9S^+$ 586.2105; Found 586.2100.

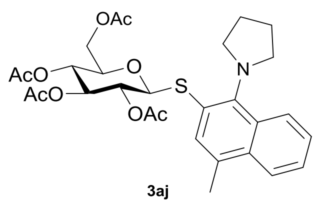
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2,5-di(pyrrolidin-1-yl)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ai)



3ai

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3ai** was isolated in 56% (97.1 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.024 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 8.7 Hz, 1H), 6.71 (d, *J* = 2.8 Hz, 1H), 6.46 (dd, *J* = 8.7, 2.8 Hz, 1H), 5.22 (t, *J* = 9.3 Hz, 1H), 5.13 – 5.06 (m, 2H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.29 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.10 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.73 – 3.69 (m, 1H), 3.25 – 3.23 (m, 4H), 3.10 – 3.06 (m, 4H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 – 1.97 (m, 7H), 1.88 – 1.86 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.5, 169.6, 169.4, 144.3, 140.0, 127.5, 119.6, 115.6, 112.0, 85.3, 75.9, 74.4, 70.2, 68.5, 62.5, 52.3, 48.0, 25.6, 24.7, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{28}H_{39}N_2O_9S^+$ 579.2371; Found 579.2367. **IR** (film) ν 3309, 2817, 1749, 1594, 1391, 1350, 1221, 1035, 761 cm^{-1}.

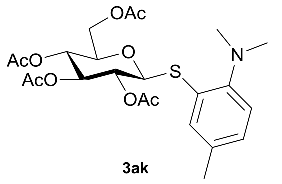
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((4-methyl-1-(pyrrolidin-1-yl)naphthalen-2-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3aj)



3aj

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 6:1 (v/v)). Compound **3aj** was isolated in 50% (86.9 mg) yield as colorless oil following the general procedure **A**; $[\alpha]_D^{20}$ -0.024 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 – 7.94 (m, 2H), 7.51 – 7.47 (m, 2H), 7.37 (s, 1H), 5.33 – 5.29 (m, 1H), 5.19 (t, *J* = 9.7 Hz, 1H), 5.14 (t, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.27 (dd, *J* = 12.3, 5.9 Hz, 1H), 4.20 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.35 – 3.32 (m, 4H), 2.67 (s, 3H), 2.12 – 2.09 (m, 7H), 2.05 (s, 6H), 2.03 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.6, 169.5, 141.8, 133.4, 133.3, 132.9, 132.8, 126.6, 126.2, 125.7, 125.1, 124.3, 85.4, 75.9, 74.2, 70.2, 68.6, 62.8, 51.4, 26.9, 20.9, 20.8, 19.9. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}NO_9S^+$ 574.2105; Found 574.2104. **IR** (film) ν 3306, 2813, 2720, 1742, 1584, 1388, 1350, 1227, 1028, 761 cm^{-1}.

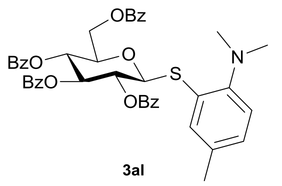
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(dimethylamino)-5-methylphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ak)



3ak

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3ak** was isolated in 65% (96.9 mg) yield as white solid following the general procedure **B**; *m.p.*: 87.1 – 92.3 ℃; $[\alpha]_D^{20}$ -0.026 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.20 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 5.26 (t, *J* = 9.3 Hz, 1H), 5.09 (t, *J* = 9.3 Hz, 2H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.24 (dd, *J* = 12.3, 5.7 Hz, 1H), 4.15 – 4.10 (m, 1H), 3.81 – 3.77 (m, 1H), 2.68 (s, 6H), 2.29 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.5, 169.4, 150.7, 133.4, 131.0, 128.8, 128.6, 119.7, 84.5, 75.8, 74.2, 70.1, 68.5, 62.6, 44.7, 21.2, 21.0, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{32}NO_9S^+$ 498.1792; Found 498.1792. **IR** (film) ν 3364, 2820, 1752, 1607, 1388, 1343, 1244, 1054, 764, cm^{-1}.

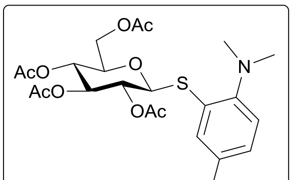
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((benzoyloxy)methyl)-6-((2-(dimethylamino)-5-methylphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3al)



3al

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 8:1 (v/v)). Compound **3al** was isolated in 72% (161.0 mg) yield as colorless oil following the general procedure **B**; $[\alpha]_D^{20}$ +0.006 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 6H), 7.83 (s, 1H), 7.55 – 7.48 (m, 3H), 7.44 – 7.41 (m, 1H), 7.39 – 7.33 (m, 6H), 7.29 – 7.24 (m, 4H), 6.96 (d, *J* = 6.1 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 5.96 (t, *J* = 9.5 Hz, 1H), 5.67 (t, *J* = 9.8 Hz, 1H), 5.64 (t, *J* = 7.3 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 4.64 (dd, *J* = 12.2, 2.8 Hz, 1H), 4.48 (dd, *J* = 12.2, 6.2 Hz, 1H), 4.26 – 4.23 (m, 1H), 2.52 (s, 6H), 2.08 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.3, 166.0, 165.4, 165.2, 151.0, 133.6, 133.3, 133.2, 132.0, 130.0, 129.9, 128.9, 128.6, 128.5, 128.4, 119.6, 85.2, 76.4, 74.4, 70.9, 69.8, 63.8, 44.5, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{43}H_{40}NO_9S^+$ 746.2418; Found 746.2412. **IR** (film) ν 3463, 1730, 1604, 1266, 1060, 703 cm^{-1}.

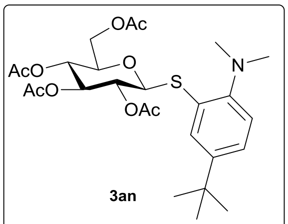
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(dimethylamino)-5-ethylphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3am)



3am

Purified by flash column chromatography R$_f$ = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3am** was isolated in 55% (84.3 mg) yield as colorless oil following the general procedure **C**; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.23 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.25 (t, *J* = 9.2 Hz, 1H), 5.11 – 5.06 (m, 2H), 4.92 (d, *J* = 9.9 Hz, 1H), 4.24 (dd, *J* = 12.7 Hz, 5.7 Hz, 1H), 4.12 (d, *J* = 12.3 Hz, 1H), 3.79 – 3.76 (m, 1H), 2.67 (s, 6H), 2.58 (q, *J* = 15.2 Hz, 7.3 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 6H), 1.99 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.4, 150.9, 139.7, 129.9, 128.7, 127.5, 119.7, 84.6, 75.8, 74.2, 70.1, 68.4, 62.5, 44.7, 28.3, 20.8, 15.6. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{24}H_{34}NO_9S^+$ 512.1949; Found 512.1946.

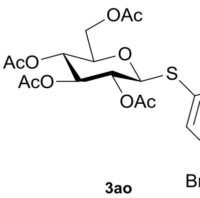
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-(tert-butyl)-2-(dimethylamino)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3an)



3an

Purified by flash column chromatography R$_f$ = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3an** was isolated in 56% (90.6 mg) yield as colorless oil following the general procedure **C**; $[\alpha]_D^{20}$ -0.022 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.23 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.25 (t, *J* = 9.3 Hz, 1H), 5.14 – 5.06 (m, 2H), 4.91 (d, *J* = 10.2 Hz, 1H), 4.30 (dd, *J* = 12.4, 4.9 Hz, 1H), 4.12 (dd, *J* = 12.5, 2.2 Hz, 1H), 3.78 – 3.74 (m, 1H), 2.69 (s, 6H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.4, 169.5, 169.4, 150.7, 146.5, 127.9, 125.1, 119.2, 85.1, 76.0, 74.3, 70.0, 68.3, 62.4, 44.6, 34.5, 31.5, 20.9, 20.8, 20.7. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{26}H_{38}NO_9S^+$ 540.2262; Found 540.2264. **IR** (film) ν 2962, 2871, 2823, 2782, 1752, 1494, 1382, 1234, 1047, 905, 825 cm^{-1}.

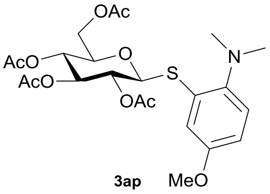
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((5-bromo-2-(dimethylamino)phenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ao)



3ao

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3ao** was isolated in 67% (112.8 mg) yield as white solid following the general procedure **C**; *m.p.*: 104.4 – 107.4 ℃; $[\alpha]_D^{20}$ -0.023 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.27 (t, *J* = 10.6 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 2H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.23 – 4.15 (m, 2H), 3.85 – 3.82 (m, 1H), 2.68 (s, 6H), 2.12 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.0, 170.4, 169.6, 169.4, 152.0, 132.2, 131.5, 130.6, 121.2, 116.3, 84.1, 76.1, 74.1, 69.9, 68.4, 62.6, 44.4, 21.0, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}BrNO_9S^+$ 562.0741; Found 562.0721. **IR** (film) ν 2949, 2852, 1762, 1372, 1240, 1031, 828 cm^{-1}.

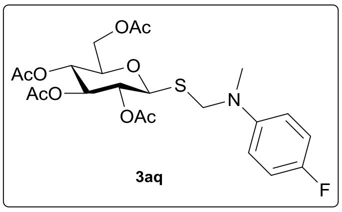
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(dimethylamino)-5-methoxyphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ap)



3ap

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3ap** was isolated in 50% (77.0 mg) yield as colorless oil following the general procedure **B**; $[\alpha]_D^{20}$ -0.014 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 2.9 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.9 Hz, 1H), 5.27 (t, *J* = 9.3 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.92 (d, *J* = 10.2 Hz, 1H), 4.23 – 4.15 (m, 2H), 3.84 – 3.81 (m, 1H), 3.76 (s, 3H), 2.62 (s, 6H), 2.08 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.4, 169.6, 169.4, 156.4, 146.0, 131.9, 120.8, 115.4, 111.6, 84.1, 75.9, 74.2, 70.0, 68.5, 62.6, 55.5, 45.0, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{32}NO_{10}S^+$ 514.1741; Found 514.1746. **IR** (film) ν 3348, 2811, 1749, 1604, 1385, 1347, 1230, 1050 cm^{-1}.

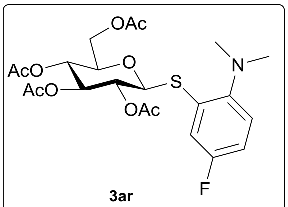
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((((4-fluorophenyl)(methyl)amino)methyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3aq)



3aq

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3aq** was isolated in 20% (30.1 mg) yield as colorless oil following the general procedure **C**; $[\alpha]_D^{20}$ -0.007 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.98 – 6.94 (m, 2H), 6.81 – 6.78 (m, 2H), 5.11 – 5.00 (m, 3H), 4.95 (t, *J* = 10.5 Hz, 1H), 4.55 (d, *J* = 13.6 Hz, 1H), 4.44 (d, *J* = 10.1 Hz, 1H), 4.21 (dd, *J* = 12.4, 5.1 Hz, 1H), 4.10 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.45 – 3.41 (m, 1H), 2.93 (s, 3H), 2.10 (s, 3H), 2.01 (s, 6H), 1.98 (s, 3H). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -126.16. **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.3, 169.5, 157.5 (d, *J* = 239.4 Hz), 144.5, 115.8 (d, *J* = 22.7 Hz), 115.3 (d, *J* = 7.6 Hz), 81.7, 75.8, 73.8, 70.4, 68.3, 62.3, 55.9, 38.0, 20.9, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}FNO_9S^+$ 502.1542; Found 502.1542.

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

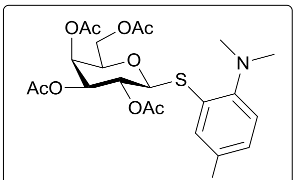


3ar

Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 5:1 (v/v)). Compound **3ar** was isolated in 25% (37.6 mg) yield as colorless oil following the general procedure **C**; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.14 (dd, *J* = 9.4, 2.9 Hz, 1H), 7.03 (dd, *J* = 8.8, 5.3 Hz, 1H), 6.87 (td, *J* = 8.3, 2.9 Hz, 1H), 5.29 – 5.26 (m, 1H), 5.13 (t, *J* = 10.2 Hz, 1H), 5.08 (t, *J* = 9.7 Hz, 1H), 4.88 (d, *J* = 10.2 Hz, 1H), 4.22 – 4.14 (m, 2H), 3.87 – 3.83 (m, 1H), 2.63 (s, 6H), 2.10 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -117.87. **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.3, 169.6, 169.4, 159.4 (d, *J* = 244.4 Hz), 148.5, 132.84 (d, *J* = 8.8 Hz), 121.1 (d, *J* = 8.8 Hz), 115.3 (d, *J* = 25.2 Hz), 113.7 (d, *J* =

25.2 Hz), 83.8, 76.1, 74.1, 69.9, 68.5, 62.6, 44.8, 20.8, 20.7. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{22}H_{29}FNO_9S^+$ 502.1542; Found 502.1542.

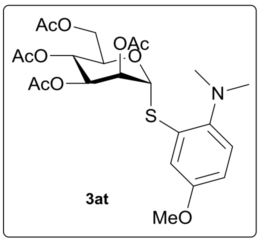
(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(dimethylamino)-5-methoxyphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3as)



3as

Purified by flash column chromatography R$_f$ = 0.2 (petroleum ether/AcOEt = 2:1 (v/v)). Compound **3as** was isolated in 70% (107.8 mg) yield as colorless oil following the general procedure **B**; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.03 (s, 1H), 7.02 (d, *J* = 5.7 Hz, 2H), 6.72 (dd, *J* = 8.8, 2.9 Hz, 1H), 5.45 (d, *J* = 3.4 Hz, 1H), 5.36 (t, *J* = 10.0 Hz, 1H), 5.09 (dd, *J* = 9.9, 3.4 Hz, 1H), 4.90 (d, *J* = 10.1 Hz, 1H), 4.18 – 4.11 (m, 2H), 4.03 – 4.01 (m, 1H), 3.76 (s, 3H), 2.62 (s, 6H), 2.16 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.4, 170.2, 169.5, 156.3, 145.9, 132.1, 120.7, 115.4, 111.4, 84.6, 72.2, 67.5, 67.1, 62.1, 55.5, 45.0, 20.9, 20.8, 20.7, 20.6. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{23}H_{32}NO_{10}S^+$ 514.1741; Found 514.1736.

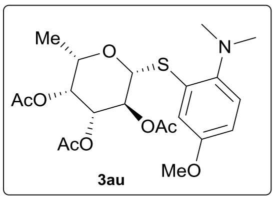
(2*R*,3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-((2-(dimethylamino)-5-methoxyphenyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3at)



3at

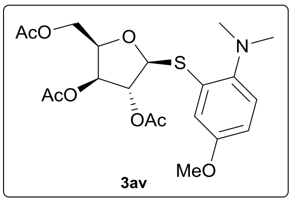
Purified by flash column chromatography R$_f$ = 0.2 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3at** was isolated in 67% (103.1 mg) yield as colorless oil following the general procedure **B**; $[\alpha]_D^{20}$ +0.111 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 2.9 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.9 Hz, 1H), 5.72 (d, *J* = 1.6 Hz, 1H), 5.51 (dd, *J* = 3.4, 1.6 Hz, 1H), 5.40 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.33 (t, *J* = 10.0 Hz, 1H), 4.50 – 4.46 (m, 1H), 4.31 (dd, *J* = 12.3, 5.5 Hz, 1H), 4.04 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.75 (s, 3H), 2.68 (s, 6H), 2.17 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.1, 169.9, 156.4, 146.2, 130.7, 120.8, 115.5, 112.7, 83.0, 71.4, 69.6, 66.5, 62.4, 55.0, 45.2, 21.1, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{32}NO_{10}S^+$ 514.1741; Found 514.1737. **IR** (film) ν 3357, 2823, 1752, 1601, 1395, 1347, 1227, 1057, 768 cm^{-1}.

(2*R*,3*S*,4*R*,5*R*,6*S*)-2-((2-(dimethylamino)-5-methoxyphenyl)thio)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3au)



Purified by flash column chromatography R_f = 0.3 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3au** was isolated in 65% (88.8 mg) yield as yellow oil following the general procedure **B**; $[\alpha]_D^{20}$ -0.009 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.05 (d, *J* = 3.0 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.9 Hz, 1H), 5.34 (t, *J* = 10.0 Hz, 1H), 5.30 (d, *J* = 3.4 Hz, 1H), 5.08 (dd, *J* = 9.9, 3.4 Hz, 1H), 4.87 (d, *J* = 10.1 Hz, 1H), 3.90 (q, *J* = 5.8, 13.1 Hz, 1H), 3.76 (s, 3H), 2.62 (s, 6H), 2.19 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.25 (d, *J* = 5.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.9, 170.3, 169.6, 156.2, 146.0, 132.0, 120.7, 115.1, 112.0, 84.4, 73.2, 72.7, 70.5, 67.1, 55.5, 45.0, 20.9, 20.8, 16.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{30}NO_8S^+$ 456.1687; Found 456.1681.

(2*R*,3*S*,4*R*,5*S*)-2-(acetoxymethyl)-5-((2-(dimethylamino)-5-methoxyphenyl)thio)tetrahydrofuran-3,4-diyl diacetate (3av)



Purified by flash column chromatography R_f = 0.5 (petroleum ether/AcOEt = 3:1 (v/v)). Compound **3av** was isolated in 60% (79.4 mg) yield as white solid following the general procedure **C**; *m.p.*: 97.0 – 99.5 ℃; $[\alpha]_D^{20}$ -0.017 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 2.9 Hz, 1H), 6.74 (dd, *J* = 8.7, 2.9 Hz, 1H), 5.21 (t, *J* = 7.8 Hz, 1H), 5.13 – 5.06 (m, 2H), 5.00 – 4.96 (m, 1H), 4.31 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.77 (s, 3H), 3.49 (dd, *J* = 11.9, 8.3 Hz, 1H), 2.65 (s, 6H), 2.07 (s, 3H), 2.06 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.1, 169.9, 169.5, 156.3, 146.2, 120.8, 115.3, 112.5, 84.1, 71.9, 69.9, 68.6, 64.9, 55.7, 45.0, 29.8, 20.9. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}NO_8S^+$ 442.1530; Found 442.1533. **IR** (film) ν 3345, 2813, 2720, 1759, 1598, 1395, 1356, 1225, 1064, 597 cm^{-1}.

10. Scale-up experiment

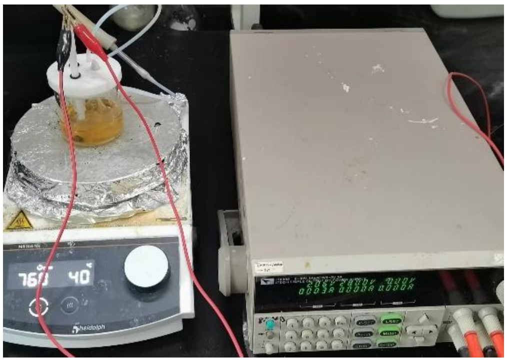
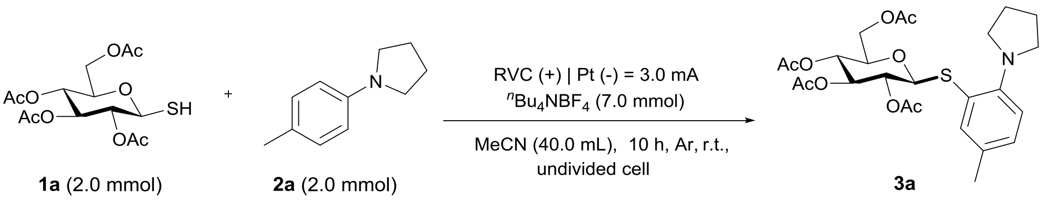


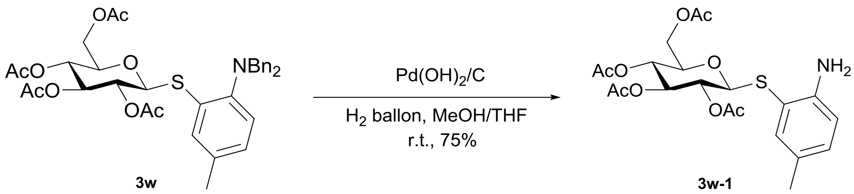
Figure S7. The ElectraSyn Set-up.



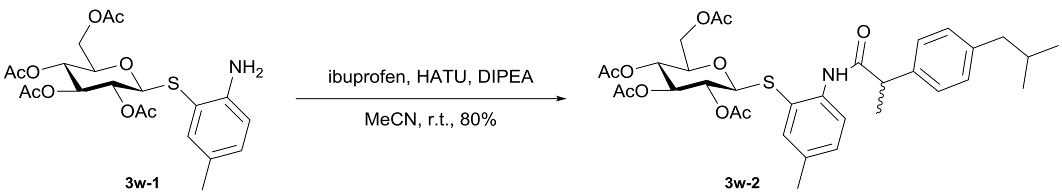
1a (2.0 mmol) **2a** (2.0 mmol) **3a**

A beaker was charged with a stir bar, **1a** (0.7 g, 2.0 mmol), **2a** (0.32 g, 2.0 mmol), $^nBu_4NBF_4$ (2.3 g, 7.0 mmol), 40.0 mL MeCN, and the suspension was stirred until the solids resolve. The assembled electrode was placed into the solution. After N_2 was bubbled through the solution for 30 min, the reaction mixture was electrolyzed under a constant current of 3.0 mA at room temperature for 10 h until the substrate was completely consumed. The bubbling of N_2 continued during the reaction. The solvent was concentrated under vacuum and the residue purified by flash column chromatography on silica gel (eluting: petroleum ether/ethyl acetate = 3: 1 (v/v)) to give product **3a** (0.47 g, 45%).

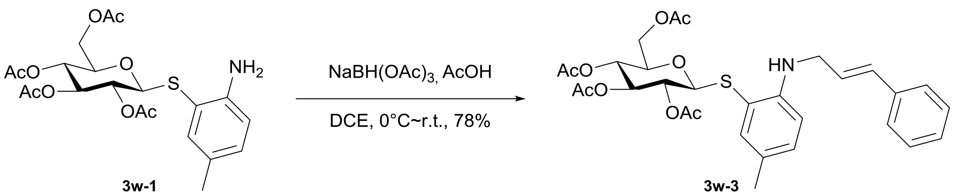
11. Characterization data for compounds in Scheme 2



Compound **3w** (0.095 g, 0.15 mmol) was dissolved in methanol (5 mL) and tetrahydrofuran (5 mL). 20% $Pd(OH)_2/C$ (0.02 g, 0.03 mmol) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere (balloon). The mixture was then filtered through a pad of Celite and the pad washed with MeOH (5 mL). The filtrate was concentrated under vacuum and the residue purified by flash column chromatography on silica gel to obtain **3w-1** (eluent: petroleum ether/ethyl acetate = 3: 1 (v/v); 52.8 mg, 75% yield). Gray solid, *m.p.*: 95.6 – 97.2 ℃; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.15 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 5.17 (t, *J* = 9.5 Hz, 1H), 5.04 (t, *J* = 10.7 Hz, 1H), 4.96 (t, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 9.3 Hz, 1H), 4.19 – 4.11 (m, 2H), 3.64 – 3.63 (m, 1H), 2.21 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.4, 169.5, 169.3, 147.4, 137.9, 132.2, 127.7, 115.6, 113.2, 86.8, 75.9, 74.1, 70.3, 68.1, 62.0, 20.9, 20.8, 20.7, 20.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{28}NO_9S^+$ 470.1479; Found 470.1480.



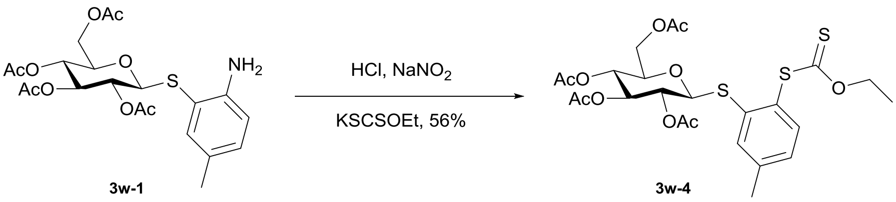
Ibuprofen (0.041 g, 0.2 mmol) was dissolved in dry CH_3CN (3 mL), then DIPEA (45 µL, 0.24 mmol), HATU (0.091 g, 0.24 mmol), and compound **3w-1** (0.096 g, 0.2 mmol) was added. After stirring at room temperature for 6 h, the mixture was diluted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel, affording product **3w-2** (eluent: petroleum ether/ethyl acetate = 5: 1 (v/v); 157.7 mg, dr = 1.3:1, 80% yield). White solid, *m.p.*: 118.2 – 120.7 ℃; ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 16.3 Hz, 2H), 8.18 (dd, *J* = 10.8, 8.4 Hz, 2H), 7.31 – 7.27 (m, 6H), 7.25 – 7.16 (m, 9H), 5.14 – 5.09 (m, 2.3H), 4.92 – 4.88 (m, 2.6H), 4.86 – 4.81 (m, 2H), 4.44 (dd, *J* = 13.1, 10.1 Hz, 2.3H), 4.13 (dd, *J* = 12.4, 6.2 Hz, 1H), 4.03 – 3.98 (m, 2.5H), 3.90 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.71 – 3.65 (m, 2.3H), 3.52 – 3.44 (m, 2.3H), 2.50 (dd, *J* = 11.5, 7.1 Hz, 5H), 2.28 – 2.27 (m, 7.3H), 2.10 (d, *J* = 6.2 Hz, 7H), 2.01 – 1.99 (m, 13.7H), 1.93 (d, *J* = 8.1 Hz, 7H), 1.90 – 1.83 (m, 2.7H), 1.58 (dd, *J* = 10.2, 7.1 Hz, 7H), 0.91 – 0.89 (m, 14.3H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 172.7, 170.5, 170.2, 169.6, 169.5, 169.4, 169.3, 141.1, 141.0, 139.4, 138.1, 137.9, 137.8, 137.6, 134.1, 134.0, 132.0, 129.9, 129.8, 128.0, 127.8, 121.3, 121.1, 118.8, 118.1, 87.3, 86.5, 76.0, 75.8, 73.9, 73.7, 70.3, 70.2, 68.1, 68.0, 62.0, 61.9, 48.0, 45.1, 30.3, 22.5, 20.9, 20.7, 20.6, 18.6, 18.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{34}H_{44}NO_{10}S^+$ 658.2680; Found 658.2674. **IR** (film) ν 3460, 1759, 1517, 1366, 1221, 1037 cm^{-1}.



3w-1 3w-3

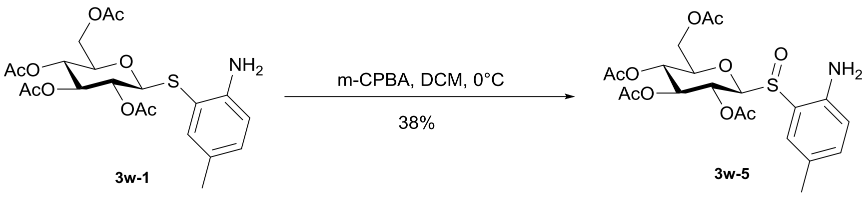
To a mixture of Cinnamaldehyde (20 μL, 0.15 mmol) and compound **3w-1** (0.048 g, 0.1 mmol) in DCE (2 mL), AcOH (11 μL, 0.2 mmol) was added, after the mixture is stirred at room temperature for 15 minutes, $NaBH(OAc)_3$ (0.043 g, 0.2 mmol) is added. After completion of the reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was quenched with a saturated aqueous solution of sodium bicarbonate. The mixture was then diluted with DCM and the organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel, affording product **3w-3** as a yellow oil (eluent: petroleum ether/ethyl acetate = 6: 1 (v/v); 45.6 mg, 78% yield). $[\alpha]_D^{20}$ -0.013 (*c* 1.0, MeCN); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.37 – 7.36 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.07 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.62

– 6.59 (m, 2H), 6.35 – 6.29 (m, 1H), 5.22 (s, 1H), 5.17 (t, *J* = 9.3 Hz, 1H), 5.05 (t, *J* = 9.8 Hz, 1H), 4.97 (t, *J* = 10.6 Hz, 1H), 4.57 (d, *J* = 10.2 Hz, 1H), 4.20 (dd, *J* = 12.4, 4.7 Hz, 1H), 4.07 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.98 – 3.90 (m, 2H), 3.62 – 3.59 (m, 1H), 2.22 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.4, 169.5, 169.3, 147.9, 138.2, 136.8, 132.4, 131.6, 128.7, 127.7, 126.7, 126.4, 126.2, 113.3, 111.1, 87.0, 76.0, 74.2, 70.3, 68.0, 62.0, 46.2, 20.9, 20.7, 20.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{30}H_{36}NO_9S^+$ 586.2105; Found 586.2100. **IR** (film) ν 3332, 2817, 2720, 1759, 1598, 1398, 1343, 1215, 1041, 758, 616 cm^{-1}.

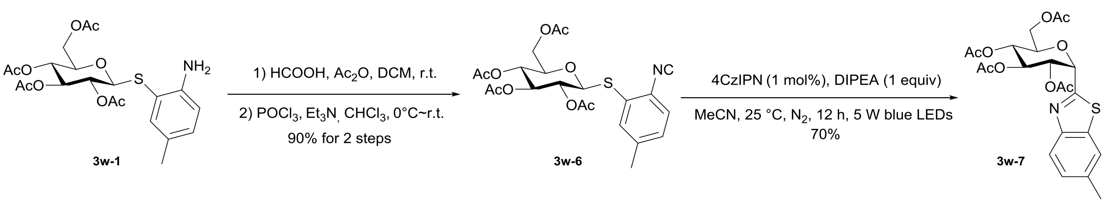


3w-1　3w-4

A suspension of compound **3w-1** (0.14 g, 0.3 mmol) in 2.7 M aqueous HCl (0.2 mL) was cooled to 0-5 ℃ and a solution of sodium nitrite (0.023 g, 0.33 mmol) in water (0.1 mL) was added dropwise. The diazonium salt solution was stirred for 30 min and then added to a solution of potassium ethyl xanthate (0.077 g, 0.48 mmol) in water (0.1 mL) stirring at 50 ℃. The reaction mixture was stirred at this temperature for 50 min, then extracted with EtOAc for three times. The combined organic extracts were washed with 1 M NaOH and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel, affording product **3w-4** as a yellow oil (eluent: petroleum ether/ethyl acetate = 3: 1 (v/v); 96.4 mg, 56% yield). $[\alpha]_D^{20}$ -0.019 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 5.20 (t, *J* = 9.3 Hz, 1H), 5.06 (t, *J* = 9.7 Hz, 1H), 4.99 (t, *J* = 10.6 Hz, 1H), 4.70 (d, *J* = 10.2 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 4.25 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.74 – 3.70 (m, 1H), 2.41 (s, 3H), 2.09 (s, 6H), 2.02 (s, 3H), 1.99 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 212.3, 170.7, 170.3, 169.5, 141.7, 138.8, 136.6, 134.4, 130.0, 86.1, 75.9, 73.9, 70.6, 69.7, 68.2, 62.4, 21.6, 20.9, 20.7, 13.8. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{24}H_{31}O_{10}S_3^+$ 575.1074; Found 575.1054. **IR** (film) ν 3319, 2817, 2733, 1755, 1601, 1388, 1350, 1221, 1050, 761 cm^{-1}.



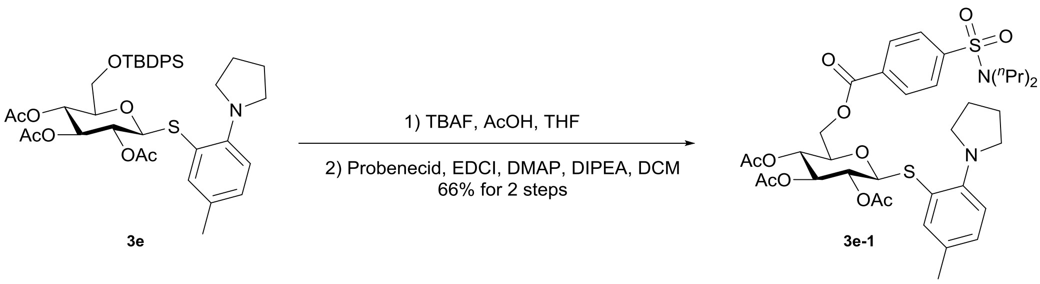
A solution of compound **3w-1** (0.11 g, 0.2 mmol) in anhydrous DCM was cooled to 0℃. m-CPBA (0.07 g, 0.4 mmol) was added under N_2 atmosphere. The reaction mixture was stirred at 0℃ for 3 h. Aqueous $Na_2S_2O_3$ was added at 0℃ and the reaction mixture was stirred for 15 min. The organic layer was separated and washed with aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel, affording product **3w-5** as a colorless oil (eluent: petroleum ether/ethyl acetate = 2: 1 (v/v); 36.9 mg, 38% yield). $[\alpha]_D^{20}$ -0.024 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 8.1 Hz, 1H), 7.02 (s, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 5.33 (t, *J* = 8.8 Hz, 1H), 5.22 (t, *J* = 9.4 Hz, 1H), 5.15 (t, *J* = 9.6 Hz, 1H), 4.83 (d, *J* = 9.9 Hz, 1H), 4.28 (dd, *J* = 12.5, 4.9 Hz, 1H), 4.15 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.79 – 3.75 (m, 1H), 2.23 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.4, 169.4, 169.1, 146.4, 134.2, 128.0, 127.3, 118.9, 117.8, 89.1, 76.6, 74.3, 67.8, 67.6, 61.8, 20.8, 20.7, 20.5, 20.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{28}NO_{10}S^+$ 486.1428; Found 486.1435. **IR** (film) ν 3351, 2817, 2720, 1755, 1581, 1398, 1347, 1221, 777, 619 cm^{-1}.



An mixture of acetic anhydride (70 μL) and formic acid (70 μL) was stirred at room temperature to form in situ acetic formic anhydride. After cooling to room temperature it was added dropwise to a stirred solution of compound **3w-1** in DCM (2 mL) at 0 ℃. After stirring 2 h at room temperature, the reaction was stopped by the addition of a satd. $NaHCO_3$. The aqueous phase was extracted three times with DCM and the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. Without further purification the residue was dissolved in THF (3 mL) and triethylamine (0.5 mL, 3.5 mmol) was added. The reaction mixture was added dropwise $POCl_3$ (95 μL, 1 mmol) in THF (2 mL) at 0 ℃ under nitrogen atmosphere over 15 mins. After stirring two hours at this temperature, the reaction mixture was poured into a satd. $NaHCO_3$. The aqueous phase was extracted three times with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography on silica gel, affording product **3w-6** as as colorless oil (eluent: petroleum ether/ethyl acetate = 4: 1 (v/v); 215.6 mg, 90% for 2 steps). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.52 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 9.5 Hz, 1H), 5.22 (t, *J* = 9.4 Hz, 1H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.95 (t, *J* = 9.5, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.25 (dd, *J* = 12.4, 5.1 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.75 – 3.71 (m, 1H), 2.38 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). The ^{1}H NMR spectroscopic data of **3w-6** are in accordance with those reported previously.[4]

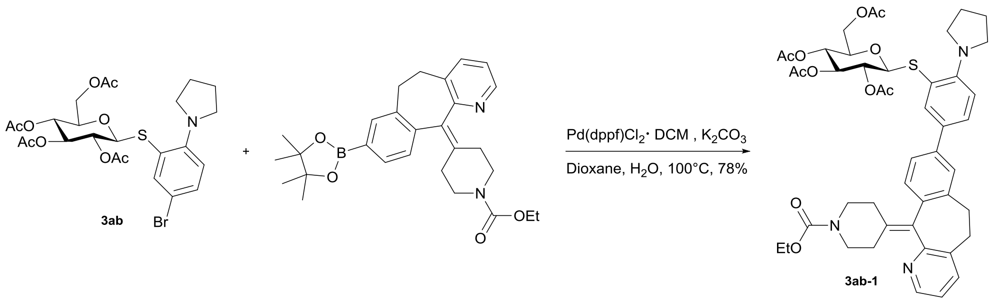
An 10 mL glass vial was charged with **3w-6** (0.096 mg, 0.2 mmol), 4CzIPN (1.6 mg, 2 μmol), DIPEA (35 μL, 0.2 mmol) and MeCN (2 mL). The vial was gently purged by N_2 for 30 seconds and sealed with a rubber stopper. The reaction was stirred vigorously and irradiated with 5 W (450 - 455 nm, approximately 4 cm away from the vial) blue LED at 25 ℃ for 12 hours. A clip fan next to the reaction setup had been kept working during the reaction, offsetting the heat generated from the LED light and to stabilize reaction temperature for reproducible results. Afterword, the reaction mixture was concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to obtain **3w-7** (eluent: petroleum ether/ethyl acetate = 2: 1 (v/v); 67.1 mg, 70% yield).[4] White solid, *m.p.*: 88.9 – 90.6 ℃; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 6.03 (t, *J* = 8.9 Hz, 1H), 5.57 (d, *J* = 6.0 Hz, 1H), 5.35 (dd, *J* = 9.3, 6.0 Hz, 1H), 5.15 (t, *J* =

9.9 Hz, 1H), 4.47 – 4.44 (m, 1H), 4.30 (dd, J = 12.5, 4.6 Hz, 1H), 4.06 (dd, J = 12.5, 2.5 Hz, 1H), 2.48 (s, 3H), 2.06 (s, 3H), 2.04 (s, 6H), 1.92 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.0, 169.8, 163.1, 151.4, 136.1, 135.2, 128.1, 123.7, 121.3, 71.6, 71.2, 70.3, 70.2, 68.6, 61.8, 21.6, 20.8, 20.7. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{26}NO_9S^+$ 480.1323; Found 480.1325.



3e **3e-1**

To a solution of compound **3e** (0.22 g, 0.3 mmol) in THF (5 mL) was added glacial acetic acid (45 µL, 0.78mmol) followed by TBAF (0.39 mL, 0.39 mmol, 1.0 M in THF). After 12 h stirring at rt, the reaction mixture was quenched with saturated $NaHCO_3$, extracted with AcOEt, dried over Na_2SO_4, filtered and concentrated. Without further purification the residue was dissolved in DCM (5 mL), probenecid (0.10 g, 0.36 mmol), EDCI (0.086 g, 0.45 mmol), DMAP (0.01 g, 0.09 mmol), and DIPEA (96 µL, 0.54 mmol) was added in succession. After stirring 12 h at room temperature, the mixture was then diluted with DCM and the organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel, affording product **3e-1** as a yellow oil (eluent: petroleum ether/ethyl acetate = 5: 1 (v/v); 148.1 mg, 66% for 2 steps). $[\alpha]_D^{20}$ -0.020 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.06 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.31 (s, 1H), 7.03 (d, J = 8.3 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 5.39 (t, J = 9.4 Hz, 1H), 5.31 (t, J = 9.7 Hz, 1H), 5.05 (t, J = 9.6 Hz, 1H), 4.80 (d, J = 10.2 Hz, 1H), 4.24 – 4.15 (m, 2H), 3.85 – 3.82 (m, 1H), 3.30 – 3.27 (m, 4H), 3.10 – 3.07 (m, 4H), 2.26 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.92 – 1.89 (m, 7H), 1.59 – 1.52 (m, 4H), 0.87 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.8, 170.4, 169.3, 164.0, 149.0, 145.0, 136.0, 132.1, 130.6, 129.9, 129.5, 127.3, 121.0, 116.7, 85.9, 75.8, 73.9, 70.3, 69.9, 62.8, 51.8, 50.2, 25.3, 22.2, 20.8, 20.7, 20.5, 11.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{36}H_{49}N_2O_{11}S_2^+$ 749.2772; Found 749.2766. **IR** (film) ν 3325, 2813, 2727, 1742, 1601, 1385, 1347, 764, 619 cm^{-1}.



Under N_2 atmosphere, compound **3ab** (0.094 g, 0.16 mmol), Loratadine boronic ester (0.27 g, 0.56 mmol), $Pd(dppf)Cl_2$ ·DCM (0.007 g, 0.008 mmol), and potassium carbonate (0.066 g, 0.48 mmol) were weighed into a screw-capped vial with a magnetic stir bar. Dioxane/H_2O (3 mL/0.6 mL) was added. The vial was tightly sealed with a Teflonlined cap and heated at 100 ℃ for 12 h. The reaction was diluted with ethyl acetate (5 mL) and washed with brine. The aqueous phase was extracted with ethyl acetate for three times. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, affording product **3ab-1** as a yellow oil (eluent: petroleum ether/ethyl acetate = 1: 2 (v/v); 106.7 mg, 78% yield). $[\alpha]_D^{20}$ -0.007 (*c* 1.0, MeCN); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 4.8 Hz, 1H), 7.73 (t, *J* = 2.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.35 – 7.33 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 8.9, 4.8 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.15 (t, *J* = 9.3 Hz, 1H), 5.00 (td, *J* = 9.8, 4.6 Hz, 1H), 4.93 (td, *J* = 9.7, 4.8 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.15 – 4.02 (m, 4H), 3.82 (s, 2H), 3.64 – 3.60 (m, 1H), 3.47 – 3.36 (m, 6H), 3.18 – 3.09 (m, 2H), 2.90 – 2.83 (m, 2H), 2.49 – 2.42 (m, 3H), 2.31 (d, *J* = 11.2 Hz, 1H), 2.02 (s, 3H), 1.98 (d, *J* = 1.2 Hz, 3H), 1.97 (s, 3H), 1.92 – 1.89 (m, 4H), 1.60 (d, *J* = 30.6 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 170.4, 169.5, 169.2, 155.6, 150.6, 146.7, 139.3, 138.0, 137.4, 136.8, 135.4, 135.3, 135.1, 133.8, 131.4, 131.3, 130.0, 127.8, 127.0, 123.9, 122.2, 116.2, 86.1, 75.7, 74.2, 70.2, 68.2, 62.3, 61.4, 51.9, 45.0, 32.2, 31.7, 30.9, 30.7, 25.6, 20.8, 20.7, 20.2, 20.1, 14.8. **HRMS**

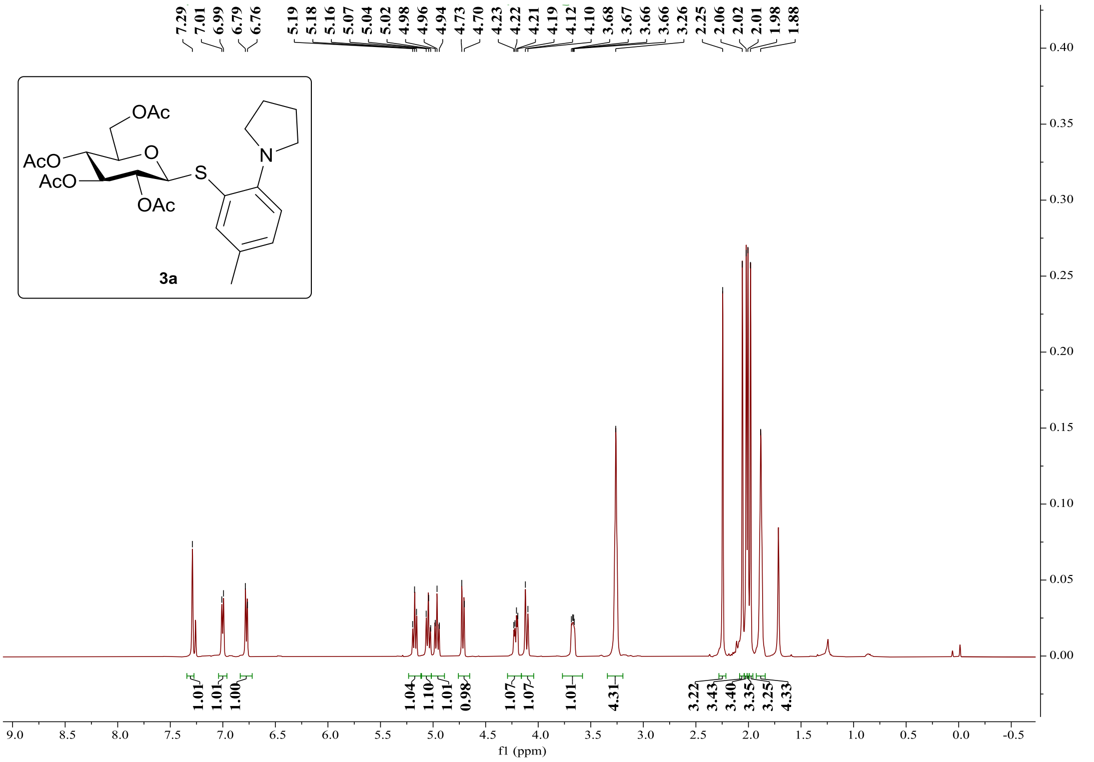
(ESI) m/z: $[M + H]^+$ Calcd for $C_{46}H_{54}N_3O_{11}S^+$ 856.3474; Found 856.3476. **IR** (film) ν 3328, 2813, 1755, 1594, 1382, 1350, 1221, 1115, 1037, 768 cm^{-1}.

12. Reference

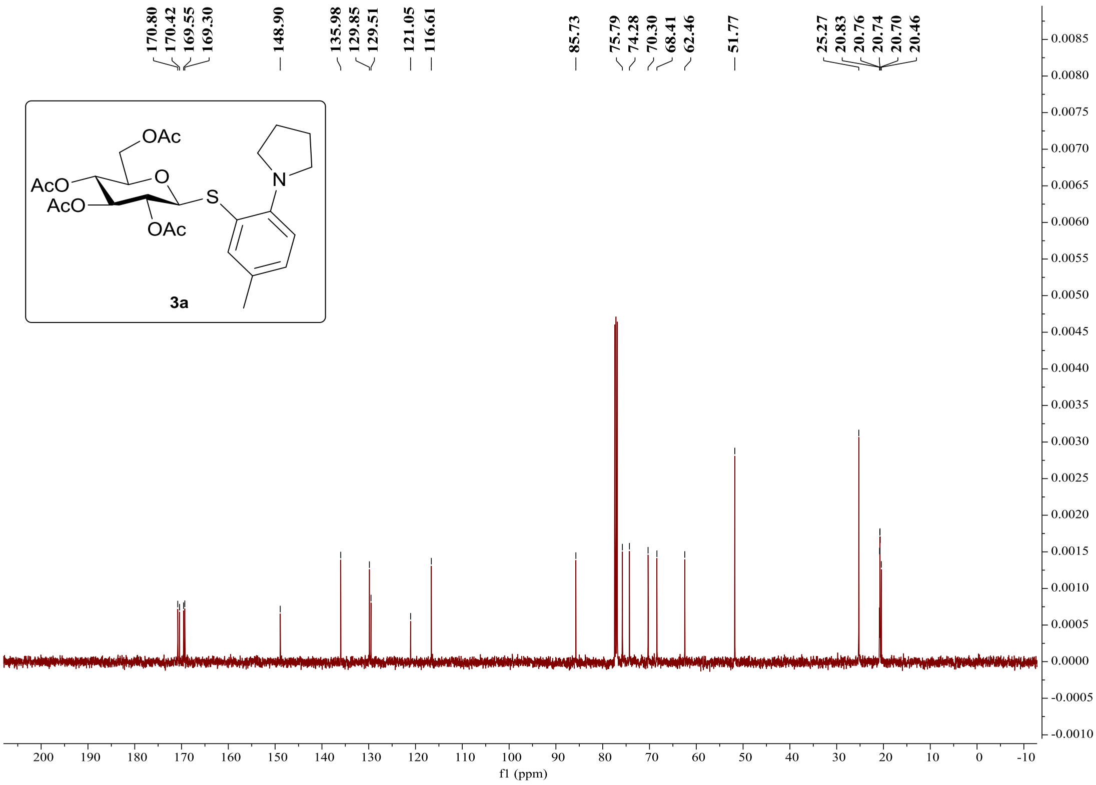
1. (a) A. Brinkø, C. Risinger, A. Lambert, O. Blixt, C. Grandjean and H. H. Jensen, *Org. Lett.*, 2019, **21**, 7544-7548; (b) N. Floyd, B. Vijayakrishnan, J. R. Koeppe and B. G. Davis, *Angew. Chem. Int. Ed.*, 2009, **48**, 7798-7802. (c) R. Q. Wang, Q. H. Jiang, H. X. Wang, X. W. Zhang and N. Yan, *Org. Lett.*, 2023, **25**, 4252–4257.
2. P. H. Shu, J. Zeng, J. Y. Tao, Y. Q. Zhao, G. M. Yao and Q. Wan, *Green Chem.*, 2015, **17**, 2545.
3. J. T. Ge, L. Zhou, F. L. Zhao and H. Dong, *J. Org. Chem.*, 2017, **82**, 12613-12623.
4. L. Y. Hu, S. Y. Zhang, L. Zhu, Y. Li, K. Luo and L. Wu, *Org. Lett.*, DOI: 10.1021/acs.orglett.3c03817.

13. NMR spectra

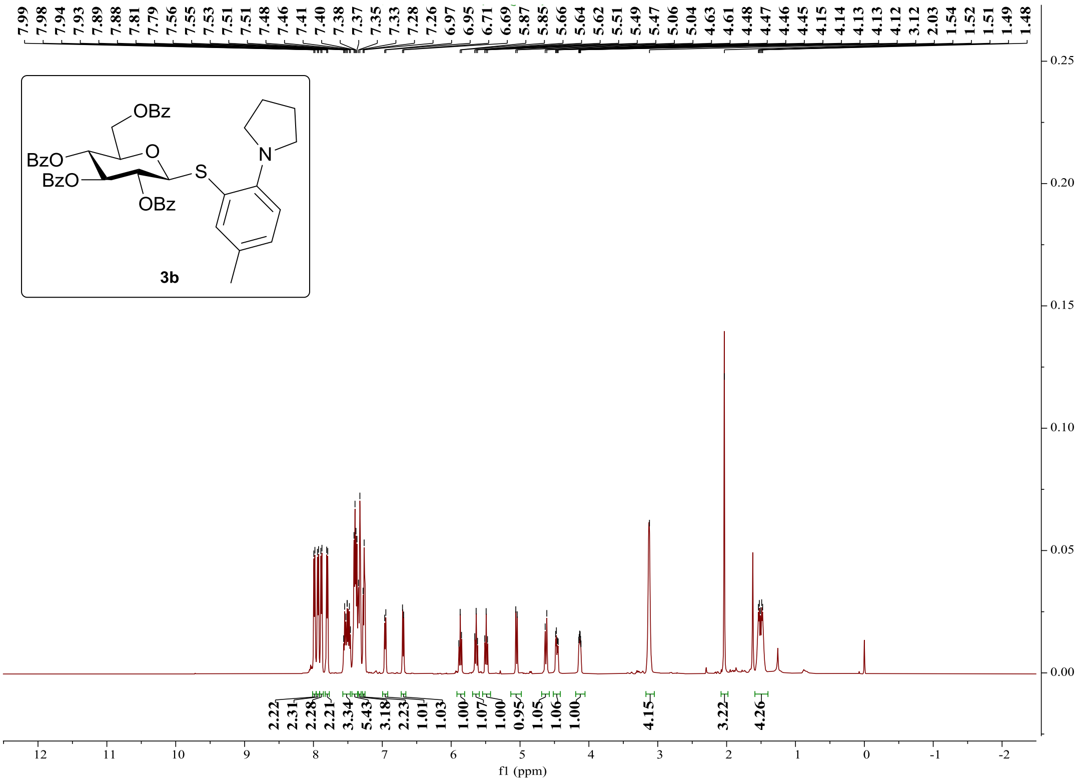
^{1}H NMR of 3a ($CDCl_3$, 500 MHz, 25 ℃)



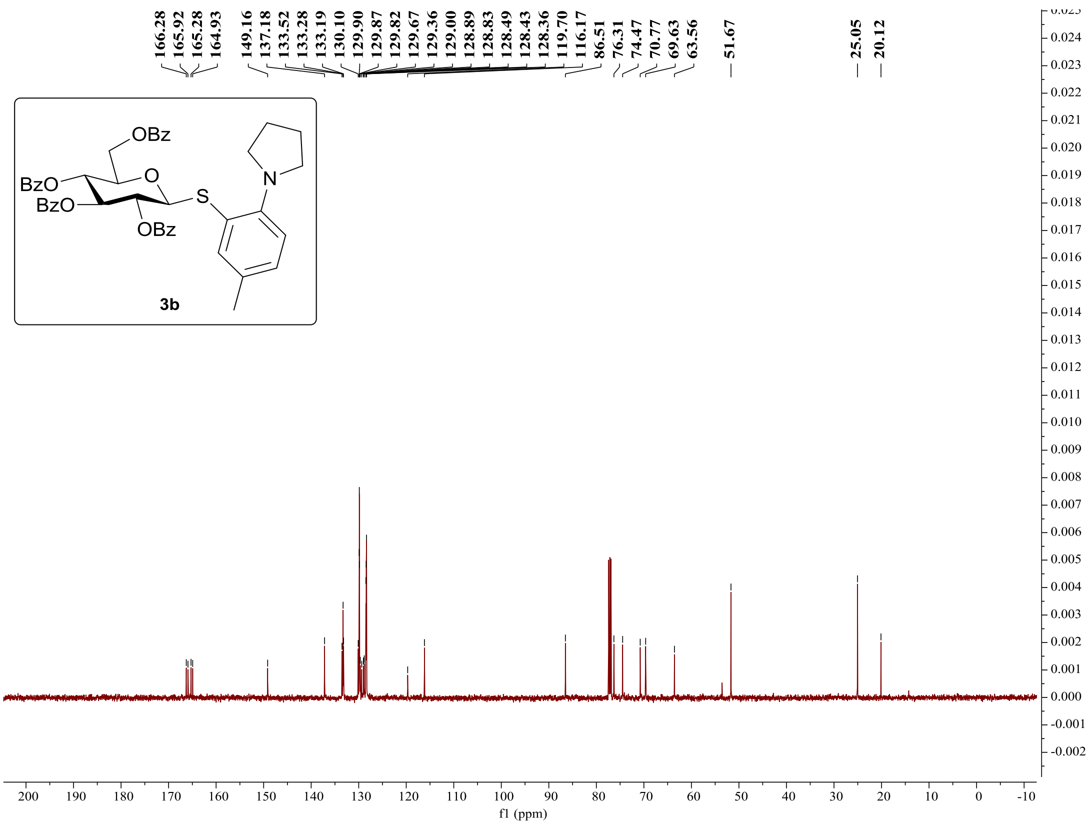
^{13}C NMR of 3a ($CDCl_3$, 126 MHz, 25 ℃)



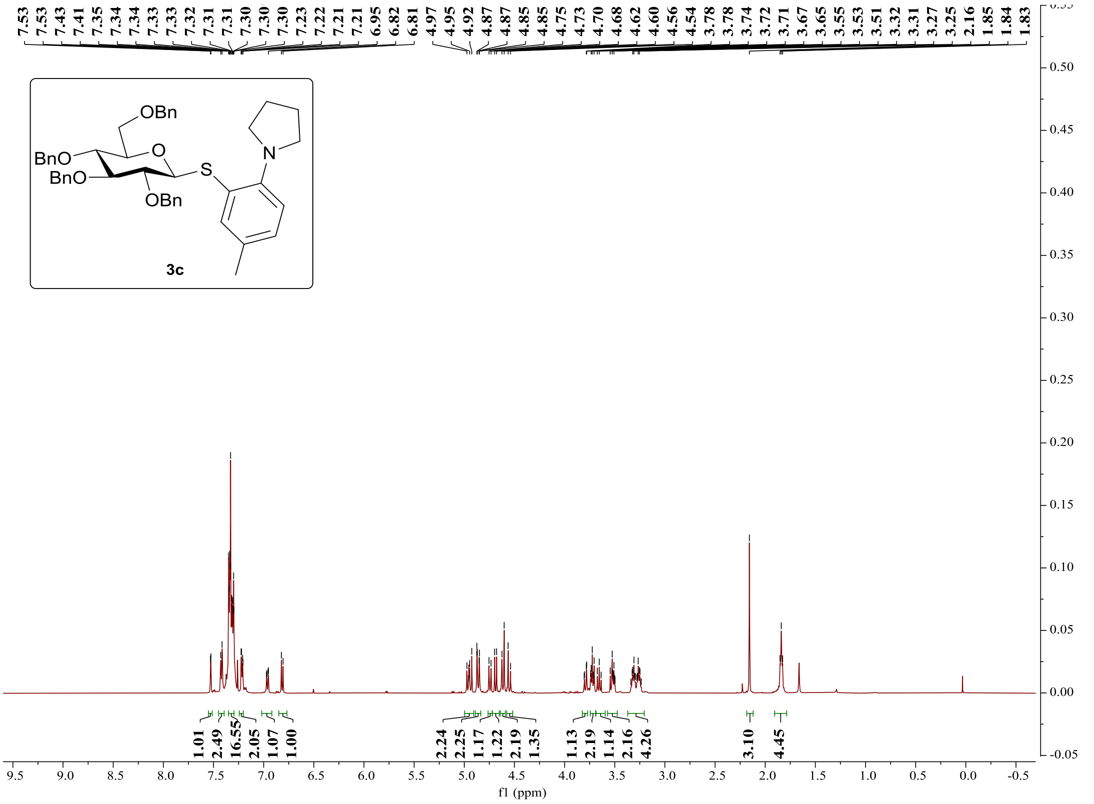
^{1}H NMR of 3b (CDCl$_3$, 500 MHz, 25 ℃)



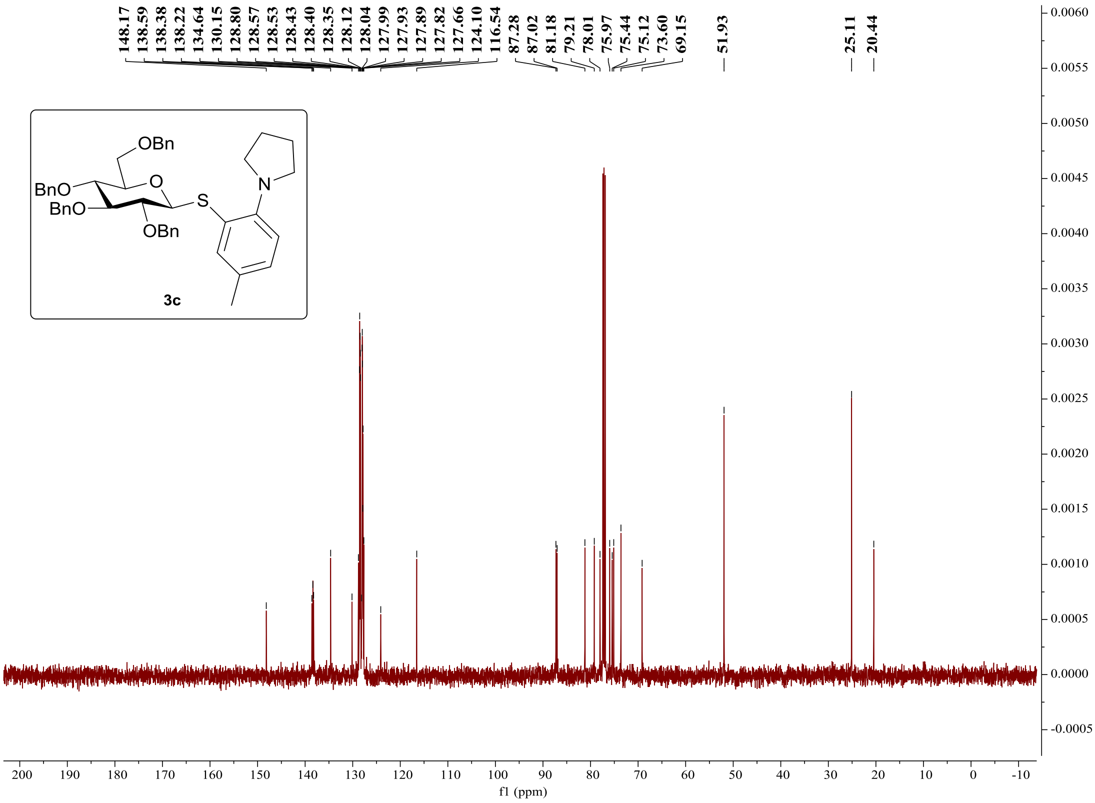
^{13}C NMR of 3b (CDCl$_3$, 126 MHz, 25 ℃)



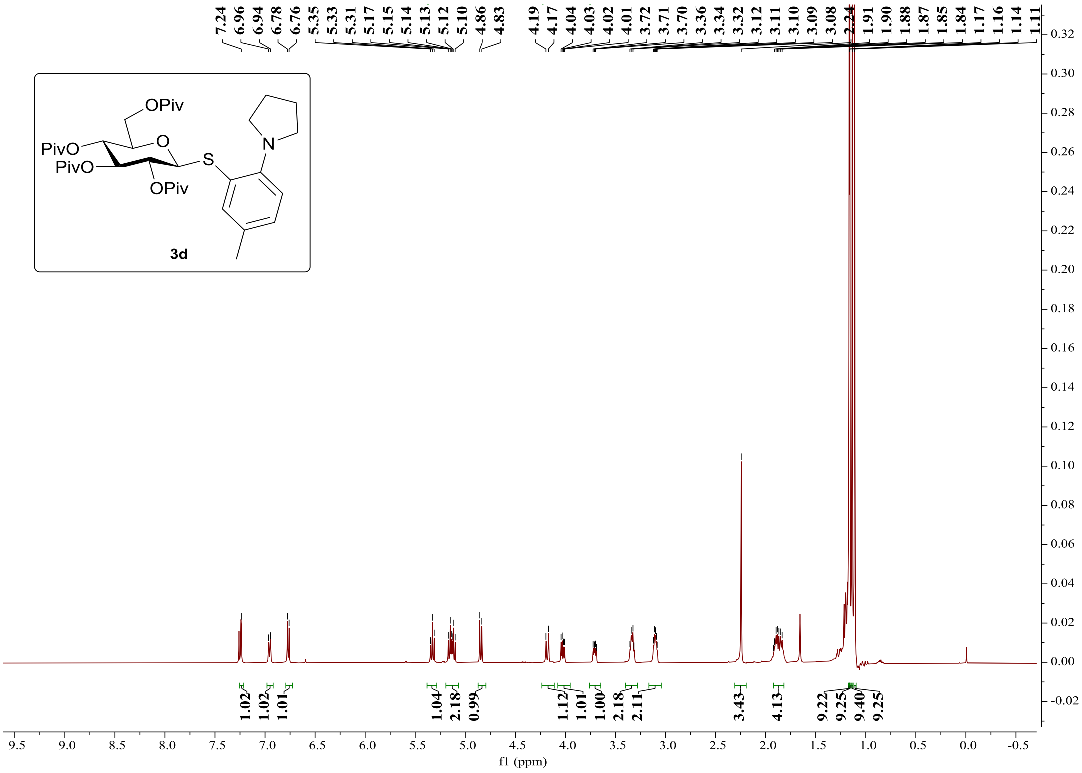
^{1}H NMR of 3c ($CDCl_3$, 500 MHz, 25 ℃)



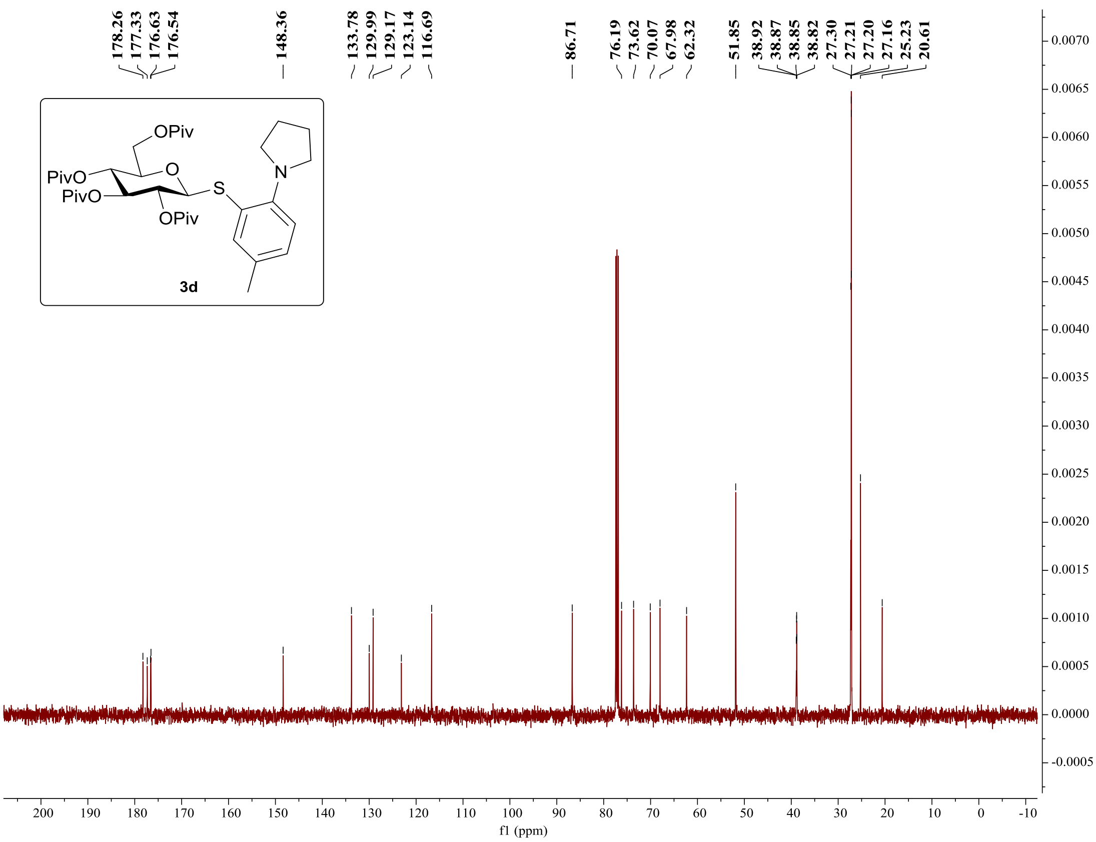
^{13}C NMR of 3c ($CDCl_3$, 126 MHz, 25 ℃)



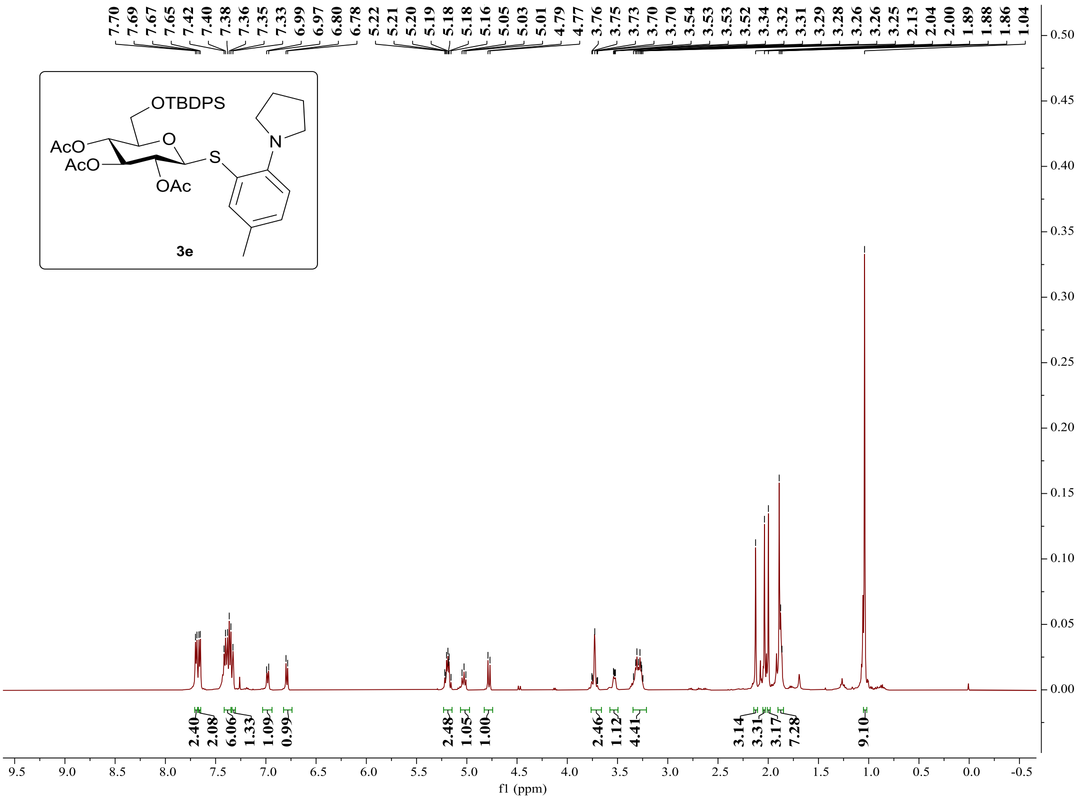
[1]H NMR of 3d (CDCl₃, 500 MHz, 25 ℃)



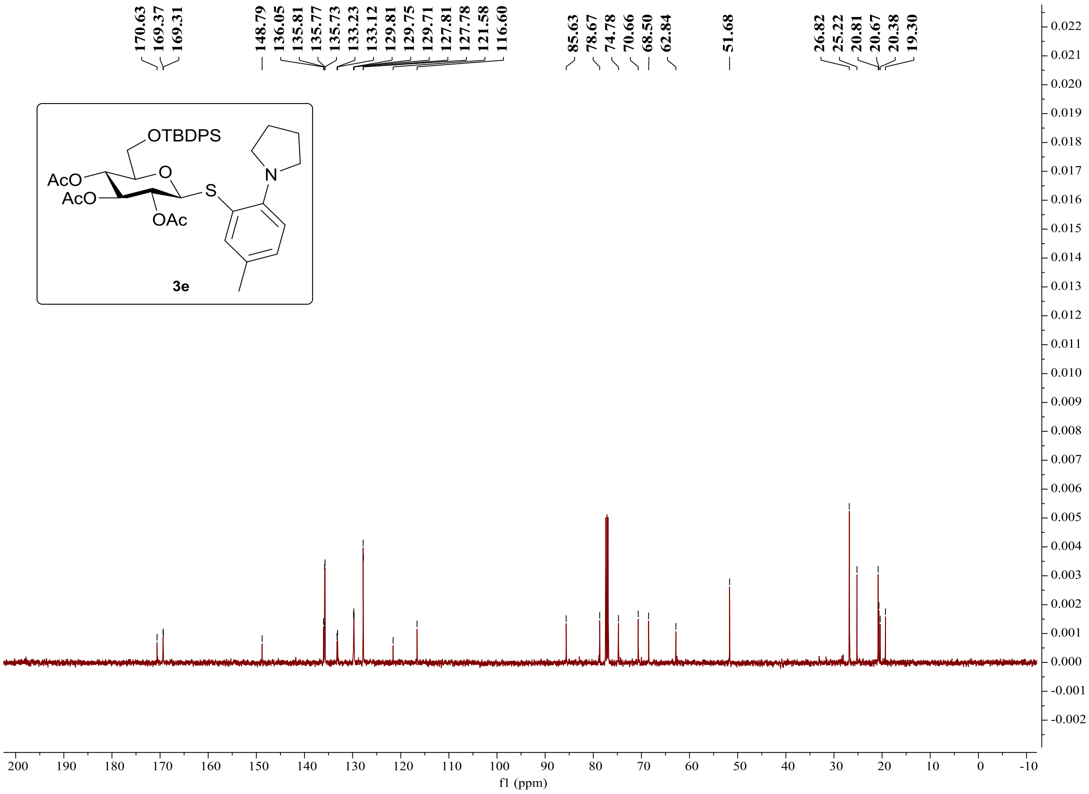
[13]C NMR of 3d (CDCl₃, 126 MHz, 25 ℃)



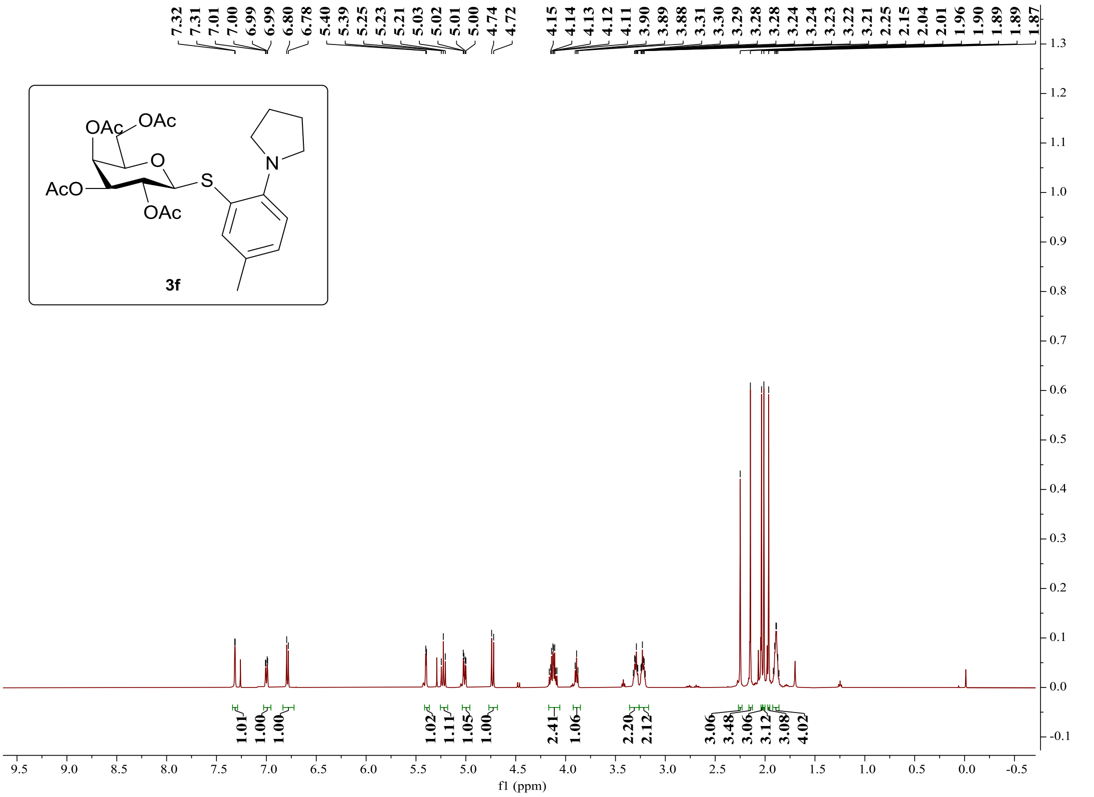
^{1}H NMR of 3e (CDCl$_3$, 500 MHz, 25 ℃)



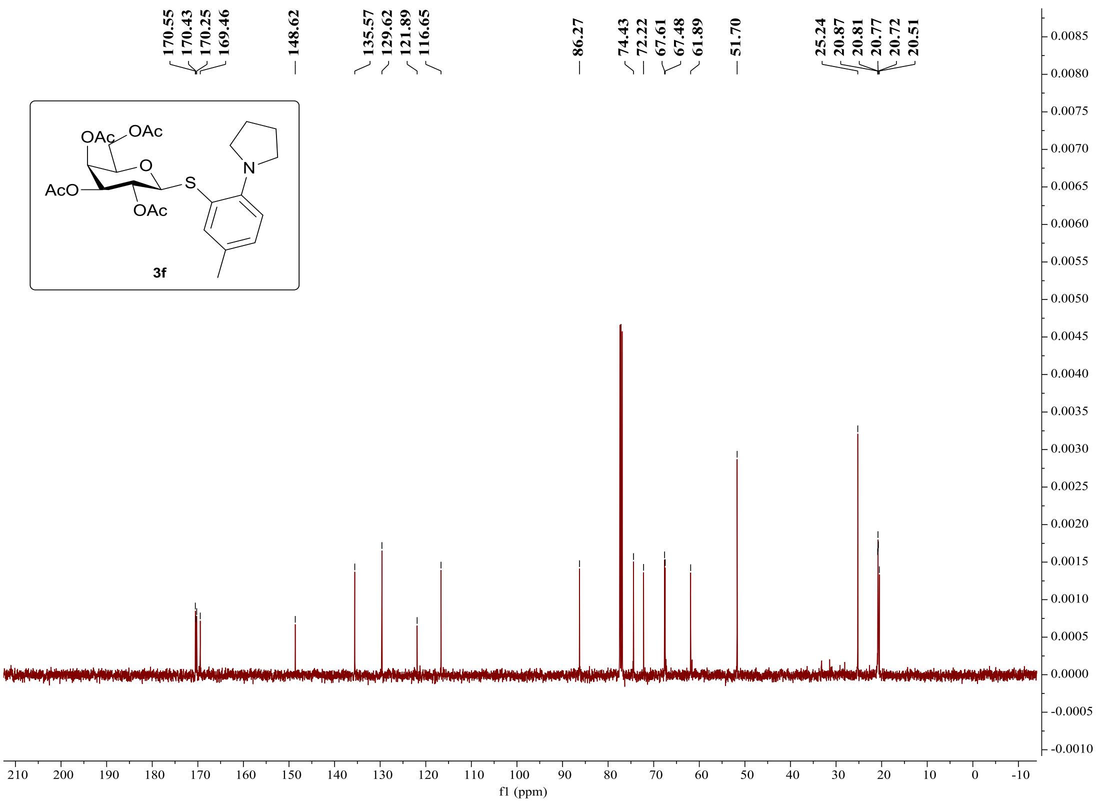
^{13}C NMR of 3e (CDCl$_3$, 126 MHz, 25 ℃)



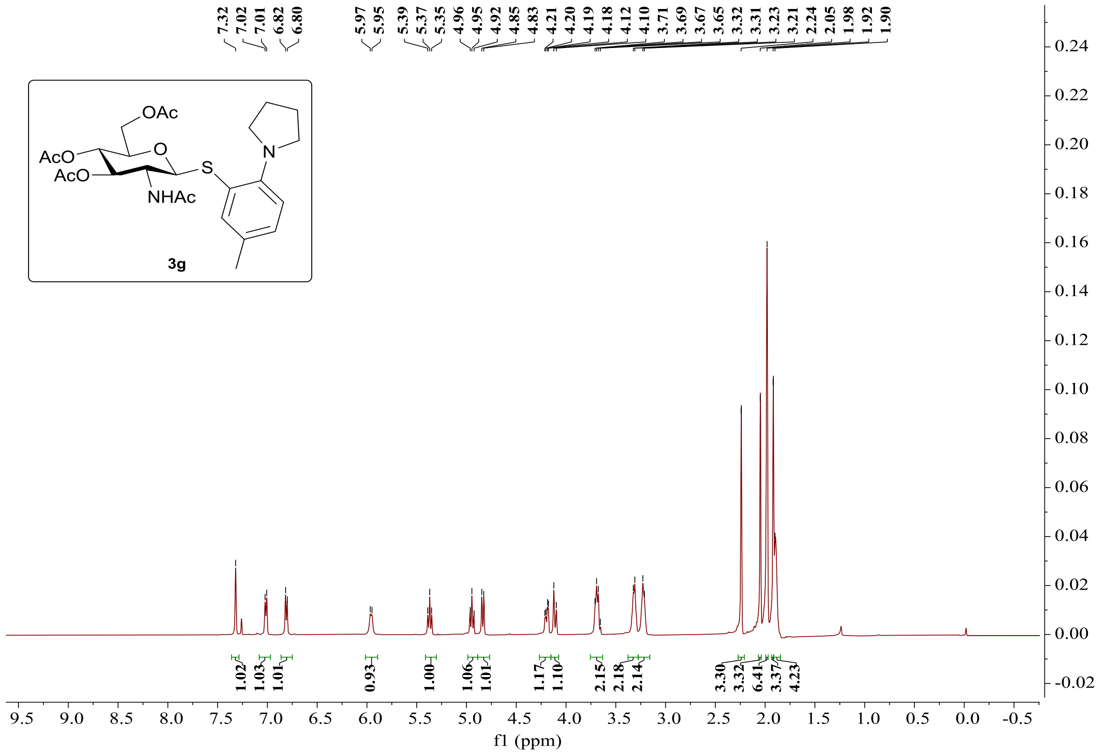
^{1}H NMR of 3f (CDCl$_3$, 500 MHz, 25 ℃)



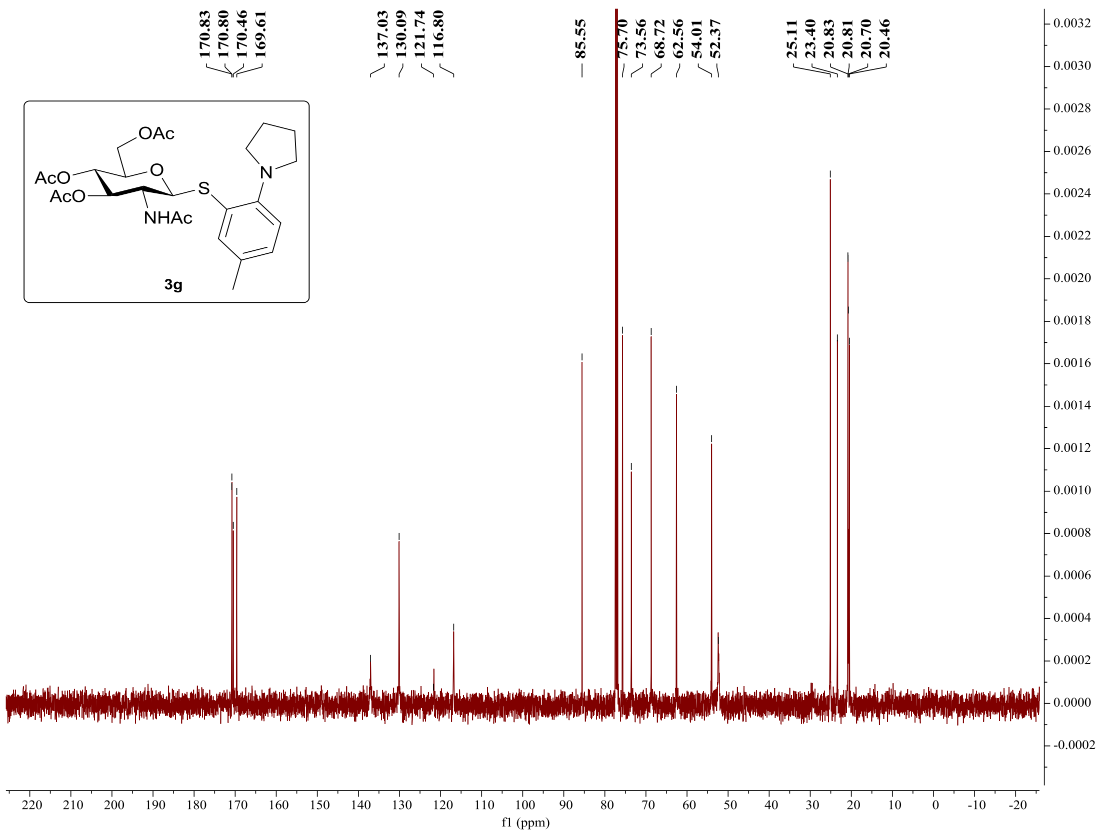
^{13}C NMR of 3f (CDCl$_3$, 126 MHz, 25 ℃)



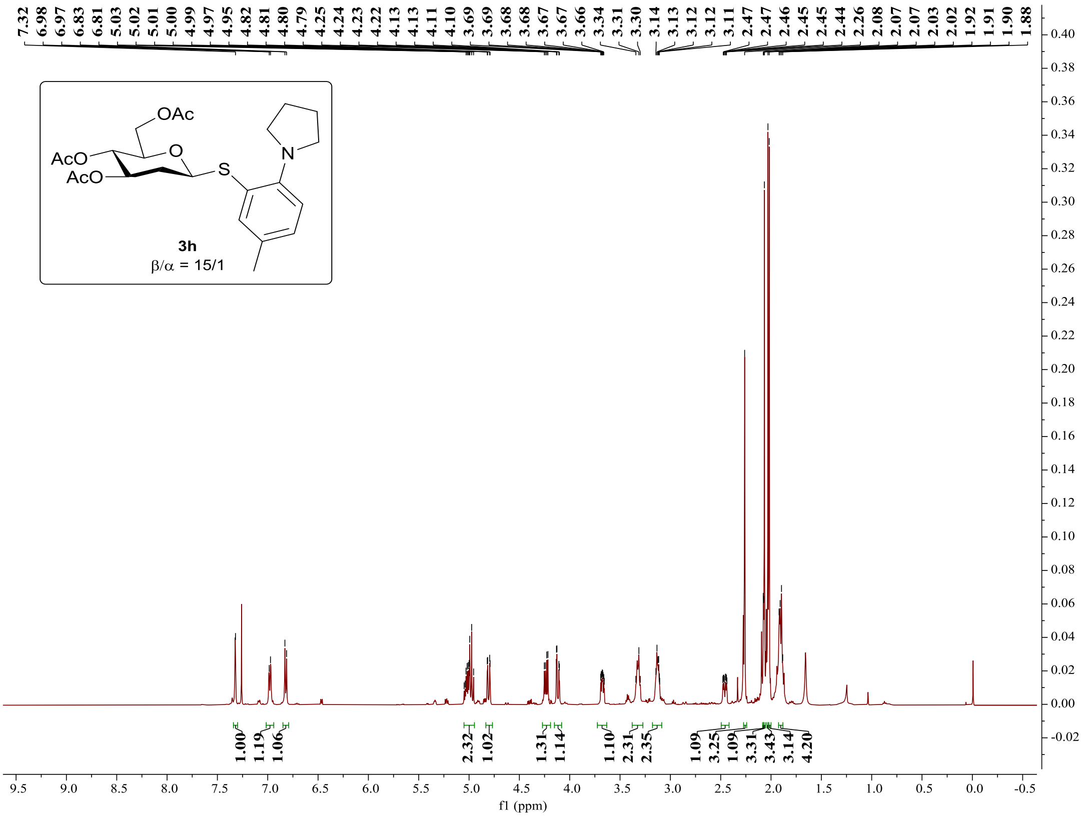
^1H NMR of 3g ($CDCl_3$, 500 MHz, 25 ℃)



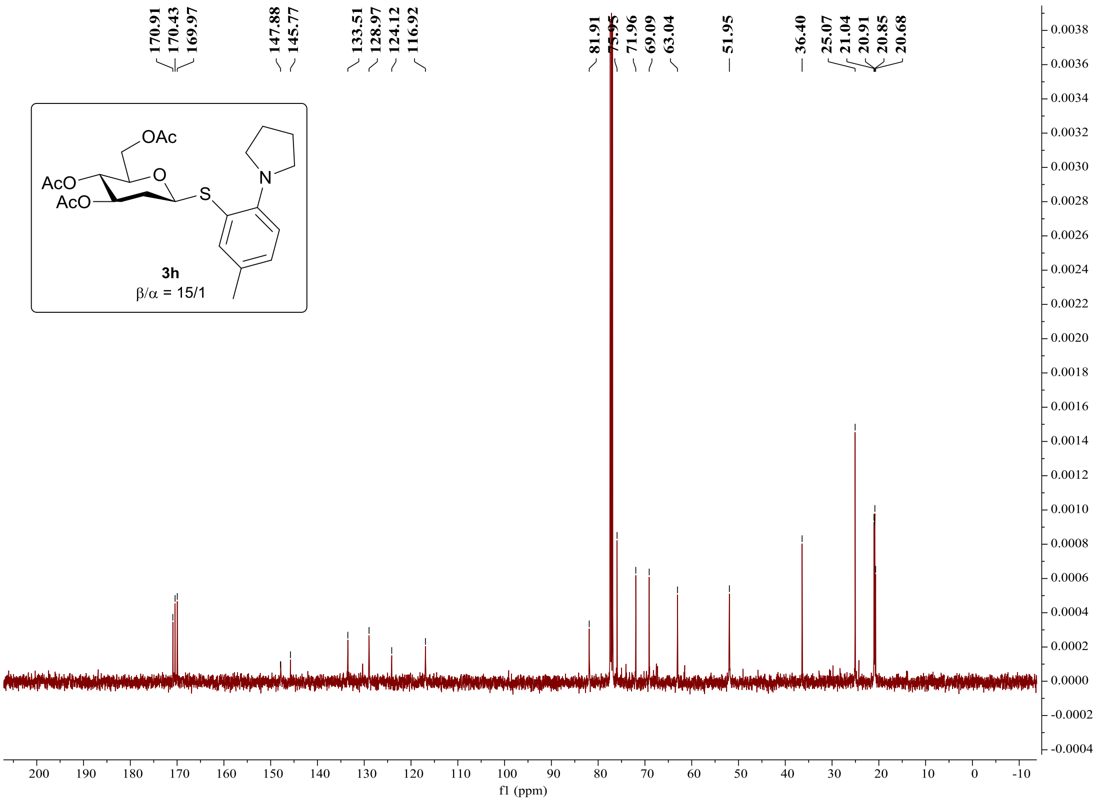
^{13}C NMR of 3g ($CDCl_3$, 126 MHz, 25 ℃)



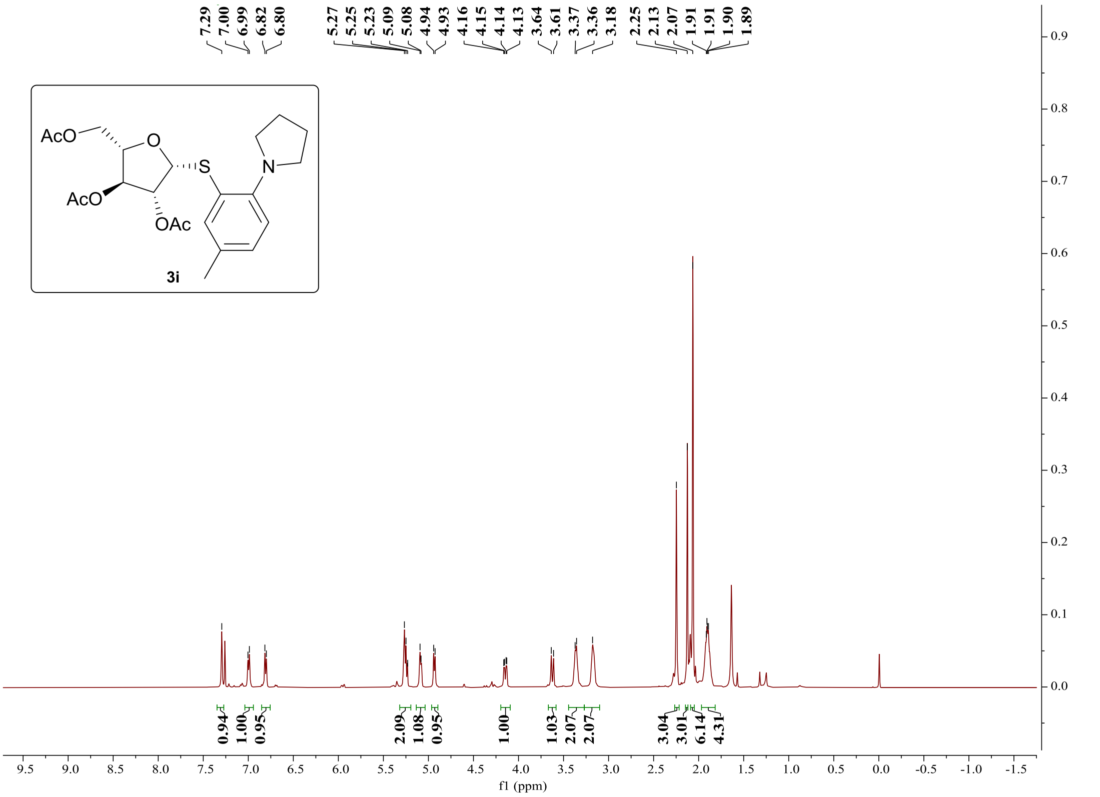
^{1}H NMR of 3h ($CDCl_3$, 500 MHz, 25 ℃)



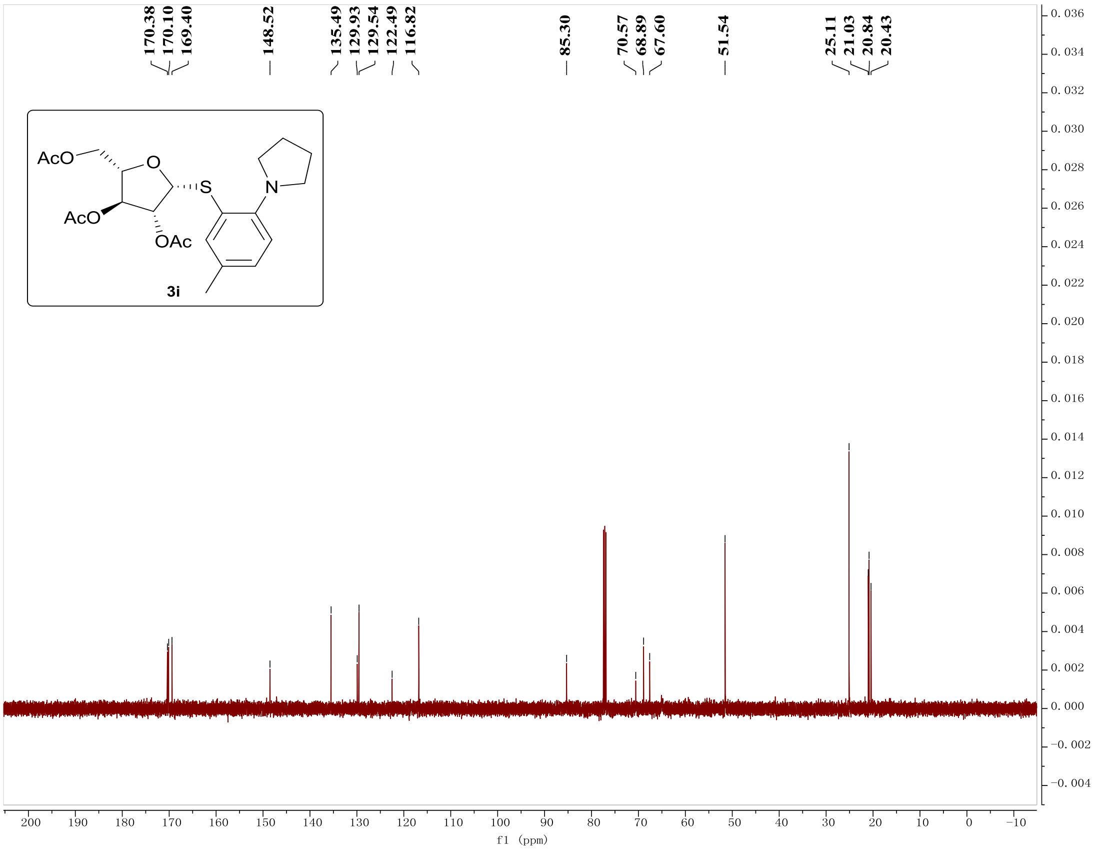
^{13}C NMR of 3h ($CDCl_3$, 126 MHz, 25 ℃)



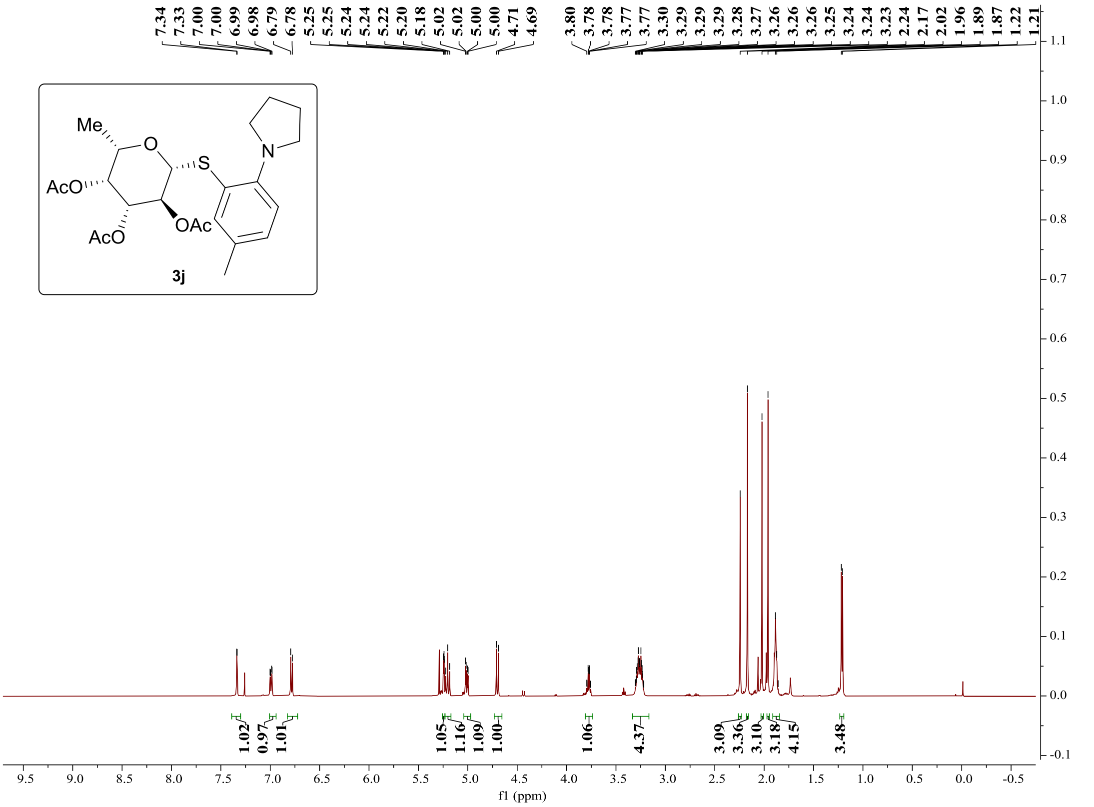
^{1}H NMR of 3i ($CDCl_3$, 500 MHz, 25 ℃)



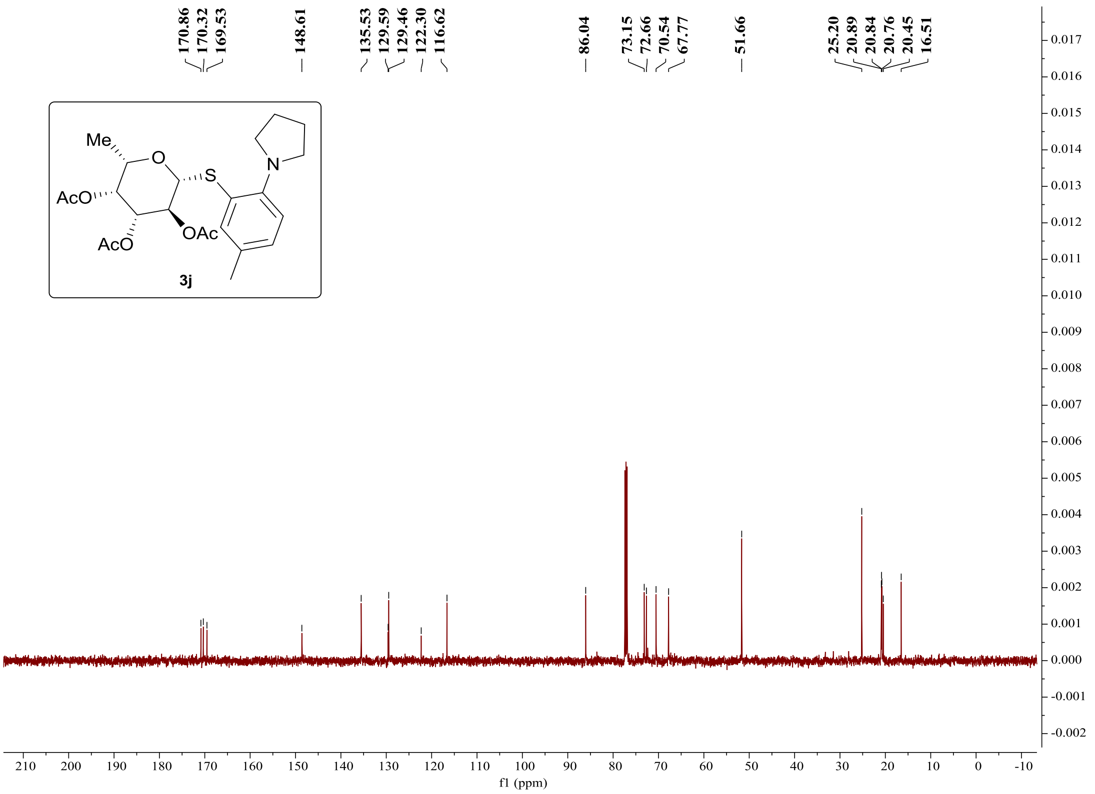
^{13}C NMR of 3i ($CDCl_3$, 126 MHz, 25 ℃)



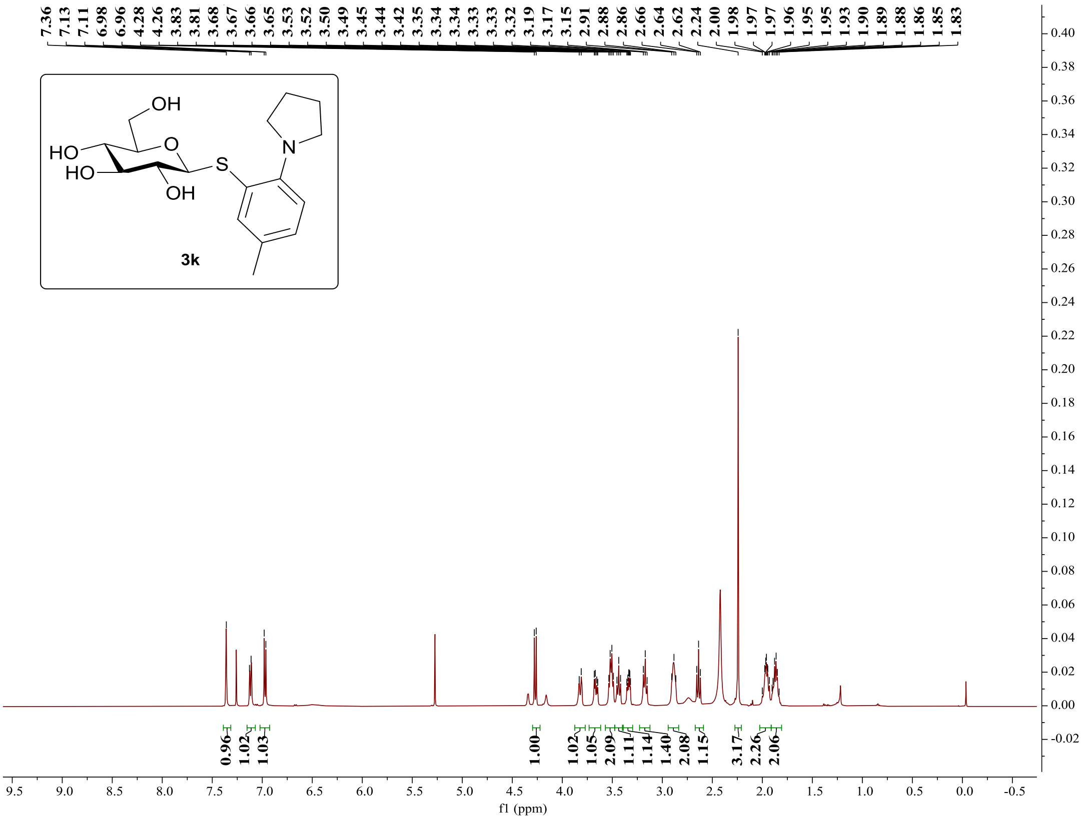
[1]H NMR of 3j (CDCl$_3$, 500 MHz, 25 ℃)



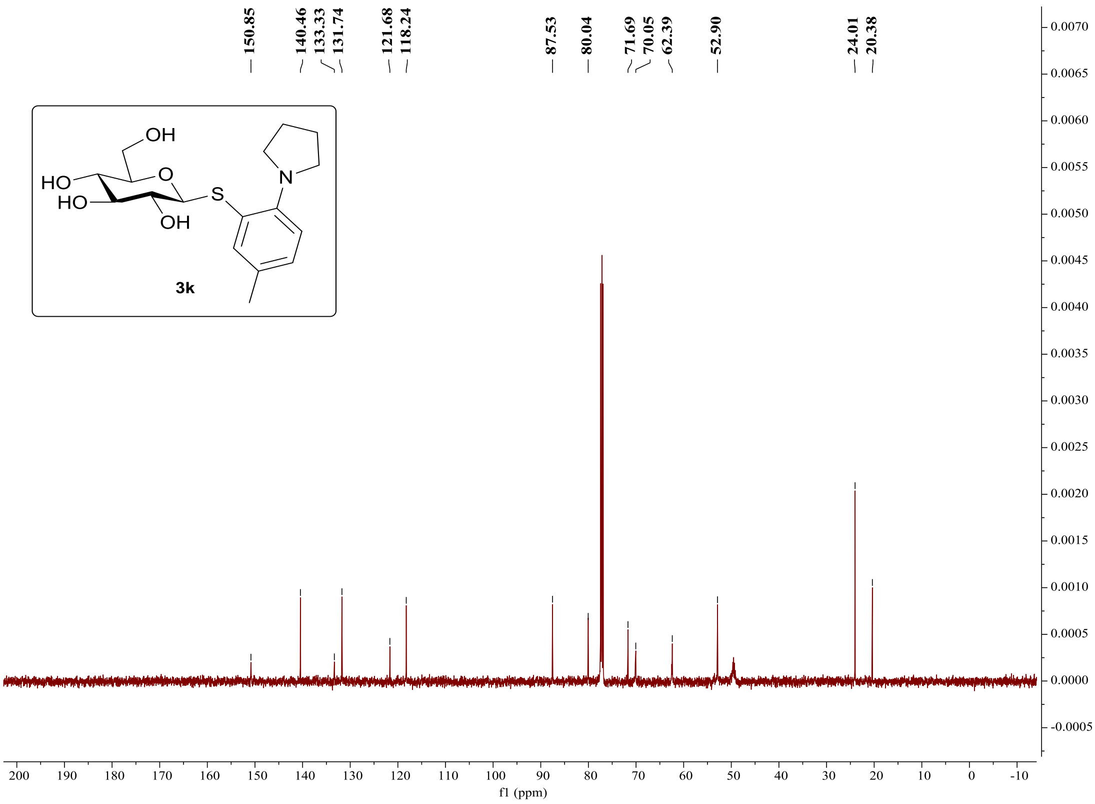
[13]C NMR of 3j (CDCl$_3$, 126 MHz, 25 ℃)



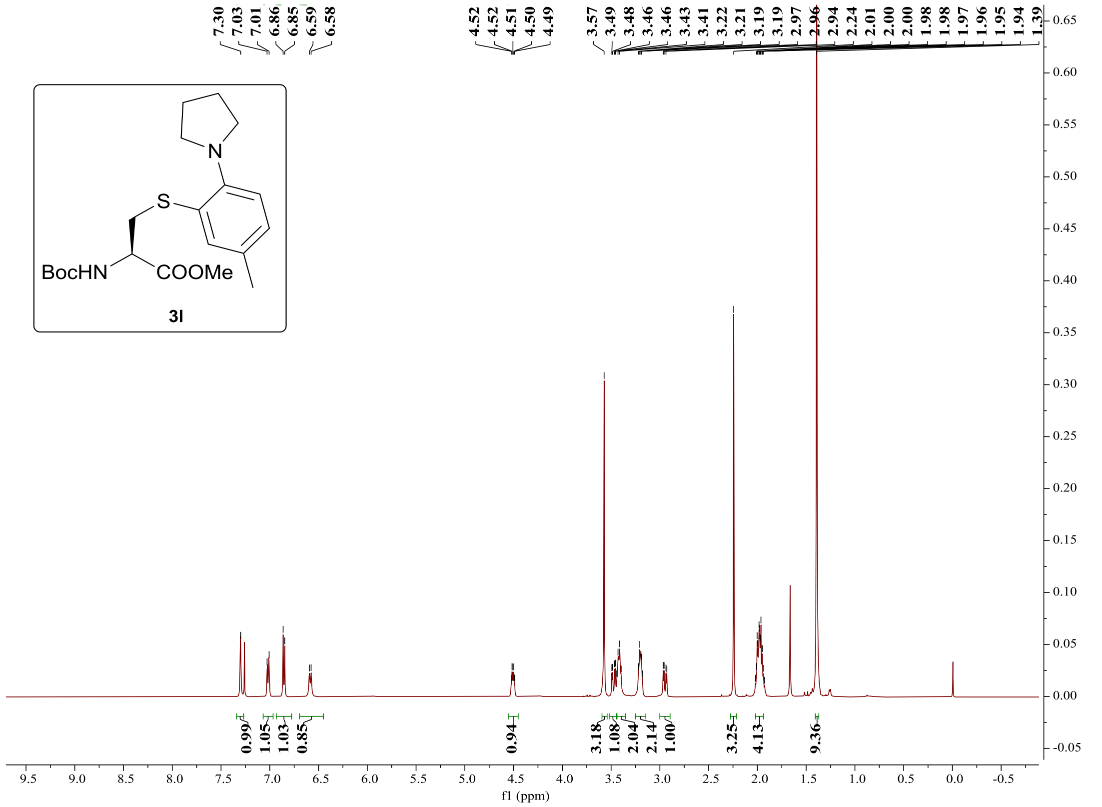
^{1}H NMR of 3k ($CDCl_3$, 500 MHz, 25 ℃)



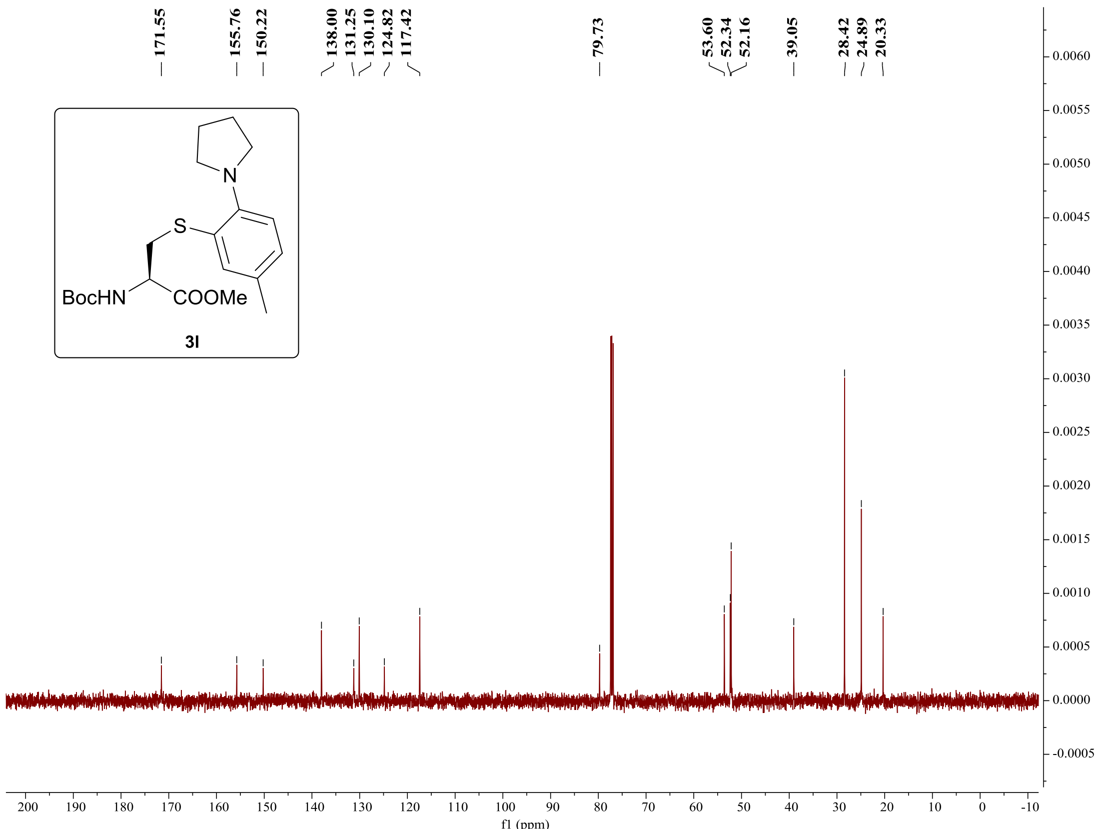
^{13}C NMR of 3k ($CDCl_3$, 126 MHz, 25 ℃)



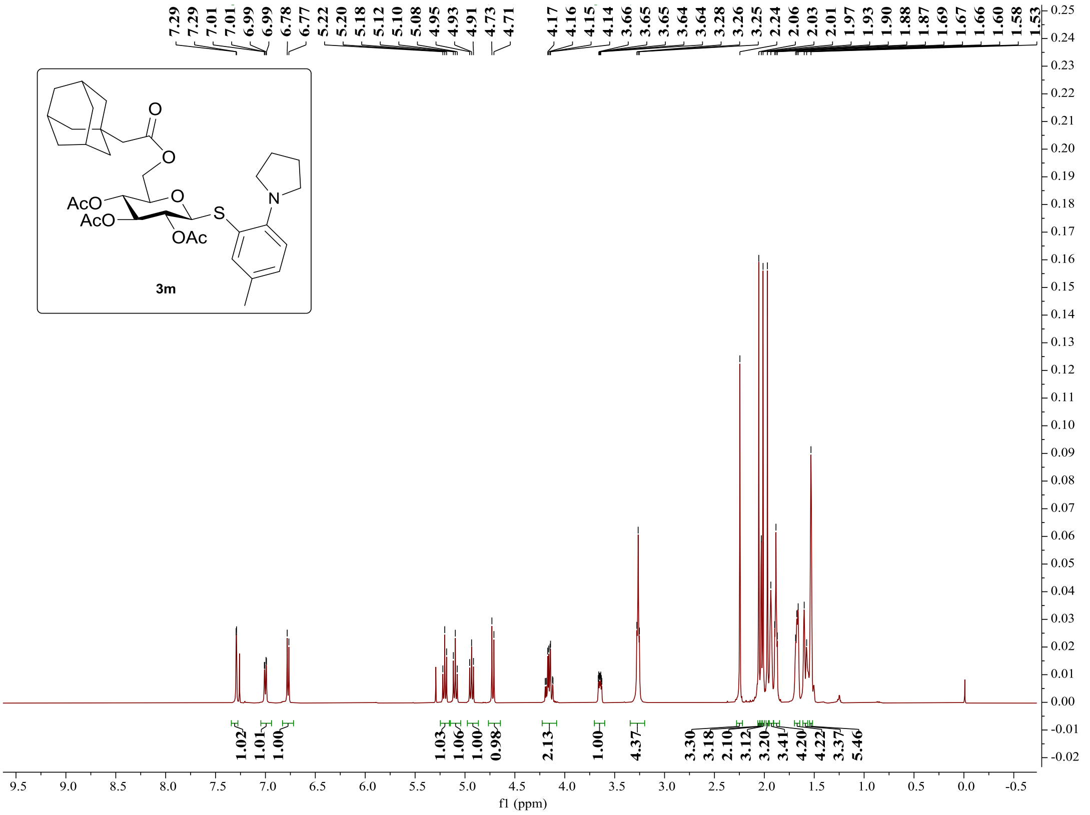
^{1}H NMR of 3l (CDCl$_3$, 500 MHz, 25 ℃)



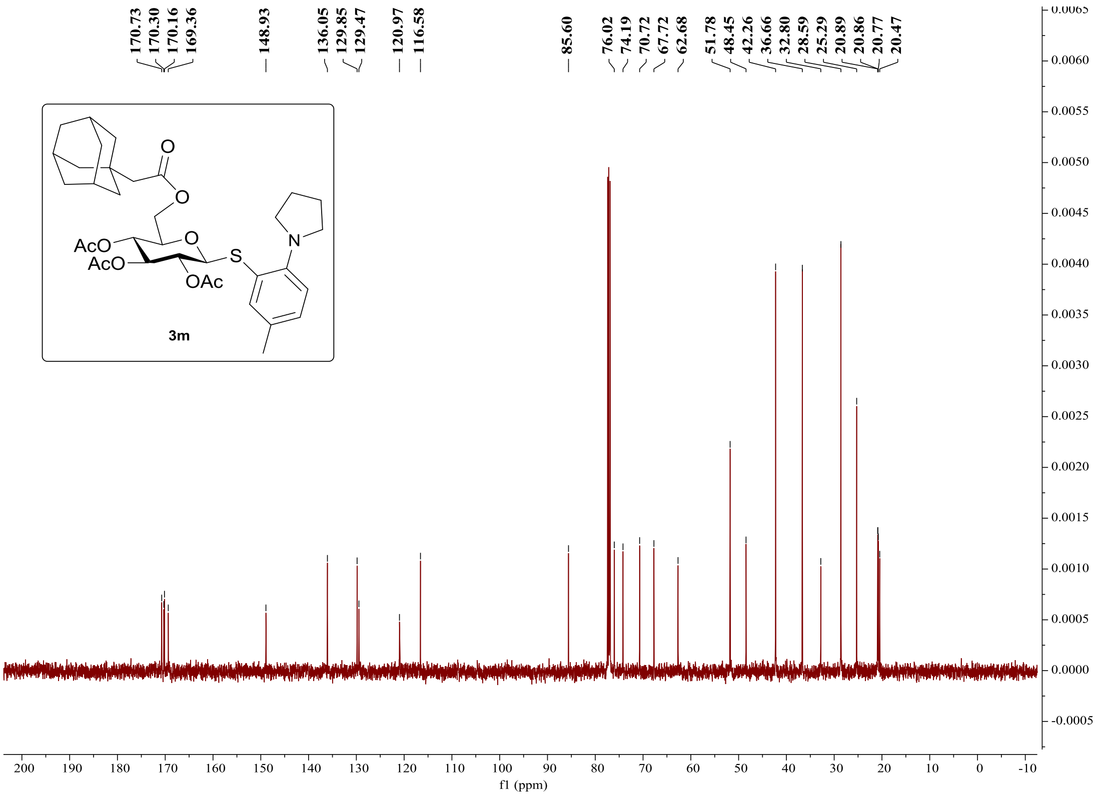
^{13}C NMR of 3l (CDCl$_3$, 126 MHz, 25 ℃)



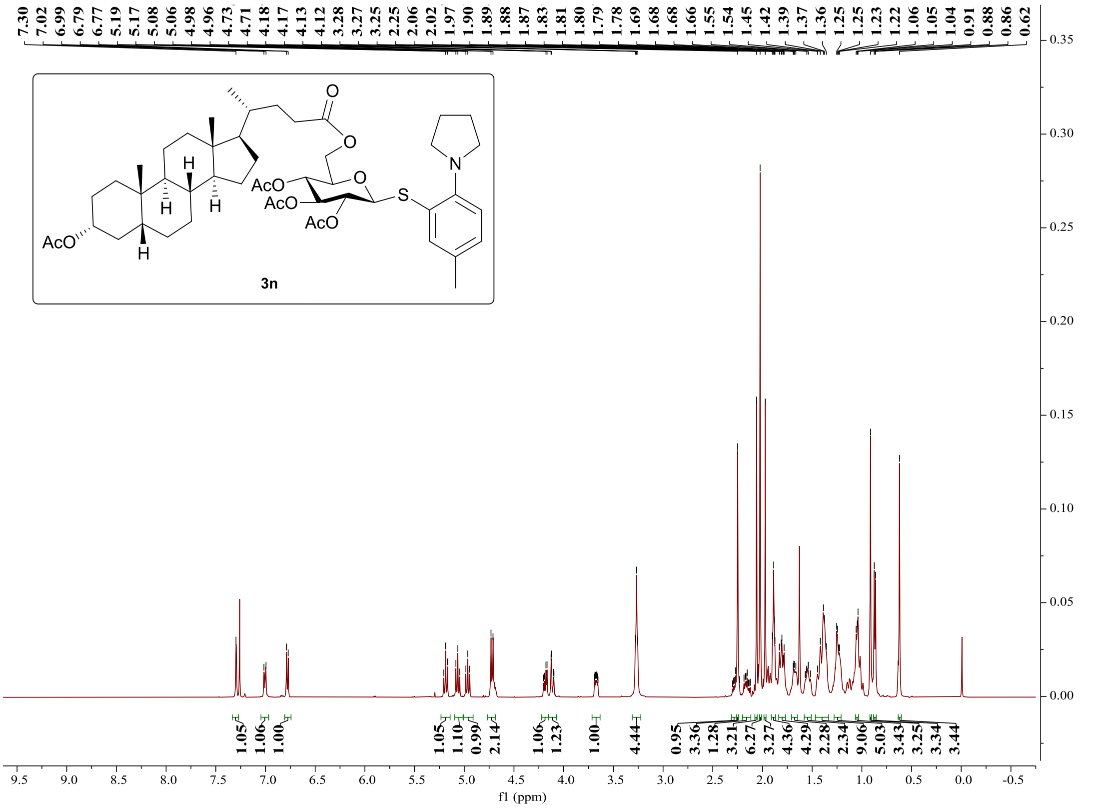
^{1}H NMR of 3m ($CDCl_3$, 500 MHz, 25 ℃)



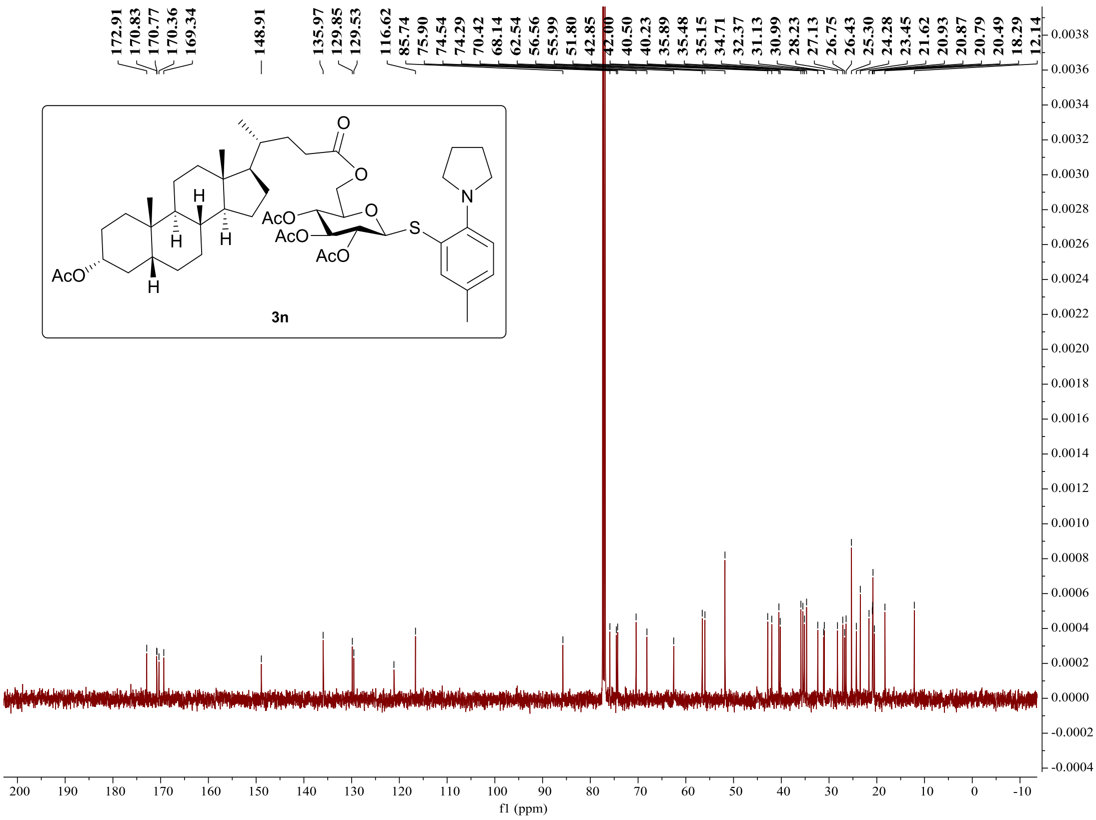
^{13}C NMR of 3m ($CDCl_3$, 126 MHz, 25 ℃)



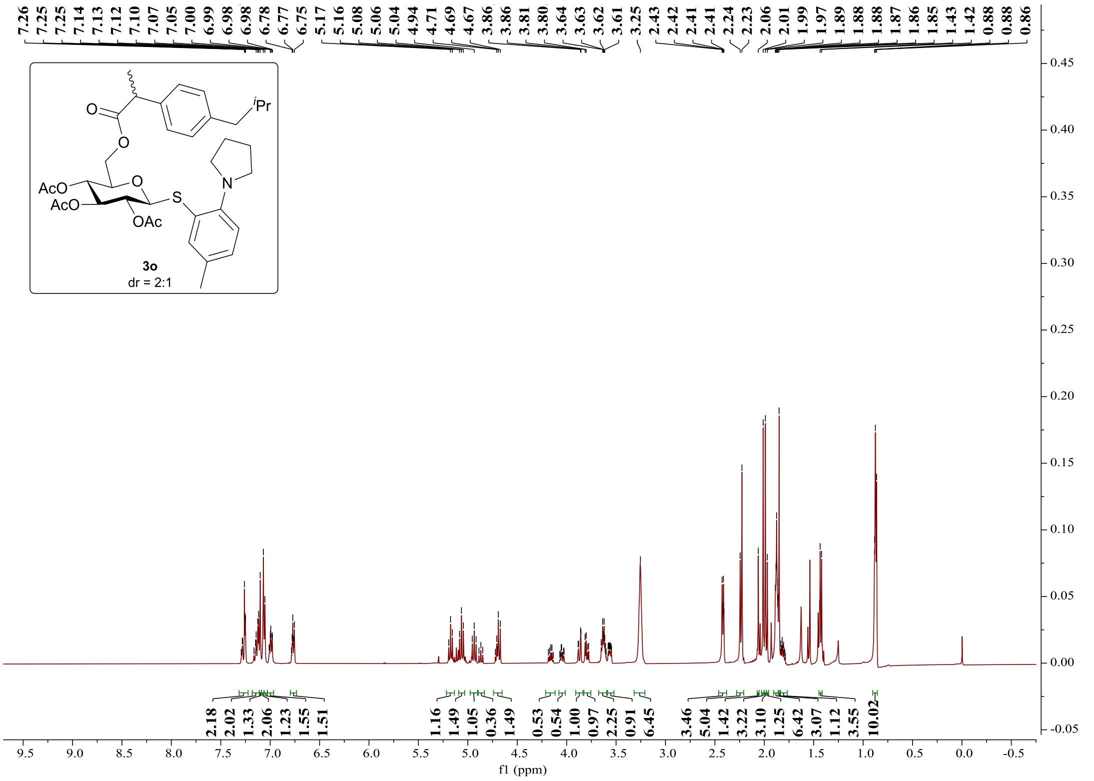
^{1}H NMR of 3n ($CDCl_3$, 500 MHz, 25 ℃)



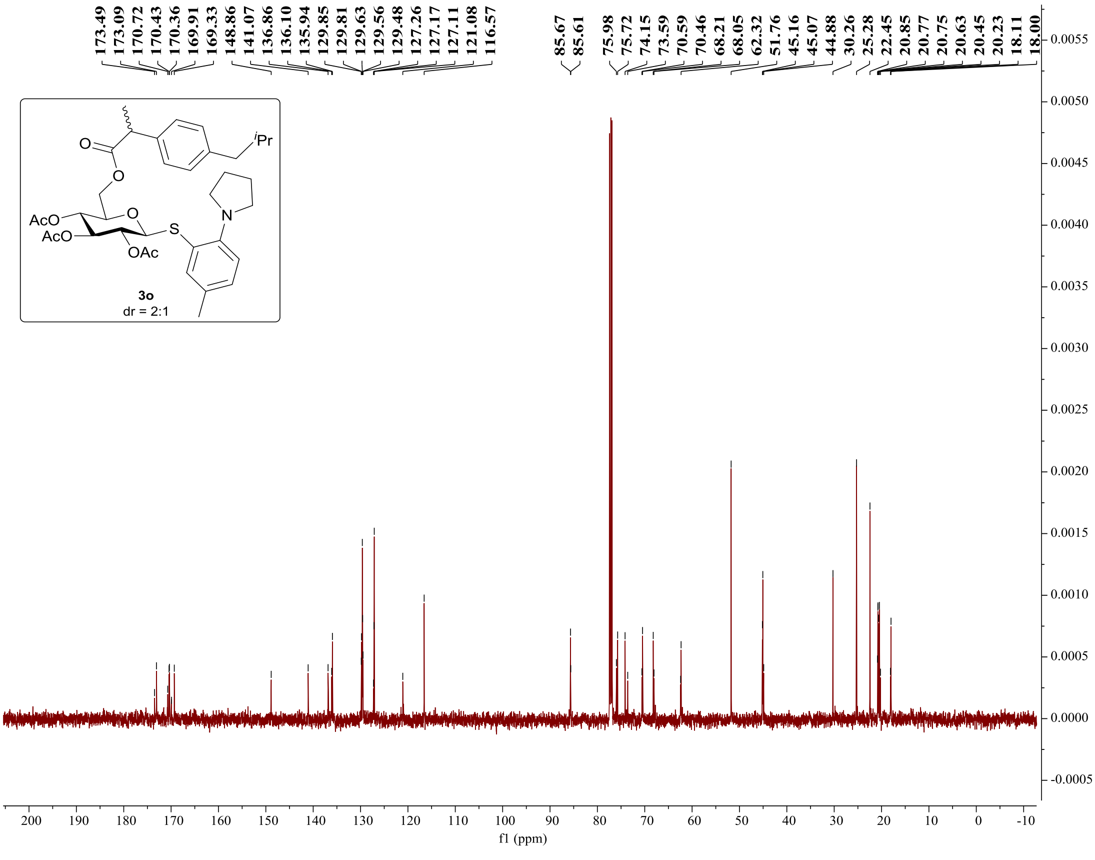
^{13}C NMR of 3n ($CDCl_3$, 126 MHz, 25 ℃)



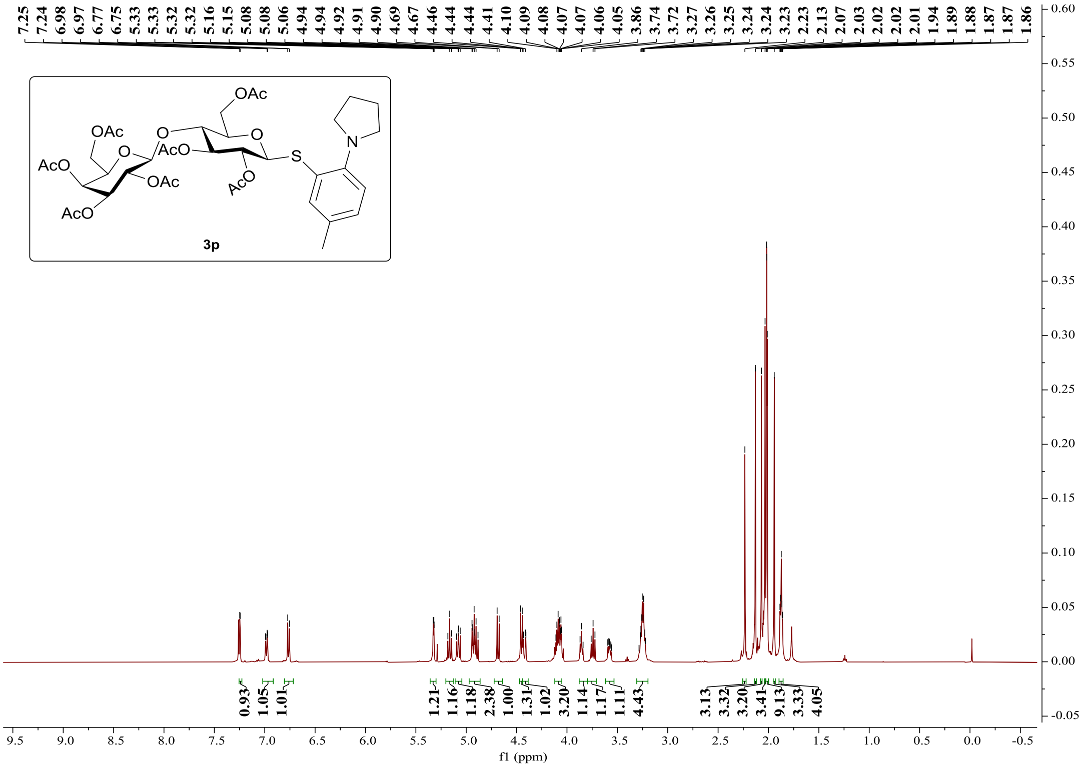
[1]H NMR of 3o (CDCl$_3$, 500 MHz, 25 ℃)



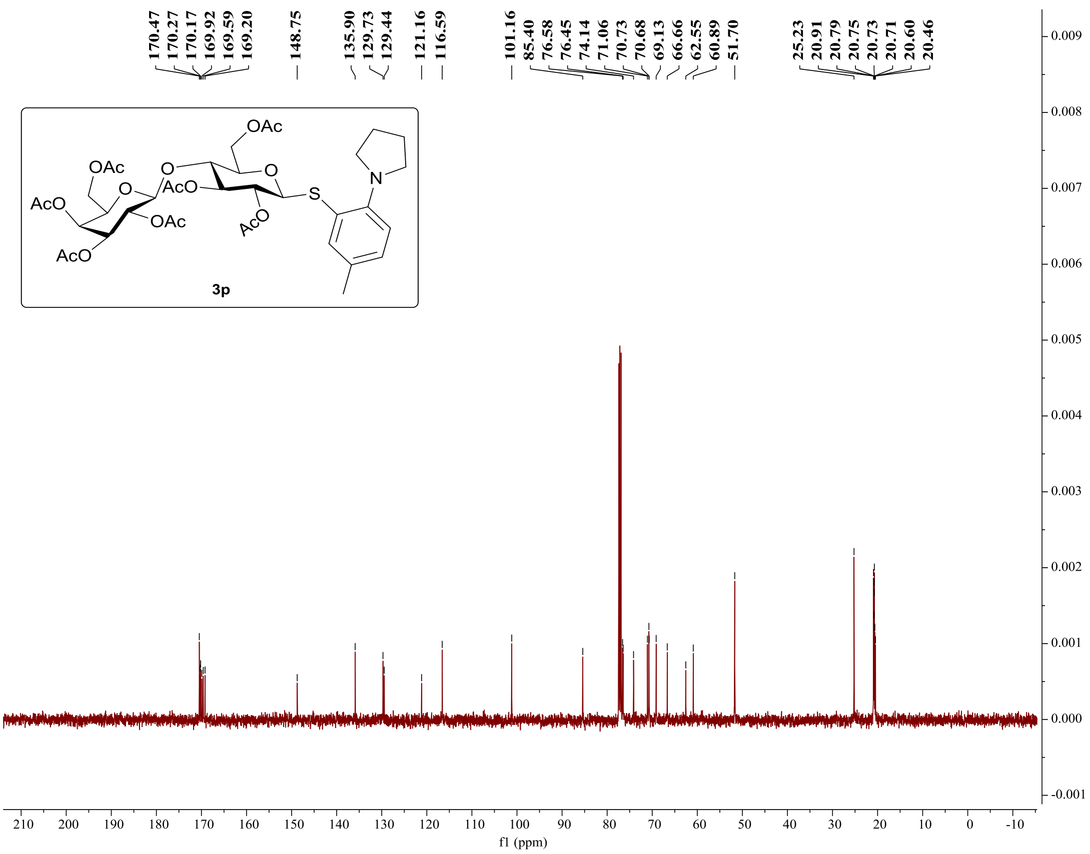
[13]C NMR of 3o (CDCl$_3$, 126 MHz, 25 ℃)



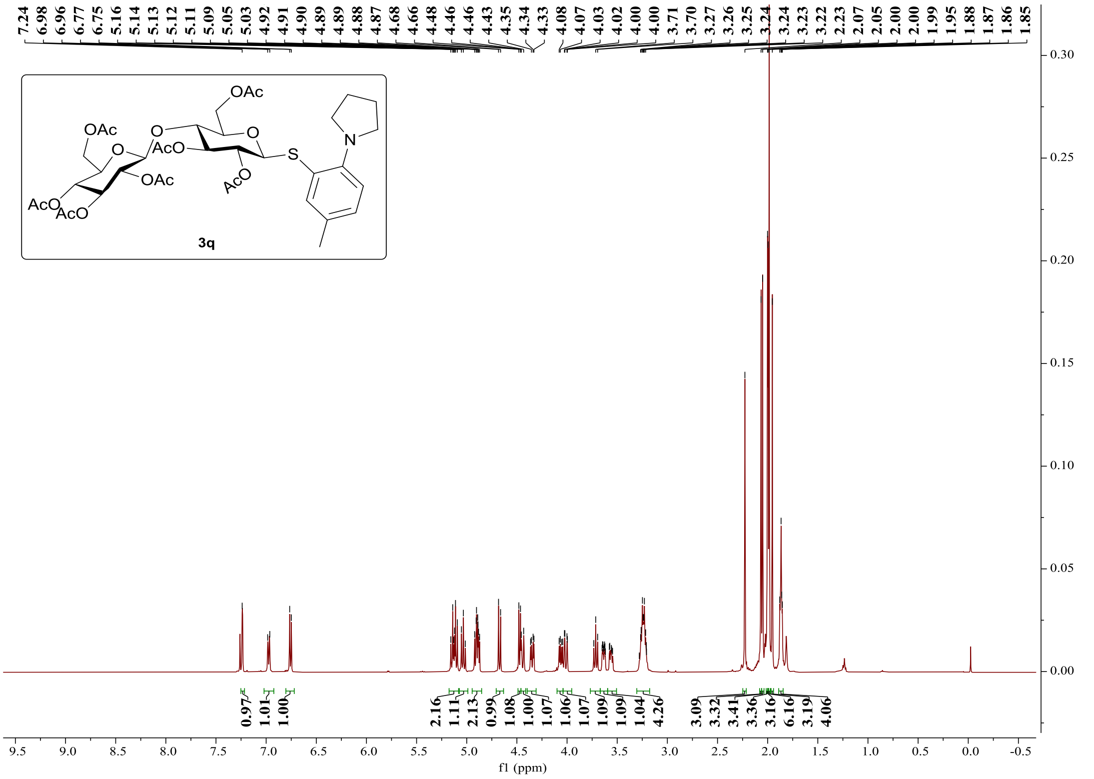
[1]H NMR of 3p ($CDCl_3$, 500 MHz, 25 ℃)



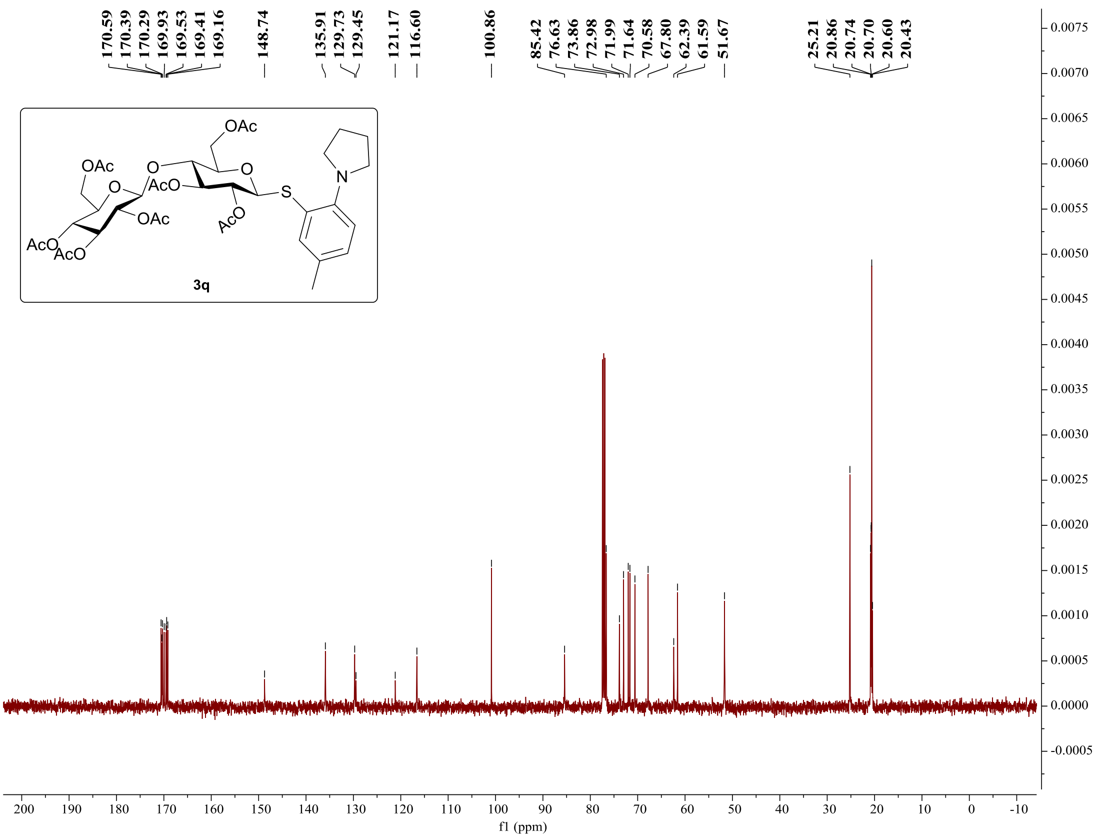
[13]C NMR of 3p ($CDCl_3$, 126 MHz, 25 ℃)



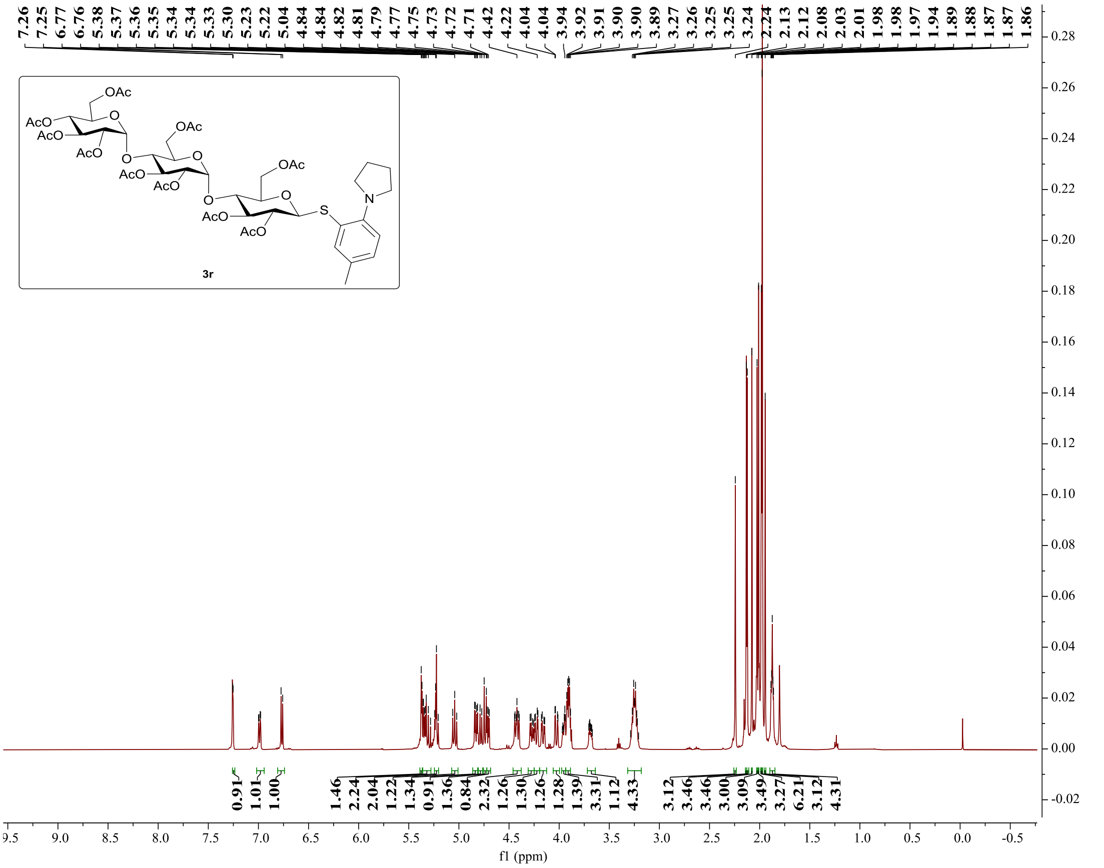
^{1}H NMR of 3q ($CDCl_3$, 500 MHz, 25 ℃)



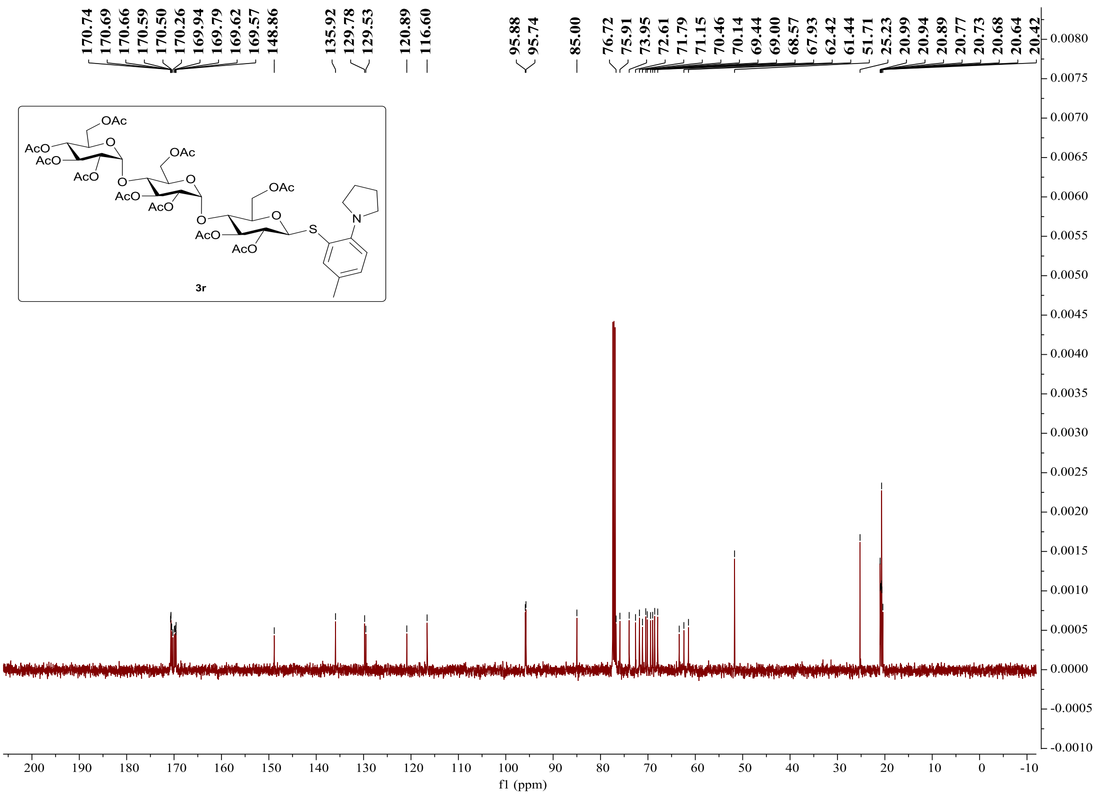
^{13}C NMR of 3q ($CDCl_3$, 126 MHz, 25 ℃)



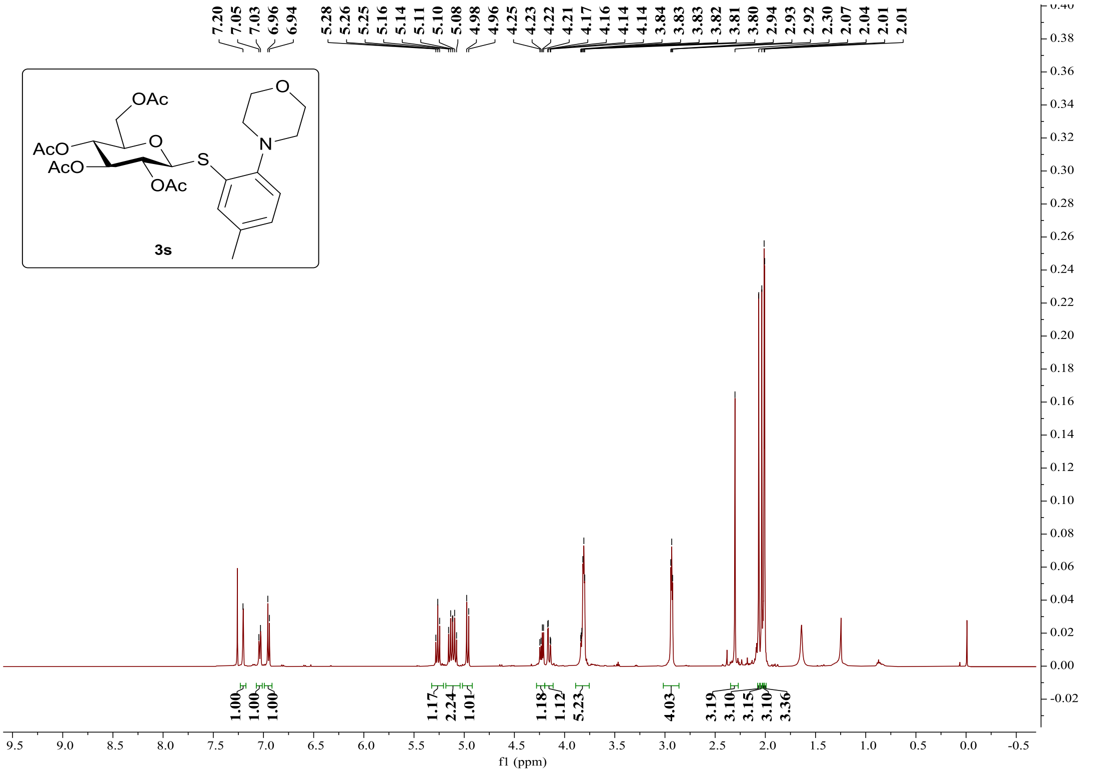
^{1}H NMR of 3r ($CDCl_3$, 500 MHz, 25 ℃)



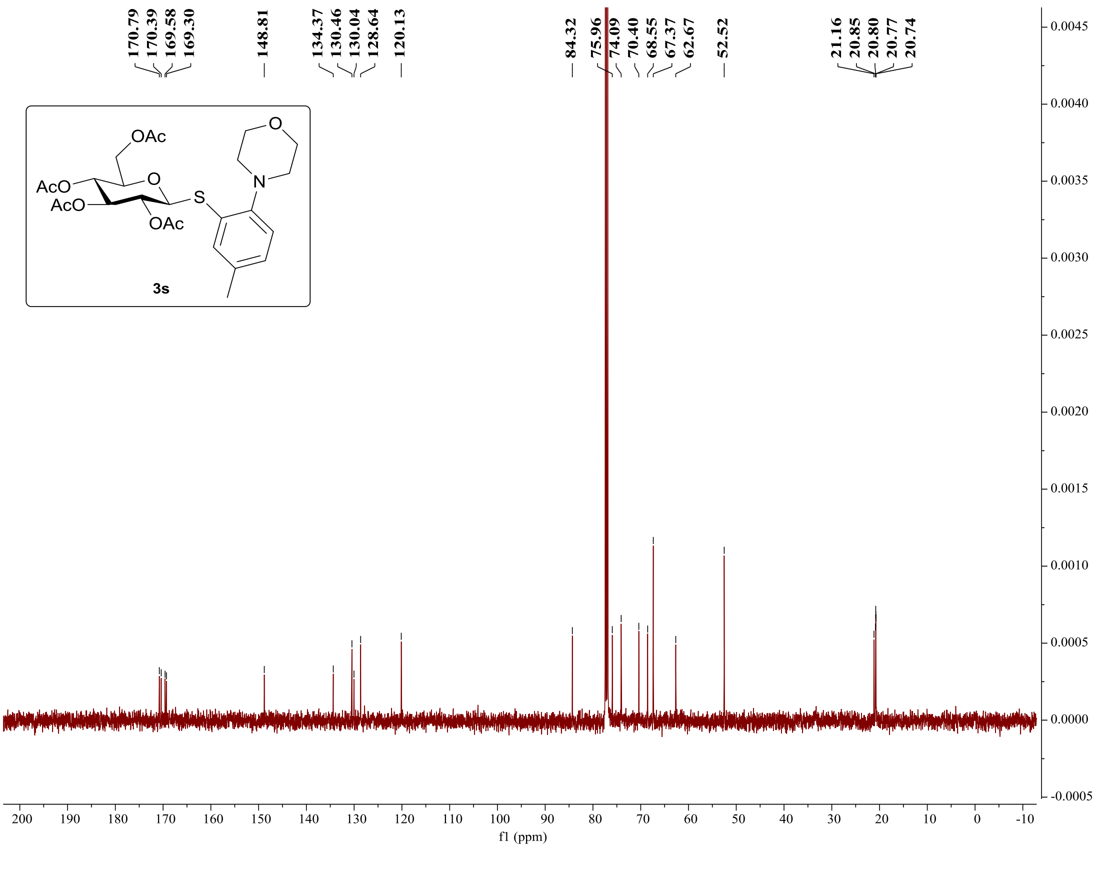
^{13}C NMR of 3r ($CDCl_3$, 126 MHz, 25 ℃)



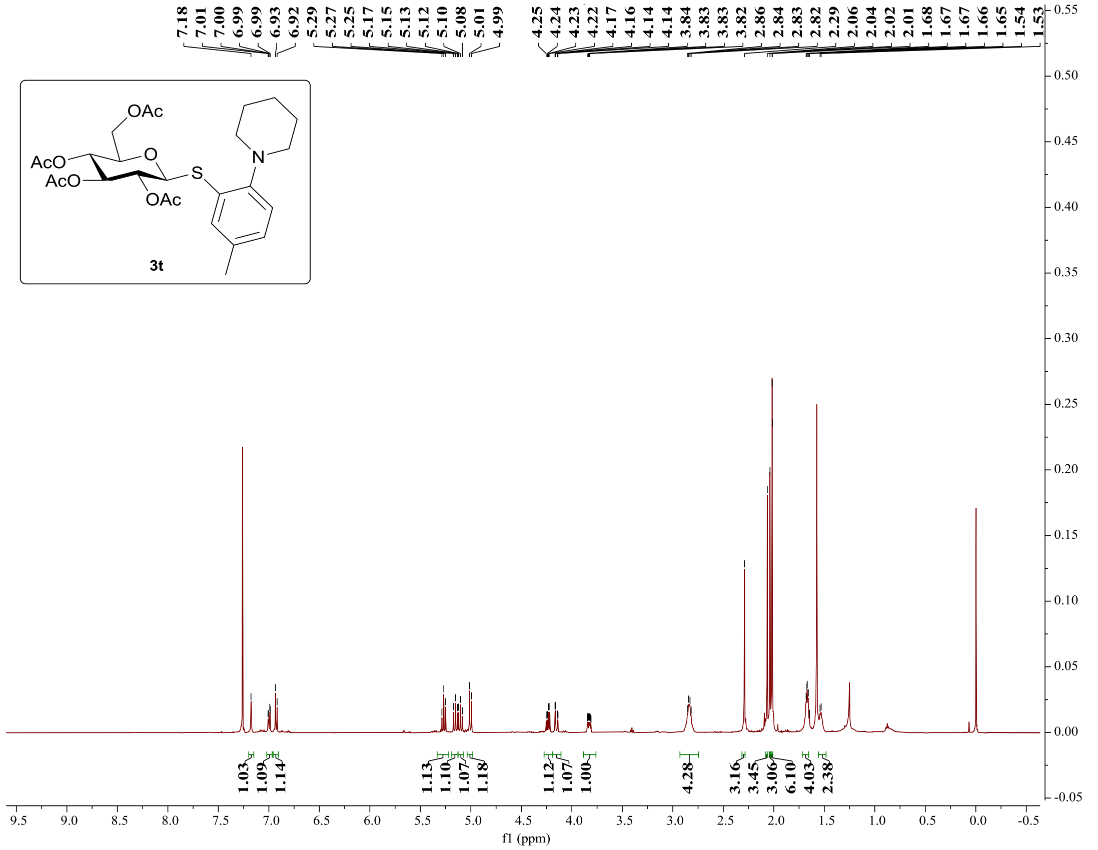
^{1}H NMR of 3s (CDCl$_3$, 500 MHz, 25 ℃)



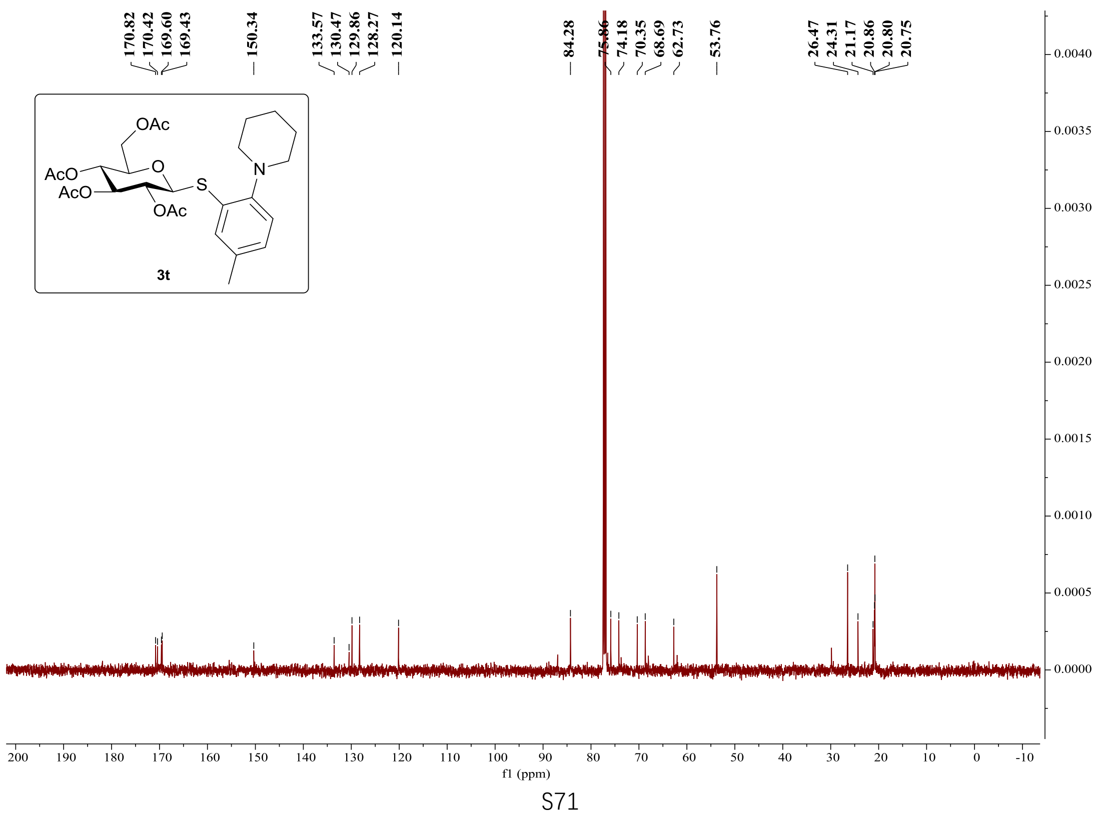
^{13}C NMR of 3s (CDCl$_3$, 126 MHz, 25 ℃)



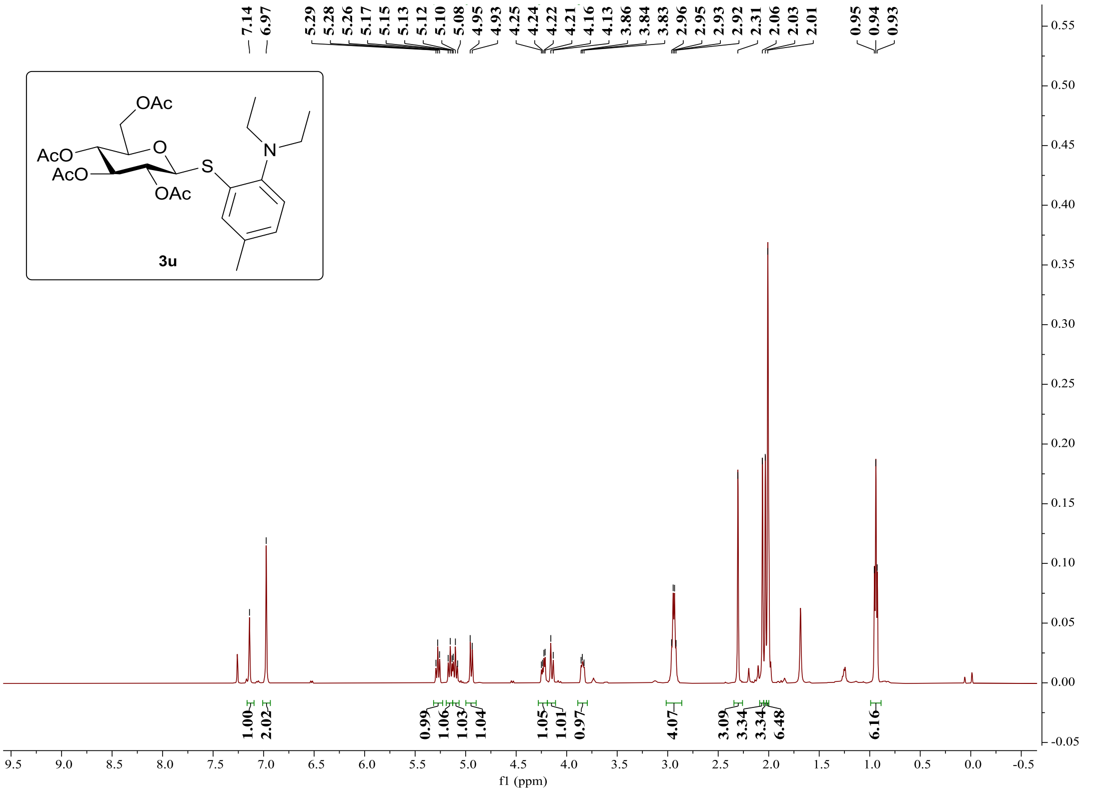
[1]H NMR of 3t (CDCl$_3$, 500 MHz, 25 ℃)



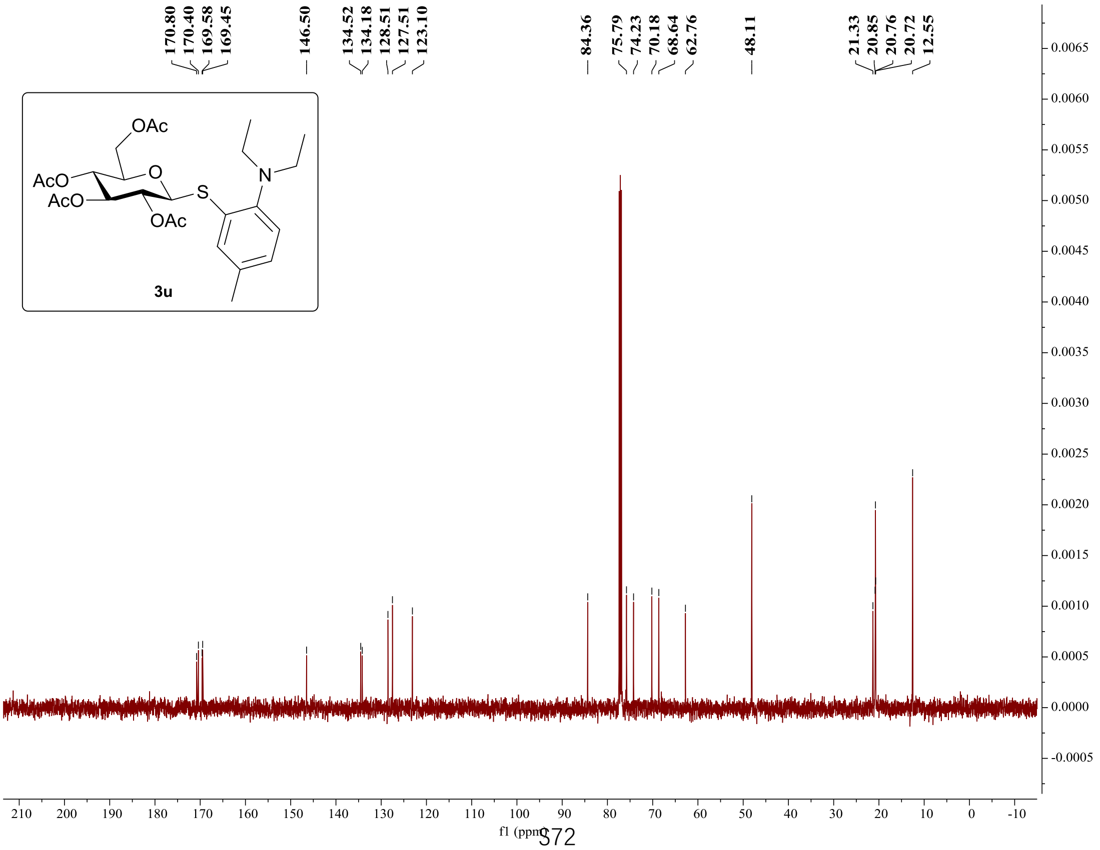
[13]C NMR of 3t (CDCl$_3$, 126 MHz, 25 ℃)



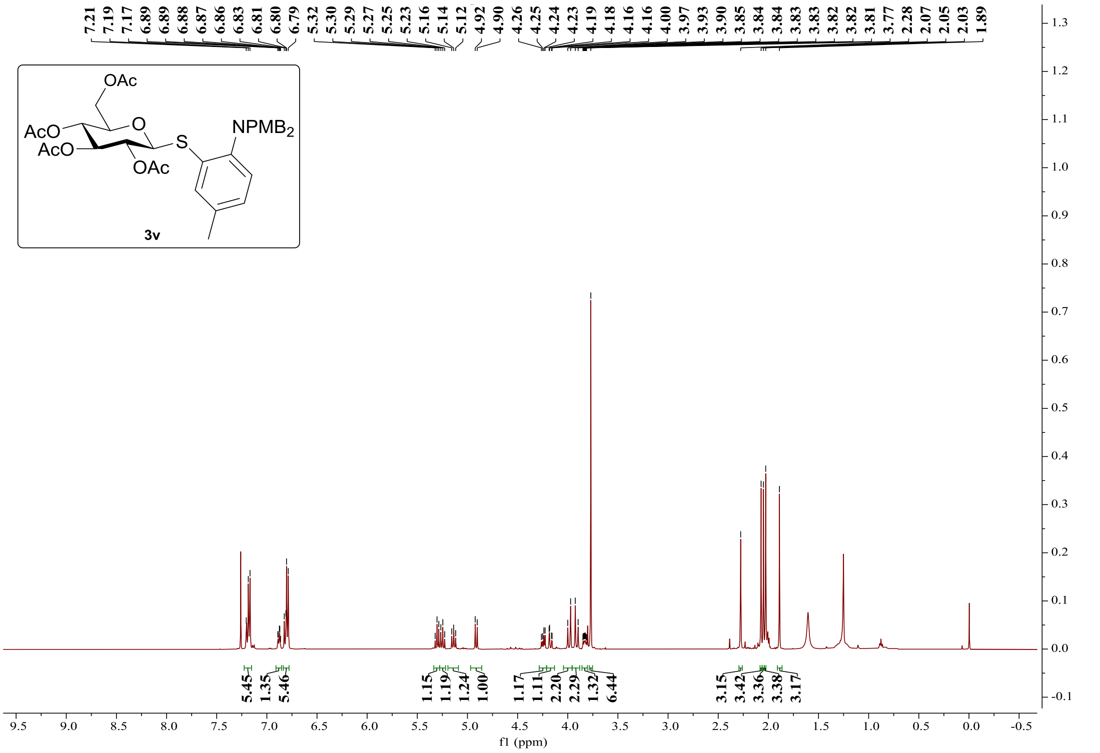
^{1}H NMR of 3u ($CDCl_3$, 500 MHz, 25 ℃)



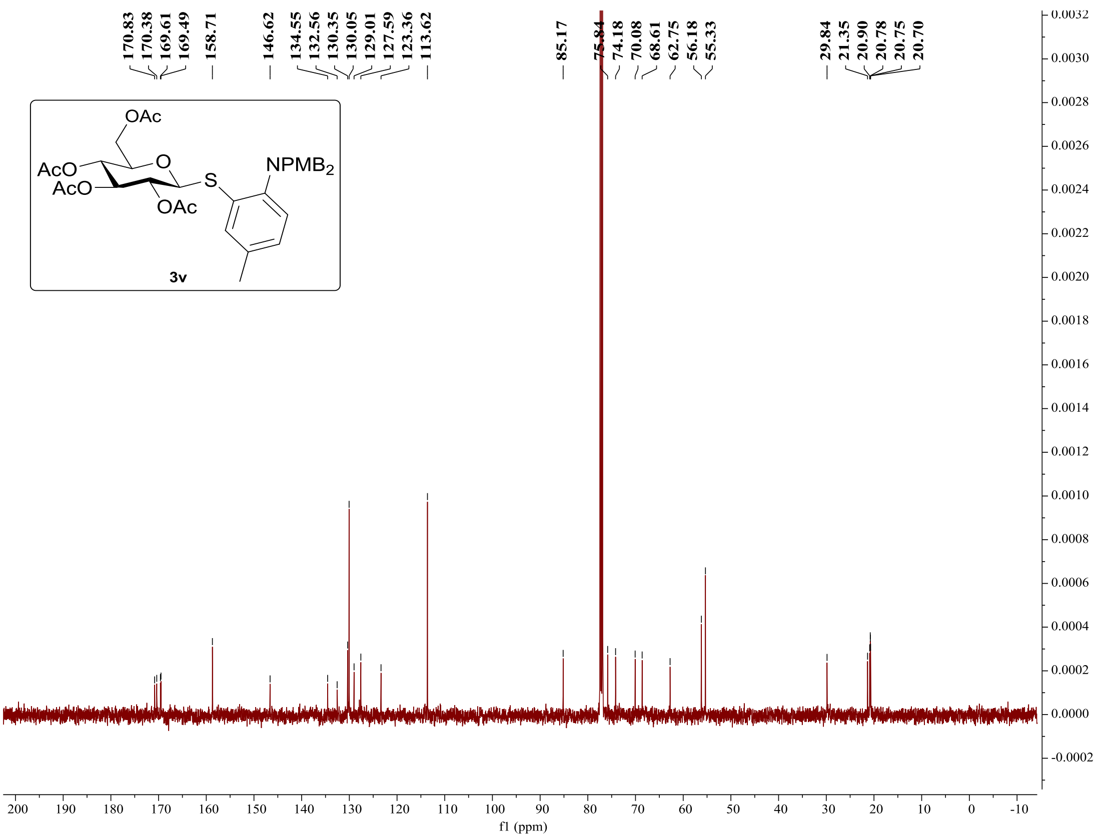
^{13}C NMR of 3u ($CDCl_3$, 126 MHz, 25 ℃)



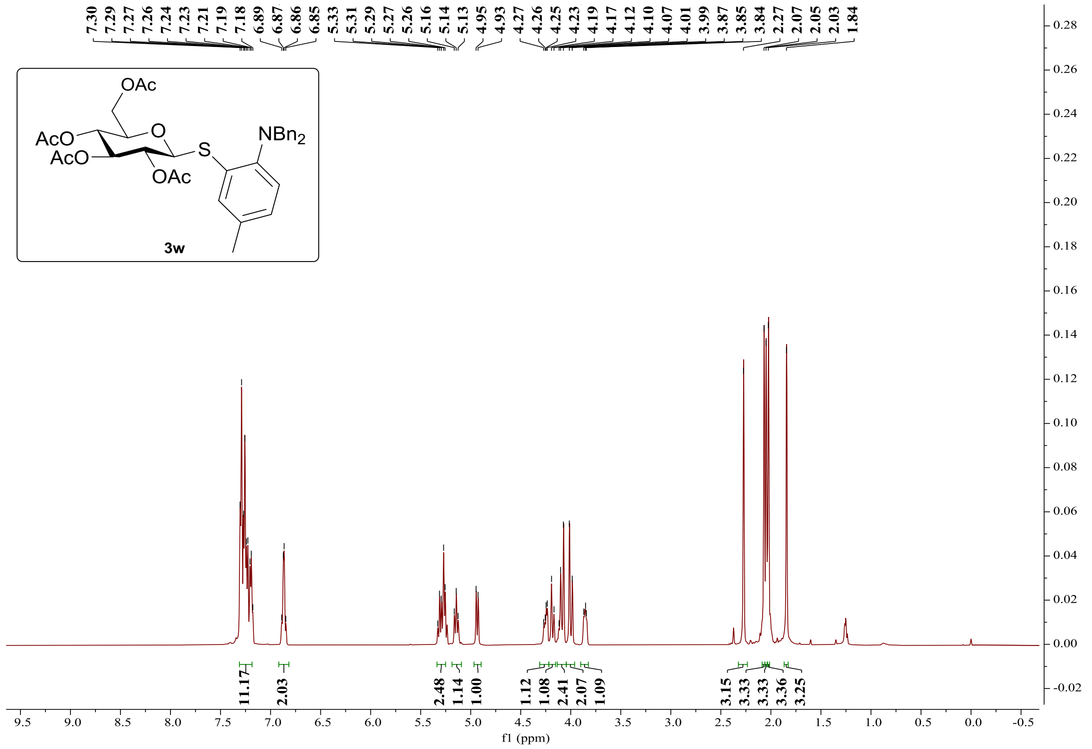
^1H NMR of 3v ($CDCl_3$, 500 MHz, 25 ℃)



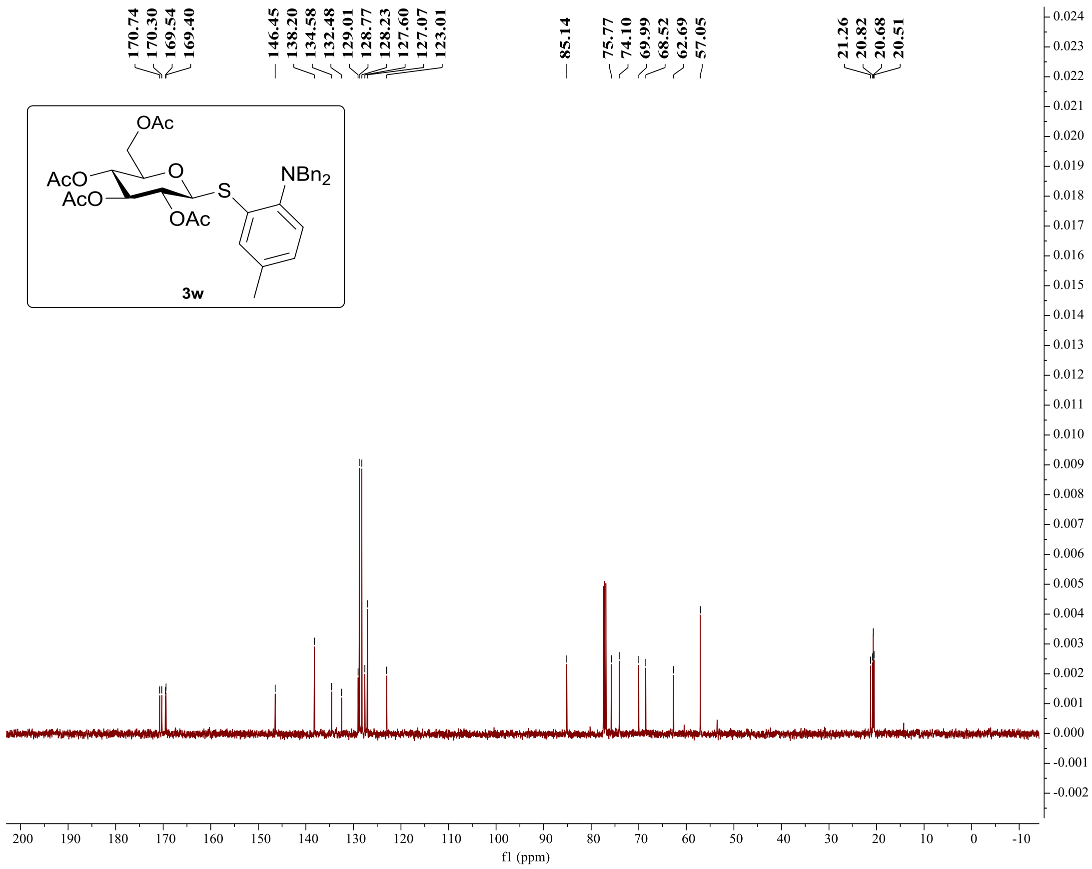
^{13}C NMR of 3v ($CDCl_3$, 126 MHz, 25 ℃)



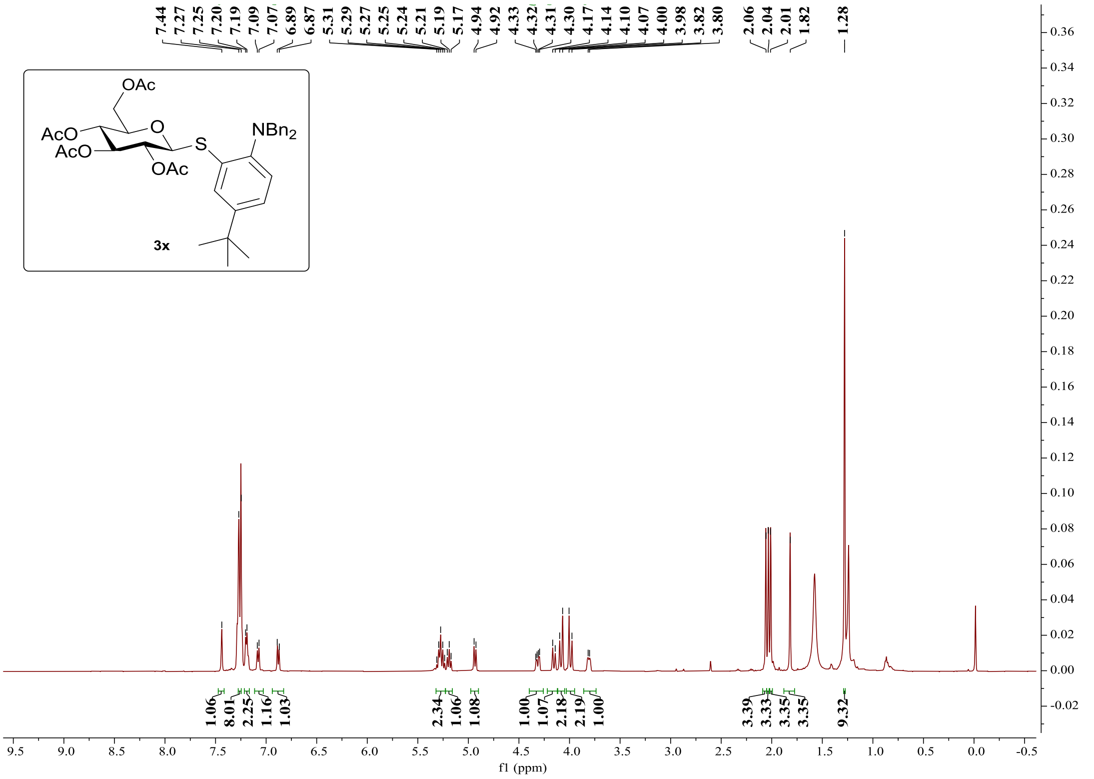
^{1}H NMR of 3w (CDCl$_3$, 500 MHz, 25 ℃)



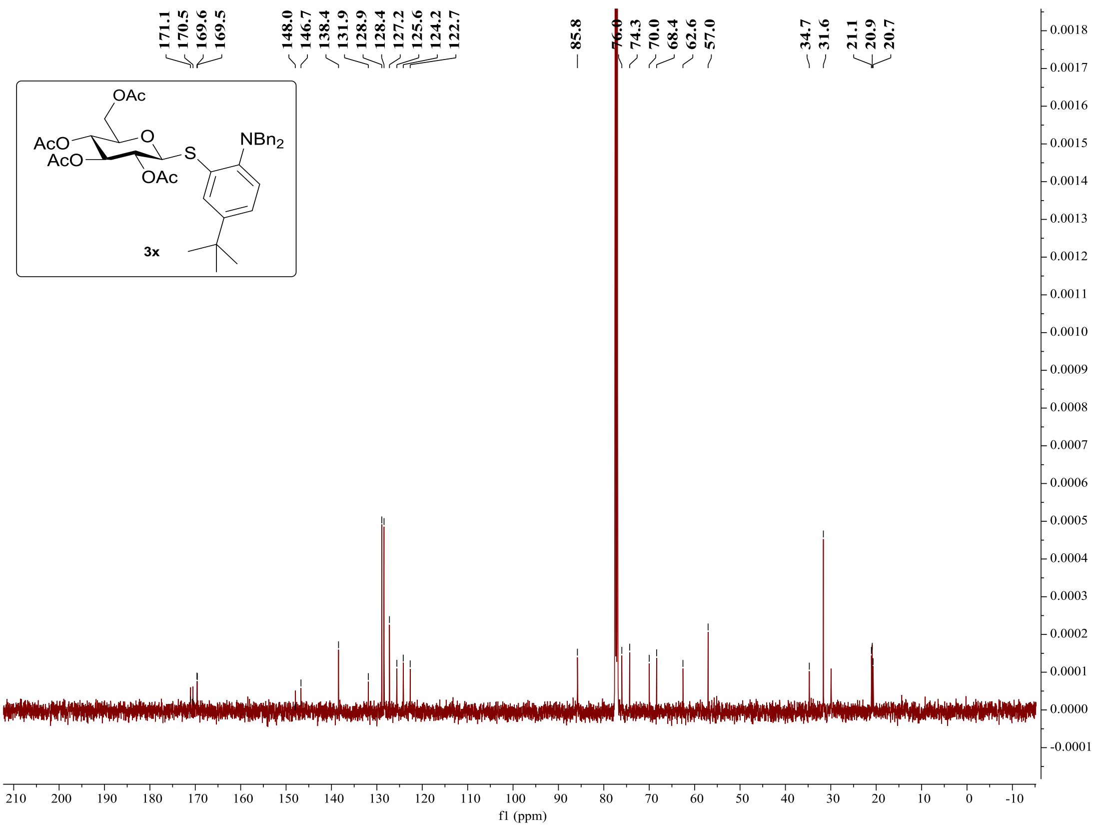
^{13}C NMR of 3w (CDCl$_3$, 126 MHz, 25 ℃)



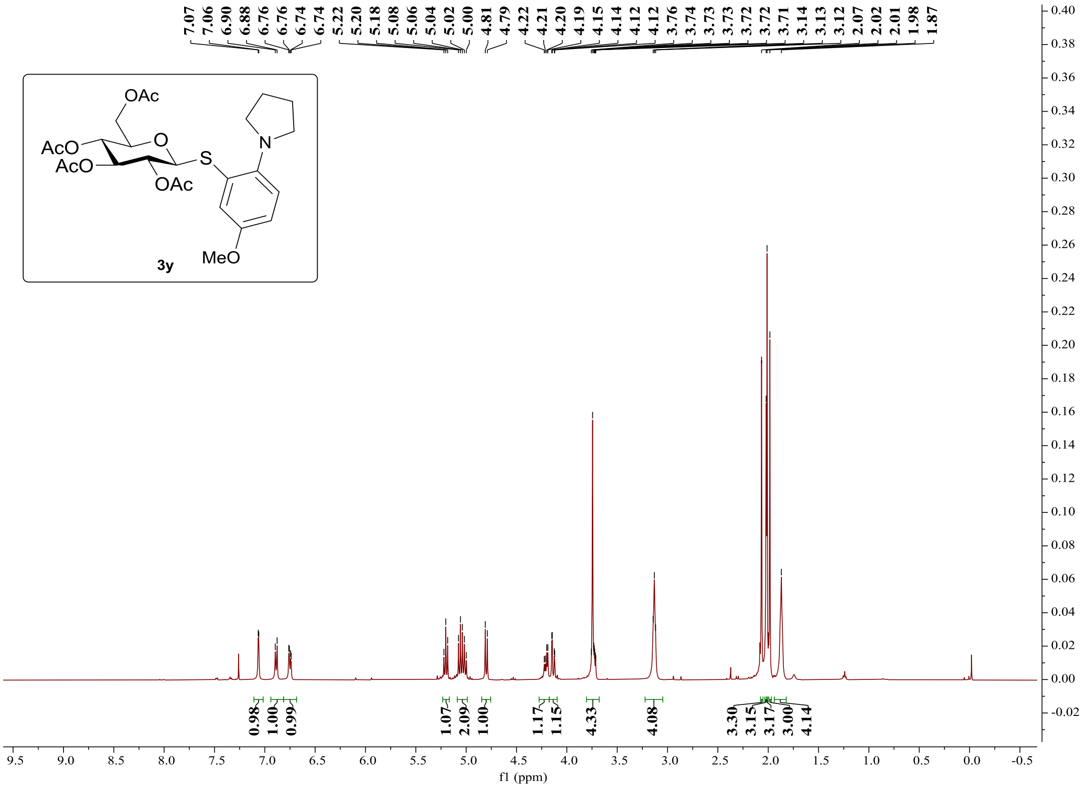
[1]H NMR of 3x (CDCl$_3$, 500 MHz, 25 ℃)



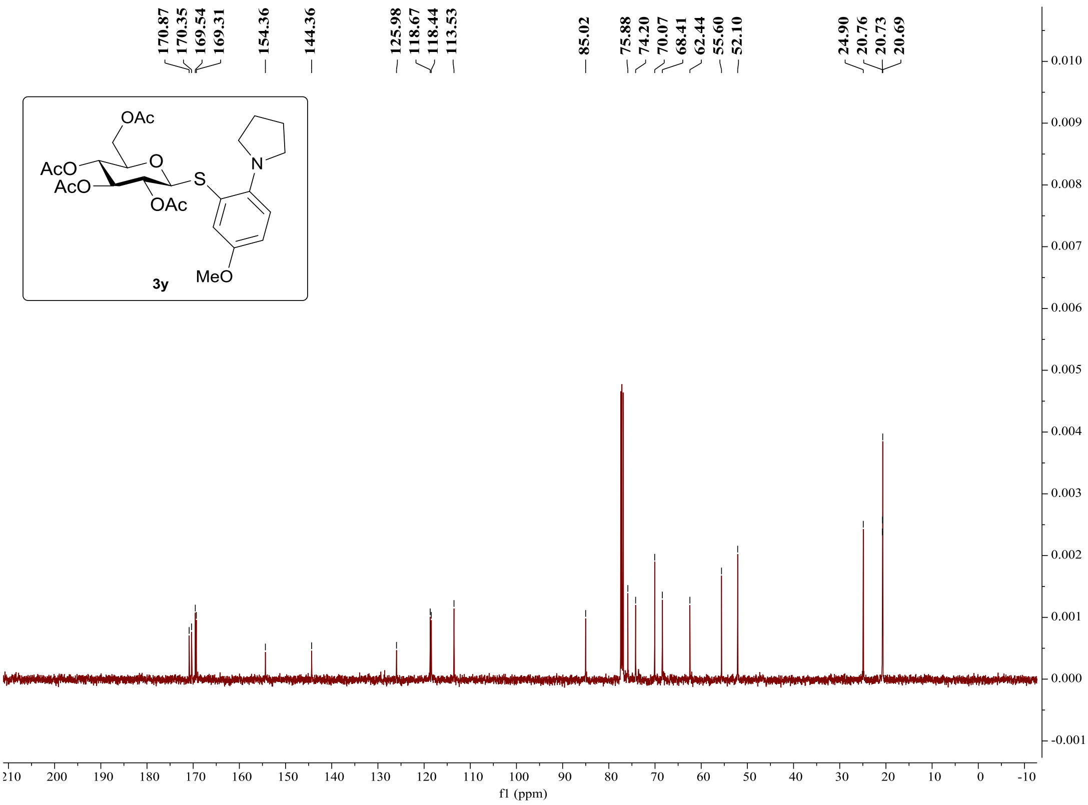
[13]C NMR of 3x (CDCl$_3$, 126 MHz, 25 ℃)



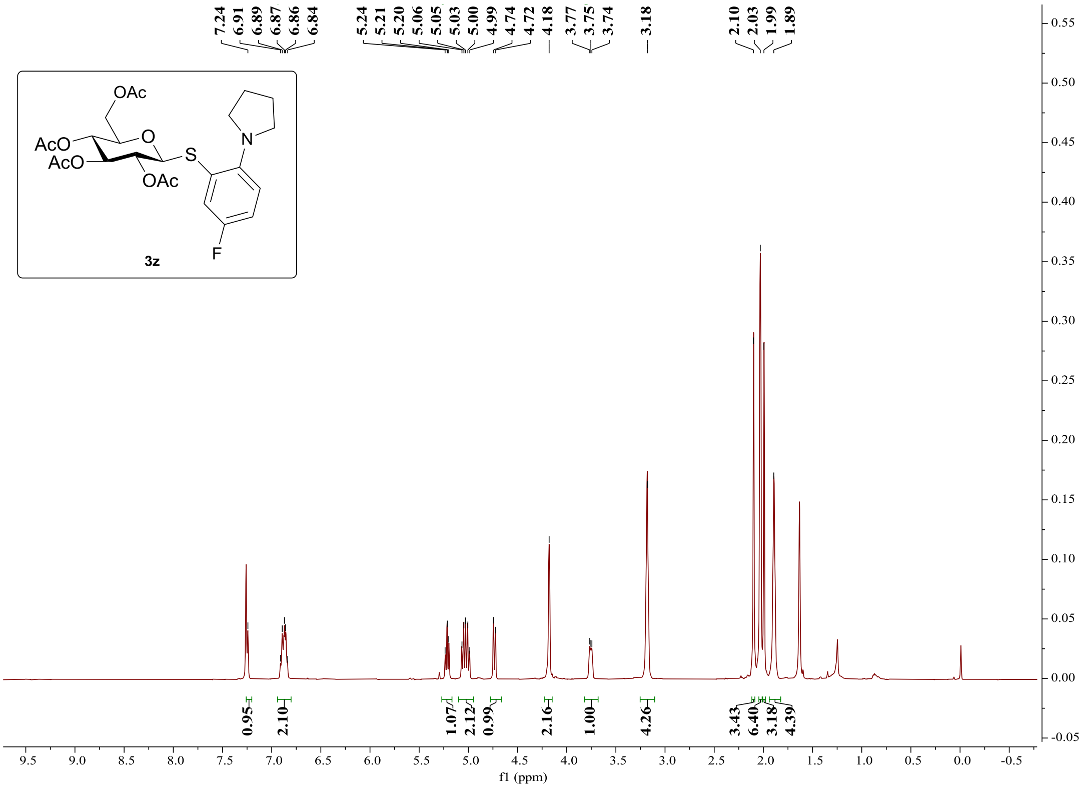
^{1}H NMR of 3y ($CDCl_3$, 500 MHz, 25 ℃)



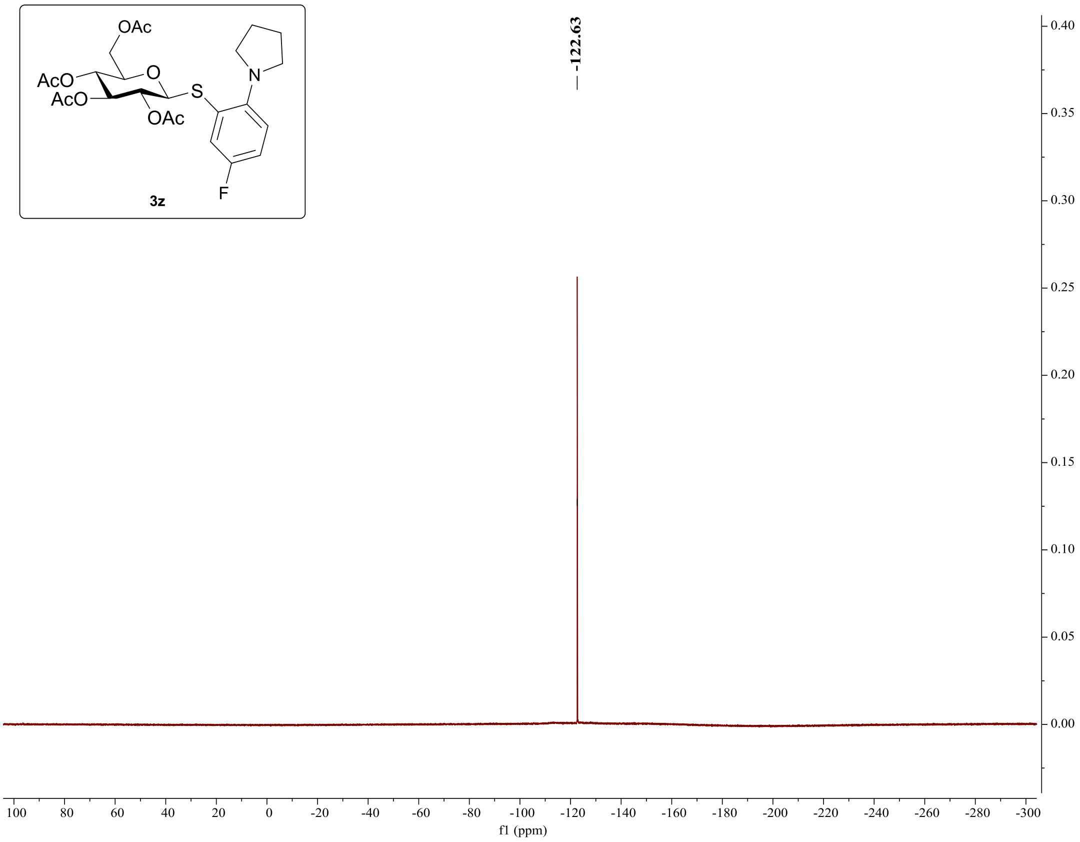
^{13}C NMR of 3y ($CDCl_3$, 126 MHz, 25 ℃)



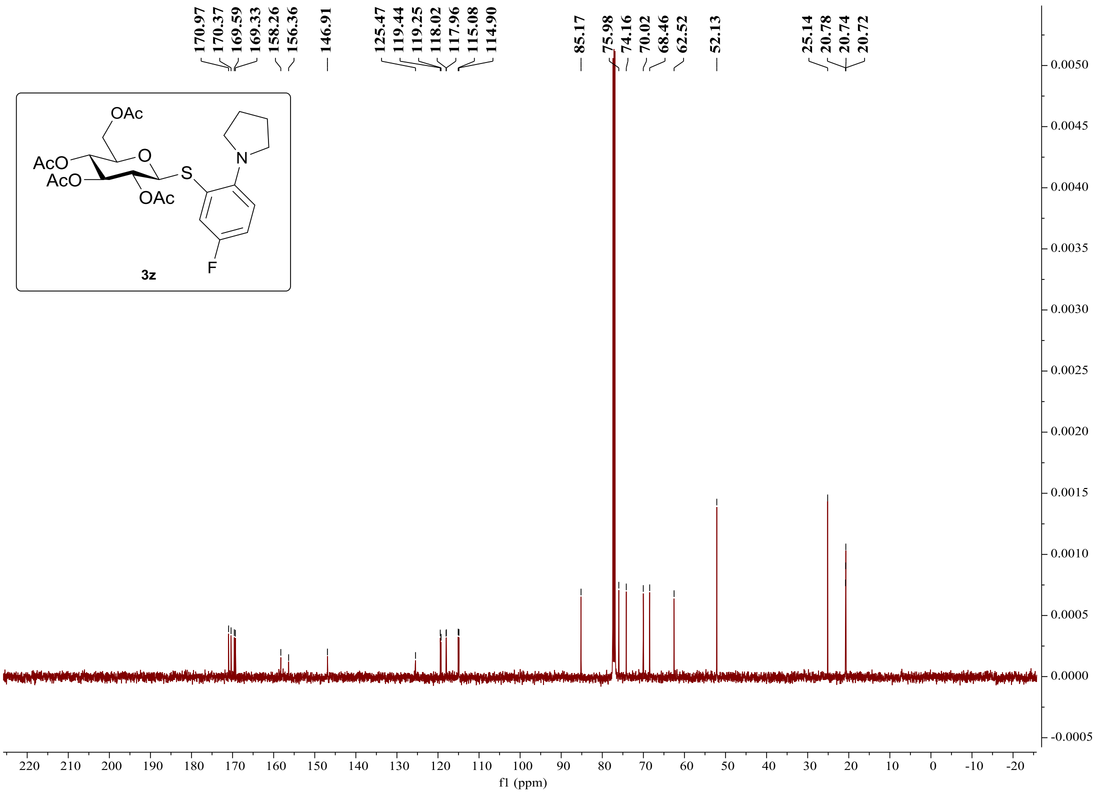
^{1}H NMR of 3z ($CDCl_3$, 500 MHz, 25 ℃)



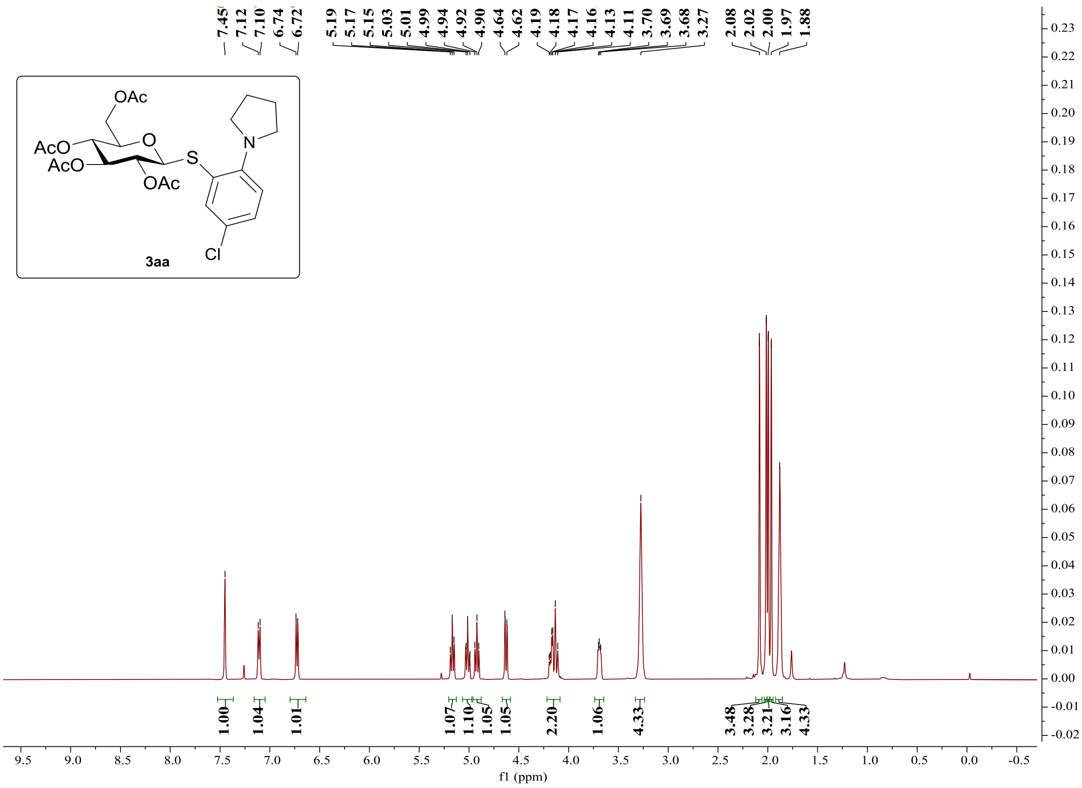
^{19}F NMR of 3z ($CDCl_3$, 471 MHz, 25 ℃)



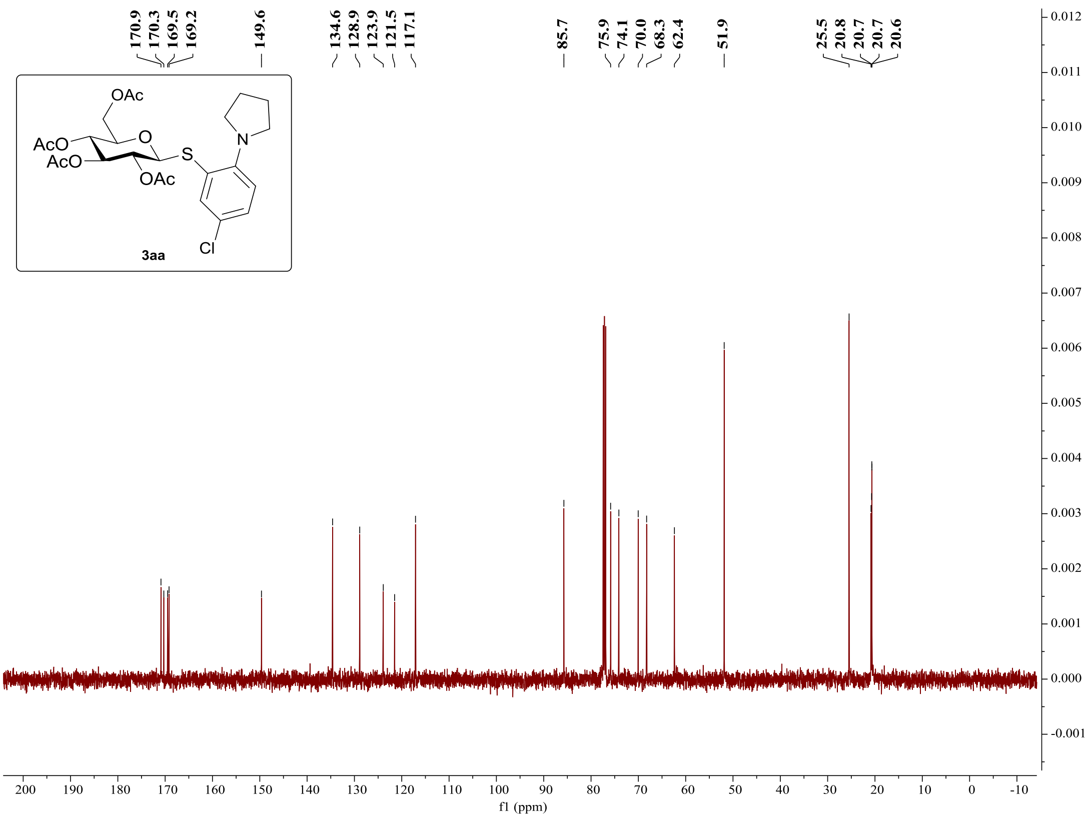
^{13}C NMR of 3z ($CDCl_3$, 126 MHz, 25 ℃)



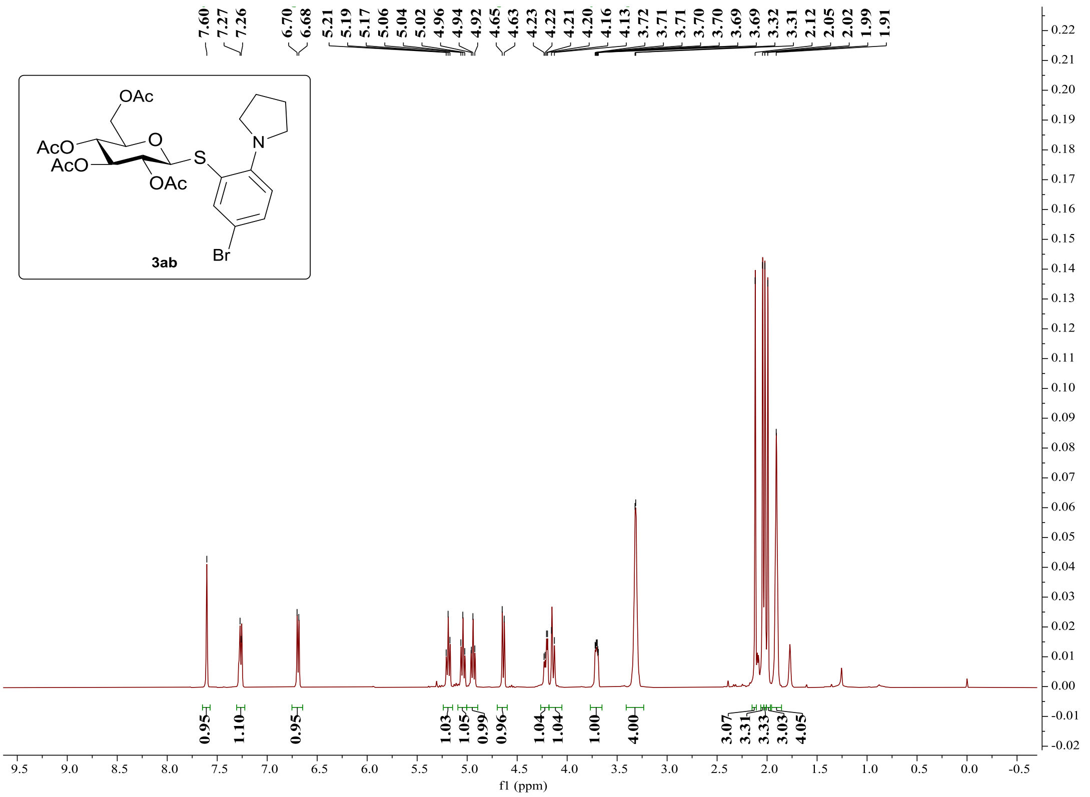
^{1}H NMR of 3aa ($CDCl_3$, 500 MHz, 25 ℃)



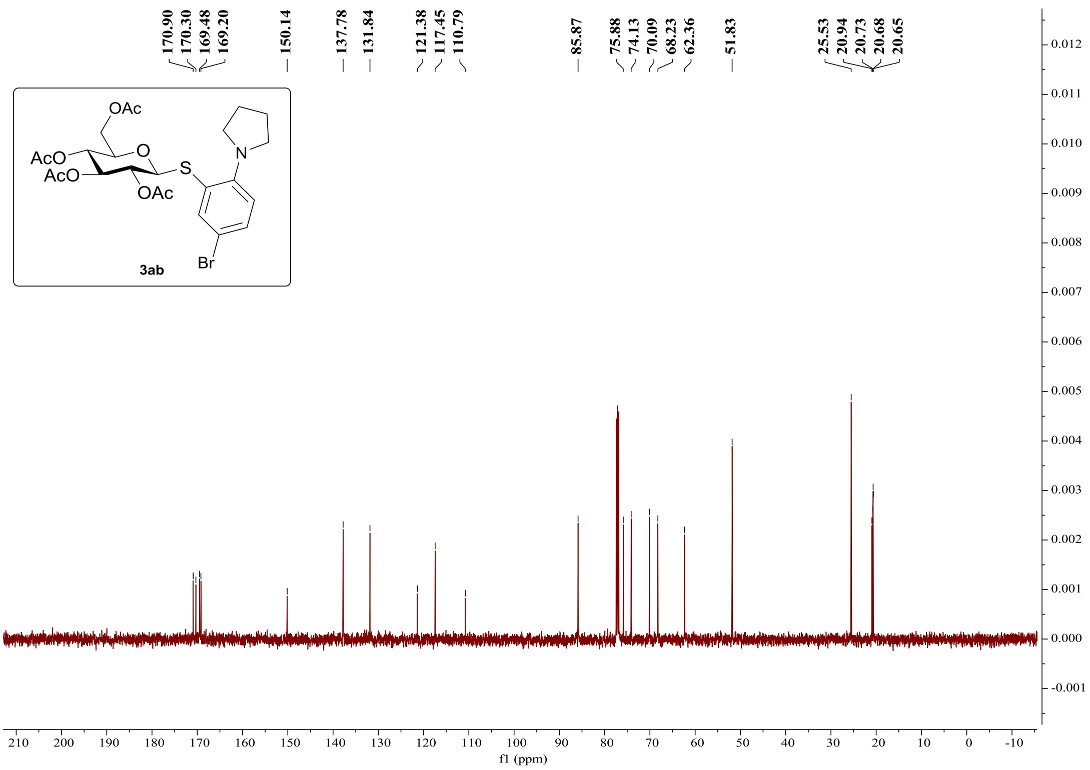
[13]C NMR of 3aa (CDCl3, 126 MHz, 25 ℃)



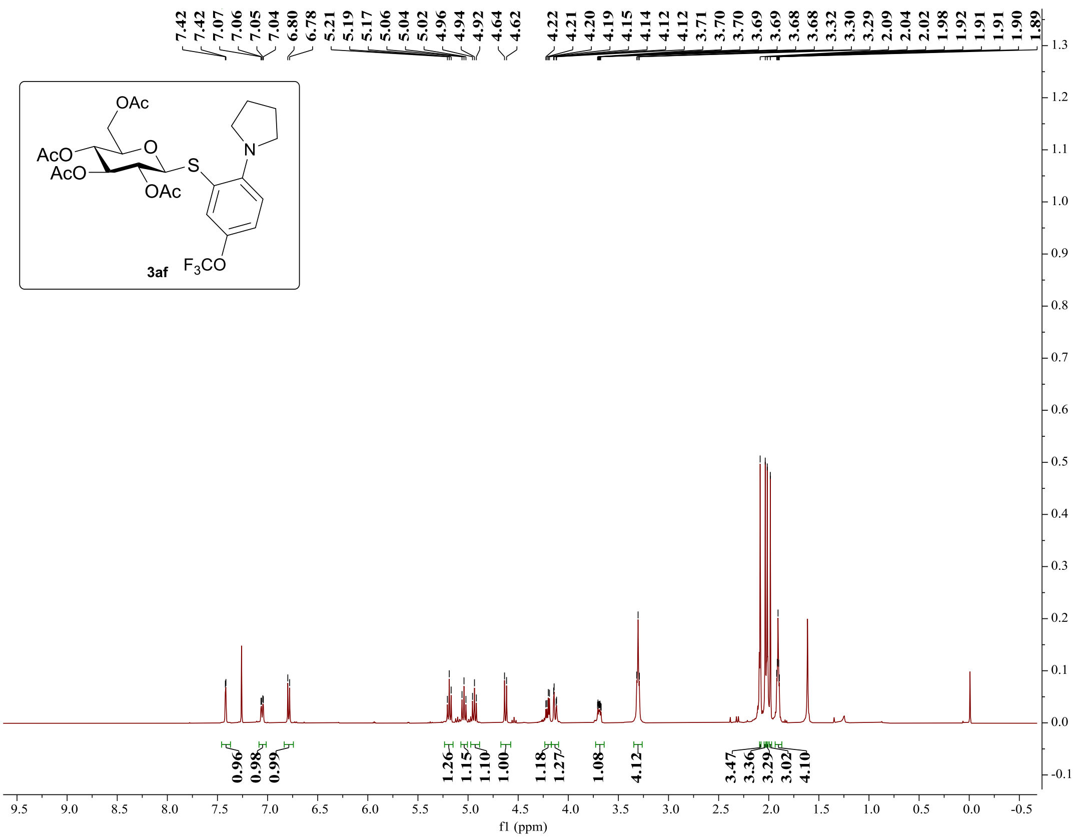
[1]H NMR of 3ab (CDCl3, 500 MHz, 25 ℃)



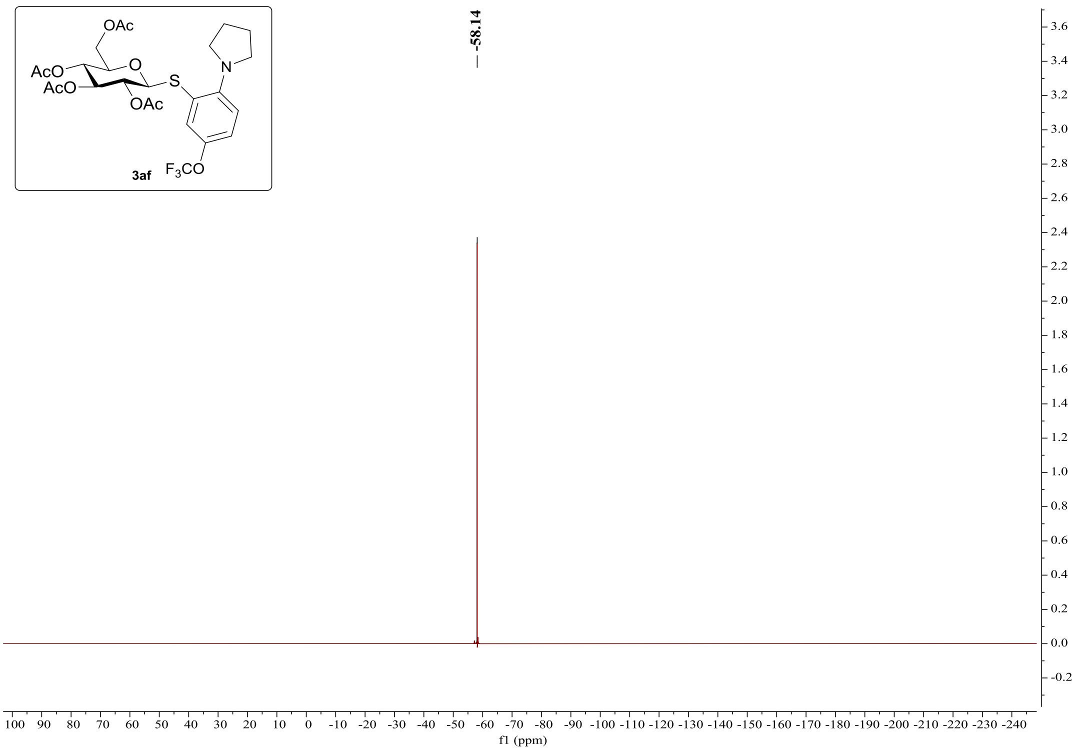
^{13}C NMR of 3ab (CDCl$_3$, 126 MHz, 25 ℃)



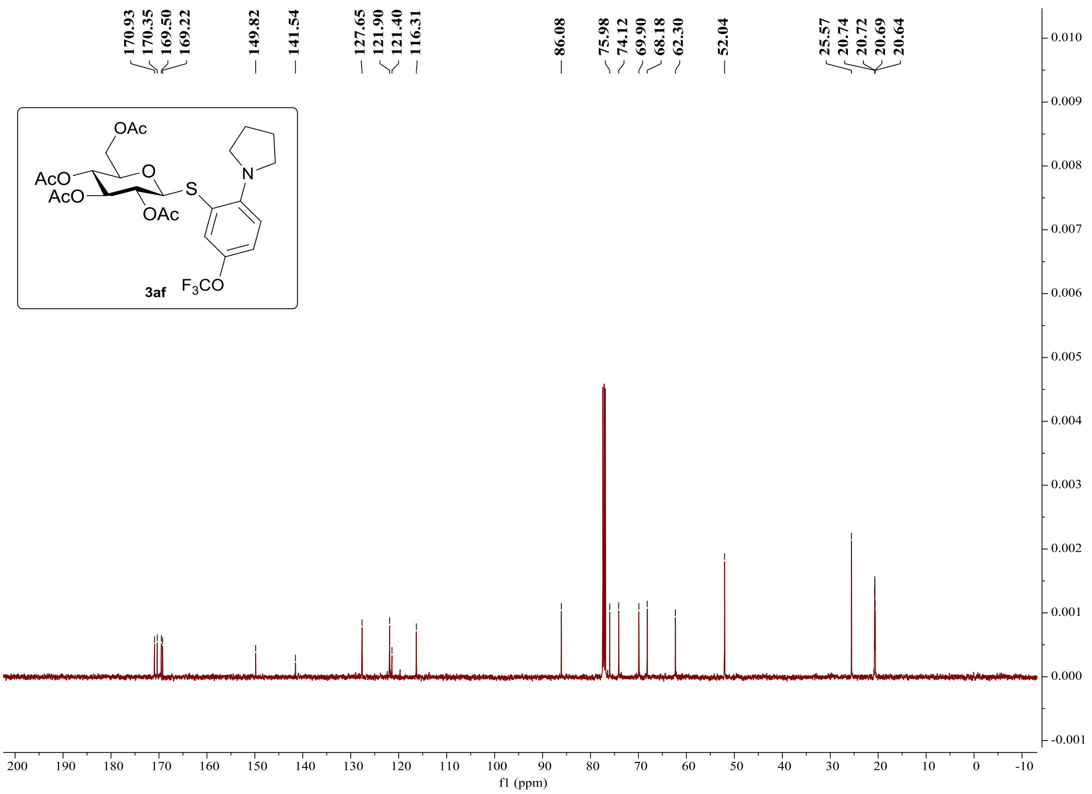
^{1}H NMR of 3af (CDCl$_3$, 500 MHz, 25 ℃)



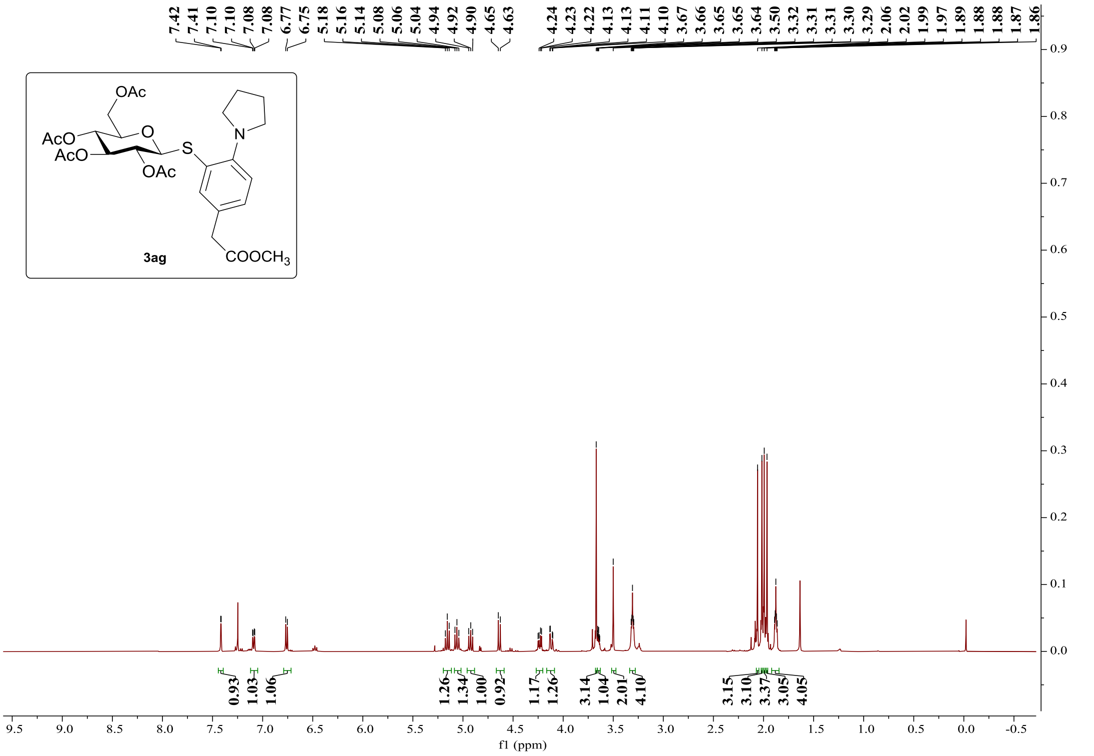
[19]F NMR of 3af (CDCl$_3$, 471 MHz, 25 ℃)



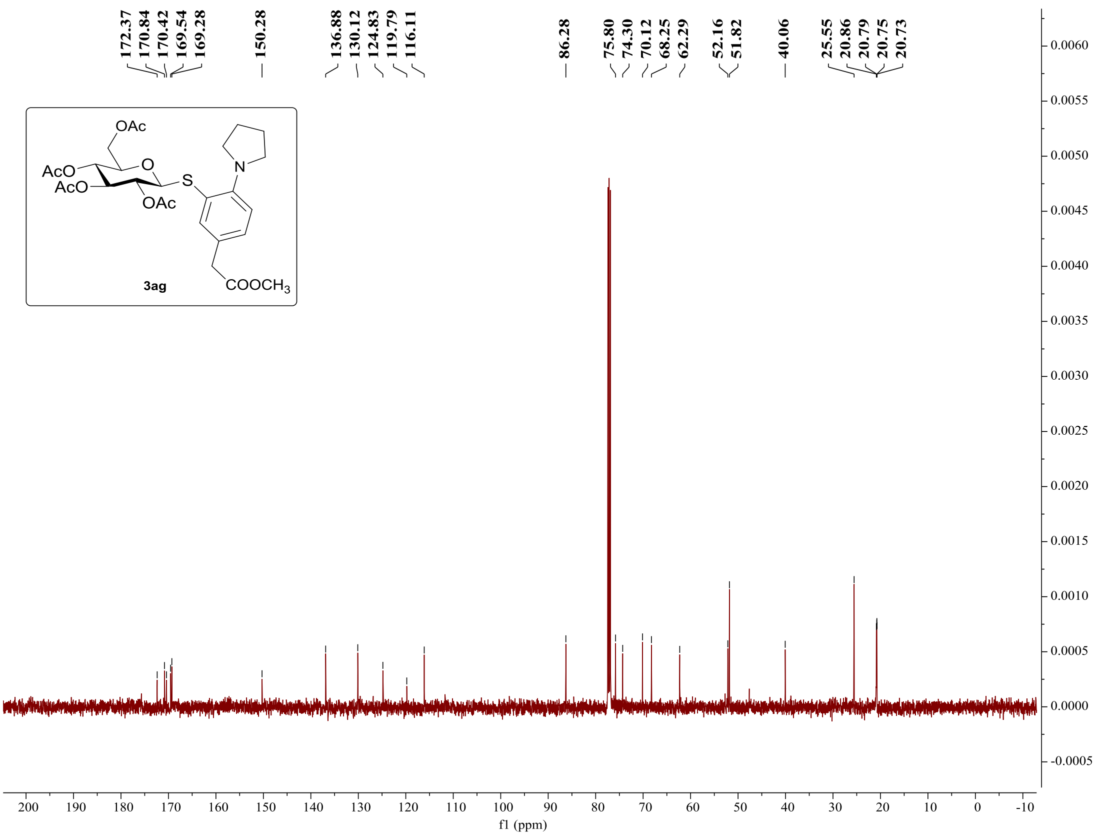
[13]C NMR of 3af (CDCl$_3$, 126 MHz, 25 ℃)



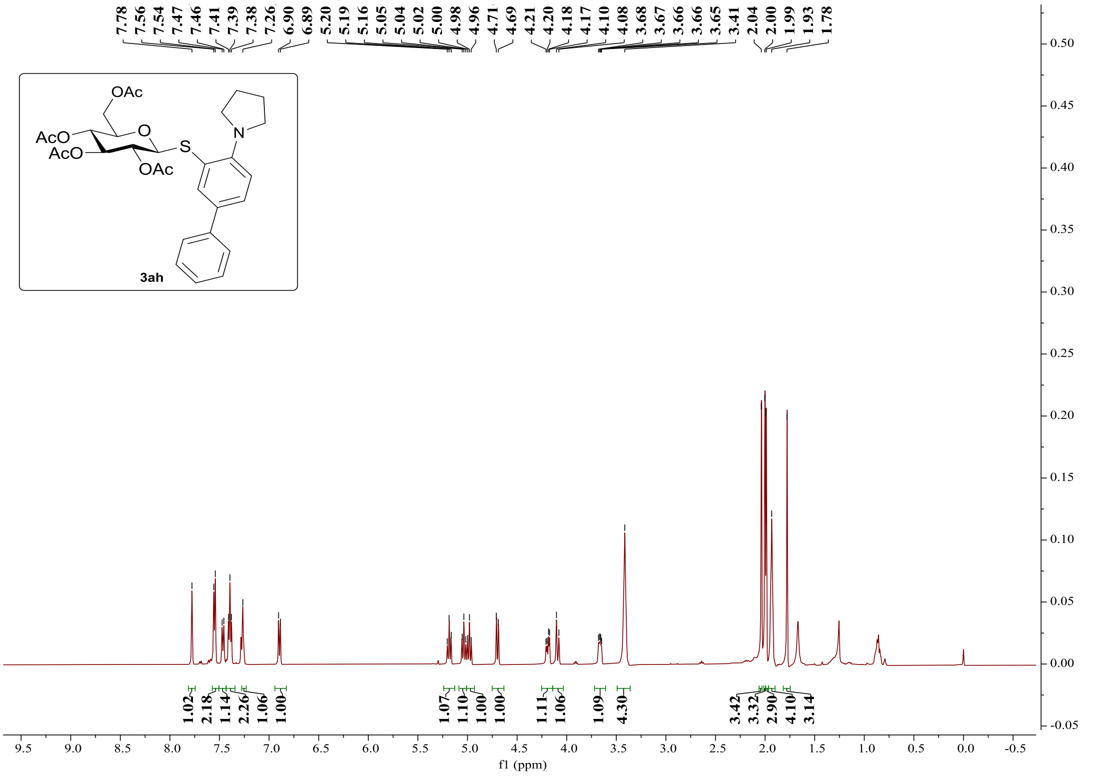
^{1}H NMR of 3ag (CDCl$_3$, 500 MHz, 25 ℃)



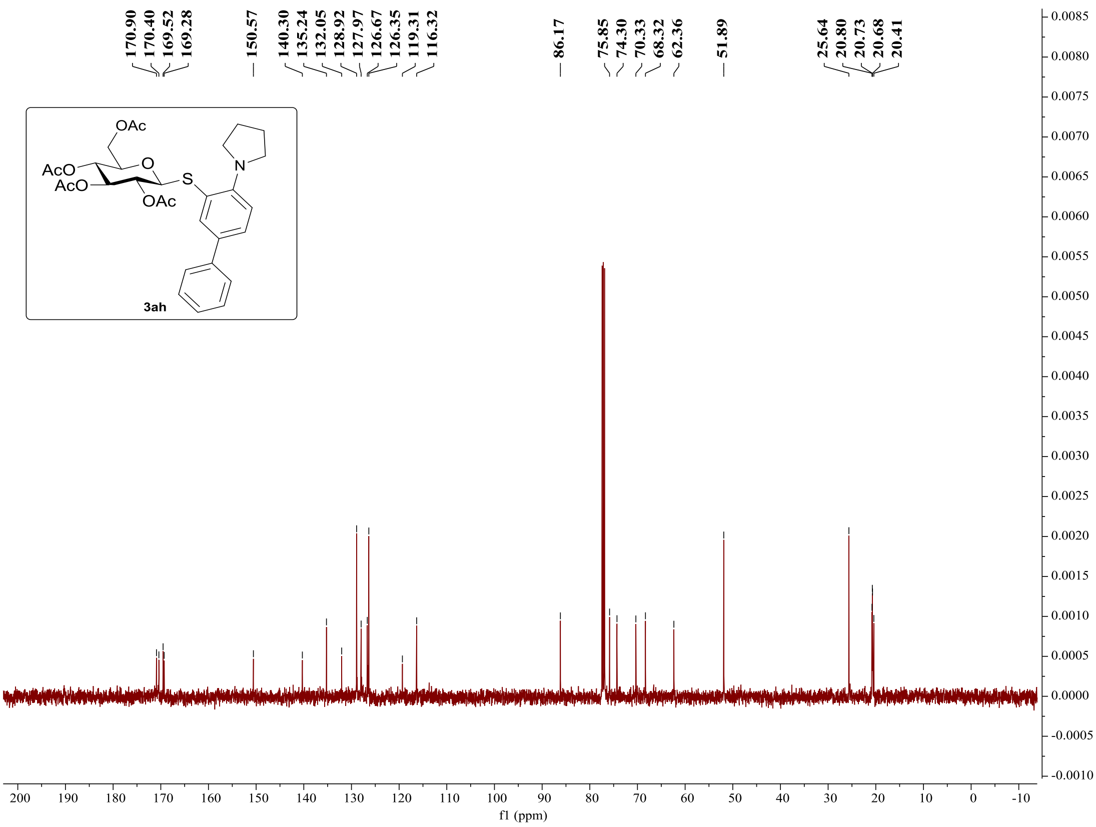
^{13}C NMR of 3ag (CDCl$_3$, 126 MHz, 25 ℃)



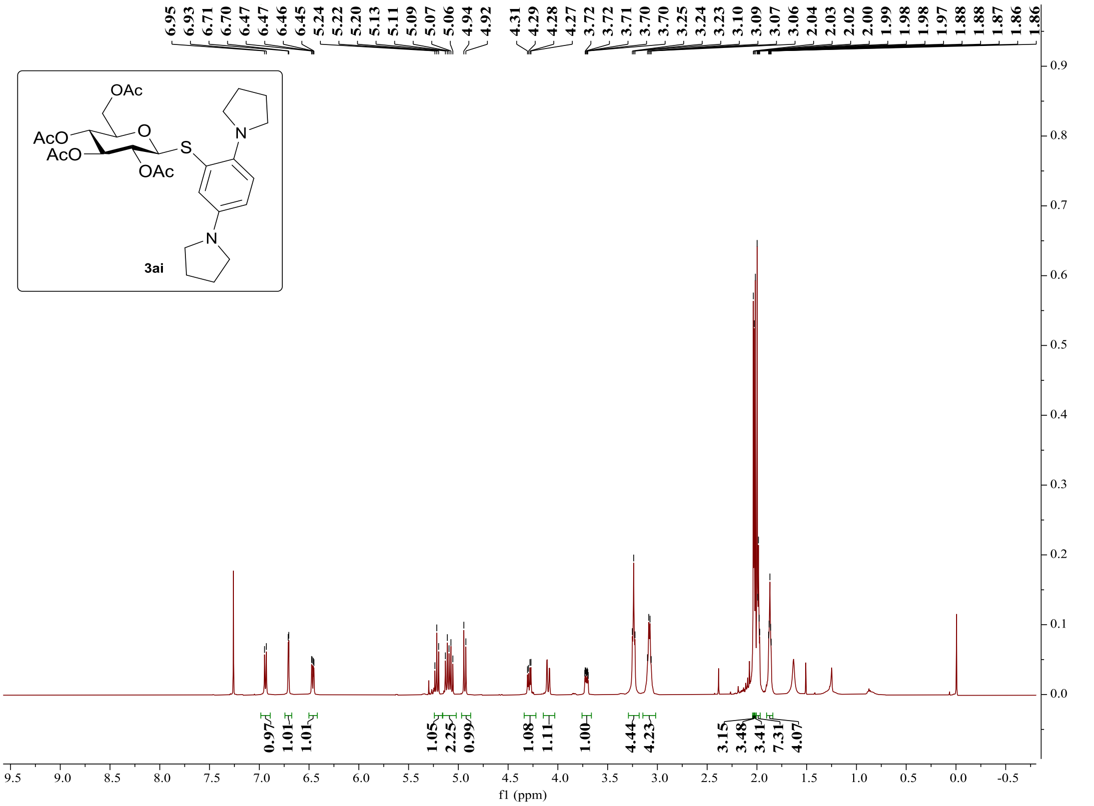
^{1}H NMR of 3ah (CDCl$_3$, 500 MHz, 25 ℃)



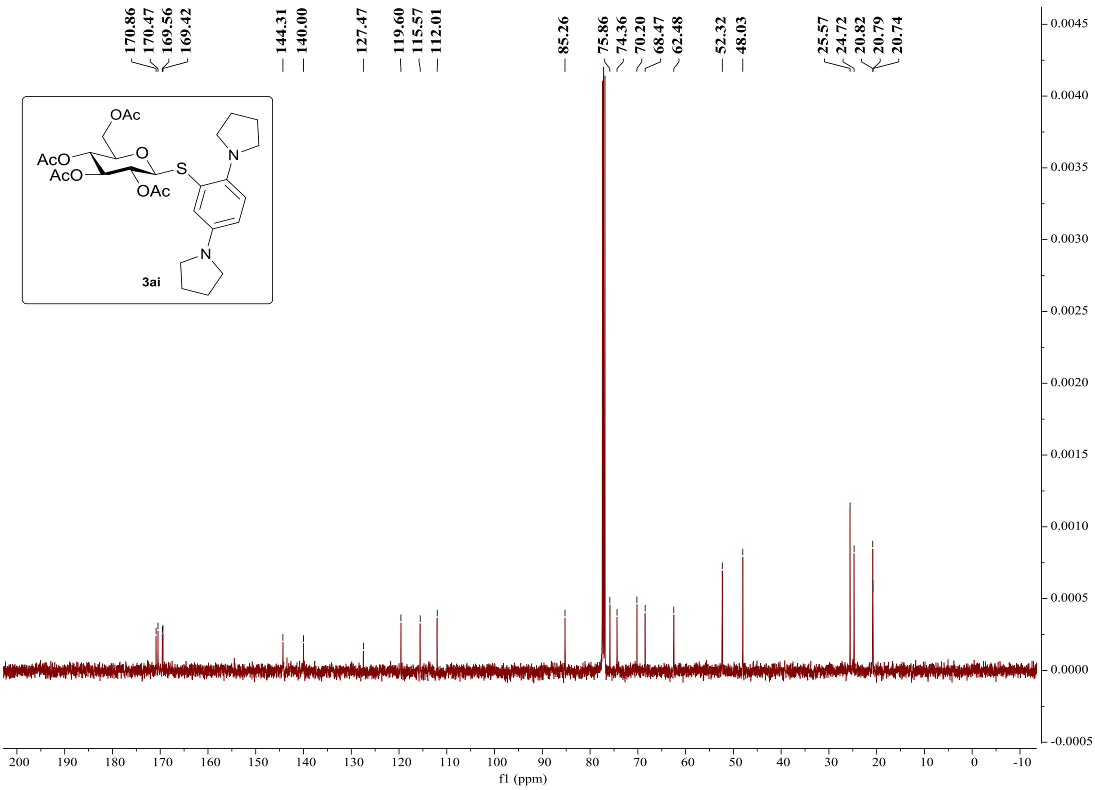
^{13}C NMR of 3ah (CDCl$_3$, 126 MHz, 25 ℃)



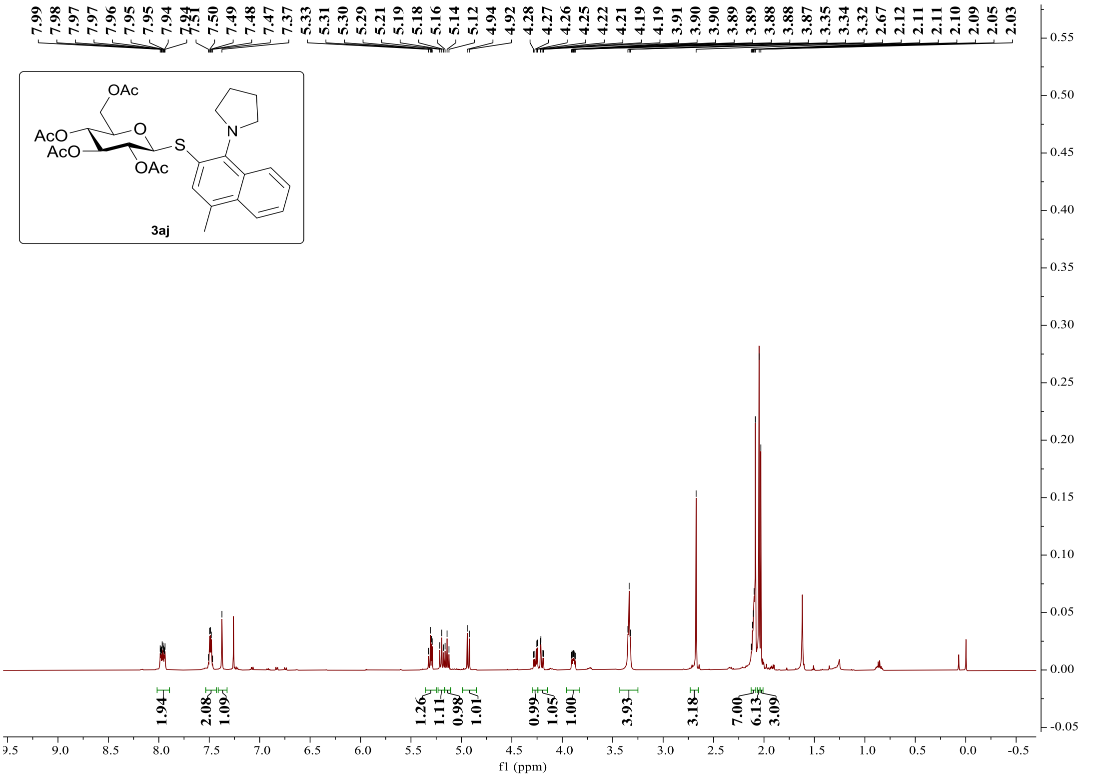
^{1}H NMR of 3ai ($CDCl_3$, 500 MHz, 25 ℃)



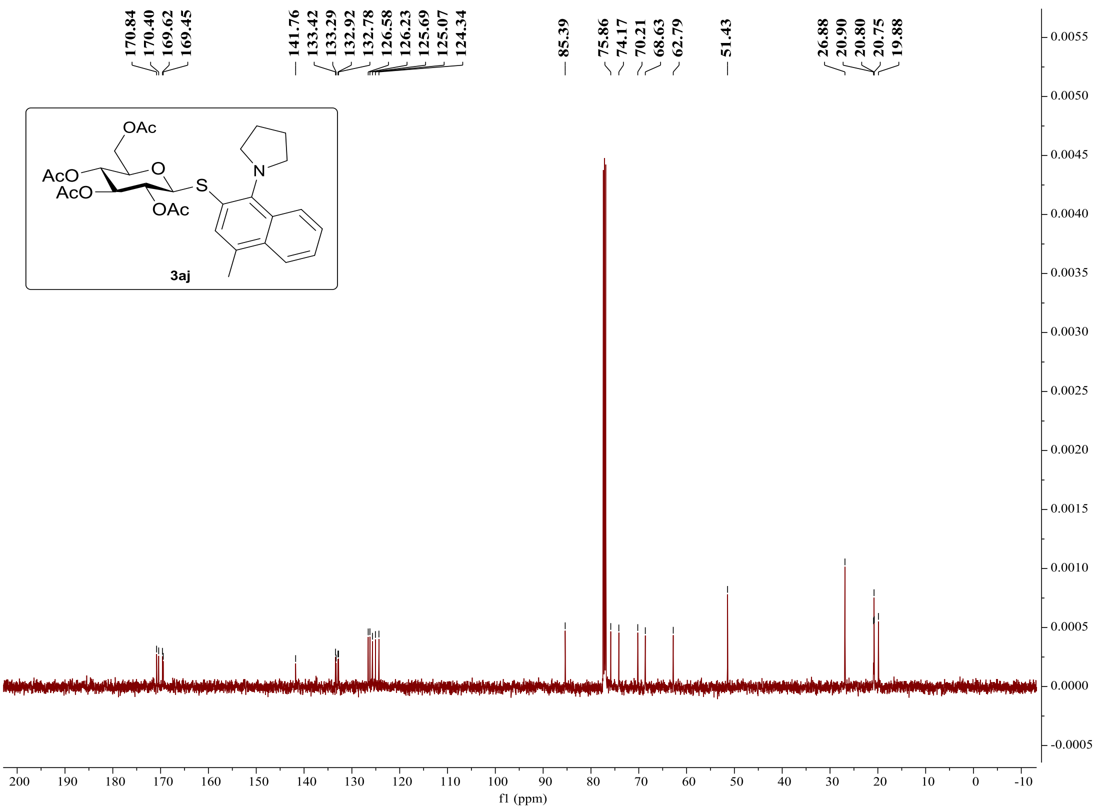
^{13}C NMR of 3ai ($CDCl_3$, 126 MHz, 25 ℃)



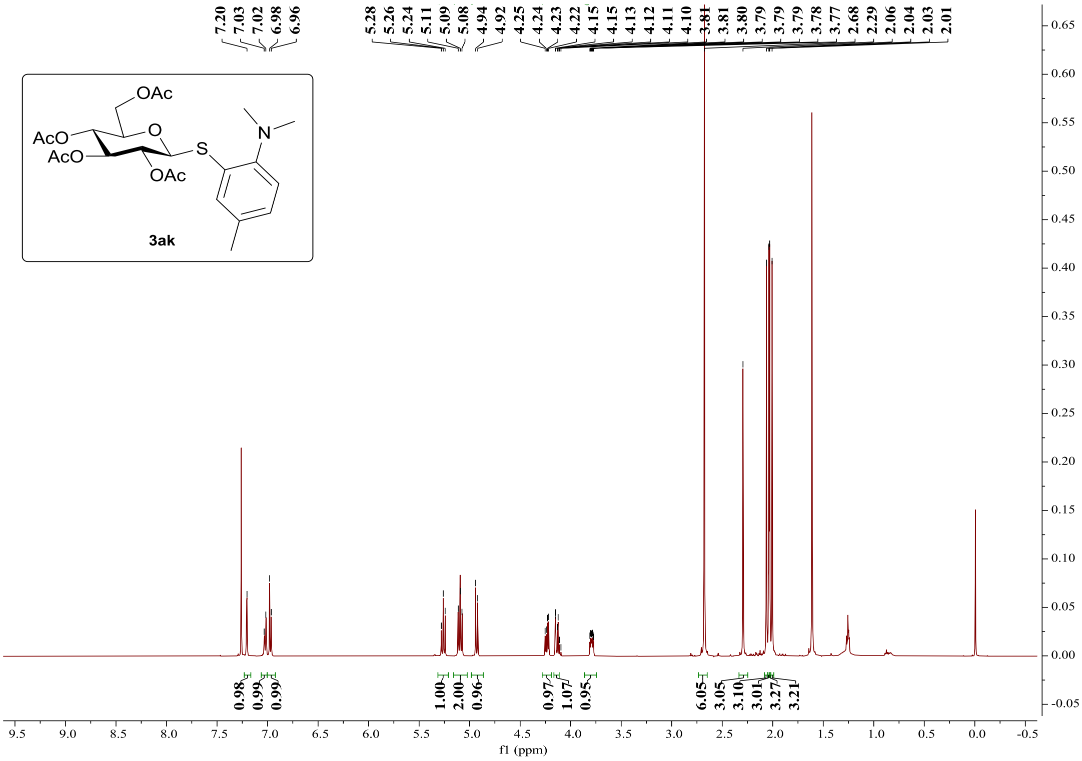
[1]H NMR of 3aj (CDCl$_3$, 500 MHz, 25 ℃)



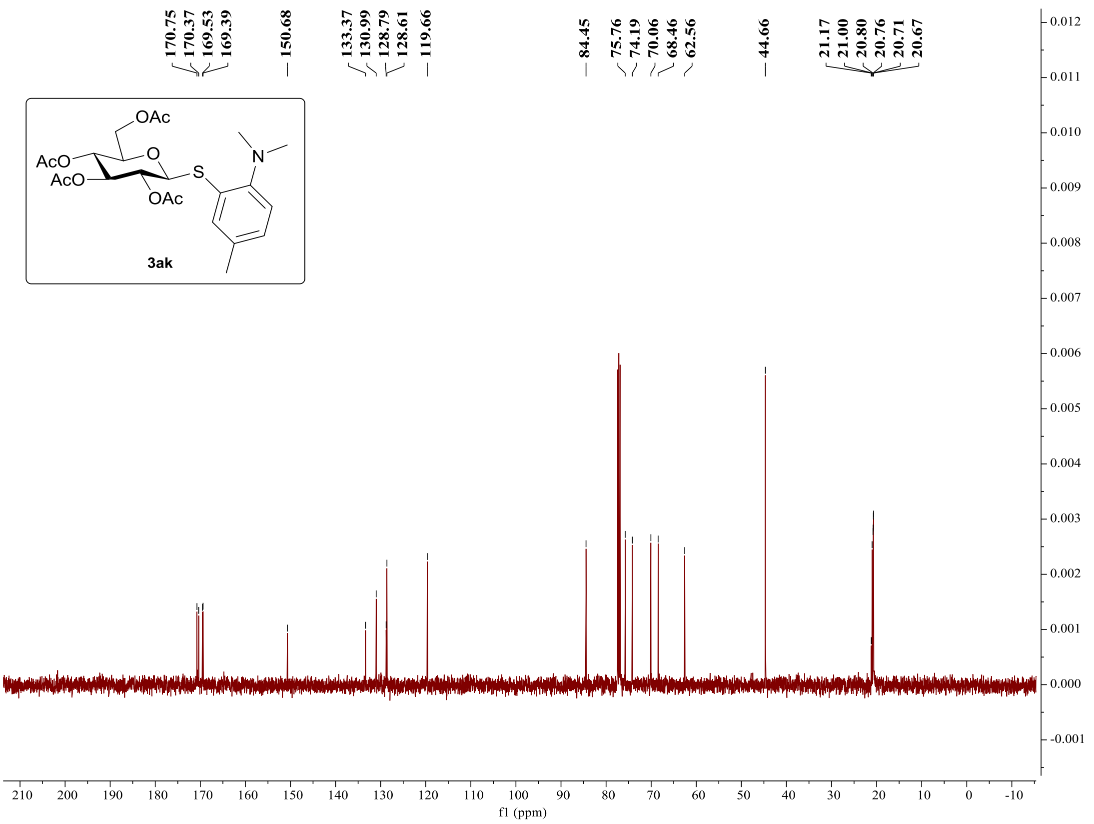
[13]C NMR of 3aj (CDCl$_3$, 126 MHz, 25 ℃)



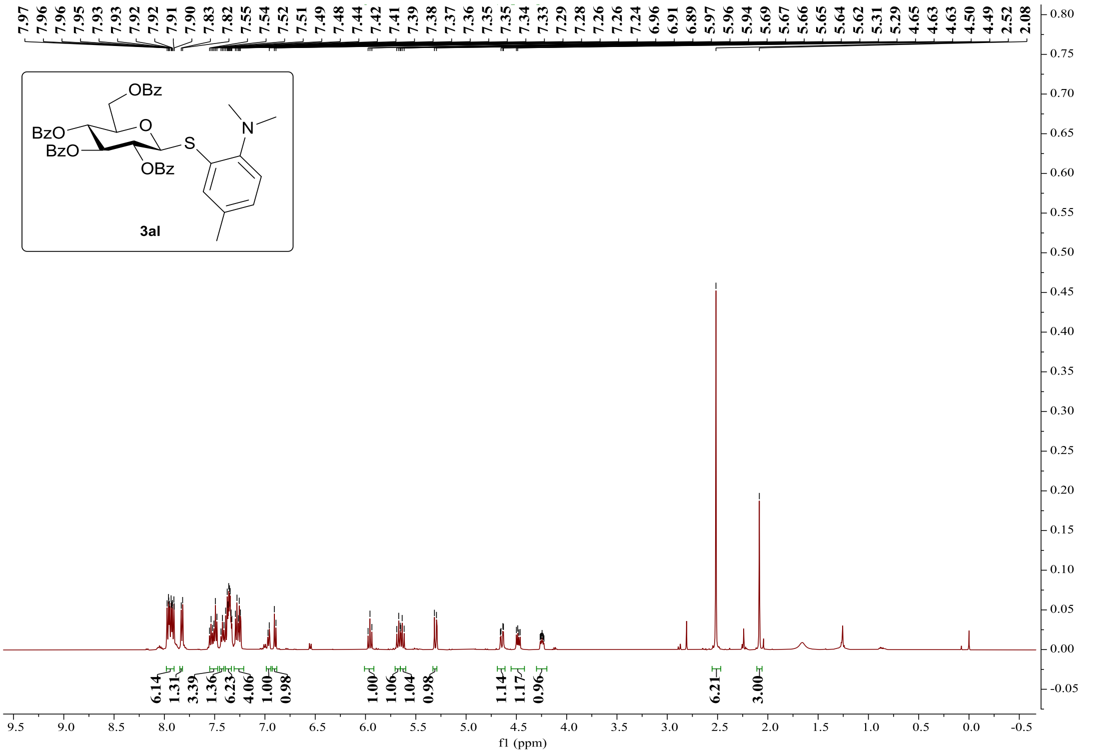
^{1}H NMR of 3ak ($CDCl_3$, 500 MHz, 25 ℃)



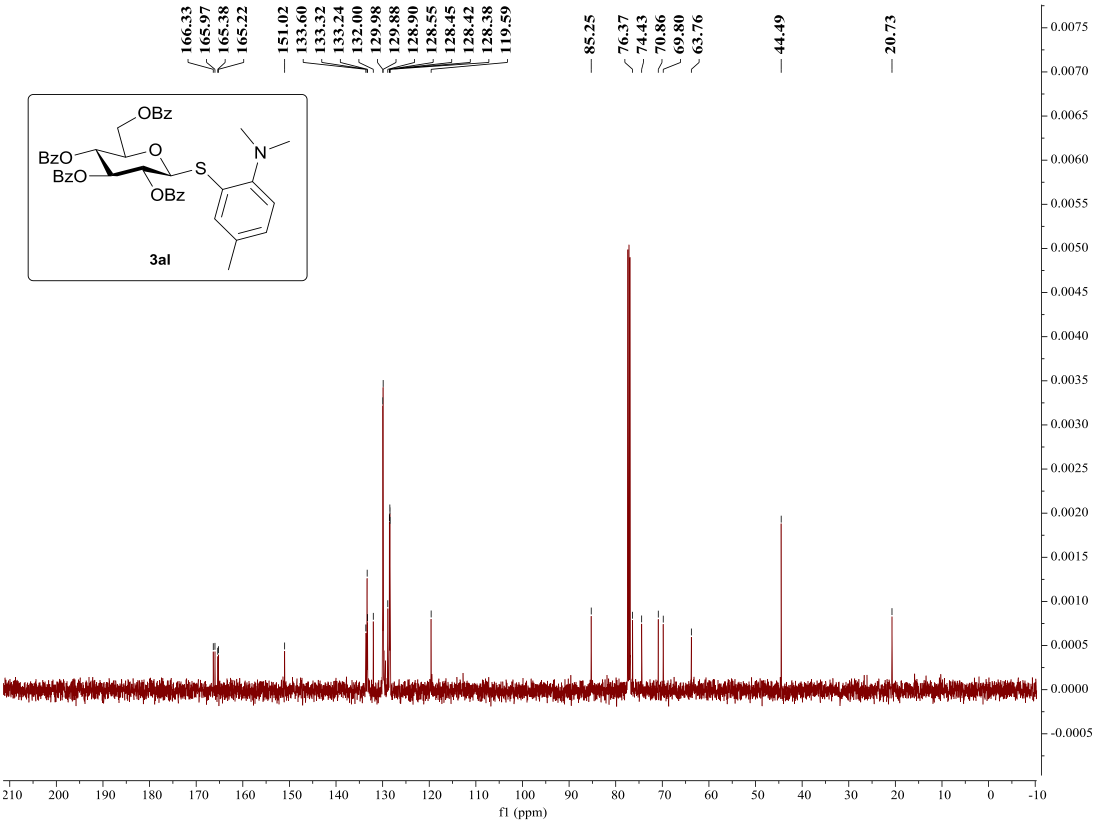
^{13}C NMR of 3ak ($CDCl_3$, 126 MHz, 25 ℃)



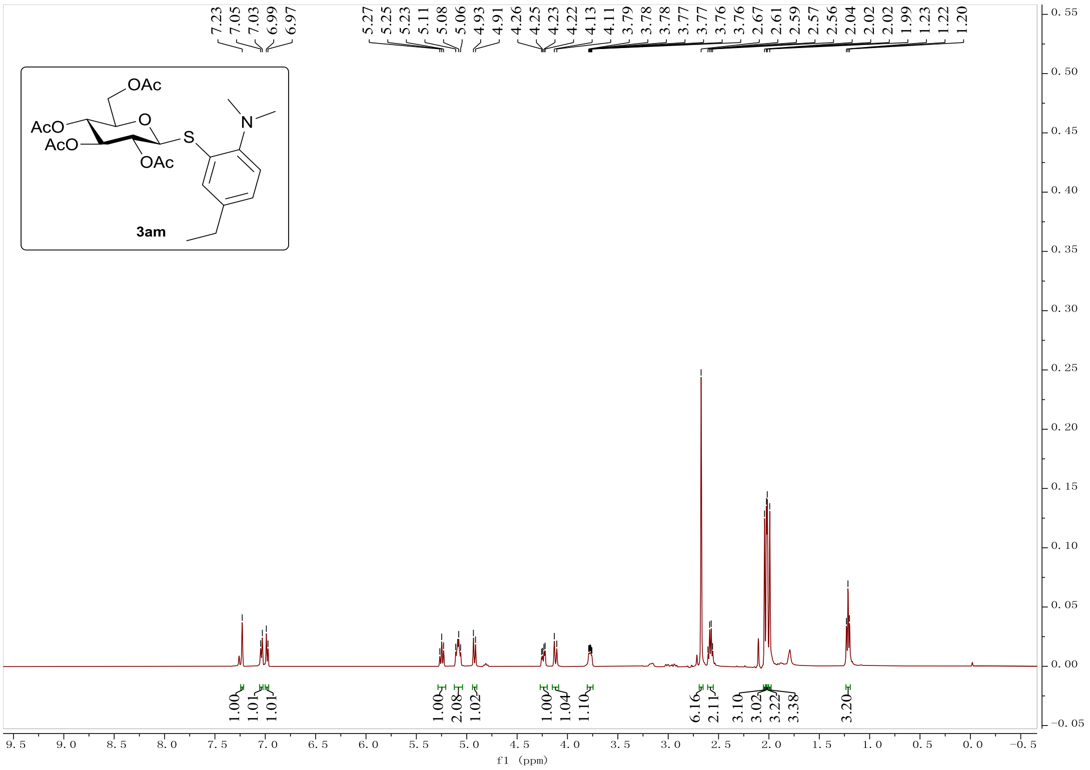
^{1}H NMR of 3ai ($CDCl_3$, 500 MHz, 25 ℃)



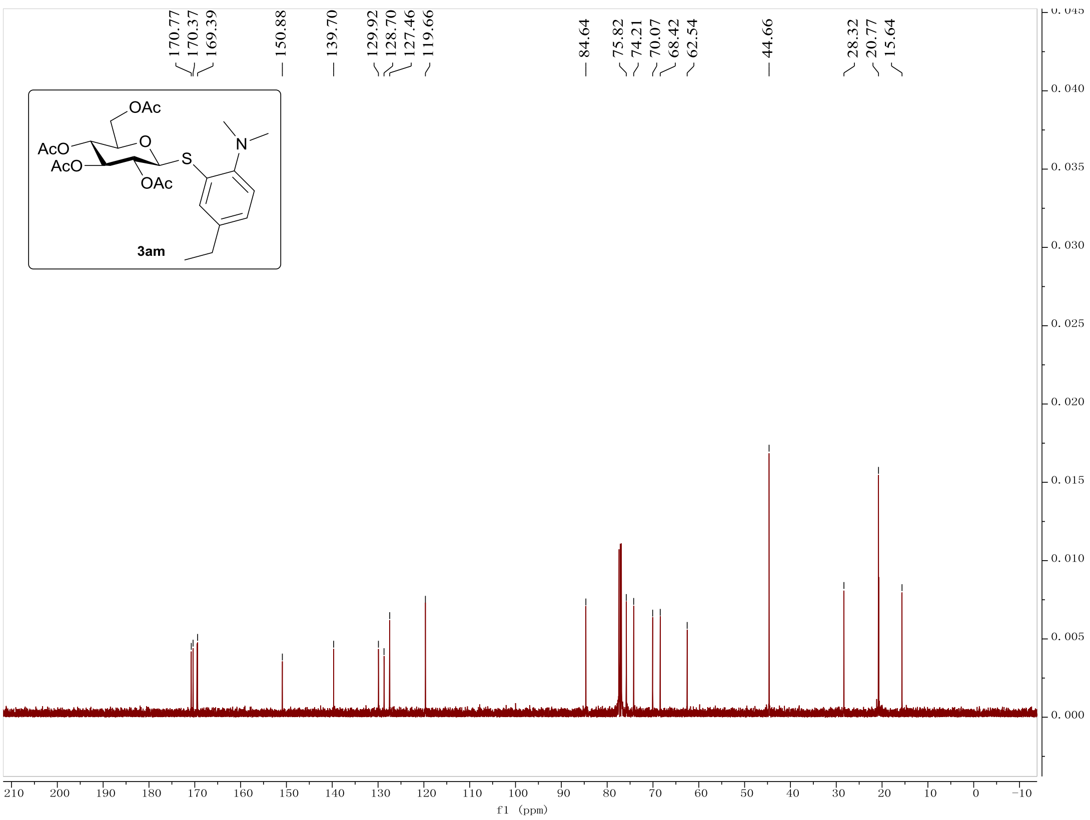
^{13}C NMR of 3ai ($CDCl_3$, 126 MHz, 25 ℃)



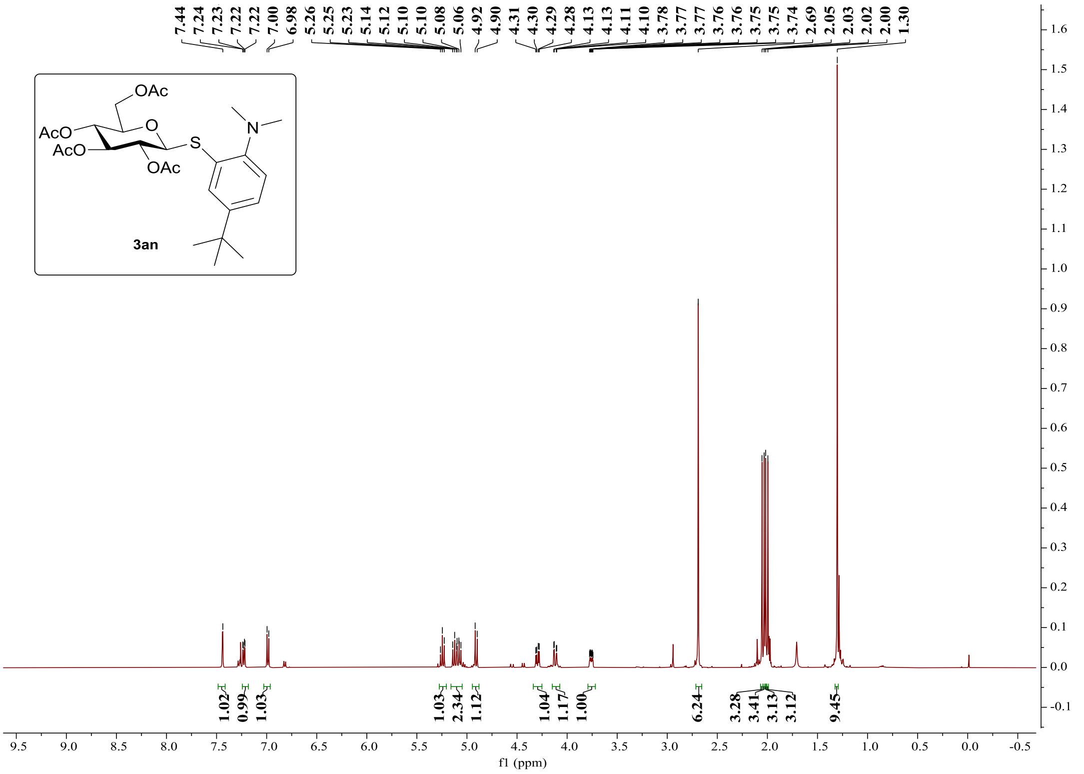
[1]H NMR of 3am (CDCl$_3$, 500 MHz, 25 ℃)



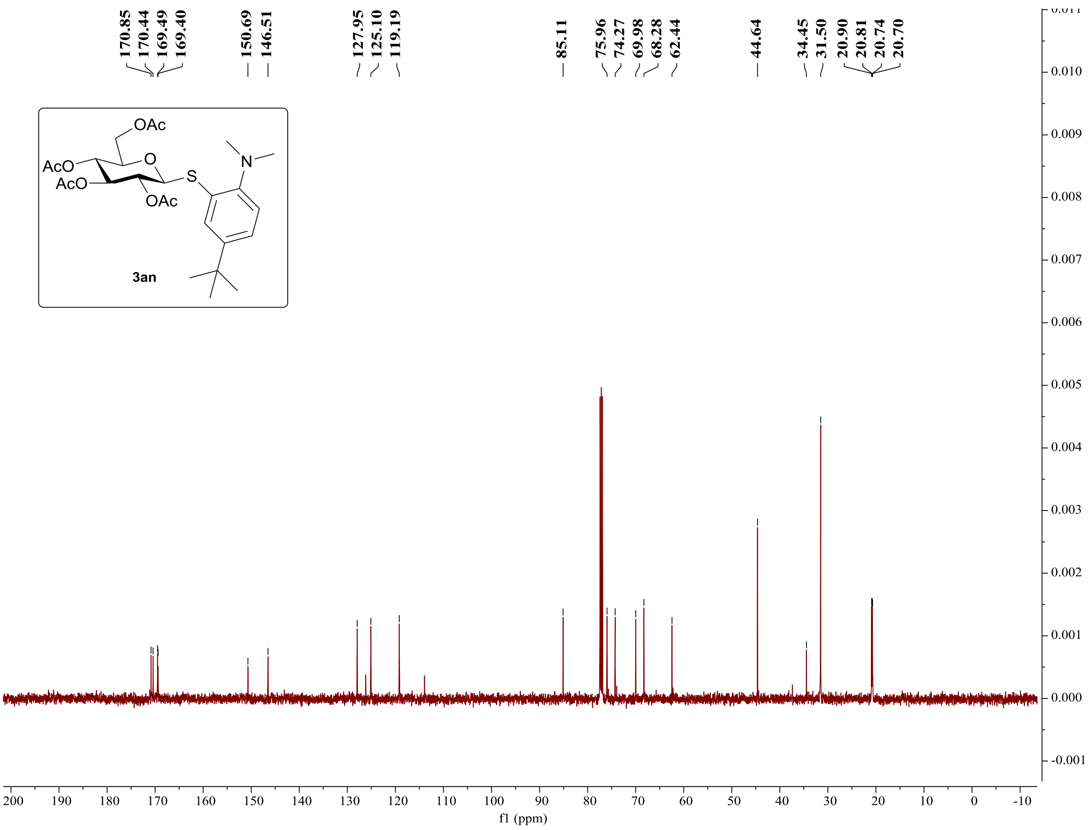
[13]C NMR of 3am (CDCl$_3$, 126 MHz, 25 ℃)



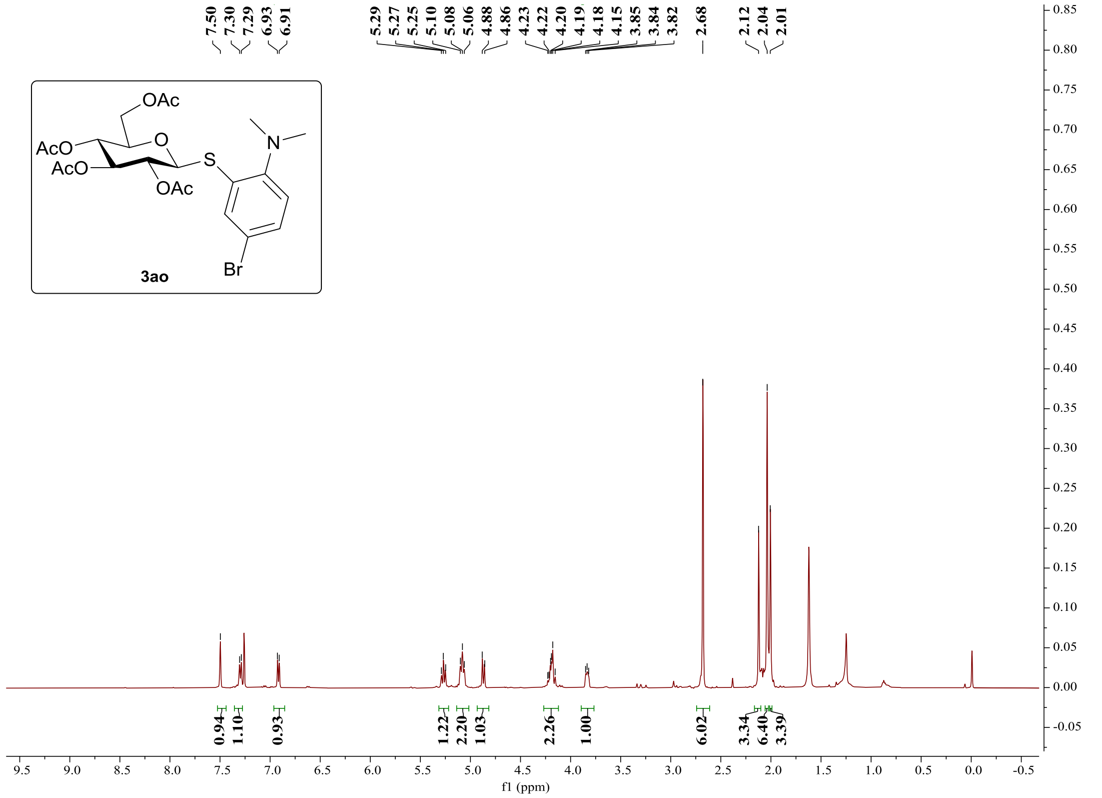
^{1}H NMR of 3an ($CDCl_3$, 500 MHz, 25 ℃)



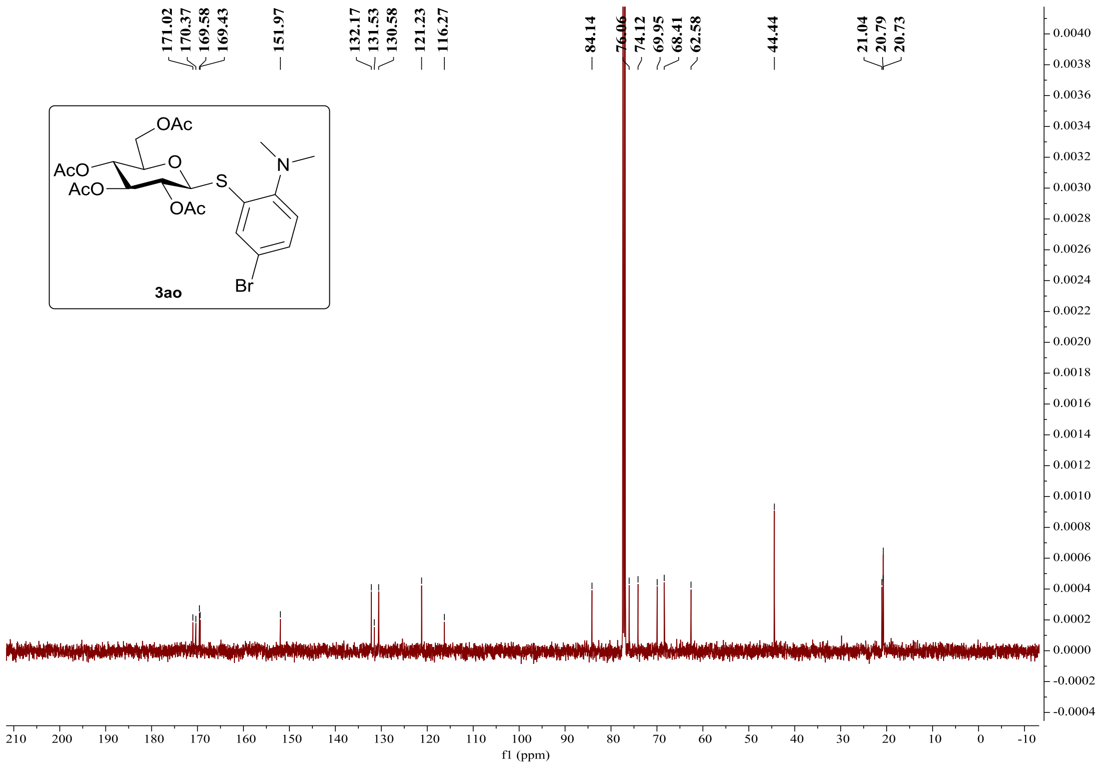
^{13}C NMR of 3an ($CDCl_3$, 126 MHz, 25 ℃)



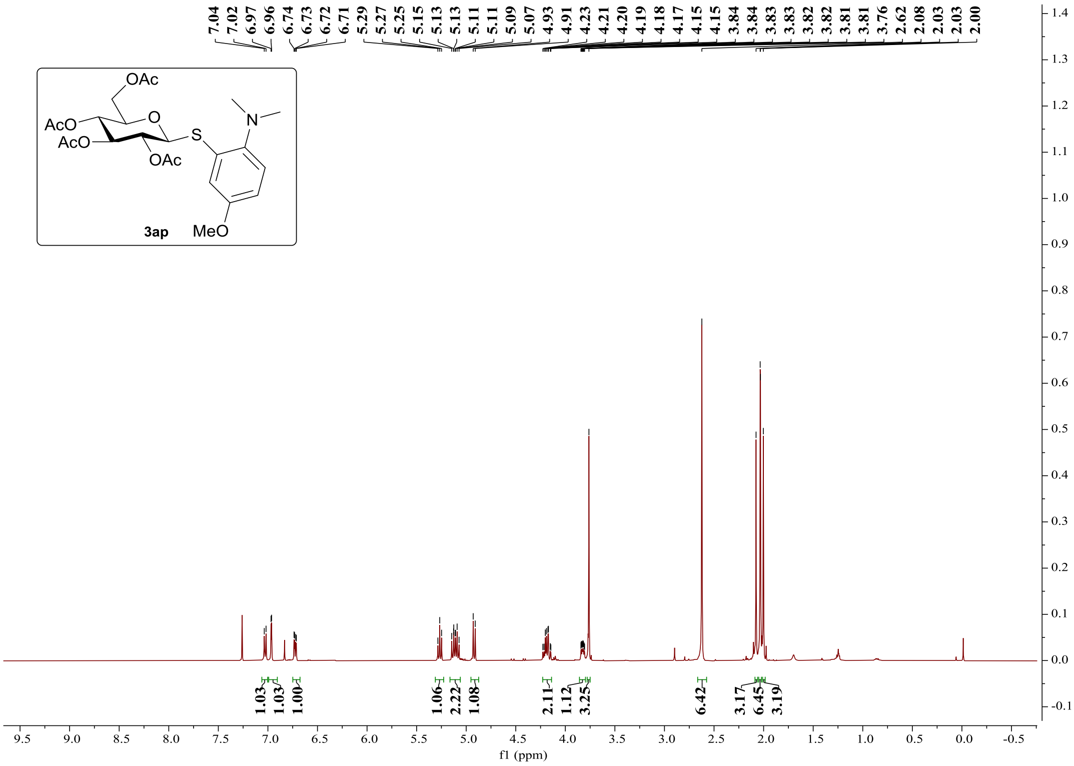
^{1}H NMR of 3ao (CDCl$_3$, 500 MHz, 25 ℃)



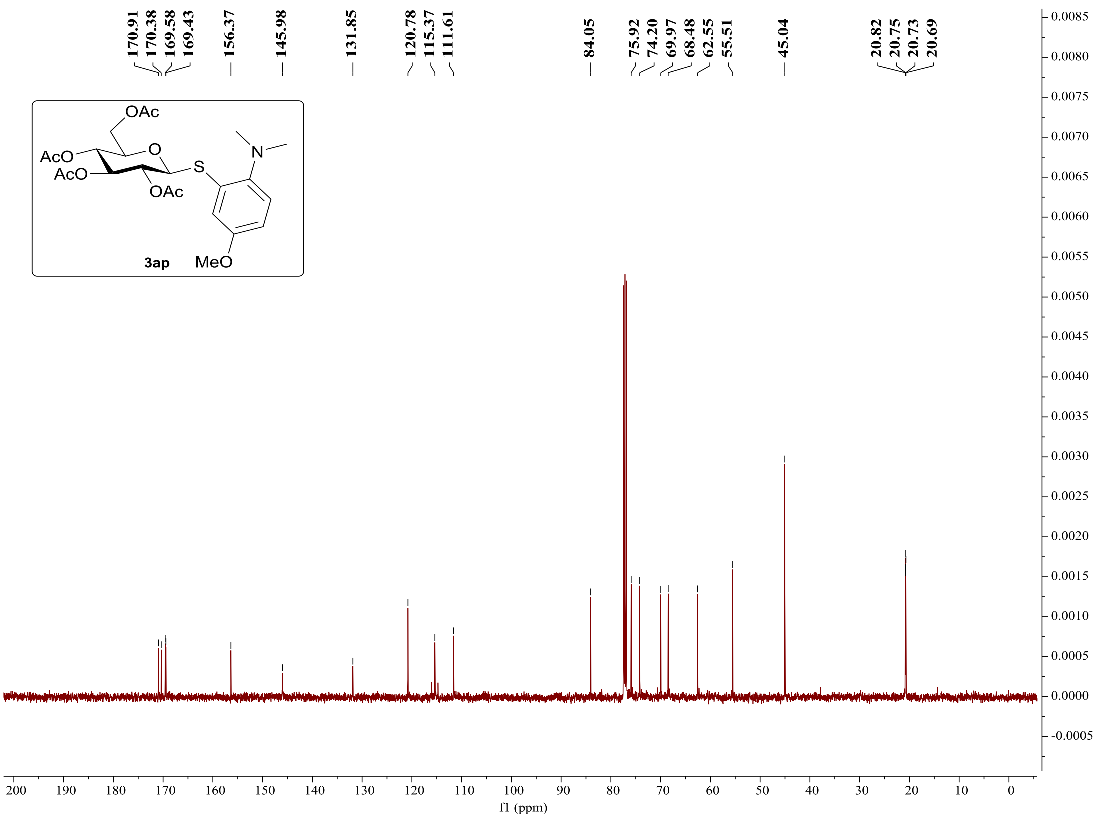
^{13}C NMR of 3ao (CDCl$_3$, 126 MHz, 25 ℃)



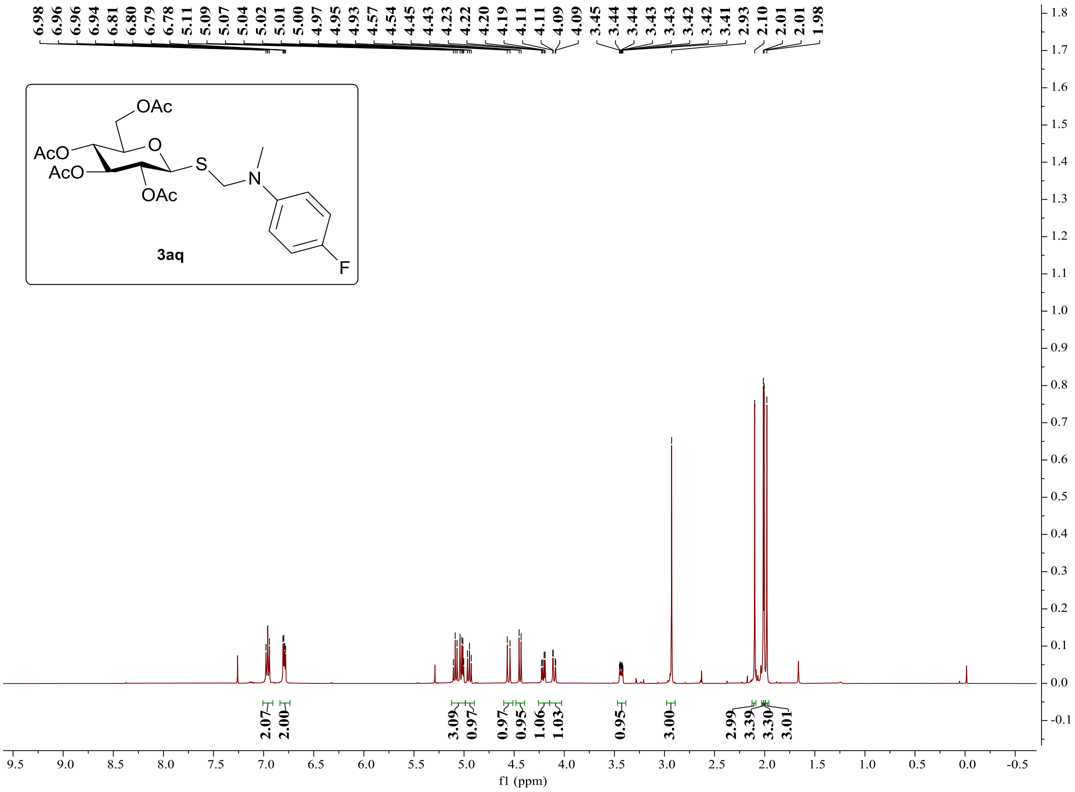
^{1}H NMR of 3ap ($CDCl_3$, 500 MHz, 25 ℃)



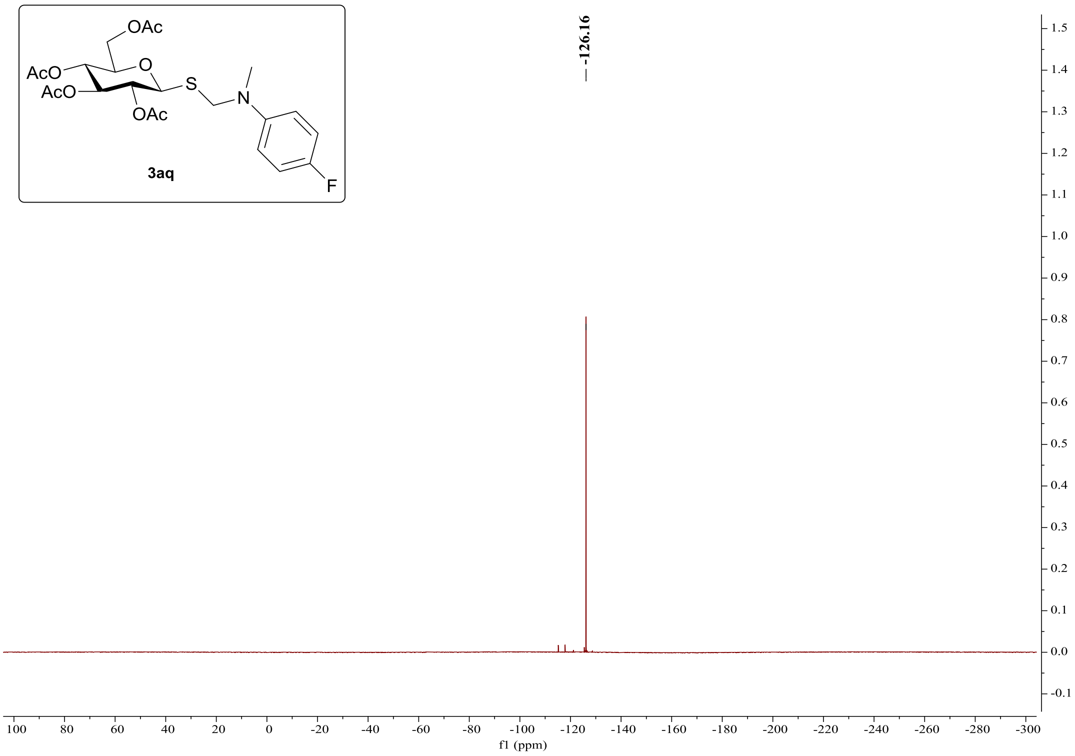
^{13}C NMR of 3ap ($CDCl_3$, 471 MHz, 25 ℃)



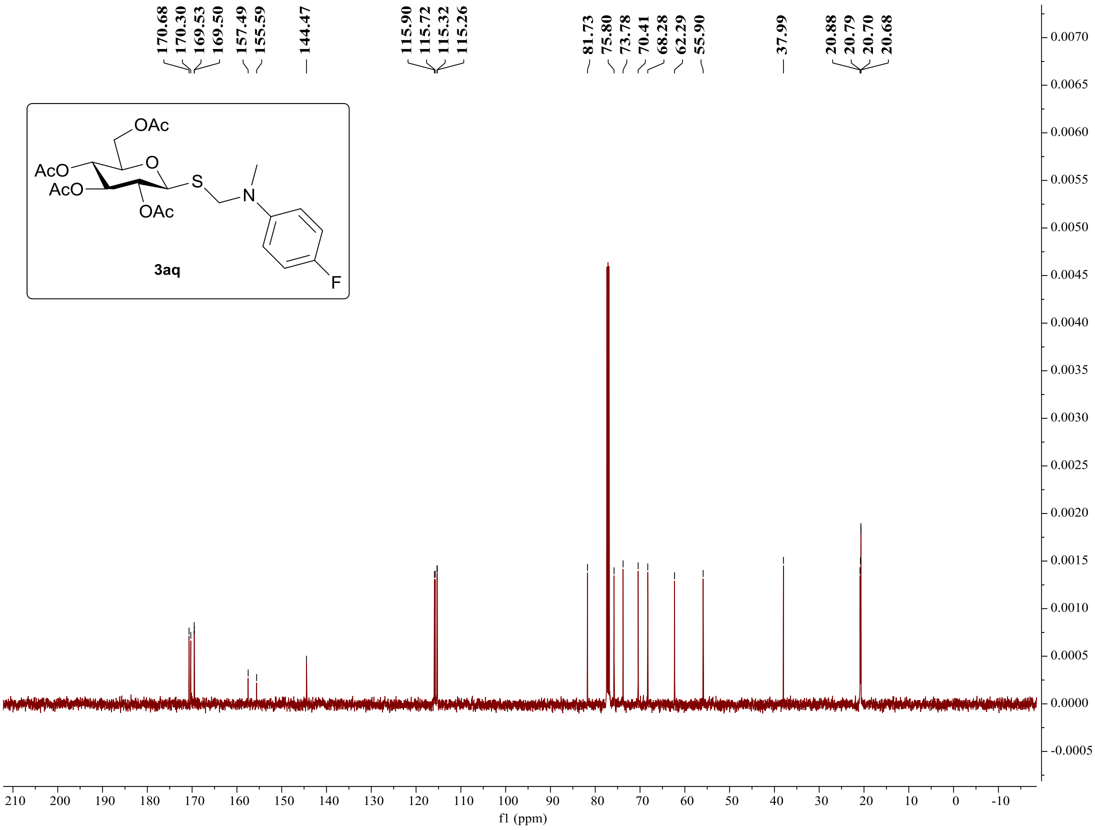
[1]H NMR of 3aq (CDCl₃, 500 MHz, 25 ℃)



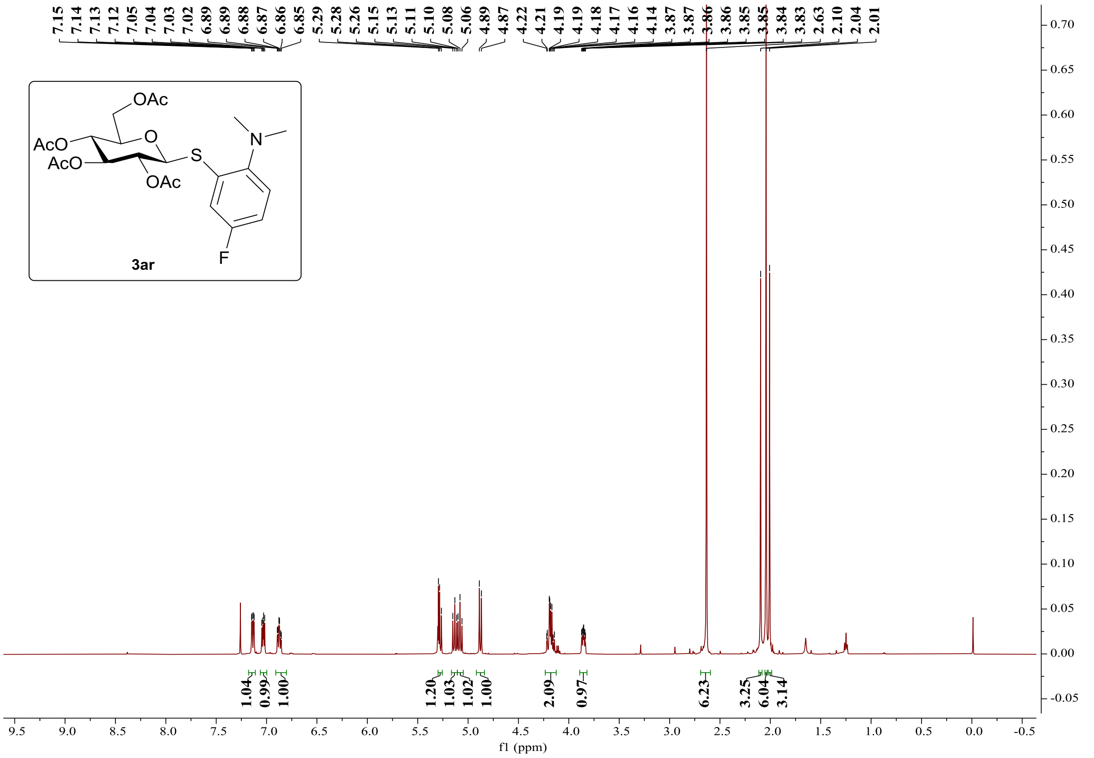
[19]F NMR of 3aq (CDCl₃, 471 MHz, 25 ℃)



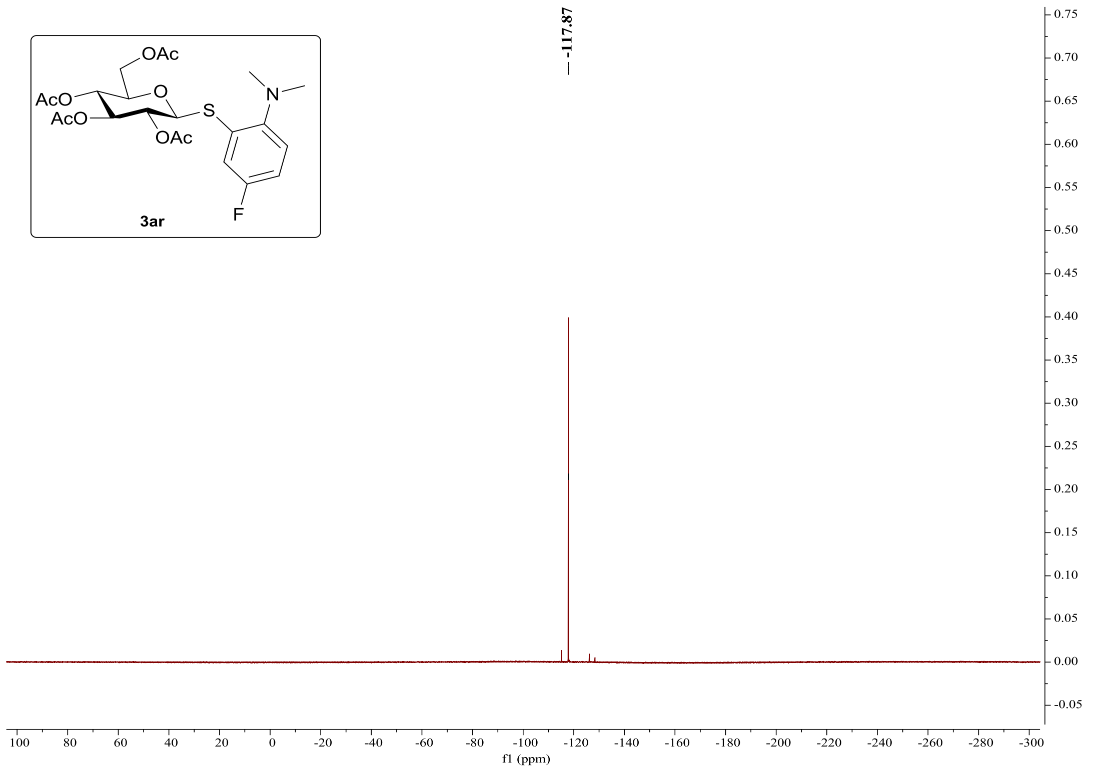
^{13}C NMR of 3aq (CDCl$_3$, 126 MHz, 25 ℃)



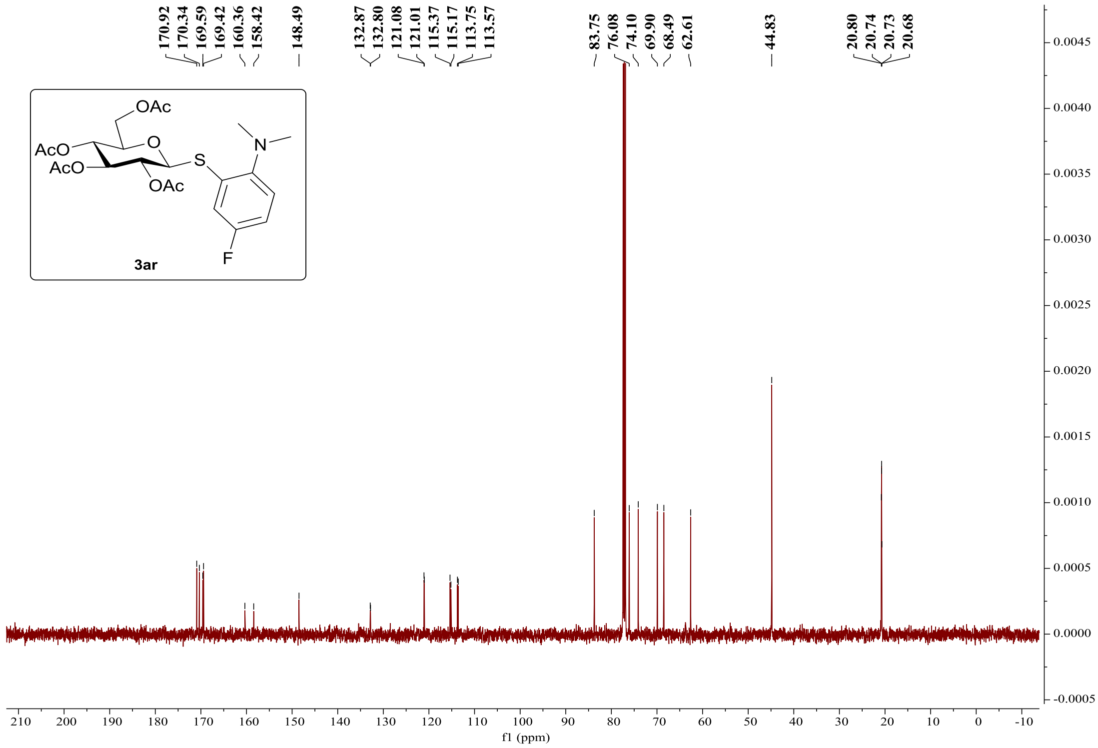
^{1}H NMR of 3ar (CDCl$_3$, 500 MHz, 25 ℃)



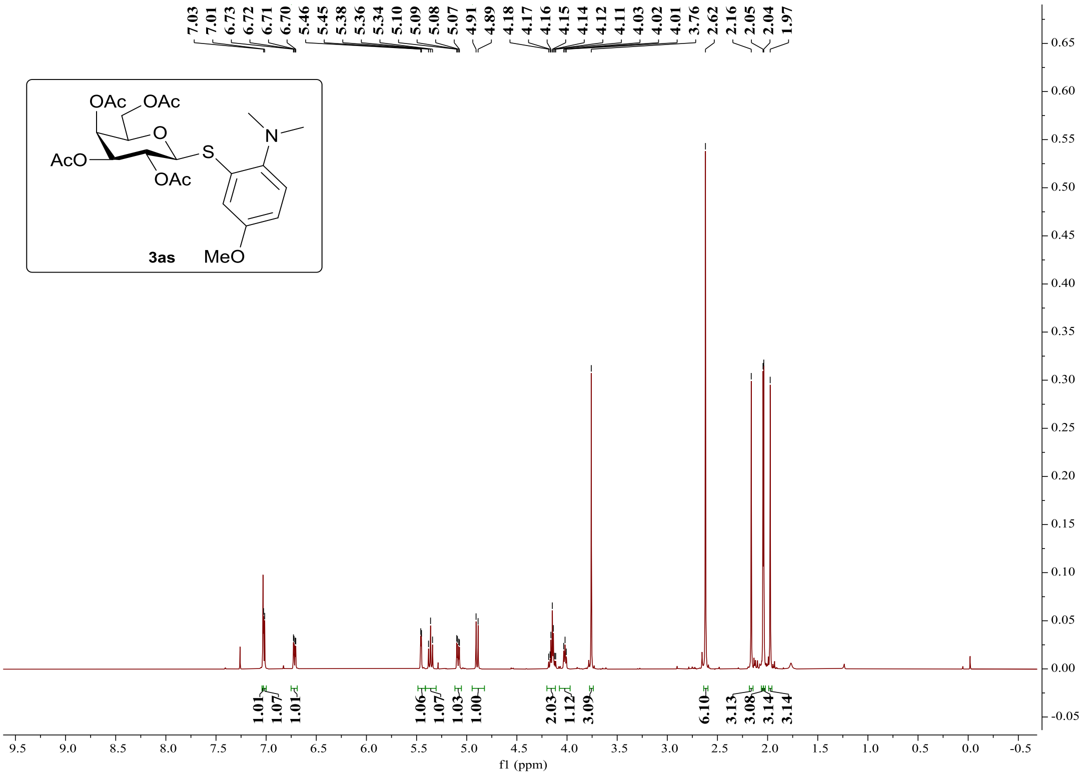
^{19}F NMR of 3ar ($CDCl_3$, 471 MHz, 25 ℃)



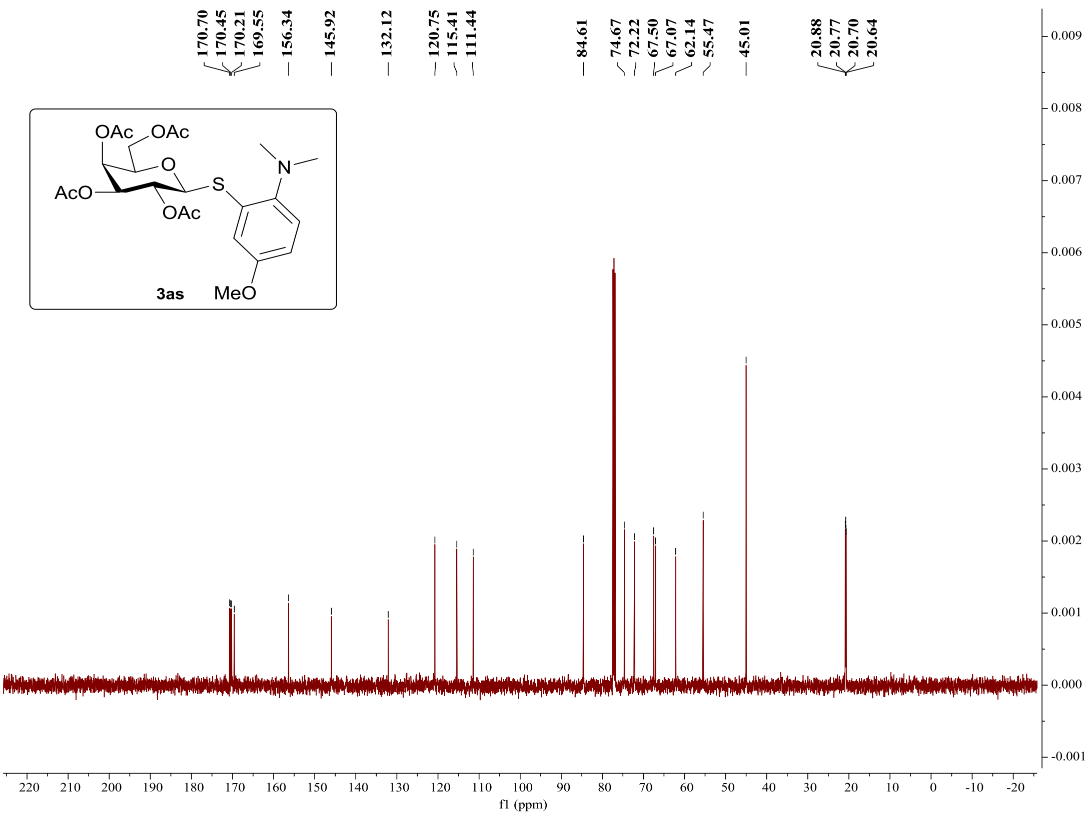
^{13}C NMR of 3ar ($CDCl_3$, 126 MHz, 25 ℃)



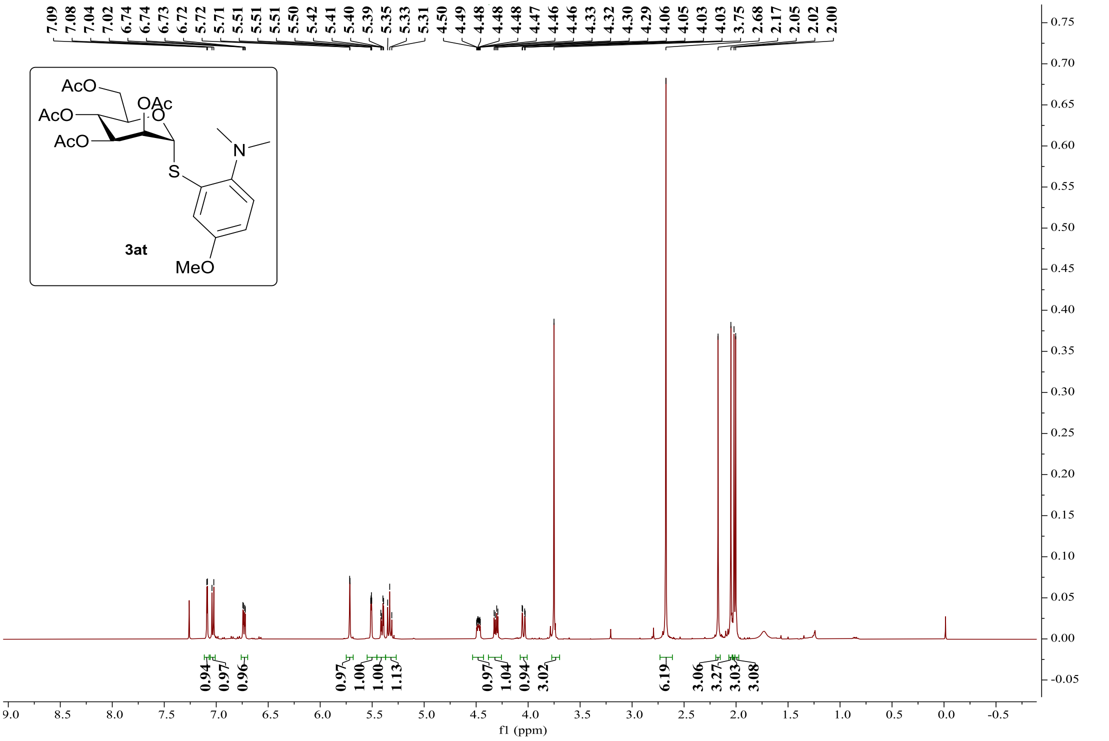
[1]H NMR of 3as (CDCl₃, 500 MHz, 25 ℃)



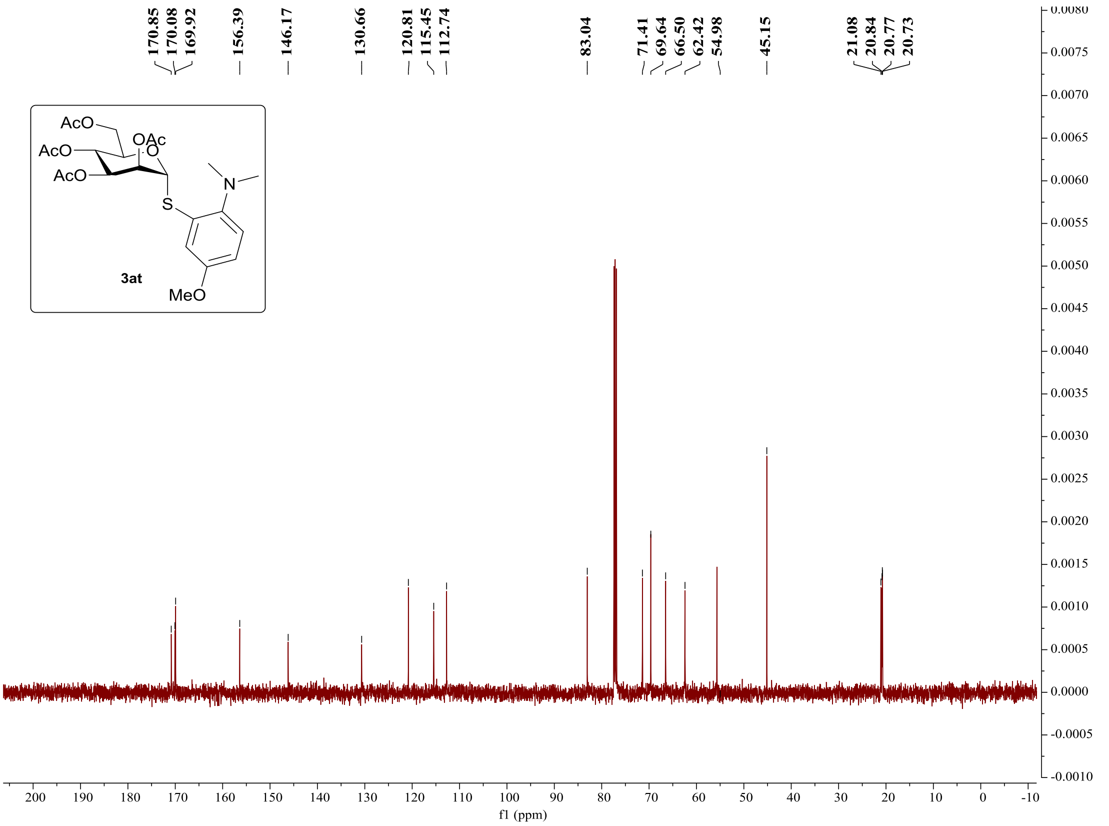
[13]C NMR of 3as (CDCl₃, 126 MHz, 25 ℃)



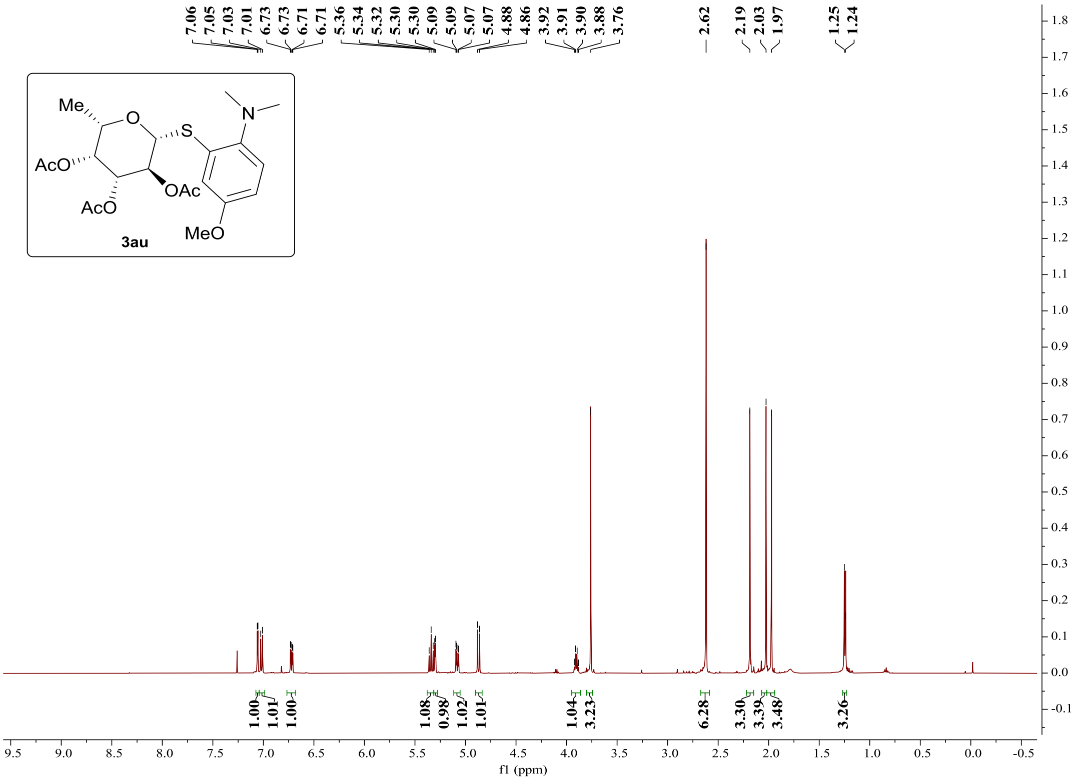
^{1}H NMR of 3at (CDCl$_3$, 500 MHz, 25 °C)



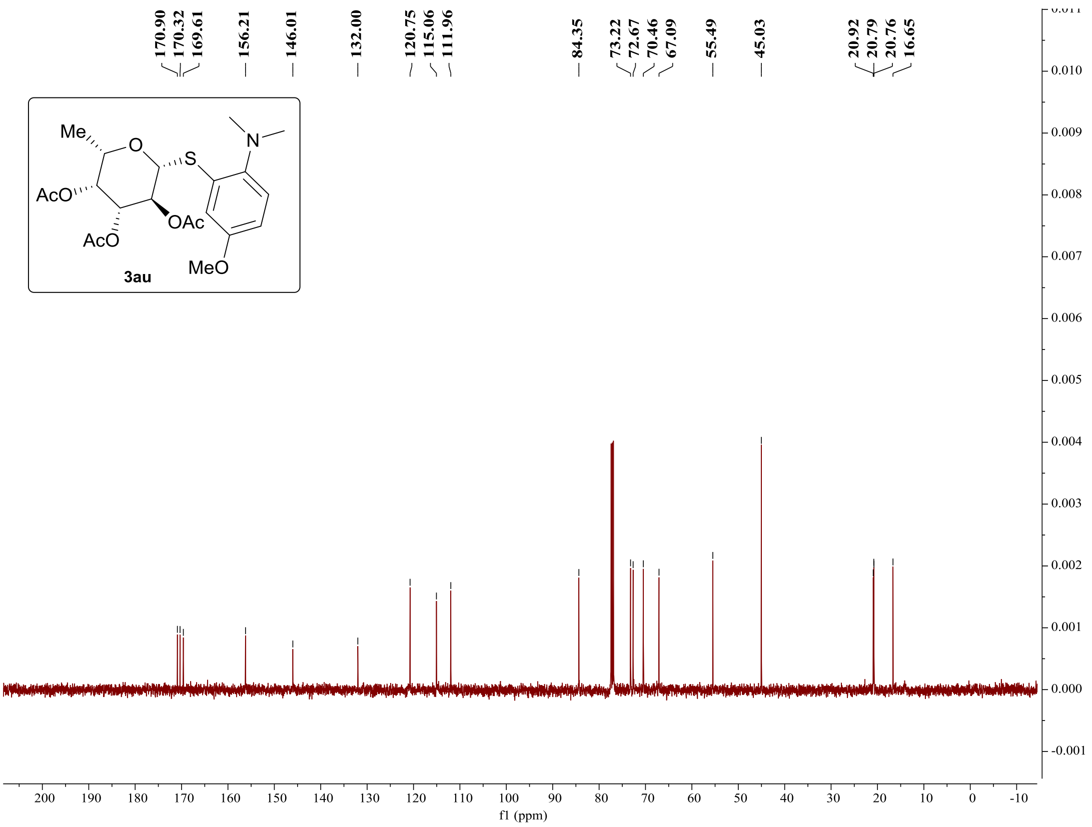
^{13}C NMR of 3at (CDCl$_3$, 126 MHz, 25 °C)



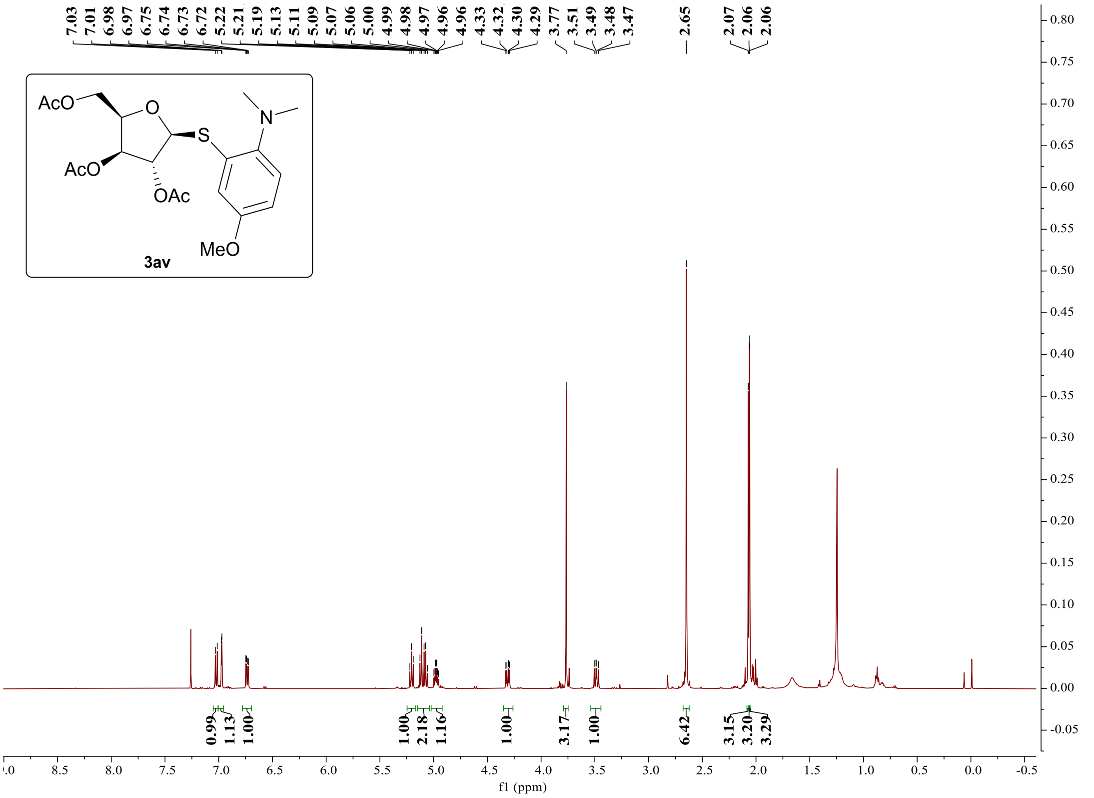
^1H NMR of 3au ($CDCl_3$, 500 MHz, 25 ℃)



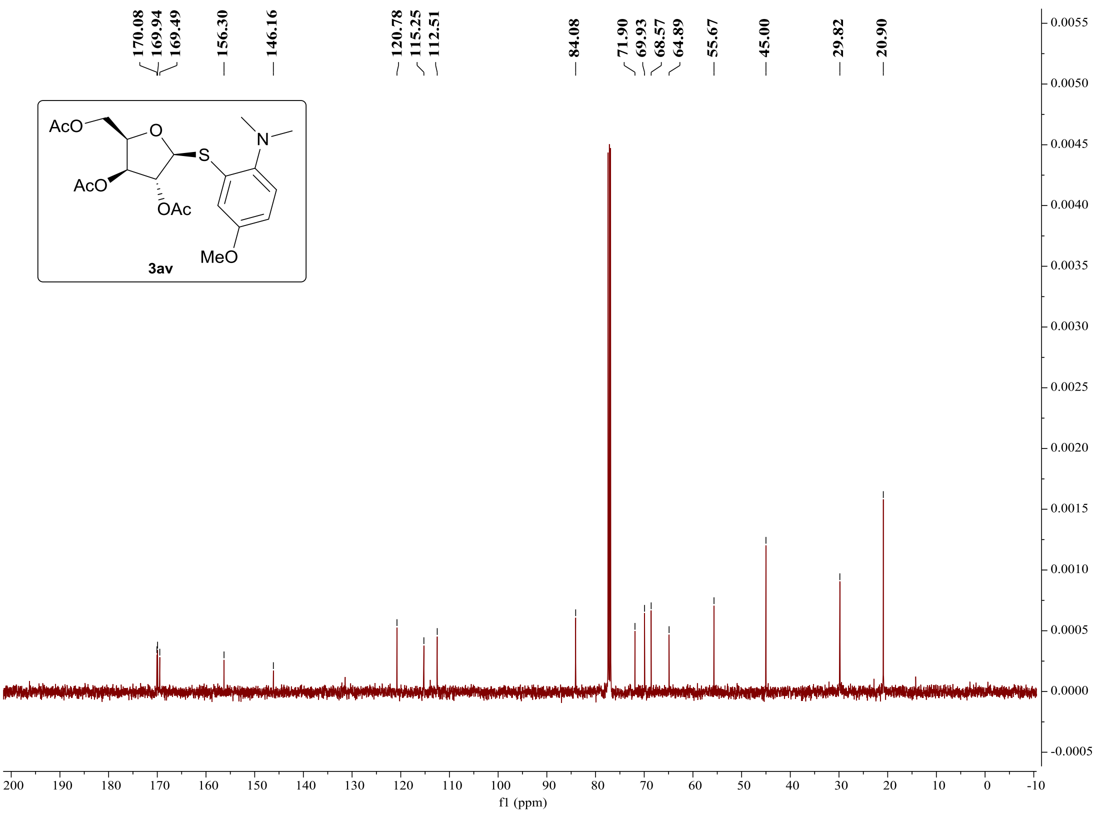
^{13}C NMR of 3au ($CDCl_3$, 126 MHz, 25 ℃)



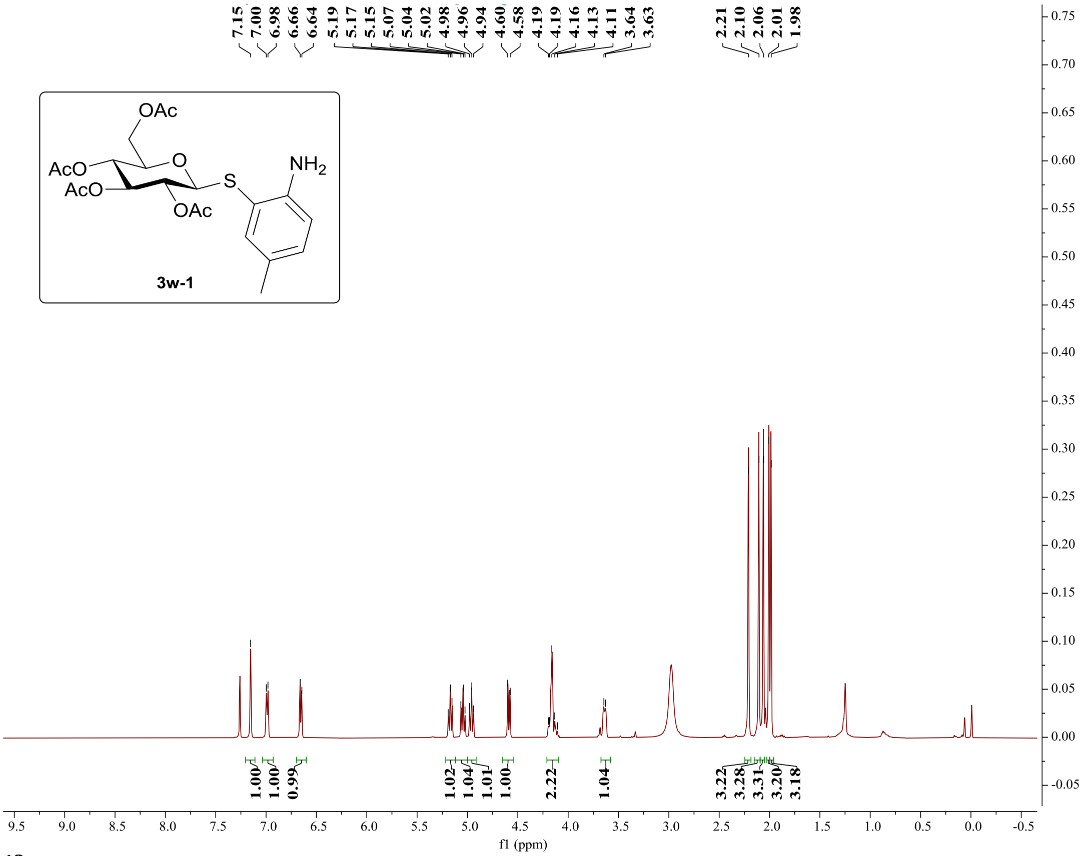
^{1}H NMR of 3av (CDCl$_3$, 500 MHz, 25 ℃)



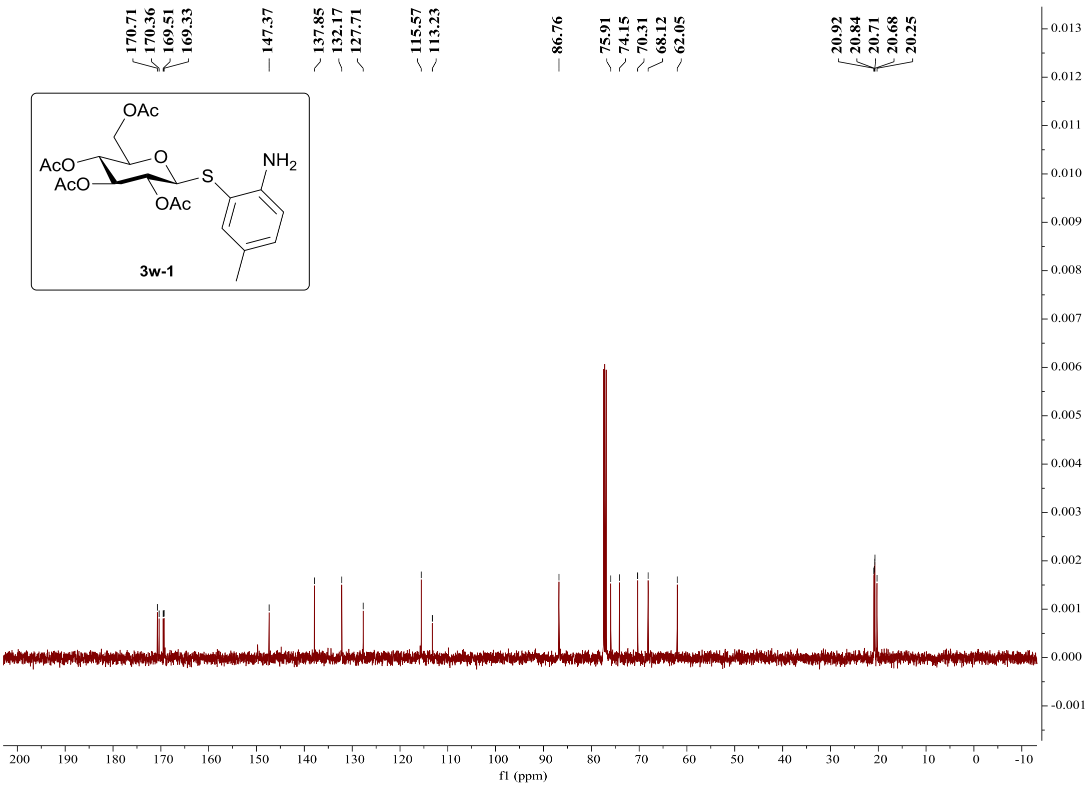
^{13}C NMR of 3av (CDCl$_3$, 126 MHz, 25 ℃)



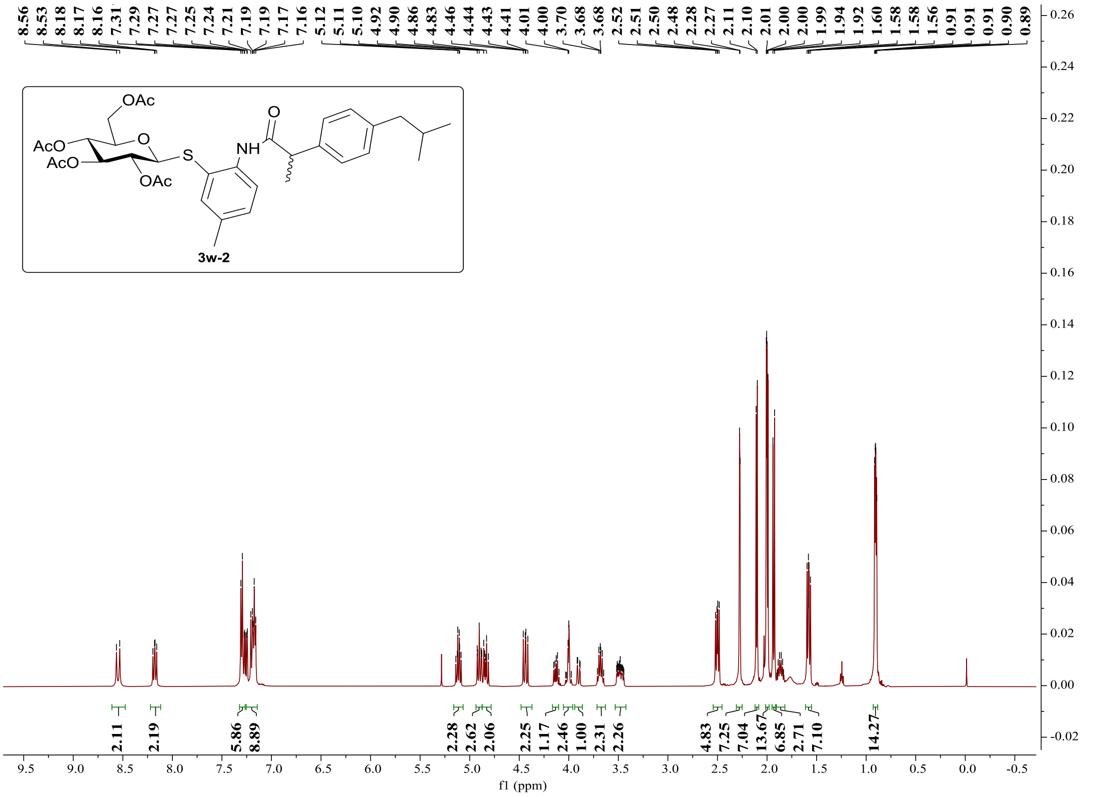
^{1}H NMR of 3w-1 ($CDCl_3$, 500 MHz, 25 ℃)



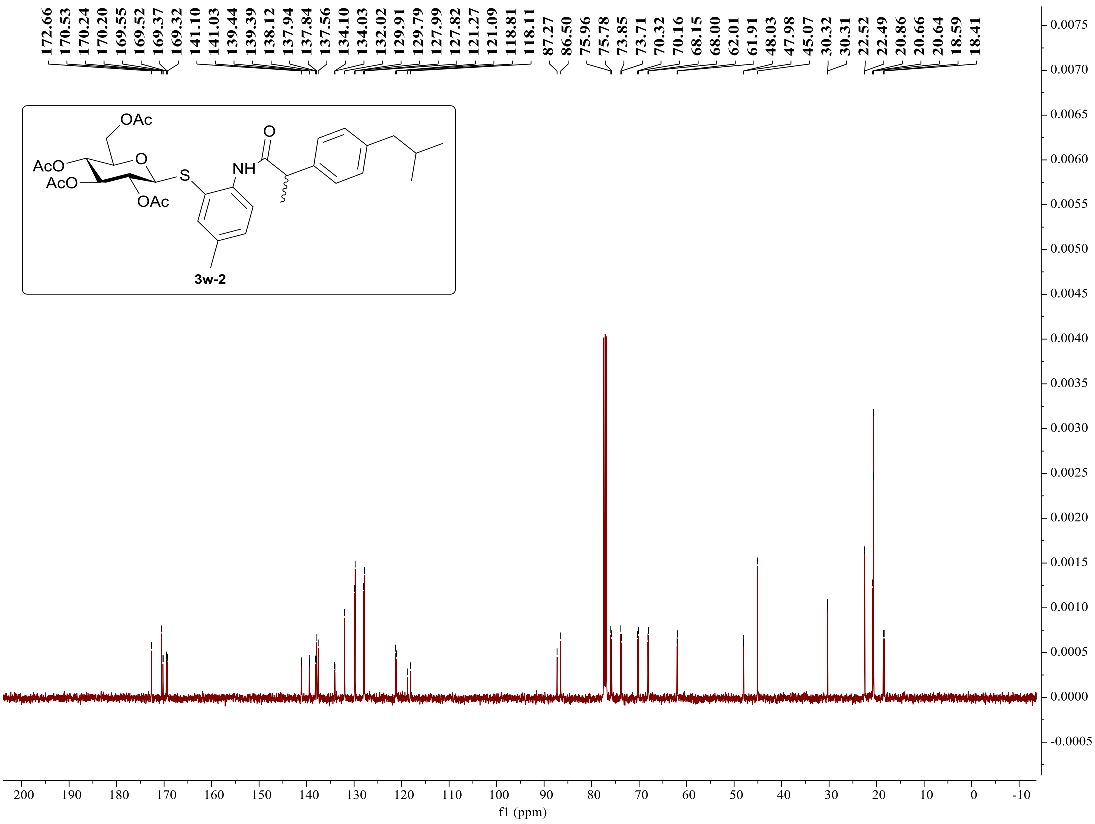
^{13}C NMR of 3w-1 ($CDCl_3$, 126 MHz, 25 ℃)



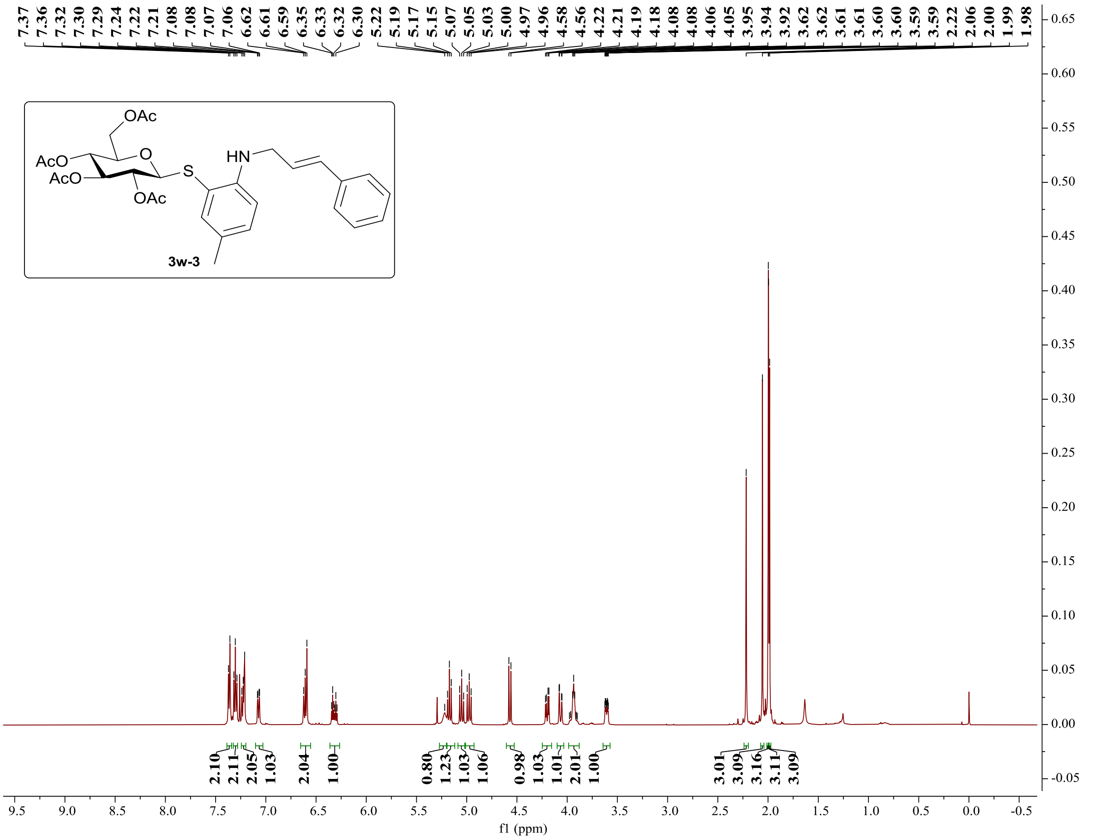
^{1}H NMR of 3w-2 (CDCl$_3$, 500 MHz, 25 ℃)



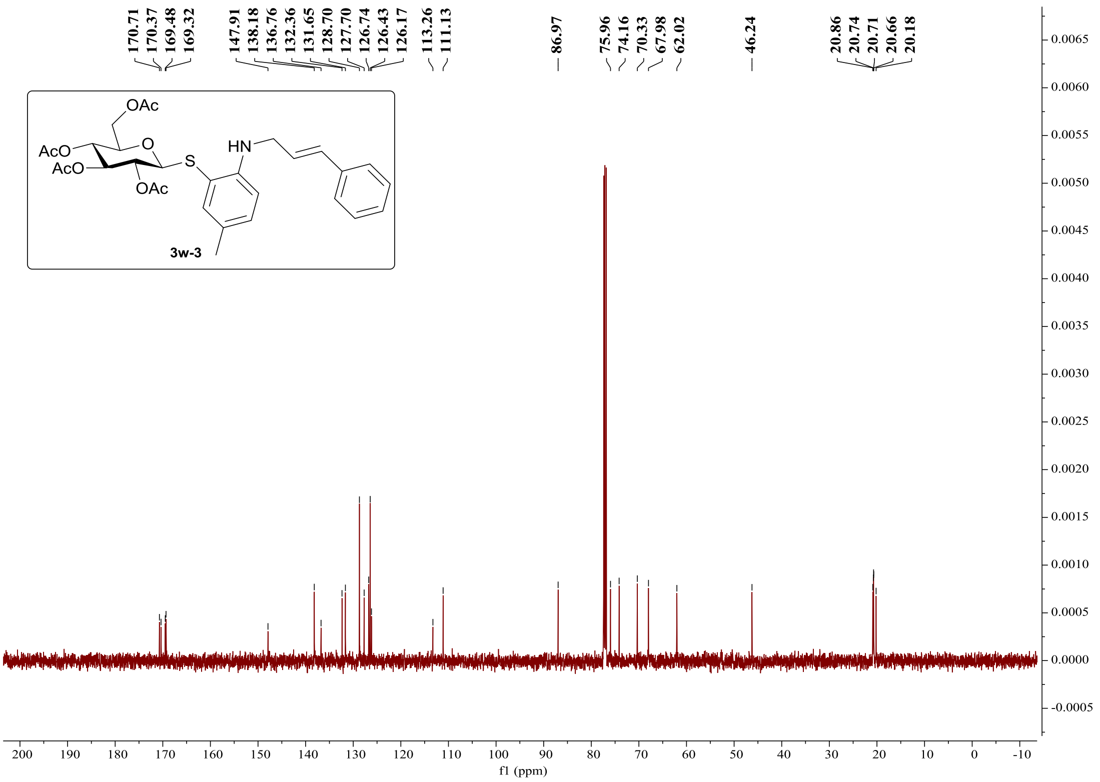
^{13}C NMR of 3w-2 (CDCl$_3$, 126 MHz, 25 ℃)



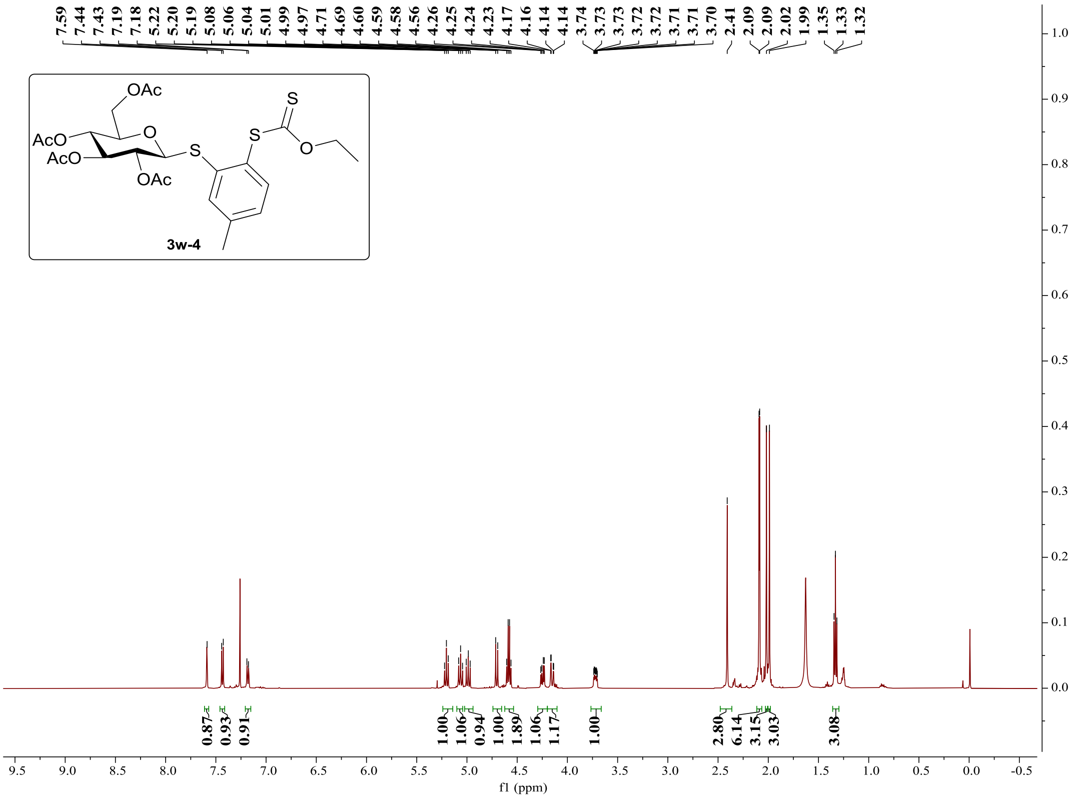
[1]H NMR of 3w-3 (CDCl3, 500 MHz, 25 ℃)



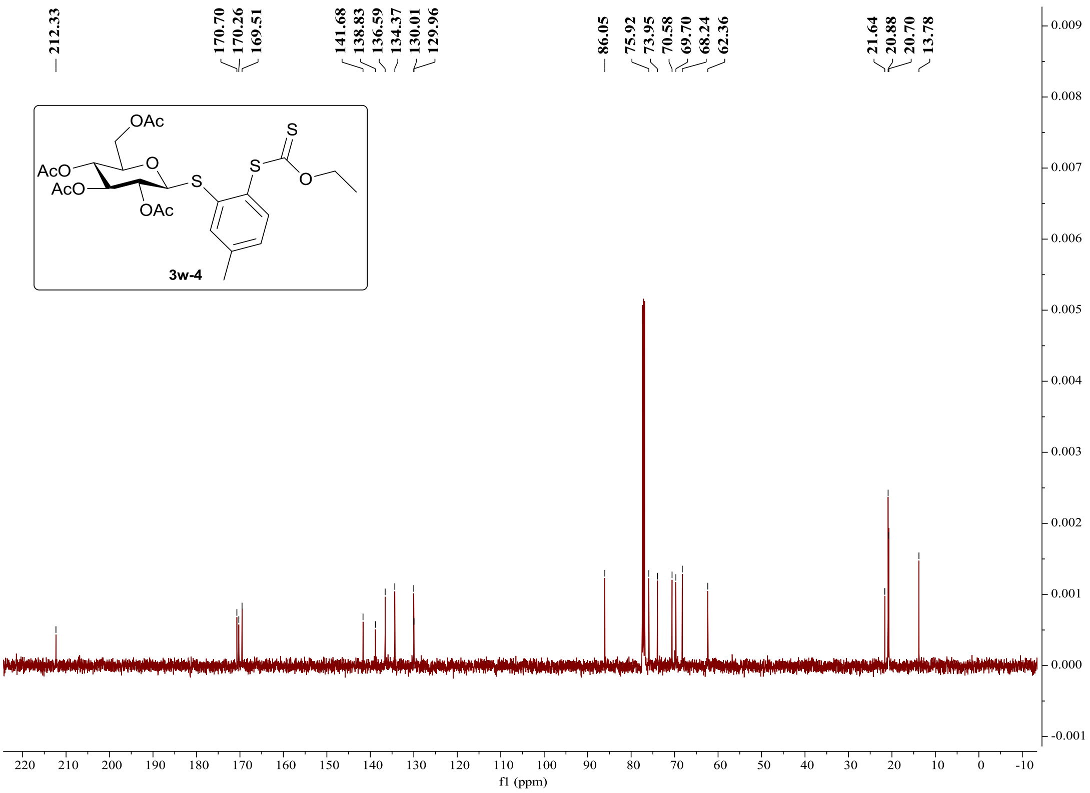
[13]C NMR of 3w-3 (CDCl3, 126 MHz, 25 ℃)



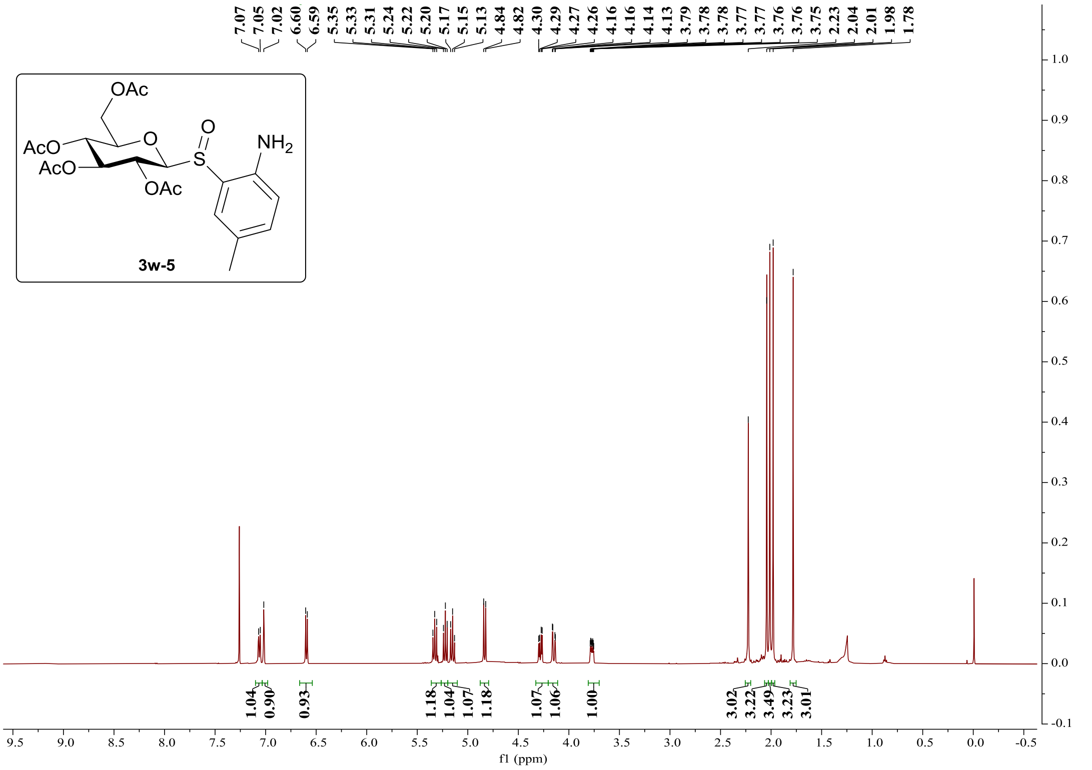
^{1}H NMR of 3w-4 ($CDCl_3$, 500 MHz, 25 ℃)



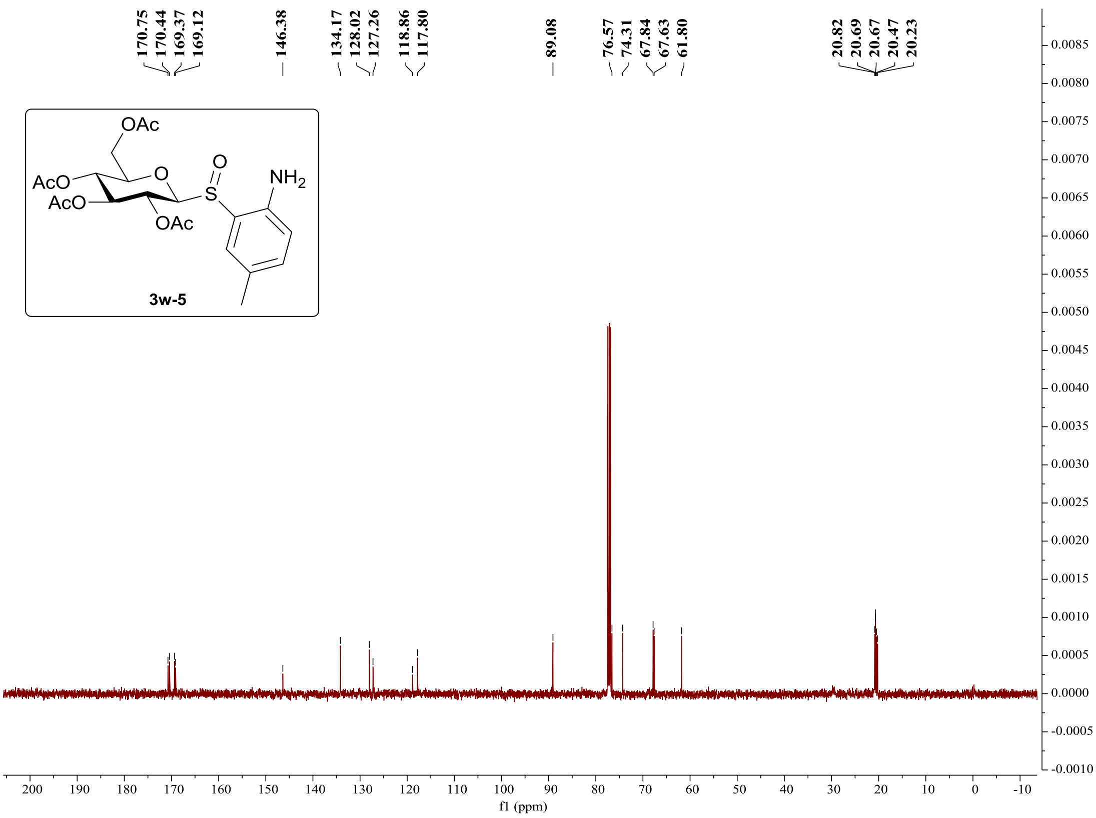
^{13}C NMR of 3w-4 ($CDCl_3$, 126 MHz, 25 ℃)



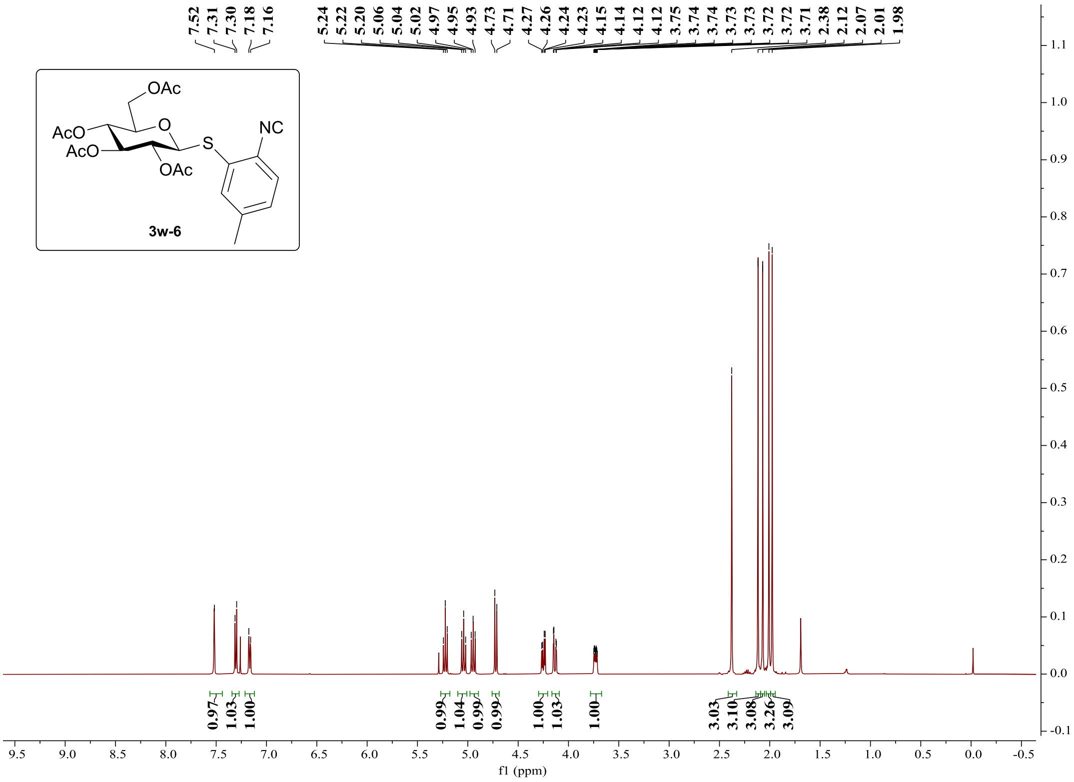
^{1}H NMR of 3w-5 (CDCl$_3$, 500 MHz, 25 ℃)



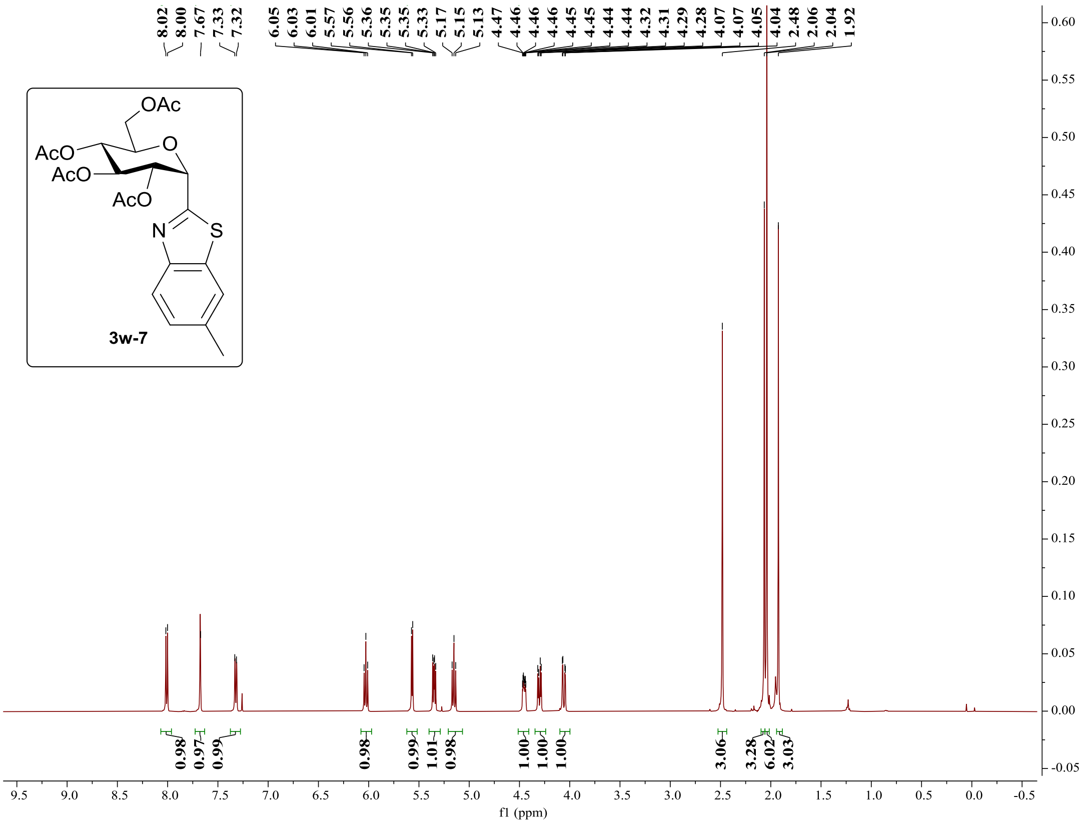
^{13}C NMR of 3w-5 (CDCl$_3$, 126 MHz, 25 ℃)



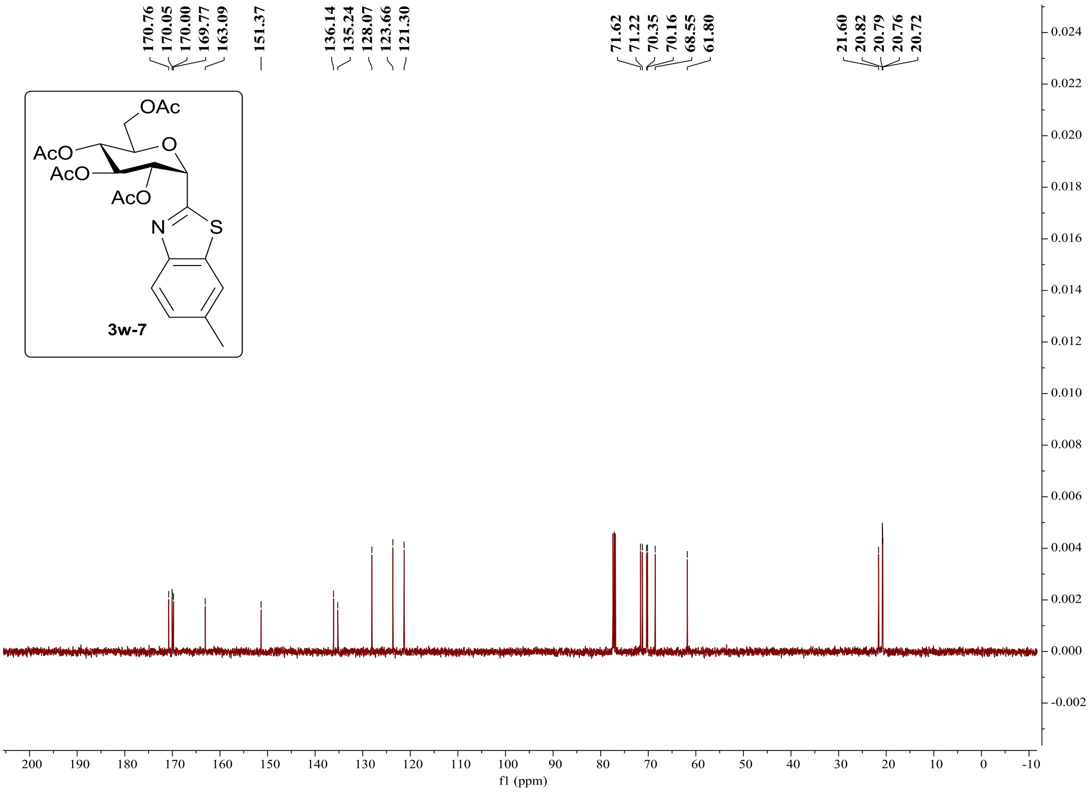
[1]H NMR of 3w-6 (CDCl$_3$, 500 MHz, 25 ℃)



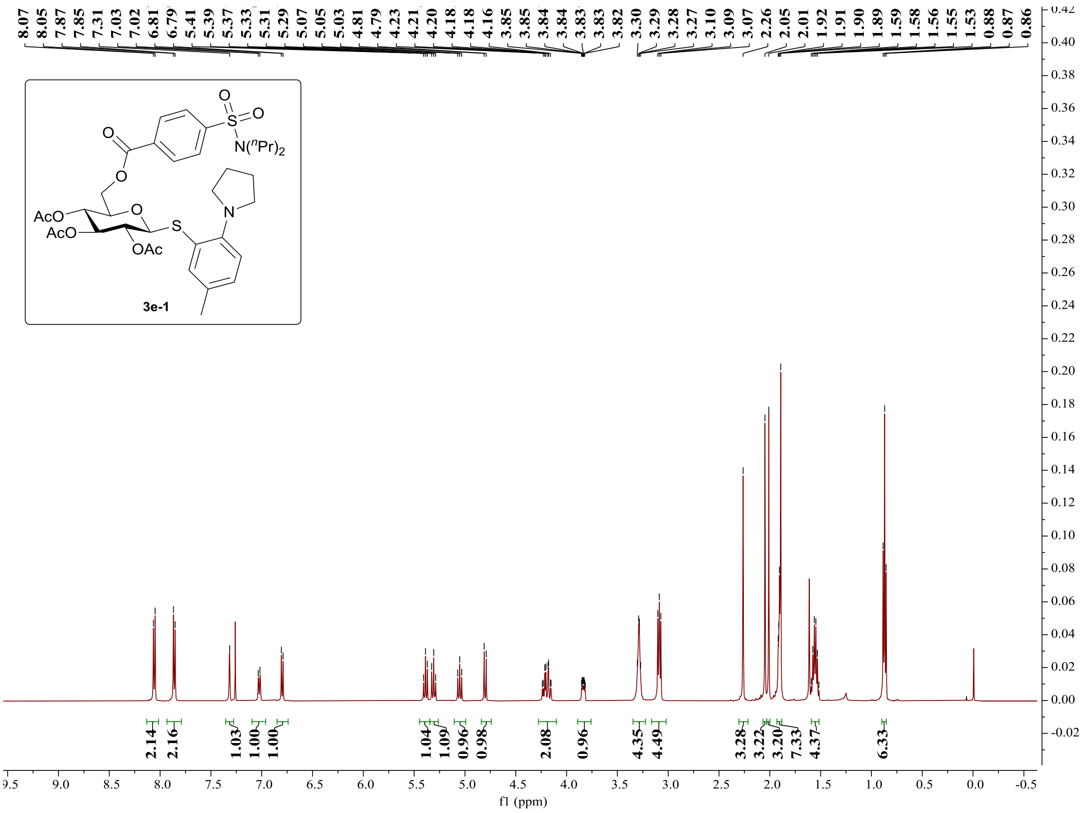
[1]H NMR of 3w-7 (CDCl$_3$, 500 MHz, 25 ℃)



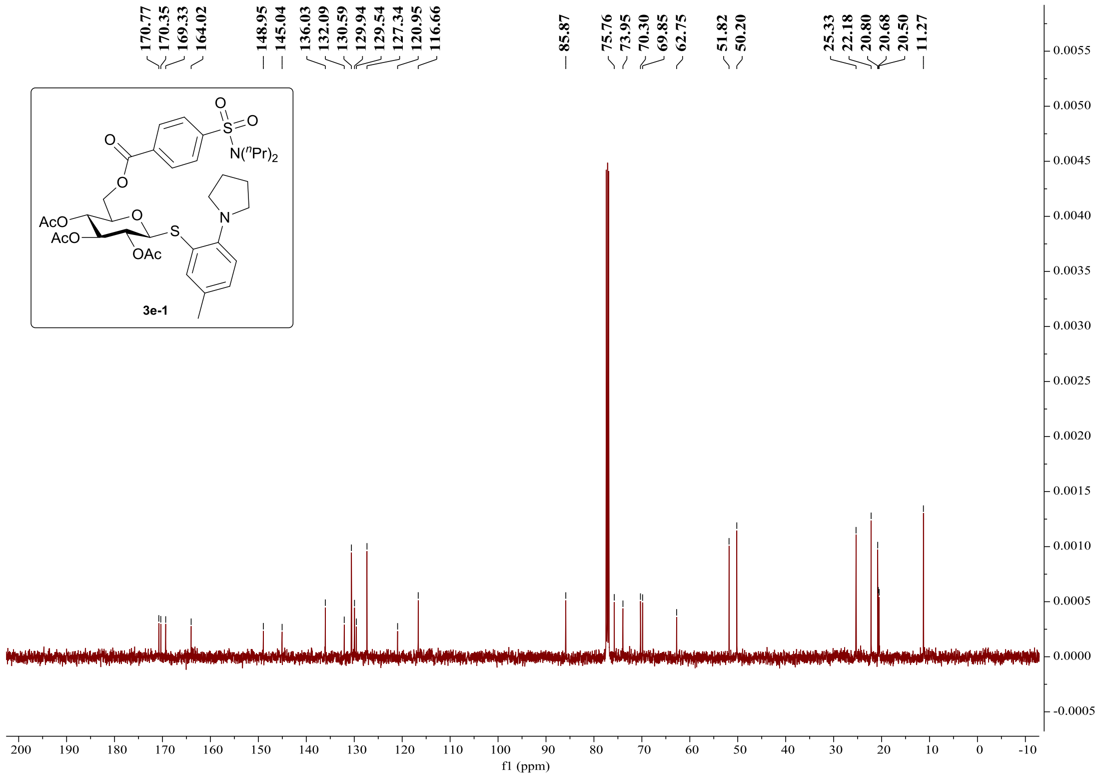
^{13}C NMR of 3w-7 ($CDCl_3$, 126 MHz, 25 ℃)



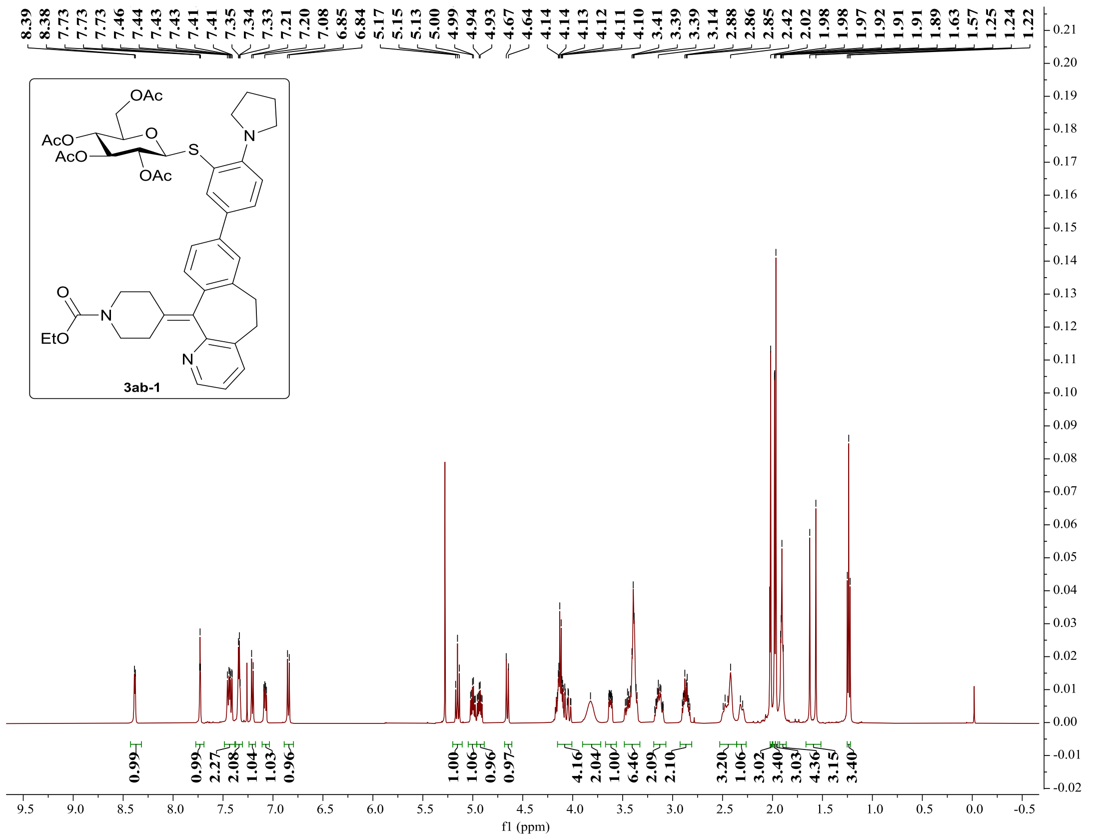
^{1}H NMR of 3e-1 ($CDCl_3$, 500 MHz, 25 ℃)



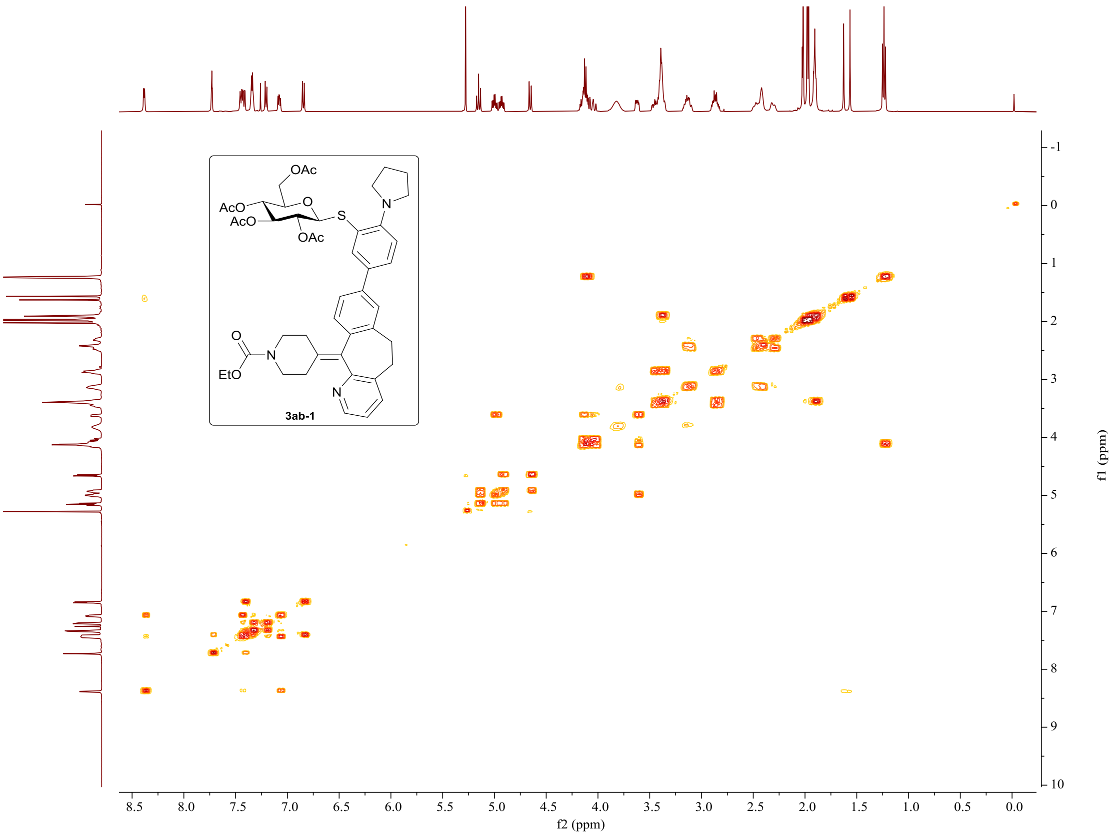
^{13}C NMR of 3e-1 (CDCl$_3$, 126 MHz, 25 ℃)



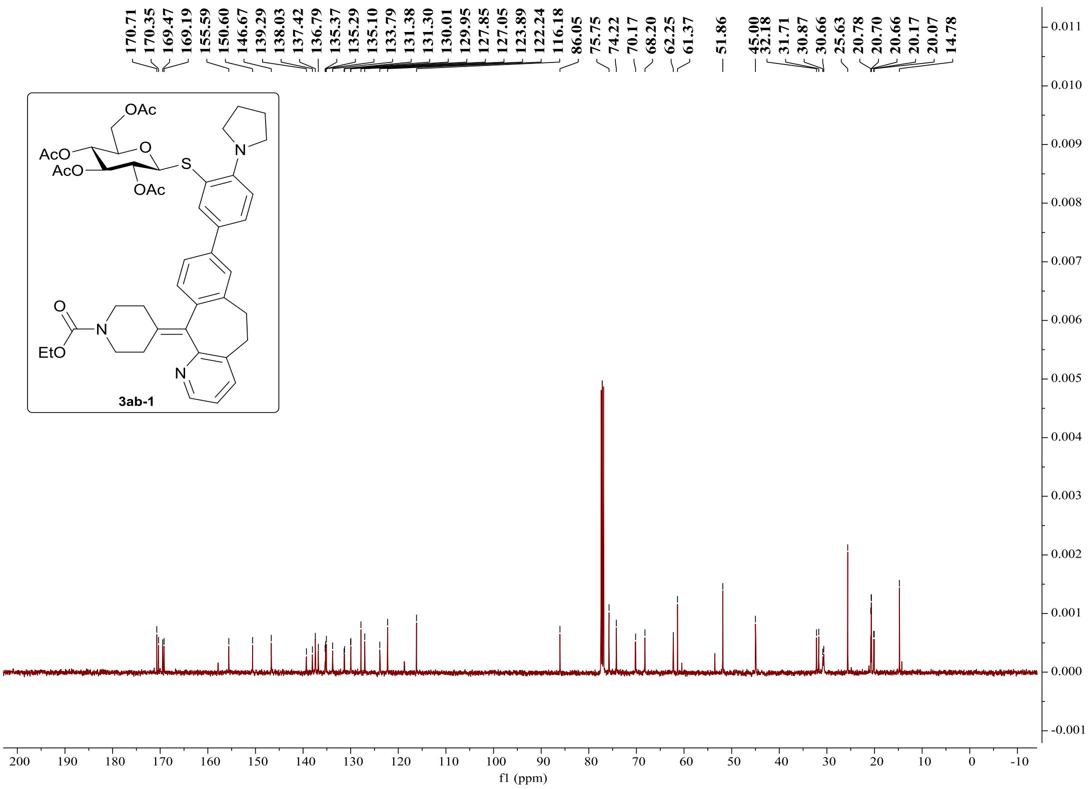
^{1}H NMR of 3ab-1 (CDCl$_3$, 500 MHz, 25 ℃)



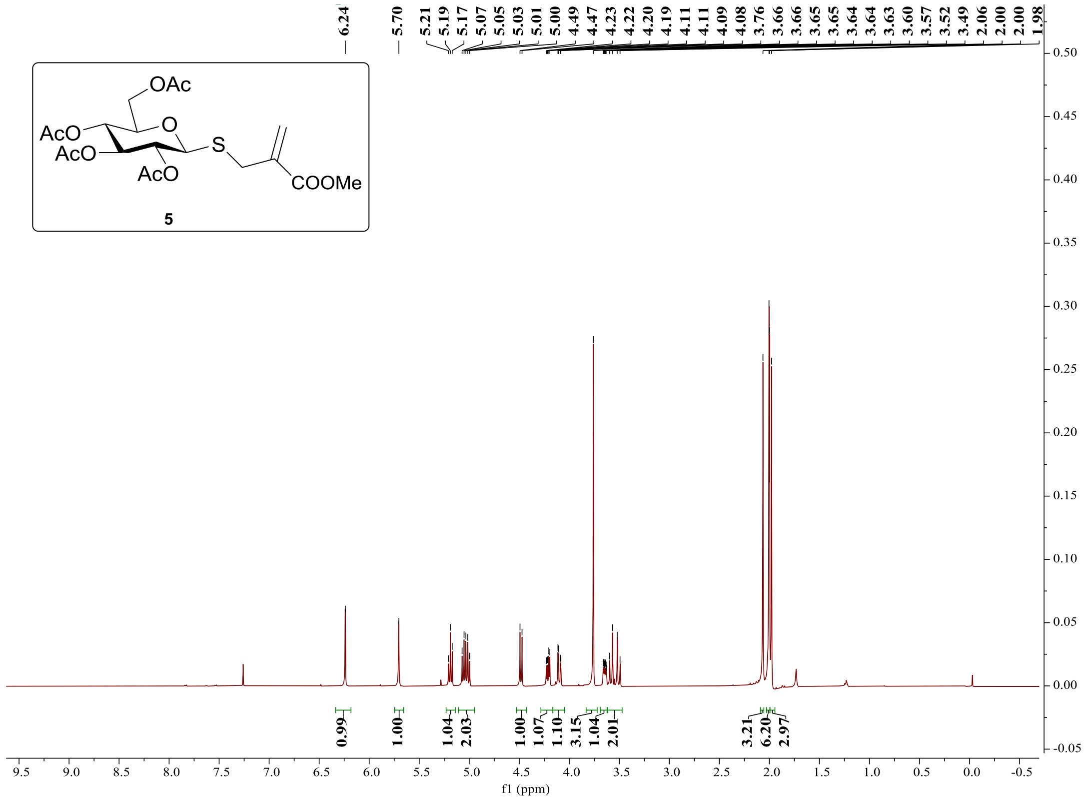
H-H COSY of 3ab-1 (CDCl$_3$, 500 MHz, 25 ℃)



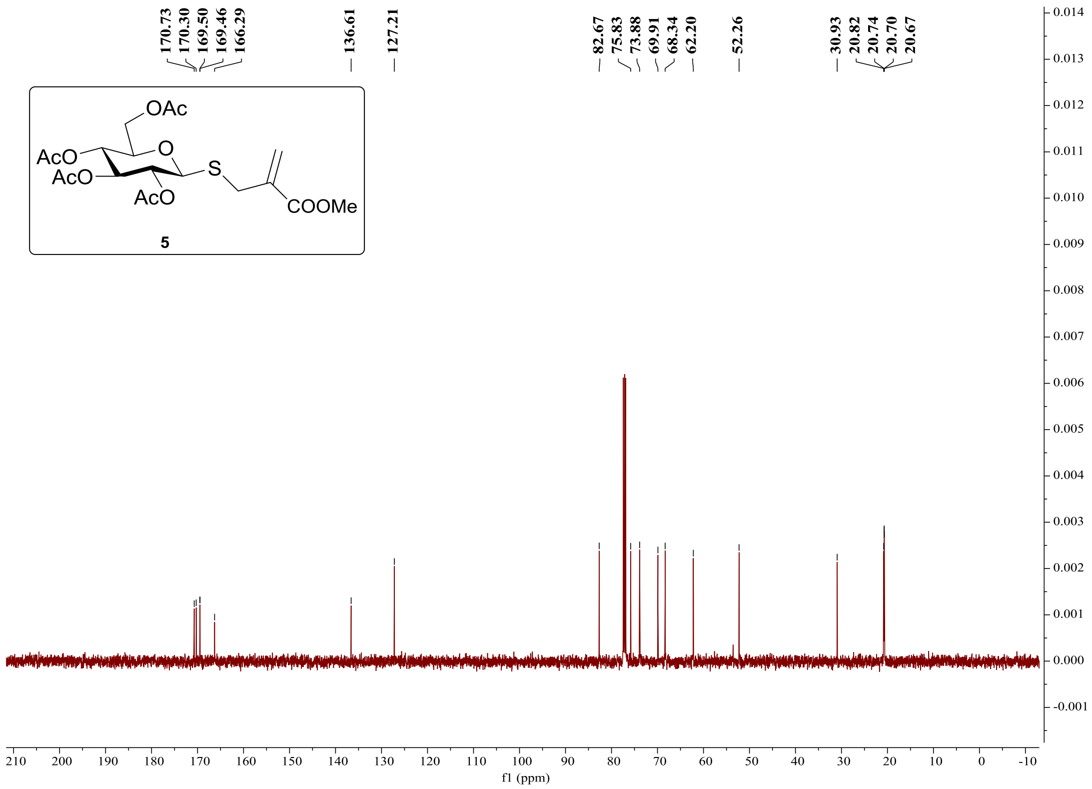
^{13}C NMR of 3ab-1 (CDCl$_3$, 126 MHz, 25 ℃)



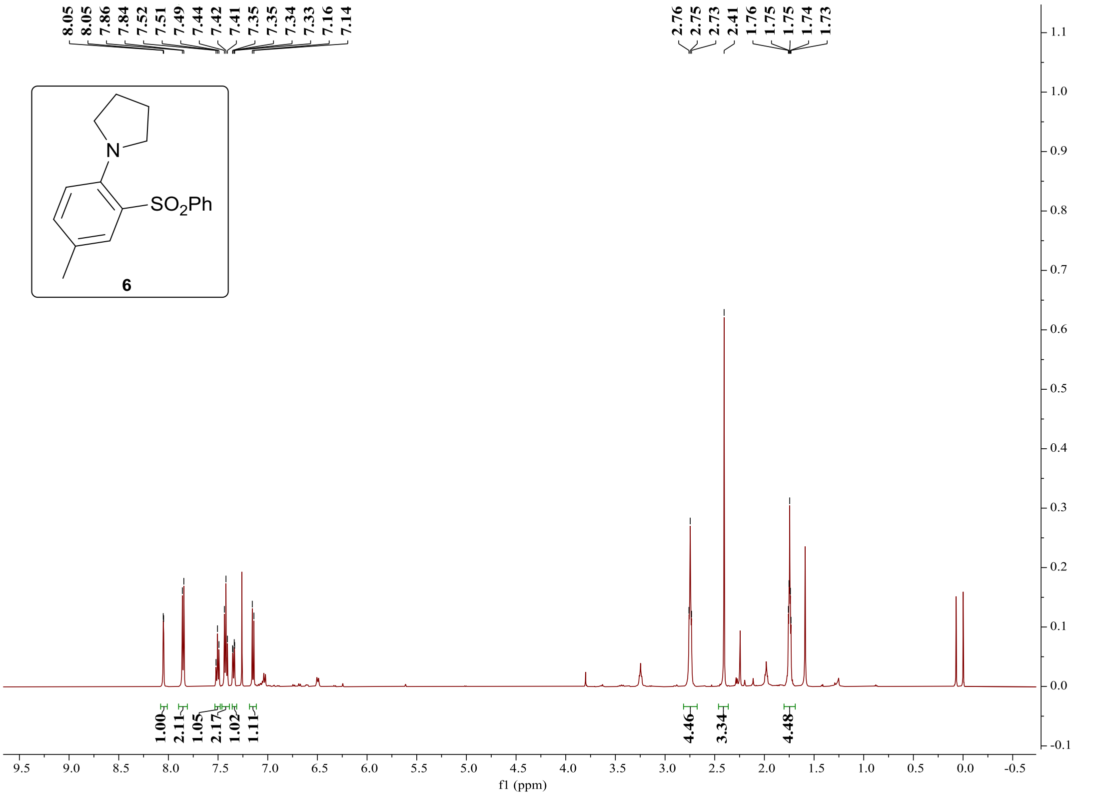
^{1}H NMR of 5 ($CDCl_3$, 500 MHz, 25 ℃)



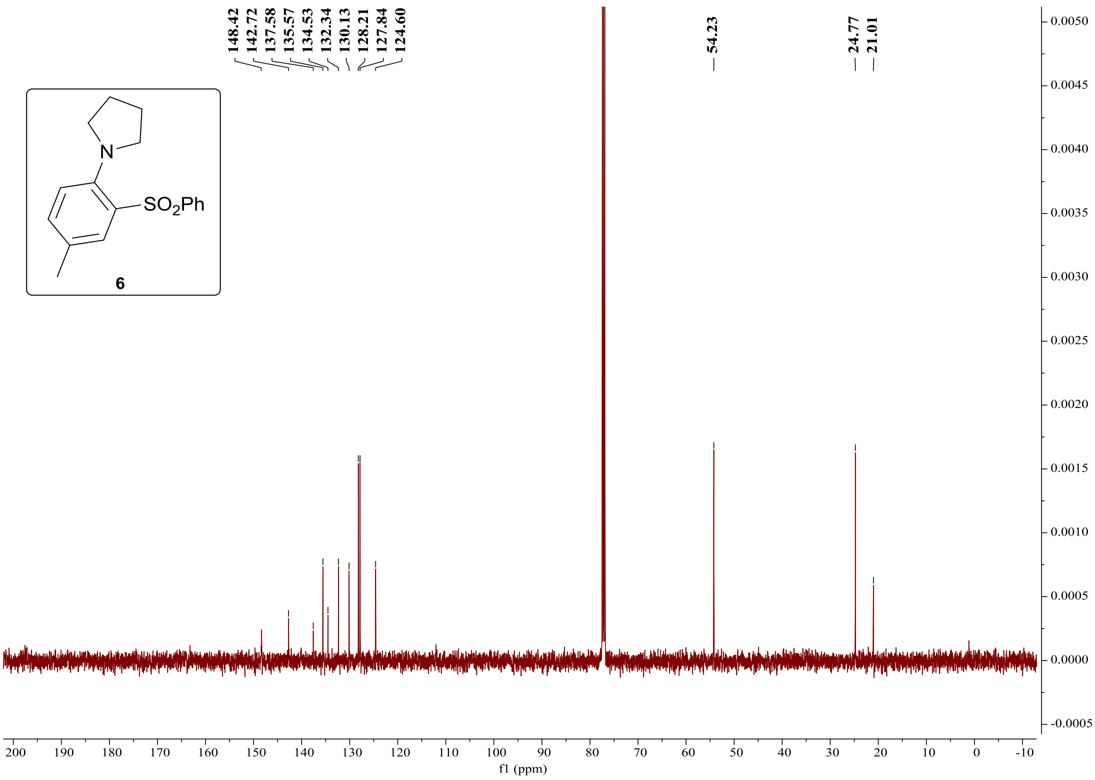
^{13}C NMR of 5 ($CDCl_3$, 126 MHz, 25 ℃)



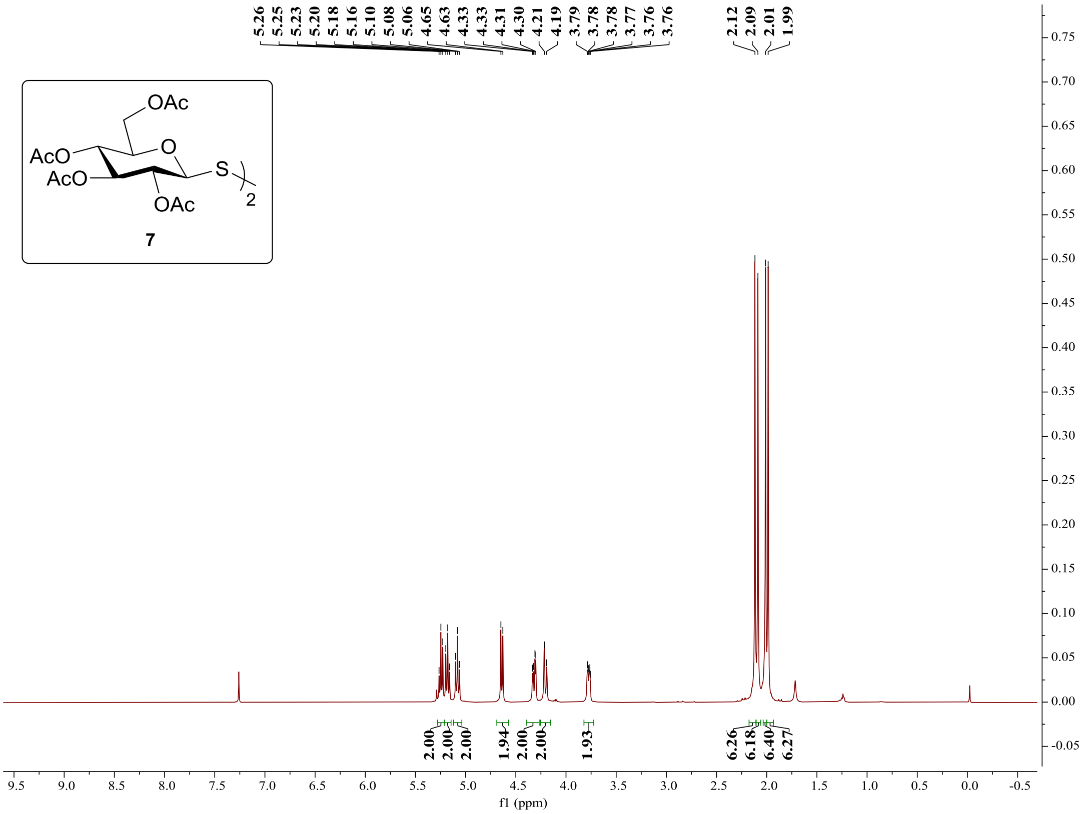
^{1}H NMR of 6 ($CDCl_3$, 500 MHz, 25 ℃)



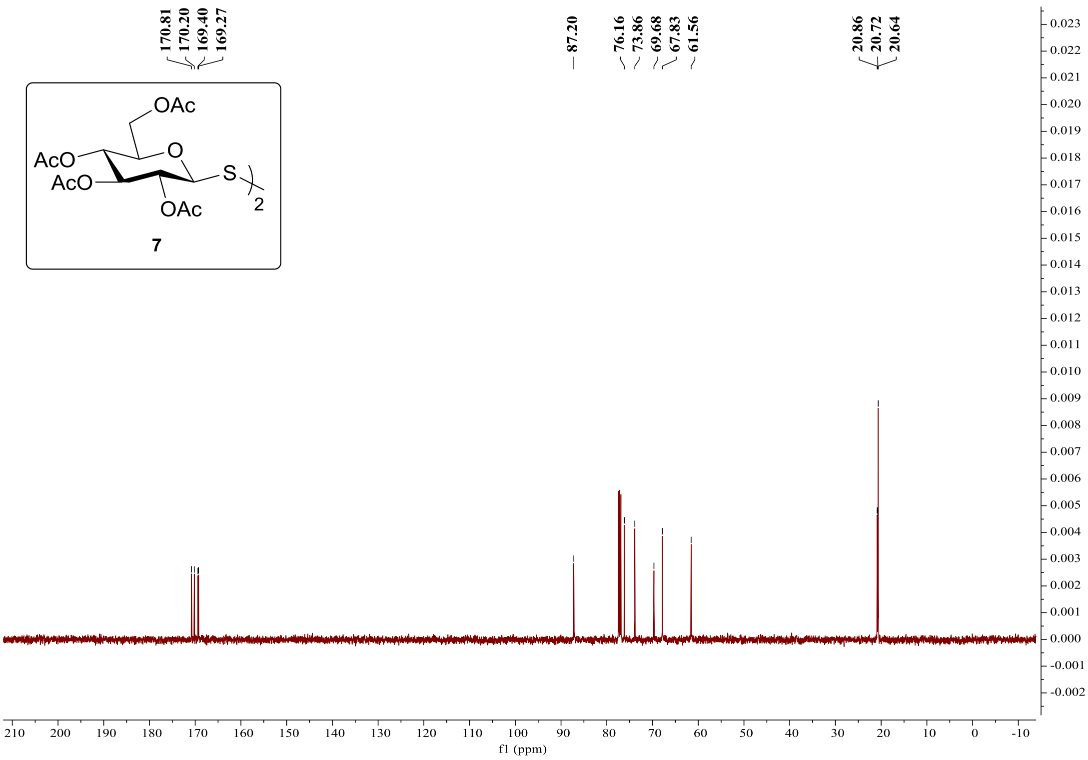
^{13}C NMR of 6 ($CDCl_3$, 126 MHz, 25 ℃)



^{1}H NMR of 7 ($CDCl_3$, 500 MHz, 25 ℃)



^{13}C NMR of 7 ($CDCl_3$, 126 MHz, 25 ℃)



14. Proof of absolute configuration

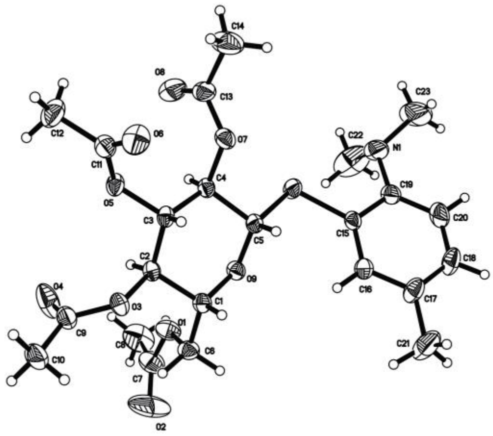


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Table S6. Crystal data and structure refinement for **3ak**.

Identification code	**3ak**	
Empirical formula	C23 H31 N O9 S	
Formula weight	497.55	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.4872(3) Å	α= 90 °.
	b = 10.4118(4) Å	β= 90 °.
	c = 29.1441(11) Å	γ = 90 °.
Volume	2575.38(17) $Å^3$	
Z	4	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	0.175 mm^{-1}	
F(000)	1056	
Crystal size	0.220 x 0.190 x 0.180 mm^3	
Theta range for data collection	2.077 to 27.520 °.	
Index ranges	-10<=h<=10, -13<=k<=12, -29<=l<=37	
Reflections collected	25923	
Independent reflections	5821 [R(int) = 0.0337]	
Completeness to theta = 25.242 °	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6919	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5821 / 0 / 314	

Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.0967
R indices (all data)	R1 = 0.0632, wR2 = 0.1046
Absolute structure parameter	0.04(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.179 and -0.210 e.Å^{-3}

Table S7. Bond lengths [Å] and angles [°] for **3ak**.

C(1)-O(9)	1.435(3)
C(1)-C(6)	1.500(4)
C(1)-C(2)	1.527(3)
C(1)-H(1)	0.9800
C(2)-O(3)	1.442(3)
C(2)-C(3)	1.507(4)
C(2)-H(2)	0.9800
C(3)-O(5)	1.441(3)
C(3)-C(4)	1.522(3)
C(3)-H(3)	0.9800
C(4)-O(7)	1.438(3)
C(4)-C(5)	1.527(3)
C(4)-H(4)	0.9800
C(5)-O(9)	1.414(3)
C(5)-S(1)	1.804(2)
C(5)-H(5)	0.9800
C(6)-O(1)	1.434(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-O(2)	1.178(5)
C(7)-O(1)	1.318(4)
C(7)-C(8)	1.472(6)
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-O(4)	1.181(4)
C(9)-O(3)	1.360(3)
C(9)-C(10)	1.475(4)
C(10)-H(10A)	0.9600

C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-O(6)	1.188(3)
C(11)-O(5)	1.358(3)
C(11)-C(12)	1.484(5)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-O(8)	1.187(4)
C(13)-O(7)	1.350(4)
C(13)-C(14)	1.494(5)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.383(4)
C(15)-C(19)	1.404(4)
C(15)-S(1)	1.769(3)
C(16)-C(17)	1.389(4)
C(16)-H(16)	0.9300
C(17)-C(18)	1.376(5)
C(17)-C(21)	1.499(5)
C(18)-C(20)	1.359(5)
C(18)-H(18)	0.9300
C(19)-C(20)	1.388(4)
C(19)-N(1)	1.422(4)
C(20)-H(20)	0.9300
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-N(1)	1.474(7)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-N(1)	1.451(5)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

O(9)-C(1)-C(6)	106.64(19)
O(9)-C(1)-C(2)	109.64(19)
C(6)-C(1)-C(2)	112.0(2)
O(9)-C(1)-H(1)	109.5
C(6)-C(1)-H(1)	109.5
C(2)-C(1)-H(1)	109.5
O(3)-C(2)-C(3)	108.69(18)
O(3)-C(2)-C(1)	106.82(19)
C(3)-C(2)-C(1)	111.76(19)
O(3)-C(2)-H(2)	109.8
C(3)-C(2)-H(2)	109.8
C(1)-C(2)-H(2)	109.8
O(5)-C(3)-C(2)	107.10(18)
O(5)-C(3)-C(4)	108.9(2)
C(2)-C(3)-C(4)	109.63(18)
O(5)-C(3)-H(3)	110.4
C(2)-C(3)-H(3)	110.4
C(4)-C(3)-H(3)	110.4
O(7)-C(4)-C(3)	108.69(19)
O(7)-C(4)-C(5)	108.64(19)
C(3)-C(4)-C(5)	110.6(2)
O(7)-C(4)-H(4)	109.6
C(3)-C(4)-H(4)	109.6
C(5)-C(4)-H(4)	109.6
O(9)-C(5)-C(4)	108.81(19)
O(9)-C(5)-S(1)	109.34(16)
C(4)-C(5)-S(1)	106.56(17)
O(9)-C(5)-H(5)	110.7
C(4)-C(5)-H(5)	110.7
S(1)-C(5)-H(5)	110.7
O(1)-C(6)-C(1)	107.3(2)
O(1)-C(6)-H(6A)	110.2
C(1)-C(6)-H(6A)	110.2
O(1)-C(6)-H(6B)	110.2
C(1)-C(6)-H(6B)	110.2
H(6A)-C(6)-H(6B)	108.5
O(2)-C(7)-O(1)	122.4(4)
O(2)-C(7)-C(8)	124.5(4)

O(1)-C(7)-C(8)	113.1(3)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(4)-C(9)-O(3)	122.6(3)
O(4)-C(9)-C(10)	125.3(3)
O(3)-C(9)-C(10)	112.1(3)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(6)-C(11)-O(5)	123.8(3)
O(6)-C(11)-C(12)	125.8(3)
O(5)-C(11)-C(12)	110.4(3)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(8)-C(13)-O(7)	123.6(3)
O(8)-C(13)-C(14)	126.3(3)
O(7)-C(13)-C(14)	110.0(3)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(19)	119.7(2)
C(16)-C(15)-S(1)	124.75(19)
C(19)-C(15)-S(1)	115.5(2)
C(15)-C(16)-C(17)	121.2(3)

C(15)-C(16)-H(16)	119.4
C(17)-C(16)-H(16)	119.4
C(18)-C(17)-C(16)	118.2(3)
C(18)-C(17)-C(21)	120.9(3)
C(16)-C(17)-C(21)	120.9(3)
C(20)-C(18)-C(17)	121.3(3)
C(20)-C(18)-H(18)	119.3
C(17)-C(18)-H(18)	119.3
C(20)-C(19)-C(15)	117.9(3)
C(20)-C(19)-N(1)	124.4(3)
C(15)-C(19)-N(1)	117.7(3)
C(18)-C(20)-C(19)	121.5(3)
C(18)-C(20)-H(20)	119.3
C(19)-C(20)-H(20)	119.3
C(17)-C(21)-H(21A)	109.5
C(17)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(17)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(1)-C(22)-H(22A)	109.5
N(1)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
N(1)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
N(1)-C(23)-H(23A)	109.5
N(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
N(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(19)-N(1)-C(23)	115.2(4)
C(19)-N(1)-C(22)	113.0(3)
C(23)-N(1)-C(22)	110.2(4)
C(7)-O(1)-C(6)	118.6(3)
C(9)-O(3)-C(2)	118.0(2)
C(11)-O(5)-C(3)	119.4(2)

C(13)-O(7)-C(4)	118.0(2)
C(5)-O(9)-C(1)	113.84(17)
C(15)-S(1)-C(5)	104.68(12)

Symmetry transformations used to generate equivalent atoms:

Table S8. Torsion angles [°] for **3ak**.

O(9)-C(1)-C(2)-O(3)	-172.62(18)
C(6)-C(1)-C(2)-O(3)	69.2(3)
O(9)-C(1)-C(2)-C(3)	-53.9(3)
C(6)-C(1)-C(2)-C(3)	-172.0(2)
O(3)-C(2)-C(3)-O(5)	-72.4(2)
C(1)-C(2)-C(3)-O(5)	169.96(19)
O(3)-C(2)-C(3)-C(4)	169.6(2)
C(1)-C(2)-C(3)-C(4)	51.9(3)
O(5)-C(3)-C(4)-O(7)	70.1(2)
C(2)-C(3)-C(4)-O(7)	-173.01(19)
O(5)-C(3)-C(4)-C(5)	-170.72(18)
C(2)-C(3)-C(4)-C(5)	-53.8(3)
O(7)-C(4)-C(5)-O(9)	177.30(19)
C(3)-C(4)-C(5)-O(9)	58.1(3)
O(7)-C(4)-C(5)-S(1)	-64.9(2)
C(3)-C(4)-C(5)-S(1)	175.88(16)
O(9)-C(1)-C(6)-O(1)	-54.7(3)
C(2)-C(1)-C(6)-O(1)	65.2(3)
C(19)-C(15)-C(16)-C(17)	2.2(4)
S(1)-C(15)-C(16)-C(17)	-176.5(2)
C(15)-C(16)-C(17)-C(18)	1.2(5)
C(15)-C(16)-C(17)-C(21)	-178.2(4)
C(16)-C(17)-C(18)-C(20)	-2.2(6)
C(21)-C(17)-C(18)-C(20)	177.2(4)
C(16)-C(15)-C(19)-C(20)	-4.6(4)
S(1)-C(15)-C(19)-C(20)	174.3(2)
C(16)-C(15)-C(19)-N(1)	174.1(3)
S(1)-C(15)-C(19)-N(1)	-7.0(4)
C(17)-C(18)-C(20)-C(19)	-0.2(6)
C(15)-C(19)-C(20)-C(18)	3.6(5)

N(1)-C(19)-C(20)-C(18)	-174.9(4)
C(20)-C(19)-N(1)-C(23)	-29.5(6)
C(15)-C(19)-N(1)-C(23)	151.9(4)
C(20)-C(19)-N(1)-C(22)	98.5(4)
C(15)-C(19)-N(1)-C(22)	-80.1(4)
O(2)-C(7)-O(1)-C(6)	4.8(6)
C(8)-C(7)-O(1)-C(6)	-174.2(3)
C(1)-C(6)-O(1)-C(7)	-175.7(3)
O(4)-C(9)-O(3)-C(2)	-3.0(4)
C(10)-C(9)-O(3)-C(2)	177.1(2)
C(3)-C(2)-O(3)-C(9)	116.9(2)
C(1)-C(2)-O(3)-C(9)	-122.4(2)
O(6)-C(11)-O(5)-C(3)	-5.0(4)
C(12)-C(11)-O(5)-C(3)	173.9(3)
C(2)-C(3)-O(5)-C(11)	146.5(2)
C(4)-C(3)-O(5)-C(11)	-95.0(3)
O(8)-C(13)-O(7)-C(4)	-0.8(4)
C(14)-C(13)-O(7)-C(4)	178.2(2)
C(3)-C(4)-O(7)-C(13)	-103.4(3)
C(5)-C(4)-O(7)-C(13)	136.2(2)
C(4)-C(5)-O(9)-C(1)	-62.4(3)
S(1)-C(5)-O(9)-C(1)	-178.39(17)
C(6)-C(1)-O(9)-C(5)	-178.3(2)
C(2)-C(1)-O(9)-C(5)	60.2(3)
C(16)-C(15)-S(1)-C(5)	12.9(3)
C(19)-C(15)-S(1)-C(5)	-165.9(2)
O(9)-C(5)-S(1)-C(15)	-78.09(19)
C(4)-C(5)-S(1)-C(15)	164.47(16)

Symmetry transformations used to generate equivalent atoms:

Table S9. Hydrogen bonds for **3ak** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(10)-H(10A)...O(2)#1	0.96	2.40	3.266(5)	150.0
C(12)-H(12B)...O(4)#1	0.96	2.48	3.272(5)	139.4
C(16)-H(16)...O(9)	0.93	2.62	3.267(3)	127.2

C(22)-H(22C)...S(1)	0.96	2.79	3.281(5)	112.6

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,-z+1