Supporting Information for

Modular Synthesis of Glycosyl Sulfonamide via Reductive Coupling of Glycosyl Sulfinate and Nitroarene

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Content

1. General information

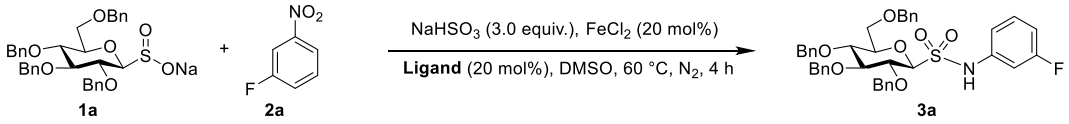
Unless otherwise stated, all reactions were set up under inert atmosphere (N_2) utilizing glassware that were oven dried and cooled under nitrogen purging. Silica Gel Flash Column Chromatography was performed on deactivated silica gel (particle size 300-400 mesh). Starting materials were purchased directly from commercial suppliers (Sigma Aldrich, Energy Chemical, Bidepharm, Tansoole) and used without further purifications unless otherwise stated. All solvents were dried according to standard procedures or brought from commercial suppliers. Reactions were monitored using thin-layer chromatography (TLC) with F254 indicator. Visualization of the developed plates was performed under UV light (254 nm) or H_2SO_4-EtOH (10% H_2SO_4 v/v).

^{1}H NMR, ^{13}C NMR were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane. Because of the special structure of sugar, the ^{13}C NMR chemical shifts retain two decimal places. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26 ppm), ^{13}C NMR ($CDCl_3$ δ 77.16 ppm), ^{1}H NMR (DMSO-d_6 δ 2.50 ppm), ^{13}C NMR (DMSO-d_6 δ 39.50 ppm), ^{1}H NMR (CD_3OD δ 4.87 ppm), ^{13}C NMR (CD_3OD δ 49.00 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS data was recorded using HRMR Exactive Plus instrument. Melting point was measured using SGW X-4A instrument.

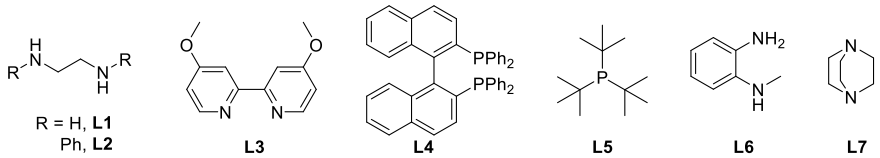
2. General procedure for optimization (Procedure A) (see Table S1 to S6)

In a glove box filled with nitrogen, to an oven-dried 10 mL tube equipped with a stirring bar were added **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), reductant, solvent (1 mL), catalyst and ligand. The tube was sealed with a Teflon screw cap and the mixture was stirred at dedicated temperature. Upon completion, the yield was determined by ^{1}H NMR spectroscopy analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S1: Effect of Ligand

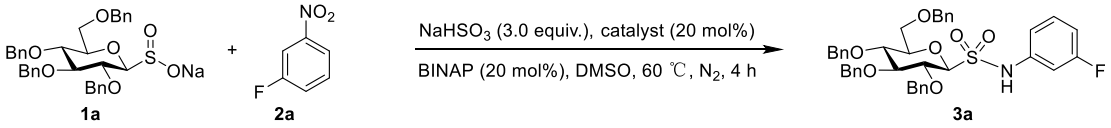


Entry	Ligand	Yield (%)[b]
1	**L1**	52
2	**L2**	77
3	**L3**	69
4	**L4**	85
5	**L5**	76
6	**L6**	32
7	**L7**	84



[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.) DMSO (1 mL), $FeCl_2$ (0.01 mmol, 20 mol%), Ligand (0.01 mmol, 20 mol%), under N_2 atmosphere, 4 h, 60 ℃; [b]Yields were determined by ^{1}H NMR spectroscopy analysis using 1,3,5-trimethoxybenzene as an internal standard.

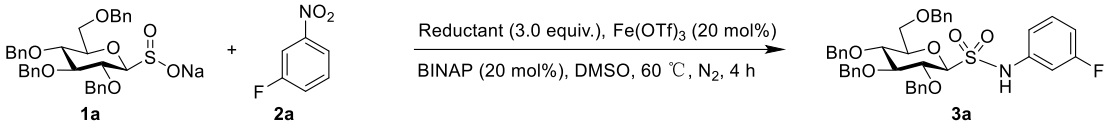
Table S2: Effect of catalyst



Entry	Catalyst	Yield (%)[b]
1	FeF_3	64
2	$Fe(acac)_3$	84
3	$Fe(OTf)_3$	91
4	$FeCl_3$	78
5	FePc	63
6	$Fe(OAc)_2$	85
7	$Fe(NO_3)_3·9H_2O$	81
8	$FePO_4$	47
9	$FeBr_2$	74
10	CuCl	60[c]

[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.) DMSO (1 mL), catalyst (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%), under N_2 atmosphere, 4 h, 60 ℃; [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield. FePc = Iron phthalocyanine.

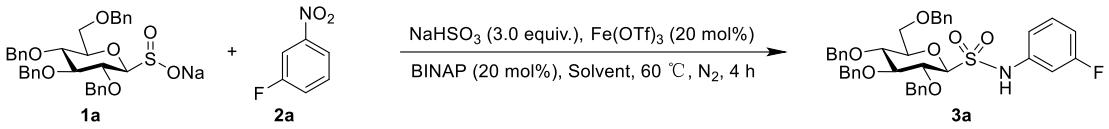
Table S3: Effect of reductant



Entry	Reductant	Yield (%)[b]
1	$NaBH_3CN$	n.d.
2	$NaBH_4$	n.d.
3	KBH_4	n.d.
4	$(i\text{-}Bu)_2AlH$	n.d.
5	NaHS	n.d.
6	$(CH_3CH_2)_3SiH$	n.d.

[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), Reductant (0.15 mmol, 3.0 equiv.) DMSO (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%), under N_2 atmosphere, 4 h, 60 ℃; [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. n.d. = not determined.

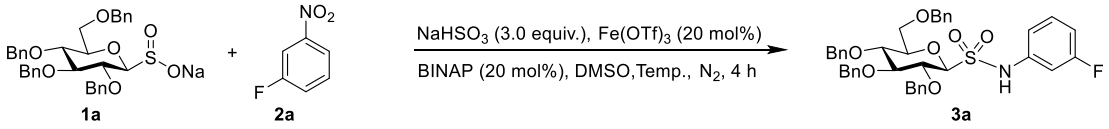
Table S4: Effect of solvent



Entry	Solvent	Yield (%)[b]
1	DMF	15
2	DMA	trace
3	THF	n.d.
4	CH_3CN	trace
5	CH_3OH	trace
6	toluene	n.d.
7	CH_2Cl_2	n.d.
8	EtOAc	trace

[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.) solvent (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%), under N_2 atmosphere, 4 h, 60 ℃; [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. n.d. = not determined.

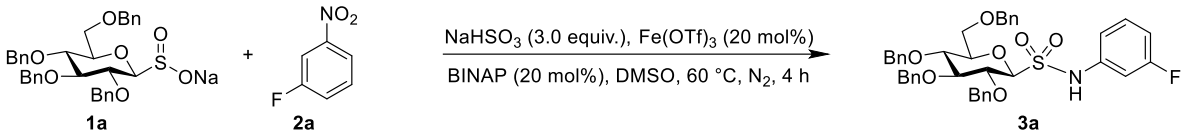
Table S5: Effect of temperature



Entry	Temp.(℃)	Yield (%)[b]
1	40	56
2	80	78
3	100	30

[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.) DMSO (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%), under N_2 atmosphere, 4 h; [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

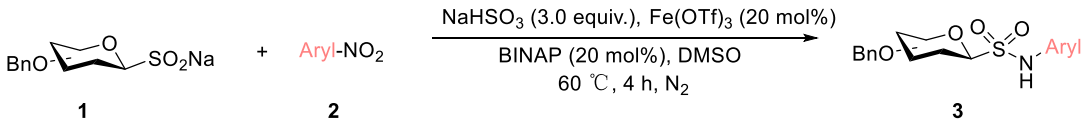
Table S6: Control experiments



Entry	Variation from standard conditions	Yield (%)[b]
1	**1a**:**2a** (1:1.2)	85
2	BINAP (10)	67
3	$Fe(OTf)_3$ (10)	66
4	$NaHSO_3$ (1.0 equiv.)	71
5	No BINAP	75
6	No $Fe(OTf)_3$	31
7	No $NaHSO_3$	n.d.
8	Air conditions	68

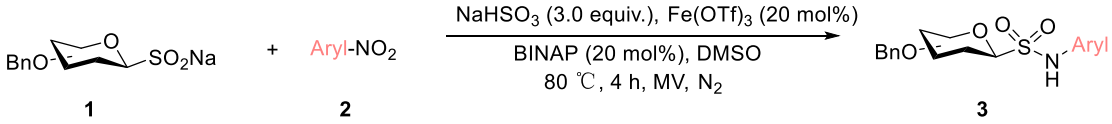
[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.) DMSO (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%), under N_2 atmosphere, 4 h, 60 ℃; [b]yield were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. n.d. = not determined.

3. General procedure for synthesis of glycosyl sulfonamide (Procedure B)



In a glove box filled with nitrogen, to an oven-dried 10 mL tube equipped with a stirring bar were added **1** (0.15 mmol, 1.5 equiv.), **2** (0.1 mmol, 1.0 equiv.), $NaHSO_3$ (0.3 mmol, 3.0 equiv.), DMSO (1 mL), $Fe(OTf)_3$ (0.02 mmol, 20 mol%), BINAP (0.02 mmol, 20 mol%). The tube was sealed with a Teflon screw cap and the mixture was stirred at 60 ℃ for 4 h. Upon completion, the reaction was extracted with ethyl acetate (3 times). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. And the residue was purified by silica gel chromatography to give the desired glycosylsulfonamide.

4. General procedure for synthesis of glycosyl sulfonamide (Procedure C)

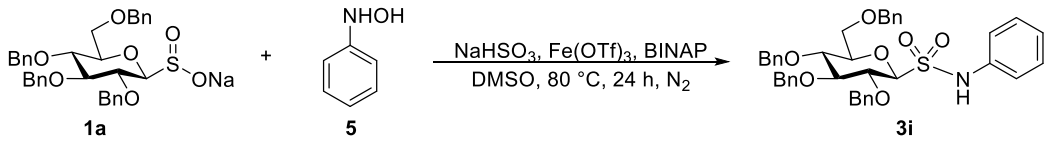


In a glove box filled with nitrogen, to an oven-dried 10 mL tube equipped with a stirring bar were

added **1** (0.15 mmol, 1.5 equiv.), **2** (0.1 mmol, 1.0 equiv.), $NaHSO_3$ (0.3 mmol, 3.0 equiv.), DMSO (1 mL), $Fe(OTf)_3$ (0.02 mmol, 20 mol%), BINAP (0.02 mmol, 20 mol%). The tube was sealed with a Teflon screw cap and the mixture was heated with microwave irradiation at 80 ℃ for 4 h. Upon completion, the reaction was extracted with ethyl acetate (3 times). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. And the residue was purified by silica gel chromatography to give the desired glycosylsulfonamide.

5. Mechanistic studies and proposed mechanism

5.1 Reaction of 1a with *N*-phenylhydroxylamine

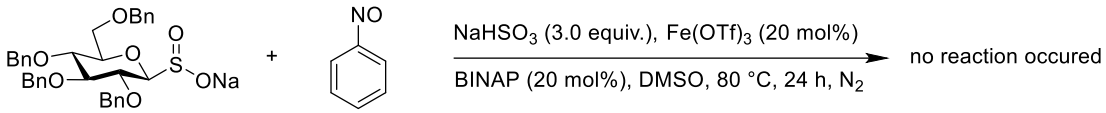


1a **5** **3i**

Entry	$NaHSO_3$ (equiv.)	$Fe(OTf)_3$ (mol%)	BINAP (mol%)	Yield (%)[b]
1	20	20	20	12
2	20	none	none	n.d.

In a glove box filled with nitrogen, to an oven-dried 10 mL tube equipped with a stirring bar were added **1a** (0.075 mmol, 1.5 equiv.), **5** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15~1 mmol, 3.0~20 equiv.), DMSO (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%). The tube was sealed with a Teflon screw cap and the mixture was stirred at 80 ℃ for 24 h. Upon completion, the reaction was extracted with ethyl acetate (3 times). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. And the residue was purified by silica gel chromatography to give the desired glycosylsulfonamide.

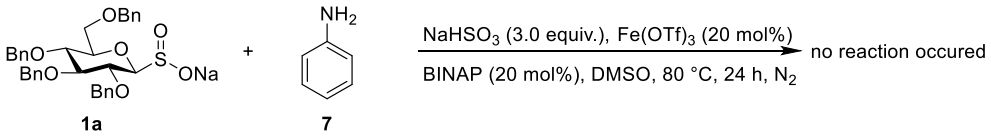
5.2. Reaction of 1a with nitrosobenzene



1a **6**

In a glove box filled with nitrogen, to an oven-dried 10 mL tube equipped with a stirring bar were added **1a** (0.075 mmol, 1.5 equiv.), **6** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.), DMSO (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%). The tube was sealed with a Teflon screw cap and the mixture was stirred at 80 ℃ for 24 h.

5.3. Reaction of 1a with aniline



In a glove box filled with nitrogen, to an oven-dried 10 mL tube equipped with a stirring bar were added **1a** (0.075 mmol, 1.5 equiv.), **7** (0.05 mmol, 1.0 equiv.), $NaHSO_3$ (0.15 mmol, 3.0 equiv.), DMSO (1 mL), $Fe(OTf)_3$ (0.01 mmol, 20 mol%), BINAP (0.01 mmol, 20 mol%). The tube was sealed with a Teflon screw cap and the mixture was stirred at 80 ℃ for 24 h.

5.4. Proposed mechanism

Based on the amalgamation of experimental results and the reported findings[1, 2], there are two possible pathways for the synthesis of glycosyl sulfonamide. In path a, initially, there is an electrostatic interaction between glycosyl sulfinate and the iron complex, forming the intermediate **A**. This interaction is crucial as the iron complex likely acts as a Lewis acid, facilitating the subsequent nucleophilic attack on the nitro group. As a result, a five membered intermediate **B** is formed. This intermediate is then reduced by $NaHSO_3$, resulting in the formation of **D**, along with the regeneration of the iron catalyst. Further reduction of **D** by $NaHSO_3$ afforded the desired glycosyl sulfonamide **3**. Alternatively, in path b, the nitroarene is directly reduced to *N*-phenylhydroxylamine, which is subsequently further converted to the final product promoted by iron catalyst.

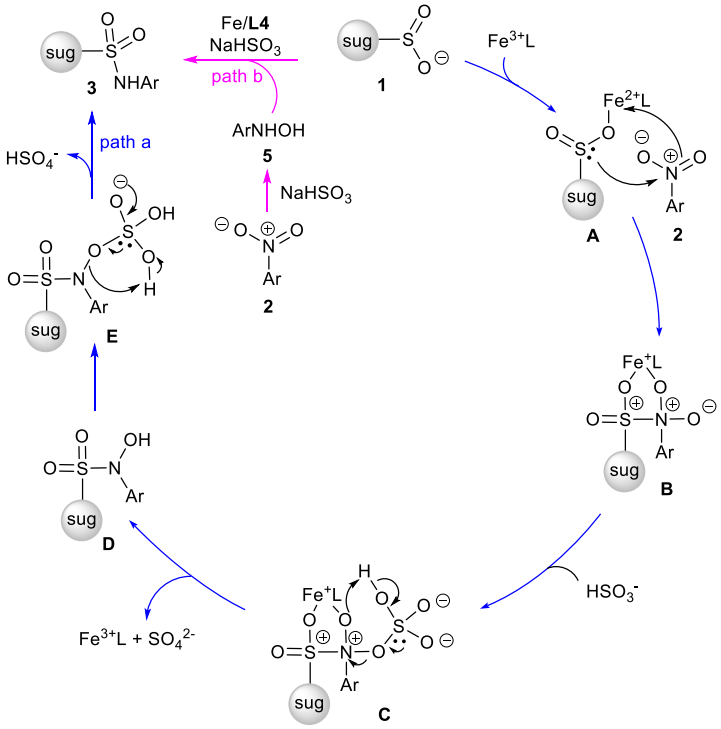
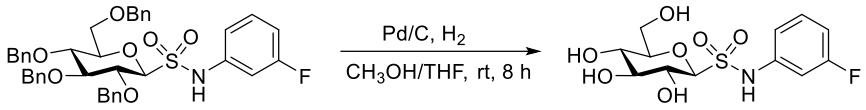


Figure S1. Plausible Mechanism

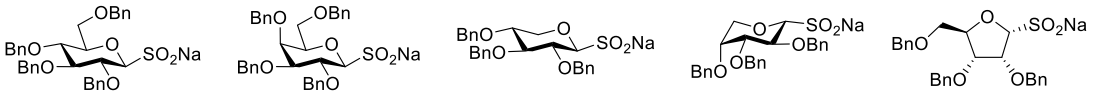
6. General procedure for debenzylation (Procedure D)



3a **4**

A suspension of **3a** (69.7 mg, 0.01 mmol) and Pd/C (5%, 86 mg) in MeOH/THF (1:1, 2 mL) was stirred at RT under hydrogen gas for 8 h. The combination was filtered via Celite, then concentrated to give a residue. The residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH, 10:1) to give the compound **4**.[3]

7. Library of glycosyl sulfinates



1a 1b 1c 1d 1e

Figure S2. Library of glycosyl sulfinates

General procedure for synthesis of glycosyl sulfinate (Procedure E)

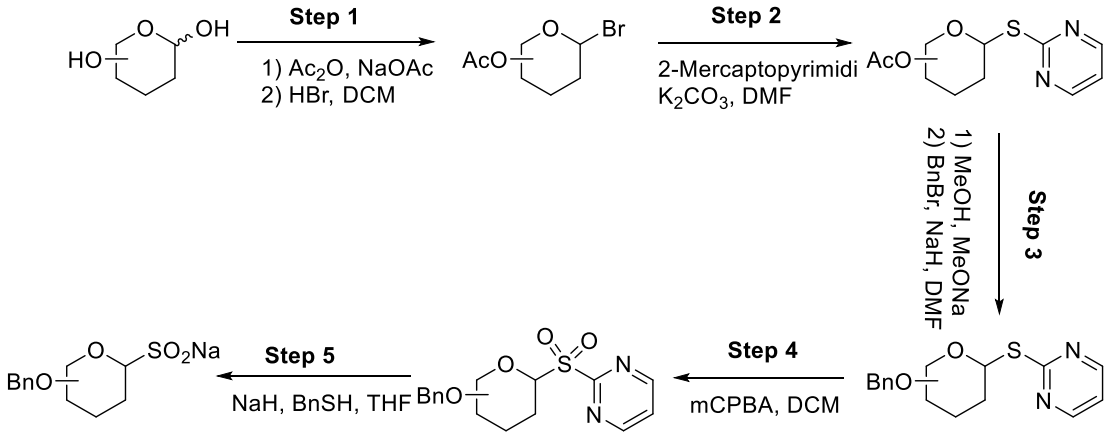


Figure S3. Synthetic route of glycosyl sulfinate

Step 1: Synthesis of glycosyl bromide

Sugar substrate (1.0 equiv.) and sodium acetate (1.1 equiv.) were dissolved in acetic anhydride (0.6 M). The reaction mixture was heated to 90°C and stirred for 5 hours. Then the mixture was poured into cold water. The water layer was extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was obtained and used directly without further purification. Crude acetylated glycoside was dissolved in CH_2Cl_2 (0.5 M) at 0 °C. Then, HBr (30% acetic acid solution, 4.5 equiv..) was slowly added and the resulting mixture was stirred at room temperature for 12 hours. Upon completion, the mixture was poured into ice water and extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with saturated $NaHCO_3$, dried with Na_2SO_4, and concentrated under rotary evaporator. The residue was obtained and used directly without further purification.

Step 2: Reaction with 2-thiopyrimidine

Under nitrogen atmosphere, 2-thiopyrimidine (1.5 equiv.), potassium carbonate (8.0 equiv.) and DMF (0.3 M) were added to a reaction flask and the mixture was stirred at 40 °C for 30 minutes. Afterwards, a DMF solution of acetylated glycosyl bromide (1.0 equiv.) was added to a reaction flask and stirred for another 12 hours. Upon completion, the reaction was quenched with water and extracted with CH_2Cl_2 (3 times). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. And the residue was purified by silica gel chromatography to give the desired thioglycoside.

Step 3: Benzylation

Sodium methoxide (0.2 equiv.) and acetylated thioglycoside (1.0 equiv.) (Obtained from step 2) were dissolved in methanol (0.25 M), and the mixture was stirred at room temperature for 2 hours. Upon completion, the mixture was concentrated under reduced pressure and further dried under vacuum. Then, the residue was dissolved in DMF (0.25 M) at 0 ℃, and NaH (8.0 equiv.) was added in batches. Afterwards, benzyl bromide (8.0 equiv.) was added dropwise at same temperature, and the reaction was allowed to warm up to room temperature (25 ℃) and stirred for 12 hours. The reaction was then quenched by water and extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with water (3 times), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give the benzylated thioglycoside.

Step 4: Oxidation

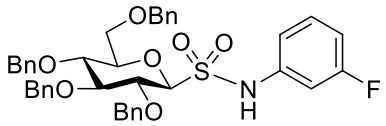
m-CPBA (3.0 equiv.) in a round bottom flask was dried under vacuum. To the flask was added a CH_2Cl_2 (0.05 M) solution of acetylated thioglycoside (1.0 equiv.) (Obtained from step 2) at 0 °C. The temperature was warmed to room temperature. After stirring for 4 hours, the reaction mixture was treated with 1 M Na_2SO_3 and saturated aqueous $NaHSO_3$ at room temperature. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography eluent: hexane/EtOAc = 1:2 to give the sulfone product.

Step 5: Removal of pyrimidine moiety

Under nitrogen atmosphere, NaH (3.0 equiv.) was dissolved in THF (0.5M) at 0 ℃, and BnSH (0.3 - 1.0 equiv.) was added dropwise. After that, a THF solution of sulfone product (Obtained from step 4) was added and the resulting mixture was stirred at 0 ℃ for 2 hours and then warmed up to room temperature for several hours until completion of sugar substrate. Afterwards, the mixture was concentrated under reduced pressure. The resulting residue was washed with petroleum ether and ethyl acetate, and dried under vacuum to give the sodium glycosyl sulfinate.

Compounds **1a-1e** were synthesized according to the literature.[4]

8. Experimental characterization data



3a

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(3-fluorophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3a)

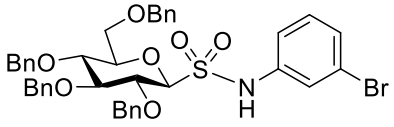
3a was synthesized according to the general procedure B and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (63.4 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.19 (m, 18H), 7.13-7.07 (m, 2H), 6.97 (d, *J* = 10.1 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 8.3 Hz, 2H), 4.88 (t, *J* = 9.9 Hz, 2H), 4.82-4.71 (m, 3H), 4.51-4.43 (m, 3H), 4.18 (d, *J* = 9.4 Hz, 1H), 3.97 (t, *J* = 9.1 Hz, 1H), 3.68 – 3.50 (m, 4H), 3.37-3.41 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.05 (d, *J* = 246.8 Hz), 138.20, 137.94 (d, *J* = 10.3 Hz), 137.76, 137.43, 130.45 (d, *J* = 9.2 Hz), 128.86, 128.65, 128.61, 128.58, 128.25, 128.13, 128.07, 128.06, 127.92, 127.75, 118.54 (d, *J* = 3.0 Hz), 112.89 (d, *J* = 21.2 Hz), 110.44 (d, *J* = 24.9 Hz), 87.46, 86.12, 79.56, 78.56, 77.37, 75.93, 75.79, 75.20, 73.55, 68.72 ppm.

$[\alpha]_D^{25}$ = +2.1 (c = 0.25, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}FNO_7SNa^+$ [M+Na^+]: 720.2401, found: 720.2380.



3b

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(3-bromophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3b)

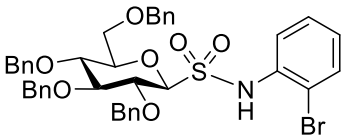
3b was synthesized according to the general procedure B and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (63.6 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.22 (m, 20H), 7.18-7.13 (m, 3H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 4.92-4.87 (m, 2H), 4.85-4.78 (m, 3H), 4.58-4.49 (m, 3H), 4.17 (d, *J* = 9.3 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.68-3.59 (m, 3H), 3.55 (t, *J* = 9.4 Hz, 1H), 3.45-3.41 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.07, 137.62, 137.30, 130.47, 129.02, 128.72, 128.55, 128.50, 128.47, 128.20, 128.14, 128.06, 127.96, 127.81, 127.65, 125.96, 122.64, 121.70, 87.33, 85.99, 79.44, 78.45, 77.23, 75.81, 75.67, 75.11, 73.45, 68.46 ppm.

$[\alpha]_D^{25}$ = +2.9 (c = 0.25, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}BrNO_7SNa^+$ [M+Na^+]: 780.1601, found 780.1589.



3c

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(2-bromophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3c)

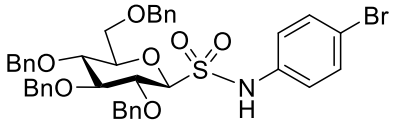
3c was synthesized according to the general procedure B and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (39.3 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41-7.19 (m, 18H), 7.14-7.12 (m, 2H), 7.02 (s, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 4.95-4.85 (m, 2H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 10.2 Hz, 2H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.49-4.30 (m, 3H), 4.02 (t, *J* = 9.0 Hz, 1H), 3.81-3.64 (m, 3H), 3.58 (d, *J* = 1.7 Hz, 1H), 3.40-3.33 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.63, 138.40, 138.33, 137.82, 135.80, 133.07, 129.19, 129.02, 128.92, 128.88, 128.85, 128.46, 128.32, 128.27, 128.24, 128.19, 128.07, 126.53, 122.55, 89.91, 86.48, 80.31, 78.75, 77.28, 76.29, 76.09, 75.51, 73.93, 68.56 ppm.

[α]$_D^{25}$ = +2.7 (c = 0.14, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}BrNO_7SNa^+$ [M+Na$^+$]: 780.1601, found: 780.1578.



3d

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-bromophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3d)

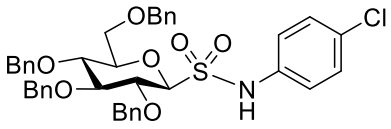
3d was synthesized according to the general procedure B and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (59 mg, 78% yield).

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.45-7.22 (m, 20H), 7.18-7.16 (m, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.67 (s, 1H), 4.94-4.90 (m, 2H), 4.86-4.73 (m, 3H), 4.59-4.47 (m, 3H), 4.17 (d, *J* = 9.4 Hz, 1H), 4.00 (t, *J* = 9.1 Hz, 1H), 3.71-3.61 (m, 3H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.45-3.42 (m,1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.18, 137.75, 137.45, 135.42, 132.34, 128.78, 128.67, 128.59, 128.23, 128.19, 128.07, 128.04, 127.90, 127.74, 124.96, 119.42, 87.42, 86.10, 79.54, 78.54, 77.36, 75.91, 75.70, 75.17, 73.63, 68.96 ppm.

[α]$_D^{25}$ = +1.4 (c = 0.12, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}BrNO_7SNa^+$ [M+Na$^+$]: 780.1601, found: 780.1587.



3e

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-chlorophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3e)

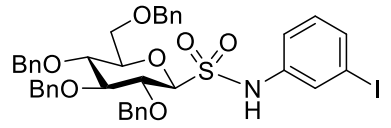
3e was synthesized according to the general procedure B and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (48.4 mg, 68% yield).

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.41-7.25 (m, 18H), 7.20-7.15 (m, 4H), 7.11 (t, *J* = 9.1 Hz, 2H), 6.71 (s, 1H), 4.94-4.92 (m, 2H), 4.86-4.73 (m, 3H), 4.57-4.49 (m, *J* = 17.8 Hz, 3H), 4.17 (d, *J* = 9.4 Hz, 1H), 4.00 (t, *J* = 9.1 Hz, 1H), 3.72-3.60 (m, 3H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.49-3.41 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.21, 137.80, 137.78, 137.48, 134.80, 131.82, 129.42, 128.82, 128.70, 128.63, 128.26, 128.23, 128.11, 128.07, 127.94, 127.78, 124.85, 87.28, 86.15, 79.63, 78.59, 77.43, 75.95, 75.75, 75.22, 73.68, 69.05 ppm.

$[\alpha]_D^{25}$ = -2.7 (c = 0.14, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}ClNO_7SNa^+$ [M+Na^+]: 736.2106, found: 736.2108.



3f

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(3-iodophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3f)

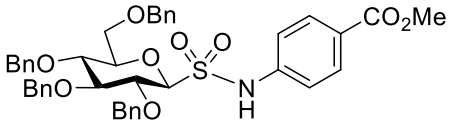
3f was synthesized according to the general procedure B and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a Colorless oil (62 mg, 77% yield).

^{1}H NMR (500 MHz,$CDCl_3$) δ 7.47-7.45 (m, 2H), 7.40-7.19 (m, 19H), 7.12-7.10 (m, 2H), 6.86 (s, 1H), 6.60 (s, 1H), 4.90-4.87 (m, 2H), 4.85-4.71 (m, 3H), 4.62-4.42 (m, 3H), 4.14 (d, *J* = 9.5 Hz, 1H), 3.96 (t, *J* = 9.1 Hz, 1H), 3.66-3.61 (m, 3H), 3.55 (t, *J* = 9.4 Hz, 1H), 3.41-3.39 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.56, 138.19, 138.11, 137.88, 137.79, 135.53, 132.22, 131.12, 129.17, 129.02, 128.96, 128.93, 128.68, 128.60, 128.52, 128.42, 128.26, 128.11, 122.94, 94.43, 87.77, 86.47, 79.96, 78.95, 77.80, 77.73, 77.48, 77.16, 76.26, 76.13, 75.58, 73.93, 68.91 ppm.

$[\alpha]_D^{25}$ = +0.7 (c = 0.20, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}INO_7SNa^+$ [M+Na^+]: 828.1462, found: 828.1454.



3g

methyl 4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran)-2-sulfonamido)benzoate (3g)

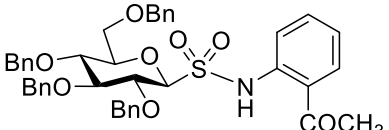
3g was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 40 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a yellow oil (52.3 mg, 71% yield).

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.44-7.21 (m, 18H), 7.15-7.11 (m, 4H), 6.91 (s, 1H), 4.88 (t, *J* = 10.0 Hz, 2H), 4.81-4.75 (m, 3H), 4.50 (d, *J* = 23.2 Hz, 3H), 4.19 (d, *J* = 9.3 Hz, 1H), 3.98 (t, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.66-3.54 (m, 4H), 3.37-3.33 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 140.86, 138.20, 137.80, 137.78, 137.46, 131.03, 128.87, 128.69, 128.64, 128.60, 128.31, 128.25, 128.22, 128.09, 128.05, 127.95, 127.77, 127.21, 121.32, 88.02, 86.13, 79.58, 78.60, 77.32, 75.94, 75.81, 75.21, 73.62, 68.72, 52.22 ppm.

$[\alpha]_D^{25}$ = +2.0 (c = 0.18, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{42}H_{43}NO_9SNa^+$ [M+Na^+]: 760.2550, found: 760.2536.



3h

(2*S*,3*R*,4*S*,5*R*,6*R*)-N-(2-acetylphenyl)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran-2-sulfonamide (3h)

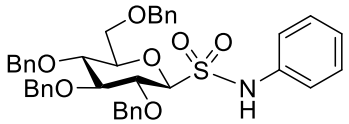
3h was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 5 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (47.2 mg, 65% yield).

^{1}H NMR (400 MHz,$CDCl_3$) δ 11.63 (s, 1H), δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.48-7.20 (m, 18H), 7.12-7.09 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 5.03 (d, *J* = 9.7 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.87-4.72 (m, 3H), 4.54 (d, *J* = 10.7 Hz, 1H), 4.47 (d, *J* = 9.4 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.06 (t, *J* = 9.1 Hz, 1H), 3.71 (t, *J* = 8.9 Hz, 1H), 3.67-3.53 (m, 2H), 3.44 (d, *J* = 11.3 Hz, 1H), 3.35-3.31 (m, 1H), 2.52 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.31, 141.01, 138.34, 138.22, 137.91, 137.65, 134.99, 131.94, 128.83, 128.61, 128.54, 128.53, 128.50, 128.07, 128.05, 127.99, 127.88, 127.75, 127.74, 127.66, 122.56, 121.95, 119.29, 89.87, 86.25, 79.92, 78.49, 75.99, 75.69, 75.21, 73.63, 68.94, 28.17 ppm.

$[\alpha]_D^{25}$ = +4.6 (c = 0.15, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{42}H_{43}NO_8SNa^+$ [M+Na^+]: 744.2601, found: 744.2597.



3i

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-phenyltetrahydro-*2H*-pyran-2-sulfonamide (3i)

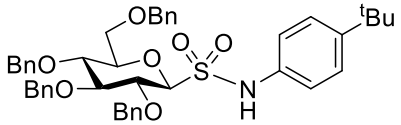
3i was synthesized according to the general procedure B with a conditions (80 °C, 24 h, 10 equiv $NaHSO_3$.) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a yellow oil (31.2 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.16 (m, 18H), 7.16-7.03 (m, 7H), 6.66 (s, 1H), 4.87-4.81 (m, 2H), 4.77-4.66 (m, 3H), 4.49-4.42 (m, 3H), 4.09 (d, *J* = 9.4 Hz, 1H), 3.92 (t, *J* = 9.1 Hz, 1H), 3.62-3.54 (m, 3H), 3.49 (t, *J* = 9.3 Hz, 1H), 3.37-3.33 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.25, 137.85, 137.82, 137.52, 136.22, 129.35, 128.86, 128.64, 128.61, 128.59, 128.20, 128.12, 128.06, 127.90, 127.76, 126.16, 123.50, 86.93, 86.20, 79.52, 78.60, 77.42, 75.92, 75.75, 75.21, 73.60, 68.89 ppm.

[α]$_D^{25}$ = +1.8 (c = 0.12, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{41}NO_7SNa^+$ [M+Na^+]: 702.2495, found 702.2486.



3j

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-(tert-butyl)phenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3j)

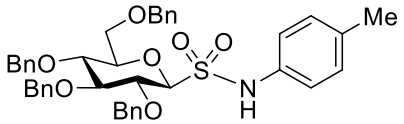
3j was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 24 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (53 mg, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.22 (m, 18H), 7.18-7.13 (m, 6H), 6.61 (s, 1H), 4.95-4.87 (m, 2H), 4.81-4.73 (m, 3H), 4.54-4.51 (m, 3H), 4.15-4.12 (m, 2H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.72-3.62 (m, 3H), 3.54 (t, *J* = 9.4 Hz, 1H), 3.47-3.43 (m, 1H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.26, 137.98, 137.60, 137.53, 137.23, 132.95, 128.65, 128.39, 128.37, 127.97, 127.95, 127.86, 127.84, 127.66, 127.52, 126.01, 123.65, 86.10, 85.97, 79.28, 78.34, 75.69, 75.52, 74.99, 73.37, 68.78, 34.30, 31.17 ppm.

[α]$_D^{25}$ = -31.7 (c = 0.19, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{44}H_{49}NO_7SNa^+$ [M+Na^+]: 758.3121, found: 758.3104.



3k

(2*S*,3*R*,4*S*,5*R*,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(p-tolyl)tetrahydro-*2H*-pyran-2-sulfonamide (3k)

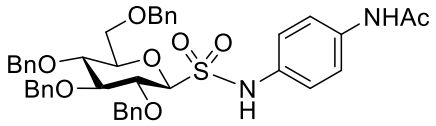
3k was synthesized according to the general procedure B with a condition (80 °C, 24 h, 10 equiv $NaHSO_3$.) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a yellow solid (35.3 mg, 51% yield).

^{1}H NMR (500 MHz,$CDCl_3$) δ 7.41-7.20 (m, 18H), 7.14-7.12 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.92-4.87 (m, 2H), 4.82-4.72 (m, 3H), 4.55-4.49 (m, 3H), 4.13 (d, *J* = 9.4 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.70-3.60 (m, 3H), 3.54 (t, *J* = 9.4 Hz, 1H), 3.43-3.39 (m, 1H), 2.25 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.29, 137.91, 137.86, 137.58, 136.16, 133.47, 129.94, 128.85, 128.65, 128.61, 128.20, 128.16, 128.11, 128.07, 127.90, 127.78, 123.89, 86.65, 86.25, 79.57, 78.64, 75.93, 75.73, 75.22, 73.61, 68.95, 20.99 ppm.

$[\alpha]_D^{25}$ = +1.8 (c = 0.12, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{41}H_{43}NO_7SNa^+$ [M+Na^+]: 716.2652, found: 716.2635.



3l

N-(4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran)-2-sulfonamido)phenyl)acetamide (3l)

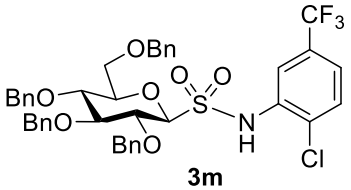
3l was synthesized according to the general procedure C with a modification of time (6 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as the eluent, giving the titled product as a yellow solid (22.8 mg, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 20H), 7.17-7.14 (m, 4H), 6.68 (s, 1H), 4.93-4.88 (m,2H), 4.84-4.75 (m, 3H), 4.55 (d, *J* = 9.7 Hz, 1H), 4.15 (d, *J* = 9.4 Hz, 1H), 3.99 (t, *J* = 9.1 Hz, 1H), 3.72-3.62 (m, 3H), 3.57 (t, *J* = 9.3 Hz, 1H), 3.45-3.43 (m, 1H), 2.98 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.30, 138.26, 137.85, 137.83, 137.54, 136.26, 132.09, 128.83, 128.68, 128.64, 128.61, 128.47, 128.22, 128.15, 128.08, 128.01, 127.91, 127.88, 127.79, 124.61, 120.64, 86.86, 86.20, 79.56, 78.65, 75.94, 75.75, 75.21, 73.61, 68.85, 24.68 ppm.

$[\alpha]_D^{25}$ = + 2.2 (c = 0.12, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{42}H_{44}N_2O_8SNa^+$ [M+Na^+]: 759.2711, found: 759.2709.



3m

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(2-chloro-5-(trifluoromethyl)phenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3m)

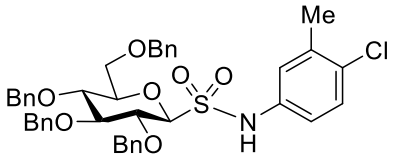
3m was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 24 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (57 mg, 73% yield).

^{1}H NMR (500 MHz,$CDCl_3$) δ 8.04 (d, *J* = 2.0 Hz, 1H), 7.3 (m, 2H), 7.34-7.23 (m, 18H), 7.12-7.10 (m, 2H), 4.96-4.88 (m, 2H), 4.84 (d, *J* = 11.1 Hz, 1H), 4.81-4.76 (m, 2H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.40 (t, *J* = 10.2 Hz, 2H), 4.34 (d, *J* = 11.9 Hz, 1H), 4.02 (t, *J* = 9.0 Hz, 1H), 3.75-3.65 (m, 2H), 3.63-3.60 (m, 1H), 3.56-3.54 (m, 1H), 3.42-3.39 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.22, 137.86, 137.34, 135.00, 130.07, 128.84, 128.64, 128.62, 128.58, 128.55, 128.25, 128.11, 128.03, 127.94, 127.75, δ 122.15 (q, *J* = 3.8 Hz), 118.93 (q, *J* = 4.2 Hz), 127.75, 90.16, 86.08, 80.02, 78.47, 75.99, 75.85, 75.24, 73.53, 68.38 ppm.

$[\alpha]_D^{25}$ = -28.4 (c = 0.29, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{41}H_{39}ClF_3NO_7SNa^+$ [M+Na^+]: 804.1980, found: 804.1980.



3n

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-chloro-3-methylphenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3n)

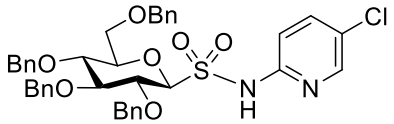
3n was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 24 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (49.4 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.22 (m, 18H), 7.16-7.11 (m, 2H), 7.08-7.05 (m, 2H), 6.95-6.92 (m, 1H), 6.63 (s, 1H), 4.91-4.87 (m, 2H), 4.83-4.73 (m, 3H), 4.55-4.46 (m, 3H), 4.14 (d, *J* = 9.4 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.67-3.58 (m, 3H), 3.52 (t, *J* = 9.4 Hz, 1H), 3.43-3.39 (m, 1H), 2.20 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.21, 137.76, 137.47, 137.31, 134.67, 132.03, 129.74, 128.83, 128.69, 128.64, 128.62, 128.60, 128.28, 128.22, 128.10, 128.08, 127.92, 127.77, 125.85, 122.22, 86.95, 86.14, 79.60, 78.57, 77.42, 75.93, 75.76, 75.23, 73.67, 68.92, 20.06 ppm.

$[\alpha]_D^{25}$ = -1.2 (c = 0.25, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{41}H_{42}ClNO_7SNa^+$ [M+Na^+]: 750.2263, found: 750.2264.



3o

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(5-chloropyridin-2-yl)tetrahydro-*2H*-pyran-2-sulfonamide (3o)

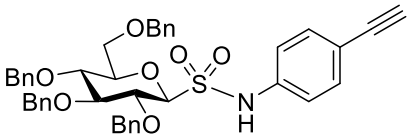
3o was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 48 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (42.8 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.5 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.41-7.34 (m, 2H), 7.32 -7.17 (m, 17H), 7.08-7.05 (m, 2H), 4.97 (d, *J* = 9.7 Hz, 1H), 4.88 (d, *J* = 11.1 Hz, 1H), 4.83-4.87 (m,2H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.56-4.49 (m, 2H), 4.33-4.21 (m, 2H), 4.05 (t, *J* = 9.0 Hz, 1H), 3.73-3.62 (m, 2H), 3.54-3.51 (m, 1H), 3.40-3.38(m. 1H), 3.37-3.31 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.42, 146.11, 138.63, 138.32, 137.88, 137.53, 128.82, 128.63, 128.60, 128.56, 128.18, 128.04, 128.01, 127.91, 127.88, 127.75, 127.71, 126.87, 114.48, 90.82, 86.16, 79.64, 78.61, 77.05, 75.99, 75.74, 75.22, 73.48, 68.53 ppm.

$[\alpha]_D^{25}$ = + 1.2 (c = 0.17, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{39}H_{39}ClN_2O_7SNa^+$ [M+Na^+]: 737.2059, found: 737.2054.



3p

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-ethynylphenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3p)

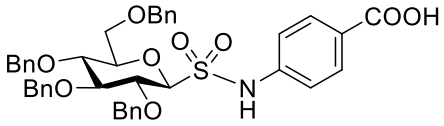
3p was synthesized according to the general procedure C with a modification of time (4.5 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (26 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.22 (m, 20H), 7.13-7.11 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.81 (s, 1H), 4.90-4.86 (m, 2H), 4.82-4.71 (m, 3H), 4.52-4.45 (m, 3H), 4.15 (d, *J* = 9.4 Hz, 1H), 3.96 (t, *J* = 9.1 Hz, 1H), 3.67-3.58 (m, 3H), 3.53 (t, *J* = 9.3 Hz, 1H), 3.39-3.35 (m, 1H), 3.03 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.21, 137.80, 137.77, 137.47, 136.84, 133.23, 128.85, 128.69, 128.65, 128.63, 128.60, 128.26, 128.22, 128.09, 128.06, 127.93, 127.78, 122.52, 119.63, 87.53, 86.14, 83.05, 79.52, 78.58, 77.66, 75.94, 75.77, 75.21, 73.63, 68.82 ppm.

$[\alpha]_D^{25}$ = +1.5 (c = 0.15, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{42}H_{41}NO_7SNa^+$ [M+Na^+]: 726.2496, found: 726.2495.



3q

4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran)-2-sulfonamido)benzoic acid (3q)

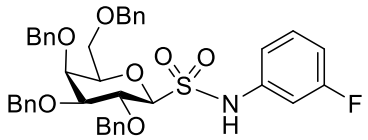
3q was synthesized according to the general procedure B with a modification of temperature and time (80 °C, 54 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (30.3 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.30-7.20 (m, 20H), 7.12 – 7.06 (m, 2H), 4.86 – 4.81 (m, 2H), 4.74 – 4.70 (m, 3H), 4.48-4.42 (m, 3H), 4.17 (d, *J* = 9.3 Hz, 1H), 3.95 (t, *J* = 9.1 Hz, 1H), 3.63-3.50 (m, 4H), 3.33-3.31m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.60, 141.60, 138.13, 137.72, 137.66, 137.37, 131.71, 128.89, 128.71, 128.65, 128.61, 128.35, 128.28, 128.26, 128.11, 128.06, 127.97, 127.78, 121.11, 88.03, 86.06, 79.52, 78.56, 77.24, 75.97, 75.85, 75.22, 73.61 ppm.

$[\alpha]_D^{25}$ = +2.0 (c = 0.13, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{41}H_{41}NO_9SNa^+$ [M+Na^+]: 746.2394, found: 746.2393.



3r

(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(3-fluorophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3r)

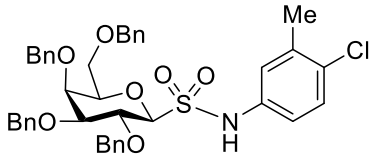
3r was synthesized according to the general procedure C with a modification of time (3.5 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (40 mg, 53% yield).

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.42 (d, *J* = 6.2 Hz, 2H), 7.38-7.26 (m, 18H), 7.08-6.98 (m, 2H), 6.91 (d, *J* = 10.1 Hz, 1H), 6.83 (d, *J* = 5.8 Hz, 1H), 6.80 (s, 1H), 4.95 (d, *J* = 11.6 Hz, 1H), 4.87 (s, 2H), 4.72 (s, 2H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.45-4.36 (m, 2H), 4.23 (d, *J* = 9.4 Hz, 1H), 3.86 (d, *J* = 2.7 Hz, 1H), 3.70-3.62 (m, 1H), 3.61 – 3.52 (m, 2H), 3.48-3.45 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.98 (d, *J* = 246.5 Hz), δ 138.32, 138.22 (d, *J* = 10.3 Hz), 137.93, 137.76, 137.62, 130.31 (d, *J* = 9.2 Hz), 128.92, 128.65, 128.61, 128.45, 128.20, 128.17, 128.10, 128.01, 127.87, 127.74, 118.37 (d, *J* = 3.0 Hz), 112.58 (d, *J* = 21.1 Hz), 110.23 (d, *J* = 25.0 Hz). 88.66, 83.64, 78.48, 75.95, 75.42, 74.68, 73.73, 73.50, 73.05, 68.96 ppm.

$[\alpha]_D^{25}$ = +1.5 (c = 0.25, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{40}H_{40}FNO_7SNa^+$ [M+Na^+]: 720.2402, found: 720.2402



3s

(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-chloro-3-methylphenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3s)

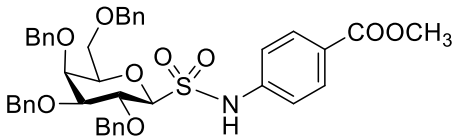
3s was synthesized according to the general procedure C with a modification of time (22 h)and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as yellow oil (34.9 mg, 48% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.29-7.16 (m, 18H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.86-6.83 (m, 1H), 6.50 (s, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.78 (s, 2H), 4.64 (d, *J* = 0.9 Hz, 2H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.36 – 4.27 (m, 2H), 4.10 (d, *J* = 9.3 Hz, 1H), 3.78 (d, *J* = 1.7 Hz, 1H), 3.61-3.58 (m, 1H), 3.51-3.44 (m, 2H), 3.40-3.37 (m, 1H), 2.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.37, 137.95, 137.80, 137.62, 137.17, 134.86, 131.78, 129.64, 128.96, 128.68, 128.64, 128.48, 128.24, 128.23, 128.20, 128.05, 127.91, 127.78, 125.74, 122.08, 88.10, 83.65, 78.62, 75.98, 75.48, 74.73, 73.85, 73.65, 73.11, 69.20, 20.04 ppm.

$[\alpha]_D^{25}$ = -172.5 (c = 0.13, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{41}H_{42}ClNO_7SNa^+$ [M+Na^+]: 750.2263, found: 750.2267.



3t

methyl 4-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran)-2-sulfonamido)benzoate (3t)

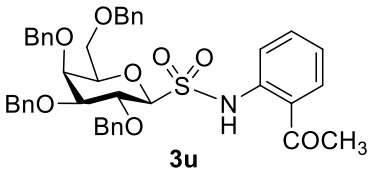
3t was synthesized according to the general procedure B with a modification of time (48 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (38.3 mg, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.42-7.38 (m, 2H), 7.36-7.23 (m, 18H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.77 (s, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.88-4.80 (m, 2H), 4.69 (s, 2H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.39-4.33 (m, 2H), 4.21 (d, *J* = 9.4 Hz, 1H), 3.88 (s, 3H), 3.85 (d, *J* = 2.6 Hz, 1H), 3.62-3.59 (m, 1H), 3.57-3.54 (m. 1H), 3.50 (t, *J* = 5.9 Hz, 1H), 3.47-3.45 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.56, 141.14, 138.34, 137.89, 137.76, 137.61, 130.93, 128.94, 128.67, 128.64, 128.47, 128.18, 128.16, 128.04, 127.90, 127.75, 126.88, 121.14, 89.20, 83.67, 78.46, 75.97, 75.41, 74.76, 73.76, 73.48, 73.02, 68.85, 52.17 ppm.

[α]$_D^{25}$ = -44.2 (c = 0.17, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{42}H_{43}NO_9SNa^+$ [M+Na^+]: 760.2550, found: 760.2533.



3u

(2*S*,3*R*,4*S*,5*S*,6*R*)-N-(2-acetylphenyl)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran-2-sulfonamide (3u)

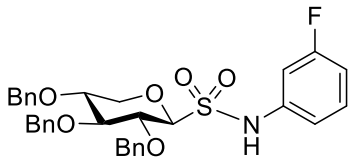
3u was synthesized according to the general procedure C with a modification of time (14 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (28.8 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.42 - 7.24 (m, 18H), 7.19-7.14 (m, 2H), 7.05 (t, *J* = 7.7 Hz, 1H), 4.99 (d, *J* = 9.7 Hz, 1H), 4.91-4.83 (m,2H), 4.70 (s, 2H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 9.3 Hz, 1H), 4.35 (t, *J* = 9.3 Hz, 1H), 4.28 (s, 2H), 3.85 (d, *J* = 2.7 Hz, 1H), 3.61-3.58 (m,1H), 3.48 (t, *J* = 6.3 Hz, 1H), 3.41-3.37 (m, 1H), 3.31-3.27 (m, 1H), 2.39 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.23, 141.21, 138.65, 138.03, 137.95, 137.77, 134.81, 131.85, 128.91, 128.64, 128.58, 128.48, 128.40, 128.00, 127.97, 127.95, 127.75, 127.69, 122.37, 121.81, 119.34, 90.78, 83.74, 77.90, 75.82, 75.00, 74.59, 73.57, 73.32, 73.03, 68.26, 28.04 ppm.

[α]$_D^{25}$ = +0.8 (c = 0.11, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{42}H_{43}NO_8SNa^+$ [M+Na^+]: 744.2602, found:744.2593.



3v

(2*S*,3*R*,4*S*,5*R*)-3,4,5-tris(benzyloxy)-N-(3-fluorophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3v)

3v was synthesized according to the general procedure C with a modification of time (18 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (31.1 mg, 54% yield).

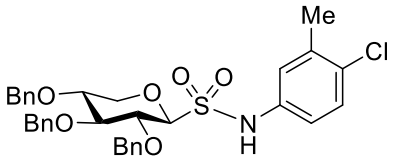
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 15H), 7.23-7.19 (m, 1H), 6.90 – 6.83 (m, 2H), 6.82 – 6.76 (m, 1H), 6.41 (s, 1H), 4.96 – 4.88 (m, 2H), 4.82 (d, *J* = 9.9 Hz, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.18 (d, *J* = 9.2 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.99 (t, *J* = 8.8 Hz, 1H), 3.73 – 3.61 (m, 2H), 3.24-3.19 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.15 (d, *J* = 247.3 Hz), δ 138.26, 137.90 (d, *J* = 15.3 Hz), 137.52, 130.69 (d, *J* = 9.3 Hz), 128.88, 128.71, 128.63, 128.52, 128.47, 128.23, 128.07, 128.01, 127.97, 127.92, 117.38 (d, *J* = 3.1 Hz), 112.72 (d, *J* = 21.2 Hz), 109.44 (d, *J* = 25.1 Hz). 88.13, 85.05, 78.38, 77.56, 76.10,

75.70, 73.53, 68.39 ppm.

[α]$_D^{25}$ = +5.1 (c = 0.18, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{32}H_{32}FNO_6SNa^+$ [M+Na^+]: 600.1827, found: 600.1817.



3w

(2*S*,3*R*,4*S*,5*R*)-3,4,5-tris(benzyloxy)-N-(4-chloro-3-methylphenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3w)

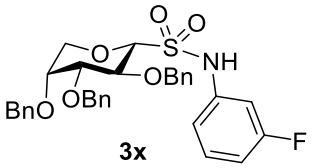
3w was synthesized according to the general procedure C with a modification of time (48 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a yellow oil (34 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 15H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.80-6.77 (m, 1H), 6.24 (s, 1H), 4.91-4.85 (m, 2H), 4.82 (d, *J* = 11.1 Hz, 2H), 4.77 (d, *J* = 9.9 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 4.09-4.05 (m, 1H), 3.95 (t, *J* = 8.7 Hz, 1H), 3.70 – 3.57 (m, 1H), 3.21-3.16 (m, 1H), 2.27 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.27, 137.84, 137.57, 137.50, 134.69, 131.80, 129.90, 128.88, 128.71, 128.63, 128.50, 128.23, 128.02, 127.98, 124.80, 120.92, 87.73, 85.05, 78.41, 77.59, 76.08, 75.68, 73.53, 68.37, 20.28 ppm.

[α]$_D^{25}$ = -43.758 (c = 0.15, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{33}H_{34}ClNO_6SNa^+$ [M+Na^+]: 630.1688, found: 630.1678.



3x

(2*R*,3*S*,4*R*,5*R*)-3,4,5-tris(benzyloxy)-N-(3-fluorophenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3x)

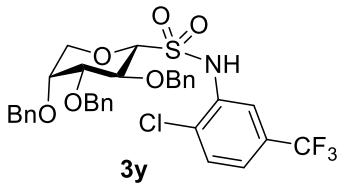
3x was synthesized according to the general procedure C with a modification of time (2 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a yellow oil (37.5 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 15H), 7.19-7.13 m, 1H), 6.87 – 6.81 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 10.1 Hz, 1H), 4.79 (d, *J* = 10.1 Hz, 1H), 4.73 (d, *J* = 12.4 Hz, 1H), 4.67-4.62 (m, 3H), 4.42 (t, *J* = 8.7 Hz, 1H), 4.25 – 4.18 (m, 2H), 3.75 (s, 1H), 3.61-3.58 (m, 1H), 3.33 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.96 (d, *J* = 246.5 Hz), 138.17 (d, *J* = 10.3 Hz), δ 137.95, 137.81, 137.76, 130.40 (d, *J* = 9.2 Hz), 128.89, 128.83, 128.67, 128.61, 128.41, 128.09, 128.06, 128.01, 127.94, 117.14 (d, *J* = 3.0 Hz), 112.22 (d, *J* = 21.0 Hz), 109.09 (d, *J* = 25.3 Hz), 89.08, 81.21, 75.88, 75.46, 72.26, 71.98, 71.68, 67.59 ppm.

[α]$_D^{25}$ = -166.923 (c = 0.13, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{32}H_{32}FNO_6SNa^+$ [M+Na^+]: 600.1827, found: 600.1820



3y

(2*R*,3*S*,4*R*,5*R*)-3,4,5-tris(benzyloxy)-N-(2-chloro-5-(trifluoromethyl)phenyl)tetrahydro-*2H*-pyran-2-sulfonamide (3y)

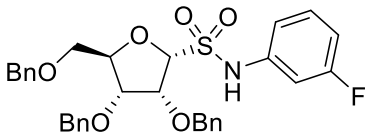
3y was synthesized according to the general procedure C with a modification of time (8 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (33.7 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.50 – 7.27 (m, 17H), 7.12 (s, 1H), 4.88 (d, *J* = 3.0 Hz, 2H), 4.72 (d, *J* = 12.7 Hz, 1H), 4.63 (d, *J* = 7.0 Hz, 3H), 4.42 (t, *J* = 8.5 Hz, 1H), 4.35 (d, *J* = 8.8 Hz, 1H), 4.18-4.14 (m, 1H), 3.73 (s, 1H), 3.62-3.60 (m, 1H), 3.30 (d, *J* = 12.6 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.93, 137.81, 137.62, 134.98, δ 130.52 (q, *J* = 33.2 Hz), 130.09, 128.78, 128.63, 128.59, 128.18, 128.09, 128.04, 127.99, 127.93, 127.82, 127.78, 124.79, 122.03, (q, d, *J* = 3.8 Hz), 118.64 (q, *J* = 3.9 Hz). 90.97, 80.74, 75.66, 74.85, 72.39, 71.86, 71.59, 67.23 ppm.

$[\alpha]_D^{25}$ = -3.050 (c = 0.20, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{33}H_{31}ClF_3NO_6SNa^+$ [M+Na$^+$]: 684.1405, found: 684.1398



3z

(2*R*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)-N-(3-fluorophenyl)tetrahydrofuran-2-sulfonamide (3z)

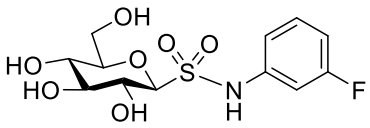
3z was synthesized according to the general procedure C with a modification of time (18 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent, giving the titled product as a white solid (24 mg, 42% yield)

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.42 – 7.22 (m, 15H), 7.20 – 7.10 (m, 1H), 6.88 – 6.75 (m, 3H), 6.35 (s, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.63 – 4.46 (m, 5H), 4.22 (s, 1H), 3.94-3.90 (m, 1H), 3.86-3.83 (m, 1H), 3.73 (t, *J* = 10.6 Hz, 1H), 3.57-3.52 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.01 (d, *J* = 246.8 Hz), δ 138.52, 137.95 (d, *J* = 10.3 Hz), 137.69, 136.82, 130.53 (d, *J* = 9.2 Hz), 129.01, 128.73, 128.69, 128.41, 128.16, 127.80, 127.77, 127.64, 117.89 (d, *J* = 3.0 Hz), 112.79 (d, *J* = 21.2 Hz), 109.92 (d, *J* = 25.0 Hz), 84.59, 77.72, 74.65, 74.37, 73.43, 72.53, 71.70, 65.33 ppm.

$[\alpha]_D^{25}$ = 11.600 (c = 0.20, $CHCl_3$).

HRMS (ESI-TOF): calculated for $C_{32}H_{32}FNO_6SNa^+$ [M+Na$^+$]: 600.1827, found: 600.1813.



4

(2*S*,3*R*,4*S*,5*S*,6*R*)-N-(3-fluorophenyl)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-sulfonamide (4)

4 was synthesized according to the general procedure D and isolated by column chromatography on silica gel using dichloromethane: methanol (10:1 v/v) as the eluent, giving the titled product as a white oil (31.3mg, 93% yield).

^{1}H NMR (400 MHz, MeOD) δ 7.42-7.36 (m, 1H), 7.20 (d, *J* = 9.0 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 1H), 4.27 (d, *J* = 9.5 Hz, 1H), 3.95 (d, *J* = 12.2 Hz, 1H), 3.80 – 3.71 (m, 2H), 3.45 – 3.42 (m, 1H), 3.30 (d, *J* = 6.1 Hz, 2H) ppm.

^{13}C NMR (101 MHz, MeOD) δ 164.37 (d, *J* = 244.6 Hz), 140.68 (d, *J* = 10.5 Hz), 131.56 (d, *J* = 9.3 Hz), 118.89 (d, *J* = 3.0 Hz), 112.72 (d, *J* = 21.4 Hz), 110.34 (d, *J* = 25.3 Hz). δ 89.68, 82.33, 78.90, 71.56, 70.96, 62.80 ppm.

$[\alpha]_D^{25}$ = +176.4 (c = 0.25, MeOH).

HRMS (ESI-TOF): calculated for $C_{12}H_{16}FNO_7SNa^+$ [M+Na^+]: 360.0524, found: 360.0519.

9. NMR Spectra

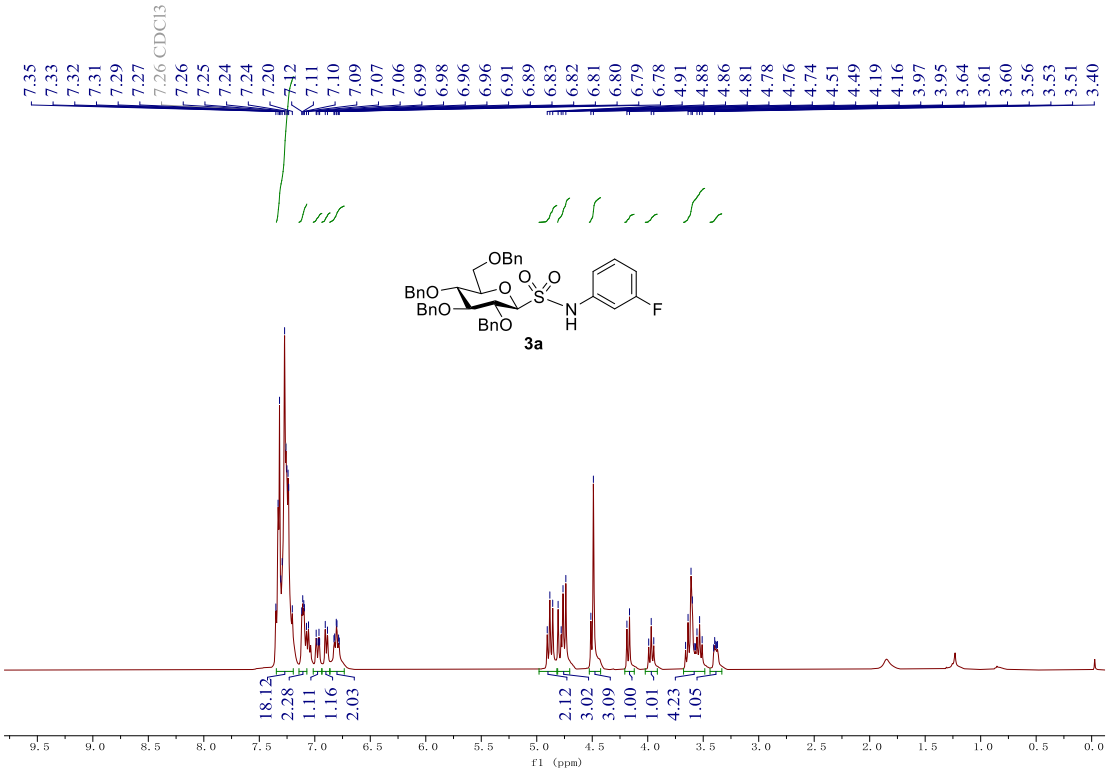


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3a**

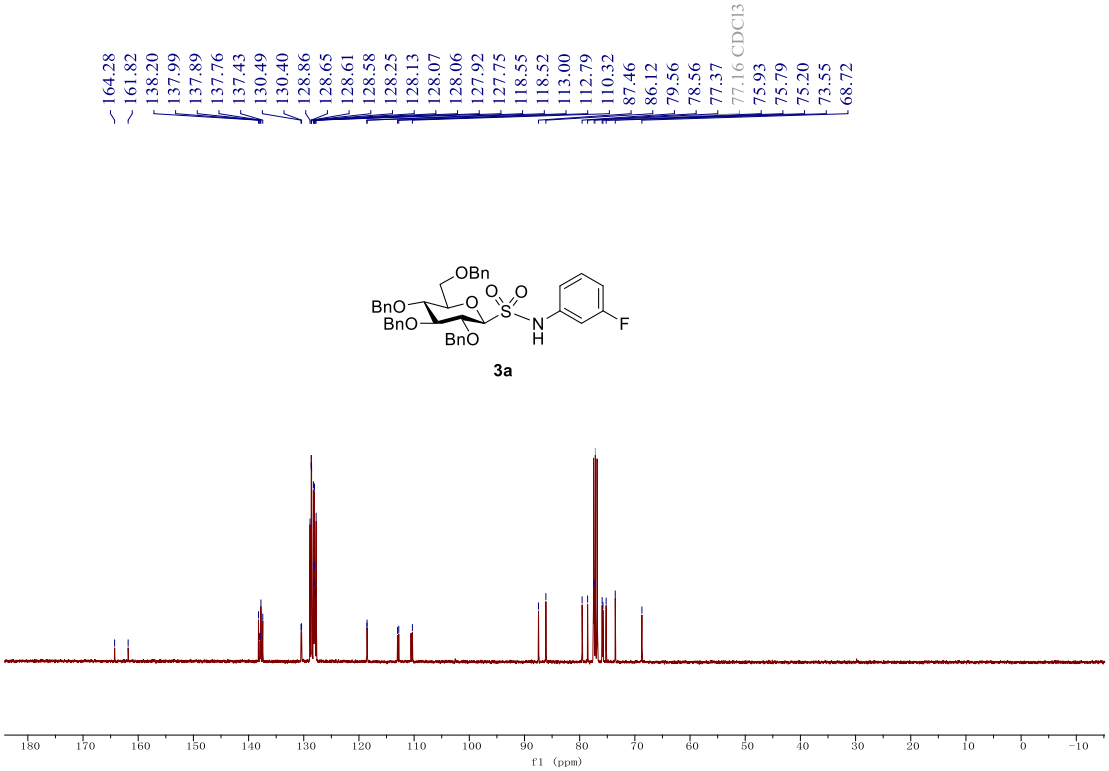


Figure S5. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3a**

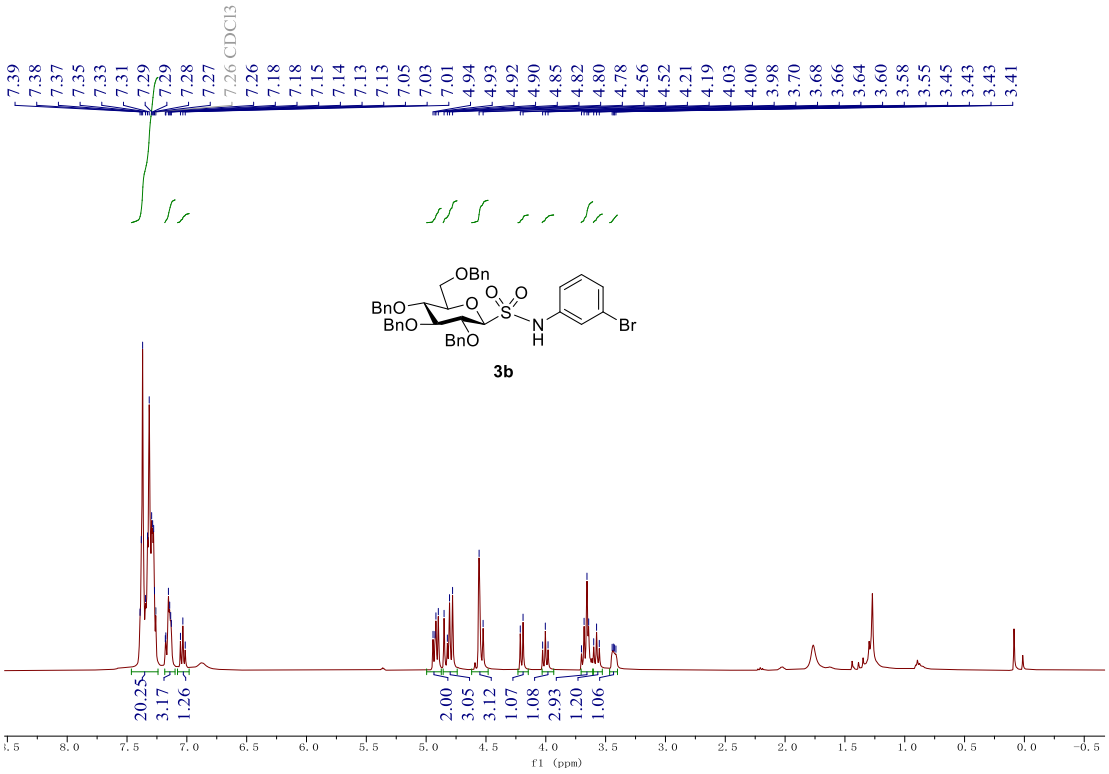


Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3b**

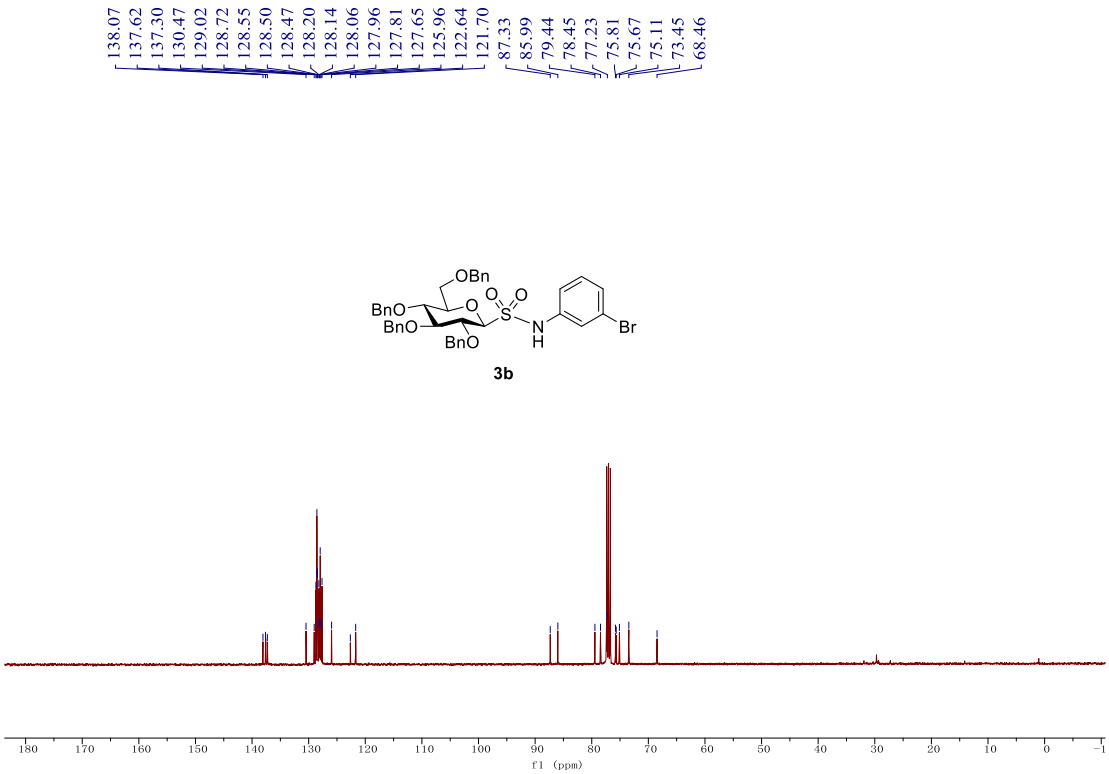


Figure S7. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3b**

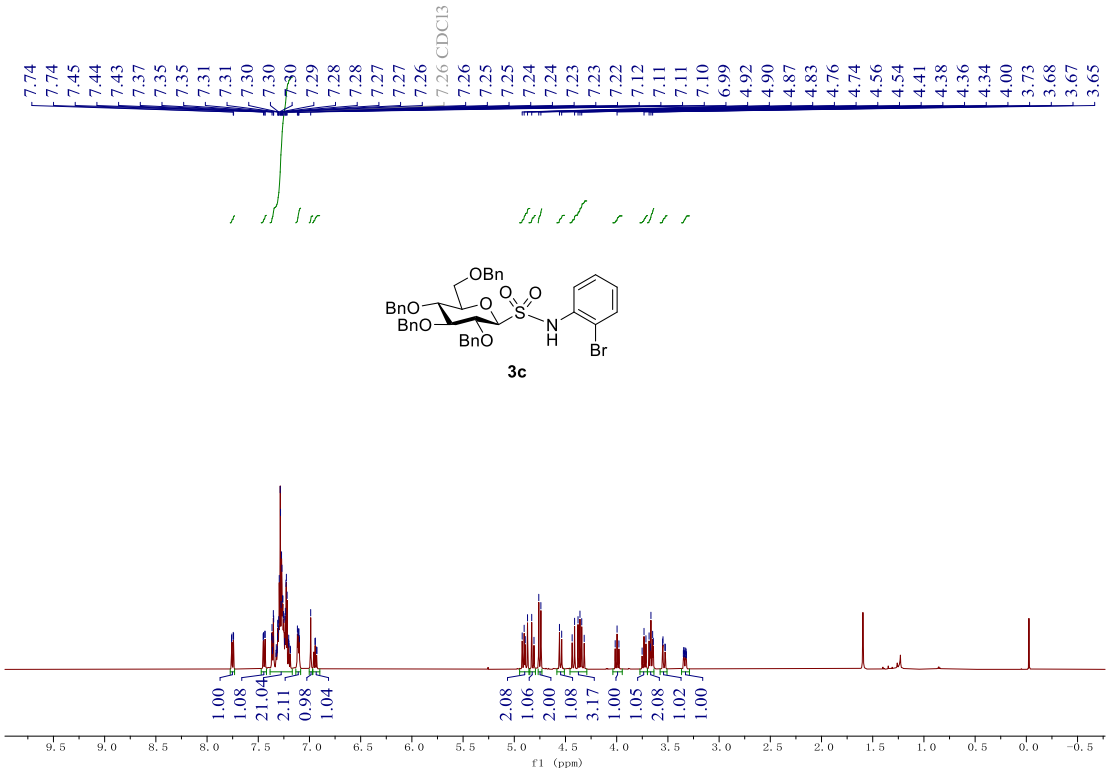


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3c**

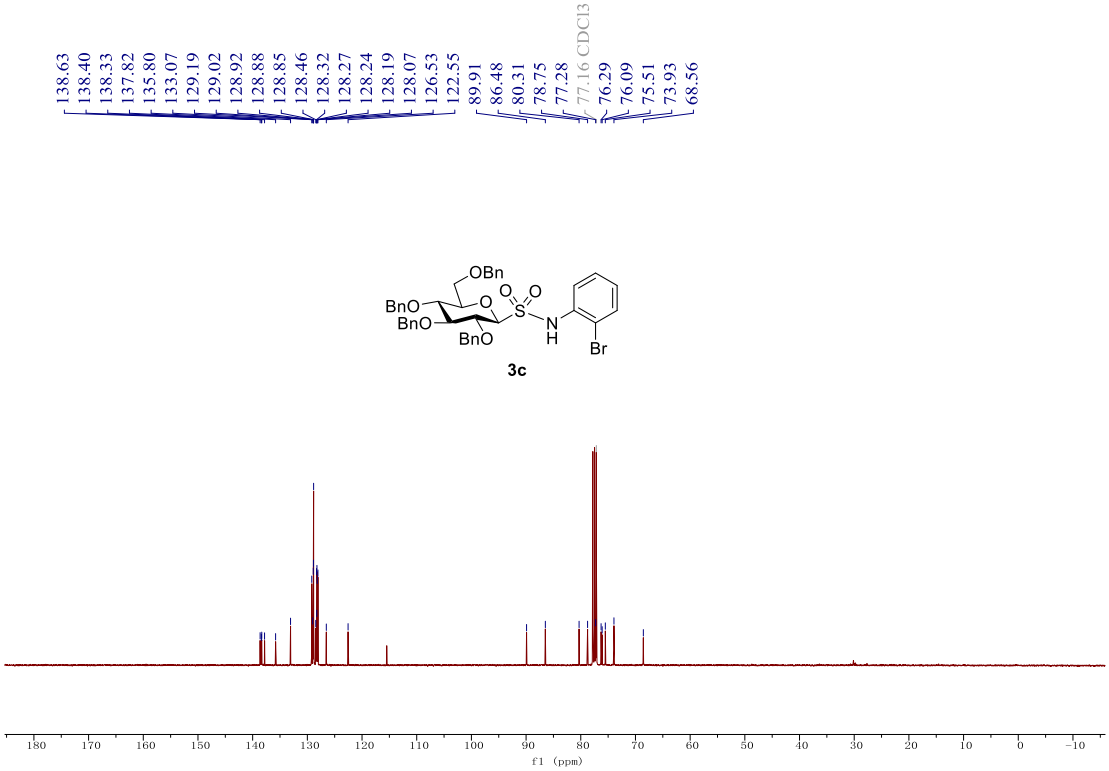


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3c**

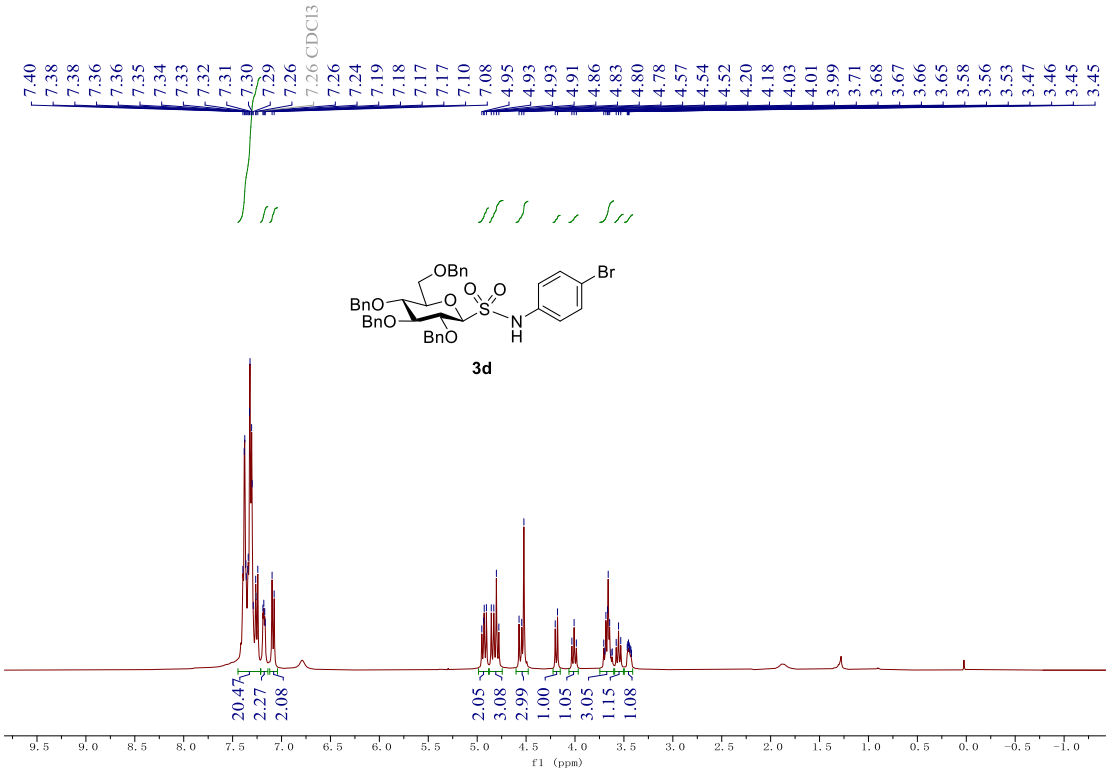


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3d**

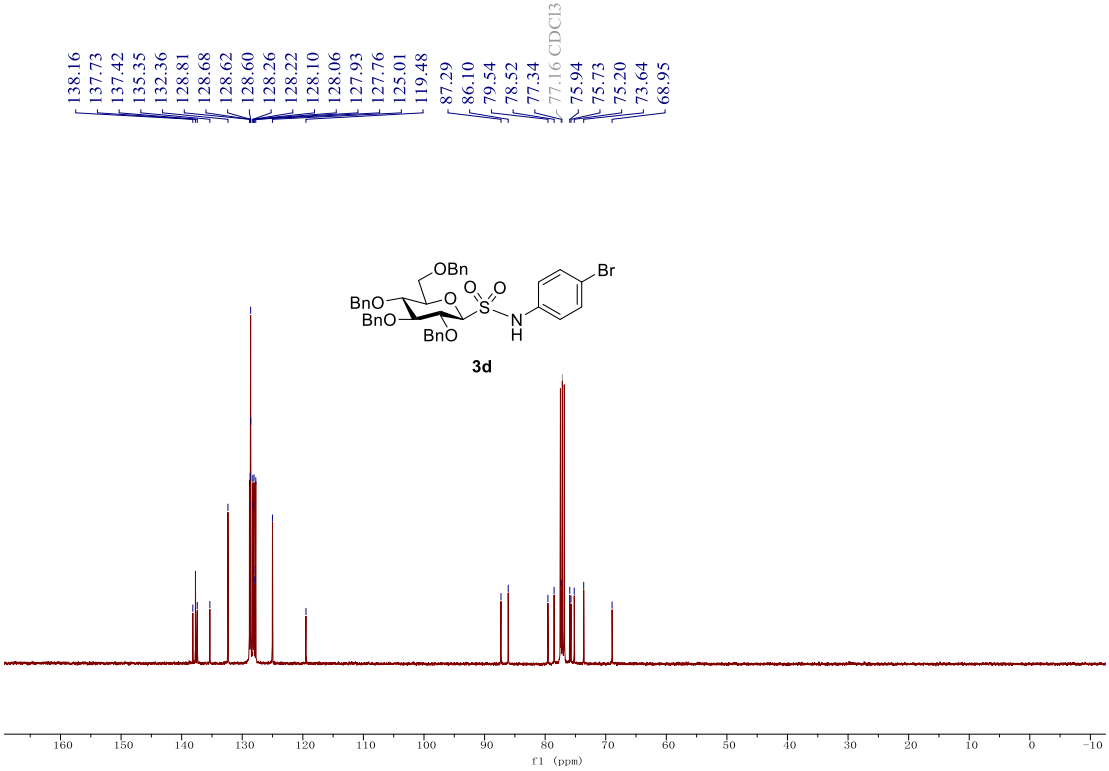


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3d**

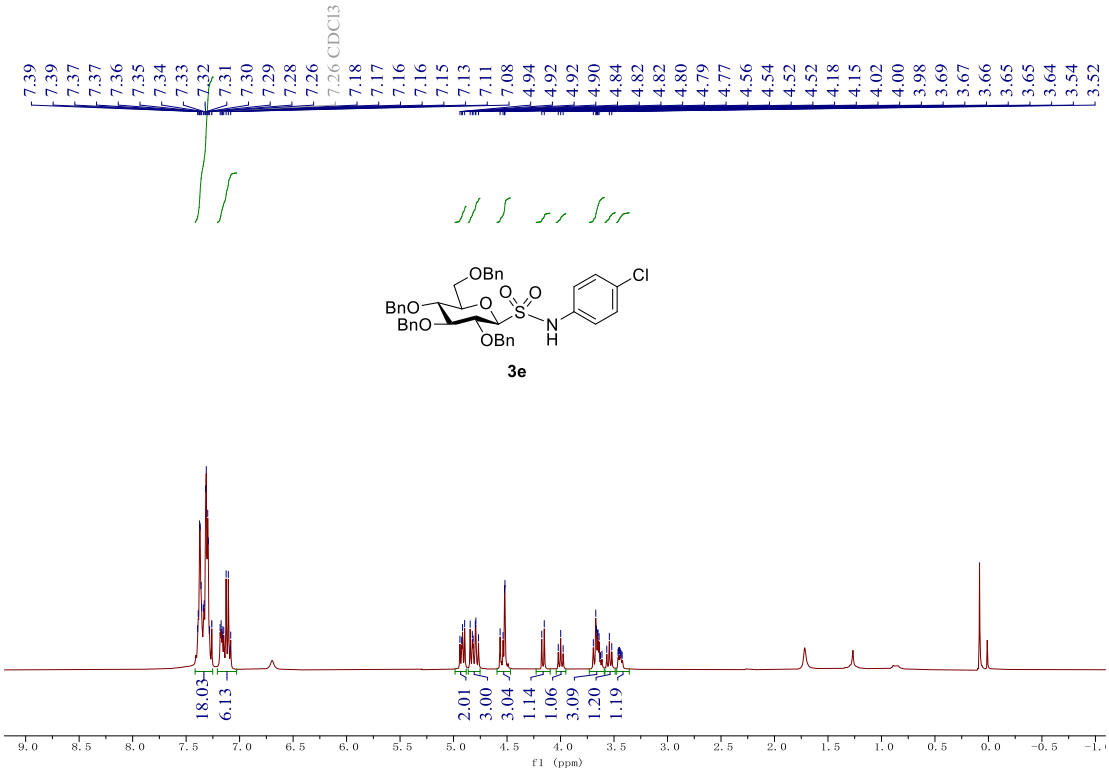


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3e**

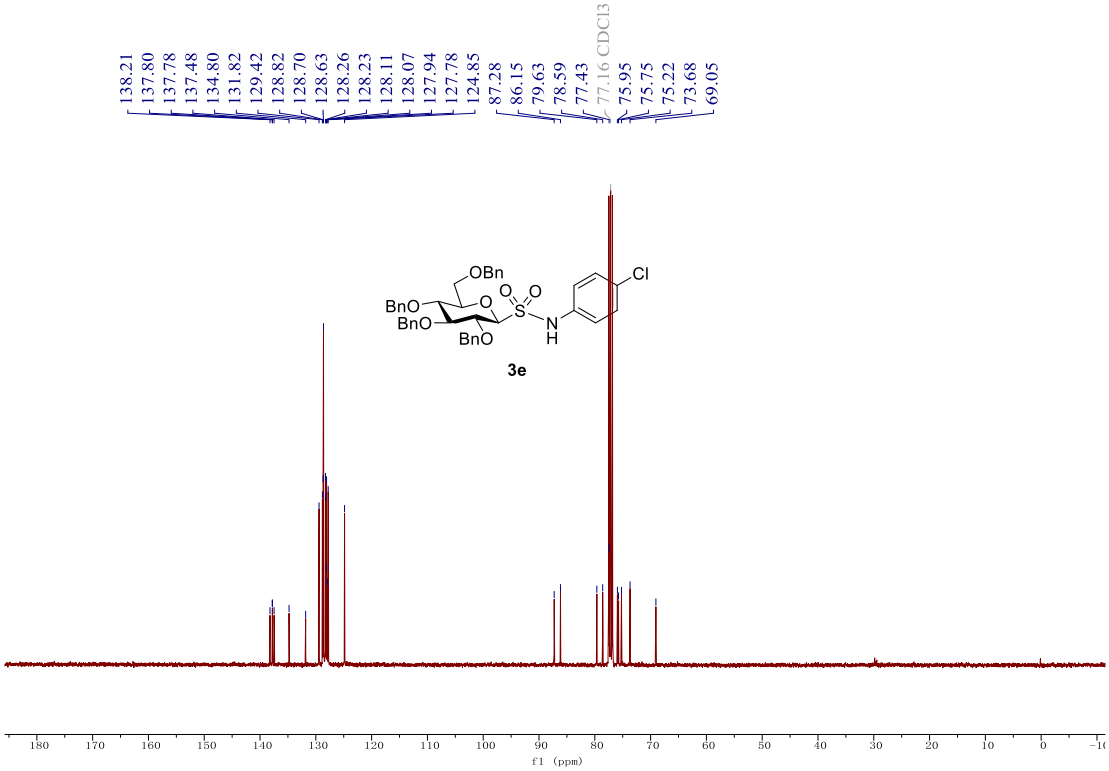


Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3e**

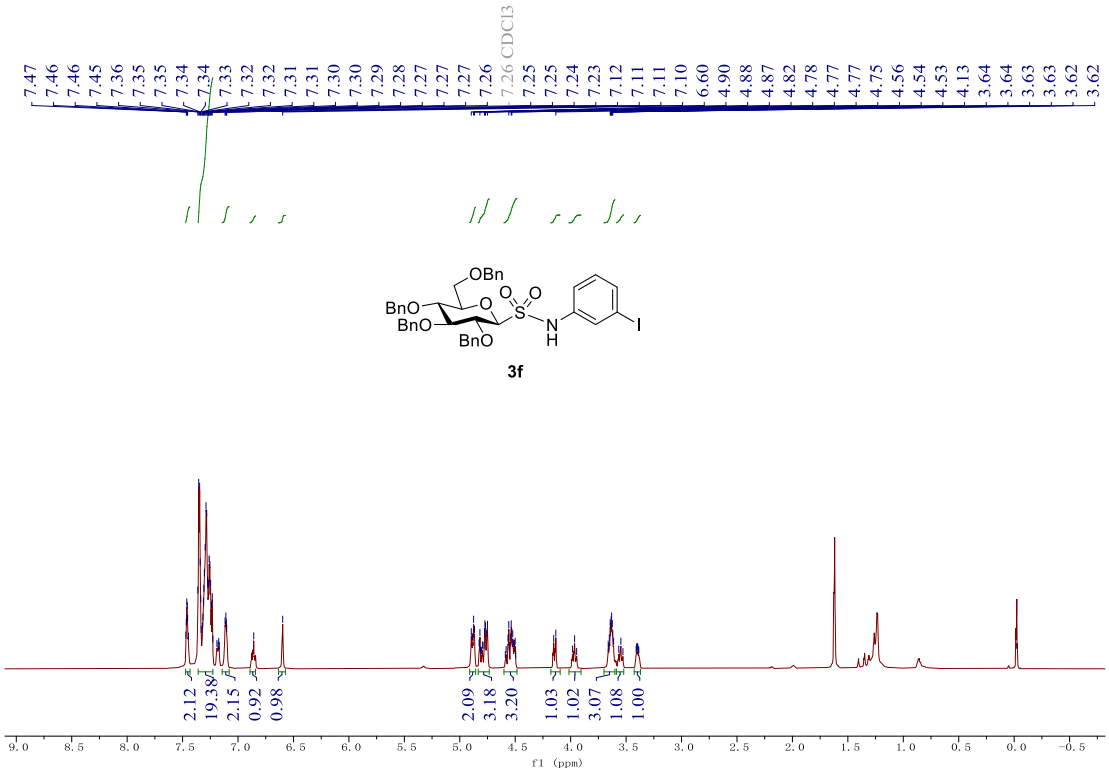


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3f**

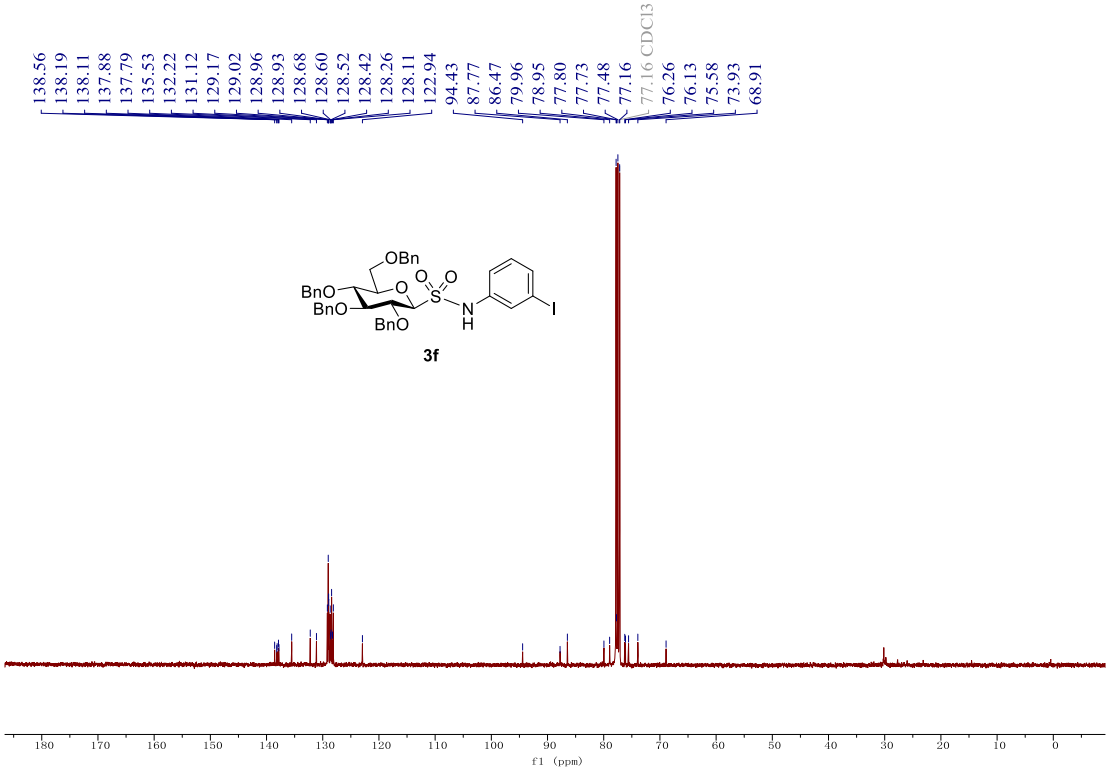


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3f**

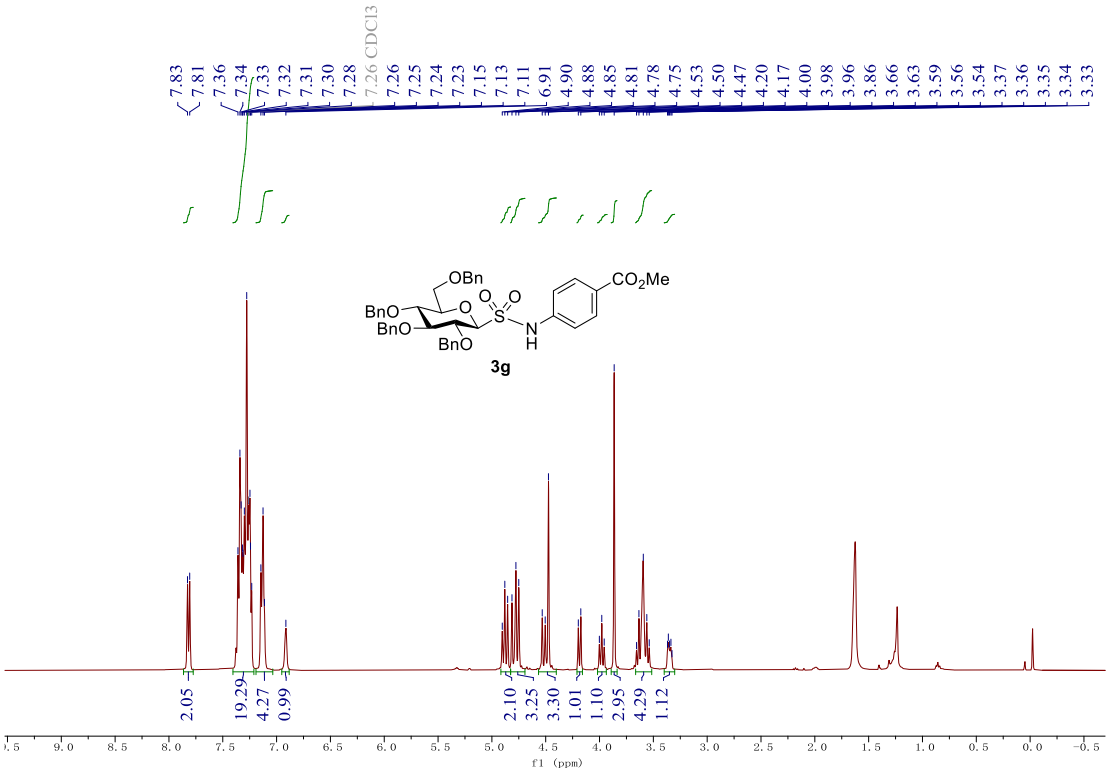


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3g**

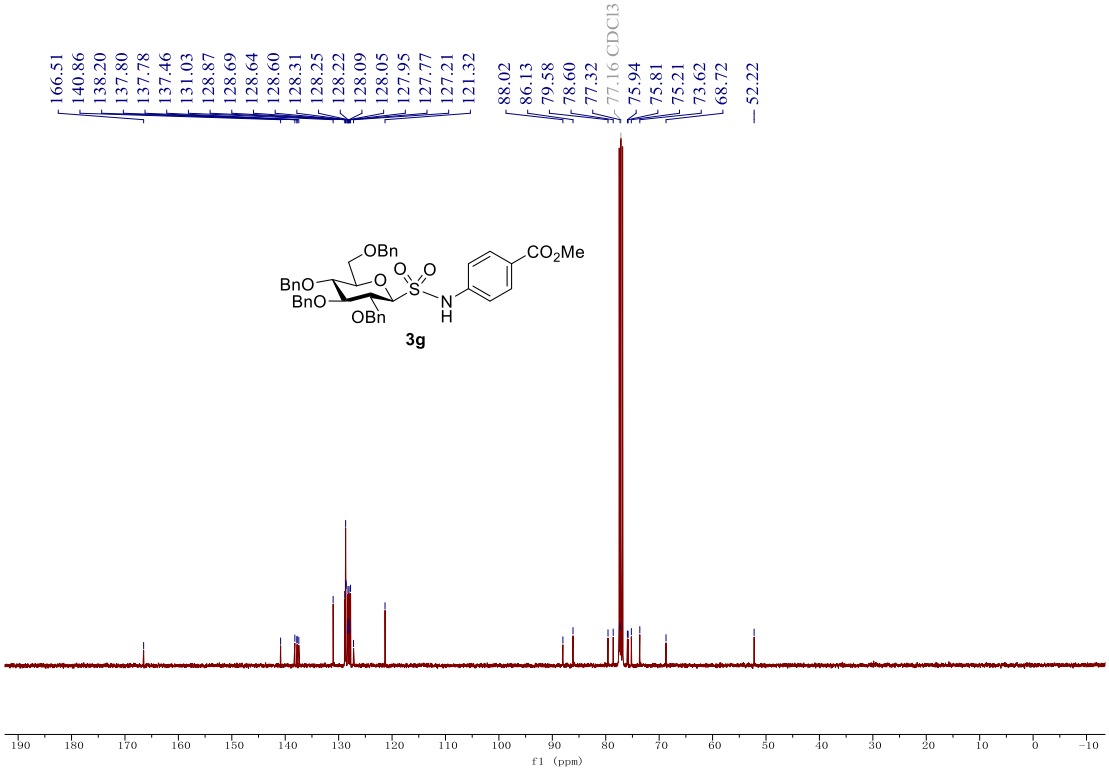


Figure S17. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3g**

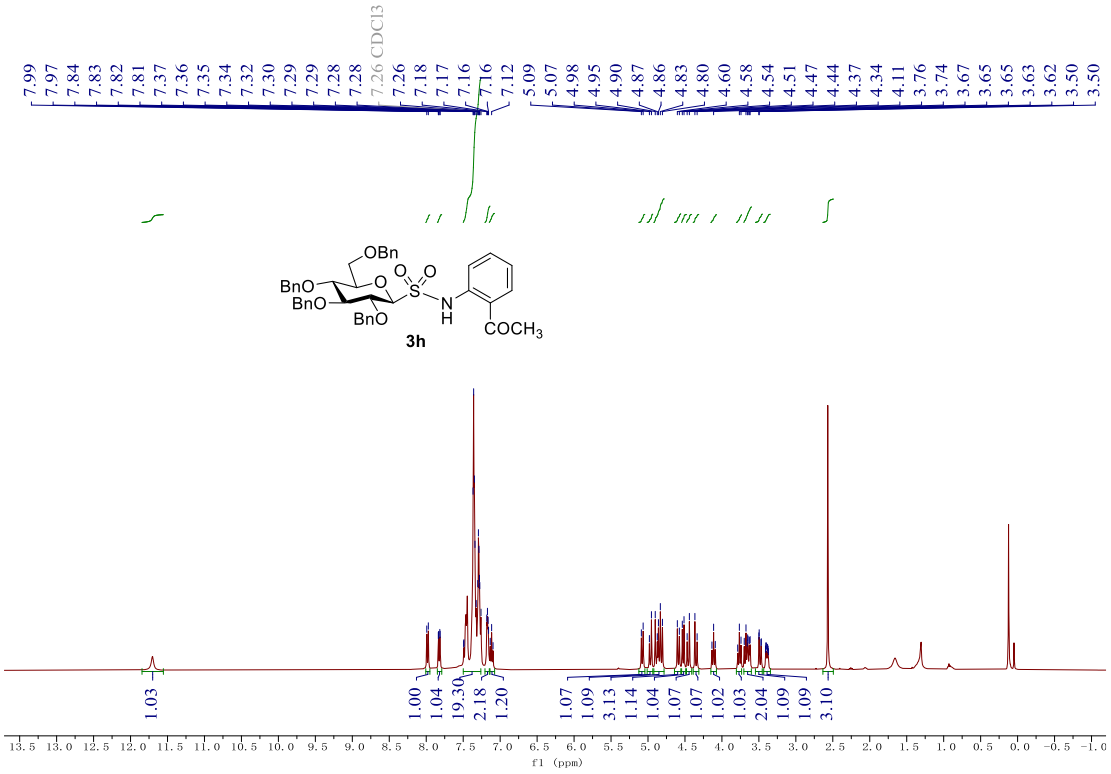


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3h**

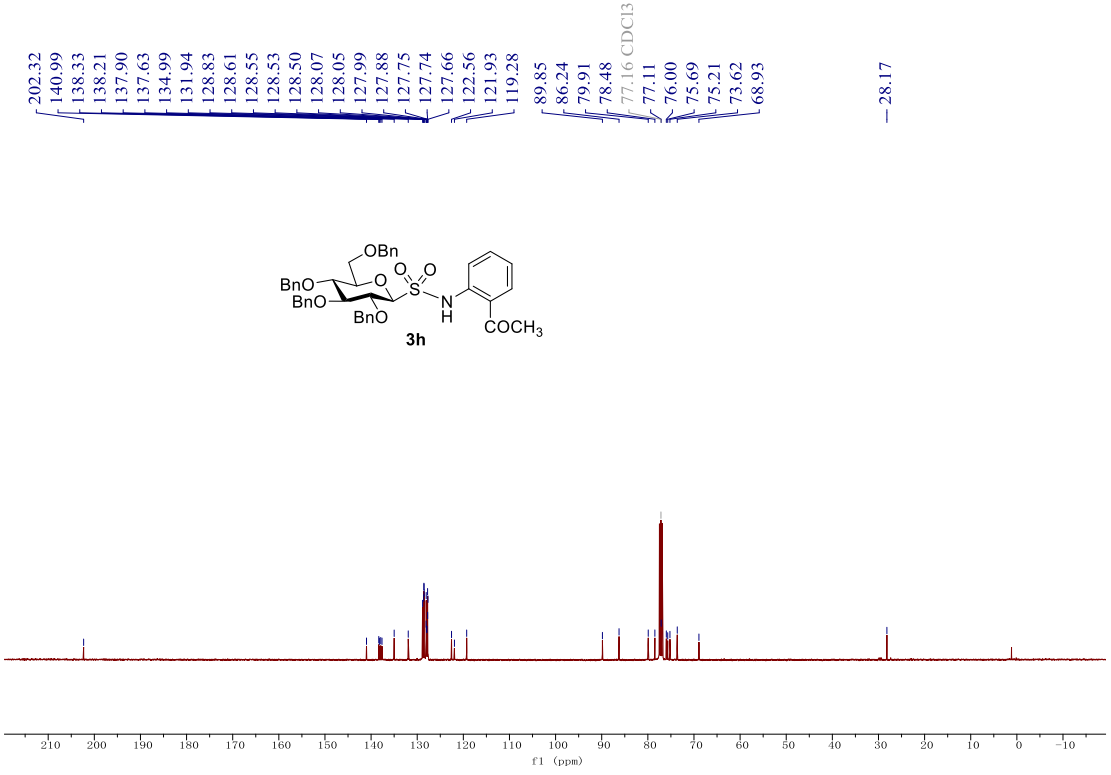


Figure S19. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3h**

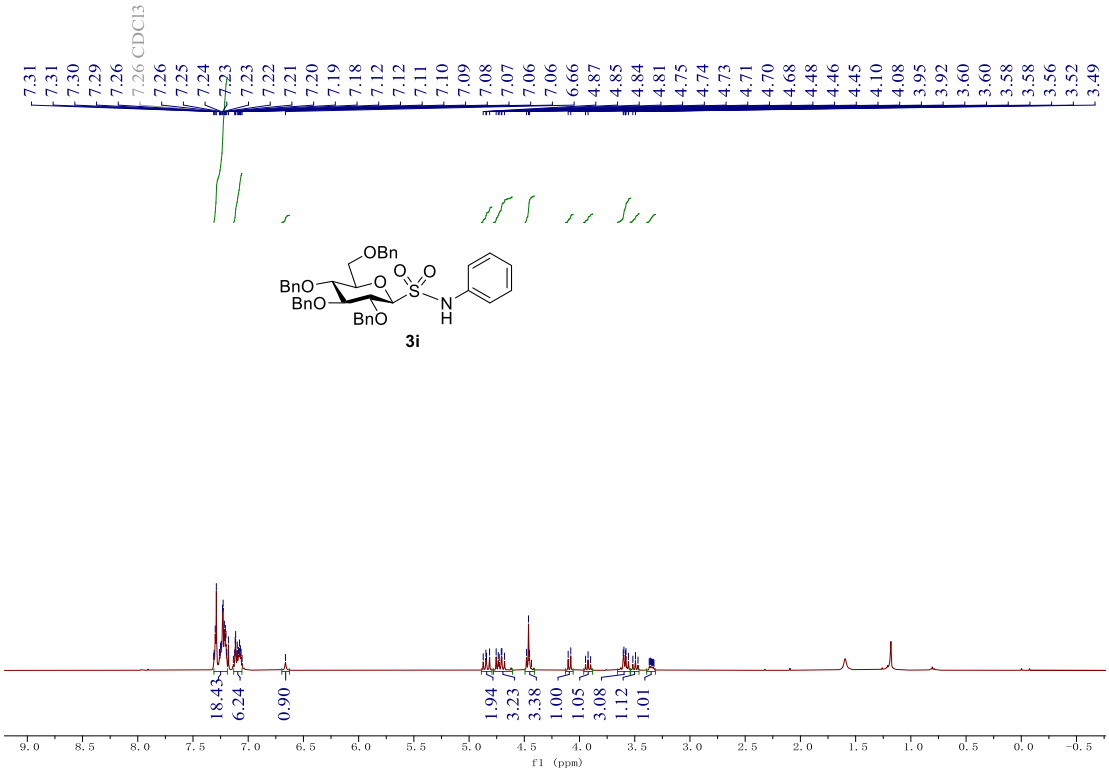


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3i**

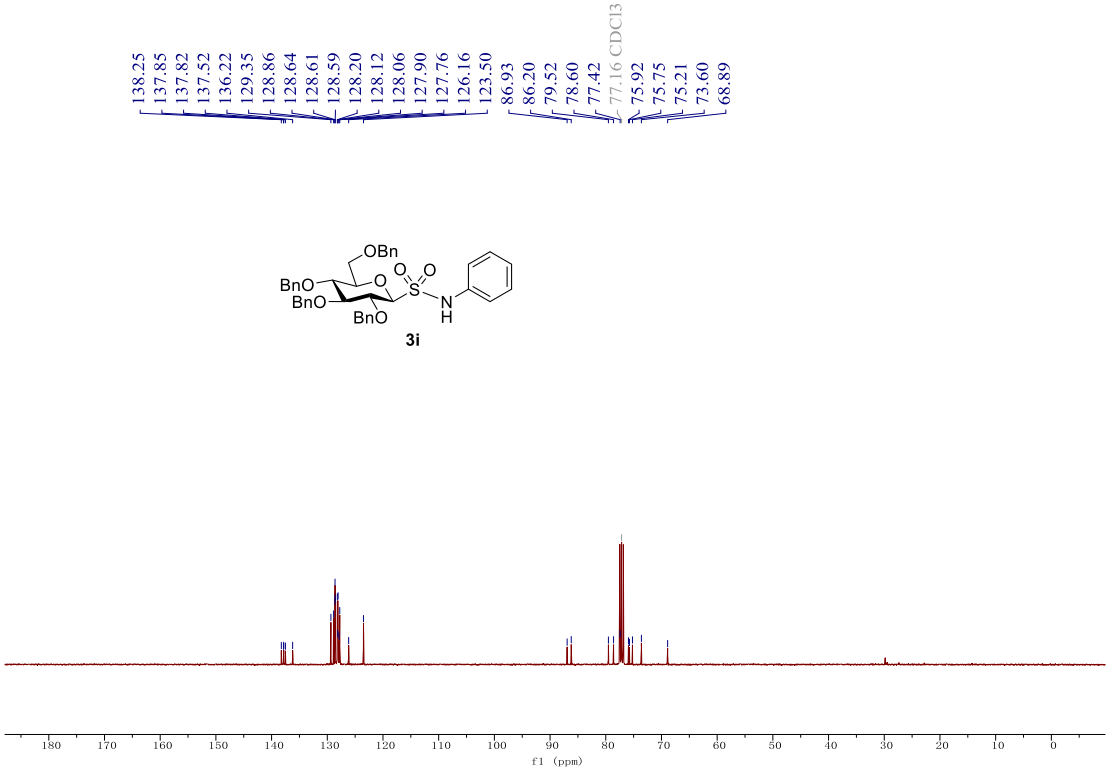


Figure S21. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3i**

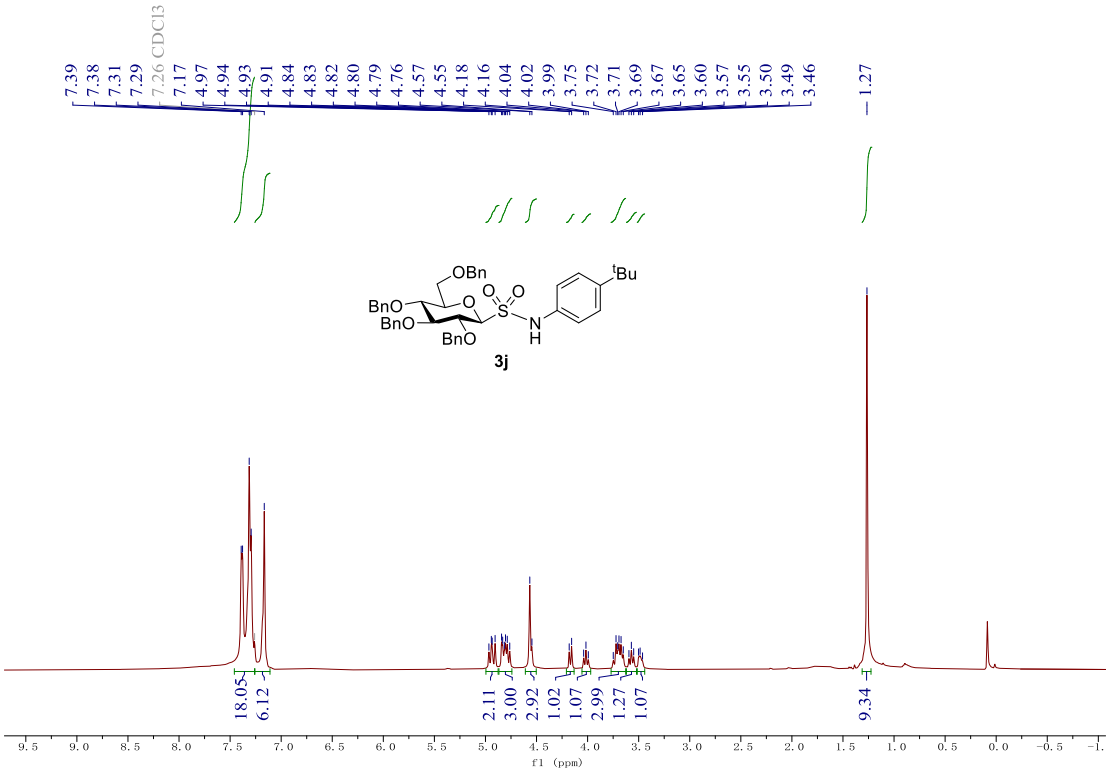


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3j**

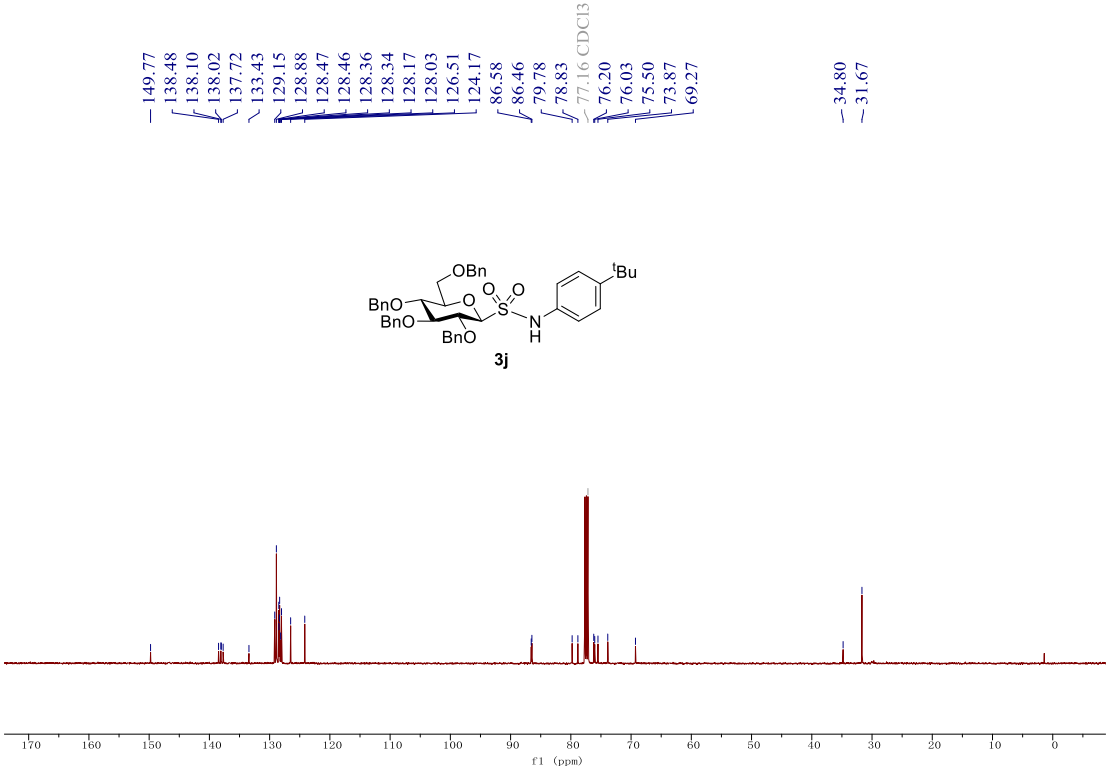


Figure S23. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3j**

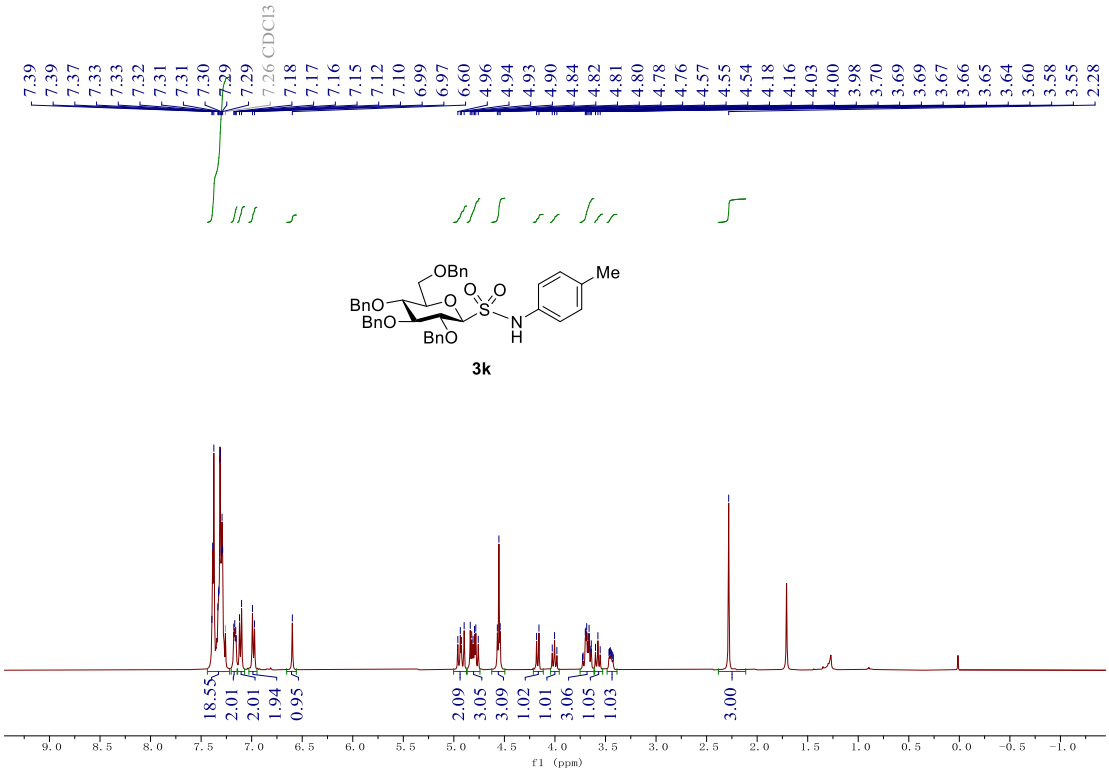


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3k**

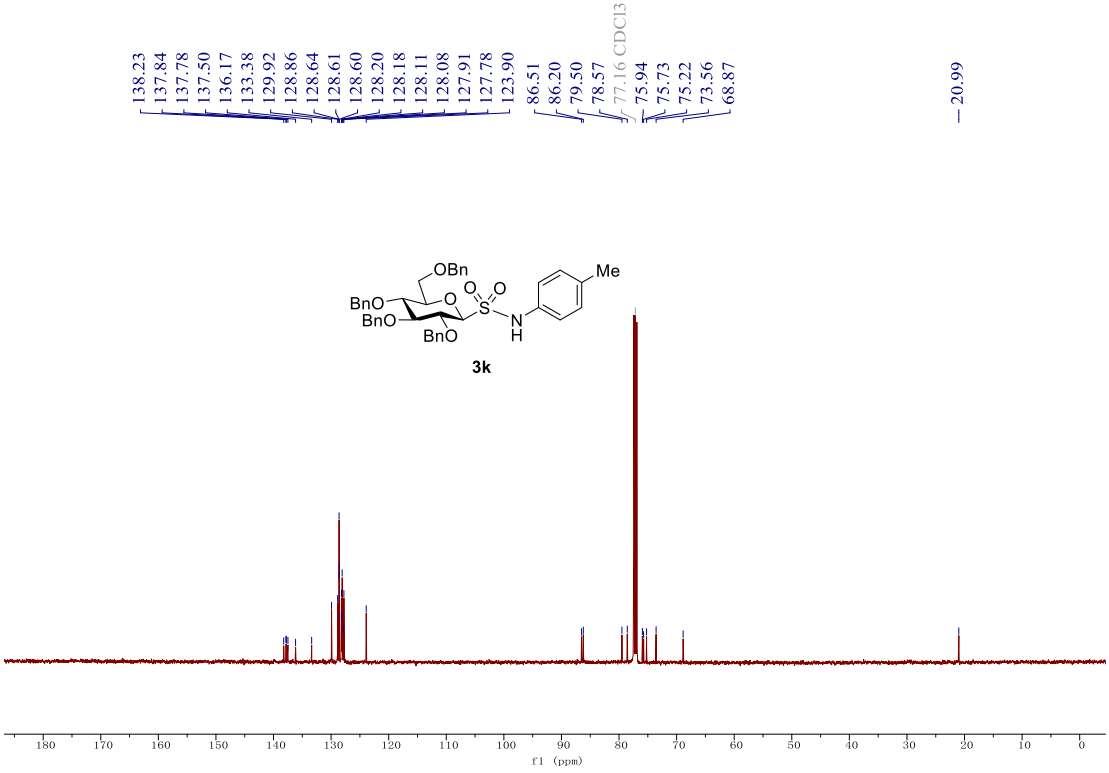


Figure S25. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3k**

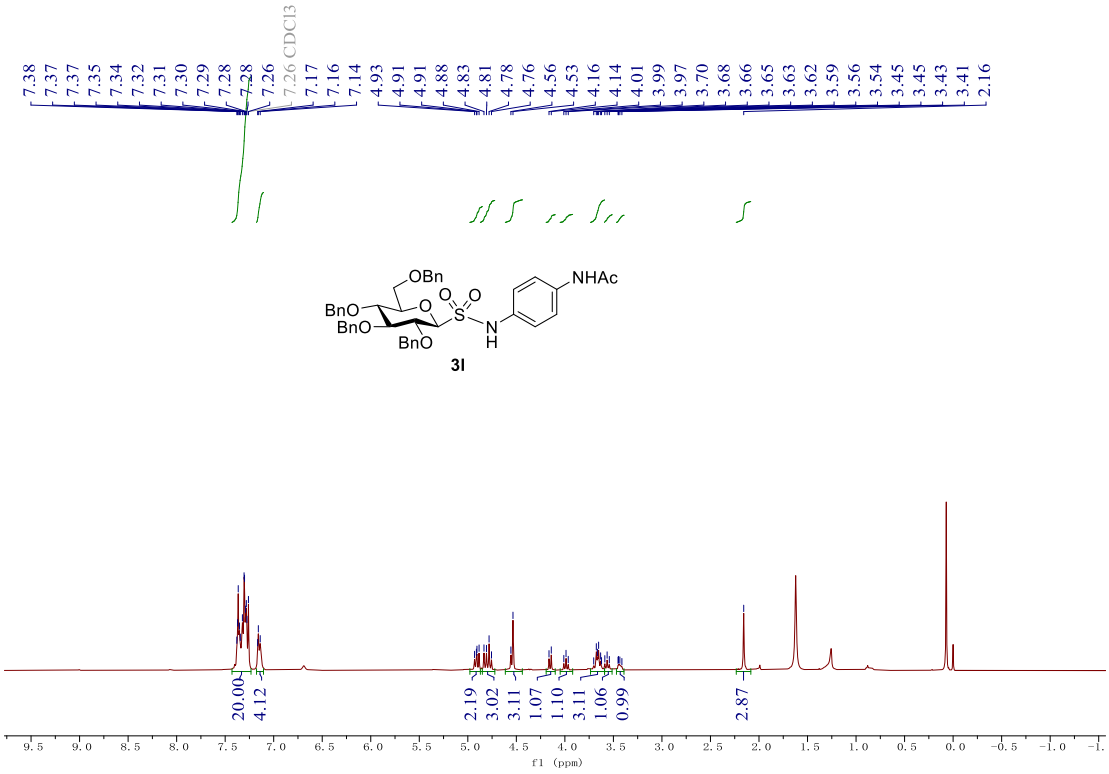


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3l**

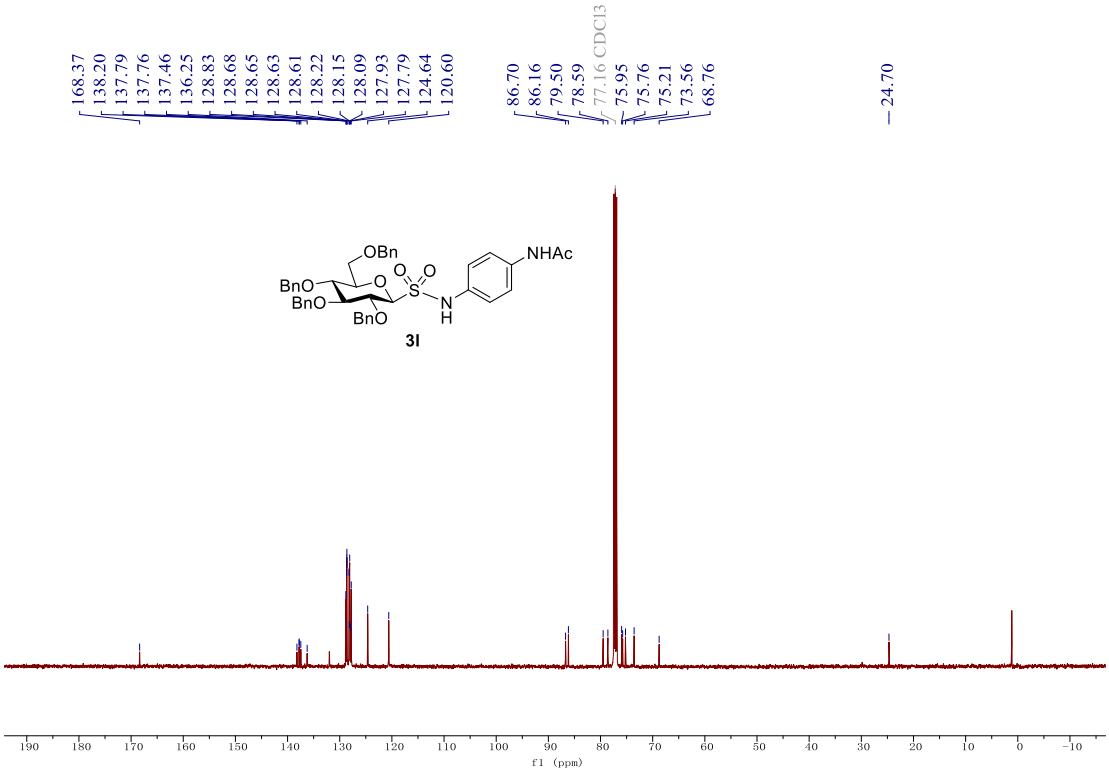


Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3l**

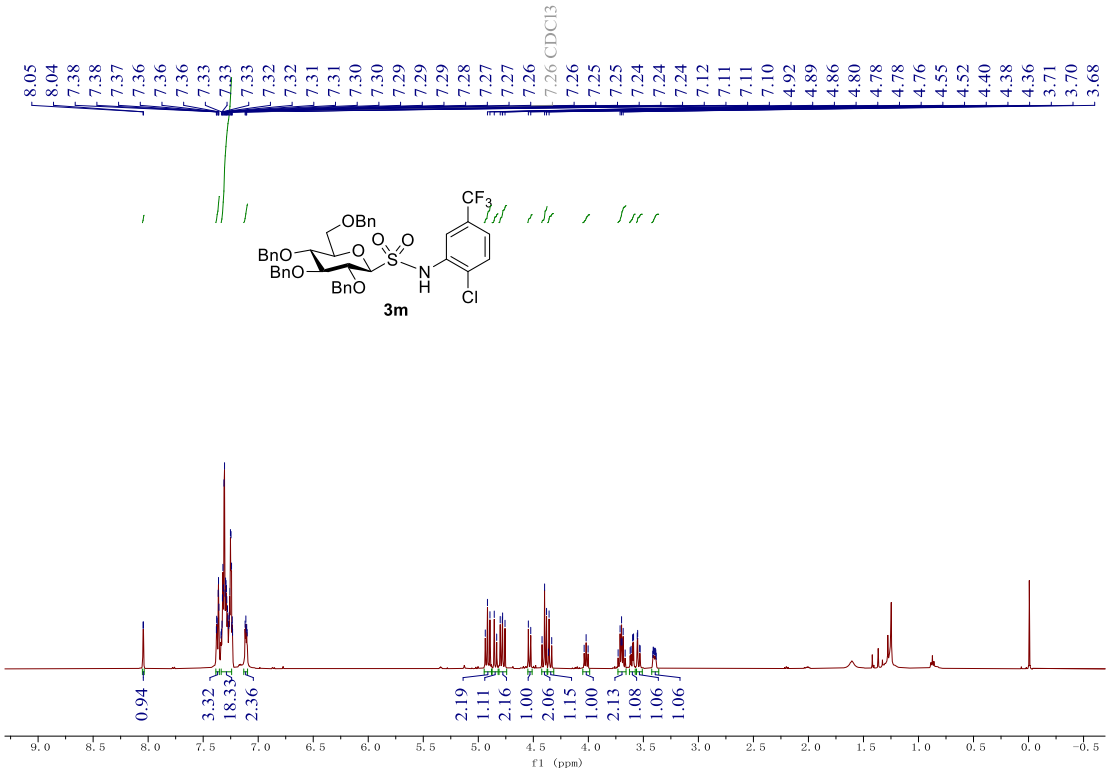


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3m**

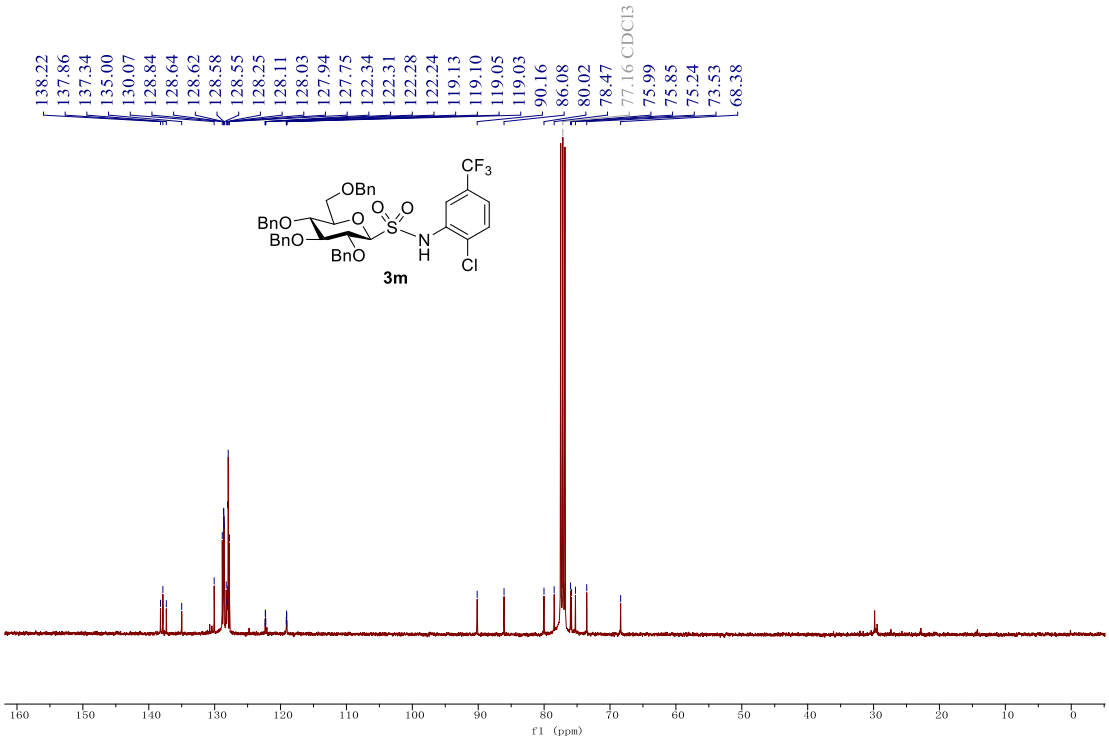


Figure S29. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3m**

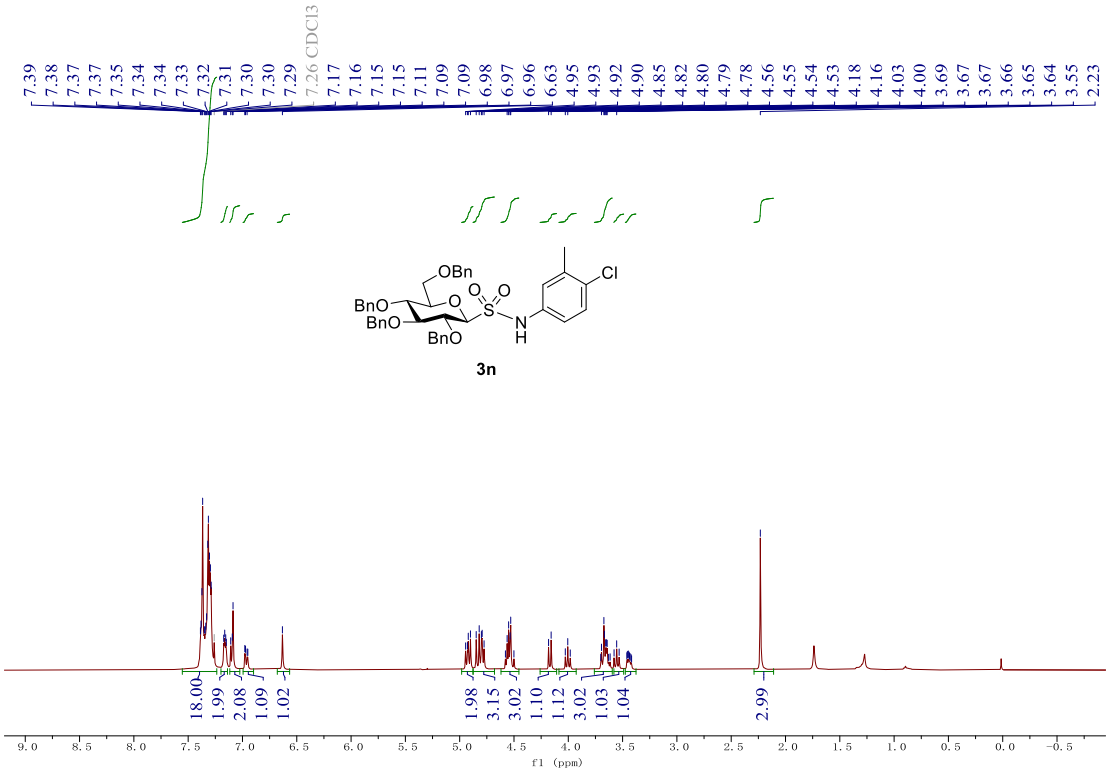


Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3n**

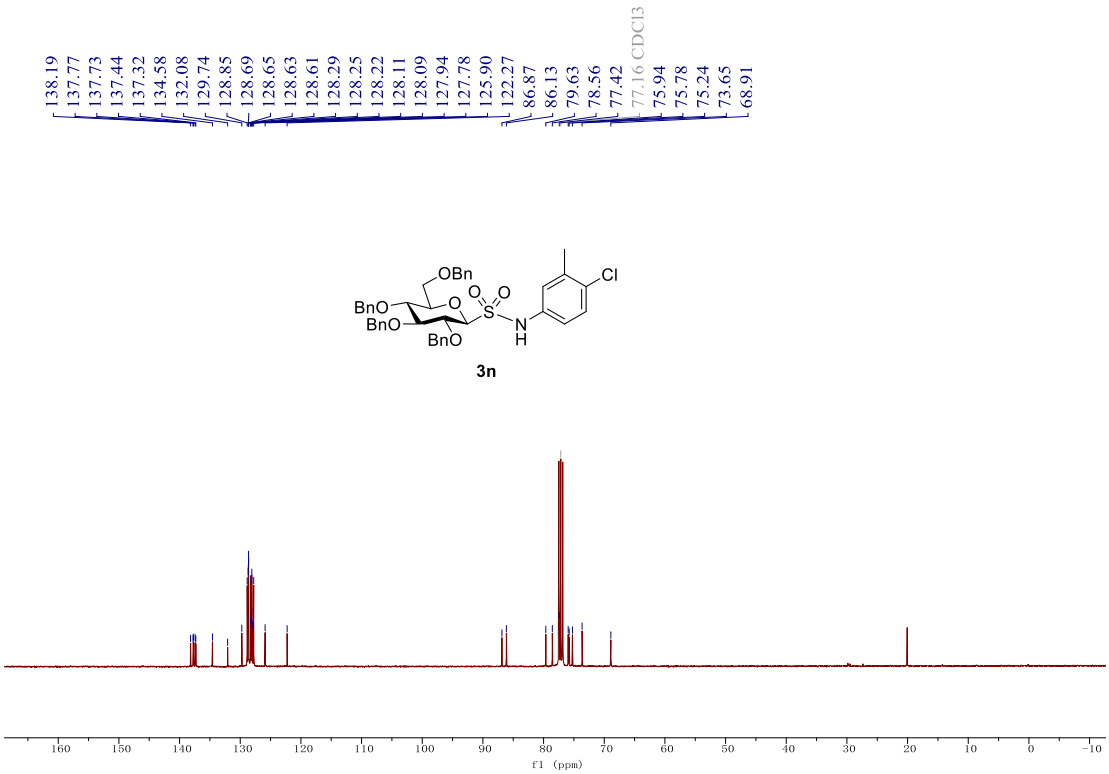


Figure S31. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3n**

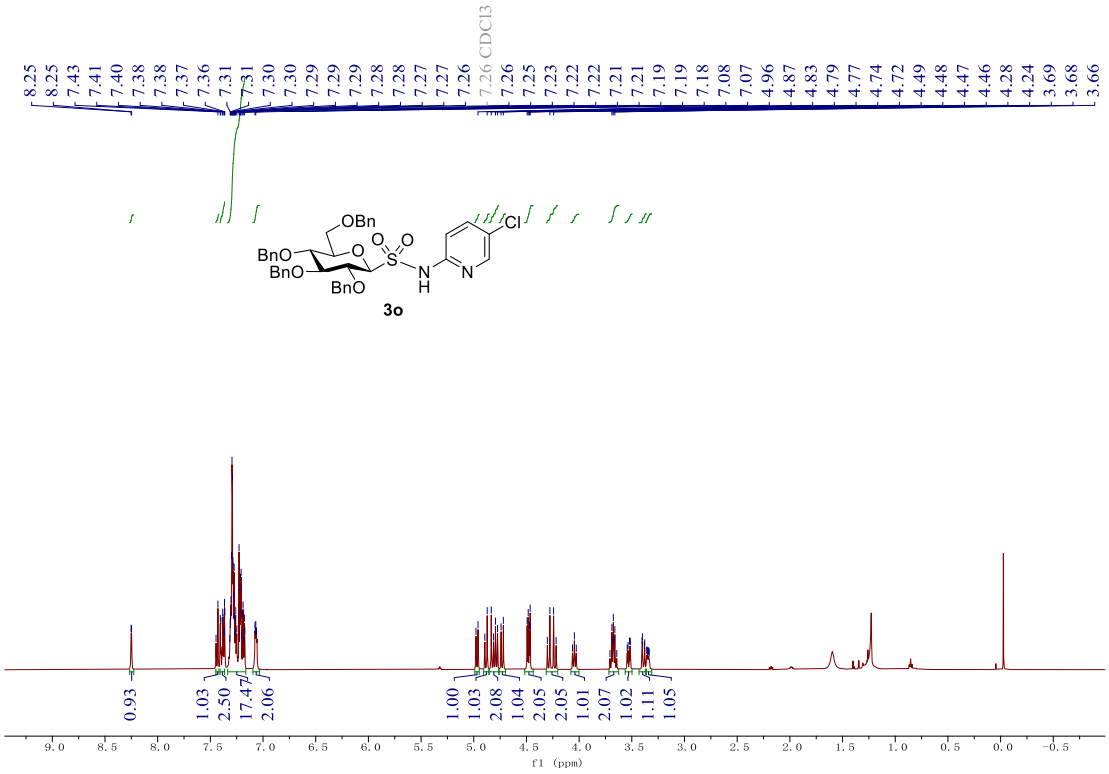


Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3o**

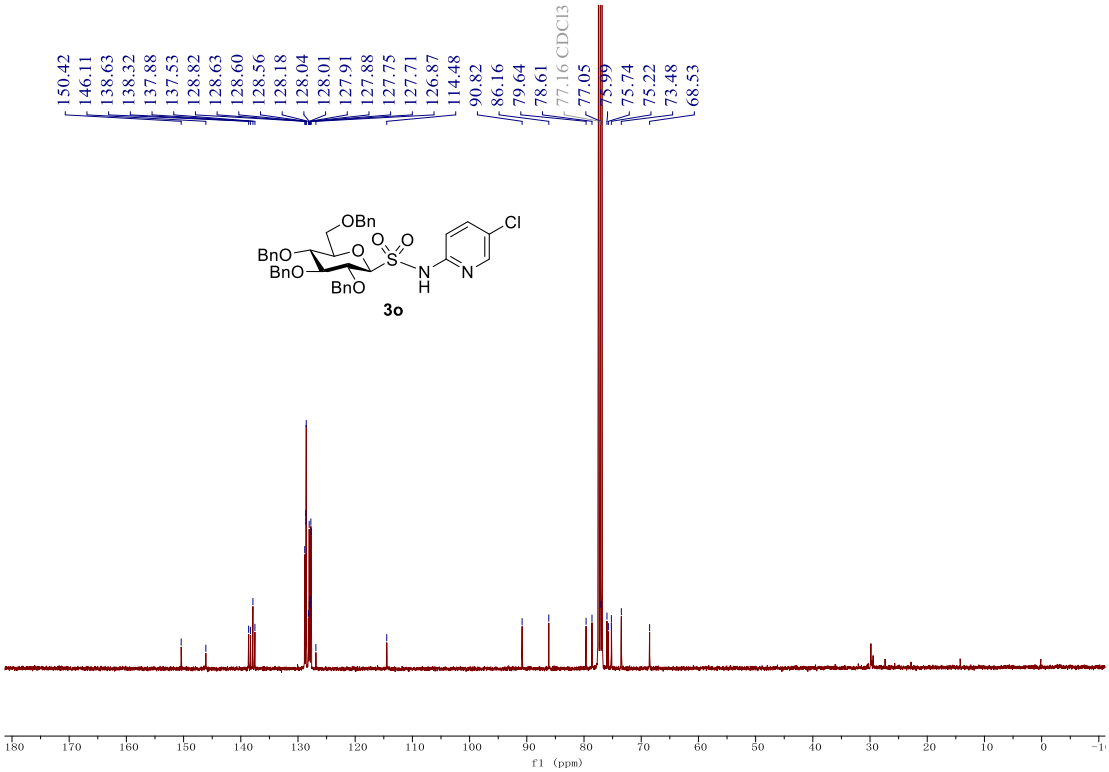


Figure S33. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3o**

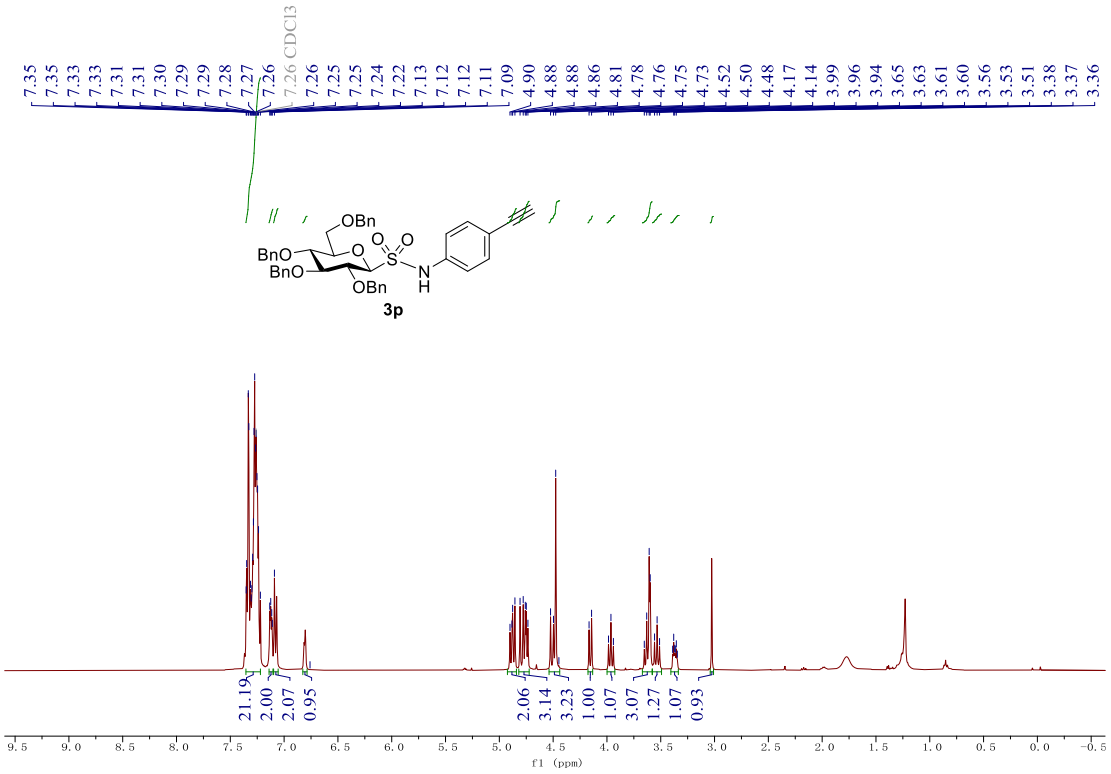


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3p**

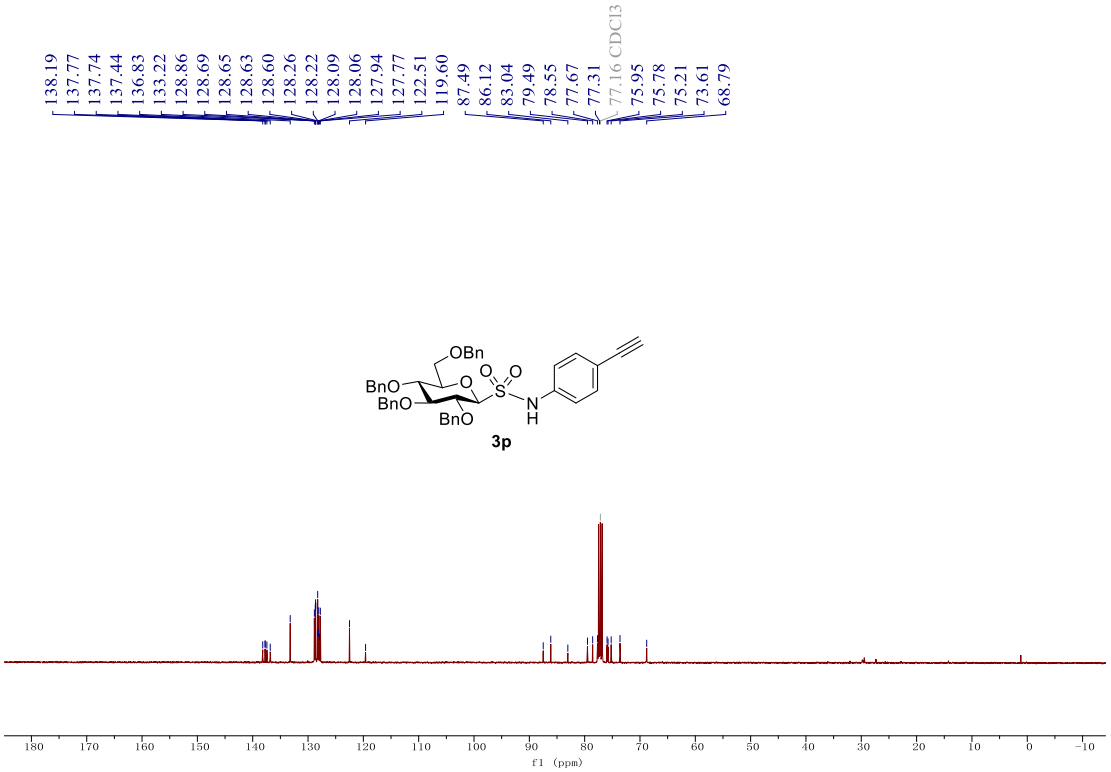


Figure S35. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3p**

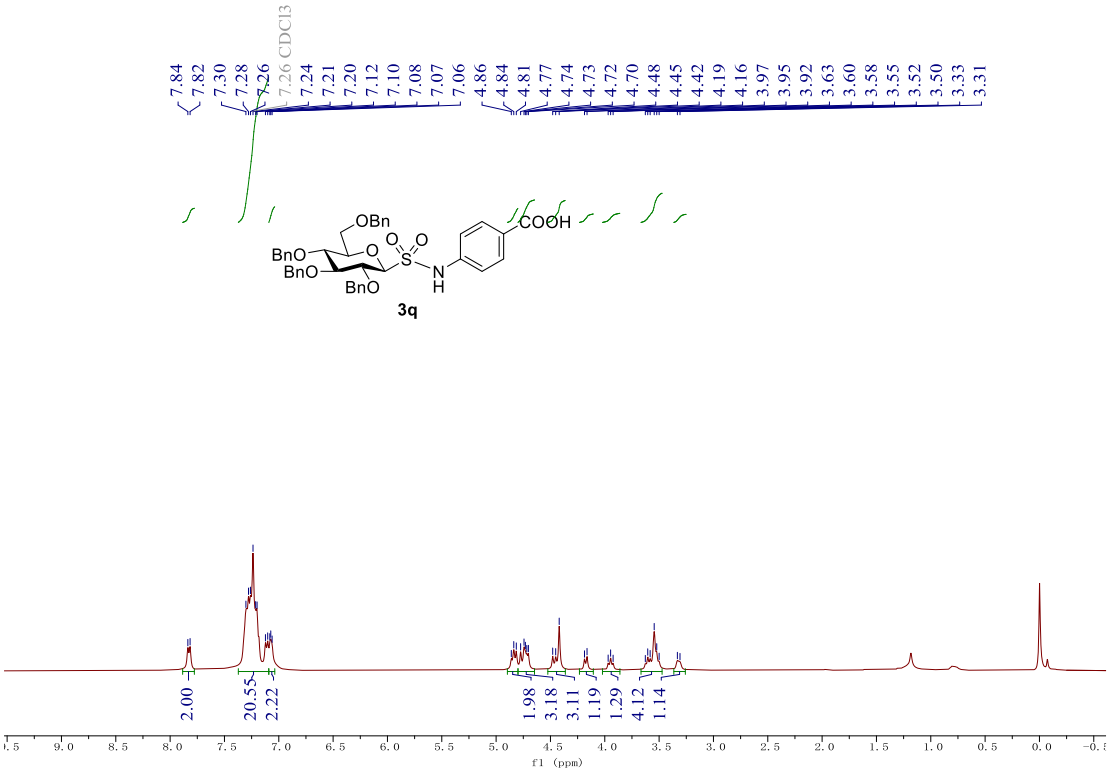


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3q**

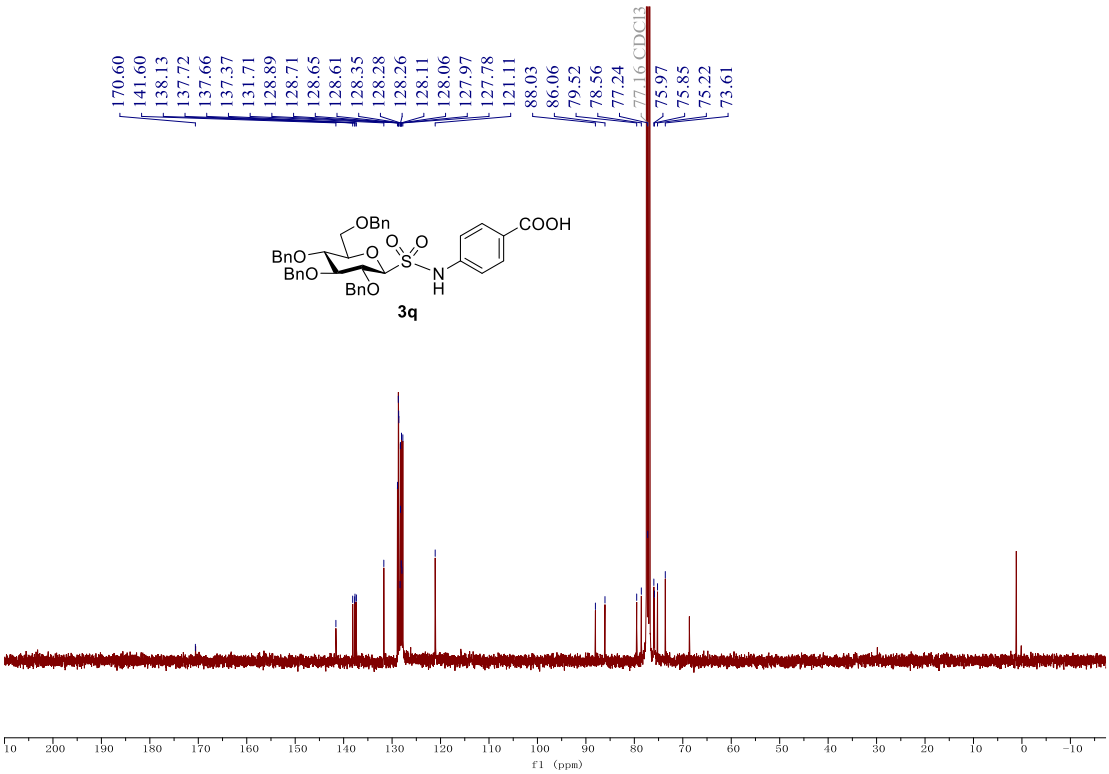


Figure S37. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3q**

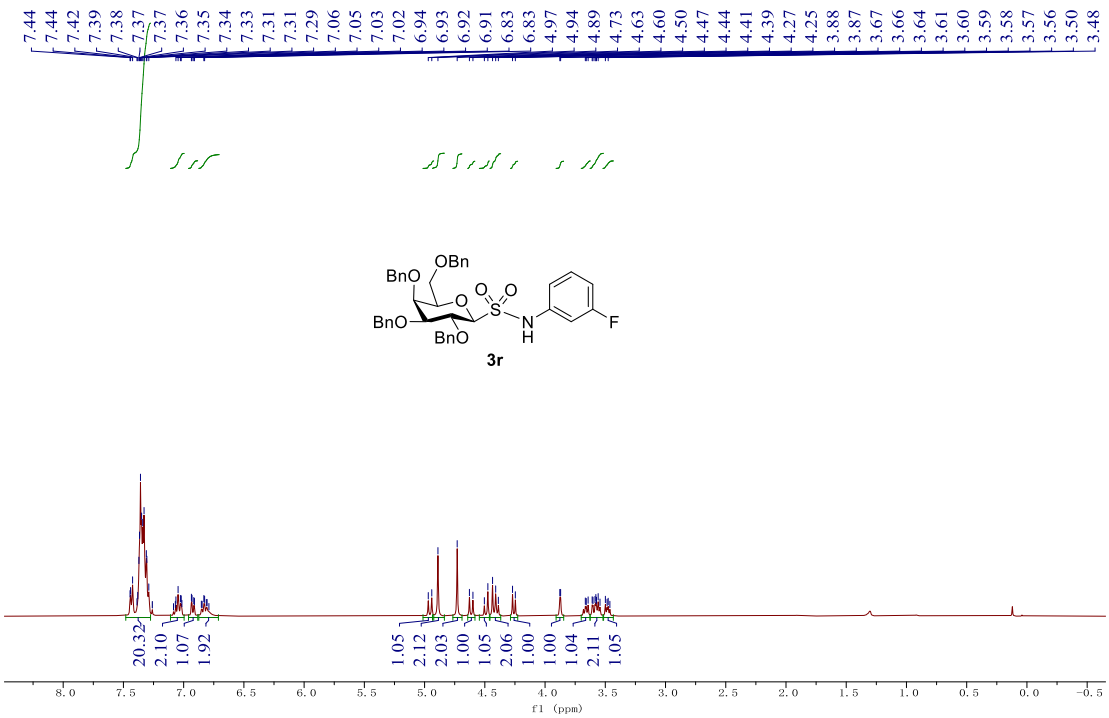


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3r**

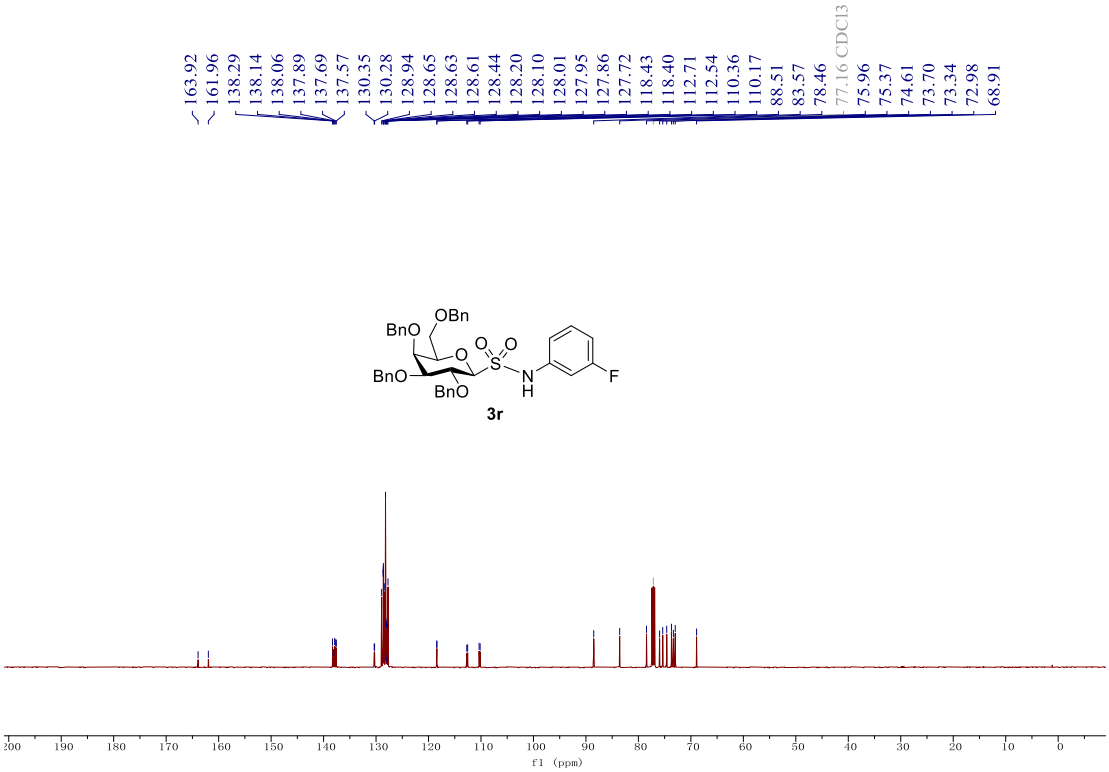


Figure S39. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3r**

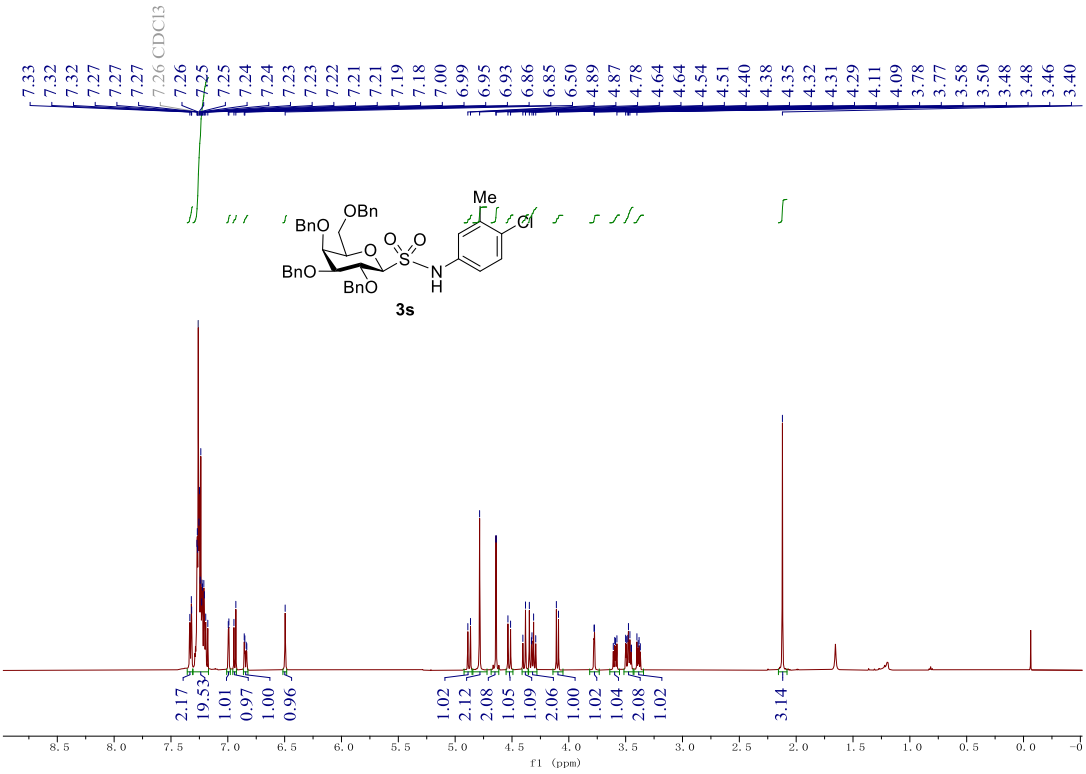


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3s**

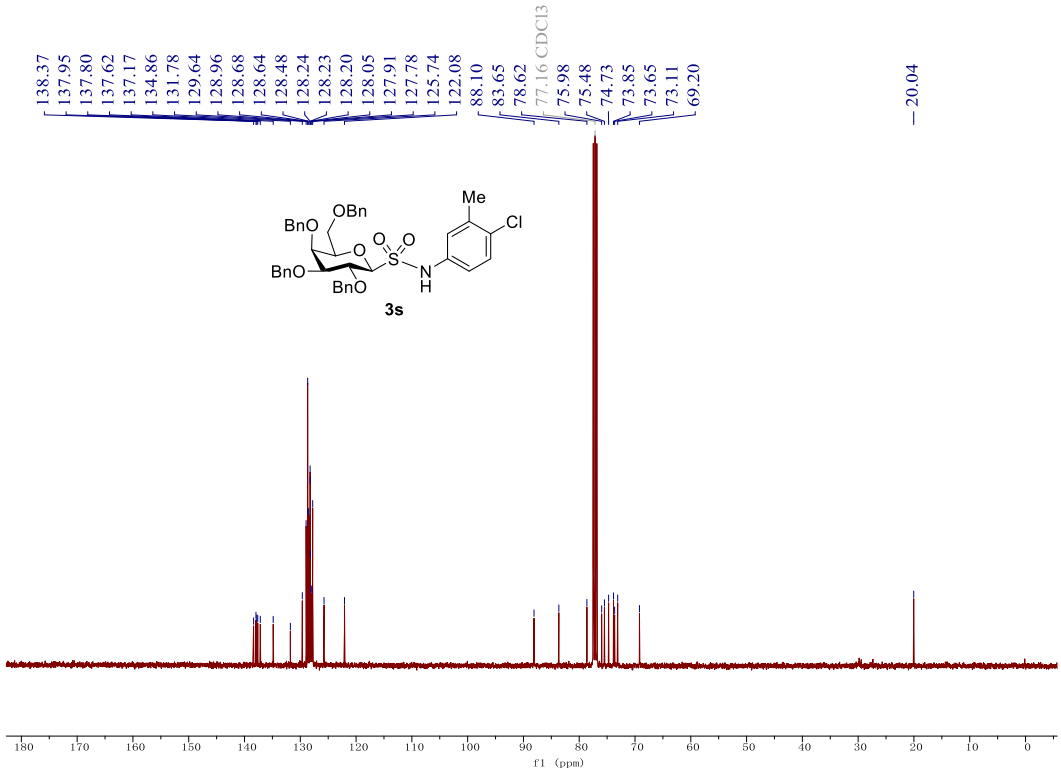


Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3s**

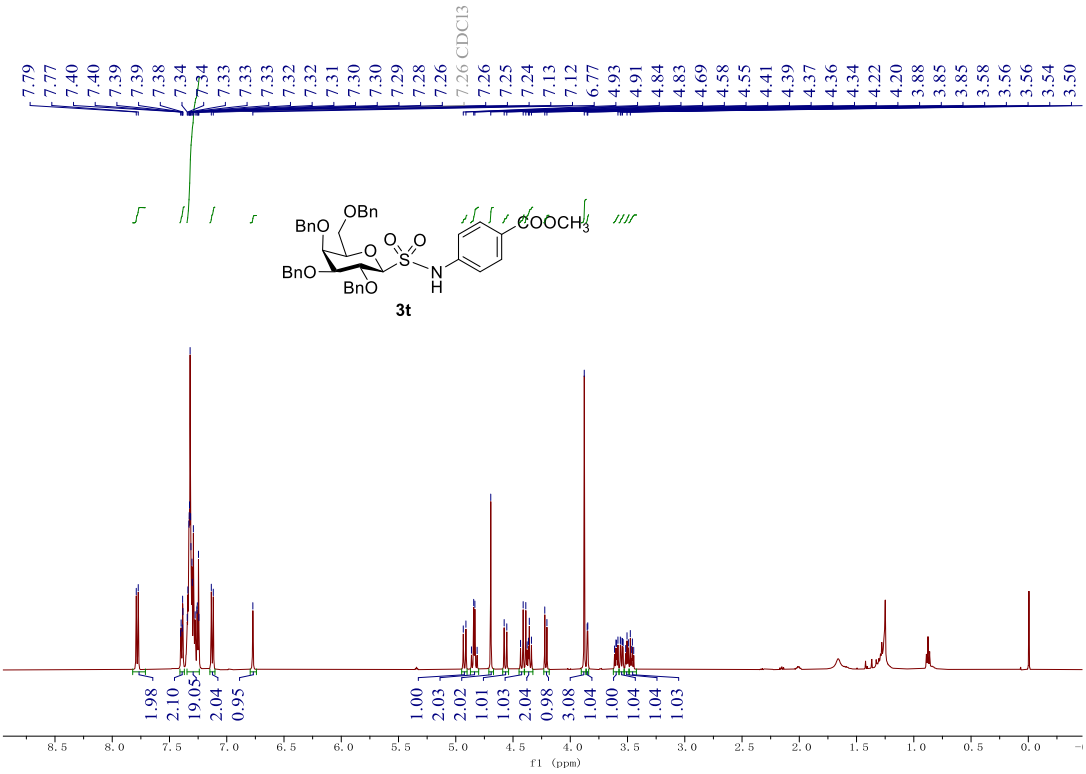


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3t**

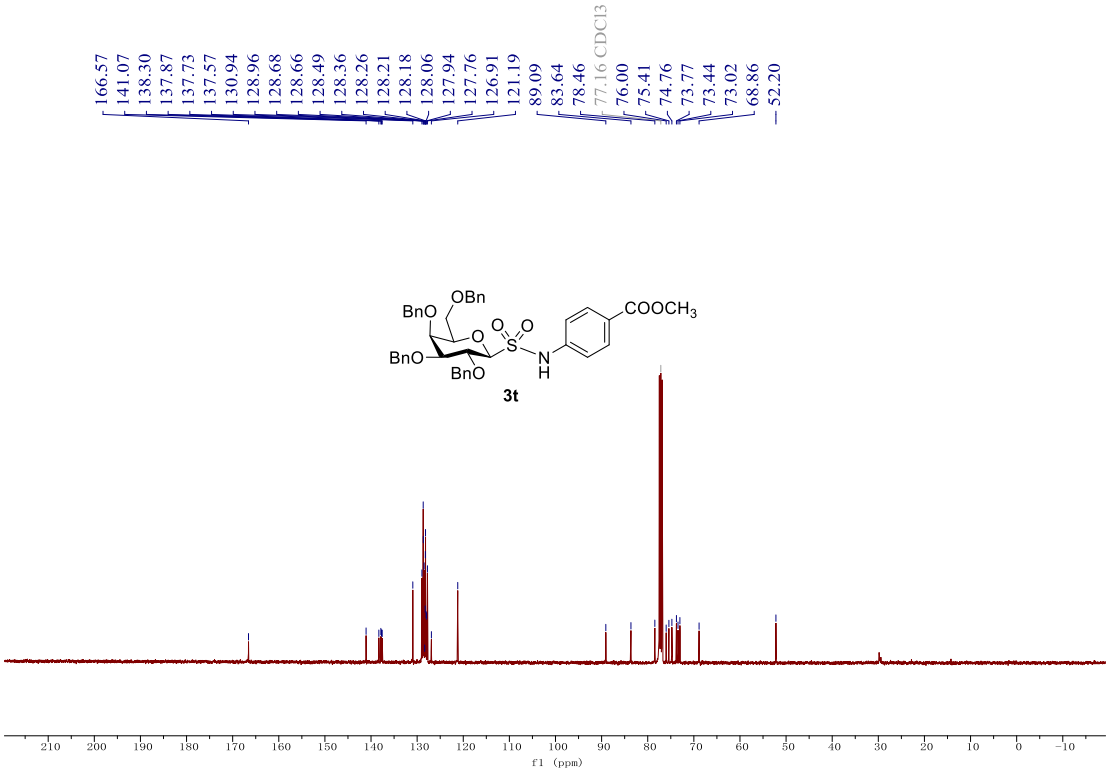


Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3t**

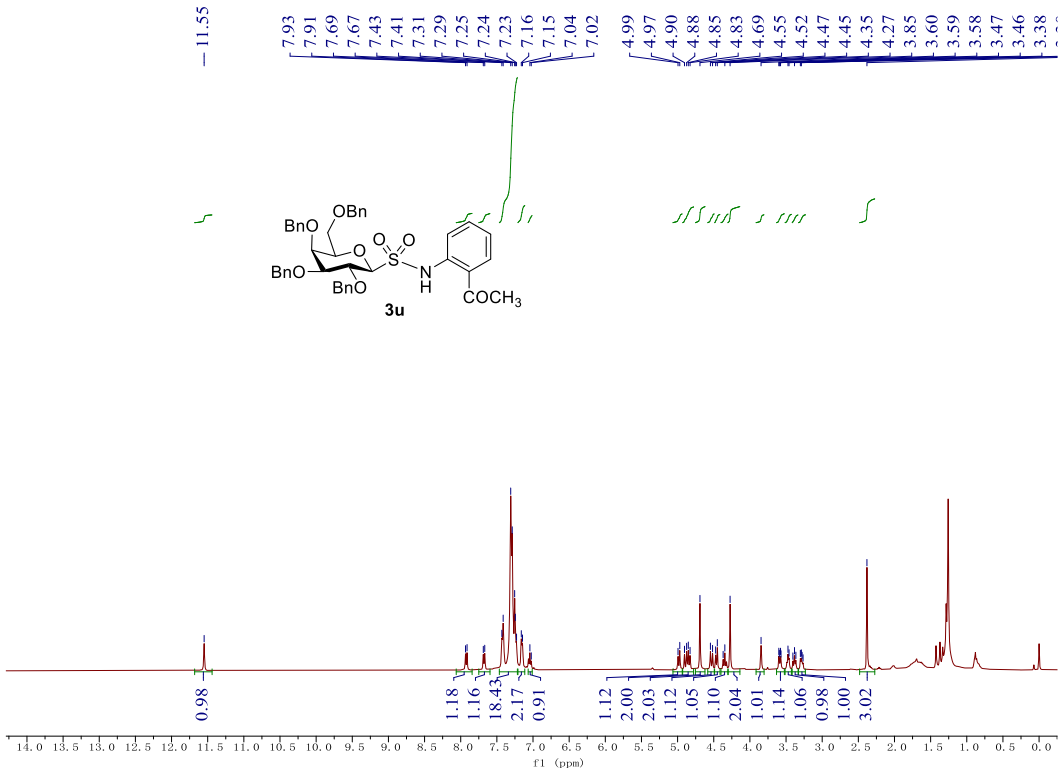


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3u**

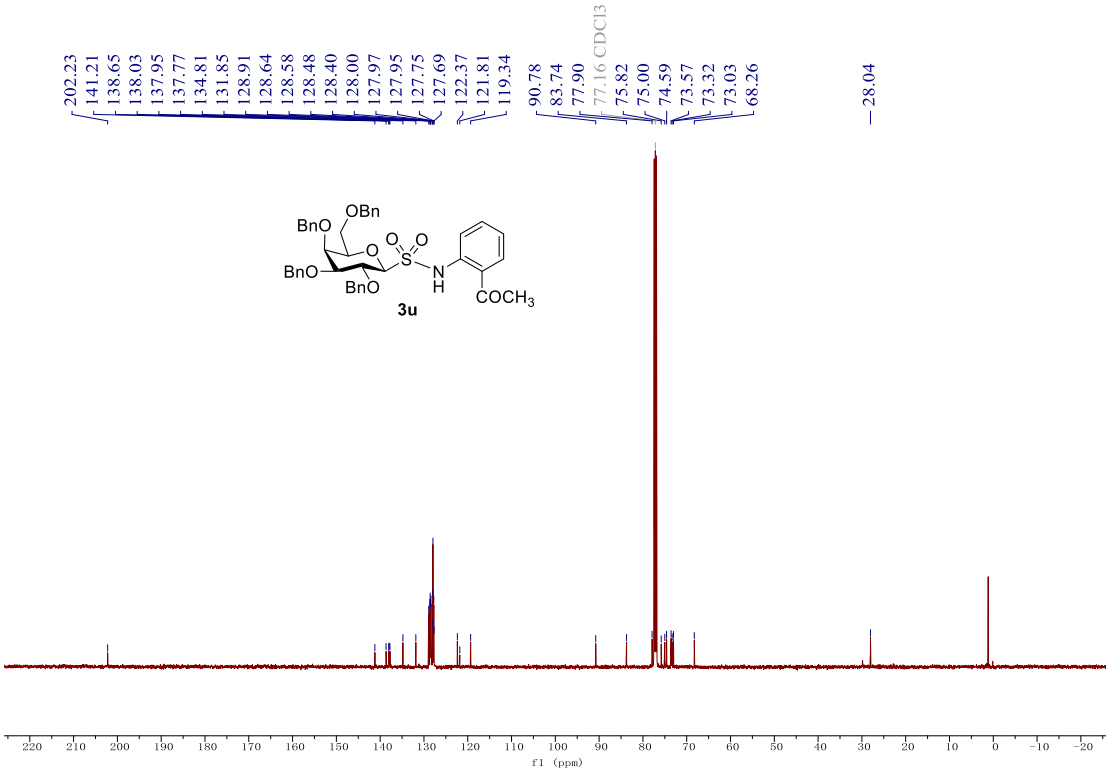


Figure S45. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3u**

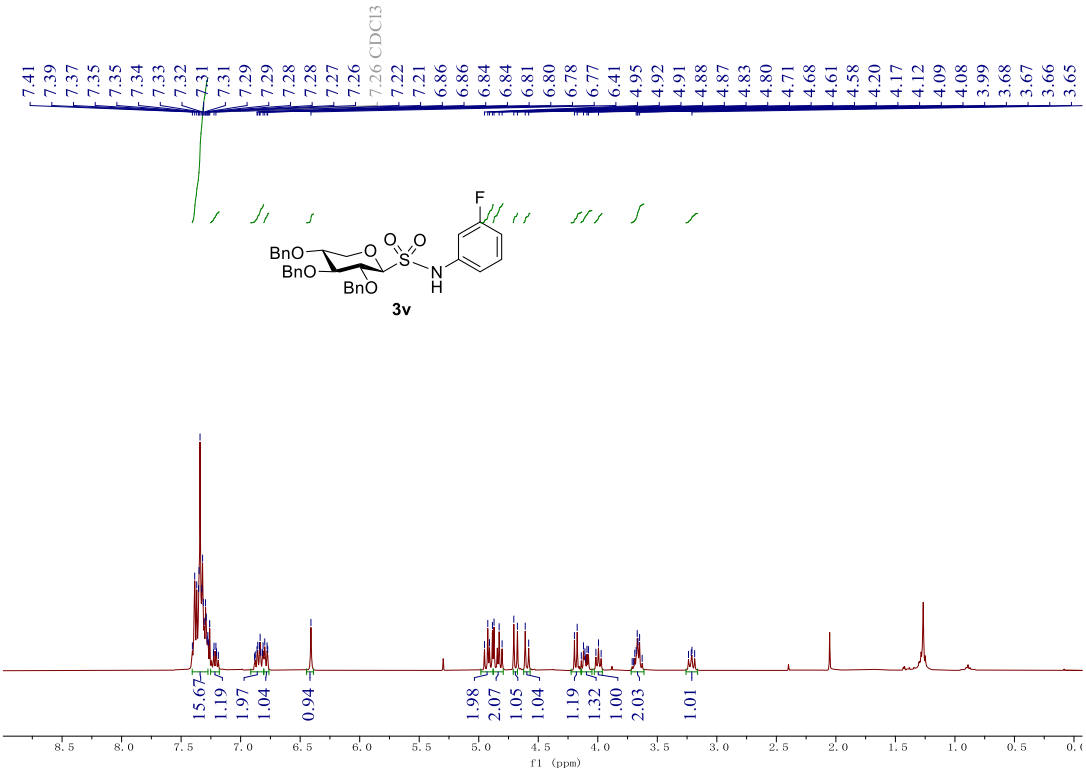


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3v**

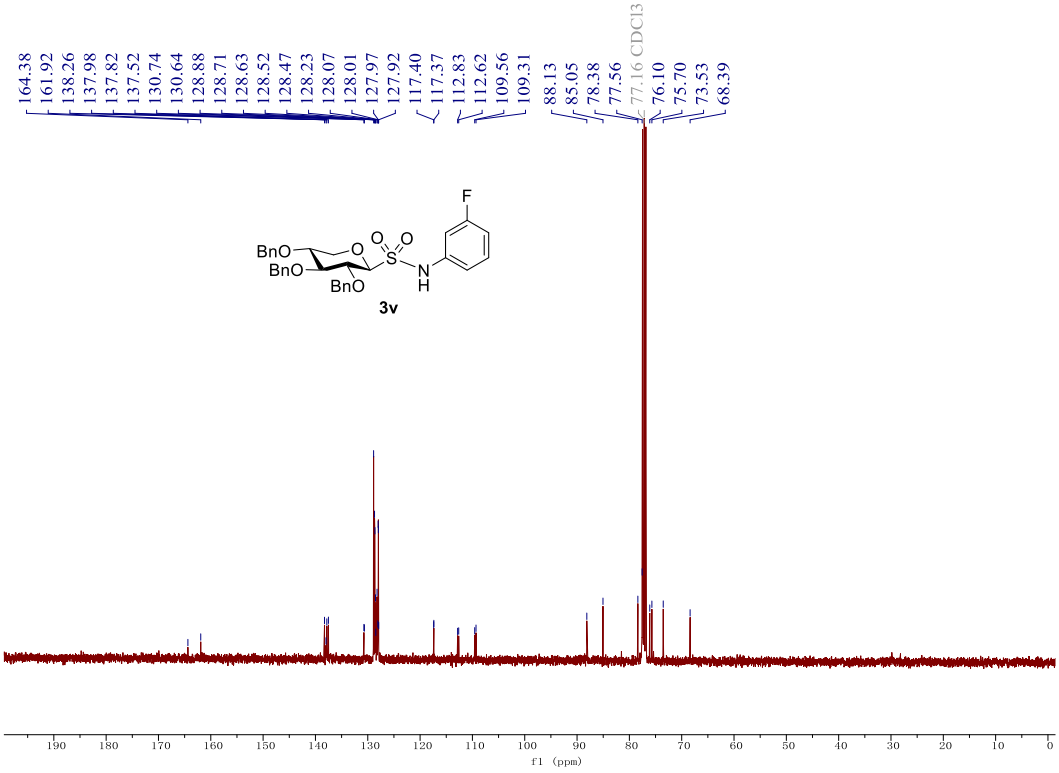


Figure S47. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3v**

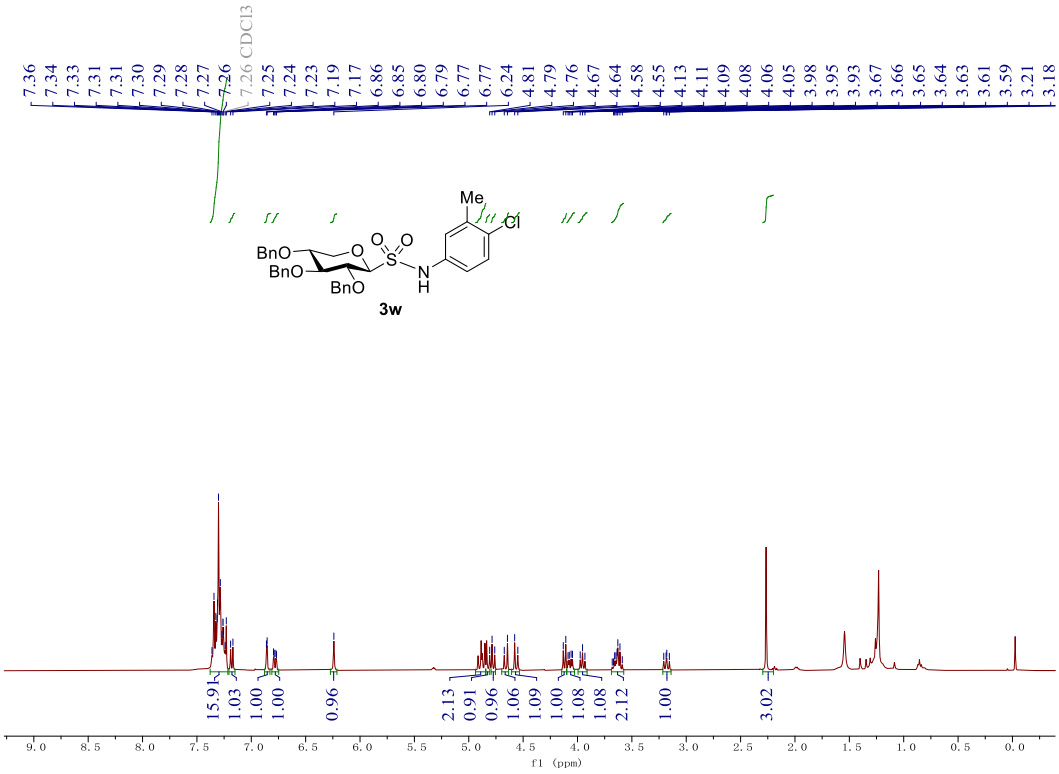


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3w**

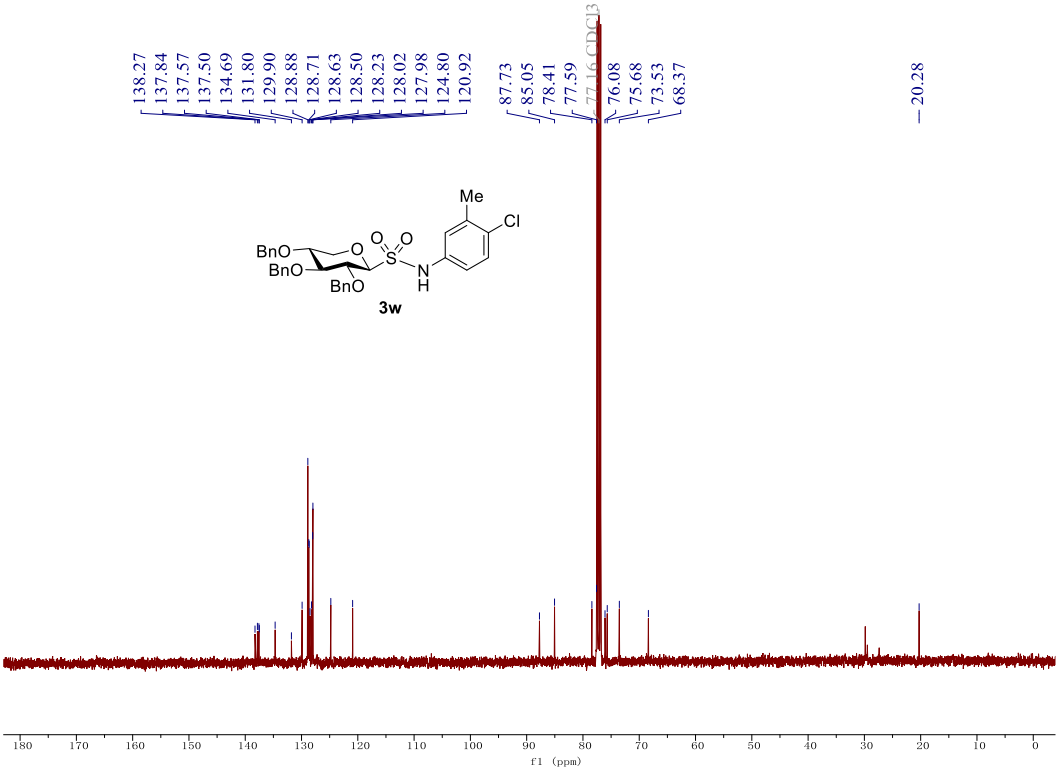


Figure S49. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3w**

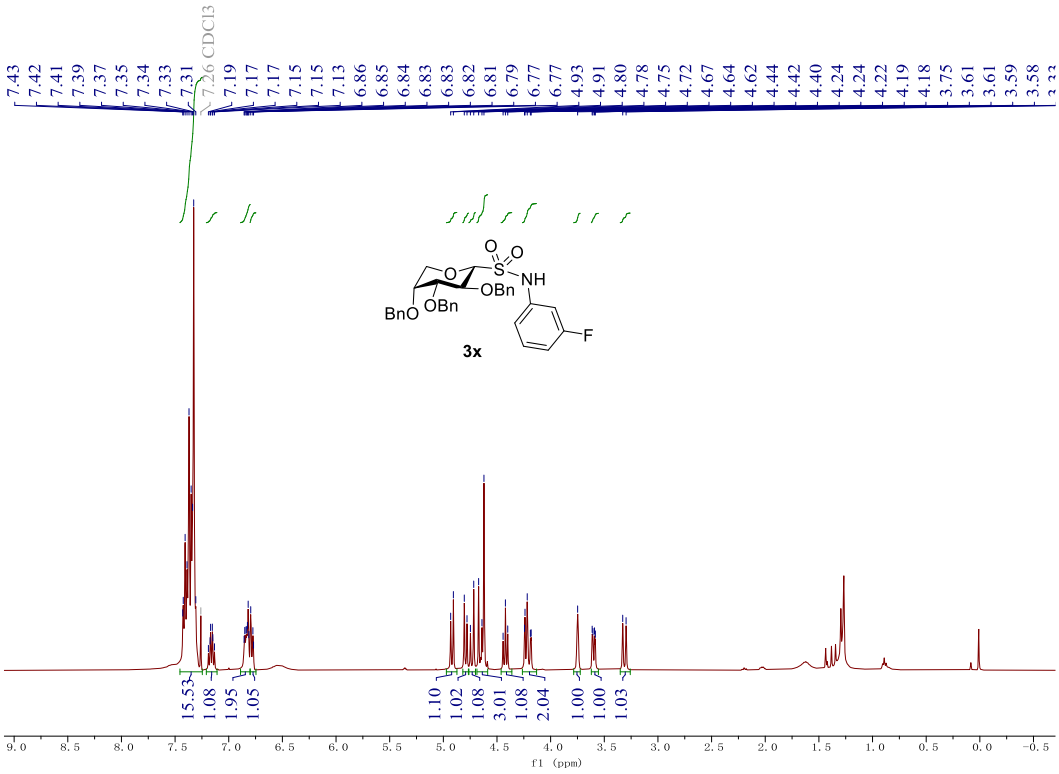


Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3x**

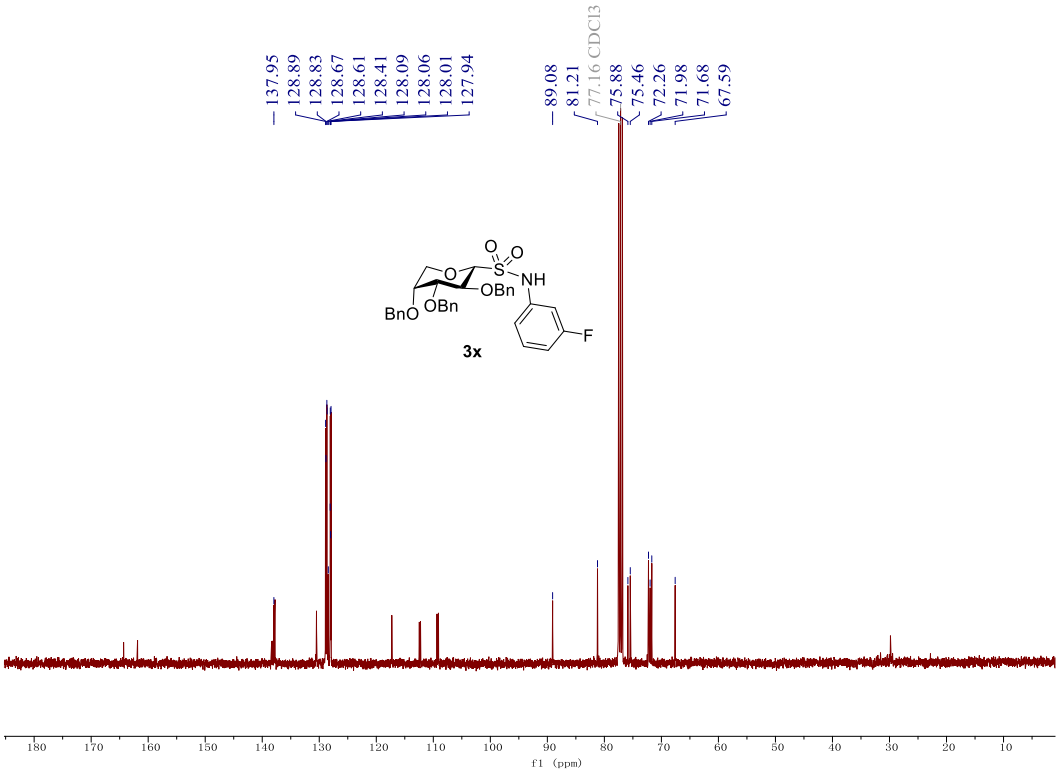


Figure S51. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3x**

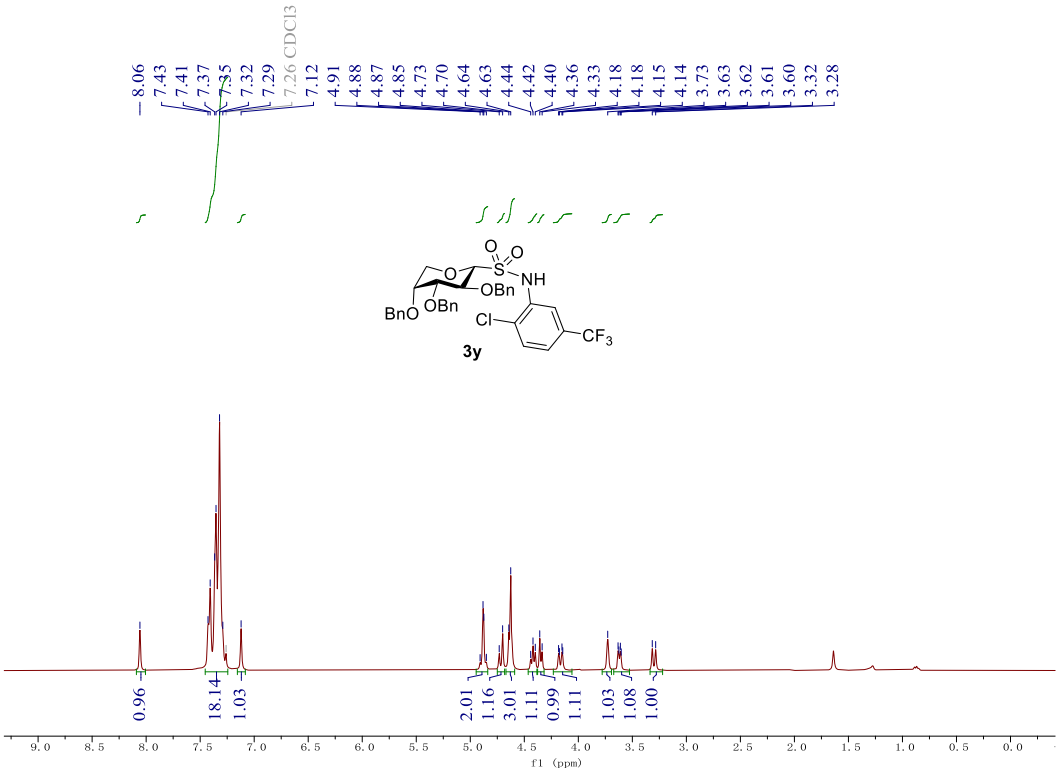


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3y**

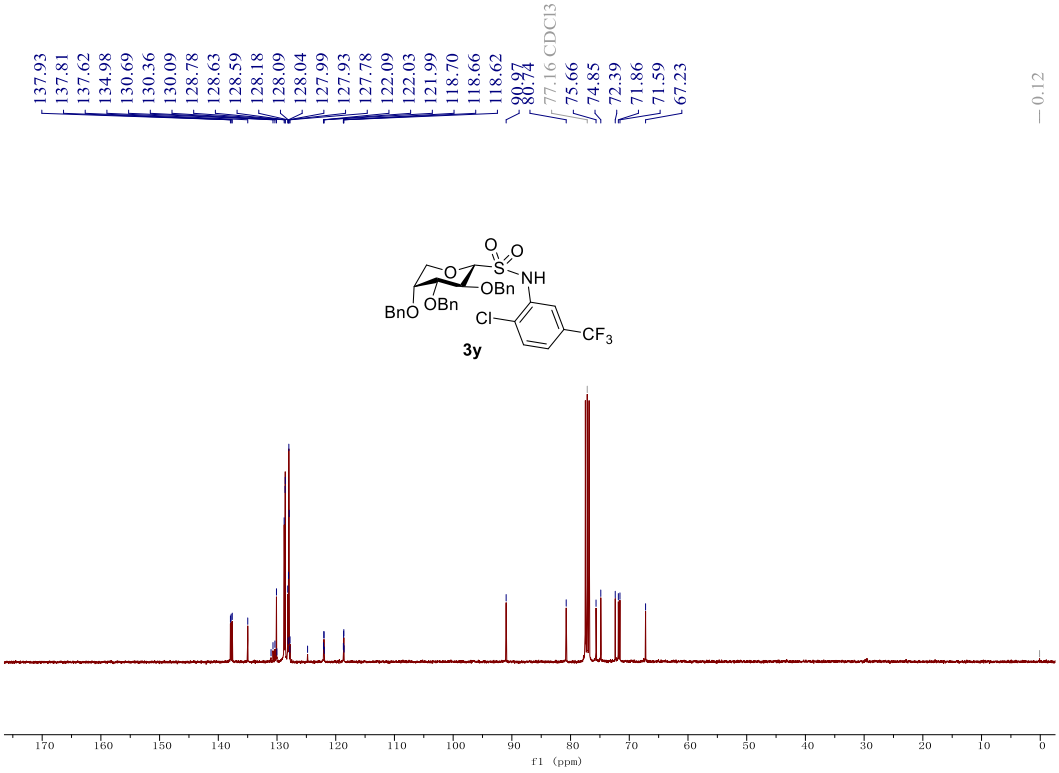


Figure S53. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3y**

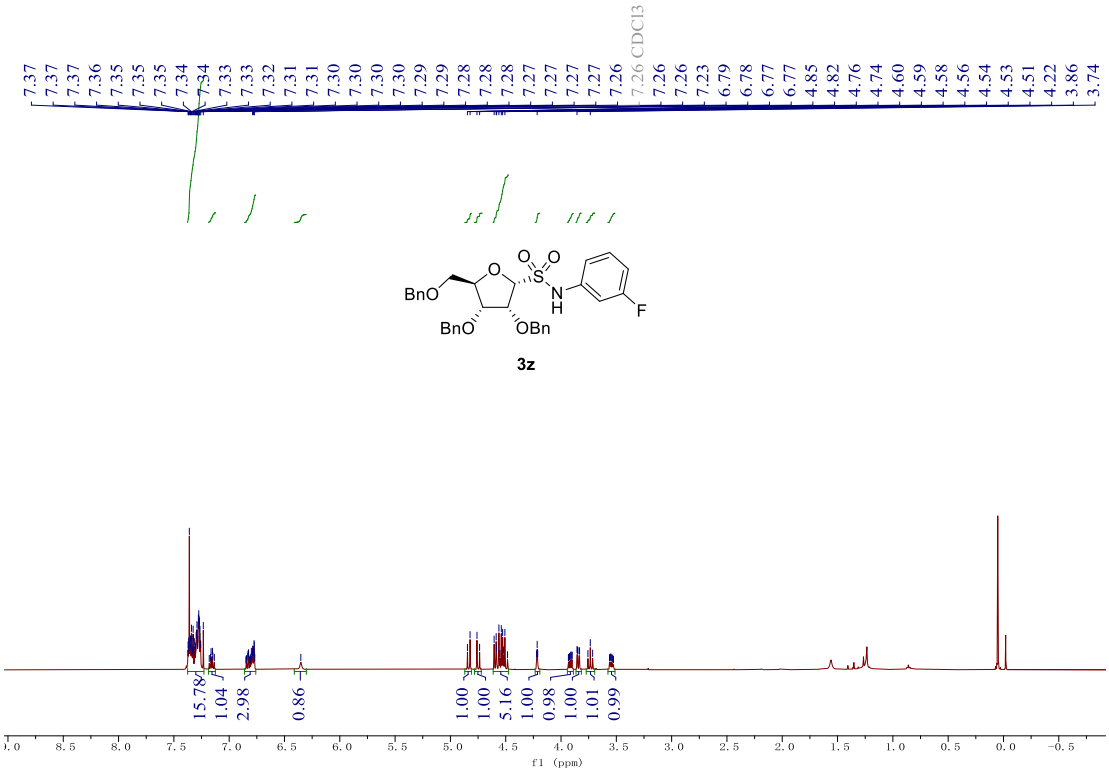


Figure S54. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3z**

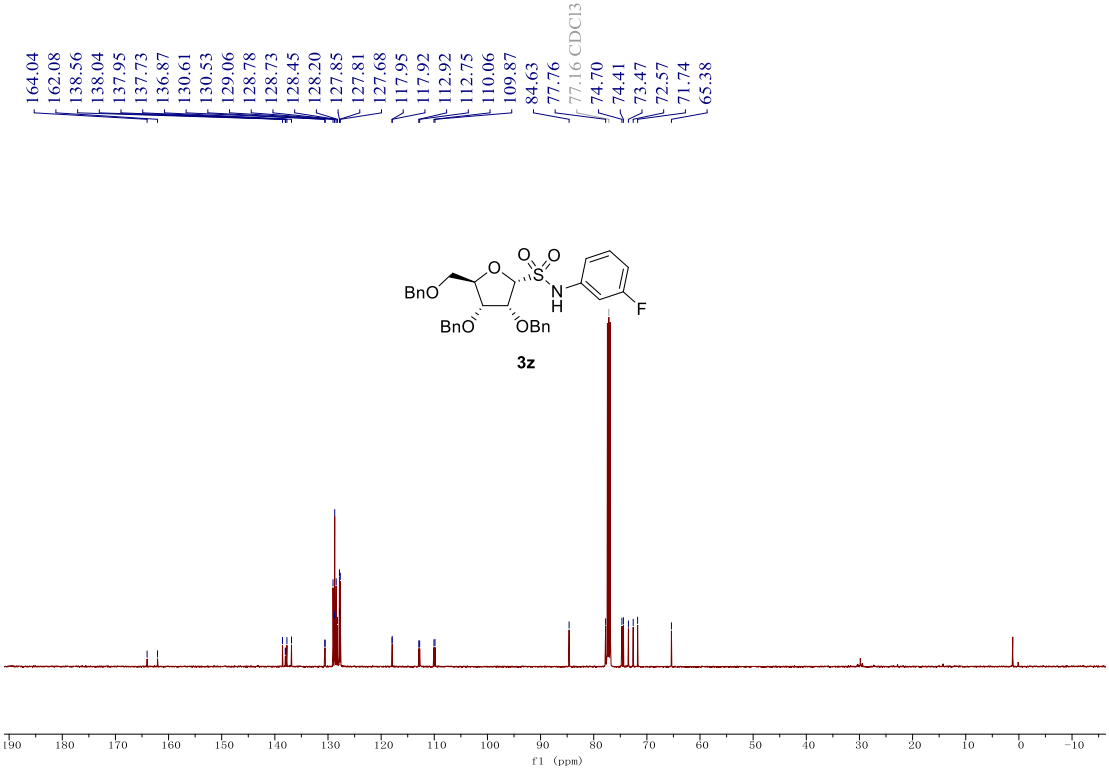


Figure S55. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound **3z**

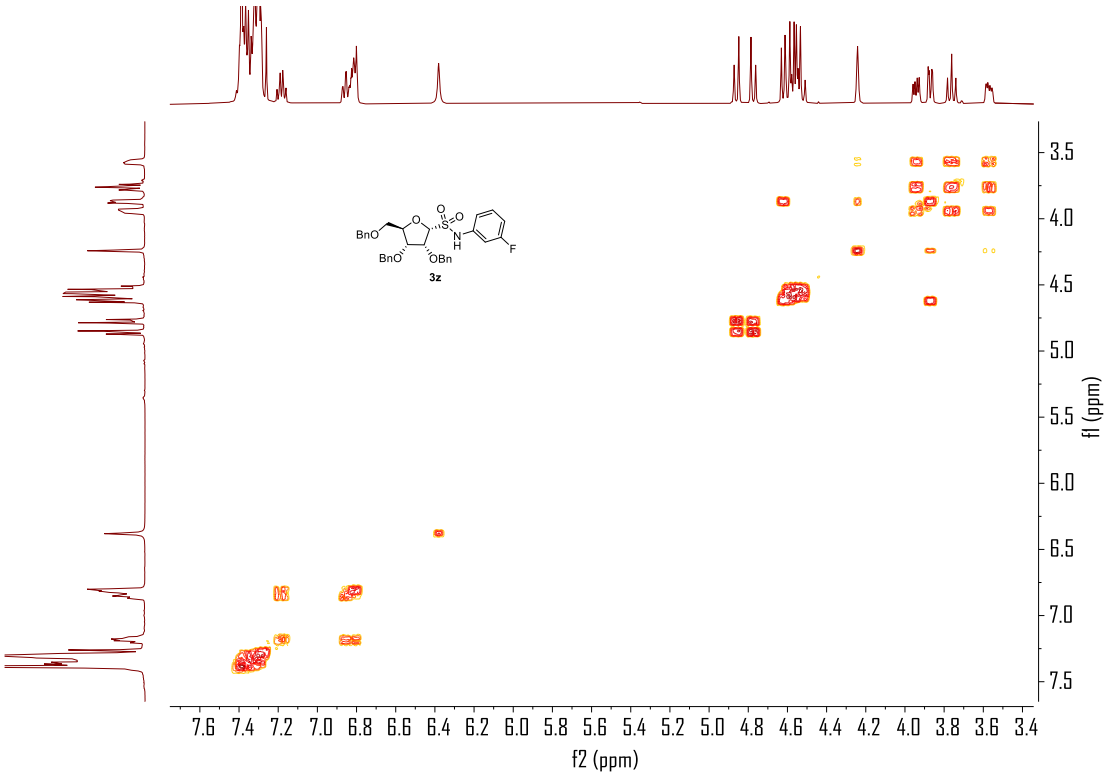


Figure S56. COSY (500 MHz, $CDCl_3$) Spectra for compound **3z**

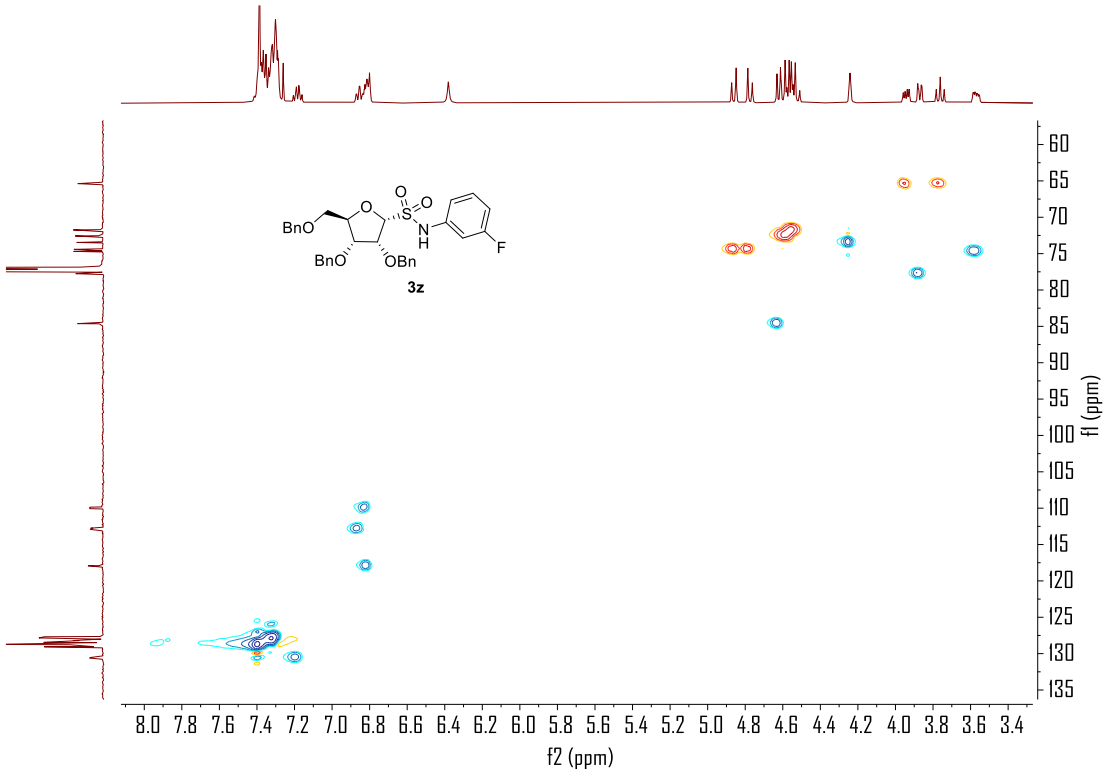


Figure S57. HSQC (500 MHz, $CDCl_3$) Spectra for compound **3z**

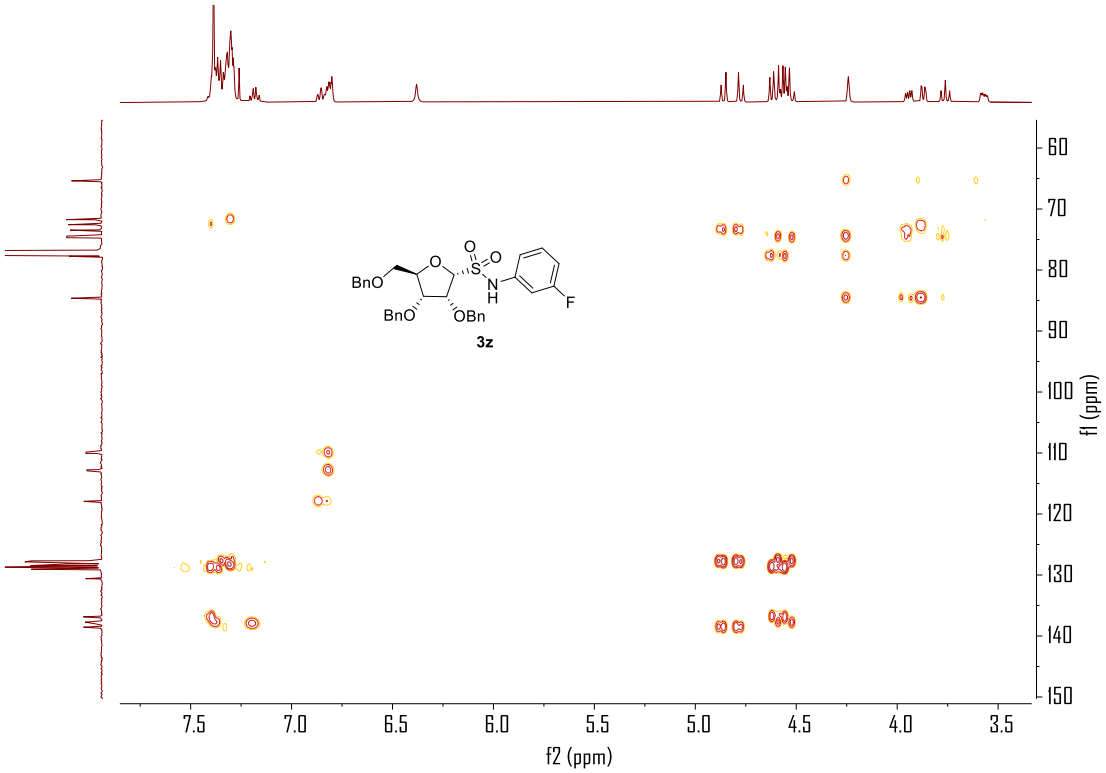


Figure S58. HMBC (500 MHz, $CDCl_3$) Spectra for compound **3z**

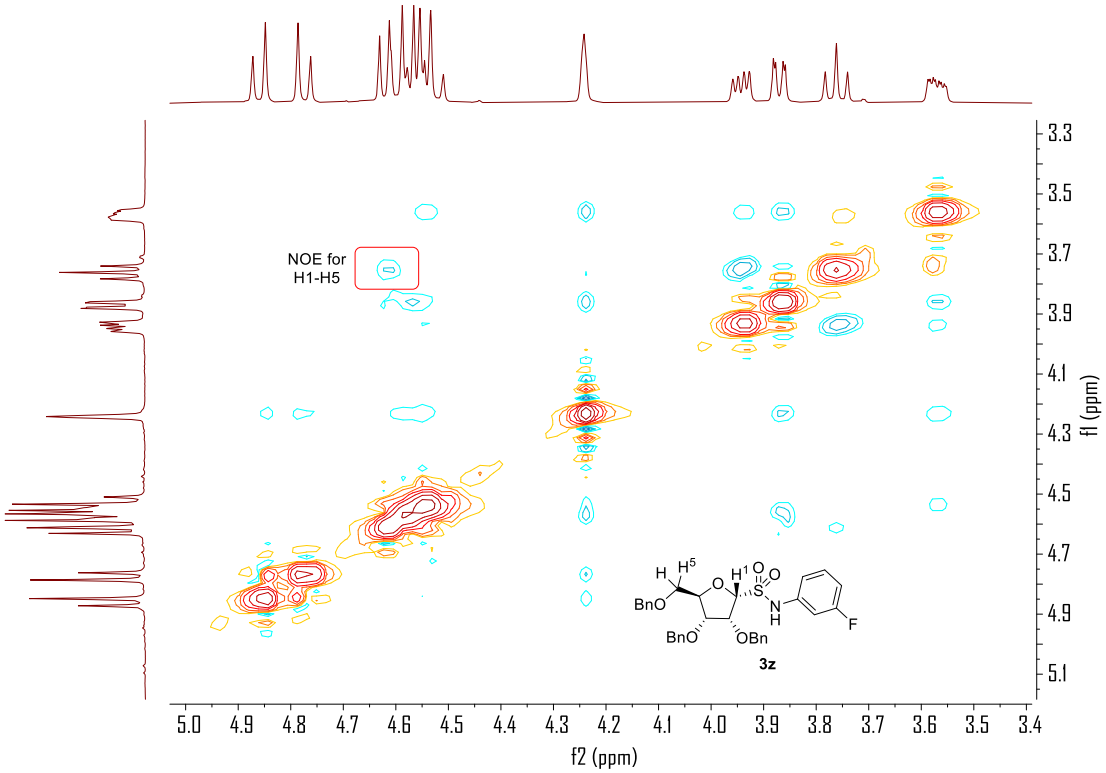


Figure S59. NOESY (500 MHz, $CDCl_3$) Spectra for compound **3z**

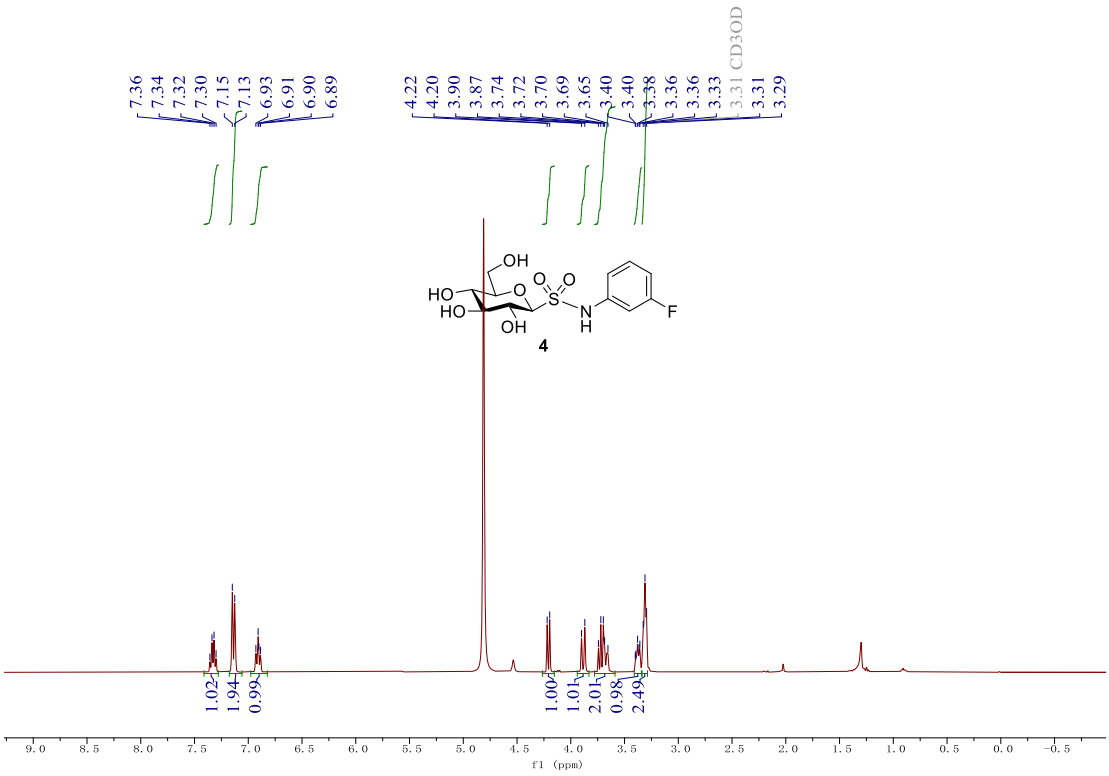


Figure S60. ^{1}H NMR (400 MHz, CD_3OD) spectra for compound **4**

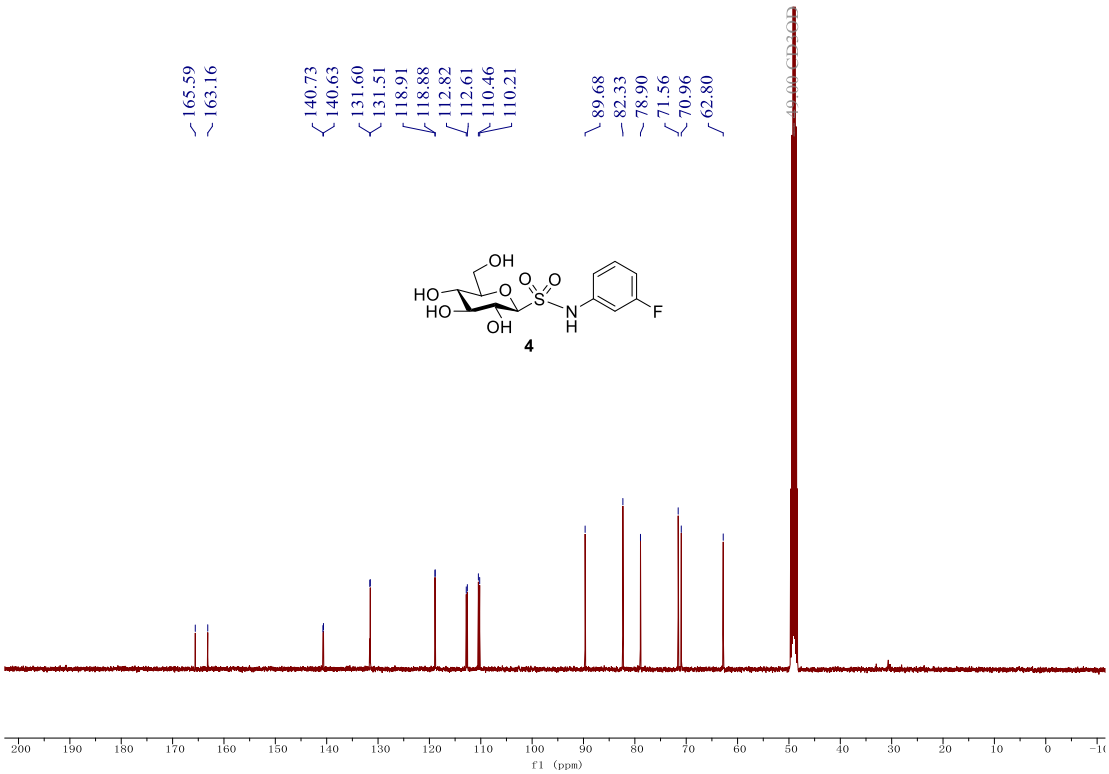


Figure S61. ^{13}C NMR (101 MHz, CD_3OD) Spectra for compound **4**

10. References

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