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General information

Unless otherwise stated, all reactions were set up under inert atmosphere (N₂) utilizing glassware that were oven dried and cooled under nitrogen atmosphere. Silica Gel Flash Column Chromatography was performed on 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 H₂SO₄-EtOH (10% H₂SO₄ v/v).

¹H NMR, ¹⁹F NMR, ¹³C NMR and 2D-NMR spectra were recorded using Bruker AVIII 400 and JEOL JNM-ECA600 spectrometer. ¹H NMR and ¹³C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ¹H NMR (CDCl₃ δ 7.26 ppm), ¹³C NMR (CDCl₃ δ 77.16 ppm), ¹H NMR (DMSO-*d*₆ δ 2.50 ppm), ¹³C NMR (DMSO-*d*₆ δ 39.50 ppm), ¹H NMR (CD₃OD δ 4.87 ppm), ¹³C NMR (CD₃OD 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. IR spectra were recorded using Nicolet iS50 spectrometer. HRMS data was recorded using HRMS Exactive Plus instrument. Melting point was measured using SGW X-4A instrument. Optical rotation was measured using MCP 150 instrument.

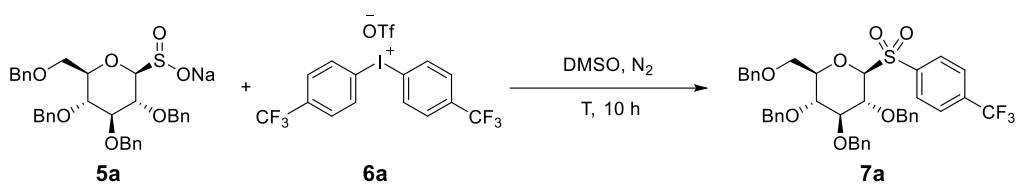
General procedure for optimization (Procedure A) (see Table S1 to S5)

In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stirring bar were added sodium glycosyl sulfinate **5a** (0.03 mmol, 1.0 equiv.), diaryliodonium salt **6a** (0.033 mmol, 1.1 equiv.) and solvent (0.3 mL). The tube was sealed with a Teflon screw cap and the mixture was stirred at an indicated temperature. Upon completion, the yield was determined by ^{19}F NMR spectroscopy with PhOCF_3 as an internal standard.

Table S1: Solvent screening

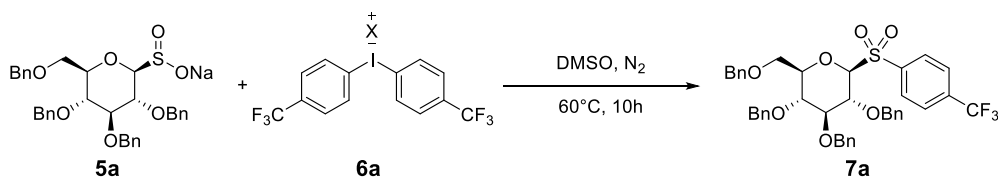
Entry	Solvent	Yield of 7a ^a
1	DMF	48%
2	DMSO	92%
3	CH_3CN	38%
4	THF	44%
5	1,4-dioxane	51%
6	DCM	81%
7	DCE	67%
8	EtOAc	40%
9	toluene	64%
10	pyridine	33%
11	CHCl_3	75%

^aReaction conditions: **5a** (0.03 mmol, 1.0 equiv.), **6a** (1.1 equiv.), solvent (0.3 mL) under N_2 atmosphere, 90°C for 10 h. The yield was determined by ^{19}F NMR spectroscopy with PhOCF_3 as an internal standard.

Table S2: Investigation of temperature

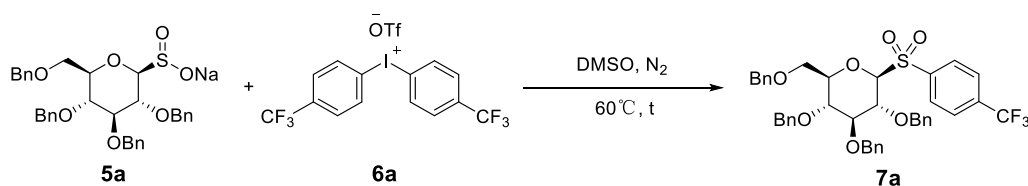
Entry	T / °C	Yield of 7a ^a
1	30	58%
2	60	95%
3	90	92%
4	130	54%

^aReaction conditions: **5a** (0.03 mmol, 1.0 equiv.), **6a** (1.1 equiv.), DMSO (0.3 mL) under N₂ atmosphere, 10 h. The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as an internal standard.

Table S3: Effect of counter anion

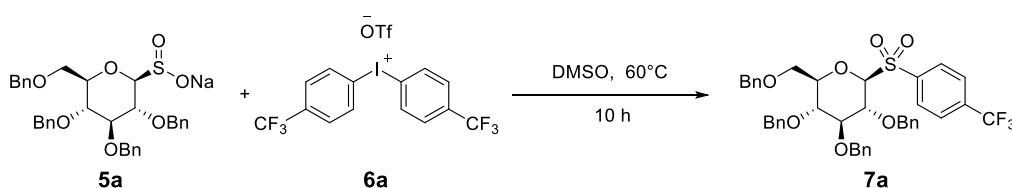
Entry	X ⁻	Yield of 7a ^a
1	⁻ OTf	95%
2	⁻ BF ₄	57%

^aReaction conditions: **5a** (0.03 mmol, 1.0 equiv.), **6a** (1.1 equiv.), DMSO (0.3 mL) under N₂ atmosphere, 60°C for 10 h. The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as an internal standard.

Table S4: Investigation of reaction time

Entry	t / h	Yield of 7a ^a
1	6	44%
2	8	90%
3	10	95%
4	12	94%
5	14	94%

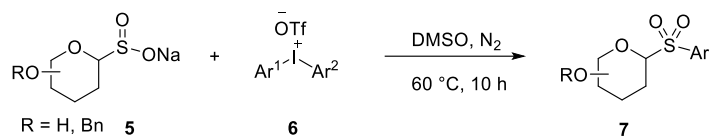
^aReaction conditions: **5a** (0.03 mmol, 1.0 equiv.), **6a** (1.1 equiv.), DMSO (0.3 mL) under N₂ atmosphere, 60°C. The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as an internal standard.

Table S5: Investigation of reaction atmosphere

Entry	environment	Yield of 7a ^a
1	N ₂	95%
2	air	37%

^aReaction conditions: **5a** (0.03 mmol, 1.0 equiv.), **6a** (1.1 equiv.), DMSO (0.3 mL), 60°C for 10 h. The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as an internal standard.

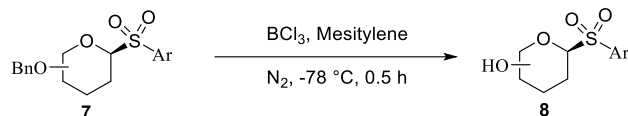
General procedure for synthesis of glycosyl aryl sulfone (Procedure B)



In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stirring bar were added sodium glycosyl sulfinate **5** (0.10 mmol, 1.0 equiv.), diaryliodonium salt **6** (0.11 mmol, 1.1 equiv.) and DMSO (1 mL). The tube was sealed with a Teflon screw cap and the mixture was stirred at 60°C for 10 h. Upon completion, the crude mixture was diluted with H₂O (15 mL) and CH₂Cl₂ (15 mL). The organic phase was separated and dried with anhydrous Na₂SO₄. The solvent was removed under reduced pressure using a rotary evaporator. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the targeted product.

Note: For benzylated sodium sulfinate as the substrate and H₂O as solvent, the reaction temperature is 120 °C and the reaction time is 10 hours. For the unprotected sodium sulfinate as the substrate and CH₃CN as solvent, the reaction temperature is 90 °C and the reaction time is 24 hours.

General procedure for protected group removal (Procedure C)



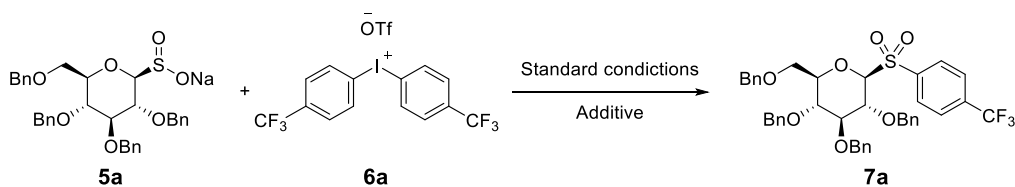
Under N₂, **7** (1.0 equiv.), CH₂Cl₂ (0.1 M), and mesitylene (12.0 equiv.) were successively added into an oven-dried glassware. The mixture was cooled to -78 °C and BCl₃ (8.0 equiv., 1.0 M in CH₂Cl₂) was added dropwise over 5 min. The resulting solution was stirred at -78 °C for 45 min until completion. The reaction was quenched by dropwise addition of MeOH (2.0 mL) at -78 °C and allowed to stir for an additional 20 min. The resulting mixture was concentrated and directly purified by column chromatography on SiO₂ (CH₂Cl₂:MeOH, 10:1) to afford **8**.

Preliminary mechanistic studies

Procedure for radical trapping experiments (see Table S6, Figure S1-2)

In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stirring bar were added sodium glycosyl sulfinate **5** (0.10 mmol, 1.0 equiv.), diaryliodonium salt **6** (0.11 mmol, 1.1 equiv.), radical scavenger and DMSO (1 mL). The tube was sealed with a Teflon screw cap and the solution was stirred at 60°C for 10 h. The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ (10 μL, 0.0756 mmol) as an internal standard.

Table S6: Radical trapping experiment



Entry	Additive	Yield of 7a ^a
1	none	99%
2	TEMPO (1.0 equiv.)	76%
3	1,1-diphenylethylene (1.0 equiv.)	100%

^aThe yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as an internal standard.

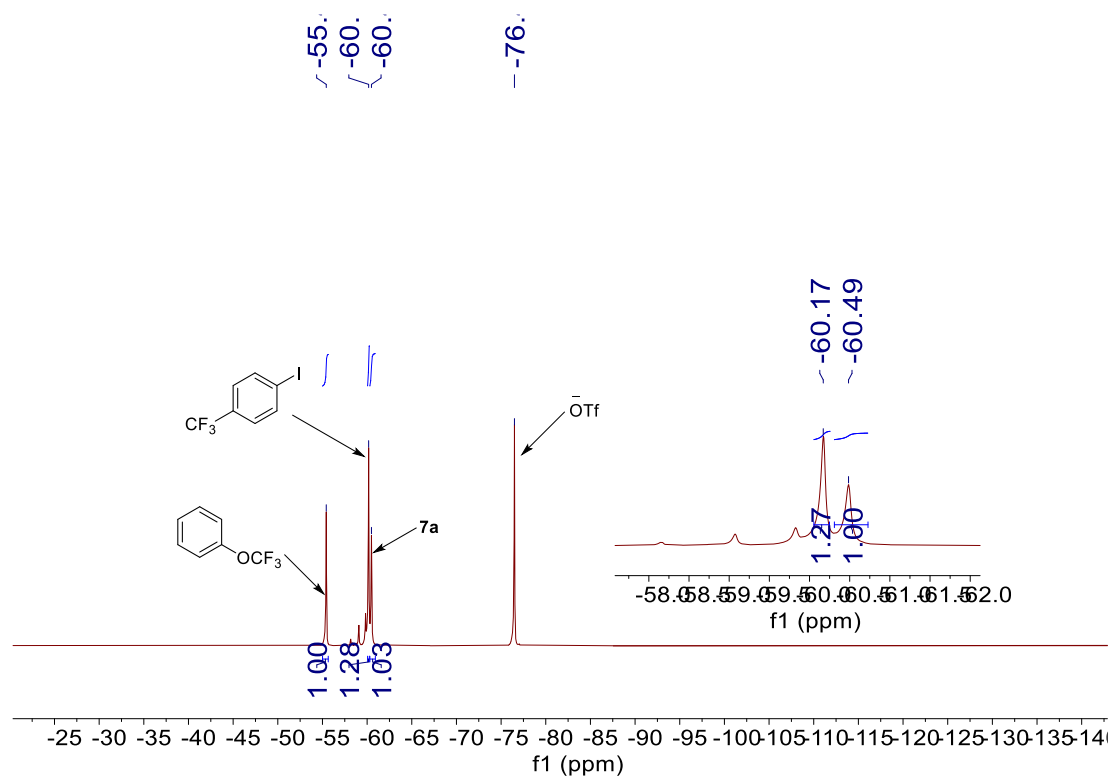


Figure S1. ¹⁹F NMR spectra for the crude mixture with 1.0 equiv. TEMPO

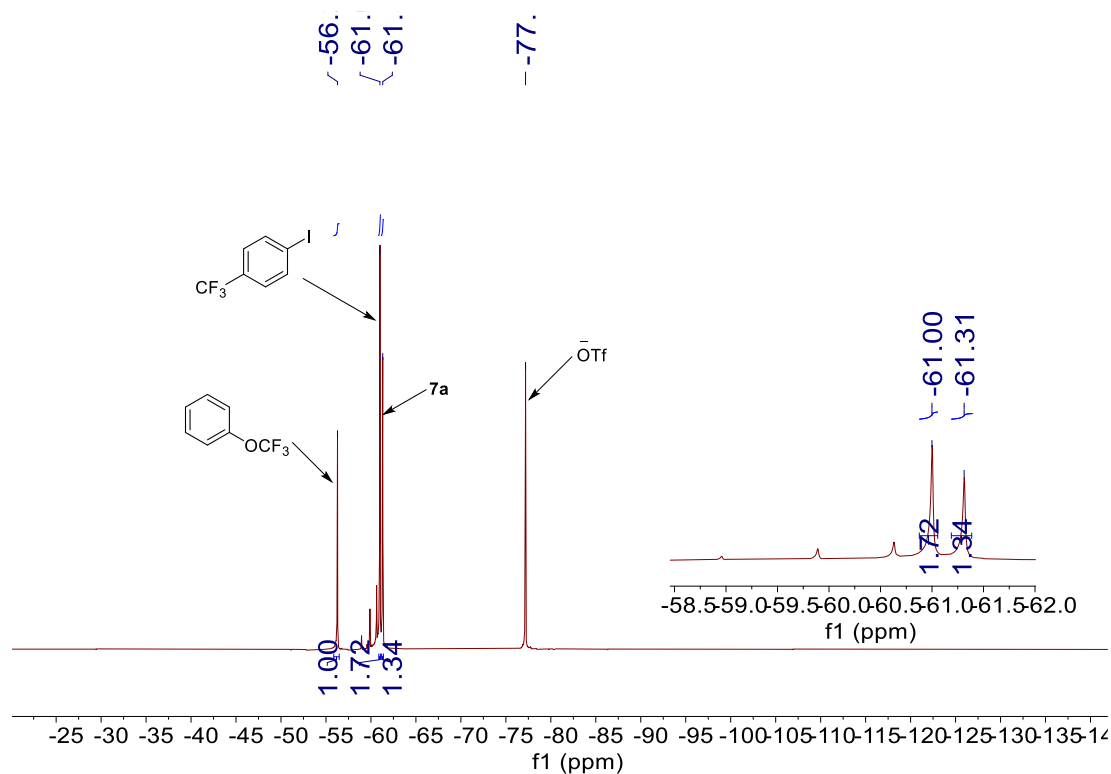
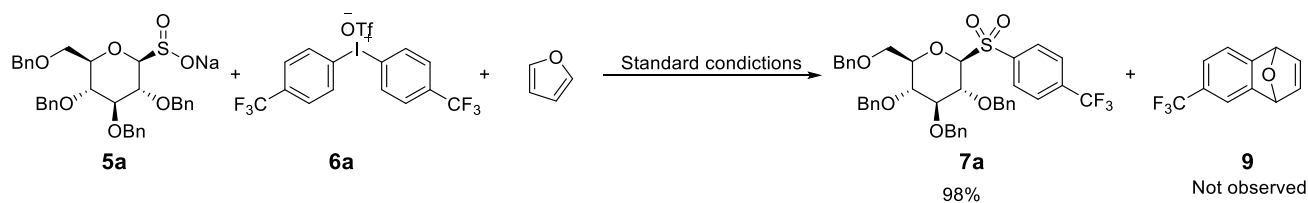


Figure S2. ^{19}F NMR spectra for the crude mixture with 1.0 equiv. 1,1-diphenylethylene

Reaction with the additive furan (see Figure S3)

In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stir bar were added sodium glycosyl sulfinate **5a** (0.10 mmol, 1.0 equiv.), diaryliodonium salt **6a** (0.11 mmol, 1.1 equiv.), furan (0.1 mmol, 1.0 equiv.) and DMSO (1 mL). The tube was sealed with a Teflon screw cap and the solution was stirred at 60 °C for 10 h. The yield was determined by ^{19}F NMR spectroscopy with PhOCF_3 (10 μL , 0.0756 mmol) as an internal standard.



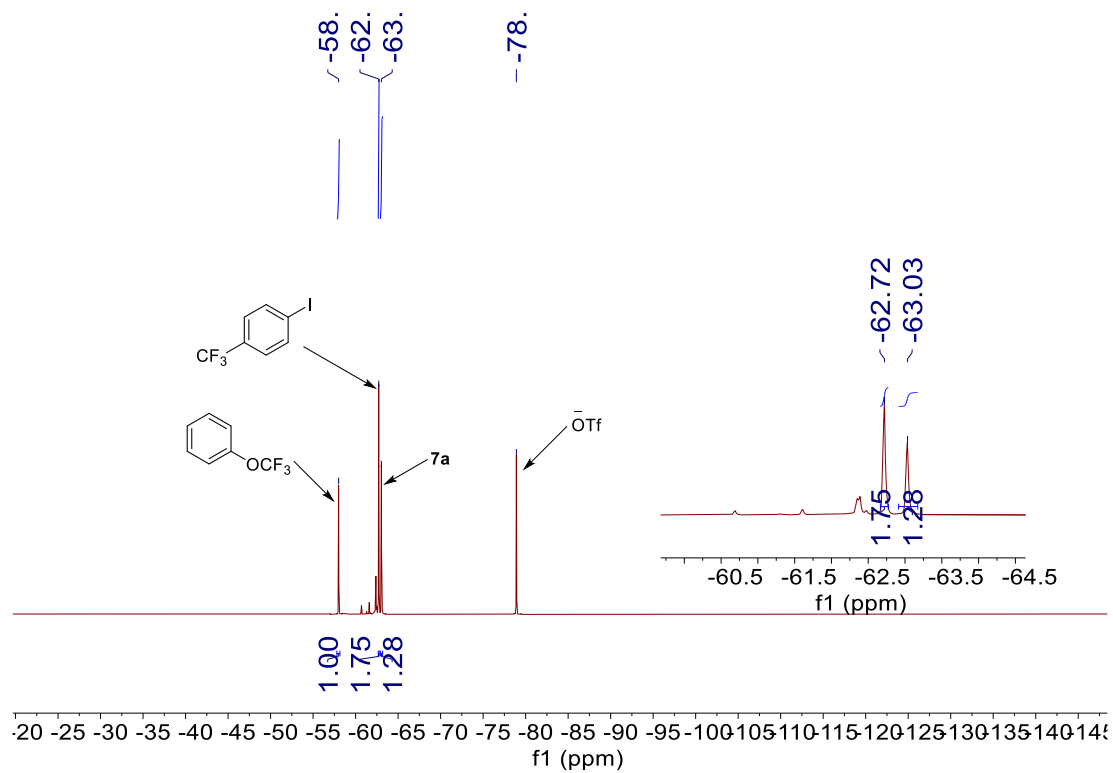


Figure S3. ^{19}F NMR spectra for the crude mixture with 1.0 equiv. furan

Library of sodium glycosyl sulfinates

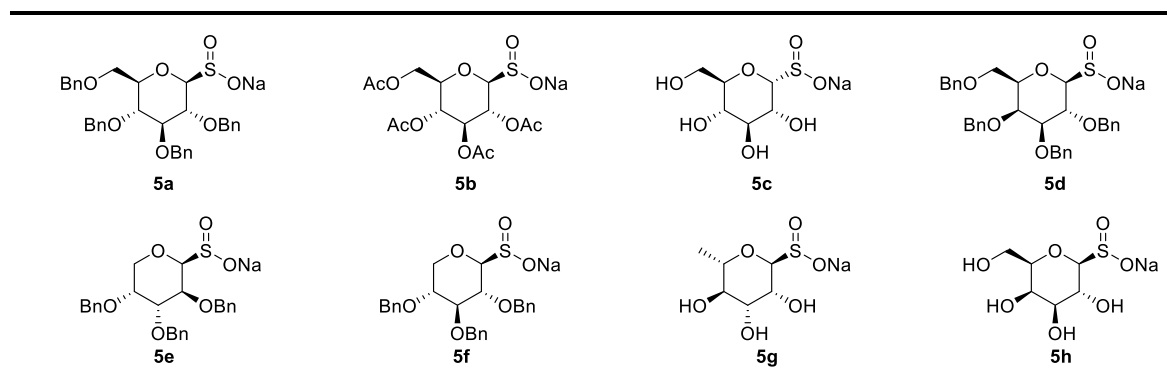
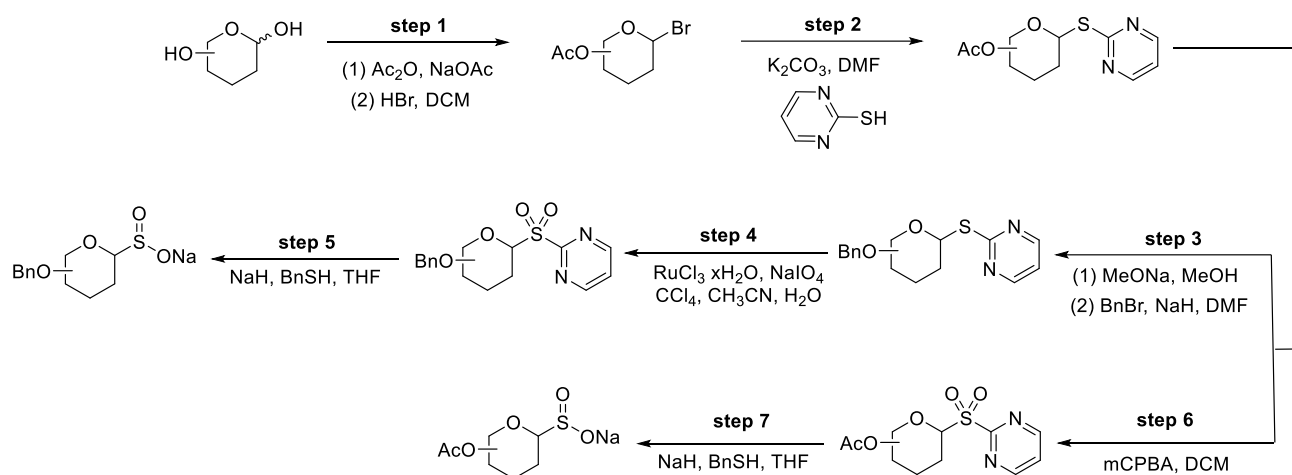


Figure S4. Library of sodium glycosyl sulfinates

General procedure for preparation of 5a-b, 5d-f (Procedure D)



Step 1: synthesis of glycosyl bromide

Sugar substrate (1.0 equiv.) and sodium acetate (1.1 equiv.) were added to 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 CH₂Cl₂ (3 times). The combined organic layers were washed with saturated NaHCO₃, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was obtained and used directly without further purification.

Crude acetylated glycoside was dissolved in CH₂Cl₂ (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 CH₂Cl₂ (3 times). The combined organic layers were washed with saturated NaHCO₃, dried with Na₂SO₄, 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 CH₂Cl₂ (3 times). The combined organic layers were dried over Na₂SO₄ 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 °C, 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 °C) and stirred for 12 hours. The reaction was then quenched by water and extracted with CH₂Cl₂ (3 times). The combined organic layers were washed with water (3 times), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give the benzylated thioglycoside.

Step 4: Oxidation

Benzylated thioglycoside (1.0 equiv.) and a catalytic amount of RuCl₃ (0.1 equiv.) were dissolved in a mixed solvent (0.1 M) (H₂O/CCl₄/CH₃CN = 3:2:2) at 0 °C. NaIO₄ (4.5 equiv.) was added in batches and the mixture was allowed to warm up to 25 °C, and stirred for 2 hours. Subsequently, the mixture was extracted with CH₂Cl₂ (3 times). The combined organic layers were washed with water, dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography 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 °C, and BnSH (0.3 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 °C 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 sulfinic acid.

Step 6: Oxidation

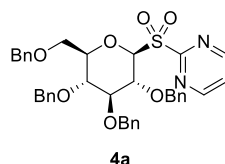
*m*CPBA (3.0 equiv.) in a round bottom flask was dried under vacuum. To the flask was added a CH₂Cl₂ (0.05 M) solution of acetylated thioglycoside (1.0 equiv.) (Obtained from step 2) at 0 °C. The temperature was warmed to room temperature. After stirring for 4 hours, the reaction mixture was treated with 1 M Na₂SO₃ and saturated aqueous NaHCO₃ at room temperature. The organic phase was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography eluent: hexane/EtOAc = 1:2 to give the sulfone product.

Step 7: Removal of pyrimidine moiety

Under nitrogen atmosphere, NaH (3.0 equiv.) was dissolved in THF (0.5M) at 0 °C, and BnSH (1.0 equiv.) was added dropwise. After that, a THF solution of sulfone product (1.0 equiv.) (Obtained from step 3) was added and the resulting mixture was stirred at 0 °C for 2.5 hours and then warmed up to room temperature for 1 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 sulfinat.

Compounds **5c**, **g-h** were synthesized according to the literature.¹

Compound 4a



4a was prepared following General Procedure D using 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide (30 mmol, 12.24 g) as starting material. Petroleum ether and ethyl acetate (2:1) were used as eluents to separate on silica gel by column chromatography to obtain the title product as a white solid (11.6 g, 58% total yield).

¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 4.9 Hz, 2H), 7.37-7.14 (m, 20H), 7.10 (t, *J* = 4.9 Hz, 1H), 5.15 (d, *J* = 9.6 Hz, 1H), 4.97 (d, *J* = 10.3 Hz, 1H), 4.92-4.76 (m, 4H), 4.57 (d, *J* = 10.9 Hz, 1H), 4.36 (d, *J* = 11.9 Hz, 1H), 4.29-4.19 (m, 2H), 3.82 (t, *J* = 8.8 Hz, 1H), 3.65-3.48 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 164.92, 158.21, 138.16, 138.13, 137.77, 137.65, 128.63, 128.60, 128.45, 128.34, 128.12, 128.09, 128.07, 127.94, 127.81, 127.78, 127.72, 123.36, 88.81, 86.38, 80.47, 77.73, 77.41, 76.05, 75.30, 75.06, 73.40, 68.68 ppm.

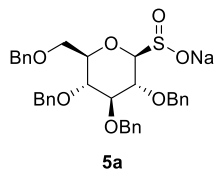
IR (thin film, cm⁻¹): 2954, 2922, 2852, 2166, 2049, 1978, 1735, 1566, 1496, 1455, 1377, 1259, 1091, 1016, 798, 757, 697, 569.

$[\alpha]_D^{25} = +11.8$ (c = 0.11, CHCl₃).

HRMS (ESI-TOF): calculated for $C_{38}H_{38}N_2O_7SNa^+$ $[M+Na]^+$: 689.2292, found: 689.2285.

m. p.: 126.5-126.9°C.

Compound 5a



5a was prepared following General Procedure D from **4a** (17.4 mmol, 11.6 g) as a white solid (10.5 g, 99% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.34-7.29 (m, 6H), 7.25-7.14 (m, 12H), 6.86 (d, *J* = 6.3 Hz, 2H), 4.94 (t, *J* = 11.0 Hz, 2H), 4.84-4.77 (m, 2H), 4.72 (d, *J* = 12.4 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 2H), 4.09 (d, *J* = 10.7 Hz, 1H), 3.89 (t, *J* = 9.5 Hz, 1H), 3.73 (q, *J* = 9.0 Hz, 3H), 3.63-3.48 (m, 3H) ppm.

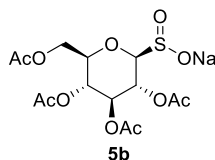
IR (thin film, cm⁻¹): 2648, 2286, 2185, 2161, 2049, 2026, 1979, 1028, 1067, 695, 529, 414.

[α]_D²⁵ = -105.4 (c = 0.10, MeOH).

HRMS (ESI-TOF): calculated for $C_{34}H_{36}NaO_7S^+$ $[M+H]^+$: 611.2074, found: 611.2064.

m. p.: 299.0-300.0 °C.

Compound 5b



5b was prepared following General Procedure D using 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (2.70 mmol, 1.11 g) as starting material. as a white solid (979 mg, 86% total yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 5.20 – 5.04 (m, 2H), 4.86 (t, *J* = 9.6 Hz, 1H), 4.15 (dd, *J* = 12.4, 4.8 Hz, 1H), 3.98 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.36 (s, 1H), 2.05 – 1.84 (m, 12H) ppm.

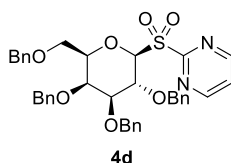
¹³C NMR (101 MHz, DMSO-*d*₆) δ 170.19, 169.71, 169.28, 169.11, 91.59, 74.60, 74.35, 68.11, 67.55, 62.15, 20.83, 20.58, 20.37, 20.37 ppm.

IR (thin film, cm⁻¹): 3321, 1644, 1559, 1410, 1241, 1014, 964, 467.

[α]_D²⁵ = +19.1 (c = 0.11, CHCl₃).

HRMS (ESI-TOF): calculated for $C_{14}H_{19}Na_2O_{11}S^+$ $[M+Na]^+$: 441.0438, found: 441.0430.

Compound 4d



4d was prepared following General Procedure D from D-Galactose (20 mmol, 3.60 g) as a solid (3.0 g, 24% total yield).

¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 4.9 Hz, 2H), 7.34-7.18(m, 20H), 7.11 (t, *J* = 4.9 Hz, 1H), 5.11 (d, *J* = 9.5 Hz, 1H), 4.92 (t, *J* = 8.3 Hz, 3H), 4.76-4.52 (m, 4H), 4.31 (s, 2H), 3.94 (d, *J* = 2.6 Hz, 1H), 3.74-3.64 (m, 2H), 3.49 (d, *J* = 6.3 Hz, 2H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 164.93, 158.07, 138.47, 137.98, 137.87, 137.78, 128.60, 128.51, 128.35, 128.19, 128.05, 127.97, 127.93, 127.70, 127.68, 127.54, 123.22, 89.47, 83.82, 78.69, 75.05, 74.64, 74.52, 73.54, 73.08, 72.69, 68.31 ppm.

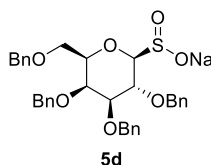
IR (thin film, cm⁻¹): 2954, 2922, 2852, 2050, 1980, 1566, 1454, 1677, 1259, 1094, 1016, 796, 757, 696, 562.

[α]_D²⁵ = +14.7 (*c* = 0.15, CHCl₃).

HRMS (ESI-TOF): calculated for C₃₈H₃₈N₂O₇SNa⁺ [*M*+Na]⁺: 689.2292, found: 689.2283.

m.p.: 158.5-162.2°C.

Compound 5d



5d was prepared following General Procedure D as a white solid (2.3 g, 79% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.32-7.26 (m, 6H), 7.25-7.12 (m, 14H), 4.94-4.91 (m, 2H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.65-4.53 (m, 3H), 4.26 (d, *J* = 12.4 Hz, 1H), 4.19 (t, *J* = 10.0 Hz, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 3.66-3.59 (m, 2H), 3.53 (dd, *J* = 9.5, 2.7 Hz, 1H), 3.45 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.03 (dd, *J* = 10.1, 4.1 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 138.71, 138.38, 137.61, 137.38, 129.29, 128.69, 128.56, 128.50, 128.44, 128.35, 128.09, 127.84, 127.78, 127.62, 93.37, 84.40, 77.83, 76.53, 75.34, 73.91, 73.20, 72.89, 72.11, 68.63 ppm.

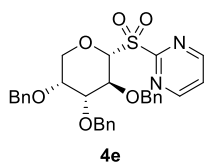
IR (thin film, cm⁻¹): 3379, 2323, 2199, 2050, 2036, 1980, 1641, 1496, 1453, 1365, 1075, 733, 697, 441.

[α]_D³⁰ = -225.96 (*c* = 0.16, MeOH).

HRMS (ESI-TOF): calculated for C₃₄H₃₆NaO₇S⁺ [*M*+H]⁺: 611.2074, found: 611.2059.

m. p.: 221.2-222.1°C.

Compound 4e



4e was prepared following General Procedure D from D-Arabinose (20 mmol, 3.0 g) as a white solid (1.9 g, 18% total yield).

¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 4.7 Hz, 2H), 7.36-7.21 (m, 14H), 7.16-7.13 (m, 2H), 5.19 (d, *J* = 8.2 Hz, 1H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.67 (d, *J* = 12.4 Hz, 1H), 4.63-4.56(m, 4H), 4.29 (dd, *J* = 12.5, 3.3 Hz, 1H), 3.79-3.75 (m, 1H), 3.69 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.44 (dd, *J* = 12.5, 1.8 Hz, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 165.32, 158.26, 137.94, 137.93, 137.84, 128.56, 128.26, 128.01, 127.91, 127.85, 127.60, 123.37, 89.20, 80.49, 74.62, 73.98, 71.98, 71.64, 71.22, 67.20 ppm.

IR (thin film, cm⁻¹): 2954, 2922, 2851, 2323, 2284, 2161, 2049, 2020, 1979, 1565, 1496, 1454, 1378, 1335, 1259, 1213, 1130, 1095, 1017, 797, 734, 697, 543, 457.

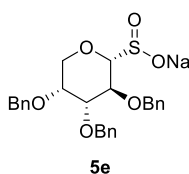
[α]_D²⁵ = -25.0 (c = 0.12, CHCl₃).

HRMS (ESI-TOF): calculated for C₃₀H₃₀N₂O₆SNa⁺ [M+Na]⁺: 569.1717, found: 569.1713.

m.p.: 166.9-167.6°C.

Note: ¹H NMR data of the precursor for preparation of **4e** is in agreement with that reported in literature.² **¹H NMR (400 MHz, CDCl₃)** δ 8.55 (d, *J* = 4.9 Hz, 2H), 7.37 – 7.23 (m, 15H), 6.99 (t, *J* = 4.9 Hz, 1H), 6.32 (d, *J* = 3.5 Hz, 1H), 4.77 – 4.52 (m, 6H), 4.23 (dd, *J* = 11.4, 8.6 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.94 (dt, *J* = 8.5, 3.5 Hz, 1H), 3.83 (dd, *J* = 5.1, 2.9 Hz, 1H), 3.66 (dd, *J* = 11.4, 3.9 Hz, 1H).

Compound 5e



5e was prepared following General Procedure D as a white solid (1.7 g, 99% yield).

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.43 – 7.20 (m, 15H), 4.74 – 4.45 (m, 7H), 4.11 – 3.96 (m, 2H), 3.80-3.75 (m, 2H), 3.02 (d, *J* = 5.4 Hz, 1H) ppm.

¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.06, 138.91, 138.77, 128.19, 128.14, 128.06, 127.64, 127.59, 127.51, 127.39, 127.33, 127.22, 97.64, 77.71, 74.56, 72.18, 72.11, 70.56, 69.95, 63.97 ppm.

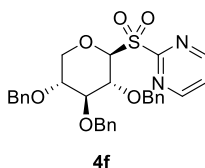
IR (thin film, cm⁻¹): 3354, 2162, 2115, 1637, 1453, 1087, 1016, 459.

[α]_D³⁰ = -346.4 (c = 0.13, MeOH).

HRMS (ESI-TOF): calculated for C₂₆H₂₈NaO₆S⁺ [M+H]⁺: 491.1499, found: 491.1493.

m. p.: 290.5-291.2°C.

Compound 4f



4f was prepared following General Procedure D from D-xylose (20 mmol, 3.0 g) as a white solid (1.1 g, 12% total yield).

¹H NMR (400 MHz, CDCl₃) δ 8.77 (d, *J* = 4.8 Hz, 2H), 7.38-7.14 (m, 16H), 5.19 (d, *J* = 9.3 Hz, 1H), 5.00-4.75 (m, 4H), 4.73-4.53 (m, 2H), 4.18 (t, *J* = 9.0 Hz, 1H), 4.07 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.77 (t, *J* = 8.7 Hz, 1H), 3.72-3.66 (m, 1H), 3.33 (dd, *J* = 11.6, 9.2 Hz, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 164.94, 158.42, 138.19, 137.79, 137.66, 128.67, 128.56, 128.29, 128.18, 128.04, 127.96, 127.92, 127.70, 123.58, 89.05, 84.96, 77.42, 76.68, 75.68, 74.97, 73.45, 68.43 ppm.

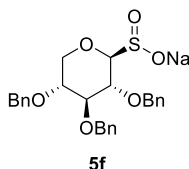
IR (thin film, cm⁻¹): 2954, 2922, 2851, 2323, 2165, 2112, 2049, 1980, 1565, 1496, 1455, 1377, 1339, 1259, 1212, 1016, 799, 756, 697, 606, 562, 458.

[α]_D²⁵ = +19.4 (c = 0.16, CHCl₃).

HRMS (ESI-TOF): calculated for C₃₀H₃₀N₂O₆SNa⁺ [M+Na]⁺: 569.1717, found: 569.1710.

m. p.: 180.9-181.5°C.

Compound 5f



5f was prepared following General Procedure D as white solid (1.2 g, 100% yield).

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.39 – 7.23 (m, 15H), 5.03 (d, *J* = 10.1 Hz, 1H), 4.81-4.71 (m, 2H), 4.65-4.59 (m, 2H), 4.52 (d, *J* = 10.3 Hz, 1H), 4.13-4.05 (m, 1H), 3.82 (d, *J* = 8.5 Hz, 1H), 3.63 – 3.50 (m, 3H), 3.23 – 3.14 (m, 1H) ppm.

¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.20, 138.97, 138.56, 128.28, 128.18, 127.99, 127.84, 127.68, 127.56, 127.53, 127.36, 127.14, 88.17, 84.89, 79.86, 77.56, 74.52, 73.62, 71.70, 66.55 ppm.

IR (thin film, cm⁻¹): 3334, 2946, 2834, 2049, 1654, 1409, 1110, 1017, 533.

[α]_D³⁰ = -458.2 (c = 0.20, MeOH).

HRMS (ESI-TOF): calculated for C₂₆H₂₈NaO₆S⁺ [M+H]⁺: 491.1499, found: 491.1494.

m. p.: 217.3-218.1°C.

Library of diaryliodonium salts

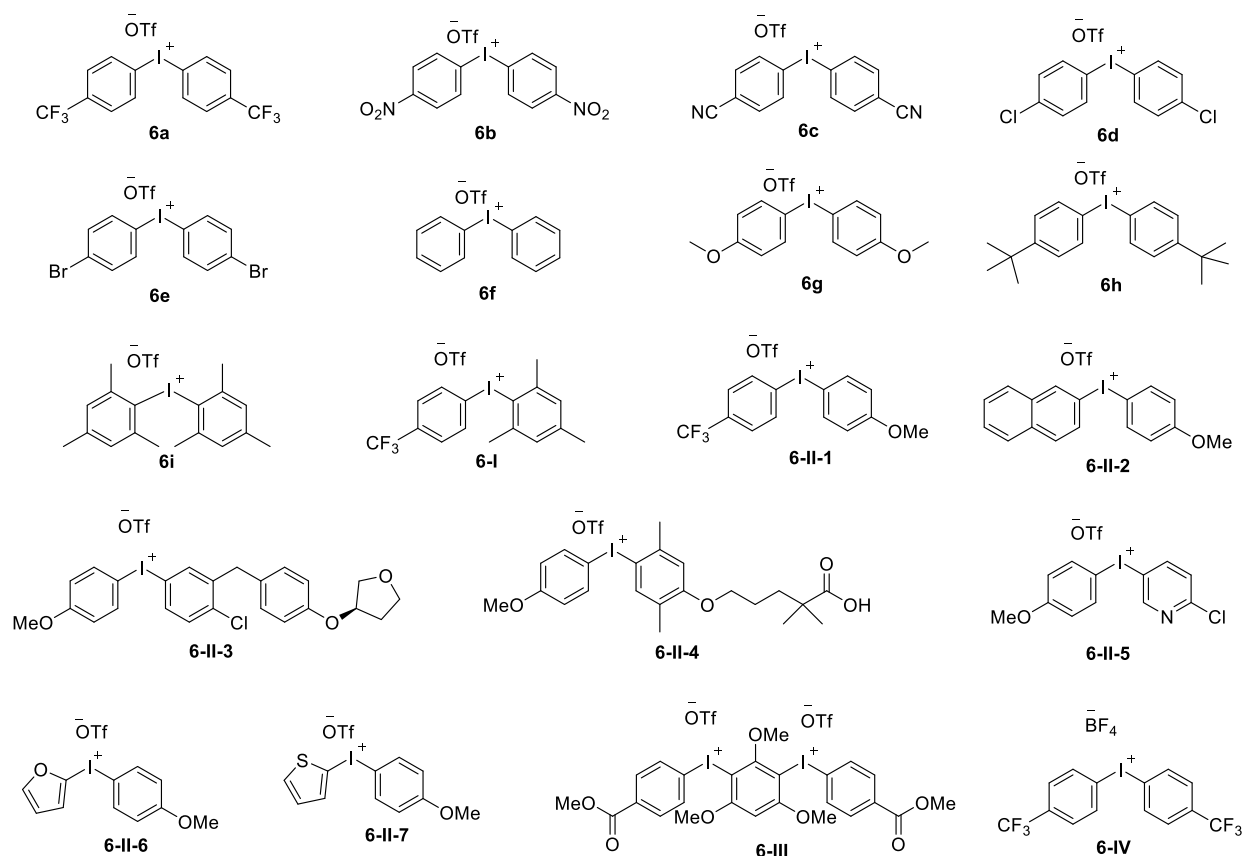
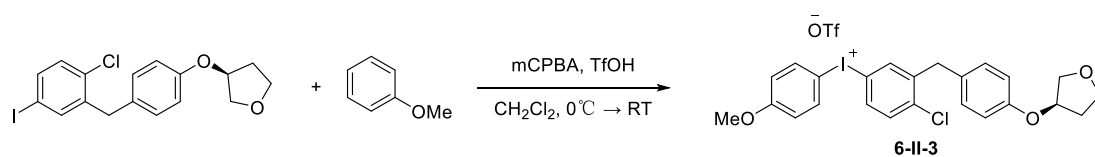


Figure S5. Library of diaryliodonium salts

The known diaryliodonium salts employed in this project were synthesized according to the reported procedures. In detail, compound **6a-e**, **6-II-1**, **6-IV** were synthesized according to the literature³. Compound **6g** was synthesized according to the literature⁴. Compound **6f** was purchased commercially. Compound **6i**, **6-I**, **6-II-3**, **6-II-5** were synthesized according to the literature⁵. Compound **6-II-2**, **6-II-6**, **6-II-7** were synthesized according to the literature⁶; Compound **6-II-4** was synthesized according to the literature⁷.

Procedure for preparation of diaryliodonium salt **6-II-3**:



(3*S*)-3-[4-[(2-chloro-5-iodophenyl) methyl] phenoxy] tetrahydrofuran (2.0 mmol, 1.0 equiv.), anisole (2.2 mmol, 1.1 equiv.), and *m*-CPBA (2.2 mmol, 1.1 equiv.) were dissolved in CH₂Cl₂ (10 mL) at 0 °C, and TfOH (3.2 mmol, 1.6 equiv.) was added dropwise. The mixture was allowed to warm up

to room temperature and stirred for several hours until completion. Then the solvent was removed and the resulting residue was suspended in ether. The precipitation was filtered, washed with ether and dried under vacuum to give **6-II-3** (524 mg, 79%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.21-8.10 (m, 3H), 8.03 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.11-7.04 (m, 4H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.99-4.95 (m, 1H), 3.99 (s, 2H), 3.91-3.69 (m, 7H), 2.24-2.15 (m, 1H), 1.95-1.88 (m, 1H) ppm.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -77.74 ppm.

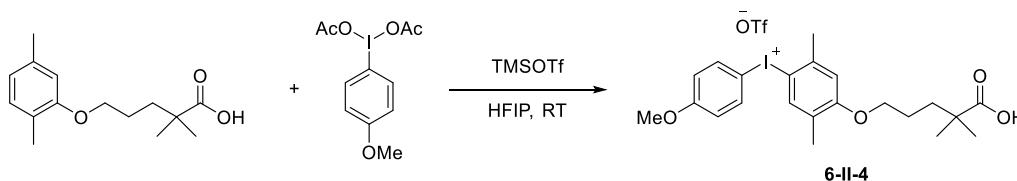
¹³C NMR (101 MHz, DMSO) δ 162.03, 155.77, 142.58, 137.17, 136.96, 136.94, 134.07, 132.33, 130.23, 129.78, 120.68 (q, *J* = 323.2 Hz), 117.49, 115.31, 114.96, 105.64, 76.97, 72.23, 66.38, 55.72, 37.36, 32.41 ppm.

IR (thin film, cm⁻¹): 3327, 2943, 2832, 2285, 2164, 2064, 2049, 1979, 1654, 1448, 1413, 1111, 1021, 603.

HRMS (ESI-TOF): calculated for C₂₄H₂₃ClIO₃⁺ [M-OTf]⁺: 521.0375, found: 521.0372.

m.p.: 214.5-215.1°C

Procedure for preparation of diaryliodonium salt **6-II-4**:



(4-Methoxyphenyl)-λ³-iodanediyl diacetate (2.2 mmol, 1.1 equiv.) was dissolved in hexafluoroisopropanol (7 mL) at 0 °C. Gemfibrozil (2.0 mmol, 1.0 equiv.) was added to the solution and stirred for 5 minutes. Then, TMSOTf (2.2 mmol, 1.1 equiv.) was added and stirred for 5 minutes at same temperature. After that, the reaction was allowed to warm up to room temperature and stirred for 4 hours. Then the solvent was removed and the resulting residue was suspended in ether. The precipitation was filtered, washed with ether and dried under vacuum to give **6-II-4** (500 mg, 41%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.13 (s, 1H), 8.12 (s, 1H), 8.10-8.02 (m, 2H), 7.10-7.01 (m, 3H), 3.98 (t, *J* = 6.0 Hz, 2H), 3.78 (s, 3H), 2.54 (s, 3H), 2.12 (s, 3H), 1.70-1.55 (m, 4H), 1.10 (s, 6H) ppm.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -77.75 ppm.

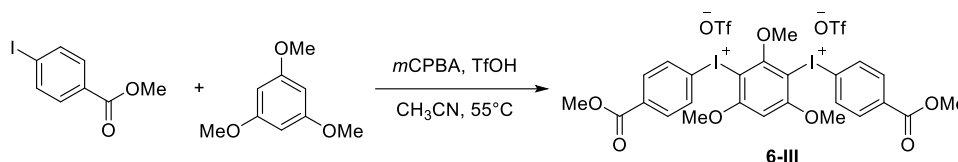
¹³C NMR (101 MHz, DMSO) δ 178.63, 161.75, 159.69, 140.13, 138.02, 136.65, 127.23, 120.68 (q, *J* = 324.2 Hz), 117.39, 113.74, 109.87, 104.96, 68.26, 55.66, 40.96, 36.28, 24.90, 24.79, 24.45, 15.13 ppm.

IR (thin film, cm⁻¹): 3326, 2944, 2832, 2323, 2050, 1980, 1654, 1448, 1412, 1258, 1112, 1020, 584.

HRMS (ESI-TOF): calculated for C₂₂H₂₈IO₄⁺ [M-OTf]⁺: 483.1027, found: 483.1022.

m.p.: 148.6-148.9°C

Procedure for preparation of diaryliodonium salt 6-III:



Methyl 4-iodobenzoate (2.0 mmol, 1.0 equiv.) and *m*-CPBA (2.4 mmol, 1.2 equiv.) were dissolved in acetonitrile (3 mL). Then, triflic acid (2.0 mmol, 1.0 equiv.) was added dropwise at room temperature. The reaction was allowed to warm up to 55°C and stirred for 1 hour. Afterwards, 1,3,5-trimethoxybenzene (2.0 mmol, 1.0 equiv.) was added and stirred for 20 minutes. Upon completion, the mixture was concentrated with rotary evaporator. And the residue was suspended in ether and stirred for 10 mins. The precipitation was filtered and dried under vacuum to give the product **6-III** as a solid (284 mg, 29%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.09 (d, *J* = 8.5 Hz, 4H), 7.90 (d, *J* = 8.5 Hz, 4H), 6.94 (s, 1H), 4.15 (s, 3H), 4.11 (s, 6H), 3.87 (s, 6H) ppm.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -77.75 ppm.

¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.95, 163.14, 159.86, 134.97, 132.57, 131.86, 121.97, 120.50 (q, *J* = 324.2 Hz), 95.48, 94.67, 64.99, 58.58, 52.76 ppm.

IR (thin film, cm⁻¹): 3329, 2944, 2832, 2323, 2167, 2050, 1979, 1654, 1448, 1411, 1278, 1109, 1020, 579.

HRMS (ESI-TOF): calculated for C₂₆H₂₄F₃I₂O₁₀S⁺ [M-OTf]⁺: 838.9126, found: 839.9105.

m.p.: 220.7-221.7°C

DFT calculations

Geometry optimizations were performed by Gaussian 16 package⁸ at the B3LYP-D3(BJ)/Def2-SVP level of theory⁹⁻¹³. Solvation effects of dimethyl sulfoxide (DMSO) were included using the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) with a standard state of 1 M¹⁴. Energy minima and transition states were verified through vibrational analysis. Frequency calculations were performed at the same theoretical level as for geometry optimizations to verify the stationary points as either minima or first-order saddle points on the potential energy surface, as well as to obtain thermal Gibbs free energy corrections at 298 K. Intrinsic reaction coordinate (IRC) computations were used to ensure that each transition state connected the correct two minima.

Highly accurate electronic energies were computed by ORCA 5.0.4 package¹⁵⁻¹⁸ at the RI- ω B97M-V/Def2-QZVPP level of theory^{19,20}. Specifically, oxygen atoms in the system were treated with the ma-Def2-QZVPP basis set²¹. Auxiliary basis sets for the RI-J approximation were generated automatically by ORCA²². Solvation effects were included using the solvation model based on density (SMD) with a standard state of 1 M²³.

Minenkov's quasiharmonic correction²⁴ and zero-point vibrational energy scale factor for the B3LYP/Def2-SVP level of theory (1.0044)²⁵⁴ were applied by using Shermo 2.4 package²⁶. Hirshfeld atomic charges²⁷ and Mayer bond orders²⁸ were computed by Multiwfn 3.8(dev) package²⁹. Optimized structures were illustrated using CYLview³⁰.

Cartesian Coordinates and Gibbs Free Energies of Optimized Structures:

DMSO

-553.1753003 Hartree

S	0.45060600	-0.00391600	0.39320600
O	-0.67593400	-0.01025000	1.41798900
C	0.08022300	1.36960800	-0.75296200
H	0.18081200	2.29429700	-0.16906400
H	0.79700300	1.36598000	-1.58644800
H	-0.95342600	1.25461600	-1.10970800
C	0.08373400	-1.36738400	-0.76602200
H	-0.95021000	-1.25164400	-1.12167100
H	0.80049500	-1.35396600	-1.59942400
H	0.18669800	-2.29734200	-0.19097300

5c

-1160.1346440 Hartree

C	-0.79740900	1.60283500	0.20974700
C	0.62452800	1.23474000	-0.18902300
C	0.92416400	-0.20178100	0.26084900
C	-1.35509100	-0.85251900	0.26488100
C	-1.78865000	0.53216300	-0.23122600
H	0.67492200	1.26265100	-1.30095800
H	-0.82536900	1.64778200	1.31816700
H	-1.40072400	-0.85427600	1.37298800

H	-1.78850200	0.50514400	-1.34127400
H	1.05759300	-0.23546700	1.36056200
O	-0.03870900	-1.13213400	-0.17858100
S	2.57955000	-0.81348100	-0.40207400
O	3.44977100	0.42453800	-0.03275900
O	2.86261400	-1.99269200	0.51657100
O	1.53531800	2.12771700	0.39638000
H	2.41426000	1.66488900	0.29568400
O	-1.15364000	2.85485400	-0.34472700
H	-2.10426600	2.95190200	-0.18162600
O	-3.05646000	0.91531300	0.26551600
H	-3.63444400	0.13601900	0.16510800
C	-2.22947900	-1.97550700	-0.27746900
H	-1.86094300	-2.94084800	0.11321200
H	-2.12940100	-1.99263600	-1.37799800
O	-3.57220200	-1.72939700	0.12104800
H	-4.15930600	-2.32849200	-0.35910000

A

-2541.2537582 Hartree

I	0.75377900	-2.14533900	-0.08717000
C	-1.02719900	-0.96421200	-0.04427700
C	-1.49185200	-0.42932500	-1.24456800
C	-1.65417100	-0.76756500	1.18427000
C	-2.64906100	0.35000800	-1.20123200
H	-0.97632000	-0.60063800	-2.18953800
C	-2.81212300	0.01350800	1.20324300
H	-1.26303900	-1.19708300	2.10649600
C	-3.30403300	0.56530200	0.01644600
H	-3.03429500	0.79024500	-2.12186000
H	-3.32386100	0.19252700	2.14942200
C	2.14663600	-0.53203500	0.07401100
C	2.67237300	0.00025600	-1.10130100
C	2.47253700	-0.06797800	1.34725300
C	3.57459400	1.06042000	-0.98581000
H	2.39416200	-0.38319900	-2.08289700
C	3.37403200	0.99380000	1.43837300
H	2.04156300	-0.50551900	2.24775800
H	3.99980400	1.50444100	-1.88648800
H	3.64362900	1.38608900	2.41979800
C	-4.58386600	1.36807200	0.03630400
F	-4.56821800	2.34791800	-0.88173500
F	-4.80032600	1.93434900	1.23350200
F	-5.64873000	0.59048500	-0.23398200

C	3.92187500	1.54988400	0.27702900
C	4.93548700	2.66387100	0.39715100
F	4.96658900	3.43226000	-0.70258500
F	6.17641200	2.17382100	0.57488600
F	4.67294800	3.46152600	1.44498600

Int1

-3148.2125513 Hartree

C	4.83841000	-2.10976300	0.98405500
C	4.69739100	-0.85383900	0.13662300
C	3.36868700	-0.89781200	-0.63289900
C	2.34076400	-2.38966500	0.92623700
C	3.58484000	-2.35275400	1.81856900
H	4.66754500	0.01289400	0.83253600
H	4.94911600	-2.96786300	0.28944300
H	2.42682100	-3.26133300	0.24907500
H	3.47195300	-1.50413500	2.52525300
H	3.45535500	-1.59601000	-1.48740300
O	2.24990200	-1.18764000	0.17058900
S	3.03925000	0.77777400	-1.40026800
O	4.30009000	0.90183200	-2.26831500
O	5.77235600	-0.76013000	-0.76311000
H	5.48958800	-0.09329000	-1.43380900
O	5.96965900	-1.99720300	1.82078100
H	5.92093700	-2.74687200	2.43359300
O	3.78352800	-3.56801100	2.50974900
H	2.91300800	-3.83169200	2.86221200
C	1.03890700	-2.48893000	1.71092300
H	0.18794000	-2.48809200	1.00667000
H	0.94466600	-1.59700800	2.35651800
O	1.08317600	-3.68326700	2.47723800
H	0.34681600	-3.68595100	3.10357300
O	1.80195800	0.47218200	-2.29160400
I	-0.58461400	0.18615700	-1.30377200
C	-2.50607900	-0.15253400	-0.35675800
C	-0.07729600	1.81037900	-0.01045700
C	-3.30491900	-1.16489500	-0.89468000
C	-2.90107100	0.57956400	0.76306600
C	-0.60920000	3.07379300	-0.27665300
C	0.81205400	1.58843100	1.04220100
C	-4.53534300	-1.43877800	-0.29425900
H	-2.96286600	-1.73320500	-1.76208100
C	-4.13474600	0.29513100	1.35363800
H	-2.27112700	1.36030800	1.18787500

C	-0.25928500	4.13993700	0.55388800
H	-1.29166700	3.23469200	-1.11235700
C	1.15671900	2.66265400	1.86500800
H	1.24957100	0.60454700	1.20718900
C	-4.95110700	-0.70941800	0.82509400
H	-5.16800300	-2.22998900	-0.69972200
H	-4.45253800	0.85705600	2.23302600
H	-0.66574900	5.13360400	0.36126700
C	0.61824600	3.93053500	1.62352600
H	1.85451200	2.50919400	2.68929400
C	-6.30251400	-0.97693200	1.43311100
C	0.95267300	5.07174400	2.55076600
F	-6.66510800	-2.26605300	1.30644100
F	-7.26751500	-0.24268100	0.84134900
F	-6.33537200	-0.67620300	2.74351400
F	0.89698800	6.26026300	1.92627500
F	2.18363000	4.94769400	3.07575400
F	0.09045200	5.13189400	3.58556500
S	-0.23727400	-2.80272200	-3.55137200
O	-1.25976900	-1.77492300	-3.01121200
C	0.75888800	-3.30833000	-2.11894300
H	0.07959400	-3.83270900	-1.43442300
H	1.55010900	-3.98932400	-2.46189400
H	1.18123700	-2.41576600	-1.64148900
C	1.02431100	-1.82921800	-4.42340100
H	1.43781900	-1.06269400	-3.74642400
H	1.80083600	-2.51993700	-4.78255400
H	0.50996400	-1.36828400	-5.27733200

Int2

-3148.2095873 Hartree

C	-4.71158500	0.38676100	-0.27509400
C	-3.26284800	0.84511500	-0.29002800
C	-3.05308800	2.02178000	0.67538600
C	-4.97021900	1.46209000	1.97757400
C	-5.20227100	0.19099500	1.15307100
H	-2.65967000	-0.00071800	0.08684800
H	-5.32841300	1.18519700	-0.73647500
H	-5.57960300	2.28029900	1.54523800
H	-4.60625600	-0.62259300	1.61311300
H	-3.40202700	2.97150600	0.22508300
O	-3.59106000	1.80311700	1.95507700
S	-1.22520300	2.24828800	1.00818900
O	-0.70939900	2.19122200	-0.49900400

O	-2.89415500	1.20049700	-1.59787300
H	-1.99500500	1.58944800	-1.49777300
O	-4.82966100	-0.81596100	-1.00927200
H	-5.69161200	-1.19179300	-0.77430200
O	-6.56741300	-0.16543400	1.07090500
H	-6.92857500	-0.07633700	1.97270900
C	-5.32295700	1.28662000	3.44902700
H	-5.12667700	2.23331300	3.98314400
H	-4.65852800	0.51155500	3.87232400
O	-6.69018300	0.90954200	3.53817300
H	-6.88235300	0.62934400	4.44307800
O	-1.11232100	3.66485100	1.53408200
I	1.41489600	0.77022100	-0.68177300
C	3.11679100	-0.57367200	-0.76503200
C	-0.01545600	-0.80307900	-0.47076700
C	4.38528900	0.00216600	-0.66577600
C	2.94146500	-1.94932700	-0.91643000
C	-0.76165100	-1.19410500	-1.58157500
C	-0.27063200	-1.30983600	0.80725800
C	5.50559900	-0.83042100	-0.71445700
H	4.49239700	1.08416900	-0.56398400
C	4.06983200	-2.77123500	-0.96188500
H	1.94862300	-2.39174100	-1.00124300
C	-1.80478200	-2.10677000	-1.40576000
H	-0.56381600	-0.77790100	-2.56948700
C	-1.30694800	-2.22861700	0.96945100
H	0.31221300	-0.98442400	1.66953800
C	5.34837900	-2.21305800	-0.85877600
H	6.50415400	-0.39652800	-0.64370300
H	3.94805900	-3.84847900	-1.08501600
H	-2.42514400	-2.39282900	-2.25383900
C	-2.07998300	-2.61153000	-0.13418400
H	-1.52769500	-2.62330700	1.96280100
C	6.55655200	-3.11198700	-0.85511500
C	-3.22824800	-3.56222000	0.08619000
F	6.85166700	-3.54181100	0.38958200
F	7.65292500	-2.48714400	-1.31949100
F	6.36912700	-4.21044700	-1.60868700
F	-4.06772500	-3.11171300	1.04085100
F	-2.78859600	-4.76697200	0.50772800
F	-3.95130900	-3.77075900	-1.02151300
S	2.92373300	4.21158500	-0.30470700
O	3.16031200	2.77445000	-0.82577000
C	2.30203800	4.07368100	1.40263100

H	2.98922900	3.39060300	1.91886300
H	2.36373300	5.07549800	1.85190700
H	1.26363500	3.71412800	1.42643300
C	1.39159400	4.78041000	-1.09912800
H	0.57413900	4.07921900	-0.87258100
H	1.16794300	5.78891300	-0.72249300
H	1.60101100	4.81788700	-2.17629500

Int3

-3148.2043705 Hartree

C	4.94322500	1.97475100	0.72771600
C	3.64883700	2.20521900	-0.03845200
C	3.70897100	1.45066500	-1.37686700
C	5.31917200	-0.11830900	-0.62138700
C	5.30853400	0.49672500	0.78161600
H	2.82640400	1.77194200	0.56748200
H	5.75007900	2.49962200	0.17589400
H	6.12455700	0.36723600	-1.20656900
H	4.53188800	-0.02121500	1.37442000
H	4.36734000	1.98975300	-2.08669200
O	4.05807000	0.09992400	-1.24707500
S	2.04585800	1.46308900	-2.22924000
O	1.69879900	2.96376300	-2.12104800
O	3.46864500	3.58076100	-0.25202100
H	2.73869400	3.63790200	-0.91372300
O	4.81980000	2.49071300	2.03776300
H	5.60152100	2.17557100	2.51718400
O	6.56793000	0.41498800	1.41635800
H	6.83406100	-0.52059600	1.33977700
C	5.49913700	-1.63556900	-0.61211600
H	5.69458800	-1.99254200	-1.63832000
H	4.54350100	-2.06669300	-0.28385800
O	6.55591700	-2.00876500	0.26616700
H	6.30527900	-2.82607100	0.71729400
O	2.36487700	1.03696400	-3.64481000
I	-0.48030500	0.00315200	-1.04675100
C	-2.23042700	-0.95894700	-0.14591700
C	0.89193800	-0.95843300	0.28054300
C	-3.47442100	-0.67143200	-0.70555300
C	-2.07765700	-1.81287800	0.94405600
C	1.26687200	-0.32284900	1.46528000
C	1.41644900	-2.19693000	-0.09219400
C	-4.60617000	-1.26742600	-0.14379100
H	-3.55314500	0.00005400	-1.56277800

C	-3.22013200	-2.40073900	1.49353000
H	-1.10152600	-2.03394200	1.37361700
C	2.21707500	-0.93532100	2.28474700
H	0.84094500	0.64003200	1.74963400
C	2.35031700	-2.81023700	0.74330700
H	1.11273300	-2.68297100	-1.02005500
C	-4.47995200	-2.12757800	0.95214500
H	-5.58915600	-1.06124600	-0.57019600
H	-3.11982500	-3.07700800	2.34363000
H	2.54566500	-0.43569800	3.19675600
C	2.76389500	-2.16891500	1.91577800
H	2.77451800	-3.77513400	0.46294400
C	-5.71143900	-2.72409100	1.58258200
C	3.81596500	-2.81137600	2.78492700
F	-6.69319600	-2.91693800	0.68429700
F	-6.21444900	-1.92121400	2.54267600
F	-5.45644800	-3.91014400	2.16248200
F	4.55568700	-1.89567500	3.43063700
F	4.66928500	-3.56417900	2.04921800
F	3.28595000	-3.62413600	3.71095100
S	-2.12221800	2.12887900	-3.82479300
O	-2.21403800	1.02407100	-2.74487700
C	-0.78360300	1.62954700	-4.94497700
H	-1.11638500	0.69114800	-5.40840700
H	-0.68087800	2.40853600	-5.71417000
H	0.16417100	1.48402600	-4.40600200
C	-1.33232600	3.55211100	-3.02621500
H	-0.32912200	3.28586100	-2.65383500
H	-1.27641400	4.36287400	-3.76705900
H	-2.00436300	3.84237000	-2.20742500

TS1

-3148.1715601 Hartree

C	4.51714100	-0.71523600	1.34236600
C	3.89707300	0.31694500	0.41337100
C	2.99378800	-0.40936500	-0.59951600
C	2.61179600	-2.28003500	0.81486000
C	3.44883600	-1.63409500	1.92547000
H	3.26624000	0.98854600	1.03133300
H	5.20346000	-1.34103600	0.73562500
H	3.26655900	-2.94345900	0.21798200
H	2.76716400	-1.01465700	2.54495100
H	3.60968500	-0.90923500	-1.37153100
O	2.05090700	-1.26723800	-0.01830500

S	1.95541000	0.84981600	-1.49186400
O	2.92259400	1.95474500	-1.85133900
O	4.91216100	1.02040300	-0.25298900
H	4.45301500	1.60418000	-0.89125800
O	5.21868800	-0.06057400	2.37523100
H	5.45043300	-0.75095100	3.01551200
O	4.12641800	-2.59040400	2.71099000
H	3.47162200	-3.27961200	2.93041900
C	1.43081600	-3.07550300	1.35661400
H	0.87545800	-3.52400400	0.51661400
H	0.75252200	-2.38017500	1.88384800
O	1.93702600	-4.07216100	2.23190000
H	1.20055200	-4.47878200	2.70797000
O	1.34080800	0.11644100	-2.67303300
I	-1.23218500	0.38303200	-1.85543400
C	-2.98239000	0.50968200	-0.64217400
C	0.01180300	1.62418100	-0.17411900
C	-3.82523400	-0.60506200	-0.63829300
C	-3.24635000	1.64198400	0.13159500
C	0.02163900	3.01205200	-0.32814600
C	-0.05441600	1.01452800	1.08111000
C	-4.96403700	-0.57908500	0.16991200
H	-3.59423000	-1.46868300	-1.26701800
C	-4.38237300	1.64895800	0.94249500
H	-2.58431800	2.50728100	0.12094000
C	-0.04272100	3.80918900	0.81575800
H	0.08331700	3.47155600	-1.31550000
C	-0.11709000	1.82766400	2.21188600
H	-0.04124800	-0.06992500	1.17996100
C	-5.23864800	0.54197000	0.96076900
H	-5.63209200	-1.44128300	0.18995700
H	-4.59447500	2.52037900	1.56394500
H	-0.03621900	4.89547400	0.71078800
C	-0.11884600	3.22368600	2.08615600
H	-0.16339700	1.36437300	3.19910800
C	-6.48768600	0.58497900	1.80122100
C	-0.27540600	4.08505000	3.30448200
F	-6.91479800	-0.64467500	2.13729100
F	-7.50433500	1.18636400	1.14918900
F	-6.30098000	1.27256300	2.94260700
F	0.28390400	5.29904500	3.14495000
F	0.28116800	3.52609300	4.39598900
F	-1.57654200	4.29931500	3.60686300
S	-1.42824900	-3.17407800	-3.37898900

O	-2.44878300	-2.05915300	-3.10845200
C	-0.37089900	-3.32873300	-1.89703100
H	-1.04813000	-3.55149700	-1.06205800
H	0.31314400	-4.17399000	-2.05931900
H	0.19052600	-2.40450800	-1.70934300
C	-0.17592200	-2.45510800	-4.49233600
H	0.31420500	-1.59875700	-4.00817100
H	0.55552900	-3.23657300	-4.74373200
H	-0.71786500	-2.14256900	-5.39457100

TS2

-3148.1713926 Hartree

C	-5.40881000	1.21302800	-1.58085200
C	-3.93125400	1.55888700	-1.69454700
C	-3.35377400	1.69435800	-0.27705300
C	-4.96596800	0.25663700	0.71254700
C	-5.60980200	0.01404600	-0.65731100
H	-3.43415900	0.71360800	-2.20727400
H	-5.92653100	2.08158000	-1.12406600
H	-5.50640800	1.08420400	1.21216400
H	-5.10304800	-0.85899300	-1.11884500
H	-3.68005300	2.65033800	0.17573100
O	-3.59246100	0.59083100	0.54976500
S	-1.49264500	1.75960700	-0.31677500
O	-1.16895700	2.46389200	-1.65087600
O	-3.76837800	2.75954900	-2.40184900
H	-2.80231400	2.91302100	-2.42471900
O	-5.93031900	0.93772100	-2.86186900
H	-6.81160600	0.56177700	-2.71232900
O	-7.00210300	-0.19591300	-0.56217700
H	-7.13101100	-0.83718500	0.16203800
C	-4.97939200	-0.98072000	1.60034500
H	-4.51172600	-0.73511300	2.57055400
H	-4.36872100	-1.76414000	1.12031700
O	-6.32989300	-1.39388200	1.76017600
H	-6.34441900	-2.28035900	2.14524300
O	-1.06509400	2.51140800	0.91028300
I	0.85858700	0.69732300	-2.26316000
C	2.28990200	-0.85324800	-1.98253000
C	-0.54474000	-0.53418100	-0.73297800
C	3.54442900	-0.49553900	-1.48368100
C	1.93957700	-2.17861200	-2.24891700
C	-1.50592700	-1.32194300	-1.36567900
C	0.07152000	-0.90817900	0.45781700

C	4.47512700	-1.50990400	-1.24501200
H	3.77738300	0.55633400	-1.29042500
C	2.87756500	-3.18074700	-1.99684200
H	0.95371100	-2.43834700	-2.63611900
C	-1.91536200	-2.49517400	-0.73332800
H	-1.94195800	-1.03432200	-2.32210200
C	-0.35182800	-2.08654100	1.07576500
H	0.84397300	-0.29390100	0.92095200
C	4.14055700	-2.84543300	-1.49525200
H	5.46404000	-1.25519900	-0.86035800
H	2.62428000	-4.22249800	-2.19787600
H	-2.67630400	-3.11761600	-1.20813300
C	-1.35120800	-2.87396100	0.49201500
H	0.10044400	-2.38507300	2.02245900
C	5.13145100	-3.93378500	-1.17264600
C	-1.85873800	-4.10759400	1.18015300
F	5.03456100	-4.32365300	0.11518300
F	6.40039300	-3.53019100	-1.36072100
F	4.94117700	-5.03053400	-1.92641900
F	-3.06940900	-3.89848800	1.75250000
F	-1.03799800	-4.52693200	2.15699500
F	-2.02269200	-5.13266900	0.32180500
S	3.11850100	3.47815800	-0.10473800
O	3.35665800	2.60221000	-1.33859100
C	2.33756800	2.43200000	1.17513700
H	2.98400200	1.55135200	1.28625000
H	2.32302900	3.00462500	2.11397700
H	1.31403800	2.15600900	0.89102400
C	1.66521800	4.50805300	-0.49617200
H	0.81420400	3.87057400	-0.77184600
H	1.42384400	5.12646600	0.38033500
H	1.96467200	5.14690300	-1.33767800

7t

-1728.7080039 Hartree

C	0.05603100	-3.00198000	1.48924800
C	1.09437900	-1.95876700	1.09632000
C	1.14248200	-1.88065000	-0.44241100
C	-1.07285100	-2.68051000	-0.74000400
C	-1.27044700	-2.75316100	0.77740600
H	0.75052300	-0.98299900	1.49357700
H	0.43436300	-3.99147800	1.16016700
H	-0.73535300	-3.66981100	-1.10289400
H	-1.66056300	-1.77091400	1.11601900

H	1.68936500	-2.75592700	-0.84421100
O	-0.09505200	-1.68766400	-1.04859600
S	2.16671700	-0.45662400	-1.00383100
O	3.36903200	-0.44640000	-0.13485400
O	2.34207200	-2.32953500	1.61917600
H	2.99185400	-1.68478300	1.28489400
O	-0.12275500	-2.97414000	2.88620100
H	-0.89264500	-3.53559100	3.06621800
O	-2.13259900	-3.80363800	1.15318400
H	-2.90644800	-3.74788600	0.56141400
C	-2.33188800	-2.25922200	-1.48585600
H	-2.12026600	-2.23308900	-2.56947400
H	-2.59997100	-1.23673100	-1.16411600
O	-3.35380200	-3.19372900	-1.17287200
H	-4.20234000	-2.85392800	-1.48751800
O	2.31751600	-0.54062500	-2.46229300
C	1.17314900	0.97828800	-0.60716100
C	1.43510100	1.67936300	0.57005000
C	0.16024300	1.35898300	-1.49178900
C	0.65010000	2.79198400	0.87709300
H	2.24280800	1.36236100	1.23014300
C	-0.62031600	2.46779000	-1.17497500
H	-0.01327300	0.79227400	-2.40579200
H	0.83450300	3.35341500	1.79321700
C	-0.37300600	3.17931000	0.00675600
H	-1.42311400	2.77804700	-1.84521500
C	-1.19785000	4.40638900	0.30906500
F	-1.17325000	4.72445600	1.61308600
F	-2.48450700	4.23821900	-0.04283400
F	-0.74438700	5.47877200	-0.36886300

B

-866.4305566 Hartree

I	-0.01233600	2.90101500	0.00000000
C	0.00735900	0.77713100	0.00000000
C	0.01525600	0.08999200	1.21780400
C	0.01525600	0.08999200	-1.21780400
C	0.02889300	-1.30587200	1.21253900
H	0.01360400	0.63028400	2.16508100
C	0.02889300	-1.30587200	-1.21253900
H	0.01360400	0.63028400	-2.16508100
H	0.04077000	-1.84860800	2.15899300
H	0.04077000	-1.84860800	-2.15899300
C	0.03431900	-2.00376300	0.00000000

C	-0.00547800	-3.50835700	0.00000000
F	0.59684300	-4.02921700	-1.08425800
F	-1.27259400	-3.97357000	0.00000000
F	0.59684300	-4.02921700	1.08425800

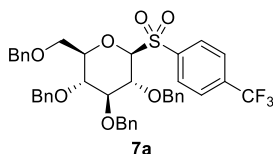
References:

- [1] Zeng, H.; Li, Y.; Wu, R.; Liu, D.; Zhang, Y.; Xu, S.; Niu, D. Carbohydrate-DNA conjugation enabled by glycosyl radicals generated from glycosyl sulfinates. *Org. Lett.* **2023**, doi.org/10.1021/acs.orglett.3c00833.
- [2] Chen, Q.; Kong, F. ; Stereoselective glycosylation using fully benzylated pyrimidin-2-yl 1-thio-13-o-glycopyranosides *Carbohydrate Research* **1995**, 272 149-157.
- [3] Ming, X.-X.; Tian, Z.-Y.; Zhang, C.-P. Base-mediated O-arylation of alcohols and phenols by triarylsulfonium triflates. *Chem. Asian J.* **2019**, 14, 3370-3379.
- [4] Duong, H. A.; Gilligan, R. E.; Cooke, M. L.; Phipps, R. J.; Gaunt, M. J. Copper(II)-catalyzed meta-selective direct arylation of alpha-aryl carbonyl compounds. *Angew. Chem., Int. Ed.* **2011**, 50, 463-466.
- [5] Lucchetti, N.; Scalone, M.; Fantasia, S.; Muniz, K. Sterically congested 2,6-disubstituted anilines from direct C-N bond formation at an Iodine(III) center. *Angew. Chem., Int. Ed.* **2016**, 55, 13335-13339.
- [6] Guan, Y.; Townsend, S. D. Metal-free synthesis of unsymmetrical organoselenides and selenoglycosides. *Org. Lett.* **2017**, 19, 5252-5255.
- [7] Zhou, J.; Bao, Z.; Wu, P.; Chen, C. The preparation and application of diaryliodonium salts derived from gemfibrozil and gemfibrozil methyl ester. *Synthesis* **2022**, 54, 1388-1394.
- [8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.
- [9] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *The Journal of Physical Chemistry* **1994**, 98 (45), 11623-11627.
- [10] Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry* **2011**, 32 (7), 1456-1465.

- [11] Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics* **2005**, *7* (18), 3297-3305.
- [12] Weigend, F., Accurate Coulomb-fitting basis sets for H to Rn. *Physical Chemistry Chemical Physics* **2006**, *8* (9), 1057-1065.
- [13] Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M., Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-d group 16–18 elements. *The Journal of Chemical Physics* **2003**, *119* (21), 11113-11123.
- [14] Tomasi, J.; Mennucci, B.; Cammi, R., Quantum Mechanical Continuum Solvation Models. *Chemical Reviews* **2005**, *105* (8), 2999-3094.
- [15] Neese, F., The ORCA program system. *WIREs Computational Molecular Science* **2012**, *2* (1), 73-78.
- [16] Neese, F., Software update: the ORCA program system, version 4.0. *WIREs Computational Molecular Science* **2018**, *8* (1), e1327.
- [17] Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C., The ORCA quantum chemistry program package. *The Journal of Chemical Physics* **2020**, *152* (22).
- [18] Neese, F., Software update: The ORCA program system—Version 5.0. *WIREs Computational Molecular Science* **2022**, *12* (5), e1606.
- [19] Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U., Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree–Fock exchange. *Chemical Physics* **2009**, *356* (1), 98-109.
- [20] Mardirossian, N.; Head-Gordon, M., ω B97M-V: A combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. *J Chem Phys* **2016**, *144* (21), 214110.
- [21] Zheng, J.; Xu, X.; Truhlar, D. G., Minimally augmented Karlsruhe basis sets. *Theoretical Chemistry Accounts* **2011**, *128* (3), 295-305.
- [22] Stoychev, G. L.; Auer, A. A.; Neese, F., Automatic Generation of Auxiliary Basis Sets. *Journal of Chemical Theory and Computation* **2017**, *13* (2), 554-562.
- [23] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *The Journal of Physical Chemistry B* **2009**, *113* (18), 6378-6396.
- [24] Otlyotov, A. A.; Minenkov, Y., Gas-phase thermochemistry of noncovalent ligand–alkali metal ion clusters: An impact of low frequencies. *Journal of Computational Chemistry* **2023**, *44* (22), 1807-1816.
- [25] Kesharwani, M. K.; Brauer, B.; Martin, J. M. L., Frequency and Zero-Point Vibrational Energy Scale Factors for Double-Hybrid Density Functionals (and Other Selected Methods): Can

- Anharmonic Force Fields Be Avoided? *The Journal of Physical Chemistry A* **2015**, *119* (9), 1701-1714.
- [26] Lu, T.; Chen, Q., Shermo: A general code for calculating molecular thermochemistry properties. *Computational and Theoretical Chemistry* **2021**, *1200*, 113249.
- [27] Hirshfeld, F. L., Bonded-atom fragments for describing molecular charge densities. *Theoretica chimica acta* **1977**, *44* (2), 129-138.
- [28] Mayer, I., Charge, bond order and valence in the AB initio SCF theory. *Chemical Physics Letters* **1983**, *97* (3), 270-274.
- [29] Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *Journal of Computational Chemistry* **2012**, *33* (5), 580-592.
- [30] Legault, C. Y. *CYLview20*, Université de Sherbrooke: Quebec, Montreal, Canada, 2020.

Characterization data



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-(trifluoromethyl)phenyl)sulfonyl)tetrahydro-2H-pyran

7a was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (63.4 mg, 86% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.47-7.24 (m, 18H), 7.21-7.19 (m, 2H), 5.09 (d, *J* = 9.7 Hz, 1H), 5.00-4.78 (m, 4H), 4.60 (d, *J* = 10.9 Hz, 1H), 4.49-4.35 (m, 3H), 4.12 (t, *J* = 9.1 Hz, 1H), 3.79 (t, 8.9 Hz, 1H) 3.66 (t, *J* = 9.4 Hz, 1H), 3.59 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.52-3.49 (m, 1H), 3.40-3.36 (m, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.03 ppm.

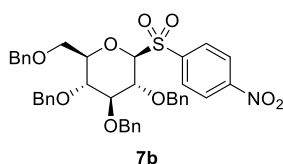
¹³C NMR (101 MHz, CDCl₃) δ 140.80, 138.13, 137.80, 137.72, 137.44, 135.51(q, *J* = 33.3 Hz), 130.44, 128.70, 128.62, 128.58, 128.56, 128.54, 128.13, 128.11, 128.08, 127.98, 127.94, 127.84, 127.74, 125.84(q, *J* = 4.0 Hz), 123.26(q, *J* = 274.7 Hz), 91.22, 86.20, 79.55, 77.48, 76.88, 76.06, 75.59, 75.24, 73.58, 68.48 ppm.

IR (thin film, cm⁻¹): 3201, 2924, 2323, 2286, 2050, 1561, 1322, 1258, 1160, 1060, 754, 697, 636, 497, 456, 422.

[α]_D²⁵ = +11.7 (c = 0.24, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₁H₃₉F₃O₇SNa⁺ [M+Na]⁺: 755.2261, found: 755.2260.

m. p.: 111.9-113.2°C.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-nitrophenyl)sulfonyl)tetrahydro-2H-pyran

7b was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (69.2 mg, 97% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 7.47-7.15 (m, 20H), 5.06 (d, *J* = 9.8 Hz, 1H), 4.99-4.78 (m, 4H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.46 (d, *J* = 9.3 Hz, 1H), 4.38 (d, *J* = 2.1 Hz, 2H), 4.13 (t, *J* = 9.1 Hz, 1H), 3.78 (t, *J* = 8.9 Hz, 1H), 3.63 (t, *J* = 9.4 Hz, 1H), 3.57-3.48 (m, 2H), 3.41-3.35 (m, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 150.97, 142.87, 138.07, 137.65, 137.62, 137.32, 131.24, 128.73,

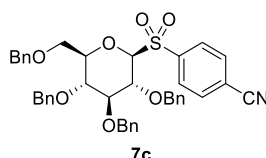
128.67, 128.64, 128.62, 128.60, 128.24, 128.18, 128.16, 128.01, 127.79, 127.76, 123.81, 91.29, 86.15, 79.56, 77.37, 76.89, 76.10, 75.66, 75.31, 73.57, 68.59 ppm.

IR (thin film, cm⁻¹): 3184, 2924, 2323, 2285, 2198, 2161, 2050, 2024, 1979, 1533, 1348, 1247, 1158, 1106, 855, 736, 647, 484, 428.

[α]_D²⁵ = +13.6 (c = 0.14, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₀H₃₉NO₉SNa⁺ [M+Na]⁺: 732.2238, found: 732.2242.

m. p.: 48.2-48.9°C.



4-(((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)sulfonyl)benzonitrile

7c was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (65.3 mg, 94% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.45-7.15 (m, 20H), 5.06 (d, *J* = 9.8 Hz, 1H), 4.98-4.78 (m, 4H), 4.59 (d, *J* = 10.9 Hz, 1H), 4.46-4.32 (m, 3H), 4.11 (t, *J* = 9.1 Hz, 1H), 3.78 (t, *J* = 8.9 Hz, 1H), 3.66-3.46 (m, 3H), 3.42-3.34 (m, 1H) ppm.

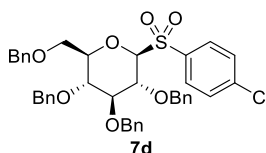
¹³C NMR (101 MHz, CDCl₃) δ 141.35, 138.07, 137.75, 137.64, 137.35, 132.40, 130.47, 128.71, 128.67, 128.66, 128.62, 128.58, 128.20, 128.14, 127.99, 127.85, 127.75, 117.63, 117.29, 91.23, 86.15, 79.49, 77.40, 76.92, 76.08, 75.63, 75.28, 73.56, 68.63 ppm.

IR (thin film, cm⁻¹): 3214, 2925, 2323, 2283, 2209, 2185, 2164, 2050, 1979, 1566, 1364, 1258, 1053, 855, 753, 644, 487, 456, 424.

[α]_D²⁵ = +13.3 (c = 0.12, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₁H₃₉NO₇SNa⁺ [M+Na]⁺: 712.2339, found: 712.2341.

m. p.: 48.5-49.6°C.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-chlorophenyl)sulfonyl)tetrahydro-2H-pyran

7d was prepared according to General procedure B as a colorless syrup using PE/EA (5:1) as the eluent (59.0 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.49-7.41 (m, 4H), 7.40-7.27 (m, 16H), 7.22 (dd, *J* = 7.1, 2.5 Hz, 2H), 5.12 (d, *J* = 9.7 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.95-4.80 (m, 3H),

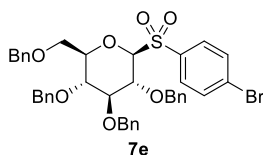
4.62 (d, $J = 11.0$ Hz, 1H), 4.45-4.39 (m, 3H), 4.12 (t, $J = 9.1$ Hz, 1H), 3.80 (t, $J = 9.0$ Hz, 1H), 3.70-3.51 (m, 3H), 3.40 (ddd, $J = 9.8, 4.6, 1.9$ Hz, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 140.84, 138.17, 137.90, 137.74, 137.50, 135.62, 131.29, 129.11, 128.75, 128.60, 128.56, 128.52, 128.09, 128.05, 127.91, 127.74, 127.72, 91.18, 86.24, 79.56, 77.57, 76.94, 76.03, 75.57, 75.21, 73.56, 68.63 ppm.

IR (thin film, cm^{-1}): 2943, 2866, 2323, 2165, 2050, 1980, 1647, 1623, 1510, 1642, 1442, 1381, 1247, 1190, 1106, 1076, 981, 884, 793, 755, 695, 573, 444.

$[\alpha]_{\text{D}}^{25} = +10.9$ ($c = 0.11$, CHCl_3).

HRMS (ESI-TOF): calculated for $\text{C}_{40}\text{H}_{39}\text{ClO}_7\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 721.1997, found: 721.1998.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-bromophenyl)sulfonyl)tetrahydro-2H-pyran

7e was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (65.0 mg, 87% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.47-7.24 (m, 18H), 7.23-7.18 (m, 2H), 5.09 (d, $J = 9.7$ Hz, 1H), 5.00-4.78 (m, 4H), 4.60 (d, $J = 10.9$ Hz, 1H), 4.46-4.37 (m, 3H), 4.10 (t, $J = 9.1$ Hz, 1H), 3.78 (t, $J = 9.0$ Hz, 1H), 3.68-3.50 (m, 3H), 3.39 (ddd, $J = 9.8, 4.6, 1.9$ Hz, 1H) ppm.

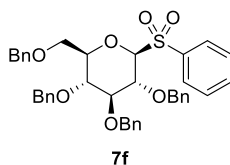
^{13}C NMR (101 MHz, CDCl_3) δ 138.18, 137.91, 137.75, 137.50, 136.18, 132.12, 131.35, 129.57, 128.76, 128.62, 128.61, 128.58, 128.54, 128.11, 128.07, 127.94, 127.92, 127.79, 127.74, 91.20, 86.25, 79.59, 77.56, 76.95, 76.05, 75.58, 75.24, 73.59, 68.63 ppm.

IR (thin film, cm^{-1}): 2943, 2866, 2323, 2166, 2050, 1980, 1647, 1623, 1568, 1462, 1442, 1381, 1247, 1106, 1076, 981, 920, 884, 793, 695, 602, 573, 444.

$[\alpha]_{\text{D}}^{25} = +9.1$ ($c = 0.11$, CHCl_3).

HRMS (ESI-TOF): calculated for $\text{C}_{40}\text{H}_{39}\text{BrO}_7\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 765.1492, found: 765.1495.

m. p.: 51.9-52.8°C.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(phenylsulfonyl)tetrahydro-2H-pyran

7f was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (58.0 mg, 87% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.01-7.95 (m, 2H), 7.64-7.54 (m, 1H), 7.51-7.08 (m, 22H), 5.14 (d, *J* = 9.7 Hz, 1H), 5.00-4.78 (m, 4H), 4.60 (d, *J* = 10.9 Hz, 1H), 4.48-4.32 (m, 3H), 4.13 (t, *J* = 9.1 Hz, 1H), 3.79 (t, *J* = 9.0 Hz, 1H), 3.69-3.49 (m, 3H), 3.40-3.34 (m, 1H) ppm.

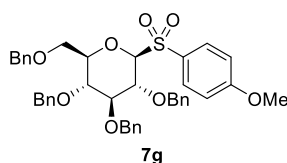
¹³C NMR (101 MHz, CDCl₃) δ 138.26, 138.11, 137.82, 137.63, 137.23, 134.01, 129.78, 128.81, 128.62, 128.56, 128.53, 128.47, 128.09, 128.06, 128.03, 127.90, 127.78, 127.76, 127.69, 91.19, 86.35, 79.76, 77.69, 77.03, 76.05, 75.58, 75.21, 73.56, 68.66 ppm.

IR (thin film, cm⁻¹): 2944, 2866, 2323, 2050, 1980, 1653, 1624, 1570, 1510, 1462, 1443, 1382, 1248, 1192, 1106, 1045, 980, 921, 884, 822, 783, 686, 610, 454.

[α]_D²⁵ = +15.0 (c = 0.10, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₀H₄₀O₇SNa⁺ [M+Na]⁺: 687.2387, found: 687.2386.

m. p.: 156.0-156.7°C.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-methoxyphenyl)sulfonyl)tetrahydro-2H-pyran

7g was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (31.0 mg, 52% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.39-7.17 (m, 18H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.12 (d, *J* = 9.7 Hz, 1H), 5.00-4.78 (m, 4H), 4.59 (d, *J* = 10.9 Hz, 1H), 4.42-4.34 (m, 3H), 4.07 (t, *J* = 9.1 Hz, 1H), 3.80-3.75 (m, 4H), 3.64-3.55 (m, 3H), 3.41-3.37 (m, 1H) ppm.

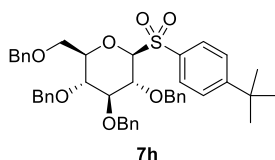
¹³C NMR (101 MHz, CDCl₃) δ 164.11, 138.31, 138.17, 137.85, 137.71, 132.05, 128.83, 128.63, 128.60, 128.58, 128.54, 128.50, 128.12, 128.05, 127.90, 127.78, 127.75, 114.08, 91.28, 86.41, 79.76, 77.86, 77.11, 76.06, 75.56, 75.23, 73.63, 68.86, 55.69 ppm.

IR (thin film, cm⁻¹): 3194, 2924, 2323, 2285, 2208, 2164, 2049, 1981, 1577, 1497, 1363, 1260, 1149, 1084, 751, 630, 512, 471, 452, 424.

[α]_D²⁵ = +10.0 (c = 0.16, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₁H₄₂O₈SNa⁺ [M+Na]⁺: 717.2493, found: 717.2493.

m. p.: 128.2 -129.7°C.



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

7h was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (62.0 mg, 86% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.40 (m, 4H), 7.39 – 7.23 (m, 16H), 7.20 - 7.14 (m, 2H), 5.09 (d, *J* = 9.7 Hz, 1H), 4.96 – 4.73 (m, 4H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.45 – 4.33 (m, 3H), 4.07 (t, *J* = 9.1 Hz, 1H), 3.76 (t, *J* = 8.9 Hz, 1H), 3.67 – 3.50 (m, 3H), 3.41 – 3.34 (m, 1H), 1.28 (s, 9H) ppm.

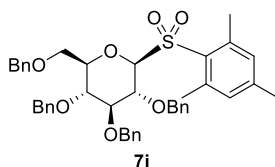
¹³C NMR (101 MHz, CDCl₃) δ 157.97, 138.28, 138.18, 137.87, 137.72, 134.25, 129.66, 128.76, 128.63, 128.58, 128.54, 128.10, 128.03, 127.92, 127.83, 127.81, 125.88, 91.27, 86.42, 79.83, 77.76, 77.06, 76.09, 75.52, 75.22, 73.69, 68.62, 35.34, 31.14 ppm.

IR (thin film, cm⁻¹): 3204, 2961, 2644, 2323, 2285, 2190, 2162, 2050, 2068, 2023, 1980, 1574, 1365, 1259, 1053, 456, 424.

[α]_D²⁵ = +7.3 (*c* = 0.11, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₄H₄₈O₇SNa⁺ [*M*+Na]⁺: 743.3013, found: 743.3015.

m. p.: 48.7-49.3°C.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(mesitylsulfonyl)tetrahydro-2H-pyran

7i was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (62.0 mg, 89% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.51-7.44 (m, 2H), 7.41-7.27 (m, 14H), 7.22-7.16 (m, 4H), 6.93 (s, 2H), 5.22 (d, *J* = 9.6 Hz, 1H), 5.00 (d, *J* = 11.1 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.88-4.80 (m, 2H), 4.61 (d, *J* = 10.9 Hz, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 4.34-4.24 (m, 2H), 4.18 (d, *J* = 11.8 Hz, 1H), 3.84 (t, *J* = 9.0 Hz, 1H), 3.66 (t, *J* = 9.4 Hz, 1H), 3.54 (d, *J* = 3.5 Hz, 2H), 3.41 (dt, *J* = 9.8, 3.2 Hz, 1H), 2.73 (s, 6H), 2.25 (s, 3H) ppm.

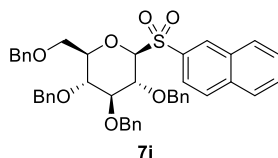
¹³C NMR (101 MHz, CDCl₃) δ 143.50, 141.62, 138.45, 138.11, 137.86, 132.08, 132.02, 128.94, 128.58, 128.54, 128.47, 128.40, 128.09, 127.99, 127.80, 127.69, 127.64, 91.39, 86.55, 79.98, 77.52, 77.10, 75.96, 75.58, 75.21, 73.61, 69.07, 23.26, 21.10 ppm.

IR (thin film, cm⁻¹): 2942, 2865, 2323, 2184, 2161, 2050, 1979, 1644, 1623, 1568, 1509, 1441, 1380, 1328, 1106, 1051, 979, 919, 883, 751, 695, 666, 579, 511, 443.

[α]_D²⁵ = +14.1 (c = 0.29, CHCl₃)

HRMS (ESI-TOF): calculated for C₄₃H₄₆O₇SNa⁺ [M+Na]⁺: 729.2856, found: 729.2858.

m. p.: 152.7-153.7°C



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-2-ylsulfonyl)tetrahydro-2H-pyran

7j was prepared according to General procedure B as a yellow solid using PE/EA (4:1) as the eluent (50.0 mg, 70% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 1.8 Hz, 1H), 8.00-7.83 (m, 4H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52-7.46 (m, 2H), 7.38-7.24 (m, 14H), 7.19 (dd, *J* = 7.0, 2.8 Hz, 2H), 7.12 (dd, *J* = 6.6, 2.7 Hz, 2H), 5.19 (d, *J* = 9.7 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.90 (dd, *J* = 10.4, 3.6 Hz, 2H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.57 (dd, *J* = 23.4, 10.1 Hz, 2H), 4.36 (d, *J* = 11.9 Hz, 1H), 4.27 (d, *J* = 11.9 Hz, 1H), 4.19 (t, *J* = 9.1 Hz, 1H), 3.82 (t, *J* = 8.9 Hz, 1H), 3.66 (t, *J* = 9.4 Hz, 1H), 3.59 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.51 (dd, *J* = 11.4, 1.8 Hz, 1H), 3.38 (ddd, *J* = 9.8, 4.6, 1.8 Hz, 1H) ppm.

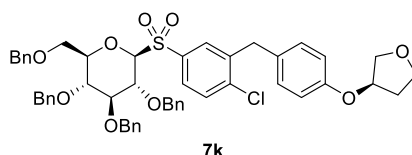
¹³C NMR (101 MHz, CDCl₃) δ 138.28, 138.02, 137.81, 137.69, 135.63, 134.38, 132.13, 131.67, 129.64, 129.42, 128.86, 128.80, 128.63, 128.57, 128.56, 128.45, 128.11, 128.08, 128.06, 128.04, 127.91, 127.77, 127.70, 127.62, 127.57, 124.58, 91.45, 86.40, 79.86, 77.79, 77.04, 76.07, 75.62, 75.23, 73.63, 68.71 ppm.

IR (thin film, cm⁻¹): 3218, 2959, 2323, 2182, 2166, 2049, 1979, 1567, 1362, 1259, 1054, 754, 643, 512, 473, 449, 438.

[α]_D²⁵ = +8.6 (c = 0.22, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₄H₄₂O₇SNa⁺ [M+Na]⁺: 737.2543, found: 737.2545.

m. p.: 52.6-53.4°C.



(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-chloro-3-(4-((R)-tetrahydrofuran-3-yl)oxy)benzyl)phenyl)sulfonyl)tetrahydro-2H-pyran

7k was prepared according to General procedure B as a white solid using PE/EA (2:1) as the eluent (55.0 mg, 63% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 2H), 7.43-7.13 (m, 21H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 5.02 - 4.83 (m, 3H), 4.82 - 4.74 (m, 3H), 4.56 (d, *J* = 10.9 Hz, 1H), 4.41-4.28 (m, 3H), 4.06-3.83 (m, 7H), 3.75 (t, *J* = 8.9 Hz, 1H), 3.66-3.49 (m, 3H), 3.37 (m, 1H), 2.26-2.00 (m, 2H) ppm.

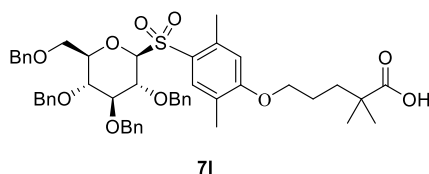
¹³C NMR (101 MHz, CDCl₃) δ 156.29, 140.72, 140.35, 138.18, 137.94, 137.74, 137.47, 135.77, 131.66, 130.34, 130.12, 130.10, 129.10, 128.74, 128.63, 128.58, 128.54, 128.10, 128.09, 128.07, 127.93, 127.89, 127.73, 127.69, 115.64, 91.16, 86.25, 79.69, 77.61, 77.34, 76.96, 76.03, 75.55, 75.23, 73.54, 73.22, 68.66, 67.28, 38.35, 33.06 ppm.

IR (thin film, cm⁻¹): 2955, 2923, 2853, 2323, 2161, 2050, 1979, 1508, 1454, 1376, 1332, 1258, 1153, 1087, 1014, 795, 755, 697, 659, 559, 461.

[α]_D²⁵ = +9.3 (c = 0.14, CHCl₃).

HRMS (ESI-TOF): calculated for C₅₁H₅₁ClO₉SNa⁺ [M+Na]⁺: 897.2835, found: 897.2839.

m. p.: 60.3-61.4°C.



5-(2,5-dimethyl-4-(((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)sulfonyl)phenoxy)-2,2-dimethylpentanoic acid

7l was prepared according to General procedure B as a white solid using PE/EA (3:1) as the eluent (31.0 mg, 39% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 1H), 7.46-7.39 (m, 2H), 7.35-7.22 (m, 15H), 7.17-7.12 (m, 4H), 6.54 (s, 1H), 5.12 (d, *J* = 9.8 Hz, 1H), 4.98-4.75 (m, 4H), 4.55 (d, *J* = 10.9 Hz, 1H), 4.44 (d, *J* = 9.3 Hz, 1H), 4.26 (d, *J* = 11.8 Hz, 1H), 4.21-4.10 (m, 2H), 3.87-3.73 (m, 3H), 3.61-3.48 (m, 3H), 3.43-3.36 (m, 1H), 2.64 (s, 3H), 2.13 (s, 3H), 1.83-1.66 (m, 4H), 1.25 (s, 6H) ppm.

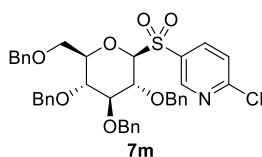
¹³C NMR (101 MHz, CDCl₃) δ 161.11, 140.19, 138.39, 138.19, 137.86, 133.59, 128.81, 128.63, 128.59, 128.52, 128.44, 128.13, 128.05, 127.99, 127.89, 127.77, 127.74, 127.71, 126.56, 124.78, 114.02, 91.77, 86.55, 80.19, 77.89, 77.36, 76.03, 75.53, 75.24, 73.65, 69.06, 68.27, 41.92, 36.85, 25.22, 25.01, 21.18, 15.72 ppm.

IR (thin film, cm⁻¹): 3278, 2923, 2161, 2049, 1979, 1631, 1497, 1453, 1375, 1257, 1088, 1045, 793, 753, 697, 664, 528, 465.

[α]_D²⁵ = +7.0 (c = 0.10, CHCl₃)

HRMS (ESI-TOF): calculated for C₄₉H₅₆O₁₀SNa⁺ [M+Na]⁺: 859.3486, found: 859.3483.

m. p.: 63.0-64.8°C.



2-chloro-5-(((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)sulfonyl)pyridine

7m was prepared according to General procedure B as a colorless syrup using PE/EA (4:1) as the eluent (47.0 mg, 67% yield).

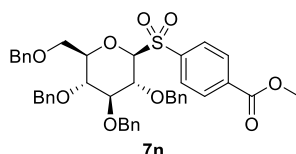
¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, *J* = 2.4 Hz, 1H), 8.08 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.44-7.21 (m, 19H), 7.18-7.15 (m, 2H), 5.05 (d, *J* = 9.7 Hz, 1H), 4.98-4.76 (m, 4H), 4.56 (d, *J* = 10.9 Hz, 1H), 4.41-4.38 (m, 3H), 4.11 (t, *J* = 9.1 Hz, 1H), 3.77 (t, *J* = 9.0 Hz, 1H), 3.65-3.47 (m, 3H), 3.41-3.36 (m, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 157.10, 150.95, 140.26, 138.11, 137.73, 137.64, 137.33, 132.70, 128.77, 128.68, 128.64, 128.62, 128.24, 128.18, 128.06, 128.01, 127.93, 127.76, 124.42, 91.42, 86.11, 79.57, 77.36, 76.90, 76.10, 75.71, 75.33, 73.68, 68.65 ppm.

IR (thin film, cm⁻¹): 3063, 2922, 2323, 2162, 2050, 2036, 1979, 1566, 1496, 1451, 1359, 1336, 1258, 1163, 1088, 1026, 797, 773, 734, 696, 639, 577, 458.

[α]_D²⁵ = +10.4 (c = 0.23, CHCl₃).

HRMS (ESI-TOF): calculated for C₃₉H₃₈ClNO₇S⁺ [M+Na]⁺: 722.1950, found: 722.1952.



Methyl 4-(((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)sulfonyl)benzoate

7n was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (63.2 mg, 88% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.48-7.42 (m, 2H), 7.41-7.27 (m, 14H), 7.24-7.18 (m, 4H), 5.11 (d, *J* = 9.7 Hz, 1H), 5.00-4.78 (m, 4H), 4.59 (d, *J* = 10.9 Hz, 1H), 4.47 (d, *J* = 9.4 Hz, 1H), 4.42-4.31 (m, 2H), 4.14 (t, *J* = 9.1 Hz, 1H), 3.96 (s, 3H), 3.79 (t, *J* = 9.0 Hz, 1H), 3.69-3.47 (m, 3H), 3.40-3.36 (m, 1H) ppm.

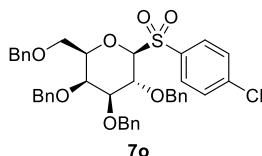
¹³C NMR (101 MHz, CDCl₃) δ 165.59, 141.10, 138.17, 137.88, 137.72, 137.49, 135.00, 129.88, 129.86, 128.75, 128.61, 128.56, 128.53, 128.49, 128.09, 128.06, 127.91, 127.81, 127.72, 127.68, 91.22, 86.24, 79.74, 77.52, 76.91, 76.03, 75.60, 75.22, 73.56, 68.60, 52.73 ppm.

IR (thin film, cm⁻¹): 3197, 2922, 2323, 2196, 2163, 2079, 2050, 2038, 1980, 1728, 1135, 1279, 1157, 1105, 734, 696, 633, 528, 501, 488, 457, 426.

$[\alpha]_D^{25} = +11.1$ ($c = 0.35$, CHCl_3).

HRMS (ESI-TOF): calculated for $\text{C}_{42}\text{H}_{42}\text{O}_9\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 745.2442, found: 745.2445.

m. p.: 43.2-45.1°C.



(2R,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-chlorophenyl)sulfonyl)tetrahydro-2H-pyran

7o was prepared according to General procedure B as a white solid using PE/EA (3:1) as the eluent (54.0 mg, 77% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.3$ Hz, 2H), 7.48 - 7.28 (m, 18H), 7.24 - 7.17 (m, 4H), 5.01 (d, $J = 9.7$ Hz, 1H), 4.94 - 4.88 (m, 2H), 4.76 - 4.70 (m, 2H), 4.55 (d, $J = 11.6$ Hz, 1H), 4.43 (d, $J = 9.3$ Hz, 1H), 4.38 - 4.26 (m, 3H), 3.88 (d, $J = 2.6$ Hz, 1H), 3.66 (dd, $J = 9.2, 2.6$ Hz, 1H), 3.54 (t, $J = 6.2$ Hz, 1H), 3.47 (d, $J = 6.1$ Hz, 2H) ppm.

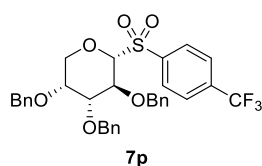
^{13}C NMR (101 MHz, CDCl_3) δ 140.65, 138.43, 137.90, 137.84, 137.67, 135.62, 131.32, 129.03, 128.79, 128.65, 128.59, 128.48, 128.39, 128.03, 128.01, 127.99, 127.90, 127.84, 127.73, 92.01, 83.82, 78.07, 75.67, 74.51, 74.31, 73.65, 73.03, 72.97, 68.62 ppm.

IR (thin film, cm^{-1}): 3221, 2923, 2323, 2285, 2185, 2166, 2050, 1979, 1572, 1365, 1258, 1089, 1053, 754, 632, 459, 449.

$[\alpha]_D^{25} = -7.6$ ($c = 0.17$, CHCl_3)

HRMS (ESI-TOF): calculated for $\text{C}_{40}\text{H}_{39}\text{ClO}_7\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 721.1997, found: 721.1996.

m. p.: 89.4-90.7°C.



(2R,3S,4R,5R)-3,4,5-tris(benzyloxy)-2-((4-(trifluoromethyl)phenyl)sulfonyl)tetrahydro-2H-pyran

7p was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (53.5 mg, 87% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.43-7.28 (m, 15H), 4.97-4.88 (m, 2H), 4.68-4.57 (m, 4H), 4.47-4.35 (m, 2H), 4.12 (dd, $J = 12.5, 3.0$ Hz, 1H), 3.73-3.62 (m, 2H), 3.28 (d, $J = 12.3$ Hz, 1H) ppm.

^{19}F NMR (376 MHz, CDCl_3) δ -63.08 ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 141.16, 137.90, 137.78, 135.38 (q, $J = 33.3$ Hz), 130.19, 128.58,

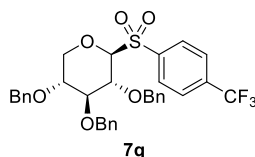
128.56, 128.54, 128.50, 128.01, 128.00, 127.93, 127.89, 127.85, 125.93 (q, $J = 4.0$ Hz), 123.30 (q, $J = 273.7$ Hz), 92.51, 80.95, 75.34, 73.79, 72.23, 71.71, 71.35, 67.07 ppm.

IR (thin film, cm^{-1}): 2954, 2921, 2851, 2322, 2162, 2049, 1979, 1735, 1496, 1455, 1403, 1376, 1321, 1259, 1130, 1086, 1061, 1016, 798, 737, 697, 558.

$[\alpha]_{\text{D}}^{25} = -6.3$ ($c = 0.16$, CHCl_3)

HRMS (ESI-TOF): calculated for $\text{C}_{33}\text{H}_{31}\text{F}_3\text{O}_6\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 635.1686, found: 635.1683.

m. p.: 160.0-160.8°C.



(2S,3R,4S,5R)-3,4,5-tris(benzyloxy)-2-((4-(trifluoromethyl)phenyl)sulfonyl)tetrahydro-2H-pyran

7q was prepared according to General procedure B as a white solid using PE/EA (5:1) as the eluent (39.0 mg, 64% yield)

^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.1$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.43-7.25 (m, 15H), 5.02 (d, $J = 9.9$ Hz, 1H), 4.96-4.84 (m, 3H), 4.68 (d, $J = 11.8$ Hz, 1H), 4.58 (d, $J = 11.8$ Hz, 1H), 4.43 (dd, $J = 9.0, 1.6$ Hz, 1H), 4.12 (t, $J = 8.9$ Hz, 1H), 4.00 (dd, $J = 11.6, 5.0$ Hz, 1H), 3.74 (t, $J = 8.7$ Hz, 1H), 3.69-3.63 (m, 1H), 3.22-3.17 (m, 1H) ppm.

^{19}F NMR (376 MHz, CDCl_3) δ -63.16 ppm.

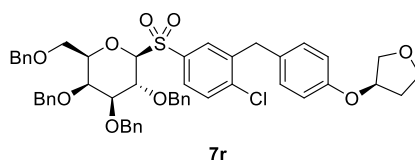
^{13}C NMR (101 MHz, CDCl_3) δ 141.00, 138.22, 137.78, 137.55, 135.65 (q, $J = 33.3$ Hz), 130.15, 128.68, 128.61, 128.54, 128.19, 128.11, 127.97, 126.11 (q, $J = 4.0$ Hz), 123.28 (q, $J = 273.7$ Hz), 91.86, 85.13, 77.26, 76.59, 75.83, 75.58, 73.40, 68.13 ppm.

IR (thin film, cm^{-1}): 2958, 2924, 2323, 2165, 2050, 2025, 1979, 1497, 1454, 1403, ,1321, 1259, 1215, 1134, 1084, 1061, 1016, 794, 753, 665, 459.

$[\alpha]_{\text{D}}^{25} = +10.6$ ($c = 0.17$, CHCl_3)

HRMS (ESI-TOF): calculated for $\text{C}_{33}\text{H}_{31}\text{F}_3\text{O}_6\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 635.1686, found: 635.1685.

m. p.: 89.7-90.6°C.



(2R,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-((4-chloro-3-(4-((S)-tetrahydrofuran-3-yl)oxy)benzyl)phenyl)sulfonyl)tetrahydro-2H-pyran

7r was prepared according to General procedure B as a yellow solid using PE/EA (2:1) as the eluent (58.0 mg, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.74-7.71 (m, 2H), 7.49-7.27 (m, 17H), 7.20 (d, *J* = 7.1 Hz, 4H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 4.97-4.84 (m, 2H), 4.83-4.64 (m, 4H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 9.3 Hz, 1H), 4.33-4.26 (m, 2H), 4.22 (t, *J* = 9.3 Hz, 1H), 4.06-3.76 (m, 7H), 3.63 (dd, *J* = 9.3, 2.5 Hz, 1H), 3.53 (t, *J* = 6.4 Hz, 1H), 3.49-3.36 (m, 2H), 2.16-2.03 (m, 2H) ppm.

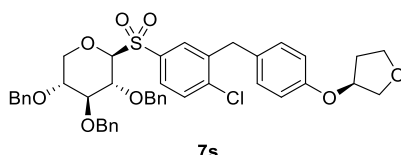
¹³C NMR (101 MHz, CDCl₃) δ 156.24, 140.44, 140.25, 138.47, 137.90, 137.80, 137.69, 135.46, 131.89, 130.39, 130.18, 129.92, 129.08, 128.75, 128.64, 128.58, 128.45, 128.40, 128.01, 127.99, 127.96, 127.84, 127.69, 127.67, 115.62, 91.85, 83.80, 77.85, 77.30, 75.59, 74.49, 74.28, 73.59, 73.19, 72.96, 72.89, 68.38, 67.26, 38.23, 33.04 ppm.

IR (thin film, cm⁻¹): 2956, 2922, 2853, 2323, 2188, 2162, 2050, 1979, 1582, 1508, 1453, 1361, 1327, 1258, 1148, 1090, 1027, 796, 752, 696, 637, 582, 440.

[α]_D²⁵ = -0.8 (c = 0.12, CHCl₃)

HRMS (ESI-TOF): calculated for C₅₁H₅₁ClO₉SNa⁺ [M+Na]⁺: 897.2835, found: 897.2838.

m. p.: 49.4-50.2°C.



(2S,3R,4S,5R)-3,4,5-tris(benzyloxy)-2-((4-chloro-3-(4-((S)-tetrahydrofuran-3-yl)oxy)benzyl)phenyl)sulfonyl)tetrahydro-2H-pyran

7s was prepared according to General procedure B as a yellow solid using PE/EA (3:1) as the eluent (44.0 mg, 58% yield)

¹H NMR (400 MHz, CDCl₃) δ 7.71-7.69 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.45-7.25 (m, 15H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 4.98-4.78 (m, 5H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.34 (d, *J* = 9.1 Hz, 1H), 4.10-3.94 (m, 7H), 3.91-3.86 (m, 1H), 3.71 (t, *J* = 8.6 Hz, 1H), 3.65-3.59 (m, 1H), 3.20-3.14 (m, 1H), 2.22-2.11 (m, 2H) ppm.

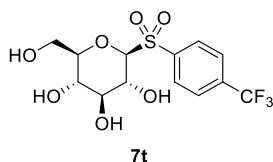
¹³C NMR (101 MHz, CDCl₃) δ 156.32, 140.75, 140.55, 138.25, 137.82, 137.58, 135.82, 131.63, 130.40, 130.30, 130.13, 128.67, 128.62, 128.59, 128.51, 128.17, 128.06, 127.94, 115.67, 91.81, 85.15, 77.40, 77.34, 76.68, 75.79, 75.50, 73.37, 73.23, 68.02, 67.30, 38.39, 33.10 ppm.

IR (thin film, cm⁻¹): 3218, 2924, 2645, 2323, 2283, 2162, 2049, 1980, 1561, 1365, 1259, 1090, 1050, 854, 625, 452, 429.

[α]_D²⁵ = +0.8 (c = 0.13, CHCl₃).

HRMS (ESI-TOF): calculated for C₄₃H₄₃ClO₈SNa⁺ [M+Na]⁺: 777.2259, found: 777.2260.

m. p.: 58.5-60.1°C.



(2R,3S,4S,5R,6S)-2-(hydroxymethyl)-6-((4-(trifluoromethyl)phenyl)sulfonyl)tetrahydro-2H-pyran-3,4,5-triol

7t was prepared according to General procedure B as a white solid using DCM/MeOH (10:1) as the eluent (28.1 mg, 76% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 5.51 (s, 1H), 5.29 (s, 1H), 5.13 (s, 1H), 4.56 (d, *J* = 9.4 Hz, 1H), 4.45 (s, 1H), 3.52 (d, *J* = 12.1 Hz, 1H), 3.43-3.37 (m, 2H), 3.27-3.16 (m, 2H), 3.04 (t, *J* = 9.3 Hz, 1H) ppm.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -61.64 ppm.

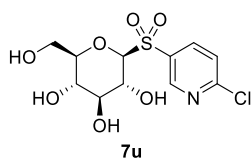
¹³C NMR (101 MHz, DMSO-*d*₆) δ 141.71, 132.32 (q, *J* = 32.2 Hz) 130.33, 125.92 (q, *J* = 4.0 Hz) 123.52 (q, *J* = 273.7 Hz), 91.30, 81.36, 77.38, 69.89, 69.00, 60.46 ppm.

IR (thin film, cm⁻¹): 3319, 2944, 2832, 2161, 2049, 1978, 1654, 1448, 1412, 1259, 1110, ,1020, 602.

[α]_D²⁹ = -64.2 (c = 0.68, MeOH).

HRMS (ESI-TOF): calculated for C₁₃H₁₅F₃O₇SNa⁺ [M+Na]⁺: 395.0383, found: 395.0381.

m. p.: 39.0-40.1°C



(2S,3R,4S,5S,6R)-2-((6-chloropyridin-3-yl)sulfonyl)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol

7u was prepared according to General procedure B as a yellow solid using DCM/MeOH (10:1) as the eluent (13.0 mg, 38% yield).

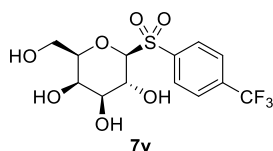
¹H NMR (400 MHz, MeOD) δ 8.89 (s, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 4.54 (d, *J* = 9.5 Hz, 1H), 3.75 (d, *J* = 12.1 Hz, 1H), 3.68-3.59 (m, 2H), 3.43 (t, *J* = 9.0 Hz, 1H), 3.37 - 3.24 (m, 2H) ppm.

¹³C NMR (101 MHz, MeOD) δ 157.83, 151.91, 141.99, 134.42, 125.91, 93.06, 82.78, 78.88, 71.25, 70.50, 62.22 ppm.

IR (thin film, cm⁻¹): 3338, 2950, 2839, 2161, 2050, 1644, 1407, 1111, 1013, 490.

[α]_D²⁹ = -73.8 (c = 0.39, MeOH).

HRMS (ESI-TOF): calculated for C₁₁H₁₄ClNO₇SNa⁺ [M+Na]⁺: 362.0072, found: 362.0070.



(2R,3R,4S,5R,6S)-2-(hydroxymethyl)-6-((4-(trifluoromethyl)phenyl)sulfonyl)tetrahydro-2H-pyran-3,4,5-triol

7v was prepared according to General procedure B as a yellow solid using DCM/MeOH (10:1) as the eluent (23.3 mg, 63% yield).

¹H NMR (400 MHz, MeOD) δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 4.59 (s, 1H), 4.45 (d, *J* = 9.5 Hz, 1H), 3.92 (t, *J* = 9.3 Hz, 1H), 3.85 (d, *J* = 3.2 Hz, 1H), 3.66-3.60 (m, 2H), 3.59-3.50 (m, 2H) ppm.

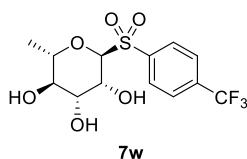
¹⁹F NMR (376 MHz, MeOD) δ -64.66 ppm.

¹³C NMR (101 MHz, MeOD) δ 142.34, 136.35 (q, *J* = 33.3 Hz), 131.74, 127.01 (q, *J* = 4.0 Hz), 124.88 (q, *J* = 273.7 Hz), 93.76, 81.45, 75.63, 69.88, 68.12, 62.22 ppm.

IR (thin film, cm⁻¹): 3363, 2479, 2219, 2071, 1324, 1119, 1062, 972, 818, 425.

[α]_D²⁹ = -137.7 (c = 0.39, MeOH)

HRMS (ESI-TOF): calculated for C₁₃H₁₅F₃O₆SNa⁺ [M+Na]⁺: 395.0383, found: 395.0380.



(2S,3R,4R,5R,6S)-2-methyl-6-((4-(trifluoromethyl)phenyl)sulfonyl)tetrahydro-2H-pyran-3,4,5-triol

7w was prepared according to General procedure B as a yellow solid using DCM/MeOH (10:1) as the eluent (16.0 mg, 45% yield).

¹H NMR (400 MHz, MeOD) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 4.92-4.88 (m, 1H), 4.65-4.61 (m, 1H), 4.29-4.22 (m, 1H), 4.02 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.47 (t, *J* = 9.3 Hz, 1H), 1.18 (d, *J* = 6.1 Hz, 3H) ppm.

¹⁹F NMR (376 MHz, MeOD) δ -64.69 ppm.

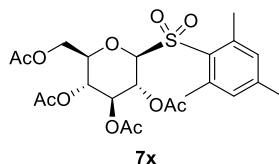
¹³C NMR (101 MHz, MeOD) δ 142.60, 136.57 (q, *J* = 33.3 Hz), 130.94, 127.51 (q, *J* = 4.0 Hz), 124.82 (q, *J* = 273.7 Hz), 95.64, 75.22, 72.73, 67.43, 18.46 ppm.

IR (thin film, cm⁻¹): 3331, 2945, 2834, 2050, 1979, 1654, 1448, 1406, 1111, 1018, 545.

[α]_D²⁹ = -121.5, (c = 0.12, MeOH)

HRMS (ESI-TOF): calculated for C₁₃H₁₅F₃O₆SNa⁺ [M+Na]⁺: 379.0434, found: 379.0434.

m. p.: 174.2-174.7°C



(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(mesitylsulfonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

7x was prepared according to General procedure B as a yellow solid using PE/EA (3:1) as the eluent (16.0 mg, 31% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.94 (s, 2H), 5.59 (t, *J* = 9.5 Hz, 1H), 5.32 (t, *J* = 9.4 Hz, 1H), 5.09 (t, *J* = 9.8 Hz, 1H), 4.56 (d, *J* = 9.7 Hz, 1H), 4.09 (dd, *J* = 12.5, 5.6 Hz, 1H), 3.92 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.64 – 3.60 (m, 1H), 2.62 (s, 6H), 2.29 (s, 3H), 2.11 – 1.87 (m, 12H) ppm.

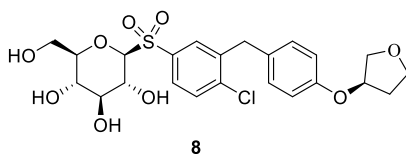
¹³C NMR (101 MHz, CDCl₃) δ 170.39, 170.36, 169.27, 169.22, 144.19, 142.01, 132.23, 130.91, 88.48, 76.11, 73.52, 67.77, 67.08, 61.69, 23.14, 21.15, 20.81, 20.68, 20.60, 20.48 ppm.

IR (thin film, cm⁻¹): 3564, 3130, 1744, 1602, 1366, 1317, 1220, 1150, 1062, 909, 594, 511.

[α]_D²⁵ = -12.7 (c = 0.15, CHCl₃).

HRMS (ESI-TOF): calculated for C₂₃H₃₀O₁₁SNa⁺ [M+Na]⁺: 537.1397, found: 537.1401.

m. p.: 253.0 – 255.5°C



(2S,3R,4S,5S,6R)-2-((4-chloro-3-(4-((R)-tetrahydrofuran-3-yl)oxy)benzyl)phenyl)sulfonyl)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol

8 was prepared according to General procedure B as a yellow solid using DCM/MeOH (10:1) as the eluent (29.9 mg, 58% yield).

¹H NMR (400 MHz, MeOD) δ 7.88 – 7.78 (m, 2H), 7.63 (dd, *J* = 8.4, 4.6 Hz, 1H), 7.13 (dd, *J* = 8.8, 3.1 Hz, 2H), 6.84 (dd, *J* = 8.6, 4.2 Hz, 2H), 5.01 – 4.94 (m, 1H), 4.40 (dt, *J* = 9.4, 2.2 Hz, 1H), 4.17 – 7.07 (m, 2H), 3.98- 3.80 (m, 4H), 3.73 – 3.63 (m, 1H), 3.62 – 3.45 (m, 2H), 3.43 – 3.36 (m, 1H), 3.27 (d, *J* = 5.4 Hz, 1H), 3.25 – 3.16 (m, 1H), 2.29 – 2.14 (m, 1H), 2.13 – 2.03 (m, 1H) ppm.

¹³C NMR (101 MHz, MeOD) δ 157.59, 141.89, 141.73, 136.93, 133.24, 132.13, 131.31, 131.12, 130.11, 116.70, 93.07, 82.74, 78.98, 78.59, 74.02, 71.39, 70.48, 68.13, 62.40, 39.07, 33.86 ppm.

IR (thin film, cm⁻¹): 3372, 2923, 2853, 1508, 1464, 1308, 1241, 1150, 1090, 1043, 897, 757, 647.

[α]_D²⁵ = -7.3 (c = 0.15, CHCl₃).

HRMS (ESI-TOF): calculated for C₂₃H₂₇ClO₉SNa⁺ [M+Na]⁺: 537.0957, found: 537.0951.

m. p.: 107.0 – 108.5°C

NMR Spectra

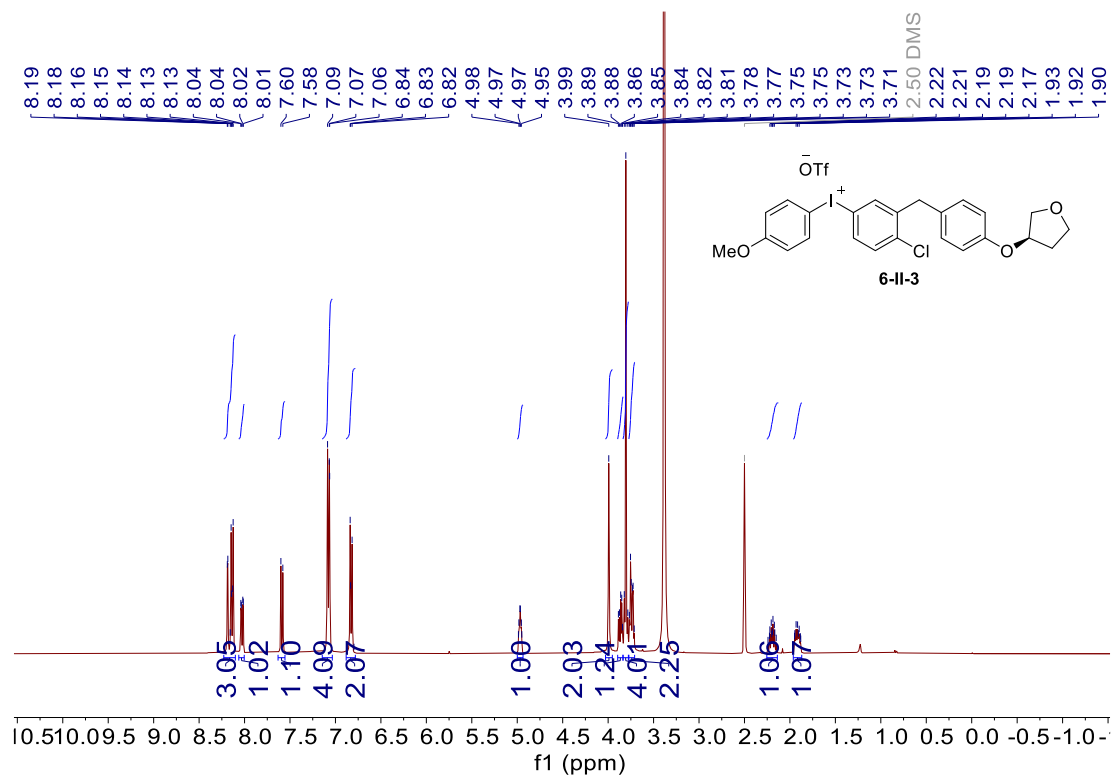


Figure S6. ¹H NMR (400 MHz, DMSO-*d*₆) Spectra for compound 6-II-3

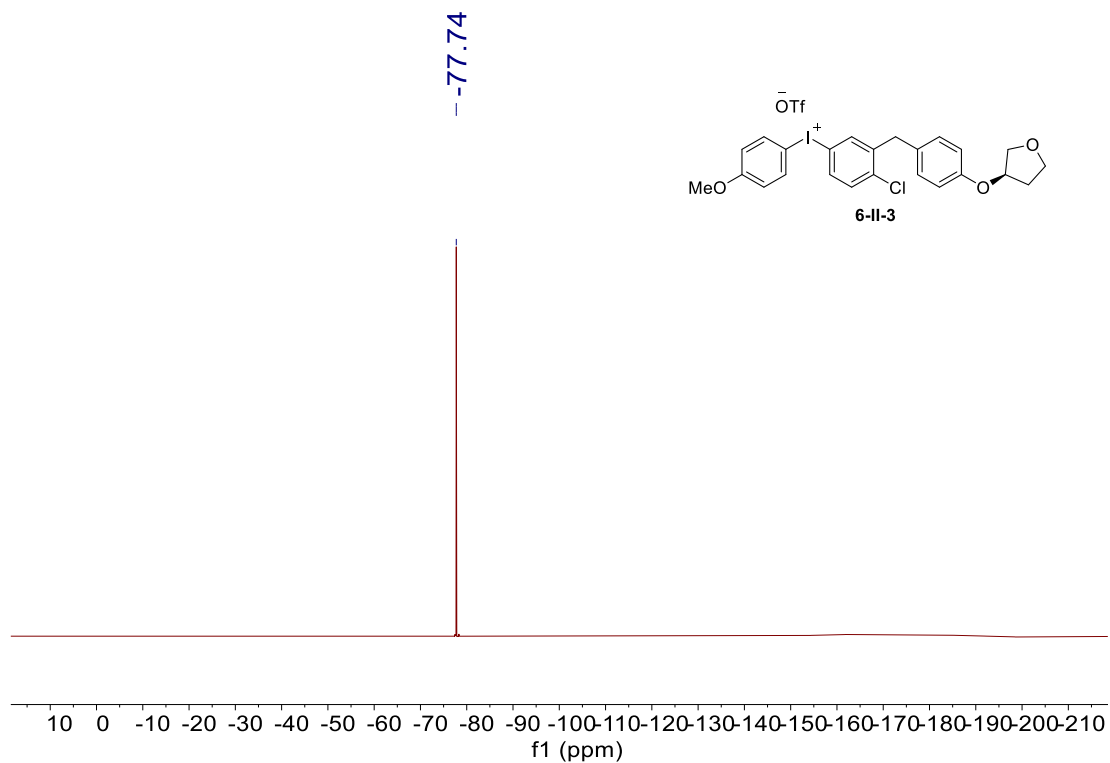


Figure S7. ¹⁹F NMR (376 MHz, DMSO-*d*₆) Spectra for compound 6-II-3

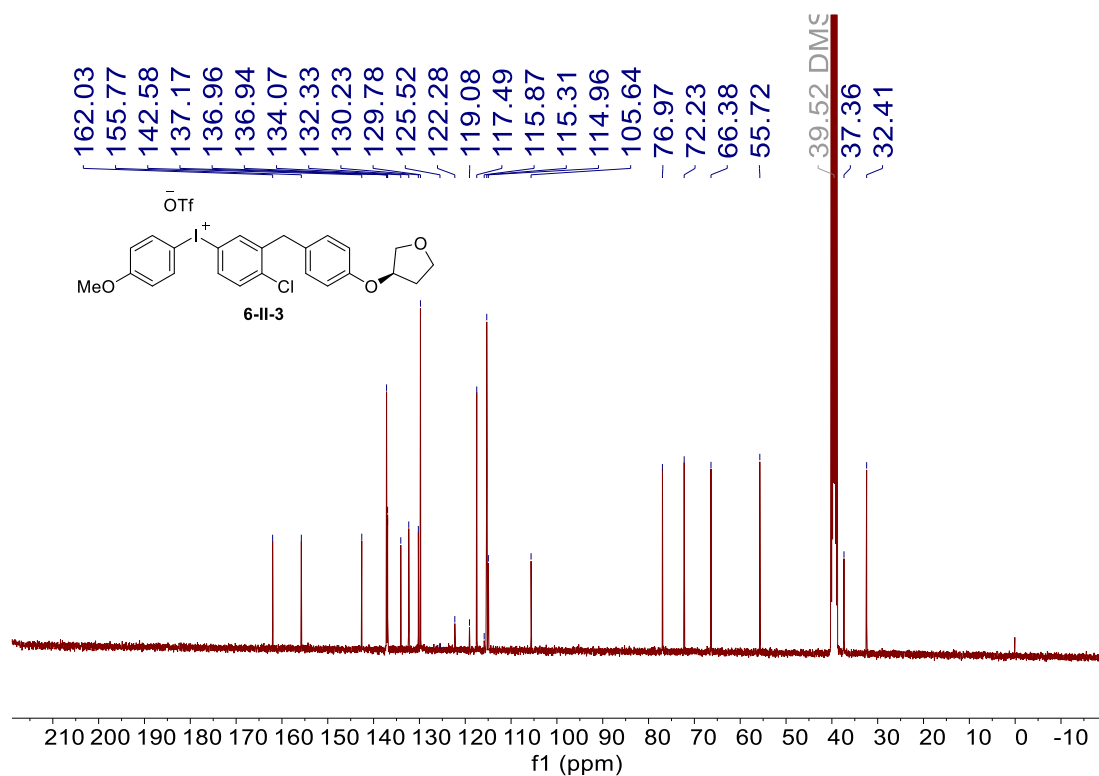


Figure S8. ¹³C NMR (101 MHz, DMSO-*d*₆) Spectra for compound 6-II-3

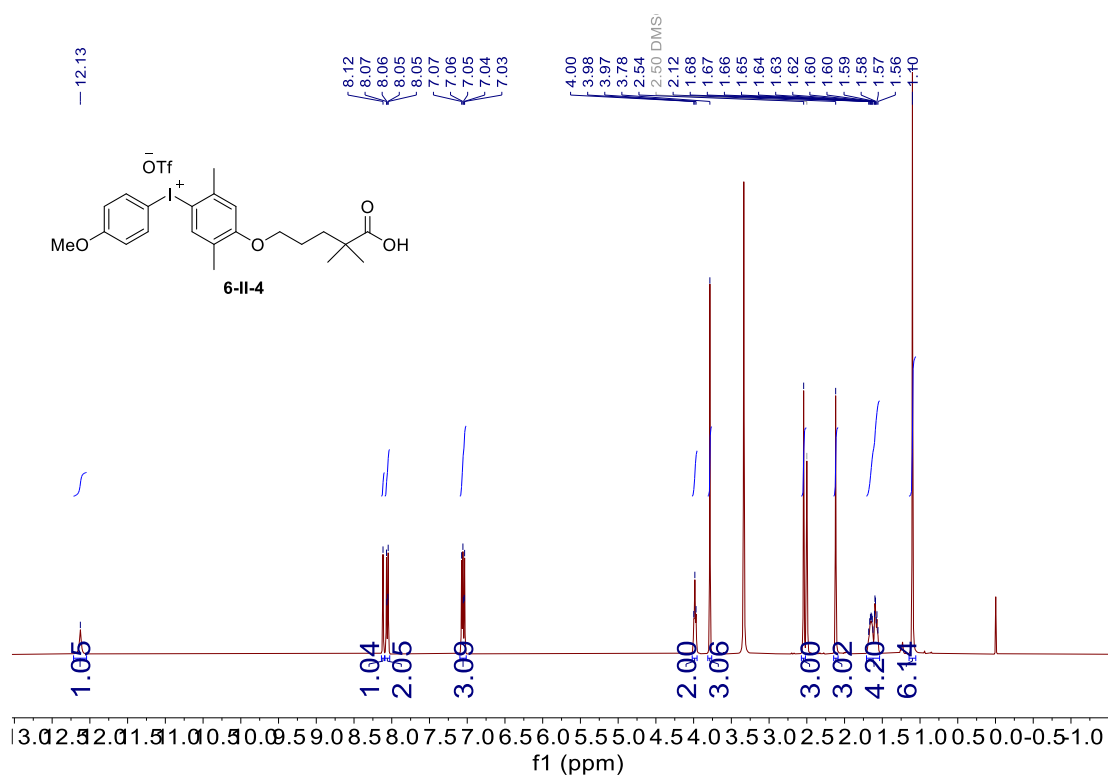


Figure S9. ¹H NMR (400 MHz, DMSO-*d*₆) Spectra for compound 6-II-4

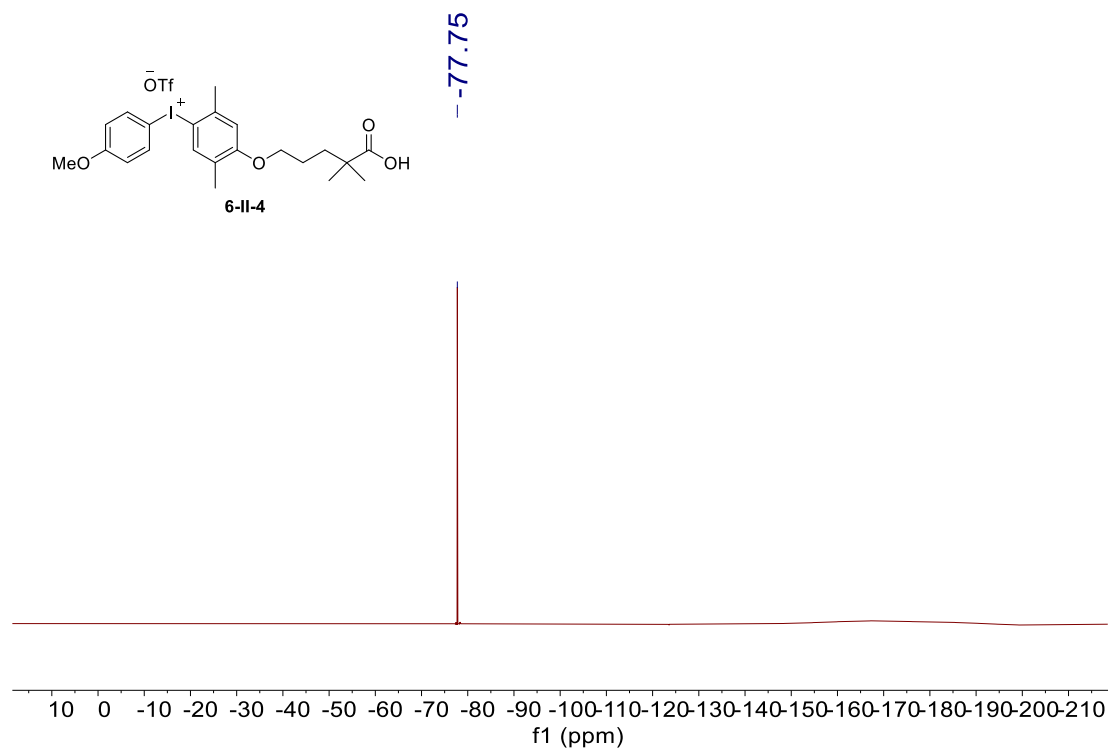


Figure S10. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) Spectra for compound 6-II-4

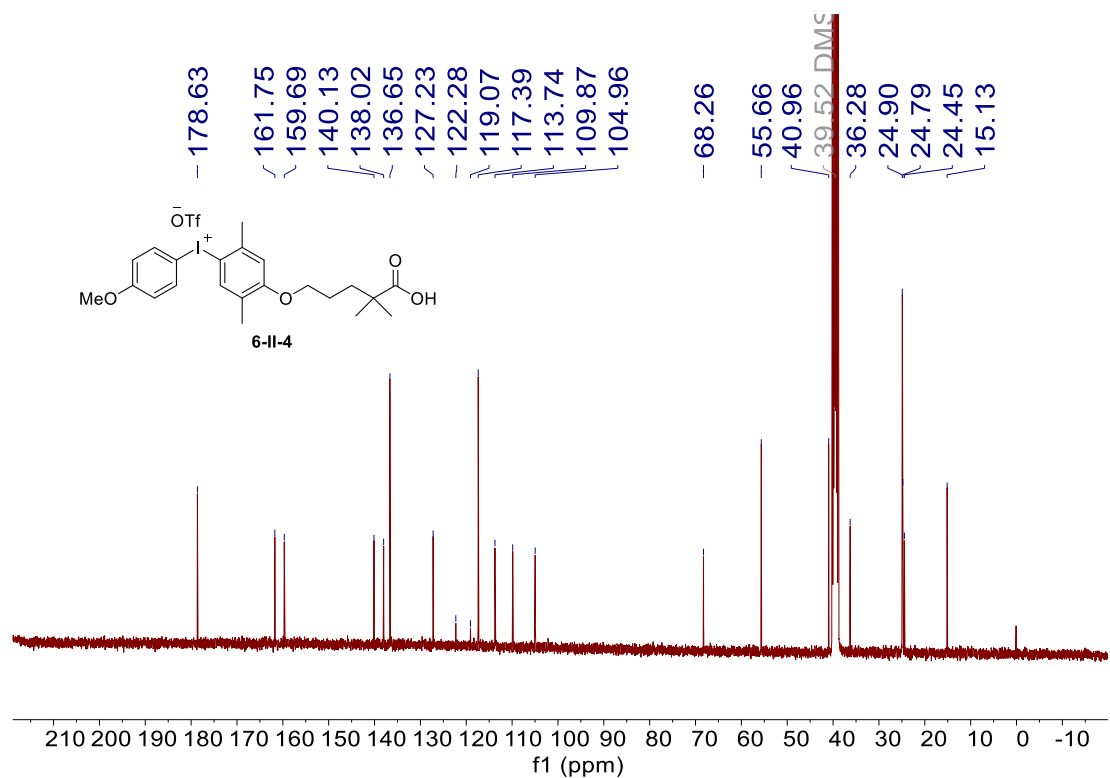
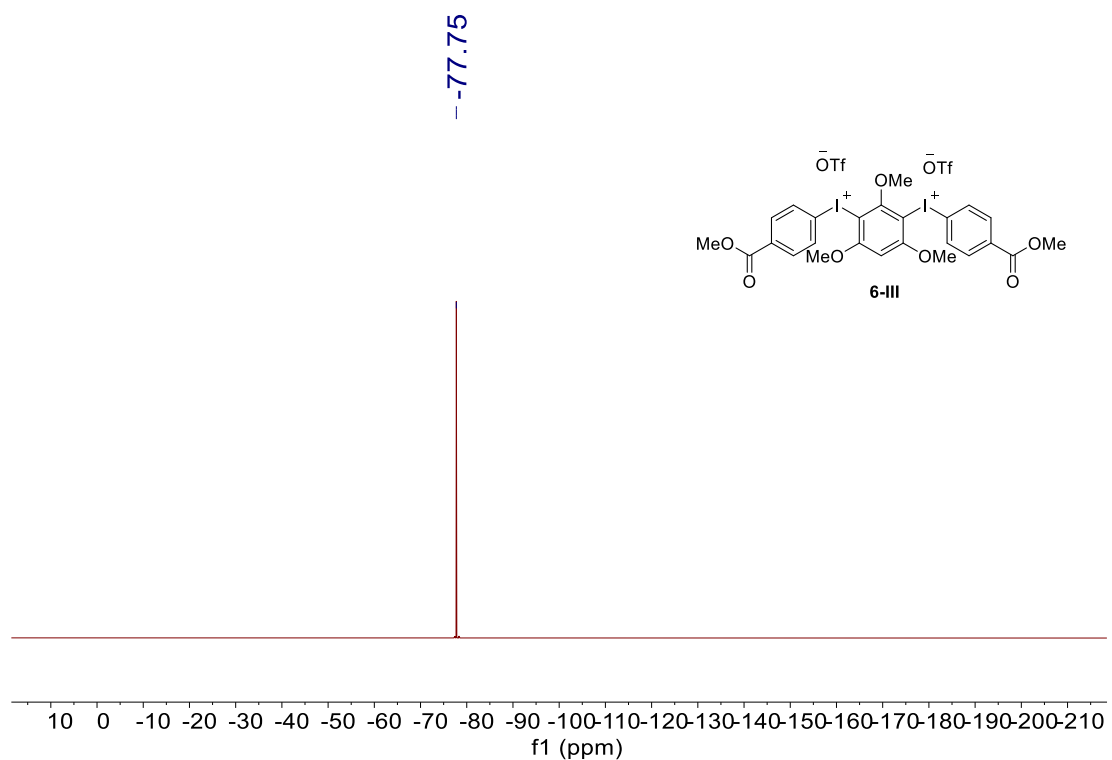
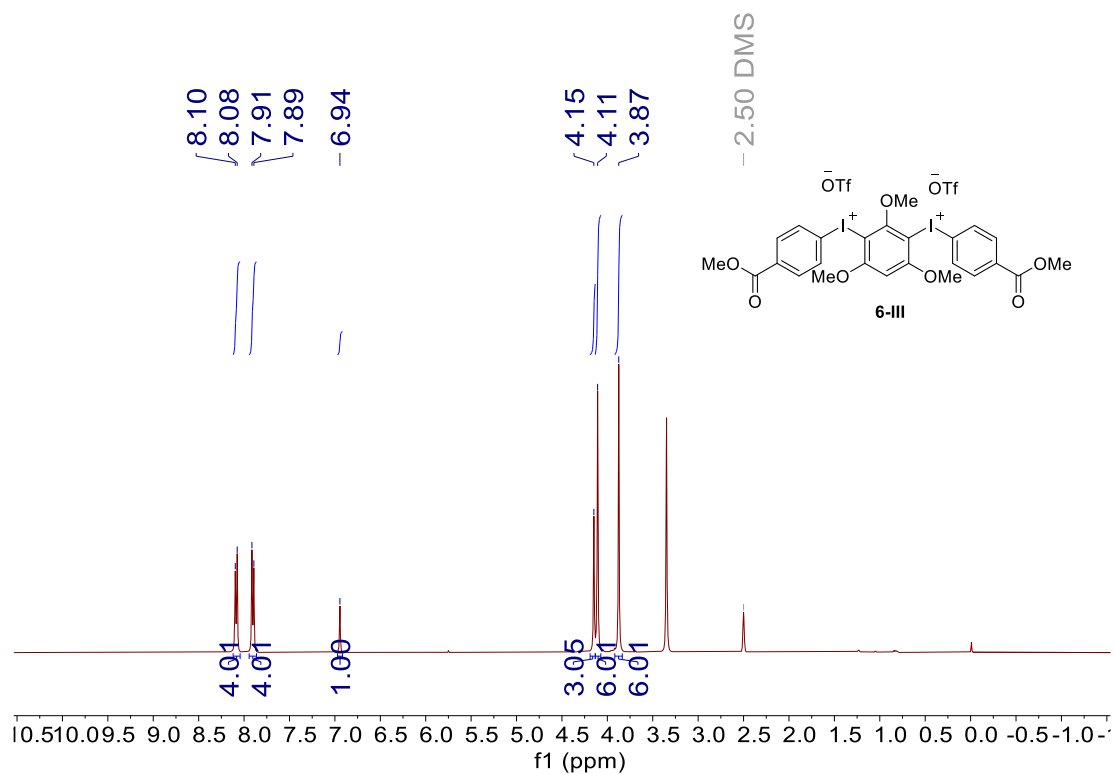


Figure S11. ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) Spectra for compound 6-II-4



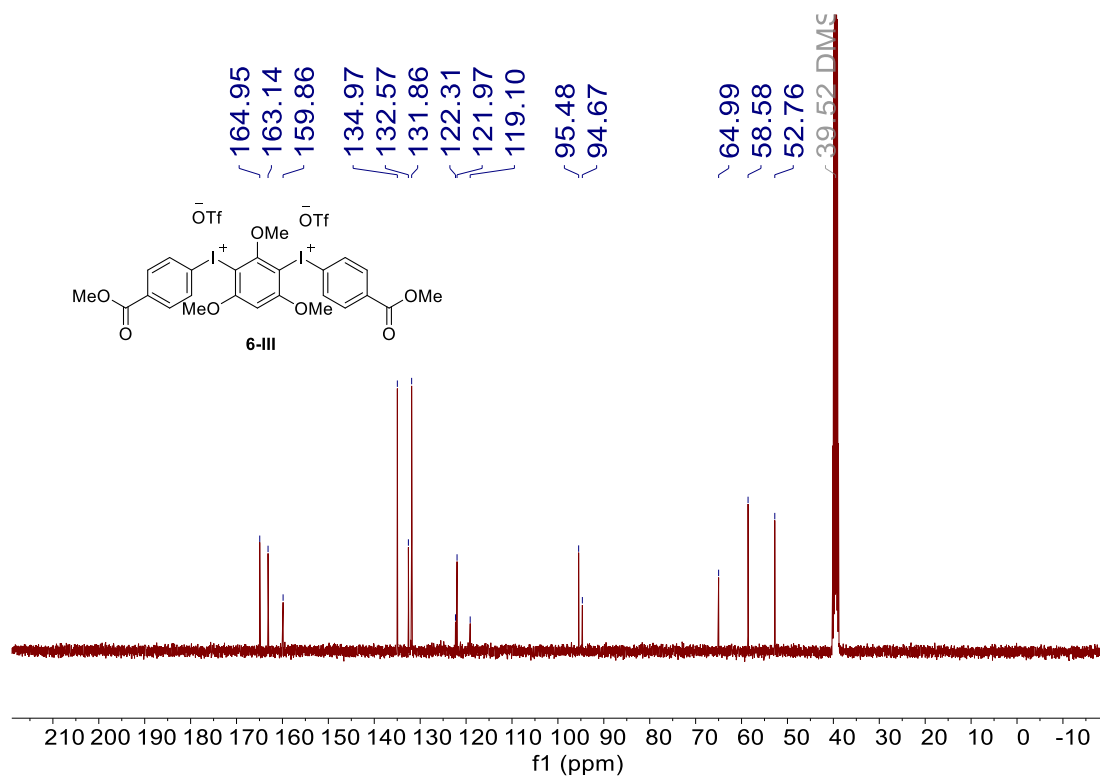


Figure S14. ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) Spectra for compound 6-III

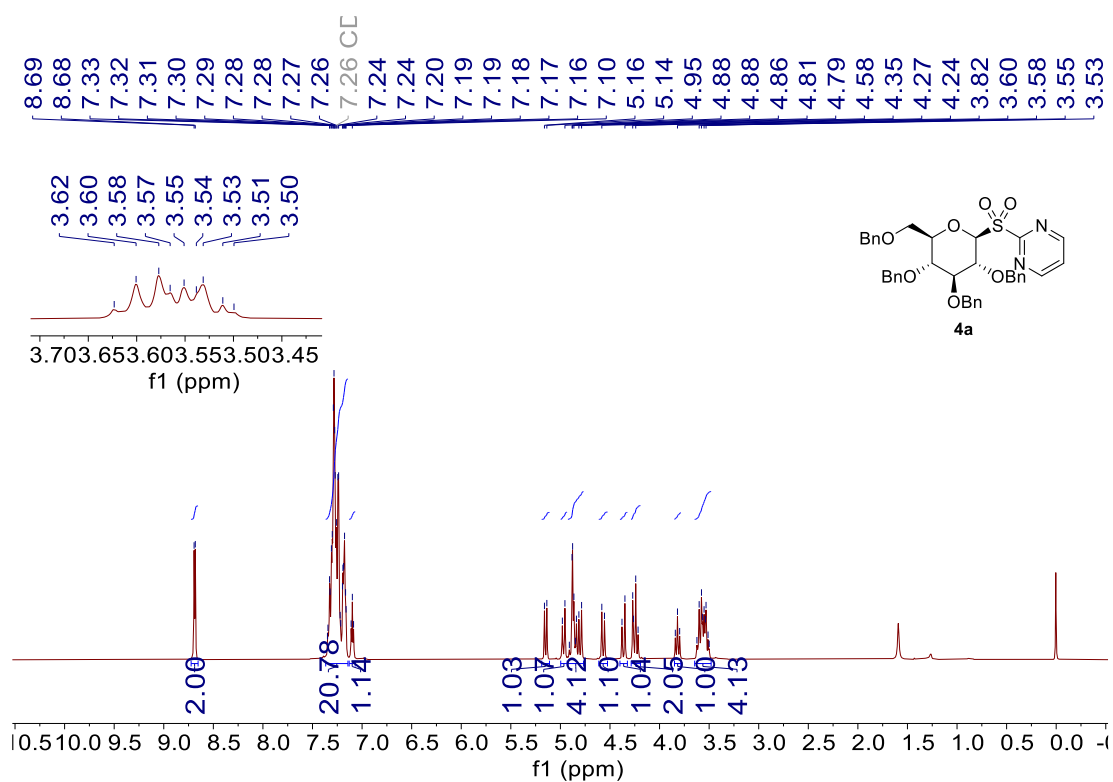


Figure S15. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 4a

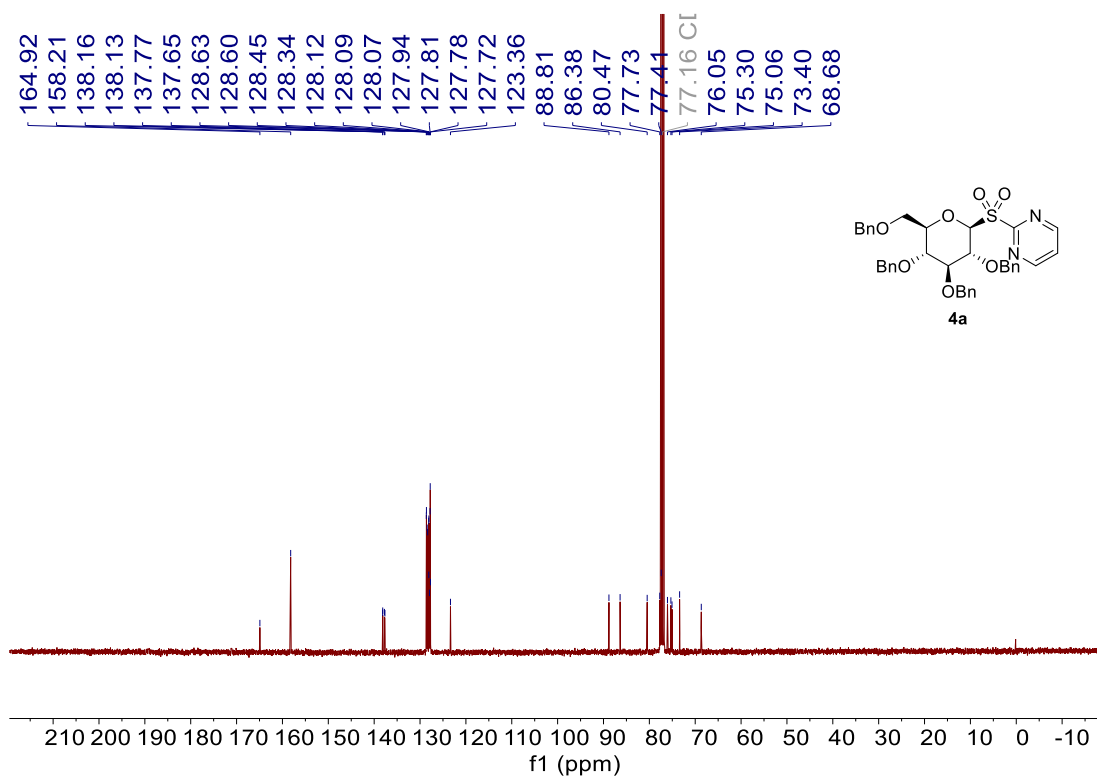


Figure S16. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 4a

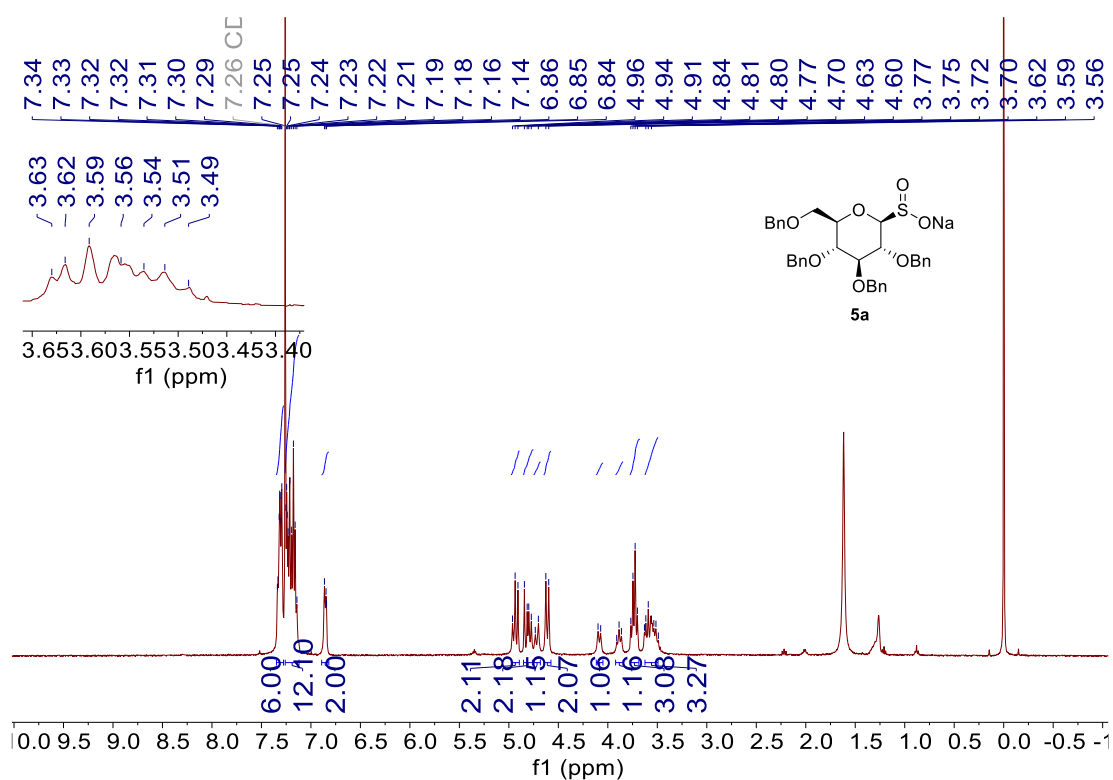


Figure S17. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 5a

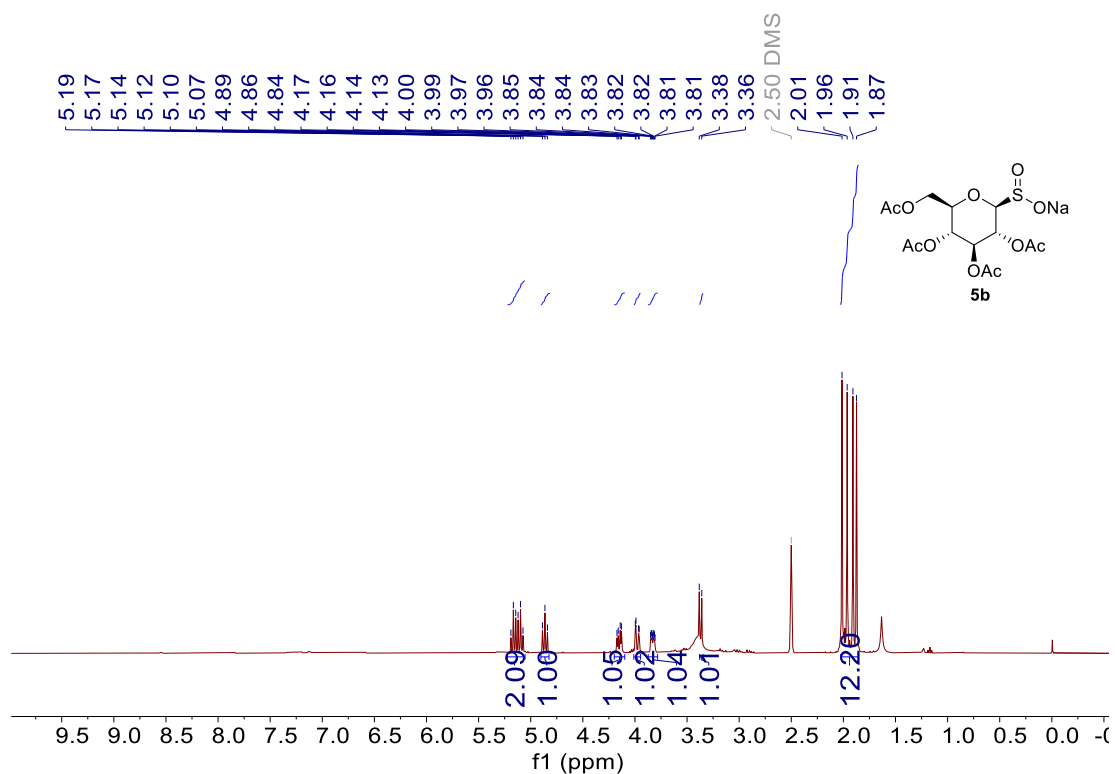


Figure S18. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) Spectra for compound 5b

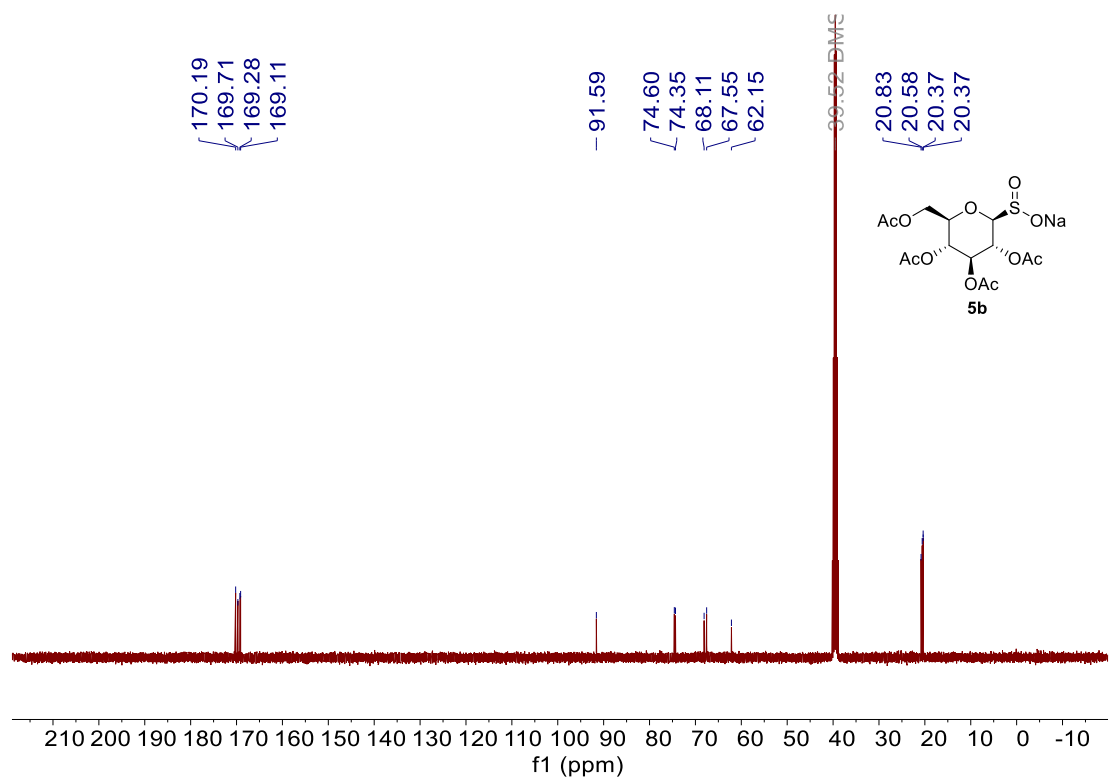


Figure S19. ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) Spectra for compound 5b

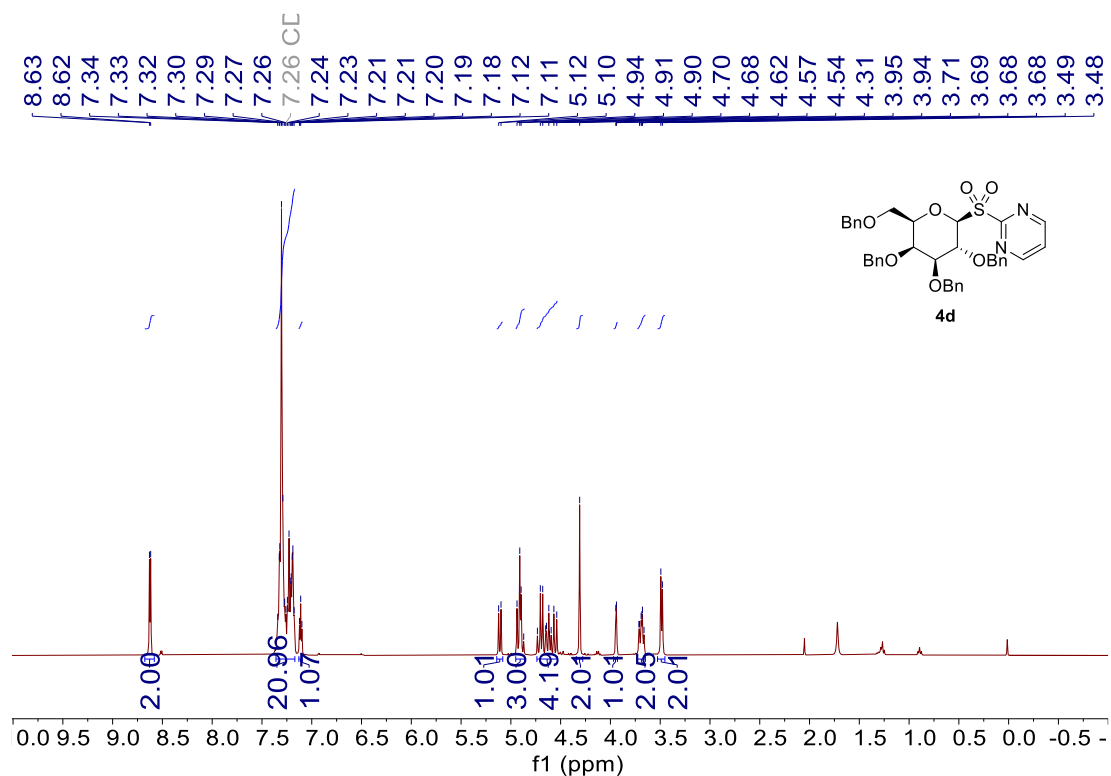


Figure S20. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 4d

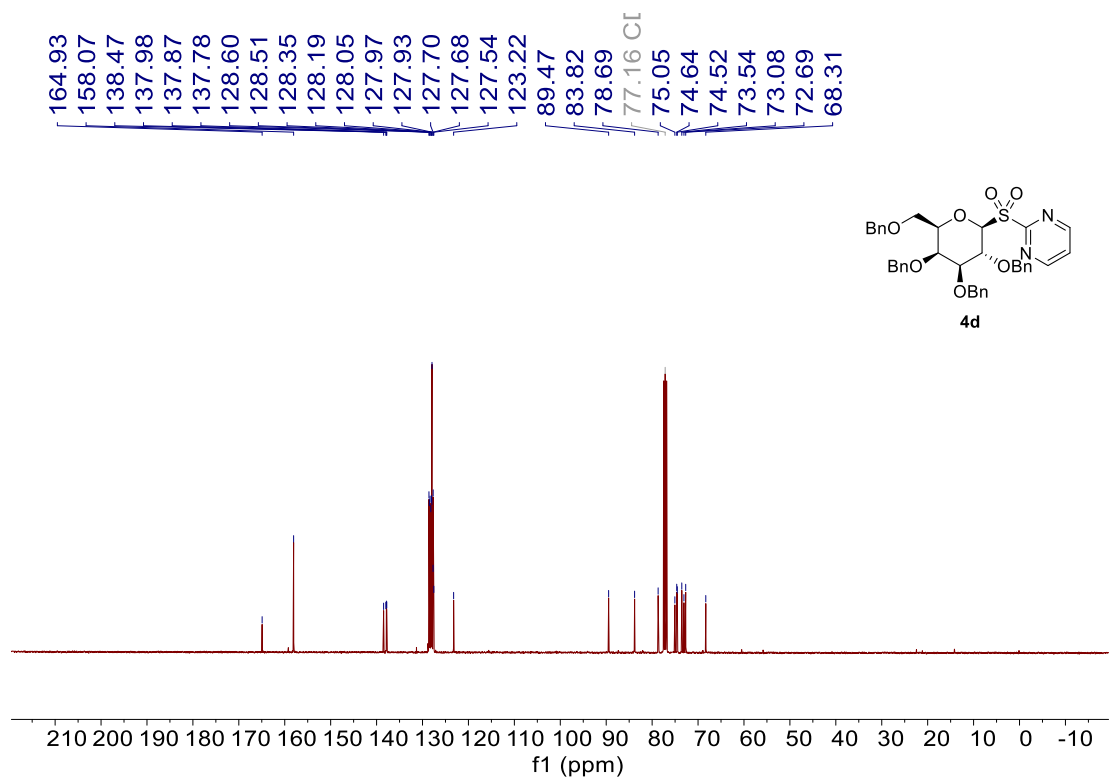


Figure S21. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 4d

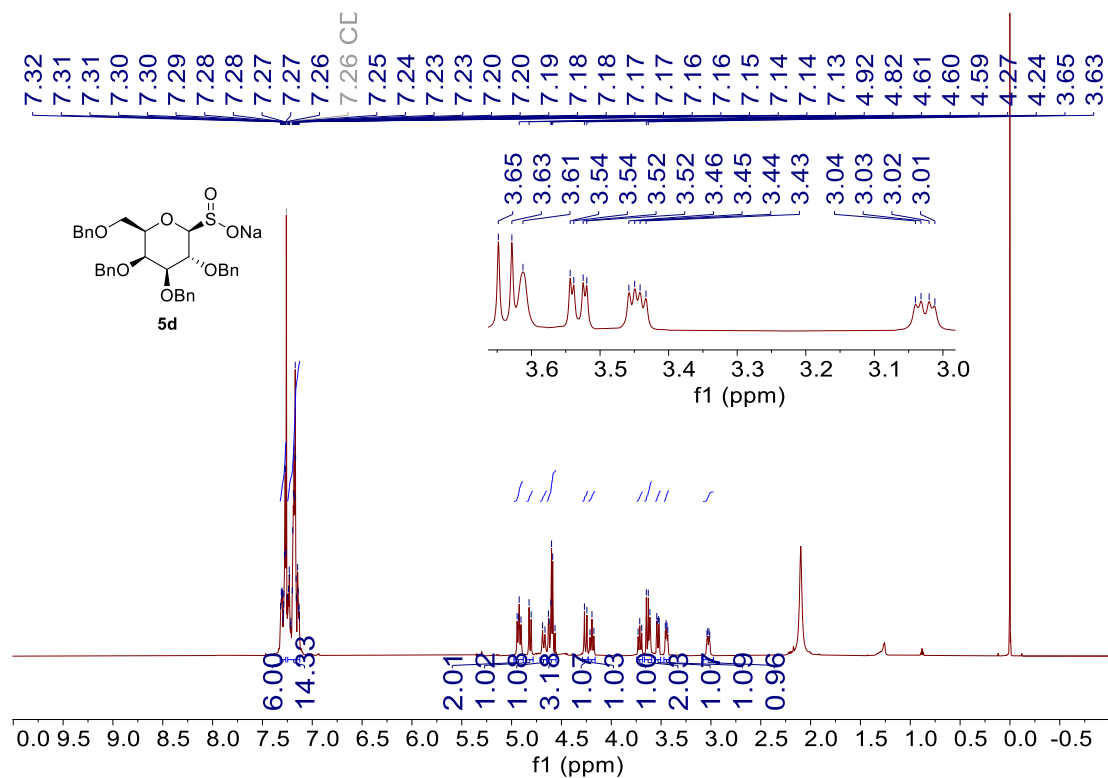


Figure S22. ¹H NMR (500 MHz, CDCl₃) Spectra for compound 5d

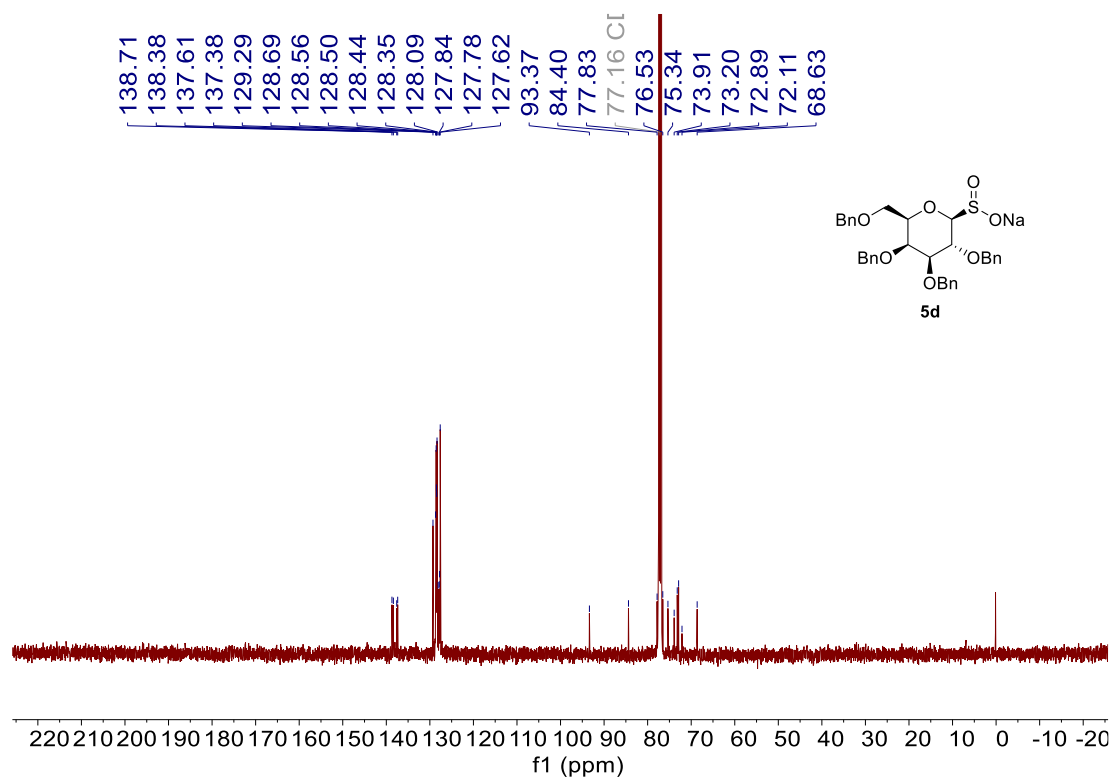


Figure S23. ¹³C NMR (126 MHz, CDCl₃) Spectra for compound 5d

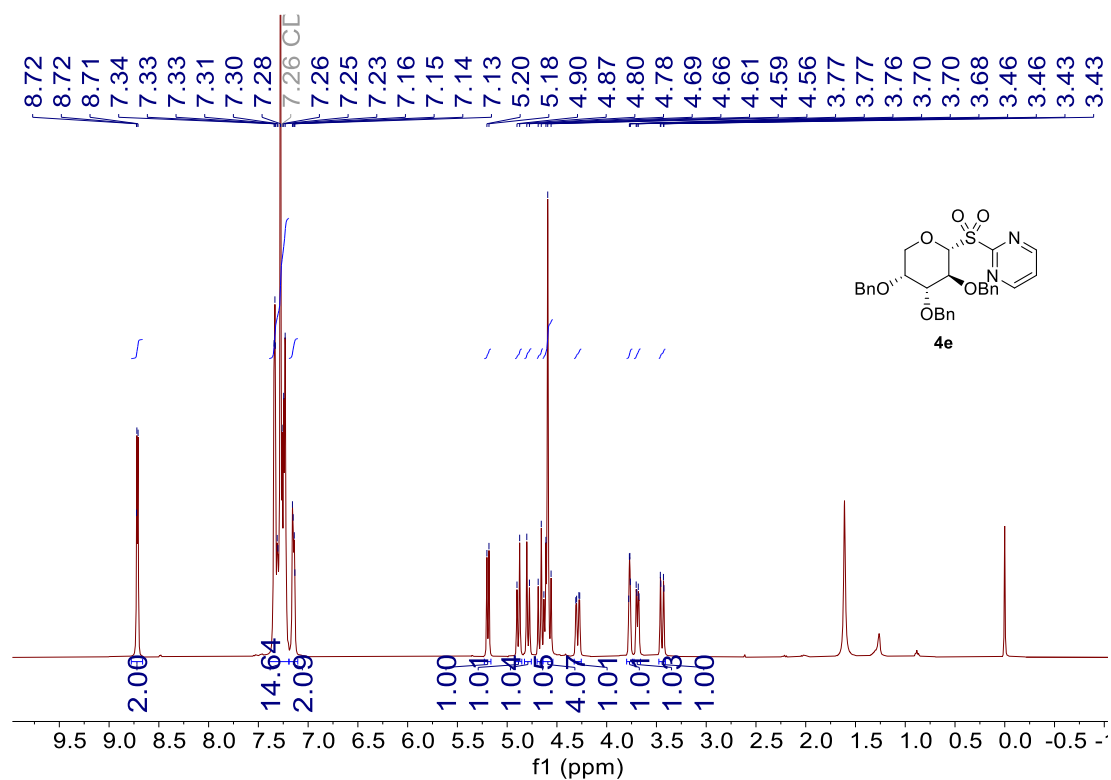


Figure S24. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 4e

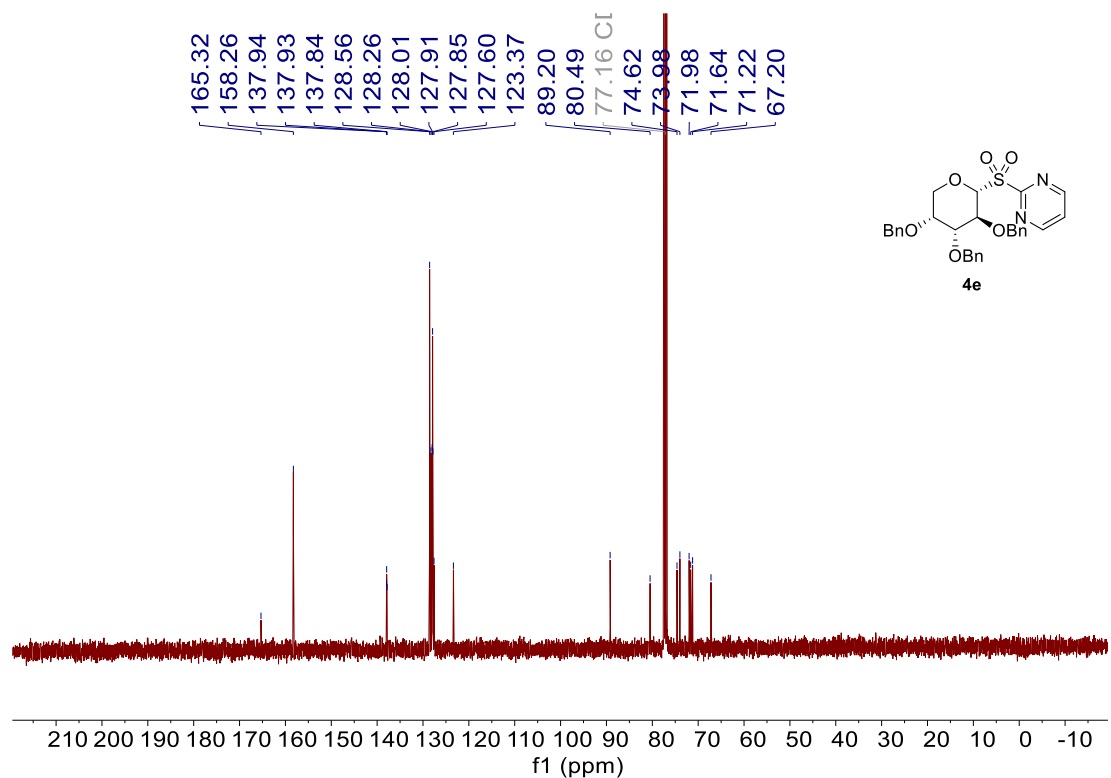


Figure S25. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 4e

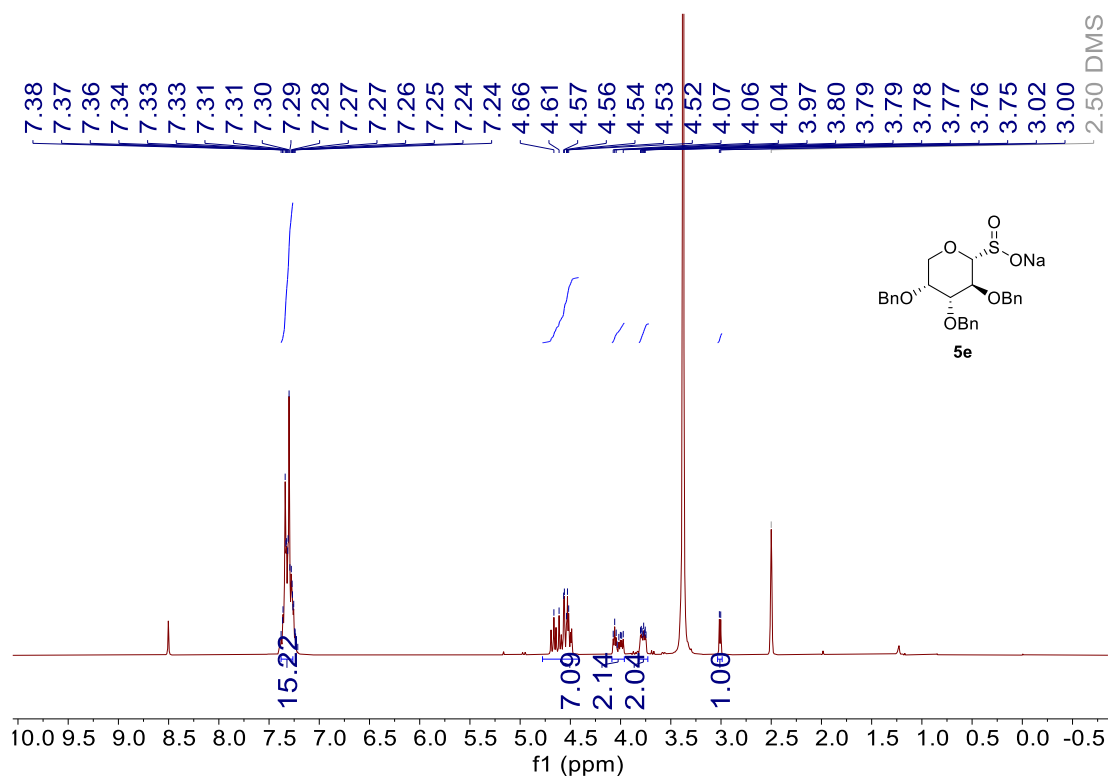


Figure S26. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) Spectra for compound 5e

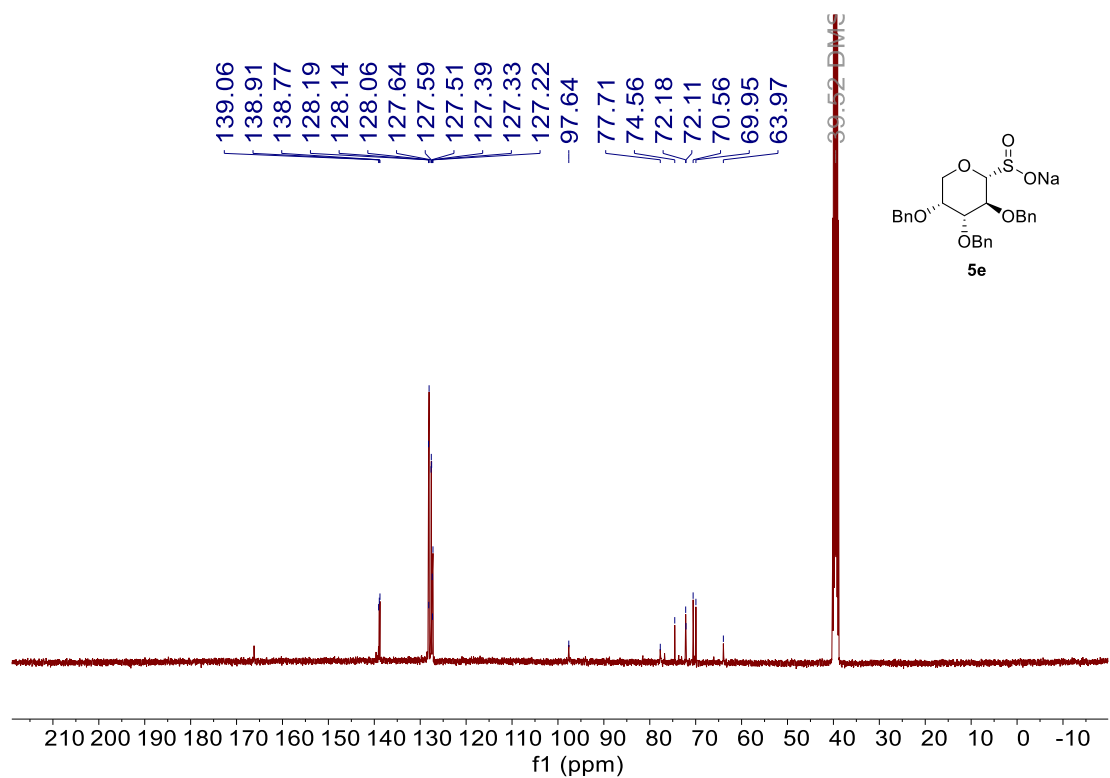


Figure S27. ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) Spectra for compound 5e

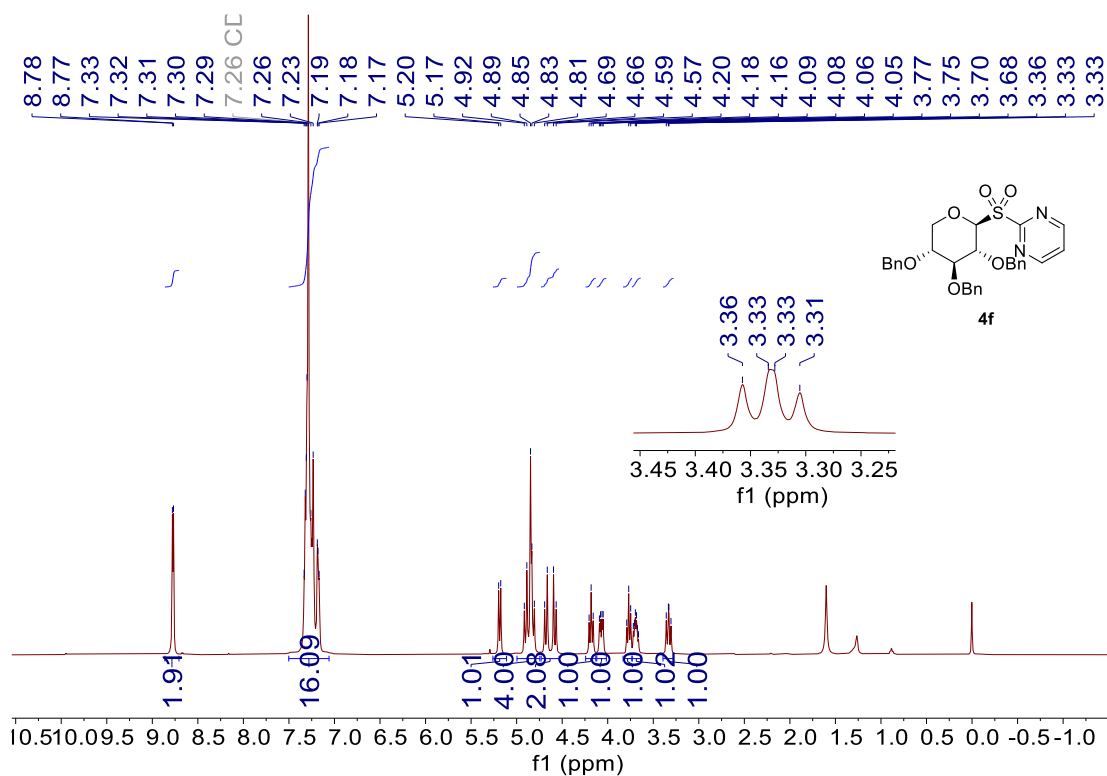


Figure S28. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 4f

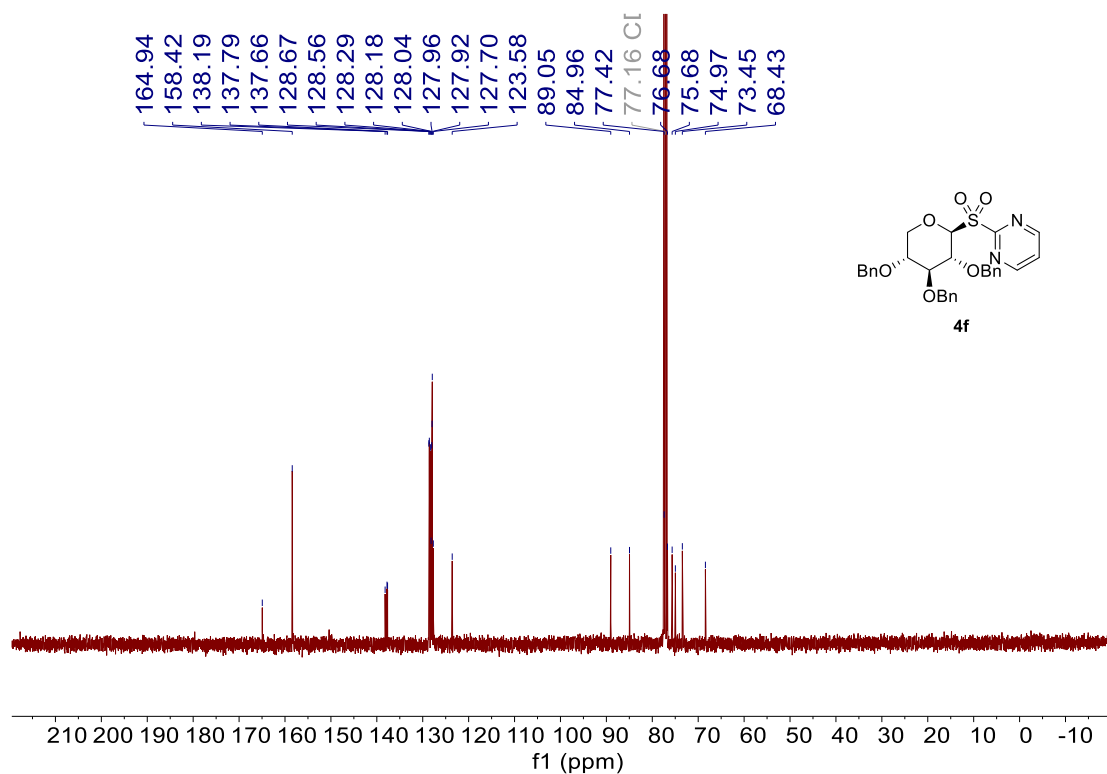


Figure S29. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 4f

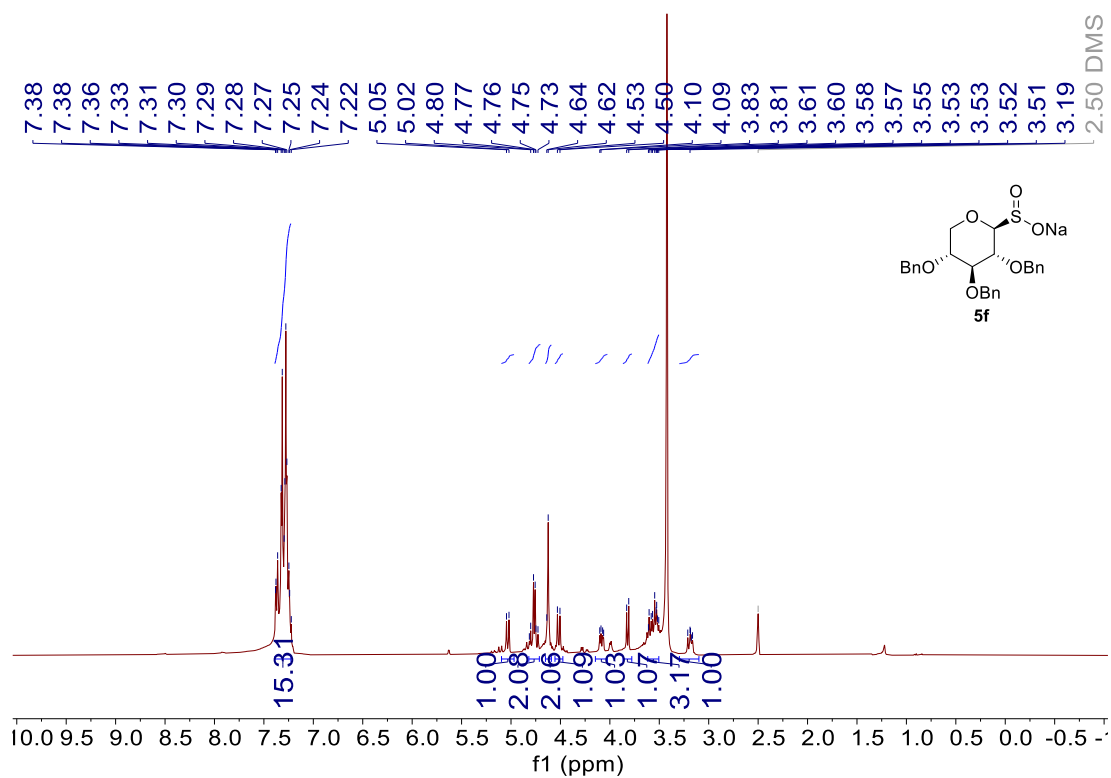


Figure S30. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 5f

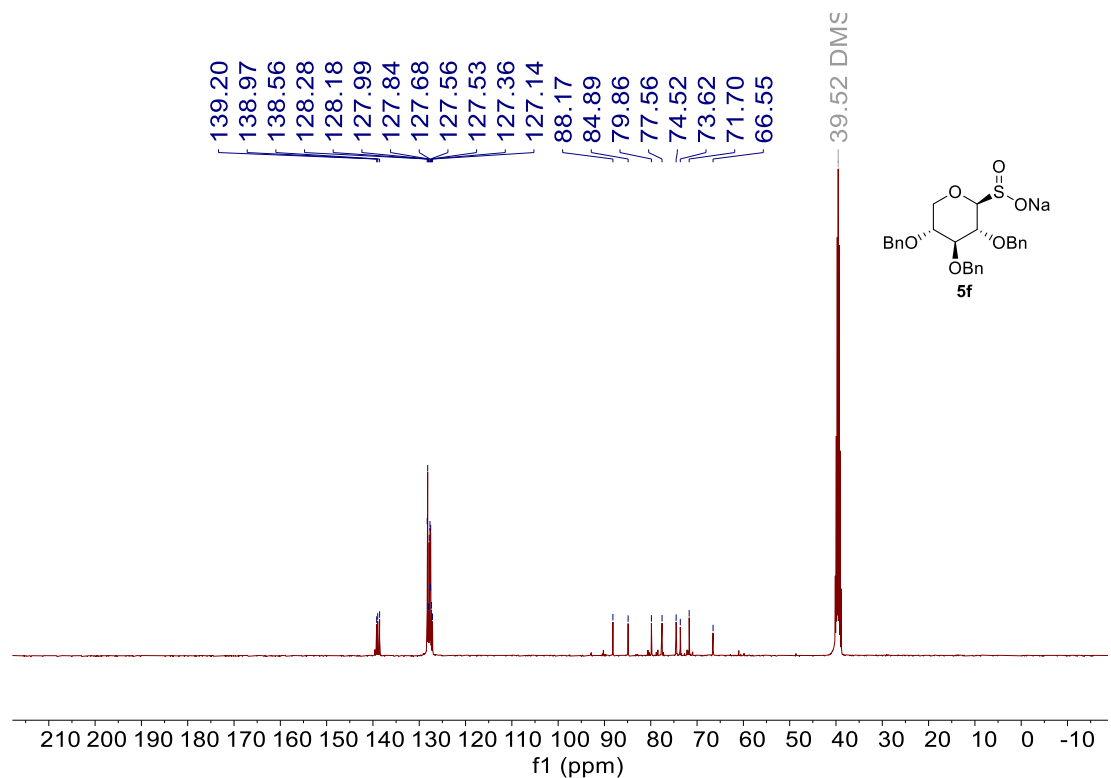


Figure S31. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 5f

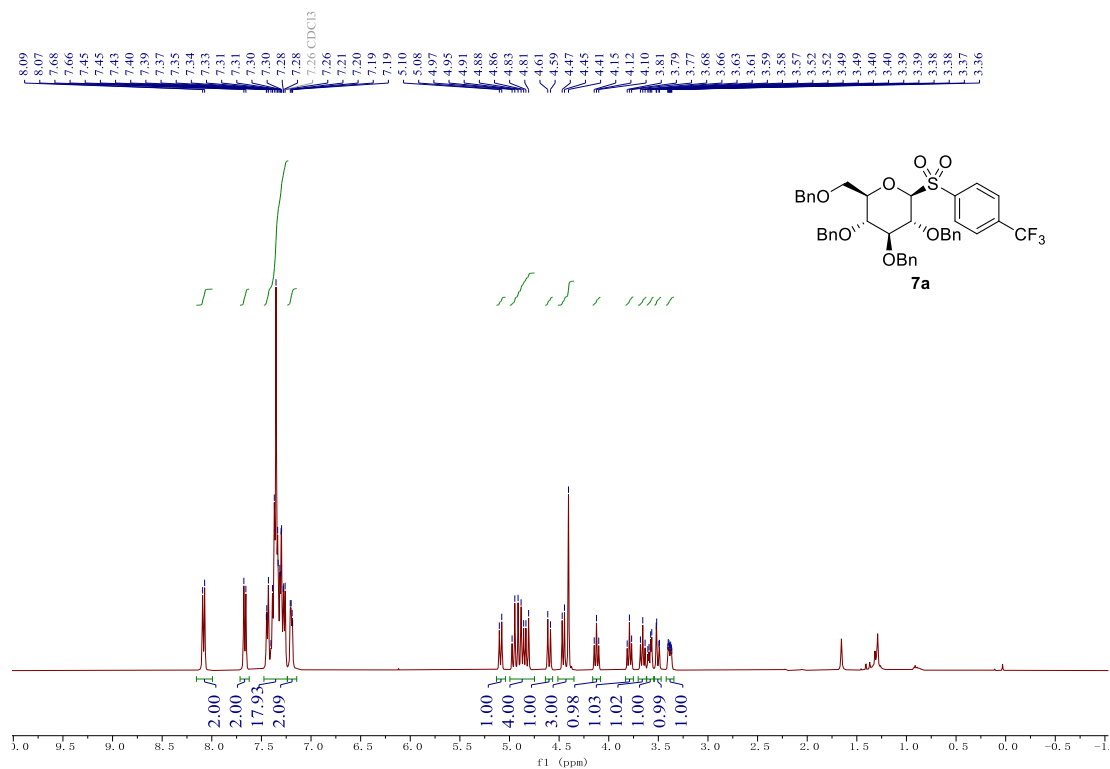


Figure S32. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7a

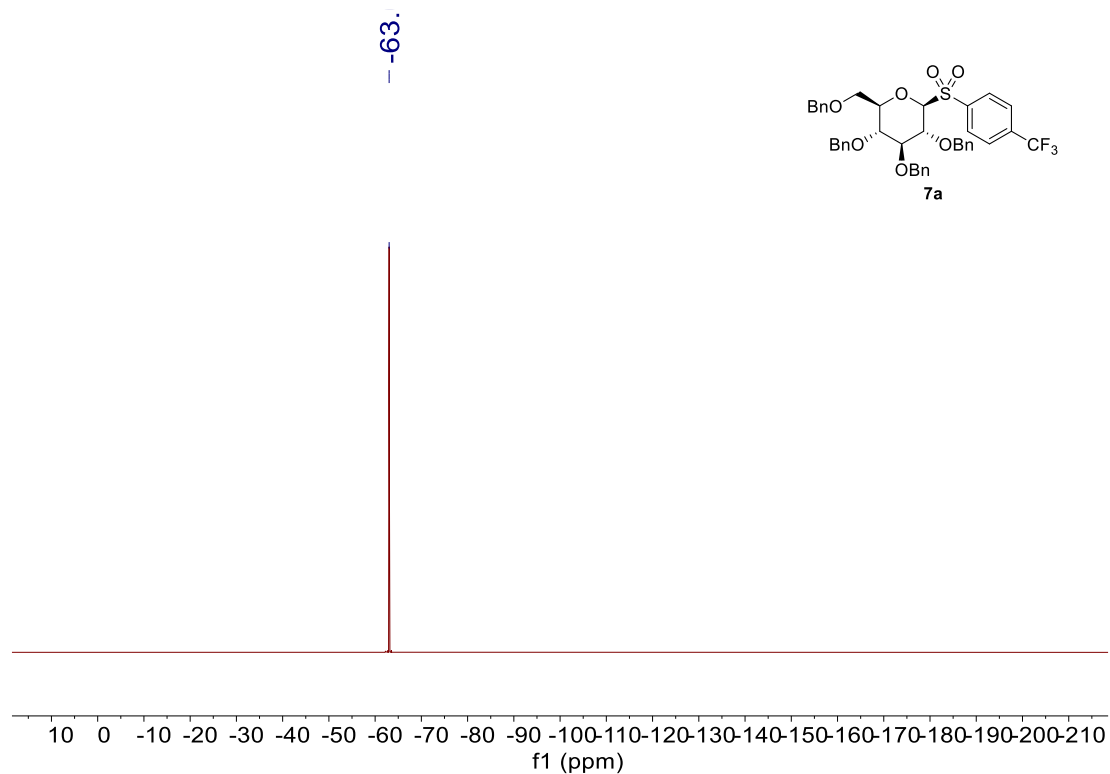


Figure S33. ¹⁹F NMR (376 MHz, CDCl₃) Spectra for compound 7a

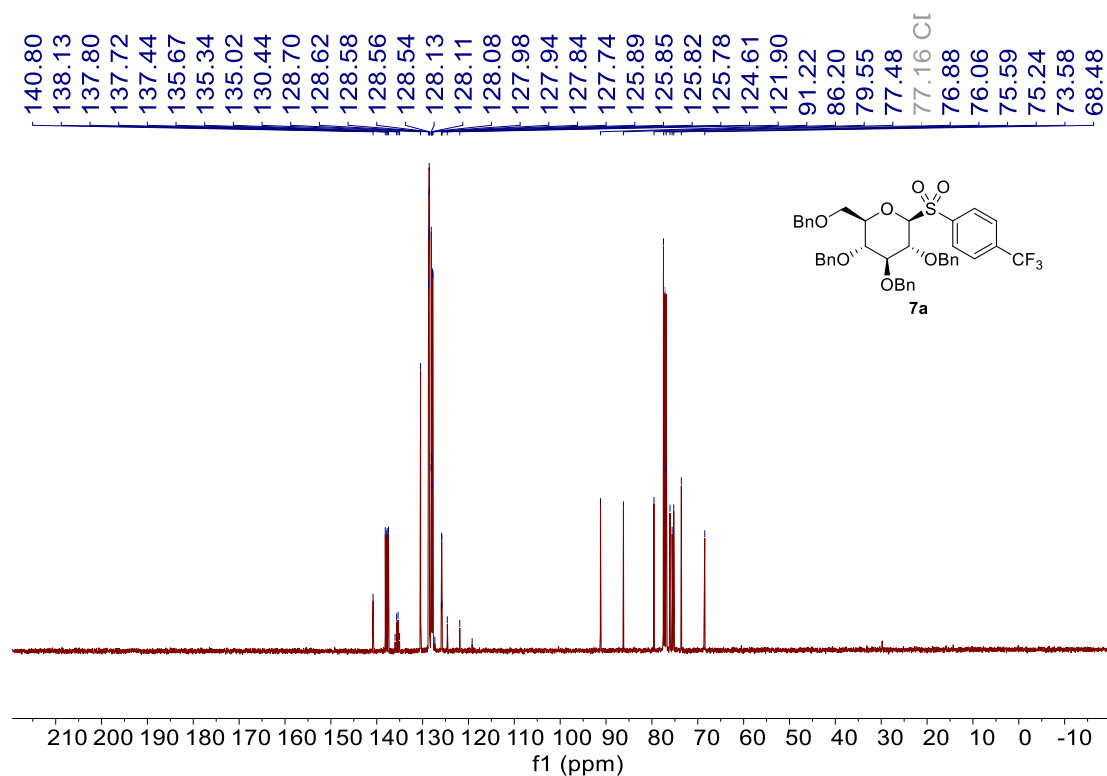


Figure S34. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 7a

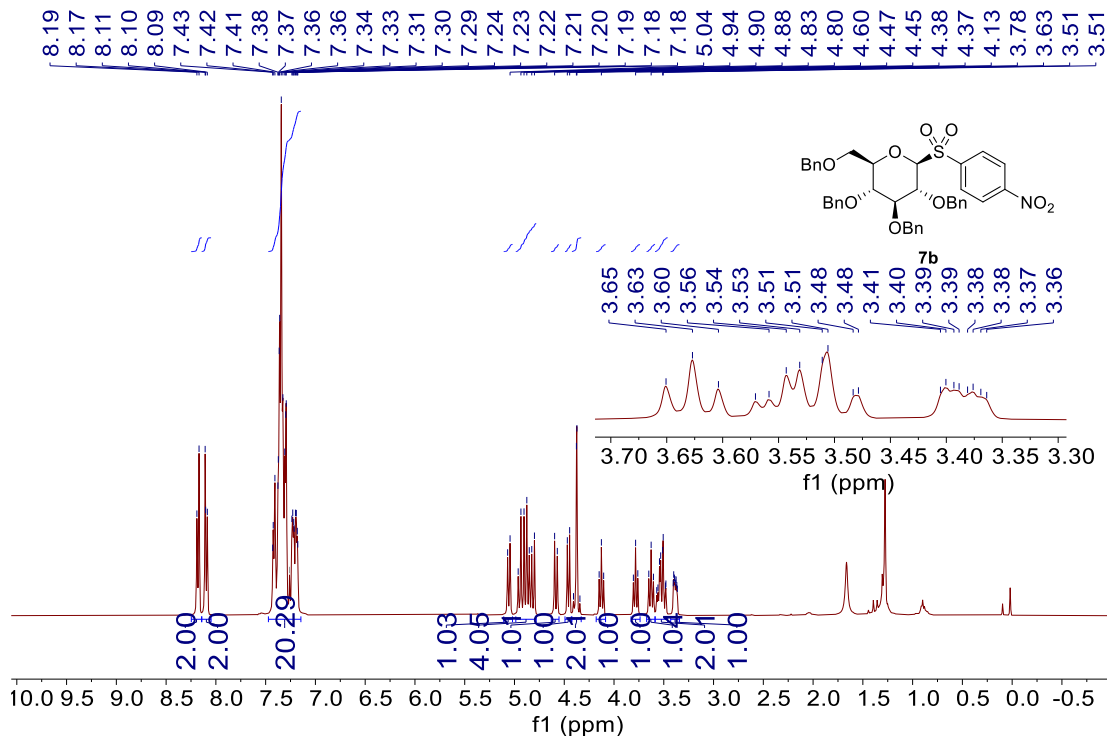


Figure S35. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 7b

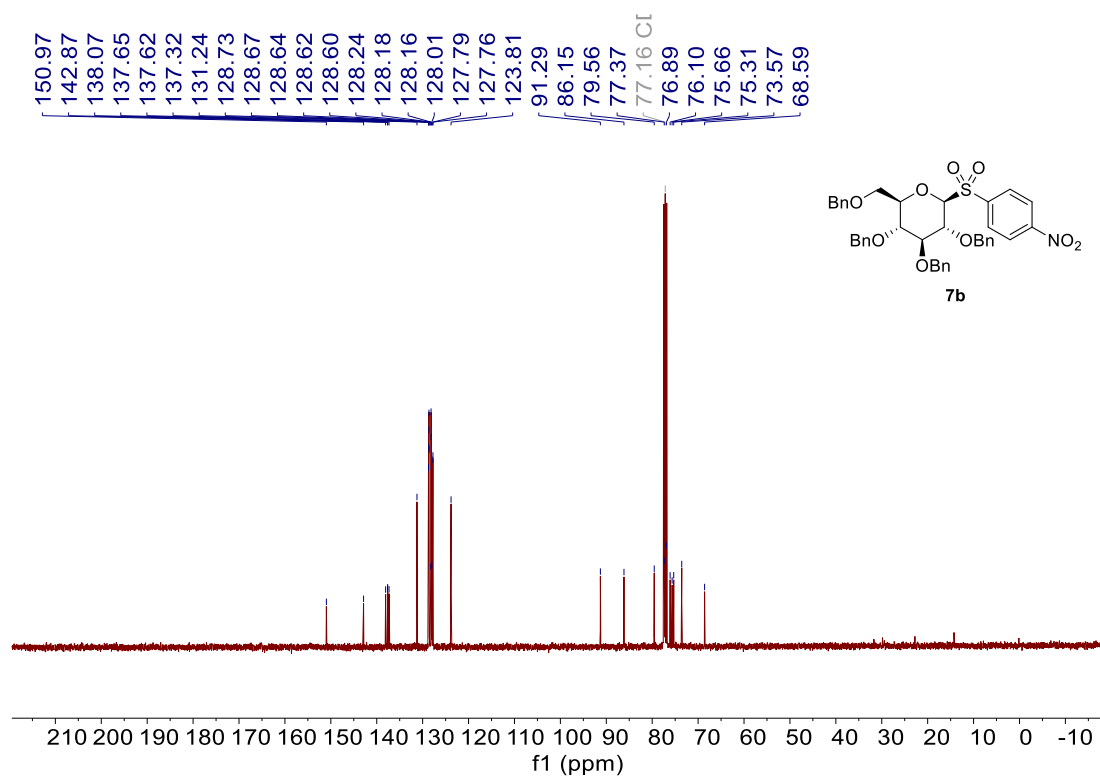


Figure S36. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound **7b**

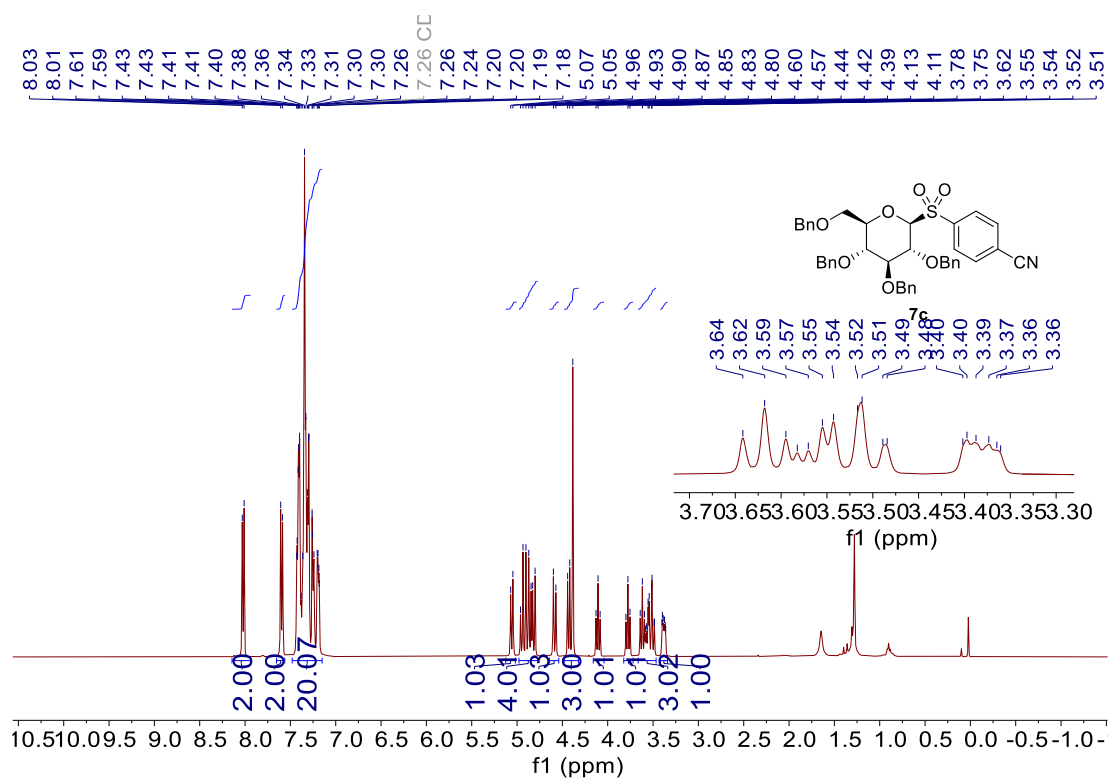
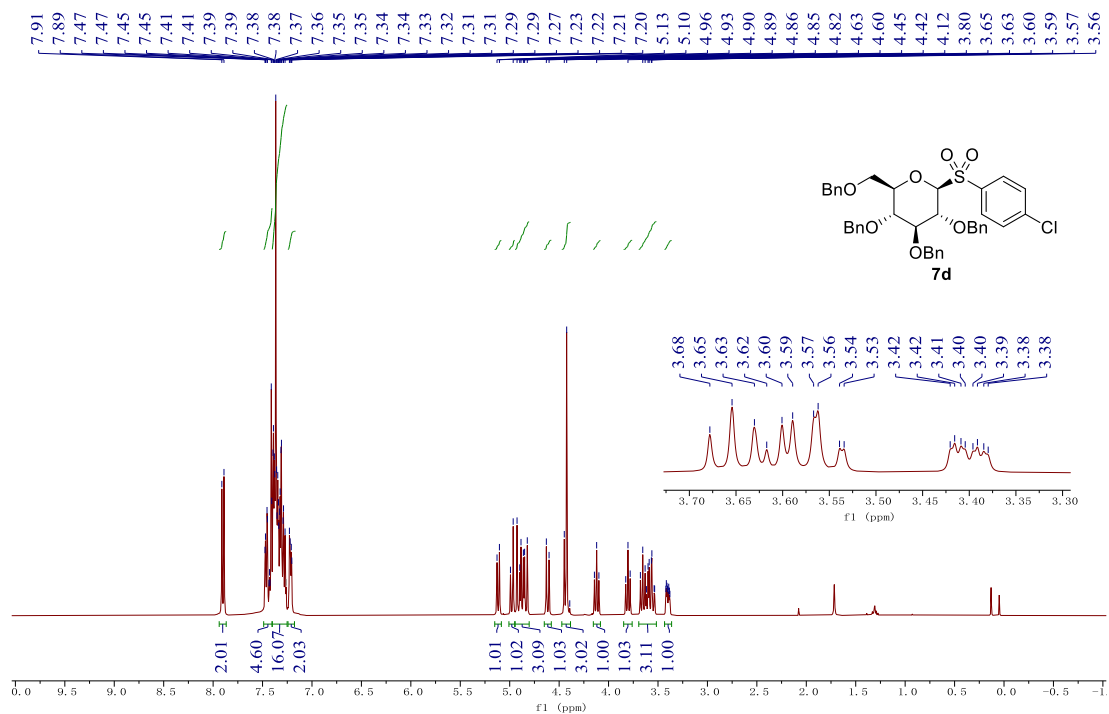
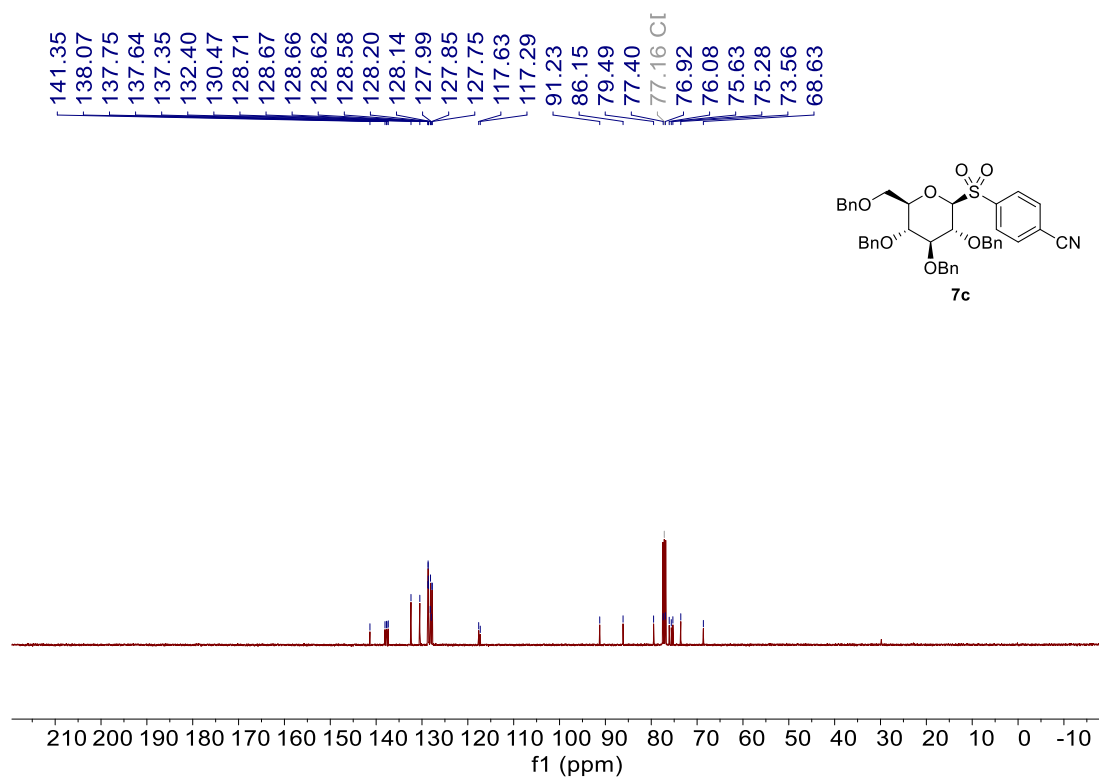


Figure S37. ^1H NMR (400 MHz, CDCl_3) Spectra for compound **7c**



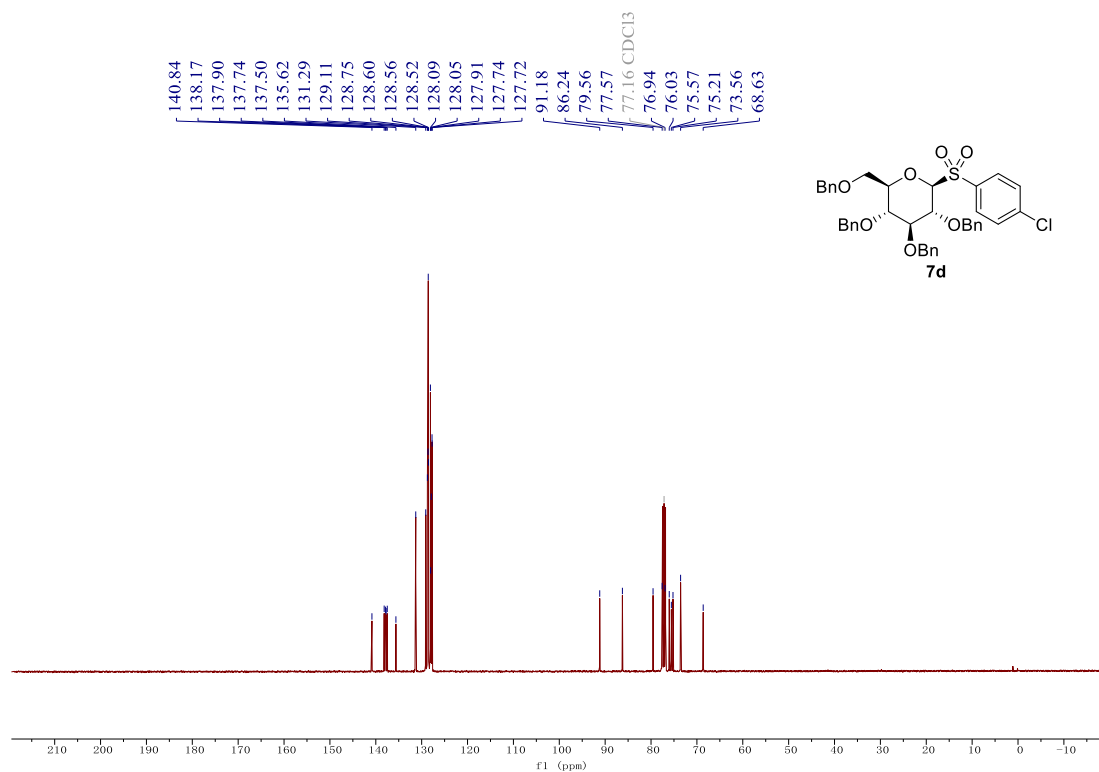


Figure S40. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound **7d**

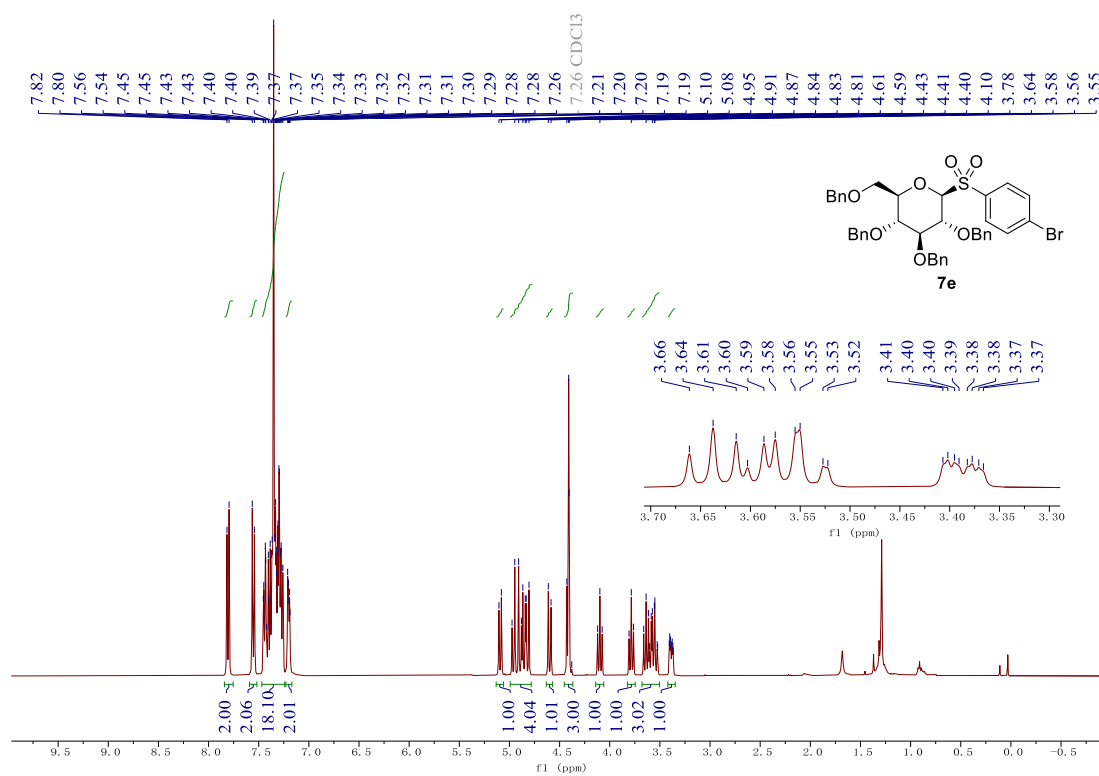


Figure S41. ¹H NMR (400 MHz, CDCl₃) Spectra for compound **7e**

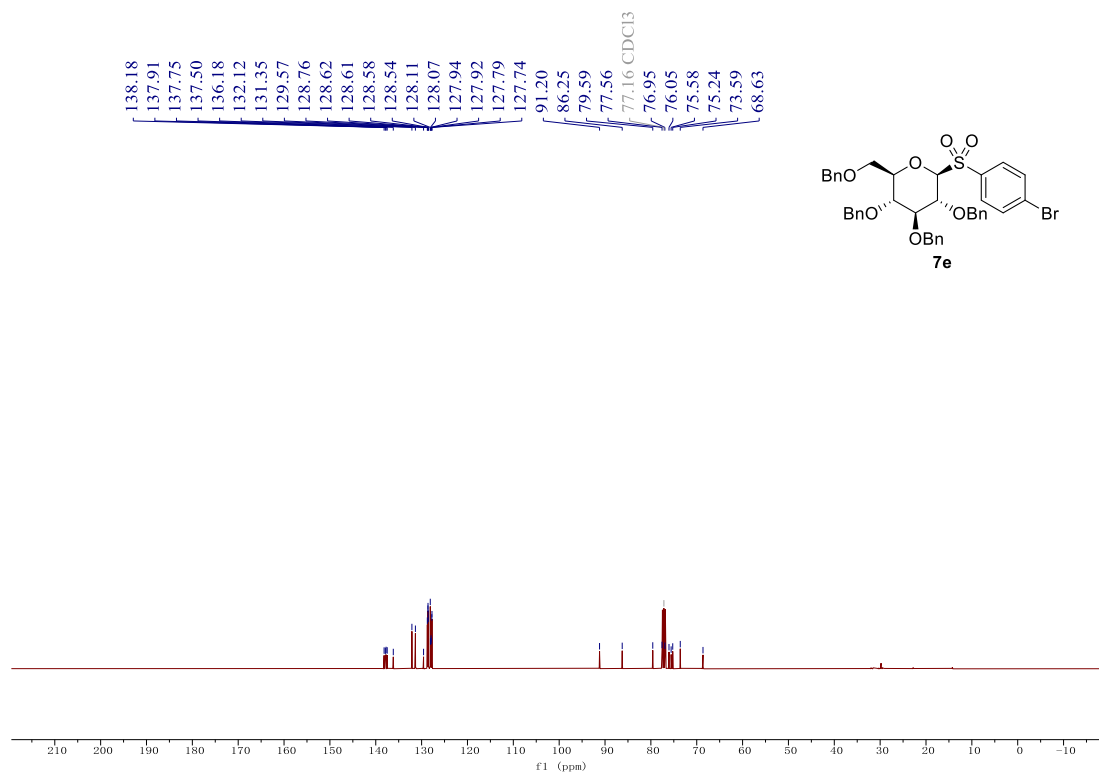


Figure S42. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound **7e**

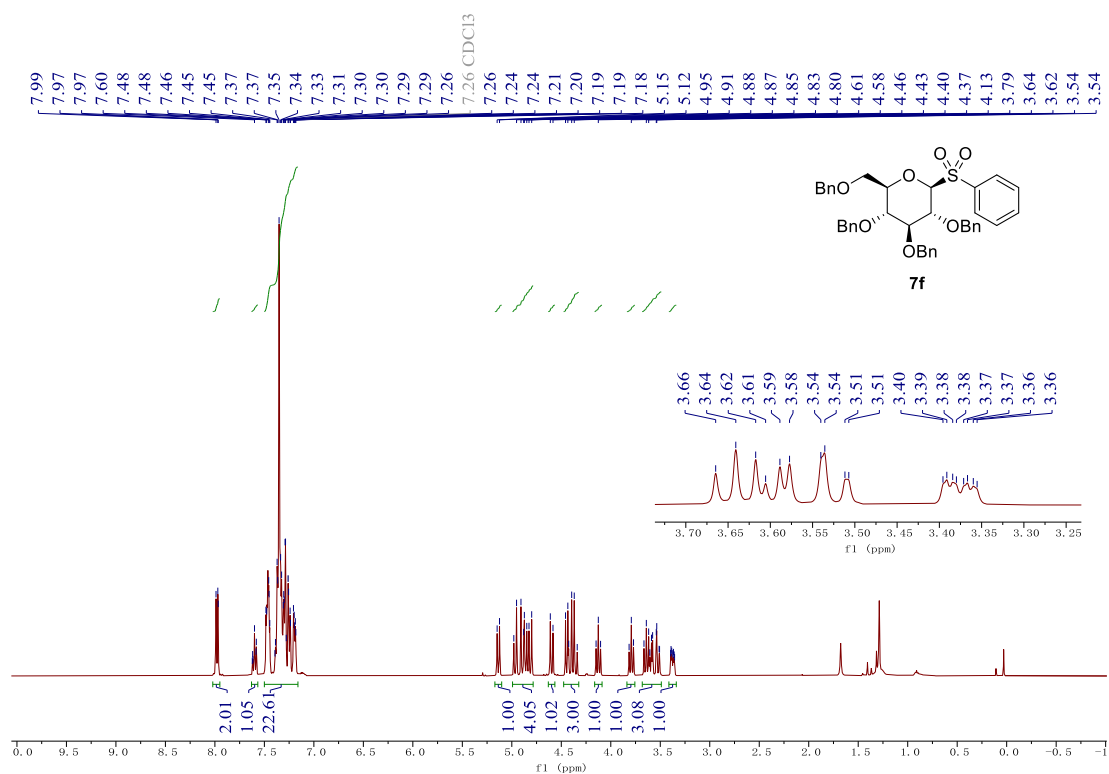


Figure S43. ¹H NMR (400 MHz, CDCl₃) Spectra for compound **7f**

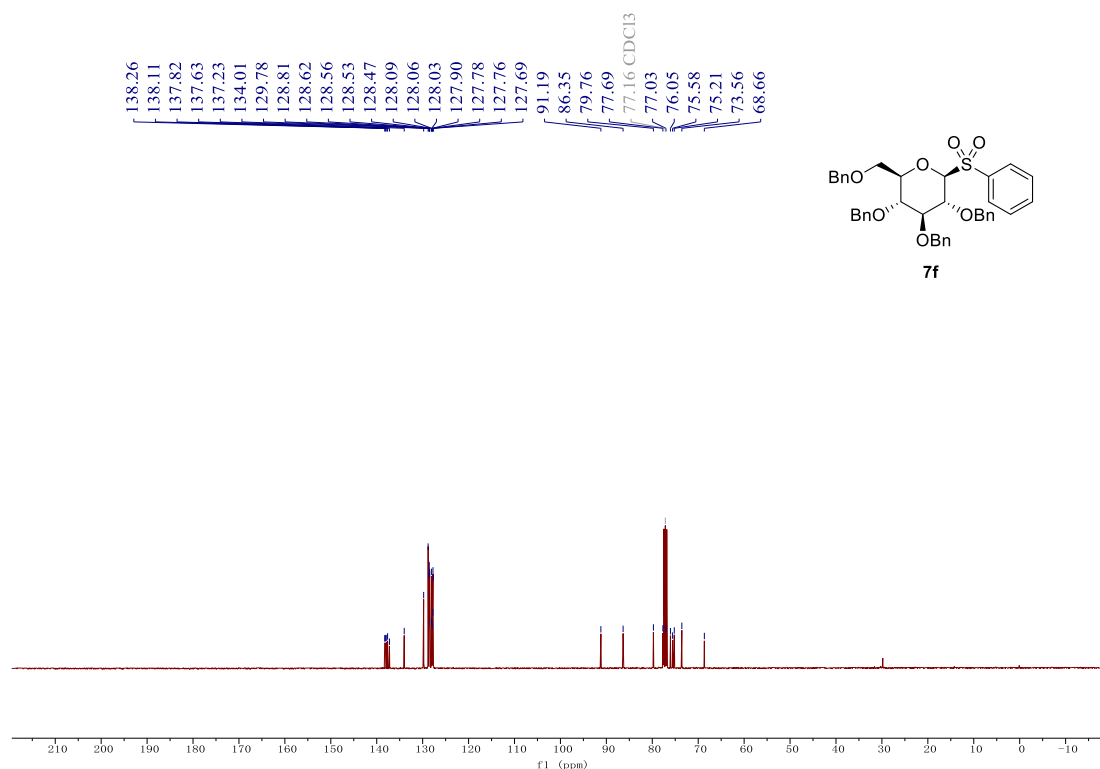


Figure S44. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 7f

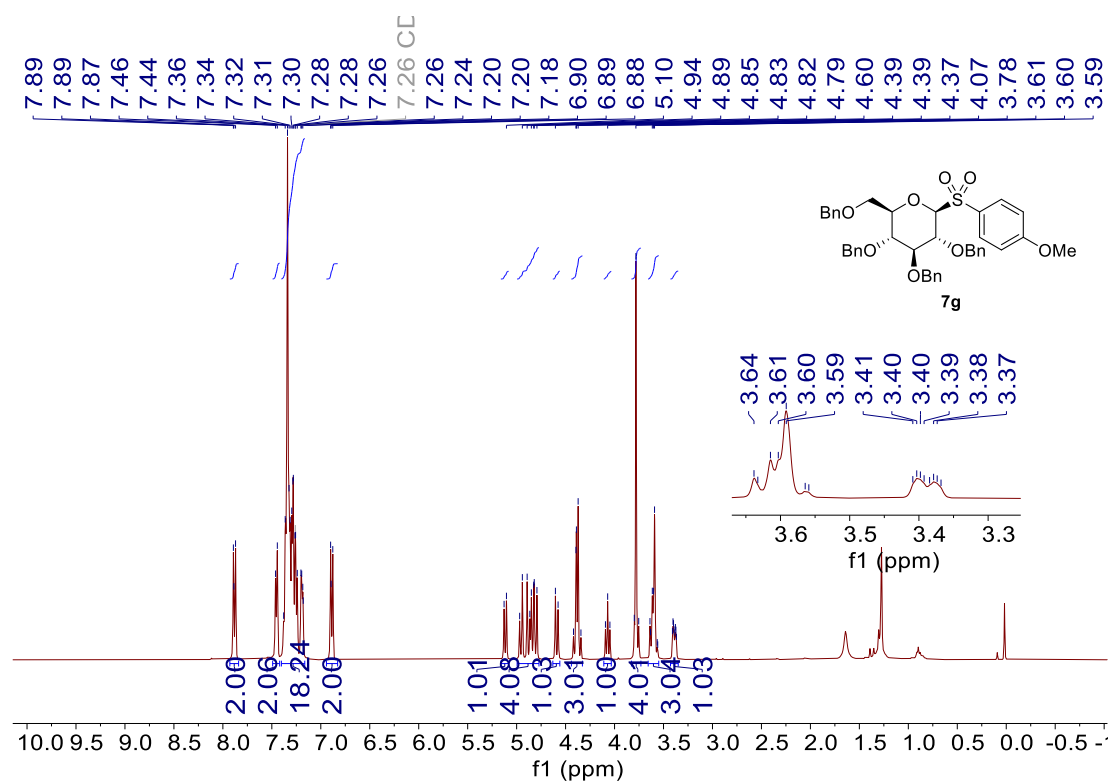


Figure S45. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7g

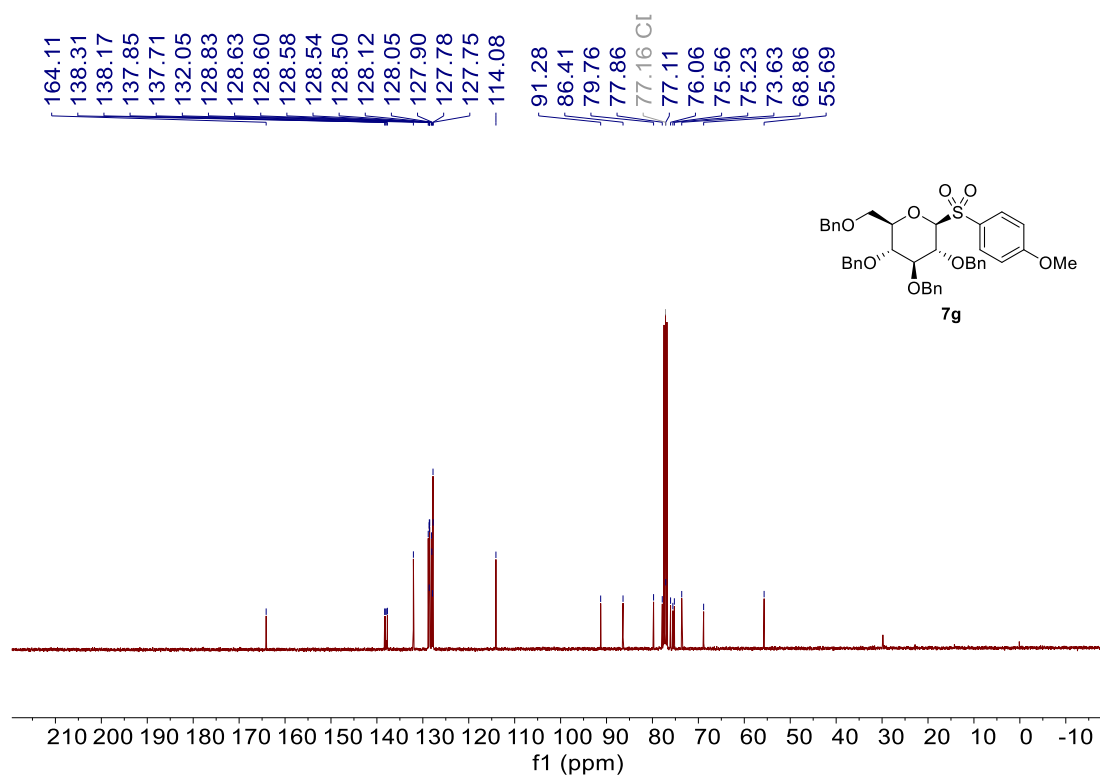


Figure S46. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 7g

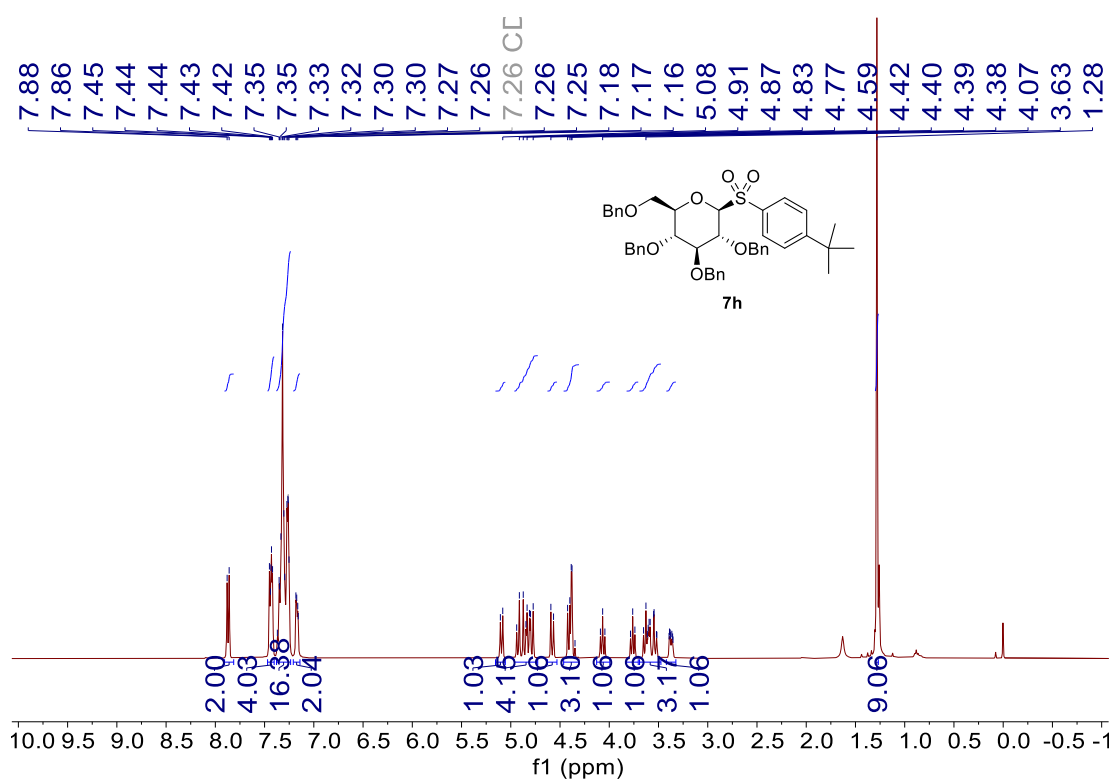


Figure S47. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 7h

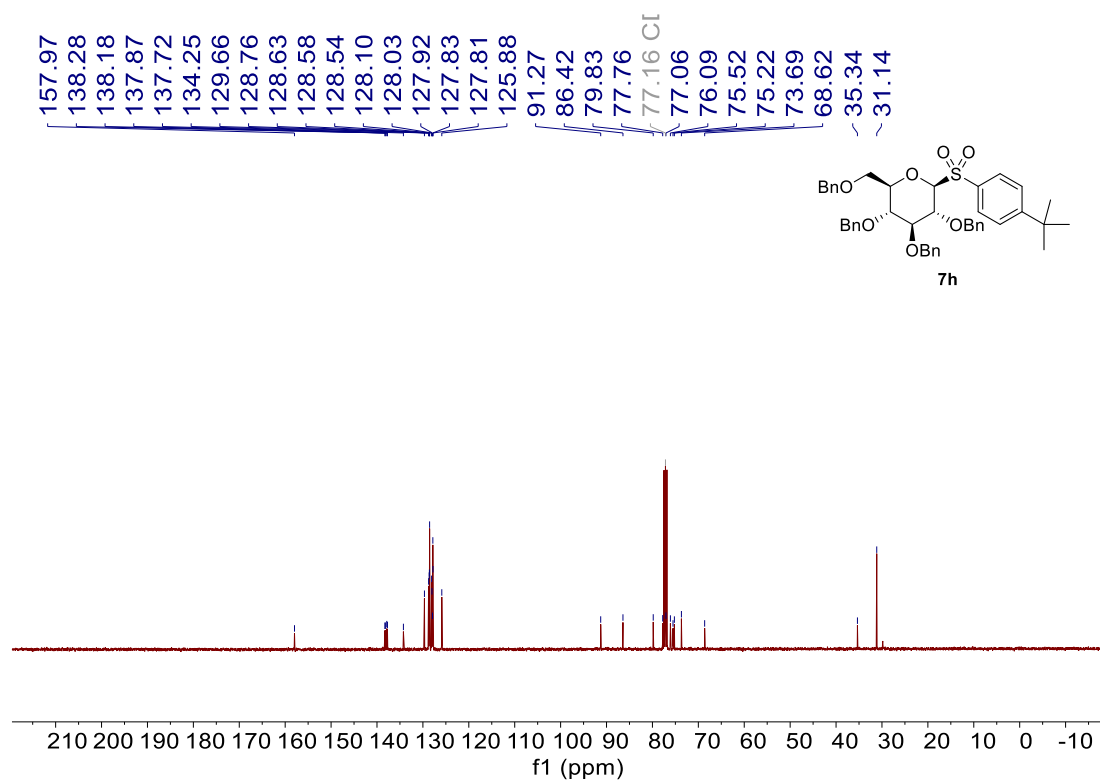


Figure S48. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound **7h**

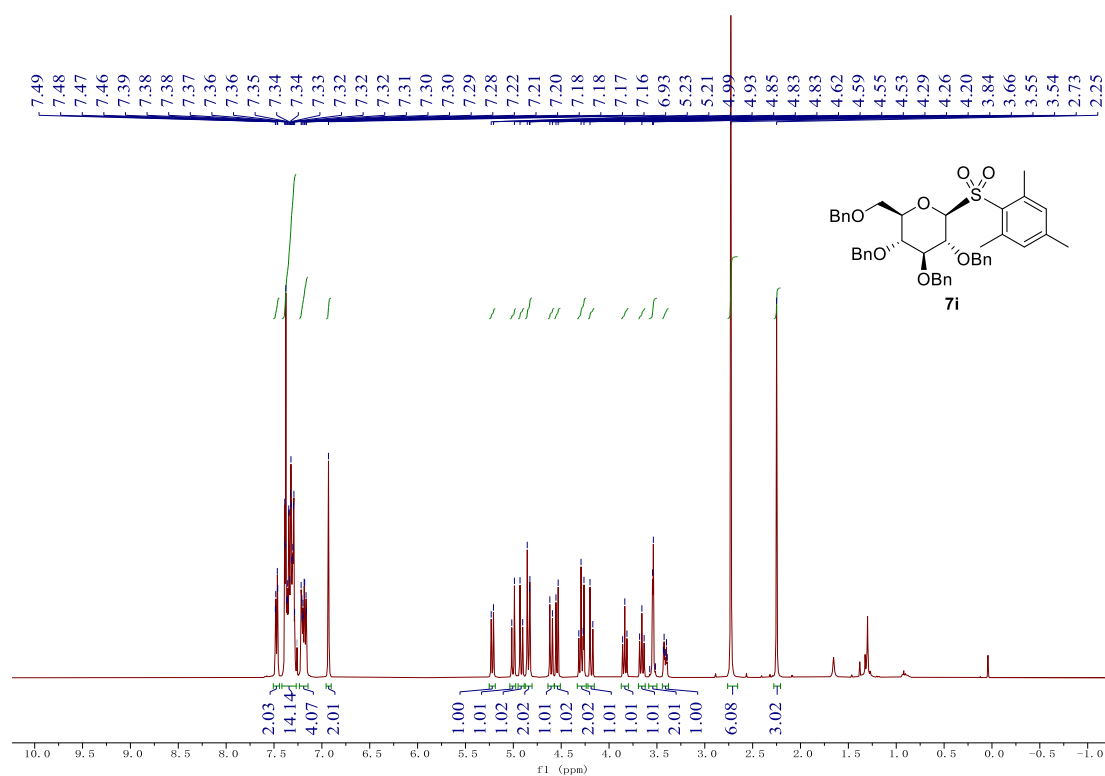


Figure S49. ^1H NMR (400 MHz, CDCl_3) Spectra for compound **7i**

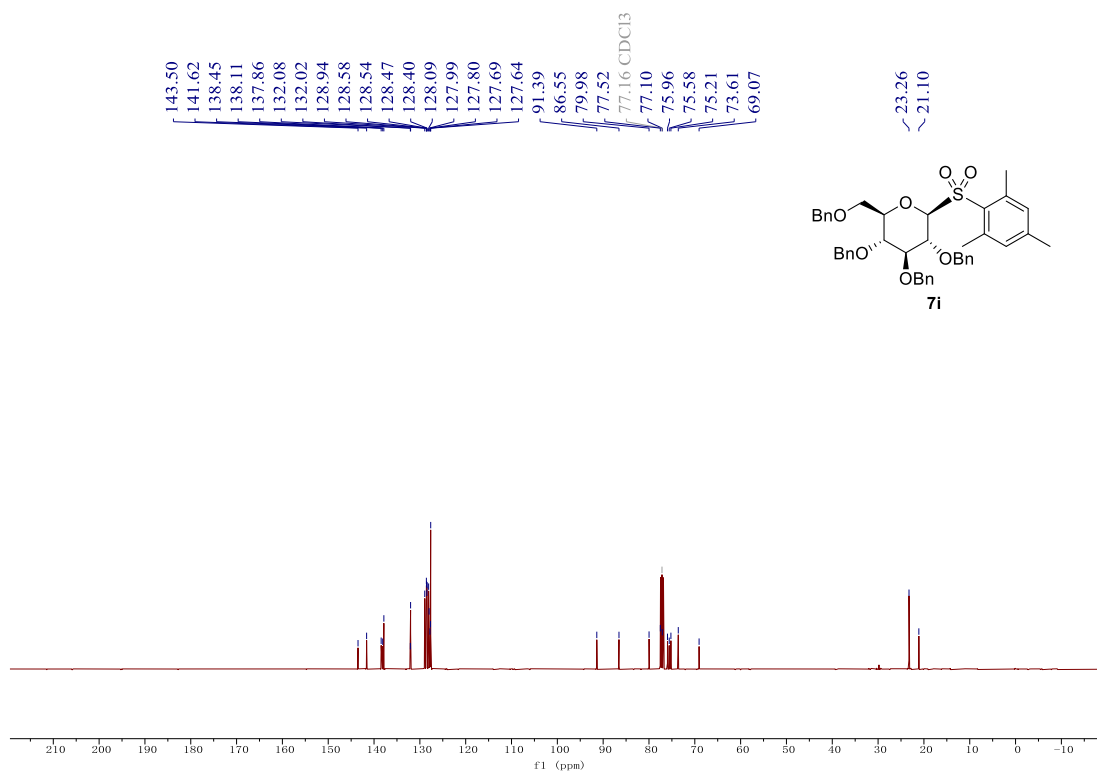


Figure S50. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 7i

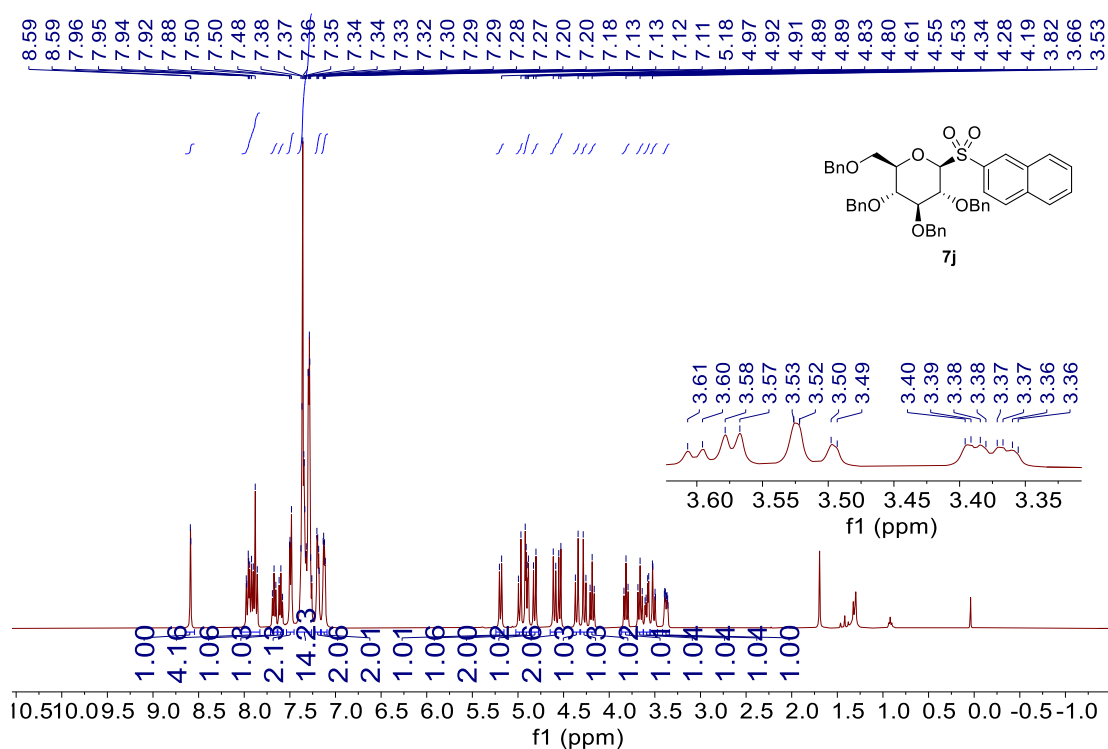


Figure S51. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 7j

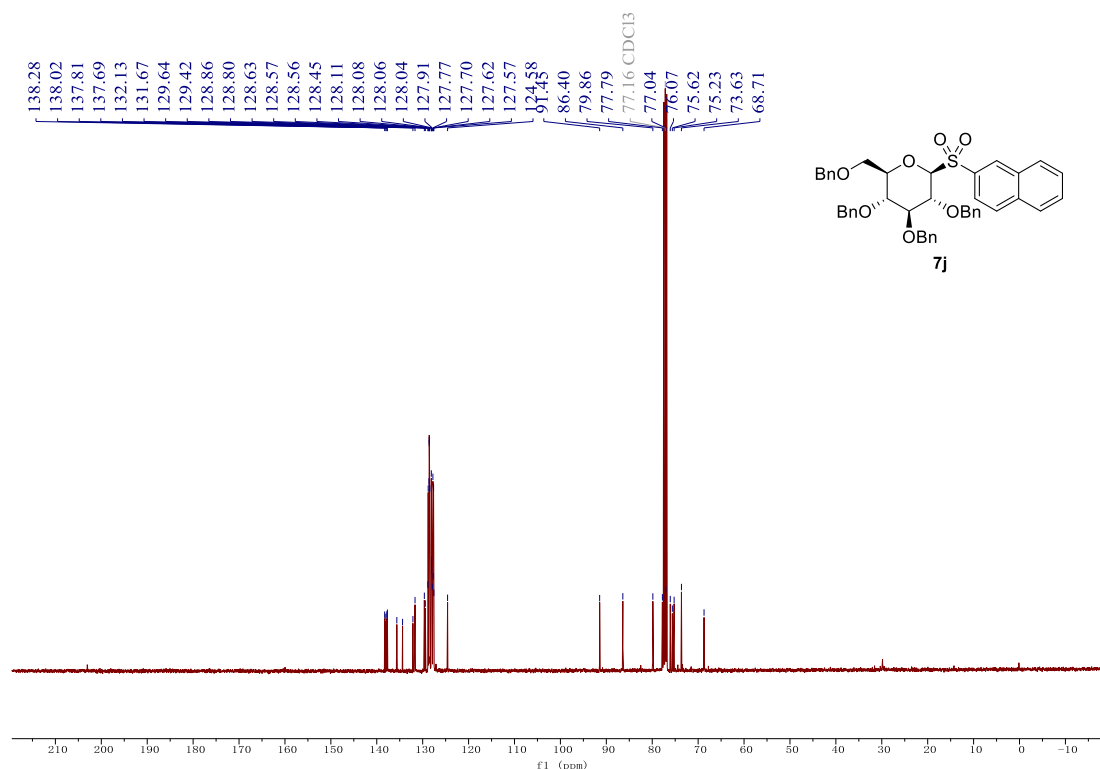


Figure S52. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 7j

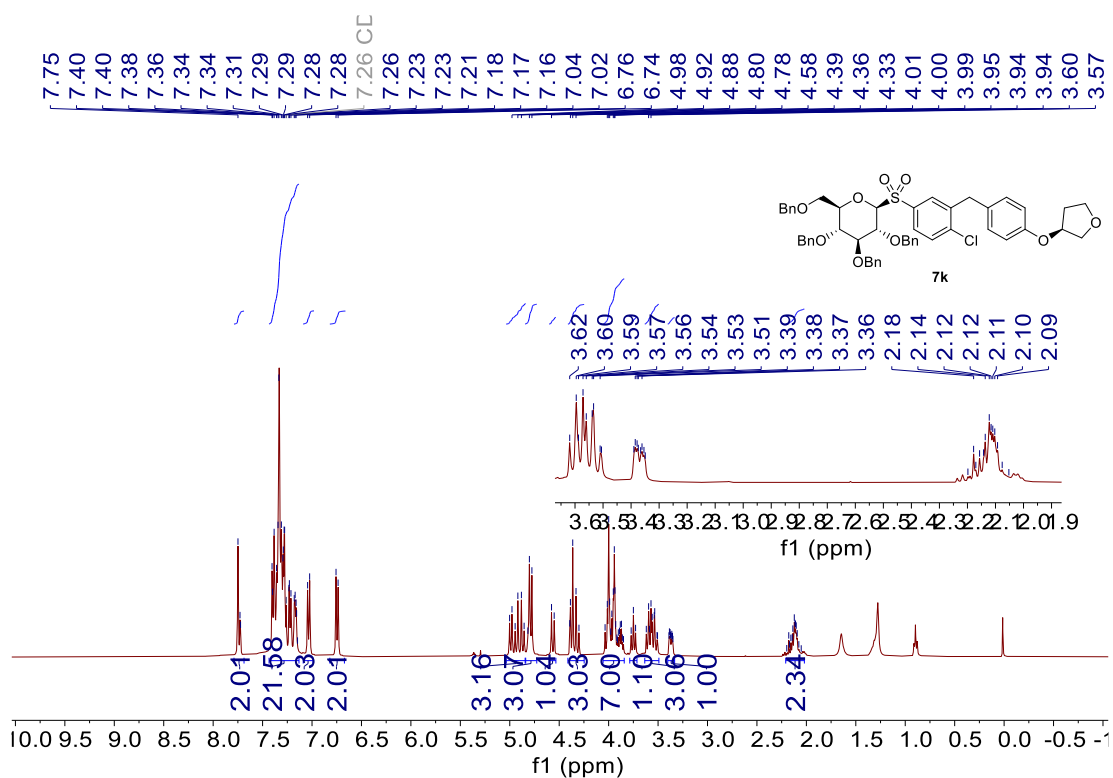


Figure S53. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7k

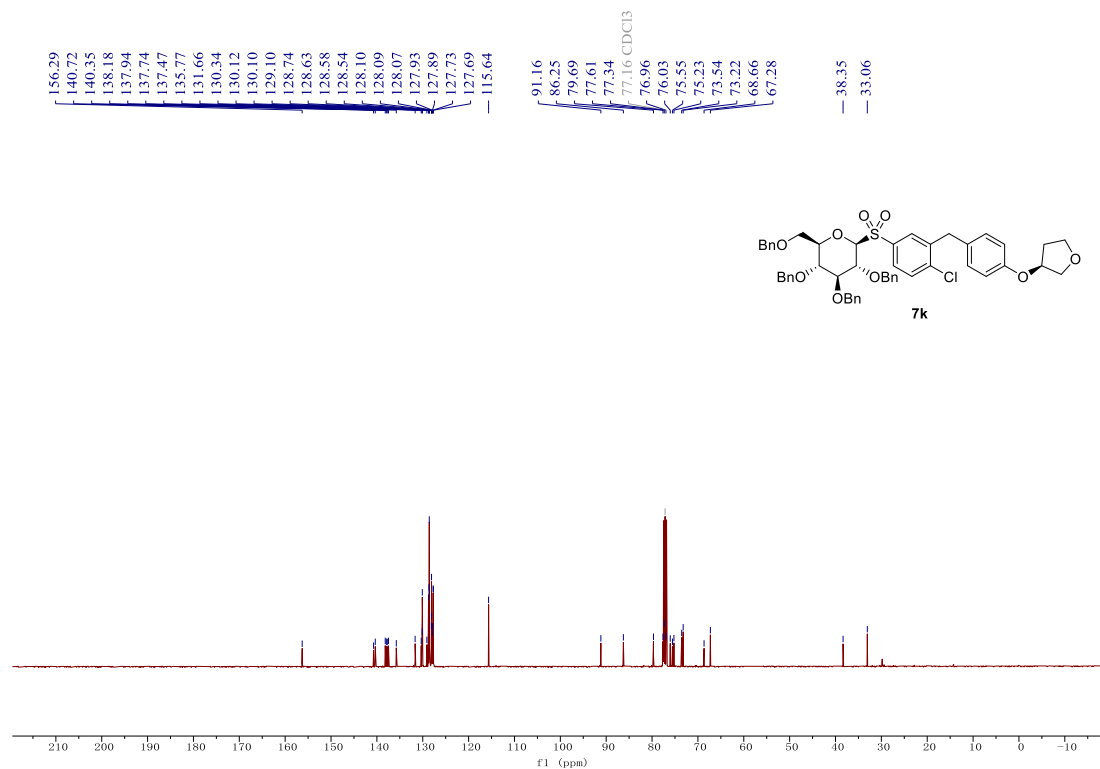


Figure S54. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 7k

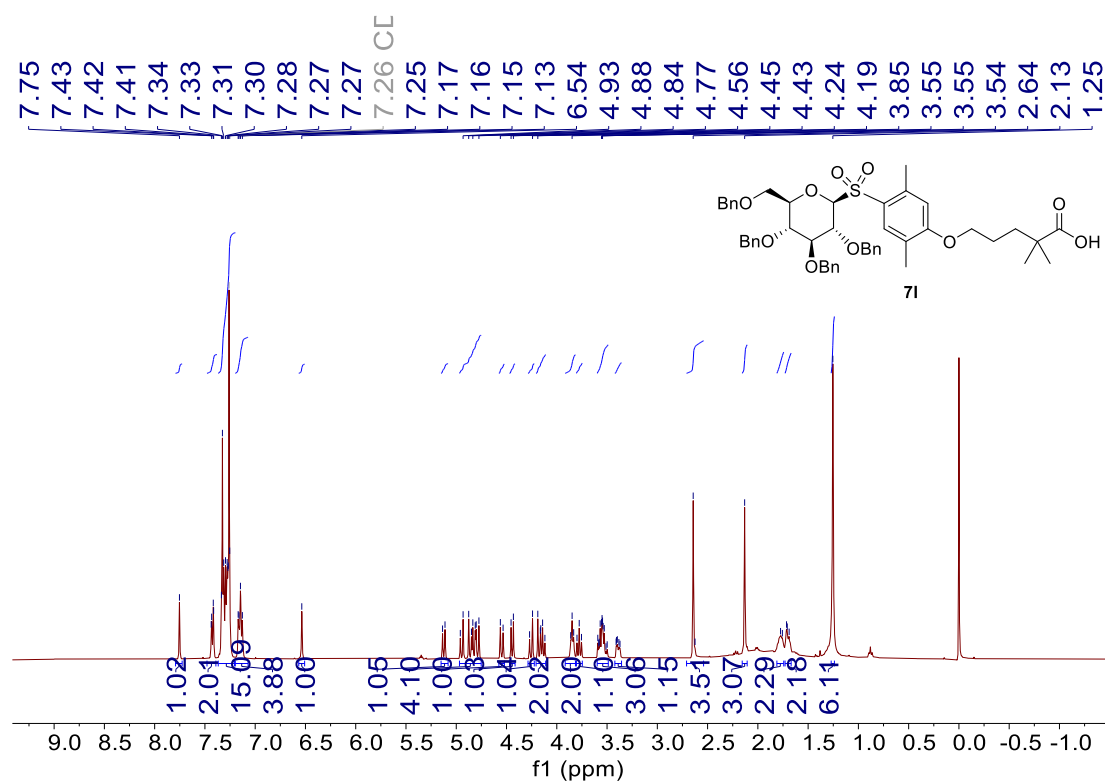


Figure S55. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7l

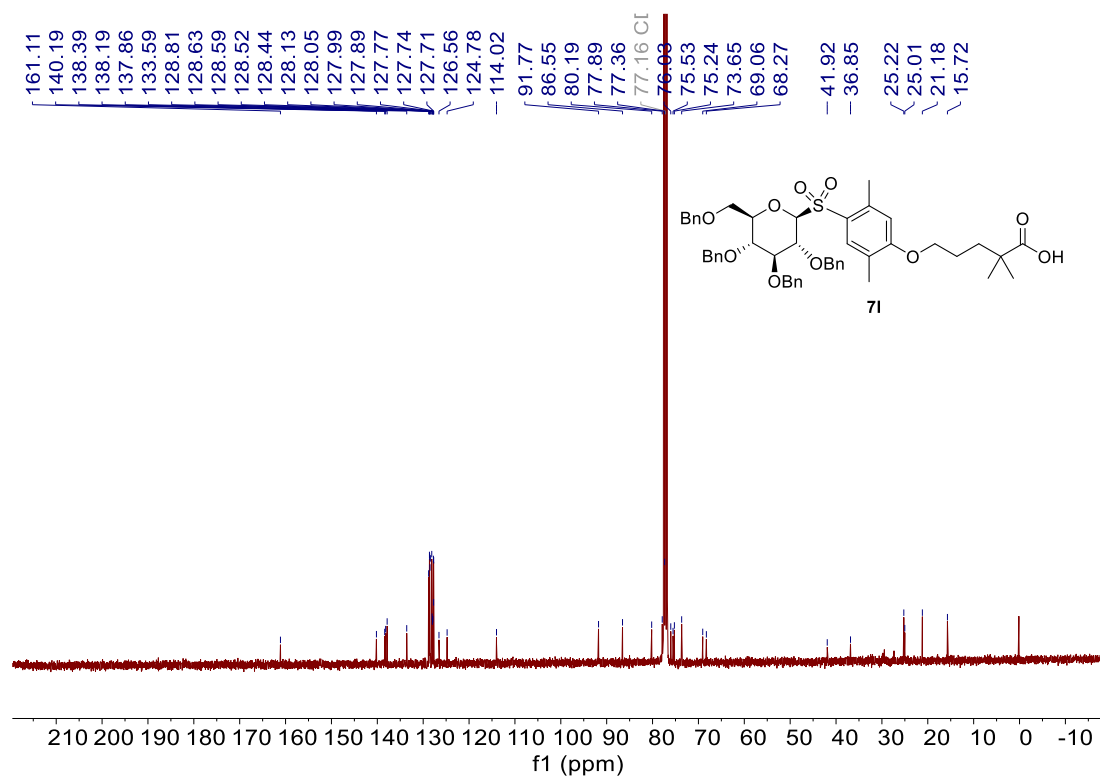


Figure S56. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 71

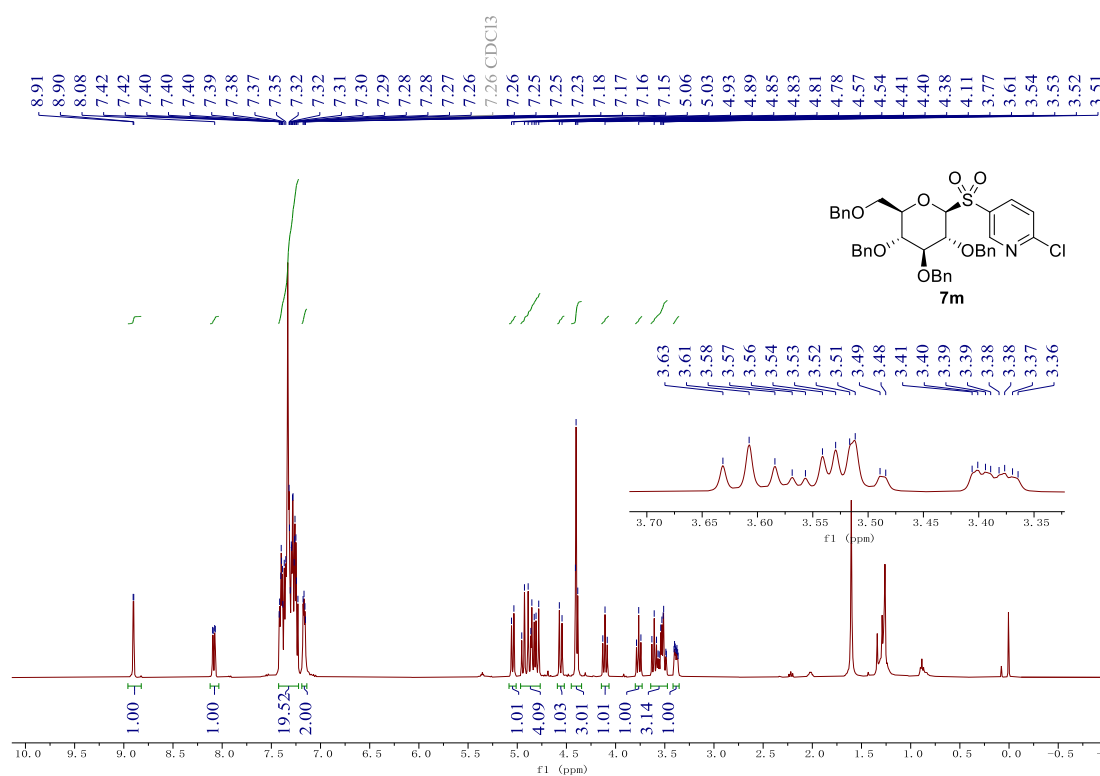


Figure S57. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 7m

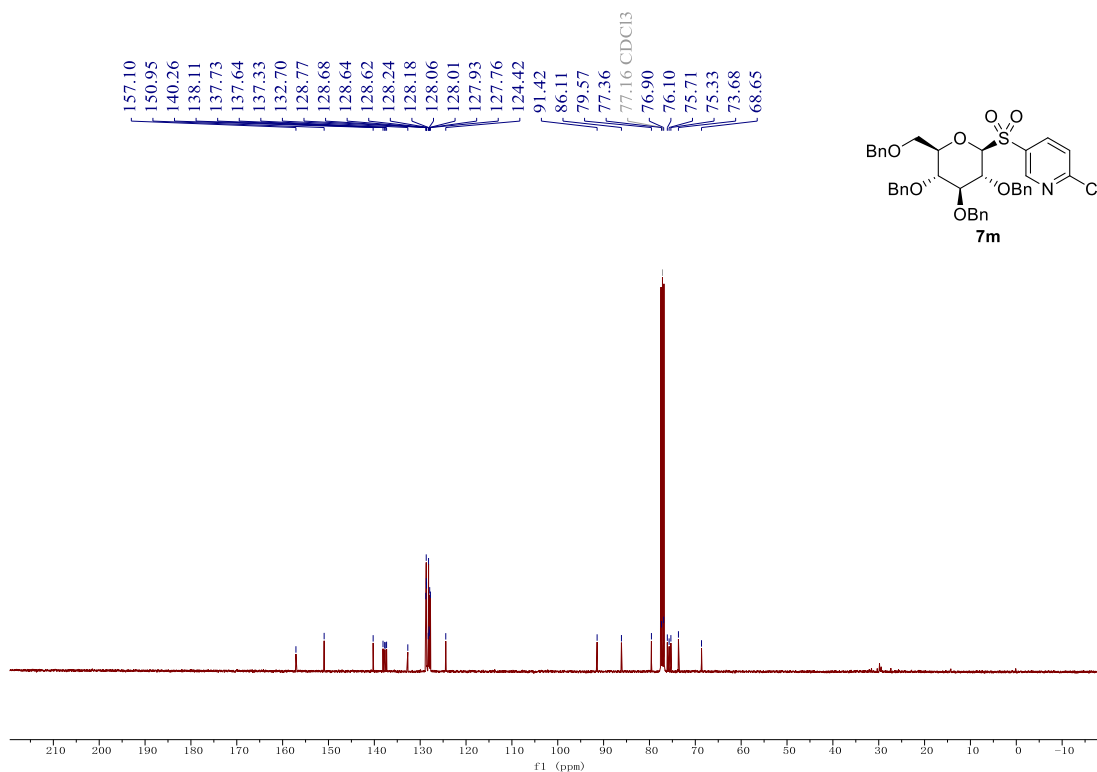


Figure S58. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 7m

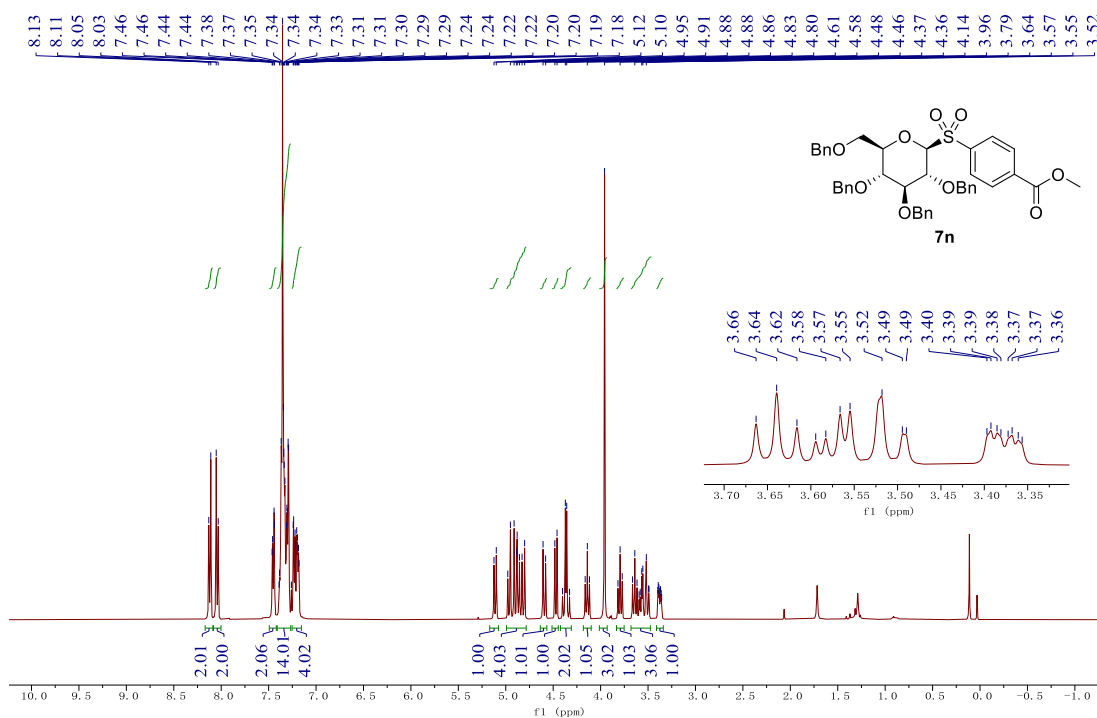


Figure S59. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7n

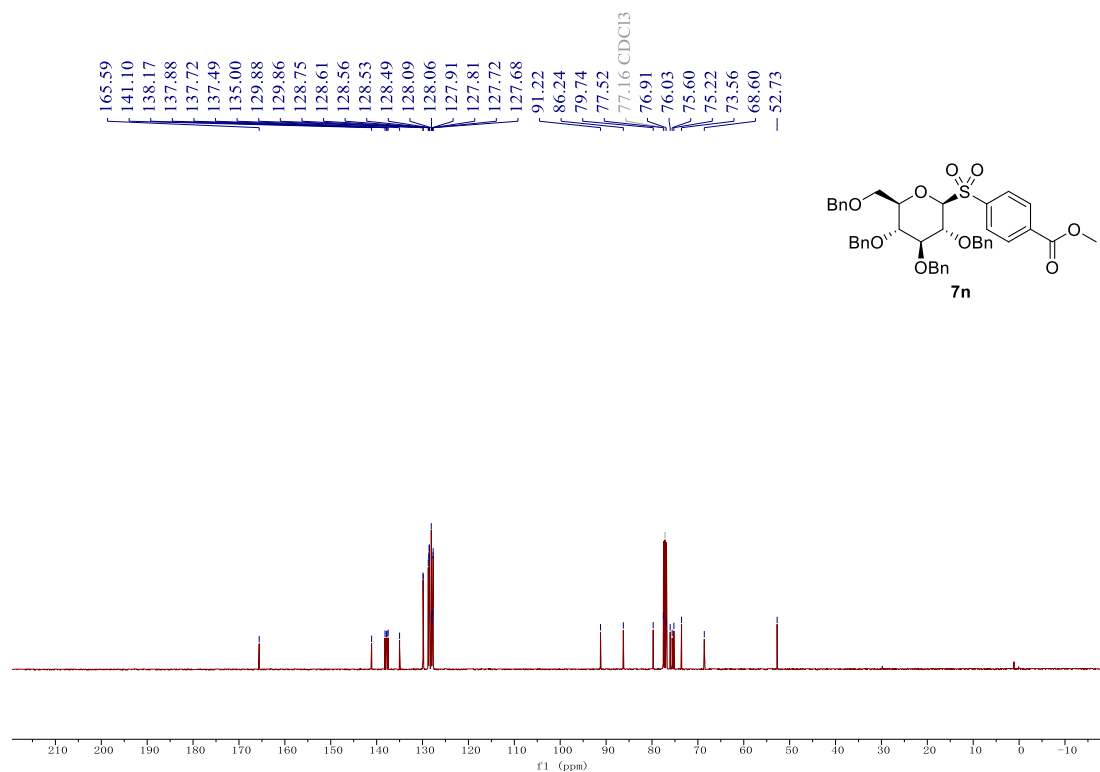


Figure S60. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound **7n**

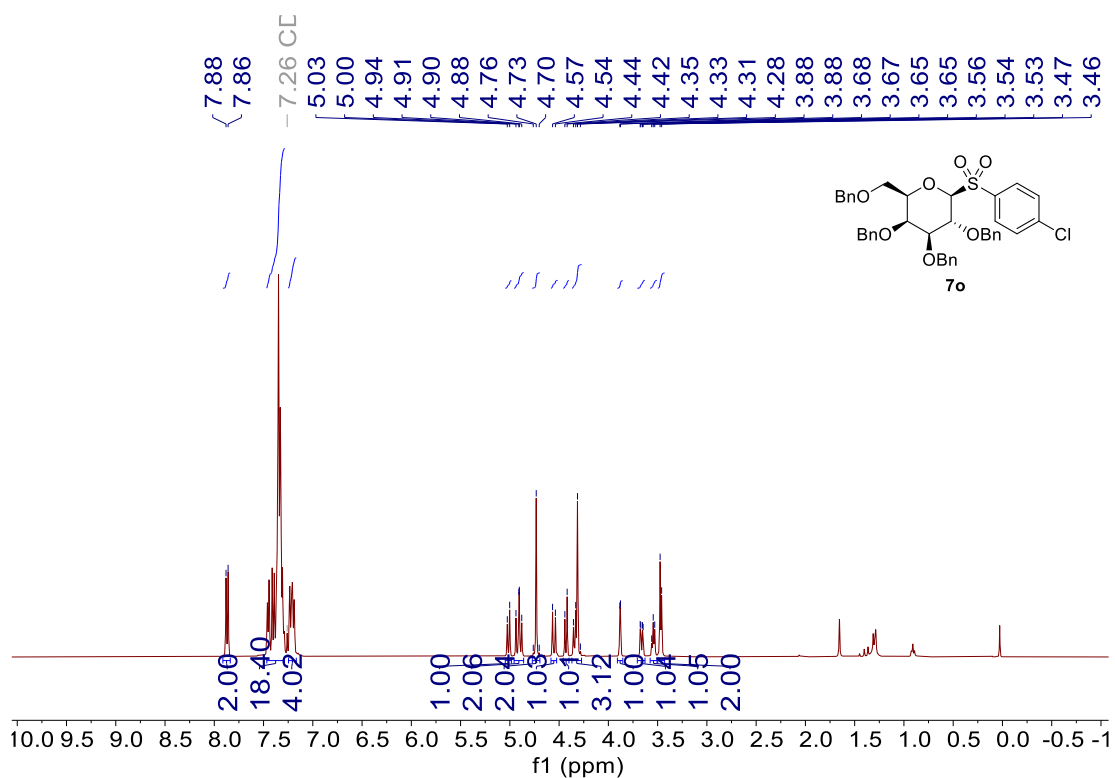
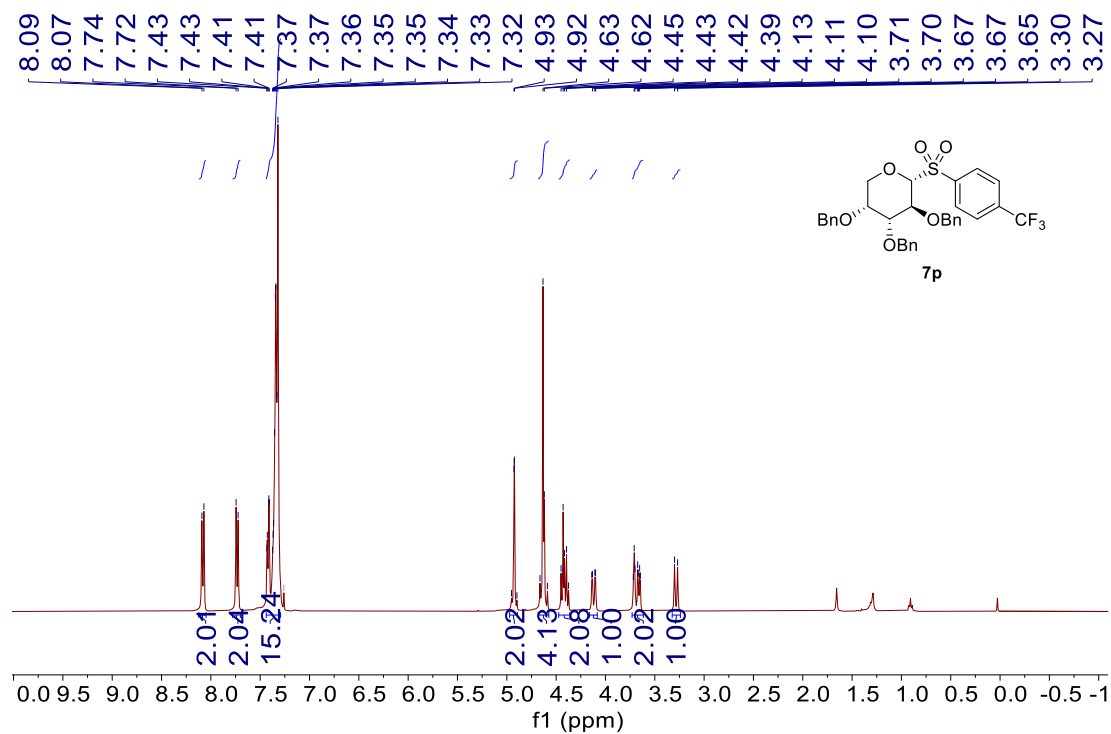
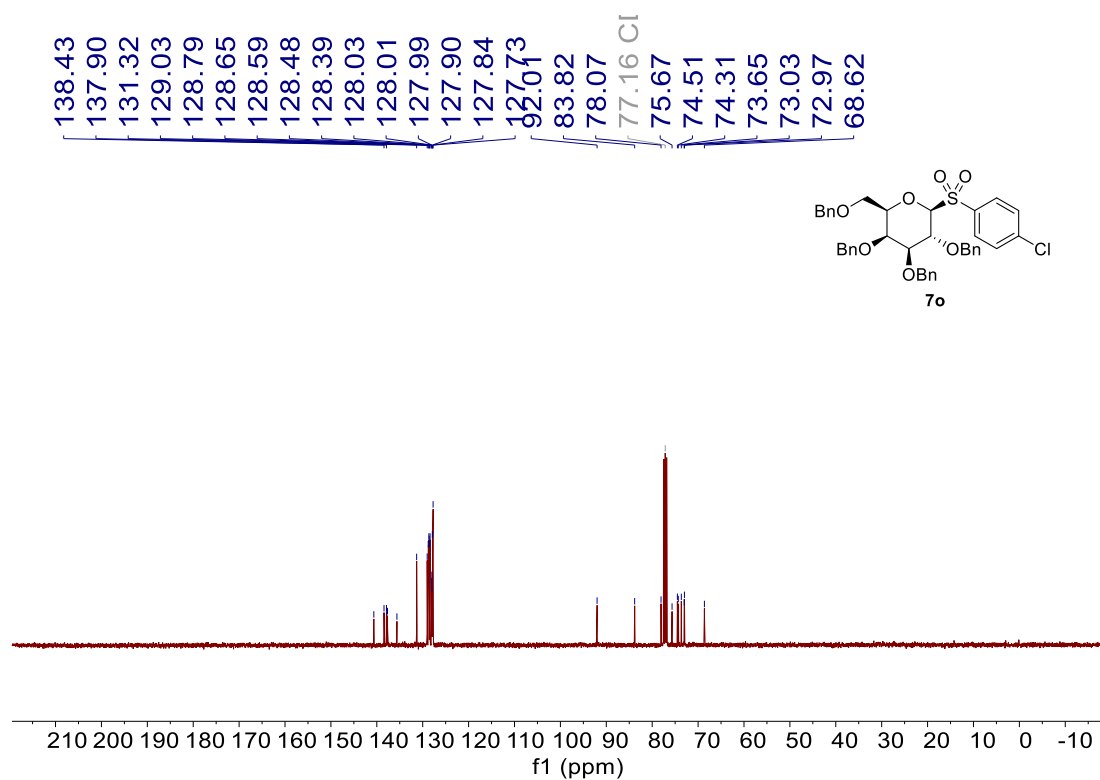
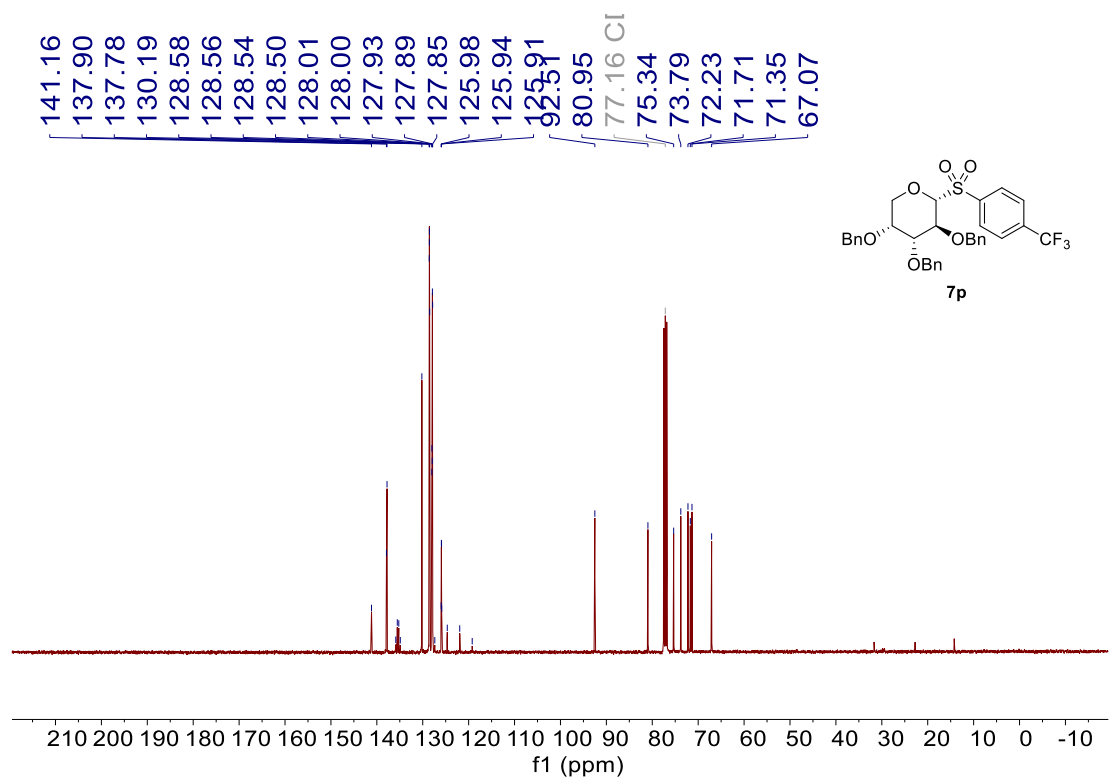
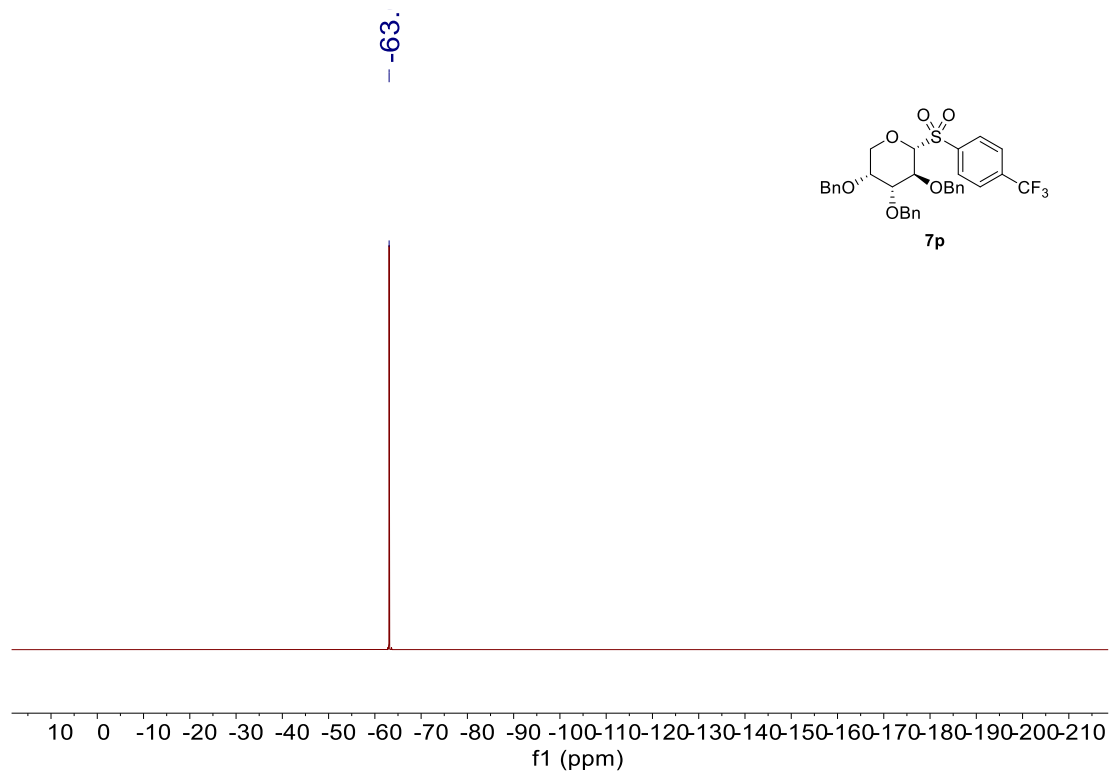


Figure S61. ¹H NMR (400 MHz, CDCl₃) Spectra for compound **7o**





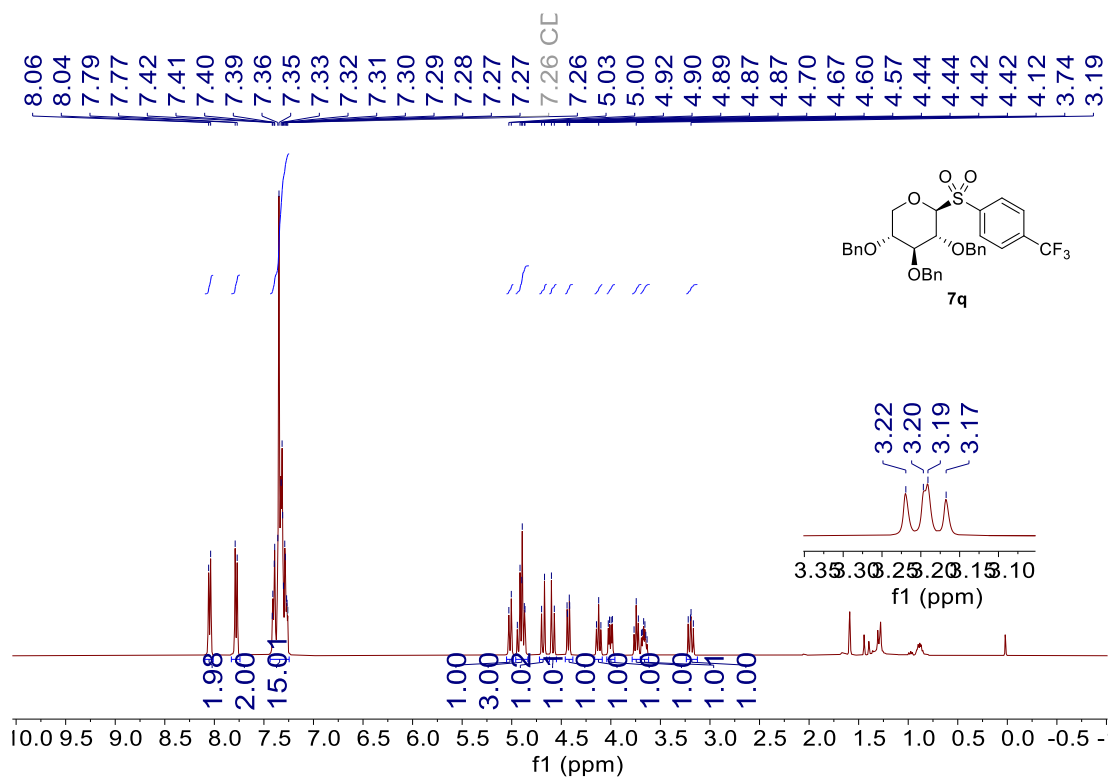


Figure S66. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 7q

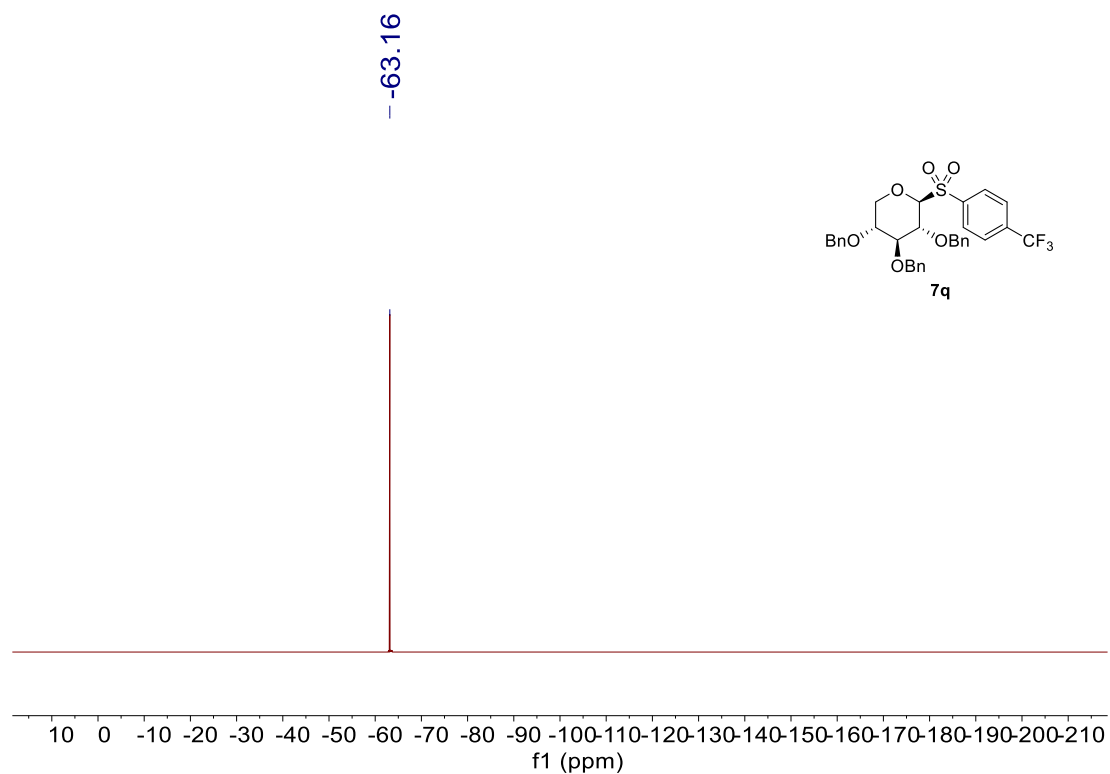


Figure S67. ^{19}F NMR (376 MHz, CDCl_3) Spectra for compound 7q

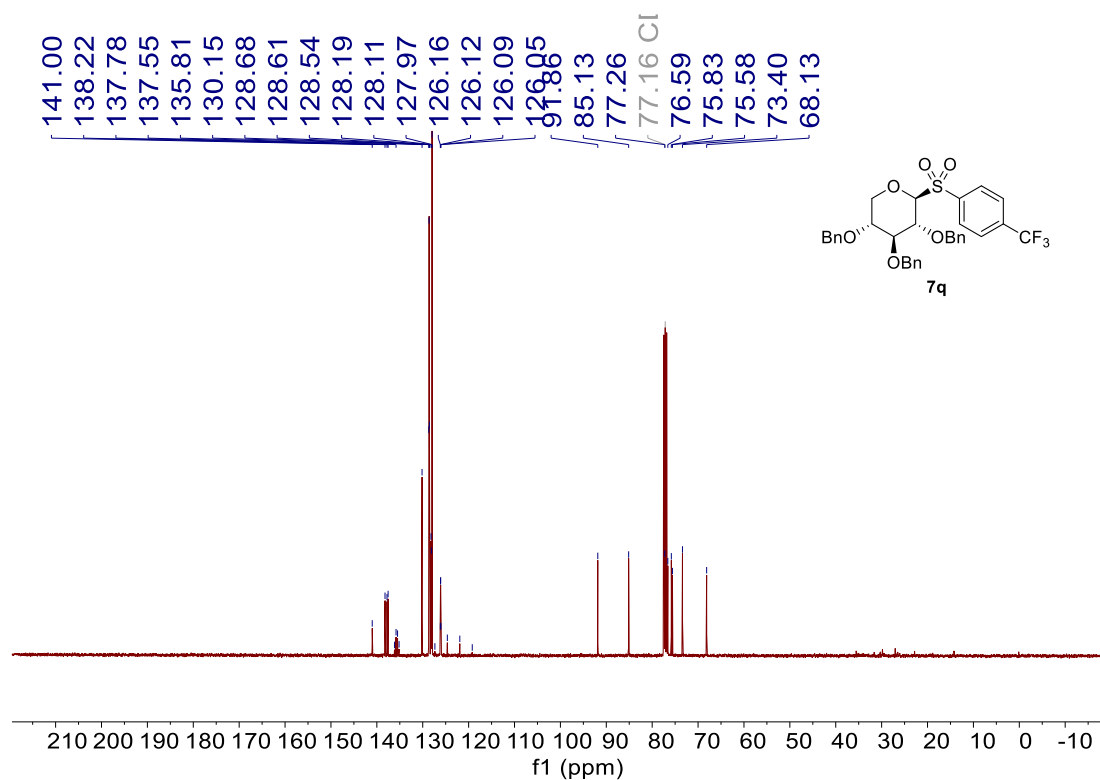


Figure S68. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 7q

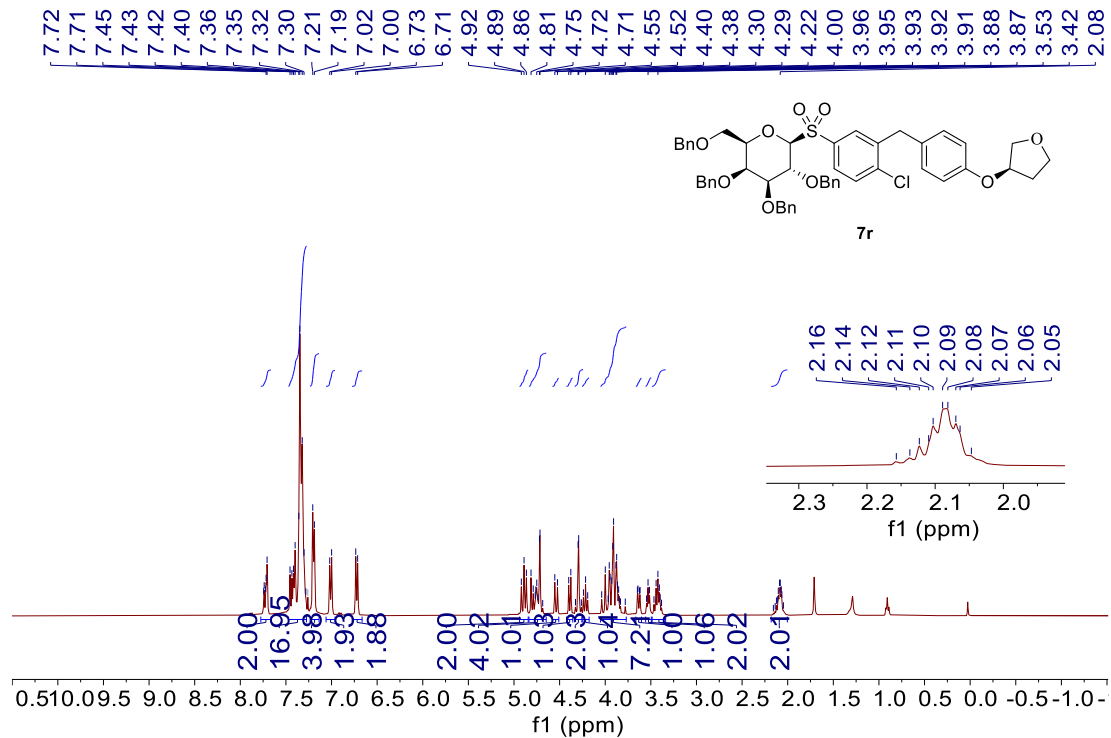


Figure S69. ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7r

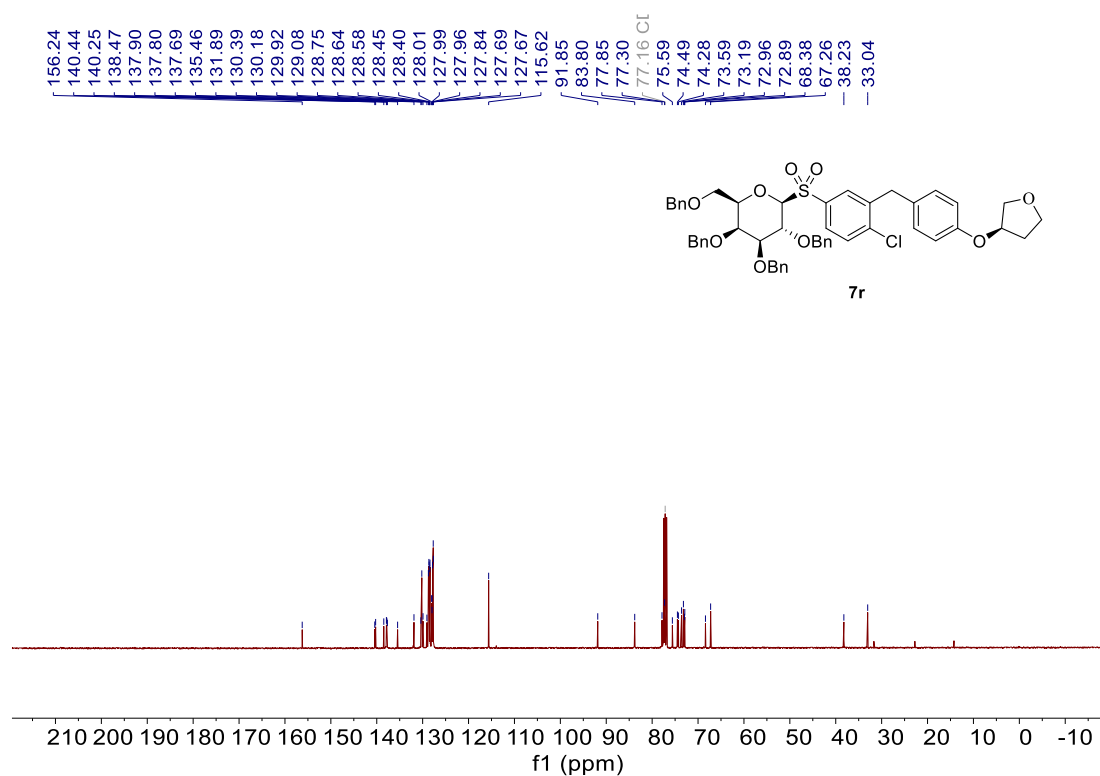


Figure S70. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 7r

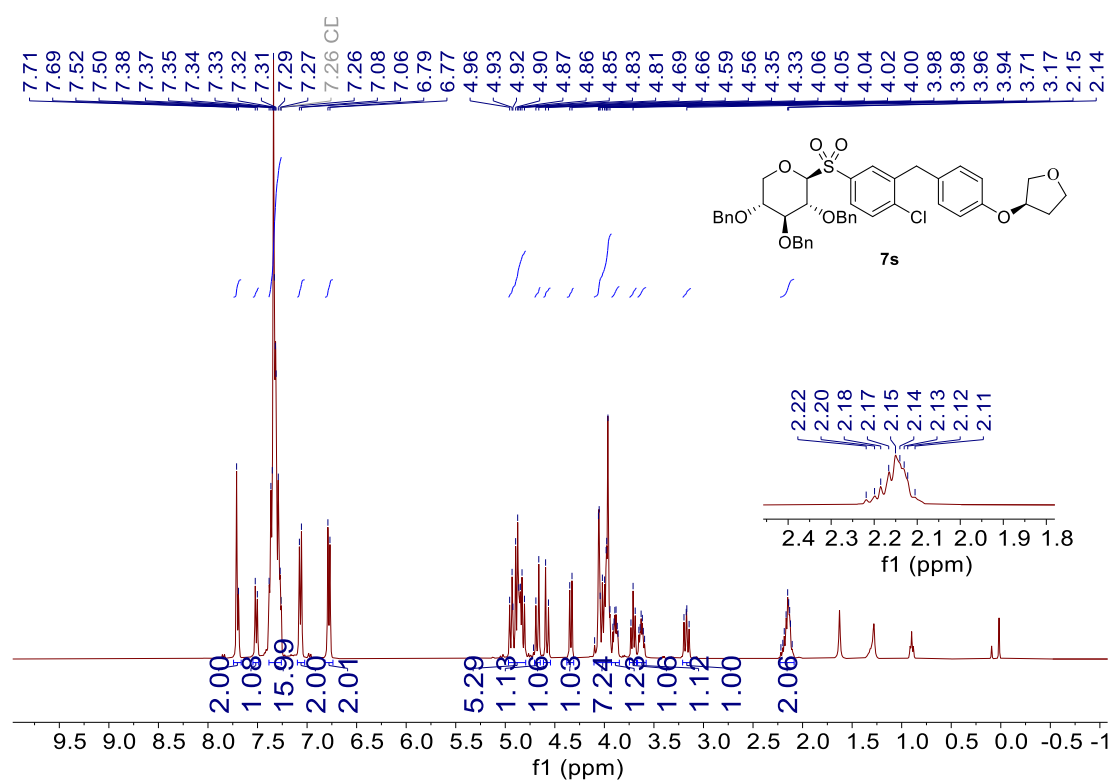


Figure S71. ^1H NMR (400 MHz, CDCl_3) Spectra for compound 7s

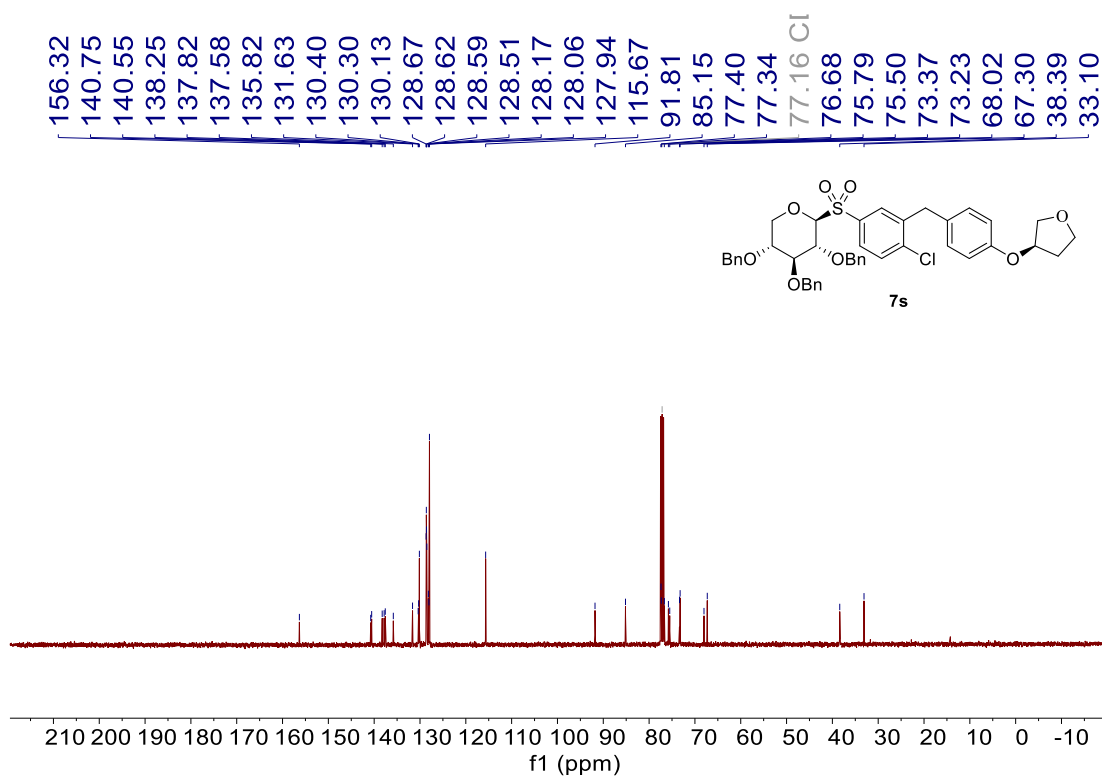


Figure S72. ^{13}C NMR (101 MHz, CDCl_3) Spectra for compound 7s

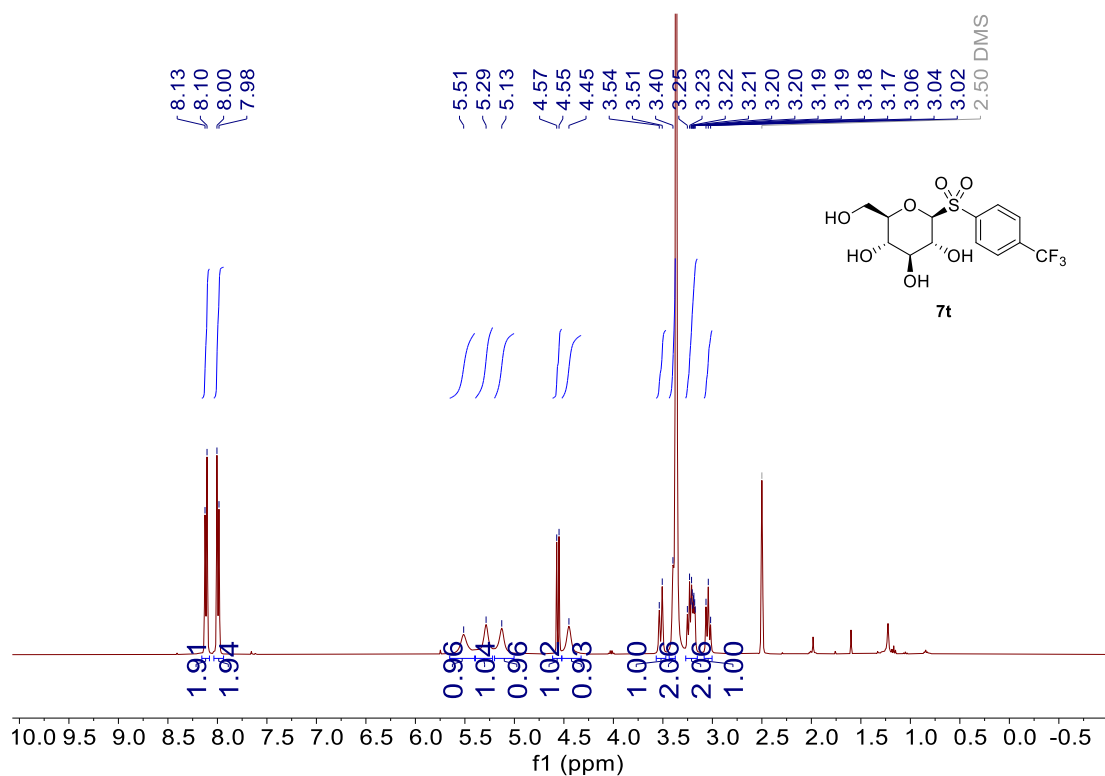


Figure S73. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) Spectra for compound 7t

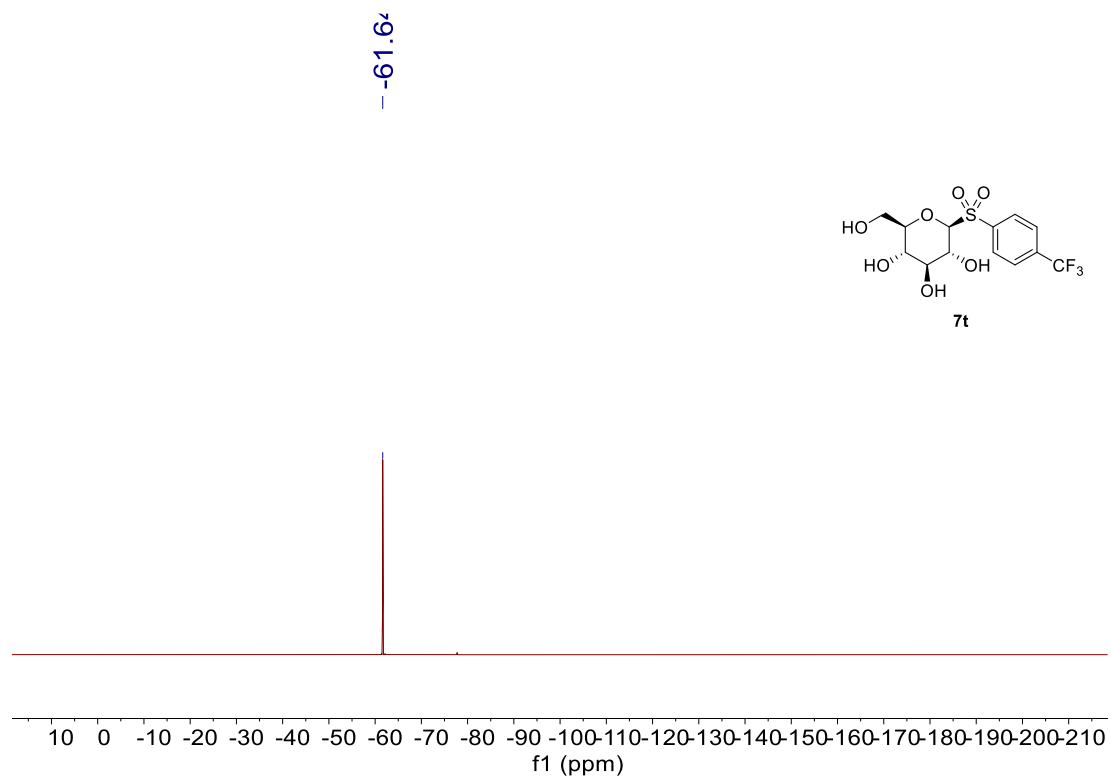


Figure S74. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) Spectra for compound 7t

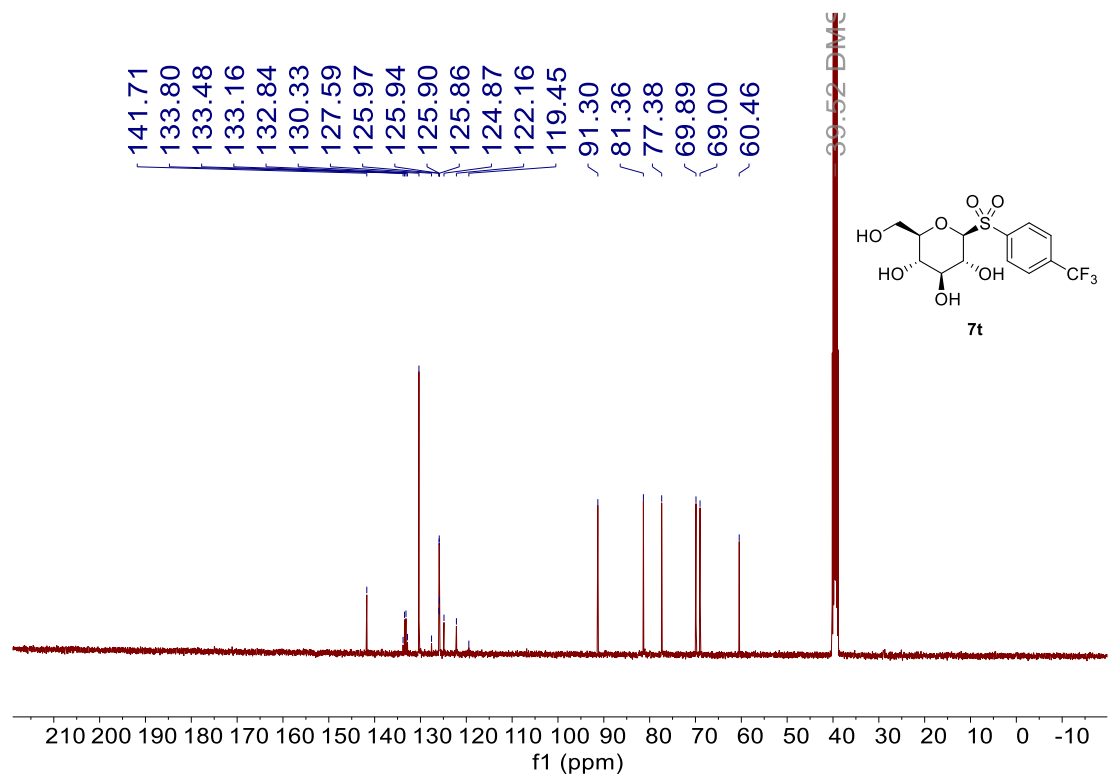


Figure S75. ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) Spectra for compound 7t

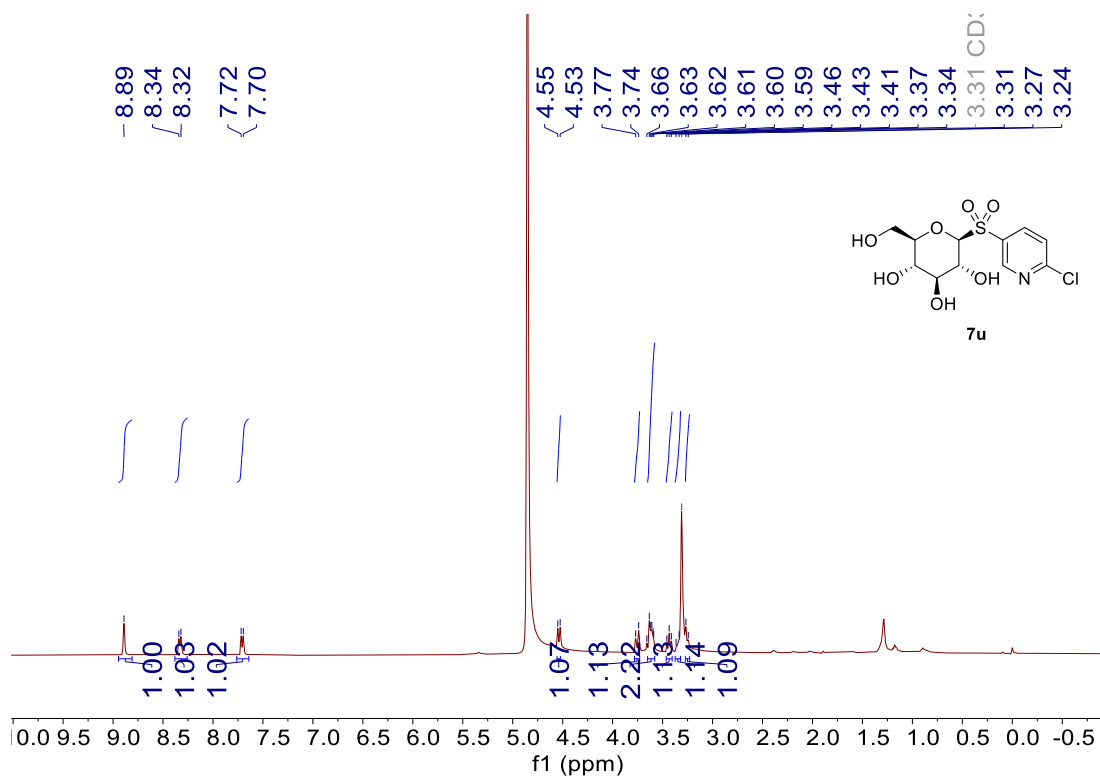


Figure S76. ¹H NMR (400 MHz, MeOD) Spectra for compound 7u

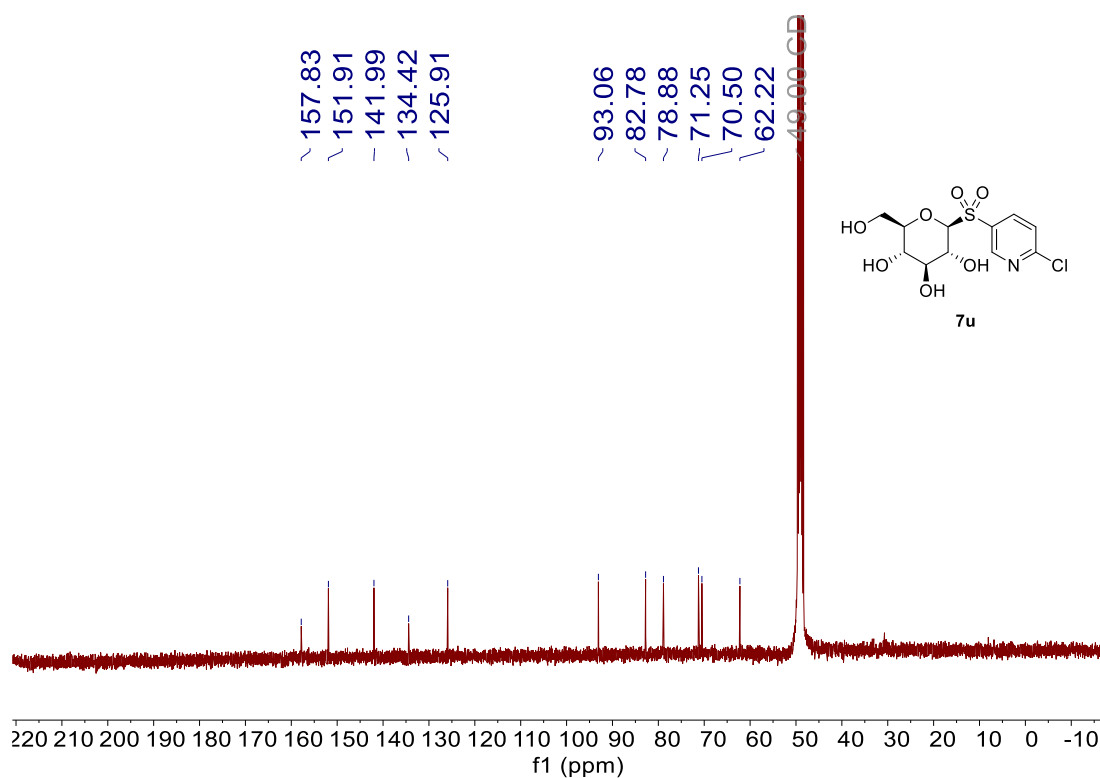


Figure S77. ¹³C NMR (101 MHz, MeOD) Spectra for compound 7u

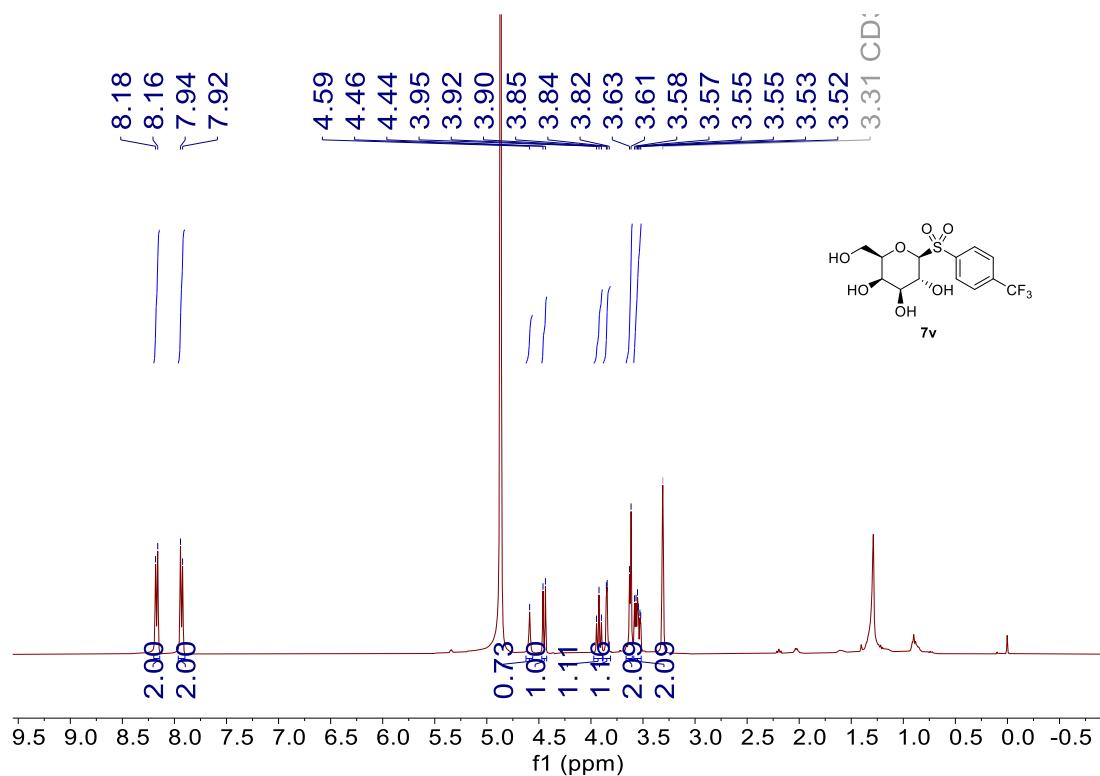


Figure S78. ¹H NMR (400 MHz, MeOD) Spectra for compound 7v

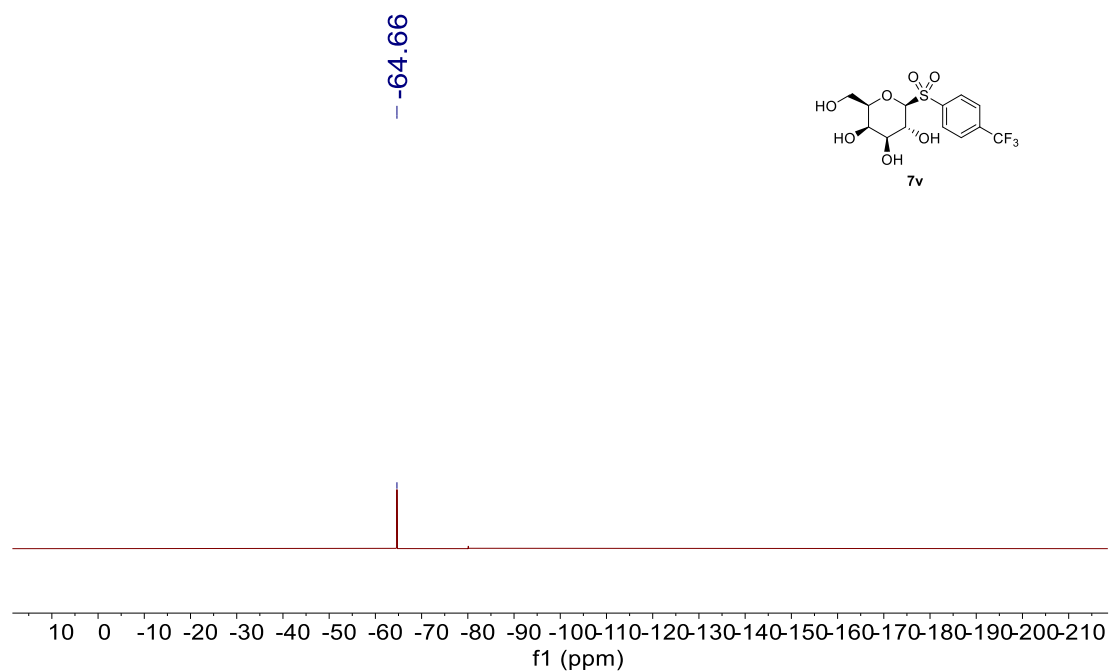


Figure S79. ¹⁹F NMR (376 MHz, MeOD) Spectra for compound 7v

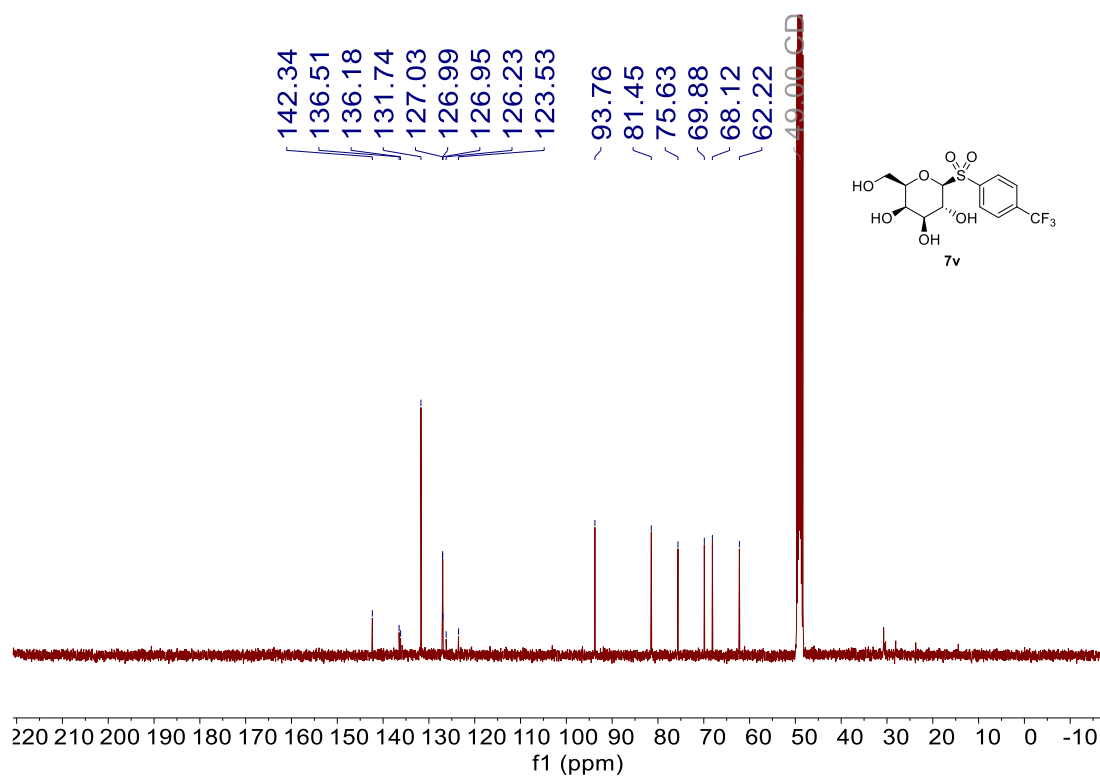


Figure S80. ¹³C NMR (101 MHz, MeOD) Spectra for compound 7v

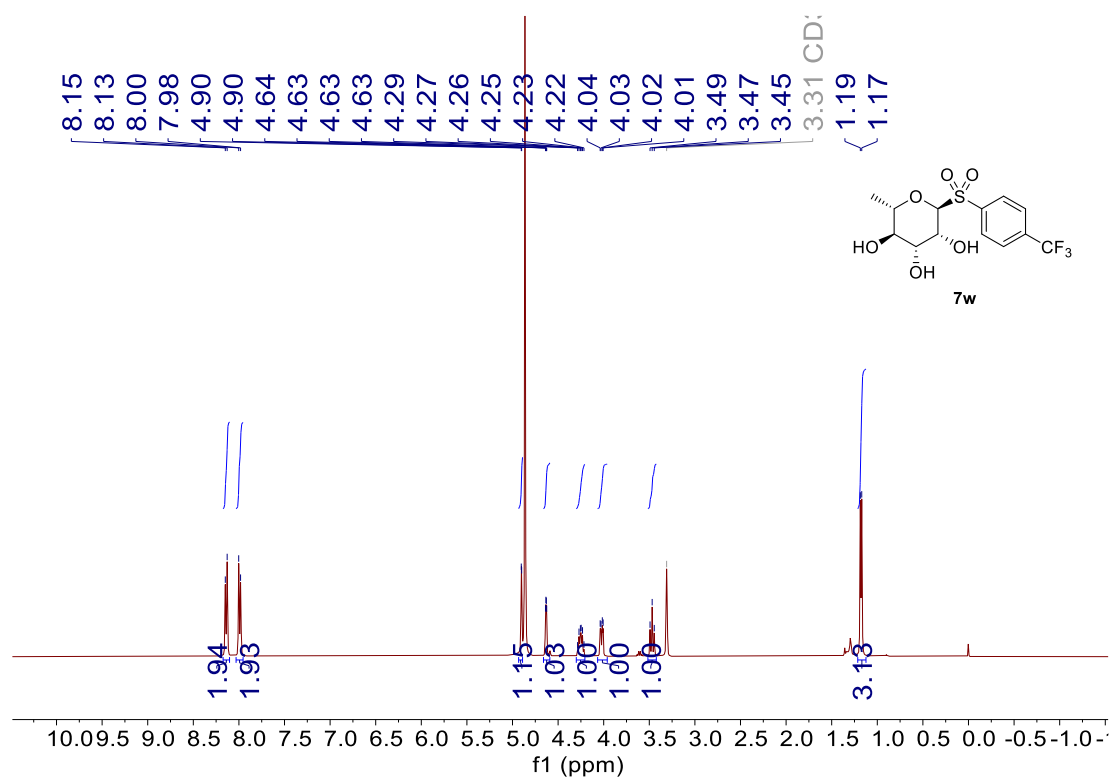
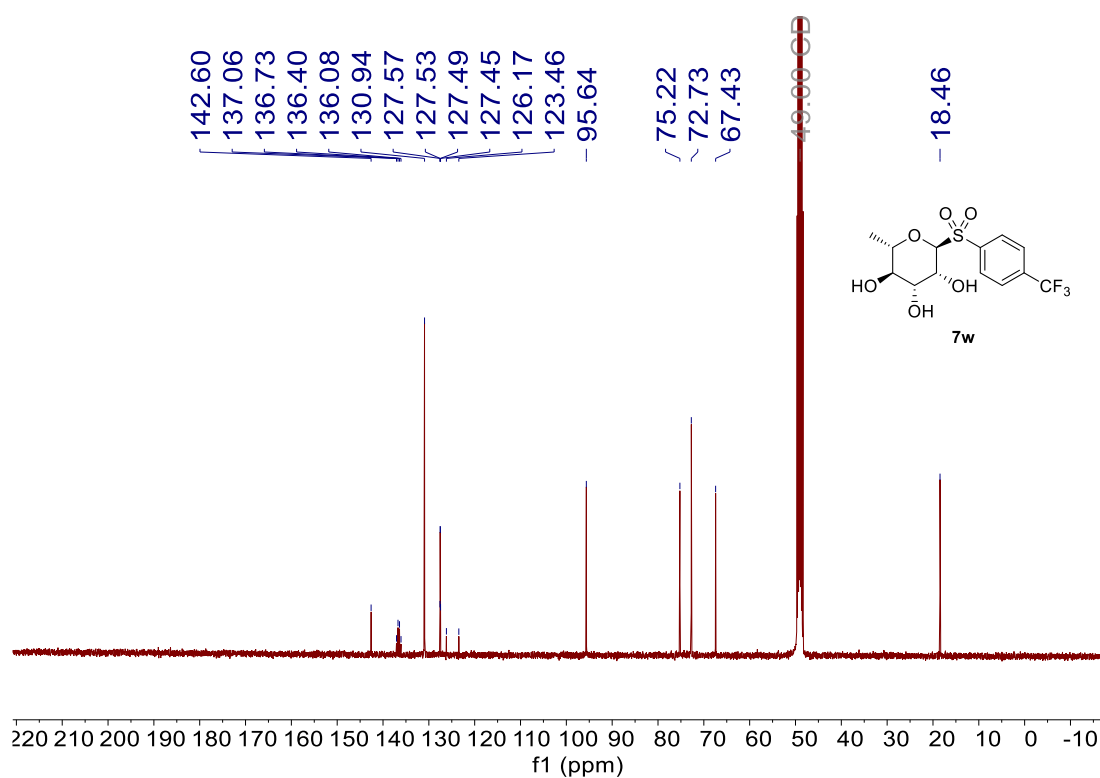
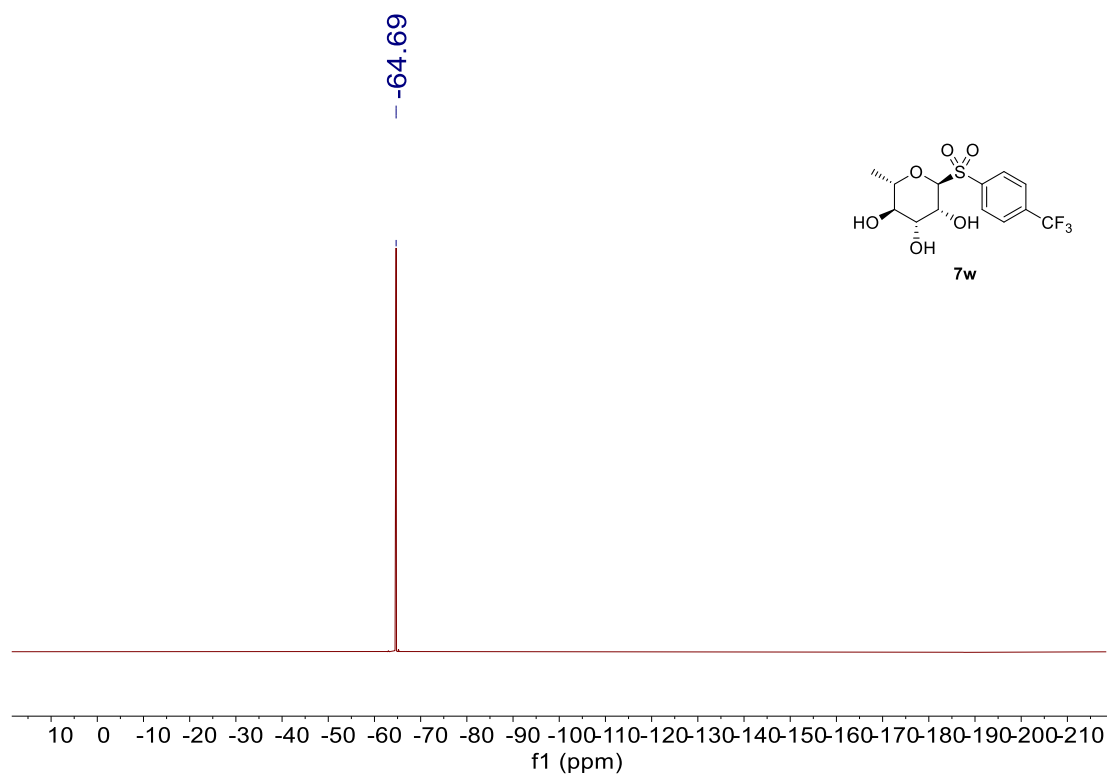


Figure S81. ¹H NMR (400 MHz, MeOD) Spectra for compound 7w



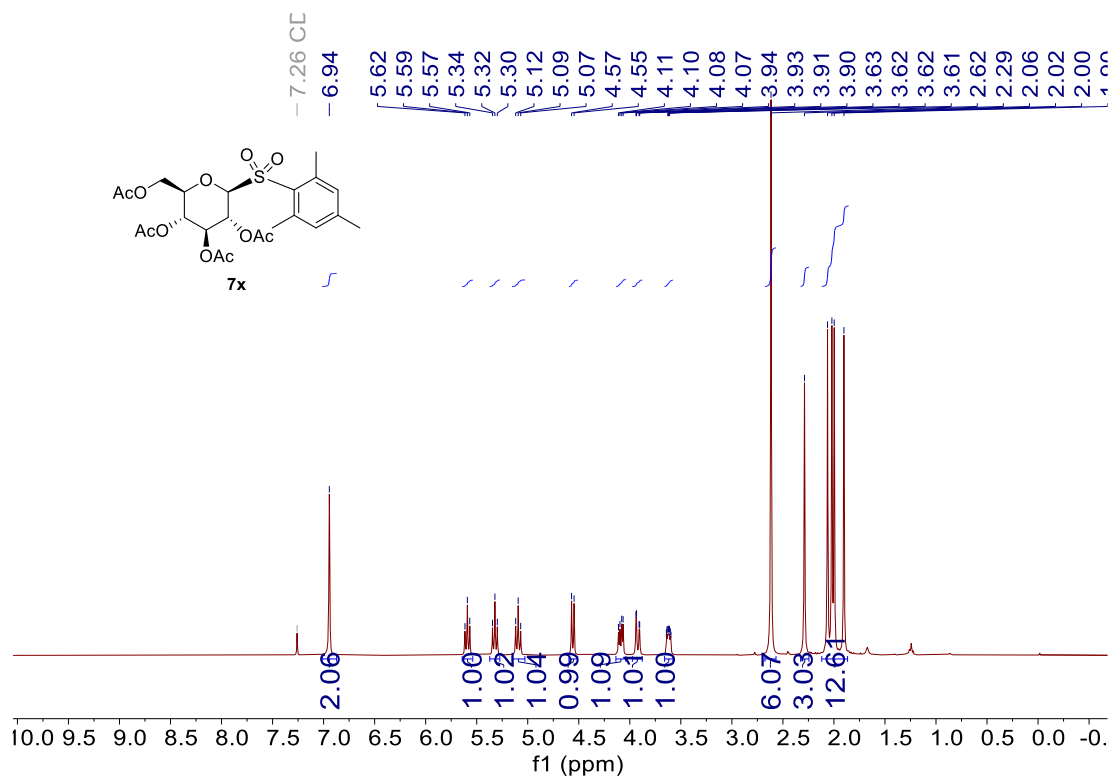


Figure S84 ¹H NMR (400 MHz, CDCl₃) Spectra for compound 7x

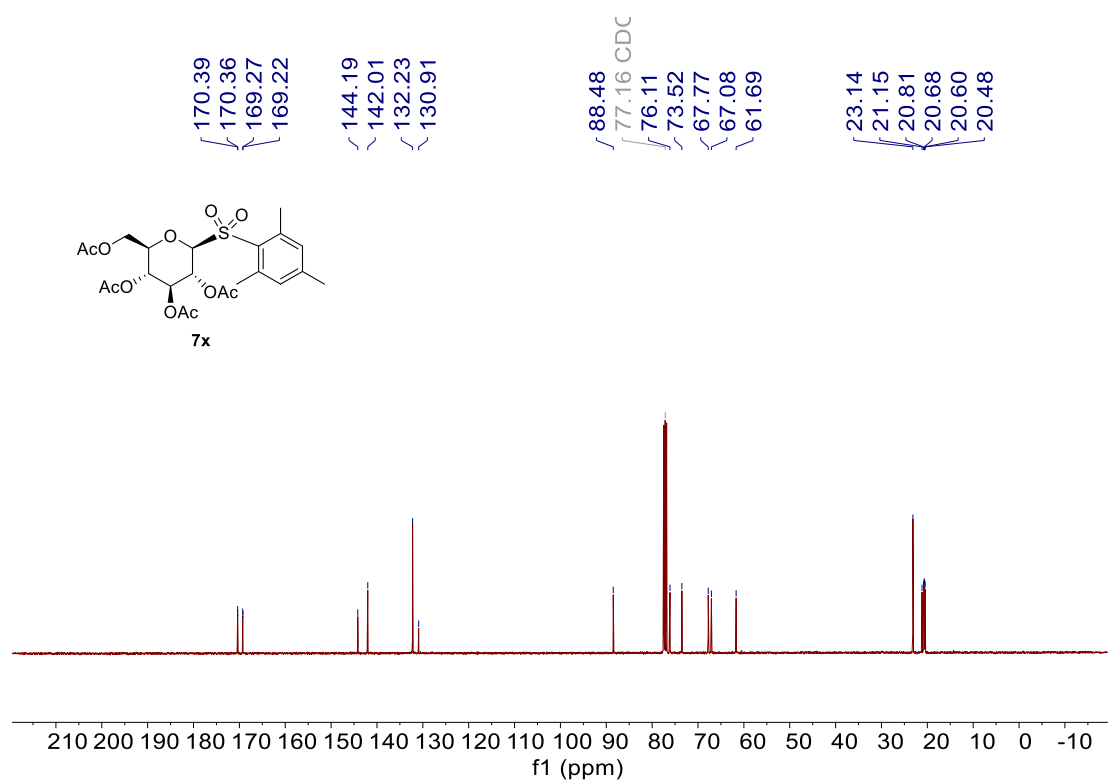


Figure S85. ¹³C NMR (101 MHz, CDCl₃) Spectra for compound 7x

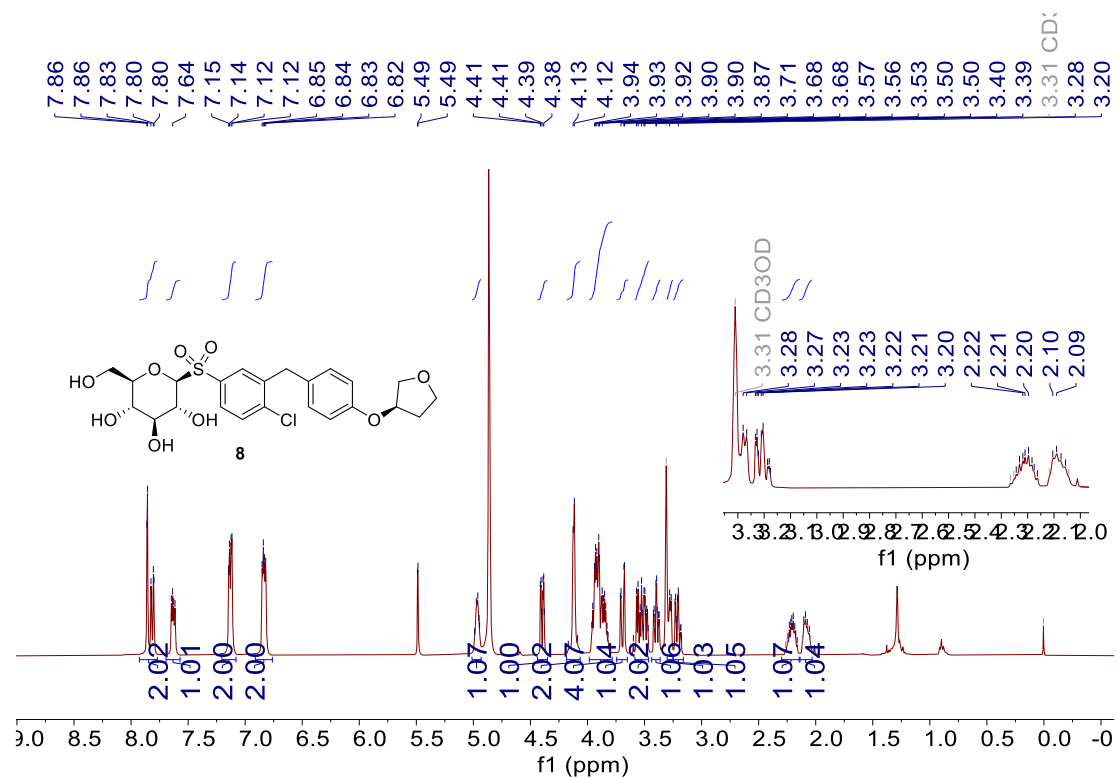


Figure S86. ¹H NMR (400 MHz, MeOD) Spectra for compound 8

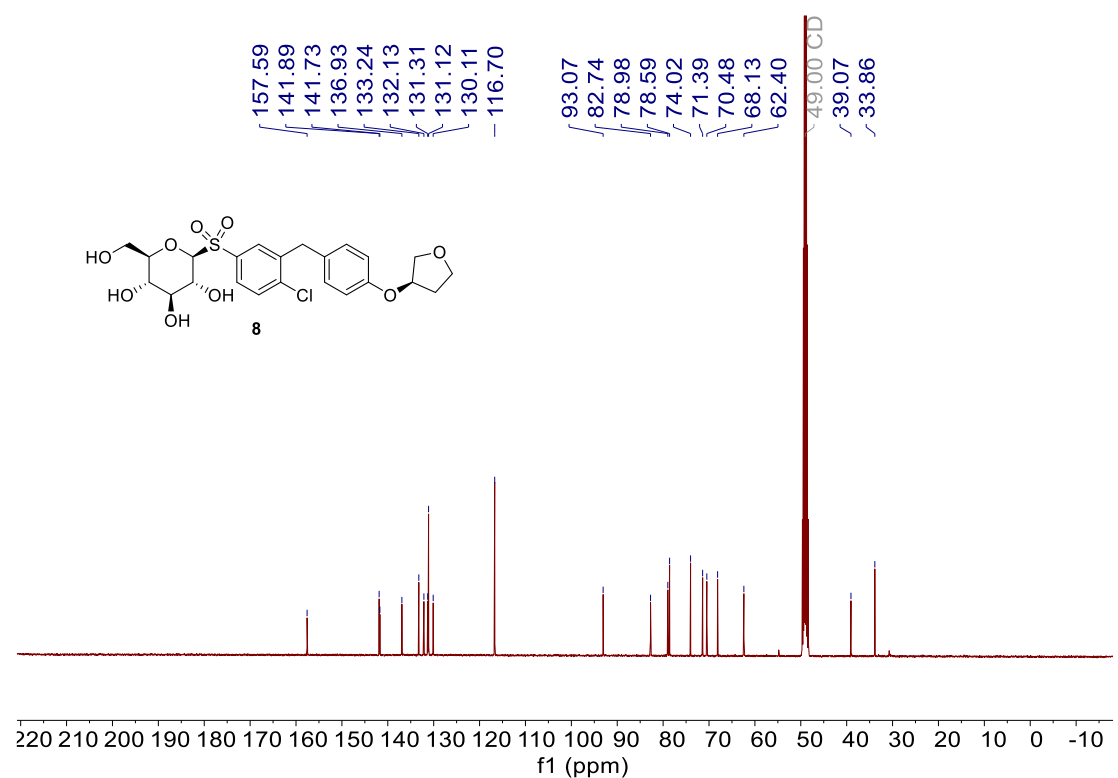


Figure S87. ¹³C NMR (101 MHz, MeOD) Spectra for compound 8