Supporting Information

Excited-State Palladium-Catalyzed 1,2-Spin-Center Shift Enables Selective C-2 Reduction, Deuteriation, and Iodination of Carbohydrates

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General Information

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin-layer chromatography (TLC) using Agela Technologies TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash column chromatography was performed on SiliaFlash® Silica Gel 40-63μm 60 Å particle size using a forced flow of eluent at 0.3–0.5 bar pressure.[1] Preparative TLC was performed on Uniplate® UV254 (20 x 20 cm) with 1000 μm thickness and visualized fluorescence quenching under UV light.

All air and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. All reaction vials were capped using green caps with F-217 PTFE liners. Isopropyl acetate was distilled from calcium chloride $CaCl_2$. Diethyl ether and THF were distilled from deep purple sodium benzophenone ketyl. Acetonitrile was dried over CaH_2 and distilled. Isopropyl acetate and acetonitrile were degassed *via* three freeze-pump-thaw cycles. All other chemicals were used as received.

All deuterated solvents were purchased from Cambridge Isotope Laboratories. NMR spectra were recorded on either a Bruker Ascend 700 spectrometer operating at 700 MHz for ^{1}H acquisitions and 175 MHz for ^{13}C acquisitions, a Bruker 500 Advance spectrometer operating at 500 MHz for ^{1}H acquisitions and 125 MHz for ^{13}C acquisitions. A Bruker 400 Nanobay spectrometer was operating at 400 MHz, 100 MHz, and 376 MHz for ^{1}H, ^{13}C, and ^{19}F acquisitions, respectively. Chemical shifts were referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.26; CD_3CN, δ 1.94) and ^{13}C solvent signals ($CDCl_3$, δ 77.16; CD_3CN, δ 118.26).[2] Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration.

UV-Vis Absorptions were measured on a Cary 100 UV-Vis spectrophotometer from Agilent Technologies. Emission intensities were recorded using a Perkin Elmer LS50B Luminescence spectrometer. High-resolution mass spectra were performed at Mass Spectrometry Services at Stony Brook University and were obtained using an Agilent LC-UV-TOF mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 °C at the appropriate pressure. Purified compounds were further dried under a high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

The blue light-emitting diodes used for the quantum yield measurements: 30 W Blue LEDs (LEDs, 30 W Royal Blue 455 nm, chip size = 45.0 x 45.0 mm) and the heat sink (diameter: 90.0 mm) were purchased from Babaoshop on eBay (https://www.ebay.com/usr/babaoshop).

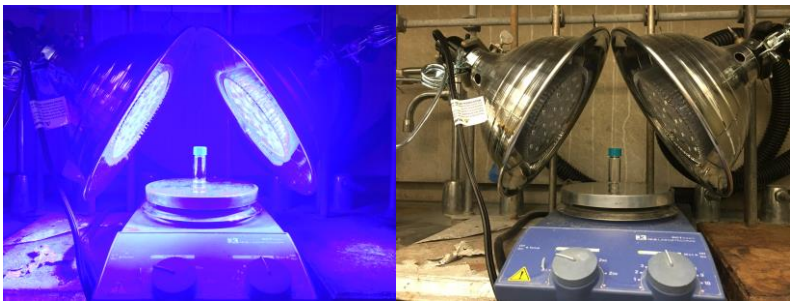
Abbreviations: DCM = dichloromethane; THF = tetrahydrofuran; MsCl = methanesulfonyl chloride; DIAD = Diisopropyl azodicarboxylate; DMAP = 4-dimethylaminopyridine; DCC = *N,N'*-Dicyclohexylcarbodiim - ide; EDCI·HCl = *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride; DIPEA = *N,N*-Diisopropylethylamine.

Photoredox Reaction Setup

LED Light: 12 W PAR38 Blue LED flood lamps from ABi® LED lighting company.

LED Light

The reaction set up: A 4 mL capped vial was placed on the stirrer. Then two 12 W PAR38 Blue LED flood lamps from ABi were placed at a 45° angle to face the vial (shown in the picture below). The distance between the blue LED lamps and the vial was 8.00 cm.

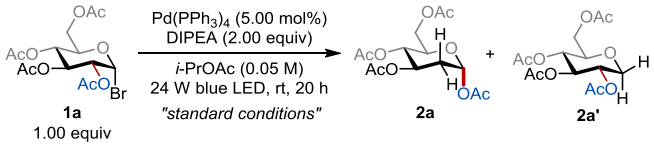


Reaction set up

Experimental Data

Optimization Table

Table S1. Selected optimization experiments.[a]

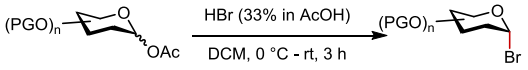


Entry	Deviation from standard conditions	Yield (%)	2a:2a'
1	None	94	>20:1
2	PPh_3 (20 mol%) instead of $Pd(PPh_3)_4$	N.R.	-
3	$(PPh_3)_2PdCl_2$ instead of $Pd(PPh_3)_4$	17	7:1
4	$Ru(bpy)_3(PF_6)_2$ instead of $Pd(PPh_3)_4$	28	10:1
5	$Ir(ppy)_2(dtbpy)PF_6$ instead of $Pd(PPh_3)_4$	52	11:1
6	Eosin Y free acid instead of $Pd(PPh_3)_4$	49	4:1
7	MeCN as solvent	50	10:1
8	Without DIPEA	N.R.	-
9	Air	N.R.	-
10	Keep in dark	N.R.	-

[a]Reaction yields and C-2:C-1 ratios were determined by ^{1}H-NMR using CH_2Br_2 as an internal standard. Ac, acetyl; DIPEA, *N*,*N*-diisopropylethylamine; *i*-PrOAc, isopropyl acetate; LED, light-emitting diode; rt, room temperature; h, hours; dtbpy, 4,4′-Di-tert-butyl-2,2′-dipyridyl; MeCN, acetonitrile; N.R., no reaction.

C-2 Reduction of 1-bromosugars via excited-state Pd-catalysis

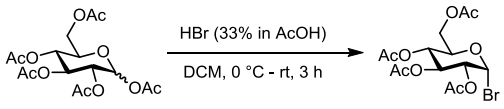
General Procedure A (for the synthesis of 1-bromosugars):



1a-1z

The C-1 acetyl protected sugar (1.00 equiv) was dissolved in dry DCM (0.500 M) and cooled to 0 °C. HBr (33% Wt in AcOH, 2.00 equiv) was added, and the reaction mixture was slowly warmed to room temp over 10 min. After stirring at room temperature for 3 h, the reaction mixture was poured onto an ice/water mixture. The organic phase was collected and the aqueous phase was extracted with DCM twice. The combined organic layers were washed with satd. $NaHCO_3$, brine, dried over Mg_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel to afford the desired compound.

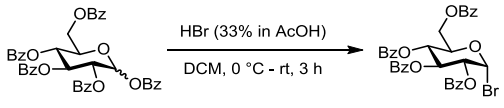
2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1a)



S1 **1a**

The reaction was performed according to the General Procedure A using **S1** (2.00 g, 5.13 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (1.85 g, 4.50 mmol, 88%) as a white solid. $\mathbf{R_f}$ = 0.65 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.58 (d, *J* = 4.0 Hz, 1H), 5.52 (t, *J* = 9.7 Hz, 1H), 5.13 (t, *J* = 9.8 Hz, 1H), 4.81 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.13 – 4.06 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.52, 169.87, 169.82, 169.50, 86.66, 72.20, 70.64, 70.21, 67.21, 61.00, 20.72, 20.70, 20.67, 20.60. The spectroscopic data corresponds to previously reported data.[3]

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (1b)

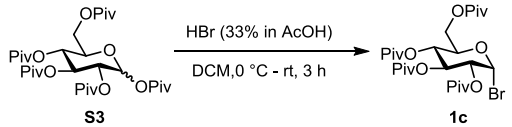


S2 **1b**

The reaction was performed according to the General Procedure A using **S2** (2.00 g, 2.86 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (1.51 g, 2.29 mmol, 80%) as a white solid. $\mathbf{R_f}$ = 0.68 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.07 (d, *J* = 7.3

Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.50 (m, 3H), 7.47 – 7.35 (m, 7H), 7.31 (t, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 4.0 Hz, 1H), 6.27 (t, *J* = 9.8 Hz, 1H), 5.83 (t, *J* = 10.0 Hz, 1H), 5.34 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.80 – 4.71 (m, 1H), 4.68 (dd, *J* = 12.5, 2.6 Hz, 1H), 4.52 (dd, *J* = 12.5, 4.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.16, 165.70, 165.44, 165.23, 133.94, 133.78, 133.49, 133.40, 130.22, 130.07, 129.97, 129.88, 129.59, 128.94, 128.70, 128.66, 128.63, 128.60, 128.50, 87.01, 72.85, 71.61, 70.76, 68.13, 62.08. The spectroscopic data corresponds to previously reported data.[4]

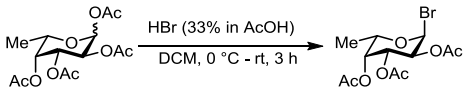
2,3,4,6-Tetra-*O*-pivotal-α-D-glucopyranosyl bromide (1c)



S3 **1c**

The reaction was performed according to the General Procedure A using **S3** (2.00 g, 3.33 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (1.35 g, 2.33 mmol, 70%) as a white solid. $\mathbf{R}_f$ = 0.65 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.61 (d, *J* = 4.1 Hz, 1H), 5.62 (t, *J* = 9.7 Hz, 1H), 5.20 (t, *J* = 10.0 Hz, 1H), 4.80 (dd, *J* = 9.9, 4.1 Hz, 1H), 4.39 – 4.26 (m, 1H), 4.20 – 4.09 (m, 2H), 1.21 (s, 9H), 1.18 (s, 9H), 1.16 (s, 9H), 1.12 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 178.04, 177.43, 176.88, 176.54, 87.01, 72.68, 71.00, 69.70, 66.65, 60.99, 39.02, 38.93, 38.87, 38.79, 27.29, 27.21, 27.17, 27.13. The spectroscopic data corresponds to previously reported data.[5]

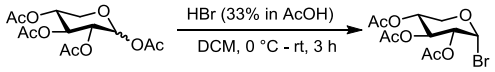
2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl bromide (1d)



S4 **1d**

The reaction was performed according to the General Procedure A using **S4** (2.02 g, 6.00 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [5:1 (v/v)] to afford the title compound (1.66 g, 4.70 mmol, 78%) as a white solid. $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 5:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.68 (d, *J* = 3.5 Hz, 1H), 5.39 (dd, *J* = 10.5, 3.5 Hz, 1H), 5.34 (d, *J* = 3.5 Hz, 1H), 5.01 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H), 1.20 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.37, 170.24, 169.91, 89.40, 70.08, 69.91, 68.51, 67.95, 20.89, 20.73, 20.67, 15.56. The spectroscopic data corresponds to previously reported data.[6]

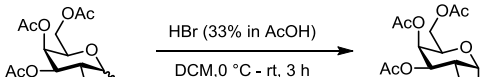
2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl bromide (1e)



S5 **1e**

The reaction was performed according to the General Procedure A using **S5** (2.20 g, 6.90 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (1.30 g, 3.85 mmol, 57%) as a white solid. $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ) 6.57 (d, *J* = 4.2 Hz, 1H), 5.55 (t, *J* = 9.8 Hz, 1H), 5.03 (td, *J* = 9.8, 6.3 Hz, 1H), 4.76 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.04 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.87 (t, *J* = 11.2 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 169.98, 169.98, 169.89, 87.70, 70.98, 69.61, 68.20, 62.64, 20.81, 20.80, 20.77. The spectroscopic data corresponds to previously reported data.[7]

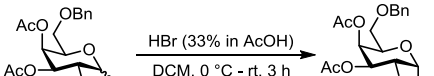
2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl bromide (1f)



S6 **1f**

The reaction was performed according to the General Procedure A using **S6** (2.00 g, 5.13 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (1.73 g, 4.21 mmol, 82%) as a white solid. $\mathbf{R}_f$ = 0.65 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.69 (d, *J* = 3.9 Hz, 1H), 5.57 – 5.48 (m, 1H), 5.40 (dd, *J* = 10.6, 3.3 Hz, 1H), 5.04 (dd, *J* = 10.6, 4.0 Hz, 1H), 4.48 (t, *J* = 6.6 Hz, 1H), 4.18 (dd, *J* = 11.4, 6.4 Hz, 1H), 4.11 (dd, *J* = 11.4, 6.8 Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.45, 170.20, 170.02, 169.89, 88.25, 71.19, 68.12, 67.90, 67.11, 60.96, 20.88, 20.77, 20.72, 20.69. The spectroscopic data corresponds to previously reported data.[3]

2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-α-D-galactopyranosyl bromide (1g)

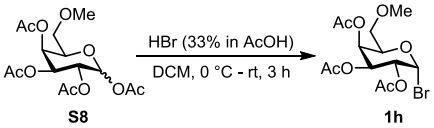


S7 **1g**

The reaction was performed according to the General Procedure A using **S7** (635 mg, 1.45 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (315 mg, 0.78 mmol 47%) as a white solid. $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (m, 3H), 6.70 (d, *J* = 3.9 Hz, 1H), 5.57 (d, *J* = 2.7 Hz, 1H), 5.40 (dd, *J* = 10.6, 2.7 Hz, 1H), 5.03 (dd, *J* = 10.6, 3.9 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.45 (t, *J* = 6.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H),

3.54 (dd, *J* = 9.8, 6.0 Hz, 1H), 3.48 (dd, *J* = 9.8, 6.0 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.23, 169.95, 169.83, 137.37, 128.60, 128.60, 128.04, 128.04, 128.04, 88.77, 73.57, 72.17, 68.29, 68.08, 67.50, 66.84, 20.88, 20.73, 20.65. The spectroscopic data corresponds to previously reported data.[8]

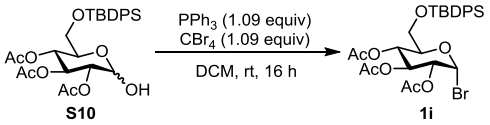
2,3,4-Tri-*O*-acetyl-6-*O*-methyl-α-D-galactopyranosyl bromide (1h)



S8 **1h**

The reaction was performed according to the General Procedure A using **S8** (307 mg, 0.85 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (207 mg, 0.54 mmol, 64%) as a white solid. $\mathbf{R}_f$ = 0.40 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.70 (d, *J* = 4.0 Hz, 1H), 5.57 – 5.46 (m, 1H), 5.39 (dd, *J* = 10.6, 3.0 Hz, 1H), 5.05 (dd, *J* = 10.6, 4.0 Hz, 1H), 4.41 (t, *J* = 6.0 Hz, 1H), 3.51 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.42 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.32 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.23, 170.03, 169.86, 88.74, 72.18, 70.15, 68.30, 68.06, 67.77, 59.44, 20.88, 20.73, 20.69. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{20}BrO_8$ [$(M + H)^+$], 383.0336, found, 383.0335.

2,3,4-Tri-*O*-acetyl-6-*O*-[(1,1-dimethylethyl)diphenylsilyl]-α-D-glucopyranosyl bromide (1i)

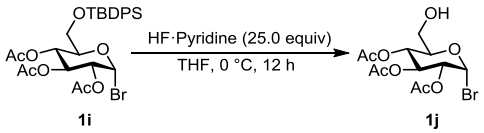


S10 **1i**

To a solution of the **S10** (571 mg, 1.05 mmol, 1.00 equiv) in dry DCM (2.00 mL) was added triphenylphosphine (301 mg, 1.15 mmol, 1.09 equiv) and tetrabromomethane (383 mg, 1.15 mmol, 1.09 equiv). The reaction mixture was stirred under nitrogen at room temperature for 16 h. Saturated $NaHCO_3$ was added until the pH of the solution became neutral. The organic layer was collected, washed with brine, dried with solid anhydrous Mg_2SO_4 and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [8:1 (v/v)] to afford the title compound (171 mg, 0.28 mmol, 27%) as a white foam. $\mathbf{R}_f$ = 0.70 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.63 (dd, *J* = 16.1, 7.0 Hz, 4H), 7.34-7.46 (m, 6H), 6.67 (d, *J* = 3.5 Hz, 1H), 5.54 (t, *J* = 9.8 Hz, 1H), 5.35 (t, *J* = 9.8 Hz, 1H), 4.82 (dd, *J* = 10.5, 4.2 Hz, 1H), 4.13 (d, *J* = 10.5 Hz, 1H), 3.76 (dd, *J* = 11.9, 1.4 Hz, 1H), 3.72 (dd, *J* = 11.9, 4.2 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.93 (s, 3H), 1.05 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.28, 170.04, 169.39, 135.81, 135.81, 135.79, 135.79, 133.00, 132.92, 129.69, 129.93, 127.88, 127.88, 127.88, 127.88 87.68, 74.85, 70.97, 70.82, 67.40, 61.54,

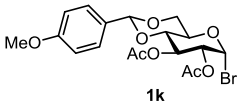
26.85, 26.85, 26.85, 20.86, 20.86, 20.67, 19.35. The spectroscopic data corresponds to previously reported data.[9]

2,3,4-Tri-*O*-acetyl-α-D-glucopyranosyl bromide (1j)



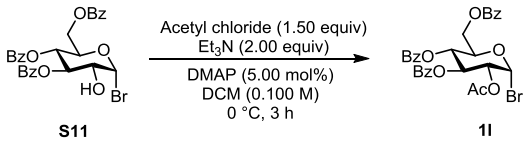
To a 50 mL round bottom flask was added compound **1i** (606 mg, 1.00 mmol, 1.00 equiv), anhydrous tetrahydrofuran (4.80 mL, 0.210 M), and HF-Py (0.66 mL, 70% HF in pyridine). The reaction mixture was stirred under nitrogen at 0 °C for 12 h. The solvent and excess HF-Py was removed by sparging N_2 gas at 0 °C and the residue was purified by silica gel column chromatography, eluting with Hexanes: EtOAc [7:1 to 2:1 (v/v)] to afford the title compound (234 mg, 0.64 mmol, 64%) as a white foam. $\mathbf{R_f}$ = 0.25 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.64 (d, *J* = 4.0 Hz, 1H), 5.63 (t, *J* = 10.0 Hz, 1H), 5.14 (t, *J* = 10.0 Hz, 1H), 4.81 (ddd, *J* = 10.0, 4.0, 0.7 Hz, 1H), 4.08 (d, *J* = 10.0 Hz, 1H), 3.78 (dd, *J* = 13.2, 0.7 Hz, 1H), 3.63 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.10 (s), 2.09 (s), 2.05 (s). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.71, 169.95, 86.98, 77.34, 77.16, 76.98, 74.48, 70.94, 69.90, 67.75, 60.42, 20.79. The spectroscopic data corresponds to previously reported data.[9]

2,3-Di-*O*-acetyl-4,6-*O*-[(*R*)-(4-methoxyphenyl)methylene]-α-D-glucopyranosyl bromide (1k)



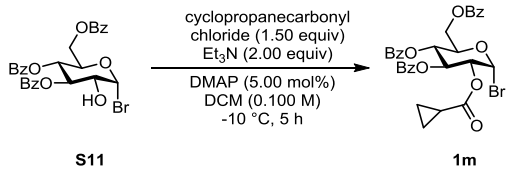
The title compound was prepared according to the literature procedure.[10] **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.37 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 4.1 Hz, 1H), 5.65 (t, *J* = 9.8 Hz, 1H), 5.47 (s, 1H), 4.84 (dd, *J* = 9.7, 4.1 Hz, 1H), 4.32 (dd, *J* = 10.2, 4.9 Hz, 1H), 4.23 (td, *J* = 9.8, 5.0 Hz, 1H), 3.86 – 3.63 (m, 5H), 2.11 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ºC, δ): 170.15, 169.61, 160.35, 129.12, 127.63, 113.75, 101.87, 87.11, 78.15, 71.52, 68.91, 67.94, 67.09, 55.41, 20.88, 20.81. The spectroscopic data corresponds to previously reported data.[10]

3,4,6-Tri-*O*-Benzoyl -2-*O*-acetyl-α-D-glucopyranosyl bromide (1l)



The title compound was prepared according to the literature procedure.[11] To a solution of **S11** (278 mg, 0.500 mmol, 1.00 equiv) in dry DCM (3.00 mL) was added Et_3N (101 mg, 1.00 mmol, 2.00 equiv), acetyl chloride (58.9 mg, 0.750 mmol, 1.50 equiv) and DMAP (3.05 mg, 0.0250 mmol, 5.00 mol%) at 0 °C. After the reaction mixture was stirred at 0 °C for 3 h, it was quenched with saturated $NaHCO_3$ solution (6.00 mL) and extracted with DCM (2 × 50 mL). The combined organic layers were washed with brine, dried with anhydrous Mg_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (194 mg, 0.330 mmol, 65%) as a white solid. $\mathbf{R_f}$ = 0.70 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C, δ): 8.08 – 8.01 (m, 2H), 7.91 (dt, *J* = 8.4, 4.3 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 (td, *J* = 7.6, 1.1 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.37 (td, *J* = 8.0, 2.4 Hz, 4H), 6.72 (d, *J* = 4.0 Hz, 1H), 6.08 (t, *J* = 9.8 Hz, 1H), 5.72 (t, *J* = 9.8 Hz, 1H), 5.12 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.72 – 4.60 (m, 2H), 4.47 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.04 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C, δ): 170.07, 166.13, 165.57, 165.23, 133.76, 133.60, 133.39, 130.08, 129.96, 129.93, 129.59, 128.95, 128.62, 128.61, 128.59, 86.84, 72.77, 71.03, 70.64, 68.24, 62.04, 20.80. **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{26}BrO_9$ [(M + H)$^+$], 597.0755, found, 597.0755. The spectroscopic data corresponds to previously reported data.[11]

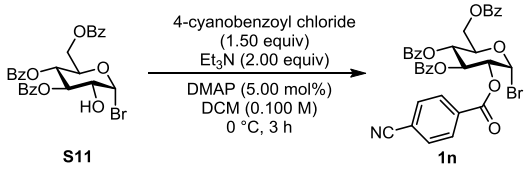
3,4,6-Tri-*O*-Benzoyl-2-*O*-cyclopropanecarbonyl-α-D-glucopyranosyl bromide (1m)



S11 **1m**

To a solution of **S11** (278 mg, 0.500 mmol, 1.00 equiv) in dry DCM (3.00 mL) was added Et_3N (101 mg, 1.00 mmol, 2.00 equiv), Cyclopropanecarbonyl chloride (78.4 mg, 0.750 mmol, 1.50 equiv) and DMAP (3.05 mg, 0.0250 mmol, 5.00 mol%) at -10 °C. After the reaction mixture was stirred at -10 °C for 5 h, work up according to the same procedure as synthesizing **1l**. The reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (224 mg, 0.359 mmol, 72%) as a white solid. $\mathbf{R_f}$ = 0.70 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C, δ):δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.93 (t, *J* = 8.0 Hz, 4H), 7.54 (dt, *J* = 25.5, 7.4 Hz, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 (td, *J* = 7.7, 4.0 Hz, 4H), 6.70 (d, *J* = 3.9 Hz, 1H), 6.07 (t, *J* = 9.8 Hz, 1H), 5.73 (t, *J* = 9.9 Hz, 1H), 5.13 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.69 – 4.58 (m, 2H), 4.47 (dd, *J* = 12.3, 4.2 Hz, 1H), 1.60 – 1.52 (m, 1H), 0.98 – 0.94 (m, 2H), 0.82 – 0.80 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C, δ): 173.69, 166.12, 165.62, 165.19, 133.74, 133.55, 133.36, 130.05, 129.92, 129.56, 128.97, 128.64, 128.60, 128.56, 87.08, 72.75, 70.74, 68.12, 62.04, 12.93, 9.19, 9.14. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{28}BrO_9$ [(M + H)$^+$], 623.0911, found, 623.0914.

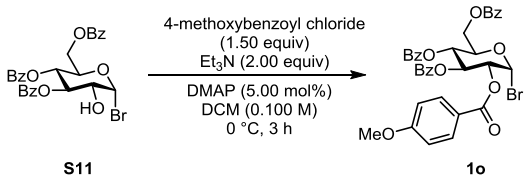
3,4,6-Tri-*O*-Benzoyl-2-*O*-(4-cyanobenzoyl)-α-D-glucopyranosyl bromide (1n)



S11 **1n**

The reaction was performed according to the same procedure as synthesizing **1l**. 4-Cyanobenzoyl chloride (124 mg, 0.750 mmol, 1.50 equiv) was used as the acylating agent. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (256 mg, 0.374 mmol, 75%) as a white solid. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.10 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.46 (q, *J* = 7.3 Hz, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 4.0 Hz, 1H), 6.25 (t, *J* = 9.8 Hz, 1H), 5.84 (t, *J* = 10.0 Hz, 1H), 5.32 (dd, *J* = 9.9, 4.1 Hz, 1H), 4.78 – 4.71 (m, 1H), 4.68 (dd, *J* = 12.5, 2.6 Hz, 1H), 4.52 (dd, *J* = 12.5, 4.5 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.13, 165.71, 165.18, 163.86, 133.89, 133.72, 133.46, 132.54, 132.30, 130.68, 130.07, 129.97, 129.89, 129.53, 128.68, 128.63, 128.61, 128.53, 117.87, 117.37, 86.42, 72.93, 72.27, 70.72, 67.85, 61.96. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{27}BrNO_9$ [$(M + H)^+$], 684.0864, found, 684.0869.

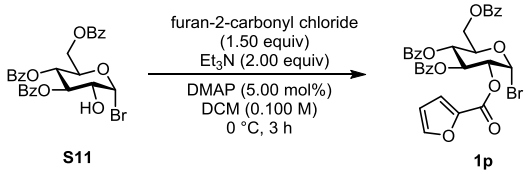
3,4,6-Tri-*O*-Benzoyl-2-*O*-(4-methoxybenzoyl)-α-D-glucopyranosyl bromide (1o)



S11 **1o**

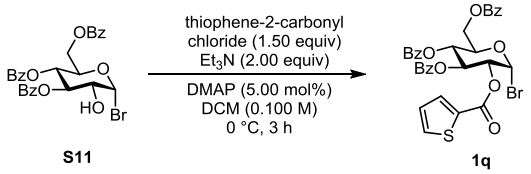
The reaction was performed according to the same procedure as synthesizing **1l**. 4-Methoxybenzoyl chloride (128 mg, 0.750 mmol, 1.50 equiv) was used as the acylating agent. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (189 mg, 0.274 mmol, 55%) as a white solid. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.07 (d, *J* = 7.9 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 4H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 3H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.24 (t, *J* = 9.7 Hz, 1H), 5.81 (t, *J* = 9.9 Hz, 1H), 5.29 (dd, *J* = 9.8, 3.4 Hz, 1H), 4.72 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.51 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.18, 165.73, 165.24, 165.11, 164.19, 133.78, 133.47, 133.40, 132.39, 130.08, 129.97, 129.89, 129.59, 128.99, 128.68, 128.63, 128.61, 128.51, 120.82, 114.00, 87.32, 72.83, 71.35, 70.80, 68.13, 62.10, 55.61. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{33}BrNO_{10}$ [$(M + NH_4)^+$], 706.1282, found, 706.1289.

3,4,6-Tri-*O*-Benzoyl-2-*O*-(furan-2-carbonyl)-α-D-glucopyranosyl bromide (1p)



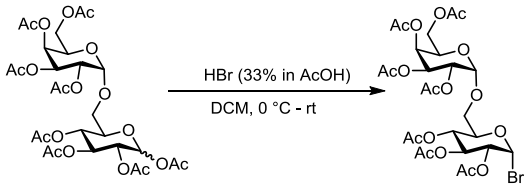
The reaction was performed according to the same procedure as synthesizing **1l**. Furan-2-carbonyl chloride (97.5 mg, 0.750 mmol, 1.50 equiv) was used as the acylating agent. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (198 mg, 0.305 mmol, 61%) as a white solid. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.06 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 10.1 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 3.1 Hz, 1H), 6.82 (d, *J* = 3.7 Hz, 1H), 6.47 (d, *J* = 1.4 Hz, 1H), 6.20 (t, *J* = 9.8 Hz, 1H), 5.79 (t, *J* = 9.9 Hz, 1H), 5.29 (dd, *J* = 9.9, 3.6 Hz, 1H), 4.71 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.50 (dd, *J* = 12.4, 4.6 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.16, 165.61, 165.20, 157.21, 147.79, 143.01, 133.80, 133.54, 133.42, 130.09, 129.98, 129.91, 129.57, 128.91, 128.64, 128.61, 128.55, 120.26, 112.31, 86.71, 72.83, 71.39, 70.65, 68.09, 62.01. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{26}BrO_{10}$ [$(M + H)^+$], 649.0704, found, 649.0704.

3,4,6-Tri-*O*-Benzoyl-2-*O*-(thiophene-2-carbonyl)-α-D-glucopyranosyl bromide (1q)



The reaction was performed according to the same procedure as synthesizing **1l**. Thiophene-2-carbonyl chloride (110 mg, 0.750 mmol, 1.50 equiv) was used as the acylating agent. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (219 mg, 0.329 mmol, 66%) as a white solid. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.06 (d, *J* = 7.2 Hz, 2H), 7.97 – 7.92 (m, 2H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.80 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 14.4, 6.3 Hz, 3H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.10 – 7.00 (m, 1H), 6.85 (d, *J* = 4.0 Hz, 1H), 6.22 (t, *J* = 9.8 Hz, 1H), 5.80 (t, *J* = 10.0 Hz, 1H), 5.26 (dd, *J* = 9.9, 4.1 Hz, 1H), 4.75 – 4.68 (m, 1H), 4.66 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.50 (dd, *J* = 12.5, 4.5 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.17, 165.60, 165.22, 160.95, 135.13, 134.24, 133.80, 133.49, 133.42, 131.81, 130.09, 129.98, 129.91, 129.58, 128.97, 128.65, 128.61, 128.53, 128.21, 86.83, 72.83, 71.70, 70.66, 68.10, 62.06. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{26}BrO_9S$ [$(M + H)^+$], 665.0475, found, 665.0477.

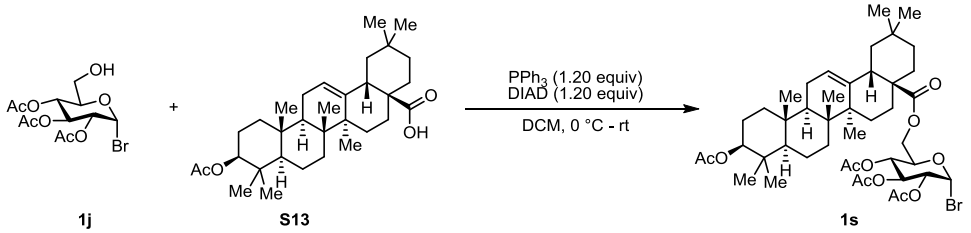
2,3,4,2',3',4',6'-Hepta-*O*-acetyl-α-D-melibiosyl bromide (1r)



S12 1r

The reaction was performed according to the General Procedure A using **S12** (1.22 g, 1.80 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [1.5:1 (v/v)] to afford the title compound (320 mg, 0.460 mmol, 25%) as a white solid. $\mathbf{R}_f$ = 0.70 [Hexanes: EtOAc 1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.58 (d, *J* = 4.2 Hz, 1H), 5.55 (t, *J* = 9.8 Hz, 1H), 5.46 (d, *J* = 3.5 Hz, 1H), 5.32 (dd, *J* = 10.5, 3.5 Hz, 1H), 5.15-5.18 (m, 2H), 5.08 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.78 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.23 (ddd, *J* = 10.5, 4.2, 2.1 Hz, 1H), 4.16 (t, *J* = 7.0 Hz, 1H), 4.06 (qd, *J* = 11.2, 7.0 Hz, 1H), 3.76 (dd, *J* = 11.9, 4.2 Hz, 1H), 3.62 (dd, *J* = 11.9, 2.1 Hz, 1H), 2.13 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.67, 170.50, 170.30, 170.02, 169.98, 169.93, 169.48, 96.37, 86.64, 73.02, 70.72, 70.33, 68.16, 68.06, 67.73, 67.55, 66.56, 65.51, 61.72, 20.93, 20.85, 20.79, 20.79, 20.76, 20.76, 20.72. The spectroscopic data corresponds to previously reported data.[4]

2,3,4-Tri-*O*-acetyl-6-*O*-[((4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-4a-carbonyl)]-α-D-glucopyranosyl bromide (1s)

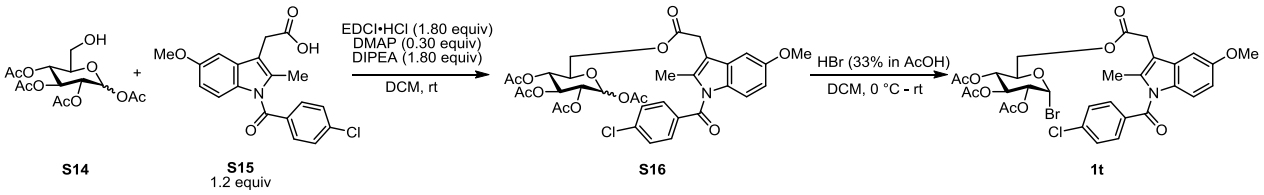


1j S13 1s

To a solution of **1j** (147 mg, 0.400 mmol, 1.00 equiv) and **S13** (239 mg, 0.480 mmol, 1.20 equiv) in dry DCM (8.00 ml, M = 0.0500) was added triphenylphosphine (126 mg, 0.480 mmol, 1.20 equiv) at 0 ºC. DIAD (94.5 ul, 0.480 mmol, 1.20 equiv) was then added dropwise to the resulting mixture. After the reaction mixture was stirred at room temperature for 12 h, the solvent was removed under vacuum. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [9:1 (v/v)] to afford the title compound as an off-white solid (129 mg, 0.152 mmol, 38% yield). $\mathbf{R}_f$ = 0.45 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.59 (d, *J* = 3.5 Hz, 1H), 5.54 (t, *J* = 9.8 Hz, 1H), 5.29 (t, *J* = 3.5 Hz, 1H), 5.12 (t, *J* = 9.8 Hz, 1H), 4.77 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.47-4.50 (m, 1H), 4.30 (dd, *J* = 12.6, 2.1 Hz, 1H), 4.27 (ddd, *J* = 10.5, 4.2, 1.4 Hz, 1H), 4.04 (dd, *J* = 12.6, 4.9 Hz, 1H), 2.83 (dd, *J* = 14.0, 4.2 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.99 (td, *J* = 14.0, 4.2 Hz, 1H), 1.82-1.92 (m, 2H), 1.50-1.71 (m, 11H), 1.45 (td, *J* = 12.6, 4.2 Hz, 1H), 1.37 (td, *J* = 12.6, 2.8 Hz, 1H), 1.33 (td, *J* = 14.0, 4.2 Hz, 1H), 1.23-1.30 (m, 1H), 1.94-1.21 (m, 1H), 1.14-1.17 (m, 1H), 1.12 (s, 3H), 1.09 (dt, *J* = 14.0, 2.8

Hz, 1H), 1.01-1.06 (m, 1H), 0.93 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H), 0.83 (d, *J* = 11.2 Hz, 1H), 0.71 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 177.15, 171.18, 170.05, 169.96, 169.41, 143.54, 122.70, 86.67, 81.07, 72.54, 70.82, 70.36, 67.63, 60.84, 55.43, 47.68, 47.06, 45.96, 41.81, 41.36, 39.41, 38.24, 37.82, 37.06, 33.98, 33.20, 32.79, 32.33, 30.80, 28.18, 27.75, 25.91, 23.69, 23.66, 23.54, 23.21, 21.47, 20.81, 20.79, 20.72, 18.36, 17.06, 16.82, 15.53. **HRMS** (ESI-TOF) *m/z* calcd for $C_{44}H_{66}BrO_{11}$ [$(M + H)^+$], 849.3783, found, 849.3776.

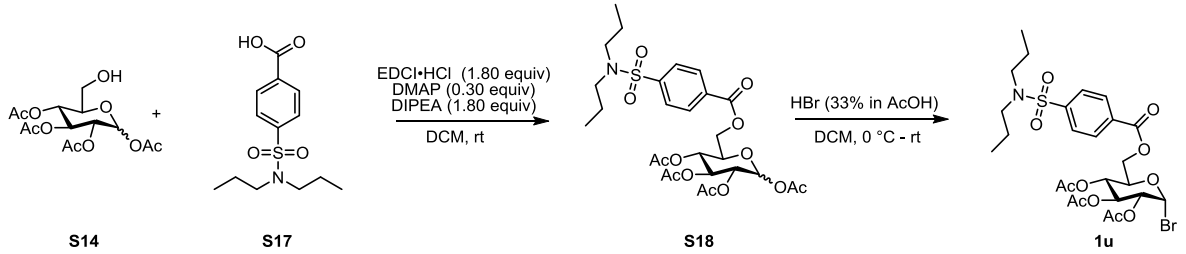
2,3,4-Tri-*O*-acetyl-6-*O*-[(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)carbonyl]-α-D-glucopyranosyl bromide (1t)



To a solution of compound **S14** (294 mg, 0.800 mmol, 1.00 equiv) in dry DCM (4.00 mL, 0.200 M) were added Indomethacin **S15** (344 mg, 0.960 mmol, 1.20 equiv), DMAP (29.3 mg, 0.240 mmol, 0.300 equiv), EDCI·HCl (276 mg, 1.44 mmol, 1.80 equiv) and DIPEA (0.250 mL, 1.44 mmol, 1.80 equiv). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine successively. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph, eluting with Hexanes: EtOAc [3:1 (v/v)] to give **S16** (330 mg, 0.480 mmol, 85% yield) as a colorless oil.

1t was synthesized according to the General Procedure A using **S16** (206 mg, 0.300 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (53.0 mg, 0.07 mmol, 25%) as a white foam. $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.68 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 2.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.67 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.54 (d, *J* = 4.2 Hz, 1H), 5.50 (t, *J* = 9.8 Hz, 1H), 5.03 (t, *J* = 9.8 Hz, 1H), 4.61 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.33 (dd, *J* = 12.6, 3.5 Hz, 1H), 4.25 (ddd, *J* = 10.5, 4.2, 2.1 Hz, 1H), 4.19 (dd, *J* = 12.6, 2.1 Hz, 1H), 3.85 (s, 3H), 3.72 (s, 2H), 2.38 (s, 3H), 2.09 (s, 3H), 2.02 (s, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.39, 169.93, 169.79, 169.44, 168.42, 156.16, 139.30, 136.30, 134.09, 131.35, 131.35, 130.94, 130.66, 129.19, 129.19, 115.12, 112.11, 111.77, 101.51, 86.66, 72.23, 70.70, 70.17, 67.15, 61.33, 55.80, 30.80, 20.78, 20.74, 20.66, 13.49. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{32}BrClNO_{11}$ [$(M + H)^+$], 708.0842, found, 708.0839.

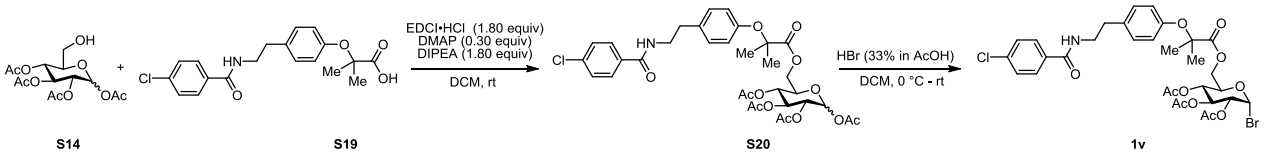
2,3,4-Tri-*O*-acetyl-6-*O*-[(4-(*N*,*N*-dipropylsulfamoyl)benzoyl)]-α-D-glucopyranosyl bromide (1u)



To a solution of compound **S14** (294 mg, 0.800 mmol, 1.00 equiv) in dry DCM (4.00 mL, 0.20 M) were added Probenecid **S17** (274 mg, 0.960 mmol, 1.20 equiv), DMAP (29.3 mg, 0.240 mmol, 0.300 equiv), EDCI·HCl (276 mg, 1.44 mmol, 1.80 equiv) and DIPEA (0.25 mL, 1.44 mmol, 1.80 equiv). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine successively. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph Hexanes: EtOAc [3:1 (v/v)] to give **S18** (209 mg, 0.340 mmol, 46.4% yield) as a colorless oil.

1u was synthesized according to the General Procedure A using **S18** (209 mg, 0.340 mmol, 46% yield) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (90.0 mg, 0.140 mmol, 40%) as a white foam. $\mathbf{R_f}$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.16 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 4.2 Hz, 1H), 5.60 (t, *J* = 9.8 Hz, 1H), 5.26 (t, *J* = 9.8 Hz, 1H), 4.85 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.55 (d, *J* = 12.6, 2.1 Hz, 1H), 4.42-4.49 (m, 2H), 3.05-3.14 (m, 4H), 2.11 (s, 2H), 2.07 (s, 1H), 2.04 (s, 2H), 1.50-1.58 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 6H).**^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 169.98, 169.96, 169.62, 164.85, 144.72, 132.78, 130.58, 130.58, 127.29, 127.29, 86.54, 72.22, 70.72, 70.25, 67.45, 62.07, 50.22, 50.22, 22.19, 22.19, 20.80, 20.76, 20.73, 11.31, 11.31.**HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{35}BrNO_{11}S$ [$(M + H)^+$], 636.1109, found, 636.1113.

2,3,4-Tri-*O*-acetyl-6-*O*-[(2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoyl)]-α-D-glucopyranosyl bromide (1v)

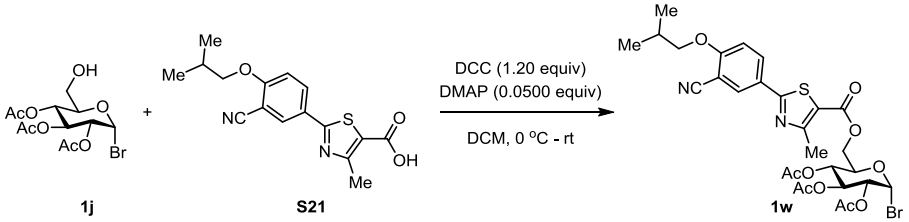


To a solution of compound **S14** (268 mg, 0.770 mmol, 1.00 equiv) in dry DCM (3.85 mL, 0.20 M) were added Bezafibrate **S19** (306 mg, 0.850 mmol, 1.10 equiv), DMAP (28.2 mg, 0.230 mmol, 0.300 equiv), EDCI·HCl (266 mg, 1.39 mmol, 1.80 equiv) and DIPEA (0.24 mL, 1.39 mmol, 1.80 equiv). After stirring at room temperature for 12 h, the reaction mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine successively. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The

residue was purified by silica gel column chromatograph Hexanes: EtOAc [1:1 (v/v)] to give **S20** (470 mg, 0.680 mmol, 88% yield) as a colorless oil.

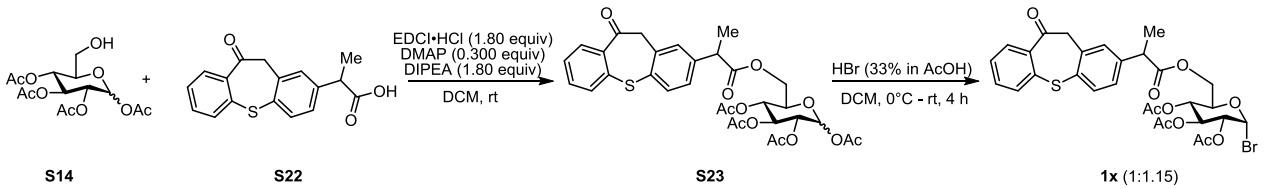
1v was synthesized according to the General Procedure A using **S20** (464 mg, 0.670 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2:1 (v/v)] to afford the title compound (331 mg, 0.460 mmol, 69%) as a white foam. $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.62 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 4.2 Hz, 1H), 6.16 (t, *J* = 5.6 Hz, 1H), 5.52 (t, *J* = 9.8 Hz, 1H), 5.07 (t, *J* = 9.8 Hz, 1H), 4.70 (dd, *J* = 10.5, 4.2 Hz, 1H), 4.19-4.37 (m, 3H), 3.55-3.73 (m, 2H), 2.86 (t, *J* = 7.0 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 173.87, 169.98, 169.95, 169.52, 166.48, 154.12, 137.73, 133.16, 132.75, 129.68, 129.68, 128.93, 128.93, 128.41, 128.41, 119.83, 119.83, 86.45, 79.28, 72.16, 70.66, 70.14, 67.52, 61.92, 41.33, 34.84, 25.85, 25.26, 20.78, 20.73, 20.69. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{36}BrClNO_{11}$ [$(M + H)^+$], 712.1155, found, 712.1158.

2,3,4-Tri-*O*-acetyl-6-*O*-[(2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)]-α-D-glucopyranosyl bromide (1w)



A suspension of febuxostat **S21** (190 mg, 0.600 mmol, 1.20 equiv) and DMAP (3.00 mg, 0.0250 mmol, 5.00 mol%) in DCM (3.00 mL) was added a solution of DCC (124 mg, 0.600 mmol, 1.20 equiv) in DCM (1.00 mL) at 0 ºC. After stirring for 10 min at 0 ºC, **1j** (185 mg, 0.50 mmol, 1.00 equiv) was added. The reaction mixture was stirred at room temperature for 12 h, quenched with saturated $NaHCO_3$ solution (6.00 mL), and extracted with DCM (2×30 mL). The organic layer was collected, washed with brine, dried with anhydrous Mg_2SO_4, and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2:1 (v/v)] to afford the title compound (214 mg, 0.320 mmol, 64%) as a white solid. $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.20 (d, *J* = 2.2 Hz, 1H), 8.11 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.63 (d, *J* = 4.0 Hz, 1H), 5.59 (t, *J* = 9.7 Hz, 1H), 5.20 (t, *J* = 9.8 Hz, 1H), 4.85 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.44 (d, *J* = 4.0 Hz, 2H), 4.40 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.75 (s, 3H), 2.26 – 2.13 (m, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 169.96, 169.94, 169.54, 168.01, 162.71, 162.32, 161.45, 132.83, 132.33, 126.00, 120.80, 115.48, 112.71, 103.13, 86.57, 75.81, 72.23, 70.75, 70.23, 67.46, 61.72, 28.28, 20.77, 20.75, 20.70, 19.17, 17.71. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{32}BrN_2O_{10}S$ [$(M + H)^+$], 667.0956, found, 667.0966.

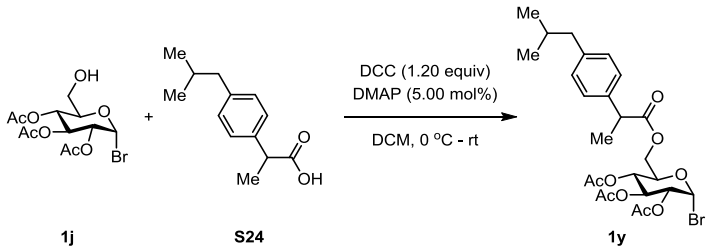
2,3,4-Tri-*O*-acetyl-6-*O*-[((2-(10-oxo-10,11-dihydrodibenzo[*b,f*]thiepin-2-yl)propanoyl)]-α-D-glucopyranosyl bromide (1x)



To a solution of compound **S14** (452 mg, 1.30 mmol, 1.00 equiv) in dry DCM (6.5 mL, 0.20 M) were added Zaltoprofen **S22** (237 mg, 1.43 mmol, 1.10 equiv), DMAP (47.6 mg, 0.390 mmol, 0.300 equiv), EDCI·HCl (448 mg, 2.34 mmol, 1.80 equiv) and DIPEA (0.480 mL, 2.34 mmol, 1.80 equiv). After stirring at room temperature for overnight, the reaction mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine successively. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography Hexanes: EtOAc [2:1 (v/v)] to give **S23** (700 mg, 1.11 mmol, 86% yield) as a colorless oil.

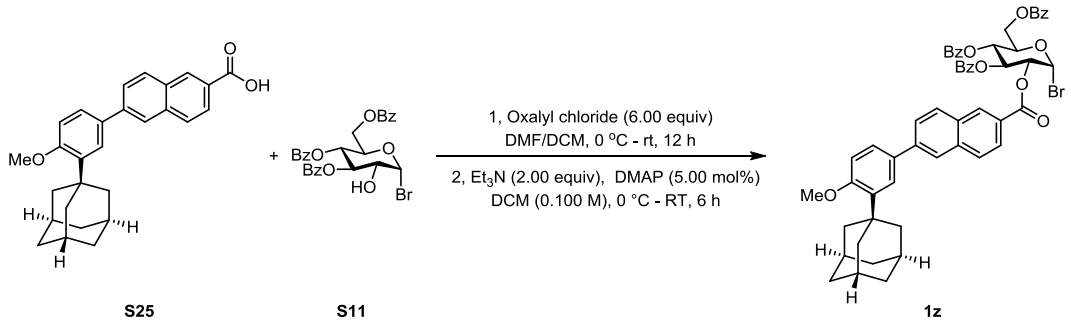
1x was synthesized according to the General Procedure A using **S23** (440 mg, 0.700 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (289 mg, 0.450 mmol, 64%) as a white foam. $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.20 (dd, *J* = 3.5, 1.4 Hz, 1H), 8.19 (dd, J = 3.5, 1.4 Hz, 1.15H), 7.58- 7.63 (m, 4.12H), 7.39-7.44 (m, 4.30H), 7.29-7.33 (m, 2.15H), 7.16 (t, *J* = 2.1 Hz, 1.15H), 7.15 (dt, *J* = 2.1 Hz, 1H), 6.55 (d, *J* = 4.2 Hz, 1H), 6.52 (d, *J* = 4.2 Hz, 1.15H), 5.49 (t, *J* = 9.8 Hz, 2.15H), 5.02 (t, *J* = 9.8 Hz, 1.15H), 4.97 (t, *J* = 9.8 Hz, 1H), 4.70 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.65 (dd, *J* = 9.8, 4.2 Hz, 1.15H), 4.38 (s, 4.30H), 4.16-4.30 (m, 6.45H), 3.77 (qd, *J* = 7.0, 2.1 Hz, 2.15H), 2.10 (s, 3H), 2.09 (s, 3.45H), 2.04 (s, 3.45H), 2.03 (s, 3.45H), 2.03 (s, 3H), 1.99 (s, 3H), 1.51 (d, *J* = 7.0 Hz, 3H), 1.49 (d, *J* = 7.0 Hz, 3.45H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.50, 191.48, 173.48, 173.41, 169.99, 169.96, 169.87, 169.85, 169.54, 169.37, 142.30, 142.08, 140.31, 140.29, 138.15, 138.10, 136.33, 136.30, 133.58, 133.55, 132.63, 132.60, 131.70, 131.67, 131.65, 131.62, 131.00, 131.00, 128.98, 128.66, 126.97, 126.96, 126.73, 126.52, 86.55, 86.51, 72.32, 72.27, 70.68, 70.67, 70.23, 70.22, 67.42, 67.19, 61.54, 61.27, 51.20, 51.19, 45.16, 45.03, 20.79, 20.79, 20.79, 20.79, 20.70, 20.61, 18.26, 18.15. **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{30}BrO_{10}S$ [$(M + H)^+$], 649.0738, found, 649.0738.

2,3,4-Tri-*O*-acetyl-6-*O*-[((2-(4-isobutylphenyl)propanoyl)]-α-D-glucopyranosyl bromide (1y)



The reaction was performed according to the same procedure as synthesizing **1w**. Ibuprofen **S24** (115 mg, 0.60 mmol, 1.50 equiv) was used as the coupling partner. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (196 mg, 0.352 mmol, 70%) as a white solid. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.21 (d, *J* = 8.4 Hz, 3H), 7.10 (d, *J* = 8.4 Hz, 3H), 6.55 (d, *J* = 4.1 Hz, 0.5H), 6.51 (d, *J* = 4.1 Hz, 1H), 5.50 (td, *J* = 9.7, 2.2 Hz, 1.5H), 5.06 – 4.99 (m, 1.5H), 4.70 (dd, *J* = 9.8, 4.1 Hz, 0.5H), 4.67 (dd, *J* = 9.8, 4.1 Hz, 1H), 4.23 (ddd, *J* = 11.9, 10.7, 5.6 Hz, 4.5H), 3.73 (q, *J* = 7.1 Hz, 1.5H), 2.43 (d, *J* = 7.2 Hz, 3.5H), 2.09 (s, 1.5H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 4.5H), 1.99 (s, 1.5H), 1.86 (dt, *J* = 13.5, 6.8 Hz, 1.5H), 1.50 (d, *J* = 7.2 Hz, 1.5H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 9.5H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 174.29, 169.95, 169.82, 169.49, 140.78, 140.76, 137.37, 137.13, 129.48, 129.44, 127.41, 127.37, 86.63, 86.58, 72.43, 72.34, 70.67, 70.26, 67.55, 67.26, 61.33, 60.98, 45.10, 44.95, 30.25, 30.23, 22.50, 20.73, 20.71, 20.65, 20.60, 18.42, 18.22. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{34}BrO_9$ [$(M + H)^+$], 557.1381, found, 557.1388.

3,4,6-Tri-*O*-benzoyl-6-*O*-[(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)]-α-D-glucopyranosyl bromide (1z)

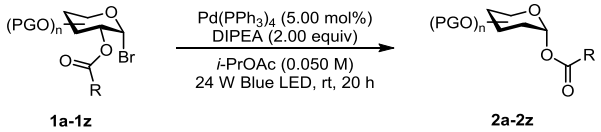


S25 **S11** **1z**

To a solution of Adapalene **S25** (248 mg, 0.6 mmol, 1.00 equiv) in dry DCM (6 mL, 0.10 M) were added DMF (60.0 uL) and oxalyl chloride (457 mg, 6.60 mmol, 6.00 equiv) at 0 ºC. After stirring at room temperature for 12 h, the solvent was removed under vacuum and the residue was directly used for next step. To a solution of crude mixture obtained above in dry DCM (6.00 mL) were added Et_3N (101 mg, 1.00 mmol, 2.00 equiv), **S11** (278 mg, 0.500 mmol, 1.00 equiv) and DMAP (3.05 mg, 0.0250 mmol, 5.00 mol%) at 0 ºC. The reaction mixture stirred at room temperature for 6 h, then quenched with saturated $NaHCO_3$ solution (6.00 mL) and extracted with DCM (2×30 mL). The organic layer was collected, washed with brine, dried with anhydrous Mg_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound **1z** (237 mg, 0.250 mmol, 50%) as a white solid. $\mathbf{R}_f$ = 0.70 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.57 (s, 1H), 8.09 (d, *J* = 7.3 Hz, 2H), 8.01 – 7.95 (m, 5H), 7.88 (dd, *J* = 15.3, 8.1 Hz, 3H), 7.79 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.55 – 7.51 (m, 2H), 7.43 (ddd, *J* = 24.4, 15.6, 7.7 Hz, 5H), 7.29 (t, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 4.0 Hz, 1H), 6.33 (t, *J* = 9.8 Hz, 1H), 5.85 (dd, *J* = 16.7, 6.7 Hz, 1H), 5.39 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.83 – 4.75 (m, 1H), 4.69 (dd, *J* =

12.5, 2.4 Hz, 1H), 4.53 (dt, *J* = 12.3, 4.4 Hz, 1H), 3.90 (s, 3H), 2.18 (s, 6H), 2.10 (s, 3H), 1.80 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.18, 165.80, 165.69, 165.25, 159.14, 141.97, 139.16, 136.46, 133.79, 133.48, 133.40, 132.50, 132.01, 131.24, 130.09, 129.98, 129.88, 129.61, 128.96, 128.70, 128.65, 128.61, 128.58, 128.51, 126.71, 126.09, 125.88, 125.61, 125.18, 124.77, 112.24, 87.14, 72.88, 71.74, 70.88, 68.17, 62.12, 55.30, 40.72, 37.34, 37.25, 29.23. **HRMS** (ESI-TOF) *m/z* calcd for $C_{55}H_{49}BrO_{10}Na$ [$(M + Na)^+$], 971.2401, found, 971.2402.

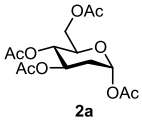
General Procedure B (for the C-2 reduction reaction):



1a-1z **2a-2z**

In a glovebox, to an oven-dried 4 mL screw cap vial was added $Pd(PPh_3)_4$ (11.6 mg, 10.0 μmol, 5.00 mol%), bromo-sugar (0.200 mmol, 1.00 equiv), and *i*-PrOAc (4.00 mL, 0.0500 M). To this suspension were added DIPEA (69.7 μL, 0.400 mmol, 2.00 equiv) and a magnetic stir bar. Next, the vial was capped, taken out of the glovebox, and sealed with parafilm. The reaction mixture was stirred at room temperature, irradiated with two 12 W Blue LEDs for 20 h. Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the desired product.

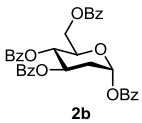
2-Deoxy-1,3,4,6-tetra-*O*-acetyl-D-glucopyranoside (2a)



2a

According to the General Procedure B, the title compound was obtained as a colorless oil (62.5 mg, 0.188 mmol, 94% yield, C2:C1 = > 20:1). **R_f** = 0.20 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.22 (d, *J* = 2.5 Hz, 1H), 5.28 (ddd, *J* = 11.6, 9.6, 5.3 Hz, 1H), 5.04 (t, *J* = 9.7 Hz, 1H), 4.32 – 4.16 (m, 1H), 4.08 – 3.94 (m, 2H), 2.24 (ddd, *J* = 13.5, 5.2, 1.2 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.93 (ddd, *J* = 13.6, 11.8, 3.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.74, 170.31, 169.75, 168.98, 90.93, 70.26, 68.74, 68.52, 61.98, 33.92, 21.08, 20.97, 20.78, 20.73. The spectroscopic data corresponds to previously reported data.[12]

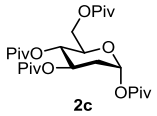
2-Deoxy-1,3,4,6-tetra-*O*-benzoyl-D-glucopyranoside (2b)



2b

According to the General Procedure B, the title compound was obtained as a white solid (110 mg, 0.190 mmol, 95% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.50 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.19 – 8.17 (m, 2H), 8.03 – 8.01 (m, 2H), 8.01 – 7.97 (m, 4H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (ddd, *J* = 10.7, 7.4, 6.2 Hz, 5H), 7.38 (dt, *J* = 17.0, 7.8 Hz, 6H), 6.66 (d, *J* = 2.6 Hz, 1H), 5.92 – 5.84 (m, 1H), 5.78 (t, *J* = 9.8 Hz, 1H), 4.62 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.58 – 4.52 (m, 1H), 4.49 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.32 (ddd, *J* = 13.7, 11.6, 3.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.21, 165.98, 165.49, 164.60, 133.82, 133.52, 133.44, 133.14, 130.07, 129.89, 129.84, 129.82, 129.77, 129.44, 129.39, 129.11, 128.78, 128.55, 128.53, 128.43, 91.76, 70.93, 69.74, 69.68, 63.01, 34.57. The spectroscopic data corresponds to previously reported data.[13]

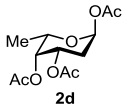
2-Deoxy-1,3,4,6-tetra-*O*-pivotal-D-glucopyranoside (2c)



2c

According to the General Procedure B, the title compound was obtained as a colorless oil (71.1 mg, 0.142 mmol, 71% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.60 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.22 (d, *J* = 2.7 Hz, 1H), 5.29 – 5.18 (m, 1H), 5.11 (t, *J* = 9.9 Hz, 1H), 4.18 – 4.07 (m, 2H), 4.07 – 3.96 (m, 1H), 2.27 (ddd, *J* = 13.3, 5.1, 1.0 Hz, 1H), 1.89 (ddd, *J* = 13.5, 11.6, 3.6 Hz, 1H), 1.25 (s, 9H), 1.19 (s, 9H), 1.17 (s, 9H), 1.14 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 178.15, 177.77, 176.81, 176.40, 90.90, 70.94, 68.60, 68.19, 62.18, 39.20, 38.95, 38.93, 38.85, 34.16, 27.22, 27.20, 27.18, 27.16. The spectroscopic data corresponds to previously reported data.[14]

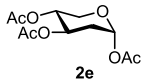
2-Deoxy-1,3,4-tri-*O*-acetyl-α-L-fucopyranoside (2d)



2d

The reaction was performed according to the General Procedure B using **1d** (70.6 mg, 0.200 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound as a colorless oil (46.6 mg, 0.170 mmol, 85% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.20 [Hexanes: EtOAc 5:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.28 (d, *J* = 2.8 Hz, 1H), 5.28 (ddd, *J* = 12.5, 4.9, 3.5 Hz, 1H), 5.21 (s, 1H), 4.16 (q, *J* = 6.5 Hz, 1H), 2.17 (dt, *J* = 13.3, 3.5 Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 2.00 (s, 3H), 1.87 (dd, *J* = 13.3, 4.9 Hz, 1H), 1.14 (d, *J* = 6.5 Hz, 3H).**^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ):170.77, 170.33, 169.48, 92.05, 69.38, 67.49, 66.35, 28.87, 21.26, 21.01, 20.84, 16.67. The spectroscopic data corresponds to previously reported data.[15]

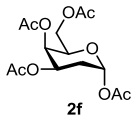
2-Deoxy-1,3,4-tri-*O*-acetyl-α-D-xylopyranoside (2e)



2e

The reaction was performed according to the General Procedure B using **1e** (67.8 mg, 0.200 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound as a yellow oil (38.0 mg, 0.146 mmol, 73% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.10 (t, *J* = 3.5 Hz, 1H), 5.24 (ddd, *J* = 9.8, 8.4, 4.9 Hz, 1H), 4.90 (td, *J* = 9.1, 4.9 Hz, 1H), 3.91 (dd, *J* = 11.9, 4.9 Hz, 1H), 3.70 (dd, *J* = 11.9, 9.1 Hz, 1H), 2.21 (ddd, *J* = 14.0, 4.9, 3.5 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 1.87 (ddd, *J* = 14.0, 10.5, 3.5 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.16, 170.06, 169.35, 90.89, 68.78, 67.97, 61.91, 33.28, 21.10, 21.09, 20.92. The spectroscopic data corresponds to previously reported data.[16]

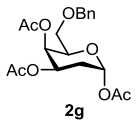
2-Deoxy-1,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (2f)



2f

According to General Procedure B, the title compound was obtained as a colorless oil (107 mg, 0.184 mmol, 92% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.28 (d, *J* = 2.7 Hz, 1H), 5.35 (s, 1H), 5.27 (ddd, *J* = 12.5, 4.9, 3.0 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 1H), 4.06 (qd, *J* = 11.3, 6.7 Hz, 2H), 2.19 (td, *J* = 13.0, 3.6 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.88 (dd, *J* = 13.3, 5.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.53, 170.29, 170.17, 169.17, 91.75, 69.02, 66.07, 65.70, 61.89, 29.08, 21.13, 20.89, 20.77, 20.74. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{21}O_9$ [$(M + H)^+$], 355.1000, found, 355.1001.

2-Deoxy-1,3,4-tri-O-acetyl-6-O-benzyl-α-D-galactopyranoside (2g)

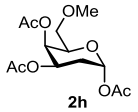


2g

The reaction was performed according to the General Procedure B using **1g** (55.0 mg, 0.120 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound as a colorless oil (32.8 mg, 0.0870 mmol, 72% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.26-7.34 (m, 5H), 6.30 (d, *J* = 3.3 Hz, 1H), 5.45 (s, 1H),

5.33-5.25 (m, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.22 (t, *J* = 5.9 Hz, 1H), 3.49 (dd, *J* = 9.5, 5.9 Hz, 1H), 3.43 (dd, *J* = 9.5, 7.3 Hz, 1H), 2.19 (td, *J* = 13.0, 3.3 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.89 (dd, *J* = 13.0, 4.7 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.31, 170.23, 169.40, 137.67, 128.56, 128.56, 128.08, 128.08, 127.94, 91.96, 73.66, 70.40, 68.04, 66.70, 65.98, 29.27, 21.25, 20.99, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{24}O_8Na$ [$(M + Na)^+$], 403.1363, found, 403.1363.

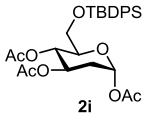
2-Deoxy-1,3,4-tri-*O*-acetyl-6-*O*-methyl-α-D-galactopyranoside (2h)



2h

The reaction was performed according to the General Procedure B using **1h** (71.8 mg, 0.190 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound as a colorless oil (46.8 mg, 0.154 mmol, 81% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.32 (d, *J* = 3.0 Hz, 1H), 5.41-5.38 (m, 1H), 5.28 (ddd, *J* = 12.5, 5.0, 3.0 Hz, 1H), 4.19 (t, *J* = 6.0 Hz, 1H), 3.44 (dd, *J* = 10.0, 6.5 Hz, 1H), 3.37 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.32 (s, 3H), 2.21 (td, *J* = 13.0, 3.5 Hz, 1H), 2.14 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H), 1.91 (dd, *J* = 13.0, 5.0 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.41, 170.24, 169.38, 92.14, 71.38, 70.52, 67.00, 65.99, 59.50, 29.18, 21.26, 20.99, 20.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{20}O_8Na$ [$(M + Na)^+$], 327.1050, found, 327.1053.

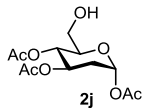
2-Deoxy-1,3,4-tri-*O*-acetyl-6-*O*-[(1,1-dimethylethyl)diphenylsilyl]-α-D- glucopyranoside (2i)



2i

The reaction was performed according to the General Procedure B using **1i** (60.6 mg, 0.100 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [5:1 (v/v)] to afford the title compound as a yellow oil (48.5 mg, 0.0910 mmol, 91% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 5:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.63-7.67 (m, 4H), 7.35-743 (m, 6H), 6.30 (d, *J* = 2.5 Hz, 1H), 5.31 (ddd, *J* = 11.5, 9.0, 5.0 Hz, 1H), 5.18 (t, *J* = 10.0 Hz, 1H), 3.89 (dt, *J* = 10.0, 3.5 Hz, 1H), 3.71 (d, *J* = 3.5 Hz, 1H), 2.23 (ddd, *J* = 13.5, 5.0, 1.0 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 3H), 1.93-1.99 (m, 1H), 1.92 (s, 3H), 1.04 (s, 9H).**^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.63, 169.67, 169.19, 135.84, 135.84, 135.81, 135.81, 133.35, 133.29, 129.28, 129.78, 127.79, 127.79, 127.78, 127.78, 91.12, 73.08, 69.19, 69.07, 62.60, 34.10, 26.85, 26.85, 26.85, 21.20, 21.13, 20.80, 19.36. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{36}O_8SiNa$ [$(M + Na)^+$], 551.2072, found, 551.2076.

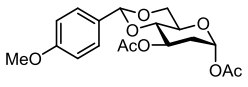
2-Deoxy-1,3,4-tri-*O*-acetyl-D-glucopyranoside (2j)



2j

The reaction was performed according to the General Procedure B using **1j** (36.8 mg, 0.100 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [1:1 (v/v)] to afford the title compound as a colorless oil (20.8 mg, 0.0720 mmol, 72% yield, C2:C1 = >20:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.25 (s, 1H), 5.28-5.42 (m, 1H), 5.02 (t, *J* = 9.8 Hz, 1H), 3.83 (d, *J* = 10.5 Hz, 1H), 3.67-3.96 (m, 1H), 3.57-3.75 (m, 1H), 2.35 (s, 1H), 2.27 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.90-1.94 (m, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.78, 170.41, 169.26, 90.98, 72.50, 69.24, 68.32, 61.21, 34.01, 21.17, 21.09, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_0H_0X_3Y_2Z_5$ [$(M + Na)^+$], 313.0894, found, 313.0888.

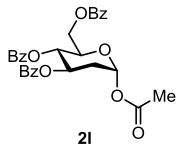
2-Deoxy-1,3-di-*O*-acetyl-4,6-*O*-[(*R*)-(4-methoxyphenyl)methylene]-α-D-glucopyranoside (2k)



2k

According to the General Procedure B, the title compound was obtained as a colorless oil (63.7 mg, 0.174 mmol, 87% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.40 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.39 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.20 (d, *J* = 3.3 Hz, 1H), 5.52 (s, 1H), 5.43 – 5.26 (m, 1H), 4.26 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.97 (td, *J* = 9.9, 4.9 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 18.6, 9.9 Hz, 2H), 2.35 (ddd, *J* = 13.6, 5.3, 0.8 Hz, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 1.90 (ddd, *J* = 13.8, 11.2, 3.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.32, 169.43, 160.27, 129.66, 127.61, 113.73, 101.84, 91.27, 79.85, 68.79, 67.54, 65.45, 55.40, 34.50, 21.21, 21.20. **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{23}O_8$ [$(M + Na)^+$], 367.1387, found, 367.1397.

2-Deoxy-3,4,6-tri-*O*-benzoyl -1-*O*-acetyl-α-D-glucopyranoside (2l)

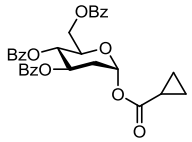


2l

According to the General Procedure B, the title compound was obtained as a white solid (93.3 mg, 0.180 mmol, 90% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.03 (d, *J* = 7.4 Hz, 2H), 7.95 (t, *J* = 7.6 Hz, 4H), 7.57 – 7.48 (m, 3H), 7.43 – 7.34 (m, 6H), 6.39 (d, *J* = 2.5 Hz, 1H), 5.83 – 5.60 (m, 2H), 4.59 (t, *J* = 6.9 Hz, 1H), 4.45 (dd, *J* = 9.3, 6.1 Hz, 2H), 2.56 (dd, *J* =

13.2, 4.4 Hz, 1H), 2.19 (s, 3H), 2.19 – 2.17 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 169.15, 166.28, 165.97, 165.49, 133.53, 133.44, 133.20, 129.90, 129.86, 129.84, 129.80, 129.42, 129.15, 128.55, 128.48, 91.14, 70.70, 69.69, 69.59, 63.10, 34.36, 21.23. **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{27}O_9$ [$(M + H)^+$], 519.1650, found, 519.1646.

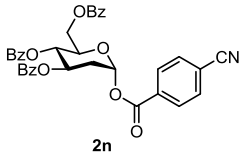
2-Deoxy-3,4,6-tri-*O*-benzoyl -1-*O*-cyclopropanecarbonyl-α-D-glucopyranoside (2m)



2m

According to the General Procedure B, the title compound was obtained as a white solid (90.4 mg, 0.166 mmol, 83% yield, C2:C1 = > 20:1). **R_f** = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.08 – 7.99 (m, 2H), 7.95 (dd, *J* = 13.0, 4.9 Hz, 4H), 7.53 (dt, *J* = 18.1, 7.4 Hz, 3H), 7.44 – 7.30 (m, 6H), 6.39 (d, *J* = 2.5 Hz, 1H), 5.92 – 5.71 (m, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 4.70 – 4.51 (m, 1H), 4.51 – 4.33 (m, 1H), 2.57 (ddd, *J* = 13.4, 5.1, 1.0 Hz, 1H), 2.17 (ddd, *J* = 13.6, 11.5, 3.7 Hz, 1H), 1.83 – 1.68 (m, 1H), 1.16 – 1.04 (m, 2H), 0.98 (dtd, *J* = 8.8, 5.7, 2.8 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 173.20, 166.30, 166.00, 165.53, 133.54, 133.43, 133.20, 129.93, 129.88, 129.85, 129.46, 129.18, 128.55, 128.47, 90.95, 70.65, 69.76, 69.70, 63.15, 34.40, 13.01, 9.42, 9.39. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{29}O_9$ [$(M + H)^+$], 545.1806, found, 545.1799.

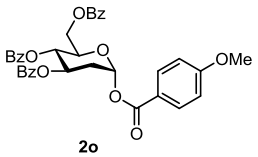
2-Deoxy-3,4,6-tri-*O*-benzoyl -1-*O*-(4-cyanobenzoyl)-α-D-glucopyranoside (2n)



2n

According to the General Procedure B, the title compound was obtained as a white solid (99.3 mg, 0.164 mmol, 82% yield, C2:C1 = > 20:1). **R_f** = 0.55 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.24 (d, *J* = 8.3 Hz, 2H), 8.05 – 7.88 (m, 6H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.53 (dt, *J* = 7.4, 5.7 Hz, 3H), 7.44 – 7.28 (m, 6H), 6.64 (d, *J* = 2.6 Hz, 1H), 5.85 – 5.79 (m, 1H), 5.76 (dd, *J* = 19.4, 9.8 Hz, 1H), 4.62 (dd, *J* = 11.6, 2.1 Hz, 1H), 4.50 – 4.44 (m, 2H), 2.76 – 2.72 (m, 1H), 2.35 – 2.29 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.22, 166.07, 165.50, 163.17, 133.68, 133.61, 133.29, 132.64, 130.58, 129.93, 129.87, 129.71, 129.26, 129.04, 128.64, 128.62, 128.51, 117.96, 117.28, 92.73, 71.28, 69.54, 69.50, 62.94, 34.48. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{27}NO_9Na$ [$(M + Na)^+$], 628.1578, found, 628.1574.

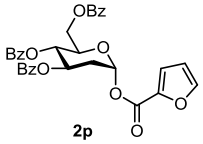
2-Deoxy-3,4,6-tri-*O*-benzoyl -1-*O*-(4-methoxybenzoyl)-α-D-glucopyranoside (2o)



2o

According to the General Procedure B, the title compound was obtained as a white solid (94.0 mg, 0.154 mmol, 77% yield, C2:C1 = 14:1). $\mathbf{R_f}$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.12 (d, *J* = 8.7 Hz, 2H), 8.01 – 7.94 (m, 6H), 7.55 – 7.48 (m, 3H), 7.41 – 7.35 (m, 6H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 2.4 Hz, 1H), 5.91 – 5.82 (m, 1H), 5.74 (t, *J* = 9.8 Hz, 1H), 4.59 (dd, *J* = 12.0, 2.2 Hz, 1H), 4.52 – 4.41 (m, 2H), 3.91 (s, 3H), 2.71 (dd, *J* = 13.4, 5.0 Hz, 1H), 2.32 – 2.24 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.27, 166.04, 165.53, 164.33, 164.12, 133.54, 133.46, 133.15, 132.24, 129.93, 129.88, 129.85, 129.46, 129.18, 128.58, 128.55, 128.45, 121.76, 114.08, 91.45, 70.85, 69.84, 69.77, 63.07, 55.67, 34.65. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{31}O_{10}$ [$(M + H)^+$], 611.1912, found, 611.1907.

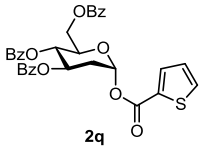
2-Deoxy-3,4,6-tri-*O*-benzoyl -1-*O*-(furan-2-carbonyl)-α-D-glucopyranoside (2p)



2p

According to the General Procedure B, the title compound was obtained as a white solid (87.8 mg, 0.154 mmol, 77% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.02 – 7.99 (m, 2H), 7.96 (dd, *J* = 11.8, 4.2 Hz, 4H), 7.68 (d, *J* = 0.8 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.42 – 7.35 (m, 7H), 6.67 – 6.52 (m, 2H), 5.91 – 5.78 (m, 1H), 5.73 (t, *J* = 9.8 Hz, 1H), 4.60 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.53 – 4.50 (m, 1H), 4.46 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.71 – 2.68 (m, 1H), 2.27 (ddd, *J* = 13.7, 11.5, 3.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.29, 165.98, 165.52, 156.67, 147.32, 143.90, 133.57, 133.47, 133.20, 129.95, 129.90, 129.87, 129.81, 129.44, 129.17, 128.58, 128.49, 119.59, 112.29, 91.74, 70.97, 69.65, 69.62, 63.00, 34.56. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{26}NO_{10}Na$ [$(M + Na)^+$], 593.1418, found, 593.1418.

2-Deoxy-3,4,6-tri-*O*-benzoyl -1-*O*-(thiophene-2-carbonyl)-α-D-glucopyranoside (2q)

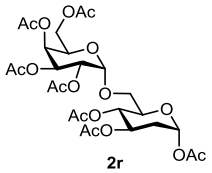


2q

According to the General Procedure B, the title compound was obtained as a white solid (86.8 mg, 0.148 mmol, 74% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.01 – 7.95 (m, 6H), 7.67 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.38 (dt, *J* = 22.5, 7.7 Hz, 6H), 7.19 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.58 (d, *J* = 2.5 Hz, 1H), 5.88 – 5.79 (m, 1H), 5.73 (t, *J* = 9.8 Hz, 1H),

4.60 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.55 – 4.49 (m, 1H), 4.46 (dd, *J* = 12.1, 4.6 Hz, 1H), 2.71 (ddd, *J* = 13.5, 5.1, 1.1 Hz, 1H), 2.27 (ddd, *J* = 13.7, 11.5, 3.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.28, 165.98, 165.53, 160.19, 134.64, 133.70, 133.58, 133.48, 133.20, 132.86, 129.96, 129.90, 129.87, 129.81, 129.43, 129.14, 128.59, 128.58, 128.49, 128.27, 91.91, 71.01, 69.70, 69.61, 63.00, 34.57. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{26}NO_9SNa$ [$(M + Na)^+$], 609.1190, found, 609.1190.

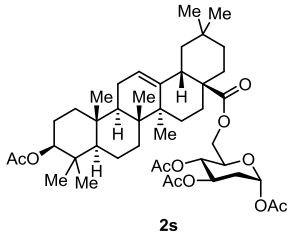
1,3,4,2',3',4',6'-Hepta-*O*-acetyl-α-D-melibiosyl bromide (2r)



2r

The reaction was performed according to the General Procedure B using **1r** (36.8 mg, 0.100 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under *vacuum* and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [1:1 (v/v)] to afford the title compound as a colorless oil (20.8 mg, 0.0720 mmol, 72% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.19 (d, *J* = 1.4 Hz, 1H), 5.28-5.35 (m, 2H), 5.15 (d, *J* = 3.5 Hz, 1H), 5.00-5.08 (m, 2H), 4.25 (t, *J* = 7.0 Hz, 1H), 4.08-4.11 (m, 1H), 4.04 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.99 (ddd, *J* = 9.8, 4.9, 2.1 Hz, 1H), 3.71 (dd, *J* = 11.2, 4.9 Hz, 1H), 3.57 (dd, *J* = 11.2, 2.1 Hz, 1H), 2.25 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.13 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 2H), 1.98 (s, 3H), 1.97-1.98 (m, 1H).**^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.65, 170.54, 170.44, 170.33, 169.99, 169.77, 169.16, 95.92, 90.77, 70.95, 69.40, 68.66, 68.32, 68.28, 67.51, 66.35, 66.28, 61.67, 33.94, 21.12, 21.07, 20.92, 20.86, 20.86, 20.80, 20.79. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{40}O_{17}N$ [$(M + NH_4)^+$], 638.2291, found, 638.2285.

2-Deoxy-3,4,6-tri-*O*-acetyl -1-*O*-[((4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-4a-carbonyl)]-α-D-glucopyranoside (2s)

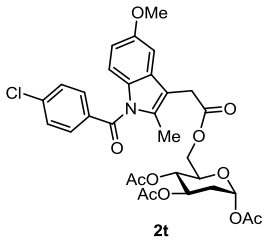


2s

The reaction was performed according to the General Procedure B using **1s** (59.5 mg, 0.0700 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title

compound as a white foam (35.0 mg, 0.0450 mmol, 64% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.24 (d, *J* = 2.8 Hz, 1H), 5.24-5.35 (m, 2H), 5.03 (t, *J* = 9.8 Hz, 1H), 4.44-4.52 (m, 1H), 4.24-4.27 (m, 1H), 4.03 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.99 (dd, *J* = 11.9, 4.9 Hz, 1H), 2.84 (dd, *J* = 14.0, 4.2 Hz, 1H), 2.25 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 1.95-2.01 (m, 1H), 1.81-1.94 (m, 3H), 1.50-1.70 (m, 9H), 1.42-1.48 (m, 1H), 1.38 (dd, *J* = 12.6, 2.8 Hz, 1H), 1.29-1.35 (m, 1H), 1.24-1.27 (m, 2H), 1.18-1.21 (m, 1H), 1.13-1.17 (m, 1H), 1.12 (s, 3H), 1.02-1.07 (m, 2H), 0.92 (d, *J* = 1.4 Hz, 6H), 0.89 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H), 0.83 (d, *J* = 11.2 Hz, 1H), 0.70 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ):177.32, 171.18, 170.50, 169.65, 169.03, 143.58, 122.66, 90.88, 81.07, 70.61, 69.18, 68.72, 61.77, 55.44, 47.68, 46.98, 45.97, 41.78, 41.36, 39.42, 38.24, 37.83, 37.05, 34.11, 34.00, 33.22, 32.82, 32.30, 30.82, 28.17, 27.72, 25.96, 23.69, 23.66, 23.52, 23.17, 21.48, 21.17, 21.12, 20.86, 18.37, 16.99, 16.82, 15.52. **HRMS** (ESI-TOF) *m/z* calcd for $C_{44}H_{66}O_{11}Na$ [$(M + Na)^+$], 793.4497, found, 793.4500.

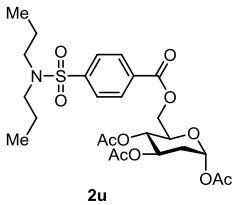
2-Deoxy-3,4,6-tri-*O*-benzoyl-1-*O*-[(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)carbonyl]-α-D-glucopyranoside (2t)



2t

The reaction was performed according to the General Procedure B using **1t** (22.7 mg, 0.0320 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound as a white foam (14.6 mg, 0.0235 mmol, 73% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.68 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 6.67 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.15 (d, *J* = 2.7 Hz, 1H), 5.27 (ddd, *J* = 11.9, 9.8, 5.6 Hz, 1H), 4.97 (t, *J* = 9.8 Hz, 1H), 4.30 (dd, *J* = 12.6, 4.2 Hz, 1H), 4.12 (dd, *J* = 12.6, 1.4 Hz, 1H), 4.01 (ddd, *J* = 10.5, 3.5, 2.1 Hz, 1H), 3.85 (s, 3H), 3.71 (s, 2H), 2.35 (s, 3H), 2.19 (m, dd, *J* = 13.3, 5.6 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 6H), 1.72 (ddd, *J* = 13.3, 11.9, 3.5 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ):170.60, 170.39, 169.72, 169.08, 168.49, 156.18, 139.30, 136.20, 134.16, 131.34, 131.34, 130.97, 130.82, 129.22, 129.22, 115.08, 112.37, 111.85, 101.49, 90.91, 70.33, 68.60, 68.49, 62.22, 55.80, 33.81, 30.12, 21.12, 21.08, 20.82, 13.51. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{33}ClNO_{11}$ [$(M + H)^+$], 630.1737, found, 630.1735.

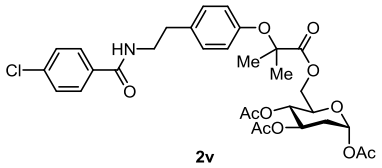
2-Deoxy-3,4,6-tri-*O*-acetyl -1-*O*-[(4-(*N*,*N*-dipropylsulfamoyl)benzoyl)]-α-D-glucopyranoside (2u)



2u

The reaction was performed according to the General Procedure B using **1u** (50.9 mg, 0.08 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3.5:1 (v/v)] to afford the title compound as a white foam (26.7 mg, 0.0480 mmol, 60% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.40 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.15 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 6.26 (d, *J* = 3.5 Hz, 1H), 5.36 (ddd, *J* = 11.2, 9.8, 4.9 Hz, 1H), 5.18 (t, *J* = 9.8 Hz, 1H), 4.48 (dd, *J* = 11.9, 2.1 Hz, 1H), 4.41 (dd, *J* = 12.6, 4.2 Hz, 1H), 4.18 (t, *J* = 9.8, 2.1 Hz, 1H), 3.03-3.13 (m, 4H), 2.30 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.94-2.01 (m, 1H), 1.51-1.58 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.37, 169.86, 169.08, 165.01, 144.53, 133.08, 130.51, 130.51, 127.20, 127.20, 90.95, 70.24, 68.98, 68.58, 63.07, 50.16, 50.16, 34.04, 22.14, 22.14, 21.16, 21.06, 20.84, 11.28, 11.28. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{36}NO_{11}S$ [$(M + H)^+$], 558.2004, found, 558.2005.

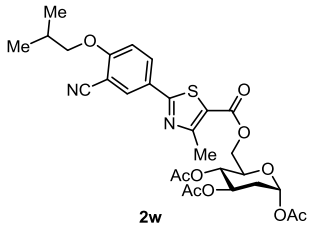
2-Deoxy-3,4,6-tri-*O*-acetyl-1-*O*-[(2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoyl)] -α-D-glucopyranoside (2v)



2v

The reaction was performed according to the General Procedure B using **1v** (71.3 mg, 0.100 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2:1 (v/v)] to afford the title compound as a white foam (44.1 mg, 0.0700 mmol, 70% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.45 [Hexanes: EtOAc 1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.62 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.22-6.25 (m, 1H), 6.16 (d, *J* = 2.8 Hz, 1H), 5.21-5.36 (m, 1H), 5.01 (t, *J* = 9.8 Hz, 1H), 4.31 (dd, *J* = 11.9, 4.9 Hz, 1H), 4.19 (dd, *J* = 11.9, 1.4 Hz, 1H), 4.05 (dd, *J* = 9.8, 2.1 Hz, 1H), 3.56-3.71 (m, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.21 (dd, *J* = 14.0, 4.9 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.82-1.88 (m, 1H), 1.59 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ):173.94, 170.38, 169.75, 169.06, 169.51, 154.11, 137.67, 133.17, 132.68, 129.59, 129.59, 128.89, 128.89, 128.44, 128.44, 119.96, 119.96, 90.72, 79.28, 70.21, 69.05, 68.49, 62.92, 41.34, 34.83, 33.88, 25.78, 25.16, 21.09, 21.03, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{37}ClNO_{11}$ [$(M + H)^+$], 634.2050, found, 634.2038.

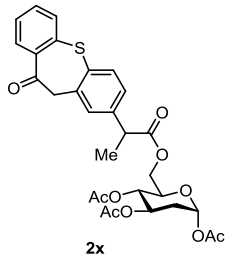
2-Deoxy-3,4,6-tri-*O*-acetyl-1-*O*-[(2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)]-α-D-glucopyranoside (2w)



2w

According to the General Procedure B, the title compound was obtained as a white foam (103.6 mg, 0.176 mmol, 88% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.18 (d, *J* = 2.2 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.28 (d, *J* = 2.5 Hz, 1H), 5.35 (ddd, *J* = 11.5, 9.7, 5.2 Hz, 1H), 5.12 (t, *J* = 9.8 Hz, 1H), 4.39 (d, *J* = 3.6 Hz, 2H), 4.29 – 4.07 (m, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.75 (s, 3H), 2.30 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.21 (dd, *J* = 13.3, 6.6 Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 – 1.95 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.41, 169.80, 169.05, 167.85, 162.67, 161.93, 161.66, 132.78, 132.33, 126.08, 121.27, 115.52, 112.72, 103.10, 90.92, 75.82, 70.31, 69.05, 68.58, 62.79, 34.05, 28.28, 21.16, 21.07, 20.85, 19.18, 17.67. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{33}N_2O_{10}S$ [$(M + H)^+$], 589.1850, found, 589.1856.

2-Deoxy-3,4,6-tri-*O*-acetyl-1-*O*-[((2-(10-oxo-10,11-dihydrodibenzo[*b,f*]thiepin-2-yl)propanoyl)]-α-D-glucopyranoside (2x)

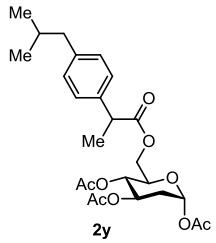


2x

The reaction was performed according to the General Procedure B using **1x** (71.3 mg, 0.100 mmol, 1.00 equiv) as the substrate. After 20 h, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2:1 (v/v)] to afford the title compound as a white foam (44.1 mg, 0.0700 mmol, 70% yield, C2:C1 = > 20:1). $\mathbf{R}_f$ = 0.40 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.20 (d, *J* = 7.0 Hz ,1H), 7.57-7.61(m, 1H), 7.39-7.44 (m, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.20 (d, *J* = 2.8 Hz, 0.45H, H-1), 6.16 (d, *J* = 2.8 Hz, 0.55H, H-1'), 5.24-5.28 (m, 1H), 4.97 (t, *J* = 9.8 Hz, 0.55 H), 4.91(t, *J* = 9.8 Hz, 0.45 H), 4.33-4.41 (m, 2H), 4.26 (dd, *J* = 4.2, 12.6 Hz, 0.55 H), 4.16 (d, *J* = 7.0 Hz, 0.9H), 4.07 (d, *J* = 12.6 Hz, 0.55 H), 3.95-4.02 (m, 1H), 3.76 (q, *J* = 7.0 Hz, 1H), 2.17-2.21 (m, 1H), 2.08 (s, 1.35H), 2.07 (s, 1.65H), 2.00-2.04 (m, 4.65H), 1.98 (s, 1.35H), 1.78-1.85 (m, 1H), 1.50 (dd, *J* = 7.0. 9.1 Hz, 3H) . **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.52, 191.48, 173.68, 173.62, 170.44, 170.43, 169.81, 169.63, 169.06, 169.04, 142.51, 142.27, 140.34, 140.30, 138.03, 137.99, 136.33, 136.29, 133.43, 133.40, 132.66, 132.63, 131.69, 131.67, 131.58, 131.56,

131.01, 131.01, 128.97, 128.96, 127.02, 126.99, 126.78, 126.69, 90.88, 90.88, 70.35, 70.25, 68.93, 68.73, 68.56, 68.54, 62.60, 62.30, 51.19, 51.19, 45.19, 45.06, 33.89, 33.89, 21.13, 21.11, 21.09, 21.09, 20.83, 20.75, 18.43, 18.25. **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{31}O_{10}S$ [(M + H)$^+$], 571.1632, found, 571.1628.

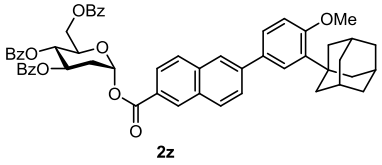
2-Deoxy-3,4,6-tri-*O*-acetyl-1-*O*-[((2-(4-isobutylphenyl)propanoyl)]-α-D-glucopyranoside (2y)



2y

According to the General Procedure B, the title compound was obtained as a white foam (80.4 mg, 0.168 mmol, 84% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.19 (d, *J* = 8.0 Hz, 3H), 7.08 (d, *J* = 8.0 Hz, 3H), 6.19 (d, *J* = 2.9 Hz, 0.5H), 6.16 (d, *J* = 2.9 Hz, 1H), 5.29 – 5.23 (m, 1.5H), 4.99 (dd, *J* = 19.1, 9.4 Hz, 1.5H), 4.23 (dd, *J* = 12.1, 4.5 Hz, 1H), 4.19 (dd, *J* = 12.5, 2.5 Hz, 0.5H), 4.14 – 4.10 (m, 1.5H), 4.02 (ddd, *J* = 10.1, 4.6, 2.4 Hz, 0.5H), 3.98 (ddd, *J* = 10.4, 4.6, 2.1 Hz, 1H), 3.75 – 3.70 (m, 1.5H), 2.43 (d, *J* = 7.2 Hz, 3H), 2.20 (ddd, *J* = 13.1, 6.3, 1.1 Hz, 1.5H), 2.09 (s, 1.5H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01 (s, 4.5H), 1.98 (s, 1.5H), 1.90 – 1.80 (m, 3H), 1.50 (d, *J* = 7.2 Hz, 1.5H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 9.5H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 174.45, 174.36, 170.35, 169.73, 169.60, 168.97, 140.60, 137.55, 137.30, 129.36, 129.36, 127.39, 127.39, 90.84, 90.84, 70.48, 70.33, 69.11, 68.83, 68.54, 68.54, 62.46, 62.05, 45.11, 45.11, 44.93, 44.93, 33.88, 33.85, 30.25, 30.25, 22.49, 22.47, 21.07, 21.04, 21.00, 20.76, 20.71, 18.54, 18.32. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{34}O_9Na$ [(M + Na)$^+$], 501.2095, found, 501.2109.

2-Deoxy-3,4,6-tri-*O*-benzoyl-1-*O*-[(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)]-α-D-glucopyranoside (2z)



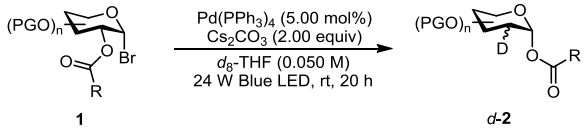
2z

According to the General Procedure B, the title compound was obtained as a white solid (111 mg, 0.128 mmol, 64% yield, C2:C1 = > 20:1). $\mathbf{R_f}$ = 0.20 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.73 (s, 1H), 8.17 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.13 – 8.05 (m, 2H), 8.05 – 7.97 (m, 7H), 7.86 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.59 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.52 (q, *J* = 7.2 Hz, 3H), 7.43 – 7.35 (m, 6H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 2.5 Hz, 1H), 6.03 – 5.89 (m, 1H), 5.79 (t, *J* = 9.8 Hz, 1H), 4.68 – 4.57 (m, 2H), 4.50 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.92 (s, 3H), 2.81 (dd, *J* = 13.4, 4.9 Hz, 1H), 2.45

– 2.30 (m, 1H), 2.21 (s, 6H), 2.13 (s, 3H), 1.82 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.28, 166.08, 165.57, 164.96, 159.17, 141.98, 139.20, 136.47, 133.56, 133.48, 133.16, 132.54, 131.62, 131.35, 130.05, 129.96, 129.89, 129.82, 129.47, 129.19, 128.72, 128.60, 128.58, 128.46, 126.85, 126.13, 125.94, 125.70, 124.91, 112.28, 91.89, 70.97, 69.89, 69.80, 63.09, 55.32, 40.75, 37.37, 37.27, 34.66, 29.25. **HRMS** (ESI-TOF) *m/z* calcd for $C_{55}H_{50}O_{10}Na$ [$(M + Na)^+$], 893.3296, found, 893.3291.

C-2 Deuteration of 1-bromosugars via excited-state Pd-catalysis

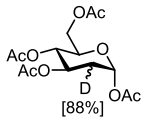
General Procedure C (for the C-2 deuteration reaction):



1 ***d*-2**

In a glovebox, to an oven-dried 4 mL screw cap vial was added $Pd(PPh_3)_4$ (1.16 mg, 1.00 μmol, 5.00 mol%), 1-bromo-sugar (0.0200 mmol, 1.00 equiv), Cs_2CO_3 (13.03 mg, 0.0400 mmol, 2.00 equiv), and d_8-THF (0.400 mL, 0.0500 M). To this suspension was added a magnetic stir bar. Next, the vial was capped, taken out of the glovebox, and sealed with parafilm. The reaction mixture was stirred at room temperature, irradiated with two 12 W Blue LEDs for 20 h. Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the desired product.

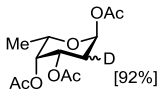
(2R,4R,5S,6R)-6-(Acetoxymethyl)tetrahydro-2H-pyran-2,4,5-triyl-3-d triacetate (*d*-2a)



***d*-2a**

According to the General Procedure C, the title compound was obtained as a colorless oil (5.70 mg, 0.017 mmol, 85% yield, C2:C1 = 8.0:1.0, 88%D). $\mathbf{R_f}$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.22 (d, *J* = 2.5 Hz, 1H), 5.28 (ddd, *J* = 11.6, 9.6, 5.3 Hz, 1H), 5.04 (t, *J* = 9.7 Hz, 1H), 4.32 – 4.16 (m, 1H), 4.08 – 3.94 (m, 2H), 2.24 (ddd, *J* = 13.5, 5.2, 1.2 Hz, 0.78H, 22%D), 2.10 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.93 (ddd, *J* = 13.6, 11.8, 3.6 Hz, 0.34H, 66%D). **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{20}DO_9$ [$(M + H)^+$], 334.1243, found, 334.1249.

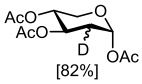
(2S,4S,5R,6S)-6-Methyltetrahydro-2H-pyran-2,4,5-triyl-3-d triacetate (*d*-2d)



d-**2d**

According to the General Procedure C, the title compound was obtained as a colorless oil (5.40 mg, 0.0196 mmol, 98% yield, C2:C1 = 10:1.0, 92%D). $\mathbf{R_f}$ = 0.20 [Hexanes: EtOAc 5:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.28 (d, *J* = 2.8 Hz, 1H), 5.28 (ddd, *J* = 12.5, 4.9, 3.5 Hz, 1H), 5.21 (s, 1H), 4.16 (q, *J* = 6.5 Hz, 1H), 2.17 (dt, *J* = 13.3, 3.5 Hz, 0.35H, 65%D), 2.16 (s, 3H), 2.09 (s, 3H), 2.00 (s, 3H), 1.87 (dd, *J* = 13.3, 4.9 Hz, 0.73H, 27%D), 1.14 (d, J = 6.5 Hz, 3H). **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{17}DNaO_7$ [(M + Na)$^+$], 298.1008, found, 298.1017.

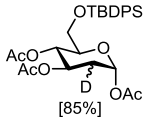
(2R,4R,5R)-Tetrahydro-2H-pyran-2,4,5-triyl-3-d triacetate (*d*-2e)



d-**2e**

According to the General Procedure C, the title compound was obtained as a colorless oil (4.60 mg, 0.0176 mmol, 88% yield, C2:C1 = 10:1.0, 82%D). $\mathbf{R_f}$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.10 (t, *J* = 3.5 Hz, 1H), 5.24 (ddd, *J* = 9.8, 8.4, 4.9 Hz, 1H), 4.90 (td, *J* = 9.1, 4.9 Hz, 1H), 3.91 (dd, *J* = 11.9, 4.9 Hz, 1H), 3.70 (dd, *J* = 11.9, 9.1 Hz, 1H), 2.21 (ddd, *J* = 14.0, 4.9, 3.5 Hz, 0.76H, 24%D), 2.10 (s, 3H), 2.05 (s, 3H), 1.87 (ddd, *J* = 14.0, 10.5, 3.5 Hz, 0.42H, 58%D). **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{15}DNaO_7$ [(M + Na)$^+$], 284.0851, found, 284.0865.

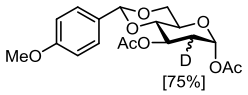
(2R,4R,5S,6R)-6-(((Tert-butyldiphenylsilyl)oxy)methyl)tetrahydro-2H-pyran-2,4,5-triyl-3-d triacetate (*d*-2i)



d-**2i**

According to the General Procedure C, the title compound was obtained as a colorless oil (9.40 mg, 0.0178 mmol, 89% yield, C2:C1 = 12:1.0, 85%D). $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 5:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.63-7.67 (m, 4H), 7.35-743 (m, 6H), 6.30 (d, *J* = 2.5 Hz, 1H), 5.31 (ddd, *J* = 11.5, 9.0, 5.0 Hz, 1H), 5.18 (t, *J* = 10.0 Hz, 1H), 3.89 (dt, *J* = 10.0, 3.5 Hz, 1H), 3.71 (d, *J* = 3.5 Hz, 1H), 2.23 (ddd, *J* = 13.5, 5.0, 1.0 Hz, 0.87H, 13%D), 2.09 (s, 3H), 2.03 (s, 3H), 1.93-1.99 (m, 0.28H, 72%D), 1.92 (s, 3H), 1.04 (s, 9H). **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{35}DNaO_8Si$ [(M + Na)$^+$], 552.2134, found, 552,2150.

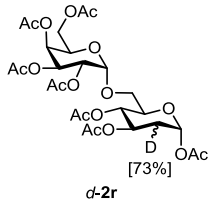
(2R,4aR,6R,8R,8aS)-2-(4-Methoxyphenyl)hexahydropyrano[3,2-d][1,3]dioxine-6,8-diyl-7-d diacetate (*d*-2k)



d-**2k**

According to the General Procedure C, the title compound was obtained as a colorless oil (7.00 mg, 0.0191 mmol, 95% yield, C2:C1 = 8.5:1.0, 75%D). $\mathbf{R_f}$ = 0.40 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.39 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.20 (d, *J* = 3.3 Hz, 1H), 5.52 (s, 1H), 5.43 – 5.26 (m, 1H), 4.26 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.97 (td, *J* = 9.9, 4.9 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 18.6, 9.9 Hz, 2H), 2.35 (ddd, *J* = 13.6, 5.3, 0.8 Hz, 0.81H, 19%D), 2.14 (s, 3H), 2.06 (s, 3H), 1.90 (ddd, *J* = 13.8, 11.2, 3.9 Hz, 0.44H, 56%D). **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{21}DNaO_8$ [(M + Na)$^+$], 390.1269, found, 390.1226.

(2R,3R,4S,5S,6S)-2-(Acetoxymethyl)-6-(((2R,3S,4R,6R)-3,4,6-triacetoxytetrahydro-2H-pyran-2-yl-5-d)methoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (*d*-2r)



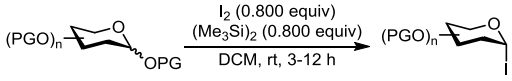
d-**2r**

According to the General Procedure C, the title compound was obtained as a colorless oil (11.2 mg, 0.0180 mmol, 90% yield, C2:C1 = 12:1.0, 73%D). $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 1:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.19 (d, *J* = 1.4 Hz, 1H), 5.28-5.35 (m, 2H), 5.15 (d, *J* = 3.5 Hz, 1H), 5.00-5.08 (m, 2H), 4.25 (t, *J* = 7.0 Hz, 1H), 4.08-4.11 (m, 1H), 4.04 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.99 (ddd, *J* = 9.8, 4.9, 2.1 Hz, 1H), 3.71 (dd, *J* = 11.2, 4.9 Hz, 1H), 3.57 (dd, *J* = 11.2, 2.1 Hz, 1H), 2.25 (dd, *J* = 13.3, 4.9 Hz, 0.80H, 20%D), 2.13 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 2H), 1.98 (s, 3H), 1.97-1.98 (m, 0.47H, 53%D). **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{35}DNaO_{17}$ [(M + Na)$^+$], 644.1907, found, 644.1911.

C-2 Iodination of 1-iodosugars via excited-state Pd-catalysis

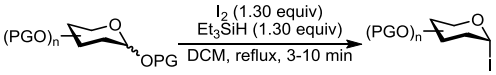
General Procedure D (for the synthesis of 1-iodosugars):

Procedure D1



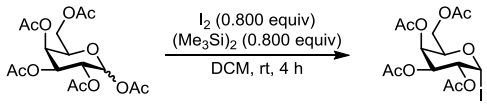
To a solution of protected sugar (1.00 equiv) in dry DCM (0.400 M), I_2 (0.800 equiv) and $(Me_3Si)_2$ (0.800 equiv) were added and the reaction mixture was stirred at room temperature for 3-12 h. The resulting mixture was diluted with $CHCl_3$ and washed with 1:1 (v/v) saturated $NaHCO_3$:10% $Na_2S_2O_3$ and saturated $NaHCO_3$ twice. The combined aqueous layers were extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over anhydrous Mg_2SO_4, and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the title compound.

Procedure D2:



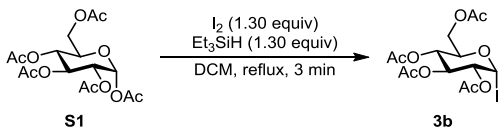
I_2 (1.30 equiv) and Et_3SiH (1.30 equiv) were added to a solution of protected sugar (1.00 equiv) in dry DCM. The reaction mixture was stirred at reflux for 3-10 min and then cooled to room temperature. The mixture was diluted with DCM and washed sequentially with 1:1 (v/v) saturated $NaHCO_3$: 10% $Na_2S_2O_3$, water, and brine. The combined organic layers were dried with Mg_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by column chromatography to afford the desired compound.

2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl iodide (3a)



The reaction was performed according to the General Procedure D1 using **S6** (2.73 g, 7.00 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (1.00 g, 2.18 mmol, 31%) as a white solid. $\mathbf{R_f}$ = 0.49 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.10 (d, *J* = 4.0 Hz, 1H), 5.49 (d, *J* = 2.5 Hz, 1H), 5.28 (dd, *J* = 3.0, 10.5 Hz, 1H), 4.37 (dd, *J* = 4.0, 11.0 Hz, 1H), 4.26-4.18 (m, 2H), 4.11 (dd, *J* = 6.5, 11.0 Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.44, 170.02, 169.99, 169.88, 75.31, 73.75, 69.87, 67.64, 66.70, 60.77, 21.05, 20.76, 20.70. The spectroscopic data corresponds to previously reported data.[17]

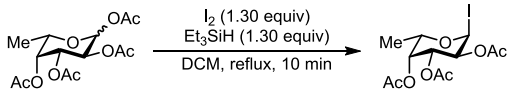
2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl iodide (3b)



The reaction was performed according to the General Procedure D2 using **S1** (9.76 g, 25.0 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica

gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (9.11 g, 19.9 mmol, 80%) as a white solid. $\mathbf{R_f}$ = 0.32 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.99 (d, *J* = 4.2 Hz, 1H), 5.47 (t, *J* = 9.8 Hz, 1H), 5.18 (t, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.21 (dd, *J* = 4.2, 9.8 Hz, 1H), 4.11 (dd, *J* = 2.1, 12.6 Hz, 1H) 4.06 (dq, *J* = 2.1, 9.8 Hz, 1H), 2.10 (d, *J* = 4.9 Hz, 6H), 2.05 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.65, 169.99, 169.75, 169.62, 75.01, 73.05, 71.84, 70.41, 67.01, 60.97, 20.97, 20.81, 20.76, 20.70. The spectroscopic data corresponds to previously reported data.[17]

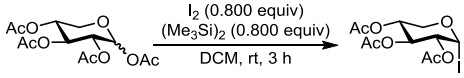
2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl iodide (3c)



S4 **3c**

The reaction was performed according to the General Procedure D2 using **S4** (1.00 g, 3.00 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (0.331 g, 0.827 mmol, 28%) as a white solid. $\mathbf{R_f}$ = 0.50 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.08 (d, *J* = 4.2 Hz, 1H), 5.34 (dd, *J* = 0.7, 2.8 Hz, 1H), 5.29 (dd, *J* = 2.8, 10.5 Hz, 1H), 4.32 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.14 (q, *J* = 6.3 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.42, 170.10, 169.97, 72.70, 70.31, 69.74, 21.12, 20.77, 20.73, 15.61. The spectroscopic data corresponds to previously reported data.[17]

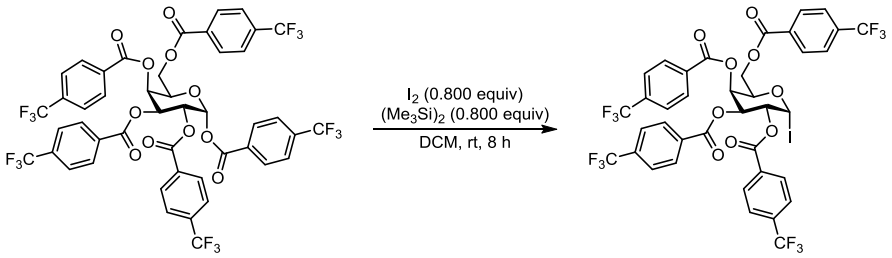
2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl iodide (3d)



S5 **3d**

The reaction was performed according to the General Procedure D1 using **S5** as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (0.631 g, 1.63 mmol, 23%) as a yellow oil. $\mathbf{R_f}$ = 0.39 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.97 (d, *J* = 4.2 Hz, 1H), 5.47 (t, *J* = 9.8 Hz, 2H), 5.05 (td, *J* = 6.3, 10.5 Hz, 1H), 4.14 (dd, *J* = 4.2, 9.8 Hz, 1H), 4.07 (dd. *J* = 6.3, 11.2 Hz, 1H), 3.62 (t, *J* = 11.2 Hz, 1H), 2.09 (s, 3H), 2.05 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.00, 169.89, 169.80, 74.64, 71.16, 70.64, 67.92, 65.35, 20.98, 20.82, 20.79. The spectroscopic data corresponds to previously reported data.[17]

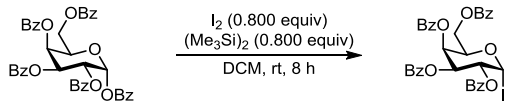
2,3,4,6-Tetra-*O*-[4-(trifluoromethyl)benzoyl]-α-D-galactopyranosyl iodide (3e)



S26 **3e**

The reaction was performed according to the General Procedure D1 using **S26** (2.91 g, 2.80 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [30:1 (v/v)] to afford the title compound (0.611 g, 0.624 mmol, 22%) as a white solid. $\mathbf{R}_f$ = 0.43 [Hexanes: EtOAc 10:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.16 (d, *J* = 7.7 Hz, 2H), 8.12 (dd, *J* = 8.4, 16.1 Hz, 4H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.0 Hz, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 4.9 Hz, 1H), 6.10 (d, *J* = 2.8 Hz, 1H), 5.95 (dd, *J* = 3.5, 10.5 Hz, 1H), 5.06 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.73-4.66 (m, 2H), 4.54 (dd, *J* = 6.3, 11.9 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 164.78, 164.40, 164.26, 164.17, 135.76 (q, $J_{C\text{-}F}$ = 33.25 Hz), 135.63 (q, $J_{C\text{-}F}$ = 33.25 Hz), 135.30 (q, $J_{C\text{-}F}$ = 33.25 Hz), 135.12 (q, $J_{C\text{-}F}$ = 33.25 Hz), 132.36, 131.79, 131.73, 131.54, 130.63, 130.63, 130.45, 130.45, 130.34, 130.34, 130.18, 130.18, 126.11 (q, $J_{C\text{-}F}$ = 3.50 Hz), 126.11 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.91 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.91 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 123.63 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.50 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.49 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.47 (q, $J_{C\text{-}F}$ = 271.25 Hz), 74.23, 73.52, 71.40, 68.36, 68.19, 61.77. **^{19}F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –63.26 (s, 3F), -63.31 (s, 3F), -63.35 (s, 6F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{27}F_{12}IO_9N$ [$(M + NH_4)^+$], 996.0533, found, 996.0509.

2,3,4,6-Tetra-*O*-benzoyl-*α*-D-galactopyranosyl iodide (3f)

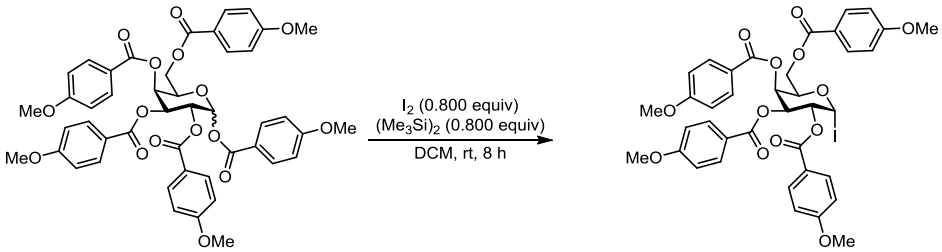


S27 **3f**

The reaction was performed according to the General Procedure D1 using **S27** (1.40 g, 2.00 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (1.00 g, 1.42 mmol, 71%) as a white solid. $\mathbf{R}_f$ = 0.43 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.07 (dd, *J* = 1.4, 8.4 Hz, 2H), 8.02 (dt, *J* = 1.4, 8.4 Hz, 4H), 7.79 (dd, *J* = 0.7, 8.4 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.56 (q, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 9.8 Hz, 2H), 7.47- 7.39 (m, 5H), 7.35 (d, *J* = 4.2 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 2H), 6.10 (dd, *J* = 0.7, 3.5 Hz, 1H), 5.95 (dd, *J* = 3.5, 10.5 Hz, 1H), 5.02 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.71-4.62 (m, 2H), 4.49 (dd, *J* = 5.6, 11.2 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.06, 165.48, 165.45, 133.97, 133.95, 133.53, 133.48, 130.24, 130.10, 129.96, 129.89, 129.38, 128.91, 128.88, 128.72, 128.63,

128.61, 128.48, 75.06, 74.62, 70.85, 68.38, 67.80, 61.68. The spectroscopic data corresponds to previously reported data.[18]

2,3,4,6-Tetra-*O*-[4-methoxybenzoyl]-α-D-galactopyranosyl iodide (3g)



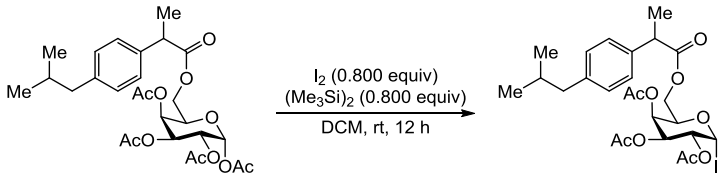
The reaction was performed according to the General Procedure D1 using **S28** (2.33 g, 2.75 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (1.68 g, 1.97 mmol, 72%) as a white solid. $\mathbf{R_f}$ = 0.31 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, CD_3CN, 25 ºC, δ): 8.01 (dt, *J* = 2.8, 8.4 Hz, 2H), 7.91 (tt, *J* = 2.8, 9.1 Hz, 4H), 7.69 (dt, *J* = 2.8, 9.1 Hz, 2H), 7.42 (d, *J* = 4.2 Hz, 1H), 7.04 (dt, *J* = 2.8, 9.1 Hz, 2H), 6.95 (dq, *J* = 7.0, 9.1 Hz, 4H), 6.81 (dt, *J* = 3.5, 8.4 Hz, 2H), 5.97 (dd, *J* = 0.7, 3.5 Hz, 1H), 5.79 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.97 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.67 (t, *J* = 6.3 Hz, 1H), 4.55-4.51 (m, 1H), 4.43 (dd, *J* = 6.3, 11.2 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (175 MHz, CD_3CN, 25 ºC, δ): 166.12, 165.98, 165.51, 165.32, 165.13, 165.11, 164.83, 164.68, 132.77, 132.74, 132.43, 132.40, 122.66, 122.08, 121.99, 121.73, 115.04, 114.96, 114.76, 114.74, 77.95, 75.59, 71.68, 68.83, 68.62, 62.11, 56.33, 56.27, 56.23, 56.21. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{36}IO_{13}$ [$(M + H)^+$], 827.1195, found, 827.1193.

2,3,6,2',4',6'-Hepta-*O*-acetyl-α-D-melibiosyl iodide (3h)

The reaction was performed according to the General Procedure D2 using **S12** (2.04 g, 3.00 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2:1 (v/v)] to afford the title compound (0.689 g, 0.923 mmol, 31%) as a white solid. $\mathbf{R_f}$ = 0.49 [Hexanes: EtOAc 1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.97 (d, *J* = 4.2 Hz, 1H), 5.46 (t, *J* = 9.8 Hz, 2H), 5.33 (dd, *J* = 2.8, 10.5 Hz, 1H), 5.20 (t, *J* = 9.8 Hz, 1H), 5.15 (d, *J* = 3.5 Hz, 1H), 5.09 (dd, *J* = 4.2, 11.2 Hz, 1H), 4.18-4.14 (m, 2H), 4.11-4.03 (m, 2H), 4.00 (dq, *J* = 2.1, 10.5 Hz, 1H), 3.78 (dd, *J* = 4.2, 11.9 Hz, 1H)**,** 3.63 (dd, *J* = 2.1, 11.9 Hz, 1H), 2.13 **(**d, *J* = 6.3 Hz, 6H), 2.10

(s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.69, 170.53, 170.33, 170.04, 170.01, 169.76, 169.52, 96.37, 75.80, 73.09, 71.94, 70.42, 68.16, 68.09, 67.56, 67.46, 66.59, 65.35, 61.75, 20.99, 20.97, 20.88, 20.81, 20.78, 20.74. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{36}IO_{17}$ [(M + H)$^+$], 747.0992, found, 747.0979.

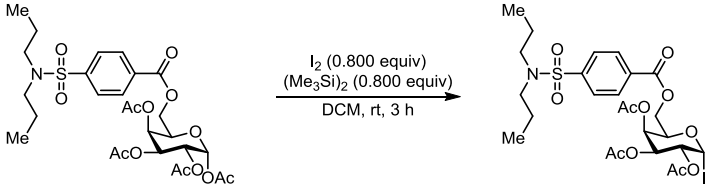
2,3,4-Tri-*O*-acetyl-6-*O*-[((2-(4-isobutylphenyl)propanoyl)]-α-D-galactopyranosyl iodide (3i)



S29 **3i**

The reaction was performed according to the General Procedure D1 using **S29** (0.939 g, 1.75 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [7:1 (v/v)] to afford the title compound (0.457 g, 0.756 mmol, 43%) as a colorless oil. $\mathbf{R_f}$ = 0.24 [Hexanes: EtOAc 8:1 (v/v)]. **^{1}H NMR** (700 MHz, Acetonitrile-*d3*, 25 ºC, δ): 7.27-7.22 (m, 2.40H), 7.14-7.11 (m, 2.40H), 7.10 (d, *J* = 4.2 Hz, 1H, H-1 for one diastereomer), 7.09 (dd, *J* = 4.2 Hz, 0.2H, H-1 for the other diastereomer), 5.43-5.40 (m, 1.20H), 5.20 (dd, *J* = 2.8, 10.5 Hz, 1H), 5.13 (dd, *J* = 3.5, 10.5, 0.20H), 4.31 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.23 (t, *J* = 6.3 Hz, 0.20H), 4.20 (t, *J* = 6.3 Hz, 1H), 4.11-4.08 (m, 0.40H), 4.02 (dd, *J* = 4.2, 10.5Hz, 0.20H), 3.89-3.79 (m, 2.20H), 3.76 (dd, *J* = 4.9, 11.9 Hz, 1H), 2.44 (d, *J* = 7.7 Hz, 2H), 2.44 (d, *J* = 7.7 Hz, 0.40H), 2.04 (s, 3H), 1.98 (s, 1.20H), 1.92 (s, 3H), 1.86 (s, 3H), 1.81 (dq, *J* = 7.0 Hz, 1.20H), 1.71 (s, 0.60H), 1.49 (d, *J* = 7.7 Hz, 3H), 1.47 (d, *J* = 7.7 Hz, 0.60H), 0.85 (d, *J* = 6.3 Hz, 6H), 0.85 (d, *J* = 6.3 Hz, 1.20H). **^{13}C NMR** (175 MHz, Acetonitrile-*d3*, 25 ºC, δ): 174.60, 174.49, 170.97, 170.73, 170.57, 170.48, 170.40, 170.19, 141.83, 141.74, 138.42, 138.29, 130.30, 130.30, 130.24, 130.24, 128.26, 128.26, 128.18, 128.18, 77.51, 77.31, 75.13, 75.10, 70.42, 70.34, 68.15, 68.08, 67.78, 67.78, 61.78, 61.45, 45.77, 45.77, 45.34, 45.34, 30.96, 30.93, 22.45, 22.45, 22.43, 22.43, 20.98, 20.90, 20.76, 20.67, 20.65, 20.54, 18.44, 17.80. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{34}IO_9$ [(M + H)$^+$], 605.1242, found, 605.1249.

2,3,4-Tri-*O*-acetyl-6-*O*-[(4-(*N*,*N*-dipropylsulfamoyl)benzoyl)]-α-D-galactopyranosyl iodide (3j)

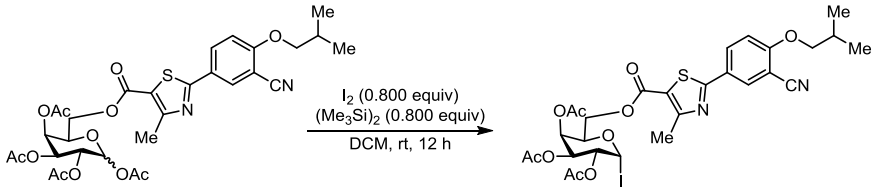


S30 **3j**

The reaction was performed according to the General Procedure D1 using **S30** (0.185 g, 0.300 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (0.0500 g, 0.0732 mmol,

25%) as a white foam. $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, CD_3CN, 25 ºC, δ): 8.21 (dt, *J* = 2.1, 9.1 Hz, 2H), 7.94 (dt, *J* = 1.4, 8.4 Hz, 2H), 7.23 (d, *J* = 4.2 Hz, 1H), 5.74 (dd, *J* = 0.56, 2.8 Hz, 1H), 5.37 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.46 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.40 (t, *J* = 6.3 Hz, 1H), 4.21 (dd, *J* = 2.1, 4.9 Hz, 2H), 3.10, (t, *J* = 7.7 Hz, 4H), 2.26 (br, 3H), 2.05, (s, 3H), 1.92 (d, *J* = 4.2 Hz, 6H), 1.53 (sextet, *J* = 7.7 Hz, 4H), 0.85 (t, *J* = 7.7 Hz, 6H), . **^{13}C NMR** (175 MHz, CD_3CN, 25 ºC, δ): 170.98, 170.61, 170.44, 165.34, 145.74, 133.19, 131.47, 128.27, 77.27, 75.15, 70.48, 69.30, 68.17, 61.98, 50.80, 22.68, 21.01, 20.71, 20.69, 11.30. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{35}INO_{11}S$ [(M + H)$^+$], 684.0970, found, 684.0972.

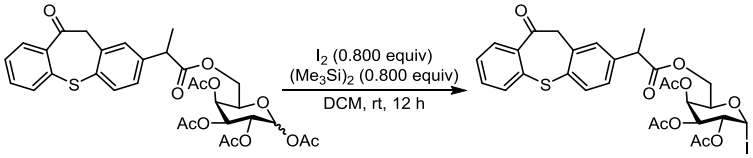
2,3,4-Tri-*O*-acetyl-6-*O*-[(2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)]-α-D-galactopyranosyl iodide (3k)



S31 **3k**

The reaction was performed according to the General Procedure D1 using **S31** (0.491 g, 0.760 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [6:1 (v/v)] to afford the title compound (0.316 g, 0.442 mmol, 58%) as a white foam. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, Acetonitrile-d_3, 25 ºC, δ): 8.24 (*d*, *J* = 2.8 Hz, 1H), 8.18 (dd, *J* = 2.8, 9.1 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 1H), 7.19 (d, *J* = 4.2 Hz, 1H), 5.67 (dd, *J* = 1.4, 2.8 Hz, 1H), 5.34 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.42 (dd, *J* = 2.8, 10.5 Hz, 1H), 4.38 (t, *J* = 6.3 Hz, 1H), 4.21 (d, *J* = 6.3 Hz, 3H), 3.98 (d, *J* = 7.0 Hz, 3H), 2.72 (s, 3H), 2.17-2.11 (m, 1H), 2.05 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.06 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, Acetonitrile-d_3, 25 ºC, δ): 171.70, 170.62, 170.46, 169.30, 163.74, 163.16, 161.84, 133.99, 132.99, 126.43, 121.27, 116.29, 114.37, 103.24, 76.90, 76.49, 75.10, 70.44, 69.04, 68.13, 61.97, 28.86, 20.99, 20.74, 20.73, 19.06, 19.06, 17.97. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{32}IN_2O_{10}S$ [(M + H)$^+$], 715.0817, found, 715.0814.

2,3,4-Tri-*O*-acetyl-6-*O*-[((2-(10-oxo-10,11-dihydrodibenzo[*b,f*]thiepin-2-yl)propanoyl)]-α-D-galactopyranosyl iodide (3l)

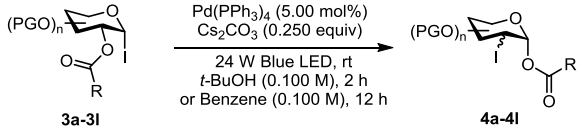


S32 **3j**

The reaction was performed according to the General Procedure D1 using **S32** (0.578 g, 0.920 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [5:1 (v/v)] to afford the title compound (0.495 g, 0.582 mmol, 63%) as a white foam. $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, Acetonitrile-d_3, 25 ºC,

δ): 8.10-8.06 (m, 1H), 7.67- 7.60 (m, 2H), 7.49 (dt, *J* = 1.5, 8.5 Hz, 1H), 7.46 (dd, *J* = 2.0, 4.5 Hz, 1H), 7.36 (dt, *J* = 1.5, 6.0 Hz, 1H), 7.24 (dt, *J* = 2.0, 8.5 Hz, 1H), 7.09 (d, *J* = 4.0 Hz, 0.7H), 7.03 (d, *J* = 4.0 Hz, 0.3H), 5.39 (dd, *J* = 1.0, 3.5 Hz, 1H), 5.20 (dd, *J* = 3.5, 10.5 Hz, 0.7H), 5.12 (dd, *J* = 3.5, 10.5 Hz, 0.3H), 4.37-4.04 (m, 4H), 3.98-3.70 (m, 3H), 2.03 (s, 2.1H), 1.97 (s, 0.9H), 1.92 (s, 0.9H), 1.87 (s, 2.1H), 1.80 (s, 2.1H), 1.65 (s, 0.9H), 1.51 (d, *J* = 6.0 Hz, 2.1H), 1.48 (d, *J* = 6.0 Hz, 0.9H).**^{13}C NMR** (125 MHz, Acetonitrile-d_3, 25 ºC, δ): 191.88, 191.88, 173.91, 173.86, 170.97, 170.71, 170.53, 170.42, 170.40, 170.11, 143.43, 143.40, 140.76, 140.76, 139.21, 139.11, 137.03, 137.00, 134.27, 134.11, 133.71, 133.71, 132.46, 132.37, 132.03, 132.03, 131.69, 131.64, 129.46, 129.37, 127.98, 127.94, 127.90, 127.64, 77.41, 77.22, 75.01, 74.99, 70.43, 70.40, 68.14, 68.10, 68.04, 67.98, 61.73, 61.39, 51.45, 51.44, 45.78, 45.37, 20.99, 20.86, 20.76, 20.63, 20.57, 20.45, 18.21, 17.65. **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{30}IO_{10}S$ [(M + H)$^+$], 697.0599, found, 697.0596.

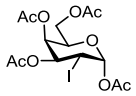
General Procedure E (for the C-2 iodination reaction):



3a-3l **4a-4l**

In a glovebox, to an oven-dried 4 mL screw cap vial was added $Pd(PPh_3)_4$ (5.00 mol%), 1-iodo-sugar (0.100 or 0.200 mmol, 1.00 equiv), Cs_2CO_3 (0.250 equiv) and *t*-BuOH (0.100 M) or benzene (0.100 M). A magnetic stir bar was then added. Next, the vial was capped, taken out of the glovebox, and sealed with parafilm. The reaction mixture was stirred at room temperature, irradiated with two 12 W Blue LEDs for 2 h (in *t*-BuOH) or 12 h (in Benzene). Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, to afford the desired product.

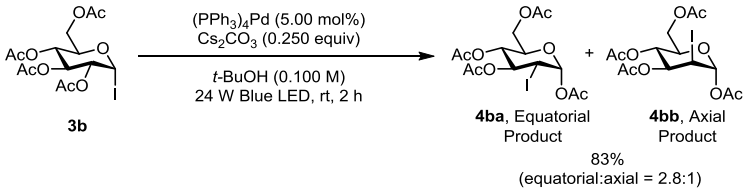
2-Deoxy-2-iodo-1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (4a)



4a

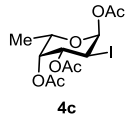
The reaction was performed according to the General Procedure E using **3a** (91.6 mg, 0.200 mmol, 1.00 equiv) as the substrate and *t*-BuOH as solvent. The title compound was obtained as a colorless oil (72.0 mg, 0.157 mmol, 79% yield, equatorial: axial = > 20:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.40 (d, *J* = 3.5 Hz, 1H), 5.36-5.33 (m, 2H), 4.42-4.38 (m, 1H), 4.36 (t, *J* = 7.0 Hz, 1H), 4.40 (dd, *J* = 3.5, 11.2 Hz, 1H), 2.19 (s, 3H), 2.15 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.52, 170.08, 169.78, 168.83, 92.49, 70.17, 68.78, 67.56, 61.30, 22.43, 20.85, 20.80, 20.78, 20.74. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{23}IO_9N$ [(M + NH_4)$^+$], 476.0412, found, 476.0412.

2-Deoxy-2-iodo-1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (4ba) and 2-Deoxy-2-iodo-1,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (4bb)



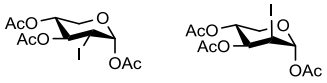
The reaction was performed according to the General Procedure E using **3b** (91.6 mg, 0.200 mmol, 1.00 equiv) as the substrate and *t*-BuOH as solvent. The title compounds as was obtained as a colorless oil (76.0 mg, 0.166 mmol, 83% yield, equatorial: axial = 2.8:1). **4ba**: $\mathbf{R_f}$ = 0.25 Hexanes: EtOAc [4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.36 (d, *J* = 2.8 Hz, 1H), 5.51 (t, *J* = 9.8 Hz, 1H), 5.10 (t, *J* = 9.8 Hz, 1H), 4.30(t, *J* = 3.5, 12.6 Hz, 1H), 4.14 (dd, *J* = 2.8, 12.6 Hz, 2H), 4.04 (d, *J* = 12.6 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.74, 169.94, 169.58, 168.67, 91.77, 72.55, 70.13, 68.60, 61.61, 23.44, 20.95, 20.83, 20.82, 20.71. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{23}IO_9N$ [$(M + NH_4)^+$], 476.0412, found, 476.0411. **4bb**: $\mathbf{R_f}$ = 0.15 Hexanes: EtOAc [4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.39 (d, *J* = 1.4 Hz, 1H), 5.45 (t, *J* = 9.8 Hz, 1H), 4.58 (dd, *J* = 4.2, 9.8 Hz, 1H), 4.52 (dd, *J* = 2.1, 4.9 Hz, 1H), 4.22 (dd, *J* = 4.9, 12.6 Hz, 1H), 4.15 (dd, *J* = 2.1, 12.6Hz, 1H), 4.11 (dq, *J* = 2.8, 9.8 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.07, 169.45, 168.32, 94.82, 71.56, 68.76, 67.13, 61.96, 27.28, 21.06, 21.00, 20.87, 20.76. These spectroscopic data correspond to previously reported data.[19]

2-Deoxy-2-iodo-1,3,4-tri-*O*-acetyl-α-L-fucopyranoside (4c)



The reaction was performed according to the General Procedure E using **3c** (80.0 mg, 0.200 mmol, 1.00 equiv) as the substrate and *t*-BuOH as solvent. The title compound was obtained as a colorless oil (65.0 mg, 0.163 mmol, 81% yield, equatorial:axial = > 20:1). $\mathbf{R_f}$ = 0.38 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.37 (d, *J* = 2.8 Hz, 1H), 5.35 (dd, *J* = 2.8, 11.9 Hz, 1H), 5.20 (d, *J* = 2.8 Hz, 1H), 4.39 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.28 (dd, *J* = 6.3, 11.9 Hz, 1H), 2.17 (s, 6H), 2.07 (s, 3H), 1.13 (d, *J* = 6.3 Hz, 3H).**^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.46, 169.84, 169.07, 92.73, 70.90, 70.70, 67.38, 22.96, 20.90, 20.84, 20.75, 16.20. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{21}IO_7N$ [$(M + NH_4)^+$], 418.0357, found, 418.0355.

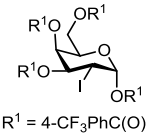
2-Deoxy-2-iodo-1,3,4-tri-*O*-acetyl-α-D-xylopyranoside (4da) and 2-Deoxy-2-iodo-1,3,4-tri-*O*-acetyl-α-D-lyxopyranoside (4db)



4da **4db**

The reaction was performed according to the General Procedure E using **3d** (77.2 mg, 0.200 mmol, 1.00 equiv) as the substrate and *t*-BuOH as solvent. The title compound was obtained as a colorless oil and inseparable mixture (60.0 mg, 0.156 mmol, 78% yield, **4da**:**4db** = 1.2:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.27 (d, *J* = 2.8 Hz, 1H, H1 of 4da), 6.10 (d, *J* = 6.3 Hz, 0.3H, H1 of 4db), 5.51 (dd, *J* = 9.1, 11.2 Hz, $1H_{4da}$), 4.98 (ddd, *J* = 10.7, 9.2, 5.9 Hz, $1H_{4da}$), 5.03-4.94 (m, $0.6H_{4db}$), 4.48 (dd, *J* = 3.5, 6.3 Hz, $0.3H_{4db}$), 4.07 (dd, *J* = 3.5, 11.2 Hz , $1H_{4da}$), 4.06 (dd, *J* = 4.2, 17.5 Hz , $0.3H_{4db}$), 3.94 (dd, *J* = 5.6, 11.2 Hz, $1H_{4da}$), 3.94 (dd, *J* = 7.7, 17.5 Hz, $0.3H_{4db}$),3.75 (t, *J* = 11.2 Hz, $1H_{4da}$), 2.19 (s, $3H_{4da}$), 2.17 (s, $1H_{4db}$), 2.15 (s, $1H_{4db}$), 2.12 (s, $3H_{4da}$), 2.11 (s, $0.9H_{4db}$), 2.03 (s, $3H_{4da}$). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 169.85 (4da), 169.85 (4da), 169.72 (4db), 169.42 (4db), 168.95 (4da), 168.84 (4db), 93.34 (4db), 92.03 (4da), 71.94 (4da), 70.17 (4db), 69.29 (4da), 67.83 (4db), 63.85 (4db), 61.08 (4da), 26.13 (4db), 23.78 (4da), 21.03 (4da), 21.00 (4db), 20.93 (4db), 20.82 (4da), 20.91 (4db), 20.79 (4da). **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{19}IO_7N$ [$(M + NH_4)^+$], 404.0201, found, 404.0203.

2-Deoxy-2-iodo-1,3,4,6-tetra-*O*-[4-(trifluoromethyl)benzoyl]-α-D-galactopyranoside (4e)



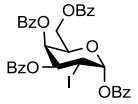
R^1 = 4-CF_3PhC(O)

4e

The reaction was performed according to the General Procedure E using **3e** (97.8 mg, 0.100 mmol, 1.00 equiv) as the substrate and benzene as solvent. The title compound was obtained as a colorless oil (74.0 mg, 0.0760 mmol, 76% yield, equatorial:axial = > 10:1). (The product contains small amount of inseparable starting material). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 20:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.27 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 3.5 Hz, 1H), 5.98 (d, *J* = 2.8 Hz, 1H), 5.89 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.81 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.77 (t, *J* = 7.0 Hz, 1H), 4.58 (dd, *J* = 7.0, 11.2 Hz, 1H), 4.41 (dd, *J* = 7.0, 11.2 Hz, 1H).**^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 164.73, 164.29, 164.23, 163.34, 135.76 (q, $J_{C\text{-}F}$ = 33.25 Hz), 135.69 (q, $J_{C\text{-}F}$ = 33.25 Hz), 135.37 (q, $J_{C\text{-}F}$ = 33.25 Hz), 135.05 (q, $J_{C\text{-}F}$ = 33.25 Hz), 132.32, 132.00, 131.86, 131.84, 130.67, 130.67, 130.38, 130.38, 130.38, 130.38, 130.23, 130.23, 126.11 (q, $J_{C\text{-}F}$ = 3.50 Hz), 126.11 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.91 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.91 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 125.73 (q, $J_{C\text{-}F}$ = 3.50 Hz), 123.60 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.56 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.54 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.51 (q, $J_{C\text{-}F}$ = 271.25 Hz), 93.72, 71.70, 69.24, 68.71, 62.04, 21.24. **^{19}F NMR** (376 MHz,

$CDCl_3$, 25 ºC, δ): –63.27, -63.28, -63.28, -63.30. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{27}F_{12}IO_9N$ [(M + $NH_4)^+$], 996.0533, found, 996.0535.

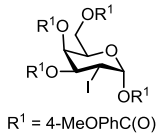
2-Deoxy-2-iodo-1,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranoside (4f)



4f

The reaction was performed according to the General Procedure E using **3f** (141 mg, 0.200 mmol, 1.00 equiv) as the substrate and benzene as solvent. The title compound was obtained as a colorless oil (110 mg, 0.156 mmol, 78% yield, equatorial:axial = > 10:1). (The product contains small amount of inseparable starting material). $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 6:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.17 (d, *J* = 7.0 Hz, 2H), 8.03 (d, *J* = 7.0 Hz, 2H), 7.93 (dd, *J* = 7.0, 18.2 Hz, 4H), 7.70- 7.61 (m, 2H), 7.58- 7.47 (m, 6H), 7.39-7.35 (m, 4H), 6.81 (d, *J* = 3.5 Hz, 1H), 5.99 (d, *J* = 2.8 Hz, 1H), 5.93 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.84 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.77 (t, *J* = 7.0 Hz, 1H), 4.55 (dd, *J* = 7.0, 11.9 Hz, 1H), 4.34 (dd, *J* = 7.0, 11.9 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 165.99, 165.42, 165.30, 164.54, 134.16, 133.88, 133.68, 133.37, 130.29, 130.29, 130.07, 130.07, 130.01, 130.01, 129.87, 129.87, 129.34, 129.10, 129.05, 128.95, 128.95, 128.84, 128.84, 128.80, 128.57, 128.57, 128.53, 128.53, 93.40, 71.30, 69.45, 68.48, 61.91, 22.42. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{31}IO_9N$ [(M + $NH_4)^+$], 724.1038, found, 724.1044.

2-Deoxy-2-iodo-1,3,4,6-tetra-*O*-[4-methoxybenzoyl]-α-D-galactopyranoside (4g)

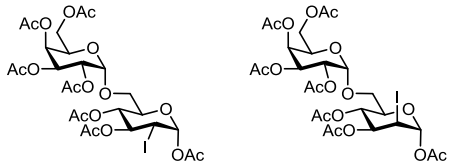


R^1 = 4-MeOPhC(O)

4g

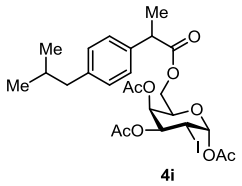
The reaction was performed according to the General Procedure E using **3g** (165.2 mg, 0.200 mmol, 1.00 equiv) as the substrate and benzene as solvent. The title compound was obtained as a colorless oil (117.3 mg, 0.142 mmol, 71% yield, equatorial:axial = > 10:1). (The product contains small amount of inseparable starting material). $\mathbf{R_f}$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.12- 8.10 (m, 2H), 8.00-7.97 (m, 2H), 7.89-7.85 (m, 4H), 7.01-6.98 (m, 2H), 6.97-6.94 (m, 2H), 6.86- 6.83 (m, 4H), 6.76 (d, *J* = 3.5 Hz, 1H), 5.93 (dd, *J* = 1.4, 3.5 Hz, 1H), 5.88 (dd, *J* = 2.8, 11.2 Hz, 1H), 4.81 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.72 (t, *J* = 7.0 Hz, 1H), 4.51 (dd, *J* = 7.0, 11.9 Hz, 1H), 4.27 (dd, *J* = 7.0, 11.9 Hz, 1H), 3.89 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H), 3.83 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 165.70, 165.08, 164.90, 164.32, 164.25, 164.03, 163.91, 163.64, 132.45, 132.45, 132.18, 132.18, 132.11, 132.11, 131.96, 131.96, 121.83, 121.52, 121.51, 121.09, 114.19, 114.19, 114.05, 114.05, 113.83, 113.83, 113.76, 113.76, 93.18, 71.03, 69.47, 68.31, 61.70, 55.70, 55.68, 55.59, 55.53, 23.08. **HRMS** (ESI-TOF) *m/z* calcd for $C_{39}H_{35}IO_{13}$ [(M + $H)^+$], 827.1195, found, 827.1196.

2-Deoxy-2-iodo-1,3,4,2',3',4',6'-hepta-*O*-acetyl-α-D-melibioside (4ha) and (2R,3S,4S,5R,6S)-2-(Acetoxymethyl)-6-(((2R,3R,4S,5S,6R)-3,4,6-triacetoxy-5-iodotetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4hb)



The reaction was performed according to the General Procedure E using **3h** (149 mg, 0.200 mmol, 1.00 equiv) as the substrate and *t*-BuOH as solvent. The title compound was obtained as a colorless oil (112 mg, 0.150 mmol, 75% yield, **4ha**:**4hb** = 2.8:1). **4ha:** $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.30 (d, *J* = 3.5 Hz, 1H), 5.51 (dd, *J* = 9.1, 11.9 Hz, 1H), 5.44 (d, *J* = 2.8 Hz, 1H), 5.33 (dd, *J* = 3.5, 11.2 Hz, 1H), 5.17 (d, *J* = 3.5 Hz, 1H), 5.12-5.01 (m, 2H), 4.18 (d, *J* = 7.0 Hz, 1H), 4.11-4.07 (m, 3H), 4.03 (dd, *J* = 7.0, 11.2 Hz, 1H), 3.70 (dd, *J* = 4.9, 11.2 Hz, 1H), 3.58 (dd, *J* = 2.8, 11.2 Hz, 1H), 2.21 (s, 3H), 2.13 (s, 3H), 2.10 (s, 6H), 2.04 (s, 6H), 1.99 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.70, 170.54, 170.33, 170.00, 169.96, 169.49, 168.77, 95.95, 91.68, 72.68, 70.81, 69.13, 68.33, 68.18, 67.47, 66.42, 65.71, 61.64, 23.52, 20.96, 20.93, 20.87, 20.81, 20.80, 20.79, 20.75. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{39}IO_{17}N$ [$(M + NH_4)^+$], 764.1257, found, 764.1245. **4hb:** $\mathbf{R}_f$ = 0.15 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.34 (d, *J* = 2.1 Hz, 1H), 5.47-5.43 (m, 2H), 5.39 (dd, *J* = 3.5, 11.2 Hz, 1H), 5.18 (d, *J* = 3.5 Hz, 1H), 5.12 (dd, *J* = 3.5, 11.2 Hz, 1H), 4.60 (dd, *J* = 4.2, 9.1 Hz, 1H), 4.52 (dd, *J* = 2.1, 4.2 Hz, 1H), 4.29 (t, *J* = 6.3 Hz, 1H), 4.12 (dd, *J* = 6.3, 11.2 Hz, 1H), 4.10-4.05 (m, 2H), 3.77 (dd, *J* = 4.8, 11.2 Hz, 1H), 3.58 (dd, *J* = 2.8, 11.2 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.62, 170.37, 170.12, 170.01, 160.41, 168.47, 95.85, 94.75, 72.05, 68.99, 68.37, 68.20, 67.68, 67.59, 66.54, 66.20, 61.90, 27.17, 21.11, 21.11, 21.00, 20.96, 20.83, 20.83, 20.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{39}IO_{17}N$ [$(M + NH_4)^+$], 764.1257, found, 764.1250.

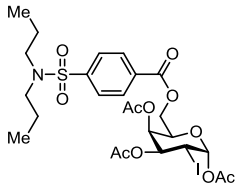
2-Deoxy-2-iodo-1,3,4-tri-*O*-acetyl-6-[((2-(4-isobutylphenyl)propanoyl)]-α-D-galactopyranoside (4i)



The reaction was performed according to the General Procedure E using **3i** (60.4 mg, 0.10 mmol, 1.00 equiv) as the substrate and *t*-BuOH as solvent. The title compound was obtained as a white foam (49.0 mg, 0.810 mmol, 81% yield, equatorial:axial = > 20:1). $\mathbf{R}_f$ = 0.70 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz,

$CDCl_3$, 25 ºC, δ): 7.21 (d, *J* = 7.7 Hz, 0.40H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 0.4H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.35 (d, *J* = 3.5 Hz, 1H, H-1 for one diastereomer), 6.29 (d, *J* = 3.5 Hz, 0.20H, H-1 for the other diastereomer), 5.35-5.26 (m, 2.20H), 5.20 (dd, *J* = 2.8, 11.9Hz, 0.20H), 4.33-4.24 (m, 2.40H), 4.05-4.00 (m, 0.40H), 3.96 (dd, *J* = 2.8, 11.9Hz, 0.20H), 3.87-3.76 (m, 2.40H), 3.59 (dd, *J* = 7.7, 11.2 Hz, 1H), 2.46 (d, *J* = 7.0 Hz, 0.40H), 2.44 (d, *J* = 7.0 Hz, 2H), 2.16 (s, 3H), 2.15 (s, 0.60H), 2.02 (s, 0.60H), 1.98 (s, 3H), 1.93 (s, 3H), 1.84 (s, 0.6H), 1.87-1.80 (m, 1.20H), 1.53 (dd, *J* = 7.0 Hz, 3H), 1.53 (dd, *J* = 7.0 Hz, 0.60H), 0.89 (dd, *J* = 7.0 Hz, 1.20H), 0.87 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 173.87, 173.76, 170.48, 170.20, 169.72, 169.70, 168.85, 168.85, 141.27, 141.20, 137.14, 136.95, 129.59, 129.59, 129.49, 129.49, 127.44, 127.44, 127.21, 127.21, 92.46, 92.44, 77.30 (overlap with $CDCl_3$), 77.20 (overlap with $CDCl_3$), 70.21, 70.14, 68.79, 68.79, 67.59, 67.52, 61.32, 61.07, 45.38, 45.14, 45.10, 44.93, 30.37, 30.32, 22.57, 22.57, 22.46, 22.46, 22.34, 22.03, 20.81, 20.78, 20.67, 20.53, 17.94, 17.47. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{37}IO_9N$ [(M + NH_4)$^+$], 622.1508, found, 622.1501.

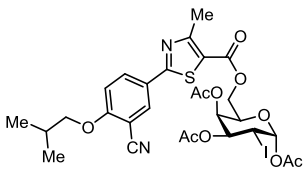
2-Deoxy-2-iodo-1,3,4-tri-*O*-acetyl-6-*O*-[(4-(*N*,*N*-dipropylsulfamoyl)benzoyl)]-α-D-galactopyranoside (4j)



4j

The reaction was performed according to the General Procedure E using **3j** (68.3 mg, 0.100 mmol, 1.00 equiv) as the substrate and benzene as solvent. The title compound was obtained as a yellow foam (50.0 mg, 0.0740 mmol, 74% yield, equatorial:axial = > 20:1). $\mathbf{R}_f$ = 0.40 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.17 (d, *J* = 9.1 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 6.49 (d, *J* = 2.8 Hz, 1H), 5.63 (dd, *J* = 1.4, 3.5 Hz, 1H), 5.46 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.51-4.45 (m, 2H), 4.15 (dd, *J* = 6.3, 11.2 Hz, 1H), 4.09 (dd, *J* = 7.0, 11.2 Hz, 1H), 3.13- 3.08 (m, 4H), 2.22 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.61-1.55 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.50, 169.82, 168.78, 164.33, 145.18, 132.19, 130.60, 130.60, 127.47, 127.47, 92.43, 70.31, 68.87, 68.85, 61.54, 50.33, 50.33, 22.27, 22.27, 22.14, 20.85, 20.77, 20.76, 11.32, 11.32. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{35}INO_{11}S$ [(M + H)$^+$], 684.0970, found, 684.0970.

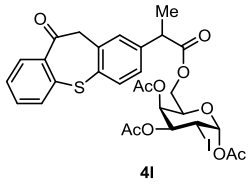
2-Deoxy-2-iodo-1,3,4-tri-*O*-acetyl-6-*O*-[(2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)]-α-D-galactopyranoside (4k)



4k

The reaction was performed according to the General Procedure E using **3k** (71.4 mg, 0.100 mmol, 1.00 equiv) as the substrate and benzene as solvent. The title compound was obtained as a white foam (61.0 mg, 0.0630 mmol, 63% yield, equatorial:axial = > 20:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, Acetonitrile-d_3, 25 ºC, δ): 8.24 (d, *J* = 2.8 Hz, 1H), 8.18 (dd, *J* = 2.8, 9.1 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 1H), 7.19 (d, *J* = 4.2 Hz, 1H), 5.67 (dd, *J* = 1.4, 2.8 Hz, 1H), 5.34 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.42 (dd, *J* = 2.8, 10.5 Hz, 1H), 4.38 (t, *J* = 6.3 Hz, 1H), 4.21 (d, *J* = 6.3 Hz, 3H), 3.98 (d, *J* = 7.0 Hz, 3H), 2.72 (s, 3H), 2.17-2.11 (m, 1H), 2.05 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.06 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, Acetonitrile-d_3, 25 ºC, δ): 171.70, 170.62, 170.46, 169.30, 163.74, 163.16, 161.84, 133.99, 132.99, 126.43, 121.27, 116.29, 114.37, 103.24, 76.90, 76.49, 75.10, 70.44, 69.04, 68.13, 61.97, 28.86, 20.99, 20.74, 20.73, 19.06, 19.06, 17.97. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{32}IN_2O_{10}S$ [(M + H)$^+$], 715.0817, found, 715.0811.

2-Deoxy-2-iodo-1,3,4-Tri-*O*-acetyl-6-*O*-[((2-(10-oxo-10,11-dihydrodibenzo[*b,f*]thiepin-2-yl)propanoyl)]-α-D-galactopyranoside (4l)



4l

The reaction was performed according to the General Procedure E using **3l** (69.7 mg, 0.10 mmol, 1.00 equiv) as the substrate and benzene as solvent. The title compound was obtained as a white foam (41.0 mg, 0.0589 mmol, 59% yield, equatorial:axial = > 20:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.20 (dd, *J* = 1.4, 7.7 Hz, 0.45H), 8.19 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.65-7.58 (m, 2.90H), 7.44-7.38 (m, 2.90H), 7.34-7.29 (m, 1.45H), 7.16 (dd, *J* = 1.4, 7.7 Hz, 0.45H), 7.13 (dd, *J* = 1.4, 7.7 Hz, 1H), 6.35 (d, *J* = 3.5 Hz, 1H, H-1 of one diastereomer), 6.28 (d, *J* = 2.8 Hz, 0.45H, H-1 of another diastereomer), 5.33-5.27 (m, 2.45H), 5.20 (dd, *J* = 2.8, 11.9Hz, 0.45H), 4.41-4.33 (m, 3.35H), 4.33-4.26 (m, 1.45H), 4.20-4.24 (m, 1H), 4.02 (dq, *J* = 7.0, 11.9 Hz, 1H), 3.85-3.80 (m, 2.35H), 3.61 (dd, *J* = 7.0, 11.2, 1H), 2.16 (s, 3H), 2.14 (s, 1.35H), 2.02 (s, 1.35H), 1.98 (s, 3H), 1.92 (s, 3H), 1.85 (s, 1.35H), 1.54 (d, *J* = 7.0 Hz, 3H), 1.52 (d, *J* = 7.0 Hz, 1.35H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.29, 191.21, 173.04, 173.04, 170.45, 170.19, 169.64, 169.61, 168.79, 168.76, 142.08, 141.85, 140.22, 140.20, 138.35, 138.28, 136.23, 136.20, 134.01, 133.98, 132.74, 132.70, 131.81, 131.77, 131.71, 131.63, 131.06, 131.02, 128.66, 128.51, 127.09, 127.03, 126.72, 126.43, 92.38, 92.34, 70.13, 70.09, 68.65, 68.62, 67.90, 67.90, 61.14, 60.96, 51.28, 51.21, 45.38, 44.98, 22.10, 21.63, 20.80, 20.80, 20.77, 20.67, 20.64, 20.54, 18.20, 17.59. **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{30}IO_{10}S$ [(M + H)$^+$], 697.0599, found, 697.0605.

Mechanistic Studies

UV-Vis Measurements

The sample of the reaction mixture was prepared by adding acetylated 1-bromoglucose (**1a**) (1.64 mg, 4.00 µmol, 1.00 equiv), $Pd(PPh_3)_4$ (0.232 mg, 0.200 µmol , 5.00 mol%), DIPEA (1.03 mg, 8.00 µmol, 2.00 equiv), and *i*-PrOAc (4.00 mL, 1.00 µM) to a cuvette. Other control samples were prepared in same way with same concentration. UV-Vis Absorptions were measured on a Cary 100 UV-Vis spectrophotometer from Agilent Technologies.

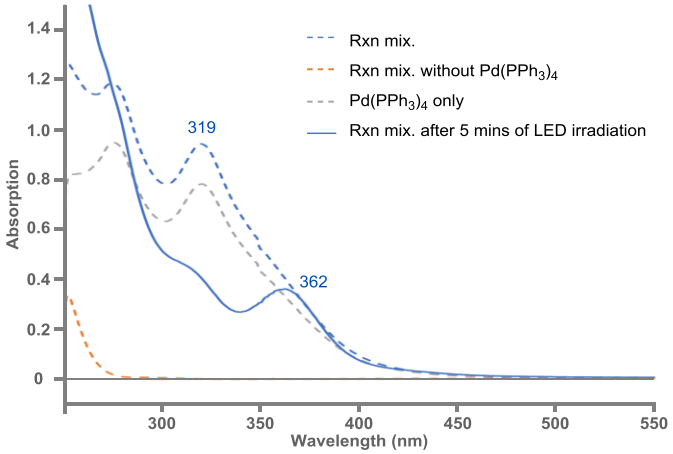


Fig. S1. UV absorption spectrums of (i) the reaction mixture, (ii) the reaction mixture without $Pd(PPH_3)_4$, (iii) a solution of $Pd(PPh_3)_4$ in *i*PrOAc, and (iv) the reaction mixture after 5 mins of LED irradiation.

Results and Conclusion: UV-Vis measurements showed that only $Pd(PPh_3)_4$ absorbs visible light and has a broad absorption band extending from the visible-light region to the UV region with a λ_{max} at 319 nm. The UV-vis absorption spectrum of the reaction mixture is similar to that of $Pd(PPh_3)_4$, indicating no reaction between the acetylated α-glucosyl bromide **1a** and the ground-state $Pd(PPh_3)_4$. However, irradiation of the reaction mixture with blue LED light for 5 mins led to a significant bathochromic shift ($\Delta\lambda_{max}$ = 43 nm) with a λ_{max} at 362 nm. The UV-Vis data suggested that an excited $Pd(PPh_3)_4$ catalyst readily undergoes a radical oxidative addition with **1a**, generating a putative Pd(II)-species.

Stern–Volmer Luminescence Quenching Experiments

All quenching data was recorded in the dark using a 1.00 cm screw-top quartz cuvette at 23 °C in the presence of $Pd(PPh_3)_4$ (0.400 µM) and varying concentration of quencher in degassed *i*-PrOAc or benzene. Excitation of the sample was performed at 375 nm and emission was detected at 580 nm. After the acquisition, the data were plotted according to the Stern-Volmer equation shown below.

$$\mathbf{I_o/I = 1 + K_{SV}[Q]}$$

$$\boldsymbol{K_{SV} = k_q \tau_o}$$

Where I_o is the luminescence intensity in the absence of the quencher, I is the intensity in the presence of the quencher, K_{SV} is the Stern−Volmer constant, k_q is the quenching rate, τ_o is the life-time of the photoredox catalyst and [Q] is the concentration of the quencher.

Results and Conclusion: The results below indicated that the 1-bromosugar and 1-iodosugar can both quench the excited state of $Pd(PPh_3)_4$, while DIPEA did not.

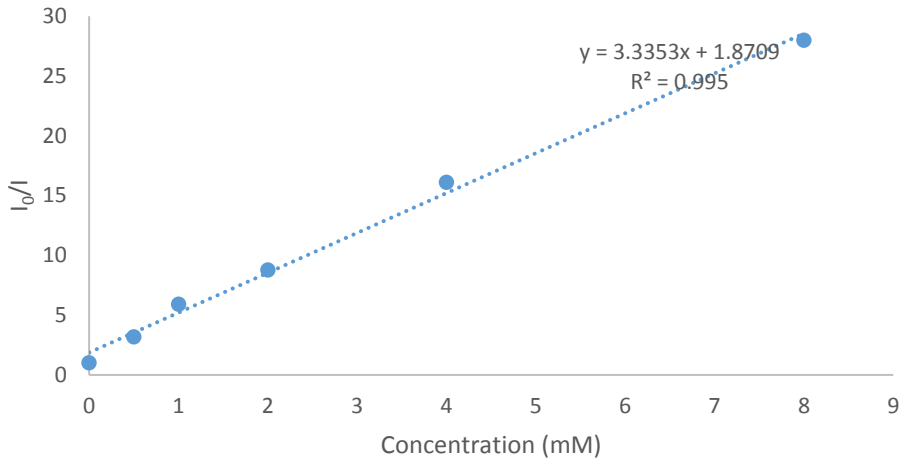


Fig. S2. Stern-Volmer plot for the emission quenching of $Pd(PPh_3)_4$ by various concentrations of acetylated 1-bromoglucose **1a** (*i*-PrOAc as solvent).

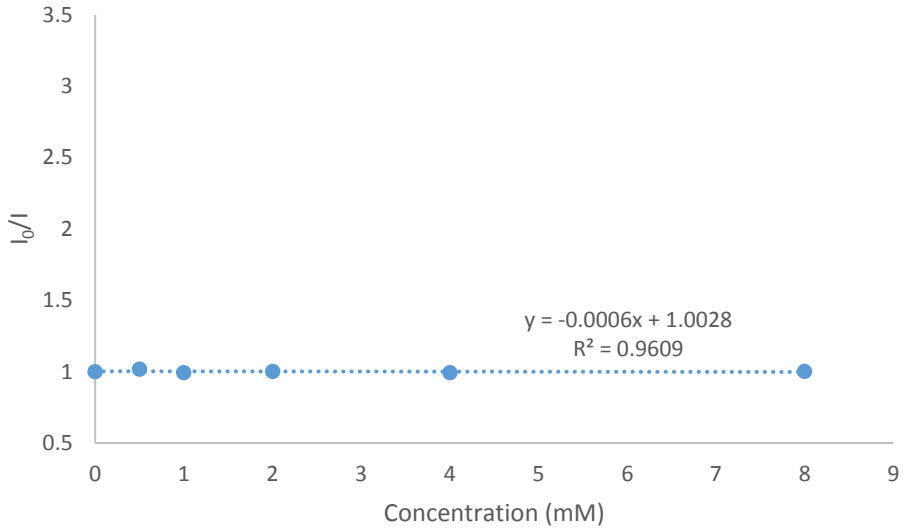


Fig. S3. Stern-Volmer plot for the emission quenching of $Pd(PPh_3)_4$ by various concentrations of DIPEA (*i*-PrOAc as solvent).

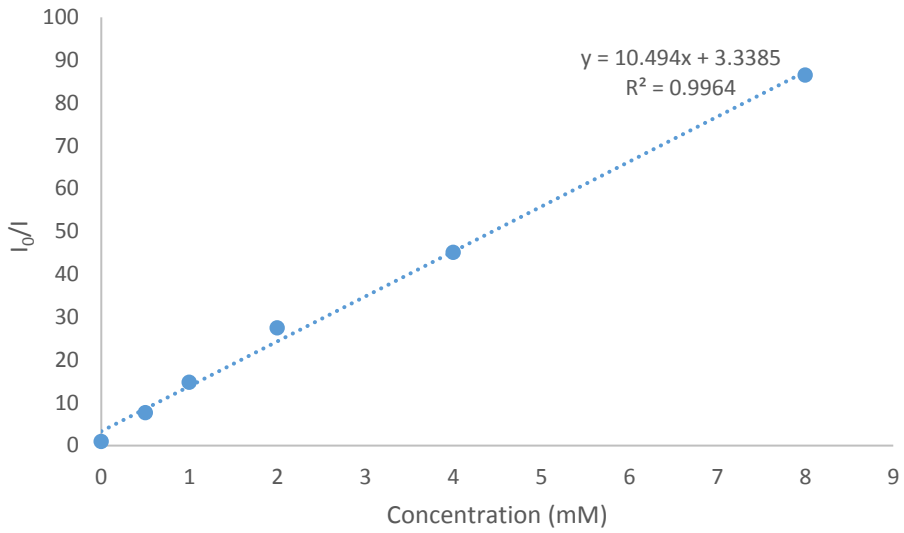


Fig. S4. Stern-Volmer plot for the emission quenching of $Pd(PPh_3)_4$ by various concentrations of acetylated 1-iodoglucose **3b** (Benzene as solvent).

Radical Trapping Experiment

The procedure is based on General Procedure B: In a glovebox, to an oven-dried 4 mL screw cap vial was added $Pd(PPh_3)_4$ (1.16 mg, 1.00 μmol, 5.00 mol%), 1-bromo-sugar **1a** (0.0200 mmol, 1.00 equiv), TEMPO (1.00 equiv) and *i*-PrOAc (2.00 mL, 0.0500 M). To this suspension was added DIPEA (5.17 mg, 0.0400 mmol, 2.00 equiv) and a magnetic stir bar. Next, the vial was capped, taken out of the glovebox, and sealed with parafilm. The reaction mixture was stirred at room temperature, irradiated with two 12 W Blue LEDs for 20 h. The yield was determined based on crude ^{1}H-NMR spectrum with dibromomethane as an internal standard.

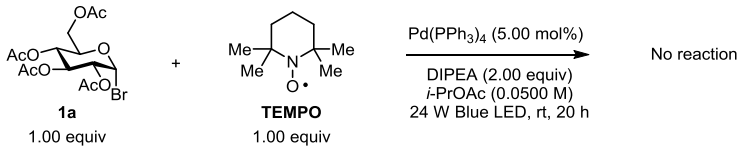


Fig. S5. Radical trapping experiment with TEMPO.

Results and Conclusion: The desired reaction was inhibited in the presence of a radical scavenger, 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO, 1.00 equiv), which indicated that the reaction likely proceeds through a radical mechanism.

Deuterium Labeling Studies

The procedure is based on General Procedure **B** with **1a** (0.0200 mol, 1.00 equiv), $Pd(PPh_3)_4$ (1.16 mg, 1.00 μmol, 5.00 mol%), DIPEA (5.17 mg, 0.0400 mmol, 2.00 equiv) or Cs_2CO_3 (13.0 mg, 0.0400 mmol, 2.00 equiv) and d_8-THF (2.00 mL, 0.0500 M) were added to the reaction vial. The ratio of **2a**:*d*-**2a** was determined based on ^{1}H-NMR spectrum of product. The yield and the ratio of C-2:C-1 were determined based on crude ^{1}H-NMR spectrum with dibromomethane as internal standard.

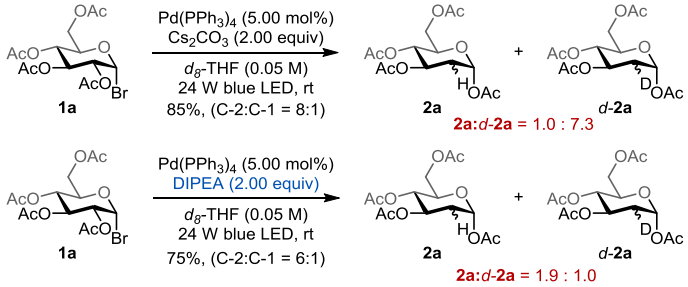


Fig. S6. Deuterium labeling studies with different bases (DIPEA and Cs_2CO_3).

Results and Conclusion: Deuterium labeling studies where replacing Cs_2CO_3 with DIPEA under deuteration reaction conditions shifted the **2a**:*d*-**2a** ratio from 1.0:7.3 to 1.9:1.0. This observation showed that DIPEA serves as a hydrogen atom donor.

Quantum Yield Experiment

The following quantum yield measurements are adapted from the procedure developed by Yoon et al.[20]

Determination of the Light Intensity at 450 nm:

The fraction of light absorbed (*f*) by ferrioxalate solution was calculated as shown in Fig. S7, where the absorbance of the ferrioxalate solution at 450 nm was measured to be 1.85441 (A), based on the equation ($f = 1\text{-}10^{-A}$), indicating $f = 0.98602$.

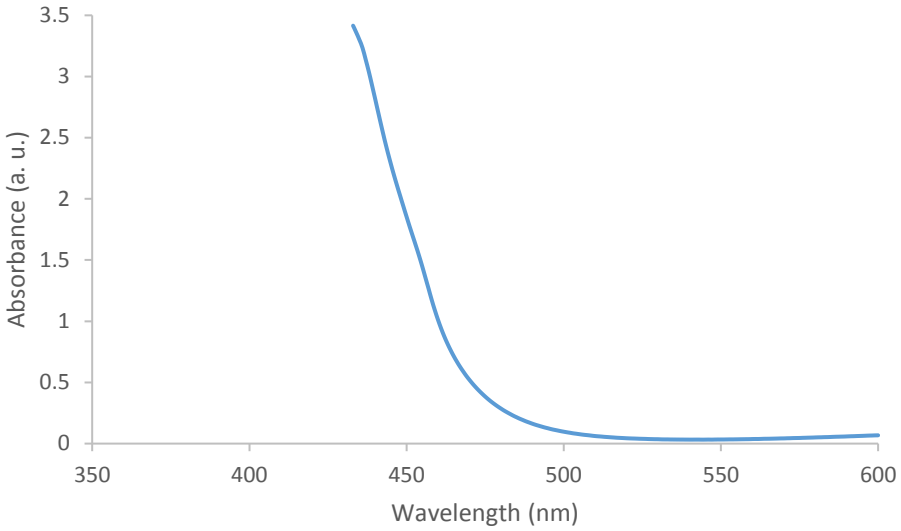


Fig. S7. Absorbance of the ferrioxalate solution at 450 nm (A = 1.85441).

The photon flux of the 30 W Blue LEDs (λ_{max} = 450 nm) was determined by standard ferrioxalate actinometry.[21] A 0.150 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate ($K_3[Fe(C_2O_4)_3]$•3 H_2O) in 30.0 mL of 0.0500 M H_2SO_4 (aq). Next, a buffered solution of phenanthroline was prepared by dissolving 50.0 mg of phenanthroline and 11.25 g of sodium acetate in 50.0 mL of 0.500 M H_2SO_4 (aq). Both solutions were stored in an amber vial in the dark. To determine the photon flux of the 30 W blue LEDs, 2.00 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 5.00 seconds at λ = 450 nm. After irradiation, 0.500 mL of the phenanthroline solution was added to the cuvette. The solution was then rested for 1 h in the dark to allow the ferrous ions to completely coordinate to the phenanthroline. A non-irradiated sample was also prepared and developed in the dark *(note: after developing the non-irradiated samples they were diluted with a dilution factor of 4 to prevent deviation from the Beer-Lambert law at high concentrations A = >2. Thus, to obtain the actual mol of* Fe^{2+} *they were multiplied by four. The values of the optical difference are the average of three trials*).

1 Ferrioxalate Actinometry

$$\text{mol of } Fe^{2+} = 4 \times \left[\frac{V \times \Delta A_{510}}{l \times \varepsilon_{510}} \right]$$

$$\text{mol of } Fe^{2+} = 4 \times \left[\frac{0.00250 \times 0.48978}{1 \times 11{,}100} \right] \text{ mol}$$

$$= 4.40 \times 10^{-7} \text{ mol}$$

V= 0.00250L *(total volume)*
ΔA_{510} = 0.48978 *(difference in absorption at 510 nm)*
l = 1.00 cm *(path length)*
ε_{510} = 11,100 L $mol^{-1}cm^{-1}$ *(molar absorptivity at 510 nm)*

2 Determination of photon flux of 30 W blue LED light

$$\text{photon flux} = \left[\frac{\text{mol of } Fe^{2+}}{\phi \times t \times f} \right]$$

$$\text{photon flux} = \left[\frac{4.40 \times 10^{-7}}{1.01 \times 5.00 \times 0.98602} \right] \text{ einstein } s^{-1}$$

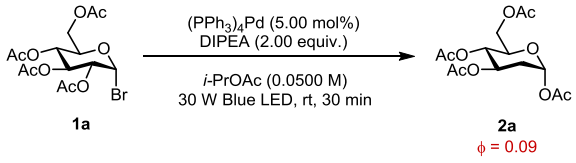
$$= 8.836 \times 10^{-8} \text{ einstein } s^{-1}$$

ϕ = 1.01 *(quantum yield of ferrioxalate actiometer)*
t = 5.00s *(time)*
f = 0.98602 *(Fraction of light absorbed)*

Fig. S8. Determination of the light intensity (photon flux) at 450 nm via ferrioxalate actinometry (ε = 11,100 L $mol^{-1}cm^{-1}$).[16a]

Afterward, the absorbance of both solutions was measured at 510 nm and with mol of Fe^{2+} known. Next the photon flux was determined to be 8.84 × 10^{-8} einstein s^{-1}. We can obtain the quantum yield of our reaction provided if it is irradiated using the same geometry (*note: although Φ = 1.01 at 436 nm was used for the calculation of the photon flux it is known that the ferrioxalate system varied little with the wavelength as the Φ remained between 0.9 and 1.1 at wavelength between 400–480 nm*).[16a]

Determination of Quantum Yield of the C-2 reduction reaction:



In a glovebox, the cuvette was charged with **1a** (41.0 mg, 0.100 mmol, 1.00 equiv), $Pd(PPh_3)_4$ (5.78 mg, 5.00 mol%) and *i*-PrOAc (2.00 mL, 0.0500 M). To this suspension was added DIPEA (25.8 mg, 0.200 mmol, 2.00 equiv). Afterward the cuvette was capped with a PTFE stopper and taken out of the glovebox. The reaction mixture was irradiated (λ_{max} = 450 nm) for 1800 s (30 min) with the same 30 W Blue LEDs. To determine the yield of the product, the solvent was removed under vacuum, an internal standard, dibromomethane (CH_2Br_2) (17.4 mg, 0.100 mmol, 1.00 equiv) was added to the cuvette, followed by 500 µL $CDCl_3$. The reaction was repeated three times with the yield of: 14%, 14.5%, 16%. The quantum yield was determined using the equation shown below.

1 Quantum Yield

$$\phi = \left[\frac{\text{mol x yield \%}}{\text{photon flux x t x f}} \right]$$

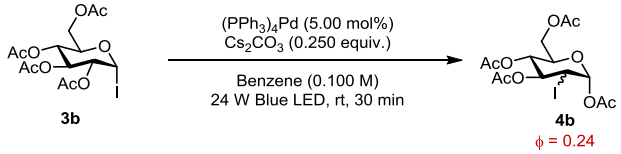
$$\phi = \left[\frac{0.0001 \times 15\%}{8.84 \times 10^{-8} \times 1800 \times 1} \right]$$

$$= 0.09$$

ϕ = quantum yield of the reaction
t = 1800s (time)
f = (Fraction of light absorbed)
yield% = averaged yield of three trials

Fig. S9. Quantum yield determination of C-2 reduction reaction**.**

Determination of Quantum Yield of the C-2 iodination reaction:



In a glovebox, the cuvette was charged with **3b** (91.6 mg, 0.200 mmol, 1.00 equiv), $Pd(PPh_3)_4$ (11.6 mg, 10.0 μmol, 5.00 mol%), Cs_2CO_3 (16.3 mg, 0.0500 mmol, 0.250 equiv) and benzene (2.00 mL, 0.100 M). Afterward the cuvette was capped with a PTFE stopper and taken out of the glovebox. The reaction mixture was irradiated (λ_{max} = 450 nm) for 1800 s (30 min) with the same 30 W Blue LEDs. To determine the yield of the product, the solvent is removed under vacuum, an internal standard, dibromomethane (CH_2Br_2) (34.8 mg, 0.200 mmol) was added to the cuvette, followed by 500 μL $CDCl_3$. The reaction was repeated three times with yield to be: 17.5%, 18%, 22%. The quantum yield was determined using the equation shown below.

1 Quantum Yield

$$\phi = \left[\frac{\text{mol x yield \%}}{\text{photon flux x t x f}} \right]$$

$$\phi = \left[\frac{0.0001 \times 19\%}{8.84 \times 10^{-8} \times 1800 \times 1} \right]$$

$$= 0.24$$

ϕ = quantum yield of the reaction
t = 1800s (time)
f = (Fraction of light absorbed)
yield% = averaged yield of three trials

Fig. S10. Quantum yield determination of C-2 iodination reaction.

Results and Conclusion: Quantum yields of the C-2 reduction and iodination reactions were 0.09 and 0.24, respectively, suggesting that an extended radical chain propagation is unlikely under our reaction conditions.

Radical Clock Experiment

The experimental procedure is the same as synthesizing **2m**.

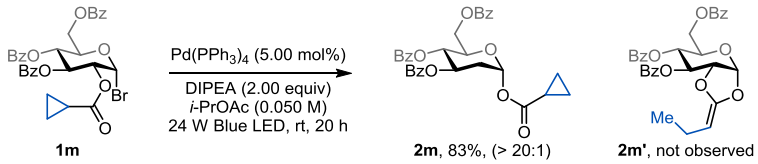


Fig. S11. Radical clock experiment using substrate **1m**.

Results and Conclusion: The radical clock experiment using a substrate bearing the cyclopropyl acetate group (**1m**) afforded the desired product **2m** without the formation of ring-opening side product **2m'**, which suggested that pathway **P2** is unlikely.

Cross-Over Experiment

The procedure is based on General Procedure **B** where **1a** (0.01 mol), **1b** (0.0100 mol), $Pd(PPh_3)_4$ (1.16 mg, 1.00 μmol, 5.00 mol%), DIPEA (5.17 mg, 0.0400 mmol, 2.00 equiv) and *i*-PrOAc (2.00 mL, 0.0500 M) were added to the reaction vial. At the end of the reaction, **5a** and **5b** were not detected on both LC-MS spectrum and crude ^{1}H-NMR spectrum. The yield of **2a** and **2b** was determined based on crude ^{1}H-NMR spectrum with dibromomethane as internal standard.

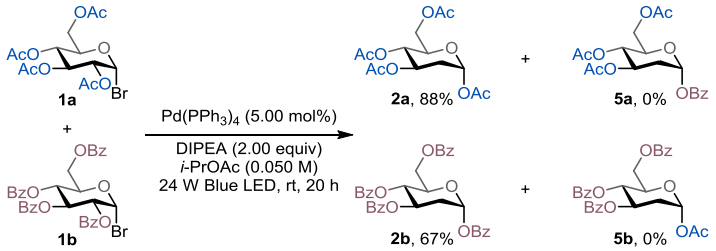
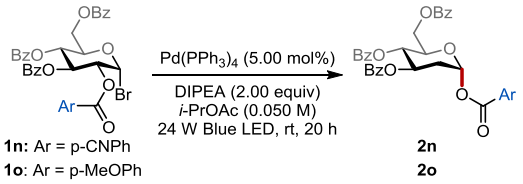


Fig. S12. Cross-over experiment with **1a** and **1b** as substrates.

Results and Conclusion: Cross-over experiments using substrates **1a** and **1b** did not give any cross-over products **5a** and **5b**, indicating that the reaction could proceed through either pathway **P3** with an "in-cage" recombination or pathway **P4**.

Reaction Rate Comparison Experiments

The procedure is based on General Procedure **B** where **1n** (0.0200 mol) or **1o** (0.0200mol), $Pd(PPh_3)_4$ (1.16 mg, 1.00 μmol, 5.00 mol%), DIPEA (5.17 mg, 0.04000 mmol, 2.00 equiv) and *i*-PrOAc (2.00 mL, 0.0500 M) were added to the reaction vial. The yield was determined based on crude ^{1}H-NMR spectrum with dibromomethane as internal standard.



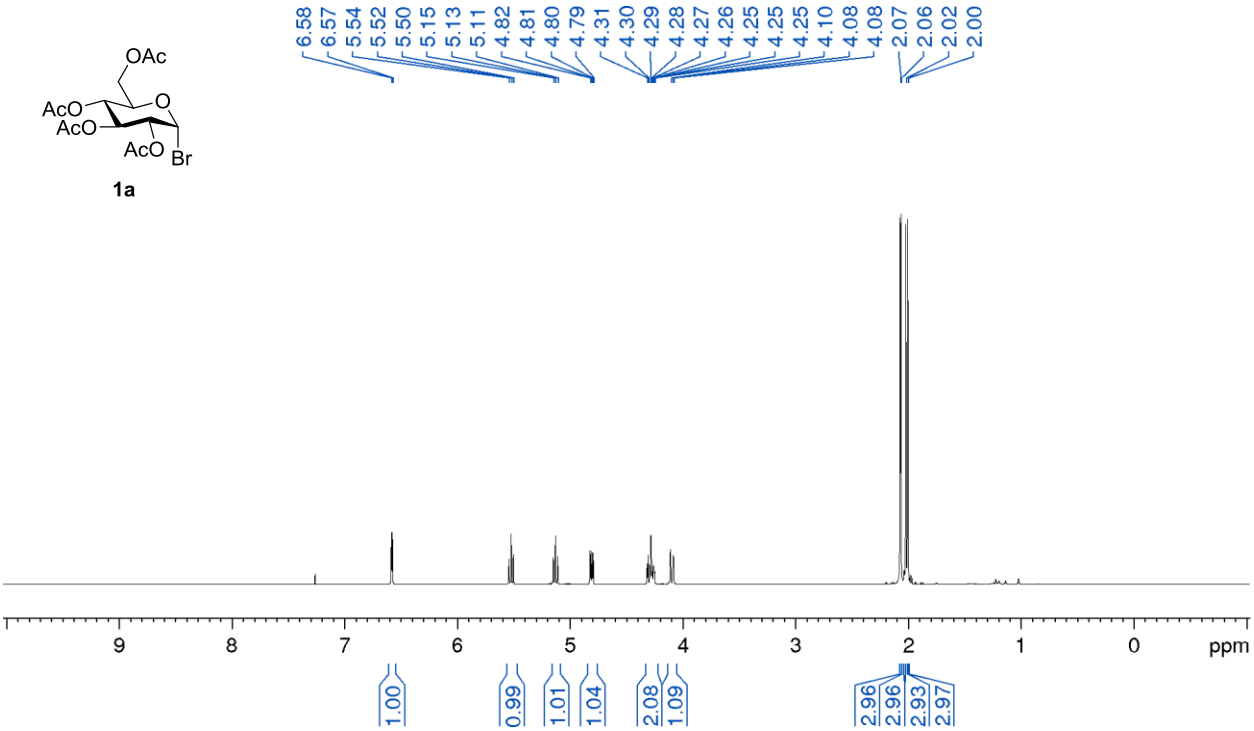
Time (h)	% yield 2n	2o
0.5	7	9
1.0	11	12
2.0	23	24
4.0	33	34
8.0	45	48

Fig. S13. Reaction rate comparison experiment with **1n** and **1o** as substrates.

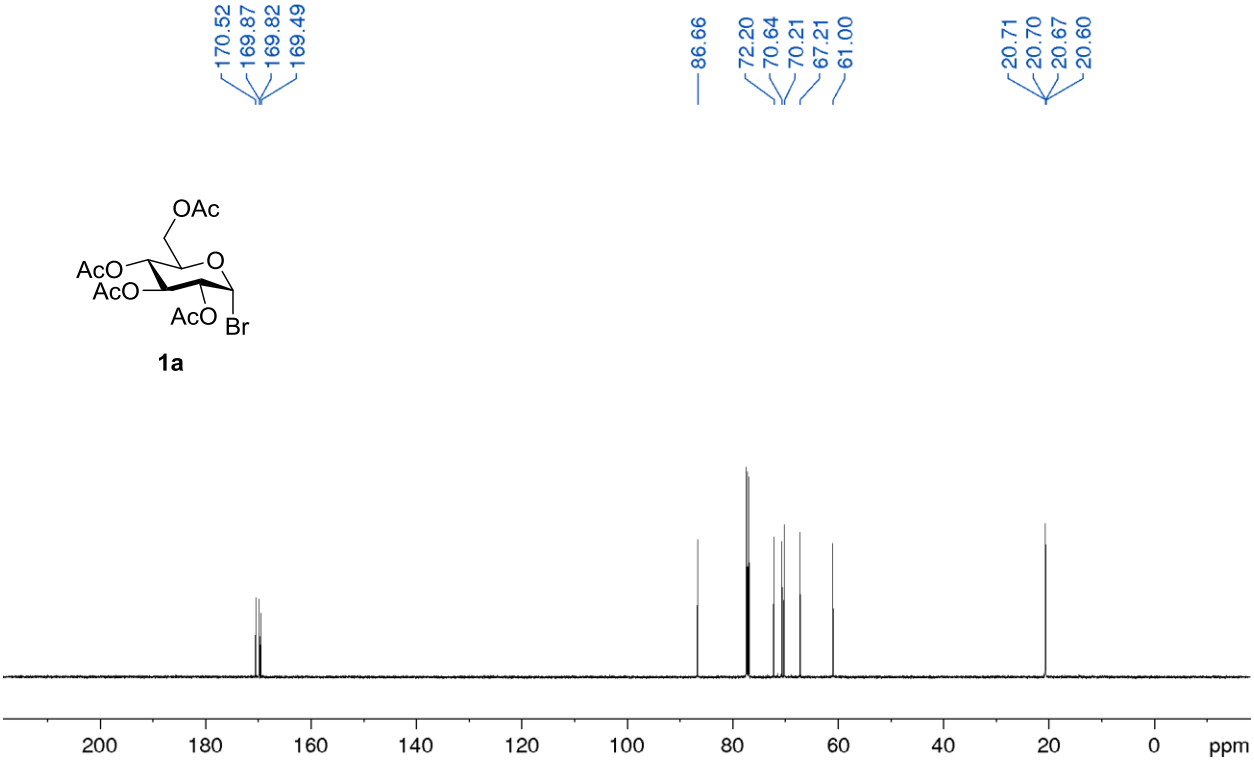
Results and Conclusion: The rate of products formation using substrates with electron deficient **1n** and electron-rich **1o** migrating groups were comparable. Thus, substituents on migrating groups with different electronics had a negligible effect on the reaction rate, which suggested that the acyloxyl migration is more likely to proceed through the concerted pathway **P4**.

Spectroscopic Data

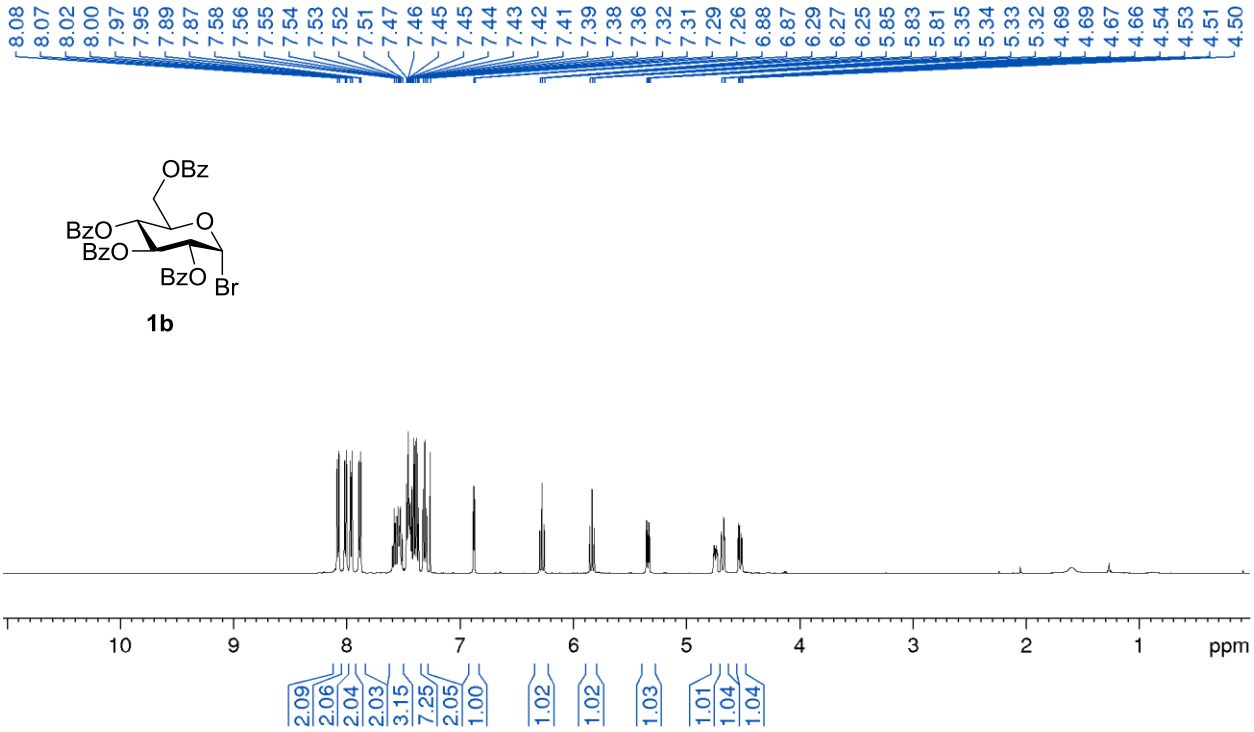
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1a)



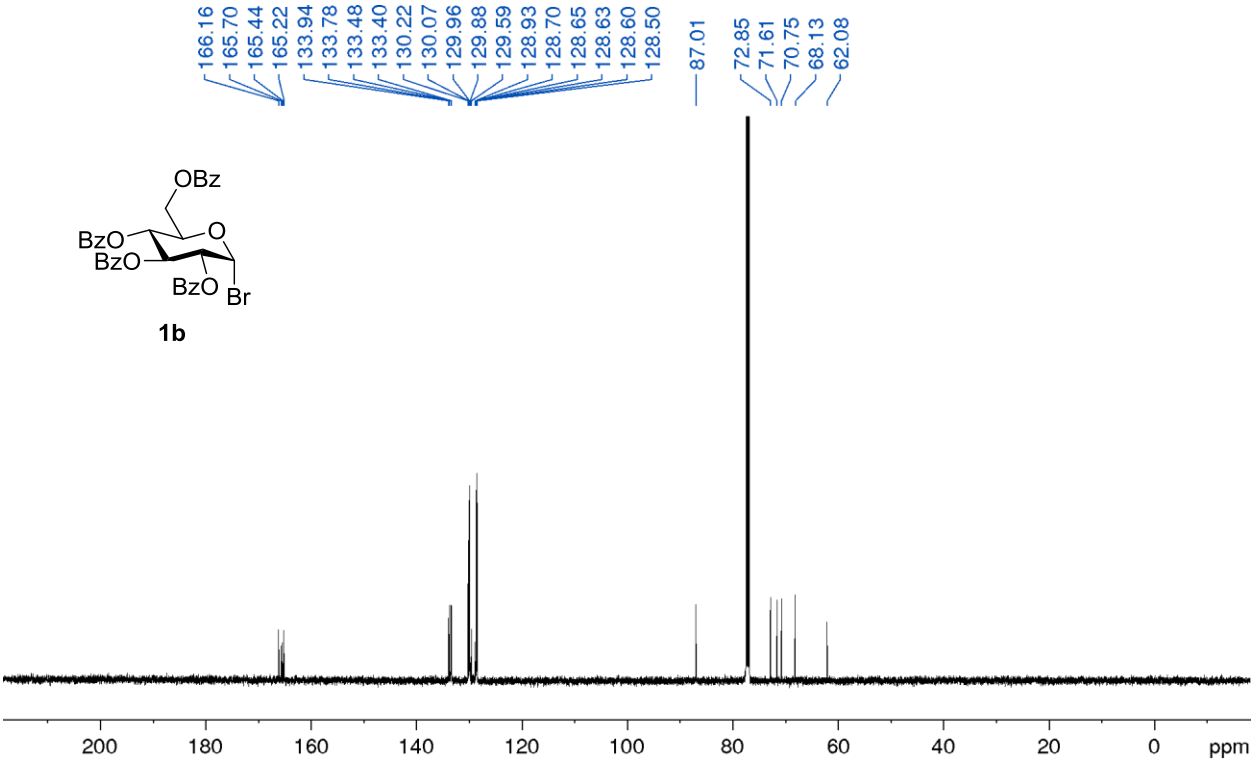
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1a)



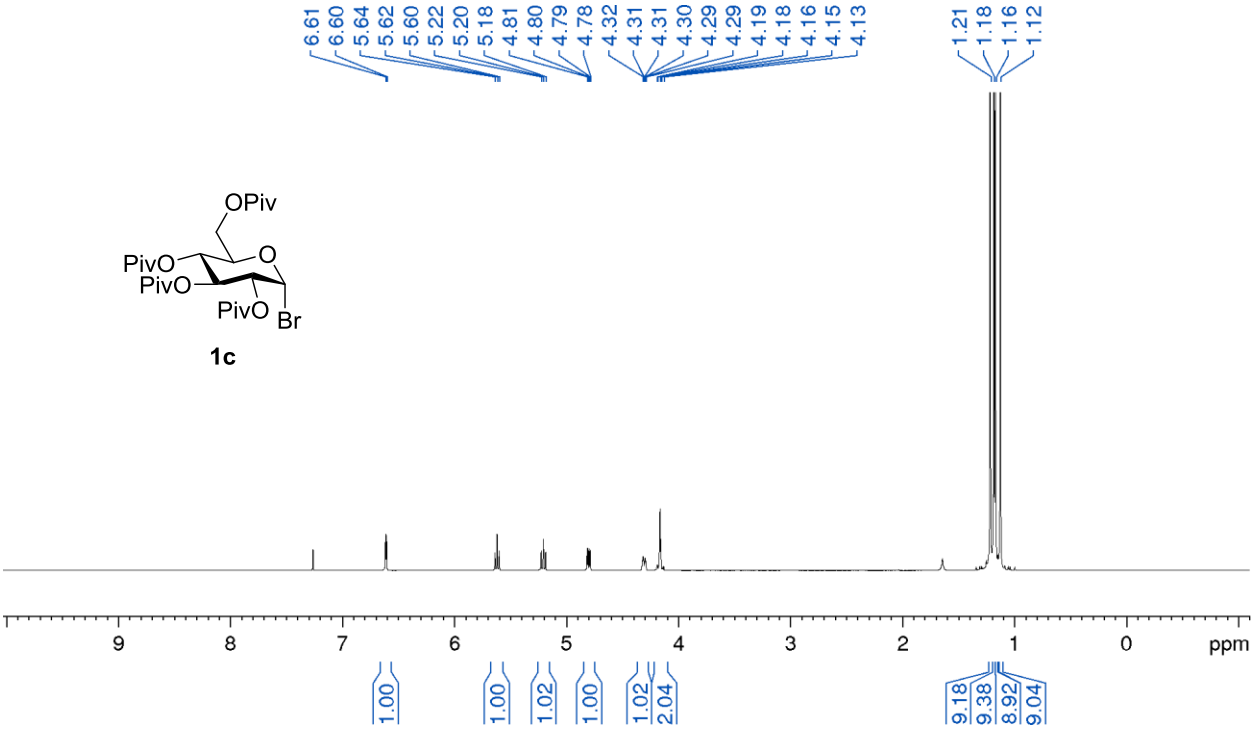
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1b)



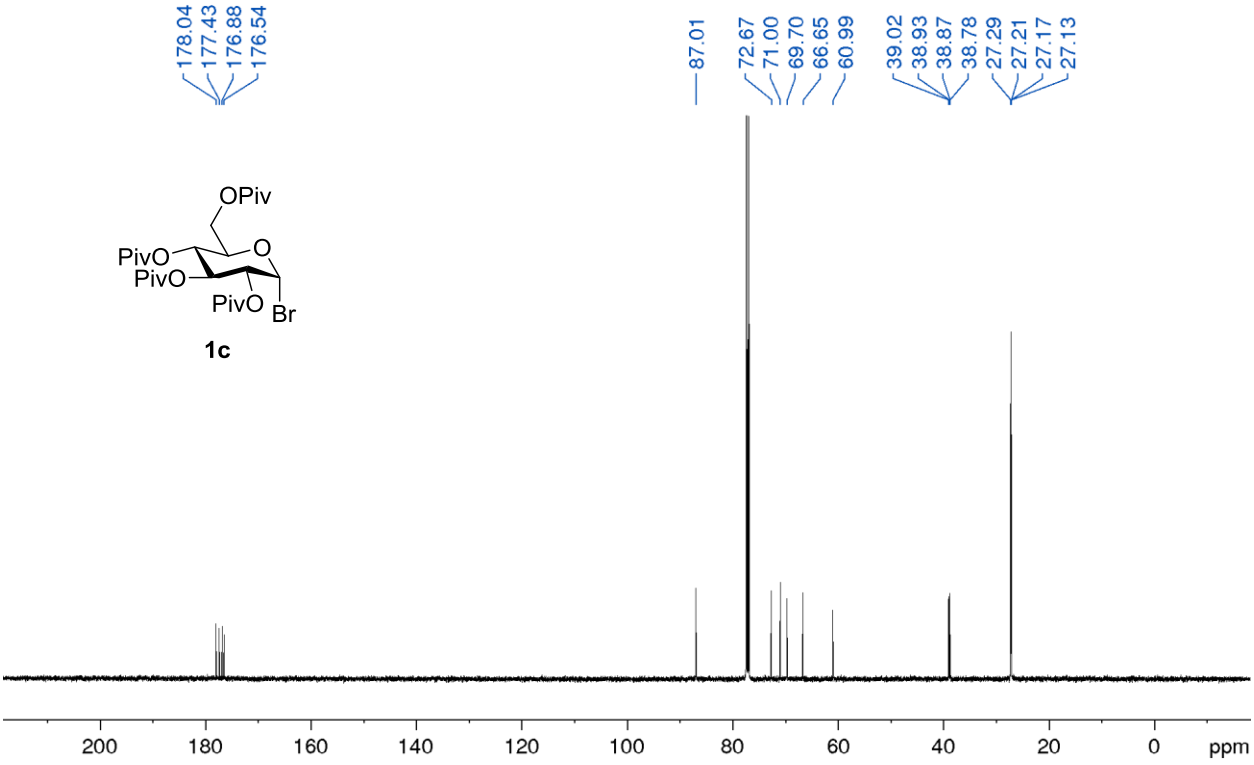
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1b)



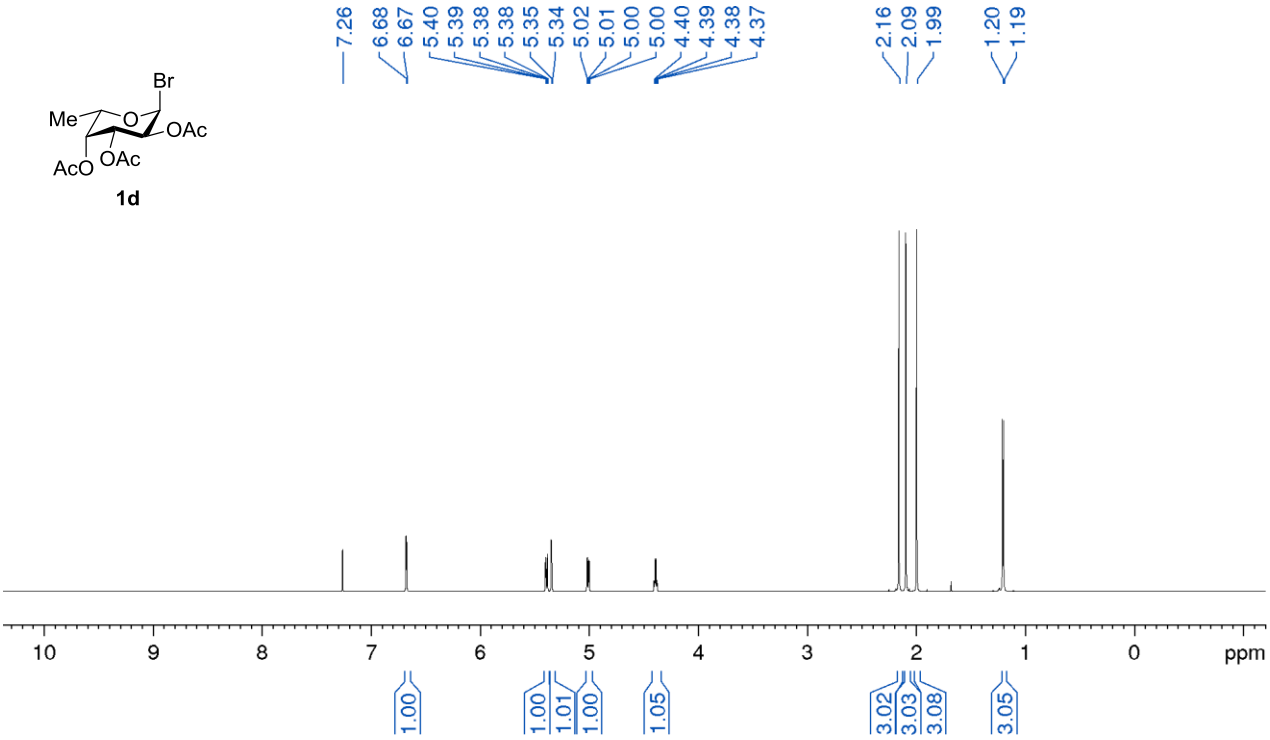
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1c)



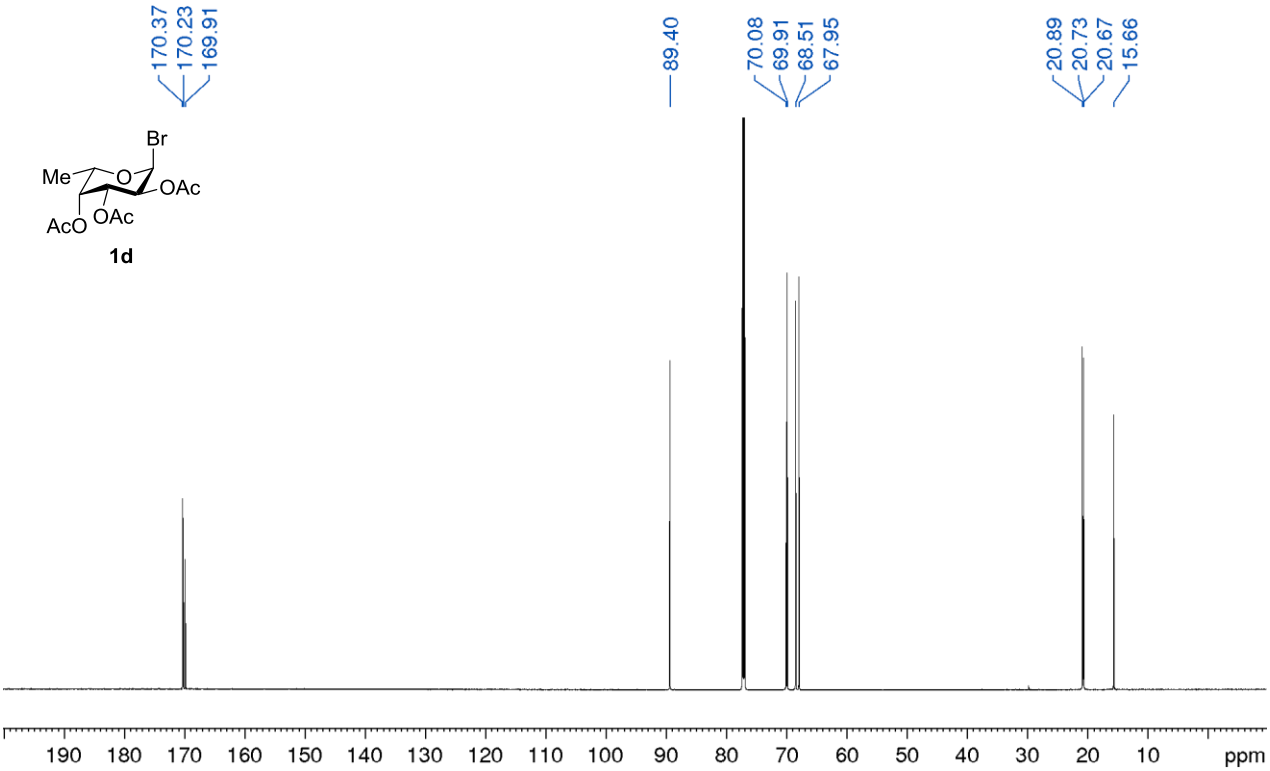
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1c)



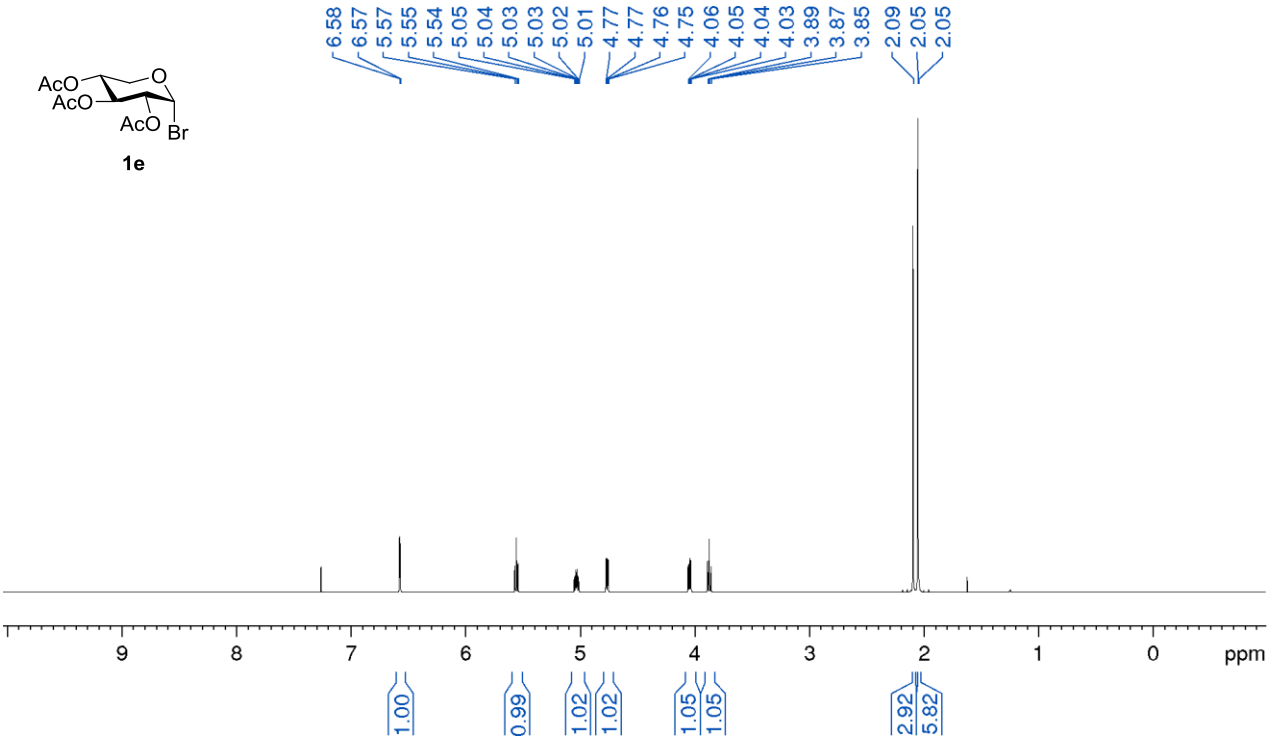
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1d)



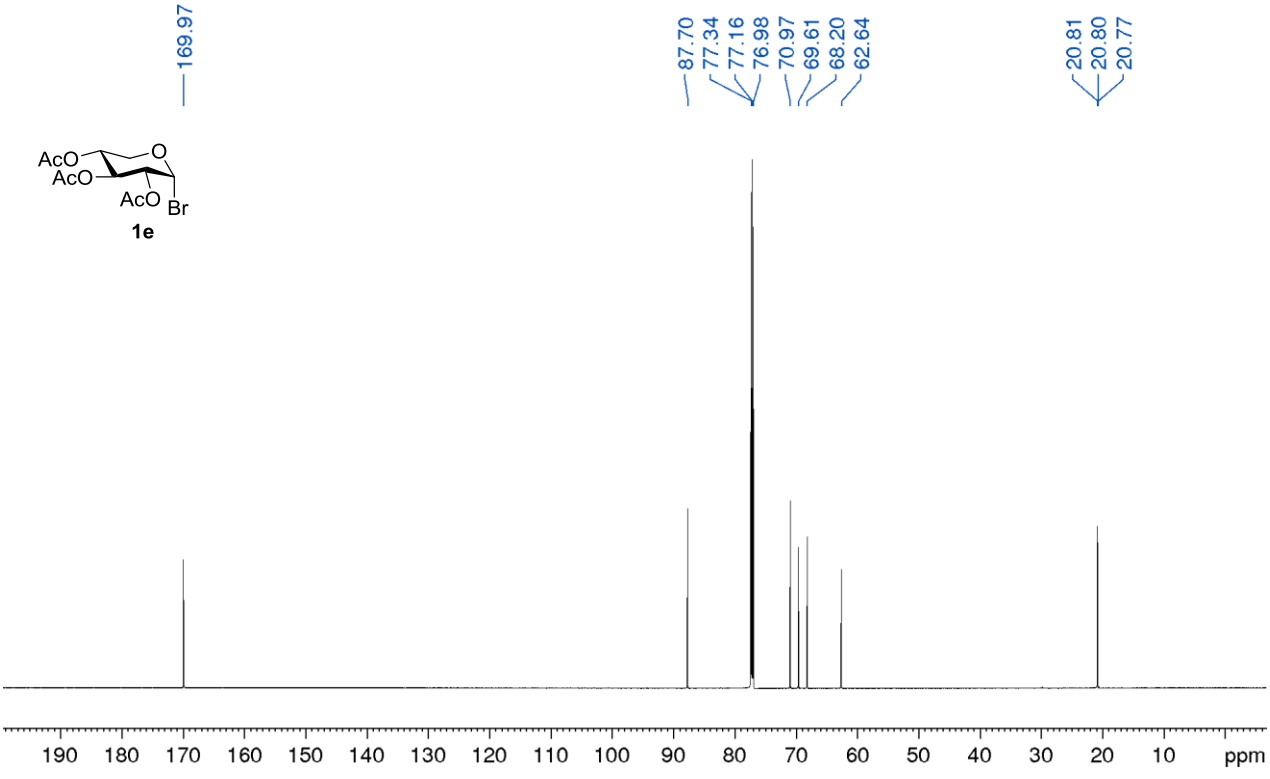
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1d)



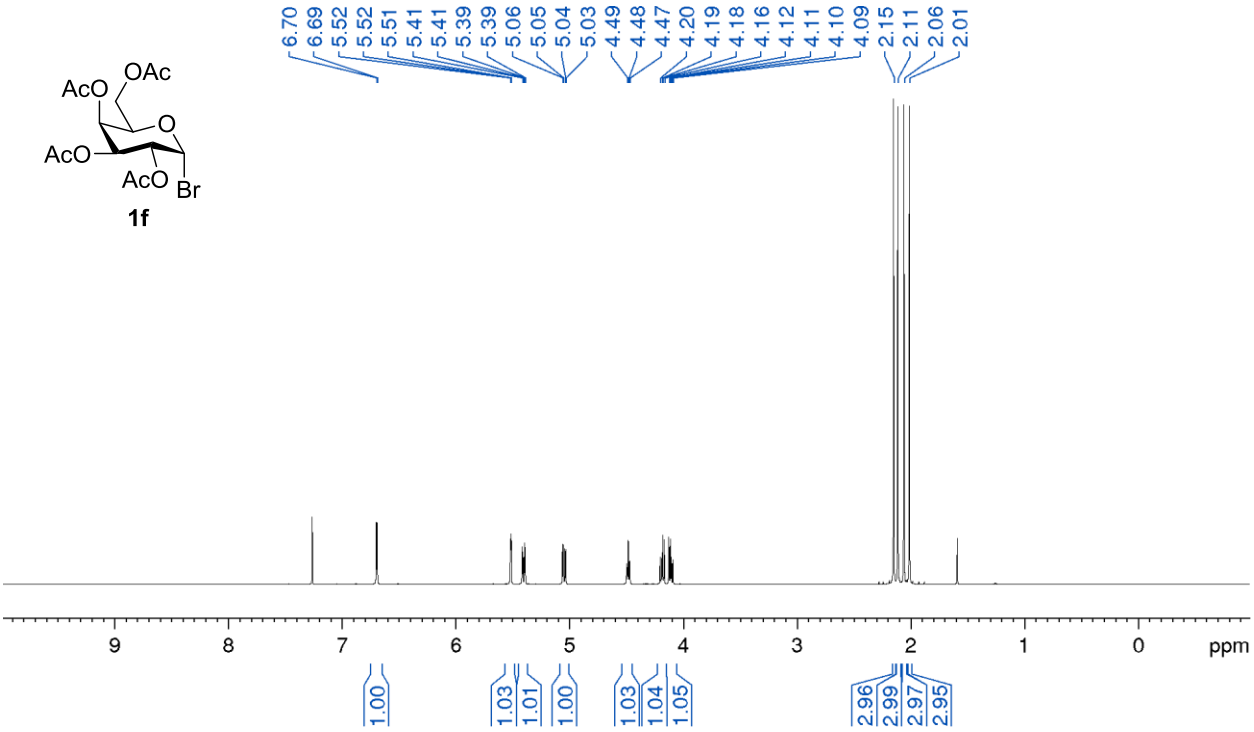
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1e)



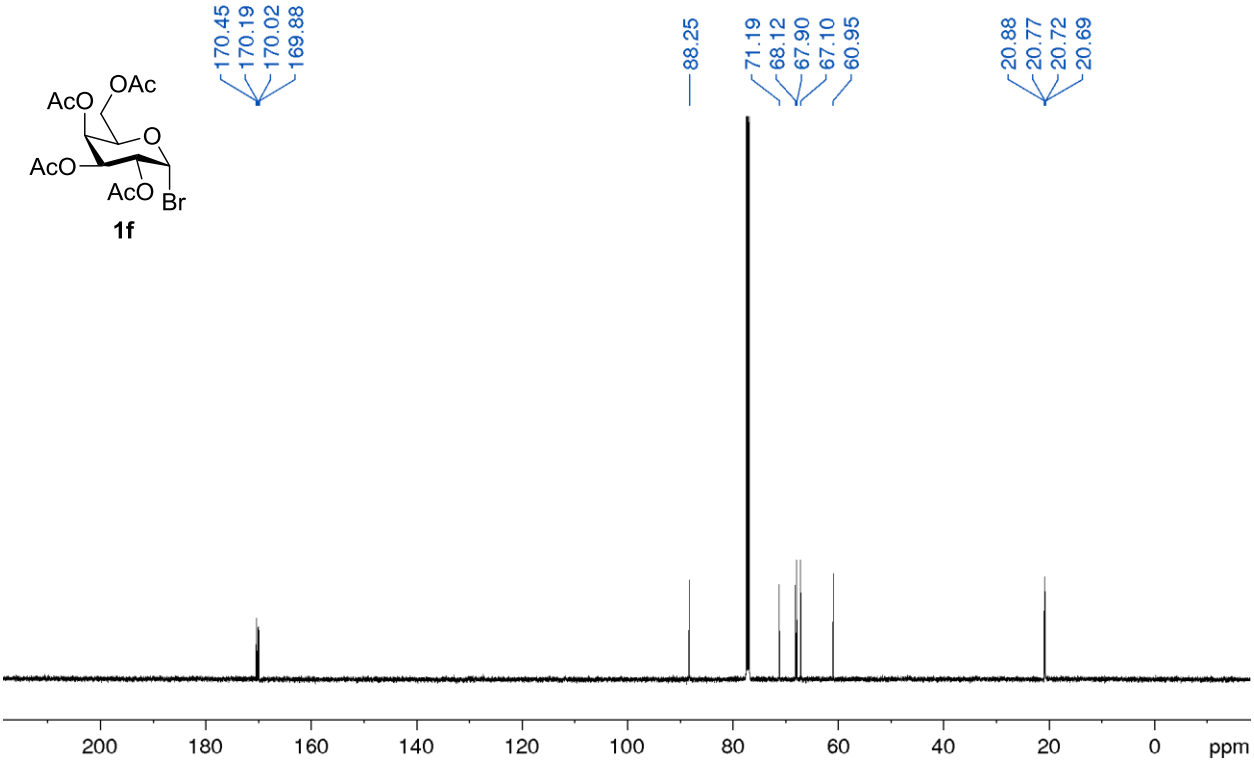
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1e)



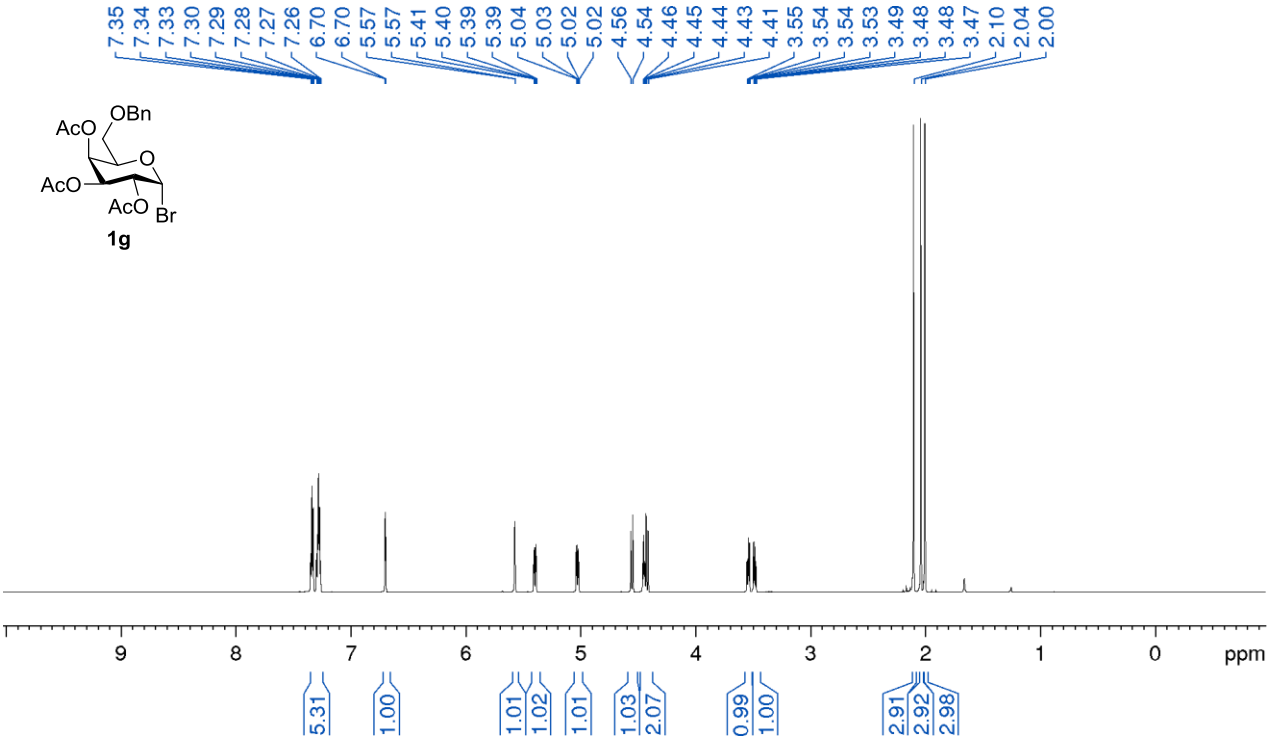
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1f)



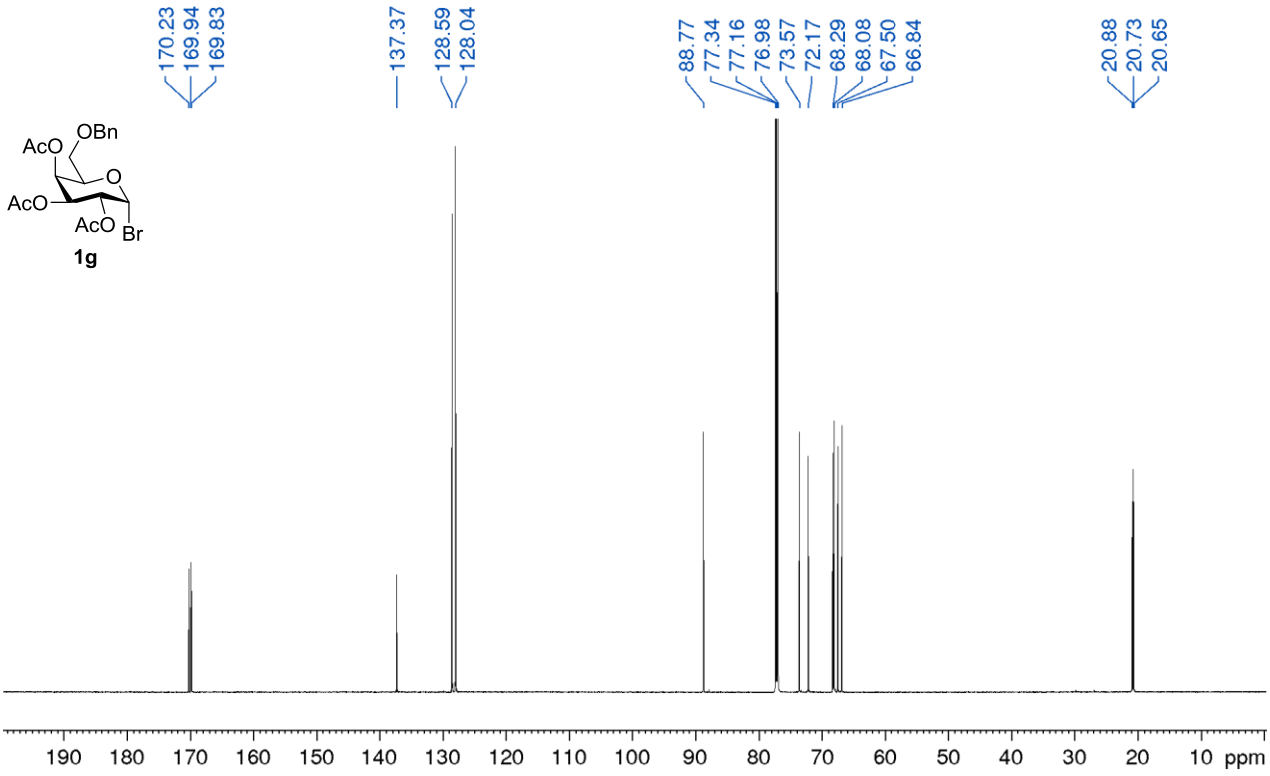
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1f)



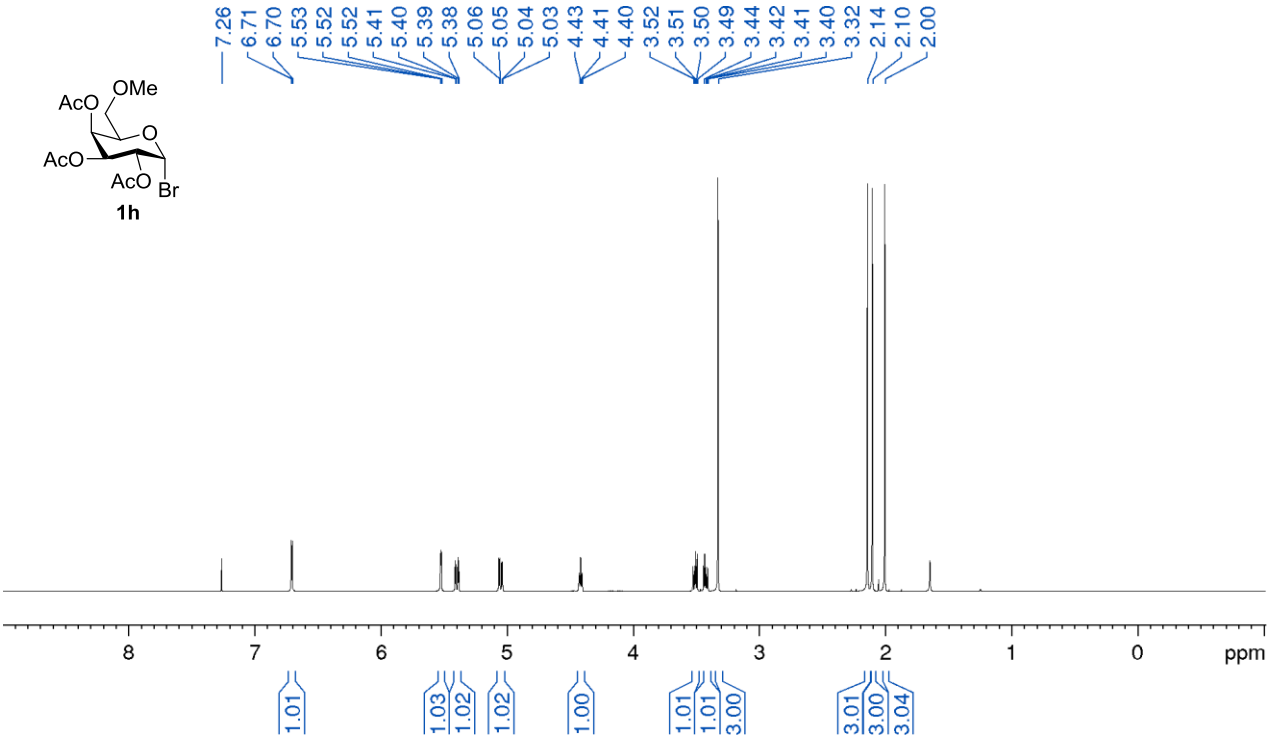
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1g)



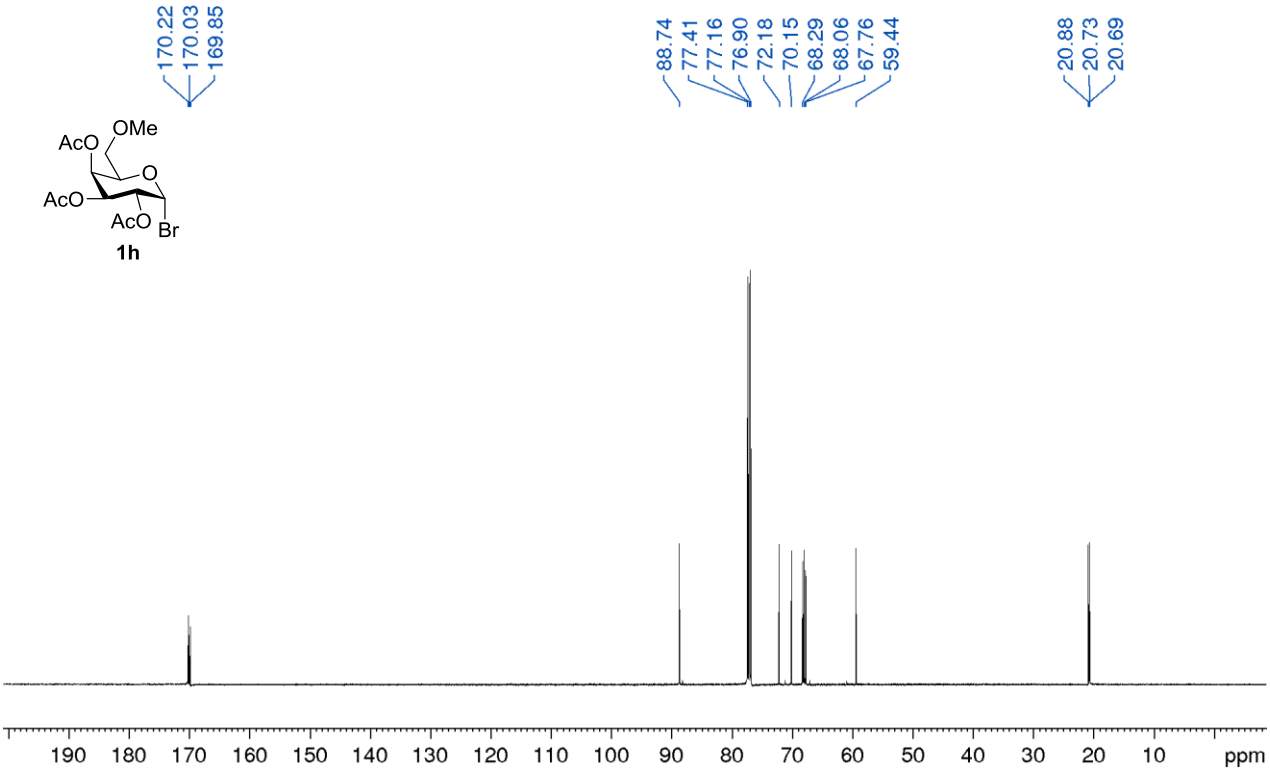
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1g)



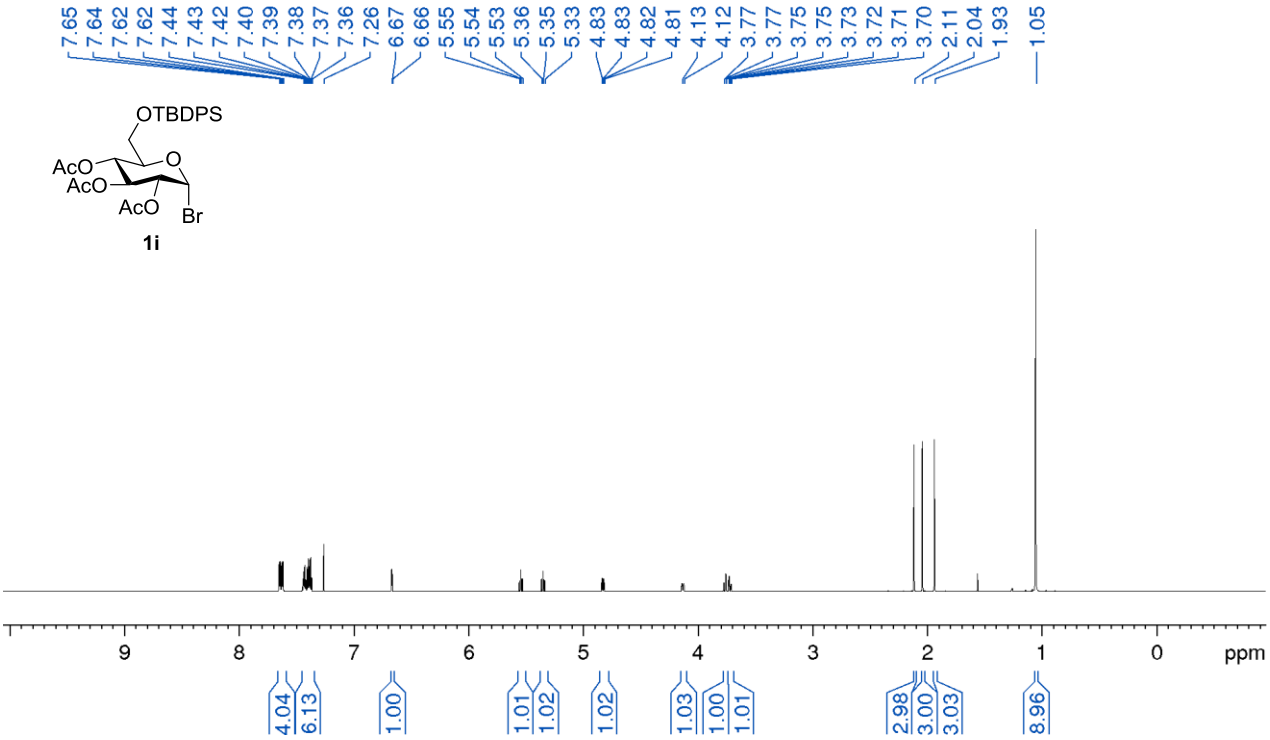
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1h)



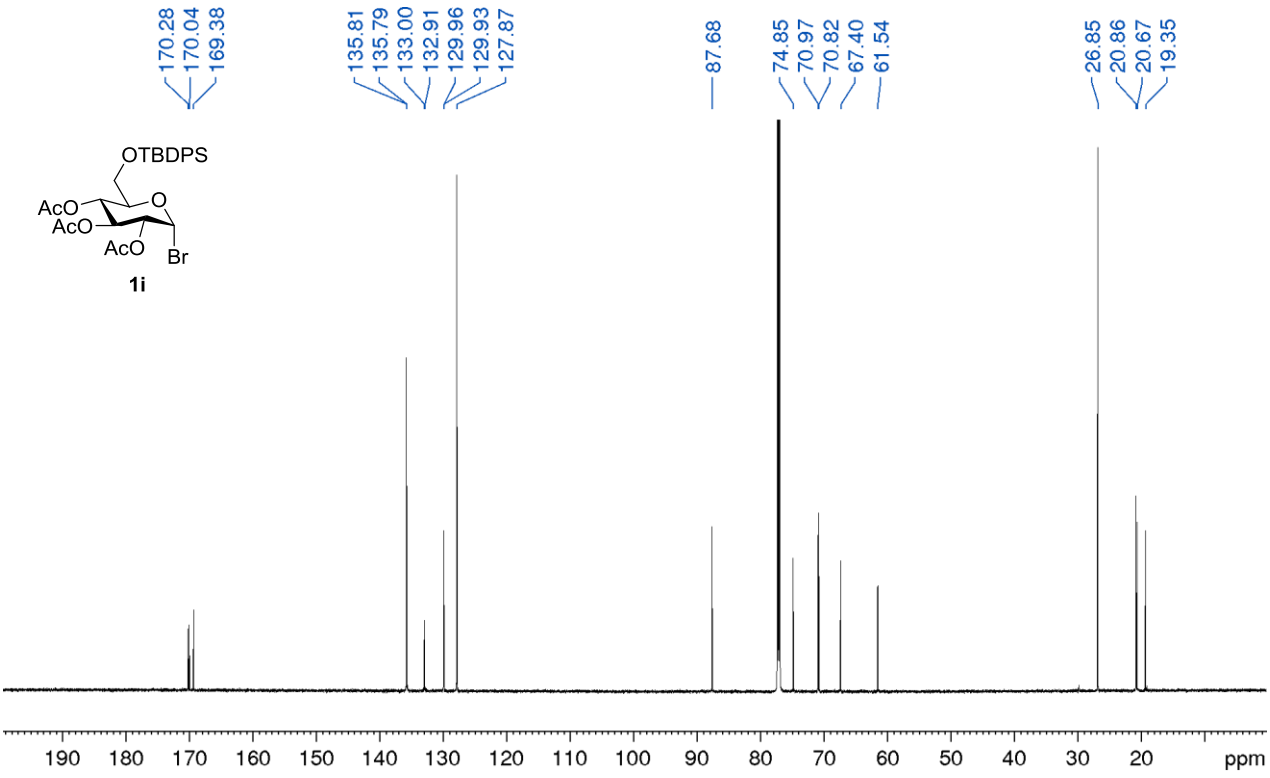
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1h)



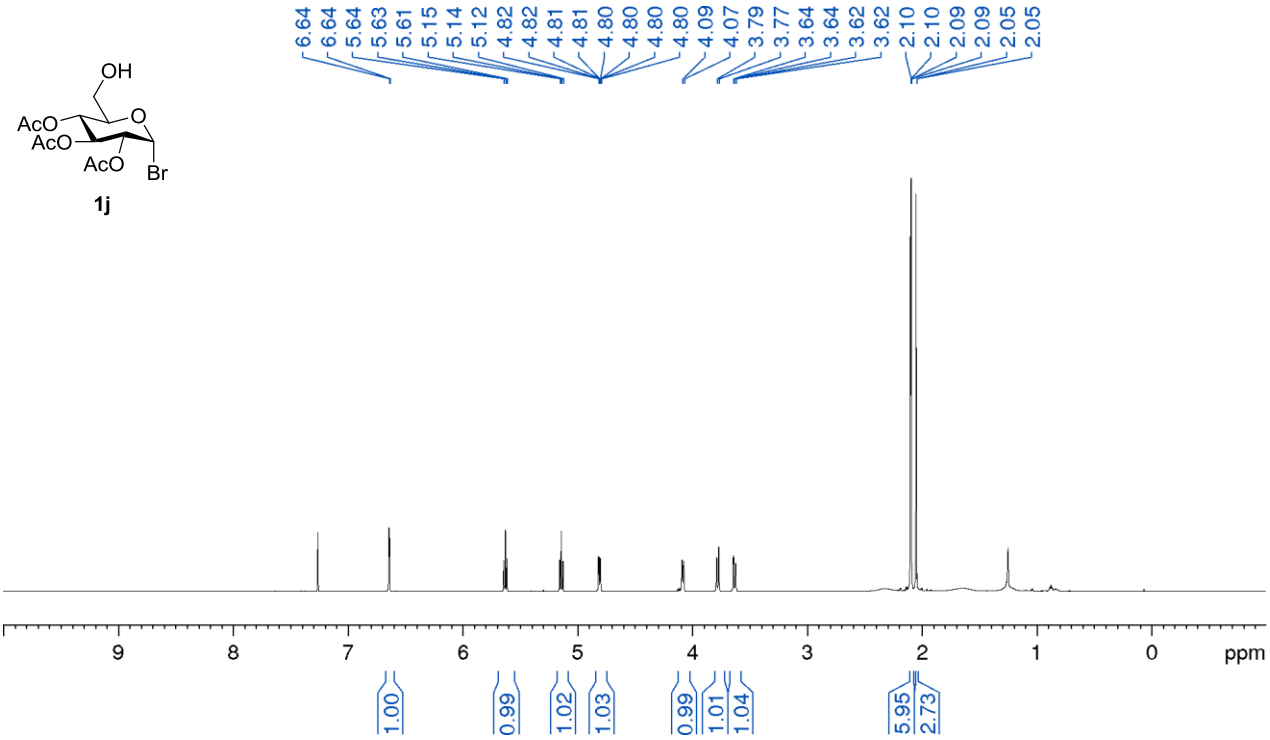
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1i)



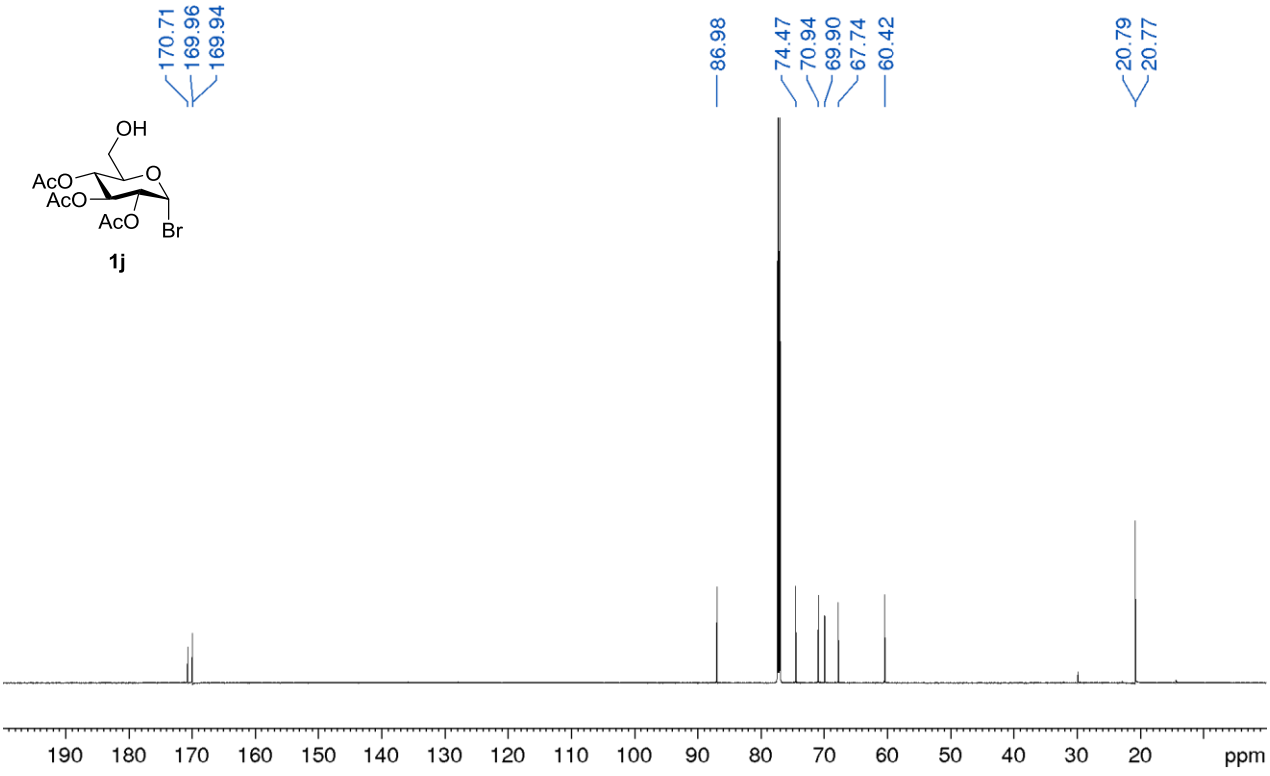
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1i)



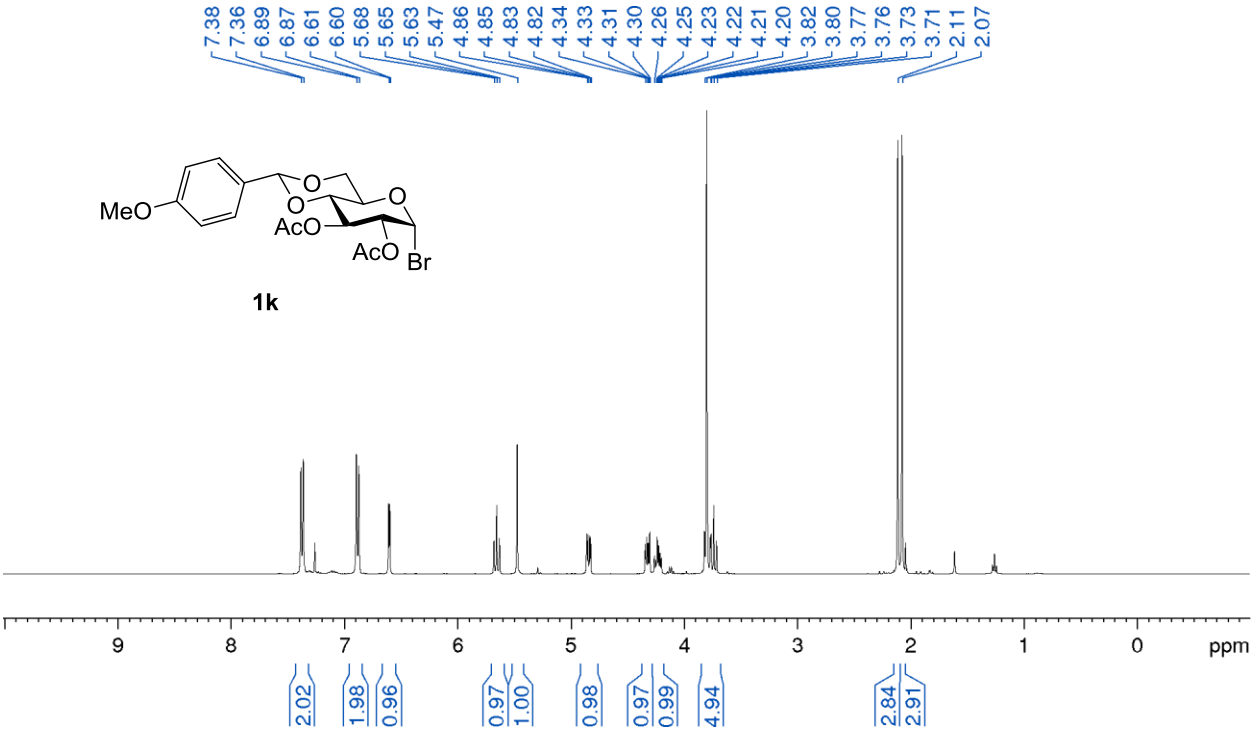
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1j)



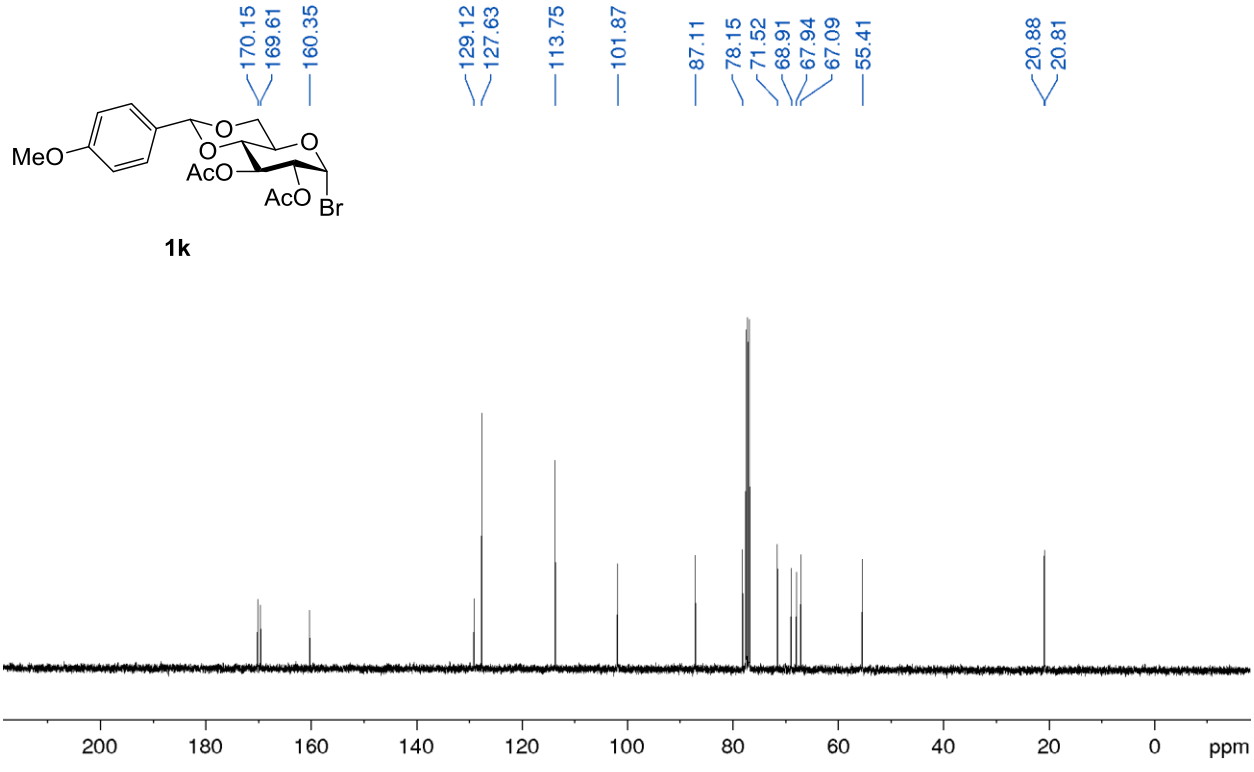
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1j)



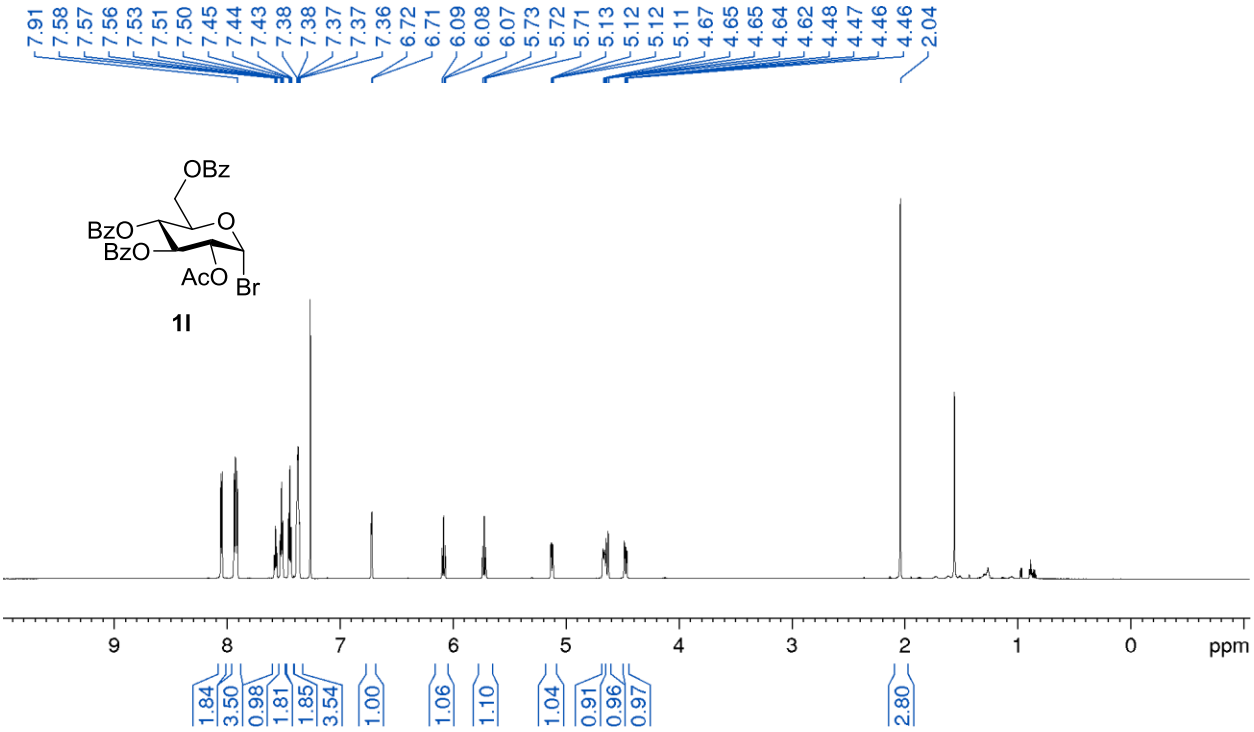
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (1k)



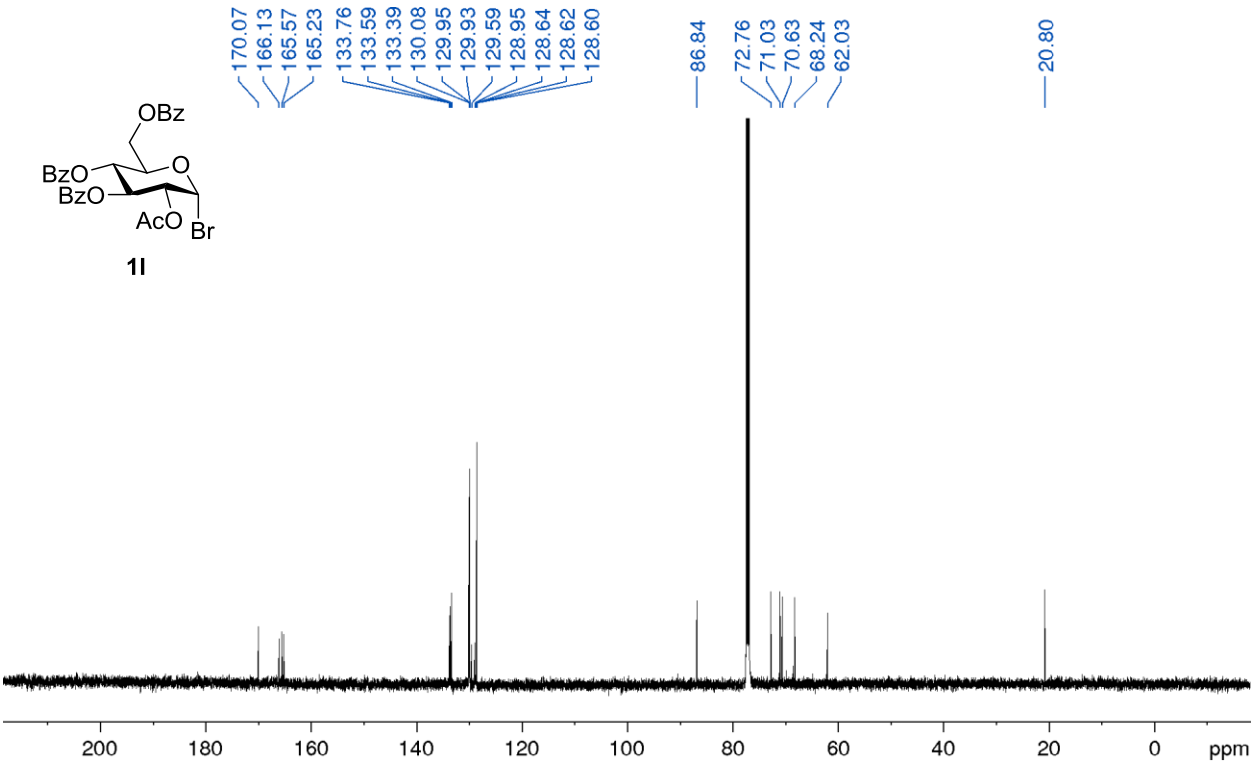
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of 1k)



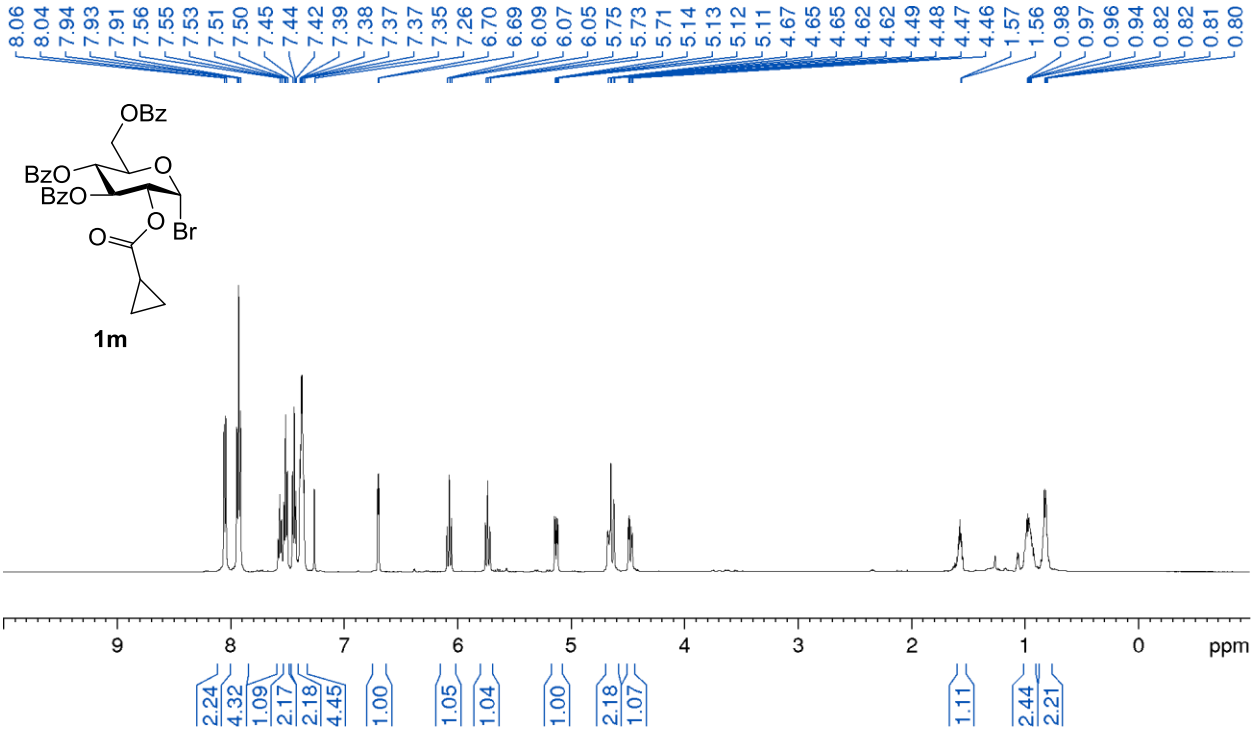
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1l)



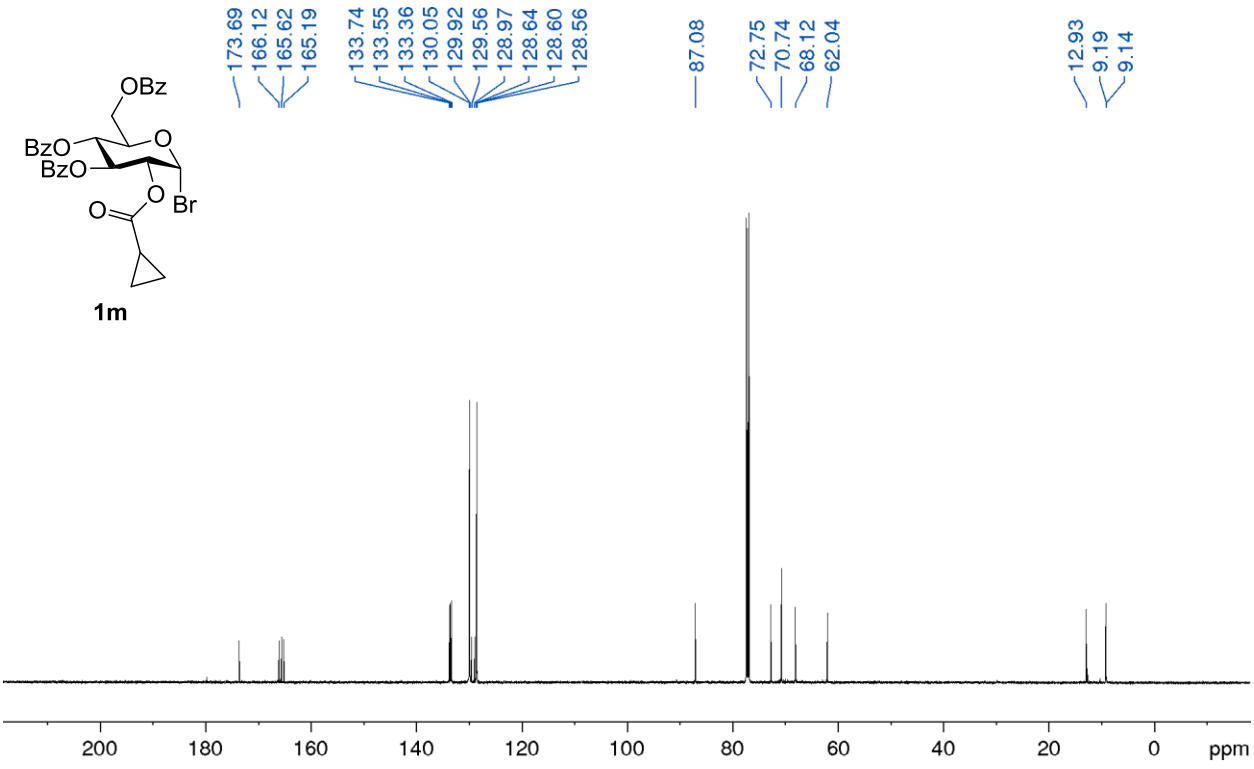
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1l)



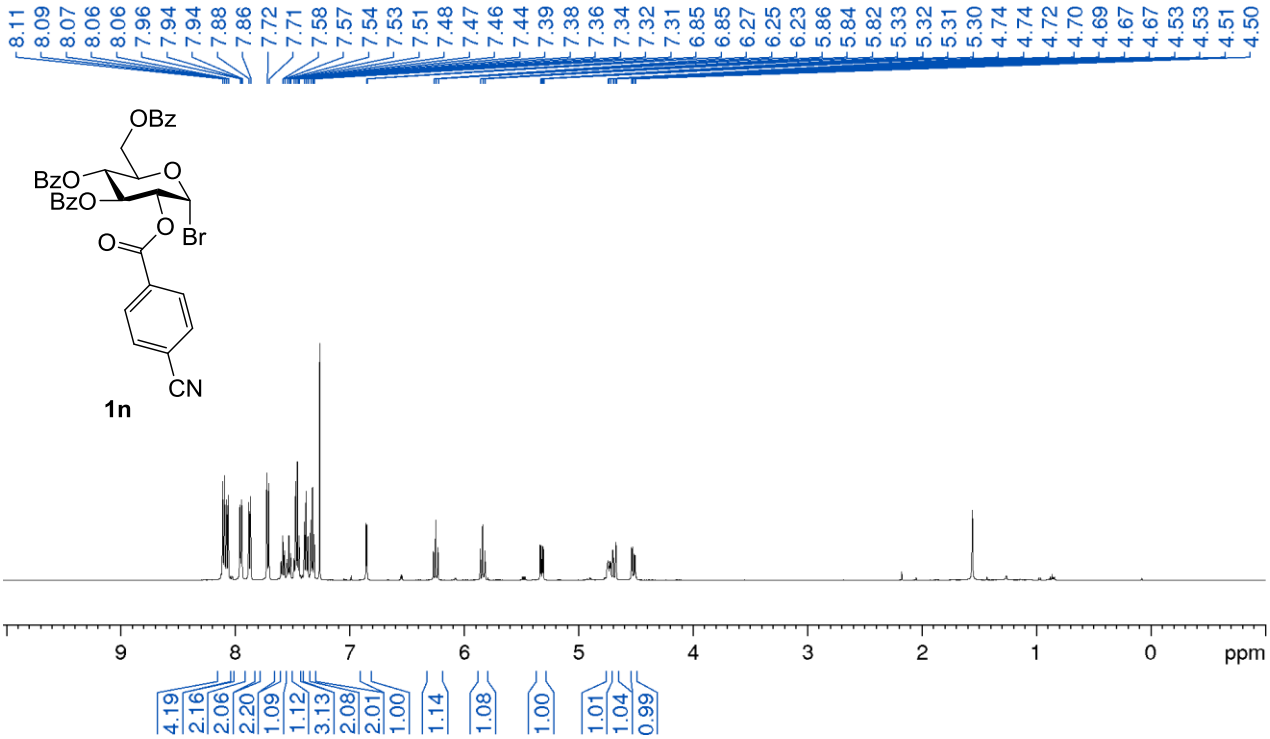
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1m)



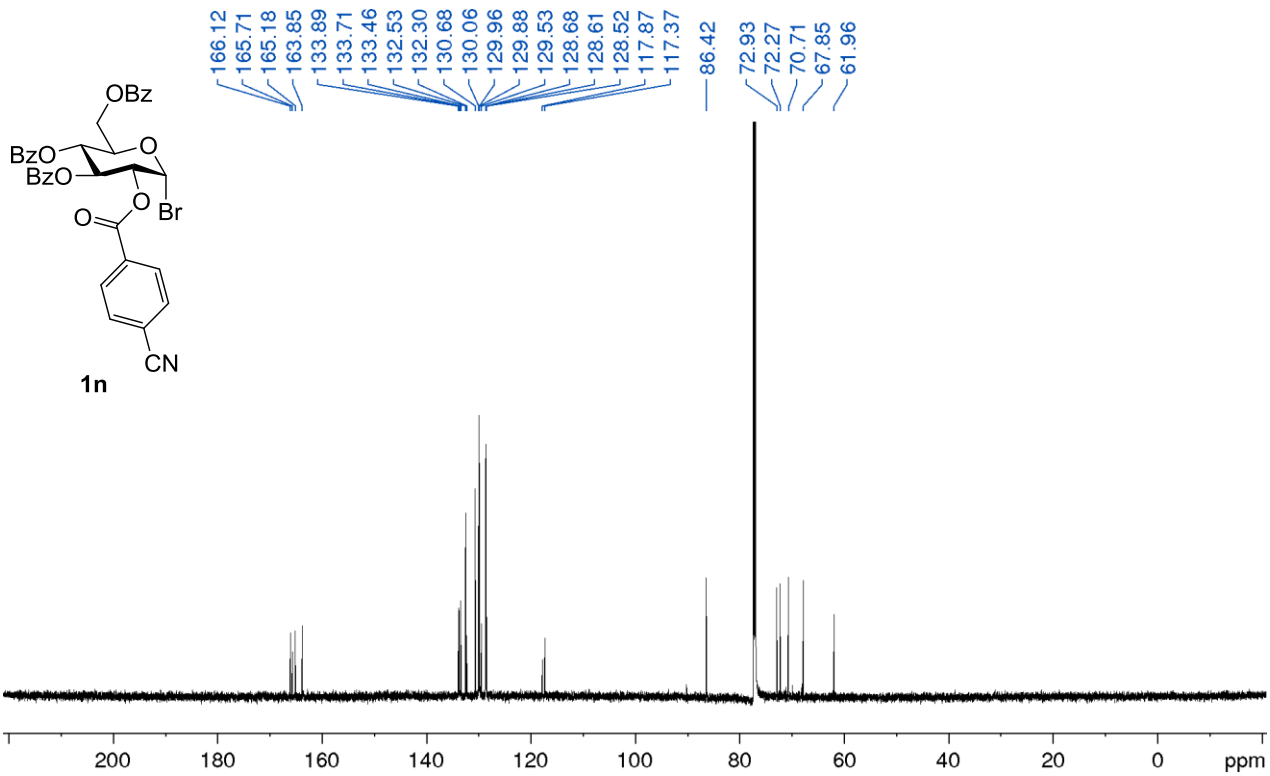
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1m)



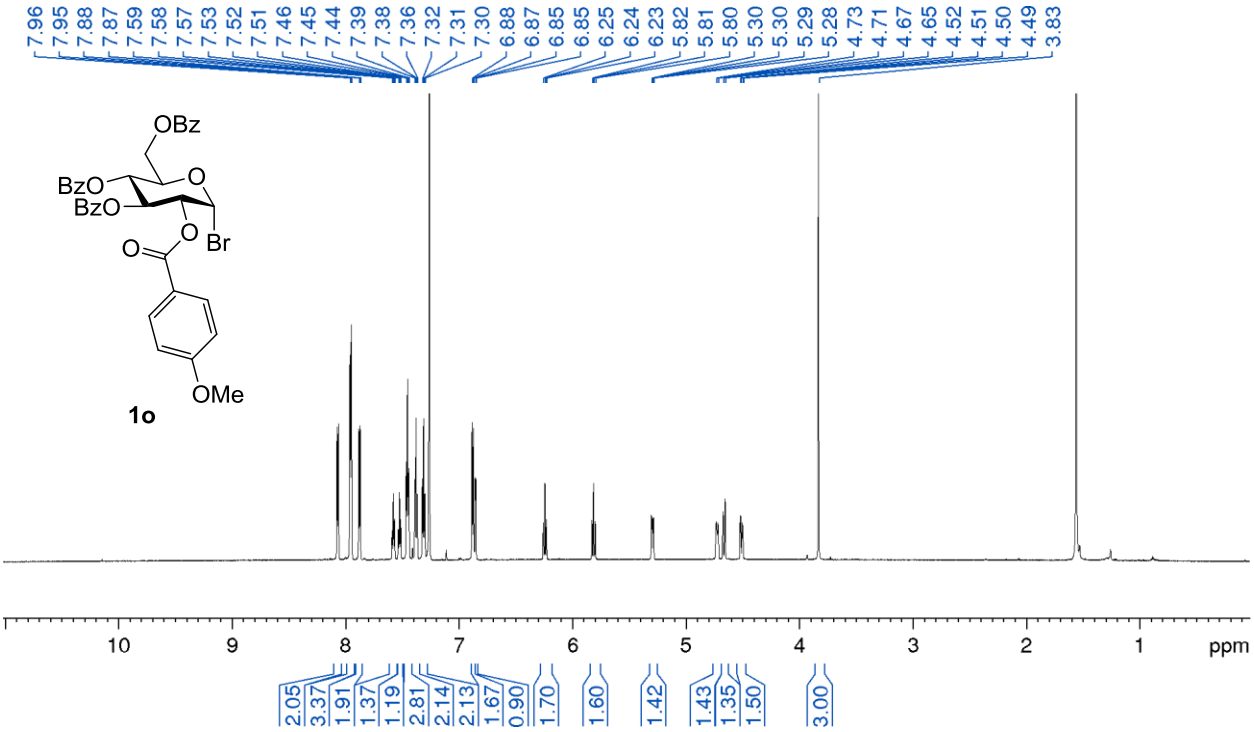
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1n)



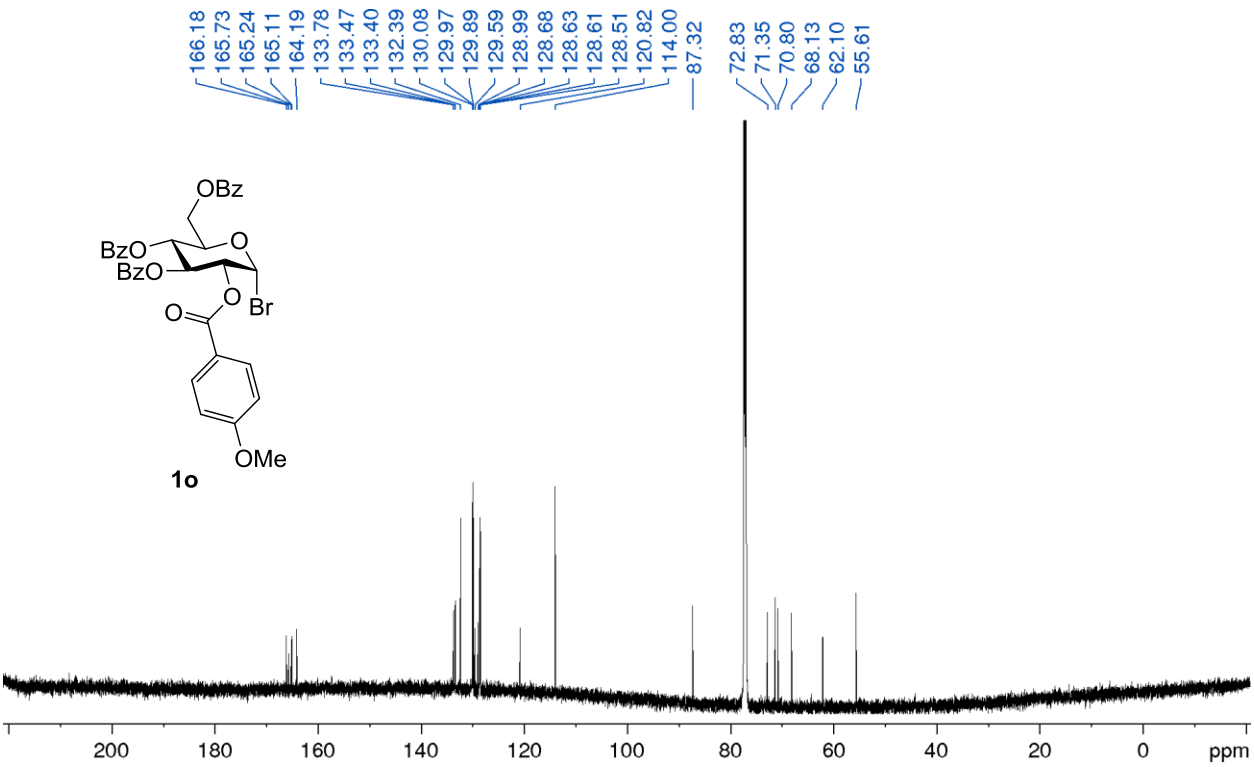
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1n)



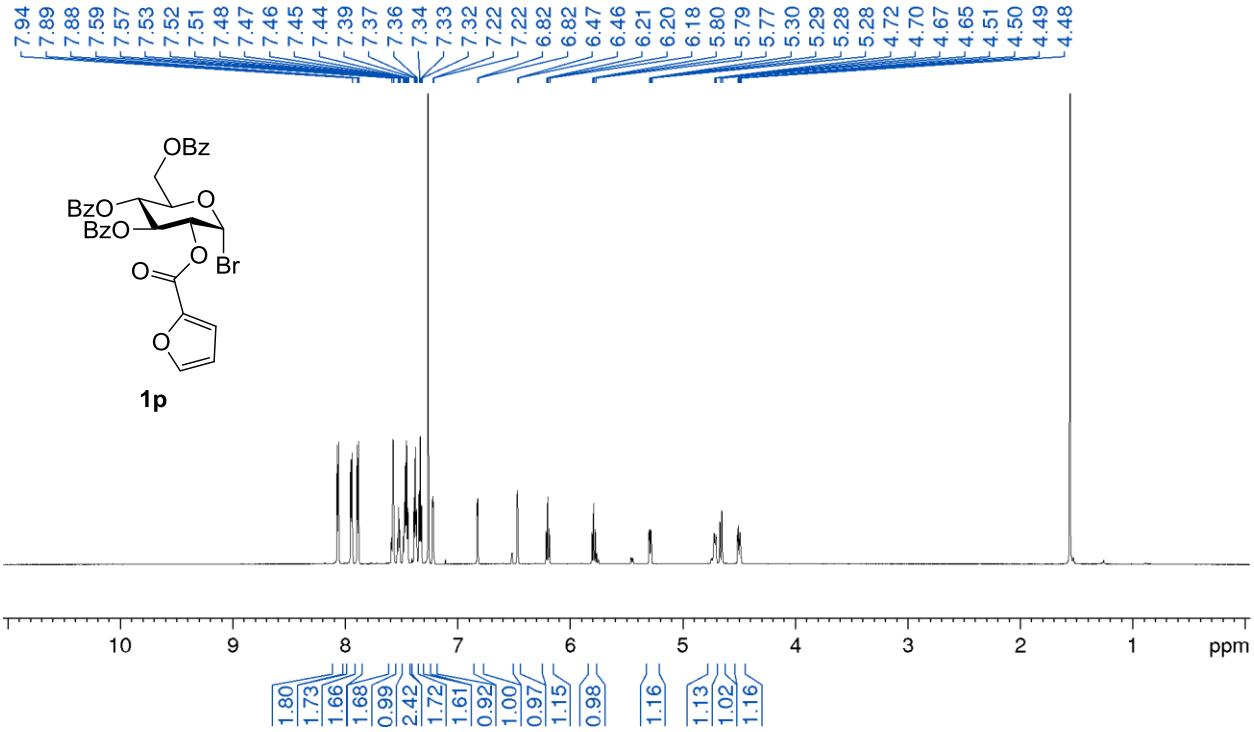
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1o)



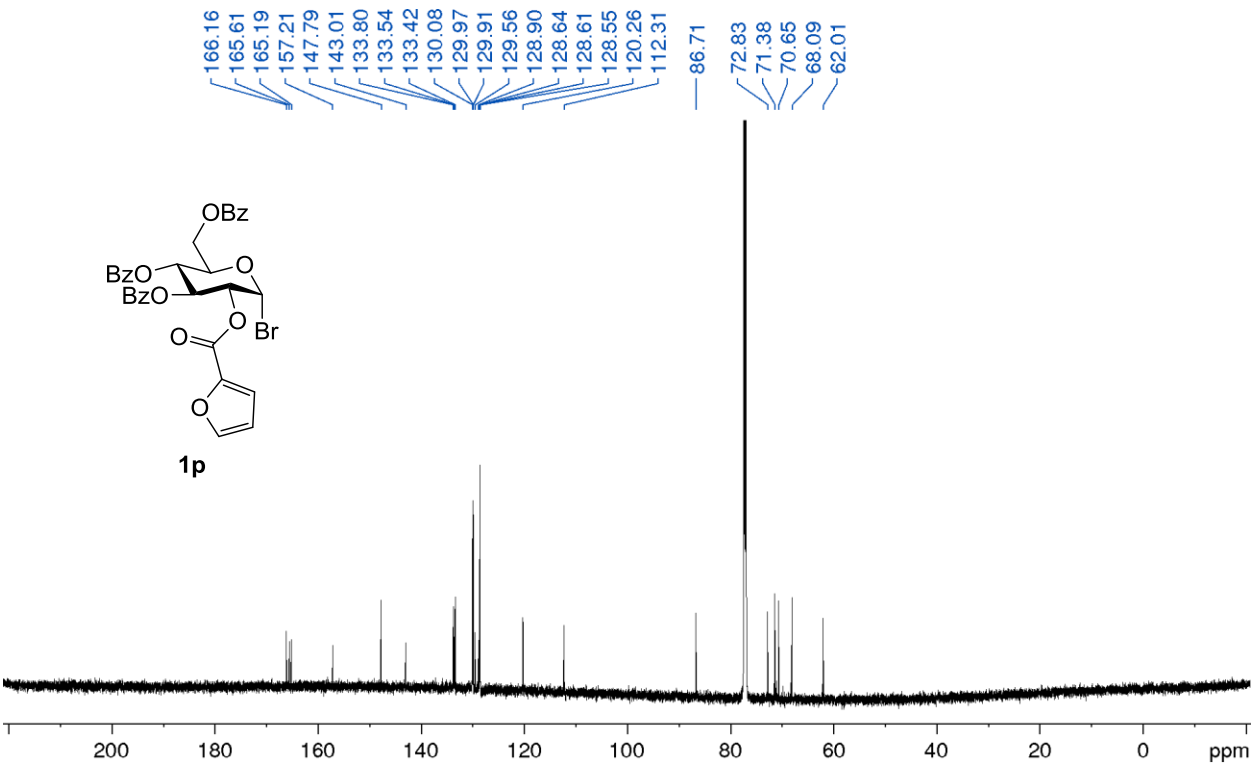
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1o)



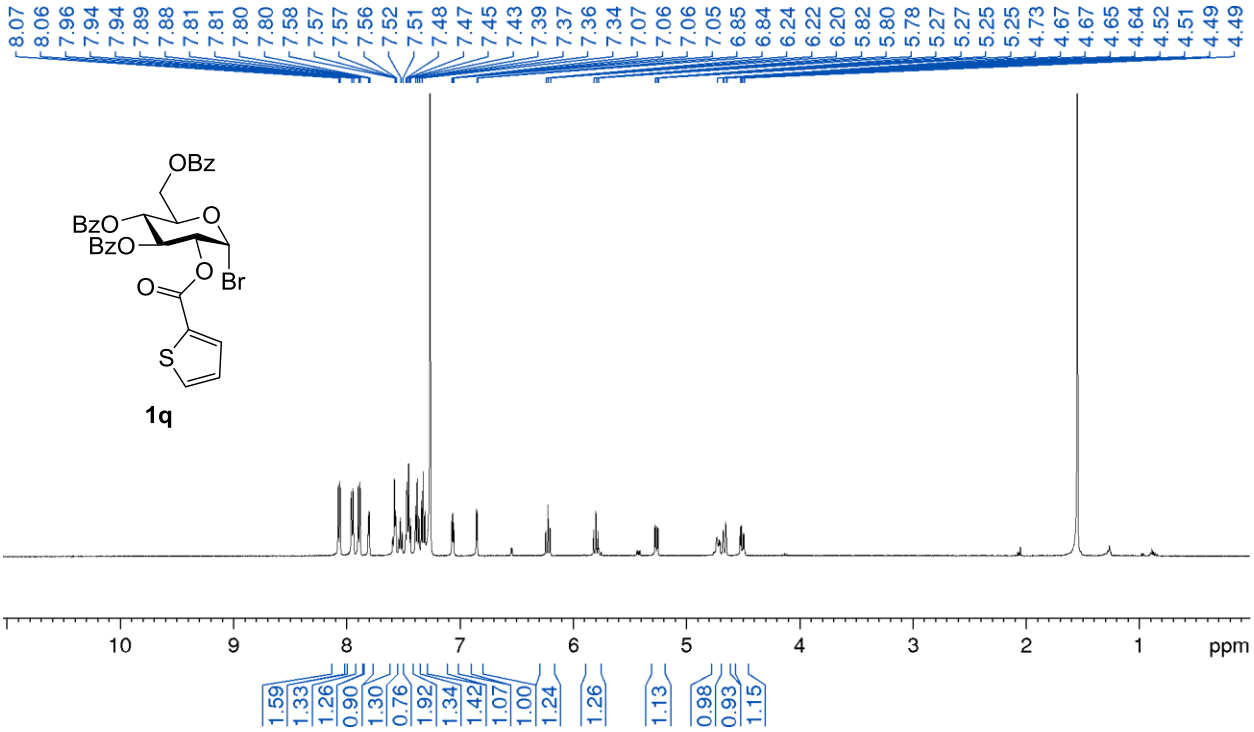
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1p)



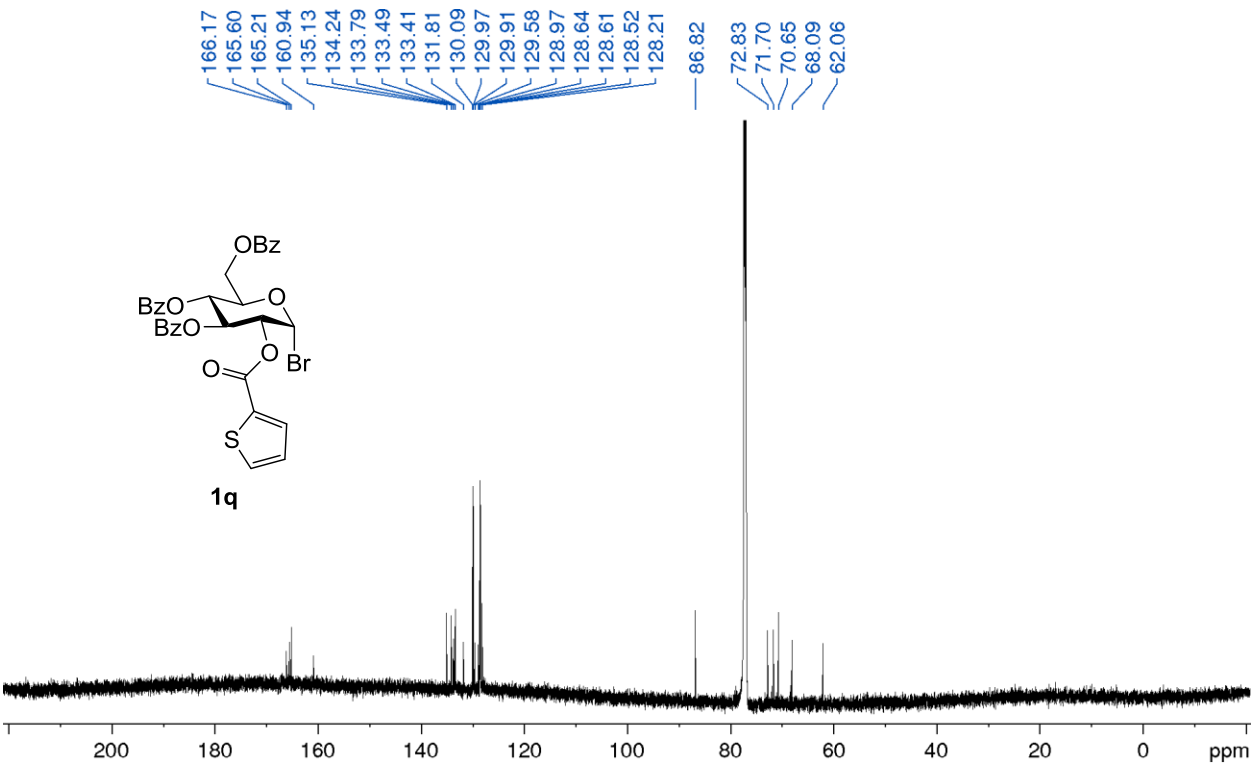
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1p)



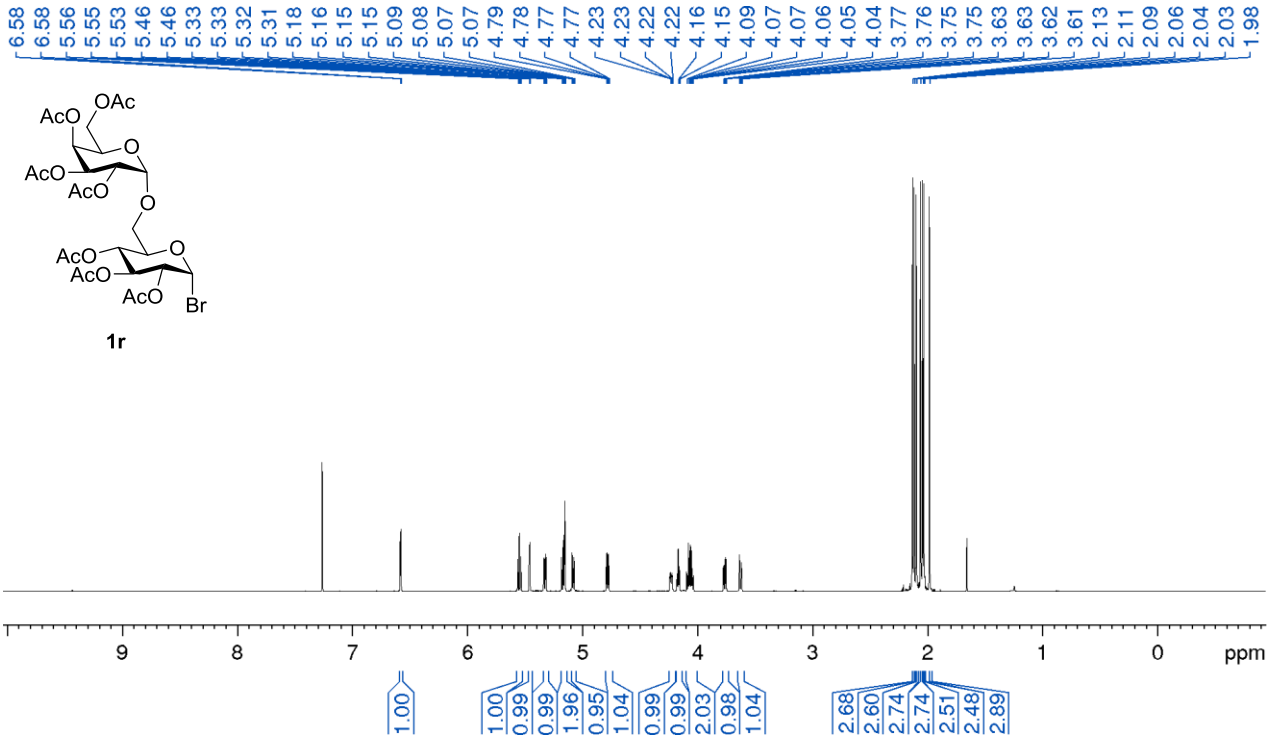
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1q)



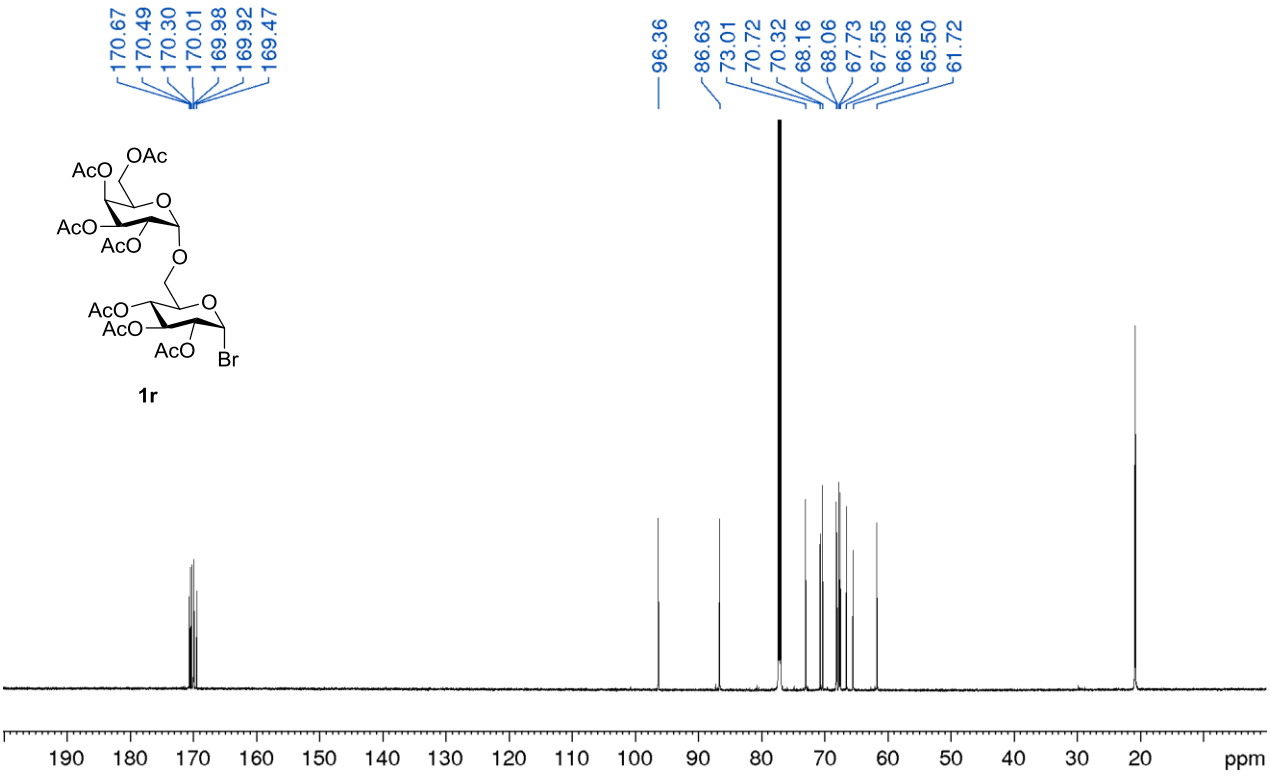
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1q)



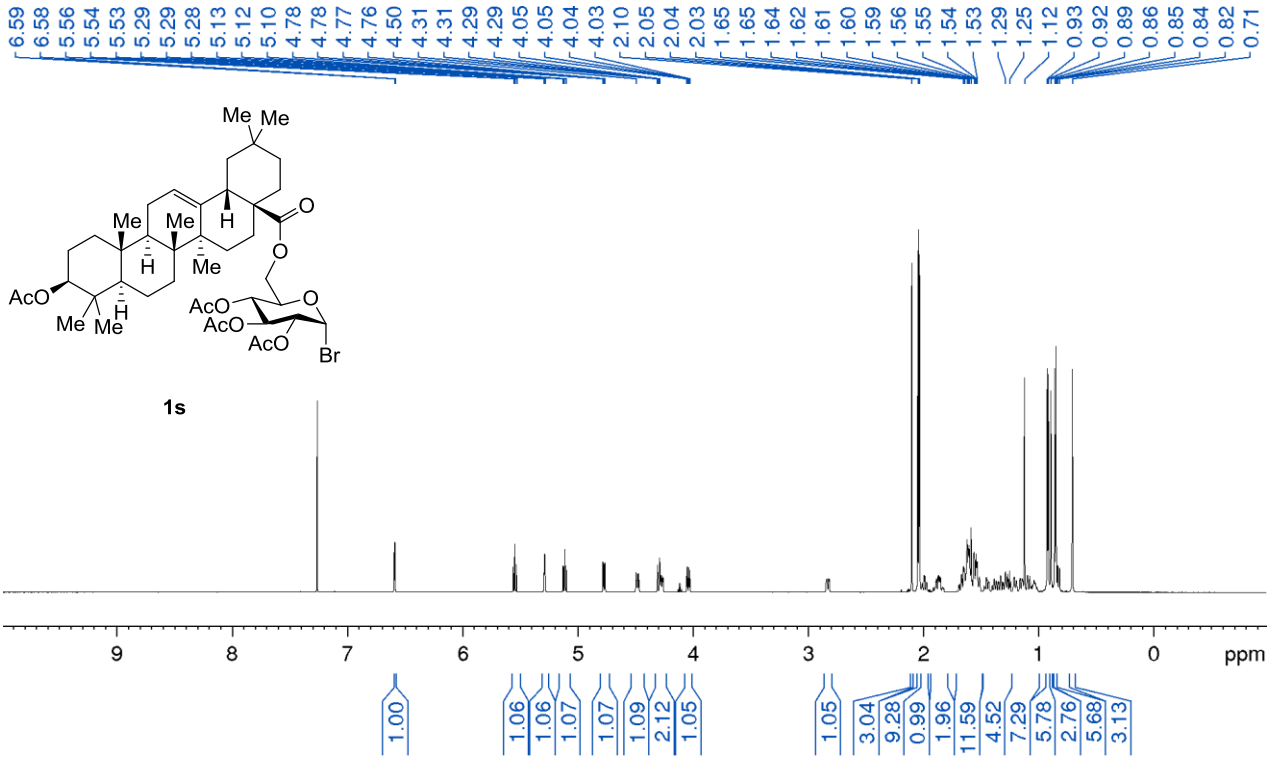
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1r)



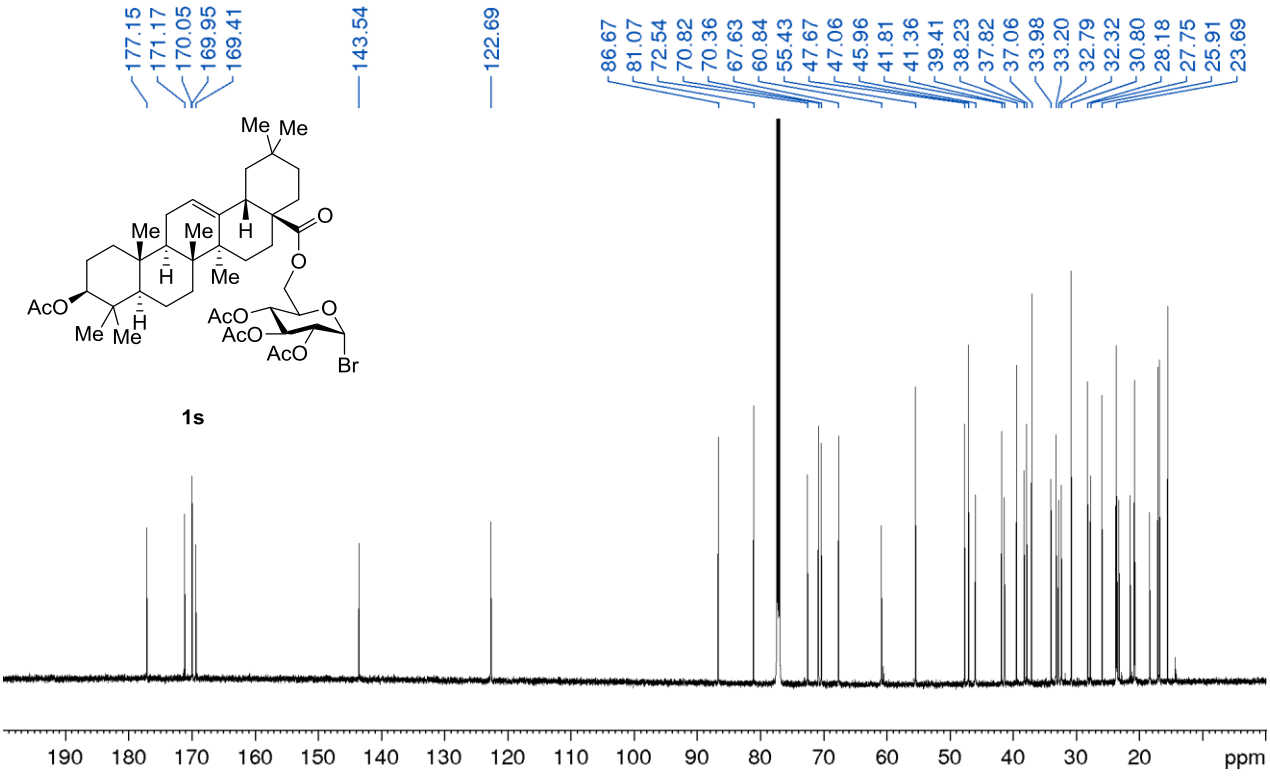
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1r)



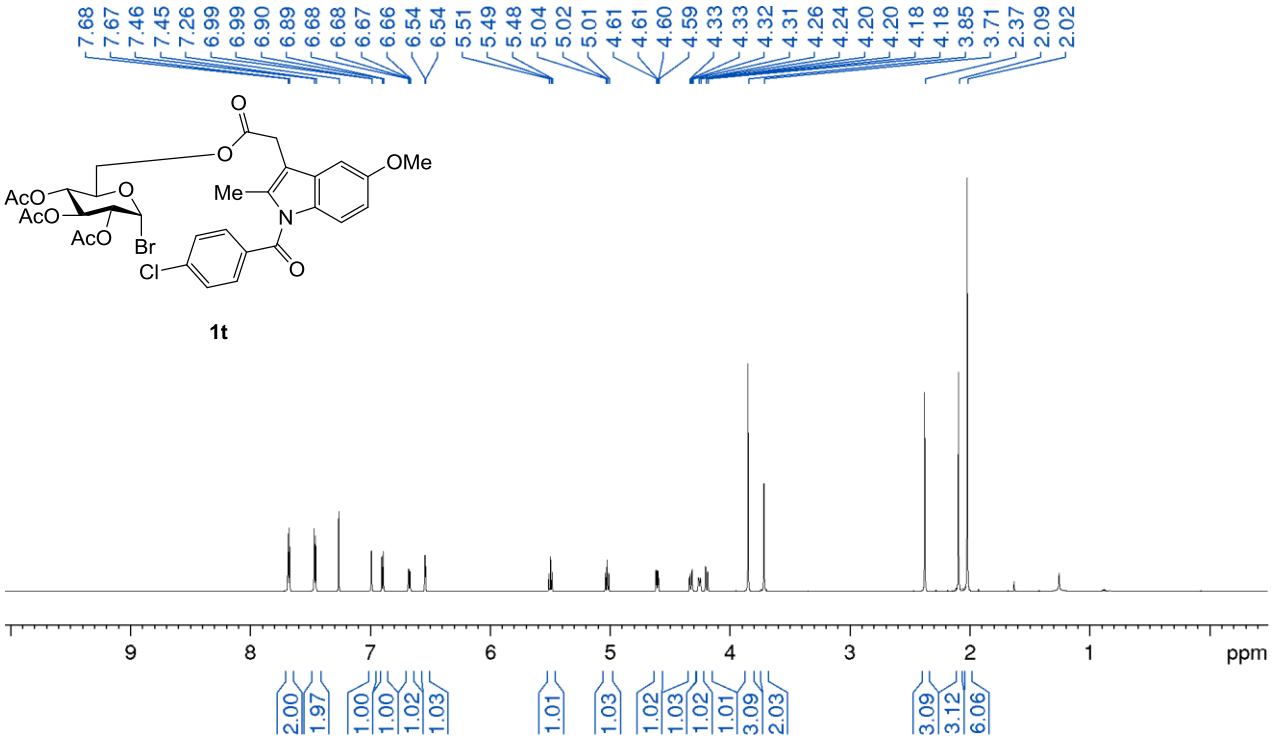
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1s)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1s)

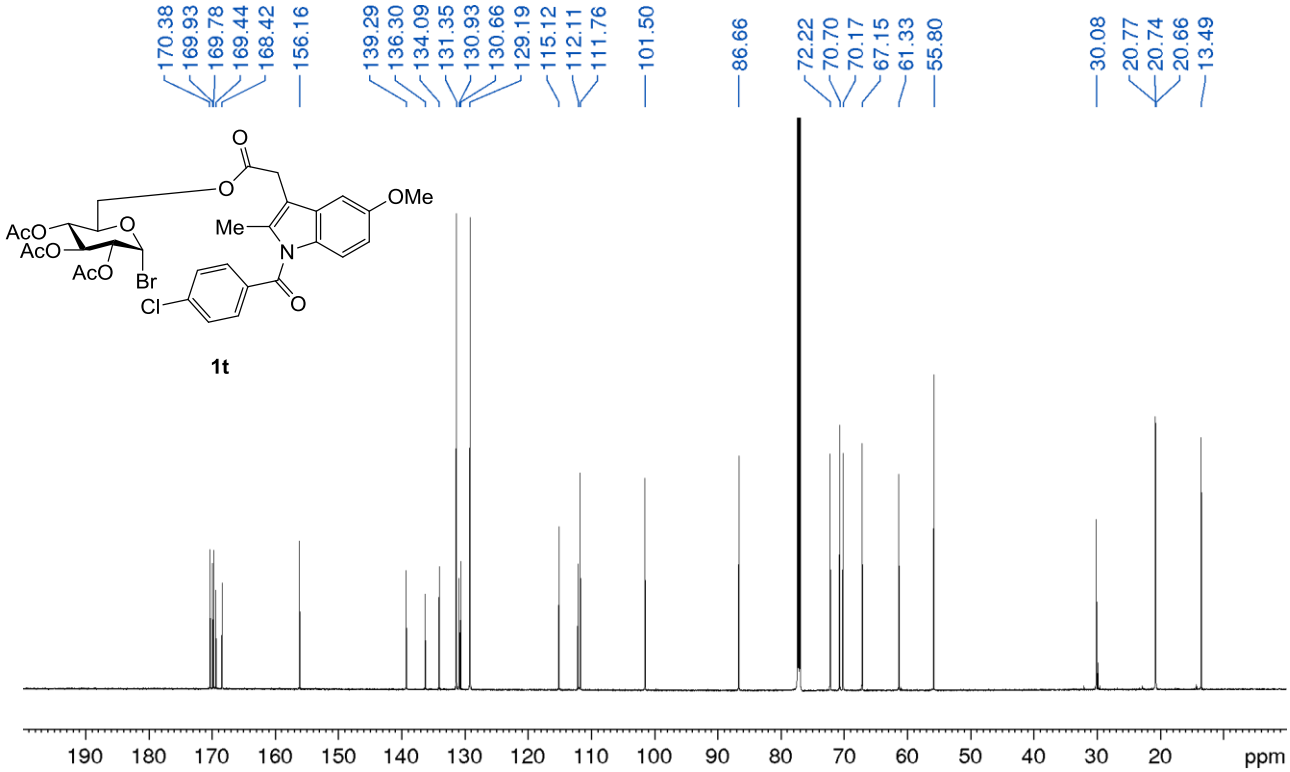


^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1t)



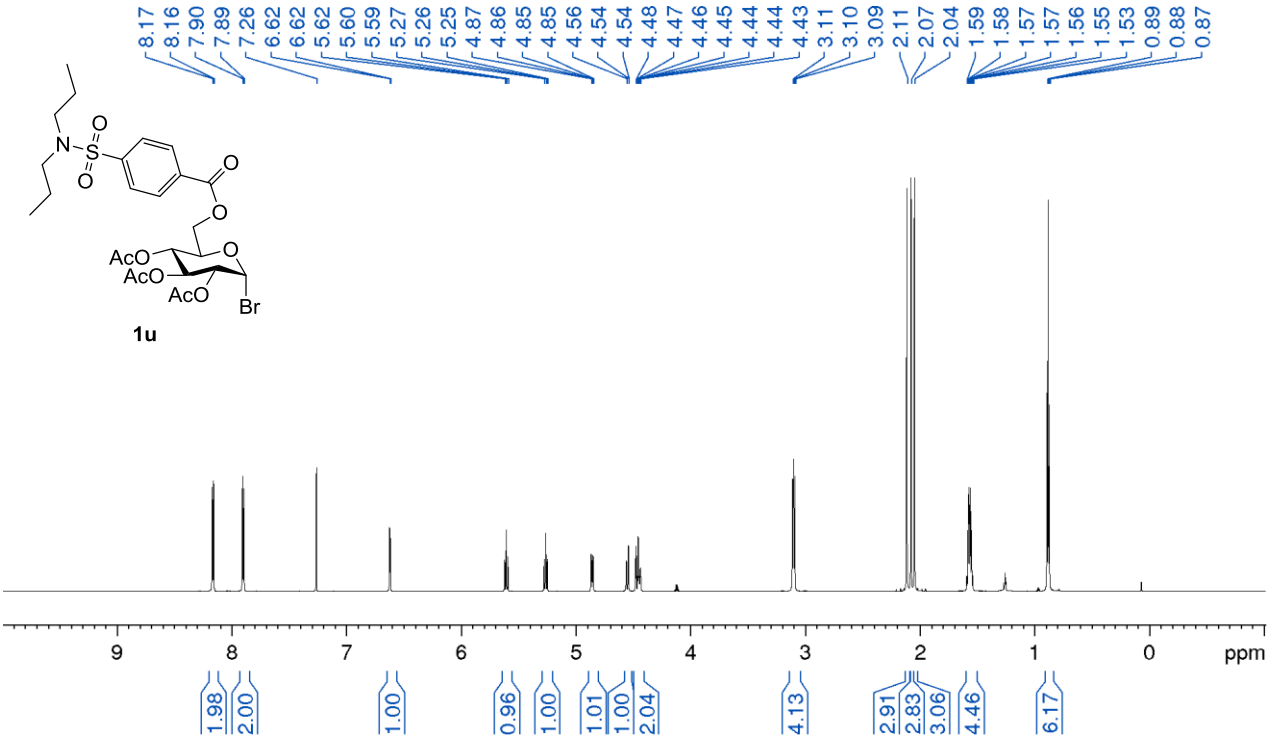
1t

^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1t)

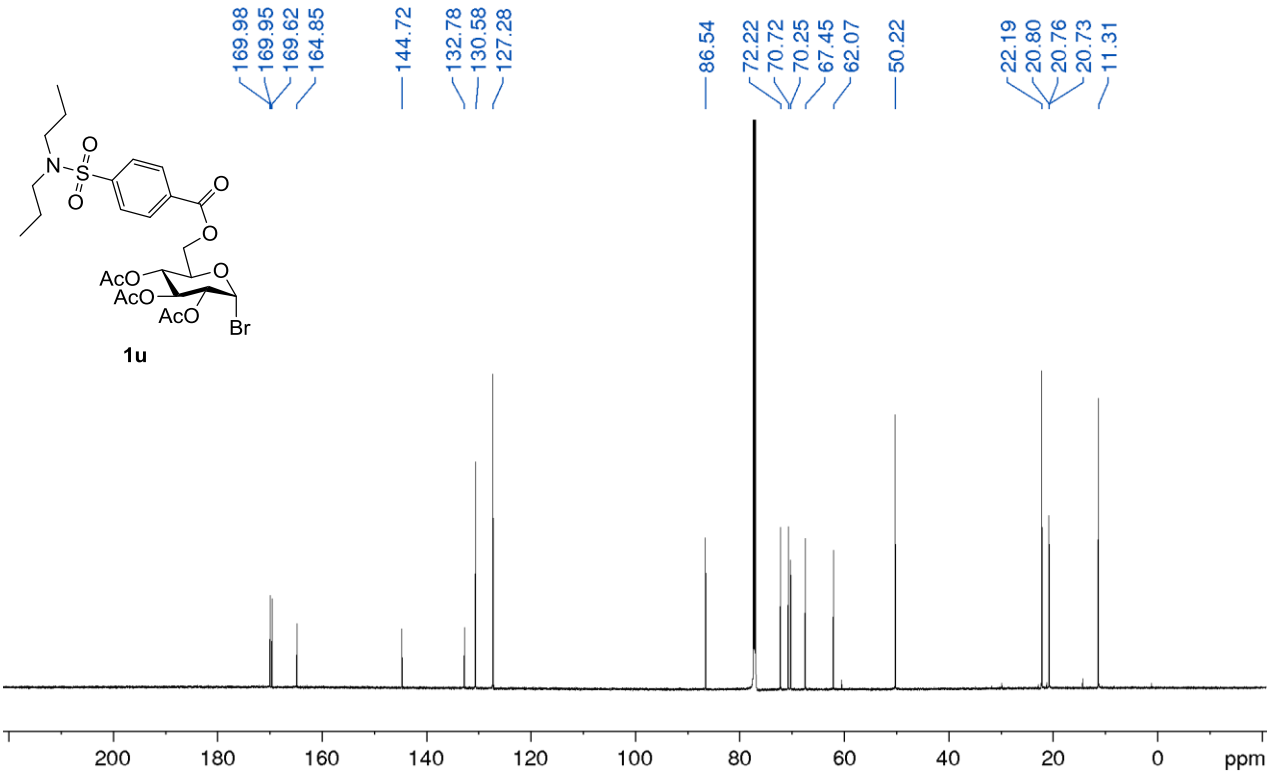


1t

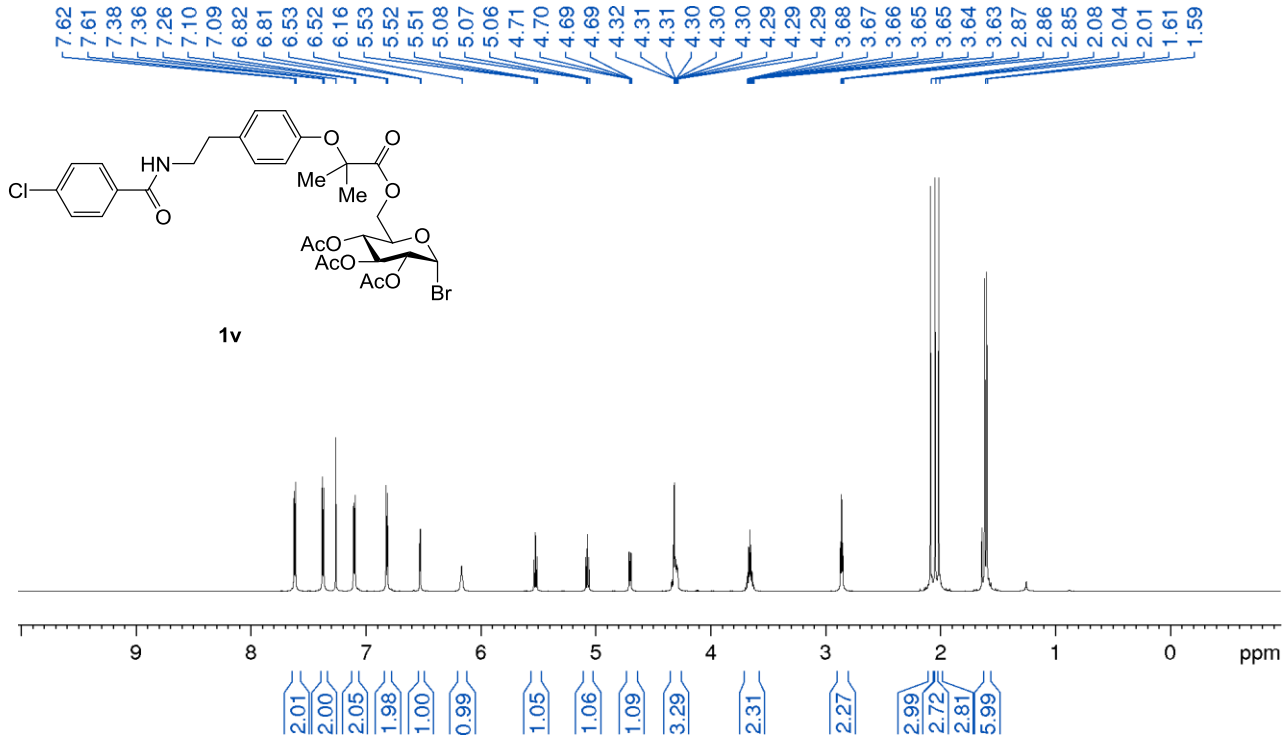
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1u)



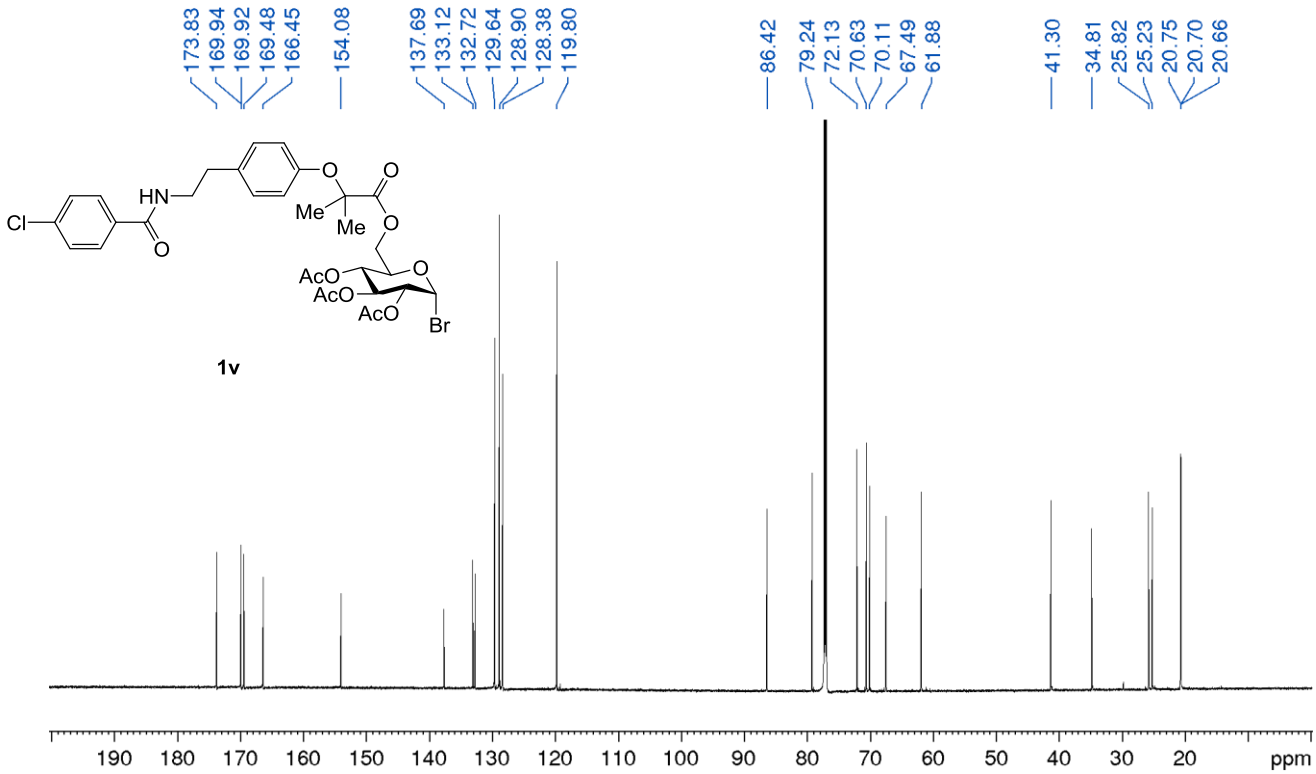
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1u)



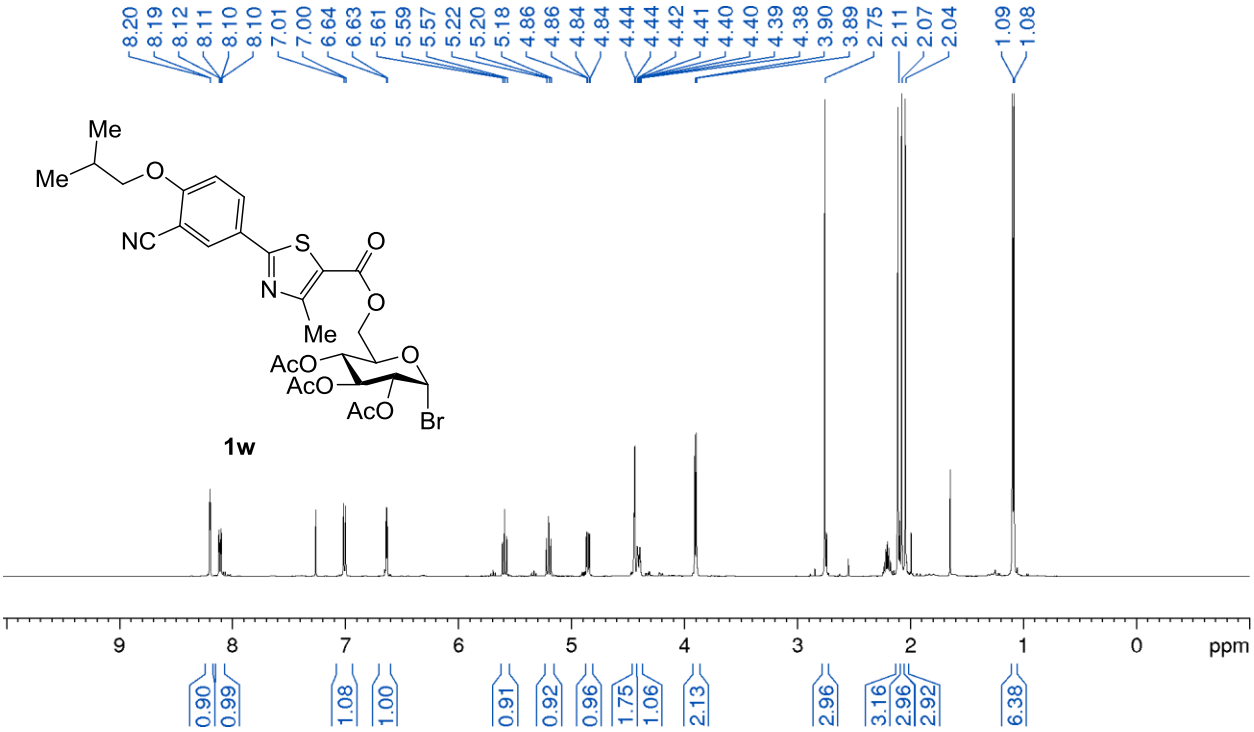
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1v)



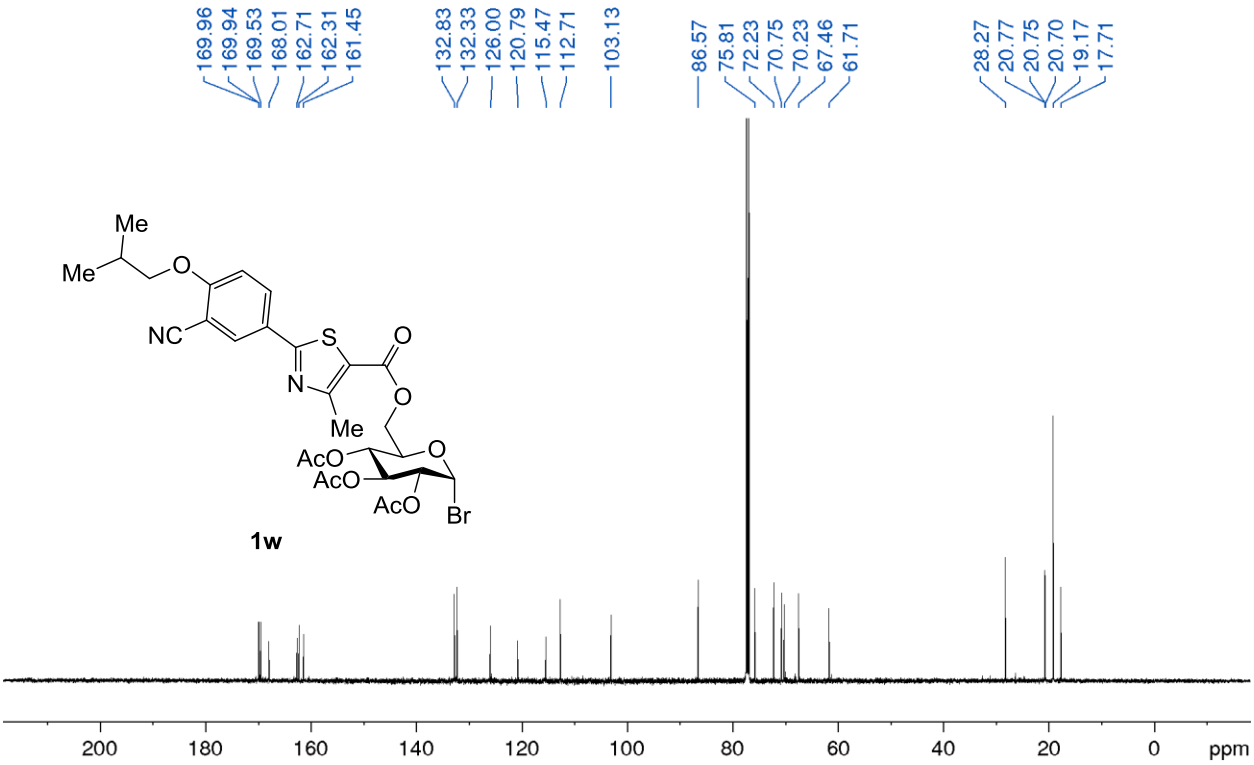
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1v)



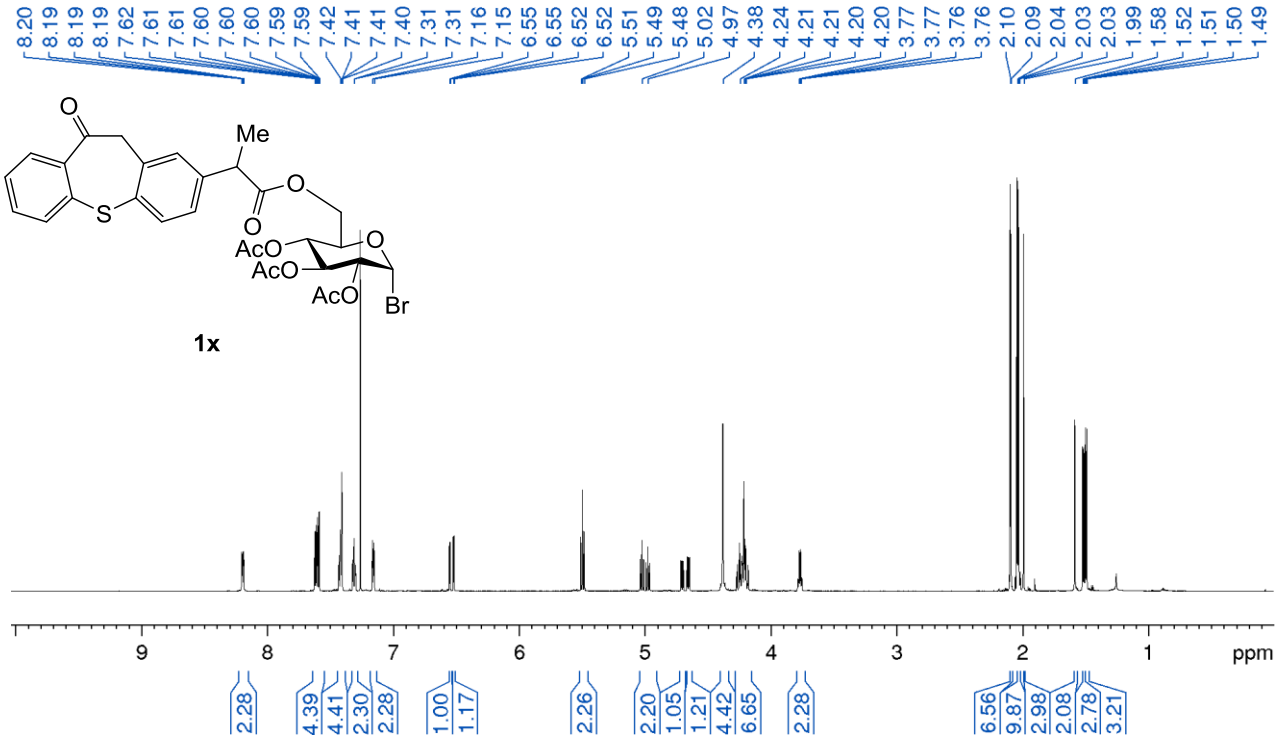
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1w)



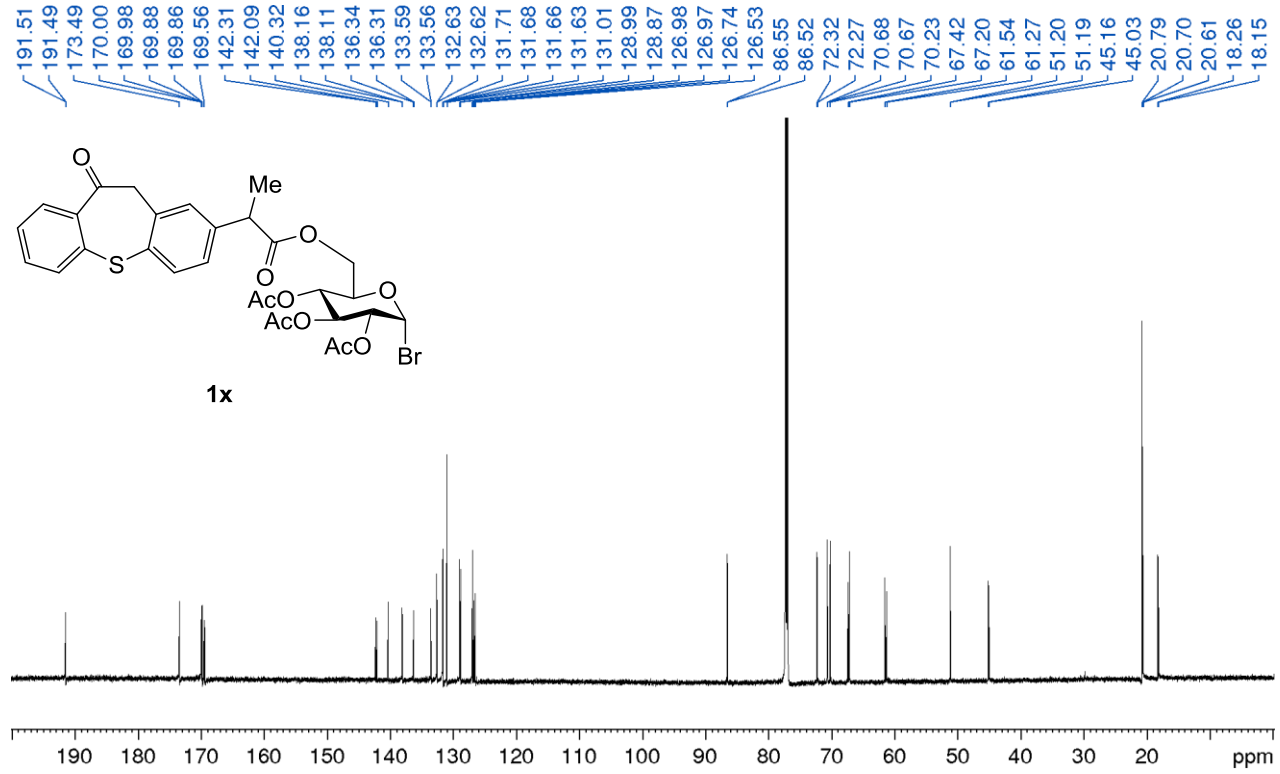
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1w)



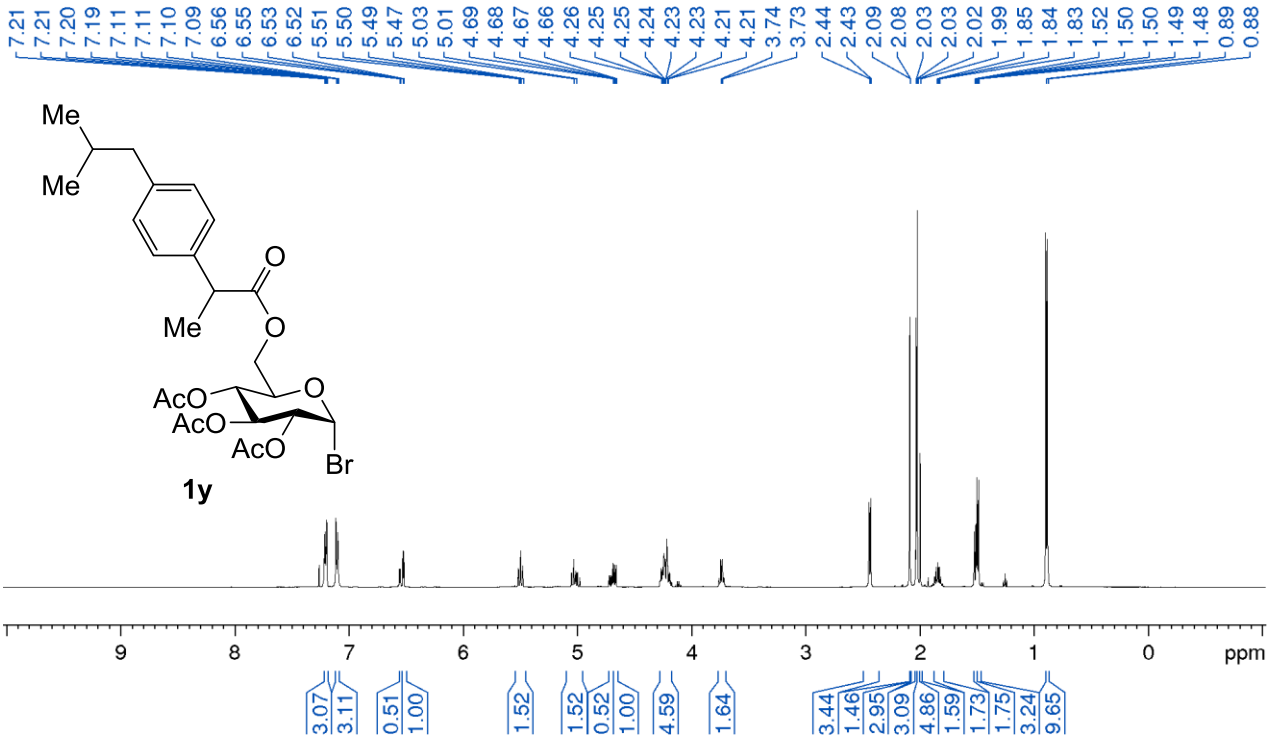
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1x)



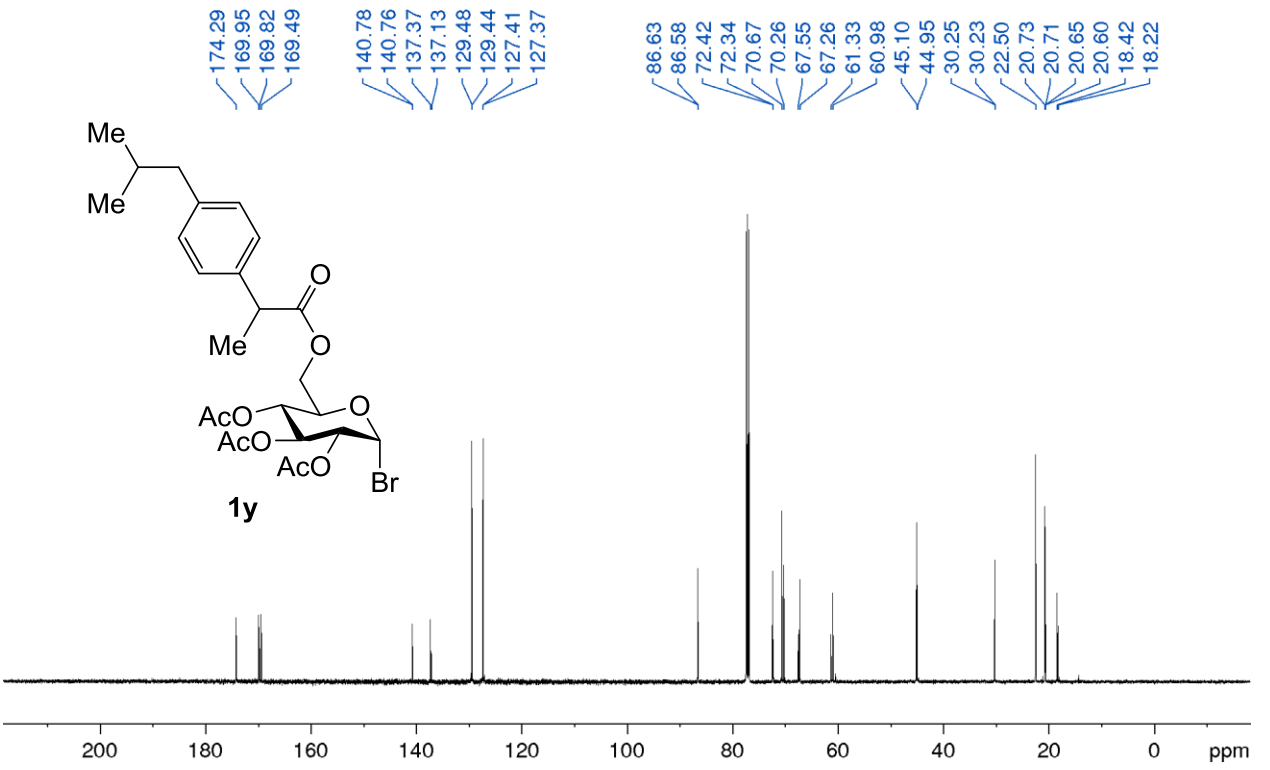
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1x)



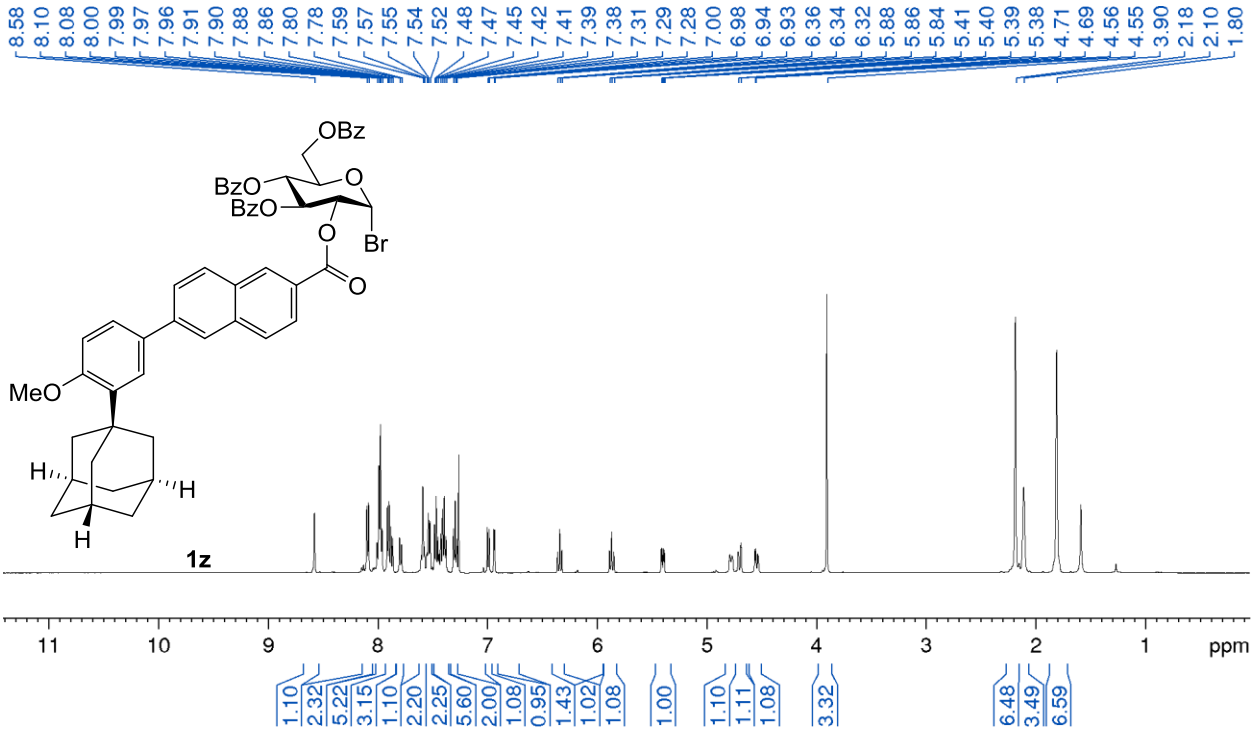
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1y)



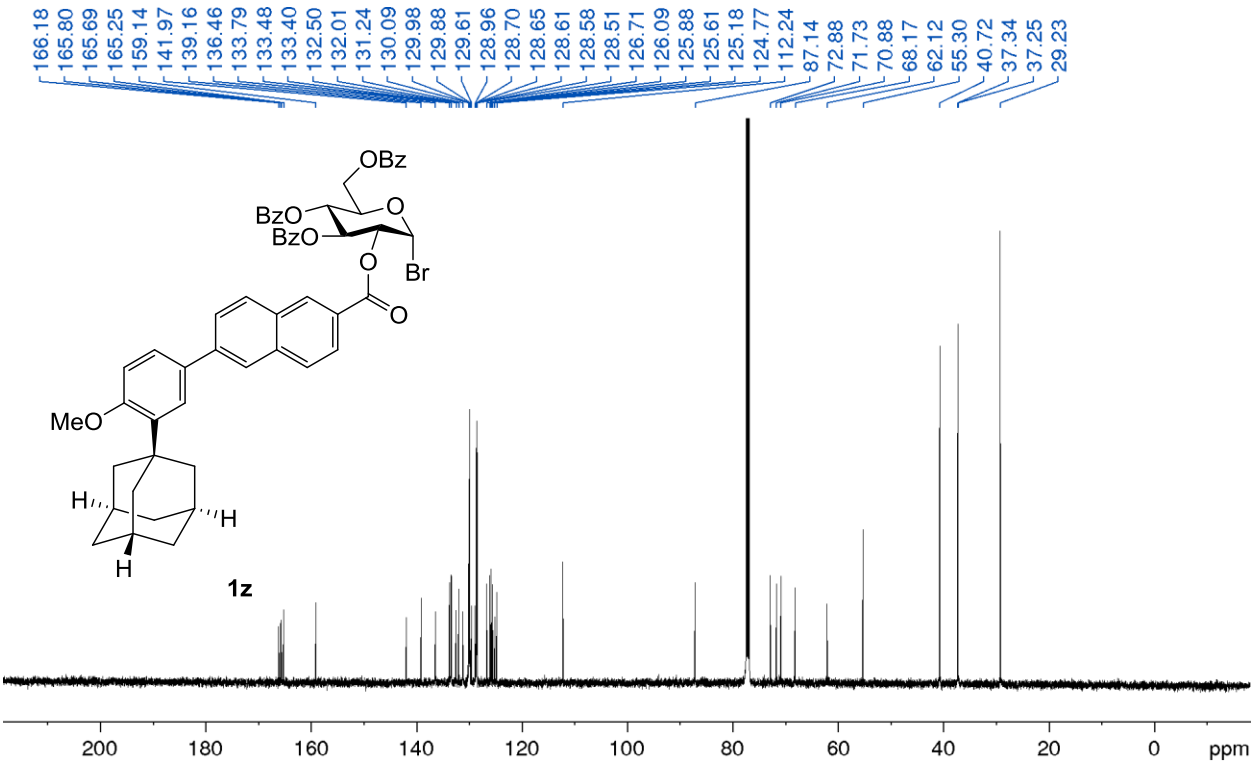
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1y)



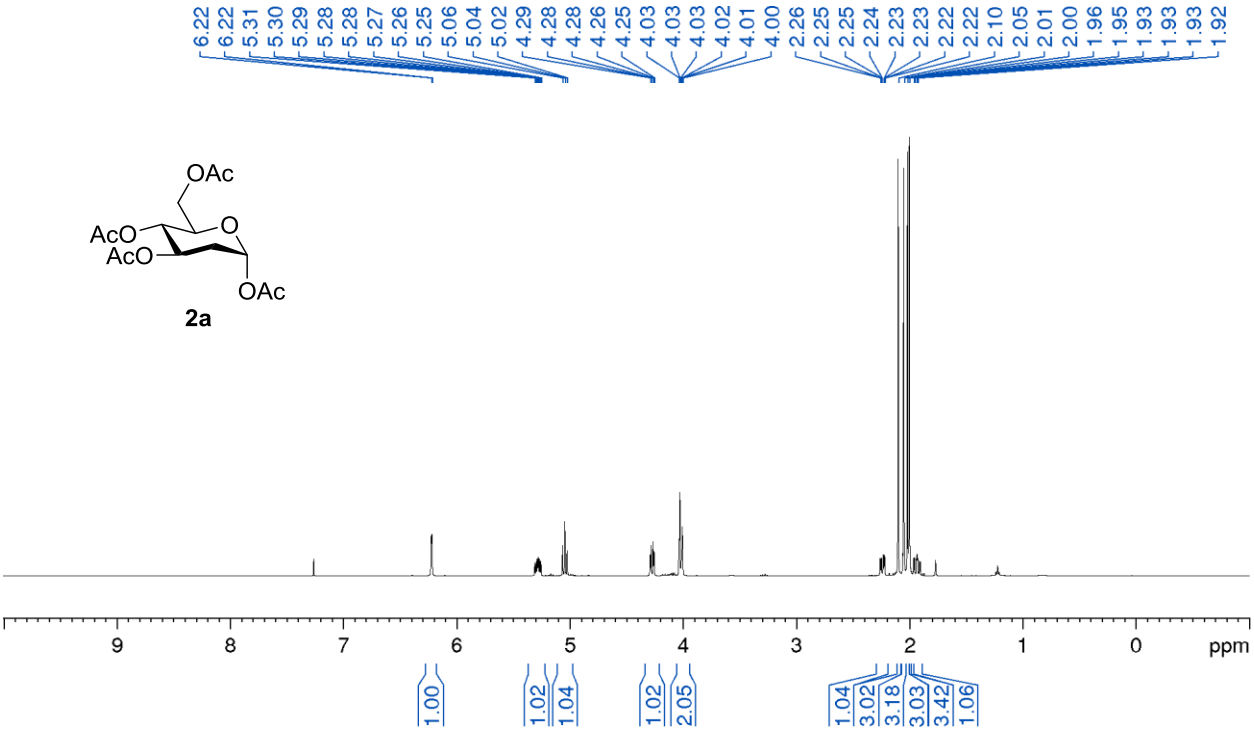
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1z)



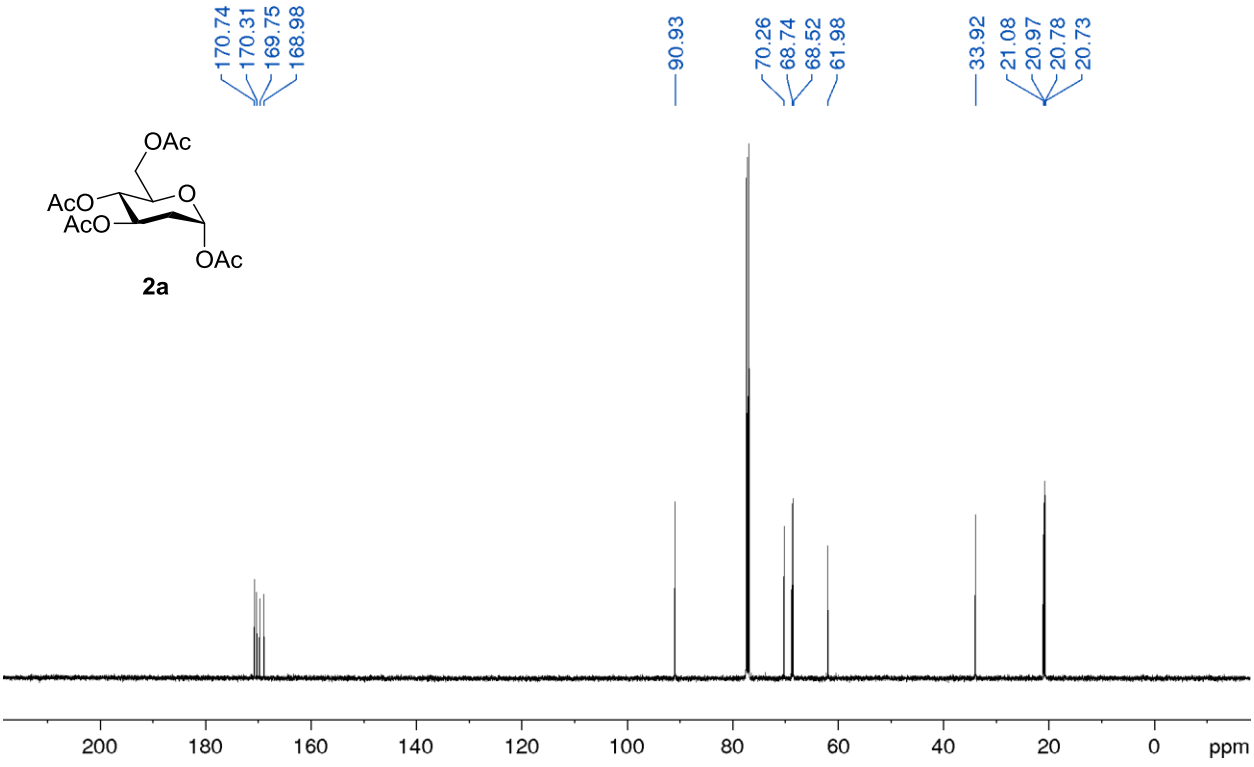
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1z)



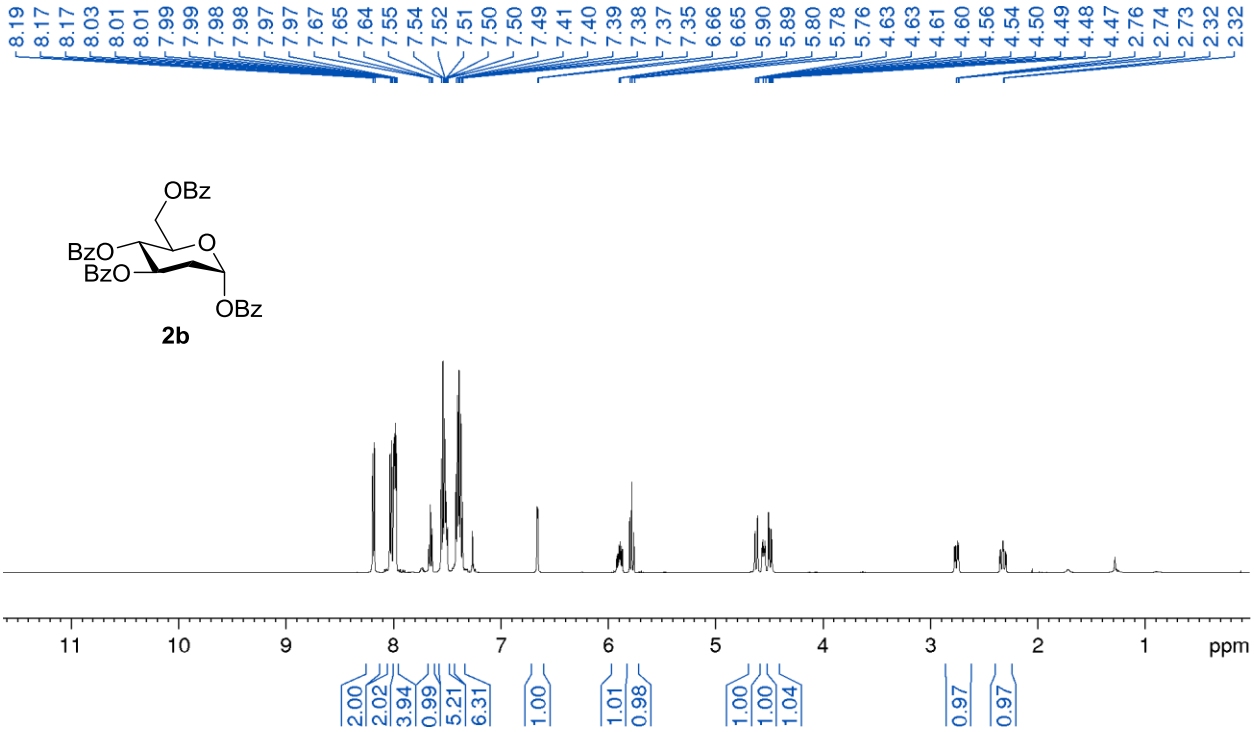
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2a)



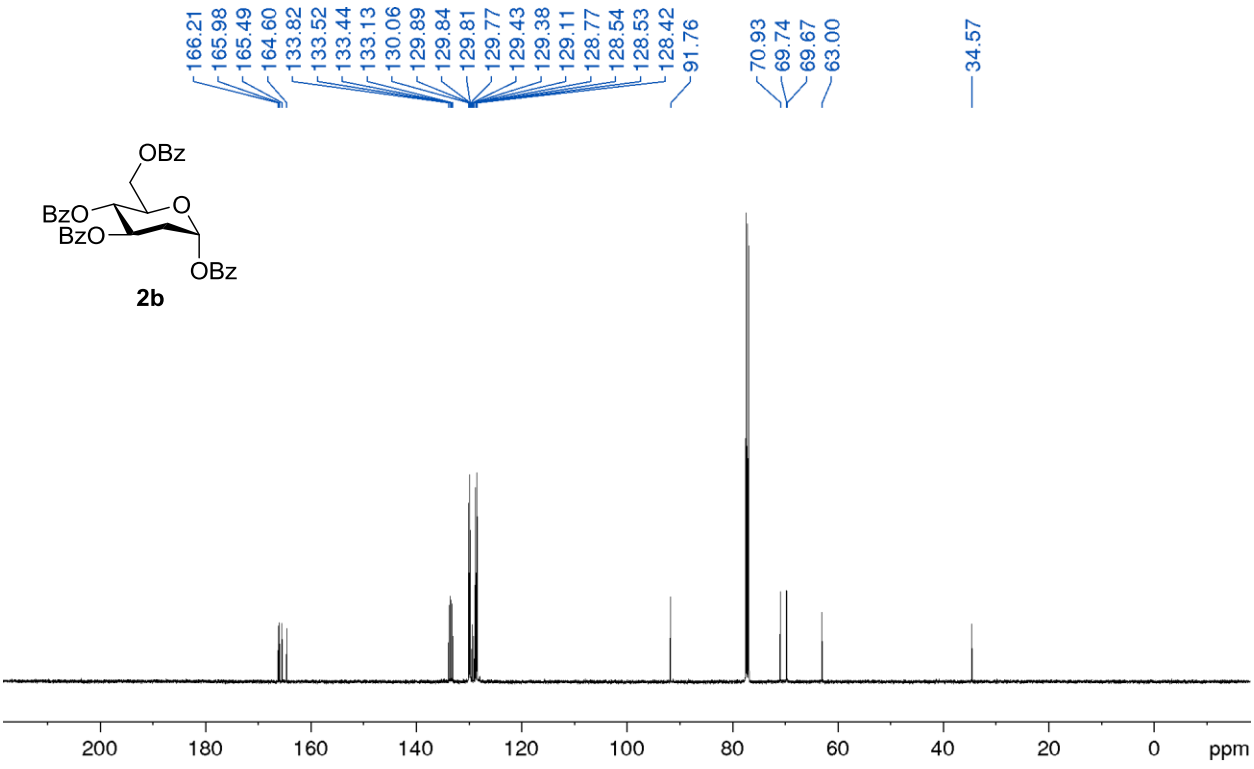
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2a)



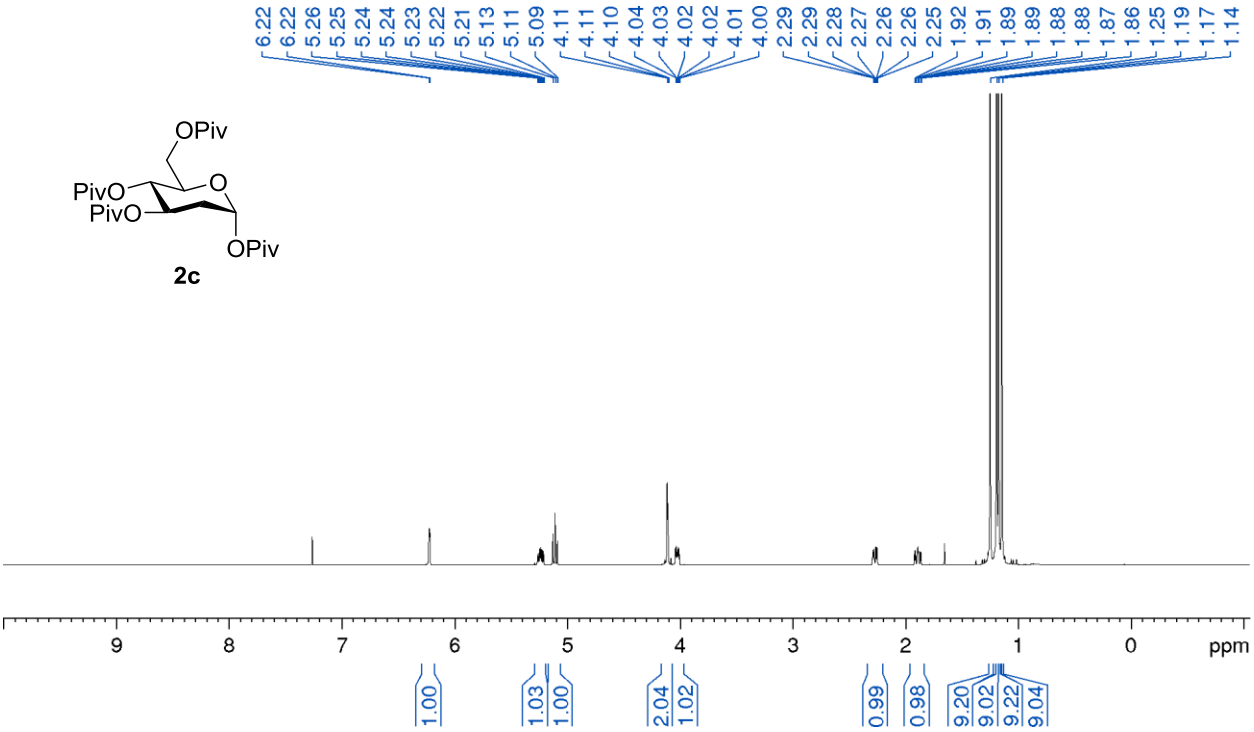
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2b)



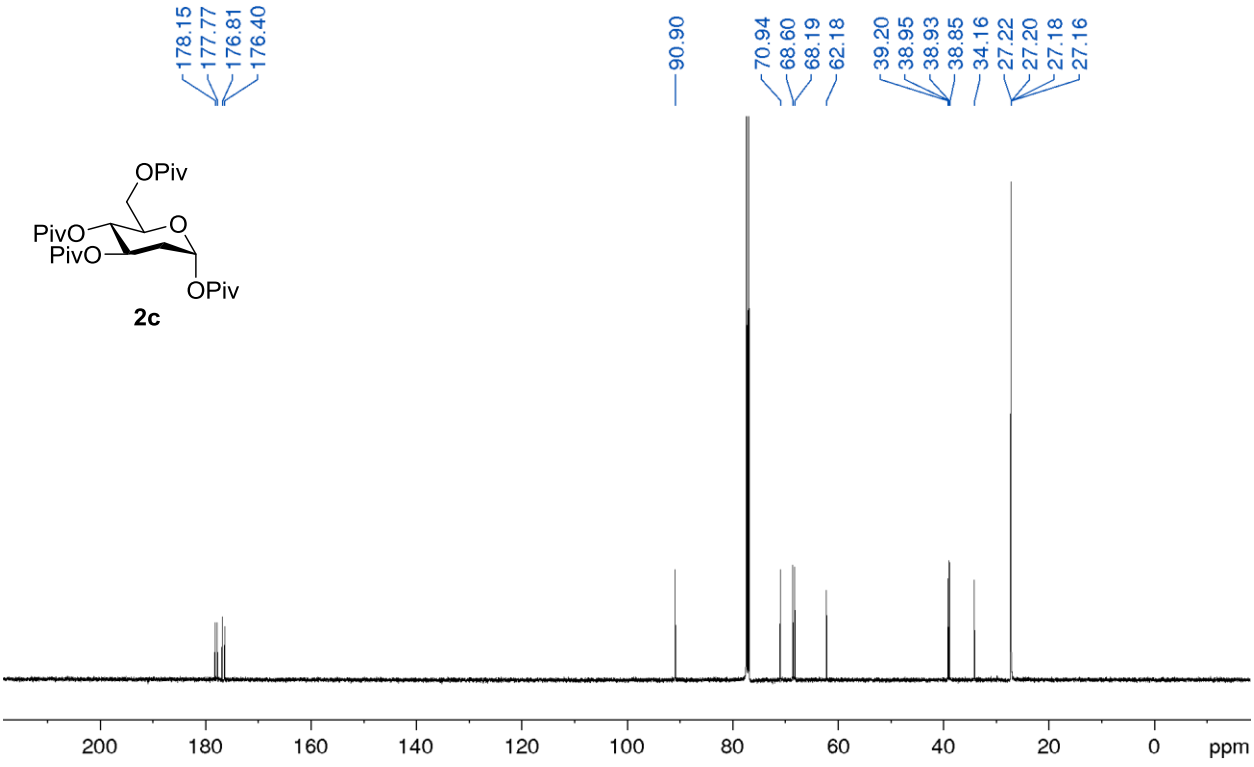
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2b)



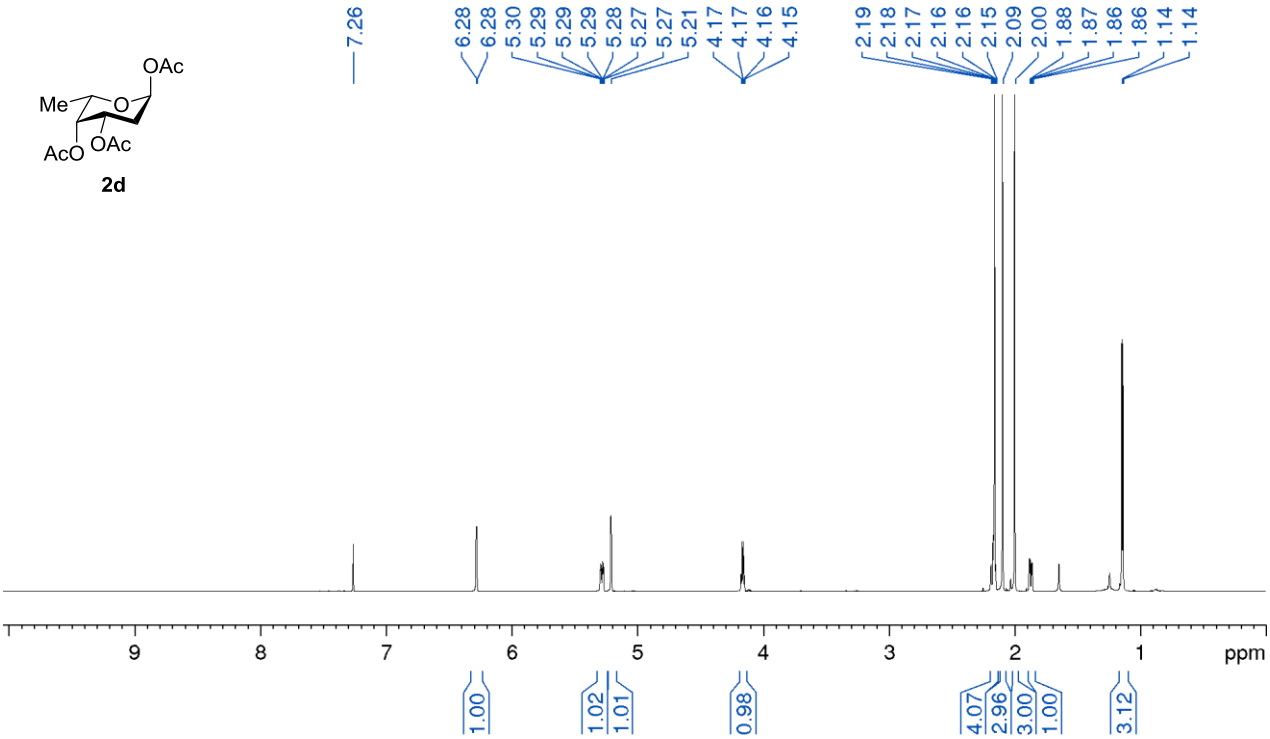
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2c)



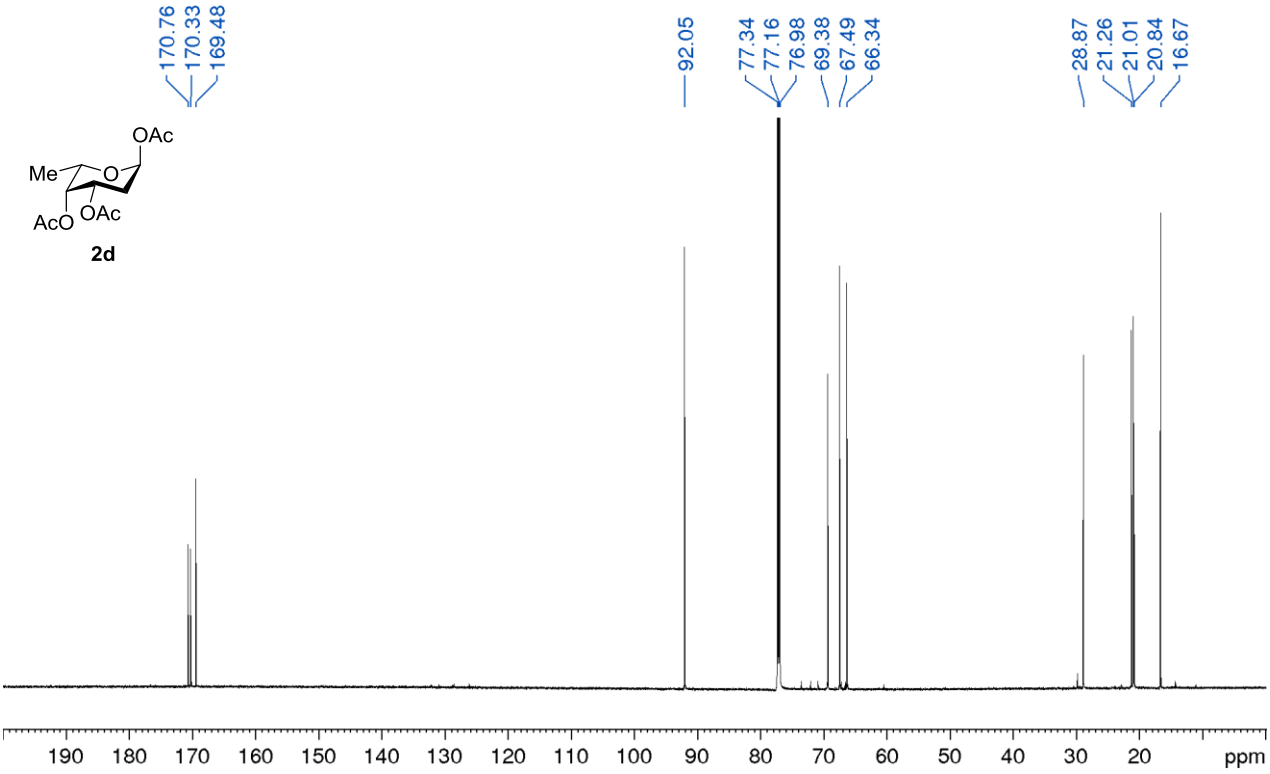
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2c)



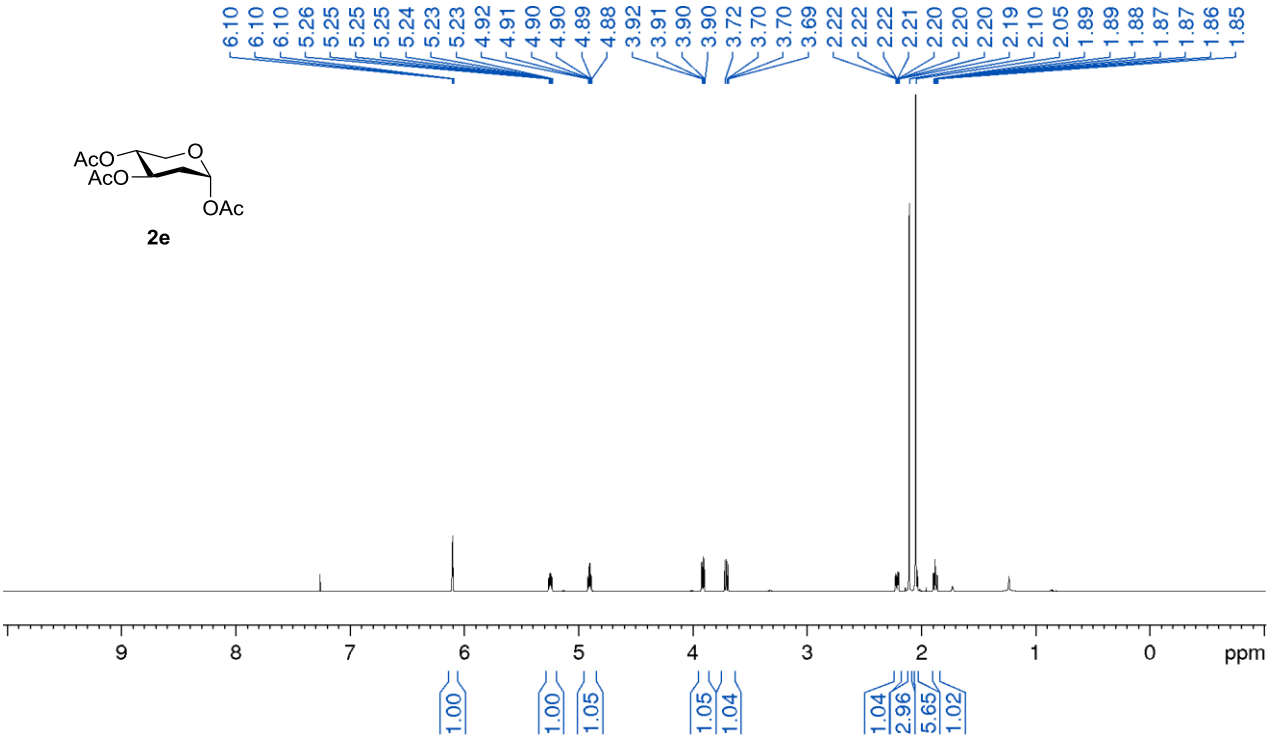
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2d)



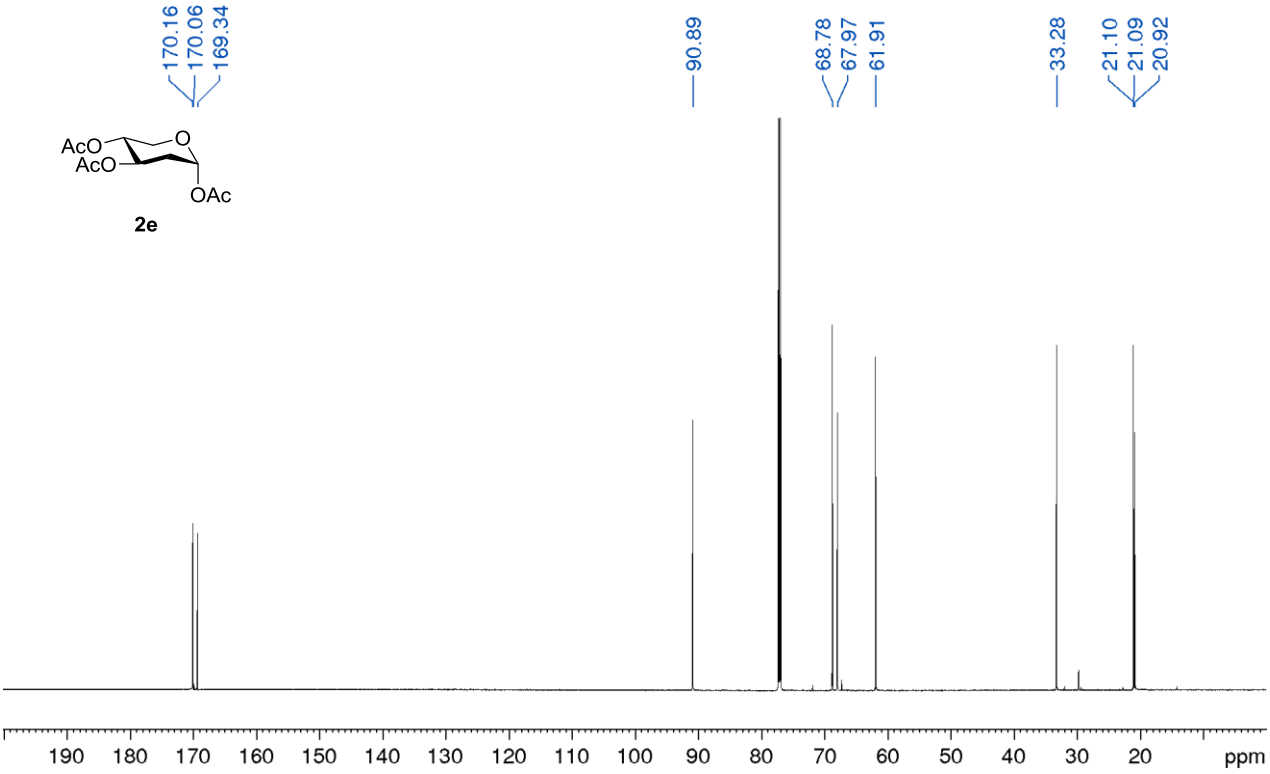
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2d)



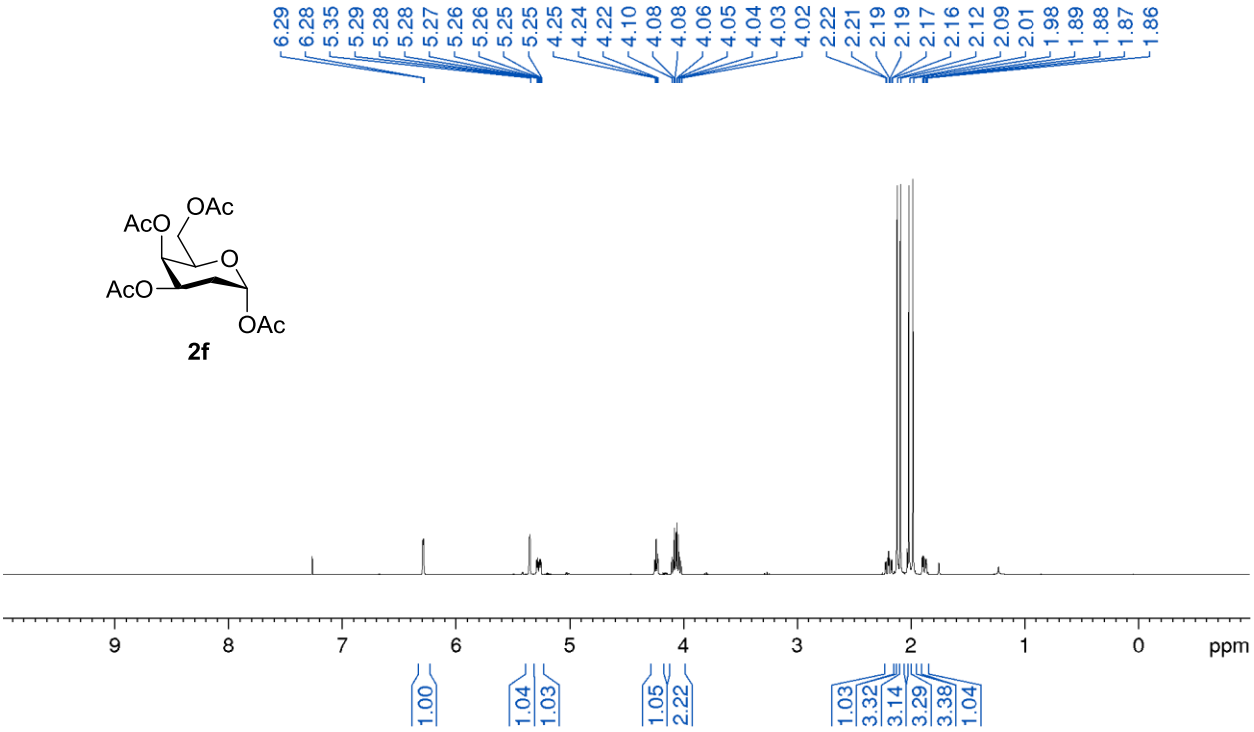
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2e)



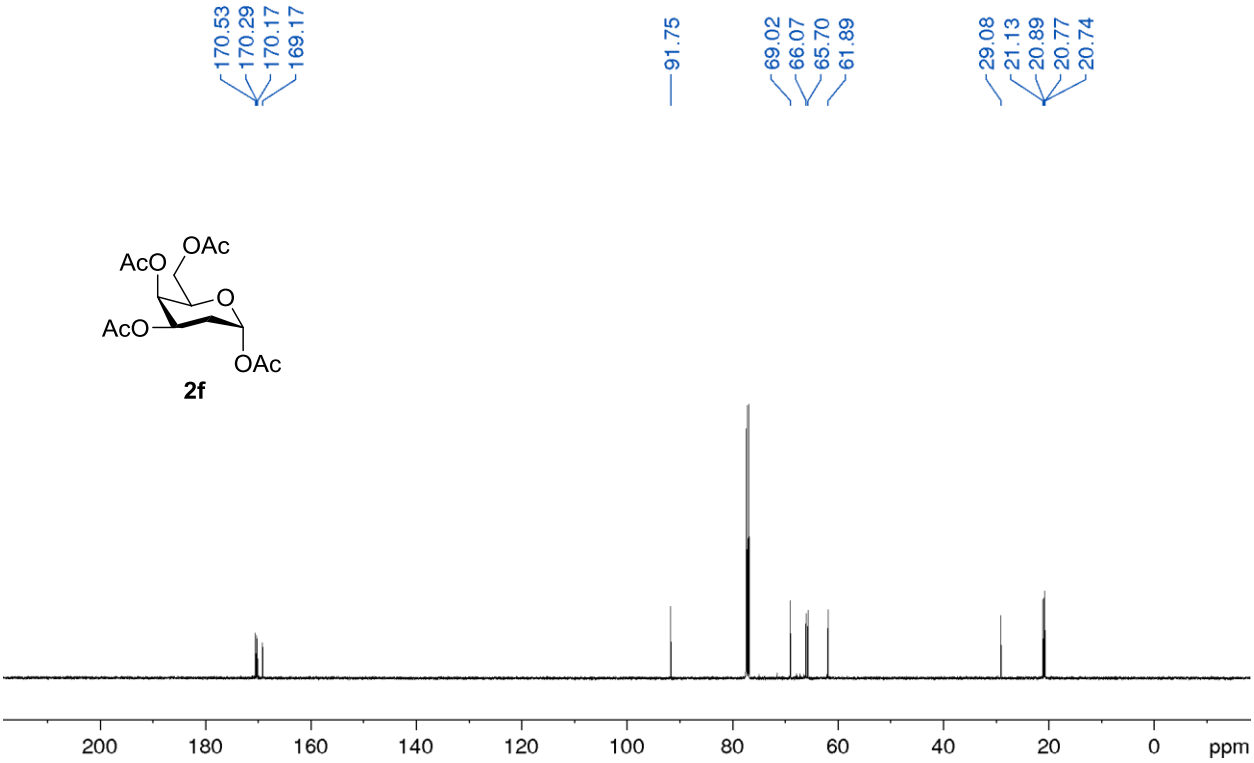
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2e)



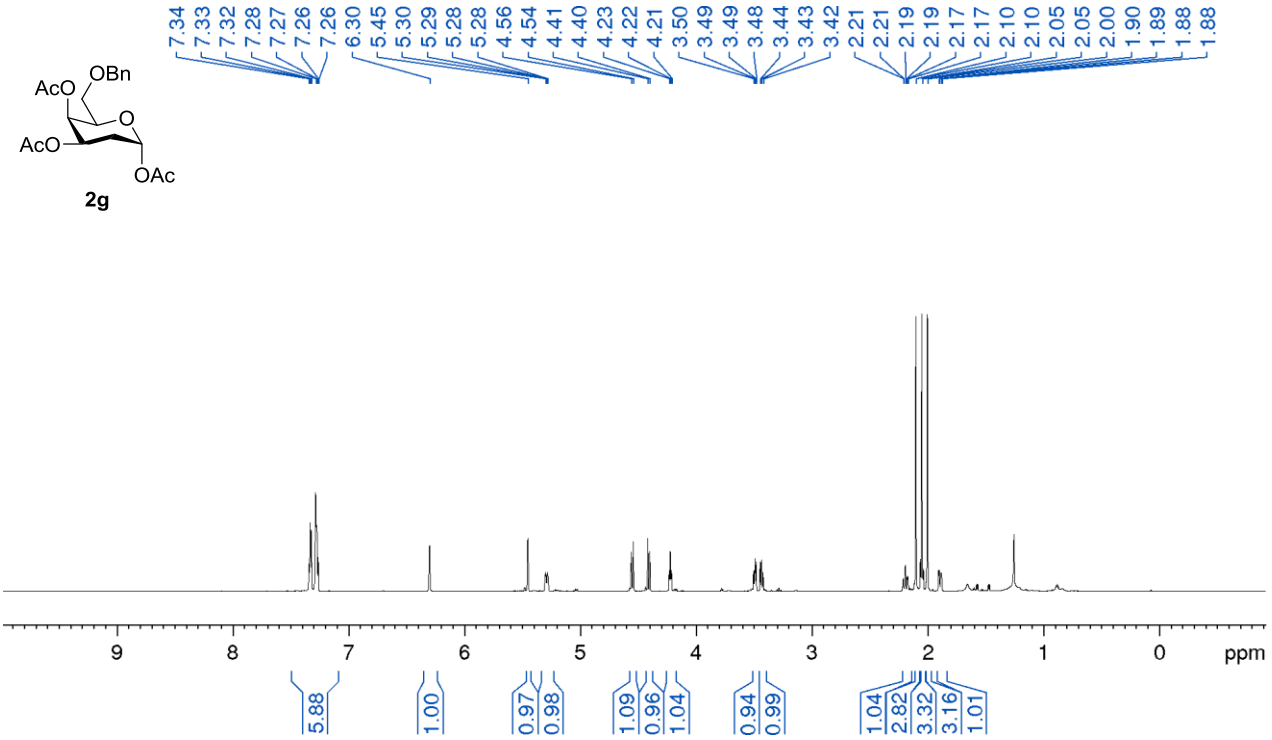
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2f)



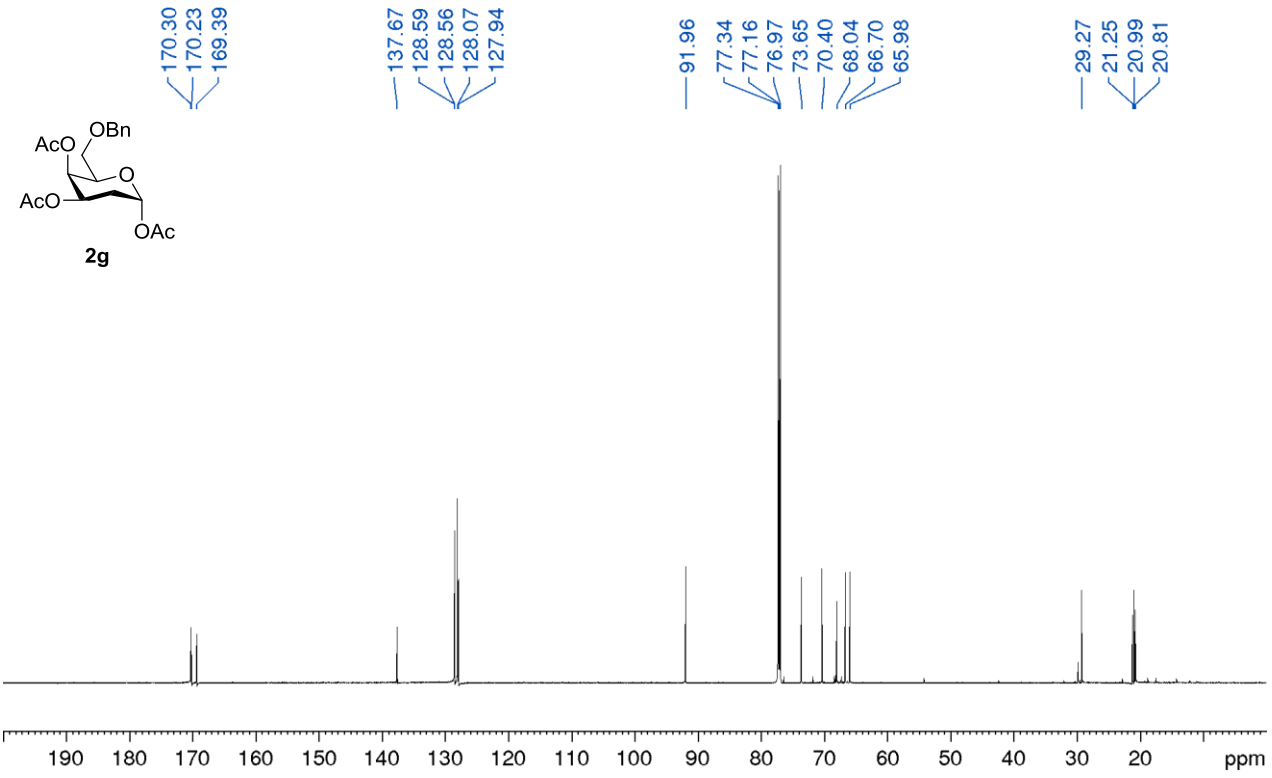
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2f)



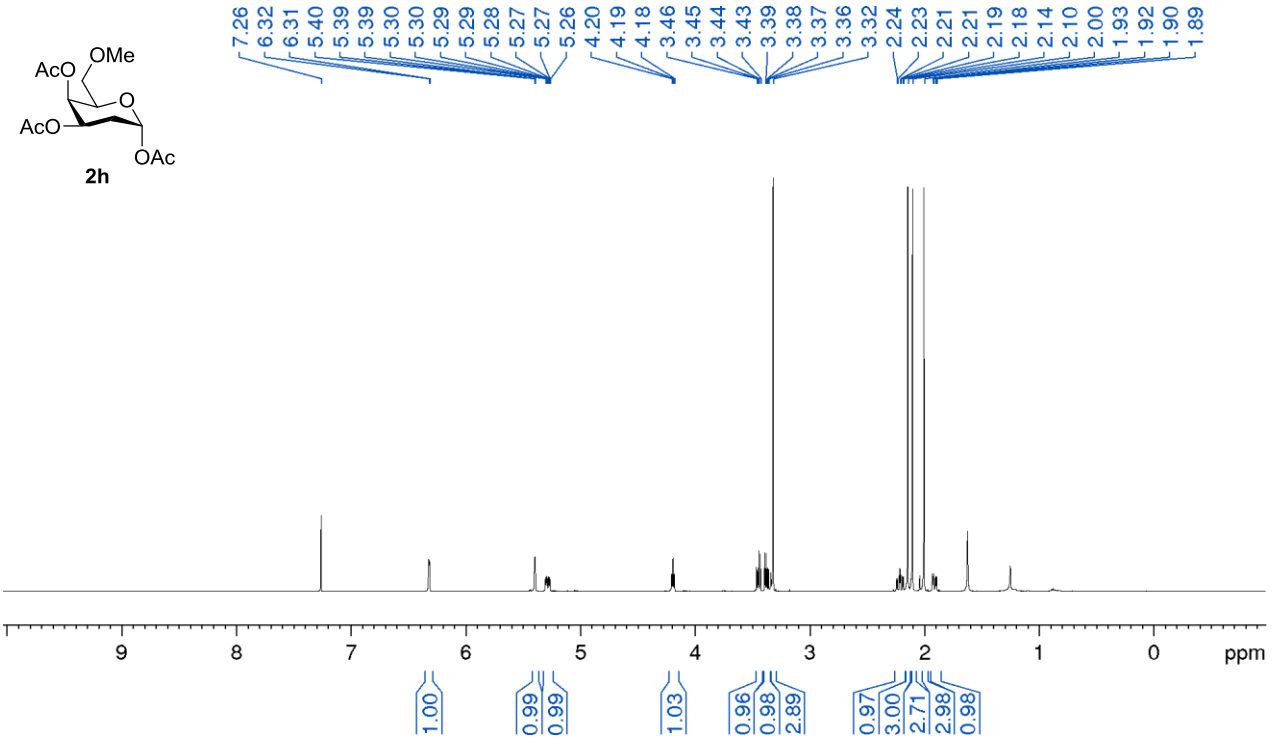
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2g)



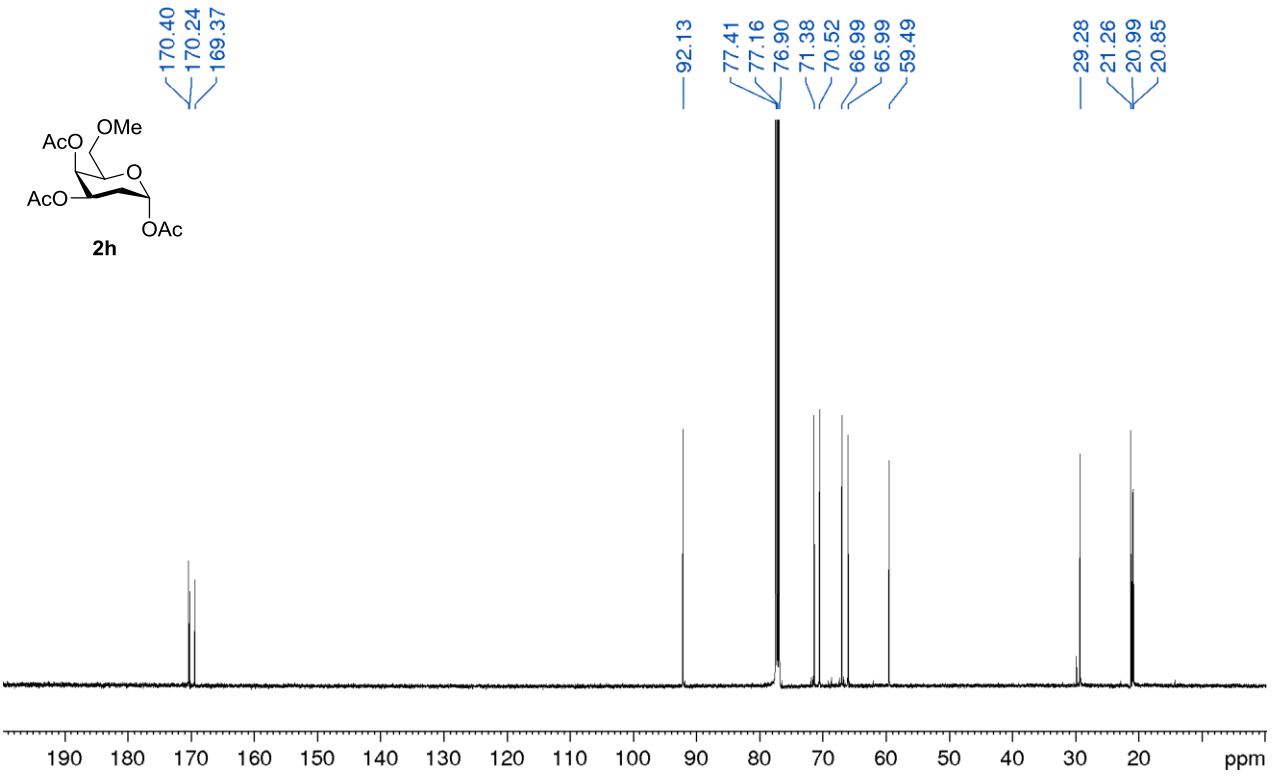
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2g)



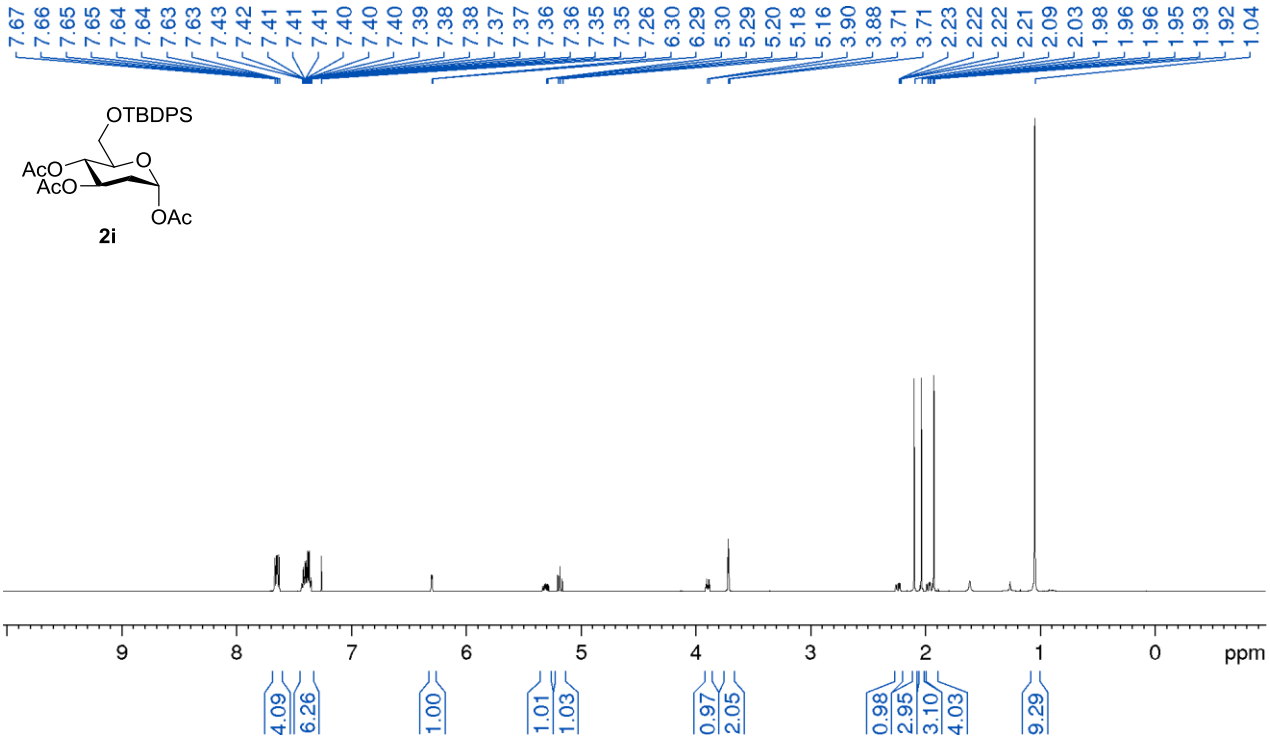
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2h)



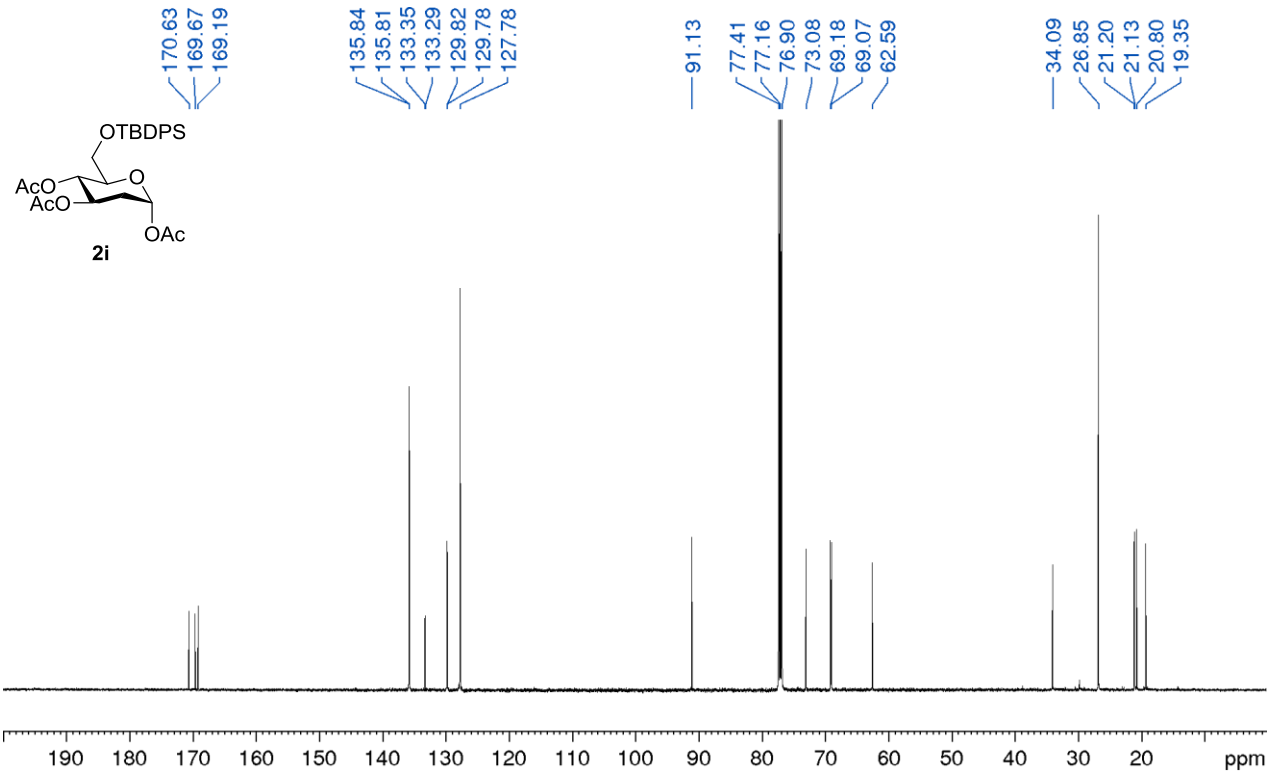
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2h)



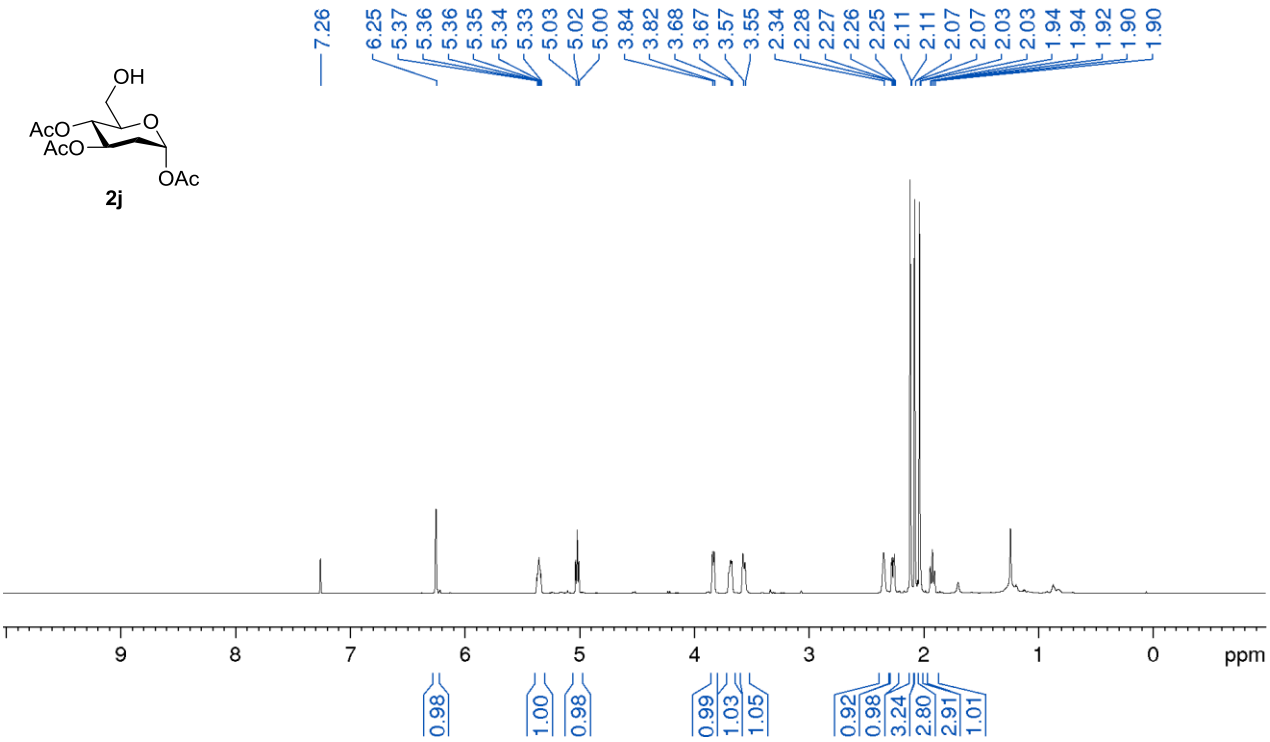
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2i)



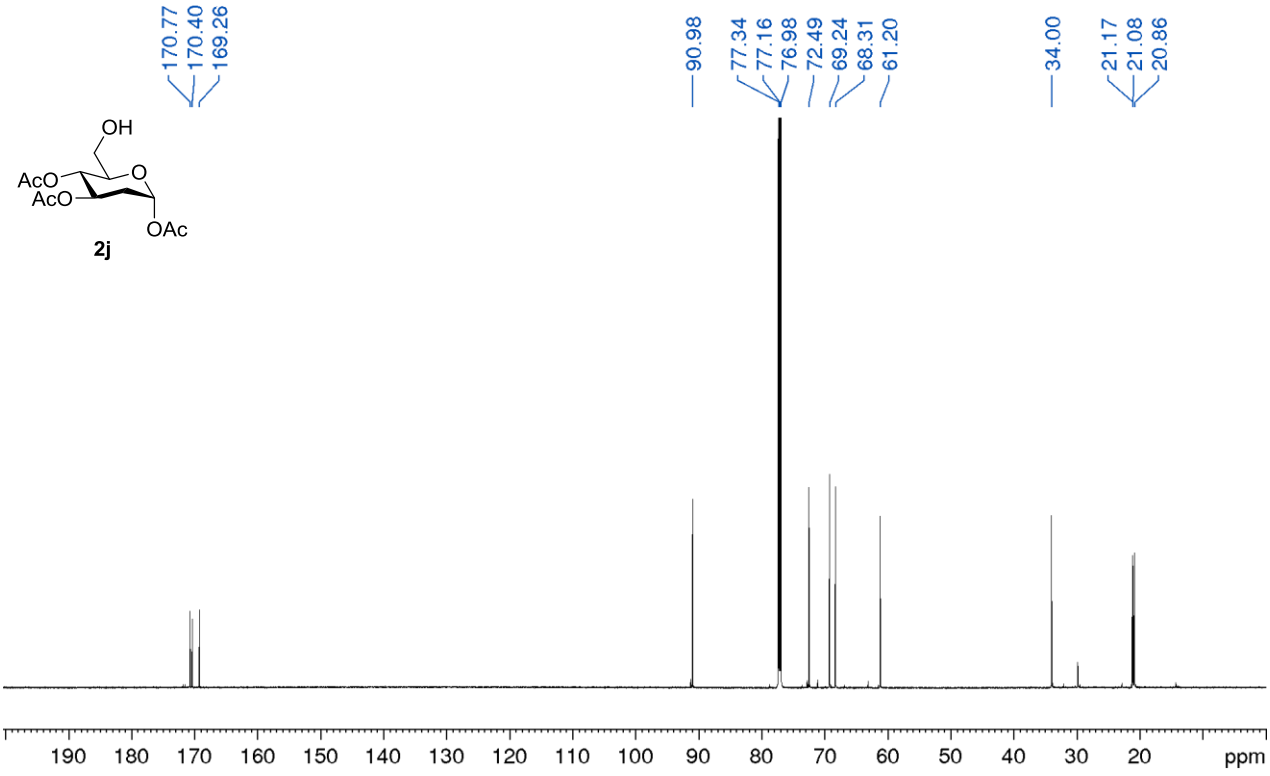
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2i)



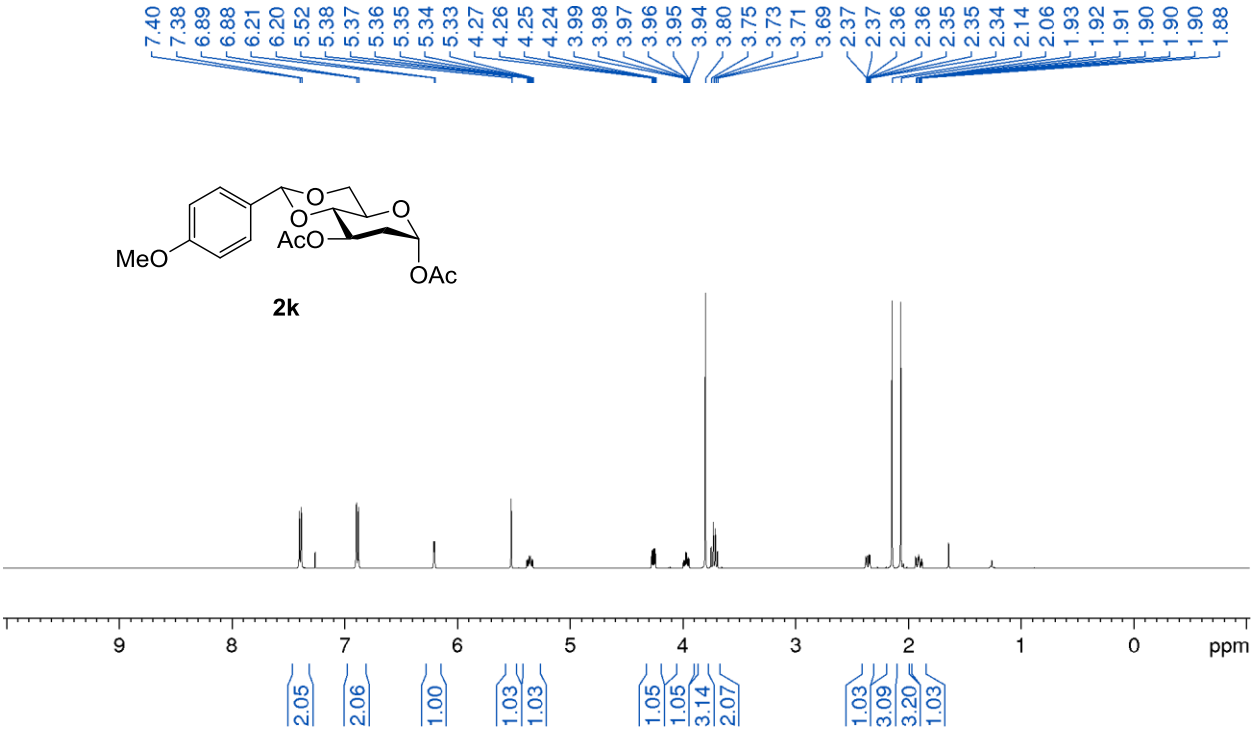
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2j)



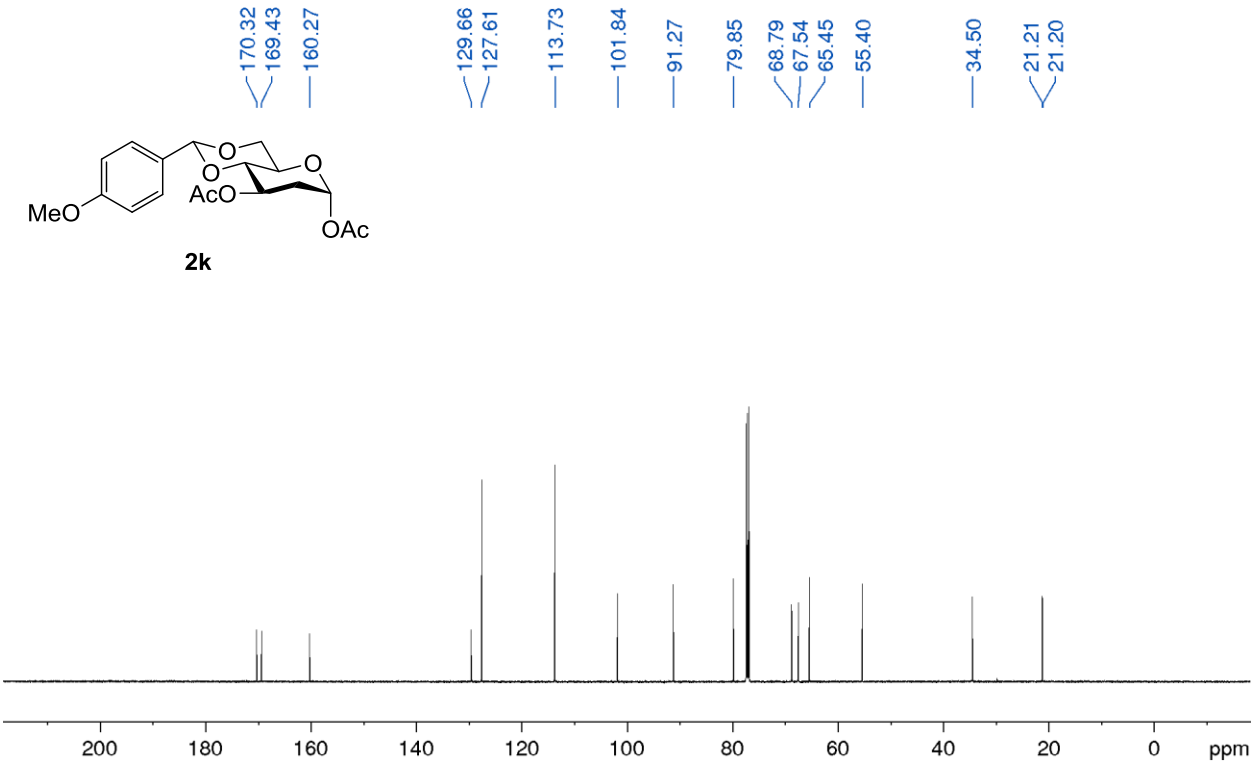
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2j)



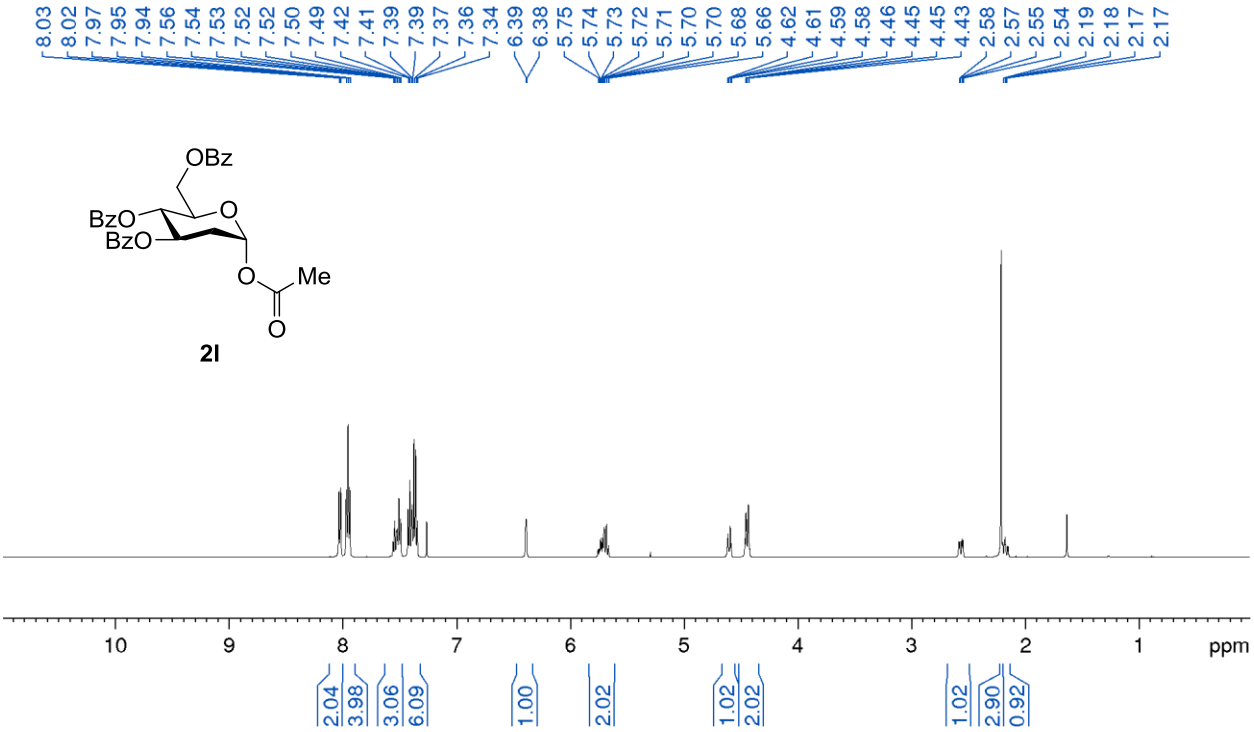
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2k)



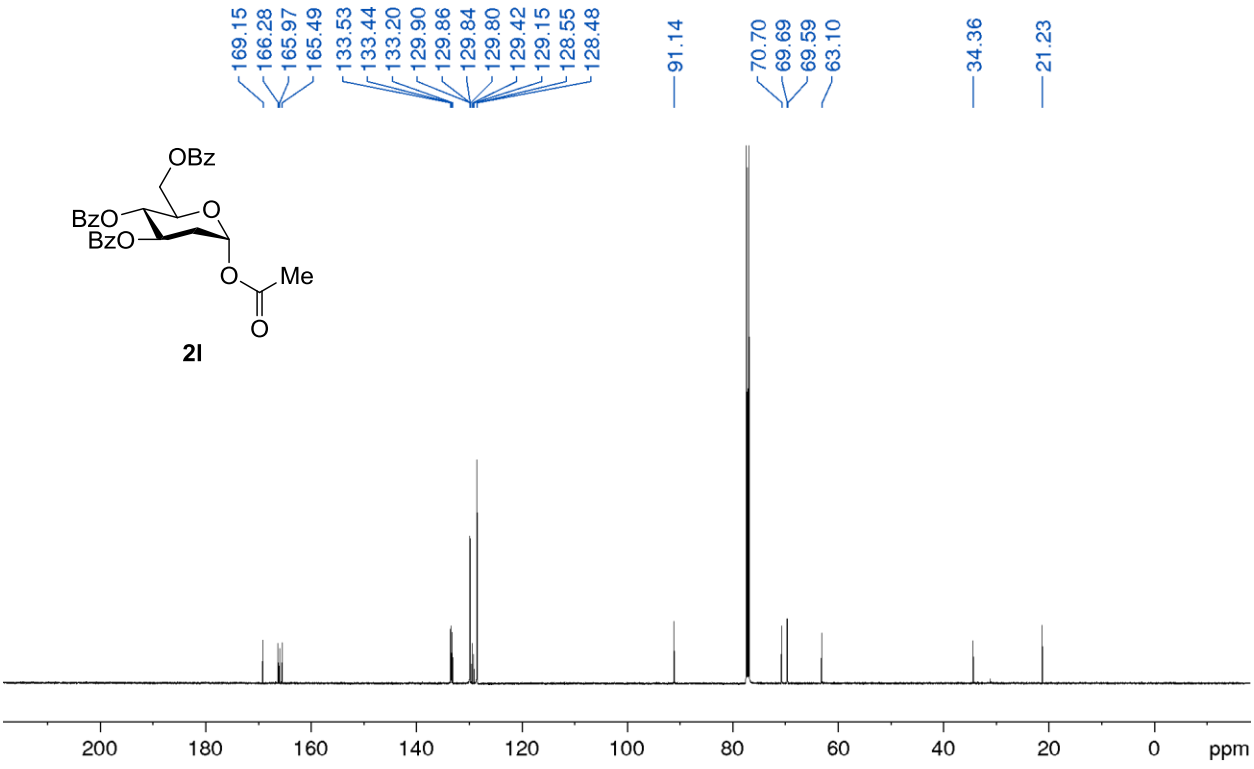
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2k)



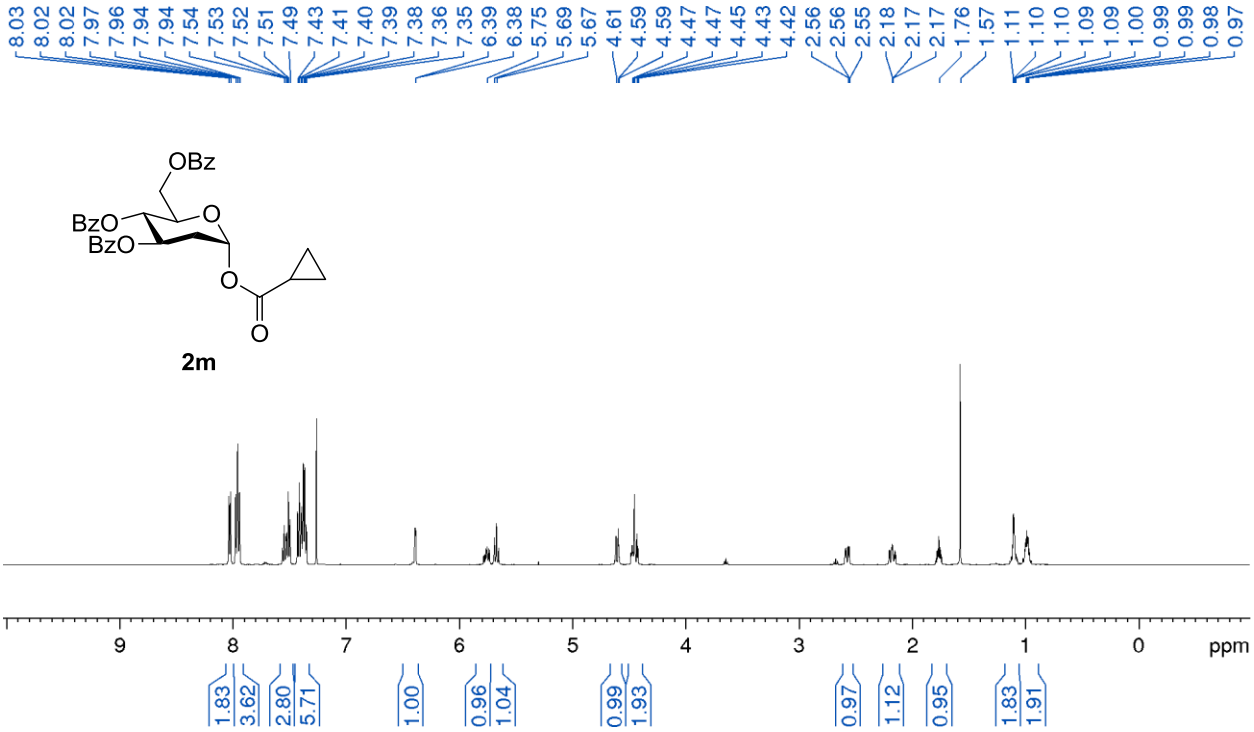
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2l)



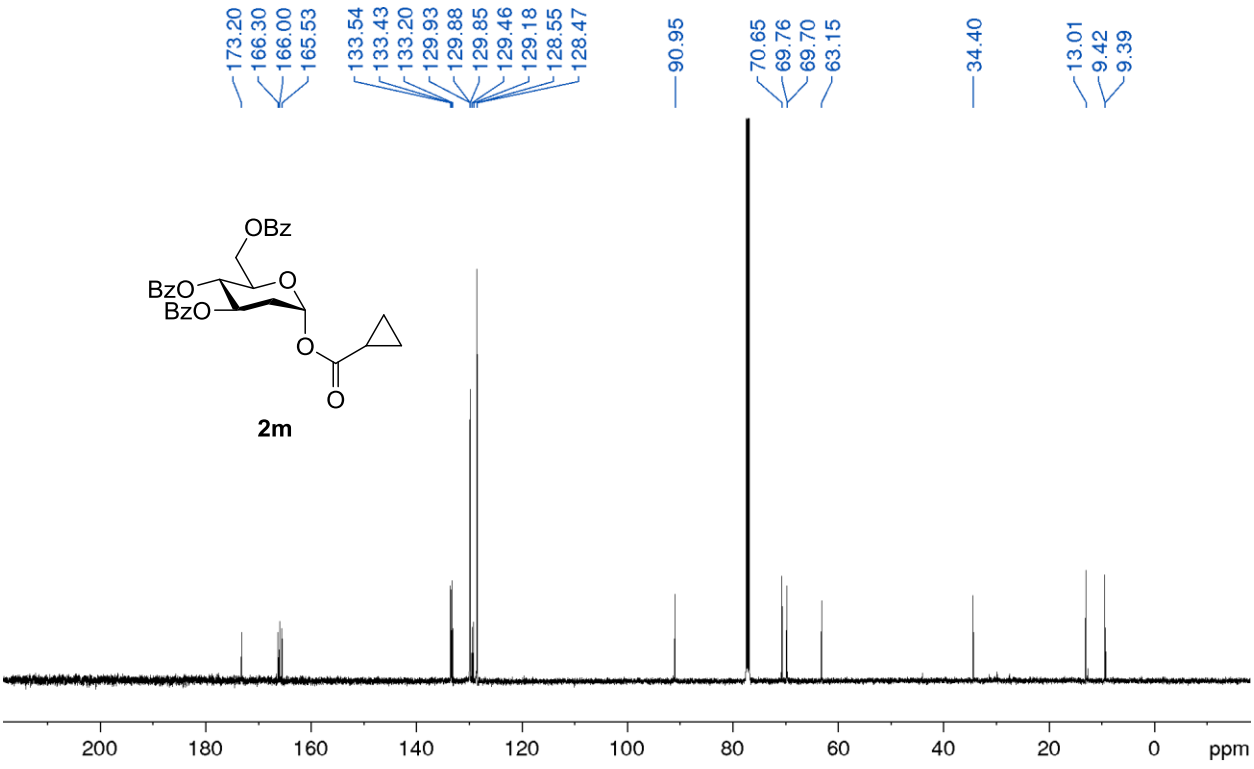
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2l)



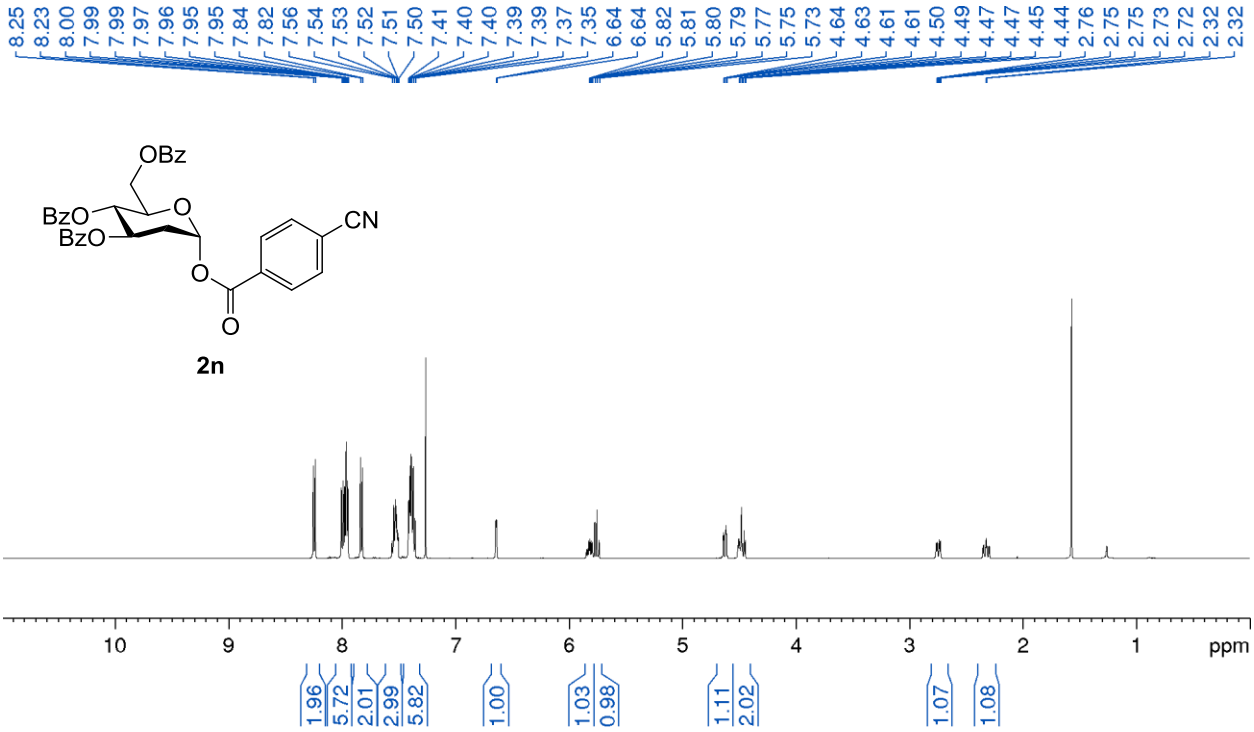
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2m)



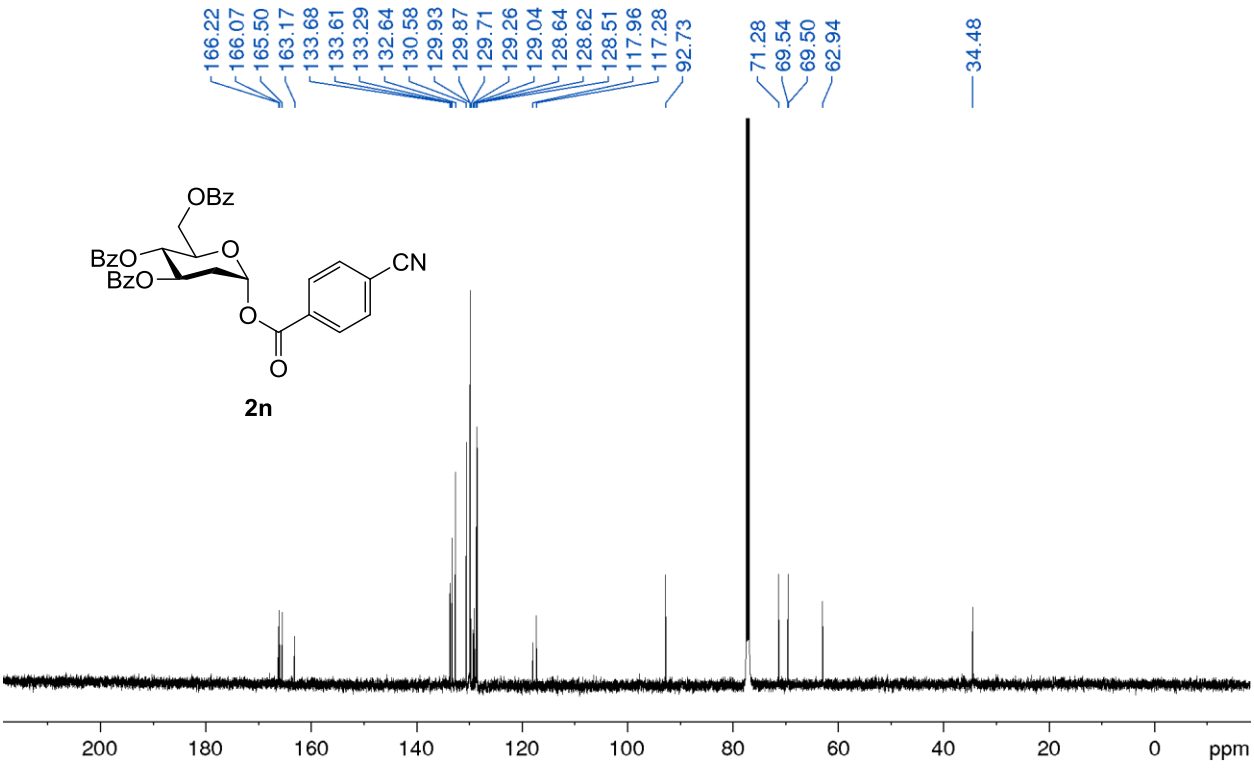
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2m)



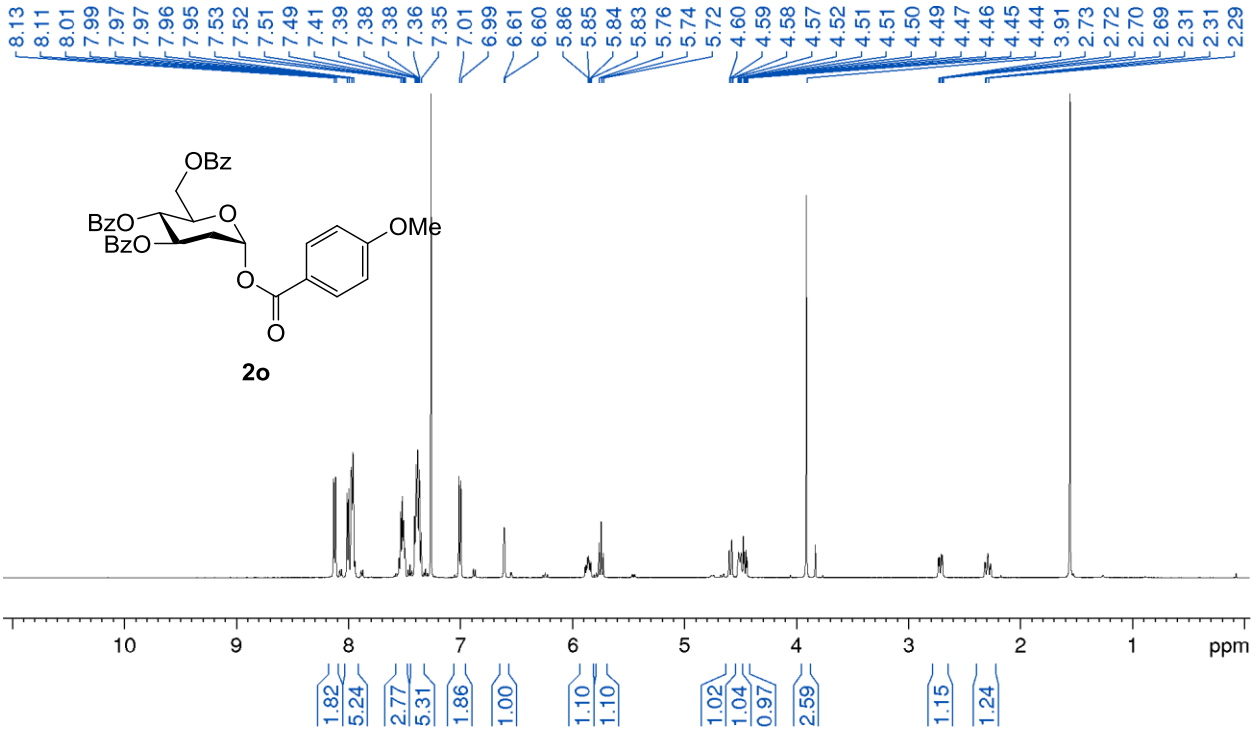
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2n)



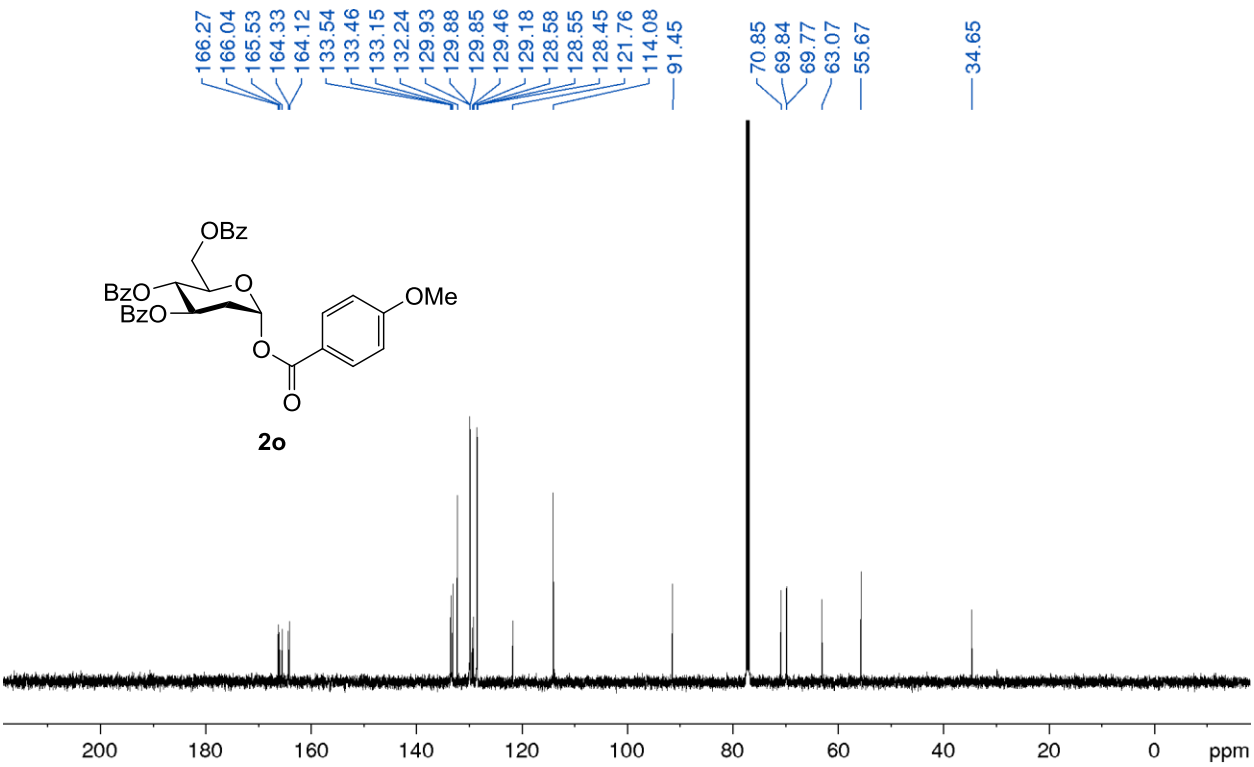
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2n)



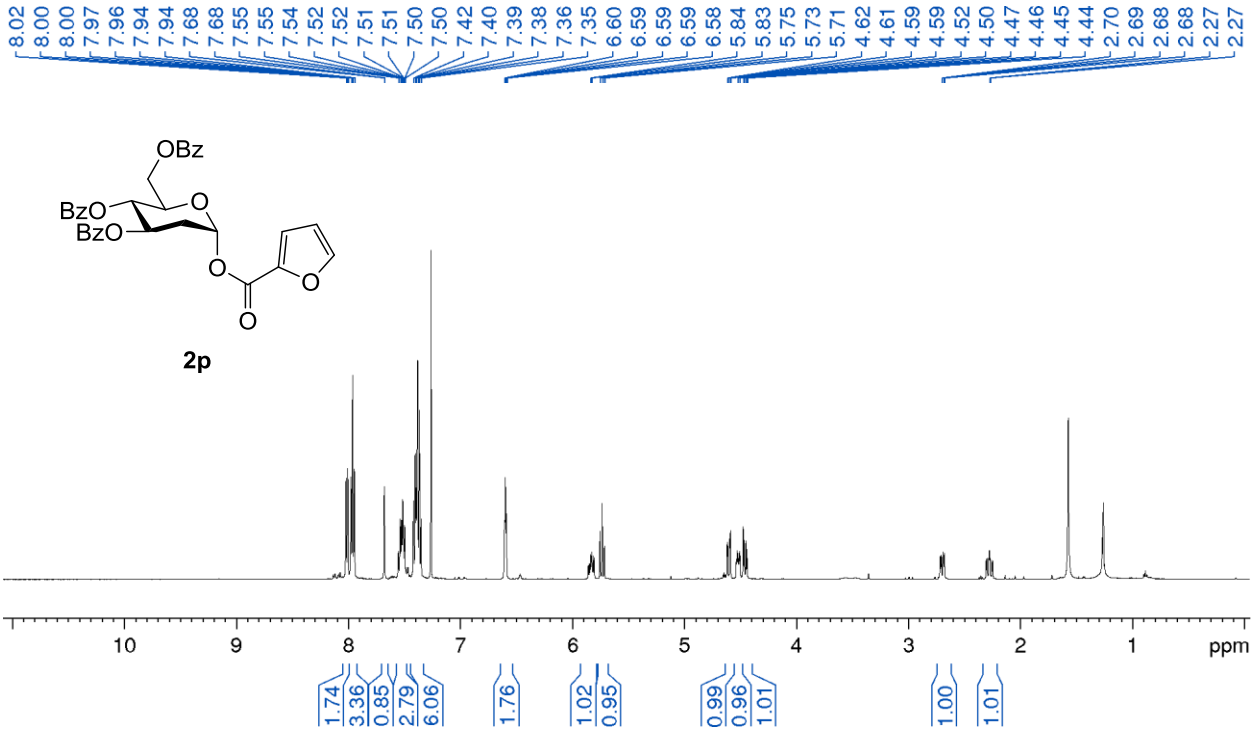
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2o)



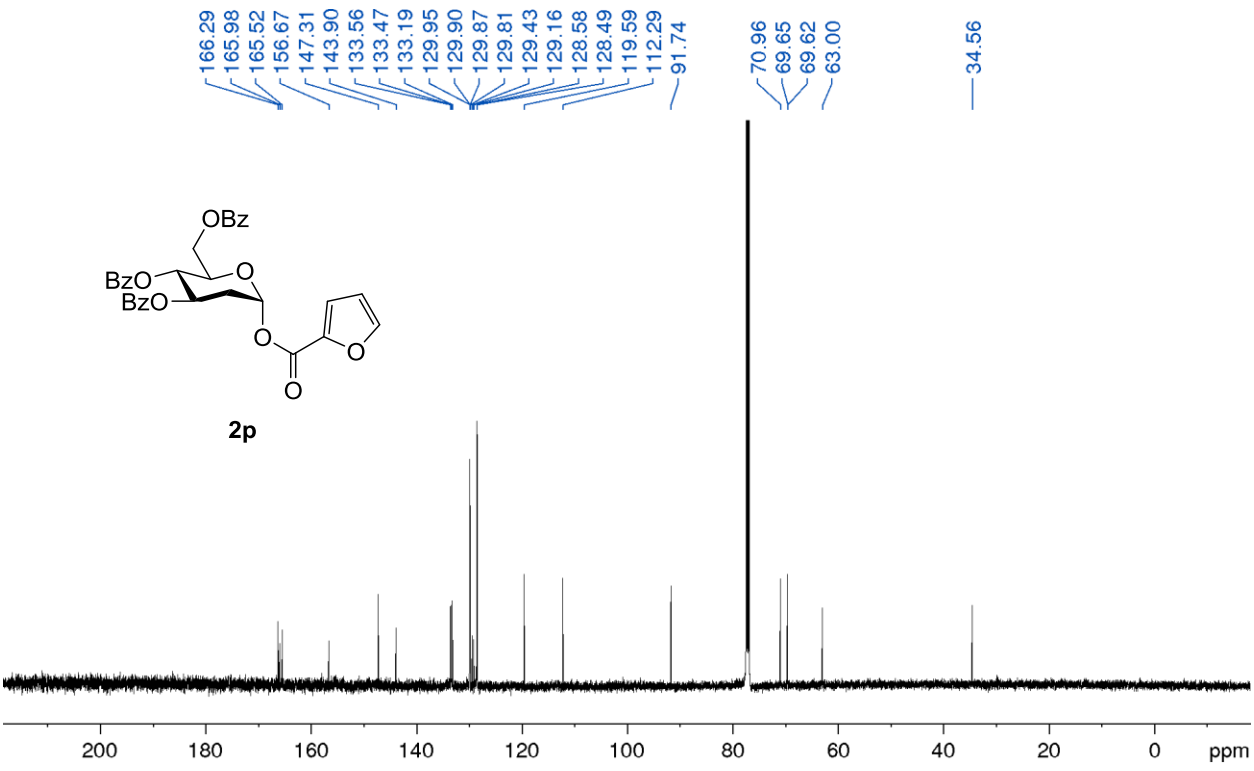
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2o)



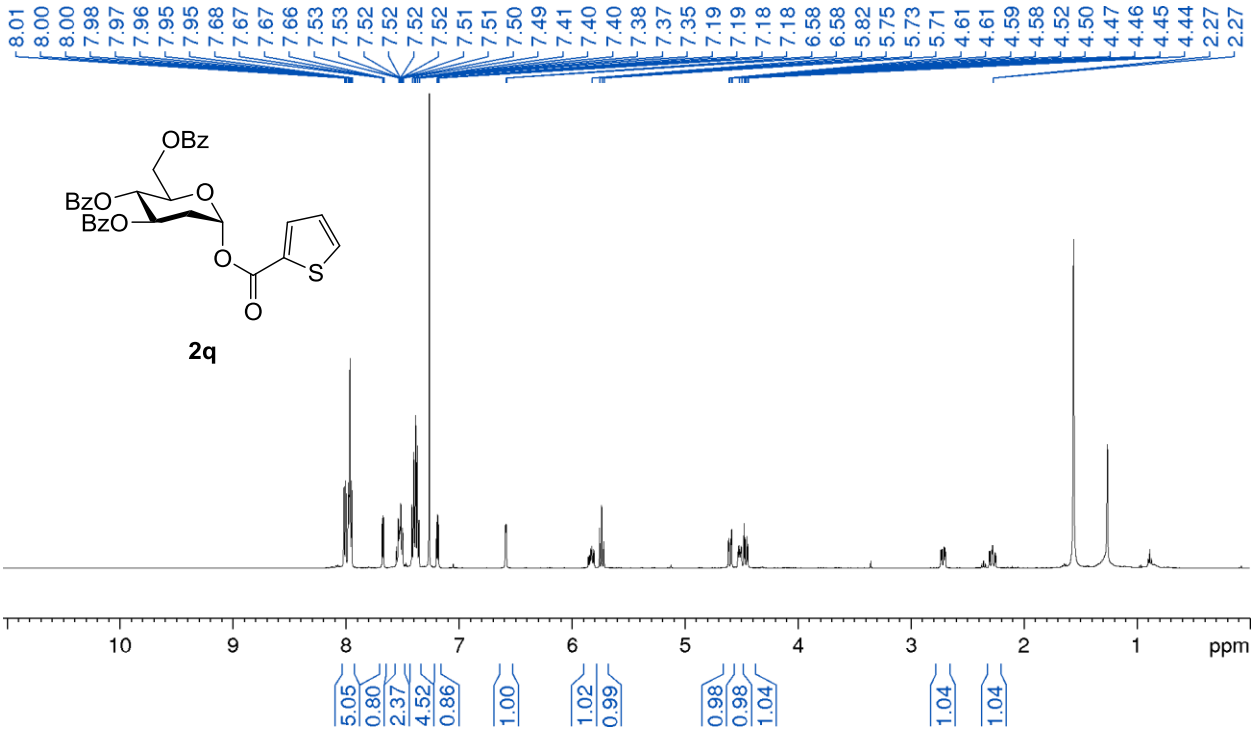
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2p)



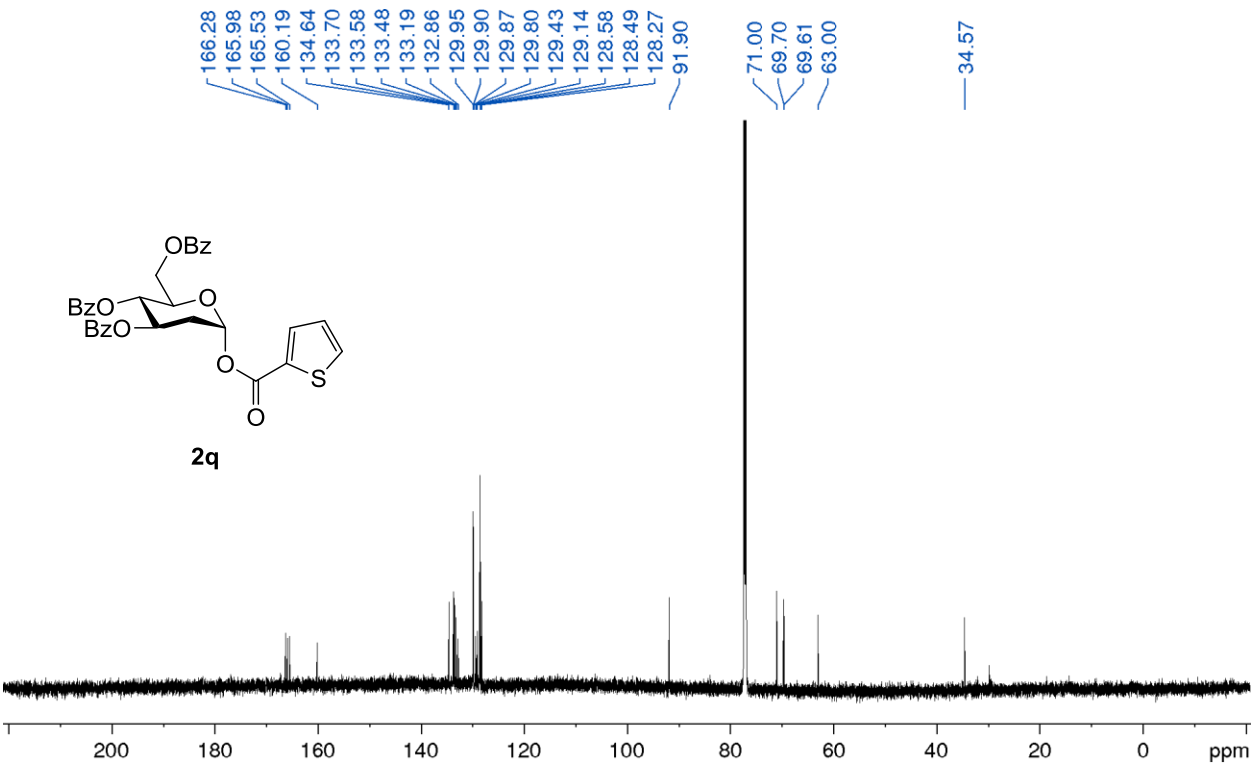
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2p)



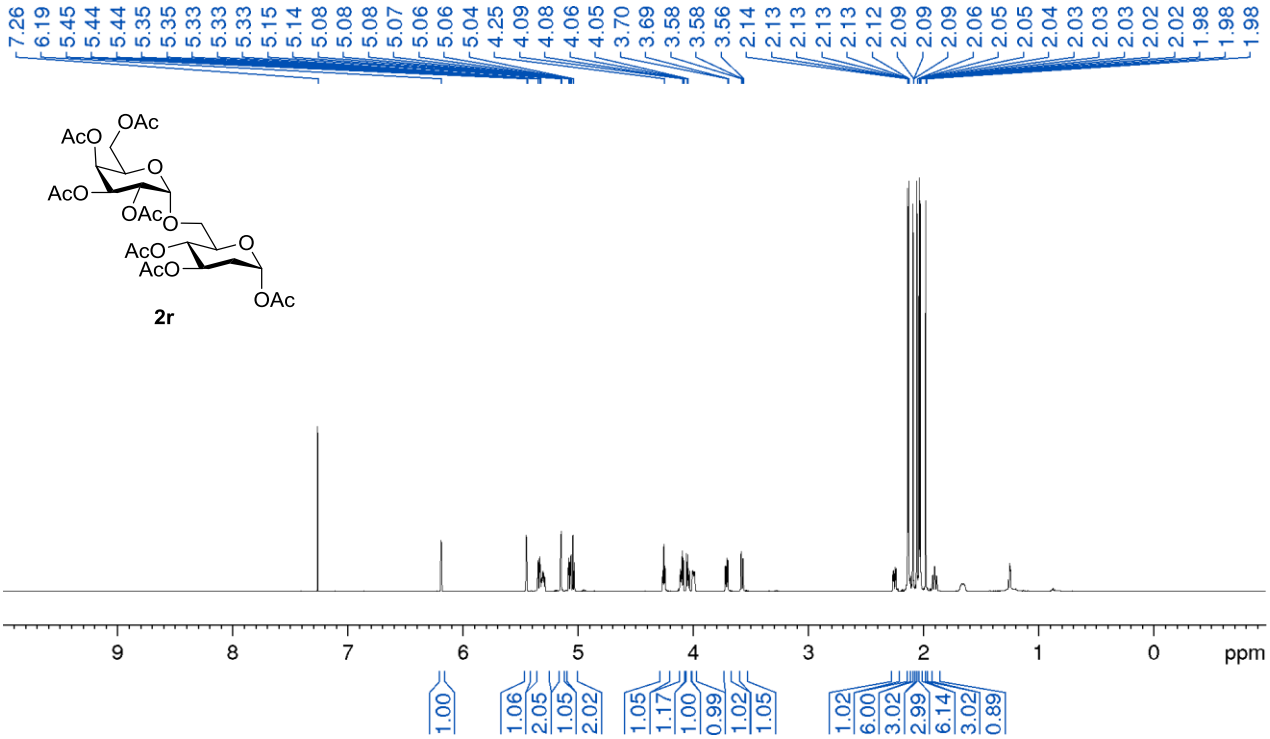
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2q)



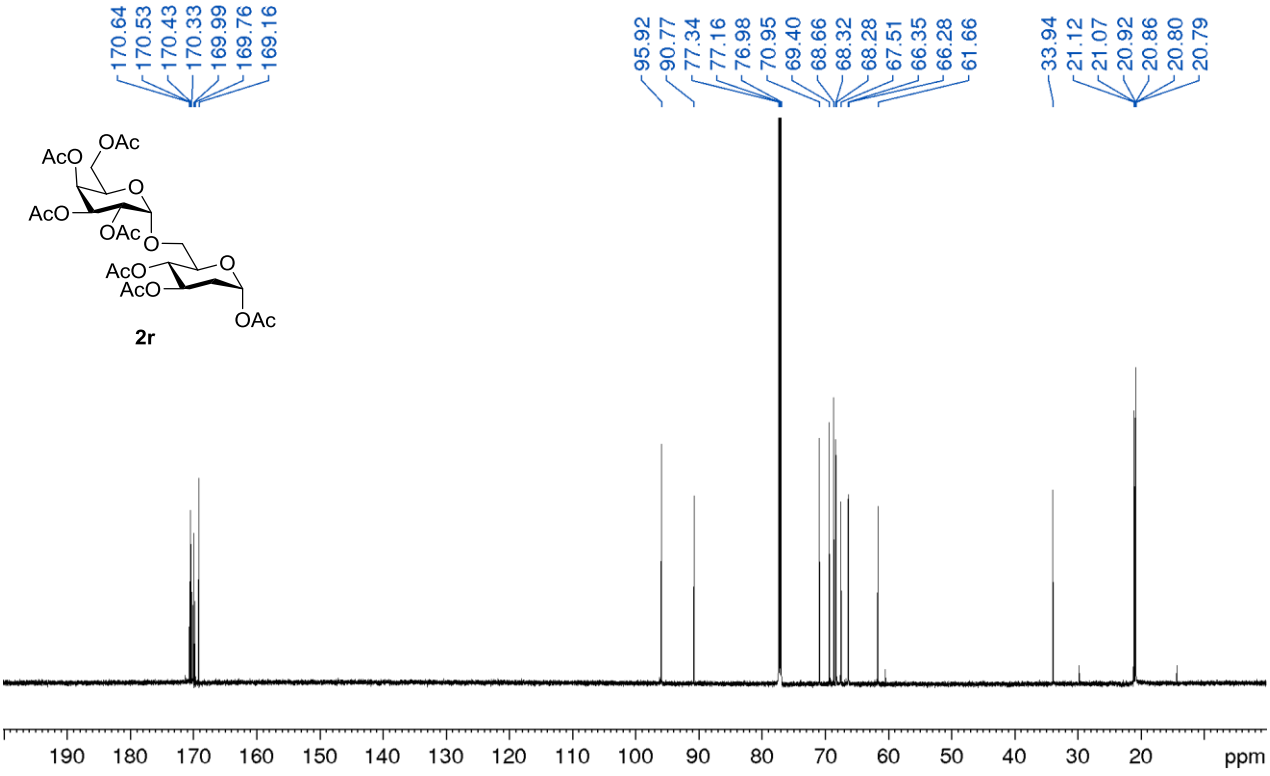
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2q)



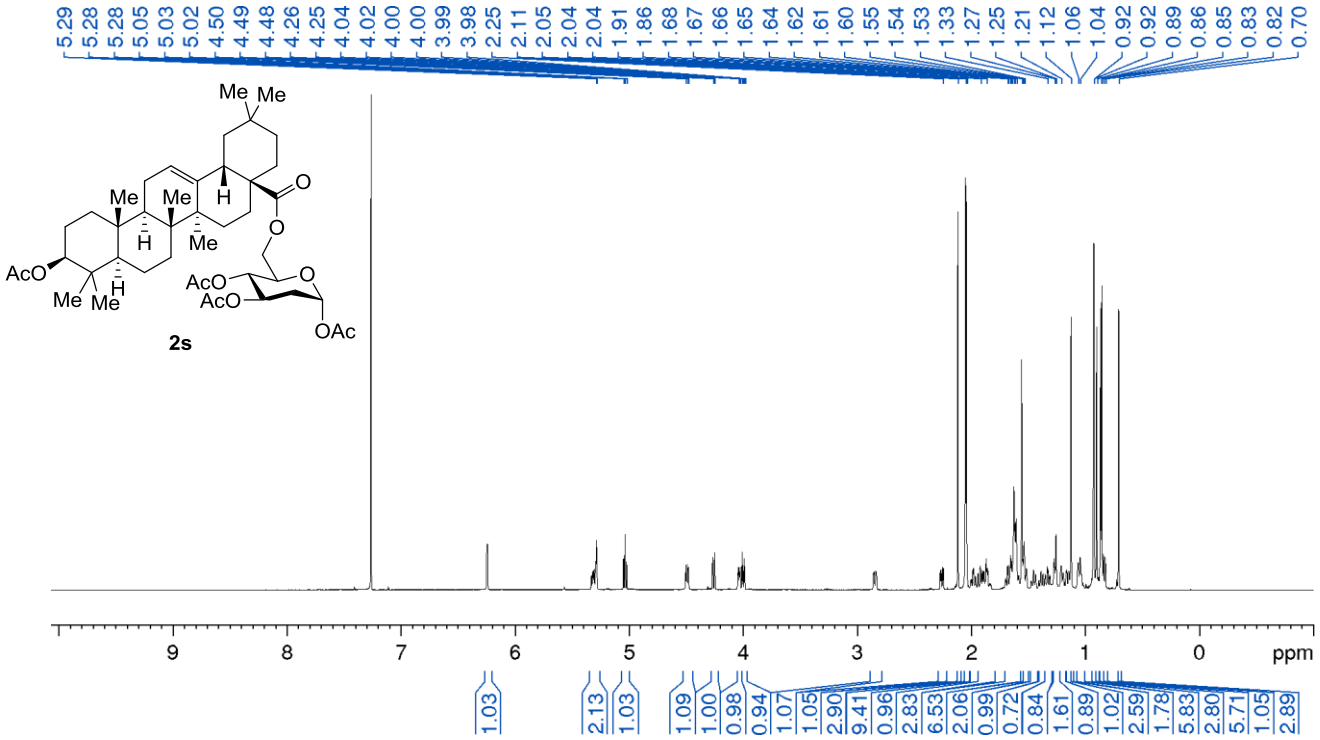
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2r)



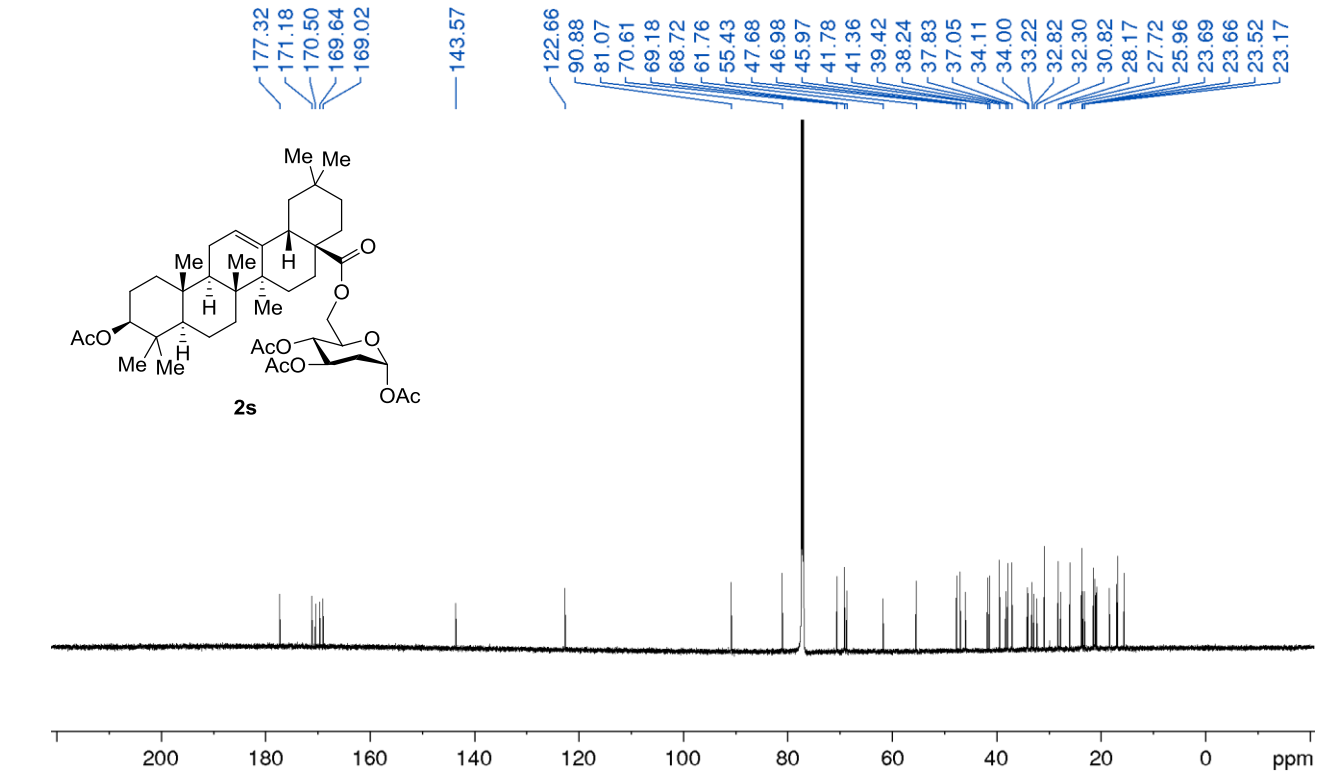
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2r)



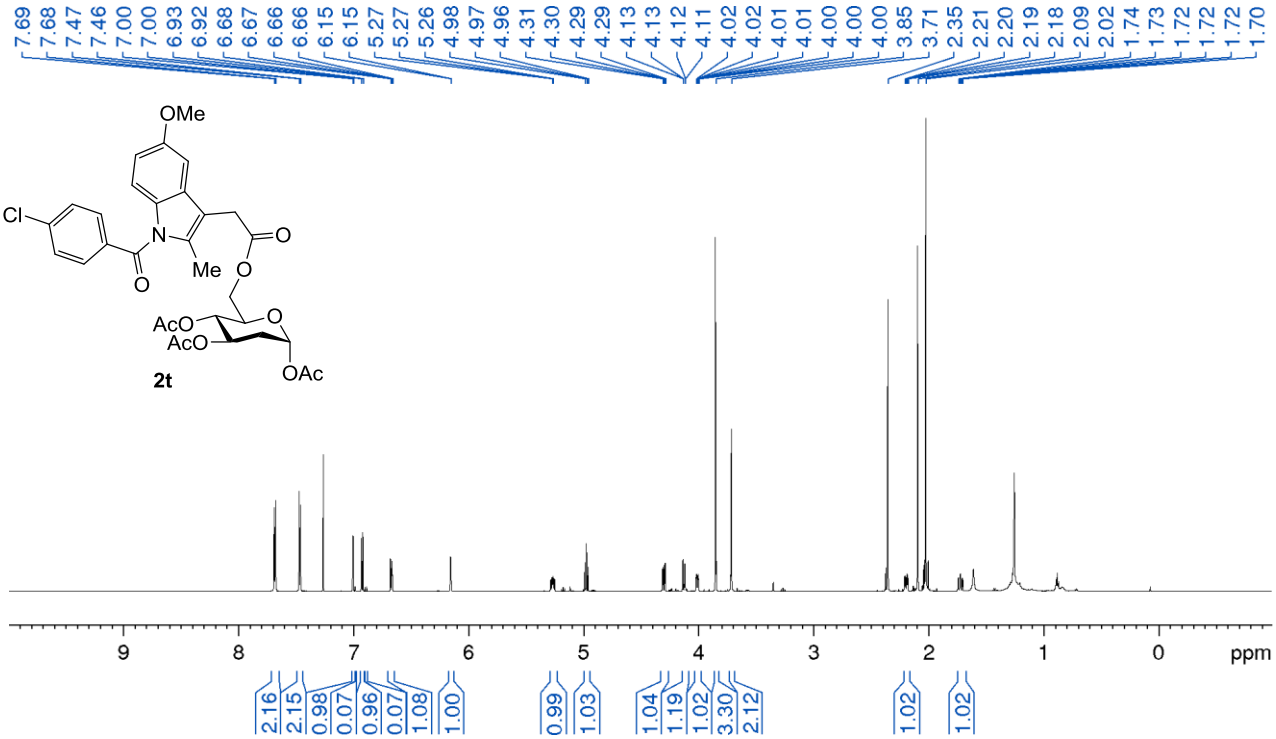
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2s)



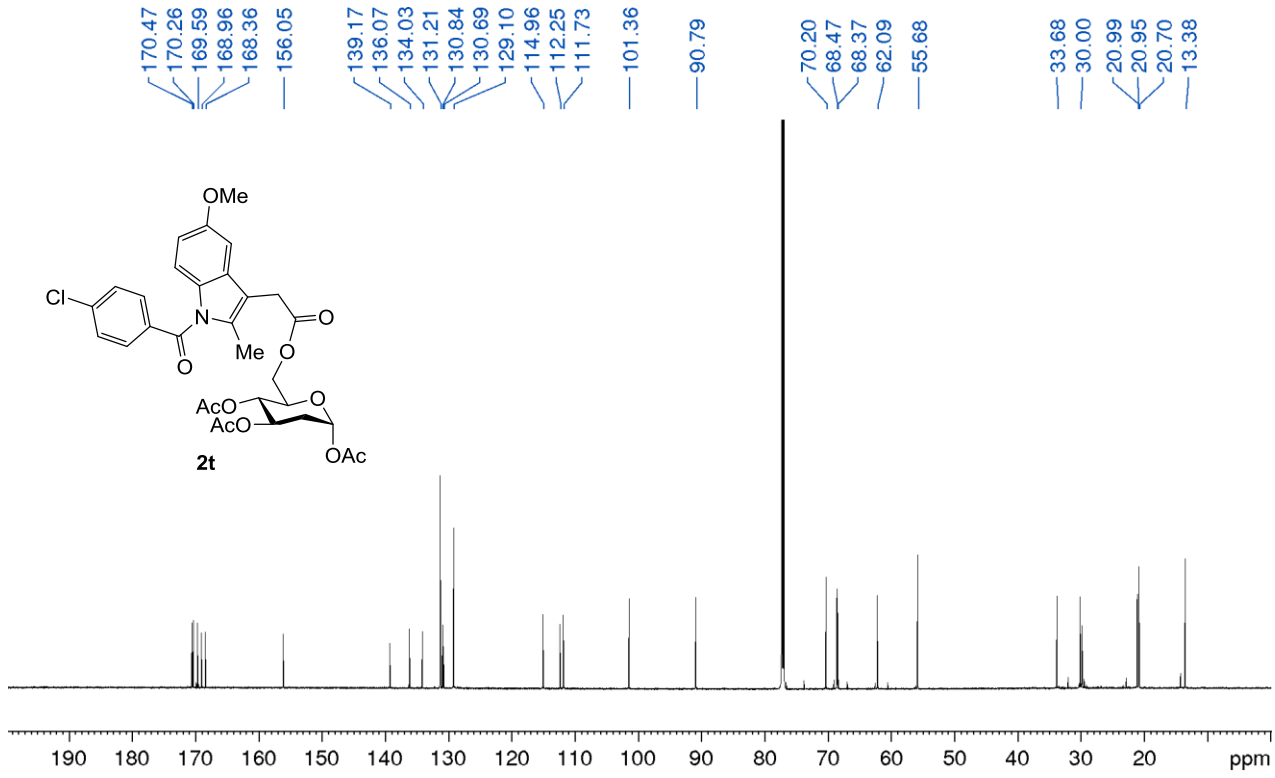
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2s)



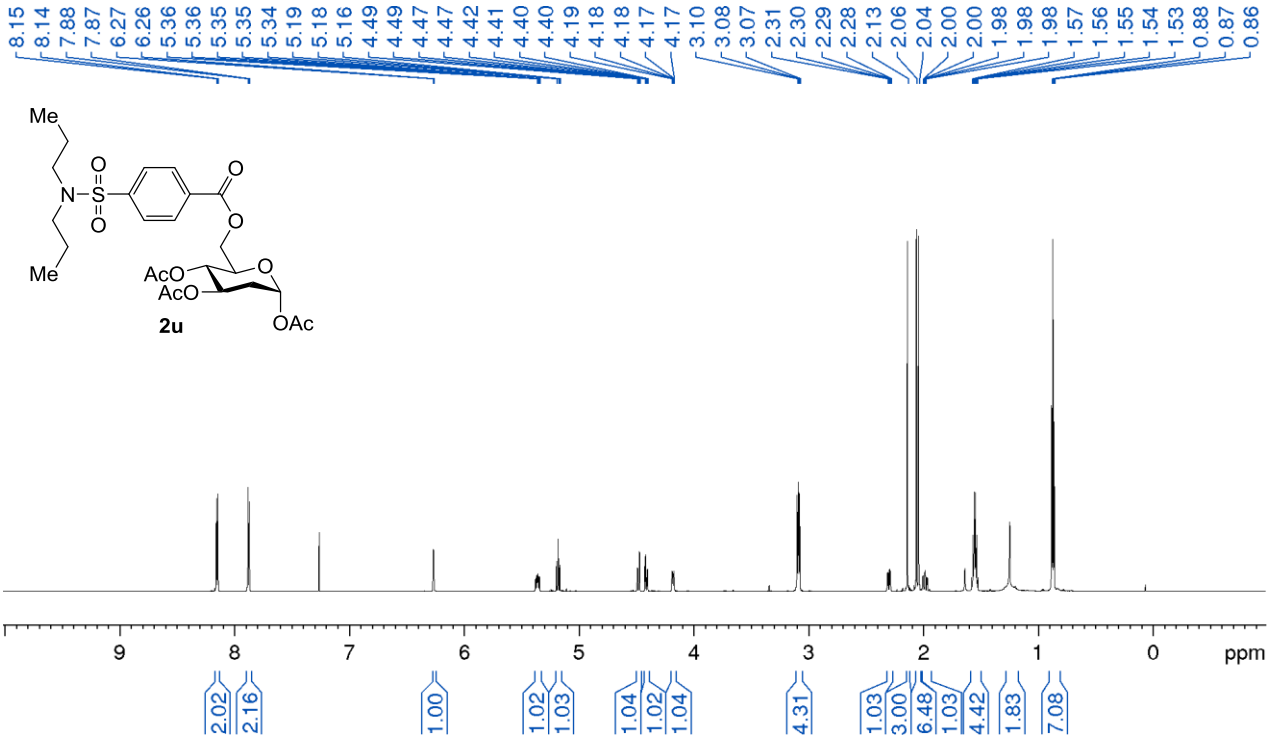
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2t)



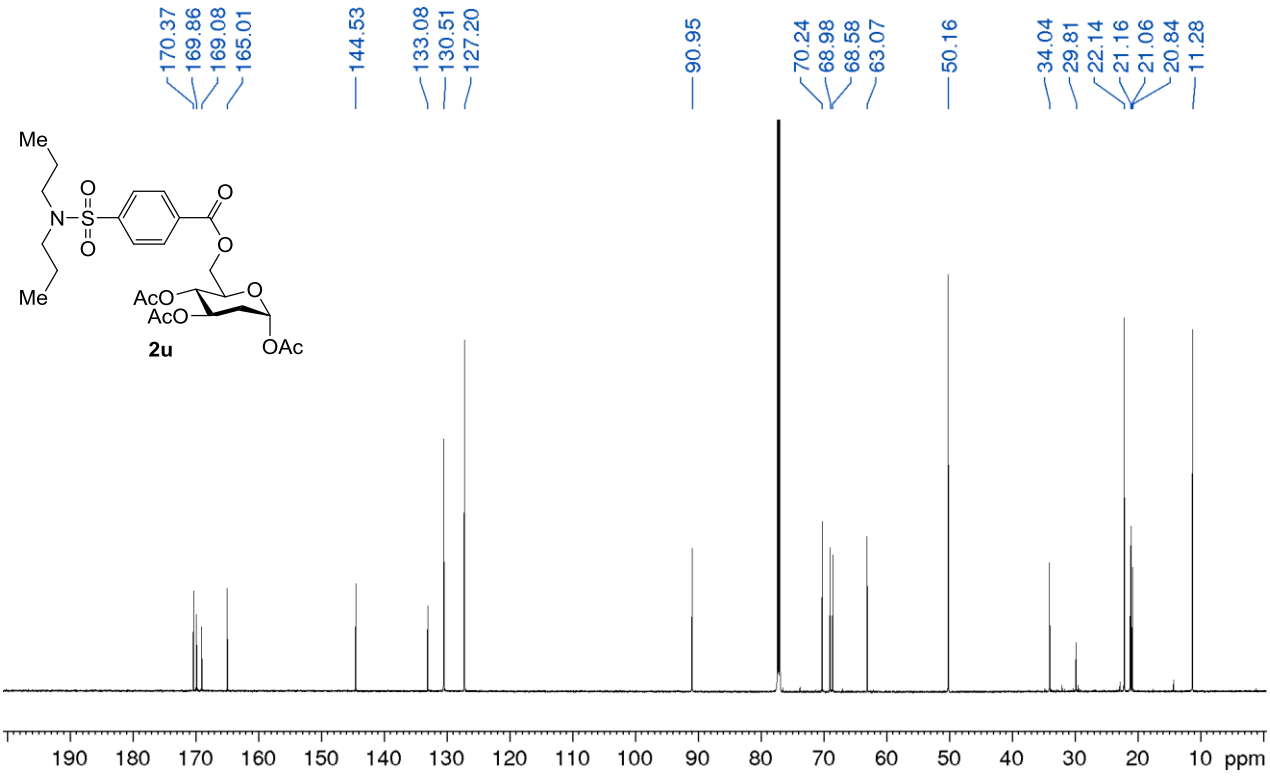
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2t)



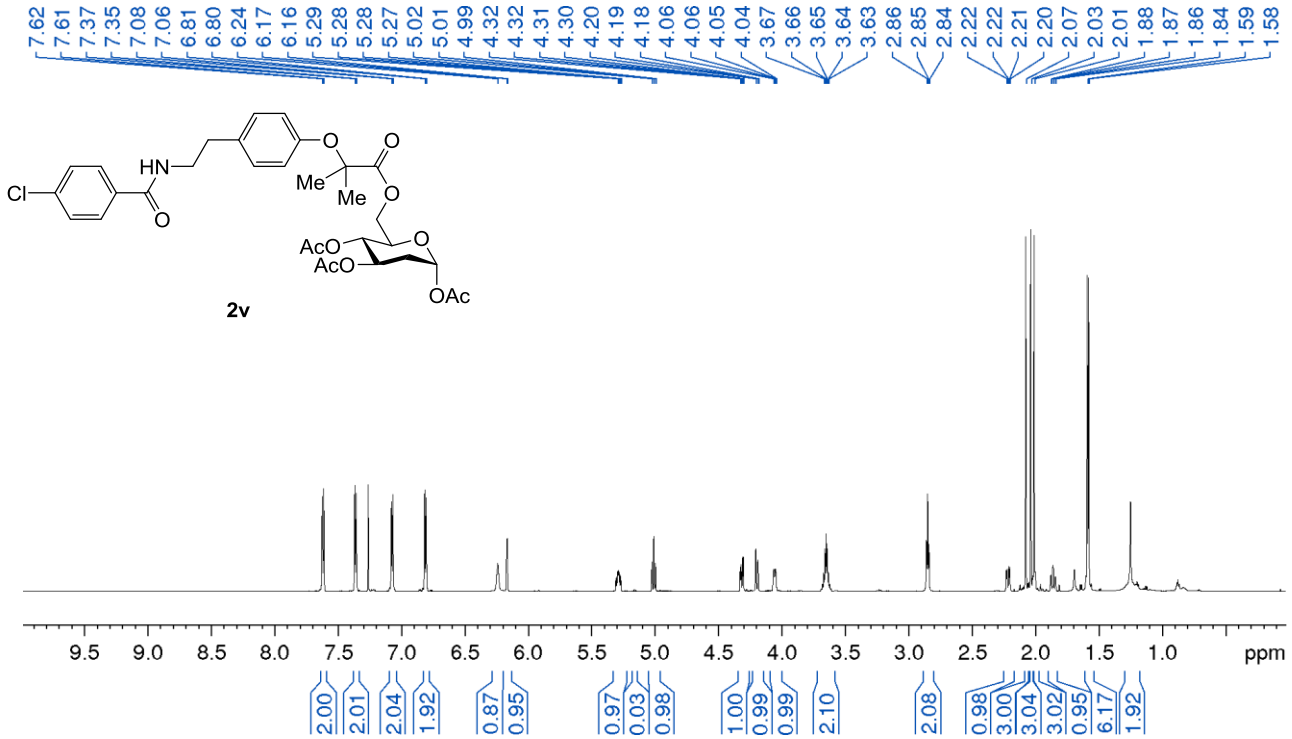
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2u)



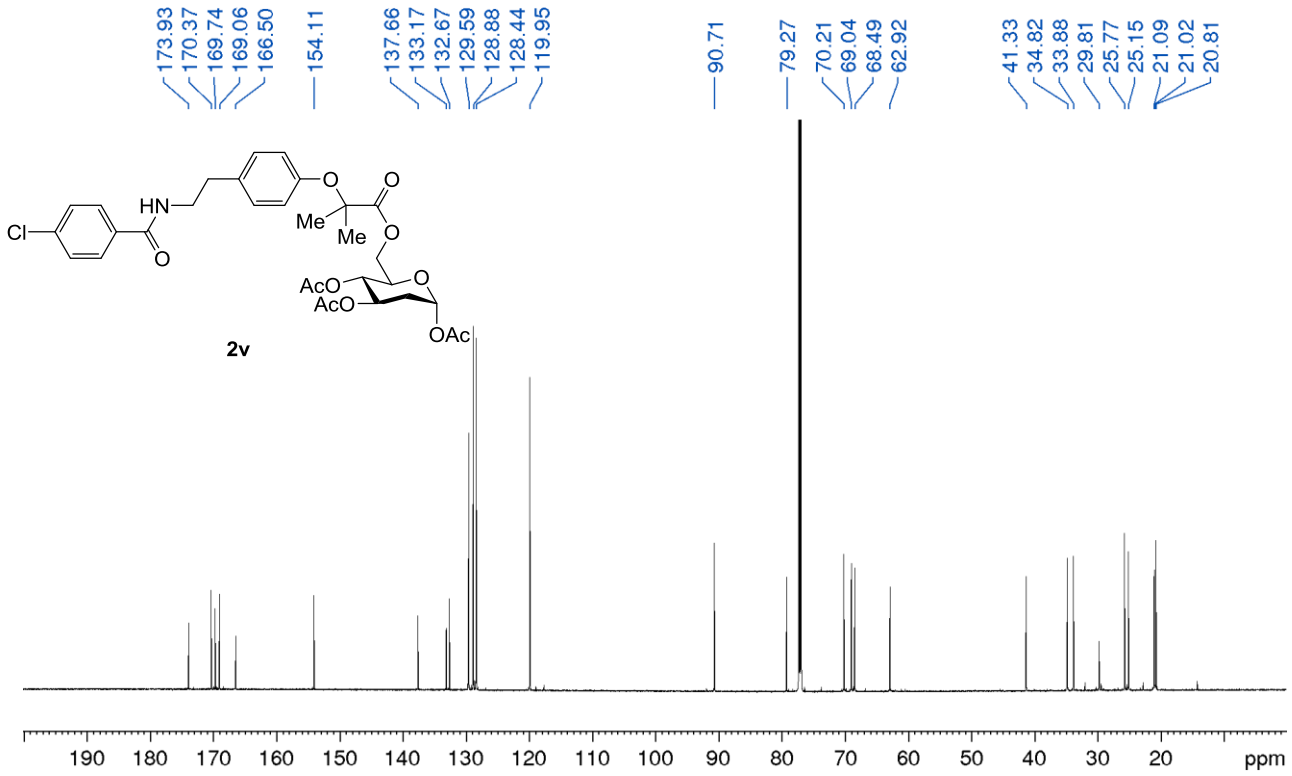
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2u)



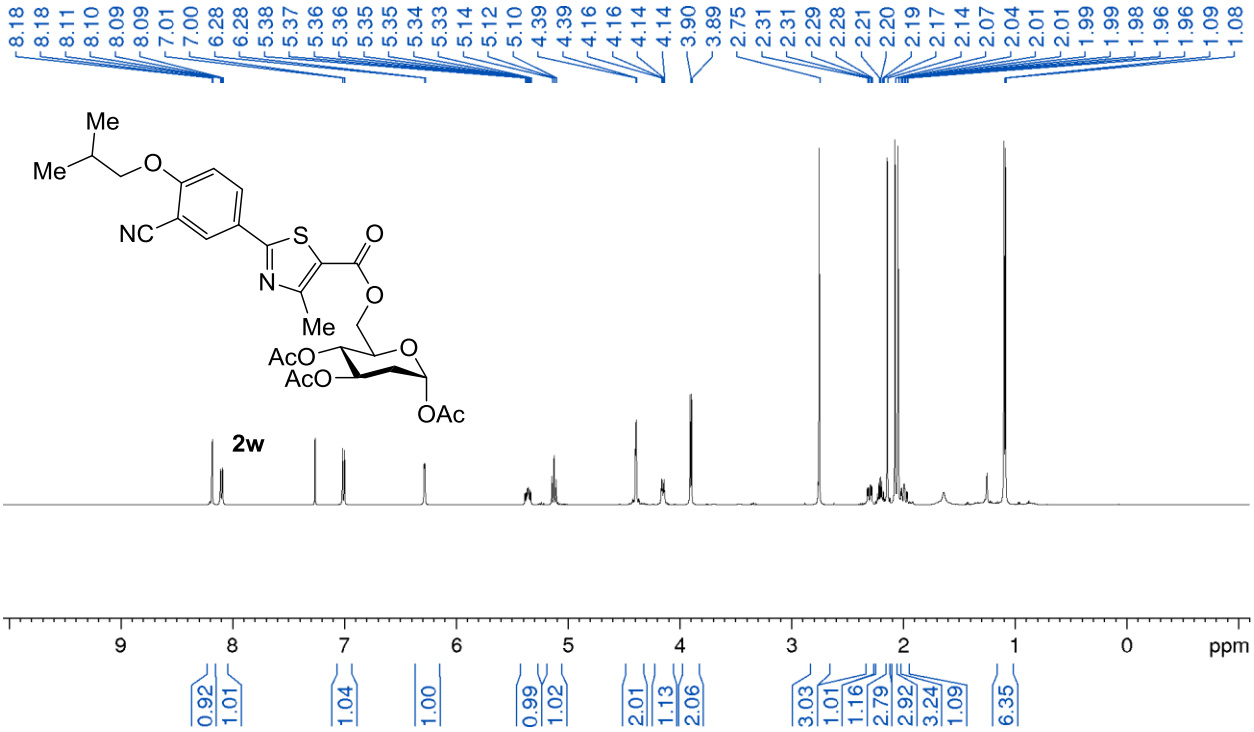
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2v)



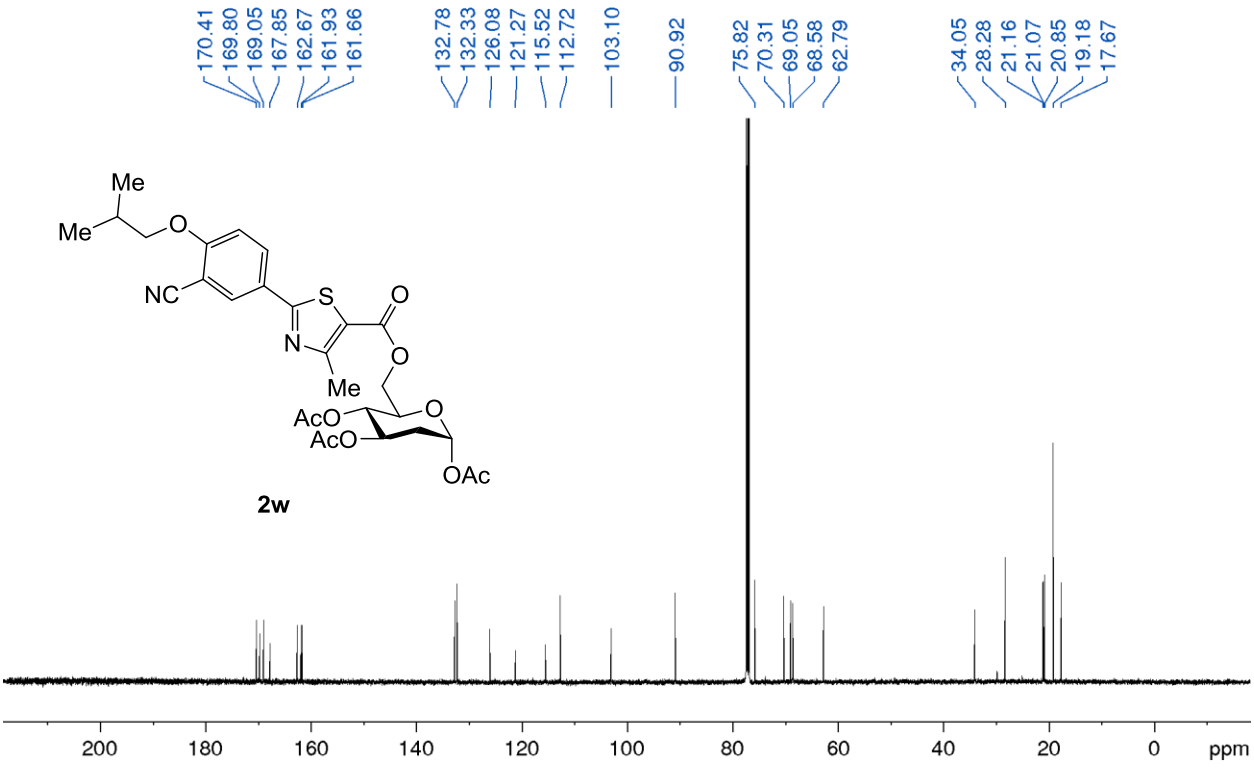
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2v)



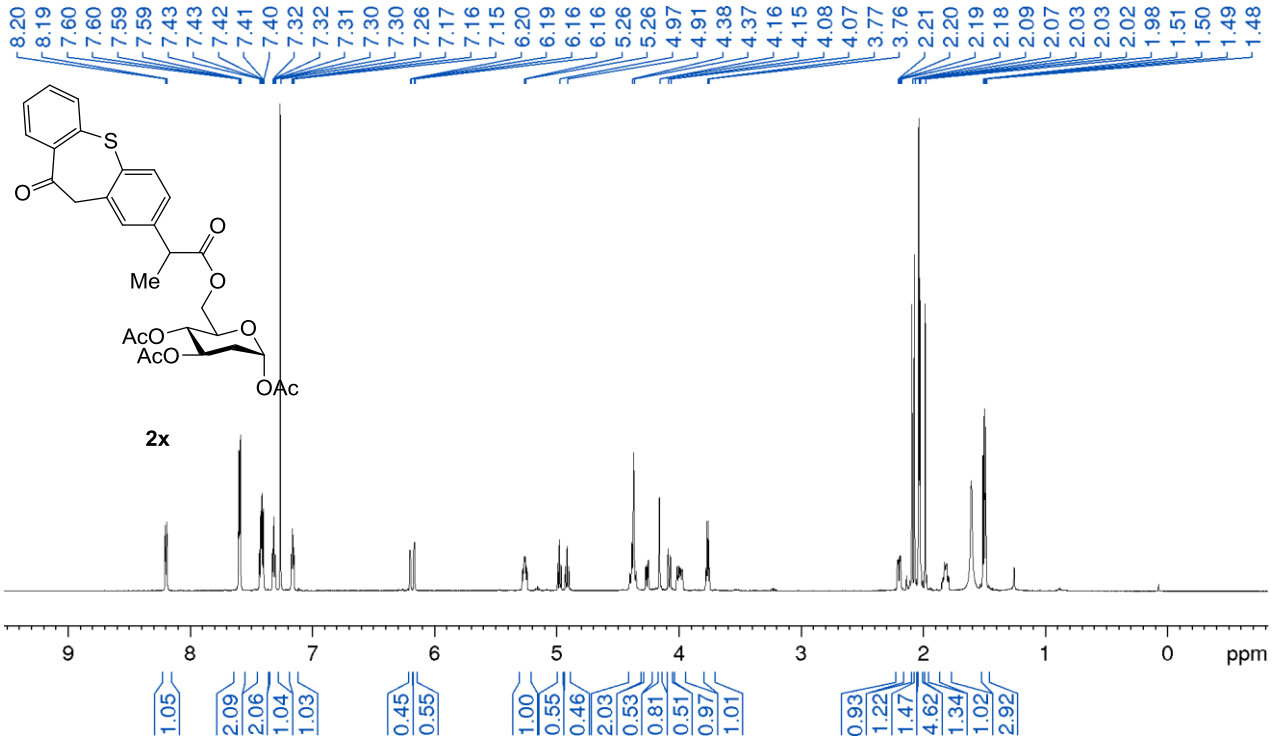
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2w)



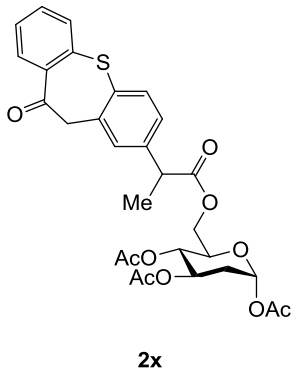
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2w)

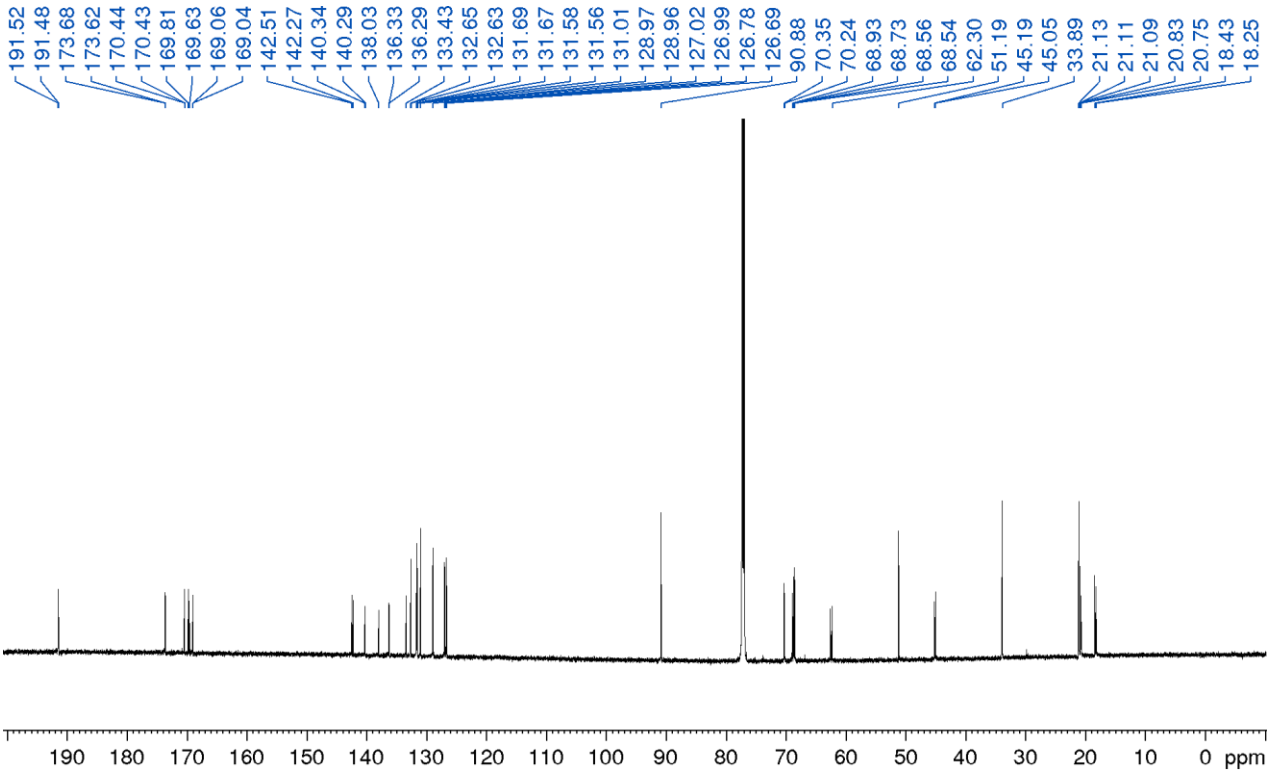


^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2x)

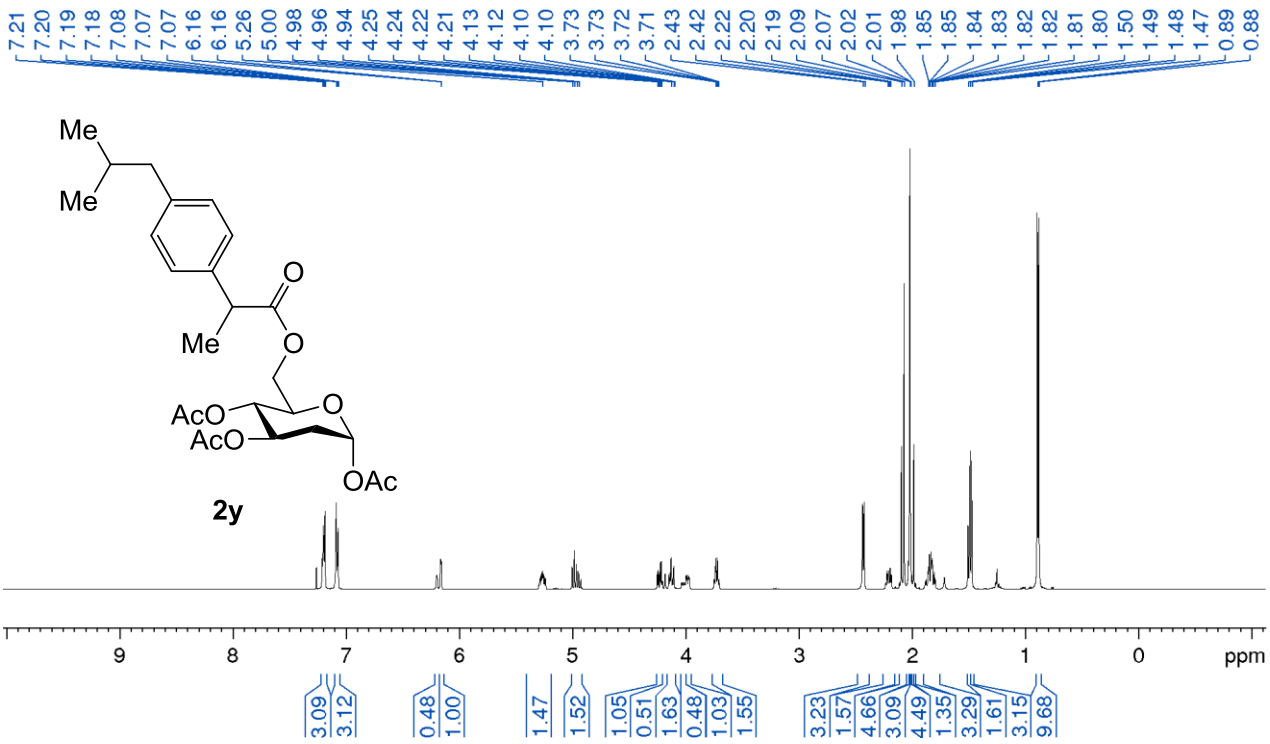


^{13}CNMR (175 MHz, $CDCl_3$, 25 °C) of (2x)

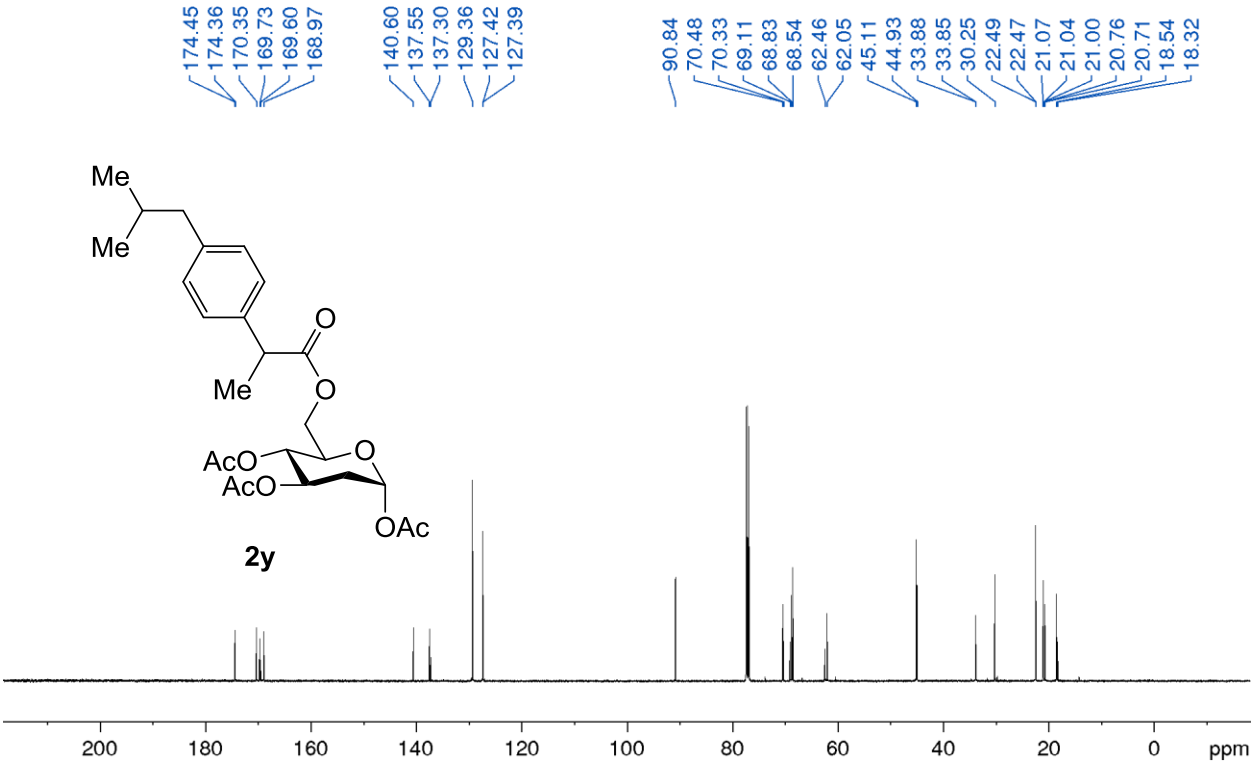




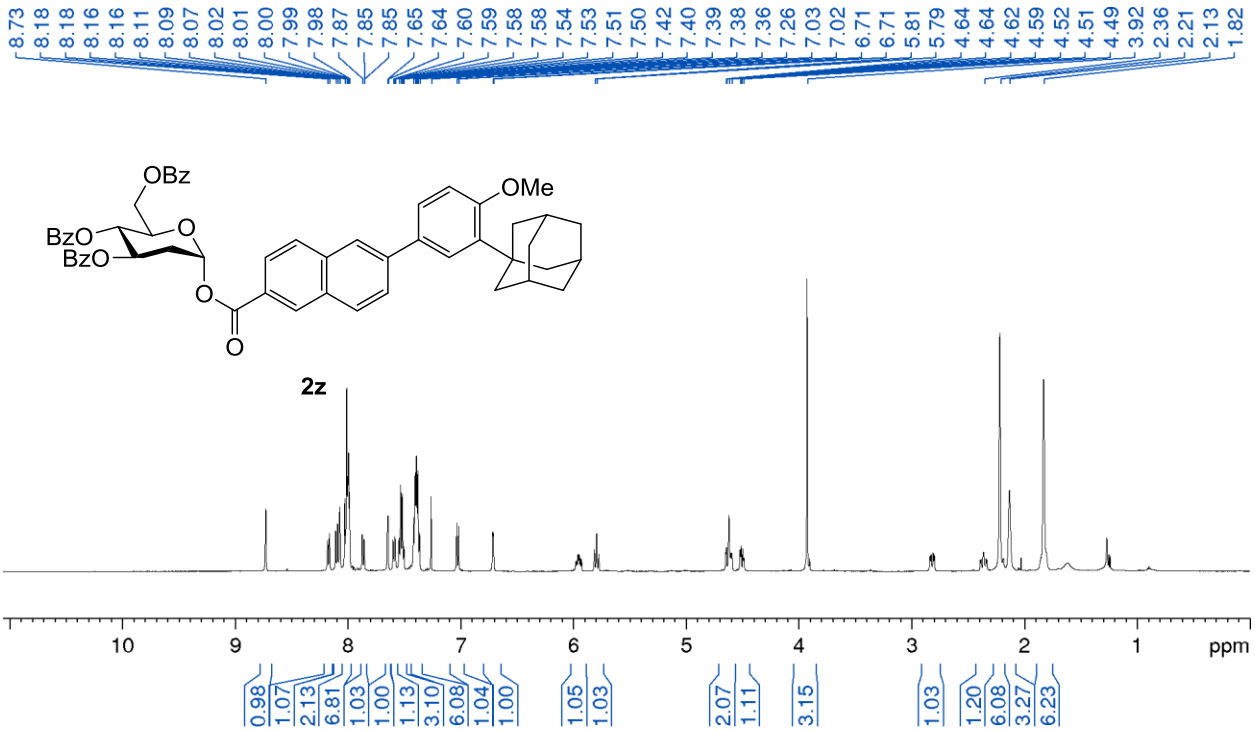
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2y)



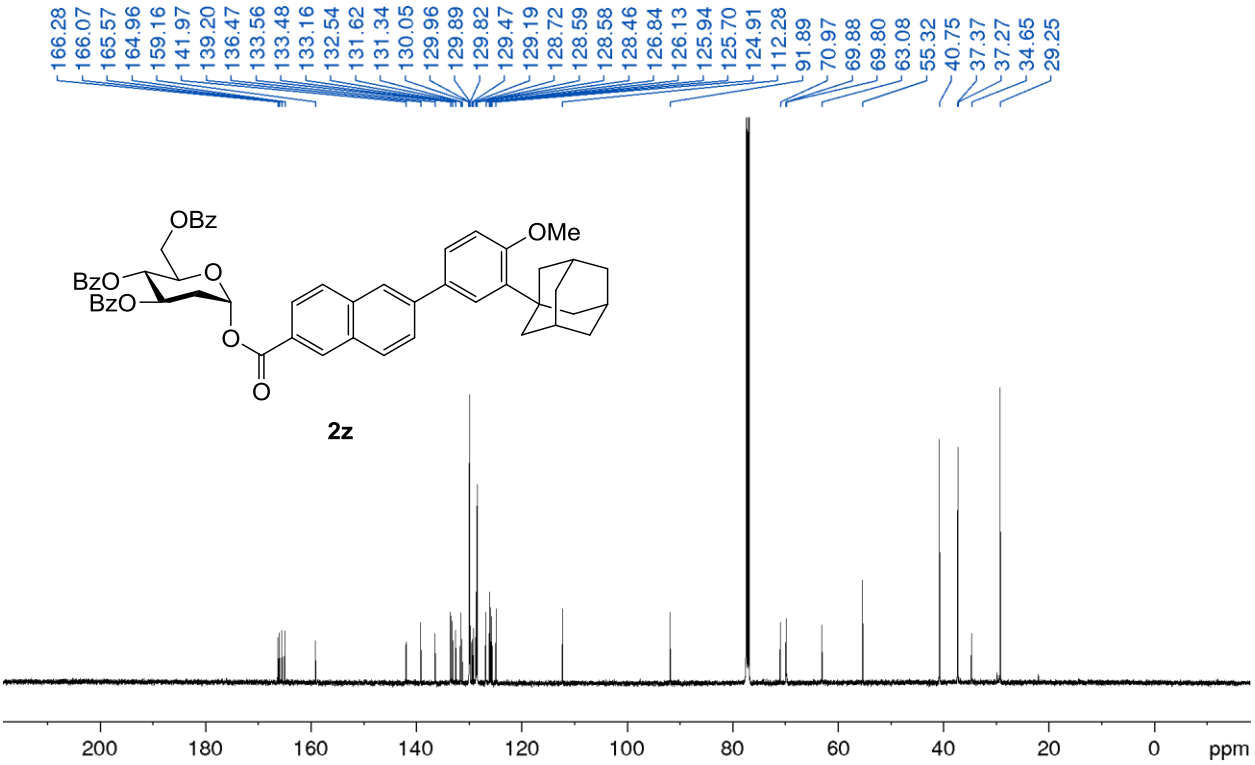
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2y)



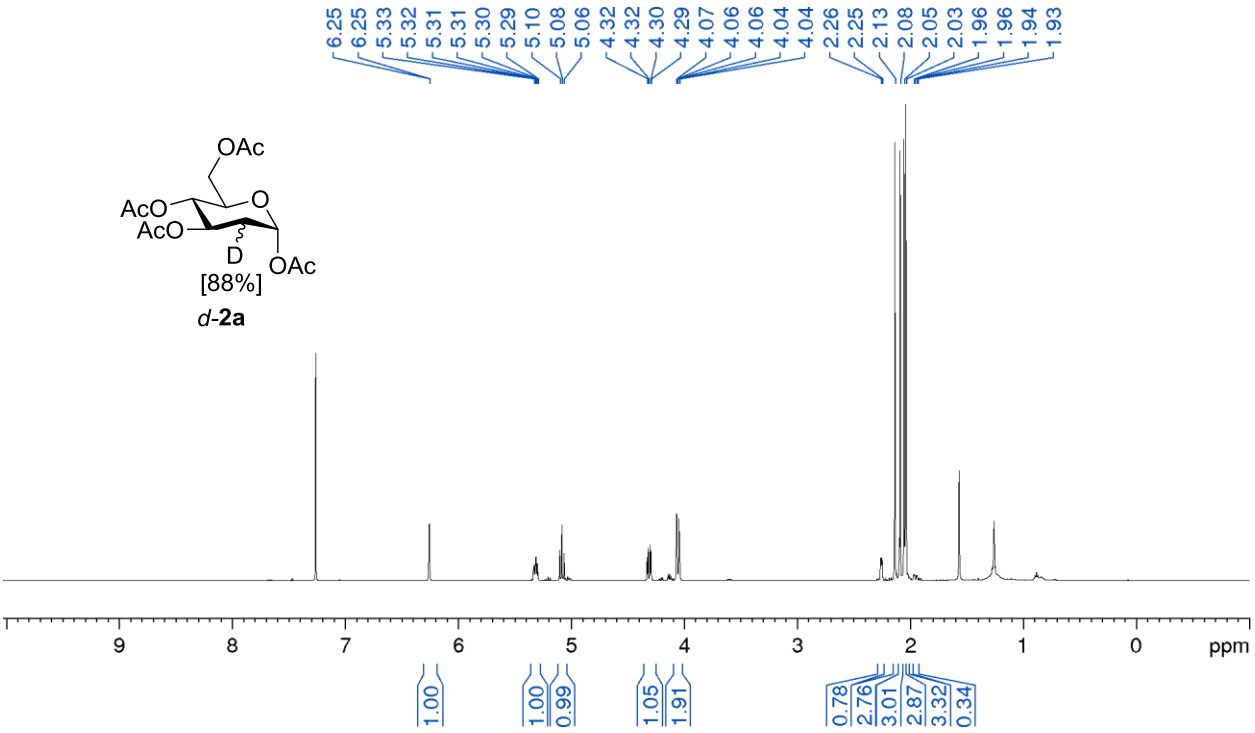
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (2z)



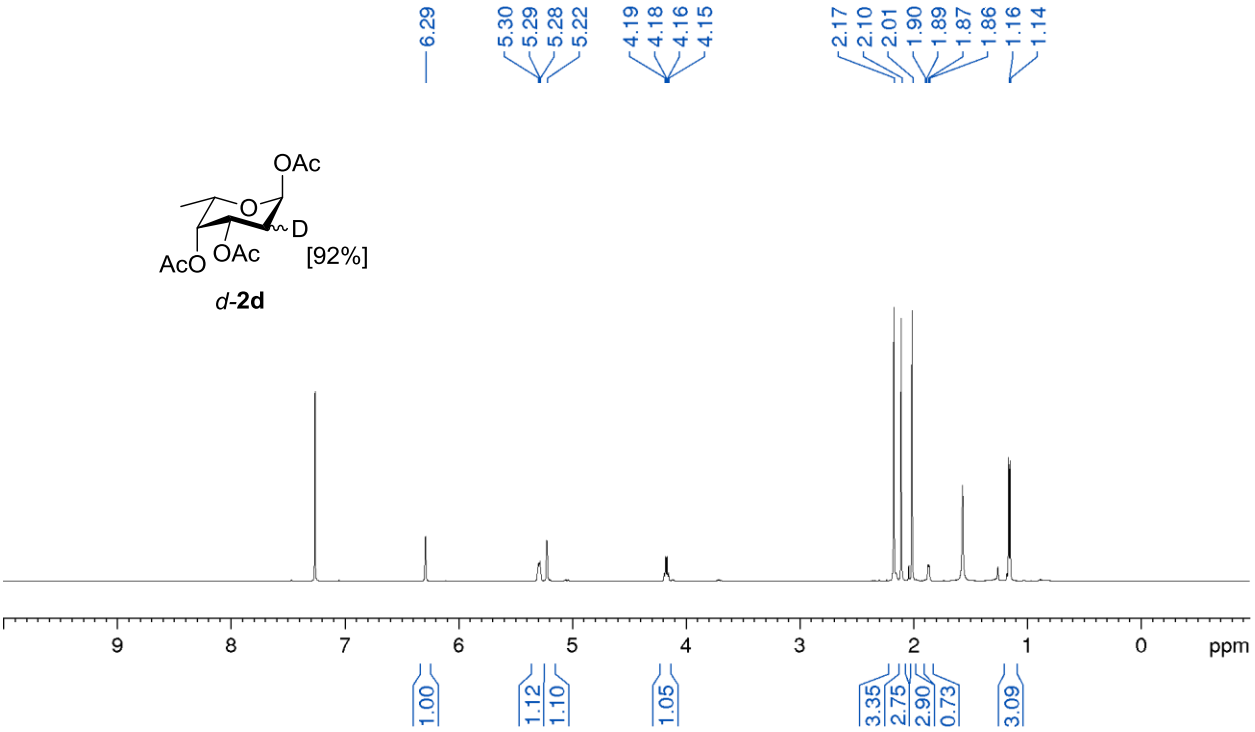
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (2z)



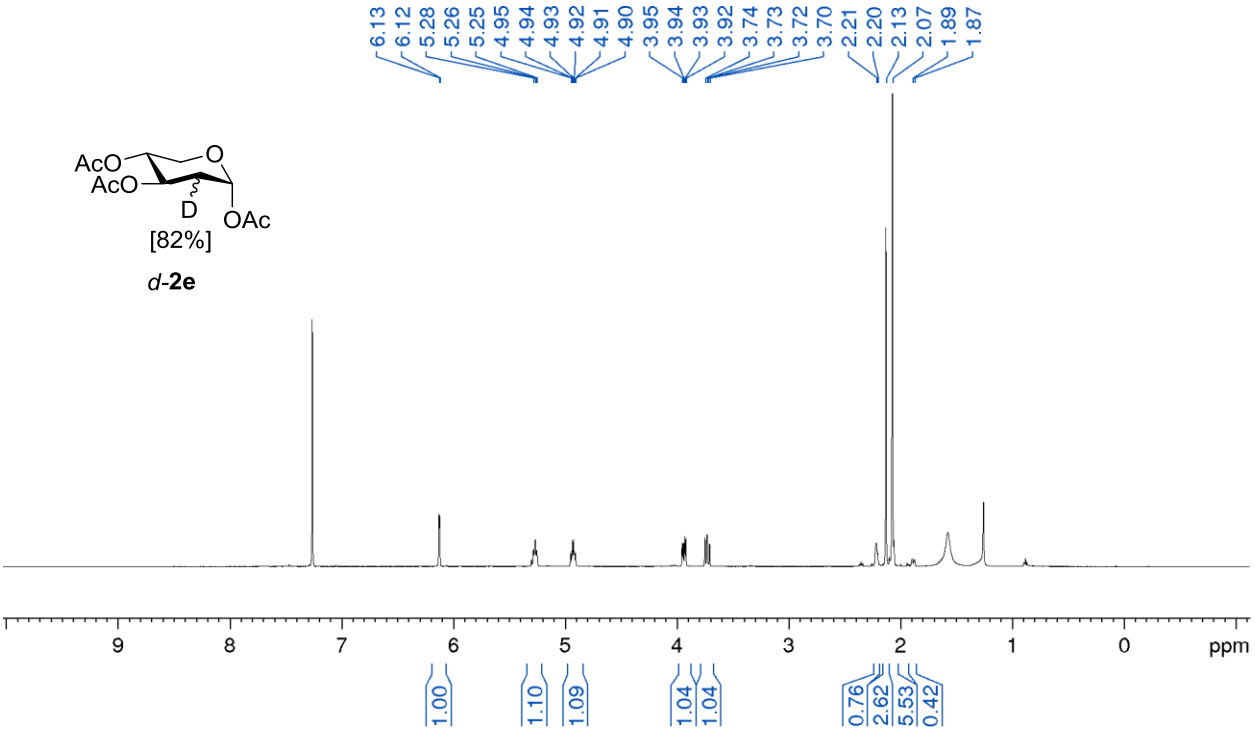
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (*d*-2a)



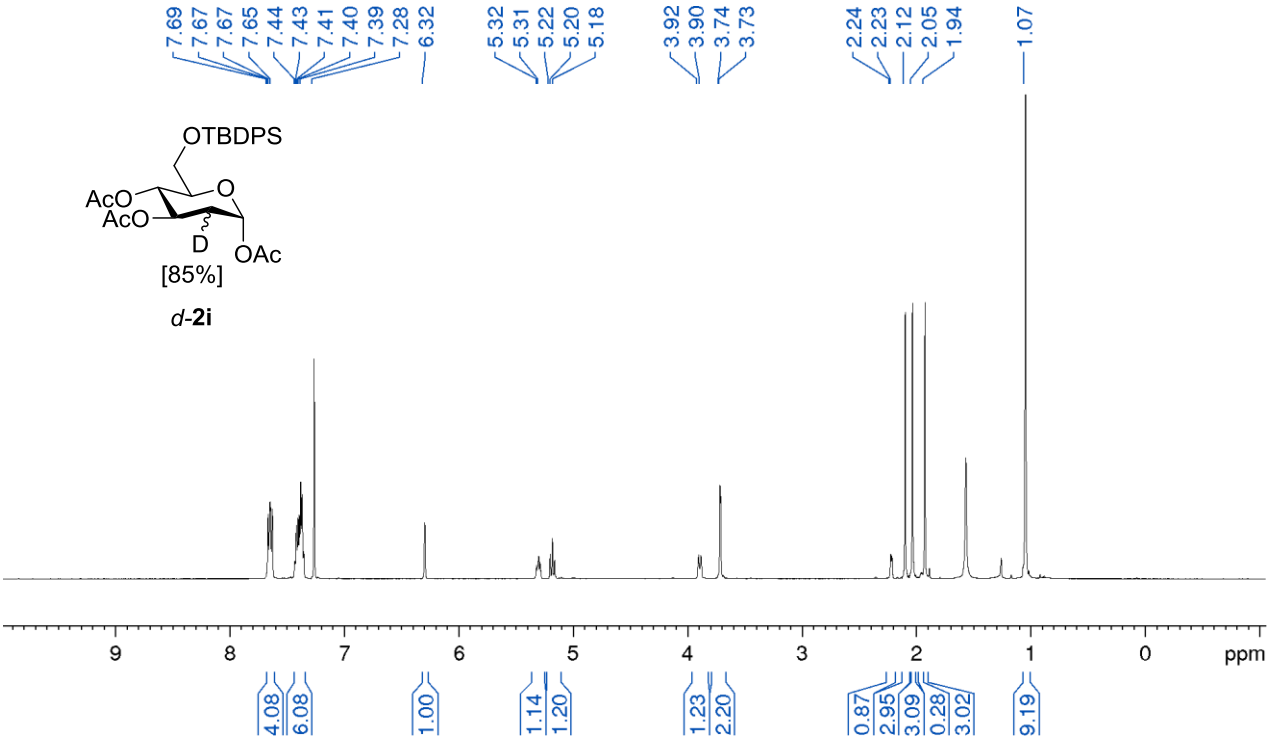
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (*d*-2d)



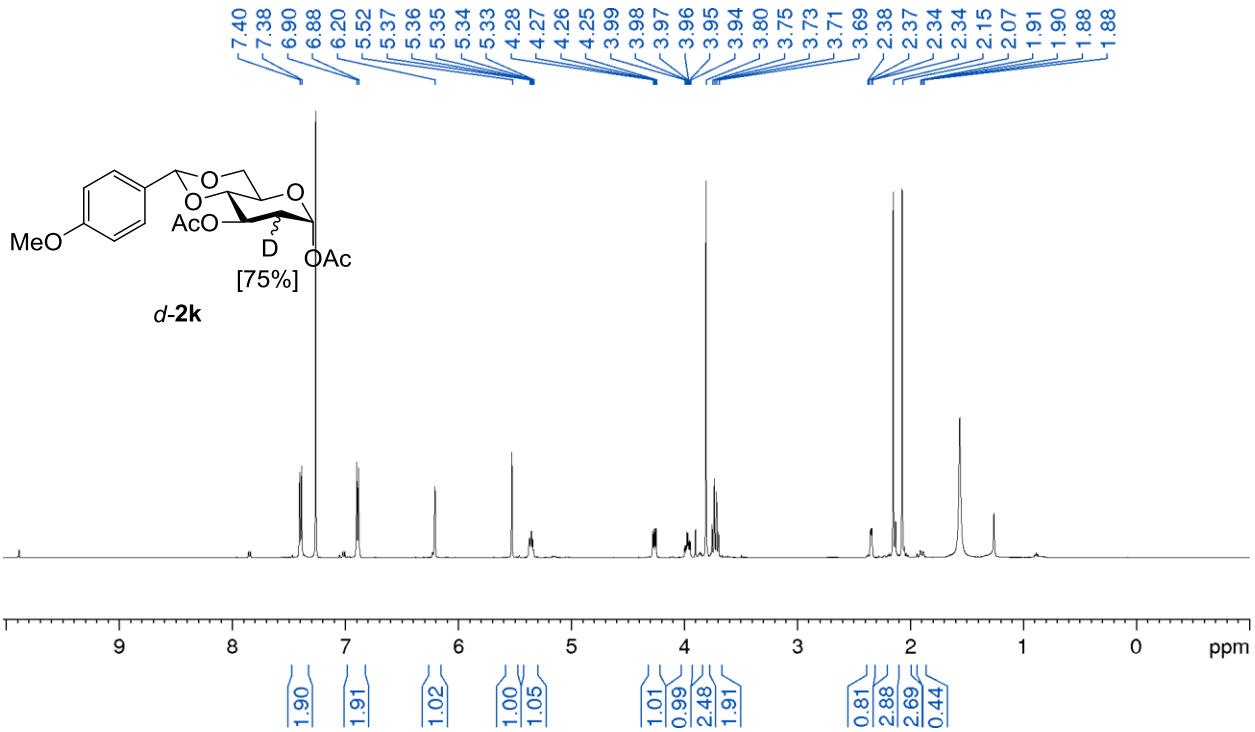
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (*d*-2e)



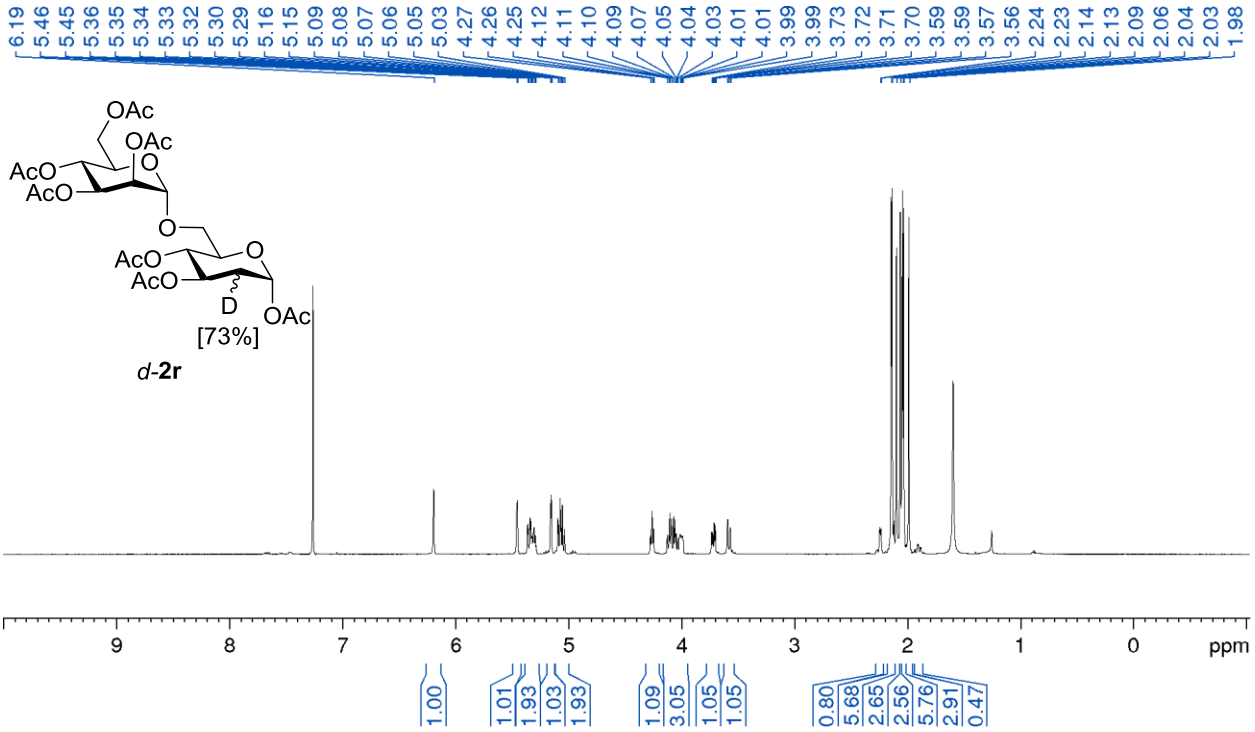
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (*d*-2i)



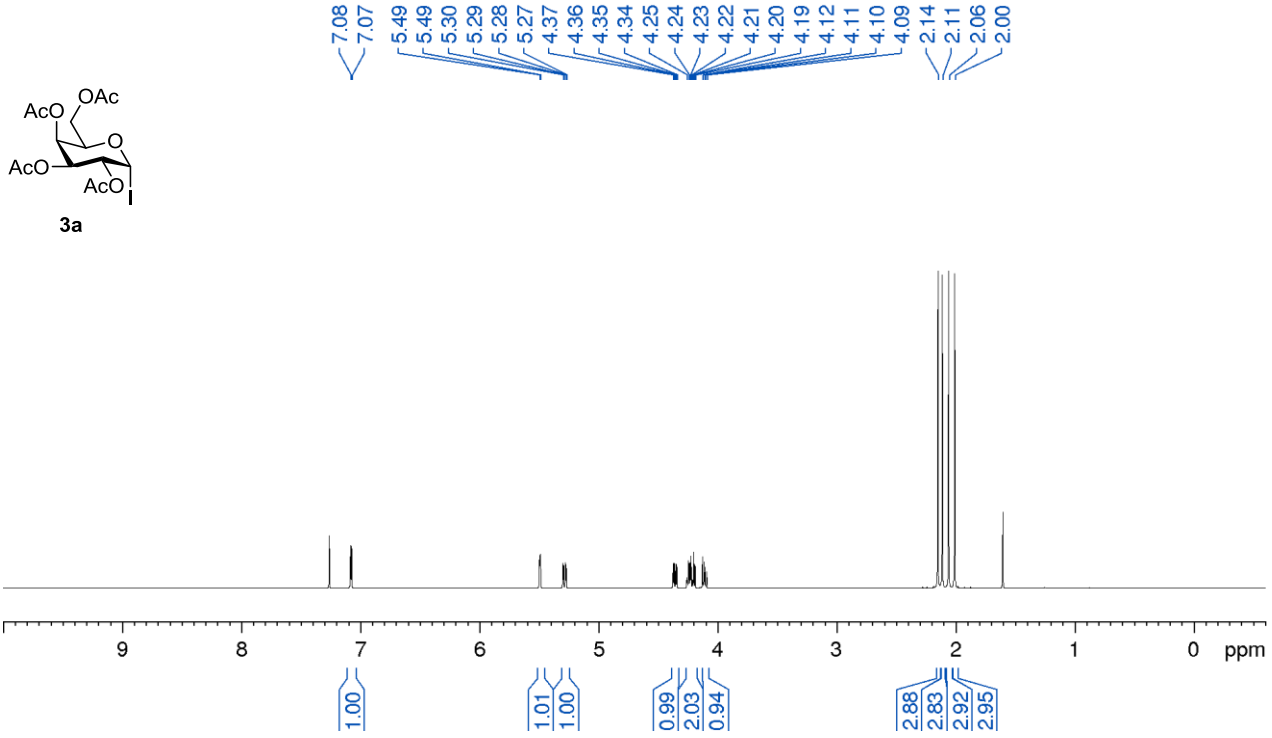
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (*d*-2k)



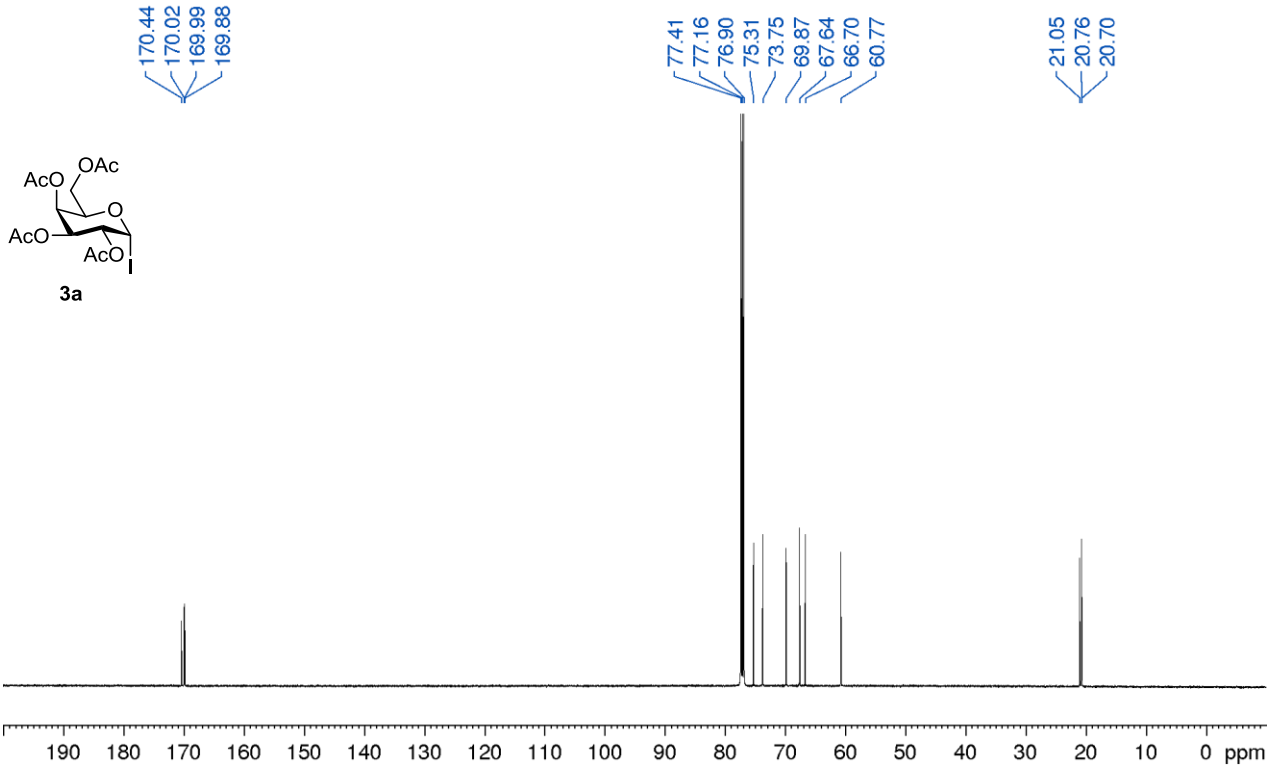
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (*d*-2r)



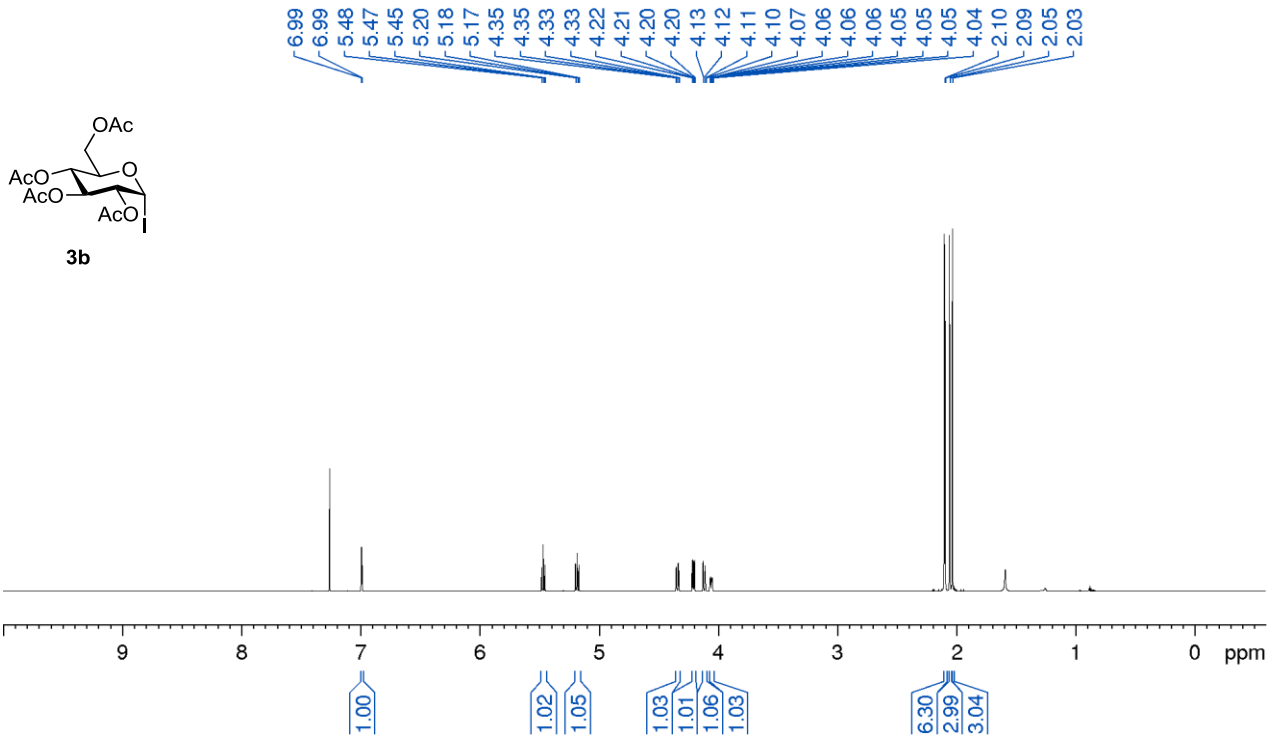
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3a)



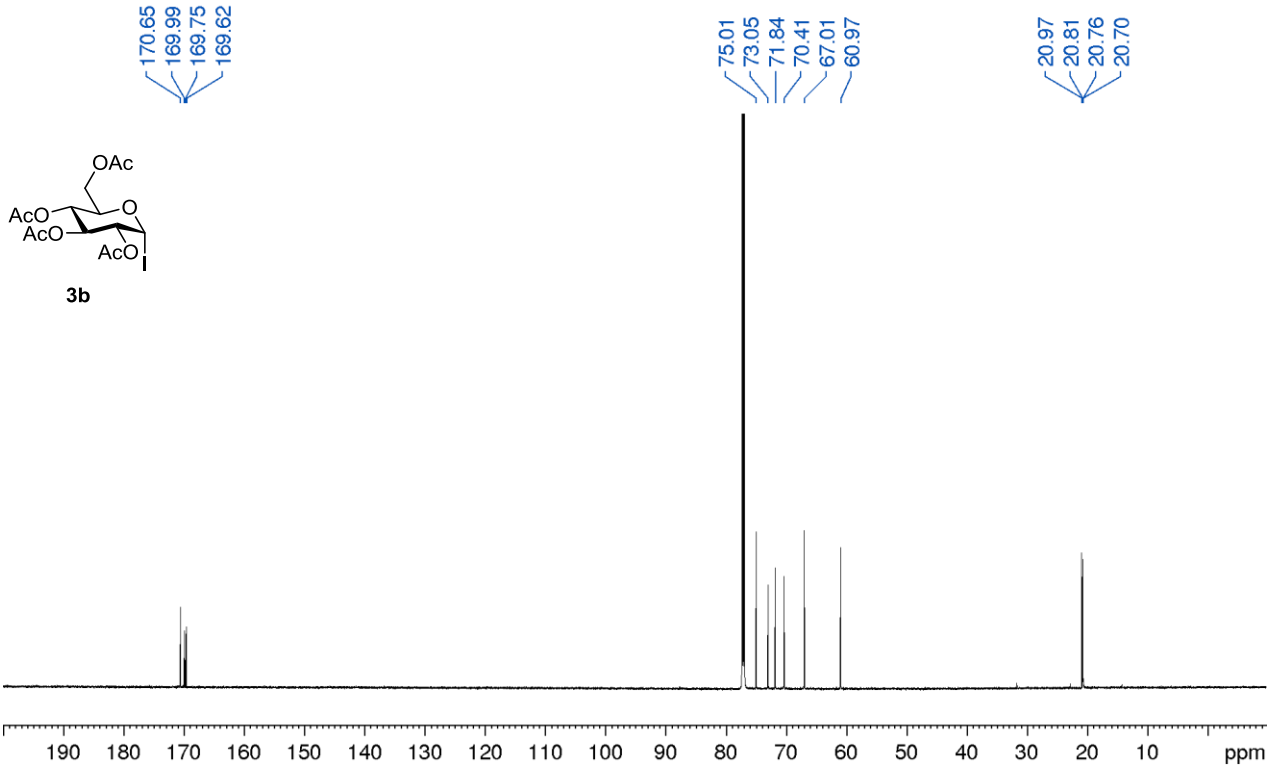
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3a)



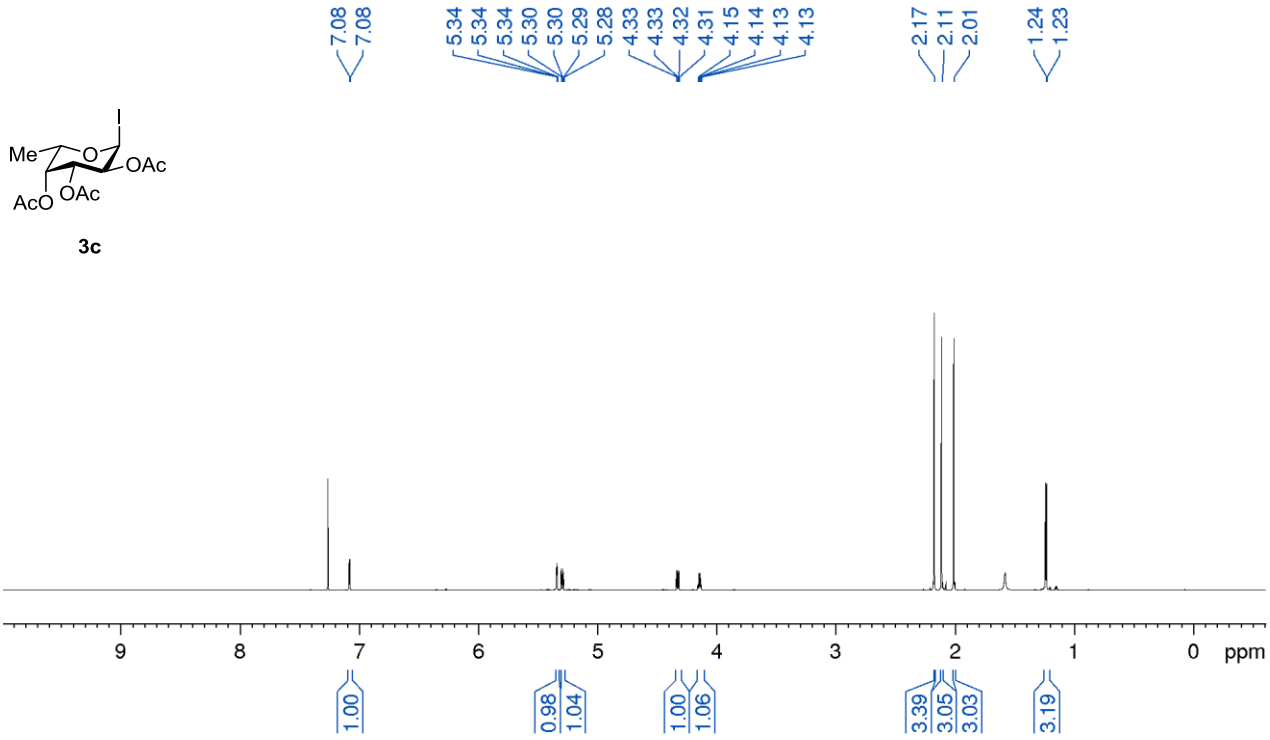
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (3b)



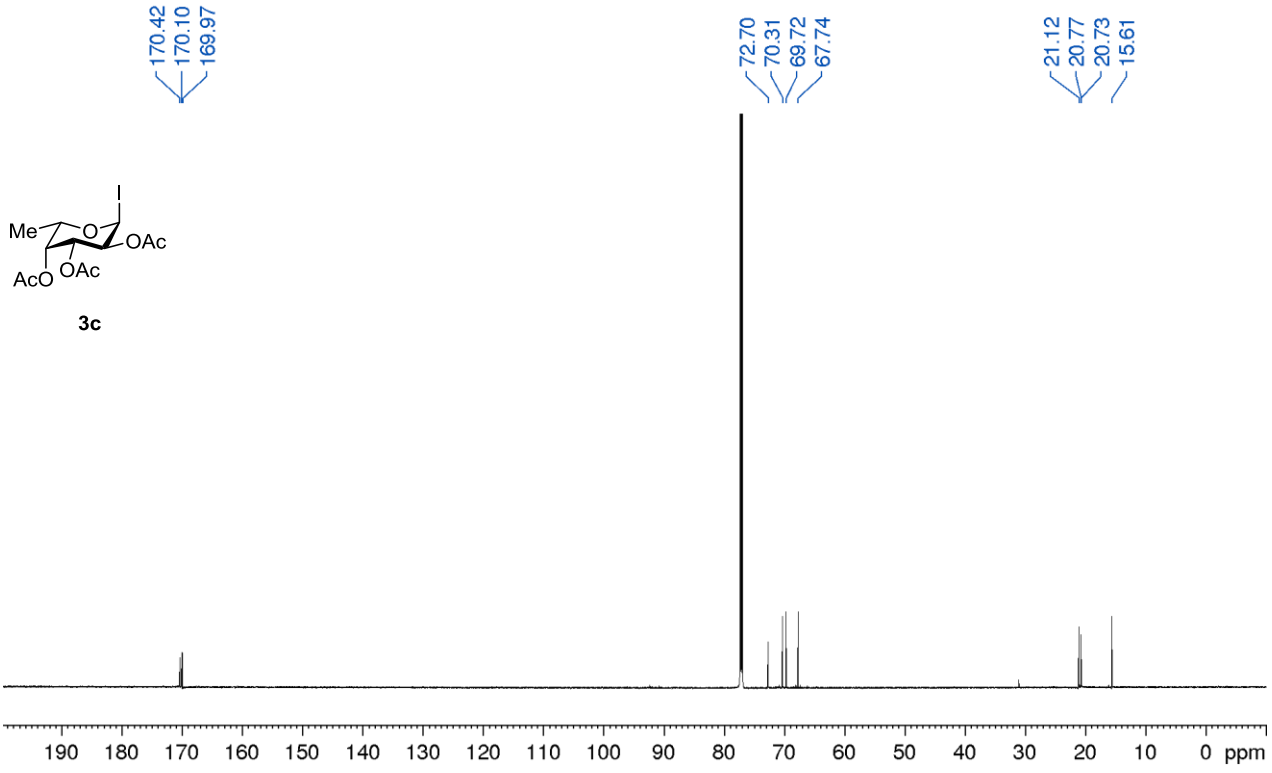
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3b)



^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3c)

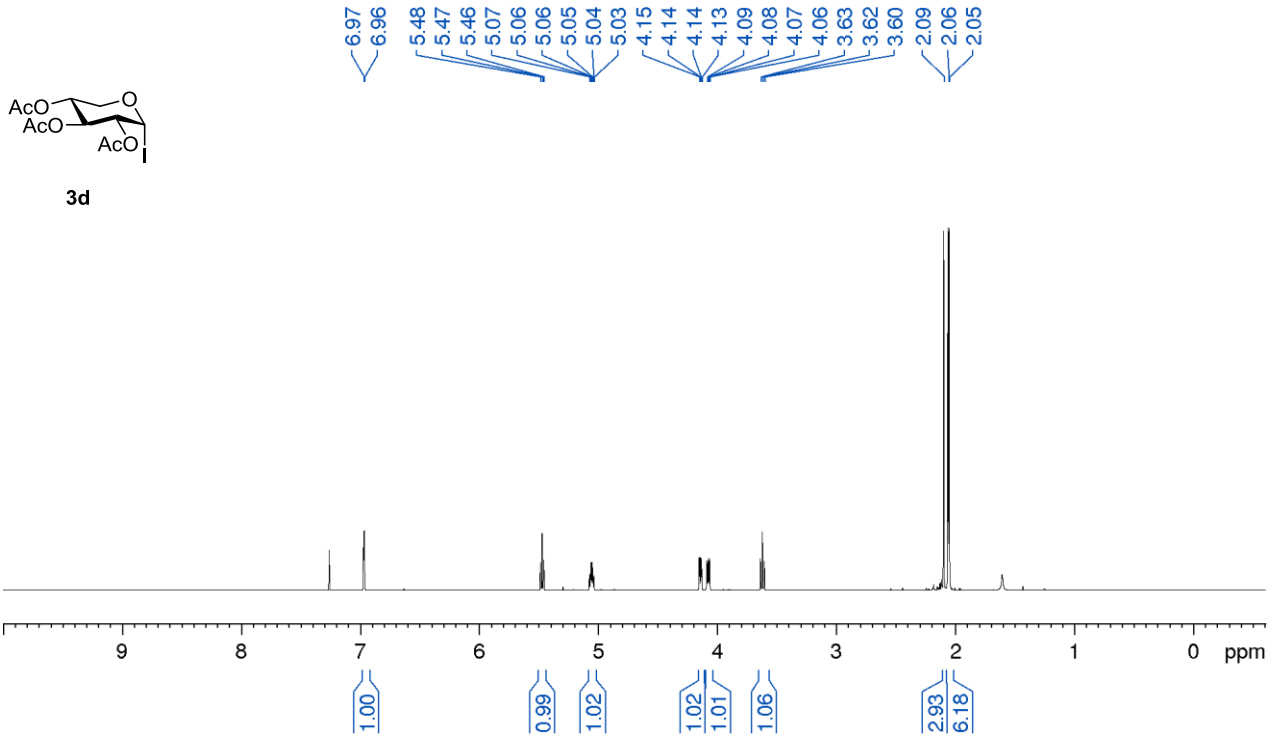


^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3c)



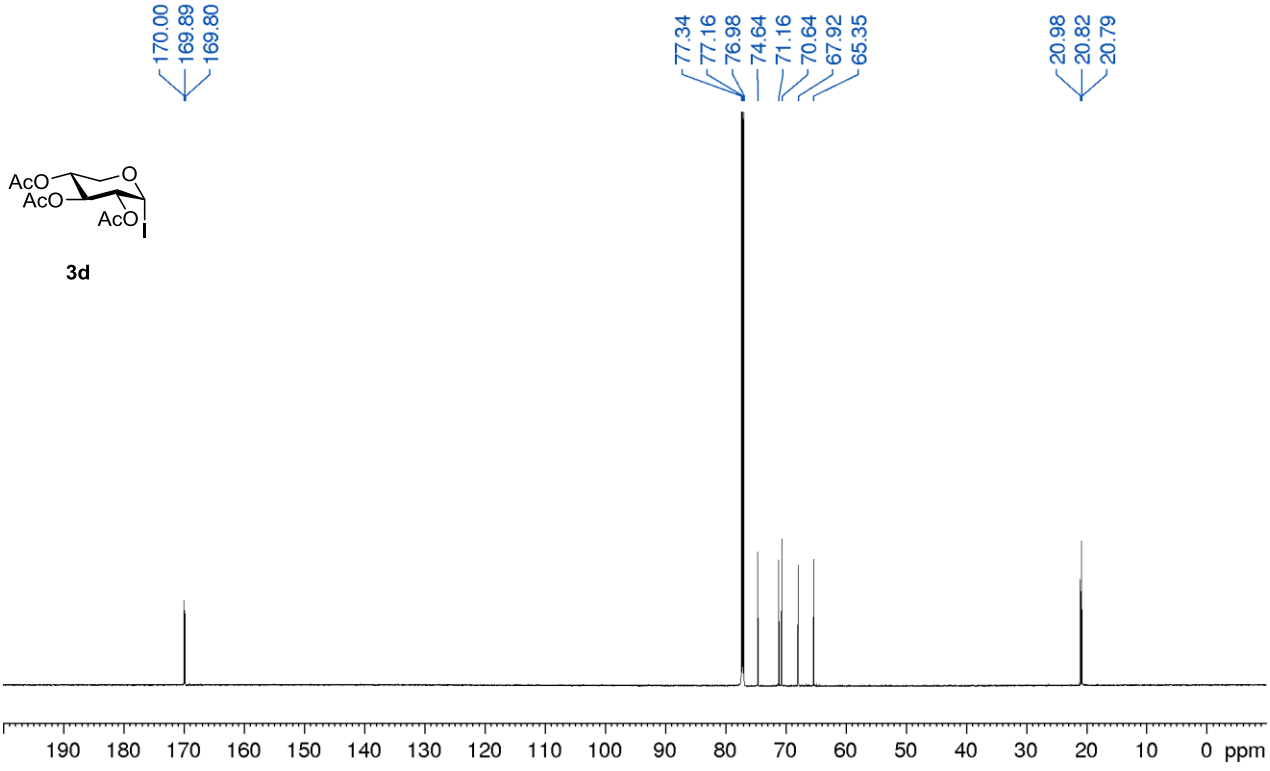
3c

^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3d)

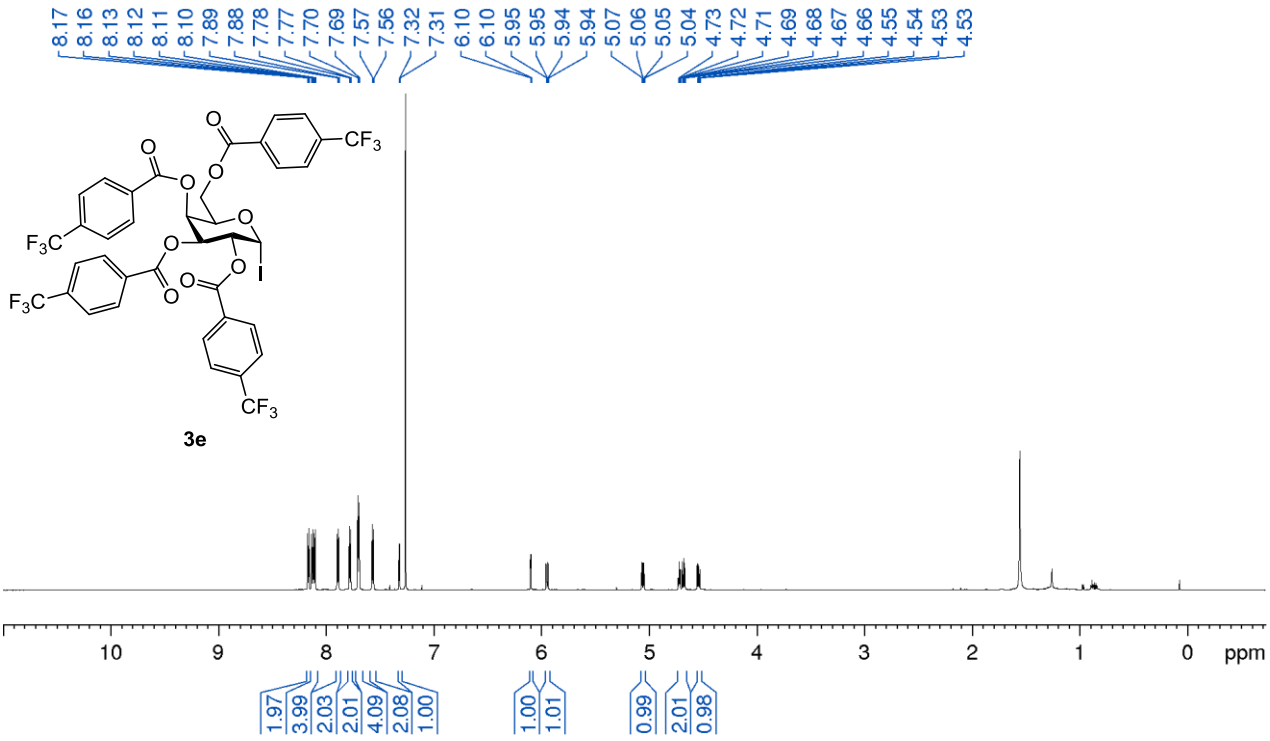


3d

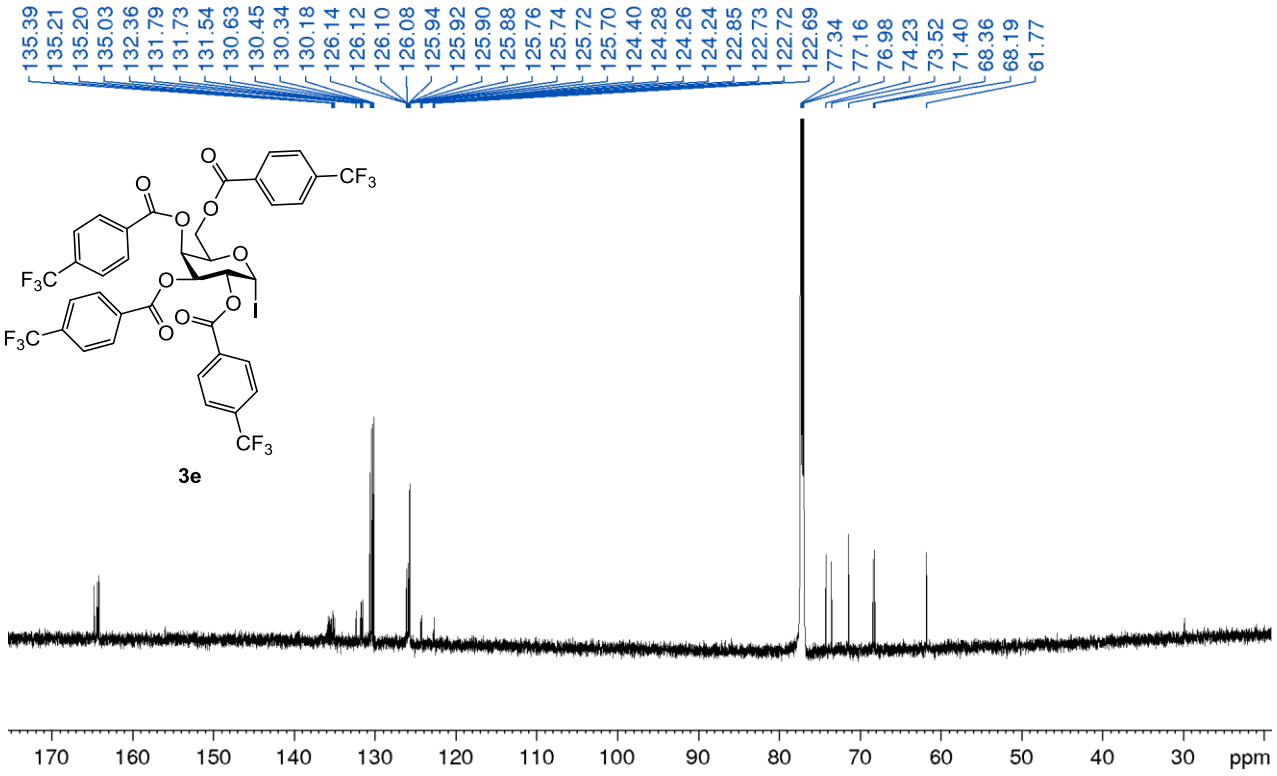
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3d)



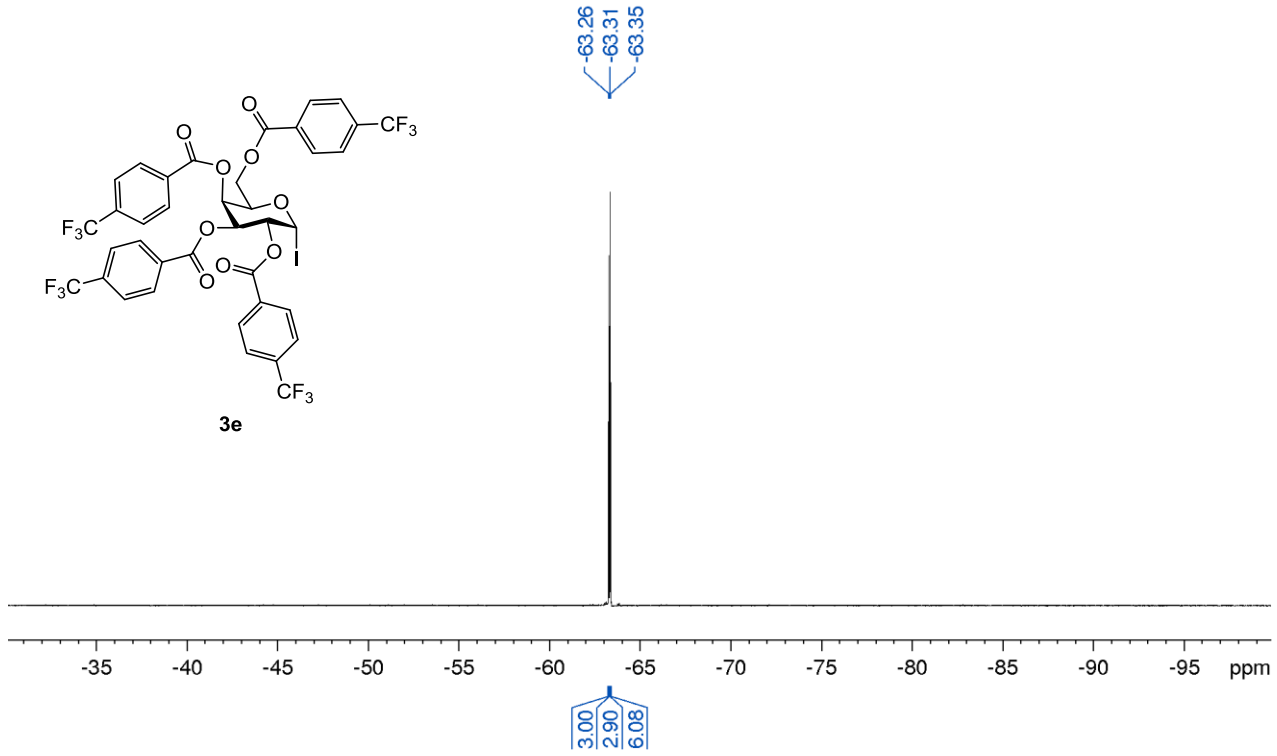
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3e)



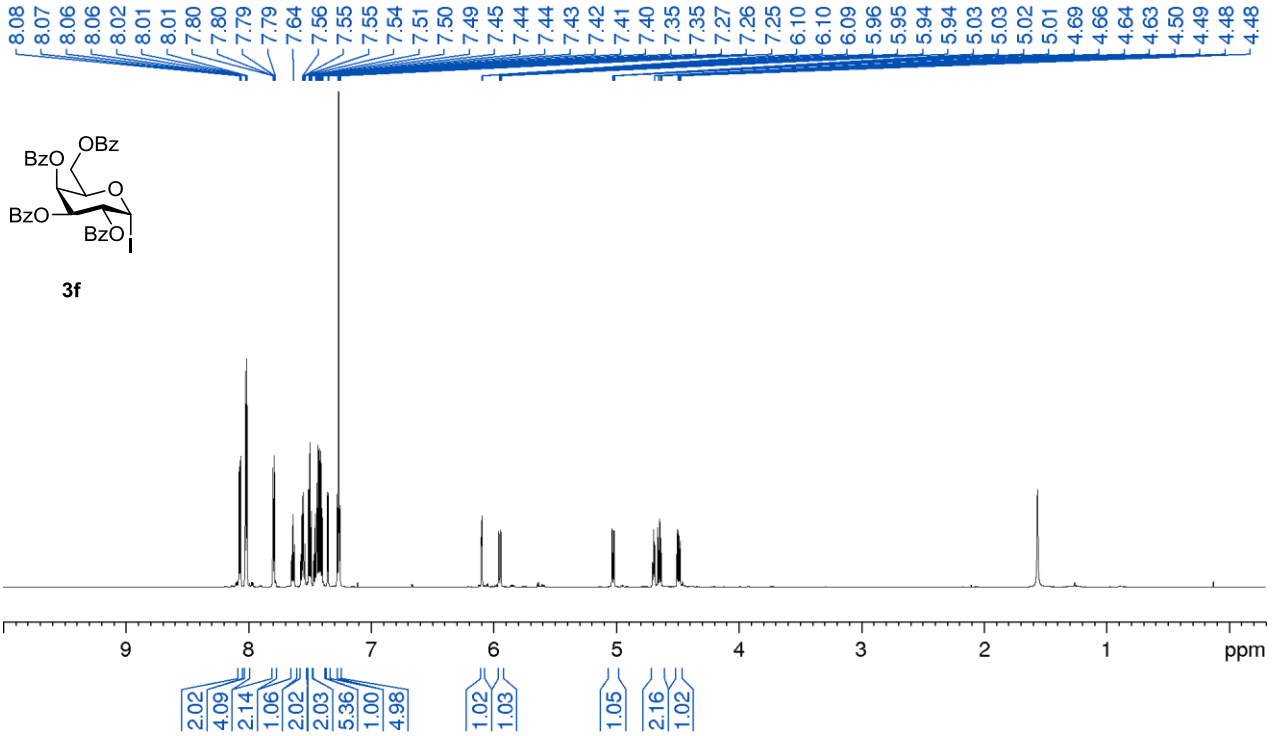
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (3e)



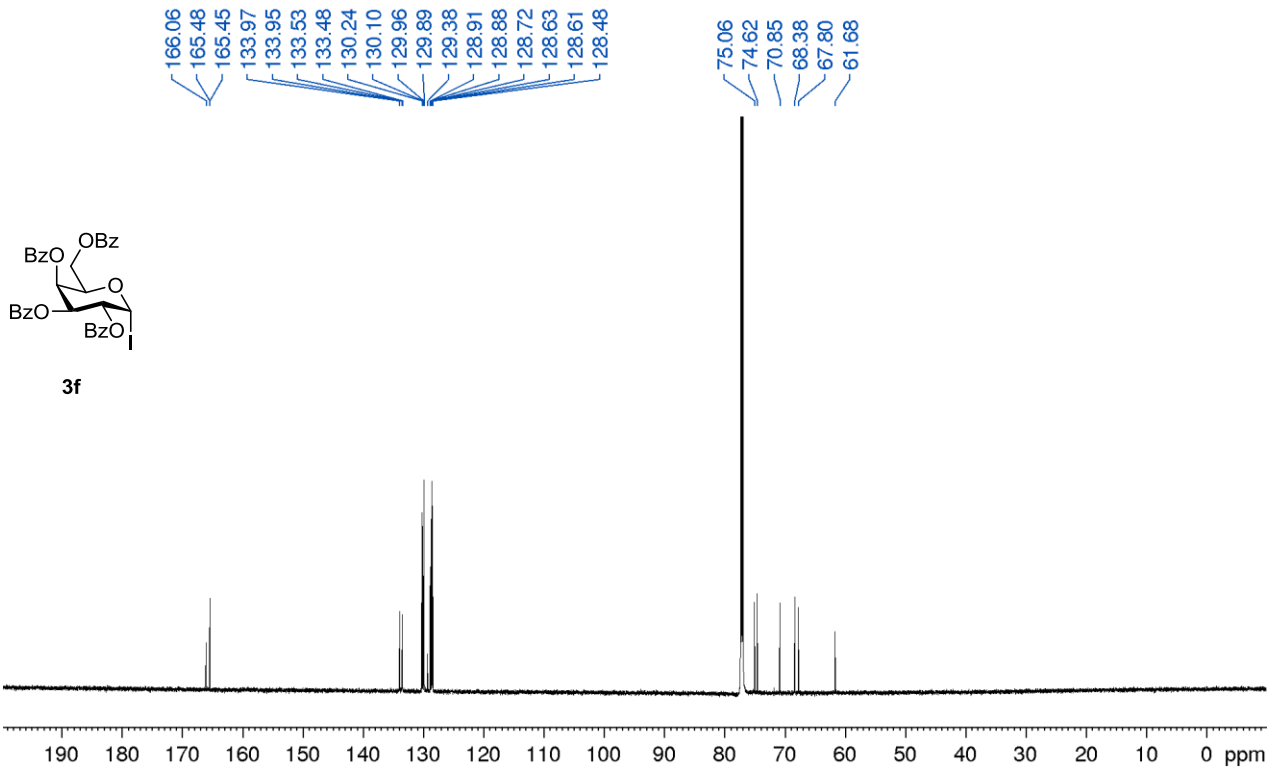
^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of (3e)



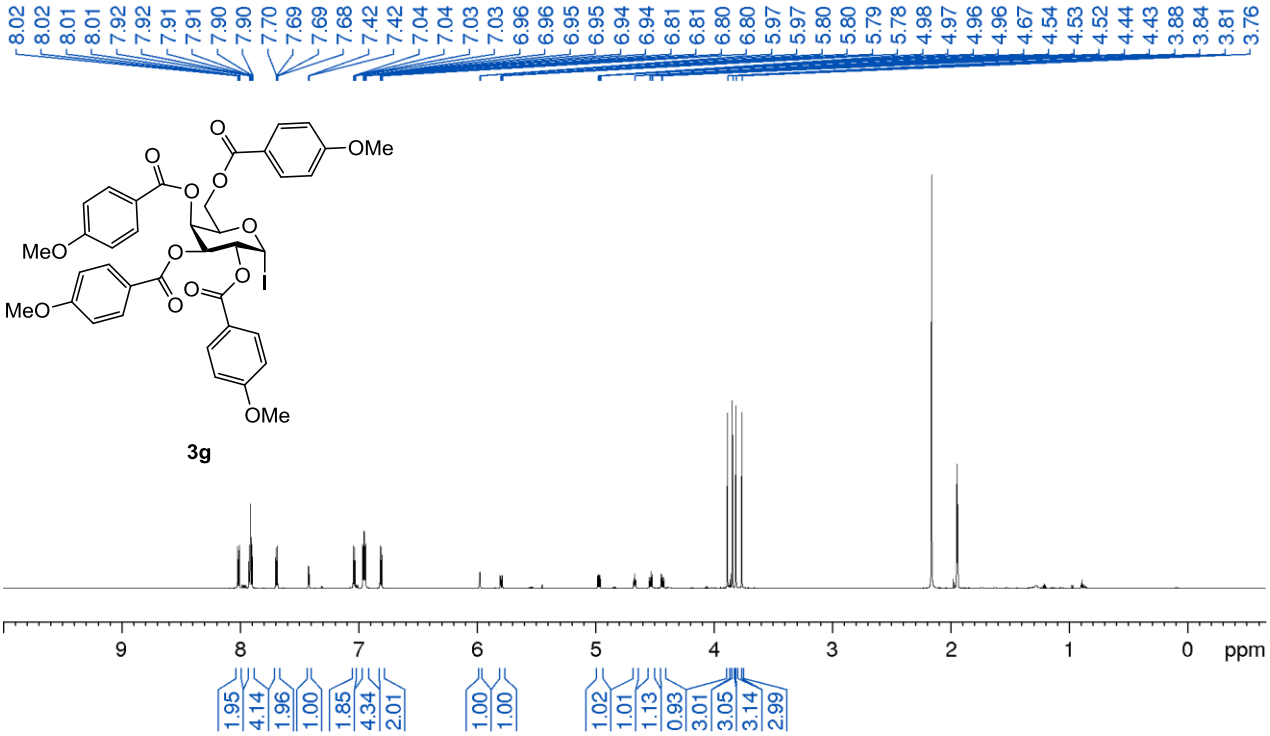
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3f)



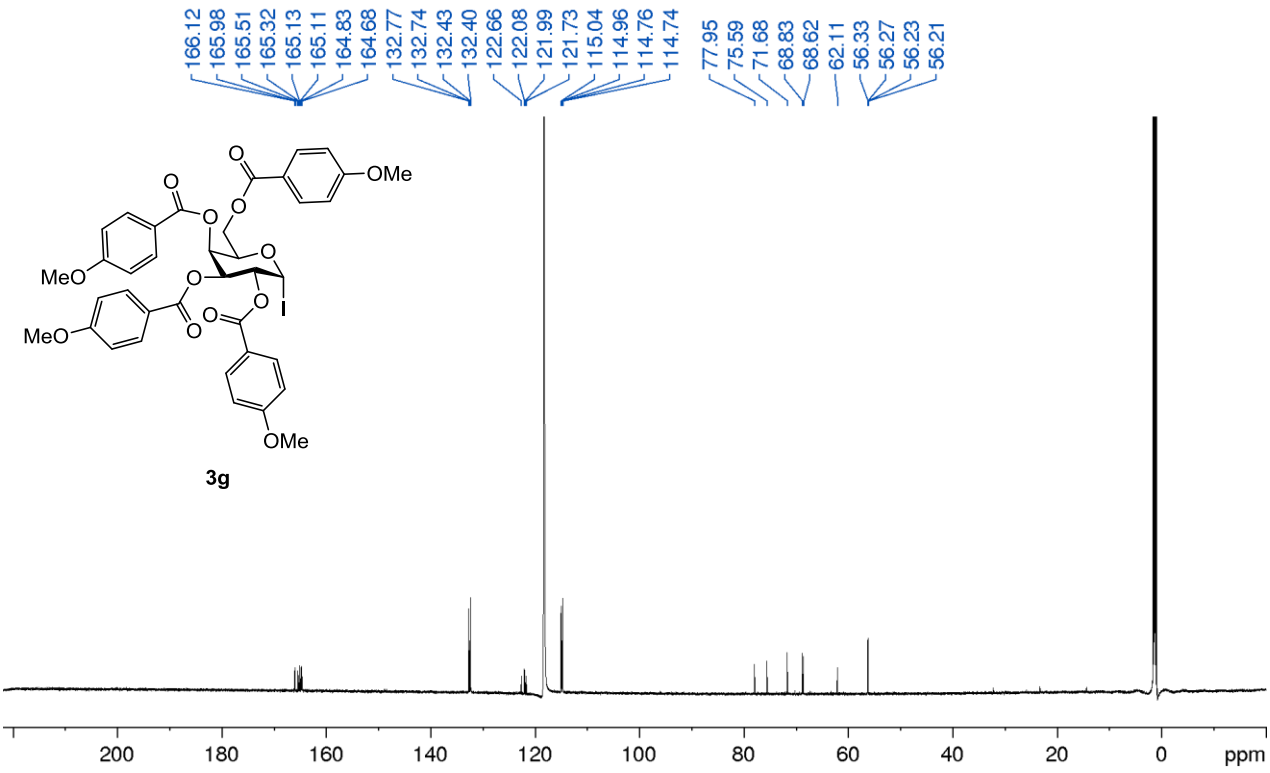
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3f)



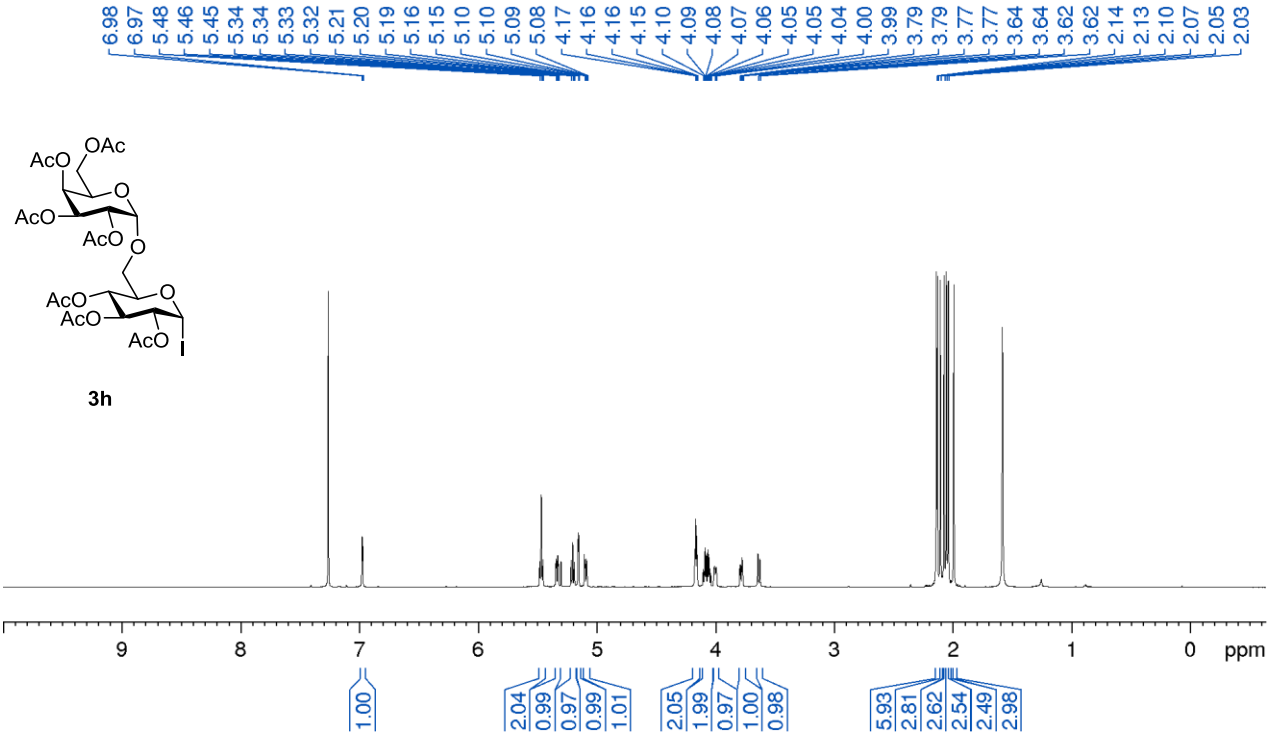
^{1}H NMR (700 MHz, CD_3CN, 25 ºC) of (3g)



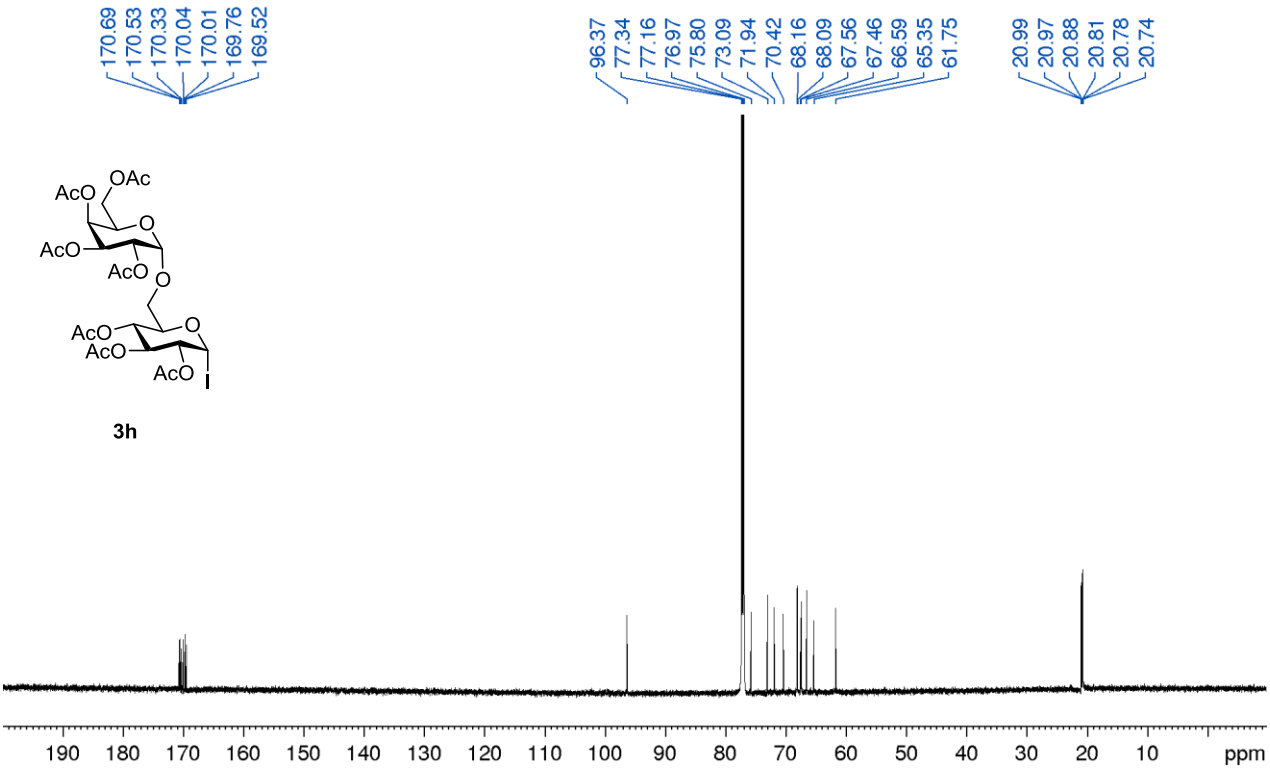
^{13}C NMR (175 MHz, CD_3CN, 25 ºC) of (3g)



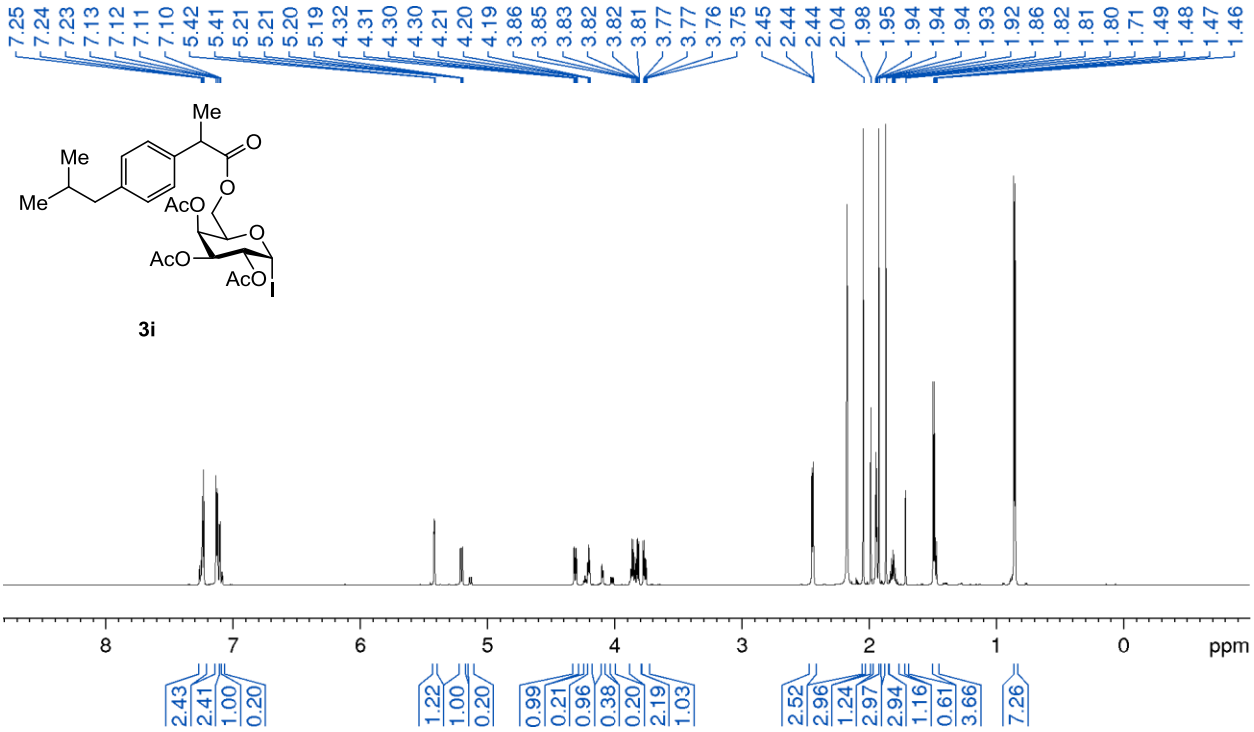
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3h)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3h)

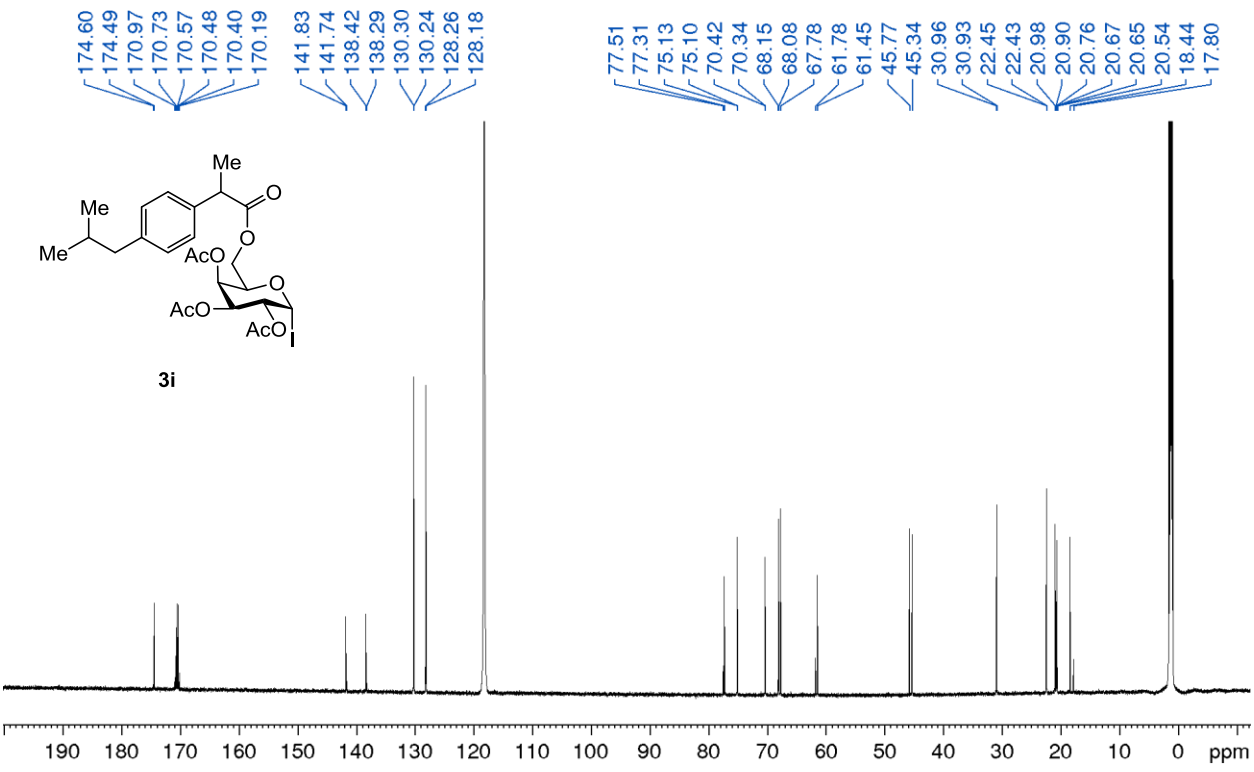


^{1}H NMR (700 MHz, CD_3CN, 25 °C) of (3i)



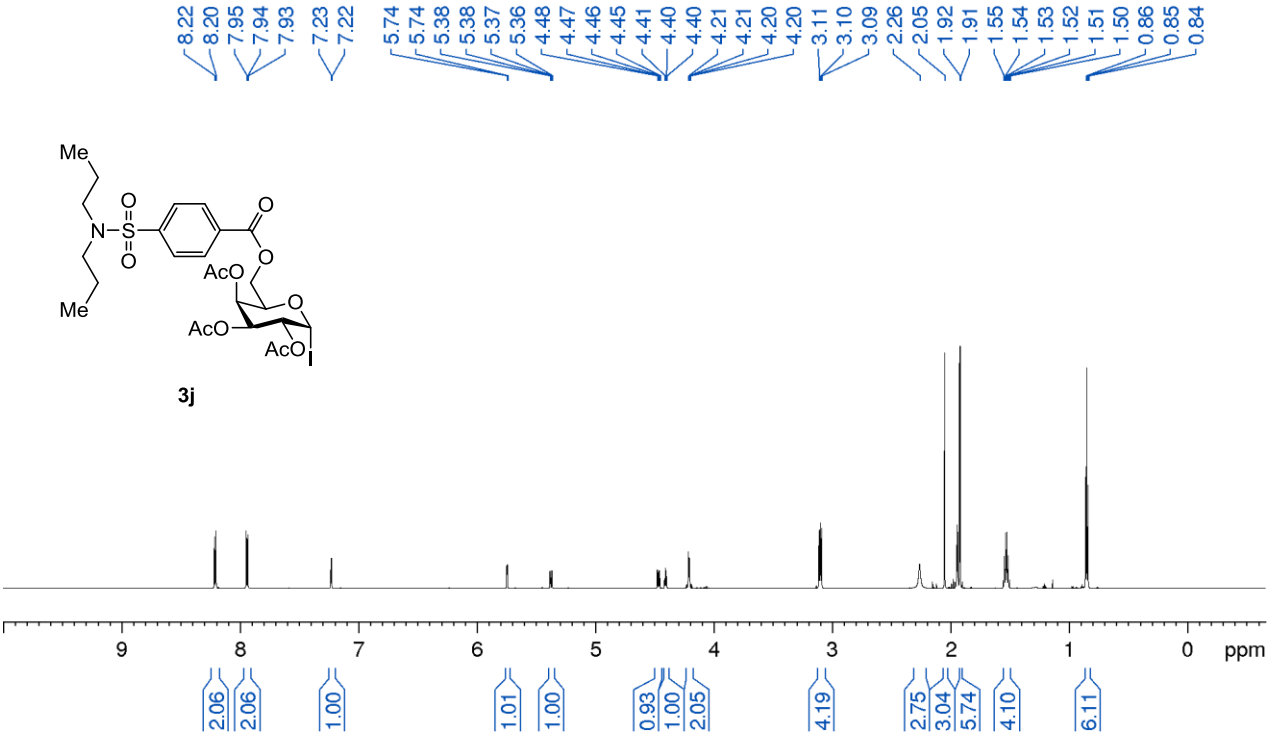
3i

^{13}C NMR (175 MHz, CD_3CN, 25 °C) of (3i)

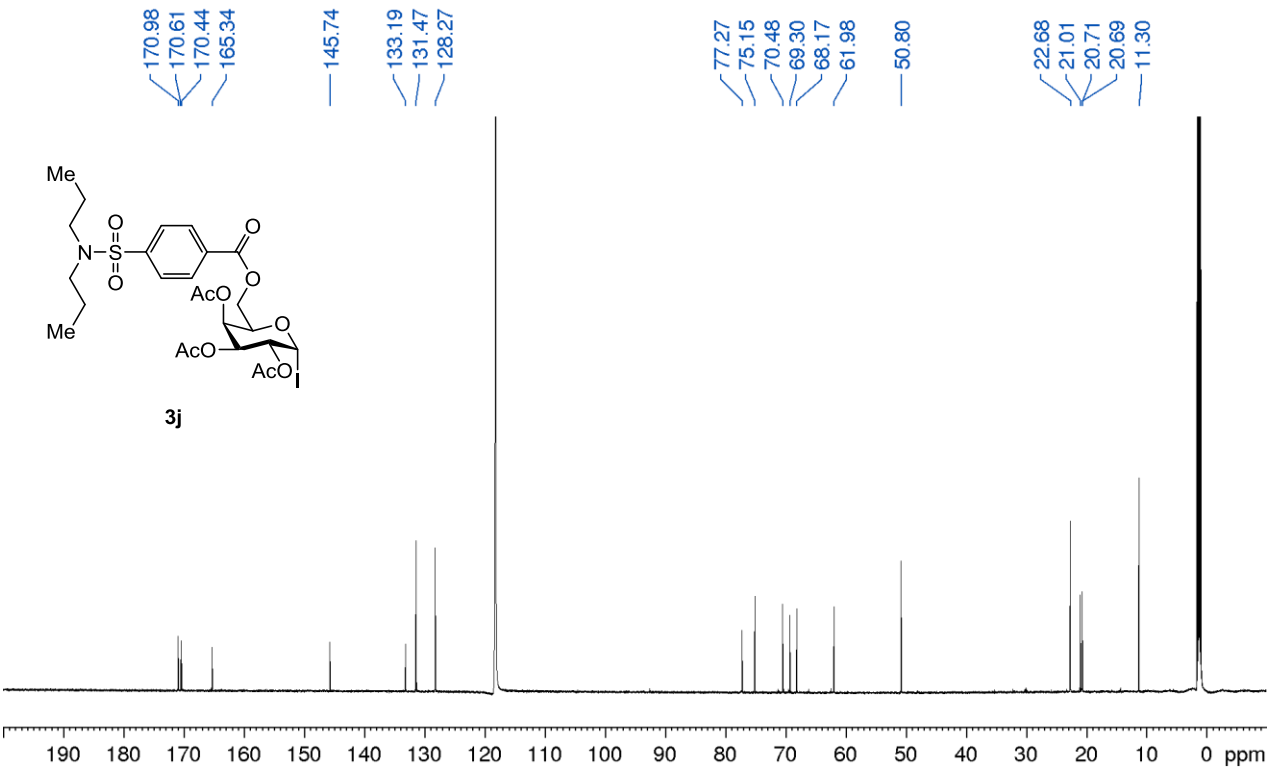


3i

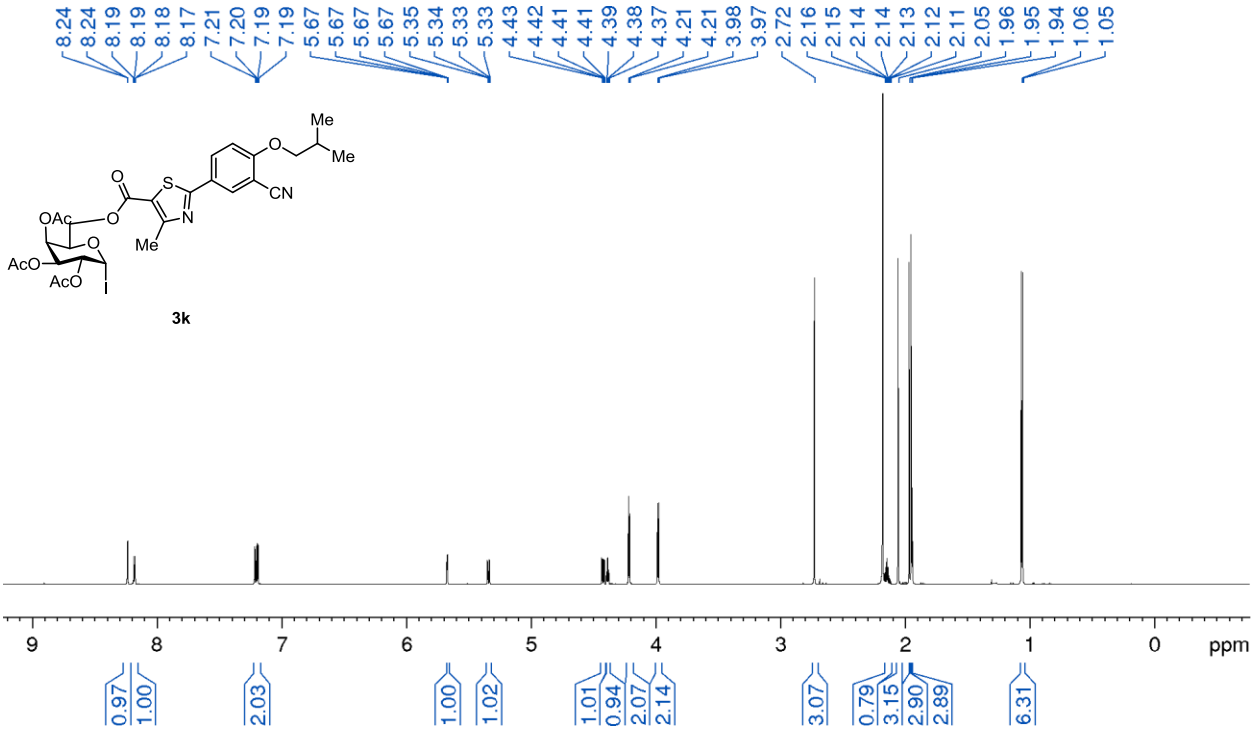
^{1}H NMR (700 MHz, CD_3CN, 25 °C) of (3j)



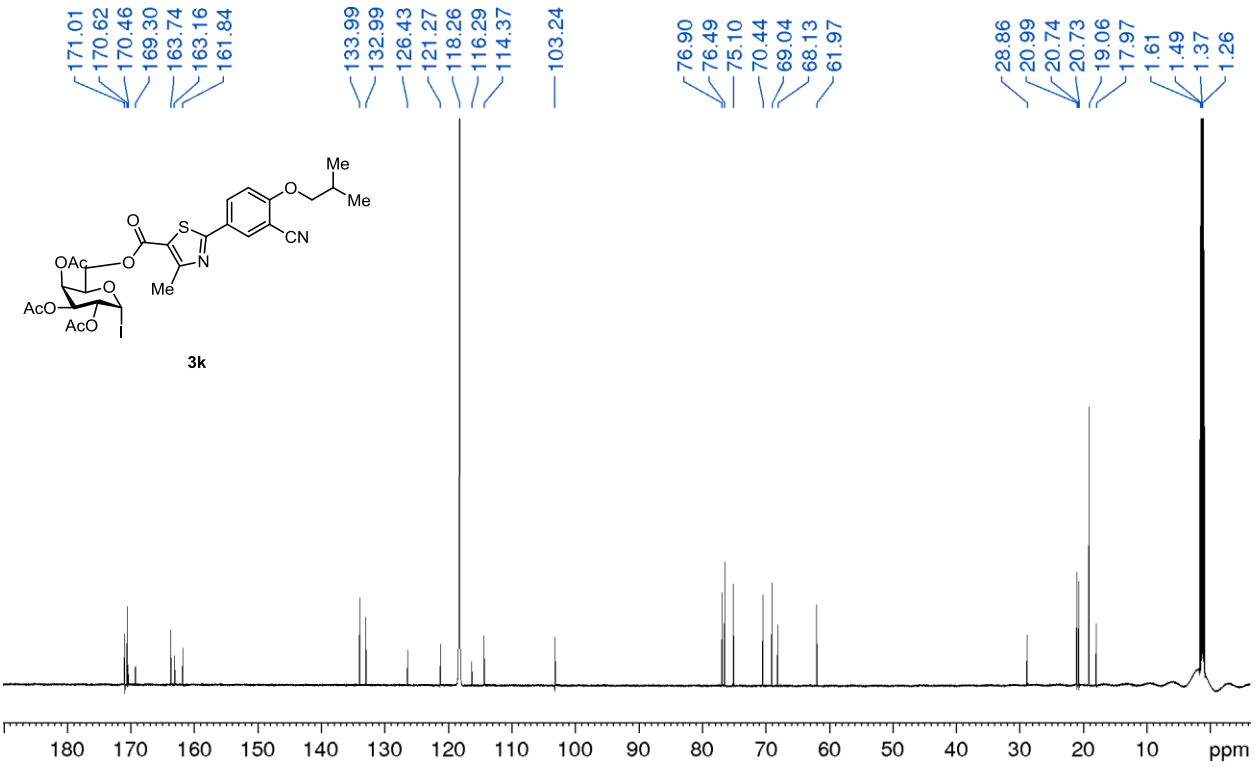
^{13}C NMR (175 MHz, CD_3CN, 25 °C) of (3j)



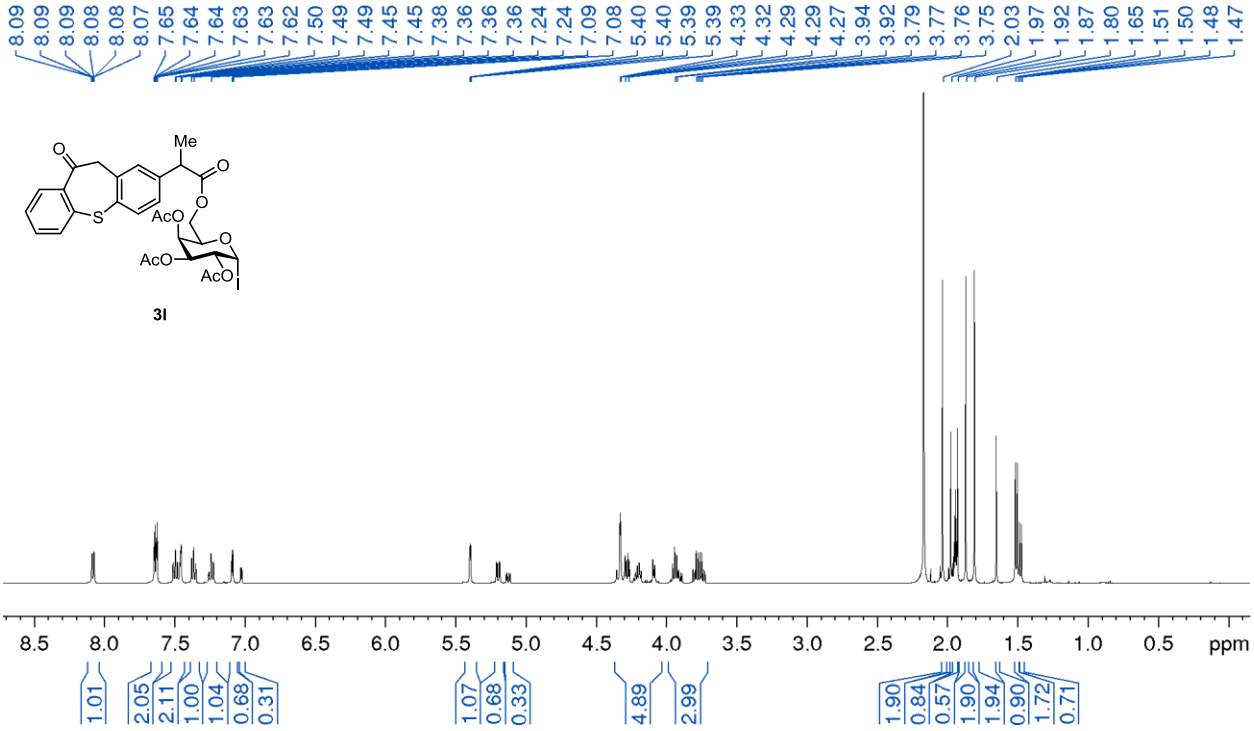
^{1}H NMR (700 MHz, CD_3CN, 25 ºC) of (3k)



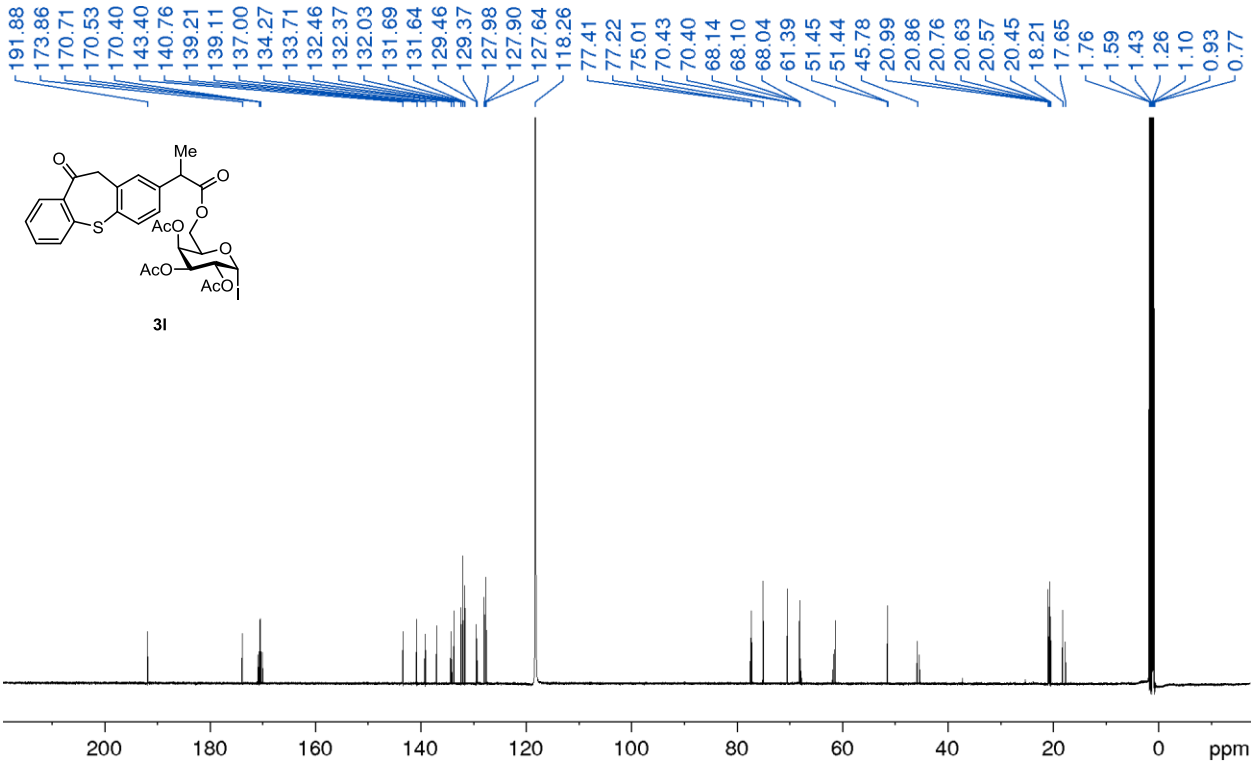
^{13}C NMR (175 MHz, CD_3CN, 25 ºC) of (3k)



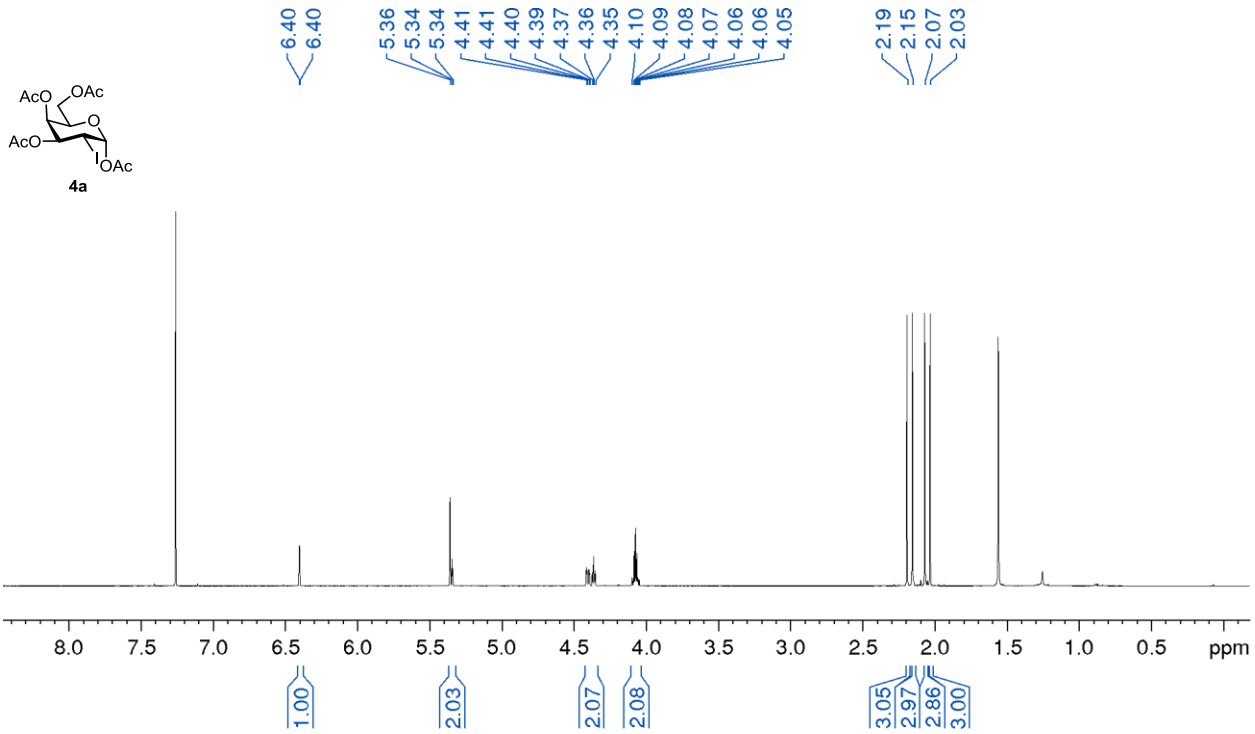
^{1}H NMR (700 MHz, CD_3CN, 25 °C) of (3l)



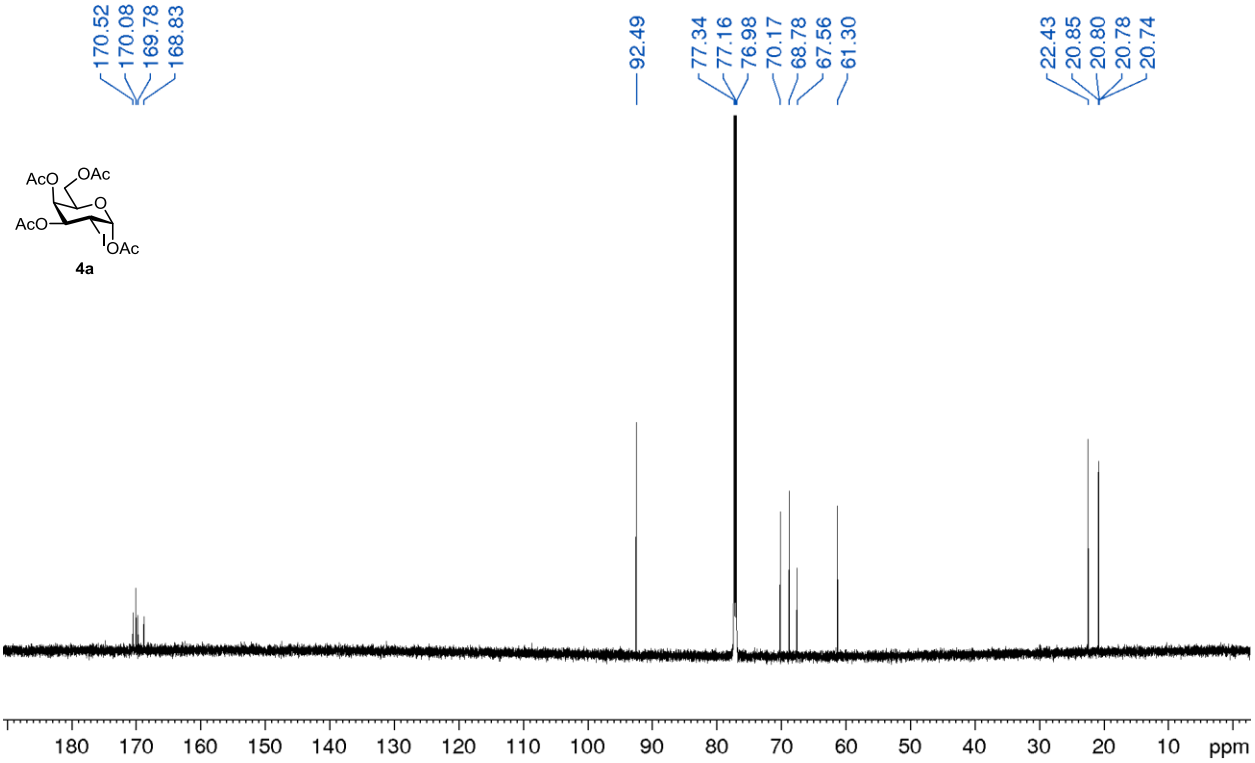
^{13}C NMR (175 MHz, CD_3CN, 25 °C) of (3l)



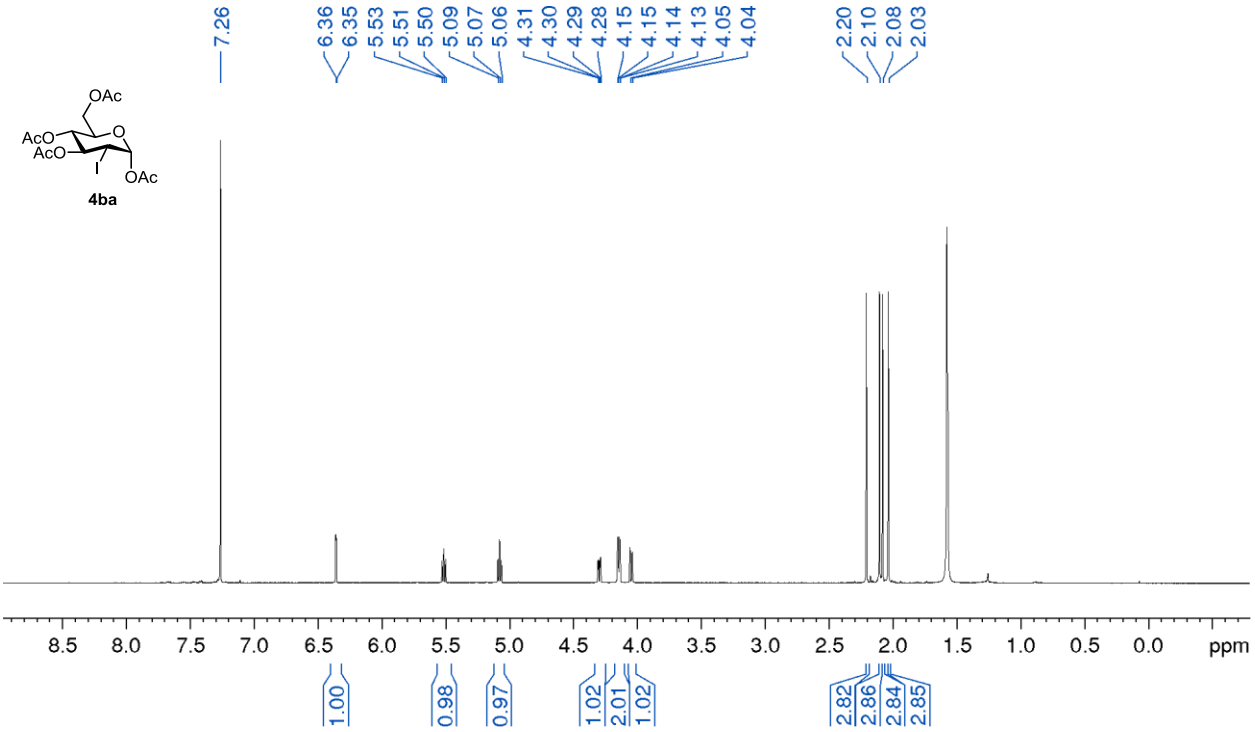
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4a)



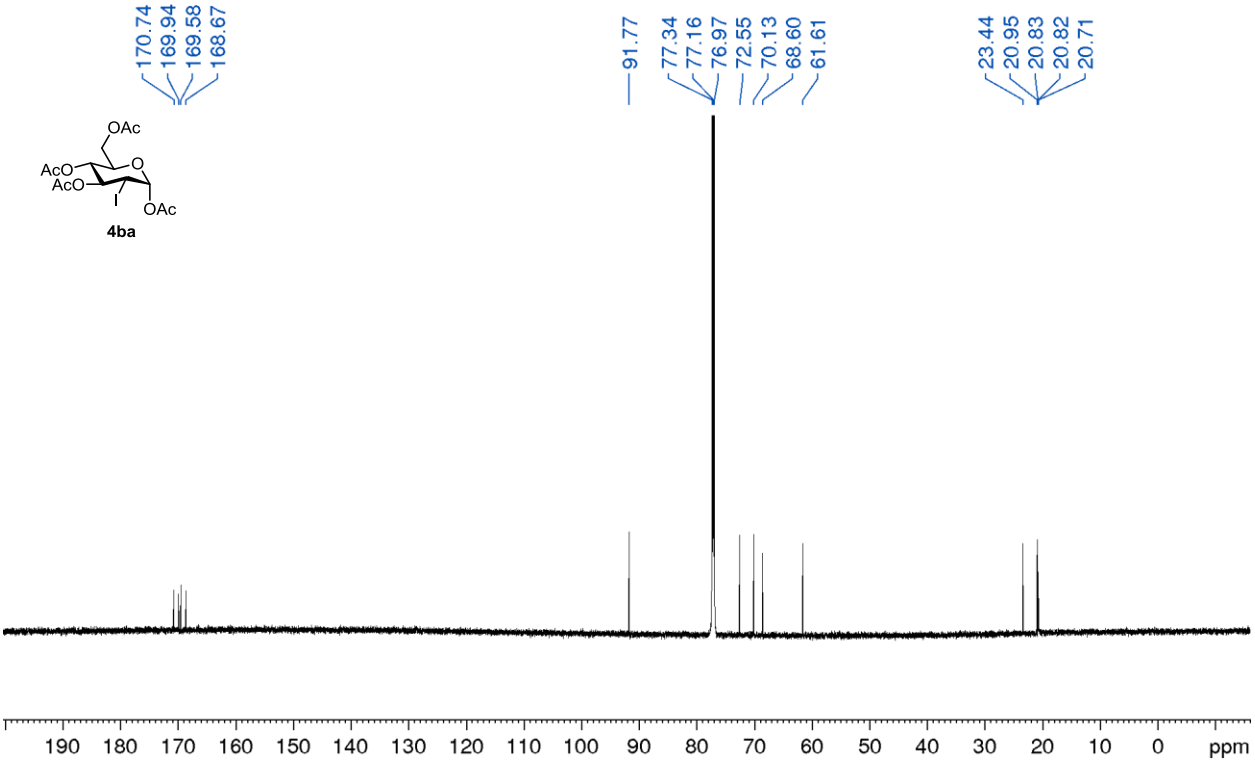
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4a)



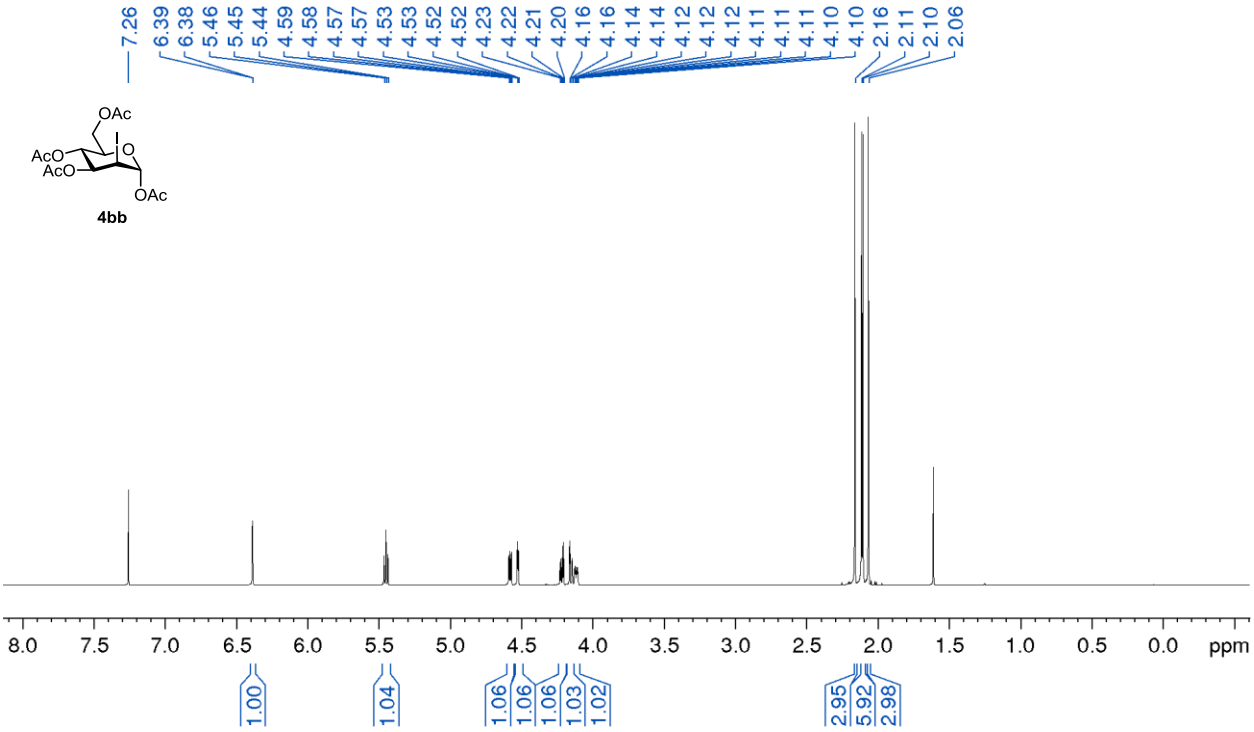
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4ba)



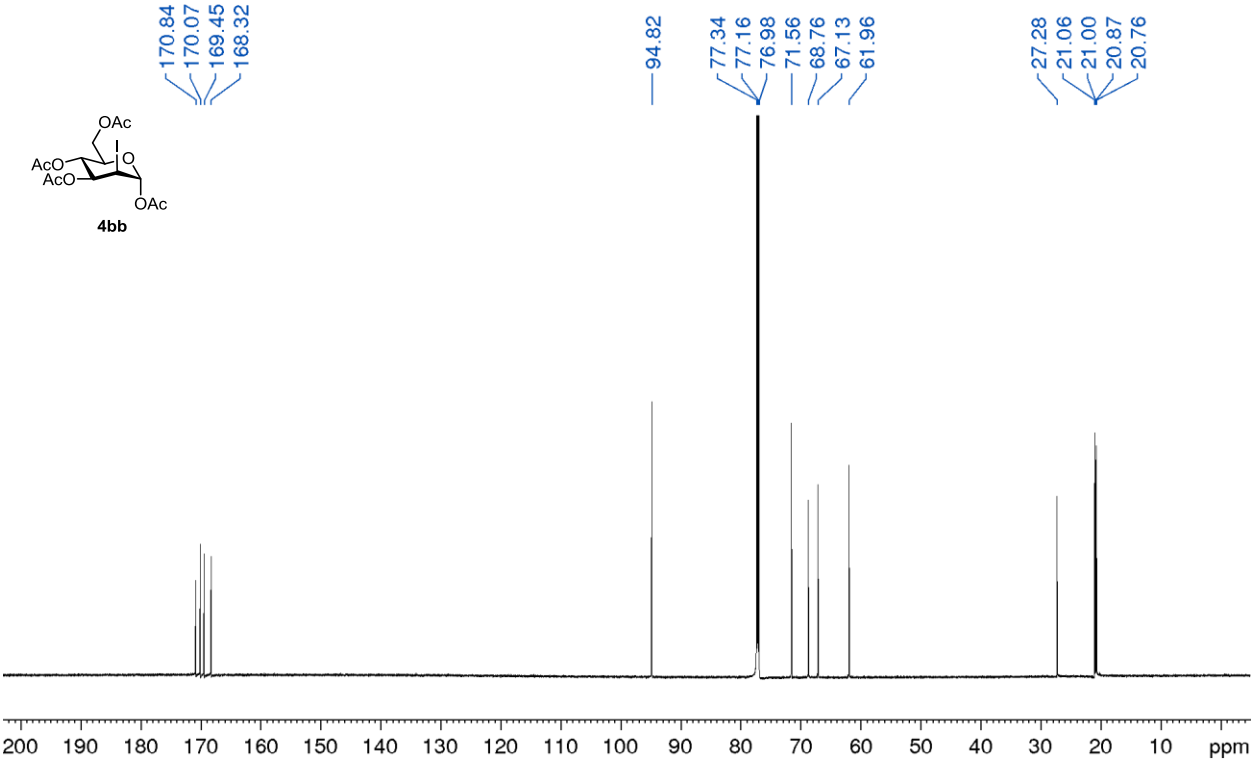
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4ba)



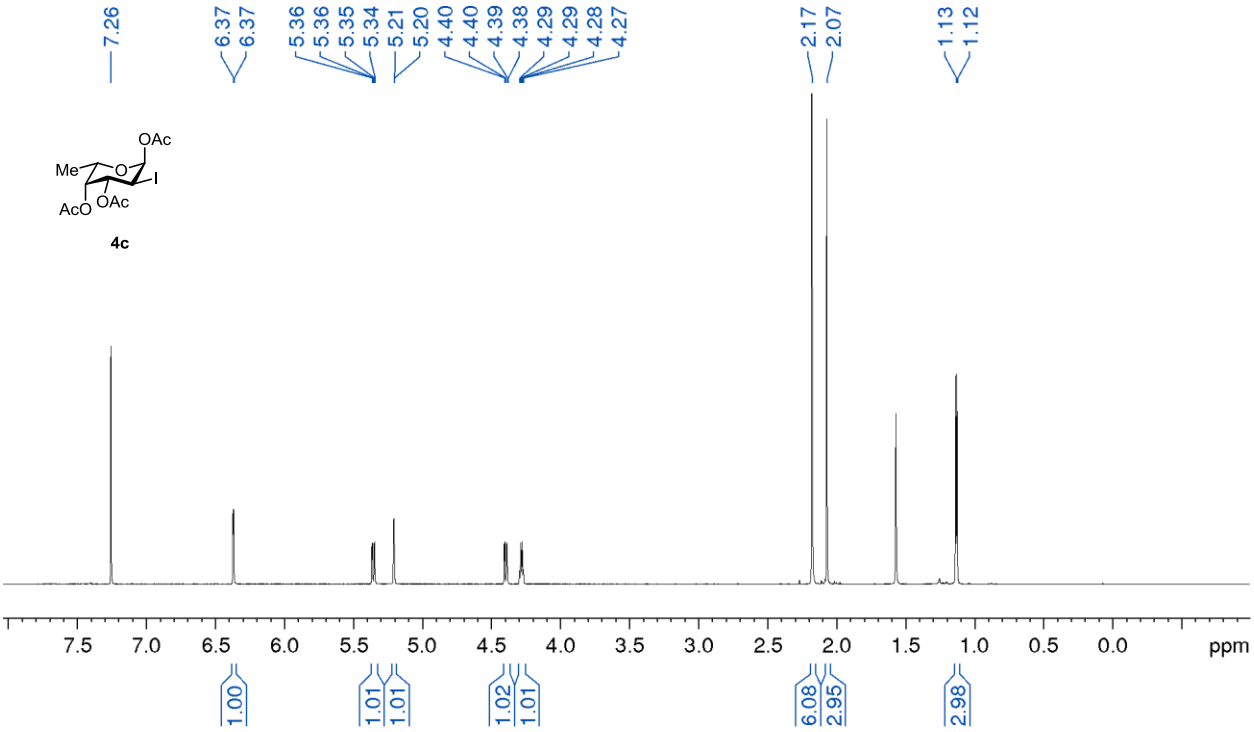
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4bb)



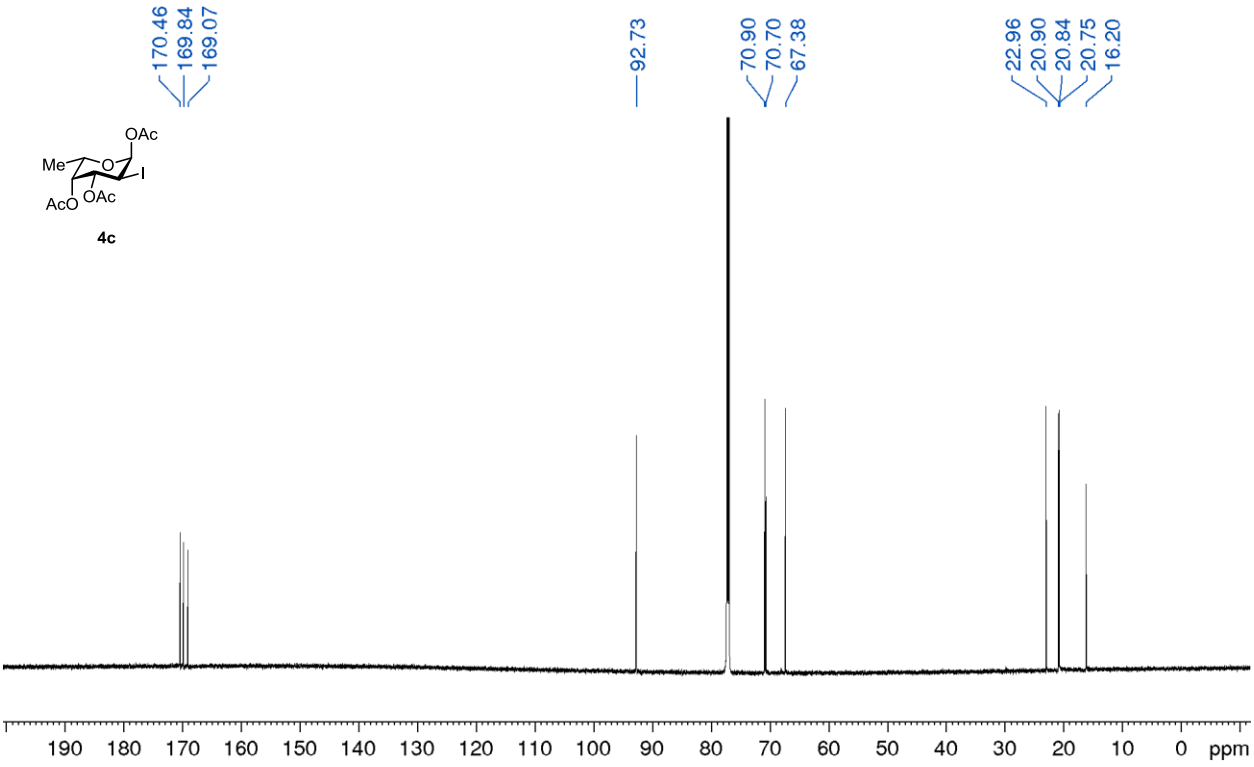
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4bb)



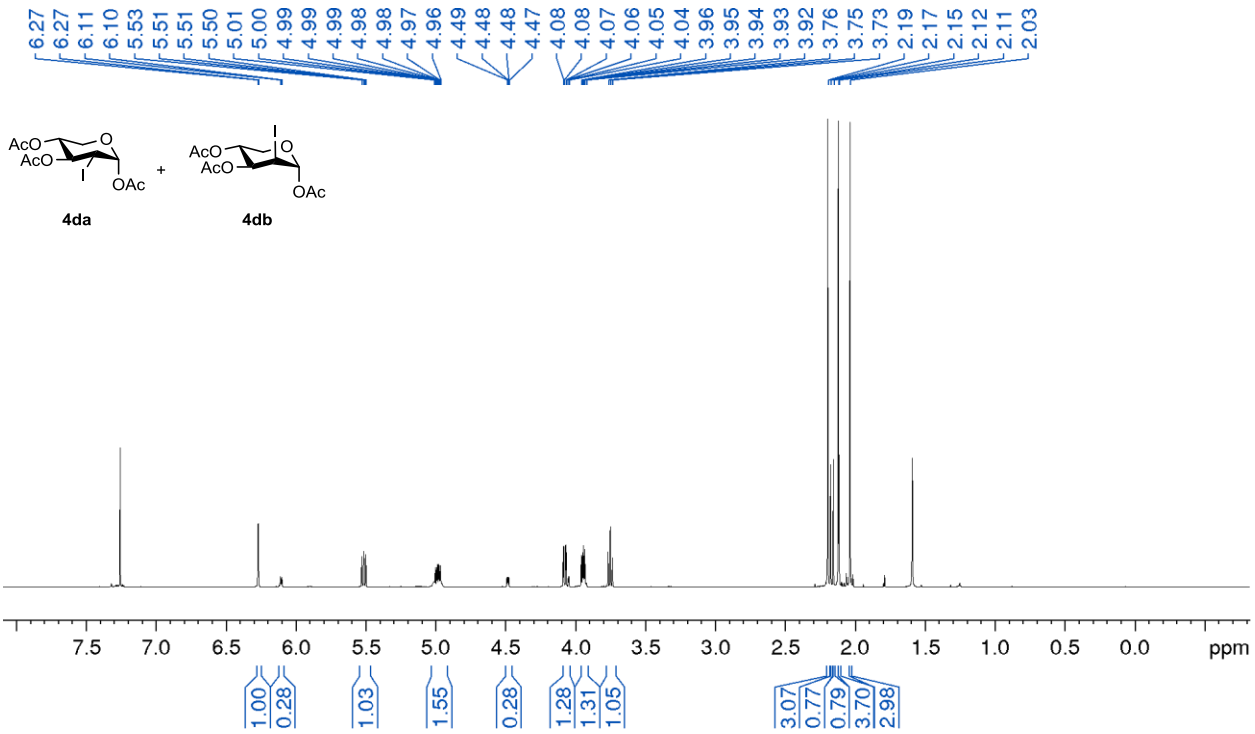
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4c)



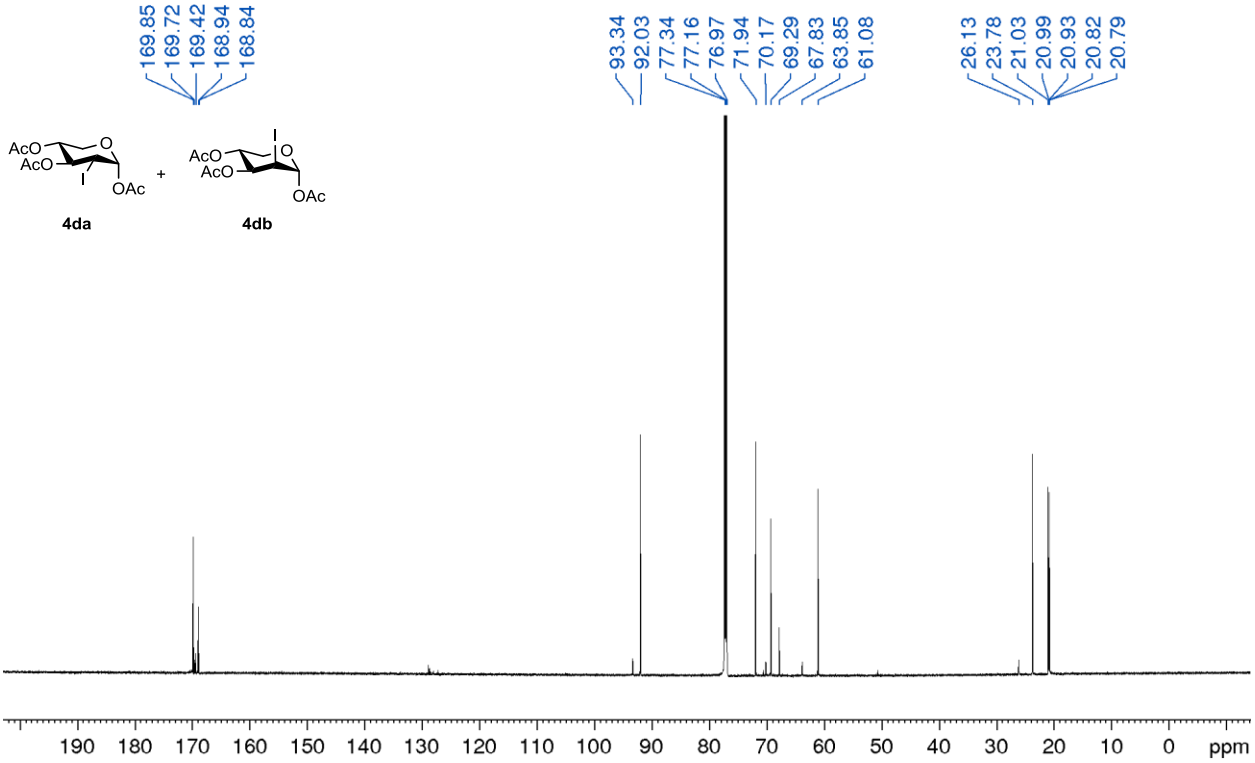
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4c)



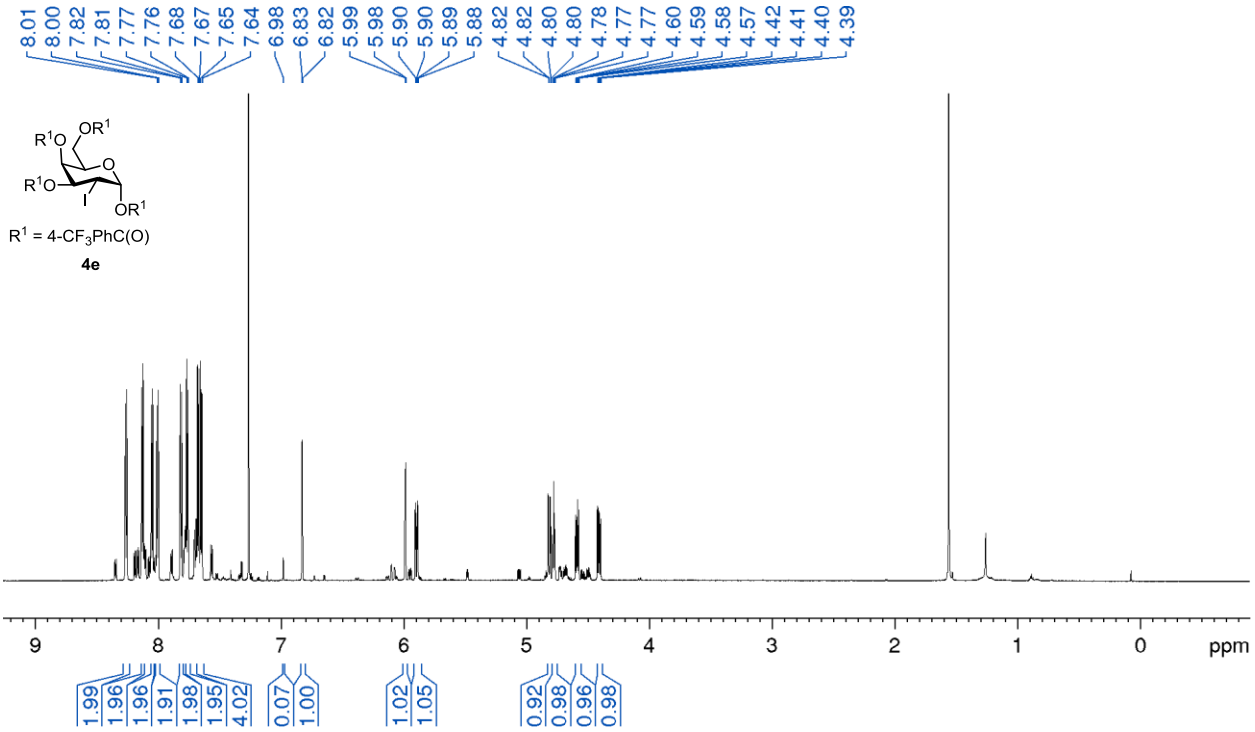
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4da+4db)



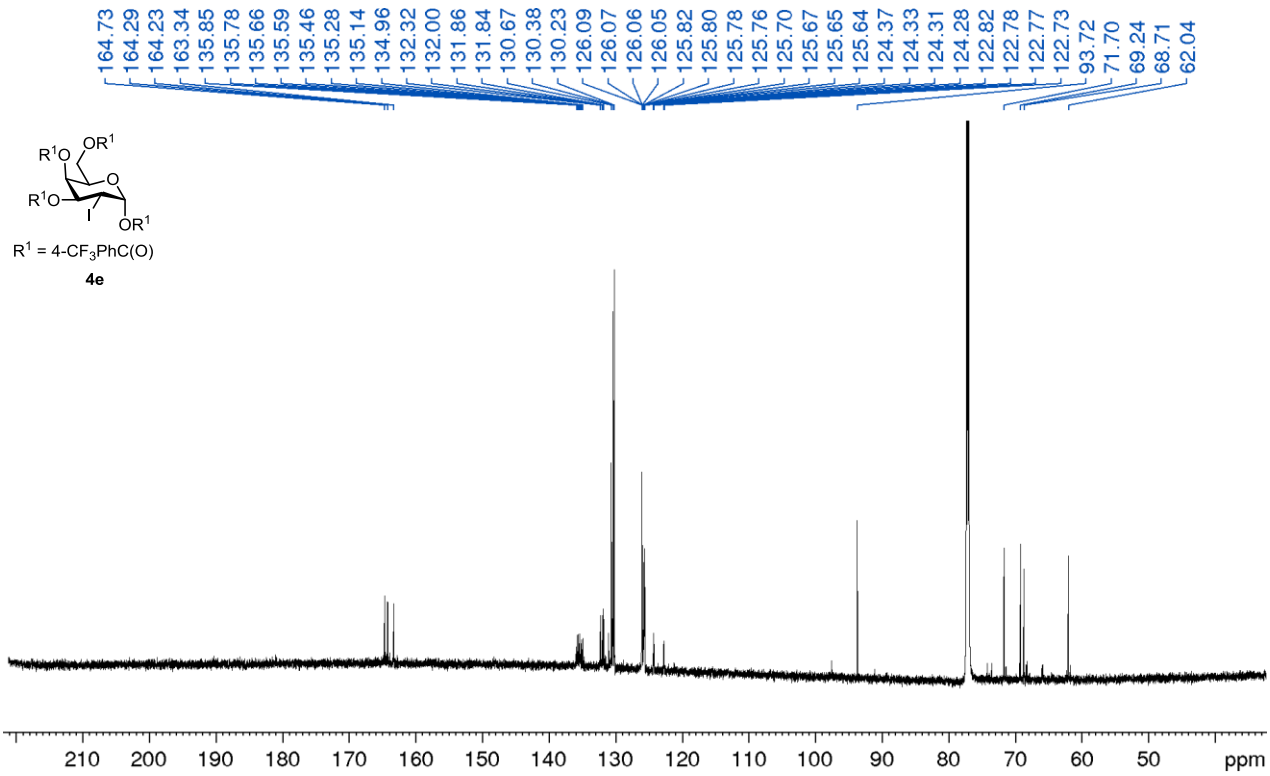
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4da+4db)



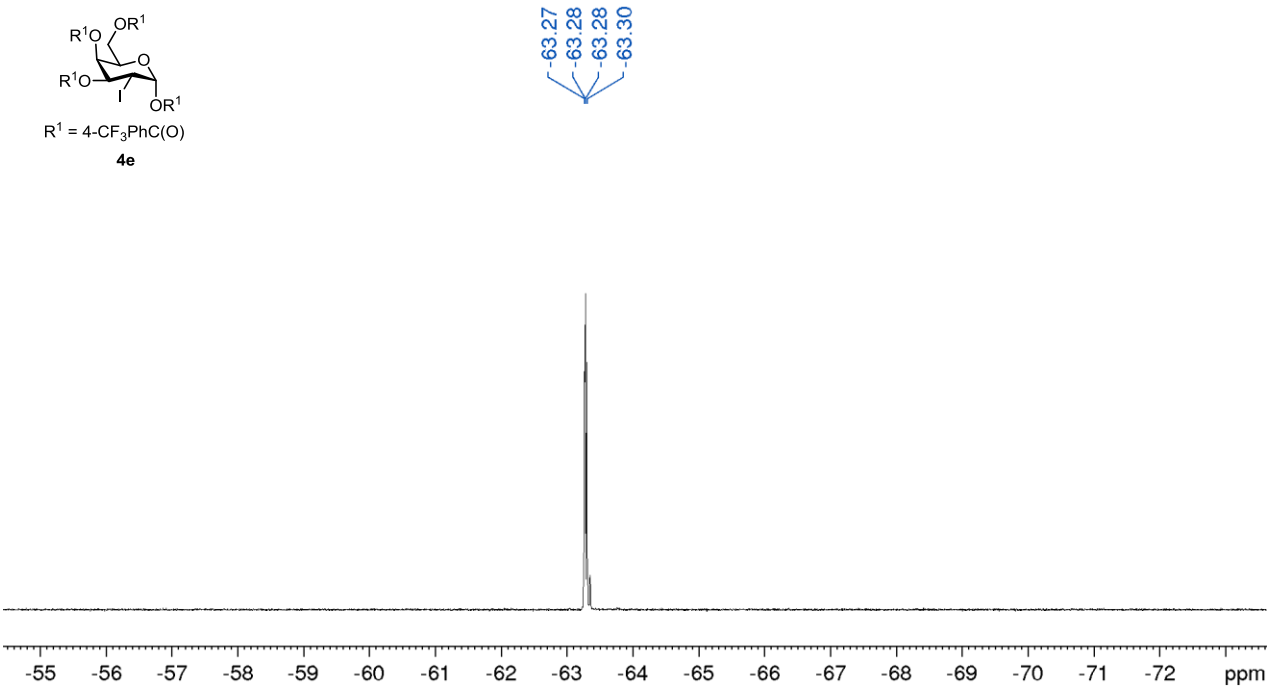
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4e)



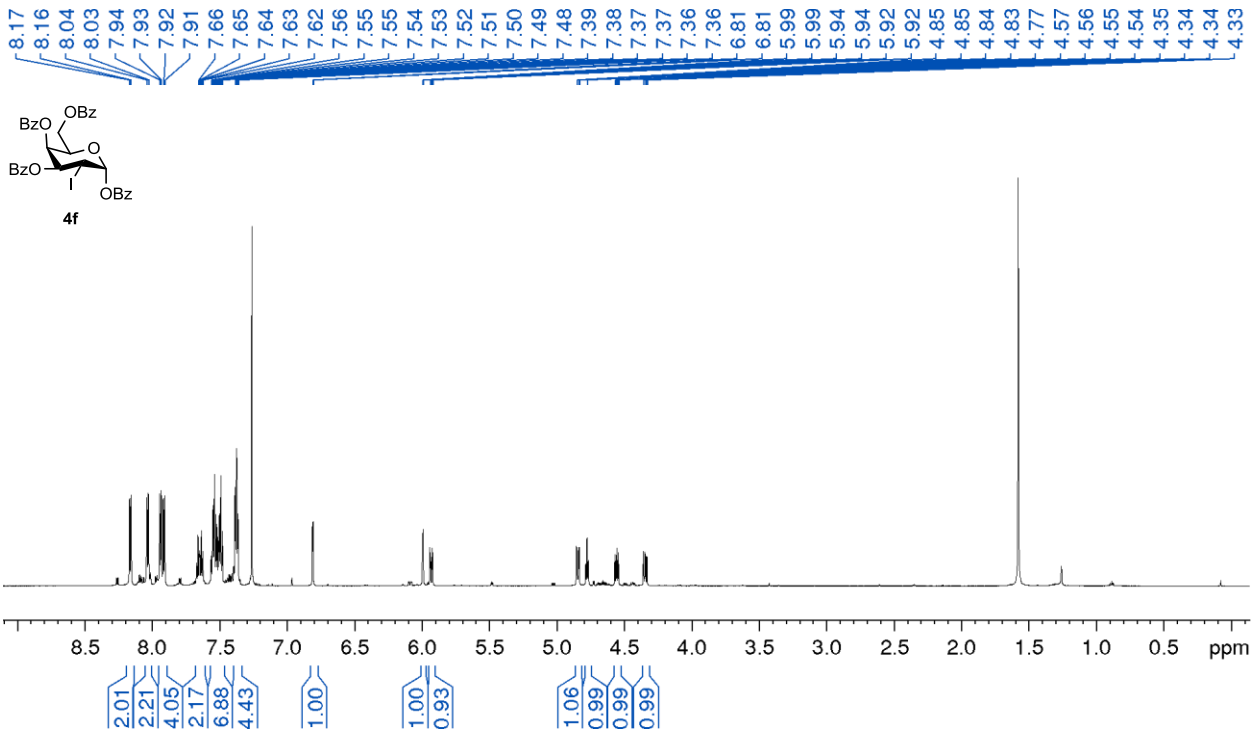
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4e)



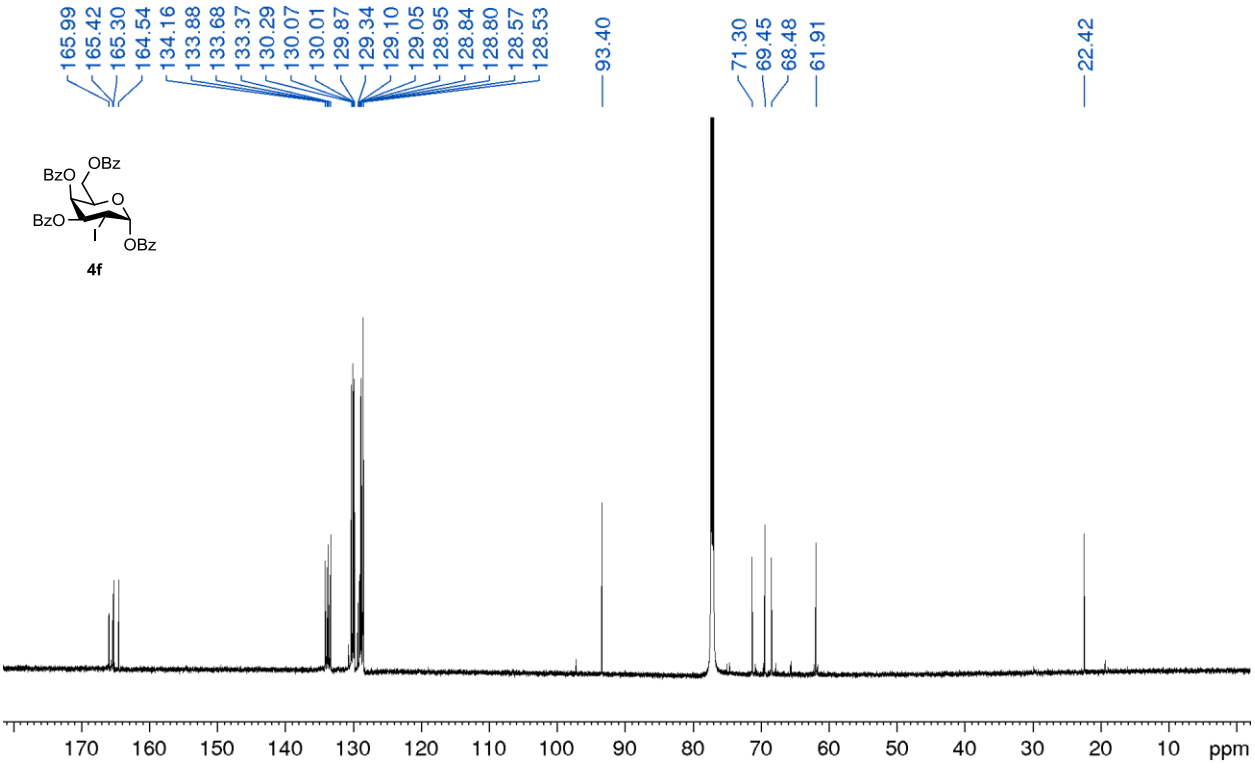
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (4e)



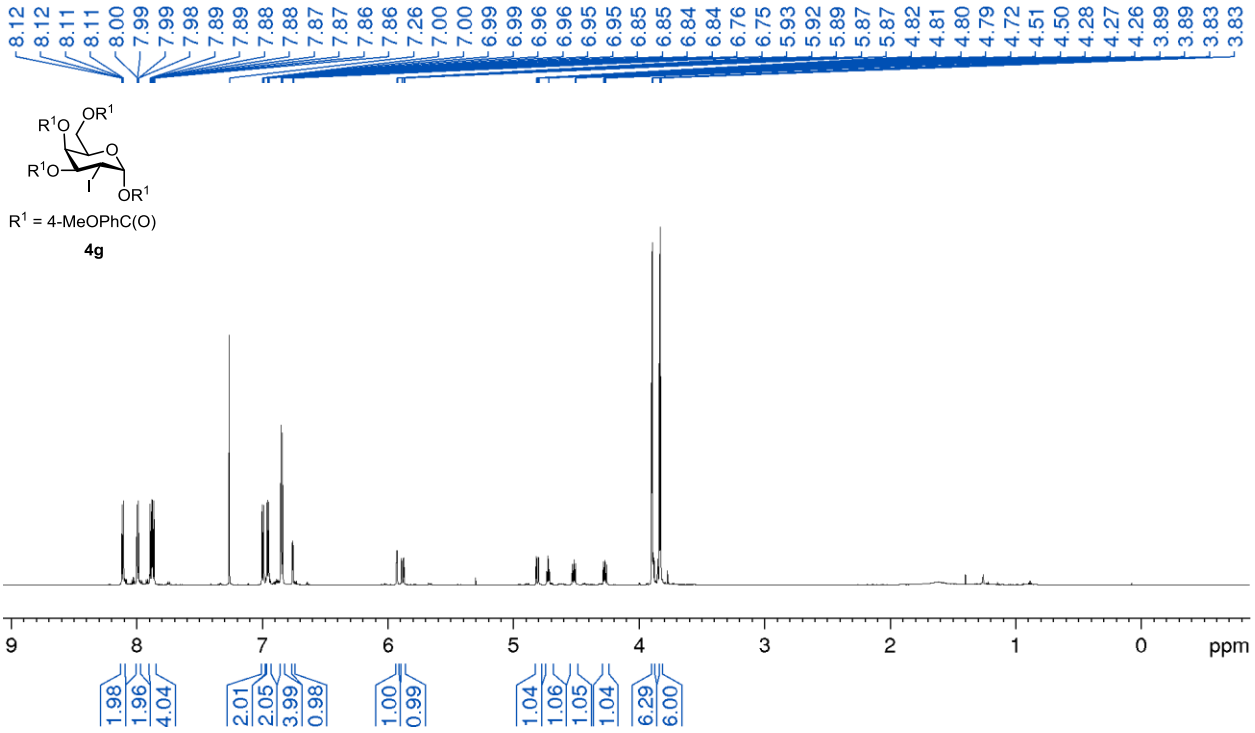
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4f)



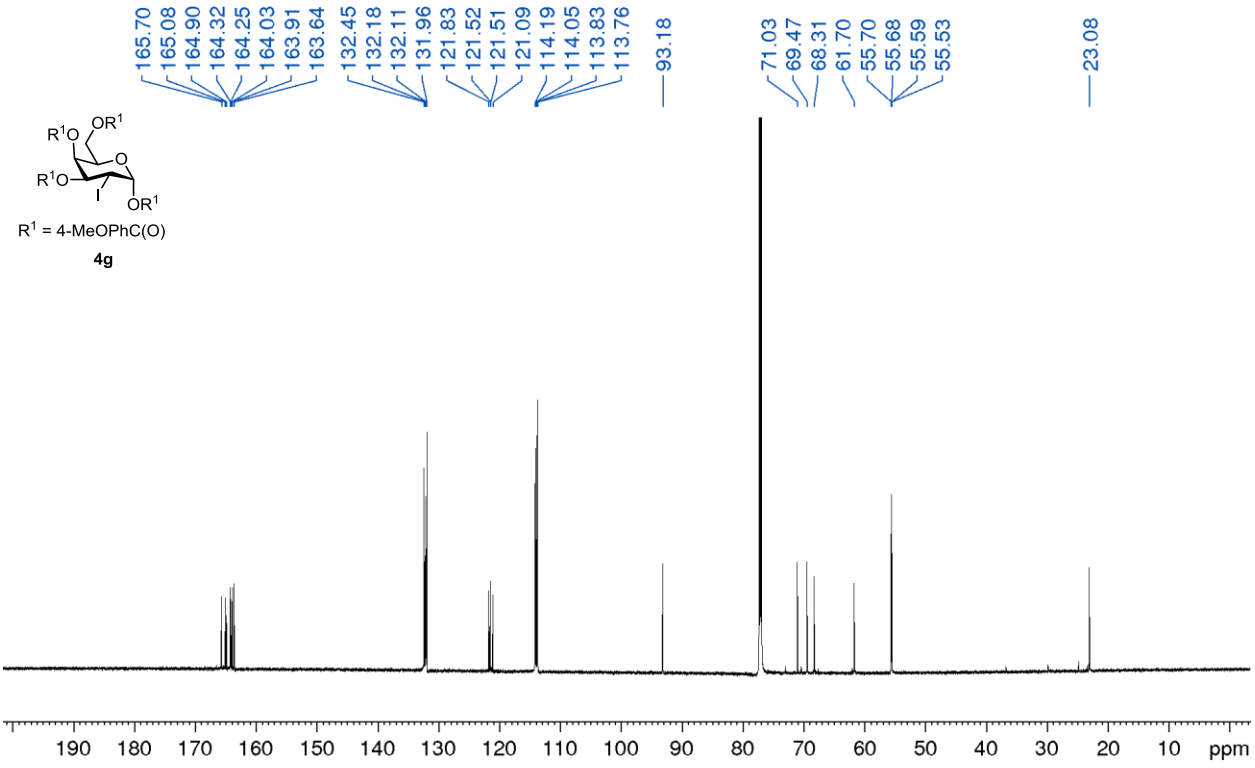
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4f)



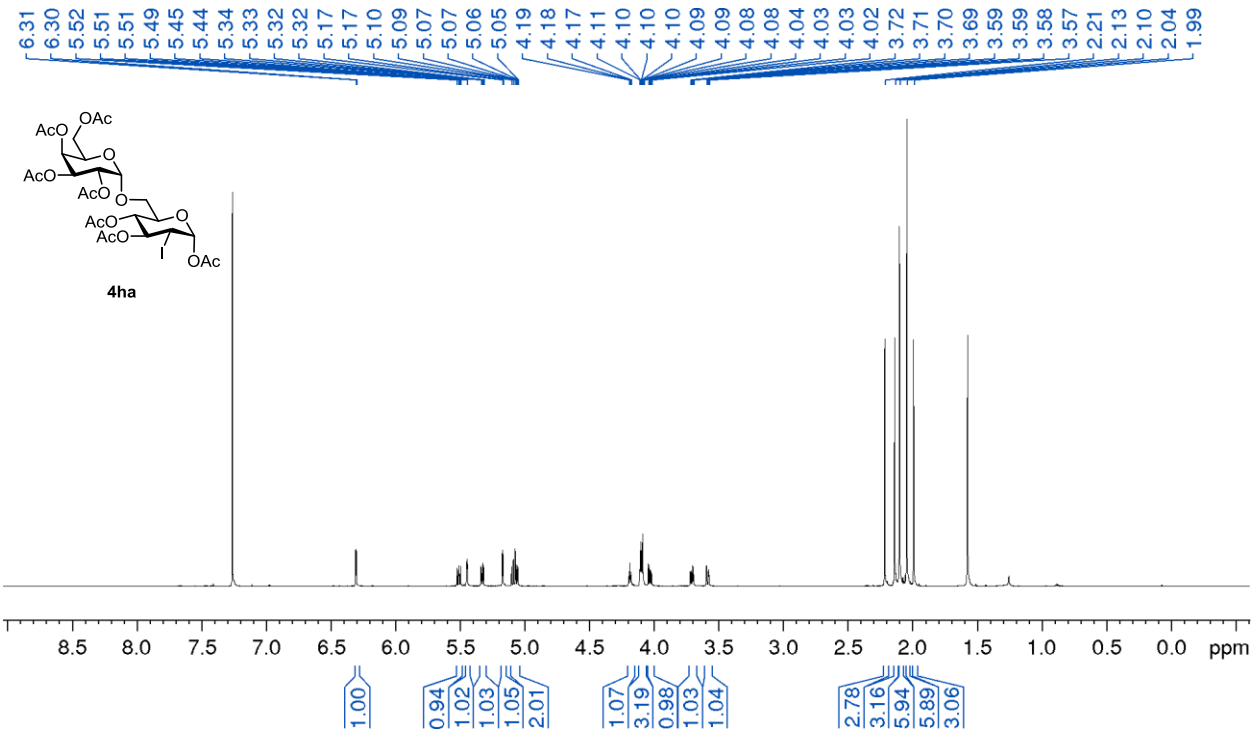
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4g)



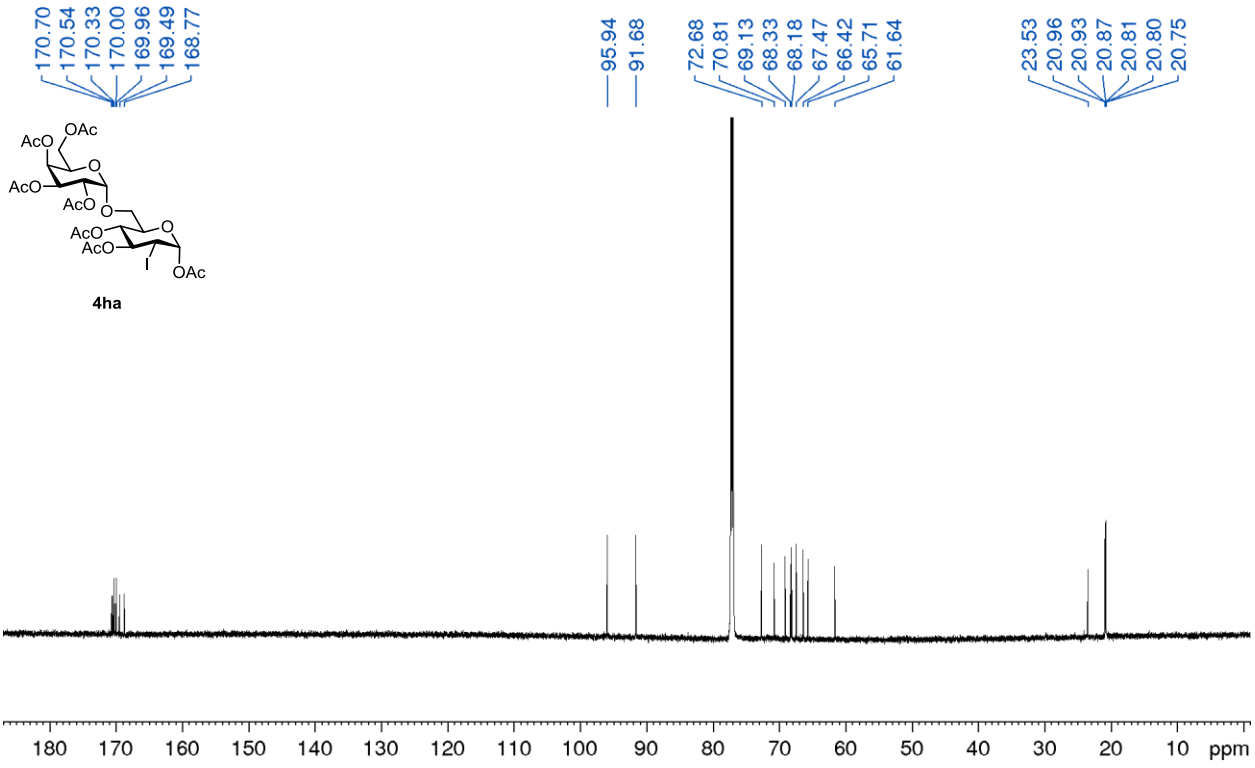
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4g)



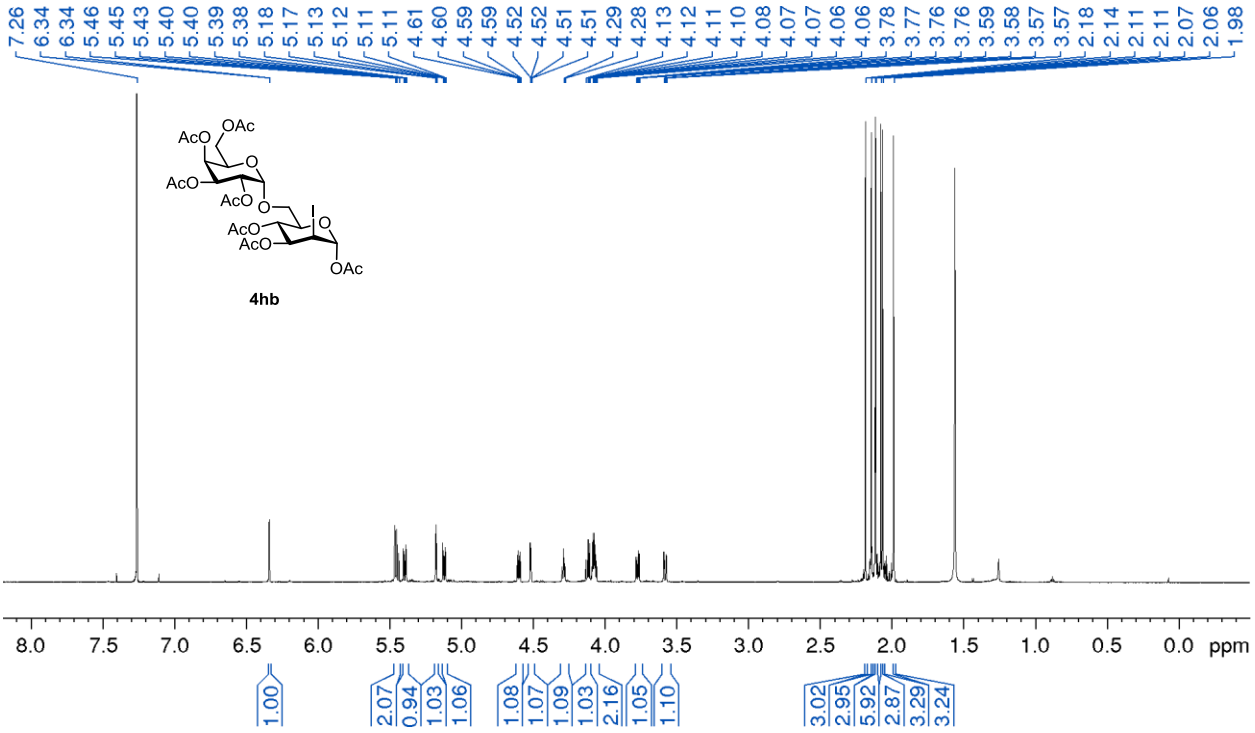
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4ha)



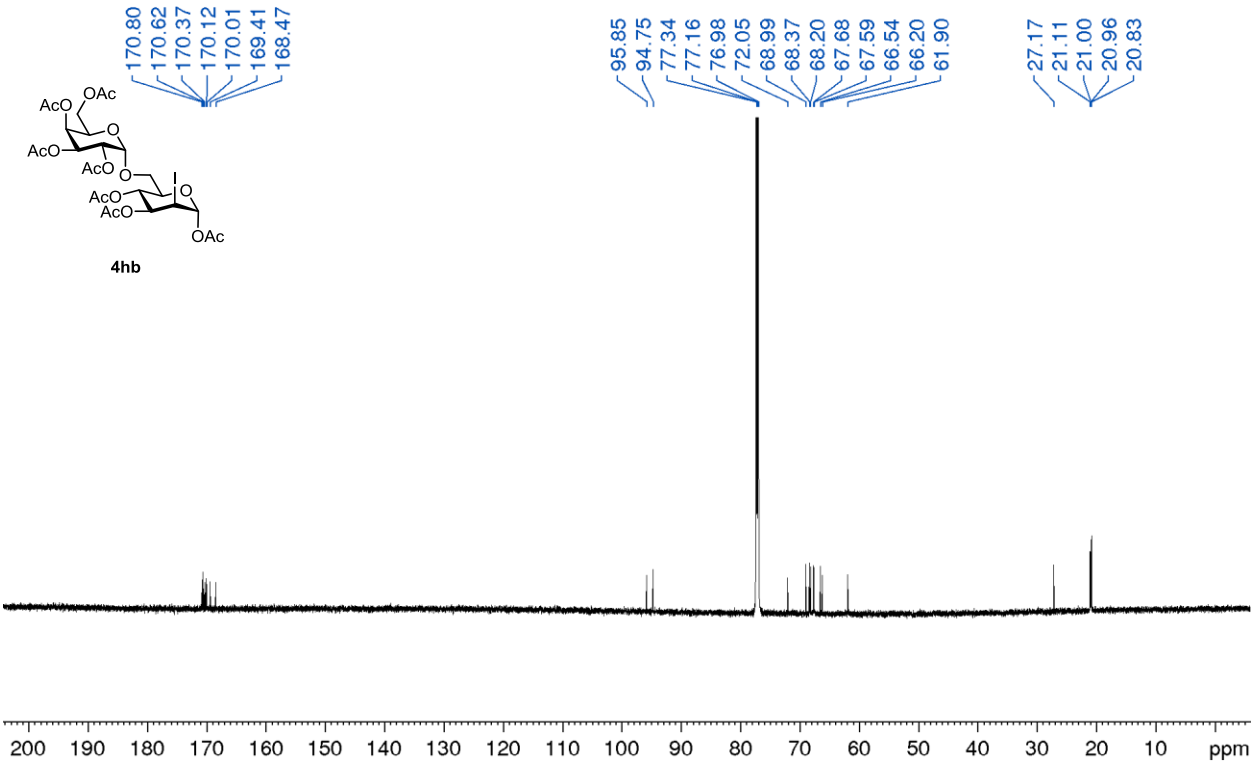
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4ha)



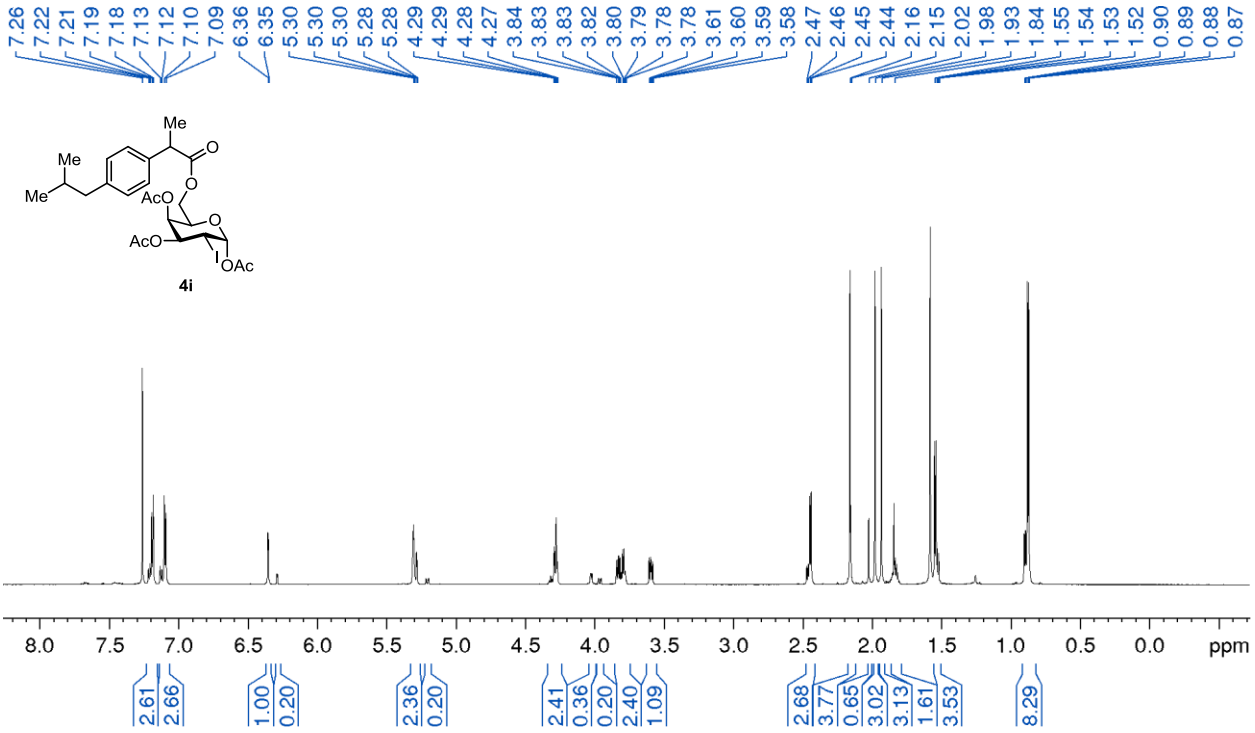
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4hb)



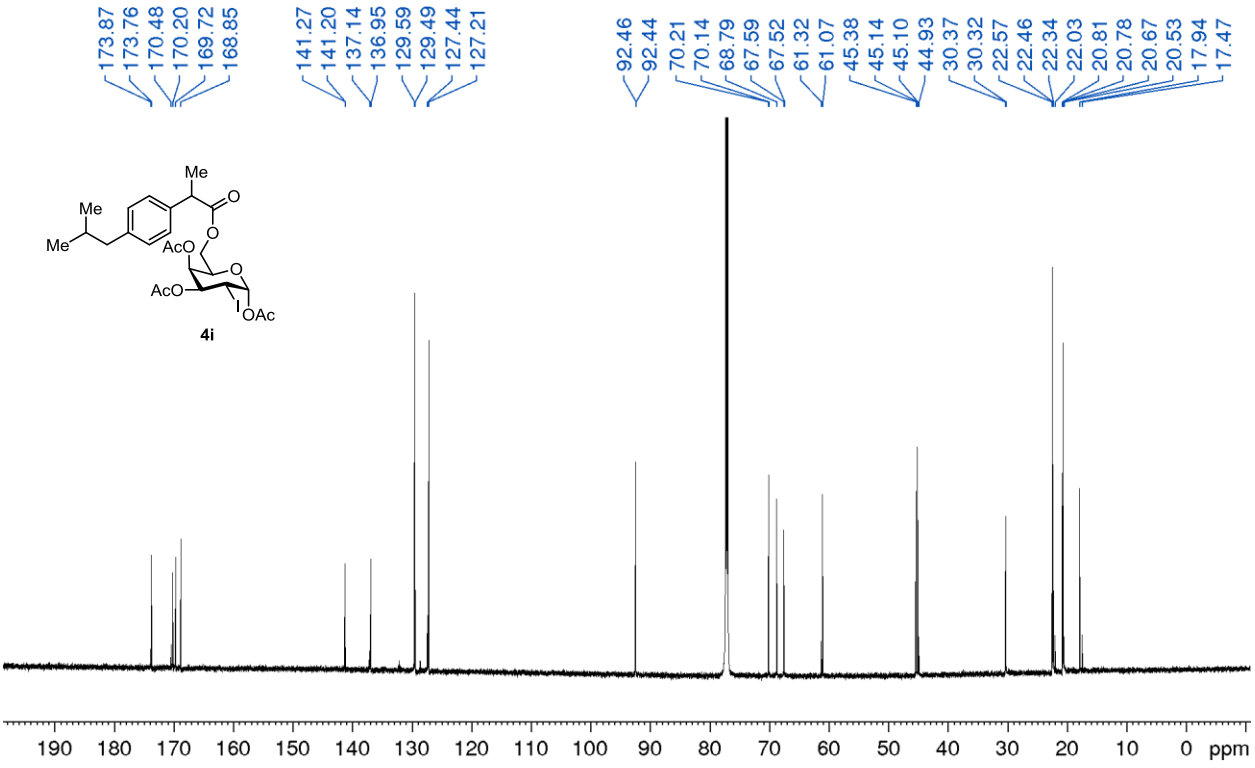
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4hb)



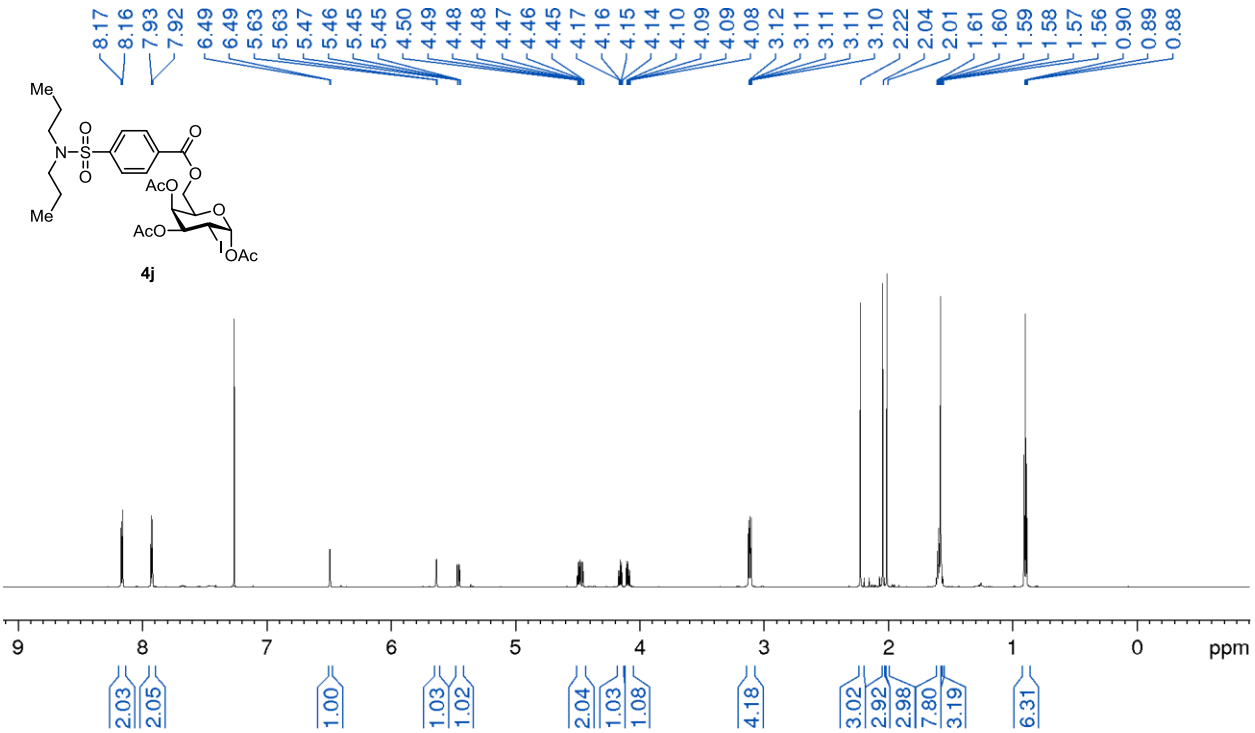
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4i)



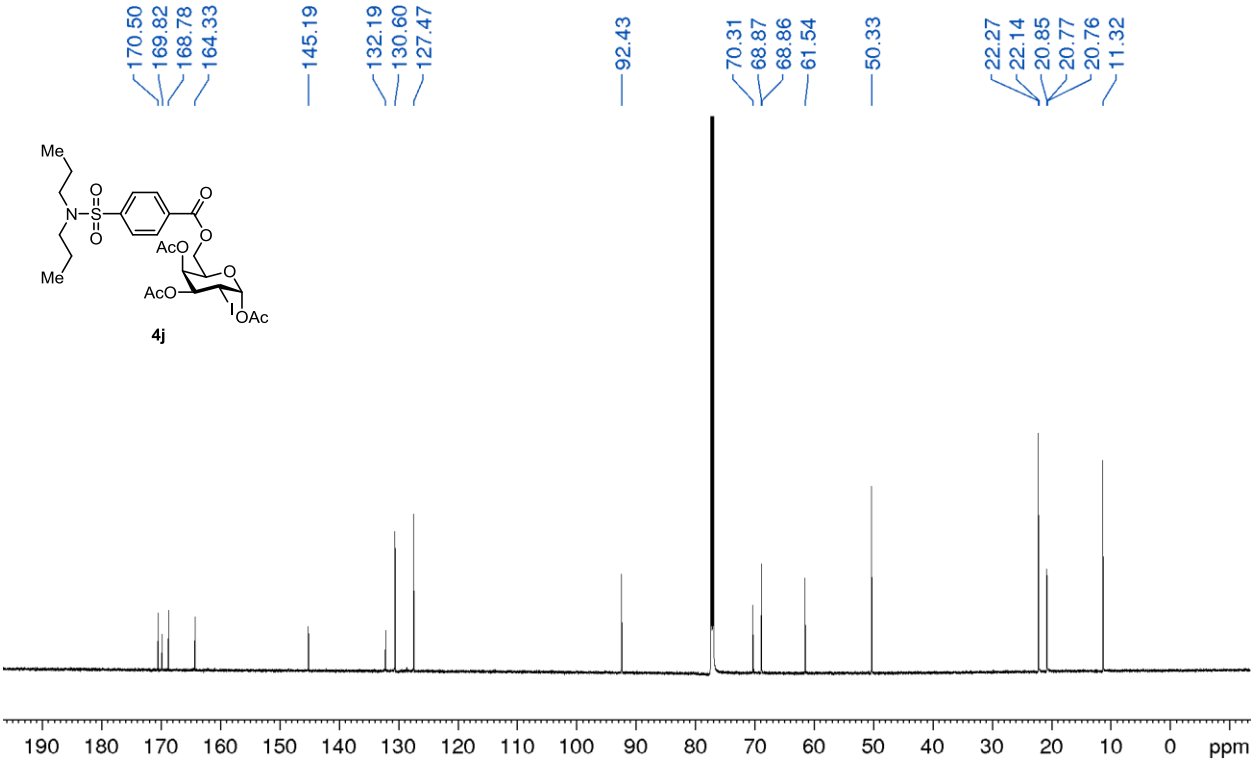
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4i)



^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4j)



^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4j)



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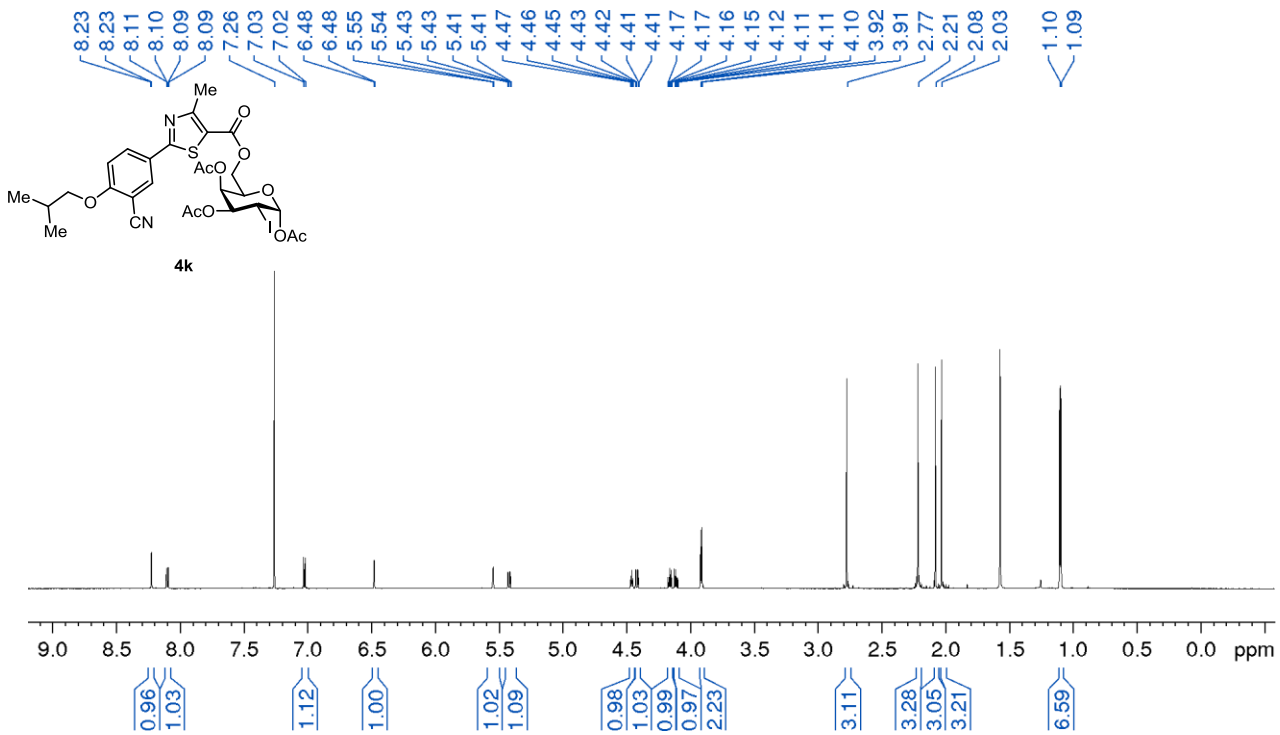
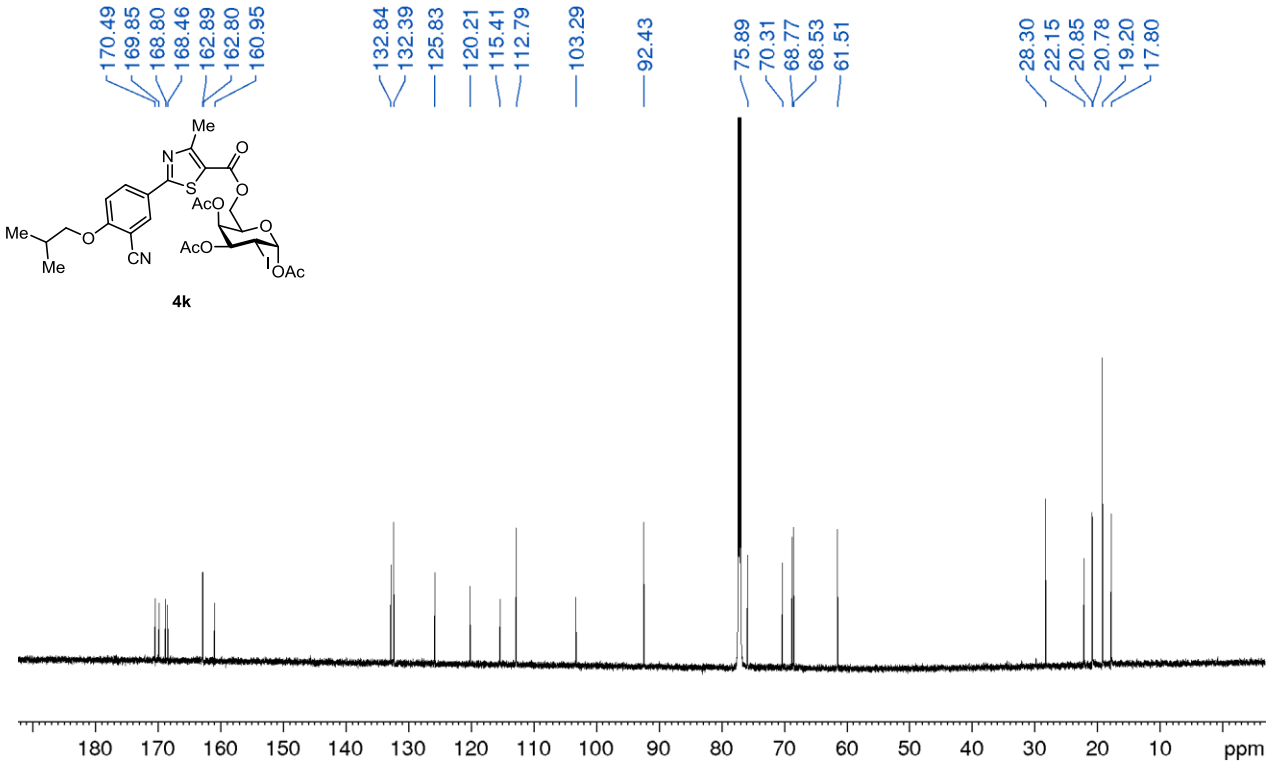


^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4k)



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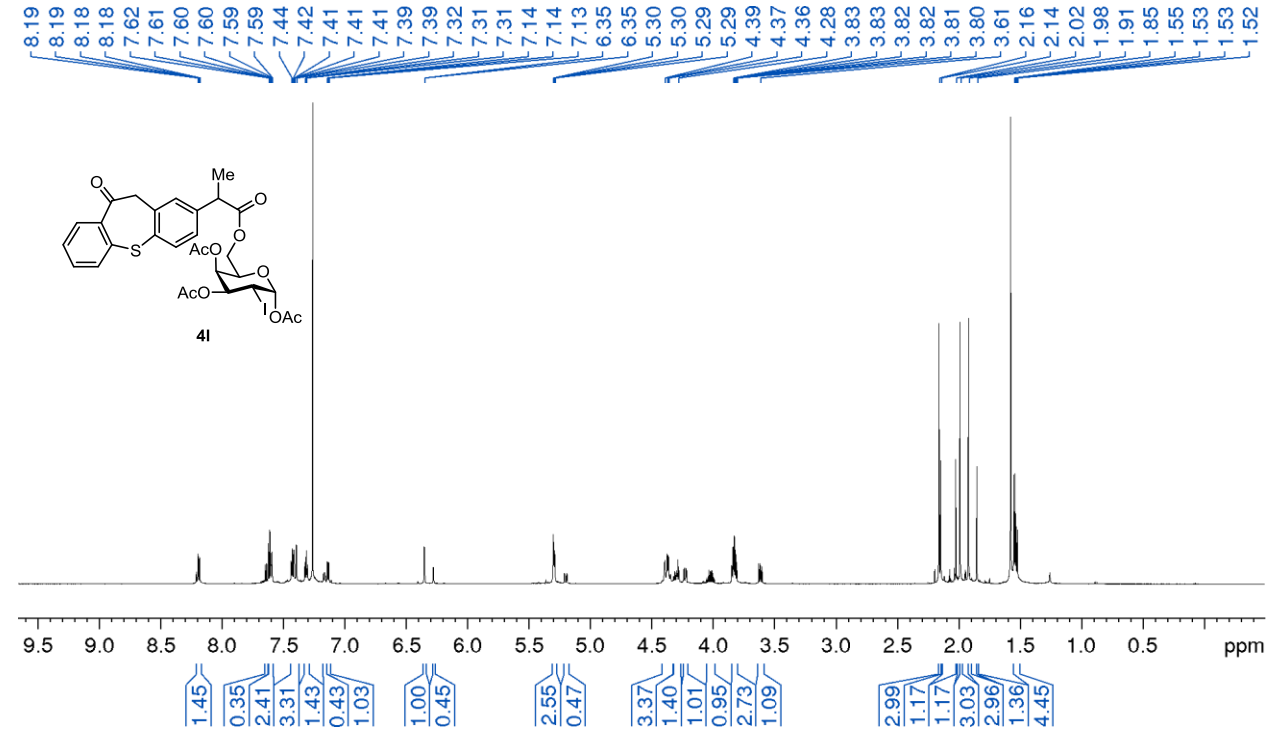
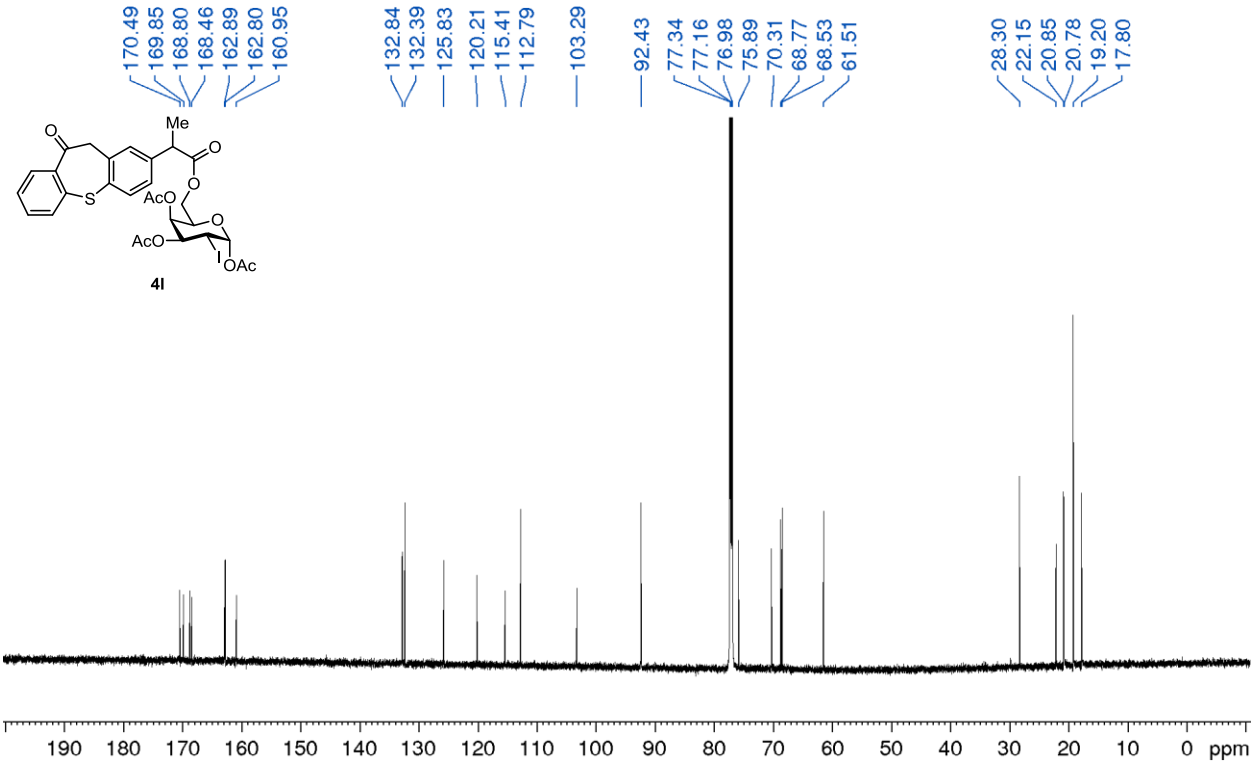


^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4l)



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