Supporting Information

Nickel-Catalyzed Radical Migratory Coupling Enables C-2 Arylation 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.

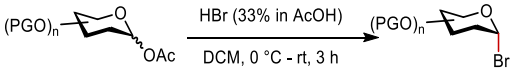
High-resolution mass spectra were performed at Mass Spectrometry Services at Stony Brook University and were obtained using an Agilent LC-UV-TOF mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 °C at the appropriate pressure. Purified compounds were further dried under a high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

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

Experimental Data

Synthesis of 1-Bromo Sugars

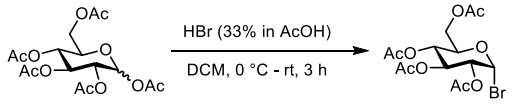
General Procedure A:



1a, 1m, 1n, 1p, 1u

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.

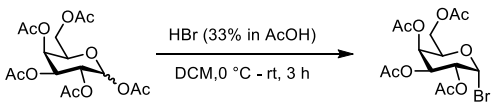
2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1a)



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*-acetyl-α-D-galactopyranosyl bromide (1m)

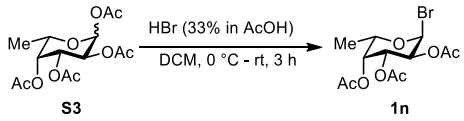


S2 **1m**

The reaction was performed according to the General Procedure A using **S2** (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]

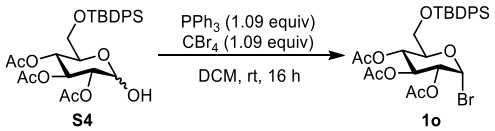
2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl bromide (1n)



S3 **1n**

The reaction was performed according to the General Procedure A using **S3** (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.[4]

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

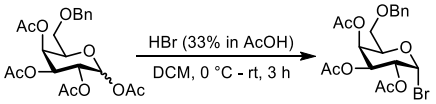


S4 **1o**

To a solution of the **S4** (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 NaHCO3 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.[5]

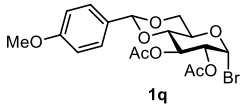
2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-*α*-D-galactopyranosyl bromide (1p)



S5 1p

The reaction was performed according to the General Procedure A using **S5** (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.[6]

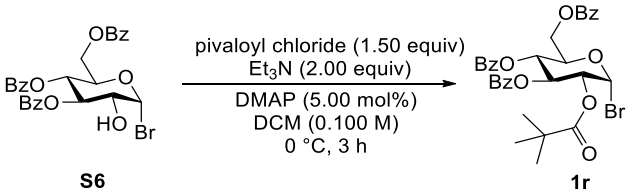
2,3-Di-*O*-acetyl-4,6-*O*-[(*R*)-(4-methoxyphenyl)methylene]-*α*-D-glucopyranosyl bromide (1q)



1q

The title compound was prepared according to the literature procedure.[7] **^{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.[7]

(2R,3R,4S,5R,6R)-2-((benzoyloxy)methyl)-6-bromo-5-(pivaloyloxy)tetrahydro-2H-pyran-3,4-diyl dibenzoate (1r)

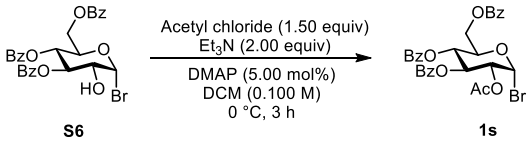


S6 1r

The compound **S6** was prepared according to the literature procedure.[8] To a solution of **S6** (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), pivaloyl

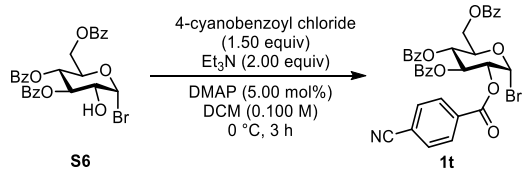
chloride (90.4 mg, 0.75 mmol, 1.50 equiv) and DMAP (3.05 mg, 0.0250 mmol, 5.00 mol%) at 0 ºC. After the reaction mixture was stirred at 0 ºC for 3 h, it was quenched with saturated $NaHCO_3$ solution (6.00 mL) and extracted with DCM (2 × 50 mL). The combined organic layers were washed with brine, dried 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 [5:1 (v/v)] to afford the title compound (256 mg, 0.40 mmol, 80%) as a white solid. $\mathbf{R_f}$ = 0.50 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.06 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 16.1, 7.5 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 (dt, *J* = 13.7, 4.6 Hz, 4H), 6.70 (d, *J* = 4.0 Hz, 1H), 6.11 (t, *J* = 9.8 Hz, 1H), 5.73 (dt, *J* = 13.9, 9.9 Hz, 1H), 5.06 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.70 – 4.58 (m, 2H), 4.48 (dd, *J* = 12.4, 4.4 Hz, 1H), 1.08 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 177.47, 166.15, 165.55, 165.22, 133.78, 133.55, 133.39, 130.09, 129.95, 129.85, 129.59, 129.01, 128.67, 128.64, 128.59, 128.58, 86.90, 72.76, 70.86, 70.63, 68.07, 62.09, 38.73, 26.87. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{32}BrO_9$ [$(M + H)^+$], 639.1224, found, 639.1227.[8]

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



The reaction was performed according to the same procedure as **1r**. acetyl chloride (58.9 mg, 0.750 mmol, 1.50 equiv). 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 title compound (194 mg, 0.330 mmol, 65%) as white solid. $\mathbf{R_f}$ = 0.70 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, 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 ºC, 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.

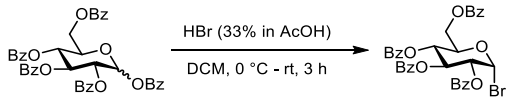
3,4,6-Tri-*O*-Benzoyl-2-*O*-(4-cyanobenzoyl)-α-D-glucopyranosyl bromide (1t)



The reaction was performed according to the same procedure as synthesizing **1r**. 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.

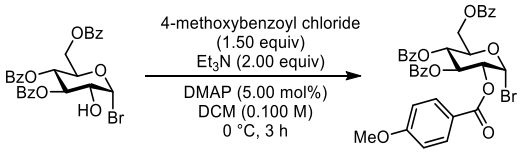
2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (1u)



S7 **1u**

The reaction was performed according to the General Procedure A using **S7** (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.[9]

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

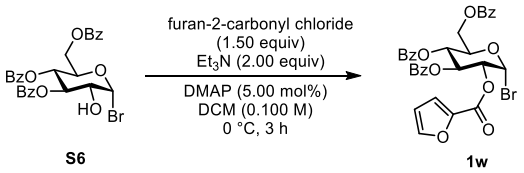


S6 **1v**

The reaction was performed according to the same procedure as synthesizing **1r**. 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

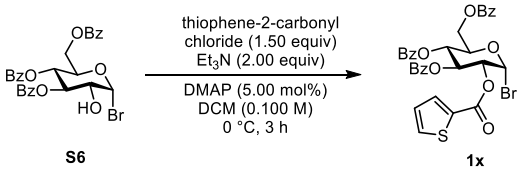
(t, *J* = 7.4 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.24 (t, *J* = 9.7 Hz, 1H), 5.81 (t, *J* = 9.9 Hz, 1H), 5.29 (dd, *J* = 9.8, 3.4 Hz, 1H), 4.72 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.51 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 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 (1w)



The reaction was performed according to the same procedure as synthesizing **1r**. 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.

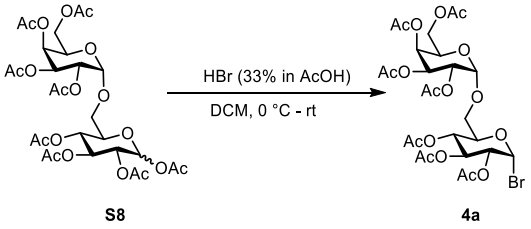
3,4,6-Tri-*O*-Benzoyl-2-*O*-(thiophene-2-carbonyl)-α-D-glucopyranosyl bromide (1x)



The reaction was performed according to the same procedure as synthesizing **1r**. 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,

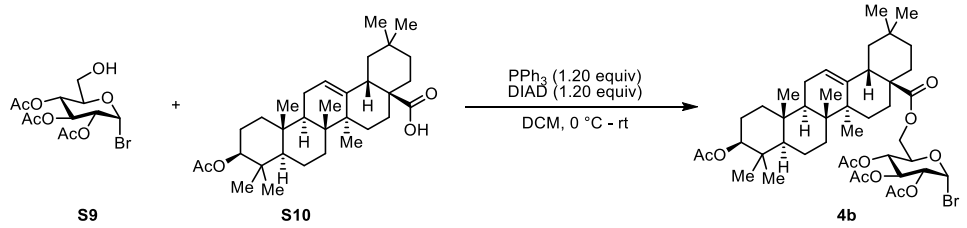
165.22, 160.95, 135.13, 134.24, 133.80, 133.49, 133.42, 131.81, 130.09, 129.98, 129.91, 129.58, 128.97, 128.65, 128.61, 128.53, 128.21, 86.83, 72.83, 71.70, 70.66, 68.10, 62.06. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{26}BrO_9S$ [$(M + H)^+$], 665.0475, found, 665.0477.

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



The reaction was performed according to the General Procedure A using **S8** (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.[9]

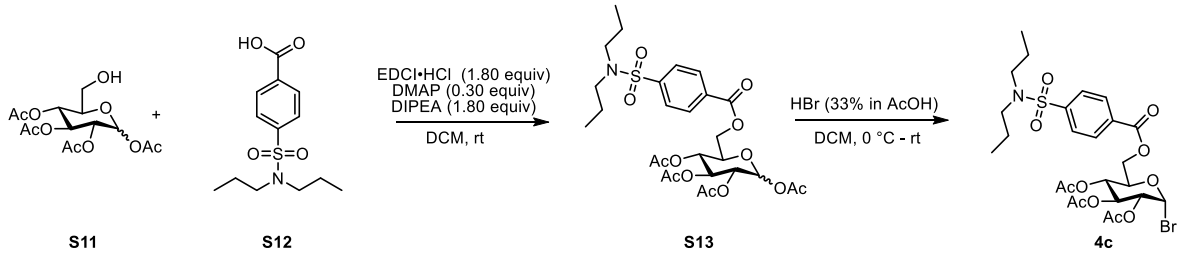
2,3,4-Tri-*O*-acetyl-6-*O*-[((4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-4a-carbonyl)]-α-D-glucopyranosyl bromide (4b)



To a solution of **S9** (147 mg, 0.400 mmol, 1.00 equiv) and **S10** (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.

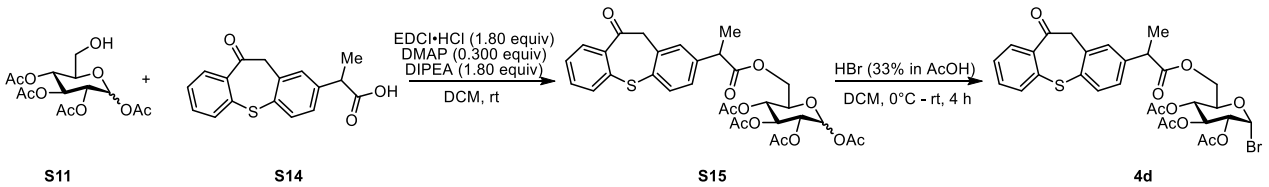
2,3,4-Tri-*O*-acetyl-6-*O*-[(4-(*N*,*N*-dipropylsulfamoyl)benzoyl)]-*α*-D-glucopyranosyl bromide (4c)



To a solution of compound **S11** (294 mg, 0.800 mmol, 1.00 equiv) in dry DCM (4.00 mL, 0.20 M) were added Probenecid **S12** (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 **S13** (209 mg, 0.340 mmol, 46.4% yield) as a colorless oil.

4c was synthesized according to the General Procedure A using **S13** (209 mg, 0.340 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 (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-(10-oxo-10,11-dihydrodibenzo[*b,f*]thiepin-2-yl)propanoyl)]-α-D-glucopyranosyl bromide (4d)

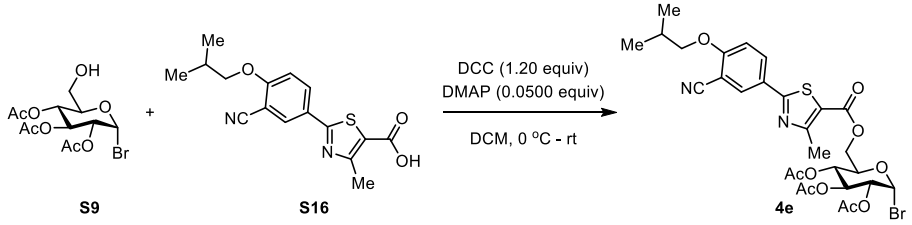


S11 S14 S15 4d

To a solution of compound **S11** (452 mg, 1.30 mmol, 1.00 equiv) in dry DCM (6.5 mL, 0.20 M) were added Zaltoprofen **S14** (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 **S15** (700 mg, 1.11 mmol, 86% yield) as a colorless oil.

4d was synthesized according to the General Procedure A using **S15** (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.

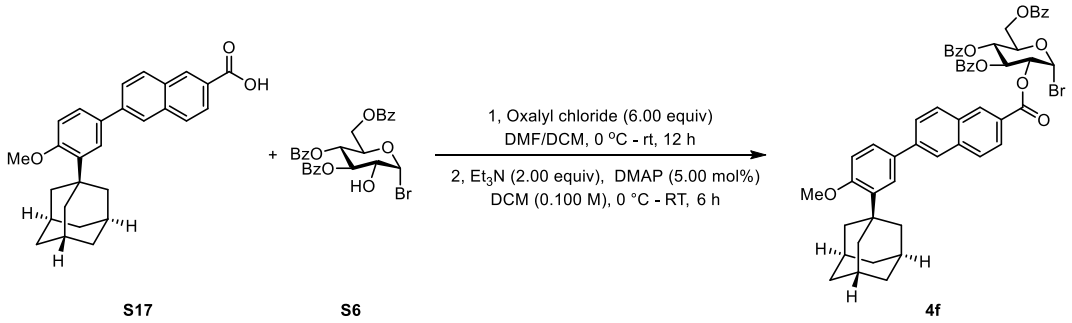
2,3,4-Tri-*O*-acetyl-6-*O*-[(2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)]-α-D-glucopyranosyl bromide (4e)



S9 S16 4e

A suspension of febuxostat **S16** (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 °C. After stirring for 10 min at 0 °C, **S9** (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 °C, 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 °C, 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.

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



S17 S6 4f

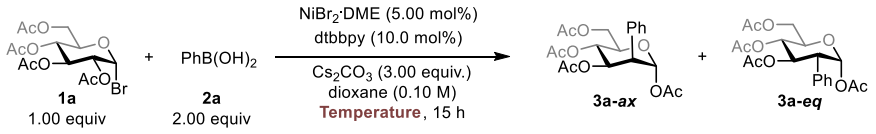
To a solution of Adapalene **S17** (248 mg, 0.6 mmol, 1.00 equiv) in dry DCM (6 mL, 0.10 M) were added DMF (60.0 uL) and oxalyl chloride (457 mg, 6.60 mmol, 6.00 equiv) at 0 °C. After stirring at room temperature for 12 h, the solvent was removed under vacuum and the residue was directly used for next 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), **S6** (278 mg, 0.500 mmol, 1.00 equiv) and DMAP (3.05 mg, 0.0250 mmol, 5.00 mol%) at 0 °C. 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 **4f** (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 °C, 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.

Nickel-Catalyzed C-2 Arylation Reaction

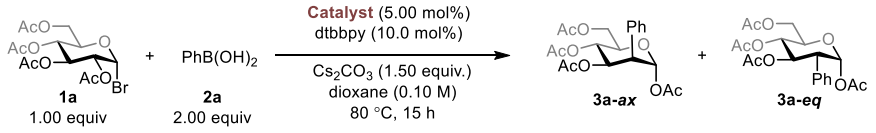
Reaction Optimization:

Table S1. Different Reaction Temperature



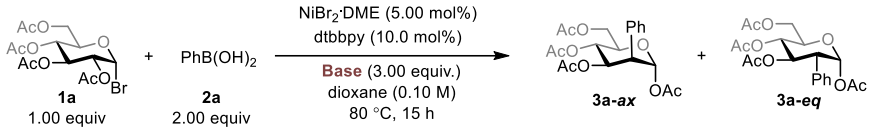
Entry	Temperature	Yield of 3a (%)	ax:eq
1	rt	<1	-
2	40 °C	7	2.5:1
3	60 °C	28	2.5:1
4	80 °C	43	2.3:1
5	100 °C	13	1.4:1

Table S2. Different Catalysts



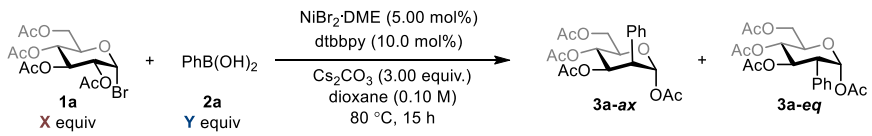
Entry	Catalyst	Yield of 3a (%)	ax:eq
1	$NiBr_2$·DME	46	2.1:1
2	$NiCl_2$·DME	43	2.3:1
3	$Ni(cod)_2$	29	2.2:1
4	$Ni(NO_2)_2·6H_2O$	20	3.0:1
5	$Ni(NH_3)_2(SO_4)_2$	0	-
6	Ni powder	0	-
7	$NiSO_4·6H_2O$	0	-
8	$Ni(OAc)_2·4H_2O$	39	2.0:1
9	$Ni(acac)_2$	13	1.6:1
10	$NiCl_4·6H_2O$	0	-
11	NiO	0	-

Table S3. Different Bases



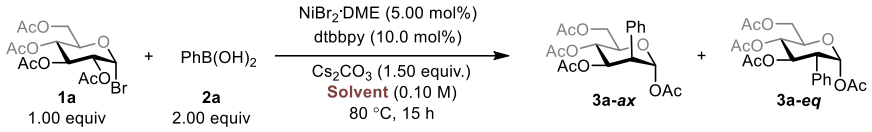
Entry	Base	Yield of 3a (%)	ax:eq
1	Cs_2CO_3	43	2.1:1
2	K_2CO_3	31	2.1:1
3	Na_2CO_3	26	3.3:1
4	Li_2CO_3	0	-
5	CsOAc	0	-
6	KOAc	0	-
7	NaOAc	0	-
8	LiOAc	0	-
9	K_3PO_4	0	-
10	Li_3PO_4	21	-
11	CsF	23	-
12	$PhCO_2Na$	0	-
13	t-BuOK	0	-
14	TMSOK	0	-
15	2,6-lutidine	0	-
16	DIPEA	0	-

Table S4. Different Stoichiometric Ratio



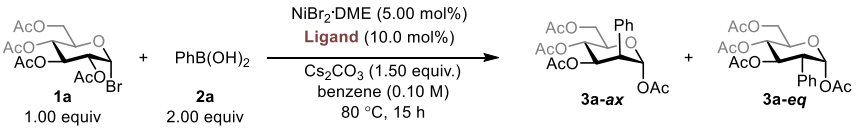
Entry	X	Y	Yield of 3a (%)	ax:eq
1	1.0	1.0	28	2.1:1
2	1.0	2.0	42	2.2:1
3	1.0	3.0	39	2.5:1
4	2.0	1.0	18	3.5:1
5	3.0	1.0	trace	-

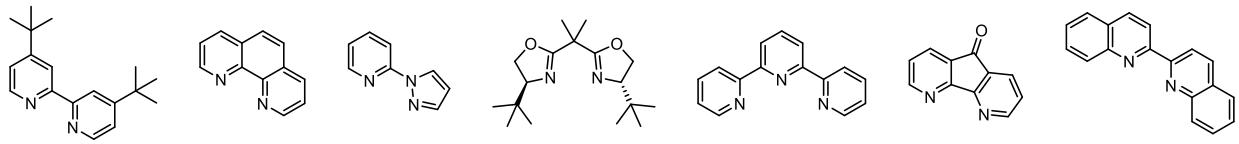
Table S5. Different Solvents



Entry	Solvent	Yield of 3a (%)	ax:eq
1	dioxane	37	3.1:1
2	*i*-PrOAc	16	3.0:1
3	triflourotoluene	36	3.5:1
4	DCE	44	2.2:1
5	MeCN	0	-
6	DMF	0	-
7	DMSO	0	-
8	DMA	0	-
9	CHCl3	0	-
10	THF	17	2.6:1
11	chlorobenzene	0	-
12	benzene	57	3.3:1
13	toluene	32	2.2:1
14	*t*-BuOH	0	-
15	DME	26	3.3:1
16	dibutyl ether	0	-

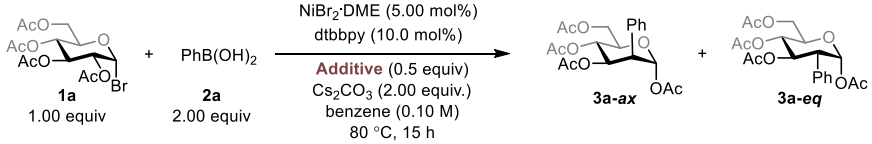
Table S6. Different Ligands





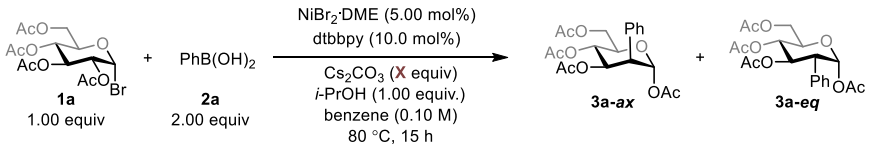
L1	L2	L3	L4	L5	L6	L7
50%, 2.6:1.0	0%	19%, 1.7:1.0	25%, 1.5:1.0	0%	0%	trace

Table S7. Different Alcohol Additives



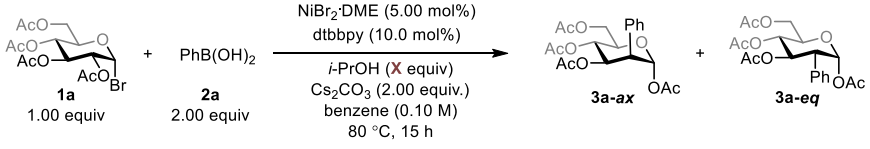
Entry	Additive	Yield of 3a (%)	ax:eq
1	*i*-PrOH	87	3.0:1
2	*t*-BuOH	35	3.4;1
3	$PhCH_2CH_2OH$	53	2.5:1
4	2-Methylbutan-2-ol	49	3.1:1

Table S8. Different Amount of Base



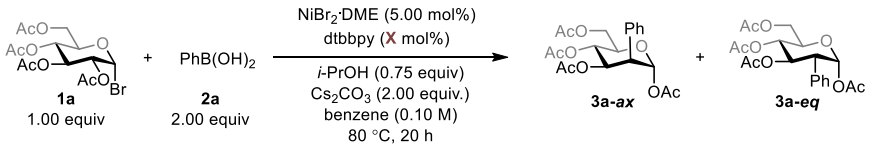
Entry	X	Yield of 3a (%)	ax:eq
1	1.5	61	2.9:1
2	2.0	67	3.0;1
3	3.0	65	3.3:1

Table S9. Different Amount of Alcohol Additives



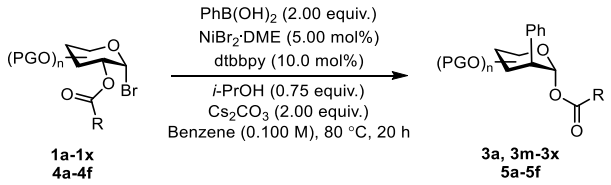
Entry	X	Yield of 3a (%)	ax:eq
1	0.25	54	2.9:1
2	0.50	87	3.0;1
3	0.75	88	3.1:1
4	1.00	79	3.6:1
5	1.25	73	3.3:1

Table S10. Different Amount of Ligand



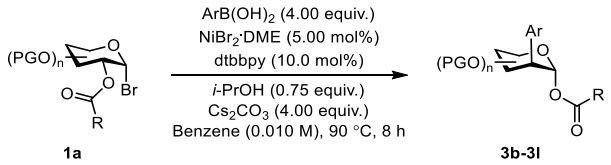
Entry	X	Yield of 3a (%)	ax:eq
1	5.0	37	4.2:1
2	7.5	51	3.0;1
3	10.0	84	3.6:1

General Procedure B:



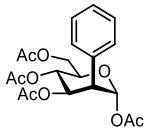
In a glovebox, to an oven-dried 4 mL screw cap vial was added $NiBr_2$•DME (3.08 mg, 10.0 μmol, 5.00 mol%), dtbbpy (5.36 mg, 20.0 μmol, 10.0 mol%), and benzene (1.00 mL). The mixture was stirred for 4 hours to get light blue catalyst solution. To another oven-dried 4 mL screw cap vial was added Cs_2CO_3 (130.3 mg, 0.400 mmol, 2.00 equiv), phenyl boronic acid (0.400 mmol, 2.00 equiv), 1-bromo sugar (0.200 mmol, 1.00 equiv), and benzene (1.00 mL). To the reaction mixture was added the prepared catalyst solution and stirred for 2 minutes. The vial was capped with a septum cap, taken out of the glovebox, and sealed with parafilm. To this suspension were added *i*-PrOH (11.4 μL, 0.150 mmol, 0.75 equiv) using a microliter syringe. The reaction mixture was stirred at 80 °C for 20 h, then, the reaction mixture was filtered through a short silica gel column and washed with ethyl acetate. The resulted solution was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the desired product. Given that many products are new and have not been characterized, if the diastereomers could not be separated by the flash column chromatography, we purified them through HPLC system [Lux® 5μm i-Amylose-1 column eluting with isopropanol:hexane (v/v) at the flow rate of 1.0 ml/min] to obtain a pure NMR spectra.

General Procedure C:



In a glovebox, to an oven-dried 4 mL screw cap vial was added $NiBr_2$•DME (3.08 mg, 10.0 μmol, 5.00 mol%), dtbbpy (5.36 mg, 20.0 μmol, 10.0 mol%), and benzene (1.00 mL). The mixture was stirred for 4 hours to get light blue catalyst solution. To another oven-dried 100 mL pressure vessel was added Cs_2CO_3 (260.6 mg, 0.800 mmol, 4.00 equiv), Aryl boronic acid (0.800 mmol, 4.00 equiv), 1-bromo sugar (0.200 mmol, 1.00 equiv), *i*-PrOH (11.4 μL, 0.150 mmol, 0.75 equiv), and benzene (19.00 mL). To the reaction mixture was added the prepared catalyst solution and stirred for 2 minutes. The pressure vessel was capped and taken out of the glovebox. After the reaction mixture was stirred at 90 °C for 8 h, it was filtered through a short silica gel column and washed with ethyl acetate. The resulted solution was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the desired product.

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



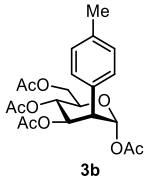
3a

According to the General Procedure B, the title compound was obtained as a white solide (68.5 mg, 0.168 mmol, 84% yield, axial: equatorial = 3.6:1). $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3a-*ax***): t_R = 12.9 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.37 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.36 – 7.31 (m, 3H), 6.36 (s, 1H, *H1*), 5.45 (dd, *J* = 9.9, 6.2 Hz, 1H, *H3*), 5.33 (t, *J* = 10.0 Hz, 1H, *H4*), 4.32 (dd, *J* = 12.4, 4.0 Hz, 1H, *H6*), 4.18 (ddd, *J* = 9.2, 7.8, 2.4 Hz, 2H, *H5*, *H7*), 3.61 (dd, *J* = 6.1, 1.0 Hz, 1H, *H2*), 2.17 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.76, 170.53, 169.50, 168.96, 134.93, 129.58, 128.69, 128.03, 93.87, 70.97, 70.85, 65.49, 62.26, 47.38, 21.21, 20.97, 20.85, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{24}O_9Na$ [$(M + Na)^+$], 431.1313, found, 431.1316.

Data for equatorial product (**3a-*eq***): t_R = 7.6 min, 5% (v/v) isopropanpl in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.32 – 7.21 (m, 5H), 6.20 (d, *J* = 3.3 Hz, 1H, *H1*), 5.91 (dd, *J* = 11.7, 9.2 Hz, 1H, *H3*), 5.21 (t, *J* = 9.7 Hz, 1H, *H4*), 4.38 (dd, *J* = 12.4, 4.0 Hz, 1H, *H6*), 4.23 – 4.16 (m, 1H, *H5*), 4.09 (dd, *J* = 12.4, 2.0 Hz, 1H, *H7*), 3.41 (dd, *J* = 11.8, 3.3 Hz, 1H, *H2*), 2.11 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.50, 169.90, 168.56, 133.63, 128.78, 128.78, 128.11, 93.15, 70.18, 69.87, 69.75, 62.02, 50.54, 20.89, 20.82, 20.63. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{24}O_9Na$ [$(M + Na)^+$], 431.1313, found, 431.1316.

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



3b

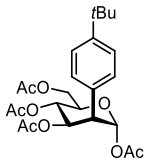
According to the General Procedure C, the title compound was obtained as a white solide (72.7 mg, 0.172 mmol, 86% yield, axial: equatorial = 4.0:1). $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3b-*ax***): t_R = 12.0 min, Lux® 3 μm Cellulose-4 column eluting with 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.34 (d, *J* = 1.4 Hz, 1H), 5.43 (dd, *J* = 5.6, 9.8 Hz, 1H), 5.32 (t, *J* = 10.5 Hz, 1H), 4.31 (dd, *J* = 4.2, 11.9 Hz, 1H), 4.14-4.20 (m, 2H), 3.57 (dd, *J* = 1.4, 6.3 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.57, 169.52, 169.01, 137.68, 131.80, 129.43, 129.43, 129.40, 129.40, 94.02, 70.96, 70.92, 65.49, 62.26, 46.98, 21.24, 21.19, 21.01, 20.88, 20.82. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{23}O_9Na$ [$(M + Na)^+$], 445.1469, found, 445.1468.

Data for equatorial product (**3b-*eq***): t_R = 10.5 min, Lux® 3 μm Cellulose-4 column eluting with 5% (v/v)

isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.07-7.12 (m, 4H), 6.17 (d, *J* = 3.5 Hz, 1H), 5.88 (dd, *J* = 9.2, 11.9 Hz, 1H), 5.20 (dd, *J* = 9.8, 10.5 Hz, 1H), 4.37 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.18 (ddd, *J* = 2.1, 3.5, 9.8 Hz, 1H), 4.09 (dd, *J* = 2.1, 12.6 Hz, 1H), 3.37 (dd, *J* = 3.5, 11.9 Hz, 1H), 2.30 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.90, 170.55, 169.93, 168.64, 137.77, 130.51, 129.48, 129.48, 128.64, 128.64, 93.25, 70.14, 69.97, 69.78, 62.05, 50.16, 21.21, 20.91, 20.88, 20.84, 20.70. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{27}O_9N$ [$(M + NH_4)^+$], 440.1915, found, 440.1919.

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



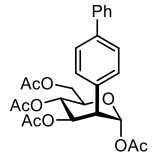
3c

According to the General Procedure C, the title compound was obtained as a white solide (69.3 mg, 0.149 mmol, 74% yield, axial: equatorial = 3.8:1). $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3c-*ax***): t_R = 5.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 5.44 (dd, *J* = 9.9, 6.1 Hz, 1H), 5.33 (t, *J* = 9.9 Hz, 1H), 4.31 (dd, *J* = 12.3, 4.1 Hz, 1H), 4.21 – 4.13 (m, 2H), 3.58 (d, *J* = 6.0 Hz, 1H), 2.17 (s, 3H), 2.15 (s, 3H), 2.03 (s, 3H), 1.93 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.59, 169.63, 168.95, 150.78, 131.76, 129.26, 125.58, 94.08, 70.98, 70.94, 65.69, 62.36, 46.93, 34.61, 31.43, 21.22, 21.03, 20.90, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{32}O_9Na$ [$(M + Na)^+$], 487.1939, found, 487.1938.

Data for equatorial product (**3c-*eq***): t_R = 7.0 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.29 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.17 (d, *J* = 3.3 Hz, 1H), 5.89 (dd, *J* = 11.8, 9.2 Hz, 1H), 5.21 (dd, *J* = 10.1, 9.3 Hz, 1H), 4.37 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.18 (ddd, *J* = 10.3, 3.9, 2.3 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.38 (dd, *J* = 11.8, 3.3 Hz, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.78 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.91, 170.61, 169.93, 168.73, 150.93, 130.44, 128.42, 125.65, 100.13, 93.30, 72.05, 70.10, 70.01, 69.86, 69.82, 68.49, 62.07, 58.05, 50.04, 34.62, 31.40, 20.93, 20.85, 20.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{32}O_9Na$ [$(M + Na)^+$], 487.1939, found, 487.1938.

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



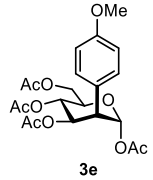
3d

According to the General Procedure C, the title compound was obtained as a white solide (77.8 mg, 0.160 mmol, 80% yield, axial: equatorial = 3.5:1). $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3d-*ax***): t_R = 6.5 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.60 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.42 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.40 (s, 1H), 5.49 (dd, *J* = 9.9, 6.1 Hz, 1H), 5.37 (t, *J* = 9.9 Hz, 1H), 4.34 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.21 (dt, *J* = 9.7, 2.7 Hz, 2H), 3.66 (d, *J* = 6.0 Hz, 1H), 2.19 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.76, 170.56, 169.53, 168.95, 140.90, 140.62, 133.92, 130.00, 128.95, 127.60, 127.38, 127.24, 93.88, 71.00, 70.87, 65.49, 62.24, 47.12, 21.21, 21.01, 20.89, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{28}O_9Na$ [$(M + Na)^+$], 507.1626, found, 507.1626.

Data for equatorial product (**3d-*eq***): t_R = 5.4 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.57 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.24 (d, *J* = 3.4 Hz, 1H), 5.95 (dd, *J* = 11.8, 9.2 Hz, 1H), 5.26 – 5.21 (m, 1H), 4.39 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.24 – 4.18 (m, 1H), 4.10 (dd, *J* = 12.4, 2.1 Hz, 1H), 3.46 (dd, *J* = 11.8, 3.4 Hz, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.89, 170.58, 169.93, 168.64, 140.84, 140.42, 132.63, 129.22, 128.96, 127.64, 127.41, 127.12, 93.14, 70.18, 69.90, 69.75, 62.03, 50.22, 20.92, 20.90, 20.85, 20.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{28}O_9Na$ [$(M + Na)^+$], 507.1626, found, 507.1622.

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



3e

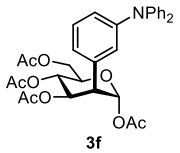
According to the General Procedure C, the title compound was obtained as a white solide (59.2 mg, 0.135 mmol, 67% yield, axial: equatorial = 2.6:1). $\mathbf{R_f}$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3e-*ax***): t_R = 9.0 min, 10% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.29 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.33 (s, 1H), 5.41 (dd, *J* = 9.9, 6.0 Hz, 1H), 5.30 (t, *J* = 10.0 Hz, 1H), 4.31 (dd, *J* = 12.4, 4.1 Hz, 1H), 4.17 (ddd, *J* = 9.1, 7.4, 2.9 Hz, 2H), 3.81 (s, 3H), 3.56 (d, *J* = 6.0 Hz, 1H), 2.17 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.76, 170.55, 169.51, 169.00, 159.30, 130.64, 126.86, 114.06, 94.10, 70.98, 70.95, 65.51, 62.29, 55.38, 46.60, 21.22, 20.99, 20.87, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for

$C_{21}H_{26}O_{10}Na$ [$(M + Na)^+$], 461.1418, found, 461.1408.

Data for equatorial product (**3e-*eq***): t_R = 9.4 min, 10% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.14 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.16 (d, *J* = 3.4 Hz, 1H), 5.85 (dd, *J* = 11.8, 9.2 Hz, 1H), 5.24 – 5.16 (m, 1H), 4.37 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.09 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.78 (s, 3H), 3.35 (dd, *J* = 11.8, 3.3 Hz, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.79 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.90, 170.54, 169.91, 168.63, 159.30, 129.88, 125.55, 114.15, 100.13, 93.28, 71.98, 70.15, 70.06, 69.74, 65.89, 62.05, 56.41, 55.32, 52.73, 49.77, 36.66, 20.91, 20.84, 20.70. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}O_{10}Na$ [$(M + Na)^+$], 461.1418, found, 461.1408.

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

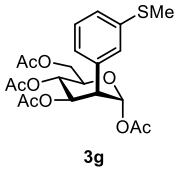


3f

According to the General Procedure C, the title compound was obtained as a white solide (94.0 mg, 0.163 mmol, 82% yield, axial: equatorial = 6.1:1). **R_f** = 0.15 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3f-*ax***): t_R = 6.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.23-7.27 (m, 3H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.99-7.09 (m, 9H), 6.33 (d, *J* = 1.4 Hz, 1H), 5.40 (dd, *J* = 6.3, 9.8 Hz, 1H), 5.18 (t, *J* = 9.8 Hz, 1H), 4.07-4.12 (m, 2H), 4.01 (dd, *J* = 5.6, 12.6 Hz, 1H), 3.45 (dd, *J* = 1.4, 6.3 Hz, 1H), 2.15 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.85 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.75, 170.46, 169.55, 168.98, 148.17, 147.84, 147.84, 136.05, 129.51, 129.51, 129.51, 129.51, 125.57, 124.40, 124.40, 124.40, 124.40, 124.40, 123.65, 123.53, 123.10, 123.10, 93.66, 71.04, 70.60, 65.80, 62.66, 47.27, 21.20, 20.94, 20.87, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{34}NO_9$ [$(M + H)^+$], 576.2228, found, 576.2226.

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



3g

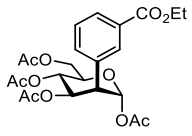
According to the General Procedure C, the title compound was obtained as a white solide (70.0 mg, 0.154 mmol, 77% yield, axial: equatorial = 2.6:1). **R_f** = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3g-*ax***): t_R = 13.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min.

^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.32 (s, 1H), 7.28 – 7.25 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 6.6 Hz, 1H), 6.35 (s, 1H), 5.44 (dd, *J* = 10.0, 6.2 Hz, 1H), 5.32 (dd, *J* = 17.2, 7.4 Hz, 1H), 4.34 (dd, *J* = 12.9, 4.2 Hz, 1H), 4.19 – 4.11 (m, 2H), 3.58 (d, *J* = 6.2 Hz, 1H), 2.48 (s, 3H), 2.18 (s, 3H), 2.17 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.95, 170.56, 169.46, 168.95, 139.24, 135.59, 129.08, 127.87, 126.40, 125.92, 93.69, 70.93, 70.78, 65.24, 62.07, 47.25, 21.22, 21.01, 20.96, 20.82, 16.01. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}O_9SNa$ [$(M + Na)^+$], 477.1190, found, 477.1188.

Data for equatorial product (**3g-*eq***): t_R = 8.9 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.21 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.19 (d, *J* = 3.3 Hz, 1H), 5.90 (dd, *J* = 11.8, 9.2 Hz, 1H), 5.25 – 5.16 (m, 1H), 4.37 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.22 – 4.13 (m, 1H), 4.09 (dd, *J* = 12.4, 2.1 Hz, 1H), 3.38 (dd, *J* = 11.8, 3.3 Hz, 1H), 2.46 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.80 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.87, 170.49, 169.88, 168.55, 139.21, 134.41, 129.14, 126.66, 126.15, 125.33, 93.02, 70.18, 69.75, 69.66, 61.98, 50.43, 20.91, 20.86, 20.82, 20.70, 15.72. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}O_9SNa$ [$(M + Na)^+$], 477.1190, found, 477.1187.

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



3h

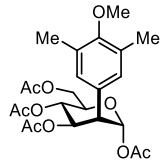
According to the General Procedure C, the title compound was obtained as a white solide (45.0 mg, 0.093 mmol, 46% yield, axial: equatorial = 2.4:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3h-*ax***): t_R = 17.7 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.01 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 6.39 (s, 1H), 5.49 (dd, *J* = 9.8, 6.1 Hz, 1H), 5.24 (t, *J* = 9.9 Hz, 1H), 4.41 – 4.30 (m, 3H), 4.21 – 4.15 (m, 2H), 3.65 (d, *J* = 6.1 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.93, 170.48, 169.45, 168.95, 166.31, 135.28, 133.47, 131.17, 129.19, 128.79, 93.49, 71.04, 70.52, 65.34, 62.13, 61.24, 47.13, 21.21, 20.93, 20.82, 14.49. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{11}Na$ [$(M + Na)^+$], 503.1524, found, 503.1522.

Data for equatorial product (**3h-*eq***): t_R = 12.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.99 – 7.94 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 6.21 (d, *J* = 3.0 Hz, 1H), 5.93 – 5.87 (m, 1H), 5.23 (t, *J* = 9.7 Hz, 1H), 4.41 – 4.34 (m, 3H), 4.21 (d, *J* = 10.5 Hz, 1H), 4.10 (d, *J* = 12.3 Hz, 1H), 3.47 (dd, *J* = 11.7, 2.9 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 6H), 1.77 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.87, 170.34, 169.88, 168.57, 166.24, 134.14, 133.17, 131.17, 130.23, 129.45, 128.84, 92.76, 70.21, 70.06, 69.58, 61.96, 61.31, 50.41, 20.91, 20.82, 20.60, 14.47. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{11}Na$ [$(M + Na)^+$], 503.1524, found,

503.1523.

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

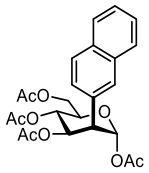


3i

According to the General Procedure C, the title compound was obtained as a white solide (63.0 mg, 0.135 mmol, 67% yield, axial: equatorial = 3.9:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3i-*ax***): t_R = 5.7 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.99 (s, 2H), 6.31 (s, 1H), 5.39 (dd, *J* = 10.0, 6.1 Hz, 1H), 5.34 (t, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 12.5, 3.8 Hz, 1H), 4.15 (dt, *J* = 12.0, 3.7 Hz, 2H), 3.73 (s, 3H), 3.51 (d, *J* = 6.8 Hz, 1H), 2.27 (s, 6H), 2.17 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.60, 169.55, 169.04, 156.67, 130.98, 130.13, 130.04, 94.09, 71.02, 70.86, 65.30, 62.18, 59.82, 46.68, 21.24, 21.02, 20.93, 20.84, 16.41. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{30}O_{10}Na$ [$(M + Na)^+$], 489.1731, found, 489.1724.

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



3j

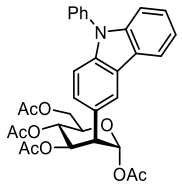
According to the General Procedure C, the title compound was obtained as a white solide (53.0 mg, 0.116 mmol, 58% yield, axial: equatorial = 3.7:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3j-*ax***): t_R = 10.0 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.95 (s, 1H), 7.79-7.86 (m, 3H), 7.48-7.52 (m, 2H), 7.40 (dd, *J* = 2.1, 8.4 Hz, 1H), 6.47 (s, 1H), 5.53 (dd, *J* = 6.3, 9.8 Hz, 1H), 5.38 (t, *J* = 9.8 Hz, 1H), 4.39 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.19-4.25 (m, 2H), 3.78 (d, *J* = 5.6, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 2.01 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.85, 170.65, 169.43, 169.05, 133.49, 132.89, 132.50, 128.54, 128.16, 128.11, 127.74, 127.68, 126.52, 126.42, 93.95, 71.03, 65.40, 62.23, 47.40, 21.25, 20.99, 20.97, 20.80. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_9Na$ [$(M + Na)^+$], 481.1469, found, 481.1476.

Data for equatorial product (**3j-*eq***): t_R = 6.7 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0

ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.77-7.82 (m, 3H), 7.70 (s, 1H), 7.46-7.50 (m, 2H), 7.37 (dd, *J* = 2.1, 8.4 Hz, 1H), 6.28 (d, *J* = 3.5 Hz, 1H), 6.05 (dd, *J* = 9.1, 11.9 Hz, 1H), 5.27 (dd, *J* = 9.1, 10.5 Hz, 1H), 4.40 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.24 (ddd, *J* = 2.1, 3.5, 10.5 Hz, 1H), 4.12 (dd, *J* = 2.1, 12.6 Hz, 1H), 3.59 (dd, *J* = 2.8, 11.9 Hz, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.73 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.91, 170.54, 169.95, 168.56, 133.39, 133.03, 131.15, 128.51, 128.39, 128.01, 127.76, 126.47, 126.42, 126.09, 93.24, 70.21, 69.91, 69.79, 62.04, 50.64, 20.93, 20.87, 20.85, 20.67. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_9Na$ [$(M + Na)^+$], 481.1469, found, 481.1478.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-(9-phenyl-9H-carbazol-3-yl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3k)



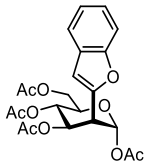
3k

According to the General Procedure C, the title compound was obtained as a white solide (48.6 mg, 0.084 mmol, 42% yield, axial: equatorial = 5.5:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3k-*ax***): t_R = 18.4 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.21 (s, 1H), 8.11-8.14 (m, 1H), 7.60-7.64 (m, 2H), 7.57-7.59 (m, 2H), 7.46-7.49 (m, 1H), 7.40-7.43 (m, 2H), 7.32-7.36 (m, 2H), 7.26-7.30 (m, 1H), 6.51 (d, *J* = 1.4 Hz, 1H), 5.52 (dd, *J* = 6.3, 9.8 Hz, 1H), 5.42 (t, *J* = 9.8 Hz, 1H), 4.43 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.19-4.26 (m, 2H), 3.83 (dd, *J* = 1.4, 6.3 Hz, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.95, 170.71, 169.46, 169.14, 141.36, 140.50, 137.68, 130.07, 127.71, 127.54, 127.24, 126.33, 126.28, 123.71, 123.28, 121.04, 120.27, 120.16, 110.08, 109.81, 94.45, 71.30, 71.09, 65.50, 62.32, 47.24, 21.29, 21.08, 21.03, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{31}NO_9Na$ [$(M + Na)^+$], 596.1891, found, 596.1901.

Data for equatorial product (**3k-*eq***): t_R = 12.5 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.11 (*d*, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.58-7.62 (m, 2H), 7.53-7.56 (m, 2H), 7.45-7.48 (m, 1H), 7.39-7.43 (m, 2H), 7.32-7.34 (m, 1H), 7.26-7.31 (m, 2H), 6.29 (d, *J* = 3.5 Hz, 1H), 6.04 (dd, *J* = 9.1, 11.9 Hz, 1H), 5.28 (dd, *J* = 9.1, 9.8 Hz, 1H), 4.41 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.25 (ddd, *J* = 2.1, 3.5, 10.5Hz, 1H), 4.13 (dd, *J* = 2.1, 12.6 Hz, 1H), 3.61 (dd, *J* = 3.5, 11.9 Hz, 1H), 2.13 (s, 4H), 2.08 (s, 3H), 2.03 (s, 4H), 1.75 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.93, 170.63, 169.96, 168.67, 141.27, 140.60, 137.60, 130.04, 130.04, 127.71, 127.15, 127.15, 126.56, 126.38, 125.03, 123.69, 123.15, 120.61, 120.32, 120.26, 110.07, 110.02, 93.57, 70.41, 70.18, 69.92, 62.12, 50.56, 20.95, 20.94, 20.87, 20.74. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{31}NO_9Na$ [$(M + Na)^+$], 596.1891, found, 596.1900.

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



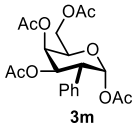
3l

According to the General Procedure C, the title compound was obtained as a white solide (36.0 mg, 0.080 mmol, 40% yield, axial: equatorial = 4.6:1). $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3l-*ax***): t_R = 13.6 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.56 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.21 (m, 2H), 6.87 (s, 1H), 6.44 (d, *J* = 1.3 Hz, 1H), 5.53 – 5.45 (m, 2H), 4.31 (dd, *J* = 12.5, 4.5 Hz, 1H), 4.22 – 4.13 (m, 2H), 3.92 (d, *J* = 3.4 Hz, 1H), 2.21 (s, 3H), 2.13 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.78, 170.58, 169.55, 168.76, 154.88, 152.11, 128.33, 124.54, 123.09, 121.19, 111.17, 106.43, 92.43, 70.85, 69.87, 65.86, 62.30, 42.41, 21.19, 21.00, 20.89, 20.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{24}O_{10}Na$ [$(M + Na)^+$], 471.1262, found, 471.1256.

Data for equatorial product(**3l-*eq***): t_R = 8.7 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.51 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.24 (m, 1H), 7.22 – 7.18 (m, 1H), 6.55 (s, 1H), 6.47 (d, *J* = 3.5 Hz, 1H), 5.87 (dd, *J* = 11.6, 9.2 Hz, 1H), 5.21 (dd, *J* = 10.2, 9.4 Hz, 1H), 4.37 (dd, *J* = 12.4, 4.1 Hz, 1H), 4.20 (ddd, *J* = 10.3, 3.9, 2.2 Hz, 1H), 4.11 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.67 (dd, *J* = 11.7, 3.4 Hz, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.85, 170.48, 169.87, 168.50, 128.05, 124.51, 123.03, 121.15, 111.31, 104.89, 91.09, 69.97, 69.24, 69.16, 61.93, 44.91, 20.91, 20.85, 20.83, 20.82. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{24}O_{10}Na$ [$(M + Na)^+$], 471.1262, found, 471.1256.

(2R,3R,4R,5R,6R)-6-(acetoxymethyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (3m)



3m

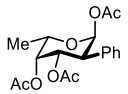
According to the General Procedure B, the title compound was obtained as a white solide (60.4 mg, 0.148 mmol, 74% yield, axial: equatorial = 1:6.0). $\mathbf{R}_f$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3m-*ax***): t_R = 11.5 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.43 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.23 (m, 3H), 6.60 (s, 1H), 5.50 (dd, *J* = 6.3, 3.3 Hz, 1H), 5.33 (d, *J* = 2.2 Hz, 1H), 4.47 (td, *J* = 6.6, 1.7 Hz, 1H), 4.29 – 4.14 (m, 2H), 3.29 (d, *J* = 6.3 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.71, 170.23, 170.07, 168.98, 136.11, 130.06, 127.61, 127.22, 94.22, 69.31, 67.70, 66.22, 62.00, 44.53, 29.86, 21.23, 20.93, 20.87, 20.12. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{24}O_9Na$ [$(M + Na)^+$], 431.1313,

found, 431.1306.

Data for equatorial product (**3m-*eq***): t_R = 10.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.32 – 7.25 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.25 (d, *J* = 3.3 Hz, 1H), 5.83 (dd, *J* = 12.3, 3.1 Hz, 1H), 5.52 (d, *J* = 1.7 Hz, 1H), 4.39 (t, *J* = 6.8 Hz, 1H), 4.15 (qd, *J* = 11.2, 6.8 Hz, 2H), 3.64 (dd, *J* = 12.3, 3.3 Hz, 1H), 2.19 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H), 1.82 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.63, 170.56, 170.42, 168.72, 134.40, 128.77, 128.56, 127.92, 93.80, 68.95, 67.22, 66.67, 61.76, 44.78, 20.90, 20.86, 20.80, 20.70. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{24}O_9Na$ [$(M + Na)^+$], 431.1313, found, 431.1310.

(2S,3S,4S,5R,6S)-6-methyl-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (3n)

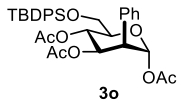


3n

According to the General Procedure B, the title compound was obtained as a white solide (44.8 mg, 0.128 mmol, 64% yield, axial: equatorial = 1:5.0). **R_f** = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for equatorial product (**3n-*eq***): t_R = 11.5 min, Lux® 3 μm i-Cellulose-5 column eluting with 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): δ 7.30-7.28 (m, 1H), 7.26-7.23 (m, 1H), 7.20-7.19 (m, 2H), 6.22 (d, *J* = 3.4 Hz, 1H), 5.83 (dd, *J* = 12.4, 3.2 Hz, 1H), 5.37 (dd, *J* = 3.2, 1.4 Hz, 1H), 4.31 (dq, *J* = 1.4, 6.3 Hz, 1H), 3.61 (dd, *J* = 12.4, 3.4 Hz, 1H), 2.21 (s, 3H), 1.94 (s, 3H), 1.82 (s, 3H), 1.21 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.82, 170.62, 168.94, 134.75, 128.69, 128.69, 128.59, 128.59, 127.77, 94.07, 69.97, 67.74, 67.40, 44.52, 20.92, 20.86, 20.76, 16.52. **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{22}O_7Na$ [$(M + Na)^+$], 373.1258, found, 373.1249.

(2R,3S,4R,5S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (3o)



3o

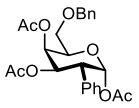
According to the General Procedure B, the title compound was obtained as a white solide (96.7 mg, 0.160 mmol, 80% yield, axial: equatorial = 2.7:1). **R_f** = 0.35 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3o-*ax***): t_R = 5.9 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.76 – 7.71 (m, 2H), 7.69 – 7.67 (m, 2H), 7.46 – 7.39 (m, 6H), 7.37 (dd, *J* = 10.4, 4.3 Hz, 2H), 7.31 – 7.24 (m, 3H), 6.41 (s, 1H), 5.59 (t, *J* = 10.0 Hz, 1H), 5.43 (dd, *J* = 9.9, 6.2 Hz, 1H), 4.02 – 3.97 (m, 1H), 3.84 (dd, *J* = 11.6, 1.9 Hz, 1H), 3.70 (dd, *J* = 11.6, 3.3 Hz, 1H), 3.58 (d, *J* = 6.2 Hz, 1H), 2.13 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.11 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ):

170.79, 169.15, 169.05, 136.01, 135.88, 135.38, 133.16, 133.03, 129.90, 129.81, 129.78, 128.69, 127.89, 127.82, 127.80, 94.17, 73.35, 71.61, 65.37, 62.03, 47.78, 26.89, 21.27, 21.05, 20.79, 19.31. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{40}O_8SiNa$ [(M + Na)$^+$], 627.2385, found, 627.2384.

Data for equatorial product (**3o-*eq***): t_R = 2.9 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.70 – 7.64 (m, 4H), 7.45 – 7.36 (m, 6H), 7.27 (dt, *J* = 11.9, 7.6 Hz, 5H), 6.25 (d, *J* = 3.3 Hz, 1H), 5.89 (dd, *J* = 11.8, 9.2 Hz, 1H), 5.34 (t, *J* = 9.7 Hz, 1H), 4.03 (dt, *J* = 10.2, 3.0 Hz, 1H), 3.79 – 3.71 (m, 2H), 3.39 (dd, *J* = 11.9, 3.3 Hz, 1H), 1.98 (s, 3H), 1.94 (s, 3H), 1.78 (s, 3H), 1.07 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.75, 169.75, 168.65, 135.85, 135.84, 134.06, 133.31, 133.30, 129.86, 129.81, 128.82, 128.70, 127.94, 127.87, 127.82, 93.24, 72.87, 70.43, 70.04, 62.55, 50.63, 26.89, 20.85, 20.81, 20.71, 19.38. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{40}O_8SiNa$ [(M + Na)$^+$], 627.2385, found, 627.2386.

(2R,3R,4R,5R,6R)-6-((benzyloxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (3p)

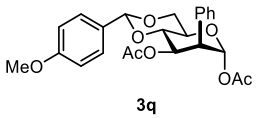


3p

According to the General Procedure B, the title compound was obtained as a white solide (36.5 mg, 0.080 mmol, 40% yield, axial: equatorial = 1:10). **R_f** = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for equatorial product (**3p-*eq***): t_R = 9.2 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.36 – 7.33 (m, 2H), 7.30 – 7.27 (m, 5H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.24 (d, *J* = 3.3 Hz, 1H), 5.83 (dd, *J* = 12.3, 3.0 Hz, 1H), 5.61 (d, *J* = 1.5 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.35 (t, *J* = 6.3 Hz, 1H), 3.62 (dd, *J* = 12.3, 3.3 Hz, 1H), 3.54 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.50 (dd, *J* = 9.3, 7.4 Hz, 1H), 2.08 (s, 3H), 1.94 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.50, 170.34, 168.85, 137.68, 134.62, 128.71, 128.60, 128.58, 128.13, 127.99, 127.82, 93.88, 73.72, 70.24, 67.84, 67.40, 67.24, 44.92, 20.89, 20.84, 20.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{28}O_8Na$ [(M + Na)$^+$], 479.1676, found, 479.1668.

(2R,4aR,6R,7S,8R,8aS)-2-(4-methoxyphenyl)-7-phenylhexahydropyrano[3,2-d][1,3]dioxine-6,8-diyl diacetate (3q)



3q

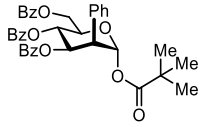
According to the General Procedure B, the title compound was obtained as a white solide (67.2 mg, 0.152 mmol, 76% yield, axial: equatorial = 1.9:1). **R_f** = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3q-*ax***): t_R = 8.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min.

^{1}H NMR (700 MHz, $CDCl_3$, 35 ºC, δ): 7.39 – 7.31 (m, 7H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.36 (s, 1H), 5.51 (dd, *J* = 10.6, 6.5 Hz, 1H), 5.48 (s, 1H), 4.37 (dd, *J* = 10.5, 4.8 Hz, 1H), 4.16 (td, *J* = 9.9, 4.8 Hz, 1H), 3.98 (t, *J* = 10.1 Hz, 1H), 3.89 (t, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.73 (d, *J* = 6.5 Hz, 1H), 2.20 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.70, 169.25, 160.31, 135.70, 129.62, 128.63, 127.88, 127.63, 113.78, 102.09, 94.38, 75.52, 69.70, 68.87, 66.43, 55.43, 47.52, 21.28, 21.21. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_8Na$ [(M + Na)$^+$], 465.1520, found, 465.1503.

Data for equatorial product (**3q-*eq***): t_R = 11.3 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.39 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.26 (m, 5H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.16 (d, *J* = 3.4 Hz, 1H), 6.03 (dd, *J* = 11.2, 9.6 Hz, 1H), 5.54 (s, 1H), 4.31 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.11 (td, *J* = 9.9, 4.9 Hz, 1H), 3.83 – 3.76 (m, 5H), 3.40 (dd, *J* = 11.5, 3.4 Hz, 1H), 2.00 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.16, 169.00, 160.22, 133.89, 129.68, 129.12, 128.69, 128.03, 127.56, 113.74, 101.78, 93.72, 80.98, 68.89, 68.44, 65.57, 55.45, 51.41, 20.86, 20.82. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_8Na$ [(M + Na)$^+$], 465.1520, found, 465.1503.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-5-phenyl-6-(pivaloyloxy)tetrahydro-2H-pyran-3,4-diyl dibenzoate (3r)

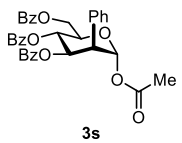


3r

According to the General Procedure B, the title compound was obtained as a white solide (48.3 mg, 0.076 mmol, 38% yield, axial only). $\mathbf{R}_f$ = 0.35 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3r-*ax***): **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.36 – 7.33 (m, 2H), 7.30 – 7.27 (m, 5H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.24 (d, *J* = 3.3 Hz, 1H), 5.83 (dd, *J* = 12.3, 3.0 Hz, 1H), 5.61 (d, *J* = 1.5 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.35 (t, *J* = 6.3 Hz, 1H), 3.62 (dd, *J* = 12.3, 3.3 Hz, 1H), 3.54 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.50 (dd, *J* = 9.3, 7.4 Hz, 1H), 2.08 (s, 3H), 1.94 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.50, 170.34, 168.85, 137.68, 134.62, 128.71, 128.60, 128.58, 128.13, 127.99, 127.82, 93.88, 73.72, 70.24, 67.84, 67.40, 67.24, 44.92, 20.89, 20.84, 20.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{36}O_9Na$ [(M + Na)$^+$], 659.2252, found, 659.2244.

(2R,3S,4R,5S,6R)-6-acetoxy-2-((benzoyloxy)methyl)-5-phenyltetrahydro-2H-pyran-3,4-diyl dibenzoate (3s)



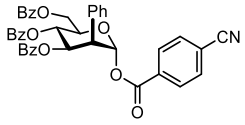
3s

According to the General Procedure B, the title compound was obtained as a white solide (97.5 mg, 0.164 mmol, 82% yield, axial: equatorial = 3.2:1). $\mathbf{R_f}$ = 0.35 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3s-*ax***): t_R = 10.7 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.15 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.42 (m, 6H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.53 (s, 1H), 6.01 – 5.92 (m, 2H), 4.75 (dd, *J* = 12.2, 2.2 Hz, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 4.45 (dd, *J* = 12.3, 2.9 Hz, 1H), 3.82 (d, *J* = 4.4 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 169.04, 166.35, 166.10, 165.25, 134.81, 133.54, 133.44, 133.33, 130.00, 129.94, 129.90, 129.84, 129.19, 129.07, 128.66, 128.63, 128.54, 128.49, 127.97, 94.12, 71.47, 71.28, 65.99, 62.53, 47.77, 21.32. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{30}O_9Na$ [$(M + Na)^+$], 617.1782, found, 617.1779.

Data for equatorial product (**3s-*eq***): t_R = 14.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.03 (d, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.32 (m, 6H), 7.28 – 7.18 (m, 6H), 6.42 (dd, *J* = 11.6, 9.5 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 5.74 (t, *J* = 9.7 Hz, 1H), 4.62 (dd, *J* = 12.1, 2.8 Hz, 1H), 4.56 – 4.51 (m, 1H), 4.47 (dd, *J* = 12.1, 4.4 Hz, 1H), 3.68 (dd, *J* = 11.8, 3.2 Hz, 1H), 2.09 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 168.69, 166.32, 166.08, 165.57, 133.55, 133.49, 133.22, 133.12, 129.97, 129.90, 129.84, 129.64, 129.29, 129.08, 128.91, 128.78, 128.50, 128.28, 128.13, 93.37, 71.12, 70.65, 70.21, 63.17, 51.12, 20.94. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{30}O_9Na$ [$(M + Na)^+$], 617.1782, found, 617.1774.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-((4-cyanobenzoyl)oxy)-5-phenyltetrahydro-2H-pyran-3,4-diyl dibenzoate (3t)



3t

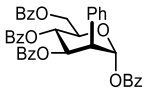
According to the General Procedure B, the title compound was obtained as a white solide (98.1 mg, 0.144 mmol, 72% yield, axial: equatorial = 5.2:1). $\mathbf{R_f}$ = 0.25 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3t-*ax***): t_R = 12.1 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.30 (d, *J* = 8.3 Hz, 2H), 8.15 – 8.12 (m, 2H), 7.94 – 7.89 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.75 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.46 (m, 5H), 7.33 (ddd, *J* = 15.5, 14.8, 7.7 Hz, 5H), 7.27 – 7.22 (m,3H), 6.79 (s, 1H), 6.12 – 5.99 (m, 2H), 4.77 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.60 (dd, *J* = 6.6, 2.8 Hz, 1H), 4.46 (dd, *J* = 12.4, 3.1 Hz, 1H), 4.01 (d, *J* = 4.1 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.27, 166.19, 165.25, 163.05, 134.42, 133.67, 133.61, 133.41, 133.27, 132.70, 130.68, 130.00, 129.91, 129.84, 129.80, 129.02, 128.94, 128.81, 128.65, 128.59, 128.57, 128.20, 117.98, 117.34, 95.58, 72.04, 71.29, 65.84, 62.38, 47.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{41}H_{31}NO_9Na$ [$(M + Na)^+$], 704.1891, found, 704.1888.

Data for equatorial product (**3t-*eq***): t_R = 9.1 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0

ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.17 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.38 (m, 4H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.56 (dd, *J* = 11.8, 9.4 Hz, 1H), 5.81 (t, *J* = 9.7 Hz, 1H), 4.63 (dd, *J* = 12.2, 2.9 Hz, 1H), 4.60 – 4.53 (m, 1H), 4.48 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.85 (dd, *J* = 11.8, 3.4 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.21, 166.18, 165.57, 162.85, 133.61, 133.30, 133.27, 133.13, 133.02, 132.69, 130.43, 129.97, 129.88, 129.73, 129.68, 129.08, 128.97, 128.93, 128.72, 128.55, 128.50, 128.36, 128.30, 117.93, 117.28, 94.93, 71.13, 71.02, 69.89, 62.95, 51.19. **HRMS** (ESI-TOF) *m/z* calcd for $C_{41}H_{31}NO_9Na$ [$(M + Na)^+$], 704.1891, found, 704.1888.

(2R,3S,4R,5S,6R)-6-((benzoyloxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl tribenzoate (3u)



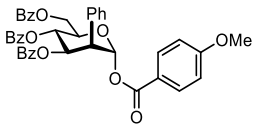
3u

According to the General Procedure B, the title compound was obtained as a white solide (111.6 mg, 0.170 mmol, 85% yield, axial: equatorial = 4.2:1). $\mathbf{R}_f$ = 0.35 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3u-*ax***): t_R = 4.8 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.27 – 8.23 (m, 2H), 8.20 – 8.16 (m, 2H), 7.98 – 7.93 (m, 2H), 7.82 – 7.77 (m, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.56 – 7.48 (m, 6H), 7.41 – 7.31 (m, 5H), 7.26 (d, *J* = 7.3 Hz, 2H), 6.81 (s, 1H), 6.15 (dd, *J* = 10.2, 5.9 Hz, 1H), 6.09 (t, *J* = 10.0 Hz, 1H), 4.77 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.65 (dt, *J* = 9.9, 2.6 Hz, 1H), 4.50 (dd, *J* = 12.4, 3.0 Hz, 1H), 4.04 (d, *J* = 6.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.31, 166.14, 165.28, 164.50, 134.83, 133.94, 133.54, 133.46, 133.30, 130.21, 130.01, 129.97, 129.91, 129.45, 129.20, 129.07, 128.88, 128.71, 128.61, 128.54, 128.52, 128.03, 94.72, 71.72, 71.49, 66.01, 62.52, 47.98. **HRMS** (ESI-TOF) *m/z* calcd for $C_{40}H_{32}O_9Na$ [$(M + Na)^+$], 679.1939, found, 679.1936.

Data for equatorial product (**3u-*eq***): t_R = 6.3 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.12 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (dt, *J* = 20.0, 7.6 Hz, 4H), 7.45 – 7.32 (m, 7H), 7.22 (dd, *J* = 14.4, 7.2 Hz, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.65 – 6.55 (m, 2H), 5.82 (t, *J* = 9.8 Hz, 1H), 4.65 – 4.55 (m, 2H), 4.49 (dd, *J* = 12.4, 4.8 Hz, 1H), 3.82 (dd, *J* = 11.8, 3.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.26, 166.15, 165.60, 164.33, 133.87, 133.49, 133.44, 133.16, 130.02, 130.00, 129.91, 129.67, 129.28, 129.08, 128.93, 128.90, 128.84, 128.50, 128.46, 128.32, 128.12, 94.09, 71.15, 70.86, 70.37, 63.08, 51.41. **HRMS** (ESI-TOF) *m/z* calcd for $C_{40}H_{32}O_9Na$ [$(M + Na)^+$], 679.1939, found, 679.1929.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-((4-methoxybenzoyl)oxy)-5-phenyltetrahydro-2H-pyran-3,4-diyl dibenzoate (3v)



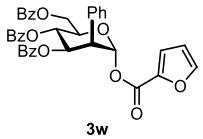
3v

According to the General Procedure B, the title compound was obtained as a white solide (96.1 mg, 0.140 mmol, 70% yield, axial: equatorial = 4.7:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3v-*ax***): t_R = 6.9 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.17 (d, *J* = 8.8 Hz, 2H), 8.16 – 8.12 (m, 2H), 7.95 – 7.88 (m, 2H), 7.80 – 7.75 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (ddd, *J* = 13.4, 12.6, 7.4 Hz, 5H), 7.37 – 7.28 (m, 5H), 7.26 – 7.21 (m, 3H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 6.12 (dd, *J* = 10.2, 6.0 Hz, 1H), 6.05 (t, *J* = 10.1 Hz, 1H), 4.73 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.63 – 4.57 (m, 1H), 4.46 (dd, *J* = 12.3, 3.0 Hz, 1H), 3.99 (d, *J* = 6.1 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.34, 166.16, 165.29, 164.19, 134.92, 133.53, 133.46, 133.29, 132.35, 130.01, 129.98, 129.94, 129.91, 129.22, 129.09, 128.68, 128.61, 128.54, 128.52, 127.99, 121.71, 114.15, 94.38, 71.60, 71.52, 66.04, 62.55, 55.72, 48.01. **HRMS** (ESI-TOF) *m/z* calcd for $C_{41}H_{34}O_{10}Na$ [$(M + Na)^+$], 709.2044, found, 709.2035.

Data for equatorial product (**3v-*eq***): t_R = 10.2 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.08 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.18 (m, 5H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.61 – 6.52 (m, 2H), 5.81 (t, *J* = 9.8 Hz, 1H), 4.60 (dd, *J* = 16.3, 4.4 Hz, 2H), 4.48 (dd, *J* = 12.4, 4.7 Hz, 1H), 3.91 (s, 3H), 3.80 (dd, *J* = 11.8, 3.2 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.28, 166.16, 165.60, 164.13, 164.02, 133.53, 133.48, 133.15, 132.15, 129.98, 129.91, 129.85, 129.65, 129.28, 129.09, 128.94, 128.79, 128.50, 128.45, 128.31, 128.06, 121.49, 114.17, 93.76, 71.18, 70.73, 70.46, 63.10, 55.70, 51.42. **HRMS** (ESI-TOF) *m/z* calcd for $C_{41}H_{34}O_{10}Na$ [$(M + Na)^+$], 709.2044, found, 709.2036.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-((furan-2-carbonyl)oxy)-5-phenyltetrahydro-2H-pyran-3,4-diyl dibenzoate (3w)



3w

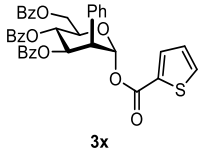
According to the General Procedure B, the title compound was obtained as a white solide (94.4 mg, 0.146 mmol, 73% yield, axial: equatorial = 4.2:1). $\mathbf{R}_f$ = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3w-*ax***): t_R = 5.2 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.19 – 8.12 (m, 2H), 7.94 – 7.89 (m, 2H), 7.78 – 7.73 (m, 2H), 7.71 (d, *J* = 0.8 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.42 (m, 7H), 7.32 (ddd, *J* = 15.6, 14.3, 7.8 Hz, 5H), 7.24 (dd, *J* = 14.2, 6.5 Hz, 2H), 6.75 (s, 1H), 6.62 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.14 – 5.98 (m, 2H), 4.75 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.62 (dt, *J* = 9.6, 2.5 Hz, 1H), 4.47 (dd, *J* = 12.4, 3.0 Hz, 1H), 3.97 (d, *J* = 5.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 166.27, 166.18, 165.25, 163.05, 134.42, 133.65, 133.59, 133.40, 133.27, 132.68, 130.66, 130.42, 129.99, 129.90, 129.84, 129.79, 129.67, 129.03, 128.94, 128.81, 128.72, 128.64, 128.58, 128.56, 128.49, 128.35, 128.19, 117.96, 117.33, 95.58, 72.04, 71.29, 65.86, 62.38, 47.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{30}O_{10}Na$ [(M + Na)$^+$], 669.1731, found, 669.1732.

Data for equatorial product (**3w-*eq***): t_R = 6.6 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.04 – 7.99 (m, 2H), 7.94 – 7.90 (m, 2H), 7.71 – 7.67 (m, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.32 (m, 8H), 7.23 (dd, *J* = 15.6, 8.0 Hz, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.59 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.53 (dd, *J* = 7.2, 2.9 Hz, 2H), 5.79 (t, *J* = 9.6 Hz, 1H), 4.62 (dt, *J* = 13.3, 3.0 Hz, 2H), 4.51 – 4.45 (m, 1H), 3.76 (dd, *J* = 11.8, 3.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.29, 166.05, 165.59, 156.34, 147.38, 143.69, 133.49, 133.30, 133.18, 133.14, 129.99, 129.92, 129.85, 129.64, 129.30, 129.11, 128.79, 128.50, 128.49, 128.30, 128.17, 119.56, 112.31, 93.95, 71.05, 70.85, 70.44, 63.06, 51.40. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{30}O_{10}Na$ [(M + Na)$^+$], 669.1731, found, 669.1724.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-5-phenyl-6-((thiophene-2-carbonyl)oxy)tetrahydro-2H-pyran-3,4-diyl dibenzoate (3x)



3x

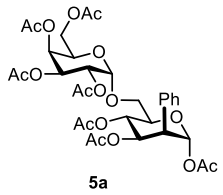
According to the General Procedure B, the title compound was obtained as a white solide (94.1 mg, 0.142 mmol, 71% yield, axial: equatorial = 4.3:1). **R_f** = 0.30 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**3x-*ax***): t_R = 5.1 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.15 (d, *J* = 7.7 Hz, 2H), 8.02 (d, *J* = 3.5 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 4.9 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.46 (m, 6H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.31 (q, *J* = 7.7 Hz, 3H), 7.25 (dd, *J* = 14.4, 6.8 Hz, 2H), 7.22 – 7.20 (m, 1H), 6.73 (s, 1H), 6.10 (dd, *J* = 10.1, 5.9 Hz, 1H), 6.05 (t, *J* = 10.0 Hz, 1H), 4.76 (dd, *J* = 12.3, 2.0 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 4.47 (dd, *J* = 12.3, 2.9 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.30, 166.06, 165.26, 159.98, 134.78, 134.70, 133.80, 133.54, 133.44, 133.30, 132.76, 129.99, 129.92, 129.90, 129.89, 129.87, 129.17, 129.03, 128.70, 128.61, 128.53, 128.49, 128.33, 128.03, 94.74, 71.73, 71.37, 65.92, 62.46, 47.91. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{30}O_9SNa$ [(M + Na)$^+$], 685.1503, found, 685.1498.

Data for equatorial product (**3x-*eq***): t_R = 7.2 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.03 – 7.99 (m, 2H), 7.95 – 7.91 (m, 3H), 7.72 – 7.68 (m, 2H), 7.67 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.19 – 7.13 (m, 2H), 6.54 (dd, *J* = 11.8, 9.3 Hz, 1H), 6.50 (d, *J* = 3.3 Hz, 1H), 5.80 (t, *J* = 9.5 Hz, 1H), 4.61 (dd, *J* = 9.7, 3.2 Hz, 2H), 4.48 (dd, *J* = 13.0, 5.3 Hz, 1H), 3.78 (dd, *J* = 11.8, 3.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 166.28, 166.04, 165.61, 159.83, 134.63,

133.65, 133.49, 133.32, 133.17, 133.14, 132.48, 130.00, 129.92, 129.85, 129.64, 129.30, 129.07, 128.83, 128.50, 128.48, 128.33, 128.30, 128.16, 94.24, 71.05, 70.90, 70.33, 63.05, 51.38. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{30}O_9SNa$ [(M + Na)$^+$], 685.1503, found, 685.1495.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3S,4R,5S,6R)-3,4,6-triacetoxy-5-phenyltetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5a)



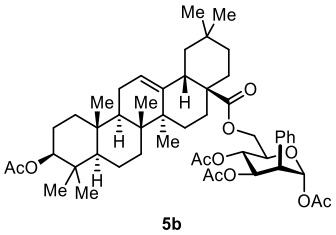
5a

According to the General Procedure B, the title compound was obtained as a white solide (72.4 mg, 0.104 mmol, 52% yield, axial: equatorial = 2.0:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**5a-*ax***): t_R = 11.5 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.41 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.35 – 7.30 (m, 3H), 6.33 (d, *J* = 0.9 Hz, 1H), 5.50 – 5.40 (m, 4H), 5.21 (d, *J* = 3.7 Hz, 1H), 5.15 (dd, *J* = 10.7, 3.8 Hz, 1H), 4.34 (t, *J* = 6.5 Hz, 1H), 4.17 – 4.08 (m, 2H), 4.02 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.86 (dd, *J* = 10.7, 3.3 Hz, 1H), 3.59 (dd, *J* = 10.7, 2.4 Hz, 2H), 2.18 (s, 3H), 2.15 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.62, 170.49, 170.37, 169.72, 169.46, 169.10, 135.01, 129.61, 128.82, 128.10, 96.51, 93.88, 71.27, 71.13, 68.58, 68.38, 67.68, 66.98, 66.46, 65.76, 61.83, 47.45, 21.21, 21.01, 20.99, 20.88, 20.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{40}O_{17}Na$ [(M + Na)$^+$], 719.2158, found, 719.2153.

Data for equatorial product (**5a-*eq***): t_R = 13.2 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.30 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.22 (m, 3H), 6.14 (d, *J* = 3.2 Hz, 1H), 5.90 (dd, *J* = 11.7, 9.2 Hz, 1H), 5.46 (d, *J* = 2.5 Hz, 1H), 5.37 (dd, *J* = 10.9, 3.3 Hz, 1H), 5.25 – 5.17 (m, 2H), 5.10 (dd, *J* = 10.9, 3.6 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 1H), 4.13 (ddd, *J* = 17.8, 7.6, 4.2 Hz, 2H), 4.06 (dd, *J* = 11.2, 6.7 Hz, 1H), 3.77 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.65 (dd, *J* = 11.3, 2.1 Hz, 1H), 3.35 (dd, *J* = 11.8, 3.2 Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.71, 170.57, 170.54, 170.37, 170.03, 169.85, 168.69, 133.72, 128.82, 128.77, 128.10, 95.99, 93.01, 70.85, 70.32, 70.02, 68.37, 68.27, 67.55, 66.41, 66.20, 61.69, 50.55, 20.99, 20.89, 20.84, 20.82, 20.65. **HRMS** (ESI-TOF) *m/z* calcd for $C_{32}H_{40}O_{17}Na$ [(M + Na)$^+$], 719.2158, found, 719.2160.

(2R,3S,4R,5S,6R)-6-((((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)oxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (5b)



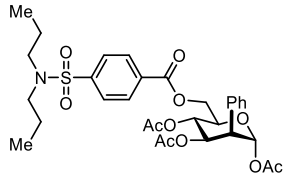
5b

According to the General Procedure B, the title compound was obtained as a white solide (130.4 mg, 0.154 mmol, 77% yield, axial: equatorial = 2.5:1). $\mathbf{R}_f$ = 0.60 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**5b-*ax***): t_R = 7.5 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.45 – 7.36 (m, 2H), 7.36 – 7.28 (m, 3H), 6.38 (s, 1H), 5.44 (dd, *J* = 9.9, 6.3 Hz, 1H), 5.34 (t, *J* = 9.9 Hz, 1H), 5.31 (s, 1H), 4.57 – 4.39 (m, 1H), 4.28 – 4.05 (m, 3H), 3.60 (d, *J* = 6.2 Hz, 1H), 2.87 (dd, *J* = 13.7, 3.7 Hz, 1H), 2.17 (s, 3H), 2.13 – 2.07 (m, 1H), 2.04 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H), 1.89 – 1.77 (m, 2H), 1.73 – 1.59 (m, 6H), 1.52 – 1.27 (m, 5H), 1.20 (dd, *J* = 14.4, 9.1 Hz, 2H), 1.16 (s, 3H), 1.08 – 1.01 (m, 1H), 0.92 (s, 6H), 0.91 (s, 3H), 0.85 (s, 3H), 0.85 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 177.42, 171.20, 170.64, 169.16, 168.94, 143.62, 135.11, 129.58, 128.66, 128.00, 122.69, 93.91, 81.09, 71.16, 70.94, 65.23, 61.85, 55.46, 47.70, 47.49, 47.00, 45.89, 41.83, 41.60, 39.45, 38.25, 37.83, 37.07, 33.93, 33.28, 32.80, 32.05, 30.82, 28.17, 27.94, 26.07, 23.80, 23.67, 23.54, 23.03, 21.48, 21.24, 21.01, 20.80, 18.36, 17.05, 16.81, 15.52. **HRMS** (ESI-TOF) *m/z* calcd for $C_{50}H_{70}O_{11}Na$ [$(M + Na)^+$], 869.4810, found, 869.4807.

Data for equatorial product (**5b-*eq***): t_R = 9.5 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.30 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.22 (d, *J* = 7.4 Hz, 2H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.90 (dd, *J* = 11.6, 9.3 Hz, 1H), 5.29 (s, 1H), 5.16 (t, *J* = 9.7 Hz, 1H), 4.53 – 4.46 (m, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.17 (dd, *J* = 10.2, 2.9 Hz, 1H), 4.07 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.35 (dd, *J* = 11.8, 3.2 Hz, 1H), 2.86 (dd, *J* = 13.8, 3.8 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.92 – 1.84 (m, 2H), 1.78 (s, 3H), 1.73 – 1.14 (m, 16H), 1.13 (s, 3H), 1.11 – 0.96 (m, 4H), 0.93 (s, 6H), 0.90 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H), 0.72 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 177.31, 171.19, 170.59, 169.70, 168.47, 143.57, 133.71, 128.78, 128.09, 122.70, 92.99, 81.08, 70.44, 70.09, 70.01, 61.76, 55.45, 50.68, 47.70, 47.02, 45.99, 41.80, 41.38, 39.44, 38.24, 37.83, 37.07, 34.01, 33.22, 32.84, 32.34, 31.73, 30.83, 28.18, 27.79, 25.96, 23.70, 23.66, 23.53, 23.21, 22.80, 21.48, 20.86, 20.82, 20.68, 18.36, 17.01, 16.82, 15.52, 14.27. **HRMS** (ESI-TOF) *m/z* calcd for $C_{50}H_{70}O_{11}Na$ [$(M + Na)^+$], 869.4810, found, 869.4813.

(2R,3S,4R,5S,6R)-6-(((4-(N,N-dipropylsulfamoyl)benzoyl)oxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (5c)



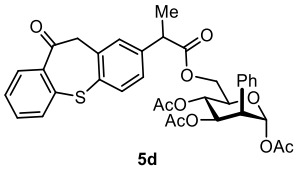
5c

According to the General Procedure B, the title compound was obtained as a white solide (88.7 mg, 0.140 mmol, 70% yield, axial: equatorial = 3.3:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**5c-*ax***): t_R = 5.6 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.23 (d, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 – 7.23 (m, 2H), 6.39 (s, 1H), 5.56 – 5.45 (m, 2H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 3.64 (s, 1H), 3.17 – 3.06 (m, 4H), 2.19 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.57 (dq, *J* = 14.4, 7.2 Hz, 4H), 0.89 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.54, 169.57, 168.93, 165.04, 144.60, 134.91, 133.25, 130.56, 129.58, 128.69, 128.13, 127.25, 93.85, 70.87, 70.75, 65.30, 62.94, 50.20, 47.32, 22.18, 21.21, 20.99, 20.81, 11.32. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{39}NO_{11}SNa$ [(M + Na)$^+$], 656.2136, found, 656.2134.

Data for equatorial product (**5c-*eq***): t_R = 6.9 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.19 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.21 (m, 3H), 6.21 (s, 1H), 5.99 – 5.91 (m, 1H), 5.35 – 5.27 (m, 1H), 4.56 – 4.43 (m, 2H), 4.33 (d, *J* = 10.2 Hz, 1H), 3.43 (d, *J* = 11.9 Hz, 1H), 3.15 – 3.06 (m, 4H), 2.07 (s, 3H), 2.03 (s, 3H), 1.79 (s, 3H), 1.60 – 1.52 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.49, 169.95, 168.61, 165.06, 144.61, 133.51, 133.10, 130.57, 128.84, 128.81, 128.20, 127.26, 93.16, 70.13, 69.96, 69.88, 63.08, 50.64, 50.20, 31.10, 22.18, 20.87, 20.86, 20.64, 11.32. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{39}NO_{11}SNa$ [(M + Na)$^+$], 656.2136, found, 656.2134.

(2R,3S,4R,5S,6R)-6-(((2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoyl)oxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (5d)



5d

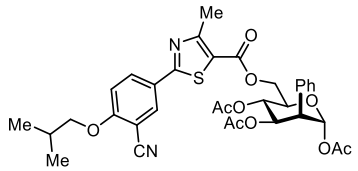
According to the General Procedure B, the title compound was obtained as a white solide (95.7 mg, 0.148 mmol, 74% yield, axial: equatorial = 2.7:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**5d-*ax***): t_R = 7.4 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): δ 8.22 – 8.18 (m, 1H), 7.60 (ddd, *J* = 9.5, 6.9, 5.6 Hz, 2H), 7.42 (dd, *J* = 11.3, 3.7 Hz, 2H), 7.36 – 7.28 (m, 6H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.36 (s, 0.5H), 6.33 (s, 0.5H), 5.43 (dd, *J* = 9.5, 6.3 Hz, 1H), 5.32 (t, *J* = 10.0 Hz, 0.5H), 5.28 (t, *J* = 9.9 Hz, 0.5H), 4.42 – 4.34 (m, 2H), 4.27 (ddd, *J* = 14.5, 12.3, 3.2 Hz, 1H), 4.20 – 4.10 (m, 2H), 3.85 – 3.77 (m, 1H), 3.60 (d, *J* = 6.1 Hz, 1H), 2.14 (s, 1.5H),

2.12 (s, 1.5H), 2.01 (s, 1.5H), 1.99 (s, 1.5H), 1.92 (s, 3H), 1.57 (d, *J* = 5.3 Hz, 1.5H), 1.53 (d, *J* = 7.2 Hz, 1.5H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.51, 191.48, 173.73, 173.62, 170.55, 169.50, 169.38, 168.93, 142.59, 142.27, 140.33, 140.30, 138.15, 138.08, 136.34, 136.32, 134.91, 133.52, 133.48, 132.65, 132.62, 131.69, 131.67, 131.04, 131.02, 129.53, 129.49, 128.88, 128.80, 128.69, 128.06, 128.04, 127.01, 126.97, 126.74, 126.62, 93.78, 93.77, 70.94, 70.90, 65.50, 65.28, 62.86, 62.68, 51.24, 51.17, 47.33, 47.31, 45.41, 45.33, 21.18, 21.15, 20.98, 20.81, 20.78, 18.81, 18.48. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{34}O_{10}SNa$ [$(M + Na)^+$], 669.1765, found, 669.1762.

Data for equatorial product (**5d-*eq***): t_R = 11.5 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.22 – 8.18 (m, 1H), 7.64 – 7.58 (m, 2H), 7.43 (t, *J* = 11.2 Hz, 2H), 7.35 – 7.28 (m, 4H), 7.23 (t, *J* = 10.4 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.15 (s, 0.5H), 6.12 (s, 0.5H), 5.86 (dd, *J* = 16.6, 10.4 Hz, 1H), 5.13 (dd, *J* = 23.0, 13.3 Hz, 0.5H), 5.04 (dd, *J* = 24.9, 15.4 Hz, 0.5H), 4.46 – 4.36 (m, 2H), 4.33 (dd, *J* = 12.1, 3.8 Hz, 0.5H), 4.24 (dd, *J* = 12.3, 3.8 Hz, 0.5H), 4.19 (d, *J* = 12.3 Hz, 1H), 4.13 (dd, *J* = 20.4, 14.5 Hz, 2H), 3.83 – 3.74 (m, 1H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.04 (s, 1.5H), 1.99 (s, 1.5H), 1.97 (s, 1.5H), 1.95 (s, 1.5H), 1.77 (s, 1.5H), 1.76 (s, 1.5H), 1.52 (d, *J* = 7.5 Hz, 1.5H), 1.51 (d, *J* = 7.2 Hz, 1.5H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.54, 191.49, 173.70, 173.63, 170.52, 169.87, 169.67, 168.55, 142.51, 142.29, 140.30, 138.08, 138.05, 136.34, 136.31, 133.62, 133.46, 133.42, 132.66, 132.62, 131.70, 131.68, 131.61, 131.57, 131.01, 129.10, 128.95, 128.81, 128.77, 128.09, 127.01, 126.98, 126.85, 126.59, 93.05, 70.21, 70.10, 69.84, 69.67, 62.53, 62.26, 51.21, 51.19, 50.46, 45.23, 45.07, 20.83, 20.80, 20.78, 20.74, 20.66, 18.44, 18.26. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{34}O_{10}SNa$ [$(M + Na)^+$], 669.1765, found, 669.1761.

(2R,3S,4R,5S,6R)-6-(((2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)oxy)methyl)-3-phenyltetrahydro-2H-pyran-2,4,5-triyl triacetate (5e)



5e

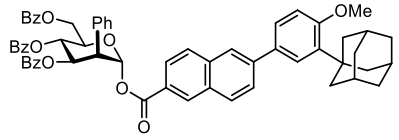
According to the General Procedure B, the title compound was obtained as a white solide (97.0 mg, 0.146 mmol, 73% yield, axial: equatorial = 2.3:1). $\mathbf{R}_f$ = 0.20 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**5e-*ax***): t_R = 10.1 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 8.21 (dd, *J* = 10.4, 2.1 Hz, 1H), 8.13 (dt, *J* = 13.4, 6.7 Hz, 1H), 7.37 (ddd, *J* = 16.8, 10.9, 6.6 Hz, 5H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.41 (s, 1H), 5.55 – 5.41 (m, 2H), 4.52 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.40 (dd, *J* = 12.4, 3.3 Hz, 1H), 4.27 (d, *J* = 9.3 Hz, 1H), 3.91 (t, *J* = 5.8 Hz, 2H), 3.65 (d, *J* = 5.7 Hz, 1H), 2.78 (s, 3H), 2.23 (dd, *J* = 13.3, 6.7 Hz, 1H), 2.19 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H), 1.10 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ºC, δ): 170.56, 169.48, 168.88, 167.81, 162.71, 162.22,

161.63, 134.98, 132.72, 132.38, 129.72, 128.78, 128.06, 126.08, 120.98, 115.49, 112.78, 103.17, 93.92, 75.86, 70.87, 65.39, 62.67, 47.37, 28.30, 21.20, 21.00, 20.79, 19.20, 17.60. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{36}N_2O_{10}SNa$ [(M + Na)$^+$], 687.1983, found, 687.1983.

Data for equatorial product (**5e-*eq***): t_R = 13.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.21 (d, *J* = 2.0 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.22 (d, *J* = 3.3 Hz, 1H), 5.95 (dd, *J* = 11.7, 9.3 Hz, 1H), 5.26 (t, *J* = 9.7 Hz, 1H), 4.47 (dd, *J* = 12.2, 4.0 Hz, 1H), 4.43 (dd, *J* = 12.2, 1.9 Hz, 1H), 4.29 (d, *J* = 10.2 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.42 (dd, *J* = 11.8, 3.2 Hz, 1H), 2.77 (s, 3H), 2.20 (ddd, *J* = 17.9, 12.3, 5.7 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 1.78 (s, 3H), 1.09 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.51, 169.87, 168.57, 167.90, 162.70, 162.03, 161.68, 133.53, 132.82, 132.37, 128.83, 128.80, 128.17, 126.07, 121.22, 115.56, 112.73, 103.11, 93.11, 75.83, 70.16, 69.97, 69.87, 62.76, 50.64, 28.30, 20.87, 20.84, 20.65, 19.20, 17.71. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{36}N_2O_{10}SNa$ [(M + Na)$^+$], 687.1983, found, 687.1977.

(2R,3S,4R,5S,6R)-6-((6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)-2-((benzoyloxy)methyl)-5-phenyltetrahydro-2H-pyran-3,4-diyl dibenzoate (5f)

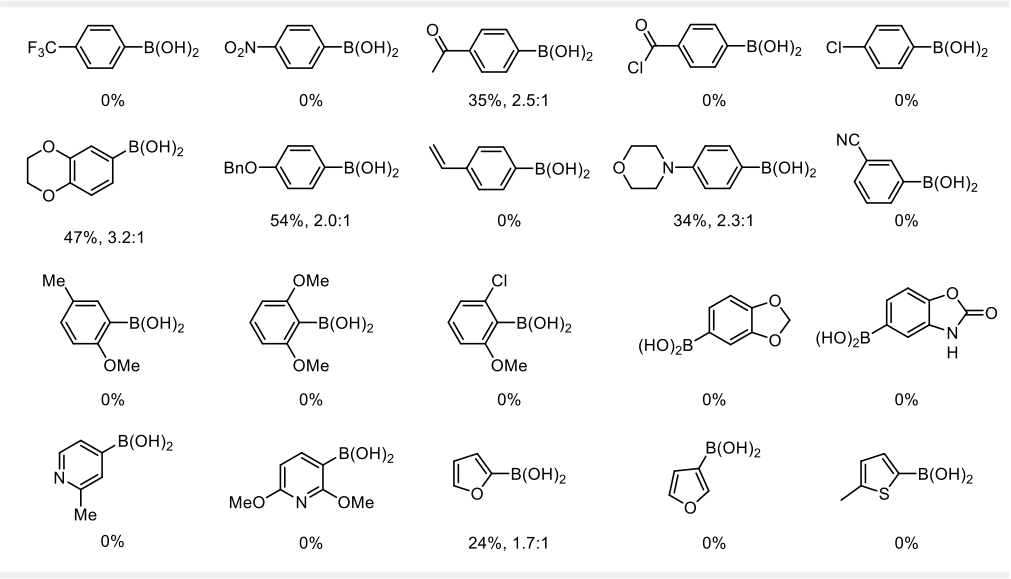


5f

According to the General Procedure B, the title compound was obtained as a white solide (106.0 mg, 0.112 mmol, 56% yield, axial: equatorial = 10:1). **R_f** = 0.40 [Hexanes: EtOAc 3:1 (v/v)].

Data for axial product (**5f-*ax***): t_R = 9.8 min, 5% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 8.80 (s, 1H), 8.26 – 8.21 (m, 1H), 8.20 – 8.08 (m, 4H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.68 – 7.55 (m, 5H), 7.50 (t, *J* = 7.4 Hz, 4H), 7.36 (dt, *J* = 15.5, 7.7 Hz, 7H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.87 (s, 1H), 6.22 (dd, *J* = 10.2, 5.9 Hz, 1H), 6.11 (t, *J* = 10.1 Hz, 1H), 4.79 (d, *J* = 12.2 Hz, 1H), 4.72 (d, *J* = 9.9 Hz, 1H), 4.52 (dd, *J* = 12.3, 2.9 Hz, 1H), 4.11 (d, *J* = 6.1 Hz, 1H), 3.95 (s, 3H), 2.23 (s, 3H), 2.15 (s, 3H), 1.85 (s, 6H), 1.57 (s, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.34, 166.17, 165.32, 164.83, 159.18, 142.03, 139.22, 136.52, 134.93, 133.55, 133.47, 133.30, 132.55, 131.79, 131.37, 130.10, 130.01, 129.94, 129.24, 129.09, 128.79, 128.73, 128.62, 128.56, 128.53, 128.04, 126.89, 126.16, 126.09, 125.96, 125.75, 124.95, 112.28, 94.84, 71.72, 71.57, 66.09, 62.57, 55.34, 48.02, 40.75, 37.38, 37.28, 29.26. **HRMS** (ESI-TOF) *m/z* calcd for $C_{61}H_{54}O_{10}Na$ [(M + Na)$^+$], 969.3609, found, 969.3610.

Other Aryl Boronic Acids Tested



Mechanistic Studies

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 $NiBr_2$•DME (0.31 mg, 1.00 μmol, 5.00 mol%), dtbbpy (0.54 mg, 2.00 μmol, 10.0 mol%), Cs_2CO_3 (13.0 mg, 0.040 mmol, 2.00 equiv), phenyl boronic acid (4.88 mg, 0.040 mmol, 2.00 equiv), TEMPO (3.12 mg, 0.020 mmol, 1.00 equiv), and benzene (0.200 mL, 0.100 M). The reaction mixture was stirred for 10 minutes. Next, 1-bromo-sugar **1a** (8.22 mg, 0.020 mmol, 1.00 equiv) was added. The vial was capped with a septum cap, taken out of the glovebox, and sealed with parafilm. To this suspension were added *i*-PrOH (1.14 μL, 0.015 mmol, 0.75 equiv) using a microliter syringe. The reaction mixture was stirred at 80 °C for 20 h, then, concentrated *in vacuo*. The yield was determined based on crude ^{1}H-NMR spectrum with dibromomethane as an internal standard.

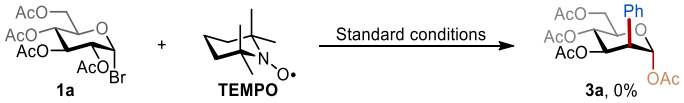


Figure S1. Radical trapping experiment.

Implication: The reaction likely proceeds through a radical mechanism.

Studies of stereochemical outcome using 2-iodo sugar

The procedure is based on General Procedure B: In a glovebox, to an oven-dried 4 mL screw cap vial was added $NiBr_2$•DME (0.31 mg, 1.00 μmol, 5.00 mol%), dtbbpy (0.54 mg, 2.00 μmol, 10.0 mol%), Cs_2CO_3 (13.0 mg, 0.040 mmol, 2.00 equiv), phenyl boronic acid (4.88 mg, 0.040 mmol, 2.00 equiv), and benzene (0.200 mL, 0.100 M). The reaction mixture was stirred for 10 minutes. Next, 2-iodo sugar **6a** or **6b** (9.16 mg, 0.020 mmol, 1.00 equiv) was added. The vial was capped with a septum cap, taken out of the glovebox, and sealed with parafilm. To this suspension were added *i*-PrOH (1.14 μL, 0.015 mmol, 0.75 equiv) using a microliter syringe. The reaction mixture was stirred at 80 °C for 20 h, then, concentrated *in vacuo*. The yield and selectivity were determined based on crude ^{1}H-NMR spectrum with dibromomethane as an internal standard.

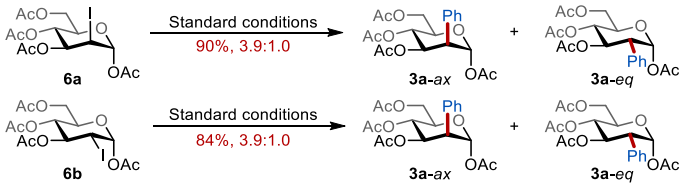


Figure S2. Studies of **s**tereochemical outcome using 2-iodo sugar.

Implication: The reaction involves the formation of a common C-2 radical species.

Cross-over experiment

The procedure is based on General Procedure B where **1a** (0.010 mol), **1u** (0.010 mol), $NiBr_2$•DME (0.31 mg, 1.00 μmol, 5.00 mol%), dtbbpy (0.54 mg, 2.00 μmol, 10.0 mol%), Cs_2CO_3 (13.0 mg, 0.040 mmol, 2.00 equiv), phenyl boronic acid (4.88 mg, 0.040 mmol, 2.00 equiv), and benzene (0.200 mL) were used. At the end of the reaction, **7a** and **3s** were not detected on both LC-MS spectrum and crude ^{1}H-NMR spectrum. The yield of **3a** and **3u** was determined based on crude ^{1}H-NMR spectrum with dibromomethane as internal standard.

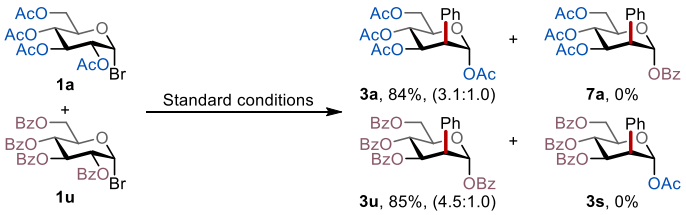


Figure S3. Cross-over experiment with **1a** and **1u** as substrates.

Implication: Acyloxyl migration undergoes a concerted mechanism.

DFT calculations

Computational Details

All density functional theory (DFT) calculations were carried out using Gaussian 16.[10] Geometries of intermediates and transition states were optimized using the dispersion-corrected B3LYP-D3 functional,[11] using Grimme's DFT-D3 dispersion correction,[12] with a mixed basis set of SDD for Ni and 6-31G(d) for other atoms in the gas phase. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure. Truhlar's quasi-harmonic corrections[13] using 100 cm^{-1} as the frequency cutoff, and temperature correction to 80 °C were applied to entropy calculations with GoodVibes,[14] Solvation energy corrections were calculated in benzene solvent with the SMD continuum solvation model[15] based on the gas-phase optimized geometries. The M06 functional[16] with a mixed basis set of SDD for Ni and 6-311+G(d,p) for other atoms was used in solvation single-point energy calculations. Conformational sampling of carbohydrate structures was carried out using the iterative metadynamic sampling and genetic crossover (iMTD-GC) method implemented in the CREST program,[17] with GFN2-xtb method[18] including additional geometry optimization of the final conformer ensemble using B3LYP-D3/SDD-6-31G(d) method. NBO analysis of some key intermediates and transition states was performed using NBO version 3 embedded in Gaussian 16.[19] DFT calculations were performed using a simplified model of glucosyl bromide (**1y**), where the OMe group was used instead of OAc group at C-3, 4, and 6 positions of the sugar backbone.

DFT calculations for the Ni-catalyzed C-2 phenylation of simplified 1-glucosyl bromide (**1y**) were performed (Figure S4). The following key information was obtained:

(i) [Ni^{I}]Br favors isopropoxide-mediated transmetallation (**TS1**) over the corresponding bromine atom abstraction (**TS2**). Prior to the transmetallation step, a base likely promotes the deprotonation of *i*-PrOH to form isopropoxide anion, which then binds to the phenylboronic acid to form a dihydroxyisopropoxyphenyl borate complex. Although the base-mediated deprotonation is challenging to calculate because the insoluble base (Cs_2CO_3) is involved, our calculations indicate that the binding of the isopropoxide anion to $PhB(OH)_2$ is highly exergonic by 23.9 kcal/mol. Therefore, we used the dihydroxyisopropoxyphenyl borate complex as the energy zero in the calculations of the transmetallation pathway. The effect of the cesium countercation was not considered in the calculations. It should be noted that the cesium counteraction may affect the reaction energy of the ligand exchange step with [Ni^{I}]Br and thus may affect the relative energies of the transmetallation and oxidative addition mechanisms (**TS1** vs **TS2**).

(ii) Oxidative insertion of [Ni^{I}]Ph into the C-Br proceeds through 1-electron bromine atom abstraction (**TS3**) rather than 2-electron S_N2 displacement (**TS4**).

(iii) 1-Glucosyl radical with a boat $B_{2,5}$-conformation (**IV**) is more stable than its chair conformation by 0.6 kcal/mol

(iv) Concerted acyloxyl migration is energetically feasible (**TS5**)

(v) Addition of Br[Ni^{II}]Ph to 2-glucosyl radical is the stereoselectivity-determining step and favors the axial addition (**TS6**). These results agree with the experimental observations of the stereoselectivity of the reaction.

(vi) The equatorial addition of 2-glucosyl radical to the apical position of Br[Ni^{II}]Ph (**TS7'**) is disfavored due to steric repulsions with the *cis* C-1 OAc group (green, Figure S6). **TS7**, which involves coordination of carbonyl oxygen in the C-1 OAc group to the nickel center, is more stable than **TS7'** (green). Nonetheless, **TS7** is still less favorable than **TS6** (purple).

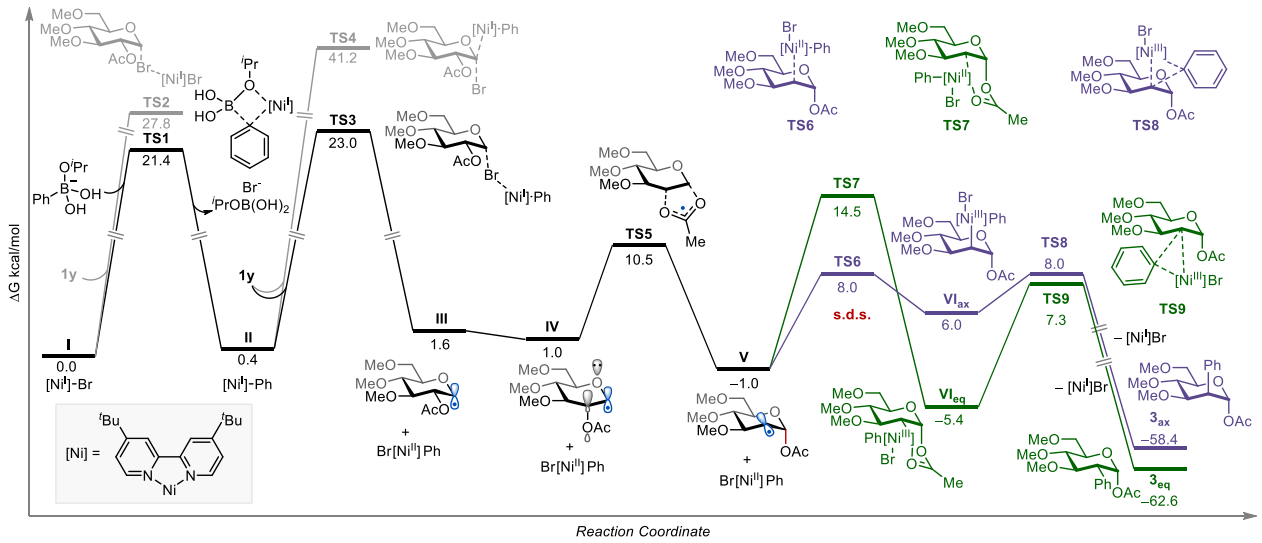
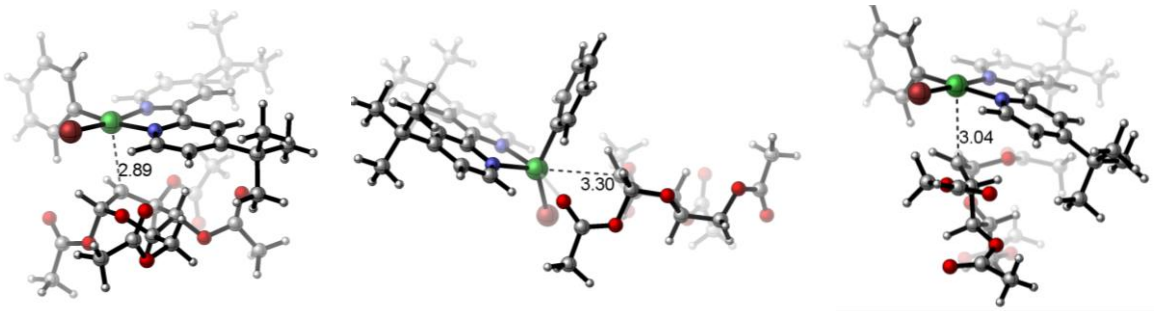


Figure S4. DFT calculations were performed at the M06/6-311+G(d,p)-SDD/SMD(benzene)//B3LYP-D3/6-31G(d)-SDD (80 °C) level of theory using 1-glucosyl bromide (**1y**) as the substrate. All energies are in kcal/mol and are with respect to **I** and the dihydroxyisopropoxyphenyl borate [$PhB(OH)_2(i\text{-}PrO)^-$].

Given that the energy difference between TS7 and TS6 ($\Delta\Delta G^{\neq}$ = 6.5 kcal/mol), which is much larger than one would expect from the experimental results (~4:1 ax:eq). To gain a better understanding of the diastereoselectivity of the reaction, we recalculated the selectivity determining transition states **TS6** and **TS7** using the whole sugar structure (i.e., the fully acetylated 2-glucosyl radical derived from substrate **1a**). We obtained a new transition states **TS6a** and **TS7a** (Figure S5). In addition to the **TS7a**, which has a similar conformation to **TS7**, we located a lower energy conformer, **TS7a'**, which is more stable than **TS7a** and is 3.6 kcal/mol less stable than **TS6a**. In **TS7a'**, the substrate is in a chair conformation and approaches $Br[Ni^{II}]Ph$ at the apical position (similar TS cannot be located when using the smaller model substrate). Although the energy difference ($\Delta\Delta G^{\ddagger}$ = 3.6 kcal/mol) is still overestimated, the new computational results with the whole sugar are in a better agreement with the experimental selectivity. Distortion/interaction analysis further revealed that the difference is interaction energy controlled. **TS7a'** has a less favorable interaction energy than **TS6**. This can be attributed to the increased Ni-C distance in **TS7a'**, which is induced by the unfavorable steric repulsions between axial acetate and the ligand.



TS6a
$\Delta\Delta G^{\ddagger}$ = 0.0
$\Delta E^{\ddagger}$ = −16.4
ΔE_{dist} = 2.0
ΔE_{int} = −18.4

TS7a
$\Delta\Delta G^{\ddagger}$ = 6.7

TS7a'
$\Delta\Delta G^{\ddagger}$ = 3.6
$\Delta E^{\ddagger}$ = −13.1
ΔE_{dist} = 1.9
ΔE_{int} = −15.0

Figure S5. Relative energies of radical rebound transition states using real substrate and distortion/interaction model analysis. DFT calculations were performed at the M06/6-311+G(d,p)-SDD/SMD(benzene)//B3LYP-D3/6-31G(d)-SDD (80 °C) level of theory using the fully acetylated 2-glucosyl radical derived from substrate **1a**. All energies are in kcal/mol and are with respect to **I**. The 3D representation was prepared using CYLview.[20]

DFT calculations were also performed to compare the energy profiles for C-1 and C-2 phenylation of 1-glucosyl radical (**III**) (Figure S6). The following key information was obtained:

(i) Reductive eliminations of the phenyl group at the C-1 of glucosyl moiety (**TS12** & **TS13**) have higher energy barriers than the radical acyloxy migration (**TS5**) and the reductive eliminations at the C-2 of glucosyl moiety (**TS8** & **TS9**).

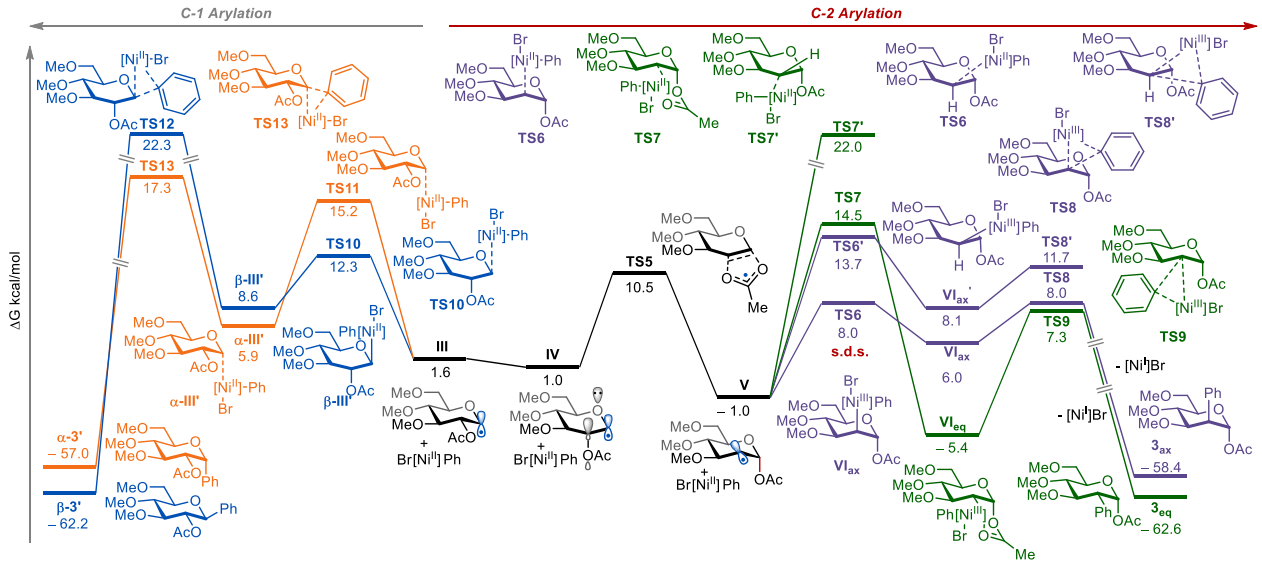
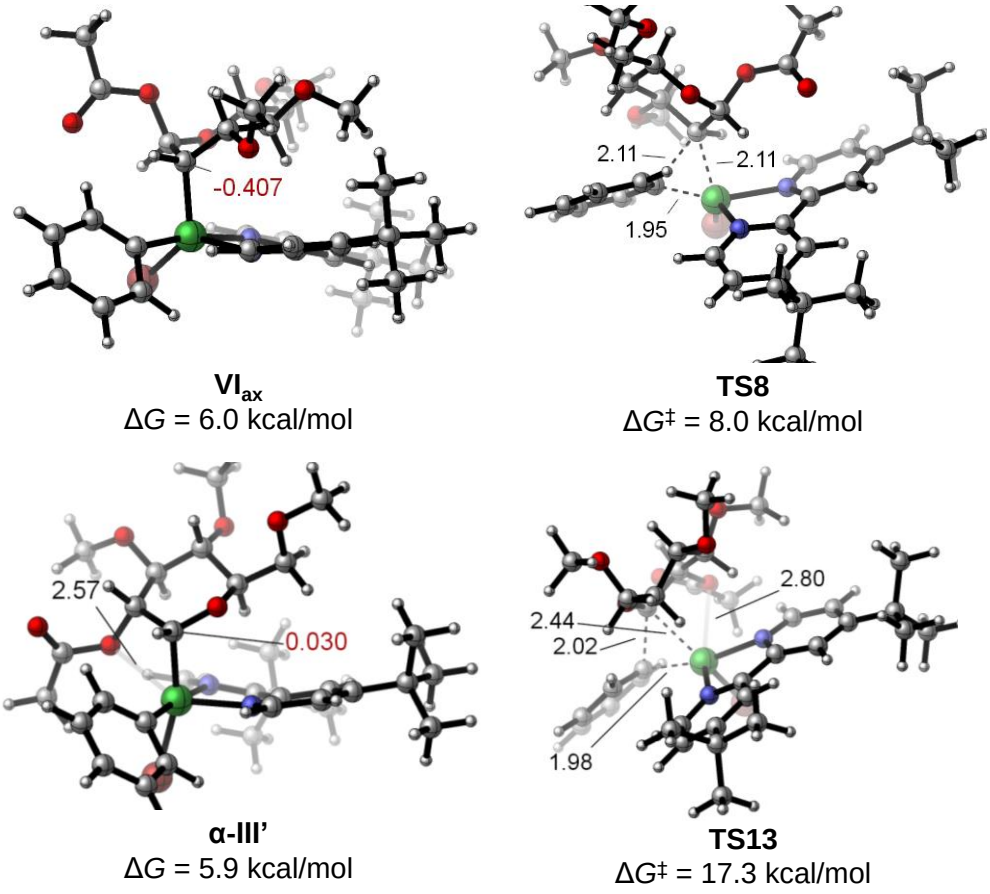


Figure S6. Gibbs free energy profiles for the Ni-catalyzed C-1 vs C-2 phenylation of glucosyl radical (**III**). DFT calculations were performed at the M06/6-311+G(d,p)-SDD/SMD(benzene)//B3LYP-D3/6-31G(d)-SDD (80 °C) level of theory using 1-glucosyl bromide (**1y**) as the substrate. All energies are in kcal/mol and are with respect to **I**.

Natural population analysis (NPA) of some key structures were performed (Figure S7) to understand the origin of relatively high barrier for reductive elimination at the C-1 of glucosyl moiety (**TS12** & **TS13**) when compared to the reductive eliminations at the C-2 of glucosyl moiety (**TS8** & **TS9)**. Following key conclusions was drawn:

(i) In complex **VI$_{ax}$** the negative charge is localized at the C-2 center (NPA charge on C-2 = −0.407), which makes this intermediate highly reactive towards reductive elimination. On the other hand, the negative charge in **α-III'** is delocalized onto the neighboring oxygen (NPA charge on C-1 = 0.030), which makes this complex less susceptible to reductive elimination, leading to a much higher barrier in spite of these two complexes (**VI$_{ax}$** & **α-III'**) having similar energies.



VI$_{ax}$
Δ*G* = 6.0 kcal/mol

TS8
Δ*G*‡ = 8.0 kcal/mol

α-III'
Δ*G* = 5.9 kcal/mol

TS13
Δ*G*‡ = 17.3 kcal/mol

Figure S7. 3D structures and NPA charge analysis of Ni(III) intermediates (**VI$_{ax}$** & **α-III'**) and reductive elimination transition states (**TS8** & **TS13**).

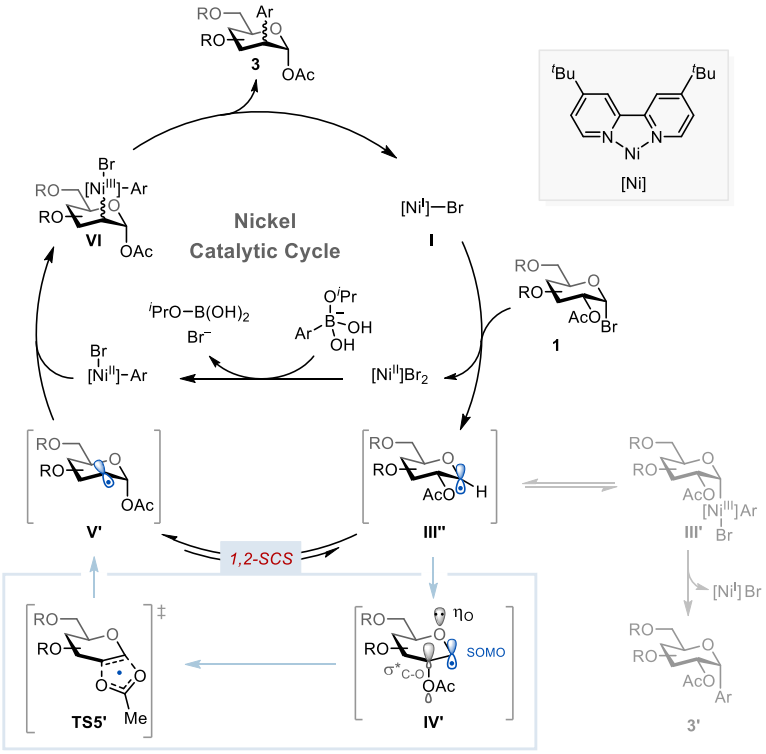
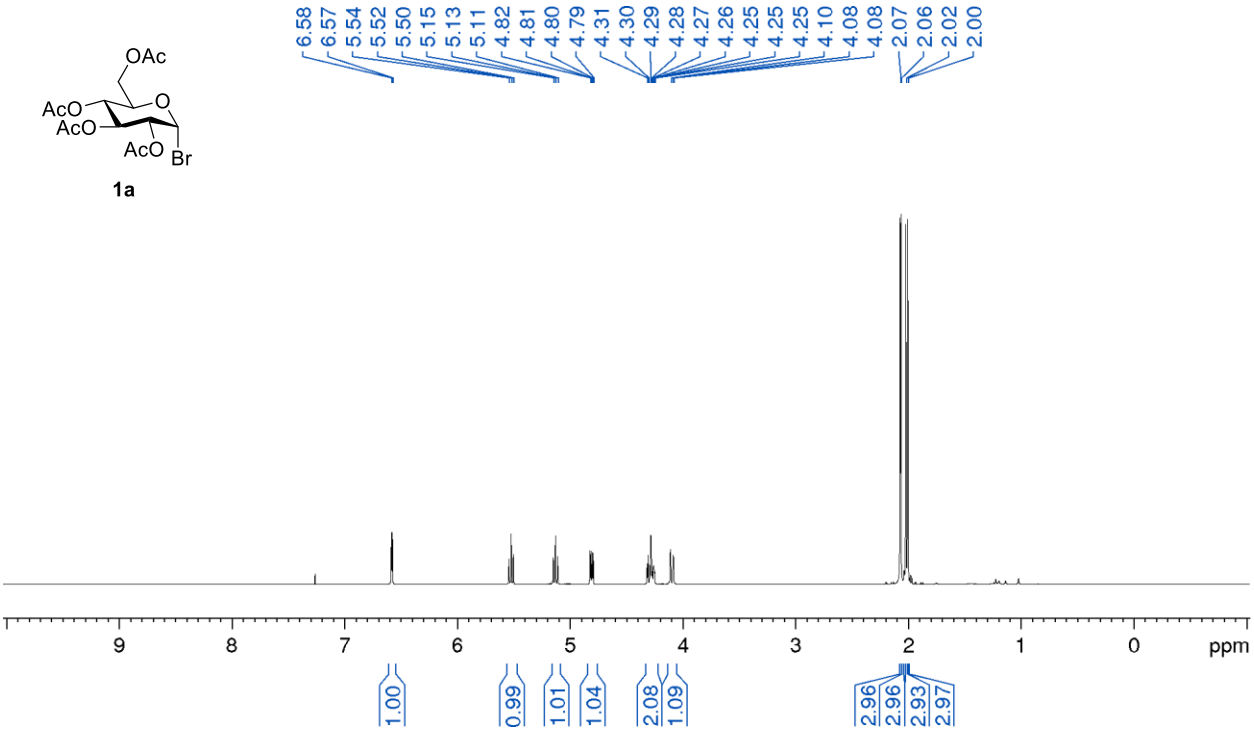


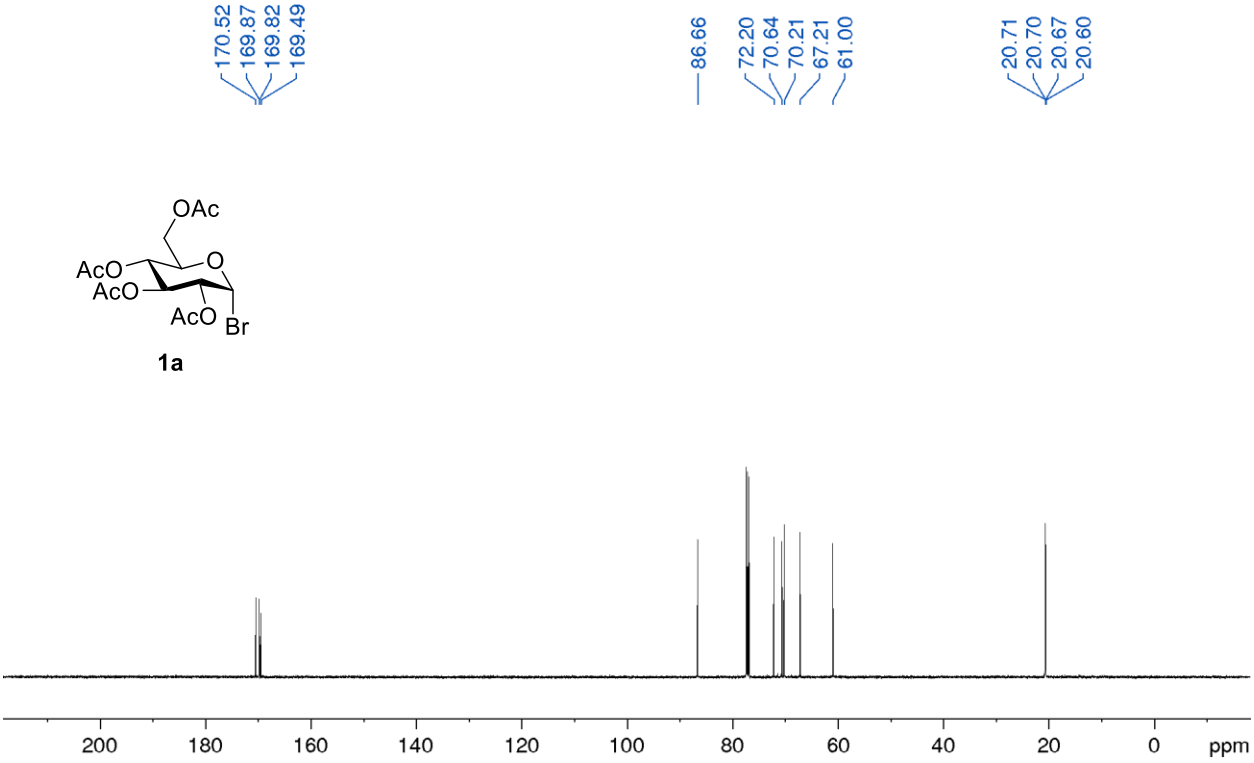
Figure S8. An alternative reaction mechanism involving first bromine atom abstraction, then transmetallation, and recombination followed by reductive elimination.

Spectroscopic Data

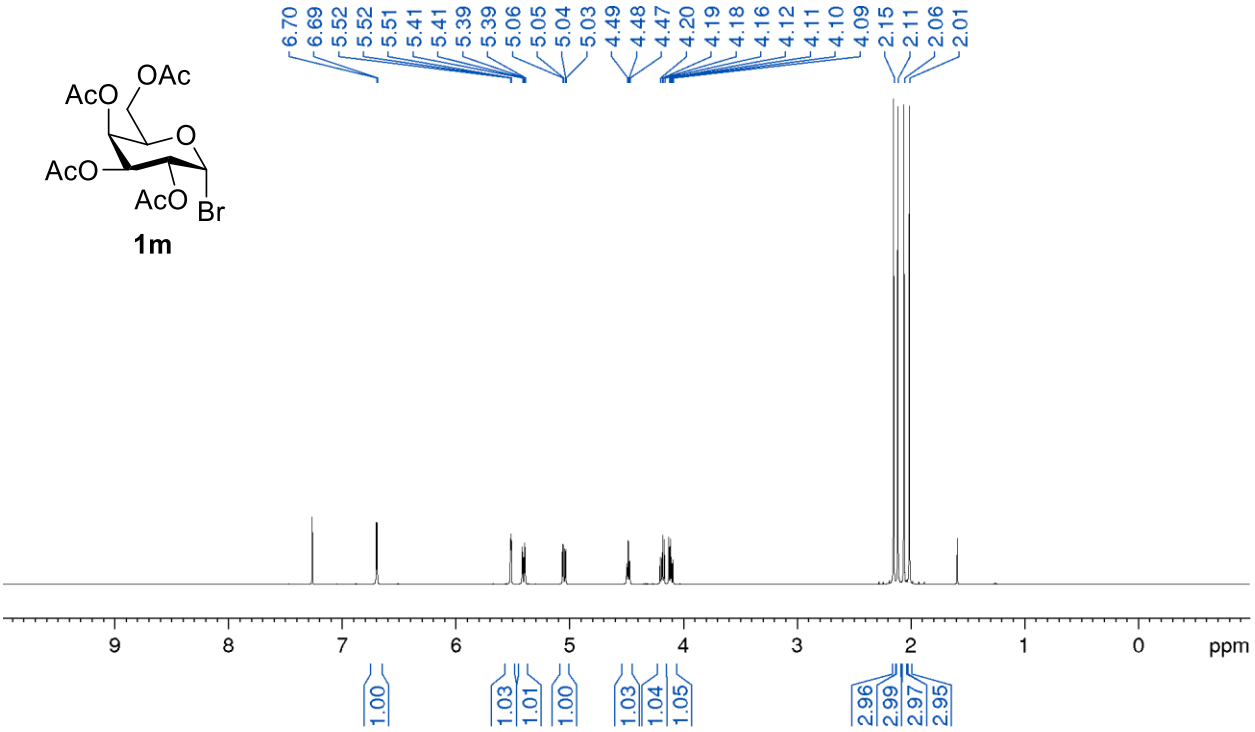
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1a)



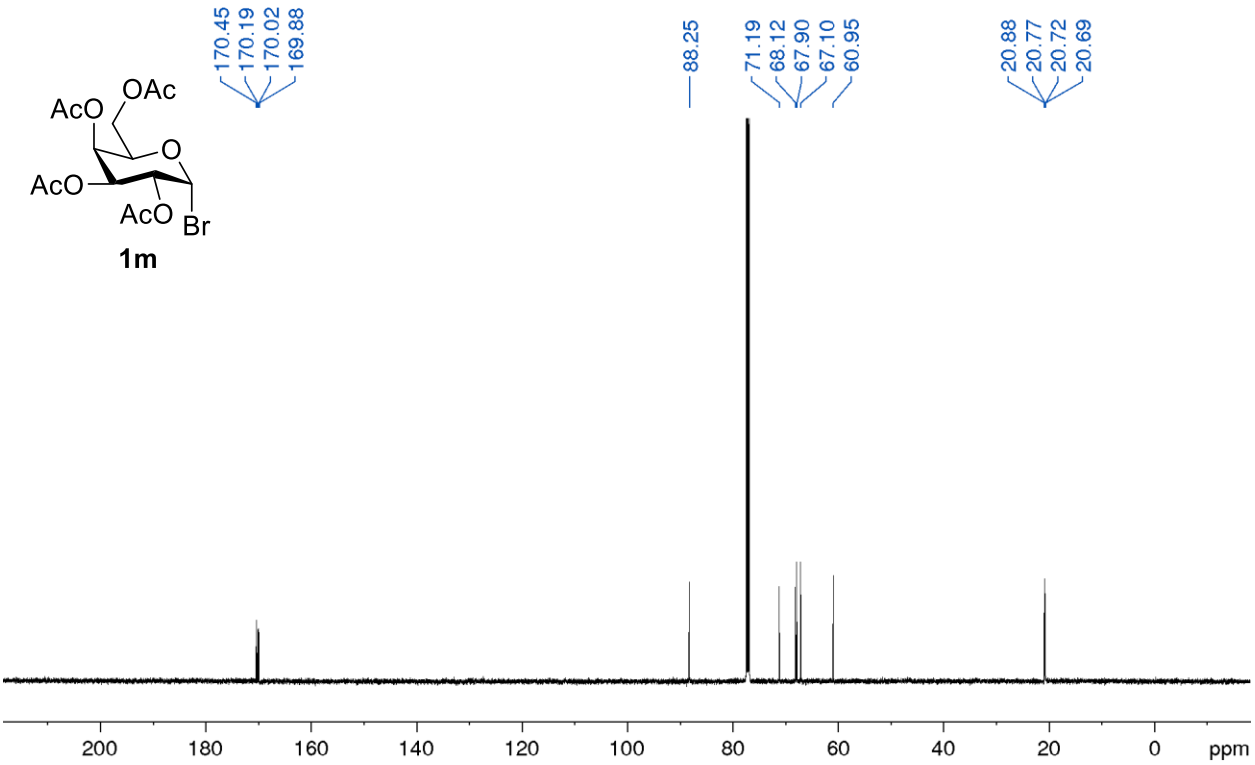
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1a)



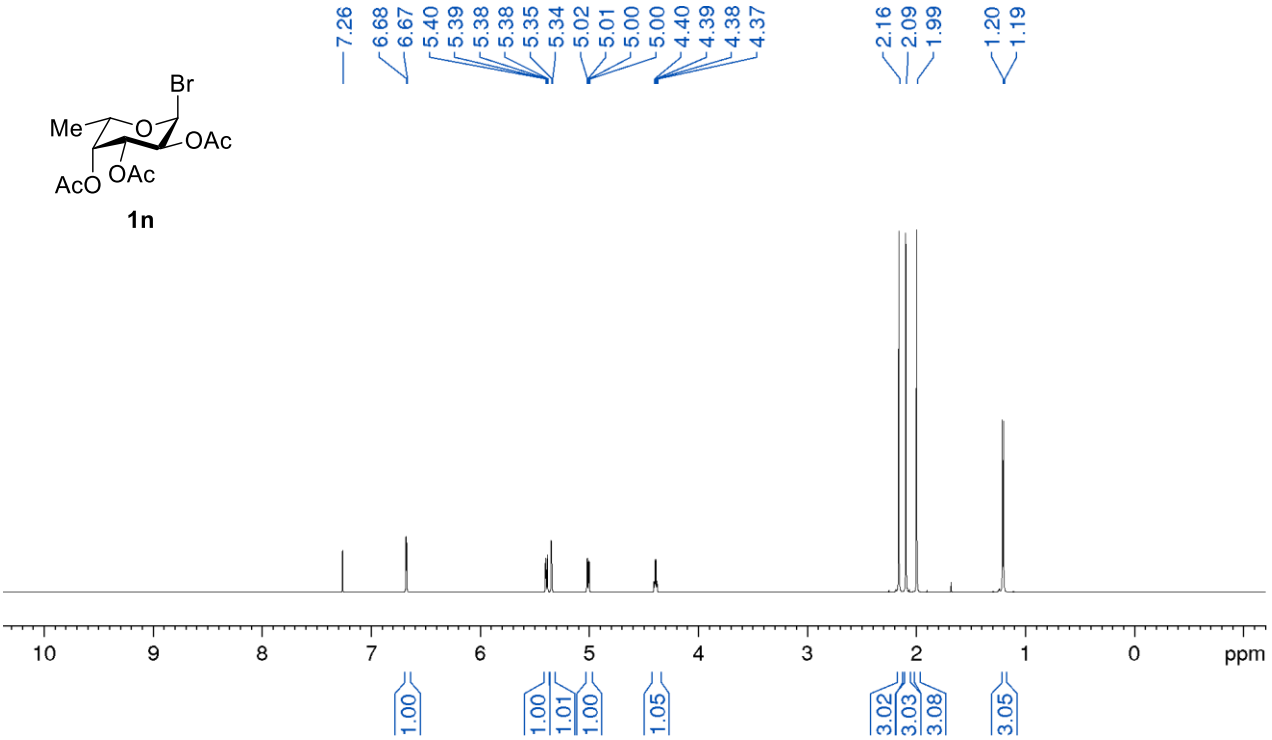
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1m)



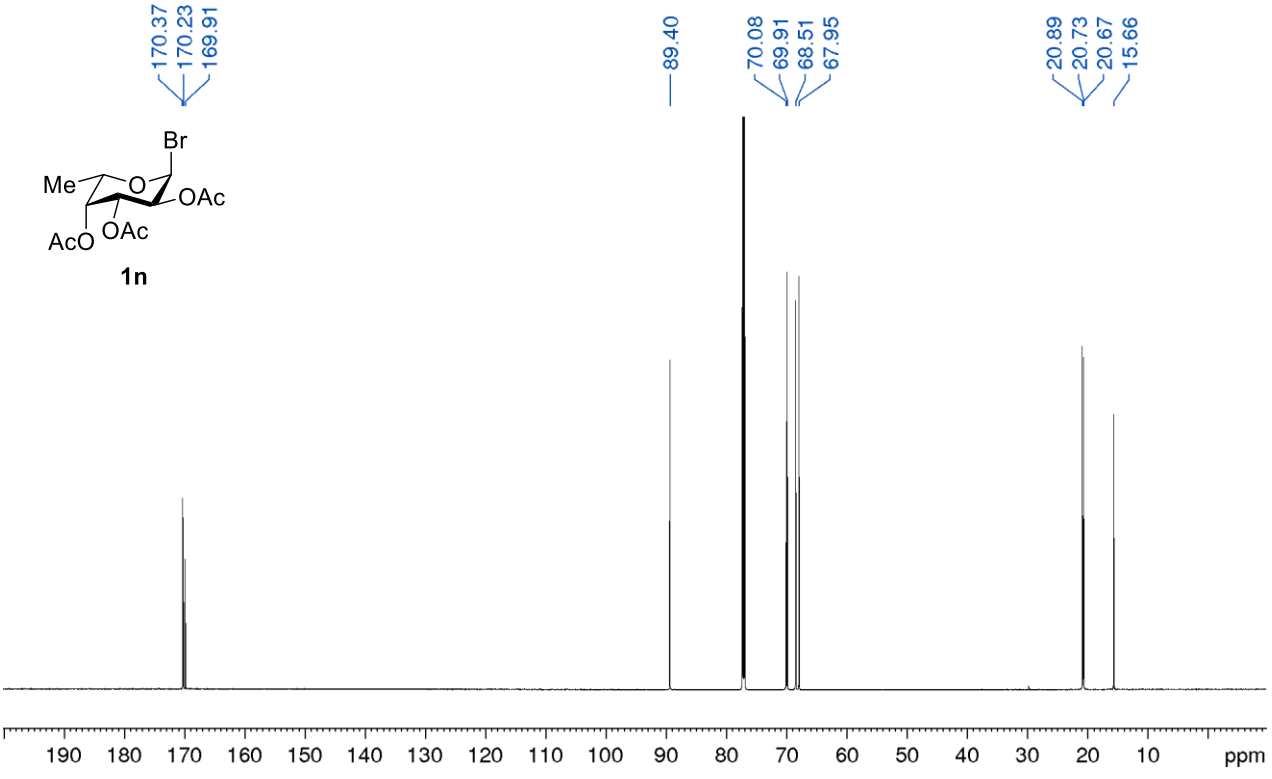
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1m)



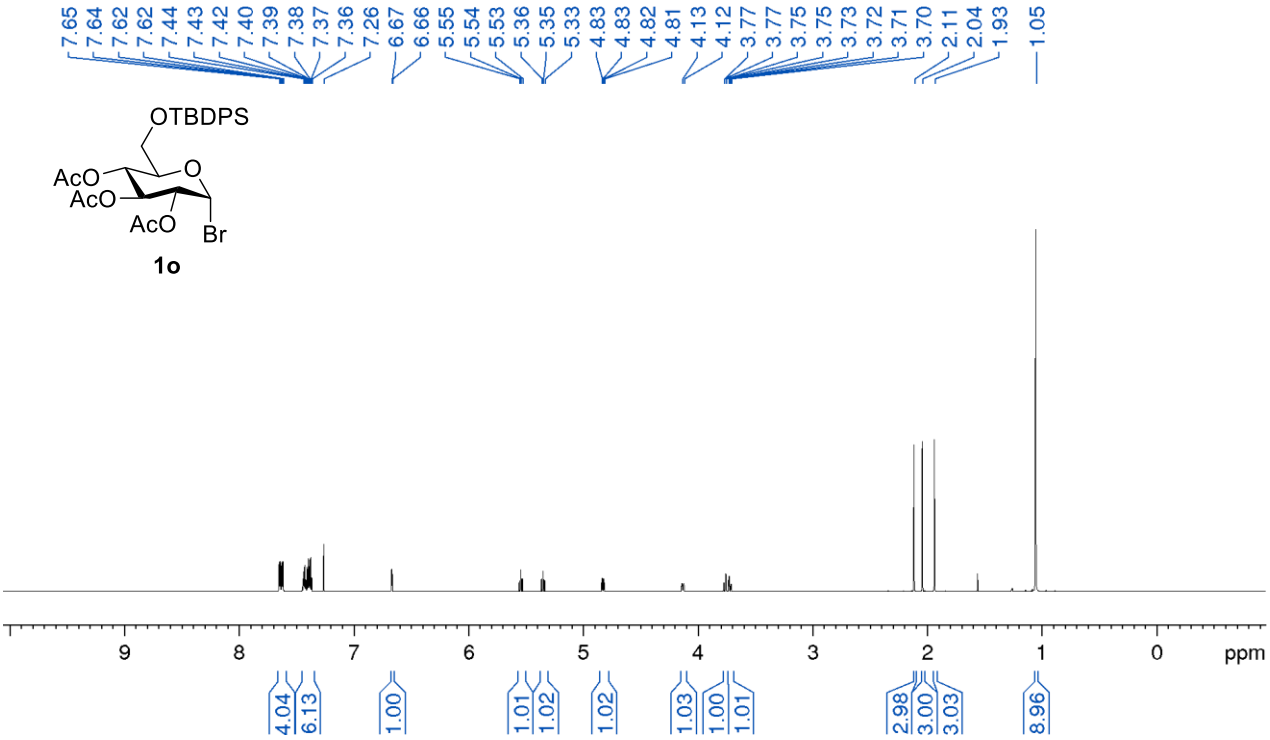
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1n)



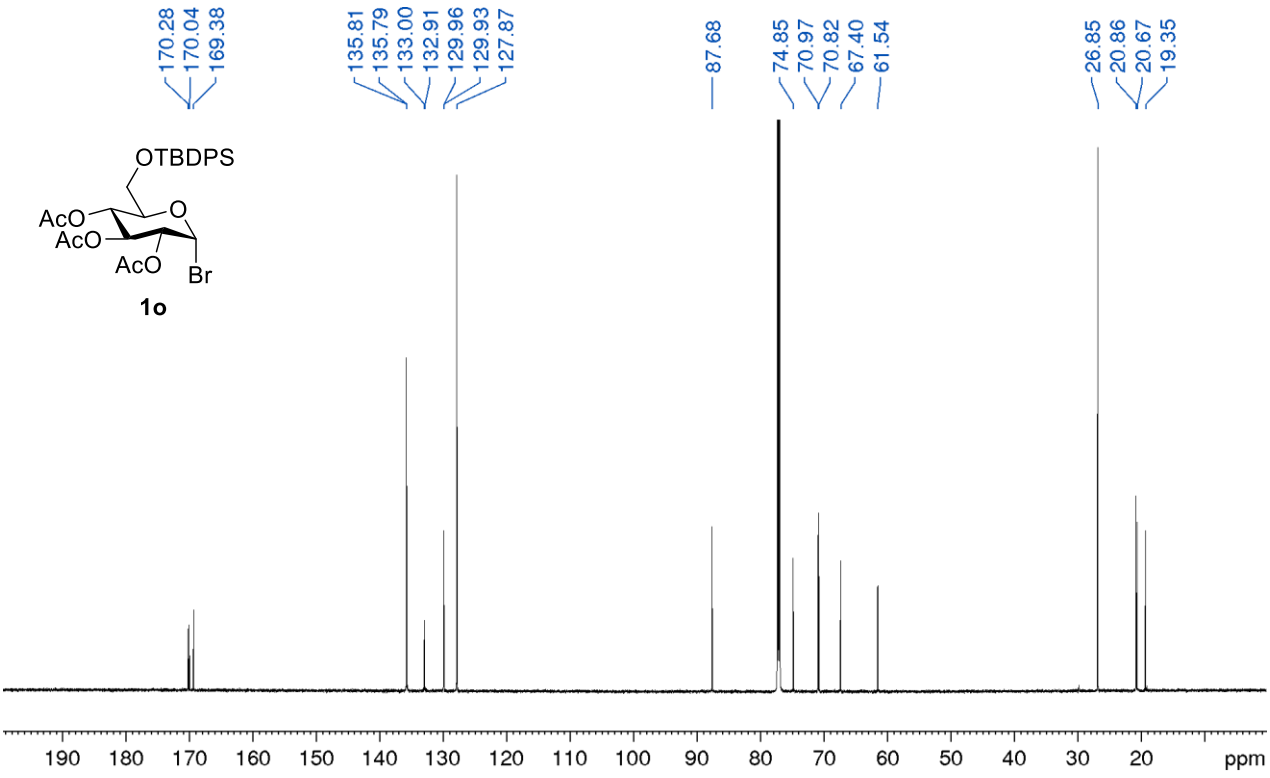
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1n)



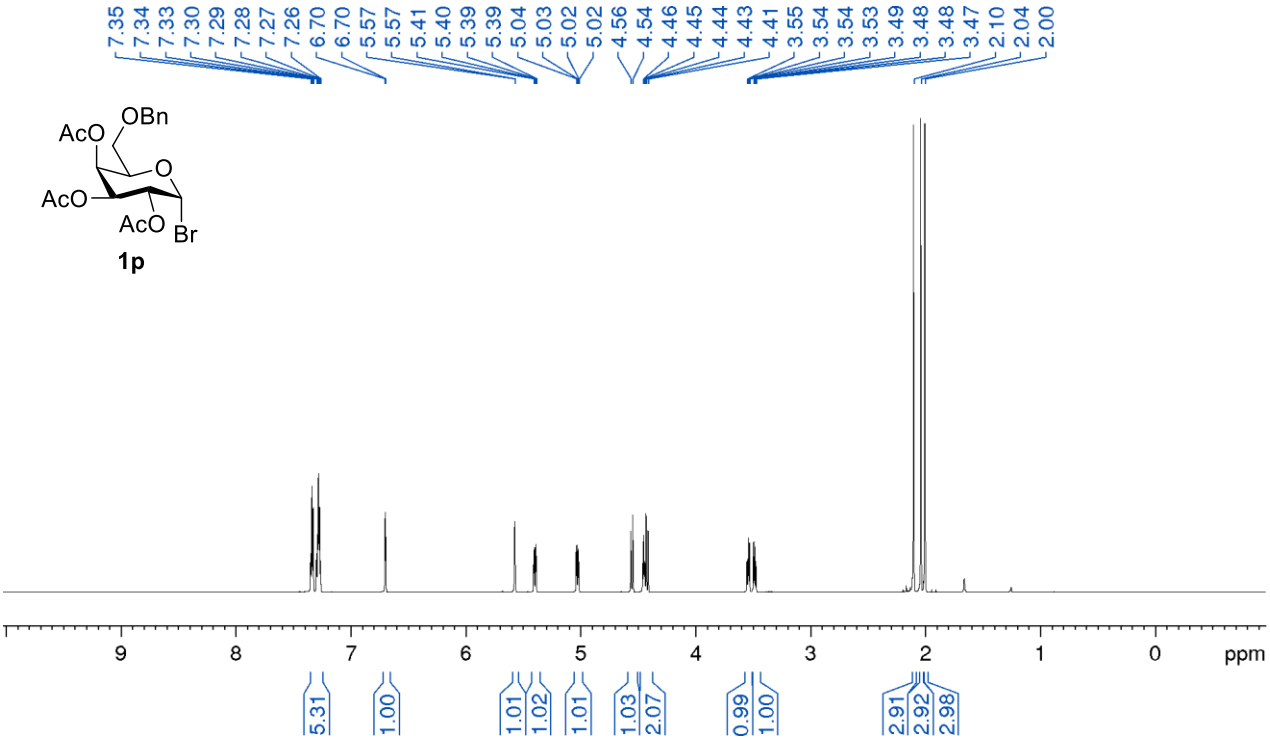
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1o)



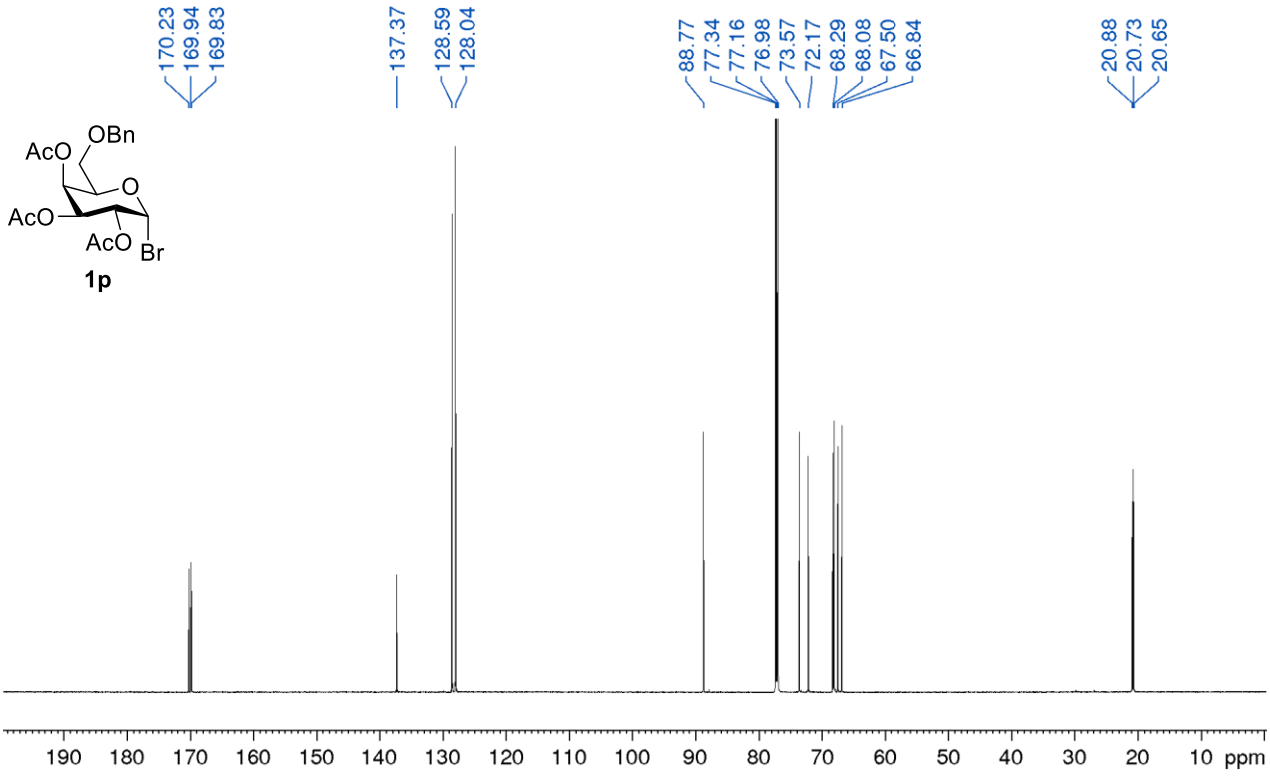
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1o)



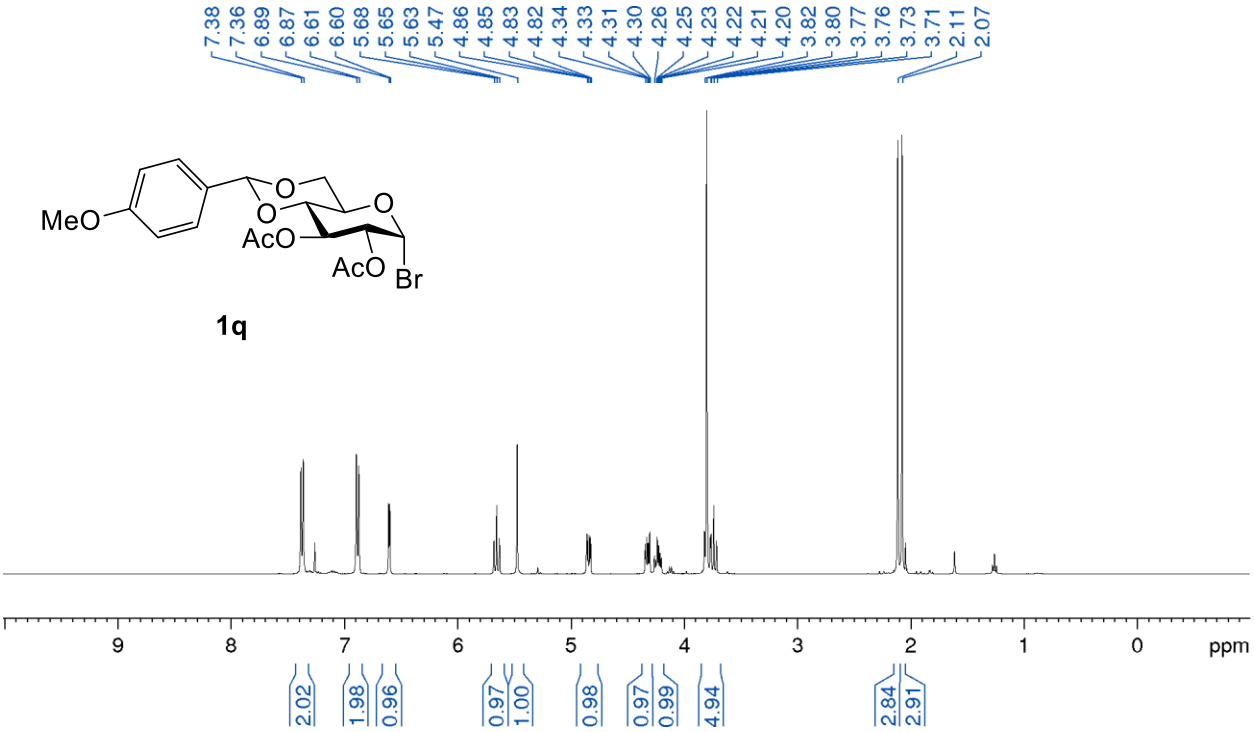
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1p)



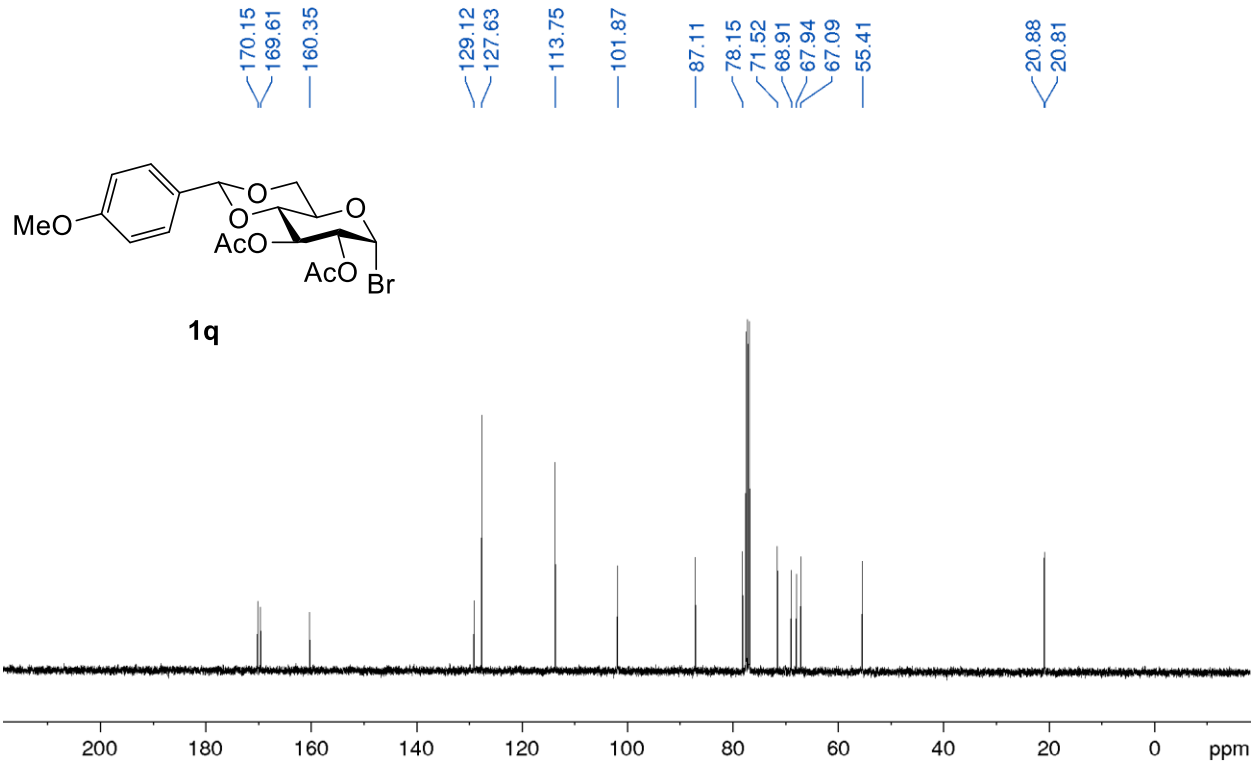
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1p)



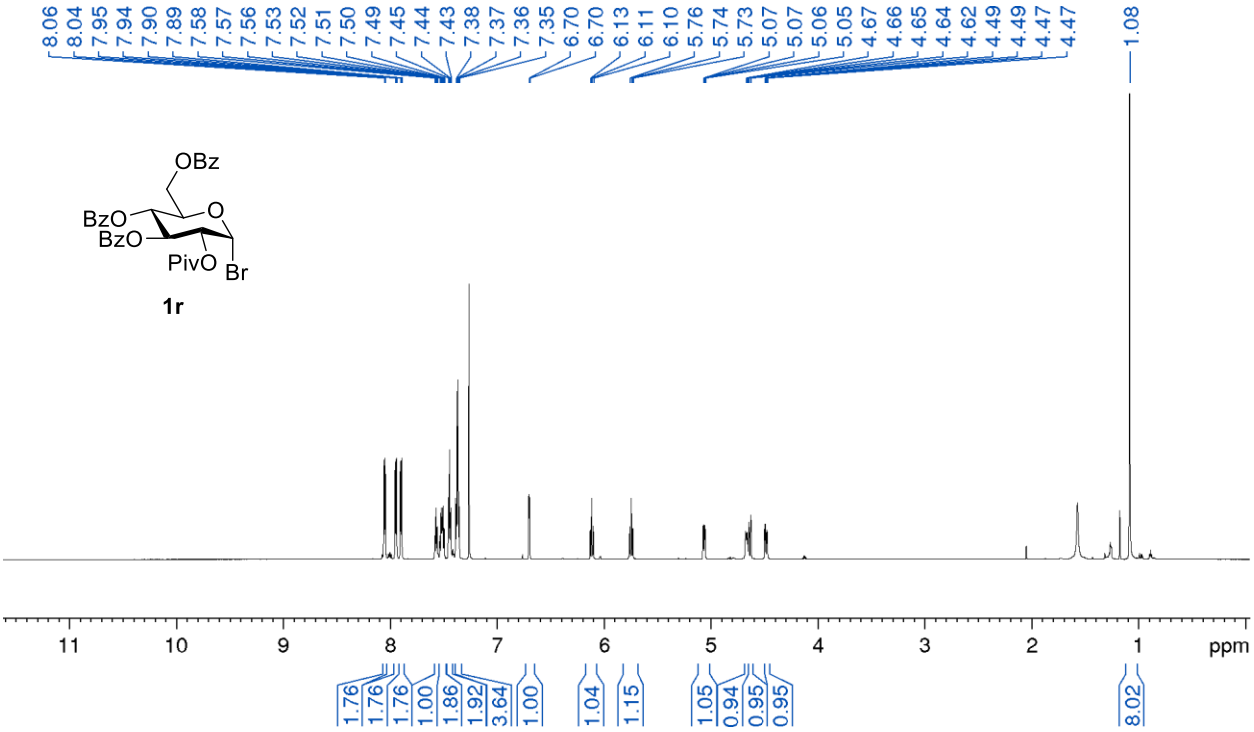
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (1q)



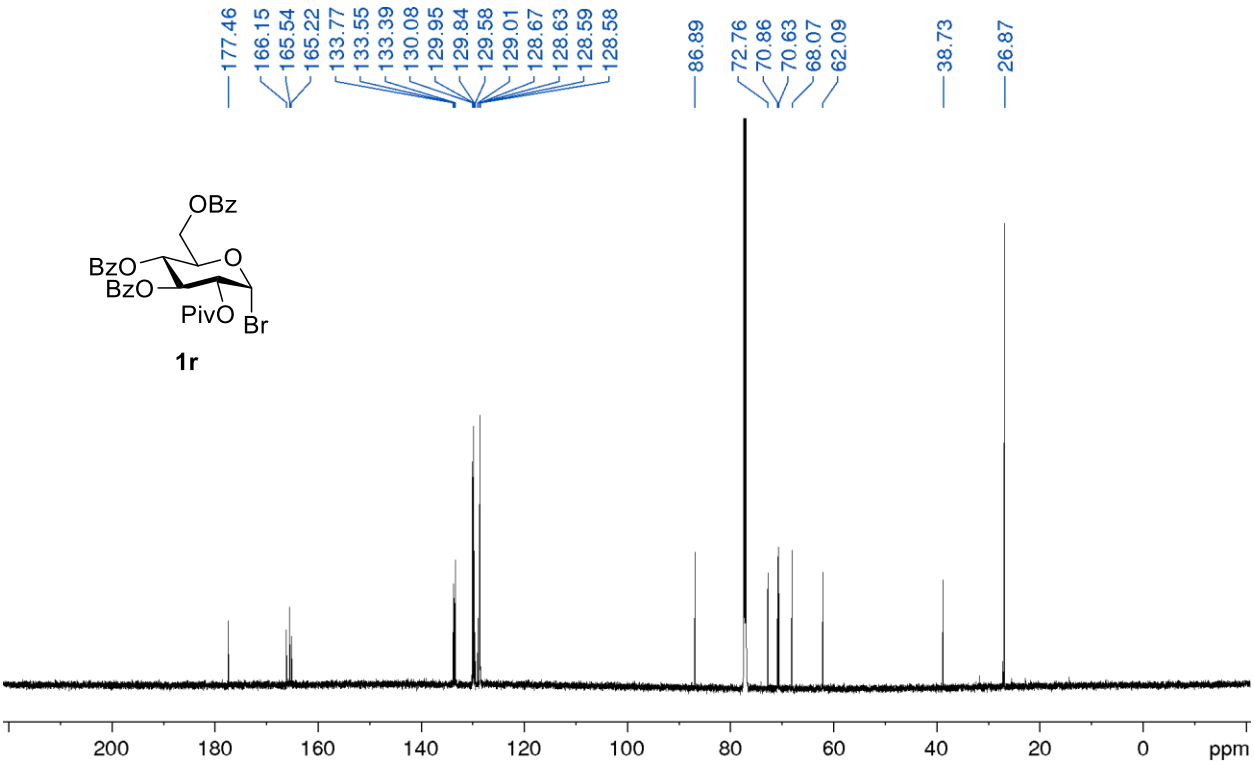
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of (1q)



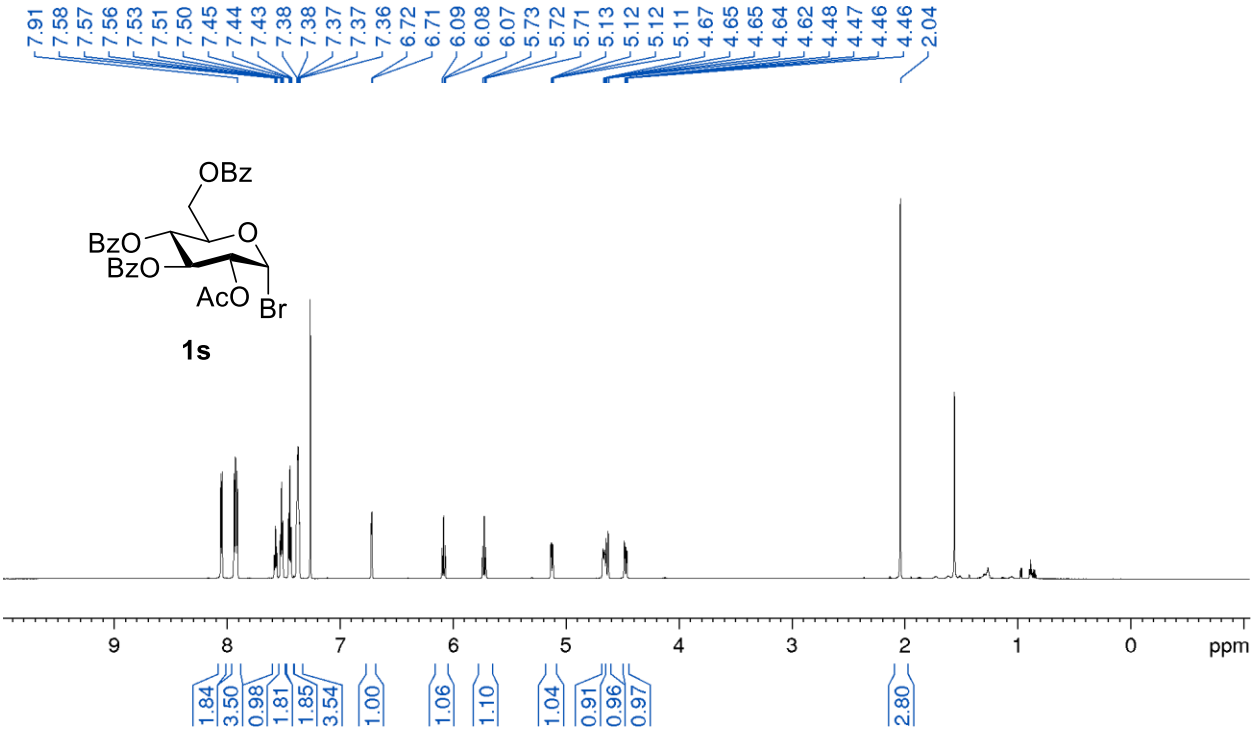
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1r)



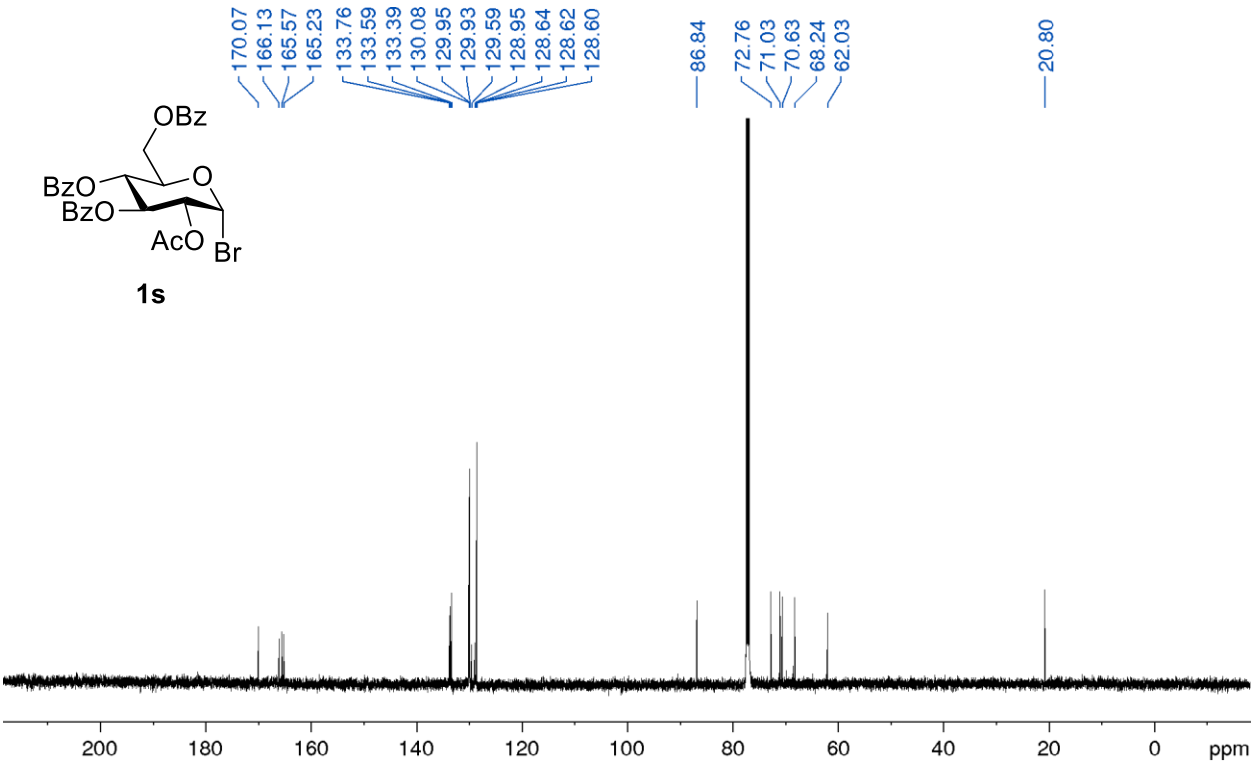
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1r)



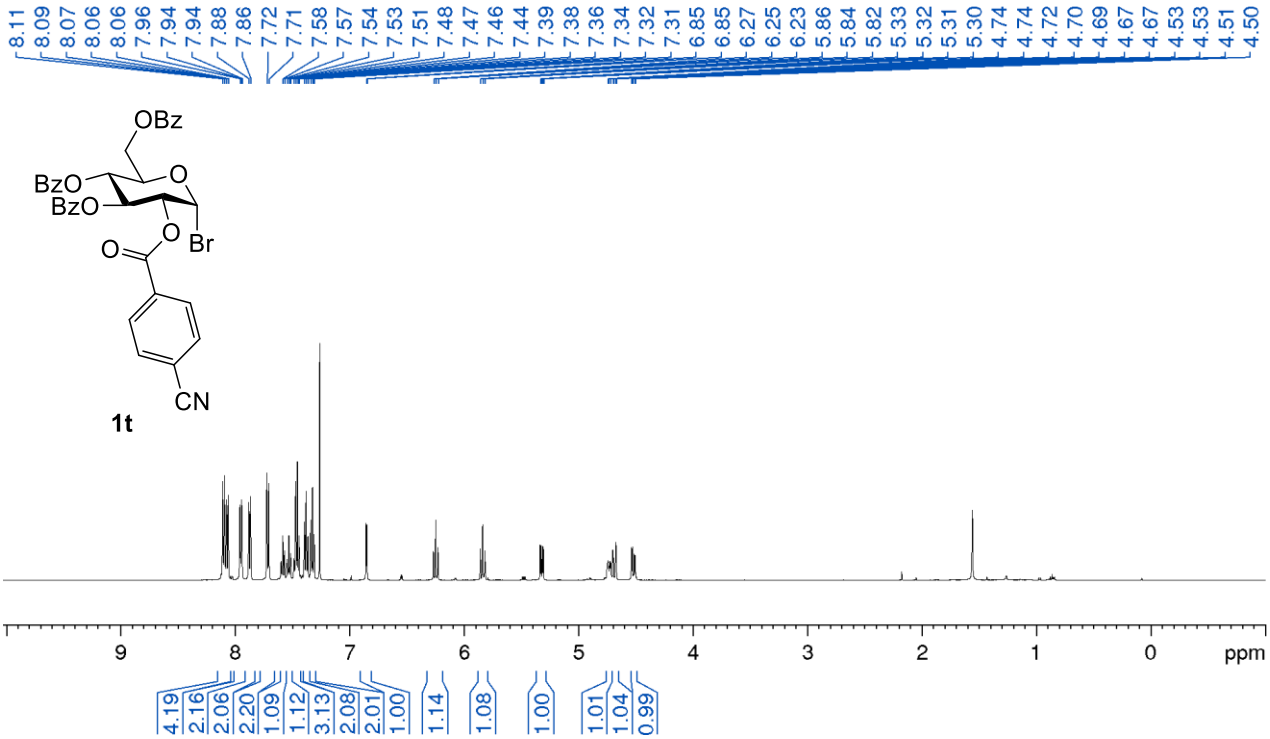
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1s)



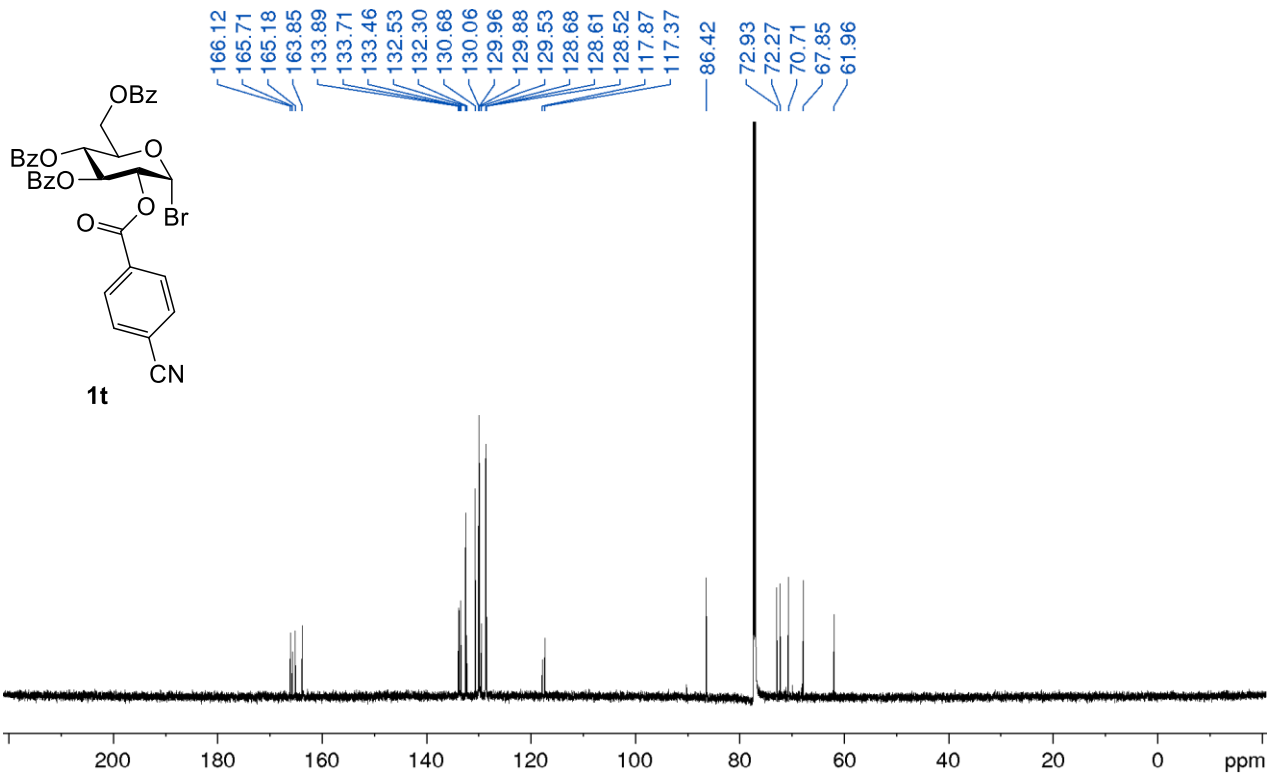
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1s)



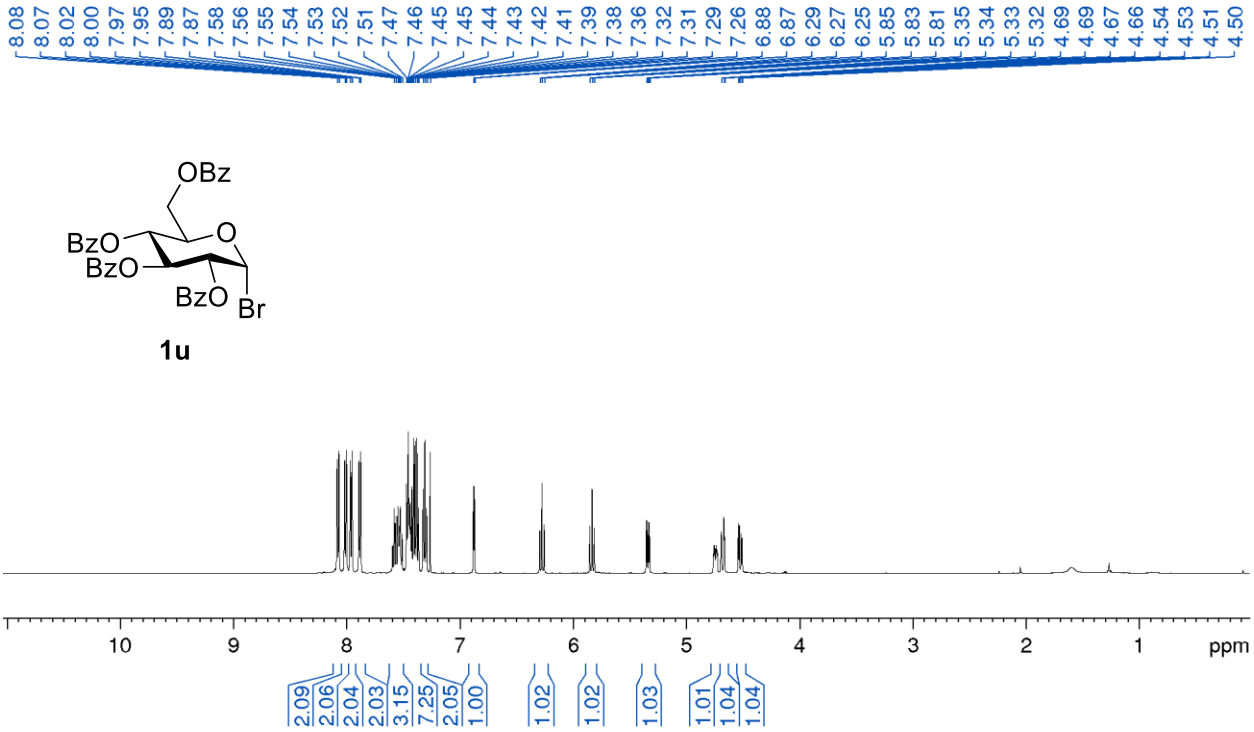
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1t)



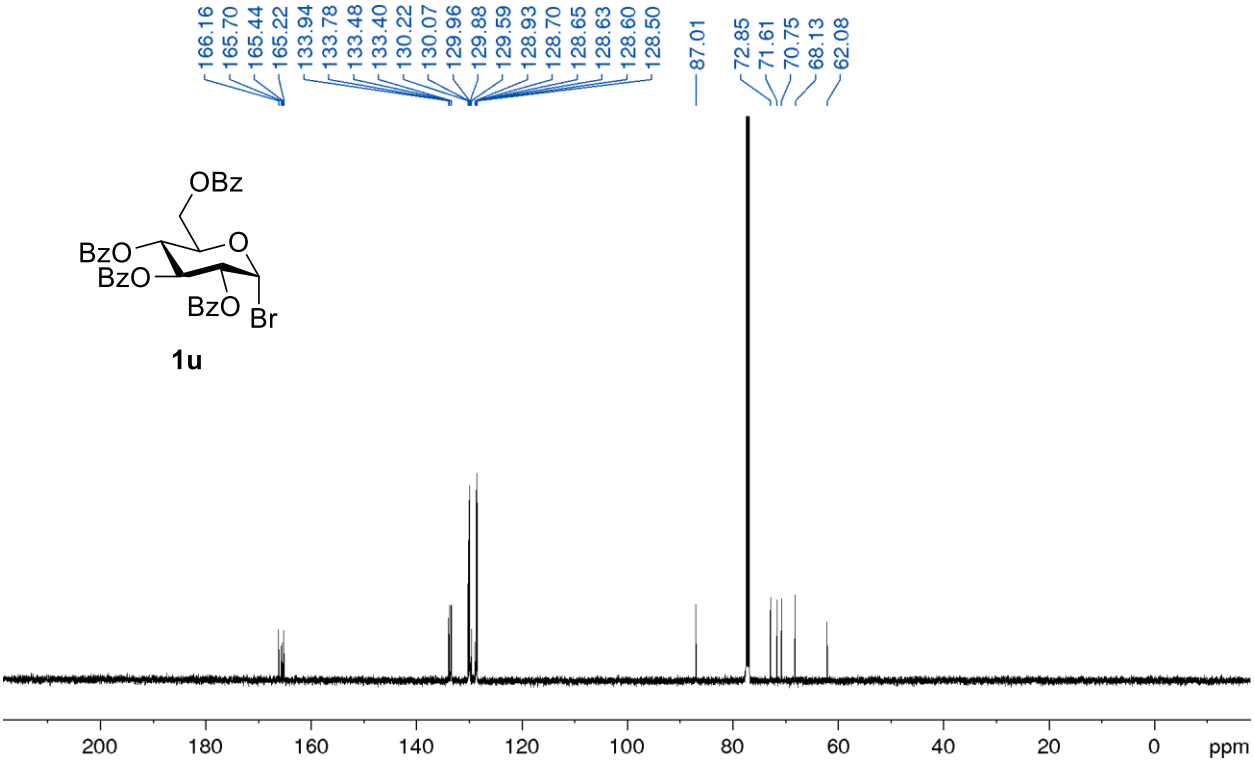
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1t)



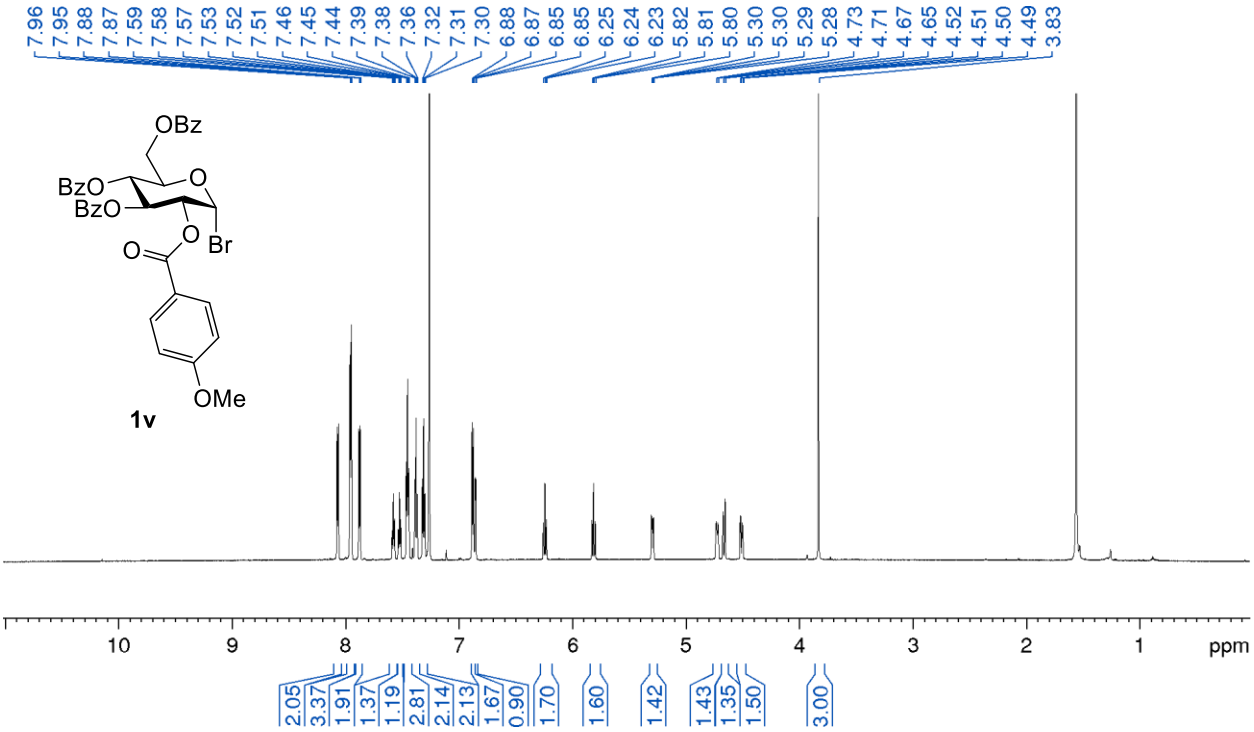
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1u)



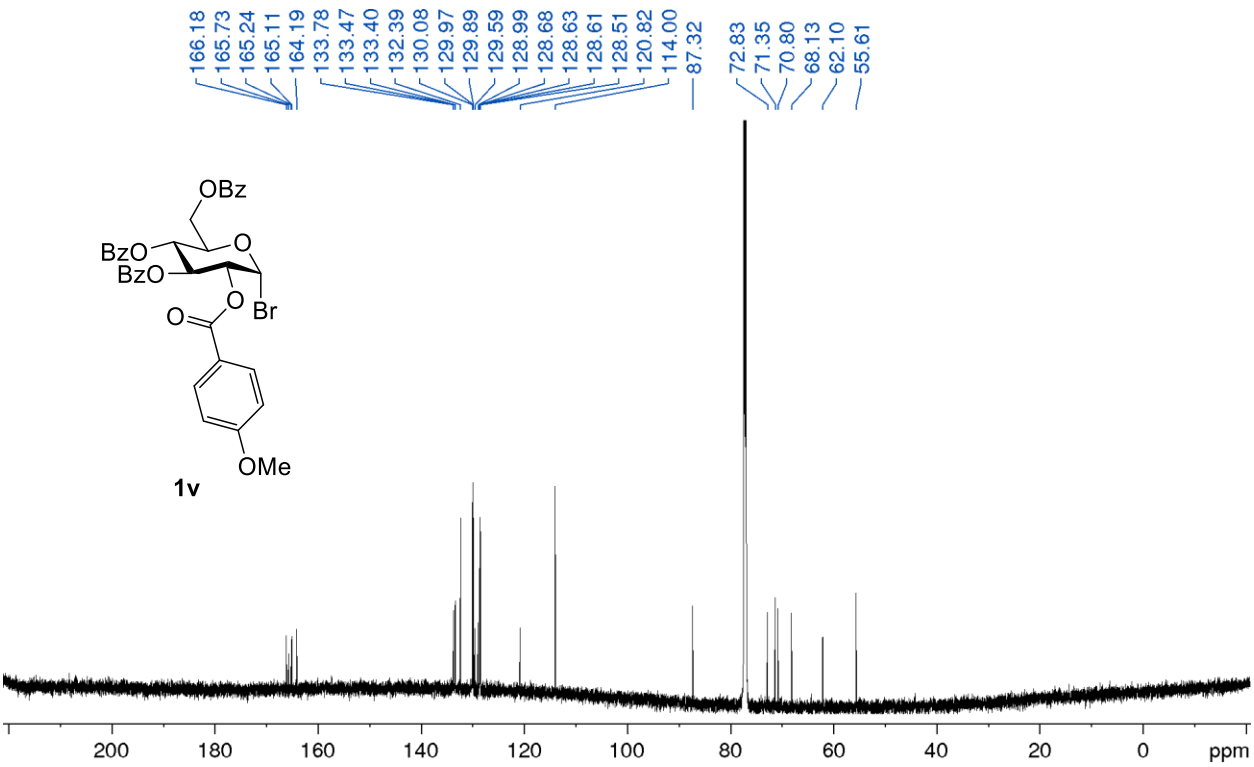
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1u)



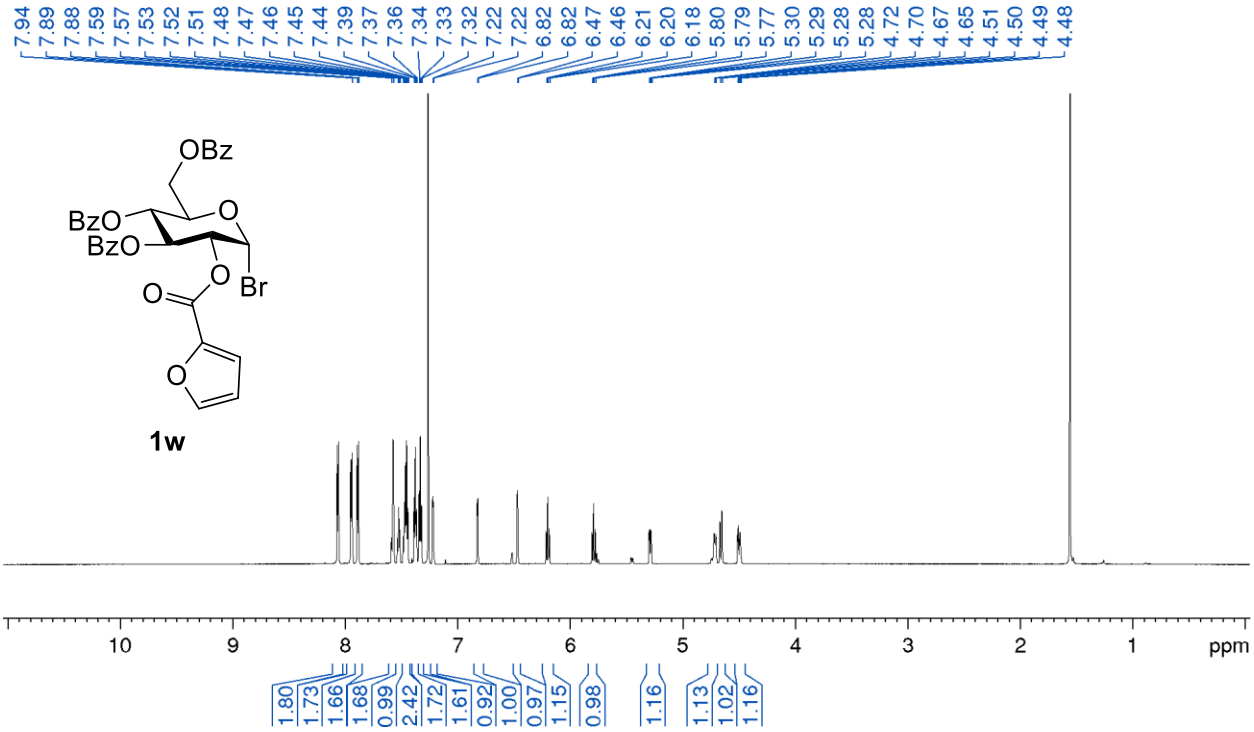
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1v)



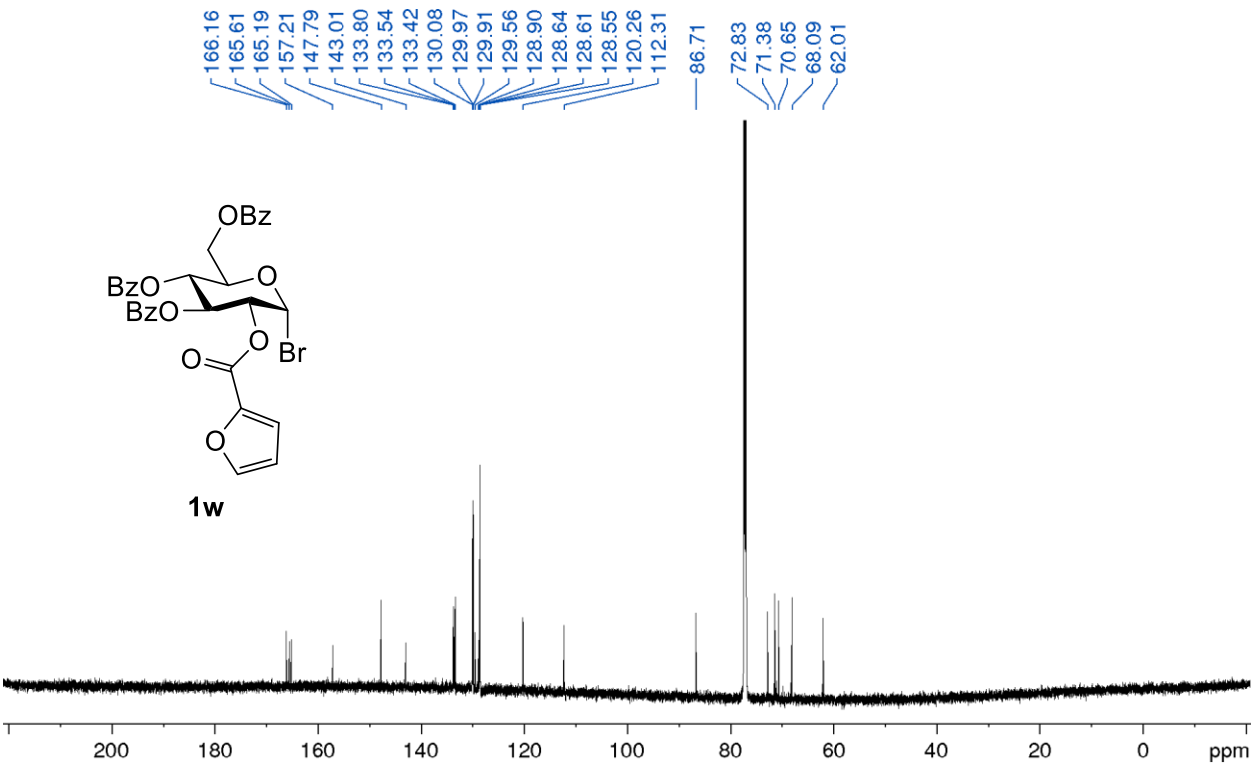
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1v)



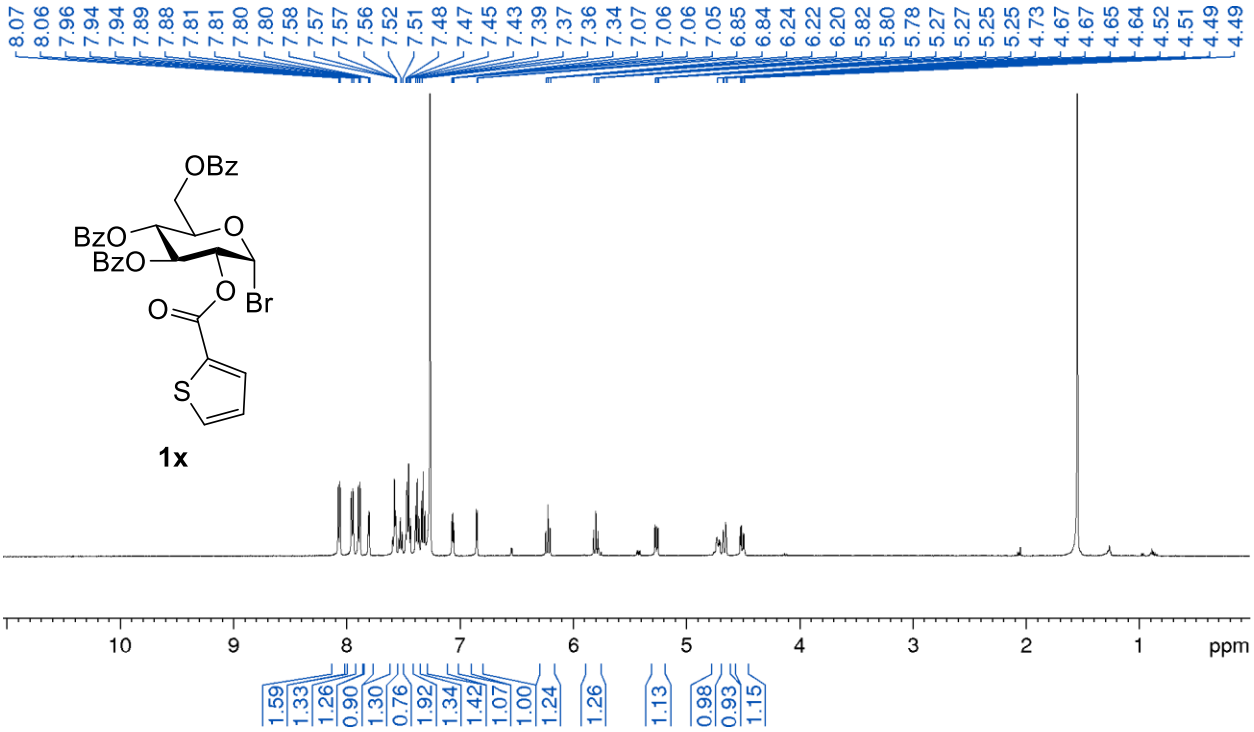
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1w)



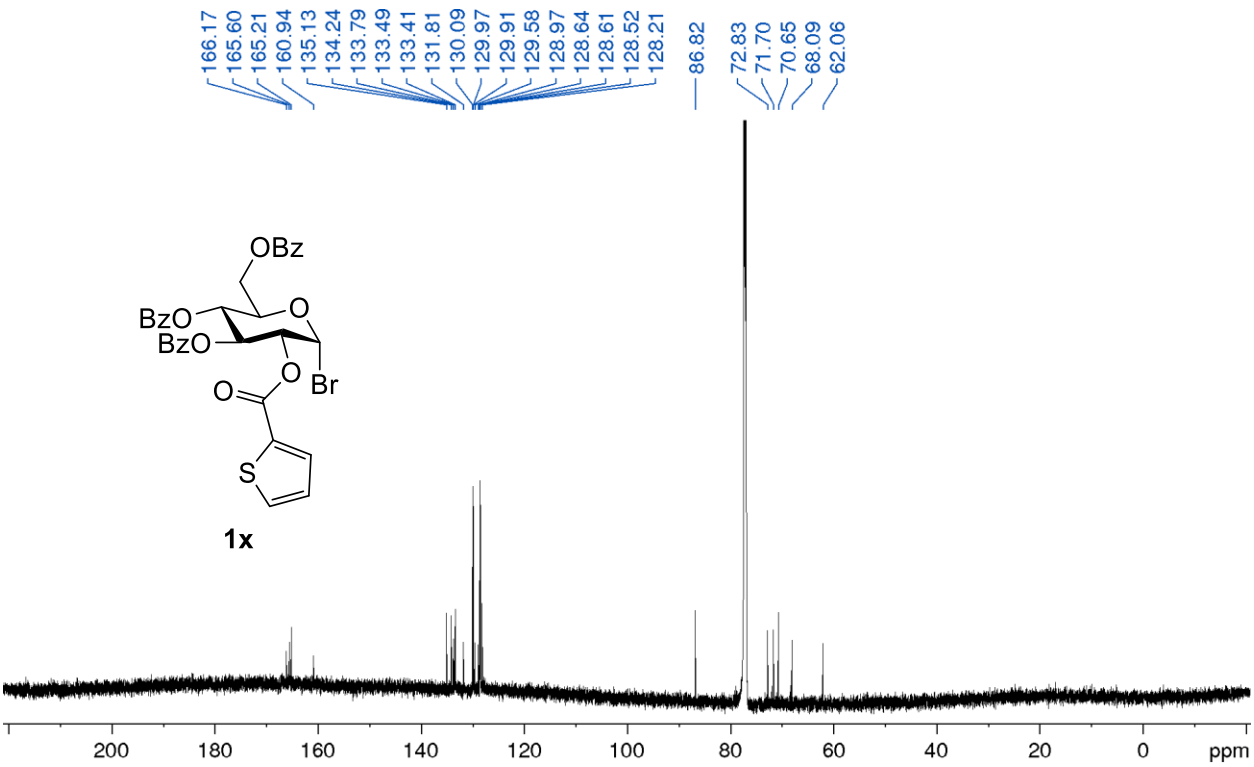
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1w)



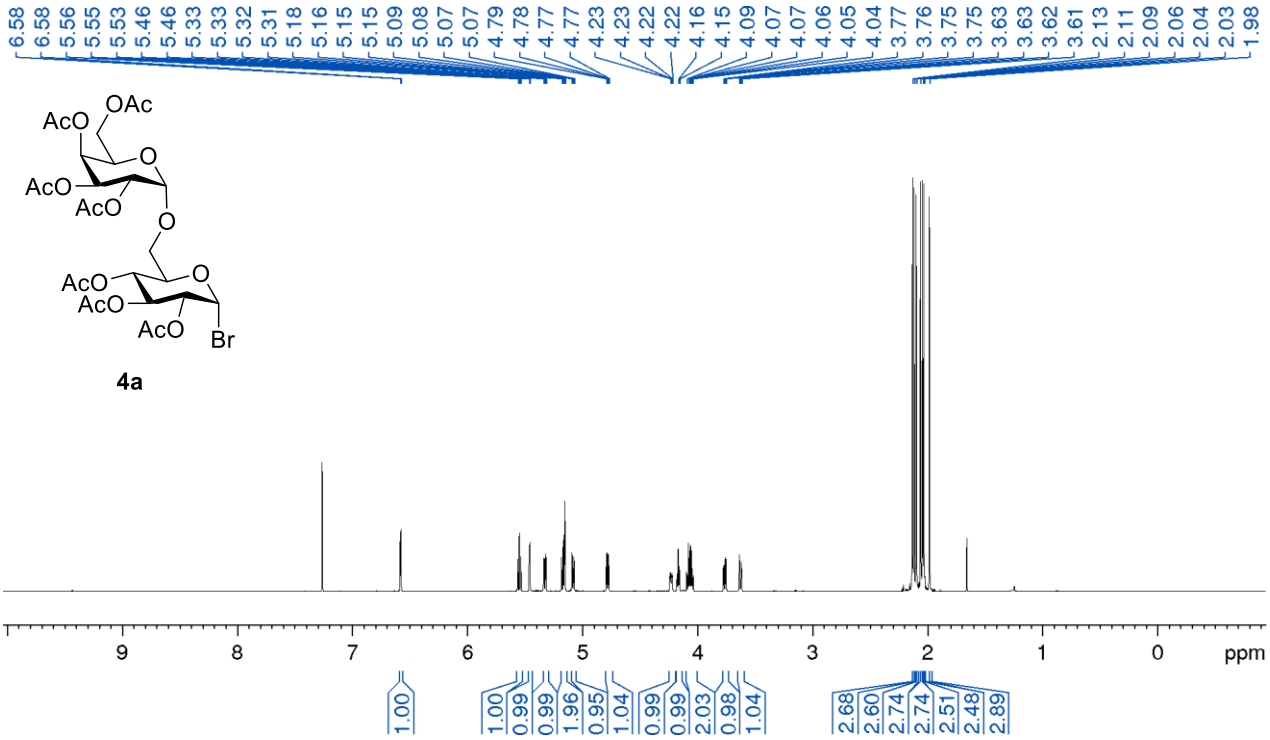
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1x)



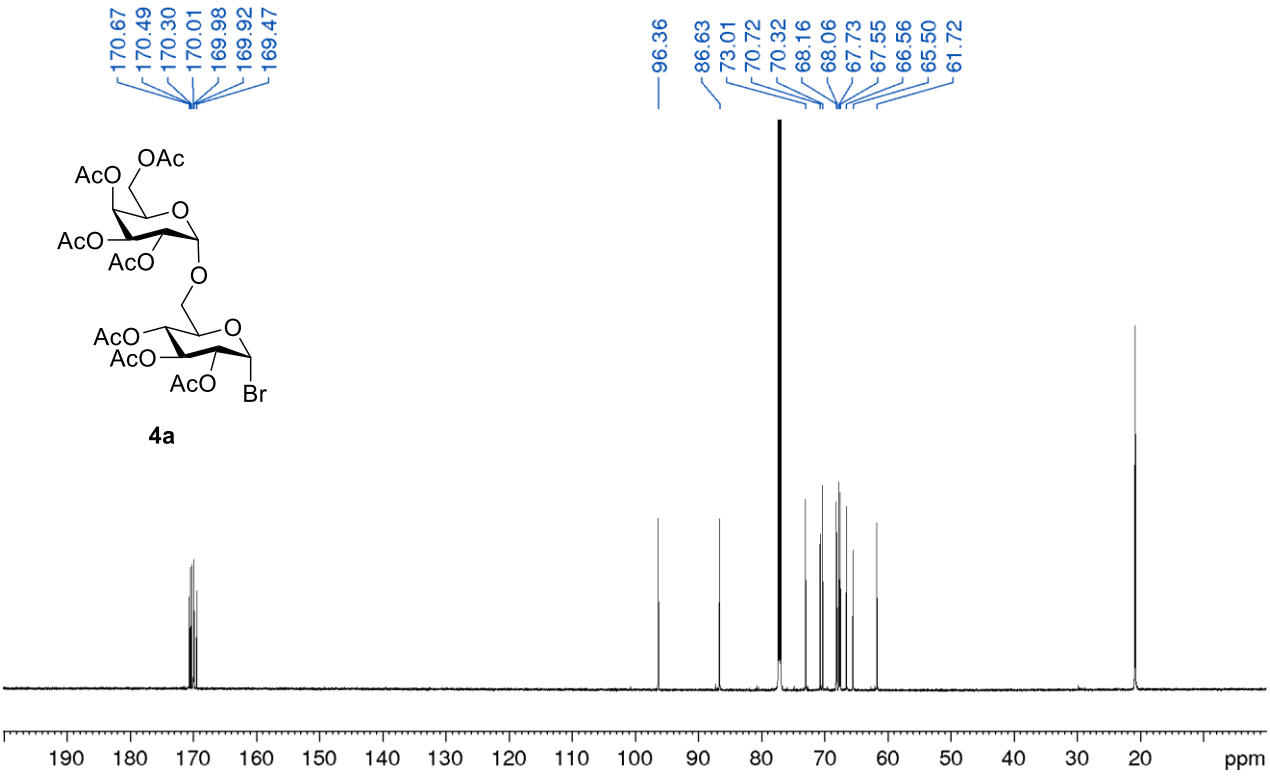
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1x)



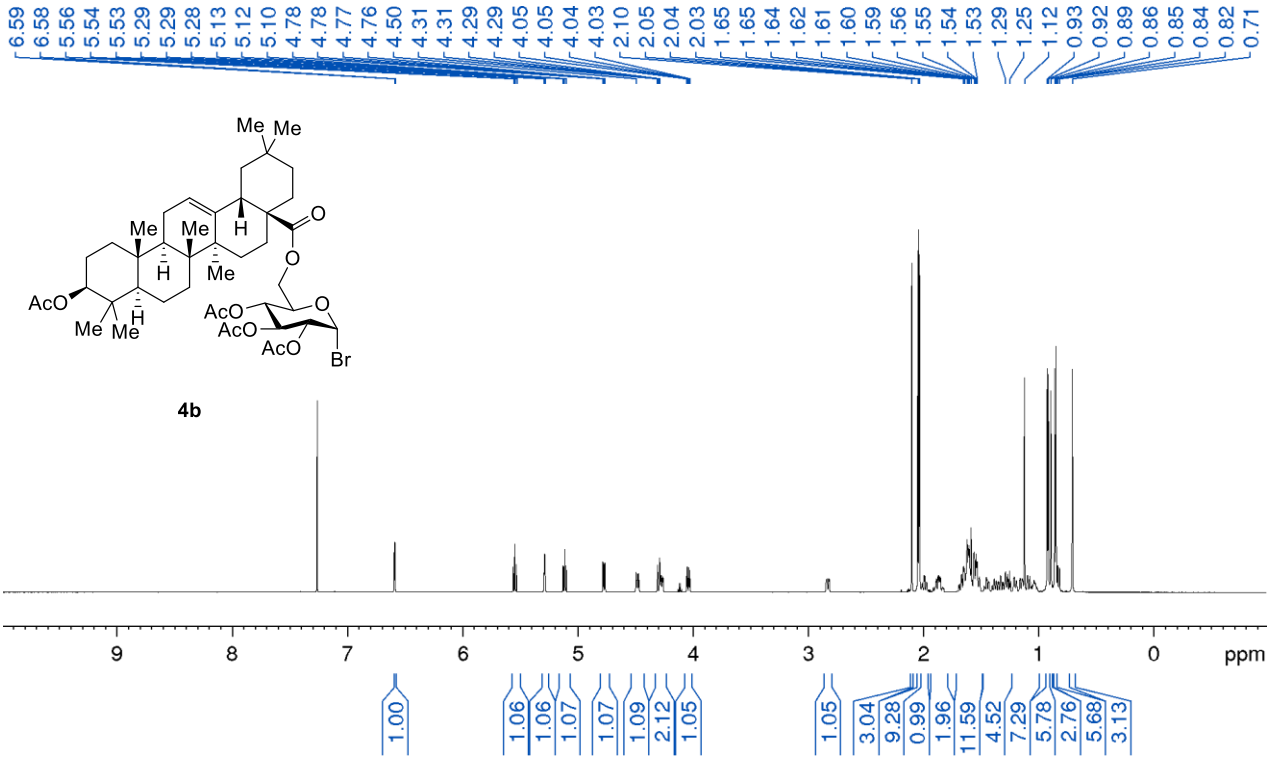
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4a)



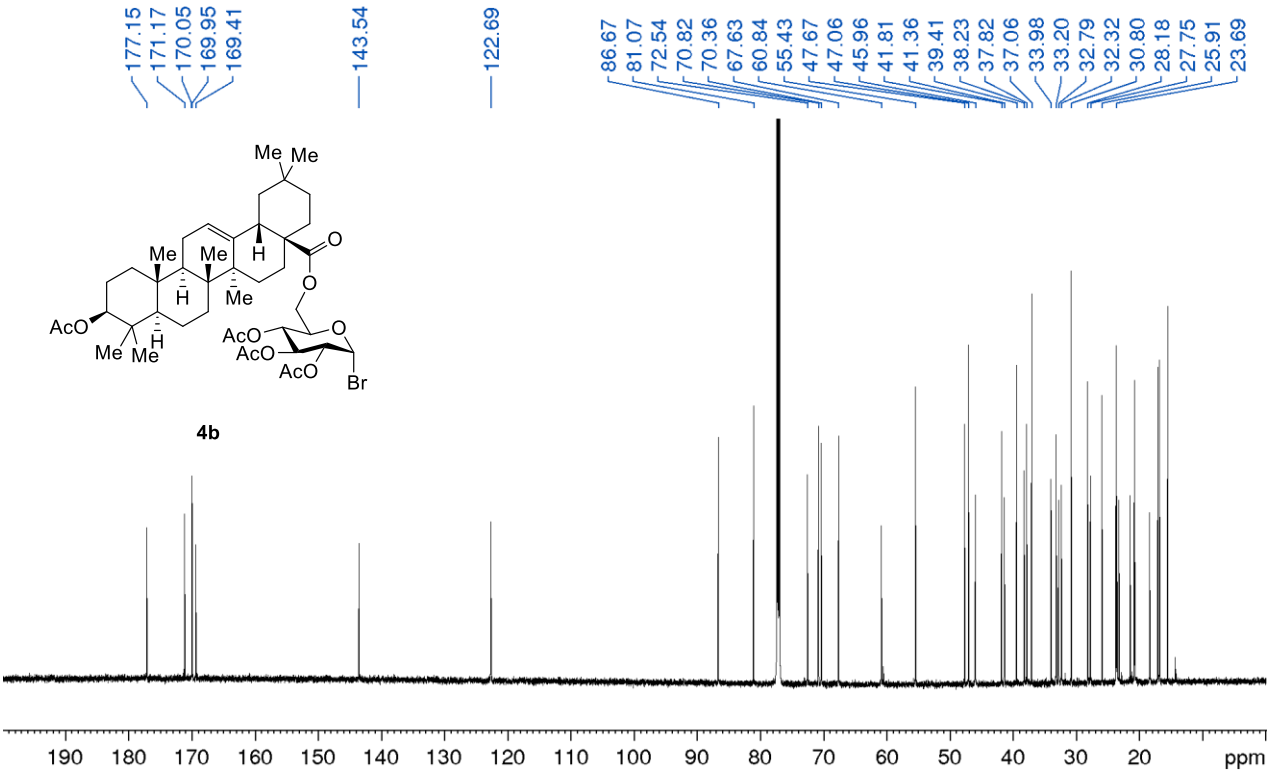
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4a)



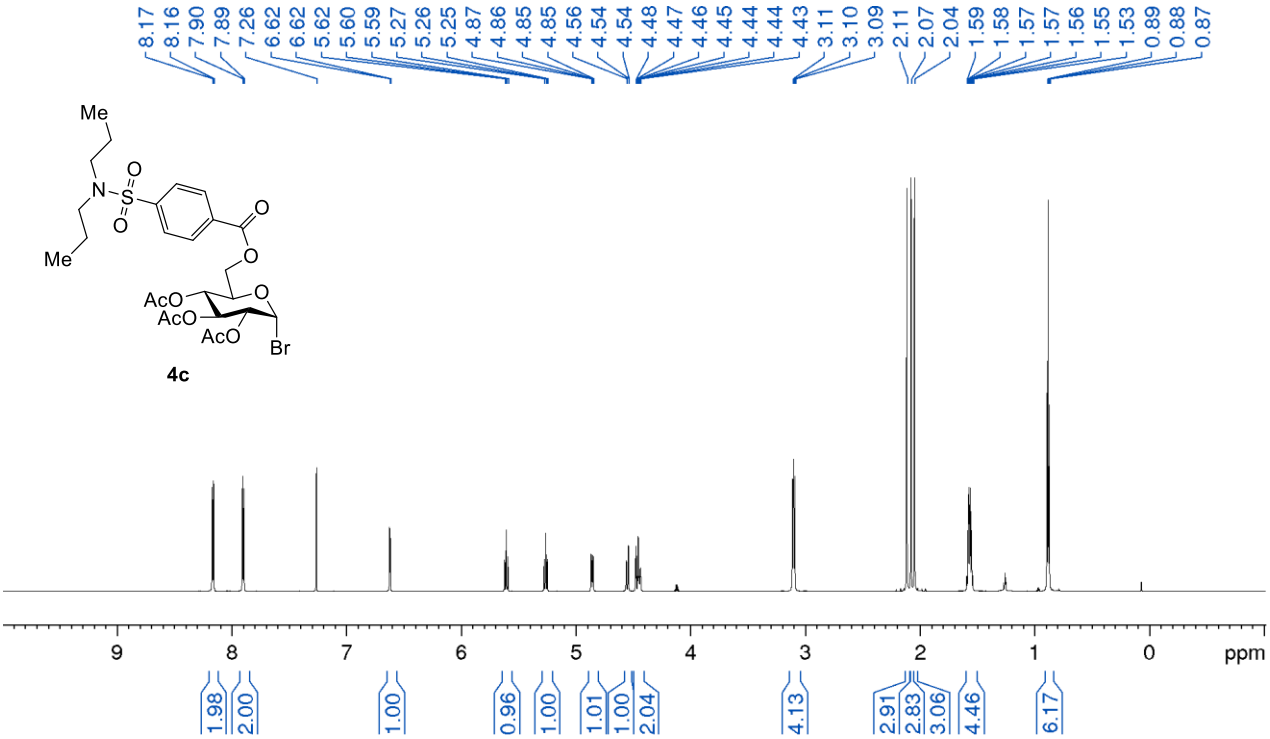
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4b)



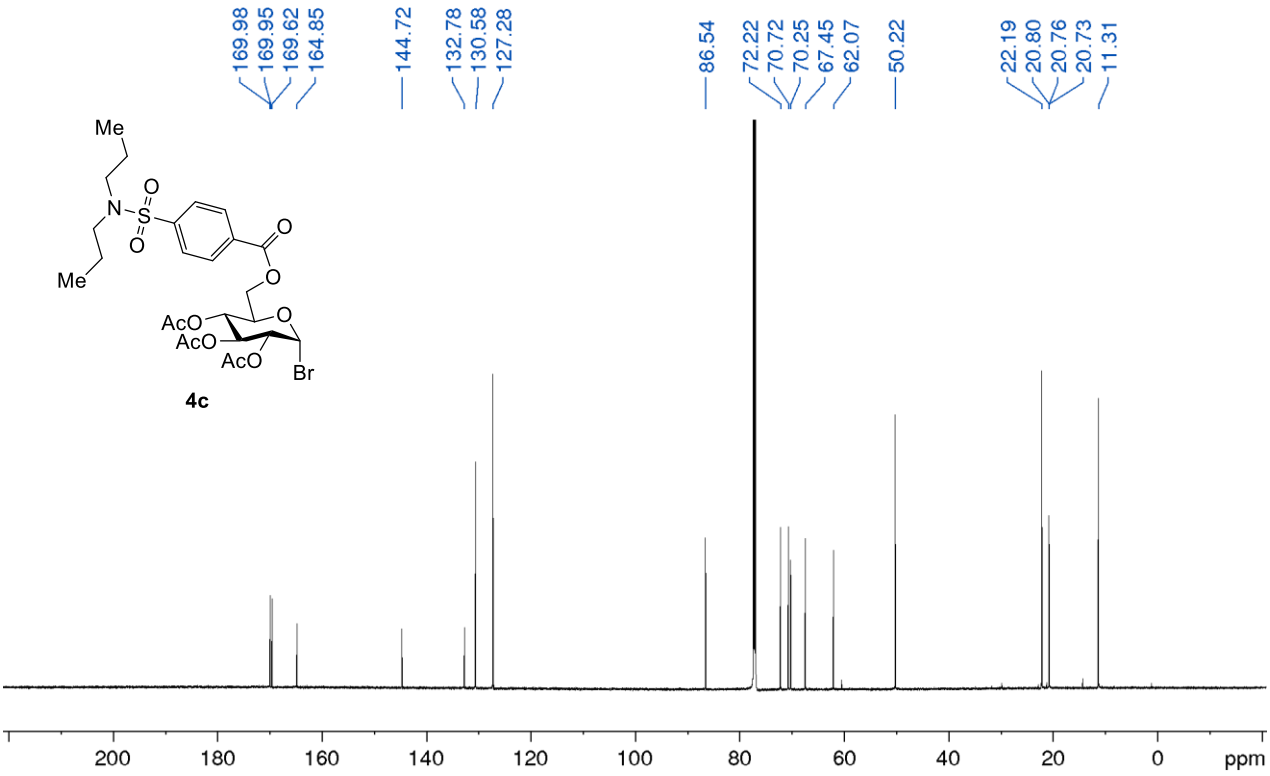
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4b)



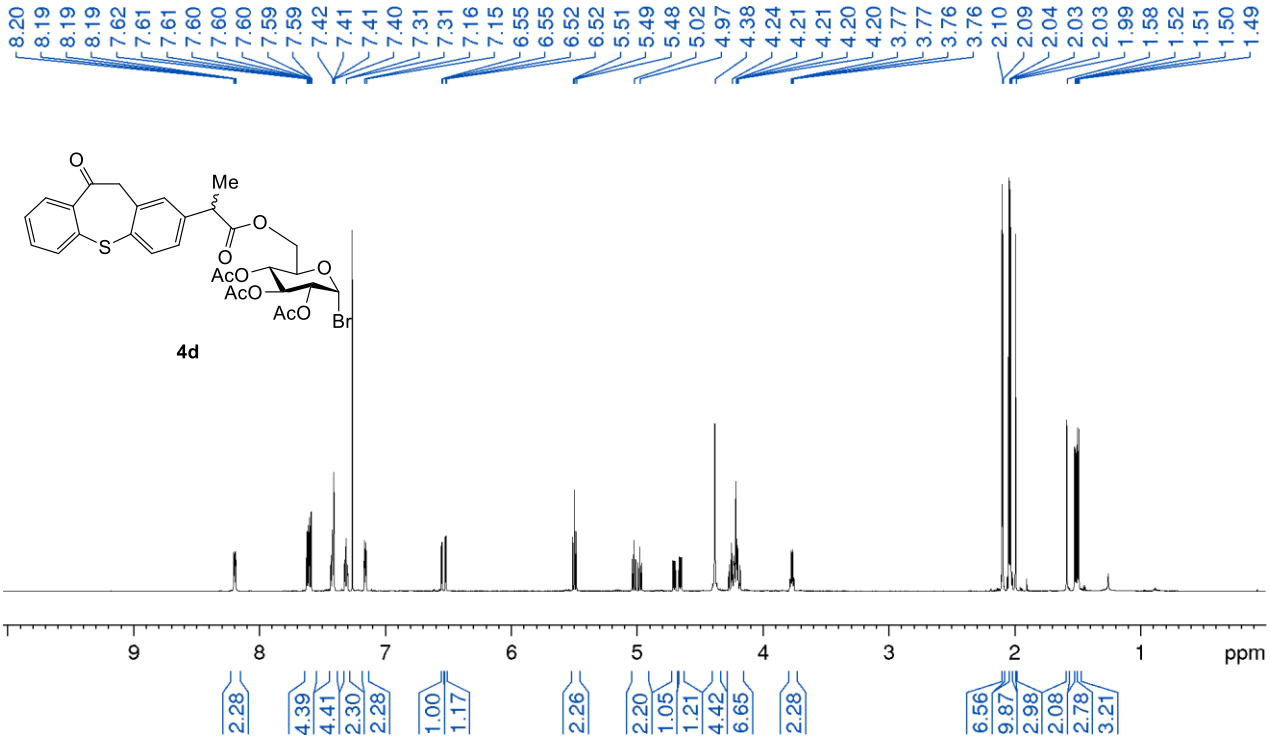
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4c)



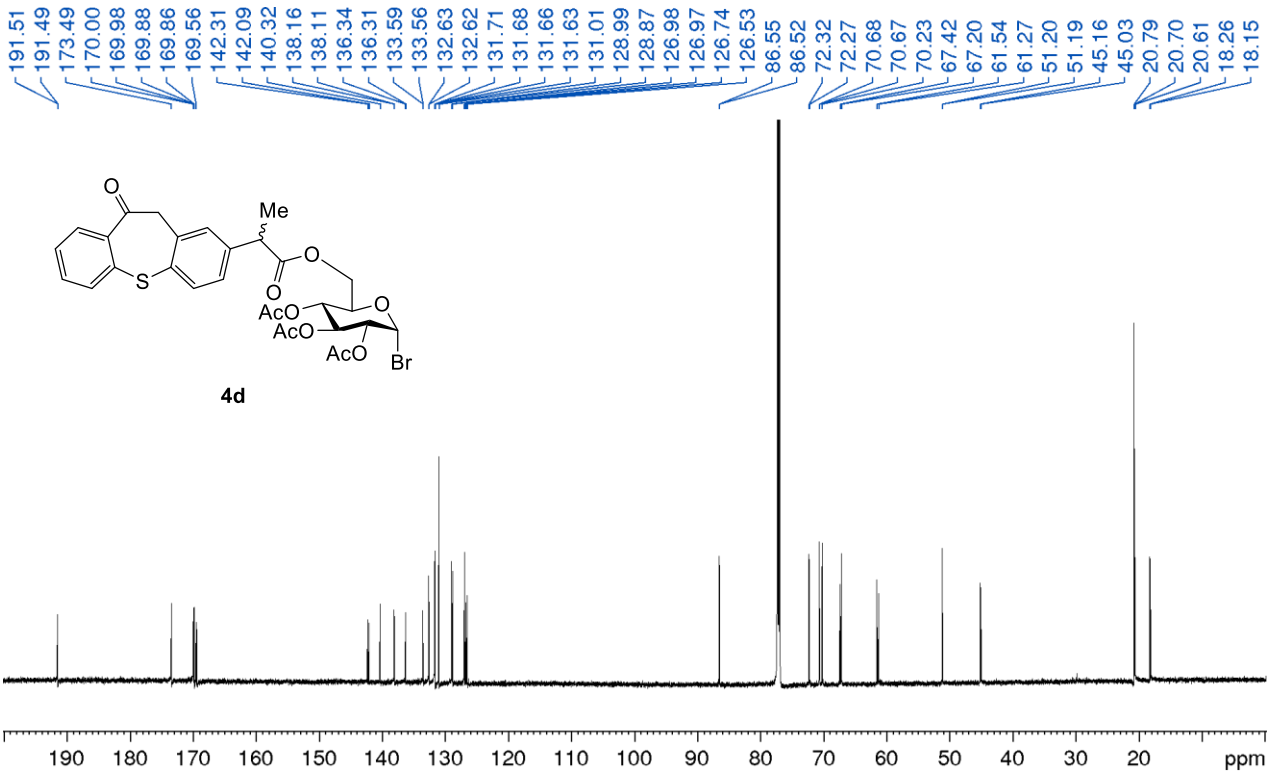
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4c)



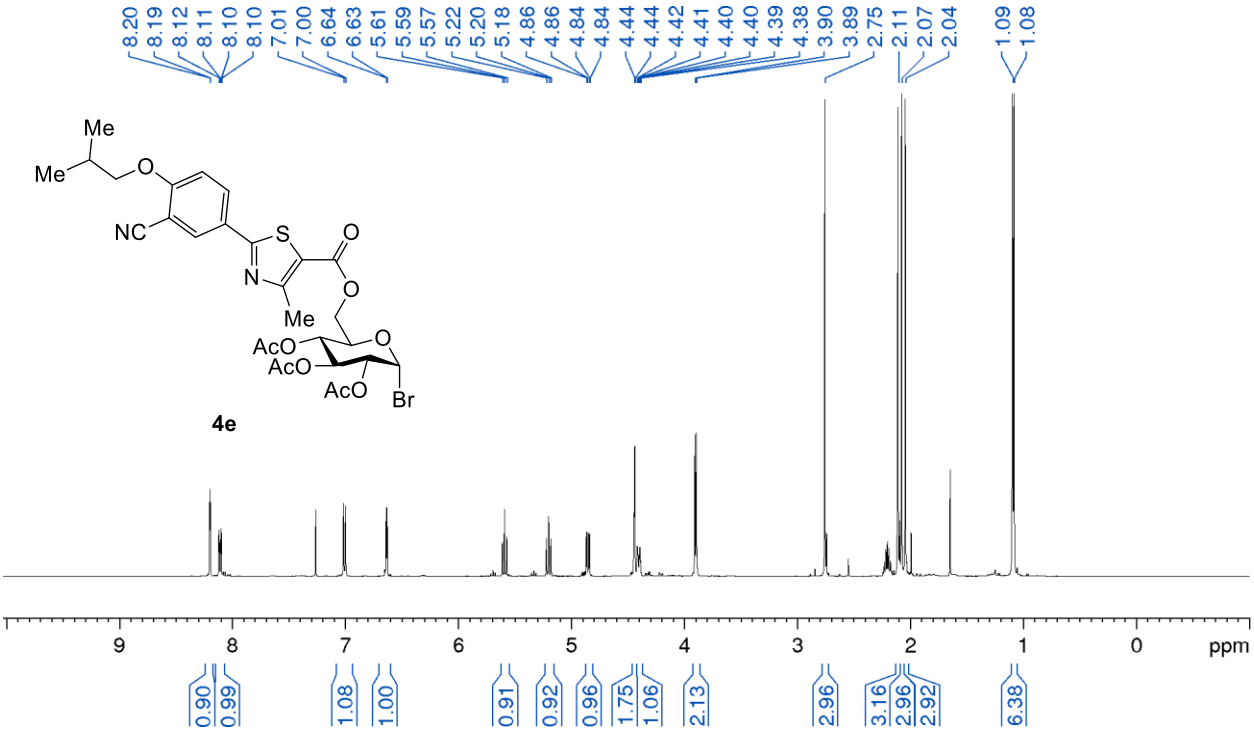
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4d)



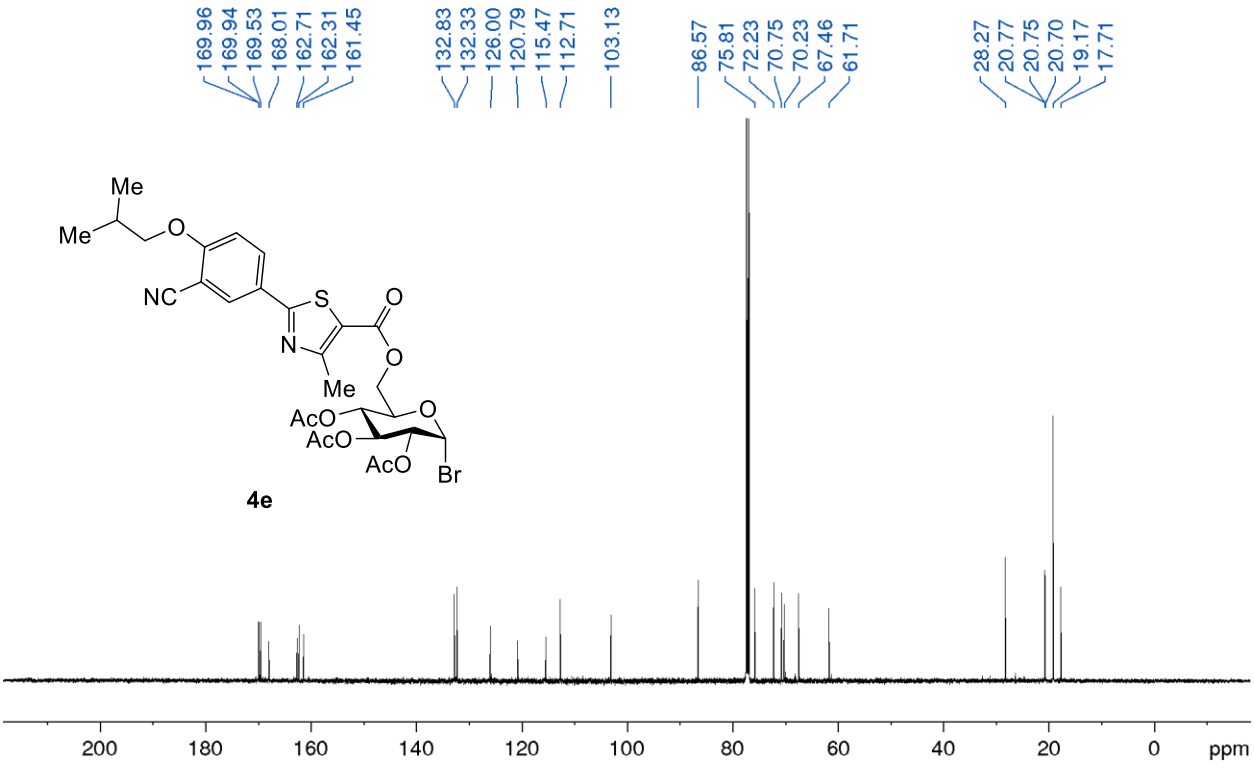
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4d)



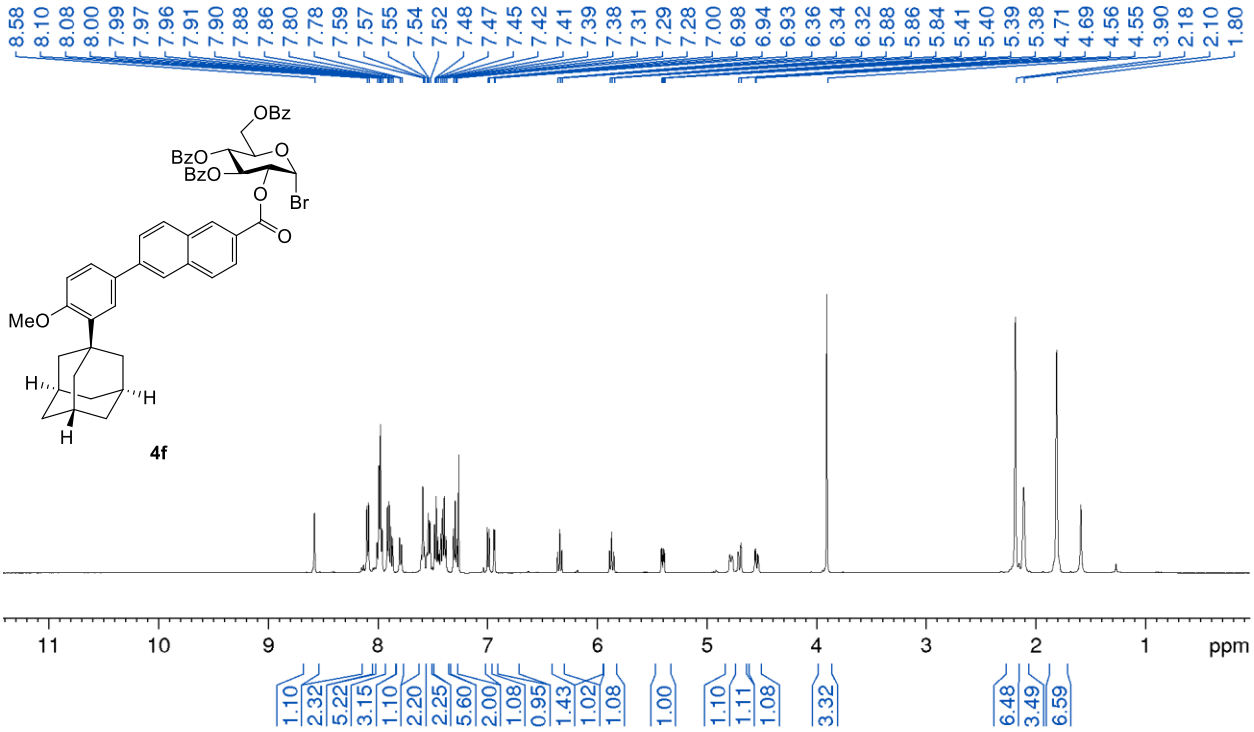
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (4e)



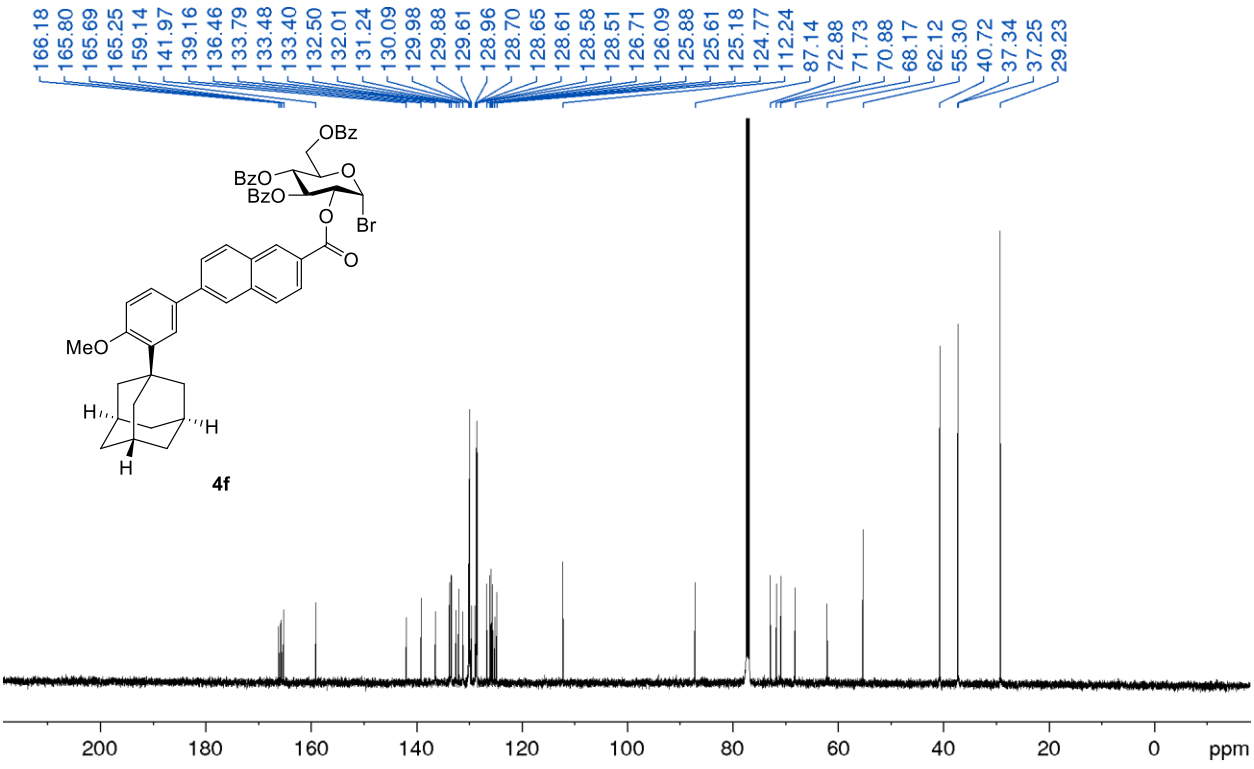
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (4e)



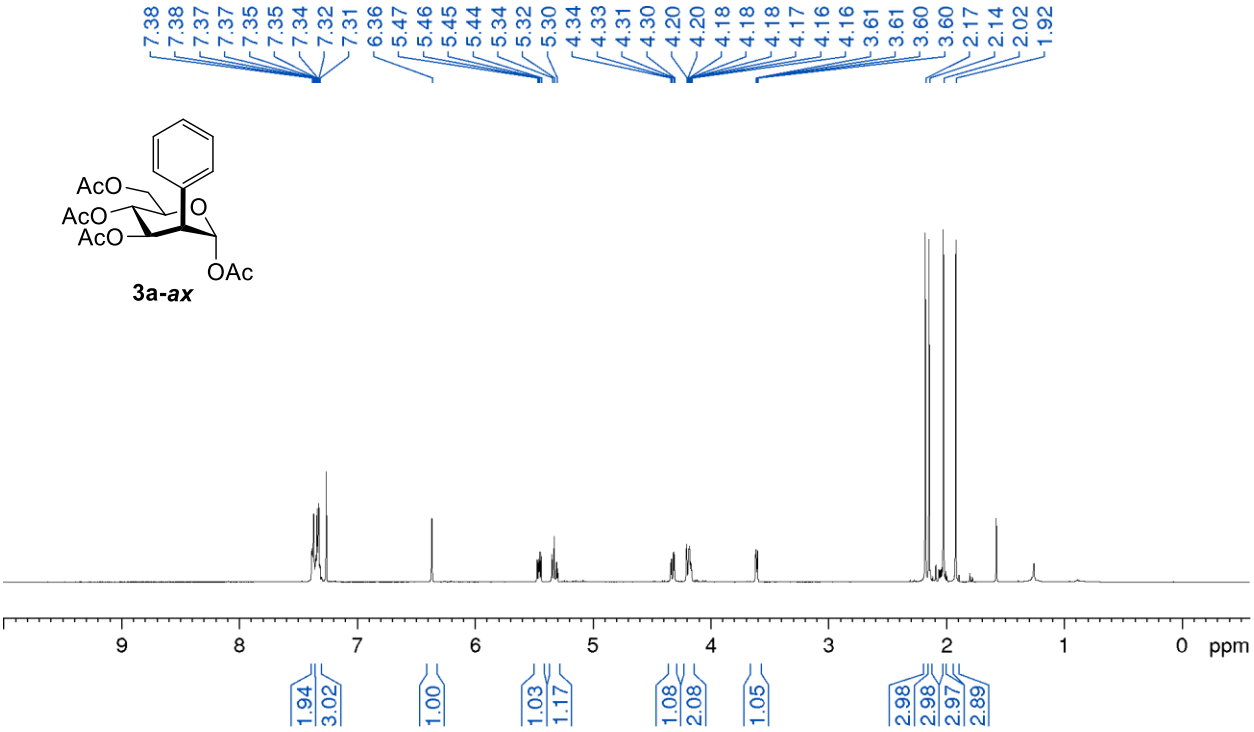
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (4f)



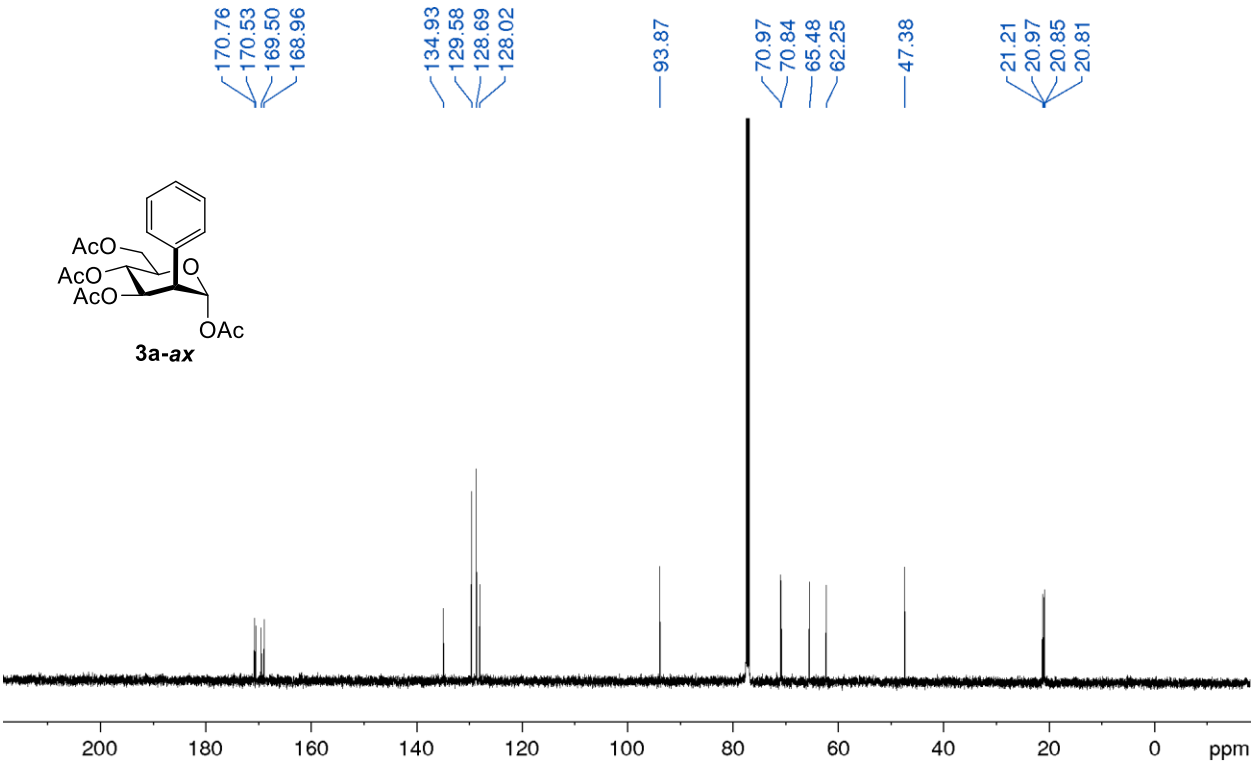
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (4f)



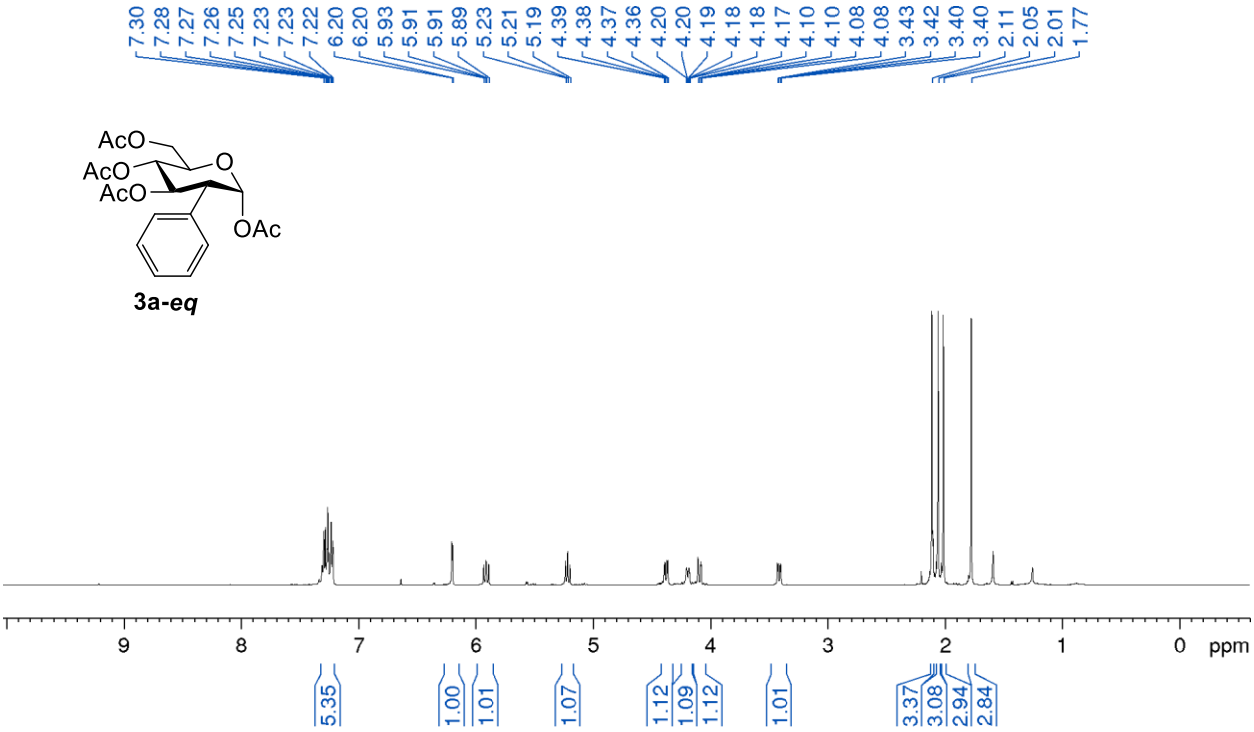
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3a-*ax*)



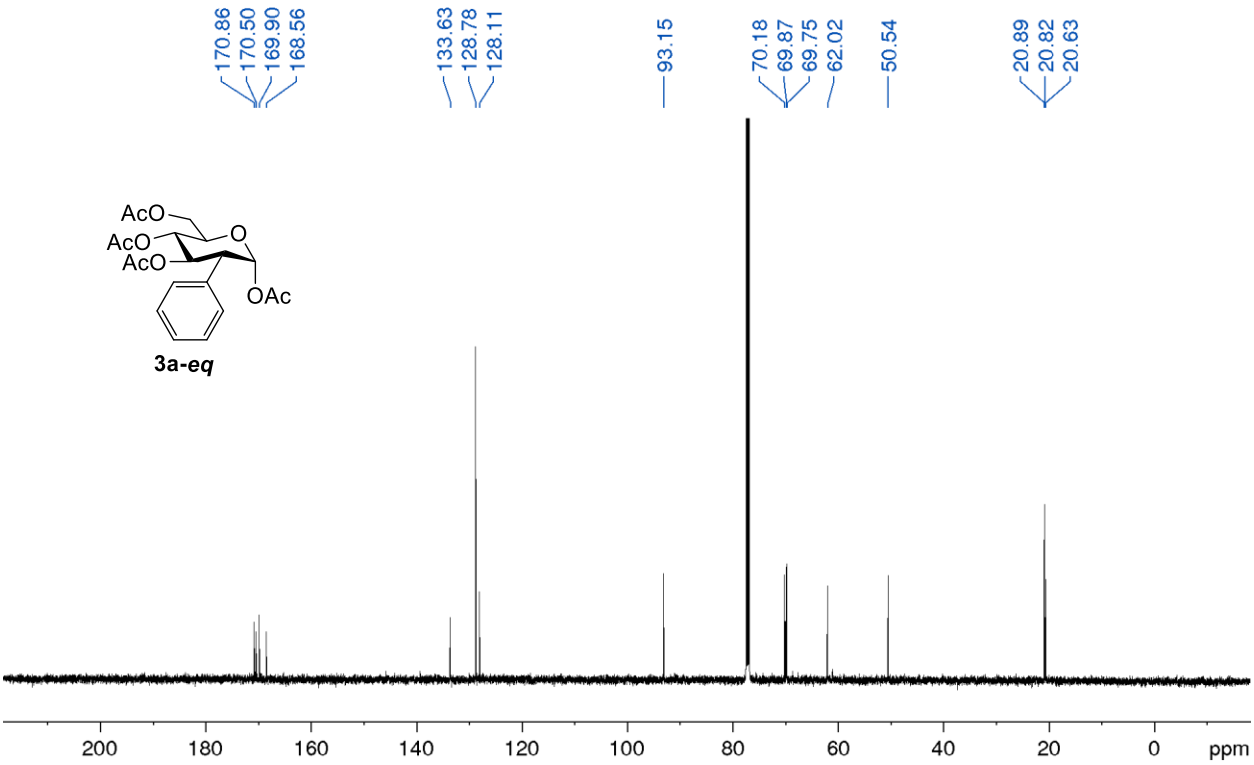
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3a-*ax*)



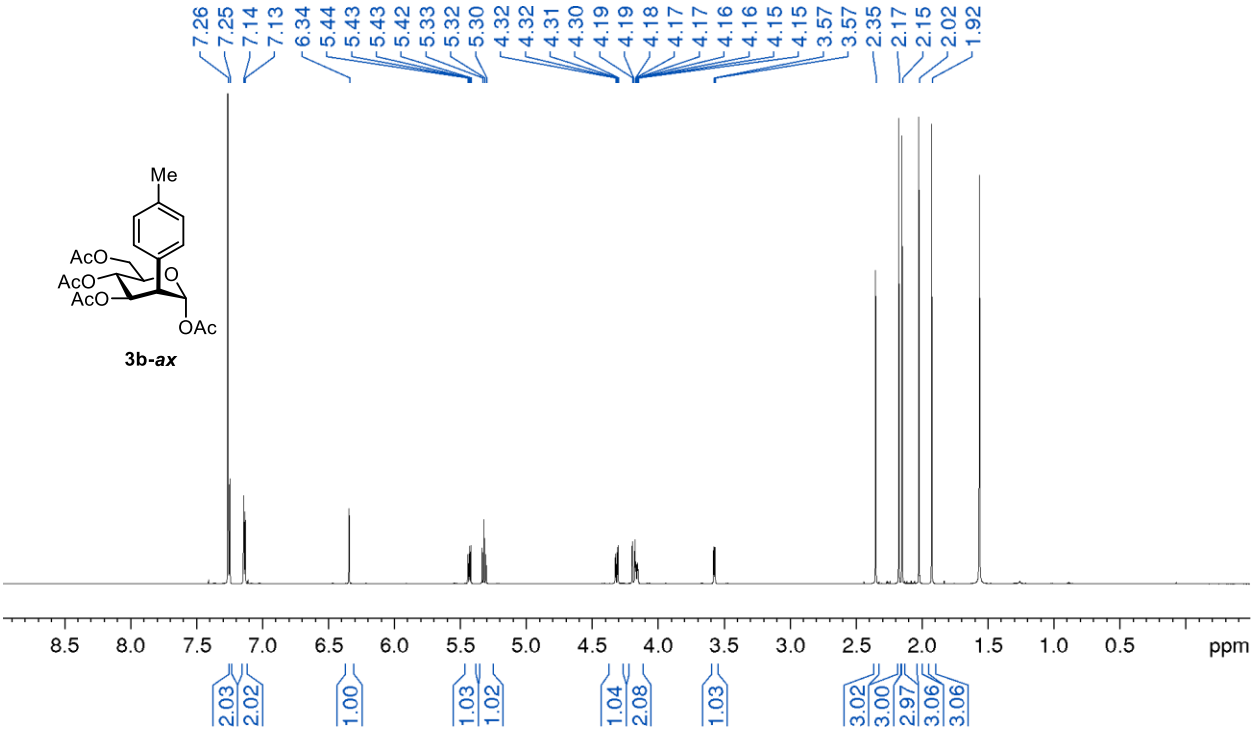
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3a-*eq*)



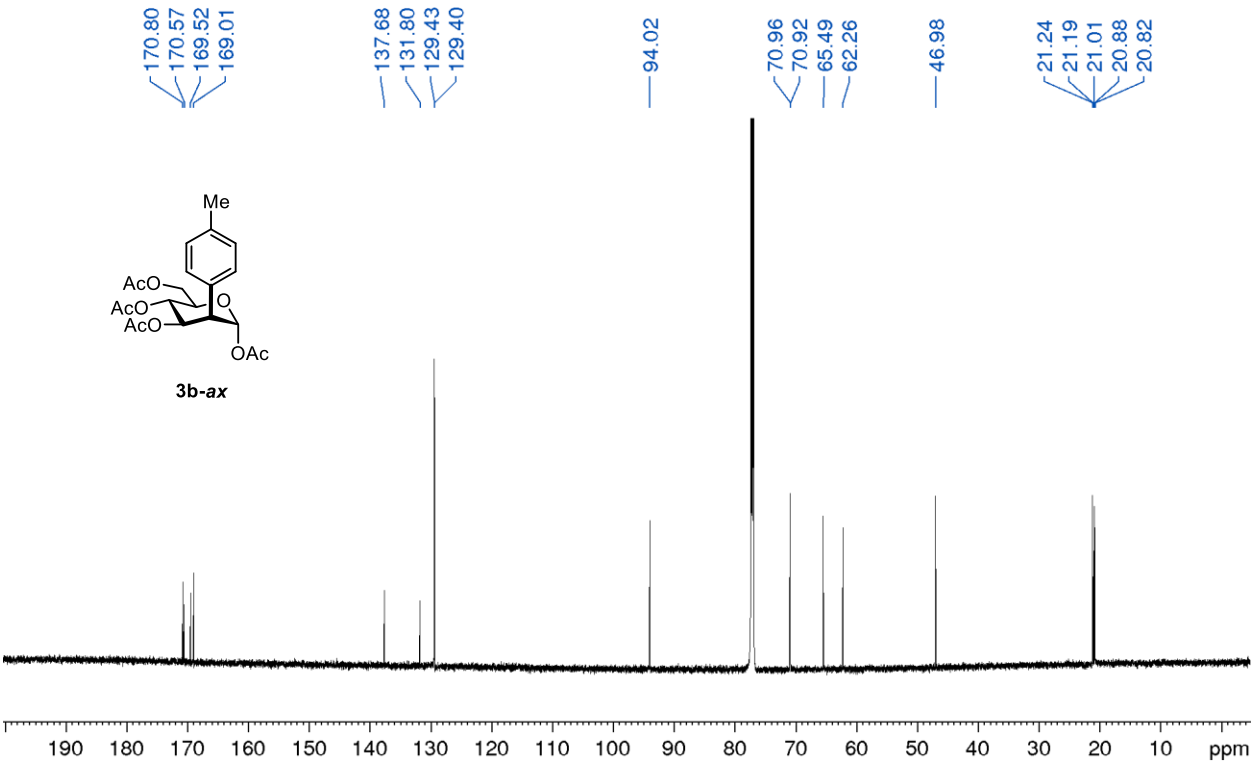
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3a-*eq*)



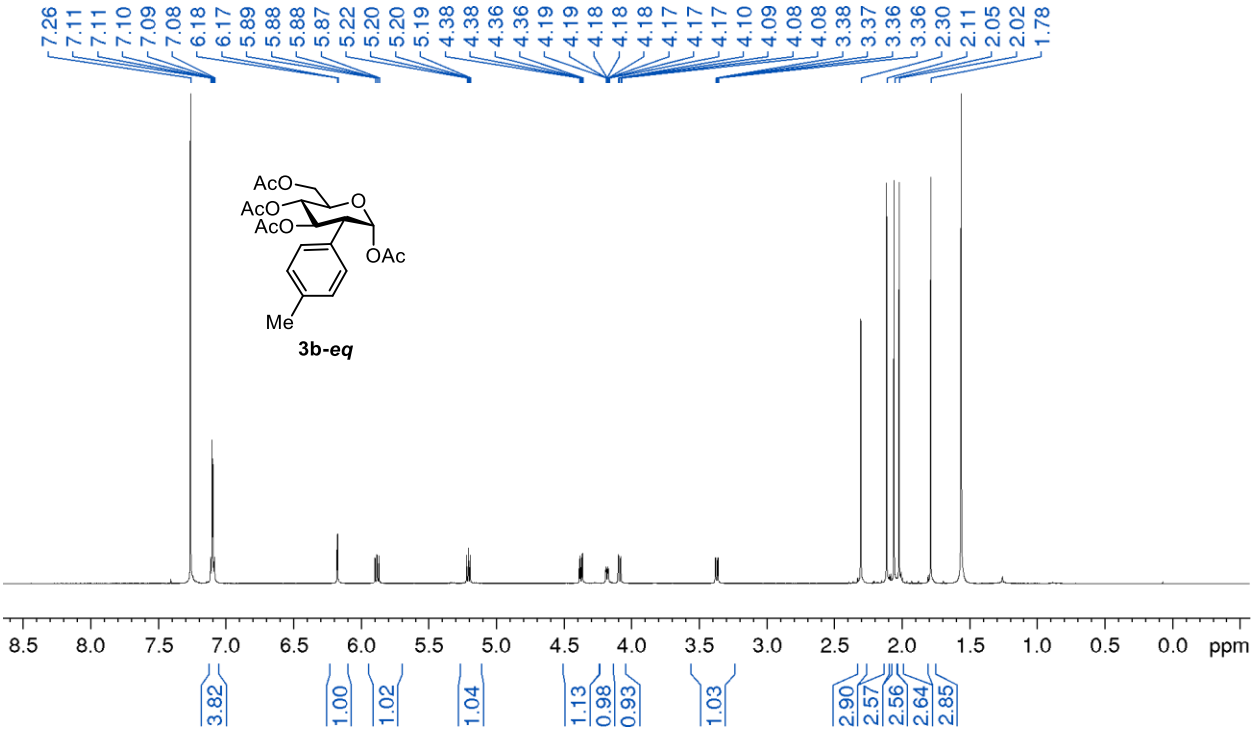
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3b-*ax*)



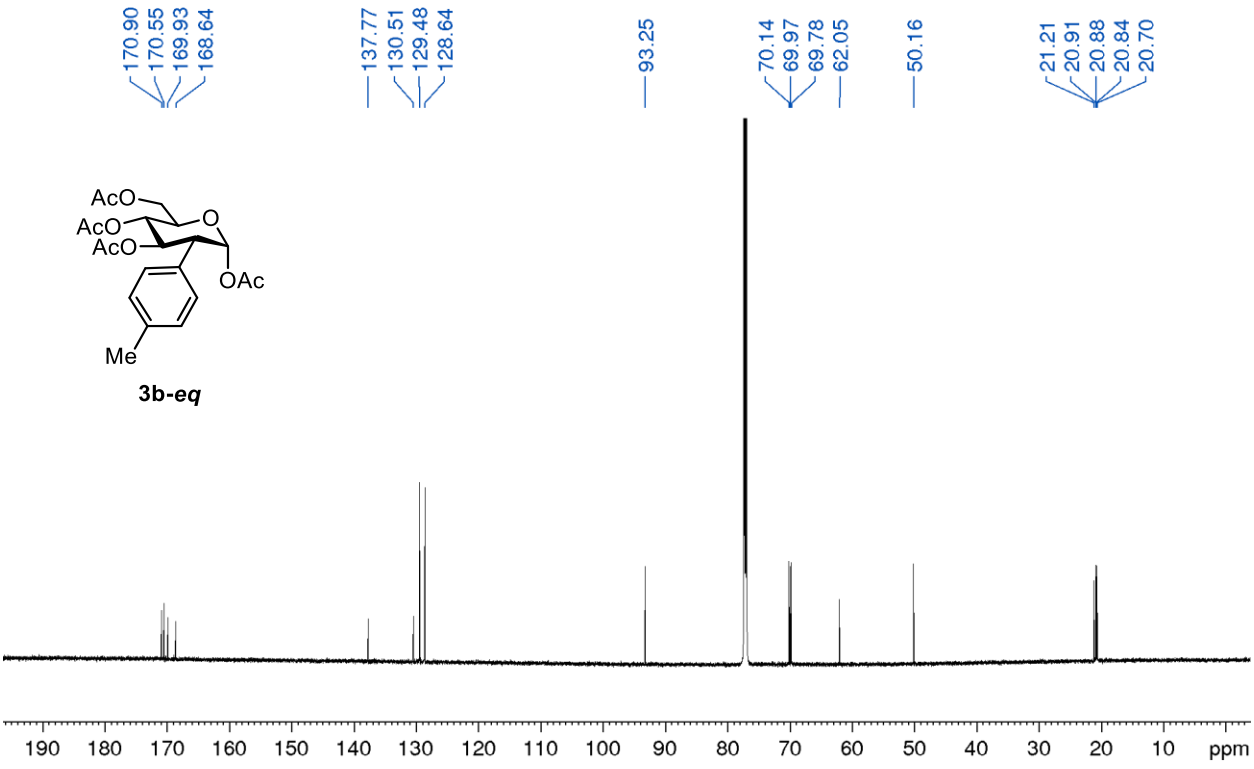
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3b-*ax*)



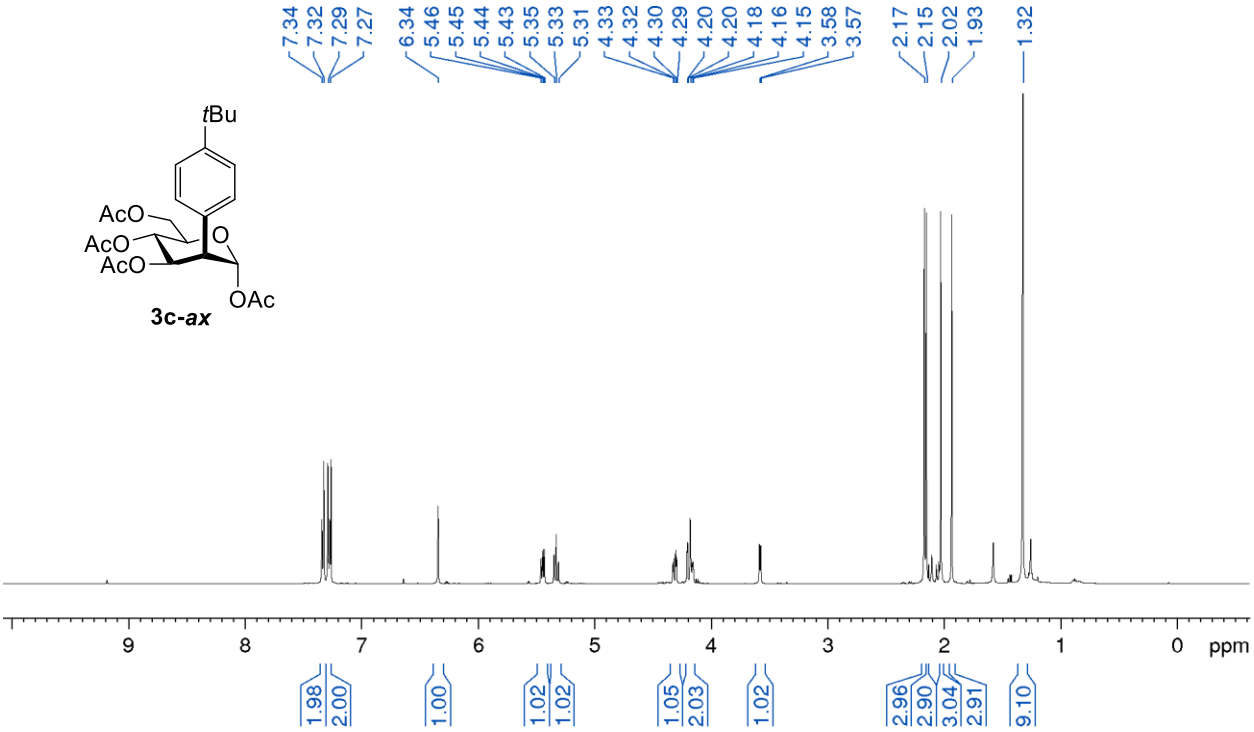
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3b-*eq*)



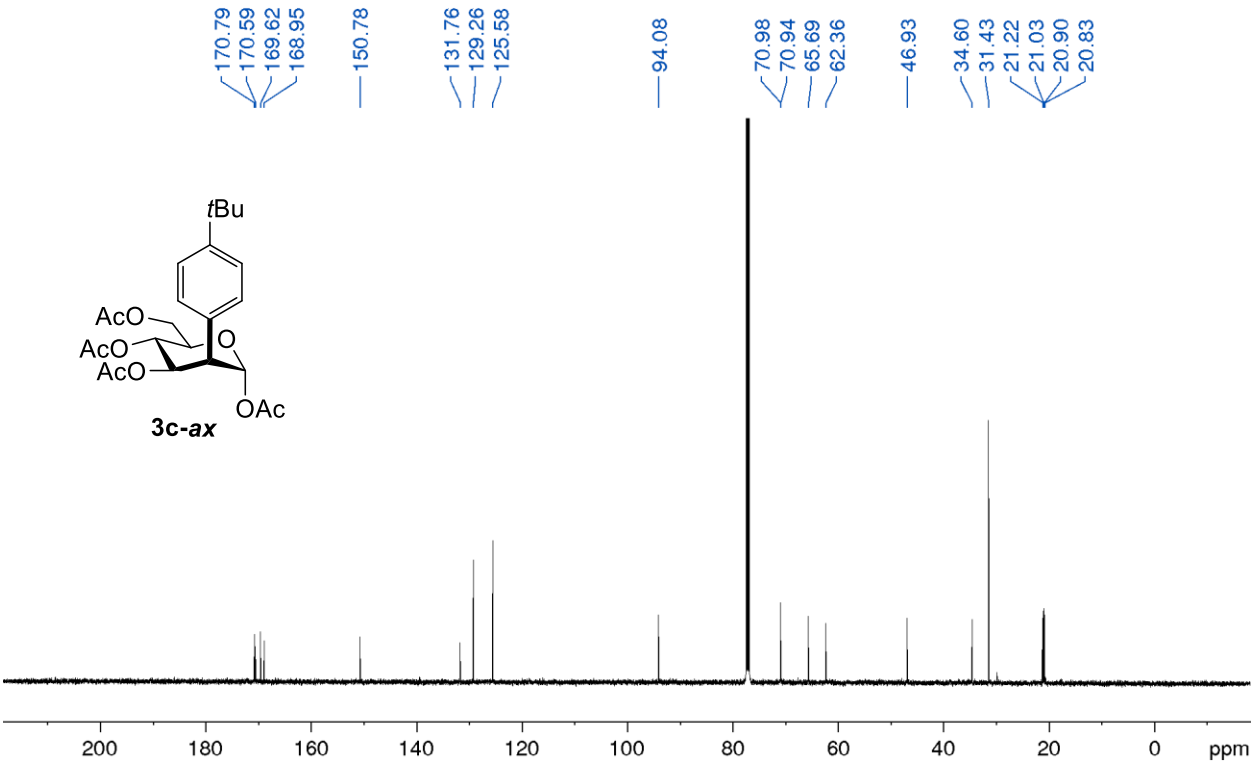
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3b-*eq*)



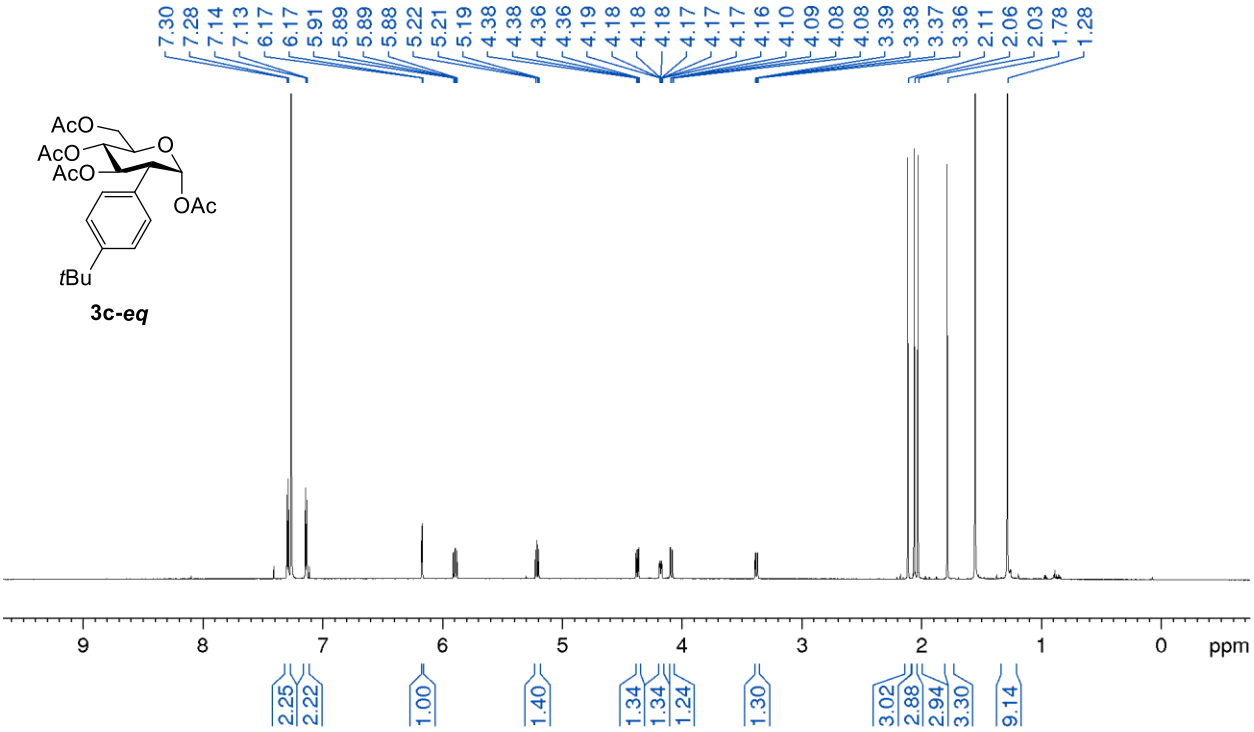
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3c-*ax*)



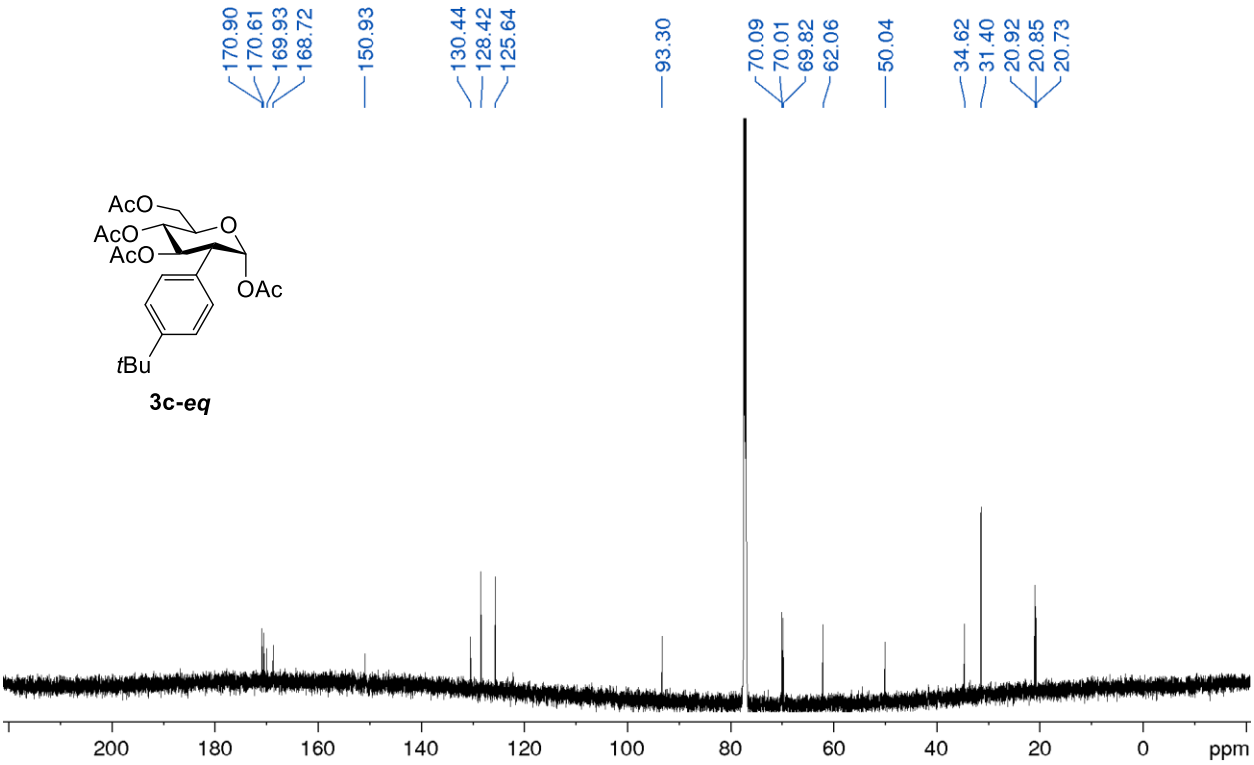
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3c-*ax*)



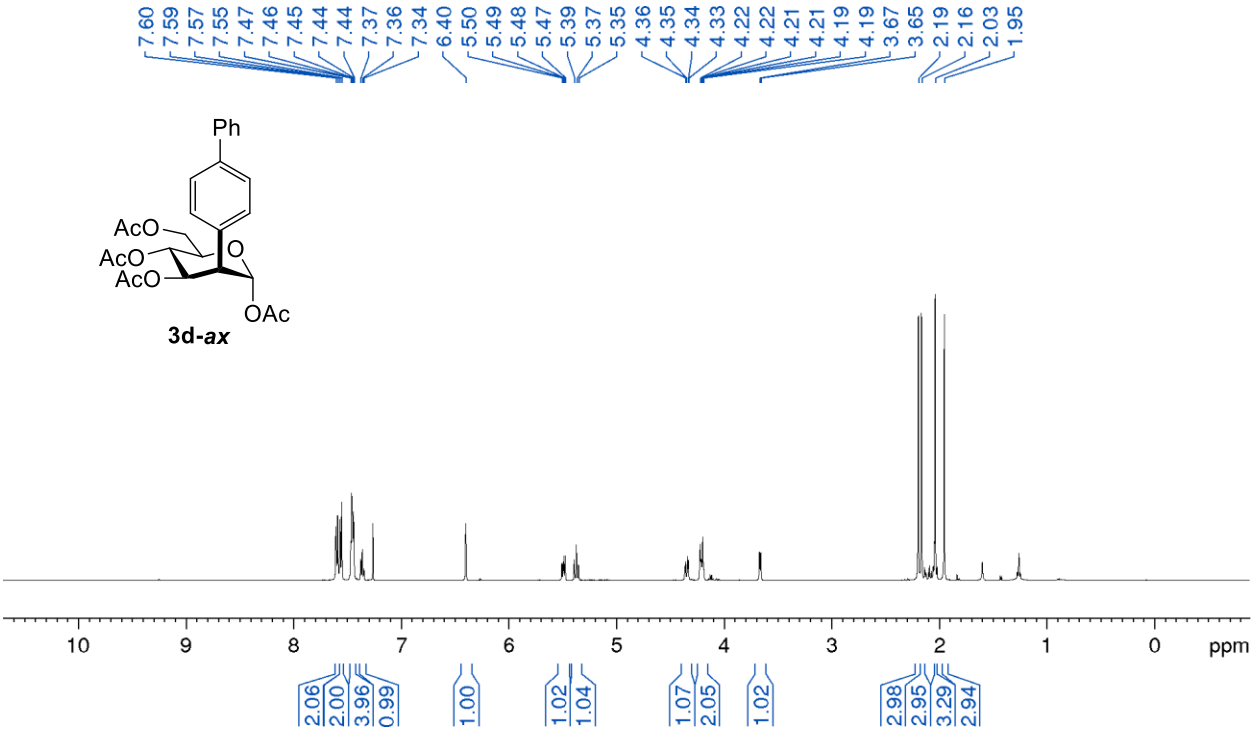
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3c-*eq*)



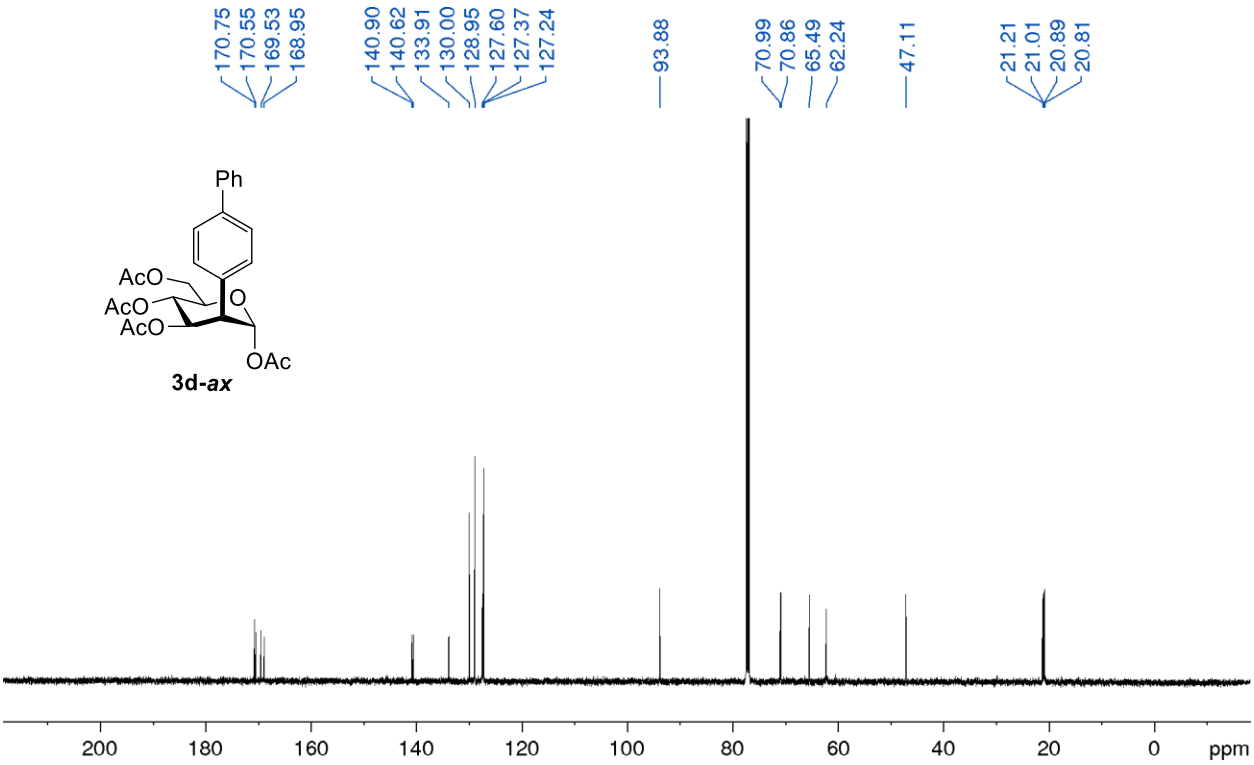
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3c-*eq*)



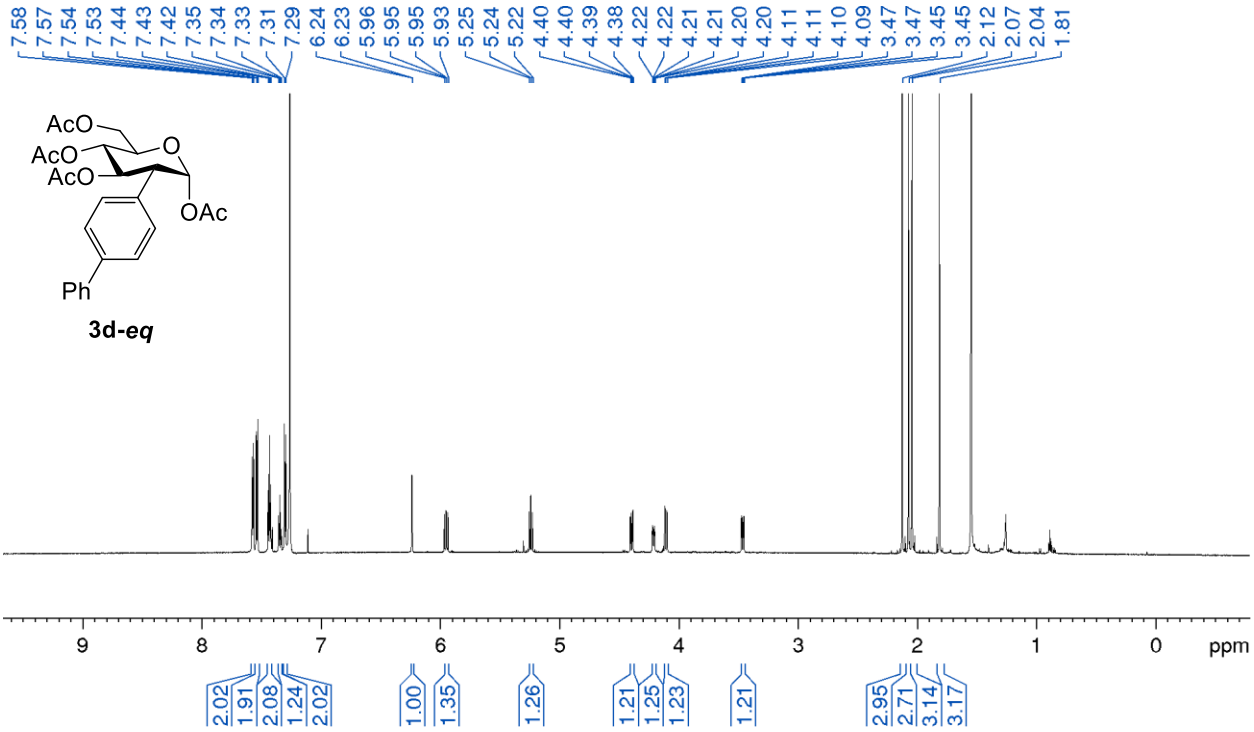
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3d-*ax*)



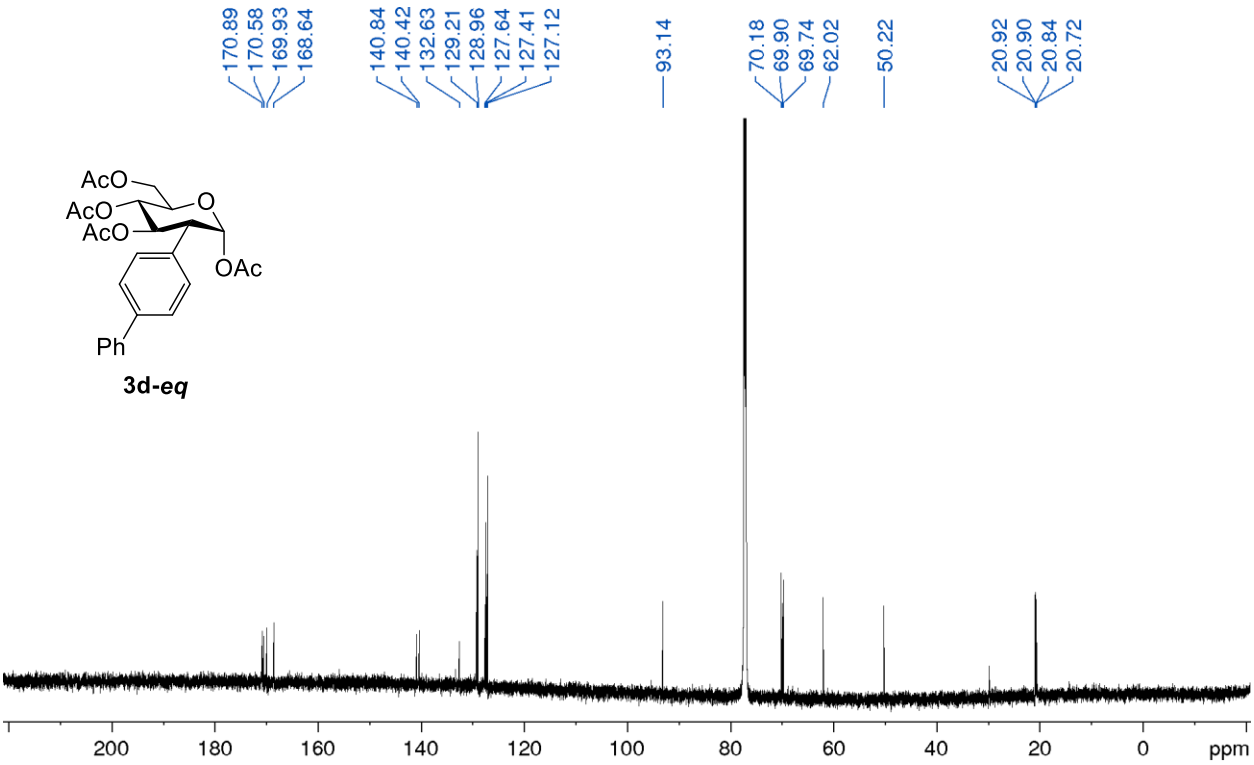
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3d-*ax*)



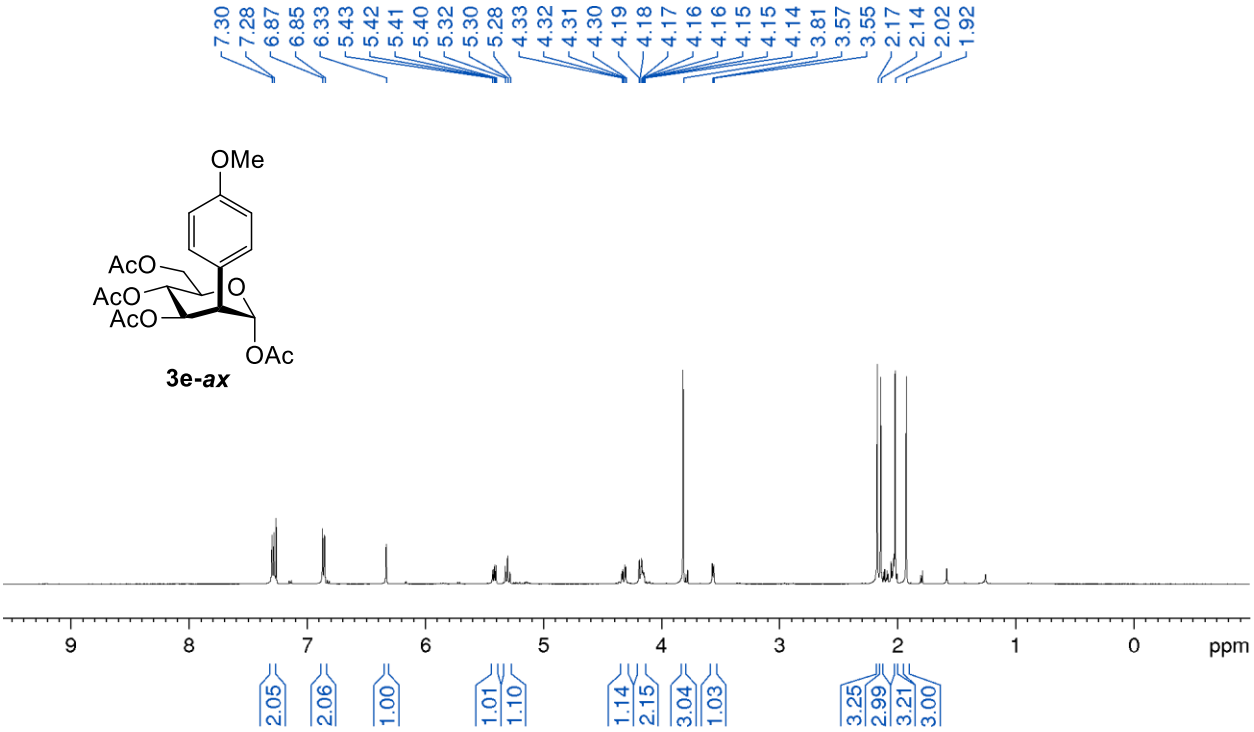
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3d-*eq*)



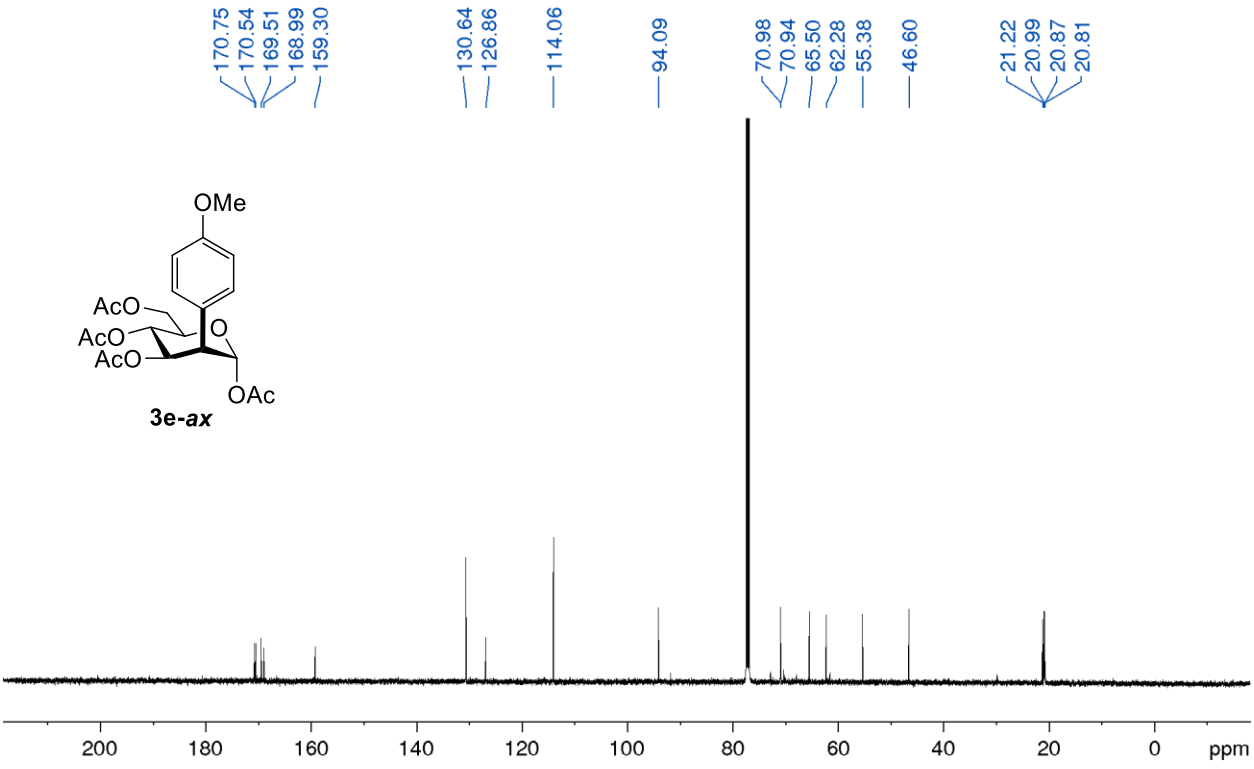
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3d-*eq*)



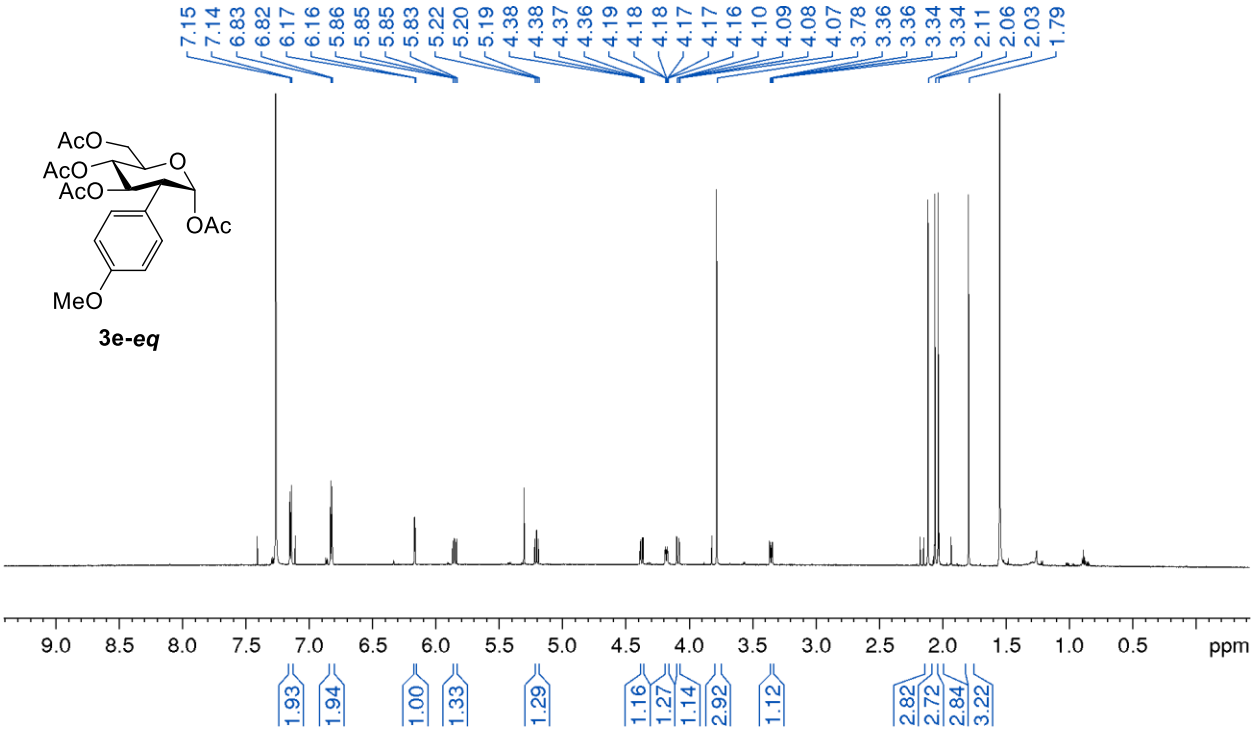
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3e-*ax*)



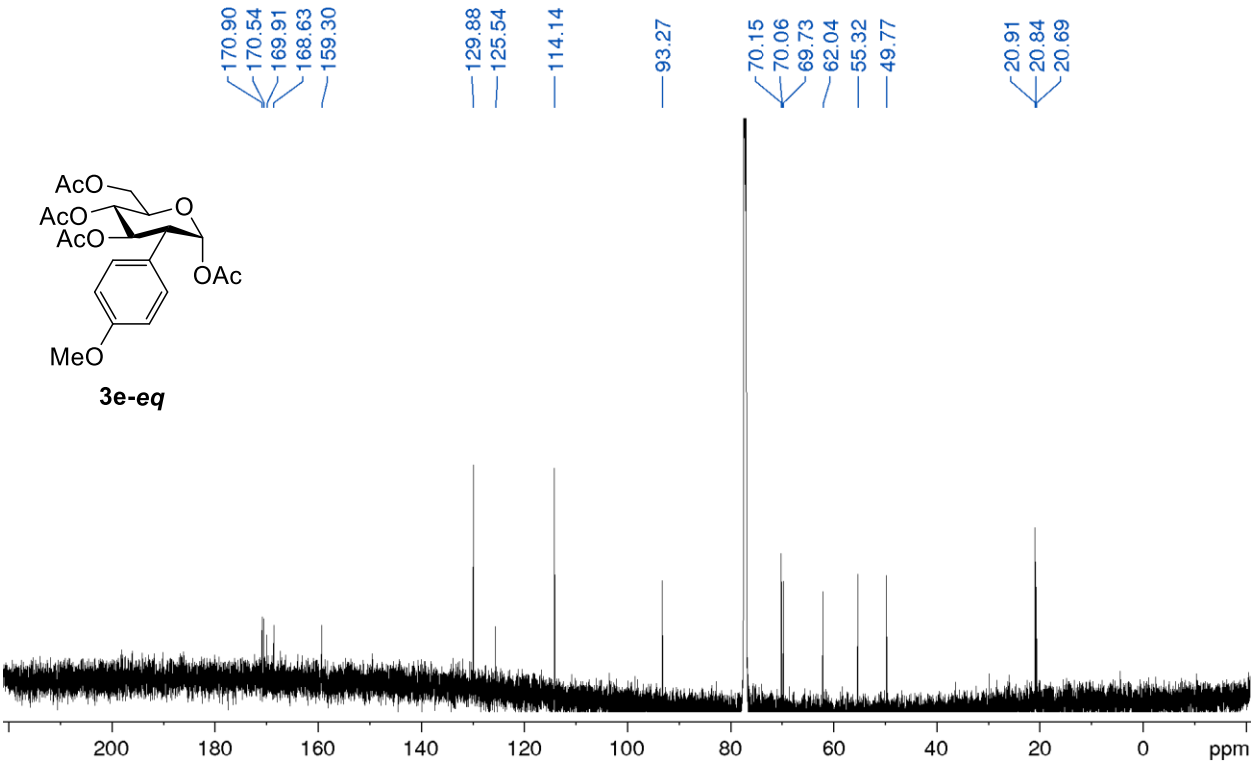
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3e-*ax*)



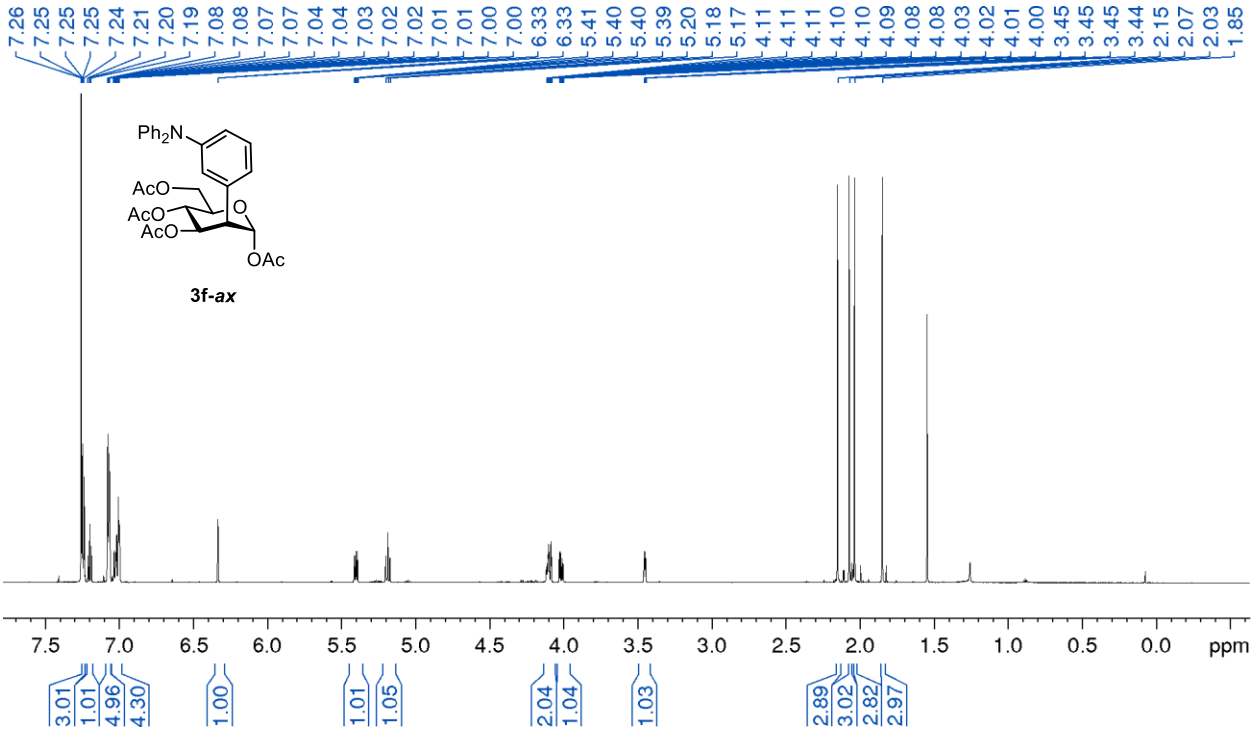
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3e-*eq*)



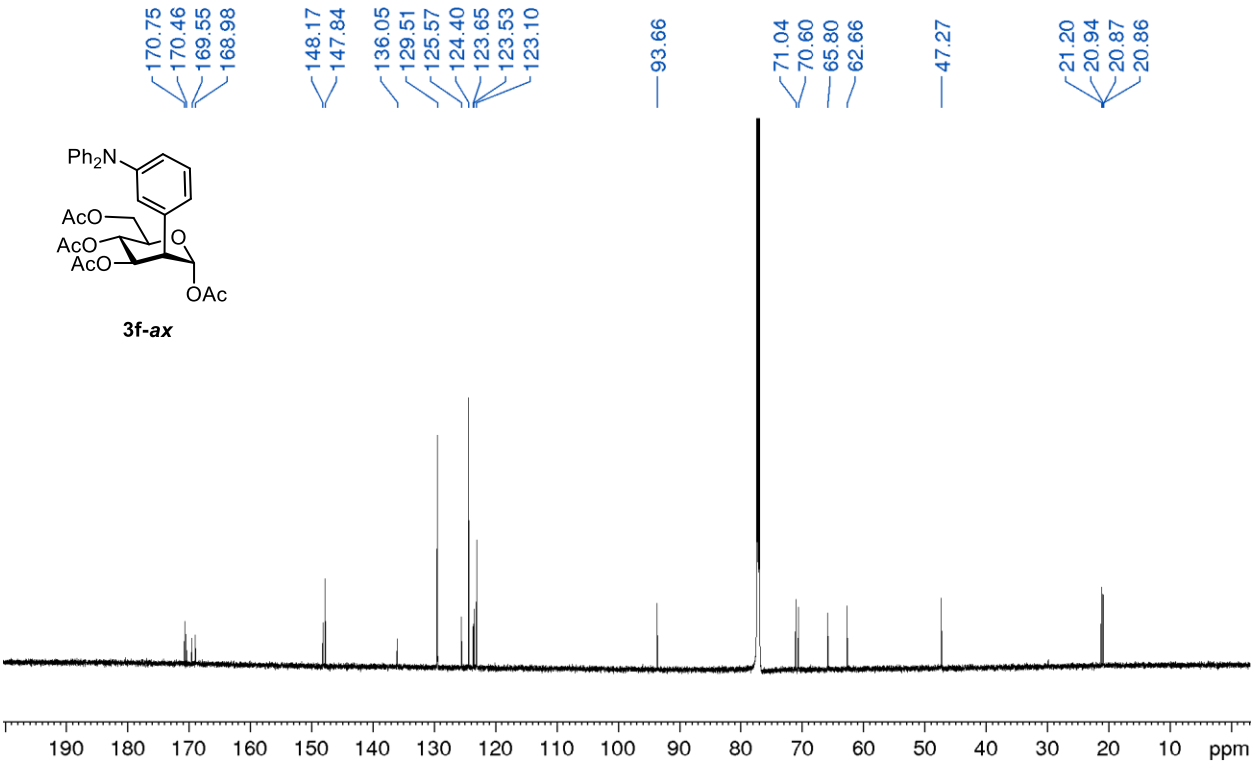
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3e-*eq*)



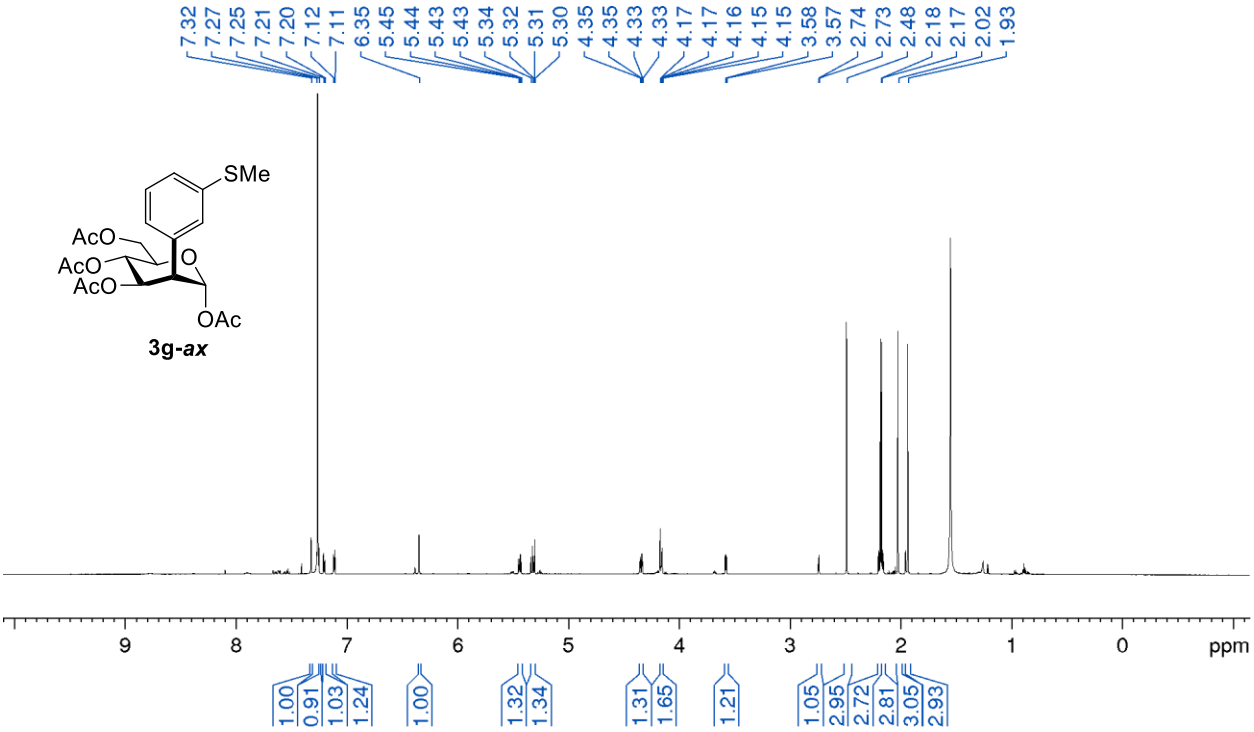
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3f-*ax*)



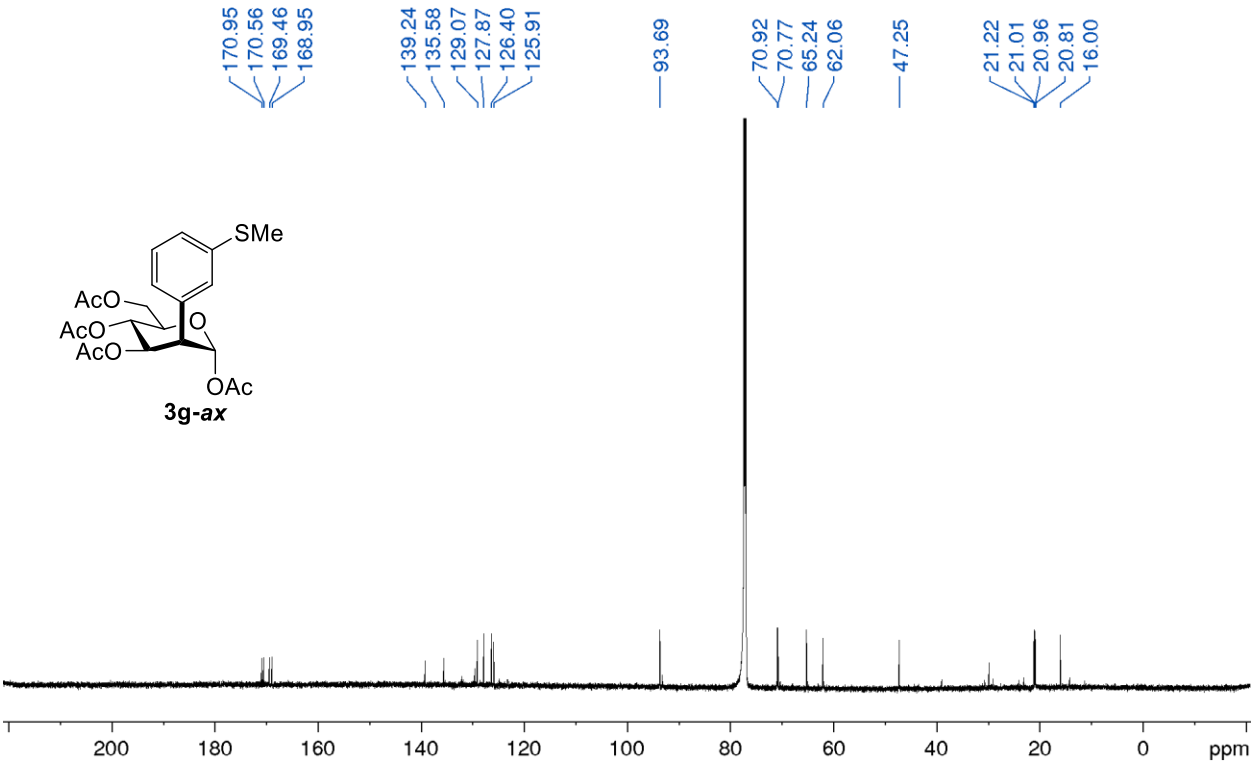
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3f-*ax*)



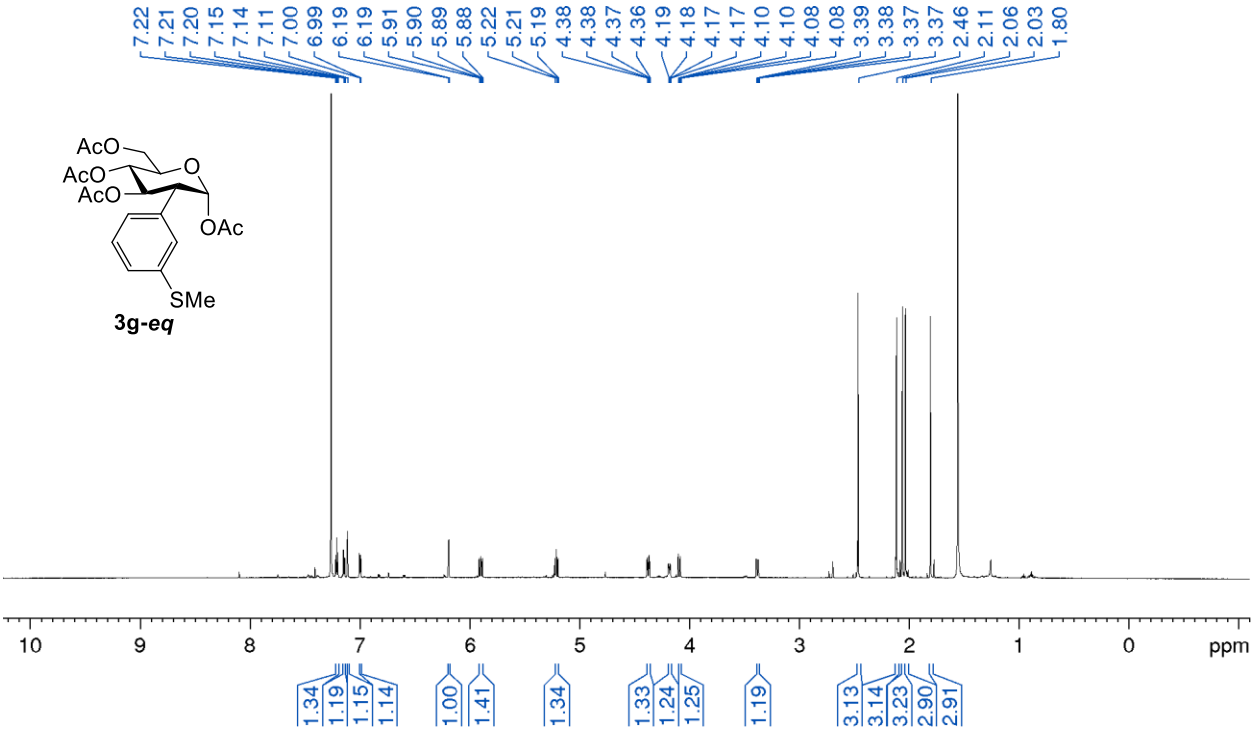
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3g-*ax*)



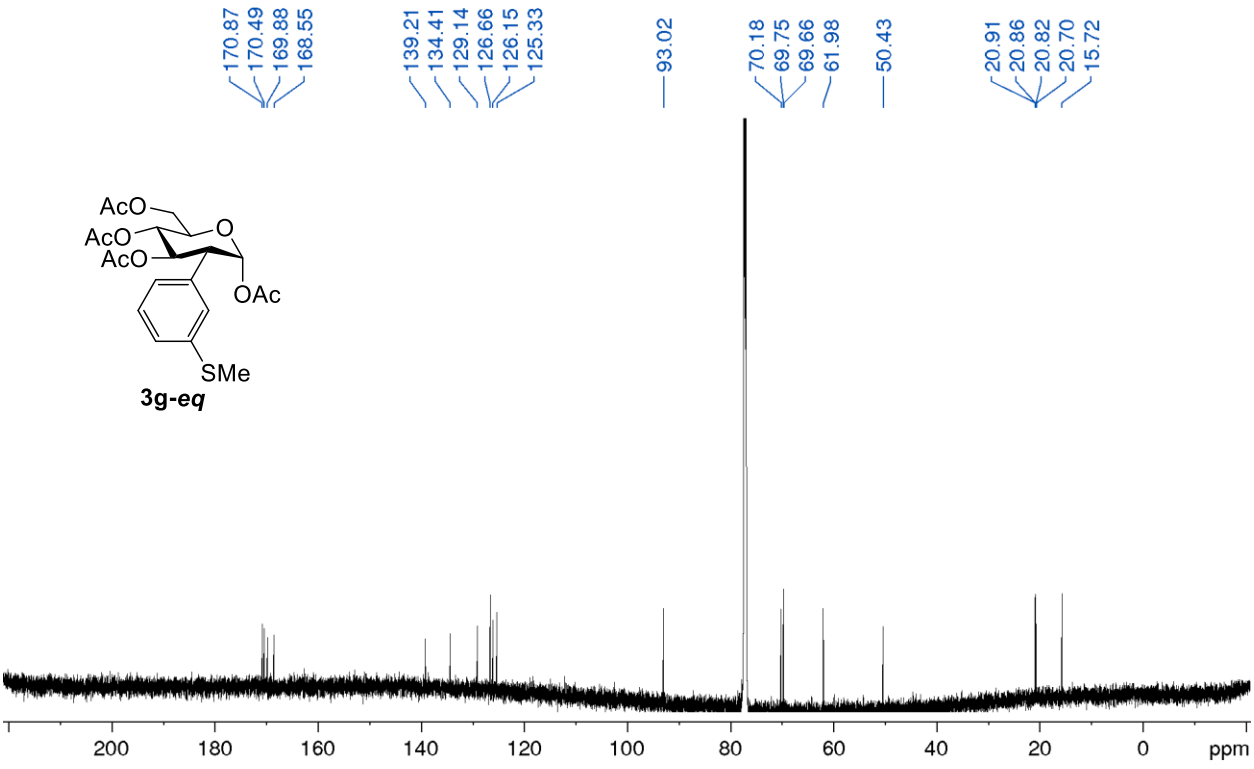
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3g-*ax*)



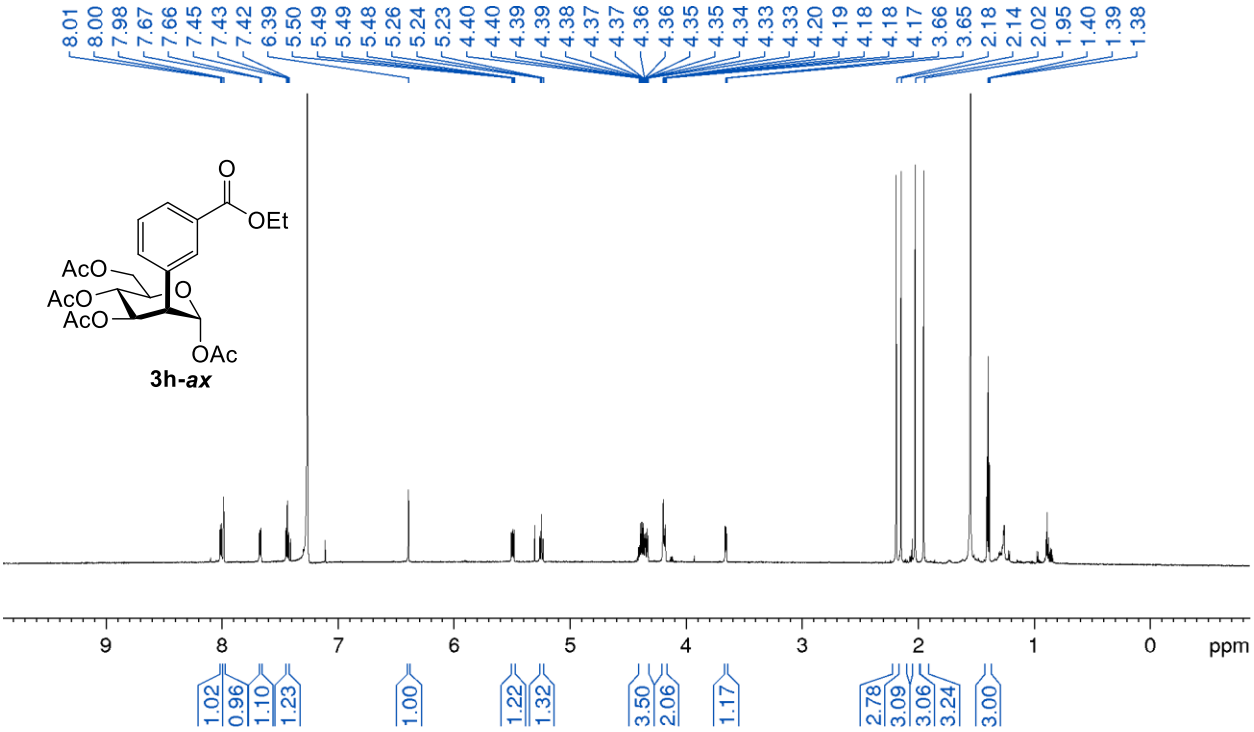
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3g-*eq*)



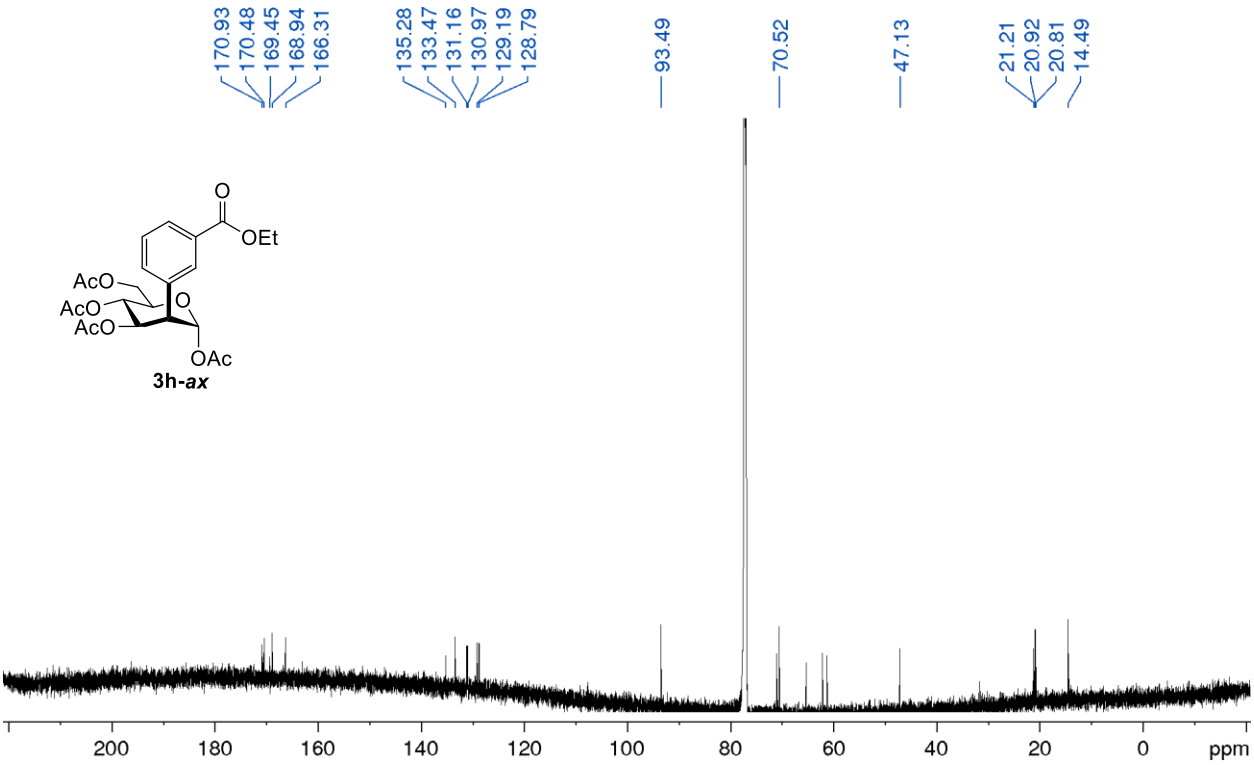
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3g-*eq*)



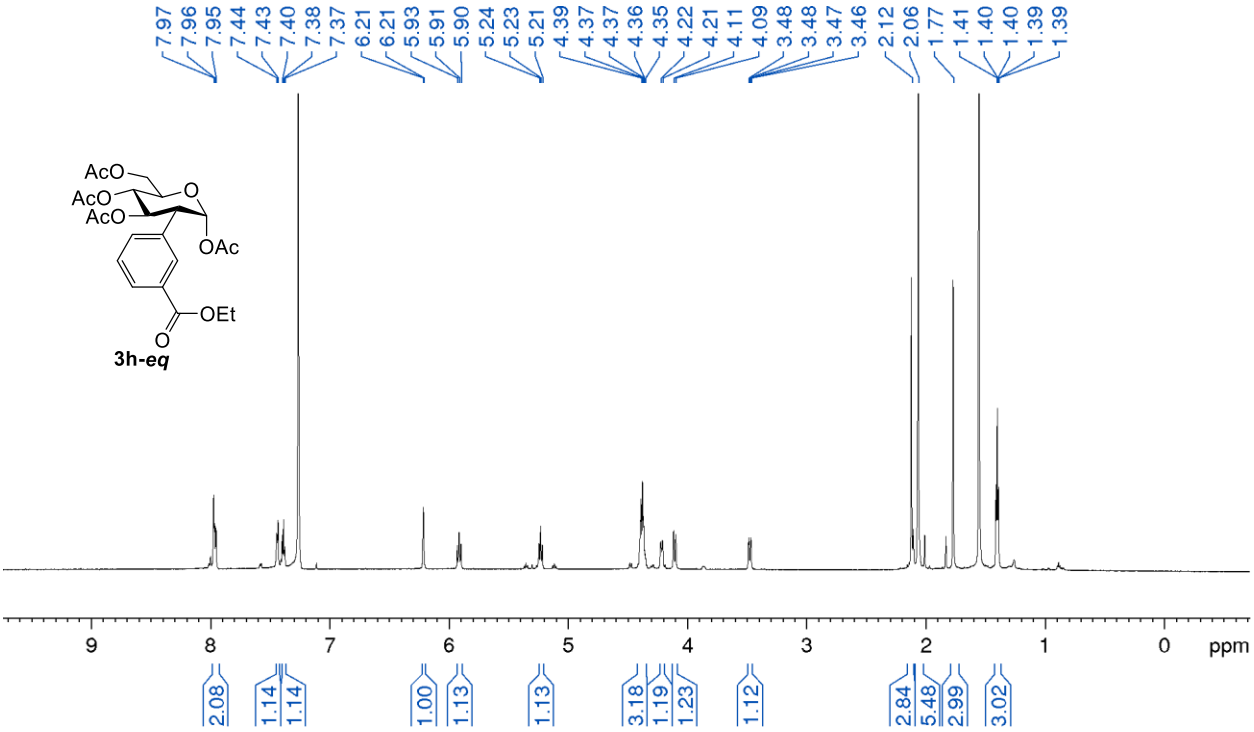
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3h-*ax*)



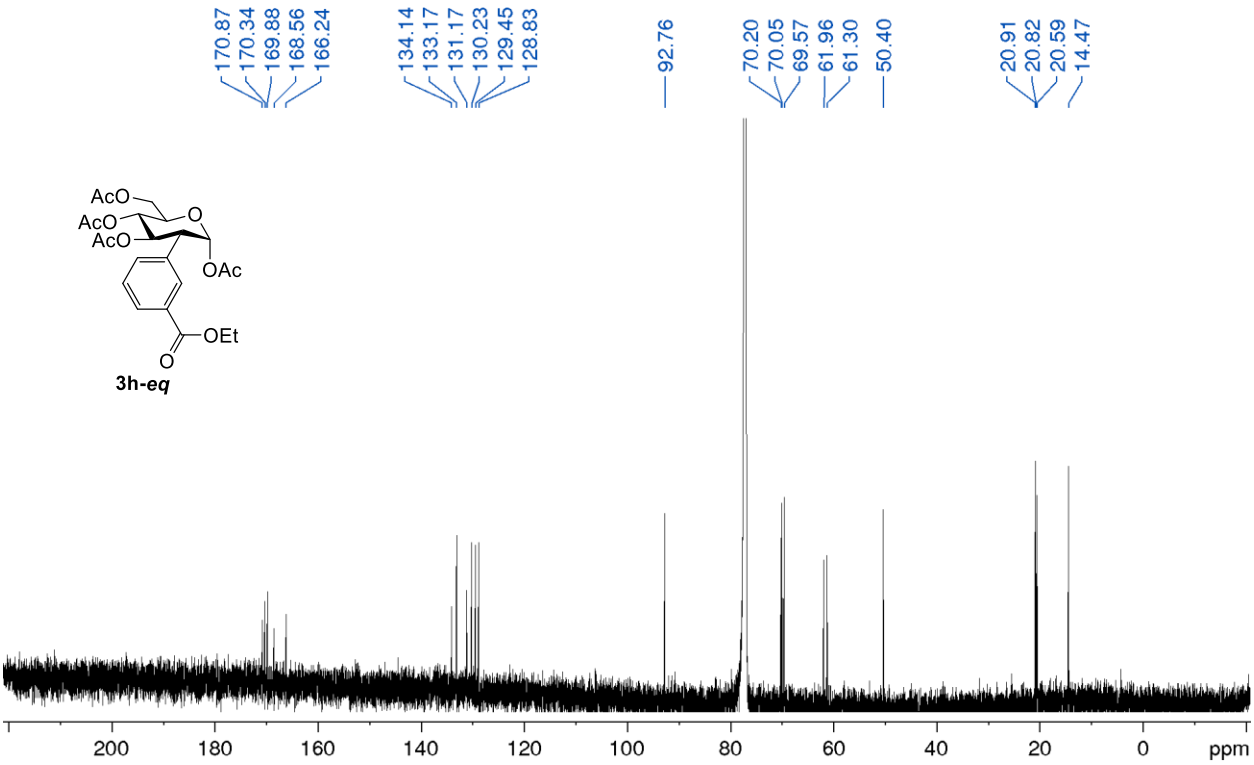
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3h-*ax*)



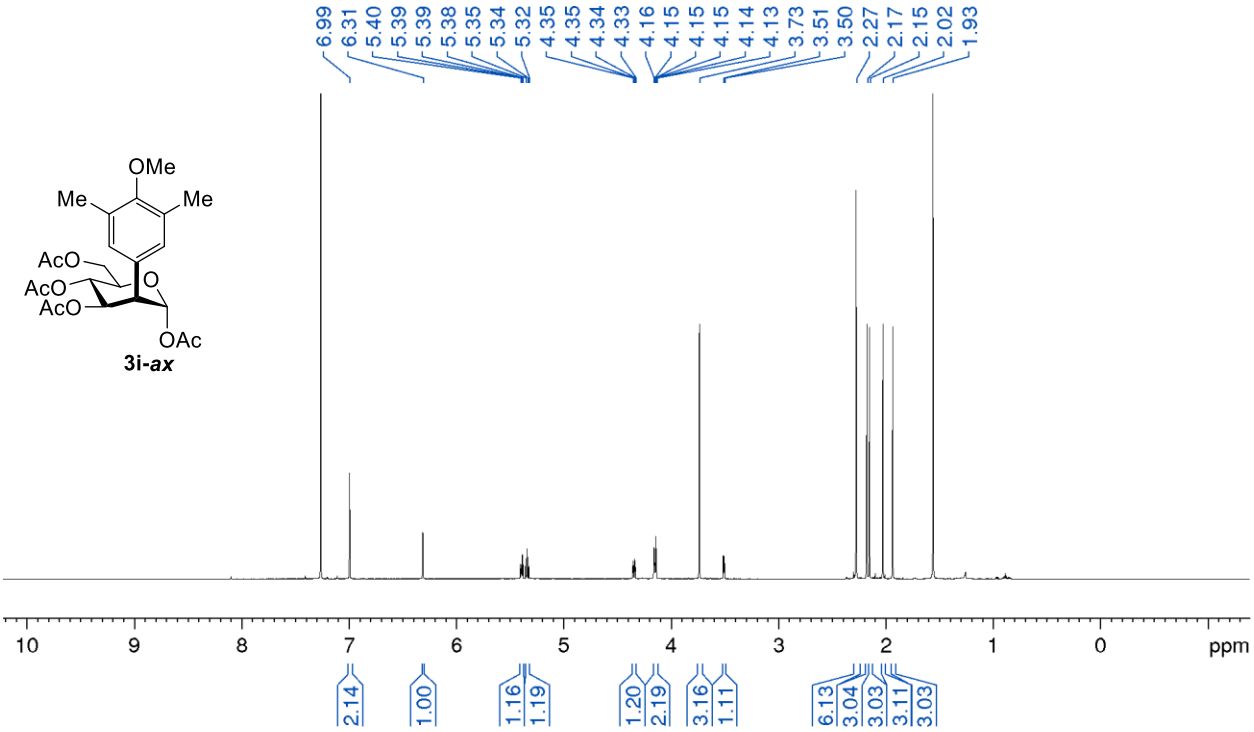
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3h-*eq*)



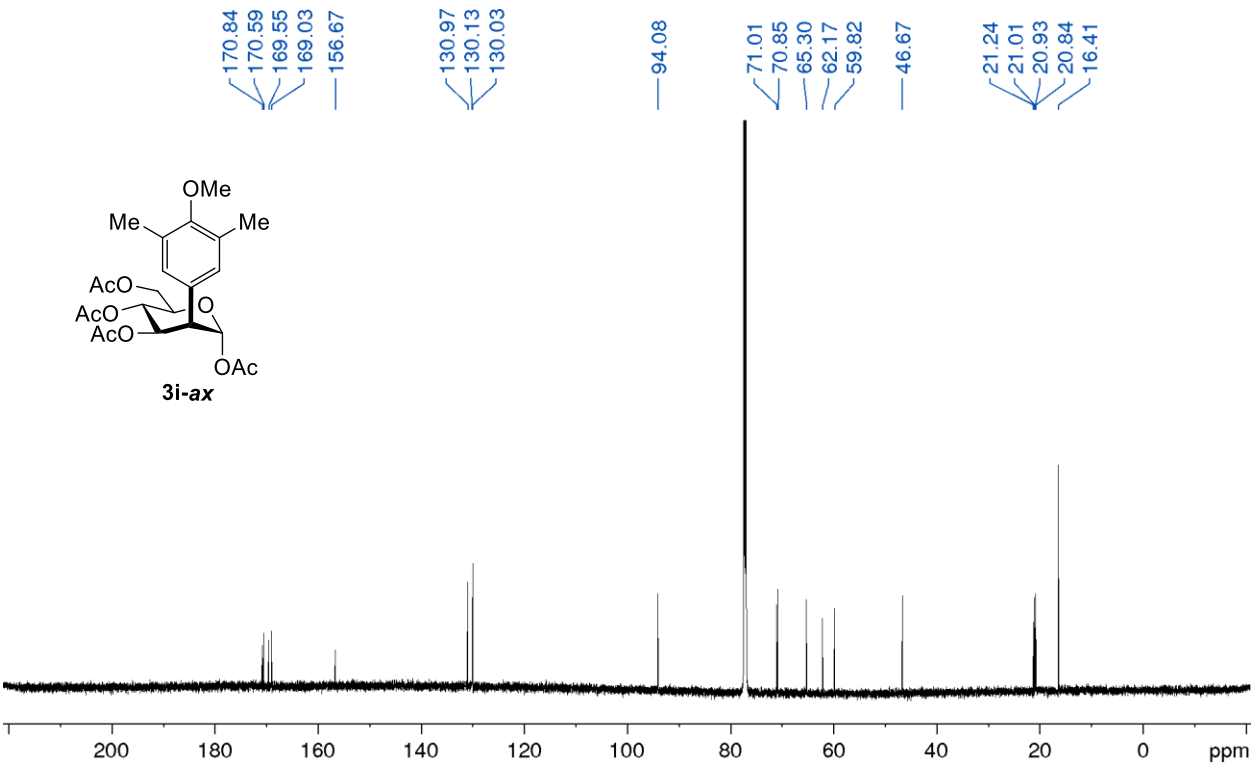
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3h-*eq*)



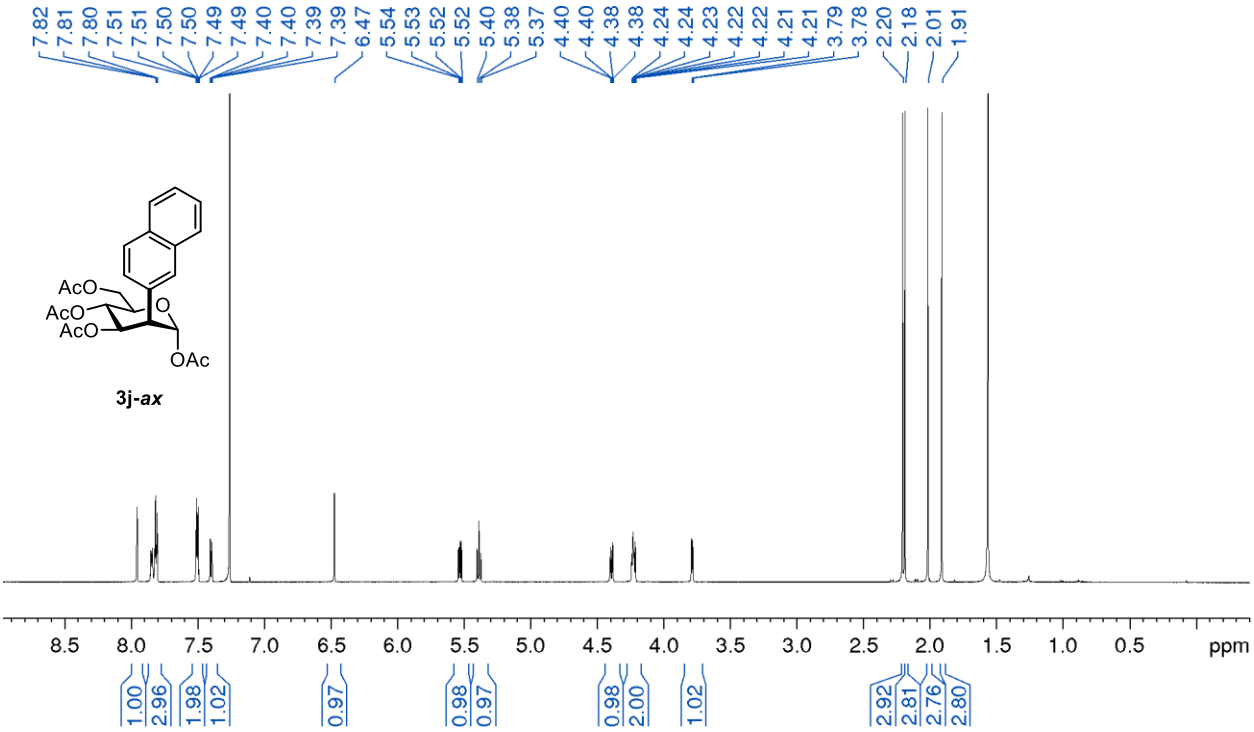
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3i-*ax*)



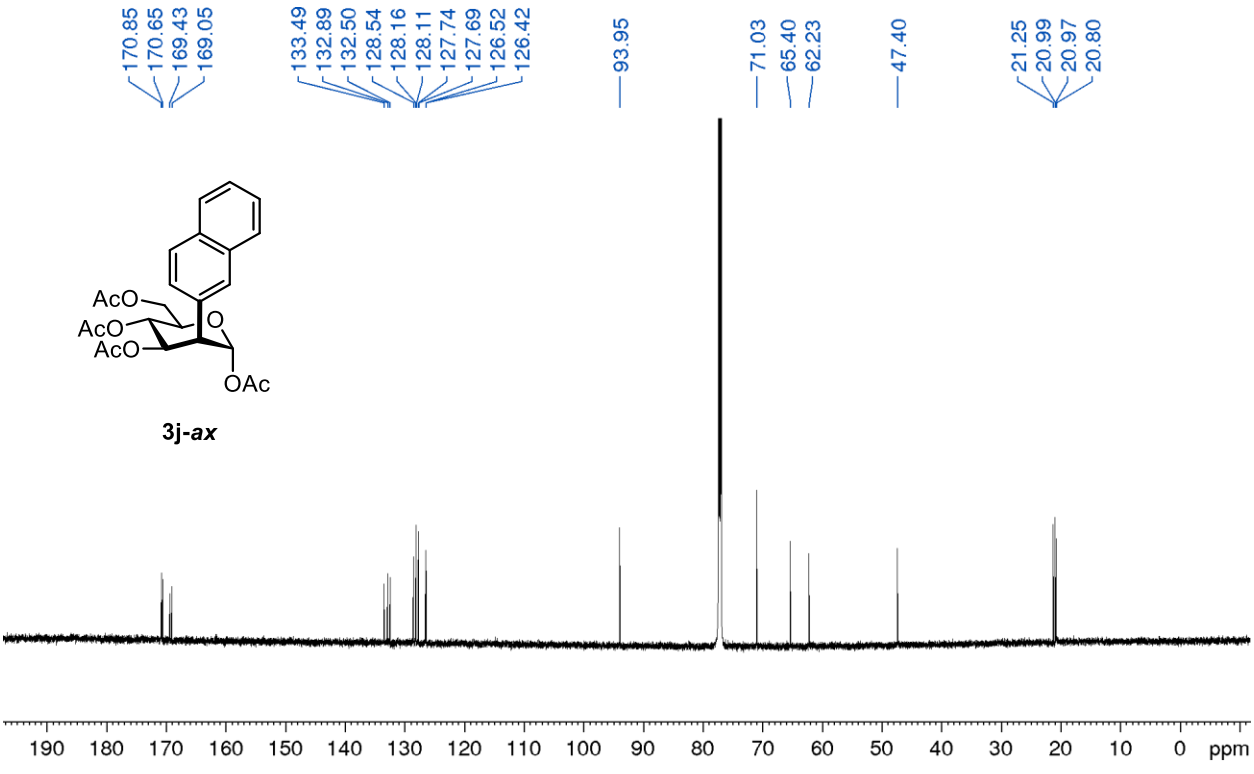
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3i-*ax*)



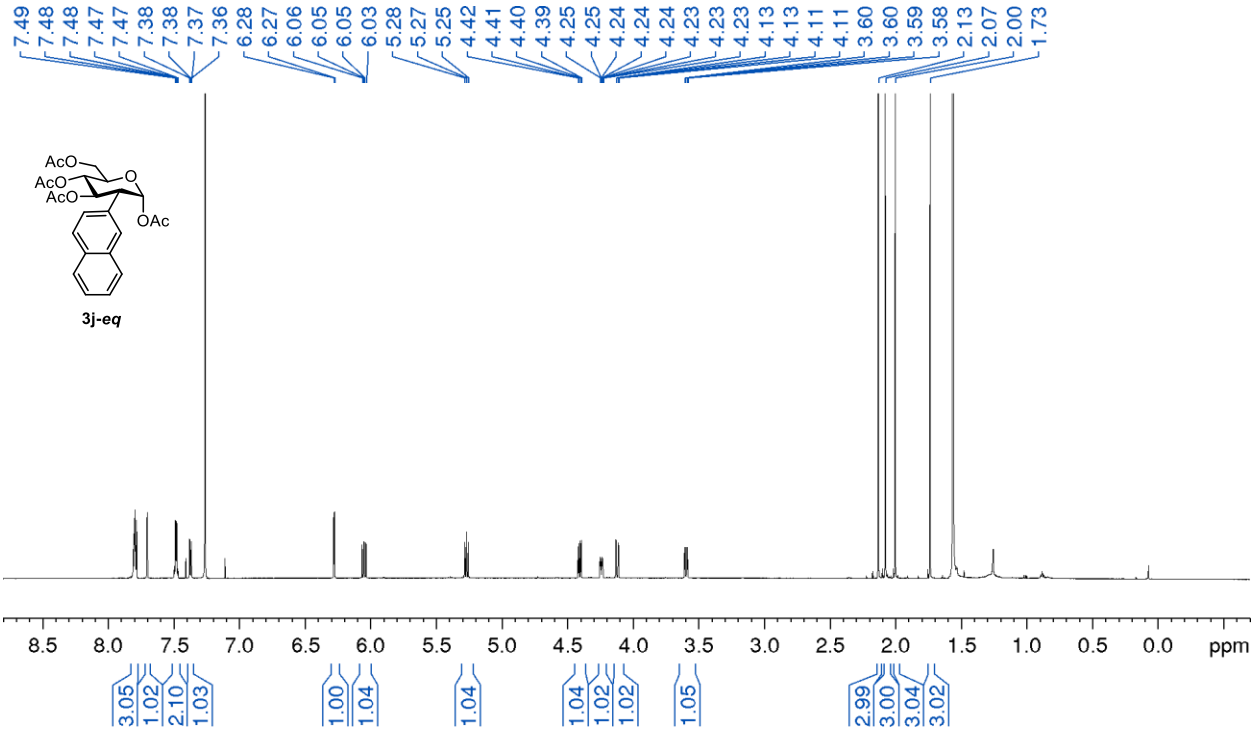
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3j-*ax*)



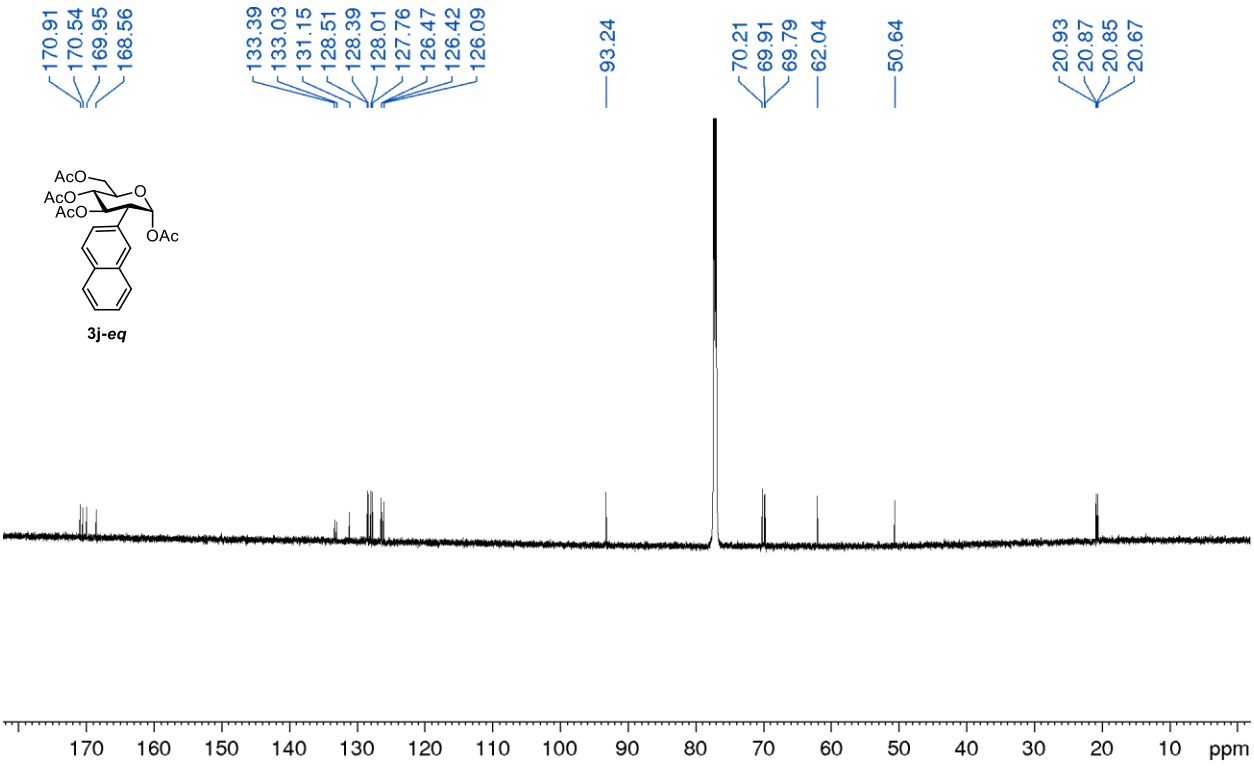
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3j-*ax*)



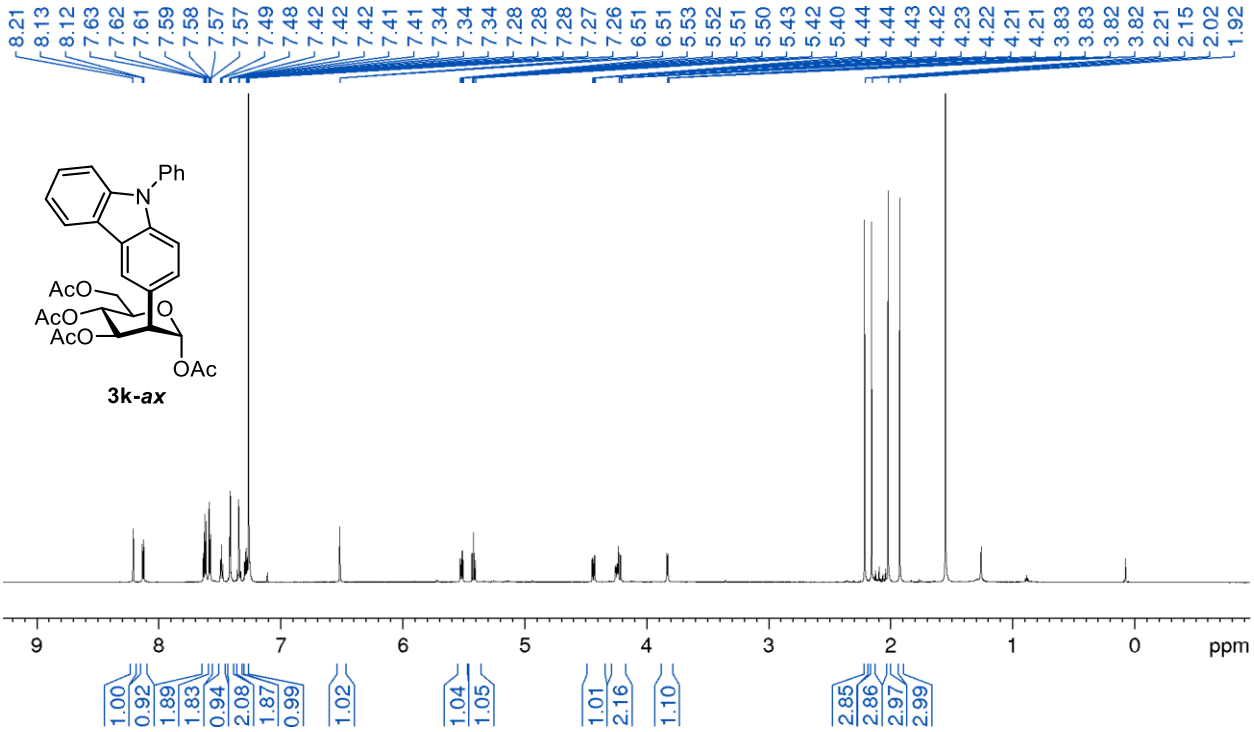
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3j-*eq*)



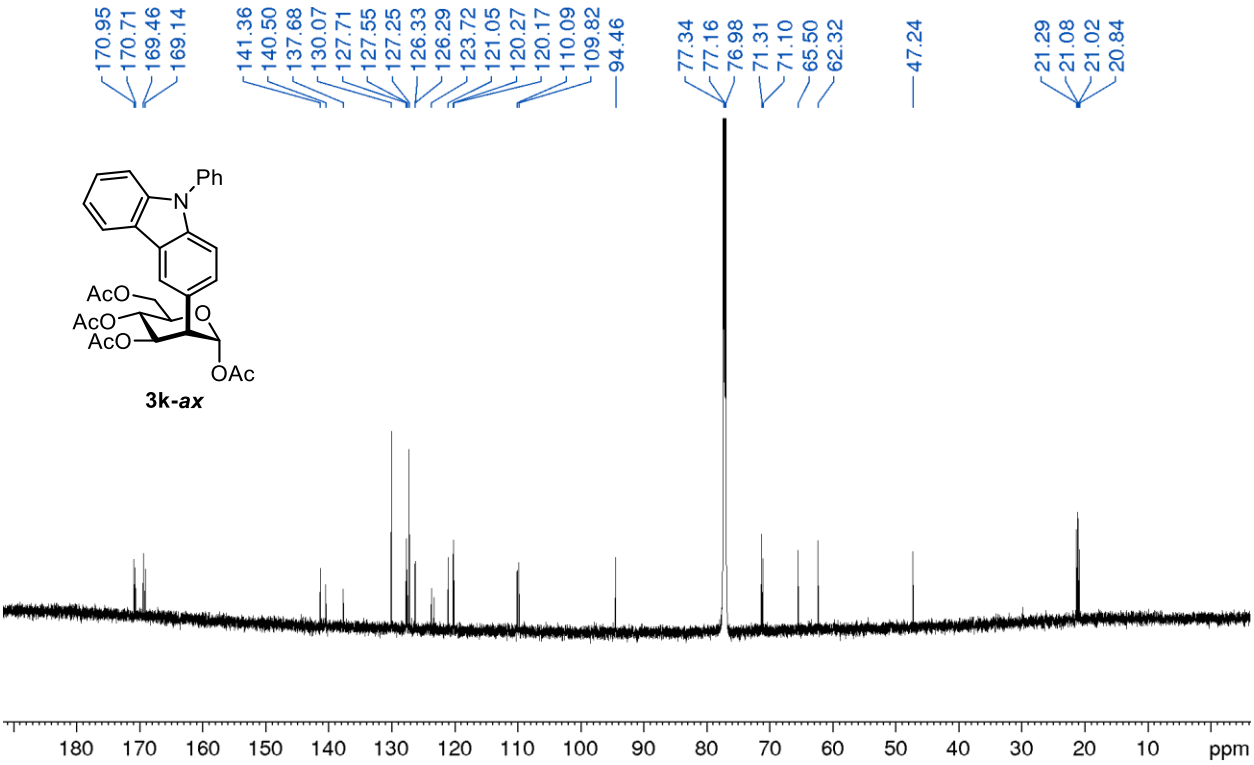
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3j-*eq*)



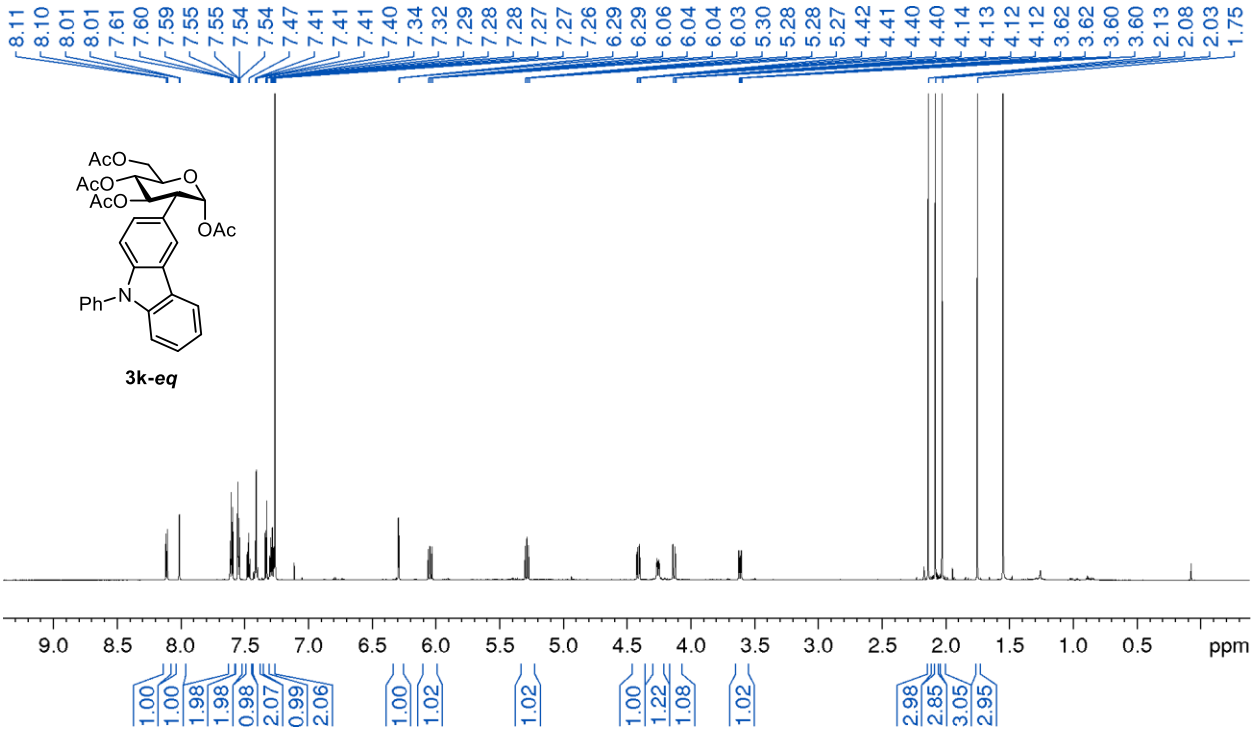
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3k-*ax*)



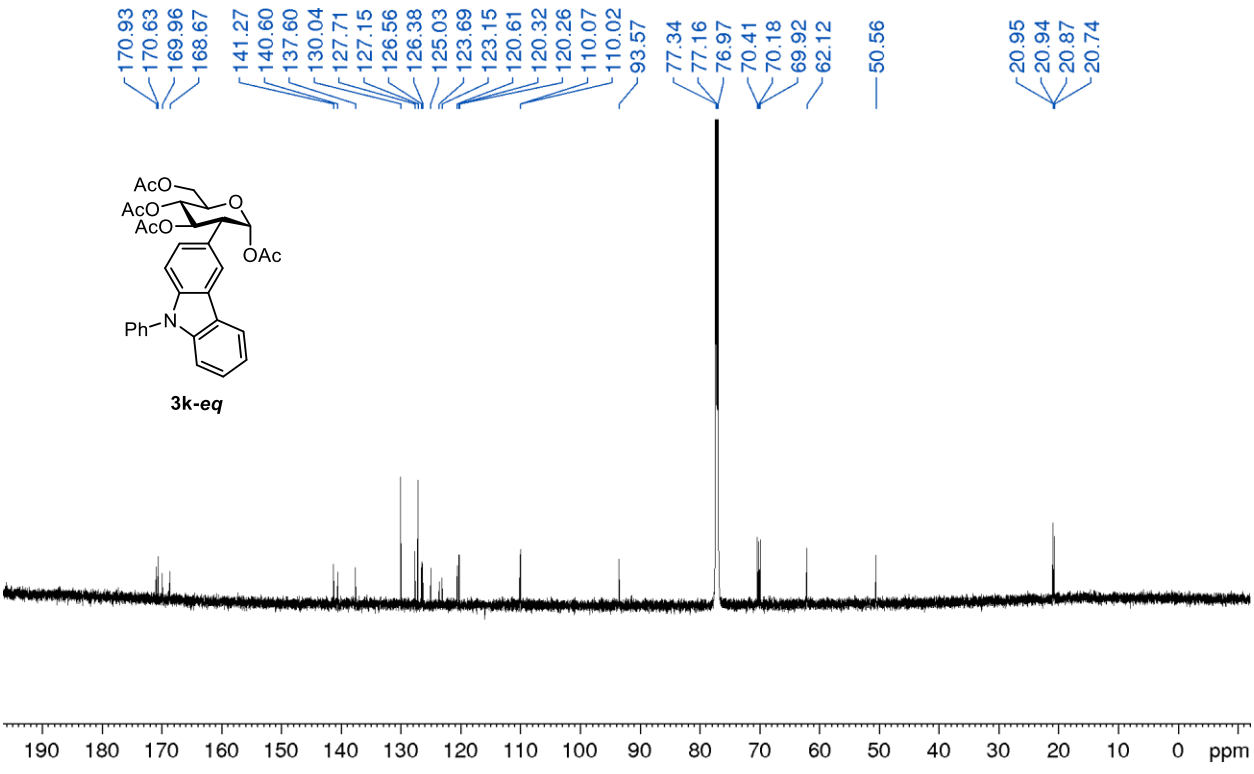
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3k-*ax*)



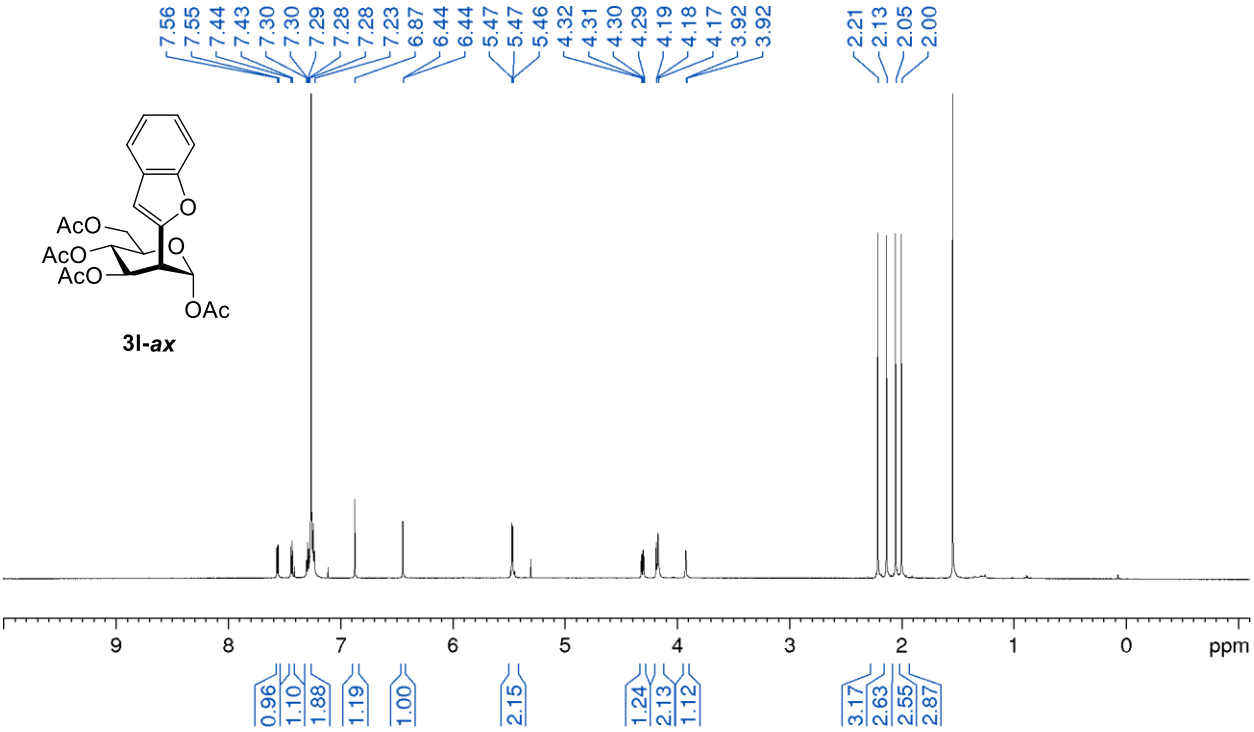
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3k-*eq*)



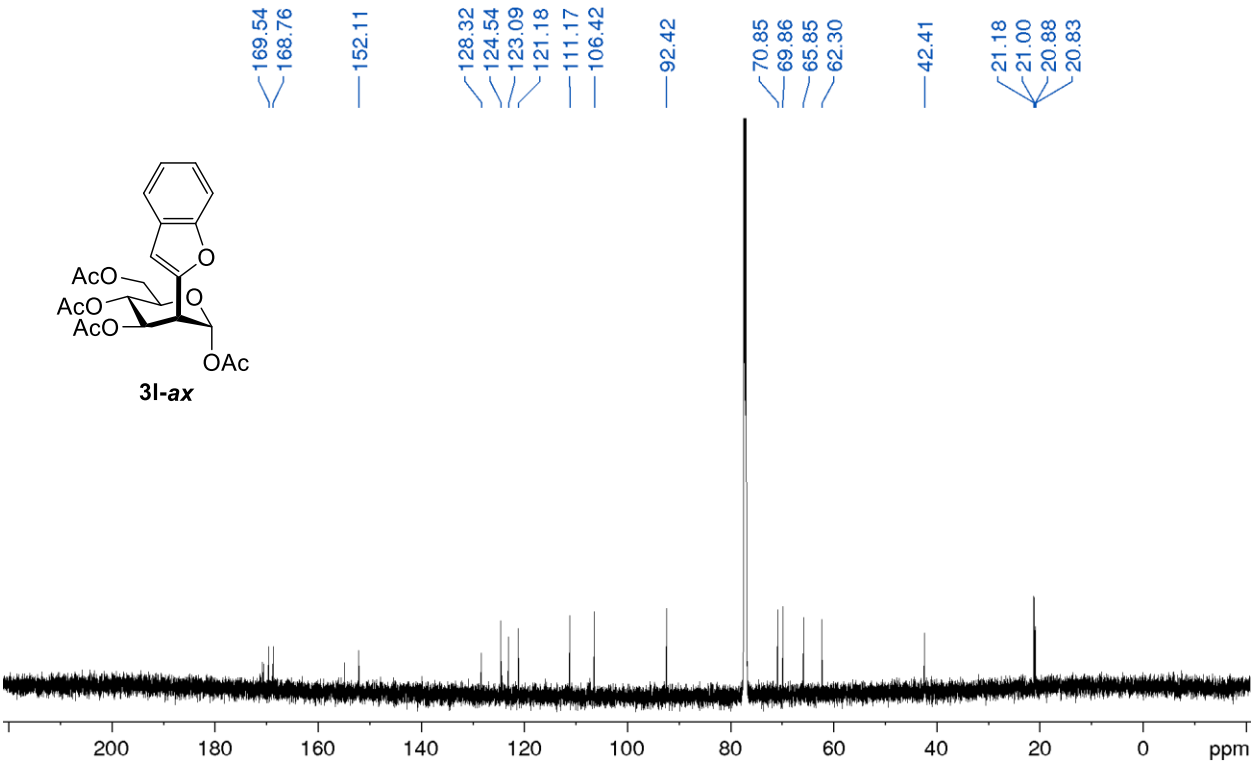
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3k-*eq*)



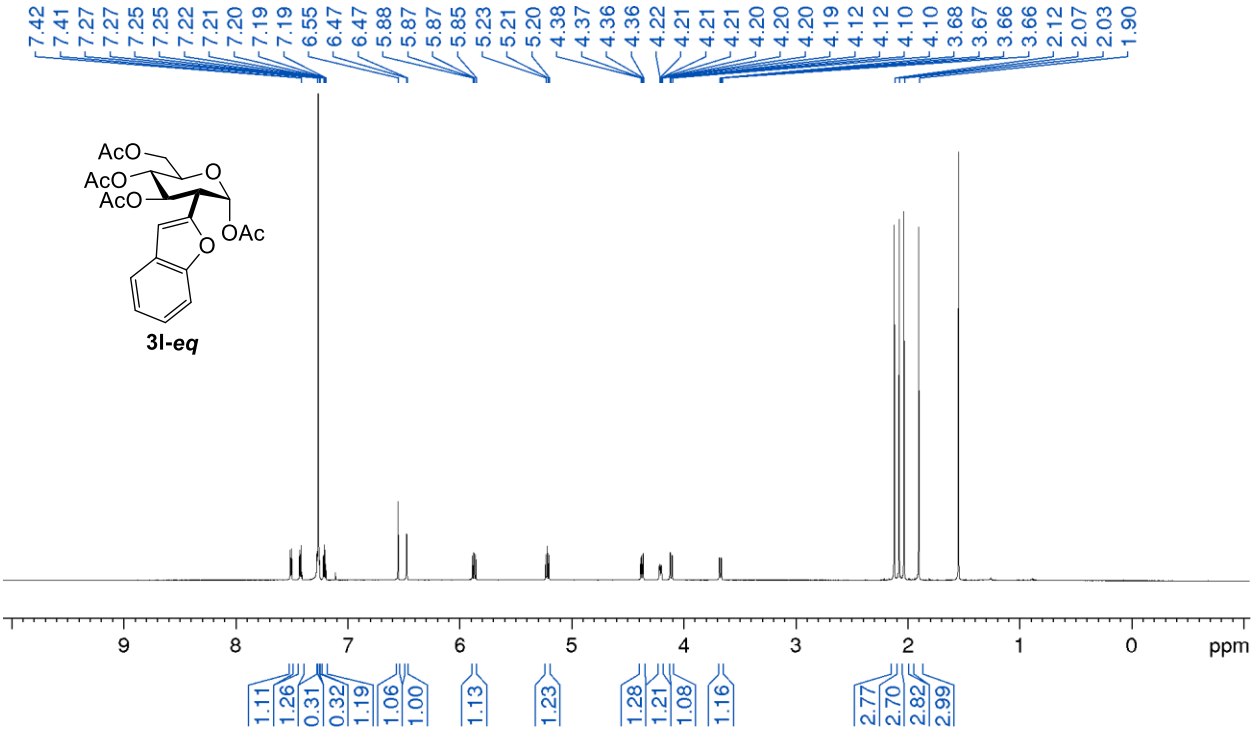
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3l-*ax*)



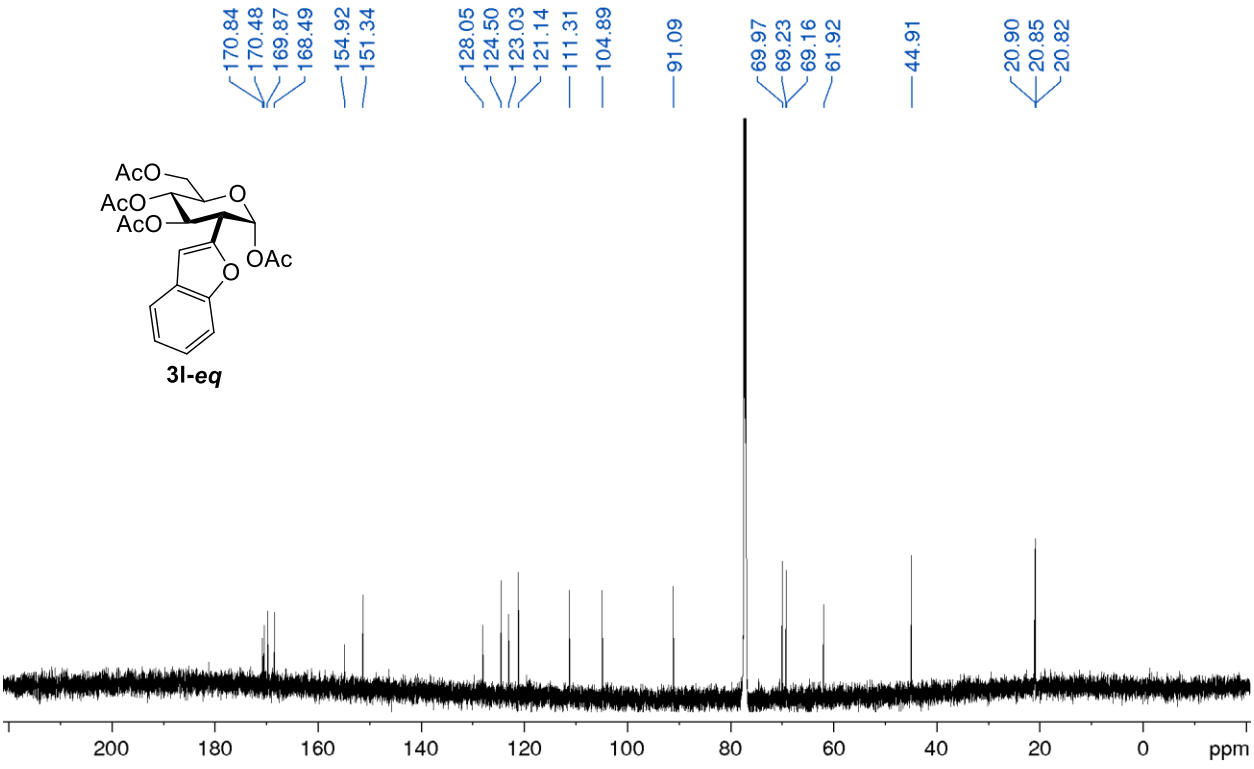
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3l-*ax*)



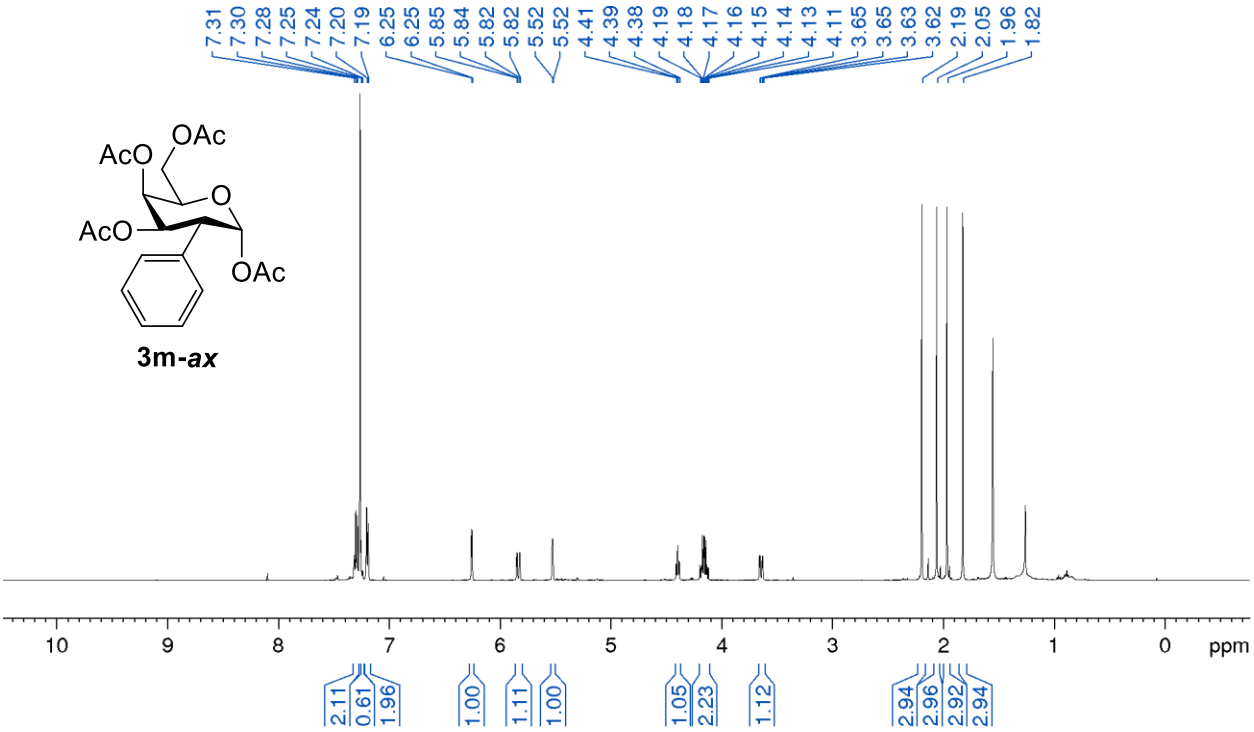
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3l-*eq*)



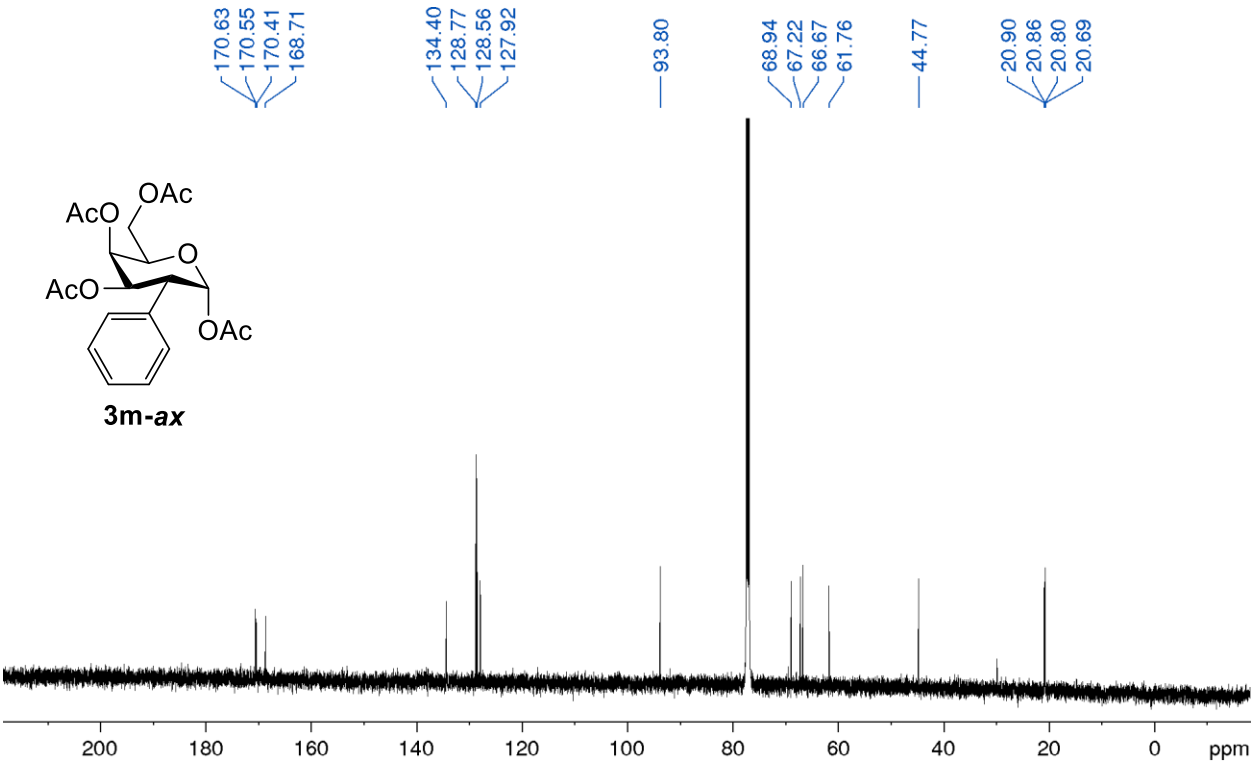
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3l-*eq*)



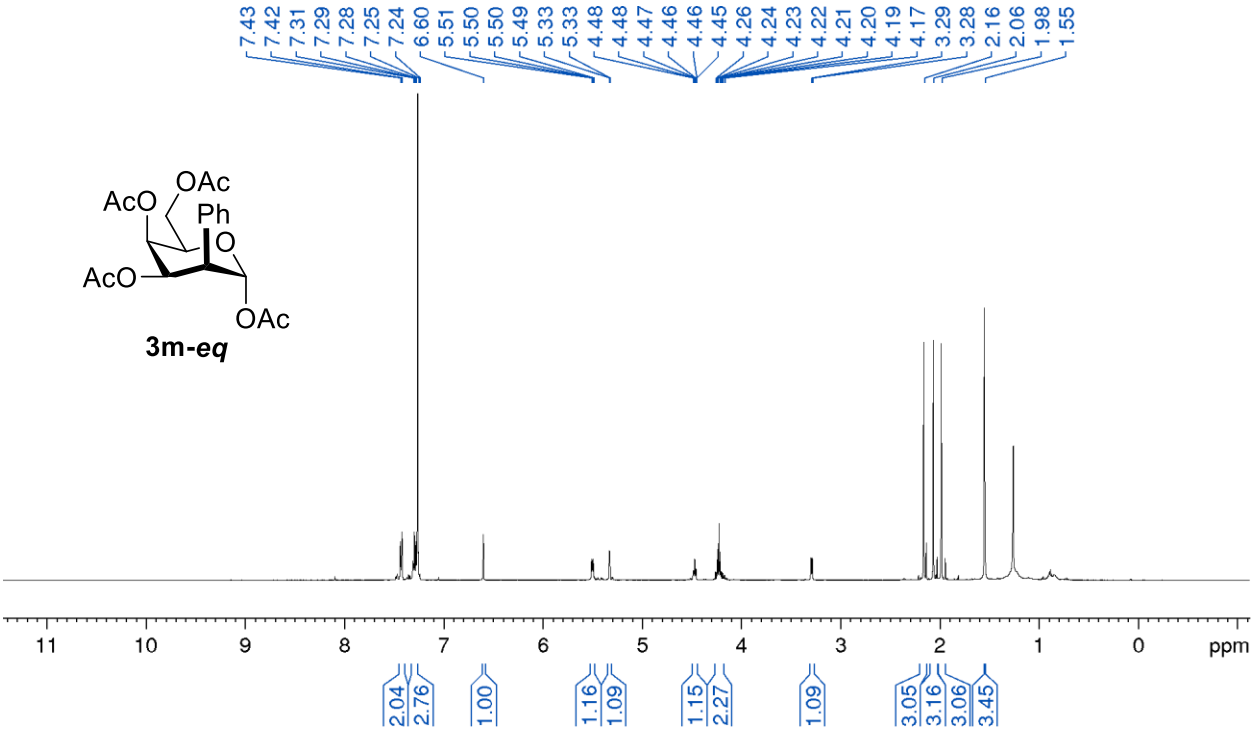
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3m-*ax*)



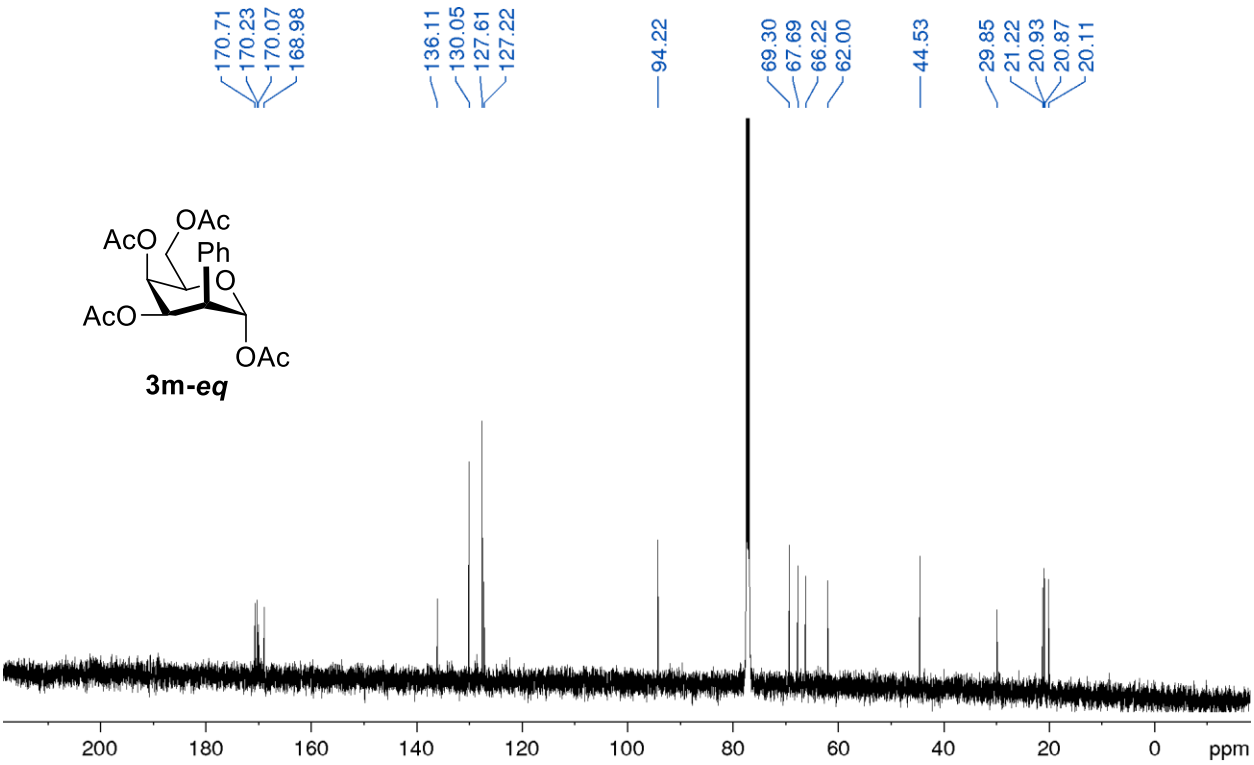
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3m-*ax*)



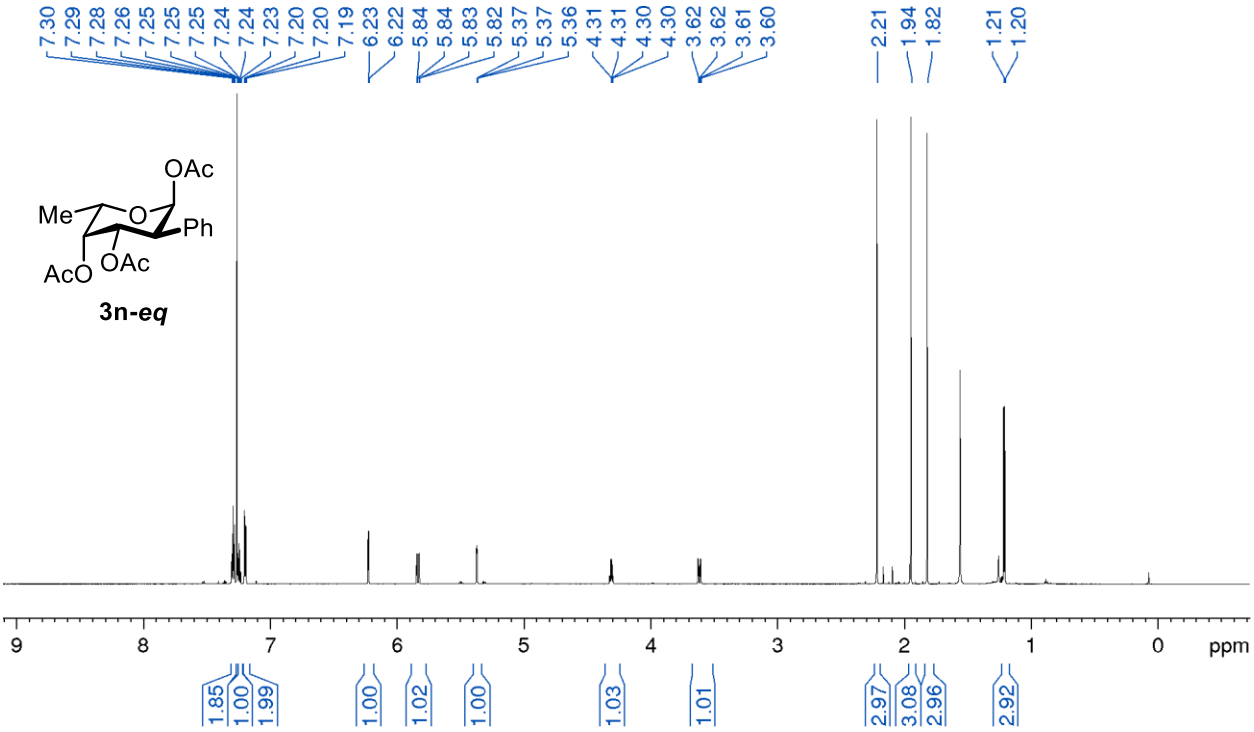
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3m-*eq*)



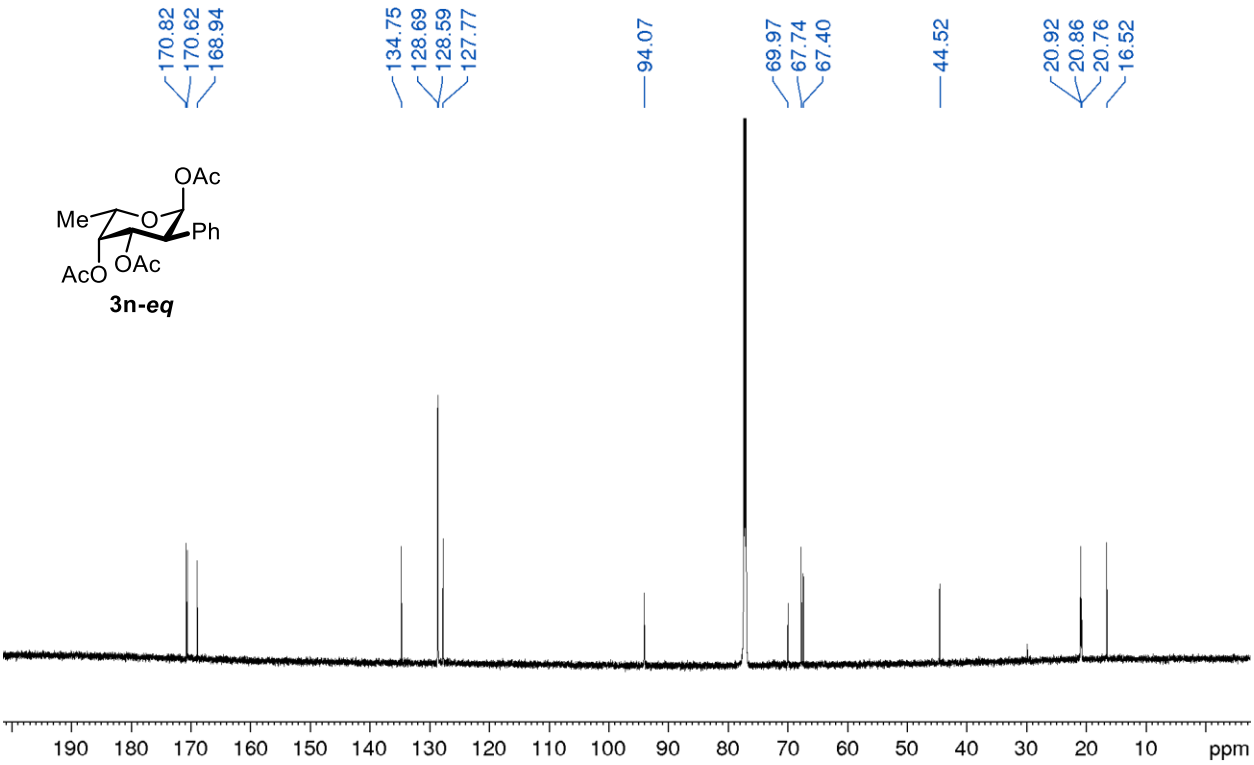
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3m-*eq*)



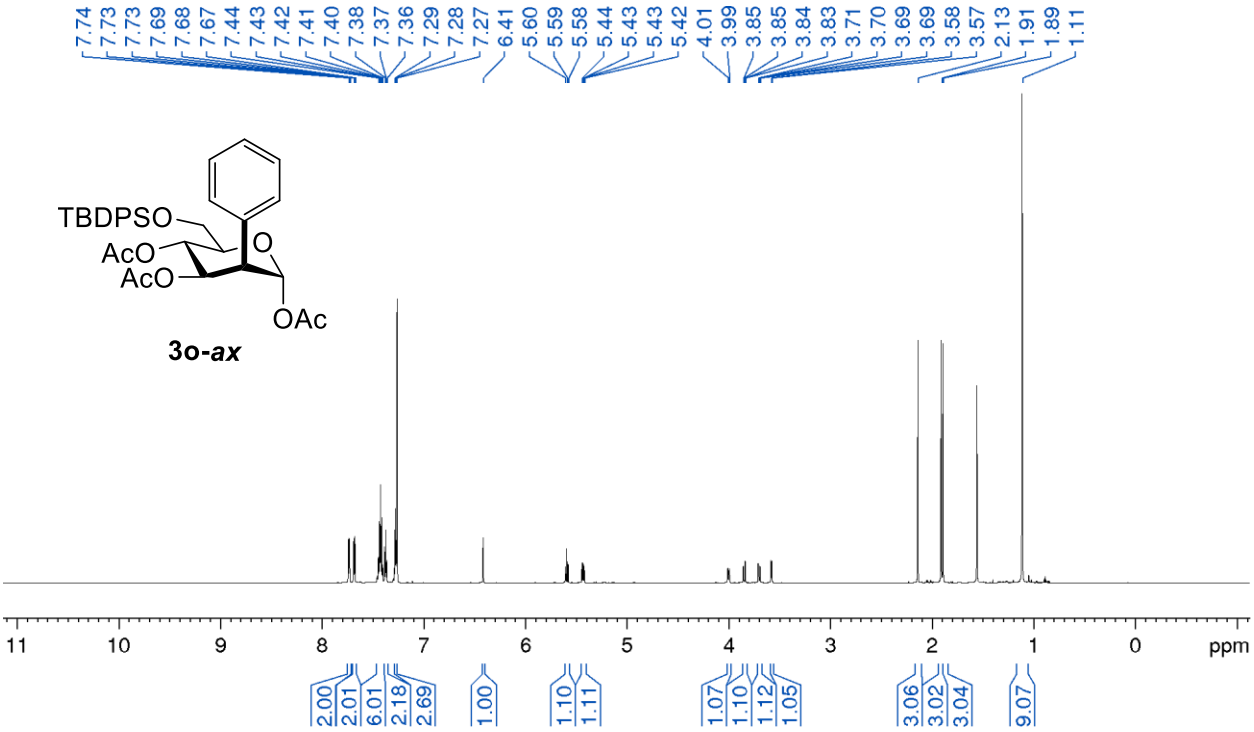
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3n-*eq*)



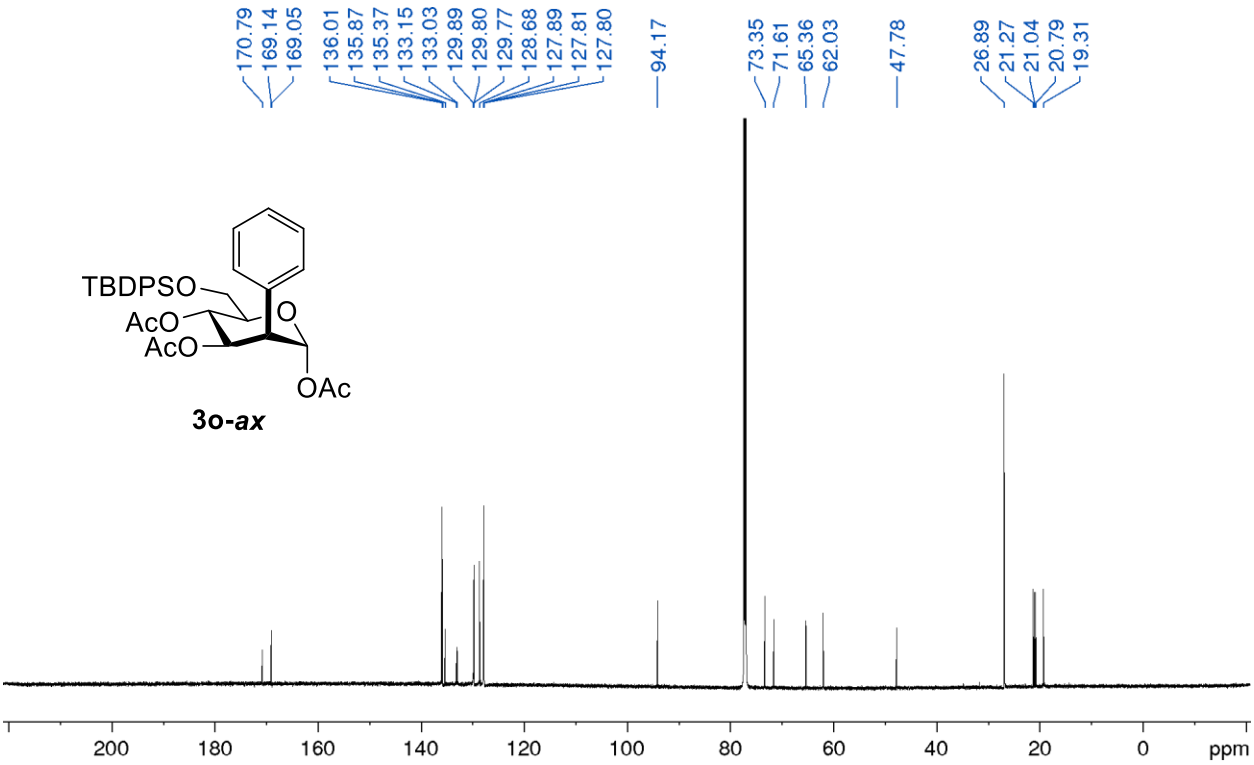
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3n-*eq*)



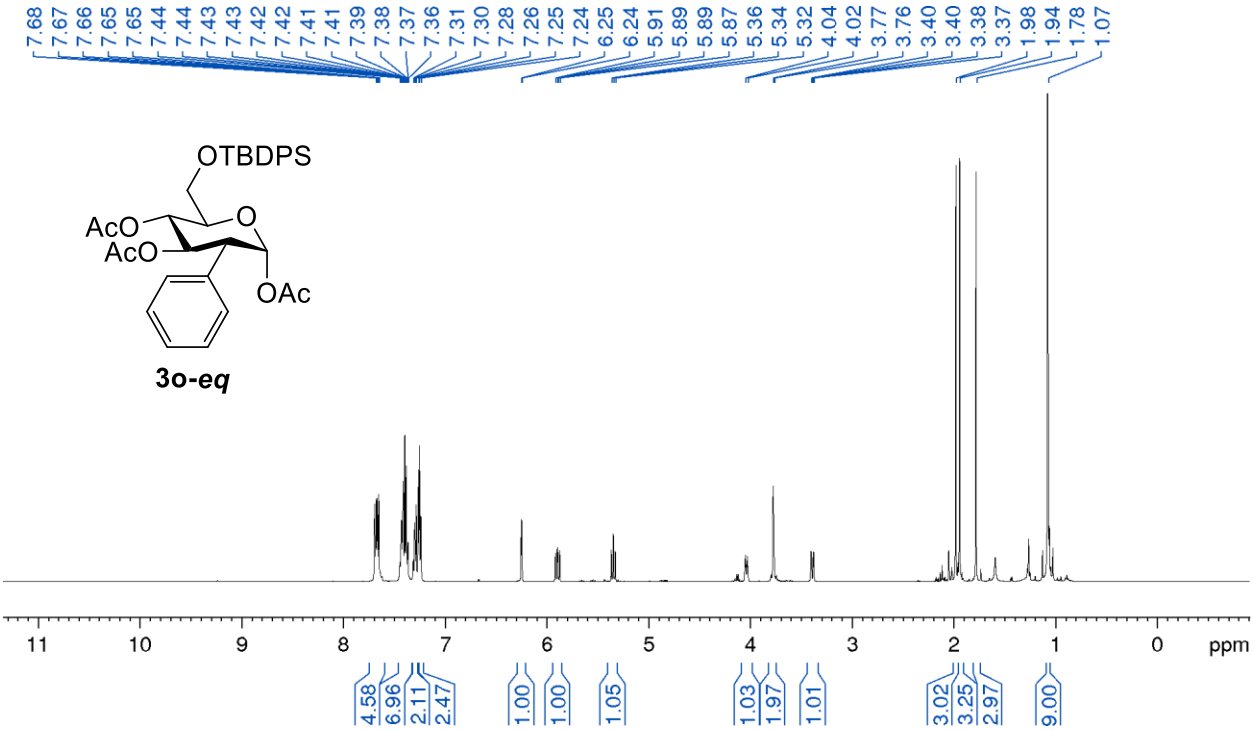
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3o-*ax*)



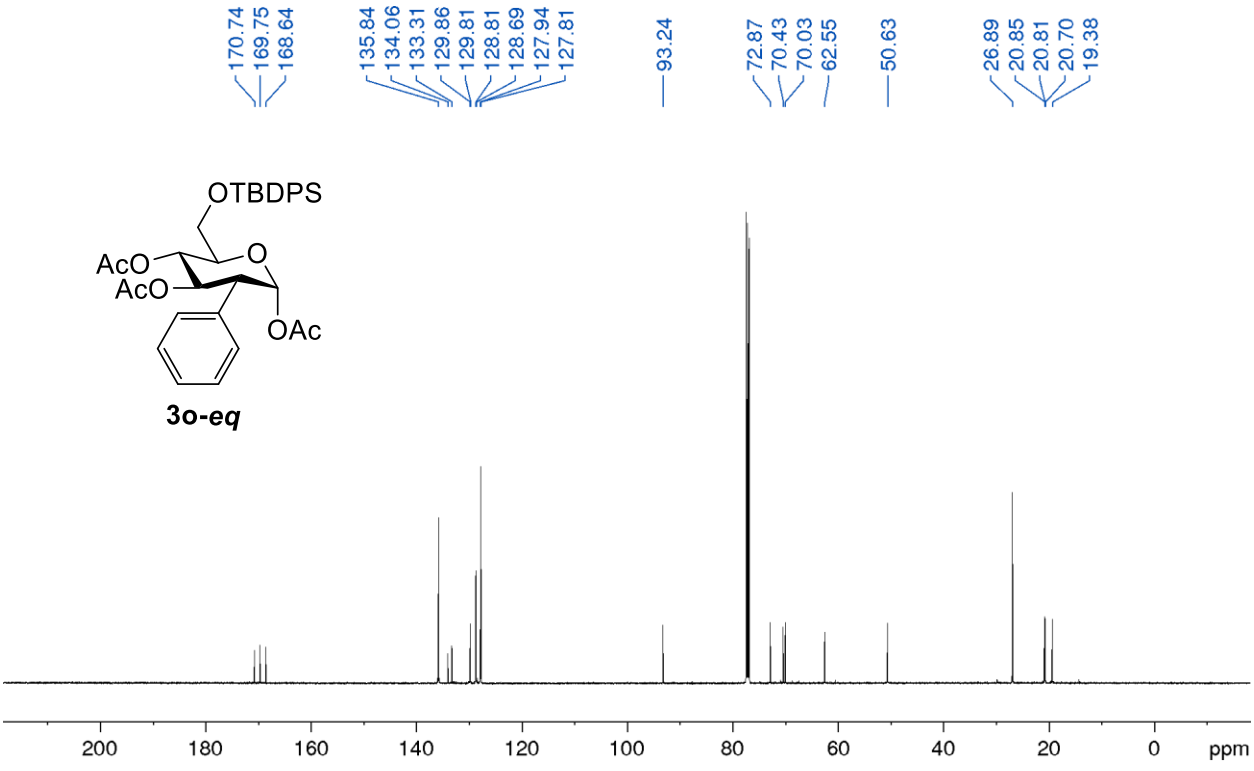
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3o-*ax*)



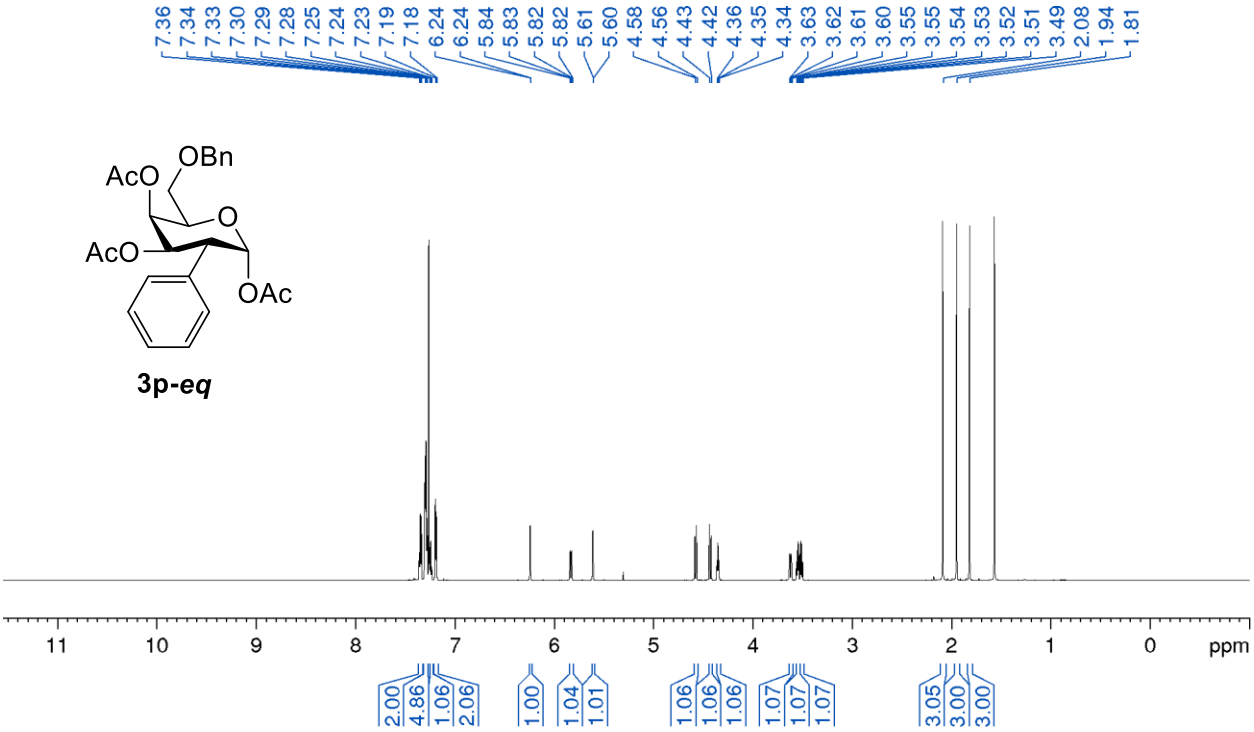
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3o-*eq*)



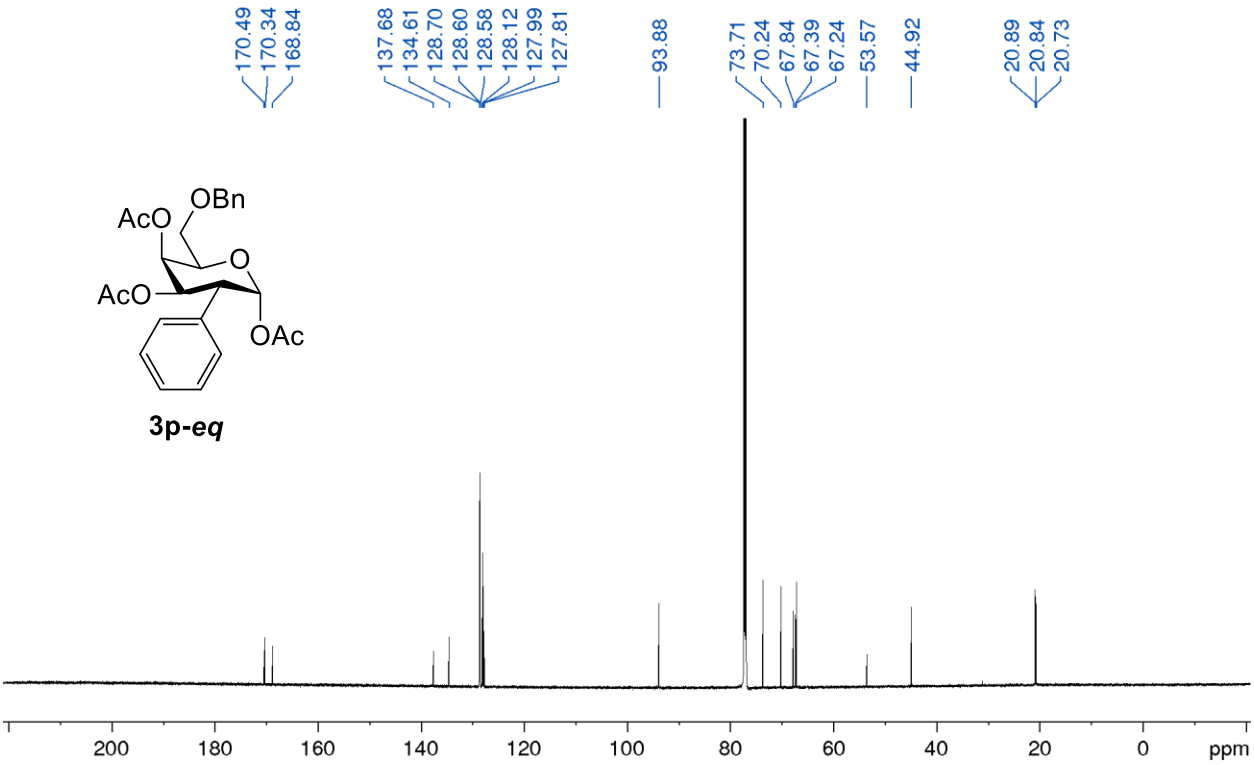
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3o-*eq*)



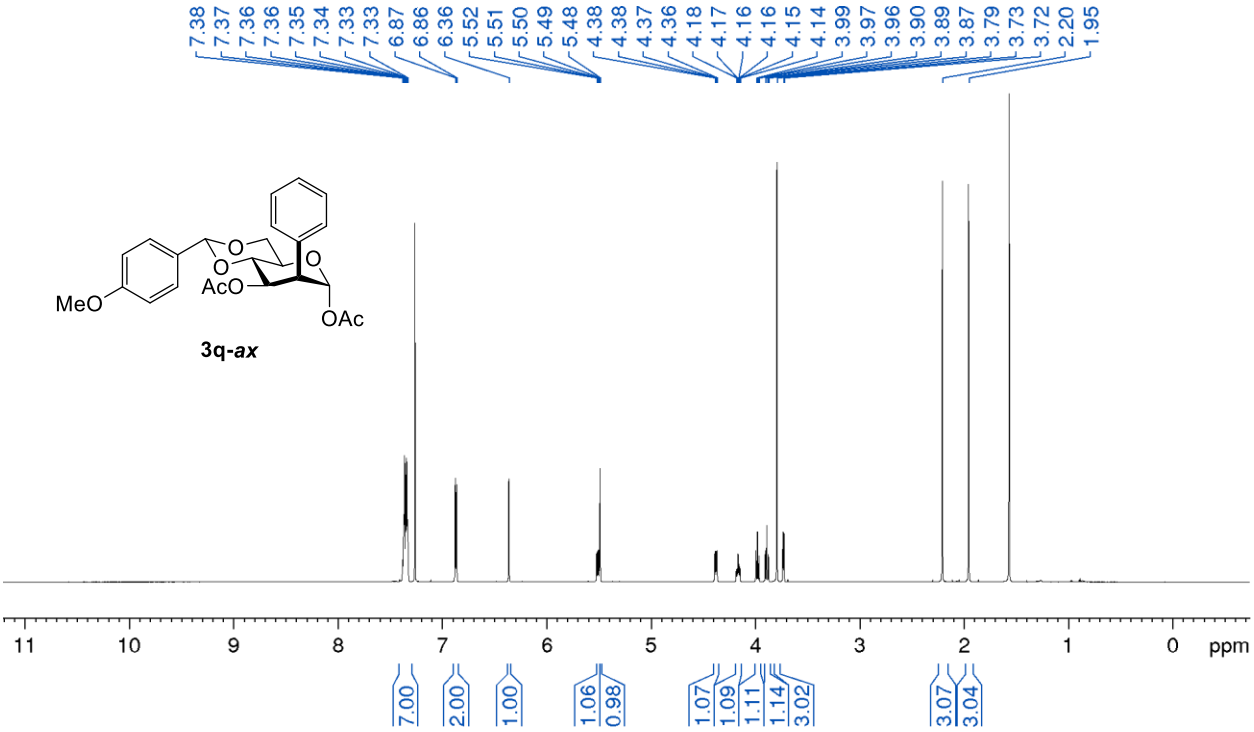
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3p-*eq*)



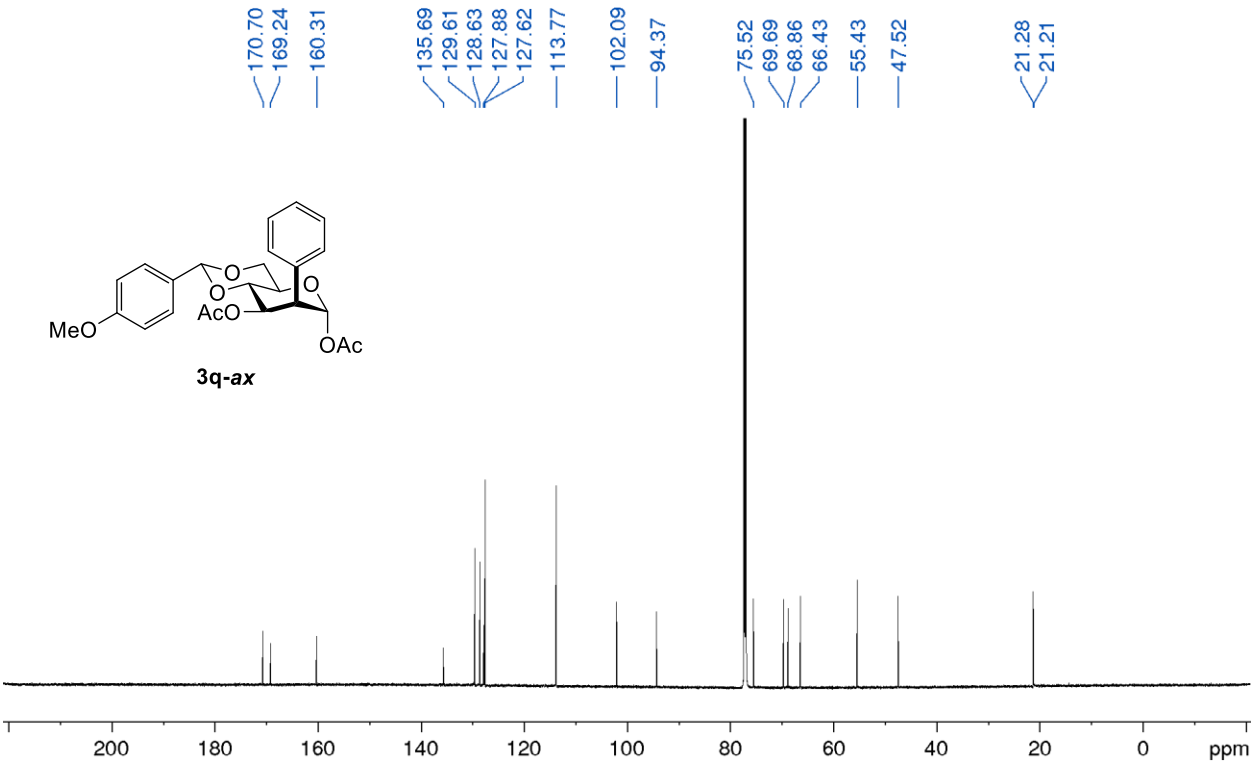
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3p-*eq*)



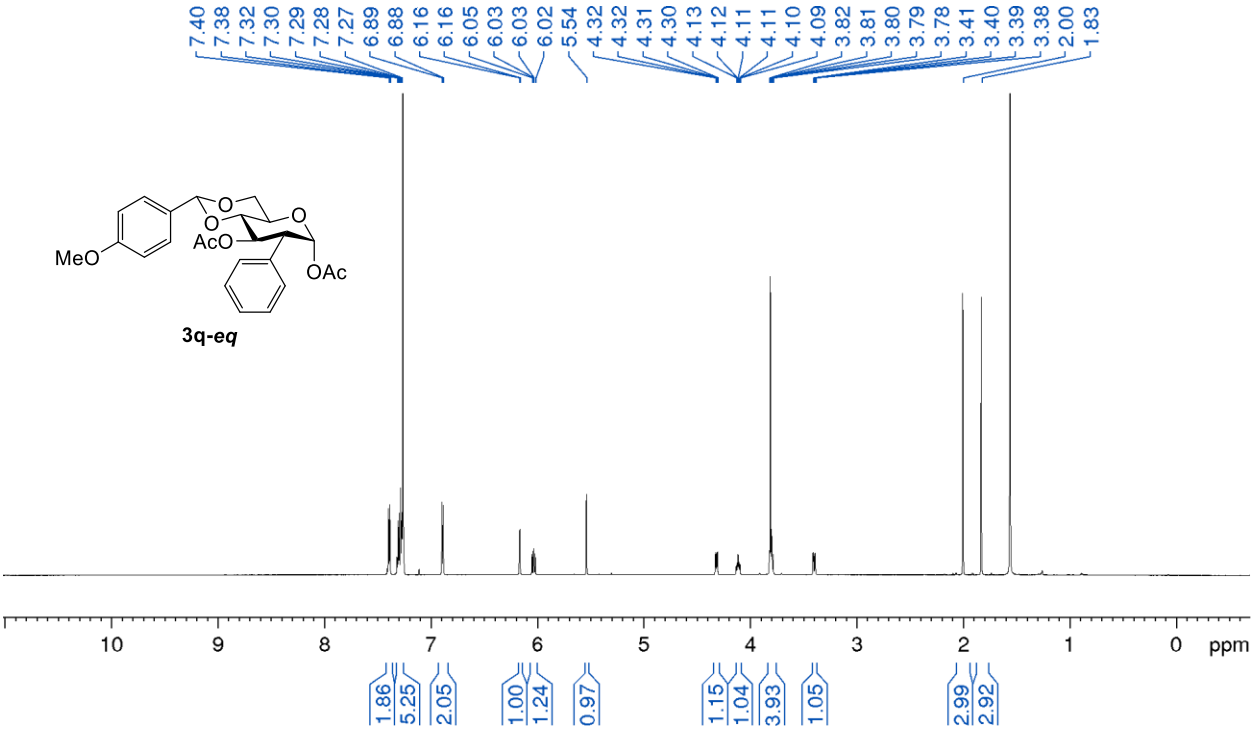
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3q-*ax*)



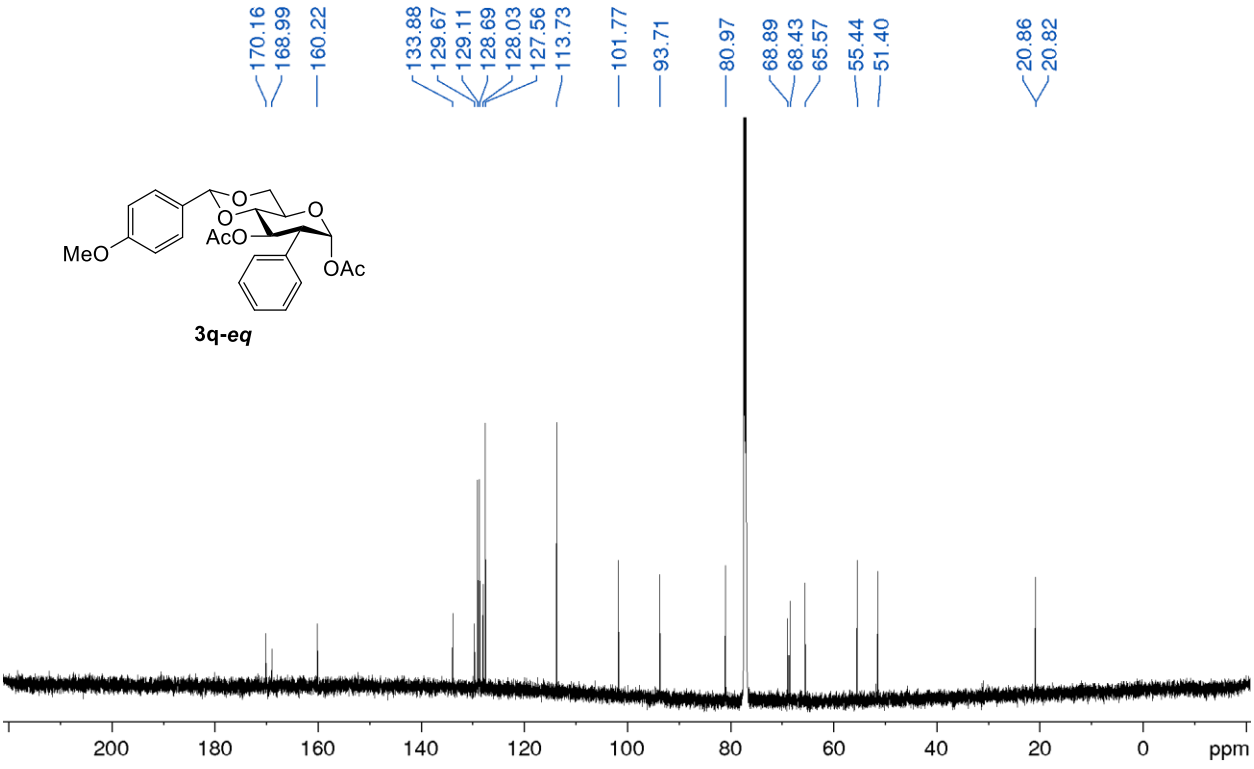
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3q-*ax*)



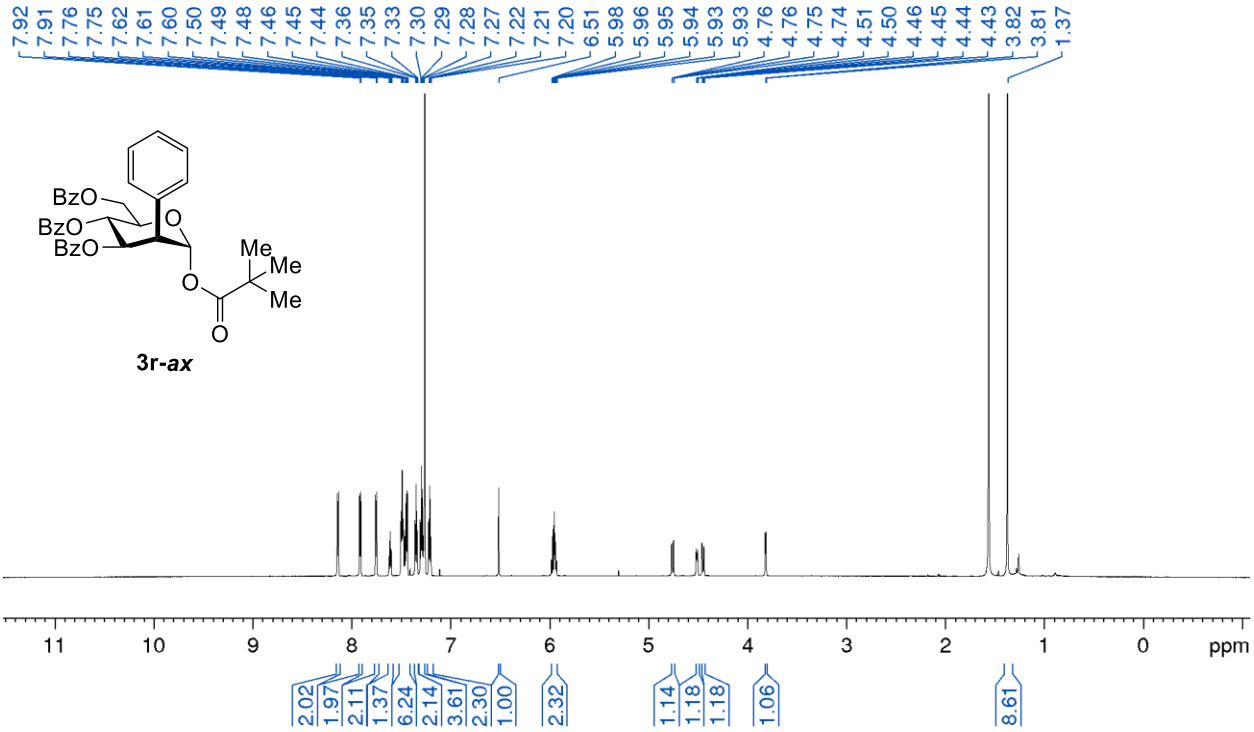
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3q-*eq*)



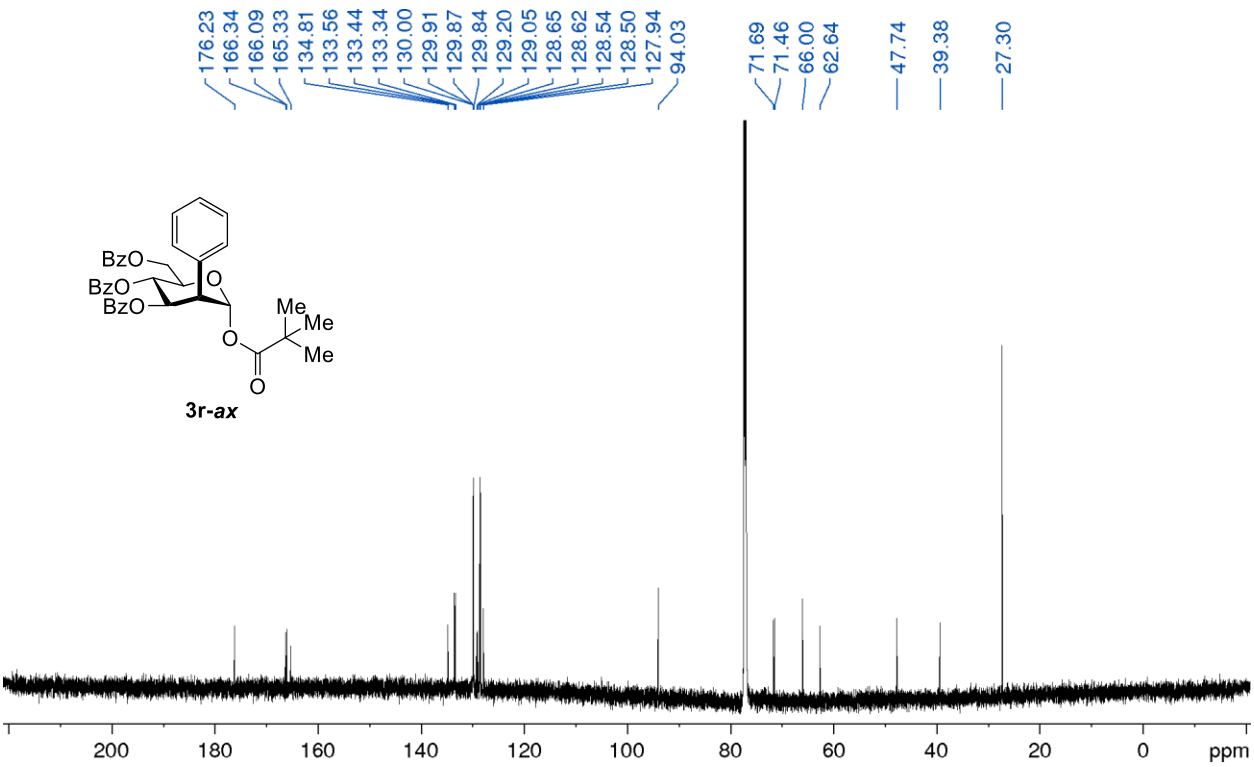
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3q-*eq*)



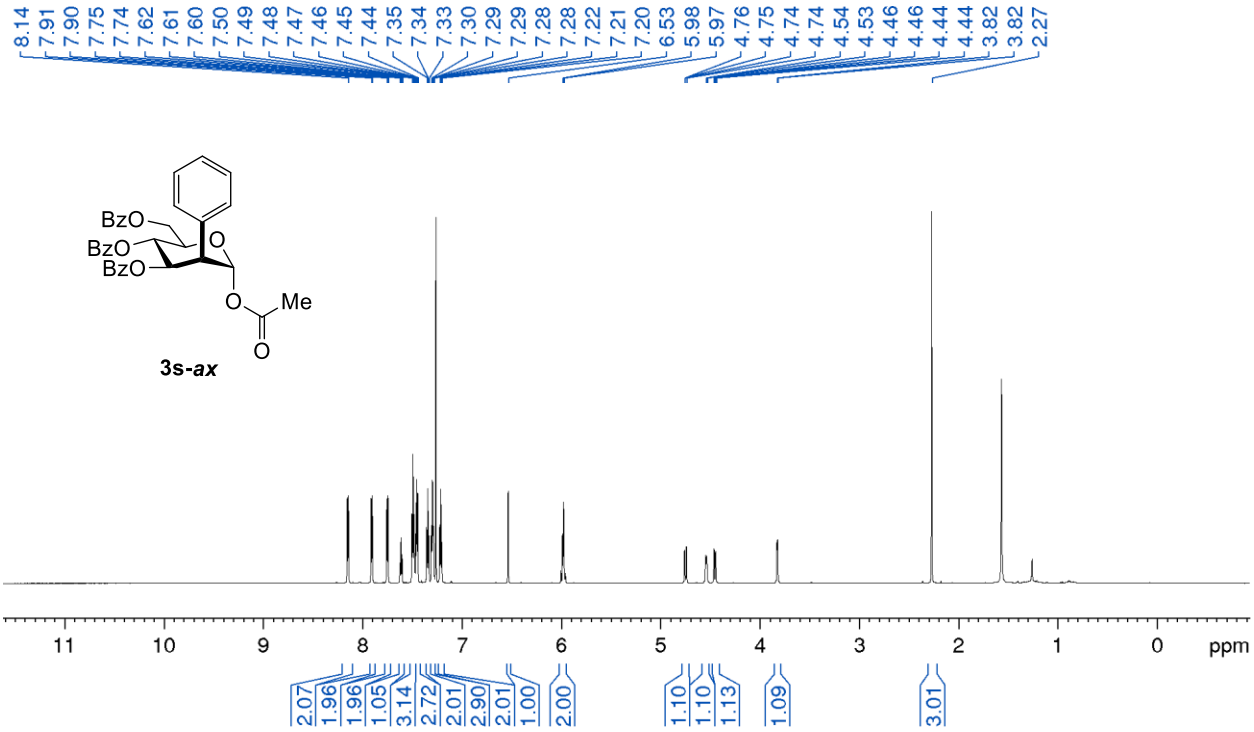
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3r-*ax*)



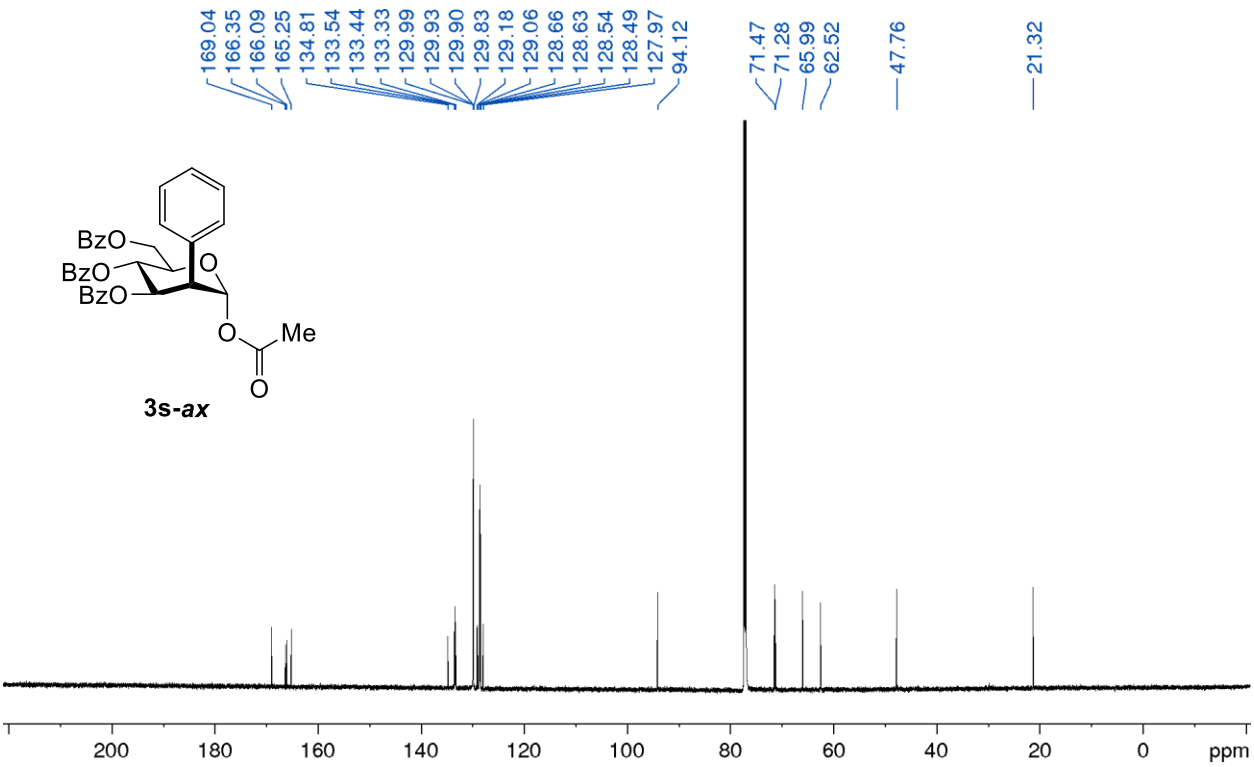
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3r-*ax*)



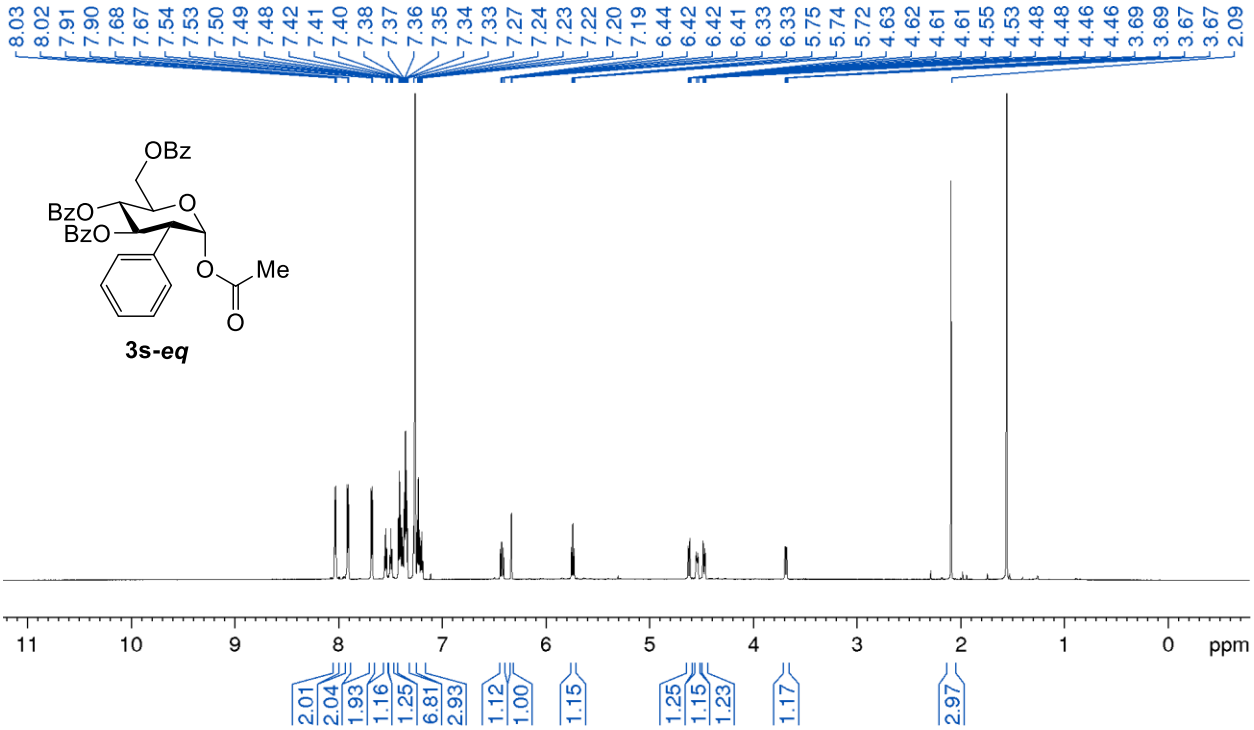
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3s-*ax*)



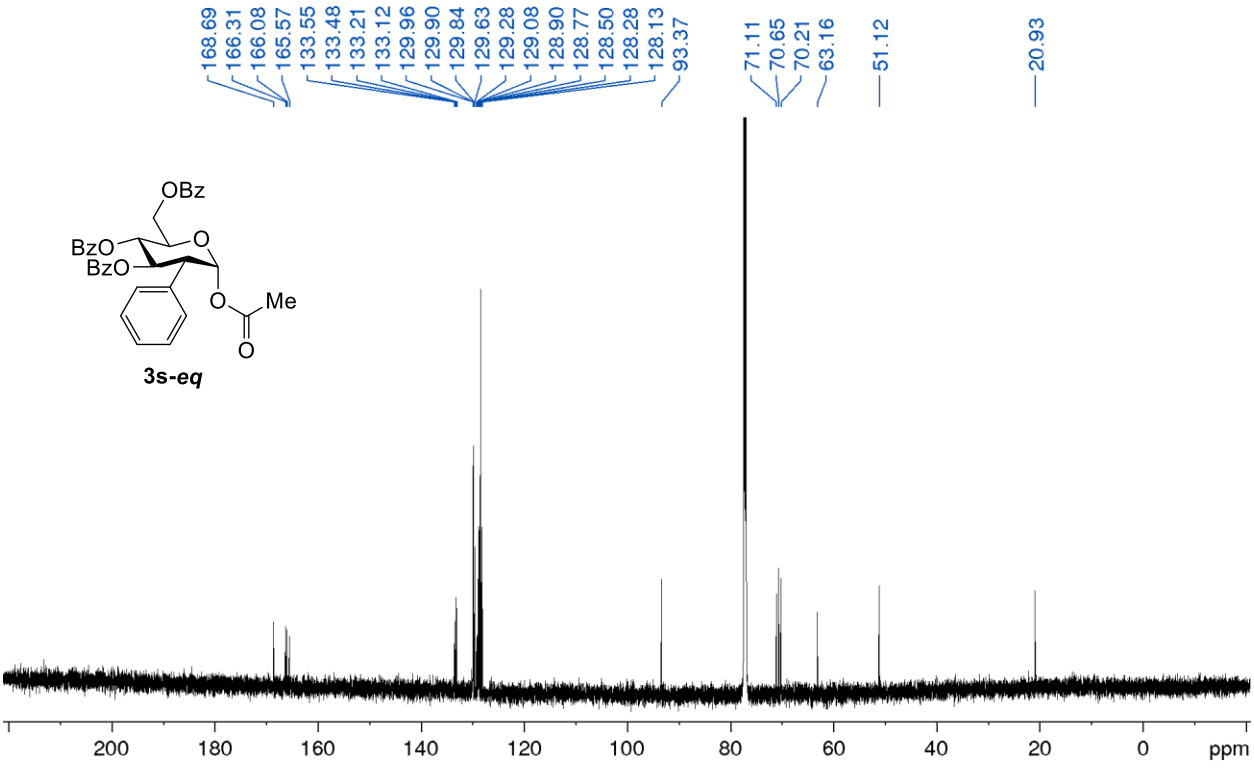
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3s-*ax*)



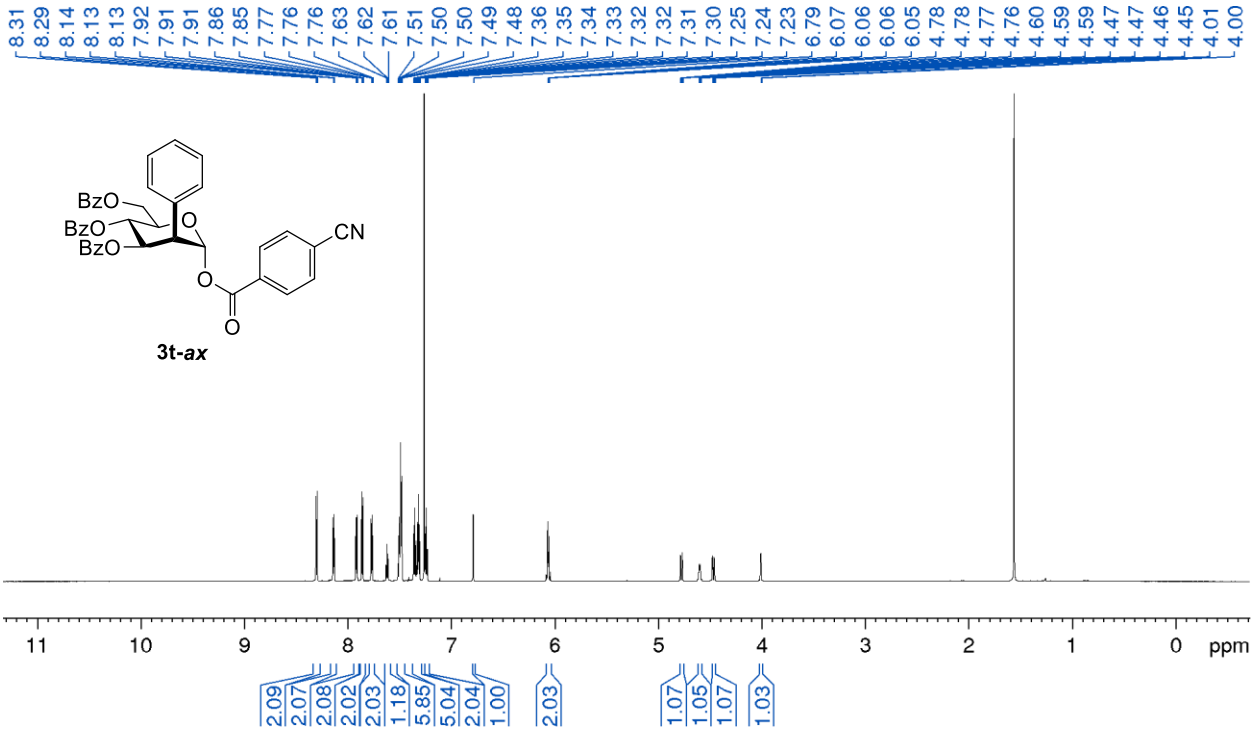
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3s-*eq*)



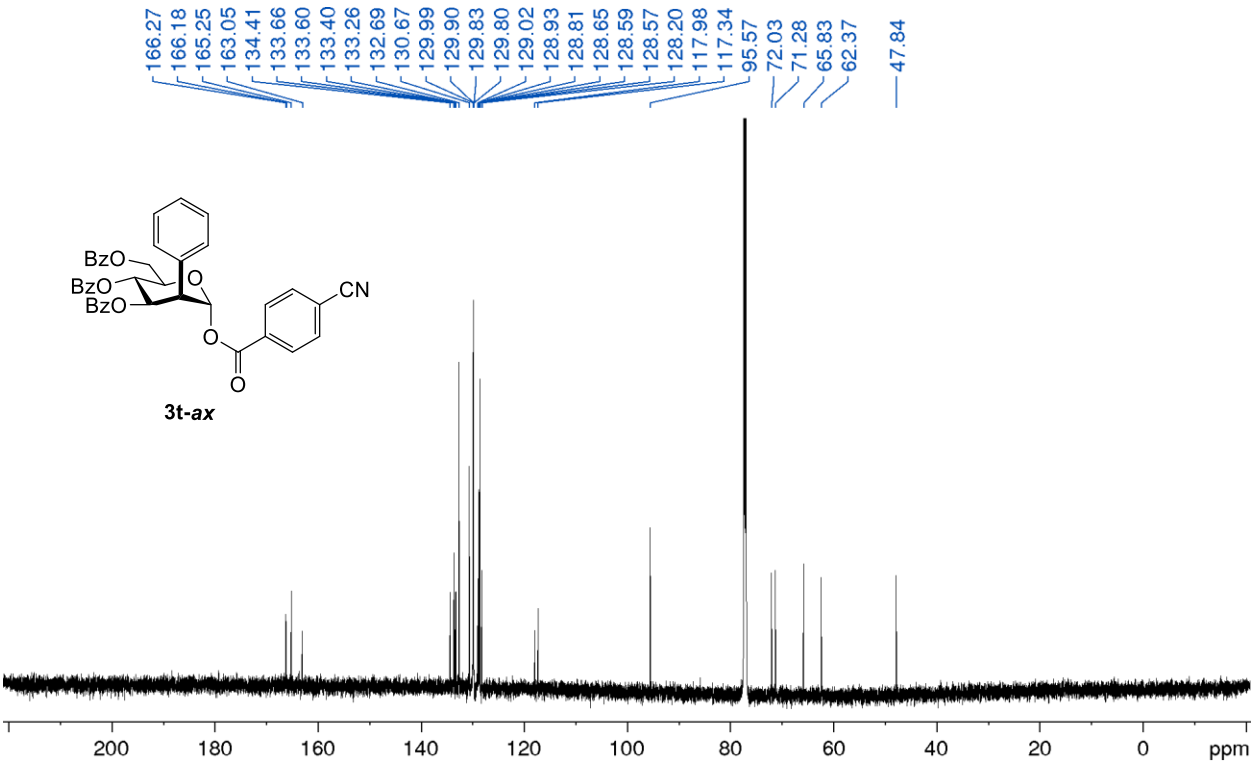
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3s-*eq*)



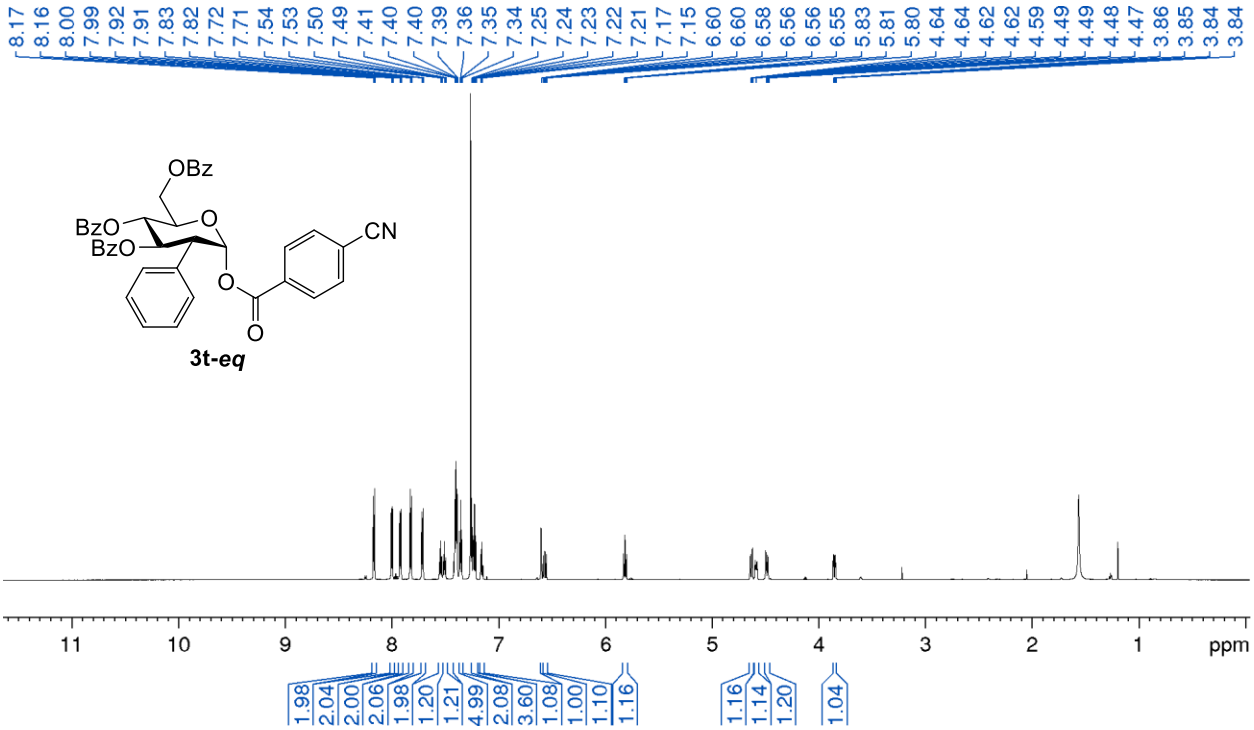
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3t-*ax*)



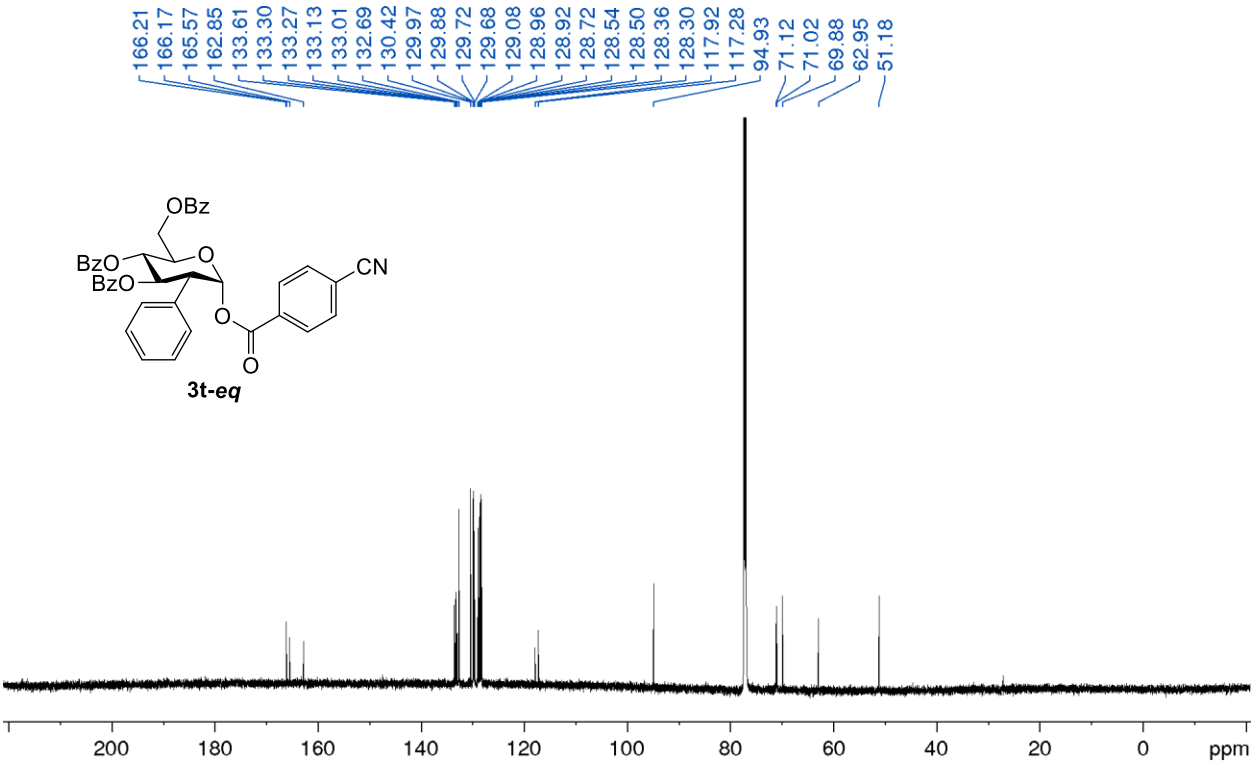
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3t-*ax*)



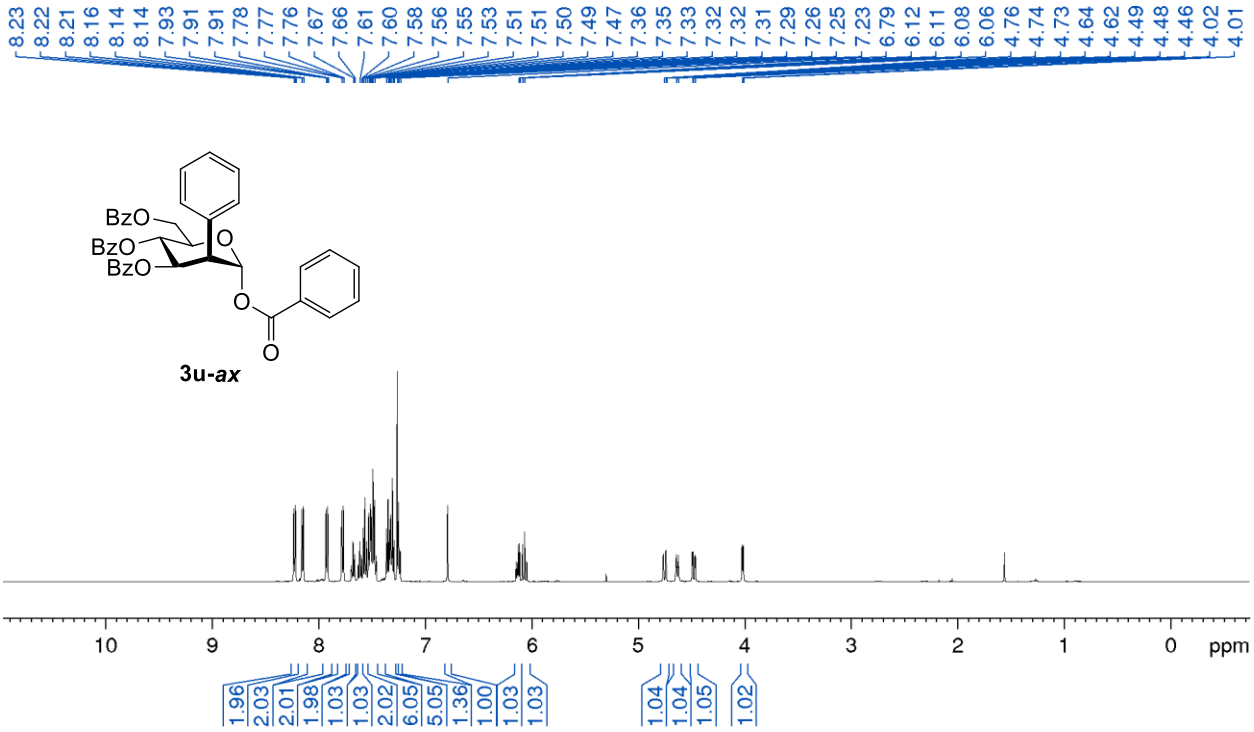
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3t-*eq*)



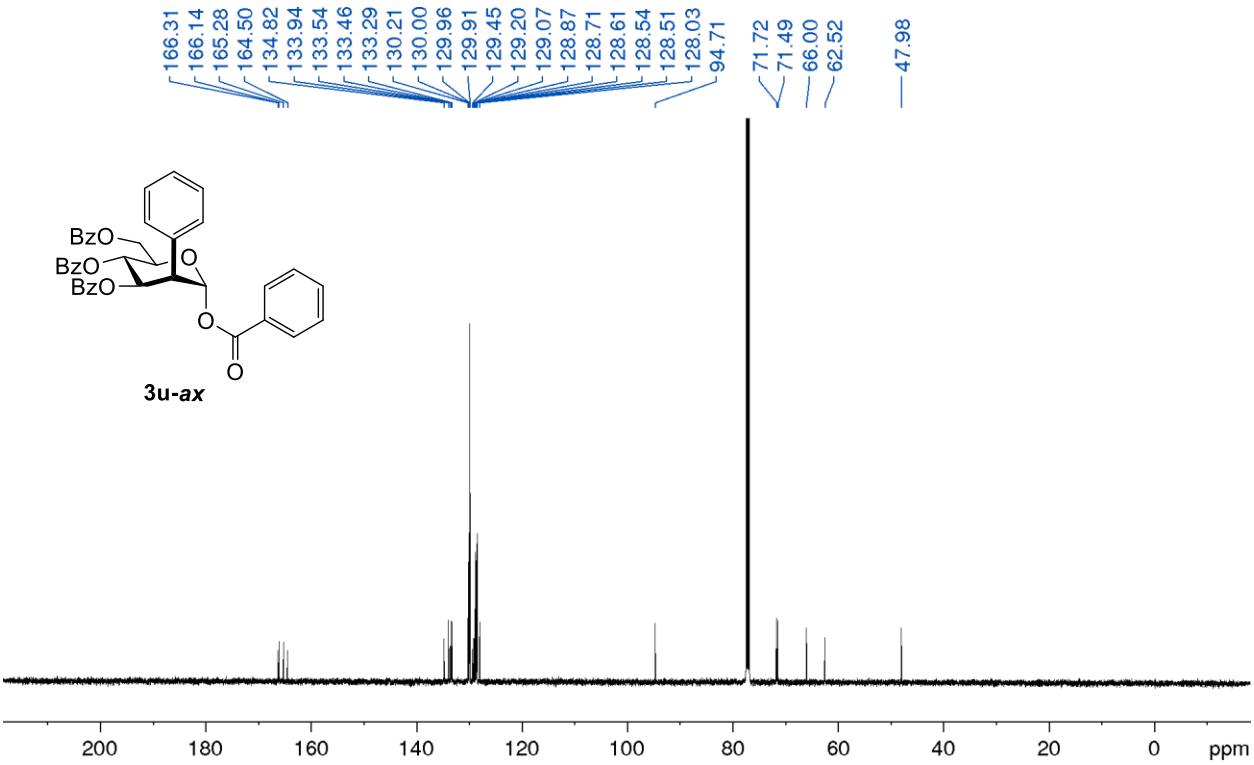
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3t-*eq*)



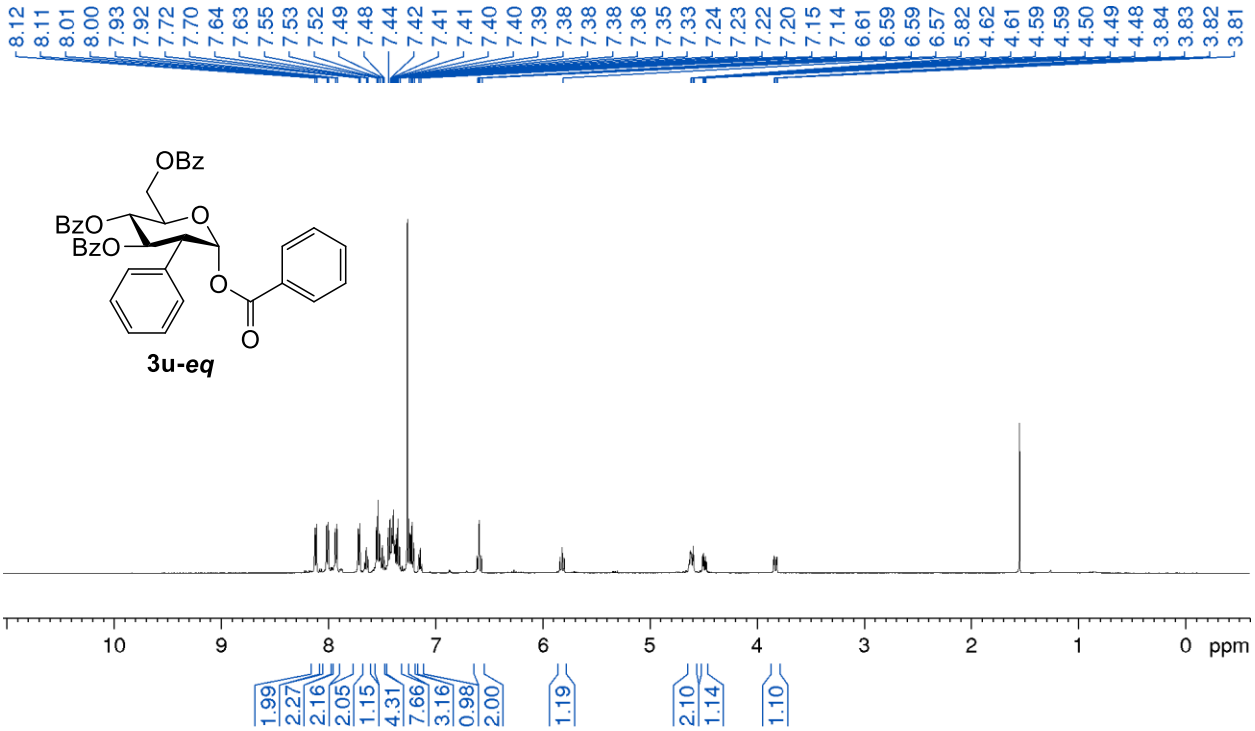
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3u-*ax*)



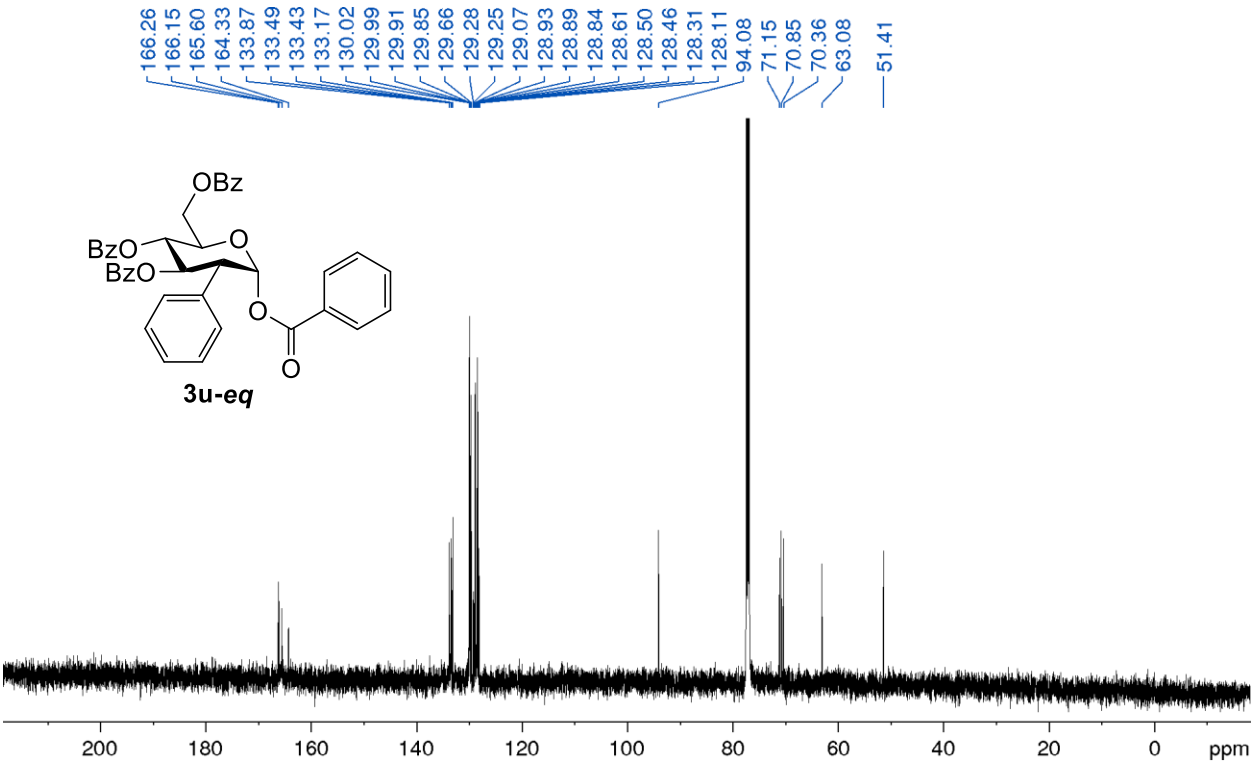
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3u-*ax*)



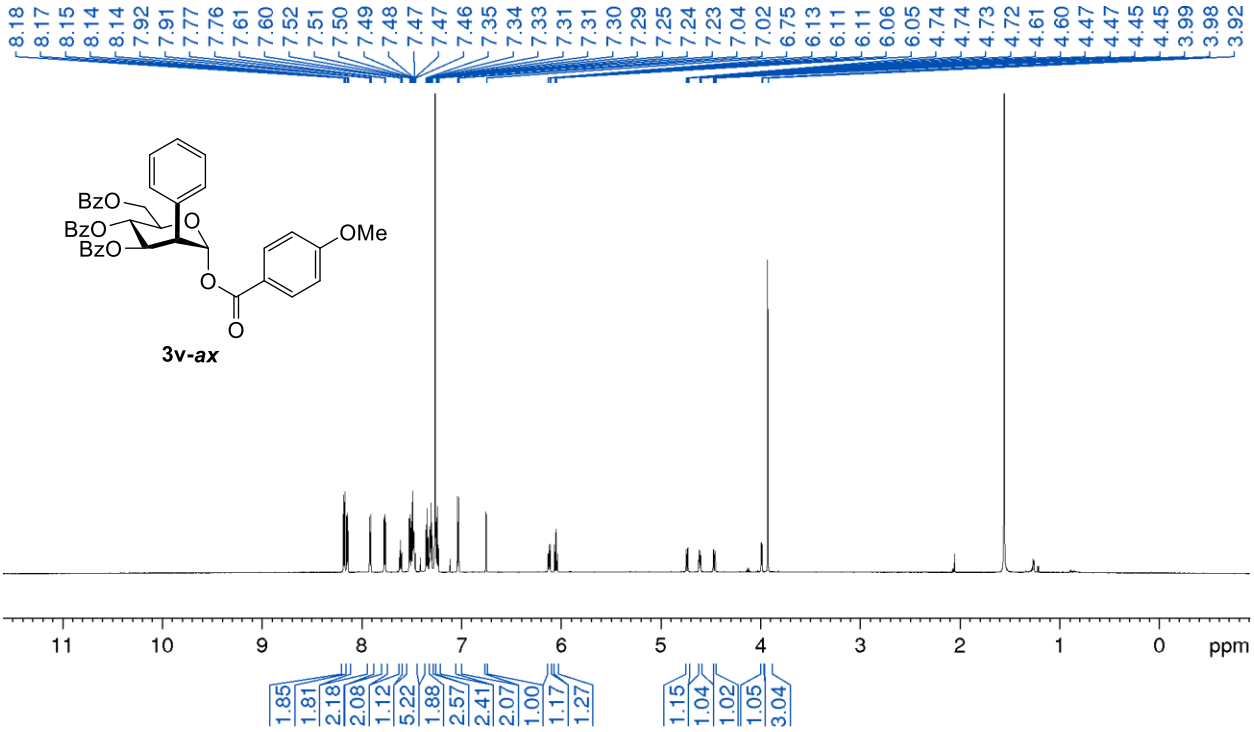
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3u-*eq*)



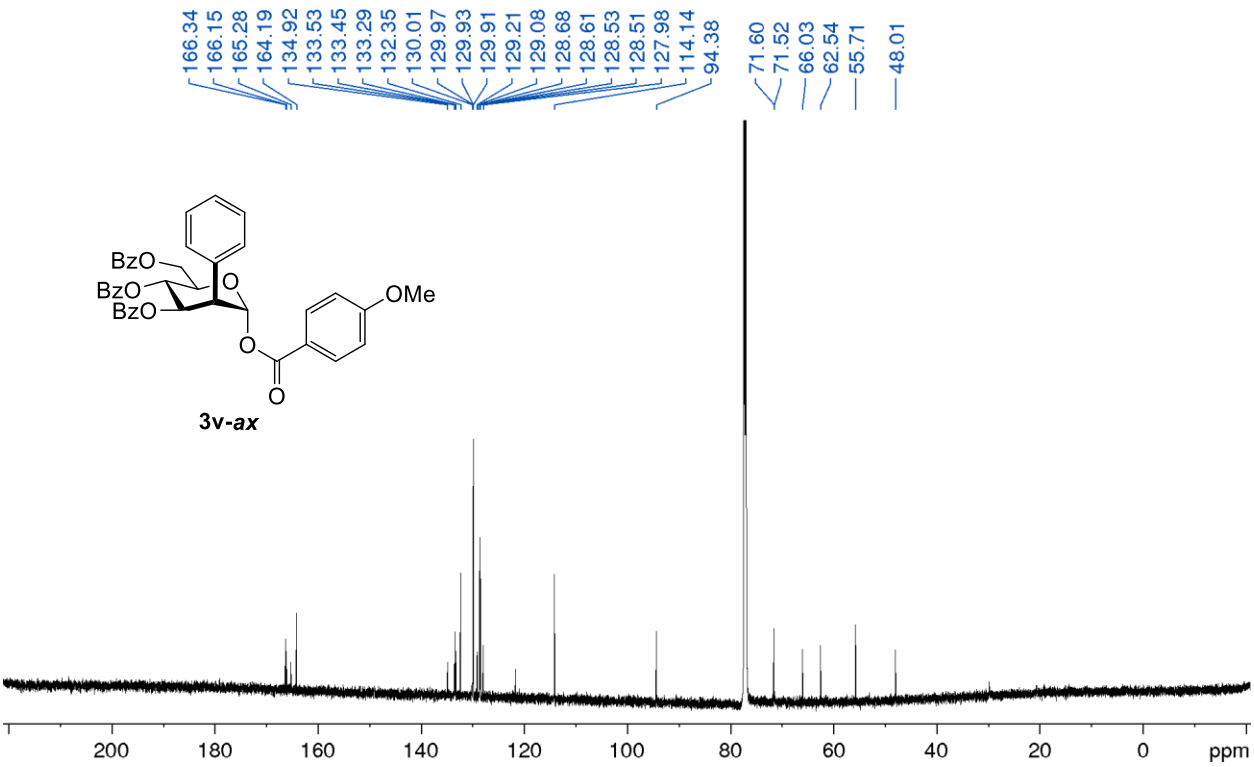
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3u-*eq*)



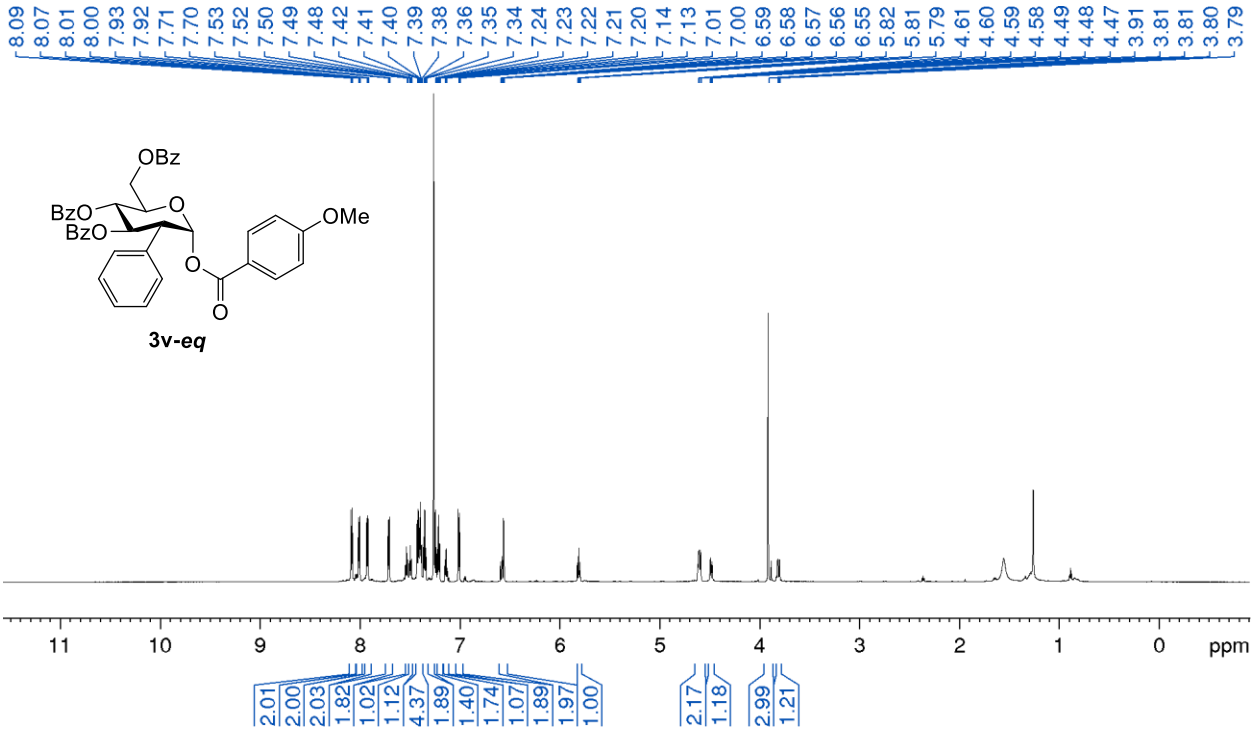
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3v-*ax*)



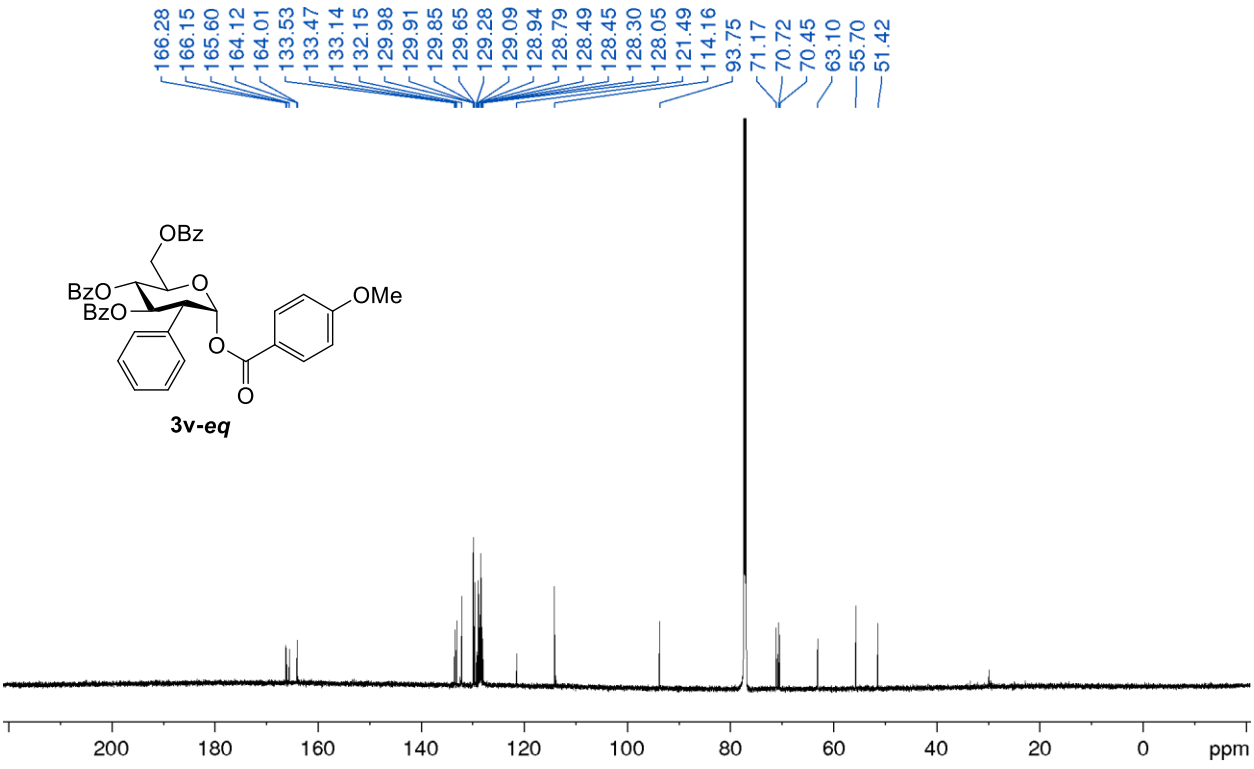
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3v-*ax*)



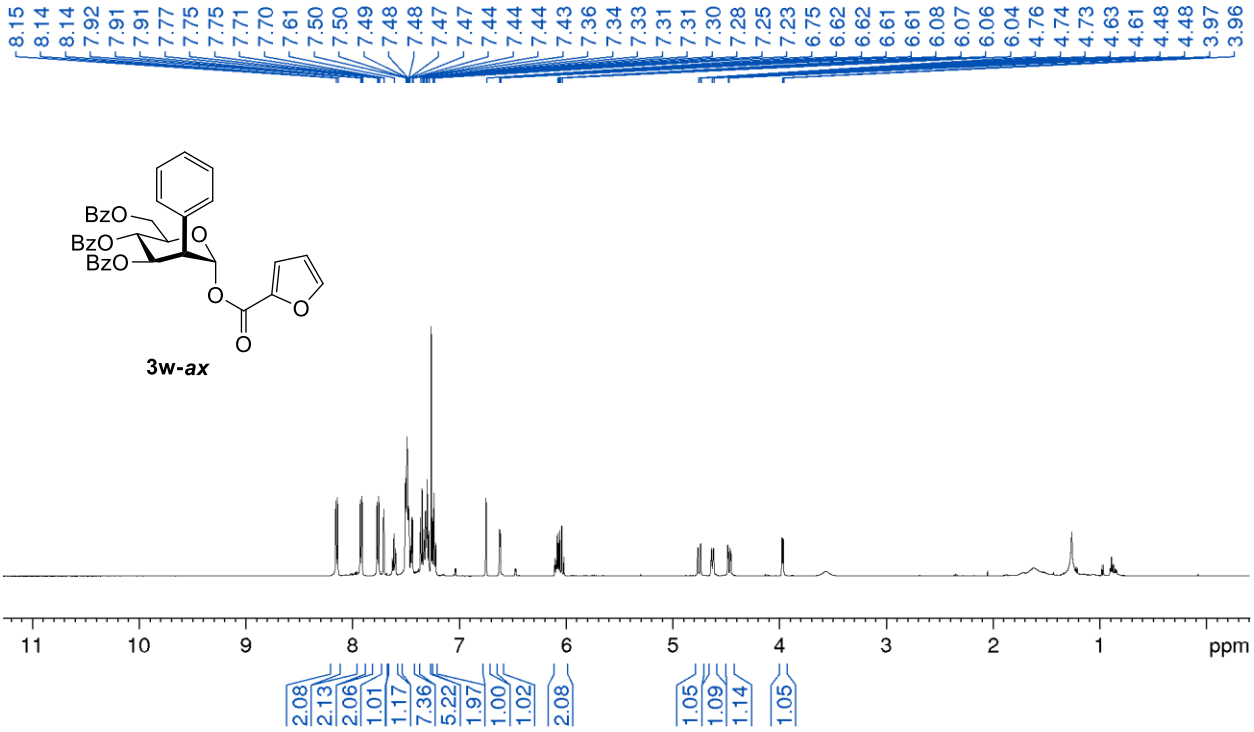
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3v-*eq*)



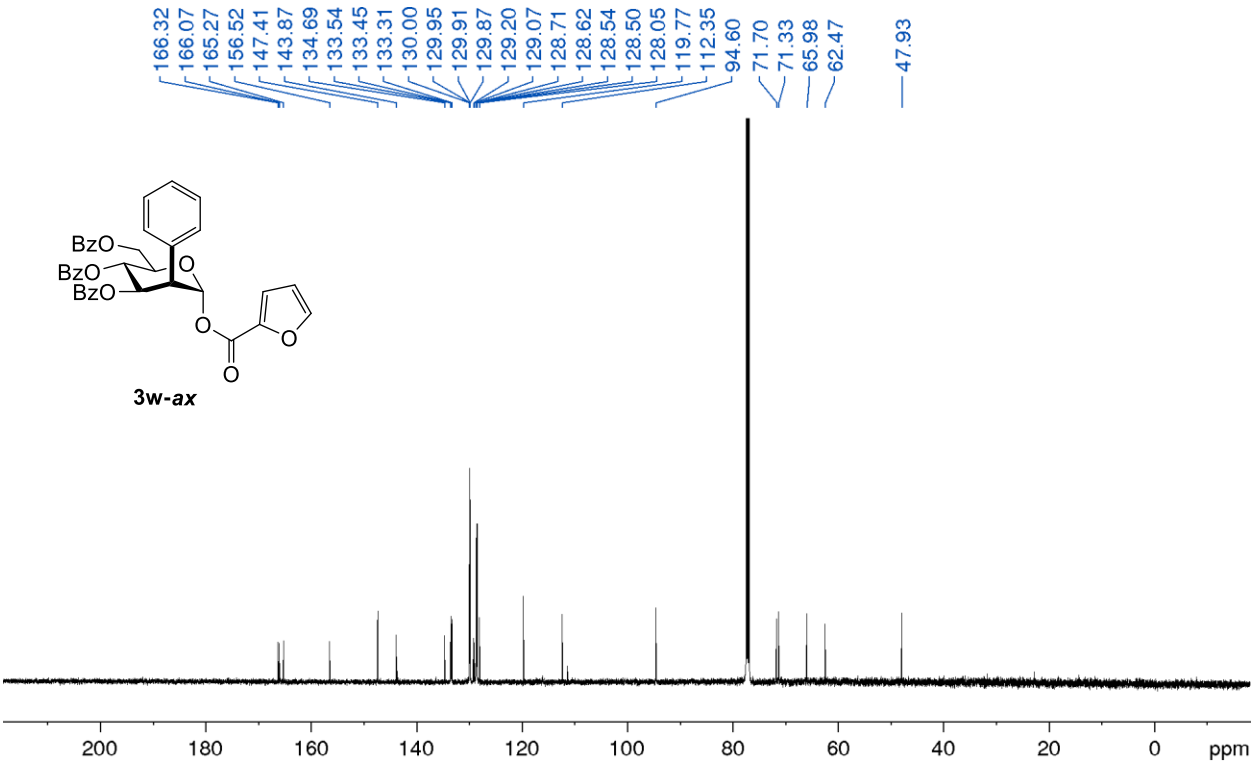
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3v-*eq*)



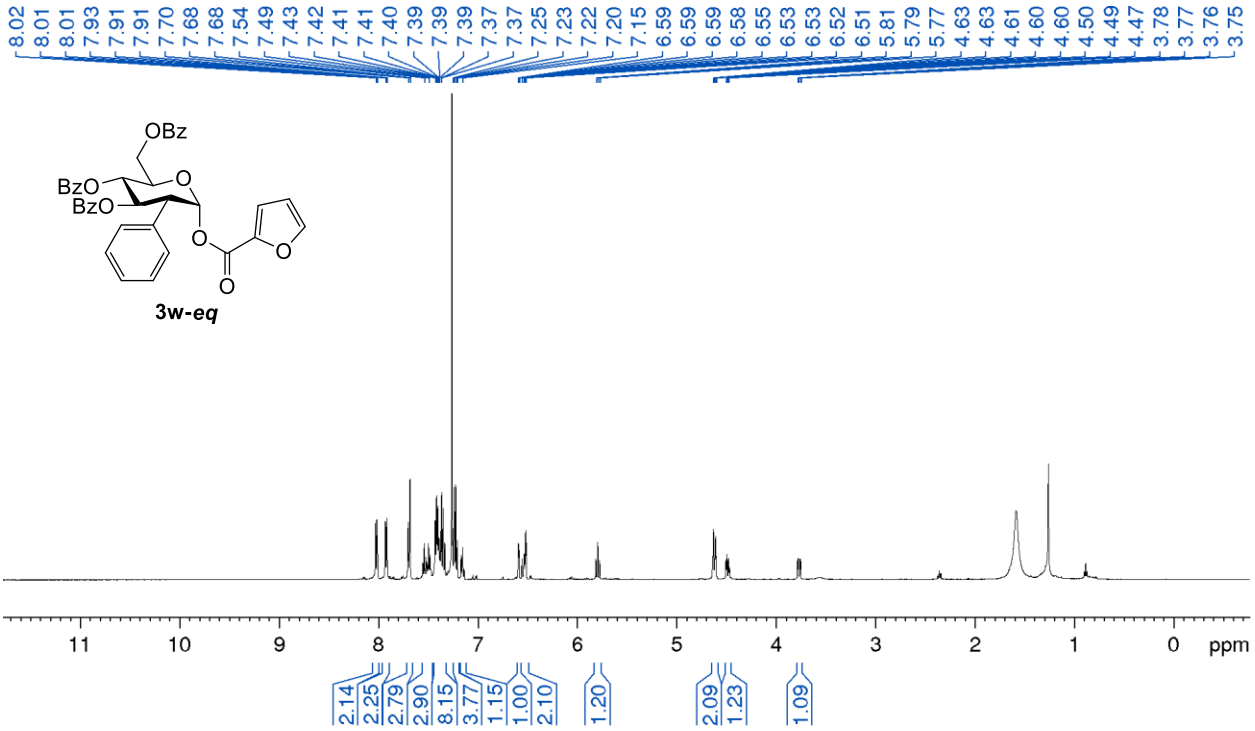
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3w-*ax*)



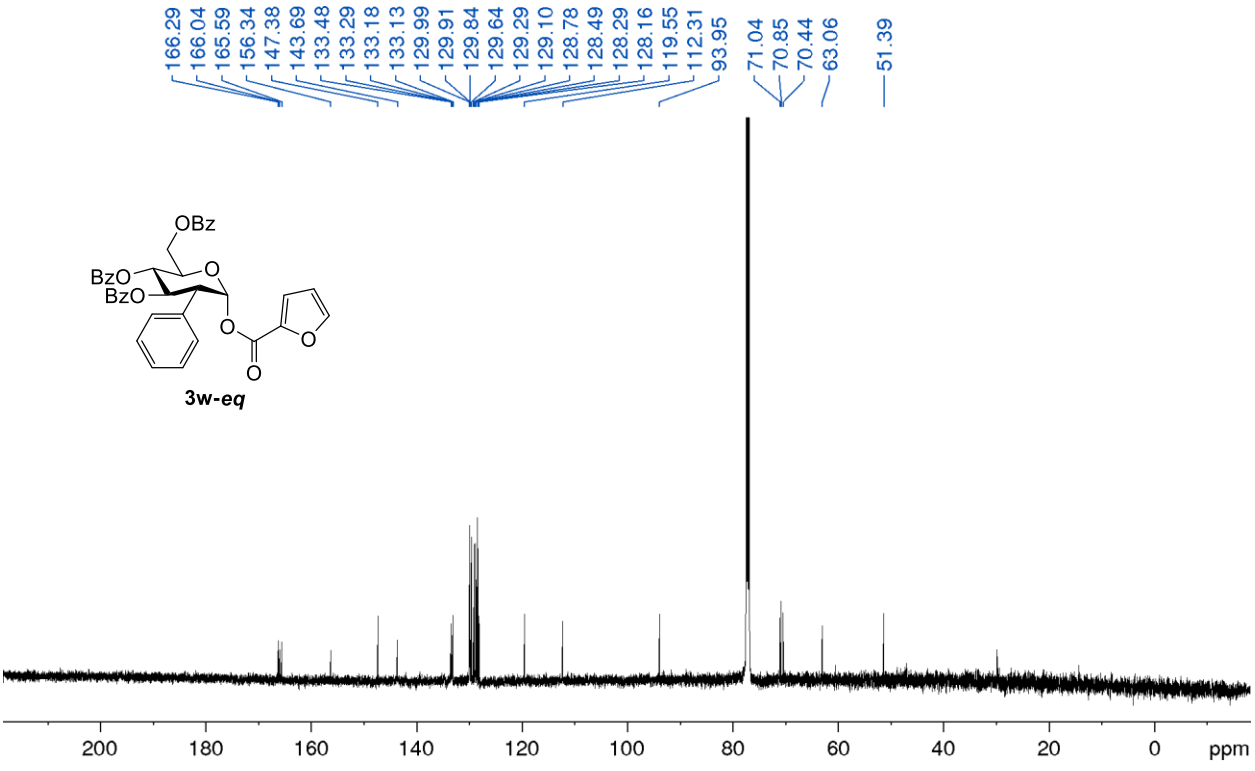
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3w-*ax*)



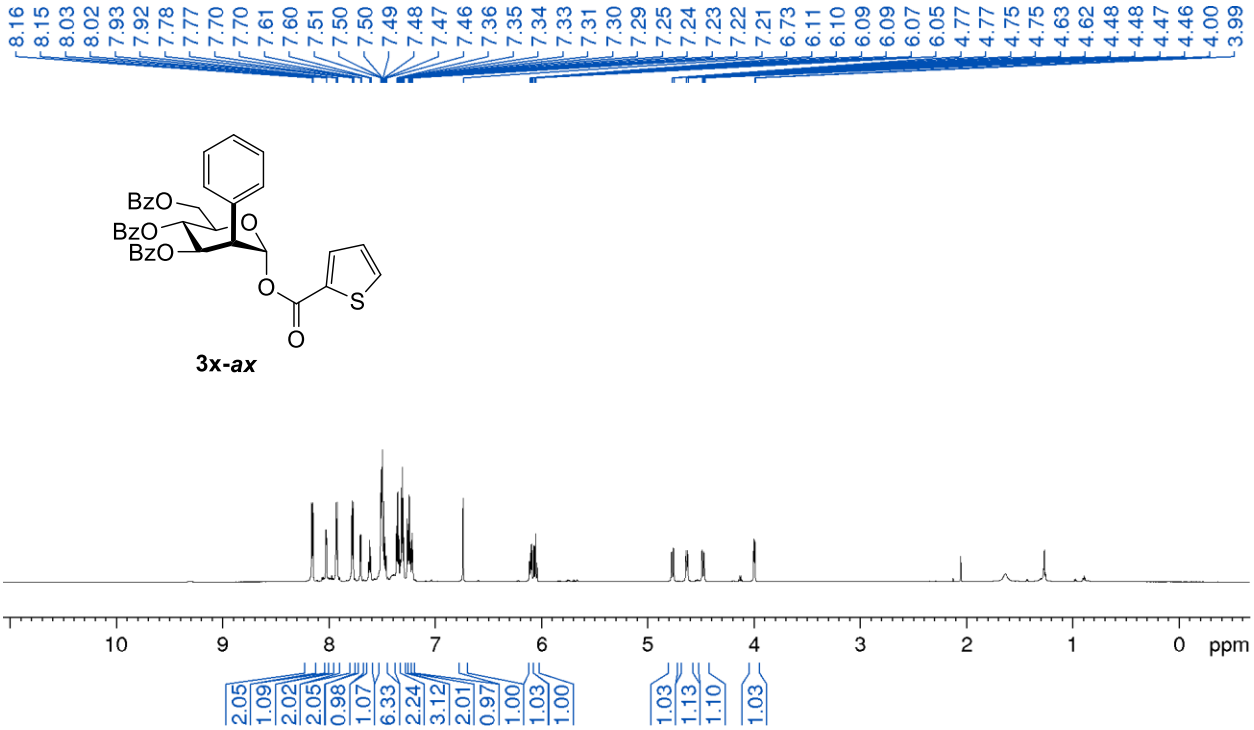
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3w-*eq*)



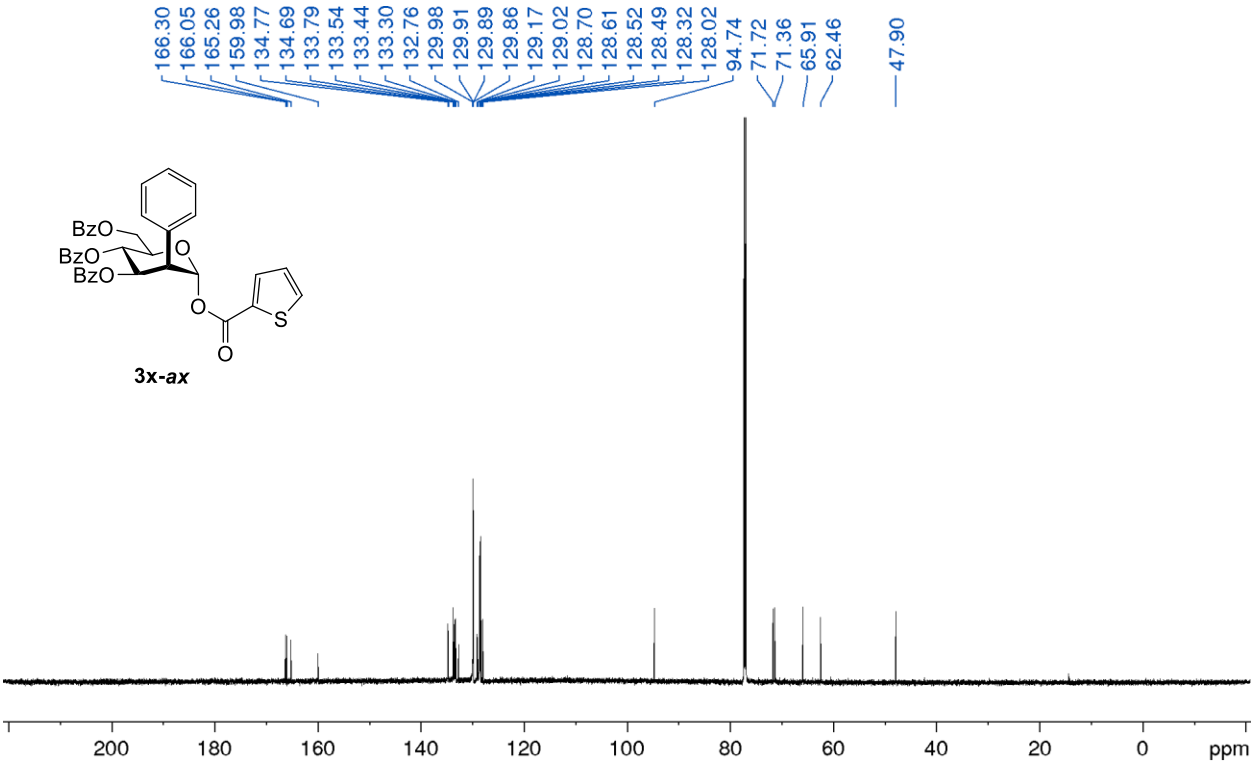
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3w-*eq*)



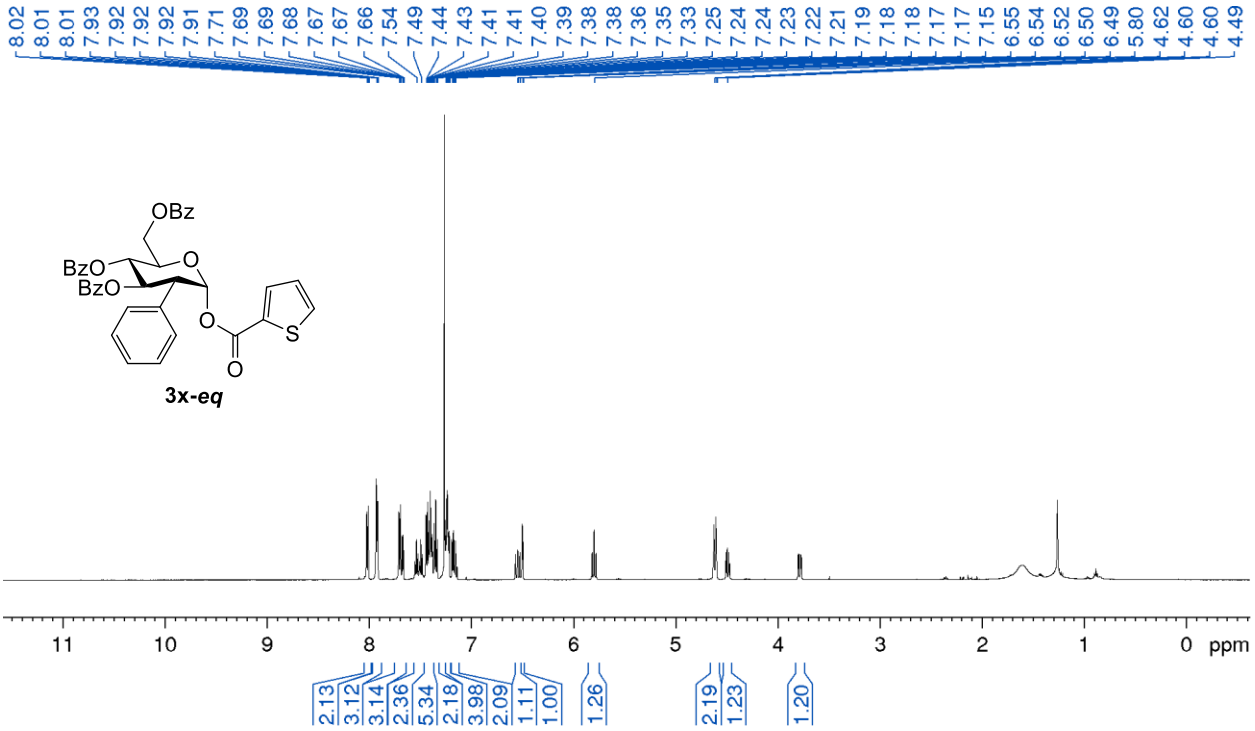
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3x-*ax*)



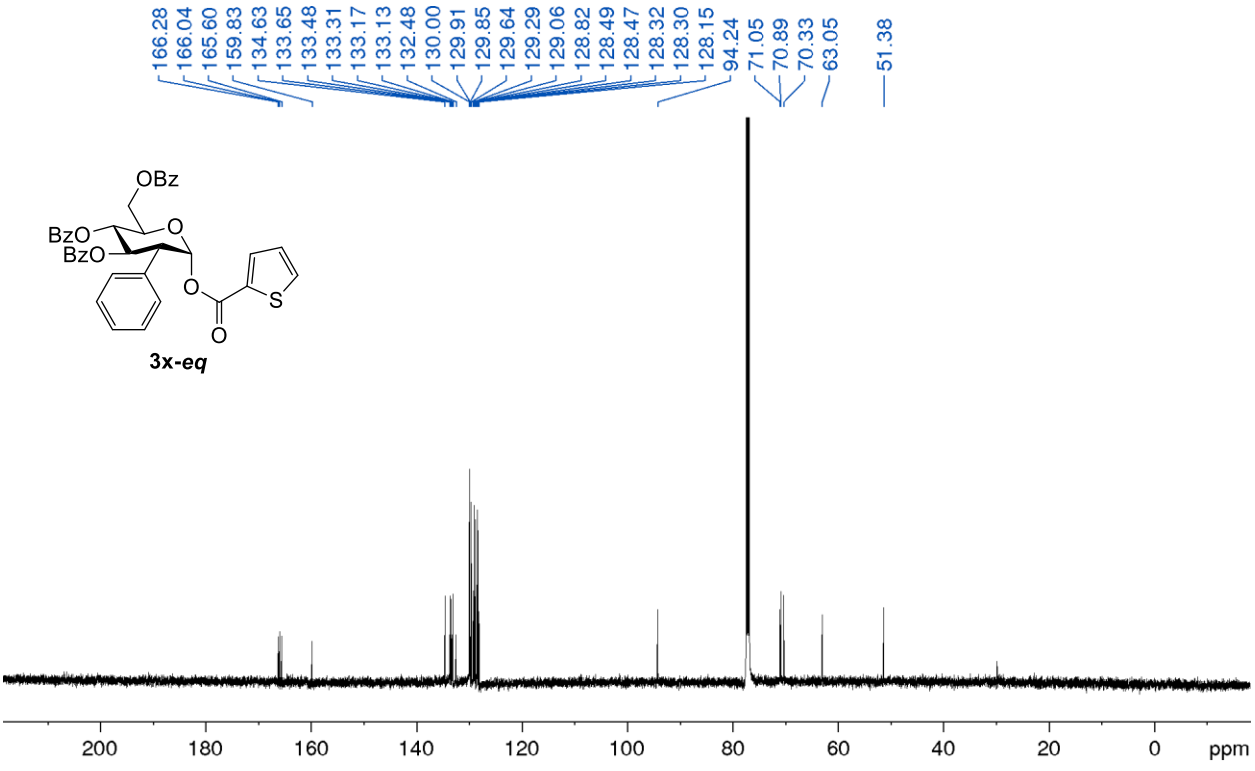
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3x-*ax*)



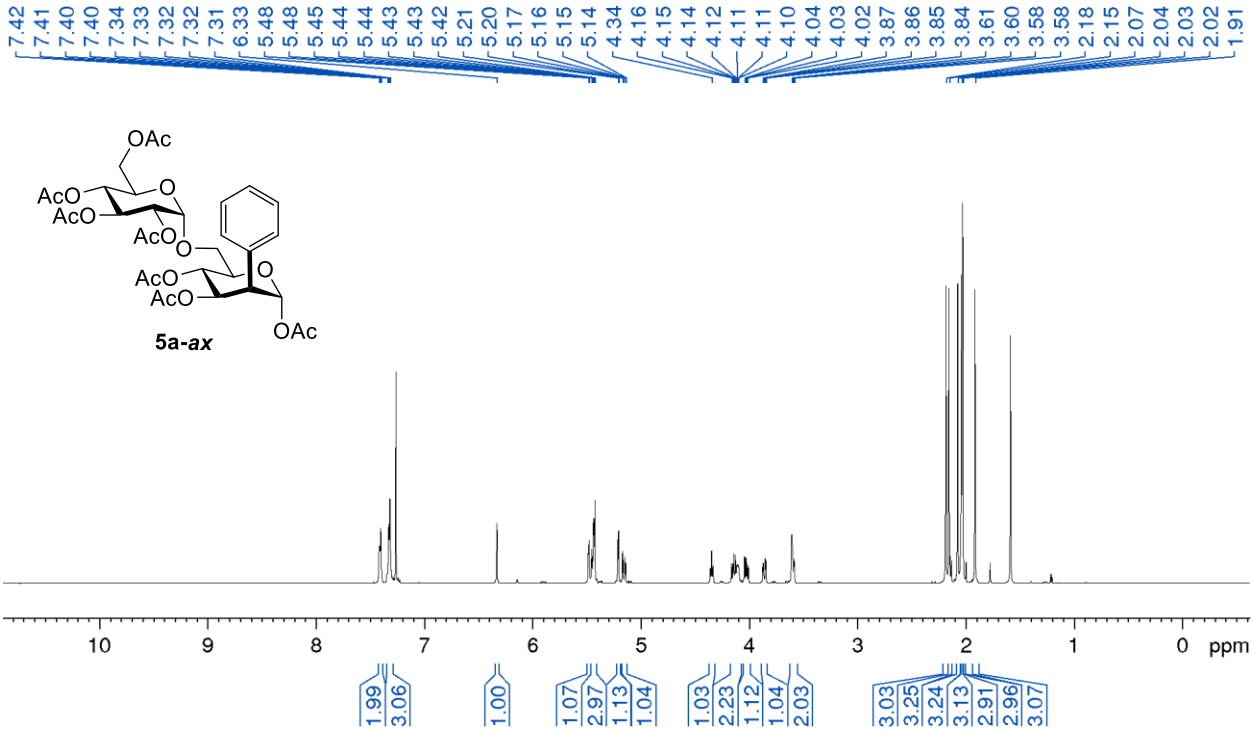
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3x-*eq*)



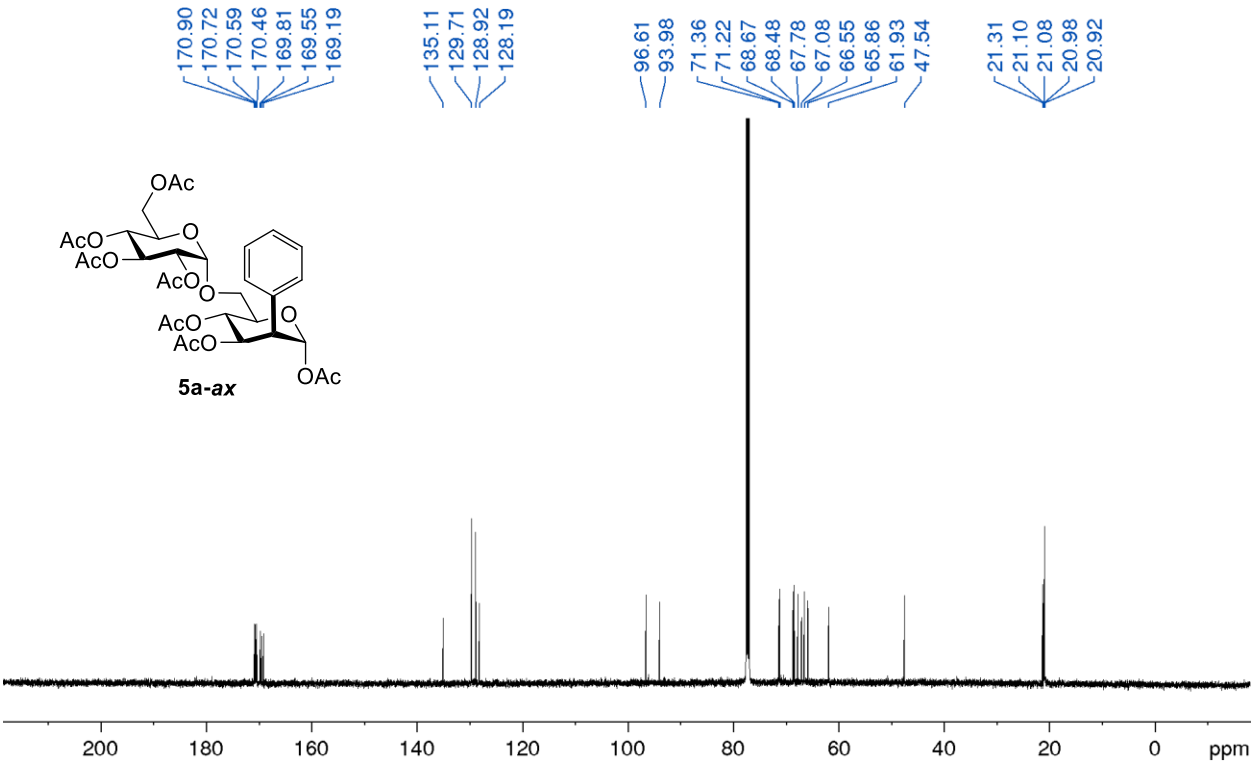
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3x-*eq*)



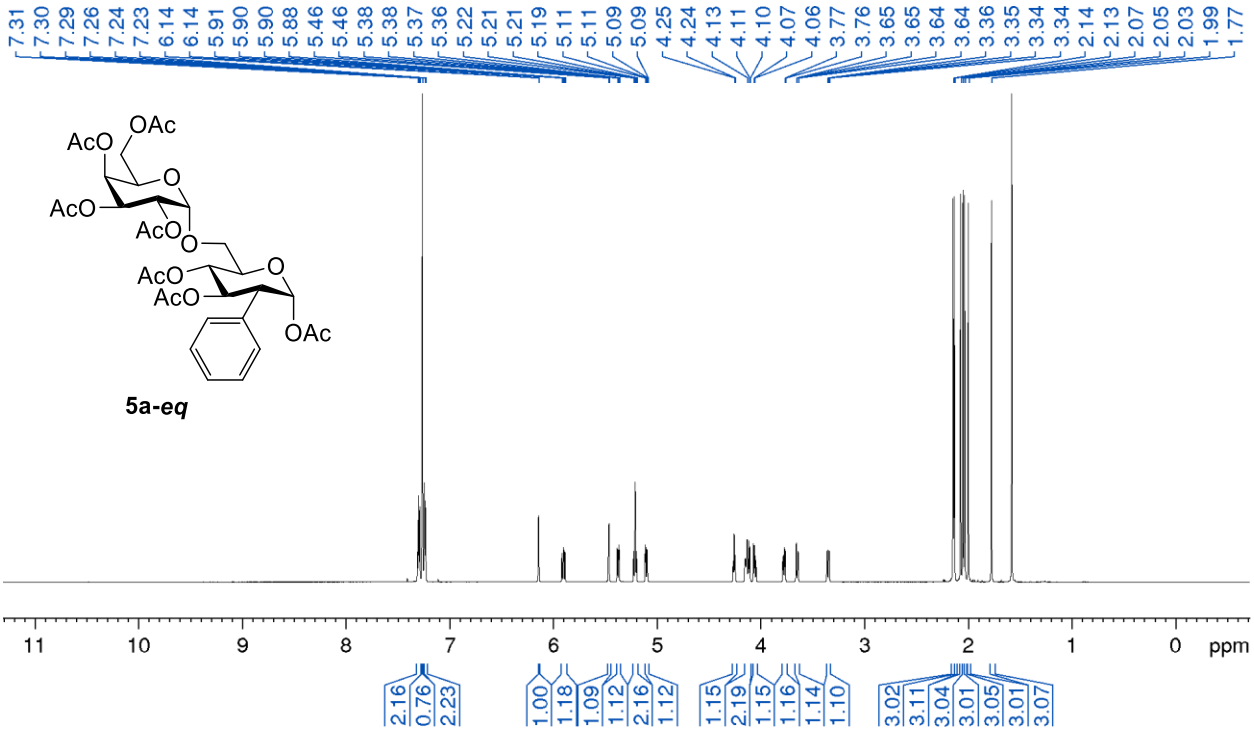
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (5a-*ax*)



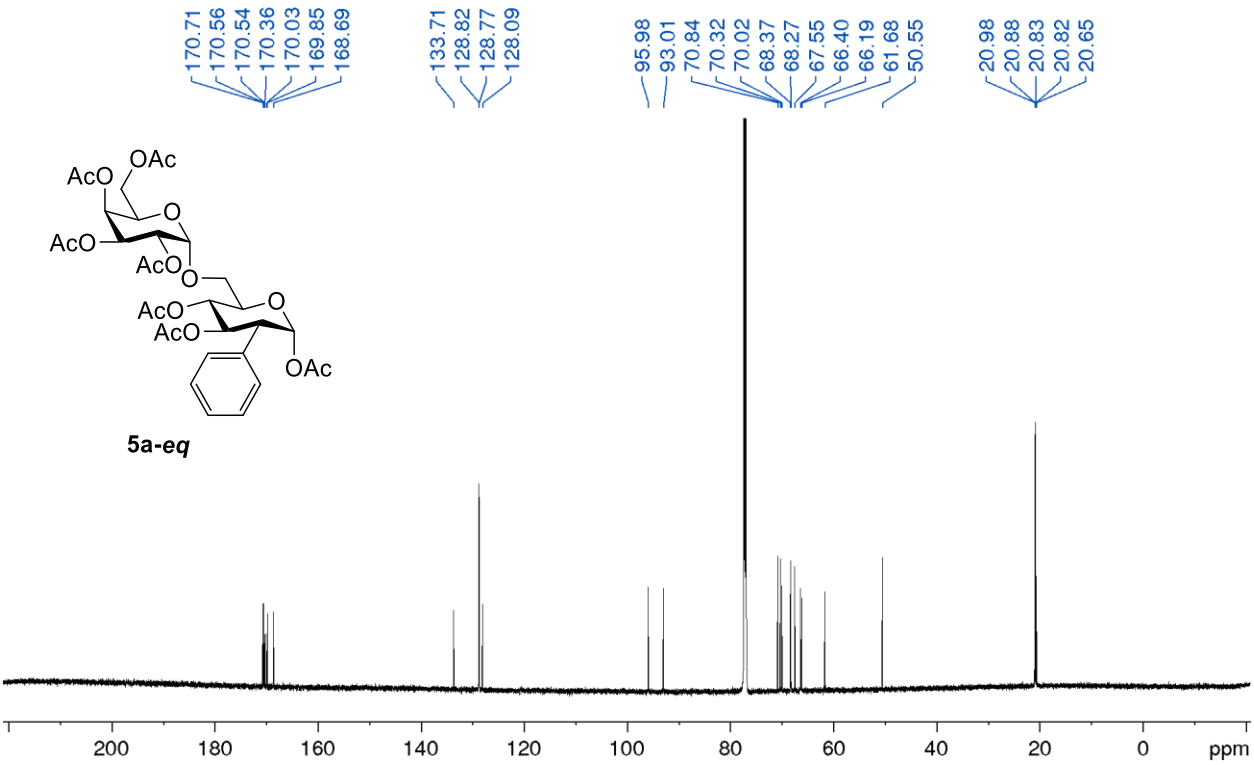
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (5a-*ax*)



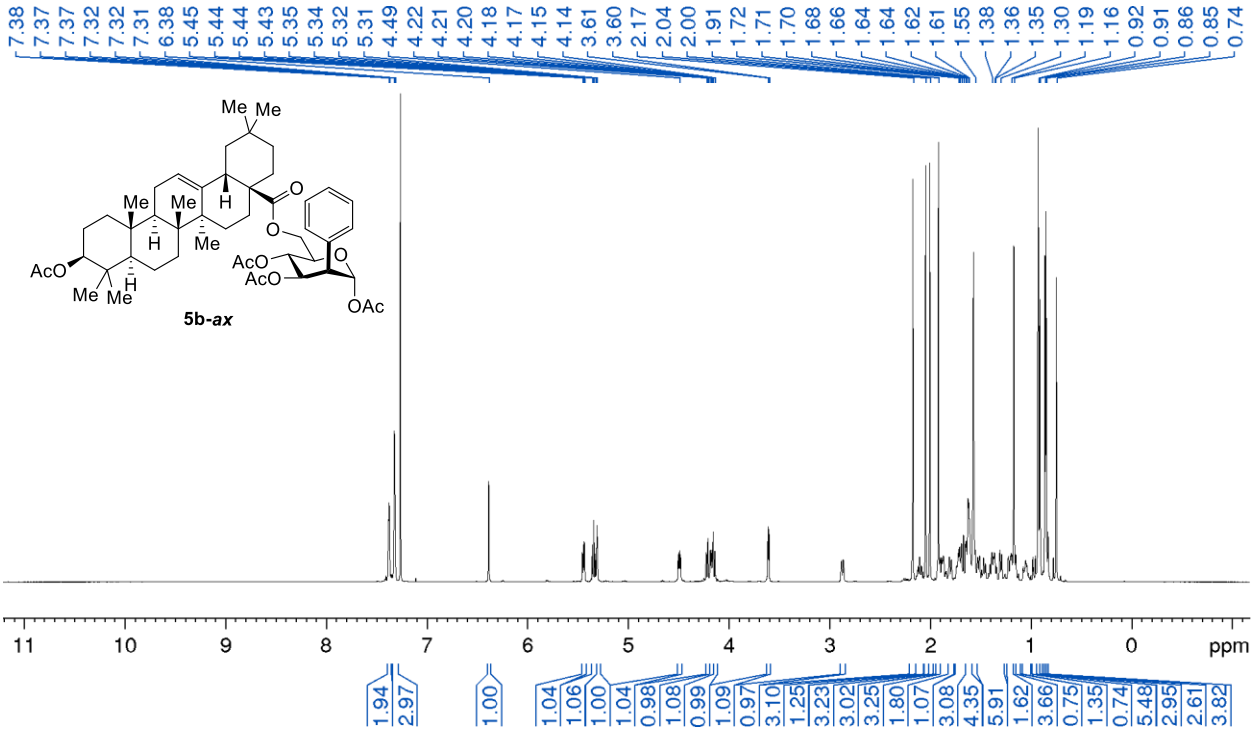
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5a-*eq*)



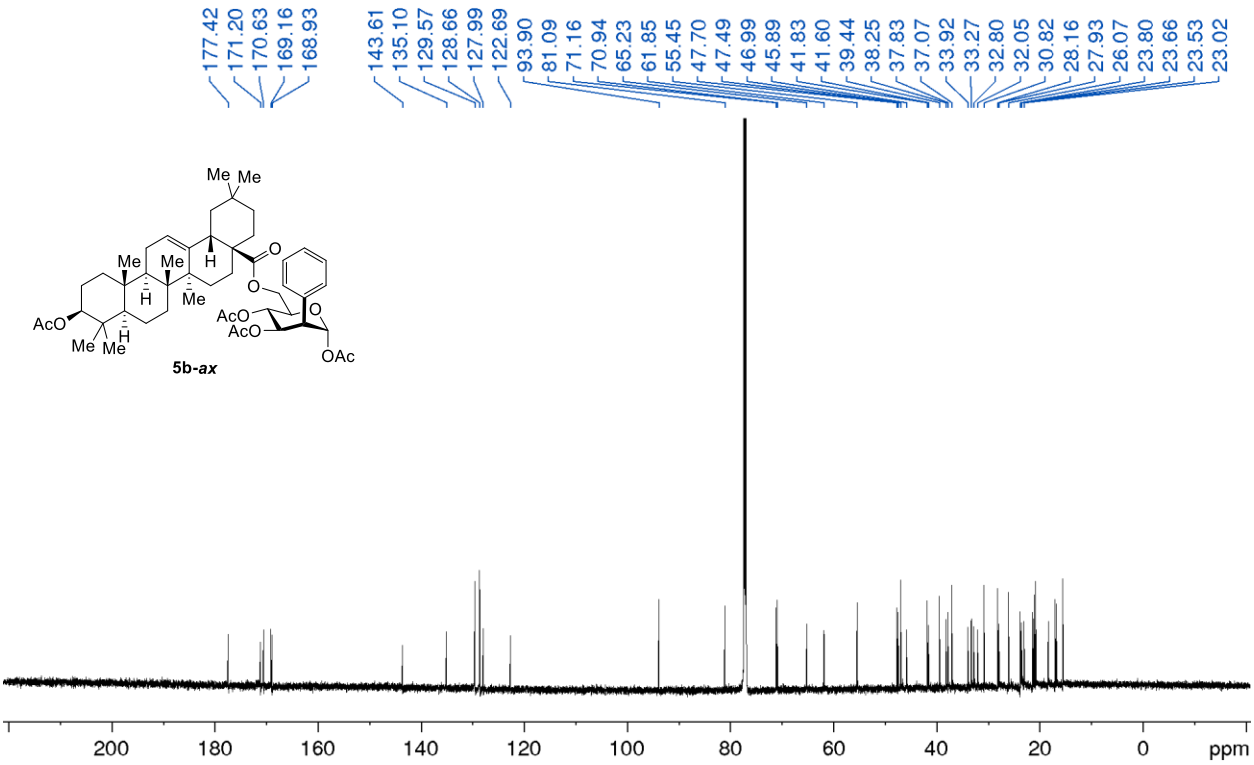
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5a-*eq*)



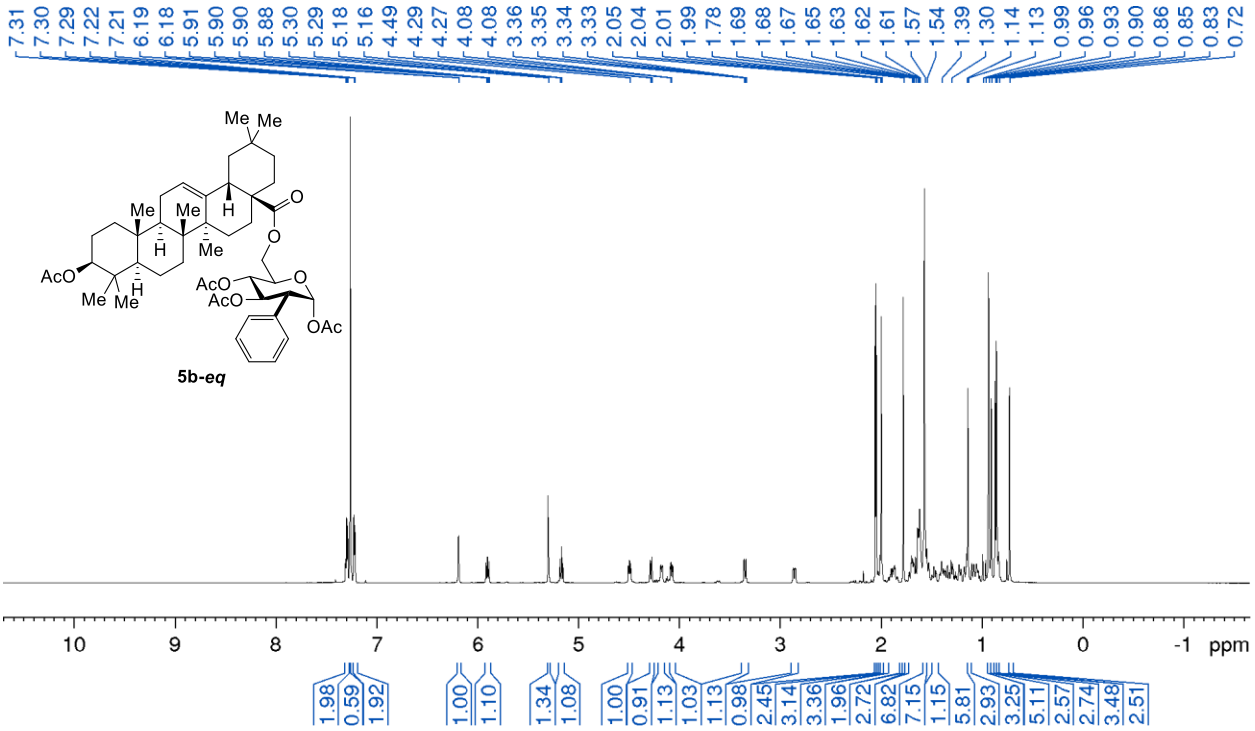
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5b-*ax*)



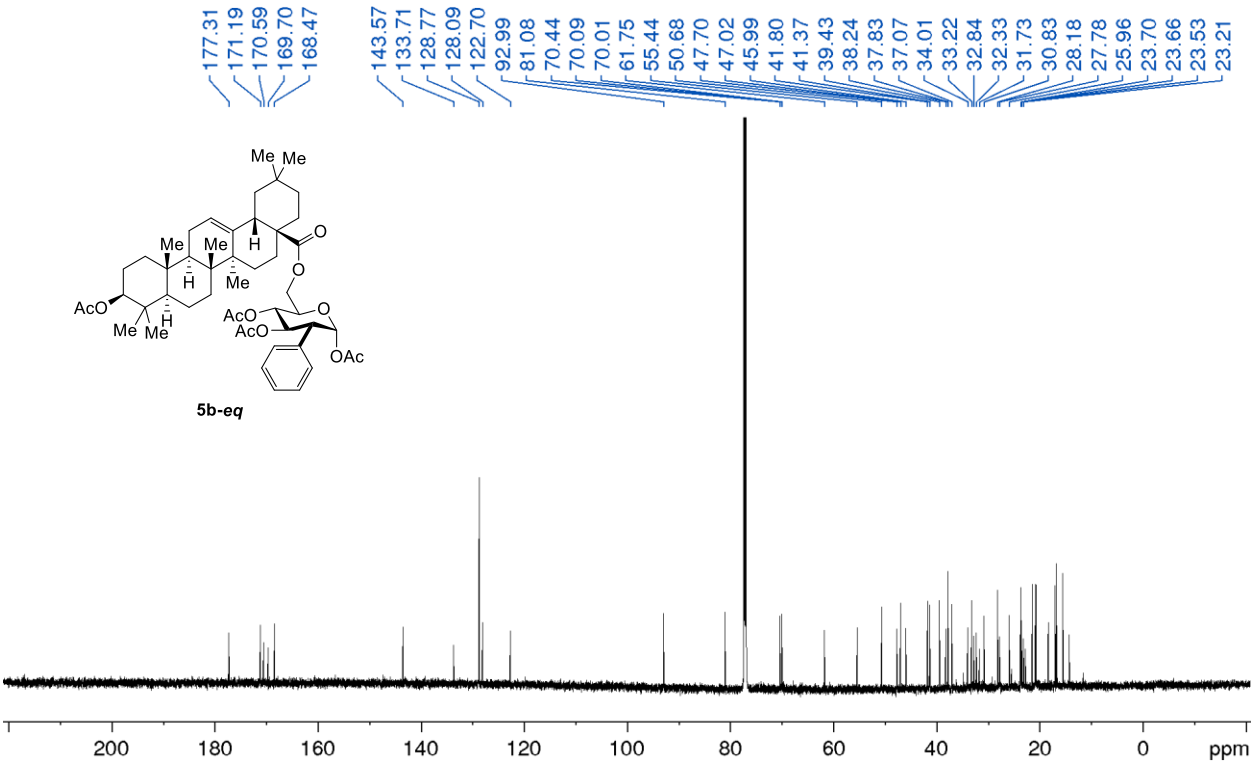
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5b-*ax*)



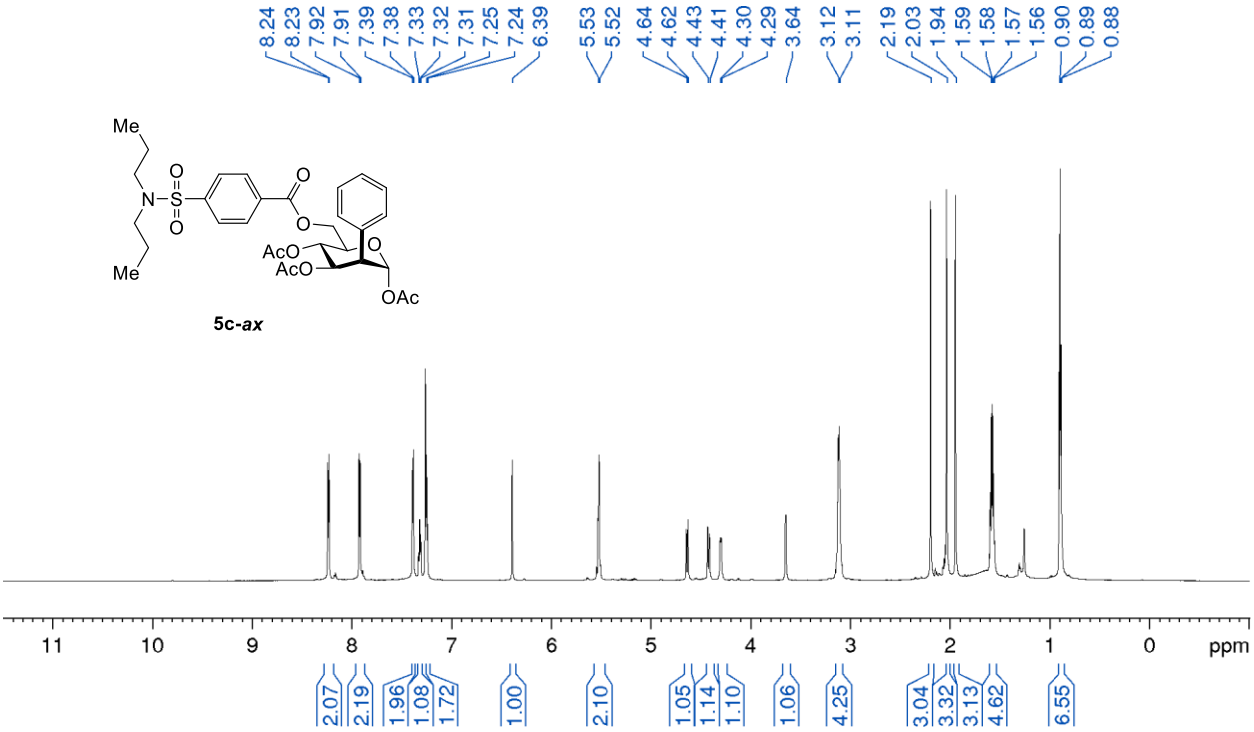
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (5b-*eq*)



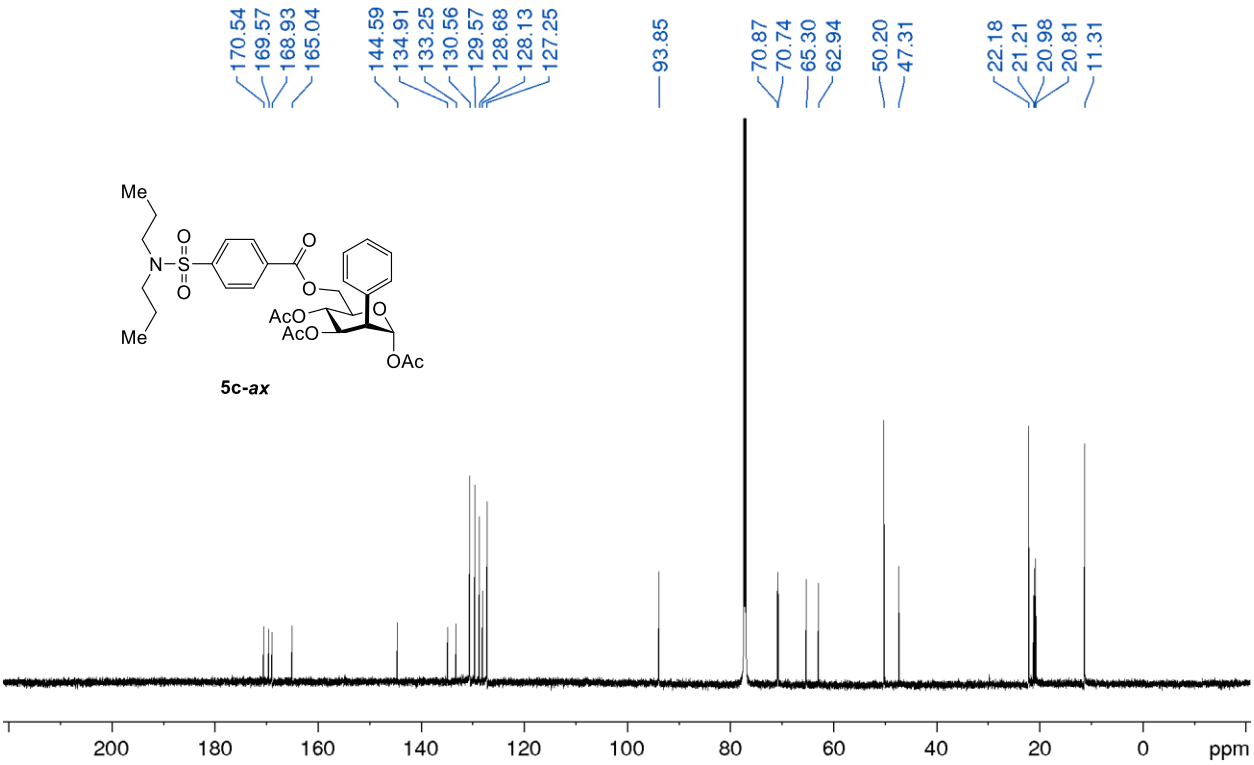
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (5b-*eq*)



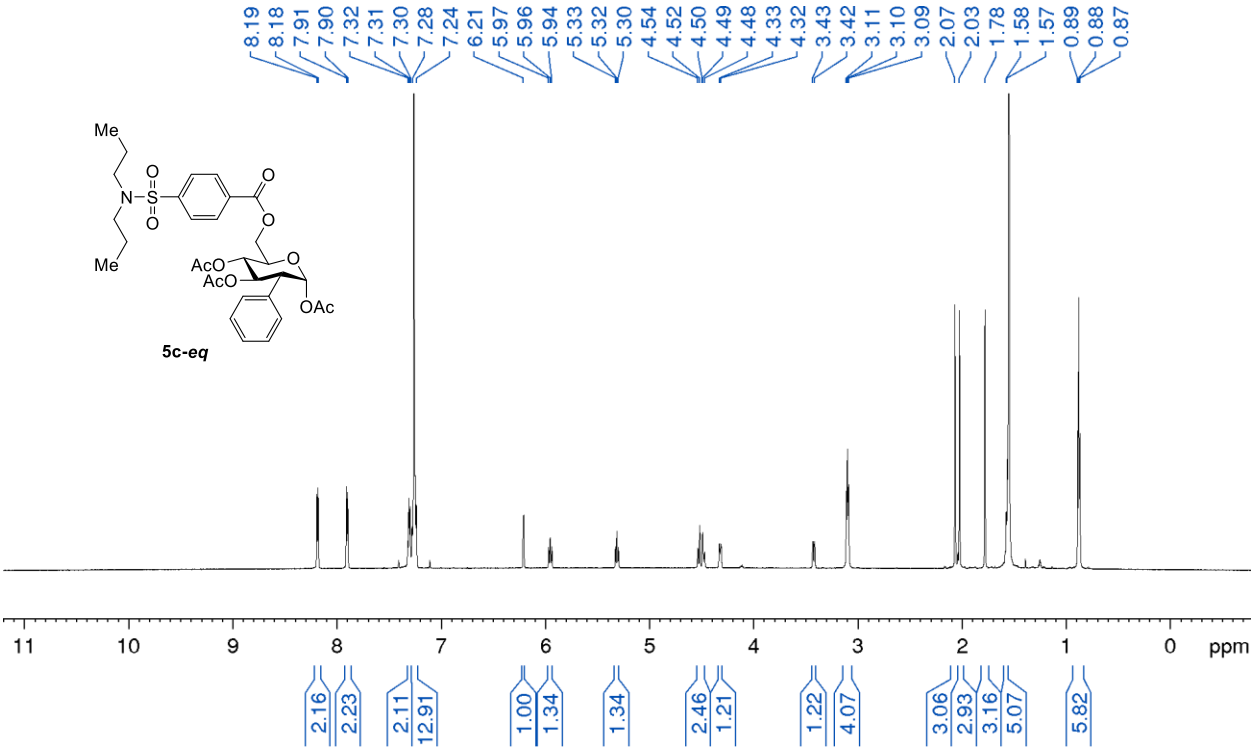
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5c-*ax*)



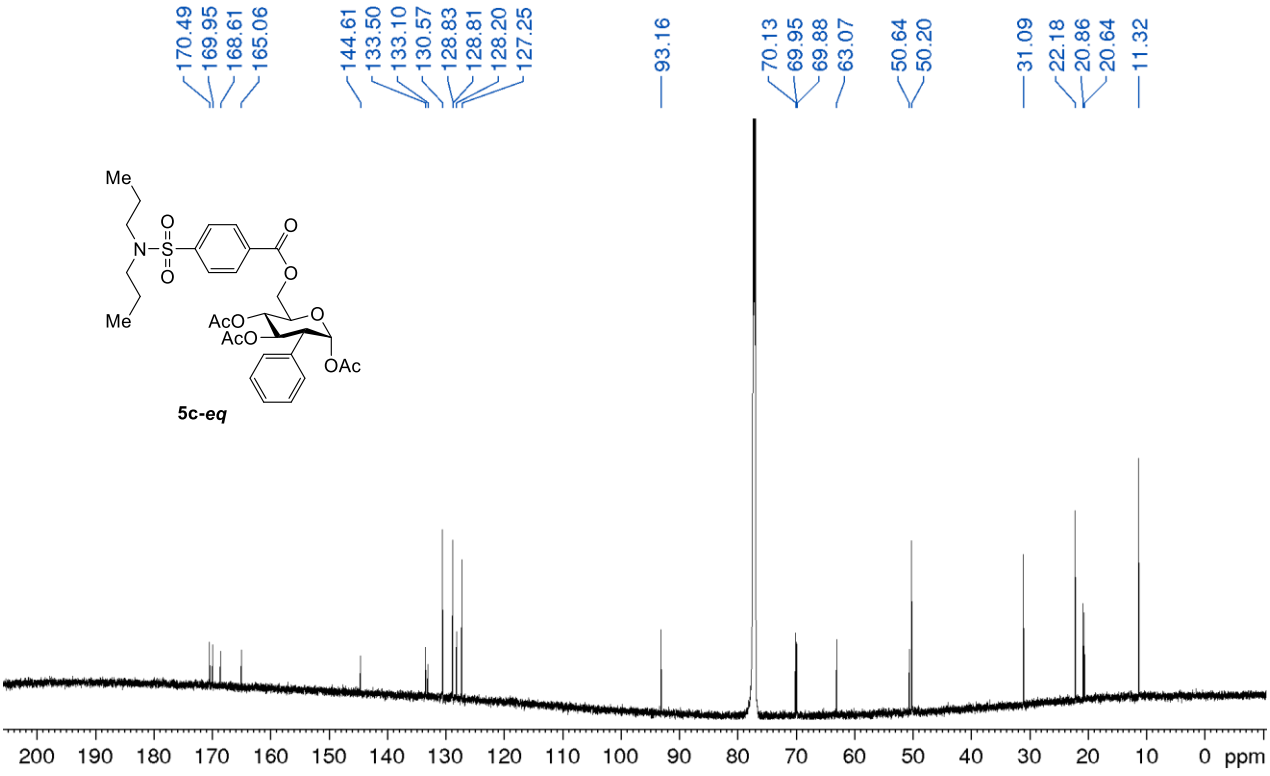
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5c-*ax*)



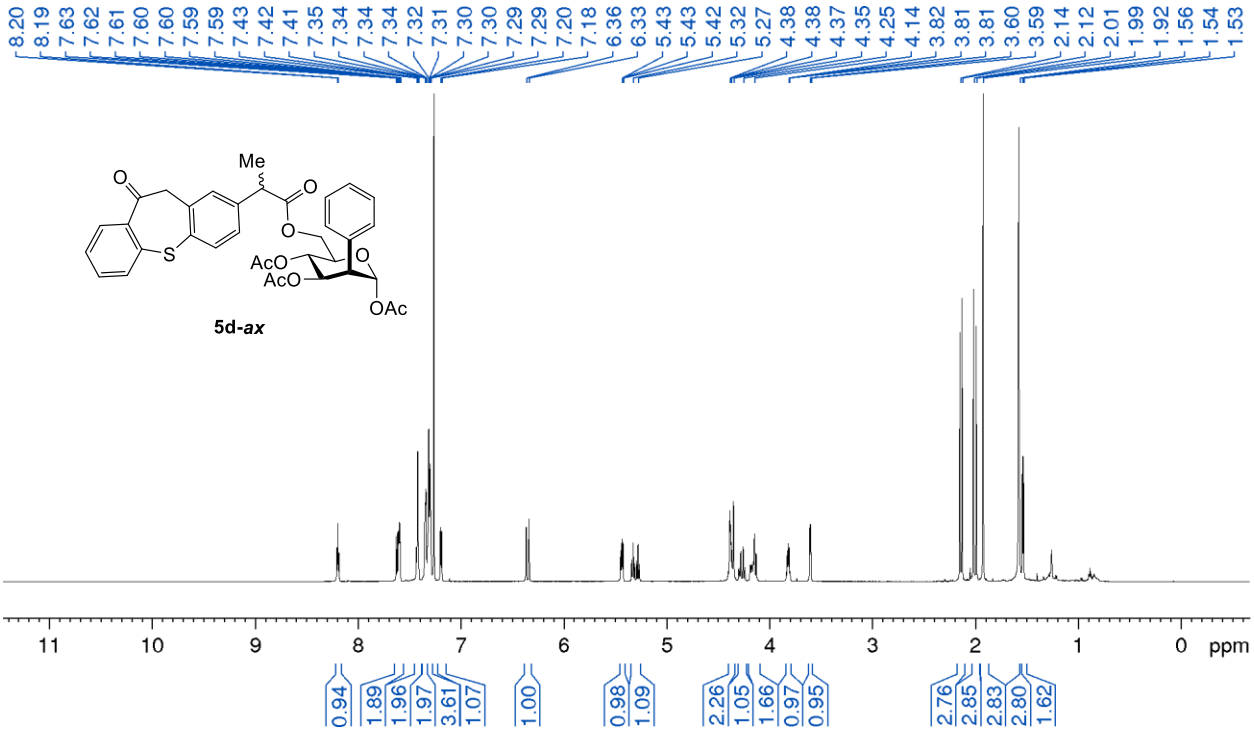
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5c-*eq*)



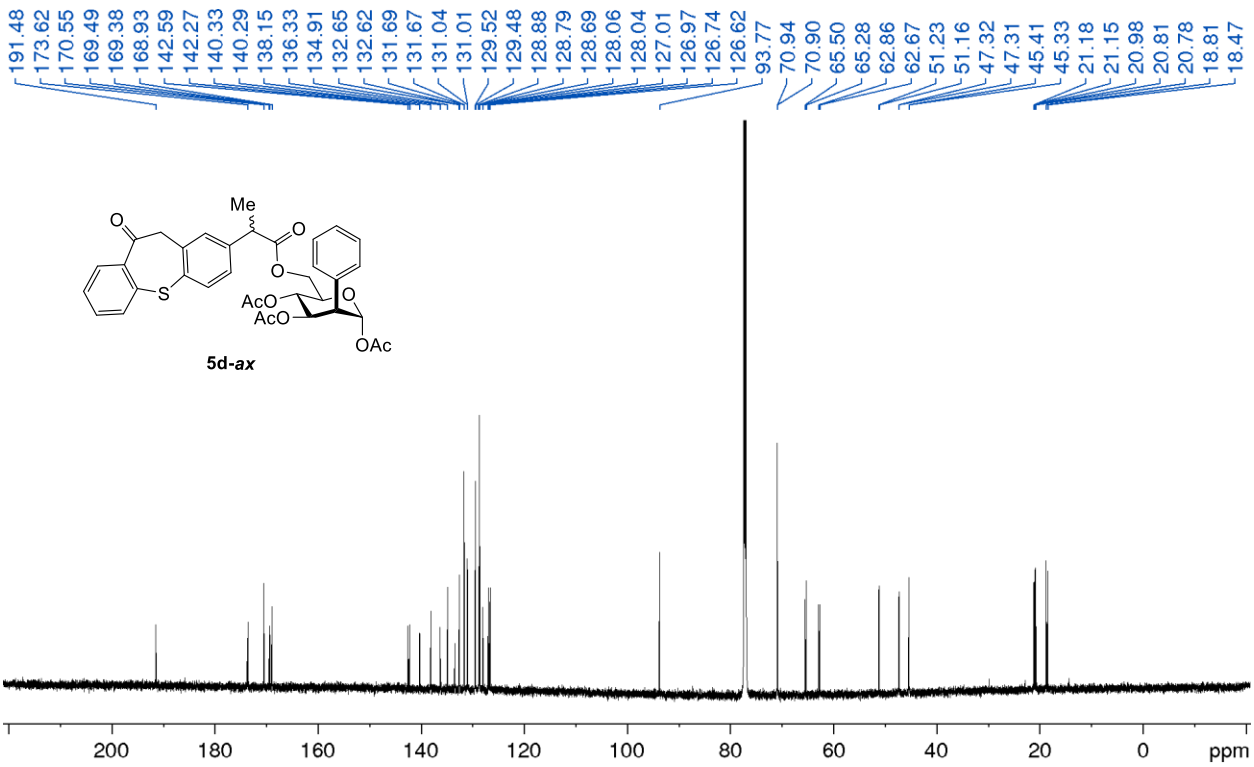
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5c-*eq*)



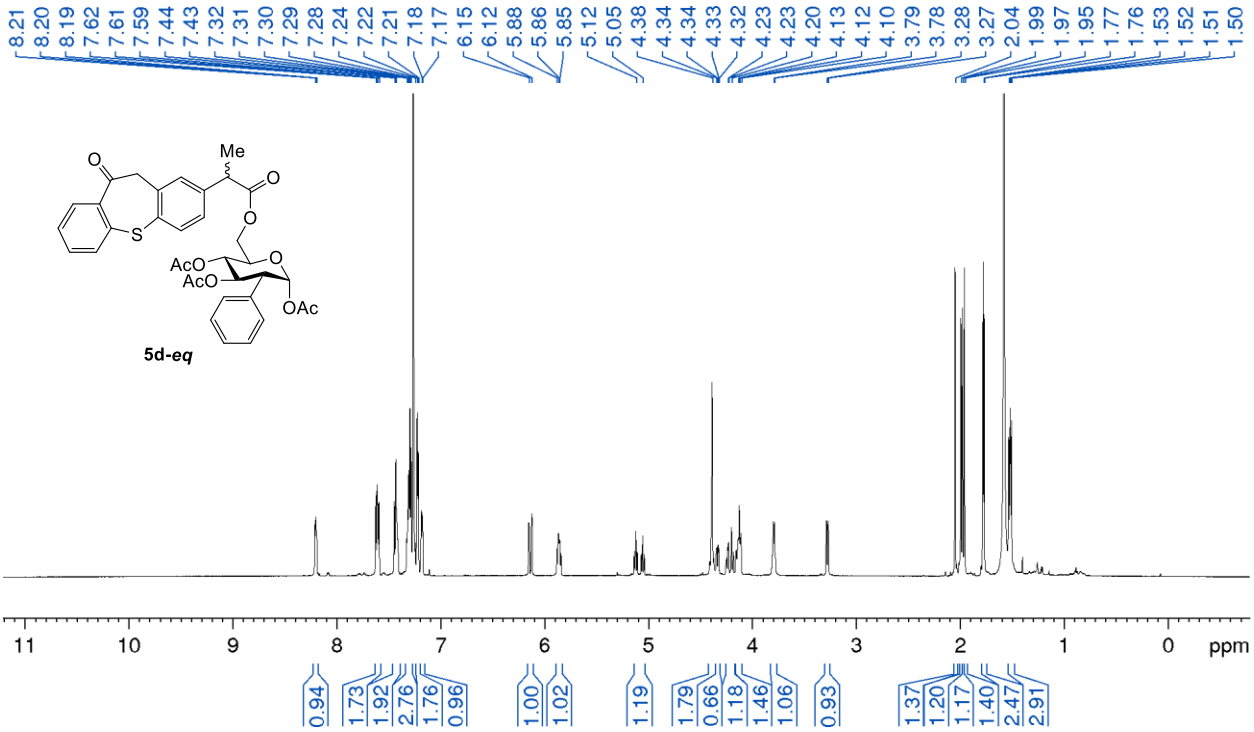
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5d-*ax*)



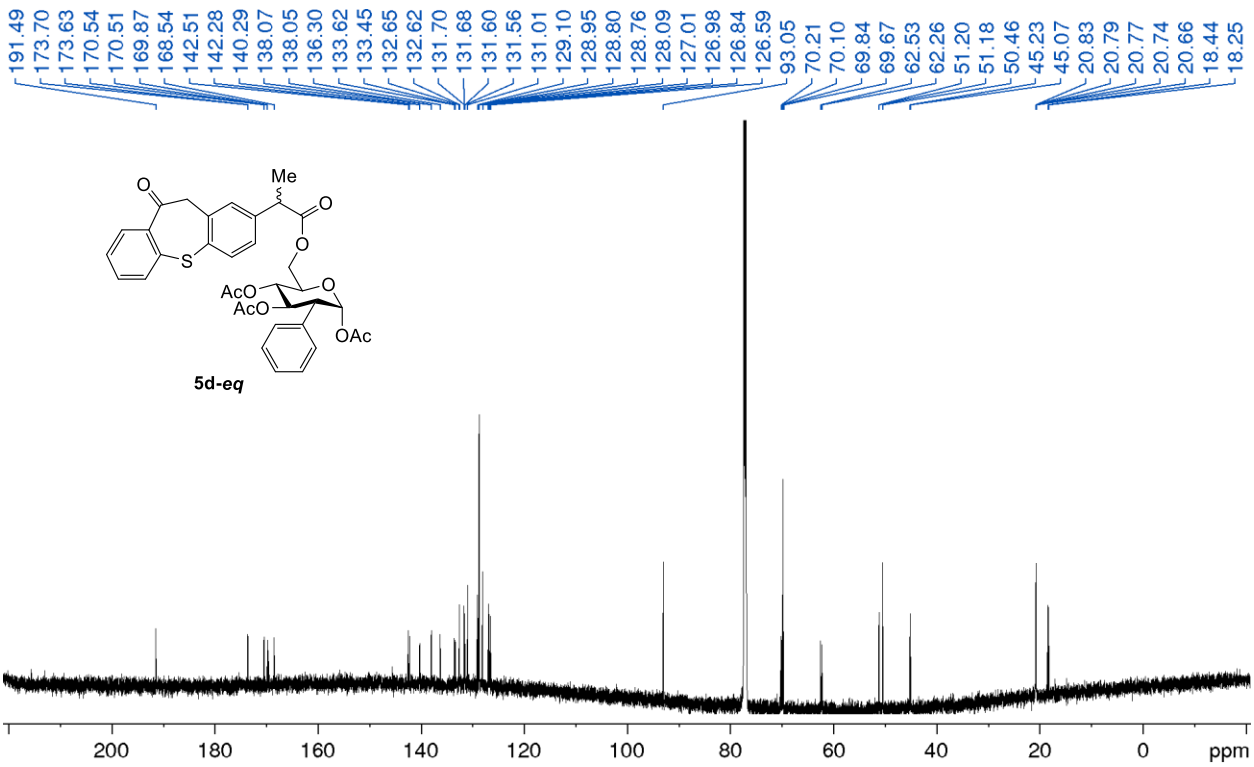
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5d-*ax*)



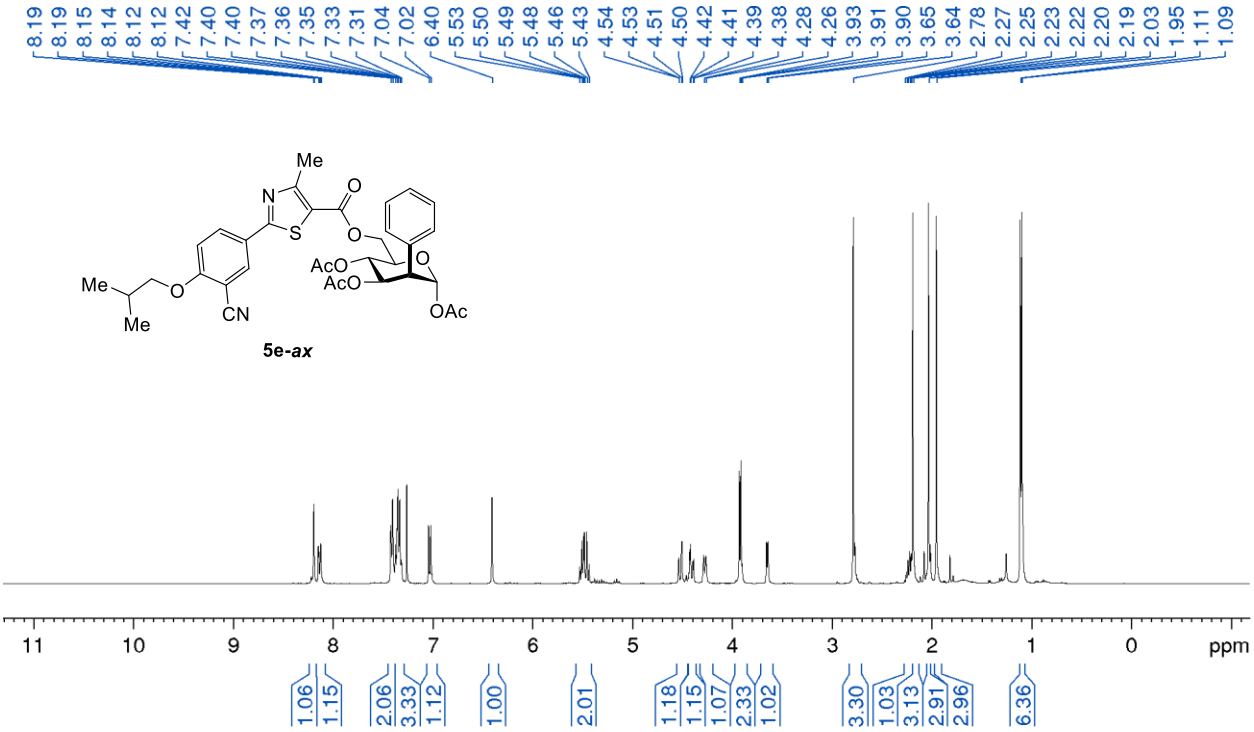
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5d-*eq*)



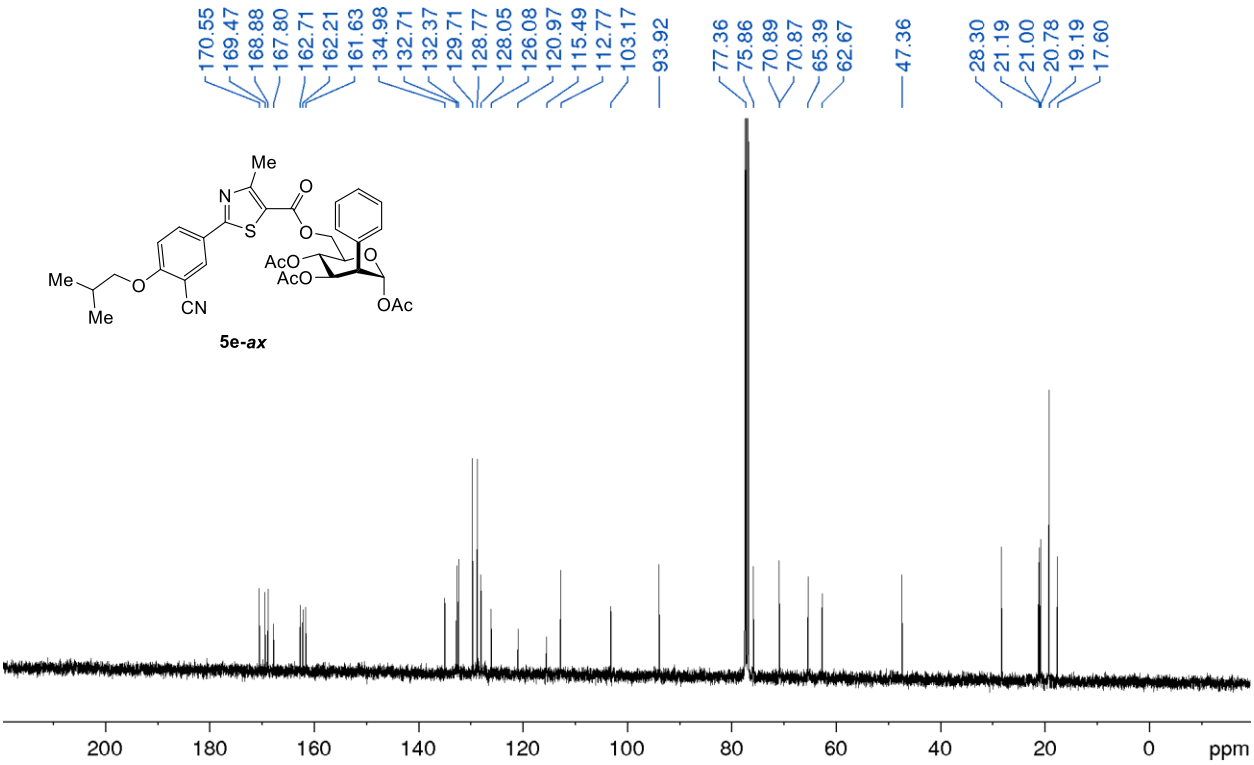
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5d-*eq*)



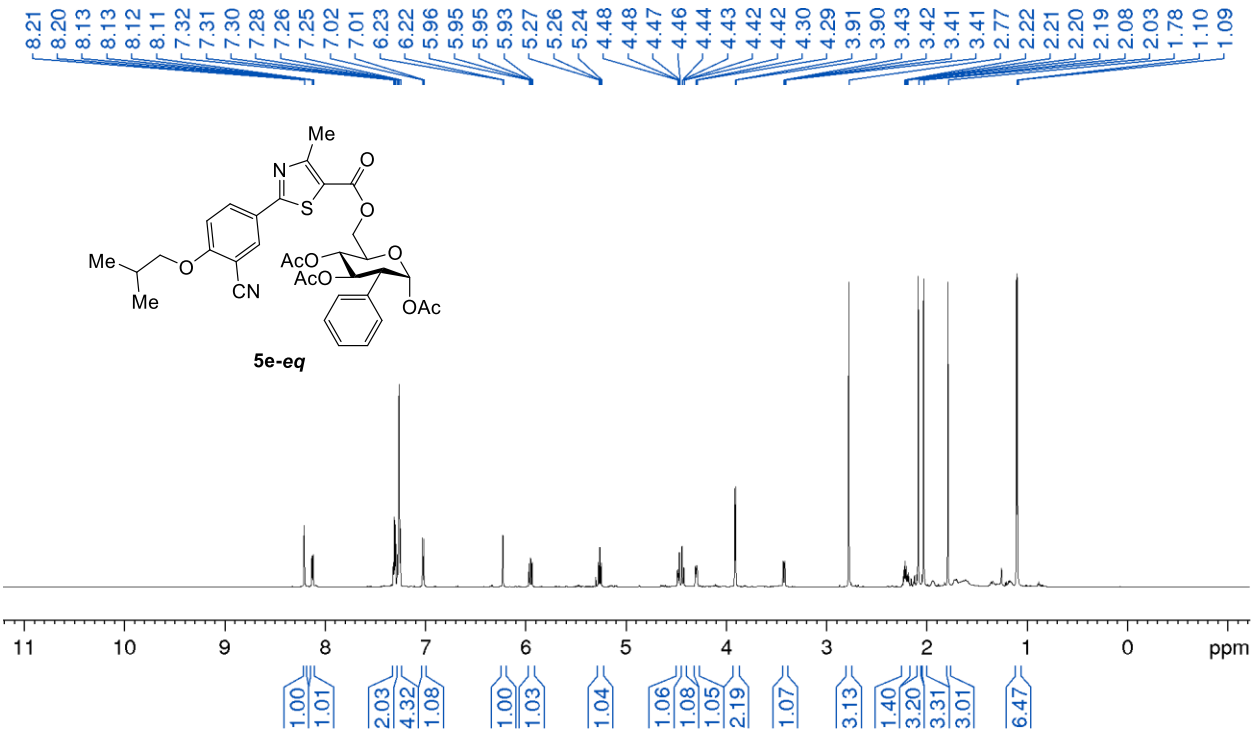
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (5e-*ax*)



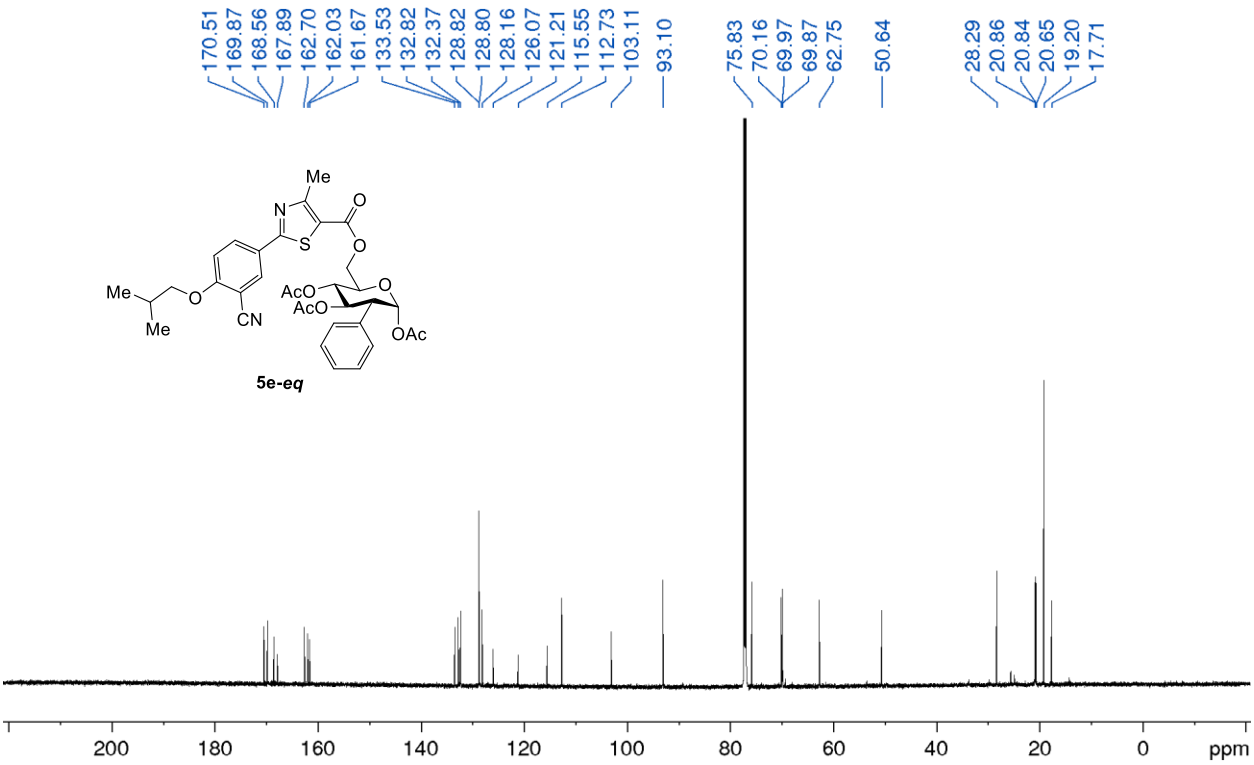
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of (5e-*ax*)



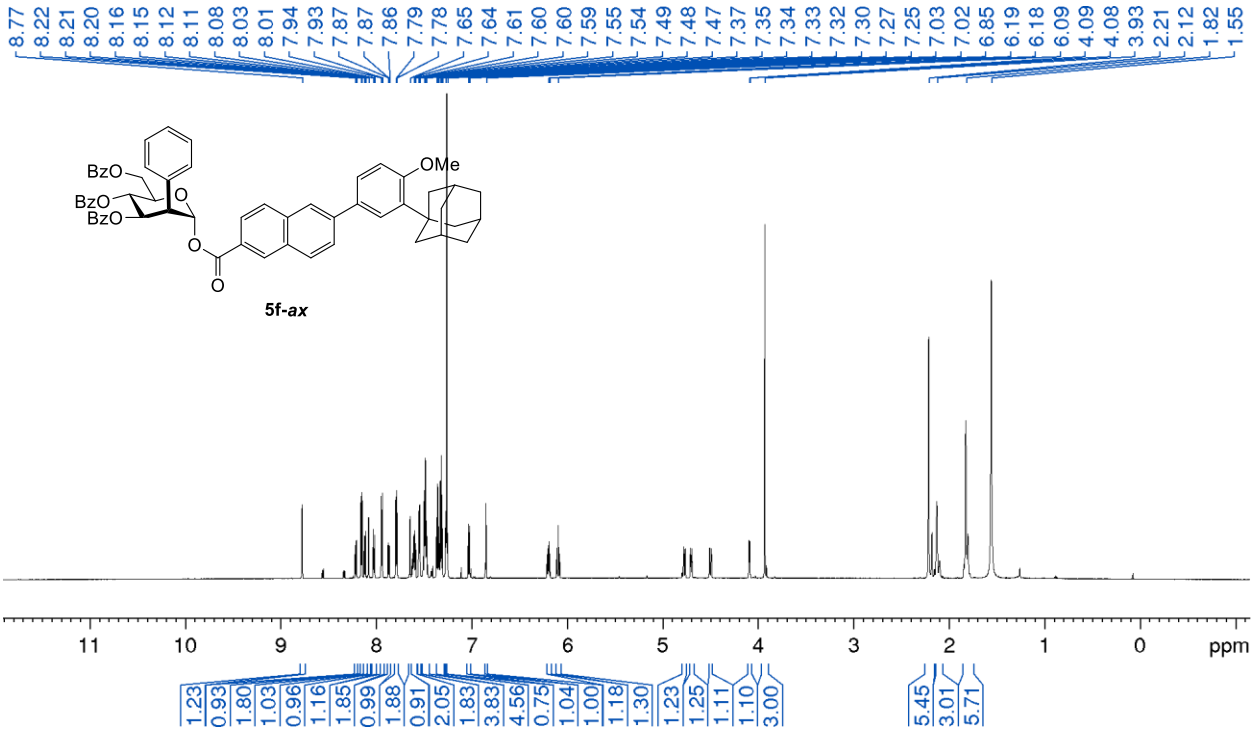
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5e-*eq*)



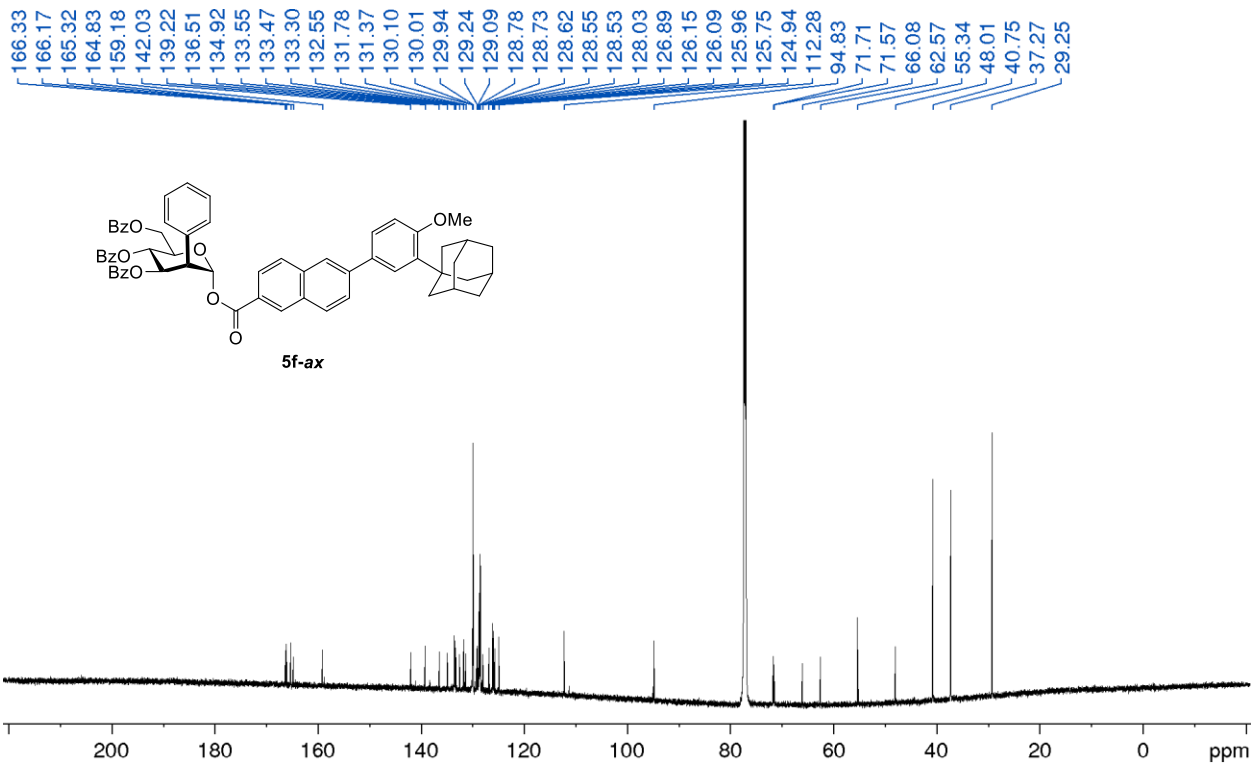
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5e-*eq*)

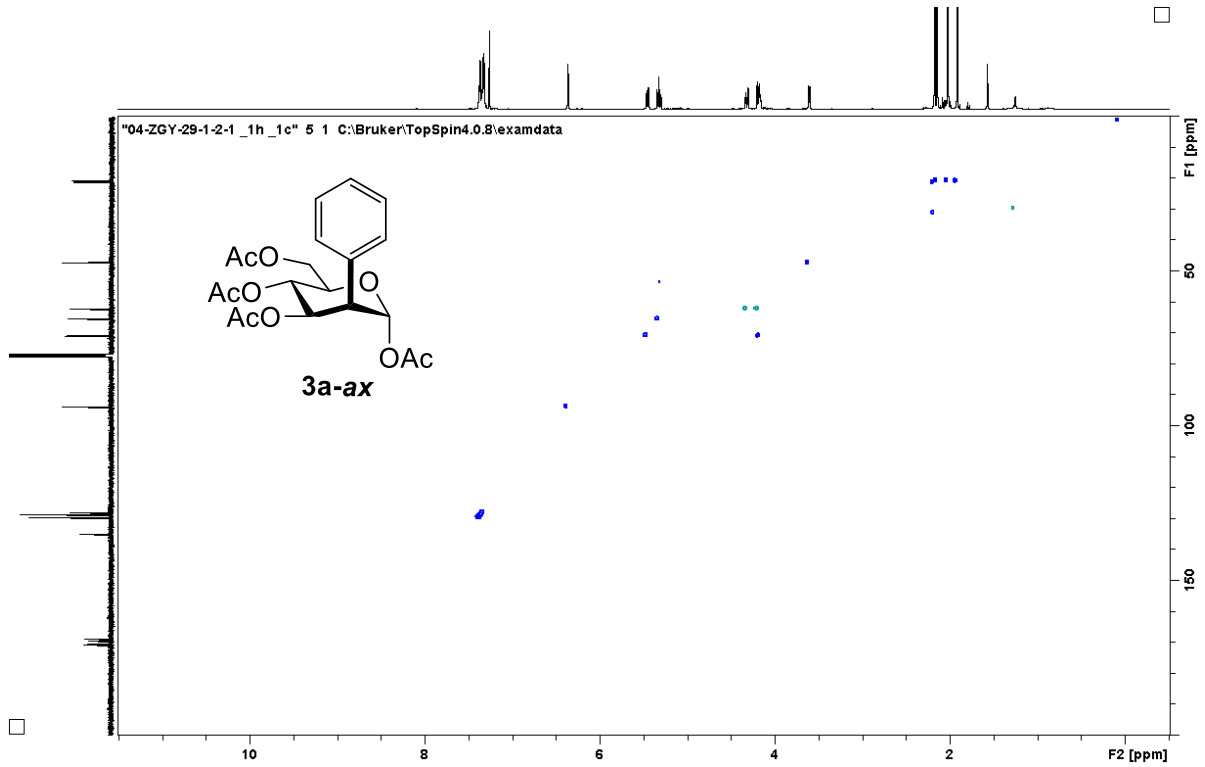


^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5f-*ax*)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5f-*ax*)

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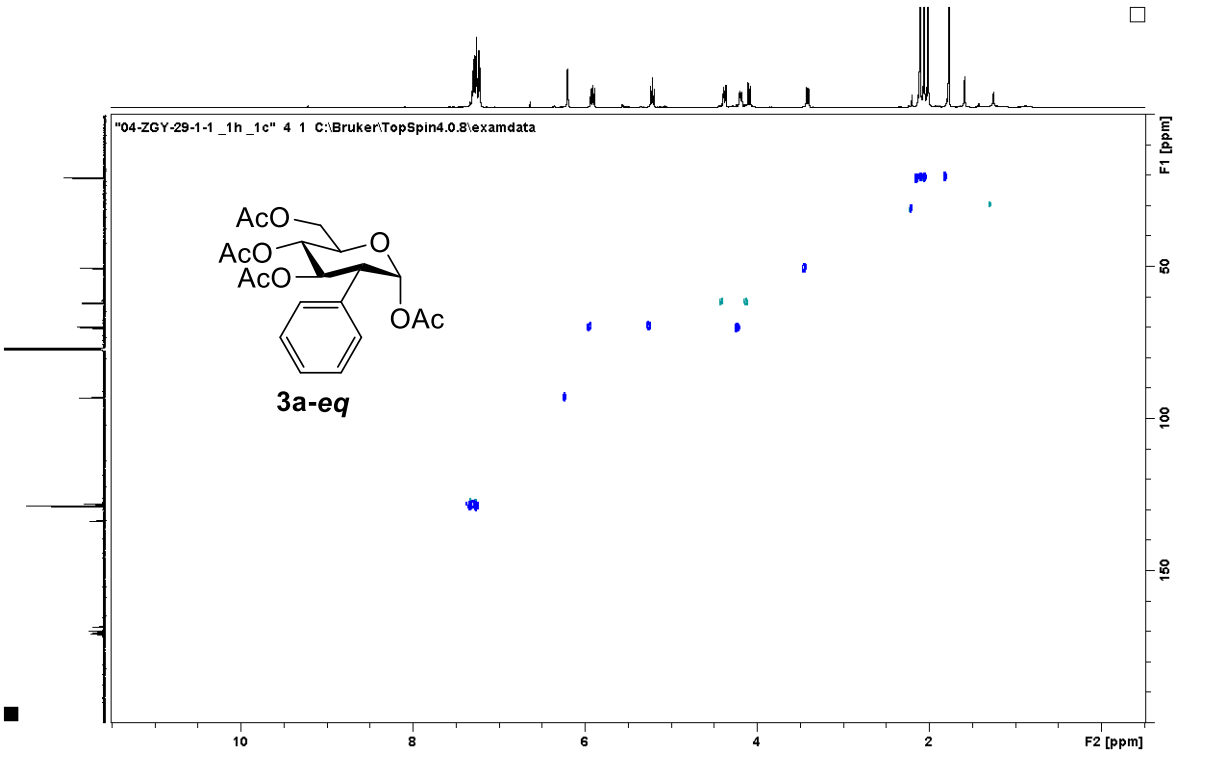
AcO
AcO
O
OAc
3a-ax
F1 [ppm]
F2 [ppm]
10
8
6
4
2
50
100
150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OAc
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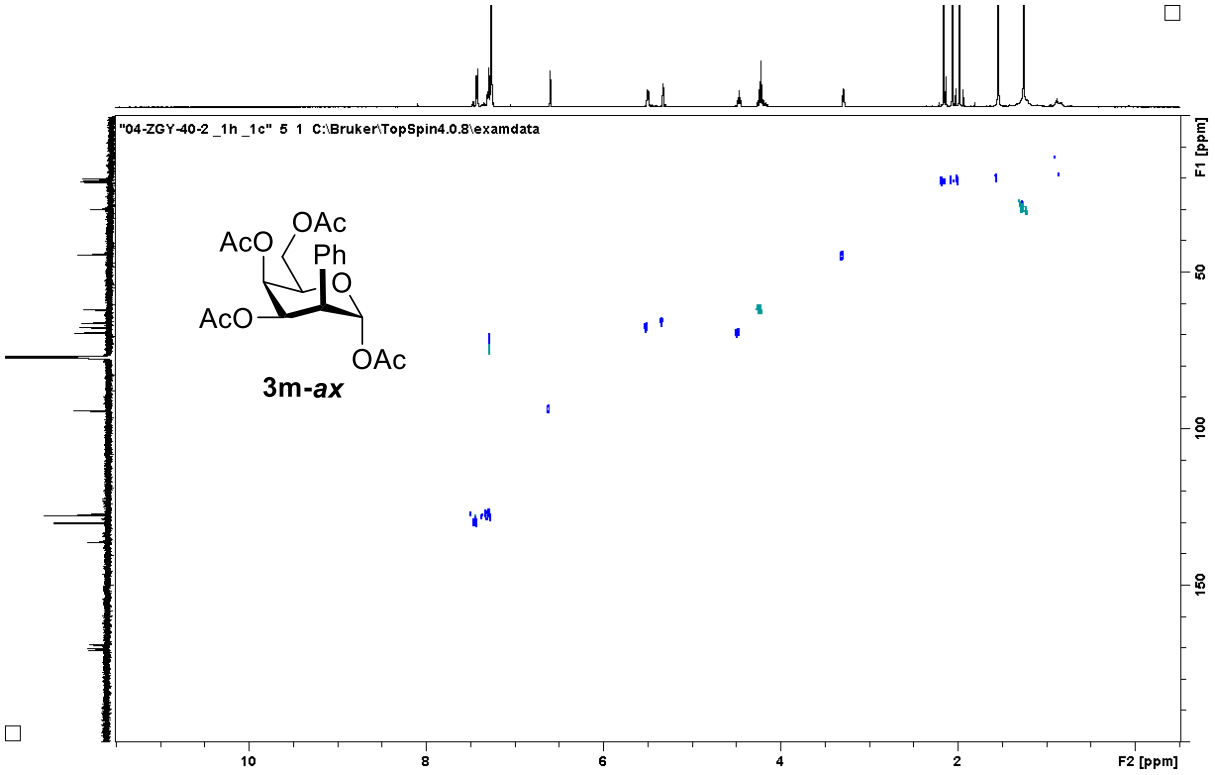
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Ph
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AcO
OAc
3m-ax
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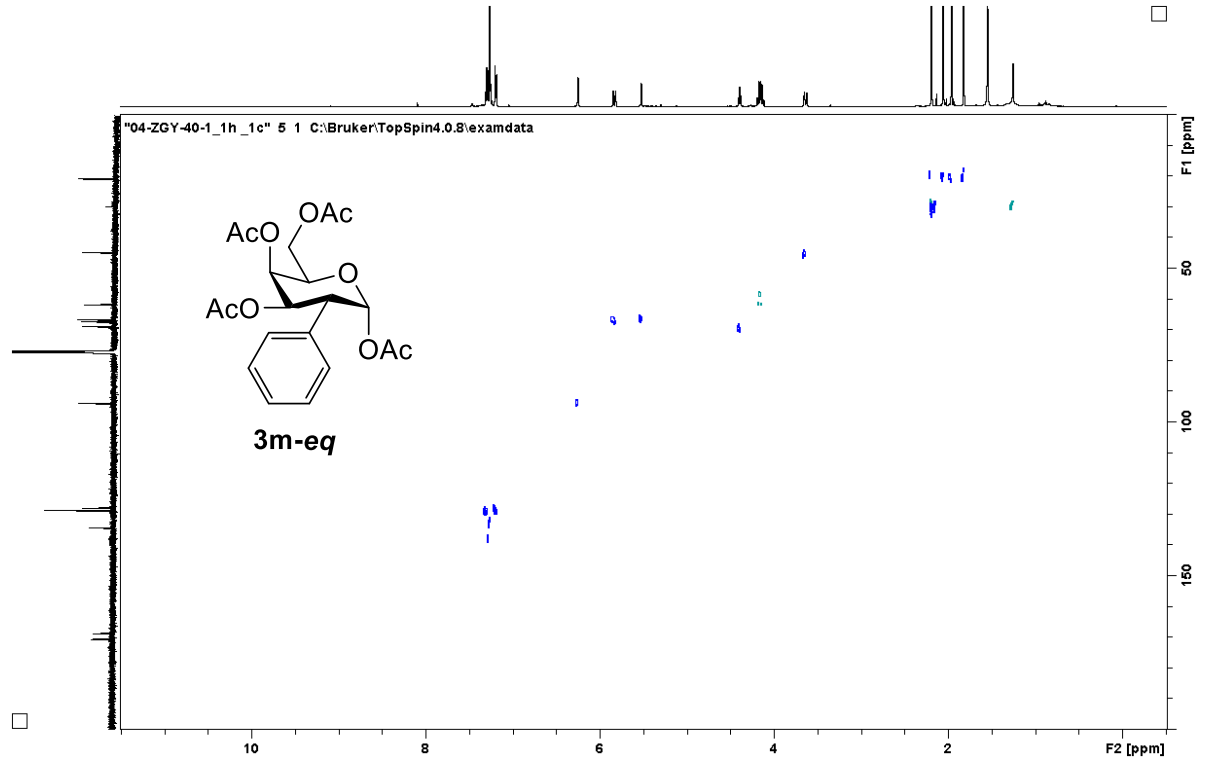
150
10
8
6
4
2
F2 [ppm]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OAc
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OAc
3m-eq
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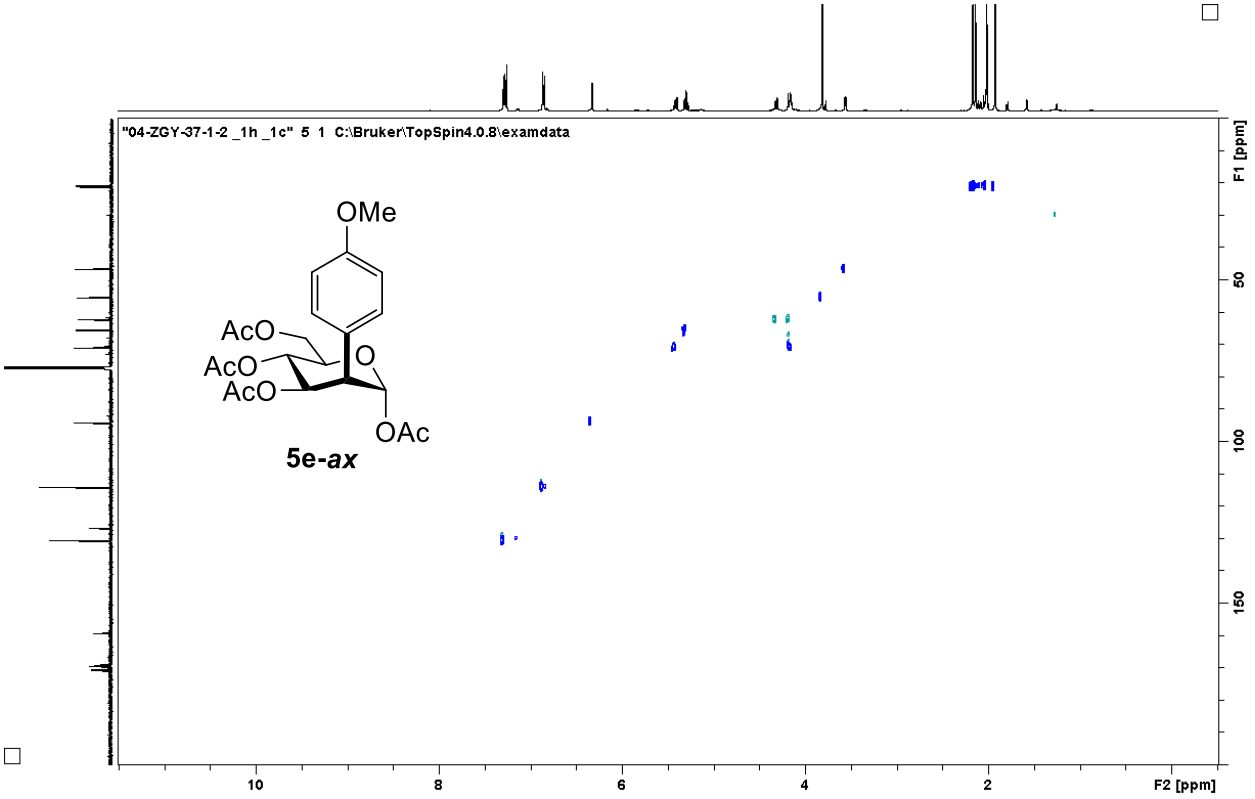
100
150
10
8
6
4
2
F2 [ppm]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AcO
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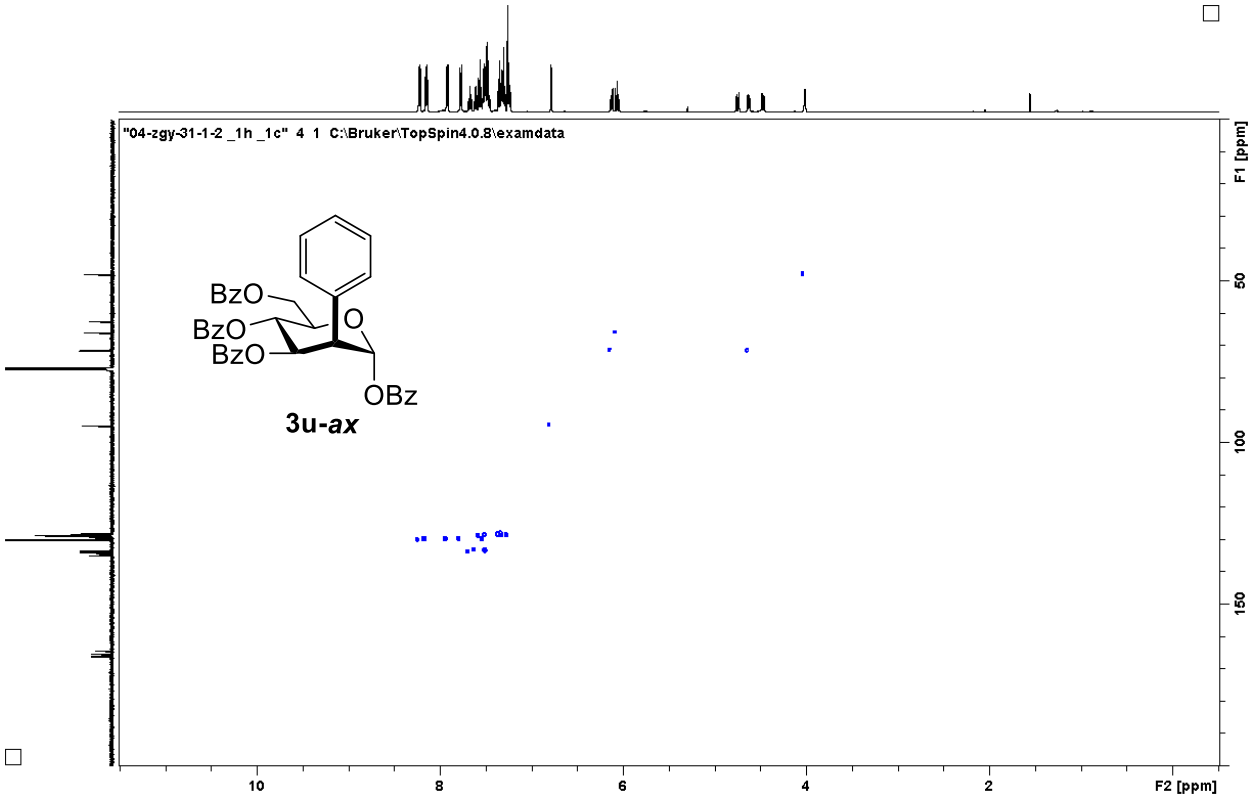
AcO
O
OAc
5e-ax
F1 [ppm]
F2 [ppm]
10
8
6
4
2
50
100
150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BzO
BzO
O
OBz
3u-ax
F1 [ppm]
F2 [ppm]
10
8
6
4
2
50
100
150

Cartesian Coordinates (Å) and Energies of the Optimized Structures

I
B3LYP-D3 SCF energy: -3552.40746220 a.u.
B3LYP-D3 enthalpy: -3551.995020 a.u.
B3LYP-D3 free energy: -3552.08333 a.u.
M06 SCF energy in solution: -3554.58711716 a.u.
M06 enthalpy in solution: -3554.174675 a.u.
M06 free energy in solution: -3554.262985 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	2.354583	0.003537	-0.000004
N	0.838030	1.293049	0.000036
C	-0.401950	0.739354	0.000002
C	0.935751	2.629403	0.000055
C	-1.550196	1.528364	-0.000024
C	-0.172303	3.471677	0.000037
H	1.948426	3.020483	0.000088
C	-1.464219	2.928326	-0.000015
H	-2.522805	1.050486	-0.000048
H	-0.006926	4.541712	0.000057
C	-0.399633	-0.740265	-0.000013
C	-1.545351	-1.532939	0.000010
N	0.842111	-1.289962	-0.000048
C	-1.454886	-2.932605	-0.000007
H	-2.519489	-1.058167	0.000046
C	0.944130	-2.626054	-0.000064
C	-0.161221	-3.471836	-0.000046
H	1.958055	-3.013865	-0.000094
H	0.007565	-4.541342	-0.000062
Br	4.629078	0.006758	0.000005
C	-2.740732	3.779181	-0.000014
C	-3.569980	3.449520	-1.263885
C	-3.570202	3.449129	1.263609
C	-2.432877	5.287794	0.000241
H	-3.001582	3.670619	-2.174118
H	-3.862691	2.394702	-1.297730
H	-4.486911	4.050083	-1.278671
H	-3.001967	3.669955	2.174010
H	-4.487143	4.049675	1.278415
H	-3.862897	2.394293	1.297073
H	-3.370406	5.853992	0.000212
H	-1.866228	5.586820	0.889272
H	-1.866015	5.587073	-0.888570
C	-2.728710	-3.787532	0.000018
C	-3.559058	-3.460296	1.263787
C	-3.559104	-3.460300	-1.263724
C	-2.416001	-5.295130	0.000014
H	-2.990023	-3.679514	2.174078
H	-3.855045	-2.406392	1.297484

H	-4.474115	-4.063712	1.278589
H	-2.990097	-3.679507	-2.174034
H	-4.474155	-4.063726	-1.278497
H	-3.855105	-2.406399	-1.297406
H	-3.351689	-5.864362	0.000031
H	-1.848281	-5.592422	-0.888914
H	-1.848251	-5.592420	0.888923

B(Ph)(OH)$_2$(O*i*-Pr)$^-$

B3LYP-D3 SCF energy: -602.09051749 a.u.
B3LYP-D3 enthalpy: -601.854245 a.u.
B3LYP-D3 free energy: -601.917718 a.u.
M06 SCF energy in solution: -601.90955383 a.u.
M06 enthalpy in solution: -601.673281 a.u.
M06 free energy in solution: -601.736754 a.u.

Cartesian coordinates

ATOM	X	Y	Z
B	-0.411307	-0.754981	0.171805
O	-0.693444	-1.112848	1.573847
H	-1.244585	-1.906457	1.509949
O	-1.298867	0.339176	-0.355215
O	-0.616361	-1.995875	-0.627465
H	-0.664093	-1.701604	-1.547846
C	1.116071	-0.171071	0.040475
C	1.423474	1.192186	0.190314
C	2.198602	-1.032271	-0.207389
C	2.733922	1.673060	0.111341
H	0.600328	1.883231	0.359551
C	3.515581	-0.570873	-0.291339
H	1.982877	-2.090191	-0.349042
C	3.791404	0.790299	-0.128887
H	2.935034	2.738313	0.232777
H	4.330572	-1.269275	-0.486541
H	4.815187	1.158503	-0.193627
C	-2.675706	0.181238	-0.165978
C	-3.398974	0.756680	-1.390394
C	-3.125326	0.872127	1.131485
H	-2.937091	-0.890968	-0.091765
H	-3.083958	0.225483	-2.296501
H	-4.492583	0.683599	-1.300326
H	-3.129586	1.813963	-1.512764
H	-2.561874	0.436791	1.960437
H	-2.893030	1.944478	1.077840
H	-4.205579	0.757159	1.311727

TS1

B3LYP-D3 SCF energy: -1582.99262973 a.u.

B3LYP-D3 enthalpy: -1582.345118 a.u.
B3LYP-D3 free energy: -1582.462758 a.u.
M06 SCF energy in solution: -1582.32746897 a.u.
M06 enthalpy in solution: -1581.679957 a.u.
M06 free energy in solution: -1581.797597 a.u.
Imaginary frequency: -187.2840 cm-1

Cartesian coordinates

ATOM	X	Y	Z
N	0.016912	1.220011	0.053213
C	-1.287506	0.848281	0.051375
C	0.305822	2.523579	0.150635
C	-2.312743	1.787547	0.152300
C	-0.671882	3.510452	0.255857
H	1.362231	2.769465	0.140702
C	-2.027087	3.156457	0.259603
H	-3.343672	1.453189	0.148879
H	-0.354698	4.543139	0.331891
C	-1.505578	-0.612498	-0.072599
C	-2.757798	-1.220621	-0.145247
N	-0.363745	-1.341723	-0.126775
C	-2.877203	-2.611206	-0.284013
H	-3.650552	-0.607932	-0.098917
C	-0.458836	-2.670969	-0.268045
C	-1.678944	-3.335796	-0.348409
H	0.492466	-3.190399	-0.314870
H	-1.673209	-4.412679	-0.462818
C	-3.169097	4.175137	0.371052
C	-4.065769	4.072073	-0.885365
C	-4.008498	3.861477	1.632032
C	-2.649735	5.620495	0.480133
H	-3.491884	4.285770	-1.793992
H	-4.505954	3.075018	-0.992627
H	-4.888022	4.794526	-0.821784
H	-3.393833	3.925247	2.536910
H	-4.831063	4.580307	1.725607
H	-4.445790	2.858185	1.592749
H	-3.496609	6.310959	0.557877
H	-2.024856	5.761254	1.369278
H	-2.066354	5.909817	-0.401209
C	-4.265185	-3.260674	-0.363199
C	-5.052671	-2.936148	0.928183
C	-5.022741	-2.693051	-1.586811
C	-4.182868	-4.791170	-0.510028
H	-4.534126	-3.326501	1.811063
H	-5.185474	-1.857800	1.065822
H	-6.048941	-3.392048	0.886914
H	-4.481396	-2.906472	-2.515220
H	-6.017913	-3.147667	-1.658266
H	-5.156331	-1.608257	-1.517515
H	-5.193428	-5.210984	-0.559767
H	-3.657582	-5.083591	-1.426183

H	-3.673608	-5.253932	0.342885
Ni	1.351166	-0.330642	-0.081300
C	3.079727	0.746770	-0.407057
C	3.170000	1.478679	-1.612078
C	3.620102	1.385870	0.735191
C	3.723009	2.761738	-1.679211
H	2.774737	1.023733	-2.519508
C	4.174146	2.669313	0.690565
H	3.593259	0.864194	1.691191
C	4.224618	3.365671	-0.522168
H	3.763422	3.292679	-2.628946
H	4.567829	3.128179	1.596022
H	4.657469	4.362578	-0.565381
B	3.458265	-1.355644	-0.709389
O	2.604579	-2.066182	0.210474
O	3.039278	-1.587550	-2.035801
H	3.711514	-1.246110	-2.639988
O	4.831402	-1.322109	-0.376032
C	3.084836	-2.360504	1.535728
C	3.861090	-3.674441	1.496640
C	1.886490	-2.413111	2.478659
H	3.760989	-1.556107	1.848148
H	4.709322	-3.582746	0.813869
H	4.236302	-3.934630	2.494093
H	3.210475	-4.484847	1.146236
H	1.355132	-1.454594	2.478171
H	1.181737	-3.191154	2.162841
H	2.212901	-2.635546	3.501059
H	5.213110	-0.459417	-0.578404

TS2

B3LYP-D3 SCF energy: -7005.77504346 a.u.
B3LYP-D3 enthalpy: -7005.033924 a.u.
B3LYP-D3 free energy: -7005.172401 a.u.
M06 SCF energy in solution: -7010.24523250 a.u.
M06 enthalpy in solution: -7009.504113 a.u.
M06 free energy in solution: -7009.642590 a.u.
Imaginary frequency: -173.9569 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.753298	-2.230920	0.478345
N	1.219517	-0.642406	1.636383
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C	2.071756	0.227854	2.180640
C	-0.601043	0.652684	2.485328
C	1.644057	1.345985	2.894142
H	3.123078	0.006494	2.025895
C	0.273788	1.583685	3.063188
H	-1.668629	0.795707	2.570042

H	2.389969	2.015449	3.303633
C	-0.962083	-1.444914	1.094978
C	-2.356235	-1.361685	1.034668
N	-0.290197	-2.458579	0.506352
C	-3.103104	-2.346474	0.379973
H	-2.846547	-0.506089	1.473724
C	-0.988348	-3.400588	-0.141130
C	-2.375051	-3.389424	-0.216796
H	-0.398710	-4.181106	-0.611302
H	-2.875245	-4.194433	-0.743020
C	-0.286729	2.778354	3.843357
C	-1.373508	3.485895	2.998575
C	-0.915394	2.251676	5.155611
C	0.808014	3.801692	4.198126
H	-1.012123	3.719469	1.993263
H	-2.266100	2.862862	2.887146
H	-1.683433	4.412471	3.495093
H	-0.163972	1.762175	5.785505
H	-1.350505	3.082403	5.723597
H	-1.711843	1.526554	4.954745
H	0.360286	4.646210	4.732449
H	1.574871	3.372324	4.852537
H	1.298164	4.195691	3.301547
C	-4.637391	-2.338424	0.346851
C	-5.133378	-3.488161	1.257934
C	-5.223946	-1.009980	0.862513
C	-5.153724	-2.572914	-1.091785
H	-4.770824	-4.460676	0.907852
H	-4.787696	-3.349956	2.288573
H	-6.229218	-3.517272	1.264616
H	-4.871672	-0.153081	0.276959
H	-6.315916	-1.038515	0.786590
H	-4.975524	-0.834465	1.915348
H	-6.249376	-2.584344	-1.091964
H	-4.824802	-1.779677	-1.769876
H	-4.817443	-3.530359	-1.501571
Br	1.667048	-0.930537	-1.648753
C	0.689314	1.073417	-2.964340
C	0.989996	2.242442	-2.049533
H	1.276499	0.985955	-3.869270
O	-0.618539	0.772459	-3.179852
C	0.069877	2.306055	-0.816761
H	0.887727	3.180458	-2.617126
O	2.334226	2.168054	-1.531135
C	-1.419799	0.641068	-1.993734
C	-1.368770	1.937224	-1.179986
H	0.450297	1.581672	-0.084483
O	0.002670	3.607438	-0.248123
C	3.358844	2.214032	-2.420473
H	-0.996436	-0.177334	-1.397870
C	-2.835714	0.254219	-2.399556
H	-1.791521	2.748985	-1.783827

O	-2.136614	1.748298	0.006141
C	1.209520	4.107420	0.310695
O	3.218594	2.497785	-3.589677
C	4.645688	1.824424	-1.741827
H	-3.341296	-0.099920	-1.499300
H	-2.777952	-0.576147	-3.120846
O	-3.637273	1.310239	-2.897961
C	-3.252452	2.623951	0.118765
H	1.920527	4.423465	-0.461693
H	0.931355	4.973444	0.918606
H	1.700020	3.356735	0.944457
H	4.758682	2.349853	-0.788720
H	4.594802	0.750464	-1.525267
H	5.490425	2.033459	-2.399110
C	-3.322361	1.723611	-4.221717
H	-2.926034	3.666415	0.227709
H	-3.795012	2.325612	1.021203
H	-3.915622	2.532475	-0.750385
H	-4.097690	2.435355	-4.517945
H	-2.339046	2.204909	-4.282321
H	-3.330461	0.870423	-4.916853
Br	3.802009	-3.246802	0.753061

$B(OH)_2(Oi\text{-}Pr)$

B3LYP-D3 SCF energy: -370.42828380 a.u.
B3LYP-D3 enthalpy: -370.284761 a.u.
B3LYP-D3 free energy: -370.334307 a.u.
M06 SCF energy in solution: -370.33389291 a.u.
M06 enthalpy in solution: -370.190370 a.u.
M06 free energy in solution: -370.239916 a.u.

Cartesian coordinates

ATOM	X	Y	Z
B	-1.294496	-0.093041	-0.036968
O	-1.466313	1.101516	-0.692976
H	-2.407364	1.313019	-0.768235
O	-0.048343	-0.609743	0.173186
O	-2.397863	-0.780228	0.413740
H	-2.128638	-1.599318	0.853070
C	1.136056	0.085661	-0.260662
C	2.235196	-0.960193	-0.402673
C	1.483921	1.179620	0.746248
H	0.934603	0.545988	-1.236537
H	1.937836	-1.735004	-1.116639
H	3.164468	-0.498431	-0.754022
H	2.428259	-1.439455	0.563837
H	0.669495	1.907324	0.811427
H	1.646546	0.741252	1.737658
H	2.396388	1.706953	0.445203

TS3
B3LYP-D3 SCF energy: -4665.93535717 a.u.
B3LYP-D3 enthalpy: -4665.102222 a.u.
B3LYP-D3 free energy: -4665.248289 a.u.
M06 SCF energy in solution: -4667.66616603 a.u.
M06 enthalpy in solution: -4666.833031 a.u.
M06 free energy in solution: -4666.979098 a.u.
Imaginary frequency: -245.9255 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	-1.004547	0.449371	-1.636116
N	-0.016228	1.904741	-0.697574
C	1.319968	1.711408	-0.545625
C	-0.566852	2.992532	-0.139470
C	2.110923	2.620229	0.156621
C	0.166424	3.921996	0.590940
H	-1.634246	3.098829	-0.295622
C	1.548762	3.754260	0.755941
H	3.175897	2.439342	0.241884
H	-0.358486	4.766720	1.019282
C	1.827409	0.481536	-1.177167
C	3.156874	0.048224	-1.100267
N	0.887220	-0.225205	-1.849991
C	3.565972	-1.122233	-1.739993
H	3.862336	0.628398	-0.521620
C	1.270202	-1.352453	-2.477921
C	2.573537	-1.821419	-2.455433
H	0.475823	-1.893982	-2.978478
H	2.806948	-2.736174	-2.989200
C	2.433008	4.734222	1.537923
C	3.111356	3.984437	2.708612
C	3.516798	5.305383	0.593477
C	1.624604	5.908966	2.118506
H	2.362653	3.569200	3.392457
H	3.740455	3.160053	2.355722
H	3.750255	4.670470	3.276999
H	3.060496	5.838585	-0.247926
H	4.157907	6.008938	1.137522
H	4.158390	4.517748	0.184357
H	2.293438	6.580118	2.668073
H	1.139962	6.496624	1.330837
H	0.853468	5.564982	2.817060
C	5.007899	-1.642804	-1.699373
C	5.576950	-1.637529	-3.138259
C	5.916690	-0.776166	-0.808608
C	5.023563	-3.087384	-1.146041
H	4.990723	-2.275315	-3.807911
H	5.578745	-0.623901	-3.554603
H	6.608220	-2.009679	-3.137453

H	5.560341	-0.749430	0.227924
H	6.929521	-1.192901	-0.800341
H	5.987941	0.253365	-1.177755
H	6.049191	-3.474234	-1.138645
H	4.639938	-3.119490	-0.120862
H	4.417042	-3.766757	-1.753249
C	-2.681457	1.389459	-1.810556
C	-3.754316	1.212488	-0.916135
C	-2.812410	2.418566	-2.762769
C	-4.891814	2.025897	-0.957478
H	-3.694099	0.419168	-0.177711
C	-3.953043	3.229101	-2.822871
H	-2.003479	2.599823	-3.470005
C	-4.997486	3.039023	-1.914763
H	-5.700724	1.864714	-0.245502
H	-4.023993	4.011779	-3.576579
H	-5.882727	3.669834	-1.954707
Br	-1.992389	-1.747518	-1.437870
C	-1.751044	-3.011740	0.736208
C	-2.232630	-1.988465	1.746243
H	-2.405898	-3.846464	0.518359
O	-0.462843	-3.401397	0.857125
C	-1.250739	-0.822751	1.898053
H	-2.343282	-2.493083	2.717959
O	-3.498300	-1.407534	1.394325
C	0.511626	-2.341157	0.928236
C	0.177618	-1.343746	2.043683
H	-1.297549	-0.211602	0.989270
O	-1.571900	-0.047537	3.045182
C	-4.586327	-2.217074	1.364348
H	0.482938	-1.811328	-0.026097
C	1.882425	-2.964537	1.086967
H	0.293598	-1.837989	3.016037
O	1.109886	-0.276315	1.905393
C	-2.226014	1.180752	2.750712
O	-4.560530	-3.385461	1.683106
C	-5.786494	-1.451758	0.867303
H	2.629100	-2.176276	0.907418
H	2.013621	-3.743916	0.319339
O	2.022087	-3.502535	2.386677
C	1.569237	0.270935	3.131770
H	-3.142279	1.026830	2.169414
H	-2.477338	1.637447	3.712448
H	-1.565294	1.858992	2.191660
H	-5.936036	-0.548469	1.467506
H	-5.603391	-1.129697	-0.163722
H	-6.670894	-2.088029	0.913240
C	3.293821	-4.072223	2.601036
H	0.738830	0.657179	3.733048
H	2.244466	1.090158	2.869959
H	2.121001	-0.480147	3.717520
H	3.310113	-4.456915	3.624281

```
H         3.493274   -4.902727    1.903923
H         4.099646   -3.326415    2.486596



 TS4
B3LYP-D3 SCF energy:    -4665.90314124 a.u.
B3LYP-D3 enthalpy:      -4665.069952 a.u.
B3LYP-D3 free energy:         -4665.216685 a.u.
M06 SCF energy in solution:         -4667.63655847 a.u.
M06 enthalpy in solution:    -4666.803369 a.u.
M06 free energy in solution:        -4666.950102 a.u.
Imaginary frequency:     -209.6924 cm-1

Cartesian coordinates
ATOM       X           Y           Z
Ni       -1.252542   -0.506358   -1.908070
N         0.230799   -1.895935   -1.604267
C         1.474355   -1.381047   -1.486451
C         0.000274   -3.138881   -1.177225
C         2.504871   -2.107722   -0.898965
C         0.988244   -3.921759   -0.583602
H        -1.023405   -3.483189   -1.286999
C         2.272428   -3.398610   -0.397809
H         3.478343   -1.651455   -0.770008
H         0.723282   -4.911946   -0.235363
C         1.580775    0.052981   -1.869019
C         2.748762    0.800859   -1.753019
N         0.401741    0.642376   -2.192640
C         2.729367    2.194804   -1.906529
H         3.668388    0.307412   -1.466265
C         0.387714    1.956165   -2.439678
C         1.512363    2.764684   -2.300840
H        -0.579687    2.372940   -2.703007
H         1.408236    3.830388   -2.459610
C         3.380325   -4.129401    0.368403
C         4.605492   -4.321310   -0.555105
C         3.778149   -3.267648    1.593077
C         2.922328   -5.509773    0.872974
H         4.348550   -4.931928   -1.428094
H         5.000738   -3.365509   -0.915811
H         5.409466   -4.827662   -0.009021
H         2.920570   -3.083335    2.248449
H         4.550381   -3.783754    2.174845
H         4.180573   -2.293539    1.296399
H         3.743272   -5.992724    1.413171
H         2.076534   -5.427671    1.564771
H         2.634833   -6.171705    0.048025
C         3.978002    3.015056   -1.570725
C         4.422984    2.645467   -0.131631
C         5.104063    2.675655   -2.573395
C         3.701393    4.528625   -1.622768
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H	3.585658	2.710677	0.570980
H	4.812788	1.623643	-0.076138
H	5.221592	3.320075	0.196422
H	4.819011	2.950544	-3.595240
H	6.015415	3.225849	-2.312892
H	5.345007	1.607034	-2.565482
H	4.610828	5.076439	-1.355438
H	3.403601	4.857616	-2.624917
H	2.917725	4.819063	-0.913455
C	-2.977156	-1.383017	-1.992318
C	-3.119347	-2.519330	-2.818750
C	-4.132236	-0.956873	-1.302772
C	-4.336653	-3.195465	-2.953675
H	-2.256106	-2.889246	-3.374816
C	-5.353418	-1.625150	-1.428992
H	-4.076927	-0.090830	-0.646767
C	-5.459708	-2.747929	-2.254292
H	-4.408407	-4.069201	-3.599204
H	-6.221886	-1.272933	-0.876354
H	-6.408104	-3.272193	-2.347763
C	-1.422436	0.076314	0.397483
C	-0.025620	0.058646	0.995558
C	0.287811	1.267000	1.895855
H	0.704406	0.164163	0.196079
C	-1.772399	2.398427	0.885879
C	-0.279673	2.518367	1.204760
H	-0.161903	1.147399	2.882529
H	-2.348291	2.238553	1.804190
H	0.270380	2.650020	0.261471
H	-2.048443	-0.802049	0.444586
Br	-2.653397	-0.280810	2.949391
O	-2.005881	1.234619	0.053960
O	-0.083126	3.653050	2.042705
O	1.705774	1.414459	1.950141
O	0.150110	-1.284624	1.464766
C	2.212595	1.811197	3.222678
H	1.986276	1.055710	3.979214
H	3.297650	1.896149	3.104129
H	1.805138	2.781356	3.531015
C	0.834593	4.603169	1.535388
H	0.501471	5.020055	0.570698
H	0.886611	5.414186	2.266867
H	1.836325	4.170688	1.405838
C	-2.294539	3.596631	0.119072
H	-2.056675	4.503085	0.698514
H	-1.771427	3.668167	-0.853719
O	-3.681310	3.454956	-0.066562
C	-4.252041	4.532022	-0.776097
H	-5.322268	4.328860	-0.860958
H	-4.108816	5.491232	-0.250448
H	-3.825339	4.625819	-1.789498
C	0.422608	-1.645364	2.749013

O	1.022405	-0.970909	3.550400
C	-0.109381	-3.032364	3.001184
H	-1.189862	-2.921506	3.152949
H	0.051427	-3.681272	2.135560
H	0.352251	-3.451142	3.896919

III

B3LYP-D3 SCF energy: -881.88808107 a.u.
B3LYP-D3 enthalpy: -881.565041 a.u.
B3LYP-D3 free energy: -881.644027 a.u.
M06 SCF energy in solution: -881.57790451 a.u.
M06 enthalpy in solution: -881.254864 a.u.
M06 free energy in solution: -881.333850 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.363205	0.914458	-0.227792
C	-1.196496	-0.325188	0.083204
C	-0.676214	-1.555158	-0.605210
C	1.484908	-0.614522	-1.000509
C	1.122905	0.578523	-0.106588
H	-1.224596	-0.460068	1.174620
H	-0.570497	1.226420	-1.261600
H	1.292456	-0.337722	-2.048691
H	1.337817	0.315131	0.936203
O	0.674268	-1.760772	-0.678047
O	1.898128	1.697861	-0.515467
O	-0.719816	1.937064	0.688613
C	2.953588	-1.014710	-0.874962
H	3.549974	-0.248039	-1.376926
H	3.102470	-1.975758	-1.391949
O	3.441852	-1.070482	0.453669
C	3.031792	-2.210596	1.198048
H	3.606877	-2.196564	2.127939
H	1.960172	-2.192512	1.429649
H	3.250183	-3.141561	0.653146
C	2.747907	2.218120	0.502704
H	2.160428	2.602306	1.348193
H	3.306381	3.042164	0.050081
H	3.447641	1.453325	0.862970
C	-0.826339	3.229554	0.110700
H	-1.633415	3.266578	-0.637225
H	-1.069888	3.916258	0.926343
H	0.113231	3.540977	-0.361569
O	-2.548098	-0.040977	-0.358801
C	-3.540680	-0.751223	0.228274
O	-3.355503	-1.632525	1.038702
C	-4.887396	-0.283745	-0.270835
H	-5.037376	0.766734	-0.000253
H	-4.926793	-0.349699	-1.362798

H	-5.672210	-0.897924	0.171710
H	-1.224112	-2.484469	-0.491401

Br[Ni^{II}]Ph

B3LYP-D3 SCF energy: -3784.04464526 a.u.
B3LYP-D3 enthalpy: -3783.535514 a.u.
B3LYP-D3 free energy: -3783.634264 a.u.
M06 SCF energy in solution: -3786.08968312 a.u.
M06 enthalpy in solution: -3785.580552 a.u.
M06 free energy in solution: -3785.679302 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.419248	-0.959848	-0.000046
N	0.677408	0.860863	-0.000012
C	-0.681013	0.955014	-0.000004
C	1.381417	2.004314	-0.000027
C	-1.327234	2.188252	-0.000005
C	0.788785	3.263660	-0.000029
H	2.456874	1.888667	-0.000036
C	-0.603699	3.388848	-0.000016
H	-2.409917	2.215309	-0.000005
H	1.438114	4.130017	-0.000041
C	-1.388598	-0.341333	-0.000007
C	-2.774849	-0.479574	0.000040
N	-0.567288	-1.417752	-0.000063
C	-3.369666	-1.750050	0.000025
H	-3.400057	0.404913	0.000097
C	-1.117720	-2.636702	-0.000076
C	-2.495942	-2.842462	-0.000034
H	-0.405264	-3.455636	-0.000123
H	-2.861200	-3.861738	-0.000053
C	-1.337656	4.734745	-0.000020
C	-2.225044	4.826828	-1.264033
C	-2.224994	4.826864	1.264026
C	-0.362373	5.926069	-0.000055
H	-1.619130	4.758651	-2.174335
H	-2.974483	4.028894	-1.297544
H	-2.757743	5.784650	-1.278672
H	-1.619045	4.758702	2.174306
H	-2.757685	5.784690	1.278664
H	-2.974439	4.028938	1.297584
H	-0.928304	6.863697	-0.000039
H	0.278521	5.926584	0.888775
H	0.278461	5.926580	-0.888928
C	-4.897518	-1.884726	0.000090
C	-5.465830	-1.196980	1.264038
C	-5.465932	-1.197222	-1.263945
C	-5.350248	-3.356295	0.000246
H	-5.072786	-1.663315	2.174249

H	-5.217230	-0.130839	1.297405
H	-6.558336	-1.284592	1.279196
H	-5.072895	-1.663677	-2.174097
H	-6.558433	-1.284916	-1.279040
H	-5.217415	-0.131068	-1.297498
H	-6.444451	-3.403614	0.000149
H	-4.995974	-3.890517	-0.888438
H	-4.996149	-3.890279	0.889142
C	3.205655	-0.363318	0.000046
C	3.865836	-0.073298	-1.204031
C	3.865642	-0.073202	1.204207
C	5.135135	0.515525	-1.206264
H	3.384668	-0.311715	-2.150247
C	5.134943	0.515617	1.206599
H	3.384318	-0.311534	2.150367
C	5.772523	0.817179	0.000207
H	5.628521	0.733657	-2.151584
H	5.628177	0.733821	2.151982
H	6.759762	1.273011	0.000269
Br	2.192115	-3.136854	-0.000159

IV

B3LYP-D3 SCF energy: -881.88688079 a.u.
B3LYP-D3 enthalpy: -881.564289 a.u.
B3LYP-D3 free energy: -881.643606 a.u.
M06 SCF energy in solution: -881.57814403 a.u.
M06 enthalpy in solution: -881.255552 a.u.
M06 free energy in solution: -881.334869 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.406904	1.150506	0.035132
C	1.388571	0.136910	-0.603897
C	0.710272	-0.976252	-1.293722
O	-0.355926	-1.601710	-0.722229
C	-0.970597	-0.923075	0.387117
C	-2.354504	-1.514098	0.585961
H	-2.741079	-1.173661	1.558158
O	-3.198174	-1.089391	-0.466664
C	-4.506693	-1.609279	-0.359256
H	-4.511949	-2.710728	-0.397743
H	-4.996533	-1.293137	0.576592
H	-5.077112	-1.222275	-1.207748
H	-2.273368	-2.613205	0.606247
C	-1.011060	0.584956	0.108436
H	-1.494741	0.722080	-0.865639
O	-1.746123	1.215702	1.143887
C	-2.671399	2.189010	0.676711
H	-3.153418	2.612829	1.562351
H	-3.434748	1.726585	0.034782

H	-2.162948	2.986689	0.120456
H	-0.372504	-1.116943	1.290433
H	1.211479	-1.587331	-2.033031
H	2.063160	0.635003	-1.301904
O	2.226280	-0.354181	0.537874
C	3.405961	-0.919292	0.200721
O	3.816498	-1.011063	-0.937011
C	4.129236	-1.419597	1.431205
H	4.229473	-0.615616	2.167034
H	5.112475	-1.796411	1.147052
H	3.546378	-2.220672	1.898628
H	0.740866	1.351655	1.063082
O	0.333071	2.359834	-0.706486
C	1.411909	3.246150	-0.465316
H	2.383513	2.808429	-0.741224
H	1.239347	4.130427	-1.084054
H	1.455101	3.547119	0.593000

TS5
B3LYP-D3 SCF energy: -881.87087668 a.u.
B3LYP-D3 enthalpy: -881.550156 a.u.
B3LYP-D3 free energy: -881.629456 a.u.
M06 SCF energy in solution: -881.56115471 a.u.
M06 enthalpy in solution: -881.240434 a.u.
M06 free energy in solution: -881.319734 a.u.
Imaginary frequency: -123.0539 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.383649	1.310667	-0.165154
C	1.200893	0.502803	-1.140034
C	0.869193	-0.814179	-1.449837
C	-0.776255	-0.876804	0.233567
C	-0.967103	0.638466	0.087528
H	1.290814	-1.327054	-2.304851
H	1.957259	0.998247	-1.731817
H	0.914623	1.367937	0.795646
H	-0.059471	-1.092739	1.036672
H	-1.621704	0.813704	-0.774548
O	-0.223691	-1.419686	-0.987816
O	-1.554557	1.110118	1.286134
O	0.131783	2.622411	-0.662681
O	2.324824	-1.889084	-0.244787
C	-2.073625	-1.608564	0.515584
H	-2.387562	-1.363924	1.541161
H	-1.893074	-2.693772	0.453213
O	-3.049588	-1.201031	-0.422762
C	3.074630	-1.063293	0.358101
O	3.031355	0.189064	0.299845
C	4.148043	-1.698095	1.258535

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H        4.794165   -2.335633    0.647288
H        4.740704   -0.927657    1.753717
H        3.661010   -2.336286    2.002088
C       -4.294306   -1.840172   -0.226777
H       -4.212488   -2.933528   -0.337041
H       -4.711914   -1.622375    0.769887
H       -4.976039   -1.456444   -0.990233
C       -2.547063    2.109443    1.086302
H       -2.132010    2.984726    0.572725
H       -2.900831    2.399980    2.079393
H       -3.391443    1.712067    0.503942
C        1.191262    3.532793   -0.410320
H        2.137395    3.208176   -0.867189
H        0.894931    4.489582   -0.848045
H        1.358721    3.662271    0.669555
```

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 V
B3LYP-D3 SCF energy:     -881.88674003 a.u.
B3LYP-D3 enthalpy:       -881.564595 a.u.
B3LYP-D3 free energy:          -881.643643 a.u.
M06 SCF energy in solution:         -881.58113589 a.u.
M06 enthalpy in solution:     -881.258991 a.u.
M06 free energy in solution:         -881.338039 a.u.

Cartesian coordinates
ATOM       X           Y           Z
C       -0.567504   -1.684858   -0.255561
C        0.635723   -1.659651    0.631278
C        1.444235   -0.420028    0.768867
O        0.680399    0.745525    0.709900
C       -0.218015    0.808742   -0.405732
C       -0.850306    2.190324   -0.409966
H       -1.397644    2.319476   -1.355849
O       -1.723945    2.309093    0.695880
C       -2.356912    3.568988    0.756173
H       -3.010852    3.559756    1.632403
H       -1.627167    4.387958    0.864662
H       -2.964948    3.764993   -0.142823
H       -0.049565    2.945921   -0.359875
C       -1.266246   -0.309740   -0.300451
H       -1.830674   -0.136765    0.623912
O       -2.104183   -0.191479   -1.437484
C       -3.426067   -0.675986   -1.250994
H       -3.970970   -0.459935   -2.174265
H       -3.922946   -0.158009   -0.415909
H       -3.437509   -1.756538   -1.065875
H        0.345345    0.689583   -1.342542
H        2.004477   -0.372332    1.703823
O        2.418923   -0.419618   -0.332041
C        3.639368    0.130571   -0.078193
```

O	3.999433	0.526518	1.005993
C	4.468014	0.159271	-1.341151
H	5.466301	0.534835	-1.113904
H	4.529117	-0.844164	-1.774103
H	3.986477	0.806178	-2.082276
H	1.053612	-2.601723	0.972729
O	-1.443915	-2.774017	0.043039
C	-2.008108	-2.771389	1.346822
H	-2.456349	-3.758116	1.489843
H	-1.249264	-2.605946	2.124705
H	-2.793130	-2.009984	1.459094
H	-0.253089	-1.890831	-1.292582

TS6

B3LYP-D3 SCF energy: -4665.95266953 a.u.
B3LYP-D3 enthalpy: -4665.119499 a.u.
B3LYP-D3 free energy: -4665.264905 a.u.
M06 SCF energy in solution: -4667.69072381 a.u.
M06 enthalpy in solution: -4666.857553 a.u.
M06 free energy in solution: -4667.002959 a.u.
Imaginary frequency: -30.3253 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.470671	0.015036	-1.366341
Br	2.066931	-1.927576	-2.501168
C	3.308585	0.475964	-1.267789
C	4.238829	-0.146536	-0.422344
C	3.751874	1.539460	-2.072563
C	5.557067	0.316300	-0.346041
H	3.953722	-1.016982	0.159977
C	5.073026	1.995837	-2.006865
H	3.055641	2.026632	-2.753603
C	5.979221	1.390526	-1.133225
H	6.258476	-0.179613	0.321828
H	5.392237	2.821497	-2.640248
H	7.006379	1.743272	-1.076947
N	0.837025	1.727304	-0.582126
C	1.601071	2.637424	0.043109
C	-0.497284	1.950919	-0.635425
C	1.087008	3.800849	0.596959
H	2.657301	2.408469	0.082589
C	-1.072048	3.108098	-0.105186
C	-0.286443	4.074062	0.527030
H	1.772827	4.486222	1.083007
H	-2.141566	3.243368	-0.182949
C	-1.287233	0.854466	-1.232255
C	-2.681433	0.866037	-1.342436
N	-0.556177	-0.220021	-1.597961
C	-3.365557	-0.256367	-1.818366

H	-3.228458	1.746119	-1.035258
C	-1.193070	-1.298819	-2.072871
C	-2.575693	-1.354137	-2.193927
H	-0.547411	-2.125645	-2.346738
H	-3.025445	-2.266957	-2.568803
C	-4.894555	-0.328109	-1.905945
C	-5.569052	0.977720	-1.447208
C	-5.308303	-0.607944	-3.369491
C	-5.390437	-1.478152	-0.996733
H	-5.267624	1.831130	-2.065518
H	-6.656445	0.878201	-1.529933
H	-5.339009	1.208455	-0.400139
H	-4.965722	0.193469	-4.033571
H	-4.892311	-1.551085	-3.737709
H	-6.399941	-0.672010	-3.445084
H	-4.982334	-2.446487	-1.303018
H	-5.099065	-1.309154	0.046230
H	-6.483547	-1.546213	-1.040260
C	-0.863715	5.362560	1.124624
C	-0.572887	5.392016	2.643365
C	-0.189613	6.577811	0.444940
C	-2.386133	5.471308	0.921053
H	0.500119	5.338922	2.854577
H	-0.954129	6.321770	3.081316
H	-1.060319	4.551904	3.150520
H	0.894105	6.581822	0.599175
H	-0.376191	6.575995	-0.634779
H	-0.589915	7.510060	0.859944
H	-2.921545	4.648147	1.408853
H	-2.749914	6.405984	1.360769
H	-2.655231	5.479585	-0.141462
C	1.231815	-0.978170	1.309046
C	0.227545	-0.392590	2.244672
C	1.059306	-2.423347	0.987724
H	2.231700	-0.566463	1.306186
C	-1.187717	-0.845366	1.868215
H	0.414748	-0.777687	3.265994
H	1.655227	-2.732241	0.130359
C	-1.218358	-2.375017	1.714881
H	-1.451046	-0.400012	0.904874
H	-0.979193	-2.847221	2.676607
O	-0.265000	-2.775917	0.722087
O	1.460120	-3.252650	2.155545
O	-2.121075	-0.443395	2.868773
O	0.314373	1.032274	2.266836
C	0.320050	1.597930	3.565382
H	0.411238	2.678916	3.432593
H	-0.604098	1.372725	4.114530
H	1.177349	1.242555	4.157653
C	-2.923702	0.657992	2.483104
H	-3.573700	0.405764	1.628805
H	-3.553040	0.910121	3.341526

H	-2.312009	1.528712	2.209190
C	-2.578782	-2.863553	1.254911
H	-3.357259	-2.361534	1.852595
H	-2.716737	-2.579209	0.200146
O	-2.649635	-4.264439	1.413877
C	-3.845556	-4.802681	0.900295
H	-3.821584	-5.880626	1.081596
H	-4.736202	-4.376542	1.394232
H	-3.940682	-4.627195	-0.185322
C	2.781386	-3.401005	2.370711
O	3.647350	-2.843413	1.728771
C	3.032692	-4.361514	3.512316
H	2.463333	-4.057672	4.396497
H	2.689977	-5.363041	3.230804
H	4.099474	-4.386564	3.738294

TS7
B3LYP-D3 SCF energy: -4665.95162331 a.u.
B3LYP-D3 enthalpy: -4665.119763 a.u.
B3LYP-D3 free energy: -4665.266673 a.u.
M06 SCF energy in solution: -4667.67753969 a.u.
M06 enthalpy in solution: -4666.845679 a.u.
M06 free energy in solution: -4666.992589 a.u.
Imaginary frequency: -16.1055 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	3.831300	1.013846	-0.217199
C	2.956329	-0.009328	0.411061
C	3.326981	-1.430658	0.246147
C	5.576928	-0.813233	-0.231841
C	5.294519	0.660780	0.107058
H	2.742005	-2.097909	0.878928
H	2.115799	0.270330	1.029079
H	3.710115	0.987779	-1.313269
H	5.444887	-0.957568	-1.313326
H	5.448782	0.806298	1.181122
O	4.676151	-1.686431	0.473713
O	6.182518	1.471390	-0.653355
O	3.517796	2.306902	0.281372
O	3.107200	-1.873149	-1.180898
C	6.994168	-1.230887	0.120411
H	7.684205	-0.739063	-0.582916
H	7.085369	-2.321737	-0.006411
O	7.289541	-0.854314	1.452373
C	1.877533	-2.138574	-1.582278
O	0.891721	-2.090923	-0.844117
C	1.795176	-2.476845	-3.045200
H	0.993223	-3.200119	-3.210405
H	1.533454	-1.544207	-3.559162

H	2.745426	-2.850965	-3.431165
C	8.575650	-1.264648	1.860965
H	8.682480	-2.361530	1.831969
H	9.366336	-0.824786	1.229821
H	8.711937	-0.922496	2.890490
C	6.986514	2.333773	0.136946
H	7.636789	2.880115	-0.552872
H	7.603214	1.763223	0.845774
H	6.370111	3.051534	0.696099
C	3.490928	3.315230	-0.720940
H	4.458479	3.397951	-1.234263
H	2.702587	3.113852	-1.458751
H	3.275437	4.257269	-0.206878
Ni	-0.341962	-0.160396	-0.453414
N	-2.068135	-1.318343	-0.582134
C	-2.094664	-2.653176	-0.683408
C	-3.213163	-0.664771	-0.293334
C	-3.254439	-3.394648	-0.503062
H	-1.138596	-3.111972	-0.906380
C	-4.412990	-1.355191	-0.092522
C	-4.461263	-2.748661	-0.191251
H	-3.204688	-4.473838	-0.599102
H	-5.306837	-0.797560	0.149814
N	-1.846785	1.287382	-0.378430
C	-1.637024	2.606955	-0.335871
C	-3.091970	0.811753	-0.200318
C	-2.659394	3.513278	-0.088222
H	-0.613214	2.915713	-0.521226
C	-4.168919	1.671679	0.043927
C	-3.971333	3.053919	0.115077
H	-2.425240	4.571768	-0.058888
H	-5.158693	1.257595	0.177204
Br	0.828580	0.984318	-2.296121
C	-0.188967	-0.364731	1.528250
C	0.010910	-1.627042	2.118844
C	-0.260082	0.732778	2.405716
C	0.141364	-1.788976	3.501960
H	0.079714	-2.504134	1.477906
C	-0.126039	0.588618	3.791782
H	-0.411229	1.733526	2.001722
C	0.075460	-0.677032	4.346048
H	0.299657	-2.781107	3.922265
H	-0.175725	1.463896	4.437528
H	0.181903	-0.795927	5.421975
C	-5.744038	-3.559970	0.028938
C	-6.952988	-2.666577	0.362307
C	-6.064298	-4.356658	-1.257829
C	-5.521777	-4.540813	1.204626
H	-7.840743	-3.290830	0.509463
H	-6.794960	-2.095772	1.284562
H	-7.175512	-1.963134	-0.448464
H	-5.256769	-5.047123	-1.521959

H	-6.976138	-4.948288	-1.115686
H	-6.222924	-3.682664	-2.107226
H	-5.285381	-3.999108	2.127177
H	-6.428803	-5.132056	1.376468
H	-4.701700	-5.237954	1.004778
C	-5.106094	4.047448	0.395258
C	-6.464143	3.347868	0.588296
C	-4.774857	4.835592	1.684720
C	-5.225791	5.027533	-0.795598
H	-6.767137	2.792521	-0.306958
H	-6.448270	2.655886	1.438250
H	-7.237511	4.097221	0.787973
H	-5.573934	5.554291	1.900949
H	-4.679366	4.160690	2.542641
H	-3.838709	5.395361	1.591466
H	-6.030108	5.748568	-0.608660
H	-4.301581	5.592398	-0.954043
H	-5.455625	4.491157	-1.723102

VI_{ax}

B3LYP-D3 SCF energy: -4665.96615636 a.u.
B3LYP-D3 enthalpy: -4665.130737 a.u.
B3LYP-D3 free energy: -4665.276909 a.u.
M06 SCF energy in solution: -4667.69545879 a.u.
M06 enthalpy in solution: -4666.860039 a.u.
M06 free energy in solution: -4667.006211 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.347734	0.171593	-1.026747
Br	2.162317	-1.189207	-2.863568
C	3.014525	1.148591	-1.174605
C	4.249564	0.818368	-0.615597
C	2.928562	2.232260	-2.057395
C	5.372394	1.609033	-0.883506
H	4.364472	-0.069228	-0.003429
C	4.052472	3.025332	-2.317068
H	1.995083	2.454742	-2.567843
C	5.277259	2.721712	-1.721425
H	6.328137	1.338018	-0.440620
H	3.966748	3.867836	-3.000124
H	6.152808	3.332848	-1.925707
N	0.030526	1.864718	-0.771636
C	0.392294	3.081183	-0.345133
C	-1.272654	1.533356	-0.710934
C	-0.513473	4.010544	0.145608
H	1.453149	3.295382	-0.390883
C	-2.237292	2.410453	-0.203464
C	-1.872425	3.679454	0.251563
H	-0.142791	4.974908	0.475716

H	-3.262887	2.076720	-0.128705
C	-1.593009	0.149914	-1.131098
C	-2.897165	-0.293587	-1.376045
N	-0.534204	-0.681040	-1.214421
C	-3.144398	-1.632465	-1.692391
H	-3.710233	0.417460	-1.327172
C	-0.750890	-1.964206	-1.535624
C	-2.021808	-2.470825	-1.769631
H	0.131532	-2.584414	-1.600569
H	-2.121414	-3.524295	-2.005994
C	-4.551607	-2.191840	-1.928698
C	-5.640644	-1.110846	-1.802888
C	-4.626090	-2.802122	-3.347775
C	-4.828405	-3.290993	-0.874860
H	-5.507208	-0.311229	-2.540599
H	-6.624610	-1.558931	-1.977010
H	-5.655362	-0.662144	-0.802650
H	-4.428562	-2.042067	-4.111797
H	-3.901040	-3.610848	-3.482849
H	-5.625552	-3.215531	-3.525959
H	-4.114100	-4.117082	-0.950733
H	-4.765047	-2.885643	0.141556
H	-5.833837	-3.703678	-1.017347
C	-2.867997	4.659964	0.881521
C	-2.431887	4.932712	2.341298
C	-2.861209	5.982421	0.080430
C	-4.304429	4.105883	0.899482
H	-1.433329	5.378873	2.390630
H	-3.132856	5.625639	2.821029
H	-2.414090	4.004307	2.923557
H	-1.870395	6.447682	0.068426
H	-3.166692	5.812976	-0.958207
H	-3.559975	6.697365	0.529968
H	-4.378522	3.186280	1.491707
H	-4.976905	4.842628	1.351484
H	-4.673079	3.898251	-0.111719
C	1.732955	-0.256763	0.945508
C	0.789309	0.167753	2.073164
C	1.893403	-1.770980	0.986716
H	2.700258	0.197391	1.149464
C	-0.507592	-0.636902	2.094746
H	1.296554	-0.048977	3.028387
H	2.463518	-2.151676	0.138881
C	-0.195951	-2.141551	2.093770
H	-1.096648	-0.397065	1.207160
H	0.277794	-2.408310	3.046772
O	0.682640	-2.473004	1.010229
O	2.599317	-2.168310	2.223806
O	-1.267466	-0.336548	3.269029
O	0.500968	1.567378	2.026394
C	0.671124	2.246825	3.255517
H	0.406747	3.293210	3.072801

H	0.021219	1.841139	4.042376
H	1.715366	2.202315	3.601925
C	-2.362100	0.527895	3.028157
H	-3.097382	0.069753	2.344923
H	-2.845762	0.707637	3.993038
H	-2.037495	1.483159	2.595469
C	-1.459964	-2.965187	1.933388
H	-2.203148	-2.600644	2.661260
H	-1.867037	-2.813184	0.921199
O	-1.164442	-4.328373	2.155128
C	-2.282672	-5.160118	1.953374
H	-1.966441	-6.186514	2.158758
H	-3.117584	-4.901807	2.627854
H	-2.654105	-5.103313	0.915423
C	3.942175	-2.249752	2.193406
O	4.628051	-1.969455	1.232011
C	4.474721	-2.736119	3.523332
H	4.151266	-2.062442	4.323902
H	4.068436	-3.728106	3.746439
H	5.563984	-2.777374	3.486168

VI_{eq}

B3LYP-D3 SCF energy: -4665.99168766 a.u.
B3LYP-D3 enthalpy: -4665.155612 a.u.
B3LYP-D3 free energy: -4665.301038 a.u.
M06 SCF energy in solution: -4667.71494946 a.u.
M06 enthalpy in solution: -4666.878874 a.u.
M06 free energy in solution: -4667.024300 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.890211	0.498988	-0.892757
C	2.137505	-0.207371	0.240914
C	2.874081	-1.489403	0.613016
C	4.995059	-0.669888	-0.079700
C	4.360419	0.667826	-0.472613
H	2.410180	-1.988713	1.462879
H	2.202878	0.432911	1.125908
H	2.835752	-0.084255	-1.816578
H	5.035953	-1.314103	-0.969161
H	4.384312	1.331527	0.398673
O	4.217851	-1.312741	0.939562
O	5.126006	1.217880	-1.544226
O	2.356896	1.806221	-1.107472
O	2.884639	-2.443135	-0.520842
C	6.413941	-0.520218	0.442143
H	7.068378	-0.250013	-0.401564
H	6.747248	-1.490245	0.844935
O	6.459055	0.479255	1.444448
C	1.779719	-3.132484	-0.760566

O	0.756729	-3.010311	-0.091663
C	1.888610	-4.030204	-1.958913
H	1.255211	-4.908889	-1.819692
H	1.500535	-3.449599	-2.804577
H	2.922351	-4.318926	-2.159149
C	7.740175	0.616494	2.017601
H	8.068780	-0.313368	2.510288
H	8.498588	0.894187	1.265937
H	7.676134	1.410515	2.766779
C	5.683117	2.489137	-1.253321
H	6.276457	2.782894	-2.124701
H	6.332471	2.446427	-0.367303
H	4.898165	3.240107	-1.083443
C	2.297826	2.215798	-2.471237
H	3.298248	2.250225	-2.916995
H	1.653317	1.544055	-3.048930
H	1.864506	3.221771	-2.471560
Ni	0.166254	-0.622453	-0.014121
N	-1.804460	-1.229728	-0.062363
C	-2.183231	-2.512281	-0.127942
C	-2.748890	-0.271306	-0.050975
C	-3.516453	-2.894854	-0.165202
H	-1.373780	-3.229968	-0.163251
C	-4.110625	-0.593568	-0.088252
C	-4.529836	-1.924444	-0.141122
H	-3.752330	-3.952186	-0.217814
H	-4.839922	0.203969	-0.085727
N	-0.903761	1.243256	-0.089885
C	-0.369460	2.470413	-0.095754
C	-2.241484	1.120575	-0.024290
C	-1.143461	3.622545	-0.027702
H	0.711708	2.496312	-0.178490
C	-3.077702	2.240991	0.052299
C	-2.540989	3.530757	0.054912
H	-0.644133	4.585593	-0.037462
H	-4.147418	2.099709	0.115999
Br	0.176127	-0.773472	-2.492415
C	0.093608	-0.675194	1.945766
C	-0.118977	-1.898553	2.593635
C	0.150772	0.486970	2.724567
C	-0.279309	-1.955710	3.983006
H	-0.151198	-2.815686	2.016625
C	-0.013020	0.433910	4.112643
H	0.331314	1.449267	2.254700
C	-0.230232	-0.789697	4.748670
H	-0.441475	-2.918192	4.464275
H	0.037164	1.351704	4.695104
H	-0.353429	-0.834354	5.827915
C	-6.006119	-2.337604	-0.180942
C	-6.955494	-1.125950	-0.142844
C	-6.273033	-3.127831	-1.483729
C	-6.309771	-3.235310	1.041773

H	-7.994162	-1.472584	-0.168399
H	-6.826634	-0.536771	0.772527
H	-6.807288	-0.465612	-1.005083
H	-5.658292	-4.031552	-1.545417
H	-7.324585	-3.434794	-1.527943
H	-6.057486	-2.513842	-2.365249
H	-6.123438	-2.697844	1.978380
H	-7.361136	-3.545699	1.028018
H	-5.694421	-4.140743	1.045512
C	-3.402505	4.796794	0.141216
C	-4.906720	4.478732	0.225376
C	-2.999955	5.594229	1.404155
C	-3.154968	5.660537	-1.117979
H	-5.257319	3.933878	-0.658786
H	-5.148509	3.887573	1.116255
H	-5.476652	5.412192	0.284637
H	-3.602379	6.507040	1.480418
H	-3.162317	5.000083	2.310527
H	-1.946293	5.890433	1.380302
H	-3.759359	6.574086	-1.071886
H	-2.105398	5.958475	-1.207806
H	-3.428587	5.114189	-2.027553

TS8
B3LYP-D3 SCF energy: -4665.95865950 a.u.
B3LYP-D3 enthalpy: -4665.124232 a.u.
B3LYP-D3 free energy: -4665.269538 a.u.
M06 SCF energy in solution: -4667.69220043 a.u.
M06 enthalpy in solution: -4666.857773 a.u.
M06 free energy in solution: -4667.003079 a.u.
Imaginary frequency: -255.4017 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.318348	0.300925	-1.580525
Br	0.602616	-0.578533	-3.846312
C	1.962312	1.194484	-1.029382
C	2.932525	1.357531	-2.037586
C	1.948825	2.114671	0.037099
C	3.833579	2.422246	-1.987401
H	2.952761	0.665971	-2.867963
C	2.852001	3.179567	0.081515
H	1.242289	1.990304	0.847817
C	3.806092	3.333541	-0.927462
H	4.563129	2.537278	-2.785408
H	2.814173	3.879098	0.913841
H	4.518407	4.153763	-0.889614
N	-1.102328	1.609271	-0.687043
C	-0.977309	2.943895	-0.649173
C	-2.279486	1.067652	-0.306618

C	-1.989694	3.786716	-0.211898
H	-0.016237	3.330570	-0.969922
C	-3.336663	1.859348	0.154249
C	-3.213471	3.250077	0.218930
H	-1.813554	4.856829	-0.210275
H	-4.262812	1.379986	0.439439
C	-2.379625	-0.404222	-0.459858
C	-3.397543	-1.174443	0.108797
N	-1.402224	-0.953862	-1.201125
C	-3.425498	-2.557612	-0.081395
H	-4.135292	-0.695445	0.736929
C	-1.435791	-2.271357	-1.429197
C	-2.414837	-3.099175	-0.893221
H	-0.646714	-2.643678	-2.076863
H	-2.375229	-4.162642	-1.103374
C	-4.458121	-3.466866	0.593826
C	-5.532372	-2.667234	1.354245
C	-5.161440	-4.344278	-0.466205
C	-3.707489	-4.361807	1.608915
H	-6.082322	-1.991269	0.688777
H	-6.257443	-3.358101	1.797576
H	-5.098698	-2.078530	2.170213
H	-5.693498	-3.726236	-1.198352
H	-4.455298	-4.978739	-1.011201
H	-5.890810	-5.003183	0.018892
H	-2.978054	-5.008679	1.109122
H	-3.169796	-3.743001	2.334138
H	-4.416385	-5.005056	2.143593
C	-4.335647	4.168735	0.716190
C	-3.822123	4.969787	1.936267
C	-4.728350	5.145243	-0.417623
C	-5.590214	3.383852	1.141364
H	-2.953800	5.586686	1.683224
H	-4.610043	5.636994	2.304402
H	-3.532938	4.298552	2.752665
H	-3.884420	5.768221	-0.730966
H	-5.089889	4.600324	-1.296798
H	-5.527741	5.812999	-0.076142
H	-5.376319	2.686991	1.959936
H	-6.356810	4.081803	1.494280
H	-6.019379	2.818339	0.306253
C	1.635143	-0.761607	-0.315316
C	3.113352	-1.193697	-0.147752
C	0.970832	-0.756519	1.062055
H	1.171527	-1.545655	-0.920262
C	3.853469	-0.387443	0.920833
H	3.067370	-2.227353	0.241205
H	-0.033664	-0.341262	1.059174
C	3.043000	-0.391292	2.231448
H	4.013358	0.638377	0.571475
H	3.110954	-1.396865	2.666340
O	1.660351	-0.053990	2.039735

O	0.865720	-2.167536	1.454024
O	5.095883	-0.999031	1.246402
O	3.885543	-1.197549	-1.325711
C	3.583776	-2.251486	-2.232218
H	4.353604	-2.220313	-3.007575
H	3.625592	-3.229479	-1.725705
H	2.605226	-2.114441	-2.707032
C	6.207208	-0.492954	0.520508
H	6.338266	0.587493	0.693412
H	7.088929	-1.020602	0.896230
H	6.098845	-0.667772	-0.554446
C	3.603553	0.610853	3.222224
H	4.698649	0.498100	3.246651
H	3.366309	1.629599	2.871481
O	3.041205	0.367412	4.495734
C	3.492428	1.281662	5.468300
H	3.014581	1.011502	6.414275
H	4.587649	1.239345	5.597166
H	3.218054	2.319910	5.214787
C	-0.255864	-2.582425	2.086572
O	-1.227505	-1.889125	2.303728
C	-0.141169	-4.048968	2.434346
H	-0.330066	-4.641702	1.531804
H	0.865881	-4.286321	2.786192
H	-0.883701	-4.308108	3.189868

TS9
B3LYP-D3 SCF energy: -4665.96204995 a.u.
B3LYP-D3 enthalpy: -4665.126893 a.u.
B3LYP-D3 free energy: -4665.271607 a.u.
M06 SCF energy in solution: -4667.69464459 a.u.
M06 enthalpy in solution: -4666.859488 a.u.
M06 free energy in solution: -4667.004202 a.u.
Imaginary frequency: -289.3533 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	2.842864	0.749706	-0.489845
C	2.346076	-0.150070	0.662675
C	3.030918	-1.516008	0.569113
C	5.019060	-0.531507	-0.306963
C	4.369241	0.863246	-0.319586
H	2.724366	-2.182826	1.372773
H	2.781874	0.283401	1.561235
H	2.614094	0.299272	-1.459488
H	4.882176	-0.979402	-1.300749
H	4.571440	1.359197	0.636473
O	4.421459	-1.379676	0.684269
O	4.954043	1.595327	-1.394801
O	2.237015	2.041704	-0.398280

O	2.780174	-2.158469	-0.704880
C	6.511049	-0.478572	-0.026196
H	7.016884	-0.041611	-0.901468
H	6.880822	-1.507103	0.111930
O	6.756841	0.301520	1.130225
C	1.936035	-3.203525	-0.770495
O	1.296712	-3.619599	0.180983
C	1.867846	-3.754692	-2.167025
H	1.364587	-4.722706	-2.155481
H	1.297664	-3.037387	-2.769051
H	2.868746	-3.841538	-2.598821
C	8.120744	0.325269	1.490431
H	8.497467	-0.683225	1.726875
H	8.749263	0.748727	0.688798
H	8.209187	0.954372	2.380401
C	5.638286	2.768660	-0.982928
H	6.088991	3.203197	-1.880082
H	6.426228	2.534697	-0.253694
H	4.947760	3.500182	-0.538127
C	2.083562	2.682118	-1.672506
H	3.039029	2.739986	-2.200066
H	1.355236	2.138072	-2.285694
H	1.719495	3.694456	-1.470143
Ni	0.178959	-0.174924	-0.064284
N	-1.626814	-1.232582	0.089055
C	-1.746949	-2.565650	0.106472
C	-2.743653	-0.483411	0.035275
C	-2.979142	-3.206227	0.079818
H	-0.818423	-3.124795	0.134407
C	-4.015941	-1.066132	0.005926
C	-4.163323	-2.455258	0.028141
H	-3.001886	-4.290595	0.094615
H	-4.888664	-0.429999	-0.041276
N	-1.224187	1.361740	-0.005061
C	-0.939390	2.668599	-0.025781
C	-2.516057	0.981961	0.000773
C	-1.917013	3.652980	-0.054204
H	0.116426	2.906301	-0.012068
C	-3.551978	1.924068	-0.020599
C	-3.273842	3.292508	-0.053963
H	-1.611811	4.693656	-0.074878
H	-4.576794	1.580670	-0.009359
Br	0.215042	-0.484143	-2.508042
C	0.739282	-0.154108	1.798598
C	0.492624	-1.361064	2.480330
C	0.609816	1.058468	2.511609
C	0.031163	-1.344078	3.799611
H	0.622819	-2.306874	1.966482
C	0.148931	1.064352	3.823408
H	0.881535	1.987665	2.021541
C	-0.152208	-0.138113	4.477468
H	-0.183195	-2.287450	4.297186

H	0.036536	2.011672	4.346510
H	-0.501256	-0.131462	5.506474
C	-5.528328	-3.153979	-0.007179
C	-6.698194	-2.154084	-0.058104
C	-5.599787	-4.054563	-1.262902
C	-5.683034	-4.022724	1.263330
H	-7.647363	-2.700286	-0.079434
H	-6.713365	-1.500365	0.821778
H	-6.658509	-1.527010	-0.956254
H	-4.817129	-4.819917	-1.260076
H	-6.568539	-4.566359	-1.303869
H	-5.486110	-3.461185	-2.176965
H	-5.631980	-3.406291	2.167983
H	-6.652039	-4.535471	1.252539
H	-4.901891	-4.786592	1.332418
C	-4.365444	4.369395	-0.085612
C	-5.782991	3.768301	-0.078898
C	-4.213844	5.278197	1.157036
C	-4.199195	5.215523	-1.369999
H	-5.958661	3.131203	-0.953308
H	-5.970249	3.177173	0.825032
H	-6.523664	4.574763	-0.104389
H	-4.984335	6.058018	1.148529
H	-4.322778	4.699460	2.081206
H	-3.237957	5.773792	1.183313
H	-4.969658	5.994486	-1.409046
H	-3.222871	5.709321	-1.409426
H	-4.296835	4.591490	-2.265303

3_{ax}

B3LYP-D3 SCF energy: -1113.61648933 a.u.
B3LYP-D3 enthalpy: -1113.193637 a.u.
B3LYP-D3 free energy: -1113.291828 a.u.
M06 SCF energy in solution: -1113.17055306 a.u.
M06 enthalpy in solution: -1112.747701 a.u.
M06 free energy in solution: -1112.845892 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.034550	0.025124	-1.574373
C	-0.115657	-1.198878	-0.624984
C	1.039235	-1.163314	0.388965
O	1.104238	0.037377	1.097192
C	1.245763	1.219265	0.301278
C	1.208736	2.395109	1.262245
H	1.482374	3.308394	0.712981
O	-0.096278	2.507833	1.803802
C	-0.211879	3.548806	2.750727
H	-1.249555	3.557283	3.094784
H	0.450755	3.387431	3.616112

H	0.027362	4.529965	2.308787
H	1.947458	2.226514	2.061431
C	0.177351	1.346557	-0.805794
H	-0.772673	1.644509	-0.348267
O	0.669651	2.391815	-1.636949
C	-0.304949	3.083678	-2.401050
H	0.195252	3.961354	-2.821138
H	-1.142474	3.422685	-1.771010
H	-0.697459	2.464433	-3.214845
H	2.226081	1.210046	-0.195224
H	0.948318	-1.945825	1.142153
O	2.260107	-1.372102	-0.361584
C	3.308740	-1.944465	0.298809
O	3.253714	-2.358689	1.431748
C	4.521962	-1.985350	-0.598901
H	5.338824	-2.492883	-0.084931
H	4.281504	-2.503692	-1.532603
H	4.822024	-0.964995	-0.860553
H	0.037892	-2.085558	-1.249399
O	-0.909204	0.074647	-2.639029
C	-2.285204	0.310392	-2.353478
H	-2.705034	0.784823	-3.246428
H	-2.823733	-0.621697	-2.155947
H	-2.439263	0.978651	-1.498757
H	0.984371	-0.113581	-2.101063
C	-1.449091	-1.366593	0.091292
C	-2.276634	-2.438751	-0.274199
C	-1.884490	-0.508593	1.114609
C	-3.514925	-2.638949	0.335296
H	-1.950257	-3.117529	-1.059125
C	-3.124516	-0.709493	1.724689
H	-1.255855	0.306848	1.453183
C	-3.947186	-1.767737	1.336741
H	-4.138668	-3.474879	0.029402
H	-3.444338	-0.032594	2.512826
H	-4.911560	-1.917601	1.814935

3_{eq}

B3LYP-D3 SCF energy: -1113.61937161 a.u.
B3LYP-D3 enthalpy: -1113.196793 a.u.
B3LYP-D3 free energy: -1113.294850 a.u.
M06 SCF energy in solution: -1113.17707265 a.u.
M06 enthalpy in solution: -1112.754494 a.u.
M06 free energy in solution: -1112.852551 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.300040	-1.040044	0.603581
C	-0.522721	-0.426181	-0.547090
C	-0.227387	1.082235	-0.632897

O	1.131530	1.347723	-0.785626
C	1.968873	0.826148	0.254515
C	3.401362	1.197682	-0.087694
H	4.035325	0.975145	0.784067
O	3.822739	0.456813	-1.217607
C	5.152398	0.745504	-1.591727
H	5.385833	0.123559	-2.460271
H	5.278332	1.805165	-1.868041
H	5.865287	0.513115	-0.782854
H	3.448946	2.279822	-0.290305
C	1.786969	-0.692357	0.430409
H	2.197074	-1.189890	-0.458469
O	2.539664	-1.028657	1.587252
C	3.072977	-2.343822	1.597390
H	3.710555	-2.413951	2.483553
H	3.688345	-2.530706	0.703146
H	2.282627	-3.100140	1.657494
H	1.712160	1.309549	1.207812
H	-0.727917	1.542453	-1.484538
O	-0.727515	1.687926	0.580855
C	-1.462501	2.831912	0.471577
O	-1.695670	3.396547	-0.570081
C	-1.962331	3.249020	1.832673
H	-2.433659	4.229974	1.764835
H	-2.693708	2.511908	2.182917
H	-1.140153	3.267526	2.554262
O	0.075493	-2.436348	0.786178
C	0.166050	-3.255958	-0.368258
H	0.120359	-4.287941	-0.010632
H	-0.672345	-3.087903	-1.057882
H	1.110379	-3.118685	-0.914939
H	-0.013148	-0.600187	1.554999
H	-0.136689	-0.825875	-1.493292
C	-2.012589	-0.701739	-0.481798
C	-2.715125	-0.974629	-1.662364
C	-2.727688	-0.644799	0.722331
C	-4.095260	-1.182721	-1.647674
H	-2.174109	-1.020940	-2.605506
C	-4.106276	-0.854745	0.741753
H	-2.204978	-0.438773	1.650107
C	-4.796001	-1.122998	-0.442817
H	-4.619917	-1.391630	-2.576193
H	-4.643163	-0.811877	1.685916
H	-5.870110	-1.286776	-0.425420

TS6'
B3LYP-D3 SCF energy: -4665.94574998 a.u.
B3LYP-D3 enthalpy: -4665.112399 a.u.
B3LYP-D3 free energy: -4665.257771 a.u.
M06 SCF energy in solution: -4667.68188280 a.u.

M06 enthalpy in solution: -4666.848532 a.u.
M06 free energy in solution: -4666.993904 a.u.
Imaginary frequency: -8.9738 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.567136	0.997059	0.137382
C	-1.089713	0.898392	0.240785
C	-0.476563	1.652354	1.370073
C	-1.883746	3.409156	0.640000
C	-2.911841	2.505659	-0.086386
H	-0.305516	1.068944	2.277250
H	-0.519945	0.771587	-0.668343
H	-2.917220	0.395584	-0.708626
H	-1.116183	3.673315	-0.100715
H	-3.918825	2.695395	0.310442
O	-1.258062	2.749051	1.751020
O	-2.834918	2.895782	-1.448257
O	-3.158144	0.537694	1.357214
O	0.827119	2.130818	0.888390
C	-2.495062	4.699903	1.151406
H	-2.832808	5.285545	0.278810
H	-1.723084	5.282811	1.680321
O	-3.578046	4.408064	2.009765
C	1.863003	2.163987	1.747837
O	1.857802	1.701710	2.870592
C	3.047066	2.859630	1.113064
H	3.959819	2.610694	1.657926
H	3.133530	2.582221	0.059735
H	2.890453	3.943411	1.160762
C	-4.206212	5.566692	2.510432
H	-3.513495	6.182454	3.107900
H	-4.614229	6.195412	1.700636
H	-5.028073	5.236643	3.151593
C	-3.854063	2.365058	-2.283028
H	-4.852697	2.515803	-1.842909
H	-3.705794	1.296605	-2.488247
H	-3.797736	2.912872	-3.227845
C	-4.523428	0.178633	1.222472
H	-5.150774	1.028173	0.914386
H	-4.651408	-0.640513	0.499859
H	-4.855373	-0.158213	2.208238
Ni	-0.530892	-1.874051	-1.170208
Br	-2.005409	-1.294219	-2.879886
C	-1.831552	-3.051062	-0.478899
C	-2.640970	-2.692259	0.610605
C	-1.958421	-4.345526	-1.003886
C	-3.544143	-3.606173	1.166053
H	-2.552295	-1.698934	1.041459
C	-2.853958	-5.263743	-0.444518
H	-1.363141	-4.636080	-1.866549
C	-3.652109	-4.896795	0.642181

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H       -4.163044   -3.306206    2.009951
H       -2.933395   -6.264676   -0.864293
H       -4.353224   -5.607960    1.072551
N        0.696822   -2.067821    0.360174
C        0.445916   -2.735821    1.500199
C        1.808745   -1.288285    0.322009
C        1.233402   -2.612723    2.636341
H       -0.437235   -3.359635    1.489271
C        2.629719   -1.117955    1.436841
C        2.346768   -1.760881    2.644922
H        0.947071   -3.170007    3.521326
H        3.471769   -0.444268    1.368117
C        2.049157   -0.616885   -0.969669
C        3.216503    0.086862   -1.279613
N        1.035674   -0.738390   -1.852336
C        3.357965    0.716230   -2.519731
H        4.012730    0.131913   -0.549663
C        1.155000   -0.142378   -3.048173
C        2.279674    0.587064   -3.409864
H        0.298611   -0.261685   -3.703589
H        2.304567    1.048511   -4.390955
C        4.603788    1.519168   -2.913039
C        5.689031    1.492276   -1.820660
C        5.203326    0.926450   -4.209920
C        4.188442    2.989454   -3.158565
H        6.030634    0.471890   -1.612073
H        6.557911    2.069744   -2.153464
H        5.338925    1.939134   -0.883235
H        5.497416   -0.118910   -4.063701
H        4.494801    0.963918   -5.043332
H        6.093574    1.494206   -4.503967
H        3.443699    3.073923   -3.956420
H        3.761361    3.434303   -2.252458
H        5.062751    3.582724   -3.450344
C        3.165182   -1.549189    3.921492
C        2.227359   -0.974362    5.011454
C        3.742846   -2.906705    4.384378
C        4.325464   -0.558426    3.712832
H        1.408639   -1.662688    5.247077
H        2.794221   -0.803075    5.934173
H        1.798609   -0.023141    4.683156
H        2.955085   -3.640006    4.586662
H        4.412106   -3.330121    3.626374
H        4.316424   -2.771116    5.308485
H        3.950225    0.430319    3.430263
H        4.882901   -0.449464    4.649374
H        5.031871   -0.910900    2.951017


 TS7'
B3LYP-D3 SCF energy:    -4665.93929367 a.u.
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B3LYP-D3 enthalpy: -4665.105439 a.u.
B3LYP-D3 free energy: -4665.250259 a.u.
M06 SCF energy in solution: -4667.66982194 a.u.
M06 enthalpy in solution: -4666.835967 a.u.
M06 free energy in solution: -4666.980787 a.u.
Imaginary frequency: -84.0036 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	2.439816	-1.122602	1.453676
C	1.656643	-0.381283	0.401108
C	1.011414	0.832658	0.995704
C	3.247615	1.291937	1.836924
C	3.638752	-0.209770	1.845289
H	2.085513	-0.284200	-0.590858
O	1.838118	1.518589	1.927596
Ni	-0.200876	-1.405210	-1.342774
Br	1.378097	-1.793306	-3.083781
C	-0.035069	-3.126395	-0.545013
C	-0.062256	-3.235517	0.856286
C	-0.009571	-4.309829	-1.298736
C	-0.059529	-4.484000	1.484903
H	-0.095384	-2.335574	1.462786
C	-0.021745	-5.561086	-0.671921
H	0.033299	-4.252693	-2.381317
C	-0.041405	-5.653108	0.721640
H	-0.060923	-4.539542	2.571552
H	-0.008107	-6.465019	-1.277658
H	-0.037935	-6.625946	1.207635
N	-2.003975	-1.047782	-0.517574
C	-2.834583	-1.963795	0.007408
C	-4.090351	-1.640253	0.505037
H	-2.454349	-2.976371	0.033990
C	-3.685341	0.620972	-0.104652
C	-4.550623	-0.314962	0.468886
H	-4.700067	-2.435162	0.920133
H	-3.976058	1.658641	-0.191138
C	-1.472483	1.174907	-1.194052
C	-1.535492	2.556151	-1.009740
N	-0.450014	0.584017	-1.847278
C	-0.504124	3.376344	-1.474104
H	-2.323817	2.967570	-0.398180
C	0.481214	1.370020	-2.408716
C	0.489245	2.749680	-2.243922
H	1.254714	0.839799	-2.954214
H	1.310400	3.317387	-2.667675
C	-0.365118	4.839934	-1.049000
C	-1.593004	5.336632	-0.263120
C	-0.155604	5.746395	-2.280705
C	0.870631	4.911734	-0.113288
H	-2.511259	5.267152	-0.859244
H	-1.452238	6.389310	0.004526

H	-1.727155	4.772073	0.665443
H	-1.020512	5.704416	-2.952746
H	0.732968	5.465277	-2.855494
H	-0.024271	6.785901	-1.959623
H	1.790267	4.639399	-0.643604
H	0.750139	4.230687	0.736468
H	0.991829	5.932433	0.268279
C	-5.925919	0.052829	1.035893
C	-5.970879	-0.338879	2.532265
C	-7.015046	-0.727198	0.262446
C	-6.221820	1.559136	0.918161
H	-5.809277	-1.411482	2.679921
H	-6.950327	-0.087632	2.954860
H	-5.205139	0.199416	3.101807
H	-6.880392	-1.810207	0.349286
H	-7.000535	-0.469394	-0.802417
H	-8.005887	-0.480359	0.660680
H	-5.486823	2.161956	1.464181
H	-7.207055	1.773442	1.345282
H	-6.236821	1.891479	-0.126164
C	3.820672	2.057646	0.640697
H	3.475840	1.611237	-0.308331
H	3.454909	3.097130	0.671368
O	5.229266	2.003549	0.736181
O	4.074479	-0.621759	3.129209
O	2.877433	-2.434403	1.195573
O	-0.125686	0.371024	1.773710
H	0.648566	1.547635	0.262365
H	3.651135	1.744384	2.746719
H	4.442962	-0.359300	1.111642
H	1.825336	-1.203467	2.357422
C	5.882566	2.612190	-0.358141
H	5.627865	3.681601	-0.440805
H	6.957995	2.515368	-0.187532
H	5.625010	2.119302	-1.309837
C	5.459267	-0.419634	3.342080
H	5.668118	-0.710482	4.375372
H	6.063123	-1.043479	2.664213
H	5.755598	0.630283	3.193996
C	3.435846	-2.689207	-0.084867
H	4.269332	-2.007471	-0.320721
H	3.824690	-3.709637	-0.043281
H	2.685749	-2.624467	-0.876935
C	-1.023381	1.289898	2.191172
O	-1.005065	2.465191	1.887410
C	-2.058482	0.635129	3.075193
H	-2.456324	-0.262460	2.593355
H	-1.587061	0.325628	4.014271
H	-2.861599	1.343523	3.284034
C	-2.432750	0.233714	-0.586001

VI$_{ax}$'
B3LYP-D3 SCF energy: -4665.97123855 a.u.
B3LYP-D3 enthalpy: -4665.135425 a.u.
B3LYP-D3 free energy: -4665.281277 a.u.
M06 SCF energy in solution: -4667.69280440 a.u.
M06 enthalpy in solution: -4666.856991 a.u.
M06 free energy in solution: -4667.002843 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.905350	-0.821338	0.384575
C	1.436290	-0.437057	0.316142
C	1.018610	0.456876	1.469816
C	2.368742	-0.902443	2.882084
C	3.144103	-1.570186	1.722421
H	0.901015	1.507573	1.216695
H	0.904987	-1.387988	0.423503
H	3.104521	-1.505625	-0.444707
H	1.494151	-1.533239	3.092585
H	4.222079	-1.550400	1.933090
O	1.907498	0.418452	2.549794
O	2.673209	-2.915813	1.671511
O	3.805839	0.277544	0.334404
O	-0.291634	-0.036608	1.915980
C	3.192357	-0.798126	4.167532
H	3.279405	-1.805183	4.590488
H	2.637870	-0.163725	4.879348
O	4.519295	-0.342750	4.011733
C	-1.160599	0.843498	2.456906
O	-1.009548	2.046664	2.487494
C	-2.359688	0.108299	3.015632
H	-3.149743	0.821006	3.257038
H	-2.717327	-0.637077	2.299092
H	-2.062695	-0.426113	3.924994
C	4.642715	1.013705	3.592070
H	4.360401	1.138454	2.541794
H	4.021663	1.679748	4.210739
H	5.695891	1.279373	3.725120
C	3.540282	-3.808694	0.995622
H	4.544338	-3.813309	1.448444
H	3.640006	-3.570704	-0.073378
H	3.102080	-4.806191	1.091386
C	4.720864	0.220496	-0.751103
H	5.418150	-0.625266	-0.640873
H	4.195749	0.133193	-1.709837
H	5.287293	1.155309	-0.732715
Ni	0.688701	0.061370	-1.456229
Br	1.865306	-1.430353	-3.056719
C	1.810100	1.601729	-1.733772
C	2.371133	2.501027	-0.821594
C	1.716068	1.980100	-3.083271

C	2.807813	3.762356	-1.243874
H	2.504290	2.227945	0.215218
C	2.140029	3.248095	-3.499710
H	1.317473	1.290926	-3.821376
C	2.685927	4.145497	-2.580776
H	3.242562	4.444617	-0.516644
H	2.051977	3.521661	-4.548742
H	3.023118	5.126917	-2.904770
N	-1.023082	1.344521	-1.044420
C	-1.004336	2.682173	-0.959113
C	-2.125157	0.692169	-0.622141
C	-2.049889	3.417241	-0.418182
H	-0.104824	3.165177	-1.319789
C	-3.212105	1.373565	-0.065944
C	-3.185165	2.763477	0.078597
H	-1.949898	4.494900	-0.356116
H	-4.062006	0.810794	0.292527
C	-2.070984	-0.783950	-0.748158
C	-3.144232	-1.618910	-0.416532
N	-0.901753	-1.285760	-1.192379
C	-3.026810	-3.008223	-0.514112
H	-4.072202	-1.176409	-0.083136
C	-0.775843	-2.615548	-1.308477
C	-1.796393	-3.496785	-0.979110
H	0.183603	-2.950783	-1.688484
H	-1.619335	-4.560904	-1.089615
C	-4.157771	-3.971552	-0.136264
C	-5.418100	-3.233831	0.351785
C	-4.533579	-4.820211	-1.373762
C	-3.663086	-4.899055	0.999198
H	-5.831799	-2.577097	-0.422251
H	-6.192160	-3.963306	0.612279
H	-5.217632	-2.633239	1.246870
H	-4.883653	-4.183910	-2.194276
H	-3.684271	-5.405465	-1.740318
H	-5.336623	-5.520838	-1.117449
H	-2.791873	-5.487829	0.695139
H	-3.384075	-4.318642	1.885886
H	-4.457250	-5.598901	1.283768
C	-4.291339	3.553022	0.784044
C	-3.660346	4.287192	1.993388
C	-4.896677	4.581398	-0.198819
C	-5.421741	2.643178	1.298613
H	-2.938782	5.044980	1.671634
H	-4.441815	4.794162	2.571434
H	-3.127245	3.586116	2.643158
H	-4.139612	5.274581	-0.579554
H	-5.359616	4.081672	-1.057589
H	-5.666965	5.174406	0.307629
H	-5.054966	1.915314	2.031684
H	-6.184986	3.252218	1.794139
H	-5.913276	2.098782	0.483547

TS8'
B3LYP-D3 SCF energy: -4665.96162304 a.u.
B3LYP-D3 enthalpy: -4665.125919 a.u.
B3LYP-D3 free energy: -4665.269730 a.u.
M06 SCF energy in solution: -4667.68907074 a.u.
M06 enthalpy in solution: -4666.853367 a.u.
M06 free energy in solution: -4666.997178 a.u.
Imaginary frequency: -266.9539 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-3.211908	0.178331	0.123765
C	-1.727175	-0.136491	0.172750
C	-1.295326	-0.484652	1.592933
C	-2.600085	1.409646	2.266604
C	-3.427550	1.466643	0.959936
H	-1.271104	-1.546207	1.814837
H	-1.256977	0.826241	-0.065809
H	-3.487186	0.374174	-0.917460
H	-1.735072	2.074156	2.134215
H	-4.495996	1.555603	1.200863
O	-2.126825	0.086106	2.557976
O	-2.979136	2.636876	0.286303
O	-3.986815	-0.886567	0.660336
O	0.049125	0.066316	1.804632
C	-3.388382	1.895198	3.484217
H	-3.507274	2.980449	3.392419
H	-2.796411	1.680414	4.389503
O	-4.699105	1.382274	3.603122
C	1.037707	-0.732142	2.252576
O	1.015932	-1.947076	2.241941
C	2.181272	0.098550	2.790904
H	3.068153	-0.526555	2.903747
H	2.387915	0.946459	2.133184
H	1.893173	0.499509	3.769543
C	-4.774417	-0.007167	3.910213
H	-4.459737	-0.627138	3.064769
H	-4.150285	-0.255683	4.782743
H	-5.822234	-0.209706	4.151814
C	-3.786301	3.048531	-0.810850
H	-4.853953	3.049949	-0.541100
H	-3.624929	2.420100	-1.695192
H	-3.482457	4.071571	-1.051014
C	-5.299364	-0.961241	0.137365
H	-5.875067	-0.041424	0.321589
H	-5.285799	-1.162528	-0.943456
H	-5.793541	-1.792287	0.646992
Ni	-0.522263	-0.466811	-1.537896
Br	-1.746229	0.821132	-3.260400

C	-1.697286	-1.924892	-0.935728
C	-2.778958	-2.169776	-1.804633
C	-1.220879	-2.993978	-0.155010
C	-3.325526	-3.447479	-1.921501
H	-3.166064	-1.361000	-2.413099
C	-1.776000	-4.271036	-0.271407
H	-0.402453	-2.843574	0.540489
C	-2.831634	-4.505426	-1.153349
H	-4.144520	-3.613253	-2.617616
H	-1.380863	-5.080105	0.338888
H	-3.267687	-5.497419	-1.238475
N	1.470297	-1.367865	-1.155557
C	1.690125	-2.688331	-1.154132
C	2.433183	-0.557033	-0.669677
C	2.820765	-3.269326	-0.597080
H	0.895963	-3.294559	-1.575329
C	3.590473	-1.078912	-0.080992
C	3.789520	-2.458849	0.010633
H	2.908974	-4.349992	-0.597681
H	4.314113	-0.401199	0.348376
C	2.164995	0.905368	-0.754137
C	3.096433	1.879309	-0.369153
N	0.952812	1.241628	-1.219796
C	2.767587	3.237681	-0.429734
H	4.075120	1.575436	-0.024727
C	0.623089	2.534492	-1.300003
C	1.486788	3.551972	-0.910253
H	-0.368785	2.730343	-1.696620
H	1.153779	4.581247	-0.988870
C	3.730591	4.349625	0.005457
C	5.080813	3.797627	0.498599
C	3.994682	5.289858	-1.193958
C	3.079882	5.149910	1.158633
H	5.603683	3.238706	-0.286088
H	5.729009	4.627646	0.799184
H	4.959553	3.142714	1.369511
H	4.452166	4.743764	-2.026517
H	3.072404	5.751289	-1.560916
H	4.676448	6.095278	-0.896881
H	2.133074	5.607104	0.854164
H	2.878961	4.502475	2.019885
H	3.750732	5.953641	1.483753
C	4.950665	-3.084794	0.788406
C	4.341376	-3.909637	1.950030
C	5.770238	-4.008466	-0.140548
C	5.896109	-2.025381	1.383467
H	3.754383	-4.755223	1.577204
H	5.139061	-4.309034	2.587241
H	3.673636	-3.292131	2.560661
H	5.155164	-4.804868	-0.571618
H	6.215740	-3.441517	-0.965972
H	6.580687	-4.483675	0.424054

H	5.378433	-1.372192	2.095751
H	6.708196	-2.521703	1.925056
H	6.351042	-1.400364	0.606025

TS10
B3LYP-D3 SCF energy: -4665.96134125 a.u.
B3LYP-D3 enthalpy: -4665.126621 a.u.
B3LYP-D3 free energy: -4665.271330 a.u.
M06 SCF energy in solution: -4667.68621262 a.u.
M06 enthalpy in solution: -4666.851492 a.u.
M06 free energy in solution: -4666.996201 a.u.
Imaginary frequency: -57.4217 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.153567	0.187145	-1.242018
Br	2.629771	-1.579252	-1.839872
C	2.586828	1.433088	-1.411641
C	3.417702	1.914824	-0.390785
C	2.756382	1.957088	-2.705319
C	4.374393	2.904485	-0.653817
H	3.337428	1.523195	0.616805
C	3.708799	2.946775	-2.968967
H	2.142320	1.583550	-3.523131
C	4.522393	3.427542	-1.939586
H	5.007371	3.261700	0.156474
H	3.819460	3.334984	-3.979673
H	5.266754	4.194485	-2.140308
N	-0.273583	1.632180	-1.164148
C	-0.045214	2.943068	-0.968337
C	-1.534223	1.173026	-0.992152
C	-1.030868	3.817360	-0.532726
H	0.974649	3.265872	-1.137225
C	-2.564613	2.000918	-0.542659
C	-2.327036	3.346970	-0.264158
H	-0.764827	4.856037	-0.368564
H	-3.526905	1.560978	-0.332236
C	-1.707848	-0.276555	-1.213965
C	-2.955547	-0.898357	-1.295347
N	-0.553168	-0.974201	-1.302882
C	-3.048985	-2.283955	-1.457416
H	-3.847546	-0.291070	-1.236568
C	-0.627016	-2.304000	-1.450505
C	-1.835557	-2.983606	-1.527779
H	0.328916	-2.810723	-1.514860
H	-1.814837	-4.061905	-1.641099
C	-4.388154	-3.023996	-1.561018
C	-5.592605	-2.068034	-1.481652
C	-4.444232	-3.774265	-2.912745
C	-4.496241	-4.040221	-0.400185

H	-5.587709	-1.338998	-2.300149
H	-6.522189	-2.642186	-1.557422
H	-5.617178	-1.523221	-0.530859
H	-4.360686	-3.075271	-3.752438
H	-3.638416	-4.509402	-3.005331
H	-5.396845	-4.308595	-3.005732
H	-3.673568	-4.762700	-0.411878
H	-4.484127	-3.527850	0.567832
H	-5.435122	-4.600569	-0.478302
C	-3.384921	4.261061	0.361943
C	-2.847836	4.763296	1.724208
C	-3.646687	5.464139	-0.571839
C	-4.712002	3.521260	0.614667
H	-1.919479	5.333168	1.614748
H	-3.587717	5.415775	2.202175
H	-2.651420	3.919243	2.394886
H	-2.737835	6.048619	-0.749833
H	-4.028776	5.130173	-1.543115
H	-4.391088	6.132451	-0.123738
H	-4.570746	2.666003	1.285177
H	-5.428809	4.204665	1.082640
H	-5.161331	3.162867	-0.319042
C	0.920694	0.496635	1.411398
C	-0.209254	-0.366967	1.869986
H	0.700879	1.545323	1.243838
C	0.243609	-1.796221	2.238718
H	-0.992207	-0.409887	1.120690
C	2.623004	-0.965301	2.284232
C	1.672751	-2.048914	1.757147
H	0.225812	-1.900376	3.334996
H	2.730816	-1.073099	3.370480
H	1.685902	-2.026762	0.661724
O	2.109365	0.366249	2.056260
O	-0.812189	0.256498	3.078141
O	-0.581068	-2.787030	1.645067
O	2.160860	-3.288613	2.241329
C	-1.881150	-2.874449	2.201707
H	-2.361540	-3.739183	1.738253
H	-1.839874	-3.027540	3.291673
H	-2.484224	-1.979498	1.991664
C	2.091140	-4.345090	1.289538
H	2.614702	-4.076491	0.360706
H	2.583362	-5.207840	1.747453
H	1.050556	-4.598327	1.053660
C	3.992410	-1.049972	1.627094
H	4.384261	-2.070876	1.758975
H	3.884825	-0.857854	0.551644
O	4.836414	-0.093424	2.240263
C	6.035146	0.100251	1.515201
H	6.624595	0.841427	2.063075
H	6.620250	-0.831301	1.435981
H	5.834645	0.477096	0.500884

C	-2.073672	0.710673	3.009466
C	-2.446460	1.441029	4.279764
H	-1.890637	2.384370	4.328993
H	-3.517635	1.647730	4.283402
H	-2.166746	0.852361	5.158184
O	-2.818742	0.570804	2.054055

TS11

B3LYP-D3 SCF energy: -4665.95427677 a.u.
B3LYP-D3 enthalpy: -4665.119584 a.u.
B3LYP-D3 free energy: -4665.263747 a.u.
M06 SCF energy in solution: -4667.68209178 a.u.
M06 enthalpy in solution: -4666.847399 a.u.
M06 free energy in solution: -4666.991562 a.u.
Imaginary frequency: -63.6638 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.846193	0.482317	-0.799280
Br	3.633840	-0.749032	-1.777654
C	3.137061	1.704686	-0.090684
C	3.934626	1.485190	1.042288
C	3.346979	2.890933	-0.814640
C	4.861208	2.441430	1.469939
H	3.865619	0.548813	1.589111
C	4.275485	3.850057	-0.394242
H	2.781263	3.071264	-1.728018
C	5.030815	3.631930	0.759247
H	5.460963	2.245967	2.356541
H	4.413365	4.760316	-0.974923
H	5.754190	4.372816	1.091229
N	0.245540	1.788437	-0.805211
C	0.217579	3.028019	-0.294635
C	-0.892536	1.294415	-1.339248
C	-0.919011	3.825068	-0.316848
H	1.146798	3.370513	0.143305
C	-2.057280	2.062922	-1.435720
C	-2.101590	3.357196	-0.911126
H	-0.868339	4.810556	0.132964
H	-2.930986	1.631670	-1.904409
C	-0.839232	-0.143832	-1.689848
C	-1.982803	-0.917457	-1.904168
N	0.388777	-0.697791	-1.629298
C	-1.881437	-2.299386	-2.084695
H	-2.953646	-0.447125	-1.845888
C	0.515699	-2.002607	-1.911690
C	-0.580233	-2.821516	-2.155957
H	1.534009	-2.373751	-1.891523
H	-0.409683	-3.878091	-2.331431
C	-3.103766	-3.222246	-2.112033

C	-4.413241	-2.450283	-1.865773
C	-3.182082	-3.940343	-3.477081
C	-2.945073	-4.260953	-0.973269
H	-4.606063	-1.706403	-2.648026
H	-5.255813	-3.149973	-1.866436
H	-4.393814	-1.945777	-0.892784
H	-3.312780	-3.221124	-4.293745
H	-2.276477	-4.521545	-3.681384
H	-4.033315	-4.630871	-3.490228
H	-2.087239	-4.920161	-1.140032
H	-2.809043	-3.759833	-0.008972
H	-3.839786	-4.892144	-0.918895
C	-3.364033	4.226177	-0.930910
C	-3.784242	4.517973	0.529923
C	-3.057763	5.555476	-1.659467
C	-4.538840	3.535062	-1.646890
H	-3.002015	5.050647	1.080399
H	-4.686605	5.140057	0.543849
H	-4.000855	3.588011	1.067976
H	-2.257646	6.116904	-1.166695
H	-2.752833	5.372879	-2.695935
H	-3.951315	6.190068	-1.672648
H	-4.829067	2.603260	-1.147527
H	-5.411897	4.196069	-1.641417
H	-4.301651	3.309556	-2.692963
C	0.989066	-0.103724	1.597154
C	0.852011	-1.587704	1.884844
H	1.906368	0.344884	1.951138
C	-1.394709	0.213262	1.713005
C	-0.529366	-2.146599	1.536227
H	1.030166	-1.758523	2.957131
C	-1.614718	-1.245600	2.120414
H	-1.564514	0.272213	0.637596
H	-0.644886	-2.167233	0.447217
H	-1.595469	-1.324408	3.213129
O	-0.073258	0.674419	2.004903
O	1.825795	-2.358107	1.150426
O	-0.766937	-3.440091	2.072863
O	-2.893309	-1.615975	1.606750
C	-0.126412	-4.525001	1.416854
H	-0.150051	-4.405089	0.325552
H	0.918571	-4.634279	1.727758
H	-0.682161	-5.427159	1.690442
C	-3.700107	-2.336595	2.530359
H	-3.914336	-1.728607	3.421423
H	-4.638370	-2.562665	2.015164
H	-3.214282	-3.270910	2.833520
C	-2.375404	1.167336	2.372005
H	-3.370976	1.004063	1.927661
H	-2.060428	2.198488	2.145325
O	-2.407831	0.939275	3.765176
C	-3.249693	1.844969	4.444954

H	-3.214906	1.585363	5.506183
H	-2.911478	2.886583	4.320222
H	-4.293040	1.775910	4.092842
C	3.093846	-2.365756	1.648460
O	3.430417	-1.703840	2.606480
C	3.979448	-3.284147	0.853102
H	3.469406	-4.228140	0.638152
H	4.202759	-2.790665	-0.099262
H	4.903716	-3.461227	1.404680

α-III'

B3LYP-D3 SCF energy: -4665.96908661 a.u.
B3LYP-D3 enthalpy: -4665.133379 a.u.
B3LYP-D3 free energy: -4665.281230 a.u.
M06 SCF energy in solution: -4667.69627013 a.u.
M06 enthalpy in solution: -4666.860563 a.u.
M06 free energy in solution: -4667.002049 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.343597	0.571118	-0.648774
Br	1.974936	-0.050160	-2.969342
C	2.583942	2.080724	-0.694447
C	3.728351	2.238820	0.096249
C	2.321847	3.055261	-1.671186
C	4.585434	3.332817	-0.079189
H	3.980310	1.517007	0.867117
C	3.159276	4.162326	-1.831732
H	1.476581	2.928521	-2.340767
C	4.299142	4.305061	-1.036344
H	5.473452	3.420539	0.543108
H	2.929562	4.902548	-2.595521
H	4.958195	5.159699	-1.167595
N	-0.535824	1.534460	-0.849641
C	-0.782753	2.818909	-0.570616
C	-1.578548	0.697344	-0.997362
C	-2.069939	3.325006	-0.444357
H	0.093030	3.444027	-0.436943
C	-2.901608	1.136896	-0.878289
C	-3.179126	2.477042	-0.593451
H	-2.195612	4.376238	-0.209399
H	-3.703000	0.416038	-0.968076
C	-1.216770	-0.725290	-1.193141
C	-2.100659	-1.680904	-1.702409
N	0.037262	-1.045686	-0.819655
C	-1.709754	-3.017125	-1.822215
H	-3.083808	-1.363894	-2.023197
C	0.435037	-2.318676	-0.948634
C	-0.399923	-3.321203	-1.417435
H	1.461687	-2.511775	-0.666303

H	-0.013393	-4.332061	-1.484062
C	-2.628330	-4.113754	-2.372205
C	-4.018358	-3.574178	-2.755874
C	-1.976082	-4.730112	-3.632509
C	-2.807709	-5.206468	-1.291728
H	-3.956725	-2.814556	-3.543515
H	-4.637375	-4.393478	-3.136532
H	-4.538793	-3.140670	-1.893778
H	-1.827807	-3.970685	-4.407967
H	-1.001840	-5.177135	-3.410373
H	-2.620521	-5.517564	-4.040374
H	-1.853227	-5.662440	-1.009671
H	-3.263639	-4.791897	-0.385524
H	-3.459165	-6.002962	-1.669553
C	-4.602666	3.016120	-0.408316
C	-4.744313	3.567945	1.030504
C	-4.850037	4.153008	-1.427365
C	-5.672075	1.928911	-0.620181
H	-4.034872	4.377764	1.228625
H	-5.755434	3.962623	1.183722
H	-4.568933	2.779203	1.771149
H	-4.145429	4.980302	-1.295502
H	-4.751038	3.786444	-2.455230
H	-5.862586	4.553956	-1.303080
H	-5.570922	1.111631	0.103353
H	-6.668526	2.363452	-0.487615
H	-5.627600	1.506147	-1.630512
C	1.330310	0.761829	1.379443
C	2.041969	-0.510726	1.895436
H	1.925805	1.637214	1.618373
C	-0.795801	-0.043805	2.229230
C	1.137419	-1.609980	2.486392
H	2.793327	-0.254900	2.646547
C	-0.110676	-1.041627	3.161857
H	-1.063692	-0.566450	1.304916
H	0.793548	-2.261915	1.670488
H	0.171904	-0.518816	4.083165
O	0.081692	1.038670	1.959105
O	2.748652	-1.072567	0.742013
O	1.801593	-2.386279	3.470830
O	-1.035416	-2.086923	3.425287
C	2.788446	-3.283711	2.988229
H	2.425690	-3.848877	2.114982
H	3.718323	-2.767293	2.721775
H	2.997201	-3.985565	3.800617
C	-1.057125	-2.517984	4.778318
H	-1.351107	-1.695918	5.448137
H	-1.805320	-3.313947	4.840936
H	-0.080649	-2.908263	5.087749
C	-2.074289	0.531326	2.813785
H	-2.836886	-0.262599	2.837288
H	-2.426882	1.337382	2.149806

O	-1.827042	1.023246	4.115711
C	-2.964615	1.622683	4.692796
H	-2.681065	1.963360	5.692279
H	-3.310084	2.490461	4.105637
H	-3.803292	0.911262	4.781716
C	4.116414	-1.075034	0.718751
O	4.798124	-0.735425	1.659941
C	4.607619	-1.559423	-0.616897
H	4.294298	-2.598678	-0.769947
H	4.152038	-0.965137	-1.417825
H	5.695614	-1.493417	-0.648668

β-III'

B3LYP-D3 SCF energy: -4665.97126077 a.u.
B3LYP-D3 enthalpy: -4665.135348 a.u.
B3LYP-D3 free energy: -4665.279165 a.u.
M06 SCF energy in solution: -4667.69207973 a.u.
M06 enthalpy in solution: -4666.856167 a.u.
M06 free energy in solution: -4667.006349 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	1.170271	0.180113	-0.893086
Br	2.561117	-1.473880	-2.058918
C	2.493959	1.547269	-1.269009
C	3.565289	2.015332	-0.510061
C	2.302883	2.044840	-2.566577
C	4.429510	2.982689	-1.040158
H	3.740190	1.635367	0.489178
C	3.163105	3.016094	-3.089605
H	1.489897	1.671389	-3.186025
C	4.232016	3.489053	-2.325158
H	5.262675	3.335973	-0.436125
H	3.001113	3.389469	-4.098546
H	4.906342	4.239068	-2.731126
N	-0.561896	1.485175	-1.192465
C	-0.520133	2.822987	-1.103003
C	-1.744686	0.873275	-0.989436
C	-1.630059	3.591882	-0.780114
H	0.452207	3.270021	-1.279801
C	-2.898787	1.585054	-0.651345
C	-2.861603	2.972932	-0.511876
H	-1.514399	4.667739	-0.704171
H	-3.799803	1.037618	-0.417054
C	-1.708532	-0.605994	-1.045648
C	-2.863726	-1.381586	-1.181664
N	-0.482971	-1.161482	-0.934291
C	-2.788589	-2.777334	-1.182918
H	-3.815442	-0.882628	-1.301331
C	-0.397105	-2.498496	-0.955267

C	-1.504586	-3.326858	-1.066932
H	0.606135	-2.900174	-0.899892
H	-1.349808	-4.400094	-1.060064
C	-4.019577	-3.683047	-1.300495
C	-5.326205	-2.880903	-1.441346
C	-3.865190	-4.592301	-2.542176
C	-4.116036	-4.556197	-0.026769
H	-5.325586	-2.257873	-2.343130
H	-6.173760	-3.570337	-1.517491
H	-5.503173	-2.235338	-0.573248
H	-3.785914	-3.995030	-3.457343
H	-2.975390	-5.226364	-2.476281
H	-4.737651	-5.249179	-2.636484
H	-3.224208	-5.175912	0.111320
H	-4.235255	-3.931930	0.866205
H	-4.982305	-5.224580	-0.093609
C	-4.059162	3.792366	-0.021138
C	-3.670234	4.452238	1.324507
C	-4.405287	4.879688	-1.063159
C	-5.303086	2.917178	0.217961
H	-2.817413	5.130529	1.213214
H	-4.513140	5.035459	1.713665
H	-3.406684	3.682553	2.056755
H	-3.565162	5.558935	-1.241604
H	-4.685310	4.430016	-2.022705
H	-5.250031	5.481868	-0.709242
H	-5.115507	2.161410	0.988515
H	-6.132046	3.545318	0.561501
H	-5.629463	2.413167	-0.699579
C	1.167025	0.775839	1.068922
C	0.018726	0.114105	1.827485
H	0.982249	1.848853	1.004388
C	0.386625	-1.285724	2.376881
H	-0.879685	0.051764	1.225823
C	2.816636	-0.665564	2.131028
C	1.757161	-1.744896	1.873879
H	0.442536	-1.222560	3.474524
H	3.041289	-0.650537	3.204784
H	1.699850	-1.934937	0.795197
O	2.351883	0.651187	1.804984
O	-0.290948	0.984077	2.973336
O	-0.557784	-2.278299	2.000127
O	2.185262	-2.913207	2.555688
C	-1.807299	-2.181298	2.662624
H	-2.410157	-3.023438	2.312326
H	-1.686127	-2.254877	3.755051
H	-2.331819	-1.244943	2.427491
C	1.933602	-4.123066	1.855573
H	2.435120	-4.126950	0.875215
H	2.348145	-4.928866	2.468006
H	0.859292	-4.287734	1.711082
C	4.099122	-0.955215	1.363485

H	4.416089	-1.989966	1.571801
H	3.903816	-0.863555	0.287192
O	5.085951	-0.029429	1.784636
C	6.208679	-0.020794	0.925181
H	6.918860	0.705244	1.331982
H	6.696354	-1.008813	0.879818
H	5.929989	0.280196	-0.096289
C	-1.519944	1.513488	3.073995
C	-1.588109	2.496841	4.219597
H	-1.198061	3.462582	3.876658
H	-2.626669	2.626597	4.528888
H	-0.971021	2.167739	5.059046
O	-2.454638	1.262075	2.331697

TS12

B3LYP-D3 SCF energy: -4665.93827986 a.u.
B3LYP-D3 enthalpy: -4665.103855 a.u.
B3LYP-D3 free energy: -4665.250109 a.u.
M06 SCF energy in solution: -4667.66840433 a.u.
M06 enthalpy in solution: -4666.833979 a.u.
M06 free energy in solution: -4666.980233 a.u.
Imaginary frequency: -264.2011 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.950428	-0.550636	-1.053814
Br	-2.615403	0.669245	-2.422014
C	-1.918990	-2.203304	-0.484109
C	-1.222704	-3.417918	-0.319857
C	-3.261962	-2.265077	-0.889723
C	-1.790601	-4.631962	-0.704515
H	-0.245820	-3.409190	0.155230
C	-3.831015	-3.479737	-1.274848
H	-3.848989	-1.358036	-0.927623
C	-3.095932	-4.665918	-1.204225
H	-1.224195	-5.553386	-0.586224
H	-4.860538	-3.496267	-1.624023
H	-3.546772	-5.610023	-1.498734
N	1.079524	-1.336950	-1.299704
C	1.417922	-2.608261	-1.547939
C	2.049683	-0.503525	-0.868314
C	2.670153	-3.133178	-1.258432
H	0.631380	-3.229056	-1.960637
C	3.315376	-0.973409	-0.506364
C	3.639963	-2.324025	-0.649828
H	2.857806	-4.181756	-1.461820
H	4.032032	-0.282693	-0.084134
C	1.683276	0.935281	-0.862129
C	2.621267	1.958930	-0.687412
N	0.388728	1.191156	-1.127306

C	2.239640	3.298457	-0.808284
H	3.651340	1.703841	-0.479674
C	0.023641	2.466411	-1.298924
C	0.902135	3.532092	-1.154864
H	-1.016232	2.608188	-1.572980
H	0.528037	4.538938	-1.306087
C	3.209411	4.469436	-0.609974
C	4.606198	4.003263	-0.160238
C	3.351259	5.235111	-1.946566
C	2.642057	5.420227	0.470460
H	5.086378	3.367365	-0.912788
H	5.252987	4.873498	-0.005517
H	4.563679	3.449003	0.784911
H	3.750985	4.582520	-2.730809
H	2.389096	5.626081	-2.292923
H	4.035040	6.083487	-1.824884
H	1.664444	5.823458	0.188670
H	2.525258	4.902711	1.429220
H	3.321951	6.266986	0.620204
C	4.948806	-2.929663	-0.135291
C	4.582881	-3.967476	0.955033
C	5.702343	-3.623799	-1.291923
C	5.877195	-1.872067	0.489082
H	4.010800	-4.802526	0.537465
H	5.493452	-4.376000	1.409137
H	3.969376	-3.505774	1.736110
H	5.103013	-4.413787	-1.755667
H	5.973453	-2.903752	-2.072481
H	6.623953	-4.083603	-0.916549
H	5.409574	-1.380066	1.349660
H	6.795594	-2.352633	0.842844
H	6.165691	-1.102810	-0.236977
C	-1.607787	-1.059670	1.160800
C	-0.435865	-0.227294	1.731337
H	-1.481268	-2.038712	1.602717
C	-0.799440	1.221110	2.099393
H	0.427403	-0.245428	1.077468
C	-3.217177	0.744532	1.678322
C	-2.058547	1.700701	1.379218
H	-1.019561	1.248194	3.177981
H	-3.503420	0.883459	2.729423
H	-1.891504	1.735569	0.298060
O	-2.865653	-0.641428	1.549794
O	-0.006104	-0.854544	2.992077
O	0.258347	2.124953	1.811806
O	-2.457455	2.969155	1.878518
C	1.406810	1.950925	2.618662
H	2.078068	2.782534	2.390993
H	1.155374	1.966345	3.690131
H	1.932706	1.010441	2.395375
C	-2.036994	4.077212	1.098175
H	-2.430988	4.015509	0.071967

H	-2.449649	4.967893	1.580765
H	-0.944434	4.152652	1.059081
C	-4.427951	1.042968	0.808753
H	-4.659340	2.117679	0.893055
H	-4.186095	0.824588	-0.239378
O	-5.510311	0.255440	1.269379
C	-6.620970	0.318834	0.402169
H	-7.400653	-0.319543	0.827947
H	-7.013156	1.346285	0.309505
H	-6.371004	-0.044014	-0.608055
C	0.905020	-1.844536	2.905599
C	1.222966	-2.398048	4.274243
H	1.503089	-1.588895	4.955779
H	0.330490	-2.879340	4.688643
H	2.030929	-3.126620	4.196226
O	1.396318	-2.235858	1.863529

TS13
B3LYP-D3 SCF energy: -4665.94397615 a.u.
B3LYP-D3 enthalpy: -4665.109509 a.u.
B3LYP-D3 free energy: -4665.254836 a.u.
M06 SCF energy in solution: -4667.67738643 a.u.
M06 enthalpy in solution: -4666.842919 a.u.
M06 free energy in solution: -4666.988246 a.u.
Imaginary frequency: -263.5454 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ni	-1.248156	0.013838	-0.900529
Br	-1.753634	1.269425	-2.983735
C	-2.736693	-1.289548	-0.761878
C	-3.917239	-0.853093	-1.404255
C	-2.481760	-2.671906	-0.731840
C	-4.730597	-1.753480	-2.084021
H	-4.169253	0.199381	-1.417529
C	-3.295833	-3.573874	-1.421943
H	-1.660830	-3.045031	-0.129832
C	-4.420886	-3.119148	-2.109784
H	-5.611313	-1.384956	-2.604106
H	-3.059372	-4.635682	-1.399189
H	-5.062764	-3.817975	-2.639348
N	0.479921	-1.150671	-1.286576
C	0.505713	-2.419433	-1.718804
C	1.657022	-0.568508	-0.964152
C	1.663754	-3.183243	-1.761063
H	-0.452010	-2.823610	-2.024499
C	2.854554	-1.293636	-0.945950
C	2.882783	-2.636829	-1.327021
H	1.600640	-4.205995	-2.116540
H	3.758565	-0.800114	-0.616965

C	1.585503	0.882894	-0.682038
C	2.714944	1.711801	-0.656004
N	0.341866	1.373643	-0.535551
C	2.579074	3.090454	-0.485172
H	3.693699	1.274416	-0.796793
C	0.192490	2.701723	-0.423651
C	1.264742	3.578829	-0.382673
H	-0.831281	3.042798	-0.346044
H	1.067962	4.640061	-0.275159
C	3.771867	4.051179	-0.422771
C	5.120397	3.319954	-0.554152
C	3.657260	5.079290	-1.572693
C	3.745931	4.788232	0.937545
H	5.210374	2.802953	-1.516450
H	5.938930	4.045048	-0.492419
H	5.265841	2.587937	0.248824
H	3.664720	4.578765	-2.547211
H	2.736114	5.666814	-1.504716
H	4.502229	5.776983	-1.538251
H	2.825433	5.366173	1.069947
H	3.820879	4.078201	1.769063
H	4.589878	5.484709	1.004388
C	4.151606	-3.495680	-1.283180
C	3.914190	-4.677580	-0.312913
C	4.449933	-4.038948	-2.700238
C	5.378619	-2.703456	-0.795970
H	3.077880	-5.306272	-0.635563
H	4.808708	-5.309227	-0.262563
H	3.693605	-4.315353	0.697873
H	3.630198	-4.654581	-3.084044
H	4.614708	-3.218552	-3.407579
H	5.352535	-4.660640	-2.680701
H	5.237064	-2.317537	0.220144
H	6.256042	-3.358688	-0.780451
H	5.607761	-1.860924	-1.458648
C	-2.418880	-0.666545	1.134588
C	-2.244257	0.721888	1.802680
H	-3.472633	-0.899733	1.219821
C	-0.367184	-1.421952	2.089079
C	-0.876079	0.999440	2.438922
H	-2.994082	0.787189	2.598622
C	-0.261582	-0.249689	3.064601
H	0.142779	-1.161821	1.152780
H	-0.181322	1.333969	1.668821
H	-0.801888	-0.516755	3.980006
O	-1.744810	-1.670958	1.819696
O	-2.509145	1.786255	0.859791
O	-0.988573	1.985436	3.461519
O	1.116161	-0.019391	3.330875
C	-0.775467	3.318291	3.026588
H	0.212712	3.433714	2.555277
H	-1.541565	3.647456	2.312508

H	-0.821728	3.949810	3.918286
C	1.405199	0.231597	4.698534
H	1.141623	-0.635853	5.321735
H	2.483458	0.405399	4.765197
H	0.868730	1.116098	5.062697
C	0.263687	-2.695045	2.622259
H	1.357498	-2.564902	2.618289
H	0.010483	-3.527087	1.944466
O	-0.203432	-2.948367	3.931534
C	0.327586	-4.134379	4.480315
H	-0.082276	-4.235887	5.488708
H	0.043653	-5.020281	3.888864
H	1.428470	-4.098908	4.542672
C	-3.819661	2.036672	0.553565
O	-4.737241	1.411882	1.034022
C	-3.912223	3.137375	-0.465609
H	-3.369213	4.024100	-0.121346
H	-3.433671	2.792800	-1.393165
H	-4.959682	3.382700	-0.644333

α-3'

B3LYP-D3 SCF energy: -1113.61228513 a.u.
B3LYP-D3 enthalpy: -1113.189715 a.u.
B3LYP-D3 free energy: -1113.288271 a.u.
M06 SCF energy in solution: -1113.16758330 a.u.
M06 enthalpy in solution: -1112.745013 a.u.
M06 free energy in solution: -1112.843569 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.227956	-1.264154	0.604760
C	1.615674	-0.656513	0.387489
C	1.513046	0.811557	-0.050513
C	2.864842	1.427204	-0.366744
H	3.421968	1.553791	0.575497
O	3.579907	0.591260	-1.258464
C	4.815655	1.148517	-1.654142
H	4.679136	2.103426	-2.186927
H	5.479825	1.325982	-0.791673
H	5.291704	0.431060	-2.327763
H	2.703092	2.422988	-0.809664
H	1.072413	1.394450	0.772949
O	0.693235	0.909632	-1.219112
C	-0.665004	0.503919	-1.000810
C	-0.638225	-0.992734	-0.620737
H	-0.216939	-1.529157	-1.475425
O	-1.952943	-1.525958	-0.355953
C	-2.732076	-1.805685	-1.429940
O	-2.394701	-1.617307	-2.577441
C	-4.061345	-2.361699	-0.980327

H	-3.907229	-3.226796	-0.328055
H	-4.651060	-2.644835	-1.852634
H	-4.598065	-1.602740	-0.400462
H	2.108375	-1.220422	-0.411935
O	2.357770	-0.740003	1.601251
C	3.580802	-1.453695	1.479146
H	3.402396	-2.509049	1.227923
H	4.077331	-1.395878	2.452094
H	4.227586	-1.010268	0.710154
H	-0.225403	-0.800239	1.491154
O	0.335115	-2.670801	0.775388
C	0.238019	-3.101400	2.123124
H	-0.753336	-2.874820	2.546405
H	0.377185	-4.186354	2.115983
H	1.007931	-2.638404	2.752966
H	-1.127298	0.571170	-1.989975
C	-1.386416	1.478981	-0.066534
C	-1.168573	2.846564	-0.300099
C	-2.249243	1.111102	0.973557
C	-1.788252	3.817779	0.482292
H	-0.491204	3.137741	-1.097656
C	-2.872388	2.086022	1.758835
H	-2.448428	0.065600	1.171724
C	-2.645736	3.439983	1.519148
H	-1.602762	4.870202	0.283352
H	-3.535824	1.778700	2.563282
H	-3.130877	4.194796	2.132293

β-3'

B3LYP-D3 SCF energy: -1113.61610584 a.u.
B3LYP-D3 enthalpy: -1113.194102 a.u.
B3LYP-D3 free energy: -1113.292941 a.u.
M06 SCF energy in solution: -1113.17502107 a.u.
M06 enthalpy in solution: -1112.753017 a.u.
M06 free energy in solution: -1112.851856 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.935977	1.454844	0.313649
C	-2.066043	0.439317	0.142402
C	-1.771773	-0.837806	0.945917
C	-2.828776	-1.911637	0.749716
H	-3.759865	-1.583359	1.238490
O	-3.039511	-2.123772	-0.634381
C	-3.954456	-3.168848	-0.891971
H	-3.594286	-4.131391	-0.494651
H	-4.945121	-2.962550	-0.453700
H	-4.055373	-3.247748	-1.977607
H	-2.485981	-2.837141	1.238991
H	-1.758507	-0.577536	2.019317

O	-0.511115	-1.382224	0.565643
C	0.583246	-0.508234	0.819549
C	0.400209	0.790326	0.002131
H	0.464884	0.566371	-1.064979
O	1.452768	1.698118	0.366850
C	2.357916	2.039594	-0.592741
O	2.314255	1.669545	-1.741244
C	3.432914	2.913062	0.006948
H	2.994647	3.692308	0.636745
H	4.030141	3.354863	-0.791454
H	4.077022	2.292589	0.640497
H	-2.126617	0.171003	-0.917789
O	-3.291171	1.007166	0.596778
C	-4.308833	1.046421	-0.395251
H	-4.025539	1.703464	-1.229724
H	-5.204355	1.446855	0.088532
H	-4.521542	0.043193	-0.788492
H	-0.923614	1.799920	1.359612
O	-1.107192	2.552188	-0.569659
C	-1.676604	3.704616	0.031076
H	-1.021428	4.110820	0.817861
H	-1.778660	4.451256	-0.761564
H	-2.661761	3.492268	0.464164
H	0.600299	-0.231096	1.887979
C	1.872718	-1.207008	0.458367
C	3.052583	-0.897170	1.143194
C	1.915471	-2.112106	-0.607541
C	4.263523	-1.478942	0.764744
H	3.021202	-0.194819	1.972524
C	3.124053	-2.700006	-0.979913
H	0.996332	-2.354039	-1.131194
C	4.301400	-2.382763	-0.298495
H	5.174176	-1.231746	1.304287
H	3.147659	-3.404335	-1.807277
H	5.242593	-2.839271	-0.593144

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